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Decarboxylative ring-opening of 2-oxazolidinones: a facile and modular synthesis of β-chalcogen amines†

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We report herein the synthesis of primary and secondary β-chalcogen amines through the regioselective ring-opening reaction of non-activated 2-oxazolidinones promoted by *in situ* generated chalcogenolate anions. The developed one-step protocol enabled the preparation of β-selenoamines, β-telluroamines and β-thioamines with appreciable structural diversity and in yields of up to 95%.

Introduction

Organochalcogen compounds (OCs) are known for their notable applications in the fields of organic synthesis,[1] catalysis,[2] and materials science.[3] In addition, a variety of biological activities are associated with OCs,[4] making them promising targets in the search for new therapeutic agents.[5] Notably, many of these valuable OCs contain a nitrogen atom close to the chalcogen in their structures, including β-chalcogen amines (β-CAs, shown in Fig. 1A). Examples of naturally occurring β-CAs include the proteinogenic amino acids L-cysteine and L-selenocysteine, which play crucial roles in the catalytic activity of enzymes such as cruzain[6] and glutathione peroxidase (GPx),[7] respectively (Fig. 1B). At the same time, synthetic β-CAs are known as a class of bioactive compounds,[8] and have been used as chiral ligands in asymmetric catalysis[9] (Fig. 1C).

Although the β-CA backbone is apparently simple, its preparation poses significant synthetic challenges, especially when the goal is to obtain primary amines (*i.e.* free amino group). In this sense, the substitution of 2-haloethylamines by chalcogenolate anions offers a direct route.[10] However, the structural variety commercially available for 2-haloethylamines is relatively limited, particularly regarding optically active substrates. β-Amino alcohols can also be used as starting materials for the synthesis of β-CAs,[11] but they require the use of protecting groups which is a disadvantage. While regioselective aminochalcogenation of alkenes has been shown to be a promising alternative for the synthesis of β-CAs, most reports are still limited to the use of soft-conjugated nitrogenous nucleophiles.[12] Ring-opening of *N*-H-aziridines, in contrast, is a well-established strategy for the synthesis of primary β-CAs,[8f,13] but the toxic and carcinogenic properties associated with these starting materials are a major concern.[14]

In view of these limitations, 2-oxazolidinones offer a safer option acting as latent aziridine equivalents, since they can undergo decarboxylative ring-opening reaction to provide aminoethylated products.[15] Although there are some reports on the synthesis of primary β-thioamines using this strategy (Scheme 1A),[16] there is a remarkable lack of synthetic studies for β-selenoamines and β-telluroamines. To the best of our knowledge, there is only one prior report on the preparation of selenium and tellurium analogues *via* the ring-opening reaction of 2-oxazolidinones (Scheme 1B).[17] And even in this report, the protocol was restricted to the use of *N*-activated 2-oxazolidinones, which does not allow for the production of primary and secondary amines. To address this clear gap and the need for more versatile synthetic routes, we focused our efforts on establishing a new methodology to allow a simple, rapid and modular synthesis of β-CAs from non-activated 2-oxazolidinone rings (Scheme 1C).

Results and discussion

To find suitable conditions to carry out the reaction, we selected (*S*)-4-benzyl-2-oxazolidinone **1a** as the standard substrate and diphenyl diselenide as the source of the selenolate anion (Table 1). We also chose $NaBH_4$ in THF : EtOH as it is an established system for *in situ* generation of chalcogenolate anions (Table 1, entries 1–8). First, we sought to determine an appropriate amount of $NaBH_4$ to promote the

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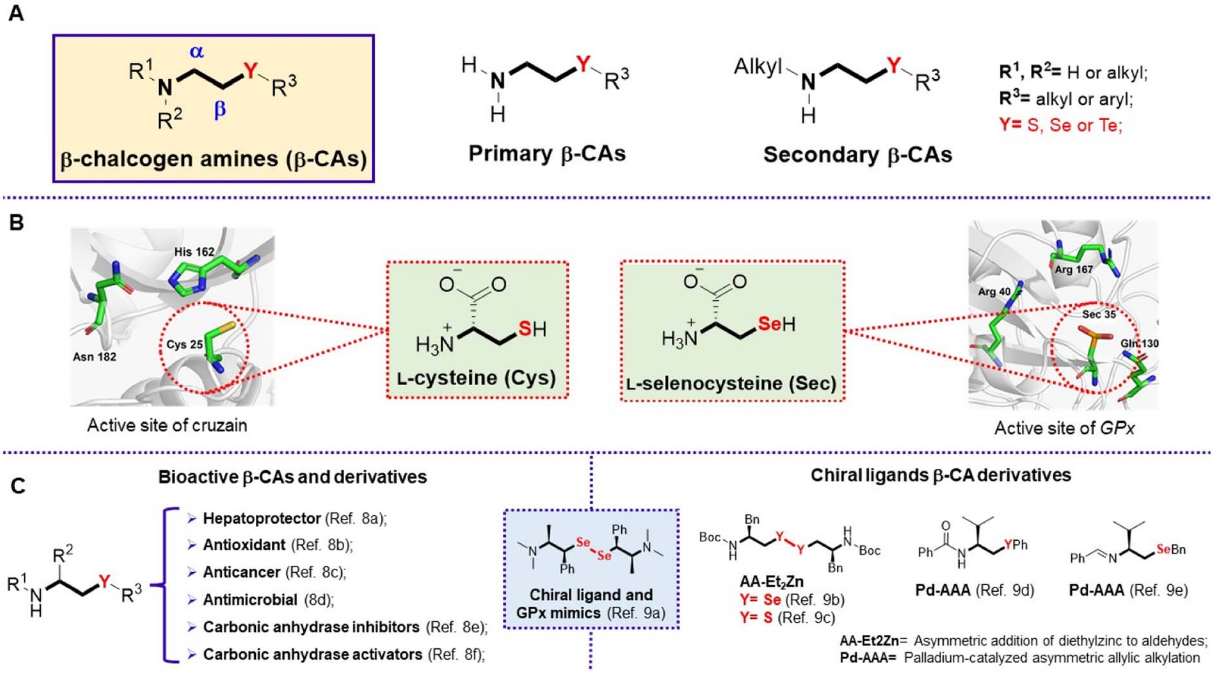
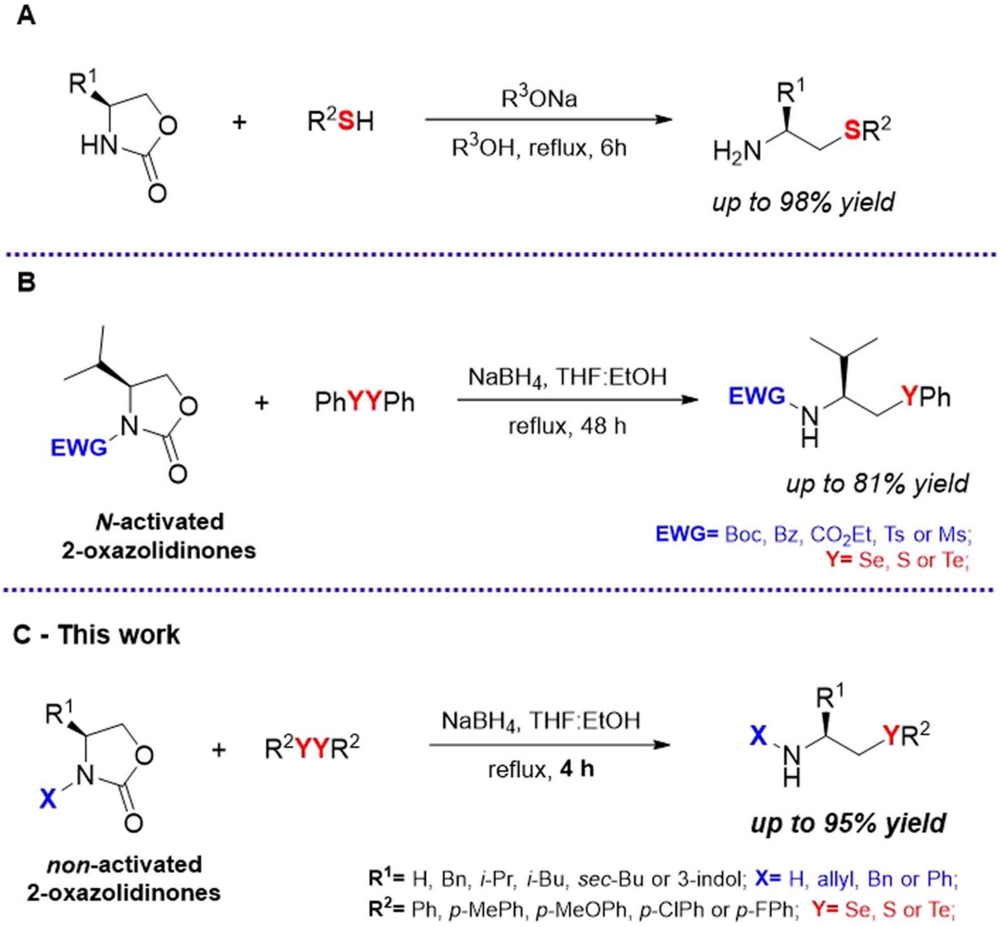
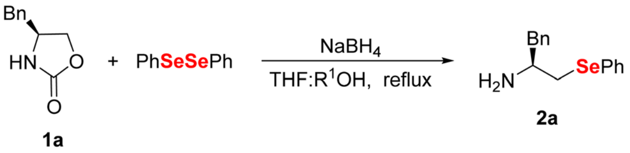


Fig. 1 (A) Structure of β-chalcogen amines; (B) structures of L-cysteine and L-selenocysteine; (C) examples of relevant synthetic β-Cas and their application fields.



Scheme 1 Preparation of β-CAs and derivatives *via* 2-oxazolidinone decarboxylative ring-opening strategy: (A) synthesis of β-thioamines; (B) synthesis of β-CA derivatives from *N*-activated 2-oxazolidinones; (C) synthesis of β-CAs from non-activated 2-oxazolidinones (this work).

Table 1 Optimization of the reaction conditions[a]



Entry	$NaBH_4$[c] (equiv.)	Time (h)	R^1	Yield[b] (%)
1	0.6	12	Et[d]	n.d.
2	1.2	12	Et[d]	n.d.
3	2.0	12	Et[d]	48
4	3.0	12	Et[d]	85
5	3.0	6	Et[d]	89
6	**3.0**	**4**	**Et**[d]	**87**
7	3.0	3	Et[d]	73
8	3.0	4	Et[e]	11
9	3.0	4	Et[f]	83
10	3.0	4	H[g]	n.d.
11	3.0	4	H[h]	73
12	3.0	4	Me[i]	75
13	3.0	4	Et[j]	n.d.

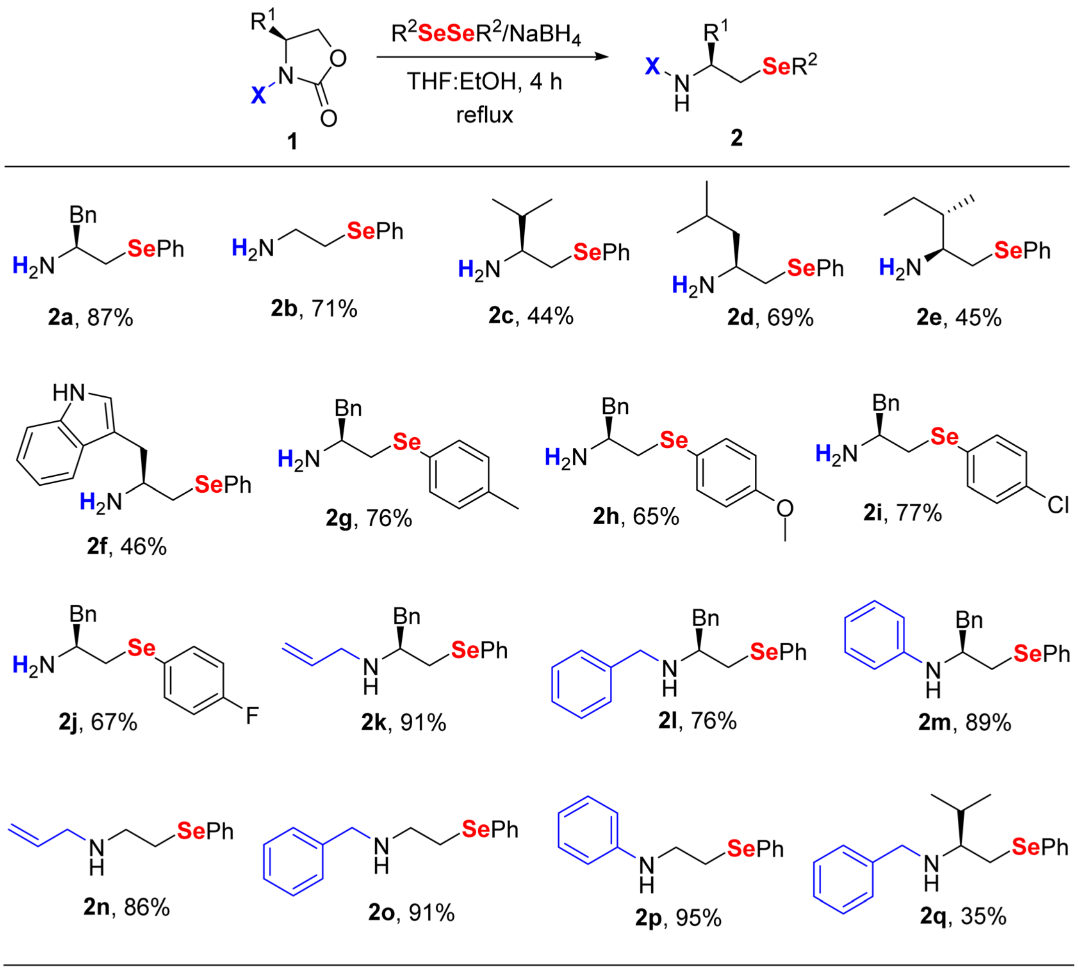
[a] Standard reaction conditions: 2-oxazolidinone **1a** (1.0 mmol), diphenyl diselenide (1.2 equiv., 0.60 mmol), $NaBH_4$, THF (7.0 mL) and R^1OH (0.6 mL) under reflux and nitrogen atmosphere. [b] Isolated yields. [c] Regarding the limiting agent, **1a.** [d] 95% ethanol. [e] Absolute ethanol was used instead of 95% ethanol. [f] 0.55 mL of absolute ethanol + 0.05 mL of distilled water. [g] 0.6 mL of distilled water was used. [h] 0.1 mL of distilled water was used. [i] 95% methanol. [j] THF was omitted and 7.6 mL of 95% EtOH was employed. n.d. = not determined.

opening reaction (entries 1–4), and we observed that the use of 3.0 equiv. produced compound **2a** in 85% yield (entry 4). Next, we focused on determining the time required for the reaction completion (entries 5–7) with the best yield for **2a** being obtained after 4 h of reaction (entry 6). Notably, the use of absolute ethanol instead of 95% ethanol led to a drastic decrease in the product yield (entry 8). This result suggests that water is crucial for this reaction, probably acting as the main source of protons to promote the decarboxylation step. To verify this hypothesis, we performed a new test with absolute ethanol, but this time by adding together a small volume of distilled water, which resulted in a significant increase in the yield of the desired product (entry 9). We also evaluated the possibility of replacing ethanol with water, but substituting the cosolvent was found to be detrimental due to the lower miscibility of water in THF (entries 10 and 11). Finally, our attempts to use methanol instead of ethanol (entry 12) as well as to conduct the reaction in ethanol alone (entry 13) did not improve the yield. As determined by chiral HPLC analysis, the ring-opening reaction proceeds with full preservation of the stereochemical integrity of the initial 2-oxazolidinone **1a** (see ESI†).

After determining suitable reaction conditions (Table 1, entry 6), the method was extended to the synthesis of a library of β-selenoamines **2** (Table 2). Initially, a few *N*-H-2-oxazolidinones derived from L-amino acids were screened to exemplify the possibilities of structural diversification in the R^1 moiety (**2a**–**2f**). Then, different diaryl diselenides were used to examine the influence of electronic effects on the selenolate anion (**2g**–**2j**). Remarkably, halogenated derivatives **2i** and **2j** were prepared in 77% and 67% of yield respectively, which is very interesting given the versatility of these blocks. In view of the challenge involved in the monoalkylation of amines, we also attempted to the use of *N*-alkylated-2-oxazolidinones, aiming to obtain secondary β-selenoamines. Surprisingly, reactions with *N*-allyl-2-oxazolidinones selectively furnished the corresponding ring-opening products **2k** and **2n** in 91% and 86% of yield, respectively. Comparable yields were obtained in the cases of *N*-benzyl-β-selenoamines **2l** and **2o**, while the L-valine derivative **2q** was obtained in moderate yield. Finally, we evaluated the possibility of preparing selenium-containing anilines from *N*-phenyl-2-oxazolidinones, and the corresponding products **2m** and **2p** were obtained in 89% and 95% of yield, respectively.

To further evaluate the scope and limitations, the established protocol was extended to the synthesis of β-telluroamines **3** and β-thioamines **4** (Table 3). In particular, primary β-telluroamines were obtained in good to excellent yields in just one step (15–89%, compounds **3a**–**3e**), with the L-valine derivative **3b** being an exception. The generality of the

Table 2 Synthesis of β-selenoamines 2[a,b]

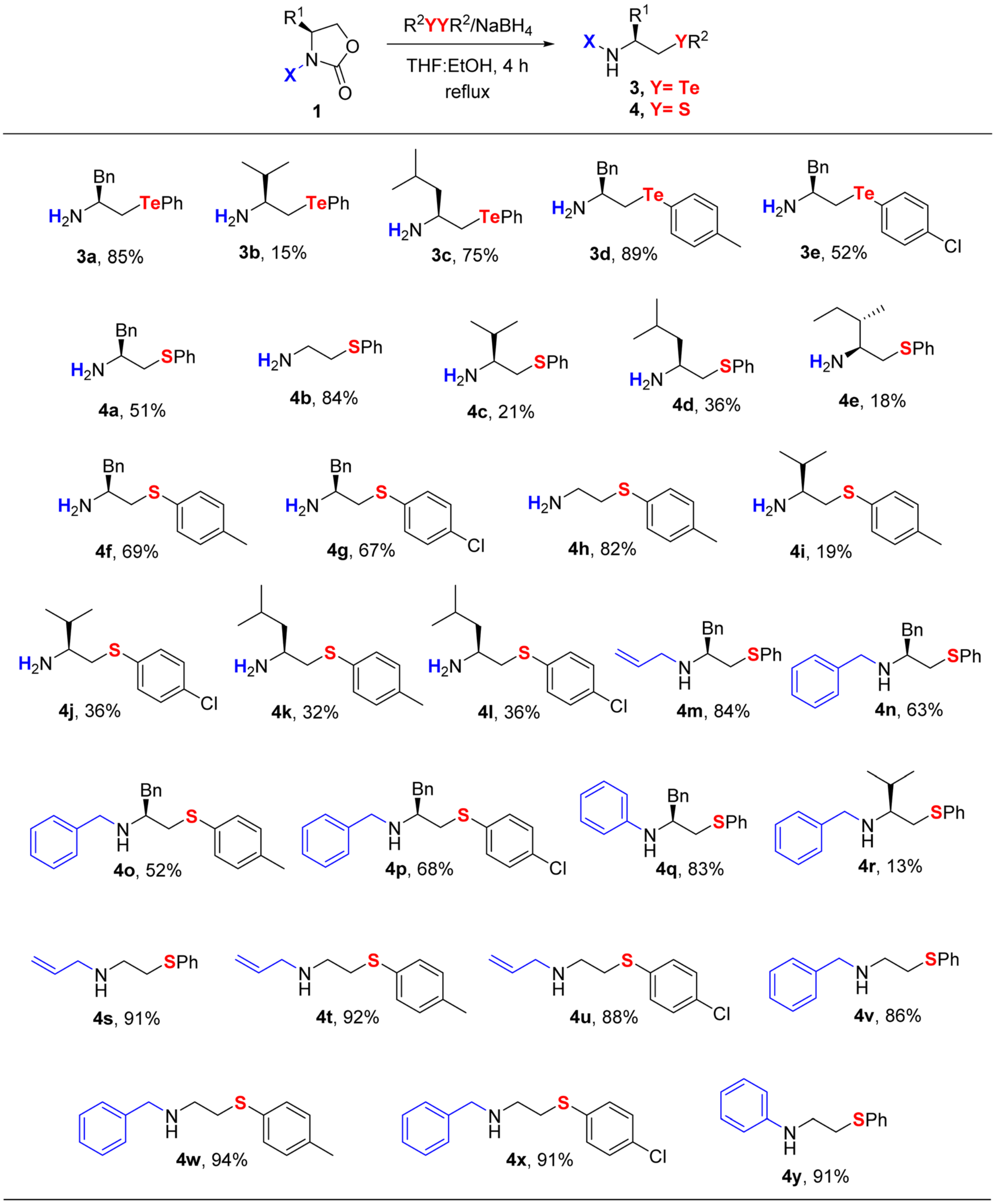


[a] Reaction scale: 2-oxazolidinone **1** (1.0 mmol), diorganoyl diselenide (1.2 equiv., 0.60 mmol), $NaBH_4$ (3.0 equiv., 3.0 mmol, 0.114 g), THF (7.0 mL) and EtOH (95.0%, 0.6 mL). [b] Isolated yields.

developed method could be demonstrated through the preparation of 25 examples of primary and secondary β-thioamines (**4a–4y**). It can be noted that the use of disulfides as source of thiolate anions instead of thiols contributes to the establishment of a safer protocol, avoiding the handling of volatile, corrosive and malodorous reagents.[18] In general, we observed that the ring-opening reaction proceeded better with tellurium and selenium than with sulfur anions, which is consistent with the relative nucleophilicity of these species. Moreover, the steric hindrance caused by the neighboring R^1 group proved to be significant, given that L-valine and L-isoleucine derivatives were normally obtained in lower yields. We also observed that secondary β-CAs were generally obtained in higher yields than their primary analogues, suggesting that electron-donating groups attached to nitrogen may also improve the reaction.

In view of the potential applications of β-CAs and derivatives,[8,9] we also carried out a scale-up study for this reaction, and the results are compiled in Table 4. Seeking to develop a more economical and environmentally sustainable process, we focused our efforts on reducing the amount of solvent employed in these experiments. In this sense, we observed that the use of 2 mL of solvent for 1 mmol of oxazolidinone was sufficient to provide the desired products in good yields. Furthermore, the β-CAs obtained from these studies were purified by acid-base extractions, showing that the chromatographic purification can be bypassed for ethanolamine derivatives (see procedure in ESI†). Fortunately, we found that reactions carried out at 30 mmol or 60 mmol of **1b** provided the products **2b**, **4b**, and **4h** in yields comparable to those obtained in milligram-scale reactions.

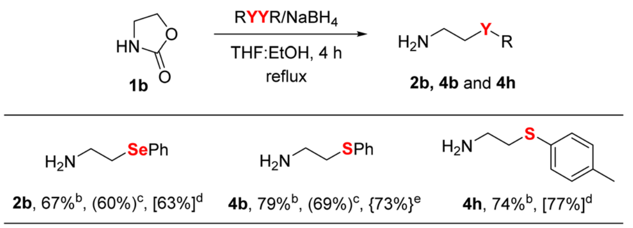
Table 3 Synthesis of β-telluroamines **3** and β-thioamines **4**[a,b]



3a, 85%
3b, 15%
3c, 75%
3d, 89%
3e, 52%
4a, 51%
4b, 84%
4c, 21%
4d, 36%
4e, 18%
4f, 69%
4g, 67%
4h, 82%
4i, 19%
4j, 36%
4k, 32%
4l, 36%
4m, 84%
4n, 63%
4o, 52%
4p, 68%
4q, 83%
4r, 13%
4s, 91%
4t, 92%
4u, 88%
4v, 86%
4w, 94%
4x, 91%
4y, 91%

[a] Reaction scale: 2-oxazolidinone **1** (1.0 mmol), diorganoyl dichalcogenide (1.2 equiv., 0.60 mmol), $NaBH_4$ (3.0 equiv., 3.0 mmol, 0.114 g), THF (7.0 mL) and EtOH (95.0%, 0.6 mL). [b] Isolated yields.

Table 4 Scale-up study of the 2-oxazolidinone ring opening-reaction[a]



2b, 67%[b], (60%)[c], [63%][d] **4b**, 79%[b], (69%)[c], {73%}[e] **4h**, 74%[b], [77%][d]

[a] Isolated yields. [b] Reaction scale: 2-oxazolidinone **1b** (30 mmol, 2.612 g), diorganoyl dichalcogenide (18 mmol), $NaBH_4$ (90 mmol, 3.420 g), THF (210 mL) and EtOH (95.0%, 18 mL). [c] Reaction scale: 2-oxazolidinone **1b** (60 mmol, 5.224 g), diorganoyl dichalcogenide (36 mmol), $NaBH_4$ (180 mmol, 6.840 g), THF (420 mL) and EtOH (95.0%, 36 mL). [d] Reaction scale: 2-oxazolidinone **1b** (30 mmol, 2.612 g), diorganoyl dichalcogenide (18 mmol), $NaBH_4$ (90 mmol, 3.420 g), THF (56 mL) and EtOH (95.0%, 4.8 mL). [e] Reaction scale: 2-oxazolidinone **1b** (60 mmol, 5.224 g), diorganoyl dichalcogenide (36 mmol), $NaBH_4$ (180 mmol, 6.840 g), THF (112 mL) and EtOH (95.0%, 9.6 mL).

Conclusions

In summary, we have developed a simple and efficient methodology for the synthesis of primary and secondary β-CAs through the decarboxylative ring-opening reaction of non-activated 2-oxazolidinones. This protocol proved to be applicable to a wide range of 2-oxazolidinone rings and diorganoyl dichalcogenides, providing quick access to structurally diverse β-CAs with good yields in most cases. Studies related to the determination of the precise reaction mechanism and on new biological applications for β-CAs are ongoing in our laboratories, as well as the possible application of these β-CAS as building blocks for functional materials.

Conflicts of interest

There are no conflicts to declare.

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