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Cycloaddition of tertiary aziridines and carbon dioxide using a recyclable organocatalyst, 1,3-di-*tert*-butylimidazolium-2-carboxylate: straightforward access to 3-substituted 2-oxazolidones†

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Imidazolium-2-carboxylates derived from *N*-heterocyclic carbenes (NHCs) and CO_2 serve as efficient catalysts for CO_2-carboxylation of tertiary aziridines bearing various substituents such as halogens, ether, olefin, ester, acetal, and nitro groups on the aziridine ring in 2-propanol, leading to 3-substituted-2-oxazolidones in good to excellent yields and with high selectivity. The NHC–CO_2 adducts facilitate nucleophilic attack of the CO_2 moiety on the aziridines, in which the substituents are intact during the carboxylation. The catalyst is successfully recycled up to five times with no apparent loss in activity.

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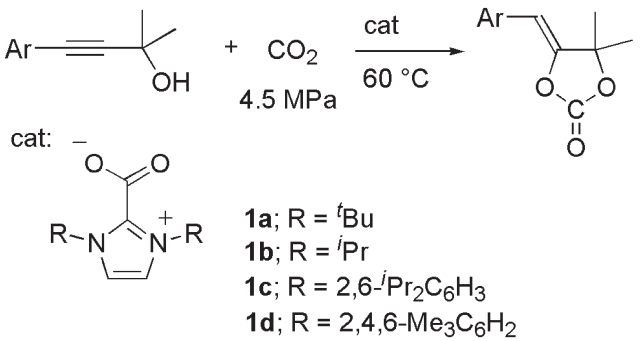
1. Introduction

Over the last few decades, there has been great interest in utilization of carbon dioxide (CO_2) as a ubiquitous C1 source in terms of synthetic challenge and environmental issues.[1] The straightforward CO_2 fixation into valuable compounds offers practical advantages in organic synthesis because of its non-toxic, abundant, and inexpensive properties. 2-Oxazolidones have been perceived as versatile intermediates for production of pharmaceuticals and fine chemicals as well as chiral auxiliaries,[2] and thus dehydrative carboxylation of amino alcohol,[3] carboxylative cyclization of propargylamines,[4] and cycloaddition of aziridines[5] have been explored for construction of the five-membered urethane ring structure. The ring-opening reaction of secondary protic aziridines with CO_2 in the presence of various catalysts or additives has been demonstrated to give 2-oxazolidones, and oligomeric or polymeric products containing urethane and amine units were also obtainable depending on the reaction conditions using high pressure or supercritical CO_2 systems.[5a,f,6,7] Recently, some advances have been made for the cycloaddition of tertiary aziridines and CO_2 promoted by several halide salts or natural α-amino acids, leading to selective formation of *N*-substituted 2-oxazolidones.[5l–w] However, the reaction scopes are mostly limited to substrates bearing simple aliphatic and aromatic groups on the nitrogen atom.[8] We have recently developed the imidazolium-2-carboxylates (**1**; NHC–CO_2) catalyzed carboxylative cyclization of propargylic alcohols and cycloaddition of epoxides to CO_2, producing cyclic carbonates as shown in Scheme 1.[9] The NHC–CO_2 adducts derived from NHCs and CO_2 are utilized as a convenient CO_2 carrier[10] to accomplish CO_2 fixation through the nucleophilic incorporation of the O=C=O unit.[9,11] These results inspired us to apply further this CO_2 fixation protocol to the synthesis of urethane using CO_2. Herein we report that the NHC–CO_2 adducts serve as efficient catalysts for cycloaddition of aziridines to CO_2 to afford the corresponding 2-oxazolidones with a variety of functional groups. Furthermore, it is successfully demonstrated that the organocatalyst can be simply recovered by precipitation and reused without a significant loss of activity.



Scheme 1 Carboxylative cyclization of propargyl alcohols catalyzed by imidazolium-2-carboxylates.

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†Electronic supplementary information (ESI) available: Synthetic procedure for new aziridine substrates, NMR spectra of aziridines (**2**) and 2-oxazolidones (**3**) and crystal structure determination of **3a**. CCDC 896141. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2gc36414j

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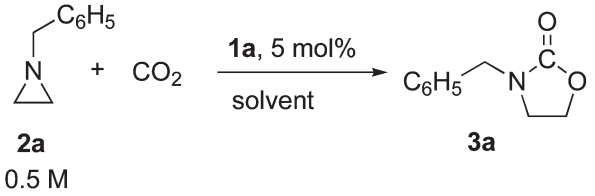
Table 1 Cycloaddition of *N*-benzylaziridine **2a** and CO_2 with catalyst **1a**[a]



Entry	Solvent	Cat	% Yield[b]
1	$(CH_3)_2CHOH$	**1a**	92
2	$(CH_3)_2CHOH$	**1b**	70
3	$(CH_3)_2CHOH$	**1c**	68
4	$(CH_3)_2CHOH$	**1d**	63
5	CH_3CH_2OH	**1a**	50
6	$(CH_3)_3COH$	**1a**	26
7	Benzene	**1a**	1
8	DMF	**1a**	66
9	THF	**1a**	23

[a] Reaction conditions: **2** (1.0 mmol), **1** (0.05 mmol), solvent (2.0 mL), 5.0 MPa, 90 °C, 20 h. [b] Determined by ^{1}H NMR spectroscopy.

2. Results and discussion

The carboxylation reaction was performed using *N*-benzylaziridine (**2a**) as a model substrate with 5.0 MPa of CO_2 at 90 °C for 20 h in the presence of an organocatalyst, 1,3-bis(*tert*-butyl)-imidazolium-2-carboxylate (**1a**) (5 mol%). The halide free catalyst **1a** was obtained by treatment of CO_2 (0.1 MPa) with the parent NHC generated from imidazolium tetrafluoroborate in THF containing an equimolar amount of $KOC(CH_3)_3$.[12] In the absence of any catalysts and additives, **2a** was hardly converted to give the cycloaddition product in less than 16% yield, and a mixture of oligomers was formed. The outcome of the reaction is highly influenced by the structure of the NHC catalysts and reaction conditions. Table 1 lists some representative results of the reaction. Catalyst screening tests revealed that the catalyst **1a** promoted the carboxylation of **2a** in 2-propanol under the standard conditions to give the desired urethane product, 3-benzyl-2-oxazolidone (**3a**), in 92% yield (entry 1), whereas 1,3-diisopropyl- and diaryl-substituted NHC–CO_2 adducts (**1b–1d**) exhibited somewhat lower catalytic activity (63–70%) (entries 2–4). A protic solvent 2-propanol is the best solvent for the reaction. In ethanol, the substrate **2a** was all consumed to yield the product **3a** in addition to the oligomeric byproducts determined by the ^{1}H NMR spectrum (entry 5). The reaction in ^{t}BuOH gave **3a** in 26% yield without formation of the undesired products (entry 6). In contrast to alcoholic solvents, the reaction in benzene was strongly retarded to give the product in less than 1% yield (entry 7). An aprotic polar solvent, DMF, gave a satisfactory chemical yield (66%) in the carboxylation of **2a** (entry 8).

Catalytic performance was markedly influenced by the reaction temperature and pressure. On increasing the temperature from 60 °C to 100 °C under 5.0 MPa for 15 h, the chemical yield of **3a** showed the maximum at around 90 °C as shown in Fig. 1. It can be reasonably assumed that a dynamic CO_2 catch-and-release phenomenon of the NHC catalyst exists in the reaction phase, and the reaction will be retarded by unfavorable decarboxylation of NHC–CO_2 at an elevated temperature above 90 °C. Although the reaction did not take place at all under an atmospheric pressure of CO_2 at 90 °C for 20 h, an increase in the pressure of CO_2 caused a positive effect on the urethane formation reaching 92% yield under 5.0 MPa (Fig. 2), indicating preferable formation of the NHC–CO_2 adduct at a higher pressure.[13]

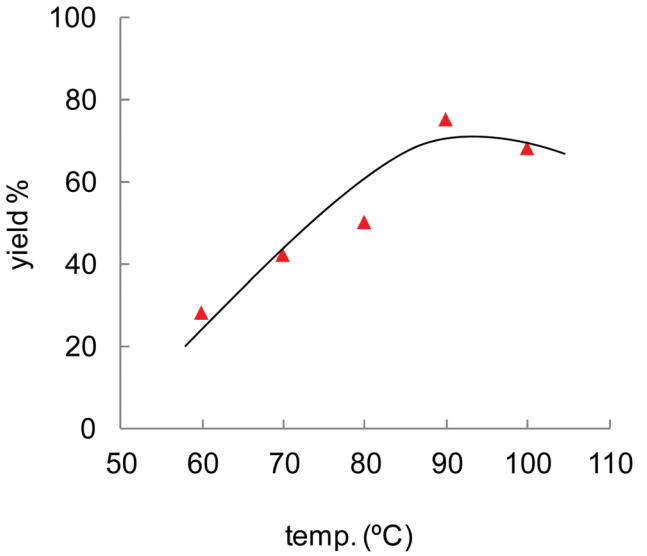


Fig. 1 Temperature effect on the yield of **3a**. Reaction conditions: **1a** (0.05 mmol), **2a** (1.0 mmol), 2-propanol (2.0 mL) under 5.0 MPa of CO_2 for 15 h.

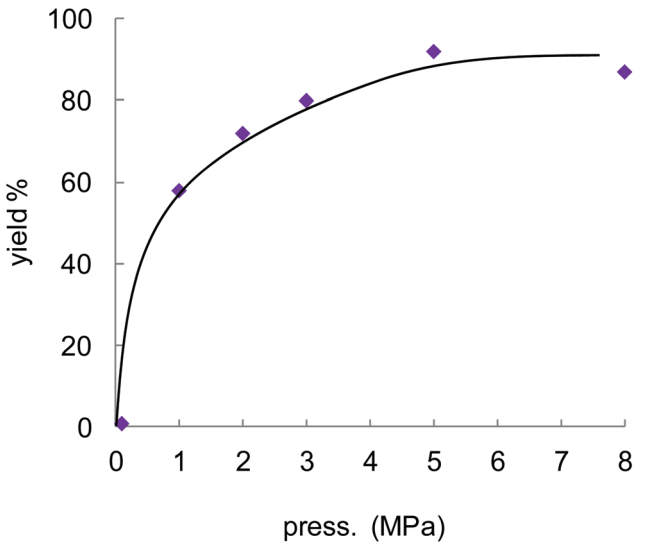


Fig. 2 CO_2 pressure effect on the yield of **3a**. Reaction conditions: **1a** (0.05 mmol), **2a** (1.0 mmol), 2-propanol (2.0 mL) at 90 °C for 20 h.

The substrate scope was then examined by using catalyst **1a** under the optimized conditions of 5.0 MPa of CO_2 at 90 °C in 2-propanol. As listed in Table 2, the reaction of **2b** having a *tert*-butyl group gave the product in a good yield (entry 2;

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Table 2 Carboxylation of *N*-substituted aziridines catalyzed by NHC–CO_2 [a]

Entry	Aziridine	R^1	Product	% Yield[b,c]
1	**2a**	$CH_2C_6H_5$	**3a**	92(85)
2	**2b**	$C(CH_3)_3$	**3b**	74
3	**2c**	CH_2CH_2OH	**3c**	40
4	**2d**	$CH_2CH_2OCH_2C_6H_5$	**3d**	81(72)
5	**2e**	$CH_2CH_2OCH_2CH{=}CH_2$	**3e**	95(88)
6	**2f**	$CH_2CH_2OSi(CH_3)_2[C(CH_3)_3]$	**3f**	90(85)
7	**2g**	$CH_2CH_2OC(=O)C_6H_5$	**3g**	91(82)
8	**2h**	$CH_2CH_2OCH_2$-3-C_6H_4F	**3h**	82(78)
9	**2i**	$CH_2CH_2OCH_2$-3-C_6H_4Cl	**3i**	90(78)
10	**2j**	$CH_2CH_2OCH_2$-3-C_6H_4Br	**3j**	75(70)
11	**2k**	$CH_2CH_2OCH_2$-3-C_6H_4I	**3k**	82(78)
12	**2l**	$CH_2CH_2OCH_2$-3-$C_6H_4NO_2$	**3l**	82(75)
13	**2m**	$CH_2CH_2OCH_2$-3-$C_6H_4OCH_3$	**3m**	80(75)
14	**2n**	$CH_2CH_2OCH_2C_6H_3(OCH_2O)$	**3n**	94(88)
15	**2o**	$CH_2CH_2OCH_2$-2-thienyl	**3o**	60(55)

[a] Reaction conditions: **2** (1.0 mmol), **1a** (0.05 mmol), 2-propanol (2.0 mL), 5.0 MPa, 90 °C, 20 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yields in parenthesis.

Table 3 Reusability of catalyst **1a** in cycloaddition of **2a** and CO_2 [a]

Cycle	% Recovery	% Yield[b]
1	99.5	92
2	99.2	91
3	99.2	92
4	99.4	90
5	99.5	90
6	99.1	90

[a] Reaction conditions: **2** (9.0 mmol), **1a** (0.45 mmol), 2-propanol (18.0 mL), 5.0 MPa, 90 °C, 20 h. [b] Determined by ^{1}H NMR spectroscopy.

74%). Although commercially available 1-(2-hydroxyethyl)aziridine **2c** resulted in a moderate yield of 40% (entry 3), the catalyst system tolerates a broad range of other functional groups. In the reaction of **2d–o** containing various substituents on the nitrogen atom, the desired urethanes were obtained in the range of 60–95% and successfully isolated in 55–88% yields after column chromatographic purification (entries 4–15). For example, carboxylation of 1-aziridineethanol derivatives protected by benzyl ether (**2d**), allyl (**2e**), and silyl (**2f**) groups efficiently proceeded to give cyclic urethane up to 95% yield. Other polar substituents including ester, halides, nitro, ether, and acetal groups as well as a heteroaromatic ring remained intact during the cycloaddition.

Potential practicability of the present carboxylation was demonstrated by a simple catalyst recovery and reuse procedure in a scale-up reaction using 1.2 g of **2a**. The imidazolium-2-carboxylate catalyst **1a** was successfully recovered by precipitation from the reaction mixture by addition of diethyl ether under a CO_2 atmosphere followed by filtration. More than 99% of the NHC–CO_2 adduct based on the amount of loading catalyst was successfully isolated after drying under reduced pressure as shown in Table 3. The catalytic

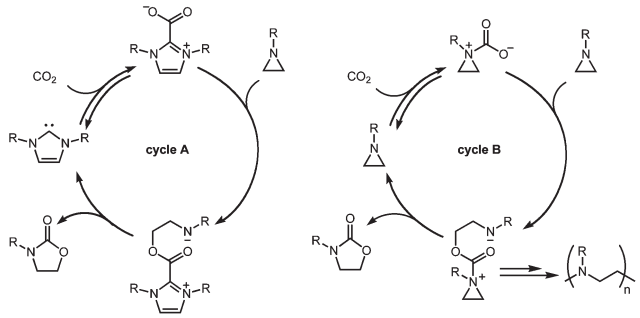

Fig. 3 Possible mechanisms of cycloaddition of tertiary aziridines with CO_2.

performance of **1a** was well maintained during the catalyst reuse six times, leading to **3a** in a range of 90–92% yields.

While the precise mechanism of the present reaction still remains obscure, the key step is probably nucleophilic attack of the CO_2 unit on the distorted aziridine ring of the substrate, as proposed in our previous work on carboxylation of propargyl alcohols and epoxides catalyzed by NHC–CO_2 adducts.[9] As shown in Fig. 3, the zwitterionic CO_2 adduct would promote the C–N bond cleavage to give an intermediate where the electrophilic carboxyl group is susceptible to attack by the nitrogen, and then the product urethane and the regenerated NHCs are released (cycle A). The positive effect on the urethane yield observed with the catalyst **1a** bearing electron donating alkyls rather than the less basic catalysts **1c** and **1d** seems to be consistent with the nucleophilic attack mechanism. Because the possible ionic intermediates are influenced by the polarity of the reaction medium, the urethane formation was significantly retarded in less polar solvents as mentioned above (Table 1, entry 7).

In an alternative mechanism (cycle B), zwitterionic aziridinium-1-carboxylate, generated from the tertiary aziridine and CO_2, acts as a catalyst to promote the ring-opening of other aziridine molecules *via* the nucleophilic attack. In the absence of NHC–CO_2 adducts, this catalytic cycle could provide the undesired oligomeric byproducts (*vide supra*). These results strongly suggest that the NHC–CO_2 catalyst accelerates the carboxylation by suppressing formation of oligomer in 2-propanol leading to the selective CO_2 fixation.

3. Conclusions

In conclusion, we demonstrated that the cycloaddition of tertiary aziridines with CO_2 can be efficiently promoted by imidazolium-2-carboxylates in 2-propanol. The NHC–CO_2 adduct facilitates incorporation of the CO_2 molecule to provide access to synthetically useful 2-oxazolidones selectively. Notably, the present organocatalysis tolerates various functional groups and heteroatoms on the substrate, leading to substituted 2-oxazolidones with high efficiency, and offers the promising product/catalyst separation method that permits catalyst reuse without a significant loss of catalytic activity.

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4. Experimental section

CAUTION: The experiments described here could involve risk of an explosion and were conducted using equipment and safety precautions suitable for high pressure CO_2 conditions.

General methods

Solvents were dried by refluxing over sodium benzophenone ketyl (THF, ether, benzene) or CaH_2 (2-propanol, ethanol, *tert*-butyl alcohol) and distilled under argon. Carbon dioxide (99.999%) was purchased from Showa Tansan. Imidazolium-2-carboxylates (**1a–1d**) were prepared according to the reported method using Schlenk techniques under an argon atmosphere.[14] The ^{1}H and ^{13}C NMR spectra were acquired on JEOL JNM-LA300 and JNM-ECX400 spectrometers as solutions in $CDCl_3$. The NMR chemical shifts were referenced to $SiMe_4$ by using residual proton impurities in the deuterated solvent. Elemental analyses were carried out using a PE2400 Series II CHNS/O Analyzer (Perkin Elmer). High-resolution mass spectra were obtained on a TOF MS instrument with an ESI source (JEOL JMS-T100LC mass spectrometer).

Typical procedure for the cycloaddition

The reaction was carried out in a 50 mL stainless steel autoclave equipped with a stirring bar. The autoclave containing the catalyst (0.05 mmol) was purged with argon gas to remove oxygen. Aziridines (1.00 mmol) and 2-propanol (2.0 mL) were introduced into the autoclave with a syringe while the vessel was purged with argon. The vessel was charged with CO_2 to the required pressure through a cooling apparatus with an HPLC pump (JASCO SCF-Get). After stirring the reaction mixture under the predetermined conditions, the autoclave was cooled in an ice bath to room temperature within a few minutes, and CO_2 was slowly vented. The reaction mixture was concentrated *in vacuo* and analyzed by ^{1}H NMR spectroscopy with Durene (11.2 mg, 0.08 mmol; an internal standard) after filtration through a PTFE filter (0.45 μm). The crude products were purified by column chromatography on silica gel (hexane–ethyl acetate = 5 : 1) and Kugelrohr distillation except the urethanes, **3b** and **3c**.

3-Benzyl-1,3-oxazolidin-2-one (3a). White solid; 85% yield (148.8 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 1.28 (t, 2H, $^3J_{HH}$ = 2.1 Hz), 1.83 (t, 2H, $^3J_{HH}$ = 2.1 Hz), 3.39 (s, 2H; CH_2C$_6$H$_5$), 7.26–7.38 (m, 5H; CH$_2$C$_6$$H_5$); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 43.9, 48.4, 61.7, 127.9, 128.1, 128.8, 135.7, 158.5 (*C*=O); HRMS (ESI) calcd for $C_{10}H_{11}NNaO$ 200.0682 (M + Na^+), found 200.0687.

3-[2-(Benzyloxy)ethyl]-1,3-oxazolidin-2-one (3d). Colorless liquid; 72% yield (159.8 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.48 (m, 2H), 3.64–3.98 (m, 4H), 4.29 (m, 2H), 4.52 (s, 2H; CH_2C$_6$H$_5$), 7.29–7.37 (m, 5H; CH$_2$C$_6$$H_5$); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 44.2, 45.9, 61.9, 68.6, 73.0, 76.6, 127.6, 127.7, 128.4, 137.8, 158.4 (*C*=O). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.66; H, 6.70; N, 6.29.

3-[2-(Allyloxy)ethyl]-1,3-oxazolidin-2-one (3e). Colorless liquid; 88% yield (147.8 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.43–3.46 (m, 2H), 3.58–3.61 (m, 2H), 3.67–3.71 (m, 2H), 3.96–3.98 (m, 2H), 4.27–4.31 (m, 2H), 5.17 (ddt, 1H, $^2J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 10.4 Hz, $^4J_{HH}$ = 1.5 Hz; HC=CH_2), 5.22 (ddt, 1H, $^2J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 17.3 Hz, $^4J_{HH}$ = 1.6 Hz; HC=CH_2), 5.81–5.92 (m, 1H; *H*C=CH$_2$); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 44.2, 46.0, 61.9, 68.6, 71.8, 117.0, 134.3, 158.5 (*C*=O); HRMS (ESI) calcd for $C_8H_{14}NO_3$ 172.0968 (M + H^+), found 172.0966.

3-[2-(*tert*-Butyldimethylsilyloxy)ethyl]-1,3-oxazolidin-2-one (3f). Colorless liquid; 85% yield (208.3 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 0.05 (s, 6H; Si(CH_3)$_2$C(CH$_3$)$_3$), 0.88 (s, 9H; Si-(CH$_3$)$_2$C(CH_3)$_3$), 3.36 (m, 2H), 3.70 (m, 2H), 3.76 (m, 2H), 4.29 (m, 2H); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ −5.56, 18.0, 25.7, 46.2, 46.7, 61.8, 61.9, 158.5 (*C*=O). Anal. Calcd for $C_{11}H_{23}NO_3Si$: C, 53.84; H, 9.52; N, 5.71. Found: C, 53.44; H, 9.52; N, 5.62.

3-[2-(Benzoyloxy)ethyl]-1,3-oxazolidin-2-one (3g). Pale yellow liquid; 82% yield (197.2 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.68 (m, 4H), 4.32 (m, 2H), 4.48 (m, 2H), 7.42–8.03 (m, 5H; COC$_6$$H_5$); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 43.5, 45.2, 61.8, 62.3, 128.5, 129.5, 129.6, 133.2, 158.3 (N*C*O), 166.2(*C*OO). Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28. Found: C, 58.73; H, 5.62; N, 5.25.

3-[2-(3-Fluorophenylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3h). Colorless liquid; 78% yield (187.2 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.49–3.50 (m, 2H), 3.65–3.72 (m, 4H), 4.29–4.33 (m, 2H), 4.51 (s, 2H; OCH_2C$_6$H$_4$F), 6.95–7.35 (m, 4H; OCH$_2$C$_6$$H_4$F); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 44.2, 46.0, 61.9, 68.8, 72.2, 114.0, 114.3 (J = 21.08), 114.4, 114.6 (J = 21.09), 122.81, 122.83 (J = 1.92), 129.9, 130.0 (J = 8.62), 140.4, 140.5 (J = 6.70), 158.5 (*C*=O), 161.6, 164.1 ($^1J_{CF}$ = 246.3 Hz). Anal. Calcd for $C_{12}H_{14}FNO_3$: C, 60.24; H, 5.90; N, 5.85. Found: C, 60.44; H, 5.70; N, 5.58.

3-[2-(3-Chlorophenylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3i). Colorless liquid; 78% yield (199.7 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.46–3.49 (m, 2H), 3.64–3.72 (m, 4H), 4.29–4.33 (m, 2H), 4.49 (s, 2H; OCH_2C$_6$H$_4$Cl), 7.15–7.31 (m, 4H; OCH$_2$C$_6$$H_4$Cl); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 44.2, 46.0, 61.9, 68.8, 72.2, 125.5, 127.5, 127.8, 129.7, 134.3, 139.9, 158.4 (*C*=O). Anal. Calcd for $C_{12}H_{14}ClNO_3$: C, 56.37; H, 5.52; N, 5.48. Found: C, 56.75; H, 5.40; N, 5.28.

3-[2-(3-Bromophenylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3j). Colorless liquid; 70% yield (210.7 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.47–3.50 (m, 2H), 3.64–3.70 (m, 4H), 4.30–4.34 (m, 2H), 4.49 (s, 2H; OCH_2C$_6$H$_4$Br), 7.19–7.47 (m, 4H; OCH$_2$C$_6$$H_4$Br); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 44.2, 46.0, 61.9, 68.8, 72.1, 122.3, 125.9, 130.0, 130.4, 130.8, 140.2, 158.5 (*C*=O). Anal. Calcd for $C_{12}H_{14}BrNO_3$: C, 48.02; H, 4.70; N, 4.67. Found: C, 47.93; H, 4.55; N, 4.63.

3-[2-(3-Iodophenylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3k). Colorless liquid; 78% yield (273.0 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.46–3.49 (m, 2H), 3.63–3.70 (m, 4H), 4.29–4.33 (m, 2H), 4.45 (s, 2H; OCH_2C$_6$H$_4$I), 7.06–7.68 (m, 4H; OCH$_2$C$_6$$H_4$I); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ 44.1, 46.0, 61.9, 68.8, 72.0, 94.3, 126.6, 130.1, 136.4, 136.7, 140.2, 158.5 (*C*=O). HRMS (ESI) calcd for $C_{12}H_{14}INO_3$ 369.9916 (M + Na^+), found 369.9929.

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3-[2-(3-Nitrophenylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3l). Orange liquid; 75% yield (201.3 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.48–3.51 (m, 2H), 3.67–3.71 (m, 4H), 4.29–4.33 (m, 2H), 4.60 (s, 2H; $OCH_2C_6H_4NO_2$), 7.49–8.16 (m, 4H; $OCH_2C_6H_4NO_2$); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$) δ 44.2, 46.1, 62.1, 69.2, 71.8, 122.1, 122.8, 129.6, 133.3, 140.3, 148.5, 158.7 (*C*=O); HRMS (ESI) calcd for $C_{12}H_{14}N_2O_5Na$ 289.0800 ($M + Na^+$), found 289.0800.

3-[2-(3-Methoxyphenylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3m). Colorless liquid; 75% yield (191.3 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.46–3.50 (m, 2H), 3.63–3.69 (m, 4H), 3.80 (s, 3H; CH_3O), 4.27–4.31 (m, 2H), 4.49 (s, 2H; $OCH_2C_6H_4OCH_3$), 6.82–7.28 (m, 4H; $OCH_2C_6H_4OCH_3$); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$) δ 44.2, 45.9, 55.1, 61.9, 68.5, 72.9, 113.1, 119.8, 129.4, 139.4, 158.5 (*C*=O), 159.7 (CH_3OC). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.03; H, 6.70; N, 5.32.

3-[2-(3,4-Methylenedioxyphenylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3n). Colorless liquid; 88% yield (234.1 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.46 (m, 2H), 3.60 (m, 2H), 3.67 (m, 2H), 4.29 (m, 2H), 4.41 (s, 2H; $CH_2C_6H_3OCH_2O$), 5.95 (s, 2H; $CH_2C_6H_3OCH_2O$), 6.76–6.80 (m, 3H; $CH_2C_6H_3OCH_2O$); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$) δ 44.2, 45.9, 61.9, 68.3, 72.9, 101.0, 108.0, 108.3, 121.2, 131.6, 147.2, 147.7, 158.5 (*C*=O). Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28. Found: C, 58.73; H, 5.62; N, 5.25.

3-[2-(Thiophen-2-ylmethyloxy)ethyl]-1,3-oxazolidin-2-one (3o). Orange liquid; 52% yield (119.6 mg); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 3.45 (m, 2H), 3.63–3.71 (m, 4H), 4.29 (m, 2H), 4.67 (s, 2H; $CH_2C_4H_3S$), 6.96–7.29 (m, 3H; $CH_2C_4H_3S$); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$) δ 44.1, 46.0, 125.9, 126.4, 126.7, 140.5, 158.5 (*C*=O). Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.95; H, 5.74; N, 6.09.

Crystal structure determination of 3a. Single crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into an ethyl acetate saturated solution of **3a**. Crystal data: $C_{10}H_{11}NO_2$ M = 177.20, orthorhombic, a = 5.955(3) Å, b = 7.460 (3) Å, c = 19.878(8) Å, V = 883.1(6) Å^3, T = 93 K, space group $P2_12_12_1$ (no. 19), Z = 4, D_c = 1.333 g cm^{-3}, λ(MoKα) = 0.71070 Å, 7147 reflections measured, 2023 unique (R_{int} = 0.029), which were used in all calculations. The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares methods on F^2 with 130 parameters. R_1 = 0.030 ($I > 2\sigma(I)$) and wR_2 = 0.092, GOF 1.00; max/min residual density 0.27/−0.28 e Å^{-3}. The details of the refinement are described in a cif file (CCDC 896141).

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