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In Situ Formation of RSCl/ArSeCl and Their Application to the Synthesis of 4-Chalcogenylisocumarins/Pyrones from *o*-(1-Alkynyl)benzoates and (*Z*)-2-Alken-4-ynoates

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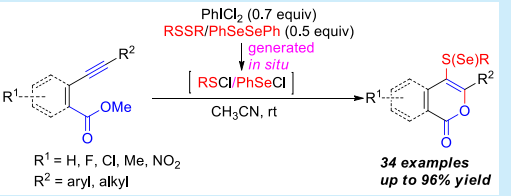
Supporting Information

ABSTRACT: The reaction of diorganyl disulfides or diselenides with $PhICl_2$ in acetonitrile was found for the first time to lead to the in situ formation of organosulfenyl chloride or selenenyl chloride, which enables the regioselective intramolecular chalcogenylacyloxylation of alkynes resulting in the formation of 4-chalcogenylisocumarins/pyrones in good to excellent yields under metal-free conditions.



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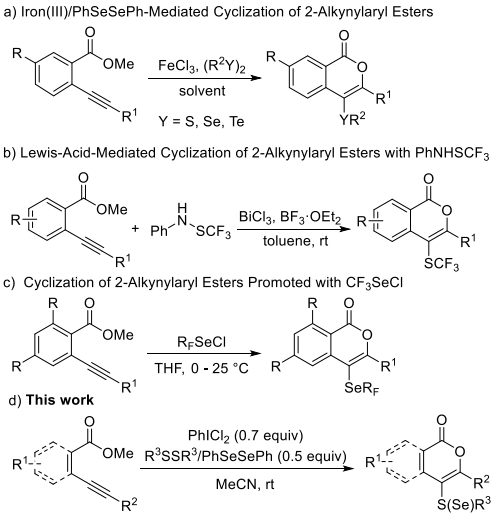
Organosulfenyl chlorides or selenenyl chlorides are versatile reagents in organic synthesis. They are commonly used to install a chalcogenyl group into various organic substrates, which can be further derivatized.[1−10] In addition, they have also been widely employed to conduct a large range of synthetic transformations.[11−16] Because of the significant usefulness of these compounds, many methods for their synthesis have been reported.[17−26] Among these approaches, the most general methods include passing chlorine gas directly through a solution of thiophenol[17] or disulfide/diselenide,[24] reacting diphenyl disulfide/diselenide with sulfuryl chloride,[18,22,23] and chlorinating thiophenol with NCS.[16,21,27] It is noteworthy that on many occasions, rather than preparing these organochalcogenyl chloride reagents in advance, protocols utilize in situ formation of such reactive reagents, for example, from the reaction of the corresponding thiol and *N*-chlorosuccinimide (NCS)[16,21,27] or disulfide/diselenide and SO_2Cl_2.[19]

Isocoumarins[28−30] and pyrones,[31,32] the core structures of many naturally occurring compounds, have been found to display a broad spectrum of biological activities including antimicrobial,[33−35] androgen-like,[36] phytotoxic,[37] antifungal,[38,39] and pheromonal[40] effects. On the other hand, the past decade has witnessed a growing interest in organochalcogenide compounds, since the installation of chalcogen functional groups into organic molecules can significantly improve their physical and chemical features as well as enhance their biological activities.[41−46]

In this regard, the development of new and efficient protocols for the synthesis of chalcogen-substituted isocoumarins or pyrones has received substantial attention during the last decades.[47−59] In 2011, Zeni's group[49] reported an $FeCl_3$-mediated cyclization of alkynylaryl esters with different diorganyl dichalcogenides to afford 4-organochalcogenyl isochromenones in good yields (Scheme 1, method a).

Scheme 1. Existing Strategies for the Synthesis of 4-Chalcogenylisocoumarins



Furthermore, in 2014, Ding and co-workers[55] reported incorporation of the CF_3S- group into the isocoumarin scaffold through an electrophilic cyclization of *o*-(1-alkynyl)-benzoates with trifluoromethanesulfanylamide in the presence of $BiCl_3$ and $BF_3{\cdot}Et_2O$ (Scheme 1, method b). However, these two methods require the inevitable use of a stoichiometric amount of the heavy metal for a complete reaction. Among the synthetic approaches, the intramolecular electrophilic addition of PhSeCl/PhSCl to *o*-(1-alkynyl)benzoates and (*Z*)-2-alken-4-ynoates has been the most extensively explored method to construct such types of interesting molecules. For example, in

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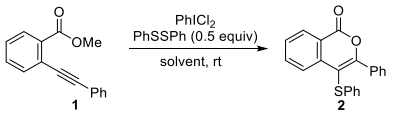
2018, Billard[58] realized the synthesis of fluoroalkylselenolated isocoumarins using CF_3SeCl or other fluorinated selenenyl chlorides (Scheme 1, method c). In addition, Melen and coauthors[52] reported that the reaction of diynyl esters and PhSeCl initially leads to the formation of isocoumarin and then to a tetracyclic skeleton with an isocoumarin subunit fused to a benzoselenopyran. Nevertheless, due to the unstable properties of organosulfenyl chlorides or selenenyl chlorides which are also costly and not easily available, both the synthesis and application of these reagents are often troublesome and require harsh conditions. Herein, we report a metal-free and atom-economical protocol to the synthesis of 4-chalcogenyl isocoumarins through regioselective intramolecular cyclization of alkynes with organosulfenyl chlorides or selenenyl chlorides generated in situ from unactivated disulfides or diselenides and $PhICl_2$, an easily prepared and nontoxic hypervalent iodine reagent (Scheme 1, method d).

Utilization of sulfenyl chlorides generated in situ from the reaction of RSSR/ArSeSeAr and $PhICl_2$ is of general significance since it avoids the direct use of moisture-sensitive RSCl/ArSeCl. Screening of the reaction conditions was initiated by reacting *o*-alkynylbenzoates **1a** with sulfenyl chlorides formed in situ by the above one-pot protocol. Considering both the two phenylthio moieties in diphenyl disulfide (PhSSPh)[60] could be incorporated into the final product, 0.5 equiv of diphenyl disulfide was introduced into the reaction system. To our delight, when a mixture of **1a** (0.5 mmol) with $PhICl_2$ (1.0 equiv) and diphenyl disulfide (0.5 equiv) in MeCN (5 mL) was stirred at rt, **2a** was obtained in a yield of 79% (Table 1, entry 1). In order to further improve the outcome of the reaction, other parameters including oxidant, solvent, and oxidant loading were screened. All attempts to perform the reaction with other oxidants including PIDA, PIFA, DDQ, Oxone, and *m*-CPBA failed to give the desired product (Table 1, entries 2–6). Next, a series of solvents including methanol, EtOAc, dioxane, toluene, DMF, THF, and DCE were surveyed; however, none of them provided superior results to MeCN (Table 1, entries 7–13). It was gratifying to find that when the loading of $PhICl_2$ was reduced from 1.0 to 0.7 equiv, an increase in yield was observed (Table 1, entries 14–16). Further reduction of the oxidant loading to 0.6 or 0.5 equiv proved to be inefficient (Table 1, entries 17 and 18). It is noteworthy that all of the reactions were carried out at rt and under air atmosphere. Finally, the optimized conditions were confirmed to be 1.0 equiv of 2-alkynoate **1a**, 0.7 equiv of $PhICl_2$, and 0.5 equiv of PhSSPh in CH_3CN at rt (Table 1, entry 16).

Table 1. Optimization of Reaction Conditions[a]



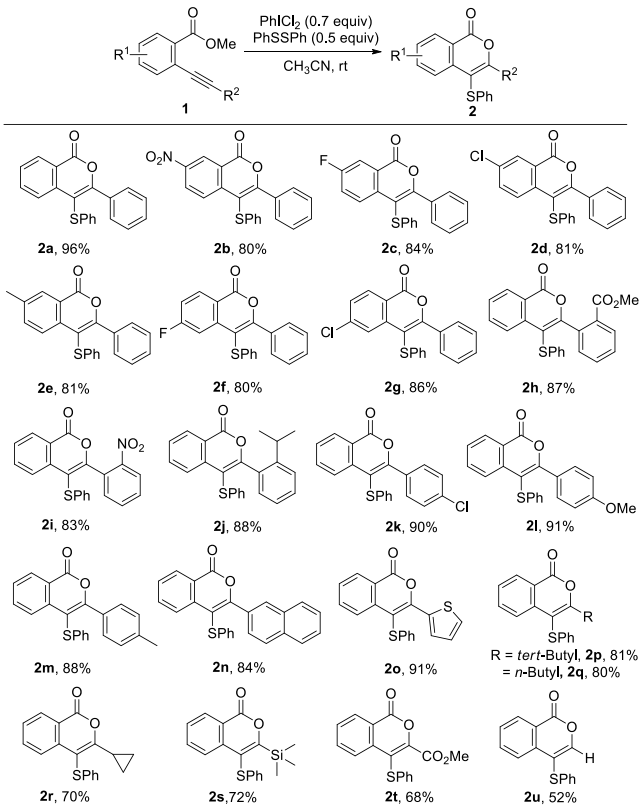
1 2

entry	oxidant (equiv)	solvent	yield[b] (%)
1	$PhICl_2$ (1.0)	CH_3CN	79
2	PIDA (1.0)	CH_3CN	ND
3	PIFA (1.0)	CH_3CN	ND
4	DDQ (1.0)	CH_3CN	ND
5	oxone (1.0)	CH_3CN	ND
6	*m*CPBA (1.0)	CH_3CN	ND
7	$PhICl_2$ (1.0)	MeOH	65
8	$PhICl_2$ (1.0)	EtOAc	72
9	$PhICl_2$ (1.0)	dioxane	ND
10	$PhICl_2$ (1.0)	toluene	67
11	$PhICl_2$ (1.0)	DMF	45
12	$PhICl_2$ (1.0)	THF	15
13	$PhICl_2$ (1.0)	DCE	75
14	$PhICl_2$ (0.9)	CH_3CN	84
15	$PhICl_2$ (0.8)	CH_3CN	90
16	**$PhICl_2$ (0.7)**	**CH_3CN**	**96**
17	$PhICl_2$ (0.6)	CH_3CN	89
18	$PhICl_2$ (0.5)	CH_3CN	80

[a]Reaction conditions: **1a** (0.5 mmol), PhSSPh (0.25 mmol), and oxidant in solvent (5 mL) for 30 min. [b]Isolated yields.

With the optimal reaction conditions established, we next examined the scope of the reaction by subjecting various *o*-alkynylbenzoate derivatives **1** to the standard conditions (Scheme 2). The effect of different substituents R^1 was first explored. Substrates with either an electron-donating methyl group or electron-withdrawing groups including F, Cl, and NO_2 substituted on the aromatic ring of the *o*-alkynylbenzoate **1** all reacted smoothly with PhSSPh under the optimized conditions, giving the corresponding products **2a–g** in good to excellent yields. Next, substitution of the alkyne motif R^2 was also investigated. To our delight, the reaction worked well with both aryl- and alkyl-substituted functional groups to generate the cyclized products **2h–p** in yields of 70–90%. Interestingly, the electronic nature of these substituents or steric effects did not have an obvious impact on the outcome of the reaction.

Scheme 2. $PhICl_2$/PhSSPh-Mediated Synthesis of Sulfenylated Isocoumarins[a]



[a]Reaction conditions: **1** (1.0 mmol), PhSSPh (0.5 mmol), and $PhICl_2$ (0.7 mmol) in CH_3CN (10 mL) for 30 min, isolated yields.

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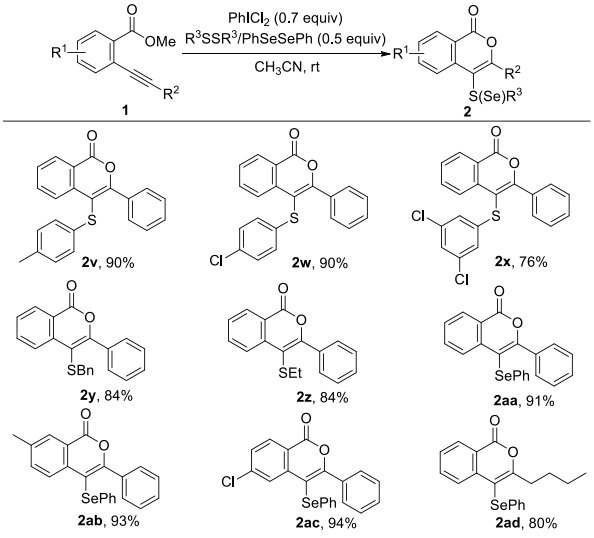
For instance, when the alkyne motif was substituted by either electron-rich/electron-poor phenyl rings with diversely substituted groups including CO_2Me, NO_2, Cl, OMe, and Me or the sterically hindered *o*-^{i}Pr-substituted aryl ring, products **2h–m** were obtained in good to excellent yields. Substrates with a naphthalene or thiophene ring linked to the alkyne moiety also proved to be well tolerated, providing the corresponding products in relatively higher yields of 84% and 91%, respectively. Most strikingly, it was found that the method could be further applied to the synthesis of 3-alkyl-substituted isocoumarins. When 2-alkynylbenzoate with a *t*/*n*-butyl R^2 group was applied, product **2p**/**2q** was obtained in a yield of 81% and 80%. Interestingly, a substrate bearing a cyclopropyl group attached to the triple bond was effective as well under the standard conditions, affording the desired product **2r** in 70% yield. Furthermore, substrates bearing a TMS R^2 group (**1s**) or methoxycarbonyl R^2 group (**1t**) were also converted to the product **2s** and **2t** in 72% and 68% yield, respectively. However, a longer time (24 h) was required for a complete reaction of substrate **1t**. It is worth noting that the method was also applicable to a terminal alkyne. When substrate **1u** was subjected to the standard conditions, the corresponding cyclized product was obtained in an acceptable 52% yield. In addition to methyl benzoate substrates, the other substrates bearing ethyl, *tert*-butyl, and benzyl esters were all tested, and the desired product was obtained in yields of 92%, 89%, and 90%, respectively.

Next, we turned our attention to investigate the scope of diorganyl dichalcogenides agents (Scheme 3). In general,

Scheme 3. Synthesis of Chalcogenyl Isocoumarins Using Various Dichalcogenide Agents[a]

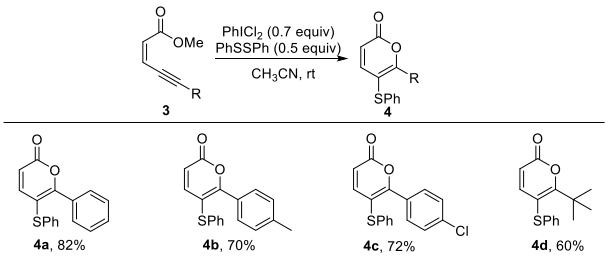


[a]Reaction conditions: **1** (1.0 mmol), PhSSPh (0.5 mmol), and $PhICl_2$ (0.7 mmol) in CH_3CN (10 mL) for 30 min, isolated yields.

diphenyl disulfide reagents bearing an electron-donating methyl group or electron-withdrawing chloro substituent on the aromatic ring as well as the dichloro-substituted diphenyl disulfide were all applicable for this conversion, with the corresponding 6-*exo*-*trig* cyclization products **2v–x** obtained in 76–90% yields. Additionally, dialkyl disulfides also served as suitable reaction partners with *o*-alkynylbenzoates **1**, giving the sulfenylated products **2y** and **2z** in good yields. Finally, we examined diselenide reagents to explore whether this strategy was amenable to introduction of selenyl groups. To our delight, the reaction of **2aa–ad** with diphenyl diselenide proceeded smoothly to provide the 4-selenylated products in yields of 80–94%. Substrates bearing either an electron-donating or electron-withdrawing substituent on the aromatic ring of the *o*-alkynylbenzoate **1** as well as both phenyl and *n*-butyl substituents attached to the alkyne moiety were investigated, and they all provided the corresponding cyclized products with good results. One might envisage that the method could be extended to install a *tert*-butoxy group into the isocoumarin skeleton by using DTBP and $PhICl_2$. However, the reaction of **1a** with DTBP (0.5 equiv) and $PhICl_2$ (0.7 equiv) in MeCN at rt to 60 °C afforded 4-chloroisocoumarin as the sole product.[61]

To further investigate whether the phenyl ring in the substrate was indispensable for this transformation, we subjected (*Z*)-2-alken-4-ynoate derivatives to the standard conditions (Scheme 4). It was found that (*Z*)-2-alken-4-

Scheme 4. Synthesis of Sulfenylated Pyrones Using Various Substrates[a]

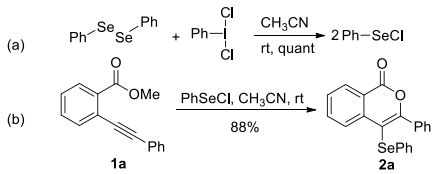


[a]Reaction conditions: **1** (1.0 mmol), PhSSPh (0.5 mmol), and $PhICl_2$ (0.7 mmol) in CH_3CN (10 mL) for 30 min, isolated yields.

ynoates bearing both a substituted phenyl group or an alkyl group on the acetylene moiety reacted well to produce the corresponding pyrones **4a–d** in good yields.

To clarify the mechanism of this process, two control experiments were conducted, and the following results were achieved: (1) When $PhICl_2$ and diphenyl diselenide reacted at rt for 20 min in the absence of starting alkynyl aryl ester **1a**, a red solid formed that was characterized as PhSeCl. This observation indicates that the pathway is consistent with the typical mechanism involving electrophilic cyclization with PhSeCl as the electrophilic source (Scheme 5a). (2) The

Scheme 5. Control Experiments



resulting PhSeCl solid was further used to react with the starting alkynyl aryl ester **1a**, and the desired product was obtained in a yield of 88% (Scheme 5b). Compared with the previous methods,[16,19,21,27,49] the in situ generation of organosulfenyl chlorides or selenenyl chlorides was achieved from easy-to-handle starting materials under mild conditions by this method.

Based on the experimental results and previous literature,[49,59] we propose that the reaction initially involves PhSCl

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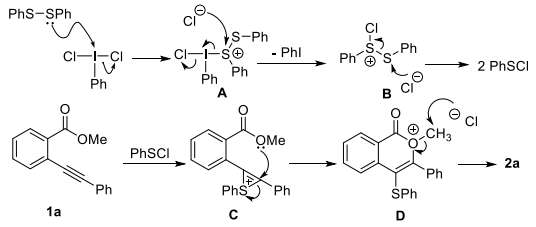
formation followed by a PhSCl-mediated electrophilic cyclization process (Scheme 6). The addition of $PhICl_2$ to

Scheme 6. Proposed Mechanism



diphenyl disulfide promotes the generation of reactive PhSCl through the attack of sulfur on the iodine center in $PhICl_2$ to give intermediate **A**, which is converted to sulfonium salt **B** after elimination of PhI. Next, the chloride anion nucleophilically attacks the sulfur atom of salt **B** to produce two molecules of PhSCl. Subsequently, intermediate **C** is generated from the reaction of substrate **1a** and PhSCl. Intramolecular nucleophilic attack of the oxygen atom from the ester moiety on the sulfonium center gives rise to intermediate **D**. Finally, removal of the methyl group from D assisted by the S_N2 attack of chloride ion leads to the formation of the title product.

In summary, we have not only developed a convenient approach to the in situ formation of sulfenyl chlorides/selenenyl chlorides from the reaction of RSSR/ArSeSeAr and $PhICl_2$ but also realized a regioselective synthesis of 4-chalcogenylisocoumarins/pyrones from reaction of in situ generated RSCl/ArSeCl with *o*-alkynylbenzoates. This one-pot strategy features a short reaction time (30 min), mild reaction conditions, a simple procedure, broad functional group tolerance, and the simultaneous introduction of a chalcogen functional group into the biologically interesting isocoumarin skeleton.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01046.

Experimental procedures; compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Armstrong, R. J.; Sandford, C.; García-Ruiz, C.; Aggarwal, V. K. *Chem. Commun.* **2017**, *53*, 4922.
(2) Gilow, H. M.; Brown, C. S.; Copeland, J. N.; Kelly, K. E. *J. Heterocycl. Chem.* **1991**, *28*, 1025.
(3) Pandey, G.; Varkhedkar, R.; Tiwari, D. *Org. Biomol. Chem.* **2015**, *13*, 4438.
(4) Nishiyama, Y.; Yokoshima, S.; Fukuyama, T. *Org. Lett.* **2016**, *18*, 2359.
(5) Halle, M. B.; Yudhistira, T.; Lee, W.-H.; Mulay, S. V.; Churchill, D. G. *Org. Lett.* **2018**, *20*, 3557.
(6) Huang, X.; Zhong, P.; Guo, W.-R. *Org. Prep. Proced. Int.* **1999**, *31*, 201.
(7) Tsizorik, N. M.; Vas'kevich, A. I.; Vas'kevich, R. I.; Vovk, M. V. *Russ. J. Org. Chem.* **2015**, *51*, 226.
(8) Gogoi, P.; Kalita, M.; Barman, P. *Synlett* **2014**, *25*, 866.
(9) Beswick, P. J.; Greenwood, C. S.; Mowlem, T. J.; Nechvatal, G.; Widdowson, D. A. *Tetrahedron* **1988**, *44*, 7325.
(10) Gerard, J.; Hevesi, L. *Tetrahedron* **2001**, *57*, 9109.
(11) Wang, B.-Y.; Turner, D. A.; Zujović, T.; Hadad, C. M.; Badjić, J. D. *Chem. - Eur. J.* **2011**, *17*, 8870.
(12) Peluso, P.; Greco, C.; De Lucchi, O.; Cossu, S. *Eur. J. Org. Chem.* **2002**, *2002*, 4024.
(13) Bertran, J. C.; Montforts, F.-P. *Eur. J. Org. Chem.* **2017**, *2017*, 1608.
(14) Mori, T.; Nishimura, T.; Yamamoto, T.; Doi, I.; Miyazaki, E.; Osaka, I.; Takimiya, K. *J. Am. Chem. Soc.* **2013**, *135*, 13900.
(15) Cookson, R. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1978**, 822.
(16) Kumamoto, H.; Onuma, S.; Tanaka, H. *J. Org. Chem.* **2004**, *69*, 72.
(17) Garratt, D. G.; Ryan, M. D.; Kabo, A. *Can. J. Chem.* **1980**, *58*, 2329.
(18) Mueller, W. H.; Butler, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2075.
(19) Iwasaki, M.; Fujii, T.; Yamamoto, A.; Nakajima, K.; Nishihara, Y. *Chem. - Asian J.* **2014**, *9*, 58.
(20) Li, Z.-S.; Wang, W.-M.; Lu, W.; Niu, C.-W.; Li, Y.-H.; Li, Z.-M.; Wang, J.-G. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 3723.
(21) Cheng, J.-H.; Ramesh, C.; Kao, H.-L.; Wang, Y.-J.; Chan, C.-C.; Lee, C.-F. *J. Org. Chem.* **2012**, *77*, 10369.
(22) Schmid, G. H.; Garratt, D. G. *Tetrahedron* **1978**, *34*, 2869.
(23) Li, L.; Wang, X.; Li, Q.; Liu, P.; Xu, K.; Chen, H.; Tang, B. *Chem. Commun.* **2015**, *51*, 11317.
(24) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(25) Makarov, A. G.; Grayfer, T. D.; Makarov, A. Y.; Bagryanskaya, I. Y.; Vasiliev, V. G.; Zibarev, A. V. *Mendeleev Commun.* **2011**, *21*, 320.
(26) Schlosser, K. M.; Krasutsky, A. P.; Hamilton, H. W.; Reed, J. E.; Sexton, K. *Org. Lett.* **2004**, *6*, 819.
(27) Yadav, J. S.; Subba Reddy, B. V.; Jain, R.; Baishya, G. *Tetrahedron Lett.* **2008**, *49*, 3015.
(28) Ohta, S.; Kamata, Y.; Inagaki, T.; Masuda, Y.; Yamamoto, S.; Yamashita, M.; Kawasaki, I. *Chem. Pharm. Bull.* **1993**, *41*, 1188.
(29) Dumontet, V.; Hung, N. V.; Adeline, M.-T.; Riche, C.; Chiaroni, A.; Sévenet, T.; Guéritte, F. *J. Nat. Prod.* **2004**, *67*, 858.
(30) Larsen, T. O.; Breinholt, J. *J. Nat. Prod.* **1999**, *62*, 1182.
(31) López-López, E. E.; Pérez-Bautista, J. A.; Sartillo-Piscil, F.; Frontana-Uribe, B. A. *Beilstein J. Org. Chem.* **2018**, *14*, 547.
(32) Das, B.; Balasubramanyam, P.; Veeranjaneyulu, B.; Reddy, G. C. *Helv. Chim. Acta* **2011**, *94*, 881.
(33) Barrero, A. F.; Oltra, J. E.; Herrador, M. M.; Cabrera, E.; Sanchez, J. F.; Quílez, J. F.; Rojas, F. J.; Reyes, J. F. *Tetrahedron* **1993**, *49*, 141.
(34) Abraham, W.-R.; Arfmann, H.-A. *Phytochemistry* **1988**, *27*, 3310.
(35) Matsuda, H.; Shimoda, H.; Yoshikawa, M. *Bioorg. Med. Chem.* **1999**, *7*, 1445.
(36) Schlingmann, G.; Milne, L.; Carter, G. T. *Tetrahedron* **1998**, *54*, 13013.
(37) Sato, H.; Konoma, K.; Sakamura, S. *Agric. Biol. Chem.* **1981**, *45*, 1675.

DOI: 10.1021/acs.orglett.9b01046
Org. Lett. XXXX, XXX, XXX–XXX

(38) Simon, A.; Dunlop, R. W.; Ghisalberti, E. L.; Sivasithamparam, K. *Soil Biol. Biochem.* **1988**, *20*, 263.
(39) Whyte, A. C.; Gloer, J. B.; Scott, J. A.; Malloch, D. *J. Nat. Prod.* **1996**, *59*, 765.
(40) Shi, X.; Leal, W. S.; Liu, Z.; Schrader, E.; Meinwald, J. *Tetrahedron Lett.* **1995**, *36*, 71.
(41) Monleón, A.; Blay, G.; Domingo, L. R.; Muñoz, M. C.; Pedro, J. R. *Eur. J. Org. Chem.* **2015**, *2015*, 1020.
(42) Lu, L.-H.; Zhou, S.-J.; Sun, M.; Chen, J.-L.; Xia, W.; Yu, X.; Xu, X.; He, W.-M. *ACS Sustainable Chem. Eng.* **2019**, *7*, 1574.
(43) Wu, C.; Xiao, H.-J.; Wang, S.-W.; Tang, M.-S.; Tang, Z.-L.; Xia, W.; Li, W.-F.; Cao, Z.; He, W.-M. *ACS Sustainable Chem. Eng.* **2019**, *7*, 2169.
(44) Wu, C.; Lu, L.-H.; Peng, A.-Z.; Jia, G.-K.; Peng, C.; Cao, Z.; Tang, Z.; He, W.-M.; Xu, X. *Green Chem.* **2018**, *20*, 3683.
(45) Bao, W.-H.; Wu, C.; Wang, J.-T.; Xia, W.; Chen, P.; Tang, Z.; Xu, X.; He, W.-M. *Org. Biomol. Chem.* **2018**, *16*, 8403.
(46) Lu, L.-H.; Zhou, S.-J.; He, W.-B.; Xia, W.; Chen, P.; Yu, X.; Xu, X.; He, W.-M. *Org. Biomol. Chem.* **2018**, *16*, 9064.
(47) Woon, E. C. Y.; Dhami, A.; Mahon, M. F.; Threadgill, M. D. *Tetrahedron* **2006**, *62*, 4829.
(48) Jean, M.; Renault, J.; van de Weghe, P.; Asao, N. *Tetrahedron Lett.* **2010**, *51*, 378.
(49) Sperança, A.; Godoi, B.; Pinton, S.; Back, D. F.; Menezes, P. H.; Zeni, G. *J. Org. Chem.* **2011**, *76*, 6789.
(50) Ismalaj, E.; Glenadel, Q.; Billard, T. *Eur. J. Org. Chem.* **2017**, *2017*, 1911.
(51) Ponra, S.; Nyadanu, A.; Maurin, S.; El Kaïm, L.; Grimaud, L.; Vitale, M. R. *Synthesis* **2018**, *50*, 1331.
(52) Wilkins, L. C.; Günther, B. A. R.; Walther, M.; Lawson, J. R.; Wirth, T.; Melen, R. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 11292.
(53) Ponra, S.; Nyadanu, A.; Kaïm, L. E.; Grimaud, L.; Vitale, M. R. *Org. Lett.* **2016**, *18*, 4060.
(54) Mitra, P.; Shome, B.; Ranjan De, S.; Sarkar, A.; Mal, D. *Org. Biomol. Chem.* **2012**, *10*, 2742.
(55) Li, Y.; Li, G.; Ding, Q. *Eur. J. Org. Chem.* **2014**, *2014*, 5017.
(56) Mehta, S.; Waldo, J. P.; Larock, R. C. *J. Org. Chem.* **2009**, *74*, 1141.
(57) Li, Z.; Hong, J.; Weng, L.; Zhou, X. *Tetrahedron* **2012**, *68*, 1552.
(58) Glenadel, Q.; Ismalaj, E.; Billard, T. *Org. Lett.* **2018**, *20*, 56.
(59) Yao, T.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 5936.
(60) It is noteworthy that disulfide in the reaction can also be replaced by thiophenol. However, it was found that more $PhICl_2$ (1.7 equiv) was required for a complete reaction of **1a**.
(61) Xing, L.; Zhang, Y.; Li, B.; Du, Y. *Org. Lett.* **2019**, *21*, 1989.

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