## Ag-Mediated Radical Cyclization of 2-Alkynylthio(seleno)anisoles: Direct Synthesis of 3-Phosphinoylbenzothio(seleno)phenes

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**Supporting Information** 

**ABSTRACT:** A new method for the direct synthesis of 3phosphinoylbenzothio(seleno)phenes has been achieved through an Ag-mediated radical addition–cyclization of 2-alkynylthio-(seleno)anisoles with secondary phosphine oxides in good yields under mild conditions. In this single reaction, benzenethiophene or benzeneselenophene skeleton,  $C(sp^2)$ –P and  $C(sp^2)$ –S bonds can



be constructed with the cleavage of the  $C(sp^3)-S$  bond, highlighting the efficiency and step-economics of this protocol.

**B** enzothiophene moieties are important skeletons that have been widely found in many pharmaceuticals, natural products, and polymers.<sup>1</sup> On the other hand, organophosphorus compounds have attracted tremendous attention because of their broad applications in the fields of organic synthesis, materials science, pharmaceuticals, and ligand chemistry.<sup>2</sup> Therefore, synthesis of diverse phosphinoylbenzothiophenes is highly desirable. However, the reported approaches for the construction of phosphinoylbenzothiophenes were very limited,<sup>3,4</sup> much less for 3-phosphinoylbenzothiophenes.<sup>4</sup> In 2016, visible-light-driven phosphonylation of 3-bromobenzothiophene with triethyl phosphite for the construction of 3-phosphonatebenzothiophene was reported by the König group (Scheme 1a).<sup>4a</sup> However, just one example was given. Subsequently, Cai's group disclosed a reaction

## Scheme 1. Route to 3-Phosphorylbenzothiophenes



between 2-substituted benzothiophenes and trialkyl phosphites for the formation of 3-phosphinoylbenzothiophenes (Scheme 1b).<sup>4b</sup> Nevertheless, a benzothiophene skeleton is required for the formation of target molecules in these above-mentioned reports, which may limit the substrate scope to synthesize more-diverse compounds. Therefore, it still remains a great challenge to develop new approaches for the synthesis of phosphinoylbenzothiophenes.

Nowadays, radical cascade reactions have become one of the most efficient routes for the construction of polycyclic and heterocyclic compounds.<sup>5</sup> Therefore, great development was made for the construction of benzothiophenes via a radical cyclization pathway.<sup>6,7</sup> On the other hand, thioanisole derivatives have been widely used in the radical cyclization process with the release of a methyl group for the construction of heterocyclic compounds.<sup>7,8</sup> As part of our interests in the synthesis of heterocycles through radical cascade processes,<sup>8a,9</sup> we questioned whether a phosphoryl radical could react with 2-alkynylthioanisoles via a radical addition to the sulfur atom, leading to the formation of 3-phosphinoylbenzothiophenes with the construction of benzenethiophene skeleton,  $C(sp^2)$ -P and  $C(sp^2)$ -S bonds in one step (Scheme 1c). However, Agmediated arylphosphine oxide radical annulation of diarylalkynes to synthesize benzo[b]phosphole oxides were wellstudied (Scheme 1d).<sup>10</sup> Therefore, considering the competition between the two reactions, the preparation of 3phosphinoylbenzothiophenes through Ag-mediated 5-exo-trig cyclization was extremely challenging.

To test this hypothesis, methyl(2-(phenylethynyl)phenyl)sulfane (1a) and diphenylphosphine oxide (2a) were chosen as reaction partners to optimize the reaction conditions (Table 1). When 3 equiv of AgOAc was employed as the initiator with HOAc as the solvent, **3a** was obtained in 56% yield after being

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#### Table 1. Optimization of Reaction Conditions<sup>a</sup>



AgOAc (3.0)	$CH_3CN$	35/39
AgOAc (3.0)	DMF	38/48
AgOAc (3.0)	DMSO	trace/0
AgOAc (3.0)	dioxane	19/20
AgOAc (3.0)	HOAc	42/8
AgOAc (3.0)	HOAc	51/15
AgNO <sub>3</sub> (3.0)	HOAc	47/10
$Ag_2CO_3$ (3.0)	HOAc	58/6
Ag <sub>2</sub> O (3.0)	HOAc	73/5
Ag <sub>2</sub> O (3.0)	TFA <sup>e</sup>	81/0
$Ag_2O$ (1.0)	TFA <sup>e</sup>	$78^{b}/0$
Ag <sub>2</sub> O (1.0)	TFA <sup>e</sup>	63/0
$\begin{array}{c} Ag_{2}O(0.2) + Zn(NO_{3})_{2} \cdot 6H_{2}O\\(2.0) \end{array}$	TFA <sup>e</sup>	24/0
$AgNO_{3}(0.1) + Mg(NO_{3})_{2} \cdot 6H_{2}O$ (0.5)	CH <sub>3</sub> CN	25/0
	AgOAc $(3.0)$ AgOAc $(3.0)$ AgOAc $(3.0)$ AgOAc $(3.0)$ AgOAc $(3.0)$ AgOAc $(3.0)$ AgOAc $(3.0)$ AgOAc $(3.0)$ Ag <sub>2</sub> CO <sub>3</sub> $(3.0)$ Ag <sub>2</sub> O $(3.0)$ Ag <sub>2</sub> O $(3.0)$ Ag <sub>2</sub> O $(3.0)$ Ag <sub>2</sub> O $(1.0)$ Ag <sub>2</sub> O $(1.0)$ Ag <sub>2</sub> O $(1.0)$ Ag <sub>2</sub> O $(0.2) + Zn(NO_3)_2 \cdot 6H_2O$ (2.0) AgNO <sub>3</sub> $(0.1) + Mg(NO_3)_2 \cdot 6H_2O$ (0.5)	AgOAc (3.0) $CH_3CN$ AgOAc (3.0) DMF   AgOAc (3.0) DMSO   AgOAc (3.0) dioxane   AgOAc (3.0) dioxane   AgOAc (3.0) HOAc   Ag2CO <sub>3</sub> (3.0) HOAc   Ag <sub>2</sub> O (3.0) HOAc   Ag <sub>2</sub> O (3.0) TFA <sup>e</sup> Ag <sub>2</sub> O (1.0) TFA <sup>e</sup> Ag <sub>2</sub> O (0.2) + Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O TFA <sup>e</sup> Ag <sub>2</sub> NO <sub>3</sub> (0.1) + Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O CH <sub>3</sub> CN   (0.5) CH <sub>3</sub> CN

<sup>*a*</sup>Reaction conditions: **1a** (0.15 mmol), **2a** (0.3 mmol), initiator in solvent (1.5 mL) stirring at 70 °C under argon for 7 h. The yield was determined via <sup>1</sup>H NMR, using CH<sub>2</sub>Br<sub>2</sub> as the internal standard. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>At 90 °C. <sup>*d*</sup>At 50 °C. <sup>*c*</sup>TFA = trifluoracetic acid. <sup>*f*</sup>Under air.

CH<sub>2</sub>CN

trace/0

 $AgNO_3 (0.1) + Na_2S_2O_8 (0.5)$ 

16

heated at 70 °C for 7 h under argon (Table 1, entry 1). Subsequently, various solvents such as CH<sub>3</sub>CN, dimethylformamide (DMF), dimethylsulfoxide (DMSO), and 1,4-dioxane were explored, revealing that HOAc was the best choice (Table 1, entries 2-5). The yield of product 3a decreased when the temperature was increased to 90 °C or reduced to 50 °C (Table 1, entries 6 and 7). By screening other silver salts, such as AgNO<sub>3</sub>, Ag<sub>2</sub>CO<sub>3</sub>, and Ag<sub>2</sub>O, Ag<sub>2</sub>O was revealed to be the most effective and gave 3a in 73% yield (Table 1, entries 8-10). Note that a small amount of benzo[b] phosphole oxides 3a' were detected under these reaction conditions through the process mentioned above (Table 1, entries 1-10).<sup>10</sup> Pleasingly, the side reaction was totally restrained by employing TFA as the solvent with a slight improvement of the yield of 3a (Table 1, entry 11). Moreover, 3a was isolated in 78% yield when the loading of Ag<sub>2</sub>O was reduced to 1 equiv (Table 1, entry 12). In addition, the yield of 3a was decreased to 61% when the reaction was conducted under air (Table 1, entry 13). Finally, the efforts to use catalytic amounts of Ag<sub>2</sub>O in the presence of oxidants such as  $Zn(NO_3)_2 \cdot 6H_2O_1$  $Mg(NO_3)_2$ ·6H<sub>2</sub>O, and  $Na_2S_2O_8$  have not been successful (Table 1, entries 14–16).

With the optimized reaction conditions in hand, we investigated the scope of this Ag-mediated radical cyclization of 2-alkynylthioanisoles, and the results are summarized in Scheme 2. First, various functional groups on the benzene ring A were examined and most of the functional groups were tolerated under the optimized conditions. With electron-donating substituents on benzene ring A, such as methyl, methoxy, ethyl, and phenyl groups, these compounds were obtained in yields of 85%-70%. Halogen atoms such as





<sup>a</sup>Reaction conditions: 1 (0.15 mmol), 2 (0.3 mmol),  $Ag_2O$  (1.0 equiv), in TFA (1.5 mL) stirring under argon at 70 °C for 7 h. <sup>b</sup>Two mmol scale.

fluorine, chlorine, and bromine have little influence under the optimized reaction conditions to afford the corresponding products 3g-3j in moderate to good yields, which could allow for further synthetic transformations. Moreover, the structure of 3h was confirmed by X-ray crystal structure analysis. Note that electron-withdrawing substituents such as CF<sub>3</sub> on the benzene ring A influenced the radical cyclization significantly by providing product 3k only in 35% yield. Compounds with functional groups such as halogen atoms and CF<sub>3</sub> on the benzene ring B were also examined and afforded the corresponding products 31-3n in good yields. In addition, compounds with the thienyl group could also provide the expected products 30 and 3p in acceptable yields. Moreover, the reactions between substituted phenylphosphine oxides 2 and 1a were also examined and gave the corresponding products 3q-3s in yields of 62%-56%. No desired products were obtained when aliphatic alkynes was employed as exemplified by 3t.

Pyridyl-based compounds also were examined; however, no desired product 3u was isolated, which might be due to the formation of ammonium salt in the strong acid TFA to restrain the reaction.

Moreover, benzoselenophenes have also been applied in medicinal chemistry and organic synthesis, as well as materials science.<sup>11</sup> For this reason, we extended the scope of application of this protocol by preparing benzoselenophenes stemming from 2-alkynylselenoanisoles **4** and secondary phosphine oxides **2** under the optimal reaction conditions (see Scheme 3). In the beginning, some substituted phenylphosphine oxides were examined and afforded the corresponding desired

# Scheme 3. Scope for the Formation of 3-Phosphinoylbenzoselenophenes $^{a}$



<sup>*a*</sup>Reaction conditions: 4 (0.15 mmol), 2 (0.3 mmol),  $Ag_2O$  (1.0 equiv), in TFA (1.5 mL) stirring under argon at 70 °C for 7 h.

products in good yields (5a-5c). Moreover, ethyl phenylphosphinate and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) also could be used in the transformation (5d, 5e). With electron-donating (methyl) or electronwithdrawing (fluorine) substituent groups on the aromatic rings of 2-alkynylselenoanisoles, these compounds reacted smoothly and provided products 5f-5h in good to moderate yields. However, no desired product (5i) was afforded when the Se atom in compound 4a was replaced by an O atom.

In order to investigate the reaction mechanism, several control experiments were performed. In the beginning, radical trapping experiments were conducted to validate our original design of the radical cyclization process (Scheme 4a). The





reaction was totally inhibited when 1.5 equiv of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) was added to the reaction, and the yield of 3a was shut down when butylated hydroxytoluene (BHT) was employed. These results indicated the Ag-mediated annulation might proceed via a radical pathway. Notably, when the methyl group at the S atom was changed to ethyl and phenyl groups, 3a was also obtained in yields of 60% and 34%, respectively (see Schemes 4b and 4c). Moreover, benzene was detected by gas chromatographymass spectrometry (GC-MS) from the reaction mixtures when **lac** was employed as the substrate. In addition, to further support the mechanism, the labeling experiment by using deuterated TAF (d-TAF) as the solvent was performed under the optimized reaction conditions (see Scheme 4d). Gladly, **3a** was obtained in 38% yield and  $d_1$ -benzene was detected by GC-MS. The results indicated the benzene might be produced from phenyl radical via H-abstraction from the solvent.

In accordance to the control experiments and corresponding literature reports, a tentative pathway was proposed for the Agmediated transformation (see Scheme 5). Initially, diphenyl-

#### Scheme 5. Proposed Mechanism



phosphine oxide 2a reacts with Ag<sub>2</sub>O to form the phosphoryl radical I, which selectively attacks the triple bond of 1a to give the vinyl radical II. The resulting vinyl radical II participates in a 5-*exo-trig* cyclization with SMe moiety to generate the product 3a, along with the release of a methyl radical. Finally, methane is generated from the methyl radical via a *H*-abstraction process from the reaction mixture.

In summary, we have successfully developed an efficient protocol for the direct synthesis of 3-phosphinoylbenzothio-(seleno)phenes through an Ag-mediated radical addition-cyclization of 2-alkynylthio(seleno)anisoles with secondary phosphine oxides involving the formation of thiophene or selenophene skeleton,  $C(sp^2)$ -P and  $C(sp^2)$ -S bonds and the cleavage of the  $C(sp^3)$ -S bond. This protocol features good functional group tolerance and easy handling with good yields under mild conditions.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b01510.

General procedure, characterization data, <sup>1</sup>H, <sup>13</sup>C <sup>31</sup>P, and <sup>19</sup>F NMR spectra (PDF)

## **Accession Codes**

CCDC 1892103 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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