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Pd-Catalyzed Highly Regio- and Stereoselective Formation of C−C Double Bonds: An Efficient Method for the Synthesis of Benzofuran-, Dihydrobenzofuran-, and Indoline-Containing Alkenes

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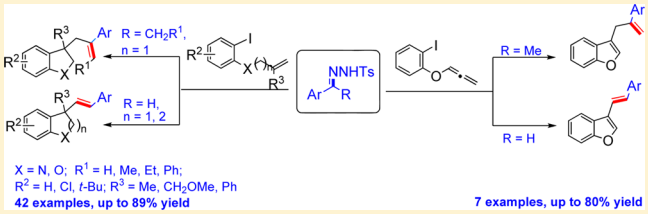
Supporting Information

ABSTRACT: A highly regio- and stereoselective C−C double bond formation reaction via Pd-catalyzed Heck-type cascade process with *N*-tosylhydrazones has been developed. Various *N*-tosylhydrazones derived from both ketones and aldehydes are found to be efficient substrates to provide di- and trisubstituted olefins with high regio- and stereoselectivity. Furthermore, this reaction has a good functional group tolerance and different benzofuran-, dihydrobenzofuran-, and indoline-containing alkene products were obtained with high selectivity.



INTRODUCTION

Carbon−carbon double bond is one of the most fundamental and versatile functional groups in synthetic organic chemistry,[1−4] owing to its widespread presence and highly developed chemistry.[5−9] In the past few years, a novel type of palladium-catalyzed cross-coupling reactions involving carbene migratory insertion process has emerged as a powerful method for the construction of C−C double bonds.[10−14] As shown in Scheme 1a, palladium-catalyzed cross-coupling reaction based on carbene migratory insertion includes the following common processes:[15] (1) metal species **A** is captured by the diazo compound to generate metal carbene species **B**; (2) migratory insertion occurs to produce a new metal species **C** which undergoes further transformations, typically β-hydride elimination; (3) the reaction releases coupling product **D** and regenerates the metal catalyst. According to this sequence, various alkene formation reactions have been designed and developed.[16−29] Nevertheless, despite the efficiency of these methods, the regio- and stereoselectivities of this type of reaction is still a challenge and has rarely been discussed. Actually, when alkyl-Pd species **A′** is employed, metal species **C′** bearing two β-hydride atoms H^a and H^b, which are electronically similar, is generated and two regioisomers **D-1** and **D-2** may be formed without selectivity in the position of the double bond (Scheme 1b). In the previous work,[30−34] *N*-tosylhydrazones derived from nonenolizable carbonyls (aldehydes or/and ketones bearing no α-hydride) are chosen as the coupling partners to avoid the regioselective problem. Significantly, to promote the regioselective β-hydride-elimination on alkylpalladium complex **C′** is the crucial step to improve the regioselectivity of this type of reaction. Therefore, we envision that the discovery of a catalyst system sensitive to the steric effect and capable of distinguishing electronically nonbiased H^a and H^b on the basis of their relative steric environments might be a strategy to solve the regioselective problem.

On the other hand, the intramolecular carbometalation of alkenes[35−48] initiated from the oxidative addition of C(sp^2)−X provides an efficient method to construct benzo-fused saturated nitrogen/oxygen heterocycles such as indolines[35−40] and dihydrobenzofurans,[41−48] which are prominent in a variety of natural products and biologically active compounds.[49−55] In 2002, Grigg and co-workers reported an interesting Pd-catalyzed queuing processes by employing allene as a relay switch and secondary amines as nucleophiles.[39] Inspired by these precedents and our continued interest in the palladium-catalyzed cross-coupling of *N*-tosylhydrazones,[56−59] we conceived that the alkyl-Pd species generated from intramolecular carbopalladation of alkene may be trapped by a diazo substrate to form a Pd carbene species, which would undergo migratory insertion and β-hydride elimination to afford the polysubstituted olefins (Scheme 1c). Herein, we present our recent progress in palladium-catalyzed Heck-type cascade reaction with various *N*-tosylhydrazones for the synthesis of functionalized olefins with high selectivity. It is worth mentioning that this reaction proceeds in a regio- and stereoselective manner which is a crucial issue in the construction of polysubstituted olefins.[60]

Results and Discussion. Our initial investigations of this Pd-catalyzed Heck-type cascade reaction commenced with substrate (**1a**) and *N*-tosylhydrazone (**2a**) derived from acetophenone as model substrates under the following conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (15 mol %), and LiO^tBu (0.9 mmol) in 1,4-dioxane (2 mL) at 90 °C. To our delight, the desired product was obtained as a mixture of diastereomers (5:1) in 66% yield

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Scheme 1. Pd-Catalyzed Heck-Type Cascade Reaction with *N*-Tosylhydrazone

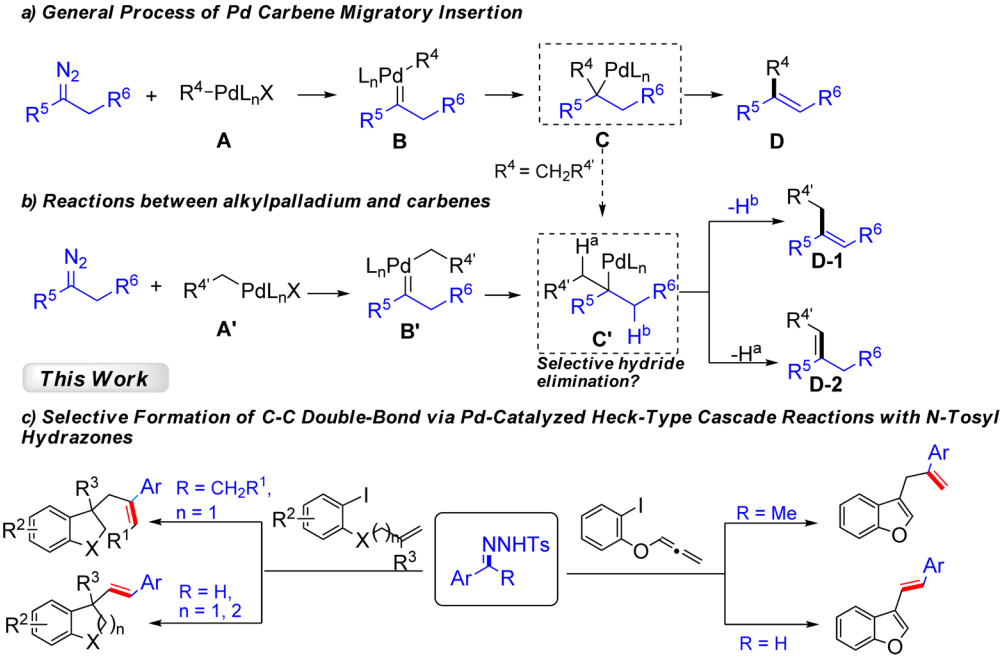
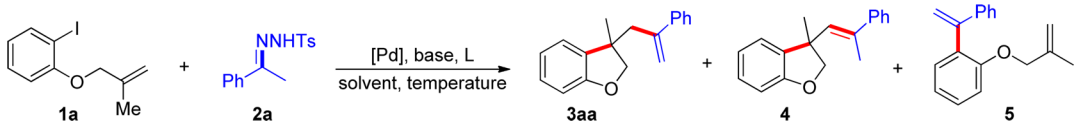
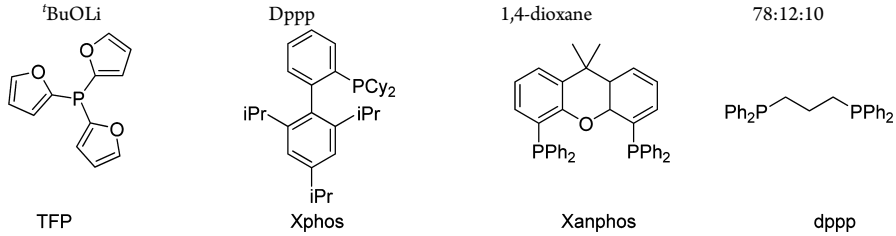


Table 1. Optimization of Reaction Conditions[a]



entry	base	ligand	solvent	3aa/4/5[b]	yield (%)[c]
1	^{t}BuOLi	PPh_3	1,4-dioxane	77:18:5	66
2	^{t}BuONa	PPh_3	1,4-dioxane	83:12:5	53
3	^{t}BuOK	PPh_3	1,4-dioxane	76:21:3	59
4	K_2CO_3	PPh_3	1,4-dioxane	70:26:4	35
5	^{t}BuOLi	PPh_3	MeCN	66:24:10	45
6	^{t}BuOLi	PPh_3	toluene	54:28:18	62
7	^{t}BuOLi	-	1,4-dioxane	75:20:5	37
8	^{t}BuOLi	TFP	1,4-dioxane	61:37:2	80
9	^{t}BuOLi	P^{t}Bu$_3$	1,4-dioxane	83:17:5	78
10	^{t}BuOLi	Xphos	1,4-dioxane	90:5:5	82
11[d]	^{t}BuOLi	Xphos	1,4-dioxane	95:4:1	88 (83)
12[e]	^{t}BuOLi	Xanphos	1,4-dioxane	83:11:6	76
13[e]	^{t}BuOLi	Dppp	1,4-dioxane	78:12:10	70



[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), ligand (15 mol %), and base (3.0 equiv) in indicated solvent (2 mL) at 90 °C for 8 h. [b]The ratio was determined by GC analysis. [c]Combined yield of **3a** and **4**. Dodecane is used as the internal standard. Data in parentheses is isolated yield. [d]5.0 equiv of water was added. [e]7.5 mol % ligand was used.

(Table 1). The structure of the major isomer was confirmed to be **3aa** by the NMR analysis, and the byproduct was the double-bond isomer **4**. Meanwhile, a small amount of **5** was also formed. Encouraged by this promising regioselectivity, we thought that the selective formation of **3aa** could be obtained through the careful screening of base, Pd source, solvent, and ligand. Among various bases tested, LiO^{t}Bu gave the highest yield (entry 1); however, the selectivity of the dominant product **3aa** was still unsatisfactory. The formation of the double-bond isomer **4** remained an issue and indicated the competition of two *β*-hydride elimination pathways. The judicious choice of a bulky ligand would promote the required

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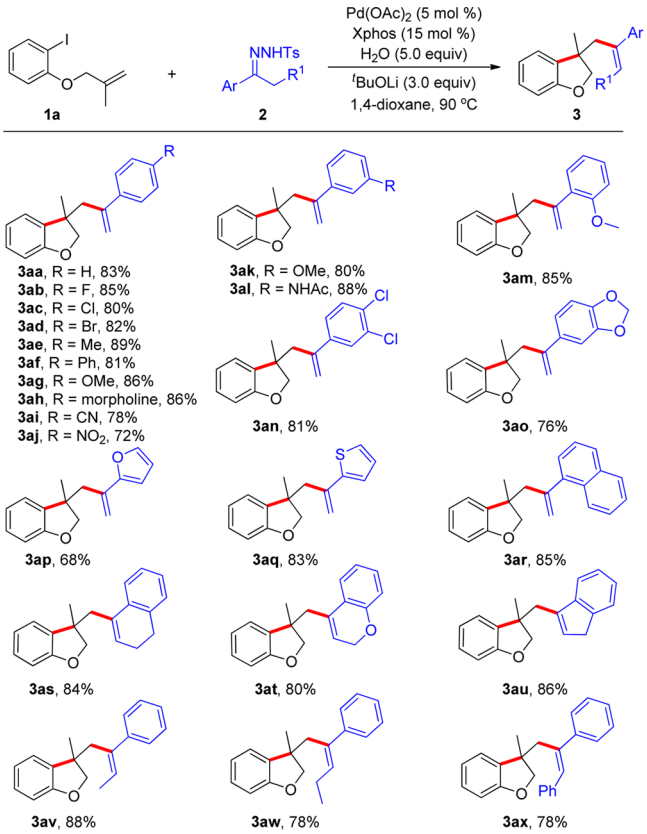
selective β-hydride elimination[61] and afford the best selectivity for **3aa**. Further optimization studies revealed that more bulky Xphos gave the highest selectivity for **3aa** (entry 10) and the presence of 5 equiv of water could further promote the ratio of **3aa** to 95% (entry 11). In addition, diphosphine ligand Xanphos and dppp were found to be effective for this reaction, but the selectivity is no better than that of Xphos (entries 12 and 13).

With the optimal reaction conditions in hand, we then examined the scope of this palladium-catalyzed Heck-type cascade reaction. Generally, various *N*-tosylhydrazones with different substituents were found to be suitable reaction partner for this transformation. As shown in Table 2, a series of para-

Table 2. Substrate Scope of *N*-Tosylhydrazones Derived from Aryl Ketones[a,b]



[a]Reaction conditions: all reactions were performed with **1a** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), Xphos (15 mol %), H_2O (5.0 equiv), and Li^{t}Bu (3.0 equiv) in 2 mL of 1,4-dioxane at 90 °C for 8 h. [b]Isolated yields are given.

substituted *N*-tosylhydrazones including both electron-donating groups (EDGs) (**3ae**–**ah**) and electron-withdrawing groups (EWGs) (**3ai** and **3aj**) could be converted to the corresponding polysubstituted olefins in good to excellent yields. Halo substituents, such as Cl and Br, were well tolerated, which provided the possibility for further functionalization (**3ab**–**ad**). No significant effect was found for the substituents at the para, meta, and ortho positions of the aromatic ring (**3ag**, **3ak**, and **3am**). When polysubstituted *N*-tosylhydrazones were used for this transformation, the corresponding products could be obtained in good yields (**3an** and **3ao**). To our delight, heterocyclic *N*-tosylhydrazones such as furan and thiophene (**3ap** and **3aq**) were found to be a suitable reaction partner for this reaction. The naphthyl *N*-tosylhydrazone **2r** also proceeded well under the optimal conditions. Notably, cyclic *N*-tosylhydrazones underwent the transformation smoothly to afford the desired products (**3as**–**au**) in good yields. It should be noted that the stereochemistry is a crucial issue in the construction of polysubstitued olefins. In this context, various trisubstituted olefins (**3av**–**ax**) were obtained in this reaction with high stereoselectivity (E/Z > 10:1 determined by NOSEY analysis, see the Supporting Information for details).

Next the generality of the reaction was additionally explored by employing various organic halide substrates to the optimized reaction conditions. Substrates bearing 4-*t*-Bu or 4-Cl underwent a smooth reaction to afford the corresponding products (**3ba** and **3ca**) in good yields (Table 3). 1-Iodo-2-(2-methylallyloxy)naphthalene was also shown to be a good substrate and gave product **3da** in 73% yield. The reaction of N–Ac protected amide **1f** afforded the desired product **3fa** in 80% yield, while an amide bearing free N–H failed to undergo this cross-coupling reaction. Acrylamide **1h** was proved to be an efficient substrate for this reaction, and **3hi** was obtained in 89% yield. Moreover, we were pleased to find that the transformations of the substrates with β-OMe or -Ph functional groups underwent the reaction efficiently and furnished the corresponding products (**3ea** and **3ia**) in good yields.

To further highlight the versatility of this reaction, various *N*-tosylhydrazones derived from benzaldehyde were applied in this reaction. As shown in Table 4, a series of nonterminal olefins were prepared and different functional groups such as (Cl, Br, NMe_2, SO_2Me, and furyl) were tolerated. It is worth mentioning that this reaction was tested to be efficient for the synthesis of six-membered chorman substituted alkenes (**6j** and **6k**).

The analogous reactions with aryl bromide or chloride starting materials were found to be inefficient, giving only a trace amount of the desired products. Interestingly, the aryl-Pd species generated from the oxidative addition of C(sp^2)–Br was first trapped by a diazo substrate and afforded **5** in 84% isolated yield, eq 1. This may be caused by the slow oxidative addition of C(sp^2)–Br and the fast formation of aryl palladium carbene species. Furthermore, the failure of **1m** to give the desired products indicated that β-hydride elimination should be faster than the carbene insertion, and blocking β-H elimination by the choice of substrate is critical for the success of this reaction eq 2.

In light of the above experimental results, we envisioned that the formation of a relatively stable alkyl palladium species is the crucial process of this reaction. The allene substrates were then tested under the standard conditions (Table 5). As we expected, various benzofuran-containing alkene products were isolated in good yields (**8a**–**f**). Furthermore, nonterminal olefins **9** could also be prepared via applying the *N*-tosylhydrazone derived from benzaldehyde as shown in eq 3.

On the basis of the above results, a tentative mechanism for this palladium-catalyzed intramolecular Heck-type cascade reaction is proposed (Scheme 2). It was initiated by the oxidative addition of **1**, affording the aryl palladium species **I**. Subsequently, the intramolecular alkene insertion into the carbon–palladium bond led to intermediate **II**, which was then captured by the diazo compound **III** to generate metal carbene species **IV**.[10−15] Next the migratory insertion occurred to give intermediate **V**, which would undergo regioselective *syn*-β-hydride elimination to form the polysubstituted olefins **3** and **6**. When **2** was derived from benzaldehyde and only H^a exists, the

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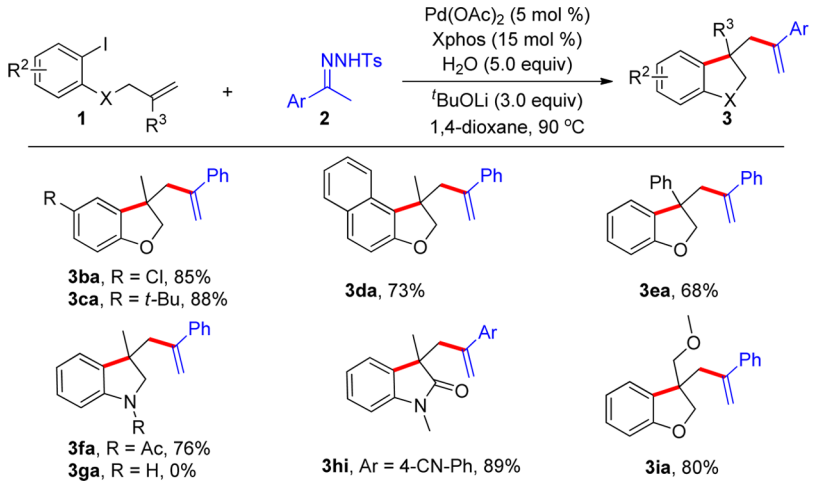
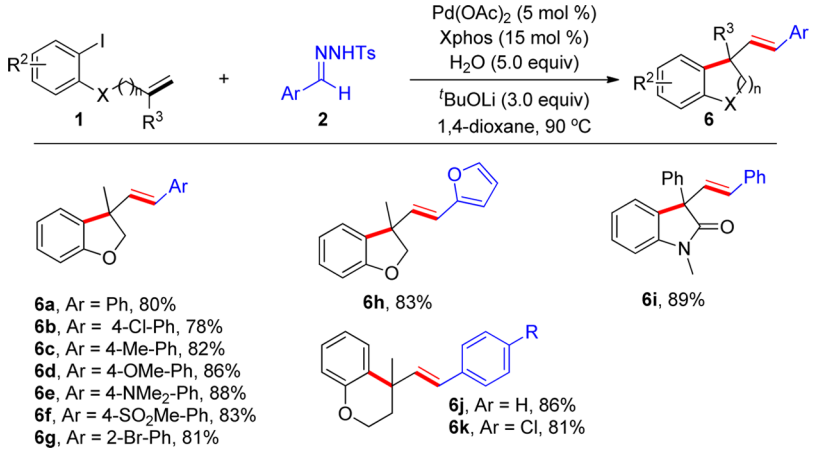
Table 3. Substrate Scope of Organic Halide Substrates[a,b]

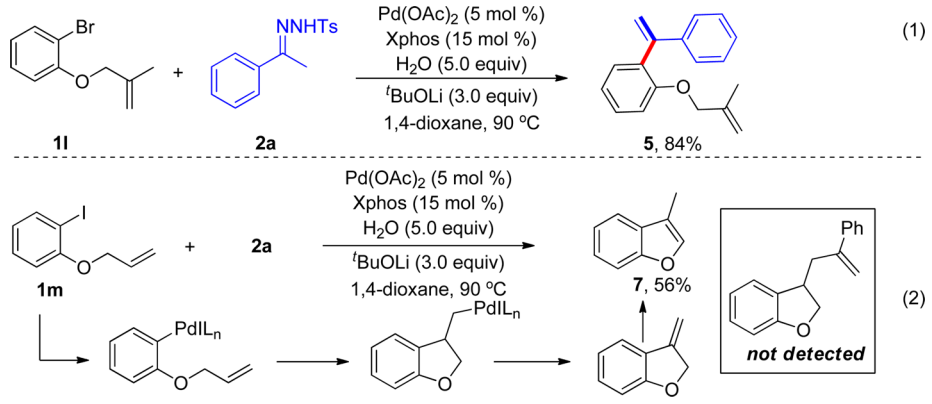


[a]Reaction conditions: all reactions were performed with **1** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), Xphos (15 mol %), H_2O (5.0 equiv), and LiO^tBu (3.0 equiv) in 2 mL of 1,4-dioxane at 90 °C for 8 h. [b]Isolated yields are given.

Table 4. Substrate Scope of *N*-Tosylhydrazones Derived from Benzaldehyde[a,b]



[a]Reaction conditions: all reactions were performed with **1** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), Xphos (15 mol %), H_2O (5.0 equiv), and LiO^tBu (3.0 equiv) in 2 mL of 1,4-dioxane at 90 °C for 8 h. [b]Isolated yields are given.



elimination of H^a occurred to afford the disubstituted alkenes **6**, and this result is in consist with Gu's work.[34] As for substrates derived from ketone with both H^a and H^b, the regioselective elimination of H^b was favored under the optimal reaction conditions, thus leading to the formation of the less-substituted terminal olefins **3**. If allene substrates were employed, **8** and **9** were obtained via the process indicated in the right cycle. The high regio- and stereoselectivity for the C−C double-bond formation observed in this reaction could be explained by the syn arrangement required for the *β*-hydride elimination in intermediate **V**, the conformation with less steric hindrance was favored to undergo the *β*-hydride elimination, and the use of a bulky ligand could further promote the selectivity.[62,63]

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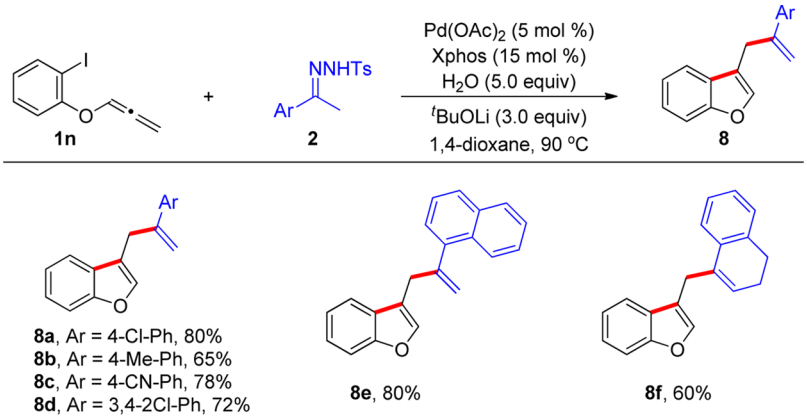
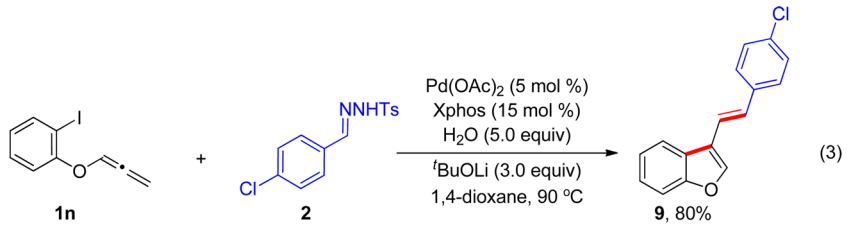
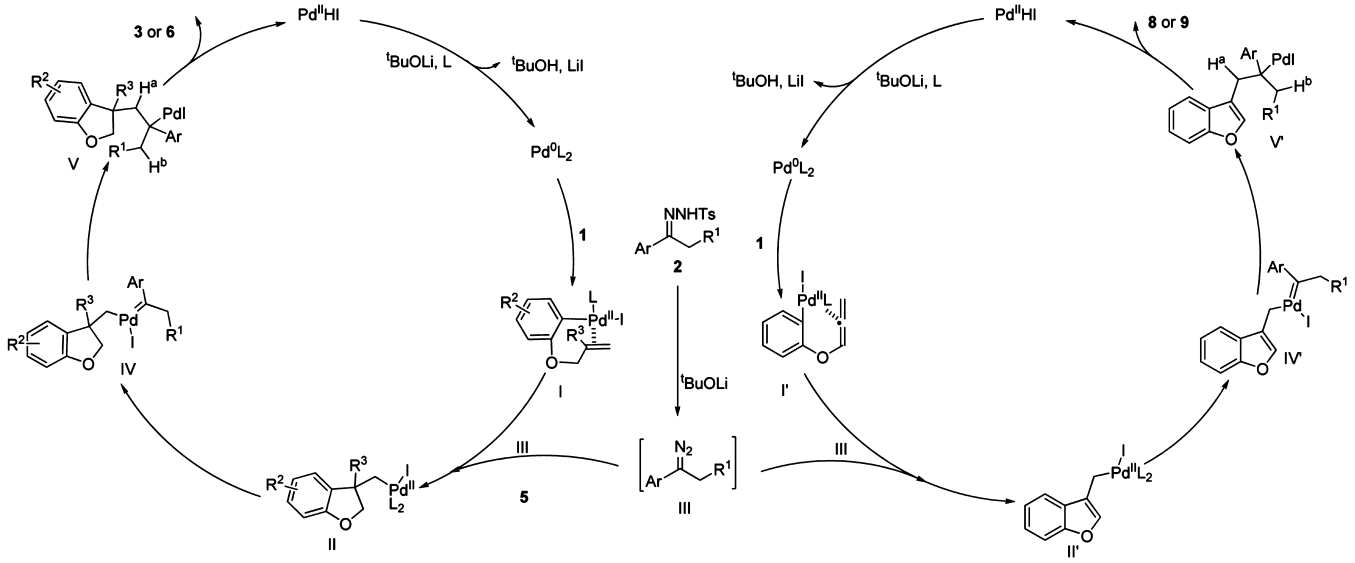
Table 5. Substrate Scope of Allene Substrates[a,b]



[a]Reaction conditions: all reactions were performed with **1i** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), Xphos (15 mol %), H_2O (5.0 equiv), and LiO^tBu (3.0 equiv) in 2 mL of 1,4-dioxane at 90 °C for 8 h. [b]Isolated yields are given.



Scheme 2. A Tentative Mechanism for the Pd-Catalyzed Intramolecular Heck-Type Cascade Reaction



CONCLUSION

In conclusion, we have developed a mild and efficient palladium-catalyzed Heck-type cascade reaction with various *N*-tosylhydrazones for the synthesis of functionalized olefins with high selectivity. This transformation involves the processes of olefin insertion/alkyl palladium carbene migratory insertion and regioselective β-hydride elimination. Different types of functionalized olefins were obtained via the switch of substrates; both inactive alkenes and allenes were proved to be efficient for this Heck-type cascade reaction. The high regio- and stereoselectivity, good functional group tolerance, mild reaction conditions, and good to excellent yields make the present protocol very attractive. Therefore, this reaction is an attractive method to prepare benzofuran-, dihydrobenzofuran-, and indoline-containing alkene products and will find its potential applications in the synthesis of more complex and significant pharmaceuticals.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR 400 MHz spectra were recorded in $CDCl_3$ at 400 MHz, and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz respectively. The chemical shifts (d) were referenced to TMS. GC−MS was performed using electron ionization. EI-HRMS for **6k**, **7a**, **7d**, APCI-HRMS for **6b**, **6h**, and ESI-HRMS for others were performed with a LCMS-IT-TOF mass spectrometer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets. TLC was performed using commercially

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prepared 100−400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

Typical Procedure for Synthesis of Aryl Iodides 1a−d, 1g, 1i, 1l, 1m.[42] The starting phenol (5 mmol, 1 equiv) and K_2CO_3 (10 mmol, 2 equiv) were suspended in DMF (0.2 M). Methallyl chloride (6.5 mmol, 1.3 equiv) was added by syringe, and the reaction was heated to 70 °C overnight. After cooling, the mixture was diluted with EtOAc and transferred to a separatory funnel. The organic phase was washed twice with H_2O and once with brine. Drying over $MgSO_4$, filtration, and rotary evaporation provided the crude material. The residue was separated by column chromatography on a silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding aryl iodides products **1a−d**, **1g**, **1i**, **1l**, **1m**.

1-Iodo-2-(2-methylallyloxy)benzene (1a).[42] Colorless oil (1.23 g, 90% yield); R_f 0.70 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 5.25 (s, 1H), 5.07 (s, 1H), 4.52 (s, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 140.1, 139.3, 128.9, 122.4, 112.8, 112.2, 86.5, 72.4, 19.4. MS (EI, 70 eV) m/z 274, 259, 220, 147, 91, 64.

4-Chloro-2-iodo-1-(2-methylallyloxy)benzene (1b). Colorless oil (1.24 g, 80% yield); R_f 0.66 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.27 (d, J = 9.5 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 5.20 (s, 1H), 5.05 (s, 1H), 4.48 (s, 2H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 139.8, 138.5, 129.0, 126.3, 113.2, 112.6, 86.6, 72.8, 19.4. MS (EI, 70 eV) m/z 308, 254, 181, 145, 97. IR (KBr, cm^{-1}): 3110, 2982, 1570, 1047, 804; ESI-HRMS calcd for $C_{10}H_{10}ClINaO$ $[M + Na]^+$ 330.9357; found, 330.9355.

4-(*tert*-Butyl)-2-iodo-1-((2-methylallyl)oxy)benzene (1c). Colorless oil (1.45 g, 88% yield); R_f 0.71 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.27 (d, J = 8.5 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 5.18 (s, 1H), 5.00 (s, 1H), 4.45 (s, 2H), 1.86 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 145.5, 140.3, 136.4, 126.1, 112.7, 111.7, 86.4, 72.6, 33.9, 31.3, 19.4. MS (EI, 70 eV) m/z 330, 315, 274, 203, 173, 105, 91, 57. IR (KBr, cm^{-1}): 3160, 2982, 1441, 1361, 803; ESI-HRMS calcd for $C_{14}H_{19}INaO$ $[M + Na]^+$ 353.0373; found, 353.0372.

1-Iodo-2-(2-methylallyloxy)naphthalene (1d). Colorless oil (1.46 g, 90% yield); R_f 0.72 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 8.9 Hz, 1H), 5.28 (s, 1H), 5.08 (s, 1H), 4.66 (s, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 140.3, 135.6, 131.1, 130.0, 129.8, 128.1, 127.9, 124.3, 114.1, 113.1, 88.2, 73.3, 19.5. MS (EI, 70 eV) m/z 324, 269, 241, 197, 142, 114. IR (KBr, cm^{-1}): 3118, 2978, 1450, 1046, 802; ESI-HRMS calcd for $C_{14}H_{13}INaO$ $[M + Na]^+$ 346.9903; found, 346.9899.

2-Iodo-*N*-(2-methylallyl)aniline (1g).[64] Colorless oil (0.54 g, 40% yield); R_f 0.68 (petroleum ether/EtOAc 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.52 (d, J = 8.2 Hz, 1H), 6.42 (t, J = 7.5 Hz, 1H), 4.93 (d, J = 20.1 Hz, 2H), 4.46 (s, 1H), 3.72 (s, 2H), 1.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 141.8, 138.9, 129.3, 118.6, 111.1, 110.9, 85.2, 49.9, 20.3. MS (EI, 70 eV) m/z 273, 232, 146, 130, 91.

1-Iodo-2-(2-(methoxymethyl)allyloxy)benzene (1i). Colorless oil (1.21 g, 80% yield); R_f 0.74 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.7 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 6.70 (t, J = 7.5 Hz, 1H), 5.44 (s, 1H), 5.29 (s, 1H), 4.58 (s, 2H), 4.07 (s, 2H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 140.7, 139.4, 129.3, 122.6, 115.0, 112.3, 86.5, 73.3, 69.4, 58.1. MS (EI, 70 eV) m/z 304, 272, 259, 145, 131, 85, 55. IR (KBr, cm^{-1}): 3110, 2961, 1489, 1047, 810; ESI-HRMS calcd for $C_{11}H_{13}INaO_2$ $[M + Na]^+$ 326.9852; found, 326.9859.

1-Bromo-2-(2-methylallyloxy)benzene (1l).[43] Colorless oil (1.04 g, 92% yield); R_f 0.70 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 8.7 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 5.16 (s, 1H), 5.01 (s, 1H), 4.49 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 140.2, 133.4, 128.3, 121.8, 113.4, 112.8, 112.3, 72.4, 19.3. MS (EI, 70 eV) m/z 226, 211, 172, 147, 133, 91, 63.

1-(Allyloxy)-2-iodobenzene (1m).[42] Colorless oil (1.17 g, 90% yield); R_f 0.72 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 1H), 7.31−7.23 (m, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.70 (t, J = 7.5 Hz, 1H), 6.06 (ddd, J = 15.7, 10.0, 4.7 Hz, 1H), 5.52 (d, J = 17.3 Hz, 1H), 5.31 (d, J = 10.6 Hz, 1H), 4.59 (d, J = 3.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 139.5, 132.6, 129.3, 122.6, 117.6, 112.5, 86.7, 69.7. MS (EI, 70 eV) m/z 260, 220, 191, 133, 105, 92.

Typical Procedure for Synthesis of Phenyl Propiolates 1h, 1j.[34] Methacryloyl chloride (0.12 mL, 1.2 mmol, 1.2 equiv) was added to a mixture of 2-iodoaniline (0.219 g, 1.0 mmol, 1.0 equiv), DMAP (6.0 mg, 0.05 mmol, 5 mol %), and Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv) in CH_2Cl_2 (2.0 mL) at −20 °C dropwise. After stirring at −20 °C for 30 min and room temperature overnight, the mixture was quenched with saturated $NaHCO_3$. The mixture was extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After filtration and concentration, the obtained crude amide was used in next step without purification. NaH (80 mg, 60% in mineral oil, 2.0 mmol, 2.0 equiv) was added to a solution of the above crude amide in THF (4.0 mL) at 0 °C in portions. After stirring for 20 min at 0 °C, MeI (0.19 mL, 3.0 mmol, 3.0 equiv) was added dropwise and the reaction mixture was allowed to warm to room temperature and stirred for another 2 h. The reaction was quenched with water, and the resulting mixture was extracted with ethyl acetate twice. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was separated by column chromatography on a silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding products **1h**, **1j**.

***N*-(2-Iodophenyl)-*N*-methylmethacrylamide (1h).**[34] Solid (0.18 g, 58% yield); R_f 0.47 (petroleum ether/EtOAc 4/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.0, 1.2 Hz, 1 H), 7.35 (dd, J = 7.6, 7.2 Hz, 1 H), 7.18 (d, J = 7.6 Hz, 1 H), 7.07−6.91 (m, 1 H), 5.05 (s, 1H), 4.98 (s, 1 H), 3.24 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 146.6, 140.0, 139.8, 129.2, 129.1, 129.1, 118.9, 98.8, 36.7, 20.3. MS (EI, 70 eV) m/z 301, 245, 174, 134, 69.

***N*-(2-Iodophenyl)-*N*-methyl-2-phenylacrylamide (1j).**[34] Solid (0.26 g, 70% yield); R_f 0.50 (petroleum ether/EtOAc 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 1H), 7.21 (d, J = 4.4 Hz, 3H), 7.13 (d, J = 4.4 Hz, 2H), 7.03 (dd, J = 14.4, 6.9 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 5.62 (s, 1H), 5.34 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 145.6, 145.3, 139.8, 136.9, 129.7, 129.0, 128.7, 128.2, 127.9, 126.0, 117.3, 99.1, 36.3. MS (EI, 70 eV) m/z 363, 263, 208, 103, 77.

Typical Procedure for Synthesis of 1-Iodo-2-(2-phenylallyloxy)benzene 1e, 1k.[42] A solution of diethyl azodicarboxylate (DEAD) (0.3 mL, 0.98 mmol, 1.3 equiv) in CH_2Cl_2 (3.0 mL) was added slowly to a mixture of 2-phenylprop-2-en-1-ol (0.27 g, 0.98 mmol, 1.3 equiv), PPh_3 (0.34 g, 2 mmol, 1.3 equiv), and 2-iodophenol (0.160 g, 1.5 mmol, 1.0 equiv) in CH_2Cl_2 (3.0 mL) at 0 °C. The resulting solution was allowed to warm to room temperature and stirred for 1 h. The reaction was quenched with water and extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was separated by column chromatography on a silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding products **1e**, **1k**.

1-Iodo-2-(2-phenylallyloxy)benzene (1e).[42] Colorless oil (0.25 g, 76% yield); R_f 0.69 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 7.4 Hz, 2H), 7.32 (m, 2H), 6.86 (d, J = 8.2 Hz, 1H), 6.72 (t, J = 7.5 Hz, 1H), 5.62 (d, J = 3.6 Hz, 2H), 4.93 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 142.4, 139.5, 138.3, 129.3, 128.4, 128.0, 126.1, 122.7, 114.6, 112.5, 86.6, 70.4. MS (EI, 70 eV) m/z 336, 259, 220, 209, 91, 64.

1-Iodo-2-(3-methylbut-3-enyloxy)benzene (1k).[65] Colorless oil (0.23 g, 80% yield); R_f 0.68 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.7 Hz, 1H), 7.27 (t, J = 7.9 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.69 (t, J = 7.5 Hz, 1H), 4.85 (d, J = 8.2 Hz, 2H), 4.11 (t, J = 6.8 Hz, 2H), 2.56 (t, J = 6.8 Hz, 2H), 1.86 (d, J = 13.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 142.0, 139.5, 129.3, 122.4, 112.4, 112.1, 86.7, 68.0, 37.1, 23.0. MS (EI, 70 eV) m/z 288, 274, 259, 228, 147, 69.

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Typical Procedure for Synthesis of *N*-(2-Iodophenyl)-*N*-(2-methylallyl)acetamide (1f).[34] To a suspension of NaH (100 mg, 60% in oil, 2 mmol) in DMF (10 mL) was added 0.52 g (2 mmol) of *N*-(2-iodophenyl)acetamide in DMF (5 mL). When the evolution of H_2 had ceased, methallyl chloride (0.4 mL, 4 mmol) was added. The reaction mixture was heated to 80 °C overnight. The reaction mixture was quenched with water and extracted with Et_2O. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was separated by column chromatography on a silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product **1f**.

***N*-(2-Iodophenyl)-*N*-(2-methylallyl)acetamide (1f).**[34] Solid (0.54 g, 87% yield); R_f 0.66 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.9 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 5.00 (d, J = 14.9 Hz, 1H), 4.84 (s, 1H), 4.67 (s, 1H), 3.35 (d, J = 14.8 Hz, 1H), 1.82 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 144.7, 140.3, 140.2, 130.2, 129.7, 129.3, 114.1, 100.0, 53.8, 22.8, 20.6. MS (EI, 70 eV) m/z 315, 273, 188, 146, 130, 91.

Typical Procedure for Synthesis of 2-Iodophenyl Propadienyl Ether 1n.[66] A suspension of 2-iodophenol (2.20 g, 10 mmol), propargyl bromide (1.79 g, 12 mmol), and potassium carbonate (1.66 g, 12 mmol) in THF (25 mL) was boiled under reflux for 16 h. Water (50 mL) and ethyl acetate (20 mL) were then added, the organic layer was separated, dried (Na_2SO_4), and evaporated under reduced pressure, and the residue was dissolved in 3:1 v/v *tert*-butyl alcohol−THF (20 mL). Potassium *tert*-butoxide (1.35 g, 12 mmol) was then added, and the resulting mixture was stirred at room temperature for 16 h. Then the solvent was evaporated under reduced pressure, and dichloromethane (20 mL) was added. The organic layer was separated, washed with water (20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was separated by column chromatography with petroleum ether/ethyl acetate as the eluent on a silica gel column to afford the corresponding product **1n**.

1-Iodo-2-(propa-1,2-dienyloxy)benzene (1n).[66] Colorless oil (1.4 g, 55% yield); R_f 0.75 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.84−6.76 (m, 2H), 5.43 (d, J = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 156.2, 139.6, 129.8, 124.7, 118.4, 116.8, 90.4, 87.2. MS (EI, 70 eV) m/z 258, 219, 190, 131, 103, 91.

Typical Procedure for Synthesis of *N*-Tosylhydrazones 2a−x..[27−29,57−59] A solution of pure $TsNHNH_2$ (5 mmol) in methanol (5 mL) was stirred and heated to 60 °C until the $TsNHNH_2$ was completely dissolved. Then carbonyl compounds were dropped into the mixture slowly. After approximately 5−30 min, the crude products were obtained as precipitates. The residue was separated by column chromatography on a silica gel to afford the corresponding *N*-tosylhydrazone products **2a**−**x** with petroleum ether/ethyl acetate as the eluent.

Typical Procedure for the Synthesis of 3-Methyl-3-(2-phenylallyl)-2,3-dihydrobenzofuran. To a Schlenk tube were added **1a** (0.3 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), Xphos (15 mol %), H_2O (5.0 equiv), and LiO^tBu (3.0 equiv) in 2 mL of 1,4-dioxane and stirred at 90 °C for the desired reaction time. After completion, the reaction was quenched with aqueous NH_4Cl, and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography using light petroleum ether/ethyl acetate as eluent to afford the desired product **3aa**−**3ia**, **5**, **6a**−**k**, **8a**−**f**, and **9**.

3-Methyl-3-(2-phenylallyl)-2,3-dihydrobenzofuran (3aa). Colorless oil (62 mg, 83% yield); R_f 0.58 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.19 (m, 5H), 7.07 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.80 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.24 (s, 1H), 4.99 (s, 1H), 4.27 (d, J = 8.8 Hz, 1H), 3.87 (d, J = 8.7 Hz, 1H), 2.86 (q, J = 13.7 Hz, 2H), 1.23 (d, J = 11.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 145.8, 142.6, 135.3, 128.2, 128.0, 127.3, 126.5, 122.9, 120.3, 117.4, 109.6, 81.7, 45.8, 45.6, 25.3; IR (KBr, cm^{-1}): 3085, 2926, 1630, 1540, 1224, 1098, 745; ESI-HRMS calcd for $C_{18}H_{18}NaO$ $[M + Na]^+$ 273.1250; found, 273.1253.

3-(2-(4-Fluorophenyl)allyl)-3-methyl-2,3-dihydrobenzofuran (3ab). Colorless oil (68 mg, 85% yield); R_f 0.60 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 7.5, 5.2 Hz, 2H), 7.05 (t, J = 7.7 Hz, 1H), 7.00−6.90 (m, 3H), 6.77 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 5.20 (s, 1H), 4.97 (s, 1H), 4.28 (d, J = 8.7 Hz, 1H), 3.90 (d, J = 8.7 Hz, 1H), 2.91−2.69 (m, 2H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 238.0 Hz), 159.2, 144.9, 138.6 (d, J = 4.0 Hz), 135.0, 128.1 (d, J = 3.0 Hz), 128.0, 123.0, 120.3, 117.4, 115.0 (d, J = 21.0 Hz), 109.6, 81.7, 45.9, 45.8, 25.4. IR (KBr, cm^{-1}): 3074, 2964, 1600, 1508, 1227, 1014, 749; ESI-HRMS calcd for $C_{18}H_{17}FNaO$ $[M + Na]^+$ 291.1156; found, 291.1156.

3-(2-(4-Chlorophenyl)allyl)-3-methyl-2,3-dihydrobenzofuran (3ac). Colorless oil (68 mg, 80% yield); R_f 0.58 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.17 (m, 4H), 7.06 (t, J = 7.7 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 5.22 (s, 1H), 4.99 (s, 1H), 4.28 (d, J = 8.8 Hz, 1H), 3.90 (d, J = 8.8 Hz, 1H), 2.88−2.73 (m, 2H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 144.7, 141.0, 134.8, 133.1, 128.3, 128.1, 127.8, 123.0, 120.3, 117.9, 109.6, 81.6, 45.8, 45.7, 25.4. IR (KBr, cm^{-1}): 3084, 2968, 1612, 1504, 1198, 745; ESI-HRMS calcd for $C_{18}H_{17}ClNaO$ $[M + Na]^+$ 307.0860; found, 307.0857.

3-(2-(4-Bromophenyl)allyl)-3-methyl-2,3-dihydrobenzofuran (3ad). Colorless oil (80 mg, 82% yield); R_f 0.59 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.06 (t, J = 7.7 Hz, 1H), 6.97 (d, J = 7.4 Hz, 1H), 6.78 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 5.23 (s, 1H), 4.99 (s, 1H), 4.28 (d, J = 8.8 Hz, 1H), 3.90 (d, J = 8.8 Hz, 1H), 2.87−2.70 (m, 2H), 1.24 (d, J = 10.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 144.8, 141.4, 134.8, 131.3, 128.1, 128.1, 122.9, 121.2, 120.3, 117.9, 109.6, 81.6, 45.8, 45.7, 25.4. IR (KBr, cm^{-1}): 3078, 2964, 1597, 1508, 1226, 748; ESI-HRMS calcd for $C_{18}H_{17}BrNaO$ $[M + Na]^+$ 351.0355; found, 351.0353.

3-Methyl-3-(2-*p*-tolylallyl)-2,3-dihydrobenzofuran (3ae). Colorless oil (70 mg, 89% yield); R_f 0.58 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.9 Hz, 3H), 7.04 (d, J = 7.6 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H), 5.22 (s, 1H), 4.94 (s, 1H), 4.27 (d, J = 8.8 Hz, 1H), 3.85 (d, J = 8.7 Hz, 1H), 2.96−2.71 (m, 2H), 2.33 (s, 3H), 1.23 (d, J = 20.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 145.6, 139.7, 137.1, 135.6, 129.0, 128.0, 126.4, 122.9, 120.3, 116.7, 109.6, 81.8, 45.8, 45.6, 25.3, 21.0. IR (KBr, cm^{-1}): 3132, 2966, 1598, 1472, 1130, 750; ESI-HRMS calcd for $C_{19}H_{20}NaO$ $[M + Na]^+$ 287.1406; found, 287.1409.

3-(2-(Biphenyl-4-yl)allyl)-3-methyl-2,3-dihydrobenzofuran (3af). Colorless oil (79 mg, 81% yield); R_f 0.62 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.7 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.34 (dd, J = 16.6, 7.9 Hz, 3H), 7.05 (dd, J = 17.2, 7.8 Hz, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H), 5.31 (s, 1H), 5.00 (s, 1H), 4.33 (d, J = 8.7 Hz, 1H), 3.91 (d, J = 8.7 Hz, 1H), 2.88 (q, J = 13.7 Hz, 2H), 1.24 (d, J = 10.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 145.3, 141.4, 140.6, 140.1, 135.2, 128.7, 128.0, 127.3, 126.9, 126.9, 123.0, 120.3, 117.3, 109.6, 81.8, 45.8, 45.6, 25.4. IR (KBr, cm^{-1}): 3033, 2964, 1680, 1477, 1127, 747; ESI-HRMS calcd for $C_{24}H_{22}NaO$ $[M + Na]^+$ 349.1563; found, 349.1570.

3-(2-(4-Methoxyphenyl)allyl)-3-methyl-2,3-dihydrobenzofuran (3ag). Yellow oil (72 mg, 86% yield); R_f 0.68 (petroleum ether/EtOAc 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 7.7 Hz, 2H), 7.10−7.00 (m, 2H), 6.82−6.77 (m, 3H), 6.73 (d, J = 7.9 Hz, 1H), 5.19 (s, 1H), 4.91 (s, 1H), 4.28 (d, J = 8.7 Hz, 1H), 3.86 (d, J = 8.7 Hz, 1H), 3.79 (s, 3H), 2.87−2.74 (m, 2H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 159.0, 145.1, 135.5, 135.0, 128.0, 127.6, 122.9, 120.3, 116.0, 113.6, 109.6, 81.8, 55.2, 45.8, 45.6, 25.3. IR (KBr, cm^{-1}): 3090, 2959, 1605, 1510, 1246, 749; ESI-HRMS calcd for $C_{19}H_{20}NaO_2$ $[M + Na]^+$ 303.1356; found, 303.1361.

4-(4-(3-(3-Methyl-2,3-dihydrobenzofuran-3-yl)prop-1-en-2-yl)phenyl)morpholine (3ah). Colorless oil (86 mg, 86% yield); R_f 0.69 (petroleum ether/EtOAc 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ

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7.24 (d, J = 8.1 Hz, 2H), 7.06 (dd, J = 17.1, 7.8 Hz, 2H), 6.82 (dd, J = 12.7, 7.5 Hz, 3H), 6.73 (d, J = 7.9 Hz, 1H), 5.20 (s, 1H), 4.90 (s, 1H), 4.29 (d, J = 8.8 Hz, 1H), 3.89−3.82 (m, 5H), 3.20−3.13 (m, 4H), 2.82 (q, J = 13.7 Hz, 2H), 1.22 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 159.2, 150.5, 145.1, 135.6, 133.9, 128.0, 127.3, 122.9, 120.3, 115.5, 115.2, 109.5, 81.8, 66.8, 49.1, 45.8, 45.4, 25.3. IR (KBr, cm^{-1}): 3084, 2931, 1603, 1248, 751; ESI-HRMS calcd for $C_{22}H_{26}NO_2$ $[M + H]^+$ 336.1958; found, 336.1962.

4-(3-(3-Methyl-2,3-dihydrobenzofuran-3-yl)prop-1-en-2-yl)-benzonitrile (3ai). Colorless oil (64 mg, 78% yield); R_f 0.43 (petroleum ether/EtOAc 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.02−6.96 (m, 1H), 6.90 (d, J = 7.4 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.65 (t, J = 6.3 Hz, 1H), 5.30 (s, 1H), 5.12 (s, 1H), 4.31 (d, J = 8.8 Hz, 1H), 3.96 (d, J = 8.8 Hz, 1H), 2.83 (q, J = 13.8 Hz, 2H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 147.0, 144.5, 133.9, 131.8, 128.2, 127.0, 123.0, 120.3, 119.9, 118.8, 110.6, 109.6, 81.39, 45.74, 25.36. IR (KBr, cm^{-1}): 3079, 2964, 1602, 1476, 751; ESI-HRMS calcd for $C_{19}H_{17}NNaO$ $[M + Na]^+$ 298.1202; found, 298.1204.

3-Methyl-3-(2-(4-nitrophenyl)allyl)-2,3-dihydrobenzofuran (3aj). Yellow oil (63 mg, 72% yield); R_f 0.52 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 6.99 (t, J = 7.7 Hz, 1H), 6.91 (d, J = 7.4 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 5.35 (s, 1H), 5.16 (s, 1H), 4.34 (d, J = 8.8 Hz, 1H), 3.98 (d, J = 8.8 Hz, 1H), 2.86 (q, J = 13.8 Hz, 2H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 149.0, 146.8, 144.3, 133.8, 128.3, 127.1, 123.3, 123.0, 120.5, 120.3, 109.6, 81.4, 46.0, 45.8, 25.4. IR (KBr, cm^{-1}): 3071, 2969, 1596, 1401, 751; ESI-HRMS calcd for $C_{18}H_{17}NNaO_3$ $[M + Na]^+$ 318.1101; found, 318.1106.

3-(2-(3-Methoxyphenyl)allyl)-3-methyl-2,3-dihydrobenzofuran (3ak). Colorless oil (67 mg, 80% yield); R_f 0.66 (petroleum ether/EtOAc 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.9 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.84−6.76 (m, 3H), 6.73 (d, J = 8.0 Hz, 1H), 5.25 (s, 1H), 4.98 (s, 1H), 4.29 (d, J = 8.8 Hz, 1H), 3.89 (d, J = 8.8 Hz, 1H), 3.80 (d, J = 7.2 Hz, 3H), 2.84 (q, J = 13.7 Hz, 2H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.2, 145.7, 144.1, 135.3, 129.2, 128.0, 123.0, 120.3, 119.1, 117.4, 112.6, 112.5, 109.6, 81.7, 55.2, 45.8, 45.7, 25.3. IR (KBr, cm^{-1}): 3073, 2960, 1597, 1479, 751; ESI-HRMS calcd for $C_{19}H_{20}NaO_2$ $[M + Na]^+$ 303.1356; found, 303.1358.

***N*-(4-(3-(3-Methyl-2,3-dihydrobenzofuran-3-yl)prop-1-en-2-yl)phenyl)acetamide (3al).** Colorless oil (81 mg, 88% yield); R_f 0.48 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.1 Hz, 2H), 7.35 (s, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.11−6.95 (m, 3H), 6.79 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 5.25 (s, 1H), 4.98 (s, 1H), 4.29 (d, J = 8.7 Hz, 1H), 3.89 (d, J = 8.7 Hz, 1H), 2.89−2.76 (m, 2H), 2.16 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 159.2, 145.3, 143.4, 137.9, 135.2, 128.9, 128.0, 123.0, 122.5, 120.3, 118.8, 118.0, 117.8, 109.5, 81.7, 45.8, 45.6, 25.4, 24.6. IR (KBr, cm^{-1}): 3302, 3082, 2964, 1667, 1600, 1481, 748; ESI-HRMS calcd for $C_{20}H_{22}NO_2$ $[M + H]^+$ 308.1645; found, 308.1649.

3-(2-(2-Methoxyphenyl)allyl)-3-methyl-2,3-dihydrobenzofuran (3am). Colorless oil (71 mg, 85% yield); R_f 0.65 (petroleum ether/EtOAc 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.9 Hz, 1H), 7.11−6.96 (m, 3H), 6.87 (t, J = 7.4 Hz, 1H), 6.78 (t, J = 7.4 Hz, 2H), 6.69 (d, J = 7.9 Hz, 1H), 5.10 (d, J = 4.1 Hz, 2H), 4.15 (d, J = 8.7 Hz, 1H), 3.82 (d, J = 8.8 Hz, 1H), 3.78 (s, 3H), 3.06 (d, J = 13.7 Hz, 1H), 2.82 (d, J = 13.7 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 156.3, 145.6, 135.8, 132.0, 130.1, 128.6, 127.8, 122.7, 120.7, 120.2, 119.0, 110.5, 109.4, 81.8, 55.2, 46.3, 45.6, 26.0. IR (KBr, cm^{-1}): 3072, 2960, 1597, 1479, 751; ESI-HRMS calcd for $C_{19}H_{20}NaO_2$ $[M + Na]^+$ 303.1356; found, 303.1360.

3-(2-(3,4-Dichlorophenyl)allyl)-3-methyl-2,3-dihydrobenzofuran (3an). Colorless oil (77 mg, 81% yield); R_f 0.60 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.25 (m, 2H), 7.04 (t, J = 8.4 Hz, 2H), 6.95 (d, J = 7.3 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 5.24 (s, 1H), 5.03 (s, 1H), 4.32 (d, J = 8.8 Hz, 1H), 3.96 (d, J = 8.8 Hz, 1H), 2.78 (q, J = 13.8 Hz, 2H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 143.8, 142.4, 134.2, 132.2, 131.1, 130.0, 128.4, 128.2, 125.8, 123.0, 120.3, 118.7, 109.6, 81.5, 45.8, 45.8, 25.4. IR (KBr, cm^{-1}): 3086, 2926, 1598, 1400, 1200, 750; ESI-HRMS calcd for $C_{18}H_{16}Cl_2NaO$ $[M + Na]^+$ 341.0470; found, 341.0467.

5-(3-(3-Methyl-2,3-dihydrobenzofuran-3-yl)prop-1-en-2-yl)-benzo[*d*][1,3]dioxole (3ao). Colorless oil (67 mg, 76% yield); R_f 0.65 (petroleum ether/EtOAc 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11−6.98 (m, 2H), 6.79 (dd, J = 15.8, 7.3 Hz, 3H), 6.72 (t, J = 8.0 Hz, 2H), 5.93 (s, 2H), 5.17 (s, 1H), 4.91 (s, 1H), 4.30 (d, J = 8.8 Hz, 1H), 3.89 (d, J = 8.8 Hz, 1H), 2.90−2.67 (m, 2H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.5, 146.9, 145.3, 136.8, 135.3, 128.0, 122.9, 120.2, 120.0, 116.5, 109.6, 108.0, 107.2, 101.0, 81.7, 45.9, 45.8, 25.3. IR (KBr, cm^{-1}): 3090, 2850, 1650, 1490, 1250, 750; ESI-HRMS calcd for $C_{19}H_{18}NaO_3$ $[M + Na]^+$ 317.1148; found, 317.1156.

3-(2-(Furan-2-yl)allyl)-3-methyl-2,3-dihydrobenzofuran (3ap). Yellow oil (49 mg, 68% yield); R_f 0.53 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.16−7.04 (m, 2H), 6.83 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 6.35−6.29 (m, 1H), 6.20 (d, J = 3.0 Hz, 1H), 5.60 (s, 1H), 4.83 (s, 1H), 4.47 (d, J = 8.7 Hz, 1H), 4.05 (d, J = 8.7 Hz, 1H), 2.78−2.59 (m, 2H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 155.1, 141.8, 135.2, 133.8, 128.1, 123.1, 120.4, 113.7, 111.2, 109.7, 106.6, 82.0, 45.7, 42.8, 24.7. IR (KBr, cm^{-1}): 3064, 2918, 1630, 1427, 1111, 717; ESI-HRMS calcd for $C_{16}H_{16}NaO_2$ $[M + Na]^+$ 263.1043; found, 263.1040.

3-Methyl-3-(2-(thiophen-2-yl)allyl)-2,3-dihydrobenzofuran (3aq). Yellow oil (63 mg, 83% yield); R_f 0.48 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.03 (m, 3H), 6.90 (d, J = 4.0 Hz, 2H), 6.84−6.73 (m, 2H), 5.45 (s, 1H), 4.84 (s, 1H), 4.44 (d, J = 8.8 Hz, 1H), 4.01 (d, J = 8.7 Hz, 1H), 2.85−2.73 (m, 2H), 1.32 (d, J = 9.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 146.2, 138.2, 135.1, 128.1, 127.3, 124.4, 123.9, 123.0, 120.3, 115.6, 109.7, 82.0, 45.9, 45.5, 24.9. IR (KBr, cm^{-1}): 3091, 2968, 2360, 1646, 1017, 747; ESI-HRMS calcd for $C_{16}H_{16}NaOS$ $[M + Na]^+$ 279.0814; found, 279.0814.

3-Methyl-3-(2-(naphthalen-1-yl)allyl)-2,3-dihydrobenzofuran (3ar). Colorless oil (76 mg, 85% yield); R_f 0.52 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−7.92 (m, 1H), 7.81 (dd, J = 6.1, 3.2 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.44 (dd, J = 6.3, 3.2 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.25−7.19 (m, 1H), 7.02 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 7.4 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 5.35 (s, 1H), 5.23 (s, 1H), 4.09 (d, J = 8.8 Hz, 1H), 3.85 (d, J = 8.8 Hz, 1H), 3.04 (d, J = 13.7 Hz, 1H), 2.94 (d, J = 13.7 Hz, 1H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 145.1, 141.1, 135.4, 133.8, 130.8, 128.4, 127.9, 127.5, 125.8, 125.6, 125.4, 125.2, 122.7, 120.2, 109.5, 81.3, 48.5, 45.9, 26.2. IR (KBr, cm^{-1}): 3092, 2964, 2863, 1640, 1054, 749; ESI-HRMS calcd for $C_{22}H_{20}NaO$ $[M + Na]^+$ 323.1406; found, 323.1412.

3-((3,4-Dihydronaphthalen-1-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3as). Colorless oil (69 mg, 84% yield); R_f 0.56 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.7 Hz, 1H), 7.15−7.00 (m, 5H), 6.85−6.71 (m, 2H), 5.72 (t, J = 4.5 Hz, 1H), 4.47 (d, J = 8.7 Hz, 1H), 3.99 (d, J = 8.7 Hz, 1H), 2.83 (d, J = 14.0 Hz, 1H), 2.75 (s, 1H), 2.71−2.64 (m, 2H), 2.17 (dd, J = 12.4, 7.7 Hz, 2H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 136.5, 135.5, 135.4, 133.1, 129.4, 128.0, 127.5, 126.5, 126.1, 123.1, 123.0, 120.2, 109.6, 82.2, 46.1, 41.7, 28.6, 25.0, 23.2. IR (KBr, cm^{-1}): 3059, 2927, 1598, 1478, 925, 745; ESI-HRMS calcd for $C_{20}H_{20}NaO$ $[M + Na]^+$ 299.1406; found, 299.1402.

4-((3-Methyl-2,3-dihydrobenzofuran-3-yl)methyl)-2*H*-chromene (3at). Colorless oil (66 mg, 80% yield); R_f 0.61 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dt, J = 13.2, 6.8 Hz, 4H), 6.81 (dt, J = 14.0, 5.2 Hz, 4H), 5.43 (t, J = 3.7 Hz, 1H), 4.65 (d, J = 3.7 Hz, 2H), 4.46 (d, J = 8.7 Hz, 1H), 4.06 (d, J = 8.7 Hz, 1H), 2.76 (d, J = 14.1 Hz, 1H), 2.67 (d, J = 14.1 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 154.3, 135.0, 130.8, 128.8, 128.2, 124.4, 123.7, 123.2, 122.2, 121.0, 120.4, 116.2, 109.7, 82.1, 65.0, 45.9, 40.3, 24.8. IR (KBr, cm^{-1}): 3053, 2928, 1596, 1109, 743; ESI-HRMS calcd for $C_{19}H_{18}NaO_2$ $[M + Na]^+$ 301.1199; found, 301.1198.

3-((1*H*-Inden-3-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3au). Colorless oil (67 mg, 86% yield); R_f 0.57 (petroleum ether/

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EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.3 Hz, 1H), 7.25 (d, J = 3.7 Hz, 2H), 7.18 (dd, J = 10.7, 6.6 Hz, 1H), 7.13 (t, J = 7.9 Hz, 1H), 7.09 (d, J = 7.4 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.08 (s, 1H), 4.55 (d, J = 8.7 Hz, 1H), 4.12 (d, J = 8.7 Hz, 1H), 3.32 (s, 2H), 2.97−2.80 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 146.0, 143.9, 140.3, 135.4, 131.7, 128.2, 126.0, 124.5, 123.6, 123.0, 120.4, 119.2, 109.7, 82.2, 45.9, 38.0, 37.5, 25.4. IR (KBr, cm^{-1}): 3058, 2925, 1599, 974, 750; ESI-HRMS calcd for $C_{19}H_{18}NaO$ [M + Na]$^+$ 285.1250; found, 285.1254.

(*E*)-3-Methyl-3-(2-phenylbut-2-enyl)-2,3-dihydrobenzofuran (3av). Colorless oil (69 mg, 88% yield); R_f 0.55 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.18 (m, 5H), 7.13−7.01 (m, 2H), 6.81 (t, J = 7.4 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 5.73 (q, J = 6.9 Hz, 1H), 4.16 (d, J = 8.7 Hz, 1H), 3.81 (d, J = 8.7 Hz, 1H), 2.95 (d, J = 13.8 Hz, 1H), 2.79 (d, J = 13.8 Hz, 1H), 1.56 (d, J = 6.9 Hz, 3H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 145.0, 138.0, 135.4, 128.2, 128.0, 127.7, 126.7, 126.6, 123.1, 120.3, 109.5, 82.6, 46.6, 39.1, 24.7, 14.6. IR (KBr, cm^{-1}): 3025, 2962, 1644, 1474, 745; ESI-HRMS calcd for $C_{19}H_{20}NaO$ [M + Na]$^+$ 287.1406; found, 287.1412.

(*E*)-3-Methyl-3-(2-phenylpent-2-enyl)-2,3-dihydrobenzofuran (3aw). Colorless oil (65 mg, 78% yield); R_f 0.54 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 4H), 7.21 (d, J = 4.0 Hz, 1H), 7.13−6.97 (m, 2H), 6.81 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H), 5.60 (t, J = 7.2 Hz, 1H), 4.15 (d, J = 8.6 Hz, 1H), 3.80 (d, J = 8.6 Hz, 1H), 2.94 (d, J = 13.7 Hz, 1H), 2.80 (d, J = 13.9 Hz, 1H), 2.09−1.87 (m, 2H), 1.13 (s, 3H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 145.0, 136.4, 135.6, 135.5, 128.2, 128.0, 126.8, 126.6, 123.0, 120.3, 109.6, 82.5, 46.4, 39.5, 24.8, 22.3, 14.0. IR (KBr, cm^{-1}): 3059, 2933, 1606, 1297, 760; ESI-HRMS calcd for $C_{20}H_{22}NaO$ [M + Na]$^+$ 301.1563; found, 301.1547.

(*E*)-3-(2,3-Diphenylallyl)-3-methyl-2,3-dihydrobenzofuran (3ax). Colorless oil (76 mg, 78% yield); R_f 0.50 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 2H), 7.43−7.27 (m, 6H), 7.22 (d, J = 7.5 Hz, 2H), 7.11 (t, J = 7.7 Hz, 1H), 6.94 (d, J = 7.3 Hz, 1H), 6.85−6.73 (m, 3H), 4.19 (d, J = 8.7 Hz, 1H), 3.80 (d, J = 8.8 Hz, 1H), 3.37 (d, J = 13.9 Hz, 1H), 3.06 (d, J = 13.9 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.3, 140.3, 137.8, 135.3, 132.7, 128.7, 128.3, 128.2, 128.0, 127.2, 127.1, 126.6, 122.9, 120.4, 109.5, 82.7, 46.2, 39.4, 25.7. IR (KBr, cm^{-1}): 3100, 2950, 2743, 1560, 1250, 749; ESI-HRMS calcd for $C_{24}H_{22}NaO$ [M + Na]$^+$ 349.1563; found, 349.1565.

5-Chloro-3-methyl-3-(2-phenylallyl)-2,3-dihydrobenzofuran (3ba). Colorless oil (72 mg, 85% yield); R_f 0.57 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.18 (m, 5H), 6.98 (d, J = 8.5 Hz, 1H), 6.90 (s, 1H), 6.61 (d, J = 8.4 Hz, 1H), 5.26 (s, 1H), 5.00 (s, 1H), 4.31 (d, J = 8.8 Hz, 1H), 3.91 (d, J = 8.8 Hz, 1H), 2.83 (q, J = 13.7 Hz, 2H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 145.6, 142.2, 137.0, 128.3, 127.8, 127.5, 126.5, 125.0, 123.4, 117.6, 110.5, 82.3, 46.1, 45.6, 25.3. IR (KBr, cm^{-1}): 3079, 2964, 1624, 1476, 742; ESI-HRMS calcd for $C_{18}H_{17}ClNaO$ [M + Na]$^+$ 307.0860; found, 307.0865.

5-*tert*-Butyl-3-methyl-3-(2-phenylallyl)-2,3-dihydrobenzofuran (3ca). Colorless oil (80 mg, 88% yield); R_f 0.58 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dt, J = 11.6, 7.5 Hz, 5H), 7.08 (d, J = 8.4 Hz, 1H), 7.02 (s, 1H), 6.65 (d, J = 8.3 Hz, 1H), 5.25 (s, 1H), 4.98 (s, 1H), 4.28 (d, J = 8.6 Hz, 1H), 3.89 (d, J = 8.6 Hz, 1H), 2.86 (q, J = 13.6 Hz, 2H), 1.26 (s, 9H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 145.9, 143.2, 142.6, 134.6, 128.2, 127.3, 126.5, 124.8, 119.8, 117.4, 108.7, 82.2, 46.0, 45.7, 34.3, 31.7, 25.3. IR (KBr, cm^{-1}): 3079, 2969, 1616, 1489, 1059, 778; ESI-HRMS calcd for $C_{22}H_{26}NaO$ [M + Na]$^+$ 329.1876; found, 329.1883.

1-Methyl-1-(2-phenylallyl)-1,2-dihydronaphtho[2,1-*b*]furan (3da). Colorless oil (65 mg, 73% yield); R_f 0.54 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.28−7.20 (m, 3H), 7.18−7.13 (m, 3H), 6.97 (d, J = 8.8 Hz, 1H), 5.18 (s, 1H), 4.98 (s, 1H), 4.53 (d, J = 8.8 Hz, 1H), 4.02 (d, J = 8.8 Hz, 1H), 3.15 (q, J = 13.8 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 146.2, 142.4, 130.6, 130.0, 129.8, 129.4, 128.0, 127.1, 126.3, 126.3, 124.4, 122.3, 121.8, 117.4, 112.3, 81.5, 47.6, 44.5, 25.8. IR (KBr, cm^{-1}): 3038, 2923, 1624, 1253, 1108, 751; ESI-HRMS calcd for $C_{22}H_{20}NaO$ [M + Na]$^+$ 323.1406; found, 323.1403.

3-Phenyl-3-(2-phenylallyl)-2,3-dihydrobenzofuran (3ea). Colorless oil (63 mg, 68% yield); R_f 0.52 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H), 7.24 (d, J = 3.2 Hz, 1H), 7.19 (s, 5H), 7.07 (dd, J = 12.4, 7.2 Hz, 2H), 6.76 (t, J = 7.6 Hz, 2H), 5.17 (s, 1H), 4.74 (s, 1H), 4.64−4.52 (m, 2H), 3.45 (d, J = 14.8 Hz, 1H), 3.25 (d, J = 14.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 145.0, 144.8, 142.6, 132.9, 128.4, 128.4, 128.1, 127.0, 126.5, 126.5, 126.6, 125.3, 120.4, 117.5, 109.9, 82.4, 54.1, 44.6. IR (KBr, cm^{-1}): 3057, 2925, 1629, 1480, 1108, 747; ESI-HRMS calcd for $C_{23}H_{20}NaO$ [M + Na]$^+$ 335.1406; found, 335.1410.

1-(3-Methyl-3-(2-phenylallyl)indolin-1-yl)ethanone (3fa). Colorless oil (66 mg, 76% yield); R_f 0.63 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 1H), 7.31−7.23 (m, 5H), 7.19−7.13 (m, 1H), 7.10 (d, J = 7.5 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H), 5.13 (s, 1H), 4.78 (s, 1H), 3.69 (d, J = 10.5 Hz, 1H), 3.35 (d, J = 10.6 Hz, 1H), 2.79 (q, J = 13.3 Hz, 2H), 1.74 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 145.2, 142.4, 142.1, 138.7, 128.3, 127.8, 127.4, 126.4, 123.5, 122.2, 117.8, 116.8, 59.9, 47.1, 44.2, 26.2, 23.7; IR (KBr, cm^{-1}): 3025, 2986, 1591, 1400, 1130, 759; ESI-HRMS calcd for $C_{20}H_{21}NNaO$ [M + Na]$^+$ 314.1515; found, 314.1523.

4-(3-(1,3-Dimethyl-2-oxoindolin-3-yl)prop-1-en-2-yl)-benzonitrile (3hi). Solid, mp =109−111 °C (73 mg, 89% yield); R_f 0.58 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.7 Hz, 2H), 6.91 (d, J = 7.3 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 5.01 (s, 1H), 4.96 (s, 1H), 3.25 (d, J = 13.7 Hz, 1H), 2.93 (d, J = 13.7 Hz, 1H), 2.87 (s, 3H), 1.36 (d, J = 12.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 146.0, 144.3, 143.0, 132.3, 131.4, 127.8, 127.2, 123.6, 122.1, 119.4, 118.8, 110.5, 107.7, 48.6, 43.7, 25.7, 24.0. IR (KBr, cm-1): 3058, 2972, 1720, 1611, 1103, 754; ESI-HRMS calcd for $C_{20}H_{18}N_2NaO$ [M + Na]$^+$ 325.1311; found, 325.1316.

3-(Methoxymethyl)-3-(2-phenylallyl)-2,3-dihydrobenzofuran (3ia). Colorless oil (67 mg, 80% yield); R_f 0.67 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.3 Hz, 2H), 7.28−7.19 (m, 3H), 7.12−6.97 (m, 2H), 6.82−6.64 (m, 2H), 5.25 (s, 1H), 4.95 (s, 1H), 4.28 (d, J = 9.1 Hz, 1H), 4.14 (d, J = 9.2 Hz, 1H), 3.32−3.23 (m, 2H), 3.10 (s, 3H), 3.04 (d, J = 13.7 Hz, 1H), 2.94 (d, J = 13.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 145.2, 142.4, 131.2, 128.5, 128.1, 127.2, 126.5, 124.6, 119.9, 117.8, 109.5, 78.7, 76.6, 58.8, 50.5, 40.5. IR (KBr, cm^{-1}): 3082, 2921, 1602, 1477, 1108, 751; ESI-HRMS calcd for $C_{19}H_{20}NaO_2$ [M + Na]$^+$ 303.1356; found, 303.1362.

1-(2-Methylallyloxy)-2-(1-phenylvinyl)benzene (5). Colorless oil (63 mg, 84% yield); R_f 0.56 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (ddd, J = 19.6, 15.4, 7.1 Hz, 7H), 6.98 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 5.68 (s, 1H), 5.32 (s, 1H), 4.73 (d, J = 6.1 Hz, 2H), 4.24 (s, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 147.4, 141.4, 140.8, 131.4, 131.3, 128.9, 128.0, 127.2, 126.4, 120.6, 115.5, 112.1, 112.0, 71.8, 18.9; IR (KBr, cm^{-1}): 3038, 2936, 1259, 1108, 765; ESI-HRMS calcd for C18H18NaO [M + Na]$^+$ 273.1250; found, 273.1247.

(*E*)-3-Methyl-3-styryl-2,3-dihydrobenzofuran (6a). Colorless oil (56 mg, 80% yield); R_f 0.55 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.7 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.22 (d, J = 7.4 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.50−6.34 (m, 2H), 4.46 (d, J = 8.6 Hz, 1H), 4.31 (d, J = 8.6 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 136.9, 134.6, 134.2, 128.5, 128.5, 128.4, 127.4, 126.3, 123.7, 120.8, 109.9, 83.4, 47.9, 24.8. IR (KBr, cm^{-1}): 3050, 2924, 1635, 1111, 750; ESI-HRMS calcd for $C_{17}H_{16}NaO$ [M + Na]$^+$ 259.1093; found, 259.1092.

(*E*)-3-(4-Chlorostyryl)-3-methyl-2,3-dihydrobenzofuran (6b). Colorless oil (63 mg, 78% yield); R_f 0.56 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 4.6 Hz, 4H), 7.17 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 7.3 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H),

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6.85 (d, J = 8.0 Hz, 1H), 6.36 (s, 2H), 4.45 (d, J = 8.6 Hz, 1H), 4.31 (d, J = 8.6 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 135.5, 135.4, 134.0, 133.1, 128.7, 128.5, 127.5, 127.4, 123.7, 120.9, 110.0, 83.3, 48.0, 24.7. IR (KBr, cm^{-1}): 3003, 2923, 1630, 1100, 732; APCI-HRMS calcd for $C_{17}H_{16}ClO$ $[M + H]^+$ 271.0884; found, 271.0888.

(*E*)-3-Methyl-3-(4-methylstyryl)-2,3-dihydrobenzofuran (6c). Colorless oil (61 mg, 86% yield); R_f 0.58 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.16 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 7.8 Hz, 3H), 6.89 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.36 (q, J = 16.1 Hz, 2H), 4.45 (d, J = 8.6 Hz, 1H), 4.31 (d, J = 8.6 Hz, 1H), 2.33 (d, J = 11.3 Hz, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 137.3, 134.4, 134.2, 133.6, 129.2, 128.4, 128.4, 126.2, 123.7, 120.8, 109.9, 83.4, 47.9, 24.8, 21.1. IR (KBr, cm^{-1}): 3038, 2981, 1635, 1098, 731; ESI-HRMS calcd for $C_{18}H_{18}NaO$ $[M + Na]^+$ 273.1250; found, 273.1250.

(*E*)-3-(4-Methoxystyryl)-3-methyl-2,3-dihydrobenzofuran (6d). Colorless oil (62 mg, 83% yield); R_f 0.62 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 7.3 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.83 (dd, J = 8.2, 3.3 Hz, 3H), 6.36 (d, J = 16.1 Hz, 1H), 6.25 (d, J = 16.1 Hz, 1H), 4.44 (d, J = 8.6 Hz, 1H), 4.30 (d, J = 8.6 Hz, 1H), 3.81−3.74 (m, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.1, 134.5, 132.6, 129.7, 128.3, 128.0, 127.4, 123.7, 120.8, 114.0, 109.9, 83.5, 55.3, 47.8, 24.9. IR (KBr, cm^{-1}): 3048, 2965, 1635, 1051, 714; ESI-HRMS calcd for $C_{18}H_{18}NaO_2$ $[M + Na]^+$ 289.1199; found, 289.1207.

(*E*)-*N*,*N*-Dimethyl-4-(2-(3-methyl-2,3-dihydrobenzofuran-3-yl)vinyl)aniline (6e). Colorless oil (73 mg, 88% yield); R_f 0.59 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.22 (m, 2H), 7.15 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 7.3 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 8.4 Hz, 2H), 6.35 (d, J = 16.1 Hz, 1H), 6.18 (d, J = 16.1 Hz, 1H), 4.43 (d, J = 8.5 Hz, 1H), 4.30 (d, J = 8.5 Hz, 1H), 2.94 (s, 6H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 150.0, 134.9, 130.4, 128.4, 128.2, 127.2, 125.5, 123.7, 120.7, 112.5, 109.8, 83.7, 47.8, 40.5, 25.0. IR (KBr, cm^{-1}): 3040, 2925, 1598, 1477, 1098, 748; ESI-HRMS calcd for $C_{19}H_{22}NO$ $[M + H]^+$ 280.1696; found, 280.1701.

(*E*)-3-Methyl-3-(4-(methylsulfonyl)styryl)-2,3-dihydrobenzofuran (6f). Colorless oil (78 mg, 83% yield); R_f 0.48 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.19 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 16.1 Hz, 1H), 6.44 (d, J = 16.1 Hz, 1H), 4.49 (d, J = 8.7 Hz, 1H), 4.33 (d, J = 8.7 Hz, 1H), 3.03 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 142.4, 139.1, 138.9, 133.4, 128.7, 127.7, 127.0, 126.9, 123.6, 121.0, 110.1, 83.0, 48.2, 44.5, 24.4. IR (KBr, cm^{-1}): 3077, 2964, 1623, 1475, 737; ESI-HRMS calcd for $C_{18}H_{18}NaO_3S$ $[M + Na]^+$ 337.0869; found, 337.0876.

(*E*)-3-(2-Bromostyryl)-3-methyl-2,3-dihydrobenzofuran (6g). Colorless oil (76 mg, 81% yield); R_f 0.56 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.13 (d, J = 7.4 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.83 (dd, J = 17.3, 12.0 Hz, 2H), 6.32 (d, J = 16.0 Hz, 1H), 4.48 (d, J = 8.6 Hz, 1H), 4.35 (d, J = 8.7 Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 137.6, 137.0, 134.0, 132.9, 128.7, 128.6, 127.8, 127.5, 127.0, 123.7, 120.9, 110.0, 83.2, 48.2, 24.7. IR (KBr, cm^{-1}): 3064, 2925, 1635, 1072, 750; ESI-HRMS calcd for $C_{17}H_{15}BrNaO$ $[M + Na]^+$ 337.0198; found, 337.0197.

(*E*)-3-(2-(Furan-2-yl)vinyl)-3-methyl-2,3-dihydrobenzofuran (6h). Colorless oil (56 mg, 83% yield); R_f 0.61 (petroleum ether/EtOAc 50/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 7.3 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.41−6.32 (m, 2H), 6.19 (dd, J = 9.6, 6.4 Hz, 2H), 4.44 (d, J = 8.6 Hz, 1H), 4.29 (d, J = 8.6 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 152.6, 141.8, 133.9, 133.5, 128.5, 123.7, 120.8, 117.4, 111.3, 109.9, 107.6, 83.4, 47.8, 24.7. IR (KBr, cm^{-1}): 3049, 2924, 1638, 1050, 746; APCI-HRMS calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1067; found, 227.1060.

(*E*)-1-Methyl-3-phenyl-3-styrylindolin-2-one (6i).[34] Solid (86 mg, 89% yield); 120−121 °C, R_f 0.47 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.33 (m, 3H), 7.33−7.22 (m, 9H), 7.13 (t, J = 7.7 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 16.1 Hz, 1H), 6.53 (d, J = 16.0 Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.2, 140.1, 136.4, 131.6, 131.5, 129.0, 128.7, 128.5, 128.4, 127.8, 127.5, 127.4, 126.6, 125.6, 122.8, 108.6, 59.7, 26.6. IR (KBr, cm^{-1}): 3056, 2987, 1712, 1585, 747; ESI-HRMS calcd for $C_{23}H_{19}NNaO$ $[M + Na]^+$ 348.1359; found, 348.1362.

(*E*)-4-Methyl-4-styrylchroman (6j). Colorless oil (64 mg, 86% yield); R_f 0.57 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 10.3 Hz, 2H), 7.20 (d, J = 7.7 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 6.17 (d, J = 16.0 Hz, 1H), 4.25−4.14 (m, 2H), 1.97 (s, 2H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 139.4, 137.2, 129.5, 128.8, 128.5, 127.9, 127.7, 127.2, 126.2, 120.3, 117.0, 62.8, 37.3, 36.4, 28.5. IR (KBr, cm^{-1}): 3034, 2923, 2023, 1635, 1208, 720; ESI-HRMS calcd for $C_{18}H_{18}NaO$ $[M + Na]^+$ 273.1250; found, 273.1245.

(*E*)-4-(4-Chlorostyryl)-4-methylchroman (6k). Colorless oil (69 mg, 81% yield); R_f 0.54 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 7.19−7.08 (m, 2H), 6.93−6.77 (m, 2H), 6.26 (d, J = 16.0 Hz, 1H), 6.11 (d, J = 16.0 Hz, 1H), 4.26−4.10 (m, 2H), 1.96 (t, J = 5.1 Hz, 2H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 140.1, 135.7, 132.8, 128.7, 128.6, 128.4, 127.8, 127.6, 127.4, 120.4, 117.0, 62.7, 37.4, 36.3, 28.1. IR (KBr, cm-1): 3023, 2926, 2023, 1635, 1403, 714; HRMS EI (m/z): calcd for $C_{18}H_{17}ClO$ 284.0962; found, 284.0966.

3-(2-(4-Chlorophenyl)allyl)benzofuran (8a). Yellow oil (64 mg, 80% yield); R_f 0.54 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 7.30 (d, J = 9.3 Hz, 3H), 7.25 (t, J = 7.5 Hz, 1H), 5.51 (s, 1H), 5.22 (s, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 144.0, 142.5, 139.0, 133.4, 128.5, 128.0, 127.3, 124.2, 122.4, 119.8, 117.8, 114.8, 111.5, 29.8. IR (KBr, cm^{-1}): 3053, 2924, 1597, 1488, 1092, 748; HRMS EI (m/z): calcd for $C_{17}H_{13}ClO$ 268.0649; found, 268.0645.

3-(2-*p*-Tolylallyl)benzofuran (8b). Yellow oil (48 mg, 65% yield); R_f 0.56 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.39−7.35 (m, 2H), 7.30−7.24 (m, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 2H), 5.46 (s, 1H), 5.10 (s, 1H), 3.85 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 144.8, 142.5, 137.7, 137.4, 129.0, 128.2, 125.9, 124.1, 122.3, 119.9, 118.2, 113.5, 111.4, 29.7, 21.1. IR (KBr, cm^{-1}): 3052, 2924, 1631, 1098, 747; ESI-HRMS calcd for $C_{18}H_{16}NaO$ $[M + Na]^+$ 271.1093; found, 271.1085.

4-(3-(Benzofuran-3-yl)prop-1-en-2-yl)benzonitrile (8c). Yellow oil (60 mg, 78% yield); R_f 0.60 (petroleum ether/EtOAc 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (q, J = 8.2 Hz, 1H), 7.55 (dt, J = 16.1, 7.8 Hz, 4H), 7.45 (d, J = 8.2 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.26−7.21 (m, 1H), 5.59 (s, 1H), 5.33 (s, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 145.0, 143.7, 142.5, 132.2, 127.7, 126.6, 124.4, 122.5, 119.7, 118.8, 117.4, 117.3, 111.6, 111.2, 29.5. IR (KBr, cm^{-1}): 3045, 2923, 1602, 1452, 745; ESI-HRMS calcd for $C_{18}H_{13}NNaO$ $[M + Na]^+$ 282.0889; found, 282.0894.

3-(2-(3,4-Dichlorophenyl)allyl)benzofuran (8d). Yellow oil (65 mg, 72% yield); R_f 0.57 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 2.5 Hz, 2H), 7.25−7.21 (m, 2H), 5.49 (s, 1H), 5.22 (s, 1H), 3.82 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 143.1, 142.5, 140.6, 132.5, 131.5 130.2, 128.0, 127.8, 125.3, 124.3, 122.4, 119.7, 117.4, 115.8, 111.5, 29.6. IR (KBr, cm^{-1}): 3047, 2926, 1643, 1097, 717; HRMS EI (m/z): $C_{17}H_{12}Cl_2O$ 302.0260; found, 302.0262.

3-(2-(Naphthalen-1-yl)allyl)benzofuran (8e). Yellow oil (68 mg, 80% yield); R_f 0.58 (petroleum ether/EtOAc 100/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.03 (m, 1H), 7.89−7.82 (m, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.47 (dd, J = 12.3, 7.4 Hz, 3H), 7.38 (t, J = 7.7 Hz, 1H), 7.34 (s, 1H), 7.29 (d, J = 7.3 Hz, 1H), 7.25−7.19 (m, 2H), 5.46 (s, 1H), 5.22 (s, 1H), 3.87 (s, 2H); ^{13}C

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NMR (100 MHz, $CDCl_3$) δ 155.4, 145.9, 142.5, 140.6, 133.7, 131.1, 128.4, 128.2, 127.4, 125.9, 125.7, 125.5, 125.3, 125.2, 124.1, 122.3, 120.0, 117.5, 117.1, 111.4, 32.7. IR (KBr, cm^{-1}): 3048, 2926, 1605, 1250, 745; ESI-HRMS calcd for $C_{21}H_{16}NaO$ $[M + Na]^+$ 307.1093; found, 307.1090.

3-((3,4-Dihydronaphthalen-1-yl)methyl)benzofuran (8f). Yellow oil (46 mg, 60% yield); R_f 0.57 (petroleum ether/EtOAc 100/1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.37 (s, 1H), 7.29 (d, J = 6.5 Hz, 2H), 7.25−7.19 (m, 2H), 7.14 (s, 2H), 5.92 (s, 1H), 3.81 (s, 2H), 2.78 (t, J = 8.0 Hz, 2H), 2.30 (t, J = 11.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.5, 136.6, 134.6, 133.5, 128.3, 127.6, 126.9, 126.8, 126.4, 124.1, 122.8, 122.3, 119.9, 118.4, 111.4, 28.3, 27.2, 23.2. IR (KBr, cm^{-1}): 3028, 2921, 1643, 1482, 1106, 745; ESI-HRMS calcd for $C_{19}H_{16}NaO$ $[M + Na]^+$ 283.1093; found, 283.1092.

***(E)*-3-(4-Chlorostyryl)benzofuran (9).** Yellow oil (61 mg, 80% yield); R_f 0.59 (petroleum ether/EtOAc 100/1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 1H), 7.77 (s, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.38−7.27 (m, 4H), 7.17 (d, J = 18.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 143.9, 136.0, 133.1, 128.9, 128.1, 127.3, 125.6, 124.8, 123.1, 120.8, 119.3, 119.0, 111.8. IR (KBr, cm^{-1}): 3046, 2983, 1641, 1403, 1051, 730; ESI-HRMS calcd for $C_{16}H_{12}ClO$ $[M + H]^+$ 255.0571; found, 255.0563.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR of compounds **3aa−ia**, **5**, **6a−k**, **7a−f**, and **8**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01024.

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Notes

The authors declare no competing financial interest.

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