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[4+2] Annulation – Convenient Synthesis of Substituted Dihydropyranones in Aqueous Media

Yan Ouyang,[a,c] Jie Huang,[a,b] Wei Pan,[a] Yongjiu Liang,[b] Yang Yang,[a] and Dewen Dong*[a,b]

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A facile and convenient synthesis of dihydropyranones has been developed by a formal [4+2] annulation of readily available α-acetyl ketene S,S-acetals with various aldehydes, involving a tandem aldol reaction and conjugate addition-elimination reaction, in the presence of NaOH in water.

Introduction

2,3-Dihydro-4*H*-pyran-4-ones have attracted considerable research attention for their presence in a diverse array of natural products and their useful bio-, physio-, and pharmacological activities.[1,2] In addition, their rich source of functionalities renders them versatile intermediates in the synthesis of a variety of biologically important compounds, such as carbohydrates,[3] antibiotics,[4] and toxins.[5] The development of efficient syntheses of 2,3-dihydro-4*H*-pyran-4-ones has been the focus of much research for many decades and continues to be an active area of research today. A pioneering synthetic approach for such heterocycles was established through the hetero-Diels–Alder reaction of carbonyl compounds and activated dienes by Danishefsky and co-workers.[6] Many papers and reviews subsequently reported on the variations and improvements of the originally published Danishefsky synthesis, which provides the basis for a number of synthetic strategies.[7] Particularly, the application of asymmetric catalysis to this protocol makes it a very powerful synthetic tool.[8] Other methods, such as Claisen rearrangements, ring opening of epoxides, iodocyclisation, olefin metathesis, and Prins cyclization have also been developed.[9] The synthesis of 2,3-dihydro-4*H*-pyran-4-ones has also been achieved by nucleophilic addition to β-ethoxy-α,β-unsaturated lactones,[10] the oxidative cyclization of β-hydroxyenones with Pd^{II},[4] the intramolecular cyclization of a keto acid onto a cyclohexenone,[11] and the aldol reaction of enones.[12]

[a] Department of Chemistry, Northeast Normal University, Changchun 130024, China
[b] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[c] Department of Chemistry, Yili Normal University, Yining 835000, China
Fax: +86-431-85098635
E-mail: dongdw663@nenu.edu.cn

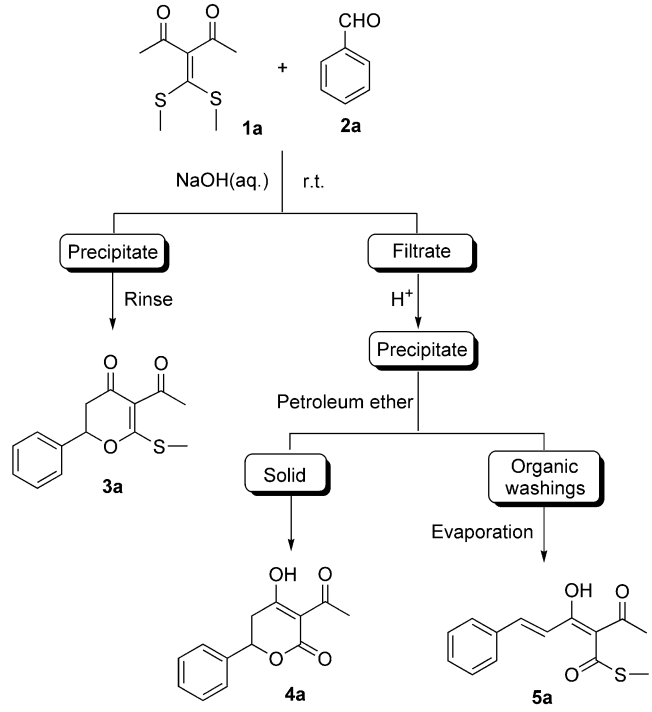
Over the past decades, the utility of α-oxo ketene S,S-acetals as versatile three-carbon 1,3-electrophilic intermediates in organic synthesis has been recognized.[13] During the course of our studies on the chemistry of α-oxo ketene S,S-acetals, we successfully developed novel strategies for highly substituted six-membered-ring carbocycles and heterocycles, relying upon the utilization of α-alkenoyl ketene S,S-acetals—aldol condensation products of α-acetyl ketene S,S-acetals—as a five-carbon 1,5-bielectrophilic species in the formal [5+1] annulation with various nucleophiles.[14] Considering the important synthetic utility of α-alkenoyl ketene S,S-acetals, we recently investigated the aldol condensation reaction of 3-(1,3-dithiolan-2-ylidene)pentane-2,4-dione in water and obtained both mono- and double-condensed products,[15] which were further used for the synthesis of thiopyrano[2,3-*b*]thiopyran-4,5-diones by a double formal [5+1] annulation.[16] In connection with our previous work and our continuing interest in the synthesis of valuable heterocycles, we examined the aldol reactions of α-oxo ketene S,S-acetals **1** with aldehydes **2** in aqueous media. As a result, we achieved a convenient one-pot synthesis of substituted dihydropyranones by a base-promoted formal [4+2] annulation of **1** with **2** in the presence of NaOH in water. Herein, we wish to report our results and propose a mechanism for the reactions.

Results and Discussion

α-Oxo ketene S,S-acetals **1a** and **1b** were prepared from commercially available acetylacetone with carbon disulfide, methyl iodide, and ethyl bromide in water in excellent yields according to our reported procedure.[17]

We initially investigated the reaction of 3-[bis(methylthio)methylene]pentane-2,4-dione (**1a**) with benzaldehyde (**2a**, 2.0 equiv.) at room temperature in the presence of

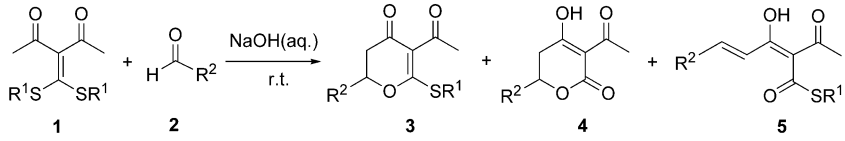
K_2CO_3 (4.0 equiv.) in water. Unfortunately, the reaction proceeded very sluggishly, and most of the substrate **1a** remained intact after one week. We then subjected **1a** and **2a** (1.0 equiv.) to NaOH (1.0 equiv.) in water at room temperature, and the reaction proceeded smoothly as indicated by TLC. As shown in Scheme 1, we filtered the resulting mixture to furnish a white solid, which was quite pure after being washed with water, and characterized it as 5-acetyl-6-(methylthio)-2-phenyl-2,3-dihydropyran-4-one (**3a**) on the basis of its spectra and analytical data (55% yield, Table 1, Entry 1). We acidified the filtrate with 10% aqueous HCl (to pH ≈ 1). We collected the resulting precipitate by filtration, washed it with water and petroleum ether several times, and dried it in vacuo to give another white solid, characterized as 3-acetyl-4-hydroxy-6-phenyl-5,6-dihydropyran-2-one (**4a**, 18% yield). We dried the combined organic washings with anhydrous Na_2SO_4 and filtered and concentrated them to afford the third white solid, which we characterized as (2*E*,4*E*)-*S*-methyl 2-acetyl-3-hydroxy-5-phenylpenta-2,4-dienethioate (**5a**, 21% yield). We established the structure of **4a** by X-ray single-crystal analyses (Figure 1) and confirmed it by NMR spectroscopy. Further experiments revealed that both high reaction temperature and excess NaOH resulted in lower yields of **3a**. It is worth noting that the one-pot reaction is associated with a very simple separation process.



Scheme 1. Reaction between **1a** and **2a** in aqueous media.

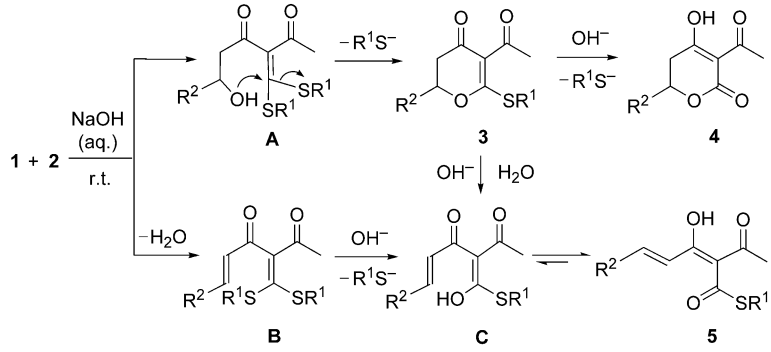
Under the conditions used for **3a** in Table 1, Entry 1, we carried out a range of reactions of **1a** with a variety of selected aldehydes **2**, and some results are listed in Table 1. We observed that all the reactions of **1a** with aromatic and heterocyclic aldehydes proceeded smoothly under the essentially mild basic conditions in water to afford the corresponding substituted dihydropyranones **3** and **4** and 2,4-dienethioesters **5** (Table 1, Entries 2–8). Interestingly, the reaction of **1a** with aqueous formaldehyde (**2i**) afforded 3-acetyl-4-hydroxy-5,6-dihydropyran-2-one (**4i**) in high yield (Table 1, Entry 9). We could not isolate products **3i** and **5i**, which might have been present in trace amounts in the reaction mixture. Based on the reaction times and yields, it seems the reactivity of aldehydes **2** follows the sequence: aromatic aldehydes with electron-withdrawing groups > heterocyclic aldehydes > halogenated aromatic aldehydes > benzaldehyde > aromatic aldehydes with electron-donating groups. In the case of 4-nitrobenzaldehyde (**2d**), the reaction

Table 1. Reactions of α-oxo ketene S,S-acetals **1** with selected aldehydes **2** in aqueous media.



Entry	**1**	R^1	**2**	R^2	Time [h]	**3**	Yield [%][a]	**4**	Yield [%][a]	**5**	Yield [%][a]
1	**1a**	Me	**2a**	Ph	8.0	**3a**	55	**4a**	18	**5a**	21
2	**1a**	Me	**2b**	4-MeC_6H_4	12.0	**3b**	53	**4b**	17	**5b**	26
3	**1a**	Me	**2c**	4-ClC_6H_4	3.0	**3c**	79	**4c**	10	**5c**	7
4	**1a**	Me	**2d**	4-$O_2NC_6H_4$	0.5	**3d**	81	**4d**	6	**5d**	8
5	**1a**	Me	**2e**	4-$MeOC_6H_4$	14.0	**3e**	46	**4e**	13	**5e**	33
6	**1a**	Me	**2f**	PhCH=CH	6.0	**3f**	45	**4f**	19	**5f**	26
7	**1a**	Me	**2g**	2-thienyl	1.5	**3g**	47	**4g**	20	**5g**	29
8	**1a**	Me	**2h**	2-furyl	1.0	**3h**	56	**4h**	16	**5h**	23
9	**1a**	Me	**2i**	H	8.0	**3i**	0	**4i**	92	**5i**	0
10[b]	**1a**	Me	**2d**	4-$O_2NC_6H_4$	1.0	**3d**	95	**4d**	0	**5d**	0
11	**1b**	Et	**2a**	Ph	16.0	**3j**	48	**4a**	9	**5j**	27
12	**1b**	Et	**2b**	4-MeC_6H_4	20.0	**3k**	54	**4b**	13	**5k**	25
13	**1b**	Et	**2c**	4-ClC_6H_4	8.0	**3l**	63	**4c**	12	**5l**	18
14	**1b**	Et	**2d**	4-$O_2NC_6H_4$	1.0	**3m**	69	**4d**	14	**5m**	12

[a] Isolated yields. [b] Aqueous K_2CO_3 (1.0 equiv.) was employed in this case.



Scheme 2. Proposed mechanism for the reaction of **1** and **2** in aqueous media.

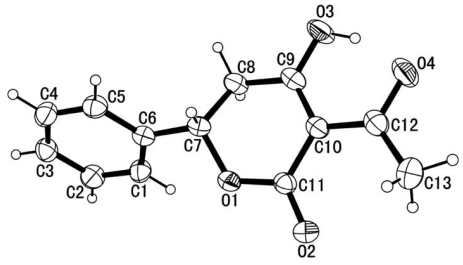


Figure 1. ORTEP drawing of **4a**.

could even proceed in aqueous K_2CO_3 (1.0 equiv.) at room temperature and exclusively furnished 2,3-dihydropyran-4-one **3d** in 95% yield (Table 1, Entry 10). It should be mentioned that we confirmed the structure of **5b** by X-ray single-crystal analysis (Figure 2).

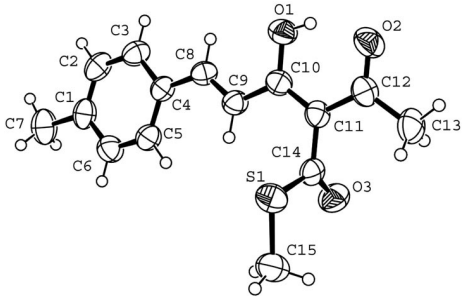


Figure 2. ORTEP drawing of **5b**.

Next, we extended the synthesis of dihydropyranones by subjecting **1b** and selected aldehydes **2** to the identical conditions. These reactions of **1b** required longer reaction times than was required for a complete conversion of **1a** (Table 1, Entries 11–14). However, the reaction of **1a** or **1b** with aliphatic aldehydes, such as acetaldehyde, under the identical conditions could not produce the corresponding substituted dihydropyranones **3** and/or **4**. All the results shown above demonstrated the efficiency and versatility of the cyclization reaction with respect to a range of heterocyclic and aromatic aldehydes. Thus, we provided a novel one-pot synthesis of substituted dihydropyranones from α-oxo ketene S,S-acetals and aldehydes in aqueous media. It is worth noting that the dihydropyranones of type **3** and **4** possess very rich functionality, such as acetyl and alkylthio or hydroxy groups, and in particular an α,β-unsaturated carbonyl moiety, which may render them extremely versatile as synthetic scaffolds in the preparation of natural and synthetic compounds with important biological and pharmacological activities.

To obtain insight into the mechanism of the one-pot reaction, we conducted a separate experiment, in which we treated **3c** with 1.0 equiv. of NaOH at room temperature for 16 h and obtained **4c** and **5c** in 64% and 33% yield, respectively. On the basis of these results, a mechanism for the reaction of **1** and **2** in water is proposed as depicted in Scheme 2. Under the basic conditions, the aldol reaction of **1** and **2** generates **A**, which undergoes an intramolecular addition-elimination (nucleophilic vinylic substitution, S_NV) reaction to afford **3**.[12a,14,18] With the attack of OH^-, **3** undergoes competitive S_NV and ring-opening reactions to give **4** and intermediate **C**, respectively. In another pathway, **C** can be formed by the S_NV reaction of **B**, derived from the aldol condensation of **1** and **2**. Finally, **C** is converted into its isomer **5**.

Conclusions

In summary, a convenient one-pot synthesis of substituted dihydropyranones of types **3** and **4** and 2,4-diene thioesters **5** was developed by a tandem aldol reaction and conjugate addition-elimination of α-acetyl ketene S,S-acetals **1** with aldehydes **2** in the presence of NaOH in water. The simple reaction procedure and product separation, mild conditions, readily available substrates, and potentially useful products make this synthetic protocol very attractive.

Experimental Section

Typical Procedure for the Synthesis of 3–5 (3a–5a as Examples): To aqueous NaOH (0.2 M, 10 mL) were added **1a** (409 mg, 2.0 mmol) and **2a** (212 mg, 2.0 mmol). The mixture was stirred at room temperature for 12.0 h. After the substrate **2a** was consumed as indicated by TLC, the resulting mixture was filtered. The precipitate was washed with water (3 × 20 mL) and dried in vacuo to give **3a** as a white solid (289 mg, 55%). The aqueous filtrate was acidified with 10% aqueous HCl (to pH ≈ 1), and a white solid precipitated. The resulting precipitate was collected by filtration, washed with water (3 × 20 mL) and petroleum ether (4 × 20 mL), and dried in

vacuo to give **4a** as a white solid (84 mg, 18%). The combined organic washings were dried with anhydrous Na_2SO_4, filtered and concentrated to afford **5a** as a white solid (110 mg, 21%).

In most cases, products **3**–**5** were obtained as quite pure solids without purification, while in some cases, oily products required further purification, which was carried out by flash chromatography over silica gel (for products **3**: ethyl acetate/petroleum ether 10%; for products **4**: ethyl acetate/petroleum ether 20%; for products **5**: petroleum ether only).

Selected Data for 3–5:

5-Acetyl-6-methylthio-2-phenyl-2,3-dihydropyran-4-one (3a): White solid; m.p. 119–121 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.29 (s, 3 H), 2.56 (s, 3 H), 2.78 (dd, J = 3.0, 17.0 Hz, 1 H), 2.98 (dd, J = 14.0, 17.0 Hz, 1 H), 5.55 (dd, J = 3.0, 14.0 Hz, 1 H), 7.40–7.43 (m, 2 H), 7.44–7.47 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.4, 32.2, 43.1, 83.4, 115.8, 126.3, 129.3, 129.7, 136.7, 187.4, 188.5, 196.8 ppm. IR (KBr): $\tilde{\nu}$ = 1658, 1634, 1500, 1428, 1344, 1185, 879 cm^{-1}. $C_{14}H_{14}O_3S$ (262.07): calcd. C 64.10, H 5.38; found C 64.24, H 5.29.

3-Acetyl-4-hydroxy-6-phenyl-5,6-dihydropyran-2-one (4a): White solid; m.p. 122–124 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.66 (s, 3 H), 2.87 (dd, J = 3.0, 17.0 Hz, 1 H), 3.05 (dd, J = 12.0, 17.0 Hz, 1 H), 5.43 (dd, J = 3.0, 12.0 Hz, 1 H), 7.39–7.42 (m, 5 H), 17.78 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 25.5, 38.8, 74.1, 102.7, 124.9, 127.8, 128.0, 136.2, 163.1, 193.8, 200.3 ppm. IR (KBr): $\tilde{\nu}$ = 1705, 1645, 1515, 1454, 1224, 1066, 763 cm^{-1}. $C_{13}H_{12}O_4$ (232.07): calcd. C 67.23, H 5.21; found C 67.48, H 5.15.

Crystal Data for 4a: $C_{13}H_{12}O_4$, colourless crystal, M = 232.23, monoclinic, $P2_1/c$, a = 11.911(3) Å, b = 16.494(4) Å, c = 5.7210(15) Å, α = 90.00°, β = 91.806(4) °, γ = 90.00°, V = 1123.4(5) Å^3, Z = 4, T = 293(2) K, F_{000} = 488, R_1 = 0.0471, wR_2 = 0.1110. CCDC-694975 contains the supplementary crystallographic data for **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(2*E*,4*E*)-*S*-Methyl 2-Acetyl-3-hydroxy-5-phenylpenta-2,4-dienethioate (5a): White solid; m.p. 93–95 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.28 (s, 3 H), 2.51 (s, 3 H), 6.81 (d, J = 15.5 Hz, 1 H), 7.38–7.39 (m, 3 H), 7.51–7.52 (m, 2 H), 7.75 (d, J = 16.0 Hz, 1 H), 16.65 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 12.4, 24.7, 116.0, 118.6, 127.4, 127.9, 129.4, 133.7, 141.5, 175.9, 192.7, 195.4 ppm. IR (KBr): $\tilde{\nu}$ = 1656, 1547, 1446, 1338, 1018, 841 cm^{-1}. $C_{14}H_{14}O_3S$ (262.07): calcd. C 64.10, H 5.38; found C 64.27, H 5.34.

5-Acetyl-6-methylthio-2-*p*-tolyl-2,3-dihydropyran-4-one (3b): White solid; m.p. 116–118 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.27 (s, 3 H), 2.39 (s, 3 H), 2.56 (s, 3 H), 2.74 (dd, J = 3.0, 17.0 Hz, 1 H), 2.98 (dd, J = 14.0, 17.0 Hz, 1 H), 5.51 (dd, J = 3.0, 14.0 Hz, 1 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.29 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.3, 21.5, 32.2, 43.0, 83.4, 115.7, 126.4, 123.0, 133.7, 139.8, 187.6, 188.6, 196.8 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1658, 1515, 1438, 1351, 1038, 860 cm^{-1}. $C_{15}H_{16}O_3S$ (276.08): calcd. C 65.19, H 5.84; found C 65.48, H 5.76.

3-Acetyl-4-hydroxy-6-*p*-tolyl-5,6-dihydropyran-2-one (4b): White solid; m.p. 102–104 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.36 (s, 3 H), 2.65 (s, 3 H), 2.85 (dd, J = 3.0, 17.0 Hz, 1 H), 3.04 (dd, J = 12.0, 17.0 Hz, 1 H), 5.40 (dd, J = 3.0, 12.0 Hz, 1 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 17.77 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.4, 26.8, 40.0, 75.3, 103.9, 110.0, 126.2, 129.7, 134.5, 139.1, 164.5, 195.2, 201.6 ppm. IR (KBr): $\tilde{\nu}$ = 1710, 1549, 1515, 1295, 1220, 1060, 813 cm^{-1}. $C_{14}H_{14}O_4$ (246.09): calcd. C 68.28, H 5.73; found C 68.52, H 5.61.

(2*E*,4*E*)-*S*-Methyl 2-Acetyl-3-hydroxy-5-*p*-tolylpenta-2,4-dienethioate (5b): White solid; m.p. 112–114 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.27 (s, 3 H), 2.37 (s, 3 H), 2.50 (s, 3 H), 6.76 (d, J = 15.5 Hz, 1 H), 7.18 (d, J = 7.5 Hz, 2 H), 7.41 (d, J = 7.5 Hz, 2 H), 7.72 (d, J = 15.5 Hz, 1 H), 16.69 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.6, 21.7, 25.9, 117.1, 118.8, 128.7, 129.9, 132.3, 141.3, 142.9, 177.5, 194.0, 196.4 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1652, 1539, 1515, 1385, 1178, 882 cm^{-1}. $C_{15}H_{16}O_3S$ (276.08): calcd. C 65.19, H 5.84; found C 65.08, H 5.92.

Crystal Data for 5b: $C_{15}H_{16}SO_3$, colourless crystal, M = 276.34, monoclinic, $P2_1/n$, a = 7.8916(19) Å, b = 10.404(3) Å, c = 17.376(4) Å, α = 90.00°, β = 93.162(4)°, γ = 90.00°, V = 1424.5(6) Å^3, Z = 4, T = 273(2) K, F_{000} = 584, R_1 = 0.0493, wR_2 = 0.1177. CCDC-694976 contains the supplementary crystallographic data for **5b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5-Acetyl-2-(4-chlorophenyl)-6-methylthio-2,3-dihydropyran-4-one (3c): White solid; m.p. 132–134 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.29 (s, 3 H), 2.56 (s, 3 H), 2.76 (dd, J = 3.0, 17.0 Hz, 1 H), 2.95 (dd, J = 14.0, 17.0 Hz, 1 H), 5.53 (dd, J = 3.0, 14.0 Hz, 1 H), 7.34 (d, J = 8.0 Hz, 2 H), 7.43 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.4, 32.2, 43.0, 82.7, 115.9, 127.7, 129.6, 135.2, 135.7, 186.9, 188.2, 196.7 ppm. IR (KBr): $\tilde{\nu}$ = 1655, 1497, 1449, 1352, 1249, 1089, 864 cm^{-1}. $C_{14}H_{13}ClO_3S$ (296.03): calcd. C 56.66, H 4.42; found C 56.45, H 4.53.

3-Acetyl-6-(4-chlorophenyl)-4-hydroxy-5,6-dihydropyran-2-one (4c): White solid; m.p. 162–164 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.66 (s, 3 H), 2.85 (dd, J = 3.0, 17.0 Hz, 1 H), 3.01 (dd, J = 12.0, 17.0 Hz, 1 H), 5.41 (dd, J = 3.0, 12.0 Hz, 1 H), 7.35 (d, J = 8.5 Hz, 2 H), 7.39 (d, J = 8.5 Hz, 2 H), 17.8 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.8, 40.0, 74.6, 103.8, 127.6, 129.4, 135.1, 136.0, 164.1, 194.9, 201.6 ppm. IR (KBr): $\tilde{\nu}$ = 1645, 1549, 1497, 1422, 1317, 1090, 826 cm^{-1}. $C_{13}H_{11}ClO_4$ (266.03): calcd. C 58.55, H 4.16; found C 58.71, H 4.05.

(2*E*,4*E*)-*S*-Methyl 2-Acetyl-5-(4-chlorophenyl)-3-hydroxypenta-2,4-dienethioate (5c): White solid; m.p. 104–106 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.28 (s, 3 H), 2.51 (s, 3 H), 6.76 (d, J = 15.5 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.43 (d, J = 8.0 Hz, 2 H), 7.68 (d, J = 15.5 Hz, 1 H), 16.61 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.7, 26.1, 117.4, 120.3, 129.4, 129.7, 133.4, 136.6, 141.2, 176.7, 193.8, 197.0 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1596, 1540, 1383, 1269, 1091, 854 cm^{-1}. $C_{14}H_{13}ClO_3S$ (296.03): calcd. C 56.66, H 4.42; found C 56.78, H 4.35.

5-Acetyl-6-(methylthio)-2-(4-nitrophenyl)-2,3-dihydropyran-4-one (3d): White solid; m.p. 180–182 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.34 (s, 3 H), 2.56 (s, 3 H), 2.83 (dd, J = 3.0, 17.0 Hz, 1 H), 2.94 (dd, J = 14.0, 17.0 Hz, 1 H), 5.68 (dd, J = 3.0, 14.0 Hz, 1 H), 7.61 (d, J = 8.5 Hz, 2 H), 8.33 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.5, 32.3, 43.2, 81.9, 116.0, 124.7, 127.0, 143.6, 148.5, 186.1, 188.0, 196.6 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1659, 1514, 1445, 1344, 1042, 854 cm^{-1}. $C_{14}H_{13}NO_5S$ (307.05): calcd. C 54.71, H 4.26, N 4.56; found C 54.92, H 4.35, N 4.68.

3-Acetyl-4-hydroxy-6-(4-nitrophenyl)-5,6-dihydropyran-2-one (4d): White solid; m.p. 126–128 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.67 (s, 3 H), 2.92 (dd, J = 4.0, 17.0 Hz, 1 H), 2.99 (dd, J = 12.0, 17.0 Hz, 1 H), 5.55 (dd, J = 4.0, 12.0 Hz, 1 H), 7.62 (d, J = 8.5 Hz, 2 H), 8.27–8.30 (m, 2 H), 17.79 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.8, 40.1, 74.2, 103.7, 124.5, 126.9, 144.5, 148.4, 163.6, 194.4, 201.8 ppm. IR (KBr): $\tilde{\nu}$ = 1701, 1558, 1520, 1347, 1294, 1064, 874 cm^{-1}. $C_{13}H_{11}NO_6$ (277.06): calcd. C 56.32, H 4.00, N 5.05; found C 56.45, H 3.89, N 5.14.

(2*E*,4*E*)-*S*-Methyl 2-Acetyl-3-hydroxy-5-(4-nitrophenyl)penta-2,4-dienethioate (5d): White solid; m.p. 146–148 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.31 (s, 3 H), 2.53 (s, 3 H), 6.92 (d, J = 15.5 Hz, 1 H), 7.65 (d, J = 8.5 Hz, 2 H), 7.73 (d, J = 15.5 Hz, 1 H), 8.24 (d, J = 9.0 Hz, 2 H), 16.46 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.8, 26.4, 118.0, 123.9, 124.4, 129.1, 139.3, 141.0, 148.6, 175.2, 193.5, 197.9 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1693, 1654, 1515, 1397, 1339, 862 cm^{-1}. $C_{14}H_{13}NO_5S$ (307.05): calcd. C 54.71, H 4.26, N 4.56; found C 54.52, H 4.32, N 4.74.

5-Acetyl-2-(4-methoxyphenyl)-6-(methylthio)-2,3-dihydropyran-4-one (3e): White solid; m.p. 124–126 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3 H), 2.56 (s, 3 H), 2.72–2.76 (m, 1 H), 3.00–3.04 (m, 1 H), 3.84 (s, 3 H), 5.49–5.51 (m, 1 H), 6.97 (d, J = 7.5 Hz, 2 H), 7.33 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.0, 30.9, 41.6, 54.3, 82.1, 113.4, 114.4, 126.9, 127.2, 159.4, 186.3, 187.2, 195.4 ppm. IR (KBr): $\tilde{\nu}$ = 1655, 1516, 1434, 1353, 1244, 1076, 863 cm^{-1}. $C_{15}H_{16}O_4S$ (292.08): calcd. C 61.62, H 5.52; found C 61.46, H 5.71.

3-Acetyl-4-hydroxy-6-(4-methoxyphenyl)-5,6-dihydropyran-2-one (4e): White solid; m.p. 142–144 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.65 (s, 3 H), 2.82 (dd, J = 3.0, 17.0 Hz, 1 H), 3.05 (dd, J = 14.0, 17.0 Hz, 1 H), 3.82 (s, 3 H), 5.38 (dd, J = 3.0, 14.0 Hz, 1 H), 6.92 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.5 Hz, 2 H), 17.78 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 25.5, 38.6, 54.3, 74.0, 102.7, 113.2, 126.5, 128.2, 159.1, 163.3, 194.0, 200.3 ppm. IR (KBr): $\tilde{\nu}$ = 1645, 1514, 1463, 1249, 1173, 1031, 827 cm^{-1}. $C_{14}H_{14}O_5$ (262.08): calcd. C 64.12, H 5.38; found C 64.35, H 5.19.

(2*E*,4*E*)-*S*-Methyl 2-Acetyl-3-hydroxy-5-(4-methoxyphenyl)penta-2,4-dienethioate (5e): White solid; m.p. 96–98 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3 H), 2.50 (s, 3 H), 3.84 (s, 3 H), 6.67 (d, J = 15.5 Hz, 1 H), 6.90 (d, J = 8.0 Hz, 2 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.71 (d, J = 15.0 Hz, 1 H), 16.77 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.7, 25.9, 55.6, 114.6, 116.9, 117.3, 127.7, 130.5, 142.7, 161.9, 177.8, 194.2, 196.1 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1693, 1514, 1465, 1292, 1024, 821 cm^{-1}. $C_{15}H_{16}O_4S$ (292.08): calcd. C 61.62, H 5.52; found C 61.49, H 5.56.

(*E*)-5-Acetyl-6-(methylthio)-2-styryl-2,3-dihydropyran-4-one (3f): White solid; m.p. 102–104 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.33 (s, 3 H), 2.55 (s, 3 H), 2.72 (dd, J = 4.0, 17.0 Hz, 1 H), 2.81 (dd, J = 12.0, 17.0 Hz, 1 H), 5.20 (dd, J = 4.0, 12.0 Hz, 1 H), 6.31 (dd, J = 6.5, 16.0 Hz, 1 H), 6.76 (d, J = 16.0 Hz, 1 H), 7.31–7.39 (m, 3 H), 7.43 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.2, 32.1, 41.9, 82.6, 115.8, 123.8, 127.2, 129.1, 129.2, 135.3, 135.6, 187.1, 188.2, 196.7 ppm. IR (KBr): $\tilde{\nu}$ = 1655, 1541, 1441, 1244, 1043, 747 cm^{-1}. $C_{16}H_{16}O_3S$ (288.08): calcd. C 66.64, H 5.59; found C 66.48, H 5.65.

(*E*)-3-Acetyl-4-hydroxy-6-styryl-5,6-dihydropyran-2-one (4f): White solid; m.p. 118–120 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.65 (s, 3 H), 2.81–2.92 (m, 2 H), 5.06–5.08 (m, 1 H), 6.21–6.26 (m, 1 H), 6.73 (d, J = 15.5 Hz, 1 H), 7.28–7.41 (m, 5 H), 17.75 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.8, 38.5, 74.2, 103.9, 124.8, 127.0, 128.8, 129.0, 134.1, 135.6, 164.5, 195.1, 201.4 ppm. IR (KBr): $\tilde{\nu}$ = 1716, 1558, 1507, 1489, 1244, 1062, 885 cm^{-1}. $C_{15}H_{14}O_4$ (258.09): calcd. C 69.76, H 5.46; found C 69.89, H 5.31.

(2*E*,4*E*,6*E*)-*S*-Methyl 2-Acetyl-3-hydroxy-7-phenylhepta-2,4,6-trienethioate (5f): White solid; m.p. 103–105 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3 H), 2.49 (s, 3 H), 6.36 (d, J = 14.5 Hz, 1 H), 6.93 (d, J = 8.0 Hz, 2 H), 7.30–7.37 (m, 3 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.51–7.53 (m, 1 H), 16.51 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.6, 26.0, 117.1, 123.2, 127.3, 127.6, 129.1, 129.5, 136.3, 141.6, 143.1, 176.9, 194.1, 196.5 ppm. IR (KBr): $\tilde{\nu}$ = 1660, 1606, 1392, 1281, 1174, 1004, 860 cm^{-1}. $C_{16}H_{16}O_3S$ (288.08): calcd. C 66.64, H 5.59; found C 66.47, H 5.75.

5-Acetyl-6-(methylthio)-2-(thiophen-2-yl)-2,3-dihydropyran-4-one (3g): White solid; m.p. 102–104 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.30 (s, 3 H), 2.54 (s, 3 H), 2.95 (dd, J = 3.0, 17.0 Hz, 1 H), 3.07 (dd, J = 12.0, 17.0 Hz, 1 H), 5.80 (dd, J = 3.0, 12.0 Hz, 1 H), 7.05–7.06 (m, 1 H), 7.12–7.14 (m, 1 H), 7.42 (d, J = 5.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.4, 32.1, 42.7, 78.9, 115.9, 126.9, 127.4, 127.6, 139.1, 186.6, 187.8, 196.6 ppm. IR (KBr): $\tilde{\nu}$ = 1731, 1659, 1537, 1431, 1342, 1071, 865 cm^{-1}. $C_{12}H_{12}O_3S_2$ (268.02): calcd. C 53.71, H 4.51; found C 53.82, H 4.53.

3-Acetyl-4-hydroxy-6-(thiophen-2-yl)-5,6-dihydropyran-2-one (4g): White solid; m.p. 80–82 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.50 (s, 3 H), 3.02–3.06 (m, 1 H), 3.14–3.19 (m, 1 H), 5.67–5.70 (m, 1 H), 7.01 (d, J = 4.0 Hz, 1 H), 7.10 (d, J = 3.0 Hz, 1 H), 7.36 (d, J = 5.0 Hz, 1 H), 17.76 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.8, 39.8, 71.4, 103.9, 126.3, 126.9, 127.2, 140.3, 163.8, 194.6, 201.6 ppm. IR (KBr): $\tilde{\nu}$ = 1652, 1558, 1540, 1457, 1354, 1062, 887 cm^{-1}. $C_{11}H_{10}O_4S$ (238.03): calcd. C 55.45, H 4.23; found C 55.28, H 4.31.

(2*E*,4*E*)-*S*-Methyl 2-Acetyl-3-hydroxy-5-(thiophen-2-yl)penta-2,4-dienethioate (5g): Yellowish solid; m.p. 84–86 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3 H), 2.50 (s, 3 H), 6.59 (d, J = 15.0 Hz, 1 H), 7.06–7.08 (m, 1 H), 7.28 (d, J = 4.0 Hz, 1 H), 7.41 (d, J = 5.0 Hz, 2 H), 7.84 (d, J = 15.0 Hz, 1 H), 16.67 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 12.4, 24.7, 115.8, 117.5, 127.4, 128.4, 130.5, 134.0, 139.3, 175.9, 192.7, 195.1 ppm. IR (KBr): $\tilde{\nu}$ = 1651, 1614, 1498, 1370, 1226, 1041, 868 cm^{-1}. $C_{12}H_{12}O_3S_2$ (268.02): calcd. C 53.71, H 4.51; found C 53.63, H 4.68.

3-Acetyl-6-(furan-2-yl)-2-(methylthio)-4*H*-pyran-4-one (3h): White solid; m.p. 100–102 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.27 (s, 3 H), 2.54 (s, 3 H), 2.83 (dd, J = 3.5, 17.0 Hz, 1 H), 3.15 (dd, J = 12.0, 17.0 Hz, 1 H), 5.60 (dd, J = 3.5, 12.0 Hz, 1 H), 6.43–6.44 (m, 1 H), 6.50 (d, J = 3.0 Hz, 1 H), 7.49–7.51 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.2, 32.2, 39.3, 76.0, 110.9, 111.0, 115.8, 144.5, 148.9, 186.8, 187.8, 196.7 ppm. IR (KBr): $\tilde{\nu}$ = 1641, 1558, 1446, 1345, 1251, 1036, 834 cm^{-1}. $C_{12}H_{10}O_4S$ (252.05): calcd. C 57.13, H 4.79; found C 57.46, H 4.89.

3-Acetyl-6-(furan-2-yl)-4-hydroxy-5,6-dihydropyran-2-one (4h): White solid; m.p. 78–80 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.64 (s, 3 H), 2.94 (dd, J = 3.5, 17.5 Hz, 1 H), 3.25 (dd, J = 10.0, 17.5 Hz, 1 H), 5.47 (dd, J = 3.5, 10.0 Hz, 1 H), 6.39 (s, 1 H), 6.44 (d, J = 2.5 Hz, 1 H), 7.45 (s, 1 H), 17.79 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.8, 36.4, 68.7, 109.8, 110.5, 110.9, 143.8, 149.7, 163.7, 194.9, 201.4 ppm. IR (KBr): $\tilde{\nu}$ = 1721, 1596, 1395, 1235, 1016, 753 cm^{-1}. $C_{11}H_{10}O_5$ (222.05): calcd. C 59.46, H 4.54; found C 59.21, H 4.67.

(2*E*,4*E*)-*S*-Methyl 2-Acetyl-5-(furan-2-yl)-3-hydroxypenta-2,4-dienethioate (5h): White solid; m.p. 92–94 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3 H), 2.49 (s, 3 H), 6.48 (d, J = 1.5 Hz, 1 H), 6.49–6.70 (m, 2 H), 7.47–7.51 (m, 2 H), 16.59 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.7, 26.0, 112.9, 116.3, 117.2, 117.5, 128.7, 145.6, 151.7, 176.9, 194.0, 196.5 ppm. IR (KBr): $\tilde{\nu}$ = 1651, 1614, 1546, 1296, 1020, 946, 866 cm^{-1}. $C_{12}H_{12}O_4S$ (252.05): calcd. C 57.13, H 4.79; found C 57.01, H 4.95.

3-Acetyl-4-hydroxy-5,6-dihydropyran-2-one (4i):[9d] White solid; m.p. 91–93 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2. 61 (s, 3 H), 2.77 (t, J = 6.0 Hz, 2 H), 4.367 (t, J = 6.0 Hz, 2 H), 17.75 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.9, 32.9, 62.7, 104.2, 164.4, 195.6, 201.7 ppm. IR (KBr): $\tilde{\nu}$ = 2915, 1716, 1652, 1558,

1388, 1056, 931, 869 cm^{-1}. $C_7H_8O_4$ (156.04): calcd. C 53.85, H 5.16; found C 53.68, H 5.25.

5-Acetyl-6-(ethylthio)-2-phenyl-2,3-dihydropyran-4-one (3j): White solid; m.p. 70–72 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.27 (t, J = 7.5 Hz, 3 H), 2.56 (s, 3 H), 2.74–2.78 (m, 1 H), 2.87 (q, J = 7.5 Hz, 2 H), 2.96–3.02 (m, 1 H), 5.53 (dd, J = 3.0, 14.0 Hz, 1 H), 6.83 (d, J = 15.0 Hz, 1 H), 7.39–7.41 (m, 2 H), 7.43–7.47 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.0, 25.2, 32.3, 43.3, 83.5, 115.9, 126.4, 129.3, 129.7, 136.8, 187.4, 196.9 ppm. IR (KBr): $\tilde{\nu}$ = 1661, 1439, 1402, 1330, 1245, 1041, 988 cm^{-1}. $C_{15}H_{16}O_3S$ (276.08): calcd. C 65.19, H 5.84; found C 65.34, H 5.79.

(2*E*,4*E*)-*S*-Ethyl 2-Acetyl-3-hydroxy-5-phenylpenta-2,4-dienethioate (5j): Liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.39 (t, J = 7.0 Hz, 3 H), 2.28 (s, 3 H), 3.07 (q, J = 7.0 Hz, 2 H), 6.83 (d, J = 15.0 Hz, 1 H), 7.38–7.39 (m, 3 H), 7.50–7.51 (m, 2 H), 7.73 (d, J = 15.5 Hz, 1 H), 16.57 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.6, 25.0, 25.7,117.2, 119.6, 128.4, 128.9, 130.4, 134.7, 142.2, 176.6, 193.4, 196.4 ppm. IR (KBr): $\tilde{\nu}$ = 1727, 1658, 1491, 1410, 1265, 1178, 877 cm^{-1}. $C_{15}H_{16}O_3S$ (276.08): calcd. C 65.19, H 5.84; found C 65.52, H 5.68.

5-Acetyl-6-(ethylthio)-2-*p*-tolyl-2,3-dihydropyran-4-one (3k): Liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.27 (t, J = 8.0 Hz, 3 H), 2.39 (s, 3 H), 2.56 (s, 3 H), 2.73 (dd, J = 3.0, 17.0 Hz, 1 H), 2.82 (q, J = 8.0 Hz, 2 H), 2.99 (dd, J = 14.0, 17.0 Hz, 1 H), 5.49 (dd, J = 3.0, 14.0 Hz, 1 H), 7.22–7.30 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.9, 21.5, 25.1, 32.2, 43.2, 83.5, 115.8, 126.5, 130.0, 133.7, 139.8, 187.6, 188.1, 196.8 ppm. IR (KBr): $\tilde{\nu}$ = 1660, 1442, 1343, 1242, 1185, 1071, 873 cm^{-1}. $C_{16}H_{18}O_3S$ (290.10): calcd. C 66.18, H 6.25; found C 66.04, H 6.37.

(2*E*,4*E*)-*S*-Ethyl 2-acetyl-3-hydroxy-5-*p*-tolylpenta-2,4-dienethioate (5k): White solid; m.p. 56–58 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.39 (t, J = 7.5 Hz, 3 H), 2.27 (s, 3 H), 2.38 (s, 3 H), 3.06 (q, J = 7.5 Hz, 2 H), 6.78 (d, J = 16.0 Hz, 1 H), 7.19 (d, J = 7.0 Hz, 2 H), 7.41 (d, J = 7.5 Hz, 2 H), 7.71 (d, J = 15.5 Hz, 1 H), 16.62 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.9, 21.8, 25.3, 25.9, 117.4, 118.9, 128.6, 129.9, 132.3, 141.3, 142.7, 177.3, 193.9, 196.4 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1645, 1515, 1394, 1174, 851 cm^{-1}. $C_{16}H_{18}O_3S$ (290.10): calcd. C 66.18, H 6.25; found C 66.41, H 6.22.

5-Acetyl-2-(4-chlorophenyl)-6-(ethylthio)-2,3-dihydropyran-4-one (3l): White solid; m.p. 120–122 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.27 (t, J = 7.5 Hz, 3 H), 2.55 (s, 3 H), 2.74 (dd, J = 3.0, 17.0 Hz, 1 H), 2.84 (q, J = 7.5 Hz, 2 H), 2.95 (dd, J = 14.0, 17.0 Hz, 1 H), 5.51 (dd, J = 3.0, 14.0 Hz, 1 H), 7.34 (d, J = 8.5 Hz, 2 H), 7.44 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.0, 25.2, 32.3, 43.1, 82.7, 115.9, 127.8, 129.6, 135.2, 135.7, 187.0, 187.9, 196.8 ppm. IR (KBr): $\tilde{\nu}$ = 1655, 1440, 1345, 1241, 1136, 1080, 835 cm^{-1}. $C_{15}H_{15}ClO_3S$ (310.04): calcd. C 57.97, H 4.86; found C 58.15, H 4.78.

(2*E*,4*E*)-*S*-Ethyl 2-Acetyl-5-(4-chlorophenyl)-3-hydroxypenta-2,4-dienethioate (5l): White solid; m.p. 66–68 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.38 (t, J = 7.5 Hz, 3 H), 2.28 (s, 3 H), 3.06 (q, J = 7.5 Hz, 2 H), 6.78 (d, J = 15. 5 Hz, 1 H), 7.35 (d, J = 8.5 Hz, 2 H), 7.43 (d, J = 8.5 Hz, 2 H), 7.66 (d, J = 15.5 Hz, 1 H), 16.53 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.6, 24.2, 24.8, 116.4, 119.2, 128.2, 128.5, 132.3, 135.4, 139.8, 175.2, 192.4, 195.7 ppm. IR (KBr): $\tilde{\nu}$ = 1656, 1540, 1497, 1397, 1296, 1090, 875 cm^{-1}. $C_{15}H_{15}ClO_3S$ (310.04): calcd. C 57.97, H 4.86; found C 58.22, H 4.67.

5-Acetyl-6-(ethylthio)-2-(4-nitrophenyl)-2,3-dihydropyran-4-one (3m): White solid; m.p. 134–136 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.29 (t, J = 7.5 Hz, 3 H), 2.54 (s, 3 H), 2.82 (dd, J = 3.0, 17.0 Hz, 1 H), 2.89 (q, J = 7.5 Hz, 2 H), 2.94 (dd, J = 14.0, 17.0 Hz, 1 H), 5.66 (dd, J = 3.0, 14.0 Hz, 1 H), 7.61 (d, J = 9.0 Hz, 2 H), 8.33 (d, J = 8.5, Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5, 24.9, 32.0, 42.9, 81.6, 115.7, 124.3, 126.7, 143.3, 148.2, 185.9, 187.3, 196.3 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1661, 1518, 1430, 1342, 1039, 851 cm^{-1}. $C_{15}H_{15}NO_5S$ (321.07): calcd. C 56.06, H 4.70, N 4.36; found C 56.15, H 4.57, N 4.38.

(2*E*,4*E*)-*S*-Ethyl 2-Acetyl-3-hydroxy-5-(4-nitrophenyl)penta-2,4-dienethioate (5m): White solid; m.p. 100–102 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.39 (t, J = 6.0 Hz, 3 H), 2.31 (s, 3 H), 3.07 (q, J = 6.0 Hz, 2 H), 6.92 (d, J = 15.5 Hz, 1 H), 7.62 (d, J = 9.0 Hz, 2 H),7.71 (d, J = 15.5 Hz, 2 H), 8.22 (d, J = 8.0 Hz, 2 H), 16.36 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.5, 25.1, 26.0, 118.3, 123.7, 124.1, 128.7, 138.7, 140.8, 148.3, 174.6, 192.8, 197.5 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1653, 1515, 1417, 1342, 1186, 862 cm^{-1}. $C_{15}H_{15}NO_5S$ (321.07): calcd. C 56.06, H 4.70, N 4.36; found C 56.24, H 4.78, N 4.47.

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