Supporting Information

Unexpected Synthesis of Novel 3-allyl-5-(arylidene)-2-thioxo-thiazolidin-4-ones in Reactions of 3-Allylrhodanine with 2-Arylidene-4-methyl-5-oxopyrazolidinium ylides

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Experimental section

Melting points were determined using a Büchi-Tottoli apparatus. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or DMSO-d₆ solution (unless otherwise specified) with TMS as an internal reference using a Bruker AC 300 (¹H) or 75MHz (¹³C) instruments. Chemical shifts are given in δ parts per million (ppm) downfield from TMS. Multiplicities of ¹³C NMR resources were assigned by distortionless enhancement by polarization transfer (DEPT) experiments. Low-resolution mass spectra (MS) were recorded on a Perkin-Elmer Sciex API 3000 spectrometer. Column chromatography was carried out on SiO₂ (silica gel 60 Merck 0.063–0.200 mm). Thin-layer chromatography (TLC) was carried out on SiO₂ (silica gel 60, F 254 Merck 0.063–0.200 mm), and the spots were visualized with UV light. Commercial reagents were used without further purification unless stated.

General procedures for the synthesis of (arylidene)-4-methyl-5-oxopyrazolidin-2-ium-2-ides (4a-k)

Cooled in an ice bath, methyl methacrylate 60 mL was added to the solution of hydrazine hydrate (80%) 26 mL in ethanol 240 mL. After addition, the mixture was refluxed for 12 h. Then the solvent and the volatile components were removed under reduced pressure. The thick colorless oil, crude 4-methyl pyrazolidin-3-one **2**, was obtained in 80% yield. CF₃COOH (1 mL) was added to a stirred mixture of 4-methyl pyrazolidin-3-one (**2**; 1.14 g, 10 mmol), substituted aromatic aldehyde **3a-k** (10 mmol), and anhydride EtOH (40 mL). The

mixture was stirred at room temperature for 8-24 h. Volatile compounds were evaporated, Et₂O (30 ml) added to the residue, and the precipitate collected by filtration and crystallized from ethanol.

(Z)-Benzylidene-4-methyl-5-oxopyrazolidin-2-ium-1-ide (4a) ^[1]

From benzaldehyde, yield: 80%, mp 123–125 °C; ¹H NMR (DMSO, 300 MHz): δ 1.15 (d, 3H, J = 7.2 Hz), 2.68–2.76 (m, 1H), 4.15–4.22 (m, 1H), 4.70–4.78 (m, 1H), 7.48–7.51 (m, 3H), 7.63 (s, 1H), 8.26–8.30 (m, 2H); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.9 (CH₃), 35.3 (CH), 64.6 (CH₂N), 129.1 (2CH), 130.3 (C), 131.4 (2CH), 131.5 (CH), 132.5 (CH), 187.5 (CO).

(Z)-(4-Methylbenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (4b)

From 4-methylbenzaldehyde, yield: 90 %, mp 160-162 °C; ¹H NMR (DMSO, 300 MHz): δ 1.14 (d, 3H, J = 7.2 Hz), 2.35 (s, 3H, CH₃), 2.66–2.74 (m, 1H), 4.16 (dd, 1H, J = 7.2 Hz, 13.5 Hz), 4.70 (dd, 1H, J = 9.3 Hz, 13.5 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.59 (s, 1H), 8.17 (d, 2H, J = 8.1 Hz); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.9 (CH₃), 21.7 (CH₃), 35.3 (CH), 64.3 (CH₂N), 127.8 (C), 129.8 (2CH), 131.5 (2CH), 132.6 (=CH), 141.8 (C), 187.2 (CO).

(Z)-(4-Methoxybenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (4c) ^[1]

From 4-methoxybenzaldehyde, yield: 84%, mp 143-145 °C; ¹H NMR (DMSO, 300 MHz): δ 1.14 (d, 3H, J = 7.2 Hz), 2.65–2.73 (m, 1H), 3.82 (s, 3H, CH₃O), 4.08-4.16 (m, 1H), 4.63-4.71 (m, 1H), 7.07 (d, 2H, J = 9.0 Hz), 7.56 (s, 1H), 8.25 (d, 2H, J = 9.0 Hz); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.9 (CH₃), 35.4 (CH), 55.9 (CH₃O), 63.9 (CH₂N), 114.7 (2CH), 123.1 (C), 132.7 (=CH), 133.6 (2CH), 161.8 (C), 186.9 (CO).

(Z)-(4-Chlorobenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (4d)

From 4-chlorobenzaldehyde, yield: 86%, mp 185-187 °C; ¹H NMR (DMSO, 300 MHz): δ 1.15 (d, 3H, J = 7.2 Hz), 2.68–2.77 (m, 1H), 4.16-4.23 (m, 1H), 4.69-4.77 (m, 1H), 7.58 (d, 2H, J = 8.7 Hz), 7.64 (s, 1H), 8.29 (d, 2H, J = 8.7 Hz); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.8 (CH₃), 35.2 (CH), 64.6 (CH₂N), 129.2 (C), 129.3 (2CH), 131.1 (=CH), 132.9 (2CH), 135.9 (C), 187.5 (CO).

(Z)-(4-Dimethylaminobenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (4e)

From 4-dimethylaminobenzaldehyde, yield: 82 %, mp 178-180 °C; ¹H NMR (DMSO, 300 MHz): δ 1.13 (d, 3H, J = 7.2 Hz), 2.60–2.68 (m, 1H), 3.00 (s, 6H, N(CH₃)₂), 3.98-4.06 (m, 1H), 4.54-4.62 (m, 1H), 6.76 (d, 2H, J = 9.3 Hz), 7.41 (s, 1H), 8.10 (d, 2H, J = 9.3 Hz); ¹³C NMR (DMSO-d₆, 75 MHz): δ 16.0 (CH₃), 35.7 (CH), 40.0 (2CH₃), 63.2 (CH₂N), 111.6 (2CH), 117.5 (C), 133.5 (2CH), 133.9 (=CH), 152.2 (C), 186.1 (CO).

(Z)-(3-Nitrobenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (4f) ^[1]

From 3-nitrobenzaldehyde, yield: 75 %, mp 187-189 °C; ¹H NMR (DMSO, 300 MHz): δ 1.18 (d, 3H, J = 7.2 Hz), 2.73–2.81 (m, 1H), 4.23–4.30 (m, 1H), 4.76–4.84 (m, 1H), 7.76–7.89 (m, 2H), 8.30 (d, 1H, J = 8.7 Hz), 8.50 (d, 1H, J = 7.8 Hz), 9.35 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.7 (CH₃), 35.1 (CH), 65.0 (CH₂N), 124.5 (C), 125.1 (CH), 125.5 (CH), 129.8 (CH), 130.7 (CH), 137.1 (CH), 148.3 (C), 187.8 (CO).

(Z)-(3-Bromobenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (4g)

From 3-bromobenzaldehyde, yield: 78 %, mp 162-164 °C; ¹H NMR (DMSO, 300 MHz): δ 1.16 (d, 3H, J = 7.2 Hz), 2.70–2.77 (m, 1H), 4.18–4.25 (m, 1H), 4.71–4.78 (m, 1H), 7.47 (t, 1H, J = 8.1 Hz), 7.63 (s, 1H), 7.69 (dd, 1H, J = 8.1 Hz, 0.9 Hz), 8.09 (d, 1H, J = 8.1 Hz), 8.68 (t, 1H, J = 1.5 Hz); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.8 (CH₃), 35.1 (CH), 64.8 (CH₂N), 122.3 (C), 130.3 (CH), 130.5 (CH), 131.2 (CH), 132.4 (C), 132.9 (CH), 133.9 (CH), 187.7 (CO).

(Z)-4-Methyl-2-(furylidene)-5-oxopyrazolidin-2-ium-1-ide (4h)

From 2-furaldehyde, yield: 96 %, mp 170-172 °C; ¹H NMR (DMSO, 300 MHz): δ 1.14 (d, 3H, J = 7.2 Hz), 2.67–2.80 (m, 1H), 4.06–4.13 (m, 1H), 4.62–4.70 (m, 1H), 6.77 (dd, 1H, J = 4.0 Hz, 3.4 Hz), 7.58 (d, 1H, J = 4.1 Hz), 7.75 (s, 1H), 7.95 (d, 1H, J = 3.0 Hz); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.8 (CH₃), 36.0 (CH), 63.0 (CH₂N), 113.8 (CH), 119.5 (CH), 121.4 (CH), 146.6 (C), 147.1 (CH), 187.1 (CO).

(Z)-4-Methyl-2-(thienylidene)-5-oxopyrazolidin-2-ium-1-ide (4k)

From 2-thiophenecarboxaldehyde, yield: 94 %, mp 178-180 °C; ¹H NMR (DMSO, 300 MHz): δ 1.15 (d, 3H, J = 7.2 Hz), 2.71–2.84 (m, 1H), 4.08–4.15 (m, 1H), 4.64–4.72 (m, 1H), 7.23 (dd, 1H, J = 5.1 Hz, 4.0 Hz), 7.68 (d, 1H, J = 4.1 Hz), 7.96 (d, 1H, J = 5.1 Hz), 8.06 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.9 (CH₃), 36.5 (CH), 62.1 (CH₂N), 127.5 (CH), 128.1 (CH), 133.9 (CH), 132.6 (C), 135.4 (CH), 185.7 (CO).

General procedure for the synthesis of 3-allyl-5-(arylidene)-2-thioxo-thiazolidin-4-ones (6a-k).

To a solution of 3-allylrhodanine (1.15 mmol) in 10 ml of THF, 4-methyl-5-oxo-1,2-pyrazolidinium ylides (1.38 mmol) was added. The mixture was refluxed for 8-12 h, monitored by TLC, the reaction completed and a yellow spot (TLC R_f = 0.3, using hexane/ethyl acetate 1:9) was generated cleanly. The solvent was evaporated in vacuo. The crude product was purified on silica gel packed column using hexane: ethyl acetate (1/9) as eluent.

(Z)-3-Allyl-5-benzylidene-2-thioxothiazolidin-4-one (6a)

Yield: 68%, yellow solid, mp 142-144°C; IR (KBr, cm^{-1}): 1694 (CO), 1265 (CS); ^1H NMR (CDCl_3 , 300 MHz): δ 4.73-4.76 (m, 2H, NCH_2), 5.24-5.35 (m, 2H, $=\text{CH}_2$), 5.80-5.93 (m, 1H, $=\text{CH}$), 7.42-7.52 (m, 5H), 7.74 (s, 1H, $=\text{CH}$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 46.4 (NCH_2), 119.4 ($=\text{CH}_2$), 123.0 (C), 129.4 (2CH), 129.6 (CH), 130.6 (2CH), 119.8 (C), 130.8 (CH), 133.3 (CH), 167.4 (CO), 192.9 (CS); EI-MS (m/z) = 262 $[\text{M}+1]^+$; Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NOS}_2$; C, 59.74; H, 4.24; N, 5.36. Found: C, 59.65; H, 4.31; N, 5.28.

(Z)-3-Allyl-5-(4-methylbenzylidene)-2-thioxothiazolidin-4-one (6b)

Yield: 75%, yellow solid, mp 116-118°C; IR (KBr, cm^{-1}): 1690 (CO), 1257 (CS); ^1H NMR (CDCl_3 , 300 MHz): δ 2.40 (s, 3H, CH_3), 4.72-4.75 (m, 2H, NCH_2), 5.23-5.32 (m, 2H, $=\text{CH}_2$), 5.80-5.93 (m, 1H, $=\text{CH}$), 7.28 (d, 2H, $J = 8.4$ Hz), 7.39 (d, 2H, $J = 8.4$ Hz), 7.71 (s, 1H, $=\text{CH}$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.7 (CH_3), 46.4 (NCH_2), 119.3 ($=\text{CH}_2$), 121.7 (C), 129.6 (CH), 130.1 (2CH), 130.7 (2CH), 133.4 (CH), 131.7 (C), 141.7 (C), 167.5 (CO), 193.0 (CS); EI-MS (m/z) = 276 $[\text{M}+1]^+$; Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NOS}_2$; C, 61.06; H, 4.76; N, 5.09. Found: C, 61.14; H, 4.68; N, 5.15.

(Z)-3-Allyl-5-(4-methoxybenzylidene)-2-thioxothiazolidin-4-one (6c)

Yield: 78%, yellow solid, mp 90-92°C; IR (KBr, cm^{-1}): 1687 (CO), 1260 (CS); ^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ 3.81 (s, 3H, CH_3O), 4.59-4.62 (m, 2H, NCH_2), 5.07-5.18 (m, 2H, $=\text{CH}_2$), 5.77-5.86 (m, 1H, $=\text{CH}$), 7.08 (d, 2H, $J = 9.0$ Hz), 7.57 (d, 2H, $J = 9.0$ Hz), 7.74 (s, 1H, $=\text{CH}$); ^{13}C NMR ($\text{DMSO}-d_6$, 75 MHz): δ 46.4 (NCH_2), 56.1 (CH_3O), 115.6 (2CH), 118.2 ($=\text{CH}_2$), 119.4 (C), 125.9 (C), 130.7 (CH), 133.4 (2CH), 133.9 (CH), 162.0 (C), 167.1 (CO), 193.3 (CS); EI-MS (m/z) = 292 $[\text{M}+1]^+$; Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}_2$; C, 57.71; H, 4.50; N, 4.81. Found: C, 57.80; H, 4.58; N, 4.72.

(Z)-3-Allyl-5-(4-chlorobenzylidene)-2-thioxothiazolidin-4-one (6d)

Yield: 72%, yellow solid, mp 97-99°C; IR (KBr, cm^{-1}): 1686 (CO), 1264 (CS); ^1H NMR (CDCl_3 , 300 MHz): δ 4.72-4.75 (m, 2H, NCH_2), 5.24-5.33 (m, 2H, $=\text{CH}_2$), 5.79-5.90 (m, 1H, $=\text{CH}$), 7.40 (d, 2H, $J = 9.0$ Hz), 7.44 (d, 2H, $J = 9.0$ Hz), 7.67 (s, 1H, $=\text{CH}$); ^{13}C NMR ($\text{DMSO}-d_6$, 75 MHz): δ 46.5 (NCH_2), 119.5 ($=\text{CH}_2$), 123.6 (C), 128.8 (C), 129.4 (CH), 129.7 (2CH), 131.5 (CH), 131.7 (2CH), 136.9 (C), 167.3 (CO), 192.3 (CS); EI-MS (m/z) = 296 (^{35}Cl) $[\text{M}+1]^+$, 298 (^{37}Cl) $[\text{M}+3]^+$; Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{ClNOS}_2$; C, 52.79; H, 3.41; N, 4.74. Found: C, 52.88; H, 3.47; N, 4.68.

(Z)-3-Allyl-5-(4-dimethylaminobenzylidene)-2-thioxothiazolidin-4-one (6e)

Yield: 82%, yellow solid, mp 118-120°C; IR (KBr, cm^{-1}): 1695 (CO), 1270 (CS); ^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ 2.99 (s, 6H, $\text{N}(\text{CH}_3)_2$), 4.59-4.62 (m, 2H, NCH_2), 5.04-5.17 (m, 2H, $=\text{CH}_2$), 5.76-5.86 (m, 1H, $=\text{CH}$), 6.79 (d, 2H, $J = 9.0$ Hz), 7.42 (d, 2H, $J = 9.0$ Hz), 7.64 (s,

1H, =CH); ¹³C NMR (DMSO-d₆, 75 MHz): δ 40.0 (N(CH₃)₂), 46.3 (NCH₂), 112.6 (2CH), 118.1 (=CH₂), 114.2 (C), 120.3 (C), 130.8 (CH), 133.7 (2CH), 135.2 (CH), 152.4 (C), 167.1 (CO), 192.7 (CS); EI-MS (m/z) = 305 [M+1]⁺; Anal. Calcd for C₁₅H₁₆N₂OS₂; C, 59.18; H, 5.30; N, 9.20. Found: C, 59.27; H, 5.34; N, 9.28.

(Z)-3-Allyl-5-(3-nitrobenzylidene)-2-thioxothiazolidin-4-one (6f)

Yield: 85%, yellow solid, mp 140-142°C; IR (KBr, cm⁻¹): 1530 (NO₂), 1684 (CO), 1266 (CS); ¹H NMR (CDCl₃, 300 MHz): δ 4.73-4.76 (m, 2H, NCH₂), 5.25-5.34 (m, 2H, =CH₂), 5.79-5.89 (m, 1H, =CH), 7.68 (t, 1H, J = 8.1 Hz), 7.14 (s, 1H, =CH), 7.79 (d, 1H, J = 8.1 Hz), 8.28 (d, 1H, J = 8.1 Hz), 8.34 (d, 1H, J = 1.2 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ 46.6 (NCH₂), 119.8 (=CH₂), 124.7 (CH), 126.6 (C), 128.8 (CH), 129.5 (CH), 130.4 (CH), 130.9 (CH), 134.9 (C), 135.4 (CH), 148.8 (C), 167.0 (CO), 191.5 (CS); EI-MS (m/z) = 307 [M+1]⁺; Anal. Calcd for C₁₃H₁₀N₂O₃S₂; C, 50.97; H, 3.29; N, 9.14. Found: C, 60.05; H, 3.36; N, 9.22.

(Z)-3-Allyl-5-(3-bromobenzylidene)-2-thioxothiazolidin-4-one (6g)

Yield: 76%, yellow solid, mp 116-118°C; IR (KBr, cm⁻¹): 1690 (CO), 1258 (CS); ¹H NMR (DMSO-d₆, 300 MHz): δ 4.61-4.64 (m, 2H, NCH₂), 5.09-5.19 (m, 2H, =CH₂), 5.77-5.87 (m, 1H, =CH), 7.49 (t, 1H, J = 8.1 Hz), 7.58 (d, 1H, J = 8.1 Hz), 7.68 (d, 1H, J = 7.8 Hz), 7.78 (s, 1H, =CH), 7.84 (d, 1H, J = 1.4 Hz); ¹³C NMR (DMSO-d₆, 75 MHz): δ 46.5 (NCH₂), 118.4 (=CH₂), 123.0 (C), 124.6 (C), 129.1 (CH), 130.6 (CH), 131.7 (CH), 132.0 (CH), 133.8 (CH), 133.9 (CH), 135.8 (C), 166.8 (CO), 193.2 (CS); EI-MS (m/z) = 341 (⁷⁹Br) [M+1]⁺, 343 (⁸¹Br) [M+3]⁺; Anal. Calcd for C₁₃H₁₀BrNOS₂; C, 45.89; H, 2.96; N, 4.12. Found: C, 45.96; H, 3.06; N, 4.18.

(Z)-3-Allyl-5-furan-2-ylmethylene-2-thioxothiazolidin-4-one (6h)

Yield: 77 %, yellow solid, mp 96-98°C; IR (KBr, cm⁻¹): 1690 (CO), 1265 (CS); ¹H NMR (CDCl₃, 300 MHz): δ 4.71-4.74 (m, 2H, NCH₂), 5.22-5.30 (m, 2H, =CH₂), 5.79-5.92 (m, 1H, =CH), 6.58 (dd, 1H, J = 4.6 Hz, 1.8 Hz), 6.84 (d, 1H, J = 4.6 Hz), 7.47 (s, 1H, =CH), 7.70 (d, 1H, J = 1.8 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ 46.3 (NCH₂), 113.3 (CH), 118.4 (CH), 118.7 (CH), 119.2 (=CH₂), 120.9 (C), 129.7 (CH), 147.1 (CH), 150.1 (C), 167.2 (CO), 194.1 (CS); EI-MS (m/z) = 252 [M+1]⁺; Anal. Calcd for C₁₁H₉NO₂S₂; C, 52.57; H, 3.61; N, 5.57. Found: C, 53.08; H, 3.56; N, 5.52.

(Z)-3-Allyl-5-thiophen-2-ylmethylene-2-thioxothiazolidin-4-one (6k)

Yield: 70%, yellow solid, mp 129-131°C; IR (KBr, cm⁻¹): 1685 (CO), 1261 (CS); ¹H NMR (CDCl₃, 300 MHz): δ 4.72-4.75 (m, 2H, NCH₂), 5.23-5.32 (m, 2H, =CH₂), 5.79-5.93 (m, 1H, =CH), 7.20 (t, 1H, J = 4.8 Hz), 7.42 (d, 1H, J = 3.9 Hz), 7.71 (d, 1H, J = 4.8 Hz), 7.91 (s, 1H, =CH); ¹³C NMR (CDCl₃, 75 MHz): δ 46.5 (NCH₂), 119.3 (=CH₂), 121.1 (C), 125.5 (CH),

128.9 (CH), 129.5 (CH), 132.9 (CH), 133.9 (CH), 138.0 (C), 167.2 (CO), 192.1 (CS); EI-MS (m/z) = 268 [M+1]⁺; Anal. Calcd for C₁₁H₉NOS₃; C, 49.41; H, 3.39; N, 5.24. Found: C, 49.48; H, 3.45; N, 5.31.

Selected ¹H NMR, ¹³C NMR and DEPT spectra of compounds **4b,4d,4g, 4k** and **6a, 6b, 6e, 6k**

Figure S1. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 4b	S7-S8
Figure S2. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 4d	S8-S9
Figure S3. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 4g	S10-S11
Figure S4. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 4k	S11-S12
Figure S5. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 6a	S13-S14
Figure S6. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 6b	S14-S15
Figure S7. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 6e	S16-S17
Figure S8. ¹ H NMR, ¹³ C NMR and DEPT spectra of compound 6k	S17-S18
Figure S9. ORTEP diagram of compound 6a	S19-S21

Figure S1. ^1H NMR (300 MHz, DMSO- d_6) spectra of compound 4b

Figure S1. ^{13}C NMR (75 MHz, DMSO- d_6) spectra of compound 4b

336RMN37
UATRS CNRST
DEPT

Figure S1. ¹³C NMR (75 MHz, DMSO-d₆, DEPT) spectra of compound 4b

256RMN05
UATRS CNRST
1h

Figure S2. ¹H NMR (300 MHz, DMSO-d₆) spectra of compound 4d

Figure S3. ¹H NMR (300 MHz, DMSO-d₆) spectra of compound 4g

Figure S3. ¹³C NMR (75 MHz, DMSO-d₆) spectra of compound 4g

336RMN35
UATRS CNRST
DEPT

Figure S3. ¹³C NMR (75 MHz, DMSO-d₆, DEPT) spectra of compound 4g

526RMN10
UATRS CNRST
1h

Figure S4. ¹H NMR (300 MHz, DMSO-d₆) spectra of compound 4k

Figure S4. ^{13}C NMR (75 MHz, DMSO- d_6) spectra of compound 4k

Figure S4. ^{13}C NMR (75 MHz, DMSO- d_6 , DEPT) spectra of compound 4k

391RMN06
UATR CNRST
DEPT

Figure S5. ¹³C NMR (75 MHz, CDCl₃, DEPT) spectra of compound 6a

Figure S6. ¹H NMR (300 MHz, CDCl₃) spectra of compound 6b

Figure S6. ^{13}C NMR (75 MHz, CDCl_3) spectra of compound 6b

Figure S6. ^{13}C NMR (75 MHz, CDCl_3 , DEPT) spectra of compound 6b

Figure S7. ^{13}C NMR (75 MHz, DMSO- d_6 , DEPT) spectra of compound **6e**

Figure S8. ^1H NMR (300 MHz, CDCl_3) spectra of compound **6k**

Crystallographic supplementary data

Figure S9. Plot of the molecule of $C_{13}H_{11}NOS_2$ compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

The crystallographic data were collected on a Bruker X8 APEX Diffractometer equipped with an APEX II CCD area-detector and a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) at 296(2) K.^[2] The data were corrected for absorption using the program SADABS.^[3] The structure is solved by direct method technique and refined by full-matrix least-squares using *SHELXS97* and *SHELXL97* program packages.^[4] All non-hydrogen atoms were refined anisotropically. H atoms were located in a difference map and treated as riding with C—H = 0.97 Å and C—H = 0.93 Å for methylene and aromatic C—H, respectively. All hydrogen with $U_{iso}(H) = 1.2$ Ueq (aromatic, methylene).

The $C_{13}H_{11}NOS_2$ compound **6a** crystallizes in triclinic system, space group P-1, unit cell parameters $a = 7.0070$ (3) Å, $b = 7.3224$ (3) Å, $c = 13.4152$ (5) Å, $\alpha = 83.815$ (2)°, $\beta = 75.567$ (2)°, $\gamma = 70.608$ (2)°, $V = 628.53$ (4) Å³, $Z = 2$, $\mu = 0.41$ mm⁻¹, $M_r = 261.35$ g, $d_{cal} = 1.381$ g/cm³, crystal dimensions $0.39 \times 0.34 \times 0.29$ mm. In the interval $2.95^\circ < 2\theta < 27.48^\circ$, 17480 ° reflections were measured of which 2876 independent reflections were obtained after merging ($R_{int} = 0.039$). The final refinement gave $R1 = 0.046$; $wR2 = 0.122$ and $S = 1.01$ with 154 least-square parameters. The atomic parameters, interatomic distances and angles are given in the crystallographic supplementary. The molecule of this compound is build up from two attached five- and six-membered rings linked to an allyl group as shown in Fig.1. The two cycles are almost coplanar as indicated by the dihedral angle between them of $5.12(11)^\circ$. The allyl chain is nearly perpendicular to the five-membered ring as indicated by the torsion angle of $C(12)C(11)N(1)C(1) = 86.0(3)^\circ$ between them.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3229 (4)	0.1135 (3)	0.78932 (18)	0.0562 (6)
C2	0.1233 (3)	0.2552 (3)	0.66735 (16)	0.0474 (5)
C3	0.3347 (3)	0.2367 (3)	0.60535 (16)	0.0420 (4)
C4	0.3671 (3)	0.2948 (3)	0.50618 (16)	0.0446 (5)
H4	0.2472	0.3495	0.4813	0.054*
C5	0.5592 (3)	0.2861 (3)	0.43124 (16)	0.0446 (5)
C6	0.5480 (4)	0.3432 (3)	0.32988 (18)	0.0594 (6)
H6	0.4195	0.3871	0.3125	0.071*
C7	0.7254 (5)	0.3355 (4)	0.2550 (2)	0.0768 (8)
H7	0.7154	0.3746	0.1877	0.092*
C8	0.9166 (4)	0.2705 (4)	0.2790 (2)	0.0749 (8)
H8	1.0360	0.2633	0.2280	0.090*
C9	0.9306 (4)	0.2164 (4)	0.3784 (2)	0.0694 (7)
H9	1.0599	0.1741	0.3950	0.083*
C10	0.7548 (3)	0.2240 (3)	0.45414 (19)	0.0562 (6)
H10	0.7666	0.1872	0.5215	0.067*
C11	-0.0593 (4)	0.1840 (4)	0.8437 (2)	0.0727 (7)
H11A	-0.0307	0.0708	0.8892	0.087*
H11B	-0.1632	0.1782	0.8091	0.087*
C12	-0.1410 (8)	0.3618 (7)	0.9051 (4)	0.152 (2)
H12	-0.0404	0.3554	0.9405	0.182*
C13	-0.2557 (10)	0.4857 (8)	0.9256 (5)	0.179 (3)
H13A	-0.3732	0.5205	0.8984	0.215*
H13B	-0.2448	0.5659	0.9717	0.215*
N1	0.1313 (3)	0.1824 (3)	0.76724 (13)	0.0516 (4)
O1	-0.0366 (2)	0.3216 (3)	0.63829 (13)	0.0657 (5)
S1	0.51434 (8)	0.13276 (8)	0.68149 (5)	0.05384 (19)
S2	0.37836 (14)	0.02363 (13)	0.89906 (6)	0.0897 (3)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0664 (14)	0.0515 (13)	0.0559 (13)	-0.0197 (11)	-0.0226 (11)	-0.0001 (10)
C2	0.0432 (11)	0.0479 (11)	0.0546 (12)	-0.0153 (9)	-0.0157 (9)	-0.0019 (9)
C3	0.0386 (10)	0.0380 (10)	0.0534 (12)	-0.0120 (8)	-0.0176 (9)	-0.0022 (8)
C4	0.0398 (10)	0.0408 (10)	0.0578 (13)	-0.0119 (8)	-0.0202 (9)	-0.0019 (9)
C5	0.0452 (11)	0.0343 (10)	0.0558 (12)	-0.0136 (8)	-0.0113 (9)	-0.0049 (8)
C6	0.0611 (13)	0.0608 (14)	0.0582 (14)	-0.0220 (11)	-0.0140 (11)	-0.0003 (11)
C7	0.089 (2)	0.0823 (19)	0.0572 (16)	-0.0348 (16)	-0.0015 (14)	-0.0030 (13)
C8	0.0639 (16)	0.0648 (16)	0.085 (2)	-0.0241 (13)	0.0133 (15)	-0.0156 (15)
C9	0.0455 (13)	0.0543 (14)	0.102 (2)	-0.0143 (11)	-0.0061 (13)	-0.0060 (14)
C10	0.0468 (12)	0.0499 (12)	0.0710 (15)	-0.0149 (10)	-0.0134 (11)	0.0008 (11)
C11	0.0674 (16)	0.0831 (19)	0.0614 (16)	-0.0277 (14)	0.0008 (13)	0.0001 (13)
C12	0.131 (4)	0.112 (4)	0.147 (4)	-0.015 (3)	0.066 (3)	-0.031 (3)
C13	0.188 (6)	0.132 (5)	0.166 (5)	-0.043 (4)	0.045 (5)	-0.022 (4)
N1	0.0510 (10)	0.0546 (11)	0.0508 (11)	-0.0188 (8)	-0.0119 (8)	-0.0012 (8)
O1	0.0403 (8)	0.0867 (12)	0.0705 (11)	-0.0181 (8)	-0.0195 (7)	0.0063 (9)
S1	0.0460 (3)	0.0561 (3)	0.0629 (4)	-0.0129 (2)	-0.0256 (3)	0.0043 (3)
S2	0.1071 (6)	0.1064 (6)	0.0627 (4)	-0.0324 (5)	-0.0429 (4)	0.0188 (4)

Geometric parameters ($\text{\AA}$, $^\circ$) for (shelx)

C1—N1	1.364 (3)	C7—H7	0.9300
C1—S2	1.630 (2)	C8—C9	1.368 (4)

C1—S1	1.740 (2)	C8—H8	0.9300
C2—O1	1.208 (2)	C9—C10	1.377 (3)
C2—N1	1.395 (3)	C9—H9	0.9300
C2—C3	1.477 (3)	C10—H10	0.9300
C3—C4	1.339 (3)	C11—N1	1.465 (3)
C3—S1	1.7450 (19)	C11—C12	1.484 (5)
C4—C5	1.452 (3)	C11—H11A	0.9700
C4—H4	0.9300	C11—H11B	0.9700
C5—C6	1.393 (3)	C12—C13	1.002 (6)
C5—C10	1.395 (3)	C12—H12	0.9300
C6—C7	1.378 (4)	C13—H13A	0.9300
C6—H6	0.9300	C13—H13B	0.9300
C7—C8	1.373 (4)		
N1—C1—S2	127.44 (19)	C7—C8—H8	120.2
N1—C1—S1	110.67 (16)	C8—C9—C10	120.5 (3)
S2—C1—S1	121.89 (15)	C8—C9—H9	119.8
O1—C2—N1	123.24 (19)	C10—C9—H9	119.8
O1—C2—C3	126.5 (2)	C9—C10—C5	120.9 (2)
N1—C2—C3	110.24 (17)	C9—C10—H10	119.6
C4—C3—C2	121.30 (18)	C5—C10—H10	119.6
C4—C3—S1	129.28 (15)	N1—C11—C12	110.7 (3)
C2—C3—S1	109.42 (15)	N1—C11—H11A	109.5
C3—C4—C5	130.44 (18)	C12—C11—H11A	109.5
C3—C4—H4	114.8	N1—C11—H11B	109.5
C5—C4—H4	114.8	C12—C11—H11B	109.5
C6—C5—C10	117.7 (2)	H11A—C11—H11B	108.1
C6—C5—C4	118.0 (2)	C13—C12—C11	148.1 (8)
C10—C5—C4	124.2 (2)	C13—C12—H12	106.0
C7—C6—C5	120.7 (2)	C11—C12—H12	106.0
C7—C6—H6	119.7	C12—C13—H13A	120.0
C5—C6—H6	119.7	C12—C13—H13B	120.0
C8—C7—C6	120.5 (3)	H13A—C13—H13B	120.0
C8—C7—H7	119.7	C1—N1—C2	116.75 (18)
C6—C7—H7	119.7	C1—N1—C11	122.6 (2)
C9—C8—C7	119.7 (2)	C2—N1—C11	120.65 (19)
C9—C8—H8	120.2	C1—S1—C3	92.91 (10)

References

- [1] Y. Xin, J. Zhao, J. Gu, S. Zhu, Catalyst free 1,3-dipolar cycloaddition of 3-oxo-1,2-pyrazolidinium ylides to β -trifluoroacetyl vinyl ethyl ether: synthesis of 6-trifluoroacetyl substituted bicyclic pyrazolidinones, *J. Fluor. Chem.* 132 (2011) 402–408.
- [2] Bruker *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA. **2009**.
- [3] Sheldrick, G. M. *SADABS*. University of Göttingen, Germany. **2003**.
- [4] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.