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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b01729 • Publication Date (Web): 07 Sep 2017

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Palladium-Catalyzed Aerobic Oxygenation of Allylarenes

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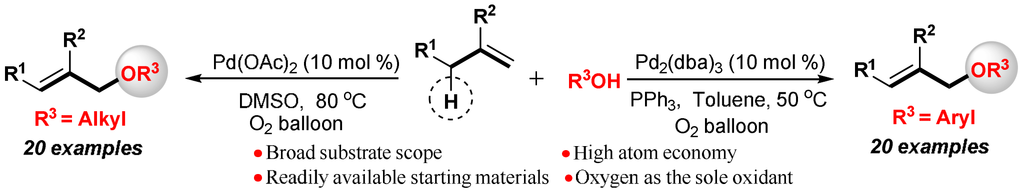
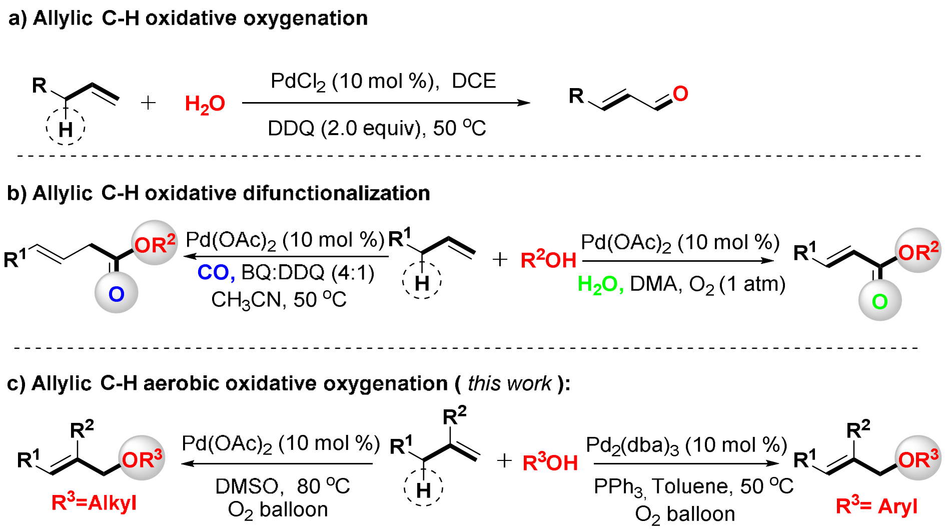


Abstract: An efficient and practical protocol for the synthesis of (*E*)-allylethers from readily available olefins with alcohols or phenols has been developed. This aerobic oxidative allylic C-H oxygenation protocol features mild conditions, broad substrate scope, as well as high atom- and step-economy, making it a valuable and convenient synthetic method. Notably, molecular oxygen is the sole oxidant in this novel transformation.

INTRODUCTION

Palladium-catalyzed oxidative allylic C-H functionalization is a well-established method that has played a vital role in synthetic chemistry due to its broad applicability[1,2], leading to allylic C-H oxygenation,[3] alkylation,[4] amination,[5] carbonylation,[6] silylation[7] and dehydrogenation[8]. This new procedure shows that unnecessary functional group manipulations (FGMs) can be bypassed, which presents a highly efficient approach for the synthesis of functionalized olefins, reducing synthetic steps and increasing overall yield. Recently, our group has reported an efficient and convenient procedure for the synthesis of cinnamic aldehydes *via* aerobic oxidative oxygenation of allylarenes (Scheme 1a).[9] More recently, we have also developed aerobic oxidative double allylic C-H oxygenation of alkenes for the construction of β-enoic acid esters and α,β-unsaturated esters with high regioselectivity (Scheme 1b).[10] However, these emerging methods utilize palladium catalysts in combination with stoichiometric oxidants, such as BQ, DDQ, $PhI(OAc)_2$, Cu^{II} , *etc*. Replacement of these oxidants with molecular oxygen represents a fundamental challenge that has important implications for environmentally benign and potential synthetic applications of these methods.[11]

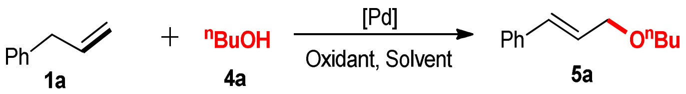
Ether compounds serve as versatile reactants in classical organic reactions or protecting reagents in organic synthesis.[12] Accordingly, many methods for the construction of ethers have been well-developed in recent years.[13] Generally, the traditional coupling of alkali metal alkoxide and alkyl halide predominated the synthesis of ether compounds due to its practicability.[14] In 2014, Hu's group presented a step-economic conversion of cinnamylbromide to the corresponding allylethers.[15] However, the harsh reaction conditions and requirement of leaving groups prohibited their applications in organic synthesis. Based on our enduring interest in palladium-catalyzed aerobic oxidative allylic C-H functionalization, we present an atom-economic and concise strategy for the synthesis of (*E*)-allylethers *via* palladium-catalyzed oxidative allylic C-H oxygenation of olefins with alcohols or phenols with the employment of atmospheric pressure of oxygen as the sole oxidant (Scheme 1c).



Scheme 1. Pd-catalyzed oxidative allylic C–H functionalization

RESULTS AND DISCUSSION

Table 1. Screening reactions for the synthesis of (*E*)-allylether [a]



Entry	Catalyst	Oxidant	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	O_2	DMSO	41
2	$PdCl_2$	O_2	DMSO	30
3	$Pd(TFA)_2$	O_2	DMSO	8
4	$Pd(CH_3CN)_2Cl_2$	O_2	DMSO	trace
5	$Pd(allyl)_2Cl_2$	O_2	DMSO	7
6	$Pd(OAc)_2$	DDQ	DMSO	5
7	$Pd(OAc)_2$	BQ	DMSO	trace
8	$Pd(OAc)_2$	$PhI(OAc)_2$	DMSO	9

9	Pd(OAc)$_2$	$K_2S_2O_8$	DMSO	8
10	Pd(OAc)$_2$	O_2	DMA	17
11	Pd(OAc)$_2$	O_2	Toluene	trace
12	Pd(OAc)$_2$	O_2	DMF	27
13	Pd(OAc)$_2$	O_2	1,4-Dioxane	16
14[c]	Pd(OAc)$_2$	O_2	DMSO	21
15[d]	**Pd(OAc)$_2$**	**O_2**	**DMSO**	**90**
16[e]	Pd(OAc)$_2$	O_2	DMSO	67

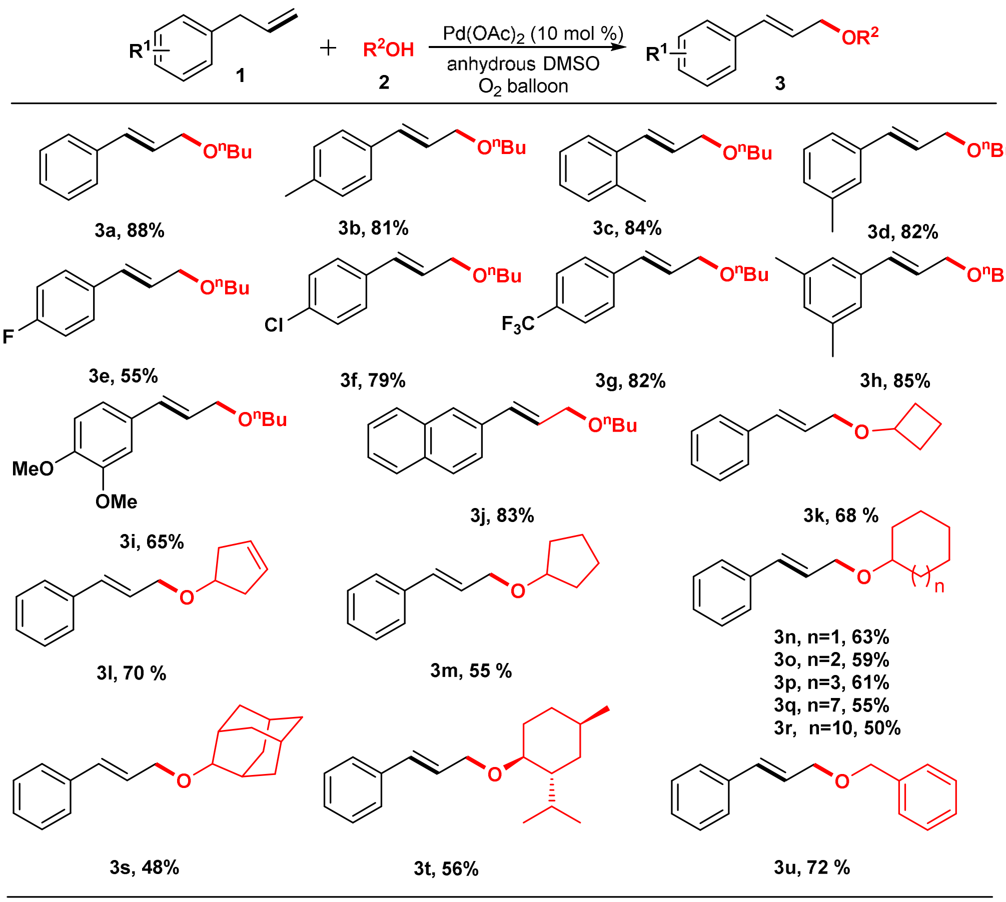
[a] Unless otherwise noted, all reactions were performed with **1a** (0.25 mmol), **2a** (0.25 mL), Pd catalyst (10 mol %), oxidant (1 equiv) or O_2 balloon in the indicated anhydrous solvent (1.0 mL) at 100 °C for 24 h. [b] Determined by GC using dodecane as the internal standard. [c] The reaction was performed at 120 °C. [d] The reaction was performed at 80 °C; [e] The reaction was performed at 60 °C.

We began our study by investigating the model reaction with allylbenzene (**1a**) and *n*-butanol (**2a**). Initially, various palladium catalysts were examined including $PdCl_2$, Pd(TFA)$_2$, Pd(PhCN)$_2$Cl$_2$, and Pd(allyl)$_2$Cl$_2$, and they were less effective than Pd(OAc)$_2$ (Table 1, entries 1-5). Furthermore, the screening of oxidants, such as DDQ, BQ, PhI(OAc)$_2$ and $K_2S_2O_8$, revealed that the molecular oxygen promoted this oxygenation reaction dramatically (Table 1, entries 6-10). Moreover, based on our initial works, the intermediate allylpalladium complex would be captured by water rather than alcohol in the presence of water.[9] Therefore, various anhydrous solvents were used for this transformation (Table 1, entries 1, 10-13), and DMSO was identified as the optimal solvent for the formation of **3a**. Further attempts to optimize the reaction condition by increasing temperature were unsuccessful (Table 1, entry 14). Fortunately, decreasing the temperature resulted in higher yields of the desired product (Table 1, entries 15 and 16). Thus, the optimal condition was obtained as

$Pd(OAc)_2$ (10 mol %) in anhydrous DMSO (2.0 mL) at 80 ^{o}C under molecular oxygen (1 atm) for 24 h.

After establishing the optimized reaction conditions, the generality and substrate scope of olefins and alcohol derivatives were investigated, and the results are summarized in Scheme 2. Gratifyingly, the allylbenzenes were amenable to a range of electron-donating groups or electron-deficient groups at the aromatic ring to generate the desired products (**3b-3i**) in moderate to good yields. Remarkably, the reaction of 4-Cl substituted allylbenzene proceeded effectively and afforded the corresponding product **3g** in good yield, highlighting the compatibility of this reaction. Additionally, 2-naphthylpropene (**1j**) could be transformed to the desired product in 83% yield. Furthermore, a series of alcohols were also found to be suitable substrates under the optimized conditions. The substrates of cyclobutanol (**2k**), cyclopent-3-en-1-ol (**2l**), cyclopentanol (**2m**), cyclohexanol (**2n**) and cycloheptanol (**2o**) were all allowed to react with **1a**, affording the corresponding (*E*)-allylether derivatives **3k-3o** in good yields. It is noteworthy that 2-adamantanol (**2s**), *L*-menthol (**2t**) and benzyl alcohol (**2u**) could also undergo this transformation, furnishing the desired allylic ester products in 48% , 56% and 72% yields, respectively.

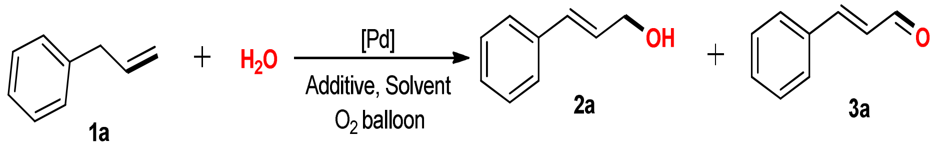
Scheme 2. Substrate scope of various allylbenzenes and alcohols [a, b]



[a] Unless otherwise noted, all reactions were performed with **1** (0.25 mmol), **2** (0.25 mL), $Pd(OAc)_2$ (10 mol %), in anhydrous DMSO (1.0 mL) with O_2 balloon at 80 °C for 24 h. [b] Isolated yields based on **1**.

Subsequently, for further demonstrating the synthetic potential of this transformation, various phenols were introduced to this oxygenation reaction. Under the optimal conditions for alcohols, a trace amount of **5a** was detected by GC-MS. Encouraged by this result, efforts were made to optimize the reaction conditions. As shown in Table 2, a range of Pd salts were examined, which demonstrated the effectiveness of $Pd_2(dba)_3$ as the catalyst, while a survey of solvents indicated that toluene was the most valid for this reaction (Table 2, entry 5). Subsequently, after the investigation of different ligands, PPh_3 was found to be the superior choice compared to dppf, dppe, 1,2-bis(phenylsulfinyl)ethane, 1,2-bis(phenylsulphonyl)ethane and 4,4'-bipyridine (Table 2, entries 11-16). Finally, declining the temperature to 50 °C gave higher yield of **5a** (Table 2, entries 17 and 18).

Table 2. Screening reaction conditions for the synthesis of (*E*)-allylethers [a]



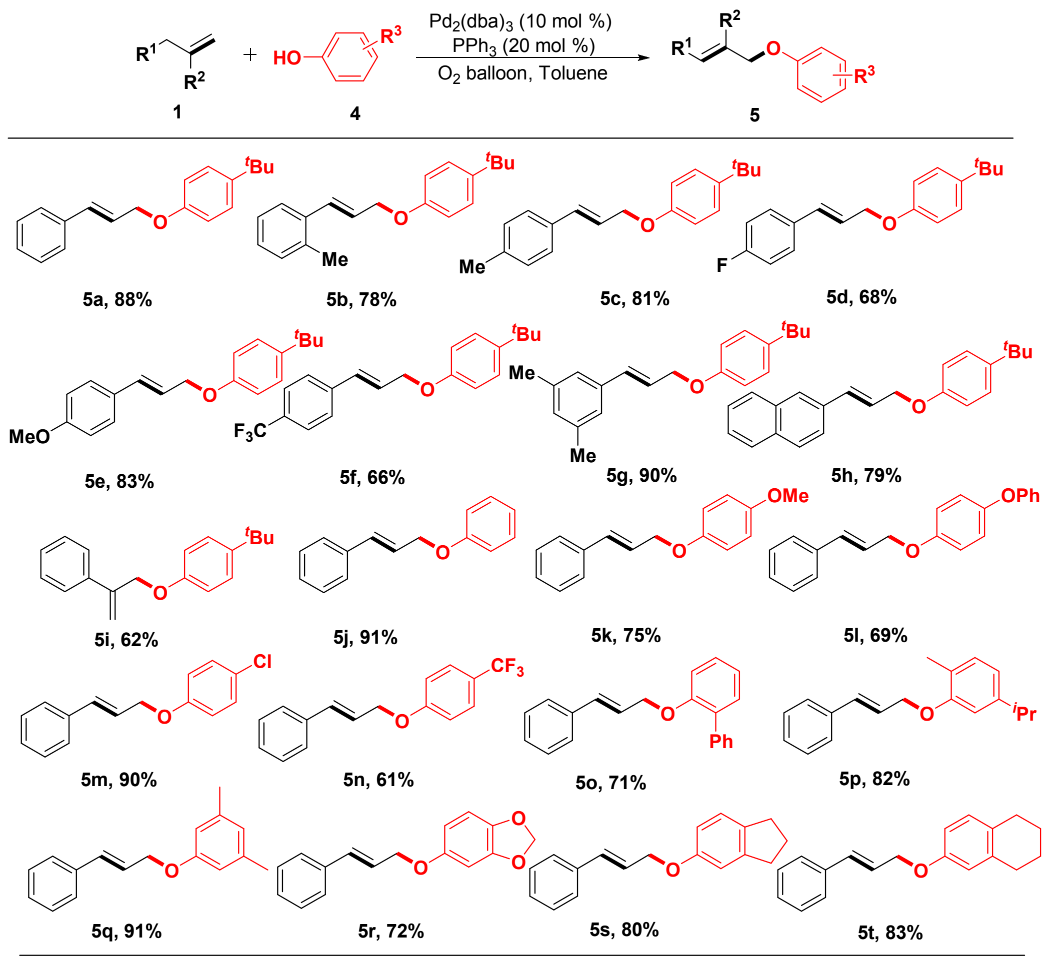
Entry	Catalyst	Ligand	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	-	DMSO	N.D.
2	$PdCl_2$	-	DMSO	N.D.
3	$Pd(TFA)_2$	-	DMSO	N.D.
4	$Pd(CH_3CN)_2Cl_2$	-	DMSO	N.D.
5	$Pd_2(dba)_3$	-	DMSO	18
6	$Pd_2(dba)_3$	-	DMF	17
7	$Pd_2(dba)_3$	-	DMA	12
8	$Pd_2(dba)_3$	-	Toluene	30
9	$Pd_2(dba)_3$	-	MeCN	25
10	$Pd_2(dba)_3$	-	1,4-Dioxane	trace
11	$Pd_2(dba)_3$	PPh_3	Toluene	67
12	$Pd_2(dba)_3$	dppf	Toluene	36
13	$Pd_2(dba)_3$	dppe	Toluene	45
14	$Pd_2(dba)_3$	1,2-bis(phenylsulfinyl)ethane	Toluene	trace
15	$Pd_2(dba)_3$	1,2-bis(phenylsulphonyl) ethane	Toluene	trace
16	$Pd_2(dba)_3$	4,4'-bipyridine	Toluene	trace
17[c]	$Pd_2(dba)_3$	PPh_3	Toluene	79
18[d]	**$Pd_2(dba)_3$**	**PPh_3**	**Toluene**	**91**

[a] Unless otherwise noted, all reactions were performed with **1a** (0.25 mmol), **4a** (0.1 mmol), Pd catalyst (10 mol %), and ligand (1 equiv) in the indicated solvent (1.0 mL) with O_2 balloon at 100 °C for 24 h. [b] Determined by isolated yields. N.D. = not detected. [c] The reaction was performed at 80 °C; [d] The reaction was performed at 50 °C.

With the above reaction conditions in hand, we sought to explore the scope and generality of different olefins. Representative results are summarized in Scheme 3.

Generally, this process is compatible with a range of allylbenzenes with electron-donating groups, giving products **5b**-**5c** in good yields. Different allylbenzenes with electron-deficient groups (**5d, 5f**) are also tolerated in this process. Pleasingly, the reaction of 1-allylnaphthalene (**1h**) proceeded efficiently to give the desired product **5h**. Additionally, it is noteworthy that another impressive feature of the current procedure is its high tolerance for *α*-methylstyrene (**5i**). Subsequently, a series of phenols were also found to be suitable in this transformation. Phenols with electron-withdrawing (**5j-5l**) and -donating groups (**5m-5n**) are perfectly compatible with the established reaction conditions. Carvacrol (**4p**) and sesamol (**4r**) were allowed to react with **1a**, affording the corresponding (*E*)-allylether derivatives in good yields. Moreover, 2,3-dihydro-1*H*-inden-5-ol (**4s**) and 5,6,7,8-tetrahydronaphthalen-2-ol (**4t**) smoothly converted into the desired products in 80% and 83% yields, respectively.

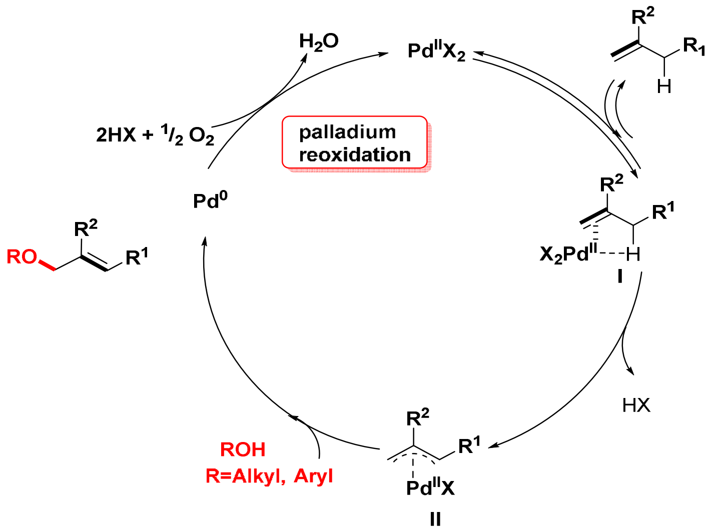
Scheme 3. Substrate scope of various olefins and phenols $^{a, b}$



5a, 88%; **5b**, 78%; **5c**, 81%; **5d**, 68%; **5e**, 83%; **5f**, 66%; **5g**, 90%; **5h**, 79%; **5i**, 62%; **5j**, 91%; **5k**, 75%; **5l**, 69%; **5m**, 90%; **5n**, 61%; **5o**, 71%; **5p**, 82%; **5q**, 91%; **5r**, 72%; **5s**, 80%; **5t**, 83%

[a] Unless otherwise noted, all reactions were performed with **1** (0.25 mmol), **4** (0.1 mmol), $Pd_2(dba)_3$ (10 mol %), PPh_3 (20 mol %) in toluene (1.0 mL) with O_2 balloon at 80 °C for 24 h. [b] Isolated yields based on **4**.

Scheme 4. Proposed Mechanism



On the basis of the current results and previous literatures, we proposed a plausible mechanism as shown in Scheme 4. Initially, palladium coordinated with olefins to generate the intermediate □. Next, the corresponding π-allylpalladium species **II** was formed by the oxidative cleavage of allylic C-H bond.[16-17] Subsequently, alcohols or phenols would undergo nucleophilic attacking to the π-allylpalladium species.[1h-i, 18] Finally, (*E*)-allylether was obtained through the reductive elimination process. Similarly, oxygen played a vital role in the regeneration of the active Pd^{II} species.[19]

In conclusion, we have developed an efficient approach to expedient and regioselective synthesis of (*E*)-allylethers from readily available olefins and alcohols or phenols *via* palladium-catalyzed aerobic oxidative allylic C-H oxygenation. This transformation provides a new synthetic strategy for the construction of (*E*)-allylethers from simple starting materials with broad substrate scope and excellent functional group tolerance.

Experimental Section

General method. Melting points were measured using a melting point instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform was used as a solvent with TMS as the internal standard. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC−MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100−400 mesh silica gel plates (GF_{254}). Unless otherwise noted, purchased chemicals were used without further purification.

General procedure for synthesis of (*E*)-allylethers 3: olefin derivatives (0.25 mmol), $Pd(OAc)_2$ (10 mol %, 0.025 mmol), and alcohol derivatives (0.25 mL) were added to anhydrous DMSO (1 mL). The mixture was stirred with O_2 balloon at 80 ^{o}C for the desired reaction time. After that, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over $MgSO_4$ and concentrated. The residue was eventually purified by flash column chromatography on a silica gel (hexanes/ethyl acetate) to afford the product.

General procedure for synthesis of (*E*)-allylether (5): olefin derivatives (0.25 mmol), $Pd_2(dba)_3$ (10 mol %, 0.010 mmol), PPh_3 (20 mol %) and phenol derivatives (0.1 mmol) were added to toluene (1 mL). The mixture was stirred under with O_2 balloon at 50 ^{o}C for the desired reaction time. After that, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over

$MgSO_4$ and concentrated. The residue was eventually purified by flash column chromatography on a silica gel (hexanes/ethyl acetate) to afford the product.

(*E*)-(3-Butoxyprop-1-en-1-yl)benzene (3a)[10]**:** Yield: 88% (41.8 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* =8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 12.0, 4.2 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.13 (d, *J* = 6.0 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 1.65 - 1.56 (m, 2H), 1.40 (dd, *J* = 14.4, 7.2 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.1, 128.5, 127.6, 126.5, 71.8, 70.9, 70.3, 31.9, 19.4, 14.0 ppm; ν_{max}(KBr)/cm^{-1} 2930, 2835, 1720, 1425, 1099, 745. MS (EI) m/z 57, 78, 91, 104, 119, 130, 190.

(*E*)-1-(3-Butoxyprop-1-en-1-yl)-4-methylbenzene (3b)[10]**:** Yield: 81% (41.3 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.24 (m, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.31 - 6.19 (m, 1H), 4.11 (d, *J* = 6.0 Hz, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 2.33 (s, 2H), 1.59 (t, *J* = 10.0 Hz, 2H), 1.40 (dq, *J* = 14.4, 7.2 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 134.1, 132.1, 129.2, 126.4, 125.4, 71.5, 70.2, 31.9, 21.2, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2925, 2845, 1652, 1450, 1117, 739; HRMS-ESI (m/z): calcd for $C_{14}H_{20}ONa$, [M+Na]+: 227.1406, found 227.1408.

(*E*)-1-(3-Butoxyprop-1-en-1-yl)-2-methylbenzene (3c): Yield: 84% (42.8 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.0 Hz, 1H), 7.14 (s, 3H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.18 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.15 (d, *J* = 6.0 Hz, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 1.65 - 1.54 (m, 2H), 1.40 (dt, *J* = 14.4, 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.4, 130.2, 129.9, 127.8, 127.5, 126.1, 125.8, 71.6, 70.2, 31.9, 19.8, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2924, 2853, 1651, 1457, 1265, 740. HRMS-ESI (m/z): calcd for

$C_{14}H_{20}ONa$, [M+Na]+: 227.1406, found 227.1405.

(*E*)-1-(3-Butoxyprop-1-en-1-yl)-3-methylbenzene (3d)[10]**:** Yield: 82% (41.8 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 5.4 Hz, 1H), 7.05 (d, J = 4.0 Hz, 3H), 6.57 (d, J = 16.0 Hz, 1H), 6.28 (dt, J = 16.0, 6.0 Hz, 1H), 4.12 (d, J = 6.0 Hz, 1H), 3.48 (t, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.64 - 1.56 (m, 2H), 1.40 (dq, J = 14.4, 7.2 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 136.8, 132.2, 128.4, 127.2, 126.3, 123.6, 71.4, 70.2, 31.9, 21.4, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2931, 2890, 1641, 1330, 1160, 744. HRMS-ESI (m/z): calcd for $C_{14}H_{20}ONa$, [M+Na]+: 227.1406, found 227.1403.

(*E*)-1-(3-Butoxyprop-1-en-1-yl)-4-fluorobenzene (3e)[10]**:** Yield: 55% (28.6 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.0, 5.6 Hz, 2H), 6.99 (t, J = 8.4 Hz, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.21 (dt, J = 16.0, 6.0 Hz, 1H), 4.11 (d, J = 6.0 Hz, 2H), 3.48 (t, J = 6.4 Hz, 2H), 1.65 - 1.53 (m, 2H), 1.46 - 1.34 (m, 1H), 0.93 (t, J = 7.23 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 245.2 Hz), 133.0, 130.9, 127.9 (d, J = 8.0 Hz), 126.2 (d, J = 2.1 Hz), 115.4 (d, J = 21.6 Hz), 71.30, 70.3, 31.9, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2920, 2851, 1730, 1459, 1009, 730. HRMS-ESI (m/z): calcd for $C_{13}H_{17}OFNa$, $[M+Na]^+$: 231.1156, found 231.1156.

(*E*)-1-(3-Butoxyprop-1-en-1-yl)-4-chlorobenzene (3f)[10]**:** Yield: 79% (44.3 mg) as a yellow oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 15.2, 8.4 Hz, 4H), 6.55 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 16.0, 6.0 Hz, 1H), 4.11 (d, J = 6.0 Hz, 2H), 3.48 (t, J = 6.4 Hz, 2H), 1.64 - 1.55 (m, 2H), 1.47 - 1.34 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 133.2, 130.7, 128.7, 127.7, 127.2, 71.2, 70.4, 31.9, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2935, 2845, 1720, 1415, 1118, 730; HRMS-EI (m/z): calcd for $C_{13}H_{17}ClO$,

$[M+Na]^+$: 224.0968, found 224.0961.

(*E*)-1-(3-Butoxyprop-1-en-1-yl)-4-(trifluoromethyl)benzene (3g): Yield: 82% (52.9 mg) as a yellow oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.39 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.15 (d, *J* = 5.6 Hz, 1H), 3.50 (t, *J* = 6.6 Hz, 2H), 1.66 - 1.56 (m, 2H), 1.40 (dt, *J* = 14.4, 7.2 Hz, 1H), 0.94 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 130.2, 129.5, 129.4, 129.2, 126.6, 125.5 (dd, *J* = 7.7, 3.9 Hz), 70.9, 70.6, 31.8, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2928, 2860, 1639, 1325, 1166, 741; HRMS-EI (m/z): calcd for $C_{14}H_{17}F_3O$, $[M+Na]^+$: 258.1231, found 258.1225.

(*E*)-1-(3-Butoxyprop-1-en-1-yl)-3,5-dimethylbenzene (3h): Yield: 85% (46.3 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 2H), 6.88 (s, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.26 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.12 (d, *J* = 6.0 Hz, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 6H), 1.62 - 1.53 (m, 2H), 1.39 (dt, *J* = 14.4, 7.2 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.7, 132.3, 129.3, 126.1, 124.4, 71.5, 70.1, 31.9, 21.2, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2956, 2923, 2856, 1639, 747. HRMS-ESI (m/z): calcd for $C_{15}H_{22}ONa$, $[M+Na]^+$: 241.1563, found 241.1569.

(*E*)-4-(3-Butoxyprop-1-en-1-yl)-1,2-dimethoxybenzene (3i): Yield: 65% (40.6 mg) as colorless oil; hexanes/ethyl acetate =25:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 - 6.81 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.10 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.04 (d, *J* = 5.4 Hz, 2H), 3.81 (d, *J* = 6.0 Hz, 6H), 3.41 (t, *J* = 6.4 Hz, 2H), 1.58 - 1.46 (m, 2H), 1.33 (dq, *J* = 14.4, 7.2 Hz, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.9, 131.9, 129.9, 124.5, 119.7, 111.1, 108.9, 71.5, 70.2, 55.9, 55.8, 31.9, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2928, 2860, 1639, 1325, 967, 741; HRMS-ESI (m/z): calcd for $C_{15}H_{22}O_3Na$, $[M+Na]^+$: 273.1461, found 273.1459.

(*E*)-2-(3-Butoxyprop-1-en-1-yl)naphthalene (3j)[10]**:** Yield: 83% (49.8 mg) as colorless oil; hexanes/ethyl acetate =100 :1; ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.78 (t, *J* = 6.4 Hz, 3H), 7.73 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.49 - 7.39 (m, 2H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.43 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.18 (d, *J* = 6.0 Hz, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 1.61 (dd, *J* = 17.2, 10.4 Hz, 2H), 1.43 (dt, *J* = 14.4, 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 134.3, 133.6, 133.0, 132.1, 128.2, 127.9, 127.7, 126.9, 126.4, 126.2, 125.9, 123.7, 71.5, 70.4, 31.9, 19.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 2933, 2860, 1714, 1425, 1089, 729. HRMS-ESI (m/z): calcd for $C_{17}H_{20}ONa$, [M+Na]+: 263.1406, found 263.1404.

(*E*)-(3-Cyclobutoxyprop-1-en-1-yl)benzene (3k): Yield: 68% (31.9 mg) as colorless oil; hexanes/ethyl acetate =100 :1; ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.23 (dd, *J* = 12.0, 5.4 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.28 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.05 (d, *J* = 6.0 Hz, 2H), 4.02 - 3.97 (m, 1H), 2.23 (dd, *J* = 16.0, 7.8 Hz, 2H), 1.98 (q, *J* = 9.2 Hz, 2H), 1.71 (q, *J* = 10.2 Hz, 1H), 1.51 (dd, *J* = 18.8, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 136.8, 132.2, 128.5, 127.6, 126.5, 126.4, 72.8, 68.5, 30.6 , 12.6 ppm; ν_{max}(KBr)/cm^{-1} 2922, 2854, 1640, 1459, 768, 729; HRMS-ESI (m/z): calcd for $C_{13}H_{16}ONa$, [M+Na]$^+$: 211.1093, found 211.1093.

(*E*)-(3-(Cyclopent-3-en-1-yloxy)prop-1-en-1-yl)benzene (3l): Yield: 70% (35.0 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.38 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.70 (s, 1H), 4.31 (d, *J* = 2.4 Hz, 1H), 4.14 (d, *J* = 6.0 Hz, 1H), 2.61 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.44 (d, *J* = 17.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 136.8, 132.1, 128.5, 128.4, 127.6, 126.5, 126.5, 78.8, 69.5, 39.3 ppm; ν_{max}(KBr)/cm^{-1} 2922, 2853, 1642, 1265, 965, 741; HRMS-ESI (m/z):

calcd for $C_{14}H_{16}ONa$, $[M+Na]^+$: 223.1093, found 223.1087.

(*E*)-(3-(Cyclopentyloxy)prop-1-en-1-yl)benzene (3m)[13e]**:** Yield: 55% (27.8 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.29 (dt, J = 16.0, 6.0 Hz, 1H), 4.10 (d, J = 6.0 Hz, 2H), 4.00 (s, 1H), 1.78 - 1.68 Hz (m, 6H), 1.53 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.8, 128.5, 127.5, 126.9, 126.5, 80.9, 69.5, 32.4, 23.6 ppm; ν_{max}(KBr)/cm^{-1} 3027, 2954, 1639, 1169, 965, 734; HRMS-ESI (m/z): calcd for $C_{14}H_{18}ONa$, $[M+Na]^+$: 225.1250, found 225.1244.

(*E*)-(3-(Cyclohexyloxy)prop-1-en-1-yl)benzene (3n)[13a]**:** Yield: 63% (34.0 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0, 6.0 Hz, 1H), 4.17 (d, J = 6.0 Hz, 2H), 3.34 (td, J = 8.8, 4.0 Hz, 1H), 1.95 (d, J = 12.0 Hz, 2H), 1.76 (d, J = 6.0 Hz, 2H), 1.55 (dd, J = 14.4, 8.0 Hz, 1H), 1.37 - 1.28 (m, 3H), 1.21 (d, J = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.6, 128.5, 127.5, 127.2, 126.5, 68.4, 32.4, 25.8, 24.2 ppm; ν_{max}(KBr)/cm^{-1} 2925, 2855, 1724, 1455, 1112, 738; MS (EI) m/z 55, 91, 92, 105, 117, 134, 216.

(*E*)-(3-(Cycloheptyloxy)prop-1-en-1-yl)benzene (3o): Yield: 59% (33.9 mg) as a yellow oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.29 (dt, J = 16.0, 6.0 Hz, 1H), 4.13 (d, J = 6.0 Hz, 2H), 3.59 - 3.45 (m, 1H), 2.00 - 1.85 (m, 2H), 1.72 - 1.60 (m, 5H), 1.54 (s, 4H), 1.43 - 1.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 131.5, 128.5, 127.5, 127.2, 126.5, 79.6, 68.8, 33.9, 28.5, 23.0 ppm; ν_{max}(KBr)/cm^{-1} 2935, 2850, 1714, 1450, 960, 740; HRMS-ESI (m/z): calcd for $C_{16}H_{22}ONa$, $[M+Na]^+$: 253.1563, found 253.1556.

(Cinnamyloxy)cyclooctane (3p): Yield: 61% (37.2 mg) as a colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 2H), 7.19 (dd, J = 8.0, 6.0 Hz, 1H), 6.57 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 6.0 Hz, 1H), 4.11 (dd, J = 6.0, 1.2 Hz, 2H), 3.52 - 3.48 (m, 1H), 1.88 - 1.81 (m, 2H), 1.77 - 1.66 (m, 4H), 1.62 - 1.39 (m, 8H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.8, 131.4, 128.3, 127.3, 127.0, 126.3, 79.1, 68.6, 31.4, 27.3, 25.4, 23.0 ppm; HRMS-ESI (m/z): calcd for $C_{17}H_{24}ONa$, $[M+Na]^+$: 267.1719, found 267.1722.

(Cinnamyloxy)cyclododecane (3q): Yield: 55% (41.3 mg) as a colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 8.0 Hz, 2H), 7.11 (dd, J = 10.0, 4.0 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H), 6.19 (dt, J = 16.0, 6.0 Hz, 1H), 4.04 (dd, J = 6.0, 0.8 Hz, 2H), 3.45 - 3.41 (m, 1H), 1.59 - 1.52 (m, 2H), 1.45 - 1.39 (m, 2H), 1.35 - 1.24 (m, 18H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.9, 131.6, 128.4, 127.3, 127.0, 126.3, 76.3, 68.9, 28.8, 24.6, 24.2, 23.1, 23.0, 20.6 ppm; HRMS-ESI (m/z): calcd for $C_{21}H_{32}ONa$, $[M+Na]^+$: 323.2345, found 323.2350.

(Cinnamyloxy)cyclopentadecane (3r): Yield: 50% (42.8 mg) as a colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.22 - 7.18 (m, 1H), 6.58 (d, J = 16.0 Hz, 1H), 6.28 (dt, J = 16.0, 5.6 Hz, 1H), 4.12 (d, J = 4.0 Hz, 2H), 3.40 (p, J = 5.8 Hz, 1H), 1.59 - 1.55 (m, 4H), 1.37 - 1.26 (m, 24H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.9, 131.6, 128.4, 127.4, 127.0, 126.4, 77.9, 68.9, 31.9, 27.4, 26.8, 26.7, 26.6, 26.5, 23.1 ppm; HRMS-ESI (m/z): calcd for $C_{24}H_{38}ONa$, $[M+Na]^+$: 365.2815, found 365.2811.

(1r,3r,5r,7r)-2-(Cinnamyloxy)adamantane (3s): Yield: 48% (32.2 mg) as a colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 8.0 Hz, 2H), 7.14 - 7.10 (m, 1H), 6.53 (d, J = 16.0 Hz, 1H), 6.24 (dt, J = 16.0, 5.6 Hz, 1H), 4.07

(dd, *J* = 5.6, 1.2 Hz, 2H), 3.44 (s, 1H), 2.04 - 1.97 (m, 4H), 1.78 - 1.72 (m, 4H), 1.63 - 1.56 (m, 4H), 1.41 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.1, 128.4, 127.3, 126.4, 81.1, 67.9, 37.6, 36.5, 31.8, 31.5, 27.4, 27.4 ppm; HRMS-ESI (m/z): calcd for $C_{19}H_{24}ONa$, $[M+Na]^+$: 291.1719, found 291.1721.

((*E*)-3-(((1S,2S,4R)-2-Isopropyl-4-methylcyclohexyl)oxy)prop-1-en-1-yl)benzene (3t)[13a]**:** Yield: 56% (38.1 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.29 (dd, *J* = 12.6, 6.0 Hz, 1H), 4.06 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.14 (td, *J* = 10.0, 4.0 Hz, 1H), 2.27 (dd, *J* = 13.4, 6.6 Hz, 1H), 2.14 (d, *J* = 12.0 Hz, 1H), 1.62 (dd, *J* = 26.2, 16.0 Hz, 4H), 1.05 - 0.86 (m, 9H), 0.84 - 0.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.7, 128.5, 127.5, 127.2, 126.5, 78.7, 69.1, 48.3, 40.6, 34.6, 31.6, 25.6, 23.4, 22.4, 21.0, 16.3 ppm; ν_{max}(KBr)/cm^{-1} 3045, 2921, 2854, 1600, 1489, 835, 767, 693; HRMS-ESI (m/z): calcd for $C_{19}H_{28}ONa$, $[M+Na]^+$: 295.2032, found 295.2025.

(*E*)-(3-(benzyloxy)prop-1-en-1-yl)benzene (3u)[13a]**:** Yield: 72% (40.3 mg) as colorless oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.44 (m, 6H), 7.40 (t, *J* = 8.0 Hz, 3H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.42 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.66 (s, 2H), 4.28 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 136.7, 132.4, 128.5, 128.3, 127.7, 127.6, 127.6, 126.4, 126.1, 72.1, 70.9.ppm; ν_{max}(KBr)/cm^{-1} 3025, 2928, 1714, 1450, 757, 673.

1-(*tert*-Butyl)-4-(cinnamyloxy)benzene (5a) [13f]**:**Yield: 88% (23.4 mg) as yellow solid; mp = 77 - 78 ^{o}C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.31 (m, 2H), 7.26 - 7.22 (m, 4H), 7.19 - 7.16 (m, 2H), 6.85 - 6.80 (m, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* =

16.0, 6.0 Hz, 1H), 4.61 (dd, *J* = 6.0, 1.6 Hz, 2H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 143.6, 136.5, 132.8, 128.6, 127.8, 126.6, 126.2, 124.8, 114.3, 68.7, 34.1, 31.5 ppm; ν_{max}(KBr)/cm^{-1} 3632, 2964, 1724, 1628, 1254, 1143, 1074, 751; HRMS-ESI (m/z): calcd for $C_{19}H_{22}ONa$, $[M+Na]^+$: 289.1563, found 289.1558.

(*E*)-1-(3-(4-(*tert*-Butyl)phenoxy)prop-1-en-1-yl)-2-methylbenzene (5b): Yield: 78% (21.8 mg) as yellow solid; mp = 73 - 74 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.35 - 7.33 (m, 1H), 7.32 - 7.30 (m, 1H), 7.20 - 7.14 (m, 3H), 6.99 - 6.88 (m, 3H), 6.31 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.72 (dd, *J* = 6.0, 1.6 Hz, 2H), 2.35 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 143.6, 135.7, 135.6, 130.9, 130.3, 127.7, 126.3, 126.1, 126.1, 125.9, 114.4, 68.9, 34.1, 31.5, 19.6 ppm; ν_{max}(KBr)/cm^{-1} 3485, 2963, 1723, 1624, 1251, 1141, 803, 750; HRMS-ESI (m/z): calcd for $C_{20}H_{24}ONa$, $[M+Na]^+$: 303.1719, found 303.1720.

(*E*)-1-(*tert*-Butyl)-4-((3-(*p*-tolyl)allyl)oxy)benzene (5c): Yield: 81% (22.7 mg) as yellow solid; mp = 110 - 111 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.30 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.93 - 6.91 (m, 1H), 6.91 - 6.88 (m, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.38 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.68 (dd, *J* = 6.0, 1.6 Hz, 2H), 2.35 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 143.5, 137.7, 133.7, 132.9, 129.3, 126.5, 126.2, 123.7, 114.3, 68.8, 34.1, 31.5, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 3035, 2954, 2862, 1604, 1509, 1240, 1185, 1005; HRMS-ESI (m/z): calcd for $C_{20}H_{24}ONa$, $[M+Na]^+$: 303.1719, found 303.1714.

(*E*)-1-(*tert*-Butyl)-4-((3-(4-fluorophenyl)allyl)oxy)benzene (5d): Yield: 68%; (19.3 mg) as yellow solid; mp = 114 - 115 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.36 (m, 2H), 7.34 - 7.29 (m, 2H), 7.05 - 6.98 (m, 2H), 6.93 - 6.88 (m, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.35 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.68 (dd, *J* = 6.0, 1.6 Hz, 2H), 1.31 (s, 9H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 247.2 Hz), 156.4, 143.7, 132.7 (d, J = 3.3 Hz), 131.7, 128.1 (d, J = 8.0 Hz), 126.3, 124.6 (d, J = 2.2 Hz), 115.49 (d, J = 21.7 Hz), 114.2, 68.6, 34.1, 31.5 ppm; ν_{max}(KBr)/cm^{-1} 3459, 3059, 2959, 2862, 1612, 1507, 1237, 1015; HRMS-ESI (m/z): calcd for $C_{19}H_{21}FONa$, $[M+Na]^+$: 307.1469, found 307.1473.

(*E*)-1-(*tert*-Butyl)-4-((3-(4-methoxyphenyl)allyl)oxy)benzene (5e): Yield: 83% (24.6 mg) as yellow solid; mp = 125 - 126 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.29 (m, 4H), 6.95 - 6.83 (m, 4H), 6.68 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0, 6.0 Hz, 1H), 4.67 (dd, J = 6.0, 1.6 Hz, 2H), 3.82 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 156.5, 143.5, 132.6, 129.3, 127.8, 126.2, 122.5, 114.2, 113.9, 68.9, 55.3, 34.1, 31.5 ppm; ν_{max}(KBr)/cm^{-1} 3546, 2956, 1723, 1610, 1511, 1246, 1011, 833; HRMS-ESI (m/z): calcd for $C_{20}H_{24}O_2Na$, $[M+Na]^+$: 319.1669, found 319.1662.

(*E*)-1-(*tert*-Butyl)-4-((3-(4-(trifluoromethyl)phenyl)allyl)oxy)benzene (5f): Yield: 66% (22.1 mg) as yellow solid; mp = 77 - 78 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 16.0 Hz, 1H), 6.51 (dt, J = 16.0, 5.6 Hz, 1H), 4.70 (dd, J = 6.0, 1.6 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 143.8, 140.0, 130.9, 127.6, 126.7, 126.3, 125.5 (dd, J = 7.5, 3.7 Hz), 114.2, 68.2, 34.1, 31.5 ppm; ν_{max}(KBr)/cm^{-1} 2959, 1608, 1511, 1328, 1235, 1167, 1115, 837; HRMS-ESI (m/z): calcd for $C_{20}H_{21}F_3ONa$, [M+Na]+: 357.1437, found 357.1441.

(*E*)-1-(3-(4-(*tert*-Butyl)phenoxy)prop-1-en-1-yl)-3,5-dimethylbenzene (5g): Yield: 90% (26.5 mg) as yellow oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 2H), 7.03 (s, 2H), 6.92 - 6.86 (m, 3H), 6.65 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 16.0, 6.0 Hz, 1H), 4.66 (dd, J = 6.0, 1.6 Hz, 2H), 2.30 (s, 6H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 143.5, 137.9, 132.9, 129.6, 126.2, 124.5, 124.4, 114.2, 68.8, 34.1, 31.5, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 3606, 2958, 1724, 1615, 1510, 1245, 1138, 826; HRMS-ESI (m/z): calcd for $C_{21}H_{26}ONa$, $[M+Na]^+$: 317.1876, found 317.1872.

(*E*)-2-(3-(4-(*tert*-Butyl)phenoxy)prop-1-en-1-yl)naphthalene (5h): Yield: 79% (25.0 mg) as yellow solid; mp = 83 - 84 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 - 8.01 (m, 1H), 7.87 - 7.81 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 7.2 Hz, 1H), 7.46 (m, 4H), 7.33 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.43 (dt, J = 16.0, 5.6 Hz, 1H), 4.79 (d, J = 5.6 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 143.6, 134.3, 133.6, 131.1, 129.9, 128.5, 128.1, 127.9, 126.3, 126.1, 125.8, 125.6, 124.0, 123.8, 114.4, 68.8, 34.1, 31.5 ppm; ν_{max}(KBr)/cm^{-1} 3542, 3049, 2956, 1510, 1240, 1182, 1015, 781; HRMS-ESI (m/z): calcd for $C_{23}H_{24}ONa$, $[M+Na]^+$: 339.1719, found 339.1721.

1-(*tert*-Butyl)-4-((2-phenylallyl)oxy)benzene (5i): Yield: 62% (16.5 mg) as yellow oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.2 Hz, 2H), 7.39 - 7.30 (m, 6H), 6.92 (d, J = 8.8 Hz, 2H), 5.62 (s, 1H), 5.48 (s, 1H), 4.89 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 143.7, 143.2, 138.4, 128.4, 127.9, 126.2, 126.0, 114.8, 114.3, 69.9, 34.1, 31.5 ppm; ν_{max}(KBr)/cm^{-1} 3632, 2956, 1725, 1613, 1509, 1460, 1243, 1023; HRMS-ESI (m/z): calcd for $C_{19}H_{22}ONa$, $[M+Na]^+$: 289.1563, found 289.1567.

(Cinnamyloxy)benzene (5j)[13f]**:** Yield: 91% (19.2 mg) as yellow solid; mp = 66 - 67 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 2H), 7.36 - 7.17 (m, 5H), 6.94 (dd, J = 13.2, 5.6 Hz, 3H), 6.72 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 16.0, 6.0 Hz, 1H), 4.68 (dd, J = 6.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 136.5, 132.9, 129.5, 128.6, 127.9, 126.6, 124.6, 120.9, 114.8, 68.5 ppm; ν$_{max}$(KBr)/cm^{-1} 3057, 2919, 2855, 1587, 1492, 1225, 1008, 744; HRMS-ESI (m/z): calcd for $C_{15}H_{14}ONa$, $[M+Na]^+$: 233.0937, found 233.0935.

1-(Cinnamyloxy)-4-methoxybenzene (5k)[13g]**:** Yield: 75% (18.0 mg) as yellow solid; mp = 86 - 87 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.38 (m, 2H), 7.31 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.28 - 7.20 (m, 1H), 6.94 - 6.86 (m, 2H), 6.86 - 6.81 (m, 2H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.40 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.64 (dd, *J* = 6.0, 1.6 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 152.8, 136.5, 132.8, 128.6, 127.8, 126.5, 124.8, 115.8, 114.7, 69.4, 55.7 ppm; ν$_{max}$(KBr)/cm^{-1} 3473, 2918, 2855, 1507, 1451, 1234, 1028, 826; HRMS-ESI (m/z): calcd for $C_{16}H_{16}O_2Na$, $[M+Na]^+$: 263.1043, found 263.1045.

1-(Cinnamyloxy)-4-phenoxybenzene (5l): Yield: 69% (20.8 mg) as yellow solid; mp = 103 - 104 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 - 7.45 (m, 2H), 7.42 - 7.28 (m, 5H), 7.13 - 7.08 (m, 1H), 7.07 - 6.98 (m, 6H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.48 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.74 (dd, *J* = 6.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 154.9, 150.4, 136.4, 133.0, 129.6, 128.6, 127.9, 126.6, 124.5, 122.5, 120.7, 117.7, 115.8, 69.1 ppm; ν$_{max}$(KBr)/cm^{-1} 3447, 2922, 1723, 1600, 1240, 964, 748, 692; HRMS-ESI (m/z): calcd for $C_{21}H_{18}O_2Na$, $[M+Na]^+$: 325.1199, found 325.1197.

1-Chloro-4-(cinnamyloxy)benzene (5m): Yield: 90% (21.9 mg) as yellow solid; mp = 95 - 96 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.36 (m, 2H), 7.31 (dd, *J* = 8.0, 6.8 Hz, 2H), 7.27 - 7.19 (m, 3H), 6.91 - 6.81 (m, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.64 (dd, *J* = 6.0, 1.6 Hz, 2H); 13C NMR (100 MHz, $CDCl_3$) δ 157.2, 136.3, 133.2, 129.3, 128.6, 127.9, 126.6, 125.7, 123.9, 116.1, 68.9 ppm; ν$_{max}$(KBr)/cm^{-1} 3456, 2914, 1594, 1491, 1240, 1011, 964, 830;

1-(Cinnamyloxy)-4-(trifluoromethyl)benzene (5n)[13f]**:** Yield: 61% (17.0 mg) as yellow solid; mp = 78 - 79 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, J = 8.8 Hz, 2H), 7.41 - 7.38 (m, 2H), 7.32 (dd, J = 10.4, 4.8 Hz, 2H), 7.28 - 7.22 (m, 1H), 6.99 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 16.0, 6.0 Hz, 1H), 4.71 (dd, J = 6.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.1, 136.2, 133.6, 128.6, 128.1, 126.9 (q, J = 3.7 Hz), 126.6, 123.6, 114.8, 68.8 ppm; ν_{max}(KBr)/cm^{-1} 2925, 1612, 1330, 1252, 1162, 1110, 970, 836;

2-(Cinnamyloxy)-1,1'-biphenyl (5o): Yield: 71% (20.3 mg) as yellow solid; mp = 67 - 68 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.36 -7.27 (m, 7H), 7.22 (t, J = 6.8 Hz, 1H), 7.08 - 6.99 (m, 2H), 6.63 (d, J = 16.0 Hz, 1H), 6.31 (dt, J = 16.0, 6.0 Hz, 1H), 4.69 (dd, J = 6.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.5, 138.5, 136.6, 131.9, 131.3, 130.9, 129.6, 128.6, 128.5, 127.9, 127.7, 126.9, 126.5, 124.6, 121.3, 113.2, 69.1 ppm; ν_{max}(KBr)/cm^{-1} 3852, 3471, 2922, 1639, 1481, 1258, 989, 747; HRMS-ESI (m/z): calcd for $C_{21}H_{18}ONa$, [M+Na]$^+$: 309.1250, found 309.1248.

2-(Cinnamyloxy)-4-isopropyl-1-methylbenzene (5p): Yield: 82% (21.8 mg) as yellow solid; mp = 83 - 84 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 2.8 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.74 (dd, J = 10.4, 5.2 Hz, 3H), 6.43 (dt, J = 16.0, 5.6 Hz, 1H), 4.70 (d, J = 5.6 Hz, 2H), 2.86 (dt, J = 13.6, 6.8 Hz, 1H), 2.23 (s, 3H), 1.23 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.7, 147.9, 136.7, 132.3, 130.5, 128.6, 127.8, 126.5, 125.2, 124.4, 118.3, 110.1, 68.7, 34.1, 24.1, 15.9 ppm; ν_{max}(KBr)/cm^{-1} 3472, 2960, 1725, 1620, 1456, 1252, 1132, 750; HRMS-ESI (m/z): calcd for $C_{19}H_{22}ONa$, [M+Na]$^+$: 289.1563, found 289.1565.

1-(Cinnamyloxy)-3,5-dimethylbenzene (5q): Yield: 91% (21.7 mg) as yellow solid; mp = 69 - 70 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.38 (m, 2H), 7.35 - 7.29 (m, 2H), 7.24 (tt, *J* = 6.8, 1.2 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 6.8 Hz, 3H), 6.41 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.66 (dd, *J* = 6.0, 1.6 Hz, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 139.2, 136.6, 132.7, 128.6, 127.8, 126.6, 124.8, 122.7, 112.6, 68.5, 21.4 ppm; ν_{max}(KBr)/cm^{-1} 3032, 2920, 2859, 1597, 1491, 1319, 1167, 747; HRMS-ESI (m/z): calcd for $C_{17}H_{18}ONa$, $[M+Na]^+$: 261.1250, found 261.1257.

5-(Cinnamyloxy)benzo[d][1,3]dioxole (5r): Yield: 72% (18.3 mg) as yellow oil; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.73 - 6.67 (m, 2H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.43 - 6.33 (m, 2H), 5.90 (s, 2H), 4.61 (dd, *J* = 6.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 148.3, 141.8, 136.5, 132.9, 128.6, 127.9, 126.6, 124.6, 107.9, 106.2, 101.1, 98.4, 69.7 ppm; ν_{max}(KBr)/cm^{-1} 2913, 1616, 1487, 1380, 1243, 1182, 1032, 743; HRMS-ESI (m/z): calcd for $C_{16}H_{14}O_3Na$, $[M+Na]^+$: 277.0835, found 277.0840.

5-(Cinnamyloxy)-2,3-dihydro-1H-indene (5s): Yield: 80% (20.0 mg) as yellow solid; mp = 90 - 91 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.38 (m, 2H), 7.31 (dd, *J* = 10.0, 4.8 Hz, 2H), 7.24 (dd, *J* = 6.0, 4.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 6.74 (dd, *J* = 16.0, 9.2 Hz, 2H), 6.41 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.66 (dd, *J* = 6.0, 1.6 Hz, 2H), 2.93 - 2.78 (m, 4H), 2.16 - 1.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 145.7, 136.6, 136.4, 132.7, 128.5, 127.8, 126.5, 124.9, 124.7, 112.8, 110.9, 68.9, 33.2, 31.9, 25.8 ppm; ν_{max}(KBr)/cm^{-1} 2927, 1725, 1605, 1457, 1254, 1073, 1024, 749; HRMS-ESI (m/z): calcd for $C_{18}H_{18}ONa$, $[M+Na]^+$: 273.1250, found 273.1248.

6-(Cinnamyloxy)-1,2,3,4-tetrahydronaphthalene (5t): Yield: 83% (21.9 mg) as yellow solid; mp = 93 - 94 °C; hexanes/ethyl acetate =100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H), 7.25 (t, J = 4.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.75 - 6.64 (m, 3H), 6.41 (dt, J = 16.0, 6.0 Hz, 1H), 4.66 (dd, J = 5.6, 1.6 Hz, 2H), 2.72 (d, J = 16.0 Hz, 4H), 1.83 - 1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 138.2, 136.6, 132.7, 129.9, 129.6, 128.5, 127.8, 126.6, 124.9, 114.8, 112.6, 68.7, 29.7, 28.6, 23.4, 23.2 ppm; ν_{max}(KBr)/cm^{-1} 3562, 2923, 2854, 1609, 1499, 1252, 964, 749; HRMS-ESI (m/z): calcd for $C_{19}H_{20}ONa$, $[M+Na]^+$: 287.1406, found 287.1409.

Acknowledgments

The authors thank the National Natural Science Foundation of China (21490572, 21502055 and 21420102003), the Fundamental Research Funds for the Central Universities (2015ZY001), the Fundamental Research Funds for the Central Universities (2015ZM150).

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Supporting Information

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

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