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Heck Reactions Catalyzed by Ultrasmall and Uniform Pd Nanoparticles Supported on Polyaniline

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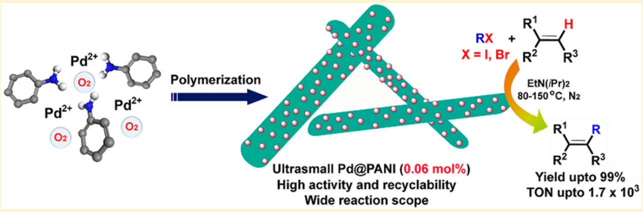
S *Supporting Information*

ABSTRACT: Using air as the oxidant instead of the traditionally employed persulfates, the smaller and more uniform Pd nanoparticles (around 2 nm) supported on polyaniline (Pd@PANI) can be easily fabricated by the oxidation−polymerization of aniline with $PdCl_2$. This material is an efficient and environmentally friendly catalyst for Heck reactions due to its recyclability, low loading, and ligand-free and mild reaction conditions. It was even tolerant to sulfur-containing substrates. This work reports the Pd@PANI-catalyzed Heck reactions with very wide substrate scopes, and discloses the catalytic mechanisms based on experimental findings and results of catalyst analysis and characterization.



1. INTRODUCTION

The Heck reaction[1,2] has been one of the most important synthetic tools to modify olefins[3] with high selectivity and efficiency. During the past 40 years, scientists have utilized this tool to synthesize a wide range of the complex molecules involving drugs and natural products.[1] Tuning the activity of the transition metal by various ligands, Heck reaction could be performed under quite mild conditions to achieve a series of challenging objectives in organic synthesis, such as the asymmetric synthesis,[2a,b] reactions with sp^3 organic halides,[2b,c] and even the highly stereoselective tandem reaction processes.[2b] In line with calls for greater environmental protection nowadays, people are interested in this synthetic methodology using environmentally friendly novel heterogeneous catalysts that are accessible, robust, and recyclable and can be employed free of ligands, and developing such catalyst systems is of both academic and industrial value.[4−6]

The development of polyaniline (PANI) as an environmentally benign supporter to anchor noble nanocatalysts[5,6] is an attractive area owing to the easily accessible monomer, low cost, and the low-toxicity carrier.[7] PANI-supported metal catalysts (M@PANIs) should be reliable catalysts with potentially comprehensive applications. However, the investigations on M@PANIs basically belong to the field of material science at present,[5,6] attracting less attention from organic chemists. In the material science field, people focused a lot on the design of the new-style M@PANI catalysts, such as the magnetic catalysts, carbon nanotube-supported catalysts, and the catalysts with fancy morphology, but ignored their applications in organic reactions. Currently, M@PANIs have been applied in limited simple organic reactions with narrow application scopes, including Suzuki cross-couplings, the hydroxylation of aryl halides, and some redox reactions.[5] Investigations of the applications of M@PANI in other organic reactions are warranted. Thus, as a part of our continuing investigation into green synthetic methodologies,[8] we wish to make a further development on the applications of this practical nanocatalyst in organic synthesis to develop reliable and eco-friendly synthetic methodologies.

The Pd@PANI-catalyzed classic Heck reaction is our first research goal because of its significance in organic chemistry. Although a few studies have been reported on this topic, there are still enough spaces to improve the currently reported works, which suffered the high catalyst loadings (0.9−5 mol %) and narrow application scopes of olefins limited to only acrylic acid and its esters and simple styrene.[6] Herein, we report a systematic study on highly efficient Pd@PANI-catalyzed Heck reactions. This Pd@PANI catalyst was prepared using air as the oxidant instead of traditionally employed ammonium persulfate. The very slow *in situ* polymerization of aniline monomer and formation of Pd nanoparticles (NPs) was the key factor to control the size of Pd and morphology of PANI, which provided an ultrasmall and uniform Pd@PANI catalyst to catalyze the Heck reaction with higher catalytic activity (TON up to 1.7×10^3) and wider substrate scopes than previous

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reports.[6] In addition, the simple preparation procedure of the reusable catalyst also allowed exploration of large-scale Heck reactions.

2. RESULTS AND DISCUSSION

We initially prepared the Pd@PANI catalyst as described in the Experimental Section (*vide infra*). After heating in oven at 100 °C for 0.5 h, it was directly used in the Heck reaction of iodobenzene **1a** with styrene **2a**. The reaction was initially performed in water, but desired product **3a** was not observed (Table 1, entry 1). Further screening of the reaction conditions showed that addition of triethylamine as the base was necessary (entry 2) and DMF was a better solvent (entry 3). Contrary to many known reports,[9] this reaction did not require excess amounts of base, and the maximum yield of **3a** was achieved by using only 1 equiv of Et_3N (entries 8 vs 3–7, 9–10). To achieve better results, a series of inorganic and organic bases were further screened (entries 11–18). Generally, the reactions afforded **3a** in rather low yields using inorganic bases (entry 11), DBU (entry 12), primary or secondary amines/amides (entry 13), and pyridines (entry 14). It was interesting that the addition of tertiary amines could improve the yield remarkably, and EtN(*i*-Pr)$_2$ was found to be best, affording **3a** in 88% yield (entries 18 vs 8, 15–17). The best reaction temperature and time were found to be 80 °C and 24 h, respectively (entries 18–25). It should be noted that although in the previous works[5,6] the PANI-supported catalyst could be directly used, for Heck reaction, baking treatment is needed to activate the catalyst (entries 26–27). The product yield did not decrease upon 25-fold increase in the reaction scale (entry 28), showing good practicability of this catalyst for organic synthesis.

Table 1. Optimization of the Reaction Conditions[a]

entry	solvent	base (equiv)[b]	T/°C	t/h	**3a**/%[c]
1	H_2O		80	24	NR[d]
2	H_2O	Et_3N (3.5)	80	24	trace[e]
3	DMF	Et_3N (3.5)	80	24	49
4	DMF	Et_3N (3.0)	80	24	52
5	DMF	Et_3N (2.0)	80	24	54
6	DMF	Et_3N (1.5)	80	24	59
7	DMF	Et_3N (1.2)	80	24	67
8	DMF	Et_3N (1.0)	80	24	76
9	DMF	Et_3N (0.5)	80	24	46
10	DMF		80	24	5
11	DMF	inorg bases (1.0)[f]	80	24	0–27
12	DMF	DBU (1.0)	80	24	NR[d]
13	DMF	1° or 2° amines/amides (1.0)[g]	80	24	0–22
14	DMF	pyridines (1.0)[h]	80	24	NR[d]
15	DMF	*n*-Bu$_3$N (1.0)	80	24	71
16	DMF	$(n\text{-}C_8H_{17})_3N$ (1.0)	80	24	69
17	DMF	$BuNMe_2$ (1.0)	80	24	72
18	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	24	88
19	DMF	EtN(*i*-Pr)$_2$ (1.0)	40	24	6
20	DMF	EtN(*i*-Pr)$_2$ (1.0)	60	24	73
21	DMF	EtN(*i*-Pr)$_2$ (1.0)	100	24	81
22	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	12	67
23	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	18	74
24	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	30	76
25	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	36	63
26[i]	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	24	21
27[j]	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	24	33
28[k]	DMF	EtN(*i*-Pr)$_2$ (1.0)	80	24	81

[a] 1 mmol of **1a**, 1 mmol of **2a**, and 1.5 mL of solvent were employed. For detailed conditional optimization table, please see Table S1 in Supporting Information. [b] Based on the amount of **1a**. [c] Average isolated yields of three repeated reactions. [d] No reaction detected. [e] Yield <3%. [f] Na_2CO_3, NaOH, NaOAc, K_2CO_3, $Ca(OH)_2$, $CaCO_3$, $MgCO_3$, Cs_2CO_3, MgO, or $Mg(OH)_2$ were tested. [g] 1-Methylpiperazine, 4-methylpiperidine, $PhCONH_2$, Et_2NH, Bu_2NH, and DMEDA were tested. [h] Pyridine, 3-acetylpyridine, and DMAP were tested. [i] The catalyst Pd@PANI was directly used without drying or baking after preparation. [j] The catalyst was dried by air at room temperature for 10 h but without baking after preparation before use. [k] Reaction scale enlarged to 25 mmol.

ICP analysis showed that the Pd@PANI catalyst contained 60.2 μg of Pd for each reaction, giving around 1555 TON at the maximum and a Pd loading for each reaction of 0.06 mol % based on the starting material **1a**. TEM was performed to study the morphology, composition, and crystal structure of Pd@PANI (Figure 1). Since the Pd NPs nucleated and grew during the *in situ* polymerization of PANI without additional chemical reagents, the distribution of Pd nanoparticles on PANI microwires was extremely uniform, and the size was ultrasmall (around 2 nm), which could be clearly seen in Figure 1b,c. Thus, it is not surprising to observe ultrahigh catalytic activity of Pd@PANI for a Heck reaction as it has been recognized that the ultrasmall particle size often results in superior performance for many catalytic applications.[10] Figure 1d showed Pd(111) lattice planes with spacing $d(111)$ = 0.224 nm, consistent with the reported literature value for nanocrystalline Pd. Scanning TEM with EDX analysis also attested to the successful loading of Pd nanoparticles on PANI microwires (Figure 1e,f).

As currently reported Heck reactions using nano-Pd@PANI catalysts have very narrow reaction scope,[6] the substrate scope of this catalyst system was our next concern. The steric hindrance effects on aryl rings were first examined: Although 4- or 3-methyl substituted iodobenzene could react with styrene **2a** smoothly to give the product **3b** or **3c** in good yields (Table 2, entries 1–2), the reaction using 2-methyl substituted iodobenzene shows much lower reactivity under the same conditions (entry 3). Higher temperature was therefore applied to address this issue, and we were very glad to find that the yield can be remarkably improved from 47% to 96% at 120 °C (entry 3). Higher temperature was also needed when employing electron-rich substrate 4-methoxyiodobenzene, affording the product **3e** in 99% yield within 12 h (entry 4). 4-Iodophenol, bearing an acidic proton that might react with base, was found to be a suitable substrate for this catalyst system, giving product **3f** in 82% yield (entry 5). Reactions of styrene **2a** with electron-poor iodobenzene was also performed, affording the corresponding products **3g**–**k** in moderate to good yields (entries 6–10). The bulky 1-iodonaphthalene could also react with styrene to afford **3l** in 77% yield (entry 11). Heteroaryl iodides were also applicable substrates (entries 12–13), and it was notable that this Pd@PANI was tolerant to sulfur-containing compounds, which were catalyst poisons in many Pd-catalyzed reactions (entry 13).[11] The application scope for olefins was further tested. Generally, reactions of iodobenzene **1a** with electron-deficient olefins were more favorable than those of electron-rich ones (entries 18–19 vs 14–17). It was interesting that, although generating the same products, the reaction of iodobenzene **1a** with (*E*)-1,2-

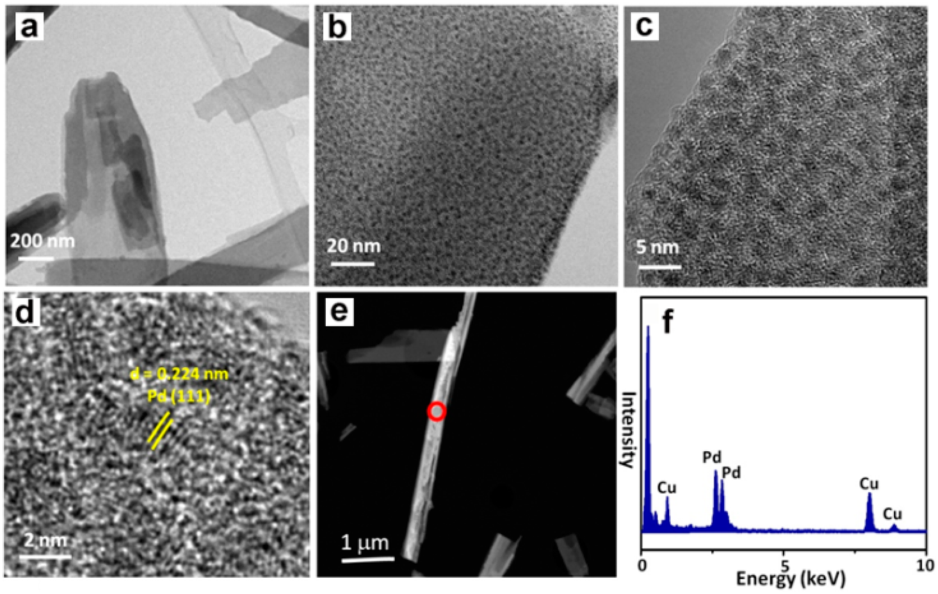


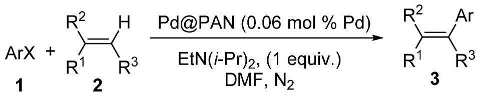
Figure 1. TEM images and EDX spectra of Pd@PANI: (a) TEM image Pd@PANI (scale bar, 200 nm), (b) magnified view of Pd@PANI (scale bar, 20 nm; Pd, small black dots), (c) magnified view of Pd@PANI (scale bar, 5 nm; Pd, small black dots), (d) HRTEM image of Pd@PANI (scale bar, 2 nm), (e) scanning TEM image Pd@PANI (scale bar, 1 *μ*m), and (f) EDX spectrum of Pd@PANI.

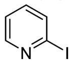
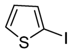
diphenylethene was favored over that with 1,1-diphenylethene (entry 20 vs 16), probably due to decreased steric hindrance of the organometallic intermediates (Figure 2). Aryl bromides were also employed, but only gave the products in low to moderate yields even at high temperature (entries 21−29), except for the reaction with 1-bromo-4-nitrobenzene, which afforded the coupling product (*E*)-1-nitro-4-styrylbenzene **3u** in 91% yield under mild conditions (entry 25). The reactions of styrene with aryl chlorides were also tested, but resulted in very low product yields, even if the electron-enriched phosphorus ligands were employed (entries 30−33).

Most impressively, PANI-supported ultrasmall Pd NPs can be reused by simple centrifugation and show excellent stability and recyclability. As can be seen in Figure 3, the recycled catalyst retained its high catalytic activity up to the sixth cycle tested, and its activity was slightly decreased in the seventh and eighth runs, probably due to a small amount of Pd leaking during reaction and separation procedures. ICP analysis demonstrated that, in each cycle, 3.2% of Pd leached into the solution, highlighting the stability of this heterogeneous Pd catalyst. To confirm that the reactions were catalyzed by Pd@PANI NPs and not by the leached homogeneous Pd species, an experiment was designed and performed to test the catalytic activity of the leaked Pd in solution (Scheme 1): A standard reaction of **1a** with **2a** was first performed under the conditions described in Table 1, entry 13. Then, the heterogeneous Pd@PANI NPs were removed by centrifugation, and a batch of fresh PhI and EtN(*i*-Pr)$_2$ was added into the supernatant liquid. The liquid was heated at 120 °C for 24 h under N_2 protection, as the conditions described in Table 2, entry 20, but the second step coupling product **3p** was obtained in only 9% yield. This indicates that the leached Pd species had low activity because, for the same reaction catalyzed by Pd@PANI NPs, the **3p** yield could reach 93%, as shown in Table 2, entry 20.

In a comparison with previous works,[6] the higher activity of this Pd@PANI catalyst was probably attributed to the very slow *in situ* polymerization of PANI polymer and formation of Pd NPs using air instead of the strong chemical oxidant ammonium persulfate, which also strengthened the interaction between supported Pd NPs and PANI surfaces and thus avoided the accumulation of Pd NPs to form stable larger clusters. The role of EtN(*i*-Pr)$_2$ was also studied. Table 1 and Figure 3 suggest several important implications: First, tertiary amines had overwhelming advantages over any other bases such as inorganic bases, DBU, pyridines and primary or secondary amines or amides (Table 1, entries 8, 15−18 vs 11−14). Second, the recovered catalyst had significantly higher activity than its first use (Figure 3). On the basis of the above results as well as the reference report,[12] we propose that trialkyl amines were able to reduce Pd(II) to activate Pd(0) in catalyst through the coordination followed by *β*-hydride transfer and reductive elimination of HX.[12] The aforementioned mechanism was clearly supported by the fact that $PdCl_2$ (1 mmol %) could efficiently catalyze the Heck reaction (77.5% isolated yield) with EtN(*i*-Pr)$_2$ as a base. The X-ray photoelectron spectroscopy (XPS) results as shown in Figure 4 further attested to the significant role of EtN(*i*-Pr)$_2$ in the Heck reaction: First, the palladium species at the surface of Pd@PANI catalyst can be very easily to be oxidized to Pd(II) with exposure to the air. This can be demonstrated by the XPS spectrum of the catalyst before and after argon ion etching the surface layers of Pd@PANI sample. The observed binding energy value of 343.0 eV (Pd 3d3) and 337.7 eV (Pd 3d5) on the XPS spectrum of the catalyst before the argon ion etching indicated the existence of palladium as Pd(II) on the surface of Pd@PANI (Figure 4a). The XPS spectrum of the catalyst after argon ion etching showed obvious binding energy peaks at 341.3 eV (Pd 3d3) and 336.0 eV (Pd 3d5), which were the characteristics of Pd(0), the real catalyst species in the Heck reaction (Figure 4b). Upon exposure to reaction conditions, the Pd(II) species on the surface of Pd@PANI can be reduced to Pd(0)[12] by EtN(*i*-Pr)$_2$ or/and etched away during the reaction to expose the Pd(0) to the reactants, supported by the fact that the content of Pd(0) was remarkably increased as shown in Figure 4c. When another base, such as DBU, was employed, Pd(II) was still the major species on the surface of the palladium

Table 2. Pd@PANI-Catalyzed Heck Cross-Couplings of Aryl Halides **1** with Olefins **2**[a]



entry	ArX	R^1, R^2, R^3	T/°C	*t* /h	**3**: /% (*E*/*Z*)[b]
1	4-MeC_6H_4I	Ph, H, H	80	24	**3b**: 71
2	3-MeC_6H_4I	Ph, H, H	80	24	**3c**: 73
3	2-MeC_6H_4I	Ph, H, H	80	48	**3d**: 47[c]
			120	12	**3d**: 96
4	4-$MeOC_6H_4I$	Ph, H, H	80	48	**3e**: 52 [c]
			120	12	**3e**: 99
5	4-HOC_6H_4I	Ph, H, H	80	24	**3f**: 82 (87:13)
6	4-FC_6H_4I	Ph, H, H	80	24	**3g**: 79
7	3-FC_6H_4I	Ph, H, H	80	24	**3h**: 60
8	2-FC_6H_4I	Ph, H, H	80	48	**3i**: 67
9	4-ClC_6H_4I	Ph, H, H	80	24	**3j**: 66
10	4-AcC_6H_4I	Ph, H, H	80	48	**3k**: 76
11	1-$C_{10}H_9I$	Ph, H, H	80	24	**3l**: 75
12		Ph, H, H	120	24	**3m**: 61
13		Ph, H, H	80	48	**3n**: 55
14	PhI	4-ClC_6H_4, H, H	80	48	**3j**: 82
15	PhI	4-BrC_6H_4, H, H	80	48	**3o**: 70
16	PhI	Ph, Ph, H	120	24	**3p**: 36[c]
17	PhI	$PhCH_2$, H, H	80	48	**3q**: 69
18	PhI	CO_2Me, H, H	80	24	**3r**: 96
19	PhI	CN, H, H	80	24	**3s**: 87 (90:10)
20	PhI	H, Ph, Ph	120	24	**3p**: 93
21[d]	PhBr	Ph, H, H	120	48	**3a**: 41[c]
			150	48	**3a**: 53[c]
22[d]	4-$MeOC_6H_4Br$	Ph, H, H	150	48	**3e**: 23 (80:20)[c]
23[d]	4-FC_6H_4Br	Ph, H, H	150	48	**3g**: 45[c]
24[d]	3,5-$(CF_3)_2C_6H_3Br$	Ph, H, H	120	48	**3t**: 39 (96:4)[c]
			150	48	**3t**: 55 (95:5)[c]
25	4-$NO_2C_6H_4Br$	Ph, H, H	80	24	**3u**: 91 (92:8)
26[d]	1-$C_{10}H_9Br$	Ph, H, H	150	48	**3l**: 60[c]
27[d]	PhBr	CO_2Me, H, H	150	48	**3r**: 30[c]
28[d]	PhBr	CN, H, H	150	48	**3s**: 58[c]
29[d]	PhBr	H, Ph, Ph	150	48	**3p**: 24[c]
30[d]	PhCl	Ph, H, H	120	48	Trace[c,e]
31[d]	4-$NO_2C_6H_4Cl$	Ph, H, H	120	48	Trace[c,e]
32[d,f]	PhCl	Ph, H, H	120	48	Trace[c,e]
33[d,g]	PhCl	Ph, H, H	120	48	Trace[c,e]
34[d,h]	PhCl	Ph, H, H	120	48	Trace[c,e]

[a] 1 mmol of **1**, 1 mmol of **2**, and 1.5 mL of DMF were employed and the reactions were monitored by TLC. [b] Isolated yields (*E*/*Z* ratio calculated by ^1H NMR in parentheses; *E*-isomers only if no *E*/*Z* was provided). [c] Reaction not completed. [d] 0.6 mol % catalyst employed. [e] Product yield <3%. [f] 0.1 mmol of dppe was employed as ligand. [g] 0.1 mmol of PCy_3 was employed as ligand. [h] 0.1 mmol of $P(n\text{-}Bu)_3$ was employed as ligand.

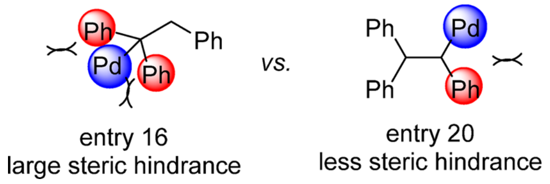


Figure 2. Comparison of the organometallic intermediates for reaction of entry 16 with entry 20.

catalyst after the reaction, as shown in its XPS spectra as well (Figure 4d).

3. CONCLUSIONS

In conclusion, we report a practical ligand-free and relatively wider-scope Heck reaction catalyzed by the recyclable heterogeneous Pd@PANI catalyst. Using air as the oxidant in the catalyst fabrication allowed Pd NPs to nucleate and grow slowly with high resistance during the *in situ* polymerization of PANI without additional chemical reagents, giving the ultrasmall and uniform Pd@PANI with ultrahigh catalytic activity. The research findings show that the Pd@PANI is an accessible, practical, and stable catalyst and might be developed to be a reliable alternative catalyst to the traditionally employed palladium complexes. Thus, more attention should be paid to extending the application scope of this catalyst in organic synthesis. More related works are ongoing in our laboratory to develop the practical green synthetic methodologies.

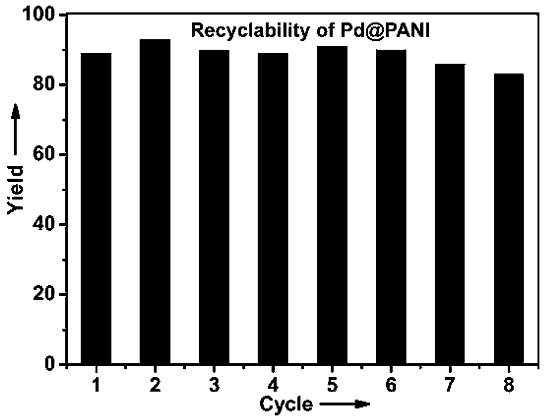
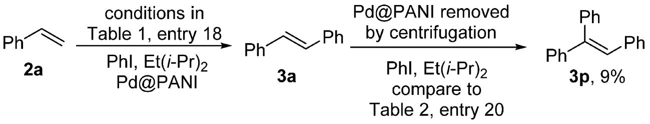


Figure 3. Recyclability of Pd@PANI in Heck reaction. Reaction scale: 10 mmol. For detailed reaction conditions, see Table 1, entry 13; yield refers to isolated yield. Pd@PANI catalyst was recovered by centrifugation.

Scheme 1. Catalytic Activity Test of the Leached Pd Species



4. EXPERIMENTAL SECTION

4.1. General Methods. Chemicals and solvents were all purchased and used as received. All reactions were monitored by TLC and/or GC analysis. Products **3** were all purified by column chromatogram. ^1H and ^{13}C NMR spectra were recorded using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Chemical shifts for ^1H and ^{13}C NMR were referred to internal Me_4Si (0 ppm), and *J*-values were shown in Hz. Melting points were measured using a digital instrument.

4.2. Preparation for the Catalyst Pd@PANI. A 465.9 mg (5 mmol) portion of aniline was dissolved in 50 mL of HCl (1 M, aq) to make solution A. A 22 mg (0.125 mmol) portion of $PdCl_2$ was dissolved in 50 mL of aqueous HCl (1 M, aq) to make solution B. Solution B was added to solution A and stirred for 2 min. The mixture stood for 24 h, and then its pH was adjusted to 7.0 with NaOH (1 M, aq). The generated precipitate was isolated by centrifugation and washed with deionized water. Then, 6 mL of deionized water was added to make a suspension. The suspension should be kept below 4 °C in a refrigerator. A 0.6 mL portion of the above suspension was diluted to 5 mL with deionized water. In each Heck cross-coupling reaction, 0.5 mL of the above diluted suspension was used. The diluted suspension was separated by centrifugation to remove water. Then, the precipitate of Pd@PANI polymer was baked in an oven at 100 °C for 0.5 h to give 0.6 mg of dried catalyst and was used in the cross-coupling reaction as catalyst.

4.3. General Procedure for Heck Cross-Couplings (Catalyst Was Not Recycled, for Table 2). Under N_2 protection, a solution of halohydrocarbons **1** (1 mmol), alkene **2** (1 mmol), and $EtN(i\text{-}Pr)_2$ (1

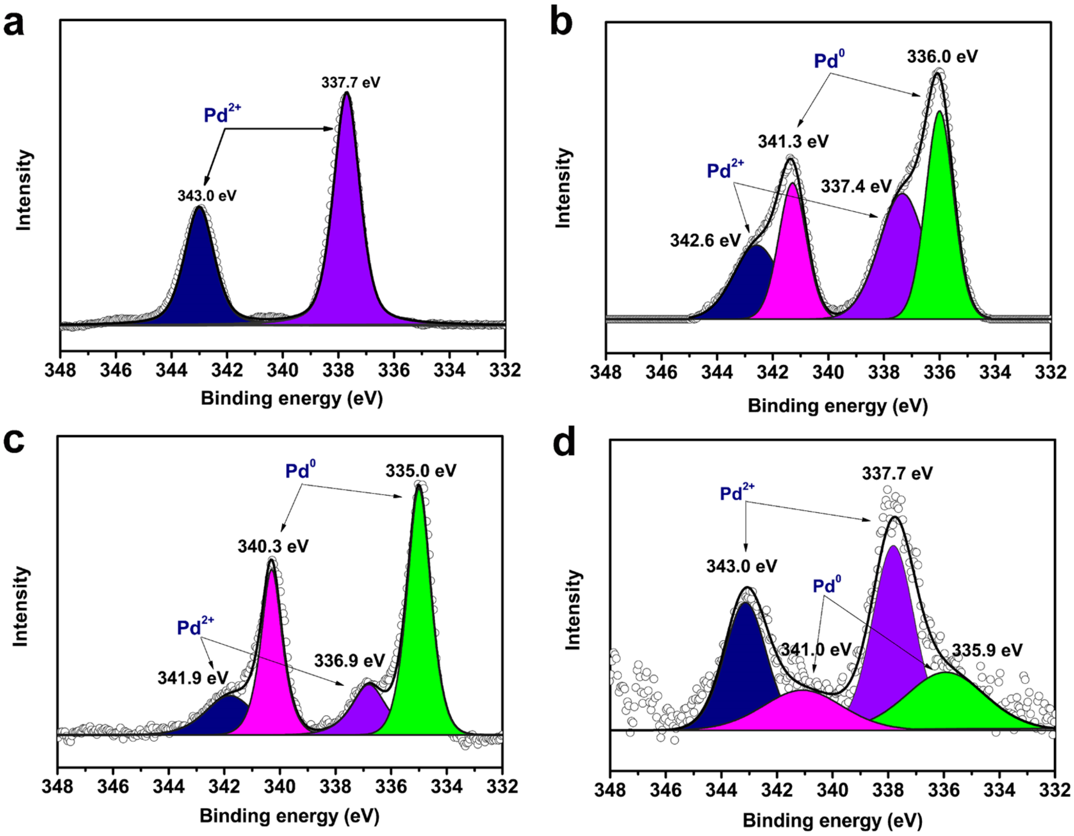


Figure 4. (a, b) XPS spectra of Pd@PANI before and after argon ion etching. (c) X-ray photoelectron spectra for Pd@PANI after reaction with EtN(*i*-Pr)$_2$ as base. (d) X-ray photoelectron spectra for Pd@PANI after reaction with DBU as base.

mmol) in DMF (1.5 mL) was injected into a reaction tube containing a magnetic bar and Pd@PANI (0.6 mg) which had been treated as described above. The mixture was stirred under N_2 at 80−120 °C for 12−48 h. After the reaction, 2 mL of saturated NaCl solution was added, and the mixture was extracted by EtOAc (2 mL × 3). Solvents in the combined organic layer were evaporated under vacuum, and the residue was purified by flash column chromatogram (eluent: petroleum ether) to afford the corresponding products **3**.

4.4. Procedure for Heck Cross-Coupling of 1a with 2a (Catalyst Recycled, for Figure 3). Under N_2 protection, a solution of **1a** (10 mmol), **2a** (10 mmol), and EtN(*i*-Pr)$_2$ (10 mmol) in DMF (15 mL) was injected into a reaction tube containing a magnetic stir bar and Pd@PANI (6.0 mg) which had been treated as described above. The mixture was stirred under N_2 at 80 °C for 24 h. After the reaction, the mixture was cooled to room temperature, and most Pd@PANI was observed to be attached on the magnetic bar and the tube wall. Then, the liquid was removed into a glass centrifuge tube for centrifugation. After centrifugation, the glass centrifugal tube and the reaction tube with magnetic bar which contained the recycled Pd@PANI catalyst were baked for the next turn of reaction. The supernatant liquid was added into saturated NaCl solution (20 mL) and extracted by EtOAc (20 mL × 3). Solvents in the combined organic layers were evaporated under vacuum, and the residue was purified by flash column chromatography (eluent: petroleum ether). The Pd@PANI in centrifuge tube could be washed into the reaction tube by DMF and reused in the next cycle of reaction together with the Pd@PANI attached on the magnetic bar and the tube wall, which was mentioned above.

4.5. Test of the Catalytic Activity of Leached Pd. A reaction was performed according to the experiment in Table 1, entry 18. Then, Pd@PANI was removed by centrifugation, and 1 mol of PhI and 1 mmol of EtN(*i*-Pr)$_2$ were added. The mixture was treated as Table 2, entry 20 in text, and after the reaction, 153 mg of **3a** (0.85 mmol) and 23 mg of **3p** (0.09 mmol) were obtained. The result indicating that the leached Pd species had very low activity because **3p** was obtained in only 9% yield, but for the same reaction catalyzed by Pd@PANI, the **3p** yield could reach 93%, as shown in Table 2, entry 20 in text.

4.6. Characterization of the Products. *(E)-1,2-Diphenylethene* ***3a***. 159 mg, 88%. White solid, mp 123.0−124.6 °C. (Lit. 124−125 °C.) IR (KBr): 3077, 3057, 3022, 1597, 1495, 1452, 1072, 1028, 984, 909, 764, 692, 540, 468 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.48 (d, *J* = 7.2 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 4H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.08 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ137.5, 128.8(d), 127.7, 126.7. MS (EI, 70 eV): *m*/*z* (%) 180 (97) [M$^+$], 179 (100), 178 (65), 165 (52). Known compound (103-30-0).[13a]

(E)-1-Methyl-4-styrylbenzene ***3b***. 138 mg, 71%. White solid, mp 121.3−122.3 °C. (Lit. 121−122 °C.) IR (KBr): 3023, 1594, 1509, 1447, 967, 808, 748, 690, 531, 494 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.30−7.33 (m, 2H), 7.21−7.22 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.01−7.08 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.6, 137.5, 134.6, 129.4, 128.7(d), 127.7, 127.4, 126.5, 126.4, 21.3. MS (EI, 70 eV): *m*/*z* (%) 195 (16) [M$^+$ + 1], 194 (96) [M$^+$], 179 (100), 178 (73). Known compound (1860-17-9).[13a]

(E)-1-Methyl-3-styrylbenzene ***3c***. 142 mg, 73%. White solid, mp 49.1−49.9 °C. (Lit. 48−49 °C.) IR (KBr): 3023, 2921, 1949, 1581, 1449, 1037, 967, 782, 749, 694, 559, 486 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.40−7.34 (m, 4H), 7.29−7.27 (m, 2H), 7.12−7.10 (m, 3H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.2, 137.5, 137.3, 128.9, 128.7, 128.6, 128.5(d), 127.6, 127.2, 126.5, 123.7, 21.5. MS (EI, 70 eV): *m*/*z* 195 (13) [M$^+$ + 1], 194 (77) [M$^+$], 179 (100), 178 (84). Known compound (14064-48-3).[13b]

(E)-1-Methyl-2-styrylbenzene ***3d***. 187 mg, 96%. Colorless oil. IR (film): 3024, 2947, 1944, 1599, 1495, 1460, 961, 758, 712, 691, 539, 490 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.33−7.29 (m, 3H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.19−7.16 (m, 1H), 7.14 (d, *J* = 4.2 Hz, 2H), 6.96 (d, *J* = 16.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.8, 136.5,

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135.9, 130.5, 130.1, 128.8, 127.7 (d), 126.7 (d), 126.4, 125.5, 20.1. MS (EI, 70 eV): *m*/*z* 195 (14) [M$^+$ + 1], 194 (85) [M$^+$], 179 (100), 178 (61). Known compound (22257-16-5).[13b]

(E)-1-Methoxy-4-styrylbenzene ***3e***. 208 mg, 99%. White solid, mp 135.1−137.0 °C. (Lit. 136−138 °C.) IR (KBr): 2836, 1905, 1809, 1606, 1508, 1449, 1289, 1249, 1180, 1114, 1028, 964, 900, 840, 783, 706, 548, 507 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.45−7.50 (m, 4H), 7.35 (t, J = 7.8 Hz, 2H), 7.24−7.25 (m, 1H), 6.96−7.08 (m, 2H), 6.90 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 159.4, 137.7, 130.2, 128.6, 128.3, 127.7, 127.2, 126.7, 126.3, 114.2, 55.3. MS (EI, 70 eV): *m*/*z* 211 (12) [M$^+$ + 1], 210 (30) [M$^+$], 44 (100), 43 (7). Known compound (1694-19-5).[13c]

(E)-4-Styrylphenol ***3f***. 161 mg, 82%. White solid, mp 184.3−185.6 °C. (Lit. 185−187 °C.) IR (KBr): 3057, 3020, 1597, 1576, 1494, 1450, 1331, 1299, 1071, 1028, 962, 908, 764, 692, 526 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.48 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.26−2.22 (m, 1H), 7.05 (d, J = 16.2 Hz, 1H), 6.96 (d, J = 16.2 Hz, 1H), 6.83 (d, J = 9.0 Hz, 2H), 4.79 (s, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ155.2, 137.6, 130.4, 128.7, 128.1, 127.9, 127.3, 126.8, 126.3, 115.6. MS (EI, 70 eV): *m*/*z* 197 (12) [M$^+$ + 1], 196 100) [M$^+$], 179 (11), 178 (12). Known compound (6554-98-9).[13d]

(E)-1-Fluoro-4-styrylbenzene ***3g***. 157 mg, 79%. White solid, mp 122.1−123.9 °C. (Lit. 123−124 °C.) IR (KBr): 2571, 1893, 1592, 1509, 1448, 1238, 1097, 967, 863, 825, 752, 691, 533, 494 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.45 (d, J = 7.8 Hz, 2H), 7.41 (dt, J = 2.4 Hz, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.03−6.95 (m, 4H). ^{13}C NMR (150 MHz, CDCl$_3$): δ162.4 (d, $J_{\mathrm{C-F}}$ = 245.6 Hz), 137.3, 133.6 (d, $J_{\mathrm{C-F}}$ = 3.2 Hz), 128.8, 128.6, 128.1 (d, $J_{\mathrm{C-F}}$ = 8.0 Hz), 127.8, 127.6, 126.6, 115.7 (d, $J_{\mathrm{C-F}}$ = 21.5 Hz). MS (EI, 70 eV): *m*/*z* 199 (14) [M$^+$ + 1], 198 (100) [M$^+$], 196 (38), 183 (37). Known compound (718-25-2).[13e]

(E)-1-Fluoro-3-styrylbenzene ***3h***. 119 mg, 60%. White solid, mp 71.0−72.2 °C. (Lit. 70−71 °C.) IR (KBr): 3023, 2413, 1956, 1581, 1450, 1266, 1205, 1147, 966, 873, 781, 753, 695, 519 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.39 (d, J = 7.8 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 7.20−7.13 (m, 3H), 7.10 (d, J = 10.2 Hz, 1H), 7.00−6.92 (m, 2H), 6.84 (t, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 163.3 (d, $J_{\mathrm{C-F}}$ = 243.8 Hz), 139.8 (d, $J_{\mathrm{C-F}}$ = 7.7 Hz), 136.9, 130.2 (d, $J_{\mathrm{C-F}}$ = 8.4 Hz), 130.1, 128.9, 128.1, 127.6 (d, $J_{\mathrm{C-F}}$ = 2.7 Hz), 126.8, 122.6 (d, $J_{\mathrm{C-F}}$ = 2.6 Hz), 114.5 (d, $J_{\mathrm{C-F}}$ = 21.3 Hz), 112.9 (d, $J_{\mathrm{C-F}}$ = 21.8). MS (EI, 70 eV): *m*/*z* 199 (14) [M$^+$ + 1], 198 (100) [M$^+$], 196 (48), 177 (38). Known compound (3041-81-4).[13f]

(E)-1-Fluoro-2-styrylbenzene ***3i***. 133 mg, 67%. White solid, mp 94.2−95.2 °C. (Lit. 94−95 °C.) IR (KBr): 3019, 1813, 1575, 1484, 1455, 1231, 1210, 1094, 968, 842, 783, 760, 690, 501 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.61 (dt, J = 1.2 Hz, J = 7.8 Hz, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.29−7.27 (m, 2H), 7.23−7.21 (m, 1H), 7.18 (d, J = 16.8 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.07 (dt, J = 1.2 Hz, J = 9.0 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 160.5 (d, $J_{\mathrm{C-F}}$ = 248.0 Hz), 137.3, 131.0 (d, $J_{\mathrm{C-F}}$ = 4.8 Hz), 128.8 (d, $J_{\mathrm{C-F}}$ = 8.4 Hz), 128.7, 127.9, 127.1 (d, $J_{\mathrm{C-F}}$ = 3.5 Hz), 126.7, 125.3 (d, $J_{\mathrm{C-F}}$ = 12.0 Hz), 124.2 (d, $J_{\mathrm{C-F}}$ = 3.5 Hz), 121.0 (d, $J_{\mathrm{C-F}}$ = 3.8 Hz), 115.8 (d, $J_{\mathrm{C-F}}$ = 22.1 Hz). MS (EI, 70 eV): *m*/*z* 199 (15) [M$^+$ + 1], 198 (100) [M$^+$], 196 (41), 183 (40). Known compound (52805-91-1).[13g]

(E)-1-Chloro-4-styrylbenzene ***3j***. 176 mg, 82%. White solid, mp 129.4−131.3 °C. (Lit. 129−131 °C.) IR (KBr): 3021, 2780, 1583, 1492, 1448, 1217, 1180, 967, 864, 817, 783, 691, 528 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.38−7.16 (m, 9H), 6.96−6.90 (m, 2H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 137.0, 135.9, 133.2, 129.4, 128.9, 128.7, 127.9, 127.7, 127.4, 126.6. MS (EI, 70 eV): *m*/*z* 215 (12) [M$^+$ + 1], 214 (69) [M$^+$], 179 (99), 176 (20). Known compound (1657-50-7).[13h]

(E)-1-(4-Styrylphenyl)ethanone ***3k***. 169 mg, 76%. White solid, mp 148.1−150.4 °C. (Lit. 149−151 °C.) IR (KBr): 1682, 1602, 1358, 1307, 1266, 1182, 958, 907, 847, 779, 701, 594 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.96 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.32−7.13 (m, 3H), 2.62 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): δ197.7, 149.2, 146.3, 140.8, 136.4, 128.4 (d), 128.3, 128.2, 128.1, 116.0, 26.7. MS (EI, 70 eV): *m*/*z* 223 (7) [M$^+$ + 1], 222 (49) [M$^+$], 179 (20), 178 (79). Known compound (20488-42-0).[13i]

(E)-1-Styrylnaphthalene ***3l***. 173 mg, 75%. White solid, mp 70.0−71.3 °C. (Lit. 70−71 °C.) IR (KBr): 3030, 2411, 1944, 1811, 1591, 1448, 1253, 1207, 1167, 1073, 1028, 959, 793, 775, 748, 692, 559, 492 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): 8.17 (d, J = 8.4 Hz, 1H), 7.83−7.73 (m, 2H), 7.67−7.53 (m, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.46−7.40 (m, 3H), 7.34 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 16.2 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 137.9, 135.3, 134.1, 132.1, 131.8, 129.1, 129.0, 128.4, 128.1, 127.0, 126.4, 126.1(d), 126.0, 124.1, 124.0. MS (EI, 70 eV): *m*/*z* 231 (18) [M$^+$ + 1], 230 (100) [M$^+$], 215 (22), 152 (26). Known compound (2840-87-1).[12j]

(E)-3-Styrylpyridine ***3m***. 111 mg, 61%. White solid, mp 81.2−82.3 °C. (Lit. 81−83 °C.) IR (KBr): 3024, 2925, 1564, 1492, 1448, 1412, 1221, 1177, 1123, 1099, 1073, 1022, 964, 801, 751, 706, 617, 530 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 8.73 (s, 1H), 8.48 (d, J = 4.2 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.31−7.28 (m, 2H), 7.16 (d, J = 16.2 Hz, 1H), 7.07 (d, J = 16.2 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 148.4, 136.6, 133.1, 132.8, 131.0, 128.8, 128.3, 126.7, 124.8, 123.6. MS (EI, 70 eV): *m*/*z* 181 (42) [M$^+$], 180 (100), 152 (20). Known compound (5097-91-6).[13k]

(E)-2-Styrylthiophene ***3n***. 102 mg, 55%. Light yellow solid, mp 112.1−113.5 °C. (Lit. 111−112 °C.) IR (KBr): 3145, 3102, 3060, 3027, 1594, 1491, 1428, 1273, 1202, 961, 839, 817, 753, 707, 692, 580, 546, 522 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.46 (d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.24−7.22 (m, 2H), 7.19 (d, J = 5.4 Hz, 1H), 7.07 (d, J = 3.6 Hz, 1H), 7.00 (t, J = 4.5 Hz, 1H), 6.93 (d, J = 16.2 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 142.9, 137.0, 128.7, 128.4, 127.6, 126.3, 126.1, 124.4, 121.8. MS (EI, 70 eV): *m*/*z* 187 (17) [M$^+$ + 1], 186 (100) [M$^+$], 185 (84). Known compound (26708-50-9).[13j]

(E)-1-Bromo-4-styrylbenzene ***3o***. 181 mg, 70%. White solid, mp 127.4−128.1 °C. (Lit. 126−128 °C.) IR (KBr): 3080, 3019, 2964, 1494, 1449, 1401, 1330, 1304, 1261, 1074, 1007, 967, 863, 814, 750, 704, 690, 528 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.50−7.46 (m, 4H), 7.38−7.35 (m, 4H), 7.27 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 7.03 (d, J = 16.2 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 137.0, 136.3, 131.8, 129.5, 128.8, 128.0, 127.9, 127.4, 126.6, 121.3. MS (EI, 70 eV): *m*/*z* 259 (6) [M$^+$ + 1], 258 (33) [M$^+$], 179 (64), 178 (100). Known compound (13041-70-8).[13l]

1,1,2-Triphenylethene ***3p***. 238 mg, 93%. White solid, mp 68.6−69.3 °C. (Lit. 69−70 °C.) IR (KBr): 3080, 3019, 2964, 1494, 1449, 1401, 1074, 1007, 967, 863, 814, 750, 704, 690, 528 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ7.26−7.20 (m, 8H), 7.14−7.13 (m, 2H), 7.07−7.02 (m, 3H), 6.95 (d, J = 6.6 Hz, 2H), 6.89 (s, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ143.4, 142.6, 140.3, 137.4, 130.4, 129.5, 128.6, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.7. MS (EI, 70 eV): *m*/*z* 257 (20) [M$^+$ + 1], 256 (100) [M$^+$], 178 (68). Known compound (58-72-0).[13m]

(E)-1,3-Diphenylprop-1-ene ***3q***. 134 mg, 69%. Colorless oil. IR (film): 3060, 3026, 2898, 1600, 1495, 1451, 1075, 1029, 965, 740, 696, 584, 494 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.32−7.15 (m, 10H), 6.43−6.30 (m, 2H), 3.50 (d, J = 7.2 Hz 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.3, 137.6, 131.2, 129.3, 128.8, 128.6, 127.2, 126.6, 126.3, 126.2, 39.5. MS (EI, 70 eV): *m*/*z* 194 (87) [M$^+$], 193 (64), 179 (45), 178 (46), 116 (48), 115 (100). Known compound (3412-44-0).[13n]

Methyl Cinnamate ***3r***. 156 mg, 96%. Colorless oil. IR (film): 3062, 3028, 2998, 2950, 1718, 1637, 1578, 1496, 1451, 1435, 1329, 1316, 1276, 1203, 1171, 1072, 1039, 1014, 980, 935, 863, 768, 712, 684, 575 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.69 (d, J = 15.6 Hz, 1H), 7.52−7.51 (m, 2H), 7.38−7.37 (m, 3H), 6.44 (d, J = 16.2 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7. MS (EI, 70 eV): *m*/*z* 162 (46) [M$^+$], 161 (28), 131 (100). Known compound (1754-62-7).[13o]

Cinnamonitrile ***3s***. 112 mg, 87%. Colorless oil. IR (film): 3055, 2217, 1674, 1618, 1494, 967, 749, 689 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$, TMS): δ 7.44−7.36 (m, 6H), 5.86 (d, J = 16.8 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 150.6, 133.6, 131.3, 129.2, 127.4, 118.2, 96.4. MS (EI, 70 eV): m/z 130 (10) [M$^+$ + 1], 129 (100) [M$^+$], 128 (26). Known compound (1885-38-7).[9d]

1-(3,5-Bis(trifluoromethyl)styryl)benzene **3t**. 174 mg, 55%. White solid, mp 51.7−53.8 °C. IR (KBr): 3089, 3043, 2929, 1777, 1638, 1616, 1577, 1497, 1469, 1447, 1378, 1279, 1218, 1184, 1165, 1119, 1030, 966, 939, 889, 847, 753, 695, 619 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 7.91 (s, 2H), 7.74 (s, 1H), 7.55 (d, J = 5.2 Hz, 2H), 7.41 (t, J = 5.0 Hz, 2H), 7.34 (d, J = 4.8 Hz, 1H), 7.24 (d, J = 16.2 Hz, 1H), 7.13 (d, J = 16.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.5, 136.0, 132.6, 132.1 (q, J_{C-F} = 33.0 Hz), 128.9, 128.8, 126.9, 126.1 (d, J_{C-F} = 2.7 Hz), 125.5, 123.4 (d, J_{C-F} = 271.1 Hz), 120.8−120.7 (m). MS (EI, 70 eV): m/z 316 (100) [M$^+$], 178 (83). Known compound (453537-08-1).[13p]

1-Nitro-4-styrylbenzene **3u**. 205 mg, 91%. Light yellow solid, mp 153.8−155.4 °C. (Lit. 154−155 °C.) IR (KBr): 3077, 3024, 2920, 1633, 1590, 1343, 1109, 971, 849, 833, 767, 695 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 8.21 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.27 (d, J = 16.4 Hz, 1H), 7.14 (d, J = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 146.8, 143.8, 136.2, 133.3, 128.9, 128.8, 127.0, 126.8, 126.3, 124.1. MS (EI, 70 eV): m/z 225 (54) [M$^+$], 179 (43), 176 (100). Known compound (1694-20-8).[13q]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01358.

Detailed conditional optimization table and ^{1}H and ^{13}C NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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