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Letter

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A Photocatalyzed Synthesis of Naphthalenes by Using Aniline as a Traceless Directing Group in [4+2] Annulation of AminoBenzocyclobutenes with Alkynes

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Abstract: We report a visible-light-promoted synthesis of substituted naphthalenes via [4+2] annulation of amino-benzocyclobutenes with alkynes. Amino-benzocyclobutenes, which are conveniently synthesized by [2+2] cycloaddition of arynes with ketenes followed by reductive amination, undergo regioselective opening of the cyclobutenyl ring to reveal a presumably distonic radical cation upon photooxidation by an excited iridium complex. The distonic radical cation undergoes the annulation with terminal and internal alkynes as well as diynes to afford structurally diverse naphthalenes. The regiochemistry of the annulation follows the pattern displayed in addition of nucleophilic carbon radicals to alkynes. The aniline group plays a dual role in which it not only directs the initial photooxidation to generate the amine radical cation but also serves as a leaving group to complete aromatization.

Keywords: substituted naphthalenes, amino-benzocyclobutenes, photocatalysis, annulation, C-C cleavage.

Substituted naphthalenes and their derivatives, such as naphthoquinones, are ubiquitous in many valuable molecules across a broad spectrum of usage.[1] Selected examples in this class of compounds include 9,10-anthraquinone-2,7-disulphonic acid (AQDS), an excellent energy storage material for flow batteries,[2] justicidin A, a potent antitumor natural product,[3] and rumexoside, isolated from the roots of a Turkish medicinal plant (Figure 1).[4] Synthesis of substituted naphthalenes remains challenging due to the limitation of functional group tolerance as well as regioselectivity.[5] Most of these syntheses fall into two categories: 1) they start from a simple naphthalene core and then often require stepwise and lengthy elaboration to install the requisite functional groups;[6] 2) they begin with a suitably functionalized arene and proceed through annulation or cyclization to install the other arene.[7] Between the two approaches, the later is generally considered to be more desirable because it is convergent and modular.

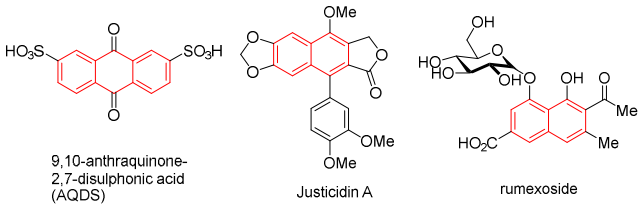
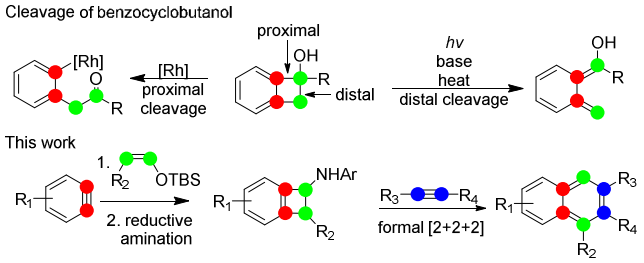


Figure 1. Selected examples of substituted naphthalenes

The embedded ring strain in benzocyclobutenes renders the usually inert C-C bonds cleavable under various conditions, thereby making them a versatile precursor in the synthesis of naphthalenes and dihydronaphthalenes.[8] Benzocyclobutenols, which bear a hydroxyl group on the cyclobutenyl ring, display similar versatility in the ring opening process.[9, 10] Photo-irradiation, base treatment, or heating generally favors cleavage of the distal C-C bond, revealing a quinodimethane intermediate that readily participates in the Diels-Alder reaction to provide dihydronaphthalenes.[11] On the other hand, cleavage of the proximal C-C bond can be realized by transition metal complexes such as Pd and Rh complexes to furnish aryl-palladium or -rhodium intermediates that can participate in a number of C-C bond formation reactions.[9a, 12] Although amino-benzocyclobutenes can be conveniently synthesized by [2+2] cycloaddition of arynes with ketenes followed by reductive amination, they have been much less exploited than benzocyclobutenols in organic synthesis (Scheme 1).[13] Two notable examples using amino-benzocyclobutenes as precursors to synthesize substituted arenes and dihydronaphthalenes include Shi's work on addition of vinylogous amides to arynes and Hsung's on syntheses of chelidonine and norchelidonine. In both works, a quinodimethane intermediate was proposed to be generated in situ via the ring opening and then was intercepted by a nucleophile or underwent the Diels-Alder reaction.[14]

Few studies on amino-benzocyclobutenes' utility as synthetic building blocks prompted us to examine their synthetic applications, particularly in the context of visible light photocatalysis. We envisioned that single electron photooxidation of amino-benzocyclobutenes would induce cleavage of the distal C-C bond to furnish a distonic radical cation.[15] This reactive species would then

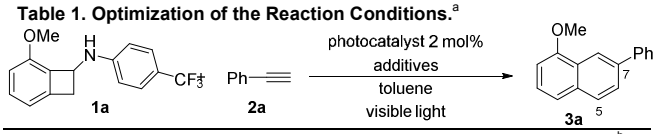
undergo two sequential C-C bond formations mediated by radicals to form a dihydronaphthalene. We expected that its reactivity would be distinct from that of a quinodimethane and thereby could furnish a completely different subclass of dihydronaphthalenes. Herein we report our studies on intermolecular annulations of amino-benzocyclobutenes with alkynes and diynes, which results in a three-component (benzynes, lithium enolates or silyl ketene acetals, and alkynes) synthesis of substituted naphthalenes. Anilines play a dual role in this reaction: it first engages in the photooxidation to induce the ring opening and then serves as a leaving group to complete aromatization.



Scheme 1. Cleavage reactions of benzocyclobutenols and amino-benzocyclobutenes

Amino-benzocyclobutene **1a** and phenylacetylene were chosen as the representative substrates to optimize the reaction conditions (Table 1). The substituent on the aniline moiety was found to greatly affect the reaction, and amino-benzocyclobutenes bearing electron-withdrawing groups performed much better than those bearing electron-donating ones (see SI). The -CF_3 group was selected as the standard substituent because of its chemical inertness under the photoredox conditions and the availability of commercially available cheap precursor, 4-(trifluoromethyl)-aniline. Among the solvents screened, toluene was found to be the best. Other aromatic solvents and polar solvents such as methanol and nitromethane all gave inferior results (see SI). For the photocatalyst, we focused on those soluble in toluene. $[Ir(ppy)_2(dtbbpy)][PF_6]$ was more effective than $[Ir\{dF(CF_3)ppy\}_2(dtbpy)][PF_6]$ (entries 1 and 2), whereas $Ru(bpy)_3(BArF)_2$ was surprisingly inactive (see SI). Addition of an inorganic base such as K_2HPO_4 increased the yield of **3a** from 37% to 48% (entry 3). However, use of more basic K_3PO_4 gave a slightly lower yield of **3a** (entry 4). Interestingly, use of a more soluble base such as Cs_2CO_3 or tetrabutylammonium hydroxide resulted in a much lower yield of **3a**, suggesting a delicate balance of the base's strength and solubility in order to achieve the optimal yield (see SI). Increasing the concentration and switching from 18 W white LED to 6 W blue LED both helped the reaction, furnishing product **3a** in 62% yield (entries 5 and 6). Control experiments showed that both light and the photocatalyst were essential to the reaction (entries 7 and 8). These results suggested that the Diels-Alder reaction pathway unlikely operated in the reaction.[14a, 14c] It was worth of note that because incomplete elimination of the aniline was observed in the conditions examined, concentrated HCl was added during the workup to ensure completion of the elimination[16].

Table 1. Optimization of the Reaction Conditions.[a]



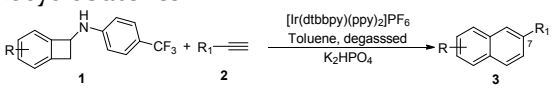
Entry	Photocatalyst	Additives (1eq.)	Yield of **3a** [%][b]
1	$[Ir\{dF(CF_3)ppy\}_2(dtbpy)][PF_6]$		22%
2	$[Ir(dtbbpy)(ppy)_2][PF_6]$		37%
3	$[Ir(dtbbpy)(ppy)_2][PF_6]$	K_2HPO_4	48%
4	$[Ir(dtbbpy)(ppy)_2][PF_6]$	K_3PO_4	36%
5	$[Ir(dtbbpy)(ppy)_2][PF_6]$	K_2HPO_4	59%[c]
6	$[Ir(dtbbpy)(ppy)_2][PF_6]$	K_2HPO_4	62%[c, d]
7	$[Ir(dtbbpy)(ppy)_2][PF_6]$	K_2HPO_4	N.R.[c, e]
8		K_2HPO_4	N.R.[c, d]

[a]Conditions: **1a** (0.1 mmol, 0.1 M in degassed toluene), **2a** (0.5 mmol), irradiation with 18 W white LED at room temperature for 36 h , concentrated HCl is added. 20 s later, the mixture is filtered through silica gel. [b]Yield determined by GC analysis using dodecane as an internal standard unless noted. [c] 0.2 M of **1a** in degassed toluene. [d]Irradiation with 6 W blue LED. [e]No light.

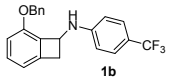
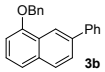
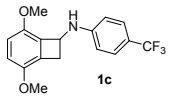
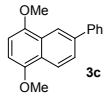
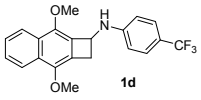
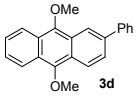
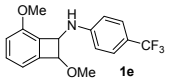
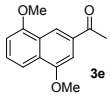
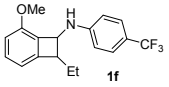
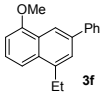
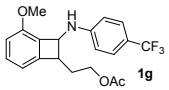
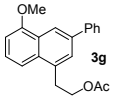
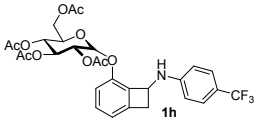
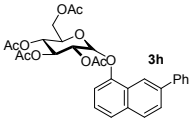
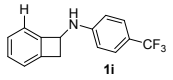
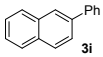
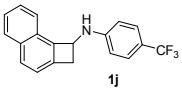
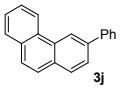
Using phenylacetylene (**2a**) as the alkyne partner, we examined the scope of amino-benzocyclobutenes (Table 2). Replacement of the -OMe substituent with a more labile -OBn group had little effect on the product's yield (**3b**). Addition of another -OMe group para to the original one (**1c**) furnished 1,4-dimethoxy-7-phenylnaphthalene **3c**, a naphthoquinone precursor in 58% yield. Fusion of a benzene ring to amino-benzocyclobutene **1d** was easily accomplished by modifying the corresponding benzyne precursor, and the expected product 9,10-Dimethoxy-2-phenylanthracene **3d**, an anthraquinone precursor was prepared in 54% yield. Additional substituents were readily incorporated into amino-benzocyclobutenes by choosing silyl ketene acetals bearing the substituents for the [2+2] cycloaddition with the corresponding benzynes. These substituted amino-benzocyclobutenes (**1e**: -OMe; **1f**: -Et; **1g**: -CH_2CH_2OAc) underwent the annulation with 3-butyn-2-one or phenylacetylene uneventfully, providing C5-substituted naphthalenes (**3e**, **3f**, and **3g**) in 54-68% yields. Aromatic O-glycosides such as naphthalene saccharides are a common structural motif in bioactive natural products. The common approach for synthesis of this motif is to form the glycosidic bond between an aglycone (e.g., naphthol) and a saccharide.[17] This method permits an alternative assembly strategy in which the glycosidic bond is formed between a simpler aglycone (e.g., a phenol derivative) and the saccharide and the subsequent annulation completes the synthesis of the more complex aglycone. Amino-benzocyclobutene **1h** bearing a tetraacetyl glucose with a β configuration at the anomeric carbon underwent the annulation with phenylacetylene to afford **3h** with the β configuration intact. Lastly, the alkoxy substituent in amino-benzocyclobutenes helped stabilize the aryne intermediate and thus improved the efficiency of the [2+2] cycloaddition to form the cyclobutenyl ring.

However, it was not required for the annulation. Amino-benzocyclobutenes (**1i** and **1j**), both lack of the alkoxy substituent, proceeded in the annulation to furnish 2-phenylnaphthalene **3i** and 3-phenylphenanthrene **3j** respectively.

Table 2. Substrate Scope of Amino-benzocyclobutenes



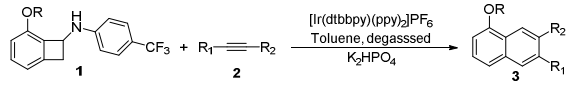
1 2 3

Entry[a]	Substrate	Product	Yield[%][b]
1	 1b	 3b	58
2	 1c	 3c	58
3	 1d	 3d	54
4	 1e	 3e	68
5	 1f	 3f	56
6	 1g	 3g	54
7	 1h	 3h	50
8	 1i	 3i	56
9	 1j	 3j	40

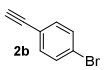
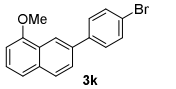
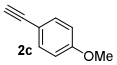
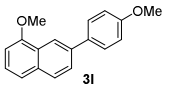
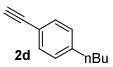
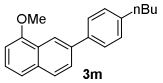
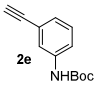
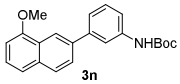
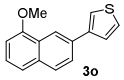
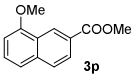
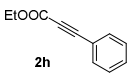
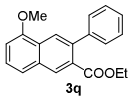
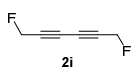
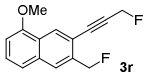
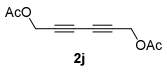
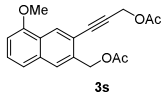
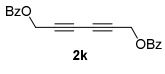
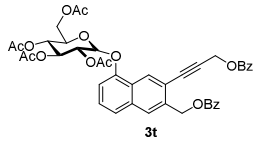
[a] Conditions: **1** (0.1 mmol, 0.2 M in degassed toluene), **2** (0.5 mmol), after irradiation with 6 W blue LED at room temperature for 60 h, concentrated HCl is added. 20 s later, the mixture is filtered through silica gel. [b] Isolated yields.

We next investigated the scope of alkynes (Table 3). The substituents on the phenyl group of phenylacetylene were well tolerated. Several groups with various electronic characters at the para or meta position (**2b-e**) were compatible with the annulation reaction to provide naphthalenes **3k-n** in 51-64% yield. In addition to the aryl group at C7, other functional groups such as thiophene and methyl esters were easily incorporated into C7 of naphthalenes, as 3-ethynylthiophene **2f** and methyl propiolate **2g** both successfully underwent the annulation with **1a**, although in somewhat lower yields than phenylacetylene. Unsymmetrical internal alkyne **2h,** despite the increase in steric hindrance, participated in the annulation to furnish only one regioisomer **3q** in 58% yield albeit in longer reaction time. To our surprise, diynes **2i-k** worked really well in this method. Alkynyl naphthalenes **3r-s**, which are usually synthesized by cross coupling of terminal alkynes with prefunctionalized naphthalenes, were obtained in one step in 62-63% yield. Not surprisingly, the glycosidic bond survived in the annulation of **1h** with diyne **2k**, which allowed for rapid increase of the structural complexity of naphthalene saccharide **3t** in a respectable yield (61%).

Table 3. Substrate Scope of Alkynes



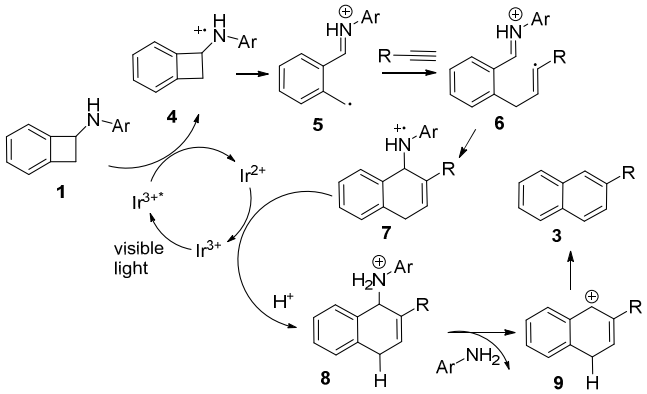
1 2 3

Entry[a]	alkynes	Product	Yield[%][b]
1	 2b	 3k	64
2	 2c	 3l	51
3	 2d	 3m	54
4	 2e	 3n	59
5	 2f	 3o	38
6	 2g	 3p	44
7	 2h	 3q	58[c]
8	 2i	 3r	62
9	 2j	 3s	63
10	 2k	 3t	61

[a] Conditions: **1** (0.1 mmol, 0.2 M in degassed toluene), **2** (0.5 mmol), after irradiation with 6 W blue LED at room temperature for 60 h, concentrated HCl is added. 20 s later, the mixture is filtered through silica gel. [b] Isolated yields. [c] 84 h

We believed that the annulation probably proceeds in a mechanism similar to our previously reported [4+2] annulation of cyclobutylanilines with alkynes, as the reactivity trend and regiochemistry with respect to alkynes completely match with those observed for the latter reaction.[15c] The photoexcited Ir(III) complex oxidizes amino-benzocyclobutene **1** to generate amino radical cat-

ion **4** followed by ring opening at the distal C–C bond to form distonic radical cation **5**, which subsequently adds to alkyne to furnish vinyl radical **6**. Ring closure is then achieved via intramolecular addition of the vinyl radical to the iminium ion to provide amino radical cation **7**, which is reduced by the Ir(II) complex to give 1,4-dihydronaphthalene **8** after protonation. Finally, elimination of the aniline group presumably by an E1-like pathway gives naphthalene **3** via benzylic carbocation **9** (Scheme 2). The [4+2] annulation of amino-benzocyclobutenes with alkynes was considerably slower than that of cyclobutylanilines with alkynes. We attributed the slower annulation of amino-benzocyclobutenes to the stability and low reactivity of the incipient benzyl radicals. It has been reported that benzyl radicals add to alkenes much slower than alkyl radicals.[18] To support the proposed mechanism, the uneliminated 1,4-dihydronaphthalene intermediate from **2h** was successfully isolated (see SI). UV-Vis absorption spectra of amino-benzocyclobutene **1a** and $[Ir(ppy)_2(dtbbpy)]PF_6$ supported that the Ir complex was photoexcited by the blue LED. The oxidation half peak potential of **1a** was found to be 1.13 V vs. SCE, which is more positive than the reduction potential of the photoexcited Ir(III) complex (Ir^{3+*}/Ir^{2+} : 0.66 V vs. SCE).[19] Although thermodynamically unfavorable, such SET processes have been reported.[15c, 20] Stern-Volmer quenching studies also showed that amino-benzocyclobutene **1a** was able to quench the photoexcited Ir(III) complex (see SI). TEMPO completely inhibited the formation of the uneliminated dihydronaphthalene and naphthalene.



Scheme 2. Proposed Reaction Mechanism

In conclusion, we report a visible-light-mediated synthesis of substituted naphthalenes via the [4+2] annulation of amino-benzocyclobutenes with alkynes. Upon one-electron photooxidation, amino-benzocylobutenes undergo ring opening to reveal presumably the distonic radical cation, which then participate in two sequential C-C bond formations en route to naphthalenes. Amino-benzocylobutenes tolerate substitution at C-2, C-5, and C-7 positions including a usually labile glycosidic bond at C-2. Terminal alkynes, internal alkynes and diynes are all shown to be a viable annulation partner, affording structurally diverse naphthalenes. The aniline moiety plays a critical role in the annulation, as it not only functions as a photo-oxidizable group to induce the ring opening but also acts as a leaving group to complete aromatization. Because a different type of the ring-opening intermediate (e.g., the distonic radical cation) is involved, amino-benzocylobutenes display distinct chemistries from benzocyclobutenols in the annulation reaction.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information.

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

Experimental procedures and spectra data

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We thank the University of Arkansas, the Arkansas Bioscience Institute, the National Institutes of Health (NIH) (grant number P30 GM103450) from the National Institute of General Medical Sciences, and NSF Career Award (Award Number CHE-1255539) for generous support of this research. We also thank Jiang Wang and Jean de Dieu Nubundiho for experimental assistance in discovering this method.

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SYNOPSIS TOC