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Base-Controlled Three Component Reactions of Amines, Elemental Sulfur, and Styrenes: Synthesis of Thioamides under Metal-Free Conditions

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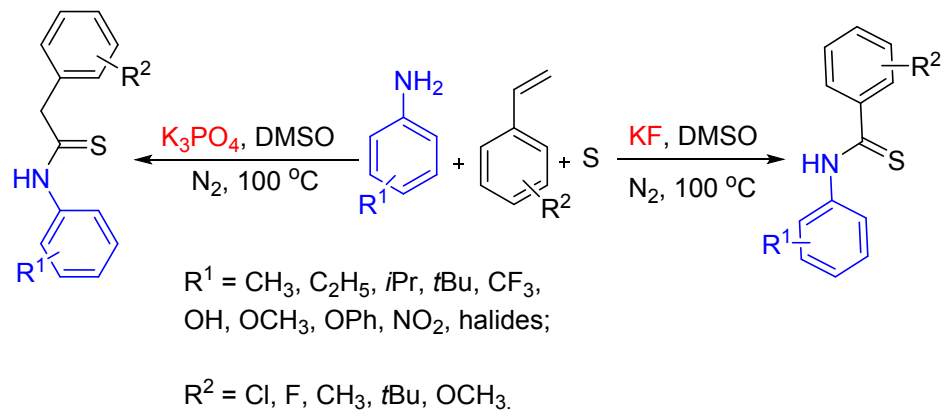


ABSTRACT: Three component reactions of olefins, amines, and sulfur were studied. Thioamidation of styrenes is base-controlled, and 2-phenylethanethioamides and benzothioamides were obtained selectively in the presence of two different bases. This protocol offers a simple and efficient procedure for the synthesis of thioamides.

Introduction

Thioamides constitute an important class of biologically active and pharmaceutical compounds.[1] Thioamides also serve as valuable synthons[2] for the synthesis of various sulfur- and nitrogen-containing heterocyclic compounds such as thioazoles,[3] thioazoline,[4] and thiophens.[5] Thioamides are small and can conceivably be scanned through a protein backbone with minimal perturbation to native structure, and thus was used to design "turn-on" fluorescent protease substrates.[6] Fluorenscence sensors based on thioamides have also been reported for the detection of inorganic ions.[7] Thioamides are typically prepared via three routes (1) reaction of amides with P_2S_5 or related Lawesson's reagent;[8] (2) Friedel–Crafts thioacylation of arenes with isothiocyanates;[9] (3) Willgerodt-Kindler reaction of aryl alkyl

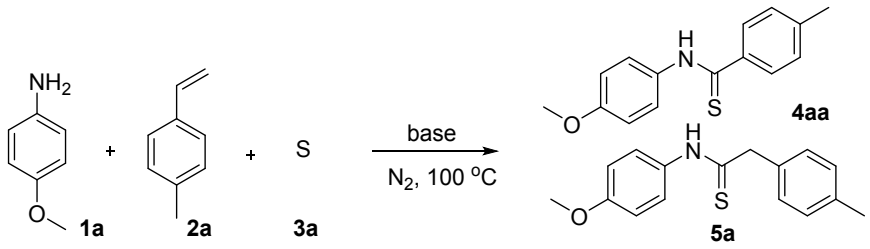
ketones, elemental sulfur, and secondary amines.[10] Other methods to prepare thioamides were also developed in recent years. Examples include three-component reactions of alkyl and aryl aldehydes, sodium sulfide, and *N*-substituted formamides,[11] and aerobic oxidative coupling of thiols and amines.[12] Taking account of environment benign, stable and nontoxic elemental sulfur is the best choice of sulfurating reagent. It has been reported that three-component reaction involving elemental sulfur and two different aliphatic amines has been successfully used for the synthesis of thioamides at 130 ^{o}C.[13] Three-component reaction between alkynes, elemental sulfur, and alkylamines could also gave thioamides, which is the atom-, step-, and redox-economical reaction.[14] It has been briefly reported that Willgerodt-Kindler reaction of styrene with morpholine afforded 2-phenylethanethioamide in moderate yields at 160- 175 ^{o}C[15a,b] or under microwave condition.[15c,d] In addition, thioamides could be easily transformed into benzothiazoles using stoichiometric amount of oxidants or under catalytic conditions.[16] We found that bases could significantly improve the efficiency and selectivity. In this paper we report the three component reactions of anilines, olefins, and sulfur, which were controlled by the bases. Two kinds of thioamides were selectively obtained in high yields through the choice of bases.

Results and discussion

Initially we investigated the reaction of 4-methoxyaniline **1a**, 4-methylstyrene **2a**, and elemental sulfur **3a** in the presence of a base to optimize the reaction conditions, and the results were listed in Table 1. Compound **1a** reacted readily and cleanly with **2a** and 6 equiv. of sulfur

to afford the unexpected product *N*-(4-methoxyphenyl)-4-methylbenzothioamide **4aa** in an almost quantitative yield at 100 °C in the presence of 3 equiv. of KF (Table 1, entry 1). When the amount of KF was decreased to 2 equiv., the yield of **4aa** was not affected (Table 1, entry 2). When the **1a:2a:3a** ratio was lowered to 1: 1.5: 3 from 1:2:6, the yield of **4aa** was reduced to 75% (Table 1, entry 3). Thus we decided to perform further studies at the **1a:2a:3a** ratio of 1:2:4, and in such case **4aa** was obtained in 95% yield (Table 1, entry 4). When KF was replaced by KOAc, the three-component reaction gave a low conversion, and **4aa** was obtained in only 45% yield. The use of K_2CO_3 as the base resulted in a mixture of **4aa** and **5a** (Table 1, entries 5 and 6). In the case of the strong base *t*-BuOK, only trace amount of **5a** was obtained (Table 1, entries 7). Organic bases such as Et_3N and pyridine did not improve the reaction efficiency (Table 1, entries 8 and 9). Without a base, we obtained a mixture of **4aa** and **5a** in 10% and 48% yields, respectively (Table 1, entry 10). Surprisingly, *N*-(4-methoxyphenyl)-2-(*p*-tolyl)ethanethioamide **5a** was the only product in the presence of 2 equiv. of K_3PO_4. In ethanol and acetone, compound **5a** was obtained in low yields. probably the cleavage of double bond was inhibited by ethanol and acetone (Table 1, entries 12-15). Further screening of solvents showed that DMSO was the optimal solvent. Finally, under an atmosphere of air or O_2 the reactions gave complex mixtues, and both the yields of **4aa** and **5a** were significantly lowered (Table 1, entries 20 and 22). Probably the oxidation of styrene, aniline and sulfur would be harmful to the reaction at 100°C under an atmosphere of O_2.

Table 1. Optimization of thioamidation of olefins[a]



Entry	**1a**: **2a**: **3a**	base (equiv.)	solvent	yields of **4aa**/**5a** (%)
1	1: 2: 6	KF (3)	DMSO	96/-
2	1: 2: 6	KF (2)	DMSO	96/-
3	1: 1.5: 3	KF (2)	DMSO	75/-
4	1: 2: 4	KF (2)	DMSO	95/-
5	1: 2: 4	KOAc (2)	DMSO	45/-
6	1: 2: 4	K_2CO_3 (2)	DMSO	<5/16
7	1: 2: 4	*t*-BuOK (2)	DMSO	-/<5
8	1: 2: 4	Et_3N (2)	DMSO	52/-
9	1: 2: 4	Pyridine (2)	DMSO	-/39
10	1: 2: 4	-	DMSO	10/48
11	1: 2: 4	K_3PO_4 (2)	DMSO	-/79
12	1: 2: 4	KF (2)	acetone	<5/21
13	1: 2: 4	KF (2)	H_2O	-/-
14	1: 2: 4	K_3PO_4 (2)	ethanol	-/56
15	1: 2: 4	KF (2)	ethanol	-/45
16[b]	1: 2: 4	KF (2)	DMSO	85/-
17[c]	1: 2: 4	KF (2)	DMSO	10/16
18[b]	1: 2: 4	K_3PO_4 (2)	DMSO	-/39
19[d]	1: 2: 4	KF (2)	DMSO	28/-
20[e]	1: 2: 4	KF (2)	DMSO	<5/-
21[d]	1: 2: 4	K_3PO_4 (2)	DMSO	-/31
22[e]	1: 2: 4	K_3PO_4 (2)	DMSO	-/<5

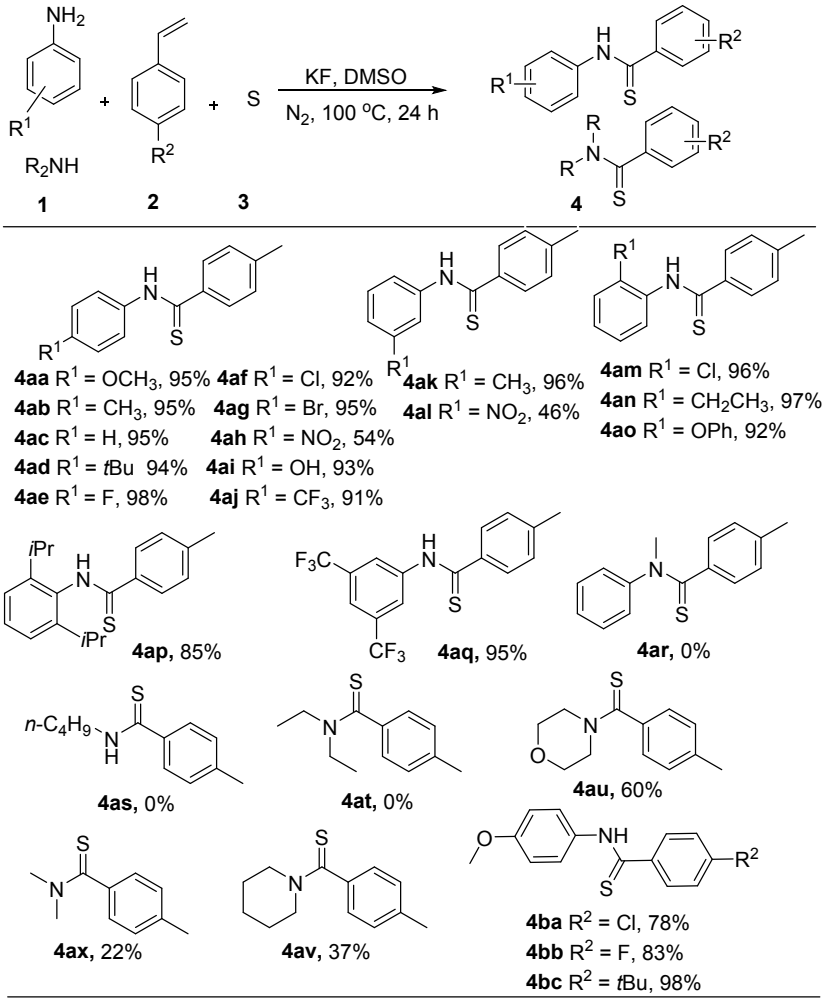
[a] Reaction conditions: amine **1a** , alkene **2a**, S_8, and base in solvent (1.5 mL) at 100 °C under N_2 for 24 h. [b] 80 °C. [c] 60 °C. [d] air. [e] O_2.

To examine the scope of the three-component reaction for the preparation of benzothioamides **4**, different amines and olefins were subjected to the reaction under the optimized conditions, and the results were summarized in Table 2. Both primary and

secondary amines with styrenes were proven to be appropriate substrates, and afforded corresponding thioamides in good to excellent yields. para-Substitutents of anilines such as alkyl, methoxy, hydroxyl, trifluoromethyl, and halogens were shown to be highly compatible with the reaction conditions, and the corresponding thioamides **4aa-4aj** were isolated in more than 90% yields. Anilines bearing alkyl, alkoxyl, and chloro groups at *meta* and *ortho* positions also gave thioamides **4ak-4ao** in excellent yields. The reaction was not much sterically sensitive as indicated by the isolation of ortho chloro-, ethyl-, and phenoxy-substituted thioamides **4am-4ao** in more than 90% yields. Even the sterically bulky 2,6-diisopropylaniline could be transformed to **4ap** in 85% yield. However, 4- and 3-nitroaniline gave quite low yields of thioamides **4ah** and **4al**. It seems that the low yields are not resulted from electronic deficiency, since anilines bearing one or two CF_3 also gave high yields of **4aj** and **4aq**. The low yields is probably due to the partial oxidation of olefin and aniline by the nitro group. Under the same conditions, *N*-methylaniline did not afford the required product. Aliphatic amines showed much lower reactivities than aromatic amines. Reaction of *n*-butylamine with 4-methylstyrene did not afford the expected *N*-butyl-4- methylbenzothioamide **4as**, instead, *N*-butyl-2-(*p*-tolyl)ethanethioamide **5j** was obtained in 64% yield. Secondary acyclic amine Et_2NH and 8-aminoquinoline were totally inactive, and the starting materials could be recovered. Reaction of benzylamine and *p*-phenylenediamine gave complicated mixtures. However, the reaction of morpholine and 4-methylstyrene could afford **4au** in moderate yield, whereas piperidine gave a mixture of **4av** and **5m** in 37 and 59% yields, respectively. Substituted styrenes containing a chloro, fluoro, and *t*Bu could also react smoothly with 4-

methoxyaniline giving the corresponding products **4ba**, **4bb**, and **4bc** in high yields. Unfortunately, aliphatic olefins such as oct-1-ene, cyclohexene, allylbenzene, and norbornene are not compatible under the optimized conditions. We also failed to observe the formation of thioamides in the reactions of DMF and styrene in DMSO, although amides are known to be an efficient partner for the synthesis of thioamides.[14c,17] However, we obtained a mixture of **4ax** and **5p** in 22% and 50% yields, respectively, when the reaction was performed in DMF.

Table 2. Synthesis of thioamides **4**

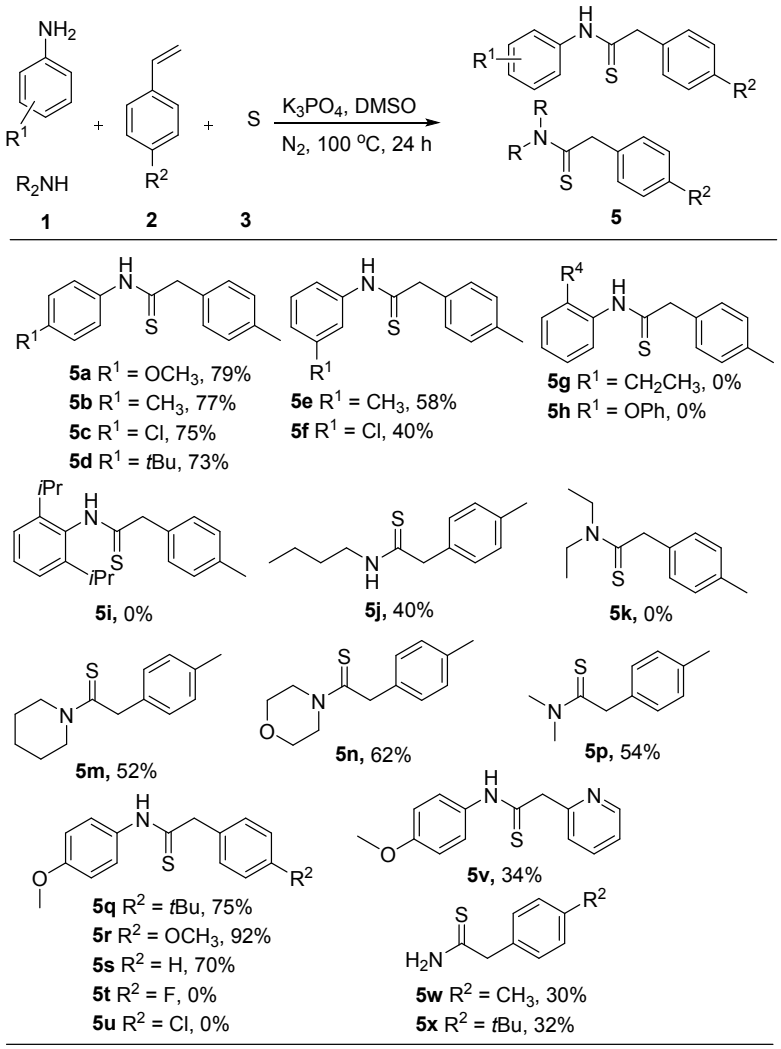


Reaction conditions: amine **1** (0.3 mmol), alkene **2** (0.6 mmol), S_8 (1.2 mmol), and KF (0.6 mmol) in DMSO (1.5 mL) at 100 °C under N_2 for 24 h.

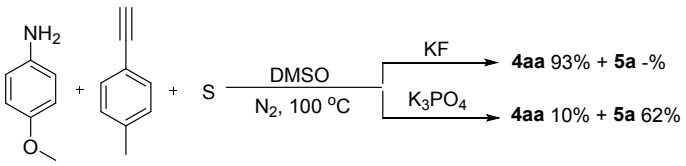
We also evaluated the substrate scope of the three component reaction for the synthesis of thioamides **5**. As shown in Table 3, when K_3PO_4 was used as the base at 100 °C, substituted anilines bearing a methyl, methoxyl, chloro, and *t*Bu could be transformed into their corresponding thioamides **5a-5d** in good yields. *meta*-Substituted anilines having a methyl and chloro also reacted with 4-methylstyrene to give **5e** and **5f** in moderate yields. Unlike KF, K_3PO_4-mediated thioamidation reaction is quite sterically sensitive, both 2-ethylaniline and 2-phenoxylaniline were not reactive, and the expected thioamides **5g** and **5h** were not detected. More steric 2,6- diisopropylaniline was also inactive. Similar to KF-mediated reaction, the reaction of *n*-butylamine with 4-methylstyrene and sulfur resulted in a low yield of **5j**, whereas the corresponding reaction of diethylamine did not occur. Interestingly, cyclic secondary amines showed their activities. In the case of piperidine a mixture of **4av** and **5m** were isolated in 14% and 52% yields, respectively. However, the reaction of morpholine, 4-methylstyrene, and sulfur afforded **5n** as the only product in 62% yield. Similar to KF-mediated reaction, two *N,N*-dimethyl thioamides **4ax** and **5p** were obtained in 12% and 54% yields, respectively, when DMF was used as the solvent. Styrene and substituted styrenes having a methoxy and tertiary butyl also reacted with 4-methoxyaniline to give corresponding thioamides in good yields. However, styrenes having a para fluoro and chloro substituents did not afford corresponding thioamides. The reason is not clearly understood at present. In

addition, 2-vinylpyridine also reacted with 4-methoxyaniline to afford **5v** in poor yield. In contrast, the same reaction of 2-vinylpyridine did not occur in the presence of KF. Again, aliphatic olefins such as oct-1-ene, cyclohexene, allylbenzene, and norbornene showed no activities under the present conditions. We were able to obtain unsubstituted thioamides **5w** and **5x** in 30% and 32% yields, when NH_4HCO_3 was employed as the NH_3 source for convenience.

Table 3. Synthesis of thioamides **5**

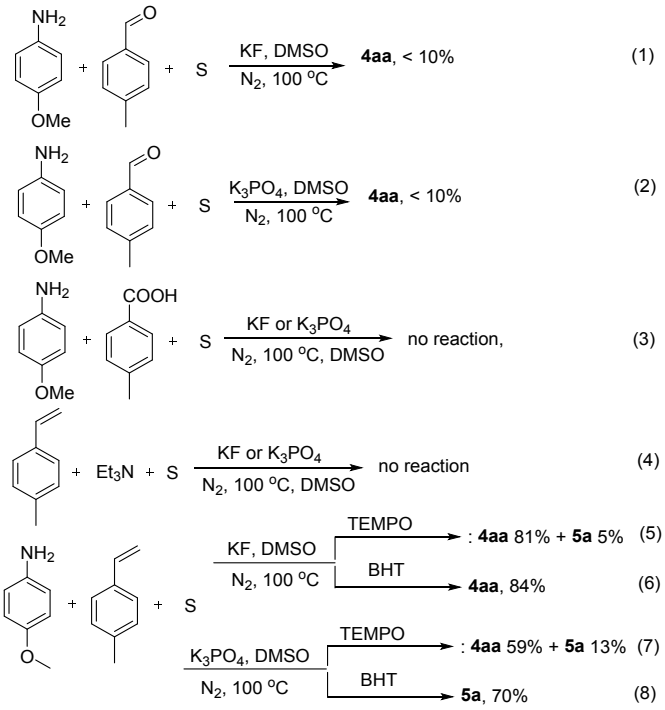


Reaction conditions: amine **1** (0.3 mmol), alkene **2** (0.6 mmol), S_8 (1.2 mmol), and K_3PO_4 (0.6 mmol) in DMSO (1.5 mL) at 100 °C under N_2 for 24 h.



Scheme 1. Thioamidation of 4-tolylacetylene

Alkyne could also be transformed to the corresponding thioamides, examples are shown in Scheme 1. Under the optimized conditions, **4aa** and **5a** were afforded in 93 % and 62% yields, respectively.

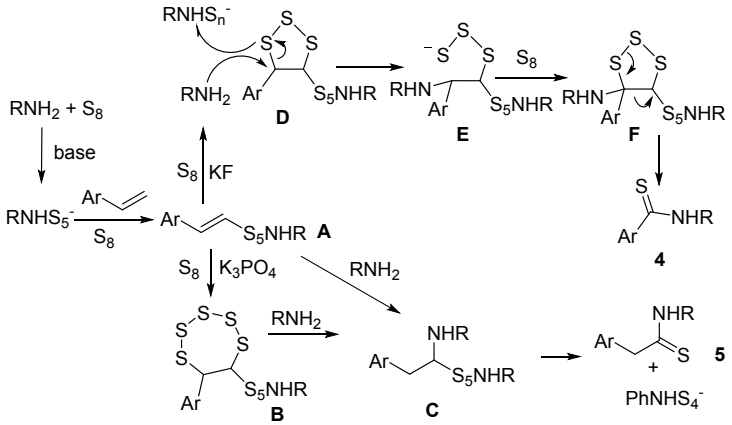


Scheme 2. Control experiments

To gain an insight on the possible mechanism of the thioamidation of olefins, a few control experiments were performed. Reactions of 4-methoxyaniline, 4-methylbenzaldehyde, and sulfur were performed using either KF or K_3PO_4 as the bases, and the results showed that **4aa**

was obtained in less than 10% yields (Scheme 2, Eqs. 1 and 2). When 4-methylbenzaldehyde was replaced by 4-methylbenzoic acid, no thioamide was observed (Eq. 3). These experiments illustrated that the thioamidation of olefins might not proceed via benzaldehyde[18] or benzoic acid from oxidation of styrene. In addition, in the reaction of 4-methylstyrene, Et_3N, and sulfur at 100 °C, 4-methylstyrene was not consumed (Eq. 4). In the presence of 2 equiv. of BHT, KF-mediated reaction of 4-methoxyaniline, 4-methylstyrene, and sulfur afforded **4aa** in 84 % yield, whereas the same reaction gave **5a** in 70% yields in the presence of K_3PO_4. For comparison, addition of 2 equiv. of TEMPO to the three-component reactions afforded mixtures **4aa** and **5a** in 81%/5% and 59%/13% yields, respectively, when KF and K_3PO_4 were used as the bases (Eqs 5-8). Obviously, the thioamidation reaction was not inhibited by the radical scavenger. ESI-MS analysis of the yellow reaction mixture resulted from 4-methoxyaniline and sulfur showed that several polysulfides were formed (Figure S1). Heating the mixture of 4-methoxyaniline, sulfur, KF or K_3PO_4 in DMSO at 100 °C for 5-20 minutes gave a red solution. Direct ESI-MS analysis of the filtrate showed a peak at *ca*. 320 due to 4-$MeOPhNHS_5K$, which was not observed in the absence of bases (Figures S2 andS4). The results illustrated that 4-$MeOPhNHS_5$- was selectively formed. The red mixture was added an excess of 4-methylstyrene, and heated at 100 °C for another 15 minutes. ESI-MS spectrua of the deep red filtrates showed peaks at ca. 523, 581, and 615 assigned to the intermediates **C**+H^+ **B**+Na^+, and **E**+H^+, respectively (Figures S3, S5 and Scheme 3). Thus based on the literature reports[14a,19] and the experimental results, a plausible reaction mechanism was proposed. As shown in Scheme 3, the reaction is probably initiated by the formation of $RNHS_5K$ from amine and

sulfur.[20] Subsequent oxidative coupling with styrene affords **A**. Nucleophilic addition of sulfur generates polysulfides **B** and **D** in the presence of K_3PO_4 and KF respectively. Nucleophilic attack of **D** by a molecule of aniline under assistance of $RNHS_4^-$ form **E**. Oxidative C-S coupling and further decomposition of **F** results in ring-opening and subsequent C-C cleavage, and finally give **4**. Nucleophilic addition of aniline towards **A** generates **C**. Elimination of a molecule of $RNHS_4^-$ yields **5**. Reaction of 4-methoxyaniline, sulfur, and KF in EtOH or acetone at 100 °C for 20 minutes gave a light yellow solution and a light brown solution, respectively. The mixture was added an excess of 4-methylstyrene, and heated at 100 °C for another 15 minutes. ESI-MS spectra of the filtrates showed that the intermediates were similar to when K_3PO_4 was acted as base in DMSO (Figures S6 and S7). However, we have not been able to understand the role of bases.



Scheme 3. Plausible mechanism

CONCLUSION

In conclusion, we have described the three component reactions of olefins, amines, and sulfur, which selectively afforded two kinds of thioamides through the choice of bases. The

starting materials are easily available and cheap, and the reactions were carried out under catalyst-free conditions. It offers an efficient synthetic protocol for thioamides. At present, we have not been able to understand how the bases control the chemoselectivity of thioamides. Further work is required to clarify the detailed mechanism.

EXPERIMENTAL SECTION

All chemicals were of reagent grade quality obtained from commercial sources and used as received.

General Procedure for Synthesis of 4. A 25 mL of Schlenk tube was charged with 4-methoxyaniline **1a** (0.3 mmol), 4-methylstyrene **2a** (0.6 mmol), S_8 (1.2 mmol), KF (0.6 mmol) and DMSO (1.5 mL). The mixture was allowed to stir at 100 °C under N_2 for 24 h, then the mixture was cooled to room temperature. Water (15 mL) was added, and the mixture was extracted with ethyl acetate (15 mL x 3). The organic phase was collected, washed with brine, and dried over Na_2SO_4, then filtered and concentrated. The crude residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (PE: EA = 50:1-3:1) as eluent to afford the desired product **4**.

General Procedure for Synthesis of 5. A 25 mL of Schlenk tube was charged with 4-methoxyaniline **1a** (0.3 mmol), 4-methylstyrene **2a** (0.6 mmol), S_8 (1.2 mmol), K_3PO_4 (0.6 mmol) and DMSO (1.5 mL). The resulting suspension was allowed to stir at 100 °C under N_2 for 24 h. The mixture was then cooled to room temperature. Water (15 mL) was added, and it was extracted with ethyl acetate (15 mL x 3). The organic phase was collected and washed

with brine, dried over Na_2SO_4, then filtered and concentrated. The crude residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (PE: EA = 50:1-3:1) as eluent to afford the desired product **5**.

***N*-(4-methoxyphenyl)-4-methylbenzothioamide (4aa)**

Light yellow solid. Mp: 144-145 °C. Yield: 73.3 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 2.83 (s, 3H), 6.95 (d, *J* = 9.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 8.95 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.23, 158.20, 141.90, 140.06, 132.12, 129.26, 126.75, 125.77, 114.18, 55.51, 21.42. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{15}H_{15}NOS^+$ 257.0874; Found 257.0874.

4-methyl-*N*-(*p*-tolyl)benzothioamide (4ab)

Light yellow solid. Mp: 133-134 °C. Yield: 68.7 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.39 (s, 3H), 7.20-7.23 (m, 4H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.75 d, *J* = 7.6 Hz, 2H), 8.98 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.19, 141.88, 140.22, 136.93, 136.61, 129.61, 129.24, 126.77, 124.00, 21.42, 21.21. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{15}H_{15}NS^+$ 241.0925; found 241.0928.

4-methyl-*N*-phenylbenzothioamide (4ac)

Light yellow solid. Mp: 128-130 °C. Yield: 64.7 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.19 (d, *J* = 6.8 Hz, 2H), 7.26-7.28 (m, 1H), 7.38-7.45 (m, 2H), 7.62-7.81 (m, 4H), 9.05 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.30, 141.95, 140.28, 139.13, 129.25, 129.03, 126.91,

126.81, 123.89, 21.44. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{13}NS^+$ 227.0769; found 227.0772.

***N*-(4-(*tert*-butyl)phenyl)-4-methylbenzothioamide (4ad)**

Light yellow solid. Mp: 117-119 °C. Yield: 79.8 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 9H), 2.32 (s, 3H), 7.15 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H), 8.90 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.83, 149.98, 141.87, 140.44, 136.54, 129.27, 126.73, 125.93, 123.30, 34.71, 31.33, 21.42. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{18}H_{21}NS^+$ 283.1395; found 283.1393.

***N*-(4-fluorophenyl)-4-methylbenzothioamide (4ae)**

Light yellow solid. Mp: 106-108 °C. Yield: 72.1 mg, 98%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39, 2.40 (both, s, 3H), 7.08-7.12 (m, 2H), 7.21 (d, J = 7.6 Hz, 1H), 7.29-7.31 (m, 1H), 7.58-7.67 (m, 3H), 7.73 (d, J = 8.0 Hz, 1H), 9.05 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.18, 198.76, 160.84 (d, J_{C-F} = 245.5 Hz, C), 142.69, 142.17, 139.78, 138.61, 135.01, 132.25, 129.28, 128.55, 127.69, 126.80, 126.26, 126.13 (d, J_{C-F} = 7.5 Hz, C), 123.62, 115.87 (d, J_{C-F} = 22.8 Hz, C), 21.44, 21.40. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}FNS^+$ 245.0674; found 245.0676.

***N*-(4-chlorophenyl)-4-methylbenzothioamide (4af)**

Light yellow solid. Mp: 155-156 °C. Yield: 72.1 mg, 92%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.37 (s, 3H), 7.28 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 11.72 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.60, 141.05, 139.60, 138.95,

129.89, 128.51, 128.38, 127.54, 125.92, 20.88. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}ClNS^+$ 261.0379; found 261.0376.

***N*-(4-bromophenyl)-4-methylbenzothioamide (4ag)**

Light yellow solid. Mp: 191-193 °C. Yield: 86.9 mg, 95%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.37 (s, 3H), 7.28 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 11.71 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.57, 141.07, 139.61, 139.36, 131.32, 128.52, 127.54, 126.22, 118.20, 20.88. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}BrNS^+$ 304.9874; found 304.9871.

4-methyl-*N*-(4-nitrophenyl)benzothioamide (4ah)

Light yellow solid. Mp: 210-211 °C. Yield: 44.1 mg, 54%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.38 (s, 3H), 7.31 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H), 8.31 (d, J = 9.2 Hz, 2H), 12.06 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.89, 145.87, 144.04, 141.53, 139.80, 128.61, 127.68, 124.22, 123.81, 20.92. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}N_2O_2S^+$ 272.0619; found 272.0620.

***N*-(4-hydroxyphenyl)-4-methylbenzothioamide (4ai)**

Orange yellow solid. Mp: 138-139 °C. Yield: 67.8 mg, 93%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.36 (s, 3H), 6.80 (d, J = 8.8 Hz, 2H), 7.26 d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 9.58 (br, 1H), 11.46 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.16, 155.51,

140.56, 139.66, 131.64, 128.41, 127.44, 125.82, 114.78, 20.85. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{13}NOS^+$ 243.0718; found 243.0720.

4-methyl-*N*-(4-(trifluoromethyl)phenyl)benzothioamide (4aj)

Light yellow solid. Mp: 178-180 °C. Yield: 80.6 mg, 91%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.38 (s, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.78-7.82 (m, 4H), 8.10 (d, J = 7.2 Hz, 2H), 11.91 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.37, 143.55, 141.27, 139.66, 128.56, 127.62, 125.94 (q, J_{C-F} = 31.6 Hz, C), 125.63 (q, J_{C-F} = 3.6 Hz, C), 124.11 (q, J_{C-F} = 270.3 Hz, C), 124.34, 20.89. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{15}H_{12}F_3NS^+$ 295.0643; found 295.0645.

4-methyl-*N*-(*m*-tolyl)benzothioamide (4ak)

Light yellow solid. Mp: 100-101 °C. Yield: 69.4 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_{3)}$: δ 2.31 (s, 6H), 7.02 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 6.8 Hz, 2H), 7.21-7.25 (m, 1H), 7.39-7.54 (m, 2H), 7.67 (d, J = 7.2 Hz, 2H), 8.91 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.19, 141.90, 140.37, 139.06, 129.25, 128.85, 127.77, 126.76, 124.40, 121.01， 21.46, 21.43. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{15}H_{15}NS^+$ 241.0925; found 241.0927.

4-methyl-*N*-(3-nitrophenyl)benzothioamide (4al)

Light yellow solid. Mp: 86-88 °C. Yield: 37.5 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.25 (d, J = 9.2 Hz, 2H), 7.60 (t, J = 8.4 Hz, 1H), 7.76 (d, J = 7.6 Hz, 2H), 8.12-8.17 (m, 2H), 8.65 (s, 1H), 9.15 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.34, 148.44, 142.68, 140.06,

129.76, 129.60, 129.45, 126.80, 121.31, 118.73, 21.47. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}N_2O_2S^+$ 272.0619; found 272.0622.

_N_-(2-chlorophenyl)-4-methylbenzothioamide (4am)

Light yellow solid. Mp: 98-99 °C. Yield: 75.2 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.21-7.25 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 8.69 (br, 1H), 9.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.04, 142.25, 135.86, 129.56, 129.40, 127.40, 127.20, 126.93, 126.90, 125.07, 21.45. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}ClNS^+$ 261.0379; found 261.0378.

_N_-(2-ethylphenyl)-4-methylbenzothioamide (4an)

Light yellow solid. Mp: 73-74 °C. Yield: 74.2 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.6 Hz, 3H), 2.42 (s, 3H), 2.66 (q, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.30-7.35 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 8.88 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.72, 142.09, 139.91, 139.28, 137.19, 129.30, 129.12, 128.37, 127.46, 126.87, 126.71, 24.52, 21.47, 14.38. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{16}H_{17}NS^+$ 255.1082; found 255.1084.

4-methyl-_N_-(2-phenoxyphenyl)benzothioamide (4ao)

Orange yellow oil. Yield: 88.1 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.94-6.97 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.16-7.21 (m, 5H), 7.36-7.40 (m, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 9.12 (br, 1H), 9.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.88, 156.13, 148.13, 141.82,

130.74, 130.13, 129.28, 126.77, 124.29, 123.35, 123.04, 118.86, 118.00, 21.41. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{20}H_{17}NOS^+$ 319.1031; found 319.1035.

***N*-(2,6-diisopropylphenyl)-4-methylbenzothioamide (4ap)**

Light yellow solid. Mp: 144-145 °C. Yield: 79.3 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (d, J = 6.8 Hz, 6H), 1.29 (d, J = 6.8 Hz, 6H), 2.44 (s, 3H), 3.05-3.12 (m, 2H), 7.27 (s, 2H), 7.29 (s, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 8.62 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.60, 145.92, 142.12, 138.84, 134.03, 129.37, 129.30, 126.76, 123.98, 28.91, 24.57, 23.30, 21.46. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{20}H_{25}NS^+$ 311.1708; found 311.1704.

***N*-(3,5-bis(trifluoromethyl)phenyl)-4-methylbenzothioamide (4aq)**

Light yellow solid. Mp: 92-93 °C. Yield: 103.5 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.24 (d, J = 8.0 Hz, 2H), 7.73-7.76 (m, 3H), 8.30 (s, 2H), 9.16 (br, 1H),. ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.52, 142.88, 140.29, 139.38, 132.22 (q, J_{C-F} = 33.5 Hz, C), 129.40, 126.81, 123.75, 123.72, 122.94 (q, J_{C-F} = 271.4 Hz, C), 119.85-119.99 (m, C), 118.88, 21.39. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{16}H_{11}F_6NS^+$ 363.0516; found 363.0513.

morpholino(*p*-tolyl)methanethione (4au)

Light yellow solid. Mp: 115-116 °C. Yield: 39.8 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 3.62 (s, 4H), 3.87 (t, J = 4.8 Hz, 2H), 4.42 (t, J = 4.8 Hz, 2H), 7.14-7.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.39, 139.69, 139.11, 129.12, 126.06, 66.78, 66.55, 52.59, 49.70, 21.28. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{12}H_{15}NOS^+$ 221.0874; found 221.0875.

piperidin-1-yl(*p*-tolyl)methanethione (4av)

Light yellow solid. Mp: 65-67 °C. Yield: 24.3 mg, 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54-1.59 (m, 2H), 1.71-1.77 (m, 2H), 1.79-1.84 (m, 2H), 2.35 (s, 3H), 3.54 (t, *J* = 5.6 Hz, 2H), 4.35 (t, *J* = 5.2 Hz, 2H), 7.13-7.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.98, 140.63, 138.47, 128.98, 125.58, 53.21, 50.76, 26.91, 25.52, 24.21, 21.25. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{13}H_{17}NS^+$ 219.1082; found 219.1085.

***N*,*N*,4-trimethylbenzothioamide (4ax)**

Light yellow oil. Yield: 11.8 mg, 22%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.17, 3.18 (both, s, 3H), 3.60, 3.60 (both, s, 3H), 7.06-7.14 (m, 2H), 7.16-7.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.60, 143.38, 140.59, 138.73, 138.20, 129.33, 128.90, 128.22, 126.39, 125.91, 122.62, 44.21, 44.15, 43.36, 43.19, 29.71, 21.40, 21.27. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{10}H_{13}NS^+$ 179.0769; found 179.0770.

4-chloro-*N*-(4-methoxyphenyl)benzothioamide (4ba)

Light yellow solid. Mp: 160-162 °C. Yield: 64.8 mg, 78%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.79 (s, 3H), 7.00 (d, *J* = 9.2 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 11.72 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.11, 157.32, 141.07, 135.36, 132.87, 129.23, 127.95, 125.60, 113.58, 55.27. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}ClNOS^+$ 277.0328; found 277.0327.

4-fluoro-*N*-(4-methoxyphenyl)benzothioamide (4bb)

Light yellow solid. Mp: 140-141 °C. Yield: 65.0 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.94 (d, J = 8.8 Hz, 2H), 7.09 (t, J = 8.4 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.83-7.87 (m, 2H), 8.94 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.96, 164.60 (d, J_{C-F} = 251.1 Hz, C), 158.34, 138.97, 131.93, 129.00 (d, J_{C-F} = 8.8 Hz, C), 125.75, 115.56 (d, J_{C-F} = 21.8 Hz, C), 114.23, 55.52. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{12}FNOS^+$ 261.0624; found 261.0624.

4-(*tert*-butyl)-*N*-(4-methoxyphenyl)benzothioamide (4bc)

Light yellow solid. Mp: 147-149 °C. Yield: 87.9 mg, 98%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 9H), 3.82 (s, 3H), 6.93 (d, J = 9.2 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 9.00 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.13, 158.17, 154.91, 140.00, 132.15, 126.61, 125.71, 125.57, 114.16, 55.52, 34.94, 31.18. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{18}H_{21}NOS^+$ 299.1344; found 299.1346.

***N*-(4-methoxyphenyl)-2-(*p*-tolyl)ethanethioamide (5a)**

Light yellow solid. Mp: 132-133 °C. Yield: 64.3 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.78 (s, 3H), 4.22 (s, 2H), 6.86 (d, J = 9.2 Hz, 2H), 7.23 (s, 4H), 7.40 (d, J = 9.2 Hz, 2H), 8.45 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.59, 158.24, 137.91, 131.76, 131.49, 130.14, 129.62, 125.55, 114.01, 55.48, 54.07, 21.20. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{16}H_{17}NOS^+$ 271.1031; found 271.1032.

***N*,2-di-*p*-tolylethanethioamide (5b)**

Light yellow solid. Mp: 73-74 °C. Yield: 58.9 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.38 (s, 3H), 4.23 (s, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.23 (s, 4H), 7.40 (d, *J* = 8.4 Hz, 2H), 8.46 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.52, 137.92, 137.01, 135.99, 131.76, 130.15, 129.62, 129.45, 123.78, 54.34, 21.19, 21.15. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{16}H_{17}NS^+$ 255.1082; found 255.1084.

N-(4-chlorophenyl)-2-(*p*-tolyl)ethanethioamide (5c)

Light yellow solid. Mp: 84-86 °C. Yield: 61.9 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 4.23 (s, 2H), 7.23 (s, 4H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 8.41 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.89, 138.14, 136.95, 132.16, 131.43, 130.27, 129.61, 128.97, 124.92, 54.58, 21.20. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{15}H_{14}ClNS^+$ 275.0535; found 275.0537.

N-(4-(*tert*-butyl)phenyl)-2-(*p*-tolyl)ethanethioamide (5d)

Brown solid. Mp: 51-53 °C. Yield: 65.1 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9H), 2.36 (s, 3H), 4.23 (s, 2H), 7.22 (s, 4H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 8.46 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.13, 150.08, 137.93, 135.90, 131.73, 130.15, 129.62, 125.76, 123.19, 54.47, 34.64, 31.28, 21.19. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{19}H_{23}NS^+$ 297.1551; found 297.1552.

N-(*m*-tolyl)-2-(*p*-tolyl)ethanethioamide (5e)

Brown oil. Yield: 44.4 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.37 (s, 3H), 4.24 (s, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.21-7.23 (m, 5H), 7.32 (br, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 8.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.98, 138.43, 137.90, 137.49, 131.15, 129.70, 129.14, 128.21, 127.36, 123.69, 120.35, 54.05, 20.87, 20.69. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{16}H_{17}NS^+$ 255.1082; found 255.1082.

N-(3-chlorophenyl)-2-(*p*-tolyl)ethanethioamide (5f)

Brown oil. Yield: 33.0 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 4.23 (s, 2H), 7.13-7.15 (m, 1H), 7.19-7.21 (m, 1H), 7.23 (s, 2H), 7.25-7.27 (m, 1H), 7.29-7.34 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.64-7.66 (m, 1H), 8.42 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.03, 201.84, 139.50, 138.17, 134.42, 131.39, 130.39, 130.29, 129.84, 129.59, 129.46, 129.09, 127.00, 126.61, 123.59, 123.55, 121.73, 55.08, 54.71, 21.45, 21.20. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{15}H_{14}ClNS^+$ 275.0535; found 275.0537.

N-butyl-2-(*p*-tolyl)ethanethioamide (5j)

Brown oil. Yield: 42.5 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 2H), 1.22-1.31 (m, 2H), 1.47-1.54 (m, 2H), 2.36 (s, 3H), 3.58-3.63 (m, 2H), 4.10 (s, 2H), 6.98 (br, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.98, 137.70, 131.54, 129.98, 129.56, 52.77, 45.91, 29.82, 21.15, 20.04, 13.69. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{13}H_{19}NS^+$ 221.1238; found 221.1236.

1-(piperidin-1-yl)-2-(*p*-tolyl)ethane-1-thione (5m)

Brown yellow solid. Mp: 117-118 °C. Yield: 41.3 mg, 59%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28-1.34 (m, 2H), 1.59-1.69 (m, 4H), 2.32 (s, 3H), 3.58 (t, *J* = 5.6 Hz, 2H), 4.27 (t, *J* = 4.8 Hz, 2H), 4.30 (s, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.63, 136.43, 133.05, 129.45, 127.75, 51.64, 51.57, 50.61, 26.25, 25.27, 23.87, 21.08. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{19}NS^+$ 233.1238; found 233.1237.

1-morpholino-2-(*p*-tolyl)ethane-1-thione (5n)

Light yellow solid. Mp: 90-91 °C. Yield 43.7 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.38 (t, *J* = 4.8 Hz, 2H), 3.62 (t, *J* = 4.8 Hz, 2H), 3.73 (t, *J* = 5.2 Hz, 2H), 4.30 (s, 2H), 4.34 (t, *J* = 4.8 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.32, 136.75, 132.66, 129.63, 127.64, 66.35, 66.15, 50.77, 50.27, 50.18, 21.08. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{13}H_{17}NOS^+$ 235.1031; found 235.1031.

***N*,*N*-dimethyl-2-(*p*-tolyl)ethanethioamide (5p)**

Light yellow oil. Yield: 29.0 mg, 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33, 2.33 (both, s, 3H), 3.20 (s, 3H), 3.49, 3.50 (both, s, 3H), 4.27, 4.28 (both, s, 2H), 7.05-7.14 (m, 2H), 7.16-7.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.99, 200.76, 138.52, 136.58, 135.57, 132.59, 129.48, 128.72, 128.67, 128.01, 127.73, 125.15, 50.98, 50.58, 44.85, 42.32, 42.26, 21.45, 21.07. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{11}H_{15}NS^+$ 193.0925; found 193.0925.

2-(4-(*tert*-butyl)phenyl)-*N*-(4-methoxyphenyl)ethanethioamide (5q)

Brown oil. Yield: 70.5 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H), 3.78 (s, 3H), 4.23 (s, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.39-7.44 (m, 4H), 8.47 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.68, 158.28, 151.10, 131.76, 131.52, 129.41, 126.40, 125.69, 114.03, 55.49, 53.99, 34.64, 31.33. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{19}H_{23}NOS^+$ 313.1500; found 313.1504.

N,2-bis(4-methoxyphenyl)ethanethioamide (5r)

Light yellow solid. Mp: 122-124 °C. Yield: 79.2 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H), 3.82 (s, 3H), 4.19 (s, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 8.47 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.75, 159.37, 158.23, 131.49, 130.90, 126.76, 125.49, 114.81, 114.01, 55.48, 55.36, 53.63. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{16}H_{17}NO_2S^+$ 287.0980; found 287.0979.

N-(4-methoxyphenyl)-2-phenylethanethioamide (5s)

Orange solid. Mp: 66-68 °C. Yield: 54.0 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H), 4.26 (s, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 7.35-7.37 (m, 3H), 7.39-7.42 (m, 4H), 8.46 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.28, 158.27, 135.01, 131.47, 129.65, 129.44, 128.08, 125.57, 114.04, 55.49, 54.47. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{15}H_{15}NOS^+$ 257.0874; found 257.0872.

N-(4-methoxyphenyl)-2-(pyridin-2-yl)ethanethioamide (5v)

Light yellow solid. Mp: 114-115 °C. Yield: 26.3 mg, 34%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 4.36 (s, 2H), 6.90 (d, *J* = 9.2 Hz, 2H), 7.26-7.29 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.72 (dt, *J* = 2.0, 8.0 Hz, 1H), 8.58 (d, *J* = 4.4 Hz, 1H), 11.85 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.82, 157.83, 156.30, 148.66, 137.74, 132.25, 124.86, 124.17, 122.53, 113.91, 55.48, 54.12. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{14}H_{14}N_2OS^+$ 258.0827; found 258.0824.

2-(*p*-tolyl)ethanethioamide (5w)

Brown oil. Yield: 15.0 mg, 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35, 2.36 (both, s, 3H), 4.07, 4.07 (both, s, 2H), 6.73 (br, 1H), 7.05-7.08 (m, 1H), 7.14-7.20 (m, 2H), 7.25-7.29 (m, 1H), 7.80 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.84, 207.61, 139.18, 137.82, 134.74, 131.76, 130.18, 130.01, 129.37, 129.23, 128.75, 126.45, 52.05, 51.69, 21.37, 21.13. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_9H_{11}NS^+$ 165.0612; found 165.0614.

2-(4-(*tert*-butyl)phenyl)ethanethioamide (5x)

Light yellow solid. Mp: 74-75 °C. Yield: 20.0 mg, 32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 4.09 (s, 2H), 6.71 (br, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.72 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.80, 151.08, 131.72, 129.19, 126.82, 126.30, 125.48, 51.63, 31.30, 29.72. HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{12}H_{17}NS^+$ 207.1082; found 207.1082.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ^{1}H NMR and ^{13}C NMR spectra for new products (PDF).

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Notes

The authors declare no competing financial interest.

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