EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Facile and Diverse Synthesis of Benzo[b]fluorenone Derivatives via Copper/Selectfluor System-Catalyzed Tandem Annulation of 1,6-Enynes

Authors: Jian Zhang; Haifeng Zhang; Dongdong Shi; Hongwei Jin; Yunkui Liu

To be cited as: Eur. J. Org. Chem. 10.1002/ejoc.201600982

Link to VoR: http://dx.doi.org/10.1002/ejoc.201600982

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

FULL PAPER

DOI: 10.1002/ejoc.200((will be filled in by the editorial staff))

Facile and Diverse Synthesis of Benzo[*b*]fluorenone Derivatives via Copper/Selectfluor System-Catalyzed Tandem Annulation of 1,6-Enynes

Jian Zhang, Haifeng Zhang, Dongdong Shi, Hongwei Jin,* and Yunkui Liu*

Keywords: benzo[*b*]fluorenone / copper / Selectfluor / 1,6-enyenes / tandem reaction

A facile and diverse synthesis of benzo[*b*]fluorenone derivatives has been developed via Cu(0)/Selectfluor system-catalyzed tandem annulation of 1,6-enynes under mild reaction conditions. Thus, for *tert*-butylethynyl group-substituted 1,6-enynes, the reaction mainly underwent tandem annulation/C-C bond cleavage/fluorination process to give fluorinated benzo[*b*]fluorenones as the major products while *tert*-butyl group-substituted benzo[*b*]fluorenones were obtained as the minor products; for aryl ethynyl-substituted 1,6-enynes, the reaction underwent tandem annulations to afford 5-aryl-substituted benzo[*b*]fluorenones in moderate to excellent yields; for (trimethylsilyl)ethynyl group-substituted 1,6-enynes, the reaction underwent tandem annulation/C-Si bond cleavage to deliver 11*H*-benzo[*b*]fluoren-11-ones in moderate yields.

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou , 310014, P. R. China
E-mail: ykuiliu@zjut.edu.cn; jhwei828@zjut.edu.cn
Homepage: http://www.zjut.edu.cn

[b] Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.xxxxxxxxx.

Introduction

Fluorenones and benzo[*b*]fluorenones are important and useful carbocycles that may have unique biological and/or pharmaceutical activities as well as optical and electronic properties.[1,2] For example, the fluorenone alkaloid cauliphine (Figure 1, **A**), an isolated natural product from *Caulophyllum robustum*, displays good antimyocardial ischemia activity;[3] the kinafluorenone (Figure 1, **B**) is an intermediate for the synthesis of prekinamycin and stealthin antibiotics;[4] the chiral compound Fluostatin **C** (Figure 1, **C**) is a new inhibitor of dipeptidyl peptidase III from human placenta.[5]

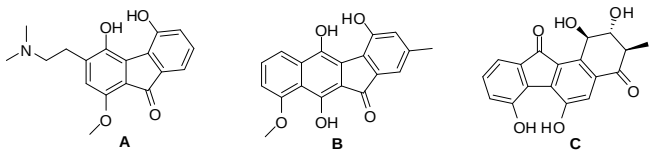
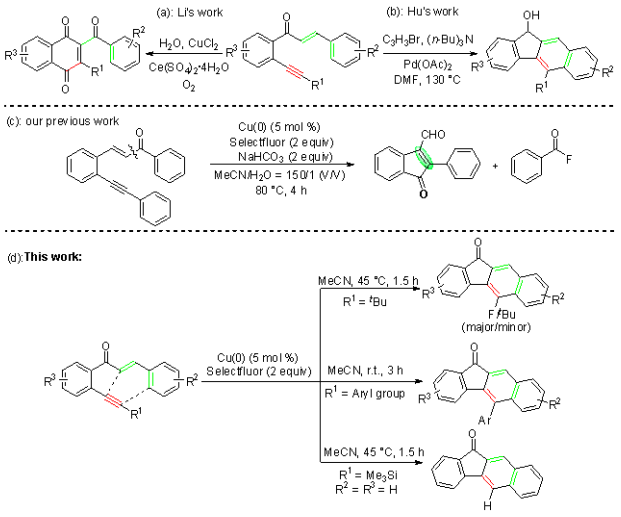


Figure 1. Bioactive Molecules Containing a Fluorenone Moiety

Regarding synthetic strategy, the classical methods for the construction of fluorenones (benzo[*b*]fluorenones) include Friedel-Crafts ring closures of biarylcarboxylic acids and derivatives,[6] oxidation of fluorenes,[7] and intramolecular [4+2] cycloaddition reaction of diarylacetylenes[8] or conjugated enynes.[9] Thanks to the high efficiency of palladium catalysts in the formation of C-C bonds,[10] several methods for the construction of fluorenones (benzo[*b*]fluorenones) involving palladium-catalyzed annulations have been developed in the past decades.[11-20] These include [2+2+2] cycloaddition of benzyne,[11] cyclocarbonylation of *o*-halobiaryls,[12] annulation of 2-haloarenecarboxaldehydes with arynes[13] or arylboronic acids,[14] intramolecular arylation of *o*-halobenzophenones,[15] dual C-H functionalization of benzophenones,[16] and directing group-assisted dual C-H activations.[17] Recently, some other methods have also been reported including DDQ-mediated oxidative radical cycloisomerization of 1,5-diynols,[18] aluminum oxide-mediated C-F bond activation of trifluoromethylated arenes,[19] and quaternary ammonium salt-promoted intramolecular dehydrogenative arylation of aldehydes.[20] Despite the capability of these methods for the synthesis of fluorenones (benzo[*b*]fluorenones), most of these procedures suffer from one or more limitations in term of harsh reaction conditions, multistep processes, low selectivity, the use of expensive catalysts, narrow scope of substrates, and/or not easy availability of the starting materials. Therefore, it is still highly desirable to develop mild and efficient methods for the construction of fluorenones (benzo[*b*]fluorenones) from easily available substrates by using inexpensive catalysts. Besides, considering that the introduction of the fluorine atom into parent molecules may significantly affect their original properties such as biological activities and physical properties,[21] it is also highly desirable to develop efficient methods for the construction of fluorinated fluorenones (benzo[*b*]fluorenones).[22]

Recently, transition-metal-catalyzed annulations of 1,*n*-enynes[23] have received increasingly attention due to their high efficiency and atom-economy for the generation of carbocycles or heterocycles.[24-27] For example, in 2011, Li[25] reported a $CuCl_2/Ce(SO_4)_2$ system-mediated oxidative annulation of 1,6-enynes in which 6-*exo*-trig cyclization products 1,4-naphthoquinones were selectively generated (Scheme 2-a). In 2012, Hu[26] described a palladium-catalyzed intramolecular cyclization of 1,6-enynes in which benzo[*b*]fluorenols were formed as the major products along with benzo[*b*]fluorenones as the byproducts (Scheme 2-b). As our research interest in the construction of carbocycles from 1,*n*-enynes, we recently developed a Cu(0)/Selectfluor system-catalyzed oxidative cyclization of 1,5-enynes to afford 3-formyl-1-indenone derivatives involving a tandem annulation/C−C bond cleavage process (Scheme 2-c).[27] Our further application of the Cu(0)/Selectfluor system in the annulation of 1,6-enynes led to a facile and diverse synthesis of

benzo[*b*]fluorenones under mild reaction conditions (Scheme 2-d).[28] Herein we would like to describe these findings.

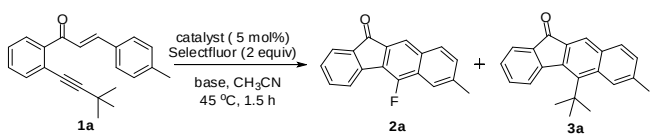


Scheme 1. Annulation of 1,5- and 1,6-Enynes

Results and Discussion

According to our previous work,[27] the present investigation began with the Cu(0)/Selectfluor system-catalyzed cyclization of 1,6-enyne **1a** (Table 1). When **1a** reacted with Cu powder (5 mol %), Selectfluor (2.0 equiv) and $NaHCO_3$ (2.0 equiv) in MeCN at 80 °C for 1.5 h, an unexpected fluorinated benzo[*b*]fluorenone **2a** was obtained in 62% yield along with a small amount of **3a** (yield: 5%) (entry 1, Table 1). A range of bases were screened, it seemed that K_2CO_3 was the most efficient base for the reaction (entries 1-6, Table 1). The reaction performed better at 45 °C while either increasing or decreasing the temperature would lead to a lower yield of **2a** (entry 6 vs 4, 7). Note that 2 equivalents of Selectfluor were necessary for the formation of **2a** otherwise the reaction would fail to give **2a** (entries 8, 9, Table 1). Several copper salts were investigated for the reaction, it was found that the use of the Cu(0) powder gave the highest yield of **2a** and selectivity (entries 10-15 vs 6, Table 1). Controlled experiments showed that the reaction failed to give either **2a** or **3a** in the absence of the Cu(0) powder (entry 16, Table 1). A controlled experiment for screening bases revealed that the reaction could perform even better without a base (entry 17 vs 6, Table 1). A series of solvents were investigated, and MeCN proved to be the most suitable solvent (entries 18-22 vs 17, Table 1). Among several electrophilic fluorination reagents screened, Selectfluor proved to be the most effectiveness for the formation of **2a** (entries 24, 25 vs 17, Table 1).

Table 1. Optimization of Reaction Conditions for the Cyclization of **1a**.[a]

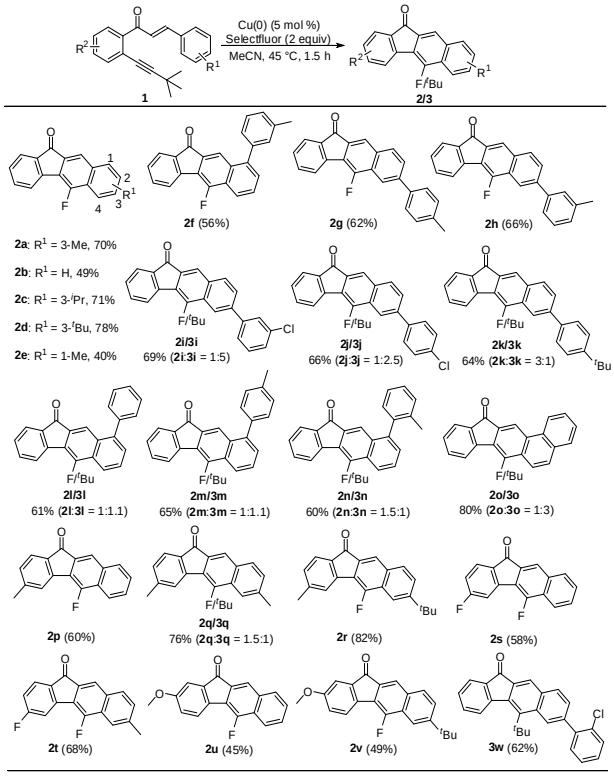


Entry	Catalyst	Base	Solvent	Yield [%][b]	
				2a	**3a**
1[c]	Cu(0)	$NaHCO_3$	CH_3CN	62	5
2[c]	Cu(0)	Na_2CO_3	CH_3CN	33	6
3[c]	Cu(0)	$KHCO_3$	CH_3CN	44	48
4[c]	Cu(0)	K_2CO_3	CH_3CN	65	28
5[c]	Cu(0)	K_3PO_4	CH_3CN	49	34
6	Cu(0)	K_2CO_3	CH_3CN	90	2
7[d]	Cu(0)	K_2CO_3	CH_3CN	13	14
8[e]	Cu(0)	K_2CO_3	CH_3CN	0	26
9[f]	Cu(0)	K_2CO_3	CH_3CN	0	0
10	CuI	K_2CO_3	CH_3CN	42	48
11	CuBr	K_2CO_3	CH_3CN	80	8
12	CuCl	K_2CO_3	CH_3CN	78	11
13	$Cu(OAc)_2$	K_2CO_3	CH_3CN	70	21
14	$CuCl_2$	K_2CO_3	CH_3CN	76	16
15	$CuSO_4$	K_2CO_3	CH_3CN	85	5
16	--	K_2CO_3	CH_3CN	0	0
17	**Cu(0)**	--	**CH_3CN**	**92(70)[g]**	**3**
18	Cu(0)	--	DMF	0	0
19	Cu(0)	--	DMSO	0	0
20	Cu(0)	--	DCE	0	0
21	Cu(0)	--	1,4-dioxane	0	0
22	Cu(0)	--	toluene	0	0
23[h]	Cu(0)	--	CH_3CN	91	2
24[i]	Cu(0)	--	CH_3CN	0	0
25[j]	Cu(0)	--	CH_3CN	42	26

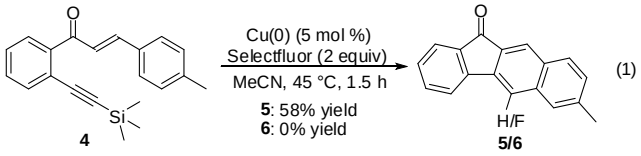
[a] All reactions were carried out with **1a** (0.2 mmol), catalyst (5 mol % based on **1a**), Selectfluor (2 equiv), base (2 equiv), in solvent (2 mL) at 45 °C for 1.5 h unless otherwise noted. [b] Determined by GC using dodecane as an internal standard. [c] The temperature is 80 °C. [d] The temperature is 25 °C. [e] Using 1 equivalent of Selectfluor. [f] In the absence of Selectfluor. [g] Isolated yield. [h] Using 3 equivalents of Selectfluor. [i] Selectfluor was replaced by 1-fluoropyridinium tetrafluoroborate, *N*-fluorobenzenesulfonimide (NFSI), and 2,6-dicholo-1-fluoropyridinium tetrafluoroborate, respectively. [j] Selectfluor was replaced by 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanebis(hexafluorophosphate) (F-TEDA-PF_6).

Under the established reaction conditions, the scope of the Cu(0)/Selectfluor system-catalyzed cyclization/fluorination of 1,6-enynes **1** was investigated and the results were summarized in Scheme 2. It was found that the electronic natures of R^1 had a great impact on the results of the fluorination process. When R^1 was aryl rings (**1f-1o**, Scheme 2) or electron-donating substituents (**1a**, **1c-1e**, **1p-1v**, Scheme 2), the reaction performed well and **2**/**3** could be obtained in modest to good yields. However, when R^1 was electron-withdrawing substituents such as Cl, F, and CF_3 etc., the reaction failed to give either **2** or **3** (not listed in Scheme 2). Note that the electronic natures of R^2 had little impact on the formation of **2** in term of yield and selectivity (**2p-2v**, Scheme 2). Regarding selectivity, when R^1 was equal to H, alkyl, *o*-methylphenyl, *m*-methylphenyl, *p*-methylphenyl, or *p*-*tert*-butylphenyl group, the reaction generally gave fluorinated products **2** as the major products (**2**:**3** ≥ 1.5:1-95:5; **2a**–**2h**, **2k**, **2n**, **2p**, **2q**, and **2r**–**2v**, Scheme 2). However, in some cases, the reaction gave non-fluorinated **3** as the predominant products (**2i**/**3i**, **2j**/**3j**, **2l**/**3l**, **2m**/**3m**, **2o**/**3o**, and **2w**/**3w**, Scheme 2). In these cases, for final characterization, we used high performance liquid chromatography (HPLC) to separate **2** and **3**.

Considering that C-Si bonds are more easily cleaved than C-C bonds, we envisioned that 1,6-enyne **4** containing a C≡C-$SiMe_3$ moiety would be more suitable for the abovementioned annulation/fluorination reaction. Thus, **4** was synthesized and subjected to the optimal reaction conditions. The annulation and C-Si bond cleavage did occurred, however, the reaction only produced 11*H*-benzo[*b*]fluoren-11-one **5** while the fluorinated product **6** was not detected (Eq. (1)).

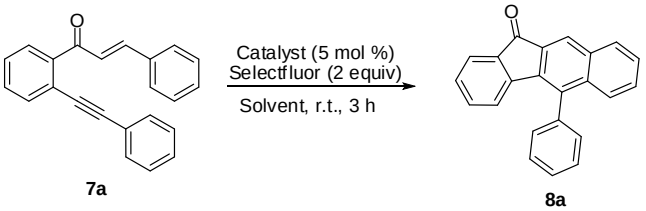


Scheme 2. Scope of the Tandem Annulation/Fluorination of **1**.[a,b] [a]: Reaction conditions: **1** (0.3 mmol), Cu(0) powder (5 mol % based on **1**), Selectfluor (2.0 equiv.), acetonitrile (2 mL) at 45 ºC for 1 h. [b]: Isolated yields.



Encouraged by the successful construction of fluorinated benzo[*b*]fluorenones from 1,6-enynes **1**, we further investigated the Cu(0)/Selectfluor system-catalyzed tandem annulation of 1,6-enynes **7** containing a C≡C-Ar moiety. When **7a** was selected as a model substrate and subjected to the standard reaction conditions for the synthesis of **2**, 5-phenyl-11*H*-benzo[*b*]fluoren-11-one **8a** was obtained in 90% GC yield (entry 1, Table 2). Note that the annulation performed even better when the reaction was conducted at room temperature for 3 h, affording **8a** in a high yield of 96% (entry 2, Table 2). Solvent screening experiments indicated that MeCN was still the best suitable solvent (3-6 vs 2). A range of copper salts were screened, most of them showed nearly equal effectiveness as the Cu(0) powder (entries 7-15 vs 2, Table 2). Controlled experiments showed that both the Cu(0) powder (5 mol %) and Selectfluor (2 equivalents) were indispensable for the completion of the reaction (entries 16-19, Table 2). The formation of benzo[*b*]fluorenone scaffold was unambiguously confirmed by the X-ray crystallography of **8a** (see Figure S1 in the Supporting Information).

Table 2. Optimization of Reaction Conditions for the Annulation of **7a** to Access **8a**.[a]



Entry	Catalyst	Solvent	Yield [%][b]
1	Cu(0)	CH_3CN	90[c]
2	Cu(0)	CH_3CN	96(76)[d]
3	Cu(0)	DCE	7
4	Cu(0)	DMF	6
5	Cu(0)	THF	<3
6	Cu(0)	1,4-dioxane	<3
7	CuBr	CH_3CN	92
8	CuCl	CH_3CN	94
9	CuCN	CH_3CN	93
10	$Cu(OAc)_2$	CH_3CN	96
11	$Cu(OH)_2$	CH_3CN	90
12	$CuSO_4$	CH_3CN	90
13	$Cu(NO_3)_2$	CH_3CN	89
14	Cu_2O	CH_3CN	91
15	CuI	CH_3CN	90
16	Cu(0)	CH_3CN	83[e], 96[f]
17	Cu(0)	CH_3CN	80[g], 96[h]
18	Cu(0)	CH_3CN	0[i]
19	--	CH_3CN	0

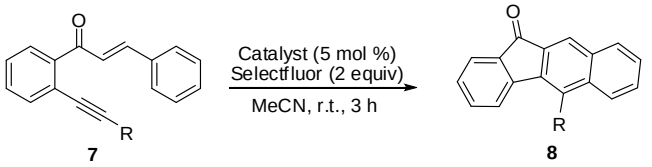
[a] All reactions were carried out with **7a** (0.2 mmol), catalyst (5 mol % based on **7a**), Selectfluor (2 equiv) in solvent (2 mL) at r.t. for 3 h unless otherwise noted. [b] Determined by GC using dodecane as an internal standard. [c] At 45 ºC for 1.5 h. [d] Isolated yield. [e] & [f] In the presence of 1 mol % and 10 mol % of Cu powder, respectively. [g] & [h] In the presence of 1.0 and 3.0 equivalensts of Selectfluor, respectively. [i] In the absence of Selectfluor.

With the optimal reaction conditions in hand, we set out to investigate the effect of the alkyne groups on the formation of **8** (Table 3). A variety of substrates bearing aromatic alkyne moieties could smoothly undergo annulations to give the desired benzo[*b*]fluorenones **8** in moderate to excellent yields (59-90%, entries 1-13, Table 3). It was found that there was no significant difference in yields between substrates bearing electron-donating groups (entries 2-9, Table 3) and those with electron-withdrawing groups (entries 11-13) except **7j** affording **8j** in an unexpected high yield of 90% (entry 10, Table 3). Notably, substrates with substitutents at different positions (*ortho*, *meta*, and *para*) on the phenyl ring of the alkyne moieties afforded the desired products in similar percent yields. A substrate **7n** containing 1-cyclohexylethynyl group could also proceed the annulating reaction smoothly to give the target product in 75% yield (entry 14, Table 3).

To broaden the scope of substrates **7**, a variety of 1,6-enynes **7** with different substituents on both aromatic rings **A** and **B** were synthesized and tested under the optimized conditions (Scheme 3). Generally, 1,6-enynes bearing electron-donating groups on the ring **B** underwent the annulation more smoothly and gave higher yields of **8** than those bearing electron-withdrawing ones (**8o**, **8r**, **8s**, **8w**, **8y** vs **8p**, **8q**, **8u**, Scheme 3). Unfortunately, substrate **8t** bearing an *ortho*-methyl group in the ring **B** afforded the desired product in only 48% yield due to formation of an unidentified byproduct. On

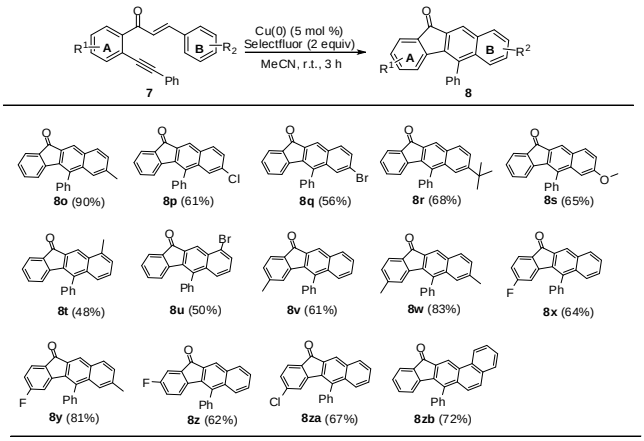
the other hand, the electronic nature of substituents on the ring **A** has little effect on the formation of **8** (**8v** vs **8x**, **8z**, **8za**; **8w** vs **8y**, Scheme 3).

Table 3. Effect of *ortho*-Substituted Alkyne Groups in 1,6-Enynes **7** on the Formation of **8**.[a]



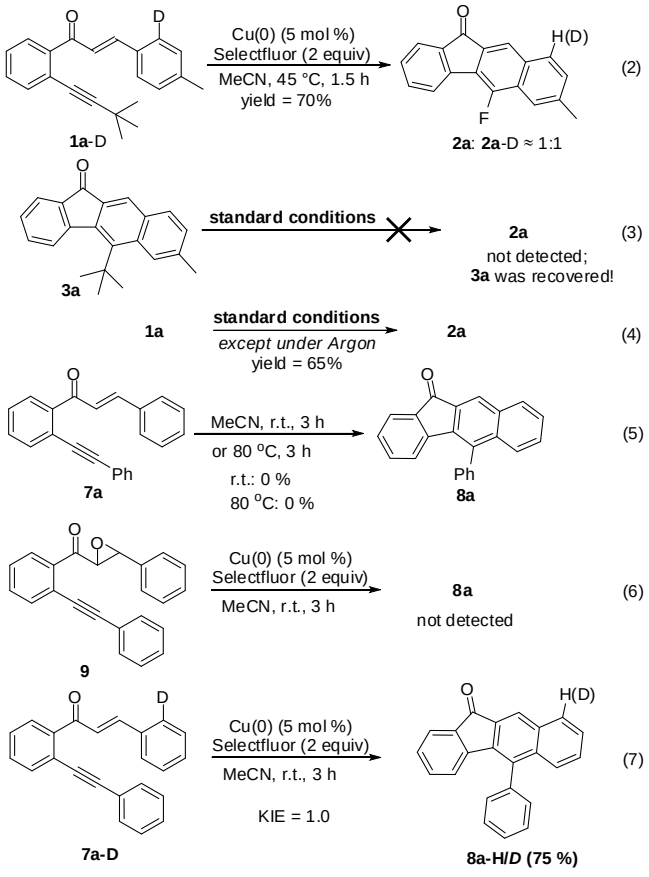
Entry	Substrate (**7**)	Product (**8**)	Yield [%][b]
1	**7a**: R = Ph	**8a**	76
2	**7b**: R = 2-MeC_6H_4	**8b**	63
3	**7c**: R = 4-MeC_6H_4	**8c**	69
4	**7d**: R = 4-(*n*-C_5H_{11})C_6H_4	**8d**	59
5	**7e**: R = 4-EtOC_6H_4	**8e**	63
6	**7f**: R = 4-MeOC_6H_4	**8f**	71
7	**7g**: R = 4-(*n*-C_3H_7)C_6H_4	**8g**	61
8	**7h**: R = 4-(*n*-$C_5H_{11}O$)C_6H_4	**8h**	59
9	**7i**: R = 4-EtC_6H_4	**8i**	63
10	**7j**: R = 2-ClC_6H_4	**8j**	90
11	**7k**: R = 4-ClC_6H_4	**8k**	73
12	**7l**: R = 3-BrC_6H_4	**8l**	67
13	**7m**: R = 4-BrC_6H_4	**8m**	70
14	**7n**: R = 1-Cyclohexenyl	**8n**	75

[a] All reactions were carried out with **7** (0.2 mmol), Cu powder (5 mol % based on **7**), Selectfluor (2 equiv) in solvent (2 mL) at room temperature for 3 h unless otherwise noted. [b] Isolated yield.



Scheme 3. Effect of Substituents on the Rings **A** and **B** on the Formation of **8**.[a,b] [a]: Reaction conditions: All reactions were carried out with **7** (0.2 mmol), Cu powder (5 mol % based on **7**), Selectfluor (2 equiv) in solvent (2 mL) at room temperature for 3 h unless otherwise noted. [b]: Isolated yields.

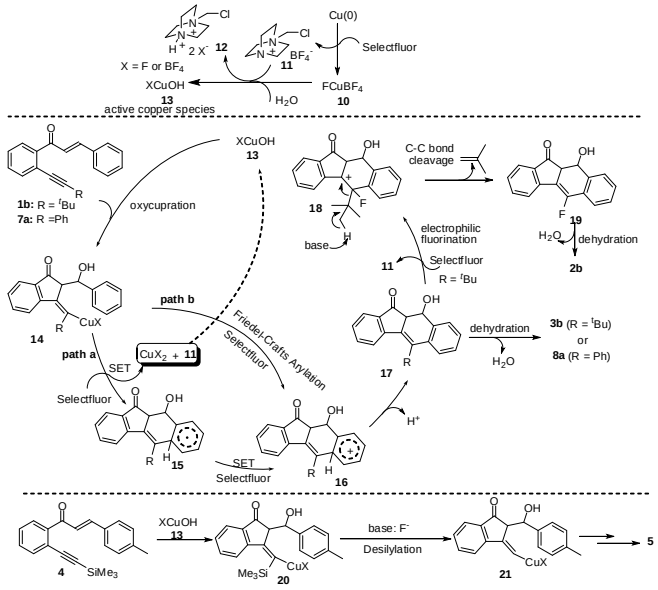
In order to elucidate the reaction mechanism, several mechanistic experiments were carried out (Scheme 4). Firstly, for the mechanistic studies on the annulation/fluorination process, an experiment determining the intramolecular kinetic isotope effects (KIE) was carried out by using **1a**-D as the substrate under the optimal reaction conditions (Eq. (2), Scheme 4). The intramolecular competitive KIE was calculated as 1.0 based on the NMR analyses (see the Supporting Information), indicating that the C-H activation is not the rate-determining step. It was found that the preparative intermediate **3a** failed to transform to **2a**, suggesting that **3a** was not likely an intermediate for the annulation/fluorination process (Eq. (3), Scheme 4). When **1a** was subjected to the optimal reaction conditions except under an argon atmosphere, the reaction could also afford **2a** in 65% yield, indicating that dioxygen was not involved in the reaction (Eq. (4), Scheme 4). Secondly, for the mechanistic studies on the annulation of **7a**, a treatment of **7a** without the participation of the Cu(0)/Selectfluor system was carried out (Eq. (5). Scheme 4). In such case, the annulation of **7a** did not occur either at room temperature or at 80 ºC, suggesting that the reaction unlikely proceeds via a direct [4+2] cyclization process because most of such [4+2] cyclizations require high temperatures.[8] In addition, an epoxy compound **9** was synthesized according to our previous work[27] and subjected to the optimal reaction conditions (Eq. (6), Scheme 4). However, the reaction resulted in complicated products without the detection of **8a**, indicating that **9** is not likely an intermediate for the annulation of **7a**.[27] Similarly, the intramolecular competitive KIE was determined as 1.0 based on the related KIE experiments of **7a**-D (Eq. (7), Scheme 4).



Scheme 4. Mechanistic Studies Based on **1a** and **7a**

Based on the abovementioned results and the previous literature,[27,29-33] a possible mechanism on the annulation of 1,6-enynes **1b** or **7a** is proposed in Scheme 5. Firstly, according to our previous work,[27,29] an active copper(II) species XCuOH (**13**, X = F or BF_4) could be generated *in situ* via the reaction of the Cu(0) powder and Selectfluor in the presence of water. This copper

species could easily undergo oxycupration toward the multiple bonds in **1b** (or **7a**) to deliver an intermediate **14**. Then **14** was further transformed to a cationic species **16** through a double SET process (path a).[30] Alternatively, the species **16** could be generated from **14** through a Friedel-Crafts arylation pathway under the oxidative conditions (path b).[31] An abstraction of a proton from the intermediate **16** delivered an intermediate **17**.[30] The direct dehydration of **17** could afford benzo[*b*]fluorenone **3b** (R = ^{t}Bu) or **8a** (R = Ph). On the other hand, if R represents a *tert*-butyl group, the intermediate **17** would undergo an electrophilic fluorination by Selectfluor to generate an intermediate **18**.[32] With the aid of a base, **18** underwent a C−C bond cleavage to afford an intermediate **19**.[33] A dehydration of **19** finally gave the fluorinated product **2b**. When substrate **4** was used, the oxycupration of **13** to the C-C double bond in **4** may result in an intermediate **20**. Intermediate **20** might easily undergo desilylation to give an intermediate **21** with the aid of F^-.[34] An annulation of **21** followed by a dehydration may deliver product **5**.



Scheme 5. Proposed Mechanism

Conclusions

In summary, we have developed a novel method for the synthesis of benzo[*b*]fluorenone derivatives via a Cu(0)/Selectfluor system-catalyzed annulations of 1,6-enynes. Notably, the type of products (5-fluorinated benzo[*b*]fluorenones, 5-*tert*-butyl-benzo[*b*]fluorenones, 5-aryl benzo[*b*]fluorenones, or 11*H*-benzo[*b*]fluoren-11-one) obtained from tandem annulations of 1,6-enynes can be controlled by the choice of substrates with different alkyne moieties (C≡C─^{t}Bu, C≡C─Ar or C≡C─$SiMe_3$). The present method has characteristic advantages of mild reaction conditions, the use of inexpensive copper catalyst, tunable generation of diverse benzo[*b*]fluorenone derivatives, and easy availability of the starting materials.

Experimental Section

General Information. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer at 25 ºC in $CDCl_3$ at 500 MHz, 125 MHz, respectively, with TMS as internal standard. ^{19}F NMR spectra were recorded on a Varian Inova 400 at 25 ºC in $CDCl_3$ at 376 MHz, with CF_3COOH as external standard. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. GC-MS experiments were performed with EI source, high resolution mass spectra (HRMS) were obtained on a TOF MS instrument with EI or ESI source.

Starting materials. All starting materials were synthesized according to the literature procedures.[25,26]

Typical experimental procedure for the synthesis of 2 or 3 or 5. 1 or **4** (0.3 mmol), Cu(0) powder (0.96 mg, 5 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and CH_3CN (2 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at 45 ºC for 1.5 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-CH_2Cl_2 (5/1, V/V) as eluent to give pure **2** (or **5**). In cases of a difficult separation of **2** and **3** with common column chromatography, a high performance liquid chromatography (HPLC) was used to separate **2** and **3** by using CH_3CN-H_2O (8/2, V/V) as eluent.

5-fluoro-7-methyl-11*H*-benzo[*b*]fluoren-11-one (2a): Yellow solid (55.1 mg, 70%); m.p. 162−163 ºC; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.88 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3, 152.6 (d, *J* = 258.8 Hz), 142.2, 139.8, 135.8, 135.2, 133.2 (d, *J* = 5.0 Hz), 132.8 (d, *J* = 5.0 Hz), 130.4 (d, *J* = 2.5 Hz), 130.0, 129.0, 128.3 (d, *J* = 16.3 Hz), 124.7 (d, *J* = 6.3 Hz), 124.5, 121.5 (d, *J* = 2.5 Hz), 121.0 (d, *J* = 13.8 Hz), 120.7 (d, *J* = 5.0 Hz), 22.1; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -129.3 (s); GC-MS (EI, 70 eV): *m/z* (%) = 262 (34) [M^+]; HRMS (EI) for $C_{18}H_{11}FO$: calcd. 262.0794, found 262.0788.

5-fluoro-11*H*-benzo[*b*]fluoren-11-one (2b): Yellow solid (37.2 mg, 50%); m.p. 222−223 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.03 (s, 1H), 7.94−7.92 (m, 2H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.66−7.64 (m, 2H), 7.57−7.54 (m, 1H), 7.40−7.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2 (d, *J* = 2.5 Hz), 153.0 (d, *J* = 258.8 Hz), 142.2 (d, *J* = 1.3 Hz), 135.8, 135.4, 135.1 (d, *J* = 3.8 Hz), 133.7 (d, *J* = 5.0 Hz), 130.6 (d, *J* = 2.5 Hz), 129.3 (d, *J* = 1.3 Hz), 129.1, 128.1 (d, *J* = 16.3 Hz), 127.9, 124.8 (d, *J* = 5.0 Hz), 124.7, 121.6 (d, *J* = 3.8 Hz), 121.5 (d, *J* = 5.0 Hz), 121.0 (d, *J* = 13.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -128.6 (s); GC-MS (EI, 70 eV): *m/z* (%) = 248 (42) [M^+]; HRMS (EI) for $C_{17}H_9FO$: calcd. 248.0637, found 248.0645.

5-fluoro-7-isopropyl-11*H*-benzo[*b*]fluoren-11-one (2c): Yellow solid (61.8 mg, 71%); m.p. 152−153 ºC; IR (KBr, cm^{-1}): ν = 1704 (C=O);^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.90(d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H),7.45 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 3.16−3.08 (m, 1H), 1.38(d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3 (d, *J* = 2.5 Hz), 152.9 (d, *J* = 258.8 Hz), 150.6(d, *J* = 1.3 Hz), 142.2(d, *J* = 2.5 Hz), 135.9, 135.3, 133.6 (d, *J* = 5.0 Hz), 132.9 (d, *J* = 5.0 Hz), 130.6 (d, *J* = 2.5 Hz), 129.0, 128.4 (d, *J* = 16.3 Hz), 127.6, 124.7 (d, *J* = 6.3 Hz), 124.5, 121.4 (d, *J* = 2.5 Hz), 121.0 (d, *J* = 13.8 Hz), 118.0 (d, *J* = 5.0 Hz), 34.6, 23.7; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -129.1 (s); GC-MS (EI, 70 eV): *m/z* (%) = 290 (16) [M^+]; HRMS (EI) for $C_{20}H_{15}FO$: calcd. 290.1107, found 290.1114.

7-(*tert*-butyl)-5-fluoro-11*H*-benzo[*b*]fluoren-11-one (2d): Yellow solid (71.2 mg, 78%); m.p.160−162 ºC; IR (KBr, cm^{-1}): ν = 1703 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.97 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.62 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2 (d, *J* = 2.5 Hz), 153.2 (d, *J* = 258.8 Hz), 152.9, 142.3 (d, *J* = 1.3 Hz), 135.9, 135.2, 133.3 (d, *J* = 3.8 Hz), 133.1 (d, *J* = 5.0 Hz), 130.3 (d, *J* = 2.5 Hz), 128.9, 128.1 (d, *J* = 16.3 Hz),

126.7, 124.7 (d, *J* = 6.3 Hz), 124.5, 121.2 (d, *J* = 2.5 Hz), 121.0 (d, *J* = 13.8 Hz), 116.7 (d, *J* = 6.3 Hz), 35.4, 31.2; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -129.1 (s); GC-MS (EI, 70 eV): *m/z* (%) = 304 (12) [M^+]; HRMS (EI) for $C_{21}H_{17}FO$: calcd. 304.1263, found 304.1258.

5-fluoro-9-methyl-11*H*-benzo[*b*]fluoren-11-one (2e): Yellow solid (31.5 mg, 40%); m.p. 185−186 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.97(d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.62−7.59 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 2.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.5 (d, *J* = 2.5 Hz), 153.3 (d, *J* = 257.5 Hz), 142.2 (d, *J* = 2.5 Hz), 137.8 (d, *J* = 2.5 Hz), 135.9, 135.4, 134.3 (d, *J* = 3.75 Hz), 133.2 (d, *J* = 6.3 Hz), 129.1, 129.0 (d, *J* = 1.3 Hz), 128.9, 128.4 (d, *J* = 15.0 Hz), 124.8 (d, *J* = 6.3 Hz), 124.6, 120.6 (d, *J* = 13.8 Hz), 119.6 (d, *J* = 6.3 Hz), 118.1 (d, *J* = 2.5 Hz), 19.7; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -127.7 (s); GC-MS (EI, 70 eV): *m/z* (%) = 262 (35) [M^+]; HRMS (EI) for $C_{18}H_{11}FO$: calcd. 262.0794, found 262.0785.

5-fluoro-9-(*m*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (2f): Yellow solid (56.8 mg, 56%); m.p. 184−185 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O);^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* =8.5 Hz, 1H), 8.07 (s, 1H), 7.90(d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.26−7.24 (m, 2H), 2.48(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2 (d, *J* = 2.5 Hz), 153.0 (d, *J* = 158.8 Hz), 143.7 (d, *J* = 2.5 Hz), 141.9 (d, *J* = 1.3 Hz), 139.5, 138.3, 135.9, 135.3, 133.5 (d, *J* = 3.8 Hz), 133.4 (d, *J* = 5.0 Hz), 130.5, 129.1, 128.9, 128.7, 128.6 (d, *J* = 1.3 Hz), 128.49 (d, *J* = 16.3 Hz), 128.48, 127.0, 124.8 (d, *J* = 5.0 Hz), 124.6, 120.56, 120.55 (d, *J* = 13.8 Hz), 120.3 (d, *J* = 3.8 Hz), 21.5; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -127.9 (s);GC-MS (EI, 70 eV): *m/z* (%) = 338 (23) [M^+]; HRMS (EI) for $C_{24}H_{15}FO$: calcd. 338.1107, found 338.1115.

5-fluoro-7-(*p*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (2g): Yellow solid (62.9 mg, 62%); m.p. 186−187 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.04 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.80 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.64−7.60 (m, 1H), 7.41−7.38 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$): δ 192.1, 153.2 (d, *J* = 258.8 Hz), 149.9, 142.1, 138.3, 137.2, 135.9, 135.3, 134.0 (d, *J* = 3.8 Hz), 133.5 (d, *J* = 5.0 Hz), 131.1 (d, *J* = 2.5 Hz), 129.8, 129.1, 128.6 (d, *J* = 16.3 Hz), 127.3, 127.3, 124.9 (d, *J* = 5.0 Hz), 124.6, 121.4 (d, *J* = 2.5 Hz), 121.3 (d, *J* = 13.8 Hz), 118.9 (d, *J* = 5.0 Hz), 21.2; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -128.8 (s); GC-MS (EI, 70 eV): *m/z* (%) = 338 (21) [M^+]; HRMS (EI) for $C_{24}H_{15}FO$: calcd. 338.1107, found 338.1113.

5-fluoro-7-(*m*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (2h): Yellow solid (67.0 mg, 66%); m.p. 180−181 ºC; IR (KBr, cm^{-1}): ν = 1708 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25(s, 1H), 8.00(s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.0 (d, *J* = 1.3 Hz), 153.1 (d, *J* = 258.8 Hz), 142.2 (d, *J* = 1.3 Hz), 142.0 (d, *J* = 1.3 Hz), 140.0, 138.7, 135.9, 135.3, 134.1 (d, *J* = 3.8 Hz), 133.5 (d, *J* = 5.0 Hz), 131.0 (d, *J* = 2.5 Hz), 129.1, 129.01, 129.0, 128.4 (d, *J* = 15.0 Hz), 128.2, 127.4, 124.84, 124.79, 124.6, 121.4, 121.3 (d, *J* = 16.3 Hz), 119.2 (d, *J* = 5.0 Hz), 21.6; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -128.7 (s);GC-MS (EI, 70 eV): *m/z* (%) = 338 (25) [M^+]; HRMS (EI) for $C_{24}H_{15}FO$: calcd. 338.1107, found 338.1116.

7-(3-chlorophenyl)-5-fluoro-11*H*-benzo[*b*]fluoren-11-one (2i): Yellow solid (12.4 mg, 11.5%); m.p. 211−212 ºC; IR (KBr, cm^{-1}): ν = 1706(C=O);^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (s, 1H), δ 8.06 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.78−7.74 (m, 2H), 7.65−7.62 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.44−7.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.0, 153.1 (d, *J* = 260.0 Hz), 150.1, 142.0 (d, *J* = 6.3 Hz), 140.7, 139.8, 135.9, 135.5, 135.1, 134.4 (d, *J* = 3.8 Hz), 131.3 (d, *J* = 2.5 Hz), 130.3, 129.3, 128.5 (d, *J* = 15.0 Hz), 128.3, 127.6, 127.1, 125.6, 124.9 (d, *J* = 5.0 Hz), 124.7, 121.6 (d, *J* = 13.8 Hz), 121.3 (d, *J* = 3.8 Hz), 119.5 (d, *J* = 5.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -128.6 (s); GC-MS (EI, 70 eV): *m/z* (%) = 358 (11) [M^+]; HRMS (EI) for $C_{23}H_{12}ClFO$: calcd. 358.0561, found 358.0554.

5-(*tert*-butyl)-7-(3-chlorophenyl)-11*H*-benzo[*b*]fluoren-11-one (3i): Yellow solid (68.5 mg, 57.5%); m.p. 159−160 ºC; IR (KBr, cm^{-1}): ν = 1707(C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.04 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.61−7.56 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.41−7.39 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 1.86 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.8, 148.1, 145.9, 143.1, 138.3, 138.0, 137.7, 136.4, 135.0, 134.8, 133.7, 133.4, 131.2, 130.3, 129.0, 128.2, 127.8, 127.5, 126.3, 125.5, 125.0, 124.2, 123.2, 37.7, 33.1; GC-MS (EI, 70 eV): *m/z* (%) = 396 (10) [M^+]; HRMS (EI) for $C_{27}H_{21}ClO$: calcd. 396.1281, found 396.1274.

7-(4-chlorophenyl)-5-fluoro-11*H*-benzo[*b*]fluoren-11-one (2j): Yellow solid (20.3 mg, 18.9%); m.p. 226−227 ºC; IR (KBr, cm^{-1}): ν = 1703(C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.05 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.0 Hz, 1H), 7.76 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.77−7.68 (m, 2H), 7.65−7.62 (m, 1H), 7.52−7.50 (m, 2H), 7.42−7.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.0, 153.1 (d, *J* = 258.8 Hz), 152.8, 142.0, 140.9, 138.5, 135.9, 135.4, 134.5, 134.3 (d, *J* = 3.8 Hz), 131.3 (d, *J* = 2.5 Hz), 129.3, 128.7, 128.6 (d, *J* = 16.3 Hz), 128.5, 127.1, 124.9 (d, *J* = 5.0 Hz), 124.7, 121.4 (d, *J* = 2.5 Hz), 120.3 (d, *J* = 15 Hz), 119.2 (d, *J* = 5.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -128.7 (s); GC-MS (EI, 70 eV): *m/z* (%) = 358 (13) [M^+]; HRMS (EI) for $C_{23}H_{12}FO$: calcd. 358.0561, found 358.0569.

5-(*tert*-butyl)-7-(4-chlorophenyl)-11*H*-benzo[*b*]fluoren-11-one (3j): Yellow solid (56.1 mg, 47.1%); m.p. 207−208 ºC; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.06 (s, 1H), 7.92−7.89 (m, 2H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.64−7.61 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 1.86 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 148.1, 145.9, 139.7, 138.4, 138.1, 138.0, 136.4, 134.7, 134.0, 133.7, 133.3, 131.2, 129.2, 129.0, 128.6, 128.2, 126.1, 125.0, 124.2, 123.3, 37.7, 33.1; GC-MS (EI, 70 eV): *m/z* (%) = 396 (12) [M^+]; HRMS (EI) for $C_{27}H_{21}ClO$: calcd. 396.1281, found 396.1276.

7-(4-(*tert*-butyl)phenyl)-5-fluoro-11*H*-benzo[*b*]fluoren-11-one (2k): Yellow soild (57.8 mg, 48%); m.p. 178−179 ºC; IR (KBr, cm^{-1}): ν = 1706 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.03 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.81−7.80 (m, 2H), 7.72−7.69 (m, 2H), 7.63−7.59 (m, 1H), 7.58−7.55 (m, 2H), 7.40−7.37 (m, 1H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.1 (d, *J* = 2.5 Hz), 153.2 (d, *J* = 258.8 Hz), 151.5, 142.1 (d, *J* = 1.3 Hz), 142.0 (d, *J* = 1.3 Hz), 137.1, 135.9, 135.3, 134.0 (d, *J* = 3.8 Hz), 133.5 (d, *J* = 5.0 Hz), 131.1 (d, *J* = 2.5 Hz), 129.1, 128.5 (d, *J* = 15.0 Hz), 127.4, 127.1, 126.1, 124.8 (d, *J* = 5.0 Hz), 124.6, 121.4 (d, *J* = 2.5 Hz), 121.3 (d, *J* = 13.8 Hz), 119.0 (d, *J* = 5.0 Hz), 34.7, 31.4; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -128.8 (s); GC-MS (EI, 70 eV): *m/z* (%) = 380 (11) [M^+]; HRMS (EI) for $C_{27}H_{21}FO$: calcd. 380.1576, found 380.1570.

5-(*tert*-butyl)-7-(4-(*tert*-butyl)phenyl)-11*H*-benzo[*b*]fluoren-11-one (3k): Yellow solid (20.1 mg, 16%); m.p. 163−164 ºC; IR (KBr, cm^{-1}): ν = 1704(C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.51(s, 1H), 8.07 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.69−7.66 (m, 3H), 7.58−7.55 (m, 3H), 7.33 (t, *J* = 7.0 Hz, 1H), 1.87 (s, 9H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.1, 150.1, 148.2, 145.9, 139.1, 138.21, 138.15, 138.1, 136.5, 134.4, 133.6, 133.0, 131.0, 129.0, 128.1, 127.1, 126.03, 125.98, 125.4, 124.1, 123.4, 37.7, 34.7, 33.1, 31.4; GC-MS (EI, 70 eV): *m/z* (%) = 418 (7) [M^+]; HRMS (EI) for $C_{31}H_{30}O$: calcd. 418.2297, found 418.2289.

5-fluoro-9-phenyl-11*H*-benzo[*b*]fluoren-11-one (2l): Yellow solid (28.2 mg, 29%); m.p. 230−231 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.67−7.64 (m, 1H), 7.61−7.58 (m, 1H), 7.56−7.45 (m, 6H), 7.36 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.1 (d, *J* = 1.3 Hz), 153.1 (d, *J* = 258.8 Hz), 143.6 (d, *J* = 2.5 Hz), 142.0 (d, *J* = 2.5 Hz), 139.6, 136.0, 135.3, 133.5 (d, *J* = 6.3 Hz), 133.4 (d, *J* = 3.8

Hz), 129.9, 129.1 (d, *J* = 12.5 Hz), 128.7, 128.65, 128.5, 128.0, 124.9, 124.8, 124.6, 120.74 (d, *J* = 6.3 Hz), 120.68 (d, *J* = 13.8 Hz), 120.2 (d, *J* = 2.5 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -127.8 (s); GC-MS (EI, 70 eV): *m/z* (%) = 324 (24) [M^+]; HRMS (EI) for $C_{23}H_{13}FO$: calcd. 324.0950, found 324.0957.

5-(*tert*-butyl)-9-phenyl-11*H*-benzo[*b*]fluoren-11-one (3l): Yellow solid (34. 8 mg, 32%); m.p. 148−149 ºC; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, *J* = 9.0 Hz, 1H), 8.10 (s, 1H), 7.91(d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.57−7.45 (m, 7H), 7.37 (dd, J_1 = 7.0 Hz, J_2 = 0.5Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 1.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.1, 148.0, 146.0, 143.0, 140.4, 138.4, 137.5, 136.4, 134.4, 133.6, 132.2, 130.1, 128.8, 128.5, 128.1, 127.6, 127.1, 126.9, 125.6, 124.1, 122.0, 37.7, 32.9; GC-MS (EI, 70 eV): *m/z* (%) = 362 (14) [M^+]; HRMS (EI) for $C_{27}H_{22}O$: calcd. 362.1671, found 362.1663.

5-fluoro-9-(*p*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (2m): Yellow solid (31.5 mg, 31%); m.p. 206−207 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 1H), 8.10 (s, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.39−7.33 (m, 5H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3 (d, *J* = 2.5 Hz), 153.1 (d, *J* = 257.5 Hz), 143.6 (d, *J* = 5.0 Hz), 142.0 (d, *J* = 2.5 Hz), 137.8, 136.6, 135.9, 135.3, 133.5 (d, *J* = 3.8 Hz), 133.4 (d, *J* = 5.0 Hz), 129.8, 129.4, 129.1, 129.0, 128.7 (d, *J* = 1.3 Hz), 128.6 (d, *J* = 15 Hz), 124.8 (d, *J* = 5.0 Hz), 124.6, 120.58 (d, *J* = 13.8 Hz), 120.57, 120.4 (d, *J* = 2.5 Hz), 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -127.9 (s); GC-MS (EI, 70 eV): *m/z* (%) = 338 (13) [M^+]; HRMS (EI) for $C_{24}H_{15}FO$: calcd. 338.1107, found 338.1116.

5-(*tert*-butyl)-9-(*p*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (3m): Yellow solid (38.4 mg, 34%); m.p. 166−167 ºC; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 9.0 Hz, 1H), 8.12 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 1H), 7.57−7.53 (m, 1H), 7.50−7.47 (m, 1H), 7.37−7.30 (m, 6H), 2.48 (s, 3H), 1.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.1, 148.0, 146.0, 143.1, 138.5, 137.5, 137.44, 137.37, 136.5, 134.3, 133.6, 132.3, 130.0, 129.3, 128.8, 128.0, 126.9, 126.8, 125.6, 124.1, 122.2, 37.7, 32.9, 21.2; GC-MS (EI, 70 eV): *m/z* (%) = 376 (11) [M^+]; HRMS (EI) for $C_{28}H_{24}O$: calcd. 376.1827, found 376.1821.

5-fluoro-9-(*o*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (2n): Yellow solid (36.5 mg, 36%); m.p. 197−198 ºC; IR (KBr, cm^{-1}): ν = 1708 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.70−7.67 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.42−7.31(m, 5H), 7.22 (d, *J* = 7.5 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3 (d, *J* = 2.5 Hz), 153.2 (d, *J* = 258.8 Hz), 143.1 (d, *J* = 2.5 Hz), 142.0 (d, *J* = 1.3 Hz), 138.9, 136.4, 135.9, 135.4, 133.9 (d, *J* = 3.8 Hz), 133.6 (d, *J* = 5.0 Hz), 130.3, 130.1, 129.1, 128.9, 128.8 (d, *J* = 1.3 Hz), 128.4 (d, *J* = 16.3 Hz), 125.9, 124.9, 124.8, 124.7, 120.74 (d, *J* = 13.8 Hz), 120.73, 120.2 (d, *J* = 3.8 Hz), 20.1; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -128.0 (s);GC-MS (EI, 70 eV): *m/z* (%) = 338 (18) [M^+]; HRMS (EI) for $C_{24}H_{15}FO$: calcd. 338.1107, found 338.1101.

5-(*tert*-butyl)-9-(*o*-tolyl)-11*H*-benzo[*b*]fluoren-11-one (3n): Yellow solid (27.1 mg, 24%); m.p. 221−222 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O);^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 9.0 Hz, 1H), 8.11 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.57−7.53 (m, 1H), 7.50−7.47 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 6.5 Hz, 1H), 7.32−7.26 (m, 4H), 2.46 (s, 3H), 1.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 148.0, 146.0, 143.3, 140.4, 138.4, 138.1, 137.5, 136.5, 134.4, 133.6, 132.3, 130.8, 128.8, 128.40, 128.38, 128.0, 127.2, 127.0, 126.8, 125.6, 124.1, 122.2, 37.7, 33.0, 21.5; GC-MS (EI, 70 eV): *m/z* (%) = 376(14) [M^+]; HRMS (EI) for $C_{28}H_{24}O$: calcd. 376.1827, found 376.1835.

7-fluoro-12*H*-indeno[*1,2-b*]phenanthren-12-one (2o): Yellow solid (17.9 mg, 20%); m.p. 227−228 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.66 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.92−7.87 (m, 3H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.5 (d, *J* = 2.5 Hz), 153.6 (d, *J* = 256.3 Hz), 142.0 (d, *J* = 1.3 Hz), 135.5, 135.4, 133.7 (d, *J* = 5.0 Hz), 132.6 (d, *J* = 3.8 Hz), 132.3, 131.0 (d, *J* =1.3 Hz), 130.5 (d, *J* = 1.3 Hz), 129.2, 129.0, 127.9, 127.7, 127.1 (d, *J* = 16.3 Hz), 126.9 (d, *J* = 15.0 Hz), 124.7, 124.6 (d, *J* = 5.0 Hz), 123.3, 118.7 (d, *J* = 7.5 Hz), 115.9 (d, *J* = 3.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -127.8 (s); GC-MS (EI, 70 eV): *m/z* (%) = 298 (31) [M^+]; HRMS (EI) for $C_{21}H_{11}FO$: calcd. 298.0794, found 298.0784.

7-(*tert*-butyl)-12*H*-indeno[*1,2-b*]phenanthren-12-one (3o): Yellow solid (60.6 mg, 60%); m.p. 202−203 ºC; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.86 (s, 1H), 8.79 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 7.90−7.86 (m, 2H), 7.79 (d, *J* = 7.0 Hz, 1H), 7.73 (t, *J* = 9.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 1.83 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.5, 148.1, 146.7, 139.3, 137.3, 136.1, 134.3, 133.7, 131.4, 131.2, 131.0, 128.5, 128.10, 128.05, 127.2, 127.0, 126.5, 125.8, 124.2, 123.3, 117.7, 37.7, 32.9; GC-MS (EI, 70eV): *m/z* (%) = 336(15) [M^+]; HRMS (EI) for $C_{25}H_{20}O$: calcd. 336.1514, found 336.1521.

5-fluoro-3-methyl-11*H*-benzo[*b*]fluoren-11-one (2p): Yellow solid (47.3 mg, 60%); m.p. 185−186 ºC; IR (KBr, cm^{-1}): ν = 1708 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 1H), 7.69 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.63−7.60 (m, 1H), 7.54−7.51 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.8 (d, *J* = 2.5 Hz), 152.8 (d, *J* = 258.8 Hz), 146.7, 142.5 (d, *J* = 1.3 Hz), 135.1 (d, *J* = 3.8 Hz), 134.3 (d, *J* = 6.3 Hz), 133.6, 130.5 (d, *J* = 2.5 Hz), 129.9, 129.1 (d, *J* = 1.3 Hz), 128.0 (d, *J* = 15.0 Hz), 127.7, 125.5 (d, *J* = 6.3 Hz), 124.5, 121.4 (d, *J* = 6.3 Hz), 121.3 (d, *J* = 3.8 Hz), 120.8 (d, *J* = 13.8 Hz), 22.3; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -129.0 (s);GC-MS (EI, 70 eV): *m/z* (%) = 262 (28) [M^+]; HRMS (EI) for $C_{18}H_{11}FO$: calcd. 262.0794, found 262.0788.

5-fluoro-3,7-dimethyl-11*H*-benzo[*b*]fluoren-11-one (2q): Yellow solid (37.8 mg, 45.6%); m.p. 188−189 ºC; IR (KBr, cm^{-1}): ν = 1706 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.83 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 2.55 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.9, 152.5 (d, *J* = 258.8 Hz), 146.5, 142.5, 139.6, 133.7, 133.4 (d, *J* = 5.0 Hz), 133.2 (d, *J* = 5.0 Hz), 130.3 (d, *J* = 2.5 Hz), 129.8, 129.7, 128.2 (d, *J* = 16.3 Hz), 125.5 (d, *J* = 5.0 Hz), 124.4, 121.2 (d, *J* = 2.5 Hz), 121.0 (d, *J* = 12.5 Hz), 120.6 (d, *J* = 5.0 Hz), 22.3, 22.0; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -129.6 9 (s);GC-MS (EI, 70 eV): *m/z* (%) = 276 (23) [M^+]; HRMS (EI) for $C_{19}H_{13}FO$: calcd. 276.0950, found 276.0958.

5-(*tert*-butyl)-3,7-dimethyl-11*H*-benzo[*b*]fluoren-11-one (3q): Yellow solid (28.7 mg, 30.4%); m.p. 157−158 ºC; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.97 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.65 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 2.54 (s, 3H), 2.49 (s, 3H), 1.81 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.8, 148.8, 145.0, 144.3, 137.95, 137.96, 136.2, 134.4, 134.2, 132.1, 130.3, 129.7, 128.8, 127.7, 127.4, 124.0, 123.2, 37.6, 33.0, 22.5, 22.4; GC-MS (EI, 70 eV): *m/z* (%) = 314(8) [M^+]; HRMS (EI) for $C_{23}H_{22}O$: calcd. 314.1671, found 314.1663.

7-(*tert*-butyl)-5-fluoro-3-methyl-11*H*-benzo[*b*]fluoren-11-one (2r): Yellow solid (78.3 mg, 82%); m.p. 205−206 ºC; IR (KBr, cm^{-1}): ν = 1706 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.93 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.62 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 2.48 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.9 (d, *J* = 2.5 Hz), 153.0 (d, *J* = 158.8 Hz), 152.7, 146.5, 142.6 (d, *J* = 1.3 Hz), 133.7, 133.2 (d, *J* = 5.0 Hz), 130.2 (d, *J* = 5.0 Hz), 129.7, 128.0 (d, *J* = 15.0 Hz), 126.6, 125.5, 125.4, 124.5, 121.0 (d, *J* = 2.5 Hz), 120.9 (d, *J* = 13.8 Hz), 116.7 (d, *J* = 5.0 Hz), 35.4, 31.1, 22.3; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -129.4 (s); GC-MS (EI, 70 eV): *m/z* (%) = 318 (12) [M^+]; HRMS (EI) for $C_{22}H_{19}FO$: calcd. 318.1420, found 318.1427.

3,5-difluoro-11*H*-benzo[*b*]fluoren-11-one (2s): Yellow solid (46.3 mg, 58%); m.p. 217−218 ºC; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.93 (d, *J* = 8.0 Hz,

1H), 7.77 (dd, J_1 = 8.0 Hz, J_2 = 5.0 Hz, 1H), 7.67−7.64 (m, 1H), 7.59-7.56 (m, 2H), 7.06−7.03 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.3 (d, *J* = 1.3 Hz), 167.5 (d, *J* = 255.0 Hz), 153.2 (d, *J* = 260.0 Hz), 144.7 (d, *J* = 11.3 Hz), 135.4 (d, *J* = 3.8 Hz), 133.7 (d, *J* = 5.0 Hz), 132.0, 130.6 (d, *J* = 2.5 Hz), 129.4 (d, *J* = 1.3 Hz), 128.3, 127.9 (d, *J* = 16.3 Hz), 126.8 (d, *J* = 10.0 Hz), 121.64. 121.61 (d, *J* = 2.5 Hz), 119.7 (dd, J_1 = 11.3 Hz, J_2 = 5.0 Hz), 116.1 (d, *J* = 23.8 Hz), 112.3 (dd, J_1 = 25.0 Hz, J_2 = 5.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -110.3 (s), -127.9 (s); GC-MS (EI, 70 eV): *m/z* (%) = 266 (35) [M^+]; HRMS (EI) for $C_{17}H_8F_2O$: calcd. 266.0543, found 266.0549.

3,5-difluoro-7-methyl-11*H*-benzo[*b*]fluoren-11-one (2t): Orange solid (57.2 mg, 68%); m.p. 199−200 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.83 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.73 (dd, J_1 = 8.0 Hz, J_2 = 5.0 Hz, 1H), 7.51 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.03−7.00 (m, 1H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.3 (d, *J* = 1.3 Hz), 167.5 (d, *J* = 258.8 Hz), 152.9 (d, *J* = 258.8 Hz), 144.7 (d, *J* = 10.0 Hz), 140.0 (d, *J* = 1.3 Hz), 133.6 (d, *J* = 3.8 Hz), 132.9 (d, *J* = 5.0 Hz), 132.1 (d, *J* = 1.3 Hz), 130.4 (d, *J* = 2.5 Hz), 130.3, 128.1 (d, *J* = 16.3 Hz), 126.6 (d, *J* = 10.0 Hz), 121.4 (d, *J* = 2.5 Hz), 120.8 (d, *J* = 6.0 Hz), 119.8 (dd, J_1 = 12.5 Hz, J_2 = 2.5 Hz), 115.9 (d, *J* = 23.8 Hz), 112.2 (dd, J_1 = 25.0 Hz, J_2 = 5.0 Hz), 22.0; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -101.7 (s), -128.6 (s); GC-MS (EI, 70 eV): *m/z* (%) = 280 (26) [M^+]; HRMS (EI) for $C_{18}H_{10}F_2O$: calcd. 280.0700, found 280.0708.

5-fluoro-2-methoxy-11*H*-benzo[*b*]fluoren-11-one (2u): Orange solid (37.6 mg, 45%); m.p. 160−161 ºC; IR (KBr, cm^{-1}): ν = 1707 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.97 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 6.5 Hz, 1H), 7.63−7.60 (m, 1H), 7.53−7.50 (m, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.13 (dd, J_1 = 8.0 Hz, J_2 = 2.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2, 160.9, 152.1 (d, *J* = 157.5 Hz), 137.5, 135.0, 134.5 (d, *J* = 3.8 Hz), 130.6 (d, *J* = 2.5 Hz), 129.3, 128.9, 128.4 (d, *J* = 16.3 Hz), 127.5, 125.8 (d, *J* = 5.0 Hz), 122.2, 121.7 (d, *J* = 2.5 Hz), 121.1 (d, *J* = 5.0 Hz), 121.1 (d, *J* = 13.8 Hz), 108.7, 55.8; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -130.7 (s); GC-MS (EI, 70 eV): *m/z* (%) = 278 (17) [M^+]; HRMS (EI) for $C_{18}H_{11}FO_2$: calcd. 278.0743, found 278.0737.

7-(*tert*-butyl)-5-fluoro-2-methoxy-11*H*-benzo[*b*]fluoren-11-one (2v): Orange solid (49.2 mg, 49%); m.p. 183−184 ºC; IR (KBr, cm^{-1}): ν = 1706 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.88 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, J_1 = 8.5 Hz, J_2 = 2.5, Hz 1H), 3.88 (s, 3H), 1.45(s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.9(d, *J* = 2.5 Hz), 160.7, 152.9, 152.2 (d, *J* = 256.3 Hz), 137.6, 135.1 (d, *J* = 1.3 Hz), 133.7 (d, *J* = 6.3 Hz), 132.6 (d, *J* = 5.0 Hz), 130.3 (d, *J* = 2.5 Hz), 128.3 (d, *J* = 15.0 Hz), 126.2, 125.6 (d, *J* = 5.0 Hz), 122.0, 121.3 (d, *J* = 2.5 Hz), 121.1 (d, *J* = 15.0 Hz), 116.5 (d, *J* = 5.0 Hz), 108.6, 55.7, 35.4, 31.1; ^{19}F NMR ($CDCl_3$, 376 MHz): *δ* -131.2 (s); GC-MS (EI, 70 eV): *m/z* (%) = 334 (8) [M^+]; HRMS (EI) for $C_{22}H_{19}FO_2$: calcd. 334.1369, found 334.1361.

5-(*tert*-butyl)-7-(2-chlorophenyl)-11*H*-benzo[*b*]fluoren-11-one (3w): Yellow solid (73.7 mg, 62%); m.p. 183−185 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (s, 1H), δ 8.09 (s, 1H), 7.90 (t, *J* = 6.5 Hz, 2H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.57-7.50 (m, 3H), 7.45 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 7.42-7.32(m, 3H), 1.83 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 148.2, 146.1, 140.5, 138.1, 137.6, 137.5, 136.4, 134.8, 133.7, 133.2, 132.7, 131.43, 130.21, 130.18, 129.0, 128.9, 128.5, 128.1, 127.4, 127.1, 124.2, 123.3, 37.7, 33.0; ESI-MS: *m/z* (%) = 397.14 (100) [M+1]$^+$; HRMS (ESI) for $C_{27}H_{22}ClO$ [M+1]$^+$: calcd. 397.1359, found 397.1364.

7-methyl-11*H*-benzo[*b*]fluoren-11-one (5):[8d] Yellow solid (46.9 mg, 60%); m.p.144−145 ºC (lit.[8d] m.p. 144−146 ºC); IR (KBr, cm^{-1}): ν = 1706 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ8.13 (s, 1H), 7.80−7.45 (m, 3H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.61 (s, 1H), 7.56−7.55 (m, 1H), 7.36−7.30 (m, 2H), 2.53 (s, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 244(38) [M^+].

General Procedure for the Synthesis of Benzo[*b*]fluorenones 8. 7 (0.2 mmol), Cu(0) powder (0.64 mg, 5 mol %), Selectfluor (141.7 mg, 0.4 mmol, 2 equiv), and CH_3CN (2 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at room temperature for 3 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc (10/1, V/V) as eluent to give pure **8**.

5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8a)[35]**:** Orange solid (46.5 mg, 76%); m.p. 222−223 ºC (Lit.[34] m.p. 232); IR (KBr, cm^{-1}): ν = 1705 (C=O), 1623, 1514, 1461, 1106, 1025, 804, 761, 699; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.97 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.76 (dd, J_1 = 6.5 Hz, J_2 = 0.9 Hz, 1H), 7.65−7.60 (m, 3H), 7.51−7.42 (m, 5H), 7.26−7.19 (m, 2H), 6.35 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 145.2, 137.4, 136.9, 136.5, 135.3,134.70, 134.66, 133.4, 132.6, 130.8, 129.7, 129.3, 128.9, 128.6, 128.3, 127.1, 126.8, 125.2, 124.2, 123.8; ESI-MS: *m/z* (%) = 307.07 (100) [M+1]$^+$.

5-*o*-tolyl-11*H*-benzo[*b*]fluoren-11-one (8b): Reddish brown solid (40.3 mg, 63%); m.p. 213−215 ºC; IR (KBr, cm^{-1}): ν = 1711 (C=O), 16667, 1625, 1601, 1513, 806, 763, 727; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.00−7.96 (m, 1H), 7.76 (dd, J_1 = 6.0 Hz, J_2 = 1.0 Hz, 1H), 7.52−7.41 (m, 5H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.28−7.20 (m, 3H), 6.27 (d, *J* = 6.5 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 145.2, 137.0, 136.7, 136.50, 136.47, 135.3, 135.0, 134.0, 133.6, 132.7, 130.9, 130.7, 129.8, 129.1, 128.70, 128.65, 126.9, 126.8, 126.7, 125.1, 124.2, 123.3, 19.6; ESI-MS: *m/z* (%) = 321.25(100) [M+1]$^+$; HRMS (ESI) for $C_{24}H_{17}O$ [M+1]$^+$: calcd. 321.1279, found 321.1275.

5-*p*-tolyl-11*H*-benzo[*b*]fluoren-11-one (8c): Orange solid (44.2 mg, 69%); m.p. 219−221 ºC; IR (KBr, cm^{-1}): ν = 1710 (C=O), 1625, 1602, 1543, 1508, 725, 670; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.95 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 7.76−7.74 (m, 1H), 7.50−7.42 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26−7.20 (m, 2H), 6.43 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.4, 145.4, 138.1, 137.2, 136.5,135.4, 134.8, 134.7, 134.3, 133.5, 132.6, 130.8, 130.0, 129.6, 128.9, 128.6, 127.2, 126.8, 125.1, 124.2, 123.9, 21.5; ESI-MS: *m/z* (%) = 321.11(100) [M+1]$^+$; HRMS (ESI) for $C_{24}H_{17}O$ [M+1]$^+$: calcd. 321.1279, found 321.1282.

5-(4-pentylphenyl)-11*H*-benzo[*b*]fluoren-11-one (8d): Orange solid (44.4 mg, 59%), m.p. 118−120 ºC; IR (KBr, cm^{-1}): ν =1710 (C=O), 1668, 1625, 1603, 1508, 701, 672; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.97−7.94 (m, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.50−7.42 (m, 5H), 7.33−7.31 (m, 2H), 7.24−7.19 (m, 2H), 6.41−6.36 (m, 1H), 2.89−2.79 (m, 2H), 1.83−1.77 (m, 2H), 1.47−1.40 (m, 4H), 0.98 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.4, 145.3, 143.1, 137.2, 136.5, 134.9, 134.7, 134.5, 133.5, 132.6, 130.8, 129.5, 129.3, 128.9, 128.7, 128.6, 127.3, 126.8, 125.1, 124.2, 123.9, 35.8, 31.6, 31.1, 22.6, 14.1; ESI-MS: *m/z* (%) = 377.15(100) [M+1]$^+$; HRMS (ESI) for $C_{28}H_{25}O$ [M+1]$^+$: calcd. 377.1905, found 377.1910.

5-(4-ethoxyphenyl)-11*H*-benzo[*b*]fluoren-11-one (8e): Orange solid (44.1 mg, 63%); m.p. 194−196 ºC; IR (KBr, cm^{-1}): ν =1705 (C=O), 1624, 1608, 1507, 1471, 703, 670; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.95 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 1H), 7.76−7.74 (m, 1H), 7.53−7.45 (m, 3H), 7.33−7.30 (m, 2H), 7.26−7.22 (m, 2H), 7.15 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 2H), 6.50−6.47 (m, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 1.54 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ193.4, 159.0, 145.4, 137.4, 136.5, 135.7, 134.7, 134.6, 133.5, 132.6, 130.9, 130.8, 129.3, 128.9, 128.6, 127.2, 126.8, 125.1, 124.2, 123.9, 115.2, 63.7, 14.9; ESI-MS: *m/z* (%) = 351.10(100) [M+1]$^+$; HRMS (ESI) for $C_{25}H_{19}O_2$ [M+1]$^+$: calcd. 351.1385, found 351.1389.

5-(4-methoxyphenyl)-11*H*-benzo[*b*]fluoren-11-one (8f): Orange solid (47.7 mg, 71%); m.p. 203−205 ºC; IR (KBr, cm^{-1}): ν =1741 (C=O), 1706, 1625, 1508, 1464, 728, 672; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.95 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 1H), 7.76−7.74 (m, 1H), 7.53−7.45 (m, 3H), 7.35−7.32 (m, 2H), 7.26−7.21 (m, 2H), 7.17−7.15 (m, 2H), 6.47 (dd, J_1 = 6.0 Hz, J_2 = 2.5 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 159.6, 145.4, 137.4, 136.6, 135.7, 134.7, 134.5, 133.5, 132.6, 130.9, 130.8, 129.4, 128.9, 128.6, 127.2, 126.8, 125.1, 124.2, 123.9, 114.7, 55.4;

ESI-MS: *m/z* (%) = 337.07(100) $[M+1]^+$; HRMS (ESI) for $C_{24}H_{17}O_2$ $[M+1]^+$: calcd. 337.1229, found 337.1224.

5-(4-propylphenyl)-11*H*-benzo[*b*]fluoren-11-one (8g): Orange solid (42.5 mg, 61%); m.p. 142−144 °C; IR (KBr, cm^{-1}): ν = 1710 (C=O), 1625, 1602, 1507, 1465, 701, 671; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.96 (dd, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 1H), 7.75 (dd, J_1 = 6.5 Hz, J_2 = 1.0 Hz, 1H), 7.52−7.42 (m, 5H), 7.32 (d, J = 8.0 Hz, 2H), 7.25−7.19 (m, 2H), 6.37 (dd, J_1 = 7.0 Hz, J_2 = 1.0 Hz, 1H), 2.80 (t, J = 7.5 Hz, 2H), 1.86−1.79 (m, 2H), 1.07 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.4, 145.3, 142.8, 137.2, 135.4, 135.4, 134.9, 134.7, 134.6, 133.5, 132.6, 130.8, 129.5, 129.4, 128.9, 128.6, 127.3, 126.8, 125.1, 124.2, 123.9, 37.9, 24.5, 13.8; ESI-MS: *m/z* (%) = 349.12(100) $[M+1]^+$; HRMS (ESI) for $C_{26}H_{21}O$ $[M+1]^+$: calcd. 349.1592, found 349.1596.

5-(4-(pentyloxy)phenyl)-11*H*-benzo[*b*]fluoren-11-one (8h): Orange solid (46.3 mg, 59%); m.p. 168−170 °C; IR (KBr, cm^{-1}): ν =1705 (C=O), 1624, 1609, 1507, 1467; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.95 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 1H), 7.76−7.74 (m, 1H), 7.54−7.45 (m, 3H), 7.33−7.30 (m, 2H), 7.26−7.22 (m, 2H), 7.16−7.13 (m, 2H), 6.50-6.48 (m, 1H), 4.12 (t, J = 6.5 Hz, 2H), 1.95−1.89 (m, 2H), 1.59−1.53 (m, 2H), 1.51−1.44 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.4, 159.2, 145.4, 137.4, 136.5, 135.6, 134.7, 134.6, 133.5, 132.6, 130.84, 130.77, 129.2, 128.9, 128.6, 127.2, 126.8, 125.1, 124.2, 123.9, 115.2, 68.2, 29.1, 28.3, 22.5, 14.1; ESI-MS: *m/z* (%) = 393.16(100) $[M+1]^+$; HRMS (ESI) for $C_{28}H_{25}O_2$ $[M+1]^+$: calcd. 393.1855, found 393.1851.

5-(4-ethylphenyl)-11*H*-benzo[*b*]fluoren-11-one (8i): Yellow solid (42.1 mg, 63%); m.p. 145−146 °C; IR (KBr, cm^{-1}): ν =1709 (C=O), 1625, 1602, 1508, 1465, 806, 765; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.96−7.95 (m, 1H), 7.75 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 7.52−7.44 (m, 5H), 7.33 (d, J = 8.0 Hz, 2H), 7.26−7.20 (m, 2H), 6.40 (dd, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 1H), 2.86 (q, J = 7.5 Hz, 2H), 1.42 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 145.3, 144.4, 137.2, 136.5, 135.4, 134.9, 134.7, 134.5, 133.4, 132.6, 130.7, 129.6, 128.8, 128.7, 128.6, 127.2, 126.8, 125.1, 124.1, 123.9, 28.8, 15.5; ESI-MS: *m/z* (%) = 335.20(100) $[M+1]^+$; HRMS (ESI) for $C_{25}H_{19}O$ $[M+1]^+$: calcd. 335.1436, found 335.1439.

5-(2-chlorophenyl)-11*H*-benzo[*b*]fluoren-11-one (8j): Reddish brown solid (61.2 mg, 90%); m.p. 228−230 °C; IR (KBr, cm^{-1}): ν = 1669 (C=O), 1600, 1581, 1512, 1429, 805; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.99 (dd, J_1 = 7.0 Hz, J_2 = 2..0 Hz, 1H), 7.78 (dd, J_1 = 6.5 Hz, J_2 = 1.5 Hz, 1H), 7.71 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.60−7.58 (m, 1H), 7.54−7.49 (m, 3H), 7.42 (dd, J_1 = 7.5 Hz, J_2 = 2..0 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.28−7.23 (m, 2H), 6.33 (d, J = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 144.8, 136.5, 136.2, 136.1, 135.9, 135.0, 134.4, 133.5, 132.6, 131.7, 131.4, 131.0, 130.3, 130.1, 129.3, 129.0, 127.7, 127.0, 126.4, 125.8, 124.3, 123.2; ESI-MS: *m/z* (%) = 341.08(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}ClO$ $[M+1]^+$: calcd. 341.0733, found 341.0738.

5-(4-chlorophenyl)-11*H*-benzo[*b*]fluoren-11-one (8k): Yellow solid (49.6 mg, 73%); m.p. 264−266 °C; IR (KBr, cm^{-1}): ν = 1707 (C=O), 1625, 1599, 1565, 1514, 805, 761; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.98−7.96 (m, 1H), 7.78−7.76 (m, 1H), 7.62−7.56 (m, 2H), 7.52−7.47 (m, 2H), 7.46−7.41 (m, 2H), 7.35−7.33 (m, 1H), 7.28−7.23 (m, 2H), 6.42−6.40 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 144.8, 136.6, 135.5, 135.3, 134.9, 133.4, 132.9, 132.5, 130.9, 130.7, 129.9, 129.2, 128.9, 128.6, 128.1, 127.0, 126.8, 125.6, 124.4, 123.7; ESI-MS: *m/z* (%) = 341.14(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}ClO$ $[M+1]^+$: calcd. 341.0733, found 341.0739.

5-(3-bromophenyl)-11*H*-benzo[*b*]fluoren-11-one (8l): Yellow solid (51.5 mg, 67%); m.p. 153−155 °C; IR (KBr, cm^{-1}): ν =1709 (C=O), 1666, 1625, 1598, 1559, 806, 765; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.96 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 1H), 7.79−7.74 (m, 2H), 7.61 (s, 1H), 7.53−7.47 (m, 3H), 7.45−7.37 (m, 2H), 7.29−7.25 (m, 2H), 6.41 (dd, J_1 = 6.0 Hz, J_2 = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 144.7, 139.7, 136.6, 135.5, 134.9, 133.4, 132.83, 132.77, 132.5, 131.6, 130.9 (3C), 129.2, 129.0, 128.6, 127.0, 126.8, 125.6, 124.4, 123.7, 123.3; ESI-MS: *m/z* (%) = 385.05(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}BrO$ $[M+1]^+$: calcd. 385.0228, found 385.0224.

5-(4-bromophenyl)-11*H*-benzo[*b*]fluoren-11-one (8m): Brown solid (53.8 mg, 70%); m.p. 290−292 °C; IR (KBr, cm^{-1}): ν = 1726 (C=O), 1622, 1598, 1446, 828, 762; ^{1}H NMR (500 MHz, $CDCl_3$): δ8.25 (s, 1H), 7.96 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 7.79−7.75 (m, 3H), 7.51−7.46 (m, 2H), 7.41 (dd, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 7.33−7.30 (m, 2H), 7.28−7.25 (m, 2H), 6.45−6.44 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.8, 144.8, 136.7, 136.6, 136.5, 135.3, 134.7, 133.9, 133.5, 133.1, 132.6, 131.6, 130.8, 129.1, 128.9, 126.9, 126.7, 125.5, 124.3, 123.7, 122.6; ESI-MS: *m/z* (%) = 385.05(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}BrO$ $[M+1]^+$: calcd. 385.0228, found 385.0223.

5-cyclohexenyl-11*H*-benzo[*b*]fluoren-11-one (8n): Yellow solid (46.5 mg, 75%); m.p. 179−181 °C; IR (KBr, cm^{-1}): ν = 2921, 1707 (C=O), 1623, 1603, 1511. 1467, 803, 751; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.91−7.87 (m, 2H), 7.78 (d, J = 7.0 Hz, 1H), 7.58−7.52 (m, 2H), 7.49−7.46 (m, 1H), 7.35−7.32 (m, 1H), 5.89 (dd, J_1 = 3.5 Hz, J_2 = 1.5 Hz,, 1H), 2.42−2.33 (m, 4H), 2.02−1.91 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ193.4, 145.5, 137.1, 136.5, 136.3, 134.9, 134.5, 133.8, 133.7, 132.7, 130.9, 128.9, 128.6, 128.5, 126.7, 126.4, 124.5, 124.3, 123.9, 29.4, 25.6, 23.2, 22.1; ESI-MS: *m/z* (%) = 311.13(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{19}O$ $[M+1]^+$: calcd. 311.1436, found 311.1432.

7-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8o): Yellow solid (57.6 mg, 90%); m.p. 155−157 °C; IR (KBr, cm^{-1}): ν = 1708 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.74 (dd, J_1 = 6.5 Hz, J_2 = 1.0 Hz, 1H), 7.65−7.61 (m, 3H), 7.43−7.40 (m, 2H), 7.32 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.23−7.17 (m, 3H), 6.29 (d, J = 7.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ193.3, 145.2, 139.4, 137.6, 137.1, 136.6, 135.6, 134.6, 134.1, 131.9, 131.6, 130.6, 129.8, 129.3, 129.0, 128.5, 128.3, 126.4, 125.1, 124.1, 123.8, 22.1; ESI-MS: *m/z* (%) = 321.25(100) $[M+1]^+$; HRMS (ESI) for $C_{24}H_{17}O$ $[M+1]^+$: calcd. 321.1279, found 321.1275.

7-chloro-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8p): Yellow solid (41.5 mg, 61%); m.p. 215−217 °C; IR (KBr, cm^{-1}): ν = 1711 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.75 (d, J = 7.0 Hz, 1H), 7.66−7.62 (m, 3H), 7.45−7.39 (m, 4H), 7.26−7.19 (m, 2H), 6.33 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.8, 144.8, 137.8, 136.7, 136.53, 136.51, 135.3, 134.8, 133.9, 132.8, 132.0, 131.7, 129.7, 129.5, 129.0, 128.7, 127.7, 126.2, 124.8, 124.3, 124.0; ESI-MS: *m/z* (%) = 341.08(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}ClO$ $[M+1]^+$: calcd. 341.0733, found 341.0736.

7-bromo-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8q): Yellow solid (43.0 mg, 56%); m.p. 213−215 °C; IR (KBr, cm^{-1}): ν = 1711 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 7.0 Hz, 1H), 7.66−7.62 (m, 3H), 7.60−7.55 (m, 2H), 7.42−7.39 (m, 2H), 7.26−7.19 (m, 2H), 6.31 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.7, 144.7, 138.1, 136.6, 136.48, 136.46, 134.8, 133.7, 132.9, 132.0, 131.9, 130.2, 129.6, 129.5, 129.4, 129.0, 128.7, 124.8, 124.3, 124.0, 123.8; ESI-MS: *m/z* (%) = 385.08(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}BrO$ $[M+1]^+$: calcd. 385.0228, found 385.0233.

7-*tert*-butyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8r): Yellow solid (49.3 mg, 68%); m.p. 158−160 °C; IR (KBr, cm^{-1}): ν = 1710 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 6.5 Hz, 1H), 7.64−7.56 (m, 4H), 7.44−7.41 (m, 3H), 7.24−7.18 (m, 2H), 6.35 (d, J = 7.5 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 193.3, 152.2, 145.3, 137.6, 136.9, 136.6, 135.3, 134.8, 134.6, 132.1, 131.5, 130.4, 129.7, 129.2, 128.5, 128.3, 125.5, 124.8, 124.1, 123.8, 122.6, 35.2, 31.0; ESI-MS: *m/z* (%) = 363.17(100) $[M+1]^+$; HRMS (ESI) for $C_{27}H_{23}O$ $[M+1]^+$: calcd. 363.1749, found 363.1753.

7-methoxy-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8s): Brown solid (43.7 mg, 65%); m.p. 129−131 °C; IR (KBr, cm^{-1}): ν =1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.65−7.59 (m, 3H), 7.43 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H),

7.24−7.12 (m, 3H), 6.78 (d, *J* = 2.5 Hz, 1H), 6.30 (d, *J* = 7.5 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 160.3, 145.0, 138.8, 137.7, 136.8, 136.2, 134.4, 133.6, 132.3, 130.7, 129.7, 129.4, 128.6, 128.5, 128.4, 125.1, 124.1, 123.7, 118.2, 107.1, 55.3; ESI-MS: *m/z* (%) = 337.12(100) $[M+1]^+$; HRMS (ESI) for $C_{24}H_{17}O_2$ $[M+1]^+$: calcd. 337.1229, found 337.1224.

9-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8t): Yellow solid (30.7 mg, 48%); m.p. 211−212 °C; IR (KBr, cm^{-1}): ν =1708 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.76 (dd, J_1 = 6.5 Hz, J_2 = 1.0 Hz, 1H), 7.63−7.59 (m, 3H), 7.43−7.40 (m, 2H), 7.35−7.32 (m, 3H), 7.25−7.18 (m, 2H), 6.31 (d, *J* = 7.5 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.6, 145.2, 137.9, 137.6, 137.3, 136.6, 135.2, 135.1, 134.7, 132.6, 132.2, 129.8 (2C), 129.2, 128.6, 128.3, 127.9, 125.6, 124.2, 123.8, 121.6, 19.8; ESI-MS: *m/z* (%) = 321.08(100) $[M+1]^+$; HRMS (ESI) for $C_{24}H_{17}O$ $[M+1]^+$: calcd. 321.1279, found 321.1275.

9-bromo-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8u): Yellow solid (38.4 mg, 50%); m.p. 189−191 °C; IR (KBr, cm^{-1}): ν = 1705 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.79−7.77 (m, 2H), 7.64−7.62 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.42−7.40 (m, 2H), 7.30−7.29 (m, 1H), 7.26−7.20 (m, 2H), 6.33 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.8, 144.7, 138.6,137.2, 136.6, 136.2, 134.9, 134.8, 133.6, 132.4, 131.0, 129.7, 129.4, 129.1, 190.0, 128.6, 127.0, 126.0, 124.5, 124.4, 124.1; ESI-MS: *m/z* (%) = 385.08(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}BrO$ $[M+1]^+$: calcd. 385.0228, found 385.0224.

3-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8v): Yellow solid (39.1 mg, 61%); m.p. 193−195 °C; IR (KBr, cm^{-1}): ν = 1735 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.96−7.94 (m, 1H), 7.65−7.60 (m, 4H), 7.50−7.45 (m, 3H), 7.43−7.41 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.10 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 145.7, 145.5, 137.6, 136.8, 135.3, 134.5, 134.3, 133.4, 133.2, 130.7, 129.8, 129.4, 129.2, 128.8, 128.2, 127.1, 126.7, 124.9, 124.7, 124.1, 22.3; ESI-MS: *m/z* (%) = 321.17(100) $[M+1]^+$; HRMS (ESI) for $C_{24}H_{17}O$ $[M+1]^+$: calcd. 321.1279, found 321.1275.

3,7-dimethyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8w): Yellow solid (55.5 mg, 83%); m.p. 134−136 °C; IR (KBr, cm^{-1}): ν = 1708 (C = O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.64−7.61 (m, 4H), 7.43−7.40 (m, 2H), 7.31 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.23 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.04 (s, 1H), 2.40 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 145.52, 145.48, 139.2, 137.7, 137.0, 135.6, 134.4, 133.9, 132.4, 131.6, 130.5, 129.8, 129.3, 129.2, 128.8, 128.2, 126.4, 124.8, 124.7, 124.0, 22.3, 22.0; ESI-MS: *m/z* (%) = 335.25(100) $[M+1]^+$; HRMS (ESI) for $C_{25}H_{19}O$ $[M+1]^+$: calcd. 335.1436, found 335.1441.

3-fluoro-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8x): Yellow solid (41.5 mg, 64%); m.p. 201−203 °C; IR (KBr, cm^{-1}): ν =1734 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, J_1 = 8.5 Hz, J_2 = 5.5 Hz, 1H), 7.65−7.63 (m, 2H), 7.52−7.48 (m, 3H), 7.43−7.40 (m, 2H), 7.26−7.21 (m, 1H), 6.93−6.89 (m, 1H), 5.97 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.5, 166.9(d, *J* = 252.5 Hz), 148.0, 147.9, 136.8, 136.75, 135.3, 134.0 (d, *J* = 2.5 Hz), 133.6, 132.7, 130.8, 129.5, 129.4, 129.0, 128.6, 128.3, 127.2 (d, *J* = 10.0 Hz), 126.2 (d, *J* = 10.0 Hz), 125.2, 115.6 (d, *J* = 23.8 Hz), 111.4 (d, *J* = 25.0 Hz); ESI-MS: *m/z* (%) = 325.17 (100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}FO$ $[M+1]^+$: calcd. 325.1029, found 325.1025.

3-fluoro-7-methyl-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8y): Yellow solid (54.8 mg, 81%); m.p. 179−181 °C; IR (KBr, cm^{-1}): ν =1711 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.72 (dd, J_1 = 8.0 Hz, J_2 = 5.0 Hz, 1H), 7.66−7.62 (m, 3H), 7.42−7.39 (m, 2H), 7.34 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.24 (s, 1H), 6.91−6.87 (m, 1H), 5.91 (dd, J_1 = 9.5 Hz, J_2 = 5.5 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.5, 166.8 (d, *J* = 252.5 Hz), 147.9 (d, *J* = 10.0 Hz), 139.5, 136.9 (d, *J* = 7.5 Hz), 134.8, 134.2 (d, *J* = 2.5 Hz), 132.8 (d, *J* = 2.5 Hz), 132.0, 131.8, 130.6, 129.6, 129.4, 129.3, 128.6, 126.6, 126.1, 126.0, 125.0, 115.4 (d, *J* = 22.5 Hz), 111.3 (d, *J* = 25.0 Hz); ESI-MS: *m/z* (%) = 339.17(100) $[M+1]^+$; HRMS (ESI) for $C_{24}H_{16}FO$ $[M+1]^+$: calcd. 339.1185, found 339.1189.

2-fluoro-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8z): Yellow solid (40.2 mg, 62%); m.p. 191−193 °C; IR (KBr, cm^{-1}): ν = 1712 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.94 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 1H), 7.65−7.59 (m, 3H), 7.49−7.45 (m, 3H), 7.43−7.37 (m, 3H), 6.90−6.86 (m, 1H), 6.28 (dd, J_1 = 8.5 Hz, J_2 = 5.0 Hz, 1H);^{13}C NMR (125 MHz, $CDCl_3$): δ 191.9 (d, *J* = 2.5 Hz), 163.1 (d, *J* = 250.0 Hz), 141.0 (d, *J* = 2.5 Hz), 138.7 (d, *J* = 6.3 Hz), 137.2, 137.0, 134.6, 134.3, 133.1, 132.6, 130.9, 129.7, 129.4, 129.2, 128.5, 127.1, 126.9, 125.6, 125.2 (d, *J* = 7.5 Hz), 121.2 (d, *J* = 23.8 Hz), 111.2 (d, *J* = 22.5 Hz); ESI-MS: *m/z* (%) = 325.17(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}FO$ $[M+1]^+$: calcd. 325.1029, found 325.1024.

3-chloro-5-phenyl-11*H*-benzo[*b*]fluoren-11-one (8za): Yellow solid (45.6 mg, 67%); m.p. 243−245 °C; IR (KBr, cm^{-1}): ν = 1710 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.67−7.63 (m, 4H), 7.54−7.48 (m, 3H), 7.43−7.39 (m, 2H), 7.21 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 6.25 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.8, 146.7, 140.9, 136.84, 136.78, 135.4, 134.8, 134.1, 133.6, 132.5, 130.8, 129.6, 129.49, 129.2, 128.72 128.66, 127.3, 127.2, 125.5, 125.2, 124.3; ESI-MS: *m/z* (%) = 341.08(100) $[M+1]^+$; HRMS (ESI) for $C_{23}H_{14}ClO$ $[M+1]^+$: calcd. 341.0733, found 341.0728.

7-phenyl-12*H*-indeno[1,2-*b*]phenanthren-12-one (8zb): Yellow solid (51.3 mg, 72%); m.p. 251−253 °C; IR (KBr, cm^{-1}): ν = 1704 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.80 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.76−7.72 (m, 3H), 7.67−7.62 (m, 4H), 7.47−7.44 (m, 3H), 7.25−7.18 (m, 2H), 6.30 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.6, 145.0, 137.8, 137.4, 136.3, 135.9, 135.4, 134.7, 132.5, 131.9, 131.4, 130.6, 129.80 (2C), 129.78, 129.3, 128.7, 128.4, 127.5, 127.3, 124.8, 124.2, 123.6, 123.2, 119.3; ESI: m/z (%) = 357.12 (100) $[M+1]^+$; HRMS (ESI) for $C_{27}H_{17}O$ $[M+1]^+$: calcd. 357.1279, found 357.1284.

Mechanistic Studies.

Studies on the Intramolecular Kinetic Isotope Effects (KIE) Based on Substrate 1a-D. 1a-D was synthesized from 1-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)ethanone and *o*-deuterated 4-methyl benzaldehyde (deuterium enrichment ≥ 99%) according to the reported procedure for the synthesis of **1**.[25,26]

Procedure: **1a-D** (91.0 mg, 0.3 mmol), Cu(0) powder (0.96 mg, 5 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and CH_3CN (2 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at 45 °C for 1.5 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-CH_2Cl_2 (5/1, V/V) as eluent to give pure mixture of **2a** and **2a-D** (55.2 mg, 70%). On the basis of ^{1}H NMR spectra analysis, the intramolecular competitive KIE was calculated as $k_H/k_D \approx 1.0$.

Direct Conversion of 3a to 2a under the Standard Reaction Conditions. Procedure: **3a** (91.1 mg, 0.3 mmol), Cu(0) powder (0.96 mg, 5 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and CH_3CN (2 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at 45 °C for 1.5 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite.After evaporation of the solvent under vacuum, the residue was prepared for GC-MS analysis. No formation of **2a** was detected by GC-MS analysis while **3a** was recovered quantitatively.

Subjection of 1a to the Standard Reaction Conditions except under Argon Atmosphere. Procedure: **1a** (90.6 mg, 0.3 mmol), Cu(0) powder (0.96 mg, 5 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and CH_3CN (2 mL) were added to a 10-mL flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the resultant mixture in the sealed tube was frozen by immersion of the flask in liquid N_2. When solvent was completely frozen, the flask was opened to the vacuum (high vacuum) and pumped for 2-3 minutes, with the flask still immersed in liquid N_2. The flask was then closed and warmed until solvent completely melted. This process was repeated three times and after the last cycle the flask was

backfilled with an inert Ar gas. The reaction mixture was stirred at 45 ºC for 1.5 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-CH_2Cl_2 (5/1, V/V) as eluent to give pure **2a** (51.1 mg, 65%).

Treatment of 7a under reaction conditions that the Cu(0)/Selectfluor system did not participate. 7a (0.2 mmol) and CH_3CN (2 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at room temperature or 80 ºC for 3 h. Upon completion, the resulting mixture was detected by GC-MS, and no formation of **8a** was confirmed either at room temperature or 80 ºC.

Preparation of epoxy compound 9. 9 was prepared according to a modified procedure of a reported literature.[27] Procedure: (*E*)-3-phenyl-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one **7a** (92.5 mg, 0.3 mmol) and THF (2 mL) were added to a screw vial equipped with a magnetic stirring bar. Urea hydrogenperoxide (31 mg, 0.33 mmol) and DBU (11.3 μL, 1.68 mmol) were added at 0 ºC, and the mixture was gradually warmed to room temperature. After being stirred for 24 h, the reaction mixture was diluted with AcOEt, and washed with saturated aqueous $Na_2S_2O_3$. Then, organic layer was evaporated to give an oily residue, whichwas purified by silica gel column chromatography (petroleum ether-EtOAc, 6:1, V/V) to afford **9** as a white solid (77.9 mg, 80% yield).

Analytical data for **9**: White solid, R_f = 0.55 (petroleum ether-EtOAc, 6:1); m.p. 98–100 ºC; IR (neat, cm^{-1}): ν = 3010, 1651, 1490, 1305, 990, 800, 755, 570; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09–8.08 (m, 2H), 7.59–7.12 (m, 12H), 4.60 (d, *J* = 2.0 Hz, 1H), 4.27 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.2, 139.9, 137.5, 135.3, 133.9, 131.9, 131.4, 128.8, 128.5, 128.42, 128.39, 128.2, 124.2, 122.4, 95.2, 85.9, 58.4 (2C); GC-MS (EI, 70 eV): *m/z* (%) = 324 (100) [M^+]; HRMS (EI) for $C_{23}H_{16}O_2$: calcd. 324.1150, found 324.1156.

Investigation of 9 as an intermediate for the formation of 8a. 9 (0.2 mmol), Cu(0) powder (0.64 mg, 5 mol %), Selectfluor (141.7 mg, 0.4 mmol, 2 equiv), and CH_3CN (2 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at room temperature for 3 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was detected by GC-MS, and the results showed the reaction gave complicated products while no formation of **8a** was detected.

Studies on the Intramolecular Kinetic Isotope Effects (KIE) Based on Substrate 7a-D. 7a-D was synthesized from 1-(2-(phenylethynyl)phenyl)ethanone and *o*-deuterated 4-methyl benzaldehyde (deuterium enrichment ≥ 99%) according to the reported procedure for the synthesis of **1**.[26,27]

Procedure: **7a-D** (92.8 mg, 0.3 mmol), Cu(0) powder (0.96 mg, 5 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and CH_3CN (2 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at room temperature for 3 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-CH_2Cl_2 (5/1, V/V) as eluent to give pure mixture of **8a** and **8a-D** (68.8 mg, 75%). On the basis of ^{1}H NMR spectra analysis, the intramolecular competitive KIE was calculated as $k_H/k_D \approx 1.0$.

Supporting Information (see footnote on the first page of this article): X-ray structural data (CIF) of compound **8a**, charts for mechanistic studies as well as copies of ^{1}H NMR, ^{13}C NMR spectra of the products.

Acknowledgments

Financial support from the Natural Science Foundation of China (No. 21172197 and 21372201) and Zhejiang Province (No. Y4100201), the Foundation of Science and Technology Department of Zhejiang Province (2011R09002-09), and the opening Foundation of Zhejiang Provincial Top Key Discipline is gratefully acknowledged.

[1] a) Y. Shi, S. Gao, *Tetrahedron* **2016**, *72*, 1717; b) P. Perry, M. Read, R. Davies, S. Gowan, A. Reszka, A. Wood, L. Kelland, S. Neidle, *J. Med. Chem.* **1999**, *42*, 2679; (c) Y. Han, A. Bisello, C. Nakamoto, M. Rosenblatt, M. Chorev, *J. Pept. Res.* **2000**, *55*, 230; (d) M. Zeng, T. E. Ballard, A. Tkachenko, V. Burns, D. Feldheim, C. Melander, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5148; (e) O. Khdour, E. B. Skibo, *Org. Biomol. Chem.* **2009**, *7*, 2140.

[2] a) A. Goel, S. Chaurasia, M. Dixit, V. Kumar, S. Parakash, B. Jena, J. K. Verma, M. Jain, R. S. Anand, S. Manoharan, *Org. Lett.* **2009**, *11*, 1289; b) D. Tilly, S. S. Samanta, F. Faigl, J. Mortier, *Tetrahedron Lett.* **2002**, *43*, 8347; c) C. D. Ertl, H. J. Bolink, C. E. Housecroft, E. C. Coustable, E. Ortí, J. M. Junquera-Hernández, M. Neuburger, N. M. Shavaleev, M. K. Nazeeruddin, D. Vonlanthen, *Eur. J. Org. Chem.* **2016**, 2037; d) M. Romain, D. Tondelier, B. Geffroy, O. Jeannin, E. Jacques, J. Rault-Berthelot, C. Poriel, *Chem.-Eur. J.* **2015**, *21*, 9426.

[3] S. Wang, B. Wen, N. Wang, J. Liu, L. He, *Arch. Pharm. Res.* **2009**, *32*, 2009.

[4] a) G. Qabaja, G. B. Jones, *J. Org. Chem.* **2000**, *65*, 7187; b) G. A. Salman, M. Hussain, A. Villinger, P. Langer, *Synlett* **2010**, 3031.

[5] T. Akiyama, S. Harada, F. Kojima, Y. Takahashi, C. Imada, Y. Okani, Y. Muraoka, T. Aoyagi, T. Takeuchi, *J. Antibotics* **1998**, *51*, 553.

[6] a) F. M. Hauser, M. J. Zhou, *Org. Chem.* **1996**, *61*, 5722; b) G. A. Olah, T. Mathew, M. Farnia, S. Prakash, *Synlett* **1999**, 1067; c) Z. Yu, D. Velasco, *Tetrahedron Lett.* **1999**, *40*, 3229; d) D. Tejedor, M. C. Prieto-Ramírez, M. Ingold, M. Chicón, F. García-Tellado, *Org. Lett.* **2016**, *18*, 2770.

[7] a) M. Hashemi, Y. Beni, *J. Chem. Res., Synop.* **1999**, 434; b) M. Nikalje, A. Sudalai, *Tetrahedron* **1999**, *55*, 5903; c) Y. Bonvin, E. Callens, I. Larrosa, D. A. Henderson, J. Oldham, A. J. Burton, A. G. M. Barrett, *Org. Lett.* **2005**, *7*, 4549.

[8] a) D. Rodríguez, A. Navarro, L. Castedo, D. Domínguez, C. Saá, *Org. Let*. **2000**, *2*, 1497; b) D. Rodríguez, A. Navarro-Vázquez, L. Castedo, D. Domínguez, C. Saá, *Tetrahedron Lett.* **2002**, *43*, 2717; c) D. Rodríguez, A. Navarro-Vázquez, L. Castedo, D. Domínguez, C. Saá, *J. Org. Chem.* **2003**, *68*, 1938; d) D. Rodríguez, M. Martínez-Esperón, A. Navarro-Vázquez, L. Castedo, D. Domínguez, C. Saá, *J. Org. Chem*. **2004**, *69*, 3842; e) C. Atienza, C. Mateo, Ó. de Frutos, A. M. Echavarren, *Org. Lett.* **2001**, *3*, 153; f) E. Gibzález-Cantalapiedra, Ó. de Frutos, C. Mateo, A. M. Echavarren, *Eur. J. Org. Chem.* **2006**, 1430.

[9] L. R. Danheiser, E. A. Gould, F. R. Pradilla, L. A. Helgason, *J. Org. Chem.* **1994**, *59*, 5514.

[10] a) F. Diederich, P. J. Stang, *Metal-catalyzed cross-coupling reactions*, Wiley-VCH, Weinheim, **1998**; b) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (eds A. de Meijere and F. Diederich), Wiley-VCH, Weinheim, **2004**.

[11] D. Peña, D. Pérez, E. Guitián, L. Castedo, *Eur. J. Org. Chem.* **2003**, 1238.

[12] M. A. Campo, R. C. Larock, *J. Org. Chem.* **2002**, *67*, 5616.

[13] J. P. Waldo, X. Zhang, F. Shi, R. C. Larock, *J. Org. Chem.* **2008**, *73*, 6679.

[14] T.-P. Liu, Y.-X. Liao, C.-H. Xing, Q.-S. Hu, *Org. Lett.* **2011**, *13*, 2452.

[15] G. Qabaja, G. B. Jones, *J. Org. Chem.* **2000**, *65*, 7187.

[16] a) H. Li, R.-Y. Zhu, W.-J. Shi, K.-H. He, Z.-J. Shi, *Org. Lett.* **2012**, *14*, 4850; b) P. Gandeepan, C.-H. Hung, C.-H. Cheng, *Chem. Commun.* **2012**, *48*, 9379.

[17] a) V. S. Thirunavukkarasu, K. Parthasarathy, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2008**, *47*, 9462; b) V. S. Thirunavukkarasu, C.-H. Cheng, *Chem.-Eur. J.* **2011**, *17*, 14723; c) C. L. Sun, N. Liu, B.-J. Li, D.-G. Yu, Y. Wang, Z.-J. Shi, *Org. Lett.* **2010**, *12*, 84; d) P. Gandeepan, P. Rajamalli, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2016**, *5*, 4308; e) D. Shabashov, O. Daugulis, S. Cheme, *J. Org. Chem.*

2008, *73*, 7818; f) D. R Kumar, G. Satyanarayana, *Org. Lett.* **2015**, *17*, 5894.

[18] H. Zhu, Z. Chen, *Org. Lett.* **2016**, *18*, 488.

[19] P. Papainina, K. Y. Armshrov, *Chem. Commun.* **2016**, *52*, 1505.

[20] Z. Shi,; F. Glorius, *Chem. Sci*. **2013**, *4*, 829.

[21] K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, U.K., **2006**.

[22] H. Jiang, Pat. Appl. CN 1055415590, **2016**.

[23] For review articles, see: a) V. Michelet, P. Y. Toullec, J.-P. Genêt, *Angew. Chem., Int. Ed.* **2008**, *47*, 4268; b) L. Anorbe, G. Dominguez, J. Perez Castells, *Chem-Eur. J.* **2004**, *10*, 4938.

[24] For selected recent examples, see: a) X.-H. Ouyang, R.-J. Song, Y. Liu, M. Hu, J.-H. Li, *Org. Lett.* **2015**, *17*, 6038; b) Y. Liu, J.-L. Zhang, M.-B. Zhou, R.-J. Song, J.-H. Li, *Chem. Commun.* **2014**, *50*, 14412; c) M. Hu, R.-J. Song, X.-H. Ouyang, F.-L. Tan, W.-T. Wei, J.-H. Li, *Chem. Commun.* **2016**, *52*, 3328; d) P. Liu, Y. Fukui, P. Tian, Z.-T. He, C.-Y. Sun, N.-Y. Wu, G.-Q. Lin, *J. Am. Chem. Soc.* **2013**, *135*, 11700; e) Y.-T. He, L.-H. Li, Z.-Z. Zhou, H.-L. Hua, Y.-F. Qiu, X.-F. Liu, Y.-M. Liang, *Org. Lett.* **2014**, *16*, 3896.

[25] Z.-Q. Wang, W.-W. Zhang, L.-B. Gong, R.-Y. Tang, X.-H. Yang, Y. Liu, J.-H. Li, *Angew. Chem. Int. Ed.* **2011**, *50*, 8968.

[26] Q. Zhao, Q. Hu, L. Wen, M. Wu, Y. Hu, *Adv. Synth. Catal.* **2012**, *354*, 2113.

[27] J. Zhang, D. Wu, X. Chen, Y. Liu, Z. Xu, *J. Org. Chem.* **2014**, *79*, 4799.

[28] Some preliminary results were published, see: J. Zhang, H. Wang, S. Ren, W. Zhang, Y. Liu, *Org. Lett.* **2015**, *17*, 2920.

[29] W. Zhang, J. Zhang, Y. Liu, Z. Xu, *Synlett* **2013**, *24*, 2709.

[30] a) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Jin, *J. Am. Chem. Soc.* **2006**, *128*, 6790; b) J. K. Kochi, R. T. Tang, T. Bernath, *J. Am. Chem. Soc*. **1973**, *95*, 7114.

[31] M. N. Hopkinson, A. Tessier, A. Salisburg, G. T. Giuffredi, L. E. Combettes, A. D. Gee, V. Gouverneur, *Chem.−Eur. J.* **2010**, *16*, 4739.

[32] a) P. T. Nyffeler, S, G. Duron, M. D. Burkart, S. P. Vincent, C.-H. Wong, *Angew. Chem. Int. Ed.* **2005**, *44*, 192; b) S. Stavber, *Molecules* **2011**, *16*, 6432.

[33] a) G. Dai, R. C. Larock, *J. Org. Chem.* **2003**, *68*, 920; b) A. L. Stein, F. N. Bilheri, J. T. da Rocha, D. F. Back, G. Zeni, *Chem.− Eur. J.* **2012**, *18*, 10602.

[34] K. Ritter, *Synthesis* **1989**, 218.

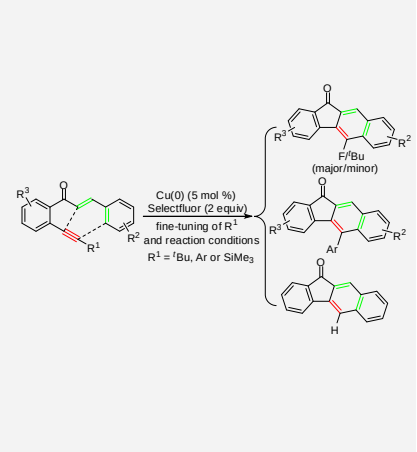
[35] W. Ried, G. Clauss, *Justus Liebigs Ann. Chem.* **1975**, 953.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Table of Contents

Annulation of 1,6-Enynes

A facile and diverse synthesis of benzo[*b*]fluorenone derivatives via copper/Selectfluor system-catalyzed tandem annulation of 1,6-enynes has been developed.



Jian Zhang, Haifeng Zhang, Dongdong, Shi, Hongwei Jin,* and Yunkui Liu* Page No. – Page No.

Facile and Diverse Synthesis of Benzo[*b*]fluorenone Derivatives via Copper/Selectfluor System-Catalyzed Tandem Annulation of 1,6-Enynes.

Keywords: benzo[*b*]fluorenone / copper / Selectfluor / 1,6-enyenes / tandem reaction