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Visible-light-induced synthesis of benzothiophenes and benzoselenophenes via the annulation of thiophenols or 1,2-diphenyldiselane with alkynes

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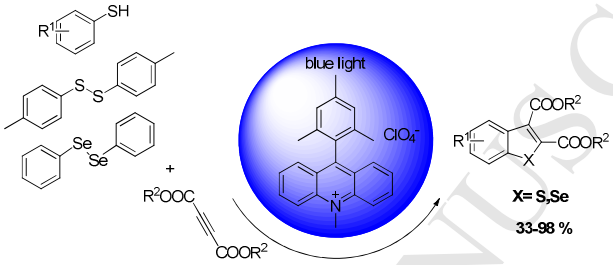

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ABSTRACT

An effective metal-free photoredox-mediated tandem addition/cyclization reaction of thiophenols or 1,2-diphenyldiselane with alkynes leads to 2,3-disubstituted benzothiophenes and benzoselenophenes. Blue light irradiation of the organic dye, Mes-Acr-Me$^+$, initiates the photoredox catalysis. A series of functional groups could be tolerated under ambient conditions, and good to excellent yields were generated.

1. Introduction

Benzothiophene derivatives have attracted considerable attention from chemists in recent years due to their wide application in biology,[1] pharmacy,[2] catalysis,[3] and especially in material science.[4] There are several active drugs on the market and potential active molecules containing the benzothiophene skeletons. For instance, Zileuton is used as a potent and selective inhibitor of 5-lipoxygenase, while raloxifene and arzoxifene are selective estrogen receptor modulators and antitubulin agents.[5] FAUC 346 and FAUC 365 can be used as D3 partial agonists, while benzothiophene biphenyl analogues are presented for inhibition of protein tyrosine phosphatase 1B (PTP1B) (Figure 1).[6] To date, lots of elegant methods have been access to the synthesis of these substituted benzothiophene cores, including intramolecular cyclizations of α-arylthioketones,[7] *o*-alkynyl (or alkenyl or ynol) benzenthiols,[3c,8] and alkynyl(aryl)thioethers,[9] and direct arylation of the benzothiophene moiety,[10] and other methods[11]. Although great progress has been achieved by using these strategies, prefunctionalized thiophenols have to be synthesized for the transformations, which limited their pervasive applications in pharmaceutical synthesis. Therefore, an efficient and practical method from thiophenols for the construction of substituted benzothiophenes was urgent in modern organic synthesis.[12]

Recently, the visible light-induced photoredox catalysis has attracted renewed interest from synthetic chemists to access challenging targets and to generate new, structurally-complex molecules with high levels of practicality and chemoselectivity.[13] In the last few years, visible light photocatalysis has also been used as a powerful tool for mild and selective synthesis of

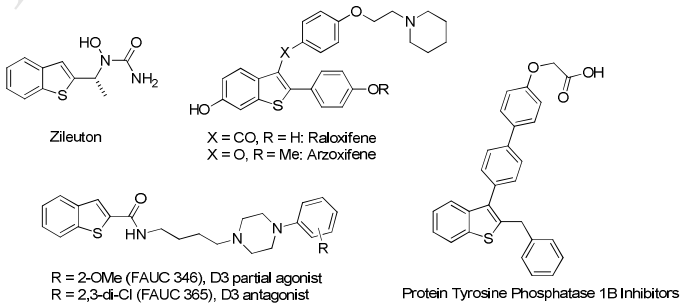

Figure 1. Biologically active molecules containing benzothiophene moiety.

substituted benzothiophenes. In 2012, König and co-workers reported a visible-light-mediated direct C-H arylation of benzothiophenes with aryl diazonium salts, but unfortunately mixtures of regioisomers were achieved in low yields (Scheme 1-a).[11a] Later, the photocatalytic reaction of *o*-methylthio-arenediazonium salts with alkynes for the synthesis of benzothiophenes was realized by the same group (Scheme 1-b).[11b] However, prefunctionalized thiophenols or unstable and insecure arenediazonium salts resulted in poor selectivity and difficulties with scale-up. Inspired by our continuous efforts in radical addition/cyclization reactions[14] and based on our previous work on photoredox catalysis,[15] we here report a straightforward photoredox-mediated tandem addition/cyclization reaction of thiophenols or 1,2-diphenyldiselane with alkynes for the

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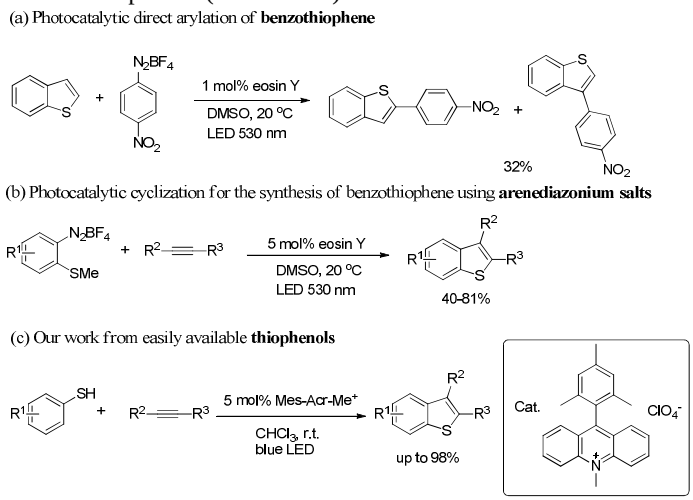
synthesis of 2,3-disubstituted benzothiophenes and benzoselenophenes (Scheme 1-c).[16]

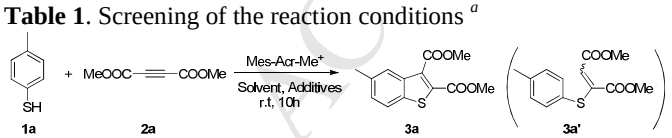


Scheme 1. Photocatalytic approaches for the synthesis of benzothiophenes.

2. Results and Discussion

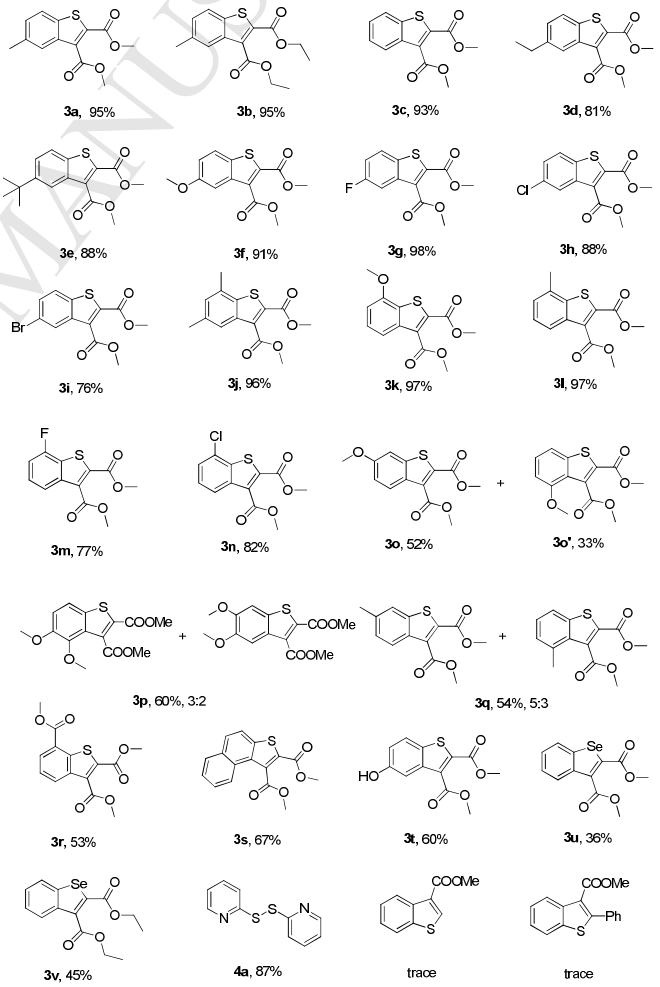
In previous report, benzenesulfanyl radical can be easily formed by SET from thiophenol ($E_{1/2}^{ox}$=+0.95 V versus the saturated calomel electrode (SCE) in MeCN for thiophenol)[17] to the excited state of the photocatalyst Mes-Acr-Me^{+*} ($E^{S}_{1/2}{}^{red}$ [Mes-Acr-Me^{+*}/Mes-Acr-Me$^{\cdot}$]=+2.18 V versus SCE in MeCN).[18] So, our initial studies focused on the reaction of the 4-methylbenzenethiol **1a** with dimethyl but-2-ynedioate using Mes-Acr-Me^{+} as a photoredox catalyst and benzoic acid as the additive by irradiating at 450 nm at 1 atm oxygen atmosphere.[19] First, several solvents were investigated including DCE, DCM, CH_3CN, $CHCl_3$, DMF, EtOAc, and toluene (Table 1, entries 1-7), where $CHCl_3$ gave a better result (entry 6). Then, we examined the amount of additive loading (entries 9 and 10) and different equivalents of alkyne (entry 8) on this photocatalysis reaction, and poor results were obtained compared with entry 6. When PivOH was used as the acid additive, a lower yield was get (entry 11). To our delight, when the reaction was performed in air or under Ar atmosphere, high yields were obtained (entries 12 and 13). In addition, 1,2-di-*p*-tolyldisulfane was also suitable in this transformation (entry 14). To prove the essential role of photocatalysis for the addition/annulation reaction, experiments without blue light irradiation or without dye under irradiation were carried out. As expected, only a 15% and 16% yield was observed, respectively (entries 15 and 16).

Table 1. Screening of the reaction conditions [a]



Entry	Conditions	Yield (%) [b]
1	2a (3.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), DCE	40 (18)
2	2a (3.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), CH_3CN	32
3	2a (3.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), DCM	44
4	2a (3.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), DMF	0 (63)
5	2a (3.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), EtOAc	16
6	2a (3.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), $CHCl_3$	63
7	2a (3.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), toluene	48
8	2a (2.0 equiv.), PhCOOH (2.0 equiv.), O_2 (1 atm), $CHCl_3$	40
9	2a (3.0 equiv.), PhCOOH (1.2 equiv.), O_2 (1 atm), $CHCl_3$	59
10	2a (3.0 equiv.), O_2 (1 atm), $CHCl_3$	20
11	2a (3.0 equiv.), PivOH (2.0 equiv.), O_2 (1 atm), $CHCl_3$	50
12	2a (3.0 equiv.), PhCOOH (2.0 equiv.), air (1 atm), $CHCl_3$	80
13	**2a (3.0 equiv.), PhCOOH (2.0 equiv.), Ar (1 atm), $CHCl_3$**	95
14[c]	2a (3.0 equiv.), PhCOOH (2.0 equiv.), Ar (1 atm), $CHCl_3$	80
15	Without LED light	15
16	Without catalyst	16

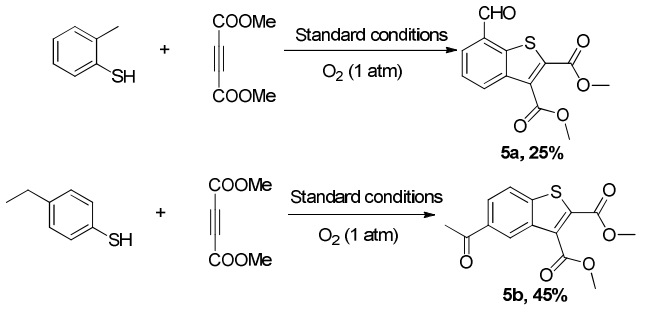
The best reaction conditions are indicated in bold.
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (3.0 equiv., 0.9 mmol), catalyst (5 mol%), oxidant, solvent (3.0 mL), r.t., for 10h.
[b] Isolated yields.
[c] 1,2-di-*p*-tolyldisulfane was used instead of **1a**.



Scheme 2. Scope of the photoannulation reactions.

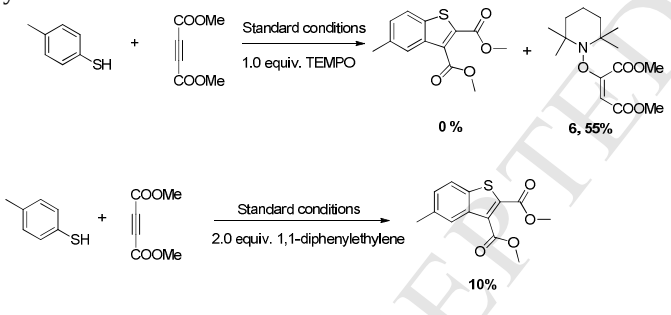
With the optimized reaction conditions in hand (Table 1, entry 13), we investigated the reaction scope for thiophenols with alkynes for the photoannulation reaction (Scheme 2). The obvious electron-effect on the benzene ring has not been observed, and both electron-donating and electron-withdrawing substituted thiophenols could produce the desired benzothiophenes **3a-n** in good to excellent yields. Ortho-

substituted thiophenols could proceed well under the optimized reaction conditions (**3k**-**3n**). However, a poor regioselectivity was observed using *m*-MeO-thiophenol, and the isomers of **3o** and **3o'** can be easily separated. When 3,4-diMeO-thiophenol and *m*-Me-thiophenol were submitted to the standard conditions, mixed isomers were produced (**3p** and **3q**). It was found that *o*-ester substituted thiophenol can also yield the target product (**3r**). *β*-Naphthiophenol was also tolerated, and selectively cyclized at the *α*-position (**3s**). Of particular note, *p*-OH-thiophenol and 1,2-diphenyldiselane can react with **2a** to give the corresponding products in moderate yields (**3t**, **3u** and **3v**). Such molecules are difficult to synthesize using previous reported methods[12,16] and very useful for further synthetic elaborations. To our disappointment, heterocyclic thiophenol such as pyridine-2-thiol failed in this transformation, but a self-coupling product **4a** was produced. In addition, methyl propiolate and methyl 3-phenylpropiolate were not suitable for this photoannulation reaction.



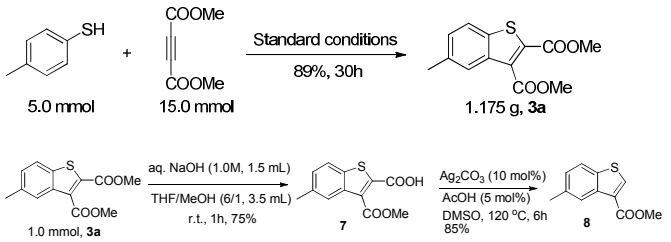
Scheme 3. Photocatalysis oxygen insertion reaction

Interestingly, when the photocatalysis reaction was carried out at 1 atm oxygen atmosphere, a cyclization/oxygen insertion phenomenon was observed (Scheme 3). Benzaldehyde and acetophenone derivatives (**5a** and **5b**) were obtained in moderate yields.



Scheme 4. Control experiments.

To gain more insights into the mechanism, the control experiments were performed (Scheme 4). The photocatalysis addition/cyclization reaction was found to be completely suppressed using 1.0 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as the typical radical scavenger, and an addition product of TEMPO with dimethyl but-2-ynedioate was separated in 55% yield. When 1,1-diphenylethylene was added into the standard conditions, no product was observed. These results indicated that a radical addition pathway might be involved in this transformation.



Scheme 5. Scale-up experiment and synthetic transformations.

To further demonstrate the utility of the present method, a scale-up experiment was investigated, and a gram scale of product **3a** can be easily prepared (Scheme 5). In addition, benzothiophene **8** can be efficiently synthesized *via* two-steps from product **3a** in good yield. [12a]

3. Conclusions

In summary, we have developed a general and efficient visible-light photoredox tandem addition/cyclization reaction of thiophenols or 1,2-diphenyldiselane with alkynes at room temperature. Interestingly, the reaction can be conducted at argon or oxygen atmosphere, and the cyclization/oxygen insertion products can be produced under 1 atm oxygen conditions. In addition, benzoselenophene derivatives can be easily synthesized *via* this transformation.

4. Experimental section

4.1. General information

Column chromatography was carried out on silica gel. Unless noted ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ or *d*-actone, ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ or *d*-actone. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a micrOTOF-Q instrument equipped with an ESI source; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided.

4.2. Typical procedure for the synthesis of product 3

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 4-methylbenzenethiol (**1a**, 0.3 mmol), dimethyl but-2-ynedioate (**2**, 0.9 mmol), 5% Mes-Acr-Me$^+$ (0.015 mmol), PhCOOH (2 equiv., 0.6 mmol). The flask was evacuated and backfilled with Ar for 3 times. Then $CHCl_3$ (3.0 mL) was added with syringe. The reaction mixture was then stirred for 10 h at room temperature. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product **(**petroleum ether/ethyl acetate as eluent (8:1)).

4.2.1 dimethyl 5-methylbenzo[*b*]thiophene-2,3-dicarboxylate, **3a**, 95%, M. P. = 85-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.80-7.66 (m, 2H), 7.32 (d, *J* = 8.3Hz, 1H), 4.02 (s, 3H), 3.93 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.0, 162.2, 137.7, 137.0, 135.7, 132.9, 129.4, 125.1, 124.0, 122.1, 52.8, 52.7, 21.4. IR: (cm^{-1}): 3021, 2953, 2920, 1913, 1714, 1565, 1536, 1456, 1434, 1358, 1197, 1236, 1168, 1104, 939, 888, 808, 765.

4.3. Typical procedure for the synthesis of product 5

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 4-ethylbenzenethiol (0.3 mmol), dimethyl but-2-ynedioate (**2**, 0.9 mmol), 5% Mes-Acr-Me$^+$ (0.015 mmol), PhCOOH (2 equiv., 0.6 mmol). The flask was evacuated and backfilled with O_2 for 3 times. Then $CHCl_3$ (3.0 mL) was added with syringe. The reaction mixture was then stirred for 24 h at room temperature. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product **(**petroleum ether/ethyl acetate as eluent (6:1)).

4.3.1 dimethyl 7-formylbenzo[*b*]thiophene-2,3-dicarboxylate, **5a**, 25%, M. P. = 152-153 °C, ^{1}H NMR (400 MHz, $CDCl_3$): 10.24 (s, 1H), 8.30-8.26 (m, 1H), 8.05-8.02 (m, 1H), 7.71-7.65 (m, 1H),

4.04 (s, 3H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 190.7, 164.5, 162.1, 138.2, 137.9, 136.9, 133.7, 131.46, 130.6, 130.5, 125.8, 53.0, 52.9. IR (cm^{-1}): 2957, 1708, 1681, 1560, 1528, 1430, 1356, 1293, 1254, 1172, 1110, 1066, 1043, 917, 863, 808, 769, 683, 576. HRMS (ESI) m/z calcd for $C_{13}H_{11}O_5S^+(M+H)^+$: 279.03217, found 279.03214.

Acknowledgments

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References and notes

1 (a) Gai, Z.; Yu, B.; Wang, X.; Deng, Z.; Xu, P. *Microbiology.* **2008**, *154*, 3804; (b) Konishi, J.; Onaka, T.; Ishii, Y.; Suzuki, M. *FEMS Microbiol. Lett.* **2000**, *187*, 151; (c) Yun, C.; You, J.; Kim, J.; Huh, J.; Kim, E. *J. Photochem. Photobiol., C* **2009**, *10*, 111.

2 (a) Xiong, R.; Patel, H. K.; Gutgesell, L. M.; Zhao, J.; Delgado-Rivera, L.; Pham, T. N. D.; Zhao, H.; Carlson, K.; Martin, T.; Katzenellenbogen, J. A.; Moore, T. W.; Tonetti, D. A.; Thatcher, G. R. J. *J. Med. Chem.* **2016**, *59*, 219; (b) Kołaczkowski, M.; Marcinkowska, M.; Bucki, A.; Pawłowski, M.; Mitka, K.; Jaśkowska, J.; Kowalski, P.; Kazek, G.; Siwek, A.; Wasik, A.; Wesołowska, A.; Mierzejewski, P.; Bienkowski, P. *J. Med. Chem.* **2014**, *57*, 4543; (c) Rackham, M. D.; Brannigan, J. A.; Moss, D. K.; Yu, Z.; Wilkinson, A. J.; Holder, A. A.; Tate, E. W.; Leatherbarrow, R. J. *J. Med. Chem.* **2013**, *56*, 371; (d) Guo, H.-F.; Shao, H.; Yang, Z.; Xue, S.; Li, X.; Liu, Z.; He, X.; Jiang, J.; Zhang, Y.; Si, S.; Li, Z. *J. Med. Chem.* **2010**, *53*, 1819.

3 (a) Sarker, M.; Shahrin, T.; Steinmetz, M. G. *Org. Lett.* **2011**, *13*, 872; (b) Likhar, P. R.; Salian, S. M.; Roy, S.; Kantam, M. L.; Sridhar, B.; Mohan, K. V.; Jagadeesh, B. *Organometallics*, **2009**, *28*, 3966; (c) Gabriele, B.; Mancuso, R.; Lupinacci, E.; Veltri, L.; Salerno, G.; Carfagna, C. *J. Org. Chem.* **2011**, *76*, 8277.

4 (a) Iwasaki, T.; Kohinata, Y.; Nishide, H. *Org. Lett.* **2005**, *7*, 755; (b) Wong, K.-T.; Chao, T.-C.; Chi, L.-C.; Chu, Y.-Y.; Balaiah, A.; Chiu, S.-F.; Liu, Y.-H.; Wang, Y. *Org. Lett.* **2006**, *8*, 5033; (c) Pu, S.; Li, M.; Fan, C.; Liu, G.; Shen, L. *J. Mol. Struct.* **2009**, *919*, 100; (d) Jung, K. H.; Kim, K. H.; Lee, D. H.; Jung, D. S.; Park, C. E.; Choi, D. H. *Org. Electron.* **2010**, *11*, 1584.

5 (a) Rossi, A.; Pergola, C.; Koeberle, A.; Hoffmann, M.; Dehm, F.; Bramanti, P.; Cuzzocrea, S.; Werz, O.; Sautebin, L. Br. *J. Pharmacol.* **2010**, *161*, 555; (b) Qin, Z.; Kastrati, I.; Chandrasena, R. E. P.; Liu, H.; Yao, P.; Petukhov, P. A.; Bolton, J. L.; Thatcher, G. R. J. *J. Med. Chem.* **2007**, *50*, 2682; (c) Flynn, B. L.; Hamel, E.; Jung, M. K. *J. Med. Chem.* **2002**, *45*, 2670.

6 (a) Bettinetti, L.; Schlotter, K.; Hübner, H.; Gmeiner, P. *J. Med. Chem.* **2002**, *45*, 4594; (b) Yang, C.; Cross, K.; Myatt, G. J.; Blower, P. E.; Rathman, J. F. *J. Med. Chem.* **2004**, *47*, 5984.

7 (a) Pinney, K. G.; Bounds, A. D.; Dingeman, K. M.; Mocharla, V. P.; Pettit, G. R.; Bai, R.; Hamel, E. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1081; (b) Capozzi, G.; Melloni, A.; Modena, G. *J. Chem. Soc. C* **1970**, 2621.

8 (a) Godoi, B.; Schumacher, R. F.; Zeni, G. *Chem. Rev.* **2011**, *111*, 2937; (b) Wang, Z.; Geng, W.; Wang, H.; Zhang, S.; Zhang, W.-X.; Xi, Z. *Tetrahedron Lett.* **2011**, *52*, 6997; (c) Bryan, C. S.; Braunger, J. A.; Lautens, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7064; (d) Newman, S. G.; Aureggi, V.; Bryan, C. S.; Lautens, M. *Chem. Commun.* **2009**, 5236; (e) Nakamura, I.; Sato, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 4473.

9 (a) Kunz, T.; Knochel, P. *Angew. Chem., Int. Ed.* **2012**, *51*, 1958; (b) Larock, R. C.; Yue, D. *Tetrahedron Lett.* **2001**, *42*, 6011; (c) Masuya, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2016**, *18*, 4312.

10 Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.

11 (a) Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc.* **2012**, *134*, 2958; (b) Hari, D. P.; Hering, T.; König, B. *Org. Lett.* **2012**, *14*, 5334; (c) Ramesh, E.; Shankar, M.; Dana, S.; Sahoo, A. K. *Org. Chem. Front.* **2016**, *3*, 1126; (d) Yang, D.; Yan, K.; Wei, W.; Tian, L.; Li, Q.; You, J.; Wang, H. *RSC Adv.* **2014**, *4*, 48547; (e) Wan, D.; Yang, Y.; Liu, X.; Li, M.; Zhao, S.; You, J. *Eur. J. Org. Chem.* **2016**, 55.

12 (a) Liu, K.; Jia, F.; Xi, H.; Li, Y.; Zheng, X.; Guo, Q.; Shen, B.; Li, Z. *Org. Lett.* **2013**, *15*, 2026; (b) Yan, K.; Yang, D.; Zhang, M.; Wei, W.; Liu, Y.; Tian, L.; Wang, H., *Synlett*, **2015**, 1890.

13 (a) Morris, S. A.; Wang, J.; Zheng, N. *Acc. Chem. Res.* **2016**, *49*, 1957; (b) Ravelli, D.; Protti, S.; Fagnoni, M. *Chem. Rev.* **2016**, *116*, 9850; (c) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 58; (d) Dai, X.; Xu, X.; Li, X. *Chin. J. Org. Chem.* **2013**, *33*, 2046; (e) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, *4*, 355; (f) Xuan, J.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2012**, *51*, 6828; (g) Xuan, J.; Zhang, Z.-G.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2015**, *54*, 15632; (h) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898; (i) Jiang, H.; An, X.; Tong, K.; Zheng, T.; Zhang, Y.; Yu, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 4055; (j) Zhao, Y.; Huang, B.; Yang, C.; Chen, Q.; Xia, W. *Org. Lett.* **2016**, *18*, 5572, and references cited therein.

14 (a) Xia, X.-F.; Zhu, S.-L.; Chen, C.; Wang, H.; Liang, Y.-M. *J. Org. Chem.* **2016**, *81*, 1277; (b) Xia, X.-F.; Zhu, S.-L.; Liu, J.-B.; Wang, D.; Liang, Y.-M. *J. Org. Chem.* **2016**, *81*, 12482.

15 Xia, X.-F.; Zhu, S.-L.; Wang, D.; Liang, Y.-M. *Adv. Synth. Catal.* **2016**, DOI: 10.1002/adsc. 201600982.

16 During preparing the manuscript, Yan's group has reported a similar strategy for the synthesis of benzothiophene from disulfides, see: Ye, L.-M.; Qian, L.; Chen, Y.-Y.; Zhang, X.-J.; Yan, M. *Org. Biomol. Chem.* **2017**, *15*, 550.

17 (a) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605; (b) Kuss-Petermann, M.; Wenger, O. S. *J. Phys. Chem. Lett.* **2013**, *4*, 2535.

18 Benniston, A. C.; Harriman, A.; Li, P.; Rostron, J. P.; Ramesdonk, H. J. van, Groeneveld, M. M.; Zhang, H.; Verhoeven, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 16054.

19 (a) Jiang, M.; Li, H.; Yang, H.; Fu, H. *Angew. Chem., Int. Ed.* **2017**, *56*, 874; (b) Keshari, T.; Yadav, V. K.; Srivastava, V. P.; Yadav, L. D. S. *Green Chem.* **2014**, *16*, 3986.