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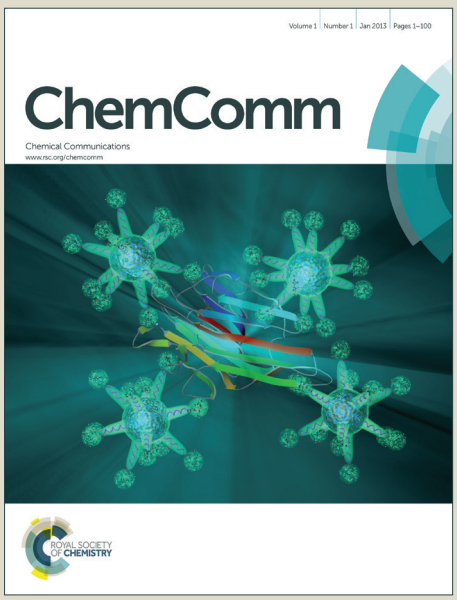





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# A facile access to substituted benzo[a]fluorenes from *o*-alkynylbenzaldehydes via *in situ* formed acetals

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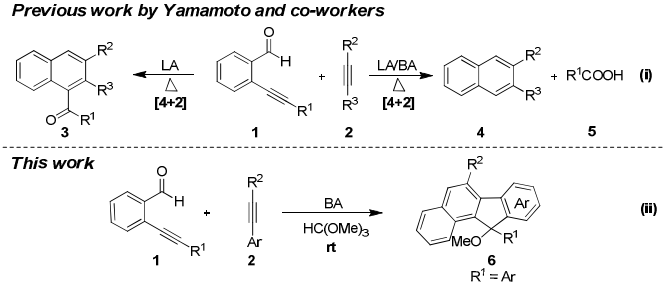
***In situ* formed acetal changes the course of Brønsted acid-catalyzed reaction of *ortho*-alkynylbenzaldehydes with arylalkynes altogether. By utilizing this, an efficient domino approach for the regioselective synthesis of substituted benzo[a]fluorenes has been developed under mild reaction conditions. *In situ* formed acetal facilitates the intermolecular heteroalkyne metathesis and subsequent trans to cis isomerization of double bond to effect the intramolecular annulation.**

Polycyclic aromatic hydrocarbons (PAHs) such as naphthalenes, fluorenes, antharacenes, phanthrenes etc. play an important role in the fields of medicinal as well as materials chemistry due to their unique properties.[1] For their synthesis in a regioselective manner, cyclization reactions of type [4+2], [2+2], [2+2+2] and domino reactions have been developed.[2] Limited methods are only available in the literature for the construction of fluorene[3] framework in general and benzo[a]fluorenes in particular.[3g, 3i, 3j] Among PAHs, fluorene derivatives have been widely utilized in the field of material science in developing optical materials.[4] Hence, development of simple method for the construction of fluorenes from readily available starting materials is highly desirable.



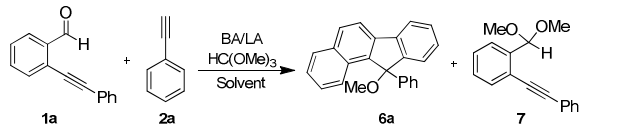

Scheme 1. Reaction of *o*-alkynylbenzaldehydes with alkynes under Lewis/Brønsted acid conditions

Yamamoto and co-workers studied extensively the cyclization involving *o*-alkynylbenzaldehydes and alkynes under Lewis/Brønsted (LA/BA) acid-catalyzed conditions for the synthesis of naphthalenes *via* [4+2] benzannulation pathway. In this reaction naphthyl ketone is the major product with LA catalyst alone whereas debenzoylated naphthalene was the major product in the presence of either BA along with LA catalyst or BA alone (Scheme 1, eq i).[5] In our endeavor to develop reactions using *in situ* generated acetals,[6] we have found that reaction of *o*-alkynylbenzaldehydes and alkynes in the presence of trimethyl orthoformate and catalytic Brønsted acid results in benzo[a]fluorene derivatives efficiently (Scheme 1, eq ii).

At the outset, *o*-alkynylbenzaldehyde **1a** was reacted with 1.5 equiv of phenylacetylene **2a** in the presence of 2.0 equiv of trimethyl orthoformate and 50 mol% of TfOH in dichloromethane solvent at room temperature. Interestingly, the reaction completed in 30 min and resulted in benzo[a]fluorene **6a** in 72% yield (Table 1, entry 1). Impressed by this result and knowing the importance of fluorene derivatives, our attention then turned to improve the yield of the product **6a** by changing various parameters. The results are summarized in the Table 1. Unfortunately, there were no reactions with trifluoroacetic acid and *p*-toluenesulfonic acid even when the reactions were allowed to stir for 24 h at room temperature in dichloromethane solvent (Table 1, entries 2 and 3). With super acid $HSbF_6{\cdot}6H_2O$ as catalyst the product **6a** was isolated in 70% yield (Table 1, entry 4). Since the reaction required strong Brønsted acids like TfOH, we then focused on finding the better solvent for TfOH-catalyzed reaction. Only moderate yields were obtained when the reaction was carried out separately in dichloroethane, nitromethane and toluene (Table 1, entries 5-7). In dioxane, as solvent, the expected product did not form and some unidentified products were obtained. There was no reaction in methanol even after 24 h (Table 1, entry 9). Interestingly, clean reaction was observed when the reaction was performed in acetonitrile for 4 h the product was isolated in 86% yield (Table 1, entry 10). For further optimization, acetonitrile was used as solvent. The amount of TfOH catalyst was reduced to 20 mol% and found that there was hardly any appreciable reduction in the product yield (85%) (Table 1, entry 11). Yield of **6a** slightly dropped to 80% when the reaction was conducted with 10 mol% TfOH (Table1, entry 12). There was no change in the yield of the product when **2a** was taken in 1.2 equiv (Table 1, entry 13). Finally, a control reaction was conducted without trimethyl orthoformate using TfOH in dichloromethane solvent. Under this condition, the reaction resulted in 36% of 2-phenylnaphthalene (Scheme 3, eq. 1). This observation clearly indicates that the benzo[a]fluorene formation does not take place through the intermediate proposed in the mechanism by Yamamoto group for naphthalene synthesis and the importance of trimethyl orthoformate

for the formation benzo[a]fluorene. The *in situ* formed acetal would generate more electrophilic oxonium ion species in the presence of BA catalyst which undergoes fast [2+2] cycloaddition reaction than their aldehyde form with alkyne to afford enone.[7] Saá group has utilized intramolecular $HBF_4$-promoted alkyne/acetal coupling in the synthesis of hydroazulenones.[8] Luo and co-workers have utilized its intermolecular version catalyzed by $In(OTf)_3$/PhCOOH to synthesize indanones.[9]

Table 1. Optimization study[a]




1a 2a 6a 7

| Entry | Solvent | Catalyst | Cat. (mol %) | Time (hours) | Yield (%)[b] 6a | 7 |
|---|---|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | TfOH | 50 | 0.5 | 72 | |
| 2 | $CH_2Cl_2$ | PTSA | 50 | 24.0 | NR | |
| 3 | $CH_2Cl_2$ | TFA | 50 | 24.0 | NR | |
| 4 | $CH_2Cl_2$ | $HSbF_6.6H_2O$ | 50 | 12.0 | 70 | |
| 5 | $C_2H_4Cl_2$ | TfOH | 50 | 0.5 | 57 | |
| 6 | $CH_3NO_2$ | TfOH | 50 | 0.5 | 54 | |
| 7 | Toluene | TfOH | 50 | 0.5 | 48 | |
| 8 | Dioxane | TfOH | 50 | 5.0 | --- | --- |
| 9 | $CH_3OH$ | TfOH | 50 | 24.0 | NR | |
| 10 | $CH_3CN$ | TfOH | 50 | 4.0 | 86 | |
| 11 | $CH_3CN$ | TfOH | 20 | 4.0 | 85 | |
| 12 | $CH_3CN$ | TfOH | 10 | 4.0 | 80 | |
| 13 | $CH_3CN$ | TfOH | 20 | 4.0 | 85[c] | |
| 14 | $CH_3CN$[d] | $AuCl_3$ | 5 | 12.0 | --- | 94 |
| 15 | $CH_3CN$[d] | $Cu(OTf)_2$ | 5 | 12.0 | --- | 99 |
| 16 | $CH_3CN$[d] | $Fe(OTf)_2$ | 5 | 12.0 | NR | |
| 17 | $CH_3CN$[d] | $Yb(OTf)_3$ | 5 | 12.0 | NR | |
| 18 | $CH_3CN$[d] | $AgSbF_6$ | 5 | 24.0 | NR | |

[a] All reactions were carried out using **1a** (1.0 equiv) **2a** (1.5 equiv) and trimethyl orthoformate (2.0 equiv) at rt unless otherwise stated. [b] isolated yield. [c] 1.2 equiv of **2a** was used. [d] The reaction was performed under reflux condition. NR: no reaction

Interestingly, no naphthalene or fluorene derivatives were obtained when the reaction was performed under different Lewis acids such as $AuCl_3$, $Cu(OTf)_2$, $Fe(OTf)_2$, $Yb(OTf)_3$ and $AgSbF_6$ (Table 1, entries 14-18). Under these conditions only acetal formation was observed at room temperature, which did not give the desired product at reflux conditions. In the reactions employing $Cu(OTf)_2$ and $AuCl_3$ catalysts, the acetal **7** was isolated in 99% and 94% respectively. On the other hand, the got acetal converted back to aldehyde with $Fe(OTf)_2$ and $Yb(OTf)_3$ under reflux condition. No reaction was observed with $AgSbF_6$ catalyst even under both reflux conditions.

The substrate scope was then studied and the results are shown in Figure 1. This cascade reaction worked with both terminal as well as internal aromatic alkynes. In general, the reaction completed in 4 h with terminal alkynes and took more time with internal alkynes. It has to be mentioned that dichloromethane is better solvent for reactions involving diarylalkynes and high yields were obtained in comparatively shorter reaction times than that in acetonitrile.[10] Substrates with substituents like F, Cl, Br, OMe, acetal, cyano and $CF_3$ tolerated and corresponding products were obtained in good to excellent yields. The benzo[a]fluorene with halo substitution (**6d**, **6e**, **6i** and **6n**) could be obtained using this method and the products can, in principle, be functionalized further by transition metal-catalyzed coupling reactions. This method is applicable to aliphatic alkynylaldehydes as well and products **6j** and **6k** were obtained in good yields. Only one of the possible regioisomeric products (**6v-6x**) were obtained in good yields with internal unsymmetrical diarylalkynes. To our delight, pharmaceutically important group such as $CF_3$ could be incorporated in benzo[a]fluorene using this methodology (**6w**). Unfortunately, this transformation is not applicable when $R^1$ is aliphatic group. Only corresponding acetal was obtained when *o*-alkynylbenzaldehyde with $R^1$ = $C_6H_{13}$ was treated with phenylacetylene under the reaction condition. In addition, there was no reaction when aliphatic terminal alkynes were used as substrates as [2+2] cycloaddition is not possible.

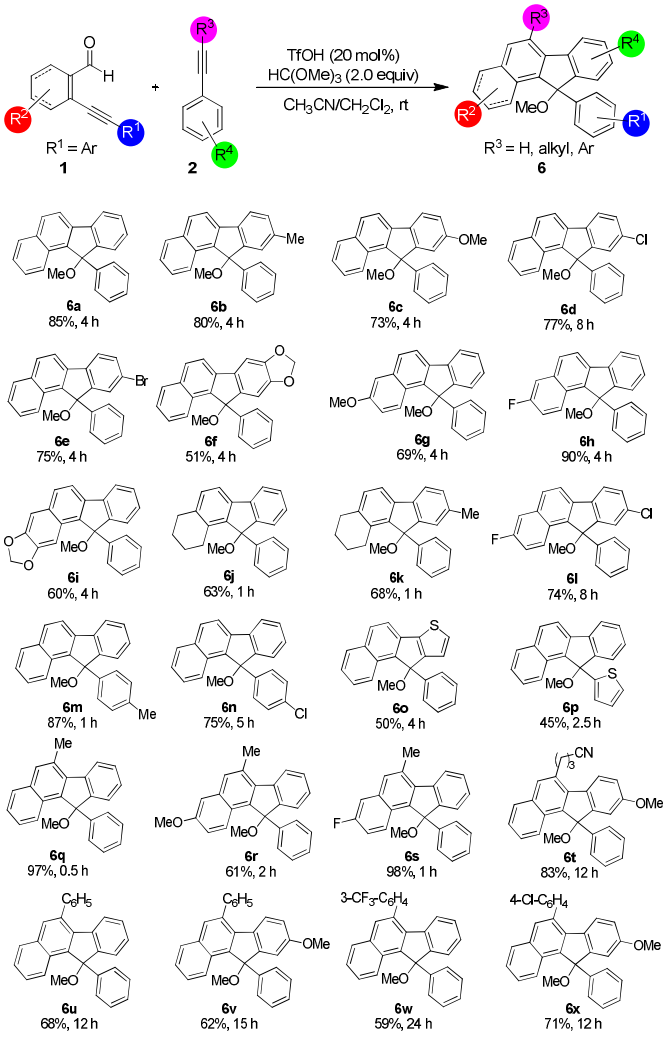
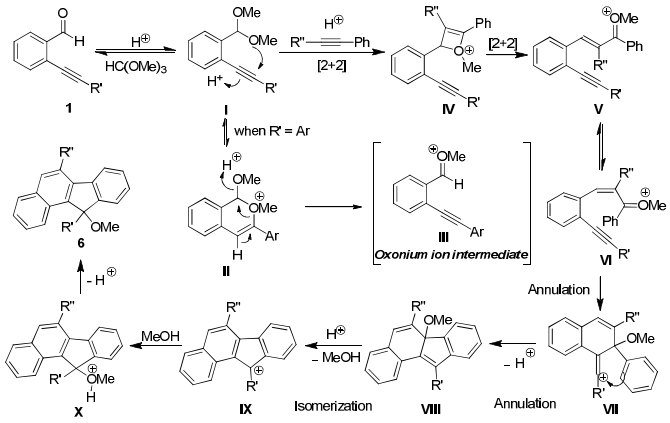



Fig 1. Substrate scope

A plausible mechanism is illustrated in Scheme 2. The acetal **I** is formed from aldehyde **1** in the presence of trimethyl orthoformate and TfOH. Intermolecular alkyne-acetal coupling ([2+2] cycloaddition) would take place between arylalkyne and oxocarbenium ion intermediate **III** generated from **I** to give oxetene intermediate **IV**. Outcome of the reaction of *o*-alkynylbenzaldehyde

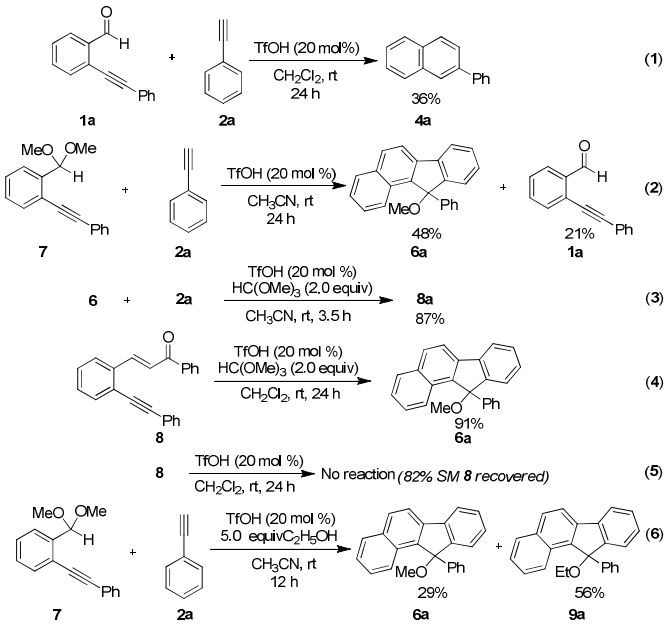
with $R^1$ = $C_6H_{13}$ suggests that the triple bond of *o*-alkynylbenzaldehyde having aryl as $R^1$ group might participate at the early stage of the reaction.[12] With R′ = Ar, the formed acetal can attack the triple bond under the influence of acid to give intermediate **II** which can result in the formation of oxocarbenium ion **III** required for the [2+2] cycloaddition. The oxetene formation is regioselective and the oxygen of oxocarbenium will be attached to the alkyne carbon which is attached to electron rich aryl ring.[9] This is the reason for the formation of benzo[a]fluorene derivatives **6q-6t** from internal alkynes having both aryl and alkyl substituents as the final cyclization to result in benzo[a]fluorene derivative is possible only with this regioselectivity. Again it is the reason for the regioselective formation of products **6v-6x** where diarylalkynes having aryl rings with different electronic properties were used. Then, [2+2] cycloreversion of **IV** will afford oxocarbenium ion intermediate **V** which will be in equilibrium with its cis isomer **VI**.[13] Subsequently, annulation reaction is initiated by intramolecular attack of alkyne on activated carbonyl group.[3g, 3i] The formed vinyl carbocation **VII** will be trapped by the aryl group by aromatic electrophilic substitution reaction to give **VIII**. Finally, the benzo[a]fluorene **6** is formed by isomerization of **VIII** through carbocation intermediate **IX** in the presence of TfOH. The structure of **6f** was confirmed by COSY and NOESY experiments. The other possible regioisomer which can form in the second annulation step (5-membered ring formation) was not detected. The structure of **6u** was confirmed by single-crystal x-ray analysis.[14]

Scheme 2. Plausible mechanism




Control experiments were carried out to check the proposed mechanistic pathway and intermediates (Scheme 3). Acetal **7** was prepared separately and reacted with phenylacetylene (1.2 equiv) and 20 mol% TfOH in acetonitrile solvent. It resulted in only 48% of benzo[a]fluorene derivative **6a** and 21% of **1a** was recovered (eq 2). In another experiment, acetal **7** was subjected to standard reaction conditions, which yielded 87% of **6a** (eq 3). Hence, in the presence of trimethyl orthoformate, the concentration of acetal will be kept high as aldehyde formed by deprotection under acidic condition will be converted back to acetal. To evaluate the formation of intermediate **VI**, the chalcone **8** was prepared and treated with TfOH and $HC(OMe)_3$ in dichloromethane. Gratifyingly, the product **6a** was isolated in 91% yield after 24 h (eq 4) which is quite higher than that took for direct conversion of **1a** into **6a**. The same reaction resulted in 69% of **6a** when the reaction was carried out in acetonitrile for 24 h and 20% of **7** was recovered. No reaction was observed in the experiment in which **8** was treated with TfOH catalyst alone in dichloromethane (eq 5). Shorter reaction time required for the direct transformation of **1a** into **6a** (Fig. 1) than **8** into **6a** might be due to ease of intermediate **V** to isomerize to cis form than the trans enone **8**. Further the trans enone **8** requires time for the formation of acetal and its conversion to oxocarbenium intermediate **V** to effect the trans to cis isomerization. In order to confirm the formation of carbocation **IX** during the reaction, 5.0 equiv of ethanol was added intentionally as external nucleophile to trap the carbocation intermediate **IX**. Indeed, ethanol quenched product **9a** formed along with **6a** in the ratio of 1:0.44 as an inseparable mixture (eq 6). Reaction of phenylacetylene alone under the reaction condition in the absence of *o*-alkynylbenzaldehyde did not give any product even after 24 h. These control experiments demonstrate that *in situ* formed acetal not only helps for [2+2] cycloaddition reaction but also assists the trans to cis isomerization[13] to undergo annulation in the present transformation. The isomerization is favored as the cis product will cyclize to result in more stable benzo[a]fluorene system.

Scheme 3. Control experiments




To summarize, a simple and efficient method has been developed for the regioselective synthesis of substituted benzo[a]fluorenes from readily accessible starting materials under mild reaction conditions. This transformation takes place *via* [2+2] cycloaddition/alkyne acetal coupling of *in situ* generated acetal followed by double bond isomerization which facilitates the intramolecular cyclization to construct benzo[a]fluorene framework. Thus the *in situ* formed acetal can advantageously be used to develop new reactions leading to interesting molecular frameworks.

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## Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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**TOC**

Brønsted acid catalysed reaction of *o*-alkynylbenzaldehydes with arylalkynes in the presence of trimethyl orthoformate takes a different reaction pathway and results in benzo[a]fluorenes.