Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201701516

Link to VoR: http://dx.doi.org/10.1002/adsc.201701516

10.1002/adsc.201701516

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Triflic acid-Mediated Expedient Synthesis of Benzo[*a*]fluorenes and Fluorescent Benzo[*a*]fluorenones

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

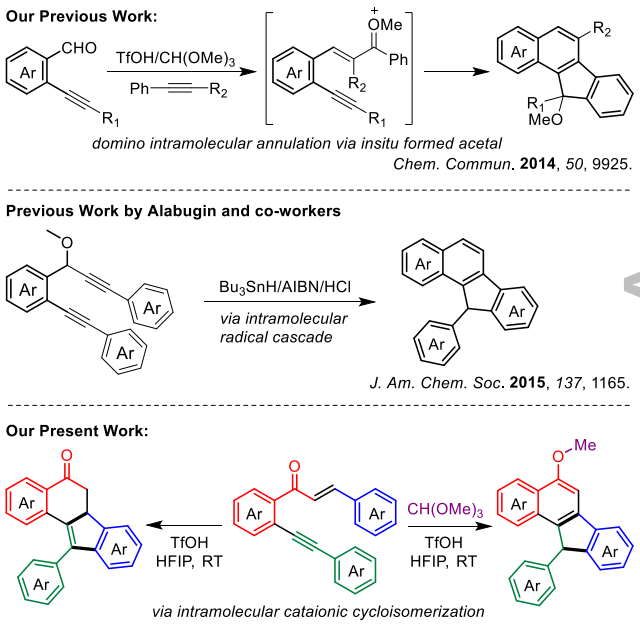
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. Fluorene-based polyaromatic hydrocarbons are renowned compounds for materials applications. Herein, a straightforward route *via* in situ acetal formation has been presented to access benzo[*a*]fluorenes by a triflic acid promoted cationic cycloisomerization of enynones in presence of trimethyl orthoformate under metal-free conditions. In the absence of trimethyl orthoformate, the same reaction results in benzo[*a*]fluorenones. All the synthesized benzo[*a*]fluorenones are highly fluorescent in solution phase with high Stokes shift while the corresponding benzo[*a*]fluorenes are not fluorescent.

Keywords: benzo[*a*]fluorene; benzo[*a*]fluorenone; triflic acid; acetal; Stokes shift

Polycyclic aromatic hydrocarbons (PAHs) have engrossed increasing attention in the field of organic materials.[1] In the fortress of PAHs family, fluorene[2] and fluorenone[3] based compounds show tremendous potential due to their extended π-conjugation which contributes to their unique optoelectronic properties.[4] This is evident from a range of potential applications of benzofluorenes such as organic lasers, blue light emitting OLEDs, in electroluminescent devices, in photochromic devices, in the treatment of osteoporosis etc.[5] In addition, this structural motif occurs in biologically active compounds as well.[6] Because of these broad utilities, synthesis of such polyarylated functional organic cores is in high need. For the synthesis of the title benzo[*a*]fluorenones, only three reports are available so far.[5e, 7] Two of these three known methods are not general and are used to make a specific derivative of benzo[*a*]fluorenones containing additional substituents such as sulfonyl and dimethylamine groups compulsorily.[7] In comparison to available methods for synthesis of benzo[*b*] and benzo[*c*] fluorenes, the methods for synthesis of benzo[*a*]fluorenes are less developed. Thus, development of efficient strategies to synthesize benzofluorenes and benzofluorenones[8] that have the scope for introducing different substituents in order to tune their optical properties is a worthy task.

We have reported the synthesis of benzo[*a*]fluorene[8g] by a triflic acid-catalyzed reaction of *o*-alkynyl benzaldehydes with alkynes in the presence of trimethyl orthoformate *via* in situ acetal formation.[9] An α,β-unsaturated ketone intermediate was proposed in resulting the benzo[*a*]fluorene product (Scheme 1). In this manuscript we present our studies on the reaction of a different α,β-unsaturated ketone system having the carbonyl and double bond positions interchanged. It was found that these substrates form a different benzo[*a*]fluorene derivative *via* in situ formed acetals.



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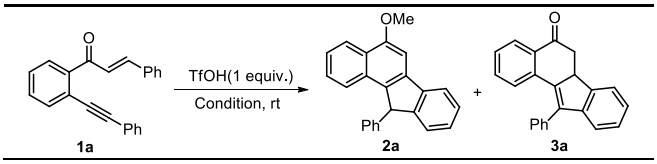
Scheme 1. Synthesis of benzo[*a*]fluorenes and benzo[*a*]fluorenones.

In extension, we have also carried out the synthesis of benzo[*a*]fluorenones under the same reaction condition in the absence of trimethyl orthoformate. Moreover, the benzo[*a*]fluorenones synthesized by us are fluorescent having high Stokes shifts which is a beneficial property in developing imaging materials, fluorescence sensors and solid state emitters etc.[10] Importantly, fluorescent active benzofluorenones (including all its sub-classes) have not been reported so far.

The enynone derivative **1a** was subjected to treatment with trimethyl orthoformate and triflic acid. It resulted in the formation of benzo[*a*]fluorene derivative **2a**. Interestingly, the same reaction in the absence of trimethyl orthoformate resulted in the formation of benzo[*a*]fluorenone **3a**. A striking feature of this compound **3a** is that it does not enolize under the reaction condition to result in the highly conjugated fluorenol system and, notably, it is fluorescent. The reaction of **1a** with TfOH was studied under different conditions in the presence and absence of trimethyl orthoformate (TMOF). Selected screening results are presented in table 1.[11] It was found that in the presence of 3 equivalents of TMOF benzo[*a*]fluorene **2a** was obtained in 98% isolated yield in 3 h (Table 1, entry 5) as only 75% of the benzo[*a*]fluorene **2a** along with 24% of benzo[*a*]fluorenone **3a** were isolated with 2 equivalent of trimethyl orthoformate (Table 1, entry 6).

Table 1. Selected optimization data

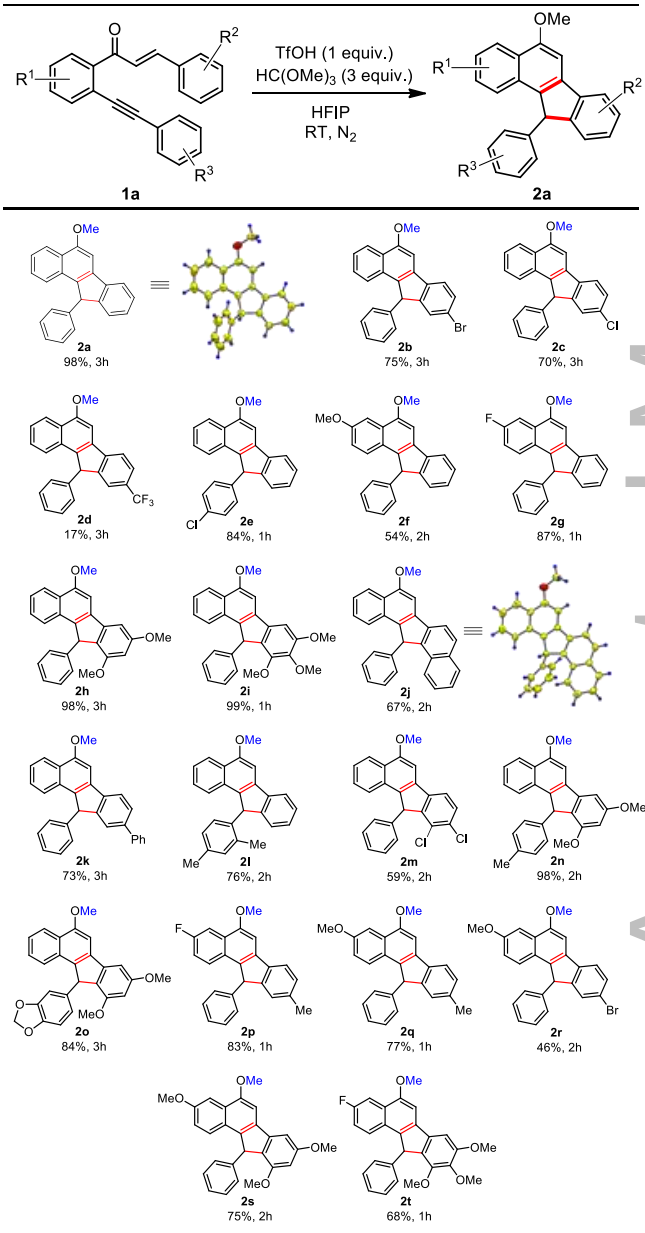


Sl. No.	Condition	Time (h)	Yield (%)[a]	
			2a	3a
1	CH_2Cl_2+TMOF (3 equiv.)	20	35	8
2	CH_3CN+TMOF (3 equiv.)	72	4	-
3	DCE+TMOF (3 equiv.)	5	33	-
4	THF+TMOF (3 equiv.)	48	NR	-
5	**HFIP+TMOF (3 equiv.)**	**3**	**98**	**-**
6	HFIP+TMOF (2 equiv.)	3	75	24
7[b]	HFIP+TMOF (3 equiv.)	3	73	-
8[c]	HFIP+TMOF (3 equiv.)	48	-	-
9	CH_2Cl_2	12	-	53
10	CH_3NO_2	3	-	45
11	Dioxane	24	-	NR
12	CH_3CN	12	-	5
13[b]	HFIP	2	-	80
14	**HFIP**	**2**	**-**	**97**

[an] isolated yield. [b] 50 mol% of TfOH was used. [c] $AgSbF_6$ (0.2 equiv.) was used in the place of TfOH.

On the other hand, in the absence of TMOF, the reaction resulted in the formation of fluorescent active benzo[*a*]fluorenone **3a** in 97% yield in 2 h (Table 1, entry 14). The reaction is high yielding only when 1 equivalent of TfOH was used in solvent HFIP. When we have used different solvents, low to moderate yields were obtained. But to our delight, HFIP solvent[12] has provided exceptionally high yield (97%). As HFIP is a highly polar solvent it stabilizes the polar intermediates involved in the present reaction more, thereby giving high yield of products. Reactions involving other solvents, Brønsted acids, and Lewis acids were found to be less effective. The optimized reaction conditions presented in entries 5 and 14 of Table 1 were used to evaluate the substrate scope for the synthesis of benzo[*a*]fluorenes and benzo[*a*]fluorenones respectively from the starting materials that could easily be accessed from *o*-bromo acetophenones or *o*-bromobenzaldehydes.

Table 2. Substrate scope for benzo[*a*]fluorene synthesis[a]



[a] isolated yield.

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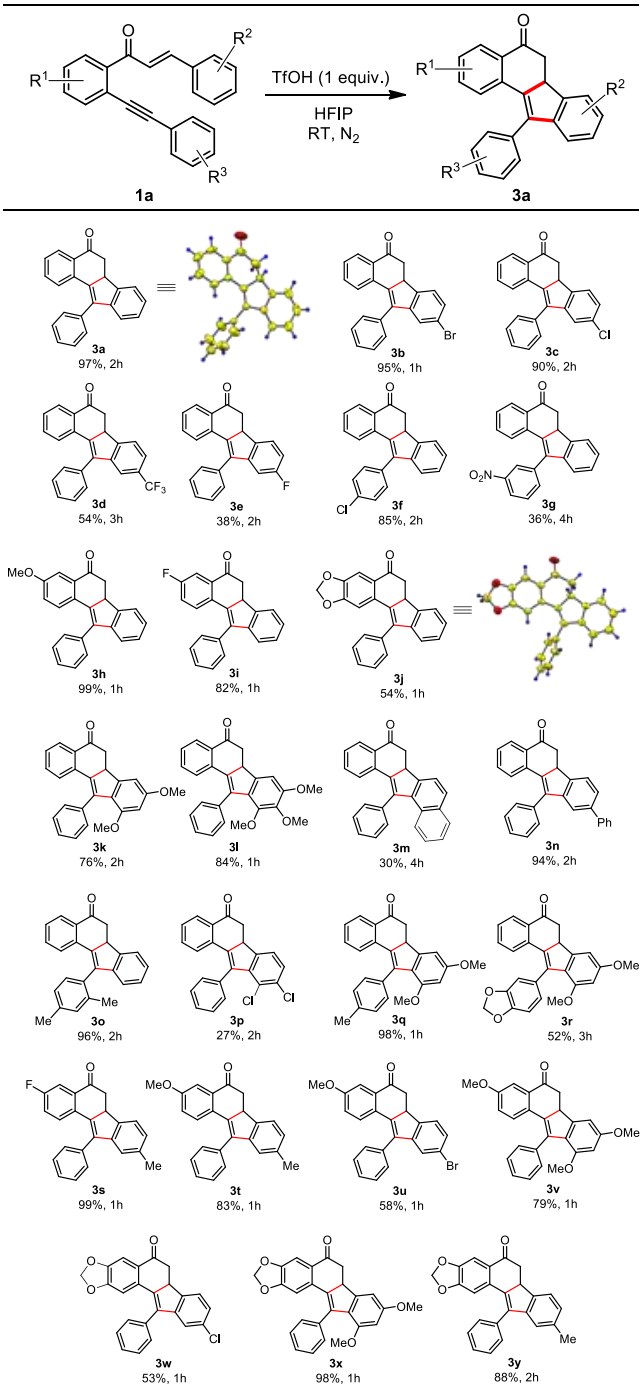
A wide range of substrates having substituents with different electronic effects that can influence the reactivities of all the three aryl rings was subjected to TfOH-promoted benzo[*a*]fluorene synthesis *via* in situ formed acetal (Table 2). The yields were generally very high with most of the substrates studied. When electron withdrawing groups are present on the aryl rings attached to alkynyl and alkenyl carbons decreased yields of benzo[*a*]fluorenes (**2c**, **2d**, **2m** and **2r**) were observed.

Table 3. Substrate scope for benzo[*a*]fluorenone synthesis[a]

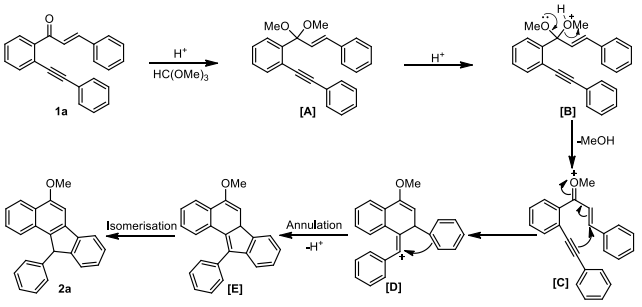


[a] isolated yield.

This is not surprising as this aromatic ring undergoes electrophilic aromatic substitution during the formation of benzo[*a*]fluorene and electron withdrawing substituents in it will suppress it. On the contrary, electron withdrawing fluoro group on the aryl ring of *o*-alkynylaryl ketone portion of the starting substrate did not have any noticeable negative effect on the yield of benzo[*a*]fluorene product (**2g**, **2p,** and **2t**). Whereas, an electron donating OMe group on the aryl ring of *o*-alkynylaryl ketone reduced the yield of the product appreciably (**2f** *vs* **2a**, **2r** *vs* **2b** and **2s** *vs* **2h**). It may be due to increase in reactivity because of the presence of OMe group which can be seen from the lesser reaction times taken by the substrates with OMe substituents (2 h vs 3 h). It was noted that several minor products were also formed in these reactions.

As mentioned in table 1, the same reactants in absence of trimethyl orthoformate resulted in the formation of corresponding fluorenone derivative (Table 1, entry 14). The scope of this reaction was also explored using substrates containing diverse substituents with different electronic effects in presence of triflic acid[13] (Table 3). The yields of the benzo[*a*]fluorenones are comparatively higher than that of the corresponding benzo[*a*]fluorenes which were obtained in the presence of trimethyl orthoformate. As observed in the benzo[*a*]fluorene formation, yields were dropped to moderate or poor whenever there were electron withdrawing substituents on the *β*-aryl ring of the enone moiety (**3d**, **3p**, **3u** and **3w**). In a similar way, the substrate containing electron withdrawing NO_2 group in the aryl ring attached to alkyne moiety resulted in a a poor yield of the product (**3g**, 36%) due to destabilization of the benzylidene carbocation intermediate which is expected to be formed after the first cyclization. Fluoro substituent is a p-donor and electrophilic aromatic substitutions are favored at the para position by a fluoro substituent.[14] The fluoro group, during the formation of **3e**, might not facilitate the cyclization as it has to happen at the meta position. Therefore the yield **3e** was poor (38%). However, a fluoro substituent on the aryl ring of *o*-alkynylaryl ketone did not decrease the yield of **3i** (82%) much. Electron donating groups on the aryl rings, on the other hand, facilitated the reaction and resulted in excellent yields of the products. Here the -OMe group present in the aryl ring of alkynylaryl ketone did not reduce the yields of the reactions more as [C] type intermediate was not forming in this case.

The structures of the compounds were further confirmed by X-ray crystallographic analysis (**2a**, **2j**, **3a,** and **3j)**. The CCDC numbers for these compounds are 1560544, 1560552, 1560545 and 1560546 respectively.



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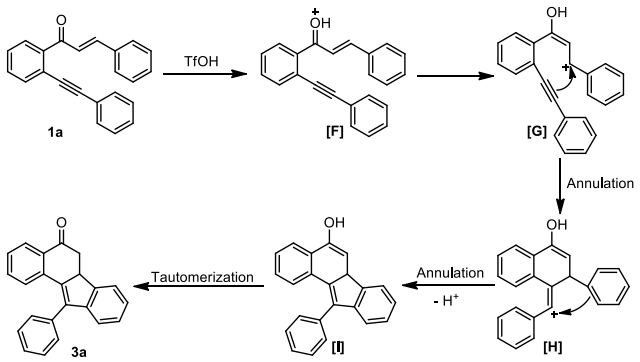
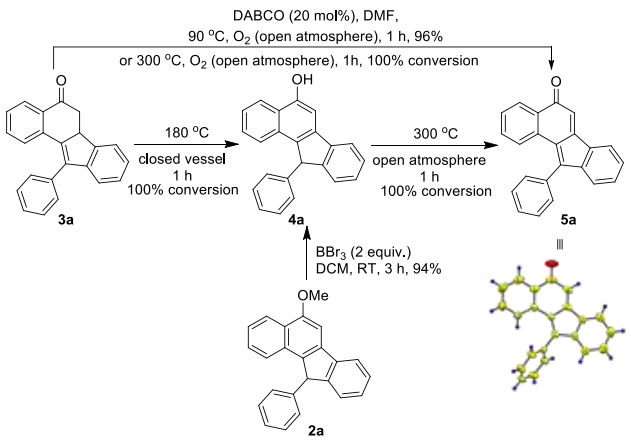
Scheme 2. Plausible reaction mechanism for the synthesis of benzo[*a*]fluorenes.

Both the transformations *i.e.*, benzo[*a*]fluorenone and benzo[*a*]fluorene formation were not feasible in presence of strong electron withdrawing substituent like 4-NO_2 as R^2. Also, this reaction failed to give any of the desired product from the substrate made from pyrene aldehyde and 1-(2-(phenylethynyl)phenyl)ethan-1-one and resulted in the complex product mixture. In addition, the reaction was not working when any one of the three aryl moieties was replaced by cyclic/acyclic aliphatic group.



Scheme 3. Plausible reaction mechanism for the synthesis of benzo[*a*]fluorenones.

A tentative mechanism for the formation of benzo[*a*]fluorene (**2a**) can be proposed as shown in Scheme 2. The acetal [A] is formed from **1a** in the presence of trimethyl orthoformate and TfOH. Then one -OMe group is protonated and departed as MeOH leading to the formation of oxonium ion intermediate [C] from the intermediate [B]. Intramolecular attack of the alkyne leads to the first annulation producing vinyl carbocation [D] which will further undergo annulation through aromatic electrophilic substitution reaction to form the intermediate [E]. Finally, benzo[*a*]fluorene derivative (**2a**) is formed from [E] through isomerization.



Scheme 4. Conversions of benzo[*a*]fluorene and fluorenone derivatives.

On the other hand, the plausible mechanistic pathway for the synthesis of benzo[*a*]fluorenone (**3a**) is illustrated in Scheme 3. **1a** undergoes triflic acid catalyzed keto-enol tautomerism to produce the intermediate [G] *via* the formation of intermediate [F].

Table 4 Stokes Shifts (nm) of the synthesized benzo[*a*]fluorenones in CH_2Cl_2, $CHCl_3$, CH_3CN and MeOH

3a (122, 92, 111, 206)	3b (70, 120, 99, 135)
3c (83, 66, 100, 136)	3d (81, 154, 28, 12)
3e (54, 83, 99, 146)	3f (143, 136, 127, 165)
3g (106, 111, 72, 149)	3h (173, 196, 198, 225)
3i (192, 207, 206, 211)	3j (129, 128, 122, 160)
3k (218, 143, 151, 226)	3l (244, 211, 182, 223)
3m (101, 154, 54, 52)	3n (137, 179, 129, 207)
3o (155, 105, 152, 163)	3p (108, 119, 123, 67)
3q (251, 222, 201, 216)	3r (183, 137, 180, 218)
3s (165, 179, 209, 212)	3t (200, 202, 172, 203)
3u (168, 143, 159, 193)	3v (191, 207, 186, 216)
3w (104, 126, 98, 153)	3x (251, 205, 215, 208)
3y (130, 239, 248, 167)	

The first annulation takes place in a similar fashion like benzo[*a*]fluorene case by the intramolecular attack of the alkyne in the intermediate [G] leads to the formation of vinyl carbocation [H]. The vinyl carbocation is then trapped by the aryl group by aromatic electrophilic substitution reaction to form the intermediate [I]. Finally the intermediate [I] will undergo tautomerization to result in the formation of benzo[*a*]fluorenone derivative (**3a**).

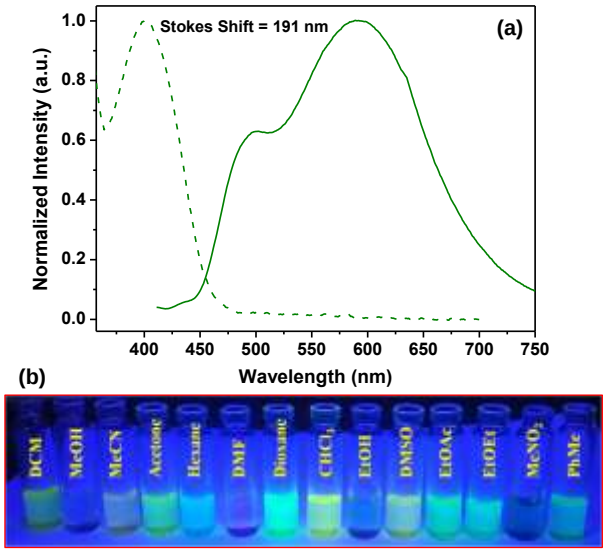


Figure 1. (a) Absorption and emission spectra of compound **3v** in CH_2Cl_2. (b) Solvent-dependent fluorescence activity of compound **3v**.

It is interesting that none of the benzo[*a*]fluorenones **3a-3y** isomerized to corresponding fluorenol

derivative under the reaction conditions. However, treatment of benzo[*a*]fluorene **2a** with BBr_3 resulted in the corresponding benzo[*a*]fluorenol derivative **4a** which is a stable compound (Scheme 4). Remarkably, the benzo[*a*]fluorenone **3a** upon heating in a closed vessel at 180 °C under nitrogen atmosphere resulted in the formation of **4a** without any side reaction. To our surprise, both **3a** and **4a** transformed into a red colored solid **5a** at 300 °C in an open atmosphere by dehydrogenation. The structure of compound **5a** was further confirmed by X-ray crystallographic analysis and its CCDC number is 1560547.

The benzo[*a*]fluorenones **3a**-**3y** are highly fluorescent in a solution state and have high Stokes shifts in different solvents (Table 4).[15] For example, compound **3a** has Stokes shifts of 122, 92, 111 and 206 nms in CH_2Cl_2, $CHCl_3$, CH_3CN and MeOH respectively when excited at 359, 361, 353 and 354 nms corresponding to the n to π* transition.

In a similar fashion, all the other benzo[*a*]fluorenones also have high Stokes shifts as shown in table 4. A representative plot containing the absorption and emission spectra of compound **3v** in CH_2Cl_2 is presented in Figure 1 (a). As seen in the plot, the overlapping region of absorption and emission peaks is very small which is highly desired for efficient applications such as fluorescent imaging and OLED etc.

In conclusion, the synthesis of benzo[*a*] fluorenes and fluorescent benzo[*a*]fluorenones have been achieved by a cationic cycloisomerization of easily accessible enynones using triflic acid as the promoter. The broad substrate scope with a tolerance of a wide array of functional groups and the moderate to high isolated yields of both the desired PAHs in lower reaction time of 1-4 h made this protocol more attractive. The synthesized benzo[*a*]fluorenones are highly florescent in solution state with high Stokes shifts. The high florescent properties of these compounds might find potential applications in imaging and sensing areas. Studies in these lines are currently in progress.

Experimental Section

Representative procedure for the synthesis of benzo[*a*]fluorene derivative 5-methoxy-11-phenyl-11*H*-benzo[*a*]fluorene 2a: To a solution of compound **1a** (100 mg, 0.325 mmol, 1.0 equiv.) in hexafluoroisopropanol solvent (1.5 mL), trimethyl orthoformate (107 µL, 0.974 mmol, 3 equiv.) followed by triflic acid (29 µL, 0.325 mmol, 1 equiv.) were added at room temperature (25 °C) under nitrogen atmosphere. The reaction mixture was stirred and the progress of the reaction was monitored by TLC. After completion of the reaction (after 3 hrs), it was quenched with a saturated $NaHCO_3$ solution (20 mL). Then it was extracted using ethyl acetate. The combined organic layers was washed with saturated brine solution and dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel, 5% EtOAc/hexanes eluent to get the pure 5-methoxy-11-phenyl-11H-benzo[*a*]fluorene **2a** (103 mg, 98%). Pale white solid (yield = 98%); M.P. = 194 - 195 °C; R_f value = 0.84 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.38 - 7.31 (m, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.22 - 7.13 (m, 5H), 7.07 (d, *J* = 6.6, 2H), 5.17 (s, 1H), 4.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 149.7, 142.0, 141.4, 139.3, 134.7, 131.0, 128.9, 128.0, 127.1, 126.9, 126.8, 126.7, 125.8, 124.9, 124.6, 124.4, 123.2, 119.3, 96.6, 55.8, 53.7; IR (Neat, cm^{-1}): 3023, 1696, 1629, 1587, 1396, 1216, 1148, 1097, 1019, 983, 823, 766, 689; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{18}O$: 323.1430; found: 323.1433.

The above procedure was followed to prepare the other benzo[*a*]fluorene derivatives **2b**-**2t** from their respective starting materials.

9-Bromo-5-methoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2b, Table 2): Brownish yellow solid (yield = 75%); M.P. = 230 - 231 °C; R_f value = 0.69 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.42 (s, 1H), 7.40 - 7.36 (m, 1H), 7.35 - 7.30 (m, 1H), 7.26 (s, 2H), 7.24 (s, 1H), 7.23 (s, 1H), 7.09 (dd, *J* = 7.7, 1.6 Hz, 2H), 5.23 (s, 1H), 4.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 151.5, 141.0, 140.4, 138.3, 134.5, 130.8, 130.2, 129.0, 128.1, 127.9, 127.1, 127.0 125.9, 124.9, 124.3, 123.2, 120.58, 120.57, 96.3, 55.8, 53.6; IR (Neat, cm^{-1}): 1577, 1463, 1407, 1376, 1272, 1216, 1086, 1024, 813, 751, 704; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{24}H_{17}BrO$: 423.0355; found: 423.0359.

9-Chloro-5-methoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2c, Table 2): Brownish yellow solid (yield = 70%); M.P. = 208 - 209 °C; R_f value = 0.75 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.40 - 7.35 (m, 1H), 7.33 - 7.29 (m, 2H), 7.25 - 7.19 (m, 4H), 7.17 (s, 1H), 7.05 (dd, *J* = 7.9, 1.5 Hz, 2H), 5.12 (s, 1H), 4.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 151.2, 141.1, 139.9, 138.3, 134.6, 132.5, 130.9, 129.0, 127.9, 127.4, 127.1, 127.0, 125.8, 125.3, 124.8, 124.3, 123.3, 120.2, 96.4, 55.8, 53.5; IR (Neat, cm^{-1}): 3049, 2941, 1577, 1463, 1396, 1376, 1262, 1210, 1143, 1092, 1071, 1019, 983, 818; HRMS: *m/z* $[M]^+$ calcd for $C_{24}H_{17}ClO$: 356.0968; found: 356.0967.

5-Methoxy-11-phenyl-9-(trifluoromethyl)-11*H*-benzo[*a*]fluorene (2d, Table 2): Brownish yellow solid (yield = 17%); M.P. = 188 - 189 °C; R_f value = 0.69 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.3 Hz, 1H), 7.85 (s, 1H), 7.74 - 7.51 (m, 5H), 7.49 - 7.31 (m, 4H), 7.10 (s, 2H), 5.29 (s, 1H), 4.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 149.8, 144.9, 140.7, 139.9, 139.2, 137.9, 136.0, 130.8, 129.6, 129.1, 127.9, 127.2, 127.1, 126.3, 125.3, 124.5, 123.3, 121.6 (q, *J* = 3.5 Hz), 119.3, 96.5, 55.8, 53.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.9; IR (Neat, cm^{-1}): 3059, 1618, 1582, 1433, 1402, 1329, 1272, 1143, 1117, 1061, 828, 746, 694; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{25}H_{17}F_3O$: 413.1124; found: 413.1125.

11-(4-Chlorophenyl)-5-methoxy-11*H*-benzo[*a*]fluorene (2e, Table 2): Reddish solid (yield = 84%); M.P. = 190 - 191 °C; R_f value = 0.66 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.39 - 7.29 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.22 - 7.20 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.11 (s, 1H), 4.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 149.2, 141.4, 140.7, 139.4, 134.1, 132.4, 130.9, 129.3, 129.1, 127.3, 127.1, 127.0, 125.9, 124.8, 124.7, 124.2, 123.3, 119.4, 96.6, 55.8, 52.9; IR (Neat, cm^{-1}): 3065, 1624, 1582, 1448, 1402, 1221, 1148, 1097, 1014, 802, 756; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{24}H_{17}ClO$: 379.0860; found: 379.0861.

3,5-Dimethoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2f, Table 2): Yellow solid (yield = 54%); M.P. = 249 - 250 °C, R_f value = 0.40 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 2.6 Hz, 1H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.22 - 7.08 (m, 6H), 7.01 (d, *J* = 6.4 Hz, 2H), 6.91 (dd, *J* = 9.1, 2.7 Hz, 1H), 5.13 (s, 1H), 4.06 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 155.4, 149.3, 142.1, 141.6, 137.1, 135.0, 128.8, 128.0, 127.0, 126.8, 126.7, 126.4, 126.3, 126.0, 124.8, 119.3, 119.0, 101.9, 97.2, 55.8, 55.3, 53.6; IR (Neat, cm^{-1}): 2920, 1587, 1474, 1371, 1210, 1174, 1019, 833, 808, 761, 730; HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{20}O_2$: 352.1463; found: 352.1461.

3-Fluoro-5-methoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2g, Table 2): Off-white solid (yield = 87%); M.P. = 224 - 225 °C; R_f value = 0.69 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 10.8, 2.7 Hz, 1H), 7.75

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(d, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 9.1, 5.6 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.26 - 7.17 (m, 5H), 7.10 - 7.04 (m, 3H), 5.17 (s, 1H), 4.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 158.9, 155.9 (d, *J* = 5.1 Hz), 149.4, 141.8, 141.2, 138.7 (d, *J* = 2.5 Hz), 134.8, 128.9, 128.0, 127.95, 127.1, 126.9, 126.8, 126.6 (d, *J* = 8.7 Hz), 124.8, 119.3, 116.9 (d, *J* = 25.0 Hz), 107.4 (d, *J* = 22.6 Hz), 97.5, 55.8, 53.7; IR (Neat, cm^{-1}): 2925, 1587, 1520, 1407, 1371, 1205, 1076, 931, 756, 730; HRMS : *m/z* [M]$^+$ calcd for $C_{24}H_{17}FO$: 340.1263; found: 340.1263.

5,8,10-Trimethoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2h, Table 2): Brownish-yellow solid (yield = 98%); M.P. = 278 - 279 °C; R_f value = 0.25 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.36 - 7.27 (m, 2H), 7.20 (s, 1H), 7.17 - 7.08 (m, 5H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.34 (d, *J* = 1.9 Hz, 1H), 5.28 (s, 1H), 4.13 (s, 3H), 3.92 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 156.8, 156.2, 143.7, 141.5, 138.9, 136.8, 130.8, 129.5, 128.1, 126.9, 126.0, 125.8, 124.5, 124.2, 123.1, 98.0, 96.63, 96.55, 55.8, 55.7, 55.5, 51.4; IR (KBr, cm^{-1}): 2930, 1582, 1489, 1447, 1419, 1344, 1246, 1210, 1132, 1075, 1034, 936, 838, 750, 693, 543, 476; HRMS: *m/z* [M+H]$^+$ calcd for $C_{26}H_{22}O_3$: 383.1642; found: 383.1641.

5,8,9,10-Tetramethoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2i, Table 2): Brownish yellow solid (yield = 99%); M.P. = 278 - 279 °C; R_f value = 0.15 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.36 - 7.28 (m, 2H), 7.22 - 7.16 (m, 3H), 7.16 - 7.11 (m, 4H), 5.32 (s, 1H), 4.14 (s, 3H), 4.02 (s, 3H), 3.87 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.4, 154.2, 150.4, 141.8, 141.7, 138.8, 137.4, 136.0, 134.9, 130.8, 128.5, 128.4, 127.0, 126.4, 125.4, 124.4, 124.0, 123.1, 99.0, 96.3, 60.9, 60.0, 56.4, 55.8, 51.9; IR (KBr, cm^{-1}): 3070, 1603, 1587, 1453, 1412, 1365, 1319, 1247, 1205, 1123, 1035, 983, 823, 756, 699, 570, 513; HRMS: *m/z* [M+Na]$^+$ calcd for $C_{27}H_{24}O_4$: 435.1567; found: 435.1567.

5-Methoxy-13-phenyl-13*H*-dibenzo[*a,i*]fluorene (2j, Table 2): Yellow solid (yield = 67%); M.P. = 250 - 251 °C; R_f value = 0.51 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 - 8.24 (m, 1H), 7.87 (s, 2H), 7.83 (dd, *J* = 8.0, 1.6, Hz, 2H), 7.78 - 7.74 (m, 1H), 7.36 - 7.27 (m, 4H), 7.21 (s, 1H), 7.17 - 7.11 (m, 4H), 7.10 - 7.05 (m, 1H), 5.36 (s, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 145.3, 142.1, 139.5, 139.1, 136.8, 133.3, 130.8, 130.2, 129.0, 128.8, 128.7, 128.6, 127.0, 126.5, 126.4, 125.5, 125.0, 124.4, 123.9, 123.6, 123.2, 118.2, 96.6, 55.7, 53.6; IR (KBr, cm^{-1}): 3064, 1582, 1515, 1458, 1380, 1220, 1096, 1019, 812, 755, 698, 631, 590, 435; HRMS: *m/z* [M]$^+$ calcd for $C_{28}H_{20}O$: 372.1514; found: 372.1518.

5-Methoxy-9,11-diphenyl-11*H*-benzo[*a*]fluorene (2k, Table 2): Dull-white solid (yield = 73%); M.P. = 248 - 249 °C; R_f value = 0.41 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.61 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.59 - 7.55 (m, 3H), 7.52 (s, 1H), 7.42 - 7.36 (m, 3H), 7.35 - 7.28 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.21 - 7.17 (m, 1H), 7.15 (d, *J* = 6.8 Hz, 2H), 5.31 (s, 1H), 4.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 150.3, 141.9, 141.4, 140.7, 140.0, 139.0, 135.0, 131.0, 128.9, 128.7, 128.1, 127.14, 127.06, 127.0, 126.7, 126.3, 125.8, 124.6, 124.4, 123.7, 123.2, 119.5, 96.7, 55.8, 53.8; IR (KBr, cm^{-1}): 1587, 1474, 1396, 1216, 1117, 1092, 828, 756, 694, 632, 503; HRMS: *m/z* [M+Na]$^+$ calcd for $C_{30}H_{22}O$: 421.1563; found: 421.1562.

11-(2,4-Dimethylphenyl)-5-methoxy-11*H*-benzo[*a*]fluorene (2l, Table 2): Reddish yellow solid (yield = 76%); M.P. = 171 - 172 °C; R_f value = 0.63 (5% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.40 - 7.29 (m, 4H), 7.28 (s, 1H), 7.24 - 7.19 (m, 1H), 6.82 (s, 1H), 6.71 (s, 2H), 5.16 (s, 1H), 4.14 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 149.9, 141.7, 141.3, 139.2, 138.2, 134.9, 131.1, 128.5, 126.93, 126.9, 126.8, 125.7, 124.8, 124.6, 124.5, 123.1, 119.2, 96.6, 55.8, 53.6, 21.3; IR (Neat, cm^{-1}): 3003, 1587, 1448, 1402, 1371, 1216, 1143, 1102, 1024, 828, 715, 699; HRMS: *m/z* [M]$^+$ calcd for $C_{26}H_{22}O$: 350.1671; found: 350.1668.

9,10-Dichloro-5-methoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2m, Table 2): Brownish yellow solid (yield = 59%); M.P. = 187 - 188 °C; R_f value = 0.56 (5% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 - 7.30 (m, 2H), 7.20 - 7.12 (m, 3H), 7.12 - 7.07 (m, 3H), 5.25 (s, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 148.5, 142.5, 138.8, 137.0, 136.2, 130.8, 130.5, 130.0, 129.6, 129.1, 128.4, 127.3, 126.8, 126.1, 125.1, 123.9, 123.2, 118.1, 96.1, 55.7, 54.4; IR (Neat, cm^{-1}): 2925, 1577, 1453, 1417, 1396, 1221, 1128, 1030, 880, 823, 761; HRMS: *m/z* [M+Na]$^+$ calcd for $C_{24}H_{16}Cl_2O$: 413.0470; found: 413.0471.

5,8,10-Trimethoxy-11-(p-tolyl)-11*H*-benzo[*a*]fluorene (2n, Table 2): Off-white solid (yield = 98%); M.P. = 162 - 163 °C; R_f value = 0.30 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.36 - 7.28 (m, 2H), 7.21 (s, 1H), 7.01 - 6.93 (m, 5H), 6.34 (d, *J* = 2.0 Hz, 1H), 5.27 (s, 1H), 4.13 (s, 3H), 3.92 (s, 3H), 3.68 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.3, 156.8, 156.1, 143.7, 138.8, 138.3, 136.9, 135.3, 130.8, 129.6, 128.8, 128.3, 126.8, 125.8, 124.5 124.3, 123.0, 98.0, 96.6, 96.5, 55.8, 55.7, 55.5, 51.0, 21.1; IR (Neat, cm^{-1}): 2956, 1582, 1453, 1278, 1252, 1200, 1148, 1071, 1040; HRMS: *m/z* [M+H]$^+$ calcd for $C_{27}H_{24}O_3$: 397.1798; found: 397.1794.

5-(5,8,10-Trimethoxy-11H-benzo[a]fluoren-11-yl)benzo[d][1,3]dioxole (2o, Table 2): Brownish yellow solid (yield = 84%); M.P. = 206 - 207 °C; R_f value = 0.21 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, *J* = 7.4 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.39 - 7.32 (m, 2H), 7.20 (s, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 1.6 Hz, 1H), 6.36 (d, *J* = 2.0 Hz, 1H), 5.83 (dd, *J* = 8.4, 1.4 Hz, 2H), 5.23 (s, 1H), 4.14 (s, 3H), 3.93 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 156.8, 156.2, 147.2, 145.7, 143.6, 138.8, 136.6, 135.2, 130.8, 129.3, 126.9, 125.8, 124.5, 124.2, 123.1, 121.9, 108.5, 107.9, 100.6, 97.9, 96.6, 96.5, 55.8, 55.7, 55.5, 51.0; IR (Neat, cm^{-1}): 2930, 1582, 1484, 1453, 1247, 1195, 1138, 1035, 926, 828, 735; HRMS: *m/z* [M+Na]$^+$ calcd for $C_{27}H_{22}O_5$: 449.1359; found: 449.1354.

3-Fluoro-5-methoxy-9-methyl-11-phenyl-11*H*-benzo[*a*]fluorene (2p, Table 2): White solid (yield = 83%); M.P. = 209 - 210 °C; R_f value = 0.66 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 10.8 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.58 - 7.53 (m, 1H), 7.30 - 7.23 (m, 4H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.15 - 7.08 (m, 4H), 5.18 (s, 1H), 4.15 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0, 159.0, 155.8 (d, *J* = 5.2 Hz), 149.6, 142.1, 138.6 (d, *J* = 27.1 Hz), 136.8, 134.4, 128.9, 128.1, 128.0, 127.9, 126.8, 126.5 (d, *J* = 8.3 Hz), 126.4, 125.6, 119.0, 116.8 (d, *J* = 25.1 Hz), 107.3 (d, *J* = 22.6 Hz), 97.5, 55.8, 53.5, 21.6; IR (Neat, cm^{-1}): 3008, 1593, 1525, 1484, 1458, 1407, 1195, 1174, 1086, 988, 926, 813, 715; HRMS: *m/z* [M]$^+$ calcd for $C_{25}H_{14}FO$: 354.1420; found: 354.1418.

3,5-Dimethoxy-9-methyl-11-phenyl-11*H*-benzo[*a*]fluorene (2q, Table 2): Yellow solid (yield = 77%); M.P. = 260 - 261 °C; R_f value = 0.67 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 2.6 Hz, 1H), 7.46 (d, *J* = 9.1 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 3H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 6.3, 3H), 6.97 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.18 (s, 1H), 4.13 (s, 3H), 3.90 (s, 3H), 2.33(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 155.4, 149.5, 142.4, 138.9, 137.2, 136.2, 134.6, 128.8, 128.0, 127.8, 126.6, 126.5 126.4, 125.9, 125.5, 119.3, 118.7, 97.2, 55.7, 55.3, 53.5, 21.6; IR (Neat, cm^{-1}): 2920, 1593, 1484, 1376, 1272, 1205, 1174, 1102, 839, 808, 678; HRMS: *m/z* [M]$^+$ calcd for $C_{26}H_{22}O_2$: 366.1620; found: 366.1621.

9-Bromo-3,5-dimethoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2r, Table 2): Off-white solid (yield = 46%); M.P. = 263 - 264 °C; R_f value = 0.74 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.59 (d, *J* = 5.8 Hz, 1H), 7.49 - 7.43 (m, 2H), 7.38 (s, 1H), 7.26 - 7.19 (m, 4H), 7.07 (dd, *J* = 7.7, 1.6 Hz, 2H), 6.99 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.17 (s, 1H), 4.13 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 155.6, 151.1, 141.2, 140.6, 136.1, 134.8, 130.2, 129.0, 128.0, 127.9, 127.0, 126.97, 126.1, 125.9, 120.2, 120.0, 119.5, 101.9, 96.9, 55.8, 55.3, 53.5; IR (Neat, cm^{-1}): 2920, 1732, 1587, 1458, 1262,

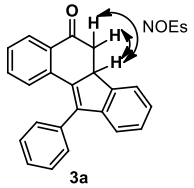
1210, 1185, 1035, 813, 699; HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{19}BrO_2$: 430.0568; found: 430.0565.

3,5,8,10-Tetramethoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2s, Table 2): Brown solid (yield = 75%); M.P. = 237 - 238 °C; R_f value = 0.5 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 2.6 Hz, 1H), 7.53 (d, *J* = 9.1 Hz, 1H), 7.21 (s, 1H), 7.18 - 7.08 (m, 5H), 6.97 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.32 (d, *J* = 2.0, 1H), 5.26 (s, 1H), 4.14 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 157.0, 156.8, 155.2, 143.9, 141.7, 137.1, 136.7, 129.0, 128.5, 128.1, 126.7, 126.1, 126.0, 125.8, 119.3, 101.7, 97.5, 97.2, 96.3, 55.8, 55.7, 55.5, 55.3, 51.3; IR (Neat, cm^{-1}): 3424, 1591, 1460, 1269, 1205, 1138, 988, 844, 734; HRMS: *m/z* $[M]^+$ calcd for $C_{27}H_{24}O_4$: 412.1675; found: 412.1673.

3-Fluoro-5,8,9,10-tetramethoxy-11-phenyl-11*H*-benzo[*a*]fluorene (2t, Table 2): Yellow solid (yield = 68%); M.P. = 231 - 232 °C; R_f value = 0.38 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 10.8, 2.7 Hz, 1H), 7.59 (dd, *J* = 9.1, 5.6 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.17 - 7.13 (m, 2H), 7.12 (d, *J* = 1.5 Hz, 1H), 7.10 (s, 2H), 7.09 - 7.04 (m, 1H), 5.26 (s, 1H), 4.11 (s, 3H), 4.01 (s, 3H), 3.87 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0, 159.1, 155.8, 154.2, 150.4, 141.7, 138.2 (d, *J* = 2.4 Hz), 137.2, 136.0, 134.6, 128.5 (d, *J* = 8.5 Hz), 127.8, 126.5, 126.3, 126.25 (d, *J* = 8.6 Hz), 126.24, 116.9 (d, *J* = 25.2 Hz), 107.2 (d, *J* = 22.7 Hz), 98.9, 97.2, 60.9, 60.0, 56.4, 55.8, 51.9; IR (Neat, cm^{-1}): 2997, 1593, 1520, 1463, 1407, 1355, 1267, 1112, 1035, 988, 833, 730, 694; HRMS: *m/z* $[M]^+$ calcd for $C_{27}H_{23}FO_4$: 430.1580; found: 430.1576.

Representative procedure for the synthesis of benzo[*a*]fluorenone derivative 11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one 3a: To a solution of compound **1a** (100 mg, 0.325 mmol, 1.0 equiv.) in hexafluoroisopropanol solvent (1.5 mL), triflic acid (29 µL, 0.325 mmol, 1 equiv.) was added and the contents were stirred at room temperature (25 °C) under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction (after 2 hrs), it was quenched with saturated $NaHCO_3$ solution. Then it was extracted using ethyl acetate. The combined organic layer was washed with saturated brine solution and dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The crude was purified by column chromatography (using silica gel, 5% EtOAc/hexanes eluent) to get pure 11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one **3a** (97 mg, 97%). Orange yellow solid (yield = 97%); M.P. = 189 - 190 °C; R_f value = 0.39 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 - 8.06 (m, 1H), 7.51 - 7.46 (m, 3H), 7.46 - 7.40 (m, 3H), 7.31 - 7.25 (m, 4H), 7.25 - 7.21 (m, 1H), 7.18 - 7.15 (m, 1H), 4.12 (dd, *J* = 14.1, 5.5 Hz, 1H), 3.50 (dd, *J* = 16, 5.5 Hz, 1H), 2.47 (dd, *J* = 16, 14.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 146.5, 146.0, 139.5, 138.1, 137.3, 134.8, 133.4, 131.0, 129.1, 129.0, 128.2, 127.83, 127.76, 127.6, 126.9, 126.1, 122.9, 121.4, 49.0, 43.0; IR (KBr, cm^{-1}): 1660, 1479, 1443, 1340, 1200, 1097, 1014, 973, 756, 704, 565, 529; HRMS: m/z $[M+H]^+$ calcd for $C_{23}H_{16}O$: 309.1274; found: 309.1271.

The structure of **2a** is also established with ^{1}H-^{1}H COSY, HETCOR and NOESY studies; intramolecular NOEs between CH_2 (δ = 2.47 and 3.50 ppm) and CH (δ = 4.12 ppm) was observed.



3a

The above procedure was followed to prepare the other benzo[*a*]fluorenone derivatives **3b**-**3y** from their respective starting materials.

9-Bromo-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3b, Table 3): Red solid (yield = 95%); M.P. = 226 - 227 °C; R_f value = 0.69 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.46 - 7.35 (m, 3H), 7.32 (d, *J* = 7.3 Hz, 3H), 7.27 (d, *J* = 9.8 Hz, 2H), 7.24 - 7.17 (m, 2H), 7.07 (d, *J* = 6.7 Hz, 1H), 4.03 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.41 (dd, *J* = 15.9, 5.4 Hz, 1H), 2.38 (dd, *J* = 15.8, 14.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 148.5, 144.5, 139.6, 138.5, 136.7, 134.1, 133.5, 130.9, 129.3, 128.9, 128.8, 128.4, 128.2, 127.9, 126.9, 124.5, 124.2, 121.7, 48.6, 42.7; IR (Neat, cm^{-1}): 3070, 1680, 1448, 1283, 1241, 1138, 1061, 926, 782, 746, 704; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{23}H_{15}BrO$: 409.0198; found: 409.0194.

9-Chloro-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3c, Table 3): Red solid (yield = 90%); M.P. = 209 - 210 °C; R_f value = 0.84 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 - 8.08 (m, 1H), 7.54 - 7.45 (m, 3H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.35 - 7 .28 (m, 2H), 7.27 - 7.24 (m, 2H), 7.19 (d, *J* = 1.8 Hz, 1H), 7.18 - 7.15 (m, 1H), 4.14 (dd, *J* = 14.0, 5.3 Hz, 1H), 3.50 (dd, *J* = 16, 5.5 Hz, 1H), 2.47 (dd, *J* = 16, 14.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.0, 148.2, 144.0, 139.7, 138.6, 136.8, 134.1, 133.7, 133.5, 130.9, 129.3, 128.9, 128.4, 128.2, 127.9, 126.9, 125.9, 123.8, 121.6, 48.6, 42.8; IR (Neat, cm^{-1}): 3054, 2915, 1680, 1489, 1448, 1283, 1241, 1071, 818, 771, 735, 709; HRMS: *m/z* $[M+H]^+$ calcd for $C_{23}H_{15}ClO$: 343.0884; found: 343.0884.

11-Phenyl-9-(trifluoromethyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3d, Table 3): Dark red solid (yield = 54%); M.P. = 171 - 172 °C; R_f value = 0.36 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 - 8.09 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.58 - 7.47 (m, 4H), 7.46 - 7.41 (m, 3H), 7.37 - 7.29 (m, 2H), 7.18 (d, *J* = 7.0 Hz, 1H), 4.21 (dd, *J* = 14.1, 5.5 Hz, 1H), 3.54 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.50 (dd, *J* = 16.0, 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 149.2, 147.0, 139.7, 138.6, 136.6, 133.9, 133.6, 130.9, 130.4, 129.4, 128.9, 128.5, 128.3, 127.9, 126.9, 125.7, 123.0, 122.95, 118.0 (q, *J* = 4.0 Hz), 48.9, 42.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.9; IR (Neat, cm^{-1}): 3059, 2925, 1686, 1433, 1319, 1278, 1174, 1123, 1055, 895, 844, 771; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{15}F_3O$: 377.1148; found: 377.1148.

9-Fluoro-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3e, Table 3): Red solid (yield = 38%); M.P. = 169 - 170 °C; R_f value = 0.59 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 - 8.08 (m, 1H), 7.54 - 7.49 (m, 2H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.45 - 7.40 (m, 3H), 7.35 7.28 (m, 2H), 7.19 - 7.16 (m, 1H), 7.00 - 6.95 (m, 1H), 6.92 (dd, *J* = 9.1, 2.4 Hz, 1H), 4.13 (dd, *J* = 14.1, 5.5 Hz, 1H), 3.50 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.48 (dd, *J* = 16.0, 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 161.9, 148.5 (d, *J* = 10.1 Hz), 141.2, 140.1, 138.8 (d, *J* = 2.9 Hz), 136.9, 134.2, 133.4, 130.9, 129.2, 128.9, 128.4, 128.1, 127.8, 126.9, 123.6 (d, *J* = 9.1 Hz), 112.7 (d, *J* = 23.2 Hz), 108.5 (d, *J* = 23.6 Hz), 48.4, 43.0; IR (Neat, cm^{-1}): 2961, 2930, 1686, 1458, 1278, 1138, 1014, 864, 777; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{15}FO$: 327.1180; found: 327.1180.

11-(4-Chlorophenyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3f, Table 3): Red solid (yield = 85%); M.P. = 112 - 113 °C; R_f value = 0.71 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 - 8.08 (m, 1H), 7.52 (d, *J* = 5.6 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.34 - 7.29 (m, 4H), 7.23 - 7.20 (m, 1H), 7.18 - 7.14 (m, 1H), 4.16 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.52 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.48 (dd, *J* = 16.0, 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 146.0, 145.9, 138.7, 138.1, 136.9, 134.1, 133.5, 133.3, 131.0, 130.5, 129.5, 128.0, 127.9, 127.6, 126.7, 126.2, 122.9, 121.2, 49.1, 42.9; IR (Neat, cm^{-1}): 2915, 2853, 1680, 1489, 1283, 1241, 1092, 1009, 844, 813, 751; HRMS: *m/z* $[M+H]^+$ calcd for $C_{23}H_{15}ClO$: 343.0884; found: 343.0880.

11-(3-Nitrophenyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3g, Table 3): Reddish yellow solid (yield = 36%); M.P. = 207 - 208 °C; R_f value = 0.47 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 - 8.32 (m, 2H), 8.12 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.57 - 7.53 (m, 1H), 7.39 - 7.29 (m, 4H), 7.21 - 7.17 (m, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 4.22 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.56 (dd, *J* = 16.1, 5.6 Hz, 1H), 2.51 (dd, *J* = 16.1, 14.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.8, 149.0, 145.8, 145.4, 140.0, 136.8, 136.6, 136.3, 135.4, 133.6, 131.1, 130.3, 128.5, 128.2, 127.8, 126.6, 126.4, 124.2, 123.2, 123.1, 120.8, 49.3, 42.9; IR (Neat, cm^{-1}): 3070, 2925, 1706,

1531, 1453, 1345, 1278, 1081, 813, 766; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{23}H_{15}NO_3$: 376.0944; found: 376.0944.

3-Methoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3h, Table 3): Brownish yellow solid (yield = 99%); M.P. = 230 - 231 °C; R_f value = 0.57 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 2.9 Hz, 1H), 7.49 (d, *J* = 7.1 Hz, 3H), 7.46 - 7.41 (m, 3H), 7.32 - 7.26 (m, 2H), 7.23 - 7.20 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.87 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.13 (dd, *J* = 14.1, 5.4, Hz, 1H), 3.85 (s, 3H), 3.52 (dd, *J* = 16.0, 5.4 Hz, 1H), 2.49 (dd, *J* = 16.0, 14.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 159.2, 146.7, 145.5, 138.0, 137.7, 135.0, 132.2, 130.6, 129.09, 129.06, 128.3, 128.0, 127.5, 125.6, 122.7, 121.7, 121.0, 109.8, 55.5, 49.1, 43.0; IR (Neat, cm^{-1}): 2956, 2848, 1680, 1603, 1484, 1453, 1319, 1278, 1221, 1143, 1019, 875, 751, 704; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{18}O_2$: 339.1380; found: 339.1384.

3-Fluoro-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3i, Table 3): Brownish solid (yield = 82%); M.P. = 185 - 186 °C; R_f value = 0.56 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.53 - 7.40 (m, 6H), 7.33 - 7.27 (m, 2H), 7.25 - 7.22 (m, 1H), 7.16 (dd, *J* = 8.7, 5.2 Hz, 1H), 6.99 (td, *J* = 8.2, 2.9 Hz, 1H), 4.13 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.52 (dd, *J* = 16.1, 5.5 Hz, 1H), 2.47 (dd, *J* = 16.1, 14.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 163.6, 160.8, 146.3, 145.5, 139.3, 137.0, 134.6, 133.6, 132.9 (d, *J* = 6.1 Hz), 129.1 (d, *J* = 26.1 Hz), 129.0, 128.3, 127.6, 126.1, 122.9, 121.4, 120.9 (d, *J* = 22.6 Hz), 113.8 (d, *J* = 22.3 Hz), 48.9, 42.8; IR (Neat, cm^{-1}): 3054, 2956, 1660, 1593, 1474, 1293, 1262, 1169, 1019, 926, 740, 704; HRMS: *m/z* $[M+H]^+$ calcd for $C_{23}H_{15}FO$: 327.1180; found: 327.1180.

11-Phenyl-6,6a-dihydro-5*H*-indeno[2',1':5,6]naphtho[2,3-*d*][1,3]dioxol-5-one (3j, Table 3): Dark brown solid (yield = 54%); M.P. = 235 - 236 °C; R_f value = 0.56 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.51 (s, 1H), 7.50 - 7.40 (m, 5H), 7.32 - 7.27 (m, 2H), 7.23 - 7.20 (m, 1H), 6.54 (s, 1H), 5.96 (d, *J* = 2.9 Hz, 2H), 4.12 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.47 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.43 (dd, *J* = 16.0, 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 151.9, 147.8, 146.5, 145.6, 138.7, 138.1, 134.6, 134.3, 129.2, 129.0, 128.2, 127.5, 126.8, 125.9, 122.7, 121.2, 106.8, 106.0, 101.7, 49.3, 42.6; IR (Neat, cm^{-1}): 3337, 1664, 1608, 1470, 1371, 1260, 1034, 931, 751, 699; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{16}O_3$: 353.1172; found: 353.1173.

8,10-Dimethoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3k, Table 3): Yellow solid (yield = 76%); M.P. = 184 - 185 °C; R_f value = 0.45 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 8.04 - 8.00 (m, 1H), 7.37 (s, 5H), 7.21 - 7.14 (m, 2H), 6.90 - 6.87 (m, 1H), 6.69 (d, *J* = 1.3 Hz, 1H), 6.37 (d, *J* = 1.2 Hz, 1H), 4.05 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.84 (s, 3H), 3.50 (s, 3H), 3.41 (dd, *J* = 15.9, 5.4 Hz, 1H), 2.47 (dd, *J* = 15.8, 14.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.6, 160.4, 156.1, 149.7, 139.4, 137.9, 137.2, 135.1, 133.2, 130.6, 129.1, 128.0, 127.6, 127.23, 127.17, 126.8, 126.6, 100.8, 98.5, 55.7, 55.5, 49.2, 43.4; IR (Neat, cm^{-1}): 3059, 2930, 1685, 1458, 1292, 1205, 1148, 1101, 827, 765, 693; HRMS: *m/z* $[M+H]^+$ calcd for $C_{25}H_{20}O_3$: 369.1485; found: 369.1483.

8,9,10-Trimethoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3l, Table 3): Pale yellow solid (yield = 84%); M.P. = 224 - 225 °C; R_f value = 0.09 (10% EtOAc in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 - 8.02 (m, 1H), 7.43 (s, 5H), 7.24 - 7.18 (m, 2H), 6.94 - 6.90 (m, 1H), 6.88 (s, 1H), 4.07 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.93 (s, 3H), 3.84 (s, 3H), 3.44 (dd, *J* = 15.9, 5.4 Hz, 1H), 3.35 (s, 3H), 2.50 (dd, *J* = 15.8, 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 153.2, 149.4, 142.6, 142.5, 139.1, 137.5, 136.8, 136.5, 133.3, 131.9, 130.6, 129.3, 128.3, 127.6, 127.5, 127.1, 126.6, 103.1, 61.1, 61.0, 56.4, 49.1, 43.4; IR (KBr, cm^{-1}): 2920, 2853, 1675, 1458, 1360, 1334, 1283, 1138, 1102, 1024, 993, 890, 751, 704, 663; HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{22}O_4$: 399.1591; found: 399.1590.

13-Phenyl-6,6a-dihydro-5*H*-dibenzo[*a,i*]fluoren-5-one (3m, Table 3): Yellow solid (yield = 30%); M.P. = 123 - 124 °C; R_f value = 0.57 (5% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 8.10 - 8.07 (m, 1H), 7.88 (d, *J* = 8.2, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.72 - 7.65 (m, 3H), 7.57 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.53 - 7.47 (m, 1H), 7.44 - 7.34 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.29 - 7.22 (m, 2H), 7.18 - 7.13 (m, 1H), 6.97 - 6.93 (m, 1H), 4.25 (dd, *J* = 14.1, 5.4 Hz, 1H), 3.62 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.46 (dd, *J* = 15.8, 14.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 145.0, 141.4, 140.7, 139.6, 138.1, 137.4, 134.0, 133.5, 130.7, 130.0, 129.3, 128.9, 128.6, 128.3, 127.8, 127.4, 127.2, 126.5, 125.8, 125.2, 123.8, 120.8, 49.2, 43.0; IR (Neat, cm^{-1}): 3426, 3049, 2920, 1627, 1582, 1463, 1272, 1117, 1081, 735, 699; HRMS: *m/z* $[M+H]^+$ calcd for $C_{27}H_{18}O$: 359.1430; found: 359.1432.

9,11-Diphenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3n, Table 3): Yellow solid (yield = 94%); M.P. = 147 - 148 °C; R_f value = 0.33 (10% EtOAc in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 - 8.08 (m, 1H), 7.60 - 7.55 (m, 2H), 7.54 - 7.50 (m, 4H), 7.49 - 7.44 (m, 3H), 7.43 - 7.38 (m, 3H), 7.35 - 7.28 (m, 3H), 7.19 - 7.16 (m, 1H), 4.22 (dd, *J* = 14.0, 5.3 Hz, 1H), 3.55 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.55 (dd, *J* = 16.0, 14.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 147.1, 144.9, 141.4, 141.2, 139.5, 138.8, 137.2, 134.7, 133.4, 131.0, 129.2, 129.0, 128.7, 128.2, 127.82, 127.81, 127.4, 127.3, 126.9, 125.3, 123.0, 120.2, 48.8, 43.1; IR (KBr, cm^{-1}): 2925, 2858, 1680, 1458, 1288, 1138, 1076, 1009, 751, 699; HRMS: *m/z* $[M+H]^+$ calcd for $C_{29}H_{20}O$: 385.1587; found: 385.1580.

11-(2,4-Dimethylphenyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3o, Table 3): Red solid (yield = 96%); M.P. = 180 - 181 °C; R_f value = 0.45 (10% EtOAc in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 - 8.05 (m, 1H), 7.49 (d, *J* = 6.7 Hz, 1H), 7.31 - 7.27 (m, 4H), 7.25 - 7.22 (m, 2H), 7.08 (s, 1H), 7.04 (s, 2H), 4.13 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.50 (dd, *J* = 15.9, 5.4 Hz, 1H), 2.47 (dd, *J* = 16, 14.2 Hz, 1H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 146.7, 145.9, 139.9, 138.6, 137.6, 137.4, 134.7, 133.3, 130.9, 129.7, 128.5, 128.4, 127.7, 127.6, 127.4, 126.9, 126.5, 125.9, 122.7, 121.5, 48.9, 43.0, 21.4; IR (Neat, cm^{-1}): 3023, 2915, 1680, 1463, 1283, 1205, 1014, 978, 849, 756, 694; HRMS: *m/z* $[M+H]^+$ calcd for $C_{25}H_{20}O$: 337.1587; found: 337.1587.

9,10-Dichloro-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3p, Table 3): Red solid (yield = 27%); M.P. = 192 - 193 °C; R_f value = 0.38 (5% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 - 8.08 (m, 1H), 7.56 (s, 1H), 7.55 - 7.46 (m, 3H), 7.40 (d, *J* = 6.9 Hz, 2H), 7.36 - 7.28 (m, 2H), 7.27 (s, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 4.15 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.48 (dd, *J* = 16.1, 5.6 Hz, 1H), 2.49 (dd, *J* = 16.0, 14.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4, 146.4, 145.2, 139.8, 138.0, 136.5, 133.8, 133.5, 131.9, 130.9, 130.0, 129.4, 128.8, 128.6, 128.4, 127.9, 126.9, 124.8, 122.9, 48.5, 42.5; IR (Neat, cm^{-1}): 3054, 2915, 1737, 1660, 1598, 1474, 1288, 1262, 1107, 1024, 952, 880, 771; HRMS: *m/z* $[M+H]^+$ calcd for $C_{23}H_{14}Cl_2O$: 377.0494; found: 377.0494.

8,10-Dimethoxy-11-(*p*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3q, Table 3): Yellow solid (yield = 98%); M.P. = 205 - 206 °C; R_f value = 0.18 (10% EtOAc in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 - 8.00 (m, 1H), 7.26 - 7.16 (m, 6H), 6.95 - 6.91 (m, 1H), 6.69 (dd, *J* = 2.0, 0.8 Hz, 1H), 6.38 (d, *J* = 2.0 Hz, 1H), 4.05 (dd, *J* = 14.1, 5.4 Hz, 1H), 3.86 (s, 3H), 3.54 (s, 3H), 3.41 (dd, *J* = 15.9, 5.5 Hz, 1H), 2.48 (dd, *J* = 15.9, 14.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 160.3, 156.1, 149.7, 139.4, 138.0, 136.8, 135.0, 134.0, 133.2, 130.6, 128.7, 127.6, 127.2, 126.7, 126.6, 100.7, 98.5, 55.7, 55.5, 49.1, 43.4, 21.4; IR (KBr, cm^{-1}): 1680, 1453, 1355, 1283, 1205, 1154, 1040, 947, 833, 766, 653, 554; HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{22}O_3$: 383.1642; found: 383.1645.

11-(Benzo[*d*][1,3]dioxol-5-yl)-8,10-dimethoxy-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3r, Table 3): Greenish yellow solid (yield = 52%); M.P. = 183 - 184 °C; R_f value = 0.21 (10% EtOAc in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 - 8.01 (m, 1H), 7.25 - 7.19 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.97 - 6.72 (m, 3H), 6.68 (dd, *J* = 2.0, 0.7 Hz, 1H), 6.39 (d, *J* = 2.0 Hz, 1H), 6.04 (s, 2H), 4.04 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.86 (s, 3H), 3.59 (s, 3H), 3.40 (dd, *J* = 15.9, 5.4 Hz, 1H), 2.46 (dd, *J* = 15.9, 14.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 160.4, 156.0, 151.9, 149.6, 147.4, 146.8, 138.8, 137.8, 135.3, 133.3, 130.7, 130.6, 127.6, 127.1, 126.9, 126.6, 110.0, 108.2, 101.0, 100.7, 98.5, 55.7, 55.6, 49.0, 43.3; IR (Neat, cm^{-1}): 2961, 2920, 1675, 1484, 1433, 1324, 1231, 1143, 1097, 1040, 942, 761, 735;

HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{20}O_5$: 413.1384; found: 413.1385.

3-Fluoro-9-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3s, Table 3): Brownish yellow solid (yield = 99%); M.P. = 140 - 141 °C; R_f value = 0.73 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.54 - 7.43 (m, 3H), 7.42 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.16 - 7.09 (m, 2H), 7.03 (s, 1H), 6.97 (td, *J* = 8.3, 2.8 Hz, 1H), 4.09 (dd, *J* = 14.1, 5.4 Hz, 1H), 3.50 (dd, *J* = 16.1, 5.4 Hz, 1H), 2.45 (dd, *J* = 16.1, 14.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 163.2, 160.7, 146.6, 142.8, 139.3, 137.5, 137.3, 134.8, 133.7 (d, *J* = 3.1 Hz), 132.9 (d, *J* = 6.3 Hz), 129.1 (d, *J* = 22.9 Hz), 128.9, 128.2, 126.9, 122.6, 122.0, 120.9 (d, *J* = 22.7 Hz), 113.8 (d, *J* = 22.3 Hz), 48.6, 43.0, 21.5; IR (Neat, cm^{-1}): 2961, 2915, 1686, 1603, 1458, 1298, 1262, 1019, 895, 823, 704; HRMS: *m/z* $[M]^+$ calcd for $C_{24}H_{17}FO$: 340.1263; found: 340.1260.

3-Methoxy-9-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3t, Table 3): Brownish white solid (yield = 83%); M.P. = 183 - 184 °C; R_f value = 0.58 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 2.8 Hz, 1H), 7.53 - 7.40 (m, 5H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 1H), 6.86 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.09 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.84 (s, 3H), 3.49 (dd, *J* = 16.0, 5.4 Hz, 1H), 2.47 (dd, *J* = 15.9, 14.1 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 159.1, 146.9, 142.7, 138.3, 137.7, 137.3, 135.1, 132.2, 130.7, 129.11, 129.07, 128.3, 127.9, 126.4, 122.4, 121.71, 121.66, 109.7, 55.5, 48.7, 43.2, 21.5; IR (KBr, cm^{-1}): 1685, 1592, 1499, 1468, 1323, 1220, 1153, 1019, 884, 807, 750, 704, 595; HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{20}O_2$: 352.1463; found: 352.1465.

9-Bromo-3-methoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3u, Table 3): Greenish yellow solid (yield = 58%); M.P. = 202 - 203 °C; R_f value = 0.76 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 2.8 Hz, 1H), 7.54 - 7.44 (m, 3H), 7.42 - 7.30 (m, 5H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.08 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.85 (s, 3H), 3.49 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.47 (dd, *J* = 16.0, 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 159.5, 148.8, 144.1, 139.5, 136.7, 134.3, 132.3, 130.0, 129.3, 129.0, 128.4, 128.33, 128.29, 124.1, 124.0, 121.8, 121.7, 109.8, 55.6, 48.7, 42.7; IR (Neat, cm^{-1}): 3018, 2930, 1680, 1587, 1484, 1453, 1319, 1283, 1241, 1210, 1040, 1014, 931, 870, 818, 746, 699; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}BrO_2$: 417.0485; found: 417.0485.

3,8,10-Trimethoxy-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3v, Table 3): Greenish yellow solid (yield = 79%); M.P. = 208 - 209 °C; R_f value = 0.42 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 2.6 Hz, 1H), 7.38 (s, 5H), 6.84 - 6.76 (m, 2H), 6.69 (d, *J* = 1.3 Hz, 1H), 6.38 (d, *J* = 2 Hz, 1H), 4.04 (dd, *J* = 14.1, 5.4 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.52 (s, 3H), 3.42 (dd, *J* = 15.9, 5.4 Hz, 1H), 2.49 (dd, *J* = 15.9, 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 160.1, 158.5, 155.8, 149.1, 137.5, 137.3, 135.0, 131.8, 131.3, 128.0, 127.3, 127.1, 121.7, 109.5, 100.8, 98.5, 55.7, 55.5, 55.46, 49.2, 43.3; IR (Neat, cm^{-1}): 2961, 2837, 1675, 1587, 1479, 1309, 1278, 1200, 1143, 1035, 823, 699; HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{22}O_4$: 399.1591; found: 399.1590.

9-Chloro-11-phenyl-6,6a-dihydro-5*H*-indeno[2',1':5,6]naphtho[2,3-*d*][1,3]dioxol-5-one (3w, Table 3): Brown solid (yield = 53%); M.P. = 265 - 266 °C; R_f value = 0.5 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.63 - 7.60 (m, 1H), 7.55 - 7.50 (m, 1H), 7.41 - 7.34 (m, 2H), 7.24 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.17 - 7.15 (m, 1H), 6.53 (s, 1H), 5.97 (s, 2H), 5.67 (s, 1H), 4.09 (dd, *J* = 13.9, 5.2 Hz, 1H), 3.44 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.41 (dd, *J* = 16, 13.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 151.9, 148.6, 143.7, 140.0, 137.7, 133.8, 132.0, 129.7, 129.5, 128.9, 128.5, 126.8, 125.8, 123.6, 121.4, 117.5, 106.9, 106.0, 101.8, 48.9, 42.4; IR (Neat, cm^{-1}): 2920, 1706, 1670, 1593, 1469, 1262, 1035, 942, 839, 813, 746, 699; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{15}ClO_3$: 387.0782; found: 387.0783.

8,10-Dimethoxy-11-phenyl-6,6a-dihydro-5*H*-indeno[2',1':5,6]naphtho[2,3-*d*][1,3]dioxol-5-one (3x, Table 3): Green solid (yield = 98%); M.P. = 199 - 200 °C; R_f value = 0.22 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.44 - 7.34 (m, 4H), 7.26 (s, 1H), 6.67 (d, *J* = 1.3 Hz, 1H), 6.37 (d, *J* = 2 Hz, 1H), 6.26 (s, 1H), 5.90 (q, *J* = 1.3 Hz, 2H), 4.03 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.86 (s, 3H), 3.51 (s, 3H), 3.37 (dd, *J* = 15.9, 5.5 Hz, 1H), 2.42 (dd, *J* = 15.9, 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 160.3, 155.9, 151.7, 149.3, 147.1, 138.5, 137.0, 135.1, 135.0, 128.1, 127.3, 127.1, 126.3, 106.6, 105.7, 101.5, 100.7, 98.5, 55.7, 55.5, 49.4, 42.9; IR (Neat, cm^{-1}): 3054, 2915, 1670, 1613, 1469, 1329, 1257, 1205, 1148, 1035, 931, 839, 735, 699; HRMS: *m/z* $[M]^+$ calcd for $C_{26}H_{20}O_5$: 412.1311; found: 412.1311.

9-Methyl-11-phenyl-6,6a-dihydro-5*H*-indeno[2',1':5,6]naphtho[2,3-*d*][1,3]dioxol-5-one (3y, Table 3): Brown solid (yield = 88%); M.P. = 291 - 292 °C; R_f value = 0.28 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 - 7.51 (m, 3H), 7.50 - 7.46 (m, 1H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.53 (s, 1H), 5.97 (d, *J* = 2.3 Hz, 2H), 4.11 (dd, *J* = 13.9, 5.5 Hz, 1H), 3.46 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.43 (dd, *J* = 16.0, 13.9 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.2, 151.8, 147.7, 146.7, 142.8, 138.7, 138.4, 137.3, 134.8, 134.4, 129.8, 129.2, 129.0, 128.1, 126.7, 122.4, 121.8, 106.8, 106.0, 101.7, 49.0, 42.8, 21.5; IR (KBr, cm^{-1}): 3385, 1701, 1629, 1484, 1267, 1169, 1035, 870, 808, 766; HRMS: *m/z* $[M+H]^+$ calcd for $C_{25}H_{18}O_3$: 367.1329; found: 367.1329.

Synthetic Procedure for the preparation of benzo[*a*]fluorenol (4a) and benzo[*a*]fluorenone (5a):

Heating Method: Benzo[*a*]fluorenone **3a** was heated under N_2 atmosphere in a closed vessel neatly. After 1 hour, **3a** was found to be fully converted into 11-phenyl-11*H*-benzo[*a*]fluoren-5-ol, **4a**. In an open vessel when **3a** was heated at 300 °C, compound 11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (**5a**) was obtained after 1 hour. The compound **4a** upon heating at 300 °C in open atmosphere converted into compound **5a**.

Chemical Method:

Synthesis of (11-Phenyl-11*H*-benzo[*a*]fluoren-5-ol) (4a): In a round bottom flask, benzo[*a*]fluorene **2a** (50 mg, 0.155 mmol) was dissolved in CH_2Cl_2 (1 mL) solvent under nitrogen atmosphere at 0 °C. Then BBr_3 (268 µL, 0.31 mmol, 1.16 M BBr_3 in CH_2Cl_2.) was added to it and allowed to stir at room temperature for 3 hours. Then the reaction mixture was quenched by a saturated $NaHCO_3$ solution and extracted with EtOAc. Then the organic layer was washed with saturated brine solution, dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, hexanes/EtOAc) to get pure 11-phenyl-11*H*-benzo[*a*]fluoren-5-ol **4a** (45.1 mg, 94%) Brown solid; M.P. = 208 - 209 °C; R_f value = 0.20 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.45 - 7.32 (m, 5H), 7.27 - 7.21 (m, 4H), 7.14 (d, *J* = 6.5 Hz, 2H), 5.47 (s, 1H), 5.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 149.6, 141.9, 140.9, 139.4, 136.1, 131.2, 128.9, 128.0, 127.1, 127.0, 126.7, 125.9, 124.9, 124.59, 124.55, 122.8, 119.8, 119.4, 101.4, 53.7; IR (Neat, cm^{-1}): 2930, 1660, 1587, 1417, 1293, 1102, 1014, 864, 751, 663; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{23}H_{16}O$: 331.1093; found: 331.1092.

Synthesis of 11-Phenyl-5*H*-benzo[*a*]fluoren-5-one (5a): Benzo[*a*]fluorenone **3a** (50 mg, 0.162 mmol) was dissolved in DMF (1 mL) in a round bottom flask. Then DABCO (6.4 mg, 0.032 mmol) was added to the reaction mixture and refluxed at 90 °C for 1 hour in an open atmosphere. After the completion of the reaction water was then added to the reaction mixture. It was extracted with EtOAc. The organic layer was washed with dil. HCl solution followed by saturated $NaHCO_3$ solution. Then the organic layer was washed with saturated brine solution, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, hexaness/EtOAc) to get pure 11-phenyl-5*H*-benzo[*a*]fluoren-5-one **5a** (48 mg, 96%). Dark red solid (yield = 96% in chemical method); M.P. = 190 - 191 °C; R_f

value = 0.31 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.0 Hz, 1H), 7.60 - 7.55 (m, 2H), 7.55 - 7.51 (m, 2H), 7.49 (d, J = 1.6 Hz, 1H), 7.48 - 7.46 (m, 1H), 7.27 (s, 1H), 7.26 (s, 1H), 7.22 - 7.16 (m, 3H), 6.88 (t, J = 4.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 153.0, 149.0, 146.0, 135.7, 134.3, 133.4, 132.3, 130.8, 130.5, 129.3, 129.2, 128.2, 127.84, 127.78, 127.5, 125.2, 122.4, 122.0, 121.3; IR (Neat, cm^{-1}): 2956, 1644, 1593, 1407, 1262, 1097, 1014, 802, 704; HRMS: m/z $[M+H]^+$ calcd for $C_{23}H_{14}O$: 307.1117; found: 307.1118.

Acknowledgements

This work was supported by the grants received from SERB-India. M. M. is grateful to the University Grants Commission (UGC-BSR), New Delhi for her fellowship.

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[15] Absorption and emission properties of compounds **3a-3y** in different solvents are given in the supporting information.

10.1002/adsc.201701516

FULL PAPER

Triflic acid-Mediated Expedient Synthesis of Benzo[*a*]fluorenes and Fluorescent Benzo[*a*]fluorenones

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