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Brønsted/Lewis Acid-Promoted Site-Selective Intramolecular Cycloisomerizations of Aryl-Fused 1,6-Diyn-3-ones for Diversity-Oriented Synthesis of Benzo-Fused Fluorenes and Fluorenones and Naphthyl Ketones

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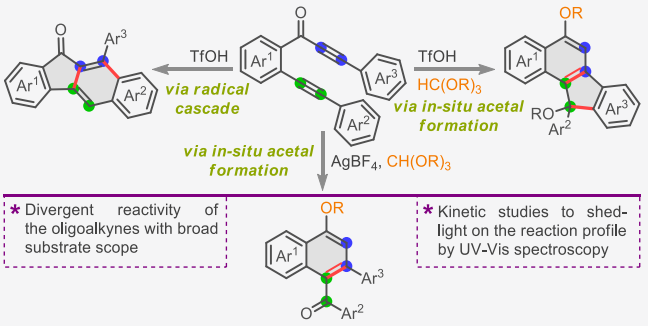
ABSTRACT: Herein, a facile diversity-oriented approach to access functionalized benzo[*a*]fluorenes, benzo[*b*]fluorenones, and naphthyl ketones has been demonstrated *via* site-selective intramolecular cyclization of aryl-fused 1,6-diyn-3-ones. Synthesis of benzo[*a*]fluorenes and naphthyl ketones has been achieved selectively using TfOH and $AgBF_4$, respectively, *via* in situ-formed acetals. Aryl-fused 1,6-diyn-3-ones undergo triflic acid-mediated intramolecular cyclization, leading to benzo[*b*]fluorenone derivatives *via* a radical intermediate as supported by EPR studies. Kinetic studies of these transformations have also been performed by UV−visible spectroscopic analysis to shed light on the reaction profile.



INTRODUCTION

Polyaromatic hydrocarbons have engrossed extensive interest due to their electrochemical and photochemical properties and utility as π-conjugated functional materials such as organic semiconductors and luminescent materials.[1] Polyarylated derivatives of aromatic cores are of particular interest because of their stability, immense ability to transport charge, and fluorescence properties due to the presence of the fused ring structures.[2] Among the polyaromatic hydrocarbons, naphthalene, fluorene, and their analogues such as benzofluorene and benzofluorenone are significant scaffolds and are often employed in developing organic materials.[3] This include electrogenerated chemiluminescence (ECL) devices,[3a] semiconductors,[3b] organic light-emitting diodes,[3c,h] organic field effect transistors,[3d] solar cells,[3i] liquid crystals,[3j,k] etc. Benzo[*a*]fluorenes have widely been employed in organic light-emitting diodes (OLEDs),[3c] potent photosensitizers in photoconductor devices,[3e] optoelectronic materials,[3f] chemo/biosensors,[3g] etc. On the other hand, benzofluorenone moieties have been applied in a range of organic electronics.[3f−h] These structural motifs are even frequently found in many natural products and also constitute the core of many pharmaceutical agents.[4] The tetracyclic core of benzo[*b*]fluorenones is found in several natural products such as stealthin C, kinoscurinone, cysfluoretin, and kinamycins,[5] which exhibits a range of vital biological activities. They have also been employed as synthetic intermediates in the development of bowl-shaped PAHs having carbon skeletons represented on the exterior of C_{60}.[6] Over the past decades, interest toward these scaffolds evoked different groups to come up with alternate protocols to the existing methodologies for the preparation of benzo[*a*]fluorene,[7] benzo[*b*]fluorenone,[8] and naphthalene cores.[9]

Easily accessible aryl fused 1,6-diyn-3-ones offer unique opportunities to synthesize different polyaromatic hydrocarbons. In 2000, Saá and co-workers synthesized benzo[*b*]-fluorenones from 1,6-diyn-3-ones *via* thermal [4 + 2] cycloaromatization by heating them at 150 °C in toluene solvent (Scheme 1II).[8h] Liu and co-workers developed a gold-catalyzed hydrative carbocyclization of 1,5- and 1,6-diyn-3-ones *via* an oxygen transfer process for the preparation of naphthyl ketones (Scheme 1III).[9h] In the recent years, use of aryl-fused 1,6-enynones in finding new transformations has gained much interest.[10] Indeno[1,2-*c*]pyrroles have been accessed from the enaminones derived from aryl-fused 1,6-enynones by Baire and co-workers.[10a] Dithiane derivatives of aryl-fused 1,6-enynones, under gold-catalyzed cyclization conditions, resulted in benzo[*a*]fluorenes.[7d] Zhao and co-workers have also utilized the enaminone derived from aryl-fused 1,6-enynones for the synthesis of dihydroisobenzofur-

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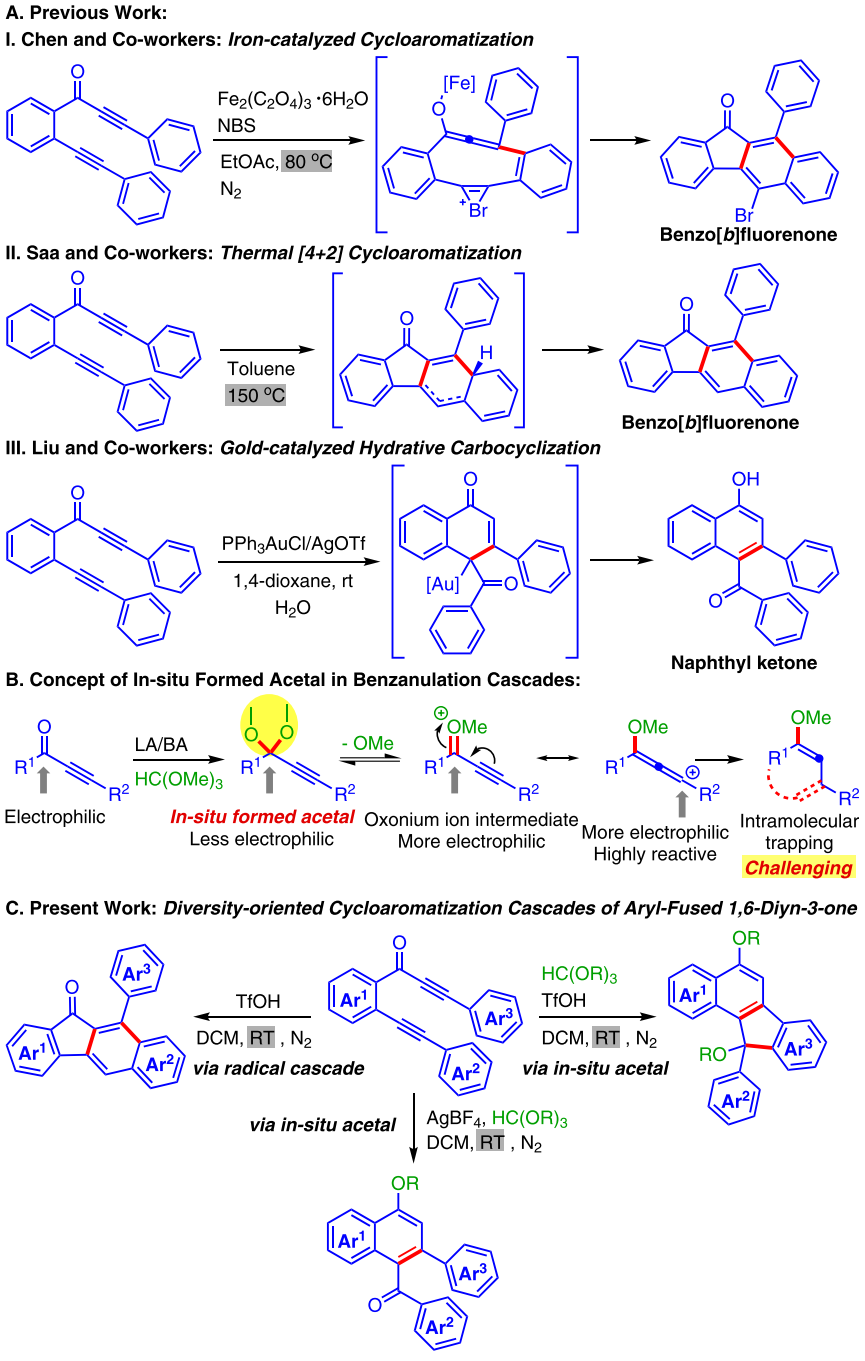
Scheme 1. Strategies for the Access of Polyaromatic Hydrocarbons from Aryl-Fused 1,6-Diynones



an,[10b] α-naphthylamines, and indeno[1,2-*c*]pyrrolones.[10c] Very recently, Chen and co-workers have disclosed the synthesis of 5-brominated benzo[*b*]fluorenones *via* an iron-catalyzed cycloaromatization of aryl-fused 1,6-enynones (Scheme 1I).[8a]

RESULTS AND DISCUSSION

In our endeavor to develop methodologies involving in situ-formed acetals,[11] we have reported alternate methods for the synthesis of benzo[*a*]fluorenes[7b,g] and substituted naphthalenes.[9e] Herein, we present a diversity-oriented approach using aryl-fused 1,6-diynones as the starting material to access benzo[*a*]fluorenes and naphthyl ketones by choosing different acid promoters for the cyclization involving in situ-formed acetal and benzo[*b*]fluorenones directly. In our earlier works, we had used alkenones,[7b,g] which upon acetal formation facilitated nucleophilic attack at the β-carbon or at the formed oxocarbenium carbon for cyclization. With alkynones present in the molecule, we were curious about the reactivity of the aryl-fused 1,6-diynones as it is expected to generate an allenyl cation *via* in situ-formed acetal as shown in Scheme 1B. Strong Brønsted acid, TfOH-promoted intramolecular cyclization of aryl-fused 1,6-diynones to afford benzo[*b*]fluorenones and a different scaffold of benzo[*a*]fluorenes in the presence of trimethyl orthoformate. Interestingly, the same starting material resulted in substituted naphthyl ketone when the reaction was catalyzed by $AgBF_4$ in the presence of trimethyl orthoformate.

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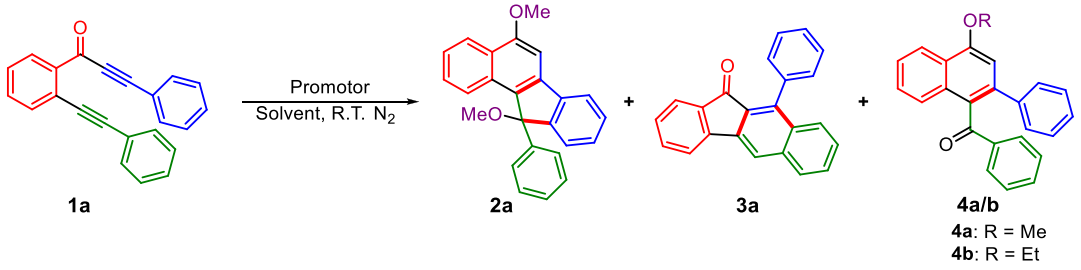
Table 1. Optimization of Conditions for the Selective Synthesis of Benzo[*a*]fluorene, Benzo[*b*]fluorenone, and Naphthyl Ketone[a]



entry	solvent	promotor (equiv)	$HC(OR)_3$ (equiv)	time (h)	yield (%) 2a	3a	4a/4b
1	DCM	TfOH (1)	TMOF (2)	3	31	-	-
2	DCM	TfOH (1)	TMOF (4)	2	79	-	-
3	DCM	-	-	24	-	-	-
4	HFIP	TfOH (1)	TMOF (4)	4	14	-	-
5	CH_3CN	TfOH (1)	TMOF (4)	4	26	19	-
6	CH_3NO_2	TfOH (1)	TMOF (4)	3	-	89	-
7	DCE	TfOH (1)	TMOF (4)	4	55	-	-
8	dioxane	TfOH (1)	TMOF (4)	4	17	51	-
9	DCM	TfOH (0.5)	TMOF (6)	4	37	31	-
10	TMOF	TfOH (1)	-	5	30	-	-
11	DCM	Tf_2NH (0.5)	TMOF (4)	3	11	60	-
12	**DCM**	**TfOH (1)**	**TMOF (6)**	**3**	**85**	-	-
13	CH_3CN[b]	TfOH (1)	TMOF (4)	2	-	90	-
14	DCM/CH_3CN (1:1)	TfOH (1)	TMOF (6)	2	77	17	-
15	DCM/HFIP (6:1)	TfOH (1)	TMOF (6)	4	17	-	-
16	toluene	TfOH (1)	TMOF (6)	4	34	57	-
17	$CHCl_3$	TfOH (1)	TMOF (6)	4	9	-	-
18	**DCM**	**TfOH (1)**	-	**1**	-	**93**	-
19	DCM	TfOH (0.5)	-	4	-	76	-
20	DCM	$AgBF_4$ (0.05)	TMOF (1)	24	-	-	70
21	**DCM**	**$AgBF_4$ (0.05)**	**TEOF (1)**	**24**	-	-	**79**
22	DCM	$AgBF_4$ (0.05)	TEOF (2)	16	-	-	69
23	DCM	$AgBF_4$ (0.05)	TEOF (3)	24	-	-	22
24	DCM	$AgBF_4$ (0.05)	TEOF (0.5)	26	-	-	75
25	DCM	$AgBF_4$ (0.05)	-	24	-	48	-
26	DCM	AgOTf (0.05)	TEOF (1)	12	-	-	56
27	DCM	$AgNTf_2$ (0.05)	TEOF (1)	11	-	-	68
28	DCM	$AgClO_4$ (0.05)	TEOF (1)	19	-	-	72
29	DCM	$AgSbF_6$ (0.05)	TEOF (1)	11	-	-	68
30	DCM	$Cu(OTf)_2$ (0.05)	TEOF (1)	24	-	-	34
31	DCM	$In(OTf)_3$ (0.05)	TEOF (1)	24	-	87	-
32	DCM	$Sn(OTf)_2$ (0.05)	TEOF (1)	24	-	88	-
33	DCM	$Sc(OTf)_3$ (0.05)	TEOF (1)	24	-	87	-
34	DCM	$BiBr_3$ (0.05)	TEOF (1)	24	-	79	-
35	DCM	$FeCl_3$ (0.05)	TEOF (1)	24	-	74	-
36	DCM	I_2 (0.05)	TEOF (1)	24	-	85	-
37	DCM	$AuCl_3$ (0.05)	TEOF (1)	24	-	88	-
38	DCM	PPh_3AuCl (0.05)	TEOF (1)	24	-	86	-
39	DCM	IprAuCl (0.05)	TEOF (1)	24	-	78	-
40	DCM	CSA (0.05)[c]	TEOF (1)	24	-	87	-
41	dioxane	$AgBF_4$ (0.05)	TEOF (1)	24	-	22	15
42	CH_3NO_2	$AgBF_4$ (0.05)	TEOF (1)	24	-	79	-
43	DCE	$AgBF_4$ (0.05)	TEOF (1)	24	-	-	63
44	CH_3CN	$AgBF_4$ (0.05)	TEOF (1)	24	-	75	-

[a]Reaction conditions: **1a** (0.1 mmol), LA/BA, $HC(OR)_3$, and solvent (1 mL) with continuous stirring at R.T. under a N_2 atmosphere. '-': No Reaction. [b]Reaction conducted at 60 °C. [c]10-(+) Camphor sulfonic acid.

A number of reactions were performed to find out the optimum condition for the selective formation of benzo[*a*]-fluorene, benzo[*b*]fluorenone, and naphthyl ketone from the aryl fused 1,6-diyn-3-one **1a**. The details of the optimization

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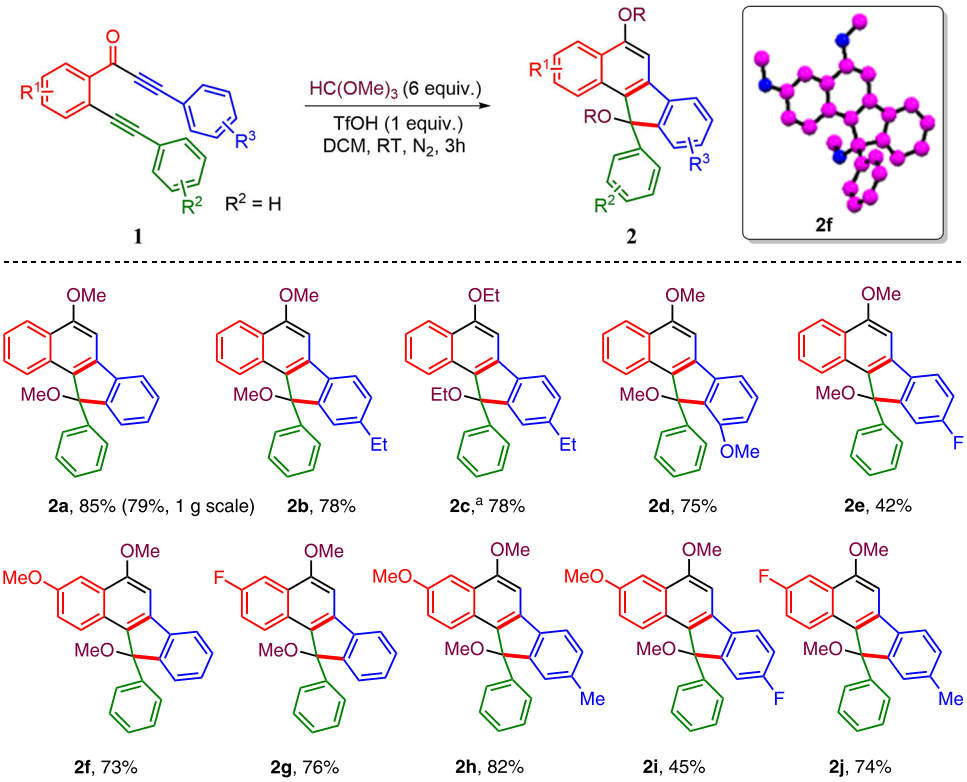
Table 2. Substrate Scope for Benzo[*a*]Fluorene Synthesis



experiments are collected in Table 1. When the aryl fused 1,6-diyn-3-one derivative **1a** was treated with 1 equiv of triflic acid in presence of 2 equiv of trimethyl orthoformate (TMOF), it led to the formation of benzo[*a*]fluorene derivative **2a** in 31% isolated yield (Table 1, entry 1). Then, the reaction was attempted with varying amounts of TMOF and triflic acid and different solvents. The highest yield of benzo[*a*]fluorene (**2a**) (85%) was achieved when the reaction was carried out in the presence of 6 equiv of TMOF and 1 equiv of TfOH in DCM solvent at room temperature under a nitrogen atmosphere (Table 1, entry 12). Remarkably, the same reaction in the absence of trimethyl orthoformate resulted in the formation of benzo[*b*]fluorenone **3a** exclusively with 93% isolated yield (Table 1, entry 18). Decreasing the amount of TfOH to 0.5 equiv decreased the yield of **3a** considerably (Table 1, entry 19). Further, catalyst screening was done with various Lewis and Brønsted acids. To our delight, we have achieved a different PAH, namely, naphthyl ketone **4a**, in 70% isolated yield from the reaction of the same aryl-fused 1,6-diyn-3-one derivative **1a** with trimethyl orthoformate in the presence of 5 mol % $AgBF_4$ catalyst (Table 1, entry 20). Using triethyl orthoformate (TEOF) in place of trimethyl orthoformate increased the yield of the product **4b** (Table 1, entry 21). Increasing or decreasing the amount of TEOF reduced the yield of the product (Table 1, entries 22−24). In the absence of TEOF, the reaction resulted in the benzofluorenone derivative **3a** only (Table 1, entry 25). Reaction parameters such as catalyst, solvent, amount of TEOF, etc. were changed and were found to be less efficient for the formation of naphthyl ketone derivative **4b**. Therefore, the condition described in reactions 12, 18, and 21 were used to evaluate the substrate scope for the synthesis of benzo[*a*]fluorene, benzo[*b*]fluorenone, and napthyl ketone derivatives, respectively.

In the case of benzo[*a*]fluorene synthesis, substrates with diverse substituents were well tolerated and provided the corresponding benzo[*a*]fluorene derivatives with moderate to excellent yields (42−85%) in a short time period (Table 2). It is important to mention that electronic and steric effects of substituents did not show an appreciable influence on the reaction outcome except for the substrates having R^2 substituents and fluorine on the aryl ring attached to the *β*-carbon of the alkynone. The fluoro substituent is a *para*-donor and reactions at the *para*-position of fluorobenzene are usually high yielding than the corresponding reaction at any other single position of benzene.[12] However, here the carbon meta to fluoro substitution is involved in the second cyclization. Thus, a decreased yield was observed in the case of **2e** and **2i**. However, a fluoro substitution on the aryl bridging the alkynone and arylalkyne did not decrease the yield of **2g** (76%) and **2j** (74%). Substrates having 4-Me, 4-F, and 2-Me-5-NO_2 as R^2 did not result in the desired products and instead resulted in complex product mixtures. This reaction failed to give the desired product when an aliphatic substituent is present at the *β*-carbon of the alkynone. Instead, naphthyl ketone derivatives **4k** and **4l** were obtained from substrates **1p** and **1q**, respectively, as there is no aryl for further benzannulation (Scheme 2). From this observation we were curious to know whether the benzo[*a*]fluorene **2a** formation is happening through the naphthyl ketone (**4a**) intermediate. For this purpose, the naphthyl ketone (**4a**) was treated with 6 equiv of TMOF and 1 equiv of TfOH. However, even after 24 h, no benzo[*a*]fluorene formation was observed; only the starting material **4a** remained. Thus, it can be concluded that

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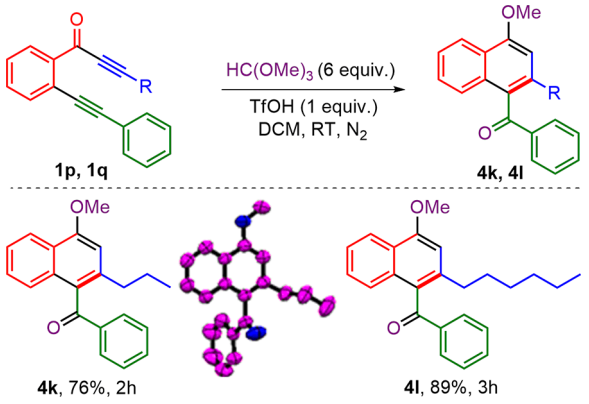
Scheme 2. Reaction of Aryl-Fused 1,6-Diyn-3-one Having an Aliphatic Substituent



benzo[*a*]fluorene formation is not happening *via* the formation of the naphthyl ketone intermediate.

On the basis of these results and our previous reports,[7b,g] we propose a plausible reaction mechanism for the formation of benzo[*a*]fluorene **2a** as shown in Scheme 3. First, in the presence of trimethyl orthoformate and TfOH, acetal [**A**] is formed from **1a**. Then, in the presence of strong acid, one of the −OMe groups is protonated and departed as MeOH leading to the formation of oxocarbenium ion intermediate [**C**] from intermediate [**B**]. At this stage, an intramolecular cyclization of the alkyne occurs on the proton-activated alkyne as shown in intermediate [**C**]. This may be facilitated by the electron-withdrawing nature of the oxocarbenium ion. Thus, generated intermediate [**D**] will undergo aromatic electrophilic substitution on the vinyl carbocation to form [**E**]. Finally, benzo[*a*]fluorene derivative (**2a**) is formed by isomerization of intermediate [**E**] followed by quenching with methanol. When an aliphatic group is present at the *β*-carbon of the enynone, second cyclization is not possible due to the absence of aryl moiety and the reaction ended up with the formation of naphthyl ketone (Scheme 2).

As stated in Table 1, in the absence of trimethyl orthoformate, the same reaction ended up with the formation of the benzo[*b*]fluorenone derivative in 93% isolated yield (Table 1, entry 18). It is worth mentioning that Saá and co-workers reported the synthesis of benzo[*b*]fluorenone from aryl-fused 1,6-diynone by refluxing it in toluene at 150 °C. However, they ended up with a mixture of two regioisomeric benzo[*b*]fluorenones in an almost quantitative combined yield (72 and 24%) in 11 h.[8h] However, in our methodology using TfOH, solely one isomer of benzo[*b*]fluorenone is obtained in excellent yield.

The scope of this reaction has been demonstrated by successful cyclization of a diverse 1,6-diyn-3-one derivatives containing different substituents on different aryl groups in the presence of triflic acid (Table 3). Exceptional yields were obtained for all the substrates studied, and there were essentially not much substituent effects on the yield of the products. When any of the benzene ring is replaced by an aliphatic group, this reaction resulted in a complex product mixture.

To understand the mechanism of the reaction, an EPR experiment was done on the reaction mixture at different times. In all the cases the outcomes of the experiments were the same. They gave a positive response with a signal having a *G* value of 2.0129 (Figure 1). Also, upon addition of triflic acid to the substrates, the color of the reaction mixture immediately changed to greenish yellow from pale yellow and finally to dark yellow. In the presence of TEMPO, the yield of the reaction decreased to 62%. Therefore, the reaction might be happening *via* Schmittel cyclization involving a diradical intermediate [H] as depicted in Scheme 4. The role of a Brønsted acid in making this reaction to happen at room temperature may be the protonation of the carbonyl facilitated the cycloisomerization to form the intermediate [H].[13] This undergoes an intramolecular radical cyclization to furnish a strained cyclic allene [**I**]. The strained allene [**I**] might lead to the formation of aromatic product **3a**. The role of acid in this reaction was evaluated by carrying out the reaction of **1a** in the presence of 2 equiv of $H_2{}^{18}O$. Significant ^{18}O labeling of carbonyl oxygen in the product was noticed from the HRMS spectra of the product (Scheme 6). The reaction took the same 1 h time for its completion without an appreciable drop in the yield. In another experiment, product **3a** was treated with TfOH (1 equiv) and 2 equiv of $H_2{}^{18}O$ in dichloromethane. Surprisingly, very little ^{18}O labeling was observed in the product. Acid-

Scheme 3. Plausible Reaction Mechanism for the Formation of Benzo[*a*]fluorenes

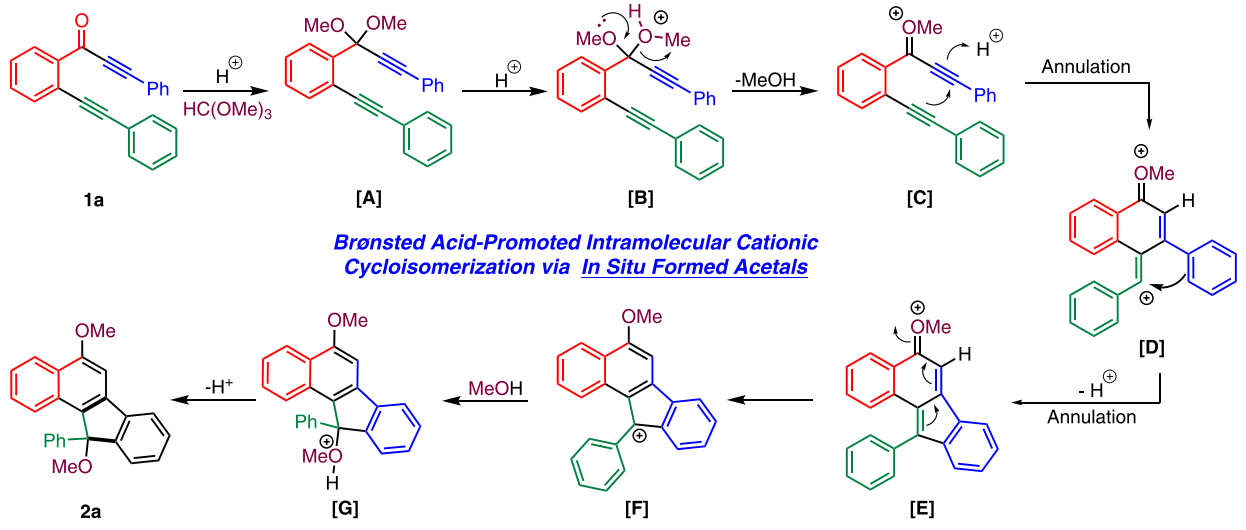


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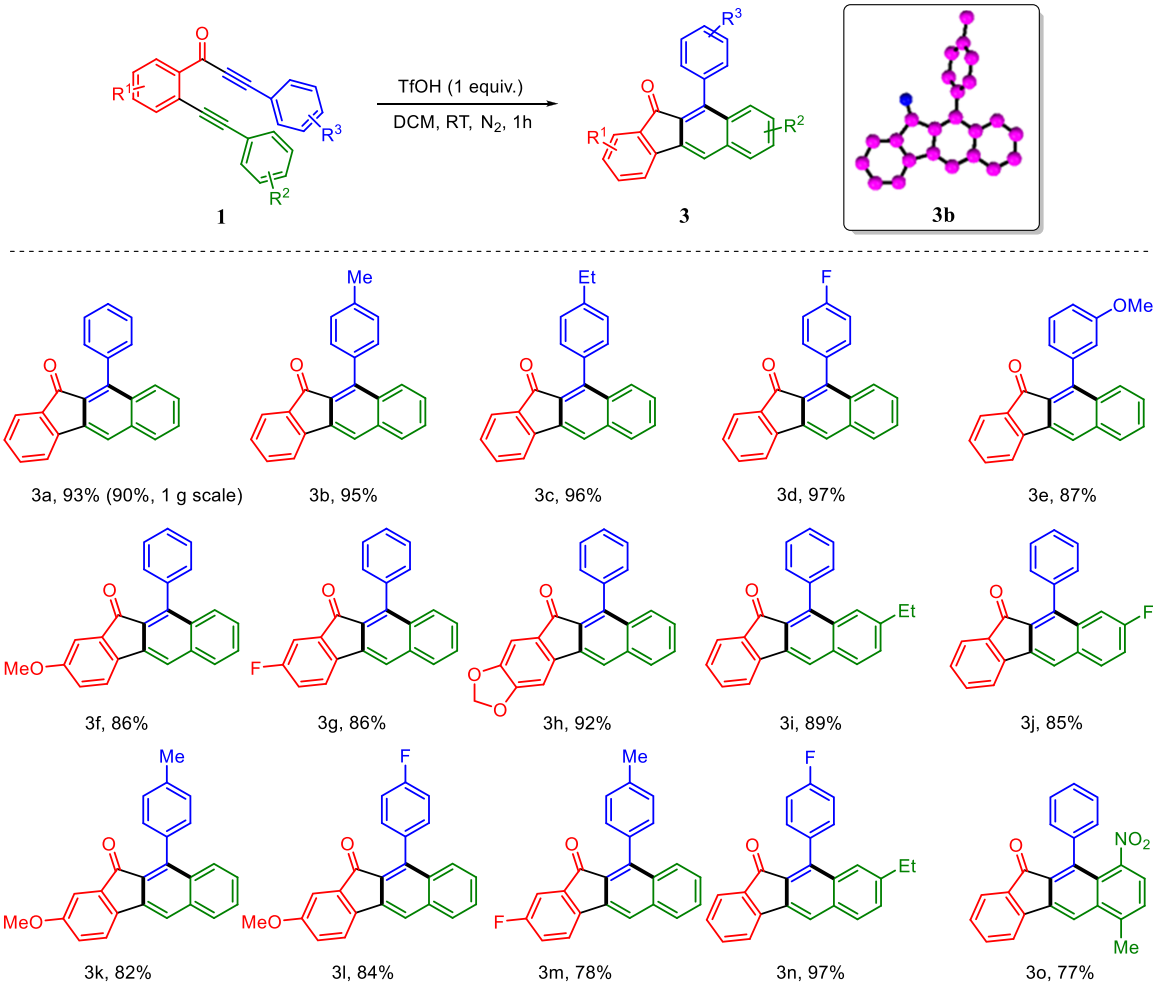
Table 3. Substrate Scope for Benzo[*b*]fluorenone Synthesis



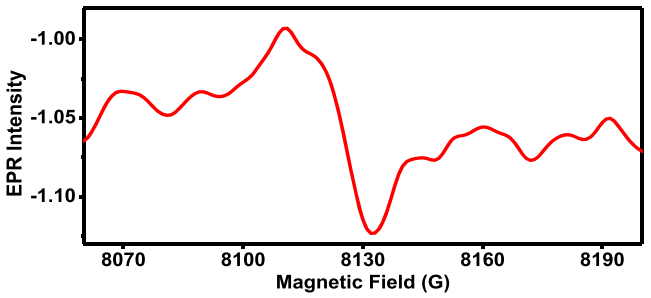
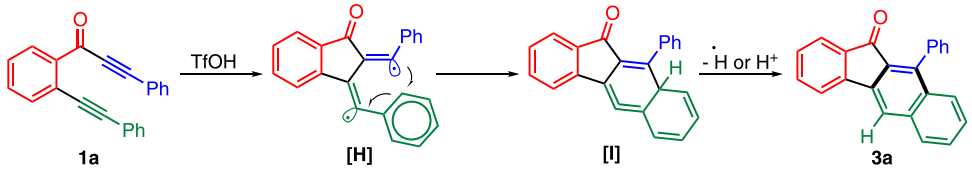


Figure 1. EPR spectra of the reaction mixture of reaction **1a** with TfOH.

promoted hydration of the carbonyl in **1a** might be the reason for the ^{18}O incorporation. This supports the role of acid in promoting the cyclization by activation of the carbonyl.

Having achieved the intramolecular cyclization of aryl-fused 1,6-diyn-3-one **1** to form benzo[*a*]fluorene **2** and benzo[*b*]-fluorenone **3**, we explored the scope of naphthyl ketone formation using various aryl-fused 1,6-diyn-3-ones **1** under the optimized reaction condition depicted in Table 1, entry 21. Substrates with donor and acceptor groups in all the three aryl rings were evaluated. Although the reaction conditions were not optimized for each of the substrates studied, the reaction showed good functional group tolerance for all types of substituents (62−80%), indicating the generality and robustness of this transformation (Table 4). In this methodology,

Scheme 4. Plausible Reaction Mechanism for the Formation of Benzo[*a*]fluorenones



Brønsted Acid-Promoted Intramolecular Cycloisomerization via Radical Intermediate

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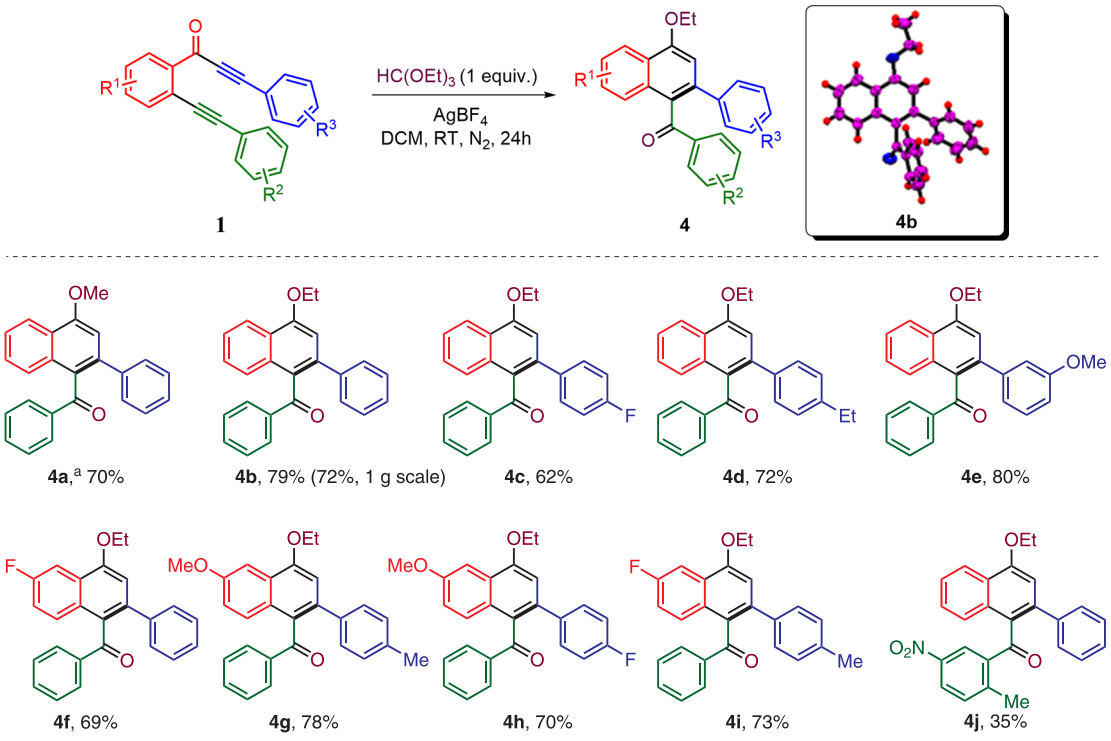
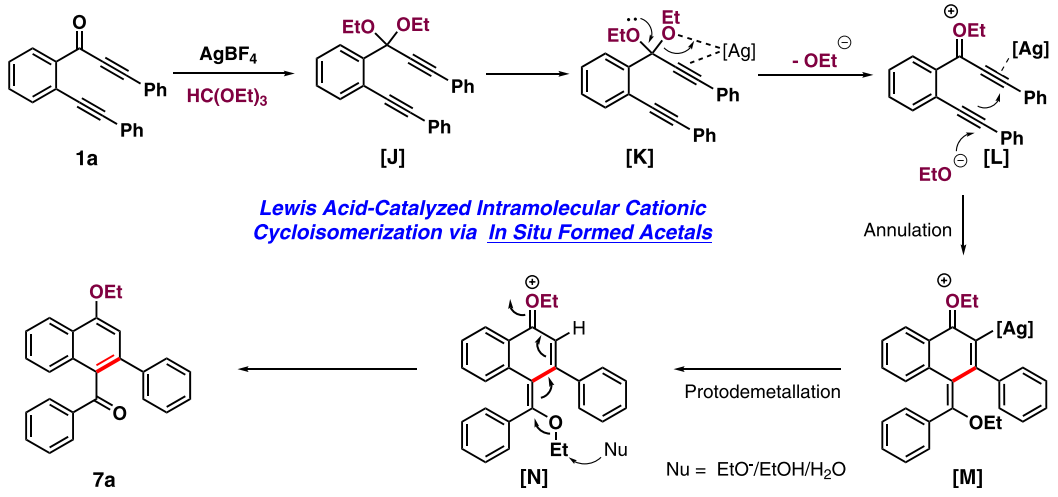
Table 4. Substrate Scope for Naphthyl Ketone Synthesis



Scheme 5. Tentative Reaction Mechanism for the Formation of Naphthyl Ketones



when any of the benzene ring is replaced with an aliphatic group, the desired product was not formed.

A tentative mechanism for the formation of naphthyl ketone (**4a**) can be proposed as shown in Scheme 5. In the presence of triethyl orthoformate and $AgBF_4$, acetal [**J**] will from. Coordination of the silver catalyst to both alkyne and acetal oxygen as in intermediate [**K**] might facilitate the removal of OEt^- to form the oxocarbenium ion intermediate [**L**]. Now, a tandem attack of OEt^- on the alkyne followed by cyclization on the silver-activated alkyne will generate intermediate [**M**]. This will undergo protodemetallation to form intermediate [**N**]. Now, aromatization will result in the formation of the naphthyl ketone product. In the TfOH-promoted formation of benzo[*a*]fluorene, TfOH was used in a stoichiometric amount and less nucleophilic MeOH is formed during the generation of the oxocarbenium ion intermediate from the in situ-formed acetal (Scheme 3). Therefore, the vinyl carbocation intermediate undergoes intramolecular benzannulation to form the benzo[*a*]fluorene. The possibility of intramolecular transfer of OEt in the acetal to the tethered alkyne as proposed by Liu and co-workers in the synthesis of 4-hydroxy-1-naphthyl ketones[9h] followed by cyclization cannot be excluded. It has to be mentioned that Yamamoto and co-workers favored the formation of 1-allenylisochromes in the silver-catalyzed reaction of the same title compounds with alcohols through a different mechanism.[14] However, the spectral characteristics of the napthyl ketone derivative **4a** matched with that of the compound obtained by them in the reaction of the same substrate involving MeOH, suggesting the possibility of naphthyl ketone formation in their study as well, at least with this particular substrate.

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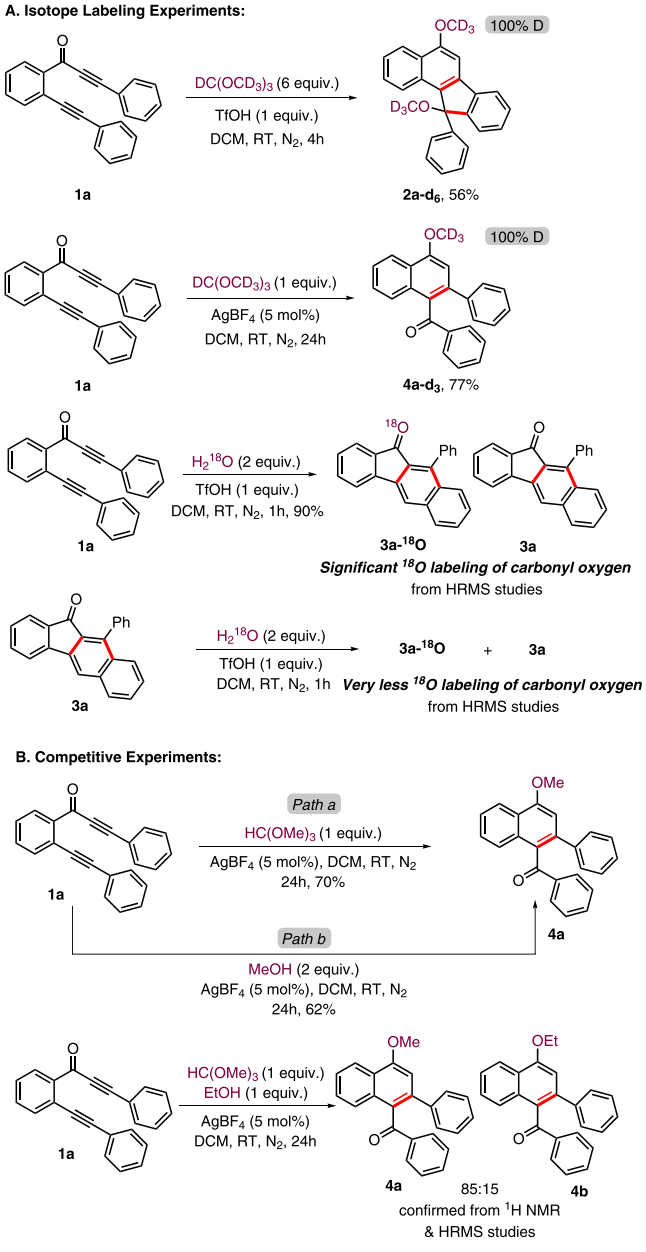
To prove the proposed mechanisms for the formation of benzo[*a*]fluorene and naphthyl ketone moieties, we did some control experiments. First, fully deuterated trimethyl orthoformate ($DC(OCD_3)_3$) was prepared following the literature-reported method.[15] Then, the reactions for the formation of benzo[*a*]fluorene **2a** and naphthyl ketone **4a** were carried out using $DC(OCD_3)_3$ under standard reaction conditions (Scheme 6A). Incorporation of -OCD_3 in both the products

Scheme 6. Control Experiments



2a-d_6 and **4a-d_3** was confirmed from the ^{1}H NMR spectrum of the respective products. The singlets at 4.14 and 2.90 ppm corresponding to the two -OCH_3 protons of **2a** disappeared in **2a-d_6** and the singlet at 4.02 ppm corresponding to the -OCH_3 protons of **4a** disappeared in **4a-d_3** in their respective ^{1}H NMR spectra.

In addition, we have performed the reactions leading to benzo[*a*]fluorene **2a** and naphthyl ketone **4a** formation in the presence of $H_2{}^{18}O$ to check whether the adventitious water present in the reaction mixture involved in the reaction. We did not observe any ^{18}O labeling in the products benzo[*a*]-fluorene **2a** and naphthyl ketone **4a** from HRMS analysis. Thus, it can be concluded that the oxocarbenium ion involved in the formation of products **2** and **4** is formed through the in situ-formed acetal and not the possible hemiacetal.

Then, to prove whether the formation of the naphthyl ketone moiety is through the formation of acetal or not, we performed a competition experiment. First, we performed a reaction under the standard condition using 2 equiv of MeOH instead of TMOF. However, we got the naphthyl ketone in 62% yield only (Scheme 6B). Another reaction was performed in the presence of 1 equiv of TMOF and 1 equiv of EtOH, keeping other reaction conditions unchanged. Both the OMe and OEt incorporated naphthyl ketone derivatives (**4a** and **4b**) involving TMOF and EtOH, respectively, were obtained. Interestingly, the ratio of OMe and OEt incorporated naphthyl ketones was found to be 85:15 (Scheme 6B), as indicated by the ^{1}H NMR spectrum of the product mixture (Figure 2). This reveals clearly that the reaction takes place *via* the formation of acetal as a ketone would form acetal readily with trimethyl orthoformate than with an alcohol. From these results we can conclude that the reaction happens *via* in situ-formed acetal only.

We then attempted some interesting transformations of the synthesized compounds. When benzo[*a*]fluorene **2a** was treated with BBr_3, it resulted in the corresponding benzo[*a*]-fluorenol derivative **5a** with the benzylic OMe group intact (Scheme 7A). Remarkably, the naphthyl ketone **4a,** upon treatment with BBr_3, produced a new class of benzo[*a*]-fluorenone **6a** instead of stopping at the OMe deprotection alone. We have also examined the scope of this transformation with a couple of more substrates, and the structures of the products are presented in Scheme 7C. A probable mechanism for its formation is also presented in Scheme 7B. This conversion requires two equivalents of BBr_3. The first equivalent of BBr_3 reacts with the OMe group, leading to intermediate [**O**]. The generated Br^- will attack methyl, thereby forming intermediate [**P**]. Activation of the carbonyl by another molecule of BBr_3 effects electrophilic cyclization. Finally, aqueous workup will generate the benzo[*a*]fluorenone with the extrusion of two molecules of boronic acid. The structures of all the synthesized compounds were confirmed by NMR, IR, and high-resolution mass spectroscopic analysis. The structures of **2f**, **3b**, **4b**, and **4k** were further confirmed by X-ray crystallographic analysis with the CCDC numbers, 1998442, 1998443, 1998444, and 1998445, respectively.

Since the starting material and the products are aromatic, having specific absorption maxima, all the three transformations have been followed by UV−visible spectroscopy to get more insight into the reactions. For each transformation, the UV spectra were recorded at regular intervals of time. An absorbance versus wavelength plot clearly revealed the smooth decrease in the intensity of starting material's absorbance with a gradual increase in the intensity of the product's absorbance. A plot of ln $[A]_t/[A]_o$ for the starting material versus time resulted in a linear fit in each case, suggesting first-order reaction kinetics (Figure 3).

Reaction Kinetics by UV−Vis Experiments for the Formation of Benzo[*a*]Fluorene, Benzo[*b*]Fluorenone, and Naphthyl Ketone. In conclusion, we have developed facile protocols for the construction of diverse molecular scaffolds such as benzo[*a*]fluorenes, benzo[*b*]fluorenones, and

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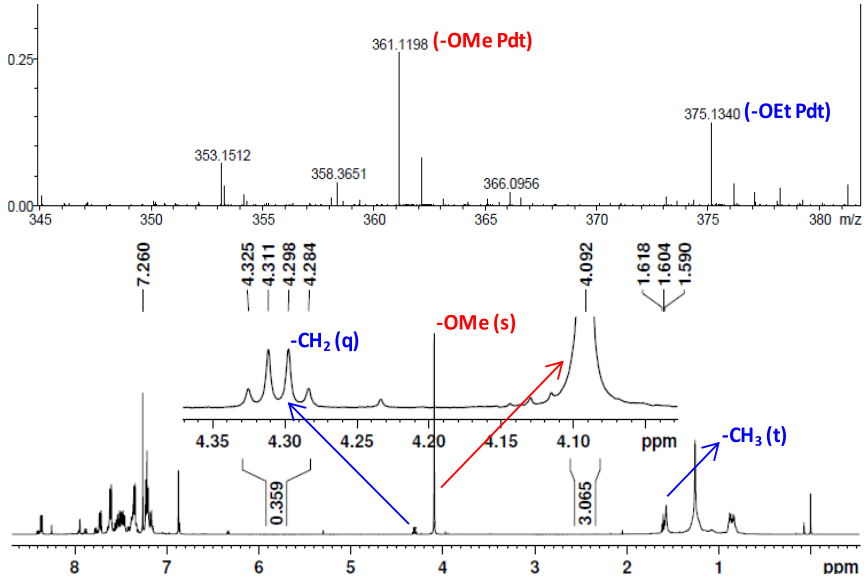
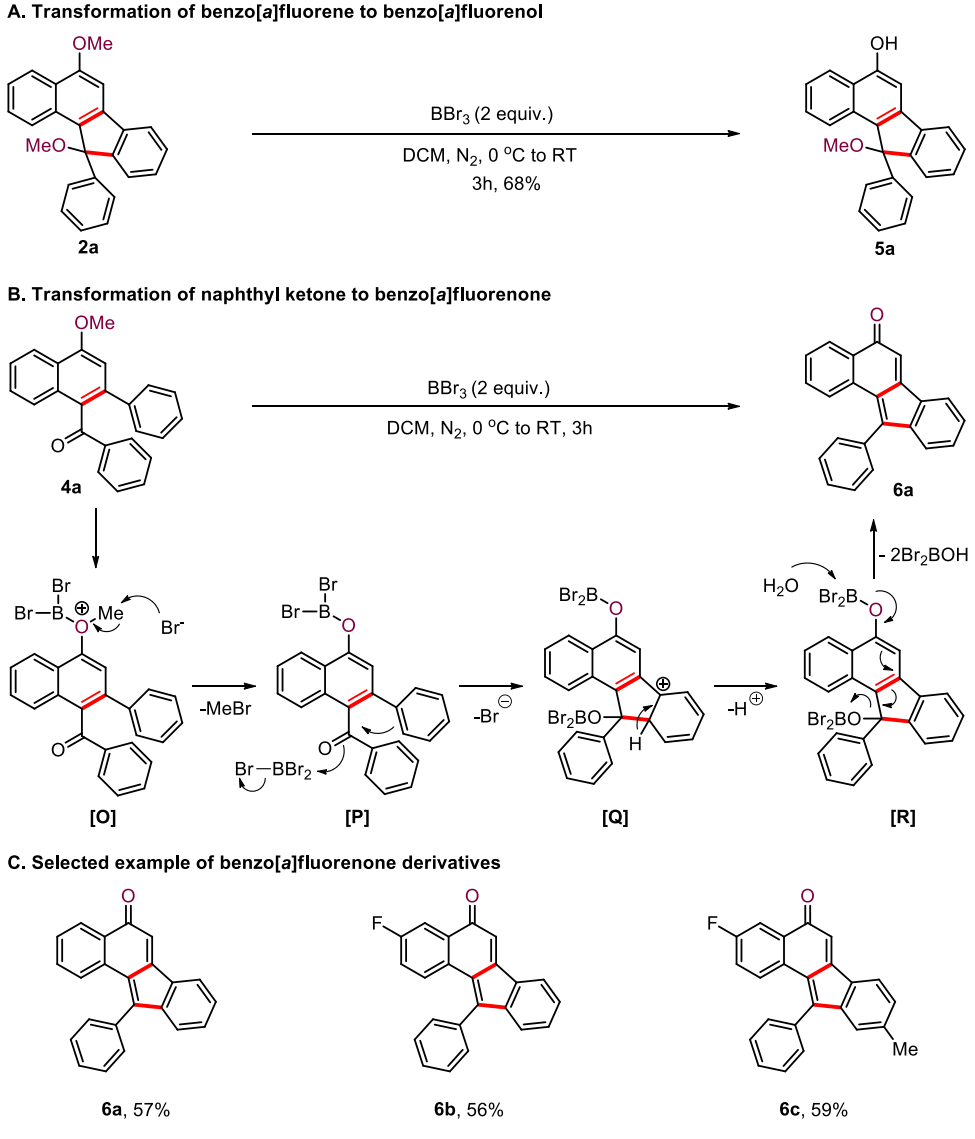


Figure 2. HRMS and ^{1}H NMR spectra of the crude product obtained in the Ag-catalyzed reaction of **1a** with TMOF and EtOH.

Scheme 7. Transformations of the Synthesized Benzo[*a*]fluorene and Naphthyl ketone



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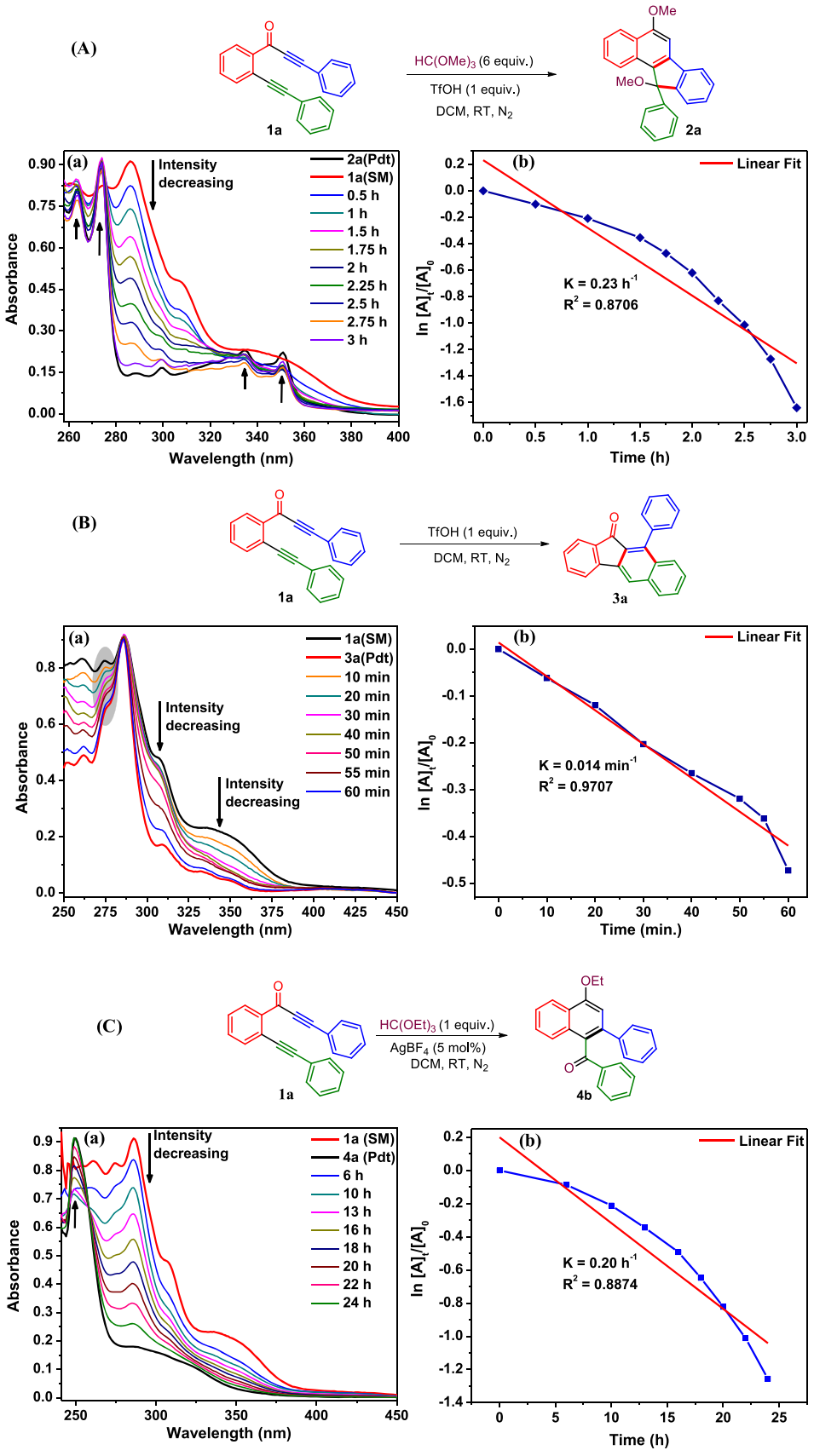

Figure 3. (a) UV profile and (b) reaction kinetics for the formation of (A) benzo[*a*]fluorene, (B) benzo[*b*]fluorenone, and (C) naphthyl ketone.

4-ethoxy arylnaphthalenes from aryl-fused 1,6-diyn-3-ones. Formation of acetal under the reaction condition using trimethyl orthoformate changes the reactivity of the title substrate under different Lewis or Brønsted acid conditions.

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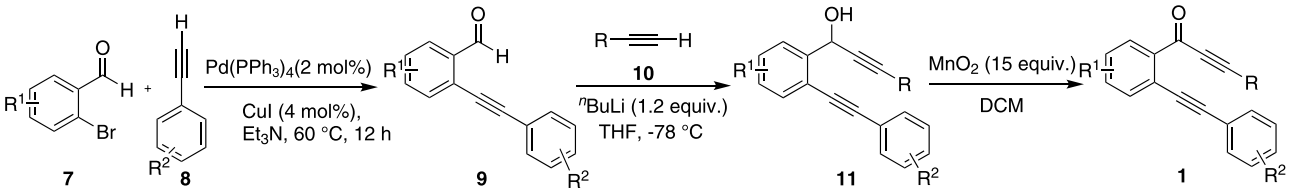
Scheme 8. Preparation of 1,6-Diyn-3-ones (1)



1a, $R^1 = R^2 = H$; R = Ph
1b, $R^1 = R^2 = H$; R = 4-Et Ph
1c, $R^1 = R^2 = H$; R = 3-OMe Ph
1d, $R^1 = R^2 = H$; R = 4-F Ph
1e, $R^1 = R^2 = H$; R = 4-Me Ph
1f, R^1 = 5-OMe; $R^2 = H$; R = Ph
1g, R^1 = 5-F; $R^2 = H$; R = Ph
1h, R^1 = 5-OMe; $R^2 = H$; R = 4-Me Ph
1i, R^1 = 5-OMe; $R^2 = H$; R = 4-F Ph
1j, R^1 = 5-F; $R^2 = H$; R = 4-Me Ph
1k, $R^1 = H$; R^2 = 4-Et; R = Ph
1l, $R^1 = H$; R^2 = 4-F; R = Ph
1m, R^1 = 3,4-O-CH_2-O-; $R^2 = H$; R = Ph
1n, $R^1 = H$; R^2 = 4-Et; R = 4-F Ph
1o $R^1 = H$; R^2 = 2-Me, 4-NO_2; R = Ph
1p, $R^1 = R^2 = H$; R = Pr
1p, $R^1 = R^2 = H$; R = Hx

Further, it has been shown that the 4-methoxy napthyl ketones can be converted into a different benzo[*a*]fluorenone derivative.

EXPERIMENTAL SECTION

General Information. Except otherwise mentioned, all the chemicals and solvents were obtained commercially and used without purification. Starting materials were prepared by following known literature procedures. THF and toluene were dried over sodium and freshly distilled before use. Dichloromethane and dichloroethane were dried over CaH_2 and freshly distilled before use. ^1H and ^{13}C NMR spectra were recorded at room temperature on 400 and 500 MHz spectrometers using $CDCl_3$ solutions containing tetramethylsilane (TMS) as an internal standard. IR spectra were recorded using an FT-IR spectrometer and are reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded using ESI-Q-TOF and ESI-Orbitrap techniques. Melting points were determined using a melting range apparatus and are uncorrected. For TLC, silica gel plates $60F_{254}$ were used and the spots were visualized by UV light and/or by treatment with Seebach solution (phosphomolybdic acid (2.5 g), $Ce(SO_4)_2$ (1 g), conc. H_2SO_4 (6 mL), and H_2O (94 mL)) followed by heating. Column chromatography was performed on silica gel (100−200 mesh) using an ethyl acetate and hexanes mixture as the eluent.

Preparation of Aryl-Fused 1,6-Diyn-3-ones (1). 2′-Bromobenzaldehyde derivative **7** (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol %), and CuI (4 mol %) were dissolved in dry THF/Et_3N (1:1) in a round-bottom flask under a nitrogen atmosphere at room temperature. After 5 min of stirring, the corresponding terminal alkyne **8** (1.2 equiv) was added and the reaction mixture was refluxed at 60 °C using an oil bath. After the completion of the reaction as indicated by TLC, the reaction mixture was filtered through Celite and the solvents were evaporated under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, hexanes/EtOAc) to get pure 2-(arylethynyl)benzaldehyde derivatives **9**.

To a solution of alkyne **10** (1.2 equiv) in dry THF at −78 °C, *n*-BuLi (2.5 M in hexanes, 1.2 equiv) was added slowly and stirred for 45 min at −78 °C and then a solution of *o*-alkynylaldehyde **9** (1 equiv) in THF was added slowly. The resulting mixture was allowed to stir for 2 h at room temperature. After completion of the reaction as mentioned by TLC, the reaction mixture was quenched by aqueous NH_4Cl solution and the organic layer was extracted with EtOAc and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure, and it was directly used for further reaction.

MnO_2 (15 equiv) was added in portions to a solution of the alcohol derivative **11** in DCM and stirred at room temperature. After completion of the reaction as indicated by TLC, the reaction mixture was filtered through Celite and concentrated under reduced pressure. The residue was purified by column chromatography to yield the corresponding 1,6-diyn-3-ones **1**.

The above procedure was used for the preparation of all the 1,6-diyn-3-one derivatives **1** employed in this study by using corresponding *o*-alkynylaldehydes and terminal alkynes (Scheme 8).

Analytical Data of Aryl-Fused 1,6-Diyn-3-ones (1). The aryl-fused 1,6-diyn-3-ones **1a**, **1d**, **1e**, **1g**, **1l**, and **1p** are reported in the literature, and the analytical data of the synthesized compounds are in good accordance with the literature data.[8a,9h,16]

*3-(4-Ethylphenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-one (**1b**, Scheme 8).* Yellow gummy (yield = 380 mg, 81%); R_f = 0.44 in 5% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 6.9 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.64−7.60 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 3H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.35−7.32 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 177.5, 147.6, 138.4, 134.2, 133.2, 132.3, 131.9, 131.5, 128.5, 128.2, 128.1, 127.9, 123.1, 122.9, 117.2, 95.4, 94.0, 88.3, 88.0, 28.9, 15.1; IR (KBr, cm^{-1}): υ 2929, 1697, 1598, 1307, 1188, 760, 726, 598; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{19}O$ 335.1430; found 335.1430.

*3-(3-Methoxyphenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-one (**1c**, Scheme 8).* Yellow gummy (yield = 402 mg, 72%); R_f = 0.31 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.59−7.51 (m, 3H), 7.47−7.42 (m, 1H), 7.30 (s, 3H), 7.26−7.20 (m, 2H), 7.10 (s, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 3.71 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 177.5, 159.3, 138.2, 134.3, 132.5, 131.9, 131.5, 129.6, 128.6, 128.2, 128.0, 125.6, 123.1, 123.0, 121.0, 117.6, 117.3, 95.5, 93.3, 88.2, 87.8, 55.2; IR (KBr, cm^{-1}): υ 2995, 1703, 1580, 1463, 1245, 1032, 756, 698, 529; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{17}O_2$ 337.1223; found 337.1229.

*1-(5-Methoxy-2-(phenylethynyl)phenyl)-3-phenylprop-2-yn-1-one (**1f**, Scheme 8).* Yellow gummy (yield = 350 mg, 83%); R_f = 0.28 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 2.7 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.61 (s, 1H), 7.56−7.53 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31−7.28 (m, 3H), 7.12 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.94 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 177.6, 159.2, 139.7, 135.7, 133.2, 131.7, 130.8, 128.6, 128.3, 128.2, 123.4, 120.2, 118.9, 115.9, 115.4, 94.0, 93.8, 88.2, 88.0, 55.7; IR (KBr, cm^{-1}): υ 2995, 1699, 1607, 1484, 1275, 1029, 747, 700, 549; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{17}O_2$ 337.1223; found 337.1226.

*1-(5-Methoxy-2-(phenylethynyl)phenyl)-3-(p-tolyl)prop-2-yn-1-one (**1h**, Scheme 8).* Yellow gummy (yield = 376 mg, 85%); R_f = 0.47 in 5% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70−7.48 (m, 6H), 7.31 (s, 3H), 7.18−7.10 (m, 3H), 3.94 (s, 3H), 2.40 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 177.5, 159.2, 141.5, 139.9, 135.7, 133.2, 131.7, 129.4, 128.2, 123.5, 118.7, 117.1, 115.9, 115.3, 94.5, 93.9, 88.2, 88.1, 85.6; IR (KBr, cm^{-1}): υ 3006, 1632, 1554, 1292, 1163, 1003, 756, 692; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{19}O_2$ 351.1380; found 351.1379.

*3-(4-Fluorophenyl)-1-(5-methoxy-2-(phenylethynyl)phenyl)-prop-2-yn-1-one (**1i**, Scheme 8).* Yellow gummy (yield = 365 mg, 81%); R_f = 0.50 in 10% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 2.7 Hz, 1H), 7.62−7.55 (m, 3H), 7.54−7.51 (m, 2H), 7.30−7.26 (m, 3H), 7.09 (d, *J* = 8.6 Hz, 1H), 7.01 (t, *J* = 8.5 Hz, 2H), 3.89 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 177.3, 163.9 (d, *J* = 253.7 Hz), 159.2, 139.7, 135.7, 135.4 (d, *J* = 8.9 Hz), 131.6, 128.2 (d, *J* = 6.9 Hz), 123.4, 118.8, 116.3 (d, *J* = 3.5 Hz), 116.1, 115.9, 115.7, 115.4, 94.1, 92.7, 88.2, 88.0, 55.6; IR (KBr, cm^{-1}): υ 2835, 1649, 1594, 1500, 1191, 1005, 831, 745, 522; HRMS

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(ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}O_2F$ 355.1129; found 355.1130.

*1-(5-Fluoro-2-(phenylethynyl)phenyl)-3-(p-tolyl)prop-2-yn-1-one (**1j**, Scheme 8).* Yellow gummy (yield = 302 mg, 77%); R_f = 0.58 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.8 Hz, 1H), 7.67−7.57 (m, 3H), 7.49 (d, J = 7.8 Hz, 2H), 7.32 (s, 3H), 7.26−7.21 (m, 1H), 7.13 (d, J = 7.7 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 175.9, 161.5 (d, J = 251.7 Hz), 141.8, 140.1 (d, J = 6.4 Hz), 136.2 (d, J = 7.5 Hz), 133.2, 131.8, 129.4, 128.6, 128.3, 123.0, 119.8 (d, J = 22.0 Hz), 119.1, 118.0 (d, J = 23.7 Hz), 116.7, 95.2, 94.8, 87.7, 87.3, 21.7; IR (KBr, cm^{-1}): υ 2919, 1706, 1604, 1478, 1262, 828, 753, 585; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}OF$ 339.1180; found 339.1185.

*1-(2-((4-Ethylphenyl)ethynyl)phenyl)-3-phenylprop-2-yn-1-one (**1k**, Scheme 8).* Yellow gummy (yield = 354 mg, 82%); R_f = 0.47 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88−7.78 (m, 1H), 7.73 (d, J = 6.8 Hz, 1H), 7.67−7.54 (m, 5H), 7.53−7.40 (m, 4H), 7.38−7.17 (m, 2H), 2.69 (q, J = 4.1 Hz, 2H), 1.26 (t, J = 6.5 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 177.6, 147.6, 138.3, 134.3, 133.2, 132.4, 131.9, 131.5, 128.5, 128.2, 128.15, 127.9, 123.1, 122.9, 117.2, 95.3, 94.1, 88.3, 88.0, 29.0, 15.1; IR (KBr, cm^{-1}): υ 2961, 1701, 1600, 1468, 1075, 759, 724, 601; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{19}O$ 335.1430; found 335.1436.

*3-Phenyl-1-(6-(phenylethynyl)benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-one (**1m**, Scheme 8).* Yellow gummy (yield = 336 mg, 72%); R_f = 0.31 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.91 (d, J = 7.0 Hz, 1H), 7.64−7.60 (m, 2H), 7.54 (s, 1H), 7.45−7.38 (m, 4H), 7.16 (s, 1H), 6.10 (d, J = 12.2 Hz, 1H), 5.97 (s, 2H), 5.71 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 177.6, 164.0, 161.5, 138.3, 134.2, 133.9, 133.1, 132.6, 131.7, 130.8, 128.6, 128.1, 122.9, 120.2, 119.3, 115.7, 115.5, 94.4, 93.4, 88.1, 88.0; IR (KBr, cm^{-1}): υ 2920, 1699, 1500, 1421, 1264, 1029, 699; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{15}O_3$ 351.1016; found 351.1021.

*1-(2-((4-Ethylphenyl)ethynyl)phenyl)-3-(4-fluorophenyl)prop-2-yn-1-one (**1n**, Scheme 8).* Yellow gummy (yield = 304 mg, 79%); R_f = 0.73 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 7.4 Hz, 1H), 7.5 (t, J = 7.4 Hz, 1H), 7.43−7.35 (m, 2H), 7.34−7.28 (m, 2H), 7.28−7.20 (m, 3H), 2.66 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 177.1, 147.2 (d, J = 300.9 Hz), 138.1, 134.8, 133.1, 132.7, 132.2, 130.9, 130.3, 128.72, 128.7, 127.2, 124.6, 123.2, 121.1(d, J = 263.7 Hz), 94.1, 93.5, 91.6, 87.8, 29.7, 21.2; IR (KBr, cm^{-1}): υ 2959, 1699, 1600, 1507, 1220, 874, 759, 556; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{18}OF$ 353.1336; found 353.1345.

*1-(2-((2-Methyl-5-nitrophenyl)ethynyl)phenyl)-3-phenylprop-2-yn-1-one (**1o**, Scheme 8).* Reddish yellow solid (yield = 328 mg, 78%); m.p. = 159−160 °C; R_f = 0.47 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, J = 2.3 Hz, 1H), 8.28 (d, J = 7.8 Hz, 1H), 8.04 (dd, J = 8.4, 2.3 Hz, 1H), 7.71 (d, J = 7.4 Hz, 1H), 7.63 (d, J = 7.1 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 8.5 Hz, 3H), 2.70 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 177.0, 148.4, 146.0, 138.0, 134.8, 133.1, 132.7, 132.2, 130.9, 130.3, 128.7, 128.67, 127.1, 124.5, 123.2, 122.1, 120.0, 94.1, 93.5, 91.7, 87.7, 21.2; IR (KBr, cm^{-1}): υ 3103, 1646, 1512, 1350, 1270, 1009, 751, 677; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}O_3N$ 366.1125; found 366.1125.

*1-(2-(Phenylethynyl)phenyl)non-2-yn-1-one (**1q**, Scheme 8, Table 2).* Yellow gummy (yield = 406 mg, 83%); R_f = 0.63 in 5% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.9, 1.0 Hz, 1H), 7.64−7.60 (m, 3H), 7.50 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.36−7.33 (m, 3H), 2.42 (t, J = 7.2 Hz, 2H), 1.62−1.55 (m, 2H), 1.43−1.36 (m, 2H), 1.32−1.22 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 177.6, 138.3, 134.2, 132.2, 131.9, 131.7, 128.6, 128.3, 127.8, 123.3, 122.8, 97.1, 95.1, 88.3, 80.7, 31.2, 28.6, 27.7, 22.4, 19.3, 14.0; IR (KBr, cm^{-1}): υ 2927, 1707, 1646, 1492, 1242, 1069, 754, 690; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}O$ 315.1743; found 315.1745.

Representative Procedure for the Synthesis of 5,11-Dimethoxy-11-phenyl-11*H*-benzo[*a*]fluorene 2a Is as Follows. To a solution of compound **1a** (100 mg, 0.326 mmol, 1.0 equiv) in dichloromethane solvent (1.5 mL), trimethyl orthoformate (214.2 μL, 1.958 mmol, 6 equiv) and triflic acid (28.8 μL, 0.326 mmol, 1 equiv) were charged sequentially at room temperature (25 °C) under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature under a nitrogen atmosphere until the completion of the reaction. The progress of the reaction was monitored by TLC. After that, it was quenched with a saturated $NaHCO_3$ solution. Then, it was extracted using ethyl acetate. The combined organic layers were 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, EtOAc/hexanes eluent) to get pure 5,11-dimethoxy-11-phenyl-11*H*-benzo[*a*]fluorene **2a** as a red solid with 85% isolated yield (97.4 mg).

The reaction was carried out using **1g** of **1a** to furnish **2a** (911 mg; 79% yield); thus, the scalability of the reaction has been checked. m.p. = 152−153 °C; R_f = 0.63 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.42−7.33 (m, 5H), 7.28 (d, J = 7.0 Hz, 1H), 7.25−7.14 (m, 5H), 4.14 (s, 3H), 2.90 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 157.7, 149.4, 143.6, 141.0, 139.8, 132.6, 130.7, 128.6, 128.2, 127.8, 127.4, 126.9, 125.9, 125.4, 124.9, 124.4, 124.39, 123.0, 119.4, 96.3, 89.9, 55.8, 51.2; IR (KBr, cm^{-1}): υ 2927, 1620, 1584, 1449, 1215, 1156, 757; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}O_2$ 353.1536; found 353.1536.

*9-Ethyl-5,11-dimethoxy-11-phenyl-11H-benzo[a]fluorene (**2b**, Table 2).* The reaction was carried out using 105 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 93.2 mg, 78%); m.p. = 178−179 °C; R_f = 0.64 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30−8.27 (m, 1H), 7.81−7.77 (m, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.39−7.32 (m, 4H), 7.23−7.15 (m, 5H), 7.11 (s, 1H), 4.15 (s, 3H), 2.90 (s, 3H), 2.64 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 157.6, 149.5, 144.2, 143.7, 139.9, 138.6, 132.4, 130.7, 128.2, 128.1, 127.3, 126.8, 125.6, 125.4, 124.7, 124.2, 124.0, 123.0, 119.2, 96.3, 89.8, 55.8, 51.2, 29.0, 15.6; IR (KBr, cm^{-1}): υ 2927, 1618, 1581, 1456, 1215, 1098, 863, 691; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}O_2$ 381.1849; found 381.1849.

*5,11-Diethoxy-9-ethyl-11-phenyl-11H-benzo[a]fluorene (**2c**, Table 2).* The reaction was carried out using 150 mg of corresponding aryl-fused 1,6-diyn-3-one. Off-white solid (yield = 143.3 mg, 78%); m.p. = 169−170 °C; R_f = 0.77 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, J = 7.7 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.38 (d, J = 7.0 Hz, 2H), 7.36−7.30 (m, 2H), 7.20−7.13 (m, 5H), 7.11 (s, 1H), 4.36 (q, J = 7.0 Hz, 2H), 3.06−2.99 (m, 1H), 2.97−2.90 (m, 1H), 2.62 (q, J = 7.6 Hz, 2H), 1.62 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H), 1.08 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 156.8, 150.4, 144.1, 139.6, 138.4, 133.1, 130.8, 128.1, 127.9, 127.1, 126.7, 125.7, 125.5, 124.5, 124.3, 123.9, 123.0, 121.9, 119.1, 96.9, 89.2, 64.0, 58.7, 29.0, 15.7, 15.6, 14.9; IR (KBr, cm^{-1}): υ 2923, 1582, 1446, 1209, 1069, 863, 761; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{29}O_2$ 409.2162; found 409.2163.

*5,10,11-Trimethoxy-11-phenyl-11H-benzo[a]fluorene (**2d**, Table 2).* The reaction was carried out using 149 mg of corresponding aryl-fused 1,6-diyn-3-one. Brown solid (yield = 127.2 mg, 75%); m.p. = 169−170 °C; R_f = 0.65 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.40−7.31 (m, 6H), 7.18 (s, 1H), 7.16−7.08 (m, 3H), 6.76 (d, J = 6.9 Hz, 1H), 4.14 (s, 3H), 3.68 (s, 3H), 2.97 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 157.5, 156.5, 143.0, 142.4, 139.0, 134.8, 133.9, 130.8, 130.4, 127.5, 127.3, 126.4, 126.1, 126.0, 124.9, 124.2, 122.9, 112.3, 111.4, 96.3, 90.6, 55.8, 51.3; IR (KBr, cm^{-1}): υ 2923, 1583, 1458, 1262, 1041, 765; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}O_3$ 383.1642; found 383.1642.

*9-Fluoro-5,11-dimethoxy-11-phenyl-11H-benzo[a]fluorene (**2e**, Table 2).* The reaction was carried out using 112 mg of corresponding aryl-fused 1,6-diyn-3-one. Brown solid (yield = 53.9 mg, 42%); m.p. = 152−153 °C; R_f = 0.85% in 10% EtOAc/hexanes; ^{1}H NMR (400

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MHz, $CDCl_3$): δ 8.29 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.63 (s, 1H), 7.39−7.32 (m, 5H), 7.91 (d, J = 6.4 Hz, 2H), 7.16 (s, 1H), 7.04 (t, J = 8.1 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 4.15 (s, 3H), 2.91 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 169.1, 157.9, 151.9, 142.9, 139.0, 136.7, 132.4, 130.7, 129.7, 128.3, 127.5, 127.2, 125.5, 125.3, 125.0, 124.2, 123.0, 120.4 (d, J = 8.6 Hz), 115.4 (d, J = 22.7 Hz), 112.2 (d, J = 23.3 Hz), 96.1, 55.8, 51.4; IR (KBr, cm^{-1}): υ 2926, 1707, 1582, 1397, 1219, 1072, 738, 696; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}FO_2$ 371.1442; found 371.1442.

3,5,11-Trimethoxy-11-phenyl-11H-benzo[a]fluorene (**2f**, Table 2). The reaction was carried out using 110 mg of corresponding aryl-fused 1,6-diyn-3-one. Pale yellow solid (yield = 91.4 mg, 73%); m.p. = 204−205 °C; R_f = 0.68 in 10% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 9.1 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 2.6 Hz, 1H), 7.36−7.31 (m, 3H), 7.25 (d, J = 6.2 Hz, 1H), 7.21 (s, 1H), 7.21−7.13 (m, 4H), 7.02 (dd, J = 9.2, 2.7 Hz, 1H), 4.15 (s, 3H), 3.91 (s, 3H), 2.88 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 157.3, 156.6, 148.9, 143.7, 141.2, 137.5, 133.0, 128.6, 128.2, 127.3, 127.0, 126.9, 126.1, 126.0, 125.4, 124.4, 119.8, 119.1, 101.7, 96.9, 89.8, 55.8, 55.3, 51.2; IR (KBr, cm^{-1}): υ 2929, 1586, 1478, 1211, 1081, 829, 752, 696; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}O_3$ 383.1642; found 383.1642.

3-Fuoro-5,11-dimethoxy-11-phenyl-11H-benzo[a]fluorene (**2g**, Table 2). The reaction was carried out using 85 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 74.2 mg, 76%); m.p. = 206−207 °C; R_f = 0.75 in 5% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 2.6 Hz, 1H), , 7.55 (d, J = 7.6 Hz, 1H), 7.40−7.33 (m, 3H), 7.22 (d, J = 7.0 Hz, 2H), 7.20−7.10 (m, 5H), 4.14 (s, 3H), 2.90 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 157.7, 149.4, 143.6, 141.0, 139.8, 132.6, 130.7, 128.6, 128.2, 127.8, 127.4, 126.9, 125.9, 125.4, 124.9, 124.4, 124.39, 123.0, 119.4, 96.3, 89.9, 55.8, 51.2; IR (KBr, cm^{-1}): υ 2911, 1589, 1452, 1170, 1069, 920, 745, 693; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}FO_2$ 371.1442; found 371.1441.

3,5,11-Trimethoxy-9-methyl-11-phenyl-11H-benzo[a]fluorene (**2h**, Table 2). The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Brown solid (yield = 92.6 mg, 82%); m.p. = 255−256 °C; R_f = 0.61 in 5% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 2.6 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 7.0 Hz, 2H), 7.21−7.13 (m, 5H), 7.07 (s, 1H), 7.01 (dd, J = 9.1, 2.6 Hz, 1H), 4.15 (s, 3H), 3.91 (s, 3H), 2.89 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 157.1, 156.6, 149.1, 143.9, 138.6, 137.6, 137.2, 132.6, 129.3, 128.2, 126.8, 126.7, 126.2, 125.9, 125.4, 125.1, 119.7, 118.8, 101.7, 96.9, 89.7, 55.8, 55.3, 51.2, 21.6; IR (KBr, cm^{-1}): υ 2921, 1581, 1461, 1207, 1079, 816, 695, 556; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}O_3$ 397.1798; found 397.1799.

9-Fluoro-3,5,11-trimethoxy-11-phenyl-11H-benzo[a]fluorene (**2i**, Table 2). The reaction was carried out using 70 mg of corresponding aryl-fused 1,6-diyn-3-one. Off-white solid (yield = 35.9 mg, 45%); m.p. = 254−255 °C; R_f = 0.50 in 5% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): 7.66 (d, J = 9.1 Hz, 1H), 7.56 (dd, J = 8, 4.8 Hz, 2H), 7.33−7.28 (m, 2H), 7.20−7.14 (m, 3H), 7.12 (s, 1H), 7.00 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 8.2 Hz, 1H), 4.11 (s, 3H), 3.87 (s, 3H), 2.88 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 164.0, 161.6, 157.3, 156.8, 151.4 (d, J = 27.6 Hz), 143.1, 137.0, 136.7, 132.7, 128.3, 127.2, 126.7, 126.1, 125.8, 125.3, 119.9 (d, J = 21.2 Hz), 115.4 (d, J = 90.7 Hz), 112.1 (d, J = 93.1 Hz), 101.7, 96.7, 89.5, 55.8, 55.3, 51.3; IR (KBr, cm^{-1}): υ 2930, 1583, 1481, 1217, 1074, 815, 695; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}FO_2$ 401.1547; found 401.1532.

3-Fluoro-5,11-dimethoxy-9-methyl-11-phenyl-11H-benzo[a]-fluorene (**2j**, Table 2). The reaction was carried out using 120 mg of corresponding aryl-fused 1,6-diyn-3-one. Brown solid (yield = 100.8 mg, 74%); m.p. = 203−204 °C; R_f = 0.64 in 5% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 7.92−7.84 (m, 2H), 7.81−7.77 (m, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 3.8 Hz, 2H), 7.20−7.17 (m, 2H), 7.15−7.10 (m, 1H), 7.09 (s, 1H), 4.15 (s, 3H), 2.90 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 161.2, 159.2, 157.0, 149.5 (d, J = 99.8 Hz), 143.6, 139.2, 138.0 (d, J = 44.7 Hz), 132.5, 129.3 (d, J = 18.4 Hz), 128.2 (d, J = 7.3 Hz), 127.7, 126.9, 126.8, 126.5 (d, J = 8.1 Hz), 125.3, 125.2, 119.2, 117.4 (d, J = 25.1 Hz), 107.3, 97.2, 89.7, 58.8, 55.8, 51.2, 21.7, 15.7; IR (KBr, cm^{-1}): υ 2924, 1591, 1457, 1202, 1072, 989, 808, 697; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}FO_2$ 385.1598; found 385.1597.

(4-Methoxy-2-propylnaphthalen-1-yl)(phenyl)methanone (**4k**, Scheme 2). The reaction was carried out using 118 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 95.3 mg, 76%); m.p. = 133−134 °C; R_f = 0.72 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.1 Hz, 2H), 7.59−7.53 (m, 1H), 7.44−7.32 (m, 5H), 6.73 (s, 1H), 4.06 (s, 3H), 2.54 (t, J = 7.8 Hz, 2H), 1.68−1.59 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 200.4, 156.0, 138.5, 138.2, 133.6, 131.9, 129.8, 128.7, 128.3, 127.2, 125.0, 124.8, 124.0, 122.1, 105.2, 55.6, 36.4, 24.6, 14.2; IR (KBr, cm^{-1}): υ 2952, 1657, 1619, 1591, 1448, 1250, 1115, 903, 769, 613; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_2Na$ 327.1356; found 327.1355.

(2-Hexyl-4-methoxynaphthalen-1-yl)(phenyl)methanone (**4l**, Scheme 2). The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 98.5 mg, 89.3%); m.p. = 156−157 °C; R_f = 0.66 in 5% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44−7.39 (m, 4H), 7.37−7.33 (m, 1H), 6.73 (s, 1H), 4.06 (s, 3H), 2.55 (t, J = 8.0 Hz, 2H), 1.61−1.54 (m, 3H), 1.26−1.16 (m, 5H), 0.82 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 200.4, 156.0, 138.5, 138.4, 133.5, 131.9, 129.8, 128.7, 128.2, 127.2, 124.9, 124.8, 123.9, 122.1, 105.1, 55.6, 34.4, 31.5, 31.3, 29.2, 22.5, 14.1; IR (KBr, cm^{-1}): υ 2924, 1663, 1582, 1376, 1242, 1107, 718, 688; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{27}O_2$ 347.2006; found 347.2006.

Representative Procedure for the Synthesis of 10-Phenyl-11*H*-benzo[*b*]fluoren-11-one 3a Is as Follows. To a solution of compound **1a** (100 mg, 0.326 mmol, 1.0 equiv) in dichloromethane solvent (1.5 mL), triflic acid (28.8 μL, 0.326 mmol, 1 equiv) was charged at room temperature (25 °C) under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature under a nitrogen atmosphere until the completion of the reaction. The progress of the reaction was monitored by TLC. After that, it was quenched with a saturated $NaHCO_3$ solution. Then, it was extracted using ethyl acetate and water. The combined organic layers were washed with saturated brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (using silica gel, EtOAc/hexanes eluent) to get pure 10-phenyl-11*H*-benzo[*b*]-fluoren-11-one (**3a**) as a yellow solid with 93% isolated yield (92.9 mg).

The reaction was carried out using **1g** of **1a** to obtain **3a** (904 mg; 90% yield). m.p. = 216−217 °C; R_f = 0.60 in 10% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 4.4 Hz, 1H), 7.62 (d, J = 3.4 Hz, 1H), 7.58−7.52 (m, 5H), 7.39−7.35 (m, 3H), 7.32 (td, J = 7.4, 0.8 Hz, 1H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 192.2, 144.1, 141.3, 138.5, 136.7, 136.4, 135.6, 134.7, 133.9, 129.7, 129.3, 129.25, 129.1, 128.8, 128.7, 128.1, 128.05, 126.9, 124.2, 120.7, 118.8; IR (KBr, cm^{-1}): υ 2920, 1697, 1620, 1599, 1443, 1187, 1158, 951, 757, 719, 699; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{15}O$ 307.1117; found 307.1117.

10-(p-Tolyl)-11H-benzo[b]fluoren-11-one (**3b**, Table 3). The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 94.8 mg, 95%); m.p. = 286−287 °C; R_f = 0.56 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.55 (q, J = 7.4 Hz, 2H), 7.40−7.30 (m, 4H), 7.29 (s, 1H), 7.26 (d, J = 1.8 Hz, 1H), 2.50 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 192.3, 144.0, 141.5, 138.5, 137.7, 136.7, 136.4, 134.7, 134.0, 132.4, 129.7, 129.5, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 126.7, 124.1, 120.7, 118.6, 21.5; IR (KBr, cm^{-1}): υ 2915, 1797, 1621, 1601, 1468, 1108, 884, 866, 756, 718, 597; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{17}O$ 321.1274; found 321.1275.

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*10-(4-Ethylphenyl)-11H-benzo[b]fluoren-11-one (**3c**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 96.2 mg, 96%); m.p. = 208−209 °C; R_f = 0.45 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.55 (q, J = 7.6 Hz, 2H), 7.40−7.35 (m, 3H), 7.34−7.29 (m, 3H), 2.81 (q, J = 7.6 Hz, 2H), 1.37 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 192.4, 144.1, 143.9, 141.6, 138.5, 136.7, 136.4, 134.7, 134.1, 132.6, 129.6, 129.2, 128.8, 128.7, 127.6, 126.8, 124.2, 120.7, 118.6, 28.8, 15.4; IR (KBr, cm^{-1}): υ 2958, 1692, 1620, 1579, 1467, 1334, 1186, 1160, 955, 832, 760, 752, 597; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{19}O$ 335.1430; found 335.1430.

*10-(4-Fluorophenyl)-11H-benzo[b]fluoren-11-one (**3d**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 97 mg, 97%); m.p. = 192−193 °C; R_f = 0.47 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.65−7.60 (m, 2H), 7.60−7.54 (m, 2H), 7.42−7.38 (m, 1H), 7.38−7.32 (m, 3H), 7.26−7.22 (m, 2H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 192.3, 163.7, 161.8, 144.1, 140.2, 138.5, 136.8, 136.3, 134.9, 131.5, 131.4 (d, J = 31.8 Hz), 131.2 (d, J = 14.1 Hz), 129.3, 128.9, 128.85, 128.8, 127.0, 124.3, 120.8, 119.0, 115.2 (d, J = 86.1 Hz); IR (KBr, cm^{-1}): υ 2922, 1701, 1623, 1597, 1499, 1208, 1093, 952, 839, 760, 720, 595; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{14}FO$ 325.1023; found 325.1025.

*10-(3-Methoxyphenyl)-11H-benzo[b]fluoren-11-one (**3e**, Table 3).* The reaction was carried out using 107 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 93.1 mg, 87%); m.p. = 238−239 °C; R_f = 0.47 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.60−7.52 (m, 2H), 7.46 (t, J = 7.9 Hz, 1H), 7.40−7.36 (m, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.08−7.05 (m, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.92 (s, 1H), 3.85 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 192.1, 159.5, 144.1, 141.0, 138.5, 137.0, 136.7, 136.4, 134.7, 133.8, 129.2, 129.18, 129.1, 128.8, 128.76, 128.6, 126.9, 124.3, 122.0, 120.7, 118.8, 115.3, 113.6, 55.3; IR (KBr, cm^{-1}): υ 2916, 1701, 1622, 1581, 1466, 1335, 1248, 1173, 1032, 957, 762, 700; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{17}O_2$ 337.1223; found 337.1225.

*2-Methoxy-10-phenyl-11H-benzo[b]fluoren-11-one (**3f**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 85.8 mg, 86%); m.p. = 240−241 °C; R_f = 0.55 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.92−7.89 (m, 1H), 7.62−7.56 (m, 3H), 7.44−7.38 (m, 5H), 7.24 (d, J = 2.6 Hz, 1H), 6.72 (dd, J = 8.5, 2.6 Hz, 1H), 6.22 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 193.2, 160.4, 138.3, 138.1, 137.6, 137.2, 135.6, 133.2, 133.1, 132.9, 130.8, 129.8, 129.3, 129.0, 128.3, 126.9, 126.5, 125.3, 124.9, 121.5, 108.1, 55.7; IR (KBr, cm^{-1}): υ 2921, 1703, 1602, 1485, 1277, 1118, 1017, 820, 745, 698, 591; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{17}O_2$ 337.1223; found 337.1224.

*2-Fluoro-10-phenyl-11H-benzo[b]fluoren-11-one (**3g**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 86.2 mg, 86%); m.p. = 294−295 °C; R_f = 0.47 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.73 (dd, J = 8.3, 4.4 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.57−7.51 (m, 4H), 7.40−7.35 (m, 3H), 7.28 (dd, J = 7.4, 2.4 Hz, 1H), 7.26−7.22 (m, 1H); ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ 190.9, 164.8, 162.8, 141.9, 140.0, 138.5 (d, J = 29.4 Hz), 137.8, 136.8, 135.4, 133.6, 129.6, 129.2, 129.1, 128.9, 128.8, 128.2, 127.0, 122.2 (d, J = 31.0 Hz), 121.5 (d, J = 94.3 Hz), 118.5, 111.3 (d, J = 91.7 Hz); IR (KBr, cm^{-1}): υ 2923, 1698, 1603, 1476, 1261, 1149, 1032, 924, 811, 777, 700, 581; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{14}FO$ 325.1023; found 325.1025.

10-Phenyl-11H-benzo[6,7]fluoreno[2,3-d][1,3]dioxol-11-one (3h, Table 3). The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 92.4 mg, 92%); m.p. = 291−292 °C; R_f = 0.27 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.89 (d, J = 6.9 Hz, 1H), 7.63−7.57 (m, 3H), 7.47−7.36 (m, 5H), 7.14 (s, 1H), 5.95 (s, 2H), 5.69 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 191.5, 153.2, 148.4, 142.6, 137.2, 136.9, 134.6, 133.3, 133.1, 131.8, 130.6, 129.7, 129.4, 128.8, 128.4, 127.0, 126.7, 124.5, 104.5, 104.3, 102.1; IR (KBr, cm^{-1}): υ 2918, 1693, 1621, 1493, 1451, 1298, 1269, 1028, 927, 818, 747, 727, 554; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{15}O_3$ 351.1016; found 351.1017.

*8-Ethyl-10-phenyl-11H-benzo[b]fluoren-11-one (**3i**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 89.2 mg, 89%); m.p. = 193−194 °C; R_f = 0.52 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H), 7.58−7.52 (m, 4H), 7.44−7.37 (m, 4H), 7.33−7.28 (m, 1H), 2.67 (q, J = 7.5 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 192.4, 144.2, 143.2, 140.9, 137.7, 136.3, 135.7, 135.1, 134.7, 134.0, 129.7, 129.6, 129.0, 128.8, 128.7, 128.1, 127.9, 127.1, 124.2, 120.6, 118.6, 29.1, 15.5; IR (KBr, cm^{-1}): υ 2962, 1702, 1599, 1468, 1231, 1023, 958, 888, 762, 700, 600; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{19}O$ 335.1430; found 335.1432.

*8-Fluoro-10-phenyl-11H-benzo[b]fluoren-11-one (**3j**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 85.2 mg, 85%); m.p. = 220−221 °C; R_f = 0.45 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.86 (dd, J = 8.9, 5.7 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.59−7.53 (m, 4H), 7.37−7.24 (m, 5H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 192.1, 161.3 (d, J = 245.8 Hz), 144.0, 140.5, 140.4, 138.0, 137.99, 136.1, 135.2 (d, J = 8.3 Hz), 135.0, 134.9, 133.5, 130.8 (d, J = 8.8 Hz), 129.5, 129.4, 129.3, 128.3, 124.3, 120.7, 118.6 (d, J = 24.6 Hz), 112.9 (d, J = 22.2 Hz); IR (KBr, cm^{-1}): υ 3052, 1698, 1599, 1514, 1468, 1226, 1102, 875, 810, 758, 722, 597; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{14}FO$ 325.1023; found 325.1021.

*2-Methoxy-10-(p-tolyl)-11H-benzo[b]fluoren-11-one (**3k**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 82 mg, 82%); m.p. = 265−266 °C; R_f = 0.38 in 5% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 1H), 7.77 (s, 1H), 7.66−7.62 (m, 2H), 7.53−7.49 (m, 1H), 7.36−7.31 (m, 3H), 7.26 (s, 2H), 7.12 (d, J = 2.3 Hz, 1H), 7.09 (dd, J = 8.3, 2.5 Hz, 1H), 3.85 (s, 3H), 2.49 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 192.2, 161.0, 141.6, 138.7, 138.2, 137.7, 137.1, 137.0, 133.5, 132.5, 129.6, 129.2, 129.15, 128.9, 128.8, 128.5, 126.4, 121.9, 121.6, 117.4, 108.0, 55.7, 21.5; IR (KBr, cm^{-1}): υ 2918, 1688, 1576, 1485, 1438, 1277, 1026, 1010, 792, 764, 586; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{19}O_2$ 351.1380; found 351.1380.

*10-(4-Fluorophenyl)-2-methoxy-11H-benzo[b]fluoren-11-one (**3l**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 84.3 mg, 84%); m.p. = 281−282 °C; R_f = 0.42 in 5% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.1 Hz, 1H), 7.79 (s, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.55−7.51 (m, 1H), 7.37−7.32 (m, 3H), 7.23 (t, J = 8.8 Hz, 2H), 7.14−7.09 (m, 2H), 3.85 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 192.2, 163.7, 161.5 (d, J = 334.3 Hz), 140.2, 138.4 (d, J = 332.6 Hz), 137.0, 133.2 (d, J = 107.1 Hz), 131.5, 129.8, 129.4 (d, J = 76.6 Hz), 128.8 (d, J = 58.3 Hz), 126.6, 125.0, 121.8 (d, J = 51.2 Hz), 121.5, 117.7, 115.3, 115.1, 111.3, 108.0, 55.8; IR (KBr, cm^{-1}): υ 2993, 1686, 1573, 1486, 1438, 1294, 1217, 1154, 1011, 837, 766, 574; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{16}FO_2$ 355.1129; found 355.1128.

*2-Fluoro-10-(p-tolyl)-11H-benzo[b]fluoren-11-one (**3m**, Table 3).* The reaction was carried out using 118 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 91.8 mg, 78%); m.p. = 284−285 °C; R_f = 0.48 in 5% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.61−7.57 (m, 2H), 7.37 (dd, J = 7.7, 1.7 Hz, 2H), 7.28 (d, J = 1.5 Hz, 1H), 7.13 (s, 2H), 5.94 (s, 2H), 5.64 (s, 1H), 2.36 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ191.5, 150.7 (d, J = 605.5 Hz), 142.5, 139.2, 137.4, 137.0, 134.9, 132.8, 132.5, 131.9, 131.2, 130.5, 129.8, 129.5, 129.3, 128.7, 128.4, 125.3 (d, J = 256.1 Hz), 117.4, 104.4 (d, J = 33 Hz), 102.0,

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22.0; IR (KBr, cm^{-1}): υ 2915, 1691, 1592, 1262, 1031, 772, 568; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{15}FONa$ 361.0999, found 361.0998.

*10-(4-Fluorophenyl)-2-methoxy-11H-benzo[b]fluoren-11-one (**3n**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow solid (yield = 96.8 mg, 97%); m.p. = 234−235 °C; R_f = 0.48 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 7.4 Hz, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.37−7.27 (m, 4H), 7.25−7.20 (m, 2H), 7.67 (q, J = 7.5 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 192.4, 162.8 (d, J = 245 Hz), 144.2, 143.3, 139.7, 137.7, 136.2, 135.1, 134.8, 134.0, 131.41 (d, J = 8.2 Hz), 131.39, 129.8, 129.0, 128.9, 128.8, 126.7, 124.2, 120.6, 118.8, 115.2 (d, J = 21.3 Hz), 29.1, 15.5; IR (KBr, cm^{-1}): υ 2959, 1700, 1599, 1508, 1468, 1185, 957, 886, 759, 725, 599; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{18}FO$ 353.1336, found 353.1337.

*6-Methyl-9-nitro-10-phenyl-11H-benzo[b]fluoren-11-one (**3o**, Table 3).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one. Pale yellow solid (yield = 77 mg, 77%); m.p. = 262−263 °C; R_f = 0.26 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (dd, J = 8.5, 2.5 Hz, 1H), 8.32 (s, 1H), 8.22 (d, J = 2.4 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 7.0 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.58−7.48 (m, 2H), 7.33−7.22 (m, 3H), 6.22 (d, J = 7.5 Hz, 1H), 2.17 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 192.7, 147.1, 145.6, 144.3, 138.4, 136.5, 135.7, 135.2, 133.6, 132.6, 131.7, 131.3, 130.9, 129.7, 129.3, 127.4, 126.1, 125.9, 125.2, 124.7, 123.7, 122.7, 20.0; IR (KBr, cm^{-1}): υ 2921, 1705, 1513, 1343, 1110, 901, 731; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}NO_3$ 366.1125; found 366.1126.

Representative Procedure for the Synthesis of (4-Methoxy-2-phenylnaphthalen-1-yl)(phenyl)methanone 4a Is as Follows. To a solution of compound **1a** (100 mg, 0.326 mmol, 1.0 equiv) in dichloromethane solvent (1.5 mL), trimethyl orthoformate (35.7 μL, 0.326 mmol, 1.0 equiv) and $AgBF_4$ (3.2 mg, 0.0163 mmol, 0.05 equiv) were charged sequentially at room temperature (25 °C) under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature under a nitrogen atmosphere until the completion of the reaction. The progress of the reaction was monitored by TLC. After that, the solvent was removed under reduced pressure and (4-methoxy-2-phenylnaphthalen-1-yl)(phenyl)-methanone (**4a**) was isolated by column chromatography (using silica gel, EtOAc/hexanes eluent) as a yellow solid with 70% isolated yield (77.6 mg); m.p. = 133−134 °C; R_f = 0.41 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 8.2 Hz, 2H), 7.48−7.38 (m, 2H), 7.29 (d, J = 7.9 Hz, 3H), 7.20−7.08 (m, 5H), 6.81 (s, 1H), 4.02 (s, 3H); IR (KBr, cm^{-1}): υ 2964, 1658, 1581, 1445, 1383, 1220, 1097, 866, 775, 695, 628; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{18}O_2Na$ 361.1199; found 361.1199.

*(4-Ethoxy-2-phenylnaphthalen-1-yl)(phenyl)methanone (**4b**, Table 4).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 91 mg, 79%); the robustness of the reaction was checked by doing the reaction with **1g** of **1a** to obtain **4b** (823 mg; 72% yield). m.p. = 235−236 °C; R_f = 0.5 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 9 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 7.4 Hz, 2H), 7.54−7.45 (m, 2H), 7.40−7.33 (m, 3H), 7.25−7.15 (m, 5H), 6.87 (s, 1H), 4.30 (q, J = 7.0 Hz, 2H), 1.61 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 199.9, 155.5, 140.9, 138.6, 132.9, 132.0, 129.6, 129.4, 128.2, 128.15, 127.7, 127.4, 125.5, 125.3, 124.6, 122.3, 106.3, 64.0, 14.9; IR (KBr, cm^{-1}): υ 2970, 1655, 1586, 1473, 1380, 1223, 1094, 866, 759, 690, 632; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{20}O_2Na$ 375.1356; found 375.1356.

*(4-Ethoxy-2-(4-fluorophenyl)naphthalen-1-yl)(phenyl)-methanone (**4c**, Table 4).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 71.2 mg, 62%); m.p. = 165−166 °C; R_f = 0.52 in 10% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, J = 7.3 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.59 (dd, J = 8.3, 1.2 Hz, 2H), 7.53−7.45 (m, 2H), 7.41−7.37 (m, 1H), 7.31−7.27 (m, 2H), 7.23 (t, J = 7.8 Hz, 2H), 6.89 (t, J = 8.8 Hz, 2H), 6.80 (s, 1H), 4.30 (q, J = 13.9, 6.9 Hz, 2H), 1.61 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 199.8, 155.6, 138.6, 137.4, 137.0, 133.1, 132.0, 131.1 (d, J = 32.3 Hz), 129.7, 129.6, 128.4, 128.3, 127.9, 125.5 (d, J = 187.5 Hz), 124.7, 122.4, 115.1 (d, J = 85.9 Hz), 106.2, 100.0, 64.1, 14.9; IR (KBr, cm^{-1}): υ 2922, 1656, 1591, 1507, 1381, 1219, 1093, 834, 721, 692; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}FO_2$ 371.1442; found 371.1443.

*(4-Ethoxy-2-(4-ethylphenyl)naphthalen-1-yl)(phenyl)methanone (**4d**, Table 4).* The reaction was carried out using 122 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 100.2 mg, 72%); m.p. = 155−156 °C; R_f = 0.65 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.48−7.39 (m, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.17 (t, J = 7.7 Hz, 2H), 7.01 (d, J = 6.2 Hz, 2H), 6.85 (s, 1H), 4.25 (q, J = 6.9 Hz, 2H), 2.51 (q, J = 7.5 Hz, 2H), 1.55 (t, J = 6.9 Hz, 3H), 1.12 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 199.9, 155.4, 143.4, 138.7, 138.6, 138.2, 132.7, 132.0, 129.5, 129.3, 128.1, 127.6, 127.56, 125.3, 125.2, 124.5, 122.3, 122.2, 106.4, 164.0, 28.4, 15.3, 14.8; IR (KBr, cm^{-1}): υ 2924, 1662, 1592, 1386, 1174, 1140, 856, 797, 724, 626; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}O_2$ 381.1849; found 381.1849.

*(4-Ethoxy-2-(3-methoxyphenyl)naphthalen-1-yl)(phenyl)-methanone (**4e**, Table 4).* The reaction was carried out using 102 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Brown solid (yield = 92.5 mg, 80%); m.p. = 203−204 °C; R_f = 0.58 in 10% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 8.35 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.37 (t, J = 7.0 Hz, 1H), 7.32 (d, J = 7.0 Hz, 1H), 7.30 (d, J = 2.5 Hz, 1H), 7.24 (s, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 6.9 Hz, 2H), 6.77 (dd, J = 8.2, 2.4 Hz, 1H), 5.21 (s, 1H), 4.38 (q, J = 7.0 Hz, 2H), 3.90 (s, 3H), 1.63 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): δ 159.5, 155.7, 142.7, 142.4, 142.1, 139.2, 135.6, 131.0, 128.8, 127.9, 126.8, 126.6, 126.0, 125.3, 124.5, 124.3, 123.3, 112.7, 104.8, 97.3, 64.1, 55.6, 52.9, 14.9; IR (KBr, cm^{-1}): υ 2979, 1606, 1583, 1476, 1425, 1234, 1204, 1136, 1029, 739, 701, 626; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}O_3$ 383.1642; found 383.1643.

*(4-Ethoxy-6-fluoro-2-phenylnaphthalen-1-yl)(phenyl)-methanone (**4f**, Table 4).* The reaction was carried out using 85 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 66.6 mg, 69%); m.p. = 154−155 °C; R_f = 0.75 in 10% EtOAc/hexanes; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, J = 10.4, 2.7 Hz, 1H), 7.72 (dd, J = 9.3, 5.3 Hz, 1H), 7.58 (dd, J = 4.3, 1.3 Hz, 2H), 7.39−7.34 (m, 1H), 7.34−7.30 (m, 2H), 7.25−7.15 (m, 5H), 6.88 (s, 1H), 4.29 (q, J = 7.0 Hz, 2H), 1.60 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 199.5, 161.8, 159.4, 154.9 (d, J = 20 Hz), 140.6, 138.5, 138.0, 133.1, 129.6, 129.4, 129.0, 128.23, 128.2, 127.9 (d, J = 34.6 Hz), 127.5, 125.9 (d, J = 44.2 Hz), 117.7 (d, J = 124.4 Hz), 107.1, 106 (d, J = 89.6 Hz), 64.2, 14.8; IR (KBr, cm^{-1}): υ 2979, 1645, 1592, 1508, 1460, 1222, 1191, 1022, 872, 792, 715, 584; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{19}FO_2Na$ 393.1261; found 393.1261.

*(4-Ethoxy-6-methoxy-2-(p-tolyl)naphthalen-1-yl)(phenyl)-methanone (**4g**, Table 4).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 88.2 mg, 78%); m.p. = 148−149 °C; R_f = 0.74 in 10% EtOAc/hexanes; ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 2.6 Hz, 1H), 7.51 (t, J = 9.3 Hz, 3H), 7.25 (t, J = 7.4 Hz, 1H), 7.14−7.08 (m, 4H), 7.00 (dd, J = 9.2, 2.6 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.75 (s, 1H), 4.19 (q, J = 6.9 Hz, 2H), 3.84 (s, 3H), 2.13 (s, 3H), 1.48 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 200.0, 157.4, 134.4, 138.6, 138.0, 136.9, 136.1, 132.9, 129.6, 129.2, 128.9, 128.1, 128.08, 127.3, 127.0, 125.8, 119.8, 107.0, 100.8, 64.0, 55.4, 21.1, 14.9; IR (KBr, cm^{-1}): υ 2917, 1651, 1593, 1506, 1384, 1280, 1219, 1052, 1024, 814, 724, 629; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{24}O_3Na$ 419.1618; found 419.1618.

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*(4-Ethoxy-2-(4-fluorophenyl)-6-methoxynaphthalen-1-yl)-(phenyl)methanone (**4h**, Table 4).* The reaction was carried out using 70 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 55.6 mg, 70%); m.p. = 146−147 °C; R_f = 0.39 in 5% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 2.7 Hz, 1H), 7.59 (d, J = 9.2 Hz, 1H), 7.56 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.28−7.23 (m, 2H), 7.20 (t, J = 7.8 Hz, 2H), 7.11 (dd, J = 9.2, 2.7 Hz, 1H), 6.86 (t, J = 8.7 Hz, 2H), 6.78 (s, 1H), 4.28 (q, J = 7.0 Hz, 2H), 3.94 (s, 3H), 1.59 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 199.8, 163.1, 161.1, 157.7, 154.6, 138.6, 137.01 (d, J = 13.3 Hz), 135.0, 133.1, 131.0 (d, J = 32.3 Hz), 129.6, 128.3, 127.9 (d, J = 556.0 Hz), 127.0, 126.0, 120.1, 115.1 (d, J = 85.8 Hz), 106.8, 100.9, 64.1, 55.4, 14.9; IR (KBr, cm^{-1}): υ 2933, 1662, 1592, 1506, 1382,1218, 1163, 1051, 841, 741, 623; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{21}FO_3Na$ 423.1367; found 423.1368.

*(4-Ethoxy-6-fluoro-2-(p-tolyl)naphthalen-1-yl)(phenyl)-methanone (**4i**, Table 4).* The reaction was carried out using 94 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 78.2 mg, 73%); m.p. = 172−173 °C; R_f = 0.78 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (dd, J = 10.4, 2.6 Hz, 1H), 7.61 (dd, J = 9.2, 5.4 Hz, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.16−7.09 (m, 5H), 6.92 (d, J = 7.9 Hz, 2H), 6.78 (s, 1H), 4.19 (q, J = 7.0 Hz, 2H), 2.15 (s, 3H), 1.49 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 199.6, 161.5, 159.5, 154.8 (d, J = 19.6 Hz), 138.4, 137.9 (d, J = 8.6 Hz), 137.7, 137.3, 133.0, 129.6, 129.2, 129.0, 128.2, 128.0, 127.8 (d, J = 33.8 Hz), 125.7 (d, J = 35.7 Hz), 117.6 (d, J = 99.6 Hz), 107.3, 106.4 (d, J = 89.4 Hz), 64.1, 21.1, 14.8; IR (KBr, cm^{-1}): υ 2920, 1696, 1651, 1600, 1509, 1447, 1224, 1186, 1025, 873, 746, 713, 659; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{21}FO_2Na$ 407.1418; found 407.1417.

*(4-Ethoxy-2-phenylnaphthalen-1-yl)(2-methyl-5-nitrophenyl)-methanone (**4j**, Table 4).* The reaction was carried out using 100 mg of corresponding aryl-fused 1,6-diyn-3-one and triethyl orthoformate. Yellow solid (yield = 39.2 mg, 35%); m.p. = 164−165 °C; R_f = 0.71 in 10% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47−8.44 (m, 1H), 8.07−8.03 (m, 1H), 7.92 (dd, J = 8.4, 2.5 Hz, 1H), 7.83 (d, J = 2.4 Hz, 1H), 7.63−7.55 (m, 2H), 7.17−7.09 (m, 6H), 6.77 (s, 1H), 4.30 (q, J = 7.0 Hz, 2H), 2.47 (s, 3H), 1.61 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 198.9, 156.5, 146.5, 145.4, 141.3, 140.8, 140.2, 132.2, 129.0, 128.5, 128.2, 127.9, 127.7, 125.9, 125.4, 125.2, 125.0, 124.8, 122.6, 106.2, 64.2, 29.7, 21.4, 14.8; IR (KBr, cm^{-1}): υ 2926, 1655, 1509, 1340, 1216, 1092, 750, 638; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{26}H_{22}FO_2$ 412.1543; found 412.1543.

*5,11-Dimethoxy-11-phenyl-11H-benzo[a]fluorene (**2a**-d_6, Scheme 6).* The reaction was carried out using 50 mg of corresponding aryl-fused 1,6-diyn-3-one. Yellow gummy (yield = 32.5 mg, 56%); R_f = 0.58 in 5% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 6.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.45−7.39 (m, 4H), 7.33 (d, J = 8.6 Hz, 1H), 7.29 (d, J = 5.1 Hz, 1H), 7.27−7.25 (m, 2H), 7.24−7.19 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 157.7, 149.4, 143.5, 140.9, 139.7, 132.6, 130.7, 128.6, 128.2, 127.7, 127.4, 126.9, 125.9, 125.4, 124.9, 124.4, 124.35, 123.0, 119.4, 96.3, 89.8; IR (KBr, cm^{-1}): υ 2922, 1583, 1446, 1110, 757, 698; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{14}D_6O_2Na$ 381.1732; found 381.1736.

*(4-Methoxy-2-phenylnaphthalen-1-yl)(phenyl)methanone (**4a**-d_3, Scheme 6).* The reaction was carried out using 50 mg of corresponding aryl-fused 1,6-diyn-3-one. Off-white solid (yield = 42.8 mg, 77%); m.p. = 227−228 °C; R_f = 0.49 in 5% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 7.1 Hz, 2H), 7.57−7.53 (m, 1H), 7.53−7.46 (m, 2H), 7.40−7.36 (m, 3H), 7.25−7.20 (m, 3H), 7.20−7.15 (m, 1H), 6.89 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 199.8, 156.1, 140.8, 138.6, 134.7, 132.9, 132.0, 129.6, 129.4, 128.8, 128.2, 127.8, 127.5, 125.7, 125.3, 124.6, 122.2, 120.7, 118.8, 105.6; IR (KBr, cm^{-1}): υ 2922, 1658, 1580, 1499, 1390, 1225, 1101, 773, 693, 610; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{15}D_3O_2Na$ 364.1387; found 364.1386.

*(R)-11-Methoxy-11-phenyl-11H-benzo[a]fluoren-5-ol (**5a**, Scheme 7).* To a solution of benzo[a]fluorene **2a** (24 mg, 0.068 mmol) in CH_2Cl_2 (1 mL) solvent under a nitrogen atmosphere at 0 °C, BBr_3 (136 μL, 0.136 mmol, 1 M BBr_3 in CH_2Cl_2) was added and the reaction was allowed to stir at room temperature. Completion of the reaction was monitored by TLC, and the reaction mixture was quenched using saturated $NaHCO_3$ solution and extracted with EtOAc. After that, the combined organic layer was washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and finally, the crude product was purified by column chromatography (silica gel, hexanes/EtOAc) to get pure 11-methoxy-11-phenyl-11H-benzo[a]fluoren-5-ol **5a** (15.6 mg, 68%). Red solid; m.p. = 212−213 °C; R_f = 0.20 in 5% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.41(d, J = 6.8 Hz, 2H), 7.38−7.31 (m, 5H), 7.24 (d, J = 7.5 Hz, 2H), 7.21 (s, 1H), 7.17 (s, 1H), 4.13 (s, 3H), 2.49 (bs, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 157.7, 152.8, 143.1, 139.7, 138.3, 136.0, 130.1, 128.7, 128.4, 128.0, 127.3, 127.0, 126.2, 125.1, 124.9, 124.5, 124.0, 123.1, 119.6, 96.4, 84.2, 55.9; IR (KBr, cm^{-1}): υ 2923, 1661, 1584, 1448, 1219, 1141, 756, 699; HRMS (ESI-TOF) m/z: [M - H]$^+$ Calcd for $C_{24}H_{17}O_2$ 337.1229; found 337.1225.

*11-Phenyl-5H-benzo[a]fluoren-5-one (**6a**, Scheme 7).* To a solution of naphthyl ketone (**4a**) (64 mg, 0.19 mmol) in CH_2Cl_2 (3 mL) solvent under a nitrogen atmosphere at 0 °C, BBr_3 (0.4 mL, 0.38 mmol, 1 M BBr_3 in CH_2Cl_2) was added and the reaction was allowed to stir at room temperature. Completion of the reaction was monitored by TLC, and the reaction mixture was quenched using saturated $NaHCO_3$ solution and extracted with EtOAc. After that, the combined organic layer was washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and finally, the crude product was purified by column chromatography (silica gel, hexanes/EtOAc) to get pure 11-phenyl-5H-benzo[a]fluoren-5-one **6a** (33 mg, 57%). Dark red solid; m.p. = 190−191 °C; R_f = 0.31 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 7.8 Hz, 1H), 7.52−7.48 (m, 2H), 7.47−7.43 (m, 2H), 7.42−7.39 (m, 2H), 7.22−7.18 (m, 2H), 7.14−7.09 (m, 3H), 6.80 (s, 2H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$): δ 186.5, 153.0, 149.0, 146.1, 135.8, 134.4, 133.5, 132.3, 130.9, 130.5, 129.4, 129.2, 128.2, 127.9, 127.6, 125.2, 122.4, 122.0, 121.3; IR (KBr, cm^{-1}): υ 2921, 1583, 1446, 1374, 1217, 1096, 1026, 741, 700; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{15}O$ 307.1117; found 307.1118.

*3-Fluoro-11-phenyl-5H-benzo[a]fluoren-5-one (**6b**, Scheme 7).* The reaction was carried out using 50 mg of naphthyl ketone (**4f**). Dark red solid (yield = 24.7 mg, 56%); m.p. = 216−217 °C; R_f = 0.51 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, J = 9.2, 2.8 Hz, 1H), 7.56−7.48 (m, 3H), 7.46−7.44 (m, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.23−7.18 (m, 1H), 7.13 (dd, J = 5.3, 3.1 Hz, 2H), 6.88−6.81 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 185.4, 163.2, 161.2, 153.4, 149.0, 145.9, 135.5, 134.0, 132.6 (d, J = 6.8 Hz), 131.0, 129.8 (d, J = 3.4 Hz), 129.4, 129.3, 128.4, 128.2, 127.4 (d, J = 7.2 Hz), 127.1, 122.5, 122.1, 121.0, 119.8 (d, J = 22.3 Hz), 113.6 (d, J = 22.7 Hz); IR (KBr, cm^{-1}): υ 2920, 1627, 1553, 1439, 1303, 1272, 1049, 758, 700, 576; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{14}FO$ 325.1023; found 325.1022.

*3-Fluoro-9-methyl-11-phenyl-5H-benzo[a]fluoren-5-one (**6c**, Scheme 7).* The reaction was carried out using 50 mg of naphthyl ketone (**4i**). Dark red solid (yield = 25.9 mg, 59%); m.p. = 222−223 °C; R_f = 0.47 in 10% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (dd, J = 9.3, 2.9 Hz, 1H), 7.62−7.53 (m, 3H), 7.47−7.43 (m, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.20 (dd, J = 8.9, 5.2 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.91−6.85 (m, 1H), 6.79 (s, 1H), 6.65 (s, 1H), 2.26 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 185.4, 163.4, 160.9, 153.5, 148.9, 146.2, 141.6, 134.2, 132.7, 132.6 (d, J = 5.9 Hz), 129.9, 129.4, 129.3, 128.7, 128.2, 127.3 (d, J = 7.3 Hz), 123.6, 122.1, 120.4, 119.7 (d, J = 22.7 Hz), 113.5 (d, J = 22.7 Hz), 21.8; IR (KBr, cm^{-1}): υ 2919, 1629, 1601, 1476, 1262, 921, 697; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{16}FO$ 339.1180; found 339.1178.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02131.

Copies of NMR spectra and HRMS analysis reports of all the prepared compounds and X-ray crystallographic data of **2f**, **3b**, **4b**, and **4k** (PDF)

Accession Codes

CCDC 1998442−1998445 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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