Base-controlled 1,6-enyne-bicyclization: divergent synthesis of benzo[*b*]fluorenones and benzo[*b*]fluorenols

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ABSTRACT

An interesting base-controlled protocol for the divergent and atom-economic synthesis of benzo[*b*]fluorenones and benzo[*b*]fluorenols with the great diversity in substitution patterns has been developed. Started from readily available 1,6-enynes, good to excellent yields of the corresponding tetracyclic benzo[*b*]fluorenones and benzo[*b*]fluorenols can be chemoselectively achieved under metal-free conditions. Notably, only K₂CO₃ or Et₃N was required as the promoter here and the reaction can work well in a high-selective manner.

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1. Introduction

The development of eco-friendly synthetic strategy for creating molecular diversity and complexity by means of the generation of several bonds and rings in an atom- and step-economic fashion is highly demanded but full of challenging task in organic chemistry.¹ One such protocol to realize this goal involves the use of domino bicyclization reactions that enable the construction of two new rings in a single operation and offers remarkable advantages such as high convergence, annulations efficiency, operational simplicity, and reduction in the generation of waste, thus rendering the transformations more environmentally friendly.² On the other hand, a high-efficient conversion demands the increase of the collision frequency of the reactants to improve the reaction efficiency. Because of the spatial proximity leading to the high collision frequency of the reaction sites, intramolecular reactions were considered to proceed faster than intermolecular.³ Therefore, the exploration of an intramolecular bicyclization strategy for the atom-economic formation of new bioactive compounds by minimizing waste and by-products continues to be of great interest and importance. Benzo[*b*]fluorene derivatives represent a privileged structure that constitutes the central core of substantial naturally and non-naturally occurring compounds exhibiting significant biological and pharmaceutical activities.⁴ For instance, these structural frameworks show potent antibacterial activity and powerful cytotoxicity against a wide range of cancer cell lines.⁵ Among these derivatives, a unique benzo[*b*]fluorenone motif commonly

Figure 1. Some Benzo[*b*]fluorenone-containing natural products

exists in natural products, represented by kinobscurinone⁶ and kinafluorenone (Figure 1)⁷; they display a variety of interesting antibiotic activities.⁸ With these attributes in mind, the scientific community devotes a numerous effort in finding new synthetic methods for the synthesis of benzo[*b*]fluorenes and their structural analogue. For example, Saa and Echavarren reported the synthesis of benzo[*b*]fluorenones *via* thermal cycloaromatization of ynone-ynes, respectively. But these reactions suffered from poor selectivity (Scheme 1a).⁹ Recently, Hu and co-workers synthesized substituted benzo[*b*]fluorenols from enone-ynes through intramolecular dehydroaromatization and carbonyl reduction, but involved the use of palladium as a metal catalyst and 3-bromoprop-1-yne as an additive (Scheme 1b).¹⁰ Particularly, these reactions only gave benzo[*b*]fluorenones or benzo[*b*]fluorenols. In sharp contrast, a convenient and selective synthesis of benzo[*b*]fluorenones and benzo[*b*]fluorenols using same reagents in a single step is virtually unexplored. During our ongoing domino bicyclization projects,¹¹ we found an efficient methodology for the divergent synthesis of benzo[*b*] fluorenones and benzo[*b*]fluorenols *via*

metal-free 1,6-enyne-bicyclization by controlling different base promoters (Scheme 1c).

Scheme 1. Methods for accessing benzo[*b*]fluorenone and benzo[*b*]fluorenols

2. Results and discussion

Initially, we commenced our evaluation with 1,6-enynes **1a** as a benchmark substrate in the presence of K_2CO_3 (0.5 equiv) in 1,4-dioxane at 100 °C (Table 1, entry 1). To our delight, only benzo[*b*]fluorenones **2a** was obtained in a 62% yield under metal-free conditions without observation of benzo[*b*]fluorenols **3a**. Encouraged by this above result, we then adjusted bases, solvents, and temperatures for the optimized conditions (Table 1). Use of 0.5 equiv of CS_2CO_3 , DBU, and *t*-BuOLi all gave inferior outcomes (entries 2–4). This reaction was met with little success using *t*-BuOK or NaH as a base promoter (entries 5–6). Without basic conditions, the reaction also proceeded but with a lower 38% yield of **2a**. Taking K_2CO_3 as the suitable base, we varied other parameters. Adjusting the amount of K_2CO_3 to 1.0 equivalent at 100 °C proved more efficient, affording the expected product **2a** in 75% yield. Further lowering or raising of the amount of K_2CO_3 or reaction temperatures ranging from 80 °C to 120 °C did not significantly change the yield (entry 1 and entries 8–11). Other solvents such as toluene, acetonitrile (CH_3CN), and *N,N*-dimethylformamide (DMF) were inferior to 1,4-dioxane in terms of reaction yields (entries 12–14). When exchanging K_2CO_3 for Et_3N (1.0 equiv), the reaction gave access to benzo[*b*]fluorenols **3a** in a 71% yield with trace amount of benzo[*b*]fluorenones **2a** (entry 15). After careful optimizations, we found that Et_3N (2.0 equiv) in 1,4-dioxane at 120 °C was the most suitable conditions for the formation of benzo[*b*]fluorenols **3a**, affording the yield of 87%.

With the optimal conditions in hand, the scope of this divergent reaction was then explored by using different base promoters, chemoselectively affording a variety of benzo[*b*]fluorenones **2** and benzo[*b*]fluorenols **3** with a broad structural diversity and good to excellent yields (Schemes 2 and 3). First, we set out to evaluate the formation of benzo[*b*]fluorenones **2** by using different 1,6-enynes in the presence of K_2CO_3 (Scheme 2). The experimental results are presented in Scheme 2 and showed that the variant of substituents on the arylvinyl moiety, including NO_2 , CN, Br, Cl, Me, and MeO, can be well-tolerated. Electronic effect of substituents on the arylvinyl moiety showed an obvious impact on the reaction efficiency. For instance, with the methoxy group on the arylalkynyl moiety (Ar) and upon treatment with

Table 1. Optimization of Reaction Conditions^a

Entry	Base (equiv)	Solvent	T / °C	Yield (%) ^b
2a/3a				
1	K_2CO_3 (0.5)	1,4-dioxane	100	62/ND
2	CS_2CO_3 (0.5)	1,4-dioxane	100	50/ND
3	DBU (0.5)	1,4-dioxane	100	41/ND
4	<i>t</i> -BuOLi (0.5)	1,4-dioxane	100	28/ND
5	<i>t</i> -BuOK (0.5)	1,4-dioxane	100	trace/ND
6	NaH (0.5)	1,4-dioxane	100	trace/ND
7	-	1,4-dioxane	100	38/trace
8	K_2CO_3 (1.0)	1,4-dioxane	100	75/trace
9	K_2CO_3 (1.5)	1,4-dioxane	100	65/trace
10	K_2CO_3 (1.0)	1,4-dioxane	80	22/ND
11	K_2CO_3 (1.0)	1,4-dioxane	120	68/trace
12	K_2CO_3 (1.0)	toluene	100	46/12
13	K_2CO_3 (1.0)	CH_3CN	100	63/trace
14	K_2CO_3 (1.0)	DMF	100	52/trace
15	Et_3N (1.0)	1,4-dioxane	120	trace/71
16	Et_3N (2.0)	1,4-dioxane	120	trace/87
17	(<i>n</i> -Pr) $_3N$ (2.0)	1,4-dioxane	120	trace/71
18	(<i>n</i> -Bu) $_3N$ (2.0)	1,4-dioxane	120	trace/65
19	(<i>i</i> -Bu) $_3N$ (2.0)	1,4-dioxane	120	trace/54
20	DIPEA (2.0) ^c	1,4-dioxane	120	trace/52
21	Et_3N (3.0)	1,4-dioxane	120	trace/76
22	Et_3N (2.0)	1,4-dioxane	100	21/62
23	Et_3N (2.0)	1,4-dioxane	130	trace/72
24	Et_3N (2.0)	DMF	120	trace/trace
25	Et_3N (2.0)	CH_3CN	120	trace/trace
26	Et_3N (2.0)	Toluene	120	17/52

^a Reaction conditions **1** (1.0 mmol), Base (1.0 mmol or 2.0 mmol), 1,4-dioxane (4.0 ml) for 6 hour under air conditions. ^b Isolated yield. ND = No Detected. ^cDIPEA = *N,N*-Diisopropylethylamine

Scheme 2. The synthesis of benzo[*b*]fluorenones **2**

substrates **1** with electron-withdrawing groups like nitro (**1c**) and cyano (**1d**), the desired products **2c** and **2d** were obtained in 66% and 58% yields, respectively. In contrast, the presence of a methoxy group of substrate **1k** resulted in an 88% yield. These observations indicated that substrates **1** bearing electron-withdrawing groups showed the lower reactivity than those with electron-donating counterparts. More sterically encumbered 2-bromophenyl (**1f**) and 2-bromo-5-chlorophenyl (**1g**) substituents were successfully engaged in these K_2CO_3 -promoted bicyclizations, affording the corresponding benzo[*b*]fluorenones **2f** and **2g** in acceptable yields. Similarly, 2-thienyl 1,6-enynes was proven to be successful in the reaction and could be readily converted into the corresponding fluoreno[2,3-*b*]thiophen-9-ones **2i** in a 81% yield. Notably, halogen-containing 1,6-enynes worked well under the optimal reaction conditions, which offer further flexibility for structural modifications by modern coupling. Electronic nature of substituents on the arylalkynyl (Ar) moiety was also probed. The reaction proceeded smoothly with a variety of functional groups on the arylalkynyl moiety of substrates **1**. The substrates **1** bearing -Cl and -F on the arylalkynyl moiety could decrease the reactivity, leading to the formation of benzo[*b*]fluorenones **2r–2u** ranging from 47–79% yields.

Scheme 3. The synthesis of benzo[*b*]fluorenols **3**

After our success with functional benzo[*b*]fluorenones **2**, we devoted our efforts to evaluate the feasibility of the synthesis of benzo[*b*]fluorenols **3** using Et_3N as a base promoter. As we had expected, a great scope is shown by various substituents, including methyl, methoxy, bromo, chloro, and cyano on both the arylalkynyl and arylvinyl moieties of the substrates, providing an easy access to a series of arylated benzo[*b*]fluorenols **3a–3j** in 76%–92% yields. Alternatively, thioenylated 1,6-enynes was also found to be suitable for this reaction. The structures of resultant benzo[*b*]fluorenones **2** and benzo[*b*]fluorenols **3** were fully characterized by their NMR spectroscopy and HRMS. Furthermore, two cases of **2a** and **3a** were determined by X-ray diffraction (Figures 2 and 3).

In general, the present two new reactions showed the following attractive characteristics: (1) the reactions proceed efficiently with formation of water as a major by-product under air conditions, which belongs to environmentally friendly chemistry; (2) the convenient workup is needed *via* simple filtration since the products directly precipitate out of solution after the reaction system is diluted with cold water, which belongs to GAP chemistry;¹² (3) up to two new rings were formed in a one-pot operation without using any metal catalysts; (4) base-controlled divergent synthesis of benzo[*b*]fluorenones and

benzo[*b*]fluorenols with important biological activity was achieved.

Figure 2. The ORTEP drawing of **2a**

Figure 3. The ORTEP drawing of **3a**

Scheme 4 control experiments

To understand the mechanism, several control experiments were performed. Treatment of 1,6-enynes **1a** in the presence of K_2CO_3 under argon conditions gave benzo[*b*]fluorenols **3a** in an 84% yield without observation of desired product **2a** (Scheme 4a). The reaction of **3a** in the presence of K_2CO_3 under air conditions delivered the desired product **2a** in a 92% yield (Scheme 4b). Both above observations indicated that oxygen play a key role in the oxidation process. Without K_2CO_3 , benzo[*b*]fluorenols **3a** was converted into product **2a** in only 48% yield, suggesting that K_2CO_3 promoted the oxidation of benzo[*b*]fluorenols into benzo[*b*]fluorenones. In addition, benzo[*b*]fluorenols **3a** did not be converted into the product **2a** using Et_3N under air conditions (Scheme 4d).

On the basis of our experimental observations and literature precedents,¹¹ a possible mechanistic pathway to products **2** and

3 is illustrated in Schemes 5. Initially, in the presence of suitable bases, 1,6-enynes **1** undergoes intramolecular Diels-Alder (D-A) reaction and enolization to give intermediate **B**, followed by 1,5-H transfer to yield benzo[*b*]fluorenols **3**, which converts into the final benzo[*b*]fluorenones **2** via K₂CO₃-promoted oxidation. With Et₃N, benzo[*b*]fluorenol products **3** was retained, which may be attributed to synergistic effect **between the basicity of Et₃N** and the presence of intermolecular N-HO hydrogen bonds between Et₃N and hydroxyl group of benzo[*b*]fluorenols **3**,¹³ **although the detailed reason is not clear for us so far.**

Scheme 5. Proposed mechanism for forming **2** and **3**

3. Conclusions

In conclusion, we have established a practical base-promoted 1,6-enyne-bicyclization, enabling a divergent pathway to generate a wide range of arylated benzo[*b*]fluorenones and benzo[*b*]fluorenols in an atom-economic and functional-group-compatible manner. The former reaction involved an intramolecular Diels-Alder (D-A) reaction/enolization/1,5-H transfer/K₂CO₃-promoted oxidation sequence, enabling a mild and high-efficient access to benzo[*b*]fluorenones with a wide diversity in substituents and good to excellent yields. The latter undergoes a similar reaction process to afford a series of arylated benzo[*b*]fluorenols, in which intermolecular hydrogen bonds prevent the oxidation of alcohols. Both protocols feature operational simplicity, easy reaction and purification procedure, broad substrate scope, and high convergence as well as annulations. Further investigation on evaluating their biological activity is underway in our laboratory.

4. Experimental section

4.1. General

¹H NMR (¹³C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl₃ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI-TOF) was determined by using microTOF-Q HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

General procedure for the synthesis of **2a** and **3a**

Example for the synthesis of **7-Bromo-5-(p-tolyl)-11H-benzo[*b*]fluoren-11-one (2a)**

A mixture of 3-(4-bromophenyl)-1-(2-(p-tolylethynyl)phenyl)prop-2-en-1-one (**1a**, 1.0 mmol), K₂CO₃ (1.0 mmol) and 1,4-dioxane (4.0 mL) were added in a sealed 20-mL reaction vial, which was sealed and heated at 100 °C (about 6 hour) until TLC (petroleum ether:

ethyl acetate 5:1) revealed that conversion of the starting material **1a** was completed. The reaction mixture was then cooled to room temperature and diluted with cold water (30 mL). The solid product was collected by Büchner filtration and was purified by recrystallization from 95% EtOH to afford the pure yellow solid **2a**. Yellow solid, mp 232-234 °C; IR (KBr, ν, cm⁻¹) 2941, 1706, 1617, 1131, 995, 624; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.16 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.75 - 7.71 (m, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.56 - 7.53 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 1H), 7.26 - 7.19 (m, 3H), 6.40 - 6.38 (m, 1H), 2.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.9, 144.8, 138.4, 138.3, 136.5, 136.4, 134.8, 133.9, 133.4, 132.9, 132.0, 131.9, 130.2, 130.2, 129.5, 128.9, 124.7, 124.2, 124.0, 123.7, 21.5; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₆BrO, 401.0359 [M+H]⁺; found 401.0372.

5-(p-Tolyl)-11H-Benzo[*b*]fluoren-11-one (**2b**)

Yellow solid, mp 240-242 °C; IR (KBr, ν, cm⁻¹) 3026, 1710, 1625, 1108, 945, 670; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.23 (s, 1H), 7.95 - 7.93 (m, 1H), 7.74-7.72 (m, 1H), 7.49-7.42 (m, 4H), 7.41 (s, 1H), 7.30-7.28 (m, 2H), 7.23-7.19 (m, 2H), 6.43 - 6.41 (m, 1H), 2.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 193.3, 145.3, 138.0, 137.2, 136.5, 135.3, 134.8, 134.7, 134.3, 133.4, 132.6, 130.7, 130.0, 129.5, 128.9, 128.6, 127.2, 126.8, 125.1, 124.2, 123.9, 21.5; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₇O, 321.1274 [M+H]⁺; found 321.1283.

5-(4-Methoxyphenyl)-7-nitro-11H-benzo[*b*]fluoren-11-one (**2c**)

Yellow solid, mp 182-184 °C; IR (KBr, ν, cm⁻¹) 3008, 1708, 1627, 1179, 964, 628; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.42 (d, *J* = 2.0 Hz, 1H), 8.27 (s, 1H), 8.24 - 8.21 (m, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.78 - 7.76 (m, 1H), 7.34 - 7.28 (m, 4H), 7.20 - 7.18 (m, 2H), 6.52 - 6.50 (m, 1H), 4.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.4, 160.1, 147.5, 144.7, 137.5, 136.8, 136.4, 136.2, 136.0, 135.6, 135.3, 132.0, 130.7, 129.5, 127.6, 124.6, 124.3, 124.1, 123.2, 120.2, 115.2, 55.5; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₆NO₄, 382.1074 [M+H]⁺; found 382.1087.

5-(4-Methoxyphenyl)-11-oxo-11H-benzo[*b*]fluorene-7-carbonitrile (**2d**)

Yellow solid, mp 230-232 °C; IR (KBr, ν, cm⁻¹) 3064, 1708, 1629, 1178, 967, 631; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.23 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.88 - 7.86 (m, 1H), 7.78 - 7.75 (m, 1H), 7.63 - 7.60 (m, 1H), 7.31 - 7.27 (m, 4H), 7.21 - 7.17 (m, 2H), 6.52 - 6.50 (m, 1H), 3.99 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.5, 160.1, 144.7, 137.2, 136.7, 136.2, 135.2, 135.1, 135.0, 134.6, 132.8, 131.6, 130.7, 129.4, 127.7, 127.4, 124.5, 124.3(2), 124.2(5), 118.9, 115.1, 112.0, 55.5; HRMS (ESI-TOF) *m/z* calcd for C₂₅H₁₆NO₂, 362.1176 [M+H]⁺; found 362.1190.

7-Bromo-5-(4-methoxyphenyl)-11H-benzo[*b*]fluoren-11-one (**2e**)

Yellow solid, mp 233-235 °C; IR (KBr, ν, cm⁻¹) 3235, 1703, 1619, 1186, 1029, 617; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.15 (s, 1H), 7.78 - 7.72 (m, 2H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.55 - 7.53 (m, 1H), 7.30 - 7.27 (m, 2H), 7.25 - 7.22 (m, 2H), 7.17 - 7.14 (m, 2H), 6.43 - 6.41 (m, 1H), 3.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.9, 159.8, 144.8, 138.5, 136.7, 136.4, 134.9, 133.6, 132.9, 132.1, 131.9, 130.8, 130.2, 129.4, 129.0, 128.5, 124.7, 124.2, 124.0, 123.8, 114.9, 55.4; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₆BrO₂, 417.0308 [M+H]⁺; found 417.0320.

9-Bromo-5-(4-methoxyphenyl)-11H-benzo[*b*]fluoren-11-one (**2f**)

Yellow solid, mp 237-239 °C; IR (KBr, ν, cm⁻¹) 3028, 1708, 1623, 1176, 904, 670; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.66 (d, *J* = 0.8 Hz, 1H), 7.76 - 7.73 (m, 2H), 7.48 - 7.45 (m, 1H), 7.31 - 7.26 (m, 3H), 7.26 - 7.22 (m, 2H), 7.16 - 7.13 (m, 2H), 6.44 - 6.42 (m, 1H), 3.97 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.9, 159.7, 144.8, 138.9, 136.5, 136.4, 134.9, 134.6, 133.5,

132.3, 130.9, 130.8, 129.0, 128.9, 127.0, 125.9, 124.3, 124.3, 124.0, 114.8, 55.4; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₆BrO₂, 417.0308 [M+H]⁺; found 417.0325.

9-Bromo-6-chloro-5-(4-methoxyphenyl)-11H-benzo[*b*]fluoren-11-one (2g)

Yellow solid, mp 240-242 °C; IR (KBr, *v*, cm⁻¹) 3005, 1715, 1628, 1172, 963, 674; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.74 (s, 1H), 7.76 - 7.74 (m, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.28 - 7.26 (m, 1H), 7.26 - 7.23 (m, 2H), 7.22 - 7.18 (m, 1H), 7.07 - 7.05 (m, 2H), 6.07 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.4, 159.7, 145.0, 139.4, 136.4, 135.1, 134.5, 134.2, 134.1, 133.4, 132.83, 132.7, 131.1, 131.0, 130.8, 129.3, 125.2, 125.1, 124.9, 124.3, 114.2, 55.4; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₄BrClO₂, 450.9918 [M+H]⁺; found 450.9937.

7-Chloro-5-(4-methoxyphenyl)-11H-benzo[*b*]fluoren-11-one (2h)

Yellow solid, mp 233-234 °C; IR (KBr, *v*, cm⁻¹) 3068, 1703, 1624, 1178, 950, 628; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.16 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.74-7.72 (m, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.42-7.39 (m, 1H), 7.30-7.28 (m, 2H), 7.25-7.20 (m, 2H), 7.17-7.13 (m, 2H), 6.45-6.42 (m, 1H), 3.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.9, 160.4, 144.6, 138.5, 136.7, 136.3, 136.1, 134.5, 134.4, 132.4, 132.0, 131.2, 130.6, 129.7, 128.8, 128.4, 125.4, 124.2, 123.5, 118.2, 106.7, 55.4; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₆ClO₂, 371.0834 [M+H]⁺; found 371.0840.

5-(4-Methoxyphenyl)-11H-benzo[*b*]fluoren-11-one (2i)

Yellow solid, mp 213-214 °C; IR (KBr, *v*, cm⁻¹) 3055, 1703, 1623, 1174, 945, 633; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.22 (s, 1H), 7.95 - 7.92 (m, 1H), 7.75 - 7.72 (m, 1H), 7.49 - 7.43 (m, 3H), 7.33 - 7.31 (m, 2H), 7.24-7.21 (m, 2H), 7.15 - 7.13 (m, 2H), 6.47-6.44 (m, 1H), 3.97 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 193.3, 159.6, 145.3, 137.4, 136.5, 135.6, 134.7, 134.5, 133.4, 132.6, 130.9, 130.8, 129.4, 128.9, 128.6, 127.5, 126.8, 125.1, 124.2, 123.9, 114.7, 55.4; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₇O₂, 337.1224 [M+H]⁺; found 337.1241.

5-(4-Methoxyphenyl)-7-methyl-11H-benzo[*b*]fluoren-11-one (2j)

Yellow solid, mp 247-249 °C; IR (KBr, *v*, cm⁻¹) 3043, 1702, 1623, 1174, 957, 636; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.18 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 - 7.71 (m, 1H), 7.32 - 7.29 (m, 3H), 7.24 (d, *J* = 0.8 Hz, 1H), 7.22 - 7.20 (m, 2H), 7.16 - 7.14 (m, 2H), 6.41 - 6.39 (m, 1H), 3.98 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 193.4, 159.5, 145.3, 139.3, 137.5, 136.6, 135.8, 134.6, 133.9, 131.8, 131.5, 130.9, 130.6, 129.6, 128.9, 128.5, 126.5, 125.0, 124.1, 123.8, 114.7, 55.4, 22.1; HRMS (ESI-TOF) *m/z* calcd for C₂₅H₁₉O₂, 351.1380 [M+H]⁺; found 351.1389.

7-Methoxy-5-(4-methoxyphenyl)-11H-benzo[*b*]fluoren-11-one (2k)

Yellow solid, mp 244-246 °C; IR (KBr, *v*, cm⁻¹) 2994, 1701, 1607, 1173, 919, 633; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.15 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.72 - 7.70 (m, 1H), 7.33 - 7.31 (m, 2H), 7.22 - 7.17 (m, 2H), 7.15 - 7.10 (m, 3H), 6.81 (d, *J* = 2.8 Hz, 1H), 6.41 - 6.39 (m, 1H), 3.97 (s, 3H), 3.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 193.2, 160.2, 159.5, 145.1, 139.2, 136.7, 136.5, 134.4, 133.3, 132.3, 130.7, 129.6, 128.6, 128.5, 125.0, 124.0, 123.8, 118.1, 114.8, 107.0, 55.4, 55.3; HRMS (ESI-TOF) *m/z* calcd for C₂₅H₁₉O₃, 367.1329 [M+H]⁺; found 367.1342.

4-(4-Methoxyphenyl)-9H-fluoreno[2,3-*b*]thiophen-9-one (2l)

Yellow solid, mp 206-208 °C; IR (KBr, *v*, cm⁻¹) 3043, 1692, 1609, 1174, 941, 632; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.17 (d, *J* = 0.8 Hz, 1H), 7.68 - 7.65 (m, 1H), 7.51 (d, *J* = 5.6 Hz, 1H), 7.38 - 7.36 (m, 2H), 7.19 - 7.17 (m, 2H), 7.11 - 7.09 (m, 2H), 7.02

-7.00 (m, 1H), 6.62 - 6.58 (m, 1H), 3.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 193.3, 159.6, 145.3, 145.0, 139.6, 136.6, 135.8, 134.5, 132.7, 131.9, 130.5, 130.4, 129.7, 128.3, 124.4, 124.1, 123.1, 118.7, 114.5, 55.4; HRMS (ESI-TOF) *m/z* calcd for C₂₂H₁₅O₂S, 343.0788 [M+H]⁺; found 343.0801.

7-Chloro-5-phenyl-11H-benzo[*b*]fluoren-11-one (2m)

Yellow solid, mp 223-224 °C; IR (KBr, *v*, cm⁻¹) 3060, 1708, 1539, 1189, 949, 622; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.20 (s, 1H), 7.89-7.86 (m, 1H), 7.75 - 7.73 (m, 1H), 7.64 - 7.61 (m, 3H), 7.44 - 7.38 (m, 4H), 7.25 - 7.18 (m, 2H), 6.32-6.30 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.8, 144.7, 137.8, 136.6, 136.5, 135.3, 134.8, 133.8, 132.8, 132.0, 131.7, 129.6, 129.5, 129.0, 128.7, 127.6, 126.2, 124.8, 124.38, 124.0; HRMS (ESI-TOF) *m/z* calcd for C₂₃H₁₄ClO, 341.0728 [M+H]⁺; found 341.0745.

7,9-Dichloro-5-phenyl-11H-benzo[*b*]fluoren-11-one (2n)

Yellow solid, mp 230-232 °C; IR (KBr, *v*, cm⁻¹) 3051, 1712, 1632, 1190, 919, 652; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.65 (d, *J* = 0.8 Hz, 1H), 7.77-7.74 (m, 1H), 7.65-7.63 (m, 3H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.39 - 7.36 (m, 2H), 7.34 - 7.33 (m, 1H), 7.30-7.26 (m, 1H), 7.23 - 7.19 (m, 1H), 6.29 (d, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.4, 144.3, 138.7, 137.3, 136.5, 136.4, 135.8, 135.0, 134.3, 133.9, 133.4, 129.6, 129.5, 129.4, 128.9, 127.6, 125.3, 124.4, 124.1, 121.5; HRMS (ESI-TOF) *m/z* calcd for C₂₃H₁₃Cl₂O, 375.0338 [M+H]⁺; found 375.0352.

7-Bromo-5-phenyl-11H-benzo[*b*]fluoren-11-one (2o)

Yellow solid, mp 227-229 °C; IR (KBr, *v*, cm⁻¹) 3008, 1705, 1618, 1187, 943, 638; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.18 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.75-7.73 (m, 1H), 7.65-7.54 (m, 5H), 7.40-7.37 (m, 2H), 7.25-7.17 (m, 2H), 6.32-6.19 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.8, 144.7, 138.1, 136.6, 136.5, 134.84, 133.7, 132.8, 132.1, 131.9, 130.2, 129.6, 129.5, 129.4, 129.0, 128.7, 124.8, 124.3, 124.0, 123.8; HRMS (ESI-TOF) *m/z* calcd for C₂₃H₁₄BrO, 387.0202 [M+H]⁺; found 387.0221.

5-Phenyl-11H-benzo[*b*]fluoren-11-one (2p)

Yellow solid, mp 208-210 °C; IR (KBr, *v*, cm⁻¹) 3043, 1706, 1623, 1160, 944, 640; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.24 (s, 1H), 7.96-7.94 (m, 1H), 7.75 - 7.73 (m, 1H), 7.63 - 7.59 (m, 3H), 7.50 - 7.44 (s, 3H), 7.42 - 7.40 (m, 2H), 7.23 - 7.16 (m, 2H), 6.34-6.32 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 193.2, 145.2, 137.4, 136.9, 136.5, 135.3, 134.7, 134.7, 133.4, 132.6, 130.8, 129.7, 129.3, 128.9, 128.7, 128.3, 127.1, 126.8, 125.2, 124.2, 123.8; HRMS (ESI-TOF) *m/z* calcd for C₂₃H₁₅O, 307.1118 [M+H]⁺; found 307.1131.

7-Methyl-5-phenyl-11H-benzo[*b*]fluoren-11-one (2q)

Yellow solid, mp 217-219 °C; IR (KBr, *v*, cm⁻¹) 3051, 1705, 1622, 1109, 902, 642; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.20 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.73-7.71 (m, 1H), 7.62-7.60 (m, 3H), 7.41-7.39 (m, 2H), 7.32 - 7.30 (m, 1H), 7.21-7.17 (m, 3H), 6.27 (d, *J* = 7.2 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 193.3, 145.2, 139.4, 137.6, 137.1, 136.6, 135.5, 134.6, 134.1, 131.8, 131.5, 130.6, 129.7, 129.3, 128.9, 128.5, 128.2, 126.4, 125.1, 124.1, 123.7, 22.1; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₁₇O, 321.1274 [M+H]⁺; found 321.1290.

7-Bromo-5-(4-chlorophenyl)-11H-benzo[*b*]fluoren-11-one (2r)

Yellow solid, mp 228-230 °C; IR (KBr, *v*, cm⁻¹) 3053, 1707, 1623, 1175, 948, 669; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.20 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.78-7.75 (m, 1H), 7.64-7.62 (m, 2H), 7.59 - 7.56 (m, 1H), 7.53 (s, 1H), 7.37-7.34 (m, 2H), 7.30 - 7.26 (m, 2H), 6.40-6.38 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 192.6, 144.4, 137.9, 136.6, 136.5, 135.1, 135.0, 134.8, 132.8, 132.3, 132.2, 131.9, 131.2, 130.4, 129.9, 129.3, 129.1, 125.2, 124.5, 124.0, 123.8; HRMS (ESI-TOF) *m/z* calcd for C₂₃H₁₃BrClO, 420.9813 [M+H]⁺; found 420.9821.

5-(4-Chlorophenyl)-11H-benzo[b]fluoren-11-one (2s)

Yellow solid, mp 194-196 °C; IR (KBr, ν , cm^{-1}) 2993, 1713, 1512, 1088, 903, 630; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.24 (s, 1H), 7.97-7.93 (m, 1H), 7.76-7.72 (m, 1H), 7.62-7.59 (m, 2H), 7.49-7.44 (m, 2H), 7.41 - 7.35 (m, 3H), 7.26 (s, 1H), 7.25-7.24 (m, 1H), 6.43-6.41 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 193.0, 144.8, 136.7, 136.5, 135.9, 135.4, 134.8, 134.5, 133.4, 133.2, 132.5, 131.2, 130.9, 129.6, 129.1, 128.9, 127.0, 126.8, 125.5, 124.4, 123.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{14}\text{ClO}$, 341.0728 $[\text{M}+\text{H}]^+$; found $\text{C}_{23}\text{H}_{14}\text{ClO}$, 341.0742.

5-(4-Chlorophenyl)-7-methoxy-11H-benzo[b]fluoren-11-one (2t)

Yellow solid, mp 178-180 °C; IR (KBr, ν , cm^{-1}) 3057, 1710, 1614, 1189, 961, 627; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.15 (s, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.73 - 7.71 (m, 1H), 7.62-7.59 (m, 2H), 7.38-7.35 (m, 2H), 7.24-7.21 (m, 2H), 7.14 - 7.11 (m, 1H), 6.70 (d, J = 2.4 Hz, 1H), 6.37 - 6.35 (m, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 192.9, 160.4, 144.6, 138.5, 136.7, 136.3, 136.1, 134.5, 134.4, 132.4, 132.0, 131.2, 130.6, 129.7, 128.8, 128.4, 125.4, 124.5, 123.5, 118.2, 106.7, 55.3; HRMS (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{16}\text{ClO}_2$, 371.0834 $[\text{M}+\text{H}]^+$; found 371.0850.

5-(4-Fluorophenyl)-11H-benzo[b]fluoren-11-one (2u)

Yellow solid, mp 189-191 °C; IR (KBr, ν , cm^{-1}) 3068, 1705, 1624, 1161, 946, 634; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.25 (s, 1H), 7.96 - 7.94 (m, 1H), 7.76-7.74 (m, 1H), 7.50-7.46 (m, 2H), 7.43-7.37 (m, 3H), 7.34-7.30 (m, 2H), 7.26-7.22 (m, 2H), 6.38-6.36 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 193.1, 162.8 ($^1J_{\text{CF}}$ = 246.2 Hz), 145.0, 137.0, 136.5, 135.6, 134.8, 133.5, 133.4, 133.3, 132.5, 131.5 ($^3J_{\text{CF}}$ = 7.9 Hz), 130.9, 129.1, 128.8, 126.9(3), 126.8(5), 125.4, 124.3, 123.6, 116.4 ($^2J_{\text{CF}}$ = 21.7); HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{14}\text{FO}$, 325.1024, $[\text{M}+\text{H}]^+$; found 325.1037.

Example for the synthesis of 7-Bromo-5-(*p*-tolyl)-11H-benzo[b]fluoren-11-ol (3a)

A mixture of 3-(4-bromophenyl)-1-(2-(*p*-tolylethynyl)phenyl)prop-2-en-1-one (**1a**, 1.0 mmol), Et_3N (2 mmol) and 1,4-dioxane (4.0 mL) were added in a sealed 20-mL reaction vial, which was sealed and heated at 120 °C (about 6 hours) until TLC (petroleum ether: ethyl acetate 5:1) revealed that conversion of the starting material **1a** was completed. The reaction mixture was then cooled to room temperature and neutralized with 10% diluted hydrochloric acid and diluted with cold water (30 mL). The solid product was collected by Büchner filtration and was purified by recrystallization from 95% EtOH to afford the pure white solid **3a**.

White solid, mp 123-125 °C; IR (KBr, ν , cm^{-1}) 2209, 1626, 1512, 1068, 877, 658; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.03 (d, J = 16.0 Hz, 1H), 7.75 - 7.72 (m, 1H), 7.67-7.62 (m, 2H), 7.54 - 7.51 (m, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.29-7.26 (m, 1H), 7.25-7.19 (m, 2H), 7.11 - 7.07 (m, 1H), 6.43 (d, J = 8.0 Hz, 1H), 5.73 (s, 1H), 2.55 (s, 3H), 2.11 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 146.5, 144.1, 139.6, 137.9, 136.3, 135.4, 134.4, 133.2, 131.6, 130.1, 130.0, 129.96, 129.8, 129.5, 129.1, 129.1, 128.6, 128.3, 125.2, 123.8, 123.7, 120.6, 74.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{16}\text{BrO}$, 401.0364 $[\text{M}+\text{H}]^+$; found 401.0372.

11-Hydroxy-5-(4-methoxyphenyl)-11H-benzo[b]fluorene-7-carbonitrile (3b)

White solid, mp 116-118 °C; IR (KBr, ν , cm^{-1}) 2223, 1609, 1512, 1053, 854, 643; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.14 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.93 (s, 1H), 7.67 (d, J = 7.2 Hz, 1H), 7.60-7.58 (m, 1H), 7.35-7.27 (m, 2H), 7.26-7.24 (m, 1H), 7.17-7.11 (m, 3H), 6.54 (d, J = 7.6 Hz, 1H), 5.82 (s, 1H), 3.99 (s, 3H), 2.12 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 159.8, 147.0, 146.3, 139.1, 137.4, 134.6, 134.0, 133.7, 132.7, 131.0,

130.7, 129.4, 129.1, 128.8, 126.3, 125.2, 124.0, 123.8, 119.5, 115.0, 114.9, 109.6, 74.4, 55.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{16}\text{NO}_2$, 362.1181 $[\text{M}+\text{H}]^+$; found 362.1195.

7-Bromo-5-(4-methoxyphenyl)-11H-benzo[b]fluoren-11-ol (3c)

White solid, mp 121-123 °C; IR (KBr, ν , cm^{-1}) 2217, 1626, 1512, 1027, 876, 658; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.05 (s, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.67-7.64 (m, 2H), 7.55-7.52 (m, 1H), 7.29 (d, J = 7.2 Hz, 2H), 7.26-7.24 (m, 1H), 7.15-7.08 (m, 3H), 6.47 (d, J = 7.6 Hz, 1H), 5.76 (s, 1H), 3.98 (s, 3H), 2.07 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 159.5, 146.5, 144.1, 139.6, 136.6, 135.6, 132.9, 131.6, 131.1, 130.8, 129.9, 129.6, 129.1, 128.6, 128.3, 125.2, 123.8, 123.7, 120.7, 114.8, 114.7, 74.4, 55.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{16}\text{BrO}_2$, 417.0313 $[\text{M}+\text{H}]^+$; found 417.0323.

9-Bromo-5-(4-methoxyphenyl)-11H-benzo[b]fluoren-11-ol (3d)

White solid, mp 118-120 °C; IR (KBr, ν , cm^{-1}) 2224, 1606, 1512, 1032, 871, 629; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.56 (s, 1H), 7.77-7.75 (m, 1H), 7.67 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.31-7.26 (m, 2H), 7.25 (d, J = 8.4 Hz, 1H), 7.22-7.18 (m, 1H), 7.13-7.09 (m, 3H), 6.47 (d, J = 7.6 Hz, 1H), 5.83 (s, 1H), 3.96 (s, 3H), 2.10 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 159.4, 146.6, 145.1, 139.5, 136.4, 135.9, 133.9, 131.7, 131.1, 130.8, 130.1, 129.9, 129.1, 128.4, 126.5, 126.3, 125.3, 123.8, 123.4, 123.1, 114.6, 114.6, 74.6, 55.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{16}\text{BrO}_2$, 417.0313 $[\text{M}+\text{H}]^+$; found 417.0328.

9-Bromo-6-chloro-5-(4-methoxyphenyl)-11H-benzo[b]fluoren-11-ol (3e)

White solid, mp 124-126 °C; IR (KBr, ν , cm^{-1}) 2220, 1611, 1515, 1032, 859, 662; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.66 (d, J = 0.8 Hz, 1H), 7.67-7.64 (m, 2H), 7.33-7.27 (m, 2H), 7.22-7.19 (m, 1H), 7.20 (s, 1H), 7.08-7.02 (m, 3H), 6.11 (d, J = 7.6 Hz, 1H), 5.80 (s, 1H), 3.95 (s, 3H), 1.74 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 159.5, 146.6, 145.2, 139.6, 139.5, 133.8, 133.4, 132.1, 131.2, 131.1, 130.9, 130.3, 129.9, 129.2, 128.7, 125.1, 124.7, 124.4, 122.7, 114.0, 114.0, 74.2, 55.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{15}\text{BrClO}_2$, 450.9923 $[\text{M}+\text{H}]^+$; found 450.9939.

8,9-Dichloro-5-(4-methoxyphenyl)-11H-benzo[b]fluoren-11-ol (3f)

White solid, mp 120-122 °C; IR (KBr, ν , cm^{-1}) 2206, 1613, 1514, 1034, 873, 658; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.60 (s, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.44-7.39 (m, 2H), 7.32-7.30 (m, 1H), 7.29-7.27 (m, 1H), 7.25 (d, J = 4.0 Hz, 1H), 7.15-7.12 (m, 3H), 6.48 (d, J = 7.6 Hz, 1H), 5.84 (s, 1H), 3.97 (s, 3H), 1.64 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 159.6, 146.5, 145.0, 139.3, 136.5, 133.9, 131.6, 131.1, 130.8, 130.4, 129.9, 129.6, 129.2, 128.5, 127.2, 126.3, 125.3, 123.8, 120.6, 114.7, 114.7, 74.6, 55.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{15}\text{Cl}_2\text{O}_2$, 405.0449 $[\text{M}+\text{H}]^+$; found 405.0456.

4-(4-Methoxyphenyl)-9H-fluoreno[2,3-*b*]thiophen-9-ol (3g)

White solid, mp 140-142 °C; IR (KBr, ν , cm^{-1}) 2223, 1609, 1509, 1036, 866, 632; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.10 (s, 1H), 7.62 (d, J = 7.2 Hz, 1H), 7.37-7.34 (m, 3H), 7.25-7.21 (m, 1H), 7.10-7.07 (m, 3H), 7.03 - 7.01 (m, 1H), 6.68 (d, J = 8.0 Hz, 1H), 5.69 (s, 1H), 3.94 (s, 3H), 2.01 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 159.3, 146.2, 143.2, 141.1, 140.0, 139.1, 134.1, 132.0, 130.9, 130.7, 130.4, 128.8, 127.4, 126.4, 125.0, 123.7, 122.8, 118.4, 114.3, 114.3, 74.5, 55.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{15}\text{O}_2\text{S}$, 343.0793 $[\text{M}+\text{H}]^+$; found 343.0808.

7-Bromo-5-phenyl-11H-benzo[b]fluoren-11-ol (3h)

White solid, mp 107-109 °C; IR (KBr, ν , cm^{-1}) 2248, 1593, 1487, 1039, 741, 699; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.08 (s, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.66-7.59 (m, 5H), 7.56-7.53 (m, 1H), 7.38-7.34 (m, 2H), 7.29-7.26 (m, 1H), 7.09-7.05 (m, 1H),

6.34 (d, $J = 7.6$ Hz, 1H), 5.78 (s, 1H), 2.04 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 146.5, 144.0, 139.4, 137.6, 136.3, 135.2, 133.1, 131.6, 130.0, 129.9, 129.7, 129.4, 129.3, 129.2, 129.1, 128.6, 128.4, 128.3, 125.2, 123.9, 123.7, 120.7, 74.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{14}\text{BrO}$, 387.0208 $[\text{M}-\text{H}]^-$; found 387.0219.

7,9-Dichloro-5-phenyl-11H-benzo[*b*]fluoren-11-ol (3i)

White solid, mp 169–171 °C; IR (KBr, ν , cm^{-1}) 2209, 1625, 1477, 1029, 857, 653; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.54 (s, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.63–7.60 (m, 3H), 7.55 (d, $J = 2.0$ Hz, 1H), 7.40–7.39 (m, 1H), 7.36–7.27 (m, 3H), 7.10–7.06 (m, 1H), 6.33 (d, $J = 8.0$ Hz, 1H), 5.81 (s, 1H), 2.14 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 146.6, 145.0, 139.0, 137.4, 137.2, 135.7, 133.4, 131.4, 129.9, 129.7, 129.5, 129.4, 129.2, 129.0, 128.8, 128.5, 126.6, 125.3, 124.6, 123.9, 120.5, 74.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{13}\text{Cl}_2\text{O}$, 375.0343 $[\text{M}-\text{H}]^-$; found 375.0350.

7-Bromo-5-(4-chlorophenyl)-11H-benzo[*b*]fluoren-11-ol (3j)

White solid, mp 170–172 °C; IR (KBr, ν , cm^{-1}) 2221, 1626, 1486, 1069, 838, 653; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.08 (s, 1H), 7.77 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.62–7.54 (m, 4H), 7.33–7.28 (m, 3H), 7.15–7.11 (m, 1H), 6.43 (d, $J = 8.0$ Hz, 1H), 5.77 (s, 1H), 2.07 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 146.6, 144.0, 139.2, 136.4, 136.1, 135.0, 134.4, 131.5, 131.2, 130.0, 129.7(3), 129.7(0), 129.3, 129.2, 128.6, 128.2, 125.3, 124.2, 123.6, 120.9, 100.0, 74.3; HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{13}\text{BrClO}$, 418.9838 $[\text{M}-\text{H}]^-$; found 418.9851.

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Graphical Abstract

Base-controlled 1,6-enyne-bicyclization: divergent synthesis of benzo[*b*]fluorenones and benzo[*b*]fluorenols

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