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Graphical Abstract

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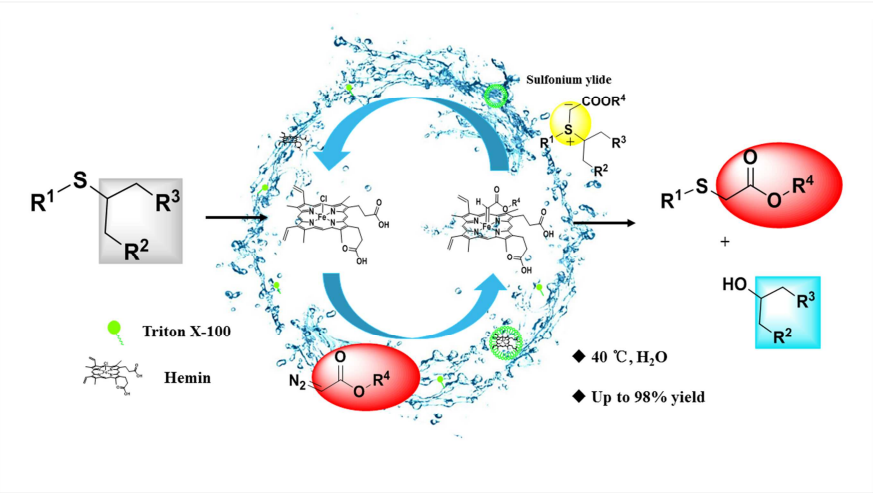

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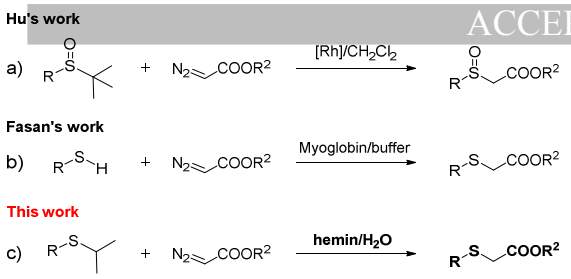
ABSTRACT

Heme is an abundant and widely existed cofactor for a variety of metalloenzymes, whose broader use is generally impeded by its high instability and poor solubility. Here we report an environment-benign and efficient strategy for the sulfonium ylide formation and subsequent C-S bond cleavage of aromatic isopropyl sulfides, which was catalyzed by hemin in assistance of Triton X-100. This aqueous catalytic system exhibited good functional group tolerance to a variety of sulfides and diazo esters. And the reaction mechanism was preliminarily proposed on the basis of designed reactions. Furthermore, the cleavage of C-S bond followed by introducing a functional ester group to aromatic sulfides, may potentially be employed for the late stage functionalization (LSF) of organosulfur drug in the future.

1. Introduction

The Late stage functionalization (LSF), which aims to generate ameliorative drug analogs without resorting to *de novo* synthesis, has received great attention lately.[1-5] However, molecules bearing C-S bonds are rarely applied in LSF, which is possibly due to the difficulty in breaking the C-S bonds and introducing another group subsequently. The C-S bond cleavage is crucial to synthetic chemistry and petroleum industry. Although C–S bond cleavage reactions mediated by third row transition metals have been reported[6-8]. Most applied C-S bond cleavage cannot be easily achieved, requiring expensive catalysts, harsh reaction conditions, and organic solvents as reported (Scheme 1a).[9-15] Thus, it is of great importance to develop mild and green methods[16] for the cleavage of C-S bond and subsequent formation of new C-S bond, which may also contribute to the LSF of organosulfur drug leads

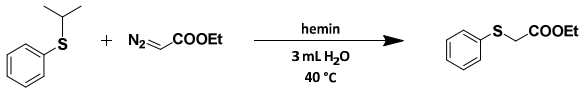
On the other hand, a great endeavor has been devoted to the modification and application of porphyrin or metallo-porphyrin enzymes in the past decade. For instance, a series of heme-based engineered metalloproteins were developed for the catalysis with excellent conversion and selectivity by Arnold group[17-21] and Fasan group[22-25]. Among them, the diazo compound-based reactions were intensively studied. Fasan group reported the myoglobin variant catalyzed S-H insertion of diazo esters with remarkable conversions (Scheme 1b).[22] Hartwig prepared modified myoglobins by replacing the iron in Fe-porphyrin IX (Fe-PIX) proteins with abiological, noble metals to catalyze the functionalization of C–H bonds.[26] Very recently, Che *et. al.* reported several cobalt (II) porphyrins catalyzed intramolecular cyclopropanation/ring opening cascade reaction, intramolecular Buchner reaction and arene cyclopropanation, affording corresponding nitrogen-containing polycyclic products in good yields.[27-29] Simple iron-porphyrin based catalysts and the reaction with diazoalkanes have also been achieved by Carreira[30] and other groups.[31, 32] However, as the most easily available form of porphyrin, only few catalytic reactions employing hemin itself as catalyst have been reported,[33, 34] in some degree owing to its high instability and poor solubility in both organic and aqueous solvent.[35-37] In recent years, our group have developed some green catalytic strategies[38, 39] based on hemin for transformation of diazo esters, especially for the formation of sulfonium ylide.[40-45] For instance, [2, 3]-sigmatropic rearrangements (Scheme 1c)[46] and Sommelet-Hauser rearrangements[39] were successfully carried out with hemin as the catalyst in aqueous system. As our continuous interest in green catalysis of hemin and sulfonium ylide formation, herein, a concise and efficient method was developed for the sulfonium ylide formation and subsequent C-S bond cleavage of aromatic isopropyl sulfide (Scheme 1d). This reaction was catalyzed by hemin and conducted in water with assistance of a surfactant Triton X-100.



Scheme 1 Strategies involving C-S bond transformation

2. Results and discussion

Table 1 Optimization of reaction conditions[a]



1a 2a 3a

Entry	2a /1a	Catalyst (mol %)	Time (d)	Additive (mol %)	Yield[b] (%)
1	1.2	hemin (10)	5	\	8
2	1.2	hemin (10)	5	β-CD (20)	17
3	1.2	hemin (10)	5	SDBS (20)	42
4	1.2	hemin (10)	5	SDS (20)	58
5	1.2	hemin (10)	5	Triton X-100 (20)	89
6	1.2	hemin (1)	5	Triton X-100(20)	70
7	1.2	hemin (5)	5	Triton X-100(20)	96
8	1.2	hemin (5)	2	Triton X-100 (20)	57
9	1.2	hemin (5)	3	Triton X-100 (20)	80
10	1.2	hemin (5)	4	Triton X-100 (20)	98
11	0.5	hemin (5)	4	Triton X-100 (20)	33
12	1.0	hemin (5)	4	Triton X-100 (20)	80
13	2.0	hemin (5)	4	Triton X-100 (20)	98
14	1.2	hemin (5)	4	Triton X-100 (5)	36
15	1.2	hemin (5)	4	Triton X-100 (10)	71
16	1.2	hemin (5)	4	Triton X-100 (30)	98
17	1.2	Cu(II)protoporphyrinIX(5)	4	Triton X-100 (20)	0
18	1.2	$FeCl_3 \cdot 6H_2O$(5)	4	Triton X-100 (20)	0

[a]Reactions were carried out with 3 mL of H_2O at 40 ℃ in a thermo shaker. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixtures.

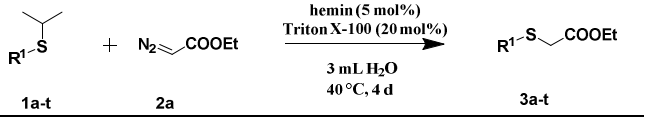
In the initial study, 0.5 mmol phenyl isopropyl sulfide (**1a**) and 0.6 mmol ethyl diazo acetate (EDA, **2a**) were employed as substrates to optimize the reaction conditions (Table 1). Upon treatment of **1a** and **2a** in 3 mL water at 40 ℃ for 5 days with 10 mol% hemin as the catalyst, the desired product, ethyl 2-(phenylthio) acetate (**3a**), was observed in 8% yield, which was determined by ^1H NMR (Table 1, entry 1). Inspired by our previous studies[38], 20 mol% β-cyclodextrin (β-CD) was added to the catalytic system. However, the yield of **3a** was only slightly raised to 17% (Table 1, entry 2). Several commercially available surfactants were screened for their ability in improvement of the catalytic effect in this reaction (Table 1, entries 3-5). Among them, Triton X-100 showed superior capacity in comparation with sodium laurylsulfonate (SDS) and sodium dodecylbenzenesulfate (SDBS), with the yield of **3a** reached as high as 89%. This result is in accordance with the reported works that Triton X-100 can inhibit the aggregation of hemin in aqueous solution[47] and further improve its catalytic capacity.[48] In addition, one similar result that appropriate amount of Triton X-100 obviously increase conversation was obtained in one of our previous studies.[46] Thus, Triton X-100 was chosen as the additive in this reaction. Several other reaction parameters were optimized, including the amount of hemin (Table 1, entries5-7), reaction time (Table 1, entries 7-10), molar ratio of **2a/1a** (Table 1, entries 10-13) and the amount of Triton X-100 (Table 1, entries 13-16). Finally, the optimized reaction condition was as follows, 5 mol% hemin and 20 mol% Triton X-100 shaken at 40 ℃ for 4 days (Table 1, entry 10). Considering the cleavage of C-S bond cannot be easily achieved in transition metal catalyzed reactions conducted in organic solvent at high temperature [9-15], it is worth mentioning that the reaction time is acceptable for diazo compound involved reactions conducted in aqueous solvent at low temperature (40 ℃) compared with previous studies.[38, 46, 49, 50] The optimized reaction yield was 98%. No desired product was observed when Cu (II) protoporphyrin IX (Table 1, entry 17) or iron salt $FeCl_3 \cdot 6H_2O$ (Table 1, entry 18) was used as catalyst in the reaction. This indicated that both porphyrin structure and iron center were crucial for the reaction. Moreover, control experiments showed that the reaction didn't proceed well in the absence of hemin or Triton X-100 (Table S1, entries 1-5). During the whole course of the experiments, only tiny amounts of the dimerization of EDA were observed in the context of excess EDA, which was added without drop wise.

Using the optimized reaction conditions, a variety of substituted isopropyl sulfides were employed in the hemin-catalyzed sulfonium ylide formation and subsequent C-S bond cleavage reaction with EDA. The results are summarized in Table 2. It is demonstrated that the catalytic system has good functional group tolerance to halogenated phenylisopropylsulfides (**3b-3g**), as well as trifluoromethyl(**3h**), ester (**3i-3j**), methoxyl(**3k-3l**) and alkylphenylisopropylsulfides (**3m-3p)**. In most cases, the *para*-, *ortho*- and *meta*-chlorophenyl isopropyl sulfides performed well, furnishing the corresponding phenylthioacetate in comparable yields (49%-58%) with no obvious position effects, while **3f** is more popular for the reaction. In general, both electron-withdrawing groups (**3b-3j**) and electron-donating groups (**3k-3p**) on the aryl ring of the initial thioether substrates were well tolerated, even though the substitution in the substrate could bring down the yield. In addition, 2-(isopropylthio) naphthalene (**3q**) was readily converted to the corresponding thioacetate in moderate yield (43%). What's more, substrates containing N- or S- heterocycles such as 2-(isopropylthio)pyridine (**3r**), 2-(isopropylthio)-6-methylpyridine(**3s**) and 2-(isopropylthio)thiophene (**3t**), which are poisonous to rhodium or other metal-based catalysts in most organic reactions,[51] could also be converted to the corresponding products in good yields(60%-68%). Subsequently, gram scale synthesis of **3a** and **3p** were realized.

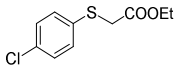
As an extension of this catalytic system, several reactants with tertiary carbon involved alkyl groups as R^2 groups were designed and their reactivities were investigated under the optimized conditions (Table 3). The results showed that 3-pentylphenylsulfide (**1u**), cyclohexylphenylsulfide (**1v**) and cyclopentylphenyl sulphide (**1w**) all generate product **3a**. However, the yields were all not as good as **1a**, which might due to the steric hinderance of the formed sulfonium ylide.

Some other thioethers were also investigated. The results are also shown in Table 3, no desired products were observed when methylphenyl sulfide (**1x**), ethyl (**1y**), vinyl (**1z**), *tert*-butyl (**1aa**) and halomethyl (**1ad-1ae**) phenyl sulfides were employed as substrates. The similar result was observed for phenylethanethioate (**1ah**). Meanwhile, diphenylsulfide (**1ab**) and diphenylmethyl phenyl sulfide (**1ac**) were also found to be incompatible, which may due to the large steric hindrance. Considering no desired reactions for (**1af**) and (**1ag**), we supposed that the aliphatic thioethers might be inapplicable to this catalytic system.

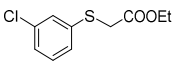
Table 2 Investigation of diverse substituted sulfides[a, b]



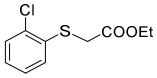
3a 98% (89%) (873 mg)



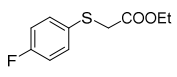
3b 49% (42%)



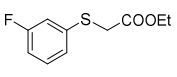
3c 58% (50%)



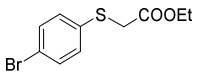
3d 51% (44%)



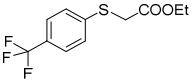
3e 54% (43%)



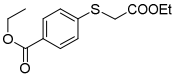
3f 98% (84%)



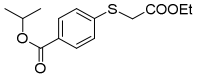
3g 72% (63%)



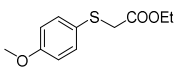
3h 52% (42%)



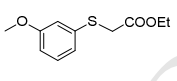
3i 74% (67%)



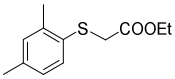
3j 81% (70%)



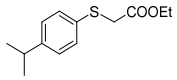
3k 34% (28%)



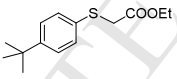
3l 40% (35%)



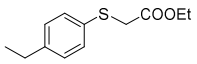
3m 58% (50%)



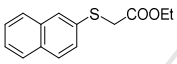
3n 44% (39%)



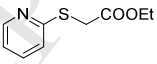
3o 50% (41%)



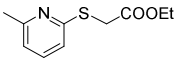
3p 78% (68%) (953 mg)



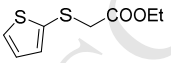
3q 43% (39%)



3r 60% (52%)



3s 69% (58%)

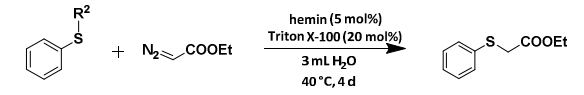


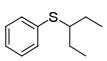
3t 68% (62%)

[a]Reactions were carried out with 3 mL of H_2O at 40 ℃ for 4 d in a thermo shaker; [b]Yields were determined by ^1H NMR analysis of the crude reaction mixtures. Values in the parentheses are isolated yields and products obtained.

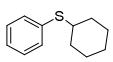
Furthermore, the reaction scope of α-diazo esters was investigated. As shown in Table 4, *tert*-butyl (**2u**), benzyl (**2v**), cyclohexyl (**2w**), cyclopentyl (**2x**), and adamantine-2-yl (**2y**) diazoacetate can react smoothly with sulfide, leading to the corresponding products in moderate to good yields (45%-80%). No reaction was detected when **2z** was employed, indicating that α-substitutions on the carbenoid moiety may be not tolerated. Several other diazo esters which are not compatible in the reaction system are listed in the supporting information (Table S2, **2b-2e**)

Table 3 Investigation of diverse substituted sulfides[a,b]

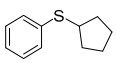




1u 24 (20)



1v 43 (37)

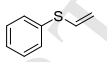


1w 74 (68)

Incompatible:

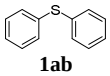
1x

1y

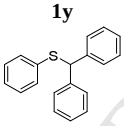


1z

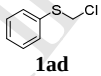
1aa



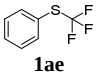
1ab



1ac

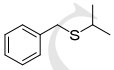


1ad



1ae

1af

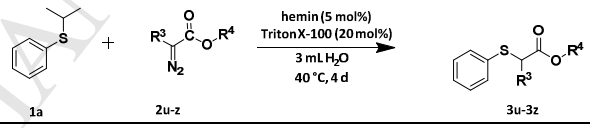


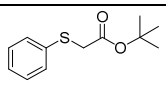
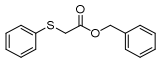
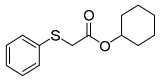
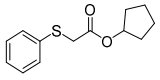
1ag

1ah

[a]Reactions were carried out with 3 mL of H_2O at 40 ℃ for 4 d in a thermo shaker; [b]Yields were determined by ^1H NMR analysis of the crude reaction mixtures. Values in the parentheses are isolated yields.

Table 4 Investigation of various diazo esters [a]



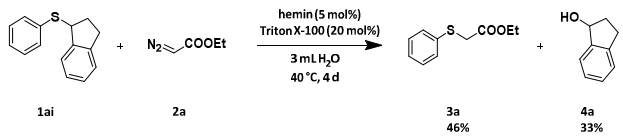
Entry	Diazo ester	Product	Yield[b] (%)
1	R^3= H, R^4= *t*Bu **2u**	 **3u**	77 (58)
2	R^3= H, R^4= Bn **2v**	 **3v**	45 (33)
3	R^3= H, R^4= C_6H_{11} **2w**	 **3w**	61 (50)
4	R^3= H, R^4= C_5H_9 **2x**	 **3x**	53 (42)
5	R^3= H, R^4= $C_{10}H_{15}$ **2y**	**3y**	80 (64)
4	R^3= Bn, R^4= Et **2z**	/	0

[a]Reactions were carried out with 3 mL of H_2O at 40 ℃ for 4 d in a thermo shaker; [b]Yields were determined by ^1H NMR analysis of the crude reaction mixtures. Values in the parentheses are isolated yields.

Even though some of the α-arylthio carbonyl compounds could be obtained from nucleophilic substitution of α-bromo-acetates with thiols and other ways, However, most of those methods must be conducted either in organic solvent with harsh

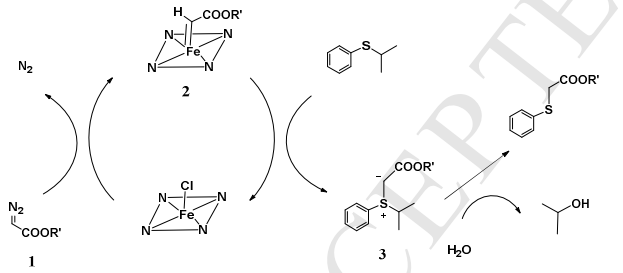
condition[52-55], or with expensive transition metal catalysts.[56] What's more, the present work consists of two parts, cleavage of non-activated C-S bond and synthesis of α-arylthio carbonyl compounds, which is different from Fasan's work(scheme 1b) and other work that only provide access to α-arylthio carbonyl compounds.[57] To our best knowledge, there is no aqueous C-S bond cleavage reaction reported yet (for reference 8, $CHCl_3$ is added).

In order to dug deeper into the mechanism of the reaction, (2, 3-dihydro-1H-inden-1-yl) (phenyl) sulfide (**1ai**) was designed to react with EDA under the standard reaction conditions. As shown in Scheme 2, the compound 1-indanol (**4a**) instead of 1-indone[58] was confirmed as the main byproduct with **3a**, **4a** in 46% and 33% yield respectively. It could be inferred that the cleaved fragment of aromatic isopropyl sulfide was further attacked by water to form the alcohol product, which is isopropanol in most cases aforementioned.



Scheme 2 Reaction between (2, 3-dihydro-1H-inden-1-yl) (phenyl) sulfide (**1ai**) and EDA

Based on the reported literatures and the observation of hydrolysed product **4a**, the proposed mechanism is depicted in Scheme 3. Initially, hemin reacts with the diazo ester (**1**) to generate hemin carbene intermediate (**2**),[59, 60] which has electrophilic character and can react with sulfide, giving rise to sulfonium ylide (**3**).[43, 46, 61] Then, the desired product from the cleavage of C-S bond and subsequent formation of new C-S bond is formed. At the same time, the attack of H_2O to sulfonium ylide led to the formation of isopropanol as byproduct.



Scheme 3 The proposed reaction mechanism

3. Conclusions

In summary， we developed an aqueous hemin-catalyzed reaction between diazo esters and aromatic isopropyl sulfides, which involved the sulfonium ylide formation and subsequent C-S bond cleavage. With the assistance of Triton X-100, the reaction is efficient under mild and eco-friendly conditions. The wide substrates scope and concise reaction conditions may contribute to a biocompatible green catalytic system for the LSF of organosulfur drug leads in the future. This study may also expand the range of carbene-mediated transformations via heme-based catalysts.

4. Experimental Section

4.1. General information

All reagents were purchased at the highest commercial quality and used without further purification. NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX-400 instrument or 600MHz and 150 MHz with Bruker Avance DMX-500 instrument. High resolution mass spectra (HRMS) were recorded on a Shimadzu LC/MS IT-TOF and a Waters Micromass GCT instrument. All reactions were monitored by TCL with silica gel-coated plates. For chromatography, 100-200 mesh silica gel (Qingdao, China) was employed.

4.2. General procedures

Sulfide (0.5 mmol) was added into 3 mL of aqueous solution of 25.0 μmol hemin and 0.1 mmol Triton X-100, followed by adding 0.6 mmol diazo ester in one portion. The reaction vial was then placed in a constant temperature shaker and left to shake at 220 rpm under 40 ℃. After 4 days, the mixture was extracted twice with EtOAc (2 mL×2). The organic layer was further washed with brine and then dried with Na_2SO_4. Then the organic solvent was removed in vacuum and hemin was removed by a short silica gel column, and eluted by petroleum ether to give the corresponding product. For gram scale synthesis **1a** and **1p** were employed with 5 mmol, 6.25 mmol respectively.

4.3. Characterization of products

*4.3.1. Ethy 2-(phenylthio) acetate (**3a**)*

Colorless oil; 873 mg; 89%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 2H), 7.34-7.27 (t, *J* = 7.5 Hz, 2H), 7.25-7.20 (t, *J* = 7.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 135.1, 130.1, 129.2, 127.1, 61.7, 36.9, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{10}H_{13}O_2S)^+$: 197.0631, found: 197.0629.

*4.3.2. Ethyl 2-(4-chlorophenylthio) acetate (**3b**)*

Colorless oil; 48.4 mg; 42%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 133.5, 133.1, 131.4, 129.1, 61.6, 36.8, 14.1. HRMS (EI) calcd. for $(M)^+$ $(C_{10}H_{11}ClO_2S)^+$: 230.0168, found: 230.0170.

*4.3.3. Ethyl 2-(3-chlorophenylthio) acetate (**3c**)*

Colorless oil; 57.6 mg; 50%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 1H), 7.32-7.28 (m, 1H), 7.27-7.19 (m, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.67 (s, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 137.3, 134.8, 130.1, 129.2, 127.6, 127.0, 61.8, 36.3, 14.2. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{10}H_{11}ClO_2SNa)^+$: 253.0060, found: 253.0044.

*4.3.4. Ethyl 2-(2-chlorophenylthio) acetate (**3d**)*

Colorless oil; 50.8 mg; 44%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 2H), 7.25-7.18 (m, 1H), 7.17-7.12 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.67 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 134.3, 129.9, 127.8, 127.4, 61.8, 35.3, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{10}H_{12}ClO_2S)^+$: 231.0241, found: 231.0230.

*4.3.5. Ethyl 2-(4-fluorophenylthio) acetate (**3e**)*

Colorless oil; 46.0 mg; 43%yield; ^{1}H NMR (400 MHz, CDCl3) δ 7.30-7.21 (m, 1H), 7.19-7.07 (m, 2H), 6.91 (td, J = 8.4, 2.3 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.65 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 164.1, 161.6,

137.6, 130.4, 124.8, 116.3, 116.0, 113.9, 113.7, 61.8, 36.2, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{10}H_{12}FO_2S)^+$: 215.0537, found: 215.0545.

*4.3.6. Ethyl 2-(3-fluorophenylthio) acetate (**3f**)*

Colorless oil; 90.0 mg; 84%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 1H), 7.19-7.08 (m, 2H), 6.95-6.87 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.66 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 130.5, 124.9, 116.3, 116.1, 113.9, 113.7, 61.9, 36.3, 14.2. HRMS (EI) calcd. for $(M)^+$ $(C_{10}H_{11}FO_2S)^+$: 214.0464, found: 214.0465.

*4.3.7. Ethyl 2-(4-bromophenylthio) acetate (**3g**)*

Colorless oil; 86.6 mg; 63%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 2H), 7.30-7.23 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.61 (s, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 134.3, 132.2, 131.7, 121.2, 61.8, 36.8, 14.2 .HRMS (EI) calcd. for $(M)^+$ $(C_{10}H_{11}BrO_2S)^+$: 273.9663, found: 273.9656.

*4.3.8. Ethyl 2-(4-Trifluoromethylphenylthio) acetate (**3h**)*

Colorless oil; 55.6 mg; 42%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.70 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 140.3, 128.2, 125.9, 62.0, 35.4, 14.2. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{11}H_{11}F_3O_2SNa)^+$: 287.0324, found: 287.0315.

*4.3.9. 4-(Ethoxycarbonylmethylsulfanyl) benzoic acid ethyl ester (**3i**)*

Colorless oil; 89.8 mg; 67%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.39 – 7.33 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.71 (s, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 169.26, 166.27, 141.98, 130.17, 128.22, 127.29, 62.00, 61.13, 35.23, 14.46, 14.23. HRMS (ESI) calcd. for $(M-H)^-$ $(C_{13}H_{15}O_4S)^-$: 267.0697, found: 267.0705.

*4.3.10. Isopropyl 4-((2-ethoxy-2-oxoethyl) thio) benzoate (**3j**)*

Colorless oil; 98.8 mg; 70%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 5.23 (hept, J = 6.3 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.71 (s, 2H), 1.35 (d, J = 6.3 Hz, 6H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.26, 165.74, 141.77, 130.15, 128.68, 127.33, 68.55, 61.98, 35.29, 22.07, 14.23. HRMS (ESI) calcd. for $(M-H)^-$ $(C_{14}H_{17}O_4S)^-$: 281.0853, found: 281.0892.

*4.3.11. Ethyl 2-(4-methoxyphenylthio) acetate (**3k**)*

Colorless oil; 31.6 mg; 28%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 8.9 Hz, 1H), 6.94-6.82 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 3.61 (s, 2H), 1.18 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 158.0, 131.7, 128.8, 121.1, 110.7, 61.4, 55.8, 35.1, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{11}H_{15}O_3S)^+$: 227.0736, found: 227.0726.

*4.3.12. Ethyl 2-(3-methoxyphenylthio) acetate (**3l**)*

Colorless oil; 39.6 mg; 35%yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.9 Hz, 1H), 6.96 (d, J = 7.2 Hz, 2H), 6.76-6.70 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 3.63 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 159.9, 136.4, 129.9, 121.7, 114.9, 112.7, 61.6, 55.3, 36.5, 14.1. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{11}H_{15}O_3S)^+$: 227.0736, found: 227.0723.

*4.3.13. Ethyl 2-[(2, 4-dimethyl) phenylthio] acetate (**3m**)*

Colorless oil; 56.0 mg; 50%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.9 Hz, 1H), 7.02 (s, 1H), 6.97 (d, J = 7.9 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.55 (s, 2H), 2.40 (s, 3H), 2.29 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.1, 137.4, 131.2, 130.3, 127.4, 61.5, 36.7, 21.0, 20.5, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{12}H_{17}O_2S)^+$: 225.0944, found: 225.0939.

*4.3.14. Ethyl 2-[4-(1-methylethyl) phenylthio] acetate (**3n**)*

Colorless oil; 46.2 mg; 39%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2H), 7.19-7.13 (m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.59 (s, 2H), 2.88 (hept, J = 6.9 Hz, 1H), 1.25-1.19 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.3, 131.6, 131.0, 127.3, 61.5, 37.4, 33.8, 24.0, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{13}H_{19}O_2S)^+$: 239.1100, found: 239.1088.

*4.3.15. Ethyl 2-[4-(1, 1-dimethylethyl) phenylthio] acetate (**3o**)*

Colorless oil; 51.8 mg; 41%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 4H), 4.16 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 1.30 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 150.5, 131.4, 130.5, 126.2, 61.5, 37.2, 34.6, 31.3, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{14}H_{21}O_2S)^+$: 253.1257, found: 253.1246.

*4.3.16. Ethyl 2-(4-ethylphenylthio) acetate (**3p**)*

Colorless oil; 953 mg; 68%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2H), 7.13 (d, J = 8.2 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 143.7, 131.5, 131.0, 128.7, 61.5, 37.4, 28.5, 15.5, 14.1. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{12}H_{17}O_2S)^+$: 225.0944, found: 225.0936.

*4.3.17. Ethyl 2-(2-naphthalenylthio) acetate (**3q**)*

Yellow oil; 48.0 mg; 39%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.81-7.75 (m, 3H), 7.53-7.42 (m, 3H), 4.18 (q, J = 7.1 Hz, 2H), 3.75 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 133.7, 132.5, 132.1, 128.6, 128.1, 127.6, 127.3, 126.6, 126.1, 61.6, 36.6, 14.1. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{14}H_{15}O_2S)^+$: 247.0787, found: 247.0767.

*4.3.18. Ethyl 2-(2-pyridinylthio) acetate (**3r**)*

Colorless oil; 51.2 mg; 52%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 4.1 Hz, 1H), 7.47 (td, J = 7.7, 1.7 Hz, 1H), 7.21 (d, J = 8.7 Hz, 1H), 7.00-6.96 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.96 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 156.9, 149.4, 136.2, 122.1, 119.9, 61.6, 32.4, 14.2. HRMS (ESI) calcd. for $(M+H)^+$ $(C_9H_{12}NO_2S)^+$: 198.0583, found: 198.0576.

*4.3.19. Ethyl 2-((6-methylpyridin-2-yl) thio) acetate (**3s**)*

Yellow oil; 61.2 mg; 58%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.82 (d, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.93 (s, 2H), 2.44 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.06, 158.42, 155.94, 136.45, 119.23, 118.88, 61.52, 32.63, 24.36, 14.28.HRMS (ESI) calcd. for $(M+H)^+$ $(C_{10}H_{14}NO_2S)^+$: 212.0745, found: 212.0746.

*4.3.20. Ethyl 2-(2-thienylthio) acetate (**3t**)*

Colorless oil; 62.8 mg; 62%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 5.4, 1.2 Hz, 1H), 7.22-7.21 (m, 1H), 6.99-6.97 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.49 (s, 2H), 1.24 (t, J =

7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 135.3, 130.7, 127.7, 61.7, 41.1, 14.3. HRMS (ESI) calcd. for $(M+H)^+$ $(C_8H_{11}O_2S_2)^+$: 203.0195, found: 203.0203.

*4.3.21. Tert-Butyl (phenylthio) acetate (**3u**)*

Colorless oil; 65.0 mg; 58%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.32-7.27 (m, 2H), 7.23-7.19 (m, 1H), 3.56 (s, 2H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 135.4, 130.0, 129.0, 126.9, 82.0, 37.9, 28.1. HRMS (ESI) calcd. for $(M+Na)^+$ $(C_{12}H_{16}O_2SNa)^+$: 247.0763, found: 247.0747.

*4.3.22. Benzyl phenylthioacetate (**3v**)*

Colorless oil; 55.6 mg; 33%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 5H), 7.22-7.10 (m, 5H), 5.05 (s, 2H), 3.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 135.5, 134.9, 130.2, 129.2, 128.7, 128.5, 128.4, 127.2, 67.3, 36.8. HRMS (ESI) calcd. for $(M+H)^+$ $(C_{15}H_{15}O_2S)^+$: 259.0787, found: 259.0781.

*4.3.23. Cyclohexyl phenylthioacetate (**3w**)*

Colorless oil; 62.6 mg; 50%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.37 (m, 2H), 7.33-7.26 (m, 2H), 7.24-7.18 (m, 1H), 4.82-4.72 (m, 1H), 3.62 (s, 2H), 1.82-1.74 (m, 2H), 1.70-1.66 (m, 2H), 1.54-1.48 (m, 1H), 1.42-1.34 (m, 3H), 1.31-1.30 (m, 1H), 1.27-1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 130.0, 129.1, 127.0, 74.1, 37.1, 31.5, 25.4, 23.7. HRMS (EI) calcd. for $(M)^+$ $(C_{14}H_{18}O_2S)^+$: 250.1028, found: 250.1029.

*4.3.24. Cyclopentyl phenylthioacetate (**3x**)*

Colorless oil; 49.6 mg; 42%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38(m, 2H), 7.25-7.19 (m, 2H), 7.33-7.26 (m, 2H), 7.25-7.19 (m, 2H), 5.20-5.12 (m, 1H), 3.60 (s, 2H), 1.86-1.74 (m, 2H), 1.69-1.49 (m, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 135.2, 130.0, 129.1, 127.0, 78.5, 36.9, 32.6, 23.7. HRMS (EI) calcd. for $(M)^+$ $(C_{13}H_{16}O_2S)^+$: 236.0871, found: 236.0872.

*4.3.25. Adamantan-2-yl phenylthioacetate (**3y**)*

Colorless oil; 96.8 mg; 64%yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 2H), 7.32-7.26 (m, 2H), 7.24-7.17 (m, 1H), 4.96-4.92 (m, 1H), 3.67 (s, 2H), 1.97-1.86 (m, 4H), 1.85-1.67 (m, 8H), 1.49 (d, J = 11.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 135.3, 129.7, 129.1, 126.9, 78.6, 37.4, 37.0, 36.4, 31. 8, 27.2, 27.0. HRMS (EI) calcd. for $(M)^+$ $(C_{18}H_{22}O_2S)^+$: 302.1340, found: 302.1341.

*4.3.26. 1-indanol (**4a**)*

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 1H), 7.26-7.21 (m, 3H), 5.25-5.20 (m, 1H), 3.09-2.99 (m, 1H), 2.88-2.76 (m, 1H), 2.53-2.42 (m, 1H), 1.99-1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.4, 128.4, 126.8, 125.0, 124.3, 76.5, 36.0, 29.9.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found.

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