

## Supporting Information

# Tandem electrocatalytic aziridination – ring expansion of simple aromatic olefins using ammonia and carbon dioxide

*Jef R. Vanhoof, Robin Dirix, Dirk E. De Vos\**

\*Centre For Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions (cMACS), KU Leuven, Celestijnenlaan 200F p.o. box 2454, 3001 Leuven (Belgium). E-mail: [dirk.devos@kuleuven.be](mailto:dirk.devos@kuleuven.be)

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## 1) General information

All reactions were carried out with commercially available chemicals and materials, unless otherwise noted. Chemicals were used without any further purification. Ring expansions of the N-H aziridines with CO<sub>2</sub> were performed in home-made pressure reactors. Ring expansions of the N-H aziridines with CS<sub>2</sub> were performed in glass vials. <sup>1</sup>H-NMR analyses of the reaction mixtures were conducted with a Bruker Avance 400 spectrometer using a zg30 pulse program (1D <sup>1</sup>H experiment using 30 degree flip angle).

## 2) General procedures

- 1) **Electrocatalytic N-H aziridination:** See Reference 1.
- 2) **Ring expansion with CO<sub>2</sub>:** After the completion of the electrocatalytic N-H aziridination (see 1), the reaction mixture was scrubbed with N<sub>2</sub>. 160 mg of sodium thiosulphate (2 equiv., optional) was added and the reaction mixture was transferred to a home-made stainless steel pressure reactor. The reactor was purged with nitrogen, after which 15 bar of CO<sub>2</sub> pressure was applied. The reactor was transferred to a heating block at 70°C and was stirred overnight. The resulting mixture was analyzed with <sup>1</sup>H NMR. Pyridine was added as an external standard from a 0.045M solution in CDCl<sub>3</sub> (200 μl of reaction mixture + 300 μl of pyridine solution in CDCl<sub>3</sub>).
- 3) **Ring expansion with CS<sub>2</sub>:** After the completion of the electrocatalytic N-H aziridination (see 2), the reaction mixture was scrubbed with N<sub>2</sub> and 160 mg of sodium thiosulphate (2

equiv., optional) were added. The solution was transferred to a glass vial and 15 equivalents of CS<sub>2</sub> was added. The reaction vial was transferred to a heating block at 40°C and was stirred for 10 minutes. The resulting mixture was analyzed with <sup>1</sup>H-NMR. Pyridine was added as an external standard from a 0.045M solution in CDCl<sub>3</sub> (200 μl of reaction mixture + 300 μl of pyridine solution in CDCl<sub>3</sub>).

- 4) **Optional adaption:** We demonstrated in our previous research that using commercial NH<sub>3</sub> solutions in dioxane or in water also results in good N-H aziridine yields around 80%, preventing the need for a homemade NH<sub>3</sub> solution in dioxane.<sup>[1]</sup> We used both commercial solutions in the protocol described herein with the model compound styrene. When performing the ring expansion with CO<sub>2</sub>, an overall yield of 74% and 75% was obtained when using the NH<sub>3</sub> commercial solution in dioxane and in water, respectively. Performing the ring expansion with CS<sub>2</sub> resulted in an overall yield of 58% and 56% when using the NH<sub>3</sub> commercial solution in dioxane and in water, respectively.
- 5) **Purification:** Isolated yields are provided for model compounds **2a** and **4a** according to the following procedure: After work-up (see Reference 1.), the mixture was purified by column chromatography on silica gel, eluting with 8:2 heptane/ethyl acetate for compound **2a** (white solid, R<sub>F</sub> = 0.21, 81% overall yield) and 6:4 heptane/ethyl acetate for compound **4a** (white solid, R<sub>F</sub> = 0.45, 58% overall yield). Copies of the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra are included.
- 6) **Scale-up:** After performing a gram scale electrocatalytic N-H aziridination reaction (see Reference 1.), the reaction mixture was transferred to a glass-lined Parr reactor (600ml)

together with additional solvent (45 ml dioxane and 5 ml water) in order for optimal mechanical stirring (300 rpm). Then, the reactor is sealed, purged and pressurized with CO<sub>2</sub> until a constant pressure of 15 bar. Afterwards, the reactor is cooled down in an ice bath and the pressure is released. The reaction mixture is analyzed with <sup>1</sup>H-NMR (see 2). Similarly for 5-phenyl-2-thiazolidinethione **4a**, 1.03 ml of CS<sub>2</sub> is added to the reaction mixture after performing the gram-scale electrocatalytic N-H aziridination. The reaction is stirred for 30 minutes at 40 °C. The reaction mixture is analyzed with <sup>1</sup>H-NMR (see 3).

### 3) Control experiments

The influence of iodide on the product formation and product distribution was investigated (Figure 1 of main text). After performing 2 standard N-H aziridination reactions with styrene, both mixtures were combined and the salts and solvents were removed following our work-up procedure (see section 2). The concentrated 2-phenylaziridine in some leftover dioxane was diluted again with the dioxane/water mixture. This homogeneous mixture was equally divided over three pressure reactors to which 0, 0.2 or 2 equivalents of LiI were added. Standard conditions for the CO<sub>2</sub> ring expansion were applied and all three mixtures were compared using <sup>1</sup>H-NMR. Since all three mixtures originate from the same starting mixture, the relative ratios of the areas assigned to 2-phenylaziridine and 5-phenyl-2-oxazolidinone can be compared. Note that for these reactions, full conversion of the aziridine (characteristic signals at  $\delta = 1.79$  (d, 1H), 2.18 (d, 1H), 3.00 (dd, 1H)) was observed, most likely due to parasitic side reactions (see main text); so for simplicity we also integrated the signal from the leftover styrene for comparison. For each spectrum, the integral of the styrene signal at  $\delta = 5.78$  (d, 1H) was calibrated to 1 and the signal for 5-phenyl-2-oxazolidinone at  $\delta = 5.66$  (t, 1H) was integrated. It is observed that with increasing amounts of LiI, the amount of 5-phenyl-2-oxazolidinone also increased. Similar experiments with CS<sub>2</sub> (signal at  $\delta = 5.18$  (dd, 1H) was used) and LiBr were also performed.

## Control experiments with CO<sub>2</sub> and LiI

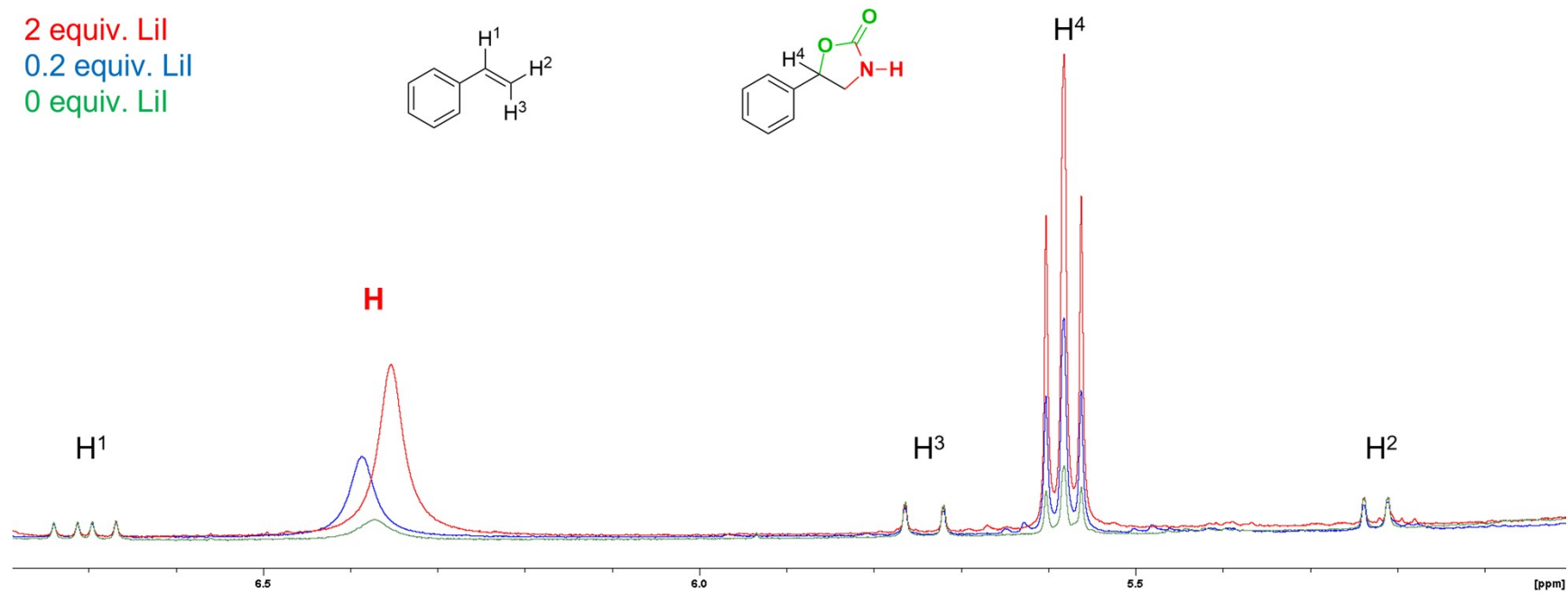


Figure S1: Control experiments with different amounts of LiI for the CO<sub>2</sub> insertion reaction.

## Control experiments with CO<sub>2</sub> and LiBr

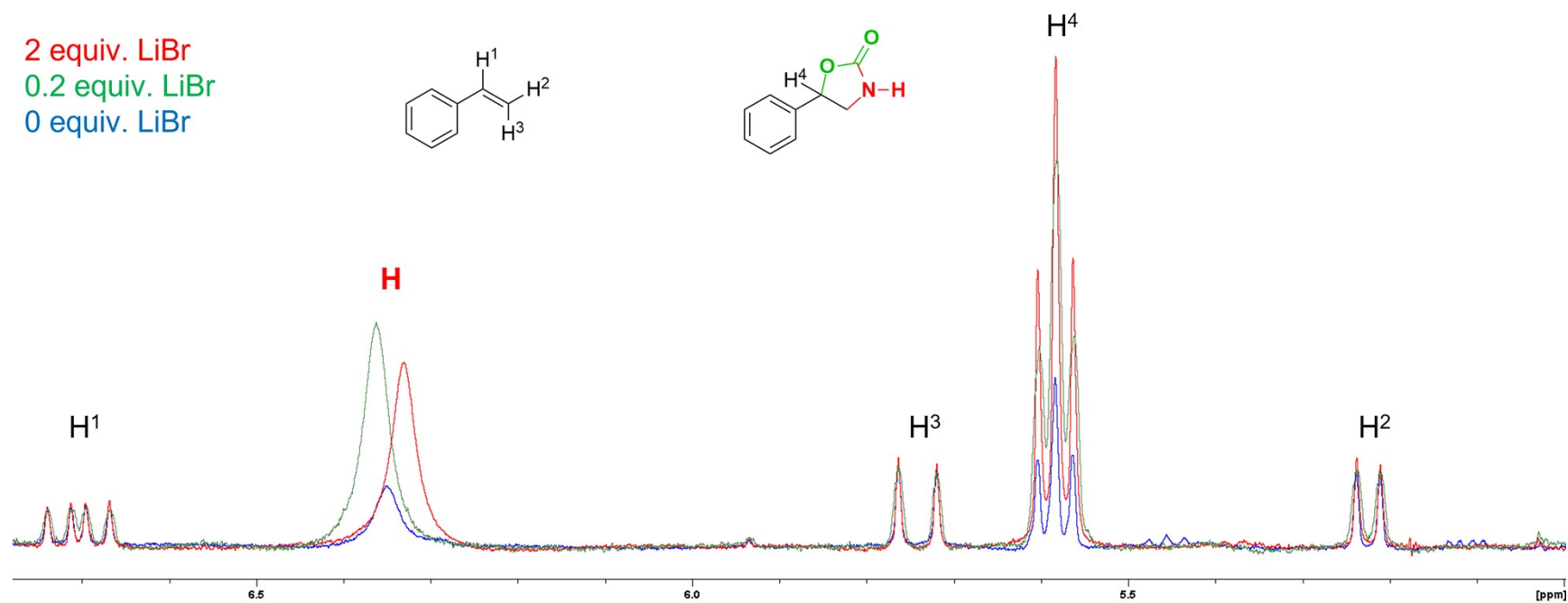
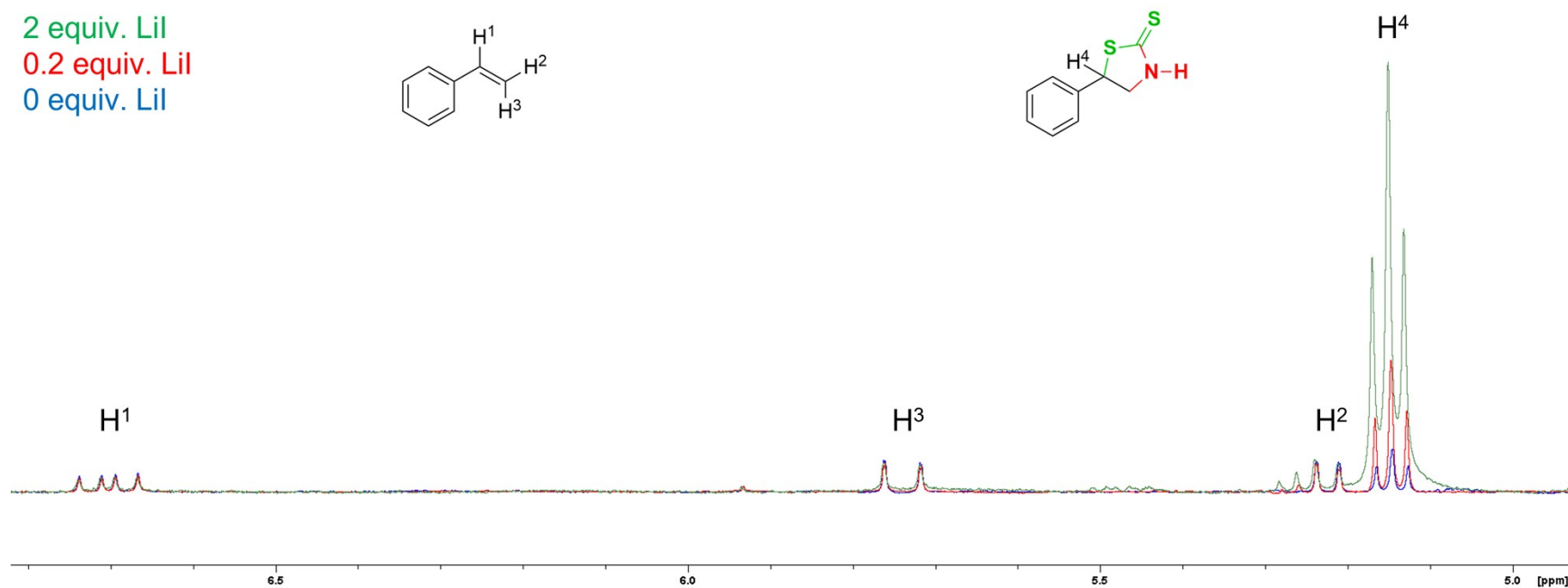
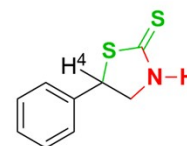
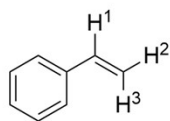


Figure S2: Control experiments with different amounts of LiBr for the CO<sub>2</sub> insertion reaction.



## Control experiments with CS<sub>2</sub> and LiI

2 equiv. LiI  
0.2 equiv. LiI  
0 equiv. LiI



**Figure S3:** Control experiments with different amounts of LiI for the CS<sub>2</sub> insertion reaction.

## Control experiments with CS<sub>2</sub> and LiBr

2 equiv. LiBr  
0.2 equiv. LiBr  
0 equiv. LiBr

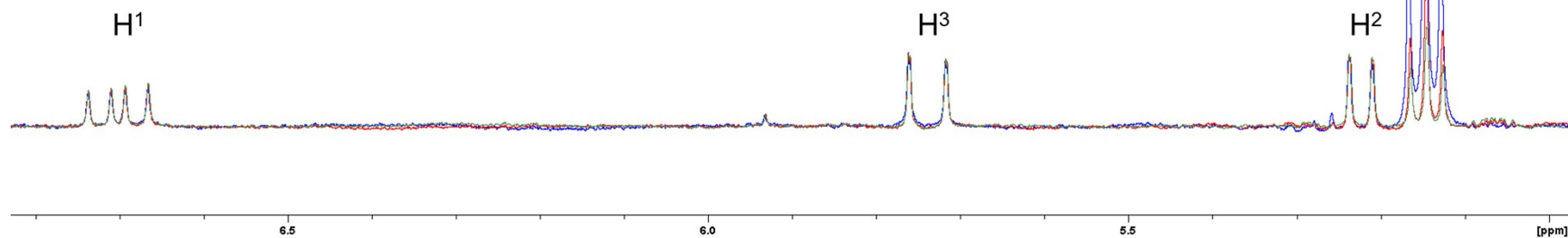
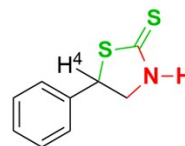
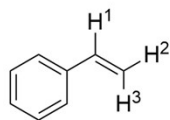
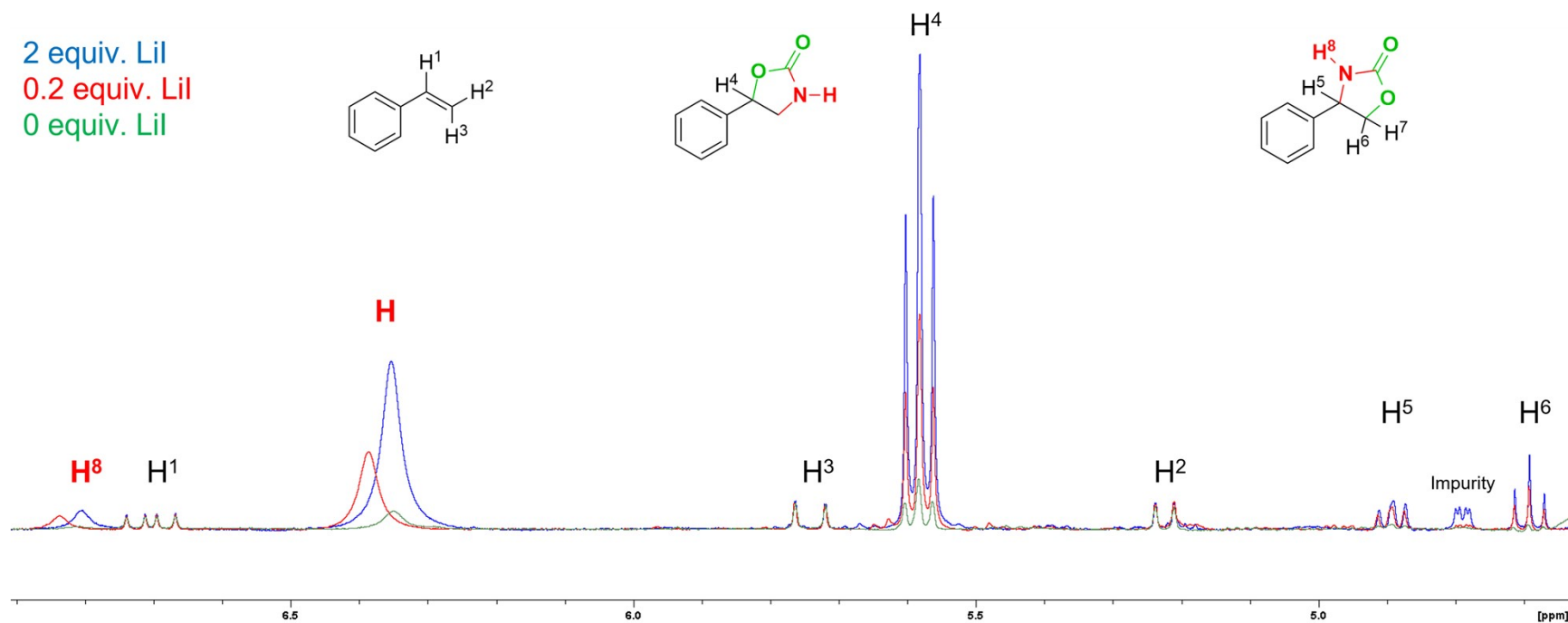


Figure S4: Control experiments with different amounts of LiBr for the CS<sub>2</sub> insertion reaction.

## Control experiments with CO<sub>2</sub> and LiI with focus on product distribution

The amount of 5-phenyl-2-oxazolidinone increases to a much larger extent with increasing amount of LiI compared to the 4-phenyl-2-oxazolidinone (signals for H<sup>4</sup> and H compared with signals for H<sup>5</sup>, H<sup>6</sup> and H<sup>8</sup>). Experiments with LiBr and CO<sub>2</sub> gave similar trends but to a lesser extent.

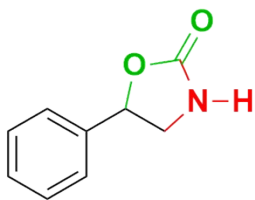


**Figure S5:** Control experiments with different amounts of LiI for the CO<sub>2</sub> insertion reaction with focus on product distribution of the 5-phenyl-2-oxazolidinone and 4-phenyl-2-oxazolidinone isomers.

## 4) Spectroscopic data

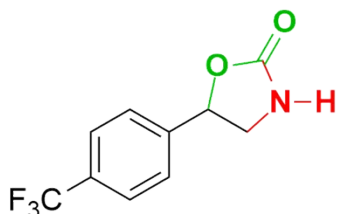
Quantification was performed by mixing 200  $\mu\text{l}$  of crude reaction mixture with 300  $\mu\text{l}$  0.0454 M solution of pyridine in  $\text{CDCl}_3$ . Characteristic signals of both starting materials and products, together with the signal for pyridine at  $\delta = 8.58$  (d, 2H), are used. For the model reaction with styrene, quantification was based on the styrene signal at  $\delta = 5.78$  (d, 1H) and the 2-oxazolidinone signal at  $\delta = 5.66$  (t, 1H). For 2-thiazolidinethiones, the characteristic signal at  $\delta = 5.30$  (t, 1H) was used. Similar strategies were used for the other substrates. For 2- and 4-vinylpyridine, a 0.0214 M solution of methyl 3,5-dinitrobenzoate in  $\text{CDCl}_3$  was used with a characteristic signal at  $\delta = 9.11$  (s, 2H).

The crude spectra for quantification were compared with literature data to prove the 2-oxazolidinones and 2-thiazolidithiones had formed<sup>2-8</sup>. The signal of the N-H proton proved difficult to discriminate from other signals, most likely because it is an exchangeable proton and due to H-bonding with both dioxane and especially water, broadening and displacing the peak. According to literature, this proton gives a broad signal at values ranging from  $\delta = 5.75$  to  $\delta = 6.68$  for the model compound **2a** (5-phenyl-2-oxazolidinone)<sup>2-4</sup>. After work-up, the N-H proton signal was found here at  $\delta = 6.34$ . However, H-bonding with leftover dioxane can still be responsible for broadening and displacing the signal. For the thiazolidinethiones, a value of the N-H signal at  $\delta = 10.53$  is reported for the model compound **4a** (5-phenyl-2-thiazolidinethione, in  $\text{DMSO-d}_6$ )<sup>4</sup>. GC-MS measurements further confirmed the formation of the desired products where the obtained mass corresponded excellently to the calculated mass.



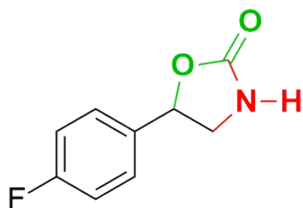
### 5-Phenyl-2-oxazolidinone (2a)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.57 (t,  $J = 8.2$  Hz, 1H), 4.01 (t,  $J = 8.6$  Hz, 1H), 5.66 (t,  $J = 8.2$  Hz, 1H), 6.34 (s br, 1H), 7.35-7.50 (m, 5H);  $^{13}\text{C-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  47.9, 76.8, 126.4, 129.2, 140.1, 159.2; GC-MS (EI, 70eV):  $m/z$  (rel. int. %): 163 (30), 133 (57), 105 (64), 104 (100), 91 (31), 78 (12), 77 (32), 65 (13), 51 (25), 50 (13).



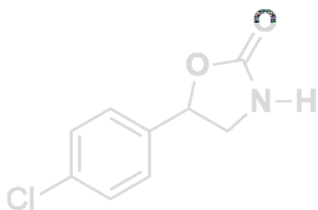
### 5-(4-trifluoromethylphenyl)-2-oxazolidinone (2b)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.43 (t,  $J = 7.9$  Hz, 1H), 3.98 (t,  $J = 8.7$  Hz, 1H), 5.67 (t,  $J = 7.9$  Hz, 1H), 6.47 (s br, 1H), 7.32-7.64 (m, 4H).



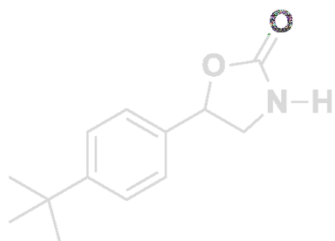
### 5-(4-fluorophenyl)-2-oxazolidinone (2c)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.50 (t,  $J = 8.1$  Hz, 1H), 3.97 (t,  $J = 8.7$  Hz, 1H), 5.59 (t,  $J = 8.1$  Hz, 1H), 6.54 (s br, 1H), 7.03-7.13 (m, 2H), 7.28-7.41 (m, 2H).



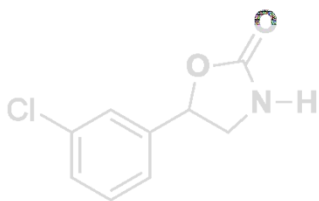
**5-(4-chlorophenyl)-2-oxazolidinone (2d)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41 (t,  $J = 7.9$  Hz, 1H), 3.92 (t,  $J = 8.7$  Hz, 1H), 5.56 (t,  $J = 7.9$  Hz, 1H), 6.42 (s br, 1H), 7.24-7.43 (m, 4H).



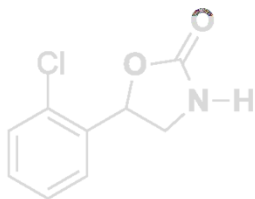
**5-(4-*tert*-butylphenyl)-2-oxazolidinone (2e)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.34 (s, 9H), 3.55 (t,  $J = 8.2$  Hz, 1H), 3.94 (t,  $J = 8.7$  Hz, 1H), 5.69 (t,  $J = 8.2$  Hz, 1H), 6.35 (s br, 1H), 7.24-7.36 (m, 2H), 7.39-7.48 (m, 2H).



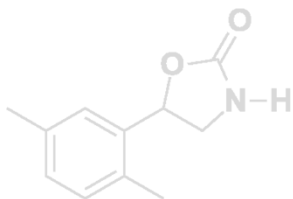
**5-(3-chlorophenyl)-2-oxazolidinone (2f)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.43 (t,  $J = 8.0$  Hz, 1H), 3.93 (t,  $J = 8.7$  Hz, 1H), 5.56 (t,  $J = 8.0$  Hz, 1H), 6.42 (s br, 1H), 7.19-7.43 (m, 4H).



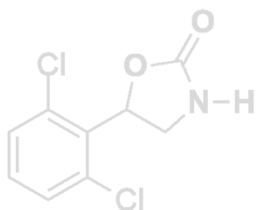
**5-(2-chlorophenyl)-2-oxazolidinone (2g)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.36 (dd,  $J = 8.9, 6.5$  Hz, 1H), 4.12 (t,  $J = 8.9$  Hz, 1H), 5.90 (dd,  $J = 8.9, 6.5$  Hz, 1H), 6.43 (s br, 1H), 7.26-7.44 (m, 3H), 7.54-7.62 (m, 1H).



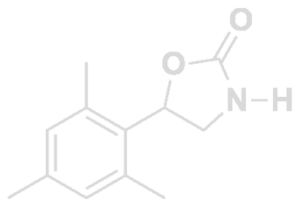
**5-(2,5-dimethylphenyl)-2-oxazolidinone (2h)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.24 (s, 3H), 2.32 (s, 3H), 3.35 (t,  $J = 8.0$  Hz, 1H), 3.94 (t,  $J = 8.6$  Hz, 1H), 5.76 (t,  $J = 8.0$  Hz, 1H), 6.38 (s br, 1H), 7.00-7.09 (m, 2H), 7.24-7.29 (m, 1H).



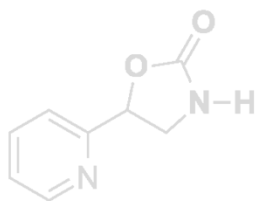
**5-(2,6-dichlorophenyl)-2-oxazolidinone (2i)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.75 (t,  $J = 8.7$  Hz, 1H), 3.88 (t,  $J = 8.9$  Hz, 1H), 6.37 (t,  $J = 9.4$  Hz, 1H) 6.49 (s br, 1H), 7.28-7.38 (m, 3H).



**5-(2,4,6-trimethylphenyl)-2-oxazolidinone (2j)**

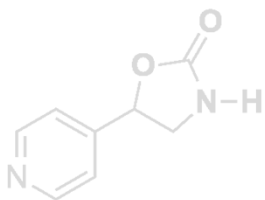
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.24 (s, 3H), 2.25 (s, 3H), 2.34 (s, 3H), 3.47 (t,  $J = 9.2$  Hz, 1H), 3.82 (t,  $J = 9.2$  Hz, 1H), 6.00 (t,  $J = 9.6$  Hz, 1H), 6.41 (s br, 1H), 7.81-7.88 (m, 2H).



**5-(2-pyridinyl)-2-oxazolidinone (2k)**

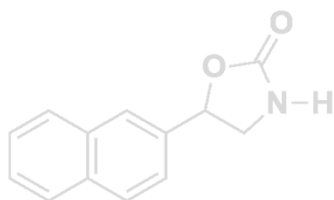
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.79 (t, 7.6 Hz, 1H), 4.09 (t,  $J = 8.8$  Hz, 1H), 5.70 (dd,  $J = 9.2, 6.7$  Hz, 1H), 5.98 (s br, 1H), 7.28 (m, 1H), 7.55 (d,  $J = 7.9$  Hz, 1H), 7.77 (t,  $J = 7.7$  Hz, 1H), 8.60 (d,  $J = 4.5$  Hz, 1H).





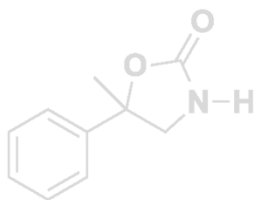
**5-(4-pyridinyl)-2-oxazolidinone (2l)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.42 (t,  $J = 8.0$  Hz, 1H), 4.01 (t,  $J = 8.4$  Hz, 1H), 5.63 (t,  $J = 8.0$  Hz, 1H), 6.44 (s br, 1H), 7.27-7.34 (m, 2H), 8.60-8.67 (m, 2H).



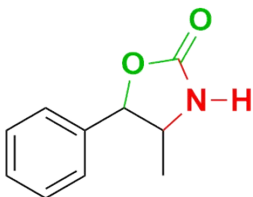
**5-(2-naphthyl)-2-oxazolidinone (2m)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.53 (t,  $J = 8.1$  Hz, 1H), 3.98 (t,  $J = 8.6$  Hz, 1H), 5.73 (t,  $J = 8.1$  Hz, 1H), 5.93 (s br, 1H), 7.38-7.53 (m, 3H), 7.78-7.91 (m, 4H).



**5-methyl-5-phenyl-2-oxazolidinone (2n)**

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.77 (s, 3H), 3.41 (d,  $J = 8.4$  Hz, 1H), 3.63 (d,  $J = 8.2$  Hz, 1H), 6.22 (s

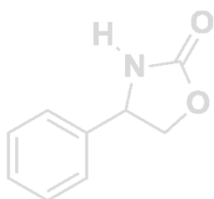


br, 1H), 7.23-7.42 (m, 5H).

#### 4-methyl-5-phenyl-2-oxazolidinone (2o)

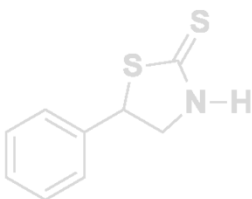
*Cis*:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (d,  $J = 6.5$  Hz, 3H), 4.23 (m, 1H), 5.74 (d,  $J = 8.0$  Hz, 1H), 5.79 (s br, 1H), 7.29-7.37 (m, 5H).

*Trans*:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.42 (d,  $J = 6.2$  Hz, 3H), 3.86 (m, 1H), 5.06 (d,  $J = 7.2$  Hz, 1H), 5.88 (s br, 1H), 7.35-7.48 (m, 5H).



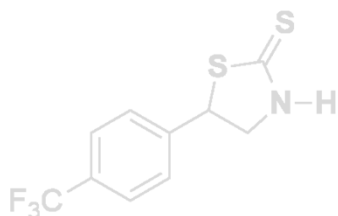
#### 4-phenyl-2-oxazolidinone (3a)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.23 (t,  $J = 7.9$  Hz, 1H), 4.78 (t,  $J = 8.7$  Hz, 1H), 4.98 (t,  $J = 7.9$  Hz, 1H), 6.78 (s br, 1H), 7.34-7.49 (m, 5H)



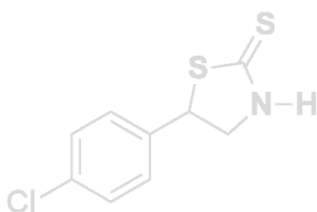
#### 5-phenyl-2-thiazolidinethione (4a)

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  3.96 (dd,  $J = 11.3, 7.3$  Hz, 1H), 4.27 (dd,  $J = 11.3, 8.1$  Hz, 1H), 5.30 (t,  $J = 7.7$  Hz, 1H), 7.30-7.46 (m, 5H), 10.27 (s br, 1H);  $^{13}\text{C-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  53.0, 58.6, 127.7, 128.7, 129.4, 140.1, 198.3



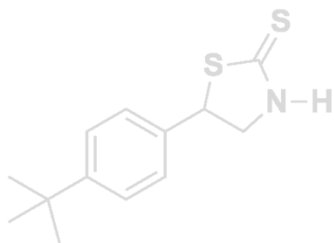
**5-(4-trifluoromethylphenyl)-2-thiazolidinethione (4b)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  3.99 (dd,  $J = 11.4, 6.5$  Hz, 1H), 4.32 (dd,  $J = 11.4, 8.1$  Hz, 1H), 5.18 (t,  $J = 7.2$  Hz, 1H), , 7.57-7.66 (m, 2H), 7.71-7.81 (m, 2H), 10.34 (s br, 1H).



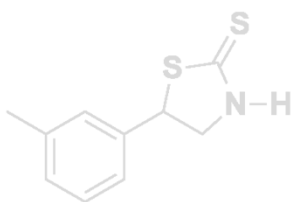
**5-(4-chlorophenyl)-2-thiazolidinethione (4c)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  3.89 (dd, 11.3, 6.8 Hz, 1H), 4.23 (dd, 11.3, 8.6 Hz, 1H), 5.12 (t,  $J = 7.6$  Hz, 1H), 7.27-7.38 (m, 4H), 10.27 (s br, 1H).



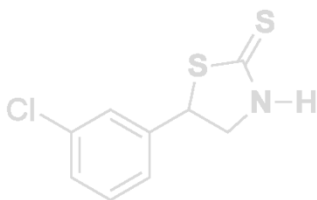
**5-(4-*tert*-butylphenyl)-2-thiazolidinethione (4d)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  1.26 (s, 9H), 3.93 (dd,  $J$  = 11.3, 7.6 Hz, 1H), 4.19 (dd,  $J$  = 11.3, 8.1 Hz, 1H), 5.14 (t,  $J$  = 7.8 Hz, 1H), 7.31-7.42 (m, 4H), 10.34 (s br, 1H).



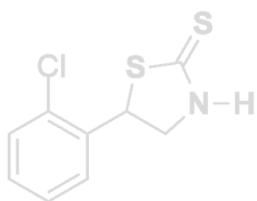
**5-(3-methylphenyl)-2-thiazolidinethione (4e)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  2.31 (s, 3H), 3.94 (dd,  $J$  = 11.6, 7.5 Hz, 1H), 4.20 (dd,  $J$  = 11.6, 8.2 Hz, 1H), 5.12 (t,  $J$  = 7.8 Hz, 1H), 7.09-7.31 (m, 4H), 10.23 (s br, 1H).



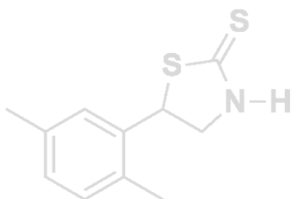
**5-(3-chlorophenyl)-2-thiazolidinethione (4f)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  3.96 (dd,  $J$  = 11.6, 6.8 Hz, 1H), 4.24 (dd,  $J$  = 11.6, 8.2 Hz, 1H), 5.29 (t,  $J$  = 7.4 Hz, 1H), 7.27-7.48 (m, 4H), 10.27 (s br, 1H).



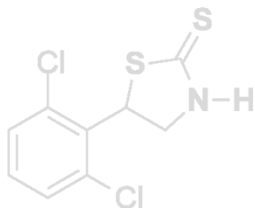
**5-(2-chlorophenyl)-2-thiazolidinethione (4g)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  3.99 (dd,  $J = 11.6, 5.1$  Hz, 1H), 4.38 (dd,  $J = 11.9, 8.3$  Hz, 1H), 5.54 (dd,  $J = 8.3, 5.1$  Hz, 1H), 7.23-7.44 (m, 3H), 7.60-7.70 (m, 1H), 10.31 (s br, 1H).



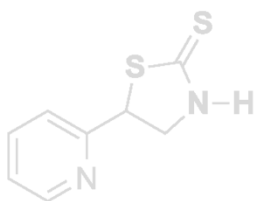
**5-(2,5-dimethylphenyl)-2-thiazolidinethione (4h)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  2.23 (s, 3H), 2.28 (s, 3H), 3.93 (dd,  $J = 11.3, 7.3$  Hz, 1H), 4.19 (dd,  $J = 11.3, 8.1$  Hz, 1H), 5.41 (t,  $J = 7.7$  Hz, 1H), 7.00-7.09 (m, 2H), 7.27-7.30 (m, 1H), 10.26 (s br, 1H).



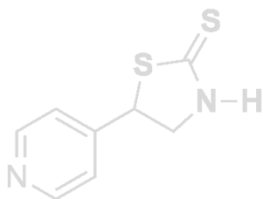
**5-(2,6-dichlorophenyl)-2-thiazolidinethione (4i)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  3.82 (dd,  $J = 12.5, 4.7$  Hz, 1H), 4.14 (dd,  $J = 12.5, 6.5$  Hz, 1H), 6.19 (dd,  $J = 11.1, 6.4$  Hz, 1H), 7.24-7.54 (m, 3H), 10.33 (s br, 1H).



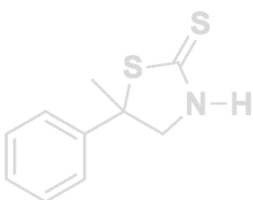
**5-(2-pyridinyl)-2-thiazolidinethione (4j)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  4.25 (dd,  $J = 11.8, 8.1$ , 1H), 4.29 (dd,  $J = 11.8, 5.8$  Hz, 1H), 5.33 (dd,  $J = 8.1, 5.8$  Hz, 1H), 7.33 (m, 1H), 7.42 (m, 1H), 7.81 (m, 1H), 8.56 (m, 1H), 10.24 (s br, 1H).



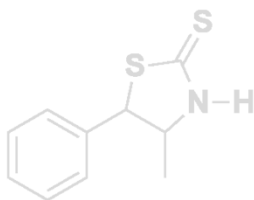
**5-(4-pyridinyl)-2-thiazolidinethione (4k)**

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  3.82 (dd,  $J = 10.2, 5.1$  Hz, 1H), 3.99 (dd,  $J = 12.6, 5.1$  Hz, 1H), 5.27 (dd,  $J = 8.2, 5.3$  Hz, 1H), 7.34-7.49 (m, 2H), 8.49-8.65 (m, 2H), 10.34 (s br, 1H).



**5-methyl-5-phenyl-2-thiazolidinethione (4l)**

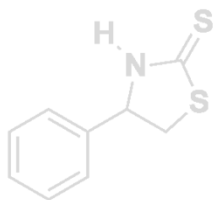
$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$  1.97 (s, 3H), 3.98 (d,  $J = 11.2$  Hz, 1H), 4.20 (d,  $J = 11.3$  Hz, 1H), 7.23-7.50 (m, 5H), 10.28 (s br, 1H).



#### 4-methyl-5-phenyl-2-thiazolidinethione (4m)

*Cis*:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.03 (d,  $J = 6.7$  Hz, 3H), 4.66 (m, 1H), 4.99 (d,  $J = 7.3$  Hz, 1H), 7.23-7.42 (m, 5H), 8.01 (s br, 1H).

*Trans*:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.42 (d,  $J = 6.3$  Hz, 3H), 4.36 (m, 1H), 4.74 (d,  $J = 8.8$  Hz, 1H), 7.23-7.42 (m, 5H), 8.01 (s br, 1H).

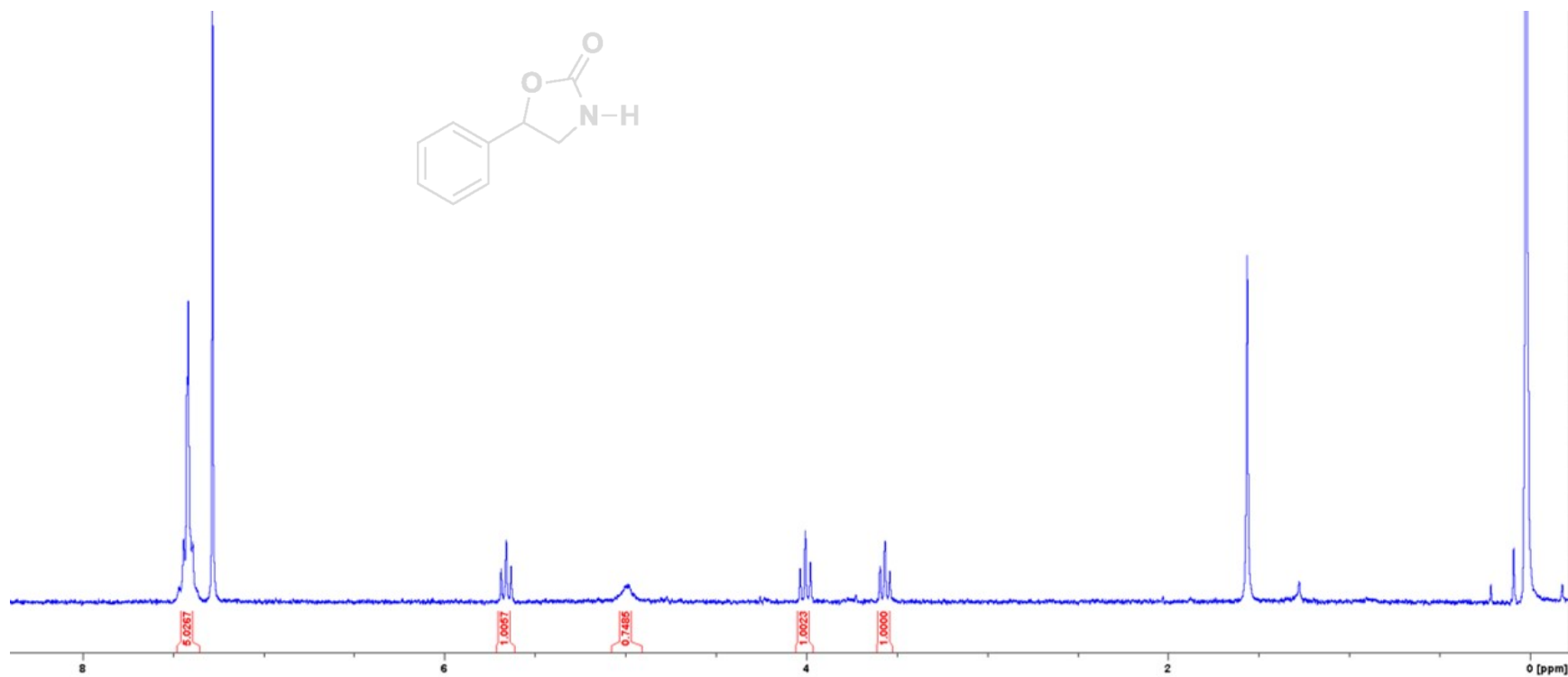


#### 4-phenyl-2-thiazolidinethione (5a)

$^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  3.04 (dd,  $J = 11.1, 6.6$  Hz, 1H), 3.71 (dd,  $J = 11.1, 8.0$  Hz, 1H), 4.54 (t, 6.5 Hz, 1H), 7.18-7.32 (m, 5H), 10.45 (s br, 1H).

## <sup>1</sup>H-NMR spectrum of purified compound **2a**

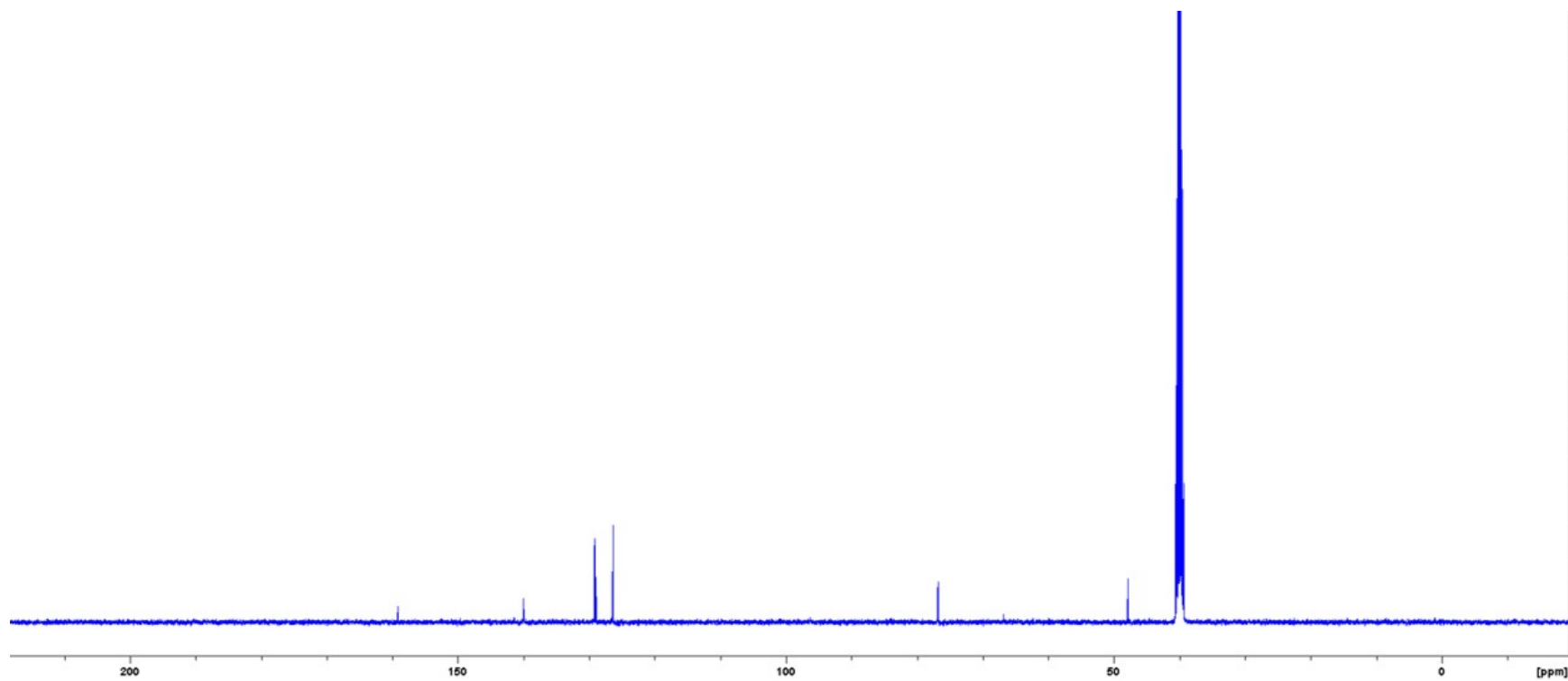
White solid,  $R_F = 0.23$ , 81% overall yield. The N-H signal at  $\delta = 4.99$  does not fully integrate for 1 proton, most likely due to H-bonding with impurity water ( $\delta = 1.57$ ) which is present in the  $\text{CDCl}_3$  bottle which might also displace the signal.



**Figure S6:** <sup>1</sup>H-NMR spectrum of the model compound **2a** in  $\text{CDCl}_3$  ( $\delta = 7.29$ )



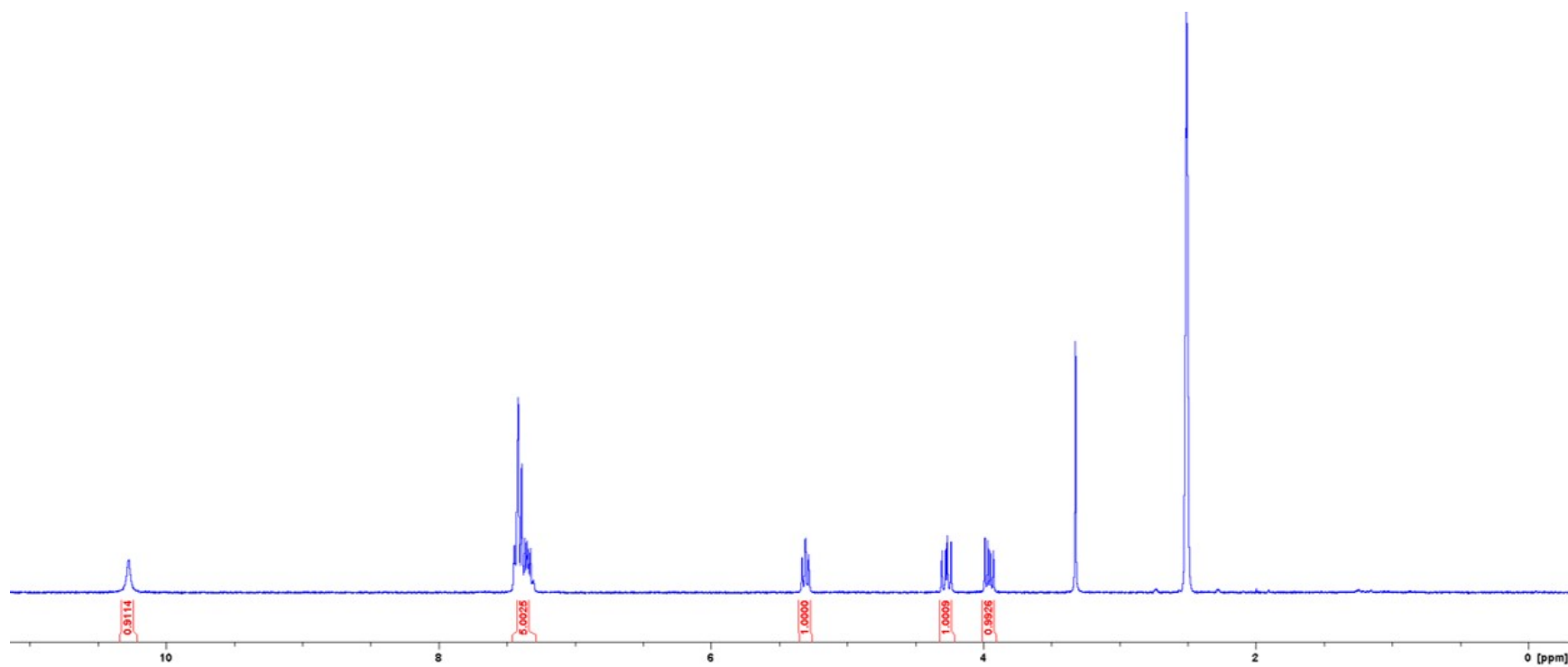
**$^{13}\text{C}$ -NMR spectrum of purified compound 2a**



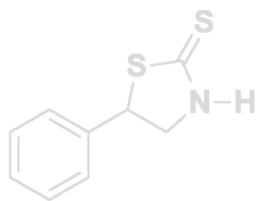
**Figure S7:**  $^{13}\text{C}$ -NMR spectrum of the model compound **2a** in  $\text{CDCl}_3$

### **<sup>1</sup>H-NMR spectrum of purified compound 4a**

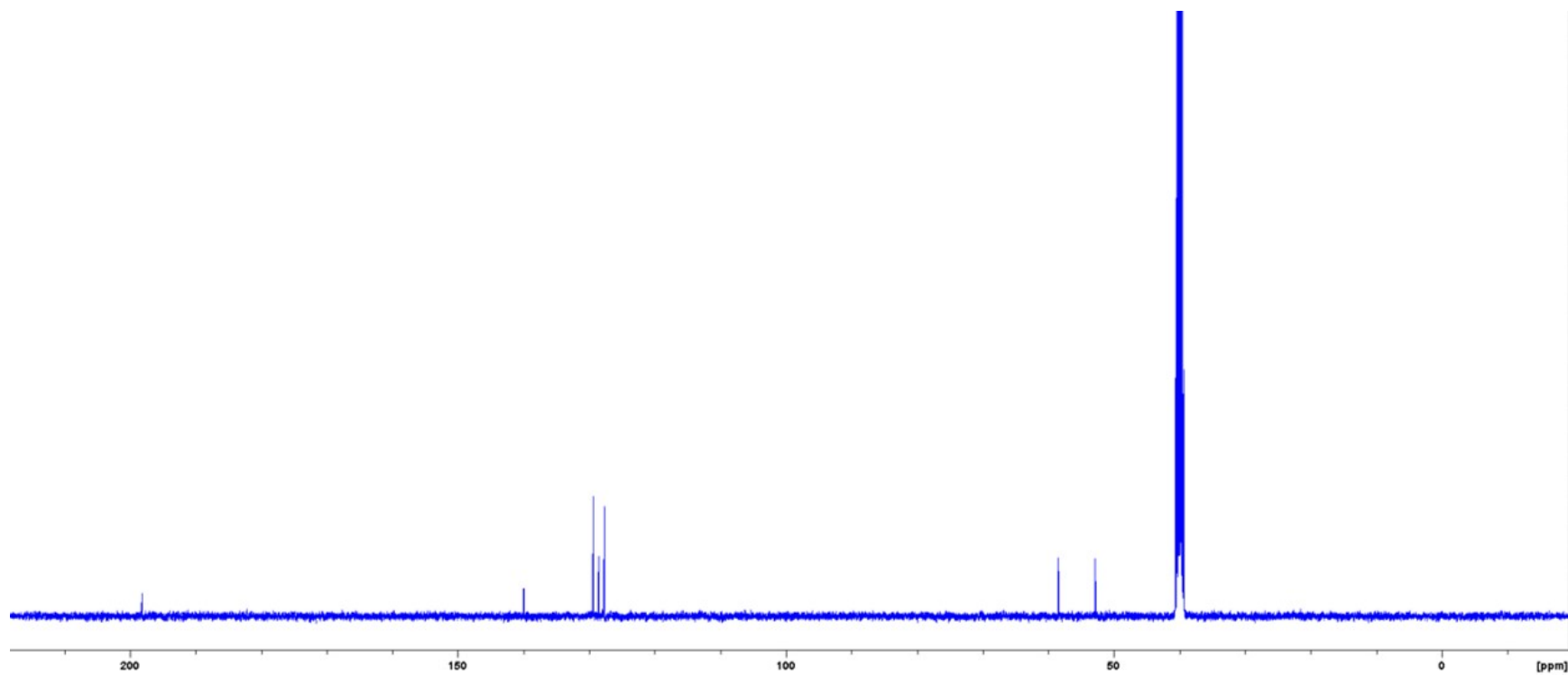
White solid,  $R_F = 0.45$ , 58% overall yield. The N-H signal at  $\delta = 10.27$  does not fully integrate for 1 proton, most likely due to H-bonding with water ( $\delta = 3.33$ ) which is present in the DMSO-d<sub>6</sub> bottle.



**Figure S8:** <sup>1</sup>H-NMR spectrum of the model compound **4a** in DMSO-d<sub>6</sub> ( $\delta = 2.51$ ).



**<sup>13</sup>C-NMR spectrum of purified compound 4a**



**Figure S9:**  $^{13}\text{C}$ -NMR spectrum of the model compound 4a in DMSO- $d_6$ .

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