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Iodine-mediated synthesis of benzo[*a*]fluorenones from yne-enones†

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The chalcones derived from *o*-alkynylacetophenones and aromatic aldehydes (yne-enones) when heated under reflux with iodine in acetic acid gave a range of benzo[*a*]fluorenone derivatives in moderate to good yields. The transformation involves the formation of a vinyl indenone intermediate through regioselective alkyne hydration and intramolecular aldol condensation followed by electrocyclic ring closure and aromatization.

Introduction

The benzo[*a*]fluorenone core is present in the fluostatin family of natural products which possess potential antibiotic and cytotoxic properties (Fig. 1).[1] In addition, few benzo[*a*]fluorene derivatives serve as active materials in the fabrication of optoelectronic devices.[2] Despite their importance in the fields of medicine and materials science, only a handful of methods are available to access benzo[*a*]fluorene derivatives, especially for benzo[*a*]fluorenones.[3] The recent methods available for the synthesis of benzo[*a*]fluorenones include thermal cyclization of diaryldiynones,[4] Suzuki coupling of functionalized arenes followed by cyclization,[5] annulation of arynes with 2-haloarenecarboxaldehydes,[6] and gold-catalyzed cyclization of trityl-substituted diynes followed by oxidative photocyclization.[7]

While exploring the synthetic potentials of *o*-alkynylchalcones,[8] we discovered that related yne-enones **1** when heated under reflux with iodine in AcOH gave benzo[*a*]fluorenones **2** through a cascade process (Scheme 1, eqn (1)). It is worthwhile to compare these results with Hu's work,[9] in which chalcones **1** have been converted into benzo[*b*]fluorenols **3** by a Pd-catalyzed intramolecular dehydroaromatization and carbonyl reduction sequence (Scheme 1, eqn (2)) and also with Li's work,[10] in which chalcones **1** have been transformed into 1,4-naphthoquinones **4** by a Cu-catalyzed intramolecular oxidative 6-*endo-trig* cyclization (Scheme 1, eqn (3)). The present work represents yet another proof of the versatility of iodine in mediating complex organic transformations.[11]

Results and discussion

The requisite starting materials **1** for the present study were prepared by the base-mediated condensation of *o*-alkynylacetophenones **5** (which were in turn prepared by the Sonogashira coupling of the corresponding *o*-haloacetophenones with terminal arylacetylenes) with aromatic aldehydes **6** (Scheme 2).

We chose the yne-enone **1a** as a model substrate for optimizing the reactions conditions for the desired transformation (Table 1). When **1a** was heated under reflux with one equiv. of iodine in AcOH for 12 h, benzo[*a*]fluorenone **2a** was produced in 75% yield (entry 1) (the starting material did not undergo any change at room temperature). When substoichiometric amounts of iodine (0.5 or 0.3 equiv.) were used, the reaction did not go to completion even after 24 h and thus gave lower yields of the product (entries 2 and 3). At the same time, the use of 1.5 or 2.0 equiv. of iodine did not alter the yield of the reaction or reaction time noticeably (entries 4 and 5). The reaction did not work when EtOH, 1,2-dichloroethane (1,2-DCE) or THF was used as the solvent (entries 6–8). Likewise, the reaction did not take place when *N*-iodosuccinimide (NIS) or ICl is employed instead of iodine (entries 9 and 10). We also screened the suitability of the hypervalent iodine reagents, namely $PhI(OAc)_2$ and 2-iodoxybenzoic acid (IBX) for the reaction, but they gave

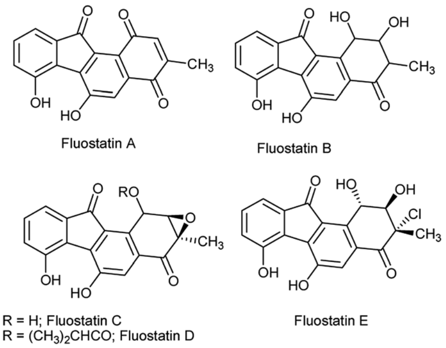

Fig. 1 Structures of fluostatin natural products.

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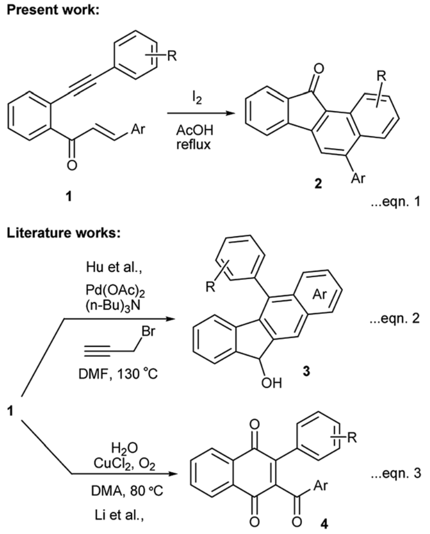
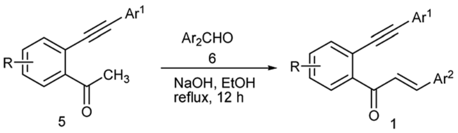
† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for all products, including copies of ^{1}H and ^{13}C NMR spectra and X-ray structural information of **2b**. CCDC 1501649. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ra02376c



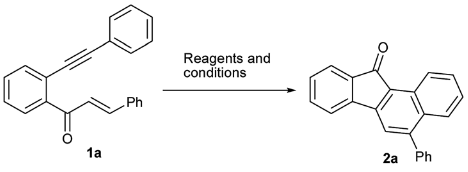
Scheme 1 Present synthesis of benzo[*a*]fluorenones and comparison with literature reports.



Scheme 2 Preparation of starting materials.

poor yields of the product (entries 11 and 12). Thus, we identified refluxing the substrate with one equiv. of iodine in AcOH as the optimal conditions for the reaction.

Table 1 Optimization of the reaction conditions

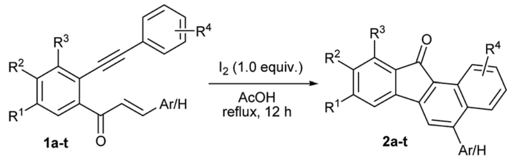


Entry	Reagents (equiv.) and conditions[a]	Yield of **2a**[b] (%)
1	I_2 (1.0), AcOH, reflux, 12 h	75
2	I_2 (0.5), AcOH, reflux, 24 h	33
3	I_2 (0.3), AcOH, reflux, 24 h	10
4	I_2 (1.5), AcOH, reflux, 12 h	75
5	I_2 (2.0), AcOH, reflux, 12 h	73
6	I_2 (1.0), EtOH, reflux, 24 h	NR[c]
7	I_2 (1.0), 1,2-DCE, reflux, 24 h	NR[c]
8	I_2 (1.0), THF, reflux, 24 h	NR[c]
9	NIS (1.0), AcOH, reflux, 24 h	NR[c]
10	ICl (1.0), AcOH, reflux, 24 h	NR[c]
11	PhI(OAc)$_2$ (1.0), AcOH, reflux, 24 h	28
12	IBX (1.0), AcOH, reflux, 24 h	15

[a] No reaction takes place at room temperature. [b] Isolated yield. [c] No reaction.

Next, we focused attention on exploring the scope of the reaction for various yne-enones (Table 2). We first examined substrates having different aryl rings (Ar) bonded to the enone unit. The reaction tolerated the presence of phenyl rings substituted with neutral, electron donating, halogen and electron withdrawing groups, bulky naphthyl ring and Heteroaromatic furyl, pyrrolyl and thienyl rings in the position and furnished the respective benzo[*a*]fluorenones **2a–k** in 50–80% yields (entries 1–11). The yield was low (50%) for the substrate containing the *p*-nitrophenyl ring due to the formation of an indenone byproduct (intermediate) in 28% yield (discussed later) (entry 6). The attachment of an aryl group to the enonoe unit is not necessary for the success of the reaction as revealed by the formation of benzo[*a*]fluorenone **2l** in 55% yield from a substrate in which Ar = H (entry 12). Next, we tested substrates containing different aryl rings attached to the alkyne unit. Though the reaction tolerated *m*-tolyl, *p*-tolyl, *m*-anisyl and *p*-chlorophenyl rings in the position and gave the respective products **2m–o** and **2q** in reasonable to good yields (entries 13–15 and 17), it gave a complicated mixture in the case of *p*-anisyl ring containing substrate (entry 16). The reason might be due to the oxidation of the *p*-anisyl ring to a quinone moiety under the reaction conditions. Finally, we investigated substrates having one or two bromo substituents on the main aryl ring and they too gave the expected benzo[*a*]fluorenones **2r** and **2s**, in 70 and 61% yields, respectively (entries 18 and 19). For one of the products **2b**, the structure was unequivocally confirmed by X-ray analysis (Fig. 2).[12]

Table 2 Synthesis of various benzo[*a*]fluorenone derivatives from yne-enones[a]



Entry	R^1, R^2, R^3, R^4, Ar/H	Time (h)	Yield[b] (%)
1	H, H, H, H, Ph (**1a**)	12	75 (**2a**)
2	H, H, H, H, 4-MeC$_6$H$_4$ (**1b**)	11	68 (**2b**)
3	H, H, H, H, 4-MeOC$_6$H$_4$ (**1c**)	9	70 (**2c**)
4	H, H, H, H, 4-N(Me)$_2$-C$_6$H$_4$ (**1d**)	12	65 (**2d**)
5	H, H, H, H, 4-BrC$_6$H$_4$ (**1e**)	12	80 (**2e**)
6	H, H, H, H, 4-NO$_2$C$_6$H$_4$ (**1f**)	24	50 (**2f**)
7	H, H, H, H, 1-naphthyl (**1g**)	10	75 (**2g**)
8	H, H, H, H, 2-furyl (**1h**)	11	57 (**2h**)
9	H, H, H, H, 2-pyrrolyl (**1i**)	12	65 (**2i**)
10	H, H, H, H, 1-methyl-2-pyrrolyl (**1j**)	12	67 (**2j**)
11	H, H, H, H, 2-thienyl (**1k**)	11	60 (**2k**)
12	H, H, H, H, H (**1l**)	9	55 (**2l**)
13	H, H, H, 3-Me, Ph (**1m**)	10	60 (**2m**)
14	H, H, H, 4-Me, Ph (**1n**)	12	73 (**2n**)
15	H, H, H, 3-OMe, Ph, (**1o**)	12	62 (**2o**)
16	H, H, H, 4-OMe, Ph, (**1p**)	12	—[c] (**2p**)
17	H, H, H, 4-Cl, Ph (**1q**)	12	74 (**2q**)
18	Br, H, H, H, Ph (**1r**)	12	70 (**2r**)
19	Br, H, Br, H, Ph (**1s**)	12	61 (**2s**)[d]

[a] The reaction was conducted with **1** (0.25 mmol), I_2 (1.0 equiv.) and solvent (5 mL). [b] Isolated yield. [c] Complicated mixture. [d] Contains *ca.* 7% inseparable impurity.

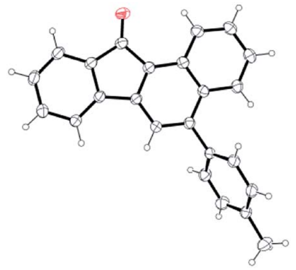
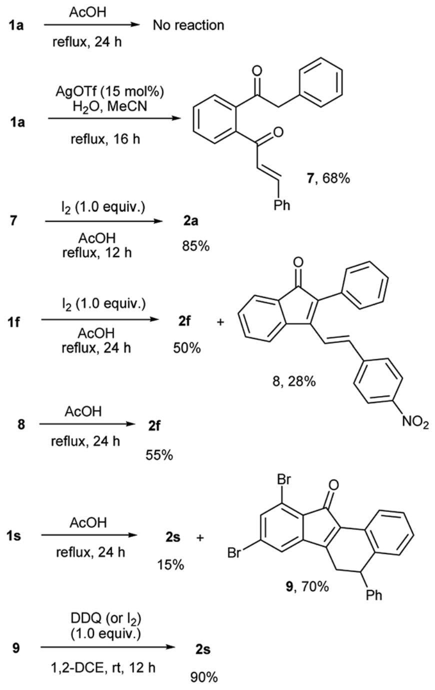
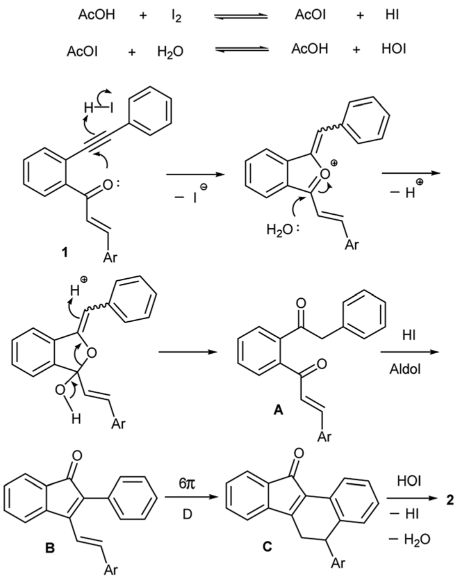


Fig. 2 X-ray structure of **2b** (30% probability level).

To probe the mechanism of the transformation, we conducted few control experiments (Scheme 3). When the reaction of **1a** was carried out under the specified conditions without iodine, the starting material did not undergo any change. Hence iodine is essential for the transformation. When **1a** was treated with silver(I) triflate (15 mol%) in the presence of water in acetonitrile,[13] it underwent regioselective triple bond hydration to give enone **7**, which when heated under reflux with iodine in AcOH afforded benzo[*a*]fluorenone **2a**. Under standard reaction conditions, **1f** (a special case) gave a mixture of **2f** (50%) and the indenone intermediate **8** (28%). The isolated intermediate **8** was slowly converted into **2f** in 55% yield when heated under reflux in AcOH for 24 h. All these reactions clearly indicate that an indenone intermediate formed by regioselective alkyne hydration and intramolecular aldol condensation is involved in the transformation.[14] To obtain evidence for the subsequent steps, we stopped the reaction of **1s** before completion (in 8 h) and analyzed. The incomplete reaction gave a mixture of **2s** (15%) and the corresponding non aromatized product **9** (70%). This indicates that the corresponding indenone intermediate should have undergone 6π electrocyclic ring closure and double bond migration to give **9**. The aromatization of **9** to **2s** could be effected using DDQ or iodine/AcOH.



Scheme 3 Control experiments.



Scheme 4 Proposed mechanism of the reaction.

The above observations indicate that the transformation proceeds through the formation of an indenone intermediate followed by electrocyclic ring closure and aromatization. Accordingly, we propose a tentative mechanism outlined in Scheme 4 for the transformation. The interaction of iodine with acetic acid under refluxing conditions generates HI and HOI.[15] The triple bond of yne-enone **1** is activated by HI, which triggers a 5-*exo-trig* nucleophilic attack by the adjacent carbonyl group to form a five-membered intermediate. Ring opening of the intermediate by a small amount of water present in AcOH (or moisture) gives enone **A** regioselectively. Acid (HI) promoted intramolecular aldol condensation of **A** leads to the indenone intermediate **B**. A 6π disrotatory electrocyclic ring closure of **B** under thermal conditions and subsequent double bond migration (re-aromatization) forms the dihydrobenzo[*a*]fluorenone derivative **C**. Dehydrogenation of **C** by HOI (or heat in case of **1f**) finally yields benzo[*a*]fluorenone **2**.

Conclusions

In summary, we have developed a convenient, environmentally benign, metal-free procedure for the synthesis of benzo[*a*]fluorenone derivatives from the chalcones derived from *o*-alkynylacetophenones and aromatic aldehydes. The reaction proceeds through the formation of a vinyl indenone intermediate and subsequent electrocyclic ring closure and aromatization. Work is in progress to apply the present methodology for the synthesis of biologically important benzo[*a*]fluorenones including natural products.

Experimental section

General procedure for the synthesis of benzo[*a*]fluorenones 2

To a solution *o*-alkynylarene chalcones **1** (0.25 mmol) in acetic acid (5 mL) was added iodine (0.25 mmol) and the reaction mixture was heated under reflux for 10–24 h. After completion of the reaction, the reaction mixture was cooled to room temperature and quenched with aq. sodium thiosulphate. The residue was diluted with water and extracted with ethyl acetate. The combined organic layer was washed with water, satd. sodium bicarbonate solution, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product obtained was purified by column chromatography (SiO_2; EtOAc : hexane, 1 : 99 v/v) to afford pure product **2**.

5-Phenyl-benzo[*a*]fluoren-11-one (2a)

Red-orange solid. Yield: 75% (57 mg). Mp: 240–242 °C. IR (KBr): 1695 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.56–7.58 (m, 3H), 7.55–7.49 (m, 5H), 7.47–7.36 (m, 3H), 7.29 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 147.4, 144.5, 142.7, 139.2, 133.9, 133.1, 131.6, 129.8, 128.7, 128.3, 128.2, 127.5, 127.1, 125.9, 125.4, 125.0, 123.5, 122.8, 118.9, 118.4 ppm. HRMS (ESI): calcd for $C_{23}H_{14}O$: 307.1117 [M + H$^+$]; found 307.1120.

5-*p*-Tolyl-benzo[*a*]fluoren-11-one (2b)

Red-orange solid. Yield: 68% (54 mg). Mp: 251–253 °C. IR (KBr): 1692 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.63–7.57 (m, 3H), 7.48–7.41 (m, 4H), 7.38–7.34 (m, 3H), 7.29 (d, J = 7.2 Hz, 1H), 2.49 (s, 3H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 148.6, 145.5, 143.7, 138.0, 137.3, 134.9, 134.1, 132.7, 130.9, 129.6, 129.3, 129.2, 129.1, 127.0, 126.3, 125.9, 124.5, 123.8, 119.9, 119.4, 21.3 ppm. HRMS (ESI): calcd for $C_{24}H_{16}O$: 321.1274 [M + H$^+$]; found 321.1309.

5-(4-Methoxy-phenyl)-benzo[*a*]fluoren-11-one (2c)

Red-orange solid. Yield: 70% (59 mg). Mp: 275–277 °C. IR (KBr): 1694 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.63–7.57 (m, 3H), 7.49–7.43 (m, 4H), 7.41–7.36 (m, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 159.7, 148.3, 145.5, 143.7, 135.0, 134.1, 132.7, 132.5, 131.0, 129.3, 129.1, 127.0, 126.3, 125.7, 124.6, 123.8, 119.9, 119.4, 114.0, 55.4 ppm. HRMS (ESI): calcd for $C_{24}H_{16}O_2$: 359.1042 [M + Na$^+$]; found 359.1049.

5-(4-Dimethylamino-phenyl)-benzo[*a*]fluoren-11-one (2d)

Red-orange solid. Yield: 65% (57 mg). Mp: 235–237 °C. IR (KBr): 1629 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.62–7.52 (m, 3H), 7.48–7.20 (m, 5H), 7.29–7.25 (m, 1H), 6.88 (d, J = 8.8 Hz, 2H), 3.07 (s, 6H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 150.4, 149.1, 145.7, 143.8, 135.1, 134.0, 132.7, 131.1, 130.8, 129.2, 129.0, 127.9, 127.3, 126.1, 125.1, 124.5, 123.7, 119.8, 119.2, 112.2, 40.5 ppm. HRMS (ESI): calcd for $C_{25}H_{19}NO$: 350.1539 [M + H$^+$]; found 350.1537.

5-(4-Bromo-phenyl)-benzo[*a*]fluoren-11-one (2e)

Red-orange solid. Yield: 80% (77 mg). Mp: 267–269 °C. IR (KBr): 1690 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.64–7.57 (m, 3H), 7.49–7.44 (m, 2H), 7.42–7.36 (m, 3H), 7.29 (t, J = 7.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 146.9, 145.4, 143.5, 139.1, 134.8, 134.2, 132.4, 131.7, 131.3, 130.8, 129.5, 129.3, 126.64, 126.55, 126.3, 124.7, 123.9, 122.5, 119.9, 119.3 ppm. HRMS (ESI): calcd for $C_{23}H_{13}BrO$: 385.0223 [M + H$^+$]; found 385.0220.

5-(4-Nitro-phenyl)-benzo[*a*]fluoren-11-one (2f)

Red-orange solid. Yield: 50% (44 mg). Mp: 243–245 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.67–7.62 (m, 3H), 7.61 (s, 1H), 7.51–7.47 (m, 2H), 7.45–7.40 (m, 1H), 7.32–7.30 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 147.8, 146.9, 145.4, 145.3, 143.3, 134.6, 134.4, 132.1, 130.8, 129.7, 129.6, 127.1, 127.0, 126.1, 124.9, 124.1, 123.8, 120.0, 119.4 ppm. HRMS (ESI): calcd for $C_{23}H_{13}NO_3$: 374.0788 [M + Na$^+$]; found 374.0794.

5-Naphthalen-1-yl-benzo[*a*]fluoren-11-one (2g)

Yellow solid. Yield: 75% (67 mg). Mp: 211–213 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.77 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.73–7.69 (m, 3H), 7.62 (d, J = 6.4 Hz, 4H), 7.44–7.42 (m, 3H), 7.25–7.13 (m, 2H), 6.28 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 145.0, 137.8, 137.4, 136.3, 135.9, 135.4, 134.6, 132.5, 131.9, 131.4, 130.7, 129.82, 129.76, 129.31, 128.7, 128.4, 127.5, 127.3, 124.8, 124.2, 123.6, 123.2, 119.3 ppm. HRMS (ESI): calcd for $C_{27}H_{16}O$: 357.1274 [M + H$^+$]; found 357.1271.

5-Furan-2-yl-benzo[*a*]fluoren-11-one (2h)

Yellow solid. Yield: 57% (42 mg). Mp: 221–223 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.68 (d, J = 2.0 Hz, 1H), 7.66–7.63 (m, 1H), 7.63–7.51 (m, 3H), 7.49 (d, J = 4.0 Hz, 2H), 7.16–7.14 (m, 2H), 6.67–6.63 (m, 1H), 6.51 (d, J = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 154.7, 148.4, 144.9, 136.8, 135.9, 135.5, 134.4, 134.0, 132.6, 130.9, 129.2, 129.0, 128.5, 128.0, 124.1, 122.7, 108.0, 107.2 ppm. HRMS (ESI): calcd for $C_{21}H_{12}O_2$: 297.0910 [M + H$^+$]; found 297.0908.

5-(1*H*-Pyrrol-2-yl)-benzo[*a*]fluoren-11-one (2i)

Yellow solid. Yield: 65% (48 mg). Mp: 227–228 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.90 (d, J = 10.0 Hz, 2H), 7.84 (d, J = 8.4 Hz, 1H) 7.77–7.72 (m, 3H), 7.59–7.54 (m, 3H), 7.48 (t, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 193.1, 144.9, 138.5, 137.0, 136.2, 135.0, 133.7, 132.9, 130.9, 129.2, 129.0, 128.8, 127.0, 125.7, 124.5, 121.0, 119.1 ppm. HRMS (ESI): calcd for $C_{21}H_{13}NO$: 318.0889 [M + H$^+$]; found 318.0899.

5-(1-Methyl-1*H*-pyrrol-2-yl)-benzo[*a*]fluoren-11-one (2j)

Yellow solid. Yield: 67% (52 mg). Mp: 199–201 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.63–7.58 (m, 3H), 7.55–7.53 (m, 2H), 7.48–7.44 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H) 7.15–7.11 (m, 1H), 7.07–7.03 (m, 1H), 6.04 (d, J = 7.6 Hz, 1H), 3.27 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1, 145.1, 142.6, 142.5, 140.2, 136.9, 136.7, 134.0, 130.4, 129.1, 128.8, 128.1, 126.4, 123.6, 123.0, 121.7, 120.7, 120.2, 117.0, 109.3, 32.1 ppm. HRMS (ESI): calcd for $C_{22}H_{15}NO$: 310.1226 [M + H^+]; found 310.1227.

5-Thiophen-2-yl-benzo[*a*]fluoren-11-one (2k)

Yellow solid. Yield: 60% (47 mg). Mp: 233–235 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.66 (d, $J = 6.8$ Hz, 1H), 7.60–7.55 (m, 3H), 7.52 (d, $J = 5.6$ Hz, 1H), 7.74–7.45 (m, 2H), 7.20–7.13 (m, 2H), 6.98 (d, $J = 5.6$ Hz, 1H), 6.49 (d, $J = 7.2$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 144.9, 144.8, 139.8, 137.7, 136.4, 135.8, 134.5, 132.9, 131.9, 130.6, 129.3, 129.1, 128.43, 128.38, 124.3, 124.1, 123.1, 118.8 ppm. HRMS (ESI): calcd for $C_{21}H_{12}SO$: 313.0682 [M + H^+]; found 313.0708.

Benzo[*a*]fluoren-11-one (2l)[3b]

Red-orange solid. Yield: 55% (32 mg). Mp: 132–134 °C [Lit. 132 °C]. ^1H NMR (400 MHz, $CDCl_3$): δ 8.95 (d, $J = 8.4$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.61–7.56 (m, 2H), 7.49–7.41 (m, 3H), 7.28–7.24 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 146.1, 143.9, 135.9, 134.6, 134.4, 134.2, 130.2, 129.4, 129.3, 128.5, 126.9, 126.4, 124.3, 123.8, 119.9, 118.1 ppm.

4-Methyl-5-phenyl-benzo[*a*]fluoren-11-one (2m)

Red-orange solid. Yield: 60% (48 mg). Mp: 255–257 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, $J = 7.6$ Hz, 1H), 8.0 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.62–7.57 (m, 2H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.46–7.42 (m, 3H), 7.29–7.25 (m, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 2.33 (s, 3H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 148.7, 145.7, 143.8, 138.2, 137.4, 135.0, 134.3, 132.8, 131.0, 129.8, 129.4, 129.34, 129.29, 127.2, 126.5, 126.0, 124.7, 123.9, 120.0, 119.5 ppm. HRMS (ESI): calcd for $C_{24}H_{16}O$: 321.1274 [M + H^+]; found 321.1308.

3-Methyl-5-phenyl-benzo[*a*]fluoren-11-one (2n)

Red-orange solid. Yield: 73% (58 mg). Mp: 219–221 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 7.2$ Hz, 1H), 7.56–7.50 (m, 6H), 7.46–7.40 (m, 3H), 7.28–7.24 (m, 2H), 2.40 (s, 3H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 147.6, 144.6, 143.9, 140.4, 136.3, 134.9, 134.1, 132.9, 131.5, 129.7, 129.1, 129.0, 128.5, 128.0, 126.0, 125.8, 124.3, 123.7, 119.7, 119.5, 22.0 ppm. HRMS (ESI): calcd for $C_{24}H_{16}O$: 321.1274 [M + H^+]; found 321.1300.

2-Methoxy-5-phenyl-benzo[*a*]fluoren-11-one (2o)

Red-orange solid. Yield: 62% (52 mg). Mp: 189–191 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, $J = 2.4$ Hz, 1H),7.68 (d, $J = 9.2$ Hz, 1H), 7.62 (d, $J = 7.2$ Hz, 1H), 7.55–7.48 (m, 5H), 7.47–7.41 (m, 3H), 7.29 (dd, $J = 7.4$, 3.8 Hz, 1H), 7.00 (dd, $J = 6.0$, 4.6 Hz, 1H), 4.0 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 158.8, 147.4, 144.6, 142.8, 134.1, 133.2, 131.8, 131.6, 130.1, 128.4, 128.2, 126.1, 125.4, 123.7, 122.9, 119.0, 118.5, 113.1, 54.5 ppm. HRMS (ESI): calcd for $C_{24}H_{16}O_2$: 337.1223 [M + H^+]; found 337.1233.

3-Chloro-5-phenyl-benzo[*a*]fluoren-11-one (2q)

Red-orange solid. Yield: 74% (63 mg). Mp: 215–217 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.00 (d, $J = 9.2$ Hz, 1H), 7.76 (d, $J = 9.2$ Hz, 1H), 7.62 (d, $J = 6.8$ Hz, 2H), 7.58–7.53 (m, 3H), 7.52–7.48 (m, 3H), 7.46–7.42 (m, 2H), 7.31–7.27 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 147.5, 145.5, 143.4, 139.5, 134.6, 134.4, 133.4, 132.7, 130.0, 129.6, 129.0, 128.7, 128.4, 126.1, 126.0, 125.8, 124.0, 120.5, 120.1 ppm. HRMS (ESI): calcd for $C_{23}H_{13}ClO$: 341.0728 [M + H^+]; found 341.0695.

8-Bromo-5-phenyl-benzo[*a*]fluoren-11-one (2r)

Orange solid. Yield: 70% (67 mg). Mp: 237–239 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, $J = 8.4$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.63–7.59 (m, 2H), 7.57 (s, 1H), 7.57–7.47 (m, 6H), 7.44–7.38 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 148.7, 145.5, 144.1, 139.9, 133.5, 132.9, 132.1, 130.7, 129.7, 129.4, 129.0, 128.5, 128.3, 127.0, 126.8, 126.3, 125.0, 124.6, 123.5, 119.4 ppm. HRMS (ESI): calcd for $C_{23}H_{13}BrO$: 385.0223 [M + H^+]; found 385.0220.

8,10-Dibromo-5-phenyl-benzo[*a*]fluoren-11-one (2s)

Orange solid. Yield: 61% (70 mg). Mp: 269–271 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.02 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.61–7.59 (m, 1H), 7.57–7.54 (m, 2H), 7.52–7.50 (m, 2H), 7.51–7.49 (m, 1H), 7.47–7.45 (m, 1H), 7.42–7.39 (m, 2H), 7.40–7.36 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 148.3, 145.1, 143.6, 139.5, 133.1, 132.5, 131.7, 130.3, 129.3, 129.0, 128.7, 128.6, 128.3, 128.1, 127.9, 126.6, 126.4, 125.9, 124.6, 124.2, 123.1, 119.0 ppm. MS (ESI): *m/z* 485 [M + Na^+]. Anal. calcd for $C_{23}H_{12}Br_2O$: C 59.52, H 2.61; found: C 59.63, H 2.55.

3-Phenyl-1-(2-phenylacetyl-phenyl)propenone (7)[10]

Compound **7** was obtained by heating under reflux **1a** (0.25 mmol) with silver(I) triflate (10 mg, 15 mol%) in the presence of water (0.25 mL) in acetonitrile (5 mL). Pale yellow solid. Yield: 68% (56 mg). Mp: 90–92 °C [Lit. 91.8–93.6 °C]. ^1H NMR (400 MHz, $CDCl_3$): δ 8.01–7.99 (m, 2H), 7.72 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.57–7.35 (m, 10H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.24 (s, 1H), 7.20 (s, 1H), 4.62 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 195.1, 145.9, 138.7, 137.0, 134.7, 134.7, 133.1, 132.5, 131.2, 130.6, 129.1, 128.9, 128.6, 128.5, 128.3, 126.9, 125.6, 43.6 ppm. Compound **7** when heated under reflux with iodine in AcOH afforded benzo[*a*]fluorenone **2a** in 85% yield.

3-[2-(4-Nitro-phenyl)-vinyl]-2-phenyl-inden-1-one (8)

Compound **8** was obtained as a byproduct in the reaction of yne-enone **1f**. Orange solid. Yield: 28% (25 mg). Mp: 115–117 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, $J = 8.8$ Hz, 2H), 7.63–7.61 (m, 4H), 7.55 (s, 1H), 7.55–7.47 (m, 5H), 7.46–7.40 (m, 2H), 7.35 (t, $J = 8.0$ Hz, 1H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 149.3, 147.7, 143.2, 142.7, 135.9, 134.1, 133.5, 131.5, 130.8, 130.2, 129.2, 128.7, 128.5, 127.7, 125.7, 124.3, 123.3, 121.5 ppm. HRMS (ESI): calcd for $C_{23}H_{15}NO_3$: 354.1125 [M + H^+]; found 354.1121. Compound **8** was converted into **2f** in 55% yield when heated under reflux in AcOH for 24 h.

8,10-Dibromo-5-phenyl-5,6-dihydro-benzo[*a*]fluoren-11-one (9)

Compound **9** was obtained from the incomplete the reaction (8 h) of yne-enone **1t**. Brown semisolid. Yield: 70% (81 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.92 (s, 1H), 7.91 (s, 1H), 7.44–7.42 (m, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.17–7.10 (m, 2H), 7.05–7.04 (m, 1H), 7.00 (d, J = 7.6 Hz, 1H), 4.39 (d, J = 4.8 Hz, 1H), 3.12 (dd, J = 18.8, 10.4 Hz, 1H), 2.89 (dd, J = 18.6, 9.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 194.4, 144.0, 143.6, 142.2, 140.6, 139.0, 135.6, 128.9, 128.8, 128.6, 128.5, 127.8, 127.0, 124.2, 122.9, 103.6, 45.9, 44.0 ppm. HRMS (ESI): calcd for $C_{23}H_{14}Br_2O$: 464.9484 [M + H$^+$]; found 464.9476. This compound (46 mg, 0.1 mmol) was mixed with DDQ (23 mg, 0.1 mmol) in 1,2-dichloroethane (2 mL) and stirred at room temperature for 12 h to give **2t** (41 mg, 90%).

Conflicts of interest

There are no conflicts to declare.

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