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Biopolymer-metal complex wool–Pd as a highly active heterogeneous catalyst for Heck reaction in aqueous media

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A B S T R A C T

Heterogeneous palladium catalysts, a biopolymer complex wool–Pd, have been applied in water-mediated coupling reactions of aryl bromides without assistance of any phosphine ligands. The catalyst was characterized by XPS, ICP. The results showed that aryl bromides could carry out the coupling reaction with a variety of alkenes at 80 °C, in aqueous media under atmospheric condition. More importantly, the cheap catalyst is stable, which shows negligible metal leaching, and retain good activity for at least ten successive runs without any additional activation treatment. This approach would be very useful from a practical viewpoint.

1. Introduction

The Heck reaction has been proven to be one of the most important methods for carbon–carbon bond formation between aryl halides and olefins in organic chemistry. It is used in a wide variety of organic transformations and thus it now belongs to an indispensable set of palladium-catalyzed cross-coupling reactions.[1]

In the past few years, homogeneous palladium-catalyzed reaction systems have been successfully established.[2] However, most of the reaction protocols suffer from the practical problems, such as catalyst separation, catalyst recycling, and product contamination, as well as the absolute necessary of specifical ligands[3] (for instance, phosphine or *N*-heterocyclic carbine, etc). To address these problems, supported palladium on a diverse array of organic and inorganic materials, such as resins,[4] carbon,[5] metal oxides,[6] clay,[7] ordered[8] or amorphous silicates,[9] and zeolites,[10] have been developed and used to catalyze the Heck reaction. The extensive explorations of heterogeneous catalytic systems are evidenced by a great number of publications and reviews in recent years. However, for the most cases, the immobilized catalysts generally encounter diffusion limitations under the reaction conditions can be a major problem, which was due to the aggregation and agglomeration of Pd particles into less active large particles (even bulk Pd) during the reaction. So the recyclability of the heterogeneous catalysts is thus discounted.

In previous research, some natural biopolymers, such as chitosan,[11,12] cellulose,[13] wool,[14–16] etc. have been used as efficient polymer supporters in the palladium-catalyzed several important transformations. Among them, wool represents the most special one, for the reasons that the biopolymers contain numerous amino acids units, the obvious interaction and affinity between supporter-itself and some more polar reaction media render wool with more fantastic properties, such as the possibility to taking organic reactions in aqueous phase with the assistance of this hydrophilous polymer. For the wool supported palladium catalyst, the loaded palladium particles could be distributed evenly in the surface of fibers due to the structurally ordered amino acids chains, so the formation and aggregation of Pd-black could be prevented, which was regarded as the most critical problem to the performance of palladium-catalyzed conversions.

In recent years, the green combination of aqueous media and heterogeneous palladium catalyst has been investigated as a modern fashion. Water as solvent in transition-metal catalysis has many advantages for the recycling of catalyst, product recovery, also concerning safety and environmental aspects.[17–20] Uozumi and Kimura[21] reported in 2002 a study comparing the performances of various polymeric supports holding monophosphine or chelating diphosphine palladium complexes for the coupling of iodobenzene and acrylic acid in water. From the interesting research programs, what could be concerned that the amphiphilic properties brought by the polyethylene glycol chains (PEG) promote the reaction in

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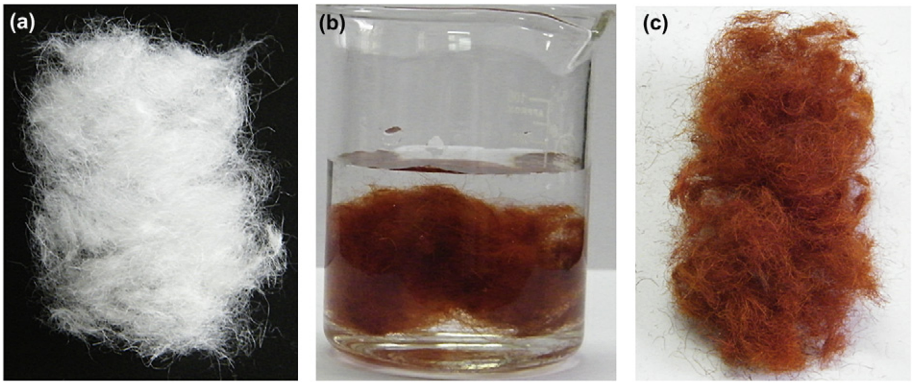
water, while polystyrene (PS) only resin catalysts were not catalytically active. In other words, the water solvated Heck reaction has decisive dependence on the supporters whether which are of hydrophilicity or lipophilicity.

Herein, we report an effective catalyst system composed of wool–palladium (wool–Pd) complex in aqueous media with very small amount of PEG-400 for the Heck reaction using NaOAc as a base. The present catalysis system could be carried out in a fashion that affords an easily separable catalyst for use in subsequent catalytic chemistry at least for 10 runs, and the total TONs is 178.

2. Results and discussion

2.1. Synthesis and characterization of the catalysts

Common commercial white wool was washed with distilled water and ethanol, and then cut to pieces. Subsequently, the wool pieces were treated by the mixture of $KMnO_4$ (3 g/L) and NaCl (25 g/L), and the pH was adjusted to 2.0, the mixture was stirred at 45 °C about 45 min, and then wool was turned to black-brown. Whereafter, the black-brown wool was dipped in the solution of Na_2SO_3 (20 g/L) and HAc (10 mol/L), stirred at 50 °C for 10 min, after the wool was returned to white, washed with water several times, and then dried at 80 °C (a, Scheme 1). 1.0 g of treated-wool pieces, 2.25 mmol $PdCl_2$ were dissolved in 30 mL of de-ionized water, the mixture was stirred at room temperature for 8 h to cause white wool pieces to become brown and the solution to become colorless and transparent (b, Scheme 1). Then, the product was filtered and washed with de-ionized water(3×20 mL) and acetone (3×20 mL), dried in a vacuum oven at 60 °C for 4 h to obtain wool supported palladium complex (c, Scheme 1).



Scheme 1. Preparation of the wool–Pd complex.

Table 1
XPS date of the wool, wool–Pd complex, and salt $PdCl_2$

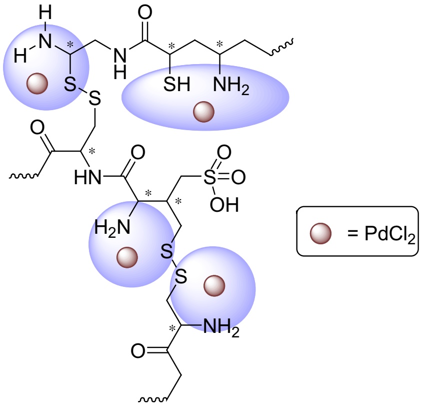
XPSPeaks		Binding energy (eV)			ΔE_b(eV)
		$PdCl_2$	Wool	Wool–Pd complex	
Pd_{3d}	$Pd_{3d\ 3/2}$	342.80		343.55	+0.75
	$Pd_{3d\ 5/2}$	337.43		338.30	+0.87
	Cl_{2p}	198.55		198.80	+0.25
N_{1s}	–NH–CO–		400.05	399.8	−0.32
	$-NH_2$		400.37	399.25	−0.55
S_{2p}	$-SO_3H$		168.18	167.87	−0.31
	–S–S–		165.05	165.75	+0.7
	–SH		163.80	163.00	−0.8
O_{1s}			531.93	532.12	+0.19

The binding energy is referred to C_{1s}=284.80 eV.

The binding energies of wool, $PdCl_2$, and wool–Pd complex were obtained by XPS analysis (Table 1). The binding energy of the $Pd_{3d\ 3/2}$ and $Pd_{3d\ 5/2}$ in the Wool–Pd complex increase 0.75 eV and 0.87 eV, respectively; the change of Pd_{3d} binding energy means the decrease of its electron density. Little change of the binding energy of the Cl_{2p} was observed, this means there are uncreative Cl exist though the chemical bond formed in this process. There are two kinds of nitrogen-containing group; –NH–CO– and $-NH_2$ in wool, and N_{1s} binding energy for them are different. Such data in wool–Pd are also different from those in wool. The difference of N_{1s} binding energies between –NH–CO– in wool and –NH–CO– in wool–Pd is 0.32 eV, and that between $-NH_2$ in wool and $-NH_2$ in wool–Pd is 0.55 eV. In the same way, there are three kinds of S containing group, $-SO_3H$, –SH, and –S–S–, in wool, and their S_{2p} binding energies are different. The difference of S_{2p} binding energy between $-SO_3H$ in wool and $-SO_3H$ in wool–Pd is only 0.31 eV, that between –SH in wool and –SH in wool–Pd is 0.8 eV, and that between –S–S– in wool and –S–S– in wool–Pd is 0.7 eV. The difference of O_{1s} binding energy between wool and wool–Pd also could not be detected. These results show that coordination or ionic bonds are formed by the connection of N atoms (in $-NH_2$) and S atoms (in –SH and –S–S–) with Pd atoms in the wool–Pd complex. The structure of wool–Pd may be shown as Scheme 2.

2.2. Heck reaction in water

To explore the catalytic activity of wool–Pd complex catalyst, we chose the coupling of bromobenzene with styrene as model reaction. In our catalysis system, it was observed clearly that base plays very important role in the transformation. We found that Cs_2CO_3, TBAB, Et_3N, and KOH were ineffective in providing the corresponding cross-coupling product. However, an increase in the cross-coupling reactivity was detected with Na_2CO_3 and K_2CO_3, under similar conditions. Finally, the reaction carried out in the



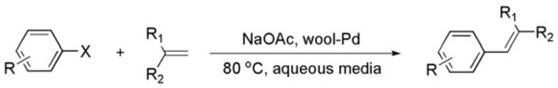
Scheme 2. The possible structure of wool–Pd.[16]

presence of different bases revealed NaOAc as a suitable base to obtain a high yield of the coupling product. Further optimization of conditions was achieved by the solvent, surprisingly, when a small quantity of PEG-400 (33 mg) were added, the coupling bromobenzene with styrene could be accelerated greatly (99% conversion). While, in the absence of PEG-400, 79% cross-coupling conversion was obtained. Thereby, the appropriate condition is optimized as bromobenzene (1.0 mmol), alkene (1.5 mmol), NaOAc (1.5 mmol), 50 mg of wool–Pd complex catalyst (Pd 11.74%), stirred in 15 mL aqueous media (PEG-400=33 mg) at 80 °C under atmospheric conditions.

Having established that the combination of wool–Pd complex catalyst and NaOAc constitutes a highly active catalyst system for the Heck reaction, we next examined the coupling of several other representative aryl bromides with different olefin substrates with the results listed in Table 2. Bromobenzene always could give excellent yield of cross-coupled product (entries 1–8). Similarly, the less reactive 4-bromotoluene was then treated with **1b**, **2b**, and **6b** (entries 9–11), and good yields were obtained: 93%, 94%, and 93%. As expected, the more reactive 4-bromobenzaldehyde underwent clean coupling with **1b**, **6b**, and **9b**, giving essentially a quantitative yield of the product (entries 12–14). Fortunately, the catalytic system can be used for selective coupling of bromo groups keeping chloro functionalities intact (entries 15–18). Notably, there was not any obvious trend or difference in reactivity between the systems of varied electronics. The coupling reaction of both electron-deficient and electron-rich aryl bromides with olefins also proceeded smoothly to furnish the Heck products with good to excellent yields. Encouraged by these results, aryl chlorides containing electron-withdrawing groups, such as *p*-nitrochlorobenzene was then treated with **1b**, **2b**, **9b**, and **4b** (entries19–22), and gave the coupling products in 93%, 95%, 91%, and 96% yields, respectively. However, for unactivated aryl chlorides (entry 23), only 20% yield of the product was obtained.

For all the olefins examined, both electron-rich and electron-poor olefins give similar yields. Even styrene derivatives are conveniently accessible in good yields. When substituted vinylic substrates, such as different acrylate esters, were employed (entries 6–8, 11, 13, and 18), high yields and only *E*-isomers were obtained. In particular, 1,1-diphenylethylene, which has some discernible steric-encumbrance, afforded the corresponding products in lower yields (entries 14, 17, and 21). All coupling products were purified and characterized; only *E*-isomers were obtained which was confirmed by NMR.

Table 2
Heck reactions of aryl halides with olefins[a]



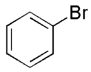
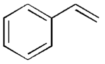
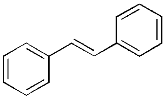
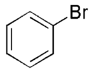
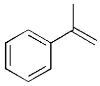
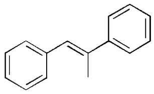
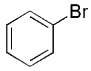
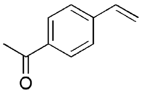
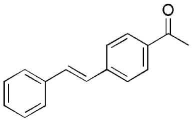
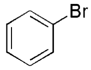
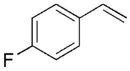
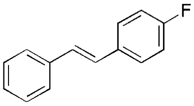
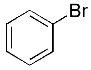
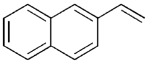
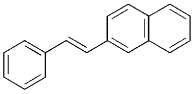
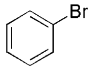
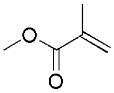
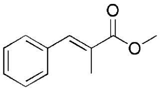
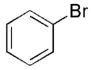
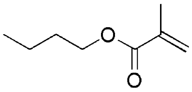
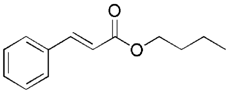
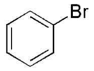
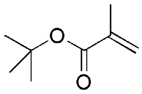
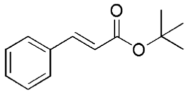
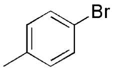
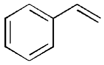
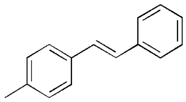
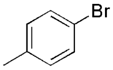
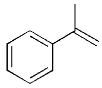
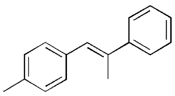
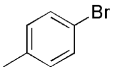
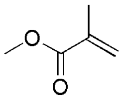
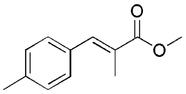
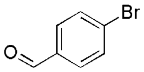
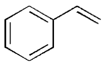
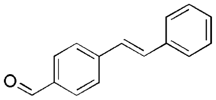
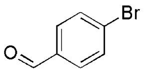
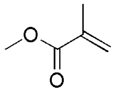
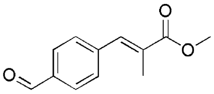
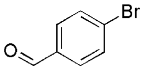
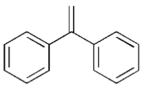
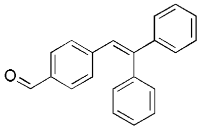
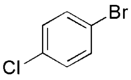
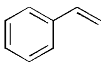
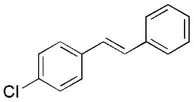
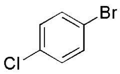
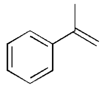
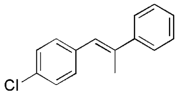
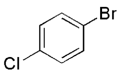
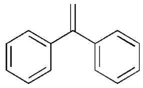
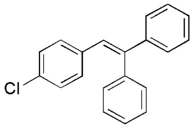
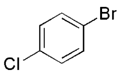
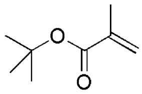
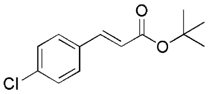
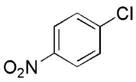
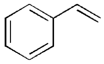
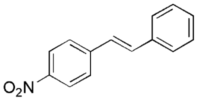
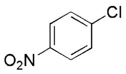
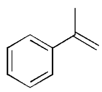
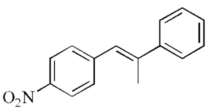
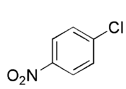
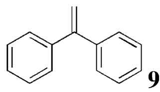
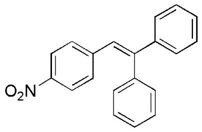
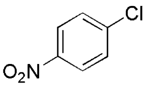
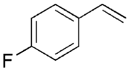
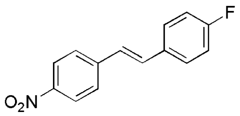
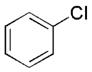
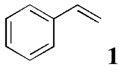
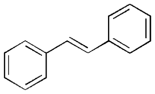
Entry	Aryl halide	Alkene	Product	Yield[b]
1	 **1a**	 **1b**	 **1c**	95
2	 **1a**	 **2b**	 **2c**	93
3	 **1a**	 **3b**	 **3c**	95
4	 **1a**	 **4b**	 **4c**	95
5	 **1a**	 **5b**	 **5c**	99
6	 **1a**	 **6b**	 **6c**	95
7	 **1a**	 **7b**	 **7c**	96

Table 2 (*continued*)

Entry	Aryl halide	Alkene	Product	Yield[b]
8	 **1a**	 **8b**	 **8c**	98
9	 **2a**	 **1b**	 **9c**	93
10	 **2a**	 **2b**	 **10c**	94
11	 **2a**	 **6b**	 **11c**	93
12	 **3a**	 **1b**	 **12c**	98
13	 **3a**	 **6b**	 **13c**	96
14	 **3a**	 **9b**	 **14c**	95
15	 **4a**	 **1b**	 **15c**	95
16	 **4a**	 **2b**	 **16c**	96
17	 **4a**	 **9b**	 **17c**	91
18	 **4a**	 **8b**	 **18c**	96
19	 **5a**	 **1b**	 **19c**	93
20	 **5a**	 **2b**	 **20c**	95

(*continued on next page*)

Table 2 (*continued*)

Entry	Aryl halide	Alkene	Product	Yield[b]
21	 **5a**	 **9b**	 **21c**	91
22	 **5a**	 **4b**	 **22c**	96
23	 **6a**	 **1b**	 **1c**	20

[a] Reaction conditions: aryl halides (1.0 mmol), alkene (1.5 mmol), NaOAc (1.5 mmol), catalyst (50 mg the amount of Pd is 0.055 mmol), stirred in 15 mL aqueous media with PEG-400 (33 mg) at 80 °C, 24 h.

[b] Yield of isolated product.

2.3. Recycling of the catalyst

An important point concerning the use of heterogeneous catalysts is its lifetime, particularly for industrial and pharmaceutical applications of the Heck reaction. For the recycling study, Heck reaction was performed with bromobenzene and styrene, maintaining the same reaction conditions as described above. The successive operations were depicted as follows: after the end of the reaction, the mixture was cooled down to room temperature and then extracted with ether (3×10 mL). The organic layer was removed, and then bromobenzene (1.0 mmol), styrene (1.5 mmol), and base (1.5 mmol) were added to the solution into the next run. TLC monitored the reaction progress, and the conversion and product selectivity were determined using GC analysis. It indicates that the catalyst is very stable and can be recycled more than nine times. ICP-AES measurement clearly verified that the Pd contents of the polymer-supported catalyst varied within very narrow scope between 11.70% and 11.18% (Fig. 1). So the catalyst leaching was almost avoided, and the contamination of palladium residues for the products also could be suppressed.

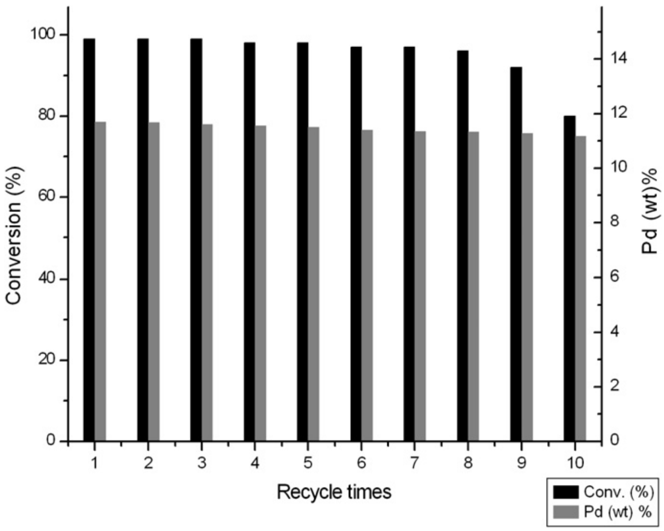


Fig. 1. Recycling test of wool–Pd complex catalyst with bromobenzene and styrene.

To further investigate the reused catalyst, XPS was employed to characterize. Fig. 2 showed the Pd_{3d} spectrum of the reused catalyst. It can be seen that a doublet for two chemically different Pd entities, with peak binding energies of 335.0 eV ($Pd_{3d\ 5/2}$) and 340.51 eV ($Pd_{3d\ 3/2}$), which confirmed the presence of Pd^0 in the reused catalyst. The XPS results indicated that Pd (0) was formed during the catalytic reaction. This was in an agreement with the previous report.

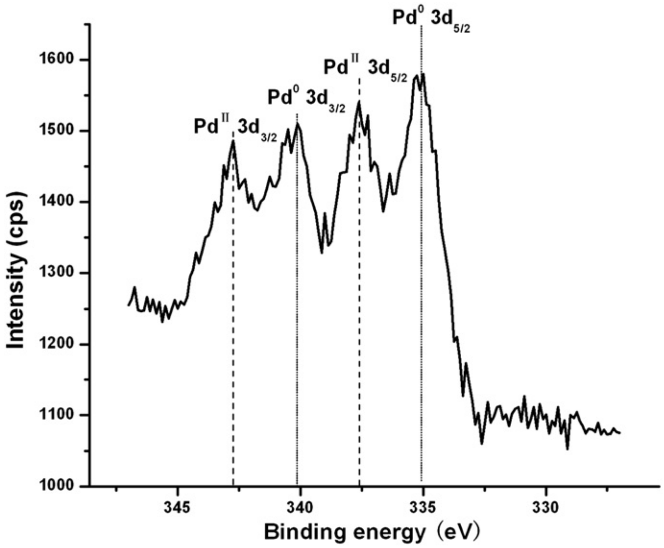


Fig. 2. XPS spectra of the reused wool–Pd complex catalyst.

3. Conclusion

In summary, we have developed a general method for the Heck coupling of aryl halide, including deactivated, electron-rich substrates, with a broad of substituted olefins. The reaction conditions were unprecedented: (1) natural biopolymer as catalyst support, and the catalyst was synthesized via simply method; (2) an environmentally safer aqueous medium was employed; (3) the catalyst was highly reusable, easy to separate, and 10 reuses did not result in any appreciable decreasing in initial activity. Further efforts to study the detailed mechanism and extend the application of the system to other coupling transformations are underway in our laboratory.

4. Experimental

4.1. Chemicals

All starting materials and reagents were commercially available and used without further purification. All products have been previously reported and characterized. All known products gave satisfactory analytical data corresponding to the reported literature values. Wool was provided by Gansu Jingyuan Woolen Mill.

4.2. Apparatus

All NMR spectra are recorded on MERCURY (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) spectrometers; chemical shifts are expressed in parts per million (δ units) relative to TMS signal as an internal reference in $CDCl_3$. Gas chromatography (GC) analysis was performed on a Shimadezu GC-2010 equipped with a 15 m×0.53 mm×1.5 μm RTX-1 capillary column and a oxyhydrogen flame detector. XPS measurement was recorded on PHI5702 photoelectron spectrometer. Binding energy was referred to C_{1s} (284.80 eV). ICP-AES were measured on IRIS Advantage.

4.3. General experimental procedure for Heck reaction

Aryl halide (1.0 mmol), alkene (1.5 mmol), and NaOAc (1.5 mmol) were added to 15 mL aqueous media (PEG-400=33 mg) in a 25 mL beaker, and then 50 mg of wool–Pd complex catalyst (Pd 0.055 mmol) was added sequentially, the mixture was stirred at 80 °C under natural condition. To study the progress of the reaction, samples of the reaction mixture were collected at different time interval and quantified by GC analysis. At the end of the reaction, the aqueous solution was cooled down to room temperature, extracted with ethyl ether (3×5 mL). The organic phases were then dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate and petroleum ether as eluent. The product was analyzed by GC–MS or NMR analysis. The conversion and selectivity were determined using GC analysis. All the prepared compounds are known and were compared with authentic samples.

4.4. The NMR data for the products[22,23]

*4.4.1. (E)-1,2-Diphenylethene (**1c**).* White solid (0.171 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53–7.51 (d, *J*=8 Hz, 4H), 7.38–7.34 (m, 4H), 7.28–7.25 (m, 2H), 7.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.27, 128.64, 127.57, 126.45.

*4.4.2. (E)-1,2-Diphenylprop-1-ene (**2c**).* Colorless oil (0.18 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54–7.52 (m, 2H), 7.45–7.43 (m, 2H), 7.39–7.35 (m, 4H), 7.31–7.30 (m, 2H), 6.84 (s, 1H), 4.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.94, 140.75, 139.47, 128.89, 128.30, 128.21, 127.41, 126.08, 17.46.

*4.4.3. 1-(4-Styrylphenyl)ethanone (**3c**).* White solid (0.21 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53–7.50 (m, 4H), 7.38–7.34 (m, 2H), 7.28–7.25 (m, 1H), 7.10–7.07 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=169.45, 149.99, 137.10, 135.11, 128.90, 128.66, 127.66, 127.60, 127.38, 126.46, 121.76, 21.14.

*4.4.4. 1-Fluoro-4-styrylbenzene (**4c**).* Colorless oil (0.188 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.35–7.31 (m, 4H), 7.25–7.22 (m, 2H), 7.04–6.88 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.84, 130.44, 129.8, 128.78, 128.20, 127.83, 127.15, 115.10.

*4.4.5. 2-Styrylnaphthalene (**5c**).* White solid (0.2268 g, 99%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.86–7.81 (m, 4H), 7.76–7.74 (m, 1H), 7.58–7.56 (m, 2H), 7.48–7.44 (m, 2H), 7.40–7.37 (m, 2H), 7.31–7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.32, 134.79, 133.68, 133.01, 129.00, 128.74, 128.70, 128.29, 127.97, 127.65, 126.60, 126.51, 126.31, 125.88, 123.47.

*4.4.6. (E)-Methyl 2-methyl-3-phenylacrylate (**6c**).* Pale-yellow oil (0.167 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.70 (s, 1H), 7.40–7.39 (d, *J*=4 Hz, 2H), 7.34–7.28 (m, 2H), 7.23–7.19 (m, 1H), 3.82 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=169.15, 138.92, 135.83, 129.60, 129.00, 128.39, 126.31, 53.07, 14.04.

*4.4.7. (E)-Butyl cinnamate (**7c**).* Yellow oil (0.196 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.70–7.66 (d, *J*=16 Hz, 1H), 7.54–7.52 (m, 2H), 7.39–7.37 (m, 3H), 6.46–6.42 (d, *J*=16 Hz, 1H), 4.23–4.20 (m, 2H), 1.71–1.67 (m, 2H), 1.47–1.41 (m, 2H), 0.97–0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.07, 144.51, 134.43, 130.17, 128.83, 128.00, 118.23, 64.40, 30.74. 19.17, 13.73.

*4.4.8. (E)-tert-Butyl cinnamate (**8c**).* Pale-yellow oil (0.20 g, 98%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.61–7.57 (d, *J*=16 Hz, 1H), 7.52–7.50 (m, 2H), 7.38–7.36 (m, 3H), 6.39–6.35 (d, *J*=16 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.29, 143.49, 129.90, 128.76, 127.90, 120.13, 120.11, 80.46, 28.15.

*4.4.9. 4-Methyl-trans-stilbene (**9c**).* White solid (0.18 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52–7.50 (m, 2H), 7.43–7.41 (m, 2H), 7.37–7.33 (m, 2H), 7.27–7.26 (m, 1H), 7.18–7.16 (d, *J*=8 Hz, 2H), 7.08–7.07 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.50, 137.47, 134.50, 129.37, 128.62, 128.58, 127.65, 127.37, 126.39, 126.36, 21.25.

*4.4.10. 1-((E)-1-p-Tolylprop-1-en-2-yl)benzene (**10c**).* Pale-yellow oil (0.196 g, 98%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53–7.51 (d, *J*=8 Hz, 2H), 7.40–7.42 (d, *J*=8 Hz, 2H), 7.37–7.35 (m, 2H), 7.10–7.08 (m, 3H), 6.81 (s, 1H), 2.37 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.06, 144.08, 140.83, 136.67, 129.03, 128.85, 128.20, 127.36, 127.01, 126.09, 29.69, 17.47.

*4.4.11. (E)-Methyl 2-methyl-3-p-tolylacrylate (**11c**).* Colorless oil (0.176 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.67 (s, 1H), 7.32–7.30 (d, *J*=8 Hz, 2H), 7.21–7.19 (d, *J*=8 Hz, 2H), 3.82 (s, 3H), 2.37 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=169.29, 141.22, 138.96, 138.43, 132.97, 129.70, 129.08, 52.02, 21.32, 14.09.

*4.4.12. 4-Styrylbenzaldehyde (**12c**).* White solid (0.204 g, 98%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.00 (s, 1H), 7.88–7.86 (d, *J*=8 Hz, 2H), 7.67–7.65 (d, *J*=8 Hz, 2H), 7.56–7.54 (d, *J*=8 Hz, 2H), 7.41–7.37 (m, 2H), 7.34–7.29 (m, 1H), 7.26–7.25 (d, *J*=4 Hz, 1H), 7.17–7.13 (d, *J*=16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.56, 143.36, 136.48, 135.27, 132.14, 130.19, 128.79, 128.45, 127.27, 126.85.

*4.4.13. (E)-Methyl 3-(4-formylphenyl)-2-methylacrylate (**13c**).* White solid (0.1958 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.03 (s, 1H), 7.92–7.90 (d, *J*=8 Hz, 2H), 7.71 (s, 1H), 7.55–7.53 (d, *J*=8 Hz, 2H), 3.84 (s, 3H), 2.14–2.13 (d, *J*=4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.60, 168.57, 141.94, 137.37, 135.63, 130.95, 130.02, 129.66, 52.29, 14.23.

*4.4.14. 4-(2,2-Diphenylvinyl)benzaldehyde (**14c**).* Yellow solid (0.27 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.89 (s, 1H), 7.64–7.62 (d, *J*=8 Hz, 2H), 7.35–7.34 (m, 8H), 7.17–7.15 (m, 4H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.63, 145.89, 143.78, 142.71, 139.64, 134.34, 130.19, 129.93, 129.39, 128.77, 128.29, 128.15, 127.93, 127.76, 126.79.

*4.4.15. 1-(4-Chlorostyryl)benzene (**15c**).* White solid (0.204 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.51–7.49 (d, J=8 Hz, 2H), 7.45–7.43 (m, 2H), 7.38–7.27 (m, 5H), 7.07–7.06 (d, J=4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.92, 135.79, 133.11, 129.25, 128.80, 128.70, 127.84, 127.62, 127.31, 126.50.

*4.4.16. 1-((E)-1-(4-Chlorophenyl)prop-1-en-2-yl)benzene (**16c**).* Pale-yellow solid (0.22 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52–7.50 (d, J=8 Hz, 2H), 7.39–7.28 (m, 7H), 6.77 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.62, 138.14, 136.72, 132.12, 130.38, 128.35, 128.30, 127.35, 126.44, 125.95, 17.47.

*4.4.17. 1-(2-(4-Chlorophenyl)-1-phenylvinyl)benzene (**17c**).* Pale-yellow solid (0.263 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83–7.81 (d, J=8 Hz, 1H), 7.63–7.58 (m, 3H), 7.52–7.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.54, 132.38, 130.02, 128.23.

*4.4.18. (E)-tert-Butyl 3-(4-chlorophenyl)acrylate (**18c**).* Colorless oil (0.228 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.55–7.51 (d, J=16 Hz, 1H), 7.45–7.43 (d, J=8 Hz, 2H), 7.35–7.33 (d, J=8 Hz, 2H), 6.36–6.32 (d, J=16 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.02, 142.06, 135.79, 133.14, 129.07, 120.75, 80.69, 28.16.

*4.4.19. 1-(4-Nitrostyryl)benzene (**19c**).* Yellow solid (0.209 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.24–8.22 (d, J=8 Hz, 2H), 7.65–7.63 (d, J=8 Hz, 2H), 7.57–7.55 (d, J=8 Hz, 2H), 7.42–7.30 (m, 4H), 7.17–7.13 (d, J=16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.72, 143.82, 136.13, 133.28, 129.62, 128.87, 126.99, 126.25, 124.13, 123.53.

*4.4.20. 1-((E)-1-(4-Nitrophenyl)prop-1-en-2-yl)benzene (**20c**).* Yellow solid (0.228 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.25–8.23 (d, J=8 Hz, 2H), 8.13–8.11 (d, J=8 Hz, 2H), 7.54–7.50 (m, 4H), 7.39–7.30 (m, 1H), 6.85 (s, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.37, 145.48, 145.08, 143.05, 129.57, 128.48, 128.41, 127.83, 126.02, 123.62, 17.82.

*4.4.21. 1-(2-(4-Nitrophenyl)-1-phenylvinyl)benzene (**21c**).* Yellow solid (0.273 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.99–7.97 (d, J=8 Hz, 2H), 7.37–7.34 (m, 8H), 7.18–7.12 (m, 4H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.25, 130.13, 129.98, 129.96, 128.92, 128.43, 128.37, 127.84, 125.72, 123.30.

*4.4.22. 1-(4-Nitrostyryl)-4-fluorobenzene (**22c**).* Yellow solid (0.233 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.23–8.21 (d, J=8 Hz, 2H), 7.63–7.61 (d, J=8 Hz, 2H), 7.55–7.51 (m, 2H), 7.25–7.21 (d, J=16 Hz, 1H), 7.11–7.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.21, 161.73, 146.77, 143.64, 132.00, 128.58, 126.77, 126.07, 124.15, 116.03.

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