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ORIGINAL PAPER

Basic Al_2O_3 promotes one-pot synthesis of thioethers via in situ generation and addition of β-acyloxy mercaptans to electron-deficient alkenes

Mohammad Abbasi[1] · **Dariush Khalili**[2]

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Abstract Thioethers were synthesized under solvent-free conditions by reacting Michael acceptors with β-acyloxy mercaptans in situ generated from the reaction of epoxides and thioacids in the presence of basic Al_2O_3 in high yields.

Keywords Thioethers · Epoxides · Thioacids · Michael addition · Al_2O_3

Introduction

Thioethers are essential building blocks for construction of organosulfur derivatives that have important roles in materials science, biology and chemistry [1, 2]. There are several commonly used methods for the synthesis of thioethers. Alkylation of thiols with electron-deficient alkenes which is known as thio or thia-Michael addition reaction is one of the most efficient methods for synthesizing thioethers. The study of thia-Michael addition has been remained a topic of research to this day in organic synthesis. The studies have been mainly limited to the introduction of new catalysts and conditions for the addition of thiols to structurally diverse Michael acceptors. Over the past few years, a handful of methods have been developed to prepare thia-Michael adducts via addition of in situ generated thiols to different acceptors. In this regards, different strategies including the hydrolysis of Bunte salts in acidic conditions [3], the treatment of elemental sulfur with aryl halides in the presence of copper ferrite nanoparticle [4], the treatment of an alkyl halide with thiourea in the presence of a base [5, 6], basic hydrolysis of *S*-alkylisothiouronium salts [7], the hydrolysis of 3-[bis(alkylthio)methylene]pentane-2,4-diones [8, 9], and 2-[bis(alkylthio)methylene]-3-oxo-*N*–*O*-tolylbutanamides [10], and reduction of disulfides [11–13] have been employed successfully to in situ generate thiols in Michael addition reactions.

Until now, the solid-phase organic synthesis [14, 15] and catalysis [16] have been the subject of intense experimental studies in organic synthesis. It is now clear that many reactions proceed more efficiently in the solid state than in solution [17–20]. A large number of organic, inorganic, or organic–inorganic hybrid materials have been employed as solid surfaces to promote or catalyze various organic reactions [16]. In this regard, alumina and silica gel has been used to promote a variety of organic reactions since many years ago [21–26]. In this goal, we recently developed a procedure for the one-pot preparation of thia-Michael adducts of β-acyloxy mercaptans using thioacids, epoxides, and electron-deficient alkenes under solvent-free conditions [27, 28]. In this method, a β-hydroxy thioester is synthesized from the reaction of a thioacid and an epoxide on silica gel surface at first which rearranges to the corresponding β-acyloxy mercaptan by using a silica gel/Et_3N combined catalyst. Several different experiments convinced us that this rearrangement proceeds efficiently only in the absence of any solvent. Now, we wish to introduce a modified procedure for one-pot synthesize of thia-Michael adducts of β-acyloxy mercaptans using heterogeneous basic Al_2O_3 without needing any co-catalyst.

✉ Mohammad Abbasi
abbassi@pgu.ac.ir

[1] Chemistry Department, Faculty of Sciences, Persian Gulf University, 75169 Bushehr, Iran

[2] Department of Chemistry, College of Sciences, Shiraz University, 71454 Shiraz, Iran

Results and discussion

To optimize conditions, several equimolar mixtures of thioacetic acid and phenyl glycidyl ether were separately treated with different amounts of basic Al_2O_3 (from 10 to 100 mol %) at room temperature and 80 °C. All reactions had not been completed within 0.5 h and other than the desired β-hydroxy thioester product and unreacted substrates, some unidentified byproducts were observed on the TLC. However, another reaction of thioacetic acid (1 mmol) and phenyl glycidyl ether (1 mmol) in the absence of basic Al_2O_3 had been completed within 0.5 h at 80 °C to generate the desired β-hydroxy thioester product cleanly. Without any separation, the crude oily product was then treated with *n*-butyl acrylate (1 mmol) under solvent-free condition. There was no reaction between them at room temperature or 80 °C within 24 h. Next, the similar reaction in the presence of basic Al_2O_3 was studied. In the presence of 0.1–0.5 g of Al_2O_3, the outcomes of the reactions were not satisfying. For example, using 0.3 g of Al_2O_3, and stirring the solid–liquid two-phase reaction mixture at room temperature, the conversion was uncompleted after 24 h and the desired product was obtained in only 48 % yield. However, using 0.6 g of basic Al_2O_3, the liquid reacting substrates were completely absorbed on the surface of Al_2O_3. The desired thia-Michael adduct was obtained in 92 % yield when the resulting powder was shaken by a mechanical shaker at room temperature for 4 h.

The reusability of the catalyst was also studied. Al_2O_3 was separated each time and after washing with EtOAc and drying at 120 °C was reused in another similar reaction. No significant decrease in catalyst activity was observed even after seven recycled runs.

The optimized conditions were then applied for the preparation of thia-Michael adducts of other β-hydroxy thioesters using structurally diverse epoxides, thioacids and electron-deficient alkenes. The results are presented in Table 1.

As the results show, the structurally diverse thia-Michael adducts of β-acyloxy mercaptans have been produced in high yields by this procedure. The reaction of structurally diverse electron-deficient alkenes with β-hydroxy acetic acid thioesters produced from thioacetic acid and different epoxides proceeded to completion within 4 h, whereas the similar reactions with β-hydroxy benzoic acid thioesters proceeded much slowly and required 7 h to reach endpoint. However, the synthesis of β-acyloxy thioethers by starting from styrene oxide under reaction conditions was not synthetically rewarding and a complex mixture of unidentified products was produced in all experiments.

A proposed reaction mechanism is shown in Scheme 1. At first, the β-hydroxy thioester is produced regioselectively by attacking thioacid to the less-hindered carbon atom of the terminal epoxide. Next, an intramolecular S→O acyl group migration generates in situ the corresponding β-acyloxy mercaptan intermediate which subsequently undergoes conjugate addition with the electron-deficient alkene to produce the corresponding thia-Michael adduct. The actual function and precise role of basic Al_2O_3 are not clear to us. In our opinion, the last two stages can be efficiently promoted by basic Al_2O_3. It accelerates the intramolecular S→O acyl group migration via activations of carbonyl group and increasing the nucleophilic character of the attacking hydroxyl group by abstraction of its proton. Similarly, it can accelerate thia-Michael addition by interaction with electron-withdrawing group of Michael acceptor and increasing the nucleophilic character of the −SH group.

Conclusion

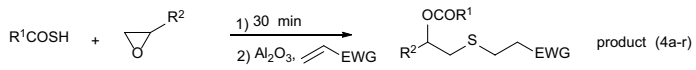
In conclusion, we have presented that basic Al_2O_3 is an efficient catalyst for high-yielding one-pot synthesis of functionalized thioethers from commercially available thioacids, epoxides and electron-deficient alkenes in solvent-free conditions. In this study, a β-hydroxy thioester is generated cleanly by heating an epoxide with a thioacid without needing any catalyst which is then treated with an electron-deficient alkene on the basic Al_2O_3 surface to obtain thia-Michael adducts of β-acyloxy mercaptans in high yields. In comparison with the previous work [28], this study demonstrated that basic Al_2O_3 is more efficient than SiO_2 and is as efficient as Et_3N/SiO_2 combined catalyst to synthesize β-acyloxy thioethers using epoxides, thioacids and electron-deficient alkenes. Advantageously, it was recoverable and reusable at least for seven runs.

Experimental

General procedure

A mixture of an epoxide (2 mmol) and a thioacid (2 mmol) in an Erlenmeyer flask (25 mL) was heated at 80 °C for 0.5 h. During this period, the starting epoxide had been completely consumed. Next, an electron-deficient alkene (2 mmol) and basic Al_2O_3 (1.2 g) were added to Erlenmeyer flask and the resulting powder was shaken at room temperature using a mechanical shaker. After consumption of β-hydroxy thioester (4–7 h), the reaction was worked up by addition of EtOAc (3 × 3 mL) to mixture and filtration. The corresponding thia-Michael adducts were obtained in high yields after purification by column chromatography on silica gel.

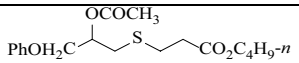
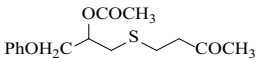
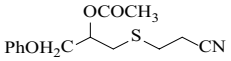
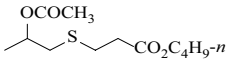
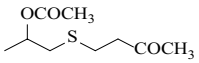
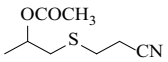
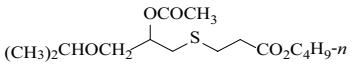
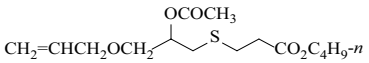
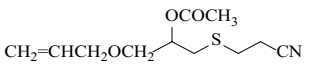
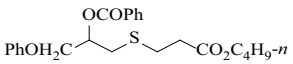
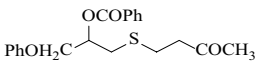
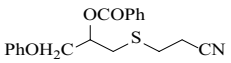
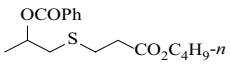
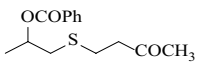
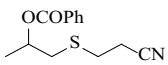
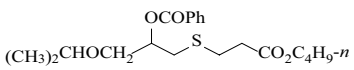
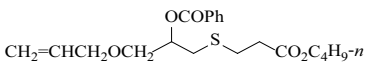
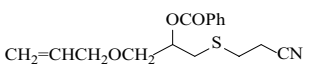
Table 1 Synthesis of thioethers via addition of in situ generated β-acyloxy mercaptans to electron-deficient alkenes

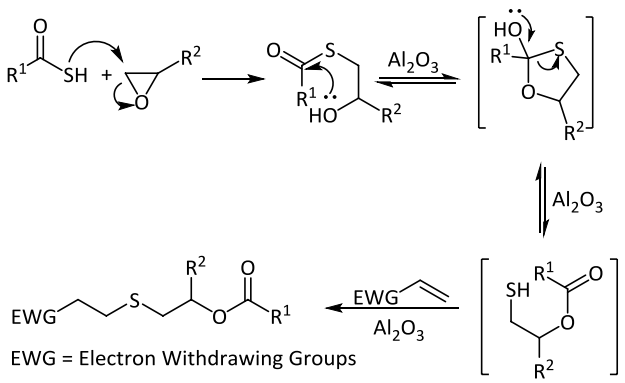


R^1: CH_3 (1a); Ph (1b)

R^2: CH_2OPh (2a); CH_3 (2b); $CH_2OCH(CH_3)_2$ (2c); $CH_2CH{=}CH_2$ (2d)

EWG: $CO_2C_4H_9$-*n* (3a), $COCH_3$ (3b), CN (3c)

Entry	R^1	R^2	EWG	Product		Yield
1	**1a**	**2a**	**3a**		**4a**	92
2	**1a**	**2a**	**3b**		**4b**	90
3	**1a**	**2a**	**3c**		**4c**	94
7	**1a**	**2b**	**3a**		**4d**	87
8	**1a**	**2b**	**3b**		**4e**	84
9	**1a**	**2b**	**3c**		**4f**	87
13	**1a**	**2c**	**3a**		**4g**	89
15	**1a**	**2d**	**3a**		**4h**	90
16	**1a**	**2d**	**3c**		**4i**	85
4	**1b**	**2a**	**3a**		**4j**	90
5	**1b**	**2a**	**3b**		**4k**	84
6	**1b**	**2a**	**3c**		**4l**	93
10	**1b**	**2b**	**3a**		**4m**	86
11	**1b**	**2b**	**3b**		**4n**	85
12	**1b**	**2b**	**3c**		**4o**	82
14	**1b**	**2c**	**3a**		**4p**	87
17	**1b**	**2d**	**3a**		**4q**	91
18	**1b**	**2d**	**3c**		**4r**	90



Scheme 1 A proposed reaction pathway

Butyl 3-{[2-(acetyloxy)-3-phenoxypropyl]sulfanyl}propanoate (4a) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.21–7.13 (m, 2H), 6.88–6.71 (m, 3H), 5.22–5.12 (m, 1H), 4.11–4.50 (m, 2H), 3.99 (t, J = 6.6 Hz, 2H), 2.88–2.69 (m, 4H), 2.54–2.48 (m, 2H), 1.98 (s, 3H), 1.56–1.45 (m, 2H), 1.34–1.17 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.7, 170.3, 158.4, 129.5, 121.3, 114.6, 71.4, 67.2, 64.5, 34.7, 32.2, 30.6, 27.6, 21.0, 19.1, 13.7; IR (neat): ν (cm^{-1}) = 1735 (C = O ester), 1597 (C = C aromatic); Anal. Calcd for ($C_{18}H_{26}O_5S$): C, 60.99; H, 7.39; S, 9.05. Found: C, 60.76; H, 7.51; S, 8.90.

2-[(3-Oxobutyl)sulfanyl]-1-(phenoxymethyl)ethyl acetate (4b) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.24–7.17 (m, 2H), 6.91–6.81 (m, 3H), 5.21–5.12 (m, 1H), 4.09–4.05 (m, 2H), 2.88–2.61 (m, 6H), 2.06 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 206.5, 170.4, 158.4, 129.5, 121.2, 114.6, 71.4, 67.2, 43.4, 32.4, 30.0, 26.3, 21.1; IR (neat): ν (cm^{-1}) = 1740 (C = O ester), 1717 (C = O ketone), 1597 (C = C aromatic); Anal. Calcd for ($C_{15}H_{20}O_4S$): C, 60.79; H, 6.80; S, 10.82. Found: C, 60.66; H, 6.96; S, 11.04.

2-[(2-Cyanoethyl)sulfanyl]-1-(phenoxymethyl)ethyl acetate (4c) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.23–7.16 (m, 2H), 6.91–6.80 (m, 3H), 5.17–5.09 (m, 1H), 4.11–4.01 (m, 2H), 2.93–2.69 (m, 4H), 2.56–2.51 (m, 2H), 2.00 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 170.3, 158.3, 129.6, 121.4, 118.6, 114.7, 71.1, 67.2, 32.0, 27.9, 21.0, 18.6; IR (neat): ν (cm^{-1}) = 2242 (CN), 1740 (C = O ester), 1597 (C = C aromatic); Anal. Calcd for ($C_{14}H_{17}NO_3S$): C, 60.19; H, 6.13; S, 11.48. Found: C, 60.31; H, 6.16; S, 11.24.

Butyl 3-{[2-(acetyloxy)propyl]sulfanyl}propanoate (4d) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.01–4.89 (m, 1H), 4.02 (t, J = 6.6 Hz, 2H), 2.91–2.49 (m, 6H), 1.97 (s, 3H), 1.56–1.50 (m, 2H), 1.34–1.17 (m, 2H), 1.23 (d, J = 6.3 Hz, 3H), 0.85 (t, J = 7.3 Hz,3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.8, 170.4, 69.9, 64.6, 37.4, 34.8, 30.6, 27.6, 21.2, 19.2, 19.1, 13.7; IR (neat): ν (cm^{-1}) = 1735 (C = O ester); Anal. Calcd for ($C_{12}H_{22}O_4S$): C, 54.93; H, 8.45; S, 12.22. Found: C, 55.05; H, 8.56; S, 12.05.

1-Methyl-2-[(3-oxobutyl)sulfanyl]ethyl acetate (4e) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 4.97–4.87 (m, 1H), 2.63–2.50 (m, 6H), 2.10 (s, 3H), 1.97 (s. 3H), 1.24 (d, J = 6.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 206.6, 170.4, 69.9, 43.6, 37.6, 30.0, 26.3,21.2, 19.1; IR (neat): ν (cm^{-1}) = 1740 (C = O ester), 1717 (C = O ketone); Anal. Calcd for ($C_9H_{16}O_3S$): C, 52.91; H, 7.89; S, 15.70. Found: C, 52.70; H, 7.96; S, 15.64.

2-[(2-Cyanoethyl)sulfanyl]-1-methylethyl acetate (4f) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 4.96–4.87 (m, 1H), 2.81–2.72 (m, 2H), 2.68–2.58 (m, 4H), 1.99 (s, 3H), 1.26 (d, J = 6.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 170.3, 118.3, 69.6, 37.2, 27.9, 21.1, 19.0, 18.7; IR (neat): ν (cm^{-1}) = 2242 (CN), 1739 (C = O ester); Anal. Calcd for ($C_8H_{13}NO_2S$): C, 51.31; H, 7.00; S, 17.12. Found: C, 51.46; H, 7.16; S, 17.01.

Butyl 3-{[2-(acetyloxy)-3-isopropoxypropyl]sulfanyl}propanoate (4g) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 4.97–4.91 (m, 1H), 4.02 (t, J = 6.6 Hz, 2H), 3.54–3.43 (m, 3H), 2.78–2.64 (m, 4H), 2.56–2.50 (m, 2H), 2.00 (s, 3H), 1.57–1.46 (m, 2H), 1.32–1.24 (m, 2H), 1.06 (d, J = 6.2 Hz, 6H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.5, 170.0, 72.1, 72.0, 67.3, 64.2, 33.4, 32.1, 30.4, 27.4, 21.8, 20.8, 18.9, 13.5; IR (neat): ν (cm^{-1}) = 1735 (C = O ester); Anal. Calcd for ($C_{15}H_{28}O_5S$): C, 56.22; H, 8.81; S, 10.01. Found: C, 56.06; H, 8.96; S, 10.04.

Butyl 3-{[2-(acetyloxy)-3-(allyloxy)propyl]sulfanyl}propanoate (4h) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.89–5.73 (m, 1H), 5.23–4.94 (m, 3H), 4.02 (t, J = 6.6 Hz, 2H), 3.95–3.92 (m, 2H), 3.58–3.46 (m, 2H), 2.80–2.61 (m, 4H), 2.57–2.50 (m, 2H), 2.01 (s, 3H), 1.60–1.49 (m, 2H), 1.38–1.24 (m, 2H) 0.68 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.7, 170.2, 134.3, 117.1, 72.1, 71.9, 69.3, 64.4, 34.7, 32.2, 30.5, 27.5, 21.0, 19.0, 13.6; IR (neat): ν (cm^{-1}) = 1735 (C = O ester), 1647 (C = C alkene); Anal. Calcd for ($C_{15}H_{26}O_5S$): C, 56.58; H, 8.23; S, 10.07. Found: C, 56.66; H, 8.16; S, 10.14.

2-(Allyloxy)-1-{[(2-cyanoethyl)sulfanyl]methyl}ethyl acetate (4i) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.90–5.74 (m, 1H), 5.25–5.19 (m, 2H), 4.99–4.94 (m, 1H), 3.97–3.93 (m, 2H), 3.62–3.50 (m, 2H), 2.86–2.71 (m, 4H), 2.65–2.59 (m, 2H), 2.02 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 170.4, 134.2, 118.2, 117.4, 72.2, 71.7, 69.1, 32.1, 27.9, 21.1, 19.7; IR (neat): ν (cm^{-1}) = 2242 (CN), 1740 (C = O ester), 1647 (C = C alkene); Anal. Calcd for ($C_{11}H_{17}NO_3S$): C, 54.30; H, 7.04; S, 13.18. Found: C, 54.21; H, 7.16; S, 13.14.

2-[(3-Butoxy-3-oxopropyl)sulfanyl]-1-(phenoxymethyl) ethyl benzoate (4j) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.97–7.92 (m, 2H), 7.46–7.40 (m, 1H), 7.34–7.28 (m, 2H), 7.17–7.12 (m, 2H), 6.87–6.80 (m, 3H), 5.44–5.36 (m, 1H), 4.26–4.13 (m, 2H), 3.97 (t, J = 6.6 Hz, 2H), 3.01–2.85 (m, 2H), 2.78 (t, J = 7.0 Hz, 2H), 2.52 (t, J = 7.0 Hz, 2H),1.53–1.44 (m, 2H), 1.30–1.16 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.7, 165.9, 158.5, 133.2, 129.9, 129.8, 129.6, 128.4, 121.3, 114.8, 72.2, 67.3, 64.6, 34.8, 32.4, 30.6, 27.8, 19.1, 13.7; IR (neat): ν (cm^{-1}) = 1735 (C = O ester), 1717 (C = O conjugated ester), 1597 (C = C aromatic); Anal. Calcd for ($C_{23}H_{28}O_5S$): C, 66.32; H, 6.78; S, 7.70. Found: C, 66.56; H, 6.60; S, 7.81.

2-[(3-Oxobutyl)sulfanyl]-1-(phenoxymethyl)ethyl benzoate (4k) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.94–7.87 (m, 2H), 7.44–7.38 (m, 1H), 7.32–7.25 (m, 2H), 7.18–7.11 (m, 2H), 7.86–6.74 (m, 3H), 5.42–3.34 (m, 1H), 4.05–3.97 (m, 2H), 2.98–2.81 (m, 2H), 2.74–2.68 (m, 2H), 2.61–2.55 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 206.6, 166.0, 158.5, 133.3, 129.8, 129.6, 129.5, 128.5, 121.3, 114.8, 71.5, 67.3, 43.6, 33.0, 30.0, 26.5; IR (neat): ν (cm^{-1}) = 1717 (C = O ketone and conjugated ester), 1597 (C = C aromatic); Anal. Calcd for ($C_{20}H_{22}O_4S$): C, 67.01; H, 6.19; S, 8.95. Found: C, 66.86; H, 6.16; S, 9.10.

2-[(2-Cyanoethyl)sulfanyl]-1-(phenoxymethyl)ethyl benzoate (4l) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.96–7.91 (m, 2H), 7.49–7.43 (m, 1H), 7.36–7.30 (m, 2H), 7.22–7.15 (m, 2H), 6.90–6.76 (m, 3H), 5.42–5.32 (m, 1H), 4.24–4.14 (m, 2H), 3.03–2.81 (m, 2H), 2.78–2.63 (m, 2H), 2.56–2.51 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 166.1, 158.4, 133.4, 129.8, 129.7, 129.7, 128.5, 121.5, 118.4, 114.8, 72.0, 67.2, 32.2, 28.1, 18.8; IR (neat): ν (cm^{-1}) = 2248 (CN), 1717 (C = O conjugated ester), 1597 (C = C aromatic); Anal. Calcd for ($C_{19}H_{19}NO_3S$): C, 66.84; H, 5.61; S, 9.39. Found: C, 66.89; H, 5.46; S, 9.44.

2-[(3-Butoxy-3-oxopropyl)sulfanyl]-1-methylethyl benzoate (4m) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.96–7.92 (m, 2H), 7.47–7.40 (m, 1H), 7.35–7.28 (m, 2H), 5.16–5.11 (m, 1H), 3.97 (t, J = 6.6 Hz, 2H), 2.76–2.61 (m, 2H), 2.54–2.48 (m, 2H), 1.50–1.43 (m, 2H), 1.34 (d, J = 6.3 Hz, 3H), 1.32–1.14 (m, 2H), 0.81 (t, J = 7.2 Hz Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.7, 165.8, 132.9, 130.3, 129.5, 128.6, 70.6, 64.4, 37.4, 34.9, 30.5, 27.7, 19.1, 13.6; IR (neat): ν (cm^{-1}) = 1735 (C = O ester), 1720 (C = O conjugated ester); Anal. Calcd for ($C_{17}H_{24}O_4S$): C, 62.93; H, 7.46; S, 9.88. Found: C, 63.06; H, 7.29; S, 9.84.

1-Methyl-2-[(3-oxobutyl)sulfanyl]ethyl benzoate (4n) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.98–7.93 (m, 2H), 7.48–7.45 (m, 1H), 7.39–7.34 (m, 2H), 5.21–5.18 (m, 1H), 2.79–2.65 (m, 6H), 2.07 (s, 3H), 1.36 (d, J = 6.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 206.5, 165.8, 132.9, 130.3, 129.5, 128.3, 70.6, 43.6, 37.7, 29.9, 26.4, 19.2; IR (neat): ν (cm^{-1}) = 1717 (C = O ketone and conjugated ester), 1601 (C = C aromatic); Anal. Calcd for ($C_{14}H_{18}O_3S$): C, 63.13; H, 6.81; S, 12.04. Found: C, 63.22; H, 6.96; S, 11.99.

2-[(2-Cyanoethyl)sulfanyl]-1-methylethyl benzoate (4o) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.96–7.89 (m, 2H), 7.49–7.43 (m, 1H), 7.38–7.29 (m, 2H), 5.21–5.09 (m, 1H), 2.83–2.64 (m, 4H), 2.57–2.53 (m, 2H), 1.35 (d, J = 6.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.9, 133.1, 130.1, 129.5, 128.5, 118.3, 70.4, 37.3, 28.1, 19.5, 19.2; IR (neat): ν (cm^{-1}) = 2242 (CN), 1717 (C = O conjugated ester); Anal. Calcd for ($C_{13}H_{15}NO_2S$): C, 62.62; H, 6.06; S, 12.86. Found: C, 62.76; H, 5.96; S, 12.80.

2-[(3-Butoxy-3-oxopropyl)sulfanyl]-1-(isopropoxymethyl) ethyl benzoate (4p) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.99–7.92 (m, 2H), 7.49–7.43 (m, 1H), 7.38–7.30 (m, 2H), 5.24–5.15 (m, 1H), 3.99 (t, J = 6.6 Hz, 2H), 3.69–3.47 (m, 3H), 2.93–2.76 (m, 4H), 2.53 (t, J = 7.1 Hz, 2H), 1.56–1.44 (m, 2H), 1.34–1.19 (m, 2H), 1.06 (d, J = 6.1 Hz, 6H), 0.82 (t, J = 7.3, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.5, 165.6, 132.9, 130.1, 129.5, 128.6, 72.9, 72.1, 67.5, 64.2, 34.7, 32.3, 30.5, 27.5, 21.9, 19.0, 13.6; IR (neat): ν (cm^{-1}) = 1735 (C = O ester), 1717 (C = O conjugated ester); Anal. Calcd for ($C_{20}H_{30}O_5S$): C, 62.80; H, 7.91; S, 8.38. Found: C, 62.63; H, 7.86; S, 8.50.

2-(Allyloxy)-1-{[(3-butoxy-3-oxopropyl)sulfanyl] methyl}ethyl benzoate (4q) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.08–8.01 (m, 2H), 7.60–7.53 (m, 1H), 7.48–7.41 (m, 2H), 5.97–5.82 (m, 1H), 5.35–5.15 (m, 3H), 4.08 (t, $J = 6.6$ Hz, 2H), 4.07–4.03 (m, 2H), 3.82–3.70 (m, 2H), 3.01–2.84 (m, 4H), 2.65–2.59 (m, 2H), 1.66–1.54 (m, 2H), 1.44–1.29 (m, 2H), 0.84 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 171.8, 165.9, 134.4, 133.1, 130.0, 129.7, 128.4, 117.2, 72.7, 72.3, 69.5, 64.6, 34.8, 32.5, 30.6, 27.7, 19.1, 13.7;; IR (neat): ν (cm^{-1}) = 1735 (C = O ester), 1717 (C = O conjugated ester), 1647 (C = C alkene); Anal. Calcd for ($C_{20}H_{28}O_5S$): C, 63.13; H, 7.42; S, 8.43. Found: C, 63.32; H, 7.31; S, 8.30.

2-(Allyloxy)-1-{[(2-cyanoethyl)sulfanyl]methyl}ethyl benzoate (4r) Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.97–7.86 (m, 2H), 7.47–7.40 (m, 1H), 7.35–7.27 (m, 2H), 5.85–5.69 (m, 1H), 5.23–5.03 (m, 3H), 3.94–3.85 (m, 2H), 3.69–3.57 (m, 2H), 2.93–2.77 (m, 2H), 2.75–2.69 (m, 2H), 2.56–2.51 (m,2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.8, 133.7, 132.8, 129.8, 129.6, 128.5, 118.4, 117.2, 72.5, 72.2, 69.3, 32.2, 28.0, 18.7; IR (neat): ν (cm^{-1}) = 2242 (CN), 1717 (C = O conjugated ester), 1647 (C = C alkene); Anal. Calcd for ($C_{16}H_{19}NO_3S$): C, 62.93; H, 6.27; S, 10.50. Found: C, 62.77; H, 6.17; S, 10.69.

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