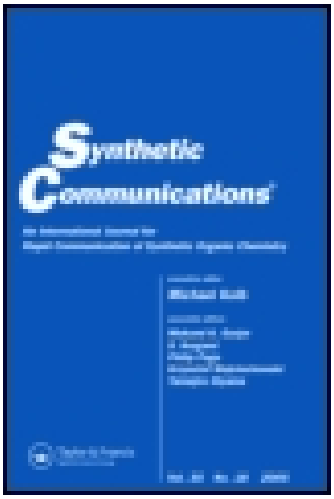

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EFFICIENT ONE-POT SYNTHESIS OF ETHYL [2-(2H-CHROMENE-3YL)-4-OXO-L,3-THIAZOLIDIN-3-YL]ACETATES

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Ethyl [2-(2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3yl]acetates (6a–e) were synthesized in a single pot by the reaction of 2H-3-chromenecarbaldehydes (3a–e), glycine ethyl ester hydrochloride (4), and mercaptoacetic acid (5) in diisopropylethylamine/benzene under refluxing conditions in a Dean–Stark trap.

Keywords: 2H-3-Chromenecarbaldehydes; Dean–Stark trap; glycine ethyl ester hydrochloride; mercaptoacetic acid; one-pot synthesis

INTRODUCTION

Thiazolidinones are one class of heterocycles that has attracted much attention because they have a wide range of biological activities including antifungal, antibacterial, antihistaminic, antimicrobial, and anti-inflammatory activities.[1] Thiazolidinone derivatives are well known in medicinal chemistry because of their diverse pharmacological action such as anticonvulsant,[2] cardiovascular,[3] and antihelminthic[4] properties. A literature survey shows that many different protocols have been developed for the synthesis of thiazolidinones.[5] Several procedures involve two steps, the first step being the synthesis of a Schiff base, which is then reacted with mercaptoacetic acid.[6,7] Homes et al. reported a solid-phase, one-pot, three-component condensation of a primary amine, an aldehyde, and mercaptoacetic acid to give thiazolidinones.[8] Earlier we reported the synthesis of new biologically active heterocycles fused or pendent at the 3-position of 2H-3-chromene carbaldehydes.[9,10]

RESULTS AND DISCUSSION

The present study involves a one-pot reaction of 2H-3-chromenecarbaldehydes (**3a**–**e**), glycine ethyl ester hydrochloride (**4**), and mercaptoacetic acid (**5**) in diisopropylethylamine/benzene with a Dean–Stark setup to afford new thiazolidinones, ethyl [2-(2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3yl]acetates (**6a**–**e**).

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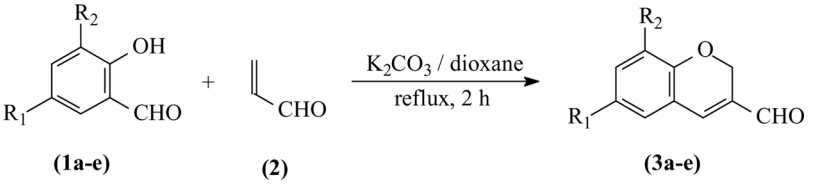
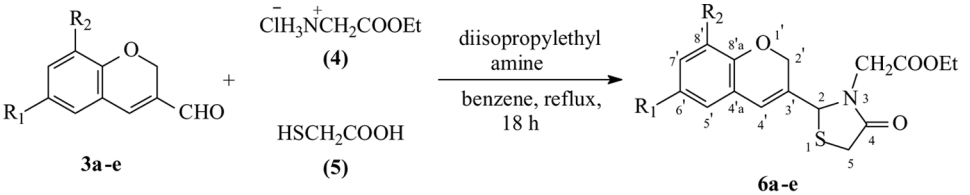


Scheme 1. Synthesis of substituted salicylaldehydes (**3a**–**e**).

Substituted phenols, on reaction with excess of chloroform in alkali medium and polyethylene glycol-400 as a phase-transfer catalyst for a Riemer–Tiemann reaction,[11–13] gave substituted salicylaldehydes (**1a**–**e**). Equimolar quantities of salicylaldehydes (**1a**–**e**), acrolein (**2**), and K_2CO_3 were refluxed in dioxane to give 2H-3-chromenecarbaldehydes[14–16] (**3a**–**e**) (Scheme 1). Their structures were established by analytical and spectral data. 2H-3-chromenecarbaldehydes (**3a**–**e**), in a one-step reaction with glycine ethyl ester hydrochloride (**4**) and mercaptoacetic acid (**5**) in the presence of diisopropylethylamine/benzene using a Dean–Stark trap, gave ethyl [2-(2H-chromene-3yl)-4-oxo-l,3-thiazolidin-3-yl)acetates (**6a**–**e**) (Scheme 2). The structures of the new compounds were confirmed on the basis of ^{1}H NMR and ^{13}C NMR data.[17]

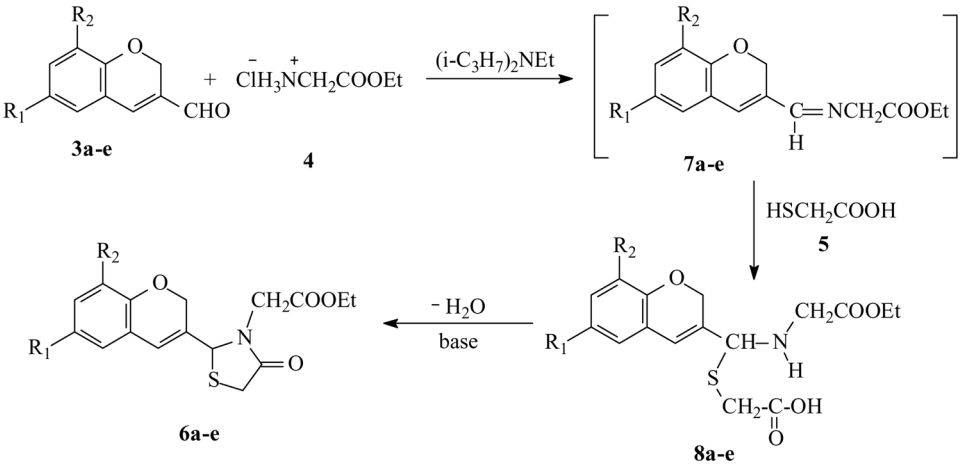
Ethyl [2-(2H-chromene-3yl)-4-oxo-l,3-thiazolidin-3yl]acetate (**6a**) in its infrared (IR) spectrum showed thiazolidinone carbonyl absorption at 1673 cm^{-1} and ester carbonyl at 1731 cm^{-1}. Its ultraviolet (UV) (MeOH) spectrum showed bands at 349 nm (log ε 4.1), 282 nm (log ε 4.4), and 235 nm (log ε 4.5). In its ^{1}H NMR spectrum, H-2 in the new thiazolidinone ring appeared as a singlet at δ 5.49. The S-CH_2 protons in thiazolidinone ring are diastereotopic: one of the S–CH_2 appeared at δ 4.40 as a doublet ($J = 17.3$ Hz), and the other overlapped with the N–CH_2 protons signal and appeared as a multiplet at δ 3.64. The chemical shifts and signal pattern of H-2, S–CH_2 suggest that a new thiazolidinone ring is formed, which is pendent at C-3 of the chromene. The N–CH_2 protons overlapped with one of the S–CH_2 proton signals and appeared at δ 3.64 as a multiplet. The OCH_2 of COOEt appeared as a quartet at δ 4.18 ($J = 6.7$ Hz), and the CH_3 appeared at δ 1.25 as a triplet ($J = 6.7$ Hz). The other signals in ^{1}H NMR spectrum are due to the chromene moiety: the OCH_2 protons at C-2′ are diastereotopic and appeared as AB quartets at



1, 3, 6a) $R_1 = R_2 = H$
b) $R_1 = Cl$, $R_2 = H$
c) $R_1 = Br$, $R_2 = H$

1, 3, 6d) $R_1 = OCH_3$, $R_2 = H$
e) $R_1 = H$, $R_2 = OEt$

Scheme 2. Synthesis of ethyl [2-(2H-chromene-3yl)-4-oxo-l,3-thiazolidin-3-yl]acetates (**6a**–**e**).



Scheme 3. Mechanism of the formation of thiazolidinones (**6a**–**e**).

δ 4.57 ($J = 13.5$ Hz) and at δ 4.83 ($J = 13.5$ Hz). H-4′ appeared at δ 6.50 as a singlet, and H-5′,6′,7′,8′ appeared as a multiplet at δ 6.75–7.20. The ^{13}C NMR spectrum of ethyl [2-(2H-chromene-3yl)-4-oxo-l,3-thiazolidin-3yl) acetate (**6a**) exhibited the thiazolidinone ring carbons as follows: δ 171.9 (C-4, carbonyl), 63.2 (C-2), and δ 32.0 (C-5). The N-CH_2 carbon appeared at δ 44.0; the ester carbons appeared at δ 167.7 (CO), 61.7 (OCH_2), and 14.0 (CH_3). The carbon signal assignments in the 2H-3-chromene moiety are as follows: δ 63.8 (C-2′), 128.8 (C-3′), 125.6 (C-4′), 121.4 (C-4′a), 127.2 (C-5′), 121.7 (C-6′), 130.3 (C-7′), 115.9 (C-8′), and 154.1 (C-8′a). In its electron-impact (EI) mass spectrum, the molecular ion appeared at m/z 319 (20%) and the other ions were observed at m/z 244 (33), 175 (100), and 131 (50).

The first step[18] is the formation of imines (**7a**–**e**) by the reaction of aldehydes (**3a**–**e**) with glycine ethyl ester hydrochloride salt (**4**) in the presence of diisopropylethylamine (base). Nucleophilic attack of the SH of mercaptoacetic acid (**5**) on the imine carbon gives an intermediate **8a**–**e**. Base-catalyzed cyclization of **8a**–**e** by the elimination of water gives rise to thiazolidinones (**6a**–**e**) (Scheme 3). The intermediates **7a**–**e** and **8a**–**e** could not be isolated.

EXPERIMENTAL

All melting points are uncorrected and were determined on a Polmon instrument (model MP 96). IR spectra were recorded on a Fourier transform (FT)–IR Perkin-Elmer model 337 spectrometer, and ultraviolet (UV) spectra were determined on a Schimadzu UV-vis 1601 spectrophotometer. The ^{1}H NMR (300 M Hz) and ^{13}C NMR (75.5 M Hz) spectra were recorded on a Varian Gemini spectrometer using $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard (chemical shifts in δ ppm). The mass spectra were recorded on a VG Micromass 7070-H instrument. Elemental analyses were performed on a PE-2400 elemental analyzer.

General Procedure for the Synthesis of 2H-3-Chromenecarbaldehydes (3a–e)

Anhydrous K_2CO_3 (13.8 g, 100 mmol) and acrolein (**2**) (5.6 g, 100 mmol) was added to a solution of salicylaldehydes (**1a**–**e**) (100 mmol) in dioxane (80 mL) and refluxed on an oil bath at 110 °C for 2 h. After completion of the reaction, the solvent was distilled off under reduced pressure, and the resultant crude was treated with crushed ice (100 g). The resultant solution was extracted with ether, dried, and concentrated. It was column chromatographed over silica gel (60–120 mesh) and eluted with chloroform to give 2H-3-chromenecarbalehydes (**3a**–**e**) as pale yellow compounds in 55–70% yield.

2H-3-Chromenecarbaldehyde (3a). Light yellowish liquid[14]; IR (KBr): 1669 cm^{-1}(C=O) and 1576 cm^{-1} (C=C); UV (MeOH): 360 nm (log ε 4.4) and 288 nm (log ε 4.6); ^{1}H NMR ($CDCl_3$): δ 9.55 (s, CHO), 7.12–7.29 (m, H-4,5,7), 6.91 (m, H-6), 6.81 (d, $J = 8.3$ Hz, H-8), 5.00 (s, OCH_2); ^{13}C NMR ($CDCl_3$): δ 189.8 (C=O), 156.0 (C-8a), 141.2 (C-4), 133.2 (C-7), 131.6 (C-3), 129.4 (C-5), 121.9 (C-6), 120.5 (C-4a), 116.5 (C-8), 63.1 (C-2); EIMS: m/z 160 ($M^{+\cdot}$) (70), 131 (100), and 104 (15). Anal. calcd. for $C_{10}H_8O_2$: C, 74.99; H, 5.03%. Found C, 74.84; H, 5.11%.

6-Chloro-2H-3-chromenecarbaldehyde (3b). Recrystallized from chloroform as pale yellow needles. Mp 89 °C (lit.[15] mp 91 °C); IR (KBr): 1672 cm^{-1} (C=O) and 1560 cm^{-1}(C=C); UV (MeOH): 384 nm (log ε 4.5) and 298 nm (log ε 4.7); ^{1}H NMR ($CDCl_3$): δ 9.57 (s, CHO), 7.07–7.28 (m, H-4,5,7), 6.78 (d, $J = 8.3$ Hz, H-8), 5.00 (s, OCH_2); ^{13}C NMR ($CDCl_3$): δ 189.4 (C=O), 154.3 (C-8a), 139.4 (C-4), 132.5 (C-7), 131.2 (C-3), 128.4 (C-5), 126.6 (C-6), 121.5 (C-4a), 117.8 (C-8), 63.4 (C-2); EIMS: m/z 194 ($M^{+\cdot}$) (60), 165 (100), and 131 (10). Anal. calcd. for $C_{10}H_7ClO_2$: C, 61.72; H, 3.63. Found C, 61.88; H, 3.47%.

6-Bromo-2H-3-chromenecarbaldehyde (3c). Recrystallized from chloroform as pale yellow needles.[16] Mp 105 °C; IR (KBr): 1666 cm^{-1} (C=O) and 1560 cm^{-1} (C=C); UV (MeOH): 364 nm (log ε 4.2), 296 nm (log ε 4.3), and 250 nm (log ε 4.5); ^{1}H NMR ($CDCl_3$): δ 9.58 (s, CHO), 7.24–7.39 (m, H-5,7), 7.12 (s, H-4), 6.74 (d, $J = 8.3$ Hz, H-8), 5.01 (s, OCH_2); ^{13}C NMR ($CDCl_3$): δ 189.3 (C=O), 154.8 (C-8a), 139.2 (C-4), 135.4 (C-7), 132.3 (C-3), 131.3 (C-5), 122.1 (C-4a), 118.2 (C-8), 113.7 (C-6), 63.3 (C-2); EIMS: m/z 239 ($M^{+\cdot}$) (100), 211 (95), and 131 (30). Anal. calcd. for $C_{10}H_7BrO_2$: C, 50.24; H, 2.95. Found C, 50.41; H, 2.73%.

6-Methoxy-2H-3-chromenecarbaldehyde (3d). Recrystallized from chloroform as pale yellow needles. Mp 52 °C (lit.[16] mp 50 °C); IR (KBr): 1667 cm^{-1} (C=O) and 1578 cm^{-1}(C=C); UV (MeOH): 369 nm (log ε 4.3) and 294 nm (log ε 4.5); ^{1}H NMR ($CDCl_3$): δ 9.49 (s, CHO), 7.10 (s, H-4), 6.71–6.82 (m, H-7,8), 6.63 (d, $J = 3.0$ Hz, H-5), 4.84 (s, OCH_2), 3.72 (s, 6-OCH_3); ^{13}C NMR ($CDCl_3$): δ 189.4 (C=O), 154.1 (C-6), 149.7 (C-8a), 140.9 (C-4), 132.1 (C-3), 120.8 (C-4a), 118.9 (C-7), 116.9 (C-8), 112.9 (C-5), 62.8 (C-2), 55.4 (6-OCH_3); EIMS: m/z 190 ($M^{+\cdot}$) (100), 161 (95), 147 (18), and 118 (55). Anal. calcd. for $C_{11}H_{10}O_3$: C, 69.47; H, 5.30. Found C, 69.55; H, 5.14%.

8-Ethoxy-2H-3-chromenecarbaldehyde (3e). Recrystallized from chloroform as pale yellow needles. Mp 87 °C; IR (KBr): 1672 cm^{-1} (C=O) and 1576 cm^{-1} (C=C); UV (MeOH): 374 nm ($\log \varepsilon$ 4.1), 299 nm ($\log \varepsilon$ 4.7), and 246 nm ($\log \varepsilon$ 4.5); ^{1}H NMR ($CDCl_3$): δ 9.58 (s, CHO), 7.23 (s, H-4), 6.72–6.91 (m, H-5,6,7), 5.07 (s, 2-OCH_2), 4.08 (q, $J = 6.7$ Hz, OCH_2 of 8-OCH_2CH_3), 1.45 (t, $J = 6.7$ Hz, CH_3 of 8-OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 189.4 (C=O), 147.2 (C-8), 145.2 (C-8a), 141.1 (C-4), 131.4 (C-3), 121.4 (C-5), 121.1 (C-7), 119.3 (C-4a), 116.9 (C-6), 64.6 (C-2), 63.3 (8-OCH_2CH_3), 14.7 (8-OCH_2CH_3); EIMS: m/z 204 ($M^{+\cdot}$) (40), 175 (20), 147 (70), and 91 (100). Anal. calcd. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found C, 70.33; H, 5.81%.

General Procedure for the Synthesis of Ethyl-[2-(2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3-yl]acetates (6a–e)

A mixture of glycine ethyl ester hydrochloride salt (**4**) (1.67 g, 12 mmol), 2H-3--chromene carbaldehydes (**3a**–**e**) (24 mmol), mercaptoacetic acid (**5**) (2.5 mL, 36 mmol), and diisopropylethyl amine (2.61 mL, 15 mmol) in 50 mL of benzene was heated to reflux with a Dean–Stark trap for 18 h. The reaction mixture was cooled to room temperature and diluted with EtOAc. The organic phase was washed with saturated $NaHCO_3$, 1 N HCl, and saturated NaCl. The organic solution was dried with $MgSO_4$ and concentrated to give a light brownish oil, which was chromatographed over silica gel (60–120 mesh) by eluting with petroleum ether–ethyl acetate (9:1) to afford ethyl [2-(2H-chromene-3yl)-4-oxo-l,3-thiazolidin-3-yl]acetates (**6a**–**e**) as a colorless oils (semi solids) in 65–75% yields.

Ethyl-[2-(2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3-yl]acetate (6a). Yield 68%; IR (KBr): 1673 cm^{-1}(thiazolidinone C=O) and 1731 cm^{-1}(ester C=O); UV (MeOH): 349 nm ($\log \varepsilon$ 4.1), 282 nm ($\log \varepsilon$ 4.4), and 235 nm ($\log \varepsilon$ 4.5); ^{1}H NMR ($CDCl_3$): δ 6.75–7.20 (m, H-5′,6′,7′,8′), 6.50 (s, H-4′), 5.49 (s, H-2), 4.83 (d, $J = 13.5$ Hz, OCH of 2′-OCH_2), 4.57 (d, $J = 13.5$ Hz, OCH of 2′-OCH_2), 4.40 (d, $J = 17.3$ Hz, S-CH), 4.18 (q, $J = 6.7$ Hz, $COOCH_2CH_3$), 3.64 (m, S-CH and N-CH_2), 1.25 (t, $J = 6.7$ Hz, $COOCH_2CH_3$); ^{13}C NMR ($CDCl_3$) (100.6 M Hz): δ 171.9 (C=O at C-4), 167.7 ($COOCH_2CH_3$), 154.1 (C-8a), 130.3 (C-7′), 128.8 (C-3′), 127.2 (C-5′), 125.6 (C-4′), 121.7 (C-6′), 121.4 (C-4′a), 115.9 (C-8′), 63.8 (C-2′-OCH_2), 63.2 (C-2), 61.7 ($COOCH_2CH_3$), 44.0 (N-CH_2), 32.0 (S-CH_2), 14.0 ($COOCH_2CH_3$); EIMS: m/z 319 ($M^{+\cdot}$) (20), 244 (35), 175 (100), 145 (45) and 131 (50). Anal. calcd. for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.36; N, 4.39. Found C, 60.31; H, 5.44; N, 4.26%.

Ethyl-[2-(6-chloro-2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3-yl]acetate (6b). Yield 63%; IR (KBr): 1684 cm^{-1} (thiazolidinone C=O) and 1739 cm^{-1} (ester C=O); UV (MeOH): 342 nm ($\log \varepsilon$ 4.6), 277 nm ($\log \varepsilon$ 4.3), and 229 nm ($\log \varepsilon$ 4.2); ^{1}H NMR ($CDCl_3$): δ 6.90–7.24 (m, H-5′,7′), 6.79 (d, $J = 8.3$ Hz, H-8′), 6.38 (s, H-4′), 5.39 (s, H-2), 4.77 (d, $J = 13.5$ Hz, OCH of 2′-OCH_2), 4.52 (d, $J = 13.5$ Hz, OCH of 2′-OCH_2), 4.32 (d, $J = 17.3$ Hz, S-CH), 4.09 (q, $J = 6.7$ Hz, $COOCH_2CH_3$), 3.58 (m, S-CH and N-CH_2), 1.17 (t, $J = 6.7$ Hz, $COOCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.3 (C=O at C-4), 168.2 ($COOCH_2CH_3$), 154.7 (C-8a), 132.5 (C-3′), 129.5 (C-7′), 128.9 (C-4′), 122.5 (C-4′a), 121.9 (C-5′), 119.0 (C-6′), 113.2 (C-8′), 64.8 (C-2′-OCH_2), 62.1 (C-2), 61.5 ($COOCH_2CH_3$), 41.5 (N-CH_2), 32.6 (S-CH_2), 13.9 ($COOCH_2CH_3$);

LSIMS: m/z 354 $[M+H]^+$. Anal. calcd. for $C_{16}H_{16}ClNO_4S$: C, 54.31; H, 4.56; N, 3.96. Found C, 54.19; H, 4.62; N, 4.05%.

Ethyl-[2-(6-bromo-2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3-yl]acetate (6c). Yield 71%; IR (KBr): 1678 cm^{-1} (C=O) (thiazolidinone C=O) and 1741 cm^{-1} (ester C=O); UV (MeOH): 338 nm (log ε 4.1), 281 nm (log ε 4.5), and 246 nm (log ε 4.1); ^{1}H NMR ($CDCl_3$): δ 7.21 (m, H-7′), 7.11 (d, $J=3.0$ Hz, H-5′), 6.70 (d, $J=8.3$ Hz, H-8′), 6.42 (s, H-4′), 5.46 (s, H-2), 4.85 (d, $J=13.5$ Hz, OCH of 2′-OCH_2), 4.59 (d, $J=13.5$ Hz, OCH of 2′-OCH_2), 4.38 (d, $J=17.3$ Hz, S-CH), 4.18 (q, $J=6.7$ Hz, $COOCH_2CH_3$), 3.66 (q, $J=6.7$ Hz, N-CH_2), 3.55 (d, $J=17.3$ Hz, S-CH), 1.26 (t, $J=6.7$ Hz, $COOCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.3 (C=O at C-4), 168.2 ($COOCH_2CH_3$), 154.8 (C-8a), 132.3 (C-3′), 130.7 (C-7′), 129.8 (C-5′), 129.3 (C-4′), 124.2 (C-4′a), 112.6 (C-8′), 109.8 (C-6′), 64.8 (C-2′-OCH_2), 62.1 (C-2), 61.6 ($COOCH_2CH_3$), 41.5 (N-CH2), 31.4 (S-CH2), 14.0 ($COOCH_2CH_3$); LSIMS: m/z 399 $[M+H]^+$. Anal. calcd. for $C_{16}H_{16}BrNO_4S$: C, 48.25; H, 4.05; N, 3.52. Found C, 48.42; H, 3.94; N, 3.38%.

Ethyl-[2-(6-methoxy-2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3-yl]acetate (6d). Yield 68%; IR (KBr): 1690 cm^{-1} (C=O) (thiazolidinone C=O) and 1736 cm^{-1} (ester C=O); UV (MeOH): 351 nm (log ε 4.4), 276 nm (log ε 4.3), and 233 nm (log ε 4.1); ^{1}H NMR ($CDCl_3$): δ 6.79–7.16 (m, H-5′,7′,8′), 6.48 (s, H-4′), 5.37 (s, H-2), 4.80 (d, $J=13.5$ Hz, OCH of 2′-OCH_2), 4.54 (d, $J=13.5$ Hz, OCH of 2′-OCH_2), 4.38 (d, $J=17.3$ Hz, S-CH), 4.10 (q, $J=6.7$ Hz, $COOCH_2CH_3$), 3.77 (s, 6′-OCH_3), 3.52 (m, S-CH and N-CH_2), 1.26 (t, $J=6.7$ Hz, $COOCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.5 (C=O at C-4), 168.4 ($COOCH_2CH_3$), 153.8 (C-6′), 150.1 (C-8a), 130.1 (C-3′), 126.3 (C-4′), 122.8 (C-4′a), 117.0 (C-7′), 114.6 (C-5′), 112.2 (C-8′), 64.6 (C-2′-OCH_2), 62.5 (C-2), 61.9 ($COOCH_2CH_3$), 55.4 (C-6′-OCH_3), 41.8 (N-CH_2), 31.6 (S-CH2), 14.3 ($COOCH_2CH_3$); LSIMS: m/z 350 $[M+H]^+$. Anal. calcd. for $C_{17}H_{19}NO_5S$: C, 58.44; H, 5.48; N, 4.01. Found C, 58.60; H, 5.29; N, 4.12%.

Ethyl-[2-(8-ethoxy-2H-chromene-3yl)-4-oxo-1,3-thiazolidin-3-yl]acetate (6e). Yield 74%; IR (KBr): 1682 cm^{-1} (C=O) (thiazolidinone C=O) and 1738 cm^{-1} (ester C=O); UV (MeOH): 344 nm (log ε 4.7), 267 nm (log ε 4.2), and 236 nm (log ε 4.1); ^{1}H NMR ($CDCl_3$): δ 6.59–6.94 (m, H-5′,6′,7′), 6.55 (s, H-4′), 5.57 (s, H-2), 4.86 (d, $J=13.5$ Hz, OCH of 2′-OCH_2), 4.65 (d, $J=13.5$ Hz, OCH of 2′-OCH_2), 4.47 (d, $J=17.3$ Hz, S-CH), 4.25 (q, $J=6.7$ Hz, $COOCH_2CH_3$), 4.12 (q, $J=6.7$ Hz, 8′-OCH_2CH_3), 3.73 (m, S-CH and N-CH_2), 1.51 (t, $J=6.7$ Hz, 8′-OCH_2CH_3), 1.32 (t, $J=6.7$ Hz, $COOCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.3 (C=O at C-4), 167.9 ($COOCH_2CH_3$), 147.2 (C-8′a), 145.6 (C-8′), 124.8 (C-3′), 122.3 (C-4′a), 121.4 (C-4′), 120.5 (C-5′), 119.8 (C-7′), 119.3 (C-6′), 64.8 (C-2′-OCH_2), 64.1 (8′-OCH_2CH_3), 62.9 (C-2), 61.7 ($COOCH_2CH_3$), 41.3 (N-CH_2), 31.2 (S-CH_2), 14.5 (8′-OCH_2CH_3), 13.8 ($COOCH_2CH_3$); LSIMS: m/z 364 $[M+H]^+$. Anal. calcd. for $C_{18}H_{21}NO_5S$: C, 59.49; H, 5.82; N, 3.85. Found C, 59.63; H, 5.61; N, 3.94%.

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