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Nickel-catalyzed carbonylation of thioacetates with aryl iodides via CO insertion and C–S bond cleavage

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Abstract

Aryl thioesters are synthesized via nickel-catalyzed carbonylation of thioacetates with aryl iodides. Alkyl thioacetates undergo coupling with carbon monoxide and aryl iodides to produce the desired aryl thioesters in moderate yields. This catalytic carbonylative coupling process provides a cost-effective and direct approach for the preparation of useful thioesters.

Keywords

carbonylation, C–S bond cleavage, disulfides, nickel, thioacetates

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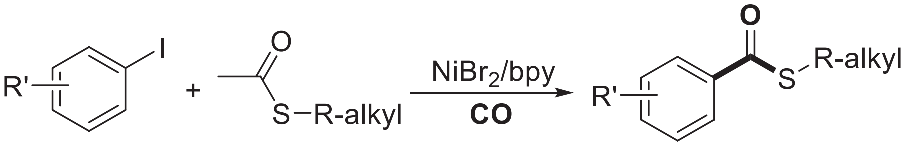

Introduction

The thioester unit is a very useful and powerful building block in organic chemistry[1] and is also an important component of many natural products[2] and agrochemicals.[3] Specifically, thioesters have often been employed as intermediates for the synthesis of amides, esters, and ketones.[4–8] In addition, thioesters also serve as important intermediates in the biosynthesis of polyketides and nonribosomal polypeptides.[9] Due to their many applications, numerous synthetic methods have been developed for the preparation of thioesters, for example, palladium-catalyzed carbonylation of aryl halides and alcohols,[10] palladium-catalyzed carbonylation of thioacetates and aryl iodides,[11] palladium-catalyzed intermolecular transthioetherification of aryl halides with thioethers,[12] condensation of carboxylic acids and alcohols,[13] copper-catalyzed esterification of disulfides and acyl chlorides,[14] and decarboxylative coupling of α-oxocarboxylic acids and disulfides.[15] These methods suffer from certain disadvantages such as harsh conditions, high costs, formation of by-products, and the use of excess reagents. More recently, new progress was reported in this field, in which some novel protocols were developed for the synthesis of thioesters.[16–19] Herein, we report a novel process for the synthesis of aryl thioesters via nickel-catalyzed carbonylation of thioacetates or dialkyl disulfides with aryl iodides under mild conditions.

Results and discussion

In previous work, Kim et al.[11] reported aryl thioacetates as the source of sulfur in the palladium-catalyzed

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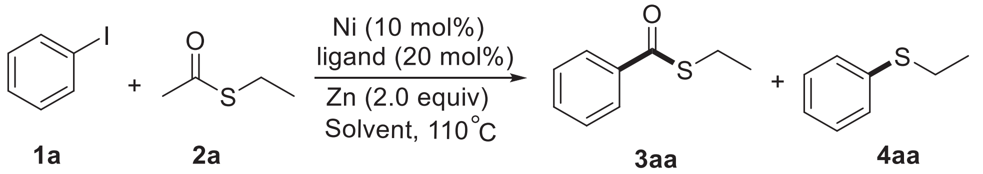
Table 1. Optimization of the reaction conditions[a].



Entry	**1a:2a**	Ni source	Ligand[b]	Solvent	Yield **3aa/4aa**(%)[c]
1	1:1	$NiCl_2$·DME	DTBPy	DMF	5/25
2	1:2	$NiCl_2$·DME	DTBPy	DMF	15/11
3	1:3	$NiCl_2$·DME	DTBPy	DMF	23/6
4	1:3	$NiBr_2$	Bpy	DMF	45/10
5	1:3	$NiBr_2$	Bpy	DMAc	33/16
6	1:3	$NiBr_2$	Bpy	Toluene	0/20
7	1:3	$NiBr_2$	Bpy	dioxane	0/13
8	1:3	NiI_2	Bpy	DMF	43/11
9	1:3	NiI_2	DTBPy	DMF	40/7
10	1:3	NiI_2	Phen	DMF	23/20
11	1:3	$NiBr_2$	Bpy	DMF/H_2O (10:1)	58/8
12	1:3	$NiBr_2$	Bpy	DMF/H_2O (5:1)	46/12
13[d]	1:3	$NiBr_2$	Bpy	DMF/H_2O (10:1)	69/8
14[d]	1:2	$NiBr_2$	Bpy	DMF/H_2O (10:1)	60/10
15[d]	1:1.5	$NiBr_2$	Bpy	DMF/H_2O (10:1)	65/5
16	1:3	$NiBr_2$	Bpy	DMF/H_2O (10:1)	0

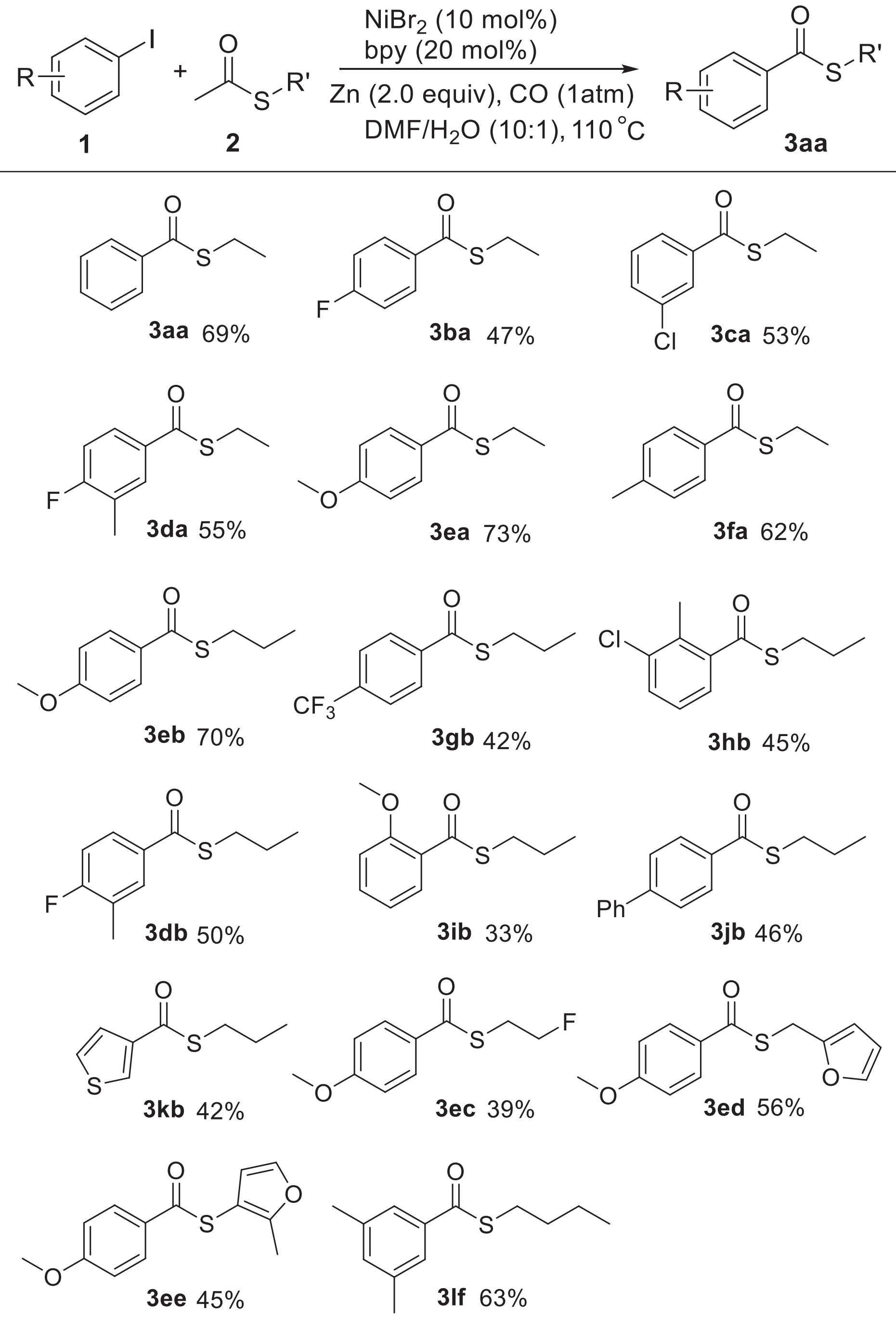
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (as needed), Ni (0.05 mmol), ligand (0.1 mmol), Zn (2.0 equiv.) in solvent (3 mL), 110 °C, and 15 h.
[b] DTBPy: 4,4'-di-*tert*-butyl-2,2'-bipyridine, Bpy: 2,2'-bipyridine, Phen: 1,10-phenanthroline.
[c] GC yield.
[d] 1 atm CO balloon.

carbonylation of aryl iodides for the formation of thioesters under CO (8 atm). Inspired by this result, we tried to use nickel as the catalyst for this transformation under 1 atm of CO; however, the reaction did not occur at all. To our surprise, alkyl thioacetates were compatible with the Ni catalyst, unlike aryl thioacetates under the same conditions. Thus, we chose iodobenzene (**1a**) and *S*-ethyl ethanethioate (**2a**) as model substrates in order to find optimized conditions for the carbonylation (Table 1). Using $NiCl_2$ (10 mol%) as the catalyst, DTBPy (4,4'-di-*tert*-butyl-2,2'-bipyridine) as the ligand, and DMF as the solvent, thioether **4aa** was detected as the main product (Table 1, entry 1). Interestingly, the amount of product **3aa** increased as the ratio of **1a**:**2a** decreased (Table 1, entries 1–3). The GC yield of product **3aa** was improved to 45% when $NiBr_2$ was used as the catalyst instead of $NiCl_2$ under the same conditions (Table 1, entry 4). Other solvents such as DMAc, toluene, and dioxane were also screened using $NiBr_2$ as the catalyst; however, no improvement in the yield of **3aa** was observed (Table 1, entries 5–7). On changing the $NiBr_2$ to NiI_2, about a 40% GC yield of product **3aa** was observed when using Bpy (2,2'-bipyridine) or DTBPy as the ligand (Table 1, entries 8 and 9). When Phen (1,10-phenanthroline) was used as the ligand, the ratio of product **3aa** to **4aa** was almost 1:1 (Table 1, entry 10). To our delight, the product yield of **3aa** was improved to 58% when DMF and H_2O were used as co-solvents (Table 1, entry 11). The yield of **3aa** was not improved when the amount of H_2O was increased in the co-solvent (Table 1, entry 12). When CO (1 atm) was introduced into the system, the GC ratio of **3aa** to **4aa** was improved to 6:1 (Table 1, entries 13–15). The Zn powder plays an important role in this transformation, and no product was observed at all (Table 1, entry 16).

To investigate the scope of this transformation, many aryl iodides were examined for the formation of the corresponding aryl thioester under the optimized reaction conditions and the results are shown in Table 2. Both aryl iodides which have electron-donating and electron-withdrawing groups were found to react with thioacetates and gave the products in moderate yields. Generally, those with electron-donating groups on the aryl ring favored the transformation. For example, 1-iodo-4-methoxybenzene (**1e**) and 1-fluoro-4-iodobenzene (**1b**) both reacted with *S*-ethyl ethanethioate (**2a**) under the optimized conditions, leading to the corresponding products in 73% and 47% yields, respectively (Table 2, **3ba** and **3ea**). Similarly, iodobenzene (**1a**) and 1-iodo-4-methylbenzene (**1f**) provided the desired products in yields of 69% and 62%, respectively. 1-chloro-3-iodobenzene (**1c**) and 1-fluoro-4-iodo-2-methylbenzene (**1d**) provided the expected products in about 55% yields when using *S*-ethyl ethanethioate (**2a**).

When *S*-propyl ethanethioate (**2b**) was selected as the substrate, different aryl iodides could also participate in this reaction with **2b**. 1-Iodo-4-methoxybenzene (**1e**) and 1-iodo-4-(trifluoromethyl)benzene (**1g**) produced the products **3eb** and **3gb** in 70% and 42% yields, respectively. However, only a 33% isolated yield of **3ib** was obtained when using 1-iodo-2-methoxybenzene (**1i**) as the

Table 2. The scope of the aryl iodides and thioacetates[a,b].

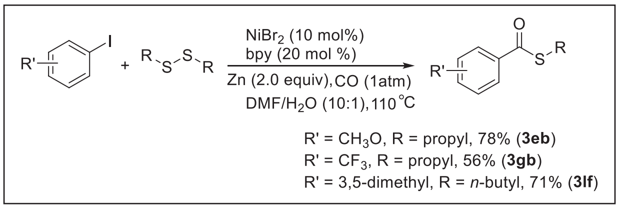


3aa 69%
3ba 47%
3ca 53%
3da 55%
3ea 73%
3fa 62%
3eb 70%
3gb 42%
3hb 45%
3db 50%
3ib 33%
3jb 46%
3kb 42%
3ec 39%
3ed 56%
3ee 45%
3lf 63%

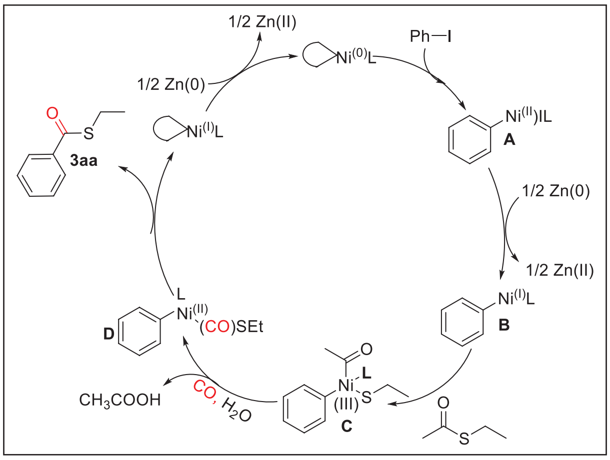
[a] Reactions were carried out using 1 (1.0 mmol), 2 (1.5 mmol), $NiBr_2$ (0.05 mmol), bpy (0.1 mmol), Zn (2.0 mmol), 1 atm CO balloon, DMF/H_2O (2 mL:0.2 mL), 110 °C, and 15 h.
[b] Isolated yield.

substrate. Moreover, 1-chloro-3-iodo-2-methylbenzene (**1h**), 1-fluoro-4-iodo-2-methylbenzene (**1d**), and 4-iodo-1,1'-biphenyl (**1j**) gave the corresponding products **3hb**, **3db**, and **3jb** in yields of about 50%. To our delight, the heteroaromatic iodide 3-iodothiophene (**1k**) reacted with **2b** to produce the desired product **3kb** in 42% yield. For other *S*-alkyl ethanethioates (**2c–d**), containing functional groups such as fluorine and furan, the reactions gave the desired products **3ec** and **3ed** in moderate yields. To our surprise, *S*-aryl ethanethioate **2e** was compatible with the present reaction conditions and the corresponding product **3ee** was obtained in 45% yield; however, other *S*-aryl ethanethioates were not compatible with this reaction.

To study further the mechanism of this transformation, alkyl sulfides were selected as one of the substrates to carry out the reaction under the optimized conditions. To our delight, the results showed that the yields of the desired products were higher in comparison with those obtained when alkyl ethanethioates were employed as substrates



Scheme 1. Alkyl sulfides as substrates.



Scheme 2. Plausible reaction mechanism.

(Scheme 1). For example, dibutylsulfane and *S*-butyl ethanethioate reacted with 1-iodo-3,5-dimethylbenzene under the same conditions, leading to the same product in 71% and 63%, respectively. These results indicated that insertion of Ni(I) into the S–S bond is easier and that the insertion of CO occurred after C–S or S–S bond cleavage.

Based on the above the experimental data and previous work,[17] a plausible reaction mechanism is proposed in Scheme 2. First, an Ni(0) species is formed by reduction with Zn powder, then, the species inserts into the Ph–I bond of the iodobenzene to form the intermediate **A**. Next, species **B** is produced rapidly in the presence of excess Zn. Intermediate **B** reacts with *S*-propyl ethanethioate and the Ni(I) inserts into the C–S bond of *S*-propyl ethanethioate, leading to the intermediate **C**. In the next step, the CO inserts into the species **C**, meanwhile, acetyl group was removed leading to the intermediate **D**. In the end, the species **D** gives the desired product **3aa** and Ni(I) via the reductive elimination. Finally, the catalytic cycle is continued through Ni(0)–Ni(I)–Ni(II) form by the assistance of Zn.

Conclusion

In conclusion, we have established a novel nickel-catalyzed carbonylation of aryl iodides and thioacetates for the synthesis of thioesters. Numerous aryl iodides reacted to give the desired *S*-alkyl thioesters in moderate yields under 1 atm of CO. This methodology is also useful with dialkyl sulfides and afforded the corresponding products in moderate yields under the same conditions. Advantageously, the reaction occurs in one pot, using a cheap catalyst, mild conditions, and a simple procedure. Unfortunately, this one-pot protocol for the formation of *S*-thioesters was unsuccessful with *S*-aryl ethanethioates as substrates as used in our previous work.[20]

Experimental

All experiments were carried out using a Schlenk flask open to air. Aryl iodides and thioacetates were purchased from commercial suppliers and were used as received, unless otherwise noted. All solvents and other commercially available reagents were purchased from TCI company and used directly. Reactions were monitored by TLC (Qingdao Haiyang Chemical Co., Ltd., Silica gel 60 F254). Products were detected using a UV-Vis lamp (254 nm). Column chromatography was performed on Qingdao Haiyang Chemical Co., Ltd., Silica Gel 60 (200–300 mesh). The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker 400 MHz NMR Fourier transform spectrometer. ^{1}H NMR data are reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz) where applicable. The spectra are referenced against the internal non-deuterated solvent ($CDCl_3$, δ $^{1}H = 7.26$ ppm, $^{13}C = 77.0$ ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. ESI-MS spectra were recorded on a Bruker Esquire 3000 instrument.

General procedures for the one-pot synthesis of thioesters **3**

A Schlenk flask equipped with a magnetic stir bar was charged with *S*-alkyl thioacetate **2** (1.5 mmol), aryl iodides **1** (1.0 mmol), $NiBr_2$ (21.8 mg, 0.1 mmol), bipyridine (31.2 mg, 0.2 mmol), and Zn powder (130 mg, 2.0 mmol). Next, the reaction flask was degassed and backfilled with CO three times, and then DMF/H_2O (2:0.2 mL) were injected sequentially. The mixture was stirred at 110 °C for 15 h. When the reaction was complete, brine (30 mL) was added and the aqueous layer was extracted with EtOAc (2×20 mL). The combined organic layer was dried and evaporated and the residue was purified by flash chromatography on silica gel (eluent:petroleum ether/EtOAc = 100:1 to 50:1, v/v) to furnish the desired product **3**.

S-ethyl benzothioate ***(3aa)****: Yield:* 114 mg (69%); yellowish liquid (lit.[13]). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J=8.0 Hz, 2H), 7.58-7.57 (m, 1H), 7.49-7.45 (m, 2H), 3.13-3.08 (m, 3H), 1.38 (t, J=8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.75, 23.44, 127.16, 128.56, 133.20, 137.30, 192.08. HRMS (EI): m/z $[M+H]^+$ calcd for $C_9H_{11}OS$: 167.0531; found: 167.0533.

S-ethyl 4-fluorobenzothioate ***(3ba)****:* Yield: 86 mg (47%); yellowish liquid (lit.[21]). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-7.99 (m, 2H), 7.14 (t, J=8.0 Hz, 2H), 3.13-3.07 (m, 2H), 1.38 (t, J=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 14.73, 23.57, 115.56 (d, $J_{C\text{-}F}$=22 Hz), 129.63 (d, $J_{C\text{-}F}$=9 Hz), 133.64, 167.12 (d, $J_{C\text{-}F}$=252 Hz), 190.57. HRMS (EI): m/z [M + H]$^+$ calcd for $C_9H_{10}FOS$: 185.0436; found: 185.0432.

S-ethyl 3-chlorobenzothioate *(3ca):* Yield: 106 mg (53%); colorless liquid. 1H NMR (400 MHz, CDC$_{13}$): δ 7.95 (s, 1H), 7.87 (d, *J*=8.0 Hz, 1H), 7.39 (t, *J*=8.0 Hz, 1H), 3.14-3.08 (m, 2H), 1.38 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 14.66, 23.68, 125.29, 127.22, 129.88, 133.11, 134.52, 138.76, 190.90. HRMS (EI): m/z [M + H]$^+$ calcd for C_9H_9ClOS: 200.0063; found: 200.0058.

S-ethyl 4-fluoro-3-methylbenzothioate *(3da):* Yield: 109 mg (55%); colorless liquid. ^{1}H NMR (400 MHz, CDC$_{13}$): δ 7.85-7.81 (m, 2H), 7.06 (t, *J*=8.0 Hz, 1H), 3.11-3.05 (m, 2H), 2.33 (s, 3H), 1.38-1.34 (m, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 14.47, 14.50, 14.75, 23.51, 115.35 (d, $J_{C\text{-}F}$=25 Hz), 125.49 (d, $J_{C\text{-}F}$=18 Hz), 127.03, 130.76, 133.32 (d, $J_{C\text{-}F}$=3.0 Hz), 165.70 (d, $J_{C\text{-}F}$=252 Hz), 190.74. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{10}H_{12}FOS$: 199.0593; found: 199.0588.

S-ethyl 4-methoxybenzothioate *(3ea):* Yield: 143 mg (73%); yellow liquid (lit.[13]). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, *J*= 8.0 Hz, 2H), 6.93 (t, *J*= 8.0 Hz, 2H), 3.88 (d, *J*=8.0 Hz, 3H), 3.09-3.05 (m, 2H), 1.37-1.33 (m, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 14.90, 23.29, 55.46, 113.71, 129.28, 130.16, 163.66, 190.55. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{10}H_{13}O_2S$: 197.0636; found: 197.0633.

S-ethyl 4-methylbenzothioate *(3fa):* Yield: 112 mg (62%); yellow liquid (lit.[14]). ^{1}H NMR (400 MHz, CDC$_{13}$): δ 7.90 (d, *J*= 12 Hz, 2H), 7.27 (t, *J*=8.0 Hz, 2H), 3.12-3.06 (m, 2H), 2.43 (s, 3H), 1.37 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 14.83, 21.67, 23.34, 127.23, 129.23, 134.75, 144.05, 191.74 HRMS (EI) m/z [M + H]$^+$ calcd for $C_{10}H_{13}OS$ 181.0687; found: 181.0685.

S-propyl 4-methoxybenzothioate *(3eb):* Yield: 147 mg (70%); yellowish liquid (lit.[13]). ^{1}H NMR (400 MHz, CDC$_{13}$): δ 7.98 (d, *J*=8.0 Hz, 2H), 6.95 (d, *J*=8.0 Hz, 2H), 3.88 (s, 3H), 3.06 (t, *J*=8.0 Hz, 2H), 1.74-1.69 (m, 2H), 1.05 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 13.47, 23.12, 30.81, 55.49, 113.71, 129.33, 130.20, 163.65, 190.65. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{11}H_{15}O_2S$ 211.0793; found: 211.0787.

S-propyl 4-(trifluoromethyl)benzothioate *(3gb):* Yield: 104 mg (42%); yellowish liquid. ^{1}H NMR (400 MHz, CDC$_{13}$): δ 8.10 (d, *J*=8.0 Hz, 2H), 7.74 (d, *J*=8.0 Hz, 2H), 3.11 (t, *J*=8.0 Hz, 2H), 1.77-1.72 (m, 2H), 1.06 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 13.41, 22.84, 31.22, 122.21 (t, $J_{C\text{-}F}$=271 Hz), 125.71 (d, $J_{C\text{-}F}$=8.0 Hz), 134.68 (d, $J_{C\text{-}F}$=32 Hz), 140.00, 191.21. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{11}H_{12}F_3OS$: 249.0561; found: 249.0558.

S-propyl 3-chloro-2-methylbenzothioate *(3hb):* Yield: 103 mg (45%); colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56 (d, *J*=8.0 Hz, 1H), 7.50 (d, *J*=8.0 Hz, 1H), 7.20 (t, *J*=8.0 Hz, 1H), 3.06 (t, *J*=8.0 Hz, 2H), 2.47 (s, 3H), 1.77-1.72 (m, 2H), 1.07 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 13.40, 16.76, 22.91, 31.82, 126.14, 126.51, 131.83, 133.88, 140.71, 194.74. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{11}H_{14}ClOS$: 229.0454; found: 229.0450.

S-(4-fluoro-3-methylphenyl)butanethioate *(3db):* Yield: 106 mg (50%); yellowish liquid. ^{1}H NMR (400 MHz, CDC$_{13}$): δ 7.87-7.82 (m, 2H), 7.10 (t, *J*=8.0 Hz, 1H), 3.07 (t, *J*=8.0 Hz, 2H), 2.35 (d, *J*=4.0 Hz, 3H), 1.75-1.70 (m, 2H), 1.06 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 13.42, 14.53 (d, $J_{C\text{-}F}$=3.0 Hz), 22.99, 31.02, 115.35 (d, $J_{C\text{-}F}$=23 Hz), 125.49 (d, $J_{C\text{-}F}$=18 Hz), 127.06, 130.80, 133.32, 163.19, 165.70, 190.82. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{11}H_{14}FOS$: 213.0749; found: 213.0745.

S-propyl 2-methoxybenzothioate *(3ib):* Yield: 69 mg (33%); yellowish liquid. ^{1}H NMR (400 MHz, CDC$_{13}$): δ 7.80-7.78 (m, 1H), 7.49-7.46 (m, 1H), 7.04-6.99 (m, 2H), 3.94 (s, 3H), 3.04 (t, *J*=8.0 Hz, 2H), 1.75-1.70 (m, 2H), 1.06 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 13.56, 22.82, 31.41, 55.84, 112.00, 120.35, 127.41, 129.65, 133.37, 157.59, 191.42. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{11}H_{15}O_2S$: 211.0793; found: 211.0790.

S-propyl (1,1'-biphenyl)-4-carbothioate *(3jb):* Yield: 118 mg (46%); yellow solid. ^{1}H NMR (400 MHz, CDC$_{13}$): δ 8.08 (d, *J*=8.0 Hz, 2H), 7.70-7.64 (m, 4H), 7.51-7.42 (m, 3H), 3.11 (t, *J*=8.0 Hz, 2H), 1.78-1.73 (m, 2H), 1.08 (t, *J*=8.0 Hz, 3H). 13C NMR (101 MHz, CDC$_{13}$): δ 13.47, 23.03, 30.97, 127.21, 127.27, 127.75, 128.23, 128.96, 136.02, 139.89, 145.98, 191.67. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{16}H_{17}OS$: 257.1000; found: 257.0997.

S-propyl thiophene-3-carbothioate *(3kb):* Yield: 78 mg (46%); yellow liquid. ^{1}H NMR (400 MHz, CDC$_{13}$): δ 8.13-8.12 (m, 1H), 7.57-7.55 (m, 1H), 7.36-7.28 (m, 1H), 3.06 (t, *J*=8.0 Hz, 2H), 1.75-1.69 (m, 2H), 1.05 (t, *J*=8.0 Hz, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 13.42, 23.08, 30.76, 126.04, 126.32, 130.26, 141.18, 185.77. HRMS (EI): m/z [M + H]$^+$ calcd for $C_8H_{11}OS_2$: 187.0251; found: 187.0250.

S-(2-fluoroethyl) 4-methoxybenzothioate *(3ec):* Yield: 84 mg (39%); yellow liquid. 1H NMR (400 MHz, CDC$_{13}$): δ 7.99 (d, *J*=8.0 Hz, 2H), 6.97 (d, *J*=8.0 Hz, 2H), 4.67 (t, *J*=8.0 Hz, 1H), 4.55 (t, *J*=8.0 Hz, 1H), 3.90 (s, 3H), 3.44-3.36 (m, 2H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 28.71, 28.93, 55.55, 82.87 (d $J_{C\text{-}F}$=170 Hz), 113.88, 129.46, 129.55, 164.04, 189.32. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{10}H_{12}FO_2S$: 215.0542; found: 215.0537.

S-(furan-2-ylmethyl) 4-methoxybenzothioate *(3ed):* Yield: 139 mg (56%); yellow liquid. ^{1}H NMR (400 MHz, CDC$_{13}$): δ 7.98 (d, *J*=8.0 Hz, 2H), 7.37 (d, *J*=8.0 Hz, 1H), 6.96-6.93 (m, 2H), 6.34-6.31 (m, 2H), 4.36 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDC$_{13}$): δ 25.63, 55.54, 108.01, 110.65, 113.83, 129.54, 142.23, 150.73, 163.92, 189.20. HRMS

(EI): m/z $[M + H]^+$ calcd for $C_{13}H_{13}O_3S$: 249.0585; found: 249.0583.

***S*-(2-methylfuran-3-yl) 4-methoxybenzothioate *(3ee)*:** Yield: 112 mg (45%); yellowish liquid. ^1H NMR (400 MHz, CDC_{13}): δ 8.04 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 4.0$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.43 (d, $J = 4.0$ Hz, 1H), 3.91 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDC_{13}): δ 12.02, 55.56, 103.66, 113.93, 115.28, 129.29, 129.76, 141.09, 156.68, 164.00, 188.01. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{13}H_{13}O_3S$: 249.0585; found: 249.0580.

***S*-butyl 3,5-dimethylbenzothioate *(3lf)*:** Yield: 140 mg (63%); colorless liquid. ^1H NMR (400 MHz, CDC_{13}): δ 7.60 (s, 2H), 7.21 (s, 1H), 3.08 (t, $J = 8.0$ Hz, 2H), 2.39 (s, 6H), 1.67-1.64 (m, 2H), 1.51-1.45 (m, 2H), 0.97 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDC_{13}): δ 13.63, 21.19, 22.05, 28.70, 31.64, 124.92, 134.85, 137.37, 138.27, 192.45. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{13}H_{19}OS$: 223.1157; found: 223.1155.

Declaration of conflicting interests

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Supplemental material

Supplemental material for this article is available online.

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