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Cascade C(sp^3)−S Bond Cleavage and Imidoyl C−S Formation: Radical Cyclization of 2-Isocyanoaryl Thioethers toward 2-Substituted Benzothiazoles

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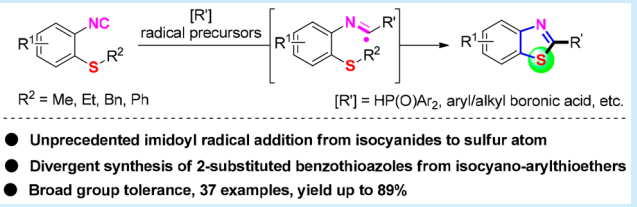
Supporting Information

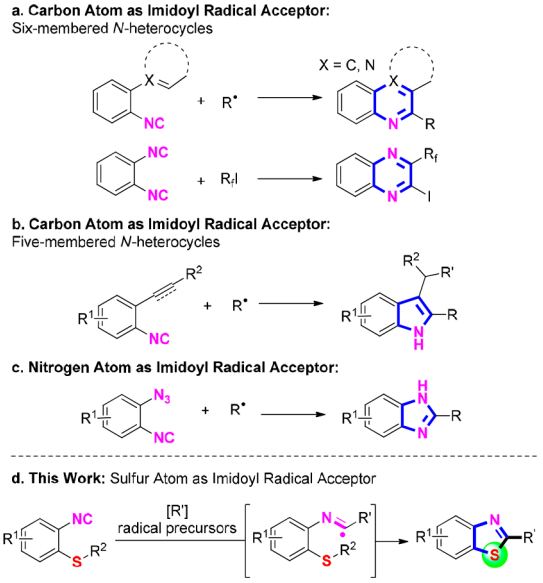
ABSTRACT: A cascade radical cyclization of 2-isocyanoaryl thioethers with *H*-phosphorus oxides, organoboronic acids, or alkyl radical precursors has been efficiently developed, providing a novel and highly efficient methodology to structurally diverse C2-substituted benzothiazole derivatives with broad functional group tolerance and good yields. This cascade radical process achieves the first cycloaddition of an imidoyl radical from isocyanide to sulfur atom, rending C(sp^2)−S bond formation.



Isocyanides as versatile building blocks have been widely applied in the synthesis of numerous nitrogen-containing compounds that are key motifs in biological and medicinal chemistry.[1] Inherently, isocyanides serve not only as nucleophiles but also as efficient radical acceptors to produce imidoyl radical intermediates for subsequent reactions.[2] As a pioneering work in a radical cascade reaction of isocyanides, in 2012, Chatani and co-workers reported a Mn(III) salt promoted cyclization of 2-isocyanobiphenyls with organoboronic acids to build phenanthridine skeletons.[3] Since then, varieties of radicals, covering aryl, phosphonate, alkyl, and trifluoromethyl radicals, have been utilized to attack isocyanides, giving six-membered *N*-heterocyclics, such as quinoline, isoquinoline, polycyclic quinoxaline, and phenanthridine derivatives (Scheme 1a).[4] Variability of the substrates offers the diversity of *N*-heterocyclics from six-membered to five-membered. Hence, cascade cycloadditions of 2-alkynylphenyl or 2-alkenylphenyl isocyanides were developed to construct substituted indoles through the imidoyl radical addition to vicinal alkynes or alkenes (Scheme 1b).[2c,5]

Mechanistically, the aforementioned cycloadditions share a common pathway in the attack of imidoyl radicals to unsaturated carbon atoms. We reasoned that the addition of imidoyl radicals to vicinal heteroatoms would provide a novel and expeditious approach to construct polyhetero compounds. However, this chemistry has been seriously underdeveloped, with only one example documented thus far. In 2017, Zhu et al. established a Mn(III)-promoted radical cyclization of 1-azido-2-isocyanoarenes with azide as an imidoyl radical acceptor, along with molecular nitrogen released spontaneously (Scheme 1c).[6]

Scheme 1. (a−c) Previous Studies on Intramolecular Radical Cascade Reactions of Isocyanides; (d) This Work



The delay in developing this chemistry might be attributed to the challenges, as follows: (1) nucleophilic addition of "free" heteroatoms (−OH, −NH$_2$, −SH, etc.) to isocyanides renders carbene intermediates,[7] resulting in inhibition of a radical

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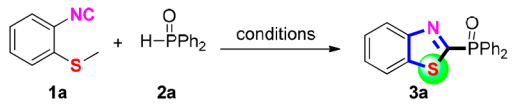
process, and (2) the "leaving moiety" on heteroatoms must be easily cleaved upon imidoyl radical attack but inert to initially generated radical species (R•).

Intriguingly, thioanisole derivatives provide much hope in this regime, since they have been applied for the construction of benzothiophenes through electrophilic cyclization or radical cyclization.[8] In elegant work, König et al. revealed a photocatalytic coupling of *o*-methylthioarenediazonium salts with alkynes, in which the radical cyclization was decreased by the addition of a vinyl radical to a sulfur atom along with the release of a methyl group.[8f] Very recently, our group disclosed a visible-light-driven synthesis of S,P-bifunctionalized butadienes using a sulfur atom as an alkenyl radical acceptor.[9d] Inspired by these studies and our continuing explorations on organophosphorus chemistry and radical chemistry,[9] herein we report unprecedented radical cascade reactions of isocyanides with *H*-phosphorus oxides, organoboronic acids, or alkyl radical precursors via an imidoyl radical addition to a sulfur atom toward diverse 2-substituted benzothiazoles.[9f,10]

An initial attempt found that the reaction of (2-isocyanophenyl)(methyl)sulfane (**1a**) and diphenylphosphine oxide (**2a**) afforded 29% yield of the target product **3a** in DMF with manganese(III) acetate hydrate as a promoter (entry 1). Systematic screenings of the conditions were further performed, as shown in Table 1. Interestingly, solvents were found to play a

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

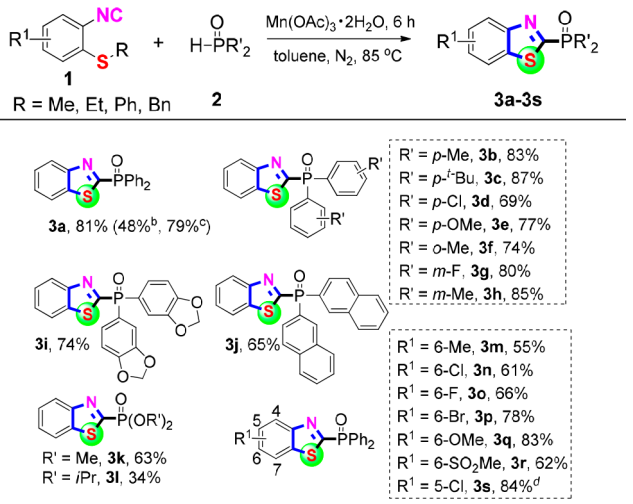
entry	promoter	solvent/temp (°C)	yield[b] (%)
1	$Mn(OAc)_3{\cdot}2H_2O$	DMF/110	29
2	$Mn(OAc)_3{\cdot}2H_2O$	DMSO/110	38
3	$Mn(OAc)_3{\cdot}2H_2O$	toluene/110	65
4	$Mn(OAc)_3{\cdot}2H_2O$	MeCN/110	47
5	$Mn(OAc)_3{\cdot}2H_2O$	THF/110	43
6	$K_2S_2O_8$	toluene/110	trace
7	$AgNO_3$	toluene/110	15
8	TBHP	toluene/110	trace
9	$Mn(acac)_3$	toluene/110	60
10	$Mn(OAc)_3{\cdot}2H_2O$	toluene/85	72
11	$Mn(OAc)_3{\cdot}2H_2O$	toluene/40	55
12[c]	**$Mn(OAc)_3{\cdot}2H_2O$**	**toluene/85**	**81**
13[d]	$Mn(OAc)_3{\cdot}2H_2O$	toluene/85	64
14		toluene/85	NR

[a]Reaction conditions: (2-isocyanophenyl)(methyl)sulfane (**1a**, 0.2 mmol), diphenylphosphine oxides (**2a**, 0.4 mmol), promoter (2.0 equiv, 0.4 mmol), 12 h, N_2. [b]Isolated yields, NR = no reaction. [c]6 h. [d]3 h.

vital role in this transformation. Polar aprotic solvents, including DMF, DMSO, and acetonitile, all gave yields lower than 50%. Toluene was proven to be the best choice and enhanced the isolated yield to 65% (entry 3). Afterward, varieties of promoters (potassium persulfate, silver nitrate, TBHP, and manganese acetylacetonate) were applied as well (entries 6–9), among which $Mn(OAc)_3{\cdot}2H_2O$ outperformed the others, leading to the highest yield. Subsequent screening of temperature and reaction time explained that a moderate temperature was enough to initiate the reaction, and the reaction could be accomplished within 6 h with an even higher yield of 81% (entry 12). This observation could be attributed to the suppression of a side reaction at high temperature between a phosphoryl radical and a thioanisole moiety. Thus, an efficient cascade reaction of isocyanide was achieved to give 2-phosphonated benzothiazoles by employing manganese(III) acetate as a promoter in warm toluene, without other additives.

Encouraged by the preliminary results, we continued to investigate the substrate scope of various *H*-phosphorus oxides and isocyanides. As shown in Scheme 2, diarylphosphine oxides

Scheme 2. Substrates Scope on *H*-phosphorus Oxides and Isocyanides[a]



[a]Reaction conditions: 2-isocyanothioanisoles (**1**, 0.2 mmol), *H*-phosphorus oxides (**2**, 0.4 mmol), R = Me, $Mn(OAc)_3{\cdot}2H_2O$ (2.0 equiv, 0.4 mmol), 2 mL of toluene, 85 °C, 6 h, N_2, isolated yields. [b]R = Ph. [c]R = Bn. [d]R = Et.

bearing electron-donating or -withdrawing groups, including methyl, *tert*-butyl, methoxy, and chloro at the *para*-position, methyl at the *ortho*-position, and fluoro at the *meta*-position were well-tolerated in the system, affording the products **3a–h** in medium to excellent yields. It is worth noting that piperonyl- and naphthyl-derivated phosphine oxides were good candidates as well, and the corresponding products **3i** and **3j** were obtained in 74% and 65% yields, respectively. In addition, phosphonate esters of methyl and isopropyl were also tested and, to our delight, were found to be applicable to the system with moderate yields ranging from 34 to 63% (**3k** and **3l**). After a broad scope of *H*-phosphorus oxides was examined, several isocyanides were further evaluated under the standard conditions. Substrates with both electron-deficient and electron-rich substituents on the aromatic ring reacted smoothly with diphenylphosphine oxide to afford the desired products (**3m–s**). We wish to note that thioethers with phenyl, benzyl, and ethyl substituents could be cleaved as well, delivering the corresponding adducts in yields of 48% (**3a**), 79% (**3a**), and 84% (**3s**).

It has been reported previously that aryl or heteroaryl radicals can be generated smoothly from organoboronic acids upon oxidation, such as in the presence of a manganese precursor.[3,4f,6] Therefore, the present system was extended with various organoboronic acids used as aryl, alkenyl, and alkyl radical sources to further explore its utility (Scheme 3). Condition optimizations explained that manganese(III) acetylacetonate exhibits better performance than that of manganese(III) acetate hydrate while changing the radical sources. When

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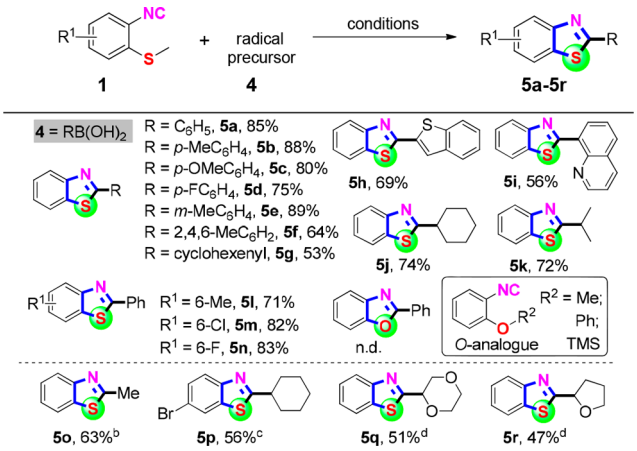
Scheme 3. Substrates Scope on Other Radical Precursors[a]

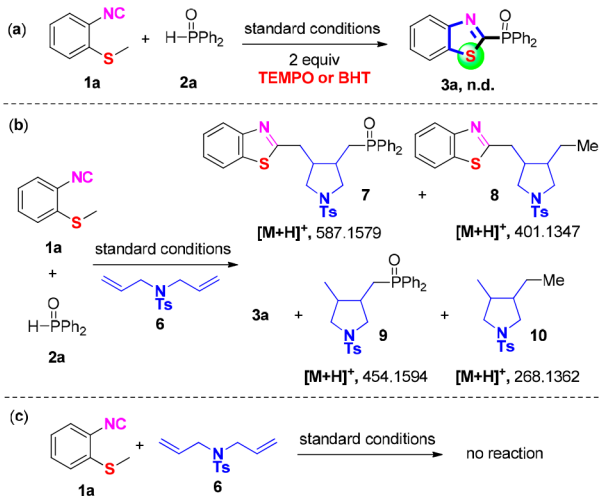


[a]Reaction conditions: 2-isocyanothioanisoles (**1**, 0.2 mmol), organoboronic regents (**4**, 0.4 mmol), $Mn(acac)_3$ (2.0 equiv, 0.4 mmol), 2 mL of toluene, 85 °C, 8 h, N_2, isolated yields. [b]**1** (0.2 mmol), $FeCl_2$ (20 mol %), DCP (3 equiv, 0.6 mmol), 2 mL of PhF, 130 °C, 12 h, N_2. [c]**1** (0.2 mmol), $CuCl_2$ (20 mol %), DCP (3 equiv, 0.6 mmol), 2 mL of cyclohexane, 110 °C, 8 h. [d]**1** (0.2 mmol), BPO (1.2 equiv), 2 mL ether 100 °C, 4 h, N_2.

2 equiv of $Mn(acac)_3$ was used, in general, electronically and sterically diverse boronic acids underwent successful cyclocoupling with (2-isocyanophenyl)(methyl)sulfane (**1**). Substrates with electron-donating and -withdrawing groups, including methyl, methoxy, and fluoro, were effective in affording the product with good yields (**5a−e**). Sterically hindered substrates was also incorporated to examine the reaction efficiency, where the 2,4,6-trimethyl-derived substrate resulted in a significant loss to medium yield (**5f**). Heteroaromatic systems of pentathiophene and quinoline were also compatible with the standard conditions, furnishing the products **5h** and **5i** in yields of 69% and 56%, respectively. It is worth mentioning that alkenyl and alkyl boronic acids also proceeded efficiently with yields ranging from 53% to 74% (**5g,j,k**). In terms of the reaction between phenylboronic acid and different isocyanides, good performance was still demonstrated with retention of good yields (**5l−n**). Note that attempts at cyclization of *O*-analogues containing methyl, phenyl, or TMS groups with phenylboronic acid failed, suggesting that the oxygen group cannot be an appropriate radical acceptor under the current conditions. Other free-radical species were evaluated to expand the application of the method for building 2-substituted benzothiazoles. Although the conditions needed to be altered, to our delight, the radical cascade cyclization of 2-isocyanothioanisoles with DCP (dicumyl peroxide), cyclohexane, or ethers proceeded smoothly to afford the corresponding **5o−r** in medium yields (see the Supporting Information for details).[4c,11]

To gain mechanistic insight into this transformation, several control experiments were conducted, and the results are depicted in Scheme 4. When 2 equiv of radical scavengers, TEMPO or BHT, were added into the model reaction (eq a), the cascade cyclization of isocyanide (**1a**) with diphenylphosphine oxide (**2a**) was completely inhibited, indicating that progress might take place through a radical pathway. Furthermore, *N*-Ts-diallylamine (**6**),[12] which is a well-known phosphoryl radical capturer, successfully trapped all of the key radical intermediates (eq b). The radical cyclization product **7**,

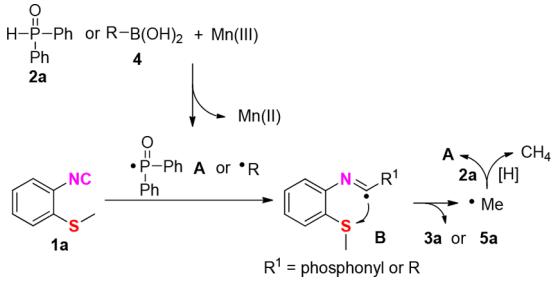
Scheme 4. Control Experiments



resulting from **1a**, **2a**, and **6**, was detected in the high-resolution mass spectrum (HR-MS). Meanwhile, the phosphonyl radical and the released methyl radical spontaneously reacted with *N*-Ts-diallylamine to give the cyclization products (**8−10**). A parallel reaction in equation c strongly supported that the phosphonyl radical initiates the cascade reaction as proposed, instead of imidoyl or methyl radicals.

On the basis of control experiments, as well as previous reports,[4j−o] a plausible mechanism for this radical cascade cyclization is proposed in Scheme 5. First, a phosphonyl radical

Scheme 5. Proposed Mechanism



A is in situ generated from diarylphosphine oxide in the presence of Mn(III) salt.[4m,n,6,13] Subsequently, the radical addition of **A** to the isonitrile functionality in **1a** generates an imidoyl radical (**B**),[2] which is further transformed into product **3a** through imidoyl radical **B** addition to a sulfur atom, along with release of a methyl radical.[8e−h] Finally, the methyl radical is deceased by abstracting a hydrogen from **2a** or the reaction medium. For cyclization with organoboronic acids or alkyl radical precursors, a sequential radical pathway is similarly taken.

In summary, we revealed unprecedented radical cascade reactions of isocyanides via an imidoyl radical addition to a sulfur atom, providing a novel and efficient method for the construction of C2-substituted benzothiazole derivatives from isocyanides, *H*-phosphorus oxides, organoboronic reagents, or alkyl radical precursors with remarkable functional group tolerance and good yields. This strategy features easily accessible substrates, operational simplicity, and expands the pool of imidoyl radical acceptors in organic synthesis.

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■ ASSOCIATED CONTENT

Supporting Information

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

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Notes

The authors declare no competing financial interest.

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