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Catalyst-Free Synthesis of 2,3-Dihydrobenzofurans *via* a Formal [4+1] Annulation of Propargylamines with Sulfur Ylides

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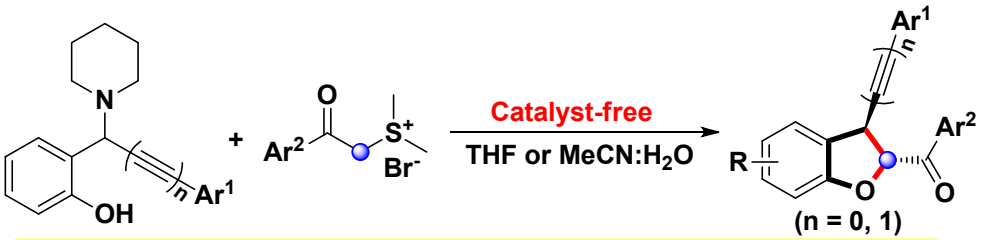
Graphic Abstract



- *Mild conditions*
- *Operational simplicity*
- *Broad substrate scope*
- *Valuable products*
- *Alkynyl and vinyl group tolerated*
- *> 50 examples, up to 95% yield, >20:1 dr*

Abstract: A simple, general route to the 2,3-dihydrobenzofurans substituted at C3 by an aryethynyl or aryl group, starting from propargylamine and its derivatives with benzoyl sulfonium salts, has been developed. This reaction involving *in situ* generated *o*-quinone methide (*o*-QM) intermediate followed by [4+1] annulation with sulfur ylides. Notably, this protocol features are moderate to excellent yields and remarkable diastereoselectivity (>20:1 *dr* in general), easy performance, as well as applicability to versatile 2,3-dihydrobenzofurans with aryethynyl or aryl group *via* C-C and C-O bond formation in one-pot without any catalyst in an aqueous mixed solvent.

INTRODUCTION

The 2,3-dihydrobenzofuran skeleton is an important structural unit that ubiquitously appears not only in numerous complex natural products but also synthetic drugs with diverse bioactivities.[1] For example, the natural product megapodiol can be used as a potential antileukemic agent,[2] (–)-tremetone and (–)-hydroxytremetone, isolated from *Eupatorium urticaefolium* (Compositae), have insecticidal properties.[3] In addition, (2*R*,3*S*)-3,4′-*di*-*O*-methylcedrusin[4] and annullatin A were isolated from the leaves of *Cordyceps annullata* and *Mitrephora teysmannii*, respectively. Moreover, the potent agonistic activity of these compounds toward the cannabinoid receptors CB1 and CB2 has been demonstrated (Figure 1).[5] Given their intriguing biological activities, highly convenient methods for their synthesis have been constantly pursued over a long time and a variety of approaches have been developed.[6] Various efficient strategies have been developed for the preparation of chiral dihydrobenzofurans, such as kinetic resolution,[7] asymmetric synthesis from chiral reagents,[8] or asymmetric catalysis.[9] Meanwhile, various 2,3-dihydrobenzofurans have been synthesized by a variety of powerful methods, such as metal-mediated transformation,[10] organocatalytic [3+2] annulations,[11] intramolecular cyclizations,[12] and electrocyclizations.[13] Recently, [4+1]-cycloannulation[14,15] of orthoquinone methides (*o*-QMs) with carbenoid compounds as an obvious strategy has been developed.[16,17] Despite the remarkable progress achieved in this area, the development of simple and efficient strategy to 2,3-disubstituted-2,3-dihydrobenzofurans using readily available *o*-QMs precursors under catalyst-free conditions remains a challenging goal.

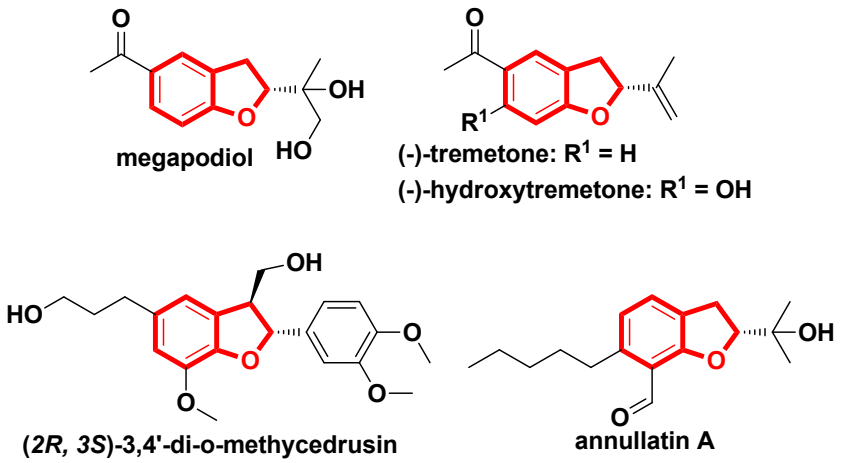
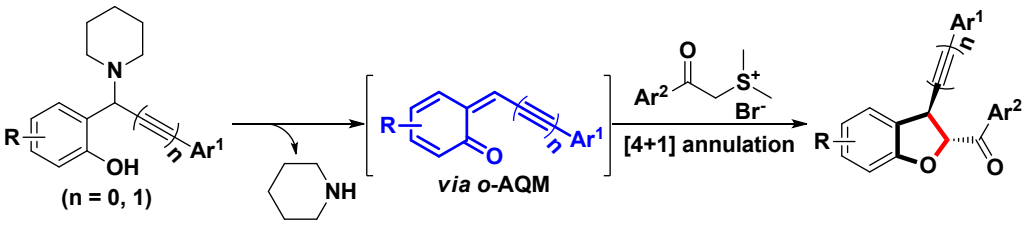


Figure 1. Selection of 2,3-dihydrobenzofuran natural products.

Propargylamines are useful and versatile building blocks in organic synthesis[18] because they have two functional groups, which are amenable to further diverse transformations.[19] Recently, we synthesized a novel propargylamines containing an hydroxy group, and demonstrated the fruitful reactions between benzoylacetonitriles or *β*-keto esters and propargylamines used as *o*-AQMs (alkynyl *o*-quinone methide) precursors for the synthesis of 2-aryl-4*H*-chromenes, polysubstituted furans, furo[3,4-*c*]coumarins, and 4-styrylcoumarins.[20] Inspired by elegant previous reports[21] and in line with our long-standing interest in propargylamine chemistry, we speculated that a novel 2-benzoyl-3-aryethynyl-2,3-dihydrobenzofurans would be synthesized from 2-(3-aryl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol and benzoyl sulfonium bromides under catalyst-free conditions (Scheme 1). Herein, we report our new results on the synthesis of 2-benzoyl-3-aryl/3-arylethynyl-2,3-dihydrobenzofurans from propargylamines and its derivatives with benzoyl sulfonium bromides under catalyst-free conditions. The starting materials propargylamines can be readily prepared from A^3-coupling reactions of commercially available salicylaldehydes, amines, and alkynes.[22]



Scheme 1. Design plan for the synthesis of 2,3-dihydrobenzofurans.

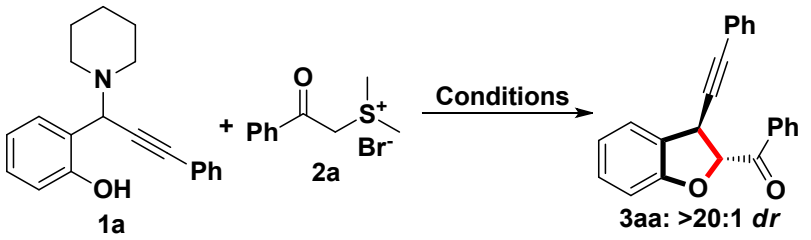
RESULTS AND DISCUSSION

At the outset of this study, we first performed a reaction between 2-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol (**1a**), dimethyl(2-oxo-2-phenylethyl) sulfonium bromide (**2a**) in aqueous acetone : water (v/v = 2:1) as mixed solvent at 100 °C for 2 h. Gratifyingly, phenyl(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3aa**) was obtained in 46% yield without forming the aromatic product (Table 1, entry 1). Inspired by this initial result, we tested the effect of different mixed solvents, including diethyl ether/H_2O, toluene/H_2O, DCM (dichlomethane)/H_2O, DMSO (dimethylsulfoxide)/H_2O, THF (tetrahydrofuran)/H_2O, and CH_3CN/H_2O (Table 1, entries 2-7). The mixed solvent of THF/H_2O was found to be the most effective one among these mixed solvents (Table 1, entry 6). To improve the yield, we carried out further optimization studies with other ratios of THF and H_2O, but they were found to be less effective at this transformation (Table 1, entries 8-12). Variation of the reaction temperature confirmed that 100 °C was the optimal condition for this protocol, with lower and higher temperatures affording decreased yields (Table, entries 13, 14). Surprisingly, when the reaction was carried out for 1 h, the highest reaction yield (82%) was observed (Table 1, entry 15), and a dramatic decrease yield was obtained by reducing the reaction time to 0.5 h (Table 1, entry 16).

Subsequently, other A^3-coupling derived propargylamines were also tested. The desired product 3aa could also be successfully attained, albeit in decreased yields when morpholine- and pyrrolidine-derived propargylamines (**1a′** and **1b′**) were used as substrates (Table 1, entries 17, 18). Tetrahydroisoquinoline-derived propargylamine **1c′**, however, failed to give the targeted product (Table 1, entry 19). Control experiments revealed that no reaction occurred when other ylides (**2a′** and **2b′**) were used as substrates (Table 1, entries 20, 21), the [4+1] annulation of the ylides to propargylamines still remains challenging. Finally, the optimized reaction conditions were achieved in the mixed solvent of THF/H_2O at 100 °C for 1 h without

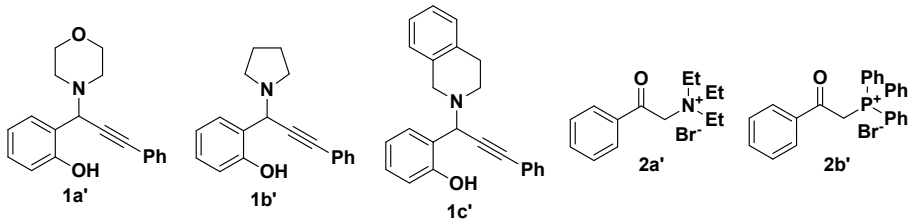
any catalyst (Table 1, entry 15).

Table 1. Optimization of the reaction conditions.[a]



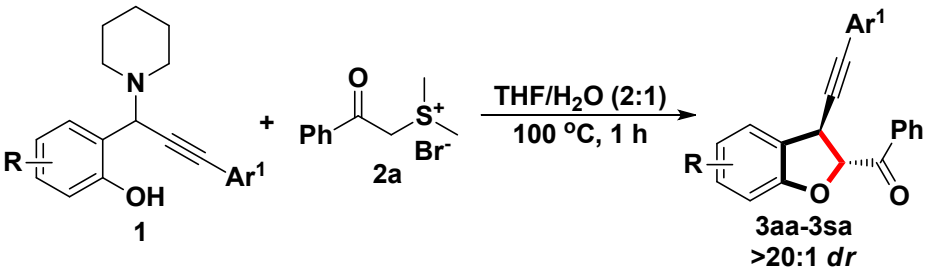
Entry	Solvent (2:1)	Temp. (°C)	Time (h)	Yield (%)[b]
1	Acetone/H_2O	100	2	46
2	Ether/H_2O	100	2	38
3	Toluene/H_2O	100	2	41
4	DCM/H_2O	100	2	51
5	DMSO/H_2O	100	2	67
6	THF/H_2O	100	2	82
7	CH_3CN/H_2O	100	2	60
8	H_2O	100	2	Trace
9	THF	100	2	Trace
10[c]	THF/H_2O	100	2	51
11[d]	THF/H_2O	100	2	NR
12[e]	THF/H_2O	100	2	54
13	THF/H_2O	80	2	66
14	THF/H_2O	120	2	68
15	THF/H_2O	100	1	82
16	THF/H_2O	100	0.5	62
17[f]	THF/H_2O	100	1	24
18[g]	THF/H_2O	100	1	45
19[h]	THF/H_2O	100	1	NR
20[i]	THF/H_2O	100	1	NR
21[j]	THF/H_2O	100	1	NR

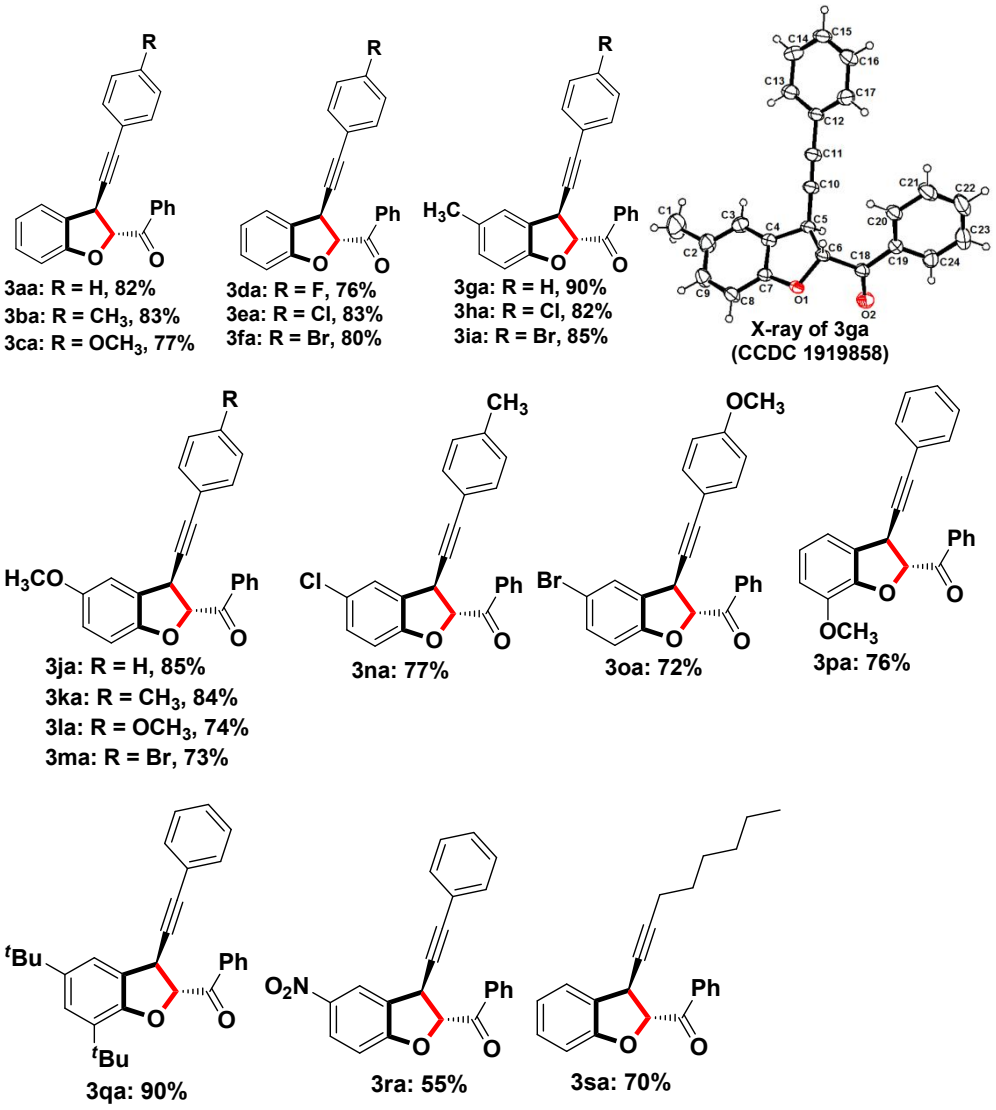
[a] Reaction conditions: 2-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol (**1a**, 0.2 mmol), dimethyl(2-oxo-2-phenylethyl)sulfonium bromide (**2a**, 0.24 mmol) in solvent (3 mL). [b] Isolated yields. [c] Solvent ratio = 1:1. [d] Solvent ratio = 1:2. [e] Solvent ratio = 4:1. [f] Using **1a′** instead of **1a**. [g] Using **1b′** instead of **1a**. [h] Using **1c′** instead of **1a**. [i] Using 2**a′** instead of 2**a**. [j] Using **2b′** instead of 2**a**.



With acceptable optimized reaction conditions in hand, we then evaluated the reaction scope for propargylamines using benzoyl sulfonium bromide **2a** as a model substrate (Table 2). The phenyl ring of Ar^1 group bearing halide substituents (F, Cl, Br) and other electron-donating groups (CH_3, OCH_3) were well tolerated and gave the corresponding products (**3ba**-**3fa**) in good yields. Propargylamines bearing various substituents with diverse electronic and steric properties at the *para*- and *ortho*-position to the hydroxy group, reacted smoothly to generate the desired products in good yields (72%-90%). It is worth mentioning that the substrate with a bulky *tert*-butyl group at the *ortho*- and *para*-position to the hydroxy of the propargylamine was also tolerated in the reaction to give the corresponding product **3qa** in 90% yield. Subsequently, we also found that when the propargylamines bearing with a strongly electron-withdrawing group (NO_2) at the *para*-position to the hydroxy group was treated with **2a**, the expected product **3ra** was obtained, albeit in lower yield (55%). Additionally, for alkynyl bearing a *n*-pentyl substituent rather than an aryl group, generally the expected product **3sa** could be obtained smoothly in 70% yields.

Table 2. Substrate scope of propargylamines.[a,b]



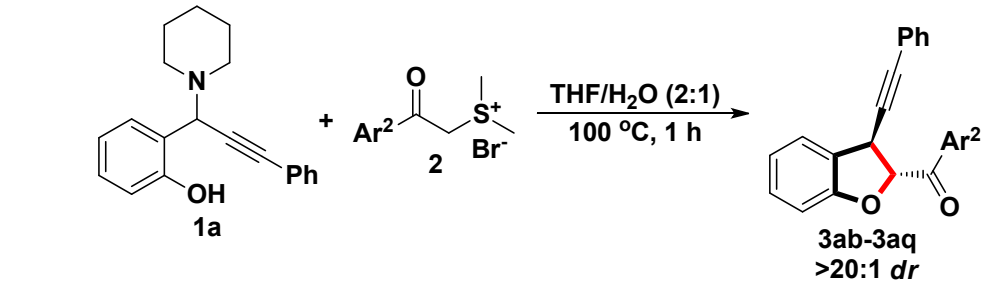


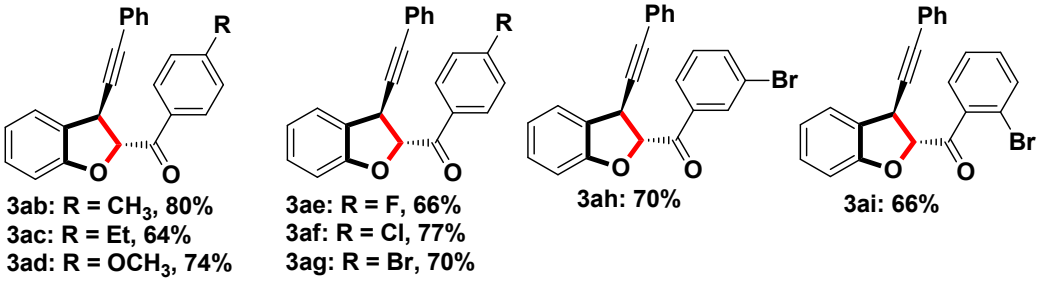
[a]Reaction conditions: propargylamines **1** (0.2 mmol), dimethyl(2-oxo-2-phenylethyl)sulfonium bromide **2a** (0.24 mmol) in THF/H_2O = 2:1 (3 mL), 100 °C for 1 h. [b]Isolated yields and all of the *dr* > 20:1.

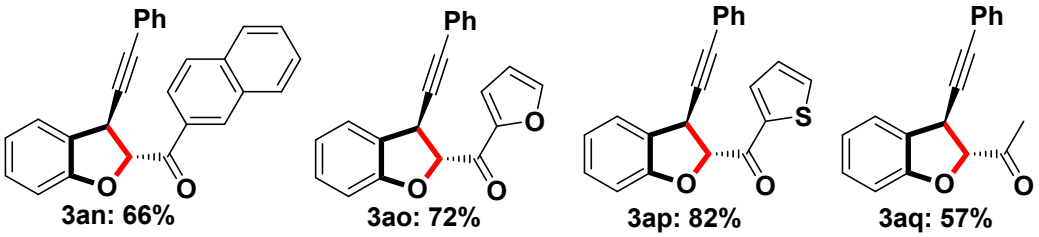
We then investigated the generality of benzoyl sulfonium bromides **2** using propargylamines **1a** as a model substrate under the optimized conditions (Table 3). The reaction proceeded smoothly with a range of substituents at the *ortho*-, *meta*-, and

para-positions on the phenyl ring of the Ar^2 group, leading to the formation of diverse 2,3-dihydrobenzofurans (**3ab-3am**) in moderate to good yields (60%-83%). Gratifyingly, phenyl, mesyl, and trifluoromethyl groups were well tolerated, generating the desired products **3ak**, **3al**, **3am** in 63%, 60%, and 76% yields, respectively. A multisubstituted benzoyl sulfonium bromide were also suitable for this annulation, giving the corresponding product **3aj** in 83% yield. In addition, benzoyl sulfonium bromide bearing *β*-2-naphthyl or heteroaromatic rings (such as 2-furyl, or 2-thienyl) also reacted efficiently, affording the products **3an**, **3ao**, and **3ap** in 66%, 72%, and 82% yields, respectively. During our study of the scope of sulfonium bromides **2** for the construction of 2,3-dihydrobenzofurans **3**, we were surprised to find that when a non-aromatic sulfonium bromide (**2q**) was treated with **1a**, the expected product **3aq** was obtained in 57% yield.

Table 3. Substrate scope of sulfur ylides.[a,b]







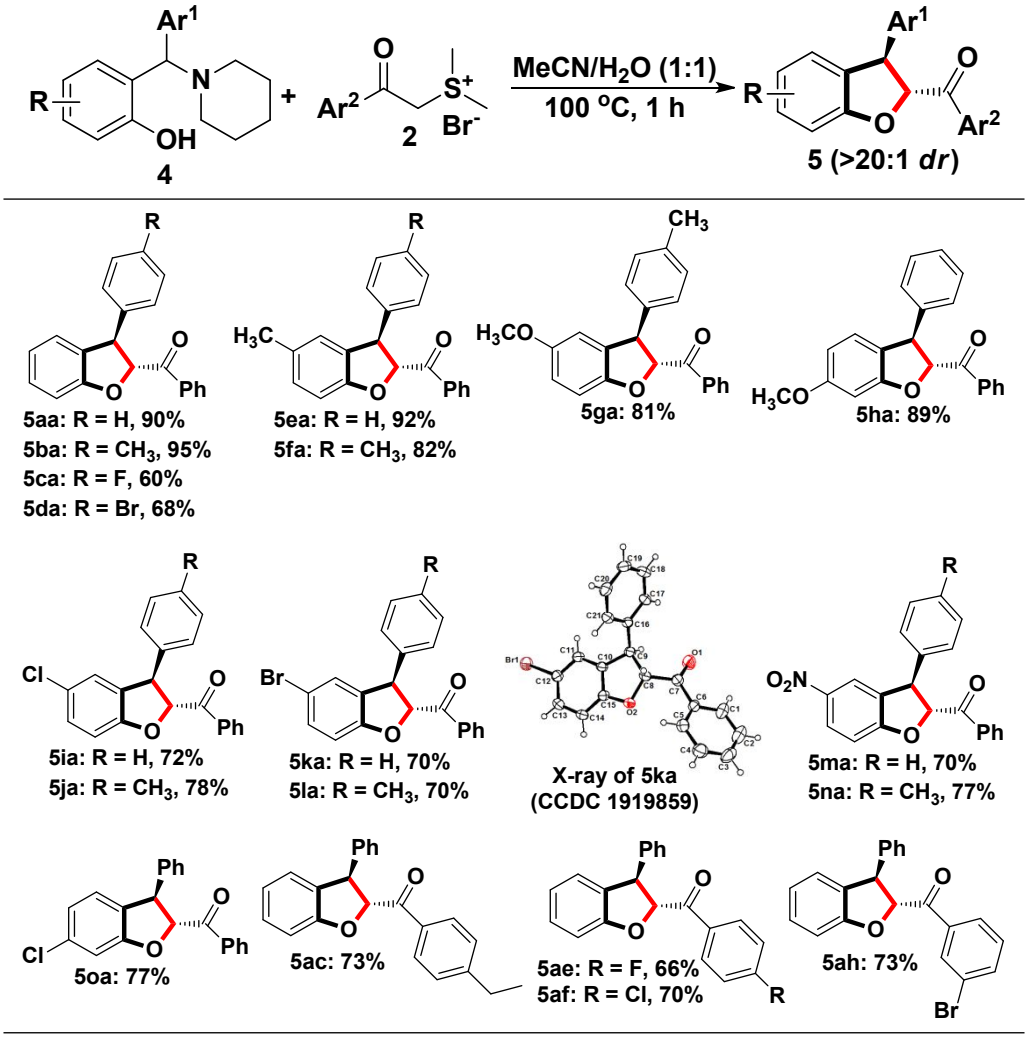
[a]Reaction conditions: 2-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol **1a** (0.2 mmol), benzoyl sulfonium bromides **2** (0.24 mmol) in THF/H_2O = 2:1 (3 mL), 100 °C for 1 h. [b]Isolated yields and all of the *dr* > 20:1.

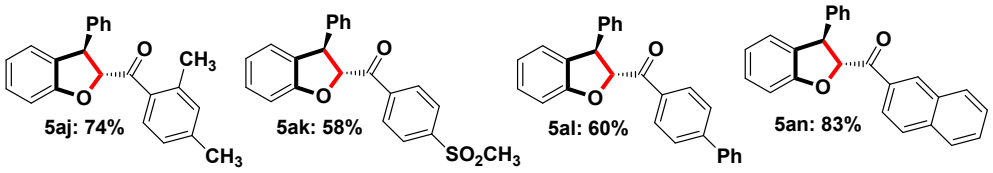
Given that the alkynyl group was retained in the present approach, we speculated that the 2-benzoyl-3-aryl-2,3-hydrobenzofurans would be obtained from 2-(aryl(piperidin-1-yl)methyl)phenols without the alkynyl group substituent on the propargylamines through the similarly process. Based on this assertion, we next subjected 2-(aryl(piperidin-1-yl)methyl)phenols **4**, which are easily available by the Petasis boronic Mannich reaction of salicylaldehydes, phenylboronic acid, and piperidine, to the otherwise identical reaction conditions above. To our delight, the desired products **5aa** was obtained in 53% yield as shown in Table S1 in the Supporting Information (SI) (entry 1). Next, we tried to optimize the reaction conditions for this reaction by changing the solvents from THF/H_2O (2:1, v/v) to CH_3CN/H_2O (1:1, v/v) at 100 °C, and the yield of the corresponding product **5aa** dramatically increased to 90% (see the SI, Table S1, entry 5).

Subsequently, using these optimized reaction conditions and by varying 2-(aryl(piperidin-1-yl)methyl)phenols **4** and benzoyl sulfonium bromides **2**, a series of 2-aroyl-3-aryl-2,3-dihydrobenzofurans **5** were prepared. As shown in Table 4, the reactions of 2-(aryl(piperidin-1-yl)methyl)phenols **4** with benzoyl sulfonium bromides **2** proceeded well to give the desired products **5** irrespective of the substitution patterns on the phenyl ring of the 2-(aryl(piperidin-1-yl)methyl)phenols. Various moderately electron-donating (Me, OMe) and electron-withdrawing (F, Cl, Br) groups were compatible, provided the corresponding products in 60%-95% yields. Notably, unlike in the case of substrate **1**, substrates **4** with a strongly electron-withdrawing

group (NO_2) in the *para*-position to the hydroxy was also tolerated in the reaction to give the desired products **5ma**, **5na** in 70% and 77% yields, respectively. Likewise, substrates **2** substituted with moderate electron-donating or electron-withdrawing groups reacted efficiently to afford the corresponding products **5ac-5ah** in 66%-73% yields. The introduction of a strongly electron-withdrawing group (e.g. mesyl) and a phenyl group resulted in decreased yields of the desired products **5ak**, **5al** which were formed in yields of 58% and 60% yields, respectively.

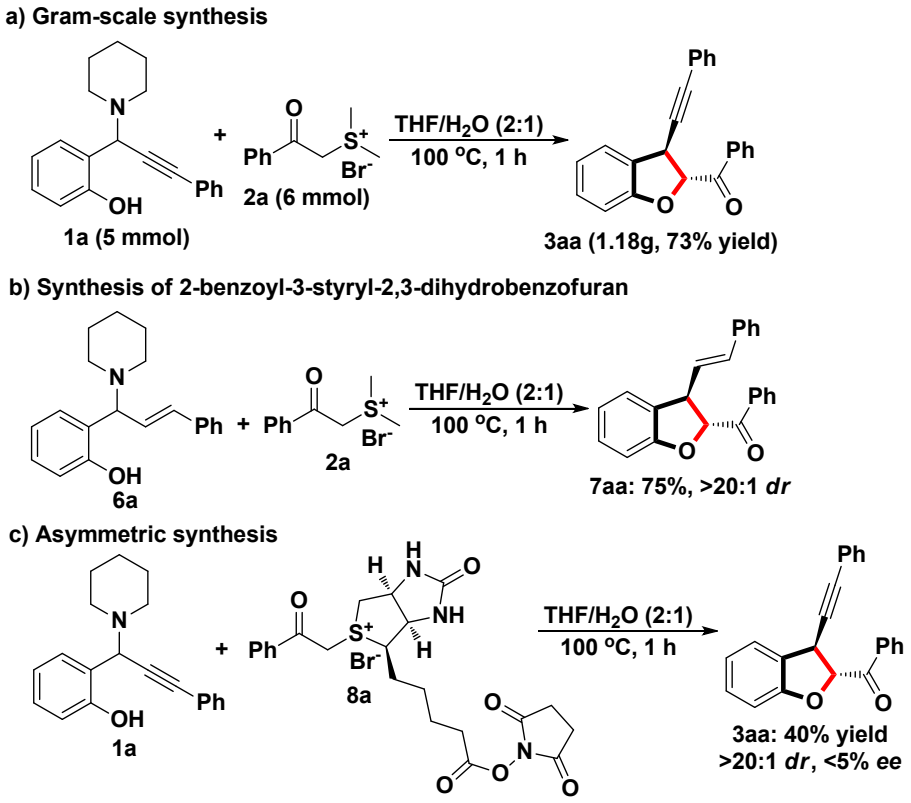
Table 4. Synthesis of 2-benzoyl-3-aryl-2,3-hydrobenzofurans from 2-(aryl(piperidin-1-yl)methyl)phenols and benzoyl sulfonium bromides.[a,b]





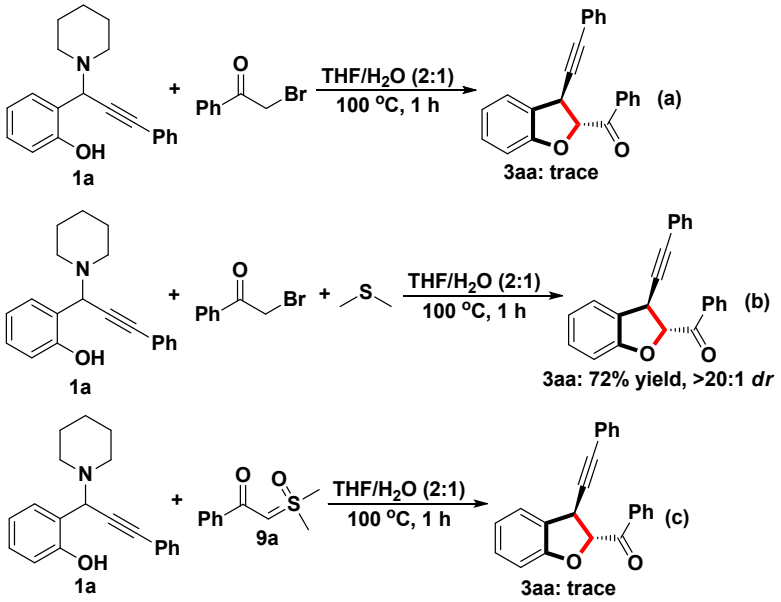
[a] Reaction conditions: 2-(aryl(piperidin-1-yl)methyl)phenol **4** (0.2 mmol), benzoyl sulfonium bromides **2** (0.24 mmol) in MeCN/H_2O = 1:1 (2 mL), 100 °C for 1 h. [b] Isolated yields and all of the *dr* > 20:1.

Furthermore, we carried out a gram-scale reaction of 2-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol (**1a**, 5 mmol) and dimethyl(2-oxo-2-phenylethyl)sulfonium bromide (**2a**, 6 mmol) under the standard conditions, and the corresponding product **3aa** was isolated in 73% (1.18 g) yield (Scheme 2), which showed promise for this synthetic methodology as a useful tool in piratical synthetic terms. In addition, by utilizing these conditions, the formal [4+1] annulation of (*E*)-2-(3-phenyl-1-(piperidin-1-yl)allyl)phenol **6a** with dimethyl(2-oxo-2-phenylethyl)sulfonium bromide **2a** also delivered the corresponding 2-benzoyl-3-styryl-2,3-dihydrobenzofuran **7aa** in 75% yield (Scheme 2b). Finally, we employed a chiral benzoyl sulfonium bromides **8a** derived from D-biotin *N*-succinimidyl ester to conduct our reaction, the desired product **3aa** was obtained in 40% yield with high diastereoselectivity (>20:1 *dr*), albeit with insufficient enantioselective control (Scheme 3c). Additional efforts are necessary to meet current challenges and explore opportunities in this emerging field.



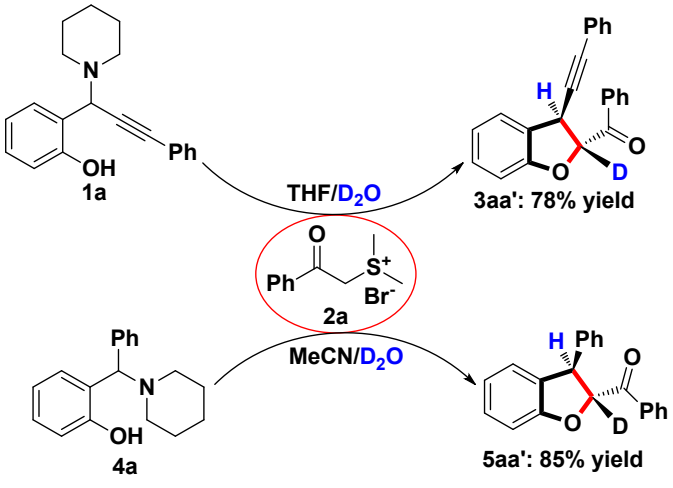
Scheme 2. Further studies of the [4+1] annulation: Gram-scale synthesis, substrate scope, and asymmetric synthesis.

Control experiments were carried out to gain preliminary insight into the reaction mechanism (Scheme 3). Initially, propargyamine **1a** reacted with 2-bromo-1-phenylethanone under the standard conditions, the final product **3aa** could be detected only in trace yield (Scheme 3a). In the presence of dimethylsulfane (1.0 equiv.), the target product **3aa** was obtained with 72% yield (Scheme 3b), illustrating that the dimethyl(2-oxo-2-phenylethyl)sulfonium bromide **2a** was initially formed and then reacted with propargylamine **1a** to provide the annulated product **3aa**. Whereas, treatment of catalytic amount of dimethylsulfane (10 mol%) in this three-component reaction, only 44% yield of the product was obtained. Next, we employed the known sulfur ylide **9a** derived from sulfoxonium salts[23] instead of **2a** to conduct our reaction (Scheme 3c). Unfortunately, only trace **3aa** could be detected.



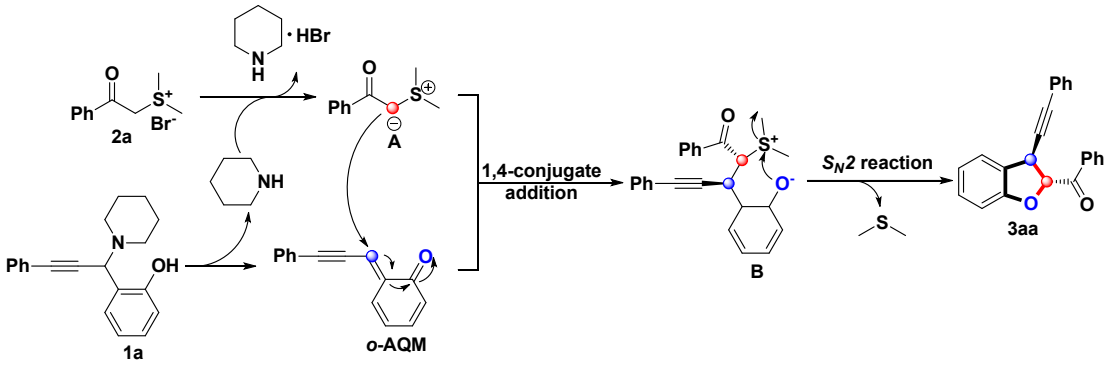
Scheme 3. Control experiments.

To elucidate the formation of the [4+1] annulation process, a deuteration study was then performed under the standard conditions as shown in Scheme 4. Initially, an H/D exchange of benzoyl sulfonium bromides **2** was carried out in the presence of D_2O. From this reaction, the ^1H NMR analysis revealed that all hydrogen atoms on the methylene group of **2** were exchanged with deuterium atoms within 10 minutes. Subsequently, when deuterium oxide was used instead of water as a part of the solvent, both more than 99% of products **3aa′** and **5aa′** were deuterated at the 2-position of the furan ring, indicating the dimethyl(2-oxo-2-phenylethyl)sulfonium bromide **2a** acted as a C1 synthon in this process.



Scheme 4. The deuteration experiments.

Based on the experimental results above and previous literature reports,[24] a plausible mechanism for this reaction was proposed as shown in Scheme 5 (**3aa** as example). Initially, propargylamine **1a** released piperidine to furnish an alkynyl *o*-quinone methide (*o*-AQM) intermediate, at the same time, benzoyl sulfonium salt **2a** transformed into the corresponding sulfur ylide **A** in the presence of piperidine as base. Subsequently, intermediate **B** resulted from an intermolecular 1,4-conjugate addition of the sulfur ylide **A** to *o*-AQM intermediate. Finally, the configuration of the intermediate **B** is stable enough to allow a stereospecific S_N2 reaction to produce the observed *trans*-selective 2,3-dihydrobenzofuran **3aa** by removing dimethyl sulfide.



Scheme 5. A plausible mechanism for the synthesis of 2,3-dihydrobenzofurans.

CONCLUSION

In summary, we have successfully developed an efficient and convergent approach for generation of *o*-AQM or *o*-QM intermediates from the readily available propargylamines or 2-(aryl(piperidin-1-yl)methyl)phenols under mild conditions, and their reactions with benzoyl sulfonium salts for the synthesis of 2,3-dihydrobenzofuran derivatives were investigated. The flexibility of this strategy permits rapid access to a variety of structurally distinct dihydrobenzofurans bearing an arylethynyl or aryl group at the C3 position. The advantages of this methodology include the readily available starting materials, operational simplicity, versatile functional groups tolerance and use of an aqueous mixed solvent under mild catalyst-free conditions.

Experiment Sections

General comments

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received, and the solvents were purified and dried using standard procedures. The chromatography solvents were technical grade and distilled prior to use. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. The ^{1}H and ^{13}C NMR data were recorded on 400 MHz or 500 MHz and 100 MHz or 125 MHz NMR spectrometers, unless otherwise specified. Chemical shifts (δ) in parts per million are reported relative to the residual signals of chloroform (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C), and all ^{13}C NMR were recorded with proton broadband decoupling and indicated as $^{13}C\{^{1}H\}$ NMR. Multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet), and the coupling constants (J) are reported in Hertz. HRMS analysis with a quadrupole time-of-flight mass spectrometer yielded ion mass/charge (m/z) ratios in atomic mass units. IR spectra were measured as dry films (KBr), and the peaks are reported in terms of wave number (cm^{-1}). The melting points were measured using SGWX-4 melting point apparatus.

Literature procedures were used for the preparation of propargylamines **1a-1s**[20, 22] and 2-(aryl(piperidin-1-yl)methyl)phenols **4a-4m**.[25] Substrates **1j-1l**, **4c**, **4d**, **4g**, **4o**, and **6a** were new compounds.

4-Methoxy-2-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol ***(1j)***. The title compound was obtained from 2-hydroxy-5-methoxybenzaldehyde (3 mmol), phenylacetylene (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[22a] as a yellow solid (818 mg) in 85% yield; mp 109-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.52 (m, 2H), 7.39–7.34 (m, 3H), 7.21–7.17 (m, 1H), 6.81–6.76 (m, 2H), 5.07 (s, 1H), 3.77 (s, 3H), 2.87–2.55 (m, 4H), 1.67 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.5, 151.4, 131.9, 128.6, 128.4, 122.6, 122.2, 116.7, 114.7, 114.0, 89.9, 82.2, 61.1, 55.8, 26.0, 24.0; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_2$ 322.1807; Found 322.1810.

4-Methoxy-2-(1-(piperidin-1-yl)-3-(p-tolyl)prop-2-yn-1-yl)phenol ***(1k)***. The title

compound was obtained from 2-hydroxy-5-methoxybenzaldehyde (3 mmol), 1-ethynyl-4-methylbenzene (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[22a] as a yellow solid (824 mg) in 82% yield; mp 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.20–7.18 (m, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.79-6.76 (m, 2H), 5.05 (s, 1H), 3.76 (s, 3H), 2.76-2.64 (m, 3H), 2.37 (s, 3H), 1.95–1.10 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.6, 151.5, 138.9, 131.9, 129.3, 122.4, 119.6, 116.8, 114.9, 114.1, 90.1, 81.6, 61.2, 55.9, 26.2, 24.2, 21.7; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_2$ 336.1964; Found 336.1967.

4-methoxy-2-(3-(4-methoxyphenyl)-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol ***(1l)***. The title compound was obtained from 2-hydroxy-5-methoxybenzaldehyde (3 mmol), 1-ethynyl-4-methoxybenzene (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[22a] as a yellow solid (916 mg) in 87% yield; mp 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.43 (m, 2H), 7.17–7.14 (m, 1H), 6.89-6.84 (m, 2H), 6.76-6.74 (m, 2H), 5.02 (s, 1H), 3.29 (s, 3H), 3.26 (s, 3H), 2.72-2.62 (m, 3H), 1.72–1.42 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 152.7, 151.7, 133.6, 122.7, 116.9, 115.1, 114.3, 114.2, 90.1, 81.0, 61.4, 56.1, 55.7, 26.3, 24.3; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_3$ 352.1913; Found 352.1915.

2-((4-Fluorophenyl)(piperidin-1-yl)methyl)phenol ***(4c)***. The title compound was obtained from salicylaldehyde (3 mmol), (4-fluorophenyl)boronic acid (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[25a] as a white solid (769 mg) in 90% yield; mp 122–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.45 (s, 1H), 7.44–7.30 (m, 2H), 7.13–7.07 (m, 1H), 7.01–6.94 (m, 2H), 6.90-6.81 (m, 2H), 6.73–6.65 (m, 1H), 4.44 (s, 1H), 2.56-2.24 (m, 3H), 1.74-1.37 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.3 ($J_{C\text{-}F}$ = 245.2 Hz), 157.0, 135.4, 130.39, 129.08 ($J_{C\text{-}F}$ = 2.4 Hz), 128.5, 125.5 ($J_{C\text{-}F}$ = 3.2 Hz), 119.2, 117.0, 115.6 ($J_{C\text{-}F}$ = 21.2 Hz), 75.7, 52.5, 26.1, 24.1; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{21}FNO$ 286.1607; Found 286.1610.

2-((4-Bromophenyl)(piperidin-1-yl)methyl)phenol ***(4d)***. The title compound was

obtained from salicylaldehyde (3 mmol), (4-bromophenyl)boronic acid (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[25a] as a light yellow solid (890 mg) in 86% yield; mp 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.34 (s, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.32–7.24 (m, 2H), 7.12–7.07 (m, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.70–6.65 (m, 1H), 4.40 (s, 1H), 2.51–2.22 (m, 3H), 1.82–1.12 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.1, 138.8, 132.1, 130.6, 129.2, 128.8, 125.3, 122.0, 119.4, 117.2, 76.1, 52.8, 26.2, 24.3; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{21}BrNO$ 346.0807; Found 346.0804.

4-Methoxy-2-(piperidin-1-yl(p-tolyl)methyl)phenol ***(4g)***. The title compound was obtained from 2-hydroxy-5-methoxybenzaldehyde (3 mmol), *p*-tolylboronic acid (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[25a] as a white solid (821 mg) in 88% yield; mp 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 1H), 7.31–7.24 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.78–6.74 (m, 1H), 6.67–6.62 (m, 1H), 6.47-6.43 (m, 1H), 4.35 (s, 1H), 3.64 (s, 3H), 2.47-2.32 (m, 3H), 2.29 (s, 3H), 1.67–1.37 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.3, 150.8, 137.6, 136.5, 129.4, 128.7, 126.4, 117.1, 115.0, 113.2, 76.3, 55.6, 52.6, 26.1, 24.2, 21.1; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{26}NO_2$ 312.1964; Found 312.1968.

5-Chloro-2-(phenyl(piperidin-1-yl)methyl)phenol ***(4o)***. The title compound was obtained from 4-chloro-2-hydroxybenzaldehyde (3 mmol), phenylboronic acid (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[25a] as a white solid (767 mg) in 85% yield; mp 118–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.00 (s, 1H), 7.37–7.25 (m, 5H), 6.83 (d, J = 2.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.63 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 4.46 (s, 1H), 2.57–2.27 (m, 3H), 1.68–1.37 (m, 7H); ^{13}C{^{1}H} NMR (100Hz, $CDCl_3$) δ 158.5, 138.8, 133.9, 130.3, 129.0, 128.3, 124.2, 119.2, 117.3, 76.0, 52.5, 26.2, 24.2; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{21}ClNO$ 302.1312; Found 302.1311.

(E)-2-(3-Phenyl-1-(piperidin-1-yl)allyl)phenol ***(6a)***. The title compound was obtained from salicylaldehyde (3 mmol), (*E*)-styrylboronic acid (3.6 mmol) and piperidine (3.6 mmol) using the general procedure described in reference[25a] as a

colorless oil (351 mg) in 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.38 (m, 2H), 7.37–7.29 (m, 2H), 7.28–7.23 (m, 1H), 7.20–7.12 (m, 1H), 7.04–6.98 (m, 1H), 6.90–6.82 (m, 1H), 6.82–6.74 (m, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.40 (dd, J = 16.0 Hz, 9.6 Hz, 1H), 4.14 (d, J = 9.6 Hz, 1H), 2.60 (s, 4H), 1.88–1.36 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.4, 136.5, 133.6, 128.7, 128.7, 128.4, 127.9, 126.6, 126.5, 124.9, 119.2, 116.6, 73.5, 51.6, 26.1, 24.3; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{23}NO$ 294.1852; Found 294.1854.

General procedure for the preparation of benzoyl sulfonium bromides 2.

Dimethyl sulfide (5 mmol) was added to a solution of 2-bromoacetophenone derivatives (5 mmol) in acetone (10 mL). After the mixture had been stirred for 12 h, the residue was filtered and washed with acetone. The solid product (**2a-2q**) was used as sulfonium bromide without further purification. All sulfonium salts were known compounds and prepared according to the previous reported method.[26]

General procedure for the synthesis of the 2-benzoyl-3-arylethynyl-2,3-dihydrobenzofuran derivatives 3.

A mixture of propargylamine **1a** (0.2 mmol) and benzoyl sulfonium salts **2** (0.24 mmol) in THF/H_2O (2:1, v/v, 3 mL) was heated to 100 °C in an oil bath for 2 h. After the reaction was complete (as determined using TLC), the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether (1:40-1:60, v/v) as the elution solvent to give desired product **3**.

*Phenyl(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3aa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 82% yield (53 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21–8.15 (m, 2H), 7.70–7.60 (m, 1H), 7.58–7.51 (m, 2H), 7.46–7.38 (m, 3H), 7.33–7.27 (m, 3H), 7.25–7.20 (m, 1H), 7.02–6.96 (m, 1H), 6.92 (d, J = 8.5 Hz, 1H), 6.02 (d, J = 7.8 Hz, 1H), 4.98 (d, J = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.9, 158.6, 134.8, 134.5, 132.2, 129.9, 129.7, 129.2, 128.8, 128.7, 126.6, 125.3,

123.1, 122.2, 110.7, 88.6, 87.9, 83.8, 37.4; IR (KBr) *v* 1692, 1598, 1477, 1446, 1225, 1052, 957, 878, 760, 744, 689 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{17}O_2$ 325.1223; Found 325.1220.

Phenyl(3-(p-tolylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone ***(3ba)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a colorless oil in 83% yield (56 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.20–8.15 (m, 2H), 7.67–7.62 (m, 1H), 7.56–7.51 (m, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.25–7.20 (m, 1H), 7.11 (d, J = 8.5 Hz, 2H), 7.02–6.97 (m, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.02 (d, J = 8.0 Hz, 1H), 4.97 (d, J = 8.0 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 194.0, 158.6, 138.9, 134.7, 134.5, 132.0, 129.9, 129.7, 129.45 129.2, 126.7, 125.4, 122.2, 120.0, 110.7, 88.6, 87.1, 83.9, 37.5, 21.9; IR (KBr) *v* 1695, 1598, 1485, 1446, 1238, 1057, 962, 865, 807, 763, 687 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}O_2$ 339.1380; Found 339.1383.

(3-((4-Methoxyphenyl)ethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone ***(3ca)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 77% yield (54 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.19–8.16 (m, 2H), 7.68–7.62 (m, 1H), 7.57–7.51 (m, 2H), 7.42–7.34 (m, 3H), 7.25–7.19 (m, 1H), 7.01–6.96 (m, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.85–6.81 (m, 2H), 6.01 (d, J = 7.5 Hz, 1H), 4.95 (d, J = 7.5 Hz, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 194.1, 160.1, 158.6, 134.8, 134.4, 133.6, 129.8, 129.7, 129.2, 126.8, 125.3, 122.2, 115.2, 114.3, 110.7, 88.7, 86.4, 83.7, 55.7, 37.5; IR (KBr) *v* 1694, 1597, 1487, 1446, 1239, 1058, 964, 878, 760, 744, 688 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}O_3$ 355.1329; Found 355.1322.

(3-((4-Fluorophenyl)ethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone ***(3da)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a colorless oil in 76% yield (52 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.19–8.15 (m, 2H), 7.68–7.63 (m, 1H), 7.57–7.51 (m, 2H), 7.43–7.38 (m, 3H), 7.25–7.20 (m, 1H), 7.03–6.97 (m, 3H), 6.92 (d, J = 8.0 Hz, 1H), 5.99 (d, J = 7.5 Hz, 1H), 4.99 (d, J = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 193.8, 162.9 (d, $J_{C\text{-}F}$ = 248.8 Hz), 134.8, 134.5, 134.1 (d, $J_{C\text{-}F}$ = 8.4 Hz),

129.9, 129.8, 129.2, 126.5, 125.3, 122.3, 119.2, 119.2, 116.1, 115.9, 110.7, 88.6, 87.6, 82.7, 37.2; IR (KBr) *v* 1700, 1593, 1501, 1472, 1225, 1154, 1086, 962, 865, 839, 684 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}FO_2$ 343.1129; Found 343.1121.

*(3-((4-Chlorophenyl)ethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ea**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 83% yield (59 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.18–8.15 (m, 2H), 7.68–7.62 (m, 1H), 7.57–7.51 (m, 2H), 7.41–7.38 (m, 1H), 7.37–7.33 (m, 2H), 7.30–7.26 (m, 2H), 7.25–7.20 (m, 1H), 7.02–6.96 (m, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.99 (d, J = 7.5 Hz, 1H), 5.01 (d, J = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 193.8, 158.6, 134.8, 134.7, 134.5, 133.4, 129.9, 129.8, 129.2, 129.0, 126.4, 125.3, 122.3, 121.6, 110.7, 88.9, 88.54, 82.7, 37.2; IR (KBr) *v* 1697, 1598, 1501, 1472, 1224, 1156, 1086, 952, 865, 747, 684 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}ClO_2$ 359.0833; Found 359.0837, 361.0830

*(3-((4-Bromophenyl)ethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3fa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow solid in 80% yield (64 mg); mp 80-82 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.18–8.15 (m, 2H), 7.69–7.63 (m, 1H), 7.57–7.51 (m, 2H), 7.46–7.42 (m, 2H), 7.41–7.37 (m, 1H), 7.30–7.27 (m, 2H), 7.25–7.21 (m, 1H), 7.01–6.97 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.99 (d, J = 7.5 Hz, 1H), 5.00 (d, J = 7.5); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 193.8, 158.6, 134.8, 134.5, 133.6, 132.0, 129.9, 129.8, 129.2, 126.4, 125.3, 123.1, 122.3, 122.1, 110.7, 89.2, 88.5, 82.8, 37.2; IR (KBr) *v* 1700, 1593, 1498, 1467, 1228, 1154, 1086, 952, 865, 839, 681 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}BrO_2$ 403.0328; Found 403.0320, 405.0311.

*(5-Methyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ga**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 90% yield (61 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.23–8.12 (m, 2H), 7.76–7.58 (m, 1H), 7.57–7.48 (m, 2H), 7.48–7.41 (m,

2H), 7.34–7.27 (m, 3H), 7.20 (s, 1H), 7.01 (d, J = 8.5 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 5.99 (d, J = 7.5 Hz, 1H), 4.95 (d, J = 7.5 Hz, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 194.1, 156.6, 134.8, 134.4, 132.2, 131.7, 130.2, 129.9, 129.2, 128.7, 128.7, 126.5, 125.7, 123.2, 110.2, 88.7, 88.0, 83.7, 37.4, 21.2; IR (KBr) v 1700, 1598, 1483, 1446, 1237, 1052, 962, 865, 807, 763, 685 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}O_2$ 339.1380; Found 339.1378.

*(3-((4-Chlorophenyl)ethynyl)-5-methyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ha**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 82% yield (61 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.22–8.10 (m, 2H), 7.72–7.59 (m, 1H), 7.58–7.50 (m, 2H), 7.40–7.32 (m, 2H), 7.30–7.26 (m, 2H), 7.19 (s, 1H), 7.02 (d, J = 8.5 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 7.5 Hz, 1H), 4.96 (d, J = 7.5 Hz, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 193.9, 156.5, 134.8, 134.5, 133.4, 131.8, 130.2, 129.9, 129.7, 129.3, 129.2, 129.0, 126.3, 125.7, 121.7, 110.3, 89.1, 88.6, 82.6, 37.2, 21.2; IR (KBr) v 1700, 1598, 1501, 1476, 1237, 1063, 962, 865, 807, 763, 684 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}ClO_2$ 373.0920; Found 373.0928, 375.0917.

*(3-((4-Bromophenyl)ethynyl)-5-methyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ia**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 85% yield (71 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 2H), 7.67–7.62 (m, 1H), 7.58–7.48 (m, 2H), 7.46–7.41 (m, 2H), 7.33 –7.27 (m, 2H), 7.19 (s, 1H), 7.01 (d, J = 8.5 Hz, 1H), 6.83–6.76 (m, 1H), 5.95 (d, J = 7.3 Hz, 1H), 4.96 (d, J = 7.3 Hz, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 193.9, 156.5, 134.8, 134.5, 133.6, 131.9, 131.8, 130.2, 129.9, 129.2, 126.3, 125.7, 123.0, 122.1, 110.3, 89.3, 88.6, 82.7, 37.2, 21.2; IR (KBr) v 1700, 1593, 1483, 1446, 1237, 1052, 962, 867, 807, 766, 683 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}BrO_2$ 417.0485; Found 417.0489, 419.0526.

*(5-Methoxy-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ja**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 85% yield (60 mg); ^1H NMR

(500 MHz, $CDCl_3$) δ 8.23–8.14 (m, 2H), 7.69– 7.60 (m, 1H), 7.57–7.50 (m, 2H), 7.48–7.40 (m, 2H), 7.35–7.27 (m, 3H), 7.01–6.94 (m, 1H), 6.86–6.78 (m, 1H), 6.79–6.74 (m, 1H), 5.99 (d, J = 7.8 Hz, 1H), 4.98 (d, J = 7.8 Hz, 1H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 194.0, 155.5, 152.7, 134.8, 134.4, 132.2, 129.9, 129.2, 128.8, 128.7, 127.5, 123.1, 115.2, 110.9, 110.8, 88.9, 87.7, 83.9, 56.5, 37.6; IR (KBr) v 1696, 1597, 1487, 1446, 1240, 1058, 964, 878, 762, 745, 683 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}O_3$ 355.1329; Found 355.1328.

*(5-Methoxy-3-(p-tolylethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ka**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 84% yield (62 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.22–8.15 (m, 2H), 7.70–7.60 (m, 1H), 7.57–7.49 (m, 2H), 7.38–7.30 (m, 2H), 7.17–7.06 (m, 2H), 6.99–6.94 (m, 1H), 6.85–6.79 (m, 1H), 6.79–6.74 (m, 1H), 5.99 (d, J = 8.0 Hz, 1H), 4.97 (d, J = 8.0 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 194.1, 155.5, 152.7, 138.9, 134.8, 134.42, 132.1, 129.9, 129.5, 129.2, 127.6, 120.0, 115.2, 111.0, 110.8, 89.0, 86.9, 84.1, 56.5, 37.8, 21.9; IR (KBr) v 1695, 1597, 1485, 1446, 1239, 1057, 964, 878, 760, 744, 687 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{21}O_3$ 369.1485; Found 369.1485.

*(5-Methoxy-3-((4-methoxyphenyl)ethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3la**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 74% yield (57 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.21–8.13 (m, 2H), 7.70–7.58 (m, 1H), 7.57–7.50 (m, 2H), 7.42–7.34 (m, 2H), 7.01–6.95 (m, 1H), 6.88–6.80 (m, 3H), 6.78–6.73 (m, 1H), 5.98 (d, J = 7.5 Hz, 1H), 4.96 (d, J = 7.5 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 194.1, 160.1, 155.5, 152.7, 134.8, 134.4, 133.6, 129.9, 129.2, 127.7, 115.1, 114.3, 111.0, 110.8, 89.0, 86.2, 83.8, 56.4, 55.7, 37.8; IR (KBr) v 1694, 1595, 1487, 1440, 1239, 1059, 964, 875, 760, 744, 688 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{21}O_4$ 385.1434; Found 385.1442.

*(3-((4-Bromophenyl)ethynyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ma**)*. This compound was purified by column chromatography (ethyl

acetate/petroleum ether = 1:60) to afford a red oil in 73% yield (63 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19–8.14 (m, 2H), 7.68–7.62 (m, 1H), 7.56–7.50 (m, 2H), 7.47–7.41 (m, 2H), 7.32–7.27 (m, 2H), 6.97–6.94 (m, 1H), 6.83–6.80 (m, 1H), 6.79–6.74 (m, 1H), 5.96 (d, J = 7.5 Hz, 1H), 5.00 (d, J = 7.5 Hz, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.8, 155.6, 152.6, 134.8, 134.5, 133.6, 132.0, 130.0, 129.2, 127.3, 123.1, 122.1, 115.2, 111.0, 110.9, 89.0, 88.8, 82.9, 56.5, 37.5; IR (KBr) v 1700, 1592, 1485, 1446, 1237, 1052, 962, 867, 803, 766, 681 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{18}BrO_3$ 433.0434; Found 433.0425, 435.0459.

*(5-Chloro-3-(p-tolylethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3na**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 77% yield (57 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19–8.13 (m, 2H), 7.74–7.62 (m, 1H), 7.58–7.50 (m, 2H), 7.38–7.31 (m, 2H), 7.21–7.10 (m, 3H), 6.86–6.81 (m, 1H), 6.04 (d, J = 7.3 Hz, 1H), 4.95 (d, J = 7.3 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.5, 156.7, 139.6, 134.6, 134.6, 132.1, 129.9, 129.7, 129.5, 129.3, 128.6, 127.0, 125.5, 119.7, 111.7, 89.1, 86.2, 84.5, 37.3, 21.9; IR (KBr) v 1700, 1598, 1511, 1467, 1228, 1112, 962, 852, 813, 766, 681 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{18}ClO_2$ 373.0920; Found 373.0919, 375.0883.

*(5-Bromo-3-((4-methoxyphenyl)ethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)meth anone (**3oa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 72% yield (62 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18–8.13 (m, 2H), 7.73–7.61 (m, 1H), 7.57–7.51 (m, 2H), 7.50–7.48 (m, 1H), 7.41–7.34 (m, 2H), 7.34–7.29 (m, 1H), 6.90–6.76 (m, 3H), 6.02 (d, J = 7.5 Hz, 1H), 4.95 (d, J = 7.5 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.4, 160.2, 157.8, 134.6, 133.6, 132.5, 129.9, 129.2, 128.4, 114.9, 114.4, 114.0, 112.2, 89.1, 85.5, 84.3, 55.7, 37.2; IR (KBr) v 1700, 1606, 1469, 1326, 1291, 1109, 962, 867, 813, 766, 687 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{18}BrO_3$ 433.0434; Found 433.0438, 435.0427.

*(7-Methoxy-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3pa**)*. This compound was purified by column chromatography (ethyl

acetate/petroleum ether = 1:40) to afford a yellow oil in 76% yield (54 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.15 (m, 2H), 7.69–7.61 (m, 1H), 7.58–7.49 (m, 2H), 7.45–7.39 (m, 2H), 7.34–7.28 (m, 3H), 7.10–6.98 (m, 1H), 6.98–6.91 (m, 1H), 6.88–6.81 (m, 1H), 6.07 (d, J = 7.6 Hz, 1H), 4.99 (d, J = 7.6 Hz, 1H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.3, 146.8, 144.8, 134.3, 134.1, 131.8, 129.5, 128.9, 128.5, 128.3, 127.3, 122.7, 122.6, 116.9, 112.5, 88.4, 87.3, 83.6, 56.2, 37.6; IR (KBr) v 1696, 1597, 1489, 1446, 1247, 1058, 964, 872, 762, 747, 683 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}O_3$ 355.1329; Found 355.1326.

*(5,7-Di-tert-butyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3qa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 90% yield (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.15 (m, 2H), 7.71–7.60 (m, 1H), 7.58–7.50 (m, 2H), 7.49–7.42 (m, 2H), 7.35–7.27 (m, 4H), 7.23–7.19 (m, 1H), 5.97 (d, J = 7.6 Hz, 1H), 4.97 (d, J = 7.6 Hz, 1H), 1.36 (s, 9H), 1.33 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.0, 153.8, 144.7, 134.6, 133.9, 132.8, 131.8, 129.5, 128.7, 128.3, 125.9, 123.2, 123.0, 119.3, 88.2, 88.2, 83.1, 36.8, 34.7, 34.3, 31.8, 29.4; IR (KBr) v 1740, 1595, 1487, 1443, 1228, 1180, 1015, 1015, 881, 762, 745, 692 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{33}O_2$ 437.2475; Found 437.2480.

*(5-Nitro-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3ra**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a Yellow oil in 55 % yield (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34–8.28 (m, 1H), 8.24– 8.13 (m, 3H), 7.72–7.67 (m, 1H), 7.60–7.54 (m, 2H), 7.48–7.42 (m, 2H), 7.38–7.29 (m, 3H), 6.99 (d, J = 8.8 Hz, 1H), 6.21 (d, J = 7.2 Hz, 1H), 5.06 (d, J = 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.0, 163.2, 143.1, 134.6, 133.8, 131.9, 129.5, 129.1, 128.9, 128.5, 128.0, 126.7, 122.0, 121.6, 110.4, 89.5, 85.6, 84.6, 36.2; IR (KBr) v 1700, 1602, 1472, 1348, 1297, 1125, 1043, 981, 874, 812, 743, 681 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{15}NO_4$ 370.1074; Found 370.1069.

*(3-(Oct-1-yn-1-yl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3sa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether =

1:60) to afford a yellow oil in 70% yield (46 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.11 (m, 2H), 7.68–7.62 (m, 1H), 7.56–7.49 (m, 2H), 7.31 (d, J = 7.6 Hz, 1H), 7.23–7.16 (m, 1H), 6.99–6.93 (m, 1H), 6.89 (d, J = 8.4 Hz, 1H), 5.88 (d, J = 7.6 Hz, 1H), 4.67 (d, J = 7.6 Hz, 1H), 2.42–2.15 (m, 2H), 1.57–1.45 (m, 2H), 1.44–1.34 (m, 2H), 1.33–1.24 (m, 4H), 0.88 (d, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.9, 158.2, 134.4, 134.0, 129.5, 129.1, 128.8, 126.9, 124.8, 121.7, 110.2, 88.5, 84.1, 78.2, 36.8, 31.3, 28.7, 28.6, 22.6, 18.8, 14.1; IR (KBr) v 1696, 1597, 1465, 1450, 1240, 1058, 964, 878, 762, 720, 683 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{25}O_2$ 333.1849; Found 333.1839.

(3-(Phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(p-tolyl)methanone ***(3ab)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 80% yield (54 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.48–7.37 (m, 3H), 7.3–7.28 (m, 5H), 7.22 (d, J = 15.6 Hz, 1H), *6.*99 (d, J = 14.8 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.01 (d, J = 7.6 Hz, 1H), 4.98 (d, J = 7.6 Hz, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.5, 158.7, 145.5, 132.3, 132.2, 130.0, 129.9, 129.7, 128.8, 128.7, 126.7, 125.3, 123.2, 122.2, 110.7, 88.5, 88.0, 83.8, 37.4, 22.2; IR (KBr) v 1700, 1593, 1483, 1450, 1237, 1052, 962, 865, 803, 763, 685 cm^{-1} ; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}O_2$ 339.1380; Found 339.1386.

(4-Ethylphenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone ***(3ac)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 64% yield (45 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H), 7.48–7.34 (m, 5H), 7.33–7.29 (m, 3H), 7.25–7.18 (m, 1H), 7.03–6.96 (m, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.01 (d, J = 7.8 Hz, 1H), 4.98 (d, J = 7.8 Hz, 1H), 2.75 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.5, 164.2, 158.7, 151.7, 132.5, 132.2, 130.1, 129.7, 128.7, 128.7, 126.7, 125.3, 123.2, 122.2, 110.7, 88.5, 88.0, 83.8, 37.41, 29.5, 15.5; IR (KBr) v 1967, 1598, 1487, 1450, 1237, 1052, 962, 865, 807, 720, 685 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{21}O_2$ 353.1536; Found 353.1541.

(4-Methoxyphenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone

*(**3ad**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 74% yield (52 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29–8.11 (m, 2H), 7.52–7.34 (m, 3H), 7.33–7.28 (m, 3H), 7.21 (d, J = 15.5 Hz, 1H), 7.06–6.94 (m, 3H), 6.91 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 7.5 Hz, 1H), 4.99 (d, J = 7.5 Hz, 1H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.3, 164.7, 158.7, 132.3, 132.2, 129.7, 128.7, 128.7, 127.9, 126.8, 125.3, 123.2, 122.2, 114.5, 110.6, 88.5, 88.1, 83.7, 56.0, 37.4; IR (KBr) v 1694, 1597, 1487, 1446, 1239, 1058, 964, 878, 760, 744, 688 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{24}H_{19}O_3$ 355.1329; Found 355.1335.

*(4-Fluorophenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3ae**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 76% yield (52 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26–8.18 (m, 2H), 7.47–7.38 (m, 3H), 7.34–7.29 (m, 3H), 7.25–7.18 (m, 3H), 7.04–6.97 (m, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 7.8 Hz, 1H), 5.01 (d, J = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.0, 166.5 (d, $J_{C\text{-}F}$ = 255.1 Hz), 158.1, 132.4, 132.3, 131.8, 131.0 (d, $J_{C\text{-}F}$ = 2.6 Hz), 129.4, 128.5, 128.4, 126.2, 125.0, 122.7, 122.0, 116.2 (d, $J_{C\text{-}F}$ = 21.8 Hz), 110.3, 88.2, 87.4, 83.5, 36.8; IR (KBr) v 1700, 1597, 1503, 1475, 1229, 1088, 964, 837, 760, 744, 688 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{23}H_{16}FO_2$ 343.1129; Found 343.1130.

*(4-Chlorophenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3af**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a colorless oil in 77% yield (55 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14–8.10 (m, 2H), 7.53–7.50 (m, 2H), 7.45–7.39 (m, 3H), 7.34–7.29 (m, 3H), 7.22 (d, J = 15.0 Hz, 1H), 7.00 (t, J = 15.0 Hz, 1H), 6.90 (d, J = 7.0 Hz, 1H), 5.94 (d, J = 7.5 Hz, 1H), 5.00 (d, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.9, 158.4, 141.1, 133.2, 132.2, 131.3, 129.8, 129.6, 128.9, 128.7, 126.5, 125.4, 123.0, 122.4, 110.7, 88.7, 87.7, 83.9, 37.2; IR (KBr) v 1700, 1596, 1501, 1472, 1224, 1156, 1086, 952, 863, 747, 692 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{23}H_{16}ClO_2$ 359.0833; Found 359.0839, 361.0829.

*(4-Bromophenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3ag**)*.

This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 70% yield (56 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–8.02 (m, 2H), 7.72–7.66 (m, 2H), 7.46–7.39 (m, 3H), 7.36–7.29 (m, 3H), 7.23 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 7.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.95 (d, J = 7.5 Hz, 1H), 4.99 (d, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.8, 158.0, 133.1, 132.2, 131.8, 131.0, 129.6, 129.4, 128.5, 128.4, 126.1, 125.0, 122.6, 122.0, 110.3, 88.2, 87.3, 83.5, 36.8; IR (KBr) v 1700, 1605, 1498, 1467, 1228, 1154, 1092, 963, 865, 849, 682 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}BrO_2$ 403.0328; Found 403.0333, 405.0303.

(3-Bromophenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone ***(3ah)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 70% yield (56 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (t, J = 2.0 Hz, 1H), 8.13–8.09 (m, 1H), 7.79–7.75 (m, 1H), 7.49–7.38 (m, 4H), 7.35–7.28 (m, 3H), 7.25–7.21 (m, 1H), 7.05–6.97 (m, 1H), 6.92 (d, J = 7.5 Hz, 1H), 5.95 (d, J = 7.5 Hz, 1H), 4.98 (d, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.4, 158.0, 136.9, 136.2, 132.50, 131.9, 130.4, 129.4, 128.5, 128.3, 128.1, 126.0, 125.0, 123.2, 122.6, 122.0, 110.4, 88.2, 87.2, 83.7, 36.9; IR (KBr) v 1701, 1604, 1503, 1467, 1228, 1154, 1086, 952, 865, 821, 685 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}BrO_2$ 403.0328; Found 403.0321, 405.0326.

(2-Bromophenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone ***(3ai)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 66% yield (53 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70–7.65 (m, 1H), 7.54–7.47 (m, 1H), 7.45–7.33 (m, 5H), 7.32–7.26 (m, 3H), 7.21 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 5.92 (d, J = 8.0 Hz, 1H), 4.90 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.2, 198.9, 158.1, 138.5, 133.8, 132.4, 131.8, 129.6, 129.4, 128.4, 128.3, 127.4, 126.1, 124.9, 122.7, 122.0, 119.8, 110.4, 89.9, 87.0, 83.4, 37.5; IR (KBr) v 1700, 1603, 1498, 1467, 1220, 1154, 1086, 952, 865, 829, 684 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}BrO_2$ 403.0328; Found 403.0334, 405.0340.

(2,4-Dimethylphenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone

*(**3aj**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a Yellow oil in 83% yield (58 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 1H), 7.47–7.41 (m, 3H), 7.36–7.30 (m, 3H), 7.27–7.22 (m, 1H), 7.21–7.16 (m, 2H), 7.03–6.99 (m, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.00 (d, J = 7.8 Hz, 1H), 4.94 (d, J = 7.8 Hz, 1H), 2.59 (s, 3H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.0, 158.4, 143.4, 140.9, 133.3, 131.8, 131.4, 130.7, 129.3, 128.3, 128.3, 126.5, 126.4, 124.9, 122.8, 121.7, 110.3, 89.0, 87.7, 83.3, 37.2, 21.9, 21.6; IR (KBr) v 1695, 1598, 1485, 1446, 1237, 1057, 962, 865, 807, 763, 685 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{21}O_2$ 353.1536; Found 353.1533.

*[1,1'-Biphenyl]-4-yl(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3ak**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 63% yield (50 mg); mp 141-143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.21 (m, 2H), 7.81–7.73 (m, 2H), 7.69–7.63 (m, 2H), 7.5–7.39 (m, 6H), 7.36–7.28 (m, 3H), 7.23 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.06 (d, J = 7.4 Hz, 1H), 5.02 (d, J = 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 158.3, 146.8, 139.7, 133.0, 131.8, 130.1, 129.4, 129.1, 128.5, 128.5, 128.4, 127.5, 127.4, 126.2, 125.0, 122.7, 121.9, 110.4, 88.2, 87.5, 83.5, 37.0; IR (KBr) v 1682, 1600, 1480, 1406, 1267, 1175, 962, 836, 807, 763, 692 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{21}O_2$ 401.1536; Found 401.1537.

*(4-(Methylsulfonyl)phenyl)(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3al**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:12) to afford a yellow oil in 60% yield (48 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.0 Hz, 2H), 8.12 (d, J = 8.0 Hz, 2H), 7.47–7.40 (m, 3H), 7.35–7.28 (m, 3H), 7.23 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.98 (d, J = 7.6 Hz, 1H), 5.04 (d, J = 7.6 Hz, 1H), 3.11 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.8, 157.8, 144.9, 138.4, 131.8, 130.5, 129.5, 128.6, 128.4, 127.9, 126.0, 125.1, 122.4, 122.3, 110.4, 88.5, 87.0, 83.7, 44.4, 36.6; IR (KBr) v 1706, 1595, 1476, 1456, 1217, 1086, 952, 865, 807, 763, 687 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}O_4S$ 403.0999; Found 403.1002.

*(3-(Phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(4-(trifluoromethyl)phenyl)methanone (**3am**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 76% yield (59 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30–8.26 (m, 2H), 7.82–7.78 (m, 2H), 7.45–7.39 (m, 3H), 7.33–7.28 (m, 3H), 7.25–7.21 (m, 1H), 7.03–6.99 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.98 (d, J = 7.5 Hz, 1H), 5.03 (d, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.3, 158.3, 137.5, 135.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 132.2, 130.3, 129.8, 128.9, 128.7, 126.4, 126.2 (q, $J_{C\text{-}F}$ = 3.5 Hz), 125.4, 124.0 (q, $J_{C\text{-}F}$ = 253.7 Hz), 122.5, 110.7, 88.8, 87.5, 84.0, 37.1; IR (KBr) v 1703, 1543, 1480, 1446, 1325, 1067, 960, 860, 807, 752, 689 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{16}F_3O_2$ 393.1097; Found 393.1091.

*Naphthalen-2-yl(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3an**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow oil in 66% yield (49 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.26–8.11 (m, 1H), 8.04–7.84 (m, 3H), 7.71–7.51 (m, 2H), 7.48–7.40 (m, 3H), 7.36–7.27 (m, 3H), 7.23 (d, J = 7.6 Hz, 1H), 7.05–6.92 (m, 2H), 6.19 (d, J = 7.6 Hz, 1H), 5.04 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.5, 158.3, 136.1, 132.5, 131.9, 131.8, 131.7, 130.0, 129.4, 129.1, 128.8, 128.4, 128.3, 127.9, 127.0, 126.3, 125.0, 124.5, 122.7, 121.9, 110.4, 88.2, 87.7, 83.6, 37.2; IR (KBr) v 1690, 1595, 1485, 1446, 1227, 1049, 965, 865, 807, 760, 687 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{19}O_2$ 375.1380; Found 375.1371.

*Furan-2-yl(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3ao**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 72% yield (45 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.71 (m, 1H), 7.54 (d, J = 3.5 Hz, 1H), 7.46–7.38 (m, 3H), 7.34–7.27 (m, 3H), 7.23 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.64–6.61 (m, 1H), 5.75 (d, J = 7.5 Hz, 1H), 4.94 (d, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.9, 158.2, 150.4, 148.1, 131.8, 129.4, 128.4, 128.3, 126.2, 125.0, 122.7, 122.0, 121.1, 112.7, 110.3, 88.3, 87.3, 83.5, 37.5; IR (KBr) v 1676, 1598, 1477, 1446, 1409, 1222, 978, 855, 823, 753, 692 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for

$C_{21}H_{15}O_3$ 315.1016; Found 315.1011.

(3-(Phenylethynyl)-2,3-dihydrobenzofuran-2-yl)(thiophen-2-yl)methanone ***(3ap)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 82% yield (54 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.07 (m, 1H), 7.80–7.76 (m, 1H), 7.47–7.39 (m, 3H), 7.35–7.28 (m, 3H), 7.25–7.19 (m, 2H), 7.00 (d, J = 7.5 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 5.80 (d, J = 7.5 Hz, 1H), 4.96 (d, J = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.5, 158.2, 140.9, 135.6, 134.6, 131.8, 129.4, 128.5, 128.5, 128.3, 126.2, 125.0, 122.7, 122.0, 110.4, 89.2, 87.3, 83.6, 37.3; IR (KBr) v 1679, 1598, 1514, 1456, 1354, 1057, 976, 865, 821, 753, 695 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{15}O_2S$ 331.0787; Found 331.0785.

1-(3-(Phenylethynyl)-2,3-dihydrobenzofuran-2-yl)ethanone ***(3aq)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:60) to afford a yellow oil in 57% yield (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.41 (m, 2H), 7.40–7.37 (m, 1H), 7.32–7.28 (m, 3H), 7.25–7.20 (m, 1H), 7.01–6.97 (m, 1H), 6.93 (d, J = 8.0 Hz, 1H), 5.14 (d, J = 7.6 Hz, 1H), 4.67 (d, J = 7.6 Hz, 1H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 205.3, 158.1, 131.8, 129.4, 128.4, 128.3, 126.2, 125.0, 122.7, 122.0, 110.3, 91.4, 87.2, 83.3, 37.3, 26.7; IR (KBr) v 1700, 1598, 1442, 1375, 1285, 1135, 1040, 973, 877, 811, 740, 671 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{14}O_2$ 263.1067; Found 263.1062.

General procedure for the synthesis of the 2-benzoyl-3-aryl-2,3-hydrobenzofuran derivatives 5.

A mixture of 2-(aryl(piperidin-1-yl)methyl)phenols **4** (0.2 mmol) and benzoyl sulfonium salts **2** (0.24 mmol) in CH_3CN/H_2O (1:1, v/v, 2 mL) was heated to 100 °C in an oil bath for 2 h. After the reaction was complete (as determined using TLC), the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether (1:40-1:60, v/v) as the elution solvent to give desired product **5**.

*Phenyl(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanon (**5aa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a ehite solid in 90% yield (54 mg); mp 129-130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.0 Hz, 2H), 7.60 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.37–7.31 (m, 2H), 7.31–7.26 (m, 1H), 7.25–7.19 (m, 3H), 7.00 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 7.5 Hz, 1H), 5.82 (d, J = 6.5 Hz, 1H), 4.98 (d, J = 6.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.1, 159.5, 142.7, 134.8, 134.2, 129.7, 129.7, 129.4, 129.3, 129.1, 128.6, 127.9, 125.8, 122.0, 110.4, 91.0, 51.3; IR (KBr) v 1703, 1593, 1474, 1451, 1225, 1178, 997, 884, 807, 750, 695 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{21}H_{17}O_2$ 301.1223; Found 301.1227.

*Phenyl(3-(p-tolyl)-2,3-dihydrobenzofuran-2-yl)methanone (**5ba**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow oil in 95% yield (59 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.65–7.56 (m, 1H), 7.50–7.42 (m, 2H), 7.25–7.09 (m, 5H), 7.05–6.95 (m, 2H), 6.94–6.85 (m, 1H), 5.81 (d, J = 6.4 Hz, 1H), 4.92 (d, J = 6.4 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.8, 159.1, 139.3, 137.2, 134.4, 133.8, 129.7, 129.5, 129.3, 128.9, 128.7, 128.0, 125.3, 121.6, 110.0, 90.7, 50.7, 21.1; IR (KBr) v 1700, 1598, 1498, 1451, 1398, 1238, 973, 874, 807, 742, 695 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{22}H_{19}O_2$ 315.1380; Found 315.1374.

*(3-(4-Fluorophenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5ca**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow oil in 60% yield (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.92 (m, 2H), 7.65–7.57 (m, 1H), 7.51–7.44 (m, 2H), 7.25–7.17 (m, 3H), 7.09–6.96 (m, 4H), 6.95–6.87 (m, 1H), 5.75 (d, J = 6.8 Hz, 1H), 5.01 (d, J = 6.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.6, 162.1 (d, $J_{C\text{-}F}$ = 245.0 Hz), 159.0, 138.0, 134.4, 133.9, 129.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.4, 129.1, 128.8, 125.3, 121.8, 115.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 110.1, 90.6, 50.0; IR (KBr) v 1694, 1590, 1404, 1329, 1230, 1070, 1044, 960, 873, 815, 750, 684 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{21}H_{16}FO_2$ 319.1129; Found 319.1137.

*(3-(4-Bromophenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5da**)*. This

compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow oil in 68% yield (51 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.93 (m, 2H), 7.65– 7.58 (m, 1H), 7.47 (t, *J* = 8.3 Hz, 4H), 7.25–7.20 (m, 1H), 7.15–7.10 (m, 2H), 7.02–6.88 (m, 3H), 5.74 (d, *J* = 6.4 Hz, 1H), 4.99 (d, *J* = 6.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* 194.5, 159.0, 141.3, 134.4, 134.0, 132.2, 129.9, 129.4, 129.2, 128.8, 128.7, 125.3, 121.8, 121.5, 110.1, 90.4, 50.2; IR (KBr) *v* 1690, 1596, 1454, 1322, 1233, 1070, 1044, 960, 873, 815, 753, 691 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{16}BrO_2$ 379.0328; Found 379.0329, 381.0306.

*(5-Methyl-3-phenyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5ea**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow solid in 92% yield (58 mg); mp 122-124 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.98–7.92 (m, 0H), 7.63–7.56 (m, 1H), 7.48–7.43 (m, 2H), 7.38–7.31 (m, 2H), 7.32–7.26 (m, 1H), 7.25–7.21 (m, 2H), 7.04–6.97 (m, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.80 (s, 1H), 5.79 (d, *J* = 9.0 Hz, 1H), 4.93 (d, *J* = 6.5 Hz, 1H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) *δ* 195.3, 157.4, 142.8, 134.8, 134.1, 131.4, 129.8, 129.7, 129.6, 129.4, 129.1, 128.5, 127.8, 126.1, 109.9, 91.1, 51.4, 21.2; IR (KBr) *v* 1700, 1598, 1498, 1398, 1238, 1107, 973, 873, 815, 742, 697 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}O_2$ 315.1380; Found 315.1383.

*(5-Methyl-3-(p-tolyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5fa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow solid in 82% yield (54 mg); mp 89-90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02–7.89 (m, 2H), 7.67–7.54 (m, 1H), 7.51–7.39 (m, 2H), 7.19–7.10 (m, 4H), 7.05–6.96 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.80 (s, 1H), 5.78 (d, *J* = 6.2 Hz, 1H), 4.87 (d, *J* = 6.2 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* 195.0, 157.0, 139.4, 137.2, 134.4, 133.8, 131.0, 129.7, 129.4, 129.3, 128.7, 128.0, 125.7, 109.5, 90.8, 50.8, 21.1, 20.8; IR (KBr) *v* 1700, 1598, 1498, 1398, 1235, 1029, 973, 873, 815, 742, 695 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}O_2$ 329.1536; Found 329.1543.

*(5-Methoxy-3-(p-tolyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5ga**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether =

1:40) to afford a white soild in 81% yield (56 mg); mp 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.92 (m, 2H), 7.64–7.54 (m, 1H), 7.50–7.40 (m, 2H), 7.19–7.07 (m, 4H), 6.89 (d, J = 8.4 Hz, 1H), 6.80–6.70 (m, 1H), 6.60–6.53 (m, 1H), 5.77 (d, J = 6.4 Hz, 1H), 4.92 (d, J = 6.4 Hz, 1H), 3.69 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.9, 155.0, 153.2, 139.1, 137.2, 134.5, 133.8, 130.3, 129.7, 129.3, 128.7, 128.1, 114.4, 110.8, 110.1, 91.0, 57.0, 51.0, 21.1; IR (KBr) ν 1692, 1595, 1485, 1451, 1246, 1109, 965, 857, 800, 752, 700 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}O_3$ 345.1485; Found 345.1488.

*(6-Methoxy-3-phenyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5ha**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white soild in 89% yield (59 mg); mp 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.88 (m, 2H), 7.70–7.56 (m, 1H), 7.52–7.41 (m, 2H), 7.38–7.26 (m, 3H), 7.24–7.19 (m, 2H), 6.93– 6.84 (m, 1H), 6.62–6.56 (m, 1H), 6.49–6.38 (m, 1H), 5.84 (d, J = 6.0 Hz, 1H), 4.87 (d, J = 6.0 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.8, 161.0, 160.5, 142.7, 134.3, 133.8, 129.3, 129.0, 128.7, 128.0, 127.5, 125.5, 121.2, 107.7, 96.2, 91.5, 55.6, 50.5; IR (KBr) ν 1697, 1595, 1498, 1397, 1325, 1041, 973, 873, 815, 750, 691 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}O_3$ 331.1329; Found 331.1324.

*(5-Chloro-3-phenyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5ia**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a colorless oil in 72% yield (48 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.90 (m, 2H), 7.67–7.57 (m, 1H), 7.51–7.42 (m, 2H), 7.40–7.28 (m, 3H), 7.25–7.20 (m, 2H), 7.19–7.14 (m, 1H), 7.00–6.86 (m, 2H), 5.86 (d, J = 6.4 Hz, 1H), 4.96 (d, J = 6.4 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 194.5, 158.1, 141.8, 134.6, 134.4, 131.6, 129.7, 129.6, 129.3, 129.2, 128.5, 128.2, 126.8, 125.8, 111.4, 91.4, 51.1; IR (KBr) ν 1698, 1595, 1473, 1391, 1322, 1039, 973, 873, 815, 742, 694 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{16}ClO_2$ 335.0833; Found 335.0836, 337.0828.

*(5-Chloro-3-(p-tolyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5ja**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether =

1:40) to afford a white solid in 78% yield (54 mg); mp 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.89 (m, 2H), 7.71–7.55 (m, 1H), 7.55–7.41 (m, 2H), 7.24–7.07 (m, 5H), 7.02–6.86 (m, 2H), 5.84 (d, J = 6.4 Hz, 1H), 4.90 (d, J = 6.4 Hz, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.3, 157.7, 138.5, 137.6, 134.2, 134.0, 131.5, 129.9, 129.3, 128.9, 128.8, 128.0, 126.4, 125.4, 111.0, 91.1, 50.5, 21.1; IR (KBr) v 1682, 1598, 1472, 1262, 1222, 1104, 955, 876, 800, 750, 676 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{22}H_{18}ClO_2$ 349.0990; Found 349.0984, 351.0992.

(5-Bromo-3-phenyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone ***(5ka)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a colorless oil in 70% yield (53 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.90 (m, 2H), 7.66–7.58 (m, 1H), 7.53–7.42 (m, 2H), 7.40–7.27 (m, 4H), 7.25–7.20 (m, 2H), 7.13–7.09 (m, 1H), 6.86 (d, J = 8.5 Hz, 1H), 5.85 (d, J = 6.5 Hz, 1H), 4.97 (d, J = 6.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 194.5, 158.6, 141.8, 134.5, 134.4 132.2, 129.7, 129.6, 129.2, 128.7, 128.5, 128.2, 113.9, 112.0, 91.3, 51.0, 31.4; IR (KBr) v 1698, 1595, 1467, 1391, 1322, 1165, 973, 873, 815, 750, 694 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{21}H_{16}BrO_2$ 379.0328; Found 379.0334, 381.0317.

(5-Bromo-3-(p-tolyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone ***(5la)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow solid in 70% yield (55 mg); mp 101-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.90 (m, 2H), 7.68–7.58 (m, 1H), 7.52–7.45 (m, 2H), 7.36–7.29 (m, 1H), 7.23–7.08 (m, 5H), 6.89 (d, J = 8.4 Hz, 1H), 5.86 (d, J = 6.2 Hz, 1H), 4.92 (d, J = 6.2 Hz, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.2, 158.2, 138.5, 137.6, 134.1, 134.0, 132.0, 131.8, 129.9, 129.3, 128.8, 128.3, 128.0, 113.5, 111.6, 91.0, 50.4, 21.2; IR (KBr) v 1679, 1600, 1469, 1298, 1225, 1149, 955, 800, 742, 689, 658 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{22}H_{18}BrO_2$ 393.0485; Found 393.0478, 395.0468.

(5-Nitro-3-phenyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone ***(5ma)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 70% yield (48 mg); mp 105-107 °C; ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.28–8.14 (m, 1H), 7.97–7.89 (m, 3H), 7.67–7.61 (m, 1H), 7.52–7.46 (m, 2H), 7.42–7.31 (m, 3H), 7.25–7.19 (m, 2H), 7.06 (d, J = 8.8 Hz, 1H), 6.04 (d, J = 6.4 Hz, 1H), 5.01 (d, J = 6.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 193.5, 164.4, 143.3, 141.0, 134.7, 134.1, 131.6, 129.8, 129.7, 129.3, 128.6, 128.4, 126.8, 122.3, 110.5, 92.3, 50.4; IR (KBr) v 1703, 1598, 1474, 1333, 1233, 1070, 1044, 960, 873, 815, 750, 684 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}NO_4$ 346.1074; Found 346.1070.

*(5-Nitro-3-(p-tolyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5na**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow oil in 77% yield (55 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28–8.12 (m, 1H), 8.01–7.84 (m, 3H), 7.71–7.58 (m, 1H), 7.57–7.42 (m, 2H), 7.22–7.16 (m, 2H), 7.16–7.01 (m, 3H), 6.02 (d, J = 6.2 Hz, 1H), 4.94 (d, J = 6.2 Hz, 1H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.2, 164.1, 142.9, 138.1, 137.7, 134.4, 133.7, 131.4, 130.1, 129.3, 128.9, 127.8, 126.3, 121.9, 110.1, 92.0, 49.8, 21.2; IR (KBr) v 1703, 1522, 1474, 1333, 1233, 1070, 1044, 973, 873, 815, 742, 697 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}NO_4$ 360.1230; Found 360.1229.

*(6-Chloro-3-phenyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**5oa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 77% yield (51 mg); mp 109-111 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00–7.89 (m, 2H), 7.68–7.56 (m, 1H), 7.54–7.43 (m, 2H), 7.38–7.27 (m, 3H), 7.24–7.19 (m, 2H), 7.01–6.85 (m, 3H), 5.86 (d, J = 6.2 Hz, 1H), 4.93 (d, J = 6.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.2, 159.9, 141.8, 134.3, 134.2, 134.0, 129.3, 129.2, 128.8, 128.1, 128.1, 127.7, 126.0, 121.9, 110.8, 91.3, 50.3; IR (KBr) v 1692, 1598, 1484, 1241, 1165, 1086, 1014, 960, 873, 815, 750, 702 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}ClO_2$ 335.0833; Found 335.0836, 337.0821.

*(4-Ethylphenyl)(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanone (**5ac**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 73% yield (48 mg); mp 68-70 ^oC; ^1H NMR (400 MHz,

$CDCl_3$) δ 7.96–7.80 (m, 2H), 7.36–7.27 (m, 4H), 7.25–7.17 (m, 3H), 7.02–6.96 (m, 2H), 6.91–6.85 (m, 1H), 5.80 (d, J = 6.4 Hz, 1H), 4.97 (d, J = 6.4 Hz, 1H), 2.71 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.3, 159.2, 151.0, 142.4, 132.1, 129.6, 129.4, 129.0, 128.9, 128.3, 128.2, 127.5, 125.4, 121.6, 110.0, 90.6, 50.3, 29.1, 15.2; IR (KBr) v 1703, 1598, 1498, 1451, 1238, 1107, 1044, 960, 873, 817, 720, 684 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}O_2$ 329.1536; Found 329.1533.

(4-Fluorophenyl)(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanone ***(5ae)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a colorless oil in 66% yield (42 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05–7.97 (m, 2H), 7.39–7.27 (m, 3H), 7.26–7.19 (m, 3H), 7.18–7.09 (m, 2H), 7.04–6.88 (m, 3H), 5.75 (d, J = 6.6 Hz, 1H), 5.02 (d, J = 6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.2, 166.1 (d, J_{C-F} = 254.9 Hz), 158.9, 142.1, 132.2, 132.1, 130.9 (d, J_{C-F} = 3.0 Hz), 129.2, 129.1, 129.0, 128.2, 127.6, 125.4, 121.8, 115.9 (d, J_{C-F} = 21.7 Hz), 110.0, 90.7, 50.7; IR (KBr) v 1692, 1598, 1482, 1453, 1247, 1107, 1054, 960, 873, 817, 720, 693 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}FO_2$ 319.1129; Found 319.1124.

(4-Chlorophenyl)(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanone ***(5af)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 70% yield (47 mg); mp 81-84 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.88 (m, 2H), 7.49–7.42 (m, 2H), 7.38–7.27 (m, 3H), 7.27–7.19 (m, 3H), 7.05 –6.96 (m, 2H), 6.94–6.89 (m, 1H), 5.75 (d, J = 6.6 Hz, 1H), 5.02 (d, J = 6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.7, 158.9, 142.1, 140.4, 132.9, 130.8, 129.2, 129.1, 129.1, 129.0, 128.2, 127.6, 125.4, 121.8, 110.0, 90.7, 50.7; IR (KBr) v 1698, 1593, 1481, 1404, 1241, 1107, 1086, 963, 873, 815, 758, 702 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}ClO_2$ 335.0833; Found 335.0827, 337.0816.

(3-Bromophenyl)(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanone ***(5ah)***. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow solid in 73% yield (55 mg); mp 82-85 ^oC; ^1H NMR (400

MHz, $CDCl_3$) δ 8.10–8.06 (m, 1H), 7.91–7.84 (m, 1H), 7.77–7.68 (m, 1H), 7.40–7.27 (m, 4H), 7.25–7.19 (m, 3H), 7.04–6.96 (m, 2H), 6.94–6.88 (m, 1H), 5.74 (d, J = 6.8 Hz, 1H), 4.99 (d, J = 6.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.6, 158.9, 142.0, 136.7, 136.2, 132.4, 130.3, 129.1, 129.1, 129.0, 128.2, 127.9, 127.6, 125.4, 123.1, 121.8, 110.1, 90.7, 50.7; IR (KBr) v 1692, 1590, 1498, 1457, 1249, 1162, 1083, 963, 883, 817, 720, 684 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{16}BrO_2$ 379.0328; Found 379.0321, 381.0286.

*(2,4-dimethylphenyl)(3-Phenyl-2,3-dihydrobenzofuran-2-yl)methanone (**5aj**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a yellow solid in 74% yield (48 mg); mp 91-93 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 1H), 7.36–7.26 (m, 3H), 7.25–7.15 (m, 3H), 7.11 (s, 1H), 7.05– 6.86 (m, 4H), 5.75 (d, J = 6.2 Hz, 1H), 4.90 (d, J = 6.2 Hz, 1H), 2.52 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.0, 142.5, 140.5, 133.2, 131.5, 130.2, 129.3, 128.9, 128.9, 128.1, 127.4, 126.3, 125.4, 121.5, 110.0, 91.4, 51.1, 21.5; IR (KBr) v 1695, 1598, 1485, 1445, 1238, 1107, 1054, 960, 873, 817, 760, 685 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}O_2$ 329.1536; Found 329.1531.

*(4-(Methylsulfonyl)phenyl)(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanone (**5ak**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 58% yield (44 mg); mp146-148 ^oC; ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.40–7.34 (m, 2H), 7.33–7.28 (m, 1H), 7.26–7.20 (m, 3H), 7.03 (d, J = 7.5 Hz, 1H), 6.99–6.89 (m, 2H), 5.76 (d, J = 7.0 Hz, 1H), 5.06 (d, J = 6.5 Hz, 1H), 3.09 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.0, 158.6, 144.6, 141.8, 138.6, 130.3, 129.2, 129.1, 129.0, 128.2, 127.8, 127.7, 125.5, 122.1, 110.1, 91.0, 50.4, 44.3; IR (KBr) v 1711, 1595, 1477, 1456, 1217, 1086, 952, 847, 765, 744, 697 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}O_4S$ 379.0999; Found 379.0996.

*[1,1'-Biphenyl]-4-yl(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanone (**5al**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 60% yield (45 mg); mp 131-133 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.10–8.05 (m, 2H), 7.74–7.70 (m, 2H), 7.69–7.66 (m, 2H), 7.55–7.49

(m, 2H), 7.48–7.43 (m, 1H), 7.42–7.36 (m, 2H), 7.36–7.29 (m, 3H), 7.28–7.24 (m, 1H), 7.09–7.02 (m, 2H), 6.98–6.92 (m, 1H), 5.99–5.83 (m, 1H), 5.07 (d, J = 6.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 194.3, 159.1, 146.5, 142.3, 139.7, 133.1, 130.0, 129.3, 129.1, 129.0, 129.0, 128.5, 128.2, 127.5, 127.4, 125.4, 121.7, 110.0, 90.7, 50.9; IR (KBr) ν 1692, 1598, 1480, 1406, 1267, 1175, 962, 836, 807, 763, 692 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{21}O_2$ 377.1536; Found 377.1538.

*Naphthalen-2-yl(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanone (**5an**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a white solid in 83% yield (58 mg); mp 145-147 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.09–8.01 (m, 1H), 7.97–7.79 (m, 3H), 7.65–7.60 (m, 1H), 7.58–7.52 (m, 1H), 7.40–7.29 (m, 3H), 7.29–7.26 (m, 1H), 7.26–7.20 (m, 2H), 7.05–6.99 (m, 2H), 6.95–6.87 (m, 1H), 5.99 (d, J = 6.6 Hz, 1H), 5.03 (d, J = 6.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 194.6, 159.2, 142.4, 135.9, 132.4, 131.6, 129.8, 129.3, 129.1, 128.9, 129.0, 128.6, 128.3, 127.8, 127.6, 126.9, 125.4, 124.5, 121.7, 110.0, 90.8, 51.3; IR (KBr) ν 1690, 1595, 1482, 1456, 1251, 1049, 983, 865, 815, 750, 702 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{19}O_2$ 351.1380; Found 351.1377.

*(E)-phenyl(3-styryl-2,3-dihydrobenzofuran-2-yl)methanone (**7aa**)*. This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:40) to afford a Yellow oil in 75% yield (49 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.02 (m, 2H), 7.64–7.60 (m, 1H), 7.52–7.47 (m, 2H), 7.41–7.37 (m, 2H), 7.36–7.26 (m, 3H), 7.21 (d, J = 7.9 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 6.98–6.88 (m, 2H), 6.57 (d, J = 16.0 Hz, 1H), 6.37 (dd, J = 15.6 Hz, 8.8 Hz, 1H), 5.75 (d, J = 6.8 Hz, 1H), 4.59–4.52 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 194.8, 158.9, 136.5, 134.5, 133.9, 132.8, 129.3, 129.1, 128.8, 128.7, 128.6, 127.9, 127.9, 126.5, 125.3, 121.5, 110.1, 88.2, 49.3; IR (KBr) ν 1710, 1663, 1327, 1301, 1269, 1123, 974, 910, 810, 721, 615 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{18}O_2$ 327.1380; Found 327.1385.

*Phenyl(3-(phenylethynyl)-2,3-dihydrobenzofuran-2-yl)methanone (**3aa'**)*. 1H NMR (400 MHz, $CDCl_3$) δ 8.20–8.16 (m, 2H), 7.69–7.62 (m, 1H), 7.57–7.52 (m, 2H),

7.46–7.38 (m, 3H), 7.33–7.28 (m, 3H), 7.25–7.20 (m, 1H), 6.99 (t, J = 7.2 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.98 (s, 1H).

*Phenyl(3-phenyl-2,3-dihydrobenzofuran-2-yl)methanon (**5aa'**)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97–7.93 (m, 2H), 7.63–7.58 (m, 1H), 7.49–7.43 (m, 2H), 7.37–7.32 (m, 2H), 7.31–7.27 (m, 1H), 7.25–7.19 (m, 3H), 7.02–6.97 (m, 2H), 6.92–6.88 (m, 1H), 4.97 (s, 1H).

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests.

Supporting Information

Spectral data for all compounds and crystallographic data of compounds **3ga**, **5ka**. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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