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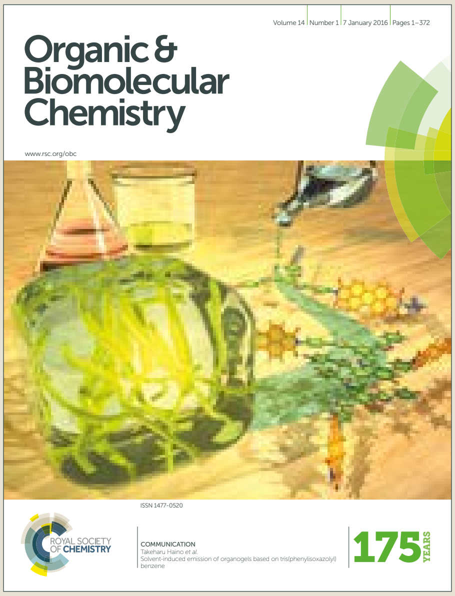

Volume 14 | Number 1 | 7 January 2016 | Pages 1–372

Organic & Biomolecular Chemistry

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ISSN 1477-0520

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DOI: 10.1039/C8OB02092B

Journal Name

ARTICLE

Efficient Assembly of Ynones *via* Palladium-Catalyzed Sequential Carbonylation/Alkynylation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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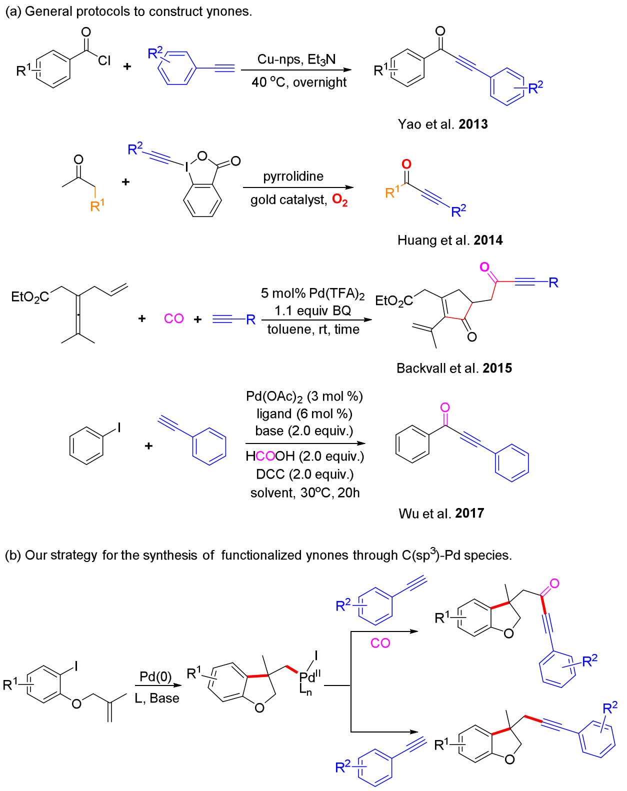
Based on intramolecular Heck-type reaction, a convenient and efficient strategy to construct functionalized ynones by palladium-catalyzed cascade annulation reaction has been developed. This reaction possesses good functional group compatibility, broad substrate scope, and high atom- and step-economy. Furthermore, this approach could also be extended to direct alkynylation that gave another route to synthesize dihydrobenzofurans.

Introduction

Ynones are privileged structural motifs which have been widely utilized as valuable framework in organic synthesis, biological and pharmaceutical research. Major advances in the construction of heterocyclic derivatives such as acylindoles,[1] thiophenes,[2] furans,[3] pyrroles[4] *etc*. have been made with significant contribution by Marinelli, Harrity, Maekawa and others through the annulation reactions of ynones. Alternatively, owing to the prevalence of ynones in natural products and bioactive molecules, the development of new transition metal-catalyzed reactions for the construction of ynones remains to be highly desirable.

The general strategies to synthesize ynones are the oxidation of propargyl alcohols.[5] However, low chemoselectivity was obtained because of the over-oxidation process. Furthermore, a series of efficient and novel methods have been designed and successfully applied to the construction of a variety of ynones.[6] Typically, Yao *et. al* reported the synthesis of ynones by direct coupling of acylchlorides and terminal alkyne in the presence of a reusable copper nanoparticle catalyst.[7] Huang group disclosed a direct synthesis of various ynones from readily available aldehydes and hypervalent alkynyl iodides by gold / amine synergistic catalysis.[8] However, both reaction partners need to be preactivated in these cases. Specifically, Bäckvall,[9] Lee,[10] Wu,[11] and others successfully synthesized a wide range of ynones by the employment of carbon monoxide or formic acid as the CO source under palladium catalysis. To the best of our knowledge, only one report has demonstrated the palladium-catalyzed oxidative cascade reaction to construct ynones *via* carbon monoxide insertion of C(sp^3)-Pd species.[9]

Scheme 1 The transformations of C(sp^3)-Pd species



Despite the remarkable progress achieved in this area, the synthesis of functionalized ynones through the insertion of carbon monoxide to C(sp^3)-Pd species remains a challenging goal. In continuation with our current research interest in the transformation of C(sp^3)-Pd species,[12, 13] we showcase a novel Pd-catalyzed cascade annulation reaction through the insertion of carbon monoxide to C(sp^3)-Pd species, which generated functional ynones in good to excellent yields under mild reaction conditions. Moreover, this protocol could also be used for direct alkynylation.

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†Electronic Supplementary Information (ESI) available: General experimental information, and NMR spectra. See DOI: 10.1039/x0xx00000x

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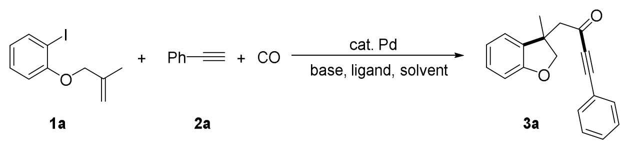
DOI: 10.1039/C8OB02092B

Results and discussion

Table 1 Optimization of the reaction conditions for the synthesis of ynones [a]

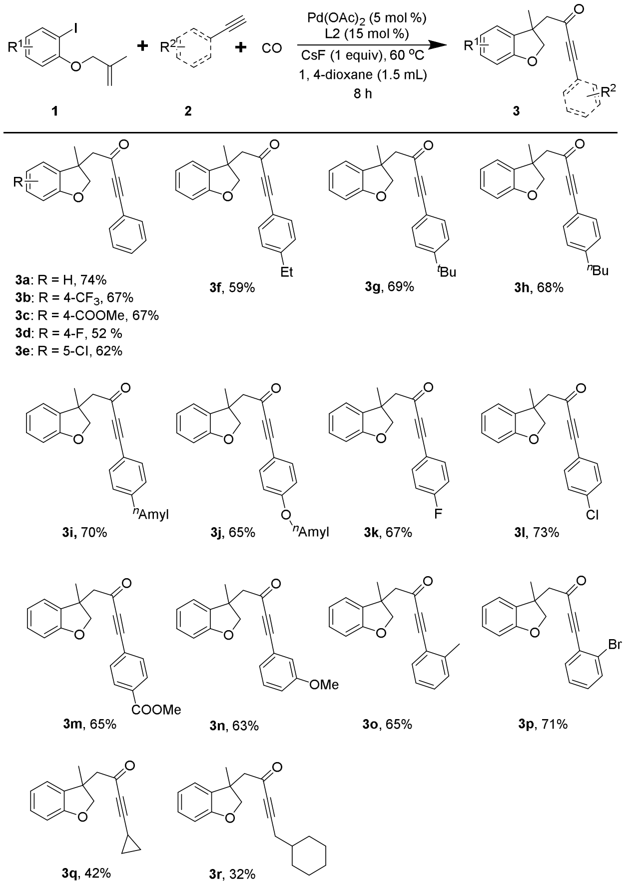


Entry	Ligand	Base	Solvent	T (°C)	Yield[b] (%)
1	PPh_3	Cs_2CO_3	toluene	80	30
2	PPh_3	KO^tBu	toluene	80	27
3	PPh_3	CsF	toluene	80	55
4	PPh_3	CsF	toluene	60	60
5	-	KO^tBu	toluene	80	20
6[c]	-	KO^tBu	toluene	80	<5
7	PPh_3	CsF	1,4-dioxane	60	68
8	L1[d]	CsF	1,4-dioxane	60	70
9	PPh_3	CsF	1,4-dioxane	60	75
10	**L2[e]**	**CsF**	**1,4-dioxane**	**60**	**78 (74)**

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ catalyst (5 mol %), ligand (15 mol %), base (1 equiv), solvent (1.5 mL), under CO (1atm), 8 h. [b] Yield was determined by NMR analysis using dibromomethane as the internal standard. Isolated yield product in parentheses. [c] $PdCl_2$ was used to replace $Pd(OAc)_2$. [d] **L1** was *N*, *N*-dimethylglycine. [e] **L2** was tris(2,4-di-*tert*-butylphenyl) phosphite.

The initial studies were conducted with 1-iodo-2-((2-methylallyl)oxy)benzene (**1a**) and ethynylbenzene (**2a**) as the model substrates in the presence of $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (1 equiv), PPh_3 (15 mol %) in toluene at 80 °C for 8 h, but the yield of the desired product **3a** was obtained only in 30% yield (Table 1, Entry 1). Under this condition, apart from the carbonylation product, the direct coupling product was also obsered, and the ratio is about 3:4. In subsequent base screening, CsF was found to be the best choice (Table 1, Entries 2-3). In addition, the reaction temperature slightly affected the reaction. We found the yield of **3a** would decrease no matter increase or decrease the temperature (Table 1, Entry 4). Among the screening solvents, 1,4-dioxane was optimal for this transformation (Table 1, Entry 7). To further improve the yield, different kinds of ligands were investigated, and **L2** (tris(2,4-di-tert-butylphenyl) phosphite) was selected (Table 1, Entries 8-10). Further control experiments showed that the reaction could not proceed smoothly without the ligand (Table 1, Entries 5-6).

Scheme 2 Substrate scope of functionalized ynones [a,b,c]



[a] Reaction condition: **1** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), **L2** (15 mol %), CsF (1 equiv), 1,4-dioxane (1.5 mL), 60 °C, CO (1atm), 8 h. [b] Yields of isolated products were given. [c] **L2** was tris(2,4-di-*tert*-butylphenyl) phosphite.

Under the optimal reaction conditions, the scope of functionalized ynones was studied with a variety of ethynylbenzene compounds **1** and 1-iodo-2-((2-methylallyl)oxy)benzene compounds **2**. Likewise, we set out to explore the substrate scope of 1-iodo-2-((2-methylallyl)oxy)benzene compounds **1**. Electron-deficient groups, such as $-CF_3$, -COOMe, -F, -Cl were well tolerated in our reaction (**3b-3e**). To our delight, the electronic effects did not affect the reaction significantly (**3f-3p**). Notably, many functional groups on ethynylbenzene ring, including alkyl (**3f-3i**, **3o**), ether (**3j** and **3n**), -F (**3k**), -Cl (**3l**), -Br (**3p**) and ester (**3m**) were tolerated. The corresponding expected products were obtained in moderate yields. It should be noted that linear alkyl substituted alkynes have been tested in the carbonylative coupling reaction, and the results indicated that they may be not suitable for this transformation (see the Supporting Information for details). Moreover, some naphthenic substituted alkynes could participate in the reaction (**3q** and **3r**). However, when using 1-bromo-2-((2-methylallyl)oxy)benzene as substrate, no desired **3a** was detected under the carbonylation process.

Encouraged by these promising results, we further attempted to apply our developed procedure to alkynylation reaction. We used 1-iodo-2-((2-methylallyl)oxy)benzene (**1a**) and ethynylbenzene (**2a**) as

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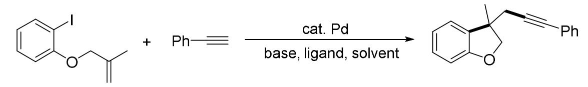
the model substrates in the presence of $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (1 equiv), PPh_3 (15 mol %) in DMF at 80 °C for 8 h. However, the desired product **4a** was obtained only in 15% yield (Table 2, Entry 1). Furthermore, other solvents such as DMSO, MeCN and toluene were investigated (Table 2, Entries 2-4). To our delight, the solvent had a significant impact on promoting the reaction efficiency, and the expected product **4a** could be detected in 85% yield when using toluene as solvent. Then the bases were examined (Table 2, Entries 5-6), and Cs_2CO_3 was the most effective base in this reaction compared with K_2CO_3 and Et_3N. Moreover, different Pd catalysts were examined as well (Table 2, Entries 7-9), such as $Pd(PPh_3)_2Cl_2$, $PdCl_2$ and $Pd(PPh_3)_4$, and $Pd(OAc)_2$ still gave the excellent yield than those of other catalysts. Experiments on ligand screening showed that PPh_3 was the best ligand (see the Supporting Information for details). Control experiments revealed that the reaction did not occur in the absence of palladium catalyst (Table 2, Entry 12). Notably, both base and ligand were required for this transformation (Table 2, Entries 13-14). Interestingly, product **4a** could be also obtained in good yield when 3-phenylpropiolic acid and trimethyl(phenylethynyl)silane were used to replace **2a** under the optimized reaction conditions (Table 1, Entries 10-11). Considering the atom economy, we chose **2a** as the best substrate in our reaction system.

Table 2 Optimization of the reaction conditions of alkynylation [a]



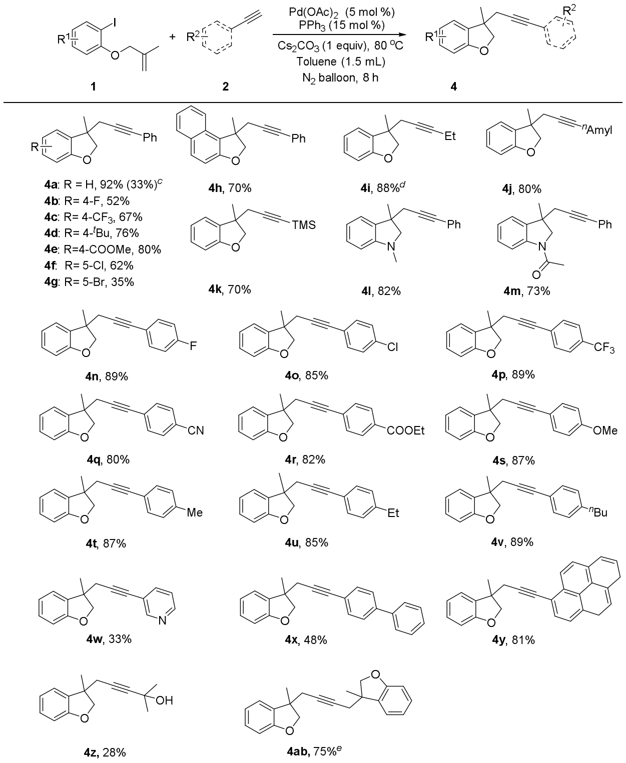
1a **2a** **4a**

Entry	Catalyst	Base	Ligand	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	Cs_2CO_3	PPh_3	DMF	15
2	$Pd(OAc)_2$	Cs_2CO_3	PPh_3	DMSO	20
3	$Pd(OAc)_2$	Cs_2CO_3	PPh_3	MeCN	38
4	**$Pd(OAc)_2$**	**Cs_2CO_3**	PPh_3	**toluene**	**85（83）**
5	$Pd(OAc)_2$	K_2CO_3	PPh_3	toluene	70
6	$Pd(OAc)_2$	Et_3N	PPh_3	toluene	78
7	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	PPh_3	toluene	75
8	$PdCl_2$	Cs_2CO_3	PPh_3	toluene	80
9	$Pd(PPh_3)_4$	Cs_2CO_3	PPh_3	toluene	82
10[c]	$Pd(OAc)_2$	Cs_2CO_3	PPh_3	toluene	83
11[d]	$Pd(OAc)_2$	Cs_2CO_3	PPh_3	toluene	78
12	-	Cs_2CO_3	PPh_3	toluene	n.d.
13[e]	$Pd(OAc)_2$	Cs_2CO_3	-	toluene	32
14	$Pd(OAc)_2$	-	PPh_3	toluene	12

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), Pd catalyst (5 mol %), PPh_3 (15 mol %) , base (1 equiv.), solvent (1.5 mL), 80 °C, under N_2, 8 h. [b] Yield was determined by NMR analysis using dibromomethane as the internal standard. Isolated yield of product was in parentheses. n.d. = not detected. [c] **2a** was replaced by 3-phenylpropiolic acid. [d] **2a** was replaced by trimethyl(phenylethynyl)silane. [e] Without ligand.

Using the optimized reaction condition, we investigated the scope of this alkynylation reaction. Different types of 1-iodo-2-((2methylallyl)oxy)benzene substrates **1** reacted smoothly with phenylacetylene (**2a**). Diverse functional groups at the *meta*- or *para*- on the benzene ring of 1-iodo-2-((2-methylallyl)oxy)benzene were successfully transformed into the corresponding products (**4a-4h**) in moderate to good yields. Moreover, a wide range of phenylacetylene compounds **2**, with no matter electron-rich or electron-deficient group on the *para*- positions of benzene ring, converted into the desired products in moderate to good yields (**4n-4v**). Remarkably, the electronic effects had little influence on the efficiency of the reaction. Moreover, some heterocycles and fused rings such as 3-ethynylpyridine (**4w**), 4-ethynyl-1,1'-biphenyl (**1x**) and 6-ethynyl-1,9-dihydropyrene (**1y**) were also applicable (**4w-4y**). However, the yields of **4w** and **4x** were only 33% and 48% when **1w** and **1x** were surveyed respectively. Notably, terminal acetylenic acid could be utilized for the construction of products with alkyl groups as well (**4i, 4j**). Delightfully, the corresponding product **4a** was obtained in 33% yield when using 1-bromo-2-((2-methylallyl)oxy)benzene as substrate under the optimized reaction conditions for alkynylation.

Scheme 3 Substrate scope of alkynylation [a, b]



[a] Reaction condition: **1** (0.3 mmol), **2** (0.36 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (15 mol %), Cs_2CO_3 (1 equiv), toluene (1.5 mL), 80 °C, N_2 balloon, 8 h. [b] Yields of isolated products were given. [c] 1-bromo-2-((2-methylallyl)oxy)benzene was uesd as **1a**. [d] Pent-2-ynoic acid was used as **2i**. [e] **1a** (0.6 mmol), propiolic acid was uesd as **2ab**.

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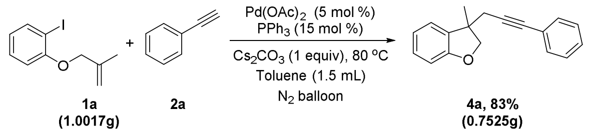
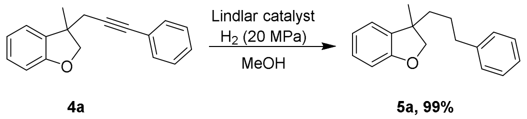
As a demonstration of the scalability of this transformation, 1-iodo-2-((2-methylallyl)oxy)benzene (**1a**) with ethynylbenzene (**2a**) was performed at the gram scale (Scheme 4). Analytically pure **4a** was isolated in 83% yield (0.7525 g) through a pad of silica gel. We also selectively reduced the alkyne in product **4a** under H_2 (20 Mpa) with Lindlar catalyst in methanol, and analytically pure **5a** was isolated in nearly 99% yield (Scheme 5).

Scheme 4 Experiment of gram scale [a]



[a] Reaction condition: **1a** (3.66 mmol), **2a** (4.39 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (15 mol %), Cs_2CO_3 (1 equiv.), toluene (1.5 mL), 80 °C, N_2 balloon.

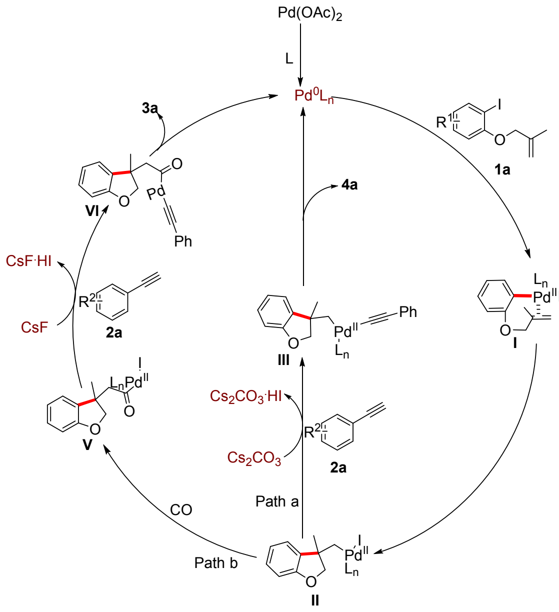
Scheme 5 Experiment of hydrogenation. [a]



[a] Reaction condition: **4a** (0.3 mmol), Lindlar catalyst (5 mol %), H_2 (20 MPa), MeOH (1.5 mL), 80 °C.

Based on the experimental results obtained above, a possible mechanism for this Pd-catalyzed Heck-type cascade annulation reaction was outlined (Scheme 6).[14] Initially, the oxidative addition of **1a** gave the aryl palladium species **I**, followed by intramolecular insertion of alkene to generate the intermediate **II**. Subsequently, the reaction might occur through two different paths. In path a, the intermediate **II** was captured by **2a** leading to the intermediate **III**, while in path b, it firstly occurred the insertion of CO to generate intermediate **V**, which went through the same route of path a to give the intermediate **VI**. Eventually, both of intermediates **III** and **VI** would undergo the reductive elimination to form **3a** and **4a**.[3-6]

Scheme 6 Possible reaction mechanism



Conclusions

In summary, we have established a simple and efficient method for the synthesis of different types ynones with high selectivity, which could be got by commercially available substrates. Notably, this protocol could also be used for direct alkynylation to construct functionalized dihydrobenzofurans. Importantly, readily available starting materials, broad substrate scope, high regioselectivity and excellent functional group compatibility make this protocol practical and attractive.

Experimental section

Materials and methods

^1H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform was used as a solvent with TMS as the internal standard. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100–400 mesh silica gel plates (GF_{254}). Unless otherwise noted, purchased chemicals were used without further purification. All terminal alkynes **2** were commercially available.

General Procedure for the Carbonylation Products 3

To a 25 mL test tube equipped with a magnetic stirring bar was added **1** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), **2** (0.45 mmol), CsF (1 equiv), **L2** (15 mol %), 1,4-dioxane (2 mL) under CO atmosphere.

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The resulting mixture was vigorously stirred at 60 °C in an oil bath. After 8 h, the resulting solution was cooled to room temperature, added water (5 mL), and extracted with EtOAc (3 × 5 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product **3**.

General Procedure for the Alkynylation Products 4

To a 25 mL test tube equipped with a magnetic stirring bar was added **1** (0.3 mmol), $Pd(OAc)_2$ (5 mol %), **2** (0.36 mmol), Cs_2CO_3 (1 equiv), PPh_3 (15 mol %), toluene (2 mL) under N_2 atmosphere. The resulting mixture was vigorously stirred at 80 °C in an oil bath. After 8 h, the resulting solution was cooled to room temperature, added water (5 mL), and extracted with EtOAc (3 × 5 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product **4**.

Procedure for the Gram-Scale Synthesis of 4a

A 100 mL round-bottom flask equipped with a magnetic stirring bar was added **1a** (3.66 mmol, 1.0017g), $Pd(OAc)_2$ (5 mol %), **2a** (4.39 mmol), Cs_2CO_3 (1 equiv), PPh_3 (15 mol %), toluene (50 mL) under N_2 atmosphere. The resulting mixture was vigorously stirred at 80 °C in an oil bath. After 8 h, the resulting solution was cooled to room temperature, added water (50 mL), and extracted with EtOAc (50 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the pure product **4a** (0.7525 g, 3.03 mmol).

1-(3-Methyl-2,3-dihydrobenzofuran-3-yl)-4-phenylbut-3-yn-2-one (3a): Yield: (61.3 mg, 74%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 6.0 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 2H), 7.20 - 7.15 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.43 (d, *J* = 8.0 Hz, 1H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 16.0 Hz, 1H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 159.0, 134.3, 133.0, 130.9, 128.6, 122.8, 120.7, 119.7, 109.9, 91.3, 88.4, 82.2, 54.9, 44.2, 25.1; ν_{max}(KBr)/cm^{-1} 3880, 3671, 3459, 2965, 2194, 1662, 1598, 1471, 1060, 751; HRMS-ESI (m/z): calcd for $C_{19}H_{16}NaO_2$, $[M+Na]^+$: 299.1043, found 299.1041.

1-(3-Methyl-5-(trifluoromethyl)-2,3-dihydrobenzofuran-3-yl)-4-phenylbut-3-yn-2-one (3b): Yield: (69.2 mg, 67%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.47 - 7.35 (m, 5H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.04 (d, *J* = 16.0 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 184.6, 161.9, 135.2, 133.1, 131.0, 128.7, 126.7 (q, *J* = 4.0 Hz), 125.9, 123.16 (q, *J* = 32.5 Hz, 1H), 120.4 (q, *J* = 4.0 Hz), 119.5, 110.1, 91.7, 88.3, 83.0, 54.6, 43.9, 25.4; ν_{max}(KBr)/cm^{-1} 3806, 3676, 3322, 2966, 2196, 1667, 1322, 1059, 977, 751; HRMS-ESI (m/z): calcd for $C_{20}H_{15}F_3NaO_2$, $[M+Na]^+$: 367.0916, found 367.0913.

3-Methyl-3-(2-oxo-4-phenylbut-3-yn-1-yl)-2,3-dihydrobenzofuran-5-carboxylate (3c): Yield: (67.2 mg, 67%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.86 (m, 2H), 7.53 - 7.50 (m, 1H), 7.47 - 7.43 (m, 1H), 7.36 (t, *J* = 6.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.68 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.21 (d, *J* = 16.0 Hz, 1H), 3.04 (d, *J* = 16.0 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.8, 166.7, 163.2, 134.7, 133.0, 131.6, 130.9, 128.6, 124.8, 122.9, 119.5, 109.6, 91.6, 88.2, 83.1, 54.7, 51.8, 43.6, 25.5; ν_{max}(KBr)/cm^{-1} 3888, 3679, 2934, 2195, 1710, 1596, 1440, 1269, 1064, 758; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaO_4$, $[M+Na]^+$: 357.1097, found 357.1089.

1-(5-Fluoro-3-methyl-2,3-dihydrobenzofuran-3-yl)-4-phenylbut-3-yn-2-one (3d): Yield: (45.9 mg, 52%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.46 (t, *J* = 6.0 Hz, 1H), 7.37 (t, *J* = 6.0 Hz, 2H), 6.87 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.81 (td, *J* = 8.8, 2.8 Hz, 1H), 6.70 (dd, *J* = 8.8, 4.0 Hz, 1H), 4.61 (d, *J* = 9.2 Hz, 1H), 4.41 (d, *J* = 9.2 Hz, 1H), 3.12 (d, *J* = 16.0 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 157.6 (d, *J* = 238 Hz), 154.9, 135.6 (d, *J* = 8 Hz), 133.0, 130.9, 128.6, 119.6, 114.8 (d, *J* = 24 Hz), 110.2 (d, *J* = 7 Hz), 110.0 (d, *J* = 9 Hz), 91.4, 88.3, 82.7, 54.5, 44.5 (d, *J* = 2 Hz), 24.9; ν_{max}(KBr)/cm^{-1} 3676, 2966, 2196, 1666, 1475, 1252, 1168, 1063, 754, 680; HRMS-ESI (m/z): calcd for $C_{19}H_{16}FO_2$, $[M+H]^+$: 295.1129, found 295.1133.

1-(6-Chloro-3-methyl-2,3-dihydrobenzofuran-3-yl)-4-phenylbut-3-yn-2-one (3e): Yield: (57.8 mg, 62%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.51 (m, 2H), 7.47 - 7.44 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.87 - 6.84 (m, 1H), 6.80 (d, *J* = 4.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 3.13 (d, *J* = 16.0 Hz, 1H), 2.99 (d, *J* = 16.0 Hz, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.8, 159.9, 133.9, 133.0, 130.9, 128.6, 123.5, 120.8, 119.5, 110.7, 91.5, 88.3, 82.9, 54.7, 43.8, 25.2; ν_{max}(KBr)/cm^{-1} 2962, 2196, 1665, 1594, 1475, 1065, 974, 861, 753, 684; HRMS-ESI (m/z): calcd for $C_{19}H_{15}ClNaO_2$, $[M+Na]^+$:333.0653, found 333.0652.

4-(4-Ethylphenyl)-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3f): Yield: (53.9 mg, 59%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16 - 7.12 (m, 2H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 0H), 4.40 (d, *J* = 8.0 Hz, 1H), 3.15 (d, *J* = 16.0 Hz, 1H), 3.01 (d, *J* = 16.0 Hz, 1H), 2.67 (q, *J* = 8.0 Hz, 2H), 1.48 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 159.0, 147.8, 134.4, 133.2, 128.6, 128.2, 122.8, 120.7, 116.7, 109.9, 92.0, 88.3, 82.2, 54.8, 44.2, 29.0, 25.1, 15.1; ν_{max}(KBr)/cm^{-1} 3876, 3676, 2964, 2873, 2193, 1665, 1596, 1470, 1063, 749; HRMS-ESI (m/z): calcd for $C_{21}H_{20}NaO_2$, $[M+Na]^+$:327.1356, found 327.1352.

4-(4-(*tert*-Butyl)phenyl)-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3g): Yield: (68.8 mg, 69%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.21 - 7.16 (m, 2H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.67 (d, *J* = 8.0 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.06 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 159.0, 154.6, 134.3,132.9, 128.5, 125.7, 122.8, 120.6, 116.5, 109.9, 91.9, 88.3, 82.2, 54.8, 44.1, 35.0, 31.0, 25.1; ν_{max}(KBr)/cm^{-1} 3681, 2957, 2191, 1665, 1592, 1489, 1061, 970, 829, 744; HRMS-ESI (m/z): calcd for $C_{23}H_{24}NaO_2$, $[M+Na]^+$: 355.1669, found 355.1661.

4-(4-Butylphenyl)-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3h): Yield: (67.8 mg, 68%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.10 - 7.12 (m, 4H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 3.15 (d, *J* = 16.0 Hz, 1H), 3.01 (d, *J* = 16.0 Hz, 1H), 2.63

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(t, *J*=8.0 Hz, 1H), 1.63 - 1.56 (m, 2H), 1.48 (s, 3H), 1.37 - 1.32 (m, 2H), 0.92 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 159.0, 146.6, 134.4, 133.1, 128.8, 128.6, 122.8, 120.7, 116.7, 109.9, 92.1, 88.4, 82.2, 54.8, 44.2, 35.7, 33.1, 25.1, 22.2, 13.8; ν_{max}(KBr)/cm^{-1} 3810, 3668, 3568, 2937, 2192, 1664, 1595, 1466, 1006, 745; HRMS-ESI (m/z): calcd for $C_{23}H_{24}NaO_2$, $[M+Na]^+$:355.1669, found 355.1675.

1-(3-Methyl-2,3-dihydrobenzofuran-3-yl)-4-(4-pentylphenyl)but-3-yn-2-one (3i): Yield: (72.8 mg, 70%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.19 - 7.14 (m, 4H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 3.12 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.62 (t, *J* = 8.0 Hz, 1H), 1.65 - 1.57 (m, 2H), 1.48 (s, 3H), 1.33 - 1.30 (m, 4H), 0.89 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 159.0, 146.6, 134.4, 133.1, 128.8, 128.6, 122.8, 120.6, 116.7, 109.9, 92.1, 88.4, 82.2, 54.8, 44.1, 36.0, 31.3, 30.7, 25.1, 22.4, 13.9; ν_{max}(KBr)/cm^{-1} 3685, 2933, 2861, 2192, 1665, 1591, 1466, 1060, 827, 744; HRMS-ESI (m/z): calcd for $C_{24}H_{26}NaO_2$, $[M+Na]^+$:369.1825, found 369.1829.

1-(3-Methyl-2,3-dihydrobenzofuran-3-yl)-4-(4-(pentyloxy)phenyl)but-3-yn-2-one (3j): Yield: (70.7 mg, 65%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 12.0 Hz, 2H), 7.17 (dd, *J* = 13.6, 7.2 Hz, 2H), 6.94 - 6.89 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.66 (d, *J* = 9.2 Hz, 1H), 4.43 (d, *J* = 9.2 Hz, 1H), 4.00 (t, *J* = 8.0 Hz, 2H), 3.17 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 1.86 - 1.79 (m, 2H), 1.51 (s, 3H), 1.49 - 1.39 (m, 4H), 0.97 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 161.3, 158.9, 135.0, 134.3, 128.4, 122.7, 120.5, 114.7, 111.0, 109.8, 92.6, 88.4, 82.1, 68.1, 54.6, 44.1, 28.6, 28.0, 25.1, 22.3, 13.9; ν_{max}(KBr)/cm^{-1} 3681, 2943, 2860, 2189, 1664, 1593, 1475, 1247, 1060, 744; HRMS-ESI (m/z): calcd for $C_{24}H_{26}NaO_2$, $[M+Na]^+$:385.1774, found 385.1781.

4-(4-Fluorophenyl)-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3k): Yield: (59.2 mg, 67%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.13 (dd, *J* = 15.6, 8.0 Hz, 2H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 6.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 4.37 (d, *J* = 9.2 Hz, 1H), 3.13 (d, *J* = 16.0 Hz, 1H), 2.99 (d, *J* = 16.0 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 163.8 (d, *J* = 254 Hz), 158.9, 135.2 (d, *J* = 9 Hz), 134.1, 128.5, 122.7, 120.5, 116.0 (d, *J* = 22 Hz), 115.6 (d, *J* = 4Hz), 109.8, 89.9, 88.2, 81.9, 54.6, 44.0, 25.0; ν_{max}(KBr)/cm^{-1} 3681, 2965, 2881, 2197, 1668, 1591, 1487, 1224, 1062, 827; HRMS-ESI (m/z): calcd for $C_{19}H_{15}FNaO_2$, $[M+Na]^+$:317.0948, found 317.0953.

4-(4-Chlorophenyl)-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3l): Yield: (68.1 mg, 73%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.16 - 7.11 (m, 2H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 4.38 (d, *J* = 8.0 Hz, 1H), 3.14 (d, *J* = 16.0 Hz, 1H), 3.00 (d, *J* = 16.0 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 159.0, 137.2, 134.1, 134.1, 129.0, 128.6, 122.8, 120.6, 118.1, 109.9, 89.7, 89.0, 82.0, 54.8, 44.1, 25.1; ν_{max}(KBr)/cm^{-1} 2960, 2197, 1666, 1590, 1475, 1069, 970, 826, 746, 597; HRMS-ESI (m/z): calcd for $C_{19}H_{15}ClNaO_2$, $[M+Na]^+$:333.0653, found 333.0659.

Methyl-4-(3-(3-methyl-2,3-dihydrobenzofuran-3-yl)prop-1-yn-1-yl)benzoate (3m): Yield: (65.2 mg, 65%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.12 – 7.17 (m, 2H), 6.89 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.50 (dd, J = 80.7, 9.2 Hz, 1H), 3.93 (s, 1H), 3.10 (dd, J = 53.0, 16.5 Hz, 1H), 1.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 165.9, 159.0, 134.0, 132.7, 131.8, 129.6, 128.6, 124.1, 122.8, 120.7, 109.9, 89.8, 89.3, 82.0, 54.9, 52.4, 44.1, 25.1; ν_{max}(KBr)/cm^{-1} 3679, 2961, 2197, 1721, 1587, 1467, 1273, 1054, 840, 755; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaO_4$, $[M+Na]^+$:357.1097, found 357.1099.

4-(3-Methoxyphenyl)-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3n): Yield: (57.9 mg, 63%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 1H), 7.17 - 7.11 (m, 3H), 7.03 - 6.99 (m, 1H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.61 (d, *J* = 8.0 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.15 (d, *J* = 16.0 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 159.4, 159.0, 134.3, 129.7, 128.6, 125.5, 122.8, 120.7, 120.6, 117.7, 117.5, 109.9, 91.2, 88.1, 82.2, 55.4, 54.9, 44.2, 25.1; ν_{max}(KBr)/cm^{-1} 3683, 2958, 2192, 1666, 1587, 1472, 1210, 1053, 749, 680; HRMS-ESI (m/z): calcd for $C_{20}H_{18}NaO_3$, $[M+Na]^+$: 329.1148, found 329.1149.

1-(3-Methyl-2,3-dihydrobenzofuran-3-yl)-4-(m-tolyl)but-3-yn-2-one (3o): Yield: (56.6 mg, 65%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.50 - 7.45 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.46 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 184.1, 161.1, 142.3, 135.8, 133.5, 130.9, 129.8, 127.9, 125.8, 121.6, 119.4, 119.4, 117.7, 92.1, 90.5, 74.0, 48.2, 44.4, 20.5, 19.1; ν_{max}(KBr)/cm^{-1} 3672, 3060, 2965, 2190, 1664, 1468, 1058, 973, 826, 746; HRMS-ESI (m/z): calcd for $C_{20}H_{18}NaO_2$, $[M+Na]^+$:313.1199, found 313.1198.

4-(2-Bromophenyl)-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3p): Yield: (75.7 mg, 71%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 - 7.62 (m, 1H), 7.56 - 7.53 (m, 1H), 7.35 - 7.28 (m, 2H), 7.17 - 7.12 (m, 2H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.64 (d, *J* = 8.0 Hz, 1H), 4.40 (d, J = 8.0 Hz, 1H), 3.20 (d, *J* = 16.0 Hz, 1H), 3.06 (d, *J* = 16.0 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 159.0, 134.9, 134.3, 132.8, 131.9, 128.6, 127.3, 126.8, 122.9, 122.2, 120.7, 110.0, 91.6, 89.1, 82.2, 54.8, 44.2, 25.1; ν_{max}(KBr)/cm^{-1} 3681, 2958, 2200, 1669, 1591, 1468, 1230, 1069, 970, 750; HRMS-ESI (m/z): calcd for $C_{19}H_{15}BrNaO_2$, $[M+Na]^+$: 377.0148, found 377.0156.

4-Cyclopropyl-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)but-3-yn-2-one (3q): Yield: (30.3 mg, 42%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 - 7.09 (m, 2H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.85 (d, *J* = 16.0 Hz, 1H), 1.42 (s, 3H), 1.35 (m, 1H), 0.96 (m, 2H), 0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 159.0, 134.4, 128.5, 122.7, 120.5, 109.8, 99.4, 82.1, 54.6, 44.0, 25.1, 9.7, 0.4; ν_{max}(KBr)/cm^{-1} 3681, 3559, 3254, 2965, 2197, 1659, 1466, 1037, 829, 754; HRMS-ESI (m/z): calcd for $C_{16}H_{16}NaO_2$, $[M+Na]^+$: 263.1043, found 263.1049.

(R)-5-cyclohexyl-1-(3-methyl-2,3-dihydrobenzofuran-3-yl)pent-3-yn-2-one (3r): Yield: (28.4 mg, 32%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 - 7.09 (m, 2H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.36 (d, *J* = 8.0Hz, 1H), 3.02 (d, *J* = 8.0Hz, 1H), 2.89 (d, *J* = 8.0 Hz, 1H), 2.22 (d, *J* = 8 Hz, 2H), 1.81 - 1.65 (m, 5H), 1.44 (s, 3H), 1.33 (s, 1H), 1.25 - 1.09 (m, 3H), 1.06 - 0.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 159.0, 134.4, 128.5, 122.8, 120.6, 109.9, 94.2, 82.5, 82.2, 54.9, 44.0, 36.7, 32.7, 26.7, 26.0, 25.9, 25.1; ν_{max}(KBr)/cm^{-1} 3729, 2921, 2349, 2207, 1756,

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DOI: 10.1039/C8OB02092B

1668, 2597, 1466, 1181, 964, 744; HRMS-ESI (m/z): calcd for $C_{20}H_{24}NaO_2$, $[M+Na]^+$: 319.1669, found 319.1674.

3-Methyl-3-(3-phenylprop-2-yn-1-yl)-2,3-dihydrobenzofuran (4a): Yield: (68.5 mg, 92%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.37 (m, 2H), 7.28 - 7.27 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 8.0 Hz, 1H), 2.67 (s, 2H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 134.0, 131.6, 128.5, 128.2, 127.8, 123.5, 122.9, 120.6, 109.8, 86.7, 82.5, 82.3, 45.3, 31.5, 24.2; ν_{max}(KBr)/cm^{-1} 3833, 3783, 3681, 3361, 2924, 2854, 1593, 1478, 1023 752; HRMS-ESI (m/z): calcd for $C_{18}H_{17}O$, $[M+H]^+$: 249.1274, found 249.1269.

5-Fluoro-3-methyl-3-(3-phenylprop-2-yn-1-yl)-2,3-dihydrobenzofuran (4b): Yield: (41.5 mg, 52%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.33 – 7.26 (m, 3H), 6.94 (dd, *J* = 8.0, 2.7 Hz, 1H), 6.84 (td, *J* = 8.8, 2.7 Hz, 1H), 6.71 (dd, *J* = 8.8, 4.0 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.25 (d, *J* = 8.0 Hz, 1H), 2.67 (s, 2H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 (d, *J* = 236 Hz), 155.3, 135.4 (d, *J* = 8.0 Hz), 131.6, 128.3, 128.0, 123.3, 114.7 (d, *J* = 24 Hz), 110.3 (d, *J* = 24 Hz), 110.0 (d, *J* = 8 Hz), 86.1, 82.8, 82.8, 45.7, 31.3, 24.1; ν_{max}(KBr)/cm^{-1} 3883, 3689, 3352, 2924, 2849, 1723, 1584, 1483, 1055, 754; HRMS-ESI (m/z): calcd for $C_{18}H_{15}FNaO$, $[M+Na]^+$: 289.0999, found 289.1004.

3-Methyl-3-(3-phenylprop-2-yn-1-yl)-5-(trifluoromethyl)-2,3-dihydrobenzofuran (4c): Yield: (63.6 mg, 67%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.38 - 7.36 (m, 2H), 7.29 - 7.28 (m, 3H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.61 (d, *J* = 8.0 Hz, 1H), 4.31 (d, *J* = 8.0 Hz, 1H), 2.69 (s, 2H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 134.8, 131.6, 128.3, 128.0, 126.6 (q, *J* = 4 Hz), 125.9, 123.25 (q, *J* = 24 Hz), 123.2, 120.6 (q, *J* = 4 Hz), 109.9, 85.8, 83.1, 83.0, 45.1, 31.6, 24.2; ν_{max}(KBr)/cm^{-1} 3926, 3711, 2968, 1614, 1490, 1326, 1267, 1160, 1115, 754; HRMS-ESI (m/z): calcd for $C_{19}H_{16}F_3O$, $[M+H]^+$: 317.1148, found 317.1145.

5-(*tert*-Butyl)-3-methyl-3-(3-phenylprop-2-yn-1-yl)-2,3-dihydrobenzofuran (4d): Yield: (69.4 mg, 76%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.0 Hz, 1H), 7.27 - 7.26 (m, 4H), 7.18 (d, *J* = 8.04 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 4.21 (d, *J* = 8.0 Hz, 1H), 2.68 (s, 2H), 1.54 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 143.6, 133.6, 131.6, 128.2, 127.8, 125.4, 123.6, 119.8, 108.9, 86.9, 82.6, 82.5, 45.4, 34.4, 31.7, 31.6, 24.0; ν_{max}(KBr)/cm^{-1}3833, 3059, 2959, 1695, 1487, 1365, 1223, 1059, 753; HRMS-ESI (m/z): calcd for $C_{22}H_{25}O$, $[M+H]^+$: 305.1900, found 305.1901.

3-Methyl-3-(3-phenylprop-2-yn-1-yl)-2,3-dihydrobenzofuran-5-yl acetate (4e): Yield: (73.5 mg, 80%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.28 (m, 2H), 7.18 (s, 3H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.23 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 2.60 (s, 2H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 163.6, 134.3, 131.6, 128.2, 127.9, 125.0, 123.2, 122.8, 109.5, 86.0, 83.2, 82.8, 51.7, 44.9, 31.6, 24.4; ν_{max}(KBr)/cm^{-1} 2953, 1713, 1604, 1446, 1253, 1107, 977, 839, 758, 686; HRMS-ESI (m/z): calcd for $C_{20}H_{19}O_3$, $[M+H]^+$: 307.1329, found 307.1341.

6-Chloro-3-methyl-3-(3-phenylprop-2-yn-1-yl)-2,3-dihydrobenzofuran (4f): Yield: (52.6 mg, 62%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.33 - 7.32 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.85 (d, *J* = 1.6 Hz, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 2H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 133.9, 132.8, 131.6, 128.3, 128.0, 123.6, 123.3, 120.7, 110.6, 86.2, 83.0, 82.7, 45.0, 31.5, 24.2; ν_{max}(KBr)/cm^{-1} 3682, 3358, 2923, 1725, 1595, 1477, 1264, 982, 754, 691; HRMS-ESI (m/z): calcd for $C_{18}H_{15}ClNaO$, $[M+Na]^+$: 305.0704, found 305.0708.

6-Bromo-3-methyl-3-(3-phenylprop-2-yn-1-yl)-2,3-dihydrobenzofuran (4g): Yield: (34.4 mg, 35%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.36 (m, 2H), 7.29 - 7.28 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.24 (d, *J* = 8.0 Hz, 1H), 2.65 (s, 2H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 133.3, 131.6, 128.3, 127.9, 124.1, 123.6, 123.3, 121.6, 113.4, 86.2, 82.9, 82.7, 45.0, 31.4, 24.2; ν_{max}(KBr)/cm^{-1} 3839, 3666, 2963, 1593, 1474, 1416, 1117, 976, 754, 691; HRMS-ESI (m/z): calcd for $C_{18}H_{15}BrNaO$, $[M+Na]^+$: 349.0198, found 349.0196.

1-Methyl-1-(3-phenylprop-2-yn-1-yl)-1,2-dihydronaphtho[2,1-b]furan (4h): Yield: (62.7 mg, 70%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.32 - 7.29 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.80 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 3.10 (d, *J* = 16.8 Hz, 1H), 2.93 (d, *J* = 16.8 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 131.6, 130.4, 130.2, 130.0, 129.5, 128.2, 127.8, 126.6, 123.6, 123.5, 122.6, 121.7, 112.5, 86.7, 82.8, 82.5, 47.3, 30.6, 24.3; ν_{max}(KBr)/cm^{-1} 3682, 3356, 2969, 1718, 1587, 1437, 1368, 1244, 999, 749; HRMS-ESI (m/z): calcd for $C_{22}H_{19}O$, $[M+H]^+$: 299.1430, found 299.1428.

3-Methyl-3-(pent-2-yn-1-yl)-2,3-dihydrobenzofuran (4i): Yield: (52.9 mg, 88%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.22 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 2H), 2.24 - 2.18 (m, 2H), 1.50 (s, 3H), 1.17 (t, *J* = 8.0 Hz, 3H); ν_{max}(KBr)/cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 134.3, 128.3, 122.8, 120.4, 109.7, 83.7, 82.2, 75.9, 45.1, 30.8, 24.2, 14.2, 12.3; ν_{max}(KBr)/cm^{-1} 3660, 3302, 2963, 1741, 1592, 1525, 1469, 1376, 822, 753; HRMS-ESI (m/z): calcd for $C_{14}H_{16}NaO$, $[M+Na]^+$: 223.1093, found 223.1099.

3-Methyl-3-(oct-2-yn-1-yl)-2,3-dihydrobenzofuran (4j): Yield: (58.2 mg, 80%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1H NMR (400 MHz, CDCl3) δ 7.15 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 2H), 2.15 - 2.12 (m, 2H), 1.49 - 1.44 (m, 5H), 1.33 - 1.32 (m, 4H), 0.90 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 134.3, 128.3, 122.8, 120.4, 109.7, 82.4, 82.2, 45.1, 30.9, 30.9, 28.6, 24.3, 22.2, 18.6, 13.9; ν_{max}(KBr)/cm^{-1} 2932, 2865, 1598, 1466, 1376, 1646, 1223, 978, 831, 750; HRMS-ESI (m/z): calcd for $C_{17}H_{13}O$, $[M+H]^+$: 243.1743, found 243.1746.

Trimethyl(3-(3-methyl-2,3-dihydrobenzofuran-3-yl)prop-1-yn-1-yl)silane (4k): Yield: (51.3 mg, 70%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.49 (d, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 2H), 1.50 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 133.9, 128.5, 122.9, 120.4, 109.7, 103.7, 86.9, 82.2, 44.9, 31.9, 23.9, -0.04; ν_{max}(KBr)/cm^{-1} 3826, 3744, 3565, 3385, 2927, 1646, 1537, 1395, 1005, 754; HRMS-ESI (m/z): calcd for $C_{15}H_{21}OSi$, [M+H]+: 245.1356, found 245.1359.

1,3-Dimethyl-3-(3-phenylprop-2-yn-1-yl)indoline (4l): Yield: (64.3 mg, 82%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.33 - 7.28 (m, 6H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz,

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DOI: 10.1039/C8OB02092B

1H), 3.26 (s, 3H), 2.94 (d, J = 16.0 Hz, 1H), 2.71 (d, J = 16.0 Hz, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.5, 143.1, 133.3, 131.5, 128.2, 128.2, 127.8, 123.4, 123.3, 122.6, 107.9, 85.4, 82.8, 47.2, 28.9, 26.3, 21.7; ν_{max}(KBr)/cm^{-1} 3667, 3308, 2951, 2836, 1677, 1469, 1242, 1141, 747, 683; HRMS-ESI (m/z): calcd for $C_{19}H_{20}N$, [M+H]$^+$: 262.1590, found 262.1591.

1-(3-Methyl-3-(3-phenylprop-2-yn-1-yl)indolin-1-yl)ethan-1-one (4m): Yield: (63.4 mg, 73%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, J = 8.0 Hz, 1H), 7.39 - 7.38(m, 2H), 7.32 - 7.30 (m, 4H), 7.27 - 7.25 (m, 2H), 7.09 (t, J = 6.0 Hz, 1H), 4.14 (d, J = 10.4 Hz, 1H), 3.80 (d, J = 10.54 Hz, 1H), 2.70 (s, 2H), 2.26 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.5, 142.0, 137.7, 131.5, 128.3, 128.2, 127.9, 123.7, 123.2, 122.2, 116.9, 86.1, 82.7, 61.2, 43.6, 32.4, 25.4, 24.2; ν_{max}(KBr)/cm^{-1} 3879, 3749, 3587, 3354, 1654, 1473, 1336, 1013, 752, 687; HRMS-ESI (m/z): calcd for $C_{20}H_{20}N$, [M+H]$^+$: 290.1539, found 290.1532.

3-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-3-methyl-2,3-dihydrobenzofuran (4n): Yield: (71.1 mg, 89%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (dd, J = 8.8, 5.6 Hz, 2H), 7.13 (d, J = 8.0 Hz, 1H), 7.07 (t, J = 8.0 Hz, 1H), 6.88 (t, J = 8.0 Hz, 2H), 6.81 (t, J = 8.0 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.44 (d, J = 8.0 Hz, 1H), 4.15 (d, J = 8.0 Hz, 1H), 2.57 (s, 2H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.2 (d, J = 248 Hz), 159.4, 133.9, 133.37 (d, J = 8 Hz), 128.6, 122.9, 120.6, 119.5 (d, J = 4Hz), 115.4 (d, J = 22 Hz), 109.8, 86.3, 82.2, 81.4, 45.3, 31.5, 24.2; ν_{max}(KBr)/cm^{-1} 3784, 3689, 3576, 3049, 2965, 1595, 1486, 1221, 827, 747; HRMS-ESI (m/z): calcd for $C_{18}H_{16}FO$, [M+H]$^+$: 267.1180, found 267.1176.

3-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-3-methyl-2,3-dihydrobenzofuran (4o): Yield: (72.1 mg, 85%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 6.88 (t, J = 6.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.52 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 8.0 Hz, 1H), 2.65 (s, 2H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.4, 133.9, 133.8, 132.8, 128.6, 128.5, 122.9, 121.9, 120.6, 109.8, 87.7, 82.2, 81.4, 45.2, 31.6, 24.2; ν_{max}(KBr)/cm^{-1} 3783, 3050, 2965, 2879, 1587, 1498, 1091, 979, 826, 749; HRMS-ESI (m/z): calcd for $C_{18}H_{16}ClO$, [M+H]$^+$: 283.0884, found 283.0886.

3-Methyl-3-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)-2,3-dihydrobenzofuran (4p): Yield: (84.5 mg, 89%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 6.95 (t, J = 6.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.58 (d, J = 8.0 Hz, 1H), 4.28 (d, J = 8.0 Hz, 1H), 2.74 (s, 2H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.5, 133.7, 131.8, 128.7, 125.2 (q, J = 3 Hz), 122.9, 120.6, 109.9, 89.5, 82.2, 81.3, 45.3, 31.6, 24.2; ν_{max}(KBr)/cm^{-1} 2880, 1605, 1473, 1323, 1228, 1124, 1064, 976, 839, 749; HRMS-ESI (m/z): calcd for $C_{19}H_{16}F_3O$, [M+H]$^+$: 317.1148, found 317.1150.

4-(3-(3-Methyl-2,3-dihydrobenzofuran-3-yl)prop-1-yn-1-yl)benzonitrile (4q): Yield: (65.6 mg, 80%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.21 - 7.15 (m, 1H), 6.91 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.24 (d, J = 8.0 Hz, 1H), 2.71 (s, 2H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.4, 133.6, 132.1, 131.9, 128.7, 128.4, 122.8, 120.6, 118.5, 111.2, 109.9, 91.8, 82.1, 81.2, 45.3, 31.7, 24.2; ν_{max}(KBr)/cm^{-1} 3927, 3680, 2962, 2223, 1597, 1473, 977, 835, 749, 553; HRMS-ESI (m/z): calcd for $C_{19}H_{16}O$, [M+H]$^+$: 274.1126, found 274.1128.

Ethyl 4-(3-(3-methyl-2,3-dihydrobenzofuran-3-yl)prop-1-yn-1-yl)benzoate (4r): Yield: (78.8 mg, 82%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.21 - 7.15 (m, 1H), 6.91 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.24 (d, J = 8.0 Hz, 1H), 2.71 (s, 2H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.0, 159.4, 133.7, 131.4, 129.5, 129.3, 128.6, 128.0, 122.8, 120.6, 109.8, 89.9, 82.2, 81.9, 61.0, 45.2, 31.6, 24.2, 14.2; ν_{max}(KBr)/cm^{-1} 3850, 2971, 1714, 1599, 1468, 1370, 1270, 1102, 845, 752; HRMS-ESI (m/z): calcd for $C_{21}H_{21}O_3$, [M+H]$^+$: 321.1485, found 321.1479.

3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-2,3-dihydrobenzofuran (4s): Yield: (72.6 mg, 87%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 4.0 Hz, 1H), 7.07 (t, J = 8.0 Hz, 1H), 6.80 (t, J = 8.0 Hz, 1H), 6.73 (d, J = 8.0 Hz, 2H), 4.45 (d, J = 8.0 Hz, 1H), 4.13 (d, J = 8.0 Hz, 1H), 3.69 (s, 3H), 2.57 (s, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.4, 159.2, 134.1, 132.9, 128.5, 122.9, 120.5, 115.6, 113.8, 109.7, 85.0, 82.3, 82.2, 55.2, 45.3, 31.5, 24.2; ν_{max}(KBr)/cm^{-1} 3882, 3681, 2942, 2838, 1724, 1594, 1505, 1246, 1035, 830, 755; HRMS-ESI (m/z): calcd for $C_{19}H_{19}O_2$, [M+H]$^+$: 279.1380, found 279.1379.

3-Methyl-3-(3-(p-tolyl)prop-2-yn-1-yl)-2,3-dihydrobenzofuran (4t): Yield: (68.5 mg, 87%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.54 (d, J = 8.0 Hz, 1H), 4.22 (d, J = 8.0 Hz, 1H), 2.66 (s, 2H), 2.33 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.4, 137.9, 134.1, 131.5, 128.9, 128.5, 123.0, 120.5, 120.4, 109.8, 85.8, 82.5, 82.3, 45.3, 31.6, 24.2, 21.4; ν_{max}(KBr)/cm^{-1} 3663, 3037, 2958, 1598, 1469, 1220, 1110, 982, 819, 748; HRMS-ESI (m/z): calcd for $C_{19}H_{19}O$, [M+H]$^+$: 263.1430, found 263.1435.

3-(3-(4-Ethylphenyl)prop-2-yn-1-yl)-3-methyl-2,3-dihydrobenzofuran (4u): Yield: (70.5 mg, 85%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.22 (dd, J = 7.2, 0.8 Hz, 1H), 7.12 (dd, J = 13.6, 4.8 Hz, 3H), 6.88 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 8.0 Hz, 1H), 2.66 (s, 2H), 2.61 (q, J = 8.0 Hz, 2H), 1.52 (s, 3H), 1.21 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.4, 144.2), 134.1, 131.5, 128.5, 127.8, 122.9, 120.7, 120.5, 109.8, 85.8, 82.5, 82.3, 45.3, 31.5, 28.7, 24.2, 15.4; ν_{max}(KBr)/cm^{-1} 3041, 2960, 1600, 1468, 1318, 1221, 980, 833, 749, 544; HRMS-ESI (m/z): calcd for $C_{20}H_{21}O$, [M+H]$^+$: 277.1587, found 277.1594.

3-(3-(4-Butylphenyl)prop-2-yn-1-yl)-3-methyl-2,3-dihydrobenzofuran (4v): Yield: (81.3 mg, 89%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 1H), 7.06 (dd, J = 11.2, 4.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.79 (t, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.45 (d, J = 8.0 Hz, 1H), 4.13 (d, J = 8.0 Hz, 1H), 2.57 (s, 3H), 2.49 (t, J = 8.0 Hz, 2H), 1.50 - 1.44 (m, 2H), 1.43 (s, 3H), 1.27 - 1.22 (m, 2H), 0.83 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.4, 142.9, 134.1, 131.5, 128.5, 128.3, 122.9, 120.6, 120.5, 109.8, 85.8, 82.6, 82.3, 45.3, 35.5, 33.4, 31.5, 24.2, 22.2, 13.9; ν_{max}(KBr)/cm^{-1} 3042, 2941, 1600, 1469, 1220, 983, 829, 749, 544; HRMS-ESI (m/z): calcd for $C_{20}H_{21}O$, [M+H]$^+$: 305.1900, found 305.1908.

3-(3-(3-Methyl-2,3-dihydrobenzofuran-3-yl)prop-1-yn-1-yl)pyridine (4w): Yield: (24.7 mg, 33%), yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.53 - 8.41 (m, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.18 - 7.06 (m, 3H), 6.82 (t, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.45 (d, J =

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8.0 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 2.62 (s, 2H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 152.2, 148.1, 138.4, 133.6, 128.6, 122.9, 122.8, 120.6, 109.8, 90.3, 82.1, 79.2, 45.2, 31.5, 24.2; ν_{max}(KBr)/cm^{-1} 3042, 2960, 2885, 1596, 1470, 1320, 1218, 979, 816, 748; HRMS-ESI (m/z): calcd for $C_{17}H_{16}NO$, $[M+H]^+$: 250.1226, found 250.1220.

3-(3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl)-3-methyl-2,3-dihydrobenzofuran (4x): Yield: (46.7 mg, 48%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 - 7.25 (m, 4H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 6.4 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.75 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 4.09 (d, *J* = 8.0 Hz, 1H), 2.54 (s, 2H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 140.6, 140.4, 134.0, 132.0, 128.8, 128.6, 127.5, 127.0, 126.9, 123.0, 122.4, 120.6, 109.8, 87.4, 82.3, 82.3, 45.3, 31.6, 24.2; ν_{max}(KBr)/cm^{-1} 3903, 3801, 3365, 2953, 1592, 1471, 1009, 830, 747, 559; HRMS-ESI (m/z): calcd for $C_{24}H_{21}O$, $[M+H]^+$: 325.1587, found 325.1592.

3-(3-(4,6-Dihydropyren-1-yl)prop-2-yn-1-yl)-3-methyl-2,3-dihydrobenzofuran (4y): Yield: (91.0 mg, 81%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.03 (dd, *J* = 11.2, 7.2 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.92 (s, 2H), 7.88 (d, *J* = 4.0 Hz, 0H), 7.86 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.14 - 7.20 (m, 1H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.23 (d, *J* = 8.8 Hz, 1H), 2.81 (m, 2H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 134.0, 131.9, 131.2, 131.0, 130.8, 129.6, 128.6, 128.1, 127.8, 127.1, 126.1, 125.4, 125.4, 125.3, 124.3, 124.2, 123.0, 120.7, 118.1, 109.9, 92.3, 82.3, 81.5, 45.6, 32.0, 24.8; ν_{max}(KBr)/cm^{-1} 3668, 3354, 2932, 1727, 1590, 1219, 1050, 915, 838, 750; HRMS-ESI (m/z): calcd for $C_{28}H_{23}O$, $[M+H]^+$: 375.1743, found 375.1746.

2-methyl-5-(3-methyl-2,3-dihydrobenzofuran-3-yl)pent-3-yn-2-ol (4z): Yield: (19.3 mg, 28%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.23 (m, 1H), 6.95- 6.84 (m, 2H), 5.22 (s, 1H), 5.02 (s, 1H), 4.49 (s, 2H), 2.17 (s, 1H), 1.89 (s, 3H), 1.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 140.6, 133.4, 129.6, 120.6, 112.5, 112.3, 112.2, 97.9, 78.6, 72.0, 65.7, 31.5, 19.3; ν_{max}(KBr)/cm^{-1}: 3851, 3072, 2920, 2855, 1662, 1579, 1447, 1248, 1146, 900, 743; HRMS-ESI (m/z): calcd for $C_{15}H_{18}NaO_2$, $[M+Na]^+$: 253.1199, found 253.1201.

1,4-bis(3-methyl-2,3-dihydrobenzofuran-3-yl)but-2-yne (4ab): Yield: (71.6 mg, 75%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 - 6.95 (m, 4H), 6.82 - 6.75 (m, 2H), 6.71 (t, *J* = 7.7 Hz, 2H), 4.33 (dd, *J* = 14.8, 8.8 Hz, 2H), 4.03 (dd, *J* = 10.1, 9.0 Hz, 2H), 2.42 - 2.23 (m, 4H), 1.28 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 134.1, 128.4, 122.7, 120.5, 109.7, 82.0, 78.7, 45.1, 30.8, 24.7; ν_{max}(KBr)/cm^{-1}: 3053, 2955, 2895, 1600, 1468, 1220, 978, 747; HRMS-ESI (m/z): calcd for $C_{22}H_{22}NaO_2$, $[M+Na]^+$:341.1512, found 341.1514.

3-Methyl-3-(3-phenylpropyl)-2,3-dihydrobenzofuran (5a): Yield: (75.0 mg, 99%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.05 – 6.99 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 0H), 6.68 (d, *J* = 8.0 Hz, 0H), 4.23 (d, *J* = 8.6 Hz, 0H), 4.04 (d, *J* = 8.6 Hz, 0H), 2.46 (t, *J* = 7.2 Hz, 1H), 1.54 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.43 – 1.29 (m, 0H), 1.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.1, 135.1, 128.3, 128.3, 127.9, 125.7, 122.8, 120.4, 109.5, 82.4, 45.1, 40.4, 36.2, 26.4, 25.6; ν_{max}(KBr)/cm^{-1} 3660, 3305, 3027, 2938, 1744, 1595, 1475, 1373, 835, 697; HRMS-ESI (m/z): calcd for $C_{18}H_{21}O$, $[M+H]^+$: 253.1587, found 253.1591.

Acknowledgements

The authors thank the National Key Research and Development Program of China (2016YFA0602900), the National Natural Science Foundation of China (21490572 and 21420102003) and Guangdong Province Science Foundation (2017B090903003) for financial support.

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