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Copper-catalyzed [3 + 2]/[3 + 2] carboannulation of dienynes and arylsulfonyl chlorides enabled by Smiles rearrangement: access to cyclopenta[*a*]indene-fused quinolinones†

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On one hand, the construction of two fused five-membered carbocyclic rings remains an extremely challenging topic in organic synthesis. On the other hand, transition-metal-catalyzed dienyne cycloaddition reactions have become one of the most powerful methods for the construction of diverse cyclic frameworks. Nevertheless, these methods are limited to noble transition-meal catalysis and non-radical cycloaddition modes. Here, a radical Smiles rearrangement strategy for allowing an unprecedented [3 + 2]/[3 + 2] carboannulation of dienynes with arylsulfonyl chlorides using cheap copper catalysis is described. This cascade method represents a novel cycloaddition mode for dienyne chemistry, which occurs by the sequence of addition of arylsulfonyl radical to a dienyne, a Smiles rearrangement and radical annulation to access cyclopenta[*a*]indene-fused quinolinones with excellent diastereoselectivity.

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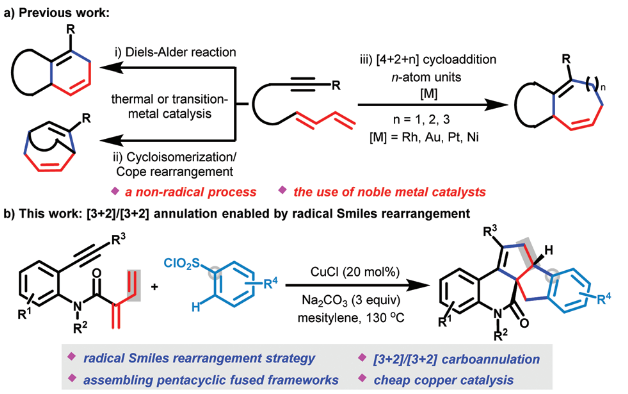
Introduction

Until now, the construction of two fused five-membered carbocyclic rings, especially with two vicinal chiral carbon atoms, has remained an extremely challenging topic in organic synthesis. Conventional methods often require multiple steps with low overall yields or the use of cyclopentane-based starting materials.[1] Therefore, the development of one-pot strategies for directly accessing two fused five-membered carbocyclic frameworks is in great demand.

The cycloaddition reaction is well-known and recognized as one of the most powerful and straightforward methodologies for efficient access to cyclic compounds in a single step, often along with the generation of multiple diastereo-centers.[2] In the past several decades, cycloaddition of dienynes (generally alkyne-tethered 1,3-dienes) has received considerable attention because this methodology is particularly appealing for rapid construction of diverse complex carbo- and hetero-cyclic structures, including the challenging seven- to nine-membered ring systems.[3–6] Typical methodologies can be divided into three types of non-radical annulation modes (Scheme 1a), including (i) Diels–Alder reaction *via* intramolecular [4 + 2] cycloaddition/isomerization,[4] (ii) intramolecular cycloisomerization/Cope rearrangement,[5] and (iii) intermolecular [4 + 2 + *n*] annulation.[6] However, these methods require expensive transition metal catalysts (such as Rh, Au, Pt, and Ni) and/or harsh



Scheme 1 Annulation modes of dienynes.

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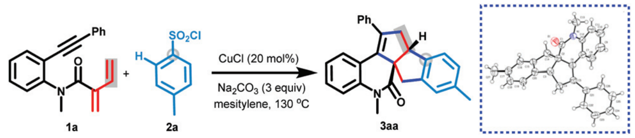
thermal conditions. Although the last [4 + 2 + *n*] cycloaddition of dienynes with external *n*-atom units can readily incorporate functional groups as well as controllably tune the ring scaffolds and has been well investigated, the scope of external *n*-atom units (such as carbene units, alkyne, ethyl cyclopropylideneacetate, and boryl(isopropoxy)silane) is limited. To the best of our knowledge, approaches that employ dienynes to undergo cycloaddition with external *x*-atom units for the construction of five-membered carbocyclic frameworks, especially those including two carbocyclic rings in a single step, have never been reported. Thus, the development of novel dienyne cycloaddition modes, especially including mechanistically distinguishable strategies using inexpensive transition metal catalysis, to widely expand the dienyne applications is desirable.

The Smiles rearrangement has emerged as one of the most powerful methods for the formation of chemical bonds in synthesis, and has been applied to difunctionalization of unsaturated hydrocarbons (such as alkenes and alkynes) by releasing SO_2 in recent years.[7–11] In a pioneering study, the group of Nevado has reported a new Smiles rearrangement tactic for enabling the addition of various radicals across the C=C bonds of *N*-(arylsulfonyl)acrylamides and their derivatives through radical addition/aryl migration/desulfonylation cascades to produce diverse N-heterocycles.[8] However, these methods largely rely on tailored acryl sulfonamide motifs.[8,9] Recently, Stephenson[11a] and Zhu[11b–e] made a significant breakthrough in the radical Smiles rearrangement to realize two-component difunctionalization of alkenes, in which external sulfonyl-based starting materials are converted to nitrogen- or sp^3 hybridized carbon-center radicals, and then they undergo addition across the C=C bonds and Smiles rearrangement cascades. On this basis, we envisioned that by the addition of the external sulfonyl radicals across the C=C bonds of the dienynes would arise an unprecedented cycloaddition reaction for the construction of new cyclic systems.

Here, we report an unprecedented copper-catalyzed [3 + 2]/[3 + 2] carboannulation of dienynes with arylsulfonyl chlorides for diastereoselectively producing cyclopenta[*a*]indene-fused quinolinones (Scheme 1b). This method enables one-pot formation of four new C–C bonds in a single step *via* radical addition cyclization, Smiles rearrangement and annulation cascades, and represents a new dienyne annulation mode to form two fused five-membered carbocyclic rings in a single step.

Results and discussion

Table 1 Optimization of reaction conditions[a]

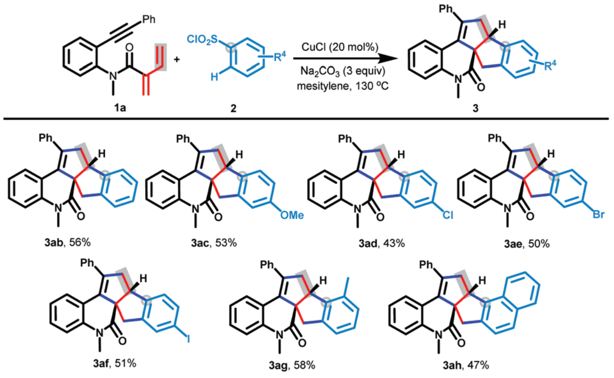


Entry	Variation from the optimal conditions	Yield (%)[b]
1	None	58 (46)[c]
2	CuBr instead of CuCl	13
3	Cu_2O instead of CuCl	36
4	CuOAc instead of CuCl	21
5	$CuCl_2$ instead of CuCl	33
6	K_2CO_3 instead of Na_2CO_3	15
7	K_3PO_4 instead of Na_2CO_3	16
8	NaOAc instead of Na_2CO_3	26
9	Cs_2CO_3 instead of Na_2CO_3	Trace
10	*o*-Xylene instead of mesitylene	40
11	*m*-Xylene instead of mesitylene	33
12	*p*-Xylene instead of mesitylene	35
13	DMF instead of mesitylene	0
14	At 120 °C	38
15	At 140 °C	49

[a] Standard conditions: **1a** (0.15 mmol), **2a** (0.3 mmol), CuCl (20 mol%), Na_2CO_3 (3 equiv.), and mesitylene (1.5 mL) at 130 °C under a N_2 atmosphere for 12 h. Only the *cis*-diastereoisomer (dr >20 : 1) was obtained, which is determined by ^1H NMR and GC-MS analyses of the crude product. [b] Yield of the isolated product. [c] **1a** (1 mmol) and mesitylene (8 mL).

We commenced our studies with the reaction of *N*-methyl-2-methylene-*N*-(2-(phenylethynyl)phenyl)but-3-enamide **1a** with 4-methylbenzenesulfonyl chloride **2a** in the presence of copper catalysts (Table 1). After investigating various reaction parameters, we were pleased to find that the [3 + 2]/[3 + 2] carboannulation could be successfully achieved by a simple catalytic system composed of CuCl (10 mol%), Na_2CO_3 (3 equiv.), and mesitylene at 130 °C, leading to the formation of **3aa** in 58% yield (entry 1). The structure of **3aa** was clearly confirmed by X-ray crystallography. Other alternative copper catalysts, including monovalent (CuBr, Cu_2O, and CuOAc) and bivalent copper salts ($CuCl_2$), did not give better results (entries 2–5). Further examination of other bases, including K_2CO_3, K_3PO_4, NaOAc, and Cs_2CO_3, revealed that all of them were less effective than Na_2CO_3 (entries 6–9). Solvents were proved to have a vital effect on this reaction: using toluene derivatives such as *o*-xylene, *m*-xylene, and *p*-xylene as media could smoothly afford the target products, albeit with greatly reduced yields (entries 10–12). However, no desired product was observed when mesitylene was replaced by DMF as medium (entry 13). Finally, this reaction showed lower conversion efficiency on changing the reaction temperature to 120 °C or 140 °C (entries 14 and 15). Notably, we attempted to perform the reaction scaling up to 1 mmol of **1a**, delivering the product **3aa** in a 46% yield (entry 1).

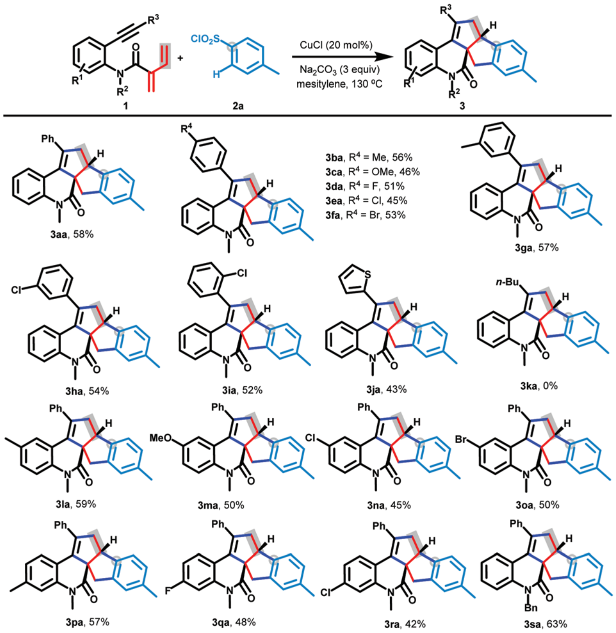
With the optimal reaction conditions identified, we set out to examine the substrate scope of this protocol with respect to arylsulfonyl chlorides. As shown in Scheme 2, a range of arylsulfonyl chlorides **2b–h** were subjected to [3 + 2]/[3 + 2] carboannulation with aniline-linked conjugated dienynes **1a** to furnish the desired products **3ab–ah** in moderate yields. For example, benzenesulfonyl chloride could afford benzo[4,5]pentaleno[6a,1-*c*]quinolin-12-one **3ab** in a 56% yield. Electron-donating methoxy and methyl substituted sulfonyl chlorides were also competent substrates, delivering the target products in 53% and 58% yields (**3ac** and **3ag**). Importantly, halogen atom substituted sulfonyl chlorides at the *para*-position of the



Scheme 2 Variations of the arylsulfonyl chlorides (**2**). Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), CuCl (20 mol%), Na_2CO_3 (3 equiv.), and mesitylene (2 mL) at 130 °C under a N_2 atmosphere for 12 h; d.r. >20 : 1.

benzene ring were smoothly converted into products **3ad–af**, which could provide a promising opportunity for further manipulation. Gratifyingly, the reaction of naphthalene-1-sulfonyl chloride **2h** with **1a** proceeded favorably, resulting in a 47% yield of **3ah**.

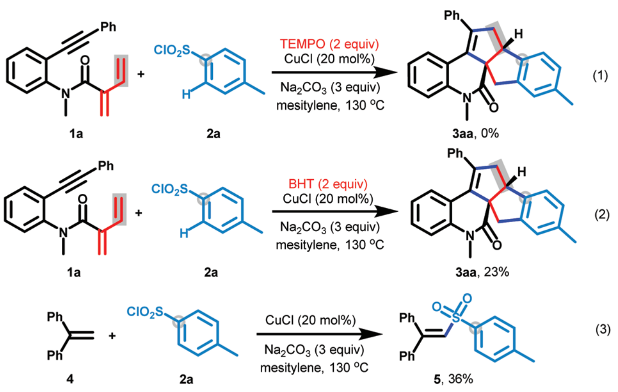
We next turned our attention to the investigation of the scope of aniline-linked conjugated dienynes **1**. To our delight, the [3 + 2]/[3 + 2] carboannulation was applicable to a wide range of conjugated dienynes **1**, thus furnishing the target products **3ba–ta** in moderate yields (Scheme 3). Initially, the alkyne moiety of conjugated dienynes **1** was studied in detail. The reaction tolerated a variety of substrates **1b–i** with different aromatic substituents (4-MeC$_6$H$_4$, 4-OMeC$_6$H$_4$, 4-FC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 3-MeC$_6$H$_4$, 3-ClC$_6$H$_4$, and 2-ClC$_6$H$_4$) at the alkyne terminus, furnishing pentacyclic-fused quinolin-12-one **3ba–ia** in moderate yields. The electronic and steric effects of substituents on the benzene ring had no significant influence on the cascade reaction. The heterocyclic thienyl group could also survive, delivering quinolin-12-one **3ja** in 43% yield. Unfortunately, chain alkynes did not give the desired product **3ka**. Afterward, we tested the variations in the aniline moiety. To our delight, various substituents such as electron-donating groups (Me and OMe) and electron-withdrawing groups (F, Cl, and Br) on the benzene ring were all well tolerated (**3la–ra**). When the methyl group on the nitrogen atom was replaced by a benzyl group, the anticipated product **3sa** could be obtained in 63% yield.



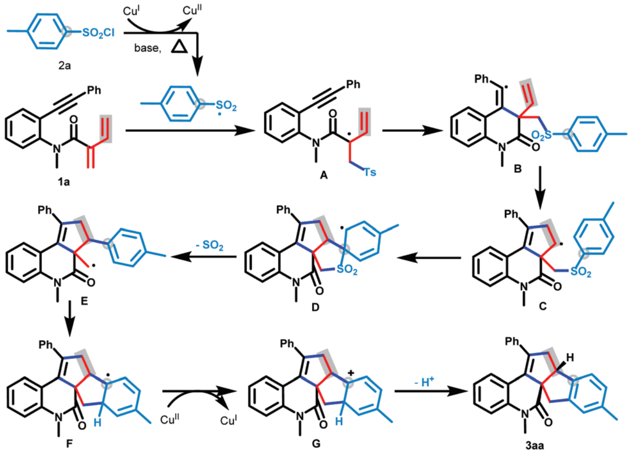
Scheme 3 Variations of the dienynes (**1**). Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), CuCl (20 mol%), Na_2CO_3 (3 equiv.), and mesitylene (2 mL) at 130 °C under a N_2 atmosphere for 12 h; d.r. >20 : 1.

Several control experiments were carried out to explore if a radical process was involved in this reaction (Scheme 4). First, the formation of product **3aa** was greatly suppressed when a stoichiometric amount of radical inhibitors such as TEMPO and BHT was added to the model reaction of **1a** with **2a** under the standard conditions (eqn (1) and (2)). 1,1-Diphenyl ethylene **4** and 4-methylbenzenesulfonyl chloride **2a** were next subjected to the above optimal reaction conditions, leading to the generation of (2-tosylethene-1,1-diyl)dibenzene **5** in 36% yield (eqn (3)). These results indicated that the [3 + 2]/[3 + 2] carboannulation possibly involved a radical pathway, which was initiated by arylsulfonyl radicals generated from arylsulfonyl chlorides **2**.

On the basis of the above results and previous reports,[10] a possible mechanism for the [3 + 2]/[3 + 2] carboannulation protocol is presented in Scheme 5. Initially, the reaction is triggered by a single electron transfer process of 4-methylbenzenesulfonyl chloride and Cu^{I} species under heating and basic conditions, thus producing 4-methylbenzenesulfonyl radicals and Cu^{II} species. Subsequently, the addition of the 4-methylbenzenesulfonyl radical to the C=C double bond of conjugated dienynes generates the allyl radical intermediate **A**, which continues to undergo a radical addition/annulation tandem reaction to form intermediate **C**. Then, the Smiles



Scheme 4 Mechanistic experiments.



Scheme 5 Proposed mechanism of [3 + 2]/[3 + 2] carboannulation.

rearrangement of intermediate **C**, including *ipso*-cyclization, 1,4-arylmigration, and SO_2-release, occurs to afford the alkyl radical intermediate **E**. The intramolecular radical addition to the vicinal benzene ring results in a cyclization of intermediate **E** to form intermediate **F**. Eventually, intermediate **F** undergoes a sequence of single electron oxidation with the Cu^{II} species and deprotonation to afford the desired fused pentacyclic product **3aa**.

Conclusions

In summary, we have developed an unprecedented copper-catalyzed [3 + 2]/[3 + 2] carboannulation of dienynes with arylsulfonyl chlorides *via* a radical Smiles rearrangement strategy. In this protocol, arylsulfonyl radicals generated from readily available arylsulfonyl chlorides undergo a radical addition cyclization/Smiles rearrangement/ring closure sequence to achieve [3 + 2]/[3 + 2] carbocyclization of dienynes, thus providing cyclopenta[*a*]indene-fused quinolinone pentacyclic frameworks with excellent diastereoselectivity. Note that four C–C bonds can be formed by this complex radical cascade process. Further applications of the dienynes are still in progress in our laboratory.

Conflicts of interest

The authors declare no competing interests.

Acknowledgements

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