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Synthesis of Bicyclic Thiazolidinethiones and Oxazolidinones by Water-Mediated Multicomponent Reactions (MCR) and Ring-Closing Metathesis (RCM)[‡]

Timo Stalling,[a] Wolfgang Saak,[a] and Jürgen Martens*[a]

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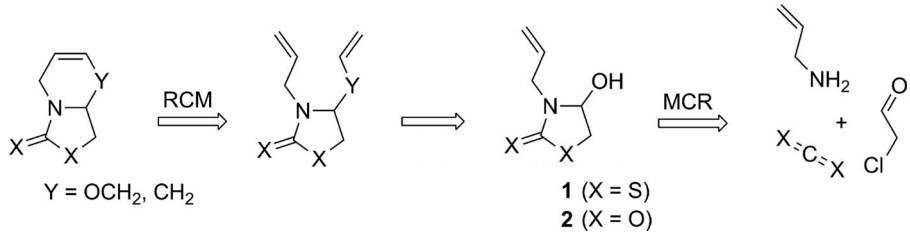
Starting with the development of new multicomponent reactions (MCR) in water, hydroxy thiazolidinethiones and oxazolidinones were prepared efficiently in a one-pot procedure. The reaction was carried out under mild conditions, consistent with the principles of "green chemistry". These precursors were converted into different dienes containing terminal C–C double bonds by modifying the hydroxy group in one- or two-step sequences. A final ring-closing metathesis (RCM) reaction led to various classes of unsaturated bicycles.

Introduction

Thiazolidinethiones and oxazolidinones are ubiquitous structures that have been widely used as chiral auxiliaries in the stereoselective synthesis of natural products, antibiotics, and pharmaceuticals.[2] Furthermore, some oxazolidinones are known as antibiotics,[3] of which linezolid is the most famous drug.[4] In addition, it has been reported that transition-metal complexes of thiazolidinethiones and oxazolidinones are very efficient reagents for stereoselective carbonyl chemistry.[5] Some thiazolidinethione derivatives have been used as tools for the modification of proteins,[6] as coupling reagents for the synthesis of peptides,[7] or as glycosyl donors for the synthesis of oligosaccharides.[8] Thiazolidinethiones also serve as excellent ligands.[9]

Consequently, the chemistry of thiazolidinethiones and oxazolidinones is a current field of research. As a result of our ongoing interest in the development of new synthetic routes involving multicomponent reactions (MCRs) and ring-closing metathesis (RCM),[1] we aimed to prepare annulated bicycles containing thiazolidinethiones and oxazolidinones by this approach (Scheme 1).

In the first step (i.e., the MCR), the one-pot reaction should be carried out within the context of sustainable development, under mild conditions. To meet these requirements, which have a bearing on "green chemistry", the essential C_1 source could be supplied by CS_2 (X = S), or by natural renewable CO_2 (X = O). CO_2 has found wide use due to its characteristics as an abundant, economical, and non-toxic reagent. However, CO_2 has attracted much attention resulting from its increasing presence as a greenhouse gas in the atmosphere.[10] We aimed to use allylamine and chloroacetaldehyde as the other necessary components in our proposed reaction. The ready accessibility of the starting materials, together with the synthetic utility of CO_2, make this approach particularly attractive. In general,



Scheme 1. Retrosynthetic analysis of the target bicycles.

[‡] Multicomponent Reaction and Ring-Closing Metathesis in the Synthesis of New Heterocycles, 5. Parts 1–4: Ref.[1]

[a] Institut für Chemie, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany
E-mail: juergen.martens@uni-oldenburg.de
www.martens.chemie.uni-oldenburg.de

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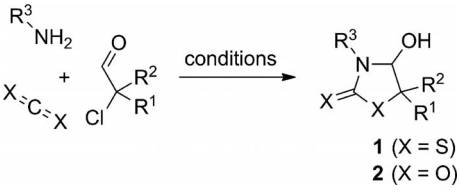
MCRs are highly atom efficient, they use readily available and structurally varied starting materials, and they also present significant advantages in terms of cost and time. MCRs are among the most versatile and powerful of synthetic procedures, and they allow the preparation of highly diverse and complex heterocyclic structures in a single synthetic operation.[11] The last step of the sequence, namely the RCM step, could be described in a similar way. RCM is one of the most preferred methods for the formation of cyclic structures from unsaturated substrates.[12] This is a consequence of the development of highly efficient catalysts.[13]

Although the preparation of hydroxy thiazolidinethiones **1** is well known,[14] most synthetic routes that start from aldehydes require multiple steps and are less efficient.[15] Other methods require drastic conditions and provide the elimination product, namely 4-thiazoline-2-thiones.[16] A new and more efficient one-pot synthesis using H_2O as solvent was recently reported by Gan and co-workers, and is based on α-bromoketones.[17] On the other hand, the formation of hydroxy oxazolidinones **2** is also a multistep process in most cases.[18] An exception was described by Toda,[19] who synthesized a few compounds from α-bromoketones by stirring under reflux in MeOH in the presence of gaseous CO_2. But notwithstanding this, the development of a synthetic method that allows the practical, flexible, and rapid preparation of hydroxy oxazolidinones from readily available starting materials under mild conditions remains an important goal.

Results and Discussion

First, we focused our attention on different hydroxy thiazolidinethiones **1** and oxazolidinones **2** that could serve as precursors for unsaturated bicycles. Their synthesis was achieved using a three-component reaction in H_2O (Scheme 2).



Scheme 2. Synthesis of thiazolidinethiones **1** (X = S) and oxazolidinones **2** (X = O). Reagents and conditions: (a) compounds **1**: amine (1.5 equiv.), CS_2 (3 equiv.), aldehyde (1 equiv.), K_2CO_3 (0.5 equiv.), H_2O, room temp., 2 h; (b) compounds **2**: amine (3 equiv.), $KHCO_3$ (10 equiv.), aldehyde (1 equiv.), H_2O, room temp., 10 h.

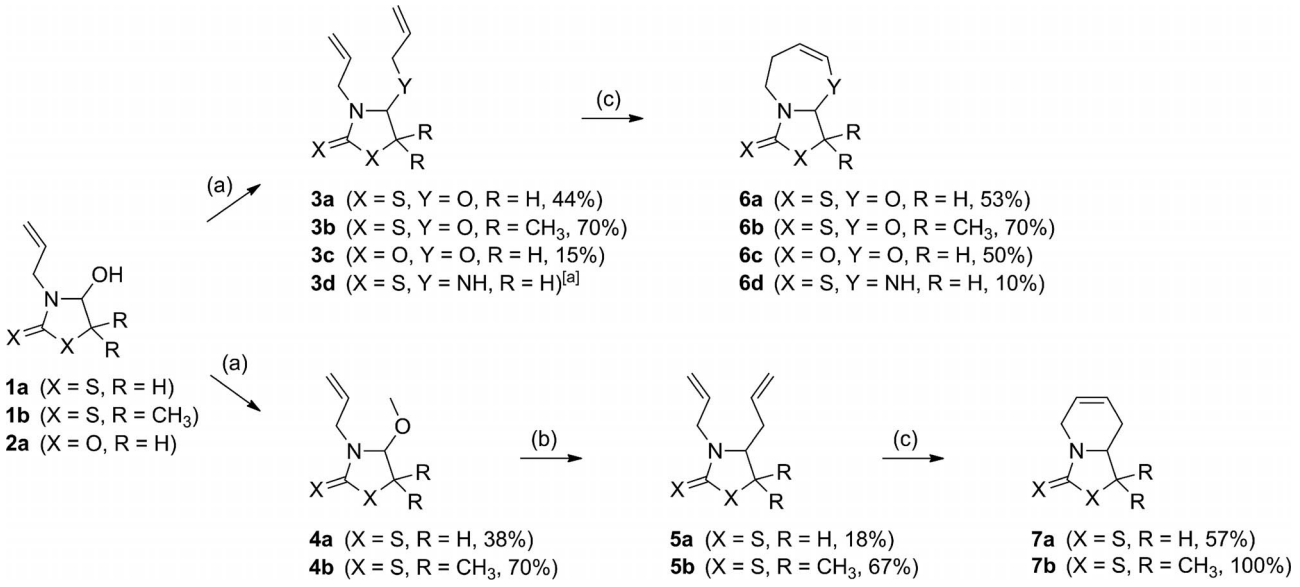
We started our investigations with allylamine[20] (R^3 = allyl; 1.5 equiv.), CS_2 (X = S; 3 equiv.), and chloroacetaldehyde (R^1 = R^2 = H; 1 equiv.), stirring in H_2O at room temp. for 2 h to access hydroxy thiazolidinethione **1a**. In spite of its toxicity, chloroacetaldehyde is an appropriate and low-cost reagent, as it is a waste product of the Wacker process[21] (synthesis of acetaldehyde). So that the results of all of the experiments run during the optimization period would be comparable, the amount of the solvent (H_2O), as well as the mixture of solvents for column chromatography (CH_2Cl_2/ethyl acetate, 19:1), were kept constant. Other parameters such as the reaction time and temperature, the solvent, and the base were varied. The stoichiometry was chosen as reported recently.[17] Initial experiments suggested that the addition of a base would lead to a more successful reaction (Table 1, entries 1–3). Of the two bases tested, we found that K_2CO_3 gave the best yield of thiazolidinethione **1a** (Table 1, entries 4 and 6 vs. entries 5 and 7). In terms of reaction time, the best result was achieved after 2 h (Table 1, entry 7). Longer or shorter times led to lower yields (Table 1, entries 5 and 8). Scaling up the procedure provided no problems, and the yield of the product was not significantly lower. We examined the sequence of addition of the starting materials (Table 1, entries 11 and 12). Interestingly, the originally chosen sequence was the most efficient method. We ascertained that heating has a significant negative influence on the yield (Table 1, entries 13 and 14). Furthermore, we observed that long reaction times and heating promote the formation of two by-products. 1,3-Diallylthiourea was isolated in some cases, and compound **3d** (see Scheme 3) was found in others. To summarize, the best yield (60%) was obtained after stirring for 2 h at room temp. using K_2CO_3 as base (Table 1, entry 7).

Table 1. Synthesis of thiazolidinethione **1a** (R^1 = R^2 = H; R^3 = allyl) under different conditions.

Entry	Molar ratio [mmol][a]	Base[b]	Conditions	Solvent	Yield [%][c]
1[d]	1.5:3.0:1.0	–	room temp., 2 h	THF[e]	14[f]
2[d]	1.5:3.0:1.0	–	room temp., 2 h	H_2O	35
3[d]	1.5:3.0:1.0	–	room temp., 1 h	H_2O	27
4[d]	1.5:3.0:1.0	Et_3N	room temp., 1 h	H_2O	30
5[d]	1.5:3.0:1.0	K_2CO_3	room temp., 1 h	H_2O	34
6[d]	1.5:3.0:1.0	Et_3N	room temp., 2 h	H_2O	46
7[d]	1.5:3.0:1.0	K_2CO_3	room temp., 2 h	H_2O	60
8[d]	1.5:3.0:1.0	K_2CO_3	room temp., 3 h	H_2O	50
9[d]	30:60:20	K_2CO_3	room temp., 2 h	H_2O	42
10[d]	30:60:20	K_2CO_3	room temp.,[g] 2 h	H_2O	34
11[h]	1.5:3.0:1.0	K_2CO_3	room temp.,[g] 2 h	H_2O	33
12[i]	3.0:6.0:2.0	K_2CO_3	room temp., 2 h	H_2O	41
13[a]	3.0:6.0:2.0	K_2CO_3	35–41 °C,[j] 2 h	H_2O	44[k]
14[h]	3.0:6.0:2.0	K_2CO_3	room temp., 2 h; 80 °C,[j] 15 min	H_2O	31[l]

[a] Amine/CS_2/aldehyde. [b] 0.5 equiv. [c] Yields based on chloroacetaldehyde. [d] Chronology: 1. Amine, 2. CS_2, 3. aldehyde, 4. base. [e] Aldehyde: 45% in H_2O. [f] No analytically pure product. [g] The reaction was started at 0–5 °C. [h] Chronology: 1. Amine, 2. K_2CO_3, 3. CS_2, 4. aldehyde. [i] Chronology: 1. K_2CO_3, 2. amine, 3. CS_2, 4. aldehyde. [j] Temperature of the oil bath. [k] 10% yield of by-product **3d**. [l] 3% yield of by-product **3d**.

Next, we focused on establishing an effective protocol for the formation of hydroxy oxazolidinones **2** (X = O). We intended to achieve this by developing a very simple experimental procedure that could be run in a single-necked flask. For the preparation of **2a**, we chose allylamine (R^3 = allyl), a suitable source of CO_2 (X = O), and chloroacetaldehyde (R^1 = R^2 = H) in H_2O. The molar ratio and the reaction conditions were varied, but the sequence of the addition of



Scheme 3. Synthesis of bicycles **6** and **7**. Reagents and conditions: (a) i) Na (1 equiv.), THF, room temp., 2 h; ii) allyl bromide/methyl iodide (1.5 equiv.), THF, room temp., overnight; (b) allyltrimethylsilane (1.5 equiv.), $TiCl_4$ (2 equiv.), CH_2Cl_2, –30 °C – room temp., overnight; (c) Ru catalyst **A** (5 mol-%), toluene, room temp. – 60 °C, 24 h. [a] Compound **3d** was isolated as by-product in the synthesis of **1a**.

the starting materials, and the amount (36 mL) of the solvent (H_2O), were kept constant during the optimization phase (Table 2). At this point, we were thinking about an efficient source of CO_2. Considering alternatives to gaseous CO_2, which has been become well known due to its many applications under sometimes toxic or radical conditions,[22] we aimed to find an easier to handle and permanently obtainable source. Other than dry ice, we recognized that $KHCO_3$ and $NaHCO_3$ could be attractive alternatives, due to their physiological non-toxicity.[23]

Our first attempts to prepare oxazolidinone **2a**, carried out at room temp., led to the conclusion that high yields could only be obtained using an excess of $KHCO_3$ (Table 2, entries 3–5). The best result was achieved after stirring for 10 h at room temp. (Table 2, entry 7). Our investigations made it clear that longer or shorter reaction times (Table 2, entries 6, 9, and 11) do not increase the yield. In terms of the source of CO_2, $KHCO_3$ seems to be a better choice than $NaHCO_3$ (Table 2, entries 7 and 8, compared to entries 9 and 10). Other sources such as K_2CO_3 and dry ice were screened, but they did not lead to any improvements (Table 2, entries 1 and 2). The yields also decreased when the reaction was heated (Table 2, entries 12 and 13). Better results were achieved when the amount of $KHCO_3$ was increased (Table 2, entries 14–16). Comparing these results to previous results (Table 2, entries 6 and 9), a cost–benefit analysis indicates that it would be preferable to use less $KHCO_3$, as the yields are comparable. Doubling the amount of the aldehyde did not increase the yield (Table 2, entries 17–19). For purification, isolation by column chromatography was the method of choice; distillation failed to give the desired product. In conclusion, the best result was obtained by using a stoichiometry of 3:10:1 (amine/$KHCO_3$/chloroacetaldehyde), and stirring for 10 h at room temp. $KHCO_3$ was the most effective source of CO_2, and no catalyst was required. To the best of our knowledge, it has never been reported before that $KHCO_3$ can serve as source of CO_2 in synthetic procedures.

Table 2. Synthesis of oxazolidinone **2a** (R^1 = R^2 = H; R^3 = allyl) under different conditions.

Entry	CO_2 source	Molar ratio [mmol][a,b]	Conditions	Yield [%][c]
1	K_2CO_3	9:30:3	room temp., 2 h	56
2	dry ice	9:18:6[d]	room temp., 2 h	48
3	$KHCO_3$	9:3:3	room temp., 19 h	42
4	$KHCO_3$	9:15:3	room temp., 2 h	45
5	$KHCO_3$	9:30:3	room temp., 2 h	61
6	$KHCO_3$	9:30:3	room temp., 6 h	72
7	$KHCO_3$	9:30:3	room temp., 10 h	73
8	$NaHCO_3$	9:30:3	room temp., 10 h	62
9	$KHCO_3$	9:30:3	room temp., 17 h	69
10	$NaHCO_3$	9:30:3	room temp., 17 h	55
11	$KHCO_3$	9:30:3	room temp., 24 h	54
12	$KHCO_3$	9:30:3	40 °C[e], 2 h	54
13	$KHCO_3$	9:30:3	40 °C[e], 20 h	46
14	$KHCO_3$	9:60:3	room temp., 6 h	74
15	$KHCO_3$	9:60:3	room temp., 16 h	71
16	$KHCO_3$	9:60:3	40 °C[e], 20 h	66
17	$KHCO_3$	9:60:6	room temp., 6 h	57
18	$KHCO_3$	9:60:6	room temp., 10 h	59
19	$NaHCO_3$	9:60:6	room temp., 10 h	47

[a] Amine/"CO_2"/aldehyde. [b] Chronology: amine first, "CO_2" second, then aldehyde. [c] Yields based on chloroacetaldehyde. [d] Additionally, K_2CO_3 (3 mmol) was added as base. [e] Temperature of the oil bath.

With the optimized conditions for both reactions (CO_2 and CS_2) defined, we went on to examine the applicability of the methods, using a wide range of amines and aldehydes, as shown in Table 3.

Table 3. Thiazolidinethiones **1** and oxazolidinones **2** as precursor.

Entry	X	R^1	R^2	R^3	GP[a]	Product (yield [%])[b,c]
1	S	H	H	allyl	A	**1a** (60)
2	S	CH_3	CH_3	allyl	A	**1b** (15)
3	S	$-(CH_2)_5-$		allyl	A	–[d]
4	S	H	H	benzyl	A	**1c** (32)
5	S	CH_3	CH_3	benzyl	A	**1d**[24] (9)
6	S	$-(CH_2)_5-$		benzyl	A	–[d]
7	S	H	H	PMB	A	**1e** (31)
8	S	CH_3	CH_3	PMB	A	**1f** (11)
9	S	$-(CH_2)_5-$		PMB	A	–[d]
10	O	H	H	allyl	C	**2a** (73)[e]
11	O	H	H	benzyl	C	**2b**[25] (64)[f]
12	O	H	H	PMB	C	**2c** (44)[g]
13	O	H	H	phenyl	C	–[d]
14	O	H	H	2-picolyl	C	**2d** (31)
15	O	H	H	cyclohexyl	C	–[d]
16	O	H	H	ethyl	C	**2e** (41)
17	O	H	H	NH-phenyl	C	**2f** (5)

[a] GP = General Procedure (for details, see Exp. Sect.). [b] Isolated yields after column chromatography. [c] References are given for known compounds. [d] No unique product was isolated. [e] 34% yield using dry ice (GP B). [f] 5% yield using dry ice (GP B). [g] 6% yield using dry ice (GP B). PMB = *para*-methoxybenzyl.

Although a wide range of hydroxy thiazolidinethiones and oxazolidinones could be synthesized by this protocol, the yields were not quite satisfactory in some cases.[26] In terms of thiazolidinethiones **1**, thiourea compounds were often isolated as by-products. The undesired formation of these compounds has previously been described in the literature.[27]

To expand the scope of the new reaction, the reactions of aniline and cyclohexylamine were also explored, but no single product was isolated from these reactions (Table 3, entries 13 and 15). The results indicate that the reaction is sensitive to the steric characteristics of the components.[28] Reinforcing this observation, the yields of products **1b**, **1d**, and **1f** starting from sterically demanding 2-chloro-2-methylpropanal were dramatically lower (15, 9, and 11%, respectively). It should also be pointed out that the formation of the latter compounds could only be achieved by performing the reactions in THF. The effect of steric hindrance could be seen in the failed production of spiro compounds (Table 3, entries 3, 6, and 9).

Dry ice was examined as an alternative to $KHCO_3$, but this led to disappointing results. Although allyl derivative **2a** was obtained in moderate yield (34%) using dry ice, the yields of compounds **2b** and **2c** were very low (5 and 6%, respectively), so we did not continue this strategy. Unexpectedly, phenylhydrazine could be converted into oxazolidinone **2f** using this new multicomponent reaction, albeit in a miserable yield of 5% (Table 3, entry 17).[29]

Gratifyingly, we were able to obtain single crystals of compound **1a**. The X-ray structure (Figure 1)[30] verifies the proposed structure of **1a** and confirms the constitution of the other thiazolidinethione **1** and oxazolidinone **2** derivatives.

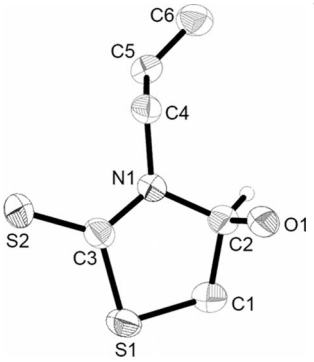
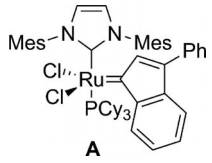


Figure 1. X-ray crystal structure of hydroxy thiazolidinethione **1a** (only one enantiomer is shown.).[30] The atom numbering in the X-ray structure does not follow IUPAC nomenclature.

To obtain dienes that could be used in the final ring-closing metathesis reaction, the hydroxy groups of thiazolidinethiones **1a**–**b** and oxazolidinones **2a** were functionalized by etherification (Scheme 3). Due to the high reactivity of alkoxide ions, the deprotonation of the hydroxy group was carried out in situ. The deprotonation was achieved using sodium in THF. Treatment with halogen compounds (allyl bromide/methyl iodide) led either to allyloxy compounds **3** or to methoxy compounds **4** in acceptable yields (up to 70%). It is worth mentioning that the best results were achieved with dimethyl-substituted derivatives, namely **3b** and **4b**. Unsubstituted compounds gave worse results due to their tendency to eliminate the hydroxy group. Interestingly, oxazolidinone derivative **2a** proved to be relatively unreactive under these conditions. The yield of **3c** was significantly lower (15%), as the crude product contained several impurities, which made multiple purifications by column chromatography necessary. An alternative process using Et_3N as base and CH_2Cl_2 as solvent was tested, but this combination did not improve the outcome of the reaction.

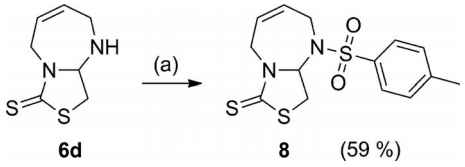
As reported in the literature,[1c,31] the Hosomi–Sakurai reaction can be used to convert the methoxy group into an allyl moiety efficiently in a single step. Therefore, methoxy compounds **4** were activated by the Lewis acid $TiCl_4$ to form iminium ions. These reactive species were trapped by the nucleophilic attack of allyltrimethylsilane to give dienes **5** (Scheme 3). Due to their terminal C–C double bonds, dienes **3** and **5** are ideal substrates for ring-closing metathesis. For this purpose, we decided to use Ru catalyst **A**[32] (Figure 2). We have reported similar procedures elsewhere.[1a] The cyclizations were performed in toluene using 5 mol-% of **A** to provide six- and seven-membered bicycles **6** and **7**, respectively, in good yields (up to 100% for **7b**). Remarkably, methyl-substituted derivatives **6b** and **7b** were obtained in higher yields than the corresponding unsubstituted examples **6a** and **7a**. This synthetic route provides products with a high degree of diversity. Both carbocyclic and heterocyclic (i.e., O- and NH-containing) annulated systems with a C–C double bond, which could offer opportunities for further functionalization, were prepared.



A

Figure 2. Ru catalyst **A** used for RCM.

To demonstrate the potential for further derivatization, an exploratory experiment was performed. Treatment of bicycle **6d** with 4-toluenesulfonyl chloride and Et_3N led to sulfonamide **8** in good yield (59%; Scheme 4).



6d **8** (59 %)

Scheme 4. Synthesis of sulfonamide **8**. Reagents and conditions: (a) TsCl (1 equiv.), Et_3N (1.75 equiv.), CH_2Cl_2, 0 °C – room temp., overnight.

Conclusions

In conclusion, we have developed synthetic sequences consisting of a multicomponent reaction followed by ring-closing metathesis to form bicyclic thiazolidinethiones and oxazolidinones. First, we established new multicomponent reactions starting from amines, CS_2/CO_2, and α-chloroaldehydes to generate hydroxy thiazolidinethiones and oxazolidinones in water. This was achieved to give a practical, simple, and efficient method, consistent with the principles of green chemistry. The precursors were converted into dienes by modifying the hydroxy group using different reactions. The synthetic route was completed using a Ru catalyst to form unsaturated bicyclic thiazolidinethiones and oxazolidinones. We successfully achieved the formation of annulated systems bearing six- and seven-membered carbocyclic and heterocyclic elements. The new one-pot procedure using $KHCO_3$ as a source of CO_2, which has been presented for the first time, is a very mild and inexpensive method. Therefore, we believe that this technique may find enormous use in heterocyclic chemistry. Investigation of some of the promising applications is in progress in our laboratories.

Experimental Section

General Remarks: Synthetic procedures carried out under an argon atmosphere were performed on a vacuum line using standard Schlenk techniques. Preparative column chromatography was carried out using Grace SiO_2 (0.035–0.070 mm, type KG 60), with CH_2Cl_2, ethyl acetate, *n*-hexane, and MTBE (methyl *tert*-butyl ether) as eluents. CH_2Cl_2, ethyl acetate, and *n*-hexane were distilled before use. TLC was performed with Macherey–Nagel aluminium-backed SiO_2 F254 plates. Melting points were determined with a Laboratory Devices melting point apparatus. ^1H and ^{13}C NMR spectra were recorded with Bruker AMX R 500 (measuring frequency: ^1H = 500.1 MHz, ^{13}C = 125.8 MHz) or Bruker Avance III 500 (measuring frequency: ^1H = 499.9 MHz, ^{13}C = 125.7 MHz) spectrometers in $CDCl_3$ or CD_3OD solution. Chemical shifts are referenced to the residual peaks of the solvent [$CDCl_3$: 7.26 ppm (^1H), 77.16 ppm (^{13}C). CD_3OD: 3.31 ppm (^1H), 49.00 ppm (^{13}C)].[33] Assignments of the signals were supported by DEPT and COSY experiments. Mass spectra were obtained with Finnigan-MAT 95 (CI) and Waters Q-TOF Premier (ESI) spectrometers. IR spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a "Golden Gate" diamond-ATR (attenuated total reflection) unit. CH_2Cl_2 was dried and distilled from CaH_2. THF and toluene were dried and distilled from sodium benzophenone. 2-Chloro-2-methylpropanal was prepared according to the published procedure.[34] Et_3N was dried with molecular sieves and freshly distilled before use. Compounds **1d**[24] and **2b**[25] have been published previously.

General Procedure A: The respective amine (1.5 equiv.), dissolved in distilled H_2O (4 mL per mmol amine), was treated with CS_2 (3 equiv.), the respective chloroaldehyde (1 equiv.), and K_2CO_3 (0.5 equiv.). The mixture was stirred for 2 h at room temp., then ethyl acetate (2 mL per mmol amine) was added. The phases were separated, and the aqueous phase was extracted with ethyl acetate (3 × 2 mL per mmol amine). The combined organic extracts were dried ($MgSO_4$). The solvent was removed on a rotary evaporator. The crude product was purified by column chromatography.

(*RS*)-3-Allyl-4-hydroxy-1,3-thiazolidine-2-thione (1a): Following GP A, allylamine (86 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol), chloroacetaldehyde (45% in H_2O; 79 mg, 1.00 mmol), and K_2CO_3 (69 mg, 0.50 mmol) were used. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate, 19:1; R_f = 0.24) to give the title compound (106 mg, 60%) as a brown solid, m.p. 38–40 °C (CH_2Cl_2/*n*-hexane). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.19 (dd, ^2J = 12.4, ^3J = 1.9 Hz, 1 H, SCH_2), 3.63 (dd, ^2J = 12.4, ^3J = 6.6 Hz, 1 H, SCH_2), 4.05–4.10 (m, 1 H, NCH_2), 4.15 (br. s, 1 H, OH), 4.81–4.86 (m, 1 H, NCH_2), 5.27–5.32 (m, 2 H, CH=CH_2), 5.64–5.64 (m, 1 H, NCH), 5.80–5.88 (m, 1 H, C*H*=CH_2) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 36.26 (SCH_2), 49.01 (NCH_2), 88.91 (NCH), 119.67 (CH=*C*H_2), 131.02 (*C*H=CH_2), 196.98 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3346, 2940, 2922, 1642, 1460, 1411, 1299, 1235, 1179, 1161, 1125, 1055, 986, 929, 882, 854 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 176.1 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_6H_{10}NOS_2$ [M + H]$^+$ 176.0198; found 176.0205.

(*RS*)-3-Allyl-5,5-dimethyl-4-hydroxy-1,3-thiazolidine-2-thione (1b): Following GP A, allylamine (1.713 g, 30.00 mmol), CS_2 (4.568 g, 60.00 mmol), 2-chloro-2-methylpropanal (45% in H_2O; 2.131 g, 20.00 mmol), and K_2CO_3 (1.382 g, 10.00 mmol) were used. THF was used as solvent. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate, 19:1; R_f = 0.34) to give the title compound (591 mg, 15%) as a brown oil. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.45, 1.51 (2 s, 6 H, 2 CH_3), 3.11 (br. s, 1 H, OH), 4.01–4.05 (m, 1 H, NCH_2), 4.91–4.96 (m, 2 H, NCH_2, NCH), 5.29–5.31 (m, 1 H, CH=CH_2^{trans}), 5.33–5.37 (m, 1 H, CH=CH_2^{cis}), 5.86 (dddd, ^3J = 5.0, ^3J = 7.9, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 17.7 Hz, 1 H, C*H*=CH_2) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.48, 28.84 (2 CH_3), 49.38 (NCH_2), 53.95 [*C*(CH_3)$_2$], 95.17 (NCH), 120.02 (CH=*C*H_2), 131.29 (*C*H=CH_2), 196.90 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3319, 3109, 3035, 3003, 2958, 2933, 2836, 1695, 1681, 1603, 1512, 1442, 1410, 1248, 1223, 1204, 1157, 1132, 1111, 1031, 813, 753, 694 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 204.1 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_8H_{14}NOS_2$ [M + H]$^+$ 204.0517; found 204.0523.

(*RS*)-3-Benzyl-4-hydroxy-1,3-thiazolidine-2-thione (1c): Following GP A, benzylamine (161 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol), chloroacetaldehyde (45% in H_2O; 79 mg, 1.00 mmol), and K_2CO_3 (69 mg, 0.50 mmol) were used. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate, 19:1; R_f = 0.29) to give the title compound (71 mg, 32%) as a brown solid, m.p. 100 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ = 3.05 (br. s, 1 H, OH), 3.13 (dd, ^2J = 12.4, ^3J = 1.9 Hz, 1 H, SCH_2), 3.55 (dd, ^2J = 12.4, ^3J = 6.3 Hz, 1 H, SCH_2), 4.53 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 5.47–5.48 (m, 1 H, NCH), 5.64 (d, ^2J = 14.8 Hz, 1 H, NCH_2), 7.31–7.37 (m, 5 H, 5 CH_{Ar}) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 36.32 (SCH_2), 49.82 (NCH_2), 88.63 (NCH), 128.44 (*p*-CH_{Ar}), 128.58 (2 *o*-CH_{Ar}), 129.16 (2 *m*-CH_{Ar}), 135.58 (C_{Ar}), 197.30 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3313, 3026, 2923, 1639, 1494, 1467, 1449, 1419, 1405, 1359, 1307, 1246, 1226, 1153, 1052, 1028, 1013, 989, 977, 907, 878, 861, 729, 693, 674, 642 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 226.2 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_{10}H_{12}NOS_2$ [M + H]$^+$ 226.0355; found 226.0365.

(*RS*)-3-Benzyl-5,5-dimethyl-4-hydroxy-1,3-thiazolidine-2-thione (1d):[24] Following GP A, benzylamine (3.215 g, 30.00 mmol), CS_2 (4.568 g, 60.00 mmol), 2-chloro-2-methylpropanal (45% in H_2O; 2.131 g, 20.00 mmol), and K_2CO_3 (1.382 g, 10.00 mmol) were used. THF was used as solvent. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 7:3; R_f = 0.31) and then by recrystallization from CH_2Cl_2/*n*-hexane to give the title compound (431 mg, 9%) as a colorless solid. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.34, 1.41 (2 s, 6 H, 2 CH_3), 3.33 (d, ^2J = 10.5 Hz, 1 H, OH), 4.43 (d, ^2J = 14.7 Hz, 1 H, CH_2), 4.77 (d, ^2J = 10.5 Hz, 1 H, NCH), 5.74 (d, ^2J = 14.7 Hz, 1 H, CH_2), 7.30–7.39 (m, 5 H, 5 CH_{Ar}) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.39, 28.72 (2 CH_3), 50.04 (CH_2), 53.83 [$C(CH_3)_2$], 94.67 (NCH), 128.32 (*p*-CH_{Ar}), 128.58 (2 *o*-CH_{Ar}), 129.03 (2 *m*-CH_{Ar}), 135.50 (C_{Ar}), 197.34 (CS) ppm.

(*RS*)-4-Hydroxy-3-(4-methoxybenzyl)-1,3-thiazolidine-2-thione (1e): Following GP A, *p*-methoxybenzylamine (4.115 g, 30.00 mmol), CS_2 (4.568 g, 60.00 mmol), chloroacetaldehyde (45% in H_2O; 1.570 g, 20.00 mmol), and K_2CO_3 (1.382 mg, 10.00 mmol) were used. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate, 19:1; R_f = 0.23) to give the title compound (1.605 g, 31%) as a colorless solid, m.p. 86–88 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.12 (dd, ^2J = 12.3, ^3J = 1.9 Hz, 1 H, SCH_2), 3.50 (dd, ^2J = 12.4, ^3J = 6.6 Hz, 1 H, SCH_2), 3.78 (s, 3 H, OCH_3), 4.23 (br. s, 1 H, OH), 4.41 (d, ^2J = 14.6 Hz, 1 H, NCH_2), 5.48–5.48 (m, 1 H, NCH), 5.55 (d, ^2J = 14.6 Hz, 1 H, NCH_2), 6.85–6.87 (m, 2 H, 2 *o*-CH_{Ar}OCH$_3$), 7.28–7.30 (m, 2 H, 2 *m*-CH_{Ar}OCH$_3$) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 36.09 (SCH_2), 49.05 (NCH_2), 55.42 (OCH_3), 88.38 (NCH), 114.36 (2 *o*-$CH_{Ar}OCH_3$), 127.30 ($C_{Ar}CH_2$), 130.00 (2 *m*-$CH_{Ar}OCH_3$), 159.53 ($C_{Ar}OCH_3$), 196.91 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3221, 3070, 3058, 3029, 3012, 2964, 2935, 2927, 2918, 2834, 1611, 1510, 1462, 1433, 1296, 1246, 1230, 1169, 1148, 1105, 1050, 1032, 1007, 982, 963, 884, 843, 827, 816, 762, 666 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 256.1 (28) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_{11}H_{14}NO_2S_2$ [M + H]$^+$ 256.0466; found 256.0471.

(*RS*)-4-Hydroxy-3-(4-methoxybenzyl)-5,5-dimethyl-1,3-thiazolidine-2-thione (1f): Following GP A, *p*-methoxybenzylamine (4.115 g, 30.00 mmol), CS_2 (4.568 g, 60.00 mmol), 2-chloro-2-methylpropanal (45% in H_2O; 2.131 g, 20.00 mmol), and K_2CO_3 (1.382 g, 10.00 mmol) were used. THF was used as solvent. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 7:3; R_f = 0.26) to give the title compound (646 mg, 11%) as a colorless solid, m.p. 124 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.32, 1.40 [2 s, 6 H, $C(CH_3)_2$], 3.14 (d, ^3J = 10.6 Hz, 1 H, OH), 3.80 (s, 3 H, OCH_3), 4.36 (d, ^2J = 14.5 Hz, 1 H, CH_2), 4.74 (d, ^3J = 10.5 Hz, 1 H, NCH), 5.66 (d, ^2J = 14.5 Hz, 1 H, CH_2), 6.87–6.88 (m, 2 H, 2 *o*-CH_{Ar}OCH$_3$), 7.30–7.31 (m, 2 H, 2 *m*-CH_{Ar}OCH$_3$) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.35, 28.70 [$C(CH_3)_2$], 49.56 (CH_2), 53.81 [$C(CH_3)_2$], 55.42 (OCH_3), 94.59 (NCH), 114.40 (2 *o*-$CH_{Ar}OCH_3$), 127.57 ($C_{Ar}CH_2$), 130.06 (2 *m*-$CH_{Ar}OCH_3$), 159.58 ($C_{Ar}OCH_3$), 196.94 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3212, 3063, 3017, 2953, 2919, 2833, 1611, 1582, 1510, 1472, 1456, 1426, 1304, 1250, 1236, 1205, 1178, 1155, 1083, 1030, 999, 888, 878, 850, 819, 762, 682 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 284.1 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_{13}H_{18}NO_2S_2$ [M + H]$^+$ 284.0779; found 284.0772.

General Procedure B: The respective amine (1.5 equiv.), dissolved in distilled H_2O (4 mL per mmol amine), was treated with dry ice (3 equiv.) at 0–5 °C. The mixture was stirred until all of the dry ice had reacted. Chloroacetaldehyde (1 equiv.) and K_2CO_3 (0.5 equiv.) were added. The mixture was stirred for 2 h at room temp., then ethyl acetate (2 mL per mmol amine) was added. The phases were separated, and the aqueous phase was extracted with ethyl acetate (5× 2 mL per mmol amine). The combined organic extracts were dried ($MgSO_4$). The solvent was removed on a rotary evaporator. The crude product was purified by column chromatography.

General Procedure C: The respective amine (3 equiv.), dissolved in distilled H_2O (4 mL per mmol amine), was treated with $KHCO_3$ (10 equiv.) and chloroacetaldehyde (1 equiv.). The mixture was stirred for 10 h at room temp., then ethyl acetate (2 mL per mmol amine) was added. The phases were separated, and the aqueous phase was extracted with ethyl acetate (5× 2 mL per mmol amine). The combined organic extracts were dried ($MgSO_4$). The solvent was removed on a rotary evaporator. The crude product was purified by column chromatography.

(*RS*)-3-Allyl-4-hydroxy-1,3-oxazolidin-2-one (2a)

Method A: Following GP B, allylamine (514 mg, 9.00 mmol), dry ice (792 mg, 18.00 mmol), chloroacetaldehyde (45% in H_2O; 471 mg, 6.00 mmol), and K_2CO_3 (415 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane, 7:3; R_f = 0.35) to give the title compound (295 mg, 34%) as a yellowish oil.

Method B: Following GP C, allylamine (514 mg, 9.00 mmol), $KHCO_3$ (3.004 g, 30.00 mmol), and chloroacetaldehyde (45% in H_2O; 235 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane, 7:3; R_f = 0.35) to give the title compound (314 mg, 73%) as a yellowish oil. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ = 3.78–3.82 (m, 1 H, NCH_2), 4.03–4.07 (m, 1 H, NCH_2), 4.17 (dd, ^2J = 10.1, ^3J = 2.1 Hz, 1 H, OCH_2), 4.38 (dd, ^2J = 10.1, ^3J = 6.4 Hz, 1 H, OCH_2), 4.58 (br. s, 1 H, OH), 5.21–5.29 (m, 3 H, NCH, CH=CH_2), 5.80 (dddd, ^3J = 5.0, ^3J = 7.3, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 17.3 Hz, 1 H, C*H*=CH_2) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 43.54 (NCH_2), 71.01 (OCH_2), 79.20 (NCH), 118.76 (CH=*C*H_2), 132.05 (*C*H=CH_2), 157.79 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3362, 2925, 2851, 1724, 1646, 1472, 1447, 1417, 1339, 1310, 1240, 1175, 1090, 1050, 1003, 940, 884, 768, 712 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 144.1 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_6H_{10}NO_3$ [M + H]$^+$ 144.0661; found 144.0657.

(*RS*)-3-Benzyl-4-hydroxy-1,3-oxazolidin-2-one (2b)[25]

Method A: Following GP B, benzylamine (964 mg, 9.00 mmol), dry ice (792 mg, 18.00 mmol), chloroacetaldehyde (45% in H_2O;

471 mg, 6.00 mmol), and K_2CO_3 (415 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane, 7:3; R_f = 0.51) to give the title compound (57 mg, 5%) as a colorless solid, m.p. 127–128 °C (MeOH/*n*-hexane).

Method B: Following GP C, benzylamine (964 mg, 9.00 mmol), $KHCO_3$ (3.004 g, 30.00 mmol), and chloroacetaldehyde (45% in H_2O; 235 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane, 7:3; R_f = 0.51) to give the title compound (369 mg, 64%) as a colorless solid. ^{1}H NMR (500.1 MHz, CD_3OD): δ = 4.07–4.09 (m, 1 H, OCH_2), 4.27 (d, ^2J = 15.3 Hz, 1 H, NCH_2), 4.40 (dd, ^2J = 10.0, ^3J = 6.5 Hz, 1 H, OCH_2), 4.65 (d, ^2J = 15.3 Hz, 1 H, NCH_2), 5.15–5.17 (m, 1 H, NCH), 7.27–7.36 (m, 5 H, 5 CH_{Ar}) ppm. ^{13}C NMR (125.8 MHz, CD_3OD): δ = 45.29 (NCH_2), 72.17 (OCH_2), 79.75 (NCH), 128.78 (*p*-CH_{Ar}), 129.06 (2 *o*-CH_{Ar}), 129.75 (2 *m*-CH_{Ar}), 137.67 (C_{Ar}), 159.73 (CO) ppm.

(*RS*)-4-Hydroxy-3-(4-methoxybenzyl)-1,3-oxazolidin-2-one (2c)

Method A: Following GP B, *p*-methoxybenzylamine (1.235 g, 9.00 mmol), dry ice (792 mg, 18.00 mmol), chloroacetaldehyde (45% in H_2O; 471 mg, 6.00 mmol), and K_2CO_3 (415 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane, 7:3; R_f = 0.48) and then by recrystallization from MeOH/*n*-hexane to give the title compound (80 mg, 6%) as a colorless solid, m.p. 120–121 °C.

Method B: Following GP C, *p*-methoxybenzylamine (1.235 g, 9.00 mmol), $KHCO_3$ (3.004 g, 30.00 mmol), and chloroacetaldehyde (45% in H_2O; 235 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane, 7:3; R_f = 0.48) to give the title compound (298 mg, 44%) as a colorless solid. ^{1}H NMR (499.9 MHz, CD_3OD): δ = 3.78 (s, 3 H, OCH_3), 4.07 (dd, ^2J = 10.0, ^3J = 1.3 Hz, 1 H, OCH_2), 4.20 (d, ^2J = 15.0 Hz, 1 H, NCH_2), 4.37 (dd, ^2J = 10.0, ^3J = 6.5 Hz, 1 H, OCH_2), 4.59 (d, ^2J = 15.0 Hz, 1 H, NCH_2), 5.13–5.14 (m, 1 H, NCH), 6.89–6.91 (m, 2 H, 2 *o*-CH_{Ar}OCH$_3$), 7.25–7.26 (m, 2 H, 2 *m*-CH_{Ar}OCH$_3$) ppm. ^{13}C NMR (125.8 MHz, CD_3OD): δ = 44.75 (NCH_2), 55.70 (OCH_3), 72.15 (OCH_2), 79.59 (NCH), 115.10 (2 *o*-*C*H$_{Ar}$OCH$_3$), 129.53 (C_{Ar}CH$_2$), 130.51 (2 *m*-*C*H$_{Ar}$OCH$_3$), 159.65 (CO), 160.83 (C_{Ar}OCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3269, 3079, 3064, 3038, 3009, 2966, 2939, 2900, 2838, 1698, 1613, 1586, 1513, 1471, 1450, 1435, 1404, 1306, 1242, 1182, 1162, 1120, 1093, 1027, 1013, 943, 837, 824, 767, 755, 704, 673 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 224.2 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_{11}H_{14}NO_4$ [M + H]$^+$ 224.0924; found 224.0921.

(*RS*)-4-Hydroxy-3-(pyridin-2-ylmethyl)-1,3-oxazolidin-2-one (2d): Following GP C, 2-picolylamine (973 mg, 9.00 mmol), $KHCO_3$ (3.004 g, 30.00 mmol), and chloroacetaldehyde (45% in H_2O; 235 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate; R_f = 0.18) to give the title compound (178 mg, 31%) as a yellowish oil. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 4.21 (dd, ^2J = 9.6, ^3J = 1.8 Hz, 1 H, OCH_2), 4.38 (dd, ^2J = 9.6, ^3J = 5.8 Hz, 1 H, OCH_2), 4.49 (d, ^2J = 16.1 Hz, 1 H, NCH_2), 4.78 (d, ^2J = 16.1 Hz, 1 H, NCH_2), 5.41 (dd, ^3J = 5.8, ^3J = 1.8 Hz, 1 H, NCH), 7.23–7.25 (m, 1 H, *p*-CH_{Ar}), 7.37–7.38 (m, 1 H, *o*-CH_{Ar}), 7.72 [ddd, ^3J = 7.7, ^3J = 9.4, ^4J = 1.7 Hz, 1 H, *m*-$CH_{Ar}(CH_{Ar})$], 8.45–8.46 [m, 1 H, *m*-CH_{Ar}(N)] ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 48.38 (NCH_2), 71.55 (OCH_2), 80.42 (NCH), 123.05, 123.13 (*o*-CH_{Ar}, *p*-CH_{Ar}), 138.00 [*m*-CH_{Ar}-(CH_{Ar})], 148.53 [*m*-CH_{Ar}(N)], 155.28 (C_{Ar}), 157.50 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3336, 3017, 2963, 2928, 1724, 1596, 1572, 1473, 1437, 1418, 1355, 1314, 1241, 1218, 1167, 1088, 1050, 1003, 940, 760, 731, 694 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 195.2 (4) [M + H]$^+$, 177.2 (100) [M + H – H_2O]$^+$. HRMS (CI, isobutane): calcd. for $C_9H_{11}N_2O_3$ [M + H]$^+$ 195.0770; found 195.0775.

(*RS*)-3-Ethyl-4-hydroxy-1,3-oxazolidin-2-one (2e): Following GP C, ethylamine (70% in H_2O; 406 mg, 9.00 mmol), $KHCO_3$ (3.004 g, 30.00 mmol), and chloroacetaldehyde (45% in H_2O; 235 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (ethyl acetate; R_f = 0.40) to give the title compound (163 mg, 41%) as a colorless oil. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.18–1.21 (m, 1 H, CH_3), 3.30 (dq, ^2J = 14.2, ^3J = 7.2 Hz, 1 H, NCH_2), 3.42 (dq, ^2J = 14.5, ^3J = 7.4 Hz, 1 H, NCH_2), 4.14 (dd, ^2J = 10.1, ^3J = 2.1 Hz, 1 H, OCH_2), 4.36 (dd, ^2J = 10.1, ^3J = 6.4 Hz, 1 H, OCH_2), 4.96–4.96 (m, 1 H, OH), 5.29–5.29 (m, 1 H, NCH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.12 (CH_3), 36.06 (NCH_2), 71.00 (OCH_2), 79.31 (NCH), 157.94 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3358, 2981, 2941, 1717, 1473, 1433, 1384, 1356, 1324, 1243, 1220, 1134, 1074, 1005 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 132.2 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_5H_{10}NO_3$ [M + H]$^+$ 132.0661; found 132.0659.

(*RS*)-4-Hydroxy-3-phenylamino-1,3-oxazolidin-2-one (2f): Following GP C, phenylhydrazine (1.947 g, 18.00 mmol), $KHCO_3$ (6.007 g, 60.00 mmol), and chloroacetaldehyde (45% in H_2O; 471 mg, 6.00 mmol) were used. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate, 4:1; R_f = 0.20) to give the title compound (59 mg, 5%) as a colorless solid, m.p. 102 °C (MeOH/*n*-hexane) ^{1}H NMR (499.9 MHz, CD_3OD): δ = 4.17–4.19 (m, 1 H, CH_2), 4.59 (dd, ^2J = 10.0, ^3J = 6.2 Hz, 1 H, CH_2), 5.38–5.39 (m, 1 H, NCH), 6.82–6.86 (m, 1 H, *p*-CH_{Ar}), 6.87–6.89 (m, 2 H, 2 *o*-CH_{Ar}), 7.19–7.22 (m, 2 H, 2 *m*-CH_{Ar}) ppm. ^{13}C NMR (125.7 MHz, CD_3OD): δ = 71.23 (CH_2), 79.83 (NCH), 114.21 (2 *o*-CH_{Ar}), 121.50 (*p*-CH_{Ar}), 130.09 (2 *m*-CH_{Ar}), 148.10 (C_{Ar}), 159.03 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3390, 3052, 2978, 2961, 2922, 1754, 1601, 1497, 1458, 1414, 1217, 1185, 1114, 1094, 1078, 1037, 993, 876, 798, 749, 723, 712, 693 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 195.3 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_9H_{11}N_2O_3$ [M + H]$^+$ 195.0770; found 195.0771.

General Procedure D: The respective hydroxy compound (1 equiv.) and sodium (1 equiv.) were dissolved in anhydrous THF (15 mL per mmol hydroxy compound) under an argon atmosphere, and the mixture was stirred for 2 h at room temp. Then the respective halogenated compound (1.5 equiv.) was added dropwise. The mixture was stirred overnight at room temp., then the solution was poured into ice-water (10 mL per mmol hydroxy compound), and the phases were separated. The aqueous phase was extracted with ethyl acetate (3 × 10 mL per mmol hydroxy compound), and the combined organic extracts were dried ($MgSO_4$). The solvent was removed on a rotary evaporator. The crude product was purified by column chromatography.

(*RS*)-3-Allyl-4-allyloxy-1,3-thiazolidine-2-thione (3a): Following GP D, hydroxy thiazolidinethione **1a** (351 mg, 2.00 mmol), sodium (46 mg, 2.00 mmol), and allyl bromide (363 mg, 3.00 mmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 5:1; R_f = 0.51) to give the title compound (188 mg, 44%) as a yellow oil. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ = 3.18 (dd, ^2J = 12.5, ^3J = 1.8 Hz, 1 H, SCH_2), 3.52 (dd, ^2J = 12.5, ^3J = 6.8 Hz, 1 H, SCH_2), 3.88–3.93 (m, 1 H, NCH_2), 3.97–4.01 (m, 1 H, OCH_2), 4.05–4.09 (m, 1 H, OCH_2), 4.84–4.89 (m, 1 H, NCH_2), 5.19–5.32 (m, 4 H, $NCH_2CH=CH_2$, $OCH_2CH=CH_2$), 5.51 (dd, ^3J = 1.8, ^3J = 6.8 Hz, 1 H, NCH), 5.80 (dddd, ^3J = 4.8, ^3J = 7.6, $^3J_{cis}$ = 9.9, $^3J_{trans}$ = 17.2 Hz, 1 H, NCH_2CH), 5.86 (dddd, ^3J = 5.6, ^3J = 10.5, ^3J = 11.2, $^3J_{trans}$ = 17.1 Hz, 1 H, OCH_2CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 32.84 (SCH_2), 49.01 (NCH_2), 67.57 (OCH_2), 93.63 (NCH), 118.12

($OCH_2CH{=}CH_2$), 119.24 ($NCH_2CH{=}CH_2$), 130.98 (NCH_2CH), 133.17 (OCH_2CH), 197.70 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3081, 3013, 2984, 2918, 2865, 1644, 1450, 1407, 1299, 1235, 1183, 1163, 1125, 1063, 1039, 926, 887 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 216.3 (100) $[M + H]^+$. HRMS (CI, isobutane): calcd. for $C_9H_{14}NOS_2$ $[M + H]^+$ 216.0517; found 216.0512.

(*RS*)-3-Allyl-4-allyloxy-5,5-dimethyl-1,3-thiazolidine-2-thione (3b): Following GP D, hydroxy thiazolidinethione **1b** (163 mg, 0.80 mmol), sodium (18 mg, 0.80 mmol), and allyl bromide (145 mg, 1.20 mmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 3:1; R_f = 0.45) to give the title compound (137 mg, 70%) as a colorless oil. ^1H NMR (499.9 MHz, $CDCl_3$): δ = 1.45, 1.50 (2 s, 6 H, 2 CH_3), 3.85–3.90 (m, 1 H, NCH_2), 4.11–4.14 (m, 1 H, OCH_2), 4.20–4.23 (m, 1 H, OCH_2), 4.81 (s, 1 H, NCH), 5.01–5.05 (m, 1 H, NCH_2), 5.22–5.32 (m, 4 H, $NCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$), 5.78–5.93 (m, 2 H, $NCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.64, 29.33 (2 CH_3), 49.44 (NCH_2), 53.05 [$C(CH_3)_2$], 71.27 (OCH_2), 100.60 (NCH), 118.28 ($OCH_2CH{=}CH_2$), 119.44 ($NCH_2CH{=}CH_2$), 131.39 (NCH_2CH), 133.28 (OCH_2CH), 197.57 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3081, 2962, 2925, 2869, 1644, 1448, 1406, 1296, 1244, 1206, 1183, 1055, 1017, 990, 930 cm^{-1}. MS (ESI): *m*/*z* (%) = 266.1 (100) $[M + Na]^+$. HRMS (ESI): calcd. for $C_{11}H_{17}NNaOS_2$ $[M + Na]^+$ 266.0649; found 266.0644.

(*RS*)-3-Allyl-4-allyloxy-1,3-oxazolidin-2-one (3c): Following GP D, hydroxy thiazolidinethione **2a** (134 mg, 0.94 mmol), sodium (22 mg, 0.94 mmol), and allyl bromide (171 mg, 1.41 mmol) were used. The crude product was purified three times by column chromatography on silica gel (1. *n*-hexane/ethyl acetate, 5:1; 2. *n*-hexane/ethyl acetate, 4:1; 3. *n*-hexane/MTBE, 1:1; R_f = 0.17) to give the title compound (26 mg, 15%) as a colorless oil. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.68–3.73 (m, 1 H, NCH_2), 3.94–3.97 (m, 1 H, $OCH_2CH{=}CH_2$), 4.00–4.04 (m, 1 H, $OCH_2CH{=}CH_2$), 4.13–4.17 (m, 1 H, NCH_2), 4.23 (dd, ^2J = 10.2, ^3J = 1.8 Hz, 1 H, OCH_2CHN), 4.31 (dd, ^2J = 10.2, ^3J = 6.1 Hz, 1 H, OCH_2CHN), 5.11 (dd, ^3J = 1.8, ^3J = 6.1 Hz, 1 H, NCH), 5.20–5.31 (m, 4 H, $NCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$), 5.79 (dddd, ^3J = 4.8, ^3J = 7.6, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 14.9 Hz, 1 H, NCH_2CH), 5.86 (m, 1 H, $OCH_2CH{=}CH_2$) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 44.25 (NCH_2), 67.38 ($OCH_2CH{=}CH_2$), 68.14 (OCH_2CHN), 84.52 (NCH), 117.96 ($OCH_2CH{=}CH_2$), 118.81 ($NCH_2CH{=}CH_2$), 132.09 (NCH_2CH), 133.57 ($OCH_2CH{=}CH_2$), 157.12 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3082, 2923, 2866, 1750, 1646, 1467, 1442, 1415, 1233, 1085, 1031, 926, 768, 712 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 184.2 (100) $[M + H]^+$. HRMS (CI, isobutane): calcd. for $C_9H_{14}NO_3$ $[M + H]^+$ 184.0974; found 184.0971.

(*RS*)-3-Allyl-4-allylamino-1,3-thiazolidine-2-thione (3d): A solution of allylamine (343 mg, 6.00 mmol) in ethanol (4 mL) was treated with CS_2 (228 mg, 3.00 mmol) at 0–5 °C. Chloroacetaldehyde (45% in H_2O; 236 mg, 3.00 mmol) was added at room temp. The mixture was stirred for 2 h at room temp., then the solution was heated at reflux for 15 min. The solvent was removed on a rotary evaporator. The crude product was dissolved in CH_2Cl_2. H_2O (10 mL) was added, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3× 10 mL). The combined organic extracts were dried ($MgSO_4$). The solvent was removed on a rotary evaporator. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate, 19:1; R_f = 0.45) to give the title compound (70 mg, 11%) as a brown oil. The major product was **1a** (205 mg, 39%). Data for **3d**: ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.95 (br. s, 1 H, NH), 3.09 (dd, ^2J = 11.8, ^3J = 3.8 Hz, 1 H, SCH_2), 3.21–3.26 (m, 1 H, $NHCH_2$), 3.30–3.35 (m, 1 H, $NHCH_2$), 3.53 (dd, ^2J = 11.8, ^3J = 8.0 Hz, 1 H, SCH_2), 3.95–3.99 (m, 1 H, NCH_2), 4.85–4.89 (m, 1 H, NCH_2), 5.06 (dd, ^3J = 3.8, ^3J = 8.0 Hz, 1 H, NCH), 5.09–5.11 (m, 1 H, $NHCH_2CH{=}CH_2^{cis}$), 5.18–5.19 (m, 1 H, $NHCH_2CH{=}CH_2^{trans}$), 5.22–5.26 (m, 2 H, $NCH_2CH{=}CH_2$), 5.78–5.87 (m, 2 H, $NHCH_2CH{=}CH_2$, $NCH_2CH{=}CH_2$) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 33.16 (SCH_2), 46.32 ($NHCH_2$), 48.75 (NCH_2), 80.12 (NCH), 116.71 ($NHCH_2CH{=}CH_2$), 118.98 ($NCH_2CH{=}CH_2$), 131.24 ($NCH_2CH{=}CH_2$), 135.62 ($NHCH_2CH{=}CH_2$), 195.47 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3313, 3079, 2981, 2916, 2844, 1642, 1453, 1407, 1286, 1230, 1166, 1119, 991, 920, 879 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 215.3 (100) $[M + H]^+$. HRMS (CI, isobutane): calcd. for $C_9H_{15}N_2S_2$ $[M + H]^+$ 215.0677; found 215.0682.

(*RS*)-3-Allyl-4-methoxy-1,3-thiazolidine-2-thione (4a): Following GP D, hydroxy thiazolidinethione **1a** (175 mg, 1.00 mmol), sodium (23 mg, 1.00 mmol), and methyl iodide (213 mg, 1.50 mmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 5:1; R_f = 0.45) to give the title compound (71 mg, 38%) as a yellow oil. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.16 (dd, ^2J = 12.6, ^3J = 1.5 Hz, 1 H, SCH_2), 3.31 (s, 3 H, OCH_3), 3.52 (dd, ^2J = 12.6, ^3J = 7.1 Hz, 1 H, SCH_2), 3.85–3.90 (m, 1 H, NCH_2), 4.85–4.88 (m, 1 H, NCH_2), 5.23–5.26 (m, 2 H, $CH{=}CH_2$), 5.46 (dd, ^3J = 1.2, ^3J = 7.0 Hz, 1 H, NCH), 5.78 (dddd, ^3J = 4.8, ^3J = 7.7, $^3J_{cis}$ = 9.8, $^3J_{trans}$ = 17.4 Hz, 1 H, $CH{=}CH_2$) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 31.79 (SCH_2), 48.93 (NCH_2), 53.09 (OCH_3), 94.43 (NCH), 119.34 ($CH{=}CH_2$), 130.78 ($CH{=}CH_2$), 197.78 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3082, 2988, 2934, 2831, 1675, 1643, 1450, 1407, 1236, 1179, 1126, 1065, 1010, 993, 964, 929 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 190.3 (100) $[M + H]^+$. HRMS (CI, isobutane): calcd. for $C_7H_{12}NOS_2$ $[M + H]^+$ 190.0360; found 190.0357.

(*RS*)-3-Allyl-5,5-dimethyl-4-methoxy-1,3-thiazolidine-2-thione (4b): Following GP D, hydroxy thiazolidinethione **1b** (61 mg, 0.30 mmol), sodium (7 mg, 0.30 mmol), and methyl iodide (64 mg, 0.45 mmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 3:1; R_f = 0.35) to give the title compound (45 mg, 70%) as a yellow oil. ^1H NMR (499.9 MHz, $CDCl_3$): δ = 1.45, 1.50 [2 s, 6 H, $C(CH_3)_2$], 3.50 (s, 3 H, OCH_3), 3.86–3.91 (m, 1 H, NCH_2), 4.71 (s, 1 H, NCH), 5.00–5.05 (m, 1 H, NCH_2), 5.28–5.32 (m, 2 H, $CH{=}CH_2$), 5.84 (dddd, ^3J = 4.7, ^3J = 8.0, $^3J_{cis}$ = 10.1, $^3J_{trans}$ = 17.3 Hz, 1 H, $CH{=}CH_2$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.24, 29.58 [$C(CH_3)_2$], 49.72 (NCH_2), 52.95 [$C(CH_3)_2$], 57.59 (OCH_3), 102.03 (NCH), 119.56 ($CH{=}CH_2$), 131.36 ($CH{=}CH_2$), 197.77 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 2962, 2931, 2836, 1681, 1643, 1445, 1406, 1366, 1296, 1245, 1181, 1078, 980, 928, 912, 888, 678 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 218.1 (100) $[M + H]^+$. HRMS (CI, isobutane): calcd. for $C_9H_{16}NOS_2$ $[M + H]^+$ 218.0673; found 218.0674.

General Procedure E: The respective methoxy thiazolidinethione (1 equiv.), dissolved in anhydrous CH_2Cl_2 (5 mL per mmol thiazolidinethione) under an argon atmosphere, was treated dropwise with a solution of the allyltrimethylsilane (1.5 equiv.) in anhydrous CH_2Cl_2 (2 mL per mmol thiazolidinethione) at –30 °C. Then a solution of $TiCl_4$ (2 equiv.) in anhydrous CH_2Cl_2 (2 mL per mmol thiazolidinethione) was added dropwise, and the solution was stirred for 1.5 h at –30 °C. The mixture was stirred overnight at room temp., then the solution was poured into ice-water (10 mL per mmol thiazolidinethione), and the phases were separated. The organic phase was washed with H_2O (2× 10 mL per mmol thiazolidinethione), and dried ($MgSO_4$). The solvent was removed on a rotary evaporator. The crude product was purified by column chromatography.

(*RS*)-3,4-Diallyl-1,3-thiazolidine-2-thione (5a): Following GP E, methoxy thiazolidinethione **4a** (71 mg, 0.38 mmol), allyltrimethylsilane (64 mg, 0.56 mmol), and $TiCl_4$ (142 mg, 0.75 mmol) were used. The crude product was purified twice by column chromatography on silica gel (1. *n*-hexane/ethyl acetate, 9:1; R_f = 0.32; 2. CH_2Cl_2/*n*-hexane, 2:1) to give the title compound (14 mg, 18%) as a brown oil. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ = 2.49–2.52 (m, 2 H, NCHCH_2CH), 3.05 (dd, ^2J = 11.2, ^3J = 4.1 Hz, 1 H, SCH_2), 3.41 (dd, ^2J = 11.2, ^3J = 8.2 Hz, 1 H, SCH_2), 3.83–3.87 (m, 1 H, NCH_2), 4.25–4.30 (m, 1 H, NCH), 5.00–5.04 (m, 1 H, NCH_2), 5.19–5.23 (m, 2 H, NCHCH_2CH=CH_2), 5.27–5.30 (m, 2 H, NCH_2CH=CH_2), 5.68–5.76 (m, 1 H, NCHCH_2CH), 5.84 (dddd, ^3J = 4.8, ^3J = 7.5, $^3J_{cis}$ = 9.9, $^3J_{trans}$ = 17.4 Hz, 1 H, NCH_2CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 31.95 (SCH_2), 35.43 (NCHCH$_2$CH), 49.82 (NCH_2), 66.31 (NCH), 119.25 (NCH_2CH=CH$_2$), 120.15 (NCHCH_2CH=CH$_2$), 131.24 (NCH_2CH), 131.94 (NCHCH_2CH), 196.73 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3078, 2979, 2926, 1641, 1456, 1409, 1313, 1236, 1179, 1128, 1025, 994, 923 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 200.0 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_9H_{14}NS_2$ [M + H]$^+$ 200.0568; found 200.0571.

(*RS*)-3,4-Diallyl-5,5-dimethyl-1,3-thiazolidine-2-thione (5b): Following GP E, methoxy thiazolidinethione **4b** (32 mg, 0.15 mmol), allyltrimethylsilane (26 mg, 0.23 mmol), and $TiCl_4$ (57 mg, 0.30 mmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 9:1; R_f = 0.32) to give the title compound (23 mg, 67%) as a yellow oil. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ = 1.41, 1.50 (2 s, 6 H, 2 CH_3), 2.49–2.60 (m, 2 H, NCHCH_2CH=CH_2), 3.76–3.81 (m, 2 H, NCH_2, NCH), 5.14–5.20 (m, 3 H, NCH_2, NCHCH_2CH=CH_2^{trans}), 5.30–5.32 (m, 1 H, NCH_2CH=CH_2^{cis}), 5.77–5.88 (m, 2 H, 2 CH=CH_2) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 22.44, 30.91 (2 CH_3), 33.16 (NCHCH$_2$), 50.85 (NCH_2), 53.13 [C(CH_3)$_2$], 74.72 (NCH), 119.07 (NCHCH_2CH=CH$_2$), 120.09 (NCH_2CH=CH$_2$), 131.11 (NCHCH_2CH), 133.19 (NCH_2CH), 195.93 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3078, 2963, 2924, 2868, 1640, 1457, 1430, 1409, 1310, 1249, 1205, 1179, 1144, 1123, 996, 921 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 228.3 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_{11}H_{18}NS_2$ [M + H]$^+$ 228.0881; found 228.0875.

General Procedure F: The respective diene (one equiv.) and ruthenium catalyst **A** (5 mol-%), dissolved in anhydrous toluene (5 mL per mmol diene), were slowly heated to 60 °C under an argon atmosphere until the reaction was finished, as shown by TLC. The mixture was then stirred overnight at room temp., and then the solvent was removed on a rotary evaporator. The crude product was purified by column chromatography.

(*RS*)-2,5,9,9a-Tetrahydro[1,3]thiazolo[4,3-*b*][1,3]oxazepin-7-thione (6a): Following GP F, diene **3a** (64 mg, 0.30 mmol) and ruthenium catalyst **A** (14 mg, 15 μmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 5:3; R_f = 0.34) to give the title compound (30 mg, 53%) as a brown solid, m.p. 71–72 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.22 (dd, ^2J = 12.4, ^3J = 2.6 Hz, 1 H, SCH_2), 3.63 (dd, ^2J = 12.4, ^3J = 7.4 Hz, 1 H, SCH_2), 3.94–4.00 (m, 1 H, NCH_2), 4.25–4.30 (m, 1 H, OCH_2), 4.37–4.42 (m, 1 H, OCH_2), 5.12–5.16 (m, 1 H, NCH_2), 5.70–5.74 (m, 1 H, NCH_2CH=CH), 5.79–5.86 (m, 2 H, NCH, NCH_2CH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 33.53 (SCH_2), 47.25 (NCH_2), 65.20 (OCH_2), 96.74 (NCH), 126.62 (NCH_2CH), 129.12 (NCH_2CH=CH), 197.18 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3015, 2954, 2925, 2902, 2879, 2856, 2834, 1453, 1416, 1287, 1250, 1233, 1190, 1163, 1103, 1050, 980, 968, 910, 853, 839, 700, 669 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 188.2 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_7H_{10}NOS_2$ [M + H]$^+$ 188.0204; found 188.0199.

(*RS*)-9,9-Dimethyl-2,5,9,9a-tetrahydro[1,3]thiazolo[4,3-*b*][1,3]oxazepin-7-thione (6b): Following GP F, diene **3b** (97 mg, 0.40 mmol) and ruthenium catalyst **A** (15 mg, 16 μmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 4:1; R_f = 0.45) to give the title compound (60 mg, 70%) as a pale brown solid, m.p. 42 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.43, 1.54 (2 s, 6 H, 2 CH_3), 4.12–4.17 (m, 1 H, NCH_2), 4.24–4.28 (m, 1 H, OCH_2), 4.46–4.50 (m, 1 H, OCH_2), 5.03–5.08 (m, 1 H, NCH_2), 5.07 (s, 1 H, NCH), 5.71–5.75 (m, 1 H, NCH_2CH=CH), 5.79–5.84 (m, 1 H, NCH_2CH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.62, 29.35 (2 CH_3), 47.44 (NCH_2), 52.56 [C(CH_3)$_2$], 67.44 (OCH_2), 102.80 (NCH), 125.76 (NCH_2CH), 129.37 (NCH_2CH=CH), 197.13 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 2989, 2954, 2922, 2867, 1673, 1444, 1402, 1387, 1371, 1296, 1243, 1164, 1090, 1073, 997, 985, 917, 787, 720, 646, 601 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 216.1 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_9H_{14}NOS_2$ [M + H]$^+$ 216.0517; found 216.0522.

(*RS*)-2,5,9,9a-Tetrahydro[1,3]oxazolo[4,3-*b*][1,3]oxazepin-7-one (6c): Following GP F, diene **3c** (26 mg, 0.14 mmol) and ruthenium catalyst **A** (7 mg, 7 μmol) were used. The crude product was purified by column chromatography on silica gel (MTBE/*n*-hexane, 7:3; R_f = 0.18) to give the title compound (11 mg, 50%) as a colorless solid, m.p. 43–44 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.80–3.86 (m, 1 H, NCH_2), 4.18–4.22 (m, 1 H, OCH_2CH=CH), 4.21 (dd, ^2J = 10.5, ^3J = 2.0 Hz, 1 H, OCH_2CHN), 4.28–4.32 (m, 1 H, OCH_2CH=CH), 4.38–4.43 (m, 1 H, NCH_2), 4.44 (dd, ^2J = 10.4, ^3J = 6.4 Hz, 1 H, OCH_2CHN), 5.35 (dd, ^3J = 6.4, ^3J = 1.9 Hz, 1 H, NCH), 5.66–5.71 (m, 1 H, NCH_2CH=CH), 5.72–5.76 (m, 1 H, NCH_2CH=CH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 43.36 (NCH_2), 64.42 (OCH$_2$CH=CH), 68.70 (OCH$_2$CHN), 86.89 (NCH), 127.69 (NCH_2CH=CH), 128.72 (NCH_2CH=CH), 157.17 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 2973, 2920, 2855, 1746, 1658, 1466, 1430, 1390, 1252, 1227, 1179, 1094, 1053, 1015, 993, 757, 744 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 156.1 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_7H_{10}NO_3$ [M + H]$^+$ 156.0661; found 156.0661.

(*RS*)-2,5,9,9a-Tetrahydro[1,3]thiazolo[4,3-*a*][1,3]diazepin-7-thione (6d): Following GP F, diene **3d** (64 mg, 0.30 mmol) and ruthenium catalyst **A** (14 mg, 15 μmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 1:1; R_f = 0.11) to give the title compound (5 mg, 10%) as a brown solid, m.p. 133–136 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.24 (dd, ^2J = 12.0, ^3J = 5.8 Hz, 1 H, SCH_2), 3.47–3.54 (m, 2 H, NHCH_2, SCH_2), 3.60–3.63 (m, 1 H, NHCH_2), 3.88–3.92 (m, 1 H, NCH_2), 5.22 (dd, ^2J = 16.8, ^3J = 6.3 Hz, 1 H, NCH_2), 5.38–5.40 (m, 1 H, NCH), 5.73–5.77 (m, 1 H, NCH_2CH=CH), 5.84–5.88 (m, 1 H, NCH_2CH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 32.89 (SCH_2), 42.89 ($NHCH_2$), 46.22 (NCH_2), 83.47 (NCH), 126.56 (NCH_2CH), 132.61 (NCH_2CH=CH), 194.65 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3275, 2954, 2927, 2889, 2853, 1651, 1466, 1443, 1412, 1377, 1282, 1263, 1219, 1158, 1010, 977, 915, 796, 734, 703 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 187.1 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_7H_{11}N_2S_2$ [M + H]$^+$ 187.0364; found 187.0368.

(*RS*)-1,5,8,8a-Tetrahydro[1,3]thiazolo[3,4-*a*]pyridin-3-thione (7a): Following GP F, diene **5a** (14 mg, 0.07 mmol) and ruthenium catalyst **A** (3 mg, 4 μmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate,

5:3; R_f = 0.58) to give the title compound (7 mg, 57%) as a brown solid, m.p. 70–71 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ = 2.41–2.45 (m, 2 H, NCHCH_2CH), 3.09 (dd, ^2J = 11.0, ^3J = 8.1 Hz, 1 H, SCH_2), 3.55 (dd, ^2J = 11.0, ^3J = 8.3 Hz, 1 H, SCH_2), 3.78–3.83 (m, 1 H, NCH_2), 4.22–4.28 (m, 1 H, NCH), 4.80–4.84 (m, 1 H, NCH_2), 5.79–5.81 (m, 1 H, NCH_2CH=C*H*), 5.84–5.88 (m, 1 H, NCH_2CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 32.09 (NCH*C*H_2CH), 34.36 (SCH_2), 47.70 (NCH_2), 63.54 (NCH), 123.13 (NCH_2CH=*C*H), 123.65 (NCH_2*C*H), 196.27 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3038, 2989, 2929, 2898, 2872, 2844, 1667, 1448, 1428, 1302, 1240, 1207, 1164, 1028, 1001, 951, 896, 839, 673 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 172.0 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_7H_{10}NS_2$ [M + H]$^+$ 172.0255; found 172.0257.

(*RS*)-1,1-Dimethyl-1,5,8,8a-tetrahydro[1,3]thiazolo[3,4-*a*]pyridin-3-thione (7b): Following GP F, diene **5b** (23 mg, 0.10 mmol) and ruthenium catalyst **A** (5 mg, 5 μmol) were used. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 4:1; R_f = 0.28) to give the title compound (20 mg, 100%) as a brown solid, m.p. 80–83 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.42, 1.56 (2 s, 6 H, 2 CH_3), 2.15–2.21 (m, 1 H, NCHCH_2), 2.43–2.51 (m, 1 H, NCHCH_2), 3.79 (dd, ^2J = 11.4, ^3J = 4.1 Hz, 1 H, NCH), 3.91 (ddd, ^2J = 19.0, ^3J = 3.4, ^4J = 1.9 Hz, 1 H, NCH_2), 4.89 (ddd, ^2J = 19.0, ^3J = 5.7, ^4J = 2.8 Hz, 1 H, NCH_2), 5.78–5.82 (m, 1 H, NCH_2CH=C*H*), 5.88–5.92 (m, 1 H, NCH_2CH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 23.66 (CH_3), 25.34 (NCH*C*H_2), 29.28 (CH_3), 48.30 (NCH_2), 52.55 [*C*(CH_3)$_2$], 72.04 (NCH), 123.53 (NCH_2CH=*C*H), 123.84 (NCH_2*C*H), 196.17 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3036, 2901, 1661, 1645, 1464, 1430, 1278, 1207, 1198, 1155, 1039, 1016, 1008, 943, 914, 669 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 200.3 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_9H_{14}NS_2$ [M + H]$^+$ 200.0568; found 200.0574.

(*RS*)-1-(4-Methylphenylsulfonyl)-2,5,9,9a-tetrahydro[1,3]thiazolo-[3,4-*a*][1,3]diazepin-7-thione (8): A solution of 4-toluenesulfonyl chloride (10 mg, 0.054 mmol) in anhydrous CH_2Cl_2 (3 mL) was treated dropwise with a solution of compound **6a** and anhydrous Et_3N (10 mg, 0.054 mmol) in anhydrous CH_2Cl_2 (2 mL) under an argon atmosphere at 0–5 °C. The mixture was stirred overnight at room temp., then the solution was washed with $NaHCO_3$ (saturated aq.; 3 mL) and H_2O (3 mL). The combined aqueous phases were extracted with CH_2Cl_2 (3 × 3 mL). The combined organic extracts were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 4:1; R_f = 0.18) to give the title compound (11 mg, 59%) as a brown solid, m.p. 150–153 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 3.21 (dd, ^2J = 12.3, ^3J = 4.5 Hz, 1 H, SCH_2), 3.24 (m, 1 H, $SCNCH_2$), 3.66 (dd, ^2J = 12.3, ^3J = 8.3 Hz, 1 H, SCH_2), 3.86–3.90 (m, 1 H, $SNCH_2$), 4.44 (dd, ^2J = 18.6, ^3J = 6.4 Hz, 1 H, $SNCH_2$), 4.95 (dd, ^2J = 17.0, ^3J = 5.8 Hz, 1 H, $SCNCH_2$), 5.48–5.52 (m, 1 H, $CSNCH_2CH$=C*H*), 5.56–5.60 (m, 1 H, $CSNCH_2CH$), 6.12 (dd, ^3J = 8.3, ^3J = 4.4 Hz, 1 H, NCH), 7.31–7.32 (m, 2 H, 2 *m*-CH_{Ar}S), 7.72–7.73 (m, 2 H, 2 *o*-CH_{Ar}S) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.78 (CH_3), 33.38 (SCH_2), 42.46 ($SNCH_2$), 47.15 ($SCNCH_2$), 80.64 (NCH), 126.65 ($CSNCH_2$*C*H), 127.01 ($CSNCH_2CH$=*C*H), 127.33 (2 *o*-CH_{Ar}S), 130.03 (2 *m*-CH_{Ar}S), 137.16, 144.67 (2 C_{Ar}), 196.53 (CS) ppm. IR (ATR): $\tilde{\nu}$ = 3034, 2955, 2922, 2852, 1597, 1449, 1396, 1354, 1339, 1234, 1217, 1178, 1154, 1089, 1037, 1015, 1003, 918, 837, 812, 672, 657, 637 cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 341.3 (100) [M + H]$^+$. HRMS (CI, isobutane): calcd. for $C_{14}H_{17}N_2O_2S_3$ [M + H]$^+$ 341.0452; found 341.0447.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all products.

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[1] a) Part 1: M. Watzke, K. Schulz, K. Johannes, P. Ullrich, J. Martens, *Eur. J. Org. Chem.* **2008**, *22*, 3859–3867; b) For a commentary, see: V. Snieckus, J. Board, *Synfacts* **2008**, *10*, 1038; c) Part 2: K. Schulz, M. Watzke, K. Johannes, P. Ullrich, J. Martens, *Synthesis* **2009**, 665–673; d) Part 3: K. Johannes, M. Watzke, J. Martens, *J. Heterocycl. Chem.* **2010**, *47*, 697–702; e) Part 4: A. Schwäblein, J. Martens, *Eur. J. Org. Chem.* **2011**, 4335–4344.

[2] a) D. A. Evans, J. Bartroli, T. L. Shih, *J. Am. Chem. Soc.* **1981**, *103*, 2127–2129; b) D. A. Evans, *Aldrichim. Acta* **1982**, *15*, 23–32; c) Y. Nagao, S. Yamada, T. Kumagai, M. Ochiai, E. Fujita, *J. Chem. Soc., Chem. Commun.* **1985**, 1418–1419; d) Y. Nagao, Y. Hagiwara, T. Kumagai, M. Ochiai, T. Inoue, K. Hashimoto, E. Fujita, *J. Org. Chem.* **1986**, *51*, 2391–2393; e) D. A. Evans, J. A. Ellman, *J. Am. Chem. Soc.* **1989**, *111*, 1063–1072; f) D. J. Ager, I. Prakash, D. R. Schaad, *Chem. Rev.* **1996**, *96*, 835–875; g) D. J. Ager, I. Prakash, D. R. Schaad, *Aldrichim. Acta* **1997**, *30*, 3–12; h) M. T. Crimmins, B. W. King, E. A. Tabet, *J. Am. Chem. Soc.* **1997**, *119*, 7883–7884; i) M. T. Crimmins, K. Chaudhary, *Org. Lett.* **2000**, *2*, 775–777; j) F. Velazquez, H. F. Olivo, *Curr. Org. Chem.* **2002**, *6*, 303–340; k) M. T. Crimmins, M. Shamszad, *Org. Lett.* **2007**, *9*, 149–152; l) A. Osorio-Lozada, H. F. Olivo, *Org. Lett.* **2008**, *10*, 617–620.

[3] a) D. J. Diekema, R. N. Jones, *Lancet* **2001**, *358*, 1975–1982; b) T. A. Mukhtar, G. D. Wright, *Chem. Rev.* **2005**, *105*, 529–542; c) R. N. Jones, G. J. Moet, H. S. Sader, R. E. Mendes, M. Castanhira, *J. Antimicrob. Chemother.* **2009**, *63*, 716–720.

[4] a) D. L. Shinabarger, K. R. Marotti, R. W. Murray, A. H. Lin, E. P. Melchior, S. M. Swaney, D. S. Dunyak, W. F. Demyan, J. M. Buysse, *Antimicrob. Agents Chemother.* **1997**, *41*, 2132–2136; b) S. M. Swaney, H. Aoki, M. C. Ganoza, D. L. Shinabarger, *Antimicrob. Agents Chemother.* **1998**, *42*, 3251–3255.

[5] M. T. Crimmins, B. W. King, E. A. Tabet, *J. Am. Chem. Soc.* **1997**, *119*, 7883–7884.

[6] R. B. Greenwald, A. Pendri, A. Martinez, C. Gilbert, P. Bradley, *Bioconjugate Chem.* **1996**, *7*, 638–641.

[7] Y. Nagao, T. Miyasaka, K. Seno, E. Fujita, D. Shibata, E. Doi, *J. Chem. Soc. Perkin Trans. 1* **1984**, 2439–2446.

[8] a) P. Pornsuriyasak, M. N. Kamat, A. V. Demchenko, *ACS Symp., Ser.* **2007**, *960*, 165–189; b) P. Pornuriyasak, A. V. Demchenko, *Chem. Eur. J.* **2006**, *12*, 6630–6646.

[9] a) J. Aznárez, J. R. Castillo, C. Luesma, *Analyst* **1981**, *106*, 1122–1125; b) R. Singh, S. K. Dikshit, *Polyhedron* **1995**, *14*, 1799–1807; c) N. A. Bell, W. Clegg, S. J. Coles, C. P. Constable, R. W. Harrington, M. B. Hursthouse, M. E. Light, E. S. Raper, C. Sammon, M. R. Walker, *Inorg. Chim. Acta* **2004**, *357*, 2091–2099; d) X.-Y. Wei, W. Chu, R.-D. Huang, S.-W. Zhang, H. Li, Q.-L. Zhu, *Inorg. Chem. Commun.* **2006**, *9*, 1161–1164.

[10] L.-L. Zhao, S.-Y. Wang, X.-P. Xu, S.-J. Ji, *Chem. Commun.* **2013**, *49*, 2569–2571.

[11] a) A. Dömling, I. Ugi, *Angew. Chem.* **2000**, *112*, 3300–3344; *Angew. Chem. Int. Ed.* **2000**, *39*, 3168–3210; b) S. S. van Berkel, B. G. M. Bögels, M. A. Wijdeven, B. Westermann, F. P. J. T. Rutjes, *Eur. J. Org. Chem.* **2012**, 3543–3559; c) C. de Graaff, E. Ruijter, R. V. A. Orru, *Chem. Soc. Rev.* **2012**, *41*, 3969–4009; d) I. Ugi, *J. Prakt. Chem.* **1997**, *339*, 499–516; e) V. Estévez,

M. Villacampa, J. C. Menéndez, *Chem. Soc. Rev.* **2010**, *39*, 4402–4421.

[12] a) M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124–2144; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2036–2056; b) U. Koert, *Nachr. Chem. Tech. Lab.* **1995**, *43*, 809–813.

[13] a) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413–4450; b) A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140–3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012–3043; c) R. R. Schrock, A. H. Hoveyda, *Angew. Chem.* **2003**, *115*, 4740–4782; *Angew. Chem. Int. Ed.* **2003**, *42*, 4592–4633; d) F. Boeda, H. Clavier, S. P. Nolan, *Chem. Commun.* **2008**, 2726–2740.

[14] a) W. J. Humphlett, R. W. Lamon, *J. Org. Chem.* **1964**, *29*, 2146–2148; b) R. W. Lamon, W. J. Humphlett, W. P. Blum, *J. Heterocycl. Chem.* **1967**, *4*, 349–354; c) G. Ege, P. Arnold, R. Noronha, *Liebigs Ann. Chem.* **1979**, 656–674; d) J. J. D'Amico, F. G. Bollinger, J. J. Freeman, W. E. Dahl, *J. Heterocycl. Chem.* **1986**, *23*, 105–112.

[15] a) S. Hünig, G. Sauer, *Justus Liebigs Ann. Chem.* **1971**, *748*, 173–188; b) M. Chanon, J. Metzger, *Bull. Soc. Chim. Fr.* **1968**, 2842–2846; c) R. A. Bafford, F. Chanon, M. Chanon, J. Metzger, *Bull. Soc. Chim. Fr.* **1973**, 971–977; d) J.-D. Bourzat, D. Farge, A. Leger, G. Ponsinet, German Patent application 2821555, **1978**; e) J.-D. Bourzat, D. Farge, A. Leger, G. Ponsinet, German Patent application 2821566, **1978**; f) J.-D. Bourzat, D. Farge, A. Leger, G. Ponsinet, German Patent application 2845624, **1978**.

[16] a) M. O. Kolosova, V. I. Stavrovskaya, *J. Gen. Chem. USSR (Engl. Transl.)* **1963**, *33*, 2778–2785, 2706–2711; b) R. W. Lamon, W. J. Humphlett, *J. Heterocycl. Chem.* **1967**, *4*, 605–609; c) J. Roschester, J. Sandstroem, *Tetrahedron* **1989**, *45*, 5081–5100.

[17] S.-F. Gan, J.-P. Wan, Y.-J. Pan, C.-R. Sun, *Synlett* **2010**, *6*, 973–975.

[18] For selected examples, see: a) S. Kano, Y. Yuasa, K. Asami, S. Shibuya, *Heterocycles* **1988**, *27*, 1437–1444; b) Y. Yuasa, S. Kano, S. Shibuya, *Heterocycles* **1991**, *32*, 2311–2314; c) Y. Yuasa, J. Ando, S. Shibuya, *J. Chem. Soc. Perkin Trans. 1* **1996**, 465–473; d) Y. Yuasa, J. Ando, S. Shibuya, *J. Chem. Soc. Perkin Trans. 1* **1996**, 793–802; e) M. A. Endoma, G. Butora, C. D. Claeboe, T. Hudlicky, K. A. Abboud, *Tetrahedron Lett.* **1997**, *38*, 8833–8836.

[19] T. Toda, *Chem. Lett.* **1977**, 957–958.

[20] In preliminary studies, allylamine gave the best results of the primary amines tested.

[21] G. Künstle, German Patent, DE 3447527C2, **1987**.

[22] For selected examples, see: a) M. A. Casadei, F. M. Moracci, G. Zappia, *J. Org. Chem.* **1997**, *62*, 6754–6759; b) M. Feroci, A. Inesi, L. Rossi, *Tetrahedron Lett.* **2000**, *41*, 963–966; c) M. Feroci, M. Orsini, L. Rossi, G. Sotgiu, A. Inesi, *J. Org. Chem.* **2007**, *72*, 200–203; d) M. Feroci, M. A. Casadei, M. Orsini, L. Palombi, A. Inesi, *J. Org. Chem.* **2003**, *68*, 1548–1551; e) K. Huang, C.-L. Sun, Z.-J. Shi, *Chem. Soc. Rev.* **2011**, *40*, 2435–2452; f) Y. Tsuji, T. Fujihara, *Chem. Commun.* **2012**, *48*, 9956–9964; g) T. Fan, X. Chen, Z. Lin, *Chem. Commun.* **2012**, *48*, 10808–10828; h) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem.* **2012**, *124*, 191–194; *Angew. Chem. Int. Ed.* **2012**, *51*, 187–190; i) M. Honda, S. Sonehara, H. Yasuda, Y. Nakagawa, K. Tomishige, *Green Chem.* **2011**, *13*, 3406–3413; j) D. Chaturvedi, N. Mishra, V. Mishra, *Monatsh. Chem.* **2007**, *138*, 57–60.

[23] The use of hydrogencarbonates is known, but the reported procedures are less efficient, due to impractical cations. See: a) S. Cesa, V. Mucciante, L. Rossi, *Tetrahedron* **1999**, *55*, 193–200; b) T. Mizuno, T. Nakai, M. Mihara, *Heteroat. Chem.* **2012**, *23*, 276–280.

[24] T. I. Orlova, S. P. Éphstein, V. P. Tashchi, A. F. Rukasov, L. Y. Bogel'fer, Y. G. Putsykin, *Chem. Heterocycl. Compd.* **1986**, *22*, 451–455.

[25] T. Matsuura, T. Kunieda, T. Takizawa, *Chem. Pharm. Bull.* **1977**, *25*, 1225–1229.

[26] A lower reactivity for aldehydes than ketones[17] has also been reported previously for similar reactions, see: D. Guérin, R. Carlier, D. Lorcy, *J. Org. Chem.* **2000**, *65*, 6069–6072.

[27] T. A. Keating, R. W. Armstrong, *J. Org. Chem.* **1998**, *63*, 867–871.

[28] Besides steric factors, the lower nucleophilicity of the amino group in the second nucleophilic attack (for mechanistic studies, see ref.[17]) seems to play a role, as the reaction of a two-component system containing aniline and CO_2 proceeds successfully, as described in the literature.[22b]

[29] The rather low yield of compound **31f** could be due to a side reaction resulting from the two amino groups of hydrazine, see: a) Z.-m. Ge, J.-l. Cui, Y.-l. Wang, T.-m. Cheng, R.-t. Li, *Synthesis* **2004**, 1257–1261; b) V. S. R. Chunduru, R. R. Vedula, *Synth. Commun.* **2012**, *42*, 2014–2021.

[30] CCDC-953093 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[31] a) D. J. Hart, Y.-M. Tsai, *Tetrahedron Lett.* **1981**, *22*, 1567–1570; b) G. A. Kraus, K. Neuenschwander, *J. Chem. Soc., Chem. Commun.* **1982**, 134–135; c) S. Kano, Y. Yuasa, S. Shibuya, *Heterocycles* **1987**, *26*, 373–376; d) C. Herborn, A. Zietlow, E. Steckhan, *Angew. Chem.* **1989**, *101*, 1392–1394; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1399–1401.

[32] a) R. Kadyrov, A. Rosiak, *Chim. Oggi/Chem. Today* **2009**, *27*, 24–26; b) R. Kadyrov, D. Wolf, C. Azap, D. J. Ostgard, *Top. Catal.* **2010**, *53*, 1066–1072.

[33] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.

[34] M. Weber, J. Jakob, J. Martens, *Liebigs Ann. Chem.* **1992**, *1*, 1–6.

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