A Platinum Open Access Journal
for Organic Chemistry

Paper

Free to Authors and Readers

DOAJ Seal

*Arkivoc* **2025** (5) 202512411

# Oxidation of cyclic ene-carbamates with Oxone

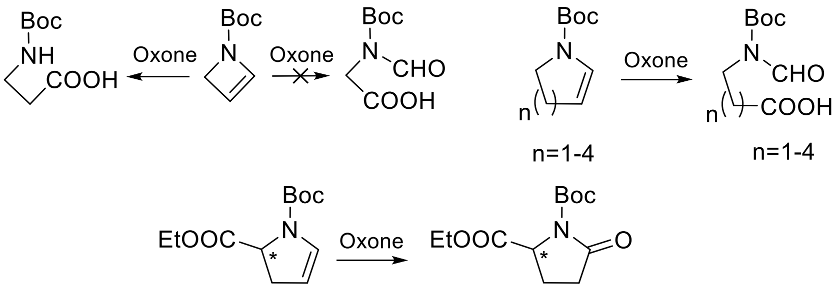
**Alessandro Giraudo, Massimiliano Sipala, Giulia Nasta, Marco Pallavicini, and Cristiano Bolchi***

*Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, via Mangiagalli 25, I-20133, Milano, Italia*
*Email: cristiano.bolchi@unimi.it*

**Received** 05-16-2025 **Accepted Manuscript** 06-11-2025 **Published on line** 06-27-2025

## Abstract

Cyclic ene-carbamates, from 4-membered to 8-membered, were submitted to metal-catalyst-free oxidation using Oxone, a stable and nonpollutant oxidizing reagent. The reaction resulted in the carbon-carbon double bond cleavage to give the corresponding *N*-formyl-ω-amino acids with the exception of the 4-membered cyclic ene-carbamate that was cleaved at the N-C(1) bond affording β-alanine instead of *N*-formylglycine. Enantiomeric 5-membered cyclic ene-carbamates having an ester function α-positioned to nitrogen were instead oxidized to pyroglutamic esters without racemization. The outcome of the Oxone oxidation of cyclic ene-carbamates is discussed and compared with those previously reported of the same substrates oxidized with $RuO_4$ and the corresponding cyclic 3-azaketones oxidized with Oxone.



**Keywords:** Cyclic ene-carbamate; Oxone; oxidative cleavage; ω-amino acid

**Cite as** *Arkivoc* **2025** (5) 202512411
**DOI:** https://doi.org/10.24820/ark.5550190.p012.411

## Introduction

A current goal of chemistry research aiming to combine efficiency with sustainability is the development of metal-catalyst-free aqueous oxidations with easy to handle and nontoxic oxidizing agents. Within these, great effort has been devoted to expanding the use of Oxone,[1-3] which meets such criterions. In fact, Oxone, the commercially available triple salt $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$, is a versatile and safe oxidizing agent, which generates $K_2SO_4$ as the only byproduct.[4,5] In the triple mixture, the anion peroxymonosulfate ($HSO_5^-$) is the active oxidant. Reactions with Oxone, which is a water-soluble, white crystalline solid, are generally performed in water, methanol, acetone, DMF or mixtures including one of these solvents.

Within the context of the many applications of this green oxidant, we have latterly been working on the transformation of cyclic ketones into the corresponding lactones by oxidation with Oxone in water at pH 7.[6] By such a novel and simple protocol of Baeyer-Villiger (BV) oxidation, we efficiently converted 4-, 5-, 6-, and 7-membered cyclic ketones to 5-, 6-, 7- and 8-membered lactones (Figure 1A). The procedure, which avoids products hydrolysis simply by buffering the reaction medium without resorting to complex reaction protocols, was successively extended to heterocyclic ketones, namely, cyclic *N*-Boc azaketones and oxoethers successfully converting 4-piperidinone and 4-, 5-, and 6-membered cyclic oxoethers to lactones (Figure 1B).[7] Upon treatment with Oxone, *N*-Boc azacyclic ketones with nitrogen α-positioned to carbonyl gave instead ring-opened oxidized products, namely, ω-amino acids or *N*-formyl ω-amino acids depending on the reaction solvent (Figure 1C).

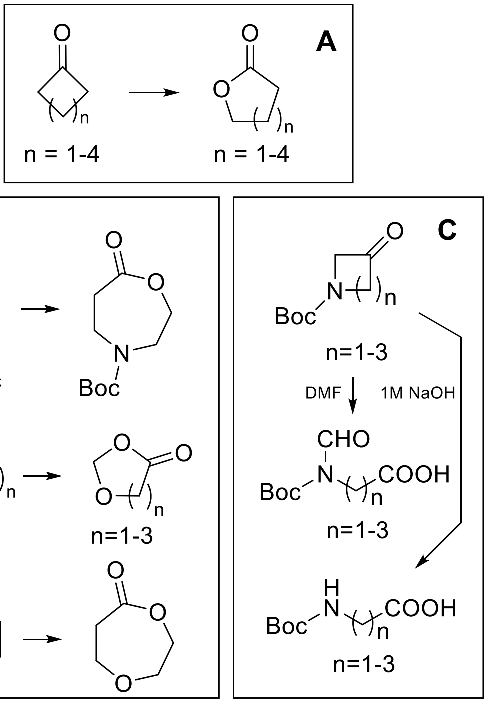
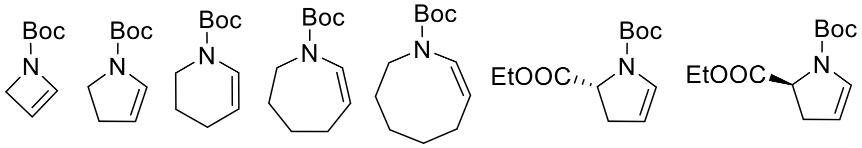


**Figure 1.** (A) Oxidation of cyclic ketones with Oxone in 1 M $NaH_2PO_4$/$Na_2HPO_4$ water solution (pH 7); (B) Oxidation of *N*-Boc-4-piperidinone and cyclic oxoethers with Oxone in 1 M $NaH_2PO_4$/$Na_2HPO_4$ water solution (pH 7); (C) Oxidation of cyclic azaketones with nitrogen α-positioned to carbonyl with Oxone under different reaction conditions.

As a continuation of this research effort, we decided to investigate the oxidation of the 4-, 5-, 6-, 7-, and 8-membered cyclic ene-carbamates **1**-**5** and the enantiomers of the cyclic 5-membered ene-carbamate **6** bearing the ethyl ester moiety α-positioned to nitrogen with Oxone (Figure 2). The substrate **2** was commercially available, while the other ene-carbamates were synthesized according to reported methods.[8-11]



**1** **2** **3** **4** **5** (*R*)-**6** (*S*)-**6**

**Figure 2.** Cyclic ene-carbamates submitted to oxidation with Oxone.

## Results and Discussion

Among the metal-free procedures for the oxidative cleavage of carbon-carbon double bond, Oxone has been reported to oxidatively cleave olefins in 1:1 acetonitrile-water at reflux to carboxylic acids without any additive.[12] According to an attested mechanism, a domino/cascade of oxidations would occur starting with epoxidation. In the acidic aqueous medium, the epoxide converts into diol intermediate, indeed isolated in some cases, and diol is oxidatively cleaved to aldehydes that undergo rapid oxidation to carboxylic acids.

The oxidative cleavage of the C=C double bond of *N*-alkoxycarbonyl protected enamines has not been so extensively studied as that of simple olefins and, in particular, that with Oxone is not described. The literature reports only examples of oxidation of 6-membered cyclic ene-carbamates to *N*-Cbz or *N*-Boc protected 2,3-dihydroxypiperidines.[13,14] For obvious structural and reactivity reasons, the outcome of the oxidative cleavage of ene-carbamates cannot be assimilated and predicted by analogy with the corresponding alkenes. Furthermore, the α or non-α position of nitrogen relative to the carbon(s) undergoing oxidation is critical as shown by the univocal and foreseen outcome of BV oxidation of *N*-Boc-4-piperidinone to *N*-Boc-4-azacaprolactone with Oxone (Figure 1B) and, instead, the different oxidatively cleaved products resultant from the same reaction on the *N*-Boc-3-piperidinone regioisomer (Figure 1C, n=3).[7] In this regard, it is instructive to compare the reported oxidative cleavage of two 6-membered cyclic ene-carbamates, **3** and its 2-methyl ethoxycarbonyl analogue,[15,16] by ruthenium tetroxide with that of cyclohexene.[17] The two 6-membered cyclic ene-carbamates undergo oxidative cleavage of the double bound both affording *N*-carbamate protected *N*-formyl-γ-aminobutyric acids (Figure 3) while cyclohexene is oxidatively cleaved to adipic acid.

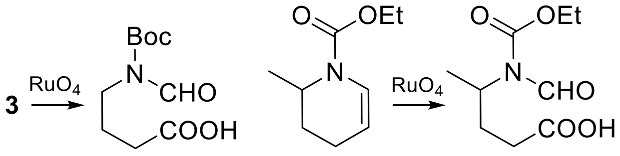


**Figure 3.** Oxidative cleavage of cyclic ene-carbamates with RuO$_4$.

Our first attempts at oxidizing *N*-Boc protected ene-carbamates with Oxone were performed on the commercially available substrate **2** in 1 M phosphate buffer (pH 7) under the conditions previously adopted for the oxidation of cyclic ketones.[6] At room temperature, total conversion into a complex mixture of products was observed (Table 1, Entry 1). In successive attempts, phosphate buffer was replaced first with 1/1 phosphate buffer/$CH_3CN$ (Table 1, Entry 2) and then 1/1 water/$CH_3CN$ mixture and the amount of Oxone increased from two to four moles per mole of **2** (Table 1, Entries 3-5). Under the last conditions (Table 1, Entry 5; Table 2, Entry 2), **2** was completely converted in 2 hours at 40 °C yielding a crude consisting of a major product, chromatographically isolated with 50% yield and identified as *N*-Boc-*N*-formyl-β-alanine (**8**).

**Table 1.** Main optimization steps of oxidation of **2** with Oxone

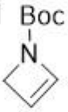
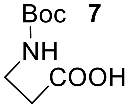
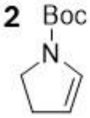
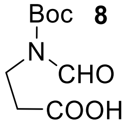
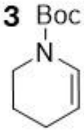
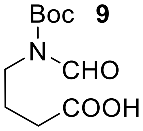
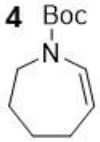
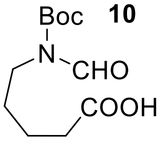
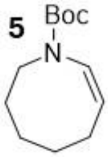
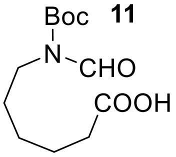
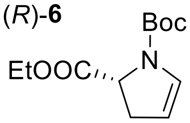
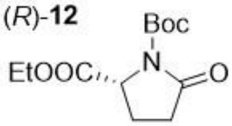
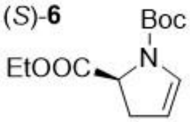
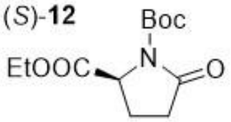
| Entry | moles Oxone / mole **2** | solvent | T °C | T hour | conversion | product |
|---|---|---|---|---|---|---|
| 1 | 2 | 1 M phosphate buffer | 20 | 6 | 100% | complex mixture |
| 2 | 2 | 1 M phosphate buffer/$CH_3CN$ | 20 | 2 | partial | complex mixture |
| 3 | 2 | water/$CH_3CN$ | 20 | 2 | partial | **2** + **8** |
| 4 | 4 | water/$CH_3CN$ | 20 | 2 | 100% | **8** [a] |
| 5 | 4 | water/$CH_3CN$ | 40 | 2 | 100% | **8** [b] |

[a] The crude product contained *N*-Boc-γ-lactam as a side-product hardly separable by chromatography. [b] The crude product contained *N*-Boc-γ-lactam only as an impurity not prejudicing the chromatographic purification of **8**.

Such reaction conditions (4 moles of Oxone per mole of substrate in 1/1 water/$CH_3CN$ for 2 hours) were then applied to oxidize the ene-carbamates **3**-**5**. For these substrates, oxidative cleavage efficiently occurred already at room temperature yielding the corresponding *N*-Boc-*N*-formyl-ω-amino acids, namely *N*-Boc-*N*-formyl-γ-aminobutyric acid (**9**), *N*-Boc-*N*-formyl-δ-aminovaleric acid (**10**), and *N*-Boc-*N*-formyl-ε-aminocaproic acid (**11**), isolated by chromatography with 70%, 55%, and 55% yield respectively (Table 2, entries 3-5). Thus, Oxone oxidatively cleaves the ene-carbamates **2**-**5** to the same products as ruthenium tetroxide.[15,16] As previously reported,[7] *N*-Boc-*N*-formyl-ω-amino acids were also the products resulting from the oxidative cleavage of cyclic *N*-Boc azaketones having nitrogen α-positioned to carbonyl by oxidation with Oxone in DMF.

To our knowledge, oxidative cleavage of 4-membered cyclic ene-carbamates is not reported in the literature. When we treated **1** with Oxone under the same conditions as **3**-**5**, we did not observe the cleavage of the C=C double bond leading to *N*-Boc-*N*-formylglycine, the product previously obtained from *N*-Boc-3-azetidinone by reaction with Oxone,[7] but the formation of *N*-Boc-β-alanine (**7**) (Figure 4). This was isolated with 57% yield by chromatography (Table 2, entry 1). We believe that the constrained ene-carbamate **1** undergoes hydration to *N*-Boc-2-hydroxyazetidine in the aqueous reaction medium made acidic by $KHSO_4$. Such hemiaminal is in equilibrium with *N*-Boc-3-aminopropionaldehyde, which is oxidized to *N*-Boc-β-alanine by Oxone (Figure 4). Such an oxidation mechanism is suggested by the fact that we detected the aldehyde signal in the $^1H$ NMR spectrum of the products mixture when we stopped the reaction after 10 minutes. Furthermore, we observed the formation of *N*-Boc-3-aminopropionaldehyde when we treated **1** in 1/1 water/$CH_3CN$ with only $KHSO_4$, in the absence of Oxone. Notably, *N*-Boc-3-aminopropionaldehyde is reported in the literature as an inseparable 1:1 mixture with the corresponding cyclic hemiaminal *N*-Boc-2-hydroxyazetidine upon reduction of *N*-Boc-2-azetidinone with $Cp_2ZrHCl$.[18]

**Table 2.** Oxidation of cyclic ene-carbamates **1**-**6** with Oxone (4 moles) for 2 hours in 1:1 water/$CH_3CN$ (entries 1-5) and in DMF (entries 6 and 7)

| Entry | Substrate | T °C | Product | Isolated yield (%) |
|---|---|---|---|---|
| 1 | **1**  | 20 | **7**  | 57 |
| 2 | **2**  | 40 | **8**  | 50 |
| 3 | **3**  | 20 | **9**  | 70 |
| 4 | **4**  | 20 | **10**  | 55 |
| 5 | **5**  | 20 | **11**  | 55 |
| 6 | (*R*)-**6**  | 20 | (*R*)-**12**  | 65 |
| 7 | (*S*)-**6**  | 20 | (*S*)-**12**  | 70 |

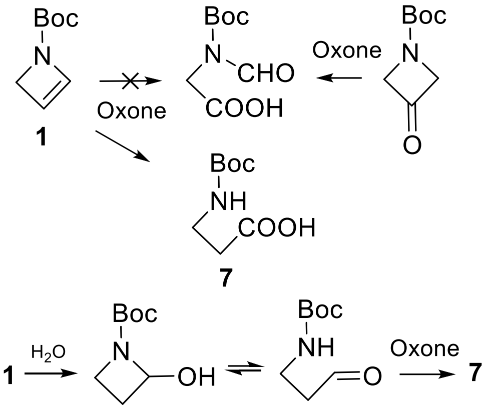


**Figure 4.** Comparison between oxidation of **1** and *N*-Boc-3-azetidinone with Oxone in 1/1 water/$CH_3CN$ and proposed mechanism of the conversion of **1** into **7**.

The two enantiomers of the cyclic ene-carbamate **6** were the last substrates submitted to oxidation with Oxone. Under the conditions previously adopted for the oxidation of the ene-carbamates **1**-**5**, the two ene-carbamates with an ester function α-positioned to nitrogen gave a crude mixture consisting of several products. Therefore, we decided to accomplish the oxidation in non-aqueous medium. Treatment of (*R*)-**6** and (*S*)-**6** with 4 moles of Oxone per mol of substrate in DMF at room temperature for 2 hours produced a univocal outcome yielding *N*-Boc-D-pyroglutamic acid ethyl ester ((*R*)-**12**) and *N*-Boc-L-pyroglutamic acid ethyl ester ((*S*)-**12**), respectively, as main products (Table 2, entries 6 and 7). The two pyroglutamates were isolated with 65% and 70% yield by chromatography, respectively. Comparison of their optical rotatory powers with those reported in the literature indicated that oxidation had occurred without racemization.

## Conclusions

In summary, we have reported here the results of the oxidative cleavage of 4-8-membered cyclic ene-carbamates by Oxone, a green oxidizing agent that, after a long dismission, has been arousing growing interest and increasing application within metal-free oxidation procedures due to its many advantages in terms of sustainability. We have shown that, under suitable conditions, Oxone cleaves the C=C double bond of cyclic ene-carbamates univocally yielding *N*-carbamate-protected *N*-formyl-ω-amino acids, which are the same products as those previously obtained from the same substrates by oxidation with $RuO_4$ and from the corresponding cyclic 3-azaketones by oxidation with Oxone. Notably, *N*-Boc-2-azetine undergoes cleavage of the C(1)-N bond to *N*-Boc-β-alanine and not of the C=C double bond to *N*-Boc-*N*-formylglycine, while the enantiomers of *N*-Boc-2-pyrroline with ethyl ester function α-positioned to nitrogen are not oxidatively cleaved but oxidized to pyroglutamates without racemization.

## Experimental Section

**General.** Heterocyclic ene-carbamates were purchased from commercial sources or synthesized as previously reported.[8-11] An aluminum heating block was used as the heating source for reactions that required heating. Flash chromatography purifications were performed using Sfär Silica D 60 µm cartridges. $^1H$-NMR and $^{13}C$-NMR spectrums were recorded in $CDCl_3$ at 300 MHz and 75 MHz respectively, with Varian Mercury 300 Spectrometer and elaborated with Mnova software. Chemical shifts are reported in ppm relative to residual solvent as internal standard. Melting points were determined by Buchi Melting Point B-540 apparatus. Thin-layer chromatography (TLC) analyses were carried out on alumina sheets precoated with silica gel 60 F254 and stained with $KMnO_4$ solution. High Resolution Mass Spectra (HRMS) were acquired by direct infusion on a Waters Q-ToF Synapt G2-Si HDMS (Waters Corporation, Milford, MA, United States) operated in positive ElectroSpray Ionization (ESI+).

**General procedure for the synthesis of compounds 7-11**. The appropriate cyclic ene-carbamate (1 mmol) was dissolved in $CH_3CN$ (0.25 M). A solution of Oxone (4 mmol) in equal volume of water was added and the reaction mixture was vigorously stirred for 2 hours at room temperature (or 40 °C for the synthesis of **8**). The mixture was poured into water and extracted with EtOAc (3 × 5–10 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated under vacuum. The desired products were obtained after purification as detailed.

***N-(tert-Butoxycarbonyl)-β-alanine (7).***[7] Obtained from *N*-Boc-2-azetine (0.15 g, 0.97 mmol) and Oxone (1.19 g, 3.87 mmol) in $CH_3CN$ (3.9 mL) and $H_2O$ (3.9 mL) at room temperature for 2 hours, following the general procedure reported above. The product was obtained after flash column chromatography purification (gradient of $CH_2Cl_2$/MeOH, from 0% to 10% MeOH) as white solid in 57% yield. $R_f$ ($CH_2Cl_2$/MeOH 95:5 stained with $KMnO_4$) 0.18. mp = 75–78 °C (lit. 73–75 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.38 (br s, 1H), 6.25 (br s, 0.3H), 5.08 (br s, 1H), 3.53 – 3.24 (m, 2H), 2.69 – 2.44 (m, 2H), 1.44 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 177.7 (major rotamer), 176.5 (minor rotamer), 156.1, 81.2 (minor rotamer), 79.8 (major rotamer), 37.3 (minor rotamer), 36.0 (major rotamer), 34.6, 28.5.

***N*-(*tert*-Butoxycarbonyl)-*N*-formyl-β-alanine (8).**[7] Obtained from *N*-Boc-2,3-dihydropyrrole (0.25 g, 1.48 mmol) and Oxone (1.82 g, 5.91 mmol) in $CH_3CN$ (6.0 mL) and $H_2O$ (6.0 mL) at 40 °C for 2 hours, following the general procedure reported above. The product was obtained after flash column chromatography purification (gradient of cyclohexane/EtOAc, from 0% to 40% EtOAc) as pale brown solid in 50% yield. $R_f$ ($CH_2Cl_2$/MeOH 95:5 stained with $KMnO_4$) 0.20. mp = 64–66 °C (lit. 68–70 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.15 (s, 1H), 3.92 (t, *J* = 7.3 Hz, 2H), 2.62 (t, *J* = 7.3 Hz, 2H), 1.55 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 176.9, 163.1, 152.0, 84.7, 36.2, 32.7, 28.0.

***N*-(*tert*-Butoxycarbonyl)-*N*-formyl-γ-aminobutyric acid (9).**[7] Obtained from *N*-Boc-3,4-dihydro-2*H*-pyridine (0.25 g, 1.36 mmol) and Oxone (1.68 g, 5.46 mmol) in $CH_3CN$ (5.5 mL) and $H_2O$ (5.5 mL) at room temperature for 2 hours, following the general procedure reported above. The product was obtained after flash column chromatography purification (gradient of cyclohexane/EtOAc, from 0% to 40% EtOAc) as white solid in 70% yield. mp = 61–63 °C. $R_f$ ($CH_2Cl_2$/MeOH 95:5 stained with $KMnO_4$) 0.25. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.16 (s, 1H), 3.65 (t, *J* = 7.1 Hz, 2H), 2.36 (t, *J* = 7.3 Hz, 2H), 1.95 – 1.78 (m, 2H), 1.53 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 178.9, 163.4, 152.5, 84.4, 39.8, 31.3, 28.1, 23.3.

***N*-(*tert*-Butoxycarbonyl)-*N*-formyl-δ-aminovaleric acid (10*).***[15] Obtained from *N*-Boc-2,3,4,5-tetrahydroazepine (0.30 g, 1.52 mmol) and Oxone (1.87 g, 6.08 mmol) in $CH_3CN$ (6.0 mL) and $H_2O$ (6.0 mL) at room temperature for 2 hours, following the general procedure reported above. The product was obtained after flash column chromatography purification (gradient of $CH_2Cl_2$/MeOH, from 0% to 5% MeOH) as yellowish oil in 55% yield. $R_f$ ($CH_2Cl_2$/MeOH 95:5 stained with $KMnO_4$) 0.33. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.17 (s, 1H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.70 – 1.58 (m, 4H), 1.54 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 179.1, 163.3, 152.6, 84.2, 40.1, 33.6, 28.1, 27.8, 21.9.

***N*-(*tert*-Butoxycarbonyl)-*N*-formyl-ε-aminocaproic acid (11).** Obtained from *N*-Boc-3,4,5,6-tetrahydro-2*H*-azocine (0.30 g, 1.42 mmol) and Oxone (1.75 g, 5.68 mmol) in $CH_3CN$ (5.5 mL) and $H_2O$ (5.5 mL) at room temperature for 2 hours, following the general procedure reported above. The product was obtained after flash column chromatography purification (gradient of $CH_2Cl_2$/MeOH, from 0% to 5% MeOH) as colorless oil in 55% yield. $R_f$ ($CH_2Cl_2$/MeOH 95:5 stained with $KMnO_4$) 0.38. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 9.16 (s, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.72 – 1.61 (m, 2H), 1.54 (s, 9H), 1.49 – 1.30 (m, 4H). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 179.6, 163.3, 152.6, 84.0, 40.4, 33.9, 28.1, 28.0, 26.2, 24.3. HRMS (ESI+) *m/z* calcd. For $C_{12}H_{21}NO_5Na$ $[M+Na]^+$ 282,1317, found 282,1311.

**General procedure for the synthesis of compounds (R)-12 and (S)-12**. The appropriate cyclic ene-carbamate (1 mmol) was dissolved in DMF (0.5 M). Oxone (4 mmol) was added and the reaction mixture was stirred at room temperature for 2 hours. The mixture was poured into water and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over $Na_2SO_4$ and the solvent was evaporated. The desired products were obtained after flash column chromatography purification (gradient of cyclohexane/EtOAc, from 0% to 30% EtOAc).

***N*-(*tert*-Butoxycarbonyl)-D-pyroglutamic acid ethyl ester ((R)-12).**[19] Obtained from (*R*)-1-*tert*-butyl 2-ethyl 2,3-dihydro-1*H*-pyrrole-1,2-dicarboxylate (0.30 g, 1.24 mmol) and Oxone (1.53 g, 4.97 mmol) in DMF (2.5 mL, 0.5 M) at room temperature for 2 hours, following the general procedure reported above. The product was obtained as off-white solid in 65% yield. $R_f$ (cyclohexane/EtOAc 6:4 stained with $KMnO_4$) 0.29. mp = 48–50 °C. $[\alpha]_D{}^{25}$ = + 45.0 (c 0.78, MeOH).[20] $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 4.58 (dd, *J* = 9.4, 3.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.69 – 2.54 (m, 1H), 2.53 – 2.40 (m, 1H), 2.39 – 2.22 (m, 1H), 2.08 – 1.95 (m, 1H), 1.48 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 173.4, 171.4, 149.4, 83.7, 61.8, 59.1, 31.3, 28.0, 21.7, 14.3.

***N*-(*tert*-Butoxycarbonyl)-L-pyroglutamic acid ethyl ester ((S)-12*).***[21] Obtained from (*S*)-1-*tert*-butyl 2-ethyl 2,3-dihydro-1*H*-pyrrole-1,2-dicarboxylate (0.30 g, 1.24 mmol) and Oxone (1.53 g, 4.97 mmol) in DMF (2.5 mL, 0.5 M) at room temperature for 2 hours, following the general procedure reported above. The product was obtained as white solid in 70% yield. $R_f$ (cyclohexane/EtOAc 6:4 stained with $KMnO_4$) 0.29. mp = 53–55 °C. $[\alpha]_D{}^{25}$ = – 44.3 (c 0.5, MeOH). Lit.[21] $[\alpha]_D{}^{25}$ = – 46.3 (c 1.4, MeOH). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 4.59 (dd, *J* = 9.3, 3.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.70 – 2.57 (m, 1H), 2.56 – 2.42 (m, 1H), 2.40 – 2.24 (m, 1H), 2.09 – 1.97 (m, 1H), 1.50 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 173.3, 171.2, 149.0, 83.2, 61.4, 58.7, 30.9, 27.6, 21.3, 13.9.

## Supplementary Material

$^1H$ NMR, $^{13}C$ NMR spectra of **7**-**12** and HRMS spectrum of **11**.

## References and Notes

1. Alvi S.; Jayant V.; Ali R. *ChemistrySelect* **2022**, *7*, No. e202200704. https://doi.org/10.1002/slct.202200704
2. Dorado V.; Herrerias C. I.; Fraile J. M. *Tetrahedron* **2023**, *139*, 133450. https://doi.org/10.1016/j.tet.2023.133450
3. Zhang M. Z.; Wang P.; Liu H. Y.; Wang D.; Deng Y.; Bai Y. D.; Luo F.; Wu W. Y.; Chen T. *ChemSusChem* **2023**, *16*, No. e202300583.

https://doi.org/10.1002/cssc.202300583

4. Hussain H.; Green I. R.; Ahmed I. *Chem. Rev.* **2013***, 113*, 3329. https://doi.org/10.1021/cr3004373
5. Goulart H. A.; Araujo D. R.; Penteado F.; Jacob R. G.; Perin G.; Lenardão E. J. *Molecules* **2021**, *26*, 7523. https://doi.org/10.3390/molecules26247523
6. Bertolini V.; Appiani R.; Pallavicini M.; Bolchi C. *J. Org. Chem*. **2021**, *86*, 15712. https://doi.org/10.1021/acs.joc.1c01469
7. Giraudo A.; Armano E.; Morano C.; Pallavicini M.; Bolchi C. *J. Org. Chem.* **2023***, 88*, 15461. https://doi.org/10.1021/acs.joc.3c01513
8. Yu J.; Truc V.; Riebel P.; Hierl E;, Mudryk B. *Tetrahedron Lett.* **2005**, *46*, 4011. https://doi.org/10.1016/j.tetlet.2005.04.030
9. Hodgson D. M.; Pearson C. I.; Kazmi M. *Org. Lett.* **2014***, 16*, 856. https://doi.org/10.1021/ol403626k
10. Asano M.; Hashimoto K.; Saito B.; Shiokawa Z.; Sumi H.; Yabuki M.; Yoshimatsu M.; Aoyama K.; Hamada T.; Morishita N.; Dougan D. R.; Mol C. D.; Yoshida S.; Ishikawa T. *Bioorg. Med. Chem.* **2013**, *21*, 5725. https://doi.org/10.1016/j.bmc.2013.07.020
11. Li G.; Kates P. A.; Dilger A. K.; Cheng P. T.; Ewing W. R.; Groves J. T. *ACS Catal.* **2019**, *9*, 9513. https://doi.org/10.1021/acscatal.9b03457
12. Parida K. N.; Moorthy J. N. *Tetrahedron* **2014**, *70*, 2280. https://doi.org/10.1016/j.tet.2014.01.042
13. Tacheuchi Y.; Azuma K.; Abe H.; Sasaki K.; Harayama T. *Chem. Pharm. Bull.* **2002**, *50*, 1011. https://doi.org/10.1248/cpb.50.1011
14. Martin C. L.; Overman L. E.; Rohde J. M. *J. Am. Chem. Soc.* **2010**, *132*, 4894. https://doi.org/10.1021/ja100178u
15. Kaname M.; Yoshifuji S.; Sashida H. *Chem. Pharm. Bull*. **2008**, *56*, 1310. https://doi.org/10.1248/cpb.56.1310
16. Torii S.; Inokuchi T.; Kondo K. *J. Org. Chem.* **1985***, 50*, 4980. https://doi.org/10.1021/jo00224a071
17. Rup S.; Sindt M.; Oget N. *Tetrahedron Lett.* **2010***, 51*, 3123. https://doi.org/10.1016/j.tetlet.2010.04.040
18. Piperno A.; Carnovale C.; Giofrè S. V.; Iannazzo D. *Tetrahedron Lett.* **2011***, 52*, 6880. https://doi.org/10.1016/j.tetlet.2011.10.006
19. Dong J.; Gong Y.; Liu J.; Chen X.; Wen X.; Sun H. *Bioorg. Med. Chem.* **2014**, *22*, 1383. https://doi.org/10.1016/j.bmc.2013.12.061
20. The $[\alpha]_D^{25}$ of commercially available *N-(*tert-Butoxycarbonyl)-D-pyroglutamic acid ethyl ester (*Florochem*) is + 44.7 (c 0.78, MeOH).
21. Jain R., *Org. Prep. Proced. Int.* **2001**, *33*, 405. https://doi.org/10.1080/00304940109356611