

# Isolation of the key intermediates in the catalyst free conversion of oxiranes to thiiranes in water at ambient temperature

- Supporting Information -

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## 1. General Methods and Procedures:

### Analytical Methods:

All compounds were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, (<sup>19</sup>F-NMR), IR, MS and CHN analysis for new compounds. NMR spectra were recorded using Bruker Avance II 200 "Microbay", Bruker Avance II 400 WB or Bruker Avance 600 MHz spectrometer at ambient temperature. All <sup>1</sup>H-NMR shifts were reported in parts per million (ppm) relative to the residual solvent peak (7.24 ppm for CDCl<sub>3</sub>, 2.05 ppm for d<sub>6</sub>-acetone). Proton-decoupled <sup>13</sup>C-NMR chemical shifts were reported relative to the solvent peak (77.1 ppm for CDCl<sub>3</sub>, 29.84 ppm for d<sub>6</sub>-acetone). Multiplicities are indicated as bs (broadened singlet), s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), quint (quintet), m (multiplet). Coupling constants (*J*) are in Hertz (Hz). Infrared spectra were recorded on a Bruker IFS 25 and IFS 48 spectrophotometer using KBr pallets, as thin film or by applying ATR technique. Absorptions were reported in reciprocal centimetres and indicated as vs (very strong), s (strong), m (middle) and w (weak), br (broad). Both conventional (LRMS) and high resolution mass spectra (HRMS) were conducted on a Finnigan MAT 95 instrument, ionization by electron impact at 70 eV. Melting points were measured with Electrothermal<sup>®</sup> melting point apparatus IA6304 and are uncorrected. Optical rotations were measured with a Jasco P-2000 Polarimeter.

Reactions were monitored by GC/MS (Hewlett Packard 5890 Series II Gas Chromatograph with Hewlett Packard 5971 A Mass Selective Detector) or TLC (silica gel coated plastic sheets, Machery-Nagel, Polygram<sup>®</sup> SIL/UV<sub>254</sub>, 40x80 mm). Thin layer plates were visualized by irradiation with UV light at 254 nm and by staining the plates with alkaline KMnO<sub>4</sub> solution followed by gentle heating. Isolation of the products was performed by flash chromatography using Merck silica gel (60, particle size 0.040 – 0.063 mm). Solvents for flash chromatography have been distilled once with a rotary evaporator prior to use. Chemical yields refer to pure isolated substances. Compound names are in agreement with the Beilstein nomenclature.

Compound *rac-1e* was prepared according to the protocol of Barkworth *et al.*<sup>1</sup> Compound *rac-1f* was prepared according to the protocol of Alexakis *et al.*<sup>2</sup>

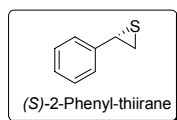
### General Procedure:

All reactions were carried out in a carousel reaction station or in 5 mL cylindrical reaction vessels. Reaction mixtures were stirred magnetically with Teflon coated stirring bars. Epoxides were purchased in highest quality available. Liquid epoxides were distilled once through a 10 cm Vigreux-column and stored under argon in a fridge prior to use. Solid epoxides were used as received. Distilled water was used as received. Ammonium thiocyanate was purchased from Riedel-de Haën in *puriss.* quality and used as received. Solvents for column chromatography were distilled once and used without further purification.

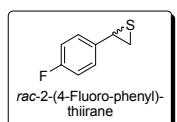
2 mL of a stock solution of ammonium thiocyanate (*c* = 1M) were placed in the reaction vessel, and 1 mmol of the respective epoxide was added at once. In the case of solid epoxides, 200 µL of dichloromethane, acetonitrile, THF or cyclopentyl-methyl-ether (CPME) were added. The heterogeneous mixture was stirred for the time indicated. After complete consumption of the starting material, monitored by GC/MS or TLC, the

reaction mixture was diluted with 5 mL of water and the aqueous phase was extracted with Et<sub>2</sub>O three times. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and after filtration the solvent was removed under reduced pressure. The crude product was subjected to flash chromatography using hexanes: ethyl acetate mixtures or pure diethyl ether as eluent or was recrystallized in the case of solid products.

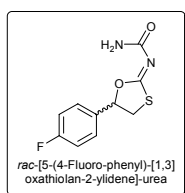
## 2. Characterization of prepared thiranes and of isolated intermediates:



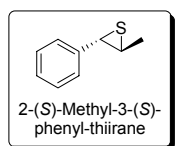
Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 126.7 mg of **2a** (0.93 mmol, 93%) as a colourless liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37 – 7.27 (5H, m), 3.95 – 3.92 (1H, dd, *J* = 6.4 Hz, 5.8 Hz), 2.92 – 2.91 (0.5H, d, *J* = 1.5 Hz), 2.90 – 2.89 (0.5H, d, *J* = 1.5 Hz), 2.70 – 2.69 (0.5H, d, *J* = 1.5 Hz), 2.68 – 2.68 (0.5H, d, *J* = 1.5 Hz). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ 139.16, 128.62, 127.66, 126.79, 36.18, 27.40. IR (cm<sup>-1</sup>): 3062 (m), 3029 (m), 2986 (m), 1602 (m), 1493 (m), 1455 (vs), 1065 (m), 1041 (s), 761 (vs), 695 (vs), 621 (vs), 610 (vs). LRMS {EI, 70 eV, *m/z* (%)}: 136 (93), 135 (100), 121 (4), 91 (48), 89 (5), 77 (14), 69 (10), 67 (6), 63 (5). HRMS (M<sup>+</sup>, C<sub>8</sub>H<sub>8</sub>S): cal.: 136.03467, found: 136.03407. [ $\alpha$ ]<sub>D</sub><sup>24</sup> = -29.26° (*c* = 6.94 g/L, CHCl<sub>3</sub>).



Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 120.1 mg of **2b** (0.78 mmol, 78%) as a colourless liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.24 – 7.19 (2H, m), 7.00 – 6.93 (2H, m), 3.87 – 3.82 (1H, t, *J* = 6.72 Hz), 2.87 – 2.82 (1H, dd, *J* = 6.52 Hz, 1.5 Hz), 2.59 – 2.54 (1H, d, *J* = 1.5 Hz). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ 162.35 (d, <sup>1</sup>*J*<sub>CF</sub> = 246.12 Hz), 134.98 (d, <sup>4</sup>*J*<sub>CF</sub> = 2.96 Hz), 128.47 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.11 Hz), 115.63 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.45 Hz), 35.63, 27.50. <sup>19</sup>F-NMR (376.46 MHz, CDCl<sub>3</sub>): δ -114.63. IR (cm<sup>-1</sup>): 3044 (w), 2987 (w), 2918 (w), 1887 (w), 1731 (w), 1649 (w), 1602 (m), 1509 (s), 1439 (w), 1416 (w), 1354 (w), 1296 (w), 1226 (s), 1158 (m), 1092 (m), 1014 (w), 834 (s), 610 (m). LRMS {EI, 70 eV, *m/z* (%)}: 154 (29), 124 (14), 123 (59), 122 (100), 109 (25), 101 (29), 96 (30), 95 (36), 75 (17), 74 (5), 69 (49). HRMS (M<sup>+</sup>, C<sub>8</sub>H<sub>7</sub>FS): cal.: 154.02525, found: 154.02496. Anal. calcd. for C<sub>8</sub>H<sub>7</sub>FS: C 62.31, H 4.53; found: C 62.24, H 4.55.

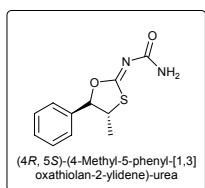


Recrystallization of the crude product from acetone afforded 33 mg of **8b** (0.14 mmol, 14%) as a colourless solid, mp: 165 °C <sup>1</sup>H-NMR (400 MHz, *d*<sub>6</sub>-acetone): δ 7.53 – 7.47 (2H, m), 7.19 – 7.13 (2H, m), 6.40 (1H, bs), 6.16 (1H, bs), 5.10 – 5.04 (1H, t, *J* = 7.03 Hz), 4.79 – 4.72 (1H, dd, *J* = 3.22 Hz, 9.38 Hz), 4.52 – 4.47 (1H, dd, *J* = 3.22 Hz, 9.66 Hz). <sup>13</sup>C-NMR (100.6 MHz, *d*<sub>6</sub>-acetone): δ 172.86, 164.20, 163.49 (d, <sup>1</sup>*J*<sub>CF</sub> = 245.41 Hz), 135.81 (d, <sup>4</sup>*J*<sub>CF</sub> = 2.41 Hz), 130.54 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.59 Hz), 116.65 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.91 Hz), 76.66, 49.95. <sup>19</sup>F-NMR (376.46 MHz, *d*<sub>6</sub>-acetone): δ -115.58. IR (cm<sup>-1</sup>): 3286 (m), 3181 (m), 2949 (w), 2922 (w), 2897 (w), 2850 (w), 1686 (s), 1636 (m), 1602 (m), 1573 (s), 1508 (s), 1390 (m), 1223 (m), 1159 (m), 1126 (m), 1068 (m), 834 (m), 668 (m). LRMS {EI, 70 eV, *m/z* (%)}: 240 (1), 197 (3), 155 (5), 154 (45), 153 (25), 139 (12), 122 (100), 121 (10), 109 (31), 101 (6), 96 (6), 95 (10), 75 (12). HRMS (M<sup>+</sup>, C<sub>10</sub>H<sub>9</sub>FN<sub>2</sub>O<sub>2</sub>S): cal.: 240.03688, found: 240.03760.

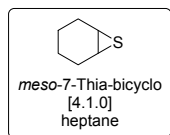


Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 121.5 mg of **2c** (0.81 mmol, 81%) as a colourless liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.24 – 7.14 (5H, m), 3.50 – 3.49 (1H, d, *J* = 5.30 Hz), 3.05 – 2.99 (1H, m), 1.57 – 1.56 (3H, d, *J* = 5.74 Hz). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ 139.25, 128.48, 127.54, 126.86, 125.81, 45.13, 39.48, 21.91. IR (cm<sup>-1</sup>): 3061 (m), 3028 (m), 2999 (m), 2958 (m), 2918 (m), 2859 (m), 1601 (m), 1497 (s), 1454 (vs), 1374 (m), 1067 (s), 979 (s), 760 (vs), 695 (vs), 603 (vs), 589 (vs), 505 (m). LRMS {EI, 70 eV, *m/z* (%)}: 150 (13), 149 (7), 135 (13), 119 (6), 118 (65), 117 (100), 116 (10), 115 (52), 91 (31), 89 (9), 78 (6),

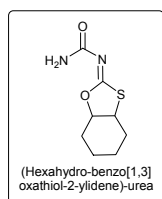
77 (8), 65 (89), 63 (8), 58 (6), 51 (8). **HRMS** ( $M^+$ ,  $C_9H_{10}S$ ): cal.: 150.05032, found: 150.05122.  
 $[\alpha]_D^{23} = -79.30^\circ$  ( $c = 4.40 \text{ g/L}$ ,  $CHCl_3$ ).



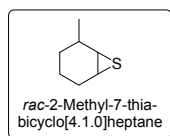
Recrystallization of the crude product from acetone afforded 23.6 mg of **8c** (0.1 mmol, 10%) as a colourless solid, mp: 213 °C **<sup>1</sup>H-NMR** (600 MHz,  $d_6$ -acetone):  $\delta$  7.42 – 7.26 (5H, m), 6.39 (1H, bs), 6.14 (1H, bs), 5.02 – 4.95 (1H, q,  $J = 6.15 \text{ Hz}$ ), 4.89 – 4.85 (1H, d,  $J = 6.15 \text{ Hz}$ ), 1.14 – 1.09 (3H, d,  $J = 6.43 \text{ Hz}$ ). **<sup>13</sup>C-NMR** (150.9 MHz,  $d_6$ -acetone):  $\delta$  177.00, 163.70, 138.08, 129.43, 128.98, 82.08, 53.61, 16.17. **IR** ( $cm^{-1}$ ): 3335 (w), 3188 (w), 1681 (s), 1635 (w), 1573 (s), 1387 (s), 1266 (w), 1216 (w), 11170 (w), 1124 (w), 1091 (w), 1045 (w), 1013 (w), 857 (w), 696 (w), 669 (w), 657 (w). **LRMS** {EI, 70 eV,  $m/z$  (%)}: 236 (1), 193 (2), 150 (18), 135 (13), 122 (18), 121 (34), 119 (10), 118 (100), 117 (57), 115 (21), 105 (12), 91 (16), 77 (10), 65 (4), 51 (5). **HRMS** ( $M^+$ ,  $C_{11}H_{12}N_2O_2S$ ): cal.: 236.06195, found: 236.06183. **Anal. calcd.** for  $C_{11}H_{12}N_2O_2S$ : C 55.19, H 5.12, N 11.86, found: C 55.38, H 5.12, N 11.86.  $[\alpha]_D^{23} = +58.69^\circ$  ( $c = 2.8 \text{ g/L}$ , acetone).



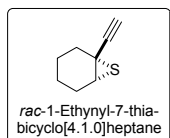
Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 106.2 mg of **2d** (0.93 mmol, 93%) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  3.23 – 3.18 (2H, m), 2.19 – 2.09 (4H, m), 1.59 – 1.49 (2H, m), 1.31 – 1.21 (2H, m). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ ):  $\delta$  37.08, 25.81, 19.43. **IR** ( $cm^{-1}$ ): 2999 (w), 2936 (vs), 2859 (s), 1442 (m), 1373 (m), 665 (m), 603 (m), 572 (m). **LRMS** {EI, 70 eV,  $m/z$  (%)}: 115 (6), 114 (73), 99 (4), 85 (12), 81 (100), 80 (72), 79 (51), 77 (10), 73 (16), 71 (9), 67 (31), 65 (5), 60 (18), 54 (23), 53 (15), 51 (6). **HRMS** ( $M^+$ ,  $C_6H_{10}S$ ): cal.: 114.05032, found: 114.05072.



Recrystallization from acetone afforded 8 mg of **8d** (0.04 mmol, 4%) as a colourless solid, mp: 160 °C **<sup>1</sup>H-NMR** (400 MHz,  $d_6$ -acetone):  $\delta$  6.28 (1H, bs), 6.04 (1H, bs), 3.88 – 3.80 (1H, dt,  $J = 11.46 \text{ Hz}$ , 22.92 Hz), 3.27 – 3.18 (1H, dt,  $J = 11.46$ , 23.77), 2.32 – 2.25 (1H, m), 2.22 – 2.15 (1H, m), 1.97 – 1.90 (1H, m), 1.87 – 1.81 (1H, m), 1.69 – 1.38 (1H, m). **<sup>13</sup>C-NMR** (100.6 MHz,  $d_6$ -acetone):  $\delta$  176.22, 164.10, 88.03, 51.98, 29.54, 28.88, 26.33, 25.14. **IR** ( $cm^{-1}$ ): 3298 (m), 3178 (m), 2940 (w), 1692 (s), 1643 (m), 1578 (s), 1380 (s), 1366 (m), 1169 (m), 1117 (m), 1065 (m), 957 (w), 685 (m). **LRMS** {EI, 70 eV,  $m/z$  (%)}: 200 (13), 157 (9), 122 (6), 114 (47), 111 (9), 109 (7), 97 (13), 83 (11), 81 (100), 80 (42), 79 (16), 73 (28), 71 (12), 69 (13), 67 (17), 57 (17), 55 (14). **HRMS** ( $M^+$ ,  $C_8H_{12}N_2O_2S$ ): cal.: 200.06195, found: 200.06189.

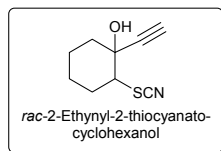


Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 119.2 mg of **2e** (0.87 mmol, 87%) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ , *syn* & *anti*):  $\delta$  3.28 – 3.20 (2.5H, m), 2.83 – 2.79 (0.4H, dd,  $J = 1.48 \text{ Hz}$ , 6.58 Hz), 2.30 – 2.15 (3.3H, m), 2.07 – 1.97 (1.6H, m), 1.75 – 1.63 (1H, m), 1.60 – 1.43 (2.3H, m), 1.41 – 1.19 (5.7H, m), 1.16 – 1.14 (3H, d,  $J = 7.21 \text{ Hz}$ ), 1.12 – 1.09 (3H, d,  $J = 6.51 \text{ Hz}$ ), 0.93 – 0.81 (1.7H, m). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ , *syn* & *anti*, ratio: 1:1.7):  $\delta$  46.02, 41.85, 38.27, 36.54, 31.68, 30.87, 30.66, 26.37, 25.60, 24.48, 22.82, 22.54, 21.21, 16.84. **IR** ( $cm^{-1}$ ): 2932 (vs), 2856 (vs), 1453 (s), 1367 (m), 1104 (m), 659 (m), 638 (m), 613 (m). **LRMS** {EI, 70 eV,  $m/z$  (%)}: 129 (8), 128 (85), 96 (30), 95 (100), 94 (71), 93 (13), 91 (13), 90 (9), 85 (14), 81 (70), 79 (83), 77 (17), 73 (10), 69 (9), 68 (40), 67 (57), 65 (9), 57 (12), 55 (29), 54 (9), 53 (15), 45 (8), 41 (17), 39 (14). **HRMS** ( $M^+$ ,  $C_7H_{12}S$ ): cal.: 128.06597, found: 128.06567.

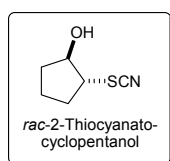


Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 85 mg of **2f** (0.62 mmol, 62%) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  3.46 – 3.43 (1H, dd,  $J = 1.68 \text{ Hz}$ , 5.74 Hz), 2.45 – 2.37 (1H, m), 2.30 – 2.29 (1H, s), 2.29 – 2.19 (2H, m), 2.14 – 2.05 (2H, m), 1.64 – 1.56 (1H, m), 1.54 – 1.47 (2H, m). **<sup>13</sup>C-NMR** (100.6

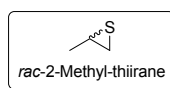
MHz, CDCl<sub>3</sub>):  $\delta$  87.75, 68.00, 44.44, 37.01, 34.67, 32.04, 19.18, 18.83. **IR** (cm<sup>-1</sup>): 3289 (w), 2927 (m), 2854 (w), 1442 (w), 1076 (w), 636 (w). **LRMS** {EI, 70 eV, m/z (%)}: 139 (3), 138 (12), 137 (10), 128 (8), 110 (13), 107 (7), 106 (54), 105 (35), 104 (13), 103 (14), 102 (8), 97(6), 92 (8), 91 (100), 79 (22), 78 (44), 77 (26), 65 (15), 64 (10), 63 (88), 57 (7), 52 (10), 51 (14), 39 (13). **HRMS** (M<sup>+</sup>, C<sub>8</sub>H<sub>10</sub>S): cal.: 138.05032, found: 138.05007.



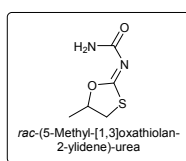
Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 25 mg of **9f** (0.14 mmol, 14%) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.23 – 3.71 (1H, dd, *J* = 12.47 Hz, 3.86 Hz), 2.74 – 2.69 (1H, bs), 2.67 – 2.65 (1H, s), 2.27 – 2.15 (2H, m), 1.88 – 1.54 (6H, m). **<sup>13</sup>C-NMR** (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  111.40, 81.61, 71.91, 58.01, 40.47, 31.81, 29.71, 25.80, 23.14. **IR** (cm<sup>-1</sup>): 3424 (s), 3291 (s), 2942 (vs), 2863 (m), 2153 (vs), 1447 (s), 1061 (s), 961 (s).



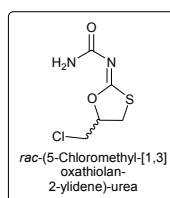
Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 117.4 mg of **9g** (0.82 mmol, 82%) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.30 – 4.26 (1H, q, *J* = 5.47 Hz, 12.02 Hz), 3.36 – 3.31 (1H, m), 2.38 – 2.28 (1H, m), 2.17 – 2.08 (2H, m), 1.91 – 1.64 (4H, m). **<sup>13</sup>C-NMR** (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  111.41, 78.61, 53.72, 32.83, 30.71, 21.42. **IR** (cm<sup>-1</sup>): 3423 (s), 2966 (s), 2875 (m), 2154 (s), 1449 (m), 1341 (m), 1303 (m), 1097 (m), 1078 (m), 986 (m). **LRMS** {EI, 70 eV, m/z (%)}: 143 (5), 116 (88), 115 (8), 1114 (19), 100 (12), 98 (33), 97 (26), 88 (67), 87 (31), 86 (11), 85 (21), 83 (89), 82 (10), 74 (7), 73 (15), 72 (19), 68 (14), 67 (77), 65 (9), 60 (100), 59 (19), 58 (11), 57 (57), 56 (10), 55 (47), 54 (21), 53 (13), 45 (21), 43 (26), 41 (52), 40 (8), 39 (40). **HRMS** (M<sup>+</sup>, C<sub>5</sub>H<sub>8</sub>S): cal.: 143.04048, found: .143.04029. **Anal. calcd.** for C<sub>5</sub>H<sub>9</sub>NOS: C 50.32, H 6.33, N 9.78; found: C 49.80, H 6.43, N 9.34.



Distillation of the crude product afforded 47.4 mg of **2h** (0.64 mmol, 28 %) as a colourless liquid. Bp.: 72 °C. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.96 – 2.88 (1H, m), 2.52 – 2.49 (1H, dd, *J* = 6.23 Hz, 1.00 Hz), 2.13 – 2.10 (1H, dd, *J* = 5.72 Hz, 0.80 Hz), 1.53 – 1.49 (3H, d, *J* = 5.79 Hz). **<sup>13</sup>C-NMR** (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  30.61, 27.20, 22.04. **IR** (cm<sup>-1</sup>): 2974 (s), 2921 (m), 2860 (m), 1454 (m), 1443 (m), 1434 (m), 1380 (m), 1347 (m), 1118 (s), 1070 (s), 598 (s). **LRMS** {EI, 70 eV, m/z (%)}: 75 (22), 74 (100), 73 (14), 70 (31), 59 (14), 46 (15), 45 (15), 44 (12), 41 (67).

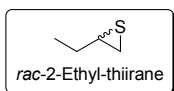


Recrystallization of the crude product from acetone afforded 44.8 mg of **8h** (0.28 mmol, 28 %) as a white solid, mp.: 166 °C (subl.). **<sup>1</sup>H-NMR** (400 MHz, d<sub>6</sub>-acetone):  $\delta$  6.36 – 6.17 (1H, bs, NH), 6.13 – 5.91 (1H, bs, NH), 4.83 – 4.70 (1H, m), 3.46 – 3.39 (1H, dd, *J* = 6.33, 11.32 Hz), 3.03 – 2.96 (1H, dd, *J* = 8.60 Hz, 11.77 Hz), 1.50 – 1.45 (3H, d, *J* = 5.88 Hz). **<sup>13</sup>C-NMR** (100.6 MHz, d<sub>6</sub>-acetone):  $\delta$  177.18, 163.79, 79.11, 36.93, 19.00. **IR** (cm<sup>-1</sup>): 3291 (s), 3182 (s), 1683 (vs), 1572 (vs), 1387 (vs), 1255 (s), 1182 (vs), 1120 (s), 1085 (s), 1038 (s), 840 (s), 671 (s). **LRMS** {EI, 70 eV, m/z (%)}: 160 (76), 144 (47), 133 (11), 119 (6), 117 (29), 115 (10), 101 (6), 87 (7), 75 (22), 74 (100), 73 (14), 70 (31), 59 (14), 46 (15), 45 (15), 44 (12), 41 (67). **HRMS** (M<sup>+</sup>, C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S): cal.: 160.03065, found: 160.03157.

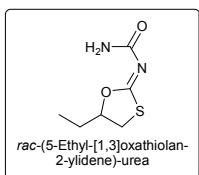


Recrystallization of the crude product from acetone afforded 145.5 mg of **8i** (0.78 mmol, 78%) as a white solid, mp: 165 °C. **<sup>1</sup>H-NMR** (400 MHz, d<sub>6</sub>-acetone):  $\delta$  6.46 – 6.30 (1H, bs, NH), 6.25 – 6.08 (1H, bs, NH), 5.01 – 4.94 (1H, m), 4.06 – 4.00 (1H, dd, *J* = 4.42 Hz, 12.36 Hz), 3.97 – 3.92 (1H, dd, *J* = 5.29Hz, 12.07), 3.55 – 3.49 (1H, dd, *J* = 7.06 Hz, 11.48 Hz), 3.43 – 3.27 (1H, dd, *J* = 7.94 Hz, 11.48 Hz). **<sup>13</sup>C-NMR** (100.6 MHz, d<sub>6</sub>-acetone):  $\delta$  176.74, 163.56, 80.86, 44.86, 32.96. **IR** (cm<sup>-1</sup>): 3339 (m), 3187 (m), 1675 (s), 1568 (s), 1387 (s), 1175 (s), 1124 (m), 1067 (m), 663 (m). **LRMS** {EI, 70 eV, m/z (%)}: 194 (36), 180 (13), 178 (35), 151 (27), 110 (20),

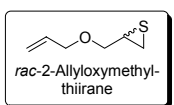
108 (58), 105 (29), 77 (15), 75 (43), 73 (100), 70 (26), 47 (12), 46 (20), 45 (24), 44 (34), 43 (12). **HRMS** ( $M^+$ ,  $C_5H_7ClN_2O_2S$ ): cal.: 193.99168, found: 193.99211. **Anal. calcd.** for  $C_5H_7ClN_2O_2S$ : C 30.85, H 3.62, N 14.39; found: C 30.78, H 3.68, N 14.90.



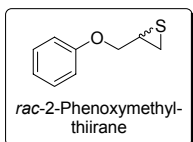
Distillation of the crude product afforded 54.6 mg of **2j** (0.62 mmol, 62 %) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  2.89 – 2.80 (1H, m), 2.50 – 2.45 (1H, d,  $J = 6.26$  Hz), 2.15 – 2.12 (1H, d,  $J = 6.12$  Hz), 1.94 – 1.82 (1H, m), 1.47 – 1.35 (1H, m), 1.10 – 1.03 (3H, t,  $J = 7.20$  Hz). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ ):  $\delta$  37.92, 29.82, 25.91, 13.50. **IR** ( $cm^{-1}$ ): 2964 (m), 2932 (w), 2873 (m), 1460 (w), 1376 (w), 1298 (w), 1073 (w), 1040 (w), 637 (w), 618 (w), 601 (w).



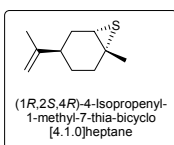
Recrystallization of the crude product from acetone afforded 29.6 mg of **8j** (0.17 mmol, 17 %) as a white solid, mp.: 176 °C (subl.). **<sup>1</sup>H-NMR** (400 MHz,  $d_6$ -acetone):  $\delta$  6.34 – 6.15 (1H, bs, NH), 6.12 – 5.94 (1H, bs, NH), 4.60 – 4.51 (1H, m), 3.44 – 3.36 (1H, dd,  $J = 6.29$  Hz, 11.13 Hz), 3.06 – 2.99 (1H, dd,  $J = 8.95$  Hz, 11.00 Hz), 1.93 – 1.74 (2H, m), 1.06 – 1.00 (3H, t,  $J = 7.38$  Hz). **<sup>13</sup>C-NMR** (100.6 MHz,  $d_6$ -acetone):  $\delta$  177.24, 163.78, 83.94, 35.05, 27.27, 10.07. **IR** ( $cm^{-1}$ ): 3311 (m), 3182 (m), 1683 (s), 1575 (s), 1384 (s), 1182 (s), 1121 (s), 687 (m). **LRMS** {EI, 70 eV, m/z (%)}: 174 (40), 158 (31), 141 (9), 131 (10), 119 (5), 88 (64), 87 (12), 73 (17), 70 (20), 60 (45), 59 (9), 55 (100), 54 (35), 47 (14), 46 (29), 45 (13), 44 (14), 41 (12). **HRMS** ( $M^+$ ,  $C_6H_{10}N_2O_2S$ ): cal.: 174.04630, found: 174.04646. **Anal. calcd.** for  $C_6H_{10}N_2O_2S$ : C 41.36, H 5.79, N 16.08, found: C 41.50, H 5.81, N 16.28.



Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 113.28 mg of **2k** (0.87 mmol, 87%) as a colourless liquid. **<sup>1</sup>H-NMR** (200 MHz,  $CDCl_3$ ):  $\delta$  6.01 – 5.82 (1H, m), 5.34 – 5.16 (2H, m), 4.07 – 4.05 (1H, t,  $J = 1.4$  Hz), 4.04 – 4.03 (1H, t,  $J = 1.4$  Hz), 3.69 – 3.61 (1H, m), 3.49 – 3.40 (1H, dd,  $J = 6.7$  Hz, 3.9 Hz), 3.14 – 3.02 (1H, m), 2.55 – 2.51 (1H, m), 2.24 – 2.23 (0.5H, d,  $J = 1.3$  Hz), 2.21 – 2.20 (0.5H, d,  $J = 1.3$  Hz). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ ):  $\delta$  134.39, 117.50, 74.68, 72.06, 32.13, 23.82. **IR** ( $cm^{-1}$ ): 3079 (m), 3011 (m), 2988 (m), 2855 (s), 2078 (w), 1860 (w), 1737 (w), 1646 (m), 1453 (m), 1438 (m), 1356 (m), 1321 (m), 1266 (m), 1247 (m), 1089 (vs), 1047 (s), 991 (m), 927 (s), 710 (m), 617 (s), 560 (w). **LRMS** {EI, 70 eV, m/z (%)}: 130 (0.04), 129 (0.05), 101 (2), 97 (2), 85 (2), 73 (100), 59 (11), 57 (14), 45 (29), 41 (81). **Anal. calcd.** for  $C_6H_{10}OS$ : C 55.35, H 7.74, found: C 55.42, H 7.97.

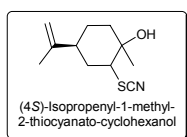


Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 146.3 mg of **2m** (0.88 mmol, 88%) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  7.32 – 7.27 (2H, m), 7.08 – 6.90 (3H, m), 4.25 – 4.20 (1H, m), 3.95 – 3.87 (1H, dd,  $J = 17.3$  Hz, 10.2 Hz, 3.1 Hz), 3.31 – 3.25 (1H, m), 2.63 – 2.61 (1H, m), 2.34 – 2.34 (0.5H, d,  $J = 1.4$  Hz), 2.33 – 2.33 (0.5H, d,  $J = 1.4$  Hz). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ ):  $\delta$  158.39, 129.57, 121.25, 114.68, 31.40, 24.02. **IR** ( $cm^{-1}$ ): 3061 (w), 3036 (w), 2989 (w), 2924 (w), 2879 (w), 1599 (vs), 1586 (s), 1496 (vs), 1466 (m), 1454 (m), 1390 (w), 1301 (m), 1290 (m), 1243 (vs), 1174 (m), 1078 (m), 1049 (s), 1035 (s), 754 (vs), 691 (s), 617 (m). **LRMS** {EI, 70 eV, m/z (%)}: 166 (11), 134 (4), 94 (7), 73 (100), 65 (4), 51 (4), 45 (23). **HRMS** ( $M^+$ ,  $C_9H_{10}OS$ ): cal.: 166.04523, found: 166.04520.

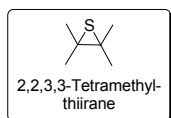


Flash chromatography of the crude product with *n*-hexane: ethyl acetate (95:5) afforded 94 mg of **2o** (0.56 mmol, 56 %) as a colourless solid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  4.80 – 4.76 (2H, m), 3.60 – 3.58 (1H, t,  $J = 4.2$  Hz), 2.35 – 2.28 (1H, m), 2.07 – 1.97 (1H, m), 1.76 – 1.59 (8H, m), 1.41 – 1.38 (3H, s). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ , *syn* (minor) & *anti* (major), ratio: 1:2.6):  $\delta$  148.09, 147.20, 112.22, 110.86, 110.25, 109.74, 71.77, 71.63, 56.71, 38.51, 37.29, 34.56, 34.03, 32.83, 32.47, 27.75, 26.80, 25.73, 21.02, 20.98. **IR** ( $cm^{-1}$ ): 3082 (w), 2963 (s), 2924 (vs), 2857

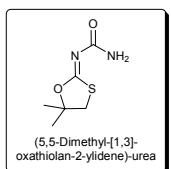
(m), 1643 (m), 1451 (m), 1436 (m), 1373 (m), 8887 (s). **LRMS** {EI, 70 eV, m/z (%)}: 168 (0.4), 152 (3), 137 (29), 123 (12), 119 (16), 108 (50), 95 (30), 94 (56), 93 (65), 91 (25), 81 (50), 79 (61), 77 (19), 68 (25), 55 (28), 51 (7), 43 (100). **HRMS** ( $M^+$ ,  $C_{10}H_{16}S$ ): cal.: 168.09727, found: 168.09804.



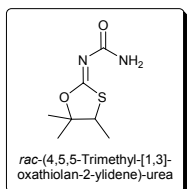
Flash chromatography of the crude reaction mixture with *n*-hexane: ethyl acetate (2:1) afforded 4 mg of **9o** (0.19 mmol, 19%) as a colourless liquid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  4.81 – 4.73 (2H, d,  $J = 19.3$  Hz), 3.60 – 3.55 (1H, t,  $J = 4.5$  Hz), 2.35 – 2.26 (1H, m), 2.21 – 2.17 (1H, bs), 2.03 – 1.96 (1H, m), 1.74 – 1.71 (3H, s), 1.71 – 1.63 (4H, m), 1.62 – 1.59 (0.5H, m), 1.53 – 1.52 (0.5H, m), 1.40 – 1.38 (3H, s). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ ):  $\delta$  147.20, 112.21, 110.26, 71.64, 56.70, 38.41, 34.57, 32.83, 25.85, 21.22. **IR** ( $cm^{-1}$ ): 3463 (s), 3085 (w), 2968 (s), 2936 (vs), 2861 (m), 2154 (vs), 1644 (m), 1452 (s), 1439 (s), 1378 (s), 1185 (m), 1109 (m), 909 (m), 889 (s). **LRMS** {EI, 70 eV, m/z (%)}: 211 (2), 168 (6), 153 (99), 140 (9), 138 (32), 137 (9), 135 (25), 126 (28), 125 (11), 113 (14), 111 (21), 109 (21), 108 (47), 107 (24), 97 (10), 95 (13), 93 (44), 91 (14), 83 (14), 82 (13), 81 (18), 79 (22), 77 (13), 71 (68), 69 (26), 68 (22), 67 (35), 65 (7), 59 (8), 58 (21), 55 (23), 53 (19), 43 (100), 41 (39), 39 (25). **HRMS** ( $M^+$ ,  $C_{11}H_{17}NOS$ ): cal.: 211.10308, found: 211.10285. **Anal. Calcd.** for  $C_{11}H_{17}NOS$ : C 62.52, H 8.11, N 6.63, found: C 62.25, H 8.11, N 6.64.



Flash chromatography of the crude product with diethyl ether afforded 87 mg of **2p** (0.75 mmol, 75%) as a waxy, white solid. **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  1.64 (12H, s). **<sup>13</sup>C-NMR** (100.6 MHz,  $CDCl_3$ ):  $\delta$  52.41, 25.79. **IR** ( $cm^{-1}$ ): 3004 (w), 2994 (w), 2961 (w), 2917 (w), 1462 (w), 1372 (w), 1168 (w), 1094 (w), 1082 (w), 569 (w), 556 (w). **LRMS** {EI, 70 eV, m/z (%)}: 116 (4), 115 (16), 83 (100), 82 (18), 69 (9), 67 (33), 64 (32), 55 (36), 41 (53). **Anal. Calcd.** for  $C_6H_{12}S$ : C 62.00, H 10.41; found: C 61.79, H 10.41.

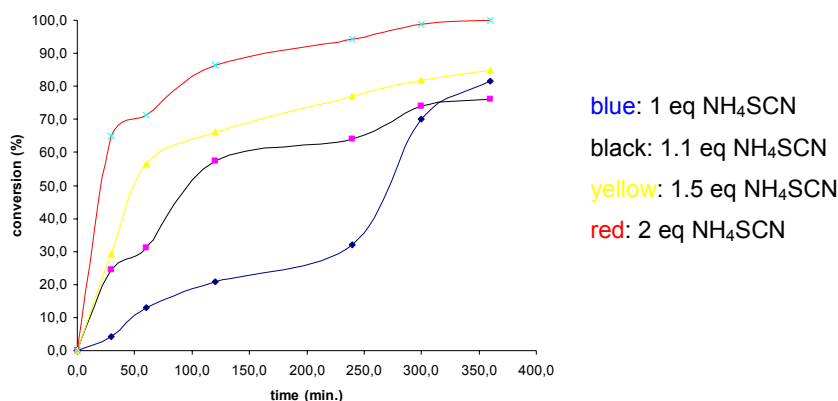


Recrystallization of the crude product from methylene chloride afforded 47 mg of **8q** (0.27 mmol, 27%) as a white solid, mp: 160 °C. **<sup>1</sup>H-NMR** (400 MHz,  $d_6$ -acetone):  $\delta$  6.22 (1H, bs, NH), 6.01 (1H, bs, NH), 3.22 – 3.19 (2H, s), 1.54 – 1.51 (6H, s). **<sup>13</sup>C-NMR** (100.6 MHz,  $d_6$ -acetone):  $\delta$  173.54, 164.50, 87.04, 42.29, 26.67. **IR** ( $cm^{-1}$ ): 3308(s), 3189(s), 2986 (m), 2972 (m), 1682 (vs), 1619 (m), 1567 (vs), 1384 (vs), 1372 (vs), 1265 (vs), 1120 (vs), 1036 (s), 864 (s), 791 (m), 730 (m), 688 (m), 664 (m). **LRMS** {EI, 70 eV, m/z (%)}: 175 (3), 174 (25), 158 (6), 119 (5), 89 (7), 88 (100), 87 (9), 84 (8), 74 (16), 73 (16), 60 (36), 59 (111), 59 (14), 55 (55), 54 (17), 44 (26), 43 (8).. **HRMS** ( $M^+$ ,  $C_6H_{10}N_2O_2S$ ): cal.: 174.04630, found: 174.04619. **Anal. Calcd.** for  $C_6H_{10}N_2O_2S$ : C 41.36, H 5.79, N 16.08, found: C 41.13, H 5.65, N 16.09.



Recrystallization of the crude product from acetone afforded 64 mg of **8r** (0.34 mmol, 34%) as a colourless solid, mp: 186 °C. **<sup>1</sup>H-NMR** (400 MHz,  $d_6$ -acetone):  $\delta$  6.31 – 6.17 (1H, bs, NH), 6.08 – 5.93 (1H, bs, NH), 3.66 – 3.59 (1H, q,  $J = 13.73$  Hz, 6.86 Hz), 1.52 – 1.50 (3H, s), 1.38 – 1.36 (3H, s), 1.32 – 1.29 (3H, d,  $J = 6.98$  Hz). **<sup>13</sup>C-NMR** (100.6 MHz,  $d_6$ -acetone):  $\delta$  175.90, 163.82, 88.39, 49.83, 25.80, 20.79, 15.80. **IR** ( $cm^{-1}$ ): 3287 (s), 3175 (s), 2988 (m), 2959 (m), 2931 (m), 1687 (vs), 1635 (s), 1551 (vs), 1391 (vs), 1282 (s), 1260 (s), 1229 (s), 1180 (m), 1119 (vs), 1080 (s), 1036 (s), 942 (m), 857 (s), 770 (m), 700 (m), 658 (m). **LRMS** {EI, 70 eV, m/z (%)}: 189 (6), 188 (31), 172 (6), 120 (8), 119 (43), 112 (7), 103 (7), 102 (100), 87 (25), 74 (63), 70 (28), 69 (84), 68 (111), 67 (5), 60 (16), 59 (56), 55 (11), 44 (10), 43 (10), 41 (24). **HRMS** ( $M^+$ ,  $C_7H_{12}N_2O_2S$ ): cal.: 188.06195, found: 188.06176. **Anal. Calcd.** for  $C_7H_{12}N_2O_2S$ : C 44.66, H 6.43, N 14.88, found: C 44.59, H 6.38, N 14.96.

### 3. Reaction diagram for the title reaction of styrene oxide with different equivalents of NH<sub>4</sub>SCN:



### 4. Computational details:

**Table S1.** Absolute energies (in – au), zero-point vibrational energies (ZPVEs, in kcal mol<sup>-1</sup>), and number of imaginary frequencies (in brackets) of all computed species.

Species (point group)	B3PW91 /cc-pVDZ	ZPVE [NIMAG]	B3PW91 /cc-pVDZ (PCM water) <sup>a</sup>	ZPVE	B3PW91 /cc-pVDZ (PCM CH <sub>2</sub> Cl <sub>2</sub> ) <sup>a</sup>	ZPVE [NIMAG]
Oxirane ( <b>A</b> , R=H), C <sub>2v</sub>	153.73880	35.9 [0]	153.74353	35.8 [0]	153.74273	35.8 [0]
Prot. Oxirane ( <b>AH</b> , R=H), C <sub>s</sub>	154.04532	43.9 [0]	154.15774	42.5 [0]	154.14501	42.9 [0]
OCN <sup>-</sup> , C <sub>∞v</sub>	168.05103	6.8 [0]	168.16210	6.9 [0]	168.15080	6.8 [0]
HOCN, C <sub>s</sub>	168.58165	13.5 [0]	168.60425	12.5 [0]	168.60028	12.8 [0]
CO <sub>2</sub> , D <sub>∞h</sub>	188.52497	7.4 [0]	188.52825	7.3 [0]	188.52773	7.3 [0]
H <sub>2</sub> O, C <sub>2v</sub>	76.39458	13.4 [0]	76.40554	12.8 [0]	76.40375	12.9 [0]
SCN <sup>-</sup> , C <sub>∞v</sub>	491.03427	5.6 [0]	491.13370	5.6 [0]	491.12358	5.6 [0]
NH <sub>3</sub> , C <sub>3v</sub>	56.53570	21.5 [0]	56.54173	21.2 [0]	56.54076	21.3 [0]
NH <sub>4</sub> <sup>+</sup> , T <sub>d</sub>	56.88345	30.9 [0]	57.00321	30.1 [0]	56.99102	30.2 [0]
<b>B</b>	645.33956	50.2 [0]	645.35588	49.4 [0]	645.35309	49.6 [0]
<b>C</b>	645.36941	52.3 [0]	645.38312	53.7 [0]	645.38071	52.0 [0]
<b>D</b>	645.32915	48.9 [0]	645.34490	48.5 [0]	645.34180	49.8 [0]
<b>E</b>	645.32914	48.9 [0]	645.34469	48.3 [0]	645.34211	48.6 [0]
Thiirane <b>F</b> (R=H), C <sub>2v</sub>	476.72925	34.4 [0]	476.73386	34.2 [0]	476.73306	34.2 [0]
Prot. Thiirane ( <b>FH</b> <sup>+</sup> ), C <sub>s</sub>	477.04570	40.5 [0]	477.14272	40.3 [0]	477.13246	40.4 [0]
Urea, C <sub>2</sub>	225.19996	40.0 [0]	225.22191	38.8 [0]	225.21807	39.1 [0]
<b>TS2</b> , C <sub>1</sub>	645.26168	47.5 [1]	645.27253	47.2 [1]	645.27061	47.4 [1]
<b>TS3</b> , C <sub>s</sub>	645.26234	47.3 [1]	645.27985	48.0 [1]	645.27603	47.9 [1]
2-(Chloromethyl)thiirane	975.59774	46.7 [0]	975.60577	46.4 [0]	975.60431	46.4 [0]

Tetramethylthiirane	633.94719	104.2 [0]	633.95151	104.0 [0]	633.95057	104.1 [0]
(Z)-1-(1,3-Oxathiolan-2-ylidene)urea	814.03520	69.3 [0]	814.05554	68.5 [0]	814.05201	68.6 [0]
(Z)-1-(5-(Chloromethyl)-1,3-oxathiolan-2-ylidene)urea	1312.90132	81.2 [0]	1312.92506	80.3 [0]	1312.92085	80.4 [0]
(Z)-1-(4,4,5,5-Tetramethyl-1,3-oxathiolan-2-ylidene)urea	971.24962	138.7 [0]	971.26877	137.8 [0]	971.26529	138.1 [0]
Oxirane ( <b>A</b> •H <sub>2</sub> O, R=H), C <sub>s</sub>	230.14498	51.4 [0]	230.15525	50.8 [0]		
Prot. Oxirane ( <b>AH</b> •H <sub>2</sub> O, R=H), C <sub>s</sub>	230.49230	58.6 [0]	230.59394	56.8 [0]		
OCN <sup>-</sup> •H <sub>2</sub> O, C <sub>s</sub>	244.47212	22.3 [0]	244.57397	21.5 [0]		
SCN <sup>-</sup> •H <sub>2</sub> O, C <sub>s</sub>	567.45210	20.5 [0]	567.54442	20.0 [0]		
NH <sub>3</sub> •H <sub>2</sub> O, C <sub>s</sub>	132.94310	37.0 [0]	132.95828	36.3 [0]		
NH <sub>4</sub> <sup>+</sup> •H <sub>2</sub> O, C <sub>s</sub>	133.31904	45.8 [0]	133.42817	44.6 [0]		
<b>B</b> •H <sub>2</sub> O	721.71904	63.5 [0]	721.77221	64.6 [0]		
<b>C</b> •H <sub>2</sub> O	721.77580	67.6 [0]	721.79432	66.2 [0]		
<b>D</b> •H <sub>2</sub> O	721.73330	64.4 [0]	721.75675	62.5 [0]		
<b>E</b> •H <sub>2</sub> O	721.73146	63.7 [0]	721.75286	62.6 [0]		
Thiirane <b>F</b> •H <sub>2</sub> O (R=H), C <sub>s</sub>	553.12734	48.7 [0]	553.14085	54.8 [0]		
Prot. Thiirane ( <b>FH</b> <sup>+</sup> •H <sub>2</sub> O), C <sub>s</sub>	553.47579	55.4 [0]	553.57599	54.8 [0]		
<b>TS2</b> , C <sub>1</sub>	721.71904	63.5 [1]	721.73860	61.8 [1]		
<b>TS3</b> , C <sub>s</sub>	721.71271	63.4 [1]	721.73547	61.7 [1]		

<sup>a</sup>Total free energy in solution including all corrections.

## 5. Single crystal structure analysis:

The X-ray crystallographic data were collected on a STOE IPDS-diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo-K<sub>α</sub> radiation ( $\lambda = 0.71069 \text{ \AA}$ ) and a graphite monochromator was used. No absorption corrections were applied. The structures were solved by Direct Methods in SHELXS97, and refined by using full-matrix least squares in SHELXL97.<sup>3</sup> The hydrogen atoms were positioned geometrically and all non-hydrogen atoms were refined anisotropically, if not mentioned otherwise.

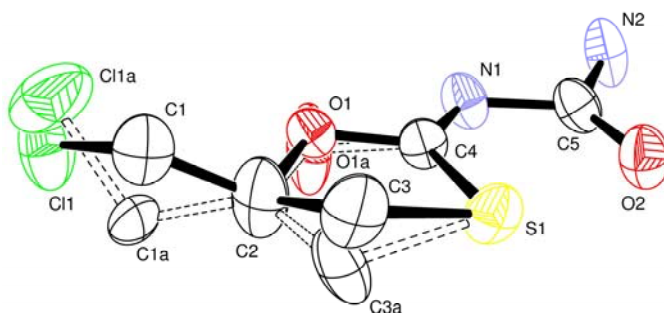
### 5.1 Crystal data and structure refinement for *rac*-(5-chloromethyl-[1,3]-oxathiolan-2-ylidene)-urea (**8i**):

Cell parameters were refined by using up to 5000 reflections. A sphere of data (210 frames) was collected with the  $\varphi$ -oscillation mode (0.9° frame width; Irradiation times/frame: 10 min). The refinement shows an asymmetric molecule in with 69 % *S*-character. The *R*-configuration was refined as disorder with 31 %. The N-H hydrogen atoms and the C-H hydrogen atom for the *S*-configuration at the asymmetric C-atom were found and isotropically refined. The C-H hydrogen atoms for the *R*-configuration are not found.

Crystallographic data for the structures reported in this publication have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC – 696272 for *rac*-(5-chloromethyl-[1,3]-



oxathiolan-2-ylidene)-urea (**8i**). Copies of the data can be obtained, free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



ORTEP plot with thermal ellipsoids set at 50% probability shows the independent unit with *R/S* – disorder.

CCDC-no.:	696272	
Empirical formula	C <sub>5</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>2</sub> S	
Formula weight	194.64	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic,	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	<i>a</i> = 7.3153(15) Å	$\alpha$ = 90°
	<i>b</i> = 7.4523(15) Å	$\beta$ = 90°
	<i>c</i> = 14.902(3) Å	$\gamma$ = 90°
Volume	812.4(3) Å <sup>3</sup>	
<i>Z</i> , Calculated density	4,	1.591 mg/m <sup>3</sup>
Absorption coefficient	0.678 mm <sup>-1</sup>	
<i>F</i> (000)	400	
Habitus, colour	Block, colourless	
Crystal size	0.64 x 0.20 x 0.16 mm <sup>3</sup>	
Theta range for data collection	3.06 to 28.02°	
Limiting indices	-9 ≤ <i>h</i> ≤ 9, -9 ≤ <i>k</i> ≤ 9, -18 ≤ <i>l</i> ≤ 19	
Reflections collected / unique	7159 / 1896 [R(int) = 0.0684]	
Completeness to theta = 28.02	95.9%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data / restraints / parameter	1896 / 0 / 149	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.096	
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0474,	<i>wR</i> 2 = 0.1125
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0613,	<i>wR</i> 2 = 0.1217
Absolute structure parameter	0.12(15)	
Largest diff. peak and hole	0.440 and -0.512 e. Å <sup>-3</sup>	

**Bond lengths [Å] and angles [°]:**

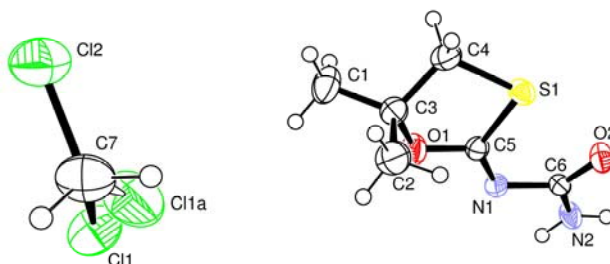
C(1)-C(2)	1.436(7)	C(2)-C(1)-Cl(1)	115.9(5)	N(1)-C(4)-O(1)	117.2(5)
C(1)-Cl(1)	1.747(6)	C(3a)-C(2)-C(1)	131.6(10)	N(1)-C(4)-O(1a)	113.3(11)
C(2)-C(3a)	1.332(19)	C(3a)-C(2)-O(1)	112.8(9)	O(1)-C(4)-O(1a)	12.3(13)
C(2)-O(1)	1.437(11)	C(1)-C(2)-O(1)	111.9(5)	N(1)-C(4)-S(1)	129.6(2)
C(2)-C(1a)	1.471(13)	C(3a)-C(2)-C(1a)	129.1(8)	O(1)-C(4)-S(1)	113.0(5)
C(2)-C(3)	1.492(9)	C(1)-C(2)-C(1a)	41.0(6)	O(1a)-C(4)-S(1)	116.6(11)
C(2)-O(1a)	1.51(3)	O(1)-C(2)-C(1a)	111.7(7)	O(2)-C(5)-N(2)	123.0(3)

C(3)-S(1)	1.788(8)	C(3a)-C(2)-C(3)	29.9(8)	O(2)-C(5)-N(1)	124.3(3)
C(4)-N(1)	1.280(4)	C(1)-C(2)-C(3)	116.4(5)	N(2)-C(5)-N(1)	112.7(3)
C(4)-O(1)	1.330(12)	O(1)-C(2)-C(3)	108.1(6)	C(2)-C(1a)-Cl(1a)	115.6(10)
C(4)-O(1a)	1.36(2)	C(1a)-C(2)-C(3)	139.7(7)	C(2)-C(3a)-S(1)	109.4(10)
C(4)-S(1)	1.733(3)	C(3a)-C(2)-O(1a)	112.4(13)	C(4)-N(1)-C(5)	117.2(3)
C(5)-O(2)	1.231(4)	C(1)-C(2)-O(1a)	115.1(11)	C(4)-O(1)-C(2)	113.5(7)
C(5)-N(2)	1.326(5)	O(1)-C(2)-O(1a)	10.9(11)	C(4)-O(1a)-C(2)	107.3(16)
C(5)-N(1)	1.403(4)	C(1a)-C(2)-O(1a)	106.8(11)	C(4)-S(1)-C(3)	91.3(2)
C(1a)-Cl(1a)	1.723(11)	C(3)-C(2)-O(1a)	113.5(10)	C(4)-S(1)-C(3a)	88.1(6)
C(3a)-S(1)	1.840(16)	C(2)-C(3)-S(1)	104.8(5)	C(3)-S(1)-C(3a)	23.6(6)

## 5.2 Crystal data and structure refinement for (5,5-Dimethyl-[1,3]-oxathiolan-2-ylidene)-urea (8r)

Cell parameters were refined by using up to 4485 reflections. A sphere of data (125 frames) was collected with the  $\varphi$ -oscillation mode (0.9° frame width; Irradiation times/frame: 40 min). The refinement shows a CH<sub>2</sub>Cl<sub>2</sub> solvent molecule in the independent unit of the elementary cell. One chloride atom of the solvent molecule is disordered in two positions (Cl1:Cl1a 95:5). All C-H hydrogen atoms were positioned geometrically; the N-H hydrogen atoms were found and isotropically refined.

Crystallographic data for the structures reported in this publication have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC – 704138 for (5,5-Dimethyl-[1,3]-oxathiolan-2-ylidene)-urea (8q). Copies of the data can be obtained, free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



ORTEP plot with thermal ellipsoids set at 50% probability shows the independent unit with disorder of the CH<sub>2</sub>Cl<sub>2</sub> solvent molecule.

CCDC-no.:	704138	
Empirical formula	C <sub>7</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S	
Formula weight	259.15	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic,	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	<i>a</i> = 7.4633(15) Å	$\alpha$ = 90°
	<i>b</i> = 9.925(2) Å	$\beta$ = 90°
	<i>c</i> = 15.920(3) Å	$\gamma$ = 90°
Volume	1179.3(4) Å <sup>3</sup>	
<i>Z</i> , Calculated density	4,	1.460 mg/m <sup>3</sup>
Absorption coefficient	0.706 mm <sup>-1</sup>	
<i>F</i> (000)	536	
Habitus, colour	Needle, colourless	
Crystal size	0.32 x 0.16 x 0.08 mm <sup>3</sup>	
Theta range for data collection	2.56 to 28.17 °	
Limiting indices	-9 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 13, -21 ≤ <i>l</i> ≤ 21	
Reflections collected / unique	10810 / 2860 [R(int) = 0.1144]	

Completeness to theta = 28.17	99.5%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameter	2860 / 0 / 147	
Goodness-of-fit on F <sup>2</sup>	0.942	
Final R indices [I > 2sigma (I)]	R1 = 0.0543,	wR2 = 0.1104
R indices (all data)	R1 = 0.0951,	wR2 = 0.1239
Absolute structure parameter	-0.09(14)	
Largest diff. peak and hole	0.431 and -0.310 e. Å <sup>-3</sup>	

### Bond lengths [Å] and angles [°]

C(1)-C(3)	1.502(7)	C(7)-Cl(1a)	1.53(4)	N(1)-C(5)-S(1)	129.5(3)
C(2)-C(3)	1.507(7)	C(7)-Cl(1)	1.741(7)	O(1)-C(5)-S(1)	113.1(3)
C(3)-O(1)	1.480(5)	C(7)-Cl(2)	1.757(5)	O(2)-C(6)-N(2)	123.9(4)
C(3)-C(4)	1.510(7)	O(1)-C(3)-C(1)	105.8(4)	O(2)-C(6)-N(1)	122.4(4)
C(4)-S(1)	1.792(5)	O(1)-C(3)-C(2)	107.9(4)	N(2)-C(6)-N(1)	113.7(4)
C(5)-N(1)	1.286(5)	C(1)-C(3)-C(2)	112.3(4)	Cl(1a)-C(7)-Cl(1)	26(4)
C(5)-O(1)	1.333(5)	O(1)-C(3)-C(4)	104.6(4)	Cl(1a)-C(7)-Cl(2)	106.8(18)
C(5)-S(1)	1.746(4)	C(1)-C(3)-C(4)	113.5(4)	Cl(1)-C(7)-Cl(2)	112.7(3)
C(6)-O(2)	1.241(5)	C(2)-C(3)-C(4)	112.0(4)	C(5)-N(1)-C(6)	118.3(4)
C(6)-N(2)	1.306(5)	C(3)-C(4)-S(1)	107.1(3)	C(5)-O(1)-C(3)	114.6(3)
C(6)-N(1)	1.399(5)	N(1)-C(5)-O(1)	117.4(4)	C(5)-S(1)-C(4)	90.6(2)

### 6. References:

1. P. M. R. Barkworth and T. A. Crabb, *J. Chem. Soc., Perkin Trans. 2*, 1982, 91-94.
2. A. Alexakis, I. Marek, P. Mangeney and J. F. Normant, *Tetrahedron*, 1991, **47**, 1677-1696.
3. G. M. Sheldrick, SHELXS97 and SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.