Reusable Visible Light Photoredox Catalysts; Catalyzed Benzylic C(sp^3)–H Functionalization/Carbocyclization Reactions

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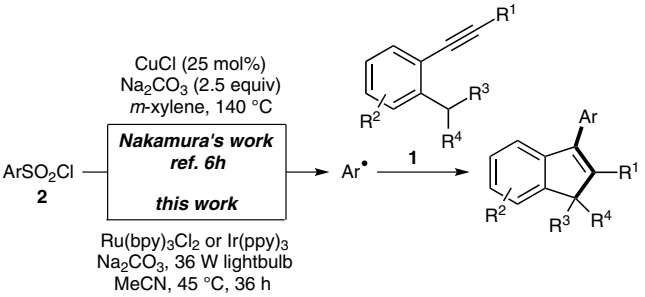
Abstract: The C(sp^3)–H functionalization/carbocyclization reaction through the oxidative quenching of visible light photoredox catalysts is established for constructing functionalized 1*H*-indenes. The process is general for a wide range of benzylic C(sp^3)–H bonds and is highly compatible with common functional groups. Importantly, the visible light photoredox catalysts can be recovered and reused at least three times without loss of catalytic activity.

Key words: photoredox, catalysis, C–H activation, cyclization, alkynes, indenes

Visible light photoredox catalyst initiated organic transformations are emerging as uniquely powerful tools for constructing new chemical bonds in organic synthesis due to their more environmentally benign sustainability and mild operating conditions.[1–4] Among these transformations, C(sp^3)–H functionalization using this visible light photoredox catalysis strategy is particularly interesting.[2,3] However, despite good progress, C(sp^3)–H functionalization methods have focused on the C(sp^3)–H bonds adjacent to either the nitrogen of amines or the oxygen atom of ethers through the reductive quenching cycles of the photocatalysts. To our knowledge, only two papers have reported on the functionalization of C(sp^3)–H bonds using visible light photoredox catalysis via an oxidative quenching cycle.[3]

Direct functionalization reactions of unactivated C(sp^3)–H bonds are highly desirable from the atom-economic point of view, and still remain an important challenge.[5,6] As an example, transition-metal-catalyzed selective carbocyclization of an alkyne with a benzylic C(sp^3)–H bond for the construction of carbocycles is particularly fascinating because saturated, less functionalized precursors would be required.[5] However, the carbocyclization reactions of alkynes involving benzylic C(sp^3)–H functionalization are rare and typically require both the use of 10–25 mol% transition-metal catalysts and elevated temperature (60–140 °C). For example, Nakamura and co-workers have reported a new Cu-catalyzed arylative cyclization of arylalkynes with aromatic sulfonyl chlorides (Scheme 1).[6h] However, the reaction required 25 mol% CuCl and harsh conditions (140 °C), and was only applied to substrates bearing the simple benzylic C(sp^3)–H group with Me or Ph substituents. In this protocol, aromatic sulfonyl chlorides were found to formally act as a donor of aryl radical groups with loss of the SO_2Cl group by heating with CuCl. In light of these results, we envisioned that aromatic sulfonyl chlorides may be transferred to aryl radical groups under visible light irradiation. As expected, we found that a variety of *ortho*-alkyl arylalkynes could undergo arylative cyclization with arylsulfonyl chlorides[7] through an oxidative quenching cycle of the visible light photocatalysts (Scheme 1). More importantly, the reaction could be employed to functionalize the C(sp^3)–H bonds of both a benzyl ether and an acetal. It is noted that the products, indene and their derivatives, are ubiquitous in natural products, functional materials, and pharmaceuticals.[8]



Scheme 1 Benzylic C(sp^3)–H functionalization and carbocyclization with aromatic sulfonyl chlorides

We began our studies with the reaction between 1-isopropyl-2-(phenylethynyl)benzene (**1a**) and 4-nitrobenzene-1-sulfonyl chloride (**2a**) to establish the optimal reaction conditions (Table 1).[9] Interestingly, substrate **1a** could successfully react with **2a**, [Ru(bpy)$_3$Cl$_2$], and NaOAc in MeCN at 30 °C under irradiation with a 36 W compact fluorescent light for 36 h, providing the desired product **3** in 37% yield (entry 1). Further screening revealed that the amount of [Ru(bpy)$_3$Cl$_2$] affected the reaction; the reaction at 5 mol% [Ru(bpy)$_3$Cl$_2$] afforded an identical yield

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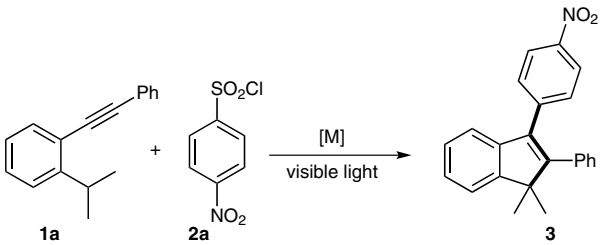
to that obtained with 3 mol% [$Ru(bpy)_3Cl_2$] (entry 2), but the yield was reduced significantly using 10 mol% [$Ru(bpy)_3Cl_2$] due to the occurrence of some side-reactions (entry 3). Subsequently, a series of other solvents, including CH_2Cl_2, *N*-methyl-2-pyrrolidinone (NMP), toluene, dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylformamide (DMF), were tested; these were found to be less effective than MeCN (entries 2 and 4–8). Among the bases examined, it turned out that Na_2CO_3 was more efficient than NaOAc or K_2HPO_4 (entries 2, 9 and 10). It is noteworthy that the yield of **3** increased to 83% by using anhydrous MeCN medium at 45 °C (entry 11), and identical results were observed at 60 °C (entry 12). Gratifyingly, [$Ru(bpy)_3Cl_2$] could be recovered and reused at least three times without loss of catalytic activity [the reaction mixture was filtered through filter paper and a short silica gel column (EtOAc), and [$Ru(bpy)_3Cl_2$] remained on the filter paper and silica gel. [$Ru(bpy)_3Cl_2$] was then recovered by washing the filter paper and silica gel with MeOH–MeCN (5 mL, 1:2 v/v) four times] (entry 12). It was noted that the reaction proceeded smoothly without base, albeit after a prolonged reaction time (entry 13). However, [$Ir(bpy)_3$] displayed less reactivity for the reaction (entry 14). Notably, the reaction did not take place without irradiation by the compact fluorescent light (entry 15).

Gratifyingly, the above visible light photocatalysis protocol was found to be applicable to a diverse range of substituted arylsulfonyl chlorides for the reaction with 1-isopropyl-2-(phenylethynyl)benzene (**1a**; Scheme 2).[8] Screening revealed that several substituents, such as NO_2, CF_3, CN, acetyl, Cl, F, I, Br, Me or MeO, on the aryl ring of the arylsulfonyl chlorides were tolerated; the electron-deficient aryl groups were more reactive than the electron-rich aryl groups (to give **4**–**13**). Notably, [$Ru(bpy)_3Cl_2$] and [$Ir(ppy)_3$] displayed different catalytic reactivity with arylsulfonyl chlorides; whereas [$Ru(bpy)_3Cl_2$] was more efficient for 4-nitrobenzene-1-sulfonyl chloride (**2a**) than [$Ir(ppy)_3$] (entries 12 and 14 in Table 1), it was inferior to [$Ir(ppy)_3$] with other arylsulfonyl chlorides, such as 4-nitro-3-(trifluoromethyl)benzene-1-sulfonyl chloride (to give **4**), 4-cyanobenzene-1-sulfonyl chloride (to give **5**) or 4-chlorobenzene-1-sulfonyl chloride (to give **7**). Consequently, [$Ir(ppy)_3$] was employed for the arylative cyclization with other arylsulfonyl chlorides to give products **6** and **8**–**15**. In the presence of [$Ir(ppy)_3$] and Na_2CO_3 under irradiation by a 36 W compact fluorescent light, 4-acetylbenzene-1-sulfonyl chloride underwent the reaction with substrate **1a**, giving the corresponding product **6** in 94% yield. Notably, when the recovery and reuse of [$Ir(ppy)_3$] was tested, 91% yield of **6** was still achieved using the recovered catalyst. Halogen substituents (F, I and Br), were compatible with the optimal conditions, giving products **8**–**10**, thereby facilitating additional modifications at the halogenated positions. Using electron-neutral or electron-rich arylsulfonyl chlorides, moderate yields of products **11**–**14** were still achieved with 10 mol% [$Ir(ppy)_3$]. Interestingly, heterocycle-containing sulfonyl chloride was suitable for the reaction, giving the expected product **15**, making this methodology more useful for pharmaceuticals and natural product preparation.

Table 1 Screening for Optimal Conditions[a]



Entry	[M] (mol%)	Base	Solvent	Temp (°C)	Yield (%)[b]
1	[$Ru(bpy)_3Cl_2$] (3)	NaOAc	MeCN	30	37
2	[$Ru(bpy)_3Cl_2$] (5)	NaOAc	MeCN	30	39
3	[$Ru(bpy)_3Cl_2$] (10)	NaOAc	MeCN	30	17
4	[$Ru(bpy)_3Cl_2$] (3)	NaOAc	CH_2Cl_2	30	5
5	[$Ru(bpy)_3Cl_2$] (3)	NaOAc	NMP	30	trace
6	[$Ru(bpy)_3Cl_2$] (3)	NaOAc	toluene	30	trace
7	[$Ru(bpy)_3Cl_2$] (3)	NaOAc	DMSO	30	trace
8	[$Ru(bpy)_3Cl_2$] (3)	NaOAc	DMF	30	trace
9	[$Ru(bpy)_3Cl_2$] (3)	Na_2CO_3	MeCN	30	60
10	[$Ru(bpy)_3Cl_2$] (3)	K_2HPO_4	MeCN	30	37
11[c]	[$Ru(bpy)_3Cl_2$] (3)	Na_2CO_3	MeCN	45	83
12[c,d]	[$Ru(bpy)_3Cl_2$] (3)	Na_2CO_3	MeCN	60	84
13[c,e]	[$Ru(bpy)_3Cl_2$] (3)	–	MeCN	45	76
14[c]	[$Ir(ppy)_3$] (3)	Na_2CO_3	MeCN	45	21
15[c,f]	[$Ru(bpy)_3Cl_2$] (3)	Na_2CO_3	MeCN	45	0

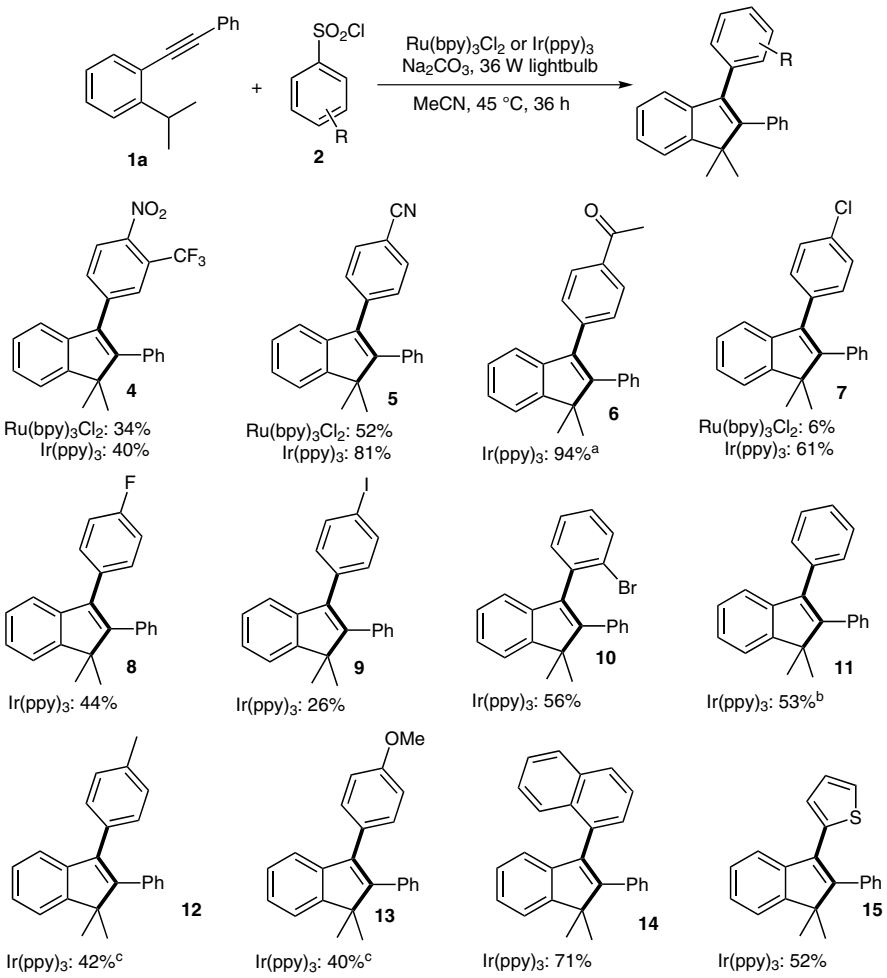
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (3 equiv), [M], base (2.5 equiv) and solvent (1 mL) irradiated with 36 W compact fluorescent light for 36 h under argon atmosphere. [$Ru(bpy)_3Cl_2$] = tris(2,2′-bipyridine)ruthenium dichloride, [$Ir(ppy)_3$] = tris(2-phenylpyridine)iridium(III).
[b] Isolated yield.
[c] Using anhydrous MeCN.
[d] The catalyst was recovered and reused three times, and the yields were 80% (run 1), 81% (run 2), and 78% (run 3).
[e] Irradiated for 42 h.
[f] Without additional light.

As shown in Scheme 3, the scope of *ortho*-alkyl arylalkynes was exploited in the presence of 4-nitrobenzene-1-sulfonyl chloride (**2a**), [$Ru(bpy)_3Cl_2$], and Na_2CO_3 under irradiation with a 36 W compact fluorescent light. The results demonstrated that both aryl and aliphatic alkynes were compatible with the standard conditions, giving products **16**–**26**. For arylalkynes, a number of substituents, including Me, MeO, F, Cl, Br and NO_2, on the aryl ring at the terminal alkyne were also well tolerated to give products **16**–**22**. Substrates with a *para*-methyl group

underwent the reaction with sulfonyl chloride **2a**, [Ru(bpy)$_3$Cl$_2$] and Na$_2$CO$_3$ under irradiation with a 36 W compact fluorescent light to afford the desired product **16** in 85% yield. MeO-substituted arylalkyne also provided good yield of **17** under the same conditions. Although the reactivity of substrates with electron-withdrawing groups or an *ortho*-methyl group was reduced, moderate to good yields were still achieved to give product **18**–**22**. Interestingly, naphthalen-1-yl- or thiophen-2-yl-substituted alkynes were also viable substrates for the arylative cyclization, giving products **23** and **24** in moderate yield. Notably, aliphatic alkynes, even with a bulky *tert*-butyl group, afforded the corresponding 1*H*-indenes **25** and **26** in moderate to good yields.

Gratifyingly, substrates with Br or Me substituents on the aromatic ring of the benzylic moiety were also compatible with the standard conditions, giving products **27** and **31**. For example, Br-substituted substrate was treated with sulfonyl chloride **2a**, [Ru(bpy)$_3$Cl$_2$], and Na$_2$CO$_3$ under irradiation with a 36 W compact fluorescent light, to smoothly furnish product **27** in 74% yield. Further screening revealed that the secondary benzylic carbon atoms, including 1-ethyl, 1-benzyl, and 1-(phenoxymethyl) groups, were viable for the arylative cyclization, giving the expected products **29**–**32**. It was noted that 1-(dimethoxymethyl)-2-(phenylethynyl)benzene, an acetal, could also undergo arylative cyclization to offer the demethylated product **33** in good yield. However, substrates with a primary benzylic carbon atom were not suitable for the arylative cyclization and only trace amounts of product **34** were obtained.

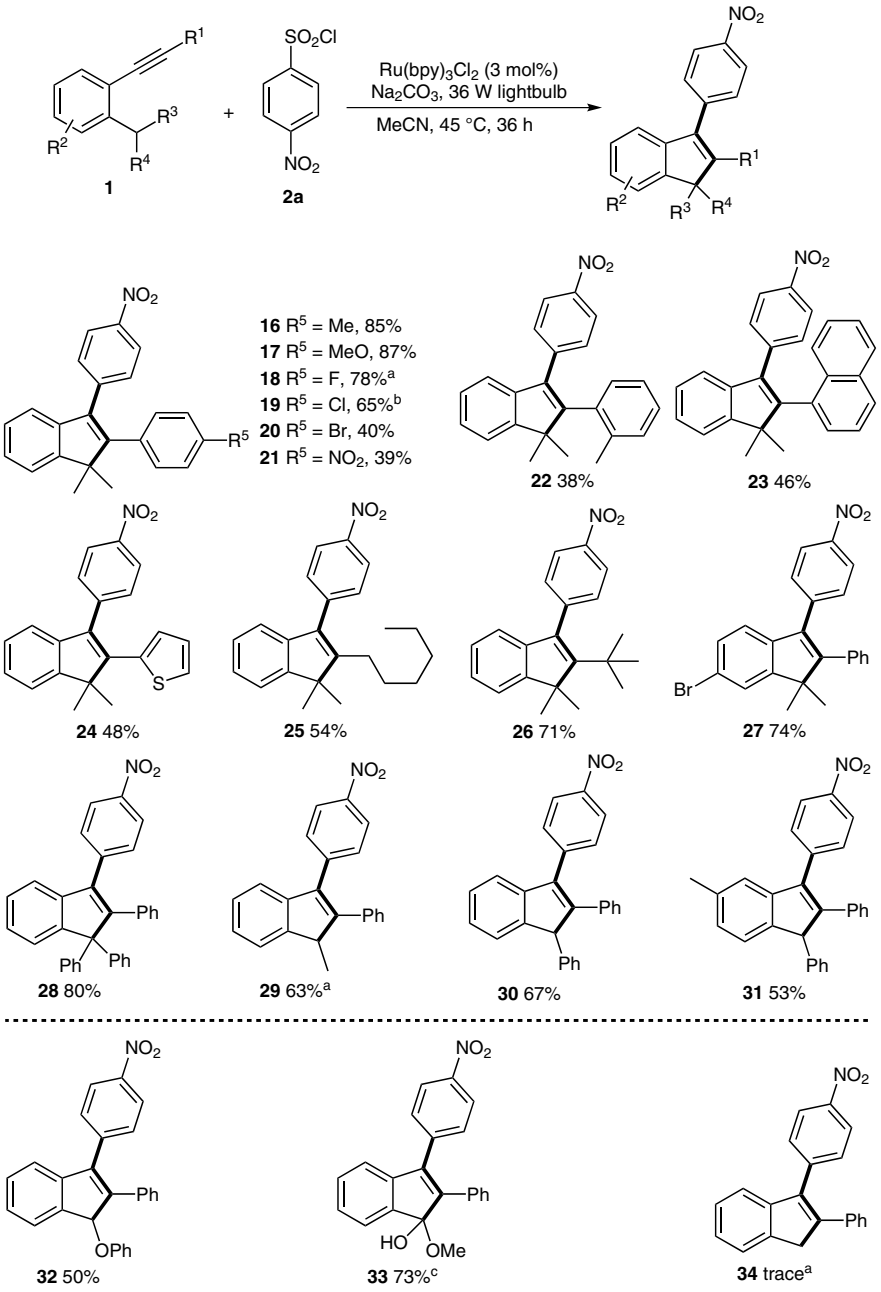
Arylative cyclization reactions of other alkynes, including double cyclization of dialkyne compounds, were also investigated (Scheme 4). In the presence of 4-nitrobenzene-1-sulfonyl chloride (**2a**), [Ru(bpy)$_3$Cl$_2$] and Na$_2$CO$_3$ under irradiation with a 36 W compact fluorescent light, both dialkyne compounds **1b** and **1c** were readily transformed into the corresponding bisindenes **36** and **38** in moderate yields together with monoindenes **35** and **37** in 32 and 31% yield, respectively. Interestingly, treatment of 1,2-diphenylacetylene (**1d**) with benzene-1-sulfonyl chloride (**2b**) and [Ir(ppy)$_3$], Na$_2$CO$_3$ and 36 W compact fluorescent light gave (2-chloroethene-1,1,2-triyl)tribenzene (**38**), a desulfitative and Cl-addition product, in 85% yield, suggesting that a vinyl cation is generated.[9]



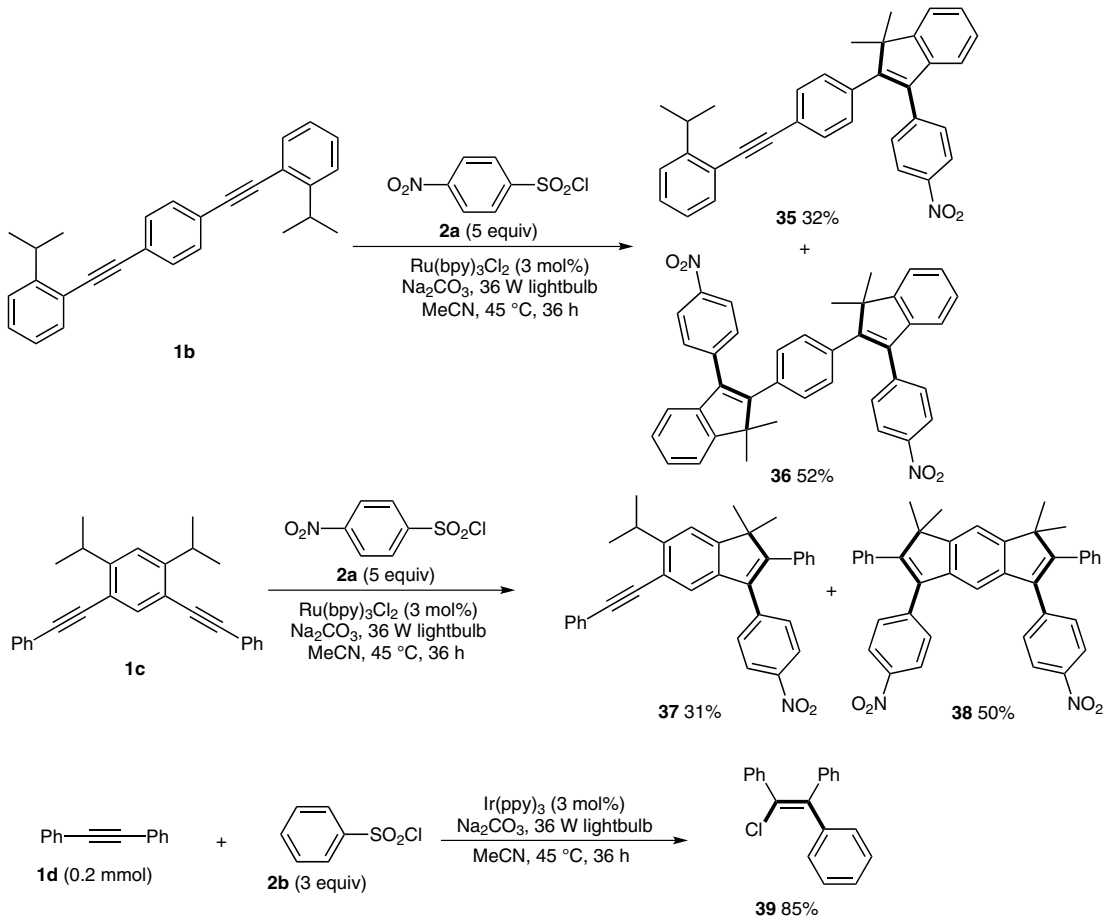
Scheme 2 Screening arylsulfonyl chlorides (**2**). *Reagents and conditions*: **1a** (0.2 mmol), **2** (3 equiv), [Ru(bpy)$_3$Cl$_2$] or [Ir(ppy)$_3$] (3 mol%), Na$_2$CO$_3$ (2.5 equiv), anhydrous MeCN (1 mL), irradiation with a 36 W compact fluorescent light at 45 °C for 36 h under argon atmosphere. [a] [Ir(ppy)$_3$] was recovered and reused to give the **6** in 91% yield. [b] [Ir(ppy)$_3$] (10 mol%) was used.

Notably, three radical inhibitors, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 1,1-diphenylalkene, and 2,6-di-*tert*-butylphenol, were also employed for the reaction of 1-isopropyl-2-(phenylethynyl)benzene (**1a**) with 4-nitrobenzene-1-sulfonyl chloride (**2a**), $[Ru(bpy)_3Cl_2]$, Na_2CO_3 under irradiation with a 36 W compact fluorescent light. Under these conditions no reaction was observed with a stoichiometric amount of these radical inhibitors, which is consistent with a radical being involved in the present reaction mechanism. In addition, a control on/off switching of the light source was tested;[2k] when the lamp was switched off at appropriate intervals (2 h every interval), the reaction did not proceed during the 'off' periods.

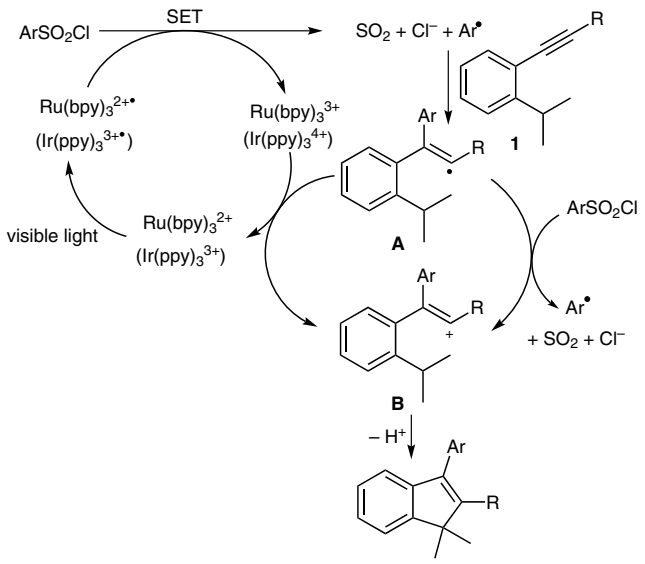
A plausible mechanism, outlined in Scheme 5, is proposed on the basis of the present results and on literature reports.[1–7,10] Aryl radical (Ar·)[9] is first formed by a single electron transfer (SET) from the excited state $[Ru(bpy)_3]^{2+}$ (or $[Ir(ppy)_3]^{3+}$) to an arylsulfonyl chloride,[1–4,10] followed by addition of Ar· to the carbon–carbon triple bond in substrate **1**, generating radical intermediate **A**. This intermediate is readily transformed into vinyl cation intermediate **B**[10] by two pathways:[1–4] oxidation of radical intermediate **A** by (i) $[Ru(bpy)_3]^{3+}$ (or $[Ir(ppy)_3]^{4+}$) cation, and (ii) aryl-



Scheme 3 $[Ru(bpy)_3Cl_2]$-Catalyzed Arylative Cyclization of *ortho*-Alkyl Arylalkynes (**1**) with Sulfonyl Chloride (**2a**). *Reagents and conditions*: **1** (0.2 mmol), **2a** (3 equiv), $[Ru(bpy)_3Cl_2]$ (3 mol%), Na_2CO_3 (2.5 equiv), anhydrous MeCN (1 mL) with 36 W compact fluorescent light at 45 °C for 36 h under argon atmosphere. [a] $[Ru(bpy)_3Cl_2]$ (10 mol%). [b] **2a** (4 equiv). [c] An acetal, 1-(dimethoxymethyl)-2-(phenylethynyl)benzene, was employed as the substrate.



Scheme 4 Arylative cyclization of other alkynes **1**



Scheme 5 Possible mechanism

sulfonyl chlorides in a radical chain transfer mechanism. Finally, deprotonation and carbocyclization of the unstable intermediate **B** takes place to furnish the desired 1*H*-indenes. The presence of base facilitates the reaction by removing HCl formed in situ from the reaction (Table 1, entries 11 and 13).

In summary, we have described a general and mild route that enables the construction of functionalized 1*H*-indenes via photoredox catalyzed arylative cyclization of *ortho*-alkyl arylalkynes with arylsulfonyl chlorides using a visible light photoredox catalysis strategy. This new protocol has several attractive features: (a) a low operating temperature (45 °C) and lower loading of catalyst is required, (b) high functional group tolerance and broad substrate scope, and (c) simple operation by reusable visible light photoredox catalysis. Applications of this mild photoredox catalyst-catalyzed arylative cyclization transformation in organic synthesis are underway in our laboratory.

Acknowledgment

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(9) **Typical Experimental Procedure for the Arylative Cyclization of *ortho*-Alkyl Arylalkynes with Arylsulfonyl Chlorides:** To a Schlenk tube were added *ortho*-alkyl arylalkyne **1** (0.2 mmol), arylsulfonyl chloride **2** (3 equiv), $[Ru(bpy)_3Cl_2]$ or $[Ir(ppy)_3]$ (3 mol%), Na_2CO_3 (2.5 equiv), and anhydrous MeCN (1 mL). The tube was charged with argon and stirred at 45 °C under irradiation with a 36 W compact fluorescent light for the indicated time (36 h) until complete consumption of starting material (reaction monitored by TLC and GC–MS analysis). When the reaction was finished, the mixture was diluted in diethyl ether, filtered through a short crude silica gel column and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane–ethyl acetate) to afford the desired product.

1,1-Dimethyl-3-(4-nitrophenyl)-2-phenyl-1*H*-indene (3): Yield: 55.7 mg (83%); yellow solid; mp 128.7–129.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.5 Hz, 2 H), 7.47–7.43 (m, 3 H), 7.32–7.29 (m, 6 H), 7.13–7.11 (m, 2 H), 1.42 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0, 153.0, 146.6, 142.3, 141.4, 136.1, 135.7, 130.2, 129.5, 128.3, 127.5, 126.8, 126.0, 123.4, 121.9, 120.2, 51.9, 24.3; MS (EI, 70 eV): *m*/*z* (%) = 341 (100) $[M]^+$,

326 (46), 279 (15), 132 (8); HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{19}NO_2$: 341.1415; found: 341.1411.

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