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# 室温下酯与伯硫醇的硫酯化反应

石义军*,[a] 孙馨悦[a] 曹 晗[a] 别福升[a]
马 杰[a] 刘 哲[b] 丛兴顺*,[a]
([a]枣庄学院鲁南煤化工工程技术研究院 化学化工与材料科学学院 山东枣庄 277160)
([b]襄阳市公共检验检测中心 湖北襄阳 441000)

**摘要** 报道了在室温下酯与伯硫醇的硫酯化反应. 该方法的优点包括不使用过渡金属、条件温和、官能团耐受性良好、底物范围广泛及对脂肪醇酯和酚酯基团的优异化学选择性. 该方法成功地应用于丙磺舒硫酯的合成和顺序键的活化.
**关键词** 硫酯化反应; 酯; 伯硫醇; 不使用过渡金属; 室温

# Thioesterification of Esters with Primary Aliphatic Thiols at Room Temperature

Shi, Yijun*,[a] Sun, Xinyue[a] Cao, Han[a] Bie, Fusheng[a]
Ma, Jie[a] Liu, Zhe[b] Cong, Xingshun*,[a]
([a] *Engineering and Technology Research Institute of Lunan Coal Chemical Engineering, College of Chemistry, Chemical Engineering and Materials Science, Zaozhuang University, Zaozhuang, Shandong 277160*)
([b] *Xiangyang Public Inspection and Testing Center, Xiangyang, Hubei 441000*)

**Abstract** The thioesterification of esters with primary aliphatic thiols at room temperature was reported. The advantages of the method include transition-metal-free, mild conditions, good functional group tolerance, broad substrate scope and excellent chemoselectivity with respect to aliphatic alcohol ester and phenolic ester groups. This method was successfully applied to the synthesis of probenecid thioester and sequential bond activation.
**Keywords** thioesterification; esters; primary aliphatic thiols; transition-metal-free; room temperature

## 1 Introduction

Sulfur is a fascinating element with a critical role in the fields of synthetic chemistry and material chemistry.[1-2] Especially in organic synthesis, organic sulfur sources were majored such as thiols,[3] thioesters,[4] thioethers,[5] disulfides,[6] sulfonyl chlorides,[7] thiosulfonates,[8] sulfonyl hydrazides,[9] thioacids[10] and $S_8$.[11] Apart from these organic sulfur sources, sodium sulfothioates[12] and potassium xanthate[13] were also applicated in synthesis (Figure 1A). In recent years, thioethers and thioesters have been found in various pharmaceuticals and bioactive molecules,[14] including thymitaq,[15] butoconazole, fluticasone[16] and formicin A[17] (Figure 1B). It is noteworthy that thioesters also played a critical role in organic synthesis as acyl donors and versatile intermediates.[18-22] For example, thioethers can be directly synthesized from thioesters by intramolecular decarbonylation.[22]

Consideration of the important role in synthetic chemistry of thioesters, many synthetic strategies have been developed over the past several decades.[23] The sulfur sources to synthesize thioesters were various and the most reported were thiols (Scheme 1A). The traditional and most efficient synthetic method was nucleophilic acylation of thiols with acylating reagents.[24] Among these synthetic strategies in Scheme 1A, oxidative acylation of thiols with alcohols or aldehyde,[25] carbonylative coupling of thiols with halides or unsaturated compounds (alkenes or alkynes),[26] thiocarbonylation of *gem*-difluoroalkene and with thiols and thioesterification of thiols with amides or esters were also efficient.[17,27] Apart from these synthetic strategies using thiols as sulfur sources, other sulfur

* Corresponding authors. E-mail: yjshi673230386@163.com; cong_xingshun@126.com
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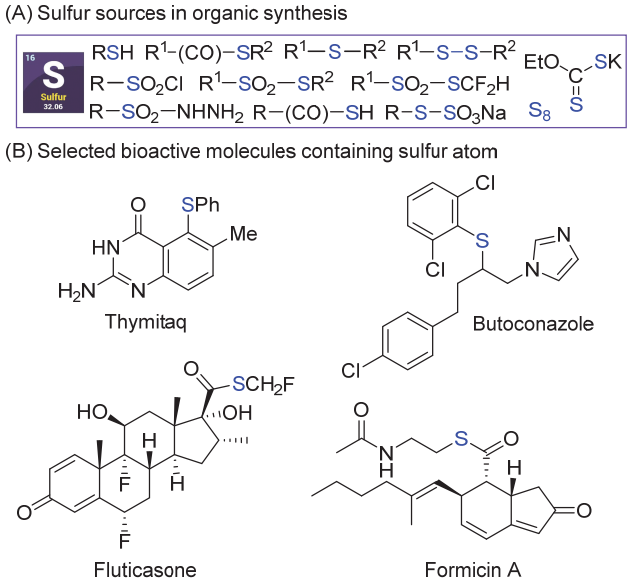
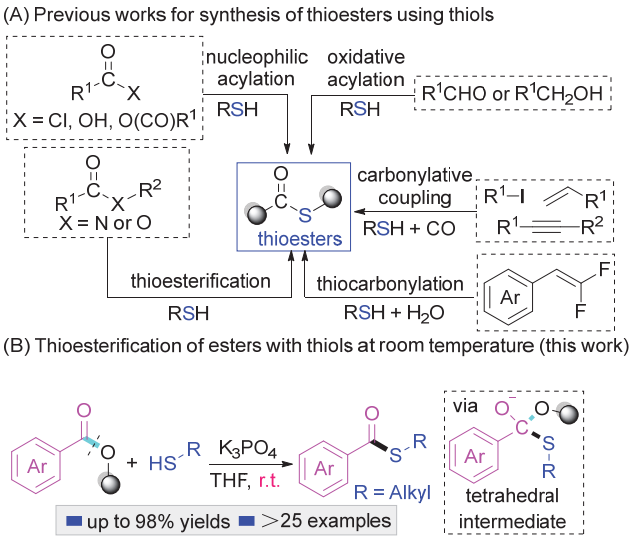



**Figure 1** (A) Sulfur sources in organic synthesis, and (B) selected bioactive molecules containing sulfur atom




**Scheme 1** Synthetic strategies of thioesters

sources were also reported to synthesize thioesters including thioethers, disulfides, sulfonyl chlorides, thiosulfonates, sulfonyl hydrazides, thioacids and $S_8$.[5-11]

So far, the thioesterification of thiols with esters was rarely reported. In 2018 and 2020, some aliphatic thiols were transformed into the corresponding thioesters by using isopropenyl acetate or vinyl ester donors.[27c-27d] But the scope of esters was very limited and the reaction must be catalyzed by triflic acid or S11C MsAcT.

Recently, our group[27f] has developed the metal-free thioesterification of thiophenols with esters at 80 ℃. For this work, only thiophenols were utilized for this transformation while the desired product (PhCOSEt) was obtained in only 22% yield at 80 ℃. To utilize the aliphatic thiols to this transformation at lower temperature, the thioesterification of primary aliphatic thiols with esters at room temperature will be reported in this paper.

## 2 Results and discussion

Initially, our studies were started with using phenyl benzoate (**1a**) and hexane-1-thiol (**2a**) as the model substrates, different parameters were optimized at room temperature (Table 1). First, $K_3PO_4$ was selected as the most appropriate base in tetrahydrofuran (THF) (Table 1, Entries 1～17). However, $K_2CO_3$ (89%), $Cs_2CO_3$ (73%), KOH (45%) and LiO*t*-Bu (88%) were also effective. Other inorganic bases such as $Na_2CO_3$, $NaHCO_3$, NaOAc, KOAc, KF and KO*t*-Bu did not show reactivity, while organic bases were also ineffective (Table 1, Entries 14～17). As expected, no reaction was observed in the absence of base (Table 1, Entry 18). Next, solvents were checked (Table 1, Entries 19～21) and THF was identified as the optimal solvent. Finally, the combination of **2a** (2.0 equiv.) and $K_3PO_4$ (0.5 equiv.) was identified in THF at room temperature as the optimum system to afford the desired product in 98% yield (Table 1, Entry 26).

**Table 1** Optimization of reaction conditions[a]

| Entry | Base | Solvent | Yield[b]/% |
|---|---|---|---|
| 1 | $Na_2CO_3$ | THF | <5 |
| 2 | $K_2CO_3$ | THF | 89 |
| 3 | $Cs_2CO_3$ | THF | 73 |
| 4 | $NaHCO_3$ | THF | <5 |
| 5 | $K_3PO_4$ | THF | 98 |
| 6 | NaOAc | THF | <5 |
| 7 | KOAc | THF | <5 |
| 8 | KF | THF | <5 |
| 9 | NaOH | THF | 8 |
| 10 | KOH | THF | 45 |
| 11 | LiO*t*-Bu | THF | 88 |
| 12 | NaO*t*-Bu | THF | 10 |
| 13 | KO*t*-Bu | THF | <5 |
| 14 | $Et_3N$ | THF | <5 |
| 15 | DIPEA | THF | <5 |
| 16 | DMAP | THF | <5 |
| 17 | Pyridine | THF | <5 |
| 18 | — | THF | <5 |
| 19 | $K_3PO_4$ | Toluene | <5 |
| 20 | $K_3PO_4$ | Dioxane | 90 |
| 21 | $K_3PO_4$ | $CH_3CN$ | 82 |
| 22[c] | $K_3PO_4$ | THF | 98 |
| 23[d] | $K_3PO_4$ | THF | 98 |
| 24[e] | $K_3PO_4$ | THF | 98 |
| 25[f] | $K_3PO_4$ | THF | 73 |
| 26[g] | $K_3PO_4$ | THF | 98 |
| 27[h] | $K_3PO_4$ | THF | 88 |

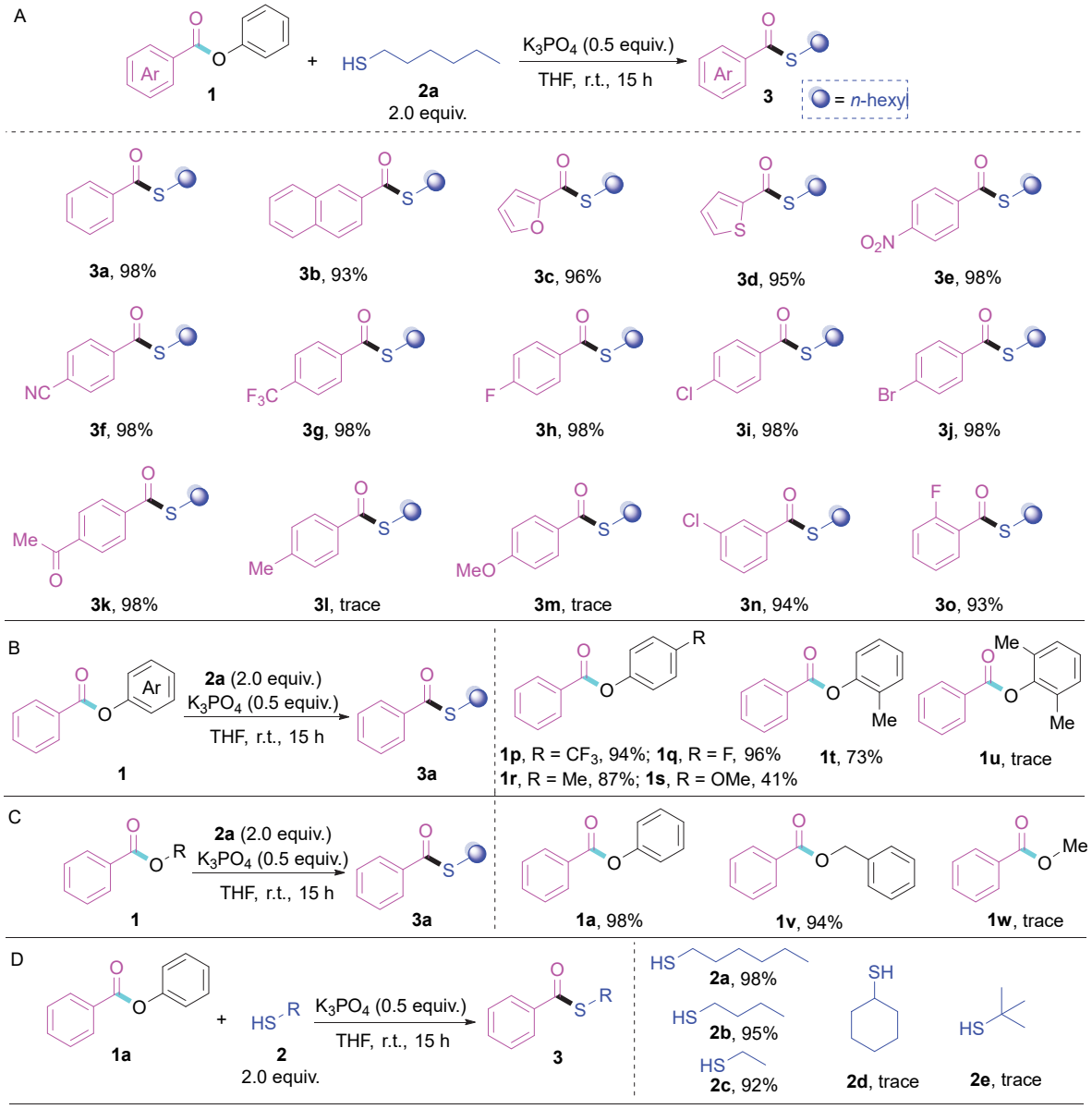
[a] Unless otherwise noted, reactions were carried out with **1a** (1.0 equiv.), **2a** (3.0 equiv.), base (3.0 equiv.), THF (0.20 mol/L), r.t., 15 h. [b] GC/$^1$H NMR yields. [c] Base (2.0 equiv.). [d] Base (1.0 equiv.). [e] Base (0.5 equiv.). [f] Base (0.25 equiv.). [g] **2a** (2.0 equiv.). [h] **2a** (1.0 equiv.).

With the optimal conditions in our hands, the scope for

the thioesterification was explored immediately and was very broad, including excellent functional group tolerance to various sensitive electronically diverse esters. As shown in Scheme 2A, electron-neutral (**3a**～**3b**) and heterocyclic (**3c**～**3d**) esters well transformed with hexane-1-thiol (**2a**) and provided the diverse thioesters in excellent yields. Furthermore, a wide range of electron-withdrawing groups (**3e**～**3k**) were well compatible with this transformation. Especially for the halides, such as fluoro (**3h**), chloro (**3i**) and bromo (**3j**) were readily accommodated, delivering handles for further modification. Moreover, electrophilic functional ketones (**3k**) can also be compatible with this method. But for the electron-donating groups, such as methyl (**3l**) and methoxy (**3m**) were not employed under these mild conditions. To our delight, 3-substituted ester (**3n**) as well as 2-substituted ester (**3o**) was well compatible.

Next, differently substituted esters on the phenol moiety were tested (Scheme 2B). Notably, a variety of esters were smoothly converted under these mild conditions to afford *S*-hexyl benzothioate (**3a**) in good to excellent yields, either electron-withdrawing groups [such as trifluoromethyl (**1p**) and fluoro (**1q**)] or electron-donating group (**1r**). Furthermore, methoxy (**1s**) was also compatible with this method, delivering *S*-hexyl benzothioate (**3a**) in 41% yield. Moreover, hindered *ortho*-substituted ester (**1t**) delivered *S*-hexyl benzothioate (**3a**) in 73% yield. But for the hindered 2,6-substituted ester (**1u**), no desired thioester could be obtained. Aliphatic esters were also tested under these mild conditions, benzyl benzoate (**1v**) delivered *S*-hexyl benzothioate (**3a**) in excellent yield while methyl benzoate (**1w**) can not (Scheme 2C). Finally, different aliphatic thiols were tested and only primary aliphatic thiols (**2a**, **2b** and **2c**) afforded the desired products in high yields. But for the secondary thiol (cyclohexanethiol, **2d**) and the ter-

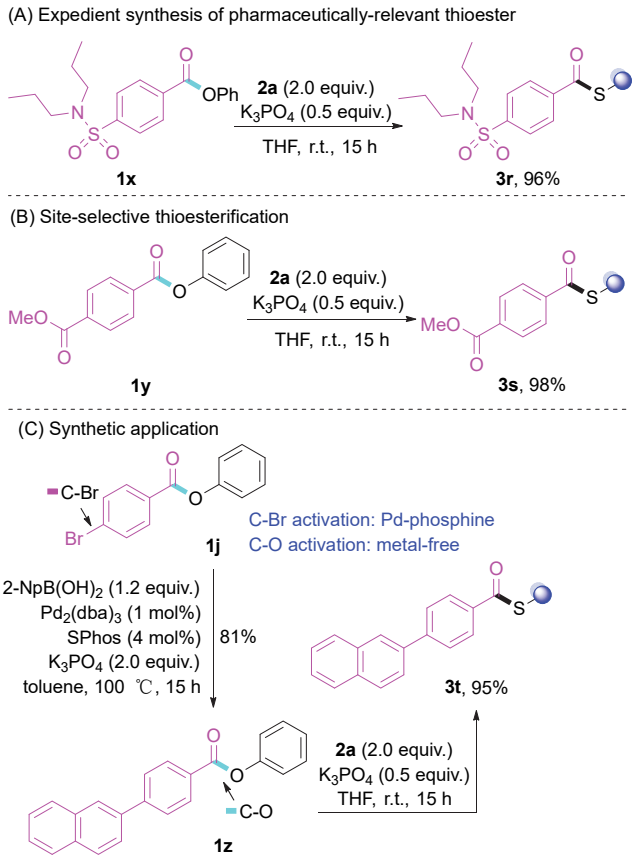



**Scheme 2** Scope of the thioesterification

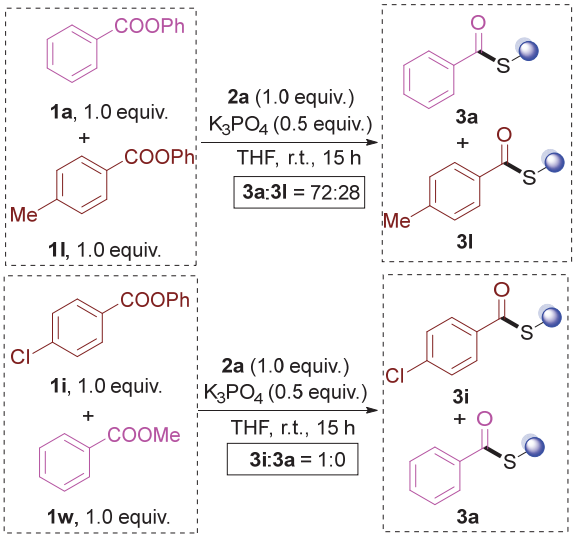
tiary thiol (2-methylpropane-2-thiol, **2e**), no products were formed due to steric hindrance and the conversation of phenyl benzoate (**1a**) was less than 5% (Scheme 2D).

To illustrate the synthetic utility of this method, probenecid (**1x**) was employed and the corresponding thioester was obtained in 96% yield (Scheme 3A). Next, the study of site-selective thioesterification was conducted (Scheme 3B), the substrate (**1y**) containing two ester functional groups showed exquisite chemoselectivity in the reaction, delivering the product (**3q**) containing ester functional group and thioester functional group in 98% yield. This result revealed that aliphatic alcohol ester remained fully intact while only the phenolic ester can be converted to the corresponding thioester under these mild conditions. Finally, the site-selective Suzuki cross-coupling and thioesterification via C—Br/acyl C—O bond cleavage was demonstrated (Scheme 3C). This sequential approach provided a very effective strategy to synthesize polycyclic aromatic thioester.




**Scheme 3** (A) Synthesis of probenecid thioester, (B) site-selective thioesterification, and (C) synthetic application

Intermolecular competition experiments were conducted to gain insight into why these esters (**1l**/**1m**/**1w**) can not work while **1a** can work well for this reaction (Scheme 4). Firstly, electron-neutral ester (**1a**) was more reactive than electron-rich ester (**1l**) (**3a** ∶ **3l**＝72 ∶ 28). Secondly, aromatic ester (**1i**) was inherently more reactive than methyl benzoate (**1w**) (**3i** ∶ **3a**＝1 ∶ 0). Finally, the tetrahedral intermediate in Scheme 1B was provided to further understand the mechanism of this transformation based on previous reports.[27b,27e-27f]




**Scheme 4** Competition experiments

## 3 Conclusions

In summary, a general and efficient thioesterification of esters with primary aliphatic thiols under mild conditions was developed. The advantages of the method include transition-metal-free, at room temperature, good functional group tolerance, broad substrate scope and excellent chemoselectivity with respect to aliphaticalcohol ester and phenolic ester groups. This method was successfully applied to the synthesis of probenecid thioester and sequential bond activation. In the future, we will focus on expanding the scope of this method as well as the high atom-economy which both acyl and phenol groups will be utilized.

## 4 Experimental section

### 4.1 General experimental details

The $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded in $CDCl_3$ on a Bruker spectrometers at 400 MHz ($^{1}$H NMR), 100 MHz ($^{13}$C NMR) and 376 MHz ($^{19}$F NMR). HRMS data were recorded on an Agilent 6530 Accurate-Mass Q-TOF LCMS spectrometer by ESI in positive mode. Melting point was recorded on an INESA (SGWX-4B) equipment without corrected. Only the ester **1w** was purchased, while other esters (**1a**～**1v**, **1x**～**1z**) were synthesized according to the previously published procedure (see ESI for details). All other chemicals were purchased at the highest commercial grade (Innochem) and used as received.

### 4.2 General procedure for thioesterification of esters

An oven-dried vial equipped with a stir bar was charged with ester (neat, 0.10 mmol, 1.0 equiv.), thiol (typically,

0.20 mmol, 2.0 equiv.) and $K_3PO_4$ (typically, 0.05 mmol, 0.5 equiv.), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.20 mol/L) was added with vigorous stirring and stirred for the indicated time at room temperature. After the indicated time, the reaction mixture was diluted with $CH_2Cl_2$ (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title products.

*S*-Hexyl benzothioate (**3a**):[25a] 98% yield (21.8 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.97 (d, $J$=7.2 Hz, 2H), 7.56 (t, $J$=7.4 Hz, 1H), 7.44 (t, $J$=7.7 Hz, 2H), 3.07 (t, $J$=7.4 Hz, 2H), 1.74～1.61 (m, 2H), 1.48～1.38 (m, 2H), 1.37～1.27 (m, 4H), 0.89 (t, $J$=6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 192.3, 137.4, 133.3, 128.7, 127.3, 31.5, 29.7, 29.2, 28.8, 22.7, 14.2.

*S*-Hexyl naphthalene-2-carbothioate (**3b**): 93% yield (23.1 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.54 (s, 1H), 8.09～7.80 (m, 4H), 7.65～7.48 (m, 2H), 3.13 (t, $J$=7.4 Hz, 2H), 1.81～1.65 (m, 2H), 1.52～1.41 (m, 2H), 1.40～1.29 (m, 4H), 0.91 (t, $J$=6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 192.3, 135.9, 134.7, 132.6, 129.7, 128.65, 128.56, 128.5, 127.9, 127.0, 123.3, 31.5, 29.7, 29.3, 28.8, 22.7, 14.2; HRMS (ESI) calcd for $C_{17}H_{20}OSNa$ $[M+Na]^+$ 295.1133, found 295.1155.

*S*-Hexyl furan-2-carbothioate (**3c**):[28] 96% yield (20.4 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.56 (s, 1H), 7.18 (d, $J$=3.4 Hz, 1H), 6.58～6.46 (m, 1H), 3.05 (t, $J$=7.3 Hz, 2H), 1.73～1.60 (m, 2H), 1.48～1.36 (m, 2H), 1.36～1.26 (m, 4H), 0.89 (t, $J$=6.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 180.9, 151.2, 146.1, 115.4, 112.3, 31.5, 29.7, 28.7, 28.3, 22.7, 14.2.

*S*-Hexyl thiophene-2-carbothioate (**3d**): 95% yield (21.7 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.79 (d, $J$=3.6 Hz, 1H), 7.59 (d, $J$=4.9 Hz, 1H), 7.14～7.07 (m, 1H), 3.06 (t, $J$=7.3 Hz, 2H), 1.76～1.61 (m, 2H), 1.49～1.37 (m, 2H), 1.36～1.26 (m, 4H), 0.89 (t, $J$=6.7 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 184.3, 142.5, 132.5, 131.0, 128.0, 31.4, 29.7, 29.3, 28.7, 22.7, 14.2; HRMS (ESI) calcd for $C_{11}H_{16}OS_2Na$ $[M+Na]^+$ 251.0540, found 251.0556.

*S*-Hexyl 4-nitrobenzothioate (**3e**): 98% yield (26.2 mg), yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.30 (d, $J$=8.8 Hz, 2H), 8.11 (d, $J$=8.8 Hz, 2H), 3.12 (t, $J$=7.4 Hz, 2H), 1.77～1.63 (m, 2H), 1.50～1.39 (m, 2H), 1.38～1.28 (m, 4H), 0.90 (t, $J$=6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 190.8, 150.6, 142.0, 128.3, 124.0, 31.4, 29.8, 29.4, 28.7, 22.6, 14.1; HRMS (ESI) calcd for $C_{13}H_{17}NO_3SNa$ $[M+Na]^+$ 290.0827, found 290.0842.

*S*-Hexyl 4-cyanobenzothioate (**3f**): 98% yield (24.2 mg), yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.05 (d, $J$=8.4 Hz, 2H), 7.75 (d, $J$=8.4 Hz, 2H), 3.10 (t, $J$=7.4 Hz, 2H), 1.75～1.62 (m, 2H), 1.48～1.37 (m, 2H), 1.37～1.27 (m, 4H), 0.89 (t, $J$=6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.0, 140.5, 132.6, 127.8, 118.0, 116.6, 31.4, 29.6, 29.4, 28.7, 22.6, 14.1; HRMS (ESI) calcd for $C_{14}H_{17}NOSNa$ $[M+Na]^+$ 270.0929, found 270.0945.

*S*-Hexyl 4-(trifluoromethyl)benzothioate (**3g**):[29] 98% yield (28.4 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.07 (d, $J$=8.1 Hz, 2H), 7.71 (d, $J$=8.2 Hz, 2H), 3.10 (t, $J$=7.4 Hz, 2H), 1.75～1.62 (m, 2H), 1.50～1.38 (m, 2H), 1.38～1.27 (m, 4H), 0.90 (t, $J$=6.7 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.4, 140.2, 134.7 (q, $J^2$=32.8 Hz), 127.7, 125.8 (q, $J^3$=3.7 Hz), 123.7 (d, $J^1$=273.1 Hz), 31.4, 29.50, 29.49, 28.7, 22.7, 14.2; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$: −63.09.

*S*-Hexyl 4-fluorobenzothioate (**3h**):[30] 98% yield (23.5 mg), yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.07～7.88 (m, 2H), 7.12 (t, $J$=8.6 Hz, 2H), 3.06 (t, $J$=7.4 Hz, 2H), 1.76～1.59 (m, 2H), 1.48～1.26 (m, 6H), 0.89 (t, $J$=6.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 190.8, 166.0 (d, $J^1$=254.9 Hz), 133.8 (d, $J^4$=2.9 Hz), 129.8 (d, $J^3$=9.4 Hz), 115.8 (d, $J^2$=21.9 Hz), 31.5, 29.6, 29.3, 28.7, 22.7, 14.2; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$: −105.15.

*S*-Hexyl 4-chlorobenzothioate (**3i**):[25a] 98% yield (25.1 mg), yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.91 (d, $J$=8.5 Hz, 2H), 7.42 (d, $J$=8.5 Hz, 2H), 3.07 (t, $J$=7.4 Hz, 2H), 1.77～1.59 (m, 2H), 1.48～1.37 (m, 2H), 1.37～1.26 (m, 4H), 0.89 (t, $J$=6.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.2, 139.7, 135.7, 129.0, 128.7, 31.5, 29.6, 29.3, 28.7, 22.7, 14.2.

*S*-Hexyl 4-bromobenzothioate (**3j**):[31] 98% yield (29.4 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.83 (d, $J$=8.6 Hz, 2H), 7.58 (d, $J$=8.6 Hz, 2H), 3.06 (t, $J$=7.4 Hz, 2H), 1.75～1.60 (m, 2H), 1.49～1.37 (m, 2H), 1.37～1.27 (m, 4H), 0.89 (t, $J$=6.7 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.3, 136.2, 132.0, 128.8, 128.3, 31.4, 29.6, 29.3, 28.7, 22.7, 14.2.

*S*-Hexyl 4-acetylbenzothioate (**3k**): 98% yield (25.9 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.23～7.78 (m, 4H), 3.09 (t, $J$=7.4 Hz, 2H), 2.64 (s, 3H), 1.76～1.62 (m, 2H), 1.50～1.38 (m, 2H), 1.37～1.28 (m, 4H), 0.90 (t, $J$=6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 197.5, 191.7, 140.7, 140.4, 128.6, 127.5, 31.5, 29.5, 29.5, 28.7, 27.0, 22.7, 14.2; HRMS (ESI) calcd for $C_{15}H_{20}O_2SNa$ $[M+Na]^+$ 287.1082, found 287.1102.

*S*-Hexyl 3-chlorobenzothioate (**3n**):[31] 94% yield (24.1 mg), yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.94 (s, 1H), 7.84 (d, $J$=7.7 Hz, 1H), 7.53 (d, $J$=7.8 Hz, 1H), 7.38 (t, $J$=7.9 Hz, 1H), 3.07 (t, $J$=7.3 Hz, 2H), 1.73～1.61 (m, 2H), 1.48～1.37 (m, 2H), 1.37～1.26 (m, 4H), 0.89 (t, $J$=6.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.1, 138.9, 135.0, 133.2, 130.0, 127.4, 125.4, 31.5, 29.5, 29.4, 28.7, 22.7, 14.2.

*S*-Hexyl 2-fluorobenzothioate (**3o**):[31] 93% yield (22.3 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.85 (t, $J$=6.7 Hz, 1H), 7.50 (d, $J$=6.0 Hz, 1H), 7.24～7.06 (m, 2H), 3.07 (t, $J$=6.9 Hz, 2H), 1.79～1.61 (m, 2H), 1.49～1.24 (m, 6H), 0.90 (t, $J$=6.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 189.3 (d, $J^5$=4.8 Hz), 160.4 (d, $J^1$=257.5 Hz), 134.2 (d, $J^4$=8.7 Hz), 129.8 (d, $J^8$=1.3 Hz), 126.0 (d, $J^3$=11.4 Hz), 124.3 (d, $J^6$=3.7 Hz), 117.0 (d, $J^2$=22.0 Hz), 31.5, 29.5 (d, $J^7$=2.8 Hz), 29.4, 28.8, 22.7, 14.2; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$: −111.10.

*S*-Butyl benzothioate (**3p**):[32] 95% yield (18.4 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.97 (d, $J$=7.1 Hz, 2H), 7.56 (t, $J$=7.4 Hz, 1H), 7.44 (t, $J$=7.7 Hz, 2H), 3.08 (t, $J$=7.3 Hz, 2H), 1.72～1.60 (m, 2H), 1.51～1.39 (m, 2H), 0.95 (t, $J$=7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 192.4, 137.4, 133.4, 128.7, 127.3, 31.8, 28.9, 22.2, 13.8.

*S*-Ethyl benzothioate (**3q**):[33] 92% yield (15.3 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.96 (d, $J$=8.5 Hz, 2H), 7.56 (t, $J$=7.4 Hz, 1H), 7.44 (t, $J$=7.7 Hz, 2H), 3.08 (q, $J$=7.4 Hz, 2H), 1.35 (t, $J$=7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 192.3, 137.4, 133.4, 128.7, 127.3, 23.6, 14.9.

*S*-Hexyl 4-(*N*,*N*-dipropylsulfamoyl)benzothioate (**3r**): 96% yield (37.0 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.06 (d, $J$=8.5 Hz, 2H), 7.87 (d, $J$=8.5 Hz, 2H), 3.26～2.65 (m, 6H), 1.74～1.63 (m, 2H), 1.59～1.49 (m, 4H), 1.47～1.38 (m, 2H), 1.36～1.28 (m, 4H), 1.05～0.67 (m, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.2, 144.4, 140.1, 127.9, 127.4, 50.1, 31.4, 29.6, 29.5, 28.7, 22.6, 22.1, 14.2, 11.3; HRMS (ESI) calcd for $C_{19}H_{31}NO_3S_2Na$ $[M+Na]^+$ 408.1643, found 408.1675.

Methyl 4-((hexylthio)carbonyl)benzoate (**3s**):[4b] 98% yield (27.5 mg), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.10 (d, $J$=8.5 Hz, 2H), 8.01 (d, $J$=8.6 Hz, 2H), 3.94 (s, 3H), 3.09 (t, $J$=7.4 Hz, 2H), 1.73～1.63 (m, 2H), 1.49～1.37 (m, 2H), 1.37～1.26 (m, 4H), 0.89 (t, $J$=6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.8, 166.3, 140.7, 134.1, 129.9, 127.2, 52.6, 31.4, 29.51, 29.45, 28.7, 22.6, 14.2.

*S*-Hexyl 4-(naphthalen-2-yl)benzothioate (**3t**): 95% yield (33.1 mg), white solid. m.p. 70～72 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.16～7.63 (m, 9H), 7.61～7.39 (m, 2H), 3.11 (t, $J$=7.4 Hz, 2H), 1.81～1.62 (m, 2H), 1.51～1.41 (m, 2H), 1.39～1.29 (m, 4H), 0.92 (t, $J$=7.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.9, 146.0, 137.3, 136.2, 133.7, 133.2, 128.9, 128.5, 128.0, 127.8, 127.6, 126.7, 126.6, 126.5, 125.3, 31.5, 29.7, 29.3, 28.8, 22.7, 14.2; HRMS (ESI) calcd for $C_{23}H_{24}OSNa$ $[M+Na]^+$ 371.1446, found 371.1469.

**Supporting Information** The $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of **1a**～**1v**, **1x**～**1z**, **3a**～**3k** and **3n**～**3t**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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