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Synthesis of 2*H*-Chromenes via Unexpected [4 + 2] Annulation of Alkynyl Thioethers with *o*-Hydroxybenzyl Alcohols

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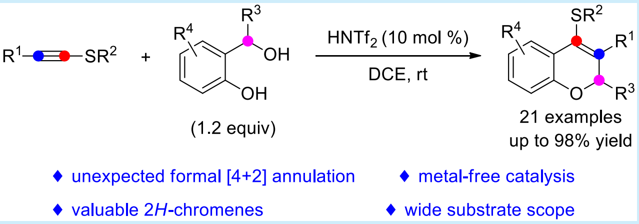
Supporting Information

ABSTRACT: A novel Brønsted acid-catalyzed reaction of alkynyl thioethers with *o*-hydroxybenzyl alcohols via an unexpected formal [4 + 2] annulation has been developed. This metal-free protocol leads to the facile and practical synthesis of valuable polysubstituted 2*H*-chromenes in mostly good to excellent yields under mild reaction conditions and features a wide substrate scope and excellent functional group tolerance.



2*H*-Chromenes, especially the 3-substituted 2*H*-chromenes, are important structural motifs which have been found in an array of bioactive molecules and natural products (Figure 1).[1,2]

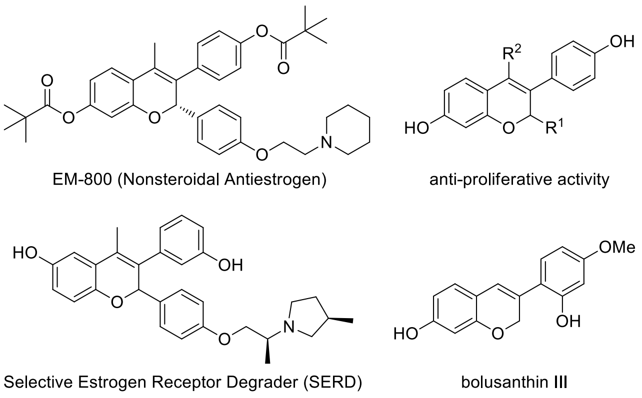


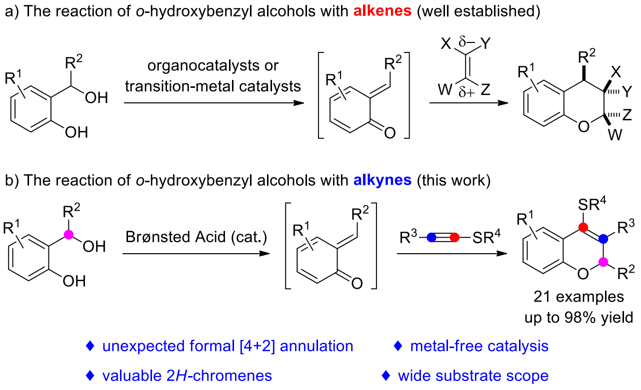
Figure 1. 2*H*-Chromenes in bioactive molecules and natural products.

Although many impressive methods have been established for their synthesis in the past decades, they still suffer from drawbacks such as multistep synthesis, limited substrate scope, harsh reaction conditions, and low yields.[2] Thus, the development of novel strategies for the construction of 2*H*-chromene scaffolds is still highly desirable, especially those with high flexibility, efficiency, and good modularity.

In recent years, *ortho*-quinone methides (*o*-QMs), a type of highly reactive intermediates which can be easily accessible from the corresponding *o*-hydroxybenzyl alcohols, have attracted much attention and have been widely used in the construction of a diverse range of synthetically useful oxo cycles.[3,4] These intermediates serve as electron-deficient oxobutadienes to participate in a broad variety of formal [4 + 2] annulation reactions in the presence of organocatalysts or transition-metal catalysts. Despite these significant achievements, these [4 + 2] annulations are generally limited to electronically rich olefins such as vinyl ethers, vinyl sulfides, enaminones, and styrenes (Scheme 1a). To date, no direct methods have been developed based on using alkynes as 2-π partners.[5]

Electronically rich heterosubstituted alkynes are versatile building blocks in organic synthesis and have attracted much

Scheme 1. Catalytic Reaction of *o*-Hydroxybenzyl Alcohols with Unsaturated CC Bonds



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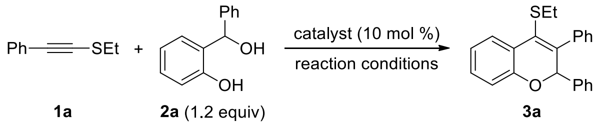
attention in the past decade. However, the chemistry of thioynol ethers has traditionally been far less explored[6−8] compared with the well-established ynamide chemistry.[9] Inspired by the above results and by our recent studies on developing heterosubstituted alkynes for heterocycle synthesis,[10] we envisioned that the catalytic reaction of *o*-hydroxybenzyl alcohols with electron-rich alkynyl thioethers might lead to the formation of 4*H*-chromenes via the above similar [4 + 2] annulation.[4d] Interestingly, the corresponding 2*H*-chromene motifs were obtained instead in this case. Herein, we would like to communicate this unexpected formal [4 + 2] annulation by Brønsted acid-catalyzed reaction of alkynyl thioethers with *o*-hydroxybenzyl alcohols (Scheme 1b). This metal-free protocol leads to the facile and practical synthesis of valuable polysubstituted 2*H*-chromenes in mostly good to excellent yields under mild reaction conditions and features a wide substrate scope and excellent functional group tolerance.

At the outset, alkynyl thioether **1a** and *o*-hydroxybenzyl alcohol **2a** were chosen as the model substrates, and some of the results are summarized in Table 1. Initially, various typical Brønsted acid catalysts were investigated in the presence of DCE as solvent at room temperature (Table 1, entries 1−4). Although TsOH failed to catalyze this reaction (Table 1, entry 1), it was found that the use of MsOH as catalyst led to the formation of the corresponding unexpected [4 + 2] annulation adduct **3a** in 30% yield (Table 1, entry 2). Pleasingly, further screening of stronger Brønsted acids (Table 1, entries 3 and 4) revealed that 92% yield of 2*H*-chromene **3a** could be achieved by employing $HNTf_2$ as catalyst (Table 1, entry 4).[11] In addition, the use of other non-noble metals, including $Cu(OTf)_2$, $Zn(OTf)_2$, $Sc(OTf)_3$, and $FeCl_3$, also produced the desired **3a** in 75−83% yields (Table 1, entries 5−8). Finally, other solvents such as THF and toluene were also examined but failed to improve the yield (Table 1, entries 9 and 10).

Table 1. Optimization of Reaction Conditions[a]

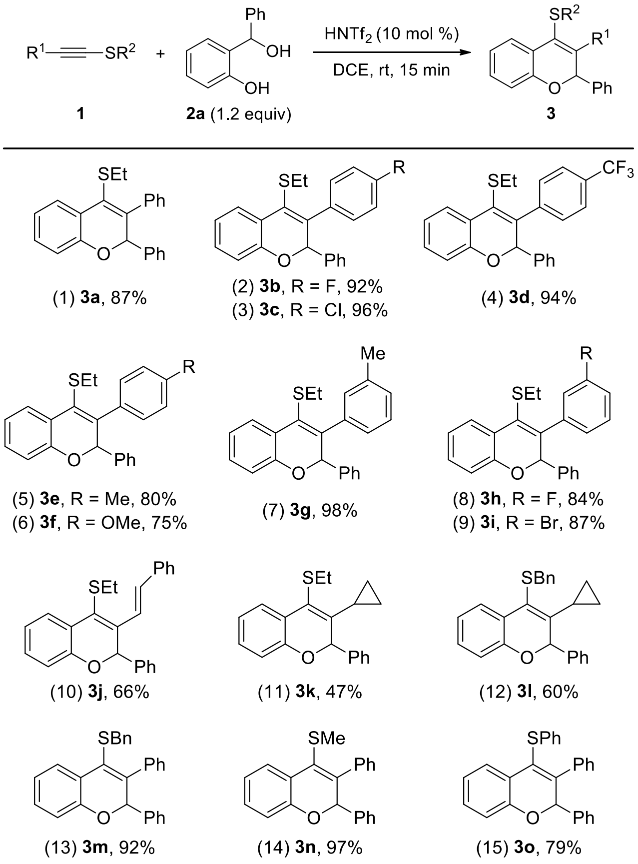


entry	catalyst	conditions	yield[b] (%)
1[c]	TsOH	DCE, rt, 24 h	<5
2[d]	MsOH	DCE, rt, 24 h	30
3	HOTf	DCE, rt, 15 min	73
4	**$HNTf_2$**	**DCE, rt, 15 min**	**92**
5	$Cu(OTf)_2$	DCE, rt, 18 h	75
6	$Zn(OTf)_3$	DCE, rt, 12 h	83
7	$Sc(OTf)_3$	DCE, rt, 12 h	79
8	$FeCl_3$	DCE, rt, 15 min	76
9	$HNTf_2$	THF, rt, 24 h	83
10	$HNTf_2$	toluene, rt, 3 h	53

[a] Reaction conditions: [**1a**] = 0.05 M. DCE: 1,2-dichloroethane. [b] Measured by ^1H NMR using diethyl phthalate as the internal standard. [c] 90% of **1a** remained unreacted. [d] 50% of **1a** remained unreacted.

With the optimal reaction conditions in hand, the scope of this metal-free [4 + 2] annulation of alkynyl thioethers **1** with *o*-hydroxybenzyl alcohols **2** was examined. First, an array of different alkynyl thioethers **1** were screened, and the desired 2*H*-chromenes **3** were afforded in mostly good to excellent yields. As shown in Scheme 2, alkynyl thioethers bearing electron-withdrawing substituents such as F, Cl, Br, and even CF_3 (entries 2−4, 8, and 9) and electron-donating substituents such as Me and MeO (entries 5−7) on the aromatic ring were compatible with this annulation to produce the corresponding 2*H*-chromenes **3a**−**3i** in 75−98% yields. In addition, the reaction also proceeded smoothly with the vinyl- and cyclopropyl-substituted thioynol ethers, leading to the expected products **3j** and **3k**/**3l** in 66 and 47−60% yields, respectively (entries 10−12). This annulation was also extended to other thioether-substituted substrates, and the desired **3m**−**3o** were formed in 79−97% yields (entries 13−15). The molecular structure of **3f** was further confirmed by X-ray crystallography (Figure 2). Attempts to extend the reaction to the ynamide substrates failed to produce the corresponding 2*H*-chromenes, and further studies in this direction are currently ongoing.

Scheme 2. Brønsted Acid-Catalyzed Formal [4 + 2] Annulation of Different Alkynyl Thioethers 1 with *o*-Hydroxybenzyl Alcohol 2a[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.24 mmol), $HNTf_2$ (0.02 mmol), DCE (4 mL), rt, 15 min, in vials; isolated yields are reported.

Then, a variety of substituted *o*-hydroxybenzyl alcohols **2** were also explored, as outlined in Scheme 3. Typical aryl-substituted *o*-hydroxybenzyl alcohols **2** (R^2 = Ar) bearing both electron-withdrawing and electron-donating groups were well tolerated in this reaction, leading to the desired 2*H*-chromenes **3p**−**3r** in 66−84% yields (entries 1−3). Of note, a longer reaction time (4 h) was needed in the case of OMe-substituted

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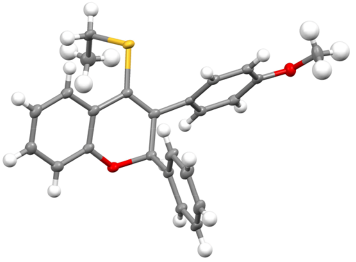
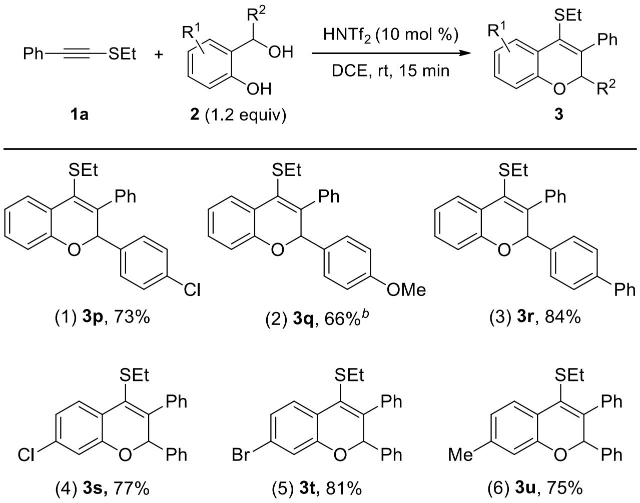


Figure 2. Structure of compound **3f** in its crystal. Thermal ellipsoids are shown at 50% probability.

Scheme 3. Brønsted Acid-Catalyzed Formal [4 + 2] Annulation of Alkynyl Thioether 1a with Different *o*-Hydroxybenzyl Alcohols 2[a]

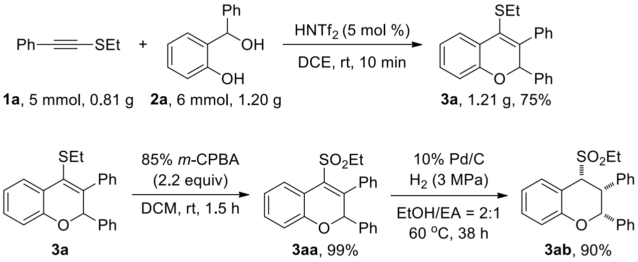


[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.24 mmol), $HNTf_2$ (0.02 mmol), DCE (4 mL), rt, 15 min, in vials; isolated yields are reported. [b]Reaction time: 4 h.

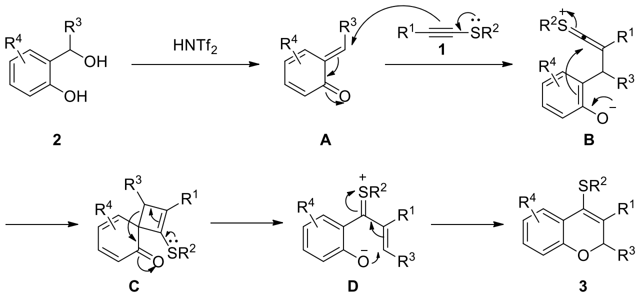
substrate (entry 2). Different substituents such as Cl, Br, and Me on the phenyl ring were also investigated, and the expected products **3s**–**3u** could be obtained in 75–81% yields (entries 4–6). Finally, it is notable that no enantioselectivity was observed when the reaction was performed in the presence of chiral Brønsted acids.

To further test the practicality of the current protocol, a gram-scale reaction of 0.81 g of **1a** with 1.20 g of **2a** was carried out with a lower catalyst loading (5 mol %), and 1.21 g of the desired 2*H*-chromene **3a** was formed in 75% yield, highlighting the synthetic utility of this chemistry (Scheme 4). Subsequently, it was found that the thioether of **3a** could be readily oxidized into the sulfonyl group by *m*-CPBA, followed by hydrogenation of the double bond, leading to the final highly functionalized chroman **3ab** in excellent yield with excellent cis diastereoselectivity (d.r. > 50:1; determined by crude ^{1}H NMR spectroscopy).

Scheme 4. Gram-Scale Synthesis and Further Transformations of the Product 3a



Scheme 5. Plausible Reaction Mechanism



On the basis of the above experimental observations, a plausible mechanism to rationalize the formation of 2*H*-chromenes **3** is proposed (Scheme 5). Initially, the *o*-hydroxybenzyl alcohols **2** are activated by the Brønsted acid to generate *o*-QM intermediates **A**. Then, intermolecular Michael addition of electron-rich thioynol ethers **1**, serving as nucleophiles, to the intermediates **A** affords the sulfonium intermediates **B**, which are further transformed into the four-membered spiro intermediates **C**. Formally, this process can be regarded as a [2 + 2] cycloaddition[12] and is kind of similar to Baire's recent work on the formal [3 + 2] annulation between alkynes and 3-indolylmethoanols involving the formation of spirocyclobutene intermediates.[5a] Here, it should be mentioned that the carbon anion of the enolate moiety selectively attacks the sulfonium moiety probably due to the fact that the sulfur is softer, compared to the nitrogen atom of ynamides, and prefers to be attacked by the carbon nucleophile but not the oxygen nucleophile. Subsequent ring opening of four-membered intermediates **C**, followed by another intramolecular Michael addition, leads to the target 2*H*-chromenes **3**. Thus, this Michael addition should be the driving force for this unexpected formal [4 + 2] annulation, as the use of vinyl sulfides as substrates only led to the normal [4 + 2] annulation.[4d]

In summary, we have developed a novel Brønsted acid-catalyzed reaction of alkynyl thioethers with *o*-hydroxybenzyl alcohols via an unexpected formal [4 + 2] annulation. This metal-free method leads to the facile and practical synthesis of valuable polysubstituted 2*H*-chromenes in mostly good to excellent yields under mild reaction conditions and features a wide substrate scope and excellent functional group tolerance. Importantly, this protocol represents the first example of direct formal [4 + 2] annulation of *o*-hydroxybenzyl alcohols with alkynes to our best knowledge, which significantly enriches the chemistry of *o*-QMs. Further investigations into the synthetic applications of the current protocol are in progress in our lab.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04421.

Experimental procedures and spectral data for all new compounds (PDF)

Accession Codes

CCDC 1967706 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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