EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201700217

Link to VoR: http://dx.doi.org/10.1002/ejoc.201700217

Supported by
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10.1002/ejoc.201700217

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Synthesis of *o*-Allyloxyethynylbenzene Derivatives *via* Cu-Catalyzed Suzuki-Miyaura-Type Reaction and Their Transformations for Heterocyclic Compounds

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Abstract: We found that a Suzuki-Miyaura-type reaction of *o*-(bromoethynyl)allyloxybenzene with arylboronic acid using a hydrazone-Cu catalyst system proceeded smoothly in *i*-PrOH under mild conditions to afford the corresponding *o*-allyloxyethynylbenzene derivatives in good yields without decomposition of the allyloxy group. We further demonstrate that three types of transformations using transition metal catalysts to *o*-allyloxyethynylbenzene derivatives lead to various respective heterocyclic compounds.

Introduction

The Internal alkyne structure is an important synthetic precursors for various natural products and pharmaceutical products,[1] and various intermolecular annulations of internal alkynes using its unique reactivity have been reported.[2] On the other hand, effective intramolecular annulations of internal alkyne have also been reported.[3] In particular, *o*-allyloxyethynylbenzene has an interesting reactivity that leads to important heterocyclic compounds such as benzofuran and benzopyran. For example, Cacchi's group,[4] Monteiro's group[5], Liang's group[6] and our group[7] reported annulation of *o*-allyloxyethynylbenzene afforded 3-allyl-2-arylbenzofuran by using a palladium (Pd) catalyst. On the other hand, Tanaka's group reported that 3-benzyl-2-vinylbenzofuran was delivered from *o*-allyloxyethynylbenzene by using a rhodium (Rh) catalyst.[8] In addition, Lovely's group reported that a benzopyran derivative could be obtained by Pauson-Khand reaction of *o*-allyloxyethynylbenzene using $Co_2(CO)_3$.[9] As demonstrated by three reports, synthetic methodology of *o*-allyloxyethynylbenzene is very important for the synthesis of various heterocyclic compounds.

Generally, a Sonogashira coupling reaction of aryl halide with terminal alkyne using a Pd/Cu (copper) catalyst system is the first choice for the synthesis of internal alkyne derivatives.[10] However, the Pd element is known as a highly toxic precious metal. Moreover, using a Pd catalyst triggers not only the formation of an internal alkyne structure, but also the decomposition of the allyloxy group *via* construction of a *π*-allyl-palladium complex. Therefore, an alternative protocol for internal alkyne using a cheaper metal catalyst instead of the expensive Pd catalyst was necessary for the preparation of an internal-alkyne-bearing allyloxy group such as *o*-allyloxyethynylbenzene. Recently, common metals such as Cu,[11] nickel (Ni)-,[12] and iron (Fe)-catalyzed[13] Sonogashira type coupling reactions were reported. However, all reactions required harsh conditions except for one example.[11k] Given this situation, protocols for internal alkyne derivatives using a common-metal catalyst remained challenging. On the other hand, Cu-catalyzed Sonogashira type reactions of terminal alkynes with arylboronic acids instead of aryl halides have also been reported.[14] Although some reactions proceeded in relatively mild conditions to afford the corresponding internal alkynes, these reactions required a large amount of amine bases, such as pyridine or lutidine. On another front, Suzuki-Miyaura-type reactions of arylboronic acid with bromoalkynes were reported as another synthetic protocol for internal alkyne derivatives.[15] In this reaction, the Pd catalyst worked well and promoted the reaction under mild conditions.[15c] Furthermore, Wang's group reported a Cu-catalyzed Suzuki-Miyaura-type reaction of bromoalkyne with aryl boronic acid for an internal alkyne derivative.[16] Although this reaction has the potential to become an effective synthetic method for *o*-allyloxyethynylbenzene, it also requires a reflux condition.

We previously demonstrated easily prepared and air-stable hydrazone compounds (**Figure 1**) as effective ligands for Pd-catalyzed C-C bond formations such as the Suzuki-Miyaura,[17] Mizoroki-Heck,[18] and Sonogashira[19] cross-coupling reactions of aryl halides. We also demonstrated that a hydrazone-Cu catalyst system was effective for C-C,[20] C-O,[20] and C-N[21] bond formations.

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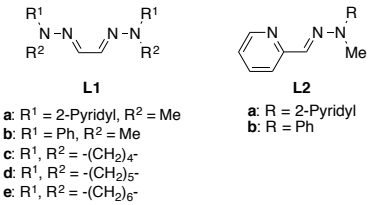
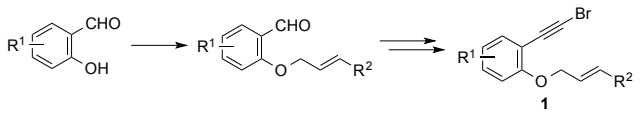


Figure 1. Hydrazone ligands.

Herein, we describe a Cu-catalyzed Suzuki-Miyaura-type reaction of *o*-allyloxy(bromoethynyl)benzene derivatives **1**, which were easily prepared from readily accessible salicylaldehyde through three step reactions[22] (Scheme 1), with arylboronic acid using a hydrazone ligand under a mild condition, that affords the corresponding *o*-allyloxyethynylbenzene derivatives without decomposition of the allyloxy group. Moreover, we demonstrate three types of transformations using transition metal catalysts to *o*-allyloxyethynylbenzene derivatives **3** for access to various heterocyclic compounds.

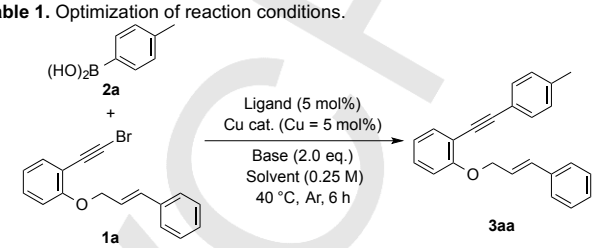


Scheme 1. Preparation of **1**

Results and discussion

Initially, we started to explore the optimizing reaction conditions for the Cu-catalyzed Suzuki-Miyaura-type reaction using *o*-(bromoethynyl)cinnamyloxybenzene (**1a**) and *p*-tolylboronic acid (**2a**) as model substrates (Table 1). Using 5 mol% of CuI and bishydrazone **L1a** as a ligand, we found that the reaction with K_3PO_4 as a base in *i*-PrOH as a solvent gave the corresponding product such as 1-cinnamyloxy-2-(*p*-tolylethynyl) benzene (**3aa**) in a 25% yield with recovery of starting material **1a** (Entry 1). We tested various bishydrazone ligands **L1b-e** (Entries 2-5). Using a phenyl-methyl type bishydrazone ligand **L1b** led to consumption of starting material **1a** completely without decomposition of the allyloxy group and afforded the corresponding product **3aa** in an 88% yield (Entry 2). When we used bishydrazone ligands **L1c-e** bearing 5-7 member rings, the desired product **3aa** was obtained in 73%, 77% and 68% yields, respectively (Entries 3-5). We also tested pyridine-methyl type monohydrazone ligands **L2a** and **L2b** (Entries 6 and 7). While the reaction using the pyridine-methyl type bishydrazone ligand **L2a** afforded a moderate yield of the corresponding product **3aa** (Entry 6), the reaction using **L2b** afforded a good yield of **3aa** (Entry 7). On the other hand, a phosphine ligand such as PPh_3 was not suitable for this reaction when compared with **L1b** (Entry 8). Furthermore, the reaction using 8-quinolinol, which was the effective ligand in Wang's report,[16] also resulted in a slightly lower yield of the desired product than using **L1b** (Entry 9). Next, we investigated the effect of the Cu catalyst (Entries 2 and 10-13) and found that only CuI was effective for this coupling reaction. Various bases were tested (Entries 2 and 14-18). While K_3PO_4 was effective for this reaction (Entry 2), the reaction using Na_3PO_4, which was effective base in the Wang's report,[16] afforded a low

Table 1. Optimization of reaction conditions.

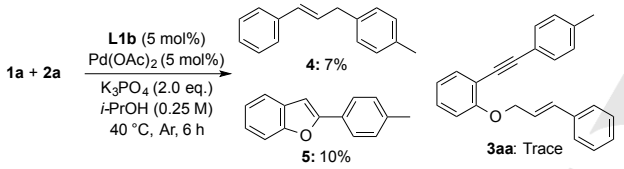


Entry	Ligand	Cu cat.	Base	Solvent	Yield (%)[a]
1	**L1a**	CuI	K_3PO_4	*i*-PrOH	25
2	***L1b***	***CuI***	***K_3PO_4***	***i-PrOH***	***88***
3	**L1c**	CuI	K_3PO_4	*i*-PrOH	73
4	**L1d**	CuI	K_3PO_4	*i*-PrOH	77
5	**L1e**	CuI	K_3PO_4	*i*-PrOH	68
6	**L2a**	CuI	K_3PO_4	*i*-PrOH	46
7	**L2b**	CuI	K_3PO_4	*i*-PrOH	80
8	PPh_3[b]	CuI	K_3PO_4	*i*-PrOH	72
9	8-Quinolinol	CuI	K_3PO_4	*i*-PrOH	82
10	**L1b**	CuBr	K_3PO_4	*i*-PrOH	9
11	**L1b**	$CuBr_2$	K_3PO_4	*i*-PrOH	17
12	**L1b**	Cu_2O	K_3PO_4	*i*-PrOH	N.D.
13	**L1b**	$Cu(OAc)_2$	K_3PO_4	*i*-PrOH	24
14	**L1b**	CuI	Na_3PO_4	*i*-PrOH	5
15	**L1b**	CuI	KOAc	*i*-PrOH	3
16	**L1b**	CuI	KF	*i*-PrOH	6
17	**L1b**	CuI	Cs_2CO_3	*i*-PrOH	8
18	**L1b**	CuI	Et_3N	*i*-PrOH	22
19	**L1b**	CuI	K_3PO_4	MeOH	9
20	**L1b**	CuI	K_3PO_4	EtOH	42
21	**L1b**	CuI	K_3PO_4	*n*-PrOH	81
22	**L1b**	CuI	K_3PO_4	*n*-BuOH	78
23	**L1b**	CuI	K_3PO_4	*i*-BuOH	39
24	**L1b**	CuI	K_3PO_4	THF	22
25	**L1b**	CuI	K_3PO_4	DMF	5
26	**L1b**	CuI	K_3PO_4	MeCN	17
27	**L1b**	CuI	K_3PO_4	Toluene	12
28	**L1b**	CuI	K_3PO_4	*i*-PrOH	83[c]

[a] Isolated yield. [b] 10 mol% of PPh_3 was added. [c] This reaction was carried out at room temperature using 10 mol% of CuI and **L1b** for 24 h.

yield of the corresponding product with recovery of **1a** because the Na_3PO_4 had poor dissolubility in *i*-PrOH and could not supply anion as a base (Entry 14). Other potassium salts such as KOAc and KF were not effective for this reaction (Entries 15 and 16). The reaction in the presence of Cs_2CO_3 afforded an 8% yield of the corresponding product (Entry 17). The reaction using an amine base such as Et_3N led to a low yield (Entry 18). Next, the effects of solvent were investigated (Entries 2 and 19-27). Firstly, we tried to use various protic solvents (Entries 2 and 19-23). The yield of product was improved as the carbon chain of protic solvents became longer until *n*-PrOH (Entries 2 and 19-21). We found EtOH was not suitable for the Cu-catalyzed Suzuki-Miyaura-type reaction under these mild conditions (Entry 20). Moreover, using a branch-type protic solvent such as *i*-PrOH improved the yield of product **3aa** (Entry 2). However, the reaction using *i*-BuOH afforded a low yield of the product (Entry 23). We also tested aprotic solvents (Entries 24-27), which proved ineffective for this reaction. Surprisingly, we found that this reaction proceeded at room temperature, although with a long reaction time, and 10 mol% of CuI and **L1b** were required (Entry 28).

In this stage, we created a reaction using $Pd(OAc)_2$ as a Pd catalyst in stead of CuI (Scheme 2).

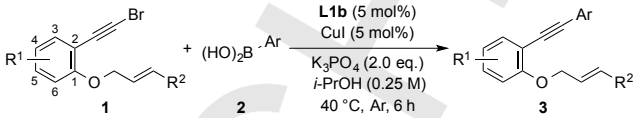


Scheme 2. Pd-catalyzed Suzuki-Miyaura-type reaction.

As we predicted, using a Pd catalyst caused not only a Suzuki-Miyaura reaction to form the target product **3aa**, but also decomposition of **3aa** to form π-allyl-palladium intermediate followed by allylic arylation[23] with *p*-tolylboronic acids **2a** to afford the 1,3-diarylpropene **4**. After decomposition of the allyloxy group, annulation of *o*-ethynylphenoxide[24] occurred to afford 2-arylbenzofuran **5**. Eventually, we could not obtain target product **3aa** and achieved only a trace amount when using the Pd catalyst. As this result shows, using the Cu catalyst was important for the preparation of *o*-allyloxyethynylbenzene derivative.

With the optimized reaction conditions in hand (Table 1, Entry 2), we investigated about scope and limitation of this reaction using various *o*-allyloxy(bromoethynyl)benzenes **1** with arylboronic acids **2** (Table 2). Bromoalkynes **1b-d** having methyl or methoxy groups were also tolerated in this reaction (Entries 2-4). Moreover, the reaction using bromoalkyne **1e** with chloro group also proceeded (Entry 5). In the case of using bromoalkyne **1f**, the coupling product was obtained in moderate yield (Entry 6). Furthermore, we tested using allyloxy compounds **1g-j** instead of cinnamyloxy compounds (Entries 7-11). As a result, allyloxybenzenes **1g-j** also reacted with arylboronic acid **2b** to give the corresponding coupling products. Coupling reactions using various arylboronic acids **2b-e** with **1a** produced high yields of the corresponding coupling products (Entries 12-15). Moreover, alkenylboronic acids **2f** and **2g** were also tolerated in this reaction and afforded corresponding products **3af** and **3ag**, respectively (Entries 16 and 17).

Table 2. Scope of coupling reaction.



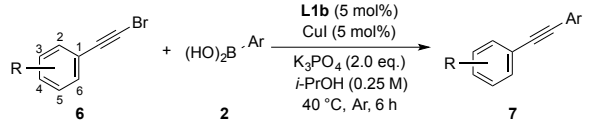
Entry	R^1	R^2 (**1**)	Ar (**2**)	Yield (%)[a] (**3**)
1	H	Ph (**1a**)	4-MeC_6H_4 (**2a**)	88 (**3aa**)
2	4-Me	Ph (**1b**)	Ph (**2b**)	76[b] (**3bb**)
3	4-OMe	Ph (**1c**)	Ph (**2b**)	62[b] (**3cb**)
4	5-OMe	Ph (**1d**)	Ph (**2b**)	83[b] (**3db**)
5	4-Cl	Ph (**1e**)	Ph (**2b**)	83[b] (**3eb**)
6	3,4-(CH=CH)$_2$	Ph (**1f**)	Ph (**2b**)	48[b] (**3fb**)
7	H	H (**1g**)	Ph (**2b**)	77 (**3gb**)
8	4-Me	H (**1h**)	Ph (**2b**)	82 (**3hb**)
9	4-Me	H (**1h**)	4-$OMeC_6H_4$ (**2c**)	86 (**3hc**)
10	4-OMe	H (**1i**)	Ph (**2b**)	50[b] (**3ib**)
11	4-Cl	H (**1j**)	Ph (**2b**)	57[b] (**3jb**)
12	H	Ph (**1a**)	Ph (**2b**)	81 (**3ab**)
13	H	Ph (**1a**)	4-$OMeC_6H_4$ (**2c**)	86 (**3ac**)
14	H	Ph (**1a**)	4-ClC_6H_4 (**2d**)	81 (**3ad**)
15	H	Ph (**1a**)	4-$CF_3C_6H_4$ (**2e**)	71 (**3ae**)
16	H	Ph (**1a**)	(*E*)-CH=CH-Ph (**2f**)	72 (**3af**)
17	H	Ph (**1a**)	(*E*)-CH=CH-*n*-Hex (**2g**)	90 (**3ag**)

[a] Isolated yield. [b] This reaction was carried out for 18 h.

Next, we investigated the generality of this reaction by using bromoalkynes **6** having a non-allyloxy group (Table 3). We found that (bromoethynyl)benzene (**6a**) and various bromoalkynes **6b-h** were tolerated in this reaction (Entries 1-8). Furthermore, the reactions using various boronic acids **2b-e** proceeded smoothly to produce good yields of the corresponding products (Entry 9-12). In particular, when using *p*-methoxyphenylboronic acid (**2c**), a 97% yield of the corresponding product **7bc** was obtained (Entry 10). *p*-Chlorophenylboronic acid (**2d**) was also tolerated in this reaction and gave the corresponding product **7bd** in 73% (Entry 11). The reaction of *p*-(trifluromethyl)phenylboronic acid (**2e**) with **6b** was carried out for 18 h and afforded **7be** in 84% yield (Entry 12). We found that 2- and 3-substituted arylboronic acids **2h** and **2i** were also tolerated in this reaction (Entries 13 and 14). Even in this reaction case, the coupling reaction proceeded

at room temperature in the presence of 10 mol% of CuI and **L1a** (Entry 2). These results indicate that this reaction is an effective synthetic method for not only an *o*-allyloxyethynylbenzene derivative, but also an internal alkyne structure.

Table 3. Scope of coupling reaction.

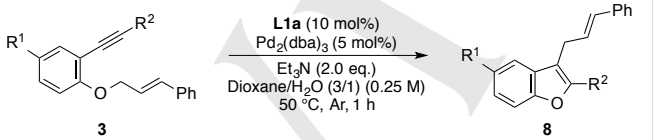


Entry	R (**6**)	Ar (**2**)	Yield (%)[a] (**7**)
1	H (**6a**)	4-MeC_6H_4 (**2a**)	71 (**7**aa)
2	4-OMe (**6b**)	4-MeC_6H_4 (**2a**)	81, 82[b] (**7ba**)
3	3-OMe (**6c**)	4-MeC_6H_4 (**2a**)	85 (**7ca**)
4	2-OMe (**6d**)	4-MeC_6H_4 (**2a**)	87 (**7da**)
5	4-^{t}Bu (**6e**)	4-MeC_6H_4 (**2a**)	90 (**7ea**)
6	4-Cl (**6f**)	4-MeC_6H_4 (**2a**)	84 (**7fa**)
7	4-CF_3 (**6g**)	4-MeC_6H_4 (**2a**)	91 (**7ga**)
8	3,4-(CH=CH)$_2$ (**6h**)	4-MeC_6H_4 (**2a**)	76 (**7ha**)
9	4-OMe (**6b**)	Ph (**2b**)	75 (**7bb**)
10	4-OMe (**6b**)	4-$OMeC_6H_4$ (**2c**)	97 (**7bc**)
11	4-OMe (**6b**)	4-ClC_6H_4 (**2d**)	73 (**7bd**)
12	4-OMe (**6b**)	4-$CF_3C_6H_4$ (**2e**)	84[c] (**7be**)
13	4-OMe (**6b**)	3-MeC_6H_4 (**2h**)	91 (**7bh**)
14	4-OMe (**6b**)	2-MeC_6H_4 (**2i**)	85 (**7bi**)

[a] Isolated yield. [b] This reaction was carried out at room temperature using 10 mol% of CuI and **L1b** for 24 h. [c] This reaction was carried out for 18 h.

Next, we demonstrated the various reactions of *o*-allyloxyethynylbenzene using transition metal catalysts for access to various heterocyclic compounds such as benzofuran and benzopyran derivatives. As described in our introduction, we already reported that annulation of an *o*-allyloxyethynylbenzene derivative in the presence of an **L1a**-Pd catalyst system afforded linear-type 3-allylbenzofuran derivatives effectively.[7] Here, we tried to use some of newly prepared *o*-allyloxyethynylbenzene derivatives **3** by a Cu-catalyzed Suzuki-Miyaura-type reaction (Table 4).

Table 4. Pd-catalyzed annulation.

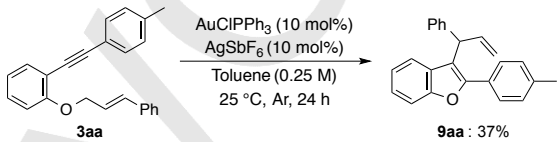


Entry	R^1	R^2 (**3**)	Yield (%)[a] (**8**)
1	OMe	Ph (**3cb**)	86 (**8cb**)
2	Cl	Ph (**3eb**)	88 (**8eb**)
3	H	(*E*)-CH=CH-Ph (**3af**)	92 (**8af**)
4	H	(*E*)-CH=CH-^{n}Hex (**3ag**)	88 (**8ag**)

[a] Isolated yield.

As a result, we achieved the corresponding 3-allylbenzofuran derivatives **8cb**, **8eb**, **8af** and **8ag** from *o*-allyloxyethynylbenzenes **3cb**, **3eb**, **3af** and **3ag** in high yields, respectively, by using a hydrazone-Pd catalyst system.

On the other hand, a gold (Au) catalyst was known to cause annulation *via* coordination of a cationic Au atom to triple bond.[25] When we use the Au catalyst to *o*-cinnamyloxyethynylbenzene derivative **3aa**, we found that branch-type 3-allylbenzofuran **9aa** could be obtained in a 37% yield (Scheme 3).

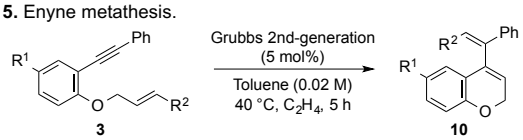


Scheme 3. Au-catalyzed annulation.

Based on the report by Roy's group,[25b] the Au-catalyst coordinated to triple bond to cause an annulation reaction, followed by the Claisen rearrangement affording the branch-type 3-allylbenzofuran in this reaction.

Furthermore, in the case of enyne metathesis[26] of *o*-allyloxyethynylbenzene derivatives **3gb**, **3ib** and **3jb** using the Grubbs 2nd catalyst, the corresponding benzopyran derivatives **10gb**, **10ib** and **10jb** were produced in high yields, respectively (Table 5, Entries 1-3). Unfortunately, the *o*-cinnamyloxyethynybenzene derivative **3ab** was not tolerated in this metathesis reaction (Entry 4).

Table 5. Enyne metathesis.



Entry	R^1	R^2 (**3**)	Yield (%)[a] (**10**)
1	H	H (**3gb**)	95 (**10gb**)
2	OMe	H (**3ib**)	96 (**10ib**)
3	Cl	H (**3jb**)	87 (**10jb**)
4	H	Ph (**3ab**)	N.R.

[a] Isolated yield.

These results, we could demonstrate three types of transformations using *o*-allyloxyethynylbenzene derivatives **3** for access to various heterocyclic compounds.

Conclusions

We found that a Cu-catalyzed Suzuki-Miyaura-type reaction of bromoalkyne with arylboronic acid using hydrazone **L1b** as a ligand proceeded smoothly in *i*-PrOH under mild conditions to afford the corresponding *o*-allyloxyethynylbenzene derivatives **3**

in good yields without decomposition of the allyloxy group. This reaction proceeded at room temperature in spite of using only a common-metal catalyst such as CuI without any amine base. Furthermore, we demonstrated three types of transformations using transition metal catalysts to *o*-allyloxyethynylbenzene derivatives for access to various heterocyclic compounds.

Experimental Section

General procedure for Cu-catalyzed Suzuki-Miyaura coupling reaction of bromoalkynes with arylboronic acids for internal alkyne 3 and 7 (Tables 2 and 3)

A mixture of bromoalkyne derivative **1** or **6** (0.25 mmol), arylboronic acids **2** (0.50 mmol), K_3PO_4 (0.50 mmol), CuI (12.5 µmol, 5 mol %) and ligand **L1b** (12.5 µmol, 5 mol %) in *i*-PrOH (1.0 mL) at 40 °C under an Ar atmosphere was stirred for 6 h. After the reaction, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane, hexane/ethyl acetate (v/v = 100-4/1) or hexane/toluene (v/v = 10-2/1)) to afford the corresponding internal alkyne products **3** or **7**.

1-Cinnamyloxy-2-(*p*-tolylethynyl)benzene[7] **(3aa)** (Table 1, Entry 2). Compound **3aa** was obtained from 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (78.3 mg) and *p*-tolylboronic acid (**2a**) (68.0 mg) according to the general procedure in 88% yield (71.4 mg, 0.220 mmol) as a white solid: m.p. 86-87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 13.0, 7.3 Hz, 1H), 7.46 (d, *J* = 7.9 Hz. 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.25-7.34 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.93-6.98 (m, 2H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.46 (dt, *J* = 16.0, 5.2 Hz, 1H), 4.81 (dd, *J* = 5.2, 1.5 Hz, 2H), 2.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 138.2, 136.6, 133.4, 132.2, 131.5, 129.4, 129.0, 128.5, 127.7, 126.5, 124.4, 120.8, 120.5, 113.3, 112.6, 93.8, 85.1, 69.1, 21.5 ppm; EI-MS *m/z* (rel intensity) 324 (M^+, 17).

1-Cinnamyloxy-4-methyl-2-(phenylethynyl)benzene (3bb) (Table 2, Entry 2). Compound **3bb** was obtained from 2-(bromoethynyl)-1-cinnamyloxy-4-methylbenzene (**1b**) (81.8 mg) and phenylboronic acid (**2b**) (61.0 mg) according to the general procedure (18 h) in 76% yield (61.7 mg, 0.190 mmol) as a white solid: m.p. 79-81 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.48-7.43 (m, 2H), 7.34-7.13 (m, 9H), 7.03 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.81-6.73 (m, 2H), 6.39 (dt, *J* = 16.0, 5.3 Hz, 1H), 4.70 (dd, *J* = 5.3, 1.6 Hz, 2H), 2.20 ppm (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 157.5, 137.0, 134.1, 132.6, 131.8, 130.76, 130.72, 129.0, 128.8, 128.5, 128.2, 126.9, 125.0, 124.0, 113.2, 113.0, 93.4, 86.5, 69.7, 20.4 ppm; EI-MS *m/z* (rel intensity) 324 (M^+, 14); HRMS (ESI-orbitrap): calcd for $C_{24}H_{20}O$+Na [*M*+Na]$^+$: 347.1406, found: 347.1399.

1-Cinnamyloxy-4-methoxy-2-(phenylethynyl)benzene (3cb) (Table 2, Entry 3). Compound (**3cb**) was obtained from 2-(bromoethynyl)-1-cinnamyloxy-4-methoxybenzene (**1c**) (86.0 mg) and phenylboronic acid (**2b**) (61.3 mg) according to the general procedure (18 h) in 62% yield (52.7 mg, 0.155 mmol) as a cream solid: m.p. 64-66 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 2H), 7.40-7.24 (m, 8H), 7.06 (d, *J* = 2.9 Hz, 1H), 6.92-6.79 (m, 3H), 6.45 (dt, *J* = 15.9, 5.4 Hz, 1H), 4.76 (dd, *J* = 5.4, 1.4 Hz, 2H), 3.79 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 153.6, 136.6, 132.3, 131.6, 128.5, 128.3, 128.2, 127.7, 126.5, 124.7, 123.4, 117.7, 115.8, 115.1, 114.2, 93.6, 85.8, 70.4, 55.7 ppm; EI-MS *m/z* (rel intensity) 340 (M^+, 23); HRMS (ESI-orbitrap): calcd for $C_{24}H_{20}O_2$+H [*M*+H]$^+$: 341.1536; found: 341.1531.

2-Cinnamyloxy-4-methoxy-1-(phenylethynyl)benzene[7] **(3db)** (Table 2, Entry 4). Compound **3db** was obtained from 1-(bromoethynyl)-2-cinnamyloxy-4-methoxybenzene (**1d**) (85.5 mg) and phenylboronic acid (**2b**) (61.0 mg) according to the general procedure (18 h) in 83% yield (70.9 mg, 0.208 mmol) as a cream solid: m.p. 85-86 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 2H), 7.46-7.23 (m, 9H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.52-6.41 (m, 3H), 4.79 (dd, *J* = 5.2, 1.1 Hz, 2H), 3.82 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.0, 160.2, 136.5, 134.1, 132.4, 131.4, 128.6, 128.2, 127.77, 127.74, 126.5, 124.1, 123.9, 105.6, 105.3, 100.1, 92.2, 85.9, 69.1, 55.4 ppm; EI-MS *m/z* (rel intensity) 340 (M^+, 21).

4-Chloro-1-cinnamyloxy-2-(phenylethynyl)benzene (3eb) (Table 2, Entry 5). Compound **3eb** was obtained from 2-(bromoethynyl)-4-chloro-1-cinnamyloxybenzene (**1e**) (86.8 mg) and phenylboronic acid (**2b**) (61.4 mg) according to the general procedure (18 h) in 83% yield (71.1 mg, 0.206 mmol) as a white solid: m.p. 95-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 2H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.40-7.21 (m. 9H), 6.88-6.80 (m, 2H), 6.42 (dt, *J* = 16.0, 5.3 Hz, 1H), 4.78 ppm (dd, *J* = 5.3, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 136.3, 132.8, 132.7, 131.7, 129.3, 128.6, 128.4, 128.3, 127.9, 126.5, 125.6, 123.8, 123.1, 114.8, 113.8, 94.7, 84.5, 69.5 ppm; EI-MS *m/z* (rel intensity) 344 (M^+, 7); HRMS (ESI-orbitrap): calcd for $C_{23}H_{17}ClO$+H [*M*+H]$^+$: 345.1041, found: 345.1039.

2-Cinnamyloxy-1-(phenylethynyl)naphthalene[7] **(3fb)** (Table 2, Entry 6). Compound **3fb** was obtained from 1-(bromoethynyl)-2-cinnamyloxynaphthalene (**1f**) (90.5 mg) and phenylboronic acid (**2b**) (61.0 mg) according to the general procedure (18 h) in 48% yield (43.5 mg, 0.121 mmol) as a white solid: m.p. 105-106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.4 Hz, 1H), 7.80 (dd, *J* = 9.2, 3.2 Hz, 2H), 7.68 (dd, *J* = 3.7, 2.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43-7.22 (m, 10H), 6.89 (d, *J* = 15.9 Hz, 1H), 6.50 (dd, *J* = 15.9, 5.3 Hz, 1H), 4.97 ppm (dd, *J* = 5.3, 1.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 136.5, 134.4, 132.5, 131.6, 130.0, 128.8, 128.6, 128.3, 128.13, 128.07, 127.8, 127.3, 126.6, 125.4, 124.5, 124.4, 123.8, 114.9, 107.5, 99.1, 84.0, 70.2 ppm; EI-MS *m/z* (rel intensity) 360 (M^+, 51).

1-Allyloxy-2-(phenylethynyl)benzene[7] **(3gb)** (Table 2, Entry 7). Compound **3gb** was obtained from 1-allyloxy-2-(bromoethynyl)benzene (**1g**) (58.6 mg) and phenylboronic acid (**2b**) (61.2 mg) according to the general procedure in 77% yield (45.1 mg, 0.193 mmol) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 2H), 7.50 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.37-7.30 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.94 (td, *J* = 7.5, 0.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz. 1H), 6.10 (dquin, *J* = 17.2, 4.8 Hz, 1H), 5.55 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.31 (dq, *J* = 10.6, 1.6 Hz, 1H), 4.64 ppm (dt, *J* = 4.8, 1.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 133.3, 132.9, 131.5, 129.5, 128.2, 128.0, 123.6, 120.7, 117.1, 113.0, 112.3, 93.4, 85.7, 69.1 ppm; EI-MS *m/z* (rel intensity) 234 (M^+, 100).

1-Allyloxy-4-methyl-2-(phenylethynyl)benzene (3hb) (Table 2, Entry 8). Compound **3hb** was obtained from 1-allyloxy-2-(bromoethynyl)-4-methylbenzene (**1h**) (62.8 mg) and phenylboronic acid (**2b**) (61.4 mg) according to the general procedure in 82% yield (50.6 mg, 0.204 mmol) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.52 (m, 2H), 7.37-

7.29 (m, 4H), 7.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.79 (d, *J* = 8.3 Hz. 1H), 6.09 (dquin, *J* = 17.2, 4.8 Hz, 1H), 5.52 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.29 (dq, *J* = 10.5, 1.6 Hz, 1H), 4.61 (dt, *J* = 4.8, 1.6 Hz, 2H), 2.27 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 157.0, 133.7, 133.2, 131.5, 130.1, 130.0, 128.2, 127.9, 123.7, 117.0, 112.8, 112.6, 93.1, 85.9, 69.4, 20.2 ppm; EI-MS *m/z* (rel intensity) 248 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{19}H_{16}O$+Na $[M+Na]^+$: 271.1093, found: 271.1093.

1-Allyloxy-2-((*p*-methoxyphenyl)ethynyl)-4-methylbenzene (3hc) (Table 2, Entry 9). Compound **3hc** was obtained from 1-allyloxy-2-(bromoethynyl)-4-methylbenzene (**1h**) (62.5 mg) and 4-methoxyphenylboronic acid (**2c**) (75.7 mg) according to the general procedure in 86% yield (59.7 mg, 0.214 mmol) as a cream solid: m.p. 36-37 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.48 (dt, *J* = 8.7, 2.7 Hz, 2H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 7.0, 2.2 Hz, 1H), 6.87 (dt, *J* = 8.7, 2,7 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.09 (dquin, *J* = 17.2, 4.8 Hz, 1H), 5.52 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.6, 1.6 Hz, 1H), 4.61 (dt, *J* = 4.9, 1.6 Hz, 2H), 3.82 (s, 3H), 2.27 ppm (s, 3H); ^{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, 84.5, 69.5, 55.3, 20.2 ppm; EI-MS *m/z* (rel intensity) 278 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{19}H_{18}O_2$+Na $[M+Na]^+$: 301.1199, found: 301.1196.

1-Allyloxy-4-methoxy-2-(phenylethynyl)benzene (3ib) (Table 2, Entry 10). Compound **3ib** was obtained from 1-allyloxy-2-(bromoethynyl)-4-methoxybenzene (**1i**) (58.6 mg) and phenylboronic acid (**2b**) (60.8 mg) according to the general procedure (18 h) in 50% yield (32.8 mg, 0.124 mmol) as a yellow oil: ^{1}H NMR (300 MHz, CD_2Cl_2): *δ* = 7.46-7.42 (m, 2H), 7.31-7.23 (m, 3H), 6.95 (t, *J* = 2.0 Hz, 1H), 6.79-6.73 (m, 2H), 6.02 (dquin, *J* = 17.2, 5.0 Hz, 1H), 5.41 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dd, *J* = 12.1, 1.6 Hz, 1H), 4.49 (dt, *J* = 5.0, 1.6 Hz, 2H), 3.68 ppm (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): *δ* = 153.94, 153.86, 133.9, 131.8, 128.8, 128.7, 123.8, 118.1, 117.2, 116.0, 114.7, 114.0, 93.6, 86.2, 70.6, 56.1 ppm; EI-MS *m/z* (rel intensity) 264 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{18}H_{16}O_2$+Na $[M+Na]^+$: 287.1043, found: 287.1036.

1-Allyloxy-4-chloro-2-(phenylethynyl)benzene (3jb) (Table 2, Entry 11). Compound **3jb** was obtained from 1-allyloxy-2-(bromoethynyl)-4-chlorobenzene (**1j**) (67.7 mg) and phenylboronic acid (**2b**) (61.4 mg) according to the general procedure (18 h) in 57% yield (38.4 mg, 0.143 mmol) as a white solid: m.p. 36-38 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.55-7.51 (m, 2H), 7.47 (d, *J* = 2.6 Hz, 1H), 7.38-7.32 (m, 3H), 7.22 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 1H), 6.07 (dquin, *J* = 17.2, 4.8 Hz, 1H), 5.52 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.32 (dq, *J* = 10.6, 1.7 Hz, 1H), 4.61 (dt, *J* = 4.8, 1.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 157.7, 132.8, 132.6, 131.6, 129.3, 128.4, 128.3, 125.5, 123.1, 117.4, 114.7, 113.6, 94.6, 84.4, 69.6 ppm; EI-MS *m/z* (rel intensity) 268 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{17}H_{13}ClO$+H $[M+H]^+$: 269.0728, found: 269.0730.

1-Cinnamyloxy-2-(phenylethynyl)benzene[7] **(3ab)** (Table 2, Entry 12). Compound **3ab** was obtained from 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (78.6 mg) and phenylboronic acid (**2b**) (61.2 mg) according to the general procedure in 81% yield (62.7 mg, 0.202 mmol) as a white solid: m.p. 100-102 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.59-7.50 (m, 3H), 7.41-7.22 (m, 9H), 6.98-6.93 (m, 2H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.46 (dt, *J* = 16.0, 5.3 Hz, 1H), 4.81 ppm (dd, *J* = 5.3, 1.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 159.1, 136.5, 133.4, 132.3, 131.6, 129.6, 128.6, 128.3, 128.1, 127.8, 126.5, 124.3, 123.6, 120.8, 113.2, 112.7, 93.6, 85.8, 69.2 ppm; EI-MS *m/z* (rel intensity) 310 (M^+, 13).

1-Cinnamyloxy-2-((*p*-methoxyphenyl)ethynyl)benzene[7] **(3ac)** (Table 2, Entry 13). Compound **3ac** was obtained from 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (77.9 mg) and *p*-methoxyphenylboronic acid (**2c**) (76.0 mg) according to the general procedure in 86% yield (73.0 mg, 0.214 mmol) as a cream solid: m.p. 84-85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.50 (d, *J* = 8.5 Hz, 3H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.34-7.24 (m, 4H), 6.97-6.92 (m, 2H), 6.87-6.82 (m, 3H), 6.45 (dt, *J* = 16.0, 5.2 Hz, 1H), 4.80 (dd, *J* = 5.2, 1.4 Hz, 2H), 3.81 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 159.5, 158.9, 136.6, 133.3, 133.0, 132.3, 129.3, 128.5, 127.7, 126.5, 124.4, 120.8, 115.8, 113.9, 113.5, 112.7, 93.6, 84.4, 69.2, 55.3 ppm; EI-MS *m/z* (rel intensity) 340 (M^+, 27).

1-((*p*-Chlorophenyl)ethynyl)-2-cinnamyloxybenzene (3ad) (Table 2, Entry 14). Compound **3ad** was obtained from 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (77.8 mg) and *p*-chlorophenylboronic acid (**2d**) (78.5 mg) according to the general procedure in 81% yield (69.9 mg, 0.203 mmol) as a white solid: m.p. 98-99 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): *δ* = 7.43-7.38 (m, 3H), 7.34-7.31 (m, 2H), 7.27-7.14 (m, 6H), 6.89 (td, *J* = 8.1, 0.9 Hz, 2H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.39 (dt, *J* = 16.0, 5.3 Hz, 1H), 4.72 ppm (dd, *J* = 5.3, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): *δ* = 161.6, 138.9, 136.4, 135.7, 135.1, 134.8, 132.4, 131.06, 130.98, 130.3, 128.9, 126.7, 124.5, 123.2, 114.98, 114.96, 94.6, 89.3, 71.5 ppm; EI-MS *m/z* (rel intensity) 344 (M^+, 8); HRMS (ESI-orbitrap): calcd for $C_{23}H_{17}OCl$+H $[M+H]^+$: 345.1041, found: 345.1041.

1-Cinnamyloxy-2-((*p*-(trifluoromethyl)phenyl)ethynyl)benzene (3ae) (Table 2, Entry 15). Compound **3ae** was obtained from 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (77.6 mg) and *p*-(trifluoromethyl)phenylboronic acid (**2e**) (95.1 mg) according to the general procedure in 71% yield (66.9 mg, 0.177 mmol) as a white solid: m.p. 114-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.65 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.52 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39-7.25 (m, 6H), 6.97 (dd, *J* = 8.7, 6.9 Hz, 2H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.45 (dt, *J* = 16.0, 5.3 Hz, 1H), 4.81 ppm (dd, *J* = 5.3, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 159.3, 136.4, 133.6, 132.6, 131.8, 130.3, 129.7 (q, *J* = 32.6 Hz), 128.6, 127.9, 127.5 (q, *J* = 1.5 Hz), 126.5, 125.2 (q, *J* = 3.9 Hz), 124.1, 124.0 (q, *J* = 272.0 Hz), 120.9, 112.6, 112.4, 92.2, 88.4, 69.2 ppm; EI-MS *m/z* (rel intensity) 378 (M^+, 8); HRMS (ESI-orbitrap): calcd for $C_{24}H_{17}OF_3$+H $[M+H]^+$: 379.1304, found: 379.1309.

1-Cinnamyloxy-2-((*E*)-styrylethynyl)benzene (3af) (Table 2, Entry 16). Compound **3af** was obtained from 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (78.0 mg) and (*E*)-styrylboronic acid (**2f**) (74.4 mg) according to the general procedure in 72% yield (60.3 mg, 0.179 mmol) as a white solid: m.p. 97-98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.45-7.39 (m, 5H), 7.36-7.23 (m, 7H), 7.06 (d, *J* = 16.2 Hz, 1H), 6.97-6.91 (m, 2H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.46 (dt, *J* = 16.2, 5.5 Hz, 2H), 4.81 ppm (dd, *J* = 5.3, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 159.0, 145.0, 136.5, 136.4, 133.4, 132.6, 129.6, 128.7, 128.6, 127.8, 126.6, 128.5, 126.3, 124.3, 120.8, 113.3, 112.6, 108.5, 93.1, 88.2, 69.2 ppm; EI-MS *m/z* (rel intensity) 336 (M^+, 7); HRMS (ESI-orbitrap): calcd for $C_{25}H_{20}O$+Na $[M+Na]^+$: 359.1406, found: 359.1407.

1-Cinnamyloxy-2-((*E*)-dec-3-en-1-yn-1-yl)benzene (3ag) (Table 2, Entry 17). Compound **3ag** was obtained from 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (78.2 mg) and (*E*)-oct-1-en-1-ylboronic acid

(**2g**) (78.2 mg) according to the general procedure in 90% yield (77.8 mg, 0.226 mmol) as a white solid: m.p. 44-46 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43-7.21 (m, 7H), 6.93-6.88 (m, 2H), 6.81 (d, J = 16.0 Hz, 1H), 6.43 (dt, J = 16.0, 5.3 Hz, 1H), 6.27 (dt, J = 15.9, 7.1 Hz, 1H), 5.76 (d, J = 15.9 Hz, 1H), 4.78 (dd, J = 5.3, 1.4 Hz, 2H), 2.16 (q, J = 7.1 Hz, 2H), 1.43-1.25 (m, 8H), 0.88 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 145.0, 136.6, 133.3, 132.4, 129.2, 128.5, 127.8, 126.5, 124.4, 120.8, 113.5, 112.5, 109.8, 92.7, 84.1, 69.2, 33.2, 31.7, 28.8, 28.7, 22.6, 14.1 ppm; EI-MS *m/z* (rel intensity) 344 (M^+, 3); HRMS (ESI-orbitrap): calcd for $C_{25}H_{28}O$+Na [M+Na]$^+$: 367.2032, found: 367.2027.

1-Methyl-4-(phenylethynyl)benzene[27] **(7aa)** (Table 3, Entry 1). Compound **7aa** was obtained from (bromoethynyl)benzene (**6a**) (45.1 mg) and *p*-tolylboronic acid (**2a**) (68.0 mg) according to the general procedure in 71% yield (34.1 mg, 0.178 mmol) as a white solid: m.p. 69-71 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.46 (m, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.38-7.31 (m, 3H), 7.15 (d, J = 7.8 Hz, 2H), 2.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.4, 131.51, 131.46, 129.1, 128.3, 128.1, 123.4, 120.1, 89.5, 88.7, 21.5 ppm; EI-MS *m/z* (rel intensity) 192 (M^+, 100).

1-Methoxy-4-(*p*-tolylethynyl)benzene[28] **(7ba)** (Table 3, Entry 2). Compound **7ba** was obtained from 1-(bromoethynyl)-4-methoxybenzene (**6b**) (52.6 mg) and *p*-tolylboronic acid (**2a**) (68.0 mg) according to the general procedure in 81% yield (45.0 mg, 0.203 mmol) as a white solid: m.p. 126-128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dt, J = 8.9, 2.6 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 6.87 (dt, J = 8.9, 2.6 Hz, 2H), 3.82 (s, 3H), 2.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 138.0, 133.0, 131.3, 129.1, 120.5, 115.6, 113.9, 88.6, 88.2, 55.3, 21.5 ppm; EI-MS *m/z* (rel intensity) 222 (M^+, 100).

1-Methoxy-3-(*p*-tolylethynyl)benzene[29] **(7ca)** (Table 3, Entry 3). Compound **7ca** was obtained from 1-(bromoethynyl)-3-methoxybenzene (**6c**) (52.5 mg) and *p*-tolylboronic acid (**2a**) (67.7 mg) according to the general procedure in 85% yield (47.4 mg, 0.213 mmol) as a brown solid: m.p. 38-40 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.1 Hz, 2H), 7.25 (t, J = 8.1 Hz, 1H), 7.17-7.04 (m, 3H), 7.05 (dd, J = 2.6, 1.4 Hz, 1H), 6.88 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H), 3.82 (s, 3H), 2.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 138.4, 131.5, 129.4, 129.1, 124.4, 124.1, 120.0, 116.2, 114.8, 89.4, 88.6, 55.3, 21.5 ppm; EI-MS *m/z* (rel intensity) 222 (M^+, 100).

1-Methoxy-2-(*p*-tolylethynyl)benzene[30] **(7da)** (Table 3, Entry 4). Compound **7da** was obtained from 1-(bromoethynyl)-2-methoxybenzene (**6d**) (52.9 mg) and *p*-tolylboronic acid (**2a**) (68.0 mg) according to the general procedure in 87% yield (48.5 mg, 0.218 mmol) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.44 (m, 3H) 7.32-7.25 (m, 1H), 7.14 (d, J = 7.8 Hz, 2H), 6.96-6.88 (m, 2H), 3.91 (s, 3H), 2.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 138.2, 133.51, 133.47, 131.5, 129.5, 129.0, 120.4, 112.6, 110.6, 93.6, 85.0, 55.8, 21.5 ppm; EI-MS *m/z* (rel intensity) 222 (M^+, 100).

1-(*tert*-Butyl)-4-(*p*-tolylethynyl)benzene[31] **(7ea)** (Table 3, Entry 5). Compound **7ea** was obtained from 1-(bromoethynyl)-4-(*tert*-butyl)benzene (**6e**) (59.5 mg) and *p*-tolylboronic acid (**2a**) (68.5 mg) according to the general procedure in 90% yield (55.8 mg, 0.225 mmol) as a white solid: m.p. 116-118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47-7.34 (m, 6H), 7.14 (d, J = 8.3 Hz, 2H), 2.36 (s, 3H), 1.32 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.3, 138.1, 131.4, 131.2, 129.1, 125.3, 120.40, 120.38, 88.85, 88.81, 34.8, 31.2, 21.5 ppm; EI-MS *m/z* (rel intensity) 248 (M^+, 68).

1-Chloro-4-(*p*-tolylethynyl)benzene[32] **(7fa)** (Table 3, Entry 6). Compound **7fa** was obtained from 1-(bromoethynyl)-4-chlorobenzene (**6f**) (53.5 mg) and *p*-tolylboronic acid (**2a**) (68.0 mg) according to the general procedure in 84% yield (47.6 mg, 0.211 mmol) as a white solid: m.p. 148-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47-7.40 (m, 4H), 7.31 (dt, J = 8.6, 2.3 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 2.37 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7, 134.0, 132.7, 131.5, 129.1, 128.6, 122.0, 119.8, 90.5, 87.6, 21.5 ppm; EI-MS *m/z* (rel intensity) 226 (M^+, 100).

1-(*p*-Tolylethynyl)-4-(trifluoromethyl)benzene[33] **(7ga)** (Table 3, Entry 7). Compound **7ga** was obtained from 1-(bromoethynyl)-4-(trifluoromethyl)benzene (**6g**) (61.9 mg) and *p*-tolylboronic acid (**2a**) (67.7 mg) according to the general procedure in 91% yield (58.9 mg, 0.227 mmol) as a white solid: m.p. 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (t, J = 9.0 Hz, 4H), 7.44 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1, 131.7, 131.6, 129.2 (q, J = 32.6 Hz), 129.2, 127.3, 125.2 (q, J = 3.7 Hz), 124.7 (q, J = 272.0 Hz), 119.4, 92.0, 87.4, 21.5 ppm; EI-MS *m/z* (rel intensity) 260 (M^+, 100).

2-(*p*-Tolylethynyl)naphthalene[34] **(7ha)** (Table 3, Entry 8). Compound **7ha** was obtained from 2-(bromoethynyl)naphthalene (**6h**) (57.7 mg) and *p*-tolylboronic acid (**2a**) (68.0 mg) according to the general procedure in 76% yield (46.2 mg, 0.191 mmol) as a white solid: m.p. 145-147 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.82-7.78 (m, 3H), 7.59-7.46 (m, 5H), 7.17 (d, J = 7.8 Hz, 2H), 2.37 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.4, 133.0, 132.7, 131.5, 131.3, 129.1, 128.4, 127.9, 127.7 × 2, 126.5, 126.5, 120.8, 120.2, 90.0, 89.1, 21.5 ppm; EI-MS *m/z* (rel intensity) 242 (M^+, 71).

1-Methoxy-4-(phenylethynyl)benzene[35] **(7bb)** (Table 3, Entry 9). Compound **7bb** was obtained from 1-(bromoethynyl)-4-methoxybenzene (**6b**) (52.8 mg) and phenylboronic acid (**2b**) (61.1 mg) according to the general procedure in 75% yield (39.1 mg, 0.188 mmol) as a white solid: m.p. 58-60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53-7.45 (m, 4H), 7.37-7.30 (m, 3H), 6.87 (dt, J = 8.9, 2.1 Hz, 2H), 3.83 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.6, 133.0, 131.4, 128.3, 127.9, 123.5, 115.3, 114.0, 89.3, 88.0, 55.3 ppm; EI-MS *m/z* (rel intensity) 208 (M^+, 100).

1,2-Bis(*p*-methoxyphenyl)acetylene[28] **(7bc)** (Table 3, Entry 10). Compound **7bc** was obtained from 1-(bromoethynyl)-4-methoxybenzene (**6b**) (52.8 mg) and *p*-methoxyphenylboronic acid (**2c**) (75.8 mg) according to the general procedure in 97% yield (57.4 mg, 0.241 mmol) as a yellow solid: m.p. 142-144 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (dt, J = 8.9, 2.7 Hz, 4H), 6.86 (dt, J = 8.9, 2.7 Hz, 4H), 3.82 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 132.8, 115.7, 113.9, 87.9, 55.3 ppm; EI-MS *m/z* (rel intensity) 238 (M^+, 100).

1-Chloro-4-((*p*-methoxyphenyl)ethynyl)benzene[36] **(7bd)** (Table 3, Entry 11). Compound **7bd** was obtained from 1-(bromoethynyl)-4-methoxybenzene (**6b**) (53.2 mg) and *p*-chlorophenylboronic acid (**2d**) (78.2 mg) according to the general procedure in 73% yield (44.3 mg, 0.183 mmol) as a white solid: m.p. 85-87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48-7.42 (m, 4H), 7.30 (dt, J = 8.5, 2.3 Hz, 2H), 6.88 (dt, J

= 8.8, 2.7 Hz, 2H), 3.83 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 133.8, 133.0, 132.6, 128.6, 122.1, 115.0, 114.0, 90.3, 87.0, 55.3 ppm; EI-MS *m/z* (rel intensity) 242 (M^+, 100).

1-Methoxy-4-((*p*-(trifluoromethyl)phenyl)ethynyl)benzene[37] **(7be)** (Table 3, Entry 12). Compound **7be** was obtained from 1-(bromoethynyl)-4-methoxybenzene (**6b**) (52.9 mg) and *p*-(trifluoromethyl)phenylboronic acid (**2e**) (94.6 mg) according to the general procedure (18 h) in 84% yield (57.9 mg, 0.210 mmol) as a yellow solid: m.p. 85-87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (t, *J* = 9.2 Hz, 4H), 7.49 (dt, *J* = 8.9, 2.7 Hz, 2H), 6.89 (dt, *J* = 8.9, 2.7 Hz, 2H), 3.83 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0, 133.2, 131.6, 129.5 (q, *J* = 32.7 Hz), 127.5 (q, *J* = 1.5 Hz), 125.2 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 272.0 Hz), 114.6, 114.1, 91.9, 86.8, 55.3 ppm; EI-MS *m/z* (rel intensity) 276 (M^+, 100).

1-Methoxy-4-(*m*-tolylethynyl)benzene[28] **(7bh)** (Table 3, Entry 13). Compound **7bh** was obtained from 1-(bromoethynyl)-4-methoxybenzene (**6b**) (53.3 mg) and *m*-tolylboronic acid (**2h**) (67.9 mg) according to the general procedure in 91% yield (50.3 mg, 0.227 mmol) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dt, *J* = 8.9, 2.7 Hz, 2H), 7.32 (d, *J* = 11.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.87 (dt, *J* = 8.9, 2.7 Hz, 2H), 3.81 (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 137.9, 133.0, 132.0, 128.8, 128.5, 128.2, 123.3, 115.4, 113.9, 89.0, 88.2, 55.3, 21.2 ppm; EI-MS *m/z* (rel intensity) 222 (M^+, 100).

1-Methoxy-4-(*o*-tolylethynyl)benzene[28] **(7bi)** (Table 3, Entry 14). Compound **7bi** was obtained from 1-(bromoethynyl)-4-methoxybenzene (**6b**) (52.6 mg) and *o*-tolylboronic acid (**2i**) (67.8 mg) according to the general procedure in 85% yield (47.3 mg, 0.213 mmol) as a yellow solid: m.p. 76-78 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (dt, *J* = 8.9, 2.7 Hz, 3H), 7.24-7.14 (m, 3H), 6.88 (dt, *J* = 8.9, 2.7 Hz, 2H), 3.82 (s, 3H), 2.50 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 139.9, 132.9, 131.6, 129.4, 127.9, 125.5, 123.3, 115.6, 114.0, 93.3, 87.0, 55.3, 20.7 ppm; EI-MS *m/z* (rel intensity) 222 (M^+, 90).

Procedure for Pd-catalyzed Suzuki-Miyaura-type reaction of *o*-cinnamyloxybromoalkyne (1a) with *p*-tolylboronic acid (2a) (Scheme 2)

A mixture of 1-(bromoethynyl)-2-cinnamyloxybenzene (**1a**) (0.25 mmol, 78.3 mg), *p*-tolylboronic acid (**2**) (0.50 mmol, 67.4 mg**),** K_3PO_4 (0.5 mmol, 0.1057 g), $Pd(OAc)_2$ (12.5 µmol, 5 mol %, 2.81 mg) and ligand **L1b** (12.5 µmol, 5 mol %, 3.34 mg) in *i*-PrOH (1.0 mL) at 40 °C under an Ar atmosphere was stirred for 6 h. After the reaction, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane) to afford 1-cinnamyl-4-methylbenzene (**4**) (3.6 mg, 0.017 mmol) in 7% and 2-(*p*-tolyl)benzofuran (**5**) (5.2 mg, 0.025 mmol) in 10%.

1-Cinnamyl-4-methylbenzene[23c] **(4)** Yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (tt, *J* = 9.9, 0.9 Hz, 2H), 7.28 (tt, *J* = 7.7, 1.5 Hz, 2H), 7.22-7.10 (m, 5H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9 and 6.4 Hz, 1H), 3.51 (d, *J* = 6.4 Hz, 2H), 2.33 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 137.0, 135.7, 130.8, 129.5, 129.1, 128.53, 128.46, 127.0, 126.1, 38.9, 21.0 ppm; EI-MS *m/z* (rel intensity) 208 (M^+, 100).

2-(*p*-Tolyl)benzofuran[38] **(5)** Yellow solid: m.p. 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.4 Hz, 2H), 7.59-7.56 (m, 1H), 7.51 (dt, *J* = 6.8, 1.3 Hz, 1H), 7.30-7.19 (m, 4H), 6.97 (d, *J* = 0.7 Hz, 1H), 2.40 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.1, 154.7, 138.6, 129.5, 129.3, 127.7, 124.9, 124.0, 122.8, 120.7, 111.1, 100.5, 21.4 ppm; EI-MS *m/z* (rel intensity) 208 (M^+, 100).

General procedure for Pd-catalyzed annulation of *o*-allyloxyethynylbenzene 3 (Table 4)

A mixture of *o*-allyloxyethynylbenzene **3** (0.25 mmol), Et_3N (0.5 mmol), Pd_2dba_3 (12.5 µmol, 5 mol %) and ligand **L1a** (25.0 µmol, 10 mol %) in 1,4-dioxane/H_2O (3/1) (1.0 mL) at 50 °C under an Ar atmosphere was stirred for 1 h. After the reaction, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane) to afford the corresponding benzofuran product **8**.

3-Cinnamyl-5-methoxy-2-phenylbenzofuran (8cb) (Table 4, Entry 1). Compound **8cb** was obtained from 1-cinnamyloxy-4-methoxy-2-(phenylethynyl)benzene **3cb** (85.2 mg) according to the general procedure in 86% yield (73.6 mg, 0.216 mmol) as a white solid: m.p. 94-95 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.4 Hz, 2H), 7.41-7.11 (m, 9H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.42-6.41 (m, 2H), 3.75 (s, 3H), 3.72-3.71 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 152.6, 149.0, 137.2, 131.0, 130.93, 130.91, 128.7, 128.5, 128.3, 127.2, 127.1, 126.9, 126.1, 113.2, 113.0, 111.5, 102.3, 55.9, 27.7 ppm; EI-MS *m/z* (rel intensity) 340 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{24}H_{20}O_2$+H $[M+H]^+$: 341.1536; found: 341.1535.

5-Chloro-3-cinnamyl-2-phenylbenzofuran (8eb) (Table 4, Entry 2). Compound **8eb** was obtained from 4-chloro-1-cinnamyloxy-2-(phenylethynyl)benzene **3eb** (86.7 mg) according to the general procedure in 88% yield (75.8 mg, 0.220 mmol) as a white solid: m.p. 115-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.2 Hz, 2H), 7.52-7.18 (m, 11H), 6.47-6.46 (m, 2H), 3.78-3.77 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.2, 152.4, 137.0, 131.8, 131.3, 130.4, 128.8, 128.7, 128.5, 128.2, 127.3, 127.0, 126.6, 126.2, 124.6, 119.3, 112.8, 112.1, 27.5 ppm; EI-MS *m/z* (rel intensity) 344 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{23}H_{17}OCl$ $[M]^+$: 344.0962; found: 344.0974.

3-Cinnamyl-2-((*E*)-styryl)benzofuran (8af) (Table 4, Entry 3). Compound **8af** was obtained from 1-cinnamyloxy-2-((*E*)-styrylethynyl)benzene **3af** (84.1 mg) according to the general procedure in 92% yield (77.7 mg, 0.231 mmol) as a yellow solid: m.p. 90-91 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 3H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.39-7.16 (m, 11H), 7.11 (d, *J* = 16.1 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.38 (dt, *J* = 15.8, 6.0 Hz, 1H), 3.71 ppm (dd, *J* = 6.0, 1.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3, 150.9, 137.1, 136.8, 131.2, 129.8, 129.5, 128.7, 128.5, 128.0, 127.3, 127.2, 126.6, 126.1, 124.8, 122.5, 119.7, 115.6, 114.3, 110.8, 27.2 ppm; EI-MS *m/z* (rel intensity) 336 (M^+, 78); HRMS (ESI-orbitrap): calcd for $C_{25}H_{20}O$-H $[M-H]^-$: 335.1430; found: 335.1429.

3-Cinnamyl-2-((*E*)-oct-1-en-1-yl)benzofuran (8ag) (Table 4, Entry 4). Compound **8ag** was obtained from 1-cinnamyloxy-2-((*E*)-dec-3-en-1-yn-1-yl)benzene **3ag** (84.4 mg) according to the general procedure in 88% yield (76.0 mg, 0.221 mmol) as a white solid: m.p. 36-38 °C; ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33-7.12 (m, 7H), 6.54-6.43 (m, 3H), 6.38- 6.29 (m, 1H), 3.60 (dd, *J* = 6.0, 1.1 Hz, 2H), 2.26 (q, *J* = 14.0, 6.8 Hz, 2H), 1.55-1.25 (m, 8H), 0.89 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0, 150.9, 137.3, 133.4, 130.8, 129.8, 128.5, 127.6, 127.1, 126.1, 124.1, 122.3, 119.4, 116.5, 112.8, 110.6, 33.3, 31.7, 29.1, 28.9, 26.9, 22.6, 14.1 ppm; EI-MS *m/z* (rel intensity) 344 (M^+, 76); HRMS (ESI-orbitrap): calcd for $C_{25}H_{28}O$-H [*M*-H]$^-$: 343.2056; found: 343.2051.

Au-catalyzed annulation of 1-cinnamyloxy-2-((*p*-tolyl)ethynyl)benzene (3aa) for synthesis of 3-(1-phenylallyl)-2-(*p*-tolyl)benzofuran (9aa) (Scheme 3)

A mixture of 1-cinnamyloxy-2-((*p*-tolyl)ethynyl)benzene (**3aa**) (32.3 mg, 0.10 mmol), $AuClPPh_3$ (5.00 mg, 10.0 μmol, 10 mol %) and $AgSbF_6$ (3.56 mg, 10.0 μmol, 10 mol %) in toluene (1.0 mL) at 25 °C under an Ar atmosphere was stirred for 24 h. After the reaction, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/ethyl acetate = (v/v = 250/1)) to afford 3-(1-phenylallyl)-2-(*p*-tolyl)benzofuran (**9aa**) in 37% yield (12.0 mg, 0.0370 mmol) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.35-7.19 (m, 9H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.53-6.42 (m, 1H), 5.30 (dt, *J* = 10.1, 1.5 Hz, 1H), 5.20 (d, *J* = 6.5 Hz, 1H), 5.13 (dt, *J* = 17.1, 1.5 Hz, 1H), 2.41 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3, 152.3, 141.6, 138.7, 138.5, 129.4, 129.9, 128.4, 128.2, 127.9, 127.7, 126.5, 123.9, 122.2, 121.6, 117.1, 115.8, 111.1, 45.3, 21.4 ppm; EI-MS *m/z* (rel intensity) 324 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{24}H_{20}O$+H [*M*+H]$^+$: 325.1587; found: 325.1587.

General procedure for enyne metathesis of *o*-allyloxyethynylbenzene 3 using Grubbs 2nd catalyst (Table 5)

To a solution of *o*-allyloxyethynylbenzene derivatives **3** (0.10 mmol) in toluene (5 mL) was added Grubbs 2nd-generation catalyst (5.0 μmol, 5.0 mol%) under nitrogen. The reaction container was filled with ethylene gas (1 atm) in three cycles. The reaction mixture was heated to 40 °C and stirred for 5 h. After cooling to room temperature, the mixture was concentrated under reduced pressure and purified by silica-gel column chromatography (hexane/ethyl acetate = (v/v = 7/3)) to afford the corresponding benzopyran product **10**.

4-(1-Phenylvinyl)-2*H*-benzopyran (10gb) (Table 5, Entry 1). Compound **10gb** was obtained from 1-allyloxy-2-(phenylethynyl)benzene **(3gb**) (23.0 mg) according to the general procedure in 95% yield (21.8 mg, 0.095 mmol) as a colorless oil; ^{1}H NMR 500 MHz, $CDCl_3$): δ = 7.44-7.42 (m, 2H), 7.30-7.23 (m, 3H), 7.05 (td, *J* = 8.0, 1.5 Hz, 1H), 6.82 (ddd, *J* = 7.6, 6.7, 1.5 Hz, 2H), 6.70 (td, *J* = 7.5, 1.2 Hz, 1H), 5.85 (t, *J* = 3.8 Hz, 1H), 5.68 (d, *J* = 1.5 Hz, 1H), 5.37 (d, *J* = 1.5 Hz, 1H), 4.87 ppm (d, *J* = 3.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.2, 146.4, 139.2, 136.7, 129.0, 128.4, 127.9, 126.5, 126.1, 123.0, 121.3, 121.2, 116.0, 115.6, 65.3 ppm; EI-MS *m/z* (rel intensity) 234 (M^+, 100); HRMS (ESI-orbitrap): calcd for $C_{17}H_{14}O$+Na [*M*+Na]$^+$: 257.0937; found: 257.0937.

6-Methoxy-4-(1-phenylvinyl)-2*H*-benzopyran (10ib) (Table 5, Entry 2). Compound **10ib** was obtained from 1-allyloxy-4-methoxy-2-(phenylethynyl)benzene (**3ib**) (25.2 mg) according to the general procedure in 96% yield (24.1 mg, 0.096 mmol) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43-7.41 (m, 2H), 7.30-7.23 (m, 3H), 6.78 (d, *J* = 8.7 Hz, 1H), 6.62 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.40 (d, *J* = 3.0 Hz, 1H), 5.90 (t, *J* = 3.9 Hz, 1H), 5.66 (d, *J* = 1.5 Hz, 1H), 4.80 (d, *J* = 3.9 Hz, 2H), 3.37 (d, *J* = 1.5 Hz, 1H), 3.53 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 148.1, 146.4, 139.3, 136.8, 128.4, 127.9, 126.6, 123.7, 122.1, 116.4, 115.8, 114.2, 111.4, 65.2, 55.4 ppm; EI-MS *m/z* (rel intensity) 264 (M^+, 100); HRMS (ESI- orbtirap): calcd for $C_{18}H_{16}O_2$+Na [*M*+Na]$^+$: 287.1043; found: 287.1043.

6-Chloro-4-(1-phenylvinyl)-2*H*-benzopyran (10jb) (Table 5, Entry 3). Compound **10jb** was obtained from 1-allyloxy-4-chloro-2-(phenylethynyl)benzene (**3jb**) (26.8 mg) according to the general procedure in 87% yield (23.3 mg, 0.087 mmol) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42-7.40 (m, 2H), 7.32-7.27 (m, 3H), 7.00 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 5.86 (t, *J* = 3.8 Hz, 1H), 5.70 (d, *J* = 1.4 Hz, 1H), 5.35 (d, *J* = 1.4 Hz, 1H), 4.86 ppm (d, *J* = 3.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.8, 145.7, 138.7, 135.9, 128.7, 128.5, 128.1, 126.5, 126.0, 125.7, 124.4, 122.3, 117.3, 116.1, 65.4 ppm; EI-MS *m/z* (rel intensity) 268 (M^+, 100); HRMS (APCI-orbitrap): calcd for $C_{17}H_{13}OCl$+H [*M*+H]$^+$: 269.0728; found: 269.0716.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 26410109) from Japan Society for the Promotion of Science (JSPS). We thank the Tonen General Sekiyu Research and Development Encouragement Foundation and the COE Program in Chiba University for financial support.

Keywords: copper • coupling reaction • alkyne • allyl • heterocycle

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[22] First step: Williamson ether synthesis of salicylaldehydes with allylbromide afforded *o*-allyloxybenzaldehydes. Second step: Corey-fucks reaction of *o*-allyloxybenzaldehydes afforded *o*-allyloxy(2,2-dibromovinyl)benzenes. Third step: HBr reduction from *o*-allyloxy(2,2-dibromovinyl)benzenes by base afforded *o*-allyloxy(bromoethynyl)benzenes **1**.

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10.1002/ejoc.201700217

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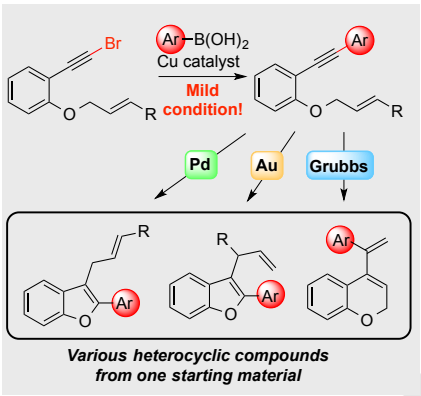
Cross-coupling

We found that Suzuki-Miyaura-type reaction of *o*-allyloxy(bromoethynyl)-benzene with arylboronic acid using a hydrazone-Cu catalyst system proceeded smoothly in *i*-PrOH under mild conditions to afford the corresponding *o*-allyloxyethynyl-benzene derivatives. We further demonstrate that three types of transformation using transition metal catalysts to *o*-allyloxyethynylbenzene derivatives lead to various respective heterocyclic compounds.



Various heterocyclic compounds from one starting material

Kohei Watanabe. Prof. Dr. Takashi Mino, Eri Ishikawa, Miyu Okano, Tatsuya Ikematsu, Prof. Dr. Yasushi Yoshida, Prof. Dr. Masami Sakamoto, Kazuki Sato and Prof. Dr. Kazuhiro Yoshida*

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Synthesis of *o*-Allyloxyethynyl-benzene Derivatives *via* Cu-Catalyzed Suzuki-Miyaura-Type Reaction and Their Transformations for Heterocyclic Compounds