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ARTICLE TYPE

Catalyst-Free Direct Decarboxylative Coupling of α-Keto Acids with Thiols: A Facile Access to Thioesters †

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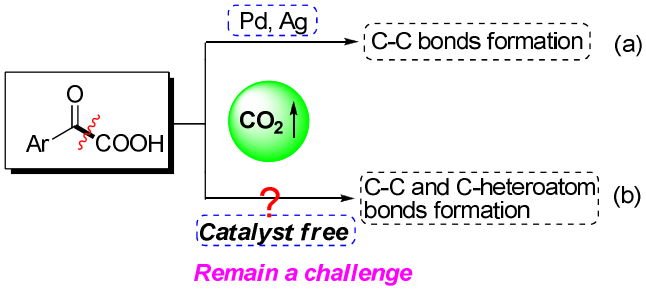
A novel, efficient, and catalyst-free strategy has been initially developed for the construction of thioesters via the direct radical oxidative decarboxylation of α-keto acids with thiols, and the corresponding target products were obtained in moderate to good yields. It offers an alternative approach for the synthesis of useful diverse thioesters.

Introduction

The C-S bond formation is of fundamental and immense importance in organic chemistry because sulfur-containing motifs are wide occurrence in natural products, biologically active molecules, and materials.[1] As a consequence, seeking mild and selective approaches for the construction of C-S bonds is still a high ongoing interest. Moreover, thiolesters as the activated carboxylic acid derivatives have attracted significant attention due to their important applications as versatile building blocks in synthetic chemistry. For example, they have been widely used as intermediates in the synthesis of esters,[2] β-lactones,[3] peptides,[4] β-lactams,[5] and ketones.[6] In addition, thiolesters popularly prevail in biochemical pathways.[7] However, extensive literature survey indicates that the traditional synthetic methods for the construction of thiolester motifs are rather limited, mainly focusing on the condensation of acyl chlorides with thiophenols.[8] Some typical drawbacks usually include the moisture-sensitive characters of acyl chlorides and the transformation producing non-environmentally friendly halide anions. These factors motivate chemists to develop more efficient, practical and green methods.

In 1976, Takagi and co-workers initially reported a photo-induced reductive acylation of disulfides with aldehydes to afford thioesters.[9] Since then, the direct oxidative cross-coupling of aldehydes with thiophenols or disulfides has been extensively studied. There is no doubt that this is an atom-economic strategy for the synthesis of thioesters. In 2005, Kita et al. developed an elegant thioesterification protocol to afford thioesters through coupling of various aromatic aldehydes and disulfides in the presence of 1 equiv of azo-type initiator.[10] In 2007, Bandgar and co-workers reported Dess-Martin periodinane mediated method for the synthesis of thioesters in the presence of 6.5 equiv of NaN_3.[11] More recently, significant progress has been made in the oxidative direct transformation. In 2013, Zhu and co-workers reported a practical method for the synthesis of thioesters by TEAB-catalyzed oxidative coupling of aldehydes with thiols or disulfides.[12] In 2014, Lee et al. described iron-catalyzed coupling reaction of thiols with aldehydes to give thioesters.[13] Subseqently, Lee's group reported an elegant procedure for the synthesis of thioesters through DTBP mediated reaction of aldehydes with disulfides.[14] Despite these methods have made various successes, the unavailable initiators, high temperature, the long reaction time, and the liquid oxidants involved in these transformations might limit their wide applications. Therefore, it is desirable to discover new methods that use new reagents and go through a new mechanism to produce thioesters.



Scheme 1 Strategies for the formation of C-C and C-heteroatom bonds via decarboxylation of α-keto acids

In recent years, decarboxylative cross-coupling reactions have emerged as an attractive method in synthetic chemistry due to carboxylic acids are more readily available and easy to handle and store. More importantly, the only by-product from the transformation is low-toxic CO_2. Though numerous fascinating works about transition-metal-catalyzed decarboxylative reactions have been successfully achieved by Gooßen,[15] Myers,[16] and other groups,[17] using α-keto acids as coupling partners in decarboxylative coupling reactions has received less attention.[18] Recently, several research groups have developed the Pd- or Ag-catalyzed methods for the formation of C-C bonds through

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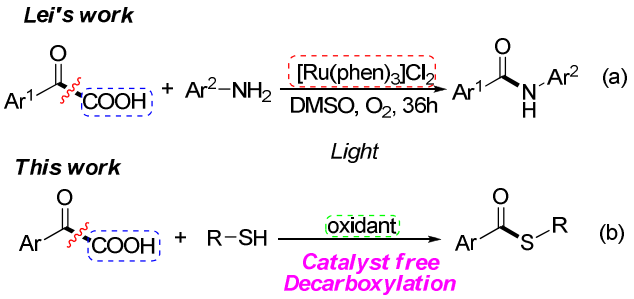
decarboxylative reaction of α-keto acids. (Scheme 1, a).[19] In 2014, Lei and co-workers demonstrated a visible-light mediated decarboxylative coupling of α-keto acids with amines in the presence of the photocatalyst $[Ru(phen)_3]Cl_2$ (Scheme 2, a).[20] Very recently, we developed silver-mediated and catalyzed radical pathways for the synthesis of coumarins and chalcones using α-keto acids as coupling partners.[21] However, to date, the formation of C-C or C-heteroatom bonds via metal-free decarboxylative coupling of α-keto acids has been scarcely studied (Scheme 1, b).[22] In fact, decarboxylative coupling of pyruvate (i.e. α-keto acetic acid) with thiol (containing in coenzyme A) to produce acetyl-CoA occurs in living organisms catalyzed by the the pyruvate dehydrogenase complex.[23] Inspired by the chemical transformation in living beings, it is highly meaningful and challenging to explore metal-free decarboxylative pathways for the formation of C-heteroatom bonds using α-keto acids as acyl surrogates. Additionally, the development of mild catalytic conditions to initiate radical intermediates and to make radical pathways more controllable have been of growing interest.[24] Herein, we disclose the first success on the preparation of thioesters via catalyst-free direct radical oxidative decarboxylative coupling of α-keto acids with thiols under mild reaction conditions (Scheme 2, b).

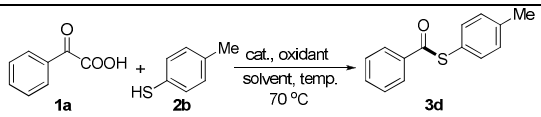


Scheme 2 Amidation and thioesterification of α-keto acids

Results and Discussion

Initially, 2-oxo-2-phenylacetic acid (**1a**) and 4-methylbenzenethiol (**2b**) were chosen as the coupling partners to optimize the reaction conditions, with the results shown in Table 1. Five oxidants of $Na_2S_2O_8$, $K_2S_2O_8$, $(NH_4)_2S_2O_8$, TBHP and O_2 were first investigated at 70 °C by using 0.1 equiv of $AgNO_3$ (relative to amount of 1a) in 2 mL CH_3CN/H_2O (v_1/v_2=1:1), and $K_2S_2O_8$ gave the highest yield (99%) (entries 1-5, Table 1). Unexpectedly, this transformation could also afford an excellent yield in the absence of $AgNO_3$ (entry 6, Table 1). The exciting results thereby confirmed it could be catalyst-free decarboxylative coupling reaction. Furthermore, different solvents including single and mixed ones were tested, showing that CH_3CN/H_2O was superior to the others (compare entries 6-12, Table 1). Subsequently, different reaction temperatures were surveyed (entries 6, 14-16, Table 1), and the best yield was isolated when the reaction was conducted at 70 °C (entry 6, Table 1). Notably, the reaction did not proceed without $K_2S_2O_8$ at 70 °C (entry 17). In contrast, only a trace amount of **3d** was detected at room temperature. Elevated temperature might not obviously improve this reaction yield (entry 16, Table 1). Highly pure $K_2S_2O_8$ (99.99% purity) was used to avoid the involvement of other transition metals in the present reaction, and the reaction provided a 99% yield (entry 18), which was the same to the yield when the analytically pure $K_2S_2O_8$ (99%) was used.

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



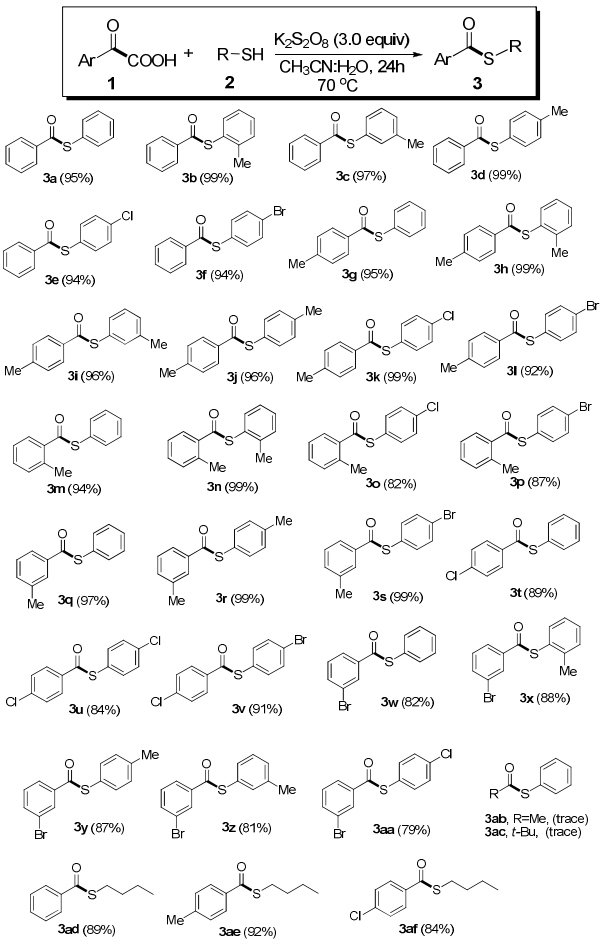
entry	catalyst	oxidant	solvent	yield [b] (%)
1	$AgNO_3$	$Na_2S_2O_8$	CH_3CN/H_2O	87
2	$AgNO_3$	$K_2S_2O_8$	CH_3CN/H_2O	99
3	$AgNO_3$	$(NH_4)_2S_2O_8$	CH_3CN/H_2O	20
4	$AgNO_3$	TBHP	CH_3CN/H_2O	trace
5	$AgNO_3$	O_2	CH_3CN/H_2O	N.R
6	none	**$K_2S_2O_8$**	**CH_3CN/H_2O**	**99**
7	none	$K_2S_2O_8$	DMSO /H_2O	31
8	none	$K_2S_2O_8$	DMF/H_2O	37
9	none	$K_2S_2O_8$	DCE/H_2O	N.R
10	none	$K_2S_2O_8$	H_2O	trace
11	none	$K_2S_2O_8$	CH_3CN	trace
12	none	$K_2S_2O_8$	DCE	N.R
14	none	$K_2S_2O_8$	CH_3CN/H_2O	72 [c]
15	none	$K_2S_2O_8$	CH_3CN/H_2O	59 [d]
16	none	$K_2S_2O_8$	CH_3CN/H_2O	98[e]
17	none	none	CH_3CN/H_2O	N.R
18	none	$K_2S_2O_8$	CH_3CN/H_2O	99[f]

[a] Reaction conditions: under nitrogen atmosphere, **1a** (0.5mmol), **2b** (1.5 equiv.), oxidant (3.0 equiv.), solvent (2 mL v_1/v_2 = 1:1), reaction time (24 h). TBHP= te*rt*-butyl hydroperoxide solution 5.5M in decane. N.R. = no reaction. [b] Isolated yield (based on the amount of **1a**). [c] 60 °C. [d] 50 °C. [e] 90 °C. [f] Use of highly pure $K_2S_2O_8$ from Aladdin company (99.99% purity).

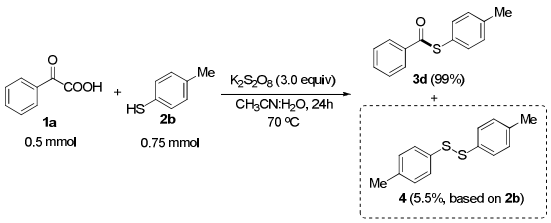
With the optimized conditions in hand, the scope and limitations of the reaction of various α-keto acids with thiols were investigated and the results were summarized in Table 2. To our delight, α-keto acids and thiols which have electron-donating or withdrawing groups could be converted to the desired products in good to excellent yields. In general, for the substituted α-keto acids, substrates with electron-donating groups, such as 2-oxo-2-*p*-tolylacetic acid and 2-oxo-2-*m*-tolylacetic acid, gave better yields than the α-keto acids with the electron-withdrawing substituent (Table 2, **3g**–**3l**, **3t**–**3v**). For the substituted thiols, electron-donating as well as electron-withdrawing groups displayed no obvious difference in the transformation. Notably, the steric hindrance in the α-keto acids and thiols did not significantly affect their efficiency, even some of the substrates could quantitatively transformed into the target products (Table 2, **3b**, **3h**, and **3m**). Aliphatic thiols also participated in this reaction (**3ad-3af**). Although aromatic α-keto acids showed high reactivity, unfortunately, aliphatic ones were poor substrates (Table 2, **3ab** and **3ac**). Further, we investigated the by-products in the present method by using the model reaction between **1a** and **2b**, the reaction afforded 9 mg of disulfides **4** in 5.5% yield as a main by-product (based on the amount of **2b**) (Scheme 3). The direct decarboxylative reactions could tolerate some functional groups,

including methyl, C-Cl bond, and C-Br bond which could be used for further modification.

Table 2. Catalyst-free synthesis of thioester derivatives via direct decarboxylative coupling of α-keto acids with thiols [a,b]

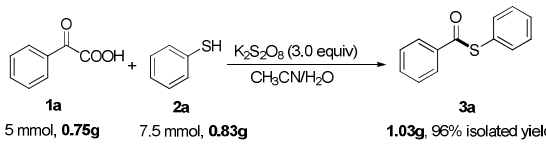


[a] Reaction conditions: under nitrogen atmosphere, substituted α-keto acids (0.5 mmol), thiols (0.75 mmol), $K_2S_2O_8$ (1.5 mmol), CH_3CN/H_2O(v_1/v_2=1:1) (2.0 mL), 70°C. [b] Isolated yield (based on the amount of **1**).



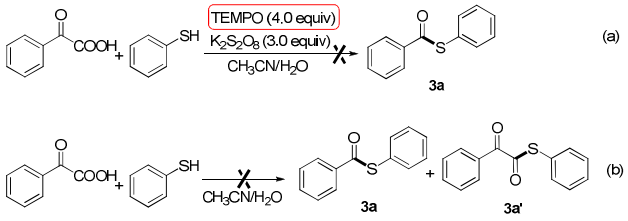
Scheme 3 Investigation of by-products in this transformation

Further, we explored the feasibility of gram-scale applications for the developed synthetic method. As shown in Scheme 4, the present reaction could afford 1.03 g of **3a** in 96 % yield under the standard conditions, without any significant loss of its efficiency. Therefore, this simple and catalyst-free synthesis protocol could be expected as a practical and efficient method to access various thioesters.



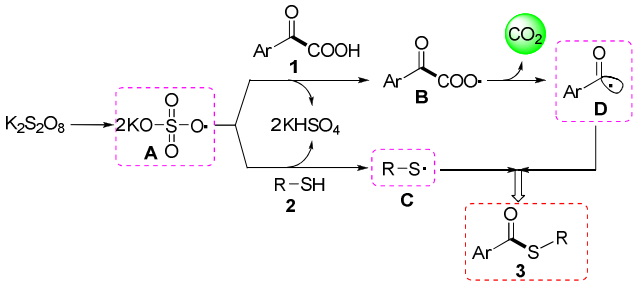
Scheme 4 Synthesis of **3a** on gram scale.

In order to investigate the mechanism further, the reaction of 2-oxo-2-phenylacetic acid (**1a**) with benzenethiol (**2a**) was tested in the presence of a radical-capturing species TEMPO (2,2,6,6-tetramethylpiperidine1-oxy). The formation of **3a** was completely compressed in the reaction, indicating that a radical process might be involved in this transformation (Scheme 5, a). Furthermore, no **3a** or **3a'** was obtained without $K_2S_2O_8$, demonstrating this process was not a traditional condensation reaction (Scheme 5, b).



Scheme 5 Investigations of the reaction mechanism.

Although the mechanism for the present catalyst-free decarboxylative pathway remains unclear, according to the previous report[25] a proposal mechanism would be herein presented (Scheme 6). Initially, $K_2S_2O_8$ was heated to generate the active radical anion $SO4^{-\bullet}$ **A**. Then, the anionic radical abstracted hydrogen from acidic C-H bond of **1** and **2**, leading to a α-keto carboxyl radical **B** and a sulfur radical **C**. Subsequently, decarboxylation of **B** afforded the corresponding acyl radical **D** by releasing one molecular CO_2. Finally, acyl radical **D** coupled with sulfur radical **C**, forming the coupling product **3**.



Scheme 6 Plausible mechanism.

Couclusions

In conclusion, a novel and efficient protocol has been firstly developed for the synthesis of thioester derivatives via catalyst-free direct decaroxylative coupling of readily prepared α-keto

acids and thiols under mild conditions. A series of thioester derivatives could be efficiently obtained in good to excellent yields. This easy and efficient approach could extend the scope of synthetic methods for the preparation of diverse thioesters.

Experimental section

General information and materials

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as internal standard (400 MHz ^{1}H, 100 MHz ^{13}C) at room temperature. All commercially available reagent and chemicals were purchased from chemical suppliers and used as received without further purification. Column chromatography was performed on silica gel (200-300 mesh). Mass analyses and HRMS were obtained by ESI on a TOF mass analyzer.

General experimental procedures.

A 25 mL Schlenk tube equipped with a magnetic strring bar was charged with $K_2S_2O_8$ (1.5 mmol, 405 mg), substituted α-keto acids (0.5 mmol), and thiols (0.75 mmol). The tube was evacuated twice and backfilled with nitrogen, and $CH_3CN/H_2O(v_1/v_2=1:1)$ (2 mL) was added under nitrogen atmosphere. Then, the tube was sealed and the mixture was stirred at 70°C for 24h. After completion of the reaction, the resulting solution was cooled to room temperature, and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**3**).

***S*-phenyl benzothioate (3a):**[12] Compound 3a was obtained in 95% yield (102 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.07 (d, 2H, J = 8.0 Hz), 7.64 (t, 1H, J = 8.0 Hz), 7.58-7.49 (m, 7H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 190.1, 136.7, 135.1, 133.7, 129.5, 129.3, 128.8, 127.5, 127.4. HRMS m/z calcd for $C_{14}H_{10}OS$ $[M + H]^+$ 215.0531, found 215.0547.

***S*-*o*-tolyl benzothioate (3b):** [26] Compound 3b was obtained in 99% yield (113 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.11 (d, 2H, J = 8.0 Hz), 7.65 (t, 1H, J = 8.0 Hz), 7.54 (t, 1H, J = 8.0 Hz), 7.43-7.42 (m, 1H), 7.34-7.432 (m, 1H), 2.46 (s, 3H),. ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.7, 142.7, 136.9, 136.5, 133.6, 130.9, 130.3, 128.8, 127.6, 126.9, 126.7. 20.9. HRMS m/z calcd for $C_{14}H_{13}OS$ $[M + H]^+$ 229.0687, found 229.0679.

***S*-*m*-tolyl benzothioat*e* (3c):** Compound 3c was obtained in 97% yield (111 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.08 (d, 2H, J = 8.0 Hz), 7.64 (t, 1H, J = 8.0 Hz), 7.53 (t, 2H, J = 8.0 Hz), 7.40-7.39 (m, 3H), 7.32-7.30 (m, 1H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 190.4, 139.2, 136.8, 135.7, 133.6, 132.2, 130.5, 129.1, 128.8, 127.5, 127.0, 21.4. HRMS m/z calcd for $C_{14}H_{13}OS$ $[M + H]^+$ 229.0687, found 229.0679.

***S*-*p*-tolyl benzothioate (3d):**[12] Compound 3d was obtained in 99% yield (114 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.08 (d, 2H, J = 8.0 Hz), 7.64 (t, 1H, J = 8.0 Hz), 7.53 (t, 2H, J = 8.0 Hz), 7.45 (d, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 190.6, 139.8, 136.8, 135.1, 133.6, 130.1, 128.8, 127.5, 123.9, 21.4. HRMS m/z calcd for $C_{14}H_{13}OS$ $[M + H]^+$ 229.0687, found 229.0679.

***S*-4-chlorophenyl benzothioate (3e):**[12] Compound 3e was obtained in 94% yield (117 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.04 (d, 2H, J = 8.0 Hz), 7.65 (t, 1H, J = 8.0 Hz), 7.56-7.47 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.6, 137.7, 136.4, 136.3, 136.0, 133.9, 129.9, 129.5, 129.3, 129.0, 128.8, 127.5, 125.9. HRMS m/z calcd for $C_{13}H_{10}ClOS$ $[M + H]^+$ 249.0141, found 249.0145.

***S*-4-bromophenyl benzothioate (3f):**[27] Compound 3f was obtained in 94% yield (138 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.04 (d, 2H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.0 Hz), 7.52 (t, 2H, J = 8.0 Hz), 7.46-7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.8, 136.5, 133.9, 132.5, 132.4. 132.3, 129.5, 128.8, 127.5, 124.3. HRMS m/z calcd for $C_{13}H_{10}BrOS$ $[M + H]^+$ 292.9636, found 292.9641, 294.9612.

***S*-phenyl 4-methylbenzothioate (3g):**[14] Compound 3g was obtained in 95% yield (109 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.97 (d, 2H, J = 8.0 Hz), 7.57-7.54 (m, 2H), 7.50-7.48 (m, 3H), 7.31 (d, 2H, J = 8.0 Hz), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.7, 144.6, 135.2, 134.2, 129.4, 129.2, 127.7, 127.6 , 21.7. HRMS m/z calcd for $C_{14}H_{13}OS$ $[M + H]^+$ 229.0687, found 229.0679.

***S*-o-tolyl 4-methylbenzothioate (3h):** Compound 3h was obtained in 99% yield (120 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.02 (d, 2H, J = 8.0 Hz), 7.55 (d, 1H, J = 8.0 Hz), 7.43-7.41 (m, 2H), 7.34-7.29 (m, 3H), 2.48 (s, 3H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.2, 144.5, 142.7, 136.5, 134.3, 130.8, 130.2, 129.4, 127.7, 127.1, 126.7, 21.8, 20.9. HRMS m/z calcd for $C_{15}H_{15}OS$ $[M + H]^+$ 243.0844, found 243.0841.

***S*-m-tolyl 4-methylbenzothioate (3i):** Compound 3i was obtained in 96% yield (116 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.98 (d, 2H, J = 12.0 Hz), 7.41-7.36 (m, 3H), 7.33-7.31 (m, 3H), 2.47 (s, 3H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.9, 144.5, 139.1, 135.7, 134.2, 132.2, 130.3, 129.4, 129.1, 127.6, 127.2, 21.7, 21.3. HRMS m/z calcd for $C_{15}H_{15}OS$ $[M + H]^+$ 243.0844, found 243.0841.

***S*-p-tolyl 4-methylbenzothioate (3j):**[28] Compound 3j was obtained in 99% yield (121 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.97 (d, 2H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.0 Hz), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 190.2, 144.5, 139.7, 135.1, 134.2, 130.1, 129.4, 127.6, 124.0, 21.7, 21.4. HRMS m/z calcd for $C_{15}H_{15}OS$ $[M + H]^+$ 243.0844, found 243.0841.

***S*-4-chlorophenyl 4-methylbenzothioate (3k):**[14] Compound 3k was obtained in 99% yield (130 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.94 (d, 2H, J = 8.0 Hz), 7.48-7.43 (m, 4H), 7.31 (d, 2H, J = 8.0 Hz), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.1, 144.9, 136.4, 135.9, 133.9, 129.5, 129.4, 127.6, 126.1, 21.8. HRMS m/z calcd for $C_{14}H_{12}ClOS$ $[M + H]^+$ 263.0297, found 263.0291.

***S*-4-bromophenyl 4-methylbenzothioate (3l):**[13] Compound 3l was obtained in 92% yield (141 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.94 (d, 2H, J = 8.0 Hz), 7.61 (d, 2H, J = 8.0 Hz), 7.40 (d, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.0, 144.9, 136.6, 133.8, 132.4, 129.5, 127.6, 126.7, 124.1, 21.6. HRMS m/z calcd for $C_{14}H_{12}BrOS$ $[M + H]^+$ 306.9792, found 306.9791, 308.9769.

***S*-phenyl 2-methylbenzothioate (3m):**[14] Compound 3m was obtained in 94% yield (108 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.00 (d, 2H, J = 8.0 Hz), 7.60-7.58 (m, 2H), 7.52-7.47 (m, 4H), 7.37-7.31 (m, 2H), 2.56 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 192.2, 137.4, 136.8, 134.9, 132.0, 131.8, 129.5, 129.3, 128.7, 128.3, 125.9, 20.8. HRMS m/z calcd for $C_{14}H_{13}OS$ $[M + H]^+$ 229.0687, found 229.0679.

***S*-*o*-tolyl 2-methylbenzothioate (3n):** Compound 3n was obtained in 99% yield (120 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.02 (d, 1H, J = 8.0 Hz), 7.56 (d, 1H, J = 8.0 Hz), 7.47 (t, 1H, J = 8.0 Hz), 7.43-7.41 (m, 2H), 7.37-7.30 (m, 3H), 2.54 (s, 3H), 2.49 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 191.9, 142.4, 137.3, 137.1, 136.3, 131.9, 131.8, 130.9, 130.2, 128.7, 127.7, 126.7, 125.9, 20.9, 20.7. HRMS m/z calcd for $C_{15}H_{15}OS$ $[M + H]^+$ 243.0844, found 243.0841.

***S*-4-chlorophenyl 2-methylbenzothioate (3o):**[29] Compound 3o was obtained in 82% yield (108 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.96 (d, 1H, J = 8.0 Hz), 7.36-7.30 (m, 2H), 2.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 191.5, 137.6, 136.4, 136.2, 135.9, 132.3, 131.9, 129.5, 128.7, 126.8, 125.9, 20.8. HRMS m/z calcd for $C_{14}H_{12}ClOS$ $[M + H]^+$ 263.0297, found 263.0291.

***S*-4-bromophenyl 2-methylbenzothioate (3p):**[14] Compound 3p was obtained in 87% yield (134 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.96 (d, 1H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.0 Hz), 7.48 (t, 1H, J = 8.0 Hz), 7.41 (d, 2H, J = 8.0 Hz), 7.36-7.30 (m, 2H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 191.4, 137.6, 136.4, 132.5, 132.3, 131.9, 128.7, 127.4, 125.9, 124.2, 20.8. HRMS m/z calcd for $C_{14}H_{12}BrOS$ $[M + H]^+$ 306.9792, found 306.9791, 308.9769.

***S*-phenyl 3-methylbenzothioate (3q):**[30] Compound 3q was obtained in 97% yield (111 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.89 (d, 2H, J = 8.0 Hz), 7.59-7.56 (m, 2H), 7.52-7.48 (m, 3H), 7.45-7.41 (m, 2H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 190.2, 138.7, 136.8, 135.1, 134.5, 129.5, 129.3, 128.7, 128.0, 127.6, 124.8, 21.4. HRMS m/z calcd for $C_{14}H_{13}OS$ $[M + H]^+$ 229.0687, found 229.0679.

***S*-phenyl 3-methylbenzothioate (3r):** Compound 3r was obtained in 99% yield (120 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.88 (d, 2H, J = 8.0 Hz), 7.46-7.38 (m, 4H), 7.31 (d, 2H, J = 8.0 Hz), 2.47 (s, 3H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 190.7, 139.8, 138.6, 136.8, 135.1, 134.4, 130.1, 128.6, 127.9, 124.7, 124.0, 21.4, 21.3. HRMS m/z calcd for $C_{15}H_{15}OS$ $[M + H]^+$ 243.0844, found 243.0841.

***S*-4-bromophenyl 3-methylbenzothioate (3s):**[29] Compound 3s was obtained in 99% yield (152 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.85 (d, 2H, J = 8.0 Hz), 7.60 (d, 2H, J = 8.0 Hz), 7.44 (d, 1H, J = 8.0 Hz), 7.42-7.38 (m, 3H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.5, 135.8, 136.5, 136.4, 134.7, 132.5, 128.7, 128.0, 126.7, 124.8, 124.2, 21.4. HRMS m/z calcd for $C_{14}H_{12}BrOS$ $[M + H]^+$ 306.9792, found 306.9791, 308.9769.

***S*-phenyl 4-chlorobenzothioate (3t):**[14] Compound 3t was obtained in 89% yield (111 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.80 (d, 2H, J = 8.0 Hz), 7.56-7.53 (m, 2H), 7.51-7.48 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.0, 140.1, 135.1, 135.0, 129.7, 129.4, 129.1, 128.9, 127.0. HRMS m/z calcd for $C_{13}H_{10}ClOS$ $[M + H]^+$ 249.0141, found 249.0145.

***S*-4-chlorophenyl 4-chlorobenzothioate (3u):**[14] Compound 3u was obtained in 84% yield (119 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.97 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.0 Hz), 7.46 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 188.5, 140.3, 136.3, 134.7, 129.6, 129.2, 128.9, 125.4. HRMS m/z calcd for $C_{13}H_9Cl_2OS$ $[M + H]^+$ 282.9751, found 282.9742.

***S*-4-bromophenyl 3-chlorobenzothioate (3v):**[14] Compound 3v was obtained in 91% yield (149 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.97 (d, 2H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.0 Hz), 7.39 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 188.4, 140.4, 136.5, 134.7, 132.6, 129.2, 128.9, 126.1, 124.5. HRMS m/z calcd for $C_{13}H_9BrClOS$ $[M + H]^+$ 326.9246, found 326.9238, 328.9226.

***S*-phenyl 3-bromobenzothioate (3w):**[12] Compound 3w was obtained in 82% yield (120 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.17 (s, 1H), 7.99 (d, 1H, J = 8.0 Hz), 7.76 (d, 1H, J = 8.0 Hz), 7.54-7.40 (m, 5H), 7.40 (t, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 188.9, 138.4, 136.5, 135.0, 130.4, 130.3, 129.8, 129.4, 126.8, 126.0, 123.0. HRMS m/z calcd for $C_{13}H_{10}BrOS$ $[M + H]^+$ 292.9636, found 292.9641, 294.9612.

***S*-o-tolyl 3-bromobenzothioate (3x):** Compound 3x was obtained in 88% yield (136 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.17 (s, 1H), 7.98 (d, 1H, J = 8.0 Hz), 7.76 (d, 1H, J = 8.0 Hz), 7.41-7.19 (m, 5H), 2.43 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.2, 139.3, 138.5, 136.4, 135.6, 132.0, 130.7, 130.4, 130.3, 129.2, 126.4, 126.0, 123.0, 21.3. HRMS m/z calcd for $C_{14}H_{12}BrOS$ $[M + H]^+$ 306.9792, found 306.9791, 308.9769.

***S*-o-tolyl 3-bromobenzothioate (3y):** Compound 3y was obtained in 87% yield (134 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.17 (s, 1H), 7.98 (d, 1H, J = 8.0 Hz), 7.75 (d, 1H, J = 8.0 Hz), 7.42-7.37 (m, 3H), 7.31 (d, 2H, J = 8.0 Hz), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.4, 140.1, 138.5, 136.4, 134.9, 130.4, 130.3, 130.2, 126.0, 123.2, 123.0, 21.4. HRMS m/z calcd for $C_{14}H_{12}BrOS$ $[M + H]^+$ 306.9792, found 306.9791, 308.9769.

***S*-m-tolyl 3-bromobenzothioate (3z):** Compound 3z was obtained in 81% yield (124 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.17 (s, 1H), 7.98 (d, 1H, J = 8.0 Hz), 7.76 (d, 1H, J = 8.0 Hz), 7.41-7.29 (m, 5H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.2, 139.3, 138.5, 136.4, 135.6, 132.0, 130.7, 130.4, 130.3, 129.2, 126.4, 126.0, 122.9, 21.3. HRMS m/z calcd for $C_{14}H_{12}BrOS$ $[M + H]^+$ 306.9792, found 306.9791, 308.9769.

***S*-4-chlorophenyl 3-bromobenzothioate (3aa):**[31] Compound 3aa was obtained in 79% yield (129 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.16 (s, 1H), 7.96 (d, 1H, J = 8.0 Hz), 7.77 (d, 1H, J = 8.0 Hz), 7.46 (m, 4H), 7.40 (t, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 188.4, 138.1, 136.7, 136.3, 130.4, 130.3, 129.6, 126.1, 125.3, 123.1. HRMS m/z calcd for $C_{13}H_9BrClOS$ $[M + H]^+$ 326.9246, found 326.9238, 328.9226.

***S*-butyl benzothioate (3ad):**[14] Compound 3ad was obtained in 89% yield (87 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.00 (d, 2H, J = 8.0 Hz), 7.59 (t, 1H, J = 8.0 Hz), 7.47 (t, 2H, J = 8.0 Hz), 3.10 (t, 2H, J = 8.0 Hz), 1.69 (dd, 2H, J = 8.0 Hz), 1.47 (dd, 2H, J = 8.0 Hz), 0.98 (t, 3H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 192.2, 137.3, 133.2, 128.6, 127.2, 31.6, 28.8, 22.1, 13.6. HRMS m/z calcd for $C_{11}H_{15}OS$ $[M + H]^+$ 195.0844, found 195.0837.

***S*-butyl 4-methylbenzothioate (3ae):**[14] Compound 3ae was obtained in 92% yield (96 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.89 (d, 2H, J = 8.0 Hz), 7.26 (d, 2H, J = 8.0 Hz), 3.09 (t, 2H, J = 8.0 Hz), 2.43 (s, 3H), 1.68 (dd, 2H, J = 8.0 Hz), 1.47 (dd, 2H, J = 8.0 Hz), 0.97 (t, 3H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 191.8, 144.0, 134.8, 129.2, 127.2, 31.7, 28.7, 22.1, 21.7, 13.6. HRMS m/z calcd for $C_{12}H_{17}OS$ $[M + H]^+$ 209.1000, found 209.1004.

***S*-butyl 4-chlorobenzothioate (3af):**[14] Compound 3af was obtained in 84% yield (96 mg) according to the general procedure: eluent petroleum ether/ethyl acetate (50:1), yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.93 (d, 2H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.0 Hz), 3.10 (t, 2H, J = 8.0 Hz), 1.68 (dd, 2H, J = 8.0 Hz), 1.47 (dd, 2H, J = 8.0 Hz), 0.97 (t, 3H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 191.0, 139.6, 135.6, 128.9, 128.5, 31.5, 28.9, 22.0, 13.6. HRMS m/z calcd for $C_{11}H_{14}ClOS$ $[M + H]^+$ 229.0454, found 229.0448.

1,2-D*ip*-tolyldisulfane (4):[32] Compound **4** was obtained in 5.5% yield (9 mg) according to the general procedure: eluent petroleum ether, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.47 (d, 4H, J = 8.0 Hz), 7.17 (d, 4H, J = 8.0 Hz), 2.39 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ137.5, 134.0, 129.9, 128.6, 21.1.

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