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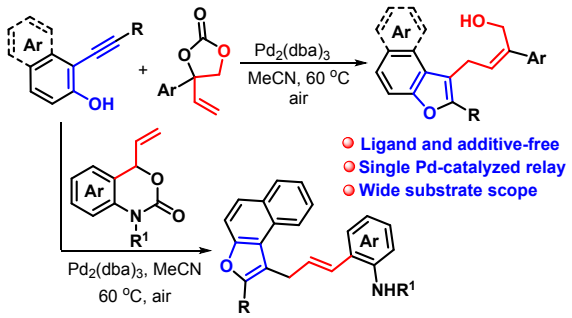


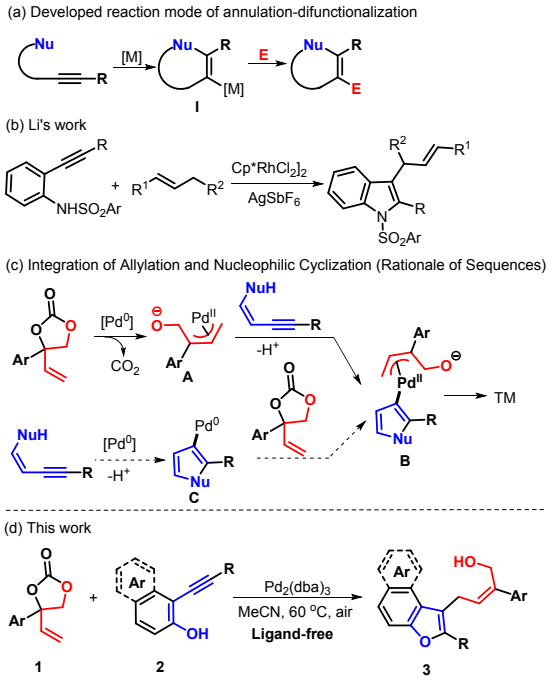
ABSTRACT. A new single Pd-catalyzed decarboxylative allylation-nucleophilic cyclization relay is reported by using α-alkynyl arylols and vinylethylene carbonates (or vinyl carbamates), and a wide range of 3-allyl benzofurans with generally good yields were stereoselectively synthesized under the mild conditions, among which the complete stereoselectivity of some cases was also observed. Notably, the present catalysis can tolerate air conditions without any ligand, additive or base, opening new avenues to build up *oxa*-heterocycle frameworks through catalytic difunctionalization of internal alkynes.

Introduction

Transition metal-catalyzed annulation-difunctionalization of alkynes linked to nucleophilic sites has proven to be one of the most straightforward and atom-economical synthetic strategies to construct a sequence of functionalized cyclic frameworks by incorporating two functional groups across the π system of the alkyne unit.[1] During these reaction processes, transition metal-catalysts with high-valence states show a strong Lewis acidity and could activate alkynes by chelation to promote its intramolecular cyclization, forming metal species **I** which capture electrophiles to give the targets (Scheme 1a).[2] For example, the group of Li reported an elegant Rh(III)-catalyzed annulation-difunctionalization of *o*-alkynylanilines and olefins toward 3-allylindoles through a nucleophilic cyclization/oxidative allylation cascade (Scheme 1b).[3] Despite these great achievements gained in this field, the development of a new catalysis for annulation-difunctionalization of alkynes remains a highly challenge because of the difficult control in the multiple catalytic behaviors of transition metal catalysts in a one-pot transformation.[4]

It is well-known that decarboxylative allylation has been recognized as a powerful and versatile synthetic tool for forging carbon−carbon and carbon−heteroatom bonds in complex molecule synthesis.[5] During them, palladium-catalyzed alkylation *via* zwitterionic allylpalladium intermediates from vinylethylene carbonates (VECs) is a reliable and valuable approach to construct functionalized allyl molecules products.[6] Zhang,[7] Zhao,[8] Kleij,[9] Glorius[10] and others[11] have independently applied palladium catalysis toward the construction of various functionalized molecules. Mechanistically, Pd(0)-catalyst enabled decarboxylation of vinylethylene carbonates (VECs) to generate an electrophilic π-allyl-palladium (II) intermediate **A** (Scheme 1c). Given the application of Lewis acidity of Pd(II) catalysts in triple C≡C bond activation,[12] π-allyl-palladium (II) intermediate may activate triple C≡C bond of alkynes to accelerate nucleophilic cyclization, giving a Pd(II) complex **B** that may reductively eliminate the product (Scheme 1c). The alternative alkyne cyclization−allylation sequence is less feasible, which is based on the following factors: i) because of its coordinative saturation, Pd(0)-catalyst is unfavorable for the formation of the cyclized intermediate **C**; ii) even if intermediate **C** is formed, it is easily (irreversibly) protonolyzed. Herein, we successfully implemented this concept with a new Pd-

catalyzed decarboxylative allylation and nucleophilic cyclization relay starting from α-alkynyl arylols and vinylethylene carbonates (VECs) without any ligand or additive (Scheme 1d). The present approach represents a precise single palladium-catalyzed relay process for the direct synthesis of a wide range of new 3-allylbenzofurans in a highly functional-group-compatible manner under ligand-free conditions.



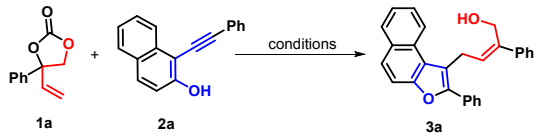
Scheme 1. Profiles for Annulation-Difunctionalization of Alkynes

Results and Discussion

We commenced our studies with the optimization investigation on the coupling of phenyl vinylethylene carbonate (**1a**) and 1-(phenylethynyl)naphthalen-2-ol (**2a**) as model substrates in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (10 mol%) as a catalyst. The reaction proceeded readily in 1,2-dichloroethane (DCE) at 60 °C under air conditions (100 °C), and the desired product **3a** was obtained in 68% yield (Table 1, entry 1). The initial outcome impelled us to further investigate the reaction conditions. Several other palladium catalysts often used in catalytic reactions, such as $Pd(OAc)_2$, $Pd(PPh_3)_4$, $(MeCN)_2PdCl_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(dppf)Cl_2$, and $Pd_2(dba)_3$ were then tested for this transformation (entries 2–8). The results revealed that the former six did not exhibit any catalytic performances as their use in fact completely suppressed the generation of **3a** whereas the last one could accelerate this reaction more efficiently, providing higher yield of 72% (entry 8), and thus it turned to be a better choice in this

transformation. Taking $Pd_2(dba)_3$ as the catalyst, the effect of the solvents was then studied (entries 9-13). The following screening of several other aprotic solvents, namely MeOH, DMSO, toluene, 1,4-dioxane and MeCN, showed that MeCN resulted in a slightly higher yield as compared with DCE (entries 1 vs 13), and the others all gave a yield of <63%. The lower conversion was observed when the reaction temperature was adjusted to be either 40 or 80 °C (entries 14-15). After that, lowering the $Pd_2(dba)_3$ loading could maintain the efficiency of this reaction (entries 16-17), and an employment of 2.5 mol% of $Pd_2(dba)_3$ produced product **3a** in 74% yield. Fine-tuning the mol ratio of **1a** and **2a** in 1:1.2 favored the transformation to give 80% yield (entry 18).

Table 1. Condition Optimization for Product **3a**[a]



entry	Pd-Cat. (mol %)	solvent	*t* (°C)	yield (%)[b]
1	$Pd_2(dba)_3 \cdot CHCl_3$ (10)	DCE	60	68
2	$Pd(OAc)_2$ (10)	DCE	60	N.D.
3	$Pd(PPh_3)_4$ (10)	DCE	60	N.D.
4	$(MeCN)_2PdCl_2$ (10)	DCE	60	N.D.
5	$Pd(PPh_3)_2Cl_2$ (10)	DCE	60	N.D.
6	$Pd(dppf)Cl_2$ (10)	DCE	60	N.D.
7	$PdCl_2$ (10)	DCE	60	N.D.
8	$Pd_2(dba)_3$ (10)	DCE	60	72
9	$Pd_2(dba)_3$ (10)	MeOH	60	63

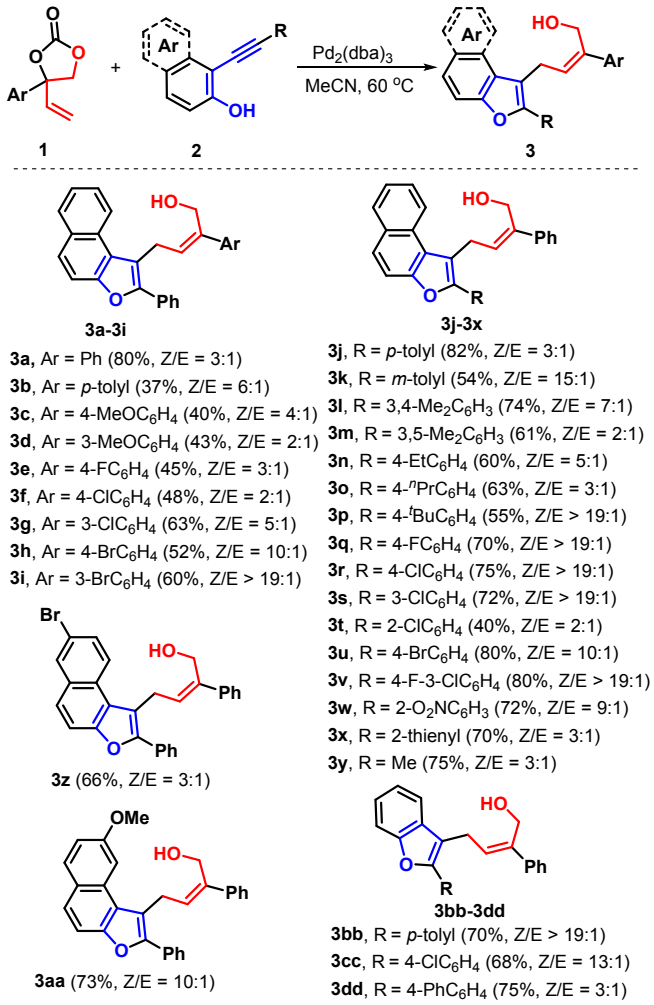
10	$Pd_2(dba)_3$ (10)	DMSO	60	57
11	$Pd_2(dba)_3$ (10)	toluene	60	52
12	$Pd_2(dba)_3$ (10)	1,4-dioxane	60	48
13	$Pd_2(dba)_3$ (10)	MeCN	60	76
14	$Pd_2(dba)_3$ (10)	MeCN	40	45
15	$Pd_2(dba)_3$ (10)	MeCN	80	50
16	$Pd_2(dba)_3$ (5)	MeCN	60	76
17	$Pd_2(dba)_3$ (2.5)	MeCN	60	74
18 [c]	$Pd_2(dba)_3$ (2.5)	MeCN	60	80

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), catalyst (*x* mol %), solvent (2.0 mL), under air conditions. [b]Isolated yield based on substrate **1a**. [c]The mol ratio of **1a** and **2a** in 1:1.2. N.D. = not detected

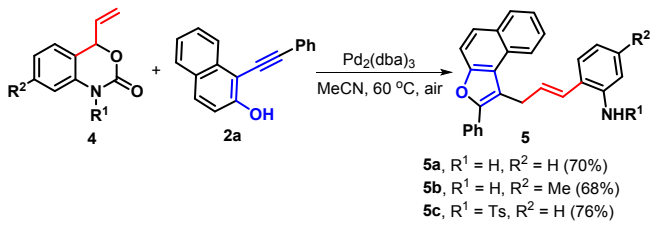
With the optimized reaction conditions in hand, we then evaluated the generality of this Pd-catalyzed allylation-cyclization cascade toward synthesizing 3-allylbenzofurans by examining a range of α-alkynylnaphth-2-ol and vinylethylene carbonate components. As depicted in Scheme 2, all tested substrates did not hamper the reaction process, enabling the Pd-catalysis to access the desired products **3** in synthetically useful yields. Firstly, vinylethylene carbonates with diverse electronic properties and different substituent patterns in the aryl ring were investigated by combining α-alkynylnaphth-2-ol **2a** under the standard conditions. Various substituents, such as methyl (**1b**), methoxy (*p*-methoxyphenyl = PMP **1c** and **1d**), fluoro (**1e**), chloro (**1f** and **1g**), and bromo (**1h** and **1i**), were well-tolerated with this catalytic conditions, delivering the corresponding products **3b−3i** in 37%-63% yields and poor to high stereoselectivities (2:1 to >19:1 *Z*/*E* ratio), among which 3-bromophenyl counterpart **1i** could

completely orient the (*Z*)-selectivity to construct the target product **3i** in 60% yield. Next, the scope regarding the α-alkynylnaphth-2-ols was detailly studied by independently installing different substituents including aryl, heteroaryl and alkyl groups into the alkynyl unit. Satisfyingly, both electron-donating (methyl **2b**–**2e**, ethyl **2f**, n-propyl **2g** and *tert*-butyl **2h**) and electron-withdrawing (fluoro **2i**, chloro **2j**–**2l** and **2n**, bromo **2m** and nitro **2o**) groups residing in various positions of the phenyl ring all accessed the corresponding products **3j-3w** with 40-82% yields and 1:1 to >19:1 *Z*/*E* ratio. Of these groups, the sterically crowded *o*-chlorophenyl functionality (**1l**) seemed reluctant to undergo this process, as product **3t** was provided in an unsatisfactory yield of 40% and 2:1 Z/E ratio. In contrast, the 2-thienyl substrate **2p** still displayed a good reactivity profile, offering product **3x** in 70% yield, but with poor stereoselectivity. Notably, substrate **2q** with a methyl group linked to the alkynyl moiety was also workable in this transformation, accessing product **3y** with 75% yield and 3:1 Z/E ratio. Moreover, *α*-alkynylnaphth-2-ols with either a C6 bromo (**2s**) or a C7 methoxy (**2t**) group were accommodated, confirming the efficiency of the reaction, as products **3z** and **3aa** were furnished in 66% and 73% yields with moderate stereoselectivities, respectively. Interestingly, *o*-arylalkynyl phenols **2u-2w** with both electron-poor and electron-rich groups at the arylalkynyl moiety (R^2) can all tolerate this catalytic system, rendering the corresponding products **3bb−3dd** in 70−75% yields and 3:1 to >19:1 Z/E ratio.

To expand the utility of this methodology, we contributed our effort to test other alkylation reagents. Fortunately, *N*-unprotected vinyl carbamates **4a** and **4b** were selected to react with **2a** under the standard conditions, providing the desired products **5a** and **5b** in 70% and 68% yields, respectively (Scheme 3). Furthermore, *N*-tosyl vinyl carbamate **4c** was appliable in this transformation as well, and the expected product **5c** was isolated in 76% yield (Scheme 3). The stereo-structure of product **5b** was assigned by X-ray diffraction analysis (CCDC 1983888).

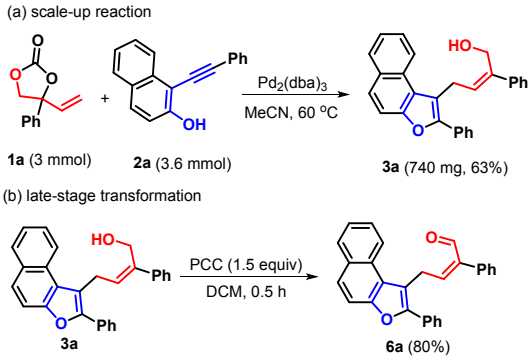


Scheme 2. Substrate Scope for the Synthesis of Products 3



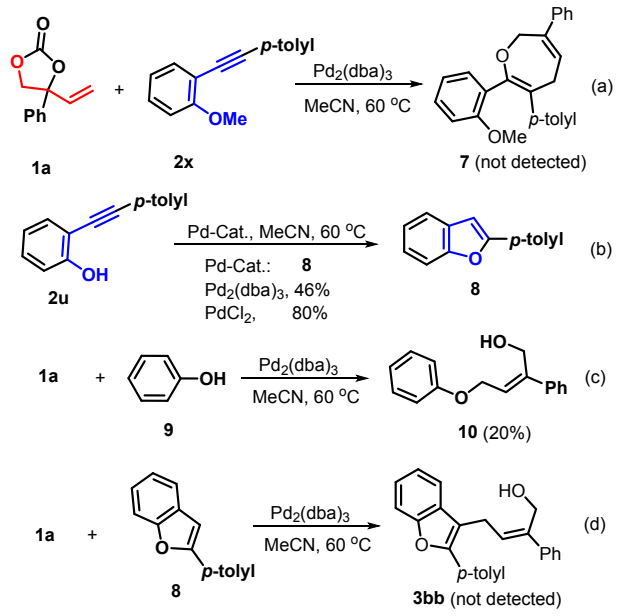
Scheme 3. Expansion of Substrate Scope

This catalytic system can be easily scaled up, as demonstrated by the synthetic utility in the amplification reaction for the synthesis of **3a** on a 3 mmol scale (63%, Scheme 4a). Next, treatment of **3a** with pyridinium chlorochromate (PCC) at 0 °C in CH_2Cl_2 afforded aldehyde product **6a** in 80% yield (Scheme 4b). These results illustrate the synthetic potential of this protocol.

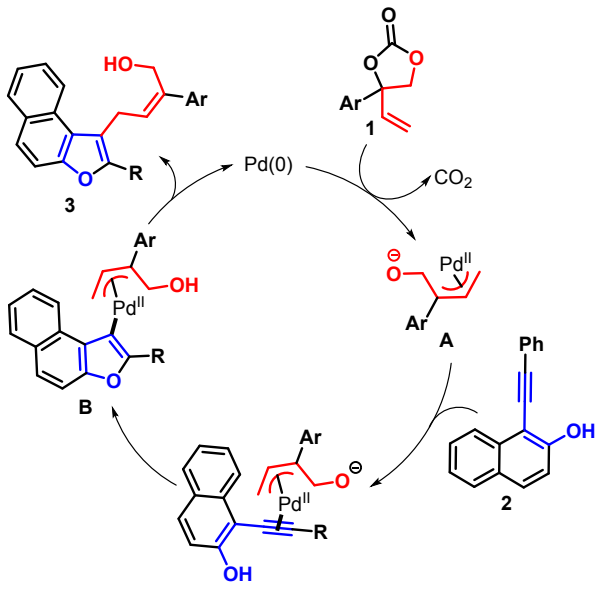


Scheme 4. Synthetic Potential of This Protocol

To ascertain the reaction process involving an allylation−cyclization sequence, several control experiments were conducted. The [5 + 2] annulation of *O*-protected *o*-arylalkynyl phenol **2x** with **1a** did not proceed and starting material **2x** was recovered, indicating the free hydroxyl group in substrates **2** was key for this successful catalysis, which could accelerate nucleophilic cyclization when carbon-carbon triple bond is activated by Pd(II) catalyst (Scheme 5a). Two palladium catalysts with different valence states were used for the cyclization of *o*-arylalkynyl phenol **2u**, and the outcomes revealed that palladium catalyst with a higher valence state favored to activate the alkyne to realize the nucleophilic cyclization (Scheme 5b). Without alkynyl moiety, phenol (**9**) gave allylic phenyl ether **10** (Scheme 5c). Furthermore, benzofuran **8** proved to be inactive for this transformation (Scheme 5d). These results showed that the reaction process should be the allylation−cyclization sequence.



Scheme 5. Preliminary Mechanistic Investigations



Scheme 6. Proposed Reaction Pathway

Based on the above experimental results and previous reports,[4,7-10] a reasonable mechanism is depicted in Scheme 6. Initially, vinylethylene carbonate **1** undergoes a decarboxylative process to afford the zwitterionic Pd-π-allyl intermediate **A**, which activates the alkynyl unit of substrate **2** via chelation. Subsequent nucleophilic cyclization and proton transfer occur to afford intermediate **B**, followed by reductive elimination to give the desired product **3** and regenerate the Pd(0) catalyst for the next catalytic cycle.

In summary, we have established a new ligand-free single Pd-catalyzed relay consisted of decarboxylative allylation and nucleophilic cyclization from α-alkynyl arylols and vinylethylene carbonates, providing a general and facile method for the synthesis of a wide range of 3-allylbenzofurans with generally good yields and stereoselectivity. In some cases, the complete stereoselectivity was observed. Very interestingly, the present catalysis can tolerate air conditions without any ligand, additive and base, featuring high atom economy, good functional group tolerance and wide substrate scope and thus opening new avenues for catalytic difunctionalization of internal alkynes. Further investigation and application of this alkylation–annulation reaction is underway in our laboratory.

Experimental Section

General Information.

All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz instrument with TMS as internal standard. Chemical shifts (δ) were reported in ppm with respect to TMS. Data are represented as follows: chemical shift, mutiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J*, Hz) and integration; HRMS analyses were carried out using a TOF-MS instrument with an ESI source. X-ray crystallographic analysis was performed with a SMART CCD and a P4 diffractometer. The compounds **1**,[13] **2**[14] and **4**[15] were prepared according to the reported procedures.

General Procedure for the Synthesis of 3

Example for the synthesis of **3a**.

Under the air conditions, 1-(phenylethynyl)naphthalen-2-ol (**1a**, 0.36 mmol, 87.8 mg), vinyl cyclic carbonate (**2a**, 0.3 mmol, 57.0 mg) and $Pd_2(dba)_3$ (2.5 mol %, 6.9 mg) were added in a 10-mL reaction vial, Then, MeCN (3.0 mL) was added into this reaction system. The reaction vial was sealed and heated at 60 ^oC in an oil bath for 5 h until TLC (petroleum ether: ethyl acetate= 5:1) revealed that conversion of the starting material **2a** was completed. Then the reaction mixture was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ ethyl acetate = 10:1) to afford the desired product **3a** as white solid.

Scale-up experiment of **3a**

Under the air conditions, 1-(phenylethynyl)naphthalen-2-ol (**1a**, 3.6 mmol, 879.5 mg), vinyl cyclic carbonate (**2a**, 3 mmol, 570.6 mg) and $Pd_2(dba)_3$ (2.5 mol %, 68.7 mg) were added in a 25-mL reaction vial, Then, MeCN (10.0 mL) was added into this reaction system. The reaction vial was sealed and heated at 60 ^oC in an oil bath until TLC (petroleum ether: ethyl acetate= 5:1) revealed that conversion of the starting material **2a** was completed. Then the reaction mixture was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ ethyl acetate = 10:1) to afford the desired product **3a** as white solid with 63% yield.

*(Z)-2-Phenyl-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3a**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3a** (93.6 mg, 80%) as a white solid, mp 129-130 °C, *Z*/*E*= 3:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17-8.13 (m, 1H), 7.97-7.93 (m, 1H), 7.81-7.76 (m, 1H), 7.71 (d, J = 3.6 Hz, 1H), 7.68-7.64 (m, 3H), 7.52 (s, 1H), 7.50 (s, 2H), 7.48 (d, J = 2.4 Hz, 2H), 7.46 (s, 1H), 7.41-7.37 (m, 3H), 6.12 (t, J = 6.4 Hz, 1H), 4.43 (s, 2H), 4.03 (d, J = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.1, 151.4, 141.9, 137.8, 130.9, 129.3, 129.0, 128.7, 128.6, 128.2, 128.0, 127.8, 127.4, 126.6, 126.3, 126.2, 125.9, 124.2, 123.6, 123.1, 116.7, 112.5, 67.8, 25.8. IR (KBr, v, cm^{-1}) 3445, 1622, 1490, 1435, 1393, 1062, 1023, 803. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{22}O_2Na$ 413.1517; Found 413.1509.

*(Z)-4-(2-Phenylnaphtho[2,1-b]furan-1-yl)-2-(p-tolyl)but-2-en-1-ol (**3b**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3b** (44.8 mg, 37%) as a white solid, mp 103-104 °C, *Z*/*E*= 6:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.64-7.61 (m, 2H), 7.59-7.44 (m, 3H), 7.44-7.36 (m, 2H), 7.35 (d, J = 2.4 Hz, 1H), 7.35-7.29 (m, 2H), 7.28 (d, J = 1.6 Hz, 2H), 7.26-7.20 (m, 3H), 5.93 (t, J = 7.2 Hz, 1H), 4.36 (d, J = 0.8 Hz, 2H), 3.70 (d, J = 7.2 Hz, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 154.0, 151.1, 141.4, 137.5, 134.8, 131.0, 130.2, 129.4(8), 129.4(6), 128.9, 128.8, 128.6, 128.2, 127.3, 127.0, 126.4, 125.2, 124.5, 122.5, 119.7, 114.5, 111.5, 67.9, 24.1, 21.3. IR (KBr, v, cm^{-1}) 3325, 3508, 1494, 1441, 1262, 1085, 1010, 732. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{24}O_2Na$ 427.1674; Found 427.1689.

*(Z)-2-(4-methoxyphenyl)-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3c**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3c** (50.4 mg, 40%) as a white solid, mp 110-111 °C, *Z*/*E*= 4:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.15 (d, J = 8.4 Hz, 1H), 7.96-7.92 (m, 1H), 7.73-7.71 (m, 1H), 7.69-7.64 (m, 3H), 7.51-7.47 (m, 2H), 7.44-7.37 (m, 5H), 7.02 (d, J = 8.8 Hz, 2H), 6.06 (t, J = 6.4 Hz, 1H), 4.40 (s, 2H), 4.03 (d, J = 6.4 Hz, 2H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 159.2, 152.0, 151.3, 141.4, 130.9, 130.1, 129.2 128.8, 128.7, 128.5, 128.1, 127.7, 127.4, 126.2, 125.8, 125.6, 124.1, 123.6, 123.1, 116.8, 114.1, 112.4, 67.9, 55.4, 25.8. IR (KBr, v,

cm^{-1}) 3444, 1611, 1514, 1393, 1250, 1027, 803, 695. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{24}O_3Na$ 443.1623; Found 443.1631.

(Z)-2-(3-methoxyphenyl)-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol ***(3d, major)*** Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3d** (54.2 mg, 43%) as a white solid, mp 136-137 °C, *Z/E*= 2:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17 (d, J = 7.6 Hz, 1H), 7.98-7.94 (m, 1H), 7.80-7.70 (m, 3H), 7.69-7.64 (m, 3H), 7.51 (d, J = 8.0 Hz, 2H), 7.44-7.39 (m, 3H), 7.07-7.01 (m, 2H), 6.11 (t, J = 6.6 Hz, 1H), 4.42 (s, 2H), 4.04 (d, J = 6.4 Hz, 2H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 159.8, 152.0, 151.3, 141.8, 139.2, 130.8, 129.7, 129.2, 128.9, 128.7, 128.1, 127.7, 127.4, 126.2, 125.8, 124.2, 123.6, 121.3, 119.0, 116.6, 114.9, 113.1, 112.4, 67.8, 55.4, 25.8. IR (KBr, v, cm^{-1}) 3445, 1606, 1577, 1491, 1395, 1285, 1203, 1002. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{24}O_3Na$ 443.1623; Found 443.1607.

(Z)-2-(4-fluorophenyl)-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol ***(3e,*** *major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3e** (55.1 mg, 45%) as a white solid, mp 111-112 °C, *Z/E*= 3:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.15-8.11 (m, 1H), 7.98-7.94 (m, 1H), 7.79-7.75 (m, 1H), 7.74-7.71 (m, 1H), 7.68-7.61 (m, 3H), 7.54-7.46 (m, 3H), 7.42-7.39 (m, 3H),-7.18-7.11 (m, 2H), 6.12 (t, J = 7.0 Hz, 1H), 4.38 (s, 2H), 4.00 (d, J = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 162.4($^1J_{CF}$ =245.8 Hz), 152.1, 151.4, 140.9, 130.9(0), 130.9(5), 130.6($^3J_{CF}$ =8.1 Hz), 129.3, 128.9, 128.7, 128.5, 128.2($^4J_{CF}$ =2.6 Hz), 127.8, 127.5,126.7, 126.3, 125.9, 124.2, 123.4, 116.4, 115.7($^2J_{CF}$ =21.4 Hz), 112.5, 67.9, 25.8. IR (KBr, v, cm^{-1}) 3390, 3050, 1601, 1508, 1393, 1222, 1157, 1008. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}FO_2Na$ 431.1423; Found 431.1403.

(Z)-2-(4-chlorophenyl)-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol ***(3f,*** *major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3f** (61.1 mg, 48%) as a white solid, mp 132-133 °C, *Z/E*= 2:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.78 (d, J = 7.2 Hz, 1H), 7.61-7.58 (m, 2H), 7.51-7.47 (m, 2H), 7.45-7.42 (m, 1H), 7.41-7.36 (m, 5H), 7.34 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 0.8 Hz, 2H), 5.99 (t, J = 7.0 Hz, 1H), 4.33 (s, 2H), 3.66 (d, J = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100

MHz, $CDCl_3$; δ, ppm) 154.0, 151.1, 140.4, 138.8, 133.6, 130.9, 130.2, 130.0, 128.9(8), 128.9(6), 128.7(2), 128.7(7), 128.4, 127.9, 127.4, 127.1, 126.4, 124.6, 122.6, 119.6, 114.1, 111.3, 67.7, 24.1. IR (KBr, v, cm^{-1}) 3343, 3058, 1489, 1441, 1263, 1092, 1009, 820. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}ClO_2Na$ 447.1128; Found 447.1113.

*(Z)-2-(3-chlorophenyl)-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3g**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3g** (80.1 mg, 63%) as a white solid, mp 155-156 °C, *Z/E*= 5:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.37 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.0Hz, 1H), 7.79-7.75 (m, 3H), 7.71 (d, J = 8.8 Hz, 1H), 7.60-7.56 (m, 1H), 7.53-7.48 (m, 3H), 7.43 (d, J = 7.2 Hz, 2H), 7.33-7.30 (m, 1H), 7.22 (d, J = 5.6 Hz, 2H), 6.23 (t, J = 6.4 Hz, 1H), 4.81 (s, 2H), 4.24 (d, J = 6.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 151.9, 142.3, 139.3, 134.6, 132.0, 131.0, 130.9, 129.8, 129.4, 128.9, 128.8, 128.6, 128.5, 127. 8, 127.6, 127.5, 126.7, 126.6, 126.1, 124.8, 124.4, 123.3, 123.0, 116.1, 112.6, 60.0, 25.0. IR (KBr, v, cm^{-1}) 3441, 1591, 1491, 1395, 1263, 1096, 1006, 808. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}ClO_2Na$ 447.1128; Found 447.1119.

*(Z)-2-(4-bromophenyl)-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3h**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3h** (73.0 mg, 52%) as a white solid, mp 127-128 °C, *Z/E*= 10:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.14-8.10 (m, 1H), 7.98-7.94 (m, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.64-7.61 (m, 2H), 7.59-7.56 (m, 2H), 7.52-7.47 (m, 2H), 7.43-7.38 (m, 3H), 7.31-7.27 (m, 2H), 6.13 (t, J = 7.0 Hz, 1H), 4.37 (s, 2H), 3.99 (d, J = 6.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 152.1, 151.4, 140.8, 136.8, 131.8, 130.9, 130.8, 130.6, 129.3, 128.7, 128.5, 128.3, 127.5, 127.0, 126.3, 125.9, 124.2, 123.4, 123.0, 122.0, 116.3, 112.5, 67.7, 25.7. IR (KBr, v, cm^{-1}) 3422, 3053, 1488, 1393, 1070, 1011, 802, 730. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}BrO_2Na$ 491.0623; Found 491.0611.

*(Z)-2-(3-bromophenyl)-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3i**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3i** (95.5 mg, 68%) as a white solid,

mp 167-168 °C, *Z/E* > 19:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.36 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.79-7.75 (m, 3H), 7.71 (d, J = 8.8 Hz, 1H), 7.60-7.56 (m, 2H), 7.54-7.49 (m, 3H), 7.43 (d, J = 7.2 Hz, 1H), 7.39-7.35 (m, 2H), 7.18-7.14 (m, 1H), 6.22 (t, J = 6.2 Hz, 1H), 4.80 (s, 2H), 4.24 (d, J = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 152.0, 142.6, 139.3, 131.0(0), 131.0(9), 130.9, 130.5, 130.1, 129.6, 129.4, 128.9, 128.6(7), 128.6(4), 127.8, 126.6, 126.1, 125.1, 124.4, 123.2, 123.0, 122.8, 116.1, 112.6, 60.0, 25.3. IR (KBr, v, cm^{-1}) 3412, 1589, 1491, 1396, 1096, 1007, 807, 697. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}BrO_2Na$ 491.0623; Found 491.0625.

*(Z)-2-phenyl-4-(2-(p-tolyl)naphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3j**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3j** (99.4 mg, 82%) as a white solid, mp 123-124 °C, *Z/E*= 3:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.14 (d, J = 7.6 Hz, 1H), 7.97-7.93 (m, 1H), 7.70 (d, J = 2.8 Hz, 1H), 7.67 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.51 (s, 1H), 7.49 (d, J = 2.4 Hz, 2H), 7.48-7.45 (m, 3H), 7.34-7.31 (m, 1H), 7.22 (d, J = 8.4 Hz, 2H), 6.10 (t, J = 6.6 Hz, 1H), 4.42 (s, 2H), 4.02 (d, J = 6.8 Hz, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 151.9, 141.8, 138.1, 130.8, 129.6, 129.4, 129.2, 128.9, 128.7, 127.9, 127.6, 127.3, 126.6, 126.3, 126.1, 125.6, 124.1, 123.6, 123.1, 116.1, 112.4, 67.8, 25.8, 21.4. IR (KBr, v, cm^{-1}) 3424, 3022, 1505, 1441, 1392, 1266, 1085, 1005. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{24}O_2Na$ 427.1674; Found 427.1665.

*(Z)-2-phenyl-4-(2-(m-tolyl)naphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3k**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3k** (65.4 mg, 54%) as a white solid, mp 149-150 °C, *Z/E*= 15:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.41 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.62-7.56 (m, 3H), 7.52-7.49 (m, 1H), 7.47-7.45 (m, 2H), 7.43-7.38 (m, 1H), 7.34-7.26 (m, 3H), 7.24 (d, J = 7.2 Hz, 1H), 6.23 (t, J = 6.2 Hz, 1H), 4.86 (s, 2H), 4.24 (d, J = 6.4 Hz, 2H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.1, 152.0, 140.3, 140.2, 138.6, 130.9, 130.8, 129.7, 129.3, 128.7, 128.6(4), 128.6(5), 128.3, 127.6, 126.6, 126.5, 125.8, 124.9, 124.3, 123.4, 123.1, 116.3, 112.5, 60.1, 25.2, 21.6. IR (KBr, v, cm^{-1}) 3416,

3058, 1608, 1488, 1393, 1265, 1172, 1005. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{24}O_2Na$ 427.1674; Found 427.1682.

*(Z)-4-(2-(3,4-dimethylphenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3l**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3l** (92.8 mg, 74%) as a white solid, mp 143-144 °C, *Z/E*= 7:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.40 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 9.2 Hz, 1H), 7.72-7.69 (m, 1H), 7.59-7.54 (m, 2H), 7.52-7.48 (m, 2H), 7.48-7.43 (m, 3H), 7.33-7.27 (m, 3H), 7.25 (s, 1H), 6.22 (t, J = 4.8 Hz, 1H), 4.85 (s, 2H), 4.23 (d, J = 6.0 Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3 152.1, 140.2, 137.3, 137.2, 130.9, 130.1, 129.9, 129.3, 128.9, 128.7, 128.6, 128.5, 127.6, 126.6, 126.5, 125.6, 125.3, 124.2, 123.4, 115.8, 112.5, 60.1, 25.3, 20.0, 19.8. IR (KBr, v, cm^{-1}) 3426, 1624, 1500, 1436, 1389, 1086, 1086, 1009. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{26}O_2Na$ 441.1830; Found 441.1847.

*(Z)-4-(2-(3,5-dimethylphenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3m**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3m** (76.5 mg, 61%) as a white solid, mp 134-135 °C, *Z/E*= 2:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.15-8.11 (m, 1H), 8.01-7.96 (m, 1H), 7.66, J = 8.8 Hz, 1H), 7.46 (d, J = 4.4 Hz, 5H), 7.41-7.37 (m, 2H), 7.32-7.28 (m, 3H), 7.02 (s, 1H), 6.08 (t, J = 6.4 Hz, 1H), 4.43 (d, J = 1.2 Hz, 2H), 4.04 (d, J = 6.4 Hz, 2H), 2.36 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.0, 151.7, 141.7, 138.5, 138.3, 130.8, 130.3, 130.0, 129.2, 128.8, 128.7, 128.5, 127.8, 126.6, 126.2, 125.5, 125.3, 124.1, 123.6, 123.1, 116.4, 112.4, 67.8, 25.7, 21.5. IR (KBr, v, cm^{-1}) 3545, 3052, 1492, 1391, 1267, 1114, 1016, 836. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{26}O_2Na$ 441.1830; Found 441.1852.

*(Z)-4-(2-(4-ethylphenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3n**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3n** (75.2 mg, 60%) as a white solid, mp 161-162 °C, *Z/E*= 5:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.40 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.73-7.69 (m, 3H), 7.58-7.54 (m, 1H), 7.51-7.44 (m, 4H), 7.37-7.28 (m, 4H), 6.23 (t, J = 6.2 Hz, 1H), 4.86 (s, 2H), 4.24 (d, J = 6.4 Hz, 2H), 2.76-2.70 (m,

2H), 1.30 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 152.1, 152.1, 144.8, 140.3, 130.9, 129.8, 129.3, 128.6, 128.4, 127.7, 127.6, 126.6, 126.4, 125.7, 124.2, 123.4, 115.9, 112.5, 60.1, 28.8, 25.3, 15.5. IR (KBr, v, cm^{-1}) 3417, 2957, 1625, 1505, 1437, 1393, 1006, 797. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{26}O_2Na$ 441.1830; Found 441.1850.

*(Z)-2-phenyl-4-(2-(4-propylphenyl)naphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3o**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3o** (81.6 mg, 63%) as a white solid, mp 89-90 °C, *Z/E*= 3:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.16-8.12 (m, 1H), 7.97-7.93 (m, 1H), 7.73-7.69 (m, 2H), 7.66 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.52-7.48 (m, 5H), 7.35-7.32 (m, 1H), 7.23 (d, J = 8.4 Hz, 2H), 6.11 (t, J = 6.6 Hz, 1H), 4.43 (d, J = 0.8 Hz, 2H), 4.03 (d, J = 6.4 Hz, 2H), 2.70-2.61 (m, 2H), 1.76-1.64 (m, 2H), 1.04-0.98 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 152.0, 151.6, 142.9, 141.8, 137.8, 130.8, 129.8, 129.2, 129.0(8), 129.0(5), 128.8, 128.7, 128.5, 128.3, 127.9, 127.6, 127.3, 126.6, 126.4, 126.1, 125.5, 124.1, 123.6, 123.2, 116.1, 112.4, 67.8, 37.9, 25.8, 24.5, 13.9. IR (KBr, v, cm^{-1}) 3427, 3052, 1623, 1505, 1436, 1392, 1267, 1087. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{28}O_2Na$ 455.1987; Found 455.1977.

*(Z)-4-(2-(4-(tert-butyl)phenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3p**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3p** (73.6 mg, 55%) as a white solid, mp 88-89 °C, *Z/E* > 19:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17-8.09 (m, 1H), 7.97-7.91 (m, 1H), 7.71 (d, J = 9.2 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.53-7.49 (m, 2H), 7.49-7.45 (m, 4H), 7.45-7.37 (m, 3H), 6.11 (t, J = 6.4 Hz, 1H), 4.43 (s, 2H), 4.03 (d, J = 6.4 Hz, 2H), 1.38 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 152.0, 151.6, 151.2, 141.7, 137.8, 130.8, 129.2, 129.0, 128.6, 128.5, 128.0, 127.8, 127.2, 126.4, 126.1, 125.6, 125.5, 124.1, 123.5, 123.2, 116.1, 112.4, 67.8, 34.8, 31.3, 25.8. IR (KBr, v, cm^{-1}) 3428, 3053, 1623, 1441, 1392, 1173, 1012, 802. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{30}O_2Na$ 469.2143; Found 469.2120.

*(Z)-4-(2-(4-fluorophenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3q**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3q** (85.7mg, 70%) as a white solid,

mp 125-126 °C *Z/E* > 19:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.18 (d, J = 8.0 Hz, 1H), 7.97-7.93 (m, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.61-7.56 (m, 2H), 7.55-7.47 (m, 4H), 7.46-7.38 (m, 3H), 7.09-7.03 (m, 2H), 6.11 (t, J = 6.4 Hz, 1H), 4.43 (s, 2H), 3.98 (d, J = 6.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 162.5 ($^1J_{CF}$ =247.1 Hz), 152.0, 150.4, 141.9, 137.7, 130.9, 129.2, 129.2($^3J_{CF}$ =8.2 Hz), 128.9, 128.7, 128.5, 128.0, 127.0($^4J_{CF}$ =3.3 Hz), 126.3, 125.9, 125.8, 124.2, 123.4, 122.9, 116.4, 115.7($^2J_{CF}$ =21.6 Hz), 112.4, 67.7, 25.7. IR (KBr, v, cm^{-1}) 3483, 3051, 1598, 1501, 1391, 1222, 1081, 993. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}FO_2Na$ 431.1423; Found 431.1407.

(Z)-4-(2-(4-chlorophenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol ***(3r)*** Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3r** (95.4 mg, 75%) as a white solid, mp 88-89 °C *Z/E* > 19:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.48-7.41 (m, 4H), 7.40 (d, J = 7.6 Hz, 3H), 7.34 (d, J = 7.2 Hz, 1H), 7.32-7.26 (m, 3H), 7.25 (d, J = 6.8 Hz, 2H), 7.21-7.17 (m, 2H), 5.89 (t, J = 7.0 Hz, 1H), 4.32 (s, 2H), 3.61 (d, J = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 153.9, 149.9, 141.6, 137.7, 134.0, 130.0, 129.3, 128.8(0), 128.8(8), 128.7, 128.1, 127.8, 124.9, 124.8, 122.7, 119.7, 114.9, 111.1, 67.7, 24.0. IR (KBr, v, cm^{-1}) 3306, 1488,1453, 1094, 1008, 830, 756, 696. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}ClO_2Na$ 447.1128; Found 447.1131.

(Z)-4-(2-(3-chlorophenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol ***(3s)*** Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3s** (91.5 mg, 72%) as a white solid, mp 107-108 °C, *Z/E* > 19:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.46 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 9.2 Hz, 2H), 7.77-7.71 (m, 2H), 7.67-7.61 (m, 1H), 7.58-7.54 (m, 1H), 7.52-7.47 (m, 3H), 7.39-7.31 (m, 4H), 6.24 (t, J = 6.6 Hz, 1H), 4.94 (s, 2H), 4.30 (d, J = 6.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 150.2, 140.8, 140.1, 134.8, 132.6, 130.9, 130.1, 129.4, 129.1, 128.7, 128.3, 127.7, 127.4, 126.7, 126.6, 126.5, 125.6, 124.4, 123.3, 117.5, 112.4, 60.2, 25.2. IR (KBr, v, cm^{-1}) 3419, 1600, 1478, 1393, 1237, 1108, 100, 803. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}ClO_2Na$ 447.1128; Found 447.1101.

*(Z)-4-(2-(2-chlorophenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3t**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3t** (50.9 mg, 40%) as a white solid, mp 87-88 °C, *Z/E*= 2:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.15 (d, J = 8.0 Hz, 1H), 8.00-7.96 (m, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.70-7.66 (m, 2H), 7.54-7.50 (m, 2H), 7.49 (s, 1H), 7.47-7.44 (m, 4H), 7.40-7.36 (m, 1H), 7.32-7.29 (m, 2H), 6.08 (t, J = 6.4 Hz, 1H), 4.43 (s, 2H), 4.00 (d, J = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 149.7, 142.4, 137.7, 134.8, 132.6, 130.9, 129.9, 129.3, 128.9, 128.8, 128.5, 128.1, 128.0, 127.3, 126.6, 126.5, 126.4, 125.4, 124.4, 123.5, 123.0, 117.7, 112.4, 67.7, 25.7. IR (KBr, v, cm^{-1}) 3408, 3053, 1599, 1472, 1392, 1081, 999, 802. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{22}ClO_2$ 425.1308; Found 425.1300.

*(Z)-4-(2-(4-bromophenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3u**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3u** (120.7 mg, 86%) as a white solid, mp 105-106 °C, *Z/E*= 10:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96 (d, J = 8.0 Hz, 1H), 7.75-7.72 (m, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 4.0 Hz, 1H), 7.33-7.26 (m, 5H), 7.26-7.17 (m, 5H), 7.04 (s, 1H), 5.88 (t, J = 6.4 Hz, 1H), 4.20 (s, 2H), 3.77 (d, J = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.1, 150.1, 142.1, 137.6, 131.8, 130.9, 129.7, 129.3, 128.9, 128.7(2), 128.7(7), 128. 5, 128.0, 126.4, 126.2, 125.4, 124.3, 123.4, 123.0, 122.2, 117.2, 112.4, 67.7, 25.7. IR (KBr, v, cm^{-1}) 3389, 1482, 1392, 1076, 1006, 837, 797, 712. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}BrO_2Na$ 491.0623; Found 491.0625.

*(Z)-4-(2-(3-chloro-4-fluorophenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3v**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3v** (106.1 mg, 80%) as a white solid, mp 119-120 °C, *Z/E* > 19:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17 (d, J = 8.0 Hz, 1H), 7.97-7.94 (m, 1H), 7.75-7.70 (m, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.54-7.46 (m, 4H), 7.45-7.38 (m, 4H), 7.11-7.06 (m, 1H), 6.07 (t, J = 6.4 Hz, 1H), 4.41 (d, J = 0.8 Hz, 2H), 3.96 (d, J = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 157.8($^1J_{CF}$ =249.8 Hz), 152.2, 149.0(9), 149.0(7), 149.0(6),142.4, 137.6, 130.9, 129.5, 129.4, 128.8($^3J_{CF}$ =7.2 Hz), 128.5, 128.2($^4J_{CF}$ =4.1 Hz), 128.1, 127.1(3), 127.1(6),

126.5, 126.4, 125.2, 124.4, 123.4, 122.8, 121.7, 121.5, 116.8 ($^2J_{CF}$ =21.3 Hz) 112.4, 67.7, 25.6. IR (KBr, *v*, cm^{-1}) 3424, 3060, 1494, 1392, 1262, 1087, 1011, 880. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{20}ClFO_2Na$ 465.1034; Found 465.1029.

*(Z)-4-(2-(2-nitrophenyl)naphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3w**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 5/1 v/v) yielded **3w** (94.1 mg, 72%) as an orange solid, mp 150-151 °C, *Z/E*= 9:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.13 (d, *J* = 8.0 Hz, 1H), 7.99-7.96 (m, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.61-7.56 (m, 2H), 7.56-7.53 (m, 2H), 7.52-7.47 (m, 3H), 7.43-7.39 (m, 2H), 7.36-7.32 (m, 3H), 6.02 (t, *J* = 6.4 Hz, 1H), 4.35 (s, 2H), 3.86 (d, *J* = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 153.0, 149.2, 147.0, 142.1, 137.8, 132.6, 132.3, 130.9, 129.7, 129.3, 128.7, 128.6, 128.5, 127.8, 126.6, 126.5, 125.1, 124.9, 124.4, 123.6, 122.2, 118.9, 112.6, 67.7(0), 67.7(9), 25.4. IR (KBr, *v*, cm^{-1}) 3450, 1619, 1528, 1393, 1026, 807, 702, 647. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}NO_4Na$ 458.1368; Found 458.1390.

*(Z)-2-phenyl-4-(2-(thiophen-2-yl)naphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3x**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3x** (89.1 mg, 75%) as a white solid, mp 88-89 °C, *Z/E*= 3:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.03-7.99 (m, 1H), 7.94-7.90 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.53-7.50 (m, 2H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.47-7.46 (m, 1H), 7.45-7.40 (m, 3H), 7.39-7.35 (m, 1H), 7.33-7.30 (m, 1H), 7.11-7.07 (m, 1H), 5.99 (t, *J* = 6.6 Hz, 1H), 4.40 (d, *J* = 1.2 Hz, 2H), 4.08 (d, *J* = 6.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ, ppm) 151.8, 146.7, 142.1, 137.8, 132.7, 130.8, 129.2, 129.0, 128.7, 128.3, 127.9, 127.7, 126.5, 126.2, 126.0, 125.8, 125.5, 125.4, 124.2, 123.5, 123.0, 116.3, 112.2, 67.7, 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}O_2S$ 397.1262; Found 397.1255.

*(Z)-4-(2-methylnaphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3y**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3y** (73.8 mg, 75%) as a white solid, mp 83-84 °C, *Z/E*= 3:1; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.05-8.00 (m, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.53-7.48 (m, 2H), 7.45-7.40 (m, 5H), 7.31-7.26 (m, 1H), 5.93 (t, *J* = 6.8

Hz, 1H), 4.33 (s, 2H), 3.72 (d, *J* = 6.8 Hz, 2H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; *δ*, ppm) 151.5, 150.4, 141.2, 138.1, 130.6, 130.1, 128.7, 128.0, 127.8, 126.5, 125.8, 124.3, 123.8, 123.5, 122.4, 115.0, 112.2, 67.8, 25.0, 11.9. IR (KBr, *v*, cm^{-1}) 3520, 1522, 1480, 1375, 1120, 1068, 953, 801. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}O_2Na$ 351.1361; Found 351.1373.

*(Z)-4-(7-bromo-2-phenylnaphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3z**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3z** (92.7 mg, 66%) as a white solid, mp 90-91 °C, *Z/E*= 3:1; ^1H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.15 (d, *J* = 1.6 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.69-7.65 (m, 4H), 7.62-7.60 (m, 1H), 7.59-7.57 (m, 1H), 7.52 (d, *J* = 1.2 Hz, 1H), 7.50 (s, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.43 (d, *J* = 2.8 Hz, 2H), 7.39-7.38 (m, 2H), 6.08 (t, *J* =6.6 Hz, 1H), 4.45 (d, *J* = 0.8 Hz, 2H), 4.01 (d, *J* = 6.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; *δ*, ppm) 152.5, 151.7, 142.0, 137.7, 131.7(9), 131.7(7), 130.7, 130.5, 128.9, 128.7, 128.4, 128.0, 127.8, 127.5, 125.9, 123.7, 123.2, 123.0, 118.8, 116.5, 116.4, 113.1, 67.7, 25.7. IR (KBr, *v*, cm^{-1}) 3423, 3053, 1564, 1499, 1391, 1296, 1168, 1068. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{21}BrO_2Na$ 491.0623; Found 491.0627.

*(Z)-4-(9-methoxy-2-phenylnaphtho[2,1-b]furan-1-yl)-2-phenylbut-2-en-1-ol (**3aa**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3aa** (91.8 mg, 73%) as a white solid, mp 99-100 °C, *Z/E*= 4:1; ^1H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.88 (d, *J* = 9.2 Hz, 1H), 7.77-7.73 (m, 3H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.60-7.57 (m, 1H), 7.53-7.49 (m, 2H), 7.47-7.40 (m, 4H), 7.32-7.27 (m, 2H), 7.16-7.13 (m, 1H), 6.23 (t, *J* = 5.8 Hz, 1H), 4.86 (s, 2H), 4.22 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; *δ*, ppm) 158.3, 152.8, 151.5, 140.8, 140.1, 130.9, 130.7, 129.8, 129.7, 128.9, 128.8(0), 128.8(5), 128.7, 128.4, 127.8, 127. 7, 127.4, 126.5, 125.9, 125.8, 122.6, 116.3, 115.3, 110.2, 110.1, 103.9, 59.9, 55.6, 25.1. IR (KBr, *v*, cm^{-1}) 3435, 3026, 1588,1493, 1385, 1260, 1057, 807. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{24}O_3Na$ 443.1623; Found 443.1615.

*(Z)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)but-2-en-1-ol (**3bb**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3bb** (74.3 mg, 70%) as a white solid, mp 84-85 °C, *Z/E* > 19:1; ^1H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 4.4 Hz, 1H), 7.45

(d, *J* = 3.6 Hz, 1H), 7.43 (s, 1H), 7.41 (s, 1H), 7.39-7.36 (m, 2H), 7.36 (s, 1H), 7.30-7.27 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.95 (t, *J* = 7.2 Hz 1H), 4.37 (s, 2H), 3.67 (d, *J* = 2.8 Hz, 2H), 2.39 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$; *δ*, ppm) 153.9, 151.3, 141.3, 138.2, 137.9, 130.2, 129.3, 128.8, 128.6, 128.1, 127.7, 126.9, 125.7, 124.2, 122.4, 119.5, 113.7, 111.0, 67.8, 24.0, 21.4. IR (KBr, *v*, cm^{-1}) 3306, 1571, 1507, 1402, 1262, 1100, 1010, 819. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{22}O_2Na$ 377.1517; Found 377.1510.

*(Z)-4-(2-(4-chlorophenyl)benzofuran-3-yl)-2-phenylbut-2-en-1-ol (**3cc**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3cc** (76.3 mg, 68%) as a white solid, mp 89-90 °C, *Z/E*= 13:1; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.52 (s, 1H), 7.50 (s, 1H), 7.48-7.47 (m, 1H), 7.46 (d, *J* = 1.6 Hz, 2H), 7.44 (s, 1H), 7.41-7.38 (m, 1H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.34 (s, 1H), 7.31 (d, *J* = 2.0 Hz, 2H), 7.29 (s, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.94 (t, *J* = 7.2 Hz, 1H), 4.38 (s, 2H), , 3.66 (d, *J* = 7.2 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$; *δ*, ppm) 153.9, 149.9, 141.6, 137.7, 134.0, 130.0, 129.3, 128.8(0), 128.8(7), 128.7, 128.1, 127.8, 124.9, 124.8, 122.7, 119.7, 114.8, 111.1, 67.7, 24.0. IR (KBr, *v*, cm^{-1}) 3445, 1543, 1488, 1400, 1259, 1093, 1008, 830. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}ClO_2Na$ 397.0971; Found 397.0961.

*(Z)-4-(2-([1,1'-biphenyl]-4-yl)benzofuran-3-yl)-2-phenylbut-2-en-1-ol (**3dd**, major)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **3dd** (81.1 mg, 65%) as a white solid, mp 95-96 °C, *Z/E*= 3:1; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$; *δ*, ppm) 7.75-7.67 (m, 3H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.62 (s, 1H), 7.60 (s, 1H), 7.50-7.47 (m, 3H), 7.46-7.42 (m, 3H), 7.38 (d, *J* = 7.6 Hz, 4H), 7.33-7.28 (m, 2H), 5.99 (t, *J* = 7.0 Hz, 1H), 4.39 (s, 2H), 3.73 (d, *J* = 7.2 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$; *δ*, ppm) 154.0, 150.8, 141.5, 140.8, 140.5, 137.9, 130.2, 129.8, 129. 3, 128.9, 128.7, 127.7, 127.6, 127.5, 127.3, 127.1, 125.4, 124.5, 122.5, 119.6, 114.6, 111.1, 67.8, 24.1. IR (KBr, *v*, cm^{-1}) 3431, 1599, 1487, 1403, 1261, 1097, 1008, 760. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{24}O_2Na$ 439.1674; Found 439.1666;

General Procedure for the Synthesis of 5

Example for the synthesis of **5a**.

Under the air conditions, 1-(phenylethynyl)naphthalen-2-ol (**1a**, 0.36 mmol, 87.8 mg), 4-vinyl-1,4-dihydro-2H-benzo[*d*][1,3]oxazin-2-one (**4a**, 0.3 mmol, 52.6 mg) and $Pd_2(dba)_3$ (2.5 mol %, 6.9 mg) were added in a 10-mL reaction vial, Then, MeCN (3.0 mL) was added into this reaction system. The reaction vial was sealed and heated at 60 °C in an oil bath for 5 h until TLC (petroleum ether: ethyl acetate= 5:1) revealed that conversion of the starting material **4a** was completed. Then the reaction mixture was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ ethyl acetate = 10:1) to afford the desired product **5a** as white solid.

*(E)-2-(3-(2-phenylnaphtho[2,1-b]furan-1-yl)prop-1-en-1-yl)aniline (**5a**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **5a** (78.8 mg, 70%) as a white solid, mp 96-97 °C, *Z/E* > 19:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.39 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 7.2 Hz, 2H), 7.79-7.72 (m, 2H), 7.58-7.46 (m, 4H), 7.44-7.39 (m, 1H), 7.30 (d, J = 6.8 Hz, 1H), 7.06-7.01 (m, 1H), 6.77-6.71 (m, 1H), 6.61-6.52 (m, 3H), 4.17 (d, J = 2.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.2, 143.5, 130.9(3), 130.9(1), 129.3, 129.2, 128.8, 128.4, 128.3, 127.7, 127.5, 127.3, 126.4, 125.9, 124.2, 124.0, 123.5, 123.4, 118.9, 115.8, 114.7, 112.5, 29.5. IR (KBr, v, cm^{-1}) 3434, 1613, 1489, 1393, 1266, 1070, 1024, 805. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{21}NONa$ 398.1521; Found 398.1518.

(E)-5-methyl-2-(3-(2-phenylnaphtho[2,1-b]furan-1-yl)allyl)aniline (***5b***) Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **5b** (84.0 mg, 68%) as a white solid, mp 101-102 °C, *Z/E* > 19:1; ^{1}H NMR (400 MHz, DMSO; δ, ppm) 8.44 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.91-7.86 (m, 2H), 7.85-7.81 (m, 2H), 7.64-7.56 (m, 3H), 7.54-7.46 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.70 (d, J = 15.6 Hz, 1H), 6.41-6.34 (m, 2H), 6.30 (d, J = 8.0 Hz, 1H), 4.78 (s, 2H), 4.11 (d, J = 4.0 Hz, 2H), 2.10 (s, 3H).^{13}C{1H} NMR (100 MHz, DMSO; δ, ppm) 152.0, 151.7, 145.7, 137.6, 131.0, 130.8, 129.6, 129.6, 129.1, 128.3, 127.9, 127.6, 127.1, 126.8, 126.6, 126.0, 124.9, 124.0, 123.3,

119.5, 118.1, 116.3, 116.1, 113.0, 29.3, 21.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{23}NO_2Na$ 412.1677; Found 412.1689.

*(E)-4-methyl-N-(2-(3-(2-phenylnaphtho[2,1-b]furan-1-yl)prop-1-en-1-yl)phenyl)benzenesulfonamide (**5c**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **5c** (120.6 mg, 76%) as a white solid, mp 97-98 °C, *Z/E* > 19:1; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.19-8.10 (m, 2H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.61-7.56 (m, 2H), 7.55-7.49 (m, 2H), 7.46-7.39 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.25-7.20 (m, 1H), 7.19-7.13 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.43-6.35 (m, 1H), 5.62 (d, *J* = 16.0 Hz, 1H), 5.41 (s, 1H), 4.03-3.97 (m, 2H), 1.89 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3 152.2, 143.5, 135.8, 133.1, 133.0, 132.5, 131.3, 130.7, 130.1, 129.2, 129.0, 128.6, 128.4, 128.0, 127.3, 127.2, 126.9, 126.7(3), 126.7(5), 126.2, 124.8, 123.3, 122.9, 113.7, 112.5, 29.4, 21.0. IR (KBr, *v*, cm^{-1}) 3311, 1485, 1385, 1183, 1090, 899, 818, 768. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}O_3Sna$ 552.1609; Found 552.1589.

General Procedure for the Synthesis of 6a

To a solution of (*Z*)-2-phenyl-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-en-1-ol (**3a**, 0.5 mmol, 195.0 mg) in DCM (5.0 mL) was added the solution of pyridinium chlorochromate (PCC, 1.5 mmol, 161.7 mg) in DCM (5.0 mL) at 0 °C. After stirring for 30 min, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ ethyl acetate = 10:1) to afford the desired product **6a** as white solid.

*(Z)-2-phenyl-4-(2-phenylnaphtho[2,1-b]furan-1-yl)but-2-enal (**6a**)* Isolation by column chromatography (petroleum ether: ethyl acetate= 10/1 v/v) yielded **6a** (116.4 mg, 95%) as a white solid, mp 92-93 °C, *Z/E* > 19:1; ^{1}H NMR (400 MHz, DMSO; δ, ppm) 9.67 (s, 1H), 8.11-8.06 (m, 2H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.63-7.59 (m, 2H), 7.58-7.52 (m, 4H), 7.49-7.45 (m, 3H), 7.44 (d, J = 1.6 Hz, 3H), 7.23 (t, *J* = 6.8 Hz, 1H), 4.30 (d, *J* = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO; δ, ppm) 194.7, 153.0, 151.9, 151.7, 144.1, 132.5, 131.0, 130.4, 130.0, 129.8, 129.4, 129.2, 128.8, 128.7, 128.1,

127.6, 127.1, 126.8, 125.0, 123.3, 122.5, 115.0, 112.9, 26.9. IR (KBr, *v*, cm^{-1}) 3650, 1683, 1492, 1394, 1239, 1083, 1024, 950. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{20}O_2Na$ 411.1361; Found 411.1338.

ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all pure products, and X-ray crystal data (CIF) for **5b**. This material is available free of charge via the Internet at http//pubs.acs.org.

Notes

The authors declare no competing financial interest.

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REFERENCES

[1] For selected reviews, see: (a) Huang, M.-H.; Hao, W.-J.; Li, G.; Tu, S.-J.; Jiang, B. Recent Advances in Radical Transformations of Internal Alkynes. *Chem. Commun.* **2018**, *54*, 10791−10811. (b) Huang, M.-H.; Hao, W.-J.; Jiang, B. Recent Advances in Radical Enabled Bicyclization and Annulation /1, n-Bifunctionalization Reactions. *Chem. Asian J.* **2018**, *13*, 2958−2977. (c) Dorel, R.; Echavarren, A. M. Gold(I)-Catalyzed Activation of Alkynes for the Construction of Molecular Complexity. *Chem. Rev.* **2015**, *115*, 9028−9072. (d) Chinchilla, R.; Najera, C. Chemicals from Alkynes with Palladium Catalysts. *Chem. Rev.* **2014**, *114*, 1783−1826. (e) Gilmore, K.; Alabugin, I. V. Cyclizations of Alkynes: Revisiting Baldwin's Rules for Ring Closure. *Chem. Rev.* **2011**, *111*, 6513−6556. (f) Wille, U. Radical Cascades Initiated by Intermolecular Radical Addition to Alkynes and Related Triple Bond Systems. *Chem. Rev.* **2013**, *113*, 813−853.

[2] (a) Li, Y.; Gryn'ova, G.; Saenz, Felipe; J. X.; Sivula, K.; Corminboeuf, C.; Waser, J. Heterotetracenes: Flexible Synthesis and in Silico Assessment of the Hole-Transport Properties. *Chem. Eur. J.* **2017**, *23*, 8058−8065. (b) Zhang, T.-S.; Wang, R.; Cai, P.-J.; Hao, W.-J.; Tu, S.-J.; Jiang, B. Silver-catalyzed Nitration/annulation of 2-alkynylanilines for Tunable Synthesis of Nitrated Indoles and Indazole-2-oxides. *Org. Chem. Front.* **2019**, *6*, 2968−2973. (c) Liu, S.; Chen, K.; Hao, W.-J.; Tu, X.-C.; Tu, S.-J.; Jiang, B. Generation of 1,3-dimethylene-substituted Isobenzofurans via Pd(II)-

Catalyzed Selective oxo-cyclization/SO_2 Insertion Ascade of β-alkynyl Ketones. *J. Org. Chem.* **2019**, *84*, 1964−1971. (d) Hao, W.-J.; Wu, Y.-N.; Gao, Q.; Wang, S.-L.; Tu, S.-J.; Jiang, B. Dual Cobalt(II)/silver Catalysis: Synthesis of Aryliminated Pyrrolo[2,3-*b*]indoles via Multicomponent Bicyclization Cascades. *Tetrahedron Lett.* **2016**, *57*, 4767−4769. (e) Cacchi, S.; Fabrizi, G.; Moro, L. Palladium-Catalyzed Cyclization of *o*-Alkynylphenols with Allyl Carbonates. A Regioselective Synthesis of 2-Substituted-3-allylbenzo[b]furans. *Synlett* **1998**, 741−745. (f) Swamy, N. K.; Yazici, A.; Pyne, S. G. Copper-Mediated Cyclization-Halogenation and Cyclization-Cyanation Reactions of *β*-Hydroxyalkynes and *o*-Alkynylphenols and Anilines. *J. Org. Chem.* **2010**, *75*, 3412−3419. (g) Xia, Z.; Khaled, O.; Mouriès-Mansuy, V.; Ollivier, C.; Fensterbank, L. Dual Photoredox/Gold Catalysis Arylative Cyclization of *o*-Alkynylphenols with Aryldiazonium Salts: A Flexible Synthesis of Benzofurans. *J. Org. Chem.* **2016**, *81*, 7182−7190, and references cited therein.

[3] Sun, J.; Wang, K.; Wang, P.; Zheng, G.; Li, X. Rhodium(III)-Catalyzed Oxidative Allylic C–H Indolylation via Nucleophilic Cyclization. *Org. Lett.* **2019**, *21*, 4662−4666.

[4] (a) Watanabe, K.; Mino, T.; Ishikawa, E.; Masuda, C.; Yoshida, Y.; Sakamoto, M. Hydrazone–Pd-catalyzed Direct Intermolecular Reaction of *o*-alkynylphenols with Allylic Acetates. *Org. Biomol. Chem.* **2018**, *16*, 575−584. (b) Tian, M.; Bai, D.; Zheng, G.; Chang, J.; Li, X. Rh(III)-Catalyzed Asymmetric Synthesis of Axially Chiral Biindolyls by Merging C−H Activation and Nucleophilic Cyclization, *J. Am. Chem. Soc.* **2019**, *141*, 9527−9532.

[5] Li, T.-R.; Wang, Y.-N.; Xiao, W.-J.; Lu, L.-Q. Transition-metal-catalyzed Cyclization Reactions using Vinyl and Ehynyl Benzoxazinones as Dipole Precursors. *Tetrahedron Lett.* **2018**, *59*, 1521–1530.

[6] Guo, W.; Glmóz, J. E.; CristÒfol, À.; Xie, J.; Kleij, A. W. Catalytic Transformations of Functionalized Cyclic Organic Carbonates. *Angew. Chem. Int. Ed.* **2018**, *57*, 13735–13747.

[7] (a) Khan, A.; Yang, L.; Xu, J.; Jin, L. Y.; Zhang, Y. J. Palladium-Catalyzed Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with Michael Acceptors: Construction of Vicinal Quaternary Stereocenters. *Angew. Chem. Int. Ed.* **2014**, *53*, 11257–11260. (b) Khan, A.; Zheng, R.; Kan, Y.; Ye, J.; Xing, J.; Zhang, Y. J. Palladium-Catalyzed Decarboxylative Cycloaddition of Vinylethylene Carbonates with Formaldehyde: Enantioselective Construction of Tertiary Vinylglycols. *Angew. Chem. Int. Ed.* **2014**, *53*, 6439–6442. (c) Khan, A.; Xing, J.; Zhao, J.; Kan, Y.; Zhang, W.; Zhang, Y. J. Palladium-Catalyzed Enantioselective Decarboxylative Cycloaddition of Vinylethylene Carbonates with Isocyanates. *Chem. Eur. J.* **2015**, *21*, 120–124. (d) Yang, L.; Khan, A.; Zheng, R.; Jin, L. Y.; Zhang, Y. J. Pd-Catalyzed Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with Imines. *Org. Lett.* **2015**, *17*, 6230−6233. (e) Khan, A.; Zhang, Y. J. Palladium-Catalyzed Asymmetric Decarboxylative Cycloaddition of

Vinylethylene Carbonates with Electrophiles: Construction of Quaternary Stereocenters. *Synlett.* **2015,** *26*, 853–860. (f) Liu, K.; Khan, I.; Cheng, J.; Hsueh, Y. J.; Zhang, Y. J. Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with *β*-Nitroolefins by Cooperative Catalysis of Palladium Complex and Squaramide. *ACS Catal.* **2018**, *8*, 11600−11604. (g) I.; Khan, Zhao, C.; Zhang, Y. J. Pd-Catalyzed Asymmetric Decarboxylative Cycloaddition of Vinylethylene Carbonates with 3-cyanochromones. *Chem. Commun.* **2018**, **54**, 4708−4711.

[8] (a) Rong, Z.-Q.; Yang, L.-C.; Liu, S.; Yu, Z.; Wang, Y.-N.; Tan, Z. Y.; Huang, R.-Z.; Lan, Y.; Zhao, Y. Nine-Membered Benzofuran-Fused Heterocycles: Enantioselective Synthesis by Pd-Catalysis and Rearrangement via Transannular Bond Formation. *J. Am. Chem. Soc.* **2017**, *139*, 15304−15307. (b) Yang, L.-C.; Rong, Z.-Q.; Wang, Y.-N.; Tan, Z. Y.; Wang, M.; Zhao, Y. Construction of Nine-Membered Heterocycles through Palladium-Catalyzed Formal [5 + 4] Cycloaddition. *Angew. Chem. Int. Ed.* **2017**, *56*, 2927–2931. (c) Yang, L.-C.; Tan, Z. Y.; Rong, Z.-Q.; Liu, R.; Wang, Y.-N.; Zhao, Y. Palladium-Titanium Relay Catalysis Enables Switch from Alkoxide-*π*-Allyl to Dienolate Reactivity for Spiro-Heterocycle Synthesis. *Angew. Chem. Int. Ed.* **2018**, *57*, 7860–7864.

[9] (a) Guo, W.; Martínez-Rodríguez, L.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Highly Efficient Catalytic Formation of (Z)-1,4-But-2-ene Diols Using Water as a Nucleophile. *Angew. Chem. Int. Ed.* **2016**, *55*, 11037–11040. (b) Guo, W.; Martínez-Rodríguez, L.; Kuniyil, R.; Martin, E.; Escudero-Adán, E. C.; Maseras, F.; Kleij, A. W. Stereoselective and Versatile Preparation of Tri- and Tetrasubstituted Allylic Amine Scaffolds under Mild Conditions. *J. Am. Chem. Soc.* **2016**, *138*, 11970−11978. (c) Cai, A.; Guo, W.; Martínez-Rodríguez, L.; Kleij, A. W. Palladium-Catalyzed Regio- and Enantioselective Synthesis of Allylic Amines Featuring Tetrasubstituted Tertiary Carbons. *J. Am. Chem. Soc.* **2016**, *138*, 14194−14197. (d) Glmóz, J. E.; Guo, W.; Kleij, A. W. Palladium-Catalyzed Stereoselective Formation of Substituted Allylic Thioethers and Sulfones. *Org. Lett.* **2016**, *18*, 6042−6045. (e) Guo, W.; Cai, A.; Xie, J.; Kleij, A. W. Asymmetric Synthesis of α,α-Disubstituted Allylic Amines through Palladium-Catalyzed Allylic Substitution. *Angew. Chem. Int. Ed.* **2017**, *56*, 11797–11801. (f) Xie, J.; Guo, W.; Cai, A.; Escudero-Adán, E. C.; Kleij, A. W. Pd-Catalyzed Enantio- and Regioselective Formation of Allylic Aryl Ethers. *Org. Lett.* **2017**, *19*, 6388−6391. (g) Miralles, N.; Gómez, J. E.; Kleij, A. W.; Fernández, E. Copper-Mediated S_N2' Allyl−Alkyl and Allyl−Boryl Couplings of Vinyl Cyclic Carbonates. *Org. Lett.* **2017**, *19*, 6096−6099. (h) Guo, W.; Kuniyil, R.; Gómez, J. E.; Maseras, F.; Kleij, A. W. A Domino Process toward Functionally Dense Quaternary Carbons through Pd-Catalyzed Decarboxylative $C(sp^3)$−$C(sp^3)$ Bond Formation. *J. Am. Chem. Soc*. **2018**, *140*, 3981−3987. (i) Cristòfol, À.; Escudero-Adán, E. C.; Kleij, A.W. Palladium-Catalyzed (Z)-Selective Allylation of Nitroalkanes: Access to Highly Functionalized Homoallylic Scaffolds. *J. Org. Chem.* **2018**, *83*, 9978−9990.

[10] Singha, S.; Patra, T.; Daniliuc, C. G.; Glorius F. Highly Enantioselective [5 + 2] Annulations through Cooperative N-Heterocyclic Carbene (NHC) Organocatalysis and Palladium Catalysis. *J. Am. Chem. Soc.* **2018**, *140*, 3551−3554.

[11] (a) Yuan C.; Wu, Y.; Wang, D.; Zhang, Z.; Wang, C.; Zhou, L.; Zhang, C.; Song, B.; Guo, H. Formal [5 + 3] Cycloaddition of Zwitterionic Allylpalladium Intermediates with Azomethine Imines for Construction of N,O-containing Eight-Membered Heterocycles. *Adv. Synth. Catal.* **2018**, *360*, 652−658. (b) Das, P.; Gondo, S.; Nagender, P.; Uno, H.; Tokunaga, E.; Shibata, N. Access to Denzo-fused Nine-membered Heterocyclic Alkenes with a Trifluoromethyl Carbinol Moiety via a Double Decarboxylativeformal Ring-expansion Process under Palladium Catalysis. *Chem. Sci.* **2018**, *9*, 3276−3281.

[12] (a) Kato, K.; Kusakabe, T.; Sekiyama, E.; Ishino, Y.; Motodate, S.; Kato, S.; Mochida, T. Cyclization-Carbonylation-Cyclization Coupling Reactions of N-Propargylanilines and *o*-Alkynylphenols with Palladium(II)-Bisoxazoline Catalysts. *Synthesis* **2012**, 1825−1832. (b) Fischer, J.; Savage G. P.; Coster M. J. A Concise Route to Dihydrobenzo[*b*]furans: Formal Total Synthesis of (+)-Lithospermic Acid. *Org. Lett.* **2011**, *13*, 3376−3379. (c) Hu, W.; Li, M.; Jiang, G.; Wu, W.; Jiang H. Synthesis of 2,3-Difunctionalized Benzofuran Derivatives through Palladium-Catalyzed Double Isocyanide Insertion Reaction. *Org. Lett.* **2018**, *20*, 3500−3503. (d) Nakamura, M.; Ilies, L.; Otsubo, S.; Nakamura, E. 3-Zinciobenzofuran and 3-Zincioindole: Versatile Tools for the Construction of Conjugated Structures Containing Multiple Benzoheterole Units. *Angew. Chem. Int. Ed.* **2006**, *45*, 944−947. (e) Hu, Y.; Nawoschik, K. J.; Liao, Y.; Ma, J.; Fathi, R.; Yang, Z. Synthesis of Conformationally Restricted 2,3-Diarylbenzo[*b*]furan by the Pd-Catalyzed Annulation of *o*-Alkynylphenols: Exploring a Combinatorial Approach. *J. Org. Chem.* **2004**, *69*, 2235−2239. (f) Watanabe, K.; Mino, T.; Ikematsu, T.; Hatta, C.; Yoshida Y.; Sakamoto, M.; Hydrazone–palladium Catalyzed Annulation of 1-cinnamyloxy-2-ethynylbenzene Derivatives. *Org. Chem. Front.* **2016**, *3*, 979−984.

[13] Niu, B.; Wu, X.-Y.; Wei, Y.; Shi, M. Palladium-Catalyzed Diastereoselective Formal [5 + 3] Cycloaddition for the Construction of Spirooxindoles Fused with an Eight-Membered Ring. *Org. Lett.* **2019**, *21*, 4859-4863.

[14] (a) Li, D.; Tan, Y.; Peng, L.; Li, S.; Zhang, N.; Liu, Y.; Yan, H. Asymmetric Mannich Reaction and Construction of Axially Chiral Sulfone-Containing Styrenes in One Pot from *α*-Amido Sulfones Based on the Waste−Reuse Strategy. *Org. Lett.* **2018**, *20*, 4959−4963. (b) Ji, C.-L.; Hao, W.-J.; Zhang, J.; Geng, F.-Z.; Xu, T.; Tu, S.-J.; Jiang, B. Catalytic Three-Component Synthesis of Functionalized Naphtho[2,1-b]oxecines via a Double Bond Cleavage–Rearrangement Cascade. *Org. Lett.* **2019**, *21*, 6494-6498.

[15] Wang, C.; Ling, Y.; Wu, Y.; Wang, Q.; Shi, W.; Yuan, C.; Yuan, C.; Xiao, Y.; Guo, H. Enantioselective Construction of Tetrahydroquinazoline Motifs via Palladium-Catalyzed [4 + 2] Cycloaddition of Vinyl Benzoxazinones with Sulfamate-Derived Cyclic Imines. *Org. Lett.* **2018**, *20*, 2880-2883.