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Silver/Scandium Co-Catalyzed Bicyclization of *β*-Alkynyl Ketones Leading to Benzo[*c*]xanthenes and Naphtho[1,2-*b*]benzofurans

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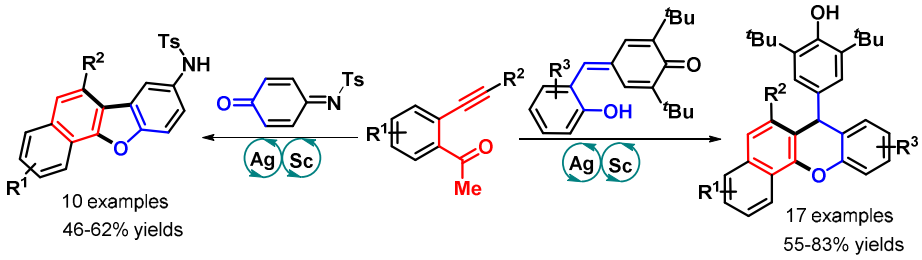


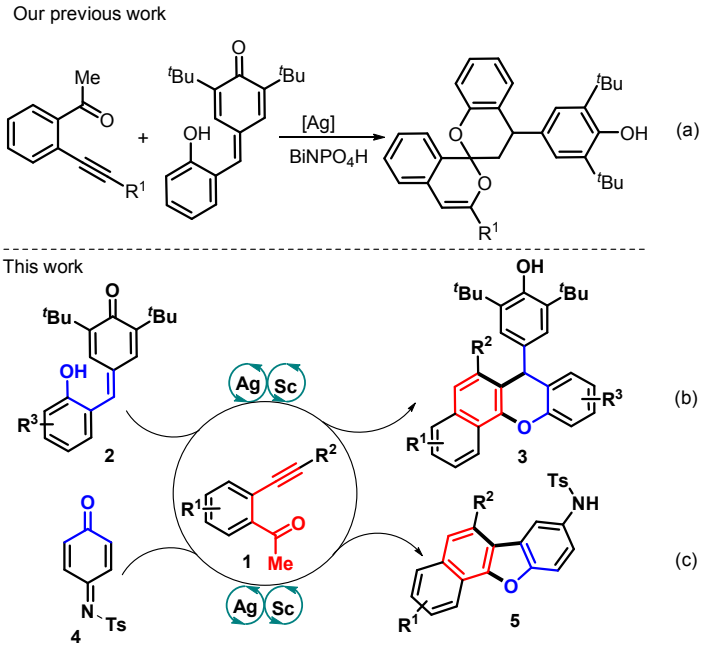
ABSTRACT. The combination of AgTFA and $Sc(OTf)_3$ enables the bimetallic synergistic catalysis of *β*-alkynyl ketones and *para*-quinone methides (*p*-QMs), allowing direct synthesis of 17 examples of benzo[*c*]xanthenes with generally good yields through a benzannulation /1,6-addition/cyclization sequence. Exchanging *p*-QMs for quinone imine ketal (QIK) resulted in 10 examples of tetracyclic naphtho[1,2-*b*]benzofurans *via* a similar benzannulation /1,4-addition/cyclization cascade. During these reaction processes, AgTFA and $Sc(OTf)_3$ could be perfectly compatible, together with the realization of $C(sp^3)$-H functionalization adjacent to carbonyl group on the *β*-alkynyl ketone unit.

Introduction

In a valuable class of oxygen-containing molecular family, xanthenes are common constituents in a broad array of natural products,[1] synthetic bioactive substances[2] and fluorescent dyes.[3] Compounds incorporating a xanthene core structure exhibit a wide range of biological and pharmacological activities including antiviral,[4] antibacterial,[5] antiplasmodial,[6] antimalarial,[7] antifungal,[8] anti-inflammatory,[9] anticancer,[10] and antihypertensive,[11] and also act as trypanothione reductase inhibitior.[12] With these contributions in mind, many chemists have contributed their efforts to develop efficient incorporation of xanthene unit into organic and medicinal targets. Most of the synthetic endeavors to assemble this bioactive core include Pd-catalyzed cyclization of polycyclic aryltriflate esters,[13] Lewis acid-catalyzed reaction of *β*-naphthol,[14a] phenol[14b] or 2-aryloxybenzaldehydes,[14c] annulation of aryne precursor,[15] ultraviolet-catalyzed tandem reaction of 2-benzylidene-1-tetralones,[16] and Brønsted acid-promoted reaction of 2-tetralone and salicylaldehydes.[17] Despite the limited preparation of xanthenes, the development of a new and versatile strategy for the direct formation of xanthene frameworks would be highly favorable.

Meanwhile, bicyclization reaction has attracted a continuation of attention as an efficient and reliable synthetic tool for the synthesis of polycyclic functional molecules of chemical and biomedical importance.[18] During this reaction process, the synergistic utilization of several reactive sites of starting materials leads to direct construction of two new rings in a single step. Thus, such reaction features bond forming/annulation efficiency and high levels of structural complexity. In recent years, widespread application of bicyclization reaction has been conducted to access various carbocycles and heterocycles.[19] In addition, synergistic catalysis enables two different catalysts to precisely activate nucleophiles and/or electrophiles, respectively, thereby facilitating their sequential coupling to build up the target compounds.[20] Obviously, merging bicyclization reaction with synergistic catalysis will provide a new protocol to construct unusual functional molecules, which are difficult to obtain through traditional methods. Very recently, we have established a AgTFA/1,1'-binaphthyl-2,2'-diyl hydrogen phosphate ($BiNPO_4H$) co-catalyzed bicyclization reaction of *β*-alkynyl ketones with *para*-quinone

methides (*p*-QMs), generating functionalized 6,6-benzannulated spiroketals (Scheme 1a).[21] To continue our efforts in this project, we found that exchanging silver/Brønsted acid catalysis for silver/scandium catalysis favored this bicyclization reaction to work in a completely different direction, allowing dual metal-catalyzed benzannulation/1,6-addition/cyclization cascades to access the unexpected benzo[*c*]xanthenes **3** (Scheme 1b). Using quinone imine ketal (QIK) **4** as a replacement for *p*-QMs **2** to expand its synthetic utility, a similar bicyclization reaction proceeded smoothly to deliver tetracyclic naphtho[1,2-*b*]benzofurans **5** with acceptable yields through synergistic silver/scandium catalysis (Scheme 1c). Herein, we elaborated these attractive and useful transformations in which the combination of dual metal catalysis with bicyclization cascades was well compatible and C(sp^3)-H functionalization adjacent to carbonyl group on the *β*-alkynyl ketone unit was simultaneously achieved.



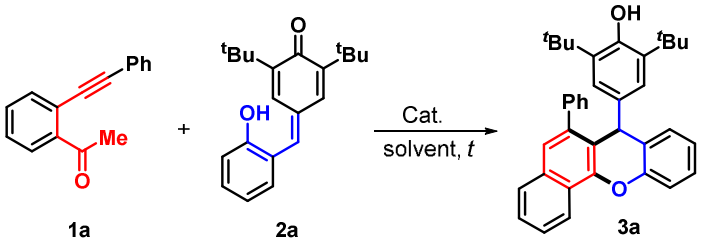
Scheme 1. Profiling Applications of Catalytic Bicyclization

Results and Discussion

To exploit metal-catalyzed bicyclization reaction, we began our investigations with the reaction of *β*-alkynyl ketone **1a** with *para*-quinone methide (*p*-QM) **2a**. In our previous report, this reaction catalyzed by AgTFA/$BiNPO_4H$ gave 6,6-benzannulated spiroketal (Scheme 1a).[21] During this project, we adjusted co-catalytic system to explore this transformation. Delightedly, when the above co-catalytic system was

replaced by silver/scandium dual metal catalysts, this bicyclization reaction proceeded smoothly to offer an unexpected benzo[*c*]xanthene **3a**. Encouraged by the interesting results, we next screened the reaction conditions for this protocol. Initially, **1a** was subjected to the reaction with *p*-QM **2a** in toluene using AgTFA (10 mol %)/$Sc(OTf)_3$(10 mol %) as a co-catalytic system at 80 ^oC under air conditions (Table 1, entry 1), and benzo[*c*]xanthene **3a** was obtained in 60% yield. Without $Sc(OTf)_3$ or AgTFA, the reaction scarcely worked to generate the desired product **3a** (entries 2-3), indicating both of these catalysts showed a synergistic catalytic performance in this reaction system. Increasing the loading of $Sc(OTf)_3$ to 20 mol% facilitated the transformation, providing **3a** in 73% yield (entry 4). Further increase of $Sc(OTf)_3$ loading was not beneficial to this reaction (entry 5). The following screening of several other silver salts such as Ag_2CO_3, AgOTf and $AgNO_3$ showed that these silver catalysts did not show any improvements in the yield of product **3a** (entries 6-8). Raising the AgTFA loading resulted in the slightly lower conversion into **3a** (entry 9). A similar inferior outcome was observed when the AgTFA loading was decreased to 5 mol % (entry 10). We next investigated the solvent effect by employing different solvents including acetonitrile (CH_3CN), tetrahydrofuran (THF), 1,4-dioxane and 1,2-dichloroethane (DCE), but < 63% yield was observed (entries 11-14). Moreover, the reaction could run at either 60 ^oC or 100 ^oC, but provided the lower yield as compared with the reaction temperature being 80 ^oC (entries 15-16). Changing Lewis acid catalyst to $Sn(OTf)_2$ gave a relatively inferior outcome regarding the yield of **3a** (61%, entry 17) whereas both $Zn(OTf)_2$ and $BF_3{\cdot}Et_2O$ as Lewis acid catalysts completely suppressed the reaction process (entries 18-19). Employment of $Pd(TFA)_2/Sc(OTf)_3$ as a co-catalytic system led to the lower conversion into **3a** (entry 20). The reaction did not work when $Cu(OTf)_2/Sc(OTf)_3$ was used as a co-catalyst (entry 21).

Table 1. Optimization of Reaction Conditions[a]



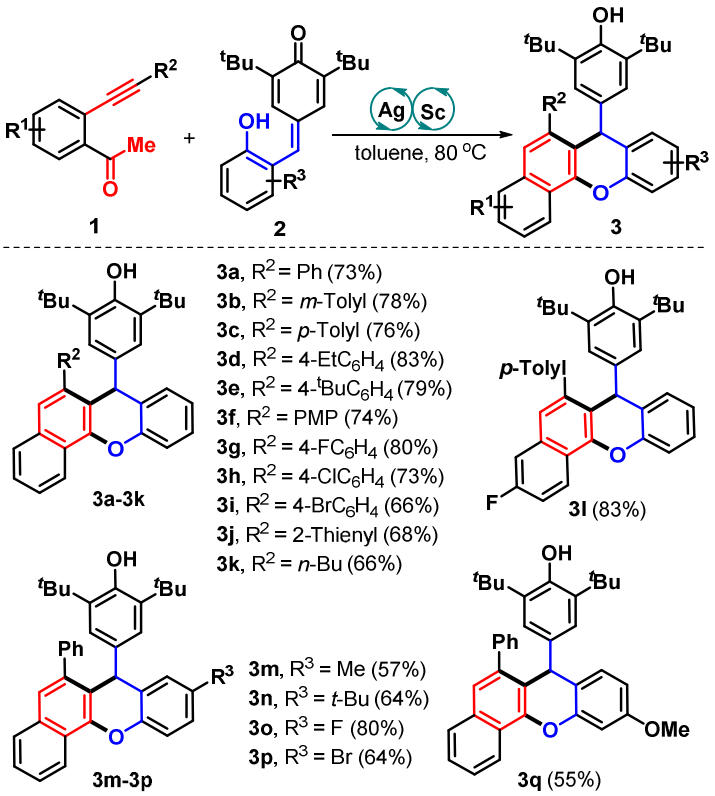
entry	catalyst (mol %)	solvent	t (^{o}C)	yield (%)[b]
1	AgTFA (10)/$Sc(OTf)_3$ (10)	toluene	80	60
2	AgTFA (10)	toluene	80	trace
3	$Sc(OTf)_3$ (10)	toluene	80	trace
4	AgTFA (10)/$Sc(OTf)_3$ (20)	toluene	80	73
5	AgTFA (10)/$Sc(OTf)_3$ (30)	toluene	80	40
6	Ag_2CO_3 (5)/$Sc(OTf)_3$ (20)	toluene	80	trace
7	AgOTf (10)/$Sc(OTf)_3$ (20)	toluene	80	30
8	$AgNO_3$ (10)/$Sc(OTf)_3$(20)	toluene	80	32
9	AgTFA (15)/$Sc(OTf)_3$ (20)	toluene	80	64
10	AgTFA (5)/$Sc(OTf)_3$ (20)	toluene	80	59
11	AgTFA (10)/$Sc(OTf)_3$ (20)	MeCN	80	22
12	AgTFA (10)/$Sc(OTf)_3$ (20)	THF	80	trace
13	AgTFA (10)/$Sc(OTf)_3$ (20)	1,4-dioxane	80	trace
14	AgTFA (10)/$Sc(OTf)_3$ (20)	DCE	80	63
15	AgTFA (10)/$Sc(OTf)_3$ (20)	toluene	60	28
16	AgTFA (10)/$Sc(OTf)_3$ (20)	toluene	100	49
17	AgTFA (10)/$Sn(OTf)_2$ (20)	toluene	80	61
18	AgTFA (10)/$Zn(OTf)_2$ (20)	toluene	80	trace
19	AgTFA (10)/$BF_3{\cdot}Et_2O$ (20)	toluene	80	N.D.[c]
20	$Pd(TFA)_2$ (10)/$Sc(OTf)_3$ (20)	toluene	80	59

21	$Cu(OTf)_2$ (10)/$Sc(OTf)_3$ (20)	toluene	80	trace

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), Ag, Pd and Cu-catalyst (x mol %), co-catalyst (y mol %), solvent (3.0 mL), under air conditions. [b]Isolated yield based on substrate **2a**. [c]Not detected (N.D.)

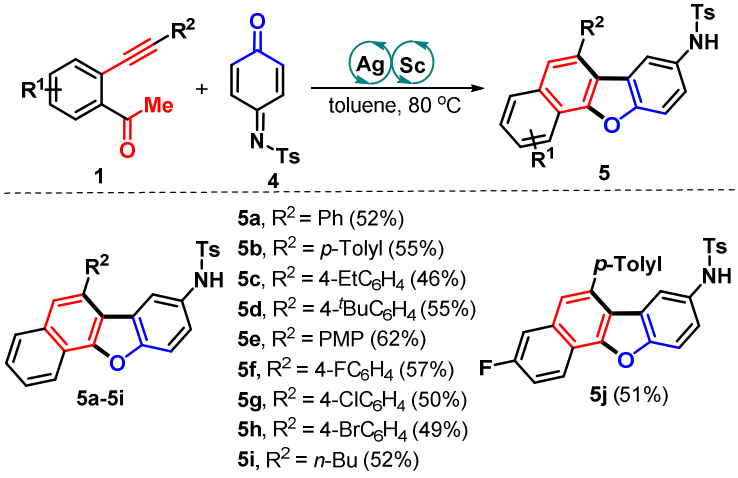
With these optimal reaction conditions in hand (Table 1, entry 4), we next turned our attention to explore the preparative scope of our silver/scandium catalysis toward benzo[*c*]xanthenes **3** by examining *β*-alkynyl ketone and *para*-quinone methide components (Scheme 2). As shown, a wide variety of *β*-alkynyl ketones possessing a diverse set of substituents at different positions of arylalkynyl (R^2) moiety could be perfectly tolerated, accessing in all cases good yields of **3a-3i**. Functional groups like methyl (**1b** and **1c**), ethyl (**1d**), *tert*-butyl (**1e**), methoxy (*p*-methoxyphenyl = PMP, **1f**), fluoride (**1g**), chloride (**1h**), and bromide (**1i**) would be accommodated with the co-catalytic conditions. Among them, an increase in the yield was obtained (**3d**, 83%) as the *p*-ethylphenyl counterpart (**1d**) was employed as a reaction partner whereas *p*-bromophenyl group resulted in a reduced yield (**3i**, 66%). Notably, substrate **1j** with a thienyl group and substrate **1k** with an *n*-butyl (*n*-Bu) group on the alkynyl moiety were also proven to be efficient components, as the corresponding products **3j** and **3k** were generated in 68% and 66% yields, respectively. Substrate **1l** having fluoro functionality at 4-position of the internal arene ring still showed high reactivity, delivering product **3l** in 83% yields. The reaction was found to tolerate various *p*-QMs **2b-2f** carrying electron-rich (Me, **2b** and *t*-Bu, **2c**) and electron-deficient (F, **2d** and Br, **2e**) groups at 4-position of the phenol ring, leading to the formation of benzo[*c*]xanthenes **3m-3p** with yields ranging from 57% to 80%. Alternatively, *p*-QM **2f** bearing a methoxy group at 5-position of the phenol ring successfully participated in the current dual catalysis, enabling 6-*endo*-*dig* cyclization/1,6-addition/cyclization cascades to access benzo[*c*]xanthene **3q** in 55% yield.

Scheme 2. Substrate Scope for Synthesis of Products 3[a]



[a] Reaction conditions: All reactions were performed with **1** (0.4 mmol), **2** (0.2 mmol), AgTFA (10 mol %), $Sc(OTf)_3$ (20 mol %), toluene (3.0 mL) at 80 °C under air conditions for 12 hours. [b]Isolated yields in brackets based on **2**.

Scheme 3. Substrate Scope for Synthesis of Products 5[a]

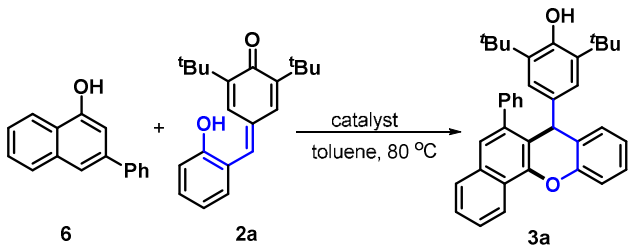


[a] Reaction conditions: All reactions were performed with **1** (0.4 mmol), **4** (0.2 mmol), AgTFA (10 mol %), $Sc(OTf)_3$ (20 mol %), toluene (3.0 mL) at 80 °C under air conditions for 12 hours. [b]Isolated yields in brackets based on **4**.

On the other hand, oxygen-rich dibenzofurans are also a class of heterocycles prevalent in natural products,[22] pharmaceutically active agents,[23] and materials science.[24] For these reasons, much effort has

been made toward identifying general methods for the synthesis of tetracyclic dibenzofuran derivatives.[25] However, the utilization of dual metal-catalyzed bicyclization cascade of β-alkynyl ketones with quinone imine ketals (QIKs) has not been documented yet. We thus considered to investigate silver/scandium catalyzed bicyclization cascades of *β*-alkynyl ketones by using QIK **4** as a cycloaddition partner to construct densely substituted dibenzofuran core. To our delight, the reaction worked well under the above-described reaction conditions. Various substituents including methyl, ethyl, *t*-butyl, methoxy, fluoro, chloro, and bromo at 4-position of arylalkynyl (R^2) moiety did not hamper the reaction process, furnishing the corresponding tetracyclic naphtho[1,2-*b*]benzofurans **5a-5h** in 46%-62% yields (Scheme 3). Similar to the above conversion of *n*-butyl (*n*-Bu) counterpart **1k** into **3k**, substrate **1k** was also smoothly transformed into naphtho[1,2-*b*]benzofuran **5i** in 52% yield. The presence of fluoro substituent at 4-position of the internal arene ring (**1l**) was also suitable for this silver/scandium catalysis under the standard conditions, confirming the success of the transformation toward product **5j** in 51% yield. The structures of products **3** and **5** have been determined by their NMR and HRMS analysis. Furthermore, in the cases of **3a**, its structure was based on X-ray diffraction analysis (see the Supporting Information).[26]

Scheme 4. Control Experiment

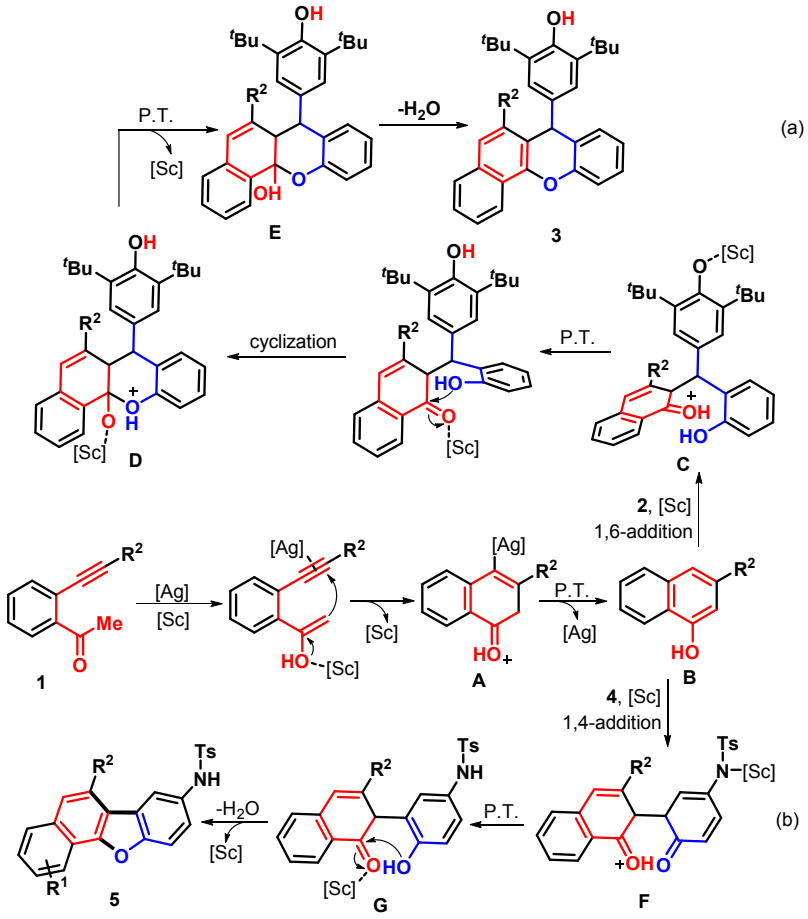


Catalyst: *i*) AgTFA/$Sc(OTf)_3$, **3a** (86%)
ii) $Sc(OTf)_3$, **3a** (85%)

To gain a mechanistic insight into the formation of **3**, treatment with 3-phenylnaphthalen-1-ol **6** with *p*-QM **2a** under the optimized conditions (Table 1, entry 4) provided the desired product **3a** in 86% yield (Scheme 4), indicating that 3-phenylnaphthalen-1-ol may behave as an intermediate for the synthesis of **3**. Without AgTFA, $Sc(OTf)_3$-catalyzed reaction of **6** with **2a** worked well, generating the corresponding

product **3a** in 85% yield, showing that AgTFA could not be involved in the catalysis for the formation of pyran ring.

Scheme 5. Plausible Reaction Pathway



Combining the aforementioned results and the previous reports about silver-catalyzed cyclization of *β*-alkynyl ketones,[27] reasonable mechanisms for forming products **3** and **5** were proposed as shown in Scheme 5. Firstly, Ag/Sc co-catalyzed 6-*endo-dig* cyclization of *β*-alkynyl ketones (**1** to **A**) occurs, giving intermediates **A**, followed by proton transfer (P.T.)-tautomerization to afford 1-naphthols **B** (detected by LC-MS, see Supporting Information). Next, Sc-catalyzed 1,6-addition of **B** into **2** yields adduct intermediates **C**, which undergo proton transfer and intramolecular *oxo*-nucleophilic addition to offer intermediates **D.** Finally, intermediates **D** would be transformed into the products **3** through deprotonation and dehydration (Scheme 5a). The mechanism for forming products **5** was similar to the above pathway, which includes 6-*endo-dig* cyclization, 1,4- nucleophilic addition and *oxo*-cyclization as

well as dehydration (Scheme 5b).

In conclusion, we have accomplished a perfectly compatible silver/scandium catalysis, which combined with bicyclization cascades to create two types of skeletally diverse *oxo*-heterocycles with generally good yields under mild conditions. Starting from *β*-alkynyl ketones and *p*-QMs, tetracyclic benzo[*c*]xanthenes were efficiently synthesized through co-catalytic benzannulation/1,6-addition/cyclization sequence. Similar to the former, synergistic silver/scandium catalysis enabled the direct transformation of *β*-alkynyl ketones and QIKs into naphtho[1,2-*b*]benzofurans with moderate to good yields. During these reaction processes, C(sp^3)-H functionalization adjacent to carbonyl group on the *β*-alkynyl ketone unit was achieved. Further investigation on mechanistic insights and their applications will be conducted in due course.

Experimental Section

General Information.

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

General Procedure for the Synthesis of 3

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

1-(2-(Phenylethynyl)phenyl)ethanone (**1a**, 0.4 mmol, 88.0 mg), 2,6-di-*tert*-butyl-4-(2-hydroxy benzylidene)cyclohexa-2,5-dienone (**2a**, 0.2 mmol, 62.0 mg), AgTFA (0.02 mmol, 4.4 mg), and $Sc(OTf)_3$ (0.04 mmol, 19.7 mg) were successively added in a 10-mL reaction vial. Toluene (3.0 mL) was then injected into the reaction system. The reaction vial was sealed and heated at 80 ^oC for 12 hours

until TLC (petroleum ether: ethyl acetate= 12:1) revealed that conversion of the starting material **2a** was completed. Then the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 100:1, v/v) to afford the desired pure products **3a** as white solid.

*2,6-Di-tert-butyl-4-(6-phenyl-7H-benzo[c]xanthen-7-yl)phenol (**3a**)*

White solid, 75.0 mg, 73%; mp 193-194 ^{o}C; IR (KBr, v, cm^{-1}) 3615 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64-7.54 (m, 2H), 7.41 (s, 1H), 7.35 (d, J = 8.0 Hz, 4H), 7.27-7.18 (m, 2H), 7.06 (m, 3H), 6.52 (s, 2H), 5.30 (s, 1H), 4.91 (s, 1H), 1.23 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 151.9, 150.9, 146.9, 140.9, 140.3, 137.3, 135.3, 132.8, 1295, 129.2, 127.8, 127.4, 127.3, 127.0, 126.4, 126.3, 125.7, 124.1, 123.8, 123.7, 123.6, 121.8, 118.4, 116.5, 42.6, 34.0, 30.1. HRMS (ESI-TOF) m/z: Calcd for $C_{37}H_{35}O_2$, 511.2637 [M-H]$^-$; found 511.2643.

*2,6-Di-tert-butyl-4-(6-(m-tolyl)-7H-benzo[c]xanthen-7-yl)phenol (**3b**)*

Pale yellow solid, 80.0 mg, 76%; mp 153-154 ^{o}C; IR (KBr, v, cm^{-1}) 3603 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.64-7.53 (m, 2H), 7.42 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.28-7.13 (m, 4H), 7.07-7.03 (m, 1H), 6.91 (d, J = 27.4 Hz, 2H), 6.54 (s, 2H), 5.36 (s, 1H), 4.91 (s, 1H), 2.34 (s, 3H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 151.9, 150.9, 146.9, 140.9, 140.4, 137.3, 135.3, 132.8, 130.2, 129.2, 127.7, 127.4, 127.3, 126.4, 126.2, 125.7, 124.1, 123.7, 123.6, 123.5, 121.8, 118.2, 116.5, 42.5, 34.0, 30.1, 21.5. HRMS (ESI-TOF) m/z: Calcd for $C_{38}H_{37}O_2$, 525.2794 [M-H]$^-$; found 525.2795

*2,6-Di-tert-butyl-4-(6-(p-tolyl)-7H-benzo[c]xanthen-7-yl)phenol (**3c**)*

White solid, 82.0 mg, 78%; mp 213-214 ^{o}C; IR (KBr, v, cm^{-1}) 3615 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.56 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.63-7.53 (m, 2H), 7.40 (s, 1H), 7.35 (m, 1H), 7.25-7.15 (m, 4H), 7.06-6.96 (m, 3H), 6.51 (s, 2H), 5.32 (s, 1H), 4.90 (s, 1H), 2.44 (s, 3H), 1.23 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 151.9, 150.9, 146.8, 140.3, 138.0, 137.4, 136.4, 135.3, 132.8, 129.3, 129.2, 128.6, 127.4, 127.2, 126.4, 126.3, 125.6, 124.2, 123.7, 123.7, 123.5, 121.8, 118.5,

116.5, 42.6, 34.0, 30.1, 21.2. HRMS (ESI-TOF) m/z: Calcd for $C_{38}H_{37}O_2$, 525.2794 $[M-H]^-$; found 525.2797.

*2,6-Di-tert-butyl-4-(6-(4-ethylphenyl)-7H-benzo[c]xanthen-7-yl)phenol (**3d**)*

Pale yellow solid, 90.0 mg, 83%; mp 233-234 ^oC; IR (KBr, v, cm^{-1}) 3614 (OH). ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.63-7.53 (m, 2H), 7.41 (s, 1H), 7.37-7.34 (m, 1H), 7.27-7.19 (m, 4H), 7.05 (m, 3H), 6.53 (s, 2H), 5.33 (s, 1H), 4.91 (s, 1H), 2.75 (m, 2H), 1.35 (m, 3H), 1.23 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 151.9, 151.0, 146.9, 142.7, 140.3, 138.2, 137.3, 135.3, 132.8, 129.4, 129.2, 127.4, 127.3, 126.5, 126.4, 125.6, 124.1, 123.8, 123.6, 121.8, 118.7, 116.5, 42.6, 34.0, 30.1, 28.6, 15.4. HRMS (ESI-TOF) m/z: Calcd for $C_{39}H_{39}O_2$, 539.2950 $[M-H]^-$; found 539.2942.

*2,6-Di-tert-butyl-4-(6-(4-(tert-butyl)phenyl)-7H-benzo[c]xanthen-7-yl)phenol (**3e**)*

White solid, 90.0 mg, 79%; mp 244-245 ^oC; IR (KBr, v, cm^{-1}) 3612 (OH). ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.56 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.62-7.58 (m, 1H), 7.53 (m, 1H), 7.42 (m, 3H), 7.37 (d, J = 8.1 Hz, 1H), 7.24 (m, 2H), 7.07 (m, 3H), 6.56 (s, 2H), 5.34 (s, 1H), 4.91 (s, 1H), 1.43 (s, 9H), 1.23 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.0, 151.4, 149.7, 147.1, 140.1, 137.9, 137.3, 135.3, 132.7, 129.2, 129.1, 127.4, 127.3, 126.8, 126.3, 125.6, 124.9, 124.0, 123.8, 123.6, 121.8, 118.9, 116.5, 42.6, 34.6, 34.1, 31.5, 30.2. HRMS (ESI-TOF) m/z: Calcd for $C_{41}H_{43}O_2$, 567.3263 $[M-H]^-$; found 567.3264.

*2,6-Di-tert-butyl-4-(6-(4-methoxyphenyl)-7H-benzo[c]xanthen-7-yl)phenol (**3f**)*

White solid, 80.0 mg, 74%; mp 216-217 ^oC; IR (KBr, v, cm^{-1}) 3614 (OH). ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.56 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.63-7.53 (m, 2H), 7.40 (s, 1H), 7.35 (m, 1.0 Hz, 1H), 7.26-7.19 (m, 2H), 7.05 (m, 1H), 7.04-6.97 (m, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.55 (s, 2H), 5.31 (s, 1H), 4.91 (s, 1H), 3.89 (s, 3H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 151.9, 150.9, 146.9, 140.9, 140.3, 137.3, 135.3, 132.8, 129.5, 129.2, 127.8, 127.4, 127.3, 127.0, 126.4, 126.3, 125.7, 124.1, 123.8, 123.7, 123.6, 121.8, 118.4, 116.5, 42.6, 34.0, 30.1. HRMS (ESI-TOF) m/z: Calcd

for $C_{38}H_{37}O_3$, 541.2743 $[M-H]^-$; found 541.2739.

*2,6-Di-tert-butyl-4-(6-(4-fluorophenyl)-7H-benzo[c]xanthen-7-yl)phenol (**3g**)*

White solid, 85.0 mg, 80%; mp 191-192 ^oC; IR (KBr, v, cm^{-1}) 3613 (OH). ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.58 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.60 (m, 2H), 7.39 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.30-7.17 (m, 3H), 7.07-6.99 (m, 4H), 6.53 (s, 2H), 5.24 (s, 1H), 4.94 (s, 1H), 1.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 162.0 ($^1J_{CF}$ = 244.3 Hz), 152.0, 150.6, 146.8, 139.3, 137.3, 136.9, 136.9, 135.5, 132.8, 131.0 ($^3J_{CF}$ = 7.9 Hz), 129.2, 127.4 ($^4J_{CF}$ = 3.6 Hz), 126.6, 125.9, 125.9, 124.1, 123.8, 123.7, 123.6, 121.9, 118.1, 116.6, 114.6 ($^2J_{CF}$ = 21.1 Hz), 42.7, 34.0, 30.1. HRMS (ESI-TOF) m/z: Calcd for $C_{37}H_{34}FO_2$, 529.2543 $[M-H]^-$; found 529.2547.

*2,6-Di-tert-butyl-4-(6-(4-chlorophenyl)-7H-benzo[c]xanthen-7-yl)phenol (**3h**)*

Pale yellow solid, 80.0 mg, 73%; mp 220-221 ^oC; IR (KBr, v, cm^{-1}) 3612 (OH). ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.58 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 1H), 7.39-7.29 (m, 4H), 7.25 (m, 1H), 7.20-7.17 (m, 1H), 7.08-6.94 (m, 3H), 6.52 (s, 2H), 5.25 (s, 1H), 4.95 (s, 1H), 1.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.0, 150.5, 146.8, 139.4, 139.1, 137.2, 135.5, 133.0, 132.8, 130.7, 129.2, 127.9, 127.4, 127.4, 126.6, 126.0, 125.7, 124.2, 123.9, 123.6, 123.6, 121.9, 117.9, 116.6, 42.6, 34.0, 30.1. HRMS (ESI-TOF) m/z: Calcd for $C_{37}H_{34}ClO_2$, 545.2247 $[M-H]^-$; found 545.2252.

*4-(6-(4-Bromophenyl)-7H-benzo[c]xanthen-7-yl)-2,6-di-tert-butylphenol (**3i**)*

Pale yellow solid, 78.0 mg, 66%; mp 234-235 ^oC; IR (KBr, v, cm^{-1}) 3611 (OH). ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.65-7.61 (m, 1H), 7.59-7.55 (m, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.37-7.32 (m, 2H), 7.24 (m, 1H), 7.19-7.16 (m, 1H), 7.04 (m, 1H), 6.92 (s, 2H), 6.51 (s, 2H), 5.24 (s, 1H), 4.94 (s, 1H), 1.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.0, 150.9, 147.2, 141.7, 137.1, 135.5, 132.5, 132.2, 129.2, 127.5, 127.3, 127.1, 126.8, 126.6, 126.3, 126.2, 125.6, 125.5, 124.2, 124.0, 123.7, 121.9, 119.0, 116.5, 42.6, 34.1, 30.2. HRMS (ESI-TOF) m/z: Calcd for $C_{37}H_{34}BrO_2$, 589.1742 $[M-H]^-$; found 589.1744.

*2,6-Di-tert-butyl-4-(6-(thiophen-2-yl)-7H-benzo[c]xanthen-7-yl)phenol (**3j**)*

White solid, 70.0 mg, 68%; mp 179-180 °C; IR (KBr, *v*, cm^{-1}) 3611 (OH). ^1H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.54 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.65-7.60 (m, 1H), 7.59-7.54 (m, 1H), 7.41 (s, 1H), 7.40-7.32 (m, 3H), 7.32-7.29 (m, 1H), 7.06 (s, 1H), 6.96-6.91 (m, 1H), 6.87 (m, 1H), 6.50 (s, 2H), 5.25 (s, 1H), 4.95 (s, 1H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 152.0, 150.5, 146.8, 139.8, 139.1, 137.2, 135.5, 132.8, 131.1, 130.9, 129.2, 127.4, 127.4, 126.6, 126.0, 125.7, 124.2, 123.9, 123.6, 123.5, 121.9, 121.2, 117.8, 116.6, 42.6, 34.0, 30.1. HRMS (ESI-TOF) m/z: Calcd for $C_{35}H_{33}O_2S$, 517.2201 $[M-H]^-$; found 517.2193.

*2,6-Di-tert-butyl-4-(6-butyl-7H-benzo[c]xanthen-7-yl)phenol (**3k**)*

White solid, 65.0 mg, 66%; mp 187-188 °C; IR (KBr, *v*, cm^{-1}) 3631 (OH). ^1H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.52-8.48 (m, 1H), 7.79-7.75 (m, 1H), 7.52 (m, 2H), 7.41-7.37 (m, 2H), 7.31 (m, 1H), 7.26-7.22 (m, 1H), 7.09 (m, 1H), 7.01 (s, 2H), 5.37 (s, 1H), 5.00 (s, 1H), 2.80 (m, 1H), 2.68-2.61 (m, 1H), 1.60 (s, 2H), 1.55-1.36 (m, 2H), 1.32 (s, 18H), 0.90 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 152.2, 151.0, 147.2, 139.3, 137.0, 135.8, 133.2, 128.9, 127.3, 126.8, 126.6, 126.1, 124.9, 124.0, 123.4, 123.1, 122.0, 121.7, 118.8, 116.6, 42.6, 34.2, 33.0, 32.3, 30.2, 22.9, 14.0. HRMS (ESI-TOF) m/z: [Calcd for $C_{35}H_{39}O_2$, 491.2950 M-H]$^-$; found 491.2954.

*2,6-Di-tert-butyl-4-(3-fluoro-6-(p-tolyl)-7H-benzo[c]xanthen-7-yl)phenol (**3l**)*

White solid, 90.0 mg, 83%; mp 235-236 °C; IR (KBr, *v*, cm^{-1}) 3614 (OH). ^1H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.56 (m, 1H), 7.43-7.36 (m, 2H), 7.35-7.32 (m, 2H), 7.27-7.22 (m, 1H), 7.20-7.13 (m, 3H), 7.07-7.03 (m, 1H), 6.97 (s, 2H), 6.49 (s, 2H), 5.30 (s, 1H), 4.91 (s, 1H), 2.44 (s, 3H), 1.23 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 161.3 ($^1J_{CF}$ = 244.4 Hz), 151.9, 150.7, 147.0, 141.8, 137.7, 137.2, 136.6, 135.3, 133.8 ($^4J_{CF}$ = 9.2 Hz), 129.2 ($^5J_{CF}$ = 8.9 Hz), 128.6, 127.3, 126.2, 124.6, 124.5, 124.2, 123.7, 123.0, 122.9, 120.7, 117.9 ($^6J_{CF}$ = 2.4 Hz), 116.5, 115.9, 115.6 ($^2J_{CF}$ = 24.9 Hz), 110.6 ($^3J_{CF}$ = 20.4 Hz), 42.4, 34.0, 30.1, 21.2. HRMS (ESI-TOF) m/z: Calcd for $C_{38}H_{36}FO_2$, 543.2699 $[M-H]^-$; found 543.2696.

*2,6-Di-tert-butyl-4-(9-methyl-6-phenyl-7H-benzo[c]xanthen-7-yl)phenol (**3m**)*

Pale yellow solid, 60.0 mg, 57%; mp 260-261 ^{o}C; IR (KBr, *v*, cm^{-1}) 3626 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.57 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.63-7.59 (m, 1H), 7.57-7.52 (m, 1H), 7.41-7.34 (m, 4H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.13-6.98 (m, 4H), 6.54 (s, 2H), 5.25 (s, 1H), 4.92 (s, 1H), 2.29 (s, 3H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 151.9, 148.9, 147.1, 140.9, 140.3, 137.4, 135.3, 132.9, 132.7, 129.5, 129.4, 128.0, 127.8, 127.38, 127.0, 126.4, 126.0, 125.7, 124.2, 123.9, 123.4, 121.9, 118.6, 116.3, 42.7, 34.1, 30.1, 20.8. HRMS (ESI-TOF) m/z: Calcd for $C_{38}H_{37}O_2$ 525.2794 $[M-H]^-$; found 525.2789.

*2,6-Di-tert-butyl-4-(9-(tert-butyl)-6-phenyl-7H-benzo[c]xanthen-7-yl)phenol (**3n**)*

White solid, 73.0 mg, 64%; mp 285-286^{o}C; IR (KBr, *v*, cm^{-1}) 3631 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.56 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.62-7.53 (m, 2H), 7.44 (s, 1H), 7.38-7.33 (m, 3H), 7.28 (s, 2H), 7.24 (s, 1H), 7.14 (s, 2H), 6.58 (s, 2H), 5.27 (s, 1H), 4.92 (s, 1H), 1.31 (s, 9H), 1.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 151.9, 149.1, 147.6, 146.2, 140.9, 140.2, 137.0, 135.3, 132.8, 129.5, 127.8, 127.4, 126.9, 126.4, 125.7, 125.6, 125.5, 124.4, 124.0, 123.9, 123.5, 121.8, 118.5, 116.0, 42.8, 34.3, 34.1, 31.5, 30.2. HRMS (ESI-TOF) m/z: Calcd for $C_{41}H_{43}O_2$, 567.3263 $[M-H]^-$; found 567.3262.

*2,6-Di-tert-butyl-4-(9-fluoro-6-phenyl-7H-benzo[c]xanthen-7-yl)phenol (**3o**)*

White solid, 85.0 mg, 80%; mp 185-186 ^{o}C; IR (KBr, *v*, cm^{-1}) 3620 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.55 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.65-7.54 (m, 3H), 7.37-7.33 (m, 2H), 7.26-7.23 (m, 1H), 7.10-7.04 (m, 2H), 6.83 (m, 1H), 6.66 (s, 2H), 5.55 (s, 1H), 4.93 (s, 1H), 1.26 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 158.7 ($^{1}J_{CF}$ = 239.3 Hz), 152.1, 146.9 ($^{6}J_{CF}$ = 2.1 Hz), 146.8, 140.7, 140.16, 136.8, 135.5, 132.8, 129.4, 127.9, 127.6 ($^{4}J_{CF}$ = 7.4 Hz), 127.5, 127.1, 126.6, 125.9, 124.1, 123.8, 123.7, 121.7, 117.6 ($^{5}J_{CF}$ = 8.4 Hz), 117.4, 115.2 ($^{2}J_{CF}$ = 23.1 Hz), 114.2 ($^{3}J_{CF}$ = 23.6 Hz), 42.9, 34.1, 30.1. HRMS (ESI-TOF) m/z: Calcd for $C_{37}H_{34}FO_2$, 529.2543 $[M-H]^-$; found 529.2548.

*4-(9-Bromo-6-phenyl-7H-benzo[c]xanthen-7-yl)-2,6-di-tert-butylphenol (**3p**)*

White solid, 75.0 mg, 64%; mp 231-232 ^{o}C; IR (KBr, *v*, cm^{-1}) 3627 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.53 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.63 (m, 1H), 7.59-7.54 (m, 1H), 7.42 (s, 1H), 7.40-7.32 (m, 4H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 20.8 Hz, 2H), 6.50 (s, 2H), 5.24 (s, 1H), 4.96 (s, 1H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 152.2 150.1, 146.5, 140.6, 140.1, 136.7, 135.6, 132.8, 131.9, 130.3, 129.4, 128.5, 127.9, 127.5, 127.1, 126.6, 125.9, 124.1, 124.0, 123.7, 121.7, 118.4, 118.0, 115.7, 42.6, 34.1, 30.1. HRMS (ESI-TOF) m/z: Calcd for $C_{37}H_{34}BrO_2$, 589.1742 [M-H]$^-$; Found 589.1736.

*2,6-Di-tert-butyl-4-(10-methoxy-6-phenyl-7H-benzo[c]xanthen-7-yl)phenol (**3q**)*

Pale yellow solid, 60.0 mg, 55%; mp 192-193 ^{o}C; IR (KBr, *v*, cm^{-1}) 3614 (OH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.56 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.57-7.53 (m, 1H), 7.40 (s, 1H), 7.34 (m, 3H), 7.07 (d, *J* = 8.5 Hz, 3H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.63 (m, 1H), 6.49 (s, 2H), 5.25 (s, 1H), 4.90 (s, 1H), 3.86 (s, 3H), 1.23 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 159.0, 151.8, 151.4, 146.7, 141.0, 140.4, 137.6, 135.3, 132.7, 129.7, 129.4, 127.78, 127.4, 126.9, 126.4, 125.7, 124.1, 123.7, 123.7, 121.8, 118.6, 118.5, 110.4, 101.4, 55.5, 42.0, 34.0, 30.1. HRMS (ESI-TOF) m/z: Calcd for $C_{38}H_{37}O_3$, 541.2743 [M-H]$^-$; found 541.2742.

General Procedure for the Synthesis of Products 5

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

1-(2-(Phenylethynyl)phenyl)ethanone (**1a**, 0.4 mmol, 88.0 mg), 4-methyl-*N*-(4-oxocyclohex-2,5-dien-1-ylidene)benzenesulfonamide (**4a**, 0.2 mmol, 52.0 mg), AgTFA (0.02 mmol, 4.4 mg), and $Sc(OTf)_3$ (0.04 mmol, 19.7 mg) were successively added in a 10-mL reaction vial. Toluene (3.0 mL) was then injected into the reaction system. The reaction vial was sealed and heated at 80 ^{o}C for 12 hours until TLC (petroleum ether: ethyl acetate= 5:1) revealed that conversion of the starting material **4a** was completed. Then the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 15:1, v/v) to afford the desired pure products **5a** as pale yellow solid.

*4-Methyl-N-(6-phenylnaphtho[1,2-b]benzofuran-8-yl)benzenesulfonamide (**5a**)*

Pale yellow solid, 48.0 mg, 52%; mp 150-151 ^{o}C; IR (KBr, *v*, cm^{-1}) 3235 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.46 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.69-7.65 (m, 2H), 7.64-7.60 (m, 2H), 7.54 (m, 7H), 7.23 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 2.2 Hz, 1H), 6.44 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 154.1, 153.1, 143.7, 139.4, 135.7, 135.3, 133.0, 131.1, 129.5, 128.9, 128.6, 128.3, 128.1, 127.4, 126.9, 126.5, 125.2, 123.7, 122.2, 120.9, 120.4, 117.1, 116.9, 112.2, 21.5. HRMS (ESI-TOF) m/z: Calcd for $C_{29}H_{20}NO_3S$, 462.1164 [M-H]$^{-}$; found 462.1162.

*4-Methyl-N-(6-(p-tolyl)naphtho[1,2-b]benzofuran-8-yl)benzenesulfonamide (**5b**)*

White solid, 52.0 mg, 55%; mp 169-170 ^{o}C; IR (KBr, *v*, cm^{-1}) 3235 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.45 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.63 (m, 4H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.25-7.18 (m, 3H), 7.15 (d, *J* = 2.1 Hz, 1H), 6.54 (s, 1H), 2.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 154.2, 153.1, 143.7, 137.8, 136.5, 135.7, 135.4, 133.1, 131.1, 129.5, 129.3, 128.8, 128.3, 127.4, 126.8, 126.4, 125.3, 123.6, 122.1, 120.9, 120.3, 117.2, 117.0, 112.2, 21.6, 21.4. HRMS (ESI-TOF) m/z: Calcd for $C_{30}H_{22}NO_3S$, 476.1320 [M-H]$^{-}$; found 476.1325.

*N-(6-(4-Ethylphenyl)naphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5c**)*

White solid, 45.0 mg, 46%; mp 207-208 ^{o}C; IR (KBr, *v*, cm^{-1}) 3239 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.45 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.64 (m, 4H), 7.50 (m, 4H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.24 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.14 (s, 1H), 6.52 (s, 1H), 2.85 (m, 2H), 2.39 (s, 3H), 1.41 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 153.1, 144.2, 143.7, 136.7, 135.7, 135.7, 133.1, 131.1, 129.5, 128.9, 128.3, 128.1, 127.4, 126.9, 126.4, 125.3, 123.6, 122.2, 122.1, 120.9, 120.3, 117.2, 117.0, 112.2, 28.7, 21.6, 15.6. HRMS (ESI-TOF) m/z: Calcd for $C_{31}H_{24}NO_3S$, 490.1477 [M-H]$^{-}$; found 490.1468.

*N-(6-(4-(tert-Butyl)phenyl)naphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5d**)*

White solid, 52.0 mg, 50%; mp 278-279 ^{o}C; IR (KBr, *v*, cm^{-1}) 3238 (NH). ^{1}H NMR (400 MHz, $CDCl_3$;

δ, ppm) 8.45 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.68-7.59 (m, 4H), 7.55-7.46 (m, 6H), 7.25 (m, 1H), 7.21-7.14 (m, 3H), 6.52 (s, 1H), 2.39 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 154.1, 153.1, 151.2, 143.6, 136.4, 135.6, 135.3, 133.1, 131.0, 129.5, 128.6, 128.3, 127.5, 126.8, 126.4, 125.5, 125.2, 123.7, 122.3, 120.9, 120.3, 117.2, 116.8, 112.2, 34.8, 31.5, 21.6. HRMS (ESI-TOF) m/z: Calcd for $C_{33}H_{28}NO_3S$, 518.1790 $[M-H]^-$; found 518.1791.

*N-(6-(4-Methoxyphenyl)naphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5e**)*

White solid, 61.0 mg, 62%; mp 167-168 ^{o}C; IR (KBr, v, cm^{-1}) 3286 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.45 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.67-7.60 (m, 4H), 7.53 (d, J = 8.3 Hz, 2H), 7.50-7.46 (m, 2H), 7.26-7.19 (m, 3H), 7.15 (d, J = 2.2 Hz, 1H), 7.06-7.03 (m, 2H), 6.45 (s, 1H), 3.98 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 159.6, 154.1, 153.1, 143.7, 135.8, 135.0, 133.1, 131.7, 131.1, 130.07, 129.5, 128.2, 127.4, 126.8, 126.3, 125.3, 123.4, 122.2, 120.9, 120.2, 117.3, 117.0, 114.0, 112.2, 55.5, 21.5. HRMS (ESI-TOF) m/z: Calcd for $C_{30}H_{22}NO_4S$, 492.1270 $[M-H]^-$; found 492.1274.

*N-(6-(4-Fluorophenyl)naphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5f**)*

White solid, 55.0 mg, 57%; mp 177-178 ^{o}C; IR (KBr, v, cm^{-1}) 3233 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.49-8.42 (m, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.69-7.60 (m, 4H), 7.53 (m, 4H), 7.27-7.13 (m, 5H), 7.08 (d, J = 2.2 Hz, 1H), 6.54 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 162.7 ($^1J_{CF}$ = 245.9 Hz), 154.2, 153.1, 143.7, 135.9, 135.4 ($^4J_{CF}$ = 3.4 Hz), 134.2, 133.0, 131.2, 130.6 ($^3J_{CF}$ = 8.0 Hz), 129.5, 128.3, 127.3, 127.0, 126.6, 125.1, 123.7, 122.5, 120.9, 120.4, 117.1, 116.9, 115.6 ($^2J_{CF}$ = 21.3 Hz), 112.3, 21.5. HRMS (ESI-TOF) m/z: Calcd for $C_{29}H_{19}FNO_3S$, 480.1070 $[M-H]^-$; found 480.1072.

*N-(6-(4-Chlorophenyl)naphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5g**)*

White solid, 50.0 mg, 50%; mp 203-204 ^{o}C; IR (KBr, v, cm^{-1}) 3286 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.45 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.69-7.62 (m, 6H), 7.56 (d, J = 8.3 Hz, 2H), 7.46-7.42 (m, 2H), 7.28-7.25 (m, 1H), 7.23 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 2.2 Hz, 1H), 6.62 (s, 1H),

2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 154.1, 153.2, 143.7, 137.8, 135.9, 134.1, 133.9, 132.9, 131.2, 130.2, 129.5, 128.8, 128.3, 127.4, 127.0, 126.8, 124.9, 123.7, 122.6, 121.0, 120.5, 116.8, 116.8, 112.3, 21.6. HRMS (ESI-TOF) m/z: Calcd for $C_{29}H_{19}ClNO_3S$, 496.0774 $[M-H]^-$; found 496.0775.

*N-(6-(4-Bromophenyl)naphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5h**)*

White solid, 53.0 mg, 49%; mp 207-208 ^oC; IR (KBr, ν, cm^{-1}) 3284 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.44 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.64 (m, 4H), 7.56 (d, J = 8.2 Hz, 2H), 7.52-7.46 (m, 4H), 7.27-7.20 (m, 3H), 7.09 (s, 1H), 6.74 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 154.2, 153.2, 143.7, 138.3, 135.9, 133.9, 132.9, 131.8, 131.2, 130.6, 129.5, 128.3, 127.4, 127.1, 126.8, 124.9, 123.7, 122.7, 122.3, 121.0, 120.5, 116.8, 116.7, 112.4, 21.6. HRMS (ESI-TOF) m/z: Calcd for $C_{29}H_{19}BrNO_3S$, 540.0269 $[M-H]^-$; found 540.0278.

*N-(6-Butylnaphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5i**)*

Pale yellow solid, 46.0 mg, 52%; mp 194-195 ^oC; IR (KBr, ν, cm^{-1}) 3240 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.40-8.37 (m, 1H), 7.93 (m, 1H), 7.75 (d, J = 2.1 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.59 (m, 3H), 7.52 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.15 (m, 1H), 6.68 (s, 1H), 3.16-3.11 (m, 2H), 2.38 (s, 3H), 1.77 (m, 2H), 1.53 (m, 2H), 1.01 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 154.1, 153.1, 143.8, 135.9, 135.8, 133.2, 131.4, 129.6, 127.7, 127.4, 126.6, 125.7, 125.7, 122.1, 122.0, 120.8, 119.9, 118.1, 117.4, 112.2, 33.7, 31.7, 22.6, 21.5, 14.0. HRMS (ESI-TOF) m/z: Calcd for $C_{27}H_{24}NO_3S$, 442.1477 $[M-H]^-$; found 442.1474.

*N-(3-Fluoro-6-(p-tolyl)naphtho[1,2-b]benzofuran-8-yl)-4-methylbenzenesulfonamide (**5j**)*

White solid, 50.0 mg, 51%; mp 212-213 ^oC; IR (KBr, ν, cm^{-1}) 3235 (NH). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.43 (m, 1H), 7.58 (m, 3H), 7.53 (d, J = 8.3 Hz, 2H), 7.46-7.39 (m, 3H), 7.33 (d, J = 7.8 Hz, 2H), 7.24-7.18 (m, 3H), 7.14 (d, J = 2.2 Hz, 1H), 6.49 (s, 1H), 2.55 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 161.4 ($^1J_{CF}$ = 245.6 Hz), 154.0, 153.1, 143.7, 138.1, 136.8, 136.1, 135.7, 134.1 ($^4J_{CF}$ = 9.2 Hz), 131.3, 129.5, 129.4, 128.7, 127.4, 125.2, 123.5 ($^5J_{CF}$ = 9.1 Hz) , 122.8, 122.7, 122.0,

117.3, 116.8, 116.7 ($^6J_{CF}$ = 2.1 Hz), 116.5 ($^2J_{CF}$ = 25.2 Hz), 112.1, 111.8 ($^3J_{CF}$ = 20.8 Hz), 21.6, 21.4. HRMS (ESI-TOF) m/z: Calcd for $C_{30}H_{21}FNO_3S$, 494.1226 $[M-H]^-$; found 494.1227.

ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all pure products, and X-ray crystal data (CIF) for **3a**. This material is available free of charge via the Internet at http//pubs.acs.org.

Notes

The authors declare no competing financial interest.

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