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FULL PAPER

Synthesis of 7-Allylated Benzofuran Derivative from *o*-Allyloxyethynylbenzene *via* Claisen Rearrangement and TBAF-Catalyzed Annulation

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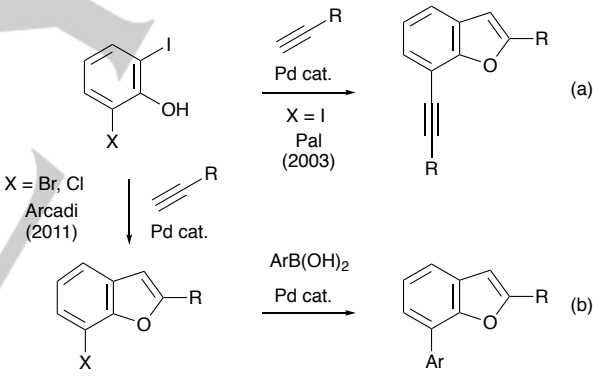
Abstract: We found that 7-allylated benzofuran derivatives *via* a continuous reaction of Claisen rearrangement and annulation using an *o*-allyloxyetynylbenzene derivatives as starting material. In addition, it was observed that annulation of *o*-alkynylphenol proceeded under mild conditions when carried out in the presence of a catalytic amount of TBAF. Furthermore, these continuous reactions could be achieved in a one-pot reaction and afforded not only 7-allylbenzofurans but also 7-alkenylbenzofurans by controlling the reaction temperature and time of the annulation reaction. Finally, we demonstrated that 7- allylbenzofuran and 7-alkenylbenzofuran could be converted to 7-(2-formylvinyl)benzofuran and 7-formylbenzofuran derivatives, respectively. Therefore, various 7-substituted benzofuran derivatives could be synthesized according to this synthetic strategy.

Introduction

The benzofuran core structure is one of the most important structures because various natural products and pharmacologically active compounds include a benzofuran skeleton.[1] In particular, 7-substituted benzofuran derivatives are known to be useful bioactive compounds.[2] For examples, various groups have reported the isolation of the 7-allylated benzofuran derivatives from the morus plants and that some of them have various bioactivities.[3] Moreover, the Arafa group synthesized 7-allylated benzofuran derivatives and found out specific bioactivity such as inhibition of GSK-3β from one of their compounds.[4] Therefore, a synthetic methodology of 7-substituted benzofurans, especially 7-allylated derivatives, is important and highly desired. Although various synthetic methodologies of 7-substituted indole derivatives *via* C-H activation using a directing group on the nitrogen atom have been reported,[5] the synthetic methodology for 7-substituted benzofuran is extremely limited. This is because, unlike a nitrogen atom, an oxygen atom cannot possess a directing group. As a result, there have been only two reports on synthetic methodology of 7-substituted benzofuran derivatives. In 2003, the Pal group reported that Pd-catalyzed tandem reaction *via* Sonogashira coupling of 2,6-diiodophenol with terminal alkynes and annulation of *o*-alkynylphenol afforded the 7-alkynylbenzofuran derivatives (Scheme 1a).[6] In 2011, the Arcadi group also reported that a tandem reaction *via* Sonogashira coupling of 2-bromo-6-iodephenol and annulation afforded 7-bromobenzofuran derivatives. Moreover, they also reported that a Pd-catalyzed coupling reaction of this product with arylboronic acids afforded 7-arylbenzofuran derivatives (Scheme 1b).[7] These synthetic strategies required a halogen atom at the corresponding position of the starting material. Therefore, finding a synthetic methodology of 7-substituted benzofuran remains a challenge.



Scheme 1. Previous reports for the synthesis of 7-substituted benzofuran.

Previously, we reported an effective synthetic methodology of *o*-allyloxyethynylbenzene derivatives *via* a Cu-catalyzed Suzuki-Miyaura coupling reaction of dibromoalkene derivatives.[8] Moreover, we reported transformations of this substrate for access to various heterocyclic compounds such as benzofuran and benzopyran derivatives.[8a,9]

On the other hand, classical Claisen rearrangement under heat conditions or high pressure is known to be a powerful strategy for the transformation of allyloxy compounds to *o*-allylphenol derivatives.[10] Actually, the Schmidt group reported that tandem Claisen rearrangement and annulation under heat conditions afforded heterocyclic compounds such as 6-allylated chromone derivatives.[11] Moreover, the Rizzacasa group applied Claisen

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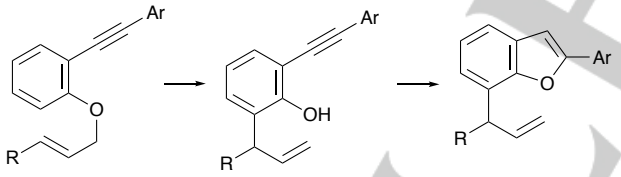
rearrangement at high temperature to synthesize chalcomoracin.[12] As another example of Claisen rearrangement, the Feng group developed Ni-catalyzed Claisen rearrangement.[13] They reported that Ni-catalyzed Claisen rearrangement of allyl vinyl ether derivatives afforded allyl substituted *β*-ketoesters.[13a] Moreover, they also reported that a tandem intermolecular reaction of alkynyl esters with allylic alcohols *via* hydroalkoxylation and Claisen rearrangement promoted by an Ni/Au catalyst system afforded *α*-allyl-*β*-ketoesters.[13b] On the other hand, the Wipf group reported that Claisen rearrangement proceeded without harsh conditions or a transition metal catalyst by utilizing Lewis acid such as an aluminum reagents.[14] After this reaction was reported, some groups have used this rearrangement in the presence of Et_2AlCl to prepare a precursor that could synthesize useful compounds.[15]

Here, we assume that 7-allylated benzofuran derivatives can be synthesized by the continuous reaction of Claisen rearrangement of *o*-allyloxyethynylbenzene derivatives using Lewis acid and annulation of *o*-alkynylphenol (Scheme 2). In this continuous reaction, the annulation of *o*-alkynylphenol is also important. Although various annulations have been reported, all of them required transition metal catalysts[16] or an excessive amount of a strong base such as Cs_2CO_3.[17] On the other hand, the Zhang[18] and Liu groups[19] reported the annulation of *o*-alkynylphenol using a catalytic amount of base such as K_2CO_3 or ^{t}BuOK proceeded. However, these reactions have required harsh conditions such as high reaction temperature. Therefore, it's clear that research on this reaction has been insufficient.



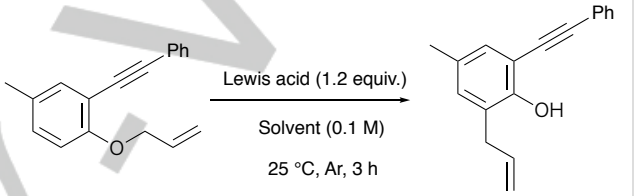
Scheme 2. Synthetic methodology of 7-allylbenzofuran.

Herein, we report that a continuous reaction of Claisen rearrangement of *o*-allyloxyethynylbenzenes using aluminum reagent and annulation in the presence of TBAF afforded the 7-allylated benzofuran derivatives.

Results and Discussion

We initiated the investigation of Claisen rearrangement using *o*-allyloxyethynylbenzene derivatives **1** as starting materials for the synthesis of 2-allyl-6-ethynylphenol derivatives **2** (Table 1). First, we tested three types of aluminum reagents as Lewis acids (Entries 1-3). As a result, we found that the reaction with Et_2AlCl as a Lewis acid in hexane afforded 2-allyl-4-methyl-6-(phenylethynyl)phenol (**2a**) in 87% yield at room temperature (Entry 1). Other aluminum reagents, such as those of trimethylaluminum reagent and tribromoaluminum reagent were not at all effective for this rearrangement at all (Entries 2 and 3). Moreover, no reaction proceeded in the presence of $BF_3{\cdot}Et_2O$ (Entry 4). Next, we investigated the effect of the solvents (Entries 5-9). We found the reaction in toluene also proceeded and delivered product **2a** in 59% yield (Entry 5). The reaction in dichloromethane produced the corresponding product **2a** in lower yield (Entry 6). Other polar solvents such as DMF, THF, DMSO and CH_3CN were not effective for this rearrangement (Entries 7-10).

Table 1. Optimization of conditions for Claisen rearrangement of **1a**.[a]

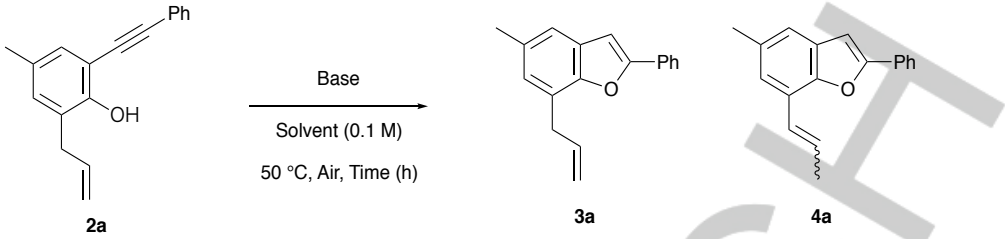


1a **2a**

Entry	Lewis acid	Solvent	Yield of **2a** (%)[b]
1	**Et_2AlCl**	**Hexane**	**87**
2	Me_3Al	Hexane	Trace
3	$AlBr_3$	Hexane	Not detected
4	$BF_3{\cdot}OEt_2$	Hexane	Not detected
5	Et_2AlCl	Toluene	59
6	Et_2AlCl	CH_2Cl_2	39
7	Et_2AlCl	DMF	No reaction
8	Et_2AlCl	THF	No reaction
9	Et_2AlCl	CH_3CN	No reaction
10	Et_2AlCl	DMSO	No reaction

[a] Reaction conditions: **1a** (0.20 mmol), Lewis acid (1.2 equiv.), solvent (2.0 mL), at 25 °C for 3 h under Ar. [b] Isolated yield.

Table 2. Optimization of reaction conditions for annulation of **2a**.[a]



2a **3a** **4a**

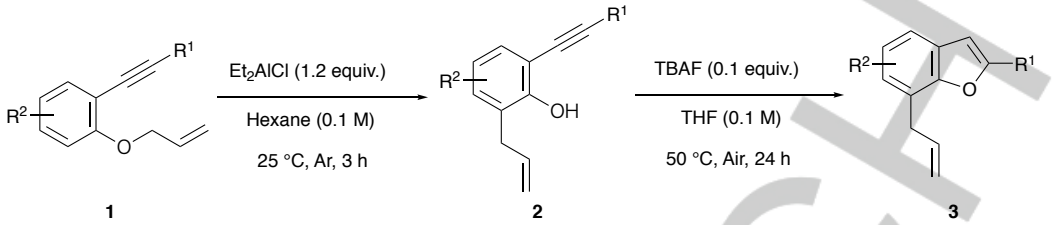
Entry	Base (equiv.)	Solvent	Time (h)	Combined yield of **3a** & **4a** (%)[b]	Ratio (**3a : 4a**)[c]
1	Cs_2CO_3 (1.0)	THF	16	25	>20 : 1
2	K_2CO_3 (1.0)	THF	16	Trace	-
3	*t*BuOK (1.0)	THF	16	9	>20 : 1
4	TBAF (1.0)	THF	16	93	>20 : 1
5	TBAC (1.0)	THF	16	No reaction	-
6	TBAB (1.0)	THF	16	No reaction	-
7	**TBAF (0.1)**	**THF**	**24**	**93**	**>20 : 1**
8	TBAF (0.1)	CH_2Cl_2	24	No reaction	-
9	TBAF (0.1)	Toluene	24	70	>20 : 1
10	TBAF (0.1)	Hexane	24	87	5.1 : 1 (*E*/*Z* =13.2)
11[d]	TBAF (0.1)	Hexane	48	88	1.1 : 1 (*E*/*Z* = 13.2)
12[d]	**TBAF (2.0)**	**Hexane**	**48**	**91**	**1 : >20 (*E*/*Z* = 13.3)**

[a] Reaction conditions: **2a** (0.1 mmol), base, solvent (1.0 mL) at 50 °C under Air. [b] Combined yield of **3a** and **4a** after purification. [c] Ratio was determined by ^{1}H NMR analysis. [d] This reaction was carried out at 80 °C.

Next, we explored the reaction conditions for the annulation of 2-allyl-4-methyl-6-(phenylethynyl)phenol (**2a**) (Table 2). Following previous reports, we tried various bases such as Cs_2CO_3,[17] K_2CO_3[18] and ^{t}BuOK[19] for annulation. However, these bases were not effective for this reaction at 50 °C (Entries 1-3). Then, we tried using tetrabutylammonium halides as bases (Entries 4-6). The reaction in the presence of TBAF proceeded and afforded 7-allyl-2-phenyl-5-methylbenzofuran (**3a**) in 93% yield (Entry 4). On the other hand, no desired product was obtained in the case of the reaction using TBAC or TBAB as a base (Entries 5 and 6). Moreover, we found that this annulation was completed with a catalytic amount of TBAF and afforded the corresponding product **2a** in the same yield as in the case of using 1.0 equiv. of TBAF (Entry 7). Next, we investigated the effect of the solvent (Entries 8-10). As a result, we found that dichloromethane was not effective for this annulation (Entry 8). On the other hand, the reaction in toluene proceeded and afforded the a nulation 7-allylbenzofuran **3a** and 7-alkenylbenzofuran **4a**, which were derived from the isomerization of the allyl moiety on **3a**, was obtained in the case of using hexane (Entry 10). From this result, fluoride anion in a non-polar solvent could abstract not only the proton from the hydroxyl group but also from the allyl group to cause isomerization of the allyl moiety to the internal alkene moiety. Then, we tried to raise the reaction temperature to 70 °C and extend the time to 48 hours to promote isomerization of **3a** (Entry 11). As a result, the remaining allylbenzofuran **3a** was still observed, although the ratio of isomer **4a** increased. Then, we increased the amount of TBAF to 2.0 equiv. and obtained 7-alkenylbenzofuran derivative **4a** selectively in 91% yield (Entry 12). At this stage, we determined that THF is the optimal solvent for the preparation of 7-allylbenzofuran **3a**, and the hexane is suitable for the preparation of 7-alkenylbenzofuran **4a**.

Under optimized reaction conditions for each reaction (Table 1, Entry 1 and Table 2, Entry 4), we investigated the scope and limitations of this continuous reaction for 7-allylbenzofuran derivatives **3** by using various *o*-allyloxyethynylbenzene derivatives **1** (Table 3). When we tried using substrates **1b** and **1c** bearing a *p*- or *m*-tolylethynyl group, the continuous reactions also proceeded and the corresponding 7-allylbenzofuran derivatives **3b** and **3c** were obtained in good yields (Entries 2 and 3). On the other hand, the annulation of **2d** bearing an *o*-tolylethynyl group afforded the product **3d** in slightly lower yield (Entry 4). The yield of **2e** bearing a methoxy group was relatively lower, since an oxygen atom of the methoxy group disturbed the coordination of the aluminum reagent to the oxygen atom of the allyloxy moiety (Entry 5). Substrates **3f** and **3g** bearing a halogen atom such as chloro and bromo groups were tolerated in this continuous reaction (Entries 6 and 7). Claisen rearrangement of **1h** afforded **2h** in relatively lower yield because **1h** possesses a methoxy group. On the other hand, annulation proceeded smoothly and gave the 7-allylbenzofuran **3h** in good yield (Entry 8). In the case of using chloro-substituted benzene derivative **1i**,

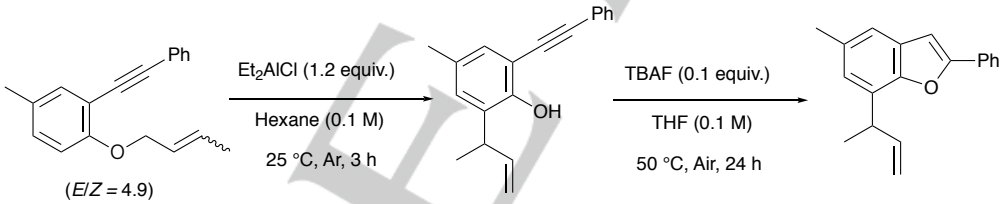
Table 3. Scope and limitation.



1 **2** **3**

Entry	R^1	R^2 (**1**)	Yield of **2** (%)[a]	Yield of **3** (%)[a]
1	Ph	4-Me (**1a**)	87 (**2a**)	93 (**3a**)
2	*p*-MeC_6H_4	4-Me (**1b**)	81 (**2b**)	90 (**3b**)
3	*m*-MeC_6H_4	4-Me (**1c**)	86 (**2c**)	89 (**3c**)
4	*o*-MeC_6H_4	4-Me (**1d**)	88 (**2d**)	78 (**3d**)
5	*p*-$MeOC_6H_4$	4-Me (**1e**)	66 (**2e**)	84 (**3e**)
6	*p*-ClC_6H_4	4-Me (**1f**)	90 (**2f**)	97 (**3f**)
7	*p*-BrC_6H_4	4-Me (**1g**)	88 (**2g**)	93 (**3g**)
8	Ph	4-OMe (**1h**)	74 (**2h**)	96 (**3h**)
9[b]	Ph	4-Cl (**1i**)	81 (**2i**)	89 (**3i**)
10	Ph	H (**1j**)	66 (**2j**) + 17 (**2j'**)	91 (**3j**)
11	Ph	5-OMe (**1k**)	26 (**2k**) + 32 (**2k'**)	95 (**3k**)

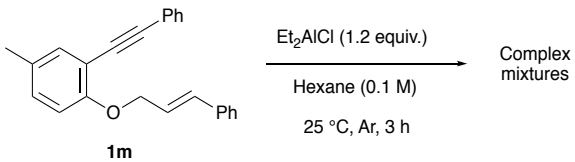
[a] Isolated yields. [b] Reaction time of annulation was shortened to 12 h.



1l **2l** : 32% **3l** : 95%

Scheme 3. Synthesis of 7-allylbenzofuran derivative **3l** from *o*-crotyloxyethynylbenzene **1l**.

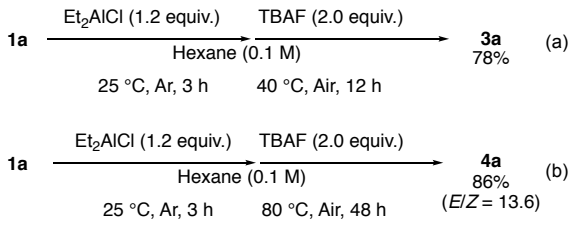
both reactions proceeded smoothly (Entry 9). Claisen rearrangement of **1j** and **1k**, bearing no substituent at the *p*-position of the allyloxy group, delivered not only *o*-allylphenols **2j** and **2k** but also *p*-allylphenols such as 4-allyl-2-(phenylethynyl)phenol (**2j'**) and 4-allyl-5-methoxy-2-(phenylethynyl)phenol (**2k'**) as side products, respectively (Entries 10 and 11). Then, we performed Claisen rearrangement of **1k** at 10 °C to suppress the side product **2k'**. However, this reaction afforded **2k** in only 20% yield along with 25% yield of **2k'**. From this result, we concluded that the selectivity of the product was not related to the reaction temperature. Then, we conducted annulations of both **2j** and **2k**. As a result, we could obtain benzofurans **3j** and **3k** in excellent yields. Furthermore, we tested crotyloxy compound **1l** (Scheme 3). Claisen rearrangement of **1l** also afforded *o*-allylphenol product **2l** bearing a branch-type allyl group in 32% yield. Because some other unidentified compounds derived from decomposition were also produced in this reaction, the yield of allylated product **2l** was reduced. The following annulation of **2l** proceeded smoothly and produced the benzofuran **3l** possessing a branch-type of allyl moiety in excellent yield. Moreover, we attempted to use a cinnamyloxy compound **1m** (Scheme 4). Although starting material **1m** was consumed completely in this reaction, unidentified complex mixtures were produced instead of the target allylated product.



1m

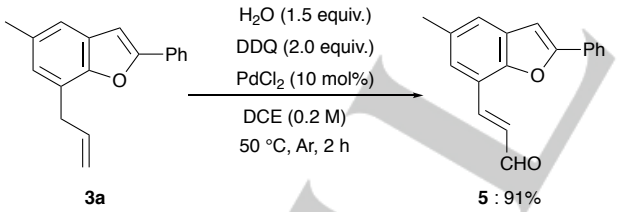
Scheme 4. Claisen rearrangement of *o*-cinnamyloxyethynylbenzene **1m**.

On the other hand, we also tried a one-pot reaction of this continuous reaction. As a first attempt, a catalytic amount (0.1 equiv.) of TBAF was added to the reaction mixture of Claisen rearrangement. As a result, this one-pot reaction afforded only phenol product **2a** because a catalytic amount of TBAF could not cleave the O-Al bond derived from the Claisen rearrangement. Then, we increased the amount of TBAF to 2 equiv. From this one-pot reaction, we could obtain 7-allylbenzofuran **3a** in 78% yield (Scheme 5a). Moreover, 7-alkenylbenzofuran **4a** was obtained in good yield *via* the same one-pot reaction by raising reaction temperature and extending reaction time of annulation using TBAF (Scheme 5b). These results indicated that both 7-allylbenzofuran **3** and 7-alkenylbenzofuran **4** could be synthesized *via* a one-pot reaction by control of the reaction temperature and the time in annulation.



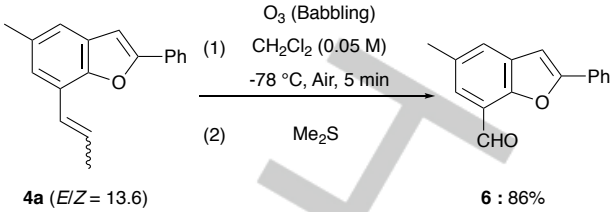
Scheme 5. One-pot reaction of **1a**.

Finally, we demonstrated the transformations of products **3a** and **4a** to 7-substituted benzofuran derivatives bearing a formyl group. As for **3a**, we conducted Pd-catalyzed allylic C-H oxygenation of **3a** according to the report of the Jiang group[20] and succeeded in transforming it to 7-(2-formylvinyl)benzofuran derivative **5** in good yield (Scheme 6).



Scheme 6. Pd-catalyzed allylic C-H oxygenation of **3a** for the preparation of 7-(2-formylvinyl)benzofuran **5**.

Moreover, we carried out the oxidative cleavage of 7-alkenylbenzofuran derivative **4a**. As a result, we succeeded in converting it to 7-formylbenzofuran derivative **6** in good yield *via* ozonolysis (Scheme 7). Since the formyl group could be transformed to various substituents, this synthetic methodology could potentially lead to various 7-substituted benzofuran derivatives.



Scheme 7. Ozonolysis of **4a** for the preparation of 7-formylbenzofuran **6**.

Conclusions

In summary, we found that 7-allylated benzofuran derivatives **3** could be provided by a continuous reaction of Claisen rearrangement using Et_2AlCl and annulation in the presence of a catalytic amount of TBAF from *o*-allyloxyethynylbenzene derivative **1**. We also demonstrated that 7-alkenylbenzofuran derivative **4** could be obtained by conducting annulation under heating conditions. Moreover, these continuous reactions could be achieved in a one-pot reaction and afford the corresponding 7-allylbenzofurans **3** and 7-alkenylbenzofurans **4** selectively through control of the reaction temperature and time in annulation. Furthermore, we demonstrated that 7-allylbenzofuran **3a** and 7-alkenylbenzofuran **4a** were converted to benzofuran derivatives bearing a formyl group. Therefore, various 7-substituted benzofuran derivatives could be synthesized by following to this synthetic method.

Experimental Section

General information: Melting points were measured with an As ONE micro melting point instrument. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX-300 NMR (300 MHz) and Bruker AVANCE III-400M (400 MHz). Chemical shifts are given in ppm downfield from TMS with chloroform as an internal standard. MS (EI) spectra were recorded with a Shimadzu GCMS-QP2010 Plus mass spectrometer. The stream of ozone was generated by the ozone generator named as an OZONE WAVE PRO SOW-10000R. Unless otherwise noted, all reagents were used without further purification.

Procedure for the preparation of starting material 1: *o*-Allyloxyethynylbenzenes **1a**, **1h-1k** and 1m were prepared according to our previous reported literature.[8a] For the preparation of **1b-1g** and **1l**, 1-allyloxy-2-(bromoethynyl)-4-methylbenzene,[8a] *N*,*N*'-(1,2-ethanediylidene)bis-1-pyrrolidinamine glyoxal[21] and bis(*N*-methyl-*N*-phenylhydrazone)[21] were prepared according to our previous reported literature.

1-Allyloxy-4-methyl-2-((*p*-tolyl)ethynyl)benzene (1b): 1-Allyloxy-2-(bromoethynyl)-4-methylbenze (0.5017 g, 2.0 mmol), *p*-tolylboronic acid (0.6078 g, 4.0 mmol), K_3PO_4 (0.8491 g, 4.0 mmol), CuI (19.04 mg, 0.10 mmol) and glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (26.65 mg, 0.10 mmol) in

i-PrOH (8 mL) at 50 °C under an Ar atmosphere was stirred. After 24 h, 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 (v/v = 40/1)) to afford **1b** in 82% yield (0.4321 g, 1.65 mmol) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (ddd, *J* = 8.4, 2.2, 0.7 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.09 (ddt, *J* = 17.2, 10.6 ,4.9 Hz, 1H), 5.53 (ddd, *J* = 17.2, 3.4 ,1.5 Hz, 1H), 5.29 (ddd, *J* = 10.6, 3.4, 1.8 Hz, 1H), 4.61 (ddd, *J* = 4.9, 1.8 ,1.5 Hz, 2H), 2.36 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.9, 138.1, 133.7, 133.2, 131.4, 130.0, 129.9, 129.0, 120.6, 117.0, 112.9, 112.6, 93.4, 85.2, 69.4, 21.5, 20.3 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H [M + H]$^+$ 263.1430, found 263.1431.

1-Allyloxy-4-methyl-2-((*m*-tolyl)ethynyl)benzene (1c): 1-Allyloxy-2-(bromoethynyl)-4-methylbenzene (0.5019 g, 2.0 mmol), *m*-tolylboronic acid (0.4080 g, 3.0 mmol), K_3PO_4 (0.8488 g, 4.0 mmol), CuI (19.10 mg, 0.10 mmol) and glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (26.62 mg, 0.10 mmol) in *i*-PrOH (8 mL) at 50 °C under an Ar atmosphere was stirred. After 24 h, 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 (v/v = 40/1)) to afford **1c** in 68% yield (0.3556 g, 1.36 mmol) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.33 (m, 2H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.05 (ddd, *J* = 8.4, 2.2, 0.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.09 (ddt, *J* = 17.2, 10.6, 4.9 Hz, 1H), 5.52 (ddd, *J* = 17.2, 3.4, 1.8 Hz, 1H), 5.29 (ddd, *J* = 10.6, 3.4, 1.5 Hz, 1H), 4.61 (ddd, *J* = 4.9, 1.8, 1.5 Hz, 2H), 2.34 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 137.8, 133.8, 133.2, 132.1, 130.03, 130.02, 128.9, 128.6, 128.1, 123.5, 117.0, 112.9, 112.7, 93.4, 85.6, 69.5, 21.2, 20.3 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H [M + H]$^+$ 263.1430, found 263.1431.

1-Allyloxy-4-methyl-2-((*o*-tolyl)ethynyl)benzene (1d): 1-Allyloxy-2-(bromoethynyl)-4-methylbenzene (0.5022 g, 2.0 mmol), *m*-tolylboronic acid (0.5439 g, 4.0 mmol), K_3PO_4 (0.8489 g, 4.0 mmol), CuI (19.05 mg, 0.10 mmol) and glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (26.58 mg, 0.10 mmol) in *i*-PrOH (8 mL) at 50 °C under an Ar atmosphere was stirred. After 24 h, 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 (v/v = 50/1)) to afford **1d** in 79% yield (0.4120 g, 1.57 mmol) as a colorless oil; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.48 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.25-7.23 (m, 2H), 7.21-7.14 (m, 1H), 7.05 (ddd, *J* = 8.4, 2.4, 0.7 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.11 (ddt, *J* = 17.4, 10.4, 5.1 Hz, 1H), 5.48 (ddd, *J* = 17.4, 3.3, 1.8 Hz, 1H), 5.29 (ddd, *J* = 10.4, 3.3, 1.5 Hz, 1H), 4.60 (ddd, *J* = 5.1, 1.8, 1.5 Hz, 2H), 2.52 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 157.8, 141.1, 134.3, 134.2, 132.3, 130.97, 130.94, 130.2, 128.9, 126.3, 124.2, 117.9, 113.6, 113.2, 92.8, 90.8, 70.3, 21.4, 20.8 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H [M + H]$^+$ 263.1430, found 263.1430.

1-Allyloxy-2-((4-methoxyphenyl)ethynyl)-4-methylbenzene (1e): 1-Allyloxy-2-(bromoethynyl)-4-methylbenzene (0.5022 g, 2.0 mmol,), 4-methoxyphenylboronic acid (0.6082 g, 4.0 mmol), K_3PO_4 (0.8488 g, 4.0 mmol), CuI (19.08 mg, 0.10 mmol) and glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (26.68 mg, 0.10 mmol) in *i*-PrOH (8 mL) at 50 °C under an Ar atmosphere was stirred. After 24 h, 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/toluene (v/v = 1/1)) to afford **1e** in 62% yield (0.3446 g, 1.24 mmol) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.30 (d, *J* = 2.2 Hz, 1H), 7.05 (ddd, *J* = 8.4, 2.2, 0.7 Hz, 1H), 6.87 (dt, *J* = 8.4, 2.2 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.10 (ddt, *J* = 17.2, 10.6, 4.9 Hz, 1H), 5.52 (ddd, *J* = 17.2, 3.4, 1.8 Hz, 1H), 5.29 (ddd, *J* = 10.6, 3.4, 1.5 Hz, 1H), 4.61 (ddd, *J* = 4.9, 1.8, 1.5 Hz, 2H), 3.83 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 156.9, 133.6, 133.3, 133.0, 130.1, 129.8, 117.0, 115.9, 113.9, 113.2, 112.7, 93.2, 84.6, 69.6, 55.3, 20.3 ppm; EI-MS *m/z* (rel intensity) 278 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O_2$+H [M + H]$^+$ 279.1380, found 279.1378.

1-Allyloxy-2-((4-chlorophenyl)ethynyl)-4-methylbenzene (1f): 1-Allyloxy-2-(bromoethynyl)-4-methylbenzene (0.5018 g, 2.0 mmol), 4-chlorophenylboronic acid (0.6260 g, 4.0 mmol), K_3PO_4 (0.8486 g, 4.0 mmol), CuI (0.10 mmol, 19.02 mg) and glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (0.10 mmol, 26.58 mg) in *i*-PrOH (8 mL) at 50 °C under an Ar atmosphere was stirred. After 24 h, 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/toluene (v/v = 4/1)) to afford **1f** in 80% yield (0.4514 g, 1.60 mmol) as a white solid; mp 70-71 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dt, *J* = 8.6, 2.2 Hz, 2H), 7.33-7.29 (m, 3H), 7.08 (ddd, *J* = 8.4, 2.2, 0.7 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.09 (ddt, *J* = 17.2, 10.6, 4.9 Hz, 1H), 5.52 (ddd, *J* = 17.2, 3.3, 1.8 Hz, 1H), 5.30 (ddd, *J* = 10.6, 3.3, 1.5 Hz, 1H), 4.61 (ddd, *J* = 4.9, 1.8, 1.5 Hz, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 157.4, 134.3, 134.1, 133.6, 133.1, 130.8, 130.5, 129.0, 122.7, 117.5, 113.0, 112.9, 92.4, 87.4, 69.9, 20.7 ppm; EI-MS *m/z* (rel intensity) 282 (M^+, 100); HRMS (APCI-Orbitrap) *m/z* calcd for $C_{18}H_{15}OCl$ $[M]^+$ 282.0806, found 282.0802.

1-Allyloxy-2-((4-bromophenyl)ethynyl)-4-methylbenzene (1g): 1-Allyloxy-2-(bromoethynyl)-4-methylbenzene (0.5021 g, 2.0 mmol), 4-bromophenylboronic acid (0.8035 g, 4.0 mmol), K_3PO_4 (0.8486 g, 4.0 mmol), CuI (19.05 mg, 0.10 mmol) and glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (26.67 mg, 0.10 mmol) in *i*-PrOH (8 mL) at 50 °C under an Ar atmosphere was stirred. After 24 h, 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 (v/v = 40/1)) to afford **1g** in 85% yield (0.5560 g, 1.70 mmol) as a white solid; mp 69-70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dt, *J* = 8.6, 2.2 Hz, 2H), 7.39 (dt, *J* = 8.6, 2.2 Hz, 2H), 7.30 (d, *J* = 2.2 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.09 (ddt, *J* = 17.2, 10.6, 4.9 Hz, 1H), 5.52 (ddd, *J* = 17.2, 3.2, 1.8 Hz, 1H), 5.30 (ddd, *J* = 10.6, 3.2, 1.5 Hz, 1H), 4.61 (ddd, *J* = 4.9, 1.8, 1.5 Hz, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.9, 133.7, 133.1, 132.9, 131.5, 130.4, 130.0, 122.6, 122.1, 117.1, 112.4, 112.3, 92.1, 87.1, 69.3, 20.3 ppm; EI-MS *m/z* (rel intensity) 326 (M^+, 100); HRMS (APCI-Orbitrap) *m/z* calcd for $C_{18}H_{15}OBr$ $[M]^+$ 326.0301, found 326.0296.

1-Crotyloxy-4-methyl-2-(phenylethynyl)benzene (1l): This compound was synthesized in three steps. First step: 5-Methylsalicylaldehyde (1.2254 g, 9.0 mmol,) and K_2CO_3 (1.8657 g, 13.5 mmol) were added into DMF (13.5 mL) in a reaction container. The mixture was stirred at room temperature. After 10 minutes, crotylchloride (1.31 mL, 13.5 mmol) were added into the reaction mixture gradually. The mixture was stirred at 50 °C. After 18 h, the reaction was quenched with distilled water and ethyl acetate. The solution was extracted with ethyl acetate, washed with saturated NaCl *aq*., dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate (v/v = 20/1)) to afford 2-crotyloxy-5-methylbenzaldehyde (*E*/*Z* = 4.7) in 98% yield (1.6731 g, 8.79 mmol) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.48 (s, 0.82H: *E*-isomer), 10.47 (s, 0.18H: *Z*-isomer), 7.63 (d, *J* = 2.2 Hz, 1H: *E*- and *Z*-isomer), 7.33 (dd, *J* = 8.5, 2.3 Hz, 0.18H: *Z*-isomer), 7.32 (dd, *J* = 8.6, 2.3 Hz, 0.82H: *E*-isomer), 6.89 (d, *J* = 8.5 Hz, 0.18H: *Z*-isomer), 6.88 (d, *J* = 8.6 Hz, 0.82H: *E*-isomer), 5.94-5.67 (m, 2H: *E*- and *Z*-isomer), 4.69 (d, *J* = 6.0 Hz, 0.36H: *Z*-isomer), 4.56 (dt, *J* = 6.0, 1.2 Hz, 1.64H: *E*-isomer), 2.30 (s, 3H: *E*- and *Z*-isomer), 1.77 (dq, *J* = 6.0, 1.2 Hz, 2.46H: *E*-isomer), 1.73 (dq, *J* = 6.0, 1.2 Hz, 0.54H: *Z*-isomer) ppm: ^{13}C NMR ($CDCl_3$): δ = 190.0 (*E*- and *Z*-isomer), 159.2 (*E*- and *Z*-isomer), 136.4 (*E*- and *Z*-isomer), 130.7 (*E*-isomer), 130.07 (*Z*-isomer), 130.02 (*E*-isomer), 129.1 (*Z*-isomer), 128.3 (*E*- and *Z*-isomer), 125.4 (*E*-isomer), 125.0 (*Z*-isomer), 124.77 (*Z*-isomer), 124.73 (*E*-isomer), 113.0 (*E*-isomer), 112.9 (*Z*-isomer), 69.3 (*E*-isomer), 64.4 (*Z*-isomer), 20.2 (*E*- and *Z*-isomer), 17.8 (*E*-isomer), 13.4 (*Z*-isomer) ppm; EI-MS *m/z* (rel intensity): 190 (M^+, 4); HRMS (APCI-Orbitrap) *m/z* calcd for $C_{12}H_{14}O_2$+H $[M + H]^+$ 191.1067, found 191.1066. Second step: 2-Crotyloxy-5-methylbenzaldehyde (*E*/*Z* = 4.7) (1.6174 g, 8.5 mmol) and CBr_4 (5.6376 g, 17.0 mmol) were added into CH_2Cl_2 (57 mL) in a reaction container. The mixture was stirred at 0 °C under Ar atmosphere. After 10 minutes, PPh_3 (8.9183 g, 34.0 mmol) was added into the reaction mixture gradually and the mixture was stirred at room temperature. After 24 h, hexane was added into reaction mixture. The mixture was stirred at room temperature. After 10 minutes, the mixture was filtered using celite and silica to remove Ph_3P=O, concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford 2-crotyloxy-1-(2,2-dibromovinyl)-4-methylbenzene (*E*/*Z* = 4.9) in 87% yield (2.5586 g, 7.39 mmol) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (s, 1H: *E*- and *Z*-isomer), 7.50 (s, 1H: *E*- and *Z*-isomer), 7.07 (d, *J* = 7.7 Hz, 1H: *E*- and *Z*-isomer), 6.76 (d, *J* = 8.2 Hz, 0.17H: *Z*-isomer), 6.75 (d, *J* = 8.4 Hz, 0.83H: *E*-isomer), 5.86-5.65 (m, 2H: *E*- and *Z*-isomer), 4.58 (d, *J* = 4.9 Hz, 0.34H: *Z*-isomer), 4.43 (d, *J* = 5.7 Hz, 1.66H: *E*-isomer), 2.29 (s, 3H: *E*- and *Z*-isomer), 1.76-1.71 (m, 3H: *E*- and *Z*-isomer) ppm; ^{13}C NMR ($CDCl_3$): δ = 153.7 (*E*- and *Z*-isomer), 133.0 (*E*- and *Z*-isomer), 130.16 (*E*- and *Z*-isomer), 130.10 (*E*-isomer), 129.5 (*E*- and *Z*-isomer), 129.4 (*E*- and *Z*-isomer), 128.3 (*Z*-isomer), 126.0 (*E*-isomer), 125.7 (*Z*-isomer), 124.51 (*E*-isomer), 124.45 (*Z*-isomer), 112.1 (*E*-isomer), 112.0 (*Z*-isomer), 89.3 (*E*- and *Z*-isomer), 69.4 (*E*-isomer), 64.5 (*Z*-isomer), 20.6 (*E*- and *Z*-isomer), 17.9 (*E*-isomer), 13.4 (*Z*-isomer) ppm; EI-MS *m/z* (rel intensity): 344 (M^+, 16); HRMS (APCI-Orbitrap) *m/z* calcd for $C_{13}H_{14}O_2Br_2O$+H $[M + H]^+$ 344.9484, found 344.9480. Third step: 2-Crotyloxy-1-(2,2-dibromovinyl)-4-methylbenzene (*E*/*Z* = 4.9) (1.0382 g, 3.0 mmol), phenylboronic (0.7312 g, 6.0 mmol), K_3PO_4 (2.5476 g, 12.0 mmol), CuI (57.0 mg, 0.30 mmol) and glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (58.5 mg, 0.30 mmol) in EtOH (12 mL) at 60 °C under an Ar atmosphere was stirred. After 24 h, 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/toluene (v/v = 4/1)) to afford 1-crotyloxy-4-methyl-2-(phenylethynyl)benzene (**1l**) (*E*/*Z* = 4.9) in 76% yield (0.5640 g, 2.27 mmol) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.52 (m, 2H: *E*- and *Z*-isomer), 7.36-7.30 (m, 4H: *E*- and *Z*-isomer), 6.80 (d, *J* = 8.4 Hz, 0.17H: *Z*-isomer), 6.79 (d, *J* = 8.4 Hz, 0.83H: *E*-isomer), 5.96-5.71 (m, 2H: *E*- and *Z*-isomer), 4.68 (d, *J* = 4.6 Hz,

0.34H: *Z*-isomer), 4.53 (dt, *J* = 5.1, 1.3 Hz, 1.66H: *E*-isomer), 2.27 (s, 3H: *E*- and *Z*-isomer), 1.76-1.73 (m, 3H: *E*- and *Z*-isomer) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2 (*E*- and *Z*-isomer), 133.8 (*E*- and *Z*-isomer), 131.5 (*E*- and *Z*-isomer), 130.1 (*E*- and *Z*-isomer), 129.97 (*Z*-isomer), 129.90 (*E*- and *Z*-isomer), 129.6 (*E*-isomer), 128.2 (*E*- and *Z*-isomer), 128.1 (*Z*-isomer), 127.9 (*E*-isomer), 126.1 (*E*-isomer), 125.9 (*Z*-isomer), 123.8 (*E*- and *Z*-isomer), 112.89 (*E*- and *Z*-isomer), 112.84 (*E*- and *Z*-isomer), 93.1 (*E*- and *Z*-isomer), 86.1 (*E*- and *Z*-isomer), 69.7(*E*-isomer), 60.1 (*Z*-isomer), 20.3 (*E*- and *Z*-isomer), 17.8 (*E*-isomer), 13.5 (*Z*-isomer) ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 57); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 163.1430.

General procedure for Claisen rearrangement: *o*-Allyloxyethynylbenzene **1** (0.20 mmol) was dissolved in hexane (2.0 mL, 0.1 M) under an Ar atmosphere. Et_2AlCl (0.24 mmol) in hexane (0.23 mL, 1.05 M) was added slowly to reaction solution with stirring at room temperature. The reaction mixture was stirred at 25 °C. After 3 h, the reaction was quenched with 2 M HCl *aq*. The solution was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to afford the *o*-allylphenol product **2**.

2-Allyl-4-methyl-6-(phenylethynyl)phenol (2a) (Table 1, Entry 1): Following the general procedure using 1-allyloxy-4-methyl-2-(phenylethynyl)benzene (**1a**) (49.5 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2a** (43.0 mg, 0.173 mmol) in 87% yield as yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.50 (m, 2H), 7.38-7.34 (m, 3H), 7.12 (d, *J* = 1.6 Hz, 1H), 6.94 (d, *J* = 1.6 Hz, 1H), 6.02 (ddt, *J* = 16.7, 10.4, 6.6 Hz, 1H), 5.80 (s, 1H), 5.14-5.06 (m, 2H), 3.40 (d, *J* = 6.6 Hz, 2H), 2.26 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 136.4, 131.9, 131.5, 129.7, 129.4, 128.6, 128.5, 125.6, 122.5, 115.7, 109.0, 95.8, 83.6, 34.3, 20.4 ppm; EI-MS *m/z* (rel intensity): 248 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O$+H $[M + H]^+$ 249.1274, found 249.1273.

2-Allyl-4-methyl-6-((*p*-tolyl)ethynyl)phenol (2b) (Table 3, Entry 2): Following the general procedure using 1-allyloxy-4-methyl-2-((*p*-tolyl)ethynyl)benzene (**1b**) (52.0 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2b** (41.9 mg, 0.160 mmol) in 81% yield as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 1.8 Hz, 1 H), 6.92 (d, *J* = 1.8 Hz, 1H), 6.01 (ddt, *J* = 16.7, 10.4, 6.6 Hz, 1H), 5.80 (s, 1H), 5.13-5.06 (m, 2H), 3.39 (d, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1, 138.9, 136.4, 131.7, 131.4, 129.6, 129.3, 129.2, 125.4, 119.4, 115.6, 109.1, 96.0, 82.9, 34.3, 21.5, 20.4 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1429.

2-Allyl-4-methyl-6-((*m*-tolyl)ethynyl)phenol (2c) (Table 3, Entry 3): Following the general procedure using 1-allyloxy-4-methyl-2-((*m*-tolyl)ethynyl)benzene (**1c**) (52.2 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v =40/1)) to afford the desired compound **2c** (44.7 mg, 0.170 mmol) in 86% yield as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 1.5 Hz, 1H), 6.93 (d, *J* = 1.5 Hz, 1H), 6.01 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.79 (s, 1H), 5.13-5.06 (m, 2H), 3.40 (d, *J* = 6.6 Hz, 2H), 2.36 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 138.2, 136.4, 132.1, 131.8, 129.63, 129.55, 129.3, 128.6, 128.4, 125.6, 122.3, 115.7, 109.1, 96.1, 83.3, 34.3, 21.2, 20.4 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1429.

2-Allyl-4-methyl-6-((*o*-tolyl)ethynyl)phenol (2d) (Table 3, Entry 4): Following the general procedure using 1-allyloxy-4-methyl-2-((*o*-tolyl)ethynyl)benzene (**1d**) (52.7 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2d** (46.2 mg, 0.176 mmol) in 88% yield as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.5 Hz, 1H), 7.29-7.17 (m, 3H), 7.14 (d, *J* = 1.5 Hz, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.03 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.80 (s, 1H), 5.16-5.08 (m, 2H), 3.42 (d, *J* = 6.6 Hz, 2H), 2.53 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1, 139.8, 136.4, 131.83, 131.81, 129.6 (2C), 129.4, 128.7, 125.7, 125.6, 122.4, 115.7, 109.3, 94.8, 87.5, 34.3, 21.0, 20.4 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1429.

2-Allyl-6-((4-methoxyphenyl)ethynyl)-4-methylphenol (2e) (Table 3, Entry 5): Following the general procedure using 1-allyloxy-2-((4-methoxyphenyl)ethynyl)-4-methylbenzene (**1e**) (55.4 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2e** (36.6 mg, 0.131 mmol) in 66% yield as a white solid; mp 66-67 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dt, *J* = 9.0, 2.2 Hz, 2H), 7.10 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 1.8 Hz, 1H), 6.89 (dt, *J* = 9.0, 2.2 Hz, 2H), 6.01 (ddt, *J* = 16.8, 10.4, 6.6 Hz, 1H), 5.79 (s, 1H), 5.13-5.06 (m, 2H), 3.83 (s, 3H), 3.39 (d, *J* = 6.6 Hz, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 152.1, 136.5, 133.0, 131.5, 129.5, 129.3, 125.4, 115.6, 114.6, 114.1, 109.3, 95.9, 82.2, 55.3, 34.3, 20.4 ppm; EI-MS *m/z* (rel intensity) 278 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O_2$+H $[M + H]^+$ 279.1380, found 279.1379.

2-Allyl-6-((4-chlorophenyl)ethynyl)-4-methylphenol (2f) (Table 3, Entry 6): Following the general procedure using

1-allyloxy-2-((4-chlorophenyl)ethynyl)-4-methylbenzene (**1f**) (56.9 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2f** (51.2 mg, 0.181 mmol) in 90% yield as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (dt, *J* = 8.6, 2.1 Hz, 2H), 7.34 (dt, *J* = 8.6, 2.1 Hz, 2H), 7.10 (d, *J* = 1.8 Hz, 1H), 6.95 (d, *J* = 1.8 Hz, 1H), 6.01 (ddt, *J* = 17.1, 10.8, 6.6 Hz, 1H), 5.71 (s, 1H), 5.06-5.13 (m, 2H), 3.39 (d, *J* = 6.6 Hz, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.3, 136.4, 134.7, 132.7, 132.1, 129.7, 129.5, 128.8, 125.7, 121.0, 115.8, 108.7, 94.6, 84.7, 34.3, 20.4 ppm; EI-MS *m/z* (rel intensity) 282 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{15}OCl$+H [M + H]$^+$ 283.0884, found 283.0879.

2-Allyl-6-((4-bromophenyl)ethynyl)-4-methylphenol (2g) (Table 3, Entry 7): Following the general procedure using 1-allyloxy-2-((4-bromophenyl)ethynyl)-4-methylbenzene (**1g**) (65.2 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2g** (57.4 mg, 0.175 mmol) in 88% yield as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.37 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.10 (d, *J* = 1.8 Hz, 1H), 6.95 (d, *J* = 1.8 Hz, 1H), 6.01 (ddt, *J* = 17.6, 9.3, 6.6 Hz, 1H), 5.72 (s, 1H), 5.06-5.13 (m, 2H), 3.39 (d, *J* = 6.6 Hz, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 136.3, 132.9, 132.1, 131.7, 129.7, 129.5, 125.6, 122.9, 121.4, 115.8, 108.6, 94.6, 84.8, 34.3, 20.4 ppm; EI-MS *m/z* (rel intensity) 326 (M^+, 99); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}OBr$+H [M + H]$^+$ 327.0379, found 327.0380.

2-Allyl-4-methoxy-6-(phenylethynyl)phenol (2h) (Table 3, Entry 8): Following the general procedure using 1-allyloxy-4-methoxy-2-(phenylethynyl)benzene (**1h**) (53.2 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2h** (39.3 mg, 0.149 mmol) in 74% yield as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.50 (m, 2H), 7.39-7.35 (m, 3H), 6.82 (d, *J* = 3.1 Hz, 1H), 6.74 (d, *J* = 3.1 Hz, 1H), 6.00 (ddt, *J* = 17.0, 9.4, 6.6 Hz, 1H), 5.63 (s, 1H), 5.14-5.08 (m, 2H), 3.76 (s, 3H), 3.40 (d, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.7, 148.8, 136.0, 131.5, 128.8, 128.5, 127.1, 122.3, 118.3, 116.1, 112.9, 109.2, 96.0, 83.6, 55.7, 34.5 ppm; EI-MS *m/z* (rel intensity) 264 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O_2$+H [M + H]$^+$ 265.1223, found 265.1222.

2-Allyl-4-chloro-6-(phenylethynyl)phenol (2i) (Table 3, Entry 9): Following the general procedure using 1-allyloxy-4-chloro-2-(phenylethynyl)benzene (**1i**) (53.7 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2i** (43.4 mg, 0.161 mmol) in 81% yield as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 2H), 7.41-7.36 (m, 3H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J* = 2.4, 0.4 Hz, 1H), 5.98 (ddt, *J* = 17.6, 9.5, 6.6 Hz, 1H), 5.91 (d, *J* = 0.4 Hz, 1H), 5.15-5.08 (m, 2H), 3.40 (d, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 135.4, 131.6, 130.7, 129.1, 128.8, 128.6, 127.8, 124.8, 121.9, 116.6, 110.7, 97.1, 82.1, 34.1 ppm; EI-MS *m/z* (rel intensity) 268 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{17}H_{13}OCl$+H [M + H]$^+$ 269.0728, found 269.0732.

2-Allyl-6-(phenylethynyl)phenol (2j) + 4-Allyl-2-(phenylethynyl)phenol (2j') (Table 3, Entry 10): Following the general procedure using 1-allyloxy-2-(phenylethynyl)benzene (**1j**) (47.1 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2j** (31.0 mg, 0.132 mmol) in 66% yield along with side product **2j'** (8.0 mg, 0.034 mmol) in 17% yield. 2-Allyl-6-(phenylethynyl)phenol (**2j**); Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.51 (m, 2H), 7.40-7.35 (m, 3H), 7.31 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.12 (ddd, *J* = 7.5, 1.6, 0.7 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.02 (ddt, *J* = 17.6, 9.5, 6.6 Hz, 1H), 5.95 (d, *J* = 0.4 Hz, 1H), 5.14-5.07 (m, 2H), 3.44 (d, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3, 136.3, 131.5, 131.0, 129.6, 128.8, 128.5, 125.9, 122.4, 120.2, 115.8, 109.3, 96.2, 83.3, 34.3 ppm; EI-MS *m/z* (rel intensity) 234 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{17}H_{14}O$+H [M + H]$^+$ 235.1117, found 235.1117. 4-Allyl-2-(phenylethynyl)phenol (**2j'**); Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 2H) , 7.39-7.35 (m, 3H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.95 (ddt, *J* = 17.4, 9.5, 6.6 Hz, 1H), 5.72 (br, 1H), 5.11-5.04 (m, 2H), 3.32 (d, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.9, 137.4, 131.9, 131.6, 131.4, 130.9, 128.8, 128.5, 122.4, 115.9, 114.7, 109.4, 96.2, 83.2, 39.1 ppm; EI-MS *m/z* (rel intensity) 234 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{17}H_{14}O$+H [M + H]$^+$ 235.1117, found 235.1117.

2-Allyl-3-methoxy-6-(phenylethynyl)phenol (2k) + 4-Allyl-5-methoxy-2-(phenylethynyl)phenol (2k') (Table 3, Entry 11): Following the general procedure using 1-allyloxy-5-methoxy-2-(phenylethynyl)benzene (**1k**) (53.1 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2k** (13.9 mg, 0.053 mmol) in 26% yield along with side product **2k'** (17.1 mg, 0.065 mmol) in 32% yield. 2-Allyl-3-methoxy-6-(phenylethynyl)phenol (**2k**); Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52-7.47 (m, 2H), 7.36-7.31 (m, 3H), 7.29 (d, *J* = 8.6 Hz, 1H), 6.47 (d, *J* = 8.6 Hz, 1H), 5.98 (ddt, *J* = 17.2, 9.9, 6.2 Hz, 1H), 5.94 (s, 1H), 5.03 (ddd, *J* = 17.2, 3.5, 1.5 Hz, 1H), 4.99 (ddd, *J* = 9.9, 3.5, 1.3 Hz, 1H), 3.82 (s, 3H), 3.45 (dt, *J* = 6.2, 1.5 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 155.2, 136.1, 131.4, 129.9, 128.4, 128.4, 122.7, 114.5, 114.0, 103.2, 102.4, 95.1, 83.6, 55.8, 27.4 ppm; EI-MS *m/z* (rel intensity) 264 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O_2$+H [M + H]$^+$ 265.1223, found 265.1223. 4-Allyl-5-methoxy-2-(phenylethynyl)phenol (**2k'**); Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53-7.50 (m, 2H), 7.39-7.34

(m, 3H), 7.17 (s, 1H), 6.52 (s, 1H), 5.97 (ddt, *J* = 17.6, 9.5, 6.6 Hz, 1H), 5.78 (s, 1H), 5.08-5.02 (m, 2H), 3.82 (s, 3H), 3.29 (d, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 156.6, 136.8, 132.0, 131.4, 128.42, 128.37, 122.8, 121.1, 115.5, 100.7, 97.6, 95.1, 83.3, 55.5, 33.3 ppm; EI-MS *m/z* (rel intensity) 264 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O_2$+H $[M + H]^+$ 265.1223, found 265.1223.

2-(But-3-en-1-yl)-4-methyl-6-(phenylethynyl)phenol (2l) (Scheme 3): Following the general procedure using 1-crotyloxy-4-methyl-2-(phenylethynyl)benzene (**1l**) (52.5 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **2l** (16.7 mg, 0.064 mmol) in 32% yield as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.50 (m, 2H), 7.38-7.34 (m, 3H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.07 (ddd, *J* = 17.2, 10.4, 6.2 Hz, 1H), 5.82 (br, 1H), 5.14-5.06 (m, 2H), 3.91-3.82 (m, 1H), 2.26 (s, 3H), 1.35 (d, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.7, 142.2, 131.5, 130.9, 129.5, 129.38, 129.41, 128.6, 128.5, 122.5, 113.3, 109.1, 95.8, 83.7, 36.4, 20.5, 19.1 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1428.

Procedure for Claisen rearrangement of 1m (Scheme 4): 1-Cinnamyloxy-2-ethynylbenzene (**1m**) (62.5 mg, 0.20 mmol) was dissolved in hexane (2.0 mL, 0.1 M) under an Ar atmosphere. Et_2AlCl (0.24 mmol) in hexane (0.23 mL, 1.05 M) was added slowly to reaction solution with stirring at room temperature. The reaction mixture was stirred at 25 °C. After 3 h, the reaction was quenched with 2 M HCl *aq*. The solution was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was pathed through the silica gel chromatography and separated some fractions. However, these fractions included some decomposed compounds that were unidentified by NMR analysis.

General procedure for TBAF-catalyzed annulation of 2: *o*-Allylphenol derivative **2** (0.10 mmol) was dissolved in THF (1.0 mL, 0.1 M). TBAF (0.01 mmol) in THF (10 µL, 1.0 M) was added to reaction solution with stirring at room temperature. The reaction mixture was stirred at 50 °C. After 24 h, the reaction was quenched with distilled water. The solution was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to afford the 7-allylbenzofuran product **3**.

7-Allyl-5-methyl-2-phenybenzofuran (3a) (Table 2, Entry 7): Following the general procedure using 2-allyl-4-methyl-6-(phenylethynyl)phenol (**2a**) (24.7mg), the residue was purified by flash chromatography on silica gel (hexane) to afford the desired compound **3a** (23.0 mg, 0.093 mmol) in 93% yield as a white solid; mp 57-58 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86-7.82 (m, 2H), 7.46-7.41 (m, 2H), 7.36-7.30 (m, 1H), 7.22 (s, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 6.12 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1H), 5.22 (ddd, *J* = 17.0, 3.2, 1.5 Hz, 1H), 5.12 (ddd, *J* = 10.0, 3.2, 1.3 Hz, 1H), 3.69 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 151.8, 136.1, 132.5, 130.7, 129.1, 128.7, 128.3, 125.6, 124.8, 123.0, 118.7, 116.1, 101.3, 34.1, 21.3 ppm; EI-MS *m/z* (rel intensity) 248 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O$+H $[M + H]^+$ 249.1274, found 249.1274.

7-Allyl-5-methyl-2-(*p*-tolyl)benzofuran (3b) (Table 3, Entry 2): Following the general procedure using 2-allyl-4-methyl -6-((*p*-tolyl)ethynyl)phenol (**2b**) (26.3 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 250/1)) to afford the desired compound **3b** (23.6 mg, 0.090 mmol) in 90% yield as a white solid; mp 76-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.25-7.20 (m, 3H), 6.90 (s, 1H), 6.88 (s, 1H), 6.12 (ddt, *J* = 17.0, 9.9, 6.8 Hz, 1H), 5.21 (ddd, *J* = 17.0, 3.2, 1.5 Hz, 1H), 5.12 (ddd, *J* = 9.9, 3.2, 1.3 Hz, 1H), 3.69 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.9, 151.6, 138.3, 136.1, 132.4, 129.4, 129.2, 128.0, 125.3, 124.7, 122.9, 118.6, 116.1, 100.5, 34.0, 21.39, 21.35 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1423.

7-Allyl-5-methyl-2-((*m*-tolyl)ethynyl)benzofuran (3c) (Table 3, Entry 3): Following the general procedure using 2-allyl-4-methyl-6-((*o*-tolyl)ethynyl)phenol (**2c**) (26.6 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 250/1)) to afford the desired compound **3c** (23.7 mg, 0.090 mmol) in 90% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.3 Hz, 2H), 7.32 (dd, *J* = 7.7, 7.3 Hz, 1H), 7.21 (s, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.92 (s, 1H), 6.91 (s, 1H), 6.13 (ddt, *J* = 17.0, 10.1 and 6.7 Hz, 1H), 5.22 (ddd, *J* = 17.0, 3.1, 1.5 Hz, 1H), 5.13 (ddd, *J* = 10.1, 3.1, 1.3 Hz, 1H), 3.70 (d, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 151.7, 138.3, 136.1, 132.4, 130.6, 129.2, 129.1, 128.6, 125.5, 125.3, 123.0, 122.0, 118.6, 116.1, 101.2, 34.0, 21.5, 21.3 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1426.

7-Allyl-5-methyl-2-((*o*-tolyl)ethynyl)benzofuran (3d) (Table 3, Entry 4): Following the general procedure using 2-allyl-4-methyl-6-((*o*-tolyl)ethynyl)phenol (**2d**) (26.0 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v =250/1)) to afford the desired compound **3d** (20.3 mg, 0.078 mmol) in 78% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84-7.80 (m, 1H), 7.30-7.23 (m, 4H), 6.93 (s, 1H), 6.82 (s, 1H), 6.13 (ddt, *J* = 17.0, 9.9, 6.7 Hz, 1H), 5.20 (ddd, *J* = 17.0, 3.2, 1.5 Hz, 1H), 5.11 (ddd, *J* = 9.9, 3.2, 1.1 Hz, 1H), 3.68 (d, *J* = 6.7 Hz, 2H), 2.58 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 151.3, 136.1, 135.7, 132.4, 131.2, 130.1,

129.0, 128.3, 128.0, 126.0, 125.5, 123.0, 118.7, 116.1, 105.0, 34.2, 22.0, 21.4 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1430.

7-Allyl-5-methyl-2-(4-methoxyethynyl)benzofuran (3e) (Table 3, Entry 5): Following the general procedure using 2-allyl-6-((4-methoxyphenyl)ethynyl)-4-methylphenol (**2e**) (26.0 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 20/1)) to afford the desired compound **3e** (23.7 mg, 0.084 mmol) in 84% yield as a white solid; mp 93-94 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (dt, *J* = 8.8, 2.7 Hz, 2H), 7.19 (s, 1H), 6.96 (dt, *J* = 8.8, 2.7 Hz, 2H), 6.88 (s, 1H), 6.80 (s, 1H), 6.12 (ddt, *J* = 17.0, 9.9, 6.8 Hz, 1H), 5.21 (ddd, *J* = 17.0, 3.1, 1.6 Hz, 1H), 5.12 (ddd, *J* = 9.9, 3.1, 1.2 Hz, 1H), 3.68 (d, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 155.8, 151.5, 136.2, 132.4, 129.3, 126.2, 125.1, 123.6, 122.8, 118.4, 116.0, 114.2, 99.7, 55.3, 34.0, 21.3 ppm; EI-MS *m/z* (rel intensity) 278 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O_2$+H $[M + H]^+$ 279.1380, found 279.1379.

7-Allyl-2-(4-chlorophenyl)-5-methylbenzofuran (3f) (Table 3, Entry 6): Following the general procedure using 2-allyl-6-((4-chlorophenyl)ethynyl)-4-methylphenol (**2f**) (28.2 mg), the residue was purified by flash chromatography on silica gel (hexane) to afford the desired compound **3f** (27.4 mg, 0.097 mmol) in 97% yield as a white solid; mp 73-74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (dt, *J* = 8.6, 2.4 Hz, 2H), 7.39 (dt, *J* = 8.6, 2.4 Hz, 2H), 7.20 (s, 1H), 6.91 (s, 2H), 6.11 (ddt, *J* = 17.0, 10.0, 6.6 Hz, 1H), 5.21 (ddd, *J* = 17.0, 3.2, 1.4 Hz, 1H), 5.13 (ddd, *J* = 10.0, 3.2, 1.2 Hz, 1H), 3.68 (d, *J* = 6.6 Hz, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.5, 151.7, 136.0, 134.0, 132.7, 129.2, 128.91, 128.89, 125.93, 125.91, 123.0, 118.8, 116.2, 101.7, 34.0, 21.3 ppm; EI-MS *m/z* (rel intensity) 282 (M^+, 100); HRMS (APPI-Orbitrap) *m/z* calcd for $C_{18}H_{15}OCl$ $[M]^+$ 282.0806, found 282.0793.

7-Allyl-2-(4-bromophenyl)-5-methylbenzofuran (3g) (Table 3, Entry 7): Following the general procedure using 2-allyl-6-((4-bromophenyl)ethynyl)-4-methylphenol (**2g**) (32.3 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 250/1)) to afford the desired compound **3g** (29.9 mg, 0.093 mmol) in 93% yield as a yellow solid; mp 83-84 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (dt, *J* = 8.7, 2.3 Hz, 2H), 7.54 (dt, *J* = 8.7, 2.3 Hz, 2H), 7.20 (s, 1H), 6.92 (s, 2H), 6.10 (ddt, *J* = 17.0, 9.9, 6.8 Hz, 1H), 5.21 (ddd, *J* = 17.0, 3.2, 1.4 Hz, 1H), 5.12 (ddd, *J* = 9.9, 3.2, 1.2 Hz, 1H), 3.67 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.5, 151.8, 136.0, 132.7, 131.8, 129.6, 128.9, 126.2, 126.0, 123.1, 122.2, 118.8, 116.2, 101.8, 34.0, 21.3 ppm; EI-MS *m/z* (rel intensity) 326 (M^+, 100); HRMS (APPI-Orbitrap) *m/z* calcd for $C_{18}H_{15}OBr$ $[M]^+$326.0301, found 326.0290.

7-Allyl-5-methoxy-2-phenybenzofuran (3h) (Table 3, Entry 8): Following the general procedure using 2-allyl-4-methoxy-6-(phenylethynyl)phenol (**2h**) (26.4 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound 3h (25.4 mg, 0.096 mmol) in 96% yield as a cream solid; mp 71-72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85-7.82 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 6.95 (s, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.12 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1H), 5.22 (ddd, *J* = 17.0, 3.2, 1.6 Hz, 1H), 5.14 (ddd, *J* = 10.0, 3.2, 1.4 Hz, 1H), 3.83 (s, 3H), 3.69 (d, *J* = 6.8 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 156.1, 148.4, 135.6, 130.6, 129.3, 128.7, 128.4, 124.7, 124.3, 116.4, 113.1, 101.7, 101.0, 55.8, 34.0 ppm; EI-MS *m/z* (rel intensity) 264 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O_2$+H $[M + H]^+$ 265.1223, found 265.1222.

7-Allyl-5-chloro-2-phenybenzofuran (3i) (Table 3, Entry 9): Following the general procedure (reaction time was 12 h) using 2-allyl-4-chloro-6-(phenylethynyl)phenol (**2i**) (26.7 mg), the residue was purified by flash chromatography on silica gel (hexane) to afford the desired compound **3i** (23.7 mg, 0.089 mmol) in 89% yield as a white solid; mp 63-65 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85-7.82 (m, 2H), 7.48-7.42 (m, 2H), 7.40-7.33 (m, 2H), 7.07 (d, *J* = 2.0 Hz, 1H), 6.94 (s, 1H), 6.08 (ddt, *J* = 17.0, 10.0, 6.7 Hz, 1H), 5.23 (ddd, *J* = 17.0, 3.2, 1.5 Hz, 1H), 5.16 (ddd, *J* = 10.0, 3.2, 1.3 Hz, 1H), 3.69 (d, *J* = 6.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.9, 151.7, 135.1, 130.14, 130.06, 128.9, 128.8, 128.5, 124.97, 124.95, 124.3, 118.4, 116.9, 101.0, 33.8 ppm; EI-MS *m/z* (rel intensity) 268 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{17}H_{13}OCl$+H $[M + H]^+$ 269.0728, found 269.0741.

7-Allyl-2-phenybenzofuran (3j) (Table 3, Entry 10): Following the general procedure using 2-allyl-6-(phenylethynyl)phenol (**2j**) (23.4 mg), the residue was purified by flash chromatography on silica gel (hexane) to afford the desired compound **3j** (21.3 mg, 0.091 mmol) in 91% yield as a cream solid; mp 26-27 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89-7.85 (m, 2H), 7.48-7.42 (m, 3H), 7.35 (tt, *J* = 7.4, 2.2 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.10 (dt, *J* = 7.3, 0.7 Hz, 1H), 7.02 (s, 1H), 6.13 (ddt, *J* = 17.0, 10.1, 6.7 Hz, 1H), 5.25 (ddd, *J* = 17.0, 3.2, 1.5 Hz, 1H), 5.13 (ddd, *J* = 10.1, 3.2, 1.3 Hz, 1H), 3.75 (d, *J* = 6.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 153.3, 136.0, 130.6, 129.0, 128.7, 128.5, 124.9, 124.2, 123.6, 123.1, 118.9, 116.2, 101.5, 34.0 ppm; EI-MS *m/z* (rel intensity) 234 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{17}H_{14}O$+H $[M + H]^+$ 235.1117, found 235.1117.

7-Allyl-6-methoxy-2-phenybenzofuran (3k) (Table 3, Entry 11): Following the general procedure using 2-allyl-3-methoxy-6-(phenylethynyl)phenol (**2k**) (26.8 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 40/1)) to afford the desired compound **3k** (25.4 mg, 0.095 mmol) in 95% yield as a cream

solid; mp 40-41 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84-7.80 (m, 2H), 7.46-7.40 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.31 (tt, *J* = 7.3, 2.0 Hz, 1H), 6.94 (s, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.11 (ddt, *J* = 17.0, 9.9, 6.4 Hz, 1H), 5.15 (ddd, *J* = 17.0, 3.3, 1.5 Hz, 1H), 5.03 (ddd, *J* = 9.9, 3.3, 1.3 Hz, 1H), 3.89 (s, 3H), 3.72 (ddd, *J* = 6.4, 1.5, 1.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.3, 155.1, 154.4, 136.0, 130.8, 128.7, 128.0, 124.5, 122.9, 118.3, 115.0, 112.0, 108.0, 101.2, 56.7, 28.0 ppm; EI-MS *m/z* (rel intensity) 264 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O_2$+H $[M + H]^+$ 265.1223, found 265.1220.

7-(But-3-en-2-yl)-5-methyl-2-phenylbenzofuran (3l) (Scheme 3): Following the general procedure using 2-(but-3-en-2-yl)-4-methyl-6-(phenylethynyl)phenol (**2l**) (26.4 mg), the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (v/v = 100/1)) to afford the desired compound **3l** (25.0 mg, 0.095 mmol) in 95% yield as a brown solid; mp 40-41 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35-7.31 (m, 1H), 7.22 (s, 1H), 6.95 (s, 1H), 6.92 (s, 1H), 6.21 (ddd, *J* = 17.1, 10.1, 6.6 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 4.08-3.98 (m, 1H), 2.42 (s, 3H), 1.53 (d, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 151.2, 142.0, 132.5, 130.8, 129.3, 128.7, 128.6, 128.3, 124.8, 123.6, 118.6, 113.4, 101.2, 38.1, 21.4, 19.7 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{19}H_{18}O$+H $[M + H]^+$ 263.1430, found 263.1430.

Procedure for annulation of 2a for synthesis of 4a

5-Methyl-2-phenyl-7-(prop-1-en-1-yl)benzofuran (4a) (*E*/*Z* = 13.3) (Table 2, Entry 12): 2-Allyl-4-methyl-6-(phenylethynyl)phenol (**2a**) (24.7 mg, 0.10 mmol) was dissolved in Hexane (1.0 mL). TBAF (0.2 mmol) in THF (0.2 mL, 1.0 M) was added to reaction solution with stirring at room temperature. The reaction mixture was stirred at 80 °C. After 48 h, the reaction was quenched with distilled water. The solution was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane) to afford the 5-methyl-2-phenyl-7-(prop-1-ene-1-yl)benzofuran (**4a**) (*E*/*Z* = 13.3) in 91% yield (22.6 mg, 0.091 mmol) as a white solid; mp 52-54 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87-7.83 (m, 2H: *E*-and *Z*-isomer), 7.46-7.41 (m, 2H: *E*-and *Z*-isomer), 7.32 (tt, *J* = 7.4, 1.2 Hz, 1H: *E*- and *Z*-isomer), 7.22 (s, 0.07H: *Z*-isomer), 7.18 (s, 0.93H: *E*-isomer), 7.05 (s, 0.07H: *Z*-isomer), 7.02 (s, 0.93H: *E*-isomer), 6.93 (s, 0.07H: *Z*-isomer), 6.91 (s, 0.93H: *E* isomer), 6.85-6.73 (m, 1H: *E*- and *Z*-isomer), 6.66 (dd, *J* = 15.9, 1.1 Hz, 1H: *E*-and *Z*-isomer), 2.43 (s, 0.21H: *Z*-isomer), 2.40 (s, 2.79H: *E*-isomer), 2.02 (dd, *J* = 6.5, 1.5 Hz, 2.79H: *E*-isomer), 1.94 (dd, *J* = 7.1, 1.8 Hz, 0.21H: *Z*-isomer) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7 (*E*- and *Z*-isomer), 150.5 (*E*- and *Z*-isomer), 132.4 (*E*- and *Z*-isomer), 130.6 (*E*- and *Z*-isomer), 129.6 (*E*- and *Z*-isomer), 129.1 (*E*-isomer), 128.9 (*Z*-isomer), 128.7 (*E*-and *Z*-isomer), 128.3 (*E*- and *Z*-isomer), 126.0 (*E*-isomer), 125.7 (*Z*-isomer), 124.8 (*E*- and *Z*-isomer), 123.9 (*E*-isomer), 123.4 (*Z*-isomer), 121.8 (*E*-isomer), 121.1 (*Z*-isomer), 119.3 (*Z*-isomer), 119.0 (*E*-isomer), 101.1 (*E*- and *Z*-isomer), 21.4 (*Z*-isomer), 21.3 (*E*-isomer), 19.3 (*E*-isomer), 15.4 (*Z*-isomer) ppm; EI-MS *m/z* (rel intensity) 248 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{16}O$+H $[M + H]^+$ 249.1274, found 249.1271.

Procedure for one-pot reaction for synthesis of 3a

7-Allyl-5-methyl-2-phenybenzofuran (3a) (Scheme 5a): 1-Allyloxy-4-methyl-2-(phenylethynyl)benzene (**1a**) (49.7 mg, 0.20 mmol) was dissolved in hexane (2.0 mL) under an Ar atmosphere. Et_2AlCl (0.24 mmol) in hexane (0.23 mL, 1.05 M) was added slowly to reaction solution with stirring at room temperature. The reaction mixture was stirred at 25 °C. After 3 h, TBAF (0.4 mmol) in THF (0.40 mL, 1.0 M) was added to reaction solution with stirring at room temperature under air. The reaction mixture was stirred at 40 °C. After 12 h, the reaction was quenched with 2 M HCl *aq.* The solution was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane) to afford 7-allyl-5-methyl-2-phenylbenzofuran (**3a**) in 79% yield (39.0 mg, 0.157 mmol) as a white solid; mp 57-58 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87-7.82 (m, 2H), 7.46-7.41 (m, 2H), 7.37-7.31 (m, 1H), 7.22 (s, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 6.12 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1H), 5.22 (ddd, *J* = 17.0, 3.2, 1.5 Hz, 1H), 5.13 (ddd, *J* = 10.0, 3.2, 1.3 Hz, 1H), 3.69 (d, *J* = 6.8 Hz, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 152.0, 136.1, 132.5, 130.7, 129.1, 128.8, 128.3, 125.6, 123.0, 118.7, 116.1, 101.4, 34.1, 124.8, 21.3 ppm; EI-MS *m/z* (rel intensity) 248 (M^+, 100).

Procedure for one-pot reaction for synthesis of 4a

5-Methyl-2-phenyl-7-(prop-1-en-1-yl)benzofuran (4a) (*E*/*Z* = 13.6) (Scheme 5b): 1-Allyloxy-4-methyl-2-(phenylethynyl)benzene (**1a**) (49.6 mg, 0.20 mmol) was dissolved in hexane (2.0 mL) under an Ar atmosphere. Et_2AlCl (0.24 mmol) in hexane (0.23 mL, 1.05 M) was added slowly to reaction solution with stirring at room temperature. The reaction mixture was stirred for 3 h at 25 °C. After the reaction, TBAF (0.4 mmol) in THF (0.4 mL, 1.0 M) was added to reaction solution with stirring at room temperature under air. The reaction mixture was stirred at 80 °C. After 48 h, the reaction was quenched with 2 M HCl *aq.* The solution was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane) to afford 5-Methyl-2-phenyl-7-(prop-1-en-1-yl)benzofuran (**4a**) (*E*/*Z* = 13.6) in 86% yield (42.6 mg, 0.171 mmol) as a white solid; mp 52-53 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88-7.84 (m, 2H: *E*-and *Z*-isomer), 7.47-7.41 (m, 2H: *E*-and *Z*-isomer), 7.34 (tt, *J* = 7.4, 1.2 Hz, 1H: *E*- and *Z*-isomer),

7.20 (s, 1H: *E*- and *Z*-isomer), 7.06 (s, 0.07H: *Z*-isomer), 7.03 (s, 0.93H: *E*-isomer), 6.96 (s, 0.07H: *Z*-isomer), 6.94 (s, 0.93H: *E* isomer), 6.84-6.76 (m, 1H: *E*- and *Z*-isomer), 6.67 (dd, *J* = 15.9, 1.3 Hz, 1H: *E*-and *Z*-isomer), 2.45 (s, 0.21H: *Z*-isomer), 2.42 (s, 2.79H: *E*-isomer), 2.02 (dd, *J* = 6.5, 1.5 Hz, 2.79H: *E*-isomer), 1.95 (dd, *J* = 7.1, 1.8 Hz, 0.21H: *Z*-isomer) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7 (*E*- and *Z*-isomer), 150.6 (*E*- and *Z*-isomer), 132.4 (*E*- and *Z*-isomer), 130.6 (*E*- and *Z*-isomer), 129.6 (*E*- and *Z*-isomer), 129.1 (*E*-isomer), 128.9 (*Z*-isomer), 128.7 (*E*-and *Z*-isomer), 128.3 (*E*- and *Z*-isomer), 126.0 (*E*-isomer), 125.7 (*Z*-isomer), 124.8 (*E*- and *Z*-isomer), 123.9 (*E*-isomer), 123.4 (*Z*-isomer), 121.8 (*E*-isomer), 121.2 (*Z*-isomer), 119.3 (*Z*-isomer), 119.0 (*E*-isomer), 101.1 (*E*- and *Z*-isomer), 21.5 (*Z*-isomer), 21.3 (*E*-isomer), 19.3 (*E*-isomer), 15.4 (*Z*-isomer) ppm; EI-MS *m/z* (rel intensity) 248 (M^+, 100).

Procedure for Pd-catalyzed allylic C-H oxygenation of 3a for synthesis of 5 (Scheme 6)

(*E*)-7-(2-Formylvinyl)-5-methyl-2-phenylbenzofuran (5) (Scheme 6): 7-Allyl-5-methyl-2-phenylbenzofuran (**3a**) (49.6 mg, 0.20 mmol), $PdCl_2$ (3.53 mg, 0.02 mmol), DDQ (90.8 mg, 0.4 mmol) and distilled water (5.5 µL, 0.30 mmol) in dichloromethane (1 mL) at 50 °C under an Ar atmosphere were stirred. After 2 h, the reaction was quenched and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/diethyl ether (v/v = 3/1)) to afford **5** in 91% yield (47.8 mg, 0.182 mmol) as a yellow solid; mp 115-117 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.75 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.47-7.43 (m, 2H), 7.40-7.35 (m, 2H), 7.24 (dd, *J* = 16.0, 7.8 Hz, 1H), 7.18 (s, 1H), 6.93 (s, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.3, 156.7, 151.2, 147.8, 132.9, 131.1, 130.3, 129.8, 128.9, 128.8, 127.3, 124.9, 124,1, 118.3, 100.9, 21.1 ppm; EI-MS *m/z* (rel intensity) 262 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{18}H_{14}O_2$+H [M + H]$^+$ 263.1067, found 263.1064.

Procedure for ozonolysis of 4a for synthesis of 6 (Scheme 7)

7-Formyl-5-methyl-2-phenylbenzofuran (6) (Scheme 7): 5-Methyl-2-phenyl-7-(prop-1-en-1-yl)benzofuran (**4a**) (*E*/*Z* = 13.6) (24.5 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (2.0 mL) and cooled to -78 °C. A stream of ozone (O_3) produced by an ozone generator was passed through the solution for 1 minute. The reaction mixture was stirred for 5 min at -78 °C. After 5 min, 10 drops of Me_2S were added to the reaction mixture to quench the reaction. After addition, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/ethyl acetate (v/v = 20/1)) to afford **6** in 86% yield (20.2 mg, 0.086 mmol) as a white solid; mp 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.55 (s, 1H), 7.90 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.63 (s, 1H), 7.61 (s, 1H), 7.47 (dd, *J* = 7.4, 7.2 Hz, 2H), 7.39 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.00 (s, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.5, 157.4, 152.9, 132.8, 131.0, 129.7, 129.0, 128.8, 127.2, 125.6, 125.1, 120.4, 100.5, 21.1 ppm; EI-MS *m/z* (rel intensity) 236 (M^+, 100); HRMS (ESI-Orbitrap) *m/z* calcd for $C_{16}H_{12}O$+H [M + H]$^+$ 237.0910, found 237.0912.

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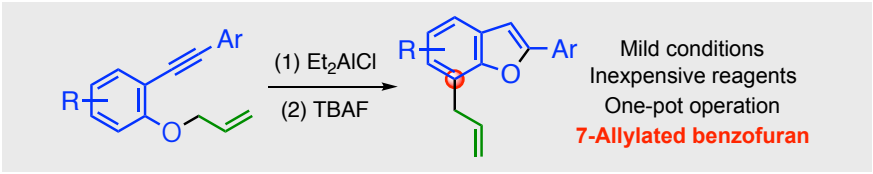

7-Allylated benzofuran derivatives can be synthesized from *o*-allyloxyethynylbenzene derivatives through two step reactions of Claisen rearrangement in the presence of Et_2AlCl and annulation using TBAF. This continuous reaction proceeded under mild conditions by utilizing only inexpensive reagents in one-pot operation.

Oxygen heterocycles

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Synthesis of 7-Allylated Benzofuran Derivative from *o*-Allyloxyethynylbenzene *via* Claisen Rearrangement and TBAF-Catalyzed Annulation