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Catalytic Arylsulfonyl Radical Triggered 1,7-Enyne Bicyclizations

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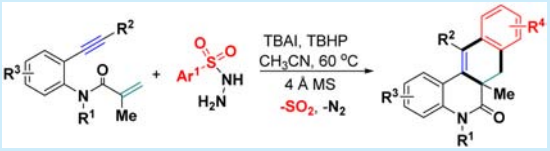
Supporting Information

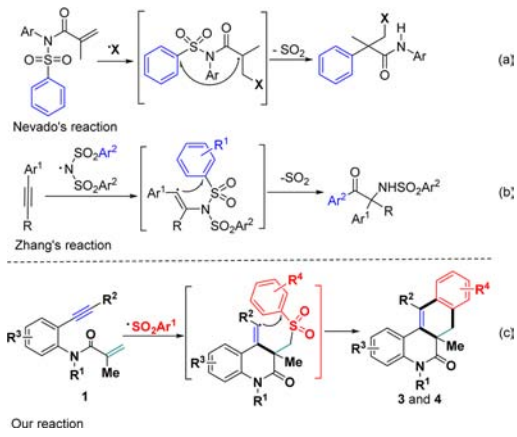
ABSTRACT: A new metal-free bicyclization reaction of 1,7-enynes anchored by *α,β*-conjugates with arylsulfonyl radicals generated in situ from sulfonyl hydrazides has been established using *tert*-butyl hydroperoxide and tetrabutylammonium iodide. The reactions occurred through sulfonylation/6-*exo*-*dig*/6-*exo*-*trig* bicyclization/in situ desulfonylation/5-*exo*-*trig* cyclization/alkyl or alkenyl migration cascade mechanism to give benzo[*j*]phenanthridines regioselectively.



The increasingly popular radical triggered bicyclization strategy represents a uniquely powerful tool to access highly functionalized polycyclic structures of chemically and biomedically importance in which the formation of multiple C−C/C−X bonds can be orchestrated in an atom-economic and highly functional group compatible manner.[1] With both unsaturated moieties, 1,*n*-enynes are significant building blocks for radical-triggered tandem additions and result in functionalized polycyclic structures via synergistic domino cyclizations across C═C and C≡C bonds of various substrates in one-pot fashions.[2] Therefore, catalytic radical bicyclizations of 1,*n*-enynes have been extensively utilized for substantially challenging and intriguing syntheses.[3]

Desulfonylation reactions have flourished in the total synthesis of many natural products and bioactive molecules through functional group transformations (FGTs).[4] Traditional desulfonylation involved a two-step process, proceeding from prefunctionalized reagents with sulfone group to modify molecular polarity and activate reaction site. After the required operation, the sulfone moiety could be removed by various methods including reductive, alkylative, and oxidative desulfonylation, etc.[5] However, these reactions suffered from the use of strong bases, transition-metal catalysts, and toxic metal salt peroxides. Recent breakthroughs were developed by Nevado and Zhang, respectively.[6,7] They reported radical-triggered aryl migration and desulfonylation reactions of sulfonyl amides, leading to the creation of carbon−carbon bonds (Schemes 1a and 1b). In sharp contrast, the radical-triggered aryl migration and desulfonylation-based bicyclization reaction of sulfones was virtually unexplored. Very recently, we developed a catalytic radical-triggered bicyclization reaction of 1,*n*-enynes toward polycyclic frameworks under mild conditions.[8] As part of our continuing interest in the design of new bicyclizations, we conceived that under suitable catalytic radical conditions the

Scheme 1. Desulfonylation-Involved Radical Reactions



arylsulfonyl radicals generated in situ from aryl sulfonhydrazides **2** could be engaged in additional bond-forming events with C═C and C≡C bonds of 1,7-enyne conjugate systems, thus facilitating the formation of multiple C−S and C−C(aryl) bonds via an aryl migration and desulfonylation process in a single operation (Scheme 1c). Herein, we present the successful implementation this concept with a novel metal-free arylsulfonyl radical-triggered 1,7-enyne bicyclization under *tert*-butyl hydroperoxide (TBHP)/tetrabutylammonium iodide (TBAI)-mediated conditions.[9]

Our study commenced with tandem cyclization reaction between 1,7-enynes (**1a**) and benzenesulfonohydrazide (**2a**) in the presence of different catalysts and oxidants to search for the optimized conditions (Table S1). First, catalytic amounts of iodine source including KI, I_2, and TBAI were evaluated in

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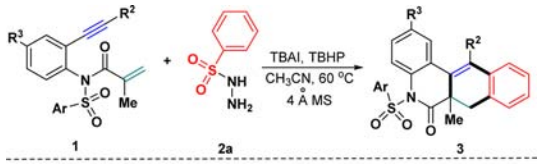
acetonitrile using TBHP[10] (5.5 M in decane) as an oxidant and 4 Å molecular sieves (MS). Use of KI gave the desired tetracyclic benzo[*j*]phenanthridines **3a** but with a low 21% yield (entry S1). The reaction worked more efficiently and delivered a 43% yield using I_2 as a catalyst (entry S2). The presence of TBAI further improved the conversion of the starting material so that **3a** could be isolated in 60% yield (entry S3). Next, several copper salts commonly used in the radical-triggered reactions were investigated,[11] and we found that $Cu(OTf)_2$ gave a similar yield (58%) compared with TBAI from acrylamide **1a** with sulfonylhydrazides **2a** in acetonitrile at 60 °C (entry S8), whereas other copper salts, like CuI, CuBr, CuCl, and $CuCl_2$, all showed poor catalytic activities (entries S4−S7). Considering both the relatively complex operation and high cost in the metal-catalyzed process, we preferred to use TBAI for the further investigation. Screening followed by other oxidants revealed that *tert*-butyl peroxybenzoate (TBPB), benzoyl peroxide (BPO), and di-*tert*-butyl peroxide (DTBP) all met little success in this radical bicyclization (entries S9−S11). Afterward, taking the combination of TBHP with TBAI, we varied other parameters. Other solvents, such as 1,4-dioxane, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1,2-dichloroethane (DCE), and toluene, were inferior to acetonitrile in terms of reaction yields (entries S12−S16). An increased or decreased load of TBAI or TBHP did not significantly improve the yield (entry S3 vs entries S17−S20). It was also found that the reaction temperature affected the reaction efficiency. The lower conversion was detected with reaction temperature being at either 40 or 80 °C (entry S3 vs entries S21 and S22). Some control reactions indicated that the transformation did not take place in the absence of either TBAI or TBHP (entries S23 and S24), and water impacted a significant influence on the reaction yield as the use of TBHP in 70% water remarkably lowered the yield (entry S25).

After determining the optimal reaction conditions, we then set out to explore the scope of the radical-triggered bicyclization toward the benzo[*j*]phenanthridine formation (Schemes 2 and 3). With the combination of TBAI and TBHP, a wide range of 1,7-enynes **1** smoothly reacted with benzenesulfonohydrazide to give access to the corresponding densely functionalized benzo[*j*]phenanthridines **3a−t** in 45%−74% yields. 1,7-Enynes **1** possessing both *N*-arylsulfonyl and arylalkynyl moieties attached by electron-donating or electron-withdrawing groups did not hamper the reaction process. A large variety of diverse functional groups directly bounded phenyl ring, including methyl, methoxy, fluoro, chloro, and bromo, can tolerate the catalytic conditions well. Electronic properties of substituents on both *N*-arylsulfonyl and the arylalkynyl moieties showed an obvious impact on the reaction efficiency and the obtained chemical yields. Upon treatment with 1,7-enynes **1a** without a functional group on the phenyl ring, the desired product **3a** was obtained in 60% yield. Interestingly, substrate **1** carrying both electron-withdrawing groups showed relatively higher reactivity than those with electron-donating counterparts (**3k** vs **3h**). Notably, thiophene-functionalized benzo[*j*]phenanthridine **3m** was successfully isolated under the optimal reaction conditions, which proved the good tolerance of the present method to heteroaryl functionalized 1,7-enynes. Besides, when the Ar fragment in the alkynyl moiety was alternated with an alkyl such as *n*-butyl, the target transformation was realized with the optimal conditions, as demonstrated by the formation of **3n** in an acceptable yield (51%). Alternatively, substrates **1** bearing methyl, fluoro, and chloro groups on the *N*-phenyl moiety were compatible and provided the corresponding tetracyclic products **3o−t** in 56−64% yields.

To expand the general applicability of the protocol, various arylsulfonyl hydrazides were subsequently examined (Scheme 3). Different substituents like Me, *t*-Bu, MeO, Cl, Br, and CF_3 in the *para*-position on the phenyl ring of sulfonyl hydrazides were compatible in these radical bicyclization reactions, but with the formation of two isomers **4a−k** and **4a′−k′** in good yields. The results revealed that the electronic nature of these substituents imposed a significant influence on the selectivity, and in cases of both stronger electron-poor and electron-rich substituents such as *tert*-butyl, methoxy and trifluoromethyl, the reactions are more facilitated leading to the higher selectivity compared to those bearing methyl, chloro, and bromo groups. For instance, arylsulfonyl hydrazides **2c** with methoxy group was treated with 1,7-enynes **1j**, affording the expected isomers **4d** and **4d′** in a 35:1 ratio, whereas a drastic decrease in the ratio (1.3:1) was

Scheme 2. Arylsulfonyl Radical Triggered Bicyclizations



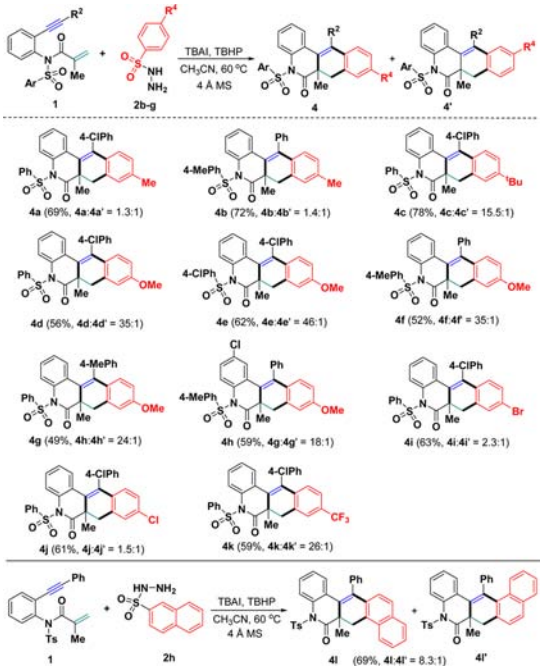
R³ = H
3a, R²/Ar = Ph/Ph (60%)
3b, R²/Ar = Ph/4-MePh (54%)
3c, R²/Ar = 4-MePh/Ph (55%)
3d, R²/Ar = 4-MePh/4-MeOPh (49%)
3e, R²/Ar = 4-MePh/4-ClPh (58%)
3f, R²/Ar = 4-MeOPh/Ph (54%)
3g, R²/Ar = 4-MeOPh/4-MePh (45%)
3h, R²/Ar = 4-MeOPh/4-MeOPh (46%)
3i, R²/Ar = 4-MeOPh/4-BrPh (63%)
3j, R²/Ar = 4-ClPh/Ph (70%)
3k, R²/Ar = 4-ClPh/4-ClPh (69%)
3l, R²/Ar = 4-FPh/Ph (74%)
3m, R²/Ar = 3-Thioenyl/4-ClPh (54%)
3n, R²/Ar = *n*-C_4H_9/Ph (51%)

R³ = Me
3o, R²/Ar = Ph/Ph (57%)
3p, R²/Ar = Ph/3-BrPh (61%)
3q, R²/Ar = 4-MePh/Ph (59%)

R³ = Cl
3r, R²/Ar = Ph/Ph (57%)
3s, R²/Ar = 4-MePh/4-MeOPh (64%)

R³ = F
3t, R²/Ar = Ph/Ph (56%)

Scheme 3. Regioselective Synthesis of Products 4



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observed using **1j** and tosylhydrazide **2b**. Alternatively, sterically encumbered naphthalene-2-sulfonohydrazide was successfully engaged in this radical bicyclization, giving access in pentacyclic isomers **4l** and **4l′** in a 8.3:1 ratio. The process involves the one-pot formation of three new C−C bonds and two new rings via a multicyclization, in situ sulfonylation and desulfonylation, and alkyl or alkenyl migration sequence. The regioselective structures were confirmed by examination of the X-ray crystal of **4e** (Figure 1).

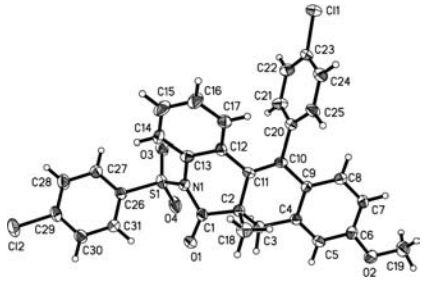
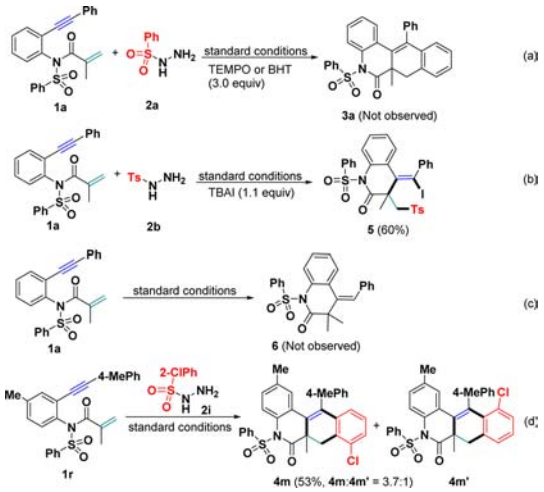


Figure 1. ORTEP drawing of **4e**.

To gain mechanistic insight into this reaction, control experiments were conducted. 1,7-Enynes **1a** was subjected to reaction with 3.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylhydroxytoluene (BHT) (Scheme 4a), but

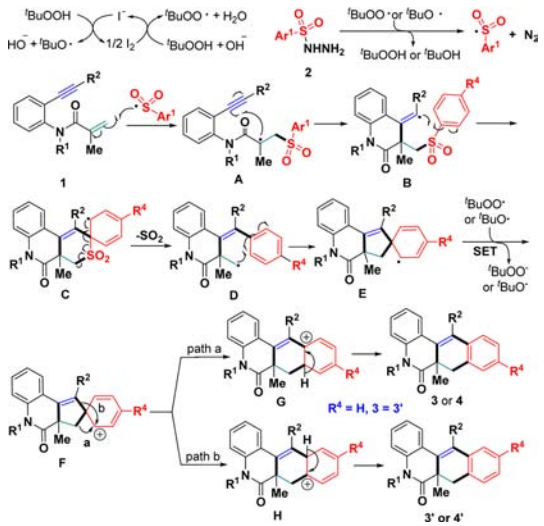
Scheme 4. Control Experiments



without observation of desired product **3a**, which indicates the possibility of an radical mechanism. Next, the reaction of **1a** with **2b** in the presence of 1.1 equiv of TBAI gave the 3,4-dihydroquinolin-2(1*H*)-ones **5** (Scheme 4b), confirming that arylsulfonyl radical, generated in situ from aryl sulfonoyl hydrazide, triggered *α,β*-conjugated addition/*6-exo-dig* cyclization to form the vinyl radical intermediate, which was captured by iodine radical. We reasoned that this reaction mechanism for constructing benzo[*j*]phenanthridines is very interesting and radically differed from Li's works involving phenyl radicals from aromatic sulfonyl chlorides.[12] To further confirm the sulfonylation and cyclization sequence, subjecting 1,7-enynes **1a** to the standard condition in the absence of **2a** failed to provide any desired 3,4-dihydroquinolin-2(1*H*)-one product **6** (Scheme 4c), suggesting that sulfonylation occurred prior to the cyclization step. Upon treatment of 1,7-enynes **1r** with 2-chloridesulfonylhydrazine **2i** proceeded readily, giving access to two isomers **4m** and **4m′** with a 53% yield and 3.7:1 ratio (Scheme 4d). This interesting observation shows that intermediate **D** undergoes *5-exo-trig* cyclization, rather than *6-endo-trig* cyclization, because *6-endo-trig* cyclization only yields product **4m′**, which is inconsistent with experimental outcomes.

On the basis of the controlled experiments and literature survey,[10,12,13] the mechanisms for the formation of desired products **3**−**4** were proposed and represented in Scheme 5. The

Scheme 5. Proposed Mechanism for Forming 3 and 4



first step is to generate the sulfonyl radical from sulfonyl hydrazides under the oxidative conditions with the release of N_2.[14] The intermolecular *α,β*-conjugated addition of the resulting sulfonyl radical onto 1,7-conjugated enynes **1** followed by *6-exo-dig* cyclization gives vinyl radical intermediate **B**. **B** undergoes continuous *6-exo-trig* cyclization (**B** to **C**)/desulfoylation (**C** to **D**)/*5-exo-trig* cyclization (**D** to **E**) and single-electron transfer (SET) oxidation (**E** to **F**) to provide spirocylic cation **F**. Two migration modes of intermediate **F** could occur to offer intermediate **G** (path a) and **H** (path b), respectively. Subsequent deprotonations of both **G** and **H** leads to the formation of two isomers **3**−**4** and **3′**−**4′** (R^4 = H, **3** = **3′**). The regioselectivity of products **4** and **4′** is attributed to the stability of intermediate **G** and **H**. Due to the bigger conjugated system, intermediate **G** is more stable than that of **H**, therefore occupying higher content of target products, especially with strong electron-poor and electron-rich substituents. Although sulfonylations of both alkenes and alkynes were well-developed,[15] sulfonyl radical-initiated 1,7-enyne bicyclizations involving an in situ desulfonylation process for the formation of fused heterocycles is unprecedented in organic synthesis.

In conclusion, we have developed a new metal-free arylsulfonyl radical triggered bicyclization of 1,7-enynes with a large variety of functional groups that offers efficient construction of densely functionalized benzo[*j*]phenanthridines via a highly efficient sequential arylsulfonyl radical triggered *α,β*-conjugated addition/*6-exo-dig*/*6-exo-trig* bicyclization/desulfonylation/*5-exo-trig* cyclization/SET/alkyl (or alkenyl) migration process. High regioselectivity (up to 46:1) was observed using aryl sulfonhydrazides with both stronger electron-poor and electron-rich substituents as a reaction partner. This method allows easy access to important functional *N*-sulfonylated fused quinolin-2(1*H*)-

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one derivatives for potential applications in organic and medicinal chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03100.

Experimental procedures and spectroscopic data for all new compounds **3a−t** and **4a−m** (PDF)
X-ray crystallographic data for **3k** (CIF)
X-ray crystallographic data for **4e** (CIF)

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Notes

The authors declare no competing financial interest.

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