

## Functionalized Arylzinc Compounds in Ethereal Solvent: Direct Synthesis from Aryl Iodides and Zinc Powder and Application to Pd-Catalyzed Reaction with Allylic Halides

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Received November 21, 2002

Arylzinc compounds,  $\text{ArZnX}$ , were conveniently prepared in high yields by the reaction of zinc powder with aryl iodides, which contain electron-withdrawing groups such as  $\text{CO}_2\text{CH}_3$ ,  $\text{CN}$ ,  $\text{Br}$ , or  $\text{CF}_3$  at the ortho-, meta- or para-position, or electron-donating groups such as  $\text{CH}_3$ ,  $\text{OCH}_3$ , or  $\text{H}$ , at  $70^\circ\text{C}$  in THF, at  $100^\circ\text{C}$ , or at  $130^\circ\text{C}$  in diglyme, respectively.  $\text{Pd}(\text{dba})_2$  exhibited an outstanding efficient catalytic effect for the cross-coupling of these ethereal solutions of  $\text{ArZnX}$  with allylic halides to afford a variety of functionalized allylbenzenes in high yields; the reactions were mostly carried out at  $0^\circ\text{C}$  for 5–30 min in the presence of 5 mol % of catalyst. The conversion of the aryl iodides to allylbenzenes via two reactions could be accomplished in one pot.

### Introduction

As a reactive and chemoselective  $\text{Ar}^-$ -supplying reagent, arylzinc compounds,  $\text{ArZnX}$ , which have been generally prepared by the metathesis of  $\text{ArLi}$  or  $\text{ArMgX}$  and  $\text{ZnX}_2$  in THF (Figure 1, path A),<sup>1</sup> are extensively utilized in organic synthesis. By comparison, the recently developed synthetic method for  $\text{ArZnX}$  of treating  $\text{ArX}$  with  $\text{Zn}$  powder in polar solvents such as HMPA, DMF, DMSO, or TMU is far more convenient and atom economic (Figure 1, path B).<sup>2</sup> Moreover, a variety of reactive functional groups such as esters, nitriles, ketones, or halogens ( $\text{Br}$  and  $\text{Cl}$ ) in  $\text{ArX}$  does not interfere with the oxidative addition of  $\text{C-X}$  bonds to  $\text{Zn}$  powder. Therefore, functionalized compounds are readily available based on this method. The obtained  $\text{ArZnX}$  has been successfully utilized in  $\text{Cu}(\text{I})$ - or  $\text{Cr}(\text{III})$ -mediated and  $\text{Pd}(\text{0})$ -catalyzed reactions with various electrophilic reagents such as acyl halides, allylic halides,  $\alpha,\beta$ -unsaturated ketones, aldehydes, or aryl halides, sometimes in place of the conventional  $\text{ArZnX}$  in THF.<sup>2,3</sup> Here it is noted that, because of the lability of the organozinc compounds to moisture, the solution containing  $\text{ArZnX}$  is used in subsequent reactions as obtained. Consequently, a given solvent must be

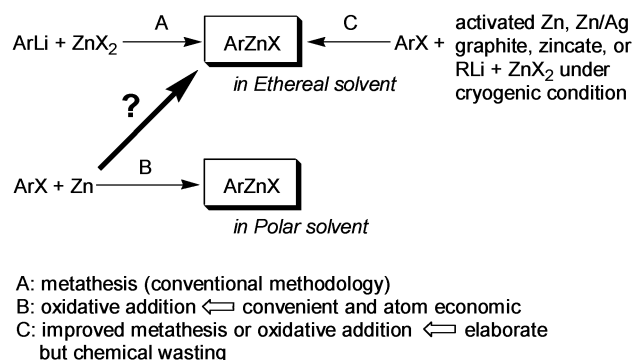


FIGURE 1. Synthesis of arylzinc compounds.

appropriate not only for the preparation but also for the utilization of  $\text{ArZnX}$ . In this context, the aforementioned polar solvents might limit the utility of  $\text{ArZnX}$ , since organometallic reactions are often carried out in less polar solvents such as THF. At present, there exist several sophisticated methods of synthesizing functionalized  $\text{ArZnX}$  in THF (Figure 1, path C),<sup>4,5</sup> however, it is desirable to disclose the most convenient and not chemical wasting synthetic method of these com-

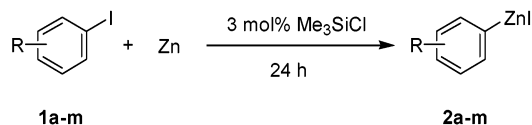
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(5) Several THF solutions of functionalized  $\text{ArZnX}$  are commercially available from Sigma-Aldrich.

**TABLE 1.** Synthesis of Arylzinc Compounds in Ethereal Solvent<sup>a</sup>

Run	R	<b>1</b>	solvent	temp, °C	<b>2</b>	yield, % <sup>b</sup>
1	2-CO <sub>2</sub> CH <sub>3</sub>	<b>1a</b>	THF	70	<b>2a</b>	87
2	2-CN	<b>1b</b>	THF	70	<b>2b</b>	94
3	2-Br	<b>1c</b>	THF	70	<b>2c</b>	95 <sup>c</sup>
4	2-CF <sub>3</sub>	<b>1d</b>	THE	70	<b>2d</b>	70
5	3-CO <sub>2</sub> CH <sub>3</sub>	<b>1e</b>	THF	70	<b>2e</b>	20
6	4-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<b>1f</b>	THF	70	<b>2f</b>	<5
7	2-Br	<b>1c</b>	diglyme	70	<b>2c</b>	82
8	2-CO <sub>2</sub> CH <sub>3</sub>	<b>1a</b>	triglyme	70	<b>2a</b>	86
9	3-CO <sub>2</sub> CH <sub>3</sub>	<b>1e</b>	diglyme	100	<b>2e</b>	84
10	4-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<b>1f</b>	diglyme	100	<b>2f</b>	89
11	4-Cl	<b>1g</b>	diglyme	100	<b>2g</b>	83
12	4-Br	<b>1h</b>	diglyme	100	<b>2h</b>	87 <sup>c</sup>
13	3-Cl	<b>1i</b>	diglyme	100	<b>2i</b>	84
14	4-CH <sub>3</sub>	<b>1j</b>	diglyme	100	<b>2j</b>	51
15		<b>1j</b>	diglyme	130	<b>2j</b>	87
16	4-OCH <sub>3</sub>	<b>1k</b>	diglyme	130	<b>2k</b>	87
17	2-OCH <sub>3</sub>	<b>1l</b>	diglyme	130	<b>2l</b>	86
18	H	<b>1m</b>	diglyme	130	<b>2m</b>	83
19 <sup>d</sup>	3-Cl	<b>1i</b>	diglyme	160	<b>2i</b>	81
20 <sup>e</sup>		<b>1i</b>	triglyme	180	<b>2i</b>	78
21 <sup>f</sup>	2-CO <sub>2</sub> CH <sub>3</sub>	<b>1a</b>	triglyme	180	<b>2a</b>	78
22 <sup>g</sup>	4-CH <sub>3</sub>	<b>1j</b>	triglyme	180	<b>2j</b>	83

<sup>a</sup> Molar ratio: 1/Zn/Me<sub>3</sub>SiCl = 1/2/0.03. Conv.: >97% except for Runs 5 (25%), 6 (8%), and 14 (68%). <sup>b</sup> GLC yield of reproduced ArI, after I<sub>2</sub> treatment of reaction mixture (see Experimental Section). <sup>c</sup> C–Br bond was retained intact. <sup>d</sup> Reaction time: 30 min. <sup>e</sup> Reaction time: 15 min. <sup>f</sup> Reaction time: 10 min. <sup>g</sup> Reaction time: 1.5 h.

pounds in weakly polar solvents. Therefore, we investigated the direct reaction between ArX and Zn powder using ethereal solvents such as THF.

## Results and Discussion

**Synthesis of ArZnX in Ethereal Solvent.** The reactions of various aryl iodides (ArI) **1** with Zn powder (2 equiv) were carried out at 70 °C (bath temperature) for 24 h in THF under nitrogen. These results are summarized in Table 1. To our delight, the oxidative addition of a ArI-containing electron-withdrawing group EWG such as CO<sub>2</sub>CH<sub>3</sub>, CN, Br,<sup>6</sup> or CF<sub>3</sub> at the ortho-position to Zn powder smoothly took place to afford the corresponding ArZnI **2** in a good yield along with a small amount of ArH (2–10%) (Runs 1–4). Other ArI, i.e., one containing EWG at the meta- or para-position or an electron-donating group EDG, however, were less reactive and the reaction was incomplete under similar conditions (Runs 5 and 6).<sup>7,8</sup> We then tried to raise the reaction temperature over 70 °C, intending to thermally activate such a reaction system. Simultaneously, the THF solvent was changed to diglyme (bp 162 °C) or triglyme

(bp 215 °C), less volatile ethereal solvents, to conduct the preparation in ordinary glassware and render the procedure simple and useful from a practical viewpoint. First of all, diglyme and triglyme were equally effective as THF for the reaction of the reactive ArI (Runs 1, 3, 7, and 8). It was ascertained that the increase in the reaction temperature by 30 °C (bath temperature 100 °C) or 60 °C (bath temperature 130 °C) was sufficient to enhance the reactivity of the electron-poor ArI (ones containing EWG such as CO<sub>2</sub>CH<sub>3</sub>, CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, Cl, or Br at the meta- or para-position) (Runs 9–13) or electron-rich ArI (ones containing EDG) (Runs 15–18) in diglyme, resulting in the completion of the reactions in 24 h, respectively. From these reactions, the desired products were obtained in good yields. Fortunately, further elevation of the reaction temperature merely shortened the reaction time, without decreasing the yield due to the thermal robustness of ArZnX in ethereal solvents (Runs 19–22). For example, a raise in the reaction temperature by 110 °C from 70 °C shortened the reaction time from 24 h in THF to 10 min in triglyme, retaining a good yield (87 or 78%) for **1a** (Runs 1 and 21). The bromo-substituent in ArI was retained intact during the reaction (Runs 3 and 12), but at the higher temperature of around 200 °C (in triglyme), the reaction of bromobenzene with Zn powder took place. However, PhZnX was obtained only in low yield (6%).

**Reaction of an Ethereal Solution of ArZnX with Allylic Halides.** Next, we investigated the utility of our ethereal solution of ArZnX for organic synthesis, taking up the cross-coupling with allylic electrophiles leading to allylbenzenes as a probe. Although the efficiency of Pd or Ni catalysis for the reaction of ordinary ArZnX (Ar = phenyl, *p*-tolyl, or 1-naphthyl) has been known for two decades,<sup>9,10</sup> the functionalized ones have been rarely applied to the reaction.<sup>1b,11</sup>

At first, the solution composed of PhZnI, allyl acetate (1.1 equiv), and Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) in diglyme was stirred at room temperature for 6 h under nitrogen. Under very typical conditions,<sup>9</sup> allylbenzene was obtained in 78% yield along with a small amount of biphenyl (7%), which showed that our ArZnX possessed reactivity similar to the conventional ones prepared from ArLi or ArMgX and ZnX<sub>2</sub> in THF (Run 1 in Table 2).<sup>9</sup> After further examination of the reaction conditions, we found that bis(dibenzylideneacetone)palladium (Pd(dba)<sub>2</sub>) exhibited an excellent catalytic efficiency for the reaction, when allyl chloride was also used as an allylic electrophile. Allylbenzene was produced in quantitative yield by stirring of the reaction solution at 0 °C for 5 min (Run 3). As a reaction medium, TMU was less effective than diglyme in terms of the reaction time required to reach

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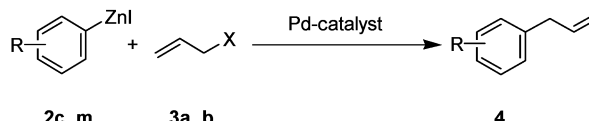
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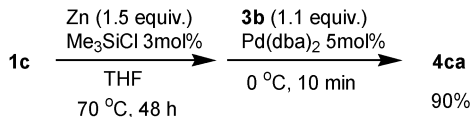
(7) As for the difference in reactivity of ArI to Zn powder during oxidative addition, see ref 2e.

(8) Besides these aryl iodides, activated alkenyl iodides are known to react with Zn powder in THF at the bond between the sp<sup>2</sup>-carbon and iodine to yield the corresponding alkenylzinc compounds: Prasad, A. S. B.; Knochel, P. *Tetrahedron* **1997**, *53*, 16711.

**TABLE 2.** Pd-Catalyzed Cross-Coupling between ArZnI and Allyl Electrophile<sup>a</sup>


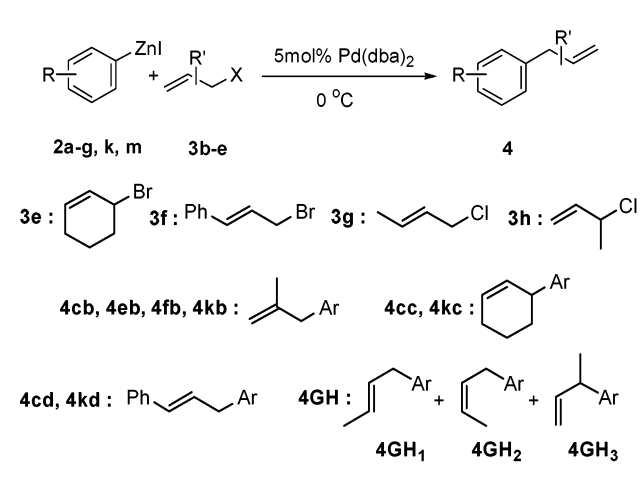
Run	R	2	X	3	catalyst	temp, °C/ time	4	yield, % <sup>b</sup>
1	H	<b>2m</b>	OAc	<b>3a</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	rt/6 h	<b>4ma</b>	78 <sup>c</sup>
2		<b>2m</b>		<b>3a</b>	Pd(dba) <sub>2</sub>	rt/6 h	<b>4ma</b>	80 <sup>d</sup>
3		<b>2m</b>	Cl	<b>3b</b>	Pd(dba) <sub>2</sub>	0/5 min	<b>4ma</b>	99
4 <sup>e</sup>		<b>2m</b>		<b>3b</b>	Pd(dba) <sub>2</sub>	0/1 h	<b>4ma</b>	91
5 <sup>f</sup>		<b>2m</b>		<b>3b</b>	Pd(dba) <sub>2</sub>	0/20 h	<b>4ma</b>	80
6 <sup>g</sup>		<b>2m</b>		<b>3b</b>		0/24 h	<b>4ma</b>	0
7		<b>2m</b>		<b>3b</b>	Pd(OAc) <sub>2</sub>	0/5 min	<b>4ma</b>	92 <sup>h</sup>
8		<b>2m</b>		<b>3b</b>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	0/5 min	<b>4ma</b>	0
9		<b>2m</b>		<b>3b</b>	Pd(dba) <sub>2</sub>	0/1 h	<b>4ma</b>	89 <sup>i</sup>
10	2-Br	<b>2c</b>		<b>3b</b>	Pd(dba) <sub>2</sub>	0/10 min	<b>4ca</b>	(91)
11		<b>2c</b>		<b>3b</b>	Pd(dba) <sub>2</sub>	0/10 min	<b>4ca</b>	(89)
12		<b>2c</b>		<b>3b</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	rt/24 h	<b>4ca</b>	9 <sup>j</sup>

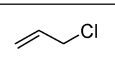
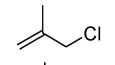
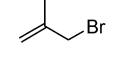
<sup>a</sup> Molar ratio: **2**/**3**/catalyst = 1/1.1/0.05. Solvent: diglyme (Runs 1–8 and 11), TMU (Run 9), or THF (Runs 10 and 12). <sup>b</sup> GLC yield. Yields in parentheses are isolated ones. <sup>c</sup> Biphenyl was obtained in 7% yield. <sup>d</sup> Biphenyl was obtained in 9% yield. <sup>e</sup> Catalyst: 1 mol % <sup>f</sup> Catalyst: 0.1 mol %. <sup>g</sup> Catalyst: 0%. <sup>h</sup> Biphenyl was obtained in 7% yield. <sup>i</sup> Biphenyl was obtained in 8% yield. <sup>j</sup> Conv.: 19%.

**SCHEME 1.** One-Pot Synthesis of Allylarene

an end and the selectivity of the desired cross-coupling product, whereas THF was equally effective as diglyme (Runs 9–11).<sup>12</sup> In other words, the present study's ArZnX is far more effective than the one in a polar solvent<sup>2</sup> for the reaction. As shown in Table 3, a variety of functionalized ArZnX were successfully utilized in the reaction in place of PhZnX to afford the corresponding allylbenzenes in good yields. Among them, the electron-rich ones (Runs 7 and 8) tended to react faster than the electron-poor ones (Runs 2–6) and the *o*-CO<sub>2</sub>CH<sub>3</sub> substituted one (Run 1) needed an exceptionally long reaction time. The reactivity of allylic bromide is higher than that of allylic chloride (Runs 9 and 10). Substituents in allylic halides caused a decreasing reactivity (Run 11 in Table 2 and Run 9 in Table 3), yet their reactions afforded the desired products in high yields (Runs 9–15), where the sterically less hindered regioisomers were selectively or mainly produced (Runs 16–19). Since both reactions of the oxidative addition of ArI to Zn powder and the cross-coupling of the resulting ArZnI with allylic halides in the presence of Pd(dba)<sub>2</sub> smoothly took place in common ethereal solvents, the one-pot synthesis of allylbenzenes starting from ArI was readily achieved (Scheme 1). It should be emphasized that the present aryl–allyl cross-coupling possesses advantages over the others using various arylmetallic compounds,<sup>13a</sup> for example, involving Mg,<sup>13b,c</sup> Cu,<sup>2e,4a,b,e–g,13e</sup> Zn,<sup>13d</sup> B,<sup>10d,13f–i</sup> Sn,<sup>10d,13j,k</sup> Tl,<sup>13l</sup>

(12) These ethereal solvents are less volatile than THF but did not cause trouble with the isolation of the reaction product, since they were readily transferred from the organic layer to the acidic aqueous one by the extraction procedure.

**TABLE 3.** Pd-Catalyzed Synthesis of Functionalized Allylbenzenes<sup>a</sup>

Run	R	2	3	Time / min.	4	Yield / % <sup>b</sup>
1	2-CO <sub>2</sub> CH <sub>3</sub>	<b>2a</b>		<b>3b</b>	18 h	<b>4aa</b> 80
2	2-CN	<b>2b</b>		<b>3b</b>	10	<b>4ba</b> 92
3	2-CF <sub>3</sub>	<b>2d</b>		<b>3b</b>	10	<b>4da</b> 94
4	3-CO <sub>2</sub> CH <sub>3</sub>	<b>2e</b>		<b>3b</b>	10	<b>4ea</b> 93
5	4-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<b>2f</b>		<b>3b</b>	10	<b>4fa</b> 87
6	4-Cl	<b>2g</b>		<b>3b</b>	10	<b>4ga</b> 90
7	4-OCH <sub>3</sub>	<b>2k</b>		<b>3b</b>	5	<b>4ka</b> 84
8	H	<b>2m</b>		<b>3b</b>	5	<b>4ma</b> 91
9	2-Br	<b>2c</b>		<b>3c</b>	20	<b>4cb</b> 87
10		<b>2c</b>		<b>3d</b>	10	<b>4cb</b> 93
11	3-CO <sub>2</sub> CH <sub>3</sub>	<b>2e</b>		<b>3d</b>	10	<b>4eb</b> 81
12	4-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<b>2f</b>		<b>3d</b>	10	<b>4fb</b> 85
13	4-OCH <sub>3</sub>	<b>2k</b>		<b>3d</b>	10	<b>4kb</b> 98
14	2-Br	<b>2c</b>		<b>3e</b>	30	<b>4cc</b> 96
15	4-OCH <sub>3</sub>	<b>2k</b>		<b>3e</b>	30	<b>4kc</b> 98
16	2-Br	<b>2c</b>		<b>3f</b>	30	<b>4cd</b> 84
17	4-OCH <sub>3</sub>	<b>2k</b>		<b>3f</b>	30	<b>4kd</b> 80
18		<b>2k</b>		<b>3g<sup>c</sup></b>	10	<b>4GH</b> 86 <sup>d</sup>
19		<b>2k</b>		<b>3h</b>	10	<b>4GH</b> 86 <sup>e</sup>

<sup>a</sup> Molar ratio: **2**/**3**/catalyst = 1/1.1/0.05. Solvent: THF (Runs 1–3, 9, 10, 14, and 16) or diglyme (Runs 4–8, 11–13, 15, and 17–19). <sup>b</sup> Isolated yield. Ratio of isomers was determined by <sup>1</sup>H NMR. <sup>c</sup> Z-isomer (16%) and **3h** (5%) were contained. <sup>d</sup> **4GH**<sub>1</sub>:**4GH**<sub>2</sub>:**4GH**<sub>3</sub> = 67:9:24. <sup>e</sup> **4GH**<sub>1</sub>:**4GH**<sub>2</sub>:**4GH**<sub>3</sub> = 40:20:40.

or Hg<sup>13m</sup> in terms of (1) the availability of starting organometallic compounds, including the functionalized ones, especially in the manner of atom economics,<sup>2e,4a,b,e–g,10d,13d–m,14</sup> (2) the mildness of the utilized reaction conditions and high degree of catalytic efficiency,<sup>2e,4a,b,e–g,13d–m,15</sup> and/or (3) the simplicity of the reaction procedure.<sup>4g,13c–e</sup>

In conclusion, application of the simple thermal condition of 70–130 °C to the reaction system composed of ArI and Zn powder in ethereal solvent achieved the first practical synthesis of various ArZnX in the solvent. The solution served as an outstandingly efficient Ar<sup>-</sup> supply reagent in the reaction with allylic halides to afford a variety of functionalized allylbenzenes by the catalysis of Pd(dba)<sub>2</sub>.

## Experimental Section

**General.** All reactions were performed under an atmosphere of nitrogen in oven-dried glassware. Triglyme was distilled under nitrogen and stored over Molecular Sieves 3A. Zn powder (from Kanto Chemical), anhydrous THF, and anhydrous diglyme were purchased and used without further purification. The NMR spectra were recorded in CDCl<sub>3</sub> at 200 MHz for <sup>1</sup>H or at 50.3 MHz for <sup>13</sup>C with TMS or chloroform-*d*<sub>1</sub> as the internal standard, respectively.

**General Procedure for Synthesis of Arylzinc Compounds in Ethereal Solvent.** Zn powder (654 mg, 10 mmol) in a reaction flask was heated by a heat-gun for 10 min under vacuum (1 Torr). To the solid were added aryl iodide (5 mmol), ethereal solvent (2.5 mL), and trimethylchlorosilane (0.015 mL, 0.15 mmol) at room temperature under nitrogen and stirred at the stated temperature (70–180 °C) for the stated period (10 min to 24 h). The presence of trimethylchlorosilane is not necessarily indispensable but provides more reproducible results. The reaction conversion was determined by adding an internal standard to the resulting mixture and then quenching the aliquot of supernatant solution with aqueous HCl, followed by GLC analysis of the remaining aryl iodide. The yield of the arylzinc compound was similarly determined by quenching the aliquot of solution with I<sub>2</sub>, followed by GLC analysis of the reproduced aryl iodide.

**Palladium-Catalyzed Reaction of Arylzinc Compound with Allyl Chloride.** A typical procedure is as follows: To Pd(dba)<sub>2</sub> (27 mg, 0.05 mmol) were added **3d** (0.11 mL, 1.1

mmol) and a 2.0 M THF solution of **2c** (0.50 mL, 1.0 mmol) at 0 °C under nitrogen with stirring for 10 min at temperature. The resulting mixture was quenched by the addition of aqueous HCl. Workup by extraction with ether, washing with water, drying with MgSO<sub>4</sub>, and evaporation of the solvent afforded a crude product, which was chromatographed on silica gel with hexane as the eluent to afford 190 mg of 3-(2-bromophenyl)-2-methyl-1-propene, **4cb** (93%): oil; IR (CDCl<sub>3</sub>) 1647, 706 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.76 (s, 3H), 3.45 (s, 2H), 4.59 (s, 1H), 4.86 (s, 1H), 7.03–7.11 (m, 1H), 7.22–7.25 (m, 2H), 7.54 (d, *J* = 7.4 Hz, 1H); <sup>13</sup>C NMR δ 22.5, 43.9, 112.4, 125.1, 127.3, 127.8, 130.9, 132.8, 139.1, 143.5; HRMS calcd for C<sub>10</sub>H<sub>11</sub>Br 210.0044, found M<sup>+</sup> 210.0025.

**Methyl 3-(2-methyl-2-propenyl)benzoate (4eb):** oil; IR (CDCl<sub>3</sub>) 1719, 1650, 708 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.67 (s, 3H), 3.36 (s, 2H), 3.91 (s, 3H), 4.74 (s, 1H), 4.84 (s, 1H), 7.36–7.39 (m, 2H), 7.92–7.92 (m, 2H); <sup>13</sup>C NMR δ 22.0, 44.3, 52.0, 112.4, 127.4, 128.3, 130.0, 130.1, 133.5, 140.1, 144.4, 167.2. Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.76; H, 7.42. Found: C, 75.72; H, 7.47.

**Ethyl 4-(2-methyl-2-propenyl)benzoate (4fb):** oil; IR (CDCl<sub>3</sub>) 1711, 1652, 706 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.39 (t, *J* = 7.2 Hz, 3H), 1.67 (s, 3H), 3.37 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.74 (s, 1H), 4.84 (s, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H); <sup>13</sup>C NMR δ 14.3, 22.0, 44.6, 60.8, 112.6, 128.4, 128.9, 129.6, 144.2, 145.1, 166.6. Anal. Calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: C, 76.44; H, 7.90. Found: C, 76.24; H, 7.94.

**3-(2-Bromophenyl)-1-cyclohexene (4cc):** oil; IR (CDCl<sub>3</sub>) 1650, 708 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.38–1.71 (m, 3H), 2.01–2.11 (m, 3H), 3.85 (ddd, *J* = 10.1, 5.4, 2.4 Hz, 1H), 5.65 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.96 (ddd, *J* = 10.0, 6.0, 3.6 Hz, 1H), 7.00–7.11 (m, 1H), 7.25 (d, *J* = 4.2 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR δ 20.7, 25.0, 30.2, 40.7, 124.4, 127.3, 127.5, 129.2, 129.3, 132.7, 145.0. Anal. Calcd for C<sub>12</sub>H<sub>13</sub>Br: C, 60.78; H, 5.53. Found: C, 60.40; H, 5.57.

**1-Allyl-2-trifluoromethylbenzene (4da):**<sup>17</sup> <sup>1</sup>H NMR δ 3.56 (d, *J* = 6.4 Hz, 2H), 5.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.12 (s, 1H), 5.95 (ddt, *J* = 16.6, 10.4, 6.4 Hz, 1H), 7.25–7.36 (m, 2H), 7.51 (t, *J* = 7.1 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H).

**(E)-1-(4-Methoxyphenyl)-2-butene (4GH1):**<sup>18</sup> <sup>1</sup>H NMR δ 1.67 (d, *J* = 6.0 Hz, 3H), 3.24 (d, *J* = 5.7 Hz, 2H), 3.77 (s, 3H), 5.43–5.59 (m, 2H), 6.80–6.85 (m, 2H), 7.05–7.13 (m, 2H).

**(Z)-1-(4-Methoxyphenyl)-2-butene (4GH2):**<sup>18</sup> <sup>1</sup>H NMR δ 1.71 (d, *J* = 5.1 Hz, 3H), 3.34 (d, *J* = 5.1 Hz, 2H), 3.78 (s, 3H), 5.44–5.59 (m, 2H), 6.82 (m, 2H), 7.10 (m, 2H).

**Methyl 2-allylbenzoate (4aa):** see ref 19.

**2-Allylbenzenecarbonitrile (4ba):** see ref 20.

**2-Bromo-1-allylbenzene (4ca):** see ref 21.

**Methyl 3-allylbenzoate (4ea):** see ref 22.

**Ethyl 4-allylbenzoate (4fa):** see ref 23.

**3-(4-Methoxyphenyl)-2-methyl-1-propene (4kb):** see ref 24.

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(14) Unlike Zn, the direct reaction between aryl halides and other metals such as Cu, B, or Sn does not take place under ordinary conditions.

(15) The catalytic cycle of the Pd-catalyzed aryl-allyl cross-coupling contains three sequential reactions of (1) oxidative addition between Pd(0) and allylic electrophiles to form the π-allylPd(II) complex, (2) transmetalation with arylmetallic compound to form the π-allyl(aryl)-Pd(II) complex, and (3) reductive elimination of the resulting complex to form the coupling product along with Pd(0).<sup>16</sup> Hegedus described the reason the conventional reaction utilizing the allylic acetates and Pd(PPh<sub>3</sub>)<sub>4</sub> as allylic electrophile and catalyst, respectively, had been slow to develop. It is due to the fact that acetate coordinates quite strongly to Pd and this, along with the presence of excess phosphine, slows down the crucial transmetalation step, already the rate-limiting step.<sup>16</sup> In contrast, the utility of not only phosphine-free Pd(0), Pd(dba)<sub>2</sub>, but also allylic halides in this study might be beneficial to accelerate the catalytic reaction by promoting the transmetalation due to rendering the Pd center more electronically positive.

**3-(4-Methoxyphenyl)-1-cyclohexene (4kc):** see ref 25.

**3-(2-Bromophenyl)-1-phenyl-1-propene (4cd):** see ref 26.

**3-(4-Methoxyphenyl)-1-phenyl-1-propene (4kd):** see ref 25.

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**3-(4-Methoxyphenyl)-1-butene (4GH3):** see ref 27.

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