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Application of thiopyrylium trifluoromethanesulfonates as Lewis acids in organocatalytic reactions

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The successful application of thiopyrylium trifluoromethanesulfonate (triflate) as organic Lewis-acidic catalysts in electro-philic aromatic bromination, acetalization, cascade, and three-component reactions is disclosed. All these transformations provided the desired products in good yield. In particular, a catalytic amount of thiopyrylium triflate was used to activate *N*-bromosuccinimide for the bromination of various aromatic compounds under ambient and dark conditions.

Catalyst-mediated organic synthesis is a widely used and versatile tool in the field of organic chemistry. In particular, the use of transition metals as Lewis-acidic catalysts has attracted considerable attention.[1] By definition, a Lewis acid has a low-lying lowest unoccupied molecular orbital (LUMO) that can accept lone-pair electrons.[2] Compared with transition-metal catalysis, synthetic chemistry using metal-free Lewis-acidic organocatalysts is less explored, despite the inherent interest of synthesizing high purity molecules without metals in the fields of materials science and pharmaceutical research.

Recently, cationic organic salts, *i.e.*, cationic organic molecules that bear counter anions, have been sporadically used for promoting specific target transformations such as electrophilic aromatic substitutions and aza-Diels–Alder reactions,[3] paving the way for the design of cationic organic Lewis-acidic catalysts. For instance, Mukaiyama and coworkers have used carbocations as Lewis acids for the first time and employed triphenylcarbenium salts as catalysts for aldol, allylations, and Michael reactions.[4] Cyclopropenium,[5] tropylium,[6] pyridinium,[7] bromonium,[8] and iodonium salts[9] have also been applied as catalysts in several organic reactions as electron-pair acceptors. In addition, organocatalysis using chalcogen(IV) species such as sulfonium,[10] selenonium,[11] and telluronium salts[12] has recently received much attention; however, reports on catalytic reactions using tertiary chalcogenium compounds remain limited.

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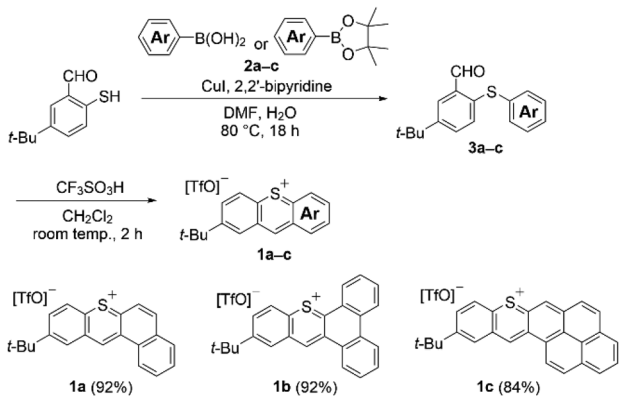
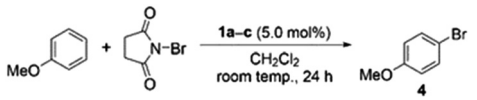
Among the aforementioned compounds, thiopyrylium salts are of interest owing to their unique electronic structure and as new building blocks for sulfur-containing aromatic molecules.[13] In 2020, we reported the synthesis of a new series of thiopyrylium salts *via* the Lewis- or Brønsted-acid-promoted intramolecular cyclization of diarylthioethers.[14] The resulting thiopyrylium compounds bear a cationic organic framework, as revealed by their spectroscopic characterization, and can be handled under atmospheric conditions. Owing to the presence of a cationic sulfur atom whose charge is delocalized over a conjugated π-electron system, we envisioned that the thiopyrylium salt could serve as a Lewis acid in solution. Here, we demonstrate for the first time that thiopyrylium trifluoromethanesulfonates (triflates) can be used as a Lewis acid in bromination, acetalization, cascade, and multi-component reactions. In particular, we describe the application of thiopyrylium triflates as a Lewis acid to activate *N*-bromosuccinimide (NBS) for bromination reactions. This reaction is especially important because traditional electrophilic brominations using molecular bromine to obtain brominated aromatic hydrocarbons, which are relevant compounds in metal-catalyzed cross-coupling reactions, pharmaceuticals, and naturally occurring products,[1] often suffer from complications associated with toxicity and operational complexity. Therefore, intense efforts have been devoted to enhancing the inherently low reactivity of NBS as an alternative bromination reagent using catalytic activators.[15]

We initially synthesized new thiopyrylium triflates **1a–c** using our previously developed intramolecular cyclization (Scheme 1).[14] Coupling reactions of 5-(*tert*-butyl)-2-sunfanylbenzaldehyde with naphthalen-2-ylboronic acid (**2a**), phenanthren-9-ylboronic acid (**2b**), and pyren-2-ylboronic acid pinacol ester (**2c**) afforded diarylthioethers **3a–c**, respectively, in moderate yields (see SI for details). Then, treatment of thioethers **3a–c** with trifluoromethanesulfonic acid (TfOH) at room temperature afforded thiopyrylium triflates **1a–c** in good yields *via* intramolecular cyclization. Thiopyrylium triflates **1a–c** are thermally stable under atmospheric conditions and do not exhibit any signs of decomposition or hygroscopicity.



Scheme 1 Synthesis of new thiopyrylium triflates **1a–c** by a TfOH-promoted cyclization.

Table 1 Bromination of anisole with NBS in the presence of 4 mol% thiopyrylium triflates **1a–c** in CH_2Cl_2 at room temperature



Entry	Thiopyrylium triflate	Additive	Yield of **4** (%)
1	—	—	1
2	—	TfOH (5.0 mol%)	63
3	—	TfOH (5.0 mol%) + 2,4,6-trimethylpyridine (5.0 mol%)	0
4	**1a**	—	48
5	**1b**	—	58
6	**1c**	—	33
7	**1b**	2,4,6-Trimethylpyridine (5.0 mol%)	52

We first investigated the Lewis acidity of thiopyrylium triflates **1a–c** using the Gutmann–Beckett method,[16] which is based on the use of trioctylphosphine oxide (n-$Oc_3P{=}O$) as a probe to detect the chemical-shift changes ($\Delta\delta_P$) in the ^{31}P NMR spectra of the evaluated systems upon addition of n-$Oc_3P{=}O$. Adding one equivalent of n-$Oc_3P{=}O$ to a solution of **1a–c** in CD_3CN resulted in downfield shifts of $\Delta\delta_P$ = 12.0, 16.3, and 19.5 ppm, respectively, compared to the chemical shift of free n-$Oc_3P{=}O$.[17] These results suggest that thiopyrylium triflates **1a–c** inherently behave as Lewis acids in solution, whereby **1b** and **1c** exhibiting higher Lewis acidity than **1a**. Thus, intermolecular interaction between these salts and trioctylphosphine oxide would be affected by their molecular structures of **1a–c**.

Then, the intermolecular interaction of thiopyrylium triflate **1b** with NBS was investigated *via* NMR spectroscopy using a 1 : 1 stoichiometric mixture of thiopyrylium salt **1b** and NBS. The ^1H and ^{13}C NMR spectra of the mixture in $CDCl_3$ showed slightly shifted signals compared with those of free **1b** and NBS, indicating that no covalent bond was formed between **1b** and NBS. Therefore, thiopyrylium triflate **1b** behaves as a soft Lewis acid toward NBS in solution. Moreover, theoretical investigations on the interactions between thiopyrylium cations **1a′–c′** and NBS were conducted using the Gaussian 16 programs suite. In all cases, the interactions were exothermic. In particular, thiopyrylium cation **1b′** and NBS showed the most effective interaction with an exothermic energy of 1.98 kcal mol^{-1}, which is consistent with the experimentally observed affinity of **1b** for NBS. Regarding the optimized structure, interaction between HOMO of **1b′** and LUMO of NBS might be caused by a planar stacked conformation of the **1b′**/NBS complex.

Having examined the Lewis acidity of **1a–c** in solution, we tested their catalytic activity in the electrophilic aromatic bromination of anisole by reacting anisole with NBS in the presence of 5.0 mol% of **1a–c** under dark conditions. The results are summarized in Table 1.

First, we confirmed that the bromination did not proceed without thiopyrylium triflate or any additive (entry 1). Using TfOH as a Brønsted acid enhanced the bromination, resulting in the formation of 4-bromoanisole in 63% yield (entry 2); however, the addition of both TfOH and 2,4,6-trimethylpyridine did not afford the desired product (entry 3). The bromination proceeded smoothly in the presence of 5.0 mol% of thiopyrylium triflate **1b** under dark conditions to furnish 4-bromoaniole in 58% yield (entry 5), whereas thiopyrylium triflates **1a** and **1c** afforded 4-bromoaniole in lower yield, *i.e.*, 48% and 33%, respectively (entries 4 and 6). The observed lower activity for **1c** might be caused by its low solubility toward CH_2Cl_2. No significant change in the yield was observed when using **1b** in the presence of 2,4,6-trimethylpyridine (entry 7). These results confirmed that thiopyrylium triflate **1b** effectively catalyzes this electrophilic aromatic bromination as a Lewis acid and that the **1b**-catalyzed bromination was not affected by the presence of a Lewis base.

With the optimized reaction conditions in hand, we next explored the substrate scope of the electrophilic bromination by NBS (Chart 1). In the presence of 5.0 mol% of **1b**, 1,3-benzodioxole, mesitylene, acetanilide and thioanisole reacted with NBS to afford monobrominated compounds **5**, **6**, **7**, and **8** in

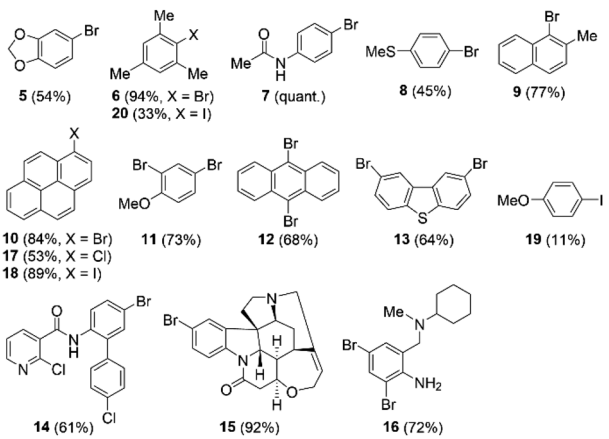
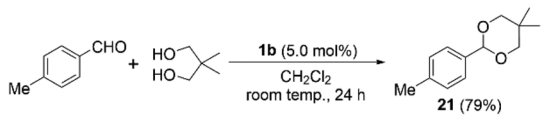


Chart 1 Substrate scope of the electrophilic bromination catalyzed by thiopyrylium triflate **1b**.

54%, 94%, quantitative, and 45% yield, respectively. Although naphthalene did not undergo the desired bromination, 2-methylnaphthalene readily furnished 1-bromo-2-methylnaphthalene (**9**) in 77% yield. When using pyrene, the reaction proceeded regioselectively to produce 1-bromopyrene (**10**) in 84% yield. In the cases of anisole, anthracene, and dibenzo[*b*,*d*]thiophene, two-fold bromination occurred preferentially to afford 2,4-dibromoanisole (**11**), 9,10-dibromoanthracene (**12**), and 2,8-dibromodibenzo[*b*,*d*]thiophene (**13**) in 73%, 68%, and 64% yield, respectively. We confirmed that the thiopyrylium-catalyzed bromination can also be applied to agricultural chemicals and alkaloid molecules. Specifically, boscalid and strychnine reacted under the applied bromination conditions to furnish brominated derivatives **14** and **15** in 61% and 92% yield, respectively. Dibromoaniline derivative **16**, an important compound in the field of pharmaceutical chemistry, was also obtained *via* two-fold bromination. Conversely, 2-methylquinoline, 9*H*-thioxanthen-9-one, 2,5-dimethylthiophene, phenanthrene, neopentylbenzene, and 1-bromo-3-chlorobenzene were not converted to the corresponding brominated products under the applied reaction conditions. The monobromination of anisole was also performed using *N*-bromophthalimide instead of NBS under the otherwise optimized conditions, to afford **4** in 74% isolated yield. Moreover, chlorination and iodination reactions using *N*-chloro- and *N*-iodosuccinimide, respectively, were successfully conducted, which furnished 1-chloropyrene (**17**), 1-iodopyrene (**18**), 4-iodoanisole (**19**), and iodomesitylene (**20**) in 53%, 89%, 11%, and 33% isolated yield, respectively (Chart 1). Thus, the thiopyrylium-triflate-promoted bromination, chlorination, and iodination is suitable for a variety of aromatic hydrocarbons, sulfur-containing heterocycles, agricultural chemicals, and alkaloids.

The robustness of the developed organic catalytic system was tested by recovering the catalyst after the reaction and using the reused catalyst for new reaction cycles. Upon completion of the bromination of pyrene in the presence of **1b**, the reaction mixture was separated by centrifugation at 0 °C, affording an orange solid. The obtained solid was then treated repeatedly with another portion of pyrene and NBS in CH_2Cl_2. The catalytic system could be reused at least five times with complete conversion and virtually no activity loss. Specifically, the product yield from the first to the fifth experiments was 91%, 100%, 86%, 86%, and 82%. These results demonstrate the robustness of catalyst **1b** in these electrophilic bromination reactions.

Having confirmed the activity and stability of thiopyrylium triflate **1b** in electrophilic bromination reactions, we examined its ability to catalyze other organic reactions. Thiopyrylium triflate **1b** was thus applied in the acetalization reaction of benzaldehyde derivatives using a diol. First, the acetalization reaction of *p*-tolualdehyde and 2,2-dimethylpropane-1,3-diol proceeded using 5.0 mol% of **1b** at room temperature (Scheme 2). The ^{1}H NMR spectrum of the reaction mixture revealed the complete conversion of the substrate within 24 h. After chromatographic purification, acetal **21** was isolated in 79% yield. Then, we evaluated the effect of different substituents on the benzene ring of the benzaldehyde precursors. Installing an



Scheme 2 Reaction of *p*-tolualdehyde with 2,2-dimethylpropane-1,3-diol in the presence of **1b**.

electron-withdrawing group on the aromatic ring did not significantly alter the cyclization outcome (*cf.* compounds **22** and **23** in Chart 2). When using 1-naphthaldehyde, the acetalization smoothly proceeded to provide acetal **24** in quantitative isolated yield. π-Expanded 1-pyrenecarboxaldehyde successfully reacted with the diol in the presence of **1b** (5.0 mol%) to afford the corresponding acetal (**25**) in 95% isolated yield. Terephthalaldehyde also proved to be a suitable substrate, which provided bisacetal derivative **26** in good yield. These results clearly demonstrate the versatility of **1b**, whose sufficient Lewis acidity renders it suitable for a variety of catalytic reactions.

Next, we turned our attention to expand the reaction of propargylic alcohols with naphthalen-2-ol in the presence of thiopyrylium triflate **1b** as a Lewis acid (Scheme 3). First, we confirmed the complete recovery of the substrates in the absence of **1b**. When using 5.0 mol% of **1b**, this cascade reaction smoothly proceeded at 80 °C within 3 h according to ^{1}H NMR spectroscopy monitoring. 3*H*-Benzochromene derivative **27** was obtained in 95% isolated yield after chromatographic separation. In addition, this direct construction of the 3*H*-benzochromene framework provided **28** and **29** in excellent yield under the applied conditions (Chart 3). Thus, propargylic alcohols could be activated by thiopyrylium triflate **1b** to undergo the Friedel–Crafts reaction with naphthalen-2-ol to give 3*H*-benzochromene derivatives.

Finally, we examined Mannich reactions catalyzed by thiopyrylium triflate **1b** as a model three-component reaction

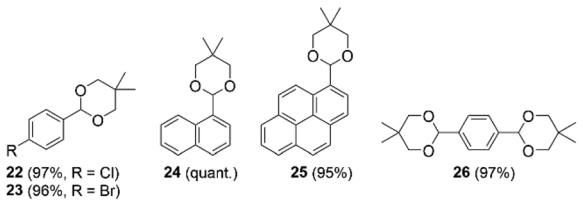
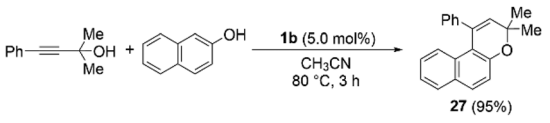


Chart 2 Substrate scope of acetalization reactions catalyzed by thiopyrylium triflate **1b**.



Scheme 3 Reactions of naphthalen-2-ol with 2-methyl-4-phenyl-3-butyn-2-ol in the presence of **1b**.

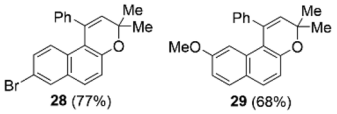
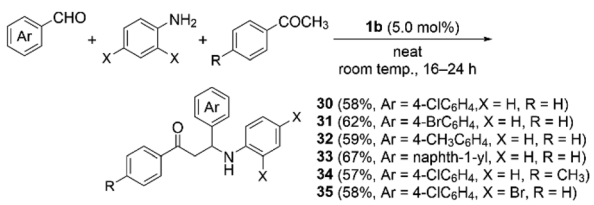


Chart 3 Substrate scope of cascade reactions catalyzed by thiopyrylium triflate **1b**.



Scheme 4 Three-component reactions in the presence of **1b**.

(Scheme 4). In the absence of **1b** at room temperature, the control reaction did not lead to the desired three-component product. Meanwhile, in the presence of 5.0 mol% of **1b**, the reaction of 4-chlorobenzaldehyde, aniline, and acetophenone furnished Mannich product **30** in 58% isolated yield. 4-Bromobenzaldehyde, *p*-tolualdehyde, and 1-naphthaldehyde were also tolerated as substrates instead of 4-chlorobenzaldehyde, providing three-component products **31**, **32**, and **33** in 62%, 59%, and 67% yield, respectively. In the case of substituted acetophenone and aniline derivatives, the reactions smoothly produced **34** and **35** in 57% and 58% yield, respectively. These results confirm that thiopyrylium triflate **1b** also works as a Lewis-acidic organocatalyst in Mannich-type condensations to afford the three-component products in moderate yield.

In summary, we have for the first time, successfully used thiopyrylium triflate **1b** as a Lewis-acidic organocatalyst in electrophilic bromination reactions of aromatic compounds, acetalization reactions of benzaldehydes, cascade reactions, and Mannich reactions. The corresponding products were obtained in good yield. DFT calculations suggested the formation of noncovalent interactions between the thiopyrylium cation fragment and the imide/carbonyl group of NBS or the benzaldehydes. Further studies on the application of thiopyrylium salts to catalyze other organic reactions are currently in progress in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental details, characterization data, and supporting figures and tables. See DOI: https://doi.org/10.1039/d5ob01353d.

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17 We also observed that adding one equivalent of *n*-$Oc_3P{=}O$ to a solution of tropylium tetrafluoroborate/triphenylcarbenium tetrafluoroborates in CD_3CN resulted in downfield shifts of $\Delta\delta_P$ = 5.01/24.4 ppm, respectively, compared to the chemical shift of free *n*-$Oc_3P{=}O$.

