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Cascade and Effective Syntheses of Functionalized Tellurophenes

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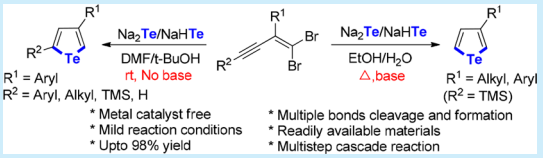
Supporting Information

ABSTRACT: A one-pot and transition-metal-catalyst-free synthetic strategy to construct functionalized tellurophenes has been developed. Substituted 1,1-dibromo-1-en-3-ynes are smoothly converted to tellurophenes with telluride salts in high yield via a series of cascade reactions through reductive debromination, hydrotelluration, nucleophilic cyclization, and aromatization. Close inspection of the results clearly showed that the reactivity of in situ prepared telluride salts are significantly influenced by the polarity of the solvent system and the electronic nature of the substituent on the enyne substrate. This method reports the first direct synthesis of 3-aryltellurophenes in high yields at room temperature. This novel reaction strategy is also found to be a promising synthetic method for multisubstituted tellurophenes and selenophenes.



Functionalized chalcogenophenes are an important class of compounds due to their wide range of applications in the fields of biochemistry, electrochemistry, and materials science.[1,2] Swapping of lighter chalcogenophenes with heavier tellurophenes for conjugated polymers has become popular in recent years, attracted by the advantages gained on red-shifted optical absorption and enhanced polarizability.[3] It is also evident, from the emerging reports, tellurophenes are captivating elevated recognition, over the widely accepted thiophene counterparts, as potential new and better optoelectronic materials due to their exceptional LUMO energy level stabilizations, lower optical band gaps, strong $\pi-\pi$ interactions, and high charge carrier mobility.[4] Although functionalized tellurophenes are highly desired by the scientific community, there remains a scarcity for a direct and customized method to prepare polysubstituted tellurophenes. Most commonly used synthetic methods for substituted tellurophenes are metal-catalyzed cross-coupling reactions with 2- and/or 5-functionalized tellurophenes, cyclization of substituted 1,3-diynes with telluride salts, and cyclization reaction of (*Z*)-telluroenynes with diorganoyl dichalcogenides.[5] However, these methods are only useful for making 2- and/or 5-substituted tellurophenes, but not for 3-substituted tellurophenes, which are greatly desirable for making highly conductive, conjugated poly(3-substituted tellurophene)s. It is conceivable that 3-alkyl- or 3-aryl-substituted tellurophenes can be prepared from 3-bromo- or 3-iodo-tellurophenes via metal-catalyzed cross-coupling reactions. However, the preparation of 3-bromotellurophene requires a complicated and multistep procedure via a series of novel intermediates such as 2,3,4,5-tetrakis(pinacolboronate)-zirconacyclopentadiene, 2,3,4,5-tetrakis(pinacolboronate)-tellurophene, and then 3-(pinacolboronate)tellurophene (Scheme S1a, Supporting Information (SI)).[6] Likewise, 3-iodo-tellurophene has to be prepared from 1,3-butadiyne and 1,2-dibutylditellane via butyltelluroenyne (Scheme S1b, SI).[5f] Alternatively, Catel *et al.* and Seferos *et al.* have demonstrated the synthesis of 3-alkyltellurophenes via 2-alkyl-1-chlorobut-3-yn-2-ol intermediate by a ring-closing reaction with NaHTe/Na_2Te that can place the desired alkyl group directly in the 3-position with low overall yields (<35%).[7b] However, these methods require the use of an expensive Weinreb amide (i.e., 2-chloro-*N*-methoxy-*N*-methylacetamide) as the starting material (Scheme S1c, SI).[7] Thus, there is still a lack of rapid and facile synthetic methods for the highly demanding 3-alkyl- and 3-aryl-substituted tellurophenes. Herein, a novel method is presented for the synthesis of 3-functionalized and 2,4-difunctionalized tellurophenes from easily made substituted 1,1-dibromo-1-en-3-ynes and telluride salts (Na_2Te/NaHTe) under mild conditions with high yields.

We have conceived that versatile 3-alkyl and 3-aryl tellurophenes can be prepared easily from the functionalizable enynes **1**, via cyclization with telluride salts. The enyne precursor, e.g., (3-(dibromomethylene)oct-1-yn-1-yl)trimethylsilane **1i**, can be synthesized by the modified literature methods,[8] and the telluride salts (Na_2Te/NaHTe) can be prepared from the reduction of Te metal with sodium borohydride in an alcoholic solvent, such as ethanol.[7] Our initial attempts to react the precursor **1i** with the telluride salts in ethanol at 75 °C, however, failed to yield 3-*n*-pentyltellurophene, but only resulted in the desilylated and monodebrominated product **3i′** (entries 1 and 2, Table 1). As desilylations can happen easily in alcoholic solvents under basic conditions, it is obvious that deprotection of the TMS group might be the first step in the reaction of **1i** with Na_2Te/NaHTe in ethanol. Furthermore, monodebromination of geminal dibromo-cyclopropanes and 1,1-dibromoalkenes can occur smoothly with telluride salts (Na_2Te/NaHTe) in ethanol even at 50 °C.[9,10] It is expected that monodebromination might be the next step in the reaction of **1i** with telluride salts at 75 °C. Therefore, desilylated and monodebrominated product **3i′** would be the key intermediate in the reaction of **1i** and telluride

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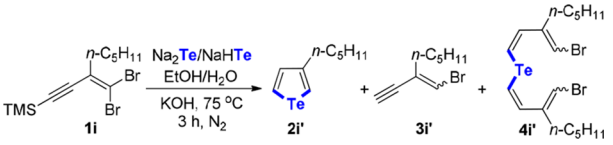
Table 1. Optimization Studies for 3-Substituted Tellurophenes[a]

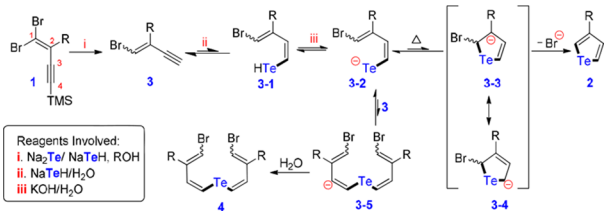


entry	Na_2Te/NaHTe (equiv)	base (equiv)	H_2O (ratio)	yield[b] (%) 2i′	3i′	4i′
1	1.2	–	–	–	81	–
2	2.5	–	–	–	84	–
3	2.5	KOH (2.0)	–	–	85	–
4	2.5	KOH (2.0)	H_2O (10%)	32	27	26
5	3.0	KOH (2.0)	H_2O (10%)	63	–	27
6	3.0	KOH (2.0)	H_2O (20%)	76	–	18
7[c]	3.0	KOH (2.0)	H_2O (30%)	62	–	32
8	3.0	NaOH (2.0)	H_2O (20%)	69	–	19
9[d]	3.0	KOH (2.0)	H_2O (20%)	–	77	–
10	3.0	–	H_2O (20%)	–	82	–

[a]Reaction conditions: **1i** (1.0 equiv), Na_2Te/NaTeH, base, and H_2O (ratios are as mentioned in the table), 75 °C, 3 h, N_2. [b]Isolated yield. [c]Reaction mixture was opaque. [d]At room temperature.

salts in ethanol at 75 °C (**3**, Scheme 1). To further promote the subsequent hydrotelluration and cyclization of the intermediate

Scheme 1. Mechanistic Rationalization



3i′, a stronger base like KOH was added in the reaction; and to our disappointment, it somewhat failed to promote any observable reaction between telluride salts and intermediate **3i′** (entry 3, Table 1). Interestingly, when we added a small amount of water (10%) as a cosolvent in the reaction medium along with KOH, the reaction between telluride salt(s) and intermediate **3i′** can be effectively triggered on to furnish the desirable cyclized compound, 3-*n*-pentyltellurophene **2i′**, in 32% yield together with a competing dimeric byproduct **4i′** (26%) (entry 4, Table 1). By increasing the telluride reagent usage from 2.5 to 3 equiv, the reaction of **3i′** can be driven to completion and could afford 63% of 3-*n*-pentyltellurophene **2i′** (entry 5, Table 1). The use of H_2O cosolvent in 20 vol % gave the best yield of **2i′** (76%; entry 6, Table 1). A Further increase in H_2O cosolvent up to 30 vol % caused the reaction solution to be opaque and somehow led to an increase in dimeric product **4i′** (32%) by sacrificing the desired cyclized product **2i′** (62%; entry 7, Table 1). Apparently, the cyclized product and the dimerized product went through a common intermediate. Also a change in the usage of base did not show any considerable effect in the conversion (entry 8, Table 1). In the presence of 20 vol % of H_2O cosolvent, control experiments were performed (entries 9–10, Table 1), and it is confirmed that use of both elevated temperature (75 °C) and strong base (KOH) are needed to trigger the reactions between telluride salts and **3i′** (for both cyclization and dimerization reactions).

To further understand the results and reaction behaviors, a preliminary mechanistic rationalization is depicted in Scheme 1. As discussed above, the first stage reactions for the formation of the compound **3** (via desilylation and reductive debromination) can be easily accomplished at 75 °C in ethanol with the telluride salts alone. While, the second stage reactions for the formation of the cyclized product **2** (via hydrotelluration, cyclization, and aromatization) and the dimerized byproduct **4** (via hydrotelluration and dimerization) have to rely on the H_2O cosolvent plus KOH to turn on the reactions. Since Te and H have the same electronegativity of 2.1 and H_2O has a similar pK_a (15.7) as ethanol (pK_a = 16.0), we have hypothesized that the main benefit provided by the H_2O cosolvent might be due to its much higher dielectric constant (ε = 79 vs 25 of ethanol), which helps to polarize the Te–H covalent bond in the telluride salt (NaTeH) or in the organic tellurol (e.g., intermediate **3-1**, Scheme 1), which in turn leads to the increased negative charge (thus with enhanced nucleophilicity) on the telluride center and the increased positive charge (thus with increased acidity) on the tellurol proton, similar to the renowned polarization effect of an approaching nucleophile has on a C–I bond (cf. both C and I have the same electronegativity of 2.5). The increased nucleophilicity of the telluride salt (NaTeH) could trigger the hydrotelluration with the alkyne group of **3**, to afford the organotellurol (intermediate **3-1**, Scheme 1), while the increased acidity of the tellurol proton should allow the KOH base to deprotonate intermediate **3-1** more effectively to form the organotelluride anion **3-2**, which in turn triggers the nucleophilic cyclization (forming **3-3**, Scheme 1) or the dimerization (forming **3-5**, Scheme 1). As the amount of H_2O cosolvent increased to 30 vol %, the resultant solution became cloudy caused by the aggregation of water-insoluble enyne **3**. The enriched local concentration of enyne **3** would naturally lead to a higher amount of dimerized byproduct **4** over the cyclized tellurophene **2**.

Although substantial studies are needed to confirm and finalize the actual reaction mechanism, the current mechanistic deduction did provide us with many useful guidelines for understanding and even improving the synthetic strategy. For example, based on the preliminary mechanistic scheme, it is conceivable that the efficiency of the cyclization path can be further improved, if the stability of the initially formed allylic anion (intermediate **3-3**, Scheme 1) can be further enhanced, e.g., by introducing an additional electron resonance effect, via replacing the alkyl group of **1i** with an aryl or a heteroaryl group. Indeed, when the *n*-pentyl group of **1i** was replaced with a phenyl group (as in **1a**), the desired cyclized product **2a′** was obtained exclusively in 96% yield, consistent with our hypothesis. Furthermore, we found that this synthetic method is also extendable to other aryl and heteroaryl substituted enynes, providing a simple and efficient way for making 3-alkyl and 3-aryltellurophenes (Scheme 2, **2a′–j′**). With the aforementioned results in hand, it is easy to envisage that the reactivity of telluride salts with compound **1** could be greatly influenced by the polarity of the solvent and the reaction temperature. To further understand and expand the scope of the reaction, we chose DMF as the reaction solvent, which can better dissolve enynes compared H_2O and has a higher dielectric constant (ε = 37) and a higher boiling point than

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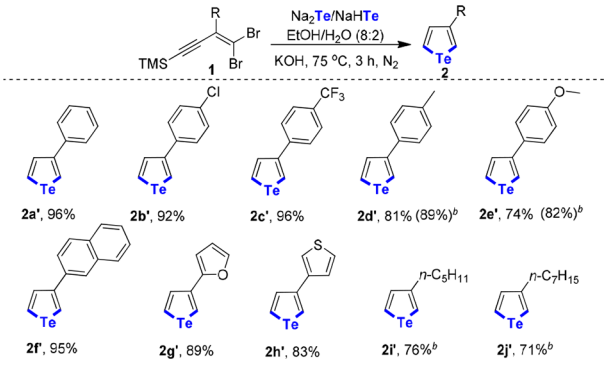
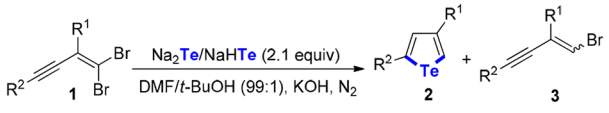
Scheme 2. Preparation of 3-Substituted Tellurophenes[a]



[a]Reaction condition: **1** (1.0 equiv), Na_2Te/NaHTe (3.0 equiv), EtOH/H_2O (8:2), KOH (2.0 equiv), 75 °C, 3 h. [b]For 8 h. See SI for detailed procedures. Isolated yields of products are given.

ethanol, and using *t*-BuOH (in 1 vol %) as the acidic proton source for making the telluride salts. Our initial trials with compound **1i** in the presence of KOH were indeed free of the dimeric byproduct **4i′** (due to its better dissolution power than H_2O), but a higher reaction temperature is required (probably due to its lower dielectric constant than that of H_2O) for obtaining a moderate yield of tellurophene **2i′** (0% at rt, 32% at 75 °C, 78% at 140 °C; entries 1−3, Table 2).

Table 2. Optimization Studies for 2,4-Substituted Tellurophenes[a]



entry	**1** (R^1/R^2)	temp/time/KOH (°C/h/equiv)	yield[b,c] (%) **2**	**3**
1	**1i** (*n*-pentyl/TMS)	25/2/2	–	**3i′** (82)
2	**1i** (*n*-pentyl/TMS)	75/2/2	**2i′** (32)	**3i′** (44)
3	**1i** (*n*-pentyl/TMS)	140/2/2	**2i′** (78)	–
4	**1a** (Phenyl/TMS)	140/0.5/2	**2a′** (97)	–
5	**1s** (Phenyl/*tert*-butyl)	140/0.5/2	**2s** (91)	–
6	**1s** (Phenyl/*tert*-butyl)	25/0.5/2	**2s** (52)	**3s** (36)
7	**1s** (Phenyl/*tert*-butyl)	25/20/2	**2s** (87)	–
8	**1s** (Phenyl/*tert*-butyl)	25/2/–	**2s** (31)	**3s** (54)
9	**1s** (Phenyl/*tert*-butyl)	25/48/–	**2s** (81)	–
10	**1i** (*n*-pentyl/TMS)	25/20/–	–	**3i′** (71)
11	**1i** (*n*-pentyl/TMS)	140/6/–	**2i′** (41)	**3i′** (32)
12	**1a** (Phenyl/TMS)	25/1/–	**2a** (47)	–
13	**1e** (4-MeOPh/TMS)	25/2/–	**2e** (39)	–
14	**1f** (2-naphth/TMS)	25/2/–	**2f** (42)	–
15	**1k** (Phenyl/Phenyl)	25/1/–	**2k** (98)	–

[a]Reaction conditions: **1** (1.0 equiv), Na_2Te/NaTeH (2.1 equiv), KOH, time and temp (values are as mentioned in the table), N_2. [b]Isolated yield. [c]Products with prime symbol (′) are TMS deprotected (i.e., with R^2 = H).

As anticipated, compound **1a** with an electron-resonance phenyl group at the 2-position could stabilize the intermediate **3-3** (Scheme 1) and, thus, facilitate the formation of the desired product **2a′** in 97% yield under the same reaction conditions in a shorter time (0.5 h; entry 4, Table 2). As deprotection of the acetylenic TMS group always occurred in the initial stage under the above reaction conditions, it is understood that terminal dibromo-enyne can undoubtedly undergo reactions with telluride salts under the appropriate conditions to afford 3-substituted tellurophenes. However, desilylation is not the requisite step for the cyclization with telluride salts to occur, because a structurally similar dibromo-enyne of **1s**, having a 2-phenyl substituent and a 4-*tert*-butyl group, could readily react with telluride salts under the same reaction conditions to give cyclized 2-*tert*-butyl-4-phenyltellurophene **2s** in 91% yield (entry 5, Table 2). The studies further indicated that the cyclization of **1s** with telluride salts was achievable even at room temperature in the presence of KOH to afford **2s** in 52%−87% yields (0.5−20 h) (entries 6 and 7, Table 2). Apparently, the electron resonance effect of the 2-phenyl group had greatly facilitated the cyclization, and the steric effect of the 4-*tert*-butyl group could at most only slow down the cyclization rate but not prevent it from happening. Most interestingly, we found that the cyclization of **1s** with the telluride salts could also proceed at 25 °C even before the addition of KOH, though at a slower pace. Further detailed studies indicated that telluride salts can cyclize **1s** at room temperature in the absence of KOH with prolonged time (2−48 h) to form **2s** in 31%−81% yields (entries 8 and 9, Table 2). The same favorable reaction behaviors however failed to occur in the case of **1i**. Even with a prolonged reaction time (20 h) at rt in the absence of KOH, it totally failed to undergo cyclization, but only yielded the monodebrominated and silylated compound in 71% yield (entry 10, Table 2). Although the cyclization reaction of **1i** in the absence of KOH could be promoted at the elevated temperature of 140 °C, the yield was still rather poor (41%; entry 11, Table 2). These results reconfirmed that the electronic nature of the substituent group at the 2-position of the dibromo-enynes also plays a very important role. With these findings, we have further conceived that syntheses of 2-silyl-4-aryltellophenes might be feasible in the DMF medium at low temperatures in the absence of a strong desilylating reagent such as KOH. Thus, the cyclization of the 2-aryl-substituted and 4-silyl-substituted enynes of **1a** (R^1 = phenyl), **1e** (R^1 = 4-methoxyphenyl), and **1f** (R^1 = 2-naphthyl) were conducted, which all gave fair yields (40−50%) of 4-aryl-2-silyltellurophenes (**2a**, **2e**, and **2f**; entries 12−14, Table 2) within 2 h at rt.

Interestingly, when both substituents are phenyl groups, as in **1k**, telluride salts can smoothly cyclize **1k** at rt without KOH in 1 h to yield **2k** in 98% yield (entry 15, Table 2). The scope of dibromo-enynes was further examined (Scheme 3), revealing the cyclization of diaryl-substituted dibromo-enynes with telluride salts occurred very smoothly at rt without KOH, regardless of the electronic nature of the substituents on the aryl groups; the corresponding products were obtained in good to excellent yields in 1 h (89−98%, **2k−r**, Scheme 3). In the case of the 2-aryl and 4-alkyl disubstituted enynes, the cyclization could still proceed in DMF at rt without KOH, but at a slower pace to give moderate yields (39%−81%, **2a**, **2e**, **2f**, and **2s**; 2−48 h, Scheme 3). Likewise, the monosubstituted 3-aryltellurophenes can also be prepared in moderate yields (82−84%, **2t−u**, Scheme 3) from the corresponding 2-aryl

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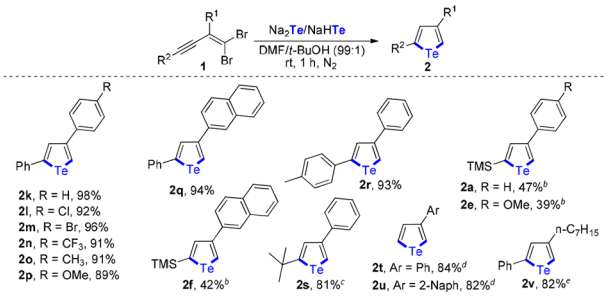
Scheme 3. Preparation of Substituted Tellurophenes at rt[a]

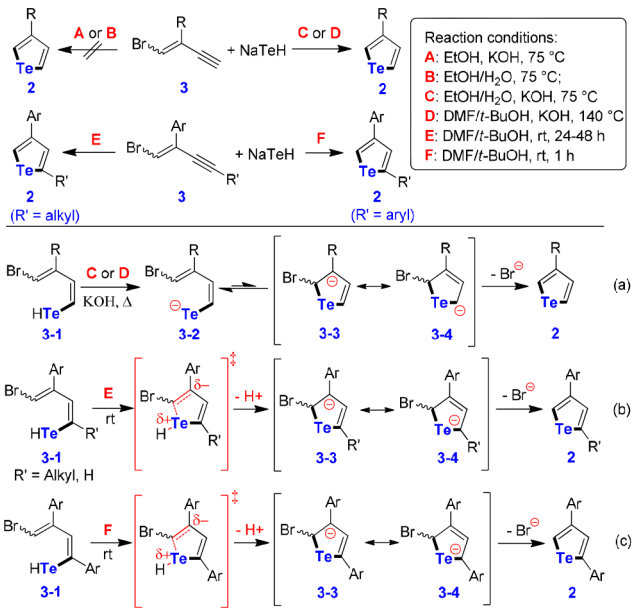


[a]Reaction conditions: **1** (1.0 equiv), $Na_2Te/NaHTe$ (2.1 equiv), DMF/*t*-BuOH (99:1), rt, 1 h. [b]For 2 h. [c]For 48 h. [d]For 24 h. [e]KOH (2.0 equiv), 140 °C for 3 h. See SI for detailed procedures. Isolated yields of products are given.

monosubstituted enyne in DMF without KOH at rt in 24 h. In contrast, the cyclization of 2-alkyl and 4-aryl disubstituted enyne (**1v**) to form **2v** (Scheme 3), however, requires the use of both KOH and elevated temperature (e.g., 140 °C) in DMF. These results suggest that the electron resonance stabilization effect for the initially formed anion at C2 is the key control factor and the additional electron resonance stabilization effect at C4 can also further facilitate the cyclization.

In summary, the cyclization of 2-alkyl-substituted enynes with NaTeH can be best performed by the use of a polar solvent (i.e., DMF or the cosolvent of H_2O/EtOH) at high temperature (140 or 75 °C respectively) with strong base KOH (Scheme 4; conditions A–D), while the same cyclization of 2-

Scheme 4. Reaction Conditions and Mechanistic Implications



aryl-substituted enynes can be readily performed in DMF at rt without KOH (Scheme 4; conditions E and F). The vastly different reaction behaviors may be accountable by our preliminarily proposed mechanisms (Schemes 1 and 4). The cyclization between enynes and NaTeH may be preceded first by a hydrotelluration to form the organotellurol (intermediate **3-1**, Scheme 4), followed by the nucleophilic addition of the tellurol to the C1 of the vinyl bromide moiety to form an anion species at C2 (intermediate **3-3**, Scheme 4), which would be destabilized by an electron-donating 2-alkyl group, but stabilized by an electron-resonance 2-aryl group. Thus, the cyclization of a 2-alkylated-enyne required the use of a much stronger nucleophile, i.e., the organotelluride **3-2** (Scheme 4), while the same cyclization of a 2-arylated-enyne can be done with a much weaker nucleophile, such as organotellurol **3-1** (Scheme 4b and 4c).

The DFT calculations also clearly indicated that the replacement of the 2-alkyl group (as in $\mathbf{A_I}$; Figure S1a, SI) with a 2-phenyl group (as in $\mathbf{B_I}$; Figure S1b, SI) would help to lower the ΔG of the cyclization reaction by 1.8 kcal/mol. The DFT calculations for the hypothetical transition states **TS1** and **TS2** (Figure S2, SI; starting from the corresponding organotellurols to the respective tellurophenes) indeed confirming that the 2-alkyl-substituted **TS1** is far more unstable than the 2-phenyl-substituted **TS2** by 5.5 kcal/mol in gas phase. Alternatively, the cyclization reaction can also be well explained by considering $S_NV\sigma$ and $S_NV\pi$ mechanism modes (see SI for detailed explanation and references).

In conclusion, we have successfully developed a new and effective method for the syntheses of a wide variety of 3-substituted and 2,4-disubstituted tellurophenes. Our preliminary studies indicated that this methodology can also be extended to prepare selenophene analogs (see Scheme S2, SI). Furthermore, research in synthesizing other chalcogeno-heterocycles by using this novel methodology is underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00279.

Experimental procedures and characterization of products (PDF)

Accession Codes

CCDC 1581863–1581864 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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