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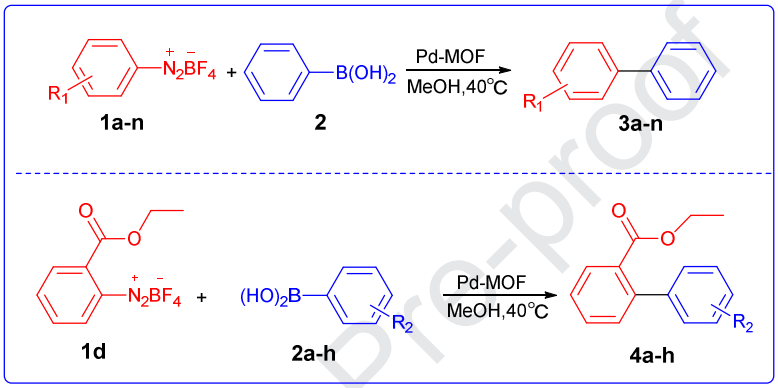

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ABSTRACT

A convenient and environmental benign synthesis of biaryls has been demonstrated by a straightforward reaction catalyzed by the palladium-containing metal-organic framework (Pd-MOF) [Pd (2-pymo)$_2$]$_n$ (2-pymo=2-pyrimidinolate). A series of functionalized biaryl derivatives have been synthesized in good to excellent yields by the Suzuki-miyaura cross-couplings of sustainable arenediazonium salts with a variety of arylboronic acids and the reactions were catalyzed by the Pd-MOF using methanol as a benign solvent. Those base- and additive-free catalytic reactions proceeded smoothly under non-anhydrous and non-degassed condition. Such transformation avoided high reaction temperature, tolerated many functional groups and presented a wide substrate scope. The catalyst could be recovered by filtration and reused for four successive cycles before collapse of the MOF structure.

1. Introduction

The palladium catalyzed Suzuki-Miyaura cross-coupling reaction is one of the most reliable and powerful methods to form C-C bonds for the synthesis of biaryls [1], which constitute a class of key structural motifs present in numerous biological important compounds [2], and advanced functional materials [3]. The vast majority of traditional Suzuki-Miyaura reactions have used costly halogenated or sulfonated electrophilic component [4]. Moreover, such methodologies that are based on aromatic halides require a base and an elevated temperature, which limited the scope of these protocols. Thus, in order to expand the scope of the Suzuki-type coupling reaction, more and more attentions have been paid to the generation of suitable electrophilic coupling partners in recent years. Among the electrophilic coupling components, aromatic diazonium salts (ADS) are found to be good choices due to their high reactivity and easy preparation [5]. In addition, ADS can be considered as super electrophiles since they are armed with diazonium function (N_2) as nucleophile, which allows the cross-coupling reactions to proceed efficiently under a simple and mild experimental procedure. Comparison to the typical Suzuki-Miyaura reaction, employing arenediazonium tetrafluoroborate salts as a coupling component provides a base-free, energy and cost-saving protocol. Although palladium-catalyzed cross-coupling reaction of arenediazonium tetrafluoroborate salts ($ArN_2^+BF_4^-$) and arylboronic acids had been successful by employing diverse homogeneous [6] or heterogeneous catalyst [7], there is a resurgent interest in the development of more efficient methods for this transformation.

Among the growing list of organometallic complexes, metal-organic frameworks (MOFs) have been investigated extensively because of their high surface areas, well-defined porosities, and chemical tenability [8]. In recent years, MOFs have been extensively demonstrated in their potential and promising applications as heterogeneous catalysts [9], especially those using MOFs as a supporting matrix for metal nanoparticles (known as metal@MOFs) [10]. However, few studies have been conducted on Pd-MOF that can be used as a new heterogeneous catalyst. Xamena et al. reported [Pd(2-pymo)$_2$]$_n$ (2-pymo=2-pyrimidinolate) as active catalyst for alcohol oxidation, Suzuki C-C coupling, and olefin hydrogenation[11]. Klemm et al. reported on the stability and reusability of this Pd-MOF in liquid-phase hydrogenation reaction [12], and the role of Pd^{2+}/Pd^0 in hydrogenation by X-ray absorption and IR spectroscopic study [13].

For our investigations, the well studied Pd-MOF [Pd(2-pymo)$_2$]$_n$ reported by Navarro et al. [14] was chosen to be the catalyst, which is an outstanding example of MOF material design for catalytic application. It was reported that the Pd^{2+}

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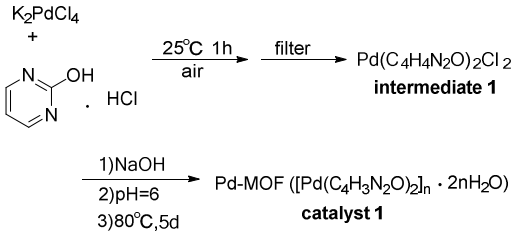
nodes of the MOF $[Pd(2\text{-pymo})_2]_n$ could be active centers in hydrogenation of 1-octene [14]. Although its catalytic performance has been tested by Xamena et al. [11] in Suzuki-Miyaura coupling between aryl halides and arylboronic acids. The methodology was base on costly aromatic halides in toxic organic solvent (o-xylene), required a base (K_2CO_3) and an elevated temperature (150□). In addition, no detailed scopes and limitations studies have been reported so far.

In the present work, Pd-MOF complex was employed to catalyze the coupling of functionalized aromatic diazonium tetrafluoroborate salts with diverse arylboronic acids under additive- and base-free condition, methanol as the solvent and a mind temperature about 40□.

2. Result and discussion

The Pd-MOF $[Pd(2\text{-pymo})_2]_n.2nH_2O$ **catalyst 1** was prepared and purified according to Jorge A. R. Navarro's reported procedure (Scheme 1) [14], and its structure was confirmed by X-ray diffraction using a PANalytical X'Pert Pro powder diffractometer and compared with literatures (see ESI†).

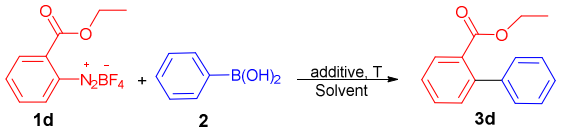


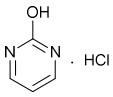
Scheme 1 Preparation of **catalyst 1**

As a starting point in the investigation of the best operating experimental conditions, the Suzuki-Miyaura cross-coupling reaction between 2-(carboxyethyl)benzenediazonium tetrafluoroborate and phenylboronic acid was selected as the representative substrate.

Firstly, the catalytic activity of the **catalyst 1** was tested, and the results are summarized in Table 1. Without catalyst, the treatment of 2-(carboxyethyl)benzendiazonium tetrafluoroborate (**1d**) and phenylboronic acid (**2**) using MeOH as solvent resulted in no reaction (Table 1, entry 1). Similarly, no biphenyl product was detected when K_2PdCl_4 or 2-pyrimidinol hydrochloride was used as the catalyst under same reaction condition (Table 1, entries 2 and 3). Excellent yields were observed for the coupling reaction when using the **catalyst 1** without base for 4 hours (Table 1, entry 5), where in the presence of **intermediate 1**, 46% yield was obtained (Table 1, entry 4). The synthetic **catalyst 1** (Pd-MOF) proved to be exceptionally active for Suzuki-Miyaura reaction in base-free condition. Note that biphenyl that may come from homocoupling of phenylboronic acid has been eliminated as supported by the fact that no biphenyl product is observed under the same experimental conditions except for the absence of 2-(carboxyethyl)benzenediazonium tetrfluoroborate (Table 1, entry 6).

Table1
Palladium-Catalyzed Suzuki-Miyaura cross-coupling reaction[a]



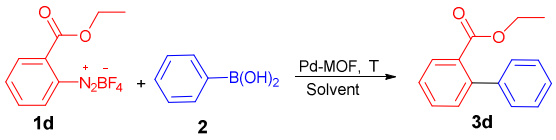
Entry	Additive	Solvent	Yield% [b]
1	nothing	MeOH	N.R
2	K_2PdCl_4	MeOH	N.R
3		MeOH	N.R
4	$Pd(C_4H_4N_2O)_2Cl_2$ **intermediate 1**	MeOH	46
5	Pd-MOF ($[Pd(C_4H_3N_2O)_2]_n \cdot 2nH_2O$) **catalyst 1**	MeOH	99
6[c]	Pd-MOF ($[Pd(C_4H_3N_2O)_2]_n \cdot 2nH_2O$) **catalyst 1**	MeOH	N.R

[a] Reaction conditions: 2-(carboxyethyl)benzenediazonium tetrafluoroborate salt (0.2 mmol), phenylboronic acid (0.3 mmol) and 3 mol% additive in solvent (1.0 ml) at 40℃ (oil temperature) for 4 hours.
[b] The yield was determined by ^{1}H NMR spectroscopy using 1,3,5-Trimethoxybenzene as an internal standard.
[c] Reaction was performed without 2-(carboxyethyl) benzenediazonium tetrafluoroborate salt

Subsequently, the effect of catalyst loading on the cross-coupling reaction was investigated under air atmosphere at 40℃ and the results are shown in Table 2. The yields were improved apparently with the increase of the catalyst, 99% of yield was obtained when as low as 3 mol% Pd-MOF was utilized (Table 2, entry 3). The investigation of some solvents usually used in Suzuki-Miyaura cross-coupling, such as MeOH, EtOH H_2O, revealed that MeOH was the best solvent (Table 2, entry 3). In sharp contrast, the yield of the model reaction was dramatically decreased when EtOH was used as solvent (Table 2, entry 6). On the other hand, when water was employed as the reaction solvent, the yield was relatively lower than MeOH (Table 2, entry 5). Comparatively, the yield of the model reaction was improved when a mixture of MeOH: H_2O was used (Table 2, entries 8-11). Temperature obviously influenced the reaction yields too. 40℃ was found to be suitable temperature (Table 2, entry 3). Reducing the reaction temperature form 40℃ to 25℃, the product yield was dramatically decreased (Table 2, entry 12). A brief survey of the bases revealed that the addition of base has significantly reduced the product formation (Table 2, entries 14-21). The loss of catalytic activity presumably resulted from the instability of Pd-MOF under alkaline conditions. After all these extensive experiments, it was discovered that the optimal conditions employed 3mol% Pd-MOF and no base in MeOH at 40℃, which provide biphenyl in 98% isolated yield.

To ascertain the scope and limitations of this reaction, a variety of arenediazonium tetrafluoroborate salts were investigated (Table 3). As described in Table 3, the nature of the substituents on the diazonium salt does not seem to affect greatly the reaction yields. Arenediazonium fluoroborate bearing either electron withdrawing functional groups or donating groups react smoothly giving moderate to excellent yields (46-98%). Additionally, compared with the corresponding meta- and para-substituted arenendiazonium tetrafluoroborate salts, the yields of the orhto-substituted derivatives gave higher yields in shorter reaction times (Table 3, entries 4, 6 and 9), probably because of the ortho-effect. Halogen atoms such as F, Cl, Br and I were also tolerated under the reaction conditions in moderate yields (Table 3, entries 11-14).

Table 2
Optimization of the cross-coupling reaction with Pd-MOF catalyst[a]

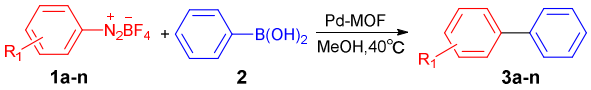


1d 2 3d

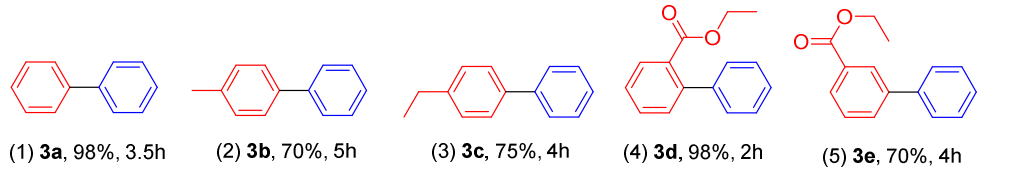
Entry	Pd-MOF(mol%)	Solvent	Bases	T [c]/℃	Yield [b](%)
1	2	MeOH	—	40	70
2	2.5	MeOH	—	40	85
3	3	MeOH	—	40	99
4	5	MeOH	—	40	98
5	3	H_2O	—	40	64
6	3	EtOH	—	40	42
7	3	EtOH /H_2O(1/1)	—	40	52
8	3	MeOH /H_2O(1/1)	—	40	70
9	3	MeOH /H_2O(2/1)	—	40	76
10	3	MeOH /H_2O(5/1)	—	40	80
11	3	MeOH /H_2O(9/1)	—	40	80
12	3	MeOH	—	25	15
13	3	MeOH	—	30	46
14	3	MeOH	K_2CO_3	40	Trace
15	3	MeOH	K_3PO_4	40	Trace
16	3	MeOH	NaOH	40	Trace
17	3	MeOH	$NaHCO_3$	40	Trace
18	3	MeOH	AcONa	40	Trace
19	3	MeOH	$NH_3·H_2O$	40	Trace
20	3	MeOH	Et_3N	40	Trace
21	3	MeOH	Py	40	Trace

[a] Reaction conditions: to the reaction mixture of 2-(carboxyethyl)benzendiazonium tetrafluoroborate salt **1d** (0.2 mmol) and Phenylboronic acid **2** (0.3 mmol) in solvent (1.0 ml).
[b] The yield was determined by 1H NMR spectroscopy using 1,3,5-Trimethoxybenzene as an internal standard.
[c] Oil temperature

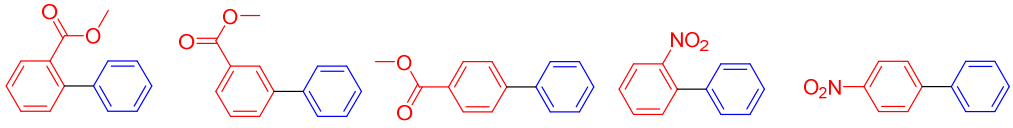
Table3
Pd-MOF catalyzed Suzuki-Miyaura cross-coupling reaction of arenediazonium tetrafluoroborate salts derivatives with arylboronic acids [a]



1a-n 2 3a-n



(1) **3a**, 98%, 3.5h (2) **3b**, 70%, 5h (3) **3c**, 75%, 4h (4) **3d**, 98%, 2h (5) **3e**, 70%, 4h



(6) **3f**, 96%, 3h (7) **3g**, 82%, 4.5h (8) **3h**, 74%, 5h (9) **3i**, 70%, 4h (10) **3j**, 46%, 8h

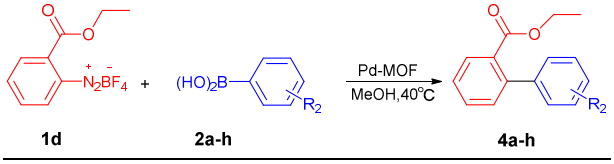
(11) **3k**, 70%, 5h (12) **3l**, 69%, 5h (13) **3m**, 58%, 5h (14) **3n**, 60%, 5.5h

[a] Reaction conditions: arenediazonium tetrafluoroborate salts **1a-n** (1.0 mmol) and Phenylboronic acid **2** (1.5 mmol) in methanol solution (5.0 ml), Pd-MOF (3 mol%), 40□ oil temperature

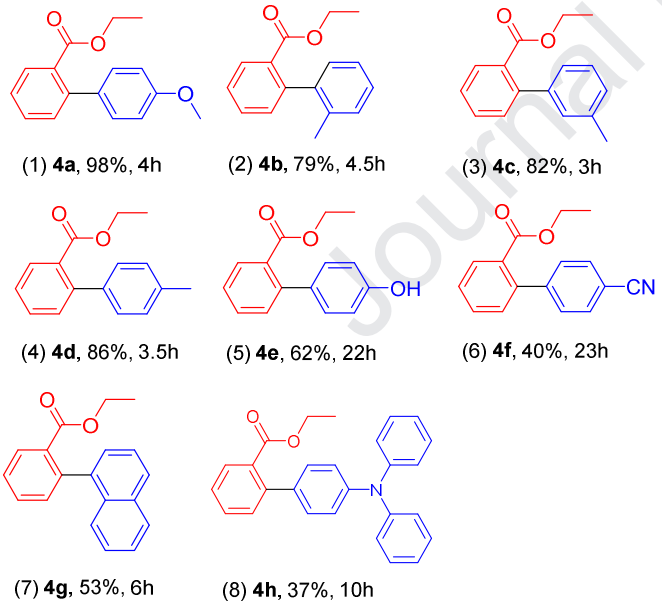
In the meantime, arylboronic acids having different substituents were examined and the results are listed in Table 4. As shown in Table 4, a series of substituted arylboronic acids bearing either electron-donating (entries 1-4) or electron-withdrawing (entries 5-6) functional groups afforded the desired products (**4a-e**) in fair to excellent yields. However, boronic acid substrates bearing electron donating groups, such as p-OMe, p-Me gave high yields of the corresponding adducts in shorter reaction times (Table 4, entries 1 and 4). The steric effect on the reaction was also investigated. When 1-naphthylboronic acid or 4-Triphenylamine was employed in the cross-coupling reaction, the product yields were dramatically decreased, demonstrating that steric effect of boronic acid was sensitive to the reaction (Table 4, entries 7-8). It is possible that **2g** and **2h** are too large to fit the pore in the Pd-MOF. Further research about the Pd-MOF catalytic mechanism is undergoing in our laboratory.

Table 4

Pd-MOF catalyzed Suzuki-Miyaura cross-coupling reaction of 2-(carboxyethyl) benzendiazonium tetrafluoroborate salt with arylboronic acids derivatives[a]



1d **2a-h** **4a-h**



(1) **4a**, 98%, 4h (2) **4b**, 79%, 4.5h (3) **4c**, 82%, 3h

(4) **4d**, 86%, 3.5h (5) **4e**, 62%, 22h (6) **4f**, 40%, 23h

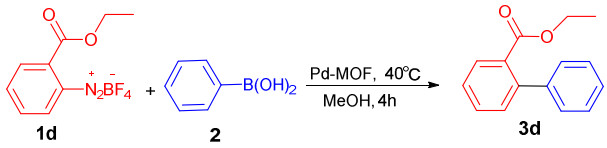
(7) **4g**, 53%, 6h (8) **4h**, 37%, 10h

[a] Reaction conditions: 2-(carboxyethyl)benzendiazonium tetrafluoroborate salt **1d** (1.0 mmol) and Phenylboronic acid **2a-h** (1.5 mmol) in methanol solution (5.0 ml), Pd-MOF (3 mol%), 40□ oil temperature.

The reusability of heterogeneous catalysts is very important, especially for commercial application. Thus, we further explored the catalyst recycling through the Suzuki-Miyaura cross-coupling of 2-(carboxyethyl) benzenediazonium tetrafluoroborate and phenylboronic acid under the optimized conditions (Table 5). The catalyst could be recovered and reused after separation, washing with MeOH, and drying under vacuum under the same reaction conditions. Although it could be recycled and reused three times without a significant reduction in the yield, the catalyst activity obviously decreased after the fourth consecutive cycles. The significant decrease of the catalytic activity was probably due to the reduction of Pd^{2+} nodes of MOF $[Pd(2\text{-}pymo)_2]_n$ and collapse of the MOF structure [11,12,13], and the decrease of the recovery percent of this catalyst during the recovery process.

Table 5

Recycling and reuse of the Pd-MOF[a]



1d **2** **3d**

Entry	Catalyst	Yield [b] (%)
1	Fresh	99
2	First Reuse	95
3	Second Reuse	90
4	Third Reuse	82
5	Fourth Reuse	64

[a] Reaction conditions: 2-(carboxyethyl)benzendiazonium tetrafluoroborate salt **1d** (0.2 mmol), phenylboronic acid **2** (0.3 mmol) and 3 mol% catalyst in Methanol solvent (1.0 ml) at 40℃ (oil temperature) for 4 hours.
[b] The yield was determined by ^{1}H NMR spectroscopy using 1,3,5-Trimethoxybenzene as an internal standard.

3. Conclusions

In summary, we have demonstrated a green and sustainable method to prepare a series of functionalized biaryls in good to excellent yields by the Suzuki-Miyaura cross-coupling reaction of arenediazonium tetrafluoroborate salts and arylboronic acids in the presence of highly active and easily synthesized Pd-MOF complex. Reactions were preformed in an open flask without the aid of any base or additive and using methanol as a green solvent. This protocol offers a practical, efficient and sustainable catalyst for Suzuki-Miyaura cross-coupling reaction with the advantages of good substrate generality, ease of experimental operation and mild alcoholic reaction conditions without inert-gas protection and any additional additives (base and ligand). More importantly, this palladium catalyst shows good to excellent yields towards a series of arenediazonium tetrafluoroborated salts and can be simply recovered and reused up to four cycles. This study indicates that the strategy can serve as a general approach for the development of Pd-MOF heterogeneous catalyst for practical catalytic applications. To our delight, this catalyst may find wide applications in synthetic and medicinal chemistry in industry and academia. Further work on exploring Pd-MOFs as heterogeneous catalysts to catalyze more significant cross-coupling reaction is currently underway.

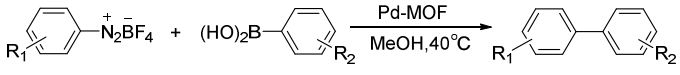
4. Experimental section

4.1. General information

Unless otherwise noted, solvents and reagents were analytical grade and used without further purification. Flash chromatography was carried out on silica gel (200–300 mesh). XRD were obtained on a D/max 2200PC X-ray diffraction. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AVANCE III (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR), and chemical shifts were reported in parts per million (ppm, δ) downfield from internal standard tetramethylsilane. Multiplicities of signals are described as follows: s --- singlet, d --- doublet, dd --- doublet d, t --- triplet, m --- multiplet. HRMS were recorded on solanX 70 FT-MS spectrometer with Methanol as solvent.

4.2. General procedure for the synthesis of Biphenyls

Compounds: **3a-n**, **4a-h**



To an Aryl diazonium salt derivative (1 mmol) and Phenylboronic acid derivative (1.5 mmol) at 25□ was added Pd-MOF (3% mmol) and Methanol (5 ml). The reaction mixture was stirred at 40□ (oil temperature) for 2h-23h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography to **3a-n**, **4a-h**. The analytical data of the products are summarized below.

1, 1'-biphenyl **3a**: Purified by column chromatography (petroleum ether/EtOAc, 300/1) as a white solid, 98% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.60 (d, J = 7.0 Hz, 4H), 7.45 (t, J = 7.5Hz, 4H), 7.35 (t, J = 7.5 Hz, 2H). ^{13}C {^{1}H} NMR (125 MHz, Chloroform-d) δ 141.57, 129.08, 127.58, 127.49.

4-methyl-1, 1'-biphenyl **3b**: Purified by column chromatography (petroleum ether/EtOAc, 300/1) as a white solid, 70% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 – 7.55 (m, 2H), 7.51 – 7.40 (m, 4H), 7.37 – 7.30 (m, 1H), 7.25 – 7.22 (m, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 141.48, 138.68, 137.32, 129.80, 129.03, 127.31, 21.42.

4-ethyl-1, 1'-biphenyl **3c**: Purified by column chromatography (petroleum ether/EtOAc, 300/1) as a white liquid, 75% yield; 1H NMR (500 MHz, Chloroform-d) δ 7.61 – 7.39 (m, 5H), 7.33 (q, J = 10.0, 7.3 Hz, 1H), 7.29 – 7.22 (m, 3H), 2.70 (d, J = 6.5 Hz, 2H), 1.27 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 143.71, 141.52, 138.94, 129.03, 128.62, 127.41, 127.34, 127.29, 28.86, 15.93.

ethyl [1, 1'-biphenyl]-2-carboxylate **3d**: Purified by column chromatography (petroleum ether/EtOAc, 150/1) as a light yellow liquid, 98% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.83 (d, J = 7.5Hz, 1H), 7.52 (t, J = 7.0 Hz, 1H), 7.44 – 7.28 (m, 7H), 4.12 – 4.03 (m, 2H), 0.99 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 169.04, 142.64, 141.77, 131.60, 130.82, 129.93, 128.63, 128.21, 127.38, 61.11, 13.88.

ethyl [1, 1'-biphenyl]-3-carboxylate **3e**: Purified by column chromatography (petroleum ether/EtOAc, 150/1) as a yellow liquid, 70% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.29 (s, 1H), 8.04 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 7.5 Hz, 2H), 7.49-7.42(m, 3H), 7.39 (t, J = 7.0 Hz, 1H), 4.42 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 166.93, 141.79, 140.55, 131.77, 131.40, 129.21, 129.13, 128.66, 128.57, 128.05, 127.52, 61.42, 14.71.

methyl [1, 1'-biphenyl]-2-carboxylate **3f**: Purified by column chromatography (petroleum ether/EtOAc, 150/1) as a light yellow liquid, 96% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.81 (d, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.42 – 7.27 (m, 7H), 3.61 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 169.37, 142.72, 141.57, 131.50, 131.13, 130.95, 130.02, 128.56, 128.29, 127.48, 127.41, 52.15.

methyl [1, 1'-biphenyl]-3-carboxylate **3g**: Purified by column chromatography (petroleum ether/EtOAc, 150/1) as a white liquid, 82% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.27 (s, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 167.34, 141.76, 140.40, 131.82, 130.99, 129.18, 129.15, 128.64, 128.56, 128.04, 127.45, 52.48.

methyl [1, 1'-biphenyl]-4-carboxylate **3h**: Purified by column chromatography (petroleum ether/EtOAc, 150/1) as a white solid, 74% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.12 (s, 1H), 8.10 (s, 1H), 7.67 (d, J = 8.5 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 3.94 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 167.34, 145.99, 140.36, 130.44, 129.26, 129.08, 128.47, 127.62, 127.39, 52.46.

2-nitro-1, 1'-biphenyl **3i**: Purified by column chromatography (petroleum ether/EtOAc, 100/1) as a pale yellow solid, 70% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.51 – 7.39 (m, 5H), 7.33 (d, J = 6.5 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 149.58, 137.67, 136.59, 132.56, 132.23, 128.96, 128.50, 128.45, 128.17, 124.33.

4-nitro-1, 1'-biphenyl **3j**: Purified by column chromatography (petroleum ether/EtOAc, 150/1) as a pale yellow solid, 46% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.30 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 7.5 Hz, 2H), 7.53 – 7.43 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 147.94, 147.40, 139.08, 129.47, 129.23, 128.11, 127.69, 124.41.

4-fluoro-1, 1'-biphenyl **3k**: Purified by column chromatography (petroleum ether/EtOAc, 300/1) as a white solid, 70% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.56 (d, J = 7.0 Hz, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5Hz, 1H), 7.15 (t, J = 8.5Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ162.82 (d, J =243.75 Hz) 140.61, 137.68, 129.05, 127.48, 115.94.

4-chloro-1, 1'-biphenyl **3l**: Purified by column chromatography (petroleum ether/EtOAc, 300/1) as a white solid, 69% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.57-7.51 (m, 4H), 7.47 – 7.39 (m, 4H), 7.36 (t, J = 7.5 Hz, 1H). ^{13}C {^{1}H}NMR (125 MHz, Chloroform-d) δ 140.14, 139.83, 133.61, 129.16, 129.13, 128.60, 127.84, 127.20.

4-bromo-1, 1'-biphenyl **3m**: Purified by column chromatography (petroleum ether/EtOAc, 300/1) as a white solid, 58% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 – 7.53 (m, 4H), 7.47–7.43 (m, 4H), 7.36 (t, J = 7.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 140.22, 140.08, 132.08, 129.12, 128.90, 127.87, 127.12, 121.79.

4-iodo-1, 1'-biphenyl **3n**: Purified by column chromatography (petroleum ether/EtOAc, 300/1) as a white solid, 60% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.77 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.44 (t, J =7.5Hz, 2H), 7.35 (dd, J = 7.5, J =8.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 140.99, 140.33, 138.14, 129.30, 129.21, 128.00, 127.19, 93.38.

ethyl 4'-methoxy-[1, 1'-biphenyl]-2-carboxylate **4a**: Purified by column chromatography (petroleum ether/EtOAc, 60/1) as a light yellow liquid, 98% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.79 (d, J = 7.5 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.25 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 4.12 (q, J = 7.0 Hz, 2H), 3.84 (s, 3H), 1.06 (t, J = 7.5Hz, 3H). ^{13}C {^{1}H}NMR (125 MHz, Chloroform-d) δ 169.14, 159.19, 142.10, 133.98, 131.54, 131.20, 130.80, 129.79, 129.69, 126.94, 113.67, 61.04, 55.40, 14.01.

ethyl 2'-methyl-[1, 1'-biphenyl]-2-carboxylate **4b**: Purified by column chromatography (petroleum ether/EtOAc, 60/1) as a white liquid, 79% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.98 (d, J = 8.5 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 6.5 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.10 (d, J = 7.5 Hz, 1H), 4.06 (q, J = 7.0 Hz, 2H), 2.10 (s, 3H), 0.97 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125MHz, Chloroform-d) δ 168.13, 142.94, 142.02, 135.74, 131.70, 131.26, 131.10, 130.27, 129.71, 128.90, 127.51, 127.45, 125.51, 61.01, 20.35, 13.91.

ethyl 3'-methyl-[1, 1'-biphenyl]-2-carboxylate **4c**: Purified by column chromatography (petroleum ether/EtOAc, 60/1) as a light yellow liquid, 82% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.83 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.32 – 7.28 (m, 1H), 7.20–7.14 (m, 3H), 4.12 (q, J = 7.5 Hz, 2H), 2.41 (s, 3H), 1.03 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125MHz, Chloroform-d) δ 169.17, 142.69, 141.65, 137.73, 131.68, 131.24, 130.77, 129.83, 129.37, 128.15, 128.11, 127.27, 125.75, 61.09, 21.65, 13.92.

ethyl 4'-methyl-[1, 1'-biphenyl]-2-carboxylate **4d**: Purified by column chromatography (petroleum ether/EtOAc, 60/1) as a white liquid, 86% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.80 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.21 (s, 4H), 4.12 (q, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.04 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 169.19, 142.69, 138.82, 137.12, 131.63, 131.33, 130.92, 129.90, 129.01, 128.57, 127.21, 61.18, 21.47, 14.03.

ethyl 4'-hydroxy-[1, 1'-biphenyl]-2-carboxylate **4e**: Purified by column chromatography (petroleum ether/EtOAc, 40/1) as a yellow liquid, 62% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (d, J = 7.5Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.19 (d, J = 6.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 5.03 (s, 1H), 4.13 (q, J = 7.0 Hz, 2H), 1.08 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-d) δ 170.06, 155.83, 142.45, 133.63, 131.51, 131.39, 131.01, 129.90, 129.86, 127.05, 115.45, 61.61, 14.12. HRMS for $C_{15}H_{14}O_3$ [M + Na] $^{+}$ calcd: 265.083515, found: 265.084025.

ethyl 4'-cyano-[1, 1'-biphenyl]-2-carboxylate **4f**: Purified by column chromatography (petroleum ether/EtOAc, 60/1-40/1) as a white liquid, 40% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.93 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.5 Hz, 1H), 4.11 (q, J = 7.0 Hz, 2H), 1.05 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H}NMR (125 MHz, Chloroform-d) δ 167.90, 146.89, 141.22, 133.62, 132.02, 131.93, 131.76, 130.83, 130.69, 129.56, 128.56, 120.40, 119.17, 111.28, 61.43, 14.06.

ethyl 2-(naphthalen-1-yl)benzoate **4g**: Purified by column chromatography (petroleum ether/EtOAc, 120/1-60/1) as a light yellow liquid, 53% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.04 (d, J = 8.0 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.61 (t, J = 7.0 Hz, 1H), 7.55 – 7.43 (m, 4H), 7.43 – 7.30 (m, 3H), 3.77 (dd, J = 7.0, 7.5 Hz, 2H), 0.53 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H}NMR (125 MHz, Chloroform-d) δ 168.09, 141.43, 140.24, 133.55, 132.56, 132.34, 132.03, 131.80, 130.38, 128.39, 127.89, 127.74, 126.28, 126.23, 125.98, 125.92, 125.41, 60.83, 13.41.

ethyl 4'-(diphenylamino)-[1, 1'-biphenyl]-2-carboxylate **4h**: Purified by column chromatography (petroleum ether/EtOAc, 60/1) as a yellow liquid, 37% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.79 (d, J = 9.0 Hz, 3H), 7.58 (dd, J = 7.0, J =7.5 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.35 – 7.29 (m, 4H), 7.18 (d, J = 7.5 Hz, 4H), 7.15 – 7.08 (m, 4H), 4.36 (dd, J = 6.5, J =7.0Hz, 2H), 1.34 – 1.30 (m, 3H). ^{13}C{^{1}H}NMR (125 MHz, Chloroform-d) δ 152.56 , 147.19 , 132.02 , 129.93 , 129.89 , 129.31 , 126.05 , 125.01 , 124.66 , 121.55 , 119.08 , 61.62 , 14.74 . HRMS for $C_{27}H_{23}NO_2$ [M + Na] $^{+}$ calcd: 416. 162100, found: 416.162309.

Conflicts of interest

There are no conflicts to declare.

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Highlights

- A convenient and environmental benign synthesis of a series of functionalized biaryl derivatives has been demonstrated by a straightforward reaction catalyzed by the palladium-containing metal-organic framework (Pd-MOF) [Pd (2-pymo)2]n (2-pymo=2-pyrimidinolate) using methanol as a benign solvent.
- The present base- and additive-free catalytic reactions proceeded smoothly under non-anhydrous and non-degassed condition. Such transformation avoided high reaction temperature, tolerated many functional groups and presented a wide substrate scope.
- The palladium catalyst (Pd-MOF) shows good to excellent yields towards a series of arenediazonium tetrafluoroborated salts and can be simply recovered and reused up to four cycles.
- This study indicates that the strategy can serve as a general approach for the development of Pd-MOF heterogeneous catalyst for practical catalytic applications. This catalyst may find wide applications in synthetic and medicinal chemistry in industry and academia.