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Hydrazone–Palladium-Catalyzed Allylic Arylation of Cinnamyloxyphenylboronic Acid Pinacol Esters

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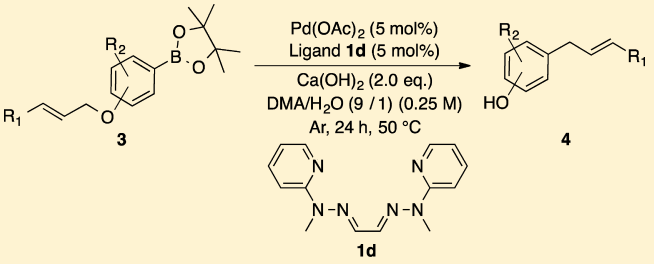
Supporting Information

ABSTRACT: Allylic arylation of cinnamyloxyphenylboronic acid pinacol esters **3**, which have arylboronic acid moiety and allylic ether moiety, using a hydrazone **1d**–$Pd(OAc)_2$ system proceeded and gave the corresponding 1,3-diarylpropene derivatives **4** with a phenolic hydroxyl group via a selective coupling reaction of the π-allyl intermediate to the boron-substituted position of the leaving group.



INTRODUCTION

1,3-Diarylpropene frameworks constitute many natural compounds.[1] In particular, 1,3-diarylpropene derivatives with a phenolic hydroxyl group are known as versatile building blocks in natural products and biologically active compounds.[2] For example, obtusastyrene and obtustyrene are isolated from *Dalbergia retusa* as natural product (Figure 1).[2a] Therefore, an

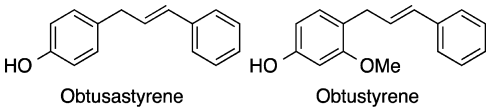


Figure 1. 1,3-Diarylpropene derivatives having a phenolic hydroxyl group.

effective approach toward synthesis of these derivatives is very important in terms of not only organic synthesis but also biological perspective. The synthesis of 1,3-diarylpropene derivatives via palladium-catalyzed allylic arylation using allylic bromides[3] or vinyl epoxides[4] with arylboronic acids were reported as pioneering studies. Recently, palladium-catalyzed allylic arylations of allylic acetates with arylboronic acids for synthesis of 1,3-diarylpropene derivatives have been reported.[5] Although allylic C–H arylation of allylbenzenes were also reported,[6] Heck-type allylic C–H arylation with arylboronic acids gave the mixture of the double-bond-migrated isomers.[6a,c] On the other hand, we demonstrated that easily prepared and air-stable hydrazones are effective ligands for palladium-catalyzed C–C bond formation reactions[7] including the allylic arylation of allylic acetates with arylboronic acids.[8] More recently, we also reported allylic arylation of allylic ethers as a starting material instead of allylic acetates using hydrazone–palladium catalyst systems.[9] Here, we report a new type of allylic arylation of cinnamyloxyphenylboronic acid pinacol esters, which have an arylboronic acid moiety and an allylic ether moiety, using bishydrazones **1a–e**[7b,c,g] and monohydrazones **2a** and **2b**[7b] as ligands (Figure 2). This procedure was

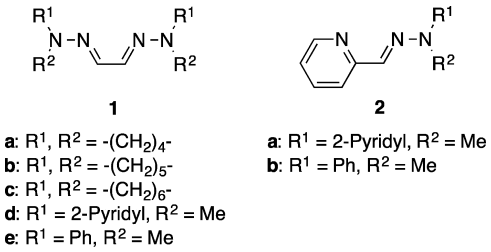


Figure 2. Hydrazones **1** and **2**.

achieved by a coupling reaction of π-allyl intermediate to the boron-substituted position of the leaving group and gave 1,3-diarylpropene derivatives with a phenolic hydroxyl group.

RESULTS AND DISCUSSION

Initially, we examined the reaction of 2-(4-(cinnamyloxy)-phenyl)-4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (**3a**) as a model substrate with 5 mol % of Pd catalyst for 24 h under Ar atmosphere at 50 °C (Table 1). Using 5 mol % of $Pd(OAc)_2$ and bishydrazone **1a** as a ligand, we observed that the reaction in the presence of $Ca(OH)_2$ as a base in DMA/H_2O (9/1) as a solvent gave corresponding product **4a** (obtusastyrene) in a 12% yield (entry 1). We tested various bishydrazones **1b–e** (entries 2–5). When we used bishydrazone **1d**, **4a** was obtained in 75% yield (entry 4). We also tested pyridine-type monohydrazone ligands **2a** and **2b**. While pyridine–methyl-type monohydrazone ligand **2a** was not effective for this reaction (entry 6), phenyl–methyl type ligand **2b** was effective

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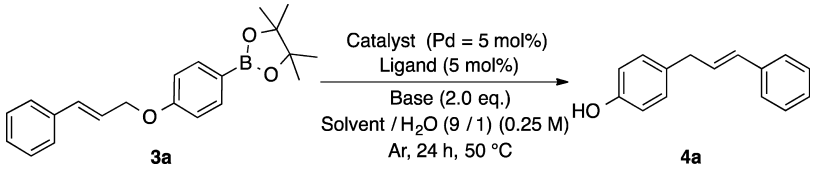
Table 1. Optimization of Palladium-Catalyzed Allylic Arylation of Cinnamyloxyphenylboronic Acid Pinacol Ester (3a) Using Hydrazone Ligand[a]



3a **4a**

entry	Pd source	ligand	base	solvent	yield of **3a** (%)
1	$Pd(OAc)_2$	**1a**	$Ca(OH)_2$	DMA	12
2	$Pd(OAc)_2$	**1b**	$Ca(OH)_2$	DMA	10
3	$Pd(OAc)_2$	**1c**	$Ca(OH)_2$	DMA	4
4	***$Pd(OAc)_2$***	***1d***	***$Ca(OH)_2$***	***DMA***	***75***
5	$Pd(OAc)_2$	**1e**	$Ca(OH)_2$	DMA	2
6	$Pd(OAc)_2$	**2a**	$Ca(OH)_2$	DMA	trace
7	$Pd(OAc)_2$	**2b**	$Ca(OH)_2$	DMA	53
8	$Pd(OAc)_2$		$Ca(OH)_2$	DMA	trace
9	$Pd(acac)_2$	**1d**	$Ca(OH)_2$	DMA	29
10	$[Pd(\eta^3\text{-allyl})Cl]_2$	**1d**	$Ca(OH)_2$	DMA	54
11	$PdCl_2$	**1d**	$Ca(OH)_2$	DMA	31
12	$Pd(tfa)_2$	**1d**	$Ca(OH)_2$	DMA	53
13	$Pd_2(dba)_3$	**1d**	$Ca(OH)_2$	DMA	72
14	$Pd(OAc)_2$	**1d**	K_2CO_3	DMA	52
15	$Pd(OAc)_2$	**1d**	K_3PO_4	DMA	27
16	$Pd(OAc)_2$	**1d**	NaOEt	DMA	32
17	$Pd(OAc)_2$	**1d**	Na_2CO_3	DMA	48
18	$Pd(OAc)_2$	**1d**	CsF	DMA	59
19	$Pd(OAc)_2$	**1d**	KF	DMA	52
20	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	2-butanol	33
21	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	DMSO	7
22	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	DMF	46
23	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	THF	63
24	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	MeCN	trace
25	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	DMA[b]	46
26	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	DMA[c]	22
27	$Pd(OAc)_2$	**1d**	$Ca(OH)_2$	DMA[d]	trace

[a]Reaction conditions: **3a** (0.25 mmol), Pd source (Pd = 5 mol %), ligand (5 mol %), base (0.50 mmol), solvent (0.9 mL), H_2O (0.1 mL) at 50 °C for 24 h under Ar. [b]Concentration of solvent was 0.125 M. [c]Concentration of solvent was 0.5 M. [d]DMA (1.0 mL) was used as solvent in the absence of water.

and gave the corresponding product in 53% yield (entry 7). Without ligand, the reaction did not give the desired product (entry 8). As a result, we decided to use pyridine−methyl-type bishydrazone ligand **1d** as the optimum ligand for this reaction. Several palladium sources were also tested (entries 4 and 9−13). $Pd(OAc)_2$ was the most effective palladium source in this reaction (entry 4). Next, the effects of various bases were investigated (entries 4 and 14−19). Using $Ca(OH)_2$ led to the highest yield in this reaction (entry 4). Various solvents were also tested (entries 4 and 20−24). DMA was the most suitable solvent for this reaction (entry 4). Additionally, the effect of concentration of solvent was investigated (entries 4, 25, and 26). When the concentration of solvent was 0.125 or 0.5 M in the reaction, the yields decreased to 46 and 22%, respectively (entries 25 and 26). The reaction without water gave the corresponding product in only trace amounts (entry 27).

Under optimized reaction conditions (Table 1, entry 4), we investigated the scope and limitation of this reaction using various substituted cinnamyloxyphenylboronic acid pinacol esters **3** (Table 2). Using 4-substituted cinnamyloxyphenylboronic acid pinacol esters led to moderate to good yields of the corresponding products **4b−e** (entries 2−5). Next, the reaction of substrates **3f** and **3g**, whose electron-donating group was substituted on phenylboronic acid pinacol ester, also proceeded smoothly and gave the corresponding products **4f** and **4g** in moderate yields (entries 6 and 7). However, in the case of using chloro-substituted pinacol ester, the desired product **4h** was obtained in low yield. (*E*,*E*)-2-Chloro-4-cinnamyl-1-(cinnamyloxy)benzene (**5h**), with which π-allyl intermediate was coupled at the boron-substituted position of starting material **3h**, was also obtained in 23% yield as a byproduct (entry 8). Pinacol esters with a cinnamyloxy group in the *m*- or *o*-position were also tested. *m*-Cinnamylphenol (**4i**) was obtained in good yield (entry 9). On the other hand, *o*-cinnamylphenol (**4j**) was obtained in 8% yield, and annulate compound (*Z*)-3-benzylidene-2,3-dihydrobenzofuran (**6**) was also generated as a byproduct in 37% yield (entry 10). When we tested allyloxyphenylboronic acid pinacol ester **3k** as starting material, 4-allylphenol (**4k**) was obtained in the same way (entry 11). Moreover, we tried to synthesize eugenol (**4l**), which is known as a medical product,[10] using 4-allyloxy-3-methoxyphenylboronic acid pinacol ester. As a result, we succeeded in obtaining eugenol in good yield accompanying the formation of 2-methoxy-4-allyl-1-(allyloxy)benzene (**5l**), which

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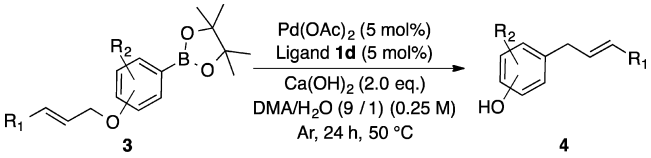
Table 2. Scope and Limitations of Palladium-Catalyzed Allylic Arylation of Pinacol Esters 3 Using Hydrazone Ligand[a]



3 4

entry	R^1	R^2	OH	yield of **4** (%)
1	C_6H_5	H	4-OH	75 (**4a**)
2	4-ClC_6H_4	H	4-OH	80 (**4b**)
3[c]	4-$CF_3C_6H_4$	H	4-OH	51 (**4c**)
4[c,f]	4-MeC_6H_4	H	4-OH	58 (**4d**)
5[c,f]	4-$MeOC_6H_4$	H	4-OH	46 (**4e**)
6	C_6H_5	3,5-diMe	4-OH	47 (**4f**)
7	C_6H_5	3-MeO	4-OH	55 (**4g**)
8[g]	C_6H_5	3-Cl	4-OH	38 (**4h**) + 23 (**5h**)
9	C_6H_5	H	3-OH	79 (**4i**)
10	C_6H_5	H	2-OH	8 (**4j**) + 37 (**6**)
11[d,e]	H	H	4-OH	43 (**4k**)
12	H	3-OMe	4-OH	57 (**4l**) + 20 (**5l**)

[a]Reaction conditions: Cynnamyloxy phenyl boronic acid pinacol ester (0.25 mmol), $Pd(OAc)_2$ (5 mol %), ligand **2d** (5 mol %), $Ca(OH)_2$ (0.50 mmol), DMA/H_2O (9/1) (1 mL) at 50 °C for 24 h under Ar. [b]This reaction was carried out at 60 °C. [c]This reaction was carried out at 70 °C. [d]This reaction was carried out for 48 h. [e]10 mol % of catalyst and ligand were used. [f]Concentration of solvent was 0.125 M.

was a coupling product from π-allyl intermediate and **3l** (entry 12). Unfortunately, the reaction using prenyloxyphenylboronic acid pinacol ester (**3m**) did not give the corresponding product (Scheme 1). When we used heterocyclic compound **3n**, such as a pyridine ring, the corresponding product **4n** was obtained in excellent yield for 48 h at 60 °C (Scheme 2).

Next, to confirm whether this reaction is an intermolecular reaction or intramolecular, a crossover reaction was carried out using **3a** and **3l** as starting materials (Scheme 3). The rate of coupling products in the reaction mixture was determined by GC–MS analysis. As a result, obtusastyrene (**4a**) and eugenol (**4l**) were detected, and two cross-coupling products **4k** and **4h** were also detected. From this result, we concluded this reaction occurred in an intermolecular fashion. Another coupling product **7** from **3a** and π-allyl intermediate of **3l** was also detected.

A plausible mechanism of allylic arylation of cinnamyloxyboronic acid pinacol ester is illustrated in Scheme 4. At first, oxidative addition at the allylic position of the starting material to Pd(0)–hydrazone complex took place to generate π-allyl phenoxy complex **I**. According to formation of compounds **5h** and **5l** in Table 2 and the crossover products in Scheme 3, the complex **I** exchanged phenoxy ion for hydroxyl ion to become π-allyl hydroxyl palladium complex **II**. On the other hand, phenoxide ion reacted with water to generate boronic acid pinacol ester ion, and this ion underwent transmetalation with palladium complex **II** to generate π-allyl aryl palladium complex **III**, followed by reductive elimination of palladium complex **III**, which gave the corresponding phenol product and regenerated Pd(0)–hydrazone catalyst. Then, the catalytic cycle was completed. We thought these palladium complexes were stabilized by hydrazone ligand, and this reaction proceeded smoothly.

In summary, we developed allylic arylation using hydrazone **1d**–$Pd(OAc)_2$ systems as catalyst and cinnamyl- and allyloxyphenylboronic acid pinacol esters, which have an arylboronic acid moiety and an allylic ether moiety as substrates. This reaction gave the desired cinnamyl- and allylphenol products including natural and medical compounds. We also certified that the reaction was intermolecular by a crossover reaction.

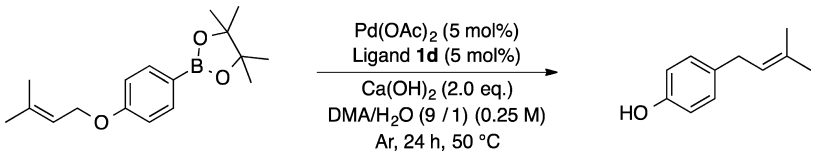
EXPERIMENTAL SECTION

Preparation of Pyridine-2-carboxaldehyde–(Pyridin-2-yl)-methylhydrazone (2a).[11] 2-Pyridinecarboxaldehyde (53.6 mg, 0.5 mmol) and 1-methyl-1-(pyridil)hydrazone (61.6 mg, 0.5 mmol) were added to EtOH (3.0 mL) in a sample tube. After the mixture was stirred for 3 h at 80 °C, the reaction was quenched with distilled water. The white solid was precipitated and collected by filtration, washed with hexane, and dried in vacuo to afford **2a** in 53% yield (55.9 mg, 0.26 mmol) as a white solid: mp 105–106 °C; ^{1}H NMR ($CDCl_3$) δ: 3.70 (s, 3H), 6.83 (ddd, J = 7.0, 4.9, 0.9 Hz, 1H), 7.19 (ddd, J = 7.4, 5.0, 1.1 Hz, 1H), 7.62 (ddd, J = 7.8, 7.1, 1.9 Hz, 1H), 7.68–7.76 (m, 3H), 8.02 (d, J = 8.04 Hz, 1H) 8.24 (dd, J = 5.0, 1.1 Hz, 1H), 8.56 (ddd, J = 5.0, 1.6, 1.0 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 29.6, 110.0, 116.1, 119.3, 122.4, 134.6, 136.3, 137.5, 147.0, 149.1, 155.3, 157.4; EI-MS m/z (rel intensity) 212 (M^+, 10).

Preparation of (*E*)-2-(4-(Cinnamyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (0.5502 g, 2.5 mmol), (*E*)-cinnamyl bromide (0.4927 g, 2.5 mmol), and potassium carbonate (0.5183 g, 3.75 mmol) were added to acetone (2.5 mL) in a sample tube. After the mixture was stirred for 24 h at 50 °C, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford **3a** in 77% yield (650 mg, 1.94 mmol) as a white solid: mp 83–84 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 4.73 (dd, J = 5.8 and 1.4 Hz, 2H), 6.37–6.46 (m, 1H), 6.73 (d, J = 15.9 Hz, 1H), 6.95 (d, J = 8.7 Hz, 2H), 7.25–7.42 (m, 5H), 7.76 (d, J = 8.7 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.8, 68.3, 83.5, 114.1, 124.2, 126.6, 127.9, 128.6, 133.1, 136.4, 136.5, 161.2; EI-MS m/z (rel intensity) 336 (M^+, 2); HRMS (ESI-orbitrap) m/z calcd for $C_{21}H_{25}O_3B$ $[M + Na]^+$ 359.1789, found 359.1771.

Preparation (*E*)-2-(4-(3-(4-Chlorophenyl)allyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b). This compound was synthesized from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenol (0.8803 g, 4.0 mmol) and (*E*)-*p*-chlorocinnamyl bromide (0.9261 g, 4.0 mmol) according to the procedure for preparation of **3a** in 38% yield (565 mg, 1.52 mmol) as a white solid: mp 111 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 4.72 (dd, J = 5.7, 1.3 Hz, 2H), 6.34–

Scheme 1. Palladium-Catalyzed Allylic Arylation of Prenyloxyphenylboronic Acid Pinacol Ester (3m)



3m **4m**, N.D.

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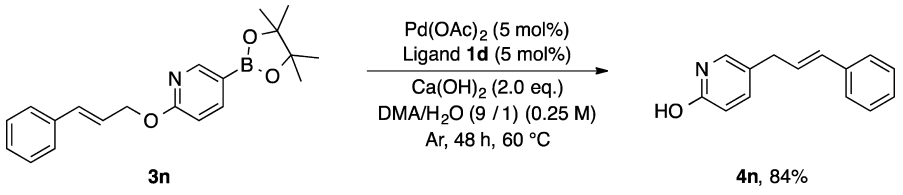
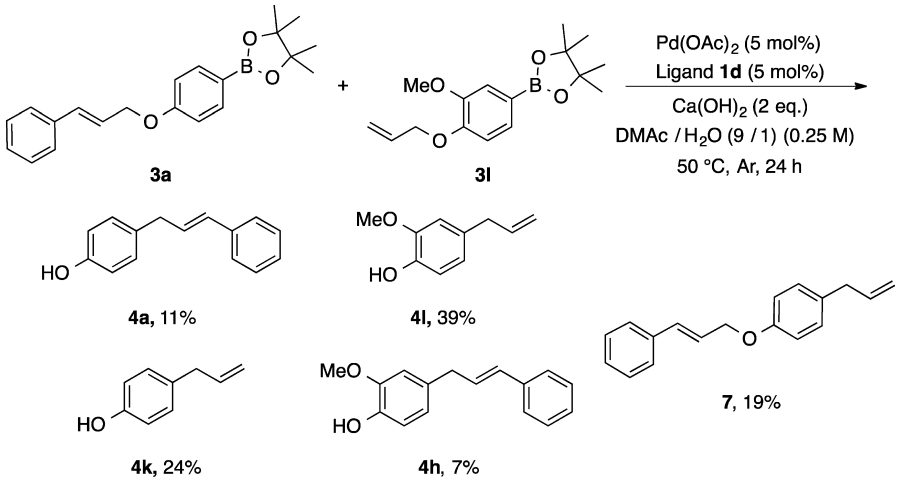
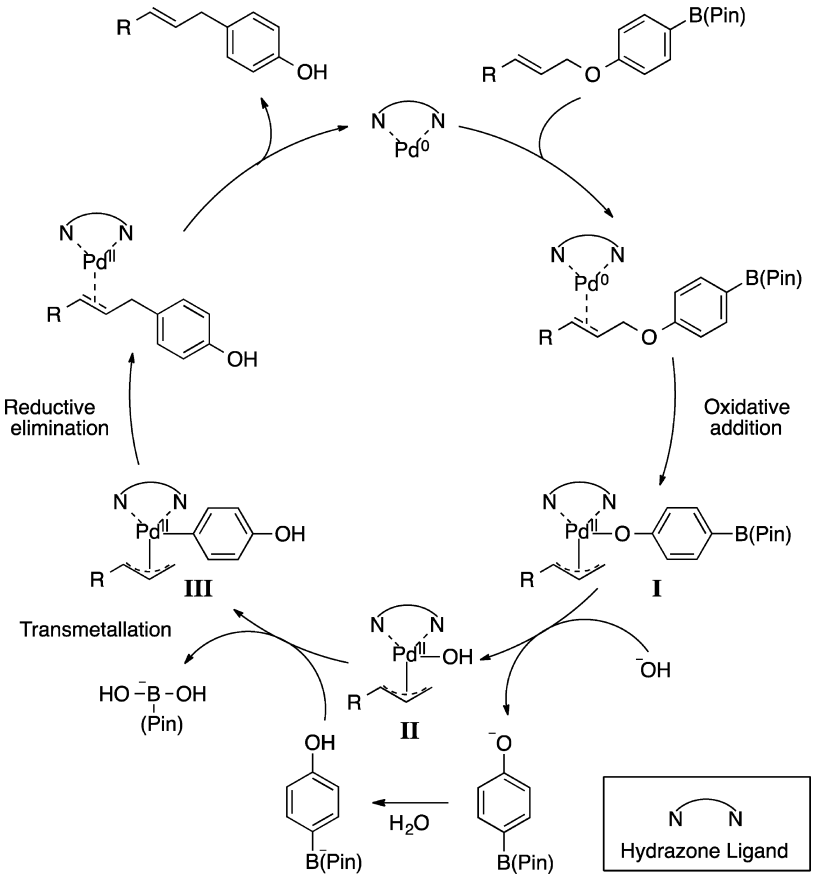
Scheme 2. Palladium-Catalyzed Allylic Arylation of Heterocyclic Compound (3n)



Scheme 3. Crossover Reaction Using 3a and 3l



Scheme 4. Plausible Reaction Mechanism



6.43 (m, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.94 (d, J = 8.7 Hz, 2H), 7.27−7.35 (m, 4H), 7.76 (d, J = 8.6 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.8, 68.1, 83.6, 114.0, 124.9, 127.8, 128.7, 131.7, 133.5, 134.9, 136.5, 161.0; EI-MS m/z (rel intensity) 370 (M^+, 2); HRMS (ESI-orbitrap) m/z calcd for $C_{21}H_{23}O_3BCl$ $[M - H]^-$ 369.1423, found 369.1433.

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Preparation of (*E*)-4,4,5,5-Tetramethyl-2-(4-((3-(4-(trifluoromethyl)phenyl)allyl)oxy)phenyl)-1,3,2-dioxaborolane (3c). This compound was synthesized from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenol (0.5067 g, 2.3 mmol) and (*E*)-*p*-(trifluoromethyl)cinnamyl chloride (0.5074 g, 2.3 mmol) according to the procedure for preparation of **3a** in 30% yield (278 mg, 0.69 mmol) as a yellow solid: mp 99 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 4.75 (dd, J = 5.4 and 1.4 Hz, 2H), 6.46−6.55 (m, 1H), 6.77 (d, J = 16.1 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.8, 67.9, 83.6, 114.0, 124.1 (q, J = 272.0 Hz), 125.5 (q, J = 3.7 Hz), 126.7, 127.0, 128.7, 129.6 (q, J = 32.3 Hz), 131.2, 136.6, 161.0; EI-MS m/z (rel intensity) 404 (M^+, 7). HRMS (APPI-orbitrap) m/z calcd for $C_{22}H_{23}O_3BF_3$ $[M - H]^-$ 403.1687, found 403.1696.

Preparation of (*E*)-2-(4-(3-*p*-Tolylallyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d). This compound was synthesized from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1.2110 g, 5.0 mmol) and (*E*)-*p*-methylcinnamyl chloride (0.8341 g, 5.5 mmol) according to the procedure for preparation of **3a** in 37% yield (648 mg, 1.85 mmol) as a white solid: mp 121−122 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 2.34 (s, 3H), 4.71 (d, J = 5.9 Hz, 2H), 6.31−6.40 (m, 1H), 6.70 (d, J = 15.9 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 21.2, 24.8, 68.5, 83.5, 114.1, 123.0, 126.5, 129.3, 133.1, 133.6, 136.5, 137.8, 161.2; EI-MS m/z (rel intensity) 350 (M^+, 1); HRMS (ESI-orbitrap) m/z calcd for $C_{22}H_{28}O_3B$ $[M + H]^+$351.2126, found 351.2122.

Preparation of (*E*)-2-(4-((3-(4-Methoxyphenyl)allyl)oxy)-phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e). This compound was synthesized via a two-step reaction. First step: A mixture of 4-(allyloxy)bromobenzene (2.1198 g, 10 mmol), 4-iodoanisole (2.3404 g, 10 mmol), K_3PO_4 (2.1227 g, 10 mmol), $Pd(OAc)_2$ (0.1123 g, 0.5 mmol, 5 mol %), and ligand **1c** (0.1250 g, 0.5 mmol, 5 mol %) in DMF (10 mL) at 70 °C under an atmosphere of air was stirred for 12 h. After the reaction, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by decantation with hexane to afford to (*E*)-1-bromo- 4-((3-(4-methoxyphenyl)allyl)oxy)benzene (**8**) in 39% yield (1.25 g 3.92 mmol) as a brown solid: mp 147−148 °C; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 4.63 (dd, J = 6.0 and 1.3 Hz, 2H), 6.20−6.30 (m, 1H), 6.75 (d, J = 15.9 Hz, 1H), 6.85 (tt, J = 8.9 and 2.1 Hz, 4H), 7.36 (tt, J = 9.4 and 2.8 Hz, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 55.3, 69.1, 112.9, 114.0, 116.6, 121.5, 127.8, 129.0, 132.2, 133.1, 157.7, 159.5; HRMS (ESI-orbitrap) m/z calcd for $C_{16}H_{15}O_2Br$ $[M - H]^-$ 317.0172, found 317.0174. Second step: (*E*)-1-Bromo-4-((3-(4-methoxyphenyl)allyl)oxy)benzene (**8**) (0.4457 g, 1.4 mmol) was added to THF (5.6 mL), the solution was stirred for 15 min at −78 °C under an Ar atmosphere, *n*-butyllithium (1.81 mmol) in hexane (1.00 mL, 1.81 M) was added gradually, and the solution was stirred at −78 °C. After 2 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.37 mL, 1.82 mmol) was added gradually, the mixture was stirred at room temperature 24 h, and the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford **3e** in 43% yield (0.204 g, 0.61 mmol) as a white solid: mp 142−143 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 3.81 (s, 3H), 4.70 (d, J = 4.9 Hz, 2H), 6.24−6.33 (m, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.8, 55.3, 68.9, 83.5, 113.9, 114.1, 121.8, 127.8, 129.1, 132.9, 136.5, 159.4, 161.2; EI-MS m/z (rel intensity) 366 (M^+, 2); HRMS (APPI-orbitrap) m/z calcd for $C_{22}H_{28}O_4B$ $[M + H]^+$ 367.2075, found 367.2061.

Preparation of (*E*)-2-(4-(Cinnamyloxy)-3,5-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f). This compound was synthesized from 3,5-dimethyl-4-(4,4,5,5- tetramethyl-1,3,2-dioxaborolan-2-yl) phenol (0.4963 g, 2.0 mmol) and (*E*)-cinnamyl bromide (0.3941 g, 2.0 mmol) according to the procedure for preparation of **3a** in 61% yield (446 mg, 1.22 mmol) as a white solid: mp 77 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 2.32 (s, 6H), 4.48 (dd, J = 6.0 and 1.2 Hz, 2H), 6.42−6.51 (m, 1H), 6.73 (d, J = 15.9 Hz, 1H), 7.25−7.36 (m, 3H), 7.42 (d, J = 7.1 Hz, 2H), 7.51 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 16.3, 24.8, 72.8, 83.6, 125.1, 126.5, 127.8, 128.6, 130.5, 132.6, 135.6, 136.6, 158.7; EI-MS m/z (rel intensity) 364 (M^+, 1); HRMS (ESI-orbitrap) m/z calcd for $C_{23}H_{30}O_3B$ $[M + H]^+$ 365.2283, found 365.2282.

Preparation of (*E*)-2-(4-(Cinnamyloxy)-3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (3g). This compound was synthesized from 3-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenol (0.5002 g, 2.0 mmol) and (*E*)-cinnamyl bromide (0.3944 g, 2.0 mmol) according to the procedure for preparation of **3a** in 33% yield (244 mg, 0.67 mmol) as a white solid: mp 104 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 3.94 (s, 3H), 4.80 (dd, J = 5.9 and 1.0 Hz, 2H), 6.41−6.50 (m, 1H), 6.72 (d, J = 16.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.24−7.41(m, 7H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.8, 55.9, 69.3, 83.6, 112.3, 116.9, 124.2, 126.6, 127.9, 128.4, 128.5, 133.4, 136.3, 148.7, 150.6; EI-MS m/z (rel intensity) 366 (M^+, 3); HRMS (ESI-orbitrap) m/z calcd for $C_{22}H_{28}O_4B$ $[M + H]^+$ 367.2075, found 367.2072.

Preparation of (*E*)-2-(3-Chlorophenyl-4-(cinnamyloxy))-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h). This compound was synthesized from 3-chloro-4-(4,4,5,5-tetramethyl- 1,3,2-dioxaborolan-2-yl) phenol (0.2545 g, 1.0 mmol) and (*E*)-cinnamyl bromide (0.1970 g, 1.0 mmol) according to the procedure for preparation of **3a** in 67% yield (249 mg, 0.67 mmol) as a white solid: mp 74 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 4.81 (dd, J = 5.6 and 1.2 Hz, 2H), 6.37−6.46 (m, 1H), 6.77 (d, J = 16.0 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 7.26−7.35 (m, 3H), 7.41 (d, J = 7.0 Hz, 2H), 7.65 (dd, J = 8.2 and 1.5 Hz, 1H), 7.83 (d, J = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.8, 69.4, 83.9, 112.9, 122.7, 123.6, 126.6, 128.0, 128.6, 133.3, 134.5, 136.2, 136.7, 156.4; EI-MS m/z (rel intensity) 370 (M^+, 1); HRMS (ESI-orbitrap) m/z calcd for $C_{21}H_{25}O_3ClB$ $[M + H]^+$ 371.1580, found 371.1583.

Preparation of (*E*)-2-(3-(Cinnamyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i). This compound was synthesized from 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (0.8803 g, 4.0 mmol) and (*E*)-cinnamyl bromide (0.7883 g, 4.0 mmol) according to the procedure for preparation of **3a** in 59% yield (796 mg, 2.37 mmol) as a white solid: mp 84−85 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 12H), 4.73 (dd, J = 5.7 and 1.3 Hz, 2H), 6.38−6.47 (m, 1H), 6.75 (d, J = 15.9 Hz, 1H), 7.07 (ddd, J = 8.2 and 2.7 and 1.1 Hz, 1H), 7.25−7.43 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.8, 68.5, 83.8, 118.5, 119.8, 124.6, 126.5, 127.4, 127.8, 128.5, 129.0, 132.8, 136.5, 158.1; EI-MS m/z (rel intensity) 336 (M^+, 2); HRMS (ESI-orbitrap) m/z calcd for $C_{21}H_{25}O_3BNa$ $[M + Na]^+$ 359.1789, found 359.1786.

Preparation of (*E*)-2-(2-(Cinnamyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j). This compound was synthesized from 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1.1004 g, 5.0 mmol) and (*E*)-cinnamyl bromide (0.9843 g, 5.0 mmol) according to the procedure for preparation of **3a**, and the residue after the concentration under reduced pressure was purified by decantation with hexane to afford **3j** in 14% yield (243 mg, 0.75 mmol) as a white solid: mp 158−159 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 12H), 4.72 (dd, J = 4.6 and 1.8 Hz, 2H), 6.41 (dt, J = 15.9 and 4.6 Hz 1H), 6.88−7.04 (m, 3H), 7.22−7.44 (m, 6H), 7.71 (dd, J = 7.3 and 1.7 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.9, 68.5, 83.5, 112.0, 120.6, 125.0, 126.4, 127.4, 128.5, 131.0, 132.5, 136.7, 137.2, 163.2; EI-MS m/z (rel intensity) 336 (M^+, 2); HRMS (ESI-orbitrap) m/z calcd for $C_{21}H_{25}O_3BNa$ $[M +Na]^+$ 359.1789, found 359.1786.

Preparation of 2-(4-(Allyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k).[12] This compound was synthesized from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1.1004 g, 5.0 mmol) and allyl bromide (0.6049 g, 5.0 mmol) according to the procedure for preparation of **3a** in 40% yield (517 mg, 2.37 mmol) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 4.56 (dt, J = 5.3 and 1.4 Hz, 2H), 5.28 (dd, J = 10.5 and 1.4 Hz, 1H), 5.41 (dd, J = 17.2 and 1.5 Hz, 1H), 5.99−6.12 (m, 1H), 6.91 (d, J = 8.7 Hz, 2H), 7.74 (d, J =

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8.6 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.8, 68.5, 83.5, 114.0, 117.7, 133.0, 136.5, 161.1; EI-MS m/z (rel intensity) 260 (M^+, 42).

Preparation of 2-(4-(Allyloxy)-3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l). This compound was synthesized from 3-methoxy-4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)phenol (0.5001 g, 2.0 mmol) and allyl bromide (0.2420 g, 2.0 mmol) according to the procedure for preparation of **3a** in 73% yield (423 mg, 1.46 mmol) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.34 (s, 12H), 3.92 (s, 3H), 4.65 (dt, J = 5.4 and 1.4 Hz, 2H), 5.28 (dd, J = 10.5 and 1.4 Hz, 1H), 5.40 (dd, J = 18.7 and 1.4 Hz, 1H), 6.02−6.15 (m, 1H), 6.88 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 1.1 Hz, 1H), 7.40 (dd, J = 8.0 and 1.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.8, 55.9, 69.5, 83.6, 112.3, 117.0, 118.1, 128.3, 133.0, 148.7, 150.6; EI-MS m/z (rel intensity) 290 (M^+, 63); HRMS (ESI-orbitrap) m/z calcd for $C_{16}H_{24}O_4B$ $[M + H]^+$ 291.1762, found 291.1763.

Preparation of 2-(4-(Prenyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m). This compound was synthesized from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1.1004 g, 5.0 mmol) and prenyl bromide (0.7452 g, 5.0 mmol) according to the procedure for preparation of **3a** in 63% yield (906 mg, 3.14 mmol) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.33 (s, 12H), 1.74 (s, 3H), 1.79 (s, 3H), 4.53 (d, J = 6.8 Hz, 2H), 5.49 (dt, J = 6.8 and 1.3 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 18.2, 24.8, 25.8, 64.5, 83.5, 114.0, 119.5, 136.4, 138.2, 161.4; EI-MS m/z (rel intensity) 288 (M^+, 3); HRMS (ESI-orbitrap) m/z calcd for $C_{17}H_{25}O_3BNa$ $[M + Na]^+$ 311.1789, found 311.1787.

Preparation of (*E*)-2-(Cinnamyloxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (3n). This compound was synthesized from 5-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-pyridin-2-ol (0.2209 g, 1.0 mmol) and (*E*)-cinnamyl bromide (0.1973 g, 1.0 mmol) according to the procedure for preparation of **3a** ,and the residue after the concentration under reduced pressure was purified by decantation with hexane to afford **3n** in 75% yield (251 mg, 0.75 mmol) as a white solid: mp 141 °C; ^1H NMR ($CDCl_3$) δ 1.30 (s, 12H), 4.72 (dd, J = 6.3 and 0.8 Hz, 2H), 6.28−6.38 (m, 1H), 6.55−6.62 (m, 2H), 7.22−7.39 (m, 5H), 7.62 (dd, J = 9.1 and 1.9 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.7, 51.3, 84.0, 119.9, 123.4, 126.6, 128.0, 128.6, 133.8, 136.0, 143.8, 145.3, 162.9; EI-MS m/z (rel intensity) 337 (M^+, 41); HRMS (ESI-orbitrap) m/z calcd for $C_{20}H_{25}O_3NB$ $[M + H]^+$ 338.1933, found 338.1919.

General Procedure for Palladium-Catalyzed Allylic Arylation of Cinnamyl- or Allyloxyphenylboronic Acid Pinacol Esters. A mixture of cinnamyl- or allyloxyphenylboronic acid pinacol ester **3** (0.25 mmol), $Ca(OH)_2$ (0.5 mmol), $Pd(OAc)_2$ (12.5 μmol, 5 mol %), and ligand **1d** (12.5 μmol, 5 mol %) in DMA/H_2O (9/1) (1.0 mL) at 50 °C under an Ar atomosphere was stirred for 24 h. After the reaction, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/ethyl acetate).

(*E*)-4-Cinnamylphenol (Obtusastyrene) (**4a**)[13] (Table 1, Entry 4). Compound **4a** was obtained according to the general procedure in 75% yield (39.5 mg, 0.188 mmol) as a yellow solid: mp 64 °C; IR (neat, cm^{-1}): 3226 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.47 (d, J = 6.3 Hz, 2H), 4.75 (s, 1H), 6.27−6.37 (m, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.77 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 7.17−7.36 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.4, 115.3, 126.1, 127.0, 128.5, 129.6, 129.8, 130.7, 132.3, 137.5, 153.8; EI-MS m/z (rel intensity) 210 (M^+, 100).

(*E*)-4-(3-(4-Chlorophenyl)allyl)phenol (**4b**) (Table 2, Entry 2). Compound **4b** was obtained according to the general procedure in 80% yield (48.8 mg, 0.199 mmol) as a yellow solid: mp 71−72 °C; IR (KBr, cm^{-1}) 3215 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.46 (d, J = 5.5 Hz, 2H), 4.84 (s, 1H), 6.25−6.40 (m, 2H), 6.78 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.22−7.29 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.4, 115.3, 127.3, 128.6, 129.5, 129.8, 130.4, 132.0, 132.6, 136.0, 153.9; EI-MS m/z (rel intensity) 244 (M^+, 100); HRMS (APPI-orbitrap) m/z calcd for $C_{15}H_{13}OCl$ $[M]^+$ 244.0649, found 244.0642.

(*E*)-4-(3-(4-(Trifluoromethyl)phenyl)allyl)phenol (**4c**) (Table 2, Entry 3). Compound **4c** was obtained according to the general procedure (60 °C) in 51% yield (35.8 mg, 0.129 mmol) as a brown solid: mp 45−46 °C; IR (KBr, cm^{-1}) 3352 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.50 (d, J = 4.0 Hz, 2H), 4.84 (s, 1H), 6.44 (t, J = 3.6 Hz, 2H), 6.79 (dt, J = 8.5 and 2.0 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.4, 115.4, 124.2 (q, J = 271.8 Hz), 125.4 (q, J = 3.8 Hz), 126.2, 128.8 (q, J = 32.7 Hz), 129.5, 129.8, 131.6, 132.5, 140.9 (q, J = 1.3 Hz), 154.0; EI-MS m/z (rel intensity) 278 (M^+, 100); HRMS (ESI-orbitrap) m/z calcd for $C_{16}H_{13}OF_3$-H $[M - H]^-$ 277.0846, found 277.0855.

(*E*)-4-(3-*p*-Tolylallyl)phenol (**4d**) (Table 2, Entry 4). Compound **4d** was obtained according to the general procedure (10 mol % of $Pd(OAc)_2$ and **1d**, 60 °C) in 58% yield (32.3 mg, 0.144 mmol) as a yellow solid: mp 81−82 °C; IR (KBr, cm^{-1}) 3231 (Ar-OH); ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H), 3.45 (d, J = 6,5 Hz, 2H), 4.86 (s, 1H), 6.22−6.31 (m, 1H), 6.39 (d, J = 15.9 Hz 1H), 6.77 (dt, J = 8.5 and 2.9 Hz, 2H), 7.09 (d, J = 8.1 Hz, 4H), 7.24 (d, J = 3.8 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 21,1, 38.4, 115.2, 126.0, 128.5, 129.2, 129.8, 130.6, 132.5, 134.7, 136.8, 153.8; EI-MS m/z (rel intensity) 224 (M^+, 100); HRMS (ESI-orbitrap) m/z calcd for $C_{16}H_{16}O$-H $[M - H]^-$ 223.1128, found 223.1130.

(*E*)-4-(3-(4-(Methoxyphenyl)allyl)phenol (**4e**) (Table 2, Entry 5). Compound **4e** was obtained according to the general procedure (10 mol % of $Pd(OAc)_2$ and **1d**, 60 °C) in 46% yield (27.9 mg, 0.116 mmol) as a cream solid: mp 62−63 °C; IR (KBr, cm^{-1}) 3372 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.45 (d, J = 6.7 Hz, 2H), 3.79 (s, 3H), 4.76 (s, 1H), 6.13−6.40 (m, 1H), 6.37 (d, J = 15.8 Hz, 1H), 6.77 (dt, J = 8.5 and 2.0 Hz, 2H), 6.83 (d, J = 8.7 and 1.9 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.4, 55.3, 113.9, 115.2, 127.2, 127.4, 129.7, 130.1, 130.3, 132.5, 153.9, 158.7; EI-MS m/z (rel intensity) 240 (M^+, 100); HRMS (APPI-orbitrap) m/z calcd for $C_{16}H_{16}O_2$ $[M]^+$ 240.1145, found 240.1139.

(*E*)-4-Cinnamyl-2,6-dimethylphenol (**4f**) (Table 2, Entry 6). Compound **4f** was obtained according to the general procedure in 47% yield (27.8 mg, 0.117 mmol) as a brown oil: IR (neat, cm^{-1}) 3479 (Ar-OH); ^1H NMR ($CDCl_3$) δ 2.22, (s, 6H), 3.40 (d, J = 6.4 Hz, 2H), 4.52 (s, 1H), 6.27−6.36 (m, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.84 (s, 2H), 7.19−7.37 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 15.9, 38.5, 123.0, 126.1, 127.0, 128.4, 128.7, 129.9, 130.5, 131.6, 137.6, 150.5; EI-MS m/z (rel intensity) 238 (M^+, 100); HRMS (APCI-orbitrap) m/z calcd for $C_{17}H_{18}O$ + Na $[M + Na]^+$ 261.1250, found 261.1243.

(*E*)-4-Cinnamyl-2-methoxyphenol (**4g**) (Table 2, Entry 7). Compound **4g** was obtained according to the general procedure in 55% yield (33.3 mg, 0.139 mmol) as a brown oil: IR (neat, cm^{-1}) 3518 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.48 (d, J = 6.3 Hz, 2H), 3.87 (s, 3H), 5.51 (s, 1H), 6.28−6.38 (m, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.74 (d, J = 7.0 Hz, 2H), 6.86 (d, J = 6.3 Hz, 1H), 7.28 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.0, 55.9, 111.1, 114.3, 121.3, 126.1, 127.1, 128.5, 129.6, 130.7, 132.0, 137.5, 144.0, 146.5; EI-MS m/z (rel intensity) 240 (M^+, 100); HRMS (ESI-orbitrap) m/z calcd for $C_{16}H_{16}O_2$-H $[M - H]^-$ 239.1067, found 239.1066.

(*E*)-2-Chloro-4-cinnamylphenol (**4h**) (Table 2, Entry 8). Compound **4h** was obtained according to the general procedure (0.125 M) in 38% (23.2 mg, 0.095 mmol) as a colorless oil: IR (neat, cm^{-1}) 3524 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.45 (d, J = 6.6 Hz, 2H), 5.49 (s, 1H), 6.24−6.33 (m, 1H), 6.43 (d, J = 15.8 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 7.04 (dd, J = 8.3 and 2.0 Hz, 1H), 7.18−7.37 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.2, 116.1, 119.7, 126.1, 127.2, 128.5, 128.62, 128.63, 128.8 131.3, 133.4, 137.2, 140.7; EI-MS m/z (rel intensity) 244 (M^+, 100); HRMS (ESI-orbitrap) m/z calcd for $C_{15}H_{13}OCl$-H $[M - H]^-$ 243.0582, found 243.0590.

(*E*,*E*)-2-Chloro-4-cinnamyl-1-(cinnamyloxy)benzene (**5h**) (Table 2, Entry 8). Compound **5h** was obtained according to the general procedure (0.125 M) in 23% yield (20.7 mg, 0.057 mmol) as a yellow solid: mp 106−107 °C; ^1H NMR ($CDCl_3$) δ 3.46 (d, J = 6.6 Hz, 2H), 4.76 (dd, J = 5.7 and 1.4 Hz, 2H), 6.27−6.46 (m, 3H), 6.75 (d, J = 16.0 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 7.06 (dd, J = 8.4 and 2.1 Hz, 1H), 7.20−7.43 (m, 11H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.1, 69.9, 114.1, 123.0, 124.0, 126.1, 126.6, 127.2, 127.7, 127.9, 128.5, 128.6, 128.7, 130.4, 131.3, 133.1, 133.7, 136.3, 137.2, 152.5; EI-MS m/z (rel

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intensity) 360 (M^+, 2); HRMS (ESI-orbitrap) m/z calcd for $C_{24}H_{21}OCl + H$ $[M + H]^+$ 361.1354, found 361.1350.

(*E*)-3-Cinnamylphenol (**4i**) (Table 2, Entry 9). Compound **4i** was obtained according to the general procedure in 79% yield (41.6 mg, 0.198 mmol) as a brown oil: IR (neat, cm^{-1}) 3291 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.49 (d, J = 6.6 Hz, 2H), 4.90 (s, 1H), 6.27−6.37 (m, 1H), 6.45 (d, J = 15.9 Hz, 1H), 6.69 (d, J = 11.7 Hz, 2H), 6.81 (d, J = 7.6 Hz, 1H), 7.14−7.36 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.1, 113.1, 115.5, 121.1, 126.1, 127.1, 128.5, 128.8, 129.7, 131.2, 137.4, 142.1, 155.6; EI-MS m/z (rel intensity) 210 (M^+, 100); HRMS (ESI-orbitrap) m/z calcd for $C_{15}H_{14}O + Na$ $[M + Na]^+$ 233.0937, found 233.0933.

(*E*)-2-Cinnamylphenol (**4j**)[13] (Table 2, Entry 10). Compound **4j** was obtained according to the general procedure 8% (4.4 mg, 0.021 mmol) as a brown oil: IR (neat, cm^{-1}) 3334 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.57 (d, J = 6.1 Hz, 2H), 4.95 (s, 1H), 6.34−6.44 (m, 1H), 6.51 (d, J = 15.9 Hz, 1H), 6.82 (d, J = 7.9 Hz, 1H), 6.91 (td, J = 8.4 and 1.0 Hz, 1H), 7.12−7.37 (m, 7H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 34.1, 115.7, 121.0, 125.6, 126.2, 127.3, 127.88, 127.91, 128.5, 130.5, 131.5, 137.0, 154.0; EI-MS m/z (rel intensity) 210 (M^+, 100).

(*Z*)-3-Benzylidene-2,3-dihydrobenzofuran (**6**)[14] (Table 2, Entry 10). Compound **6** was obtained according to the general procedure in 37% yield (19.0 mg, 0.091 mmol) as a white solid: mp 129−131 °C; ^1H NMR ($CDCl_3$) δ 5.43 (d, J = 3.1 Hz, 2H), 6.84 (t, J = 3.1 Hz, 1H), 6.95 (q, J = 8.0 Hz, 2H), 7.20−7.28 (m, 4H), 7.41 (t, J = 7.5 Hz, 2H), 7.53 (d, J = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 74.6, 110.4, 116.6, 120.2, 120.9, 126.7, 127.0, 128.0, 128.8, 130.2, 136.6, 136.9, 162.5; EI-MS m/z (rel intensity) 208 (M^+, 86); HRMS (ESI-orbitrap) m/z calcd for $C_{15}H_{12}O + H$ $[M + H]$ 209.0961, found 290.0960.

4-Allylphenol (**4k**)[15] (Table 2, Entry 11). Compound **4k** was obtained according to the general procedure (48 h, 70 °C) in 43% yield (14.3 mg, 0.107 mmol) as a colorless oil: IR (neat, cm^{-1}) 3536 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.31(d, J = 6.7 Hz, 2H), 5.02−5.09 (m, 3H), 5.88−6.01 (m, 1H), 6.77 (dt, J = 8.5 and 2.5 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.3, 115.2, 115.4, 129.7, 132.2, 137.8, 153.8; EI-MS m/z (rel intensity) 134 (M^+, 100).

4-Allyl-2-methoxyphenol (Eugenol) (**4l**)[16] (Table 2, Entry 12). Compound **4l** was obtained according to the general procedure in 57% yield (23.2 mg, 0.141 mmol) as a colorless oil: IR (neat, cm^{-1}) 3523 (Ar-OH); ^1H NMR ($CDCl_3$) δ 3.32 (d, J = 6.7 Hz, 2H), 3.87 (s, 3H), 5.07 (t, J = 7.0 Hz, 2H), 5.50 (s, 1H), 5.88−6.01 (m, 1H), 6.68 (q, J = 2.4 Hz, 2H), 6.84 (t, J = 4.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.9, 55.8, 111.1, 114.2, 115.5, 121.1, 131.9, 137.8, 143.9, 146.4; EI-MS m/z (rel intensity) 164 (M^+, 100).

2-Methoxy-4-allyl-1-(allyloxy) benzene (**5l**)[17] (Table 2, Entry 12). Compound **5l** was obtained according to the general procedure in 20% yield (10.5 mg, 0.051 mmol) as a colorless oil: ^1H NMR ($CDCl_3$) δ 3.33 (d, J = 6.7 Hz, 2H), 3.86 (s, 3H), 4.59 (d, J = 5.4 Hz, 2H), 5.08 (td, J = 8.9 and 1.2 Hz, 2H), 5.27 (dd, J = 10.5 and 1.3 Hz, 1H), 5.39 (dd, J = 17.2 and 1.5 Hz, 1H), 5.89−6.15 (m, 2H), 6.70 (d, J = 9.2 Hz, 2H), 6.82 (d, J = 7.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.8, 55.8, 70.0, 112.2, 113.5, 115.6, 117.8, 120.3, 133.1, 133.5, 137.6, 146.3, 149.3; EI-MS m/z (rel intensity) 204 (M^+, 45).

(*E*)-5-Cinnamylpyridine-2-ol (**4n**) (Scheme 2). Compound **4n** was obtained according to the general procedure (60 °C, 48 h) 84% (44.5 mg, 0.211 mmol) as a gray oil: IR (neat, cm^{-1}) 3462 (Ar-OH); ^1H NMR ($CDCl_3$) δ 4.73 (dd, J = 6.4 and 1.2 Hz, 2H), 6.19 (td, J = 6.7 and 1.3 Hz, 1H), 6.27−6.36 (m, 1H), 6.56−6.63 (m, 2H), 7.22−7.39 (m, 7H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 50.6, 106.2, 121.0, 123.5, 126.5, 128.1, 128.6, 134.0, 135.9, 136.9, 139.5, 162.5; EI-MS m/z (rel intensity) 211 (M^+, 33); HRMS (ESI-orbitrap) m/z calcd for $C_{14}H_{13}NO + H$ $[M + H]^+$ 212.1070, found 212.1068.

Preparation of 7 for Authentic Sample. A mixture of (cinnamyloxy)phenylboronic acid pinacol ester **3a** (0.0841 g, 0.25 mmol), allylic acetate (0.0300 g, 0.30 mmol), $Ca(OH)_2$ (0.0370 g, 0.5 mmol), $Pd(OAc)_2$ (2.81 mg, 12.5 μmol, 5 mol %), and ligand **1d** (3.35 mg, 12.5 μmol, 5 mol %) in DMA/H_2O (9/1) (1.0 mL) at 20 °C under an Ar atomosphere was stirred for 6 h, and the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/ethyl acetate) to afford 1-allyl-4-(cinnamyloxy)benzene (**7**) in 29% yield (18.4 mg, 0.074 mmol) as a cream solid: mp 44−45 °C; ^1H NMR ($CDCl_3$) δ 3.33 (d, J = 6.7 Hz, 2H), 4.68 (dd, J = 5.8 and 1.4 Hz, 2H), 5.02−5.10 (m, 2H), 5.89−6.02 (m, 1H), 6.37−6.46 (m, 1H), 6.73 (d, J = 16.0 Hz, 1H), 6.90 (dt, J = 8.7 and 2.1 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 7.22−7.35 (m, 3H), 7.41 (dd, J = 8.6 and 1.5 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.3, 68.7, 114.7, 115.4, 124.6, 126.5, 127.8, 128.6, 129.5, 132.4, 132.9, 136.5, 137.8, 157.0; EI-MS m/z (rel intensity) 250 (M^+, 3); HRMS (ESI-orbitrap) m/z calcd for $C_{18}H_{18}O + H$ $[M + H]^+$ 251.1430, found 251.1426.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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