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COMMUNICATION

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Copper-Catalyzed Defluorinative Thioannulation of Trifluoropropynes for the Synthesis of 1,2-Dithiole-3-thiones

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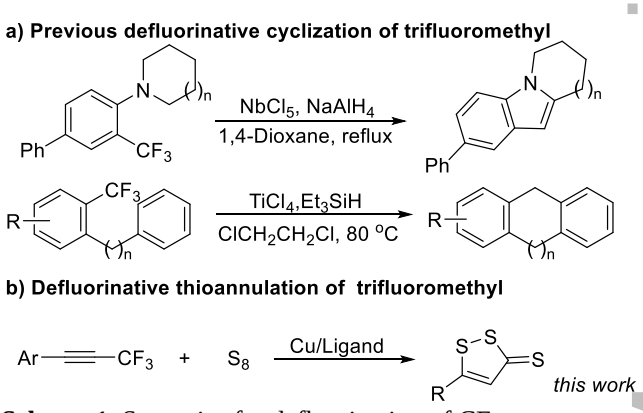
Abstract: A simple and practical strategy for the preparation of 1,2-dithiole-3-thiones *via* copper-catalyzed defluorinative thioannulation of trifluoropropynes has been developed using elemental sulfur as the sole sulfur source. This reaction displays a wide substrate scope and high functional group tolerance to afford the corresponding S-heterocycles in moderate to good yields and features efficient construction of multiple C–S bonds through C–F bond cleavage of CF_3 groups.

Keywords: defluorination; thioannulation; C–F bond activation; sulfur heterocycles.

As one of the major challenges in modern organic chemistry,[1] the activation of carbon-fluorine bonds and subsequent transformation has profound significance for organic synthesis, as well as the destruction of atmospheric pollutants such as CFCs and perfluoroalkanes. Consequently, a number of methods have been developed for the conversion of C–F bonds,[2] most of which are focused on hydrodefluorination[3] and the functionalization of aryl fluorides.[4] However, the functional group transformation through activation of three C–F bonds of trifluoromethylated compounds is less studied.[5] Recently, Akiyama and co-workers developed the hydrodefluorinative cyclization of trifluorotoluene derivatives for the synthesis of *N*-fused indoles and fused carbocycles *via* a C–F bond activation and C–H bond insertion approach (Scheme 1a).[5a, 6] In past decades, transition-metal-catalyzed cross-coupling reactions of organic halides with sulfur-surrogates have been developed as powerful tools for the synthesis of sulfur-containing compounds.[7] Nevertheless, the introduction of sulfur to organofluorine compounds through the cleavage of C–F bonds is rarely reported [8] due to the thermodynamic and chemical stability of fluorocarbons,[9] and thus, sulfuration of the CF_3 group remains unexplored.

1,2-Dithiole-3-thiones (D3T) are essential structural motifs in numerous pharmaceuticals with remarkable biological and medicinal utility, including chemotherapy, antioxidant, and radiation protection.[10] For instance, Oltipraz exhibits anti-HIV activity,[11] NOSH-1 shows excellent anti-inflammatory effects,[12] Anethole dithiolethione ADT is used as cholagogue,[13] and S-Danshensu has some effects on male infertility (Figure 1).[14] The traditional synthetic method involving multi-step reactions of terminal alkynes or *β*-ketoesters with sulfurating reagents suffers from harsh reaction conditions, low yields and poor functional group tolerance.[15] In 2016, Singh and co-workers reported an efficient synthesis of 1,2-dithiole derivatives by $InCl_3$-catalyzed heterocyclization of *α*-enolic dithioesters with elemental sulfur.[16] As part of our continue interest in the synthetic utility of fluorine and sulfur-containing molecules,[17] we wondered if the conversion of fluoride to sulfide could be achieved through multiple carbon-fluorine bond cleavages of trifluoromethyl compounds. Herein, we wish to report a copper-catalyzed defluorinative thioannulation of trifluoropropynes with elemental sulfur for the efficient and practical synthesis of 1,2-dithiole-3-thiones (Scheme 1b).



Scheme 1. Strategies for defluorination of CF_3 groups.

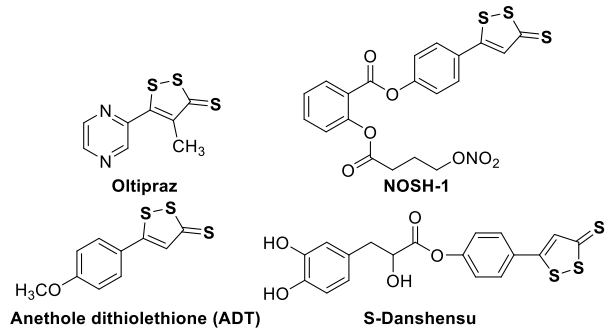


Figure 1. Representative drugs containing the D3T moiety.

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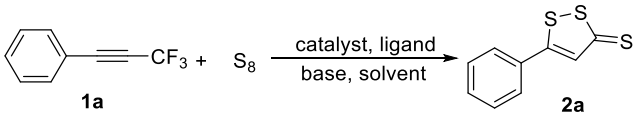
Table 1. Optimization of reaction conditions.[a]



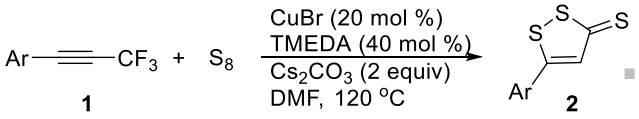
1a 2a

Entry	Catalyst	Ligand	Base	Solvent	Yield (%)
1	CuOAc	-	Cs_2CO_3	DMF	49
2	CuCl	-	Cs_2CO_3	DMF	42
3	CuBr	-	Cs_2CO_3	DMF	59
4	CuI	-	Cs_2CO_3	DMF	43
5	-	-	Cs_2CO_3	DMF	Trace
6	CuBr	1,10-Phen	Cs_2CO_3	DMF	56
7	CuBr	bipyridine	Cs_2CO_3	DMF	62
8	CuBr	TMEDA	Cs_2CO_3	DMF	88
9	CuBr	TMEDA	K_2CO_3	DMF	62
10	CuBr	TMEDA	K_3PO_4	DMF	36
11	CuBr	TMEDA	-	DMF	NR
12	CuBr	TMEDA	Cs_2CO_3	DMSO	65
13	CuBr	TMEDA	Cs_2CO_3	MeCN	23
14	CuBr	TMEDA	Cs_2CO_3	Toluene	Trace
15[b]	CuBr	TMEDA	Cs_2CO_3	DMF	52
16[c]	CuBr	TMEDA	Cs_2CO_3	DMF	63
17[d]	CuBr	TMEDA	Cs_2CO_3	DMF	72
18[e]	CuBr	TMEDA	Cs_2CO_3	DMF	ND

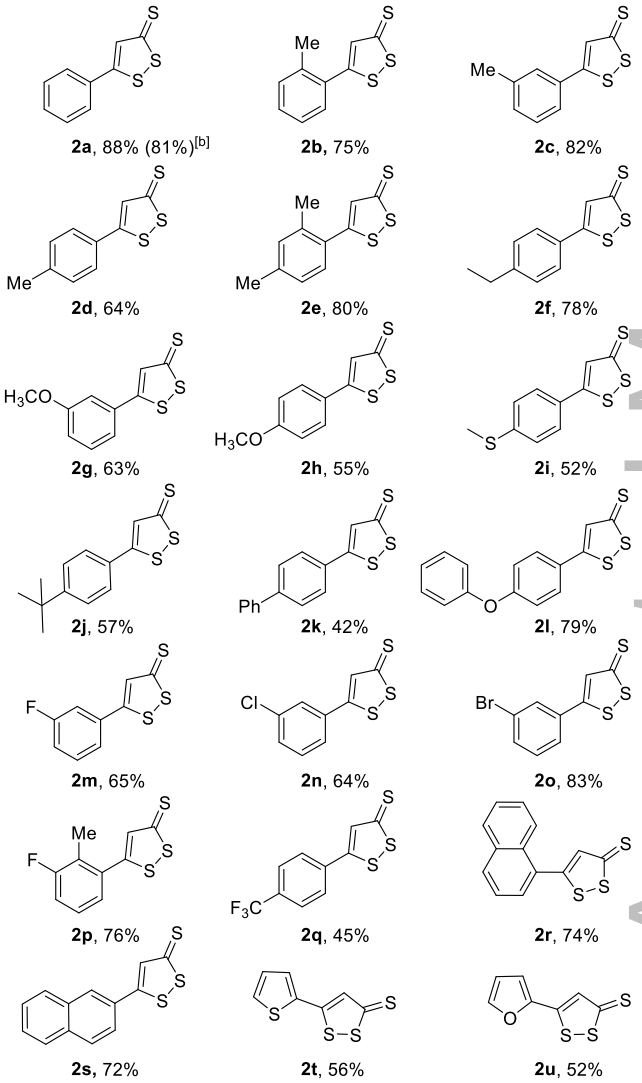
[a] Reaction conditions: **1a** (0.2 mmol), S_8 (1.5 equiv), CuBr (20 mol %), ligand (40 mol %), base (2.0 equiv), solvent (2 mL) at 120 °C for 12 h, isolated yield.
[b] CuBr (10 mol %).
[c] At 100 °C.
[d] S_8 (1.2 equiv).
[e] Na_2S or NaHS was used as the sulfur source; NR = no reaction; ND = not detected.

Inspired by the high efficiency of C–S bond formation catalyzed by cuprous salts,[18] we carried out our research by testing the reaction of (3,3,3-trifluoroprop-1-yn-1-yl)benzene **1a**[19] with sulfur in the presence of 20 mol% CuOAc and 2 equiv of Cs_2CO_3 in DMF at 120 °C. We were pleased to find that the desired product **2a** was isolated in 49% yield (Table 1, entry 1), and the structure was confirmed by X-ray diffraction analysis. Encouraged by these results, various copper catalysts were investigated, and CuBr proved to be the best catalyst for delivering product **2a** in 59% yield (entry 3). However, only trace amounts of 1,2-dithiole-3-thiones could be detected in the absence of a catalyst (entry 5). To further enhance the reaction yield, several *N*,*N*-bidentate ligands were examined, such as 1,10-Phen, bipyridine and TMEDA (entries 6-8). The results showed that TMEDA was the optimal ligand, and an 88% yield was obtained (entry 8). During the testing of different bases, the reaction yields were decreased when K_2CO_3 and K_3PO_4 were used (entries 9 and 10). The reaction did not proceed without a base, suggesting that strong base was crucial for the process of defluorinative thioannulation (entry 11). When the solvent was changed to DMSO, MeCN or toluene, the reaction afforded lower yields or trace amounts of product (entries 12-14). Lower yields were also observed when the loading of CuBr was reduced to 10 mol% or when the reaction temperature was reduced to 100 °C (entries 15 and 16). A 72% yield was obtained when l.2 equiv of S_8 was used (entry 17), while the desired product was not detected using Na_2S or NaHS as the sulfurating reagent (entry 18).

Table 2. Synthesis of 1, 2-dithiole-3-thione derivatives.[a]



1 2



[a] Reaction conditions: **1** (0.2 mmol), S_8 (1.5 equiv), CuBr (20 mol %), TMEDA (40 mol %), Cs_2CO_3 (2 equiv) in DMF (2 mL) at 120 °C for 12 h, isolated yields.
[b] 15 mmol scale, 2.55g of **2a** was isolated.

Under the optimal conditions, we next explored the substrate scope of this defluorinative thioannulation by

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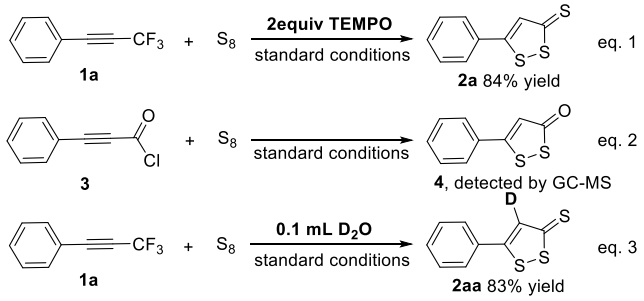
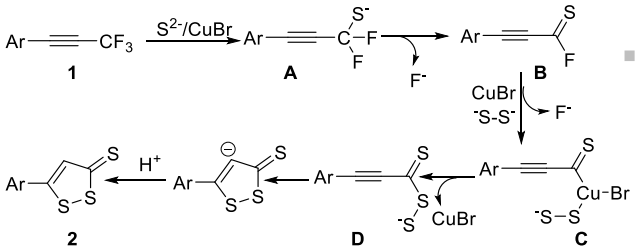
testing the reaction with a series of aryl trifluoropropynes. As shown in Table 2, the results revealed that various functional groups including electron-donating or electron-withdrawing substituents in different positions of the phenyl group could be well tolerated. For example, methyl or ethyl substituted phenyls afforded the 1,2-dithiole-3-thiones **2b**-**2f** in 64%-82% yield. Even substrates **1b** and **1e** with a steric *ortho*-methyl group underwent the reaction smoothly to give products **2b** and **2e** in 75% and 80% yields, respectively. Significantly, *meta*- or *para*-methylthio and methoxy substituted products **2g**-**2i** were obtained in 52%-63% yields, especially product **2h**, which has been applied as a commercial prescription drug. The *para*- *tert*-butyl, phenyl and phenoxy substituted products **2j**-**2l** were isolated in 42%-79% yields. Moreover, F, Cl and Br substituents were compatible for the thioannulation to give products **2m**-**2p** in yields of 64%-83%. Pleasingly, substrate **1q** with an electron-withdrawing trifluoromethyl group successfully afforded product **2q** in 45% yield. During the examination of other aryl groups, the results indicated that the reaction could proceed smoothly under the standard conditions for naphthyl or heteroaryl groups. For instance, 1-naphthyl and 2-naphthyl provided the products **2r** and **2s** with 74% and 72% yields, respectively. As expected, the thiophen-2-yl and furan-2-yl substituted **2t** and **2u** were prepared successfully by this defluorinative thioannulation, albeit in low yields of 56% and 52%.

In order to probe the mechanism of this defluorinative thioannulation, the following control experiments were conducted (Scheme 2). First, we carried out the reaction of **1a** with S_8 under the standard conditions by adding 2 equiv. of 2,2,6,6-tetramethylpiperidine oxide (TEMPO), a radical scavenger. The desired product **2a** was still isolated in 84% yield, which implied that this transformation might not proceed through a free radical pathway. According to previous reports,[20] we speculated that thionyl fluoride was formed as a highly active intermediate before cyclization. Unfortunately, we did not detect or isolate 3-phenylprop-2-ynethionyl fluoride owing to its extreme reactivity. Therefore, the reaction of 3-phenylpropynoyl chloride **3** with S_8 was carried out under standard conditions. As expected, the corresponding product **4** was detected by GC-MS (eq. 2) these results partly proved our hypothesis. Moreover, when the reaction of **1a** with S_8 was conducted in anhydrous DMF and 0.1 mL D_2O under standard conditions, the deuterated product **2aa** was isolated in 83% yield, suggesting that the proton was derived from water in the solvent (eq. 3).



Scheme 2. Control experiments.

On the basis of the experimental results and the relevant reports,[21] a plausible mechanism was proposed in Scheme 3. It is well-known that S_8 can undergo a disproportionation reaction under alkaline conditions to produce SO_3^{2-} and S^{2-}, and S^{2-} could further react with S_8 to give polysulfides including $^{-}S\text{-}S^{-}$.[22] Next, the substrate trifluoropropyne **1** could undergo copper-catalyzed defluorinative C–S formation with S^{2-} to form intermediate **A** in the presence of TMEDA and Cs_2CO_3. The thionyl fluoride **B** could be formed through the F^- leaving intermediate **A**.[23] Then, the oxidative addition with CuBr and ligand exchange with $^{-}S\text{-}S^{-}$ provides intermediate **C**, and the following reductive elimination delivers dithioperoxothioate **D**. Finally, the intramolecular nucleophilic addition of sulfide to the triple bond and protonation affords the cyclization product **2**.



Scheme 3. Possible mechanism.

In conclusion, we have successfully developed a copper-catalyzed defluorinative thiocyclization for the synthesis of 1,2-dithiole-3-thione derivatives using odorless, nontoxic and readily available S_8 as the sole sulfur source. The reaction provides an efficient pathway for the construction of the D3T moiety and shows a broad substrate tolerance to give the corresponding products in moderate to good yields. This protocol may offer a method for the formation of C–S bonds from the cleavage of C–F bonds, and also for the conversion of trifluoromethylated compounds to sulfur-containing heterocyclic compounds.

Experimental Section

Typical Experimental Procedure for the Synthesis of 2a: To a flame-dried Schlenk tube with a magnetic stirring bar was charged with **1a** (34.0 mg, 0.2 mmol), S_8 (76.8 mg, 0.3 mmol), CuBr (5.7 mg, 20 mol %), TMEDA (9.3 mg, 40 mol %), Cs_2CO_3 (130.3 mg, 2 equiv) in DMF (2 mL) under air atmosphere. The reaction mixture was stirred at 120 °C for 12 hours. After the reaction was completed, the mixture was poured into ethyl acetate, which was washed with brine (2 x 15 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under *vacuum*. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product **2a** (37.0 mg) as a red solid. Yield 88%; m.p. 122-124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.0 Hz, 2H), 7.48-7.47 (m, 1H), 7.42-7.39 (m, 2H), 7.35 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.5, 172.8, 135.9, 132.1, 131.6, 129.5, 126.8; LRMS (EI 70 ev) m/z (%): 210 (M^+, 79), 146 (20), 145 (100), 122 (29).

X-Ray structure: Supplementary crystallographic data was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC-1840046 (**2a**) and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

Acknowledgements

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References

[1] a) V. J. Scott, R. Çelenligil-Çetin, O. V. Ozerov, *J. Am. Chem. Soc.* **2005**, *127*, 2852; b) T. Ahrens, J. Kohlmann, M. Ahrens, T. Braun, *Chem. Rev.* **2015**, *115*, 931; c) T. A. Unzner, T. Magauer, *Tetrahedron Lett.* **2015**, *56*, 877.

[2] For selected reviews on C–F bond activation, see: a) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119; b) T. Hendrik, F. T. Klare, M. Oestreich, *ACS Catal.* **2013**, *3*, 1578; c) M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem., Int. Ed.* **2013**, *52*, 3328.

[3] For selected examples, see: a) G. Meier, T. Braun, *Angew. Chem., Int. Ed.* **2009**, *48*, 1546; b) C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* **2010**, *132*, 4946; c) W. Zhao, J. Wu, S. Cao, *Adv. Synth. Catal.* **2012**, *354*, 574; d) J. Xiao, J. Wu, W. Zhao, S. Cao, *J. Fluorine Chem.* **2013**, *146*, 76; e) T. Akiyama , K. Atobe, M. Shibata, K. Mori, *J. Fluorine Chem.* **2013**, *152*, 81; f) S. M. Senaweera, A. Singh, J. D. Weaver, *J. Am. Chem. Soc.* **2014**, *136*, 3002.

[4] a) N. Yoshikai, H. Mashima, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 17978; b) T. Schaub, M. Backes, U. Radius, *J. Am. Chem. Soc.* **2006**, *128*, 15964; c) M. Tobisu, T. Xu, T. Shimasaki, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 19505; d) Y. Nakamura, N. Yoshikai, L. Ilies, E. Nakamura, *Org. Lett.* **2012**, *4*, 3316; e) Z.-J. Luo, H.-Y. Zhao, X. Zhang, *Org. Lett.* **2018**, *20*, 2543.

[5] a) K. Fuchibe, T. Akiyama, *J. Am. Chem. Soc.* **2006**, *128*, 1434; b) J. Terao, M. Nakamura, N. Kambe, *Chem. Commun.* **2009**, 6011; c) W. Gu, M. R. Haneline, C. Douvris, O. V. Ozerov, *J. Am. Chem. Soc.* **2009**, *131*, 11203; d) J. Zhu, M. Pérez, C. B. Caputo, D. W. Stephan, *Angew. Chem., Int. Ed.* **2016**, *55*, 1417; e) F. Forster, T. T. Metsänen, E. Irran, P. Hrobárik, M. Oestreich, *J. Am. Chem. Soc.* **2017**, *139*, 16334.

[6] a) K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama, *Angew. Chem., Int. Ed.* **2009**, *48*, 8070; b) T. Yamada, K. Saito, T. Akiyama, *Adv. Synth. Catal.* **2016,** *358*, 62; c) K. Saito, T. Umi, T. Yamada, T. Suga, T. Akiyama, *Org. Biomol. Chem.* **2017**, *15*, 1767.

[7] a) I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.* **2011**, *111*, 1596; b) Y.-Y. Lin, Y.-J. Wang, C.-H. Lin, J.-H. Cheng, C.-F. Lee, *J. Org. Chem.* **2012**, *77*, 6100; c) Z. Qiao, J. Wei, X. *Org. Lett.* **2014**, *16*, 1212; d) F.-F. Duan, S.-Q. Song, R.-S. Xu, *Chem. Commun.* **2017**, *53*, 2737; e) B.-B. Liu, X.-Q. Chu, H. Liu, L. Yin, S.-Y. Wang, S.-J. Ji, *J. Org. Chem.* **2017**, *82*, 10174.

[8] a) M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc.* **2008**, *130*, 12214; b) C. Yu, C. Zhang, X. Shi, *Eur. J. Org. Chem.* **2012**, 1953; c) C. Yu, G. Hu, C. Zhang, R. Wu, H. Ye, G. Yang, X. Shi, *J. Fluorine Chem.* **2013**, *153*, 33; d) X. Zhang, G.-P. Lu, C. Cai, *Green Chem.* **2016**, *18*, 5580; e) Z. Liu, K. Ouyang, N. Yang, *Org. Biomol. Chem.* **2018**, *16*, 988.

[9] For selected examples, see: a) H. Amii, Y. Hatamoto, M. Seo, K. Uneyama, *J. Org. Chem.* **2001**, *66*, 7216; b) C. Douvris, O. V. Ozerov, *Science* **2008**, *321*, 1188; c) T. Stahl, H. F. T. Klare, M. Oestreich, *J. Am. Chem. Soc.* **2013**, *135*, 1248; d) R. Doi, M. Ohashi, S. Ogoshi, *Angew. Chem., Int. Ed.* **2016**, *55*, 341; e) S. Yoshida, K. Shimomori, Y. Kim, T. Hosoya, *Angew. Chem., Int. Ed.* **2016**, *55*, 10406.

[10] a) T. W. Kensler, J. D. Groopman, B. D. Roebuck, T. J. Curphey, *ACS Symp. Ser.* **1993**, *546*, 154; b) Y. Y. Maxiutenko, A. H. Libby, H. H. Joyner, T. J. Curphey, D. L. MacMillan, T. W. Kensler, B. D. Roebuck, *Carcinogenesis* **1998**, *19*, 1609; c) M. A. Otieno, T. W. Kensler, K. Z. Guyton, *Free Radical Biol. Med.* **2000**, *28*, 944; d) A. Begleiter, L. Lange, *Int. J. Oncol.* **2002**, *20*, 835.

[11] a) H. J. Prochaska, Y. Yeh, P. Baron, B. Polsky, *Proc. Natl. Acad. Sci. U.S.A* **1993**, *90*, 3953; b) H. J. Prochska, C. L. Fernandes, R. M. Pantoja, S. J. Chavan, *Biochem. Biophys. Res. Comm.* **1996**, *221*, 548.

[12] R. Kodela, M. Chattopadhyay. K. Kashfi, *ACS Med. Chem. Lett.* **2012**, *3*, 257.

[13] a) R. Häusler, J. Ritschard, *Rev. Suisse Praxis Med.* **1979**, *68*, 1063; b) Z. X. Ma, S. L. Zhu, Y. L. Wang, J. L. You, W. B. Lu, CN 101463030A.

[14] J. Bian, Z. Cai, H. Wu, CN 102417501A.

[15] a) C. TH. Pedersen, *Adv. Heterocycl Chem.* **1982**, *31*, 63; b) T. J. Curphey, *Tetrahedron Lett.* **2002**, *43*, 371; c) T. J. Curphey, *J. Org. Chem.* **2002**, *67*, 6461; d) D. A. Brown, S. Betharia, J.-H. Yen, Q. Tran, H. Mistry, K. Smith, *Bioorg. Med. Chem. Lett.* **2014**, *24*, 5829; e) H. Adams, A. J. Hughes, M. J. Morris, S. I. A. Quenby, *Tetrahedron Lett.* **2014**, *55*, 5283.

[16] S. Koley, T. Chanda, S. Samai, M. S. Singh, *J. Org. Chem.* **2016**, *81*, 11594.

[17] a) C.-L. Li, X.-G. Zhang, R.-Y. Tang, P. Zhong, J.-H. Li, *J. Org. Chem.* **2010**, *75*, 7037; b) S. Shi, L.-L. Sun, Z.-Y. Liao, X.-G. Zhang, *Synthesis* **2012**, *44*, 0966; c) Z.-J. Yang, B.-L. Hu, C.-L. Deng, X.-G. Zhang, *Adv. Synth. Catal.* **2014**, *356*, 1962; d) H.-Y. Tu, B.-L. Hu, C.-L. Deng, X.-G. Zhang, *Chem. Commun.* **2015**, *51* 15558.

[18] For selected examples, see: a) F. Y. Kwong, S. L. Buchwald, *Org. Lett.* **2002**, *4*, 3517; b) C. Chen, Y. Xie, L. Chu, R.-W. Wang, X. Zhang, F.-L. Qing, *Angew. Chem., Int. Ed.* **2012**, *51*, 2492; c) Z. Zhou, Y. Liu, J. Chen, E. Yao, J. Cheng, *Org. Lett.* **2016**, *18*, 5268; d) E. Guzmán-Percástegui, D. J. Hernández, I. Castillo, *Chem. Commun.* **2016**, *52*, 3111; e) C. Ravi, N. N. K. Reddy, V. Pappula, S. Samanta, S. Adimurthy, *J. Org. Chem.* **2016**, *81*, 9964.

[19] This compound was prepared from the reaction of terminal alkynes with Me_3SiCF_3, please see: L. Chu, F.-

10.1002/adsc.201800846

L. Qing, *J. Am. Chem. Soc.* **2010**, *132*, 7262.
[20] a) W. J. Middleton, E. G. Howard, W. H. Sharkey, *J. Am. Chem. Soc.* **1961**, *83*, 2589; b) W. J. Middletone, E. G. Howard, W. H. Sharkey, *J. Org. Chem.* **1965**, *30*, 1375.
[21] a) M. Arisawa, T. Yamada, M. Yamaguchi, *Tetrahedron Lett.* **2010**, *51*, 6090; b) M. Arisawa, T. Ichikawa, M. Yamaguchi, *Org. Lett.* **2012**, *14*, 5318; c) L. Meng, T. Fujikawa, M. Kuwayama, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2016**, *138*, 10351; d) L. Xu, Q. Zhang, Q. Xie, B. Huang, J.-J. Dai, J. Xu, H.-J. Xu, *Chem. Commun.* **2018**, *54*, 4406.
[22] Y. Jiang, Y. Qin, S. Xie, X. Zhang, J. Dong, D. Ma, *Org. Lett.* **2009**, *11*, 5250.
[23] J. Zheng, R. Cheng, J.-H. Lin, D.-H. Yu, L. Ma, L. Jia, L. Zhang, L. Wang, J.-C. Xiao, S. H. Liang, *Angew. Chem., Int. Ed.* **2017**, *56*, 3196.

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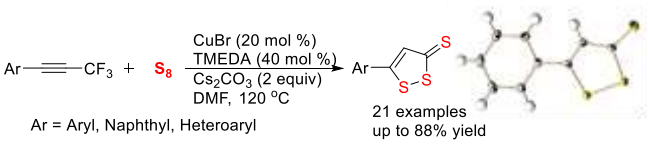

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