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Access to 2-Aroylthienothiazoles via C−H/N−O Bond Functionalization of Oximes

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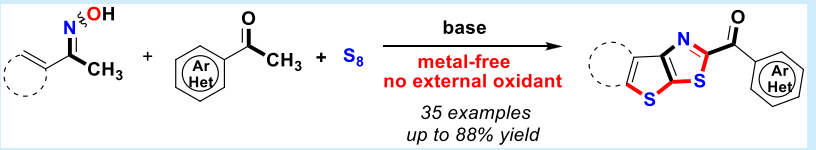
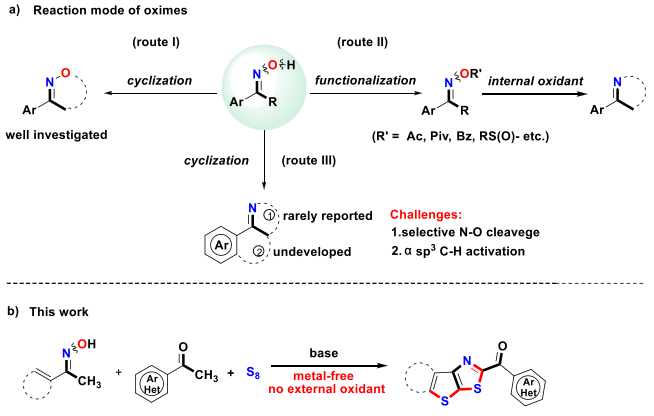
Supporting Information



ABSTRACT: A novel strategy for the synthesis of 2-aroylthienothiazoles via C−H/N−O bond functionalization of ketoximes is developed. This reaction features excellent step- and atom-economy, as well as broad substrate scope. Various common ketoximes, even vinyl ketoximes, were efficiently converted to 2-aroylthienothiazoles. Preliminary mechanistic studies indicated that the radical process should be involved in this transformation. Moreover, the product exhibited good coordination with Cu(II), showing the potential application in the metal coordination field.

Oximes are versatile and fascinating building blocks in organic synthesis with the advantages of easy availability, convenient storage, and high reactivity. With base or free radical initiator added, the oximes could be converted into various N−O bond-bearing compounds (Scheme 1, route I).[1]

Scheme 1. Reaction Mode of Oximes



On the other hand, another common strategy to activate oxime is based on O-functionalization, obtaining oxime esters with a reactive N−O bond. Undergoing *in situ* imino intermediate generation and the α-sp^3 C−H bond activation process, oxime esters efficiently construct various *N*-heterocycles (Scheme 1, route II).[2] Despite significant advances, the prefunctionalization operation and harsh storage conditions of oxime esters (usually below 10 °C) make this strategy relatively uneconomical and inconvenient. In contrast, synthetic methods that directly allow N−OH cleavage of oximes to construct N-bearing heterocycles have been rarely achieved (Scheme 1, route III−①),[3] probably due to the competitive O−H bond cleavage, making the single electron transfer (SET) of the N−OH bond on oxime difficult. To date, the direct employment of cyclobutanone oxime to form an iminyl radical under photocatalysis developed by Chen has been the only example.[4] Therefore, the development of more types of transformations of oximes is highly desirable. To the best of our knowledge, the study of C−H functionalization of oxime to incorporate both α-C(sp^3) and β-C(sp^2) into the final cyclic product remains unexplored (Scheme 1, route III−②).

2-Aroylthiazoles are an important class of thiazole derivatives existing in a myriad of clinical drugs and bioactive molecules, such as anti-infectives, immune agents, cardiovascular drugs, enzyme inhibitors, etc.[5] Despite their good synthetic utility, only one example is reported by Krayushkin for the synthesis of 2-aroylthienothiazole through four steps with the thiophene ring as the starting skeleton.[6] Until now, the polycyclization strategy for the preparation of 2-aroylthienothiazoles would be a high atom- and step-economic method, but still undeveloped. Herein, we reveal a multicomponent tandem cyclization to assemble the 2-aroylthienothiazole framework, using readily available oximes, S_8, and aromatic ketones as substrates (Scheme 1, route III). This type of annulation successfully achieves three Csp^3−H and a single Csp^2−H bond cleavage in unactivated oximes. Also, this method can be efficiently carried out in a metal-free manner without external oxidant, which simplifies the experimental protocol and improves the atom economy of the process.

In our initial studies, the reaction of acetophenone oxime (**1a**), acetophenone (**2b**), and S_8 was chosen as a model to optimize the reaction conditions, and the results are

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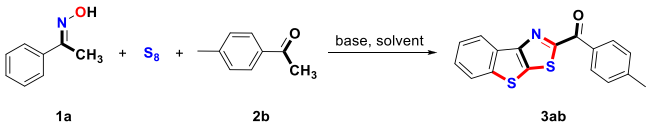
summarized in Table 1. The solvent was first screened, including nonpolar solvents (toluene and DCE, Table 1,

Table 1. Optimization of Reaction Conditions[a]



1a 2b 3ab

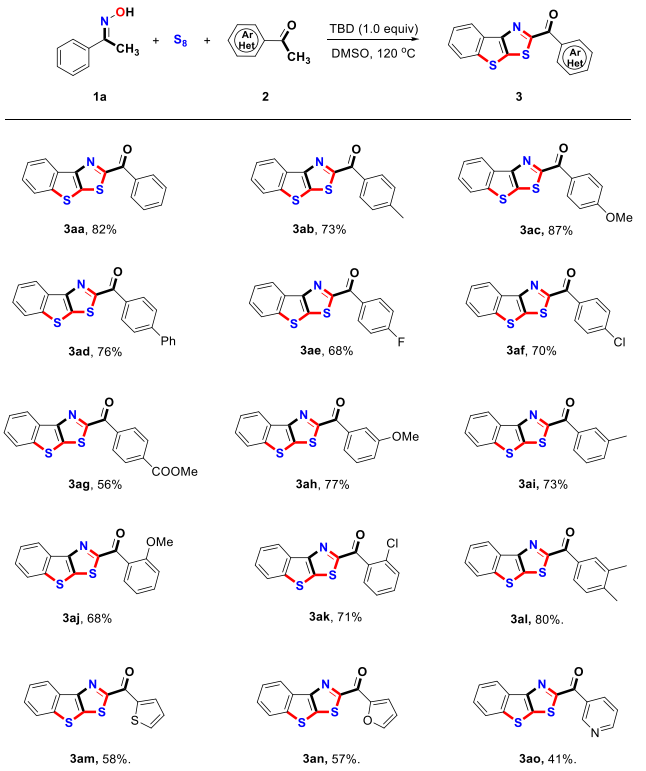
entry	solvent	base[b]	additive	yield [%][c]
1	toluene	DBU	-	trace
2	DCE	DBU	-	n.d.
3	1,4-dioxane	DBU	-	n.d.
4	MeCN	DBU	-	18
5	DMSO	DBU	-	41
6	DMSO	DBU	$FeCl_2$	26
7	DMSO	DBU	$CuCl_2$	22
8	DMSO	DBU	I_2	11
9	DMSO	DBU	NaI	15
10	**DMSO**	**TBD**	-	**78 (73)**
11	DMSO	MTBD	-	33
12	DMSO	Li_2CO_3	-	31
13	DMSO	^{t}BuOLi	-	52

[a]Reaction conditions: **1a** (0.4 mmol), S_8 (0.2 mmol), **2b** (0.2 mmol), base (1.0 equiv), and additive (20 mol %) in 1.0 mL of solvent at 120 °C under N_2 for 26 h unless otherwise noted. [b]MTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene. TBD = 1,5,7-triazabicyclo[4.4.0]-dec-5-ene. [c]^{1}H NMR yield using nitromethane as an internal standard. The number in parentheses is isolated yield.

entries 1 and 2) and polar solvents (DMSO, MeCN, and 1,4-dioxane, Table 1, entries 3−5). DMSO was effective for this transformation, providing the desired product in 41% yield. Different additives were then examined. It was found that $CuCl_2$, $FeCl_2$, NaI, and I_2 had a negative effect on the reaction (Table 1, entries 6−9). The effect of base was investigated (Table 1, entries 10−13), and a lower yield was obtained when using Li_2CO_3, ^{t}BuOLi, DBU, or MTBD as base. TBD was found to be the optimal choice, and the reaction gave **3ab** in 78% NMR yield.

With the optimized conditions in hand, the substrate scope of this protocol was explored. As presented in Scheme 2, the reaction was compatible with different aromatic ketones equipped with either electron-rich or electron-poor substituents. Thus, the substrates with a methyl, methoxy, or phenyl group *para* to the acyl group converted to the corresponding 2-aroylthienothiazoles **3ab**, **3ac**, and **3ad** in 73%, 87%, and 76% yields, respectively. The structure of **3aa** was confirmed by single-crystal X-ray diffraction analysis. Substrates with electron-withdrawing groups, such as fluoro-, chloro-, and methoxyformyl, were also well tolerated, obtaining **3ae**, **3af**, and **3ag** in 68%, 70%, and 56% yields. The compatibility of halogen substituents provides a potential handle for further synthetic transformations through cross-coupling techniques. Delightfully, acetophenones bearing electron-rich or electron-poor substituents such as methyl, methoxy, and halogen at *meta*- or *ortho*-positions reacted well with oxime, giving the corresponding products (**3ah**−**3ak**) in good yields. In addition, this transformation could be successfully extended to multi-substituted aromatic ketone, furnishing the corresponding product **3al** in 80% yield. The substrate scope regarding the heteroarenes was next investigated. Gratifyingly, the reaction

Scheme 2. Substrate Scope of Acetophenones[a]



[a]Reaction conditions: **1a** (0.6 mmol), S_8 (0.3 mmol), **2** (0.3 mmol), and TBD (1.0 equiv) in 1.5 mL of DMSO at 120 °C under N_2 for 26 h unless otherwise noted.

tolerated many heteroarenes such as thiophene (**3am**), furan (**3an**), and pyridine (**3ao**) and afforded the desired products in moderate yields.

Next, we examined the substrate scope of aromatic oximes bearing different substituents (Scheme 3). To our delight, electron-withdrawing (fluoro, chloro) and electron-donating (methyl, methoxy, and phenyl) groups at different positions of the aromatic ring were tolerated, providing the desired products in yields from 42% to 88%. Even sterically hindered 2-methyl, 2-methoxy, and 3,5-dimethyl oximes worked efficiently in this reaction and converted to **3ga**, **3ha**, and **3ia** in 88%, 73%, and 75% yields, respectively. Fused ring oximes such as naphthalene and benzofuran oximes also reacted smoothly, affording the larger conjugated fused rings **3ja** and **3ka** in moderate yields. However, heterocyclic ketoximines, such as pyridine and thiophene oximes, failed to obtain the corresponding product (**3la**, **3ma**). Notably, vinyl ketoximes were also well tolerated in this protocol and converted to the linear heteroaromatic structures **3na** and **3oa** in 77% and 52% yields. Moreover, the ionone oxime, derived from naturally occurring molecules, could be transformed to the desired product **3pa** in 80% yield, indicating the potential of this method in the elaboration of complex molecules.

Linear domino sequence reaction is an attractive research topic, which, significantly, provides an efficient tool for constructing complex molecules with simple raw materials. Considering acetophenone is a synthetic precursor of oxime, we envisioned that the present reaction protocol could be readily extended to a four-component tandem cyclization. Gratifyingly, a series of ketoximes reacted well under the standard conditions, providing the expected 2-aroylthienothia-

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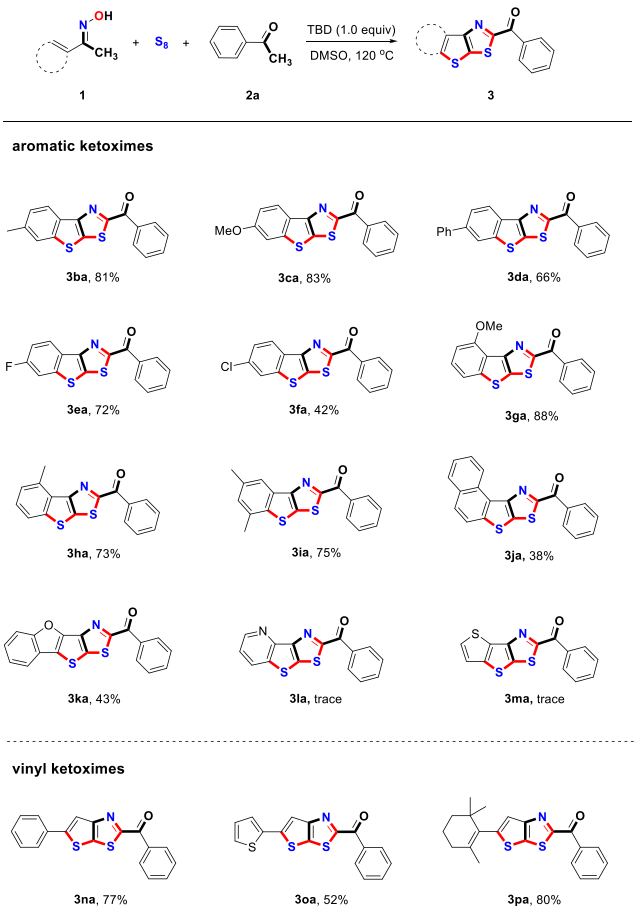
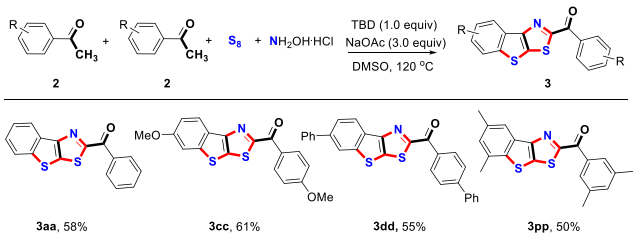
Scheme 3. Substrate Scope of Different Oximes[a]



[a]Reaction conditions: **1** (0.6 mmol), S_8 (0.3 mmol), **2a** (0.3 mmol), and TBD (1.0 equiv) in 1.5 mL of DMSO at 120 °C under N_2 for 26 h unless otherwise noted.

zole products **3aa**−**3pp** in modest yields (Scheme 4). Different substituents such as methyl, methoxyl, and phenyl on the

Scheme 4. One-Step Synthesis of 2-Aroylthienothiazoles[a]

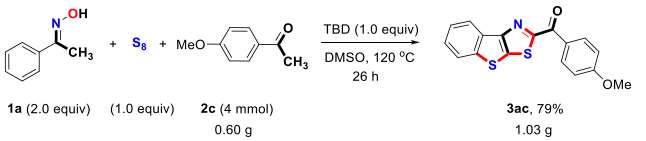


[a]Reaction conditions: **2** (0.6 mmol), S_8 (0.3 mmol), $NH_2OH{\cdot}HCl$ (0.9 mmol), NaOAc (3.0 equiv), and TBD (1.0 equiv) in 1.5 mL of DMSO at 120 °C under N_2 for 26 h unless otherwise noted.

aromatic ring of acetophenone were well tolerated in this reaction. Notably, this process could efficiently afford symmetrically substituted 2-aroylthienothiazoles without preparation of the starting materials, which simplified the procedure further.

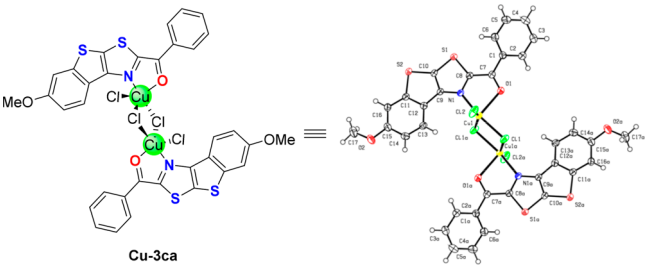
To test the scalability of the present reaction, a gram-scale reaction was carried out with 4 mmol of 4-methoxy acetophenone (**2c**) as substrate, and the desired product **3ac** was obtained in 79% isolated yield, which indicated the practical value of this approach (Scheme 5).

Scheme 5. Gram-Scale Synthesis of 2-Aroylthienothiazoles



Due to their unique 1,4-diheteroatom structures, 2-aroylthienothiazoles **3** should have important metal coordination properties. To our delight, the reaction of $CuCl_2$ with 2-aroylthienothiazole (**3ca**) afforded a copper(II) complex (**Cu-3ca**) (Scheme 6). As shown by single-crystal X-ray analysis, the

Scheme 6. Coordination of 2-Aroylthienothiazole with Copper[a]

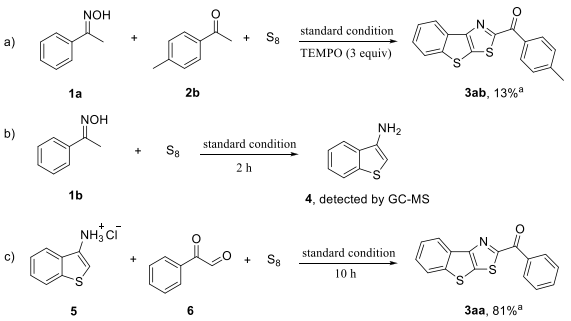


[a]The crystal structure of **Cu-3ca** is drawn with 50% probability ellipsoids.

N and O atoms of **3ca** were coordinated with copper, which indicated that 2-aroylthienothiazoles **3** could serve as an [N, O] chelate ligand with potential applications in the metal ion probe,[7] bioinorganic chemistry,[8] and metal-complex materials.[9]

To investigate the reaction mechanism, several control experiments were conducted (Scheme 7). Initially, when the

Scheme 7. Control Experiments



[a]^{1}H NMR yield using nitromethane as an internal standard.

radical scavenger TEMPO was added, the reaction system became complex, and the yield of **3ab** was decreased to 13% yield (Scheme 7a), which indicated that a radical pathway might be involved in this reaction. Next, we blended the oximes and S_8 under the standard conditions, and compound **4** was detected by GC-MS (Scheme 7b). Subsequently, when **5** was used as the substrate to react with **6**, the target product **3aa** was obtained in 81% yield, suggesting that **4** and **6** might be the intermediates in the reaction (Scheme 7c).

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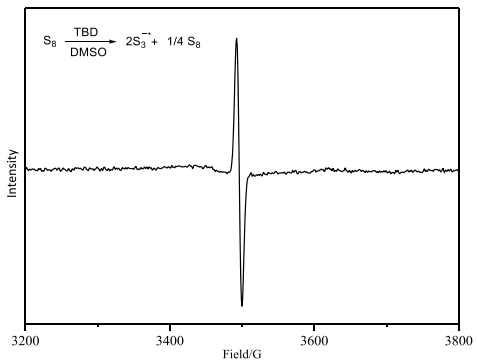
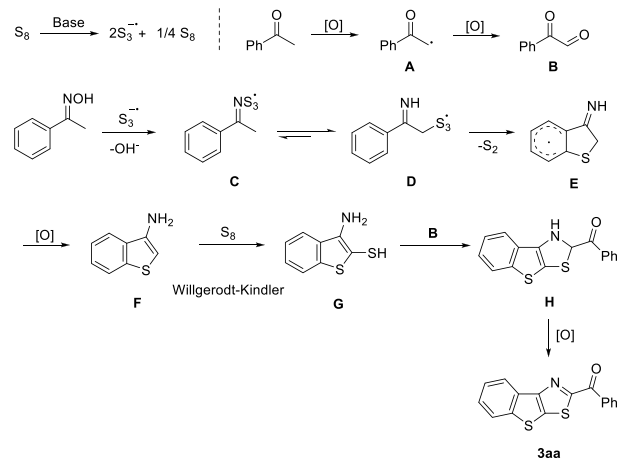
Considering the $S_3^{\bullet-}$ can be generated by the reaction of S_8 with base in polar solvent,[10] the electron paramagnetic resonance (EPR) experiment was carried out. Fortunately, an EPR signal was observed when the mixture of S_8 and TBD was tested (Scheme 8). Therefore, we confirmed that a radical process was involved in this transformation, and $S_3^{\bullet-}$ might be the key intermediate.

Scheme 8. EPR Studies of Interaction between S_8 and Base



Based on the above experimental results, a tentative mechanism is proposed in Scheme 9. First, **B** is generated

Scheme 9. Proposed Mechanism



under oxidative conditions,[11] where oxime or elemental sulfur serves as internal oxidant. Meanwhile, S_8 reacts with the base to provide $S_3^{\bullet-}$, which has been confirmed by the EPR experiment. Interaction between oxime and $S_3^{\bullet-}$ gives iminosulfur radical intermediate **C**, followed by tautomerization to form **D**.[2p] Next, intramolecular cyclization of **D** and subsequent oxidative aromatization afford intermediate **F**, which then undergoes Willgerodt−Kindler-type sulfuration of the enamine moiety to generate intermediate **G**.[12] Condensation annulation between **B** and **G**, followed by oxidative aromatization, finally produces the desired product **3aa**.

In summary, we have developed a novel approach for the synthesis of 2-aroylthienothiazoles using aromatic ketones, oximes, and S_8. Inexpensive reagents, simple operations, broad substrate scope, and good scalability make the transformation attractive. In this protocol, oximes, instead of prefunctionalized oxime esters, efficiently construct the N-heterocycles. This new type of annulation involving three Csp^3−H and a single Csp^2−H/N−OH cleavage in unactivated ketoximes is first reported, which shows high atom- and step-economy for the synthesis of N-heterocycles. Preliminary mechanistic studies suggest the involvement of $S_3^{\bullet-}$, and a radical mechanism for this reaction is proposed. Moreover, 2-aroylthienothiazoles show good coordination property with transition metal copper. Further applications of the metal complex are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b03900.

Experimental procedures, condition screening table, characterization data, and copies of NMR spectra for all products (PDF)

Accession Codes

CCDC 1921834−1921835 contain 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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