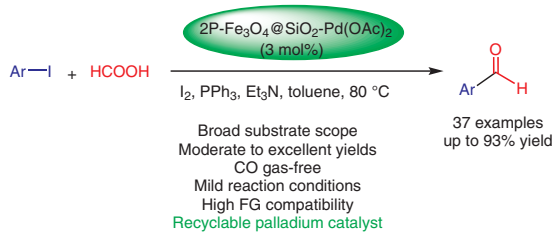
Synthesis S. You et al. Paper

A Magnetically Recyclable Palladium-Catalyzed Formylation of Aryl Iodides with Formic Acid as CO Source: A Practical Access to Aromatic Aldehydes

Shengyong You[a,b]
Rongli Zhang[a]
Mingzhong Cai[*a]

[a] Key Laboratory of Functional Small Organic Molecule, Ministry of Education and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P. R. of China
mzcai@jxnu.edu.cn
[b] Institute of Applied Chemistry, Jiangxi Academy of Sciences, Nanchang 330029, P. R. of China



Received: 03.10.2020
Accepted after revision: 10.11.2020
Published online: 13.01.2021
DOI: 10.1055/s-0040-1706621; Art ID: ss-2020-g0521-op

Abstract A magnetically recyclable palladium-catalyzed formylation of aryl iodides under CO gas-free conditions has been developed by using a bidentate phosphine ligand-modified magnetic nanoparticles-anchored palladium(II) complex [2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$] as catalyst, yielding a wide variety of aromatic aldehydes in moderate to excellent yields. Here, formic acid was employed as both the CO source and the hydrogen donor with iodine and PPh_3 as the activators. This immobilized palladium catalyst can be obtained via a simple preparative procedure and can be facilely recovered simply by using an external magnetic field, and reused at least 9 times without any apparent loss of catalytic activity.

Key words formylation, palladium, magnetic nanoparticles, heterogeneous catalysis, aromatic aldehyde

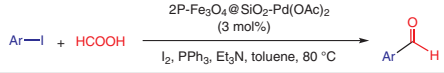
Aromatic aldehydes are a class of important chemical intermediates that are widely employed for the synthesis of chemical materials, pharmaceuticals, pesticides, food additives, and so on.[1] The conventional methods for the preparation of aromatic aldehydes involve an electrophilic formylation of electron-rich aromatic rings including Gattermann–Koch reaction, Reimer–Tiemann reaction, Vilsmeier reaction, and Duff reaction, which generally suffer from some inherent drawbacks such as the use of high amounts of reagents and formation of wastes and by-products, multiple steps, low yields and/or poor selectivity as well as the incompatibility of many functional groups.[2] In addition, some other synthetic routes such as the reduction of aromatic carboxylic acids or esters[3] and the direct formylation of aryl halides via a halogen/lithium exchange followed by addition of formylating agents[4] are also well represented. But these approaches usually require low reaction temperatures and a stoichiometric amount of reductive agents or metal reagents, and have limited functional groups tolerance. Therefore, there has been a continuing quest for simple and efficient approaches.

Since the discovery of palladium-catalyzed carbonylation of aryl halides by Heck in 1974,[5] the palladium-catalyzed formylation of aryl halides with carbon monoxide has been developed into an alternative and more efficient route to aryl aldehydes,[6] and has been widely employed to construct carbonyl-containing compounds.[7] However, laboratorial use of CO gas suffers from transportation, handling, storage, and safety regulations due to its high toxicity and flammable characters. For reasons of safety and operation, a variety of CO surrogates have been extensively utilized in palladium-catalyzed reductive carbonylation of aryl halides towards aryl aldehydes, including *N*-formylsaccharin,[8] paraformaldehyde,[9] 9-methylfluorene-9-carbonyl chloride,[10] acetic formic anhydride,[11] formic acid,[12] $Fe(CO)_5$,[13] CO_2,[14] *S*-phenyl thioformate,[15] and isocyanide.[16] Although these palladium-catalyzed formylations of aryl halides under CO gas-free conditions are highly efficient for the synthesis of aromatic aldehydes, in almost all cases homogeneous palladium complexes such as $Pd(OAc)_2$/$BuPAd_2$, $PdCl_2$(dppp), $Pd(OAc)_2$/dppb, and $Pd(MeCN)_2Cl_2$/dppb were used as the catalysts, which suffered from the high cost, difficulty with separation and non-recyclability of the palladium catalysts as well as palladium contamination of the desired product due to palladium leaching, thereby restricting their applications in large-scale synthesis or in industry. Therefore, the development of an efficient, economic, and practical route to aromatic aldehydes is highly desirable.

Anchoring homogeneous palladium catalysts through covalent bond formation onto a solid support is one of the most effective ways to solve these problems. The employment of the immobilized catalysts could result in convenient separation, recovery, and recycle of the palladium catalysts, thereby preventing contamination of the desired

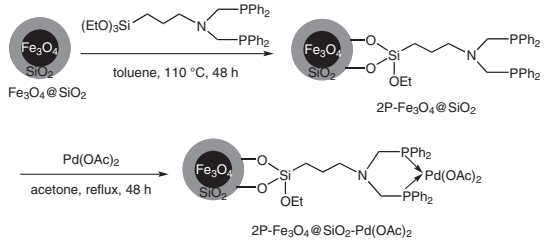
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

product from palladium and minimizing waste derived from reaction workup.[17] The use of magnetic nanoparticles as the support is particularly attractive in this regard because the catalysts anchored onto magnetic nanoparticles can be facilely separated and recovered from the product simply by using an external magnetic field, which avoids filtration or centrifugal operation, thereby effectively preventing loss of catalyst and greatly improving the recyclability.[18] During recent years, some functionalized magnetic nanoparticles-anchored palladium complexes have been successfully utilized as recyclable catalysts in various carbon–carbon coupling reactions.[19] Very recently, we reported the synthesis of a bidentate phosphine ligand-modified magnetic nanoparticles-anchored palladium(II) complex [2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$] and its catalytic behavior in Heck coupling polycondensation of bis(acrylamide)s with aromatic diiodides towards polycinnamamides.[20] To extend the application of this supported palladium catalyst, we herein report a recyclable palladium-catalyzed formylation of aryl iodides by using 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ as the heterogeneous catalyst with formic acid as both the CO source and the hydrogen donor in the presence of iodine and PPh_3 as the activators (Scheme 1). This heterogeneous formylation reaction proceeded smoothly under CO gas-free conditions, delivering a wide variety of aryl aldehydes in moderate to excellent yields with high functional group tolerance and easy recycle of the palladium catalyst.



Scheme 1 Heterogeneous palladium-catalyzed formylation of aryl iodides with HCOOH as CO source

The bidentate phosphine ligand-modified magnetic nanoparticles-anchored palladium(II) complex [2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$] was prepared by referring to our previously reported route as depicted in Scheme 2.[20] The silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2) was reacted with *N*,*N*-bis[(diphenylphosphino)methyl]-3-(triethoxysilyl)propan-1-amine in anhydrous toluene at 110 °C for 48 hours to give the bidentate phosphine ligand-modified magnetic nanoparticles (2P-Fe_3O_4@SiO_2). The 2P-Fe_3O_4@SiO_2 was then complexed with palladium acetate in acetone at reflux for 48 hours to furnish the bidentate phosphine ligand-modified magnetic nanoparticles-anchored palladium(II) complex [2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$]. Figure 1 shows the FT-IR spectra of Fe_3O_4@SiO_2 (a) and 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ (b). In the FT-IR spectrum of 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$, absorptions at 2924 cm^{-1} (CH_2), 1605 and 1559 cm^{-1} (benzene ring) were observed indicating the presence of silylated phosphine-palladium groups. The XRD patterns of Fe_3O_4@SiO_2 (a) and 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ (b) are presented in Figure 2. No peaks characteristic for palladium(0) nanoparticles were observed from the XRD pattern of 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$, which shows the excellent dispersion of the palladium sites on the magnetic nanoparticles. These results indicate that the bidentate phosphine-palladium complex has been successfully anchored onto the magnetic nanoparticles.



Scheme 2 Preparation of the 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ complex

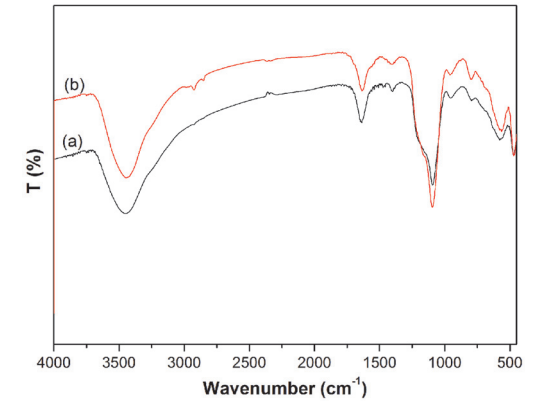


Figure 1 FT-IR spectra of Fe_3O_4@SiO_2 (a) and 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ (b)

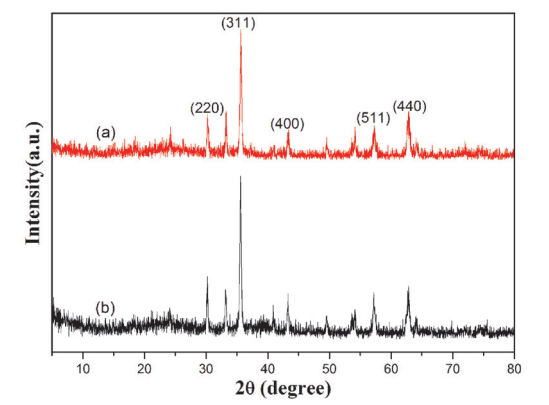


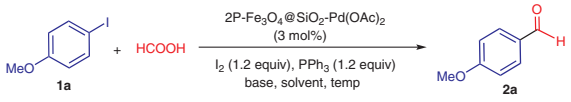
Figure 2 XRD patterns of Fe_3O_4@SiO_2 (a) and 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ (b)

The 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ complex was then utilized as the catalyst for the formylation of aryl iodides by using HCOOH as both the CO source and the hydrogen donor in the presence of iodine and PPh_3 as the activators. Initially,

the formylation of 4-iodoanisole with HCOOH was chosen as the model reaction to determine the optimal reaction conditions including solvents, bases, reaction temperatures, and catalyst loadings. The results are summarized in Table 1. At first, the effect of various bases on the model reaction was evaluated in toluene as the solvent at 80 °C in the presence of I_2 (1.2 equiv) and PPh_3 (1.2 equiv) as the activators (Table 1, entries 1–7). The use of DIPEA, DBU, Et_3N, or TMEDA as the base afforded the desired **2a** in 62–86% yields and Et_3N gave the best result (entry 5), while DABCO, DMAP, and K_2CO_3 proved to be ineffective (entries 3, 4, and 7). Replacement of toluene with THF, MeCN, DMF, DCM, or 1,4-dioxane resulted in a decreased yield of **2a** (entries 8–12), so toluene as solvent was the best option in this transformation (entry 5). Further examination of reaction temperatures showed that lowering the temperature to 70 °C led to a decreased yield, whilst raising the temperature to 90 or 100 °C did not enhance the yield of **2a** (entries 13–15). When the amounts of HCOOH or Et_3N were further increased, no improvement in the yield of **2a** was observed (entries 16 and 17). Also, the amounts of the palladium catalyst were tested. Reducing the amount of the catalyst to 1 mol% lowered the yield of **2a** to 62% and needed a long reaction time (12 h, entry 18). Increasing the amount of the catalyst to 5 mol% could enhance the reaction rate, but the reaction did not give an increased yield (entry 19). The use of homogeneous $Pd(OAc)_2$ (3 mol%) as the catalyst also furnished the desired **2a** in 87% yield (entry 20), which indicated that the catalytic efficiency of 2P-Fe_3O_4@SiO_2-$Pd(OAc)_2$ was comparable to that of $Pd(OAc)_2$. Thus, the optimized reaction conditions were established as 2P-Fe_3O_4@SiO_2-$Pd(OAc)_2$ (3 mol%), HCOOH (4 equiv), Et_3N (6 equiv), I_2 (1.2 equiv), and PPh_3 (1.2 equiv) in toluene at 80 °C for 3 hours (entry 5).

With the optimized conditions in hand, we next explored the generality and scope of this heterogeneous formylation reaction with a wide variety of aryl iodides. The results are shown in Scheme 3. As depicted in Scheme 3, iodobenzene (**1b**) and a wide variety of substituted iodobenzenes **1c–r** underwent the heterogeneous formylation smoothly under the optimal conditions to give the corresponding aromatic aldehydes **2b–r** in 56–93% yields. For example, various *para*- or *meta*-substituted electron-rich aryl iodides **1c–h** afforded the desired products **2c–h** in 79–87% yields. Aryl iodides with weak electron-withdrawing substituents **1i–m** delivered various halosubstituted aryl aldehydes **2i–m** in 74–93% yields. Notably, aryl iodides bearing strong electron-withdrawing groups **1n–r**, which are traditionally considered as forbidden substrates in this type of conversion also reacted well, thereby furnishing the expected products **2n–r** in 56–77% yields. In addition, bulky 1-iodonaphthalene (**1s**) and 2-iodonaphthalene (**1t**) gave the desired naphthyl aldehydes **2s** and **2t** in 71 and 74% yield, respectively. Sterically hindered *ortho*-substituted iodobenzenes **1u–x** displayed a relatively lower reactivity than the *para*- or *meta*-substituted ones and produced the corresponding aromatic aldehydes **2u–x** in 67–80% yields on a longer reaction time. Furthermore, highly sterically congested 2,6-disubstituted iodobenzenes **1y** and **1z** could also undergo the formylation effectively to give the target products **2y** and **2z** in 63–68% yields. It is also noteworthy that aryl iodides bearing active functional groups **1a′–e′** underwent the formylation smoothly to give the functionalized aryl aldehydes **2a′–e′** in 75–88% yields. In addition to aryl iodides, heteroaryl iodides such as 3-iodopyridine, 2-iodothiophene, and 2-iodofuran were also compatible in this reaction and provided the corresponding heteroaryl aldehydes **2f′–h′** in 61–71% yields. A wide variety of functional groups such as methyl, methoxy, acetyloxy, dimethylamino, fluoro, chloro, bromo, trifluoromethyl, ester, ketone, cyano,

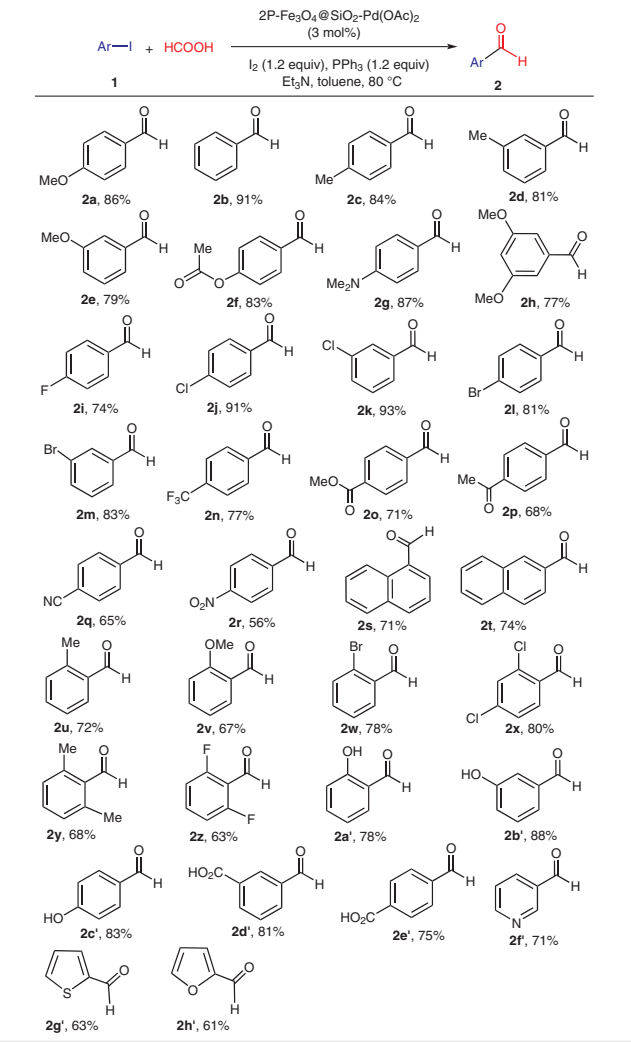
Table 1 Optimization of the Reaction Conditions[a]



Entry	Solvent	Base	Temp (°C)	Yield (%)[b]
1	toluene	DIPEA	80	78
2	toluene	DBU	80	62
3	toluene	DABCO	80	0
4	toluene	DMAP	80	0
5	**toluene**	**Et_3N**	**80**	**86**
6	toluene	TMEDA	80	67
7	toluene	K_2CO_3	80	0
8	THF	Et_3N	80	60
9	MeCN	Et_3N	80	65
10	DMF	Et_3N	80	53
11	DCM	Et_3N	80	74
12	1,4-dioxane	Et_3N	80	57
13	toluene	Et_3N	70	59
14	toluene	Et_3N	90	85
15	toluene	Et_3N	100	86
16[c]	toluene	Et_3N	80	86
17[d]	toluene	Et_3N	80	85
18[e]	toluene	Et_3N	80	62
19[f]	toluene	Et_3N	80	86
20[g]	toluene	Et_3N	80	87

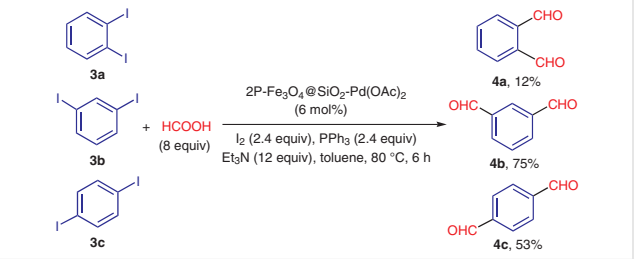
[a] Reaction conditions: **1a** (1 mmol), HCOOH (4 mmol), I_2 (1.2 mmol), PPh_3 (1.2 mmol), base (6 mmol), 2P-Fe_3O_4@SiO_2-$Pd(OAc)_2$ (3 mol%), solvent (4 mL), 3 h.
[b] Isolated yield.
[c] HCOOH (6 mmol) was used.
[d] Et_3N (8 mmol) was used.
[e] 2P-Fe_3O_4@SiO_2-$Pd(OAc)_2$ (1 mol%) was used for 12 h.
[f] 2P-Fe_3O_4@SiO_2-$Pd(OAc)_2$ (5 mol%) was used for 2 h.
[g] $Pd(OAc)_2$ (3 mol%) was used for 2 h.

nitro, hydroxy, and carboxy were tolerated well in this transformation. Encouraged by the above results, we also performed the formylation of aryl bromides with HCOOH under the optimized conditions, unfortunately, the formylation reaction did not occur at all even at elevated temperatures, which may be due to the fact that oxidative addition of aryl bromides to a heterogeneous palladium complex did not take place. So, substrates **1l–m** and **1w** could be chemoselectively converted into the corresponding bromo-substituted aryl aldehydes in good yields.



Scheme 3 Heterogeneous palladium-catalyzed formylation of aryl iodides with HCOOH. *Reagents and conditions*: **1** (1 mmol), HCOOH (4 mmol), I_2 (1.2 mmol), PPh_3 (1.2 mmol), Et_3N (6 mmol), 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ (3 mol%), toluene (4 mL), 80 °C, 3 h. Isolated yields are shown. For **2n–r**: The reaction was conducted at 70 °C. Reaction time for **2s–z,a'**: 5 h.

In order to expand application of this methodology, aromatic diiodides were used as substrates to perform the diformylation reaction (Scheme 4). It was found that 1,2-diiodobenzene (**3a**) displayed poor reactivity, providing the desired *o*-phthalaldehyde (**4a**) in low yield of 12%, probably owing to the interference of palladium oxidative addition by the neighboring carbonyl group, and 2-iodobenzaldehyde was isolated as a by-product in 34% yield. To our delight, 1,3-diiodobenzene (**3b**) and 1,4-diiodobenzene (**3c**) could undergo the diformylation smoothly to afford isophthalaldehyde (**4b**) and terephthalaldehyde (**4c**) in 75 and 53% yield, respectively.

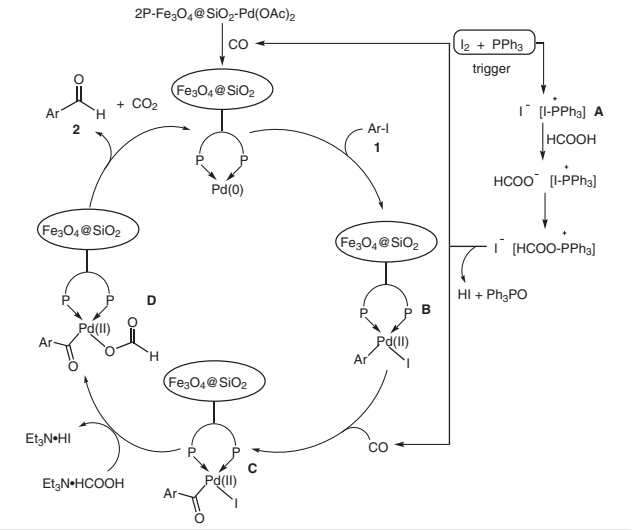


Scheme 4 Heterogeneous palladium-catalyzed diformylation of aromatic diiodides with HCOOH

To identify whether the observed formylation was due to the heterogeneous 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ complex or a leached palladium species from this catalyst, we performed the hot filtration test.[21] For this, the formylation of 4-iodoanisole (**1a**) was conducted until a conversion of 60%. The palladium catalyst was then separated magnetically from the reaction solution at 80 °C and the solution was transferred into another reaction tube. After the addition of I_2 (0.6 equiv), PPh_3 (0.6 equiv), HCOOH (2 equiv), and Et_3N (3 equiv), the catalyst-free solution was stirred at 80 °C for another 3 hours. In this case, further increase in conversion of 4-iodoanisole (**1a**) was not observed, indicating that the soluble palladium species leached from 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ was not responsible for the observed reductive carbonylation. Furthermore, ICP-AES analysis of the reaction solution showed that no palladium species could be detected (below the detection limit). These results indicate that the 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ complex was stable during the formylation and the nature of the reaction was heterogeneous.

A plausible reaction mechanism for this heterogeneous palladium-catalyzed formylation of aryl iodides with HCOOH is illustrated in Scheme 5. First, I_2 and PPh_3 form the complex **A**, which can trigger the release of CO from HCOOH. Then the 2P-Fe_3O_4@ SiO_2-Pd$(OAc)_2$ complex is easily reduced by CO to 2P-Fe_3O_4@SiO_2-Pd(0). Oxidative addition of Ar-I **1** to 2P-Fe_3O_4@SiO_2-Pd(0) generates a magnetic nanoparticle-bound arylpalladium(II) complex **B**, which is followed by migratory insertion of CO to give a magnetic nanoparticles-bound acylpalladium(II) complex **C**. Subsequent reaction between intermediate **C** and HCOOH with the aid of Et_3N produces a magnetic nanoparticles-bound acylpalladium(II) formic acid complex intermediate **D** and releases HI simultaneously. Finally, intermediate **D** under-

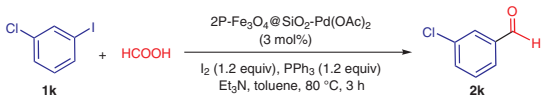
goes decarboxylation and reductive elimination to afford the desired aryl aldehyde **2** and regenerates the 2P-Fe_3O_4@SiO_2-Pd(0) complex that launches next catalytic cycle.



Scheme 5 Proposed catalytic cycle

For the application of a heterogeneous palladium catalyst in the large-scale synthesis or in industry, its ease of separation from the product and the ability to recycle it are significant factors that need to be examined. We next evaluated the recyclability of the palladium catalyst in the formylation reaction of 3-chloroiodobenzene (**1k**) with HCOOH under the standard conditions and the results are listed in Table 2. Upon completion of the first reaction cycle, the reaction mixture was cooled to room temperature. As expected, more than 99% of the palladium catalyst could be facilely recovered simply by fixing a magnet to the outside of the reaction tube. The recovered palladium catalyst was washed with toluene, distilled water and ethanol, dried under vacuum at 80 °C, and used directly in the next cycle. As seen from Table 2, the yield of the desired product **2k** in ten consecutive cycles was over 89%, which reveals that this heterogeneous palladium catalyst can be reused at least nine times with only a slight drop in catalytic efficiency. Figure 3 shows TEM images of the fresh catalyst (a) and the recovered catalyst after ten cycles (b). No obvious differences in the morphology and dispersion of particles were observed from their TEM images, which show that the structural regularity of the recovered catalyst is consistent with the fresh catalyst. In addition, the palladium leaching in this supported Pd catalyst was also examined and the Pd content of the recovered catalyst after ten consecutive cycles was measured to be 0.37 mmol/g by ICP-AES analysis, revealing a negligible palladium leaching. The excellent reusability of the 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ catalyst might arise from the chelating action of the bidentate phosphine ligand on the palladium center.

Table 2 Recycle of the 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ Catalyst[a]



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

[a] Reaction conditions: **1k** (1 mmol), HCOOH (4 mmol), I_2 (1.2 mmol), PPh_3 (1.2 mmol), Et_3N (6 mmol), 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ (3 mol%), toluene (4 mL), 80 °C, 3 h.
[b] Isolated yield.

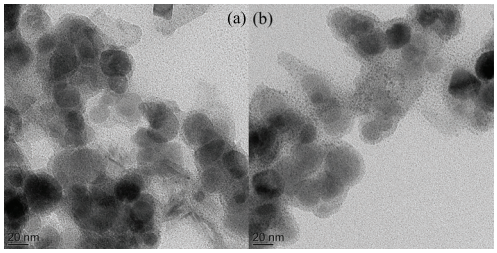


Figure 3 TEM images of the fresh catalyst (a) and the recovered catalyst after ten cycles (b)

In summary, we have developed a novel, facile, and practical method for the synthesis of aromatic aldehydes through a heterogeneous palladium-catalyzed formylation of aryl iodides with dual-role HCOOH by using a bidentate phosphine ligand-modified magnetic nanoparticles-anchored palladium(II) complex [2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$] as catalyst under CO gas-free conditions. In contrast to the conventional route to aromatic aldehydes, this heterogeneous formylation strategy has some attractive features, such as: (1) the scope of substrates is broad, and a wide range of aryl iodides are allowed; (2) a wide variety of aromatic aldehydes are obtained in moderate to excellent yields under mild conditions; (3) the reaction avoids the use of CO gas and additional reductant; (4) many functional groups including active hydroxy and carboxy are well tolerated; and (5) this heterogeneous palladium catalyst can be facilely recovered simply by fixing a magnet to the outside of the reaction tube and recycled up to ten times without any apparent decrease in catalytic activity. Thus, the current methodology is an attractive alternative to synthesize aromatic aldehydes.

All starting materials were purchased from various commercial sources and used as received without further purification. All solvents were dried and distilled prior to use. The silica-coated magnetic Fe_3O_4 nanoparticles (Fe_3O_4@SiO_2)[19f] and *N*,*N*-bis[(diphenylphosphino)methyl]-3-(triethoxysilyl)propan-1-amine[22] were prepared by referring to literature procedures. The products were purified by silica gel column chromatography with a mixture of light petroleum ether (PE) and EtOAc as eluent. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker Avance 400 NMR spectrometer in $CDCl_3$ as solvent with TMS as internal reference. Melting points were measured on a Beijing Tech Instrument Co., LTD X-6 melting point apparatus and are uncorrected. Pd content was measured on a Jarrell-Ash 1100 ICP. FT-IR spectra were obtained with a Horiba FT-720 FTIR spectrophotometer. X-ray diffraction (XRD) patterns were recorded at r.t. on a Rigaku D/MAX-IIA X-ray diffractometer with nickel-filtered CuKα radiation (40 KV and 20 mA). TEM images were recorded in a transmission electron microscope operated at an accelerated voltage of 200 kV.

2P-Fe_3O_4@SiO_2-Pd(OAc)$_2$

A mixture of Fe_3O_4@SiO_2 (1.12 g) and *N*,*N*-bis[(diphenylphosphino)methyl]-3-(triethoxysilyl)propan-1-amine (0.928 g, 1.5 mmol) in anhyd toluene (50 mL) was stirred at 110 °C under argon atmosphere for 48 h. The resulting product was then magnetically separated, followed by washing with toluene (2 × 15 mL) and dried in vacuo at 120 °C for 4 h to furnish 1.327 g of the bidentate phosphine ligand-modified Fe_3O_4@SiO_2 (2P-Fe_3O_4@SiO_2). The phosphorus content of 2P-Fe_3O_4@SiO_2 was measured to be 0.97 mmol g^{-1} by elemental analysis.

A mixture of 2P-Fe_3O_4@SiO_2 (1.08 g) and Pd(OAc)$_2$ (91 mg, 0.4 mmol) in anhyd acetone (50 mL) was stirred at reflux under argon atmosphere for 48 h. After cooling to r.t., the solid product was magnetically separated from the solution, followed by washing with distilled water (2 × 15 mL) and acetone (15 mL), and dried in vacuo at 70 °C for 6 h to afford 1.064 g of 2P-Fe_3O_4@SiO_2-Pd(OAc)$_2$. The palladium content of 2P-Fe_3O_4@SiO_2-Pd(OAc)$_2$ was determined to be 0.38 mmol g^{-1} based on ICP-AES analysis.

Heterogeneous Palladium-Catalyzed Formylation of Aryl Iodides with HCOOH; General Procedure

A dried 10 mL reaction tube was charged with I_2 (152 mg, 1.2 mmol), PPh_3 (315 mg, 1.2 mmol), and toluene (4 mL) under argon. The mixture was stirred at r.t. for 10 min. Then aryl iodide **1** (1 mmol), 2P-Fe_3O_4@SiO_2-Pd(OAc)$_2$ (79 mg, 3 mol%), and Et_3N (606 mg, 6 mmol) were added to this solution. After the addition of HCOOH (184 mg, 4 mmol), the reaction tube was immediately sealed and the reaction mixture was stirred at 80 °C for 3–5 h. After cooling to r.t., the Pd catalyst was magnetically separated from the mixture, washed with toluene (2 mL), distilled H_2O (2 × 2 mL) and EtOH (2 × 2 mL), dried under vacuum at 80 °C, and used directly in the next cycle. The reaction mixture was then filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography (light PE/EtOAc 10:1) to afford the desired product **2**.

4-Methoxybenzaldehyde (2a)[12c]

Yield: 118.2 mg (86%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (d, *J* = 2.0 Hz, 1 H), 7.82–7.78 (m, 2 H), 6.99–6.95 (m, 2 H), 3.84 (t, *J* = 2.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 164.5, 131.8, 129.9, 114.3, 55.5.

Benzaldehyde (2b)[12c]

Yield: 96.6 mg (91%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1 H), 7.88–7.85 (m, 2 H), 7.63–7.59 (m, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 136.4, 134.4, 129.7, 129.0.

4-Methylbenzaldehyde (2c)[12c]

Yield: 100.9 mg (84%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 7.6 Hz, 2 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 145.6, 134.2, 129.8, 129.7, 21.8.

3-Methylbenzaldehyde (2d)[12c]

Yield: 97.4 mg (81%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 7.68–7.63 (m, 2 H), 7.43–7.37 (m, 2 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 138.9, 136.5, 135.3, 130.0, 128.9, 127.2, 21.1.

3-Methoxybenzaldehyde (2e)[12c]

Yield: 107.6 mg (79%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (d, *J* = 0.8 Hz, 1 H), 7.47–7.43 (m, 2 H), 7.40–7.38 (m, 1 H), 7.20–7.16 (m, 1 H), 3.86 (d, *J* = 0.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 160.2, 137.8, 130.0, 123.5, 121.5, 112.1, 55.5.

4-Acetyloxybenzaldehyde (2f)[23]

Yield: 136.3 mg (83%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1 H), 7.88 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0, 168.6, 155.3, 133.9, 131.1, 122.3, 21.0.

4-Dimethylaminobenzaldehyde (2g)[12d]

Yield: 129.8 mg (87%); white solid; mp 73–75 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (s, 1 H), 7.73 (d, *J* = 8.8 Hz, 2 H), 6.70 (d, *J* = 8.8 Hz, 2 H), 3.08 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 154.4, 132.0, 125.2, 111.0, 40.1.

3,5-Dimethoxybenzaldehyde (2h)[24]

Yield: 127.9 mg (77%); white solid; mp 45–46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1 H), 7.01 (d, *J* = 2.0 Hz, 2 H), 6.70 (s, 1 H), 3.84 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 161.3, 138.4, 107.2, 107.1, 55.6.

4-Fluorobenzaldehyde (2i)[12c]

Yield: 91.8 mg (74%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1 H), 7.94–7.90 (m, 2 H), 7.24–7.19 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 166.5 (d, *J* = 255.2 Hz), 133.0 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 9.7 Hz), 116.3 (d, *J* = 22.1 Hz).

4-Chlorobenzaldehyde (2j)[12c]

Yield: 128.6 mg (91%); white solid; mp 47–48 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 141.0, 134.7, 130.9, 129.5.

3-Chlorobenzaldehyde (2k)[12c]

Yield: 130.7 mg (93%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1 H), 7.85 (t, *J* = 2.0 Hz, 1 H), 7.78–7.75 (m, 1 H), 7.61–7.58 (m, 1 H), 7.48 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 137.8, 135.4, 134.4, 130.4, 129.3, 128.0.

4-Bromobenzaldehyde (2l)[12c]

Yield: 149.8 mg (81%); light yellow solid; mp 57–58 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1 H), 7.76–7.73 (m, 2 H), 7.70–7.67 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 135.1, 132.4, 131.0, 129.8.

3-Bromobenzaldehyde (2m)[24]

Yield: 153.6 mg (83%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (d, *J* = 2.4 Hz, 1 H), 7.98 (d, *J* = 1.6 Hz, 1 H), 7.80 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.75–7.71 (m, 1 H), 7.44–7.38 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 138.0, 137.2, 132.3, 130.6, 128.4, 123.3.

4-(Trifluoromethyl)benzaldehyde (2n)[12d]

Yield: 134.1 mg (77%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.11 (s, 1 H), 8.02 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0, 138.7, 135.6 (q, *J* = 32.5 Hz), 129.9, 126.1 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 271.2 Hz).

Methyl 4-Formylbenzoate (2o)[12d]

Yield: 116.5 mg (71%); white solid; mp 60–62 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.11 (s, 1 H), 8.19 (dd, *J* = 8.2, 1.4 Hz, 2 H), 7.97–7.94 (m, 2 H), 3.96 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 166.0, 139.1, 135.1, 130.2, 129.5, 52.6.

4-Acetylbenzaldehyde (2p)[12d]

Yield: 100.7 mg (68%); white solid; mp 34–36 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.12 (s, 1 H), 8.11 (d, *J* = 8.4 Hz, 2 H), 7.99 (d, *J* = 8.4 Hz, 2 H), 2.67 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 191.6, 141.2, 139.1, 129.8, 128.8, 27.0.

4-Cyanobenzaldehyde (2q)[12c]

Yield: 85.2 mg (65%); light yellow solid; mp 98–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.11 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 138.8, 132.9, 129.9, 117.7, 117.6.

4-Nitrobenzaldehyde (2r)[12c]

Yield: 84.6 mg (56%); yellow solid; mp 104–105 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.18 (s, 1 H), 8.41 (d, *J* = 8.8 Hz, 2 H), 8.10 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 151.1, 140.1, 130.5, 124.3.

1-Naphthaldehyde (2s)[12a]

Yield: 110.9 mg (71%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.28 (t, *J* = 4.0 Hz, 1 H), 9.20 (d, *J* = 8.4 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.84–7.76 (m, 2 H), 7.61–7.56 (m, 1 H), 7.51–7.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 136.7, 135.3, 133.7, 131.3, 130.5, 129.1, 128.5, 127.0, 124.9.

2-Naphthaldehyde (2t)[12d]

Yield: 115.6 mg (74%); pale yellow solid; mp 59–60 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.15 (s, 1 H), 8.32 (s, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.96–7.87 (m, 3 H), 7.66–7.55 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.2, 136.5, 134.5, 134.2, 132.7, 129.5, 129.1, 128.1, 127.1, 122.8.

2-Methylbenzaldehyde (2u)[12c]

Yield: 86.5 mg (72%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.26 (s, 1 H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.49–7.44 (m, 1 H), 7.37–7.33 (m, 1 H), 7.25 (d, *J* = 7.6 Hz, 1 H), 2.66 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 140.6, 134.1, 133.7, 132.1, 131.8, 126.3, 19.6.

2-Methoxybenzaldehyde (2v)[12c]

Yield: 91.3 mg (67%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.47 (s, 1 H), 7.82 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.57–7.52 (m, 1 H), 7.04–7.01 (m, 1 H), 6.99 (d, *J* = 8.8 Hz, 1 H), 3.92 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8, 161.8, 136.0, 128.5, 124.8, 120.7, 111.7, 55.6.

2-Bromobenzaldehyde (2w)[24]

Yield: 144.3 mg (78%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1 H), 7.88–7.85 (m, 1 H), 7.62–7.59 (m, 1 H), 7.44–7.37 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 135.3, 133.8, 133.4, 129.8, 127.9, 127.0.

2,4-Dichlorobenzaldehyde (2x)[25]

Yield: 140.1 mg (80%); pale yellow solid; mp 65–67 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.41 (s, 1 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.48 (d, *J* = 2.0 Hz, 1 H), 7.37 (dd, *J* = 8.2, 1.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.4, 141.1, 138.5, 131.0, 130.5, 130.3, 127.9.

2,6-Dimethylbenzaldehyde (2y)[26]

Yield: 91.3 mg (68%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.61 (d, *J* = 1.6 Hz, 1 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.08 (d, *J* = 7.6 Hz, 2 H), 2.60 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 141.1, 133.0, 132.5, 129.7, 20.5.

2,6-Difluorobenzaldehyde (2z)[27]

Yield: 89.5 mg (63%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.36 (s, 1 H), 7.62–7.54 (m, 1 H), 7.01 (t, *J* = 8.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.5 (t, *J* = 4.5 Hz), 163.2 (dd, *J* = 261.5, 5.6 Hz), 136.3 (t, *J* = 11.3 Hz), 114.2, 112.5 (dd, *J* = 22.5, 2.3 Hz).

2-Hydroxybenzaldehyde (2a')[12c]

Yield: 95.2 mg (78%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.02 (s, 1 H), 9.86 (s, 1 H), 7.54–7.47 (m, 2 H), 7.01–6.94 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 161.6, 137.0, 133.7, 120.7, 119.9, 117.6.

3-Hydroxybenzaldehyde (2b')[12c]

Yield: 107.4 mg (88%); white solid; mp 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1 H), 7.46–7.40 (m, 3 H), 7.19–7.15 (m, 1 H), 6.64 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 156.7, 137.7, 130.4, 123.5, 122.4, 114.8.

4-Hydroxybenzaldehyde (2c')[12c]

Yield: 101.4 mg (83%); white solid; mp 115–117 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 6.18 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 161.5, 132.5, 130.0, 116.0.

3-Formylbenzoic Acid (2d')[12c]

Yield: 121.5 mg (81%); white solid; mp 170–172 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.12 (s, 1 H), 8.62 (t, *J* = 1.8 Hz, 1 H), 8.40–8.37 (m, 1 H), 8.18–8.14 (m, 1 H), 7.69 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 170.2, 136.7, 135.7, 133.8, 132.0, 130.4, 129.5.

4-Formylbenzoic Acid (2e')[12c]

Yield: 112.6 mg (75%); white solid; mp 244–245 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.10 (s, 1 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 193.4, 167.0, 139.3, 136.1, 130.4, 130.0.

Pyridine-3-carbaldehyde (2f')[12c]

Yield: 76.1 mg (71%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.14 (s, 1 H), 9.10 (dd, *J* = 2.2, 1.0 Hz, 1 H), 8.86 (dd, *J* = 5.0, 1.8 Hz, 1 H), 8.21–8.18 (m, 1 H), 7.53–7.49 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 154.7, 152.1, 135.8, 131.4, 124.1.

Thiophene-2-carbaldehyde (2g')[12c]

Yield: 70.6 mg (63%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1 H), 7.80–7.76 (m, 2 H), 7.23–7.20 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.0, 144.0, 136.4, 135.1, 128.4.

Furan-2-carbaldehyde (2h')[12c]

Yield: 58.6 mg (61%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.67 (d, *J* = 0.8 Hz, 1 H), 7.72 (t, *J* = 0.8 Hz, 1 H), 7.28 (dd, *J* = 3.6, 0.8 Hz, 1 H), 6.62 (dd, *J* = 3.6, 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 152.9, 148.1, 121.2, 112.6.

Compounds 4a–c; General Procedure

A dried 20 mL reaction tube was charged with I_2 (304 mg, 2.4 mmol), PPh_3 (630 mg, 2.4 mmol), and toluene (6 mL) under argon. The mixture was stirred at r.t. for 10 min. Then aryl diiodide **3** (1 mmol), 2P-Fe_3O_4@SiO_2-Pd$(OAc)_2$ (158 mg, 6 mol%), and Et_3N (1.2 g, 12 mmol) were added to this solution. After the addition of HCOOH (368 mg, 8 mmol), the reaction tube was immediately sealed and the reaction mixture was stirred at 80 °C for 6 h. After cooling to r.t., the Pd catalyst was magnetically separated and the reaction mixture was then filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography (light PE/EtOAc 10:1) to give the desired product **4**.

***o*-Phthalaldehyde (4a)**[12c]

Yield: 16.1 mg (12%); white solid; mp 51–53 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.54 (s, 2 H), 8.01–7.96 (m, 2 H), 7.82–7.76 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 136.4, 133.8, 131.1.

***m*-Phthalaldehyde (4b)**[12c]

Yield: 100.5 mg (75%); white solid; mp 88–89 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 2 H), 8.39 (t, *J* = 1.8 Hz, 1 H), 8.17 (dd, *J* = 7.6, 1.6 Hz, 2 H), 7.75 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 137.0, 134.6, 131.0, 129.9.

Terephthalaldehyde (4c)[12c]

Yield: 71.5 mg (53%); white solid; mp 113–115 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.15 (s, 2 H), 8.07 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 140.0, 130.1.

Funding Information

We thank the National Natural Science Foundation of China (No. 21462021), the Natural Science Foundation of Jiangxi Province of China (No. 20161BAB203086) and Key Laboratory of Functional Small Organic Molecule, Ministry of Education (No. KLFS-KF-201704) for financial support.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1706621.

References

(1) (a) Ferguson, L. N. *Chem. Rev.* **1946**, *38*, 227. (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Springer: Heidelberg, **2007**.

(2) (a) Vilsmeier, A.; Haack, A. *Bull. Soc. Chim. France* **1962**, 1989. (b) Crawford, L. P.; Richardson, S. K. *Gen. Synth. Methods* **1994**, *16*, 37. (c) Aldabbagh, F. In *Comprehensive Organic Functional Group Transformations II, Vol. 3, Part 1, Chap. 3*; Jones, K., Ed.; Elsevier: Amsterdam, **2005**, 99. (d) Fetter, J.; Bertha, F.; Poszavacz, L.; Simig, G. *J. Heterocycl. Chem.* **2005**, *42*, 137. (e) Singh, A. S.; Bhanage, B. M.; Nagarkar, J. M. *Tetrahedron Lett.* **2011**, *52*, 2383.

(3) (a) Amakasu, T.; Sato, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1428. (b) Peters, J. A.; Van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 21. (c) Osman, M. A. *Helv. Chim. Acta* **1982**, *65*, 2448.

(4) (a) Xi, H.; Gibb, L. D.; Gibb, B. C. *J. Org. Chem.* **1999**, *64*, 9286. (b) Mizuno, T.; Takeuchi, M.; Shinkai, S. *Tetrahedron* **1999**, *55*, 9455. (c) Albrecht, M.; Rodriguez, G.; Schoenmarker, J.; Van Koten, G. *Org. Lett.* **2000**, *2*, 3461. (d) Hoye, T. R.; Humpal, P. E.; Moon, B. *J. Am. Chem. Soc.* **2000**, *122*, 4982.

(5) (a) Schoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318. (b) Schoenberg, A.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3327. (c) Schoenberg, A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 7761.

(6) (a) Cacchi, S.; Fabrizi, G.; Goggiamani, A. *Org. Lett.* **2003**, *5*, 4269. (b) Sergeev, A. G.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2008**, *130*, 15549. (c) Neumann, H.; Kadyrov, R.; Wu, X.-F.; Beller, M. *Chem. Asian J.* **2012**, *7*, 2213. (d) Klaus, S.; Neumann, H.; Zapf, A.; Strbing, D.; Huebner, S.; Almena, J.; Riermeier, T.; Grob, P.; Sarich, M.; Krahnert, W.-R.; Rossen, K.; Beller, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 154. (e) Han, W.; Liu, B.; Chen, J.; Zhou, Q. *Synlett* **2017**, *28*, 835. (f) Ashfield, L.; Barnard, C. F. J. *Org. Process Res. Dev.* **2007**, *11*, 39. (g) Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 452.

(7) (a) Wu, X. F.; Neumann, H. *ChemCatChem* **2012**, *4*, 447. (b) Wu, X. F.; Neumann, H.; Beller, M. *ChemSusChem* **2013**, *6*, 229. (c) Wu, X. F.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 4986. (d) Wu, X. F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1.

(8) (a) Ueda, T.; Konishi, H.; Manabe, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 8611. (b) Ueda, T.; Konishi, H.; Manabe, K. *Org. Lett.* **2013**, *15*, 5370.

(9) Natte, K.; Dumrath, A.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 10090.

(10) Korsager, S.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. *J. Org. Chem.* **2013**, *78*, 6112.

(11) Cacchi, S.; Fabrizi, G.; Goggiamani, A. *J. Comb. Chem.* **2004**, *6*, 692.

(12) (a) Qi, X.; Li, C.-L.; Wu, X.-F. *Chem. Eur. J.* **2016**, *22*, 5835. (b) Wu, F.-P.; Peng, J.-B.; Meng, L.-S.; Qi, X.; Wu, X.-F. *ChemCatChem* **2017**, *9*, 3121. (c) Sun, G.; Lv, X.; Zhang, Y.; Lei, M.; Hu, L. *Org. Lett.* **2017**, *19*, 4235. (d) Ying, J.; Fu, L.-Y.; Zhou, C.; Qi, X.; Peng, J.-B.; Wu, X.-F. *Eur. J. Org. Chem.* **2018**, 2780. (e) Dey, T. K.; Basu, P.; Riyajuddin, S.; Ghosh, A.; Ghosh, K.; Islam, S. *New J. Chem.* **2019**, *43*, 9802. (f) Sadhasivam, V.; Balasaravanan, R.; Siva, A. *Appl. Organomet. Chem.* **2019**, *33*, e4994.

(13) Iranpoor, N.; Firouzabadi, H.; Etemadi-Davan, E. D.; Rostami, A.; Moghadam, K. R. *Appl. Organomet. Chem.* **2015**, *29*, 719.

(14) (a) Yu, B.; Zhao, Y. F.; Zhang, H. Y.; Xu, J. L.; Hao, L. D.; Gao, X.; Liu, Z. M. *Chem. Commun.* **2014**, *50*, 2330. (b) Yu, B.; Yang, Z. Z.; Zhao, Y. F.; Hao, L. D.; Zhang, H. Y.; Gao, X.; Han, B. X.; Liu, Z. M. *Chem. Eur. J.* **2016**, *22*, 1097. (c) Kumar, S.; Verma, S.; Jain, S. L. *Tetrahedron Lett.* **2015**, *56*, 2430.

(15) Qi, X. X.; Li, C. L.; Wu, X. F. *Chem. Eur. J.* **2016**, *22*, 5835.

(16) Jiang, X.; Wang, J.-M.; Zhang, Y.; Chen, Z.; Zhu, Y.-M.; Ji, S.-J. *Org. Lett.* **2014**, *16*, 3492.

(17) (a) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217. (b) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (c) Liu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815. (d) Molnar, A. *Chem. Rev.* **2011**, *111*, 2251.

(18) (a) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.-M. *Chem. Rev.* **2011**, *111*, 3036. (b) Nasi Baig, R. B.; Varma, R. S. *Chem. Commun.* **2013**, *49*, 752. (c) Wang, D.; Astruc, D. *Chem. Rev.* **2014**, *114*, 6949.

(19) (a) Stevens, P. D.; Li, G.; Fan, J.; Yen, M.; Gao, Y. *Chem. Commun.* **2005**, 4435. (b) Liu, J.; Peng, X.; Sun, W.; Zhao, Y.; Xia, C. *Org. Lett.* **2008**, *10*, 3933. (c) Baruwati, B.; Guin, D.; Manorama, S. V. *Org. Lett.* **2007**, *90*, 5377. (d) Jin, M.-J.; Lee, D.-H. *Angew. Chem. Int. Ed.* **2010**, *49*, 1119. (e) Shylesh, S.; Wang, L.; Thiel, W. R. *Adv. Synth. Catal.* **2010**, *352*, 425. (f) Li, P.; Wang, L.; Zhang, L.; Wang, G.-W. *Adv. Synth. Catal.* **2012**, *354*, 1307. (g) Zhang, L.; Li, P.; Li, H.; Wang, L. *Catal. Sci. Technol.* **2012**, *2*, 1859. (h) Zhang, L.; Li, P.; Yang, J.; Wang, M.; Wang, L. *ChemPlusChem* **2014**, *79*, 217. (i) Zhang, L.; Li, P.; Liu, C.; Yang, J.; Wang, M.; Wang, L. *Catal. Sci. Technol.* **2014**, *4*, 1979.

(20) Tang, H.; Yao, F.; Liu, L.; Cai, M. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2020**, *57*, 198.

(21) Lempers, H. E. B.; Sheldon, R. A. *J. Catal.* **1998**, *175*, 62.

(22) Posset, T.; Guenther, J.; Pope, J.; Oeser, T.; Blumel, J. *Chem Commun.* **2011**, *47*, 2059.

(23) Kawajiri, T.; Kato, M.; Nakata, H.; Goto, R.; Aibara, S.; Ohta, R.; Fujioka, H.; Sajiki, H.; Sawama, Y. *J. Org. Chem.* **2019**, *84*, 3853.

(24) Li, F.; Zhou, Y.; Yang, H.; Wang, Z.; Yu, Q.; Zhang, F.-L. *Org. Lett.* **2019**, *21*, 3692.

(25) Mu, B.; Li, J.; Zou, D.; Wu, Y.; Chang, J.; Wu, Y. *Org. Lett.* **2016**, *18*, 5260.

(26) Wadhwa, K.; Verkade, J. G. *J. Org. Chem.* **2009**, *74*, 4368.

(27) Bunnett, J. F.; Miles, J. H.; Nahabedian, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2512.

