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Pd-catalyzed substitution of the OH group of non-derivatized allylic alcohols by phenols

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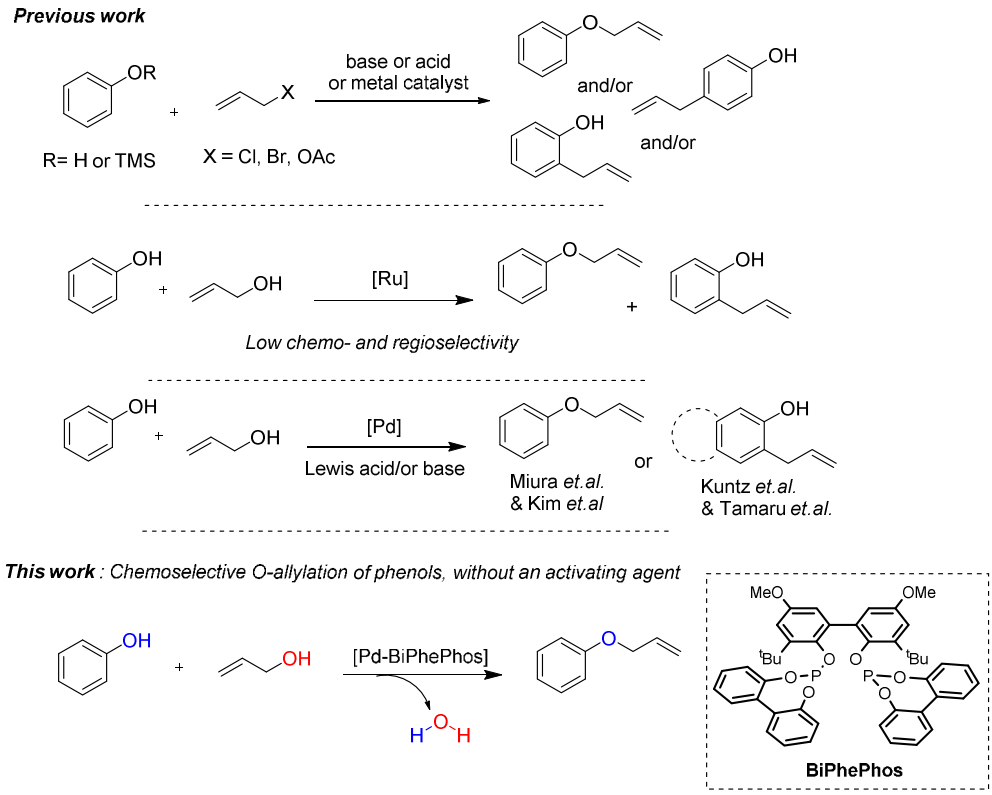
Abstract: *Non-activated phenols have been employed as nucleophiles in the allylation of non-derivatized allylic alcohols to generate allylated phenolic ethers with water as the only by-product. A Pd[BiPhePhos] catalyst was found to be reactive to give the O-allylated phenols in good to excellent yields in the presence of molecular sieves. The reactions are chemoselective in which the kinetically favored O-allylated products are formed exclusively over the thermodynamically favored C-allylated products.*

Aryl allyl ethers are important precursors in organic synthesis,[1] for example as monomers for the preparation of epoxy resins,[2] and as substrates in Claisen rearrangements.[3] Traditionally, the aryl allyl ethers are prepared by Williamson's ether synthesis in which potassium phenoxide (ArOK) and allylic halides as substrates are used.[4] Aryl allyl ethers can also be synthesized via metal[5] or zeolite catalyzed reactions.[6] However, these methodologies require multi-step procedures in which the hydroxyl (OH) group is derivatized to promote the leaving group ability and the phenols are deprotonated to enhance the nucleophilicity. These additional steps do not only lead to a lower atom economy but also an increased environmental factor due to additional purification steps.[7]

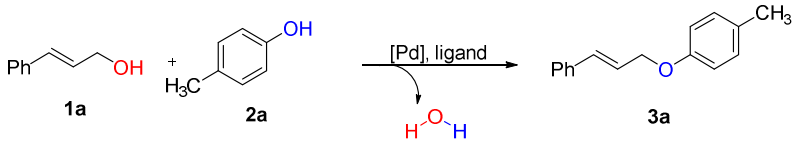
The direct substitution of the OH group in alcohols without prior derivatization with uncharged nucleophiles has attracted considerable attention with respect to lowering the number of reaction steps and chemicals used where water is generated as the only by-product.[8] In the allylation of phenols, there are several challenges that need to be addressed. In addition to the poor leaving group ability of the OH group of allylic alcohols and the poor nucleophilicity of the phenol, a competition between the kinetically favored O-allylation and the thermodynamically favored C-allylation needs to be taken into account. Only a few reports with respect to a direct substitution of the OH group in allylic alcohols by phenols are found in the literature (Scheme 1). In 1997, Miura reported an O-allylation of phenols using allylic alcohols by palladium.[9] To activate the OH group, $Ti(O\textit{i}Pr)_4$ was required. Recently, Kim reported a palladium catalyzed O-allylation of phenols activated in situ by amide acetal.[10] A C-allylation was reported by Kuntz in which a palladium TPPTS was used.[11] In this case, the presence of base was needed to activate the nucleophile. A Pd-catalyzed C-allylation reaction was reported by Tamaru using BEt_3 as additive.[12] Bouwman and coworkers have reported the direct substitution of allylic alcohols by phenols using Ru-catalysts under acidic conditions in which mixtures of O-allylation and C-allylation products were observed.[13] Ru-catalyzed formation aryl allyl ether without any additive was reported by Kitamura. Unfortunately, low yields were obtained with phenolic substrates.[14] Thereby, previous reports show that there are both challenges in activating substrates as well as obtaining high chemoselectivity especially when O-allylation is desired. This encouraged us to study this reaction and to develop an efficient methodology for the selective O-allylation of phenols. Herein we report an efficient Pd[BiPhePhos] catalyzed O-allylation of phenols using non-derivatized allylic alcohols without acidic or basic activation.



Scheme 1. Previous reported methodologies struggle with chemo-/regioselectivity (above), current report gives the kinetically favored O-allylated product (below).

Cinnamyl alcohol **1a** and *p*-cresol **2a** were used as substrates for the optimization of the reaction conditions. We have previously reported a successful allylic amination using $Pd[P(OPh)_3]_3$ as catalyst precursor.[15] In the present reaction, low conversion to **3a** was observed using the monodentate phosphite-based ligand (Table 1, entry 1). The ligand and catalyst precursor were changed to $[Pd(allyl)Cl]_2$ and bidentate BINAP without any success (Table 1, entry 2). Next, the bidentate phosphite-based BiPhePhos ligand was tested in combination with $Pd(dba)_2$ and a 34% conversion to **3a** was observed (Table 1, entry 3). Changing the palladium precursor had a significant effect on the reaction outcome where $[Pd(allyl)Cl]_2$ gave best results together with the BiPhePhos ligand (Table 1, entries 3-6). As expected, the reaction is sensitive to water and the addition of molecular sieves had a dramatic influence on the reaction, however, full conversion was not reached (Table 1, entry 7). Therefore, a gentle heating was employed and full conversion to product **3a** was obtained (Table 1, entry 8). Noteworthy, no traces of C-allylation was observed using the employed reaction conditions. Taking into account that the molecular sieves easily can be regenerated, this is a remarkable mild and atom efficient reaction giving high chemoselectivity towards the kinetically favored product. An excess of the phenol is necessary to inhibit self-condensation of the allylic alcohols (Table 1, entry 9).

Table 1. Optimization of the reaction conditions.[a]

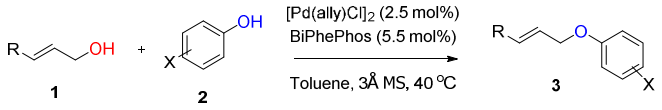


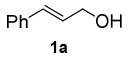
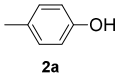
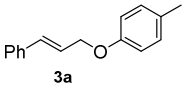
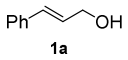
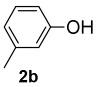
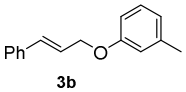
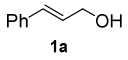
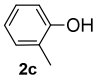
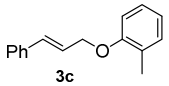
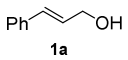
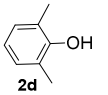
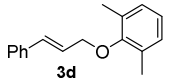
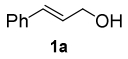
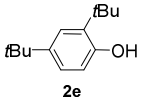
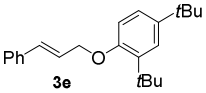
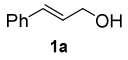
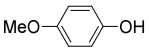
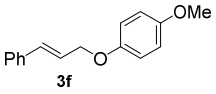
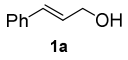
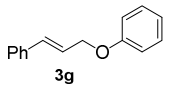
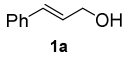
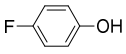
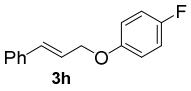
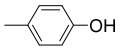
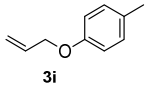
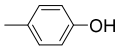
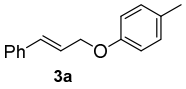
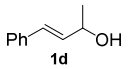
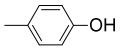
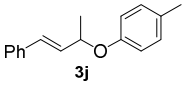
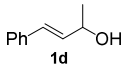
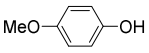
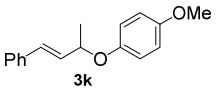
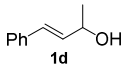
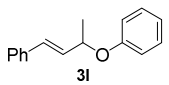
Entry	[Pd] (mol %)	Ligand (mol %)	Additive	Temp (°C)	Conversion (%)[b] **3**
1	$Pd(dba)_2$ (5)	$P(OPh)_3$ (40)	-	rt	15
2	$[Pd(allyl)Cl]_2$ (2.5)	BINAP (5.5)	-	rt	0
3	$Pd(dba)_2$ (5)	BiPhePhos (5.5)		rt	34
4	$Pd(OAc)_2$ (5)	BiPhePhos (5.5)	-	rt	0
5	$PdCl_2$ (5)	BiPhePhos (5.5)	-	rt	0
6	$[Pd(allyl)Cl]_2$ (2.5)	BiPhePhos (5.5)	-	rt	40
7[c]	$[Pd(allyl)Cl]_2$ (2.5)	BiPhePhos (5.5)	3Å MS	rt	64
8[c]	$[Pd(allyl)Cl]_2$ (2.5)	BiPhePhos (5.5)	3Å MS	40	>95
9[d]	$[Pd(allyl)Cl]_2$ (2.5)	BiPhePhos (5.5)	3Å MS	40	13[e]

[a] Reaction condition: allylic alcohol (0.25 mmol), nucleophile (0.5 mmol), toluene (0.5 ml) 24 hours. [b] Determined by ^{1}H-NMR. [c] 3Å MS (60 mg). [d] allylic alcohol (0.25 mmol), nucleophile (0.25 mmol), 3Å MS (60 mg), toluene (0.5 ml) 24 hours. [e]Homocoupling of allylic alcohol was obtained as a major product.

With the optimized reaction conditions in hand, the substrate scope of the phenolic allylation was studied (Table 2). Cresols **2a-2c** (*o*- ,*m*-, and *p*-) gave O-allylated products **3a-3c** in 93-99% yield (Table 2, entries 1-3). This shows that the reaction has tolerance to phenols substituted in the sterically demanding *ortho*-position. To further test this, sterically hindered 2,6-dimethylphenol **2d** was employed as substrate. Even this substrate gave the desired product, albeit in a lower yield (Table 2, entry 4). Also, the challenging 2,4-di-*tert*butylphenol **2e** worked as nucleophile in the present reaction and gave product **3e** in a 70% yield (Table 2, entry 5). Next, the electronic effect of the phenol was studied. As expected, the electron-rich *para*-methoxy-phenol was very reactive in the allylation reaction and gave substituted product **3f** in excellent yield (Table 2, entry 6). When the phenol was substituted in the *para*-position with an electron-withdrawing fluoride, product **3h** could be isolated in 74% isolated yield, showing that the catalyst is very reactive also with challenging phenols (Table 2, entry 8). The substrate scope with respect to the allyl alcohol was then studied. Allyl alcohol **1b** reacted smoothly with **2a** to give product **3i** in a good yield (Table 2, entry 9). Secondary allylic alcohols were even more reactive in the reaction with phenols than the primary allylic alcohols where the reactions were finished within two hours and the products **3a**, **3j**, **3k**, **3l, 3m** and **3n** were isolated in moderate to good yields (Table 2, entries 10-15). Noteworthy, the substrates **1c** and **1a** in which the OH and the double bond have been juxtapositioned, gave the same product (Table 2, entries 1 and 10). This shows that the reaction proceeds through a Pd-π-allyl intermediate. The same trend with respect to the electronic effect of the phenol was observed (Table 2, entries 12-14). Cyclic non-aromatic cyclohexenol **1e** reacted with **2a** to yield product **3n** in a good yield (Table 2, entry 15). Thereby, the employed catalyst shows a remarkable reactivity with respect to both the electrophile as well as the nucleophile.

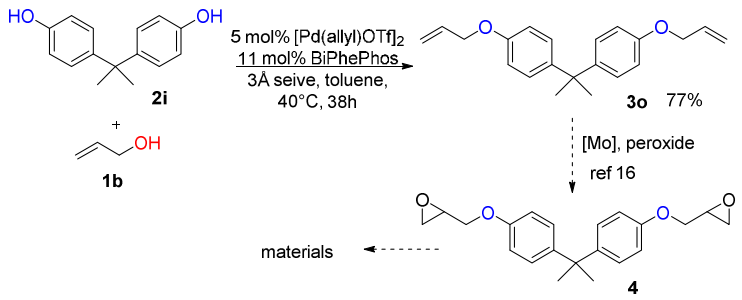
Table 2 Palladium catalyzed allylation of phenols.[a]



Entry	Allylic alcohol	Phenol	Product	Time (h)	Yield (%)[b]
1	 1a	 2a	 3a	24	93
2	 1a	 2b	 3b	24	99
3	 1a	 2c	 3c	24	96
4	 1a	 2d	 3d	24	55
5	 1a	 2e	 3e	24	70
6	 1a	 2f	 3f	24	99
7	 1a	 2g	 3g	24	97
8	 1a	 2h	 3h	24	74
9	 1b	 2a	 3i	20	86
10	 1c	 2a	 3a	2	90
11	 1d	 2a	 3j	2	87
12	 1d	 2f	 3k	2	81
13	 1d	 2g	 3l	2	70
14	1d	2h	3m	2	63
15	1e	2a	3n	2	71

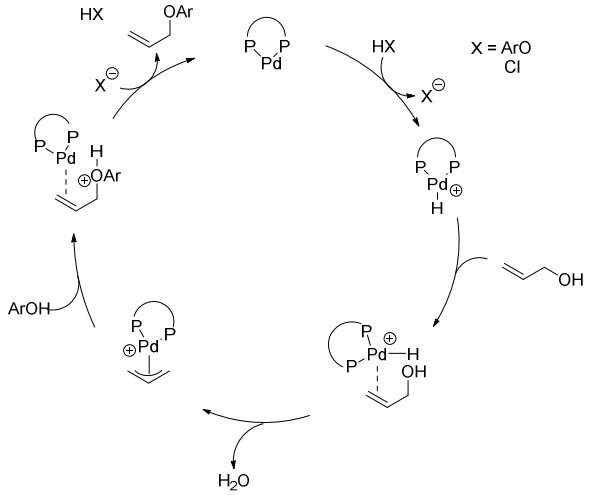
[a] Reaction condition: allylic alcohol (0.25 mmol), nucleophile (0.5 mmol), $[Pd(\pi\text{-allyl})Cl]_2$ (2.5 mol%), BiPhePhos (5.5 mol%), 3Å MS (60 mg), toluene (0.5 mL). [b] Isolated yield.

Allylation of Bisphenol A **2i** with allyl alcohol **1b** gave the diallylated product **3o** in 77% yield (Scheme 2). This intermediate can then be epoxidized using a Mo-catalyst to yield the diepoxy precursor **4** using known literature procedures.[16] As epoxy resins are commonly synthesized by the reaction of a biphenolic precursor with epichlorohydrin that is produced from allyl chloride, this result opens up green synthetic pathways to Bisphenol derivatives where the allylic alcohol easily can be varied.

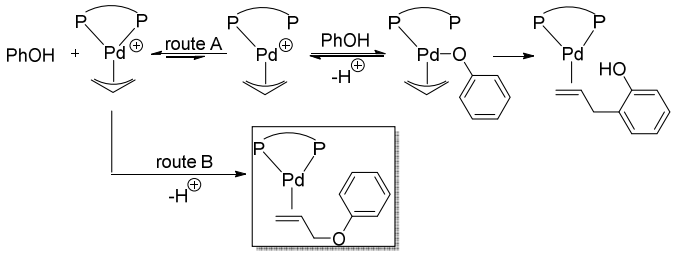


Scheme 2 Synthesis of bisallyl ether of bisphenol A (**3o**), a precursor to epoxy resin.

The mechanism of the C–O bond cleavage of allylic alcohol has been proposed in which the OH group of allylic alcohol was activated by palladium hydride intermediate (Scheme 3). The intermediacy of a palladium hydride in C–O bond cleavage of allylic alcohol has previously been proposed by Ozawa and Yoshifuji.[17,15a] The phenol attacks the Pd-π-allyl in an outersphere mechanism (Table 2, entries 1 and 10).[8j] Regarding the chemoselectivity of the O-allylation of phenols, the reactions that give the thermodynamically favored C-allylation with phenols have been proposed to proceed through an innersphere reaction mechanism (Scheme 4, route A). In the case of palladium, decoordination of one of the ligands must precede the coordination of the phenol. From this intermediate, an ortho allylation or a Fiedel-Craft reaction takes place to generate the ortho allylated phenol.[13] With the present Pd[BiPhePhos] catalyst, this pathway is inhibited. The π-acidic bidentate phosphite ligand is less prone to decoordinate as compared to monodentate phosphite ligands or even bidentate phosphine ligands. Thereby the present catalytic system is tuned to promote O-allylation where the phenol attacks the Pd-π-allyl in an outersphere reaction mechanism (Scheme 4, route B). Also, the mild reaction conditions without requirement of acids, inhibit thermal or acid-catalyzed Claisen rearrangement to form the C-allylated product.



Scheme 3. The proposed mechanism.



Scheme 4. C-allylation by the phenoxy-Pd intermediate requires a vacant cooridination site on palladium (route A). The bidentate π-acidic BiPhePhos ligand inhibits the decoordination and hence favor route B.

To our knowledge, this is the first report of a selective O-allylation of phenols using non-derivatized allylic alcohols as substrates without addition of either acids or bases. Due to the nature of the catalyst, where a π-acidic bidentate phosphite ligand is used, no free coordination sites are available and thus the C-allylation route is inhibited and only O-allylation is observed. The substrate scope is broad with respect to both the phenol and the allylic alcohol. Application towards epoxy resins using a halide free route has been demonstrated.

EXPERIMENTAL SECTION

General information

Toluene and dichloromethane were distilled from calcium hydride under argon. The reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Thin-layer chromatography (TLC) was conducted using Merck analytical TLC plates (silica gel 60 F-254). Compounds were visualized by ultraviolet light and/or by heating the plate after dipping in a 1% solution of vanillin in 0.1 M sulfuric acid in ethanol. Flash column chromatography was performed on silica gel (35-70 micron). Infrared (IR) spectra were recorded on a Perkin–Elmer FT-IR spectrometer. Proton and carbon nuclear magnetic resonance (NMR) spectra were obtained using a Varian 400 MHz spectrometer and Bruker 400 MHz spectrometer. Chemical shifts were recorded as δ values in ppm. Coupling constants (J) are given in Hz, and multiplicity is defined as follows: br = broad, s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, dq = doublet of quintet, t = triplet, td = triplet of doublet, tt = triplet of triplet, q = quartet, quint = quintet, hep = heptet, m = multiplet. High resolution mass spectrometry was recorded on Bruker Daltonics MicrOTOF.

General procedure of allylation of phenol derivatives: A dried schelenk tube was charged with $[Pd(allyl)Cl]_2$ (2.3 mg, 2.5 mol%) and BiPhePhos (11 mg, 5.5 mol%) and CH_2Cl_2 (0.5 mL). The mixture was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 30 min, after which the solvent was removed under vacuum. A solution of allylic alcohol (0.25 mmol) in toluene (0.5mL, 0.5 *M*), phenol (0.50 mmol) and 3Å molecular sieve (60 mg) were added to the schelenk tube. The mixture was degassed by three freeze-pump-thaw cycles and stirred at 40°C for 2-24 h. The reaction mixture was purified by column chromatography on silica gel.

1-(cinnamyloxy)-4-methylbenzene (3a) Purification by flash column chromatography (1-2% EtOAc/pentane) gave a white solid (52.1 mg 93%). mp: 76-77 °C. IR (neat.) *v* 3037, 2935, 2863, 1611, 1512, 1448, 1242, 1015, 966, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.34 (m, 2H), 7.35 – 7.26 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 16.1 Hz, 1H), 6.47 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.73 (dd, *J* = 5.8, 1.5 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 156.7, 136.7, 133.0, 130.3, 130.1, 128.7, 128.0, 126.7, 124.9, 114.8, 68.9, 20.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}ONa$ 247.1093; Found 247.1096.

(*E*)-1-(cinnamyloxy)-3-methylbenzene (3b) Purification by flash column chromatography (1-2% EtOAc/pentane) gave a colorless oil (55.5 mg 99%). IR (neat.) *v* 3027, 2921, 2854, 1599, 1489, 1449, 1260 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.26 – 7.17 (m, 1H), 6.87 – 6.72 (m, 4H), 6.45 (dt, *J* = 16.0, 5.7 Hz, 1H), 4.71 (dd, *J* = 5.8, 1.6 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 139.6, 136.6, 132.9, 129.3, 128.6, 127.9, 126.6, 124.7, 121.8, 115.7, 111.7, 68.5, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}ONa$ 247.1093; Found 247.1088.

1-(cinnamyloxy)-2-methylbenzene (3c) Purification by flash column chromatography (1-2% EtOAc/pentane) gave a white solid (53.8 mg 96%). mp: 40-41 °C. IR (neat.) *v* 3026, 2925, 1601, 1495, 1450, 1241, 1122, 965 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$,) δ 7.43 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 7.17 – 7.10 (m, 2H), 6.92 – 6.83 (m, 2H), 6.72 (d, *J* = 15.8, 1.6 Hz, 1H), 6.42 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.68 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 136.7, 132.4, 130.9, 128.7, 127.9, 127.1, 126.9, 126.7, 125.1, 120.7, 111.6, 68.7, 16.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}ONa$ 247.1093; Found 247.1091.

2-(cinnamyloxy)-1,3-dimethylbenzene (3d) Purification by flash column chromatography (1 % EtOAc/pentane) gave a brown oil (32.7 mg, 55%). IR (neat.) *v* 3025, 2921, 2855, 1591, 1495, 1475, 1262, 1196 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.12 (m, 1H), 6.93 (d, *J* = 7.4 Hz, 2H), 6.89 – 6.78 (m, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.39 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.38 (d, *J* = 5.9 Hz, 1H), 2.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 136.8, 132.6, 131.2, 128.9, 128.7, 127.9, 126.7, 125.5, 124.0, 73.0, 16.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}ONa$ 261.1250; Found 261.1243.

2,4-di-*tert*-butyl-1-(cinnamyloxy)benzene (3e) Purification by flash column chromatography (1 % EtOAc/pentane) gave a white solid (56.4 mg 70%). mp: 111-112 °C IR (neat.) *v* 3005, 2963, 1601, 1496, 1455, 1217, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.9 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.29 – 7.22 (m, 1H), 7.17 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.46 (dt, *J* = 16.0, 5.5 Hz, 1H), 4.72 (dd, *J* = 5.5, 1.6 Hz, 2H), 1.43 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.9, 137.7, 136.9, 132.2, 128.7, 127.9, 126.7, 125.5, 124.1, 123.5, 112.1, 68.9, 35.3, 34.4, 31.8, 30.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{30}ONa$ 345.2189; Found 345.2197.

1-(cinnamyloxy)-4-methoxybenzene (3f) Purification by flash column chromatography (1-4% EtOAc/pentane) gave a colorless solid (59.4 mg 99%). mp: 107-108 °C. IR (neat.) *v* 3072, 2955, 1638, 1512, 1449, 1240, 1039, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.31 (m, 2H), 7.31 – 7.22 (m, 1H), 6.97 – 6.88 (m, 2H), 6.90 – 6.81 (m, 2H), 6.73 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.43 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.66 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$,) δ 154.1, 152.9, 136.6, 132.9, 128.7, 128.0, 126.7, 124.9, 116.0, 114.8, 69.5, 55.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}O_2Na$ 263.1043; Found 263.1048.

(cinnamyloxy)benzene (3g) Purification by flash column chromatography (1-2% EtOAc/pentane) gave a white solid (51.0 mg 97%)**.** mp: 67-68 °C**.** IR (neat.) *v* 3027**,** 2098, 1599, 1448, 1241, 1041, 963 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.37 (m, 2H), 7.35 – 7.21 (m, 5H), 6.99 – 6.88 (m, 3H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.40 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.68 (dd, *J* = 5.8, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 136.6, 133.1, 129.6, 128.7, 128.0, 126.7, 124.6, 121.0, 114.9, 68.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}ONa$ 233.0937; Found 233.0934.

1-(cinnamyloxy)-4-fluorobenzene (3h) Purification by flash column chromatography (1-2% EtOAc/pentane) a yellow light solid. mp: 84-85 °C. IR (neat.) *v* 3064, 3028, 2926, 2836, 1598, 1506, 1449, 1217, 831 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.19 (m, 1H), 6.99 – 6.92 (m, 2H), 6.89 – 6.84 (m, 2H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.37 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.63 (dd, *J* = 5.8, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5 (d, $^1J_{CF}$ = 238.4 Hz), 154.9 (d, $^4J_{CF}$ = 2.1 Hz), , 136.5, 133.2, 128.7, 128.1, 126.7, 124.4, 115.96 (dd, $^2J_{CF}$ = 23.1, $^3J_{CF}$ = 7.9 Hz), 69.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{13}FONa$ 251.0843; Found 251.0831.

1-(allyloxy)-4-methylbenzene (3i) Purification by flash column chromatography (0.5 % EtOAc/ pentane) gave a clear oil (32.0 mg 86%). IR (neat.) *v* 3082, 3028, 2923, 2861, 1874, 1614, 1455, 1241, 817 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.06 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.41 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.51 (dt, *J* = 5.3, 1.5 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 156.6, 133.7, 130.2, 130.0, 117.6, 114.7, 69.1, 20.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{12}ONa$ 171.0772; Found 171.0780.

(*E*)-1-methyl-4-((4-phenylbut-3-en-2-yl)oxy)benzene (3j) Purification by flash column chromatography (1-4 % EtOAc/pentane) gave a colorless oil (51.8 mg 87%). IR (neat.) *v* 3028, 2956, 2924, 1613, 1584, 1509, 1449, 1236, 966 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$,) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 1H), 7.07 – 6.97 (m, 2H), 6.92 – 6.80 (m, 2H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.28 (dd, *J* = 16.1, 6.2 Hz, 0H), 4.97 – 4.84 (m, 1H), 2.27 (s, 3H), 1.51 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 136.7, 131.1, 130.7, 130.2, 130.0, 128.7, 127.8, 126.6, 116.2, 74.9, 21.8, 20.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}ONa$ 261.1250; Found 261.1258.

(*E*)-1-methoxy-4-((4-phenylbut-3-en-2-yl)oxy)benzene (3k) Purification by flash column chromatography (1-4 % EtOAc/pentane) gave a colorless oil (50.6 mg 81%). IR (neat.) *v* 3026, 2979, 2833, 1592, 1505, 1448, 1227, 968 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$,) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 6.96 – 6.86 (m, 2H), 6.85 – 6.76 (m, 2H), 6.58 (d, *J* = 16.1 Hz, 1H), 6.28 (dd, *J* = 16.1, 6.3 Hz, 1H), 4.90 – 4.79 (m, 2H), 3.76 (s, 3H), 1.51 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 152.2, 136.7, 131.1, 130.8, 128.7, 127.8, 126.6, 117.7, 114.7, 75.9, 55.8, 21.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}O_2Na$ 277.1199; Found 277.1210.

(*E*)-(3-phenoxybut-1-en-1-yl)benzene (3l) Purification by flash column chromatography (0.5 % EtOAC/pentane) gave a colorless oil (36.8 mg 70%). IR (neat.) *v* 3029, 2979, 2929, 1597, 1494, 1448, 1239 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 2H), 7.31 – 7.16 (m, 5H), 7.01 – 6.83 (m, 3H), 6.59 (dd, *J* = 16.1, 1.1 Hz, 1H), 6.27 (dd, *J* = 16.1, 6.2 Hz, 1H), 4.95 (td, *J* = 6.3, 1.2 Hz, 1H), 1.51 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 136.7, 130.9, 130.8, 129.5, 128.7, 127.8, 126.6, 120.9, 116.2, 74.6, 21.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}ONa$ 247.1093; Found 247.1100.

(*E*)-1-fluoro-4-((4-phenylbut-3-en-2-yl)oxy)benzene (3m) Purification by flash column chromatography (0.5-2 % EtOAC/pentane) gave a yellow oil (38.2 mg 63%). IR (neat.) *v* 3057, 3028, 2980, 2929, 1600, 1504, 1449, 1206, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 7.01 – 6.88 (m, 4H), 6.60 (d, *J* = 16.1 Hz, 1H), 6.28 (dd, *J* = 16.1, 6.4 Hz, 1H), 4.95 – 4.82 (m, 1H), 1.54 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 157.4 (d, $^1J_{CF}$ = 238.5 Hz),154.2 (d, $^4J_{CF}$ = 2.1 Hz), 154.2, 136.5, 131.0, 130.6, 128.7, 127.9, 126.6,), 117.6 (d, $^3J_{CF}$ = 7.9 Hz) , 115.8 (d, $^4J_{CF}$ = 22.9 Hz)., 75.7, 21.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}FONa$ 265.0999; Found 265.1000.

1-(cyclohex-2-en-1-yloxy)-4-methylbenzene (3n) Purification by flash column chromatography (0.5-2 % EtOAC/pentane) gave a yellow oil (33.4 mg 71%) IR (neat.) *v* 3029, 2932, 1614, 1451, 1233, 1175, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$,) δ 7.13 – 7.00 (m, 2H), 6.92 – 6.77 (m, 2H), 5.96 (dtd,

J = 10.2, 3.6, 1.3 Hz, 1H), 5.87 (dq, *J* = 10.1, 2.3 Hz, 1H), 4.75 (ddd, *J* = 4.2, 3.0, 1.6 Hz, 1H), 2.29 (s, 3H), 2.20 – 1.75 (m, 5H), 1.72 – 1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 132.1, 130.1, 126.7, 116.1, 71.2, 28.5, 25.3, 20.6, 19.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}ONa$ 211.1093; Found 211.1101.

4,4'-(propane-2,2-diyl)bis((allyloxy)benzene) (3o) A flame-dried schelnk tube was charged with $[Pd(allyl)Cl]_2$ (4.6 mg, 10 mol%), BiPhePhos (22 mg, 11 mol%), AgOTf (32 mg, 50 mol%) and CH_2Cl_2 (0.5 mL). The mixture was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 30 min then AgCl was filtered off through syringe filter and the solvent was removed under vacuum. A solution of allylic alcohol (0.2 mL, 3 mmol) in toluene (1 mL, 0.25 *M*), bisphenol A (58 mg, 0.25 mmol) and 3 Å molecular sieve (1 g) were added to the $Pd[\kappa^2$-BiPhePhos$][\eta^3$-$C_3H_5]^+$ + $[OTf]^-$ complex. The slurry was degassed by three freeze-pump-thaw cycles and stirred at 40°C for 38 h. The reaction mixture was purified by column chromatography on silica gel eluting with 10% EtOAC/pentane to give diallylated product as a brown oil (59 mg, 0.19 mmol, 77% yield) IR (neat.) *v* 2966, 2928, 2870, 1608, 1509, 1458, 1298, 1247, 1182, 1024bcm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.20 (d, *J*= 8.9 Hz, 4H), 6.87 (d, *J*= 8.9 Hz, 4H), 6.17-6.05 (m, 2H), 5.47 (dq, *J*= 1.6, 17.2 Hz), 5.34 (ddd, *J*= 1.3, 1.4, 10.5 Hz), 4.56 (dt, *J*= 1.4, 5.4 Hz), 1.69 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 143.3, 133.4, 127.8, 117.9, 113.9, 68.8, 41.7, 31.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{24}O_2Na$ 331.1674; Found 331.1664.

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of the products (PDF)

Acknowledgements

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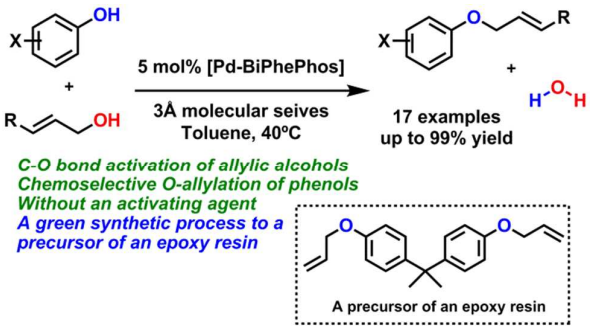

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