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$AlCl_3$-promoted thiolation of acyl C–H bonds with arylsulfonyl hydrazides

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ABSTRACT

$AlCl_3$-promoted thiolation of acyl C–H bonds with arylsulfonyl hydrazides was developed, which represents an effective synthesis of *S*-aryl thiocarbamates via C–S bond formation reaction.

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1. Introduction

S-aryl thiocarbamate is a key structural unit that is widely found in some biologically active molecules such as herbicides thiobencarb and orbencarb (Fig. 1).[1] A considerably large number of methodologies have been developed to construct the *S*-aryl thiocarbamate core structure and the emphasis of research has been on the reactions of amines with thiols and phosgene or with carbonyl sulfide,[2,3] the reactions of dialkylamines with carbon monoxide and sulfur,[1,4] two-step synthesis of *S*-alkyl thiocarbamates,[5] and metal-catalyzed thiolation of acyl compounds.[6] However, the reported protocols usually suffer from some drawbacks such as low efficacy caused by two-step synthetic routes, tedious operations, issues of unavoidable side-reaction or environmental unfriendliness.[1–5]

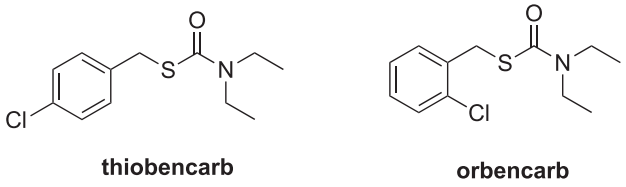

Fig. 1. The representative known compounds containing thiocarbamate moiety.

Owing to the increasing importance of the C–S bond forming process in organosulfur-containing medicinal synthesis,[7] intensive research efforts have been focused on metal-promoted cross coupling for C–S bond formation in recent years. The metal catalyst systems developed thus far mainly involve Pd, Cu, Ni, Fe, Mn, Rh and so on.[8–12] More recently, C–H bond activation as a powerful tool in organic synthesis has been exploited for the cross coupling C–S bond formation. Both sp^2 and sp^3 C–H bond sulfenylations have been achieved towards the construction of diverse sulfide derivatives.[13] In addition, the formamide acyl C–H bond activation was carried out to produce a class of *S*-aryl thiocarbamates by copper catalyzed reactions with thiols as a sulfur source.[6] However, the use of the volatile, foul-smelling and expensive arenethiols in this work largely limited the practical applications of this method. The development of new synthetic methods utilizing alternative sulfur sources such as sulfonyl hydrazides that are safe, reliable and less expensive is desirable. To continue our recent efforts on the cross coupling C–S bond formation processes in our group,[14] we, herein, report a novel aluminum-promoted thiolation of formamide C–H bonds with arylsulfonyl hydrazides.

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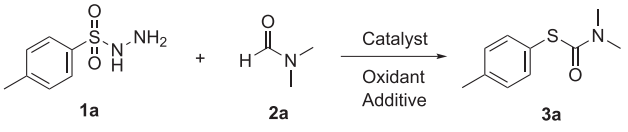
2. Results and discussion

Initially, phenylsulfonyl hydrazide was reacted with *N*,*N*-dimethylformamide (DMF) at 150 °C in the air, in the presence of catalytic amount of $PdCl_2$ and an oxidant DTBP (2.0 equiv), and to our delight the desired product **3a** was isolated in 25% yield (Table 1, entry 1). In order to optimize the reaction conditions, various oxidants were tested for this transformation (Table 1, entries 2–5), however, none of them was effective. It was further observed that the reaction also proceeded in the absence of a palladium catalyst, whilst the yield was slightly lower (Table 1, entry 6). We next screened some other catalysts such as $Pd(OAc)_2$, $(Ph_3P)_2PdCl_2$, I_2,[15] $Cu(OAc)_2$, CuI and $FeCl_3$, yet either inferior results or no reaction were revealed (Table 1, entries 7–12). Interestingly, changing the reaction conditions by the addition of an extra Lewis acid aluminum trichloride (0.2 equiv) into the catalyst system resulted in a small improvement of the yield (Table 1, entry 13), and the yield was slightly higher while using $AlCl_3$ alone as a catalyst (Table 1, entry 14). Consequently, several other Lewis acids were examined and it turned out that $AlCl_3$ was the best additive for the reaction (Table 1, entries 14–18). In addition, the loading amounts of both the additive and oxidant were evaluated, it was found that 53% yield of 3a was gained when 3.0 equivalents of DTBP and 1.0 equivalent of $AlCl_3$ were utilized (Table 1, entries 19–23). At this end, the yield was further improved to 65% when conducted under Ar atmosphere (Table 1, entries 24–25).

Table 1
Optimization of the reaction conditions[a]



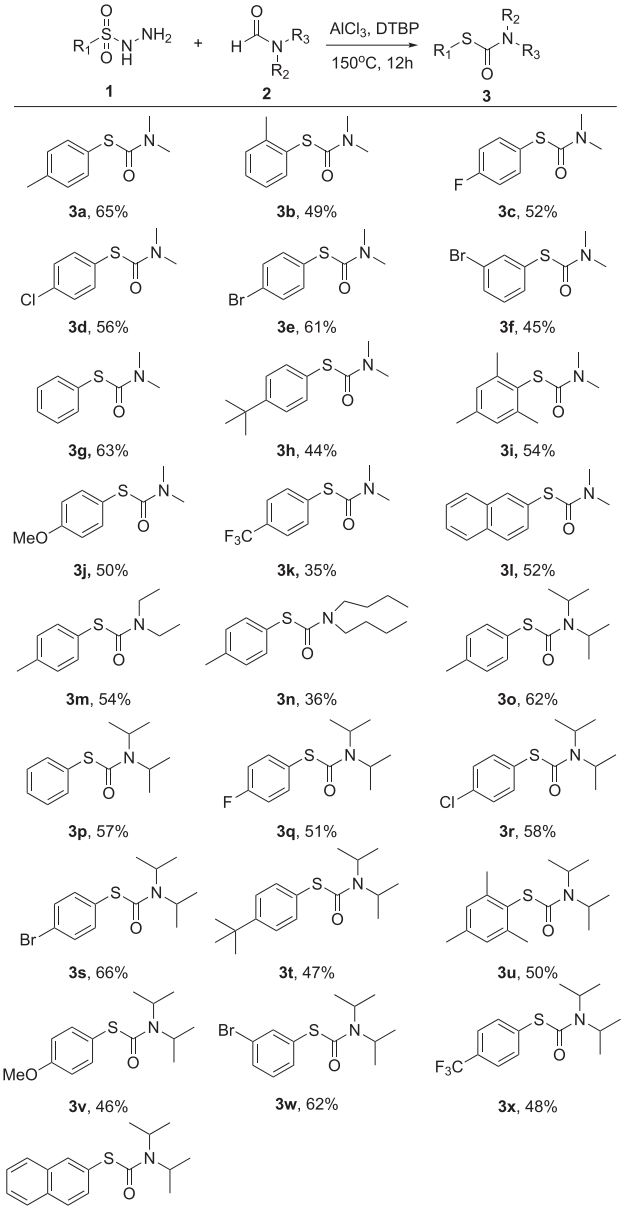
1a 2a 3a

Entry	Oxidant (equiv)	Catalyst (mol %)	Additive (equiv)	Yield[b] (%)
1	DTBP(2.0)	$PdCl_2$(10)	—	25
2	TBHP(2.0)[c]	$PdCl_2$(10)	—	ND
3	DCP(2.0)	$PdCl_2$(10)	—	Trace
4	$Na_2S_2O_8$(2.0)	$PdCl_2$(10)	—	ND
5	$PhI(OAc)_2$(2.0)	$PdCl_2$(10)	—	ND
6	DTBP(2.0)	—	—	17
7	DTBP(2.0)	$Pd(OAc)_2$(10)	—	22
8	DTBP(2.0)	$(Ph_3P)_2PdCl_2$(10)	—	20
9	DTBP(2.0)	I_2(10)	—	22
10	DTBP(2.0)	$Cu(OAc)_2$(10)	—	ND
11	DTBP(2.0)	CuI(10)	—	Trace
12	DTBP(2.0)	$FeCl_3$(10)	—	ND
13	DTBP(2.0)	$PdCl_2$(10)	$AlCl_3$(0.2)	26
14	DTBP(2.0)	—	$AlCl_3$(0.2)	34
15	DTBP(2.0)	—	$BF_3{\cdot}Et_2O$(0.2)	27
16	DTBP(2.0)	—	$ZnCl_2$(0.2)	Trace
17	DTBP(2.0)	—	HOAc(0.2)	22
18	DTBP(2.0)	—	H_2SO_4(0.2)	Trace
19	DTBP(2.0)	—	$AlCl_3$(0.5)	38
20	DTBP(2.0)	—	$AlCl_3$(1.0)	42
21	DTBP(2.0)	—	$AlCl_3$(2.0)	40
22	DTBP(3.0)	—	$AlCl_3$(1.0)	53
23	DTBP(4.0)	—	$AlCl_3$(1.0)	51
24[d]	DTBP(3.0)	—	$AlCl_3$(1.0)	65
25[e]	DTBP(3.0)	—	$AlCl_3$(1.0)	48

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (1 mL), oxidant (2–4 equiv), additive (0.2–2 equiv), heated at 150 °C for 12 h.
[b] Isolated yield.
[c] 70% in water solution.
[d] Under Ar atmosphere.
[e] Under O_2 atmosphere. DTBP: di-*tert*-butyl peroxide; TBHP: *tert*-butyl hydroperoxide; DCP: dicumyl peroxide.

With the optimized conditions in hand, we then explored the substrate scope of the present protocol (Table 2). When electron-neutral and -rich phenylsulfonyl hydrazides were used to react

Table 2
Substrate scope for the synthesis of *S*-aryl thiocarbamate compounds[a]



[a] Reaction conditions: **1** (0.3 mmol), **2** (1 mL), $AlCl_3$ (1 equiv), DTBP (3 equiv), 150 °C, Ar, 12 h; Isolated yield based on **1**.

with DMF under the optimized conditions, modest to good yields have been obtained (**3a, 3b, 3j, 3g**–**3i**). In addition, halo substituents, F, Cl, or Br at the *para*-positions of phenylsulfonyl hydrazide were also compatible with the optimal conditions, affording the desired products in good yields (**3c**–**3e**), although the reaction with *meta*-bromophenylsulfonyl hydrazide was less efficient (**3f**). It is worth noting that this protocol is also applicable to heterocyclic aromatics such as naphthalene, give 52% yield of the corresponding product (**3l**). Next, a variety of formamides were also investigated. Under the optimized conditions, new formamides including *N*,*N*-diethylformamide, *N*,*N*-dibutylformamide, and *N*,*N*-diisopropylformamide were found to react smoothly with toluenesulfonyl hydrazide to generate the coupling products with 36–61% yields (**3m**–**3o**). Encouraged by the relatively high yield of **3o**, the scope and versatility of this method was extended to the reactions of *N*,*N*-diisopropylformamide with

various substituted phenylsulfonyl hydrazides and accordingly, a diverse range of *S*-aryl thiocarbamate compounds were generated in reasonable yields (**3p**–**3y**). The single-crystal X-ray structure of the thiocarbamate product **3l** was obtained and the ORTEP presentation of the molecule is illustrated in Fig. 2. The result matches with the proposed molecular structure, being in full agreement with the spectroscopic data.

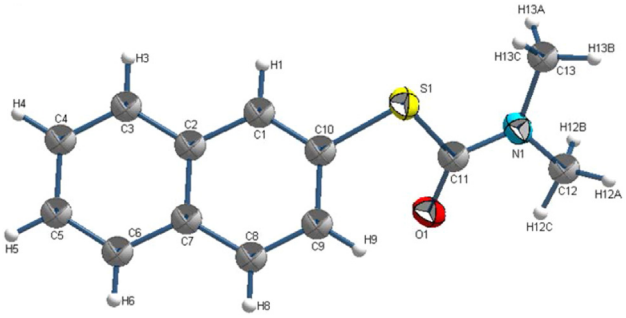
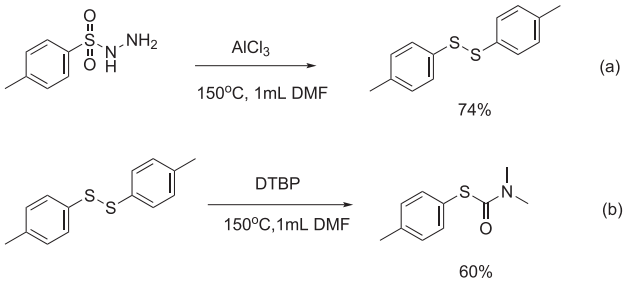


Fig. 2. An ORTEP diagram of product **3l**.

To gain insights on the reaction mechanisms, control experiments were carried out as shown in Scheme 1.[16] When the reaction between phenylsulfonyl hydrazide and DMF was performed under the standard reaction conditions without the addition of DTBP, a disulfide product was obtained in 74% yield. Subsequently, the



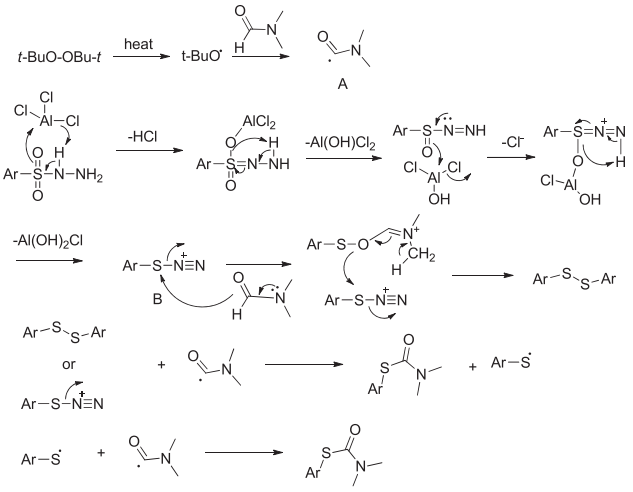
Scheme 1. Control experiments.

disulfide was used to further react with DMF in the presence of DTBP, and the same thiocarbamate product 3a was harvested in 60% yield, comparable to the result above when the reaction was carried out in one pot. This result indicates that the reduced disulfide has participated in the reaction as an intermediate.

A proposed reaction mechanism is outlined in Scheme 2 based upon both the results obtained here and the literature reports.[17] The aluminum trichloride is responsible for the sequential removal of hydrogen and oxygen atoms from phenylsulfonyl hydrazide to genete intermediate **B**, which reacted further with the metal to form aryl disulfide as confirmed previously through the elimination of N_2 molecules. On the other side, DTBP would experience hemolytic cleavage to give *tert*-butoxyl radicals upon heating, which abstracts hydrogen from formamide to generate the crucial radical **A**. Consequently, radical **A** reacts with either the intermediate **B** or aryl disulfide, resulting in the formation of **3a** and ArS• free radical. The ArS• free radical also readily combines with another radical A to form the product **3a** and the reaction is terminated.

3. Conclusions

In conclusion, we have disclosed a direct approach for synthesizing *S*-aryl thiocarbamate compounds from $AlCl_3$-promoted



Scheme 2. The Plausible mechanism.

thiolation of acyl C–H bonds using arylsulfonyl hydrazides as thiol surrogates. This work represents a new example for the C–S bond formation. Further investigations are in progress to expand the scope of the reaction.

4. Experiment

4.1. General information

All reactions were carried out under Ar atmosphere. Solvents were dried and degassed by standard methods. Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Melting points were measured using a XT-4 micro melting point apparatus and were uncorrected. The ^1H and ^{13}C NMR spectra of the new compounds were measured at 400 MHz and 100 MHz in $CDCl_3$ with TMS as the internal standard. HRMS analyses were carried out using a Bruker micrOTOF-Q instrument.

4.2. General procedure for the synthesis of 3

A 25 mL tube was charged with phenylsulfonyl hydrazide (0.3 mmol), $AlCl_3$ (1 equiv), DTBP (3 equiv) and DMF (1 mL) under Ar atmosphere. The resulting reaction mixture was kept stirring at 150 °C for 12 h. Upon completion of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the desired product in high purity.

4.3. *S*-*p*-Tolyl dimethylcarbamothioate (3a)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J=8.0 Hz, 2H), 7.24 (d, J=8.0 Hz, 2H), 3.13 (s, 3H), 3.08 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 138.9, 135.2, 129.3, 124.7, 36.4, 20.8; HRMS calcd for $C_{10}H_{13}NOS$ $[M+H]^+$: 196.0791, found: 196.0788.

4.4. *S*-*o*-Tolyl dimethylcarbamothioate (3b)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J=7.6 Hz, 1H), 7.40–7.34 (m, 2H), 7.27–7.23 (m, 1H), 3.18 (s, 3H), 3.08 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 142.6, 136.6, 130.1,

129.4, 127.7, 125.9, 36.5, 20.6; HRMS calcd for $C_{10}H_{13}NOS$ $[M+H]^+$: 196.0791, found: 196.0790.

4.5. *S*-(4-Fluorophenyl) dimethylcarbamothioate (3c)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.15–7.10 (m, 2H), 3.13 (s, 2H), 3.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 163.0 (d, J=247.9 Hz), 137.3 (d, J=8.5 Hz), 123.6 (d, J=3.4 Hz), 115.6 (d, J=21.9 Hz), 36.4; HRMS calcd for $C_9H_{10}FNOS$ $[M+H]^+$: 200.0540, found: 200.0555.

4.6. *S*-(4-Chlorophenyl) dimethylcarbamothioate (3d)

White solid, mp=76–78 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.42–7.38 (m, 2H), 3.13 (s, 2H), 3.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 136.4, 135.1, 128.6, 126.8, 36.5; HRMS calcd for $C_9H_{10}ClNOS$ $[M+H]^+$: 216.0244, found: 216.0252.

4.7. *S*-(4-Bromophenyl) dimethylcarbamothioate (3e)

White solid, mp=84–86 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J=8.4 Hz, 2H), 7.40 (d, J=8.8 Hz, 2H), 3.12 (s, 2H), 3.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 136.7, 131.6, 127.5, 123.4, 36.5; HRMS calcd for $C_9H_{10}BrNOS$ $[M+H]^+$: 259.9739, found: 259.9752.

4.8. *S*-(3-Bromophenyl) dimethylcarbamothioate (3f)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, J=1.6 Hz, 1H), 7.58–7.55 (m, 1H), 7.49–7.41 (m, 1H), 7.34–7.29 (m, 1H), 3.12 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 137.6, 133.8, 131.7, 130.3, 129.7, 121.8, 36.5; HRMS calcd for $C_9H_{10}BrNOS$ $[M+H]^+$: 259.9739, found: 259.9752.

4.9. *S*-Phenyl dimethylcarbamothioate (3g)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.43–7.39 (m, 3H), 3.11 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 135.3, 128.7, 128.4, 128.3, 36.4; HRMS calcd for $C_9H_{11}NOS$ $[M+H]^+$: 182.0634, found: 182.0646.

4.10. S-(4-(*tert*-Butyl)phenyl) dimethylcarbamothioate (3h)

White solid, mp=68–70 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.44 (m, 4H), 3.13 (s, 3H), 3.09 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 151.8, 134.9, 125.6, 124.8, 36.4, 34.2, 30.8; HRMS calcd for $C_{13}H_{19}NOS$ $[M+H]^+$: 238.1260, found: 238.1257.

4.11. *S*-Mesityl dimethylcarbamothioate (3i)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 2H), 3.21 (s, 3H), 3.07 (s, 3H), 2.44 (s, 6H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 142.9, 139.0, 128.6, 124.2, 36.5, 21.4, 20.7; HRMS calcd for $C_{12}H_{17}NOS$ $[M+H]^+$: 224.1104, found: 224.1122.

4.12. *S*-(4-Methoxyphenyl) dimethylcarbamothioate (3j)

White solid, mp=88–90 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=9.2 Hz, 2H), 6.96 (d, J=9.2 Hz, 2H), 3.86 (s, 3H), 3.12 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 160.1, 136.9, 118.9, 114.1, 54.9, 36.4; HRMS calcd for $C_{10}H_{13}NO_2S$ $[M+H]^+$: 212.0740, found: 212.0751.

4.13. *S*-(4-(Trifluoromethyl)phenyl) dimethylcarbamothioate (3k)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70–7.65 (m, 4H), 3.15 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 135.2, 133.1 (d, J=1.3 Hz), 130.5 (q, J=32.4 Hz), 125.1 (q, J=3.7 Hz), 123.4 (q, J=270.6 Hz), 36.5; HRMS calcd for $C_{10}H_{10}F_3NOS$ $[M+H]^+$: 250.0508, found: 250.0524.

4.14. *S*-Naphthalen-2-yl dimethylcarbamothioate (3l)

White solid, mp=106–108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.92–7.87 (m, 3H), 7.63–7.53 (m, 3H), 3.17 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 134.8, 133.0, 132.8, 131.8, 128.0, 127.5, 127.3, 126.5, 125.9, 125.6, 36.5; HRMS calcd for $C_{13}H_{13}NOS$ $[M+H]^+$: 232.0791, found: 232.0803.

4.15. *S*-*p*-Tolyl diethylcarbamothioate (3m)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J=8.0 Hz, 2H), 7.25 (d, J=7.6 Hz, 2H), 3.51–3.46 (m, 4H), 2.42 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 138.8, 135.3, 129.2, 124.8, 41.8, 20.8, 13.4, 12.7; HRMS calcd for $C_{12}H_{17}NOS$ $[M+H]^+$: 224.1104, found: 224.1121.

4.16. *S*-*p*-Tolyl dibutylcarbamothioate (3n)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J=8.0 Hz, 2H), 7.24 (d, J=7.6 Hz, 2H), 3.40 (t, J=7.6 Hz, 4H), 2.41 (s, 3H), 1.72 (s, 2H), 1.61 (s, 2H), 1.44 (s, 2H), 1.34 (s, 2H), 1.05 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.7, 135.3, 129.2, 124.9, 47.6, 47.4, 30.2, 29.4, 20.8, 19.7, 13.3; HRMS calcd for $C_{16}H_{25}NOS$ $[M+H]^+$: 280.1730, found: 280.1738.

4.17. *S*-*p*-Tolyl diisopropylcarbamothioate (3o)

White solid, mp=95–97 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J=8.0 Hz, 2H), 7.25 (d, J=8.0 Hz, 2H), 4.25 (s, 1H), 3.55 (s, 1H), 2.41 (s, 3H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 138.6, 135.5, 129.2, 125.3, 49.0, 47.1, 20.9, 20.2; HRMS calcd for $C_{14}H_{21}NOS$ $[M+H]^+$: 252.1417, found: 252.1429.

4.18. *S*-Phenyl diisopropylcarbamothioate (3p)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2H), 7.47–7.42 (m, 3H), 4.25 (s, 1H), 3.57 (s, 1H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 135.4, 128.8, 128.4, 128.4, 49.2, 47.1, 20.2; HRMS calcd for $C_{13}H_{19}NOS$ $[M+H]^+$: 238.1260, found: 238.1275.

4.19. *S*-(4-Fluorophenyl) diisopropylcarbamothioate (3q)

Pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.12–7.06 (m, 2H), 4.18 (s, 1H), 3.53 (s, 1H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.9 (d, J=247.5 Hz), 137.4 (d, J=8.5 Hz), 124.1 (d, J=3.4 Hz), 115.5 (d, J=21.9 Hz), 49.3, 47.0, 20.2; HRMS calcd for $C_{13}H_{18}FNOS$ $[M+H]^+$: 256.1166, found: 256.1163.

4.20. *S*-(4-Chlorophenyl) diisopropylcarbamothioate (3r)

White solid, mp=110–112 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.41–7.58 (m, 2H), 4.20 (s, 1H), 3.56 (s, 1H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 136.6, 134.9, 128.6, 127.4, 49.4, 47.2, 20.2; HRMS calcd for $C_{13}H_{18}ClNOS$ $[M+H]^+$: 272.0870, found: 272.0865.

4.21. *S*-(4-Bromophenyl) diisopropylcarbamothioate (3s)

White solid, mp=131–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2H), 7.42–7.39 (m, 2H), 4.20 (s, 1H), 3.55 (s, 1H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 136.9, 131.5, 128.0, 123.2, 49.5, 47.2, 20.2; HRMS calcd for $C_{13}H_{18}BrNOS$ $[M+H]^+$: 316.0365, found: 316.0364.

4.22. *S*-(4-(*tert*-Butyl)phenyl) diisopropylcarbamothioate (3t)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.45 (m, 4H), 4.27 (s, 1H), 3.56 (s, 1H), 1.38 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 151.4, 135.1, 125.6, 125.3, 49.2, 47.1, 34.2, 30.8, 20.2; HRMS calcd for $C_{17}H_{27}NOS$ $[M+H]^+$: 294.1886, found: 294.1901.

4.23. *S*-Mesityl diisopropylcarbamothioate (3u)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 2H), 4.41 (s, 1H), 3.55 (s, 1H), 2.45 (s, 6H), 2.34 (s, 3H), 1.40 (s, 6H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 142.9, 138.7, 128.5, 125.0, 49.4, 47.1, 21.4, 20.7, 20.3; HRMS calcd for $C_{16}H_{25}NOS$ $[M+H]^+$: 280.1730, found: 280.1728.

4.24. *S*-(4-Methoxyphenyl) diisopropylcarbamothioate (3v)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2H), 6.99–6.95 (m, 2H), 4.24 (s, 1H), 3.86 (s, 3H), 3.54 (s, 1H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 159.9, 137.0, 119.5, 114.1, 54.8, 49.1, 46.9, 20.2; HRMS calcd for $C_{14}H_{21}NO_2S$ $[M+H]^+$: 268.1366, found: 268.1365.

4.25. *S*-(3-Bromophenyl) diisopropylcarbamothioate (3w)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, J=1.6 Hz, 1H), 7.56–7.53 (m, 1H), 7.50–7.48 (m, 1H), 7.30 (t, J=8.0 Hz, 1H), 4.18 (s, 1H), 3.56 (s, 1H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 137.7, 134.1, 131.5, 131.0, 129.6, 121.8, 49.4, 47.2, 20.2; HRMS calcd for $C_{13}H_{18}BrNOS$ $[M+H]^+$: 316.0365, found: 316.0360.

4.26. *S*-(4-(Trifluoromethyl)phenyl) diisopropylcarbamothioate (3x)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 4H), 4.22 (s, 1H), 3.57 (s, 1H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 135.4, 133.7, 130.2 (q, J=32.4 Hz), 125.0 (q, J=3.8 Hz), 123.5 (q, J=270.6 Hz), 49.6, 47.3, 20.1; HRMS calcd for $C_{14}H_{18}F_3NOS$ $[M+H]^+$: 306.1134, found: 306.1151.

4.27. *S*-Naphthalen-2-yl diisopropylcarbamothioate (3y)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.93–7.88 (m, 3H), 7.66–7.63 (dd, J=8.8, 2.0 Hz, 1H), 7.58–7.52 (m, 2H), 4.31 (s, 1H), 3.58 (s, 1H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 134.9, 133.1, 132.8, 132.2, 127.9, 127.5, 127.2, 126.4, 126.2, 125.7, 49.4, 47.1, 20.2; HRMS calcd for $C_{17}H_{21}NOS$ $[M+H]^+$: 288.1417, found: 288.1434.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.10.030.

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