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Iron-Catalyzed Synthesis of Thioesters from Thiols and Aldehydes in Water

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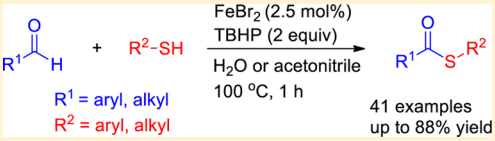
Supporting Information

ABSTRACT: The preparation of thioesters through the iron-catalyzed coupling reaction of thiols with aldehydes is described. The reactions were carried out by using *tert*-butyl hydroperoxide (TBHP) as an oxidant and water as a solvent in most cases. This system is compatible with a variety of functional groups.



INTRODUCTION

Thioesters are important building blocks for organic synthesis[1] and chemical biology.[2] Recently, the direct coupling of aldehydes with sulfur surrogates has become an atom-economic strategy for the preparation of thioesters.[3−8] It is shown that thioesters can be prepared via photoirradiation of thiols with aldehydes. However, the scope of the substrate is limited to benzaldehyde, and it is not applicable to substituted aryl aldehydes. Moreover, recquisite dilute reaction conditions make photoirradiation difficult to scale up.[4] Takemote et al. described the carbene-catalyzed coupling reaction of thiols with aldehydes. Some synthetic limitations are presented in this system: (1) carbenes used in this system are expensive; (2) electron-rich carbenes are necessary for alkyl aldehydes.[5] Kita and co-workers reported the C−S bond formation between pentafluorophenyl disulfide and aldehydes; however, other diaryl and dialkyl disulfides are not suitable as the coupling partners in this system.[6] Bandgar and co-workers demonstrated that a combination of Dess−Martin periodinane and NaN_3 is able to promote the synthesis of thioesters from aryl thiols and aldehydes. However, 6 equiv of Dess−Martin periodinane and 6 equiv of NaN_3 are required. Moreover, the substrate is limited to aryl thiols.[7] Recently, we reported the copper-catalyzed coupling of aldehydes with thiols in water by using TBHP as an oxidant.[8a] However, owing to the high binding affinity between copper and heteroatoms, a low product yield was obtained when the reaction was carried out by using 2-thiophenecarboxaldehyde and 4-methylbenzenethiol as the coupling partners (31% yield).[8a] Moreover, only trace amounts of products were detected when pyridine- or furan-containing substrates were employed. Alternatively, iron is cheap and nontoxic, and iron salts have been utilized for many useful reactions.[9,10] As part of our ongoing progress toward C−S bond coupling reactions,[10f,g,11] we report herein the iron-catalyzed coupling reaction of thiols with aldehydes.

RESULTS AND DISCUSSION

We initially examined the coupling reaction of benzaldehyde with 1-dodecanethiol in the presence of iron salt and oxidant in water at 100 °C for 1 h. The study of iron salts (Table 1, entries 1−11) suggested that $FeBr_2$ was the best catalyst, providing the product in 82% yield (Table 1, entry 9). A comparative yield was obtained when extra pure $FeBr_2$ was employed as a catalyst, and this result eliminated the contribution from other transition-metal contaminants in $FeBr_2$ (Table 1, entry 12). Screening oxidants (Table 1, entries 13−18) indicated that TBHP was superior to DTBP, AcOOH, BPO, H_2O_2, $K_2S_2O_8$, and TBPB. An 85% yield of product was afforded when the reaction was carried out at 110 °C (Table 1, entry 19). Shorter reaction times reduced the yield of the product (Table 1, entry 20). Interestingly, it was observed that a higher amount of TBHP (Table 1, entry 21) and lower $FeBr_2$ loadings (Table 1, entry 22) diminished the yield of the product. Control experiments showed that 28% yield was obtained in the absence of catalyst (Table 1, entry 23).

With the optimized reaction conditions in hand, we explored the scope of the substrates possible with this novel system. The results are summarized in Table 2. A variety of alkyl thiols were coupled with aldehydes. Aryl aldehydes containing electron-donating or electron-withdrawing groups also reacted smoothly with alkyl thiols, giving thioesters in moderate to excellent yields. Functional groups including chloro (Table 2, entries 1 and 13), bromo (Table 2, entries 5 and 16), trifluoromethyl (Table 2, entries 6 and 17), nitrile (Table 2, entry 7), and ester (Table 2, entry 20) are all tolerated under the reaction conditions. Sterically demanding substrates slightly reduce the product yield (Table 2, entry 3). Alkyl aldehydes were also coupled with thiols to give the corresponding thioesters along with disulfides as the byproducts (Table 2, entries 9−11). In general, the product yields for the coupling of alkyl aldehydes with thiols are lower than those of coupling between aryl aldehydes and thiols.

On the basis of promising results for alkyl thiols, we then turned our attention to aryl thiols. As shown in Table 3, the system once again shows good functional group compatibility. Chloro (Table 3, entries 1, 3, 5, 6, 9, 13, 15−17, and 20), trifluoromethyl (Table 3, entries 2, 4, 7, and 8), nitrile (Table 3,

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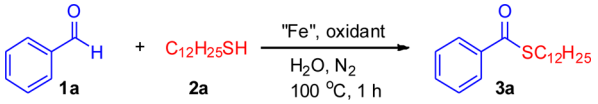
Table 1. Optimization of Iron-Catalyzed Coupling of 1-Dodecanethiol with Benzaldehyde[a]



entry	"Fe" (concn, mol %)	oxidant	yield (%)
1	$FeCl_2$ (2.5)	TBHP (1.0)	66
2	$Fe(OAc)_2$ (2.5)	TBHP (1.0)	53
3	Fe_2O_3 (2.5)	TBHP (1.0)	52
4	$Fe_2(CO)_9$ (2.5)	TBHP (1.0)	32
5	$Fe_3(CO)_{12}$ (2.5)	TBHP (1.0)	25
6	$Fe(acac)_3$ (2.5)	TBHP (1.0)	78
7	$Fe(NO_3)_3{\cdot}9H_2O$ (2.5)	TBHP (1.0)	70
8	$FeCp_2$ (2.5)	TBHP (1.0)	69
9	$FeBr_2$ (2.5)	TBHP (1.0)	82
10	$FeBr_3$ (2.5)	TBHP (1.0)	41
11	$FeCl_3$ (2.5)	TBHP (1.0)	79
12[b]	$FeBr_2$ (2.5)	TBHP (1.0)	78
13	$FeBr_2$ (2.5)	DTBP (1.0)	–
14	$FeBr_2$ (2.5)	AcOOH (1.0)	trace
15	$FeBr_2$ (2.5)	BPO (1.0)	12
16	$FeBr_2$ (2.5)	H_2O_2 (1.0)	–
17	$FeBr_2$ (2.5)	$K_2S_2O_8$ (1.0)	–
18	$FeBr_2$ (2.5)	TBPB (1.0)	58
19[c]	$FeBr_2$ (2.5)	TBHP (1.0)	85
20[c,d]	$FeBr_2$ (2.5)	TBHP (1.0)	54
21[c,e]	$FeBr_2$ (2.5)	TBHP (1.5)	62
22[c]	$FeBr_2$ (1.25)	TBHP (1.0)	75
23[c]		TBHP (1.0)	28

[a]Reaction conditions: iron source (0.0125 mmol, 2.5 mol %), oxidant (1.0 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and benzaldehyde (0.26 mL, 2.5 mmol) under a nitrogen atmosphere in H_2O (1.5 mL) for 1 h. [b]$FeBr_2$ (99.999%). [c]Temperature 110 °C. [d]Time 30 min. [e]A 1.5 mmol portion of TBHP (70% in H_2O) was used. TBHP = *tert*-butyl hydroperoxide. DTBP = di-*tert*-butyl peroxide. AcOOH = peracetic acid. BPO = benzoyl peroxide. H_2O_2 = hydrogen peroxide. $K_2S_2O_8$ = potassium persulfate. TBPB = *tert*-butyl perbenzoate.

entry 6), and bromo (Table 3, entries 8, 12, 14, 18, 19, and 21) are all tolerated under the reaction conditions. Remarkably, thiophene-, furan-, and pyridine-containing aldehydes could not serve as good coupling partners with thiols through copper catalysis;[8] however, such heterocyclo-containing aldehydes were reacted with thiols to give the corresponding thioesters in moderate to good yields (Table 3, entries 9–11, 16, and 17). Alkyl aldehydes could also be used as the coupling partners with thiols to provide the corresponding thioesters in moderate to excellent yields (Table 3, entries 14, 15, and 18–21).

A plausible mechanism for iron-catalyzed coupling of an aldehyde with a thiol is shown in Scheme 1. Iron(IIII) complex **A** is formed when $FeBr_2$ is reacted with TBHP, and *t*-BuOO$^{\bullet}$ radical is generated at the same time.[12] A hydrogen atom is then abstracted from the aldehyde to give an acyl radical. Complex **A** further reacts with the thiol to give an iron(III) thiolate complex, **B**. This complex traps the acyl radical to provide a thioester, along with the generation of iron complex **C**.[13] $FeBr_2$ is regenerated when complex **C** is reacted with HBr from the first step of the catalytic cycle. A radical coupling of an acyl radical with a thiyl radical is also possible in this reaction.[6c]

CONCLUSION

In summary, we have developed a generally applicable iron-catalyzed coupling reaction of aldehydes with thiols in water. Functional groups including chloro, bromo, trifluoromethyl, and nitrile and heteroaryls including thiophene, furan, and pyridine are all tolerated under the reaction conditions.

EXPERIMENTAL SECTION

General Information. All reagents and solvents were purchased from commercial suppliers and used without additional purification. The acetonitrile used for the reactions was dried by distillation over CaH_2 and stored in the presence of activated molecular sieves. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on silica gel 60 (230–400 mesh).

Analysis. NMR spectra were recorded using $CDCl_3$ as the solvent. Chemical shifts are reported in parts per million and referenced to the residual solvent resonance. Coupling constants (J) are reported in hertz. $^{13}C\{^1H\}$ NMR spectra were recorded on a 100 MHz spectrometer using broad-band proton decoupling. Standard abbreviations indicating multiplicity are used as follows: br s (broad singlet), s (singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet), m (multiplet). Melting points (mp's) were determined using an apparatus and are reported uncorrected. High-resolution mass spectrometry (HRMS) was performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer.

General Procedure for Table 1. A Schlenk tube equipped with a magnetic stir bar was charged with iron salt (0.0125 mmol) in a nitrogen-filled glovebox. The Schlenk tube was then covered with a rubber septum and removed from the glovebox. Under a nitrogen atmosphere, 1-dodecanethiol (0.125 mL, 0.5 mmol), benzaldehyde (0.26 mL, 2.5 mmol), oxidant (1.0 mmol), and solvent (1.5 mL) were added via syringe, and the Schlenk tube was connected to a nitrogen-filled balloon and heated at 100 °C in an oil bath. After being stirred at this temperature for 1 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of silica gel, then washed with ethyl acetate (20 mL), and concentrated to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to yield **3a**.

*Representative Example for Table 1. S-Dodecyl Benzothioate (**3a**) (Entry 19).*[8a] The general procedure for Table 1 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), benzaldehyde (0.26 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3a** as a yellow oil (131 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26–1.44 (m, 18 H), 1.63–1.69 (m, 2H), 3.07 (t, J = 7.2 Hz, 2 H), 7.44 (t, J = 7.6 Hz, 2 H), 7.55 (t, J = 7.4 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 28.9, 29.0, 29.1, 29.3, 29.5, 29.5, 29.5, 29.6, 29.6, 31.9, 127.1, 128.5, 133.1, 137.2, 192.1.

General Procedure for Table 2. A Schlenk tube equipped with a magnetic stir bar was charged with $FeBr_2$ (2.8 mg, 0.0125 mmol) in a nitrogen-filled glovebox. The Schlenk tube was then covered with a rubber septum and removed from the glovebox. Under a nitrogen atmosphere, thiol (0.5 mmol), aldehyde (2.5 mmol), TBHP (0.14 mL, 1.0 mmol), and H_2O (1.5 mL) were added via syringe, and the Schlenk tube was connected to a nitrogen-filled balloon and heated at 110 °C in an oil bath. After being stirred at this temperature for 1 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of silica gel, then washed with ethyl acetate (20 mL), and concentrated to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to yield **3**.

*S-Dodecyl 4-Chlorobenzothioate (**3b**) (Table 2, Entry 1).*[8a] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-chlorobenzaldehyde (359 mg, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column

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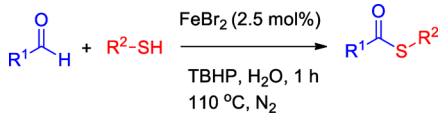
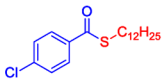
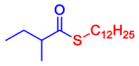
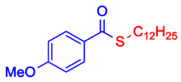
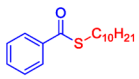
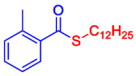
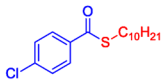
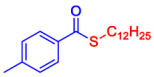
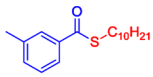
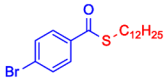
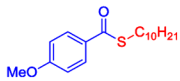
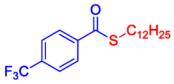
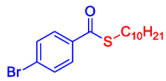
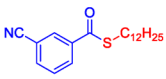
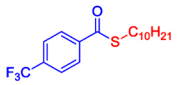
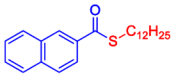
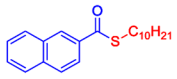
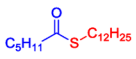
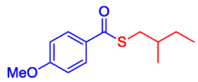
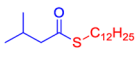
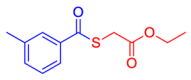
Table 2. Substrate Scope of Aldehydes and Alkyl Thiols[a]



Entry	Product		Yield (%)	Entry	Product		Yield (%)
1		**3b**	82	11		**3l**	49
2		**3c**	88	12		**3m**	75
3		**3d**	55	13		**3n**	83
4		**3e**	79	14		**3o**	80
5		**3f**	83	15		**3p**	64
6		**3g**	50	16		**3q**	73
7		**3h**	56	17		**3r**	68
8		**3i**	51	18		**3s**	45
9		**3j**	63	19		**3t**	50[b]
10		**3k**	66	20		**3u**	40[b]

[a]Reaction conditions unless otherwise stated: $FeBr_2$ (0.0125 mmol, 2.5 mol %), TBHP (1.0 mmol, 70% in water), thiol (0.5 mmol), and aldehyde (2.5 mmol) under a nitrogen atmosphere in H_2O (1.5 mL) for 1 h. [b]In acetonitrile (1.5 mL) at 90 °C for 1 h.

chromatography (SiO_2, hexane) to provide **3b** as a yellow oil (140 mg, 82% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.0 Hz, 3 H), 1.26−1.43 (m, 18 H), 1.62−1.68 (m, 2 H), 3.06 (t, J = 7.4 Hz, 2 H), 7.40 (dd, J = 1.6, 6.4 Hz, 2 H), 7.90 (dd, J = 2.0, 6.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 28.9, 29.1, 29.1, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 128.5, 128.8, 135.5, 139.5, 190.8.

*S-Dodecyl 4-Methoxybenzothioate (**3c**) (Table 2, Entry 2).*[8a] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methoxybenzaldehyde (0.31 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **3c** as a yellow oil (148 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26−1.43 (m, 18 H), 1.61−1.67 (m, 2 H), 3.04 (t, J = 7.4 Hz, 2 H), 3.83 (s, 3 H), 6.90 (d, J = 8.8 Hz, 2 H), 7.94 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 28.8, 28.9, 29.1, 29.3, 29.5, 29.5, 29.6, 29.6, 29.6, 31.9, 55.3, 113.6, 129.2, 130.1, 163.5, 190.5.

*S-Dodecyl 2-Methylbenzothioate (**3d**) (Table 2, Entry 3).*[8a] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-methylbenzaldehyde (0.30 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3d** as a colorless oil (89 mg, 55% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.2 Hz, 3 H), 1.26−1.44 (m, 18 H), 1.63−1.68 (m, 2 H), 2.48 (s, 3 H), 3.03 (t, J = 7.2 Hz, 2 H), 7.21−7.24 (m, 2 H), 7.36 (t, J = 7.6 Hz, 1 H), 7.76 (d, J = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.5, 22.7, 28.9, 29.2, 29.3, 29.5, 29.6, 29.6, 31.9, 125.6, 128.3, 131.4, 136.6, 137.8, 194.5.

*S-Dodecyl 4-Methylbenzothioate (**3e**) (Table 2, Entry 4).*[8a] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methylbenzaldehyde (0.30 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3e** as a yellow oil (126 mg, 79% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.26−1.43 (m, 18 H), 1.64−1.67 (m, 2 H), 3.85 (s, 3 H), 3.04 (t, J = 7.4 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.86 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.5, 22.6, 28.9, 28.9, 29.1, 29.3, 29.5, 29.6, 29.6, 31.9, 127.2, 129.1, 134.7, 143.8, 191.5.

*S-Dodecyl 4-Bromobenzothioate (**3f**) (Table 2, Entry 5).*[8a] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-bromobenzaldehyde (467 mg, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column

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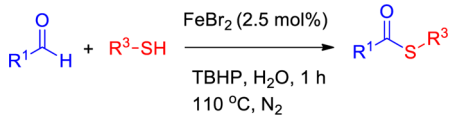
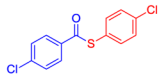
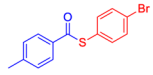
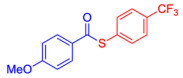
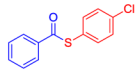
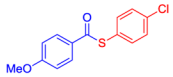
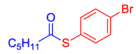
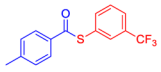
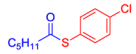
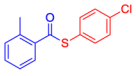
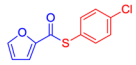
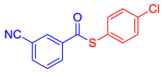
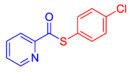
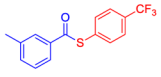
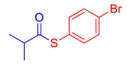
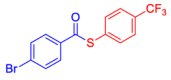
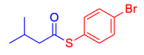
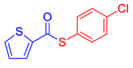
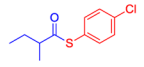
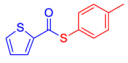
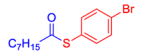
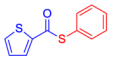
Table 3. Iron-Catalyzed C−S Bond Formation between Various Aldehydes and Aryl Thiols[a]



Entry	Product		Yield (%)	Entry	Product		Yield (%)
1		**5a**	62[b]	12		**5l**	60[b]
2		**5b**	75	13		**5m**	51[b]
3		**5c**	59	14		**5n**	85[b]
4		**5d**	70[b]	15		**5o**	85[b]
5		**5e**	66[b]	16		**5p**	42[b]
6		**5f**	40[b]	17		**5q**	31[b]
7		**5g**	61[b]	18		**5r**	64[b]
8		**5h**	64	19		**5s**	59[b]
9		**5i**	79[b]	20		**5t**	56[b]
10		**5j**	52[b]	21		**5u**	46[b]
11		**5k**	46[b]				

[a]Reaction conditions unless otherwise stated: $FeBr_2$ (0.0125 mmol, 2.5 mol %), TBHP (1.0 mmol, 70% in H_2O), thiol (0.5 mmol), and aldehyde (2.5 mmol) under a nitrogen atmosphere in H_2O (1.5 mL) for 1 h. [b]In acetonitrile (1.5 mL) at 90 °C for 1 h.

chromatography (SiO_2, hexane) to provide **3f** as a yellow oil (160 mg, 83% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H), 1.25−1.42 (m, 18 H), 1.62−1.69 (m, 2 H), 3.05 (t, J = 7.4 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.9, 29.1, 29.1, 29.3, 29.4, 29.5, 29.5, 29.6, 29.6, 31.9, 128.1, 128.6, 131.7, 135.9, 190.9.

*S-Dodecyl 4-(Trifluoromethyl)benzothioate (**3g**) (Table 2, Entry 6).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-(trifluoromethyl)benzaldehyde (0.35 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3g** as a white solid (93 mg, 50% yield). Mp: 39−40 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.0 Hz, 3 H), 1.26−1.45 (m, 18 H), 1.65−1.72 (m, 2 H), 3.10 (t, J = 7.4 Hz, 2 H), 7.70 (d, J = 8.4 Hz, 2 H), 8.06(d, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.7, 28.9, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 31.9, 123.5 (q, J = 271.3 Hz), 125.6 (q, J = 3.7 Hz), 127.5, 134.5 (q, J = 32.6 Hz), 140.0, 191.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −65.6 (s). HRMS (EI-TOF) (m/z): calcd for $C_{20}H_{29}F_3OS$, 374.1891; found, 374.1887.

*S-Dodecyl 3-Cyanobenzothioate (**3h**) (Table 2, Entry 7).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 3-formylbenzonitrile (331 mg, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **3h** as a white solid (92 mg, 56% yield). Mp: 36−37 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26−1.45 (m, 18 H), 1.65−1.72

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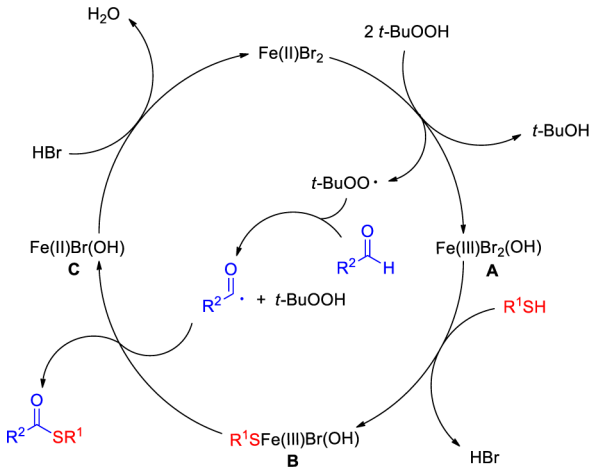
Scheme 1. Plausible Mechanism



(m, 2 H), 3.11 (t, J = 7.4 Hz, 2 H), 7.59 (t, J = 7.8 Hz, 2 H), 7.82−7.85 (m, 1 H), 8.16−8.24 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 28.8, 29.0, 29.3, 29.4, 29.4, 29.5, 29.5, 31.8, 113.1, 117.7, 129.5, 130.7, 131.0, 135.9, 138.0, 190.1. HRMS (EI-TOF) (m/z): calcd for $C_{20}H_{29}NOS$, 331.1970; found, 331.1979.

*S-Dodecyl Naphthalene-2-carbothioate (**3i**) (Table 2, Entry 8).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-naphthaldehyde (398 mg, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **3i** as a yellow oil (91 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26−1.46 (m, 18 H), 1.67−1.72 (m, 2 H), 3.12 (t, J = 7.4 Hz, 2 H), 7.51−7.59 (m, 2 H), 7.84−7.87 (m, 2 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.99 (dd, J = 1.2, 8.8 Hz, 1 H), 8.53 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 29.0, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 123.2, 126.8, 127.7, 128.3, 128.4, 128.4, 129.5, 132.4, 134.5, 135.7, 192.0. HRMS (EI-TOF) (m/z): calcd for $C_{23}H_{32}OS$, 356.2174; found, 356.2183.

*S-Dodecyl Hexanethioate (**3j**) (Table 2, Entry 9).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), hexaldehyde (0.31 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3j** as a yellow oil (95 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.91 (m, 6 H), 1.26−1.36 (m, 22 H), 1.54−1.57 (m, 2 H), 1.64−1.68 (m, 2 H), 2.53 (t, J = 7.6 Hz, 2 H), 2.86 (t, J = 7.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.1, 22.3, 22.7, 25.4, 28.8, 28.8, 29.1, 29.3, 29.5, 29.5, 29.6, 29.6, 29.6, 31.1, 31.9, 44.1, 199.7. HRMS (EI-TOF) (m/z): calcd for $C_{18}H_{36}OS$, 300.24787; found, 300.2477.

*S-Dodecyl 3-Methylbutanethioate (**3k**) (Table 2, Entry 10).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), isovaleraldehyde (0.27 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol). and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3k** as a colorless oil (94 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 6 H), 1.26−1.34 (m, 18 H), 1.52−1.57 (m, 2 H), 2.13−2.19 (m, 1 H), 2.41 (d, J = 7.2 Hz, 2 H), 2.86 (t, J = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.2, 22.7, 26.4, 28.8, 29.1, 29.3, 29.5, 29.5, 29.6, 31.9, 52.9, 199.1. HRMS (EI-TOF) (m/z): calcd for $C_{17}H_{34}OS$, 286.2330; found, 286.2336.

*S-Dodecyl 2-Methylbutanethioate (**3l**) (Table 2, Entry 11).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-methylbutyraldehyde (0.27 mL, 2.5 mmol), 1-dodecanethiol (0.125 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3l** as a colorless oil (70 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.93 (m, 6 H), 1.16 (d, J = 7.2 Hz, 3 H), 1.26−1.37 (m, 18 H), 1.43−1.59 (m, 3 H), 1.70−1.77 (m, 1 H), 2.52−2.58 (m, 1 H), 2.85 (t, J = 7.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 14.1, 17.2, 22.7, 27.2, 28.5, 28.8, 29.1, 29.3, 29.5, 29.6, 31.9, 50.2, 204.0. HRMS (EI-TOF) (m/z): calcd for $C_{17}H_{34}OS$, 286.2330; found, 286.2336.

*S-Decyl Benzothioate (**3m**) (Table 2, Entry 12).*[14] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), benzaldehyde (0.26 mL, 2.5 mmol), 1-decanethiol (0.108 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3m** as a yellow oil (95 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26−1.44 (m, 14 H), 1.63−1.70 (m, 2H), 3.06 (t, J = 7.4 Hz, 2 H), 7.43 (t, J = 7.8 Hz, 2 H), 7.55 (t, J = 7.4 Hz, 1 H), 7.97 (d, J = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 28.9, 29.0, 29.1, 29.3, 29.5, 29.5, 29.5, 31.8, 127.1, 128.5, 133.1, 137.2, 192.0.

*S-Decyl 4-Chlorobenzothioate (**3n**) (Table 2, Entry 13).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-chlorobenzaldehyde (359 mg, 2.5 mmol), 1-decanethiol (0.108 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3n** as a colorless oil (130 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26−1.43 (m, 14 H), 1.63−1.70 (m, 2 H), 3.06 (t, J = 7.4 Hz, 2 H), 7.26−7.43 (m, 2 H), 7.89−7.92 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 28.9, 29.1, 29.1, 29.3, 29.5, 29.5, 31.9, 128.5, 128.8, 135.5, 139.5, 190.8. HRMS (EI-TOF) (m/z): calcd for $C_{17}H_{25}ClOS$, 312.1315; found, 312.1320.

*S-Decyl 3-Methylbenzothioate (**3o**) (Table 2, Entry 14).* The general procedure for Table 2 was followed using $FeBr_2$(2.8 mg, 0.0125 mmol), 3-methylbenzaldehyde (0.30 mL, 2.5 mmol), 1-decanethiol (0.108 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3o** as a yellow oil (117 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26−1.43 (m, 14 H), 1.62−1.68 (m, 2 H), 2.39 (s, 3 H), 3.05 (t, J = 7.2 Hz, 2 H), 7.28−7.36 (m, 2 H), 7.76−7.77 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.2, 22.6, 28.9, 29.0, 29.1, 29.3, 29.5, 29.5, 29.7, 31.8, 124.3, 127.6, 128.3, 133.9, 137.2, 138.3, 192.1. HRMS (EI-TOF) (m/z): calcd for $C_{18}H_{28}OS$, 292.1861; found, 292.1852.

*S-Decyl 4-Methoxybenzothioate (**3p**) (Table 2, Entry 15).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methoxybenzaldehyde (0.31 mL, 2.5 mmol), 1-decanethiol (0.108 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **3p** as a yellow oil (99 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26−1.42 (m, 14 H), 1.64−1.68 (m, 2 H), 3.04 (t, J = 7.4 Hz, 2 H), 3.85 (s, 3 H), 6.91 (d, J = 7.0 Hz, 2 H), 7.95 (d, J = 7.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 28.9, 28.9, 29.1, 29.3, 29.5, 29.5, 29.7, 31.8, 55.4, 113.6, 129.3, 130.1, 163.6, 190.6. HRMS (EI-TOF) (m/z): calcd for $C_{18}H_{28}O_2S$, 308.1810; found, 308.1801.

*S-Decyl 4-Bromobenzothioate (**3q**) (Table 2, Entry 16).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-bromobenzaldehyde (467 mg, 2.5 mmol), 1-decanethiol (0.108 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3q** as a colorless oil (130 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.0 Hz, 3 H), 1.26−1.41 (m, 14 H), 1.62−1.68 (m, 2 H), 3.06 (t, J = 7.2 Hz, 2 H), 7.55−7.59 (m, 2 H), 7.81−7.84 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 28.9, 29.1, 29.2, 29.3, 29.4, 29.5, 29.5, 31.9, 128.2, 128.6, 131.8, 136.0, 191.1. HRMS (EI-TOF) (m/z): calcd for $C_{17}H_{25}BrOS$, 356.0809; found, 356.0803.

*S-Decyl 4-(Trifluoromethyl)benzothioate (**3r**) (Table 2, Entry 17).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-(trifluoromethyl)benzaldehyde (0.35 mL, 2.5 mmol), 1-decanethiol (0.108 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol)

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in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3r** as a yellow oil (118 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.27−1.44 (m, 14 H), 1.65−1.72 (m, 2 H), 3.10 (t, J = 7.2 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H), 8.06 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 28.9, 29.1, 29.3, 29.4, 29.4, 29.5, 29.5, 31.9, 123.5 (q, J = 271.2 Hz), 125.6 (q, J = 3.8 Hz), 127.5, 134.5 (q, J = 32.6 Hz), 140.0, 191.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.7 (s). HRMS (EI-TOF) (m/z): calcd for $C_{18}H_{25}F_3OS$, 346.1578; found, 346.1587.

*S-Decyl Naphthalene-2-carbothioate (**3s**) (Table 2, Entry 18).* The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-naphthaldehyde (398 mg, 2.5 mmol), 1-decanethiol (0.108 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **3s** as a yellow oil (74 mg, 45% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.25−1.44 (m, 14 H), 1.68−1.72 (m, 2 H), 3.11 (t, J = 7.2 Hz, 2 H), 7.52−7.57 (m, 2 H), 7.84−7.87 (m, 2 H), 7.94 (d, J = 8.0 Hz, 1 H), 7.99 (d, J = 8.4 Hz, 1 H), 8.52 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 29.0, 29.2, 29.3, 29.5, 29.5, 29.6, 29.7, 31.9, 123.2, 126.8, 127.7, 128.3, 128.3, 128.4, 129.5, 132.4, 134.5, 135.7, 192.0. HRMS (EI-TOF) (m/z): calcd for $C_{21}H_{28}OS$, 328.1861; found, 328.1850.

*S-(2-Methyl-1-butyl) 4-Methoxybenzothioate (**3t**) (Table 2, Entry 19).*[8a] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methoxybenzaldehyde (0.31 mL, 2.5 mmol), 2-methyl-1-butanethiol (0.065 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **3t** as a yellow oil (60 mg, 50% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.4 Hz, 3 H), 0.99 (d, J = 6.4 Hz, 3 H), 1.23−1.30 (m, 1 H), 1.47−1.54 (m, 1 H), 1.65- 1.70 (m, 1 H), 2.93 (dd, J = 7.2, 12.8 Hz, 1 H), 3.11 (dd, J = 5.6, 12.8 Hz, 1 H), 3.84 (s, 3 H), 6.91 (d, J = 10.2 Hz, 2 H), 7.96 (d, J = 10.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.8, 28.7, 35.1, 35.4, 55.4, 113.6, 129.3, 130.1, 163.6, 190.6.

*Ethyl 2-((3-Methylbenzoyl)thio)acetate (**3u**) (Table 2, Entry 20).*[8a] The general procedure for Table 2 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 3-methylbenzaldehyde (0.30 mL, 2.5 mmol), ethyl 2-mercaptoacetate (0.056 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **3u** as a yellow oil (48 mg, 40% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.30 (t, J = 6.8 Hz, 3 H), 2.41 (s, 3 H), 3.88 (s, 2 H), 4.23 (q, J = 7.2 Hz, 2 H), 7.32−7.41 (m, 2 H), 7.77−7.79 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.2, 31.4, 61.8, 124.6, 127.8, 128.5, 134.5, 136.1, 138.6, 168.8, 190.2.

General Procedure for Table 3. A Schlenk tube equipped with a magnetic stir bar was charged with $FeBr_2$ (2.8 mg, 0.0125 mmol) in a nitrogen-filled glovebox. The Schlenk tube was then covered with a rubber septum and removed from the glovebox. Under a nitrogen atmosphere, thiol (0.5 mmol), aldehyde (2.5 mmol), TBHP (0.14 mL, 1.0 mmol), and H_2O (1.5 mL) were added via syringe, and the Schlenk tube was connected to a nitrogen-filled balloon and heated at 110 °C in an oil bath. After being stirred at this temperature for 1 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of silica gel, then washed with ethyl acetate (20 mL), and concentrated to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to yield **5**.

*S-(4-Chlorophenyl) 4-Chlorobenzothioate (**5a**) (Table 3, Entry 1).*[8a] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-chlorobenzaldehyde (359 mg, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5a** as a white solid (87 mg, 62% yield). Mp: 135−136 °C (lit.[8a] 136−137 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 4 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.94 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.3, 128.8, 129.1, 129.5, 134.6, 136.1, 136.2, 140.3, 188.5.

*S-(4-(Trifluoromethyl)phenyl) 4-Methoxybenzothioate (**5b**) (Table 3, Entry 2).*[8a] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methoxybenzaldehyde (0.31 mL, 2.5 mmol), 4-(trifluoromethyl)benzenethiol (0.071 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **5b** as a white solid (118 mg, 75% yield). Mp: 105−106 °C (lit.[8a] 105−106 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3 H), 6.92 (d, J = 10.2 Hz, 2 H), 7.60 (d, J = 8.4 Hz, 2 H), 7.65 (d, J = 8.4 Hz, 2 H), 7.96 (d, J = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 114.0, 123.9 (q, J = 271.0 Hz), 125.9 (q, J = 3.7 Hz), 127.9, 128.9, 129.8, 131.2 (q, J = 32.6 Hz), 132.5, 135.2, 164.3, 187.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.3 (s).

*S-(4-Chlorophenyl) 4-Methoxybenzothioate (**5c**) (Table 3, Entry 3).*[8a] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methoxybenzaldehyde (0.31 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **5c** as a white solid (83 mg, 59% yield). Mp: 94−95 °C (lit.[8a] 96−97 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3 H), 6.96 (d, J = 8.8 Hz, 2 H), 7.42 (s, 4 H), 7.99 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 114.0, 126.1, 129.1, 129.4, 129.7, 135.8, 136.4, 164.1, 188.0.

*S-(3-(Trifluoromethyl)phenyl) 4-Methylbenzothioate (**5d**) (Table 3, Entry 4).*[8a] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methylbenzaldehyde (0.30 mL, 2.5 mmol), 3-(trifluoromethyl)benzenethiol (0.070 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5d** as a yellow solid (104 mg, 70% yield). Mp: 59−60 °C(lit.[8a] 62−63 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.55 (t, J = 7.8 Hz, 1 H), 7.68(d, J = 8.0 Hz, 2 H), 7.78 (s, 1 H), 7.91 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 123.6 (q, J = 271.2 Hz), 126.1 (q, J = 3.7 Hz), 127.6, 129.0, 129.3, 129.3, 129.5, 129.5, 131.5 (q, J = 32.5 Hz), 131.7 (q, J = 3.8 Hz), 133.6, 138.5, 145.1, 188.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.2 (s).

*S-(4-Chlorophenyl) 2-Methylbenzothioate (**5e**) (Table 3, Entry 5).*[8a] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-methylbenzaldehyde (0.30 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5e** as a white solid (86 mg, 66% yield). Mp: 90−91 °C (lit.[8a] 90−91 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3 H), 7.25−7.32 (m, 2 H), 7.41−7.45 (m, 5 H), 7.93 (d, J = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 125.9, 126.6, 128.6, 129.5, 131.8, 132.2, 135.9, 136.1, 136.3, 137.6, 191.5.

*S-(4-Chlorophenyl) 3-Cyanobenzothioate (**5f**) (Table 3, Entry 6).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 3-formylbenzonitrile (331 mg, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **5f** as a white solid (47 mg, 40% yield). Mp: 128−129 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 4H), 7.64 (t, J = 8.0 Hz, 1 H), 7.89 (d, J = 7.6 Hz, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 8.28 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.3, 117.5, 124.5, 129.7, 129.8, 130.9, 131.3, 136.1, 136.4, 136.6, 137.1, 187.9. HRMS (EI-TOF) (m/z): calcd for $C_{14}H_8ClNOS$, 273.0015; found, 273.0007.

*S-(4-(Trifluoromethyl)phenyl) 3-Methylbenzothioate (**5g**) (Table 3, Entry 7).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 3-methylbenzaldehyde (0.30 mL, 2.5 mmol), 4-(trifluoromethyl)benzenethiol (0.071 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5g** as a white solid (90 mg, 61% yield). Mp: 72−73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3 H), 7.36−7.45 (m, 2 H), 7.67 (dd, J = 8.0, 24.0 Hz, 4 H), 7.82−7.83 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 123.8 (q, J = 271.2 Hz), 125.9 (q, J = 3.7 Hz), 128.0, 128.7, 131.3 (q, J = 32.5 Hz), 132.3, 134.8, 135.2, 136.2, 138.8, 189.0. ^{19}F NMR (376

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MHz, $CDCl_3$): δ −64.2 (s). HRMS (EI-TOF) (m/z): calcd for $C_{15}H_{11}F_3OS$, 296.0483; found, 296.0491.

*S-(4-(Trifluoromethyl)phenyl) 4-Bromobenzothioate (**5h**) (Table 3, Entry 8).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-bromobenzaldehyde (467 mg, 2.5 mmol), 4-(trifluoromethyl)benzenethiol (0.071 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in H_2O (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5h** as a white solid (115 mg, 64% yield). Mp: 94−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62−7.71(m, 6 H), 7.87 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 114.0, 123.8 (q, J = 225.7 Hz), 123.7 (q, J = 271.1 Hz), 126.0 (q, J = 3.6 Hz), 128.6, 129.2, 131.6 (t, J = 16.3 Hz), 132.2, 134.9, 135.1, 187.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.4 (s). HRMS (EI-TOF) (m/z): calcd for $C_{14}H_8BrF_3OS$, 359.9431; found, 359.9439.

*S-(4-Chlorophenyl) Thiophene-2-carbothioate (**5i**) (Table 3, Entry 9).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-thiophenecarboxaldehyde (0.24 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **5i** as a yellow oil (100 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, J = 4.2 Hz, 1 H), 7.39−7.45 (m, 4 H), 7.67 (d, J = 4.4 Hz, 1 H), 7.89 (d, J = 3.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.3, 128.0, 129.4, 131.8, 133.5, 136.0, 136.2, 140.9, 181.4. HRMS (EI-TOF) (m/z): calcd for $C_{11}H_7ClOS_2$: 253.9627; found, 253.9620.

*S-4-Tolyl Thiophene-2-carbothioate (**5j**) (Table 3, Entry 10).*[8a] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-thiophenecarboxaldehyde (0.24 mL, 2.5 mmol), 4-methylbenzenethiol (0.063 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **5j** as a yellow oil (61 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3 H), 7.14 (t, J = 4.4 Hz, 1 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 4.8 Hz, 1 H), 7.89 (d, J = 4.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 123.3, 127.9, 130.1, 131.5, 133.0, 135.0, 139.9, 141.4, 182.5.

*S-Phenyl Thiophene-2-carbothioate (**5k**) (Table 3, Entry 11).*[15] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-thiophenecarboxaldehyde (0.24 mL, 2.5 mmol), benzenethiol (0.06 mL, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **5k** as a yellow oil (50 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, J = 4.2 Hz, 1 H), 7.44 (t, J = 3.2 Hz, 3 H), 7.51−7.53 (m, 2 H), 7.65 (d, J = 5.2 Hz, 1 H) 7.90 (d, J = 4.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.9, 128.0, 129.2, 129.6, 131.6, 133.2, 135.0, 141.3, 182.0.

*S-(4-Bromophenyl) 4-Methylbenzothioate (**5l**) (Table 3, Entry 12).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 4-methylbenzaldehyde (0.30 mL, 2.5 mmol), 4-bromobenzenethiol (0.099 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5l** as a white solid (92 mg, 60% yield). Mp: 120−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.4 Hz, 2 H), 7.90 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 124.1, 126.6, 127.6, 129.4, 132.4, 133.7, 136.5, 144.8, 189.0. HRMS (EI-TOF) (m/z): calcd for $C_{14}H_{11}BrOS$, 305.9714; found, 305.9718.

*S-(4-Chlorophenyl) Benzothioate (**5m**) (Table 3, Entry 13).*[16] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), benzaldehyde (0.26 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5m** as a white solid (64 mg, 51% yield). Mp: 72−73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.50 (m, 6 H), 7.59−7.63 (m, 1 H), 8.00 (d, J = 5.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.7, 127.4, 128.8, 129.5, 133.8, 135.9, 136.2, 136.3, 189.6.

*S-(4-Bromophenyl) Hexanethioate (**5n**) (Table 3, Entry 14).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), hexaldehyde (0.31 mL, 2.5 mmol), 4-bromobenzenethiol (0.099 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5n** as a yellow oil (121 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89−0.92 (m, 3 H), 1.25−1.36 (m, 4 H), 1.69−1.73 (m, 2 H), 2.65 (t, J = 7.6 Hz, 2 H), 7.26 (d, J = 7.2 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.3, 25.2, 31.0, 43.7, 123.9, 127.0, 132.3, 135.9, 196.8. HRMS (EI-TOF) (m/z): calcd for $C_{12}H_{15}BrOS$, 286.0027; found, 286.0028.

*S-(4-Chlorophenyl) Hexanethioate (**5o**) (Table 3, Entry 15).*[17] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), hexaldehyde (0.31 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5o** as a yellow oil (103 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83−0.92 (m, 3 H), 1.26−1.34 (m, 4 H), 1.69−1.72 (m, 2 H), 2.64 (t, J = 7.4 Hz, 2 H), 7.34 (dd, J = 8.4, 19.6 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.3, 25.2, 31.0, 43.7, 126.4, 129.4, 135.7, 197.0.

*S-(4-Chlorophenyl) Furan-2-carbothioate (**5p**) (Table 3, Entry 16).*[18] The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-furancarboxaldehyde (0.21 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 100:1) to provide **5p** as a white solid (50 mg, 42% yield). Mp: 102−103 °C (lit.[18] 106−107 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (q, J = 1.7, 1 H), 7.27 (dd, J = 0.8, 4.0 Hz, 1H), 7.42 (s,4H), 7.63 (dd, J = 0.8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.5, 116.5, 124.6, 129.5, 136.1, 136.3, 146.6, 150.0, 178.1.

*S-(4-Chlorophenyl) Pyridine-2-carbothioate (**5q**) (Table 3, Entry 17).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-pyridinecarboxaldehyde (0.24 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc, 10:1) to provide **5q** as a white solid (39 mg, 31% yield). Mp: 105−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.47 (m, 4 H), 7.57 (t, J = 6.0 Hz, 1 H), 7.88 (t, J = 7.6 Hz, 1 H), 7.96 (d, J = 8.0 Hz, 1 H), 8.74 (d, J = 4.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.8, 126.7, 128.2, 129.4, 135.8, 136.1, 137.4, 149.2, 151.3, 191.5. HRMS (EI-TOF) (m/z): calcd for $C_{12}H_8ClNOS$, 249.0015; found, 249.0020.

*S-(4-Bromophenyl) 2-Methylpropanethioate (**5r**) (Table 3, Entry 18).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), isobutyraldehyde (0.23 mL, 2.5 mmol), 4-bromobenzenethiol (0.099 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5r** as a colorless oil (83 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (d, J = 6.8 Hz, 6 H), 2.81−2.88 (m, 1 H), 7.26 (d, J = 8.4 Hz, 2 H), 7.52 (d, J = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 43.0, 123.8, 126.9, 132.2, 136.0, 201.2. HRMS (EI-TOF) (m/z): calcd for $C_{10}H_{11}ClOS$, 257.9714; found, 257.9708.

*S-(4-Bromophenyl) 3-Methylbutanethioate (**5s**) (Table 3, Entry 19).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), isovaleraldehyde (0.27 mL, 2.5 mmol), 4-bromobenzenethiol (0.099 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5s** as a colorless oil (81 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, J = 6.4 Hz, 6 H), 2.17−2.24 (m, 1 H), 2.53 (d, J = 7.2 Hz, 2 H), 7.25 (d, J = 7.4 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 26.5, 52.4, 123.9, 127.0, 132.3, 135.8, 196.2. HRMS (EI-TOF) (m/z): calcd for $C_{11}H_{13}BrOS$, 271.9870; found, 271.9872.

*S-(4-Chlorophenyl) 2-Methylbutanethioate (**5t**) (Table 3, Entry 20).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), 2-methylbutyraldehyde (0.27 mL, 2.5 mmol), 4-chlorobenzenethiol (0.074 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5t** as a colorless oil (64 mg,

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56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, J = 7.6 Hz, 3 H), 1.22−1.26 (m, 3 H), 1.50−1.57 (m, 1 H), 1.76−1.83 (m, 1 H), 2.65−2.70 (m, 1 H), 7.31−7.38 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 17.1, 27.1, 50.0, 126.4, 129.3, 135.5, 135.7, 201.0. HRMS (EI-TOF) (m/z): calcd for $C_{11}H_{13}ClOS$, 228.0376; found, 228.0378.

*S-(4-Bromophenyl) Octanethioate (**5u**) (Table 3, Entry 21).* The general procedure for Table 3 was followed using $FeBr_2$ (2.8 mg, 0.0125 mmol), octanaldehyde (0.39 mL, 2.5 mmol), 4-bromobenzenethiol (0.099 g, 0.5 mmol), and TBHP (0.14 mL, 1.0 mmol) in ACN (1.5 mL). The product was then purified by column chromatography (SiO_2, hexane) to provide **5u** as a colorless oil (73 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87−0.88 (m, 3 H), 1.28−1.32 (m, 8 H), 1.67−1.74 (m, 2 H), 2.65 (t, J = 7.4 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 25.5, 28.9, 31.6, 43.7, 123.9, 127.0, 132.3, 135.9, 196.8. HRMS (EI-TOF) (m/z): calcd for $C_{14}H_{19}BrOS$, 314.0340; found, 314.0335.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and $^{13}\{^1$H$\}$ NMR spectra of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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