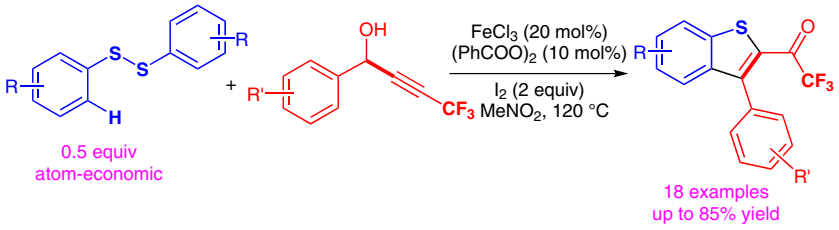
Synlett Y.-F. Lin et al. Letter

Iron-Catalyzed Thiocyclization for the Synthesis of Trifluoromethylated Benzothiophenes by C–H Functionalization of Aryl Disulfides

Yan-Feng Lin
Chong Wang
Bo-Lun Hu
Peng-Cheng Qian
Xing-Guo Zhang*

College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. of China
zxg@wzu.edu.cn



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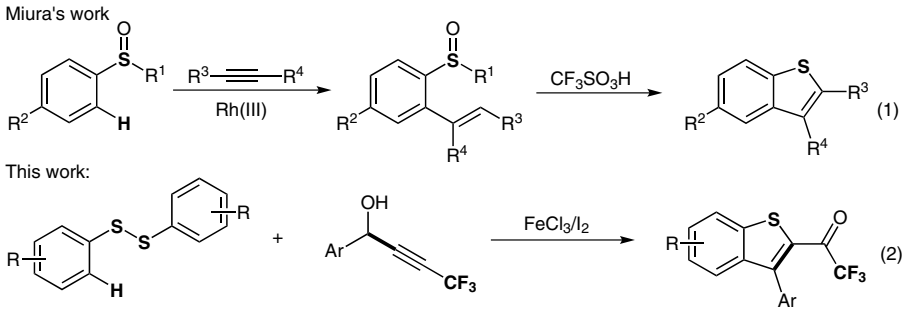
Abstract An iron-catalyzed thiocyclization of propynols with aryl disulfides has been developed for the synthesis of trifluoromethylated benzothiophenes. The one-pot tandem reaction involves Meyer–Schuster rearrangement of propynols and radical cyclization through C–H functionalization of aryl disulfides. A variety of 2-trifluoroacyl benzothiophenes were prepared in moderate to good yields with good functional-group tolerance.

Key words annulations, C–H functionalization, iron, radical, trifluoromethyl

Benzothiophene derivatives represent an important class of heterocyclic compounds, which widely exist in a large number of pharmacologically active molecules[1] and organic functional materials.[2] Therefore, a number of synthetic methods have been developed for constructing benzothiophene skeletons. Most of them involve the electrophilic cyclization of *o*-alkynyl thioanisole[3] or transition-metal-catalyzed annulations of *o*-halo alkynylbenzenes with thiol surrogates.[4] However, only a few effective approaches have been reported for the synthesis of trifluoromethylated benzothiophenes,[5] although the introduction of a CF_3 group into organic molecules often enhances their biological activities and manifests some changes in chemical and physical properties.[6] In order to overcome the limitations of some direct trifluoromethylation reactions including narrow substrate scope and/or poor regioselectivity,[7] the transformation of synthons bearing a CF_3 group at the right position has been recognized to be an alternative strategy towards targeted trifluoromethylated molecules.[8]

Recently, transition-metal-catalyzed aromatic C–H functionalization has been emerged as a powerful synthetic tool due to its step- and atom-economical advantages.[9] A variety of nitrogen- and oxygen-containing aromatic compounds could be prepared in a single-step reaction through the cleavage of C–H bonds. Whereas the C–H functionalization of sulfur-containing aromatics is rarely reported,[10] possibly due to the strong coordination ability of sulfur atom which causes poisoning of metal catalysts.[3a] Recently, Miura and coworkers reported a rhodium-catalyzed C–H alkenylation of aryl sulfoxides with alkynes, the resulted *o*-alkenylphenyl sulfoxides could be transformed into benzothiophenes via another step Pummerer cyclization (Scheme 1, eq. 1).[10a] Herein, we wish to report an iron-catalyzed C–H functionalization of aryl disulfides with trifluoromethyl propynols, which are versatile and easily prepared CF_3-containing building blocks.[11] The present one-pot tandem reaction proceeded through Meyer–Schuster rearrangement of propynols, radical addition to allenol, and intramolecular electrophilic cyclization process, leading to trifluoroacyl benzothiophenes (Scheme 1, eq. 2).

We began the study by examining the reaction between 1,2-diphenyldisulfane (**1a**) and 4,4,4-trifluoro-1-phenylbut-2-yn-1-ol (**2a**) to optimize the reaction conditions (Table 1). Treatment of diphenyl disulfide (**1a**) with substrate **2a**, 20 mol% of FeF_3 and two equivalents of I_2 afforded product **3** in 22% yield (Table 1, entry 1). These results prompted us to investigate some Lewis acids which could promote the Meyer–Schuster rearrangement process,[12] and $FeCl_3$ was found to be a more effective catalyst (65%, Table 1, entry 2). Lower yields were observed in the presence of $FeBr_3$ or FeI_3 which was prepared in situ from Fe powder and I_2 (Table 1, entries 3 and 4). While the reaction nearly did not work when $Cu(OAc)_2$ was used as catalyst or without catalyst (Table 1, entries 5 and 6). With the aim of increasing the reaction yield, we subsequently investigated some radical initiators. When 10 mol% of azodiisobutyronitrile (AIBN) or benzoyl peroxide (BPO) was added, the desired product **3** was isolated in 68% and 85% yield, respectively (Table 1, entries



Scheme 1 C–H functionalization of S-containing aromatics

7 and 8). However, the reaction yield was decreased dramatically when di-*tert*-butyl peroxide (DTBP) or *tert*-butyl hydroperoxide (TBHP) was used as additive (Table 1, entries 9 and 10). Other iodine sources were also tested, including ICl, NIS and $PhI(OAc)_2$, but all of them were less effective than elemental iodine (Table 1, entries 11–13). During the screening of solvent (Table 1, entries 14–17), low yields were obtained in MeCN and DCE, and only trace amount of product were detected in DMSO and AcOH. Further investigation revealed that the reaction yield was reduced slightly to 71% when the reaction was performed at 100 °C (Table 1, entry 18). Lower yield was obtained when the loading of elemental iodine was reduced to one equivalent (Table 1, entry 19), and the reaction did not proceed in the absence of I_2 (Table 1, entry 20).

Under these optimized conditions, the substrate scope of diaryl disulfides and trifluoromethylated arylpropynols was explored, and the results are summarized in Scheme 2. Initially, the reactions between diphenyl disulfides **1** and a number of arylpropynols were investigated under the standard conditions. The results disclosed that both rich-electronic and poor-electronic aryl groups were suitable substrates to afford the corresponding products in moderate to good yields. For example, *p*-tolyl propynol provided the product **4** in 81% yield, *m*-tolyl propynol gave the products

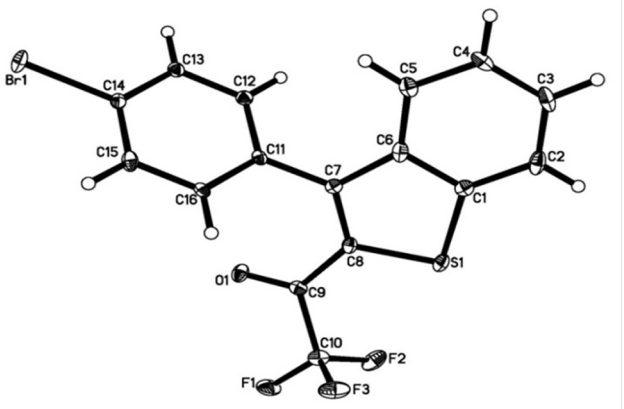
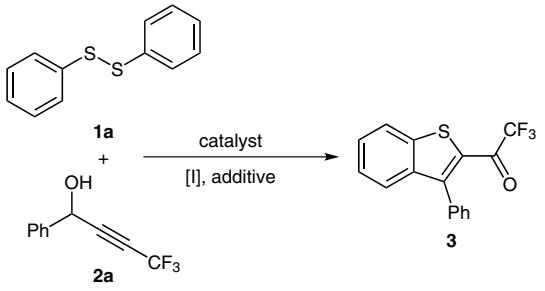


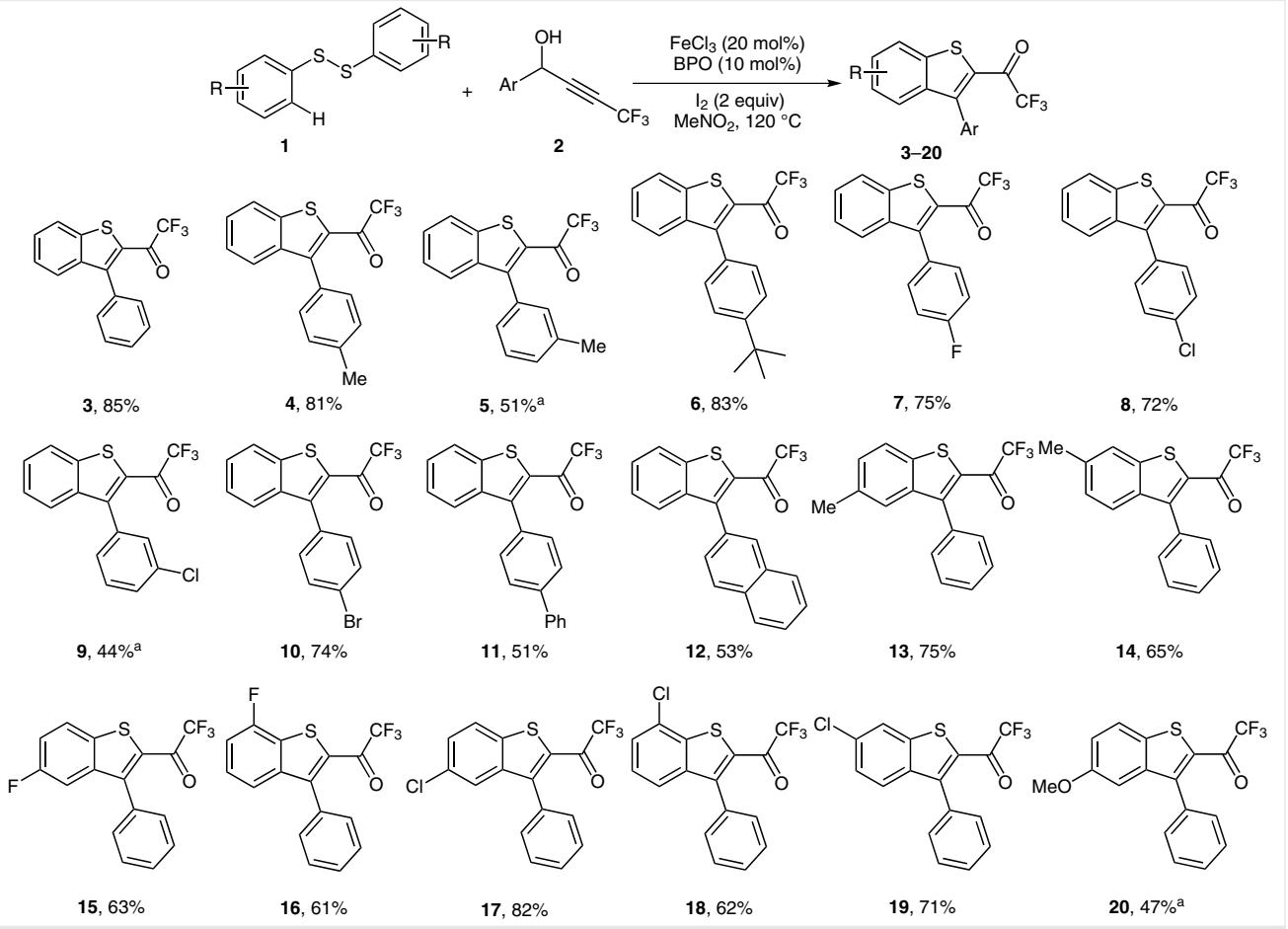
Figure 1 X-ray crystallographic structure of compound **10**

Table 1 Screening Conditions[a]



Entry	Catalyst	[I] source	Additive	Solvent	Yield (%)[b]
1	FeF_3	I_2	–	$MeNO_2$	22
2	$FeCl_3$	I_2	–	$MeNO_2$	65
3	$FeBr_3$	I_2	–	$MeNO_2$	58
4	Fe	I_2	–	$MeNO_2$	36
5	$Cu(OAc)_2$	I_2	–	$MeNO_2$	10
6	–	I_2	–	$MeNO_2$	trace
7	$FeCl_3$	I_2	AIBN	$MeNO_2$	68
8	$FeCl_3$	I_2	BPO	$MeNO_2$	85
9	$FeCl_3$	I_2	DTBP	$MeNO_2$	23
10	$FeCl_3$	I_2	TBHP	$MeNO_2$	trace
11	$FeCl_3$	ICl	BPO	$MeNO_2$	48
12	$FeCl_3$	NIS	BPO	$MeNO_2$	10
13	$FeCl_3$	$PhI(OAc)_2$	BPO	$MeNO_2$	trace
14	$FeCl_3$	I_2	BPO	MeCN	12
15	$FeCl_3$	I_2	BPO	DCE	25
16	$FeCl_3$	I_2	BPO	DMSO	trace
17	$FeCl_3$	I_2	BPO	AcOH	trace
18[c]	$FeCl_3$	I_2	BPO	$MeNO_2$	71
19[d]	$FeCl_3$	I_2	BPO	$MeNO_2$	59
20	$FeCl_3$	–	BPO	$MeNO_2$	trace

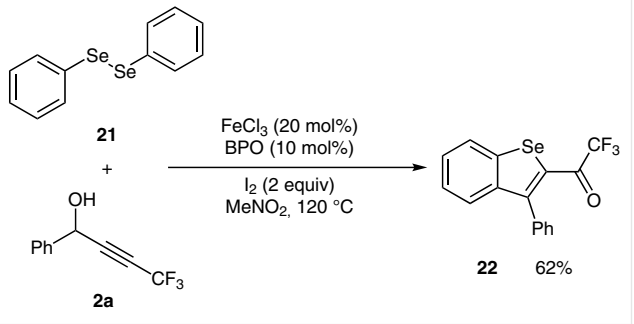
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (20 mol%), I_2 (0.4 mmol), and additive (10 mol%) in solvent (2 mL) under N_2 atmosphere at 120 °C for 12 h.
[b] Isolated yield.
[c] At 100 °C.
[d] 1.0 equiv of I_2.



Scheme 2 Thiocyclization of propynols with disulfides. *Reagents and conditions*: **1** (0.1 mmol), **2** (0.2 mmol), $FeCl_3$ (20 mol%), I_2 (0.4 mmol), and BPO (10 mol%) in $MeNO_2$ (2 mL) under N_2 atmosphere at 120 °C for 12 h, isolated yield. [a] 0.2 mmol disulfide were used.

5 in 51%. 4-*tert*-Butylphenyl also produced product **6** in 83% yield. Fluorinated and chlorinated phenylpropynol afforded the products **7**–**9** in 44–75% yields. Thiocyclization of 4-bromophenyl propynol proceeded smoothly to give the corresponding benzothiophene **10** in 74% yield, and the structure of product **10** was confirmed by X-ray single-crystal diffraction analysis (Figure 1).[13] The reaction of disulfide **1** with 4-biphenyl and naphtha-2-yl propynols produced the desired products in 51% and 53% yield, respectively (**11** and **12**). Subsequently, the substrate scope of diaryl disulfides was investigated by examining their reaction with trifluoromethylated propynol **2** under the optimal conditions. As expected, all of *ortho*-, *meta*- and *para*-substituted diphenyl disulfides underwent the thiocyclization successfully to produce 2-trifluoroacyl benzothiophenes in moderate to good yields. *p*-Tolyl and *m*-tolyl substrates afforded product **13** and **14** in 75% and 65% yields, respectively. 4-Fluoro- and 2-fluorophenyl-substituted disulfides gave 63% and 61% yields (**15** and **16**). Good yields were observed when 2-chloro-, 3-chloro- and 4-chlorophenyl disulfides were used as substrates (62–82%, **17**–**19**). While only 47% yield of product **20** was obtained when 4-methoxylphenyl disulfide was reacted with propynol **2a**, probably due to decomposition of anisole in the presence of oxidant. In addition, diphenyl diselenide **21** underwent the cyclization reaction smoothly, and the product **22** could be isolated in 62% yield under the standard conditions (Scheme 3).

In order to get more insight into the mechanism of this thiocyclization, several control experiments were conducted as shown in Scheme 4. Firstly, we tested the reaction of propynol **2a**, $FeCl_3$, BPO, and I_2 in the absence of disulfide, but only trace amount of iodo Meyer–Schuster rearrangement product **23** was observed (Scheme 4, eq. 1).[14] With the aim of disclosing whether the key C–S bond-forming process in this reaction follows a direct C–H sulfenylation of enone generated from the previous rearrangement, 4-phenyltrifluorobut-3-en-2-one (**24**) was treated with diphenyl disulfide (**1a**) under the standard conditions, but the product **3** could not be detected (Scheme 4, eq. 2). All of the above results suggested that the thiocyclization did not



Scheme 3 Cyclization of diphenyl diselenide with propynol **2a**

undergo a coupling reaction of aryl disulfide with vinyl iodide or trifluoromethyl propenone. Subsequently, the reaction of disulfide **1a** with propynol **2a** was performed under the optimal conditions in the presence of 2.5 equivalents of 2,2,6,6-tetramethylpiperidine oxide (TEMPO), a radical scavenger (Scheme 4, eq. 3). The thiocyclization was suppressed completely, and only trace amount of product **3** was observed along with 9% yield of iodization product **25**. These results indicated that the thiocyclization of trifluoromethyl propynols might be involved in a free-radical process.

Based on the obtained experimental results and previous reports,[15] a plausible mechanism was outlined in Scheme 5. Firstly, trifluoromethylated propargyl alcohol undergoes a $FeCl_3$-catalyzed Meyer–Schuster rearrangement to produce active allenol intermediate **A**. Meanwhile, diphenyl sulfide is decomposed to yield free radical PhS$^{\bullet}$ in the presence of BPO and I_2. Then, the selective addition of PhS$^{\bullet}$ to the double bond of allenol **A** gives allyl radical **B**. Subsequently, keto–enol tautomerism and intramolecular radical electrophilic cyclization of intermediate **B** take place to afford cyclohexadienyl radical **C**. With the aid of $FeCl_3$ and I_2, cyclohexadienyl radical **C** is converted into dihydroindenone **D** through single-electron transfer and deprotonation process.[16] Finally, the oxidative dehydrogenation of dihydroindenone **D** by $FeCl_3/I_2$ affords the desired product **3**.

In summary, we developed an aryl C–H bond functionalization of aryl disulfides by $FeCl_3$-catalyzed one-pot tandem Meyer–Schuster rearrangement and radical cyclization. A variety of trifluoromethylated propynols underwent the thiocyclization with various aryl disulfides successfully to afford the corresponding trifluoroacyl benzothiophenes in moderate to good yields.[17] Both two sulfur atoms of sulfides were incorporated onto benzothiophenes, which were the significant advantages of this atom-economic reaction. The present transformation provided a novel valuable one-pot method for the synthesis of trifluoromethylated benzothiophenes from commercially available aryl disulfides and easily prepared CF_3-containing propargyl alcohols.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588923.

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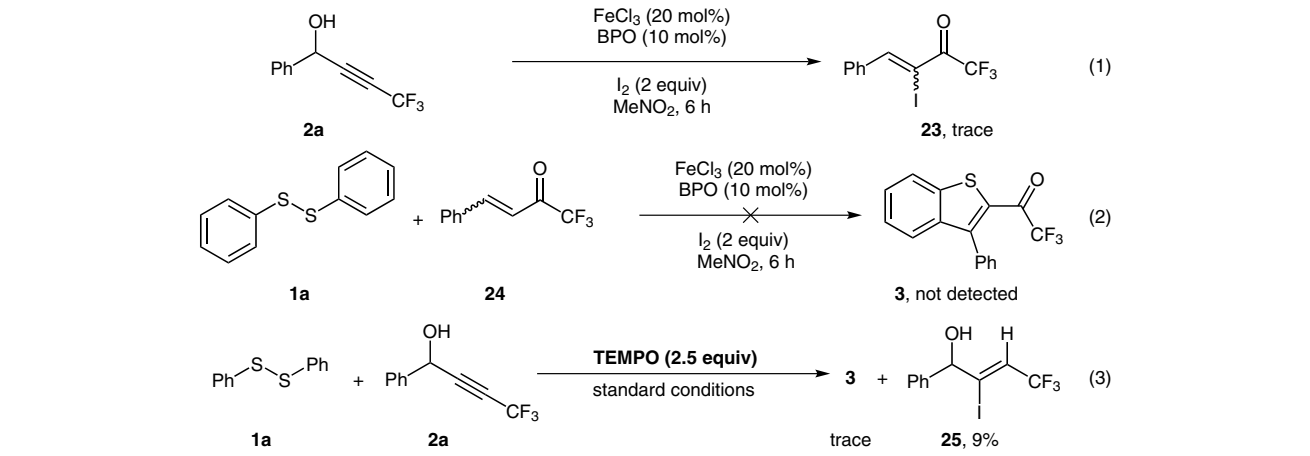
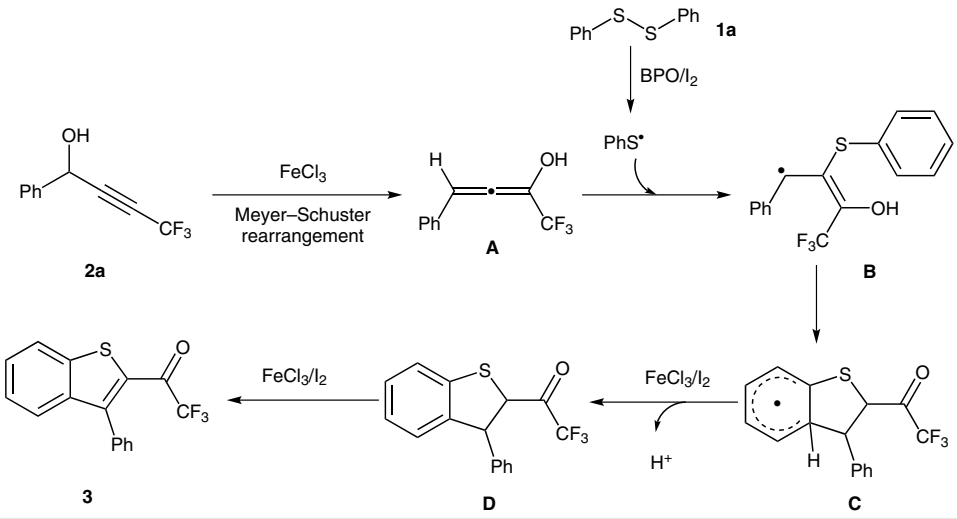


Scheme 4 Control experiment



Scheme 5 Proposed mechanism

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(17) **General Procedure for the Synthesis of 2-Trifluoroacylbenzothiophenes**

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with **1** (0.1 mmol), **2** (0.2 mmol), $FeCl_3$ (6.4 mg, 0.04 mmol), BPO (0.02 mmol, 4.8 mg), and I_2 (101.6 mg, 0.4 mmol) in $MeNO_2$ (2 mL) under N_2 atmosphere. The reaction mixture was stirred at 120 °C until complete consumption of starting material as detected by TLC or GC–MS analysis. After the reaction was finished, the mixture was poured into EtOAc, which was washed with sat. $Na_2S_2O_3$ (2 × 15 mL) and brine (1 × 15 mL). After the aqueous layer was extracted with EtOAc, the combined organic layers were dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography (PE–EtOAc) to afford the desired products **3**–**20**.

2,2,2-Trifluoro-1-(3-phenylbenzo[*b*]thiophen-2-yl)ethanone (3)

Yellow solid (52.0 mg, 85% yield); mp 65–68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1 H), 7.51–7.47 (m, 2 H), 7.43–7.40 (m, 3 H), 7.33–7.32 (m, 1 H), 7.29–7.27 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.6 (q, J_{C-F} = 37.1 Hz), 148.6, 141.9, 139.6, 133.8, 129.5, 129.0, 128.7, 128.4, 127.9, 126.4, 125.6, 122.5, 116.0 (q, J_{C-F} = 289.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.10 (s, 3 F). LRMS (EI, 70 eV): *m/z* (%) = 306 (57) [M^+], 237 (100), 165 (48), 163 (12), 104 (17). ESI-HRMS: *m/z* calcd for $C_{16}H_9F_3NaOS^+$ [M + Na]$^+$: 329.0218; found: 329.0223.