Synthesis and Stereospecific Ring Opening of the (*Z*/*E*)-Isomers of 2-Methyl(Phenyl)-4-(thienylmethylene)-5(4*H*)-oxazolones

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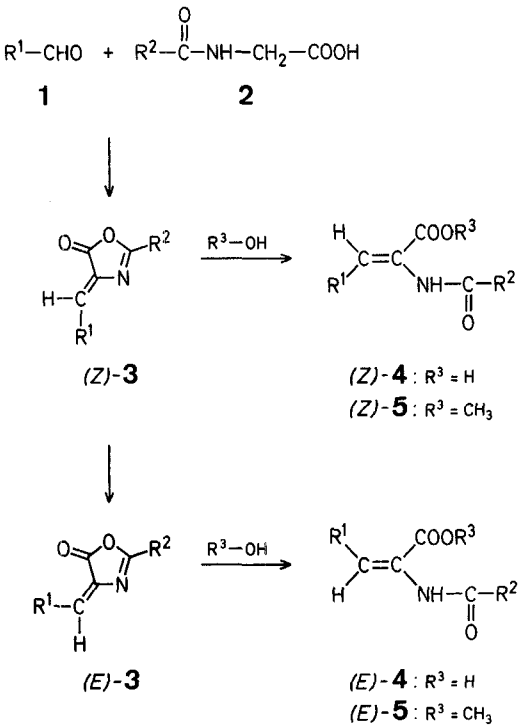
Unsaturated 5(4*H*)-oxazolones[1] are of interest as intermediates in the synthesis of *N*-acyl-2,3-dehydroamino acids[2]. These latter compounds are precursors of 2,3-dehydroamino acids which have been found in natural products which possess antimicrobial activity[3,4]. They are also precursors of optically pure α-amino acids[5]. We are particularly interested in the enantioselective synthesis of β-thienylalanine derivatives, which are antagonists of phenylalanine[6], via homogeneous asymmetric hydrogenation of the 2,3-dehydroanalogs using rhodium-phosphine complexes as catalysts; these catalysts are insensitive to poisoning by sulfur[7].

Some 2-phenyl-4-(thienylmethylene)-5(4*H*)-oxazolones have been described[8-12], without regard to stereochemistry. Usually, the (*Z*)-isomers are thermodynamically more stable; the (*E*)-isomers could hitherto not be obtained. Further, a reliable synthesis of 2-methyl-4-(thienylmethylene)-5(4*H*)-oxazolones has up to now not been reported. We describe here the synthesis, physical characteristics, and stereospecific ring-cleavage reactions of (*Z*)- and (*E*)-2-methyl(phenyl)-4-(thienylmethylene)-5(4*H*)-oxazolones **(3)**. (*Z*)-2-Methyl(Phenyl)-4-(2- or 3-thienylmethylene)-5(4*H*)-oxazolones [(*Z*)-**3**] were easily obtained from thiophenecarboxaldehydes **(1)** and *N*-acetylglycine **(2a)** or hippuric acid **(2b)** in acetic anhydride. The 2-phenyl compounds (*Z*)-**3** ($R^2 = C_6H_5$) were isomerized to (*E*)-2-phenyl-4-(2- or 3-thienylmethylene)-5(4*H*)-oxazolones [(*E*)-**3**, $R^2 = C_6H_5$] by a slight modification of the previously reported method[1]; in contrast, all attempts to obtain (*E*)-2-methyl-4-(2- or 3-thienylmethylene)-5(4*H*)-oxazolones [(*E*)-**3**, $R^2 = CH_3$] were unsuccessful.

Although alkaline hydrolysis and alcoholysis of (*Z*)- and (*E*)-5(4*H*)-oxazolones is assumed to give the individual isomeric



1	R^1
a	
b	
c	
d	
e	

2	R^2
a	CH_3
b	C_6H_5

acids and esters with retention of configuration[2], this is not always true. Alkaline hydrolysis under "standard" conditions[2] with aqueous sodium hydroxide of both (*Z*)- and (*E*)-2-phenyl-4-(thienylmethylene)-5(4*H*)-oxazolones **(3)** gives (*Z*)-2-benzoylamino-3-thienyl-2-propenoic acids [(*Z*)-**4**] which shows that the reaction proceeds with isomerization. Stereospecific hydrolysis of (*Z*)- and (*E*)-2-methyl(phenyl)-4-thienylmethylene-5(4*H*)-oxazolones [(*Z*)-**3** and (*E*)-**3**] to afford (*Z*)- and (*E*)-2-acetylamino(benzoylamino)-3-(2- or 3-thienyl)-2-propenoic acids [(*Z*)-**4** and (*E*)-**4**], respectively, can be achieved with sodium hydroxide in methanol/water at room temperature; similarly, stereospecific methanolysis of (*Z*)-**3** and (*E*)-**3** to afford methyl (*Z*)- and (*E*)-2-acetylamino(benzoylamino)-3-(2- or 3-thienyl)-2-propenoates [(*Z*)-**5** and (*E*)-**5**], respectively, proceeds readily on treatment of compounds **3** with sodium methoxide in absolute methanol.

The structural assignments of the (*Z*)- and (*E*)-2-phenyl-4-(thienylmethylene)-5(4*H*)-oxazolones [(*Z*)-**3** and (*E*)-**3**, $R^2 = C_6H_5$] were made on the basis of the ^{1}H-N.M.R.-spectral data. The vinylic proton of the (*E*)-isomer gives rise to a low field signal because it is in a *"trans"* position with respect to the carbonyl group, in agreement with similar observations on related compounds[13]. Structural assignments of the (*Z*)- and (*E*)-2-benzoylamino-3-thienyl-2-propenoic acids **(4)** and their methyl esters **(5)** were also made on the basis of the ^{1}H-N.M.R.-spectral data, but in this case our observations are not in total agreement with other spectral data. The vinylic proton of the (*Z*)-isomers give rise to a low-field signal, in a contrast to observations on related compounds[13]. Again, according to one of our earlier investigations[2] the amidic proton was used to decide between the two isomeric structures since this proton always give rise to a low-field signal in the (*E*)-isomer.

Melting points were determined on a Mettler FP61 apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240-B analyzer. The I.R. spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer Model 283. The ^{1}H-N.M.R. spectra were measured on a Perkin-Elmer R-12B spectrometer.

(*Z*)-2-Methyl(or Phenyl)-5-oxo-4-(2- or 3-thienylmethylene)-4,5-dihydro-1,3-oxazoles [(*Z*)-3]; General Procedure:

A mixture of the aldehyde **1** (1 mmol), *N*-acetylglycine or hippuric acid (**2**; 1 mmol), acetic anhydride (3 mmol), and anhydrous sodium acetate (1 mmol) is heated at 100°C for 2 h. The mixture is then allowed to cool to room temperature, and poured into ethanol/water (2/3; 20 ml). The solid azlactone is isolated by suction, washed with ethanol, dried, and recrystallized from acetonitrile to give the analytically pure product (*Z*)-**3**.

(*E*)-2-Phenyl-5-oxo-4-(2- or 3-thienylmethylene)-4,5-dihydro-1,3-oxazole [(*E*)-3]; General Procedure:

A suspension of the (*Z*)-isomer (*Z*)-**3** in 48% hydrobromic acid (20 ml/g azlactone) is saturated with anhydrous hydrogen bromide; the suspension is left at 0°C overnight and the product is isolated by suction, washed with ethanol, dried, and recrystallized from acetonitrile to give the analytically pure product (*E*)-**3**.

(*Z*)- and (*E*)-2-Acetylamino(or benzoylamino)-3-(2- or 3-thienyl)-propenoic Acids [(*Z*)-4 and (*E*)-4]; General Procedure:

A suspension of the unsaturated azlactone (*Z*)-**3** or (*E*)-**3** (4 mmol) in aqueous 1% sodium hydroxide (32 ml) + methanol (16 ml) is stirred at room temperature until the compound **3** has completely dissolved. Then, 5% hydrochloric acid (10 ml) is added. The resultant precipitate

Table 1. (*Z*)- and (*E*)-2-Methyl(Phenyl)-5-oxo-4-(2- or 3-thienylmethylene)-4,5-dihydro-1,3-oxazoles **(3)**

Product[a]	Yield [%]	m.p. [°C]	Molecular formula[b] or Lit. m.p. [°C]	I.R. (Nujol) $\nu_{C=O}$ [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
(*Z*)-**3aa**	57	132–133°	134°[7]	1800, 1770	2.40 (s, 3 H, CH_3); 7.12 (m, 1 H); 7.35 (s, 1 H, HC=); 7.55 (d, 1 H, J=4 Hz); 7.65 (d, 1 H, J=4.5 Hz)
(*Z*)-**3ab**	79	176–177°	174–175°[12]	1790, 1770	7.12 (m, 1 H); 7.44 (s, 1 H, HC=); 7.45–7.55 (m, 3 H); 7.60 (d, 1 H, J=4 Hz); 7.68 (d, 1 H, J=4.5 Hz); 8.05–8.20 (m, 2 H)
(*E*)-**3ab**	96	151–153°	$C_{14}H_9NO_2S$ (255.3)	1790, 1765	7.15 (m, 1 H); 7.40–7.55 (m, 3 H); 7.64 (d, 1 H, J=4 Hz); 7.67 (s, 1 H, HC=); 7.93 (d, 1 H, J=4.5 Hz); 8.0–8.15 (m, 2 H)
(*Z*)-**3ba**	61	120–122°	$C_9H_7NO_2S$ (193.2)	1770	2.33 (s, 3 H, CH_3); 7.15 (s, 1 H, HC=); 7.33 (m, 1 H); 7.80 (d, 1 H, J=6 Hz); 8.04 (d, 1 H, J=3 Hz)
(*Z*)-**3bb**	89	192–194°	(188–190°)[10]	1795, 1760	7.28 (s, 1 H, HC=); 7.42 (m, 1 H); 7.45–7.55 (m, 3 H); 7.95 (d, 1 H, J=6 Hz); 8.12 (d, 1 H, J=3 Hz); 8.10–8.25 (m, 2 H)
(*E*)-**3bb**	97	144–146°	$C_{14}H_9NO_2S$ (255.3)	1810	7.4–7.7 (m, 5 H); 8.0–8.20 (m, 3 H); 8.46 (s, 1 H, HC=)
(*Z*)-**3ca**	58	128–129°	$C_{10}H_9NO_2S$ (270.2)	1790, 1765	2.35 (s, 3 H, CH_3); 2.52 (s, 3 H, CH_3); 6.76 (d, 1 H, J=3 Hz); 7.22 (s, 1 H, HC=); 7.30 (d, 1 H, J=3 Hz)
(*Z*)-**3cb**	83	151–152°	152–153°[11]	1790, 1770	2.52 (s, 3 H, CH_3); 6.75 (d, 1 H, J=4.5 Hz); 7.30 (s, 1 H, HC=); 7.34 (d, 1 H, J=4.5 Hz); 7.40–7.55 (m, 3 H); 8.0–8.15 (m, 2 H)
(*E*)-**3cb**	95	190–192°	$C_{15}H_{11}NO_2S$ (269.3)	1800, 1765	2.57 (s, 3 H, CH_3); 6.84 (d, 1 H, J=4.5 Hz); 7.4–7.7 (m, 4 H); 7.57 (s, 1 H, HC=); 7.95–8.15 (m, 2 H)
(*Z*)-**3da**	63	132–134°	$C_9H_6BrNO_2S$ (272.1)	1760	2.33 (s, 3 H, CH_3); 7.28 (d, 1 H, J=3 Hz); 7.51 (s, 1 H, HC=); 7.55 (d, 1 H, J=3 Hz)
(*Z*)-**3db**	91	184–186°	186–187°[11]	1785, 1760	7.32 (d, 1 H, J=3 Hz); 7.43 (d, 1 H, J=3 Hz); 7.51 (s, 1 H, HC=); 7.7–7.9 (m, 3 H); 8.30–8.50 (m, 2 H)
(*E*)-**3db**	95	180–182°	$C_{14}H_8BrNO_2S$ (334.2)	1800, 1770	7.03 (d, 1 H, J=3 Hz); 7.31 (d, 1 H, J=3 Hz); 7.6–7.8 (m, 3 H); 8.05 (s, 1 H, HC=); 8.0–8.2 (m, 2 H)
(*Z*)-**3ea**	84	215–217°	213–214°[12]	1790, 1765	2.41 (s, 3 H, CH_3); 7.62 (s, 1 H, HC=); 7.73 (d, 1 H, J=3 Hz); 8.11 (d, 1 H, J=3 Hz)
(*Z*)-**3eb**	97	234–236°	234–236°[12]	1790, 1765	7.31 (s, 1 H, HC=); 7.37 (d, 1 H, J=4.5 Hz); 7.5–7.7 (m, 3 H); 7.86 (d, 1 H, J=4.5 Hz); 8.1–8.3 (m, 2 H)

[a] The first letter in (*Z*)-**3aa** etc. refers to R^1 from **1**, the second letter to R^2 from **2** (see Scheme).

[b] All compounds gave satisfactory microanalyses: C, ±0.22; H, ±0.10; N, ±0.13; S, ±0.27.

Table 2. (*Z*)- and (*E*)-2-Acetylamino(Benzoylamino)-3-(2- or 3-thienyl)-propenoic Acids (**4**)

Product	Yield [%]	m.p. [°C]	Molecular formula[a] or Lit. m.p. [°C]	I.R. (Nujol) ν [cm^{-1}] NH, C=O$_{acid}$, C=O$_{amide}$	^{1}H-N.M.R. (DMSO-d_6/TMS$_{int}$) δ [ppm]
(*Z*)-**4aa**	66	230–231°	230–231°[7]	3270, 1675, 1625	2.02 (s, 3H, CH$_3$); 7.07 (m, 1H); 7.43 (d, 1H, J=4.5 Hz); 7.66 (d, 1H, J=4.5 Hz); 7.76 (s, 1H, HC=); 9.24 (s, 1H, NH)
(*Z*)-**4ab**	79	237–238°	237–238°[7]	3250, 1685, 1655	6.95–7.15 (m, 1H); 7.4–7.7 (m, 5H); 7.88 (s, 1H, HC=); 7.9–8.1 (m, 2H); 9.70 (s, 1H, NH)
(*E*)-**4ab**	47	173–175°	$C_{14}H_{11}NO_3S$ (273.3)	3260, 1685, 1635	6.90 (s, 1H, HC=); 7.1–7.2 (m, 1H); 7.3–7.5 (m, 5H); 7.8–8.0 (m, 2H); 10.04 (s, 1H, NH)
(*Z*)-**4ba**	73	215–216°	$C_9H_9NO_3S$ (211.2)	3270, 1680, 1635	1.95 (s, 3H, CH$_3$); 7.32 (s, 1H, HC=); 7.4–7.7 (m, 2H); 7.85 (d, 1H, J=3 Hz); 9.26 (s, 1H, NH)
(*Z*)-**4bb**	83	238–240°	$C_{14}H_{11}NO_3S$ (273.3)	3260, 1685, 1640	7.4–7.6 (m, 6H); 7.88 (s, 1H, HC=); 7.9–8.1 (m, 2H); 9.75 (s, 1H, NH)
(*E*)-**4bb**	61	181–182°	$C_{14}H_{11}NO_3S$ (273.3)	3280, 1720, 1635	6.72 (s, 1H, HC=); 7.2–7.3 (m, 1H); 7.4–7.7 (m, 5H); 7.9–8.1 (m, 2H); 10.25 (s, 1H, NH)
(*Z*)-**4ca**	53	242–244°	$C_{10}H_{11}NO_3S$ (225.3)	3290, 1680, 1625	2.06 (s, 3H, CH$_3$); 2.53 (s, 3H, CH$_3$); 6.97 (d, 1H, J=3 Hz); 7.44 (d, 1H, J=3 Hz); 7.80 (s, 1H, HC=); 9.30 (s, 1H, NH)
(*Z*)-**4cb**	76	228–230°	$C_{15}H_{13}NO_3S$ (287.3)	3180, 1680, 1640	2.44 (s, 3H, CH$_3$); 6.96 (d, 1H, J=3 Hz); 7.48 (d, 1H, J=3 Hz); 7.6–7.8 (m, 3H); 7.96 (s, 1H, HC=); 8.1–8.3 (m, 2H); 9.80 (s, 1H, NH)
(*E*)-**4cb**	59	170–171°	$C_{15}H_{13}NO_3S$ (287.3)	3280, 1685, 1645	2.46 (s, 3H, CH$_3$); 6.87 (d, 1H, J=3 Hz); 7.11 (s, 1H, HC=); 7.24 (d, 1H, J=3 Hz); 7.5–7.8 (m, 3H); 8.0–8.2 (m, 2H); 10.22 (s, 1H, NH)
(*Z*)-**4da**	50	222–223°	$C_9H_8BrNO_3S$ (290.1)	3260, 1670, 1620	2.06 (s, 3H, CH$_3$); 7.33 (d, 1H, J=3 Hz); 7.44 (d, 1H, J=3 Hz); 7.77 (s, 1H, HC=); 9.35 (s, 1H, NH)
(*Z*)-**4db**	92	238–239°	$C_{14}H_{10}BrNO_3S$ (352.2)	3180, 1680, 1640	7.3–7.8 (m, 5H); 7.95 (s, 1H, HC=); 8.0–8.2 (m, 2H); 9.85 (s, 1H, NH)
(*E*)-**4db**	63	188–189°	$C_{14}H_{10}BrNO_3S$ (352.2)	3260, 1705, 1690	7.1–7.3 (m, 2H); 7.25 (s, 1H, HC=); 7.5–7.7 (m, 2H); 7.9–8.2 (m, 2H); 10.24 (s, 1H, NH)
(*Z*)-**4ea**	56	218–220°	218–220°[12]	3300, 1720, 1650	2.02 (s, 3H, CH$_3$); 7.48 (d, 1H, J=3 Hz); 7.65 (s, 1H, HC=); 8.02 (d, 1H, J=3 Hz); 9.50 (s, 1H, NH)
(*Z*)-**4eb**	64	230–232°	230–232°[12]	3220, 1690, 1645	7.5–7.7 (m, 4H); 7.8–8.1 (m, 3H); 7.96 (s, 1H, HC=); 10.07 (s, 1H, NH)

[a] All compounds gave satisfactory microanalyses: C, ±0.26; H, ±0.19; N, ±0.21; S, ±0.28.

Table 3. Methyl (*Z*)- and (*E*)-2-Acetylamino(Benzoylamino)-3-(2- or 3-thienyl)-propenoates (**5**)

Product	Yield [%]	m.p. [°C]	Molecular formula[a]	I.R. (Nujol) ν [cm^{-1}] NH, C=O$_{ester}$, C=O$_{amide}$	^{1}H-N.M.R. (DMSO-d_6/TMS$_{int}$) δ [ppm]
(*Z*)-**5aa**	81	118–119°	$C_{10}H_{11}NO_3S$ (225.3)	3230, 1710, 1650	2.05 (s, 3H, CH$_3$); 3.71 (s, 3H, OCH$_3$); 7.1–7.2 (m, 1H); 7.45 (d, 1H, J=4 Hz); 7.77 (s, 1H, HC=); 7.81 (d, 1H, J=5 Hz); 9.35 (s, 1H, NH)
(*Z*)-**5ab**	87	187–188°	$C_{15}H_{13}NO_3S$ (287.3)	3250, 1705, 1645	3.71 (s, 3H, OCH$_3$); 7.1–7.2 (m, 1H); 7.5–7.8 (m, 5H); 7.93 (s, 1H, HC=); 7.9–8.2 (m, 2H); 9.84 (s, 1H, NH)
(*E*)-**5ab**	54	113–114°	$C_{15}H_{13}NO_3S$ (287.3)	3290, 1720, 1650	3.73 (s, 3H, OCH$_3$); 7.02 (s, 1H, HC=); 7.2–7.3 (m, 1H); 7.45–7.7 (m, 5H); 7.8–8.05 (m, 2H); 10.40 (s, 1H, NH)
(*Z*)-**5ba**	73	114–115°	$C_{10}H_{11}NO_3S$ (225.3)	3300, 1720, 1650	2.05 (s, 3H, CH$_3$); 3.75 (s, 3H, OCH$_3$); 7.42 (s, 1H, HC=); 7.4–7.8 (m, 2H); 8.0 (d, 1H, J=3 Hz); 9.60 (s, 1H, NH)
(*Z*)-**5bb**	65	157–159°	$C_{15}H_{13}NO_3S$ (287.3)	3260, 1715, 1640	3.77 (s, 3H, OCH$_3$); 7.5–7.8 (m, 6H); 8.04 (s, 1H, HC=); 8.05–8.2 (m, 2H); 10.05 (s, 1H, NH)
(*E*)-**5bb**	52	139–140°	$C_{15}H_{13}NO_3S$ (287.3)	3300, 1720, 1635	3.73 (s, 3H, OCH$_3$); 6.78 (s, 1H, HC=); 7.05–7.2 (m, 1H); 7.5–7.7 (m, 5H); 7.9–8.1 (m, 2H); 10.45 (s, 1H, NH)
(*Z*)-**5ca**	68	122–123°	$C_{11}H_{13}NO_3S$ (239.2)	3270, 1705, 1660	2.06 (s, 3H, CH$_3$); 2.51 (s, 3H, CH$_3$); 3.76 (s, 3H, OCH$_3$); 6.97 (d, 1H, J=3 Hz); 7.51 (d, 1H, J=3 Hz); 7.82 (s, 1H, HC=); 9.42 (s, 1H, NH)
(*Z*)-**5cb**	72	138–140°	$C_{16}H_{15}NO_3S$ (301.4)	3200, 1710, 1635	2.42 (s, 3H, CH$_3$); 3.75 (s, 3H, OCH$_3$); 6.89 (d, 1H, J=4 Hz); 7.46 (d, 1H, J=4 Hz); 7.5–7.7 (m, 3H); 7.91 (s, 1H, HC=); 8.0–8.2 (m, 2H); 9.83 (s, 1H, NH)
(*E*)-**5cb**	57	144–145°	$C_{16}H_{15}NO_3S$ (301.4)	3300, 1730, 1640	2.45 (s, 3H, CH$_3$); 3.78 (s, 3H, OCH$_3$); 6.84 (d, 1H, J=3 Hz); 7.02 (s, 1H, HC=); 7.13 (d, 1H, J=3 Hz); 7.5–7.8 (m, 3H); 7.9–8.2 (m, 2H); 10.30 (s, 1H, NH)

Table 3. (Continued)

Product	Yield [%]	m.p. [°C]	Molecular formula[a]	I.R. (Nujol) ν [cm^{-1}] NH, C=O$_{ester}$, C=O$_{amide}$	^{1}H-N.M.R. (DMSO-d_6/TMS$_{int}$) δ [ppm]
(*Z*)-**5da**	64	157–159°	$C_{10}H_{10}BrNO_3S$ (304.2)	3260, 1715, 1650	2.12 (s, 3H, CH$_3$); 3.80 (s, 3H, OCH$_3$); 7.44 (d, 1H, J=4 Hz); 7.57 (d, 1H, J=4 Hz); 7.91 (s, 1H, HC=); 9.71 (s, 1H, NH)
(*Z*)-**5db**	71	164–165°	$C_{15}H_{12}BrNO_3S$ (366.2)	3200, 1710, 1635	3.77 (s, 3H, OCH$_3$); 7.32 (d, 1H, J=4 Hz); 7.53 (d, 1H, J=4 Hz); 7.6–7.8 (m, 3H); 7.95 (s, 1H, HC=); 8.05–8.2 (m, 2H); 9.93 (s, 1H, NH)
(*E*)-**5db**	60	112–113°	$C_{15}H_{12}BrNO_3S$ (366.2)	3240, 1695, 1620	3.77 (s, 3H, OCH$_3$); 7.07 (s, 1H, HC=); 7.13 (d, 1H, J=4 Hz); 7.23 (d, 1H, J=4 Hz); 7.5–7.8 (m, 3H); 8.0–8.2 (m, 2H); 10.35 (s, 1H, NH)
(*Z*)-**5ea**	76	161–163°	$C_{10}H_{10}N_2O_5S$ (270.3)	3220, 1715, 1660	2.06 (s, 3H, CH$_3$); 3.75 (s, 3H, OCH$_3$); 7.66 (d, 1H, J=4 Hz); 7.80 (d, 1H, J=4 Hz); 8.18 (s, 1H, HC=); 9.77 (s, 1H, HC=)
(*Z*)-**5eb**	82	185–186°	$C_{15}H_{12}N_2O_5S$ (332.3)	3220, 1720, 1665	3.73 (s, 3H, OCH$_3$); 7.6–7.8 (m, 4H); 8.00 (d, 1H, J=4 Hz); 8.08 (s, 1H, HC=); 8.1–8.2 (m, 2H); 10.22 (s, 1H, NH)

[a] All compounds gave satisfactory microanalyses: C, ±0.28; H, ±0.23; N, ±0.26; S, ±0.30.

is isolated by suction, dried, and recrystallized from ethanol/water or ethyl acetate/petroleum ether to give the analytically pure acid (*Z*)-**4** or (*E*)-**4**.

Methyl (*Z*)- and (*E*)-2-Acetylamino(or Benzoylamino)-3-(2- or 3-thienyl)-propenoates [(*Z*)-5 and (*E*)-5]; General Procedure:

A suspension of the unsaturated azlactone (*Z*)-**3** or (*E*)-**3** (4 mmol) in a solution of sodium methoxide (0.01 g) in absolute methanol (15 ml) is stirred at room temperature until the compound **3** has completely dissolved. The solution is filtered and evaporated in vacuo and the resultant solid was recrystallized from ethyl acetate/petroleum ether to give the analytically pure ester (*Z*)-**5** or (*E*)-**5**.

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