Organic LETTERS

Letter

pubs.acs.org/OrgLett

Thiocarbonyl Surrogate via Combination of Sulfur and Chloroform for Thiocarbamide and Oxazolidinethione Construction

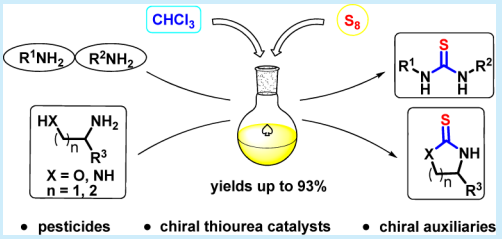
Wei Tan,[†] Jianpeng Wei,[†] and Xuefeng Jiang*[,†,‡]

[†]Shanghai Key Laboratory of Green Chemistry and Chemical Process, School of Chemistry and Molecular Engineering, East China Normal University, 3663 North Zhongshan Road, Shanghai, 200062, P. R. China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China

Supporting Information

ABSTRACT: An efficient and practical thiocarbonyl surrogate via combination of sulfur and chloroform has been developed. A variety of thiocarbamides and oxazolidinethiones have been established, including chiral thiourea catalysts and chiral oxazolidinethione auxiliaries with high selectivity. Meanwhile, pesticides Diafenthiuron (an acaricide), ANTU (a rodenticide), and Chloromethiuron (an insecticide) were practically synthesized through this method in gram scale. Dicholorocarbene, as the key intermediate, was further confirmed via a carbene-trapping control experiment.



Thiocarbamides and oxazolidinethiones are of great importance due to their unique thiocarbonyl motif.[1] Thiocarbamides are extensively studied in medicinal chemistry,[2] stemming from their selective biological activities such as clinically applied hyperthyroidism drug Propylthiouracil/Carbimazole,[2a] and sedative hypnotics drug Thiopental (Figure 1).[2b]

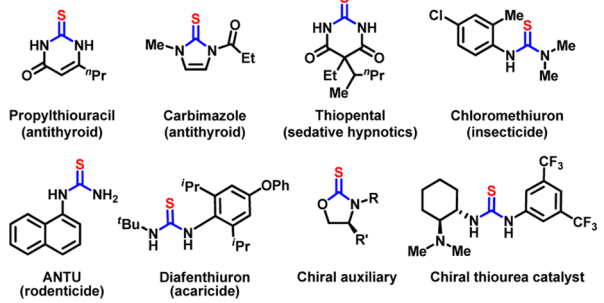
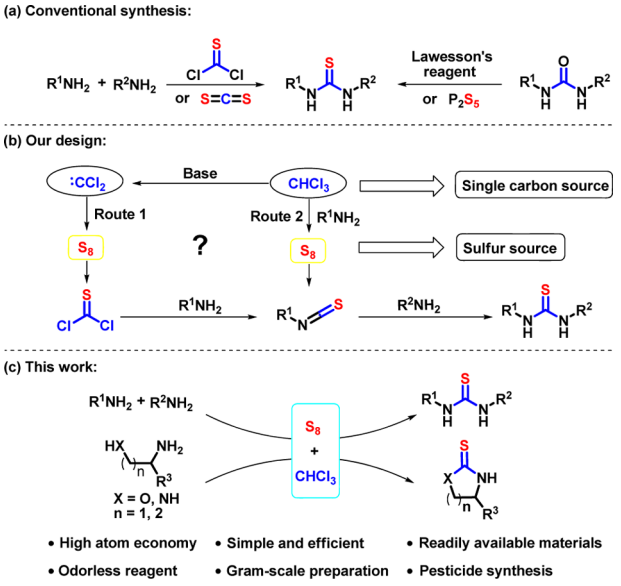


Figure 1. Representative thiocarbamides and oxazolidinethiones.

Meanwhile, thiocarbamide also played an important role in pesticide chemistry[3] such as the acaricide Diafenthiuron,[3d,e] the rodenticide ANTU,[3a,b] and the insecticide Chloromethiuron.[3c] Furthermore, optically active thiocarbamides and oxazolidinethiones, which serve as a crux in asymmetric synthesis, have been developed as a chiral thiourea catalyst[4] and chiral oxazolidinethione auxiliary.[5] In addition, they were widely applied for the synthesis of significant sulfur-containing heterocycles[6] such as aminobenzothiazole,[6c] thiazoline,[6d] and thiazolidinone,[6d] whose diverse biological activities promoted them as privileged scaffolds in drug discovery.

Accordingly, numerous procedures[7] have been developed for the synthesis of thiocarbamides and oxazolidinethiones. However, these reported methods scarcely avoid the utilization of volatile and flammable carbon disulfide,[7j] toxic and corrosive thiophosgene,[7c] or their derivates[7d] as starting materials (Scheme 1a). Alternatively, Lawesson reagents[7e] and P_2S_5[7f] were other choices for transforming the carbonyl to thiocarbonyl with the defect of low economy and odor. Therefore, a practical and environment-friendly process for thiocarbamide and oxazolidinethione construction is highly desirable but still remains a challenge in organic synthesis. Based on continuous study on

Scheme 1. Strategies for Thiocarbonyl Construction



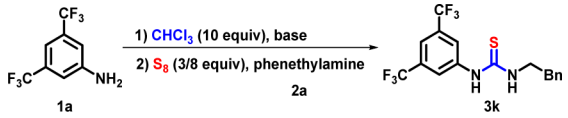
Received: March 18, 2017

DOI: 10.1021/acs.orglett.7b00819
Org. Lett. XXXX, XXX, XXX−XXX

organic sulfur chemistry,[8] development of a thiocarbonyl surrogate is one of our goals.[9] Construction of a thiocarbonyl group was orientated to the establishment of a carbon−sulfur double bond. We envisioned this target could be achieved through the combination of a single carbon source and sulfur source. Chloroform and elemental sulfur, which are a potential single carbon source[10,11] and nature-abundant sulfur source[12] respectively, could be candidates in the establishment of the thiocarbonyl group (Scheme 1b). Subsequently, two possibilities were followed: (1) Dicholorocarbene stemming from chloroform combined with sulfur directly to form a carbon−sulfur bond.[13] (2) Dicholorocarbene was effected with one amine affording isocyanide, followed by sulfur for isothiocyanate, which was captured by another amine.[14] Herein, we report an efficient and practical thiocarbonyl surrogate via combination of sulfur and chloroform for thiocarbamide and oxazolidinethione construction (Scheme 1c).

We commenced our studies by subjecting 3,5-di(trifluoromethyl)aniline, chloroform, and potassium *tert*-butoxide in acetonitrile at 55 °C for 2 h, followed by addition of sulfur and phenethylamine affording product **3k** in 36% isolated yield (Table 1, entry 1). When the reaction solvent was altered to a mixture of *tert*-butyl alcohol/1,4-dioxane, **3k** could be afforded in 59% yield with cleaner thin-layer chromatography (Table 1, entries 2−4). However, only a trace amount of the desired product could be detected in water (Table 1, entry 5). Notably, no reaction was detected with potassium carbonate or trimethylamine as the base, which were probably unable to afford carbene from chloroform (Table 1, entries 6−7). A 51% yield of **3k** could be afforded with potassium hydroxide (Table 1, entry 8). Delightedly, the yield was further improved to 78% via adjusting the ratio of two different amines (**1a**/**2a**) to 2/1 (Table 1, entries 9−11). Finally, the optimized conditions were achieved when the reaction time was extended to 4 h with an 82% isolated yield (Table 1, entries 12−14).

Table 1. Discovery of Thiocarbonyl Surrogate[a]

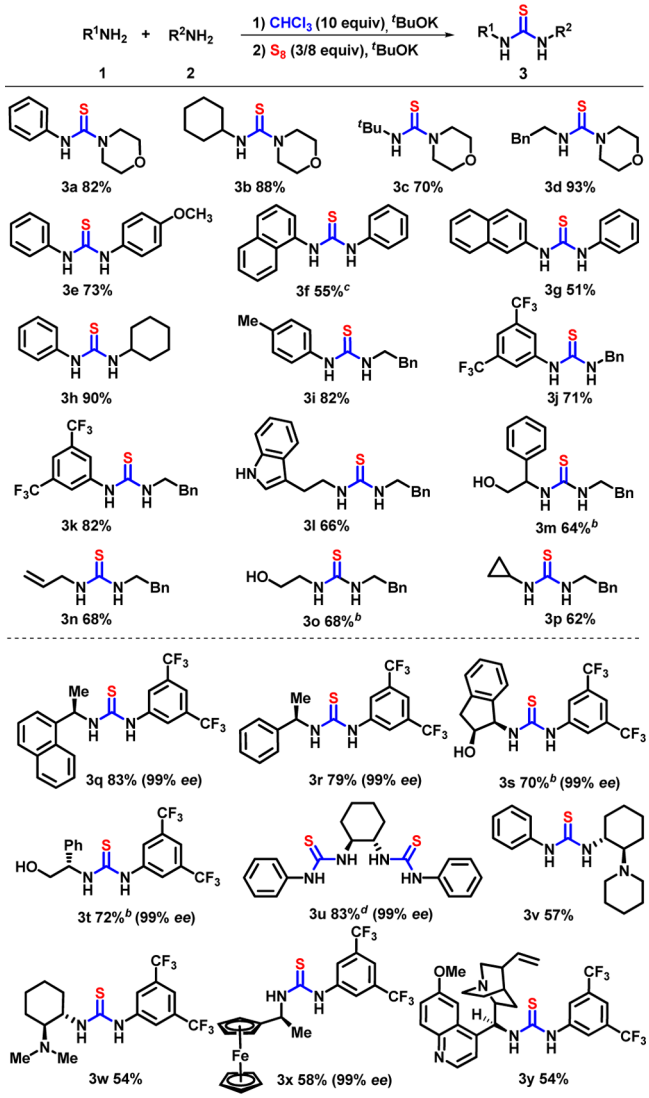


entry	solvent	base	ratio **1a**/**2a** (x/y)	yield[b] (%)
1	CH_3CN	^{t}BuOK	1/2	36
2	^{t}BuOH	^{t}BuOK	1/2	48
3	1,4-dioxane	^{t}BuOK	1/2	41
4	^{t}BuOH/1,4-dioxane	^{t}BuOK	1/2	59
5	H_2O	^{t}BuOK	1/2	trace
6	^{t}BuOH/1,4-dioxane	K_2CO_3	1/2	–
7	^{t}BuOH/1,4-dioxane	TEA	1/2	–
8	^{t}BuOH/1,4-dioxane	KOH	1/2	51
9	^{t}BuOH/1,4-dioxane	^{t}BuOK	1/1.2	47
10	^{t}BuOH/1,4-dioxane	^{t}BuOK	2/1	78
11	^{t}BuOH/1,4-dioxane	^{t}BuOK	3/1	78
12[c]	^{t}BuOH/1,4-dioxane	^{t}BuOK	2/1	78
13[d]	^{t}BuOH/1,4-dioxane	^{t}BuOK	2/1	82
14[e]	^{t}BuOH/1,4-dioxane	^{t}BuOK	2/1	81

[a]Reaction conditions: It was carried out on a 0.2 mmol scale. **1a** (*x* mmol), base (1.2 mmol), and $CHCl_3$ (2.0 mmol) were stirred in solvent (0.8 mL) at 55 °C for 2 h, then **2a** (*y* mmol), S_8 (0.6 mmol), and base (0.4 mmol) were added to the reaction mixture, and the reaction continued at this temperature. [b]Isolated yields. [c]3 h. [d]4 h. [e]6 h (TEA = triethylamine).

Based on the optimized conditions, an intermolecular thiocarbamide library was established, as shown in Table 2.

Table 2. Intermolecular Thiocarbamide Library[a]



[a]Reaction conditions: **1** (0.4 mmol), ^{t}BuOK (1.2 mmol), and $CHCl_3$ (2 mmol) in ^{t}BuOH/1,4-dioxane (0.4/0.4 mL) were stirred at 55 °C for 3−4 h, then S_8 (0.6 mmol), ^{t}BuOK (0.4 mmol), and **2** (0.2 mmol) were added to the reaction mixture, and the reaction continued at this temperature for 6−15 h. Isolated yields. [b]No ^{t}BuOK (0.4 mmol) was added. [c]KOH (1.2 mmol) was used instead of ^{t}BuOK (1.2 mmol). [d]The amounts of reagents were doubled except for (1*S*,2*S*)-(+)-1,2-diaminocyclohexane in ^{t}BuOH/1,4-dioxane (0.5/0.5 mL).

Not only aniline (**3a**) and phenethylamine (**3d**) but also sterically hindered cyclohexylamine (**3b**) and *tert*-butylamine (**3c**) could afford the corresponding thiocarbamides with morpholine in good to excellent yields. Furthermore, the combination of various aryl- and aryl amines (**3e**−**3g**), aryl- and alkyl amines (**3h**−**3k**), and alkyl- and alkyl amines (**3l**−**3p**) could be efficiently transformed to the desired products in moderate to excellent yields. Notably, the amine with an allylic group, which was prone to react with carbene, could be tolerated in this transformation (**3n**). Moreover, the amines containing an

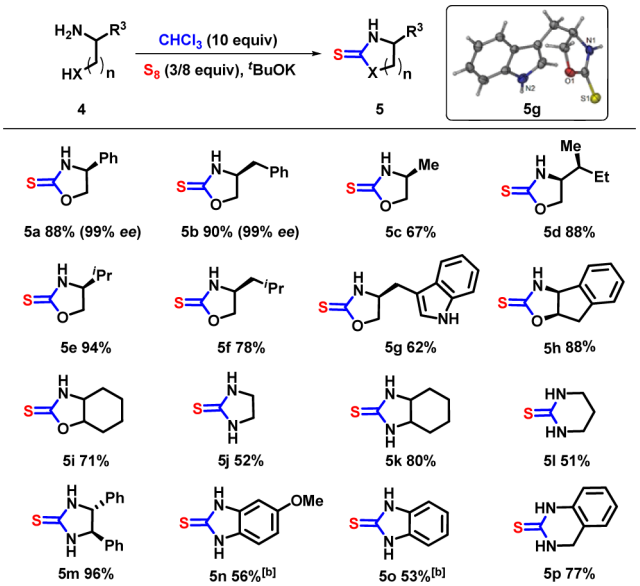
DOI: 10.1021/acs.orglett.7b00819
Org. Lett. XXXX, XXX, XXX−XXX

unprotected hydroxyl (**3m,** and **3o**), indolyl (**3l**), and cyclopropyl (**3p**) group could afford products as well.

With great compatibility, the chiral thiourea catalyst library was consequently established. 3,5-Di(trifluoromethyl)aniline could be assembled with both optically pure (*R*)-1-(naphthalen-1-yl)ethanamine and (*R*)-(+)-1-phenylethylamine to afford the desired products (**3q**−**3r**), which were highly important catalysts as a hydrogen bond donor[4h] in an asymmetrically catalytic reaction. Delightedly, the enantiomeric excess of the initial materials were completely maintained even in the presence of potassium *tert*-butoxide (detection by HPLC; see Supporting Information). Meanwhile, optical pure (1*S*, 2*R*)-(−)-*cis*-1-amino-2-indanol and (*S*)-(+)-2-phenylglycinol were chosen as substrates to afford chiral thiourea derivatives (**3s**−**3t**), which could be used as the bifunctional chiral catalysts with an unprotected hydroxyl group.[4d] Since rigid frame (1*S*, 2*S*)-(+)-1,2-diaminocyclohexane was widely applied to the construction of chiral thiourea catalyst, the corresponding product (**3u**)[4e] was also synthesized without loss of enantioselectivity through this method in 83% yield. Notably, chiral tertiary amine was efficiently introduced into a thiourea skeleton to afford other bifunctional chiral catalysts (**3v**−**3w**).[4a] Amazingly, chiral ferrocene (**3x**)[4e] and natural quinolone (**3y**)[4a] skeletons were both compatible in the system.

An intramolecular thiocarbamide and oxazolidinethione library was further established, as shown in Table 3. This process

Table 3. Intramolecular Thiocarbamide and Oxazolidinethione Library[a]

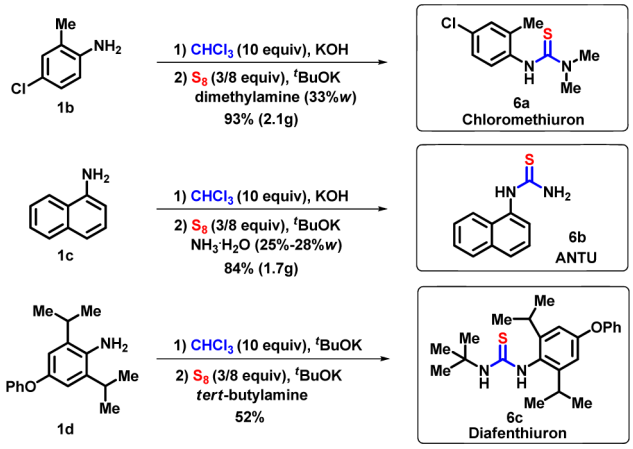


[a]Reaction conditions: **4** (0.3 mmol), S_8 (0.9 mmol), $CHCl_3$ (3 mmol), and ^{t}BuOK (1.35 mmol) in 2-ethoxyethanol/1,4-dioxane (0.5/0.5 mL) were added to $CHCl_3$ (3.0 mmol, 10.0 equiv) dropwise at 0 °C, and then the reaction mixture was heated to 50 °C for 8−16 h. Isolated yields. [b]S_8 (1.5 mmol) and ^{t}BuOK (1.8 mmol) were used.

was successfully applied to synthesis of optically pure oxazolidinethione derivatives from various chiral amino alcohols (**5a**−**5h**), which were widely used as an excellent chiral auxiliary for asymmetric synthesis.[5] The structure of compound (**5g**) was further confirmed through X-ray crystallographic analysis.[15] Fortunately, the *ee* values of the representative products (**5a**−**5b**) were retained in the presence of potassium *tert*-butoxide. Moreover, various intramolecular thiocarbamides (**5j**−**5p**) could also be obtained from the corresponding amines. Importantly, key intermediates (**5n**−**5o**) for pharmaceuticals such as Omeprazole and Lansoprazole were also afforded.[16]

Afterward, three significant thiocarbonyl-containing pesticides were efficiently synthesized via commercially available amines as starting materials in a one-pot procedure (Scheme 2).

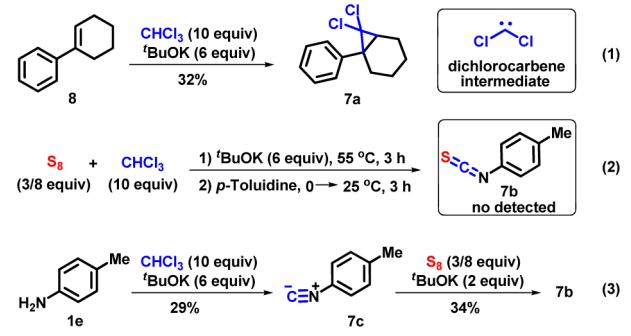
Scheme 2. Application of Gram-Scale Synthesis of Pesticides



Chloromethiuron (cas: 28217-97-2) as an insecticide was afforded on the 10 mmol scale in excellent yield (93%, 2.1 g) with 4-chloro-2-methylaniline and a 33% aqueous solution of dimethylamine as starting materials. ANTU (cas: 86-88-4) as a rodenticide could be highly efficiently achieved in 84% (1.7 g) isolated yield on the 10 mmol scale with a 25−28% aqueous solution of ammonia. Diafenthiuron (cas: 80060-09-9) with a high resistance space structure, which serves as widely used acaricide, was obtained in 52% isolated yield by using sterically hindered 2,6-diisopropyl-4-phenoxyaniline and *tert*-butylamine.

To gain mechanistic insight into this protocol, a carbene trapping experiment was introduced with activated cyclohexenylbenzene, in which 7,7-dichloro-1-phenylbicyclo[4.1.0]heptane **7a** was obtained in 32% isolated yield (Scheme 3, eq 1). *p*-

Scheme 3. Control Experiment



Toluidine was subjected with S_8 and chloroform under the given conditions without isothiocyanate **7b** being detected, which indicated that thiophosgene was not formed in the system (Scheme 3, eq 2). Furthermore, the 1-isocyano-4-methylbenzene **7c** was obtained in 29% isolated yield without addition of S_8, which showed that isocyanide might be the key intermediate during this process. Then, **7c** was subjected to the standard conditions without chloroform affording a 34% isolated yield of

DOI: 10.1021/acs.orglett.7b00819
Org. Lett. XXXX, XXX, XXX−XXX

isothiocyanate **7d**, which demonstrated that isothiocyanate could be formed in the reaction (Scheme 3, eq 3).

In summary, we have developed an efficient and practical thiocarbonyl surrogate for the construction of various thiocarbamides and oxazolidinethiones via combination of sulfur and chloroform. Moreover, the procedure was successfully applied for the establishment of chiral thiourea catalysts, chiral oxazolidinethione auxiliaries, and a commercial pesticides library. Further studies on other thiocarbonyl surrogates are ongoing 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.7b00819.

Experimental procedures, NMR spectral, X-ray, and analytical data for all new compounds (PDF)
Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xfjiang@chem.ecnu.edu.cn.

ORCID

Xuefeng Jiang: 0000-0002-1849-6572

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support provided by NSFC (21672069, 21472050), DFMEC (20130076110023), Fok Ying Tung Education Foundation (141011), Program for Shanghai Rising Star (15QA1401800), Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, and the National Program for Support of Top-notch Young Professionals.

■ REFERENCES

(1) Reviews: (a) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359. (b) Maciejewski, A.; Steer, R. P. *Chem. Rev.* **1993**, *93*, 67. (c) Sakamoto, M. In *Topics in Current Chemistry*; Toda, F., Ed.; Springer: Berlin, Heidelberg, 2005; Vol. *254*, pp 207−232. (d) Li, A. F.; Wang, J. H.; Wang, F.; Jiang, Y. B. *Chem. Soc. Rev.* **2010**, *39*, 3729. (e) Sahu, S.; Sahoo, P. R.; Patel, S.; Mishra, B. K. *J. Sulfur Chem.* **2011**, *32*, 171.

(2) Reviews: (a) Rodríguez-Fernández, E.; Manzano, J. L.; Benito, J. J.; Hermosa, R.; Monte, E.; Criado, J. J. *J. Inorg. Biochem.* **2005**, *99*, 1558. (b) D'Cruz, O. J.; Uckun, F. M. *Curr. HIV Res.* **2006**, *4*, 329. (c) Manna, D.; Roy, G.; Mugesh, G. *Acc. Chem. Res.* **2013**, *46*, 2706. For selected examples: (d) Weiss, M.; Buhl, R.; Medve, M.; Schneider, E. M. *Crit. Care Med.* **1997**, *25*, 128. (e) Harper, L.; Chin, L.; Daykin, J.; Allahabadia, A.; Heward, J.; Gough, S. C.; Savage, C. O.; Franklyn, J. A. *Clin. Endocrinol.* **2004**, *60*, 671. (f) Van Daele, I. V.; Munier-Lehmann, H.; Froeyen, M.; Balzarini, J.; Van Calenbergh, S. V. *J. Med. Chem.* **2007**, *50*, 5281. (g) Touati-Jallabe, Y.; Bojnik, E.; Legrand, B.; Mauchauffée, E.; Chung, N. N.; Schiller, P. W.; Benyhe, S.; Averlant-Petit, M. C.; Martinez, J.; Hernandez, J. F. *J. Med. Chem.* **2013**, *56*, 5964. (h) Ma, L. Y.; Zheng, Y. C.; Wang, S. Q.; Wang, B.; Wang, Z. R.; Pang, L. P.; Zhang, M.; Wang, J. W.; Ding, L.; Li, J.; Wang, C.; Hu, B.; Liu, Y.; Zhang, X. D.; Wang, J. J.; Wang, Z. J.; Zhao, W.; Liu, H. M. *J. Med. Chem.* **2015**, *58*, 1705.

(3) For selected examples: (a) Gaines, T. B.; Hayes, W. J., Jr. *Public Health Rep.* **1952**, *67*, 306. (b) Gratz, N. G. *Bull. World Health Organ.* **1973**, *48*, 469. (c) Schuntner, C. A.; Thompson, P. G. *Pestic. Sci.* **1979**, *10*, 519. (d) Pascual, A.; Rindlisbacher, A. *Pestic. Sci.* **1994**, *42*, 253. (e) Kayser, H.; Eilinger, P. *Pest Manage. Sci.* **2001**, *57*, 975. (f) Wang, B. L.; Zhu, H. W.; Ma, Y.; Xiong, L. X.; Li, Y. Q.; Zhao, Y.; Zhang, J. F.; Chen, Y. W.; Zhou, S.; Li, Z. M. *J. Agric. Food Chem.* **2013**, *61*, 5483.

(4) Reviews: (a) Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713. (b) Chauhan, P.; Mahajan, S.; Enders, D. *Chem. Rev.* **2014**, *114*, 8807. For selected examples: (c) Inokuma, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2006**, *128*, 9413. (d) Sibi, M. P.; Itoh, K. *J. Am. Chem. Soc.* **2007**, *129*, 8064. (e) Zhang, Y.; Liu, Y. K.; Kang, T. R.; Hu, Z. K.; Chen, Y. C. *J. Am. Chem. Soc.* **2008**, *130*, 2456. (f) Zhao, Q.; Wen, J.; Tan, R.; Huang, K.; Metola, P.; Wang, R.; Anslyn, E. V.; Zhang, X. *Angew. Chem., Int. Ed.* **2014**, *53*, 8467. (h) Madarász, Á.; Dósa, Z.; Varga, S.; Soós, T.; Csámpai, A.; Pápai, I. *ACS Catal.* **2016**, *6*, 4379.

(5) (a) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835. (b) Velázquez, F.; Olivo, H. F. *Curr. Org. Chem.* **2002**, *6*, 303. (c) Sakamoto, M. In *Comprehensive Chirality*; Carreira, E. M., Yamamoto, H., Eds.; Elsevier B.V.: Amsterdam, The Netherlands, 2012; Vol. 3, pp 19−41.

(6) (a) Yella, R.; Ghosh, H.; Patel, B. K. *Green Chem.* **2008**, *10*, 1307. (b) Cano, I.; Gómez-Bengoa, E.; Landa, A.; Maestro, M.; Mielgo, A.; Olaizola, I.; Oiarbide, M.; Palomo, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 10856. (c) Zhao, J.; Huang, H.; Wu, W.; Chen, H.; Jiang, H. *Org. Lett.* **2013**, *15*, 2604. (d) Appalanaidu, K.; Dadmal, T.; Babu, N. J.; Kumbhare, R. M. *RSC Adv.* **2015**, *5*, 88063.

(7) Reviews: (a) Schroeder, D. C. *Chem. Rev.* **1955**, *55*, 181. (b) Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 351. (c) Sharma, S. *Synthesis* **1978**, *1978*, 803. (d) Ortiz, A.; Sansinenea, E. *J. Sulfur Chem.* **2007**, *28*, 109. (e) Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2007**, *107*, 5210. (f) Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2010**, *110*, 3419. For selected examples: (g) Ballabeni, M.; Ballini, R.; Bigi, F.; Maggi, R.; Parrini, M.; Predieri, G.; Sartori, G. *J. Org. Chem.* **1999**, *64*, 1029. (h) Katritzky, A. R.; Ledoux, S.; Witek, R. M.; Nair, S. K. *J. Org. Chem.* **2004**, *69*, 2976. (i) Maddani, M. R.; Prabhu, K. R. *J. Org. Chem.* **2010**, *75*, 2327. (j) Chau, C. M.; Chuan, T. J.; Liu, K. M. *RSC Adv.* **2014**, *4*, 1276.

(8) Reviews: (a) Liu, H.; Jiang, X. *Chem. - Asian J.* **2013**, *8*, 2546. (b) Feng, M.; Tang, B.; Liang, S.; Jiang, X. *Curr. Top. Med. Chem.* **2016**, *16*, 1200. (c) Qiao, Z.; Jiang, X. *Org. Biomol. Chem.* **2017**, *15*, 1942. For representative examples: (d) Qiao, Z.; Liu, H.; Xiao, X.; Fu, Y.; Wei, J.; Li, Y.; Jiang, X. *Org. Lett.* **2013**, *15*, 2594. (e) Qiao, Z.; Wei, J.; Jiang, X. *Org. Lett.* **2014**, *16*, 1212. (f) Li, Y.; Pu, J.; Jiang, X. *Org. Lett.* **2014**, *16*, 2692. (g) Zhang, Y.; Li, Y.; Zhang, X.; Jiang, X. *Chem. Commun.* **2015**, *51*, 941. (h) Qiao, Z.; Ge, N.; Jiang, X. *Chem. Commun.* **2015**, *51*, 10295. (i) Xiao, X.; Feng, M.; Jiang, X. *Chem. Commun.* **2015**, *51*, 4208. (j) Li, Y.; Xie, W.; Jiang, X. *Chem. - Eur. J.* **2015**, *21*, 16059. (k) Qiao, Z.; Jiang, X. *Org. Lett.* **2016**, *18*, 1550. (l) Wang, M.; Fan, Q.; Jiang, X. *Org. Lett.* **2016**, *18*, 5756. (m) Xiao, X.; Feng, M.; Jiang, X. *Angew. Chem., Int. Ed.* **2016**, *55*, 14121. (n) Wang, M.; Wei, J.; Fan, Q.; Jiang, X. *Chem. Commun.* **2017**, *53*, 2918.

(9) Wei, J.; Li, Y.; Jiang, X. *Org. Lett.* **2016**, *18*, 340.

(10) Fedoryński, M. *Chem. Rev.* **2003**, *103*, 1099.

(11) (a) Gockel, S. N.; Hull, K. L. *Org. Lett.* **2015**, *17*, 3236. (b) Liu, X.; Li, B.; Gu, Z. *J. Org. Chem.* **2015**, *80*, 7547. (c) Zhao, H.; Du, H.; Yuan, X.; Wang, T.; Han, W. *Green Chem.* **2016**, *18*, 5782. (d) Sun, G.; Lei, M.; Hu, L. *RSC Adv.* **2016**, *6*, 28442.

(12) (a) Meyer, B. *Chem. Rev.* **1976**, *76*, 367. (b) Boyd, D. A. *Angew. Chem., Int. Ed.* **2016**, *55*, 2.

(13) (a) Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Inorg. Chem.* **2000**, *39*, 1042. (b) Takikawa, Y.; Yamaguchi, M.; Sasaki, T.; Ohnishi, K.; Shimada, K. *Chem. Lett.* **1994**, *23*, 2105.

(14) (a) Weber, W. P.; Gokel, G. W. *Tetrahedron Lett.* **1972**, *13*, 1637. (b) Lipp, M.; Dallacker, F.; zu Kocker, I. M. *Monatsh. Chem.* **1959**, *90*, 41. (c) Weith, W. *Chem. Ber.* **1873**, *6*, 212. (d) Hofmann, A. W. *Ann. Chem.* **1867**, *144*, 114.

(15) CCDC-1524792 (**5g**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(16) (a) Prasad, K. D. 2001 US 6303787 B1. (b) Gangula, S.; Elati, C. R.; Neredla, A.; Baddam, S. R.; Neelam, U. K.; Bandichhor, R.; Dongamanti, A. *Org. Process Res. Dev.* **2010**, *14*, 229.

DOI: 10.1021/acs.orglett.7b00819
Org. Lett. XXXX, XXX, XXX−XXX