

Article

Reusable Polymer-Supported Terpyridine Palladium Complex for Suzuki-Miyaura, Mizoroki-Heck, Sonogashira, and Tsuji-Trost Reaction in Water

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Received: 10 January 2011; in revised form: 8 February 2011 / Accepted: 9 March 2011 /

Published: 14 March 2011

Abstract: A novel heterogeneous transition-metal catalyst comprising a polymer-supported terpyridine palladium(II) complex was prepared and found to promote the Suzuki-Miyaura, Mizoroki-Heck, Sonogashira, and Tsuji-Trost, reactions in water under aerobic conditions with a high to excellent yield. The catalyst was recovered by simple filtration and directly reused several times without loss of catalytic activity.

Keywords: palladium; terpyridine; cross-coupling; polymer-supported synthesis

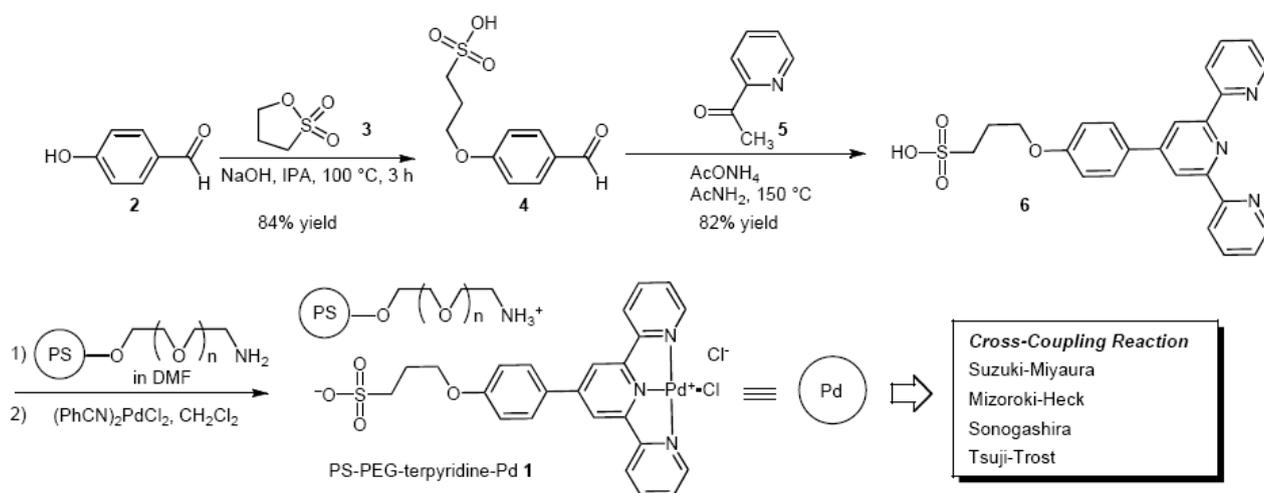
1. Introduction

Palladium-catalyzed reactions that form carbon-carbon bonds, such as Suzuki-Miyaura, Mizoroki-Heck, Sonogashira, and Tsuji-Trost cross-coupling, are of considerable importance in organic chemistry [1-11]. These cross-coupling reactions are generally catalyzed with soluble palladium complexes in an organic solvent or in a mixture of water and an organic solvent [12-15]. However, there has been a continuing challenge with such catalyst systems regarding their efficient separation and recycling, which are important considerations for economic and ecological reasons.

Heterogeneous palladium-catalyst systems have been found to be highly effective for overcoming some of these problems [16-20]. Heterogeneous catalysts generally comprise an organic or inorganic solid support, a linkage moiety, and a catalytic center prepared from a transition metal and a

phosphine-based ligand. Therefore, catalytic reactions are carried out under nitrogen to avoid oxidizing the phosphine ligands. We recently developed an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported terpyridine-metal complex and found it to be an effective catalyst for coupling reactions in water under heterogeneous and aerobic conditions with high recyclability [21,22]. As an extension of that study, we investigated this catalytic utility of the PS-PEG-terpyridine-palladium(II) complex for the cross-coupling reaction in aqueous solution, with the aim to achieve more environmentally friendly reaction media. We report herein the results of these investigations and demonstrate that the complex effectively catalyzes the cross-coupling reaction in water (Scheme 1). This catalytic system offers three benefits: (1) It produces neither organic solvent waste nor metal-contaminated waste; (2) It is unharmed by oxygen and moisture; (3) It thus enables the cross-coupling reaction to meet green chemical requirements; and (4) It enables the cross-coupling reaction with high level of safety.

Scheme 1. Preparation of PS-PEG resin-bound terpyridine palladium complex.



2. Results and Discussion

2.1. Preparation of PS-PEG Resin-Bound Terpyridine Palladium Complex

The amphiphilic PS-PEG resin-bound terpyridine ligand was prepared from *p*-hydroxybenzaldehyde (**2**), propane sultone (**3**), 2-acetylpyridine (**5**), and PS-PEG-NH₂ resin, and the coordination of the synthesized polymeric terpyridine ligand with palladium species proceeded to give the PS-PEG resin-supported terpyridine palladium complex **1**, which exhibited good catalytic activity for the cross-coupling reaction. Thus, the reaction of *p*-hydroxybenzaldehyde (**2**) with propane sultone (**3**) in isopropyl alcohol (IPA) at 100 °C for 3 h under alkaline conditions followed by treatment of the obtained 3-(4-formylphenoxy)propane-1-sulfonic acid (**4**) with 2-acetylpyridine (**5**) and AcONH₄ in acetamide at 150 °C for 5 h gave terpyridine ligand **6** in a 68% yield in two steps. Immobilization of terpyridine ligand **6** onto an amphiphilic PS-PEG resin through ionic bonds to the sulfonate group was performed in DMF at room temperature for 1 h and the complexation of an amphiphilic PS-PEG resin-bound terpyridine ligand and Pd(II) occurred in CH₂Cl₂ to give PS-PEG-terpyridine-Pd(II) complex **1** as a brown solid [23-26].

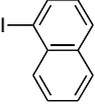
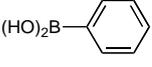
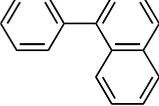
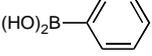
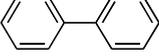
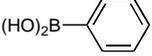
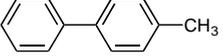
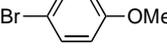
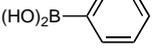
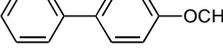
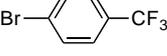
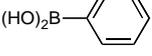
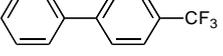
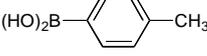
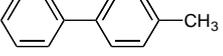
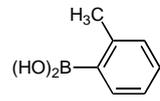
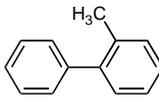
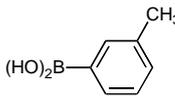
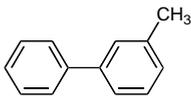
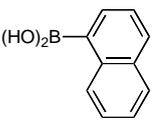
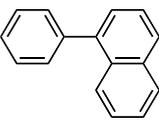
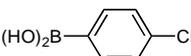
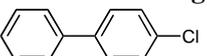
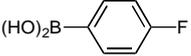
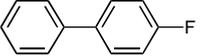
2.2. Suzuki-Miyaura Cross-Coupling Reaction Using Polymer-Supported Terpyridine Palladium Complex

The scope of aryl halides and arylboronic acids was examined for the Suzuki-Miyaura cross-coupling reaction in water using the PS-PEG-terpyridine-Pd(II) complex **1** under aerobic conditions. Representative results are summarized in Table 1. PS-PEG resin-supported terpyridine palladium(II) complex **1** efficiently catalyzed the coupling of iodobenzene (**7a**) with phenylboronic acid (**8a**). Thus, the Suzuki-Miyaura cross-coupling reaction of **7a** with **8a** was carried out with K_2CO_3 (2 equiv.) in the presence of polymeric catalyst **1** (5 mol% Pd) in water to give the biphenyl (**9a**) in a 93% yield (Table 1, entry 1). The Suzuki-Miyaura cross-coupling reaction of phenylboronic acid (**8a**) with iodobenzene derivatives **7b–d** bearing electron donating and withdrawing substituents at their *para*-positions gave the 4-methylbiphenyl (**9b**), 4-methoxybiphenyl (**9c**), and 4-trifluoromethylbiphenyl (**9d**) in 82%, 92%, and 93% yields, respectively (Table 1, entries 2–4). The coupling reaction of *meta*- and *ortho*-substituted iodobenzene derivatives **7e–g** having *meta*-alkyl and *ortho*-alkyl groups took place with phenylboronic acid (**8a**) to give the 2-methylbiphenyl (**9e**), 3-methylbiphenyl (**9f**), and 1-phenylnaphthalene (**9g**) in 80%, 93%, and 98% yields, respectively (Table 1, entries 5–7). The coupling reaction of bromoarenes **7h–k** with **8a** was also performed to give the corresponding biaryls **9a–d** in 74%, 85%, 69%, and 82% yields, respectively (Table 1, entries 8–11). The reactivity of several boronic acids **8b–g** was also examined under similar conditions to furnish the coupling products **9b** and **9e–i** in 91%, 87%, 90%, 92%, 99%, and 96% yields, respectively (Table 1, entries 12–17).

Table 1. Suzuki-Miyaura coupling reaction using polymeric catalyst **1** in water ^{a, b}.

entry	aryl halide (7)	arylboronic acid (8)	temp (°C)	time (h)	product (9)	yield (%)
1			100	6		93
2			100	6		82
3			100	6		92
4			100	6		93
5			100	6		80
6			100	6		93

Table 1. Cont.

entry	aryl halide (7)	arylboronic acid (8)	temp (°C)	time (h)	product (9)	yield (%)
7	 7g	 8a	100	6	 9g	98
8	 7h	 8a	100	6	 9a	74
9	 7i	 8a	100	6	 9b	85
10	 7j	 8a	100	6	 9c	69
11	 7k	 8a	100	6	 9d	82
12	 7a	 8b	100	6	 9b	91
13	 7a	 8c	100	6	 9e	87
14	 7a	 8d	100	6	 9f	90
15	 7a	 8e	100	6	 9g	92
16	 7a	 8f	100	6	 9h	99
17	 7a	 8g	100	6	 9i	96

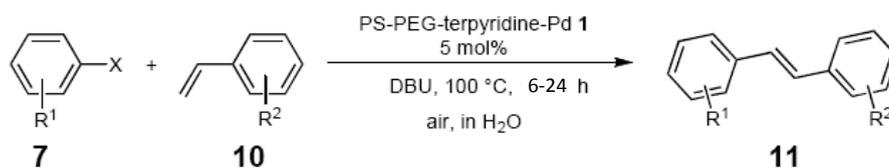
^a All reactions were carried out with ArX (**7**; 0.4 mmol), ArB(OH)₂ (**8**; 0.8 mmol), and K₂CO₃ (0.8 mmol) in the presence of the polymeric catalyst **1** in 3.0 mL of H₂O at 100 °C for 6 h under aerobic conditions. ^b The 0.005 mol% of polymeric catalyst **1** (0.08 mg) was used, the reaction gave 74% yield of biphenyl **9a** (TON 14800). ^c The iodobenzoic acid as water soluble substrate was used, the reaction afforded 59% yield of biphenyl-4-carboxylic acid **9j**.

2.3. Mizoroki-Heck Reaction Using Polymer-Supported Terpyridine Palladium Complex

The scope of suitable aryl halides and styrenes for the Mizoroki-Heck reaction in water using catalyst **1** was also examined (Table 2). The general process was to conduct the reaction of an aryl halide and a styrene with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2 equiv.) in the presence of catalyst **1** (5 mol% Pd) in water to afford the corresponding products. The results for various aryl halides and

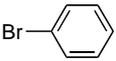
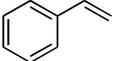
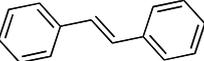
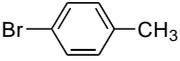
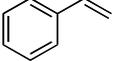
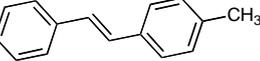
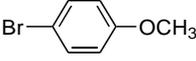
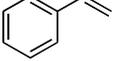
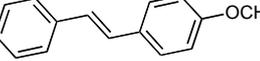
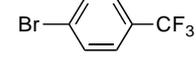
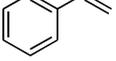
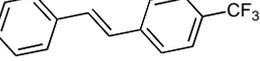
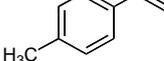
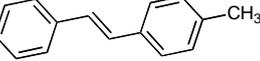
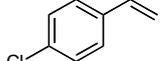
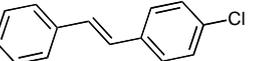
styrenes are as follows. For aryl halides **7a–g** in reaction with styrene **10a**, iodobenzene (**7a**) gave 1,2-diphenylethene (**11a**) in a 90% yield (Table 2, entry 1); iodobenzene derivatives **7b–d** bearing electron donating and withdrawing substituents at their *para*-positions gave 1-methyl-4-styrylbenzene (**11b**), 1-methoxy-4-styrylbenzene (**11c**), and 1-trifluoromethyl-4-styrylbenzene (**11d**) in 78%, 88%, and 76% yields, respectively (Table 2, entries 2–4); in addition, *meta*- and *ortho*-substituted iodobenzene **7e–g** having *meta*-methyl and *ortho*-methyl groups gave 1-methyl-2-styrylbenzene (**11e**), 1-methyl-3-styrylbenzene (**11f**), and 1-styrylnaphthalene (**11g**) in 60%, 90%, and 99% yields, respectively (Table 2, entries 5–7). Bromoarenes **7h–k** in reaction with **10a**, carried out over longer reaction times (24 h), gave the corresponding stilbene derivatives **11a–d** in 80%, 57%, 75%, and 87% yields, respectively (Table 2, entries 9–12). Styrenes **10b** and **10c** under similar conditions gave **11b** and **11h** in 80% and 77% yields, respectively (Table 2, entries 13 and 14).

Table 2. Mizoroki-Heck reaction using polymeric catalyst **1** in water ^{a, b, c}.



entry	aryl halide (7)	styrenes (10)	temp (°C)	time (h)	product (11)	yield (%)
1			100	6		90
2			100	6		78
3			100	6		88
4			100	6		76
5			100	6		60
6			100	6		90
7			100	6		99
8			100	12		37

Table 2. Cont.

entry	aryl halide (7)	styrenes (10)	temp (°C)	time (h)	product (11)	yield (%)
9	 7h	 10a	100	24	 11a	80
10	 7i	 10a	100	24	 11b	57
11	 7j	 10a	100	24	 11c	75
12	 7k	 10a	100	24	 11d	87
13	 7a	 10b	100	12	 11b	80
14	 7a	 10c	100	12	 11h	77

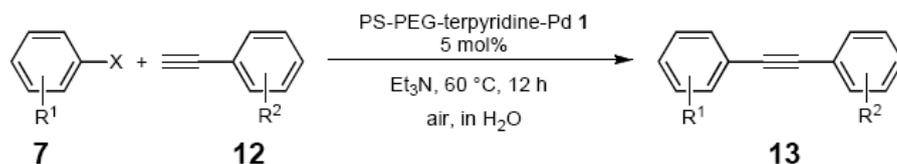
^a All reactions were carried out with ArX (**7**; 0.4 mmol), styrenes (**10**; 0.8 mmol), and DBU (0.8 mmol) in the presence of the polymeric catalyst **1** in 3.0 mL of H₂O at 100 °C for 12 h under aerobic conditions. ^b The 0.05 mol% of polymeric catalyst **1** (0.8 mg) was used, the reaction gave 4% yield of stilbene **11g** (TON 80).

2.4. Sonogashira Coupling Reaction Using Polymer-Supported Terpyridine Palladium Complex

The palladium-catalyzed coupling of an aryl halide with a terminal alkyne, the so-called Sonogashira reaction, is recognized as the most successful method for forming an sp^2 carbon- sp^3 carbon bond. Since its discovery by Sonogashira and co-workers in 1975, a vast amount of research has been devoted to the synthetic application as well as the improvement of the reaction efficiency. Our continuing interest in the catalytic utility of PS-PEG-terpyridine-Pd(II) complex **1** led us to examine the Sonogashira coupling reaction in water with the PS-PEG-terpyridine-Pd(II) complex **1** under copper-free conditions. Thus, the copper-free Sonogashira coupling was examined with several haloarenes in the presence of catalyst **1** in water under aerobic conditions. The representative results are summarized in Table 3. The coupling of iodobenzene (**7a**) with phenylacetylene (**12**) took place smoothly in water at 60 °C in the presence of 3 equiv. of Et₃N and 5 mol% palladium of the PS-PEG-terpyridine-Pd(II) complex **1** to give a 78% yield of diphenylacetylene (**13a**) (Table 3, entry 1). The Sonogashira coupling reaction of *p*-methyliodobenzene (**7b**) bearing electron donating groups at their *para*-positions gave the corresponding biarylacetylene **13b** in a 65% yield (Table 3, entry 2). *p*-(Trifluoromethyl)iodobenzene (**7d**) and *p*-(methoxycarbonyl)iodobenzene (**7l**) having electron deficient aromatic rings also underwent the Sonogashira coupling with phenylacetylene under similar conditions to afford the corresponding biarylacetylenes **13c** and **13d** in 82% and 69% yields, respectively (Table 3, entries 3 and 4). The coupling of *meta*- and *ortho*-substituted iodobenzenes **7e–g**, **m**, **n** having *meta*-methyl, *meta*-chloro, *ortho*-methyl, and *ortho*-chloro groups took place with phenylacetylene to give the corresponding products **13e–i** in 51%, 51%, 72%, 83%, and 76% yields, respectively (Table 3, entries 5–9). However, Bromoarene **7h** in reaction with **12**, carried out over

longer reaction times (24 h) and at a higher temperature (100 °C), gave the corresponding stilbene **13a** in a low yield (<5% yield) (Table 3, entry 11).

Table 3. Sonogashira coupling reaction using polymeric catalyst **1** in water ^{a, b}.



entry	aryl halide (7)	1-alkyne (12)	temp (°C)	time (h)	product (13)	yield (%)
1			60	12		78
2			60	12		65
3			60	12		82
4			60	12		69
5			60	12		51
6			60	12		51
7			60	12		72
8			60	12		83
9			60	12		76
10			60	12		<5
11			100	24		<5

^a All reactions were carried out with ArX (**7**; 0.4 mmol), phenyl acetylene (**12**; 0.8 mmol), and Et₃N (1.2 mmol) in the presence of the polymeric catalyst **1** in 3.0 mL of H₂O at 60 °C for 12 h under aerobic conditions. ^b The 0.005 mol% of polymeric catalyst **1** (0.08 mg) was used, the reaction gave 28% yield of diphenyl acetylene **13a** (TON 5600).

2.5. Tsuji-Trost Reaction Using Polymer-Supported Terpyridine Palladium Complex

The palladium-catalyzed allyl esters via π -allylpalladium intermediates, the so-called Tsuji-Trost reaction, are a powerful synthetic means for forming carbon–carbon as well as carbon–nitrogen bonds. While extensive research has been devoted to the π -allylic alkylation and amination, research on π -allylic azidation has been limited to isolated reports. We also describe herein our preliminary results demonstrating that allylic azidation of several allyl esters with sodium azide proceeded in water in the presence of a polymeric catalyst **1**. Thus, the coupling of allyl acetate **14a** and **14b** with sodium azide **15** took place smoothly in water at 70 °C in the presence of 5 mol% palladium of the PS-PEG-terpyridine-Pd(II) complex **1** to give the allyl azides **16a** and **16b** in 78% and 36% yields, respectively (Table 4, entries 1 and 2). The Tsuji-Trost reaction of 1-tolylallyl acetate (**14c**) bearing electron donating groups at their *para*-positions gave the 3-(*p*-tolyl)allyl azide (**16c**) in a 65% yield (Table 4, entry 3). 1-(4-(trifluoromethyl)phenyl)allyl acetate (**14d**) having electron deficient aromatic rings also underwent the Tsuji-Trost reaction with sodium azide under similar conditions to afford the 3-(*p*-trifluoromethylphenyl)allyl azide (**16d**) in an 18% yield (Table 4, entry 4).

Table 4. Tsuji-Trost reaction using polymeric catalyst **1** in water ^{a,b}.

Reaction scheme: Allyl acetate (**14**) + NaN₃ (**15**) $\xrightarrow[\text{air, in H}_2\text{O}]{\text{PS-PEG-terpyridine-Pd } \mathbf{1} \text{ (5 mol\%)}}$ Allyl azide (**16**)

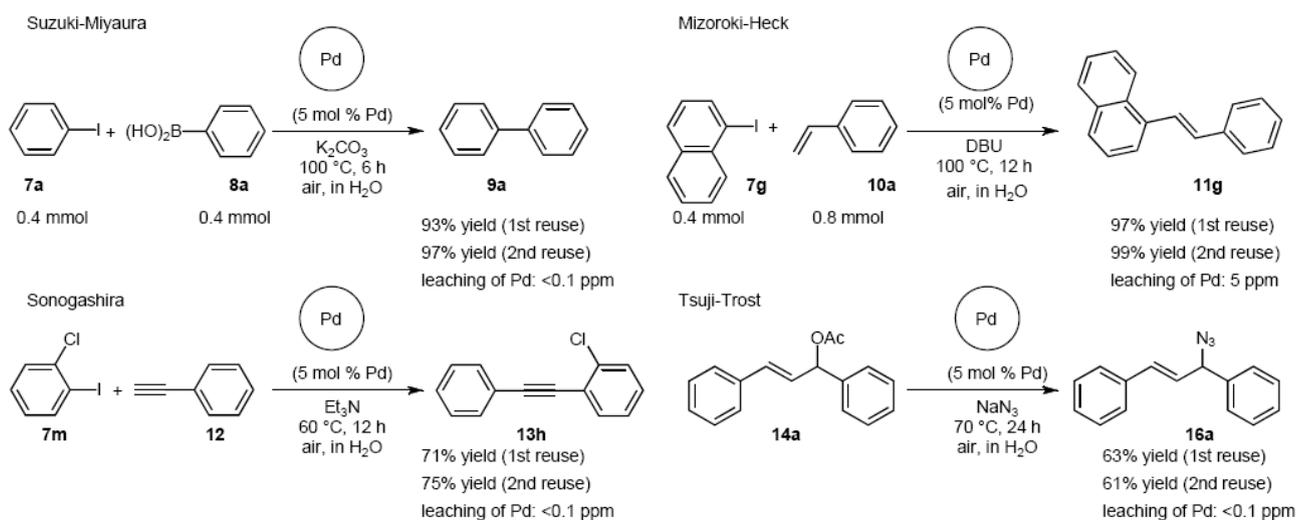
entry	allyl acetate (14)	nucleophile (15)	temp (°C)	time (h)	product (16)	yield (%)
1		NaN ₃ 15	70	24		78
2		NaN ₃ 15	70	24		36
3		NaN ₃ 15	70	24		65
4		NaN ₃ 15	70	24		18

^a All reactions were carried out with allyl acetate (**14**; 0.4 mmol) and sodium azide (**15**; 0.6 mmol) in the presence of the polymeric catalyst **1** in 3.0 mL of H₂O at 70 °C for 24 h under aerobic conditions. ^b The 0.05 mol% of polymeric catalyst **1** (0.8 mg) was used, the reaction gave 73% yield of azide **16a** (TON 1460).

2.6. Recycling Experiments for Cross-Coupling Reaction in Water

The recyclability of the PS-PEG-terpyridine-Pd(II) complex **1** was also tested for the Suzuki-Miyaura, Mizoroki-Heck, Sonogashira, and Tsuji-Trost coupling reaction, respectively. Thus, after the first reaction, which gave a good yield of the coupling product **9a**, **11g**, **13h**, and **16a** (Table 1, entry 1 (93% yield); Table 2, entry 7 (99% yield); Table 3, entry 8 (83% yield); and Table 4, entry 1 (78% yield)), the catalyst beads were recovered by simple filtration and directly applied for the reaction under the similar conditions to afford **9a**, **11g**, **13a**, and **16a** in high yields (Scheme 2), during which palladium residue could hardly be detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (detection limit of Pd: <3 µg/L) from aqueous nor organic filtrates, excluding the Mizoroki-Heck reaction (leaching of Pd: 5 ppm).

Scheme 2. Recycling experiments for cross-coupling reaction in water.



3. Experimental Section

3.1. General Methods

All manipulations were carried out under aerobic conditions. Water was deionized with a Millipore MilliQ gradient A10 as Milli-Q grade. NMR spectra were recorded on a BURKER AVANCE spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) and NMR spectra were recorded on a BURKER AVANCE spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C), and HITACHI R1900 spectrometer (90 MHz for ^1H and 22 MHz for ^{13}C). ^1H and ^{13}C NMR spectra were recorded in CDCl_3 or dimethyl sulfoxide- d_6 (DMSO- d_6) at 25 °C. Chemical shifts of ^{13}C NMR were given relative to CDCl_3 and DMSO- d_6 as an internal standard (δ 77.0 ppm and 39.7 ppm). Mass spectral data were measured on a JEOL JMS-T100GCv MS detector (GC-MS) and a JEOL JMS-T100LP MS detector (LC-MS); the abbreviation ‘bp’ is used to denote the base peak. GC analysis was performed on a Shimadzu GC-2014. IR analysis was performed on a JASCO FTIR-410. ICP-AES spectral data were measured on a Shimadzu ICPE-9000.

3.2. Materials

PS-PEG-supported terpyridine-palladium complex (PS-PEG-terpyridine-Pd) **1** was prepared from PS-PEG amino-resin (Tenta Gel S NH₂, average diameter 90 μm, 1% divinylbenzene cross-linked, loading value of amino residue 0.31 mmol/g; purchased from Rapp Polymer), polymeric terpyridine ligand, and (C₆H₅CN)₂PdCl₂ according to the reported procedures [22]. The loading level of Pd in polymeric catalyst **1** was 0.25 mmol/g.

3.3. Suzuki-Miyaura Cross-Coupling Reaction

To a mixture of the polymeric catalyst **1** (80 mg, 0.020 mmol), K₂CO₃ (110 mg, 0.8 mmol), and iodobenzene (**7a**; 81 mg, 0.4 mmol) in H₂O (3.0 mL) was added phenyl boronic acid (**8a**; 97 mg, 0.8 mmol). The reaction mixture was shaken at 100 °C for 6 h and filtered. The recovered resin beads were rinsed with H₂O and extracted three times with EtOAc (6 mL). The EtOAc layer was separated and the aqueous layer was extracted with EtOAc (3 mL). The combined EtOAc extracts were washed with brine (2 mL), dried over MgSO₄, and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel (hexane) to give 57 mg (93% yield) of biphenyl (**9a**).

3.4. Spectral and Analytical Data for the Biaryls

3.4.1. biphenyl (9a)

¹H NMR (CDCl₃) δ 7.60–7.57 (m, 2 H), 7.45–7.41 (m, 4 H), 7.35–7.31 (m, 4 H); ¹³C NMR (CDCl₃) δ 141.2 (2 C), 128.7 (4 C), 127.2 (4 C), 127.1 (2 C). MS (EI): *m/z* (rel%) 154 (bp, M⁺), 153 (39), 77 (6). IR (ATR): (cm⁻¹) ν 3061, 1475.

CAS registry number: 92-52-4.

3.4.2. 4-methylbiphenyl (9b)

¹H NMR (CDCl₃) δ 7.60–7.55 (m, 2 H), 7.50–7.47 (m, 2 H), 7.43–7.39 (m, 2 H), 7.33–7.29 (m, 1 H), 7.25–7.20 (m, 2 H), 2.38 (s, 3 H); ¹³C NMR (CDCl₃) δ 141.1, 138.3, 136.9, 129.4 (2 C), 128.7 (2 C), 128.6 (2 C), 126.9 (2 C), 126.9, 21.0. MS (EI): *m/z* (rel%) 168 (bp, M⁺), 167 (69), 165 (24), 153 (13), 83 (9). IR (ATR): (cm⁻¹) ν 3026, 1486.

CAS registry number: 644-08-6.

3.4.3. 4-methoxybiphenyl (9c)

¹H NMR (CDCl₃) δ 7.52 (t, *J* = 8.6 Hz, 4 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 6.96 (d, *J* = 8.6 Hz, 2 H), 3.82 (s, 3 H); ¹³C NMR (CDCl₃) δ 159.1, 140.7, 133.7, 128.6 (2 C), 128.0 (2 C), 126.6 (2 C), 126.6, 114.1 (2 C), 55.2. MS (EI): *m/z* (rel%) 184 (bp, M⁺), 169 (53), 141 (46), 115 (29). IR (ATR): (cm⁻¹) ν 3065, 1603.

CAS registry number: 613-37-6.

3.4.4. 4-trifluoromethylbiphenyl (9d)

^1H NMR (CDCl_3) δ 7.67 (br, 4 H), 7.59–7.57 (m, 2 H), 7.47–7.43 (m, 2 H), 7.40–7.37 (m, 1 H): ^{13}C NMR (CDCl_3) δ 144.7, 139.7, 129.3 (q, $J = 32.5$ Hz, 1 C), 128.9 (2 C), 128.1 (2 C), 127.5, 127.2 (2 C), 125.6 (q, $J = 3.7$ Hz, 2 C), 124.4 (q, $J = 271.8$ Hz, 1 C). MS (EI): m/z (rel%) 222 (bp, M^+), 203 (8), 153 (17). HRMS (EI): calcd for $\text{C}_{13}\text{H}_9\text{F}_3$ 222.0656, found 222.0655. IR (ATR): (cm^{-1}) ν 3034, 1613, 1111.

3.4.5. 2-methylbiphenyl (9e)

^1H NMR (CDCl_3) δ 7.57–7.38 (m, 2 H), 7.35–7.30 (m, 3 H), 7.24–7.20 (m, 4 H), 2.26 (s, 3 H): ^{13}C NMR (CDCl_3) δ 141.9, 141.9, 135.3, 130.2, 129.7, 129.1, 128.7, 128.0, 127.2, 127.1, 126.7, 125.7, 20.4. MS (EI): m/z (rel%) 168 (bp, M^+), 165 (38), 152 (30). IR (ATR): (cm^{-1}) ν 3061, 1598, 1478, 1073.

CAS registry number: 643-58-3.

3.4.6. 3-methylbiphenyl (9f)

^1H NMR (CDCl_3) δ 7.58–7.56 (m, 2 H), 7.42–7.37 (m, 4 H), 7.32–7.29 (m, 2 H), 7.15–7.13 (m, 1 H), 2.40 (s, 3 H): ^{13}C NMR (CDCl_3) δ 141.3, 141.2, 138.2, 128.6 (2 C), 127.96 (2 C), 127.16 (2 C), 124.26 (2 C), 21.4. MS (EI): m/z (rel%) 168 (bp, M^+), 167 (58), 165 (24), 115 (6), 91 (5). IR (ATR): (cm^{-1}) ν 3057, 1600, 1481, 1027.

CAS registry number: 643-93-6.

3.4.7. 1-phenylnaphthalene (9g)

^1H NMR (CDCl_3) δ 7.88 (t, $J = 9.0$ Hz, 2 H), 7.82 (d, $J = 8.2$ Hz, 1 H), 7.56–7.33 (m, 9 H): ^{13}C NMR (CDCl_3) δ 140.7, 140.2, 133.7, 131.6, 130.0 (2 C), 128.7, 128.2 (2 C), 127.6, 127.1, 127.1, 126.8, 125.9, 125.7, 125.3. MS (EI): m/z (rel%) 204 (bp, M^+), 203 (99), 201 (12), 101 (23). IR (ATR): (cm^{-1}) ν 3055, 1590, 1493, 1019.

CAS registry number: 605-02-7.

3.4.8. 4-fluorobiphenyl (9i)

^1H NMR (CDCl_3) δ 7.72–7.50 (m, 4 H), 7.43–7.41 (m, 2 H), 7.39–7.30 (m, 1 H), 7.17–7.08 (m, 2 H): ^{13}C NMR (CDCl_3) δ 162.4 (d, $J = 246.3$ Hz, 1 C), 140.2, 137.3 (d, $J = 3.2$ Hz, 2 C), 128.7, 128.6, 128.5, 127.2, 126.9 (2 C), 115.5 (d, $J = 21.4$ Hz, 2 C). MS (EI): m/z (rel%) 172 (bp, M^+), 171 (47), 85 (9). IR (ATR): (cm^{-1}) ν 3042, 1596, 1482, 1233.

CAS registry number: 324-74-3.

3.4.9. 4-chlorobiphenyl (9h)

^1H NMR (CDCl_3) δ 7.57–7.49 (m, 4 H), 7.46–7.34 (m, 5 H): ^{13}C NMR (CDCl_3) δ 139.9, 139.6, 133.3, 128.8 (4C), 128.3 (2C), 127.5, 126.9 (2C). MS (EI): m/z (rel%) 188 (bp, M^+), 153 (23), 151 (12), 94 (4), 51 (4). IR (ATR): (cm^{-1}) ν 3065, 3038, 1475, 1096.

CAS registry number: 2051-62-9.

3.4.10. biphenyl-4-carboxylic acid (9j)

^1H NMR (CDCl_3) δ 12.5 (br, 1 H), 8.09 (d, $J = 8.5$ Hz, 1 H), 7.72–7.65 (m, 4 H), 7.39–7.29 (m, 4 H); ^{13}C NMR (CDCl_3) δ 146.7, 141.3, 134.6, 131.2, 130.0, 129.1 (2 C), 128.5 (2 C), 128.1 (2 C), 127.9 (2 C). MS (ESI): 221.0 ($\text{M}+\text{Na}^+$). IR (ATR): (cm^{-1}) ν 3446, 3080, 1677, 1602.

CAS registry number: 92-92-2.

3.5. Mizoroki-Heck Reaction

The general procedure to obtain Mizoroki-Heck reaction products **11a–h** is as described here for **11a**. Styrene (**11a**; 83 mg, 0.8 mmol) was added to a mixture of polymeric catalyst (**1**; 80 mg, 0.020 mmol), base DBU (121 mg, 0.8 mmol), and iodobenzene (**7a**; 81 mg, 0.4 mmol) in H_2O (3.0 mL). The reaction mixture was shaken at 100 °C for 12 h and then filtered. The recovered resin beads were rinsed with H_2O and extracted three times with EtOAc (6 mL). The EtOAc layer was separated and the aqueous layer was extracted with EtOAc (3 mL). The combined EtOAc extracts were washed with brine (2 mL), dried over MgSO_4 , and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel (hexane) to give 64.8 mg (90% yield) of (*E*)-1,2-diphenylethene (**11a**).

3.6. Spectral and Analytical Data for the Stilbenes

3.6.1. (*E*)-1,2-diphenylethene (11a)

^1H (CDCl_3) δ 7.57–7.39 (m, 4 H), 7.36–7.21 (m, 6 H), 7.14 (s, 2 H); ^{13}C (CDCl_3) δ 137.5 (2 C), 128.8 (2 C), 128.7 (4 C), 127.6 (2 C), 126.6 (2 C). MS (EI): m/z (rel%) 180 (bp, M^+), 179 (96), 165 (44). IR (ATR): (cm^{-1}) ν 2922, 1737, 1450.

CAS registry number: 103-30-0.

3.6.2. (*E*)-1-methyl-4-styrylbenzene (11b)

^1H NMR (CDCl_3) δ 7.53–7.08 (m, 9 H), 7.04 (s, 2 H), 2.33 (s, 3 H); ^{13}C NMR (CDCl_3) δ 137.7, 137.5, 134.8, 129.4 (2 C), 128.8, 128.6 (2 C), 127.9, 127.4, 126.5 (2 C), 126.4 (2 C), 21.0. MS (EI): m/z (rel%) 194 (98, M^+), 193 (23), 179 (bp). IR (ATR): (cm^{-1}) ν 3020, 1592, 1508, 1448.

CAS registry number: 4714-21-0.

3.6.3. (*E*)-1-methoxy-4-styrylbenzene (11c)

^1H NMR (CDCl_3) δ 7.50–7.20 (m, 7 H), 7.00–6.81 (m, 4 H), 3.79 (s, 3 H); ^{13}C NMR (CDCl_3) δ 159.2, 137.8, 128.6 (2 C), 128.4, 127.7 (2 C), 127.2 (2 C), 126.8, 126.3 (2 C), 114.3 (2 C), 55.2. MS (EI): m/z (rel%) 210 (bp, M^+), 195 (20), 167 (31), 165 (32). IR (ATR): (cm^{-1}) ν 2935, 1599, 1509.

CAS registry number: 1142-15-0.

3.6.4. (*E*)-1-trifluoromethyl-4-styrylbenzene (11d)

^1H NMR (CDCl_3) δ 7.55–7.29 (m, 9 H), 7.11–7.10 (m, 2 H): ^{13}C NMR (CDCl_3) δ 140.8, 131.9, 129.2 (q, $J = 32.3$ Hz, 1 C), 128.7 (2 C), 128.3 (2 C), 127.1, 126.9 (2 C), 126.5 (2 C), 125.6 (q, $J = 3.9$ Hz, 2 C), 124.2 (q, $J = 271.5$ Hz, 1 C). MS (EI): m/z (rel%) 248 (bp, M^+), 179 (74), 178 (62). HRMS (EI): calcd for $\text{C}_{15}\text{H}_{11}\text{F}_3$ 248.0812, found 248.0818. IR (ATR): (cm^{-1}) ν 2923, 1611, 1132.

3.6.5. (*E*)-1-methyl-2-styrylbenzene (11e)

^1H NMR (CDCl_3) δ 7.56–7.11 (m, 11 H), 2.41 (s, 3 H): ^{13}C NMR (CDCl_3) δ 130.4, 130.1, 128.6 (4 C), 127.5 (2 C), 126.7, 126.5, 126.2 (2 C), 125.5, 19.6. MS (EI): m/z (rel%) 194 (82, M^+), 179 (bp), 115 (22). IR (ATR): (cm^{-1}) ν 3023, 1494.

CAS registry number: 74685-42-0.

3.6.6. (*E*)-1-methyl-3-styrylbenzene (11f)

^1H NMR (CDCl_3) δ 7.53–7.11 (m, 9 H), 7.05 (s, 2 H), 2.34 (s, 3 H): ^{13}C NMR (CDCl_3) δ 138.2, 137.6, 137.5, 129.0, 128.6 (3 C), 128.6, 128.4, 127.5, 127.3, 126.5 (2 C), 123.8, 21.2. MS (EI): m/z (rel%) 194 (93, M^+), 193 (28), 179 (bp). IR (ATR): (cm^{-1}) ν 3022, 1598, 1493, 1448, 964.

CAS registry number: 14064-48-3.

3.6.7. (*E*)-1-styrylnaphthalene (11g)

^1H NMR (CDCl_3) δ 8.24–7.16 (m, 14 H): ^{13}C NMR (CDCl_3) δ 137.5, 135.1, 133.9, 132.2, 131.9, 128.8 (2 C), 128.6, 128.0, 127.7, 126.7 (2 C), 126.0, 125.9, 125.9, 125.7, 123.8, 123.7. MS (EI): m/z (rel%) 230 (99, M^+), 229 (bp), 228 (31), 152 (25). IR (ATR): (cm^{-1}) ν 3055, 3022, 1493, 957.

CAS registry number: 2043-00-7.

3.6.8. (*E*)-1-chloro-4-styrylbenzene (11h)

^1H NMR (CDCl_3) δ 7.52–7.26 (m, 9 H), 7.01 (s, 2 H): ^{13}C NMR (CDCl_3) δ 136.9, 135.7, 133.1, 129.2, 128.7 (2 C), 128.6 (2 C), 127.8, 127.6 (2 C), 127.2, 126.5 (2 C). MS (EI): m/z (rel%) 214 (85, M^+), 179 (99), 89 (27), 76 (23). IR (ATR): (cm^{-1}) ν 3021, 2923, 1488, 1087.

CAS registry number: 4714-23-2.

3.7. Sonogashira Coupling Reaction

The general procedure to obtain Sonogashira coupling reaction products **13a–g** is as described here for **13a**. phenylacetylene (**12**; 81.7 mg, 0.8 mmol) was added to a mixture of polymeric catalyst (**1**; 80 mg, 0.024 mmol), base Et_3N (121 mg, 1.2 mmol), and iodobenzene (**7a**; 81.6 mg, 0.4 mmol) in H_2O (3.0 mL). The reaction mixture was shaken at 60 °C for 12 h and then filtered. The recovered resin beads were rinsed with H_2O and extracted three times with EtOAc (6 mL). The EtOAc layer was

separated and the aqueous layer was extracted with EtOAc (3 mL). The combined EtOAc extracts were washed with brine (2 mL), dried over MgSO₄, and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel (hexane/AcOEt:100/1) to give 55.3 mg (77% yield) of diphenylacetylene (**13a**).

3.8. Spectral and Analytical Data for the Biarylacetylenes

3.8.1. Diphenylacetylene (13a)

¹H NMR (CDCl₃) δ 7.55–7.51 (m, 4 H), 7.36–7.29 (m, 6 H): ¹³C NMR (CDCl₃) δ 131.5, 128.3, 128.2, 123.2, 89.4. MS (EI): *m/z* (rel%) 178 (bp, M⁺), 152 (24). IR (ATR): (cm⁻¹) ν 3062, 1598, 1491.

CAS registry number: 64666-02-0.

3.8.2. 1-Phenyl-2-(*p*-tolyl)acetylene (13b)

¹H NMR (CDCl₃) δ 7.52 (dd, *J* = 8.1, 1.9 Hz, 2 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 7.38–7.30 (m, 3 H), 7.15 (d, *J* = 7.8, 2 H), 2.36 (s, 3 H): ¹³C NMR (CDCl₃) δ 138.3, 134.8, 131.5, 131.4, 129.1, 128.3, 128.0, 127.7, 120.1, 89.5, 21.5. MS (EI): *m/z* (rel%) 192 (bp, M⁺), 165 (27), 39 (21). IR (ATR): (cm⁻¹) ν 3052, 3029, 2215, 1594, 1509, 1441, 1380.

CAS registry number: 185817-85-0.

3.8.3. 1-Phenyl-2-(*p*-trifluoromethylphenyl)acetylene (13c)

¹H NMR (CDCl₃) δ 7.62 (dd, *J* = 14.1, 8.2 Hz, 4 H), 7.56–7.54 (m, 2 H), 7.37 (m, 3 H): ¹³C NMR (CDCl₃) δ 132.5, 131.8, 131.7, 129.8 (q, *J* = 33.1 Hz, 1 C), 128.8, 128.4, 126.4 (q, *J* = 272 Hz, 1 C), 125.2 (q, *J* = 272 Hz, 1 C), 122.5, 91.7, 87.9. MS (EI): *m/z* (rel%) 246 (73, M⁺), 176 (43), 98 (bp), 75 (49), 51 (46). IR (ATR): (cm⁻¹) ν 3080, 2219, 1508.

CAS registry number: 370-99-0.

3.8.4. 1-(*p*-Methoxycarbonylphenyl)-2-phenylacetylene (13d)

¹H NMR (CDCl₃) δ 8.02 (d, *J* = 8.5 Hz, 2 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.57–7.53 (m, 2 H), 7.38–7.36 (m, 3 H), 3.93 (s, 3 H): ¹³C NMR (CDCl₃) δ 166.5, 131.7, 131.4, 129.5, 129.4, 128.7, 128.4, 127.9, 122.6, 92.4, 88.6, 52.9. MS (EI): *m/z* (rel%) 236 (80, M⁺), 205 (bp), 176 (91), 151 (34). IR (ATR): (cm⁻¹) ν 2949, 2217, 1718, 1606, 1508, 1455, 1374, 1280.

CAS registry number: 42497-80-3.

3.8.5. 1-Phenyl-2-(*o*-tolyl)acetylene (13e)

¹H NMR (CDCl₃) δ 7.44–7.39 (m, 3 H), 7.25–7.21 (m, 3 H), 7.12–7.10 (m, 2 H), 7.08–7.04 (m, 1 H), 2.41 (s, 3 H): ¹³C NMR (CDCl₃) δ 166.5, 131.7, 131.4, 129.5, 129.4, 128.7, 128.4, 127.9, 122.6, 92.4, 88.6, 52.9. MS (EI): *m/z* (rel%) 192 (bp, M⁺), 165 (27), 115 (11). IR (ATR): (cm⁻¹) ν 3055, 2919, 1600, 1492.

CAS registry number: 14309-60-5.

3.8.6. 1-Phenyl-2-(*m*-tolyl)acetylene (13f)

^1H NMR (CDCl_3) δ 7.51 (d, $J = 5.8$ Hz, 2 H), 7.35–7.28 (m, 5 H), 7.21 (t, $J = 7.5$ Hz, 1 H), 7.12 (d, $J = 7.5$ Hz, 1 H), 2.33 (s, 3 H): ^{13}C NMR (CDCl_3) δ 137.9, 132.1, 131.5, 129.3, 128.6, 128.2, 128.2, 128.1, 123.3, 122.9, 89.5, 89.0, 21.1. MS (EI): m/z (rel%) 192 (bp M^+), 165 (13), 115 (5). IR (ATR): (cm^{-1}) ν 3003, 2919, 1492.

CAS registry number: 14635-91-7.

3.8.7. 1-(1-Naphthyl)-2-phenylacetylene (13g)

^1H NMR (CDCl_3) δ 8.44 (d, $J = 8.3$ Hz, 1 H), 7.83 (ddd, $J = 13.2, 13.2, 4.9$ Hz, 2 H), 7.75 (d, $J = 7.1$ Hz, 1 H), 7.64 (d, $J = 7.3$ Hz, 2 H), 7.58 (t, $J = 7.3$ Hz, 1 H), 7.52 (t, $J = 7.3$ Hz, 1 H), 7.44 (t, $J = 7.6$ Hz, 1 H), 7.39–7.34 (m, 3 H): ^{13}C NMR (CDCl_3) δ 133.1, 131.7, 131.6, 130.3, 128.7, 128.4, 128.3, 128.2, 128.2, 126.7, 126.4, 126.1, 125.2, 125.2, 94.3, 87.5. MS (EI): m/z (rel%) 228 (bp, M^+), 202 (6), 113 (13). IR (ATR): (cm^{-1}) ν 3055, 1488, 1396.

CAS registry number: 4044-57-9.

3.8.8. 1-(*o*-chlorophenyl)-2-phenylacetylene (13h)

^1H NMR (CDCl_3) δ 7.57–7.55 (m, 3 H), 7.53–7.50 (m, 1 H), 7.34–7.32 (m, 3 H), 7.22–7.18 (m, 2 H): ^{13}C NMR (CDCl_3) δ 135.9, 133.2, 131.7, 129.2, 128.6, 128.3, 126.4, 123.1, 122.8, 94.5, 86.2. MS (EI): m/z (rel%) 212 (bp, M^+), 176 (38), 151 (11). IR (ATR): (cm^{-1}) ν 3057, 1491, 1468.

CAS registry number: 10271-57-5.

3.8.9. 1-(*m*-chlorophenyl)-2-phenylacetylene (13i)

^1H NMR (CDCl_3) δ 7.46–7.43 (m, 3 H), 7.34–7.32 (m, 1 H), 7.29–7.27 (m, 3 H), 7.23–7.16 (m, 2 H): ^{13}C NMR (CDCl_3) δ 134.1, 131.6, 131.4, 129.6, 129.5, 128.5, 128.4, 128.3, 124.9, 122.7, 90.5, 87.8. MS (EI): m/z (rel%) 212 (bp, M^+), 176 (46), 151 (13). IR (ATR): (cm^{-1}) ν 3055, 1490.

CAS registry number: 51624-34-1.

3.9. Tsuji-Trost Coupling Reaction

The general procedure to obtain Tsuji-Trost reaction products **16a–d** is as described here for **16a**. 1,3-Diphenyl-2-propenyl acetate (**14a**; 100 mg, 0.4 mmol) was added to a mixture of polymeric catalyst (**1**; 80 mg, 0.024 mmol), and sodium azide (**15**; 39 mg, 0.6 mmol) in H_2O (3.0 mL). The reaction mixture was shaken at 70 °C for 24 h and then filtered. The recovered resin beads were rinsed with H_2O and extracted three times with EtOAc (6 mL). The EtOAc layer was separated and the aqueous layer was extracted with EtOAc (3 mL). The combined EtOAc extracts were washed with brine (2 mL), dried over MgSO_4 , and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel (hexane) to give 72.7 mg (77% yield) of 1,3-diphenyl-2-propenyl azide (**16a**).

3.10. Spectral and Analytical Data for the Allyl Azide

3.10.1. 1,3-Diphenyl-2-propenyl azide (16a)

^1H NMR (CDCl_3) δ 7.41–7.23 (m, 10 H), 6.71 (d, $J = 15.6$ Hz, 1 H), 6.28 (dd, $J = 15.6, 7.3$ Hz, 1 H), 5.20 (d, $J = 7.3$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 138.6, 135.9, 133.0, 128.8, 128.7, 128.3, 128.2, 127.1, 126.9, 126.8, 67.2. MS (EI): m/z (rel%) 207 (58, M+), 193 (bp), 130 (40), 115 (85). IR (ATR): (cm^{-1}) ν 3028, 2093, 1882, 1809.

CAS registry number: 120990-01-4.

3.10.2. Cinnamyl azide (16b)

^1H NMR (CDCl_3) δ 7.39 (d, $J = 7.3$ Hz, 2 H), 7.32 (t, $J = 7.3$ Hz, 2 H), 7.26 (t, $J = 7.3$ Hz, 1 H), 6.63 (d, $J = 15.8$ Hz, 1 H), 6.23 (td, $J = 6.7, 15.8$ Hz, 1 H), 3.92 (d, $J = 6.7$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ 135.9, 134.4, 128.6, 128.1, 126.5, 122.3, 52.9. IR (ATR): (cm^{-1}) ν 3061, 2927, 2092.

CAS registry number: 28022-21-1.

3.10.3. 3-(*p*-Tolyl)allyl azide (16c)

^1H NMR (CDCl_3) δ 7.29 (d, $J = 8.0$ Hz, 2 H), 7.14 (d, $J = 8.0$ Hz, 2 H), 6.61 (d, $J = 15.8$ Hz, 1 H), 6.18 (td, $J = 6.7, 15.2$ Hz, 1 H), 3.92 (d, $J = 6.1$ Hz, 2 H), 2.33 (s, 3 H); ^{13}C NMR (CDCl_3) δ 138.1, 134.5, 133.2, 129.3, 126.5, 121.2, 53.1, 21.2. MS (EI): m/z (rel%) 173 (10, M+), 144 (63), 131 (bp), 116 (23). HRMS (EI): calcd for $\text{C}_{10}\text{H}_{11}\text{N}_3$ 173.0953, found 173.0960. IR (ATR): (cm^{-1}) ν 3026, 2922, 1652, 1512.

3.10.4. 3-(*p*-Trifluoromethylphenyl)allyl azide (16d)

^1H NMR (CDCl_3) δ 7.58 (d, $J = 7.9$ Hz, 2 H), 7.48 (d, $J = 7.9$ Hz, 2 H), 6.67 (d, $J = 15.8$ Hz, 1 H), 6.32 (td, $J = 6.1, 15.8$ Hz, 1 H), 3.98 (d, $J = 6.1$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ 139.4, 132.3, 129.9 (q, $J = 33.0$ Hz), 126.7, 125.6 (q, $J = 4.1$ Hz), 125.2, 124.0 (q, $J = 270$ Hz), 52.6. MS (EI): m/z (rel%) 227 (23, M+), 206 (42), 185 (bp). HRMS (EI): calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{N}_3$ 227.0670, found 227.0674. IR (ATR): (cm^{-1}) ν 2099, 1321. 227.06703.

3.11. Recycling Experiments for Cross-Coupling Reaction

The general procedure for recycling experiments to obtain cross-coupling coupling reaction products is as described here for **13a** (Suzuki-Miyaura coupling product). To a mixture of the polymeric catalyst **1** (80 mg, 0.020 mmol), K_2CO_3 (110 mg, 0.8 mmol), and iodobenzene (**7a**; 81 mg, 0.4 mmol) in H_2O (3.0 mL) was added phenylboronic acid (**8a**; 97 mg, 0.8 mmol). The reaction mixture was shaken at 100 °C for 6 h and filtered. The recovered resin beads were rinsed with H_2O and extracted three times with EtOAc (6 mL). The EtOAc layer was separated and the aqueous layer was extracted with EtOAc (3 mL). The combined EtOAc extracts were washed with brine (2 mL), dried

over MgSO_4 , and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel (hexane) to give 57 mg (93% yield) of biphenyl (**9a**). After first run, the recovered resin beads were dried *in vacuo* and directly applied in the next reaction under similar conditions. The reaction of iodobenzene (**7a**; 81 mg, 0.4 mmol) and phenylboronic acid (**8a**; 48 mg, 0.4 mmol) with the recovered catalyst **1** took place in K_2CO_3 (110 mg, 0.8 mmol) aqueous solution (3.0 mL) to give the biphenyl in 57 mg (93% yield) of biphenyl (**9a**). For second and third runs, these reaction conditions and procedures were also the same as first reuse procedures.

4. Conclusions

We developed a novel polymer-supported terpyridine palladium complex through ionic bonds to a sulfonate group, which efficiently catalyzed the Suzuki-Miyaura, Mizoroki-Heck, Sonogashira, and Tsuji-Trost, cross-coupling reactions in water under aerobic and mild reaction conditions to give the corresponding cross-coupling product with a high to excellent yield. This catalyst was recovered and reused several times without any loss of catalytic activity. Efforts to further extend the scope of the cross-coupling reactions and the application of this catalyst for other organic transformations are in progress in our lab.

Acknowledgements

We are grateful for the financial support from the Cooperative Research Program of Institute for Materials Chemistry and Engineering, Kyushu University. This work was the Joint Study Program of the Institute for Molecular Science. We also thank the Cooperative Research Center for their financial support for this work.

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26. For control experiments for entry 1 in Table 1; 1) the Suzuki-Miyaura cross-coupling reaction of phenylboronic acids with iodobenzene was performed with 5 mol% of Pd(NCCH₃)₂Cl₂ and PS-PEG-NH₂ resin at 100 °C for 6 h to give the biphenyl in 33% yield. ICP-AES analysis of the filtrate showed that the Pd content was 2.2 ppm.

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