Synthesis of (4*Z*)-4-(Arylmethylidene)-5-ethoxy-1,3-oxazolidine-2-thiones by the Reaction of Ethyl (2*Z*)-3-Aryl-2-isothiocyanatoprop-2-enoates with Organolithium Compounds

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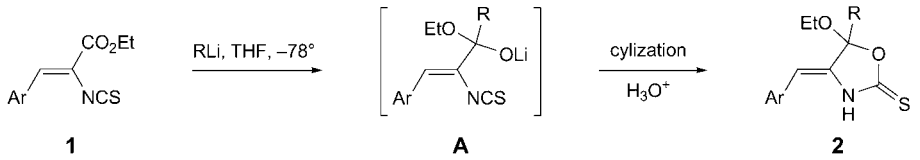
A convenient one-pot method for the preparation of (4*Z*)-4-(arylmethylidene)-5-ethoxy-1,3-oxazolidine-2-thiones **2** and **3** from ethyl (2*Z*)-3-aryl-2-isothiocyanatoprop-2-enoates **1**, which can be easily prepared from ethyl 2-azidoacetate and aromatic aldehydes, has been developed. Thus, these α-isothiocyanato α,β-unsaturated esters were treated with organolithium compounds, including lithium enolates of acetates, to provide 5-substituted (4*Z*)-4-(arylmethylidene)-5-ethoxy-1,3-oxazolidine-2-thiones, **2**, and 2-[(4*Z*)-(4-arylmethylidene)-5-ethoxy-2-thioxo-1,3-oxazolidin-5-yl]acetates, **3**.

Introduction. – 1,3-Oxazolidine-2-thiones are important heterocycles, because some compounds with this heterocyclic unit have been reported to exhibit biological activities [1]. The most common method for the preparation of 1,3-oxazolidine-2-thiones is based on the reaction of 2-aminoethanols with $CSCl_2$ or CS_2 [2][1]). On the other hand, we recently demonstrated that 4-substituted 4-alkoxy-1,4-dihydrobenzoxazine-2-thiones could be obtained by the reaction of 2-isothiocyanatobenzoates with organolithium compounds, including lithium enolates of esters and tertiary acetamides [3]. This success encouraged us to investigate the possibility of the formation of 4-(arylmethylidene)-1,3-oxazolidine-2-thiones by the reaction of 3-aryl-2-isothiocyanatoprop-2-enoates with organolithium compounds. In this article, we wish to describe the results of our study, which provide a convenient method for the preparation of 5-alkyl(or aryl)-(4*Z*)-4-(arylmethylidene)-5-ethoxy-1,3-oxazolidine-2-thiones **2** and ethyl 2-[(4*Z*)-4-(arylimethylidene)-5-ethoxy-2-thioxo-1,3-oxazolidin-5-yl]acetates **3** by the reaction of ethyl (2*Z*)-3-aryl-2-isothiocyanatoprop-2-enoates **1** with alkyl(or aryl)lithium and lithium enolates of acetates, respectively. To date, there have been no reports on the synthesis of these types of 1,3-oxazolidine-2-thiones.

Results and Discussion. – The one-pot synthesis of (4*Z*)-5-alkyl(or aryl)-4-(arylmethylidene)-5-ethoxy-1,3-oxazolidine-2-thiones **2** from ethyl (2*Z*)-3-aryl-2-isothiocyanatoprop-2-enoates **1** was accomplished as outlined in *Scheme 1*. The starting materials **1** were easily prepared by the successive treatment of ethyl (2*Z*)-3-aryl-2-azidoprop-2-enoates, derived from ethyl 2-azidoacetate and aromatic aldehydes [4],

[1]) A method *via* the reaction of NH_4SCN, acid chloride, and bromopyruvate or 2-chloroacetoacetate has been published [2d].

Scheme 1



1 **A** **2**

with Ph_3P and CS_2 under conditions reported by *Sun* and co-workers [5]. We started this study by reacting (2*Z*)-2-isothiocyanato-1-phenylprop-2-enoates (**1a**) with BuLi in THF at $-78°$. After aqueous workup, followed by purification using column chromatography, the desired product, (4*Z*)-5-butyl-5-ethoxy-4-(phenylmethylidene)-1,3-oxazolidine-2-thione (**2a**), was obtained as a single stereoisomer in 77% yield. The structure of **2a** was determined on the basis of its spectroscopic data. Mass spectrometry and elemental analysis established the molecular formula of the product as $C_{16}H_{21}NO_2S$. The IR spectrum showed absorption bands at 3216, 1685, and 1190 cm^{-1} due to N–H, C=C, and C=S groups, respectively. The ^{13}C-NMR spectrum exhibited 14 signals including a signal at 185.81 ppm assignable to the thiocarbamate C-atom. The ^{1}H-NMR data are in good agreement with the structure of **2a** (see *Exper. Part*). We determined the configuration of the C=C bond as (*Z*), because isomerization, during the reaction sequence, or the workup and purification process appears to be impropable. When the other four starting materials, **1b**–**1e**, were treated with five organolithium compounds including BuLi, the corresponding desired products **2b**–**2h** were obtained in comparable yields, as compiled in *Table 1*. The highly selective attack of an organolithium compound on the ester C=O group of **1** in a 1,2-addition fashion, followed by the quick cyclization of the resulting lithium 1-aryl-3-ethoxy-2-isothiocyanatoalk-1-en-3-yl oxide intermediates **A** by the attack of alkenyl oxide on the isothiocyanate C-atom (before elimination of ethoxide), is assumed to take place to give the expected products **2**.

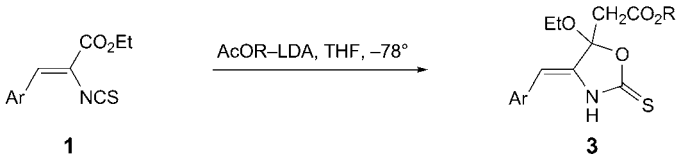
Table 1. *Preparation of (4Z)-4-Arylidene-1,3-oxazolidine-2-thiones* **2**

Entry	**1**	Ar	R	**2**	Yield[a]) [%]
1	**1a**	Ph	Bu	**2a**	77
2	**1b**	4-Me–C_6H_4	Ph	**2b**	72
3	**1b**	4-Me–C_6H_4	*t*Bu	**2c**	71
4	**1b**	4-Me–C_6H_4	Thiophen-2-yl	**2d**	67
5	**1c**	4-Cl–C_6H_4	Me	**2e**	63
6	**1d**	4-MeO–C_6H_4	Me	**2f**	64
7	**1e**	Thiophen-2-yl	Bu	**2g**	68
8	**1e**	Thiophen-2-yl	Ph	**2h**	79

[a]) Yields of isolated products.

With the above-mentioned results in hand, the preparation of 2-[(4*Z*)-4-(arylmethylidene)-5-ethoxy-2-thioxooxazolidin-5-yl]acetates **3** by the reaction of **1** with lithium enolates of acetates was then addressed, as depicted in *Scheme 2*. A similar

Scheme 2



1 **3**

addition–cyclization sequence, as described above for the preparation of **2**, also proceeded cleanly to afford, after the subsequent aqueous workup, the desired products **3** in fair yields, as collected in *Table 2*. Unfortunately, it should be noted that attempts to obtain 2-[(4*Z*)-4-(arylmethylidene)-2-thioxo-1,3-oxazolidin-5-yl]-*N*,*N*-dimethylacetamides using *N*,*N*-dimethylacetamide in place of acetates were unsuccessful. The reactions resulted in the formation of rather complicated mixtures of products, from which only a very low yield of the desired product contaminated with structurally undefined products was obtained in each case (results not shown in *Table 2*).

Table 2. *Preparation of 2-[(4Z)-4-Arylidene-2-thioxo-1,3-oxazolidin-5-yl]acetates* **3**

Entry	**1**	Ar	R	**3**	Yield[a])[%]
1	**1a**	Ph	^{t}Bu	**3a**	77
2	**1c**	4-Cl–C_6H_4	^{t}Bu	**3b**	62
3	**1d**	4-MeO–C_6H_4	^{t}Bu	**3c**	69
4	**1d**	4-MeO–C_6H_4	Et	**3d**	61
5	**1e**	Thiophen-2-yl	^{t}Bu	**3e**	68

[a]) Yields of isolated products.

In conclusion, the aforementioned results demonstrate that the reaction of (2*Z*)-3-aryl-2-isothiocyanatoprop-2-enoates with organolithium compounds, including lithium enolates of acetates, provides a facile method for the preparation of a new type of 1,3-oxazolidine-2-thiones, *i.e.*, 5-substituted (4*Z*)-4-(arylmethylidene)-1,3-oxazolidine-2-thiones. As the starting materials are readily available, and the manipulations are very simple, the present method may be valuable in organic synthesis.

Experimental Part

General. All of the org. solvents used in this study were dried on appropriate drying agents and distilled prior to use. TLC: *Merck* silica gel *60 PF_{254}*. Column chromatography (CC): *Wako Gel C-200E*. M.p.: *Laboratory Devices MEL-TEMP II* apparatus; uncorrected. IR Spectra: *Perkin–Elmer Spectrum65* FT-IR spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR Spectra: *JEOL ECP500* FT NMR spectrometer, at 500 MHz or *JEOL LA400* FT NMR spectrometer at 400 MHz; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ^{13}C-NMR Spectra: *Bruker Biospin AVANCE II 600* at 150 MHz, *JEOL ECP500* FT NMR spectrometer at 125 MHz, or *JEOL LA400* FT NMR spectrometer at 100 MHz; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard. EI-MS (70 eV): *JEOL JMS AX505 HA* spectrometer; in *m*/*z* (rel. %). HR-MS (*DART*®, pos.): *Thermo Scientific Exactive* spectrometer; in *m*/*z*.

Ethyl (2Z)-2-isothiocyanato-3-phenylprop-2-enoate (**1a**) was prepared from ethyl (2*Z*)-2-azido-3-phenylprop-2-enoate as described in [5]. BuLi was supplied by *Asia Lithium Corporation*. All other chemicals used in this study were commercially available.

(2Z)-3-Aryl-2-isothiocyanatoprop-2-enoates **1b**–**1e** were prepared from the respective azides under the conditions used for the preparation of **1a**.

Ethyl (2Z)-2-Isothiocyanato-3-(4-methylphenyl)prop-2-enoate (**1b**). Yield: 49%. White solid. M.p. 53–54° (hexane). IR (KBr): 2030, 1724, 1260. ^{1}H-NMR (400 MHz): 1.41 (*t*, *J* = 6.8, 3 H); 2.40 (*s*, 3 H); 4.38 (*q*, *J* = 6.8, 2 H); 7.24 (*s*, 1 H); 7.26 (*d*, *J* = 7.3, 2 H); 7.72 (*d*, *J* = 7.3, 2 H). Anal. calc. for $C_{13}H_{13}NO_2S$ (247.31): C 63.13, H 5.30, N 5.66; found: C 62.91, H 57.38, N 5.61.

Ethyl (2Z)-3-(4-Chlorophenyl)-2-isothiocyanatoprop-2-enoate (**1c**). Yield: 64%. White solid. M.p. 107–109° (hexane/Et_2O). IR (KBr): 2047, 1718, 1626, 1260. ^{1}H-NMR (500 MHz): 1.41 (*t*, *J* = 6.9, 3 H); 4.38 (*t*, *J* = 6.9, 2 H); 7.21 (*s*, 1 H); 7.40 (*d*, *J* = 8.4, 2 H); 7.76 (*d*, *J* = 8.4, 2 H). Anal. calc. for $C_{12}H_{10}ClNO_2S$ (267.73): C 53.83, H 3.76, N 5.23; found: C 53.65, H 4.04, N 5.22.

Ethyl (2Z)-2-Isothiocyanato-3-(4-methoxyphenyl)prop-2-enoate (**1d**). Yield: 56%. Pale-yellow oil. R_f (THF/hexane 1:20) 0.25. IR (neat): 2062, 1716, 1617, 1269. ^{1}H-NMR (500 MHz): 1.40 (*t*, *J* = 7.4, 3 H); 3.86 (*s*, 3 H); 4.37 (*q*, *J* = 7.4, 2 H); 6.95 (*d*, *J* = 8.6, 2 H); 7.23 (*s*, 1 H); 7.80 (*d*, *J* = 8.6, 2 H). Anal. calc. for $C_{13}H_{13}NO_3S$ (263.31): C 59.30, H 4.98, N 5.32; found: C 59.23, H 4.94, N 5.54.

Ethyl (2Z)-2-Isothiocyanato-3-(thiophen-2-yl)prop-2-enoate (**1e**). Yield: 78%. Pale-yellow solid. M.p. 150–152° (hexane/Et_2O). IR (KBr): 2057, 1721, 1615, 1254. ^{1}H-NMR (500 MHz): 1.40 (*t*, *J* = 6.9, 3 H); 4.37 (*q*, *J* = 6.9, 2 H); 7.12 (*dd*, *J* = 4.6, 3.8, 1 H); 7.43 (*d*, *J* = 3.8, 1 H); 7.51 (*s*, 1 H); 7.57 (*d*, *J* = 4.6, 1 H). Anal. calc. for $C_{10}H_9NO_2S_2$ (239.31): C 50.19, H 3.79, N 5.85; found: C 50.02, H 3.93, N 5.55.

(4Z)-5-Butyl-5-ethoxy-4-(phenylmethylidene)-1,3-oxazolidine-2-thione (**2a**). *Representative Procedure.* To a stirred soln. of **1a** (0.12 g, 0.51 mmol) in THF (4 ml) at −78° was added BuLi (1.6M in hexane, 0.51 mmol) dropwise. After 15 min, sat. aq. NH_4Cl (10 ml) was added, and the mixture was warmed to r.t. and extracted with AcOEt (3 × 10 ml). The combined extracts were washed with brine (10 ml), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by PLC (SiO_2; AcOEt/hexane 1:10) to give **2a** (0.12 g, 77%). Pale-yellow oil. R_f (AcOEt/hexane 1:10) 0.42. IR (neat): 3216, 1685, 1465, 1190. ^{1}H-NMR (500 MHz): 0.92 (*t*, *J* = 7.4, 3 H); 1.24 (*t*, *J* = 6.9, 3 H); 1.34–1.51 (*m*, 4 H); 1.90–1.96 (*m*, 1 H); 2.10–2.16 (*m*, 1 H); 3.51–3.63 (*m*, 2 H); 5.66 (*s*, 1 H); 7.26 (*d*, *J* = 7.4, 2 H); 7.30 (*t*, *J* = 7.3, 1 H); 7.41 (*t*, *J* = 7.4, 2 H); 8.72 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 13.84; 14.89; 22.40; 24.54; 39.23; 59.81; 102.93; 116.22; 127.43; 127.79; 129.33; 134.00; 134.11; 185.81. HR-MS: 292.1354 ($[M+H]^+$, $C_{16}H_{22}NO_2S^+$; calc. 292.1371). Anal. calc. for $C_{16}H_{21}NO_2S$ (291.41): C 65.96, H 7.26, N 4.81; found: C 65.82, H 7.30, N 4.71.

(4Z)-5-Ethoxy-5-phenyl-4-[(4-methylphenyl)methylidene]-1,3-oxazolidine-2-thione (**2b**). White solid. M.p. 147–148° (hexane/Et_2O). IR (KBr): 3120, 1685, 1463, 1174. ^{1}H-NMR (400 MHz): 1.35 (*t*, *J* = 7.3, 3 H); 2.35 (*s*, 3 H); 3.68–3.83 (*m*, 2 H); 5.59 (*s*, 1 H); 7.11 (*d*, *J* = 8.3, 2 H); 7.19 (*d*, *J* = 8.3, 2 H); 7.41–7.44 (*m*, 3 H); 7.56–7.58 (*m*, 2 H); 8.79 (br. *s*, 1 H). ^{13}C-NMR (150 MHz): 14.98; 21.22; 60.54; 105.52; 114.14; 125.74; 127.35; 128.60; 129.71; 129.93; 130.91; 134.12; 137.60; 137.95; 185.30. HR-MS: 326.1227 ($[M+H]^+$, $C_{19}H_{20}NO_2S^+$; calc. 326.1215). Anal. calc. for $C_{19}H_{19}NO_2S$ (325.42): C 70.12, H 5.88, N 4.30; found: C 70.03, H 5.65, N 4.15.

(4Z)-5-(1,1-Dimethylethyl)-5-ethoxy-4-[(4-methylphenyl)methylidene]-1,3-oxazolidine-2-thione (**2c**). White solid. M.p. 148–150° (hexane/CH_2Cl_2). IR (KBr): 3230, 1680, 1454, 1176. ^{1}H-NMR (500 MHz): 1.10 (*s*, 9 H); 1.24 (*t*, *J* = 6.9, 3 H); 2.37 (*s*, 3 H); 3.48–3.61 (*m*, 2 H); 5.68 (*s*, 1 H); 7.14 (*d*, *J* = 8.0, 2 H); 7.22 (*d*, *J* = 8.0, 2 H); 8.67 (br. *s*, 1 H). ^{13}C-NMR (150 MHz): 14.82; 21.22; 23.65; 40.28; 60.33; 104.95; 120.17; 127.37; 129.98; 131.09; 131.75; 137.79; 185.94. HR-MS: 306.1509 ($[M+H]^+$, $C_{17}H_{24}NO_2S^+$; calc. 306.1528). Anal. calc. for $C_{17}H_{23}NO_2S$ (305.44): C 66.85, H 7.59, N 4.59; found: C 66.80, H 7.78, N 4.58.

(4Z)-5-Ethoxy-4-[(4-methylphenyl)methylidene]-5-(thiophen-2-yl)-1,3-oxazolidine-2-thione (**2d**). Pale-yellow, viscous oil. R_f (AcOEt/hexane 1:10) 0.33. IR (neat): 3239, 1684, 1461, 1166. ^{1}H-NMR (500 MHz): 1.34 (*t*, *J* = 6.9, 3 H); 2.37 (*s*, 3 H); 3.69–3.81 (*m*, 2 H); 5.78 (*s*, 1 H); 7.02 (*dd*, *J* = 5.4, 3.8, 1 H); 7.16 (*d*, *J* = 7.6, 2 H); 7.21–7.22 (*m*, 3 H); 7.41 (*d*, *J* = 5.4, 1 H); 8.83 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 14.55; 20.86; 60.53; 105.64; 111.91; 126.52; 126.58; 127.10; 127.35; 129.61; 130.37; 132.89;

137.76; 140.31; 184.24. HR-MS: 332.0765 ($[M+H]^+$, $C_{17}H_{18}NO_2S_2^+$; calc. 332.0779). Anal. calc. for $C_{17}H_{17}NO_2S_2$ (331.45): C 61.60, H 5.17, N 4.23; found: C 61.54, H 5.46, N 4.19.

(4Z)-4-[(4-Chlorophenyl)methylidene]-5-ethoxy-5-methyl-1,3-oxazolidine-2-thione (**2e**). Pale-yellow solid. M.p. 109–111° (hexane). IR (KBr): 3225, 1687, 1461, 1189. ^{1}H-NMR (500 MHz): 1.25 (*t*, *J* = 6.9, 3 H); 1.81 (*s*, 3 H); 3.54–3.58 (*m*, 2 H); 5.62 (*s*, 1 H); 7.19 (*d*, *J* = 8.4, 2 H); 7.38 (*d*, *J* = 8.4, 2 H); 8.70 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 14.87; 26.13; 60.04; 101.66; 113.83; 128.73; 129.48; 132.29; 133.53; 135.43; 185.51. HR-MS: 284.0508 ($[M+H]^+$, $C_{13}H_{15}ClNO_2S^+$; calc. 284.0512). Anal. calc. for $C_{13}H_{14}ClNO_2S$ (283.77): C 55.02, H 4.97, N 4.94; found: C 54.91, H 5.04, N 4.83.

(4Z)-5-Ethoxy-4-[(4-methoxyphenyl)methylidene]-5-methyl-1,3-oxazolidine-2-thione (**2f**). Pale-yellow solid. M.p. 99–101° (hexane/CH_2Cl_2). IR (KBr): 3239, 1686, 1463, 1178. ^{1}H-NMR (500 MHz): 1.24 (*t*, *J* = 7.4, 3 H); 1.80 (*s*, 3 H); 3.52–3.59 (*m*, 2 H); 3.84 (*s*, 3 H); 5.63 (*s*, 1 H); 6.93 (*d*, *J* = 8.6, 2 H); 7.19 (*d*, *J* = 8.6, 2 H); 8.74 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 14.87; 26.21; 55.35; 59.88; 102.85; 113.80; 114.71; 126.26; 128.75; 133.31; 159.10; 185.44. HR-MS: 280.1008 ($[M+H]^+$, $C_{14}H_{18}NO_3S^+$; calc. 280.1007). Anal. calc. for $C_{14}H_{17}NO_3S$ (279.35): C 60.19, H 6.13, N 5.01; found: C 59.98, H 6.14, N 4.98.

(4Z)-5-Butyl-5-ethoxy-4-[(thiophen-2-yl)methylidene]-1,3-oxazolidine-2-thione (**2g**). Pale-yellow, viscous oil. R_f (AcOEt/hexane 1:10) 0.33. IR (neat): 3239, 1679, 1452, 1189. ^{1}H-NMR (500 MHz): 0.90 (*t*, *J* = 7.6, 3 H); 1.22 (*t*, *J* = 6.9, 3 H); 1.32–1.47 (*m*, 4 H); 1.87–1.93 (*m*, 1 H); 2.08–2.14 (*m*, 1 H); 3.50–3.56 (*m*, 2 H); 5.81 (*s*, 1 H); 7.02 (*d*, *J* = 3.1, 1 H); 7.08 (*dd*, *J* = 5.3, 3.1, 1 H); 7.34 (*d*, *J* = 5.3, 1 H); 8.81 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 13.78; 14.82; 22.35; 24.46; 39.14; 59.84; 96.21; 116.18; 125.15; 126.57; 127.93; 132.47; 136.60; 185.36. HR-MS: 298.0932 ($[M+H]^+$, $C_{14}H_{20}NO_2S_2^+$; calc. 298.0935). Anal. calc. for $C_{14}H_{19}NO_2S_2$ (297.44): C 56.53, H 6.44, N 4.71; found: C 56.46, H 6.53, N 4.61.

(4Z)-5-Ethoxy-5-phenyl-4-[(thiophen-2-yl)methylidene]-1,3-oxazolidine-2-thiones (**2h**). Pale-yellow, viscous oil. R_f (AcOEt/hexane 1:5) 0.41. IR (neat): 3248, 1678, 1449, 1175. ^{1}H-NMR (500 MHz): 1.34 (*t*, *J* = 7.6, 3 H); 3.67–3.78 (*m*, 2 H); 5.76 (*s*, 1 H); 6.96 (*d*, *J* = 3.8, 1 H); 7.04 (*dd*, *J* = 5.3, 3.8, 1 H); 7.32 (*d*, *J* = 5.3, 1 H); 7.41–7.42 (*m*, 3 H); 7.56 (*dd*, *J* = 7.6, 1.5, 2 H); 8.87 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 14.93; 60.62; 98.63; 114.10; 125.33; 125.68; 126.91; 127.93; 128.65; 129.80; 133.27; 136.62; 137.37; 184.93. HR-MS: 318.0630 ($[M+H]^+$, $C_{15}H_{16}NO_2S_2^+$; calc. 318.0622). Anal. calc. for $C_{16}H_{15}NO_2S_2$ (317.43): C 60.54, H 4.76, N 4.41; found: C 60.37, H 4.85, N 4.17.

1,1-Dimethylethyl 2-[(4Z)-5-Ethoxy-4-(phenylmethylidene)-2-thioxo-1,3-oxazolidin-5-yl]acetate (**3a**). *Representative Procedure.* To a stirred soln. of LDA (LiN^iPr_2; 0.51 mmol), generated by the standard method from BuLi and $^iPr_2NH$, in THF (2 ml) at −78°, was added AcO^{t}Bu (60 mg, 0.51 mmol) dropwise. After 15 min, a soln. of **1a** (0.12 g, 0.51 mmol) in THF (2 ml) was added, and stirring was continued for 10 min before sat. aq. NH_4Cl (10 ml) was added. The mixture was warmed to r.t. and extracted with AcOEt (3 × 10 ml). The combined extracts were washed with brine (10 ml), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by PLC (SiO_2; AcOEt/hexane 1:5) to give **3a** (0.13 g, 77%). White solid. M.p. 90–92° (hexane). IR (KBr): 3230, 1732, 1691, 1470, 1149. ^{1}H-NMR (500 MHz): 1.24 (*t*, *J* = 6.9, 3 H); 1.42 (*s*, 9 H); 2.99 (*d*, *J* = 16.0, 1 H); 3.21 (*d*, *J* = 16.0, 1 H); 3.52–3.63 (*m*, 2 H); 5.72 (*s*, 1 H); 7.26 (*d*, *J* = 8.0, 2 H); 7.30 (*t*, *J* = 7.4, 1 H); 7.41 (*dd*, *J* = 8.0, 7.4, 2 H); 8.78 (br. *s*, 1 H). ^{13}C-NMR (150 MHz): 14.81; 27.95; 45.03; 59.42; 82.11; 103.20; 111.59; 127.39; 127.86; 129.33; 133.87; 133.92; 166.22; 185.69. LR-MS: 349 (46, M^+), 293 (68), 247 (100). Anal. calc. for $C_{18}H_{23}NO_4S$ (349.44): C 61.87, H 6.63, N 4.01; found: C 61.80, H 6.69, N 3.97.

1,1-Dimethylethyl 2-{(4Z)-4-[(4-Chlorophenyl)methylidene]-5-ethoxy-2-thioxo-1,3-oxazolidin-5-yl}acetate (**3b**). White solid. M.p. 128–130° (hexane/AcOEt). IR (KBr): 3200, 1733, 1692, 1465, 1142. ^{1}H-NMR (500 MHz): 1.24 (*t*, *J* = 6.9, 3 H); 1.41 (*s*, 9 H); 2.98 (*d*, *J* = 16.8, 1 H); 3.20 (*d*, *J* = 16.8, 1 H); 3.52–3.59 (*m*, 2 H); 5.65 (*s*, 1 H); 7.18 (*d*, *J* = 8.4, 2 H); 7.38 (*d*, *J* = 8.4, 2 H); 8.88 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 14.80; 27.95; 44.97; 59.48; 82.17; 101.88; 111.62; 128.67; 129.52; 132.33; 133.59; 134.40; 166.20; 185.70. HR-MS: 384.1029 ($[M+H]^+$, $C_{18}H_{23}ClNO_4S^+$; calc. 384.1036). Anal. calc. for $C_{18}H_{22}ClNO_4S$ (383.89): C 56.32, H 5.78, N 3.65; found: C 56.17, H 6.01, N 3.64.

1,1-Dimethylethyl 2-{5-Ethoxy-(4Z)-4-[(4-methoxyphenyl)methylidene]-2-thioxo-1,3-oxazolidin-5-yl}acetate (**3c**). Pale-yellow solid. M.p. 121–123° (hexane/Et_2O). IR (neat): 3283, 1733, 1608, 1466, 1179. ^{1}H-NMR (500 MHz): 1.23 (*t*, *J* = 7.4, 3 H); 1.41 (*s*, 9 H); 2.97 (*d*, *J* = 16.6, 1 H); 3.19 (*d*, *J* = 16.6, 1 H); 3.51–3.60 (*m*, 2 H); 3.85 (*s*, 3 H); 5.66 (*s*, 1 H); 6.93 (*d*, *J* = 8.6, 2 H); 7.19 (*d*, *J* = 8.6, 2 H); 8.75 (br. *s*, 1 H). ^{13}C-NMR (100 MHz): 14.80; 27.95; 45.10; 55.37; 59.34; 82.02; 103.17; 111.59; 114.74; 126.28;

128.72; 132.25; 159.15; 166.27; 185.64. HR-MS: 380.1531 ($[M+H]^+$, $C_{19}H_{26}NO_5S^+$; calc. 380.1532). Anal. calc. for $C_{19}H_{25}NO_5S$ (379.47): C 60.14, H 6.64, N 3.69; found: C 60.12, H 6.72, N 3.43.

Ethyl 2-{5-Ethoxy-(4Z)-4-[(4-methoxyphenyl)methylidene]-2-thioxo-1,3-oxazolidin-5-yl}acetate (**3d**). Pale-yellow, viscous oil. R_f (AcOEt/hexane 1:5) 0.23. IR (neat): 3271, 1740, 1687, 1607, 1468, 1176. ^{1}H-NMR (500 MHz): 1.22, 1.23 (2*t*, $J=6.9$ each, total 6 H); 3.05 (*d*, $J=16.8$, 1 H); 3.25 (*d*, $J=16.8$, 1 H); 3.53–3.61 (*m*, 2 H); 3.83 (*s*, 3 H); 4.10–4.17 (*m*, 2 H); 5.66 (*s*, 1 H); 6.93 (*d*, $J=8.4$, 2 H); 7.20 (*d*, $J=8.4$, 2 H); 8.7 (br., 1 H). ^{13}C-NMR (125 MHz): 14.03; 14.75; 43.71; 55.38; 59.34; 61.07; 103.25; 111.28; 114.67; 126.17; 128.81; 132.05; 159.13; 167.23; 185.68. HR-MS: 352.1225 ($[M+H]^+$, $C_{17}H_{22}NO_5S^+$; calc. 352.1219). Anal. calc. for $C_{17}H_{21}NO_5S$ (351.42): C 58.10, H 6.02, N 3.99; found: C 58.01, H 6.06, N 3.92.

1,1-Dimethylethyl 2-{(4Z)-5-Butyl-5-ethoxy-4-[(thiophen-2-yl)methylidene]-2-thioxo-1,3-oxazolin-5-yl}acetate (**3e**). Pale-yellow solid. M.p. 90–92° (hexane/Et_2O). IR (KBr): 3261, 1733, 1683, 1461, 1151. ^{1}H-NMR (500 MHz): 1.22 (*t*, $J=7.4$, 3 H); 1.40 (*s*, 9 H); 2.97 (*d*, $J=16.6$, 1 H); 3.20 (*d*, $J=16.6$, 1 H); 3.51–3.56 (*m*, 2 H); 5.89 (*s*, 1 H); 7.02 (*d*, $J=4.0$, 1 H); 7.08 (*dd*, $J=5.1$, 4.0, 1 H); 7.35 (*d*, $J=5.1$, 1 H); 8.80 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 14.75; 27.90; 45.08; 59.51; 82.22; 96.57; 111.63; 125.24; 126.74; 127.97; 132.18; 136.45; 166.06; 185.19. HR-MS: 350.0971 ($[M+H]^+$, $C_{16}H_{22}NO_4S_2^+$; calc. 356.0990). Anal. calc. for $C_{16}H_{21}NO_4S_2$ (355.47): C 54.06, H 5.95, N 3.94; found: C 54.15, H 6.16, N 3.75.

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