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Preparation of polystyrene-supported soluble palladacycle catalyst for Heck and Suzuki reactions

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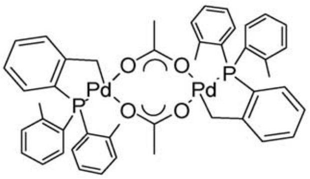
Abstract—A polystyrene-supported palladium complex soluble in tetrahydrofuran and *N*,*N*-dimethylacetamide and precipitated in diethyl ether or acetonitrile was prepared from two routes as an excellent and recyclable palladacycle catalyst for carbon–carbon bond formation in Heck and Suzuki reactions to give high yields of the desired products.

1. Introduction

The advantage of using soluble polymers to recover catalysts and ligands has its origins in the synthetic approaches to peptide and oligonucleotide synthesis that were developed in the labs of Merrifield and Letsinger in the 1960s.[1,2] Although soluble polymers were common 40 years ago, but they did not receive as much attention for using as catalyst supports as was the case for their cross-linked, insoluble analogues. However, the uses of soluble polymer systems have substantially expanded in recent years due to the point that soluble polymers are no longer uncommon as supports for catalysts and ligands.[3–5] On the other hand, palladacycles have been known for over 20 years; yet they have been used as catalysts recently.[6–10] Nitrogen-, phosphorus-, and sulfur-containing palladacycles are emerging as a new family of palladium catalyst precursors, and they have recently, become the most simple and efficient catalyst in applying to Heck-Mizoroki, Suzuki-Miyaura and Sonogashira reactions.[11] Herrmann and his co-workers have demonstrated that Herrmann's palladacycle catalyst **1** is thermally stable and efficient catalyst for Heck-Mizoroki, Suzuki-Miyaura, and Sonogashira reactions.[12–15] It also had been shown to have high reactivity toward arylation of olefins with aryl chlorides.[16] Although the palladacycle catalyst, as Herrmann reported, have high reactivity to promote a lot of reactions, only a few reports on the recovery of palladacycle catalysts were reported in the literature.[17–23] In addition, phosphorus-containing polystyrene was generally used as the ligand to trap and reuse Pd catalysts after the reaction.[24–30] In this paper, we summarized two synthetic routes for the synthesis of a polystyrene-supported palladacycle catalyst **2** which can be used as an efficient recyclable palladium catalyst for running Heck-Mizoroki and Suzuki-Miyaura reaction.[31]



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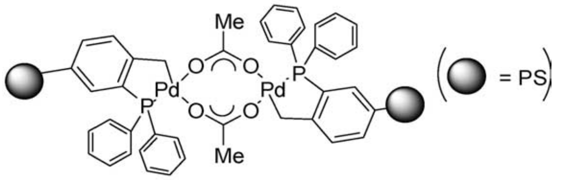

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2. Results and discussion

The two synthetic routes of the polystyrene-supported palladacycle catalyst are shown in Scheme 1. In the first

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Keywords: Supported catalyst; Heck reaction; Suzuki reaction; Recyclable catalyst; Polystyrene-bound catalyst; Palladacycle catalyst.

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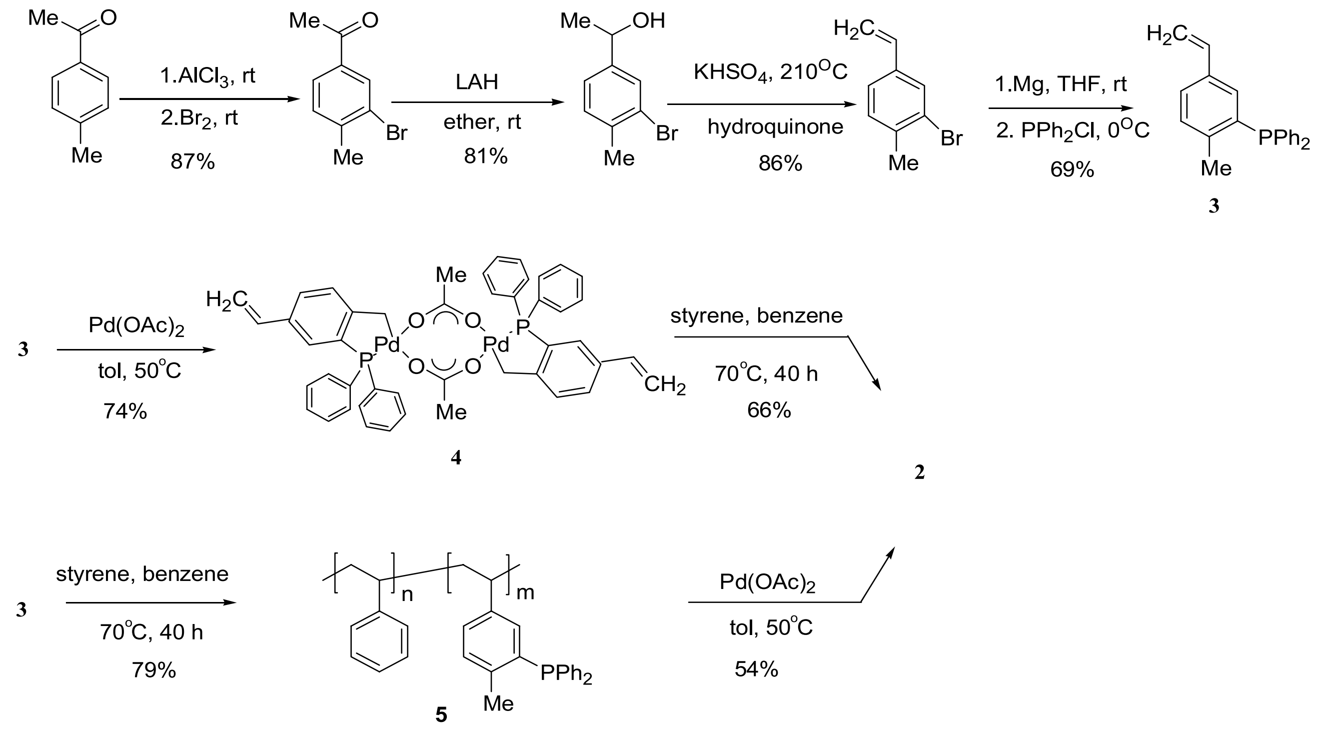
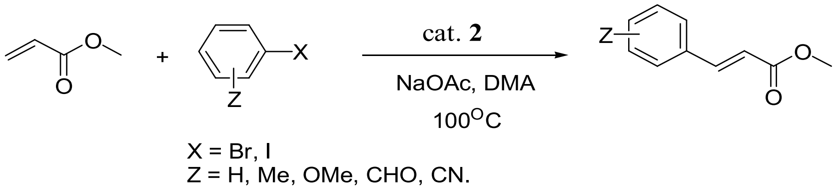


Scheme 1. Two routes for the synthesis of polystyrene-supported pallacycle catalyst **2**.

route, *trans*-di(μ-acetato)-bis[2-(diphenylphosphino)-4-vinylbenzyl]dipalladium(II) **4** was synthesized from 3-(diphenylphosphino)-4-methylstyrene **3** by heating with palladium acetate in toluene at 50 °C.[32] Compound **3** was prepared in moderate yield by bromination ($Br_2/AlCl_3$)[33] of 4-methylacetophenone followed by the reduction (LAH/ether), dehydration ($KHSO_4$)[34] and coupling with chlorodiphenylphosphine (Mg/THF; $ClPPh_2$).[35] Considering the proper space around the palladium in the catalyst, the palladacycle precursor **4** was copolymerized with 6 equiv of styrene at 70 °C (Route 1) to give polystyrene-supported palladacycle catalyst **2**. Alternatively, the phosphine-containing monomer **3** was copolymerized with 6 equiv of styrene at 70 °C to form the phosphine-bound polystyrene **5**, which was then heating with Pd(II) acetate in toluene at 50 °C (Route 2) to form polystyrene-supported palladacycle catalyst **2**. The exterior deep dark brown color and their ^{31}P NMR and ^{1}H NMR spectral data are the same for the catalyst **2** obtained from Route 1 and Route 2. The total yields for two routes via **4** and **5** for the preparation of polystyrene-supported palladacycle catalyst **2** were 21 and 18%, respectively, on the basis of atomic absorption analysis of palladium in **2**. The phosphorous-containing compounds were analyzed by solution phase ^{31}P NMR in $CDCl_3$. The chemical shift of phosphous in **3** appeared at −12 ppm as a singlet, while it was shifted to 17 ppm as a singlet in **4**. On the other hand, the methyl protons in **3** appeared at 2.36 ppm as a singlet, while the methylene protons in **4** appeared at 3.63 ppm as a broad singlet in ^{1}H NMR spectrum. The signal of catalyst **2** in ^{31}P NMR spectrum was observed at 53 ppm before and after Heck reaction, while the signal of catalyst **4** in ^{31}P NMR spectrum observed at 17 ppm before Heck reaction but appeared at 17 ppm along with a new peak at 53 ppm after Heck reaction (the peaks ratio at 17 and 53 ppm is about 7:3). The peak at 53 ppm in ^{31}P NMR spectrum became the sole peak after six times recycling of the catalyst **4**. Thus, the catalyst **4** was polymerized completely under the reaction conditions. On the other hand, the chemical shift of phosphorus in **5** appeared at −12 ppm as a singlet. Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicated that M_w of catalyst **2** prepared from Route 1 and Route 2 was 1.434×10^4 and 1.529×10^4 g/mol, respectively. Atomic absorption spectrophotometer analysis showed that palladium was containing at 86.39 and 82.91 mg of Pd per gram of **2** prepared from Route 1 and Route 2, respectively.

To test the applicability of polystyrene-supported palladacycle catalyst **2** obtained from the above two routes, we examined the Heck reaction of methyl acrylate and various aryl halide in the presence of NaOAc in *N*,*N*-dimethylacetamide as shown in Table 1. Under various reaction conditions, all the desired products were isolated in more than 90% yields. Thus, the polystyrene-supported catalyst **2** can easily promote the Heck reaction of aryl bromides- and iodides-containing with either electron-rich or electron-withdrawing group (Eq. 1), which produced only one major product as determined from GC and crude ^{1}H NMR spectral analysis. The polystyrene-supported catalyst **2** prepared with other ratio of styrene (mole ratio of styrene/**4** = 3 and 9) were also synthesized and were run as the catalyst in the above Heck reaction. Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicated that M_w of catalyst **2** prepared from mole ratio of styrene/**4** = 3 and 9 was 1.126×10^4 and 1.578×10^4 g/mol, respectively. No obvious difference was observed in the results of the above Heck reaction among these polystyrene-supported catalysts prepared from different ratio of styrene/**4**. Thus, the reactivity of catalyst

Table 1. Heck reaction of using polystyrene-supported catalyst **2**



X = Br, I
Z = H, Me, OMe, CHO, CN.

(**eq 1**)

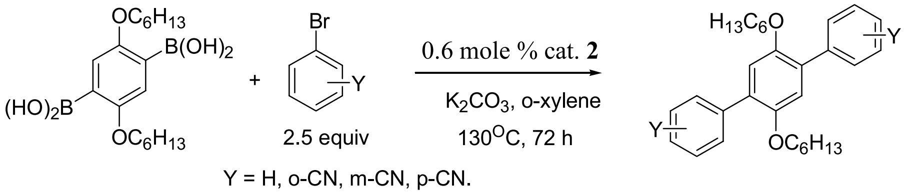
Entry	Haloarene	Catalyst **2** (equiv)	Temp (°C)	Time (h)	Iso. Yield (%)	
					Route 1	Route 2
1	Iodobenzene	0.02	100	8	>99	99
2	Bromobenzene	0.05	130	48	97	98
3	4-Bromotoluene	0.05	130	48	95	93
4	4-Bromoanisole	0.05	130	48	92	92
5	2-Bromobenzaldehyde	0.002	100	10	>99	99
6	4-Bromobenzonitrile	0.02	100	10	>99	98

2 was proved to be similar to Herrmann's palladacycle catalyst **1**. Furthermore, we also found that the reactivity of polystyrene-supported palladacycle catalyst **2** obtained from two different precursors were similar to each other based on the yields of the above model Heck reaction, although the catalyst **2** obtained from Route 2 gave a little lower yields than that from Route 1.

The polystyrene-supported catalyst **2** was soluble in tetrahydrofuran, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, toluene, chloroform, dichloromethane and not very soluble in methanol, acetonitrile, hexane, and diethyl ether. Diethyl ether and acetonitrile were used here, to precipitate our new catalyst **2**. Salt removal was skipped due to the palladacycle catalyst, which can be deactivated easily by water. Probably, the phosphine ligand may form phosphine oxide in the presence of water. The Heck reaction of 4-bromobenzonitrile and methyl acrylate (1.5 equiv) with 2 mol% of catalyst **2** and NaOAc (1.5 equiv) in *N*,*N*-dimethylacetamide at 100 °C was proceeded as the model reaction. The results showed that the yield of the product can be isolated more than 80% after recycled four times with diethyl ether as the solvent to precipitate our polystyrene-supported catalyst **2**. Using acetonitrile as the solvent may drop the yield of the product below 60% after the 2nd run. The reactivity of Herrmann's catalyst **1** diminished thoroughly after recycled two times in the model reaction. We also found that the yield can be kept more than 99% after recycling 6 times, using Et_3N instead of NaOAc as the base in the model Heck reaction. The ^1H NMR and IR spectra of the recycled palladium catalysts showed no difference before and after recycling five times. The elemental analysis for the repeating unit ($C_{142}H_{138}O_4P_2Pd$) in the polystyrene-supported palladium catalyst found C, $82.12 \pm 0.5\%$ and H, $6.70 \pm 0.5\%$ before and after recycling one to three times clearly indicated the composition of the copolymer. Atomic absorption spectrophotometer analysis showed that palladium was containing at 85.43, 80.78, 74.13 mg of Pd per gram of polymer after recycling one to three times, respectively.

We also tested the applicability of catalyst **2** in Suzuki-Miyaura cross-coupling reaction. Thus, the cross-coupling of 2,5-dihexyloxy-1,4-benzenediboronic acid, prepared in 79% yield from the lithium–halogen exchange reaction of 2,5-dibromo-1,4-dihexyloxybenzene with *n*-butyllithium followed by the treatment of trimethylborate and dilute acid (2 N HCl), with 2.5 equiv of bromoarene with or without cyano groups at *o*-, *m*-, or *p*-positions in the presence K_2CO_3 as the base and catalyst **2**, prepared from Route 1 and Route 2, in *o*-xylene could give *p*-terphenyls in fair to good yields (72 to 88%) as shown in Table 2. The results showed that the activities of the catalyst **2** prepared

Table 2. Suzuki reaction of using polystyrene-supported catalyst **2**



Y = H, o-CN, m-CN, p-CN.

(**eq 2**)

Entry	Haloarene	Iso. Yield (%)	
		Route 1	Route 2
1	Bromobenzene	85	88
2	2-Bromobenzenecarbonitrile	72	78
3	3-Bromobenzenecarbonitrile	74	83
4	4-Bromobenzenecarbonitrile	76	84

from Route 1 and Route 2 were similar. Attempts to change the base as Et_3N or other solid bases (K_3PO_4, Cs_2CO_3) in the above Suzuki-Miyaura cross-coupling reaction gave very low yields ($<20\%$).

3. Conclusion

We have synthesized via two routes in six steps with high yields to a new polystyrene-supported palladacycle catalyst **2** which was successfully employed in the carbon–carbon bond formation to give good yields in the Heck-Mizoroki and Suzuki-Miyaura model studies. The simple precipitation and filtration process to recycle the catalyst after our model reactions for these reactions were noteworthy. Our catalyst exhibited a high reactivity as Herrmann's palladacycle catalyst and, in addition, to its high reactivity, it gave us a promising solution to lower the reaction cost by its good recyclabilities in Heck-Mizoroki reaction of using pertinent organic bases.

4. Experimental

4.1. General

4.1.1. Synthesis of 3-bromo-4-methylacetophenone. Anhydrous aluminum chloride (30 g, 225 mmol) and one magnetic stirrer bar were put into a 100 mL of two necked round bottomed flask equipped with one septum at one neck and a pressure-equalizer dropping funnel at the other neck. Then, the flask was flushed with nitrogen through the septum. 4-Methylacetophenone (13.3 mL, 100 mmol) was added slowly from the dropping funnel to the stirred solid over a period of 10 min. The flask was stirred continuously for another 30 min after completion of the addition. Bromine (5.7 mL, 110 mmol) was added, dropwise, to the stirred, molten mass over a period of 5 min. The reaction was completed when the stirred mass solidified and no more hydrogen bromide was emitted. The solidified mass was dropped, portionwise, into 3 N HCl aqueous solution (250 mL). The dark oil at the bottom of the solution was extracted by ether (3×30 mL). The organic layer was then washed by saturated NH_4Cl aqueous solution (50 mL), dried over with $MgSO_4$, and concentrated to get the crude product. The crude product was further purified by distillation at low pressure [118 °C (3 mm Hg)] to give 18.53 g (87% yield) of the desired product. Mp 38–40 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 2.58 (s, 3H), 7.33 (d, $J=4.7$ Hz, 1H), 7.79 (dd, $J=4.7$, 0.99 Hz, 1H), 8.12 (d, $J=0.99$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.19, 26.52, 123.21, 127.08, 130.87, 132.32, 136.46, 143.53, 196.4; IR (neat) 3024, 1684, 1599, 1383, 1521, 1039, 958, 907, 831 cm^{-1}; MS *m/z* 212 (M^+), 199, 197, 171, 169, 89; HRMS calcd for C_9H_9OBr: 211.9837, found: 211.9840.

4.1.2. Synthesis of 1-(3-bromo-4-methyl-phenyl)ethanol. LAH (6.45 g, 170 mmol) and one magnetic stirrer bar were added into a 250 mL of round bottomed flask, which was then closed with one septum and dried under vacuum followed by filling with nitrogen. One part of dry ether (50 mL) was first injected into the stirred LAH. The mixture of 3-bromo-4-methylacetophenone (38 g, 180 mmol) in dry ether (50 mL) was injected into the flask dropwisely. Stirring was continued after the completion of addition of 3-bromo-4-methylacetophenone until no more gas was generated. The mixture was poured into 2 N HCl aqueous solution (240 mL), extracted with EAC (4×30 mL), washed over saturated NH_4Cl aqueous solution (50 mL), dried over anhydrous $MgSO_4$, and concentrated at low pressure. The crude product was further purified by distillation at low pressure [130 °C (4 mm Hg)] to give 31.35 g (81% yield) of the desired product as clear and pale yellow liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 1.47 (t, $J=6.4$ Hz, 3H), 1.76 (s, 1H), 2.38 (s, 3H), 4.84 (q, $J=6.4$ Hz, 1H), 7.20 (s, 2H), 7.55 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.54, 25.16, 69.33, 124.30, 124.93, 129.34, 130.82, 136.88, 145.27; IR (neat) 3024, 2997, 2927, 1605, 1562, 1494, 1452, 1381, 1331, 1255, 1091, 1038, 1009, 908, 822, 733 cm^{-1}; MS *m/z* 214 (M^+), 199, 197, 171, 169, 119, 91; HRMS calcd for $C_9H_{11}OBr$: 213.9993, found: 213.9995.

4.1.3. Synthesis of 3-bromo-4-methyl-styrene. $KHSO_4$ (0.55 g, 34 mmol), hydroquinone (0.142 g, 1.3 mmol), and 1-(3-bromo-4-methyl-phenyl)ethanol (17.2 g, 80 mmol) were delivered into a 25 mL round bottomed flask, equipped with a distillation equipment. The mixture was kept stirring. The system was vacuumed at 3 mm Hg. The dehydration and distillation processes [102 °C (3 mm Hg)] were proceeded at the same time. The isolated product was obtained in 13.6 g (86% yield) as clear and golden yellow liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.23 (d, $J=10.9$ Hz, 1H), 5.69 (d, $J=17.6$ Hz, 1H), 6.60 (dd, $J=10.9$, 17.6 Hz, 1H), 7.16 (d, $J=7.8$ Hz, 1H), 7.21 (d, $J=7.8$ Hz, 1H), 7.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.63, 114.32, 125.04, 125.09, 129.92, 130.76, 135.30, 137.11, 137.22 ppm; IR (neat) 3091, 3063, 3016, 2985, 2964, 1899, 1833, 1701, 1629, 1602, 1554, 1492, 1450, 1380, 1304, 1278, 1205, 1037, 989, 914, 833, 854, 826 cm^{-1}; MS *m/z* 197 (M^++1) 171, 169, 117, 115, 91, 89; HRMS calcd for C_9H_9Br: 195.9888, found: 195.9887.

4.1.4. Synthesis of 3-(diphenylphosphino)-4-methyl-styrene 3. Mg (0.72 g, 30 mmol) was added into a 50 mL of round bottomed flask, which was dried and filled with nitrogen. Dry THF (10 mL) was injected first and then stirred with Mg. Half mixture of 3-bromo-4-methyl-styrene (3.94 g, 20 mmol) in dry THF (10 mL) was injected dropwisely. After an exothermic reaction starts, the rest of the mixture was injected. The Grignard reagent was reversely added into the mixture of chlorodiphenylphosphine (5.25 g, 25 mmol) in dry THF (10 mL) at 0 °C. After completion of the addition, the temperature was raised to the room temperature. After stirring for another 20 h, the mixture was poured into a saturated NH_4Cl aqueous solution (10 mL) at 0 °C and extracted with dry THF (3×20 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated to 5 mL only. Hexane was added into the organic solution to deposit the by-products. After filtration and concentration, the residue was purified by a flash column chromatography (hexane/EAC=4:1). The isolated product was 2.42 g (39% yield). Mp 48–49 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.06 (d, $J=10.9$ Hz, 1H), 5.42 (d, $J=17.6$ Hz, 1H), 6.48 (q, $J=10.9$, 17.6 Hz, 1H), 6.79 (q, $J=2.1$, 5.8 Hz, 1H), 7.20–7.34 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 21.1, 113.0, 126.2, 128.5, 128.6, 128.8, 130.2, 130.3, 130.7, 133.9, 134.1, 135.1, 136.0, 136.3, 136.5, 141.7 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ -12.34 ppm; IR (neat) 3057, 3016, 2974, 1957, 1900, 1819, 1629, 1589, 1479, 1435, 1380, 1306, 1262, 1179, 1152, 1093, 1028, 992, 911, 830, 699 cm^{-1}; MS *m/z* 302 (M^+) 223, 183, 165, 152, 115, 78; HRMS calcd for $C_{21}H_{19}P$: 302.1224, found: 302.1227.

4.1.5. Synthesis of *trans*-di(μ-acetato)-bis[3-(diphenylphosphino)-4-styryl]dipalladium (II) 4. $Pd(OAc)_2$ (0.225 g, 1 mmol) was solvated in stirring dry toluene (20 mL) in a 50 mL round bottomed flask. The mixture of 3-(diphenylphosphino)-4-methyl-styrene **3** (0.333 g, 1.1 mmol) and dry toluene (4 mL) was injected into the flask. After that, the mixture was heated at 50 °C for 5 min, and then cooled slowly to the room temperature. The mixture was concentrated to one third of the original volume. Hexane (25 mL) was added to the mixture for precipitation of the product. The recrystallization was proceeded repeatedly in the system of toluene/hexane or dichloromethane/hexane. The isolated product was 0.34 g (74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.61 (s, 6H), 3.63 (br s, 4H), 5.06 (d, $J=11.1$ Hz, 2H), 5.42 (d, $J=17.6$ Hz, 2H), 6.48 (q, $J=11.1$, 17.6 Hz, 2H), 7.1–7.8 (m, 26H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.41 ppm. IR ($CHCl_3$) ν 3058, 2921, 2860, 1653, 1561, 1435 cm^{-1}. Anal. Calcd for $C_{46}H_{42}O_4P_2Pd_2$: C, 59.18; H, 4.53. Found: C, 59.33; H, 4.68.

4.1.6. Synthesis of phosphine-bound polystyrene 5. 3-(Diphenylphosphino)-4-methyl-styrene **3** (0.33 g, 1.1 mmol) was added to a test tube and flushed with nitrogen. A mixture of styrene (0.68 g, 6.6 mmol) and benzene (2 mL) was injected into the test tube. Then, a mixture of AIBN (0.18 g, 0.1 mmol) and benzene (10 mL) was injected into the stirring test tube. The reaction mixture was then heated at 70 °C for 40 h. The mixture was concentrated to dryness. The dry solid was repeatedly washed by the solvent (THF/hexane = 1:30). The isolated polymer was 0.8 g (79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.1–1.7 (m, phenylC*H*C*H*$_2$), 2.2–2.4 (br s, Ar-C*H*$_3$), 6.2–6.7 (m, Ar-*H*), 6.8–7.3 (m, Ar-*H*) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ -12.23 ppm; IR ($CHCl_3$) ν 3023, 2924, 2846, 1653, 1561, 1492, 1452, 756, 699 cm^{-1}. Anal. Calcd for $C_{69}H_{68}P$ (repeating unit): C, 89.28; H, 7.38. Found: C, 89.60; H, 7.84.

4.1.7. Synthesis of polystyrene-supported palladacycle catalyst 2. *trans*-Di(μ-acetato)-bis[3-(diphenylphosphino)-4-styryl]dipalladium(II) **4** (93 mg, 0.1 mmol) was added to a test tube and flushed with nitrogen. A mixture of styrene (62 mg, 0.6 mmol) and benzene (2 mL) was injected into the test tube. Then, a mixture of AIBN (18 mg, 0.01 mmol) and benzene (1 mL) was injected into the stirring test tube. The reaction mixture was then heated at 70 °C for 40 h. The mixture was concentrated to dryness. The dry solid was repeatedly washed by the solvent (THF/hexane = 1:15). The isolated polymer was 0.11 g (66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.1–2.0 (m, phenylC*H*C*H*$_2$), 2.2–2.4 (br s, Ar-C*H*$_3$), 6.3–6.7 (m, Ar-*H*), 6.8–7.4 (m, Ar-*H*) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ 53.01 ppm. IR ($CHCl_3$) ν 3027, 2921, 2858, 1447, 912, 743 cm^{-1}; Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicated that M_w of catalyst **2** prepared from Route 1 and Route 2 was 1.434×10^4 and 1.529×10^4 g/mol, respectively. Atomic absorption spectrophotometer analysis showed that palladium was containing at 86.39 and 82.91 mg of Pd per gram of polymer prepared from Route 1 and Route 2, respectively.

4.1.8. Typical procedure for use of polystyrene-supported palladacycle catalyst 2 in the Heck reaction. Polystyrene-supported palladacycle catalyst **2** (30 mg, 24 μmol Pd), iodobenzene (0.20 g, 1 mmol), methyl acrylate (0.13 g, 1.5 mmol), sodium acetate (0.12 g, 1.5 mmol), and *N*,*N*-dimethylacetamide (3 mL) were sequentially added into a 15 mL septum-sealed test tube under nitrogen atmosphere. The mixture was then heated at 100 °C for 8 h. After cooling to the room temperature, the mixture was added 8 mL of dry ether to precipitate the polystyrene-supported palladacycle catalyst. After the catalyst was further precipitated by a centrifuge, the upper liquid layer of the reaction mixture was transferred via a syringe into another 20 mL round bottom flask. Repeat the above precipitation procedure one more time. The combined liquid layer was concentrated under reduced pressure. Saturated ammonium chloride solution (5 mL) was then added to the oil mixture. The organic product was extracted three times by ethyl acetate (10 mL × 3), dried over magnesium sulfate, filtrated, and concentrated to give the crude product. The crude product was further purified by column chromatography (silica gel, hexane/EAC = 4:1) to give 0.16 g (99% yield) of *trans*-methyl cinnamate.[36]

4.1.9. Typical procedure for the use of polystyrene-supported palladacycle catalyst 2 from Route 1 in the Suzuki-Miyaura reaction for the preparation of 2,5-dihexyloxy-1,4-di-phenylbenzene. *o*-Xylene (5 mL) was added to a mixture of 2,5-dihexyloxy-1,4-benzenediboronic acid (0.44 g, 1 mmol), bromobenzene (0.39 g, 2.5 mmol), and K_2CO_3 (0.83 g, 6 mmol) in a 10 mL round-bottomed flask under nitrogen atmosphere. A solution of catalyst **2** (0.007 g) in 1 mL of *o*-xylene was added into the above mixture at 130 °C. The mixture was cooled to room temperature after it was stirred and heated for 72 h. The mixture was added 16 mL of dry diethyl ether to precipitate the polystyrene-supported palladacycle catalyst. After the catalyst was further precipitated by a centrifuge, the upper liquid layer of the reaction mixture was transferred via a syringe into another 20 mL round bottom flask. Repeat the above precipitation procedure one more time. The combined organic layer was dried over $MgSO_4$, filtrated, and concentrated before recrystallized by EAC and MeOH to give 0.37 g (85% yield) of the desired product. Mp 67–68 °C; $R_f=0.9$ (hexane/EAC = 4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (t, $J=7$ Hz, 6H), 1.26–1.36 (m, 12H), 1.65–1.68 (m, 4H), 3.90 (t, $J=6.4$ Hz, 4H), 6.98 (s, 2H), 7.32 (t, $J=7.1$ Hz, 2H), 7.41 (t, $J=7.5$ Hz, 4H), 7.60 (d, $J=7.75$ Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.96, 22.56, 25.72, 29.33, 31.45, 69.70, 116.44, 126.88, 127.89, 129.53, 130.91, 138.46, 150.31 ppm; IR ν 1484.8, 1400.4, 1211.4, 1054.1, 763.9, 698.1 cm^{-1}; MS *m/z* 430 (M^+), 347, 262; HRMS Calcd for $C_{30}H_{38}O_2$: 430.2872, found: 430.2869.

4.1.10. 2-[4-(2-Cyanophenyl)-2,5-dihexyloxyphenyl]-benzenecarbonitrile. Following the procedure as described for the preparation of 2,5-dihexyloxy-1,4-diphenylbenzene by using 2,5-dihexyloxy-1,4-benzenediboronic acid (0.37 g, 1 mmol), 2-bromobenzene-carbonitrile (0.45 g, 2.5 mmol), catalyst **2** (0.007 g), and K_2CO_3 (0.83 g, 6 mmol) to obtain 0.35 g (72% yield) of the desired product. Mp 129–131 °C; $R_f=0.6$ (*n*-hexane/EAC = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.83 (t, $J=7$ Hz, 6H), 1.21–1.28 (m, 12H), 1.64–1.67 (m, 4H), 3.94 (t, $J=6.5$ Hz, 4H), 6.94 (s, 2H), 7.44 (t, $J=7.6$ Hz, 2H), 7.56 (d, $J=7.7$ Hz, 2H), 7.64 (t, $J=7.7$ Hz, 2H), 7.74 (d, $J=7.6$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.88, 22.47, 25.53, 29.05, 31.35, 69.19, 113.21, 115.51, 118.61, 127.42, 128.52, 131.11, 132.17, 132.74, 142.17, 149.80 ppm; IR ν 2228.1, 1513.9, 1390.7, 1215.4, 1035.9, 762.8 cm^{-1}; MS *m/z* 480.2 (M^+), 412.0, 395.2, 313.1; HRMS Calcd for $C_{32}H_{36}O_2N_2$: 480.2777, found: 480.2786.

4.1.11. 3-[4-(3-Cyanophenyl)-2,5-dihexyloxyphenyl]-benzenecarbonitrile. Following the procedure as described for the preparation of 2,5-dihexyloxy-1,4-diphenylbenzene by using 2,5-dihexyloxy-1,4-benzenediboronic acid (0.37 g, 1 mmol), 3-bromobenzene-carbonitrile (0.45 g, 2.5 mmol), catalyst **2** (0.007 g), and K_2CO_3 (0.83 g, 6 mmol) to give 0.35 g (74% yield) of the desired product. Mp 100–103 °C; $R_f=0.525$ (*n*-hexane/EAC = 4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, $J=7.5$ Hz, 6H), 1.26–1.68 (m, 12H), 1.67–1.71 (m, 4H), 3.94 (t, $J=6$ Hz, 4H), 6.94 (s, 2H), 7.52 (t, $J=7.7$ Hz, 2H), 7.63 (d, $J=7.7$ Hz, 2H), 7.7 (d, $J=7.7$ Hz, 2H), 7.89 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.96, 22.53, 25.75, 29.17, 31.40, 69.58, 112.21, 115.48, 118.93, 128.77, 129.21, 130.57, 133.14, 133.89, 139.29, 150.16 ppm; IR ν 2232.1, 1478.3, 1397.7, 1216.6, 1037.7, 785.9 cm^{-1}; MS *m/z* 480.2 (M^+), 397.1, 325.1, 312.1; HRMS Calcd for $C_{32}H_{36}O_2N_2$: 480.2777, found: 480.2772.

4.1.12. 4-[4-(4-Cyanophenyl)-2,5-dihexyloxyphenyl]-benzenecarbonitrile. Following the procedure as described for the preparation of 2,5-dihexyloxy-1,4-diphenylbenzene by using 2,5-dihexyloxy-1,4-benzenediboronic acid (0.37 g, 1 mmol), 4-bromobenzene-carbonitrile (0.45 g, 2.5 mmol), catalyst **2** (0.007 g), and K_2CO_3 (0.83 g, 6 mmol) to give 0.37 g (76% yield) of the desired product. Mp 152–154 °C; $R_f=0.68$ (*n*-hexane/EAC = 4:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, $J=7$ Hz, 6H), 1.25–1.33 (m, 12H), 1.67–1.68 (m, 4H), 3.93 (t, $J=6$ Hz, 4H), 6.93 (s, 2H), 7.69 (s, 8H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.89, 22.48, 25.65, 29.11, 31.31, 69.56, 110.70, 115.55, 118.96, 129.82, 130.13, 131.70, 142.80, 150.18 ppm; IR ν 2226.4, 1647.6, 1601.0, 1214.5, 776.0 cm^{-1}; MS *m/z* 480.2 (M^+), 397.1, 325.1, 312.1; HRMS Calcd for $C_{32}H_{36}O_2N_2$: 480.2777, found: 480.2772.

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