Study of the $Rh_2(OAc)_4$- or $BF_3{\cdot}OEt_2$-Mediated Reaction of Thioacetic *S*-Acid with α-Diazocarbonyl Compounds

Wengang Yao,[a] Mingyi Liao,[a] Xiaomei Zhang,[a] Hao Xu,[a] and Jianbo Wang*[a]

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The $Rh_2(OAc)_4$-catalyzed reaction of methyl aryldiazoacetates with thioacetic *S*-acid gives exclusively the S–H insertion products in high yields, while the corresponding reaction mediated by $BF_3{\cdot}OEt_2$ gives *O*-esters. The mechanism of the reaction is discussed.

Introduction

The S−H insertion of diazo carbonyl compounds with thiols is a synthetically useful reaction that can introduce a sulfur-containing substituent adjacent to the carbonyl group of ketones or esters.[1] Similarly to the corresponding O−H insertions of alcohols,[2] this type of insertion reaction can be promoted by photolysis or by transition metal catalysis. It has been reported by McKervey et al. that the $Rh_2(OAc)_4$-catalyzed reaction of diazo carbonyl compounds with thiophenol gives α-phenylthio ketones and esters in good yields.[3] The intramolecular S−H insertion reaction is also known to be highly efficient.[4] Although the S−H insertion into thiols and the O−H insertion into the O−H bond of carboxylic acids have been well investigated,[5] the corresponding reactions of α-diazo carbonyl compounds with thiocarboxylic acids have received only limited attention. In 1977, Sheehan et al. reported the photoinduced reaction of 6-diazopenicillinate with thiocarboxylic acids, from which the *S*-esters were obtained in moderate yields.[6] In 1978, Thomas and coworkers reported the reaction between that same diazo compound and thioacetic acid in the presence of $BF_3{\cdot}OEt_2$. In Thomas's case, the corresponding *S*-ester was isolated in low yield.[7] Since thiocarboxylic acids may exist as a tautomeric mixture of thiol and thione forms,[8] it is interesting to investigate the chemoselectivity of this reaction. Here we report our study on the reaction of thioacetic *S*-acid with α-diazo carbonyl compounds, catalyzed by an Rh^{II} catalyst and a Lewis acid.

[a] Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Department of Chemical Biology, College of Chemistry,
Peking University, Beijing 100871, China
Fax: (internat) + 86-10/6275-1708
E-mail: wangjb@pku.edu.cn

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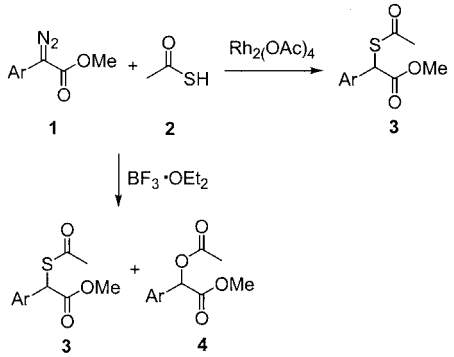
Results and Discussion

Methyl phenyldiazoacetate **1a** was used as the first substrate in this investigation (Scheme 1). When the diazo compound was slowly added to a stirring solution under reflux of freshly distilled thioacetic *S*-acid in CH_2Cl_2 containing 1 mol % $Rh_2(OAc)_4$, the reaction was complete within 60 min to give a single product, which was isolated in 93% yield. Spectroscopic data confirmed that the product was *S*-ester **3a**, which was formed through normal S−H insertion by an Rh^{II}−carbene. When the same substrate was reacted, however, with thioacetic *S*-acid in the presence of 30 mol % of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at room temperature, an unexpected product, methyl α-acetoxyphenyl acetate **4a**, was isolated. The structure of **4a** was confirmed by spectral data and by the comparison with a sample prepared independently by O−H insertion catalyzed by $Rh_2(OAc)_4$ of **1a** into acetic acid.[5] In the $BF_3{\cdot}OEt_2$-catalyzed reaction, careful inspection of the ^1H NMR spectra of the reaction mixture before purification revealed that *O*-ester **5** was formed initially.



a. Ar = C_6H_5; b. Ar = *m*-ClC_6H_4; c. Ar = *p*-ClC_6H_4
d. Ar = *p*-$MeOC_6H_4$; e. Ar =  ; f. Ar = 

Scheme 1

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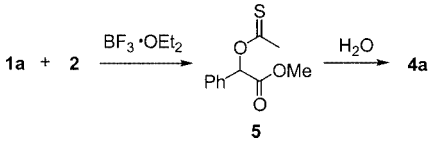
The C=S group in **5** was readily replaced by a C=O group during the workup and column chromatography (Scheme 2). Moreover, from the ^1H NMR spectrum of the crude product, we determined that the thioester **3a** was the minor product. Interestingly, if the reaction time was prolonged from 10 min to 12 h, the *S*-ester **3a** became the main product. It is likely that the excess thioacetic *S*-acid can further attack the initially formed *O*-ester **5** or α-acetoxyphenyl acetate **4a** to give **3a**. To substantiate this hypothesis, isolated **4a** was treated with excess thioacetic *S*-acid in CH_2Cl_2 containing $BF_3{\cdot}OEt_2$. We found that **4a** was converted slowly into **3a**. This transformation was accelerated by the addition of Et_3N to the reaction mixture.



Scheme 2

Another pathway for the formation of **3a** in the $BF_3{\cdot}OEt_2$-catalyzed reaction is an intramolecular rearrangement of **5**. Since **5** could not be isolated in a pure form, we could not confirm this pathway experimentally.

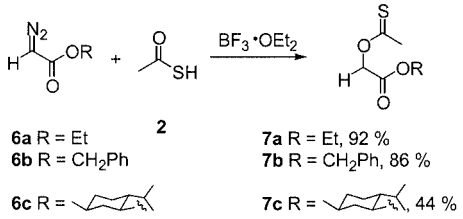
To demonstrate the generality of the reaction, we investigated the reaction of thioacetic *S*-acid with other methyl arylacetates under conditions of $Rh_2(OAc)_4$ or $BF_3{\cdot}OEt_2$ catalysis, and the results are summarized in Table 1. We see that $Rh_2(OAc)_4$-catalyzed reactions all give the S−H-insertion products in good to excellent yields, while the $BF_3{\cdot}OEt_2$-catalyzed reactions gave the methyl α-acetoxyphenylacetates **4a−f** in low to moderate yields. Various amounts of **3a−f** were detected from the reaction mixture when $BF_3{\cdot}OEt_2$ was used as the catalyst.

Table 1. The reaction of methyl aryldiazoacetate **1** with thioacetic *S*-acid

Entry	Diazo substrate	Catalyst[a]	**3**:**4**[b]	Main product yield (%)[c]
1	1a	$Rh_2(OAc)_4$	100:0	93
2	1a	$BF_3{\cdot}OEt_2$	16:84	43
3	1b	$Rh_2(OAc)_4$	100:0	77
4	1b	$BF_3{\cdot}OEt_2$	14:86	64
5	1c	$Rh_2(OAc)_4$	100:0	85
6	1c	$BF_3{\cdot}OEt_2$	11:89	41
7	1d	$Rh_2(OAc)_4$	100:0	89
8	1d	$BF_3{\cdot}OEt_2$	50:50	37[d]
9	1e	$Rh_2(OAc)_4$	100:0	79
10	1e	$BF_3{\cdot}OEt_2$	25:75	24
11	1f	$Rh_2(OAc)_4$	100:0	57
12	1f	$BF_3{\cdot}OEt_2$	20:80	59

[a] 1 mol % $Rh_2(OAc)_4$ or 30 mol % $BF_3{\cdot}OEt_2$ was used. [b] The ratio was determined from a ^1H NMR spectrum of the crude product. [c] Isolated yield. [d] Yield refers to compound **4**.

Next, we extended this investigation to other diazo carbonyl compounds **6a−c**. In contrast to the reaction of methyl arylacetate **1**, the $Rh_2(OAc)_4$-catalyzed reaction of ethyl diazoacetate **6a** gave a complex mixture of products. We also have tried $Rh_2(O_2CCF_3)_4$ as the catalyst, but it gave a similar complex mixture. When the reaction was catalyzed, however, by $BF_3{\cdot}OEt_2$, the *O*-ester **7a** was isolated as the main product (Scheme 3). We found **7a** to be stable under normal workup and separation conditions. Diazoacetates **6b** and **6c** gave similar results, although in the case of **6c** the yield was somewhat low. The structures of **7a−c** were confirmed by spectral data, and by comparison of **7b** with benzyl α-*S*-thioacetoxyacetic ester, which was prepared by the reaction of thioacetic *S*-acid with benzyl chloroacetate under basic conditions.



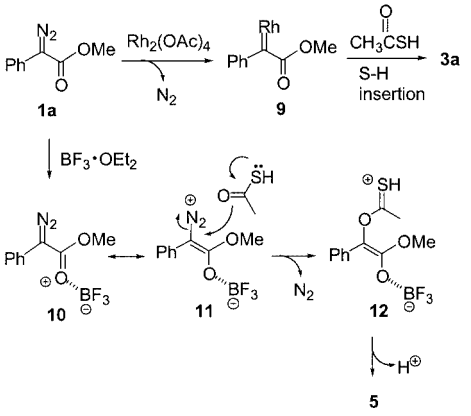
Scheme 3

These experimental results raise intriguing questions regarding the reaction mechanism. Although there is evidence to show that simple thiocarboxylic acids may exist as an equilibrium between thiol form **2** and thione form **8** in solution, it is generally believed that the thiol structure predominates (Scheme 4).[8] By observing the ^{13}C NMR spectrum, we confirmed that a catalytic amount of $Rh_2(OAc)_4$ or $BF_3{\cdot}OEt_2$ does not change thioacetic acid, which shows a peak at $\delta = 194.09$ ppm in $CDCl_3$ at room temperature. Based on this information, we suggest that for both $Rh_2(OAc)_4$- and $BF_3{\cdot}OEt_2$-catalyzed reactions, the thioacetic acid participates in the reaction in its thiol form **2**.

Scheme 4

We propose that the mechanism of the reaction of methyl aryldiazoacetate with thioacetic *S*-acid, catalyzed by $Rh_2(OAc)_4$, proceeds through a typical S−H insertion by Rh^{II}−carbene **9** (Scheme 5). It has been suggested that an X−H (X = O, S, N, etc.) insertion reaction of a diazocarbonyl compound, catalyzed by a transition metal complex, follows a stepwise processes in which nucleophilic attack of a heteroatom X at the electrophilic metal carbene forms an ylide, which subsequently undergoes 1,2-rearrangement to transfer a proton from X to the carbon atom to give the formal insertion product.[1,2,9] For the reaction of

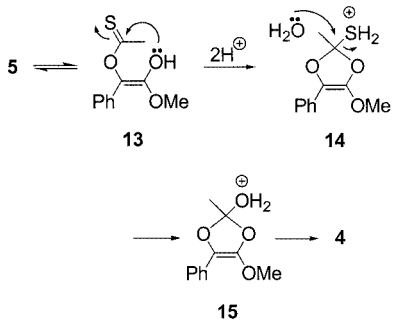
Rh^{II}−carbene with thioactic *S*-acid, however, it is more likely that direct insertion into the S−H bond occurs, because the electron-withdrawing acetyl group decreases the electron density of the sulfur atom, and thus makes it less nucleophilic toward the electron-deficient carbenoid carbon atom.



Scheme 5

The $BF_3{\cdot}OEt_2$-catalyzed reaction follows a different mechanism. The $BF_3{\cdot}OEt_2$ unit complexes with the carbonyl group of the diazo compound,[1] followed by nucleophilic attack of thioacetic *S*-acid's carbonyl-group oxygen atom to generate **11**, which deprotonates to give **5**.

On the other hand, although a theoretical study suggests that a C=O bond is more stable than a C=S bond in general,[10] it is not clear why, in the $BF_3{\cdot}OEt_2$-catalyzed reaction of methyl phenyldiazoacetate, the C=S bond in the initially formed product **5** can be easily replaced by C=O, while the C=S bond is relatively stable in **7a**, **7b** and **7c**. In the case of **5**, we speculate that enolization occurs readily because of the stabilizing effect of the phenyl ring. In the enol structure **13**, the thioacetyl group is close to the hydroxyl group. The ester group may accelerate the conversion of C=S to C=O through neighboring-group participation (Scheme 6). In *O*-esters **7a**, **7b** and **7c**, the enolization is more difficult because of lack of stabilization by a phenyl ring. Consequently, in these cases, the *O*-esters with a C=S group are relatively stable.



Scheme 6

Conclusions

We have carried out a study on the reaction of thioacetic *S*-acid with α-diazo carbonyl compounds under conditions of $Rh_2(OAc)_4$ or $BF_3{\cdot}OEt_2$ catalysis. We found the reaction to be dependant on both the diazo substrate and the catalysts used. The $Rh_2(OAc)_4$-catalyzed reaction of methyl aryldiazoacetate with thioacetic *S*-acid, which may find its utility in organic synthesis, gave a good yield of the *S*-ester.

Experimental Section

General Remarks: All reactions were performed under a nitrogen atmosphere in flame-dried reaction flasks, and the components were added by syringe. All solvents were distilled prior to use. CH_3COSH was purchased from Aldrich, and was distilled with collection of the fraction boiling at 88−92 °C. CH_2Cl_2 was distilled from CaH_2. $BF_3{\cdot}Et_2O$ was distilled before use. For chromatography, 100−200 mesh silica gel (Qindao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz with a Varian Mercury 200 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as the internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer.

General Procedure for the $Rh_2(OAc)_4$-Catalyzed Reaction of Diazo Compounds with Thioacetic *S*-Acid: CH_3COSH (1.0 mmol) and $Rh_2(OAc)_4$ (≈ 0.005 mmol) were dissolved in CH_2Cl_2 (5 mL). The solution was heated under gentle reflux under N_2. To this solution was added dropwise a solution of diazo compound (0.5 mmol) in CH_2Cl_2 (5 mL) over 30 min. The reflux was continued for 30 min after addition. CH_2Cl_2 (20 mL) was added, and the solution was washed with 1 N NaOH and then with brine. A typical work-up gave a crude product that was purified on a silica gel column eluting with petroleum ether/diethyl ether (40:1). The structures of the products were confirmed by IR, ^1H NMR and ^{13}C NMR spectroscopy and mass spectrometry.

General Procedure for the $BF_3{\cdot}OEt_2$-Catalyzed Reaction of Diazo Compounds with Thioacetic *S*-Acid: The diazo compound (0.33 mmol) in CH_2Cl_2 (3 mL) was added dropwise over 5−10 min at room temperature to a solution of CH_3COSH (3.3 mmol) and $BF_3{\cdot}Et_2O$ (0.1 mmol) dissolved in CH_2Cl_2 (2 mL). Stirring was continued for another 5 min under N_2 at room temperature, then water (5 mL) and CH_2Cl_2 (20 mL) were added. The same procedure as described above gave pure products whose structures were confirmed by IR, ^1H NMR, and ^{13}C NMR spectroscopy and mass spectrometry.

Methyl (Acetylthio)(phenyl)acetate (3a):[11] From the $Rh_2(OAc)_4$-catalyzed reaction: colorless oil, 93%. IR: $\tilde{\nu}$ = 2955, 1743, 1698, 1241, 1134, 786 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.33 (s, 3 H), 3.72 (s, 3 H), 5.32 (s, 1 H), 7.29−7.38 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.9, 51.0, 53.0, 128.3, 128.4, 129.9, 134.7, 170.4, 193.8 ppm. MS: *m*/*z* = 224 (2) [M^+], 192 (51), 182 (51), 150 (30), 123 (81), 90 (10), 77 (14), 43 (100).

Methyl (Acetyl)(phenyl)acetate (4a):[12] From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 43%. IR: $\tilde{\nu}$ = 2955, 1757, 1233, 786 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.20 (s, 3 H), 3.72 (s, 3 H), 5.93 (s, 1 H), 7.36−7.47 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7, 52.6, 74.4, 127.6, 128.8, 129.2, 133.7, 169.3, 170.3 ppm. MS: *m*/*z* = 208 (4) [M^+], 176 (31), 166 (52), 149 (62), 107 (100).

Methyl (Acetylthio)(*m*-chlorophenyl)acetate (3b): From the $Rh_2(OAc)_4$-catalyzed reaction: colorless oil, 77%. IR: $\tilde{\nu}$ = 2954, 1743, 1698, 1132, 770 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.36 (s, 3 H), 3.75(s, 3 H), 5.29 (s, 1 H), 7.27−7.40 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.9, 50.3, 53.2, 126.6, 128.5, 128.6, 130.0, 134.6, 136.9, 169.8, 193.2 ppm. MS: *m*/*z* = 258 (1) [M^+], 226 (9), 216 (13), 184(6), 157 (15), 84 (76), 77 (1), 43 (100). HRMS calcd. for $C_{11}H_{11}O_3SCl$ [M^+] 258.0117; found 258.0114.

Methyl (Acetyl)(*m*-chlorophenyl)acetate (4b): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 64%. IR: $\tilde{\nu}$ = 2956, 1751, 1232 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.21 (s, 3 H), 3.74 (s, 3 H), 5.90 (s, 1 H), 7.34−7.48 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7, 52.8, 73.6, 125.7, 127.6, 129.4, 130.0, 134.7, 135.5, 168.8, 170.1 ppm. MS: *m*/*z* = 242 (1.5) [M^+], 210 (4), 200 (11), 183 (10), 141(9), 124 (2), 111 (7), 77 (6), 43 (100). HRMS calcd. for $C_{11}H_{11}O_4Cl$ [M^+] 242.0345; found 242.0340.

Methyl (Acetylthio)(*p*-chlorophenyl)acetate (3c): From the $Rh_2(OAc)_4$-catalyzed reaction: colorless oil, 85%. IR: $\tilde{\nu}$ = 2957, 1740, 1696 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.35 (s, 3 H), 3.74 (s, 3 H), 5.29 (s, 1 H), 7.30−7.40 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.9, 50.2, 53.1, 129.0, 129.7, 133.5, 134.4, 169.9, 193.4 ppm. MS: *m*/*z* = 258 (3) [M^+], 226 (30), 216 (27), 184 (16), 157 (44), 123 (7), 111 (12), 84(100). HRMS calcd. for $C_{11}H_{11}O_3SCl$ [M^+] 258.0117; found 258.0122.

Methyl (Acetyl)(*p*-chlorophenyl)acetate (4c): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 41%. IR: $\tilde{\nu}$ = 2919, 1749, 1225, 787 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.21 (s, 3 H), 3.73 (s, 3 H), 5.90 (s, 1 H), 7.34−7.42 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7, 52.7, 73.7, 128.9, 129.0, 132.2, 135.3, 168.9, 170.1 ppm. MS: *m*/*z* = 242 (6) [M^+], 210 (21), 200 (30), 183 (29), 141 (97), 124 (3), 111(9), 77 (17), 43 (100). HRMS calcd. for $C_{11}H_{11}O_4Cl$ [M^+] 242.0345; found 242.0348.

Methyl (Acetylthio)(*p*-methoxyphenyl)acetate (3d): From the $Rh_2(OAc)_4$-catalyzed reaction: colorless oil, 89%. IR: $\tilde{\nu}$ = 2955, 1741, 1695, 1512, 1253 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.34 (s, 3 H), 3.73 (s, 3 H), 3.79 (s, 3 H), 5.27 (s, 1 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 7.30 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.9, 50.4, 53.0, 55.2, 114.3, 126.5, 129.5, 159.6, 170.6, 194.1 ppm. MS: *m*/*z* = 254 (2) [M^+], 222 (15), 212 (4), 179 (13), 151 (20), 119 (7.83), 86 (100), 84 (100). HRMS calcd. for $C_{12}H_{14}O_4S$ [M^+] 254.0612; found 254.0627.

Methyl (Acetyl)(*p*-methoxyphenyl)acetate (4d): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 37%. IR: $\tilde{\nu}$ = 2957, 1747, 1515, 1233, 760 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.18 (s, 3 H), 3.72 (s, 3 H), 3.81 (s, 3 H), 5.88 (s, 1 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 7.37 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7, 52.5, 55.3, 74.1, 114.2, 125.9, 129.1, 160.3, 169.6, 170.4 ppm. MS: *m*/*z* = 238 (30) [M^+], 206 (77), 196 (19), 179 (50), 137 (100). HRMS calcd. for $C_{12}H_{14}O_5$ [M^+] 238.0841; found 238.0842.

Methyl (Acetylthio)(3-thienyl)acetate (3e): From the $Rh_2(OAc)_4$-catalyzed reaction: colorless oil, 79%. IR: $\tilde{\nu}$ = 2953, 1742, 1696, 1132 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.35 (s, 3 H), 3.76 (s, 3 H), 5.45 (s, 1 H), 7.06−7.32 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.9, 45.9, 53.0, 124.0, 126.5, 127.2, 134.3, 170.1, 193.6 ppm. MS: *m*/*z* = 230 (7) [M^+], 198 (54), 188 (39), 156 (26), 129 (60), 43 (100). HRMS calcd. for $C_9H_{10}O_3S_2$ [M^+] 230.0071; found 230.0065.

Methyl (Acetyl)(3-thienyl)acetate (4e): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 24%. IR: $\tilde{\nu}$ = 2955, 1750, 1229 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.12 (s, 3 H), 3.68 (s, 3 H), 5.98 (s, 1 H), 7.09−7.35 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7, 52.7, 70.4, 124.6, 126.3, 126.6, 134.0, 169.0, 170.2 ppm. MS: *m*/*z* = 214 (3) [M^+], 182 (14), 172 (31), 155 (19), 113 (89), 96 (4), 85 (22), 43 (100). HRMS calcd. for $C_9H_{10}O_4S$ [M^+] 214.0299; found 214.0292.

Methyl (Acetylthio)(1-naphthyl)acetate (3f): From the $Rh_2(OAc)_4$-catalyzed reaction: colorless oil, 57%. IR: $\tilde{\nu}$ = 2953, 1743, 1694, 1132 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.38 (s, 3 H), 3.72 (s, 3 H), 6.09 (s, 1 H), 7.38−8.05 (m, 7 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.8, 48.2, 53.2, 123.1, 125.3, 126.0, 126.8, 127.0, 129.0, 129.3, 130.7, 130.8, 134.0, 170.7, 194.0 ppm. MS: *m*/*z* = 274 (30) [M^+], 242 (54), 232 (32), 200 (55), 173 (62), 171 (100). HRMS calcd. for $C_{15}H_{14}O_3S$ [M^+] 274.0663; found 274.0658.

Methyl (Acetyl)(1-naphthyl)acetate (4f): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 59%. IR: $\tilde{\nu}$ = 2955, 1748, 1229, 1055 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.20 (s, 3 H), 3.69 (s, 3 H), 6.68 (s, 1 H), 7.43−8.19 (m, 7 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7, 52.7, 72.4, 123.7, 125.2, 126.1, 126.9, 127.5, 128.8, 129.9, 130.1, 131.0, 134.0, 169.6, 170.3 ppm. MS: *m*/*z* = 258 (20) [M^+], 226 (9), 216 (11), 199 (10), 157 (100). HRMS calcd. for $C_{15}H_{14}O_4$ [M^+] 258.0892; found 258.0888.

Ethyl (*O*-Thioacetyl)acetate (7a): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: light-yellow oil, 92%. IR: $\tilde{\nu}$ = 2254, 1755, 1194, 1080 (C=S), 651 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.27 (t, *J* = 7.2 Hz, 3 H), 2.64 (s, 3 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 5.00 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1, 33.9, 61.5, 67.1, 166.7, 219.2 ppm. MS: *m*/*z* = 162 (20) [M^+], 117 (13), 104 (29), 83 (6.5), 59 (100), 43(99). HRMS calcd. for $C_6H_{10}O_3S$ [M^+] 162.0350; found 162.0357.

Benzyl (*O*-Thioacetyl)acetate (7b): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 86%. IR: $\tilde{\nu}$ = 2958, 1765, 1287, 1176, 1079 (C=S), 808 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.57 (s, 3 H), 5.00 (s, 2 H), 5.13 (s, 2 H), 7.28 (s, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 33.8, 67.0, 67.1, 115.9, 128.4, 128.52, 128.58, 128.6, 134.9, 166.5, 219.1 ppm. MS: *m*/*z* = 224 (8) [M^+], 168 (15), 148 (14), 108 (13), 91 (100). HRMS calcd. for $C_{11}H_{12}O_3S$ [M^+] 224.0507; found 224.0500.

Menthyl (*O*-Thioacetyl)acetate (7c): From the $BF_3{\cdot}Et_2O$-catalyzed reaction: colorless oil, 44%. IR: $\tilde{\nu}$ = 2959, 1750, 1196, 1080 (C=S), 650 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.74−2.39 (m, 18 H), 2.66 (s, 3 H), 4.77 (dt, *J* = 11, 4.4 Hz, 1 H), 5.01 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.2, 20.7, 21.9, 23.4, 26.2, 31.4, 33.9, 34.1, 40.6, 46.9, 67.2, 75.8, 166.3 ppm. MS: *m*/*z* = 272 (3) [M^+], 138 (84), 123 (39), 109 (9), 95 (100), 81 (86). HRMS calcd. for $C_{14}H_{24}O_3S$ [M^+] 272.1446; found 272.1445.

Preparation of Benzyl (Acetylthio)acetate:[13] $ClCH_2CO_2Bn$ (1.84 g, 10 mmol) in THF (2 mL) was added dropwise to a solution of CH_3COSH (760 mg, 10 mmol) and NaOH (400 mg, 10 mmol) dissloved in THF (5 mL). After the addition was complete, the solution was stirred overnight. The reaction mixture was extracted with CH_2Cl_2, and then the organic solution was washed with water and dried by Na_2SO_4. Evaporation of the solvent gave a crude product that was purified on a silica gel column (petroleum ether/Et_2O, 40:1) to give a colorless oil (1.92 g, 86%). IR: $\tilde{\nu}$ = 2935, 1750, 1696, 1291, 1132 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.38 (s, 3 H), 3.75 (s, 2 H), 5.12 (s, 2 H), 7.36 (s, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ =30.0, 31.5, 67.5, 128.2, 128.4, 128.6, 135.4, 168.5, 193.5 ppm. MS: *m*/*z* = 224 (3) [M^+], 181 (27), 148 (2), 136 (3), 107 (10), 91 (100). HRMS calcd. for $C_{11}H_{12}O_3S$ [M^+] 224.0507; found 224.0501.

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