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Regioselective synthesis of polycyclic sulfones via radical-induced three-component bicyclization cascades†

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New radical-triggered three-component bicyclization cascades of 2-alkynyl aryldiazonium tetrafluoroborates with a sulfur dioxide surrogate DABCO-(SO₂)₂ and internal alkynes such as haloalkynes and ynones have been reported for the first time, leading to 49 examples of polycyclic sulfones with moderate to good yields and high levels of regioselectivity. This transformation initiated by an *in situ* generated arylsulfonyl radical proceeds efficiently under mild and neutral redox conditions, which provide an easy and metal-free pathway toward the formation of a range of richly decorated indeno[1,2-*c*]thiochromene 5,5-dioxides.

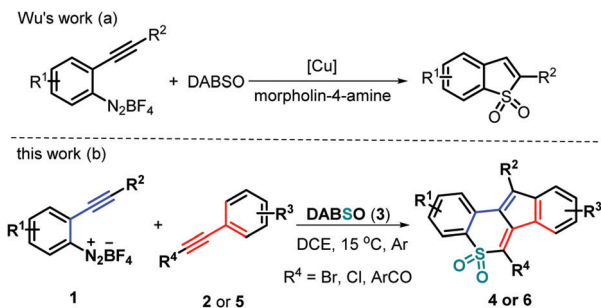
The development of robust, environmentally friendly, and atom-economical synthetic strategies is a constant driving force in chemical sciences.¹ In this regard, bicyclization reaction cascades have proven to be an indispensable and versatile tool for assembling a high degree of complex polycyclic systems and natural products with elaborate cyclic frameworks, owing to their atom-economy, step economy, and high bond-forming and annulation efficiency (two new rings are formed in a single step).² Specifically, with the resurgence of reliable and controllable radical chemistry, radical-triggered bicyclization reactions have received increased attention in recent years as such transformations could provide efficient preparative protocols for the direct collection of cyclic targets of chemical and biological importance which are difficult to obtain through traditional methods.³ A survey of literature reports reveals that the majority of current bicyclization reactions involve the radical-induced two-component transformations of enynes,⁴ *N*-cyanamides⁵ and *N*-(2-cyanobiphenyl)-acrylamides.⁶ In sharp contrast, radical-induced multicomponent bicyclization cascades have received very little attention⁷ as such reactions encounter a great challenge in controlling the behavior of the radicals when

trapped in the selection of radical acceptors. Therefore, the design and development of new radical multicomponent bicyclizations is of utmost interest to the organic chemist community.

As a valuable class of sulfone-containing molecules, cyclic sulfones are widely prevalent in pharmaceutically important compounds, which have been found to exhibit a broad spectrum of biological activities.⁸ Moreover, some aryl-annulated sulfones have been widely applied in the field of organic photoconducting materials due to their unique electrical and optical properties.⁹ In addition, they have also served as versatile intermediates in Diels–Alder reactions¹⁰ and Ramberg–Bäcklund rearrangement.¹¹ With these contributions in mind, much effort has been contributed toward identifying efficient methods for assembling structurally important cyclic sulfones, including ring-closing metathesis of acyclic sulfones,¹² LDA-induced cyclization of alkynyl sulfones,¹³ domino cyclization of β-keto sulfones¹⁴ or alkynyl-(aryl)iodonium salts,¹⁵ and the recent SO₂ insertion of cyclic diaryliodonium salts¹⁶ and others.¹⁷ Furthermore, addition of arylsulfonyl radicals, starting from aryldiazonium salts and DABCO-bis(sulfur dioxide) (DABSO), into unsaturated systems has proven to be a reliable and practical SO₂ insertion pathway for obtaining structurally diverse sulfones and sulfonamides in a convergent manner.¹⁸ For example, Wu and co-workers reported an elegant copper(i)-catalyzed annulation of 2-alkynylaryldiazonium tetrafluoroborates with DABSO in the presence of morpholin-4-amine to afford cyclic sulfonamides through SO₂ insertion (Scheme 1a).¹⁹ In continuation with our efforts on bicyclization reactions²⁰ and inspired by Wu's work,¹⁹ we have considered treating 2-alkynylaryldiazonium tetrafluoroborates **1** with DABSO (**3**) and haloalkynes **2** to realize the radical three-component bicyclization cascade. Interestingly, this transformation proceeded readily in a highly regioselective manner, resulting in a set of structurally diverse polycyclic sulfones **4** in moderate to good yields (Scheme 1b). Upon using ynones **5** as a radical acceptor to expand the synthetic utility of this protocol, the three-component bicyclization of **1** with **3** and **5** proceeds well through a similar radical addition–cyclization, furnishing good yields of the expected tetracyclic sulfones **6** in a highly regioselective manner (Scheme 1b).

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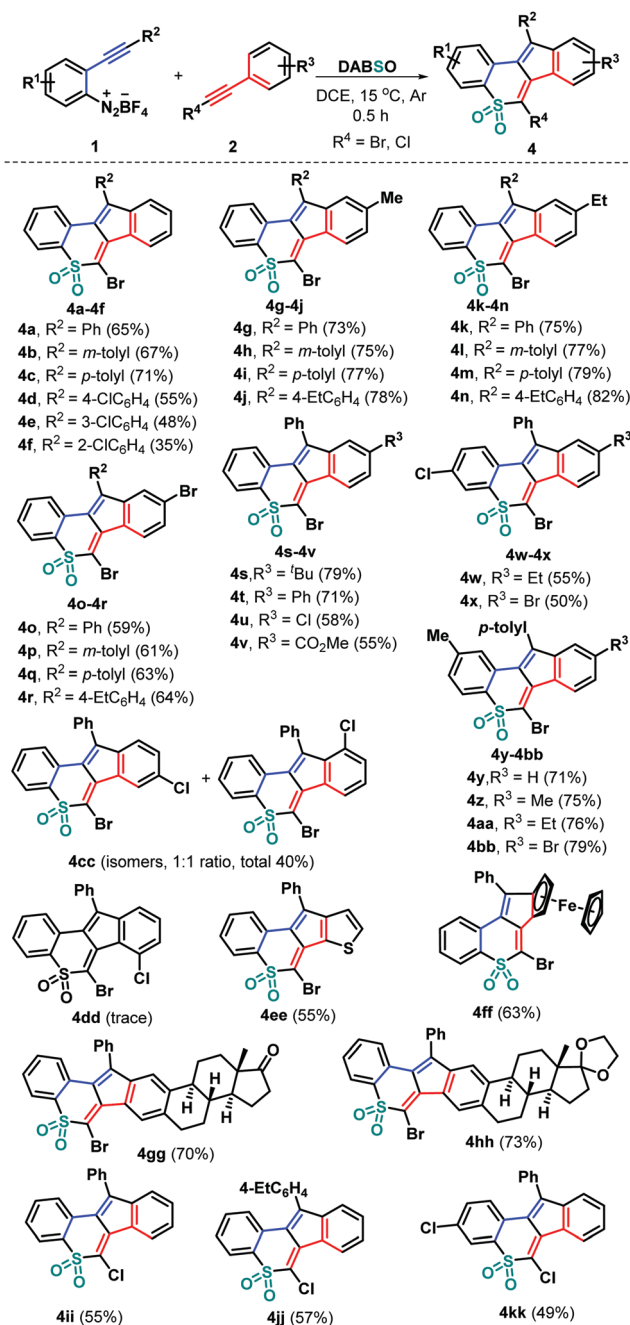


Scheme 1 Profiles for the synthesis of cyclic sulfones.

Herein, we report these two types of new metal-, catalyst-, and additive-free transformations.

Our initial investigation commenced with the treatment of 2-(phenylethynyl)benzenediazonium tetrafluoroborate (**1a**) with (bromoethynyl)benzene (**2a**) and DABSO (**3**) at 1:1:1 ratio at room temperature using 1,2-dichloroethane (DCE) as the reaction medium. The reaction generated indeno[1,2-*c*]thiochromene 5,5-dioxide **4a** in 48% yield (Table S1, entry S1, see ESI[†]). When the substrate ratio of **1a**, **2a** and **3** was adjusted to 1.1:1:1.1, the reaction proceeded more efficiently, providing the desired product **4a** in a slightly higher yield (52%, entry S2, ESI[†]). Further increasing the amount of **2a** and **3** led to a relatively lower conversion into product **4a** (entries S3 and S4, ESI[†]). Subsequently, the effect of solvent on this radical transformation was investigated by screening various solvents such as dichloromethane (DCM), acetonitrile (CH₃CN), tetrahydrofuran (THF), and 1,4-dioxane. The use of DCM as the reaction medium resulted in a decreased yield of product **4a** (45%, entry S5, ESI[†]), whereas the other three solvents completely suppressed the reaction process (entries S6–S8, ESI[†]). Elevating the reaction temperature to 30 °C was not beneficial for the transformation, affording **4a** in a reduced yield (46%, entry S9, ESI[†]). In contrast, a decrease of the reaction temperature seems to promote the conversion of **1a** into product **4a** as a higher yield (60%) was obtained when the reaction temperature was 15 °C (entry S10, ESI[†]). Further lowering the reaction temperature to 10 °C led to a reduced yield of 52% (entry S11, ESI[†]). An identical reaction was performed under Ar, delivering product **4a** in a slightly higher yield (65%, entry S12, ESI[†]).

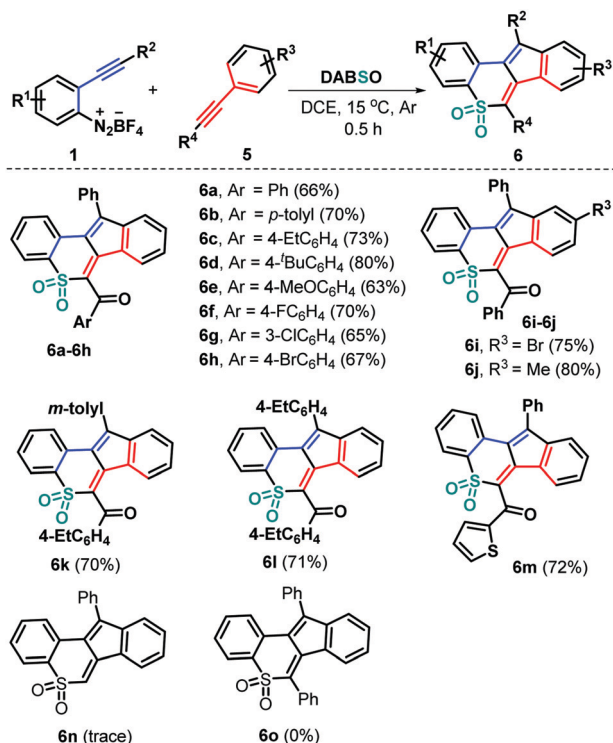
With these acceptable reaction conditions in hand, we then systematically investigated the generality of this metal-free three-component bicyclization cascade toward synthesizing polycyclic sulfones **4** by examining 2-alkynyl aryldiazonium tetrafluoroborate and haloalkyne components (Scheme 2). Different functional groups attached on both 2-aryldiazonium tetrafluoroborates **1** and bromoalkynes **2** were evaluated by combining with DABSO. Electronically neutral, rich (methyl and ethyl), or poor (chloro) groups at different positions of the arylalkynyl moiety of substrates **1** could show good reactivity, generating the corresponding tetracyclic sulfones **4b–4cc** in 35–82% yields. Among them, bromoalkynes bearing both electron-donating (methyl **2b**, ethyl **2c**, *tert*-butyl **2d**, and phenyl **2e**) and electron-withdrawing (chloro **2f**, bromo **2g** and ester **2h**) groups at the *para* position of the phenyl ring could be successfully engaged in

Scheme 2 Substrate scope for forming products **4**.

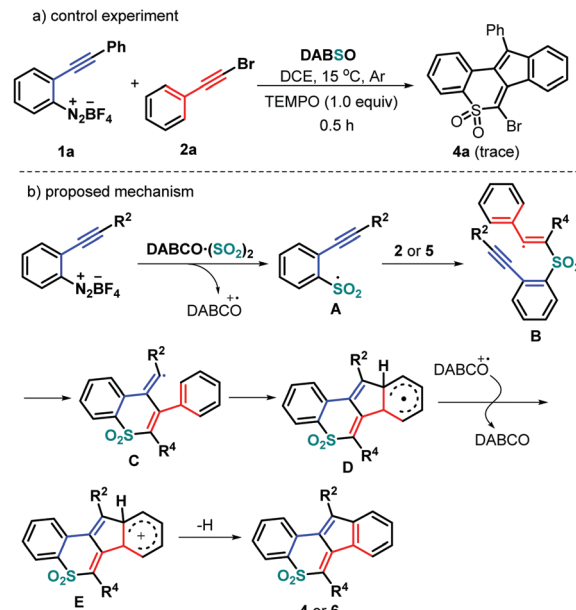
this transformation. The representative chloro and methyl substituents were independently introduced into the internal aryl ring of substrates **1** and were then employed to react with **2** and DABSO under standard conditions. The reactions worked well to deliver the corresponding products **4w–4bb** in 50–79% yields. Due to the presence of a chloro group at the *meta* position of the phenyl ring in the bromoalkyne unit (**2i**) two inseparable isomers **4cc** were obtained in a total yield of 40%. However, bromoalkyne **2j** having a 2-chlorophenyl group only provided a trace amount of product **4dd**, which failed to be isolated. Moreover, 2-thienyl bromoalkyne **2k** proved to be suitable for this transformation, affording tetracyclic sulfone **4ee** in 55% yield. Besides, ferrocenyl

bromoalkyne **2l** would be accommodated, confirming the efficiency of the transformation, as the product **4ff** was obtained in 63% yield. The feasible modification of important bioactive molecular frameworks is a basis for the evaluation of a practical protocol. In this context, estrone-derived bromoalkynes **2m** and **2n** were prepared, which tolerated this radical bicyclization cascade well, giving complex products **4gg** and **4hh** that comprise both estrone and cyclic sulfone units in 70% and 73% yields, respectively. Notably, chloroalkyne **2o** was a good candidate for this radical transformation (**4ii–4kk**), further highlighting the generality and great potential of the developed synthetic strategy.‡

To expand the utility of this methodology, we devoted our next efforts to assessing the feasibility of the current three-component bicyclization cascade toward cyclic sulfone syntheses by exploiting ynones to replace the haloalkyne component (Scheme 3). As anticipated, the reaction of the preformed ynones **5** with substrates **1** and DABSO (**3**) proceeded readily under the standard reaction conditions, leading to structurally diverse tetracyclic sulfones **6a–6m** with generally good yields. Ynones **5** having electron-neutral (H **5a**), electron-rich (Me **5b**, Et **5c**, *t*-Bu **5d**, and MeO **5e**) and electron-deficient (F **5f**, Cl **5g**, and Br **5h**) groups attached to the aryl moiety can participate in the current bicyclization chemistry, thus resulting in the corresponding products **6a–6h** in 63–80% yields. Alternatively, the presence of functional groups (R^3) including methyl (**5i**) and bromo (**5j**) groups residing in the arylalkynyl moiety of the substrates **5** was compatible in this transformation (**6i** and **6j**). Furthermore, the reaction proceeded readily with a variety of functional groups (R^2) on the arene ring of substrates **1**, giving access to



Scheme 3 Substrate scope for forming products **6**.



Scheme 4 Mechanism pathway.

the products **6k** and **6l** in 70% and 71% yields, respectively. Similarly, the 2-thienyl ynone **5k** showed high reactivity, enabling direct radical bicyclization to access the corresponding 2-thienyl substituted product **6m** in 72% yield. However, phenylene acetylene **5l** and 1,2-diphenylethyne **5m** were proved to be ineffective, as the generation of the corresponding products **6n** and **6o** was completely suppressed under the standard conditions (Scheme 3).

On the basis of the above observations and literature reports, a reasonable mechanism is proposed as shown in Scheme 4. It is well known that the combination of DABSO with aryldiazonium tetrafluoroborates would provide the arylsulfonyl radical **A** and a tertiary amine (DABCO) radical cation.¹⁸ Still, the presence of 2.0 equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) completely suppressed the formation of the normal product **4a** (Scheme 4a), indicating that the reaction process could include a radical mechanism. Therefore, the regioselective radical addition of the *in situ* generated sulfonyl radical **A**, from 2-alkynyl aryldiazonium tetrafluoroborates and DABSO, into the triple bond of haloalkynes **2** (or ynones **5**) yields the alkenyl radical intermediate **B**. Intermediate **B** undergoes a 6-*exo-dig* cyclization/5-*endo-trig* cyclization to give the radical intermediate **D**, followed by a single electron transfer (SET) in the presence of a tertiary amine (DABCO) radical cation to access intermediate **E**. Finally, the desired products **4** or **6** are produced through a deprotonation process (Scheme 4b).

In conclusion, we have developed two new types of radical three-component bicyclization cascades of 2-alkynyl-aryldiazonium tetrafluoroborate, DABSO and internal alkynes under oxidant- and catalyst-free conditions. This transformation initiated by the *in situ* generated arylsulfonyl radical proceeds efficiently under mild and neutral redox conditions, regioselectively giving access to indeno[1,2-*c*]thiochromene 5,5-dioxides with different substituent patterns in moderate to good yields. A tandem radical process with

the insertion of sulfur dioxide and 6-*exo-dig*/5-*endo-trig* bicyclization is proposed, with the formation of multiple chemical bonds. The transformation is attractive since it provides an easy and metal-free pathway toward the formation of a range of richly decorated polycyclic sulfones. Further investigation on their applications will be carried out in due course.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ The crystal of compound **4g** belongs to the monoclinic space group $P2_1(1)/n$ with dimensions of $0.42 \times 0.25 \times 0.14$ mm and a total of 9016 reflections were collected in the $2.63 < \theta < 25.02^\circ$ range by using an ω scan mode and 3240 were independent ($R_{\text{int}} = 0.0441$), $a = 8.4326(7)$ Å, $b = 11.5349(9)$ Å, $c = 18.9409(15)$ Å, $a = g = 90^\circ$, $\beta = 91.0070(10)^\circ$, $V = 1842.1(3)$ Å³, $M_r = 435.32$, $Z = 4$, $D_c = 1.570$ g cm⁻³, $\mu(\text{MoK}\alpha) = 2.361$ mm⁻¹, $F(000) = 880$, the final $R = 0.0324$ and $wR = 0.0769$.

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