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Synthesis of Oxazolidinones using Carbon Dioxide as a C-1 Building Block and an Aluminium-based Catalyst.

Mani Sengoden,[a] Michael North,*[a] and Adrian C. Whitwood[a]

Abstract: Oxazolidinone synthesis by the coupling of carbon dioxide and aziridines is catalysed by an aluminium(salphen) complex at 50-100 °C and 1-10 bar pressure under solvent-free conditions. The process is applicable to a variety of substituted aziridines, giving products with high regioselectivity. It involves the use of a sustainable and reusable aluminium-based catalyst, uses carbon dioxide as a C-1 source and provides access to pharmaceutically important oxazolidinones as illustrated by a total synthesis of toloxatone. This protocol is scalable and the catalyst can be recovered and reused. A catalytic cycle is proposed based on stereochemical, kinetic and Hammett studies.

Introduction

Utilization of carbon dioxide as a chemical feedstock is currently attracting much interest[1] in both industry and academia, since it is a safe, inexpensive and ubiquitous C-1 resource as well as being the main greenhouse gas. The commercially viable exploitation of carbon dioxide as a feedstock requires both the production of large volume, low value chemicals and the production of lower volume, high value products.[2] The reaction of carbon dioxide with aziridines falls into the latter category and is an efficient, atom-economic route for the preparation of oxazolidinones which are important heterocyclic motifs found in commercial pharmaceuticals[3] and which have a range of other synthetic applications.[4] For example, antimicrobials such as radezolid,[3b,c] linezolid[3d] and eperezolid[3e] and the antidepressant, toloxatone[3f] all contain an oxazolidinone scaffold (Figure 1). Hence, the development of an environmentally friendly approach for the synthesis of oxazolidinones under mild reaction conditions is highly desirable.

The uncatalysed reaction of carbon dioxide with aziridines requires specialized conditions (ball milling[5] or supercritical carbon dioxide[6]) and is only applicable to a small number of substrates. The reaction can be induced by catalytic or stoichiometric amounts of metal salts,[7] metal complexes,[8] solid metal phosphonates,[9] MOFs,[10] onium salts,[11] iodine,[12] α-amino acids,[13] *N*-heterocyclic carbenes[14] or polymers.[15] However, all these systems have deficiencies with respect to catalyst loading, carbon dioxide pressure, substrate scope and/or need for toxic solvents.[16] Building on our experience in the development of catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide,[17] the conversion of aziridines to oxazolidinones presented a new challenge with additional complications due to the presence of a substituent on the nitrogen atom of the aziridine and the possibility of forming regioisomeric products. Herein we present an aluminium-based catalyst for the coupling of aziridines with carbon dioxide at moderate temperature under solvent-free conditions. The reactions efficiently gave the corresponding oxazolidinones in high yields.

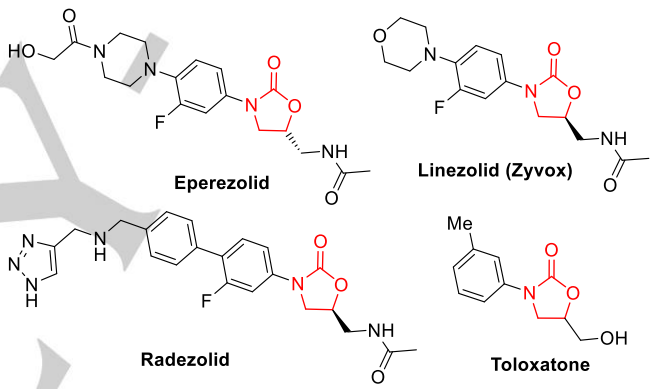

Figure 1. Examples of medicinally important oxazolidinones.

Results and Discussion

Initial reactions were carried out using 1-benzyl-2-phenylaziridine[15a] (**1a**) as substrate (Table 1). Pleasingly, 3-benzyl-5-phenyloxazolidin-2-one (**2a**) was obtained as a single regioisomer with 100% conversion when substrate **1a** and carbon dioxide (10 bar) were stirred with 2.5 mol% of aluminium complex **3**[18] (Figure 2) for 24 hours at 50 °C (entry 1). A similar result was obtained, when the carbon dioxide pressure was reduced to 5 bar (entry 2), though the conversion dropped significantly when the carbon dioxide pressure was reduced to 1 bar (entry 3). The conditions of Table 1, entry 3 were then used to screen the catalytic activity of complexes **4**[19] and **5**[20] (entries 4,5) and complex **5** was found to restore the complete conversion of **1a** into **2a** (entry 5). Use of 1.5 mol% of catalyst **5** still gave 97% conversion (entry 6), but a significant reduction in conversion to 77% was apparent when the catalyst loading was further reduced to 1 mol% (entry 7). At room temperature, no reaction occurred (entry 8) and a control experiment confirmed that no reaction occurred in the absence of catalyst (entry 9). Despite its rather complex looking structure, catalyst **5** is readily available in just two steps from commercially available chemicals.[16,20]

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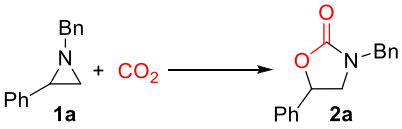
Table 1. Optimization of the reaction conditions.



Entry	CO_2 [bar]	Catalyst [mol %]	*T* [°C]	*t* [h]	Conv. (%)[a]
1	10	**3** (2.5)	50	24	100
2	5	**3** (2.5)	50	24	100
3	1	**3** (2.5)	50	65	41
4	1	**4** (2.5)	50	24	59
5	1	**5** (2.5)	50	24	100
6	**1**	**5 (1.5)**	**50**	**24**	**97**
7	1	**5** (1.0)	50	24	77
8	1	**5** (1.5)	23	24	n.r.
9	1	-	50	24	n.r.

[a] Determined by ^{1}H NMR spectroscopy. n.r. = no reaction.

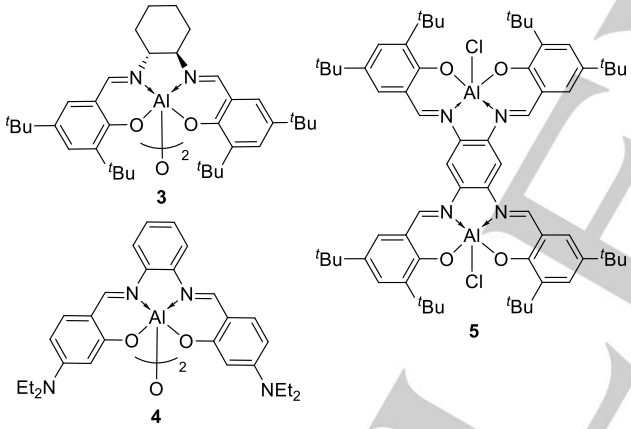
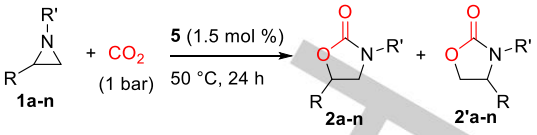
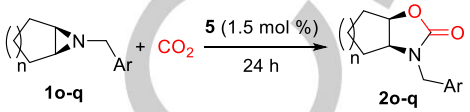


Figure 2. Structures of complexes **3-5**.

The generality of the reaction under the conditions of Table 1, entry 6 was examined using 17 aziridines[14c,15a,16, 21] **1a-q** (Scheme 1) and the results are presented in Table 2. Variously *N*-substituted 2-phenylaziridines **1a-f** underwent coupling with CO_2 to give products **2a-f** in 72-91% isolated yields and with regioselectivities of 95-100%. Substrates **1e,f** with a secondary alkyl group on the nitrogen atom required longer reaction times to give complete conversions and substrate **1g** with a *tert*-butyl group on its nitrogen atom failed to react. These results are clearly indicative of a mechanism in which complex **5** coordinates to the nitrogen atom of the aziridine. 2-Alkyl aziridines, **1h,i** were also good substrates, giving oxazolidinones **2h-i** in 89-94% isolated yields with regioselectivities of at least



a: R=Ph; R'=Bn. **b:** R=Ph; R'=Allyl. **c:** R=Ph; R'=Et. **d:** R=Ph; R'=Bu.
e: R=Ph; R'=cyclopropyl. **f:** R=Ph; R'=isopropyl. **g:** R=Ph; R'=*tert*-butyl.
h: R=Bu; R'=Bn. **i:** R=Oct; R'=Bn. **j:** R=4-MeOC_6H_4; R'=Bu.
k: R=4-MeC_6H_4; R'=Bu. **l:** R=4-ClC_6H_4; R'=Bu. **m:** R=4-BrC_6H_4; R'=Bu.
n: R=4-$NO_2C_6H_4$; R'=Bu.



o: n=1; Ar=Ph. **p:** n=2; Ar=Ph. **q:** n=2; Ar=4-$NO_2C_6H_4$.

Scheme 1. Substrate scope of the coupling of CO_2 with aziridines catalysed by complex **5**.

Table 2. Synthesis of oxazolidinones **2a-r**.

Substrate	CO_2 [bar]	*T* [°C]	*t* [h]	Conv. (%)[a]	Regioselectivty (**2**:**2'**)[a]	Yield (%)[b]
1a	1	50	24	97	100:0	89
1b	1	50	24	100	95:5	84
1c	1	50	24	99	94:6	91
1d	1	50	24	100	96:4	89
1e	1	50	44	100	95:5	72
1f	1	50	32	100	100:0	83
1g	1	50	24	0		
1h	1	50	24	100	80:20	89
1i	1	50	24	100	86:14	94
1j	1	50	24	100	100:0	78
1k	1	50	24	100	98:2	88
1l	1	50	24	100	94:6	91
1m	1	50	24	100	94:6	93
1n	1	50	40	100	90:10	86
1o	1	50	24	100		72
1p	10	100	24	100		72
1q	10	100	24	100		86

[a] Determined by ^{1}H NMR spectroscopy of the reaction mixture before purification. n.r. = no reaction. [b] Total isolated yield of **2** and **2'** (when present).

80%. *N*-Butyl 2-arylaziridines **1j-n** with either electron-donating or electron-withdrawing substituents on the aryl group gave

oxazolidinones **2j-n** in 78-93% yields and with at least 90% regioselectivity. Notably, however, substrate **1n** with a 4-nitrophenyl substituent required a reaction time of 40 hours, suggestive of a mechanism which involves a build-up of positive charge at the benzylic position of the aziridine during the mechanism. Bicyclic 2,3-disubstituted aziridines **1o-q** were also suitable substrates, giving oxazolidinones **2o-q**. Cyclopentyl aziridine **2o** was highly reactive under the standard reaction conditions (50 °C, 1 bar CO_2, 24 hours), whilst cyclohexyl aziridines **2p,q** were less reactive and required a temperature of 100 °C with 10 bar CO_2 pressure for 24 hours. The stereochemistry of products **2p,q** provides useful mechanistic information and for both products, ^{1}H and ^{13}C NMR spectroscopy indicated the formation of a single diastereomer. In the case of **2q**, this was unambiguously determined to be cis by single crystal X-ray analysis (Figure 3).[16,22]

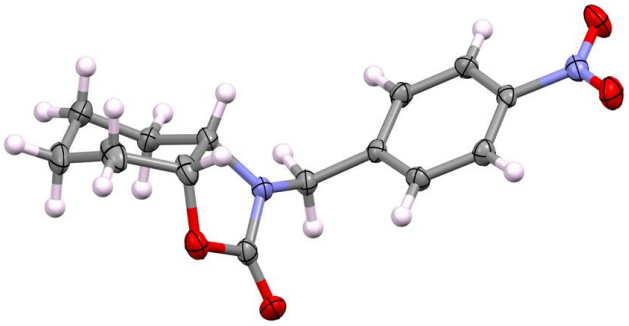
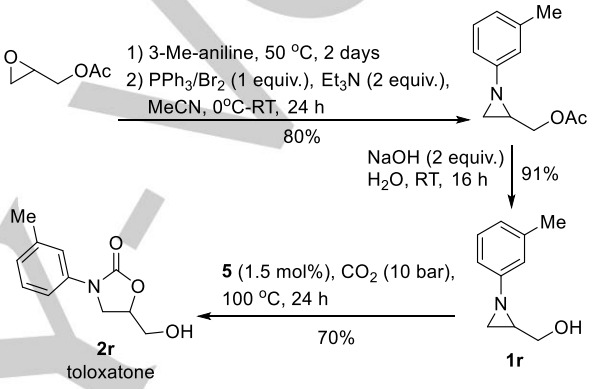


Figure 3. Ellipsoid diagram of the X-ray structure of compound **2q**.

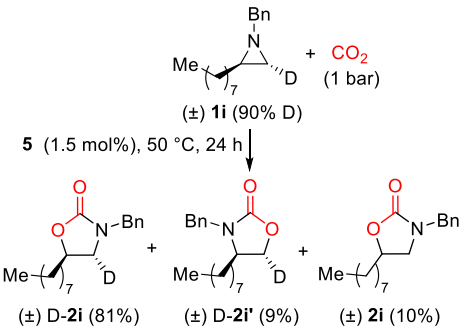
The above reactions were all carried out on a 0.5 mmol (ca 100 mg) scale. However, the reaction was found to be scalable without difficulty. Thus, a reaction at 50 °C and 1 bar CO_2 pressure using 4.18 g (20 mmol) of aziridine **1a** gave 99% conversion to oxazolidinone **2a** which was isolated in 96% yield. Catalyst **5** could be recovered in 95% yield simply by adding acetonitrile to the reaction mixture and was then used to convert aziridine **1d** into oxazolidinone **2d** with 100% conversion (87% isolated yield) and 95% regioselectivity under the conditions of Table 1, entry 6. Thus, complex **5** can be recovered and reused without loss of catalytic activity.

To illustrate the applicability of the methodology, a total synthesis of toloxatone[23] **2r** was undertaken as shown in Scheme 2. Thus, glycidyl acetate was converted in two steps into aziridine **1r**. Compound **1r** could then be converted into toloxatone **2r** in 70% isolated yield by treatment with carbon dioxide in the presence of catalyst **5**. The optimal conditions for this conversion were found to be 100 °C and 10 bar of carbon dioxide pressure.

The regiochemistry observed in reactions using substrates **1a-n** and the slower rate of reaction of substrate **1n** are indicative of a mechanism that involves cleavage of the more substituted C-N bond of the aziridine and at least partial cleavage of this bond during the rate determining step of the catalytic cycle. In contrast, the complete retention of stereochemistry observed with bicyclic substrates **1p,q** is the result found in related reactions between carbon dioxide and epoxides when the reaction occurs at the less substituted end of the heterocycle.[24] To investigate this further, reactions were carried out using deuterated *trans*-**1i** (90% deuterium incorporation). As shown in Scheme 3, both regioisomeric products: deuterated **2i** and deuterated **2i'** were formed exclusively as the *trans*-isomer. Deuterated **2i** was again the major product and arises from insertion of carbon dioxide into the more substituted C-N bond of the aziridine. Hence, whichever C-N bond of the aziridine carbon dioxide inserts into, the reaction occurs with complete retention of the stereochemistry of the aziridine.



Scheme 2. Total synthesis of toloxatone.



Scheme 3. Reaction with deuterated trans-aziridine **1i**.

To further probe the reaction mechanism, a Hammett plot was constructed using kinetic data obtained using substrates **1a,j-n** from reactions carried out at 50 °C and 1 bar carbon dioxide pressure with dichloroethane as solvent.[16] The general rate equation for the reaction is: rate = k[aziridine]^a[CO_2]^b[**5**]^c. Since species **5** is a catalyst, and a large excess of carbon dioxide was present, this simplifies to: rate = k_{obs}[aziridine]^a where k_{obs} = k[CO_2]^b[**5**]^c. The disappearance of the aziridine was monitored by ^{1}H NMR spectroscopy and all reactions were found to show a good fit to first order kinetics implying that a=1. The resulting first order rate constants are given in Table 3.

Table 3. Kinetic data for the reaction of substrates **1a,j-n**.

Substrate	Aromatic substituent	k_{obs} x 10^3 min^{-1} [a]	σ	log[(k_{obs}X)/(k_{obs}H)]
1a	H	-3.630 ± 0.000	0.00	0.00
1j	4-OMe	-29.365 ± 1.145	-0.27	0.91
1k	4-Me	-9.930 ± 0.540	-0.17	0.44
1l	4-Cl	-1.084 ± 0.185	0.23	-0.55
1m	4-Br	-0.606 ± 0.022	0.23	-0.78
1n	4-NO_2	-0.179 ± 0.001	0.78	-1.31

[a] Average of two, mutually consistent, separate experiments.

The Hammett plot constructed from the relative rate data in Table 3 is shown in Figure 4 and has a negative slope, indicative of a build-up of positive charge at the more hindered carbon atom of the aziridine during the catalytic cycle. However, the magnitude of the reaction constant (-2.1) is considerably smaller than the -4 to -5 which is characteristic of reactions which involve formation of a full positive charge at a benzylic position during the rate determining step of the reaction.[25]

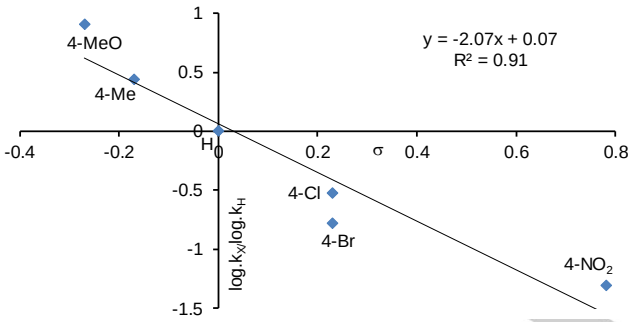
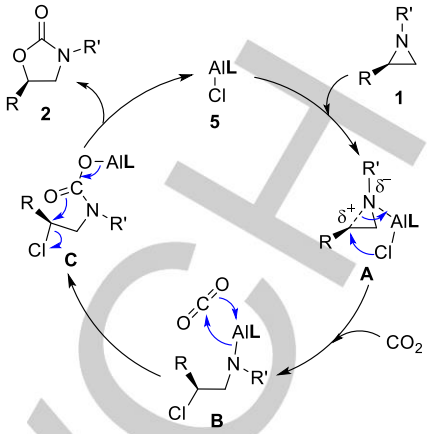


Figure 4. Hammett plot for the synthesis of oxazolidinones **2a,j-n** catalysed by complex **5**.

On the basis of the stereochemical, regiochemical and kinetic evidence, the catalytic cycle shown in Scheme 4 is proposed as the simplest mechanism that fits all of the data. Chelation of aziridines **1** to complex **5** results in formation of intermediate **A** in which the aziridine C–N bond best able to support a partial positive charge is preferentially lengthened. Intermediate **A** then undergoes aziridine ring-opening selectively at the lengthened C–N bond to give intermediate **B**. Reaction of intermediate **B** with carbon dioxide forms intermediate **C** which can cyclize to form oxazolidinone **2** and regenerate catalyst **5**. Overall the catalytic cycle involves two substitution reactions, each of which occurs with inversion of configuration, at the more hindered carbon atom of the aziridine ring, explaining both the regio- and stereochemistry. The build-up of partial positive charge in intermediate **A** correctly accounts for the observed kinetic data.



Scheme 4. Proposed catalytic cycle.

Conclusions

An efficient procedure for the synthesis of oxazolidinones by the reaction of carbon dioxide with aziridines under mild reaction conditions has been developed. The reaction is regioselective, scalable and gives oxazolidinones in good to high yields. The homogeneous catalyst can be recovered and reused and the methodology has been used to prepare the antidepressant, toloxatone. Mechanistic studies involving studies of the reaction stereochemistry and kinetics suggested that the reaction occurs at the more substituted carbon of the aziridine with overall retention of configuration at this position. A catalytic cycle is proposed which accounts for all of the experimentally observed features. Compared to previously reported systems, the reaction has wide substrate scope, requires a low catalyst loading, low carbon dioxide pressure and occurs under solvent-free conditions.

Experimental Section

General Information. All chemicals were purchased from Sigma-Aldrich and used as received. Aziridines **1a–g** and **1j–n** were prepared by the method of Du et al.[15a] Aziridines **1h,l**,**o-q** and 1-(3-methylphenyl)-2-(acetoxymethyl)aziridine were prepared by the method of Anaya de Parrodi *et al*.[21b] Metal complexes were prepared as previously reported.[18,19,20] Reactions were monitored by analytical TLC on Merck silica gel 60 F_{254} plates. Column chromatography was performed with Aldrich silica gel (220-440 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-400 spectrometer Chemical shifts (δ) are reported relative to solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR and $CDCl_3$ 77.23 ppm for ^{13}C NMR). Melting points were determined with a Stuart SMP20 apparatus and are uncorrected. FT-IR spectra were recorded using PerkinElmer 400 spectrometer.

X-Ray Crystallography. Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-Kα radiation (λ= 1.54184 Å) using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "Crysalis".[26] Face-indexed absorption corrections were

applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[27] OLEX2[28] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithms used for structure solution were "ShelXT dual-space".[29] Refinement by full-matrix least-squares used the SHELXL-97[30] algorithm within OLEX2.[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed by difference map and allowed to refine.

General procedure for the coupling of aziridines with CO_2 at atmospheric pressure. A mixture of aziridine (0.5 mmol), and catalyst **5** (0.015 mmol) was stirred at 50 °C under CO_2 (1 atm) for the appropriate time, then the reaction was allowed to cool to room temperature. The conversion of aziridine to oxazolidinones and the regioselectivity were determined by ^{1}H NMR analysis. The residue was purified by silica gel column chromatography using EtOAc and petroleum ether as eluents to give the corresponding oxazolidinones.

General procedure for the synthesis of oxazolidinones under pressure. A mixture of aziridine (0.5 mmol), and catalyst **5** (0.015 mmol) was placed in a stainless steel autoclave and the reactor was heated to the desired temperature, then pressurised with CO_2 to the required pressure. The reaction mixture was stirred for 24 h, then the autoclave was cooled in liquid nitrogen and excess CO_2 vented. Conversion of aziridine to oxazolidinones was determined by ^{1}H NMR analysis. The residue was purified by silica gel column chromatography using EtOAc and petroleum ether as eluents to give the corresponding oxazolidinones.

Synthesis of 1-(3-Methylphenyl)-2-(hydroxymethyl)aziridine (1r). A mixture of 1-(3-methylphenyl)-2-(acetoxymethyl)aziridine (1 equiv.) and NaOH (2 equiv.) in H_2O was stirred at room temperature overnight. Then, the reaction mixture was extracted with EtOAc (3x10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using EtOAc and petroleum ether (2:3) as eluent to give 1-(3-Methylphenyl)-2-(hydroxymethyl)aziridine (1r) as a colourless liquid in 91% yield.

Reaction kinetics. Catalyst **5** (0.015 mmol) was added to a 1M solution of aziridine (0.5 mmol) in dichloroethane. The resulting solution was stirred at 50 °C under CO_2 (1 atm) and at appropriate time intervals, samples were removed and analysed by ^{1}H NMR spectroscopy to determine the relative amounts of aziridine and oxazolidinones present. All kinetic experiments were carried out in duplicate and gave consistent results.

Characterizing data for previously unreported aziridines.

1-Butyl-2-(4-methoxyphenyl)aziridine (1j). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (d *J* = 8.8 Hz, 2H, ArH), 6.84 (d *J* = 8.8 Hz, 2H, ArH), 3.78 (s, 3H, OCH_3), 2.51-2.45 (m, 1H, NC*H*$_2$CH$_2$), 2.32-2.23 (m, 2H, NC*H*$_2$CH$_2$ + CHN), 1.85 (d *J* = 3.6 Hz, 1H, CH_2N), 1.61-1.55 (m, 3H, CH_2N, NCH$_2$C*H*$_2$), 1.42-1.33 (m, 2H, CH_2Me), 0.91 (t *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7, 132.7, 127.4, 113.9, 61.7, 55.5, 41.0, 37.5, 32.2, 20.8, 14.3 ppm. IR (neat): υ_{max} = 2932 and 2869 cm^{-1}; MS (ESI): calcd. for $C_{13}H_{20}NO$ (MH^+) 206.1539, found 206.1540, 411.307 $[2M+H]^+$.

1-Butyl-2-(4-chlorophenyl)aziridine (1l). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 (d *J* = 8.4 Hz, 2H, ArH), 7.17 (d *J* = 8.8 Hz, 2H, ArH), 2.50-2.44 (m, 1H, NC*H*$_2$CH$_2$), 2.33-2.27 (m, 1H, NC*H*$_2$CH$_2$), 2.25 (dd *J* = 6.4, 3.2 Hz, 1H, CHN), 1.82 (d *J* = 4.0 Hz, 1H, CH_2N), 1.65 (d *J* = 6.8 Hz, 1H, CH_2N), 1.60-1.53 (m, 2H, NCH$_2$C*H*$_2$), 1.42-1.32 (m, 2H, CH_2Me), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.3, 132.5, 128.5, 127.7, 61.6, 40.7, 38.1, 32.1, 20.7, 14.3 ppm. IR (neat): υ_{max} = 3038, 2962, 2931, 2859 and 2817 cm^{-1}; MS (ESI): calcd. for $C_{12}H_{17}N^{35}Cl$ (MH^+) 210.1044, found 210.1043, 419.2011 $[2M+H]^+$.

1-Butyl-2-(4-bromophenyl)aziridine (1m). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d *J* = 8.4 Hz, 2H, ArH), 7.12 (d *J* = 8.4 Hz, 2H, ArH), 2.51-2.45 (m, 1H, NC*H*$_2$CH$_2$), 2.34-2.27 (m, 1H, NC*H*$_2$CH$_2$), 2.24 (dd *J* = 6.4, 3.2 Hz, 1H, CHN), 1.82 (d *J* = 3.6 Hz, 1H, CH_2N), 1.66 (d *J* = 6.4 Hz, 1H, CH_2N), 1.61-1.54 (m, 2H, NCH$_2$C*H*$_2$), 1.42-1.33 (m, 2H, CH_2Me), 0.90 (t *J* = 7.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.8, 131.4, 128.0, 120.5, 61.5, 40.7, 38.1, 32.1, 20.7, 14.3 ppm. IR (neat): υ_{max} = 3045, 2957, 2930, 2867 and 2821 cm^{-1}; MS (ESI): calcd. for $C_{12}H_{17}N^{79}Br$ (MH^+) 254.0539, found 254.0536.

1-Butyl-2-(4-nitrophenyl)aziridine (1n). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d *J* = 8.8 Hz, 2H, ArH), 7.39 (d *J* = 8.8 Hz, 2H, ArH), 2.52-2.45 (m, 1H, NC*H*$_2$CH$_2$), 2.40-2.33 (m, 2H, NC*H*$_2$CH$_2$, CHN), 1.87 (d *J* = 2.8 Hz, 1H, CH_2N), 1.78 (d *J* = 6.4 Hz, 1H, CH_2N), 1.61-1.53 (m, 2H, NCH$_2$C*H*$_2$), 1.42-1.33 (m, 2H, CH_2Me), 0.90 (t *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9, 146.9, 126.9, 123.7, 61.3, 40.6, 39.2, 32.0, 20.7, 14.2 ppm. IR (neat): υ_{max} = 2958, 2932, 2871 and 1601 cm^{-1}; MS (ESI): calcd. for $C_{12}H_{17}N_2O_2$ (MH^+) 221.1285, found 221.1288.

7-(4-Nitrobenzyl)-7-azabicyclo[4.1.0]heptane (1q). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d *J* = 8.8 Hz, 2H, ArH), 7.53 (d *J* = 8.8 Hz, 2H, ArH), 3.54 (s, 2H, NCH_2), 1.89-1.76 (m, 4H, 2 x CH_2), 1.66-1.64 (m, 2H, 2xNCH), 1.44-1.35 (m, 2H, CH_2), 1.25-1.16 (m, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.0, 146.9, 128.1, 123.6, 63.7, 38.9, 24.5, 20.6 ppm. IR (neat): υ_{max} = 2933, 2855 and 1601 cm^{-1}; MS (ESI): calcd. for $C_{13}H_{17}N_2O_2$ (MH^+) 233.1285, found 233.1284.

1-(3-Methylphenyl)-2-(hydroxymethyl)aziridine (1r). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (t *J* = 7.6 Hz, 1H, ArH), 6.84-6.80 (m, 3H, ArH), 3.99-3.94 (m, 1H, CH_2O), 3.59-3.50 (m, 2H, CH_2O + OH), 2.39-2.34 (m, 1H, CHN), 2.30-2.28 (m, 4H, CH_3, CH_2N), 2.08 (d, *J* = 6.4 Hz, 1H, CH_2N) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.8, 139.0, 128.9, 123.8, 121.7, 118.1, 63.0, 41.0, 31.4, 21.5 ppm. IR (neat): υ_{max} = 3339 and 2920 cm^{-1}; MS (ESI): calcd for $C_{10}H_{14}NO$ (MH^+) 164.1070, found 164.1068, 186.0887 $[M+Na]^+$, 327.2062 $[2M+H]^+$, 349.1881 $[2M+Na]^+$.

Characterizing data for oxazolidinones 2a-r.

3-Benzyl-5-phenyloxazolidin-2-one (2a).[15a] Analytical TLC on silica gel, 1:4 EtOAc/petroleum ether, R_f = 0.33; colourless solid; yield 89% (112 mg); M.p 68–69 °C (lit.[15a] 60–64 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.34 (m, 5H, ArH), 7.32-7.28 (m, 5H, ArH), 5.47 (t *J* = 8.4 Hz, 1H, CHO), 4.57 (d *J* = 15.2 Hz, 1H, NCH_2Ph), 4.42 (d *J* = 15.2 Hz, 1H, NCH_2Ph), 3.77 (t *J* = 8.8 Hz, 1H, CH_2N), 3.31 (dd *J* = 8.8, 7.6 Hz, 1H, CH_2N) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 138.7, 135.7, 129.0, 128.9, 128.3, 128.2, 125.6, 74.7, 51.7, 48.5 ppm; IR (neat): υ_{max} = 1739 cm^{-1}; MS (ESI): calcd. for $C_{16}H_{16}NO_2$ (MH^+) 254.1176, found 254.1163, 276.0981 $[M+Na]^+$.

3-Allyl-5-phenyloxazolidin-2-one (2b).[31] Analytical TLC on silica gel, 1:4 EtOAc/petroleum ether, R_f = 0.23; pale yellow liquid; yield 84% (86 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.32 (m, 5H, ArH), 5.82-5.72 (m, 1H, =CH_2), 5.48 (t *J* = 7.6 Hz, 1H, CHO), 5.25-5.20 (m, 2H, CH=CH_2), 3.96-3.82 (m, 3H, CH_2N, CH_2), 3.39 (t *J* = 7.6 Hz, 1H, CH_2N) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 138.8, 131.9, 129.0, 128.9, 125.6, 118.9, 74.6, 51.9, 47.0 ppm; IR (neat): υ_{max} = 1739 cm^{-1}; MS (ESI): calcd. for $C_{12}H_{14}NO_2$ (MH^+) 204.1019, found 204.1019, 226.0840 $[M+Na]^+$.

3-Ethyl-5-phenyloxazolidin-2-one (2c).[8b] Analytical TLC on silica gel, 3:7 EtOAc/petroleum ether, R_f = 0.40; colourless liquid; yield 91% (87 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.33 (m, 5H, ArH), 5.47 (t *J* = 8.4 Hz, 1H, CHO), 3.91 (t *J* = 8.8 Hz, 1H, CH_2N), 3.44-3.29 (m, 3H, CH_2N, CH_2), 1.16 (t *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 138.9, 129.0, 128.9, 125.6, 74.4, 51.7, 39.0, 12.7 ppm; IR (neat): υ_{max} = 1738 cm^{-1}; MS (ESI): calcd. for $C_{11}H_{14}NO_2$ (MH^+) 192.1019, found 192.1018, 214.0839 $[M+Na]^+$.

3-Butyl-5-phenyloxazolidin-2-one (2d).[10c] Analytical TLC on silica gel, 1:4 EtOAc/petroleum ether, Rf = 0.29; colourless liquid; yield 89% (98 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.33 (m, 5H, ArH), 5.47 (t *J* = 8.0 Hz, 1H, CHO), 3.90 (t *J* = 8.8 Hz, 1H, CH_2N), 3.41 (dd *J* = 8.4, 7.6 Hz, 1H, CH_2N), 3.37-3.22 (m, 2H, CH_2), 1.57-1.49 (m, 2H, CH_2), 1.39-1.30 (m, 2H, CH_2), 0.93 (t *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.0, 139.0, 129.0, 128.9, 125.6, 74.4, 52.3, 44.0, 29.5, 20.0, 13.8 ppm; IR (neat): υ_{max} = 1740 cm^{-1}; MS (ESI): calcd. for $C_{13}H_{18}NO_2$ (MH^+) 220.1332, found 220.1332, 242.1152 $[M+Na]^+$.

3-Cyclopropyl-5-phenyloxazolidin-2-one (2e).[15a] Analytical TLC on silica gel, 1:4 EtOAc/petroleum ether, R_f = 0.25; colourless solid; yield 72% (73 mg); M.p 60–61 °C (lit.[15a] 52–55 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.31 (m, 5H, ArH), 5.42 (t *J* = 8.0 Hz, 1H, CHO), 3.88 (t *J* = 8.4 Hz, 1H, CH_2N), 3.43 (dd *J* = 8.4, 7.6 Hz, 1H, CH_2N), 2.59-2.54 (m, 1H, NCH), 0.85-0.68 (m, 4H, 2xCH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 138.7, 129.0, 128.9, 125.6, 74.6, 53.6, 26.0, 6.2, 5.7 ppm; IR (neat): υ_{max} = 1734 cm^{-1}; MS (ESI): calcd. for $C_{12}H_{14}NO_2$ (MH^+) 204.1019, found 204.1022, 226.0841 $[M+Na]^+$.

3-Isopropyl-5-phenyloxazolidin-2-one (2f).[15a] Analytical TLC on silica gel, 3:7 EtOAc/petroleum ether, R_f = 0.35; colourless liquid; yield 83% (85 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.33 (m, 5H, ArH), 5.46 (t *J* = 8.4 Hz, 1H, CHO), 4.16 (septet *J* = 6.8 Hz, 1H, NCH), 3.85 (t *J* = 8.8 Hz, 1H, CH_2N), 3.36 (dd *J* = 8.4, 7.6 Hz, 1H, CH_2N), 1.22 (d *J* = 7.2 Hz, 3H, CH_3), 1.16 (d *J* = 6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.3, 139.1, 129.0, 128.9, 125.6, 74.6, 47.5, 45.0, 20.2, 19.7 ppm; IR (neat): υ_{max} = 1736 cm^{-1}; MS (ESI): calcd. for $C_{12}H_{16}NO_2$ (MH^+) 206.1176, found 206.1179, 228.1000 $[M+Na]^+$.

3-Benzyl-5-butyloxazolidin-2-one (2h).[32] Analytical TLC on silica gel, 1:4 EtOAc/petroleum ether, R_f = 0.29; colourless liquid; yield 89% (104 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37-7.27 (m, 5H, ArH), 4.49-4.35 (m, 3H, CHO, NCH_2Ph), 3.45 (t *J* = 8.4 Hz, 1H, CH_2N), 3.00 (dd *J* = 8.4, 7.2 Hz, 1H, CH_2N), 1.76-1.64 (m, 1H, CH_2), 1.60-1.52 (m, 1H CH_2), 1.41-1.24 (m, 4H, 2xCH_2), 0.88 (t *J* = 6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.3, 135.9, 128.9, 128.2, 127.9, 73.7, 49.3, 48.3, 34.7, 26.6, 22.4, 13.9 ppm; IR (neat): υ_{max} = 1738 cm^{-1}; MS (ESI): calcd. for $C_{14}H_{20}NO_2$ $(MH)^+$ 234.1489, found 234.1479, 256.1297 $[M+Na]^+$.

3-Benzyl-5-octyloxazolidin-2-one (2i). Analytical TLC on silica gel, 1:4 EtOAc/petroleum ether, R_f = 0.33; colourless liquid; yield 94% (136 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37-7.25 (m, 5H, ArH), 4.49-4.36 (m, 3H, CHO, NCH_2Ph), 3.45 (t *J* = 8.8 Hz, 1H, CH_2N), 3.00 (dd *J* = 8.4, 7.2 Hz, 1H, CH_2N), 1.74-1.66 (m, 1H, CH_2), 1.58-1.51 (m, 1H, CH_2), 1.42-1.24 (m, 12H, 6xCH_2), 0.86 (t *J* = 6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.3, 136.0, 128.9, 128.2, 128.0, 73.8, 49.4, 48.4, 35.1, 31.9, 29.5, 29.4, 29.3, 24.6, 22.8, 14.2 ppm; IR (neat): υ_{max} = 1741 cm^{-1}; MS (ESI): calcd. for $C_{18}H_{28}NO_2$ $(MH)^+$ 290.2115, found 290.2113, 312.1931 $[M+Na]^+$.

3-Butyl-5-(4-methoxyphenyl)oxazolidin-2-one (2j). Analytical TLC on silica gel, 1:3 EtOAc/petroleum ether, R_f = 0.27; colourless solid; yield 78% (98 mg); M.p 58–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d *J* = 8.8 Hz, 2H, ArH), 6.92 (d *J* = 8.8 Hz, 2H, ArH), 5.42 (t *J* = 8.4 Hz, 1H, CHO), 3.85 (t *J* = 8.4 Hz, 1H, CH_2N), 3.81 (s, 3H, OCH_3), 3.41 (dd *J* = 8.4, 7.6 Hz, 1H, CH_2N), 3.39-3.22 (m, 2H, NCH_2), 1.58-1.50 (m, 2H, CH_2), 1.40-1.31 (m, 2H, CH_2), 0.94 (t *J* = 7.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1, 158.1, 130.9, 127.3, 114.4, 74.5, 55.5, 52.3, 44.1, 29.6, 20.0, 13.9 ppm; IR (neat): υ_{max} = 1728 cm^{-1}; MS (ESI): calcd. for $C_{14}H_{20}NO_3$ $(MH)^+$ 250.1438, found 250.1435, 272.1258 $[M+Na]^+$.

3-Butyl-5-(4-methylphenyl)oxazolidin-2-one (2k).[14c] Analytical TLC on silica gel, 1:3 EtOAc/petroleum ether, R_f = 0.40; colourless solid; yield 88% (103 mg); M.p 46–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 (d *J* = 8.4 Hz, 2H, ArH), 7.20 (d *J* = 8.0 Hz, 2H, ArH), 5.44 (t *J* = 8.0 Hz, 1H, CHO), 3.87 (t *J* = 8.8 Hz, 1H, CH_2N), 3.40 (dd *J* = 8.4, 7.2 Hz, 1H, CH_2N), 3.37-3.22 (m, 2H, NCH_2), 2.35 (s, 3H, CH_3), 1.57-1.49 (m, 2H, CH_2), 1.40-1.30 (m, 2H, CH_2), 0.93 (t *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 138.8, 136.0, 129.7, 125.7, 74.5, 52.3, 44.1, 29.6, 21.3, 20.0, 13.9 ppm; IR (neat): υ_{max} = 1728 cm^{-1}; MS (ESI): calcd. for $C_{14}H_{20}NO_2$ $(MH)^+$ 234.1489, found 234.1484, 256.1306 $[M+Na]^+$.

3-Butyl-5-(4-chlorophenyl)oxazolidin-2-one (2l). Analytical TLC on silica gel, 3:7 EtOAc /petroleum ether, R_f = 0.33; colourless solid; yield 91% (115 mg); M.p 53–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d *J* = 8.8 Hz, 2H, ArH), 7.29 (d *J* = 8.8 Hz, 2H, ArH), 5.45 (t *J* = 8.8 Hz, 1H, CHO), 3.90 (t *J* = 8.8 Hz, 1H, CH_2N), 3.39-3.22 (m, 3H, CH_2N, NCH_2), 1.56-1.49 (m, 2H, CH_2), 1.38-1.29 (m, 2H, CH_2), 0.93 (t *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 137.6, 134.8, 129.3, 127.0, 73.7, 52.2, 44.1, 29.5, 20.0, 13.8 ppm; IR (neat): υ_{max} = 1727 cm^{-1}; MS (ESI): calcd. for $C_{13}H_{17}{}^{35}ClNO_2$ $(MH)^+$ 254.0942, found 254.0940, 276.0761 $[M+Na]^+$.

5-(4-Bromophenyl)-3-butyloxazolidin-2-one (2m). Analytical TLC on silica gel, 1:3 EtOAc/petroleum ether, R_f = 0.22; colourless solid; yield 93% (139 mg); M.p 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d *J* = 8.4 Hz, 2H, ArH), 7.23 (d *J* = 8.4 Hz, 2H, ArH), 5.43 (t *J* = 8.4 Hz, 1H, CHO), 3.90 (t *J* = 8.8 Hz, 1H, CH_2N), 3.38-3.21 (m, 3H, CH_2N, NCH_2), 1.56-1.48 (m, 2H, CH_2), 1.38-1.29 (m, 2H, CH_2), 0.92 (t *J* = 7.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 138.1, 132.2, 127.3, 122.9, 73.7, 52.2, 44.1, 29.5, 20.0, 13.8 ppm; IR (neat): υ_{max} = 1724 cm^{-1}; MS (ESI): calcd. for $C_{13}H_{17}{}^{79}BrNO_2$ $(MH)^+$ 298.0437, found 298.0435, 320.0258 $[M+Na]^+$.

3-Butyl-5-(4-bromophenyl)oxazolidin-2-one (2n). Analytical TLC on silica gel, 2:3 EtOAc/petroleum ether, R_f = 0.24; yellow liquid; yield 86% (114 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d *J* = 8.8 Hz, 2H, ArH), 7.54 (d *J* = 8.8 Hz, 2H, ArH), 5.59 (dd *J* = 8.8, 7.6 Hz, 1H, CHO), 4.00 (t *J* = 8.8 Hz, 1H, CH_2N), 3.38 (dd *J* = 8.8, 7.2 Hz, 1H, CH_2N), 3.37-3.21 (m, 2H, CH_2), 1.55-1.47 (m, 2H, CH_2), 1.34-1.28 (m, 2H, CH_2), 0.90 (t *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.4, 148.1, 146.2, 126.3, 124.3, 73.1, 51.9, 44.1, 29.4, 19.9, 13.7 ppm; IR (neat): υ_{max} = 1743 cm^{-1}; MS (ESI): calcd. for $C_{13}H_{17}N_2O_4$ $(MH)^+$ 265.1183, found 265.1181, 287.1004 $[M+Na]^+$.

3-Benzylhexahydro-2*H*-cyclopenta[*d*]oxazol-2-one (2o).[33] Analytical TLC on silica gel, 2:3 EtOAc/petroleum ether, R_f = 0.38; colourless liquid; yield 72% (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36-7.27 (m, 5H, ArH), 4.87-4.84 (m, 1H, CHO), 4.76 (d *J* = 15.2 Hz, 1H, NCH_2Ph), 4.06 (d *J* = 15.2 Hz, 1H, NCH_2Ph), 3.96 (t *J* = 6.8 Hz, 1H, CHN), 2.08-2.04 (m, 1H, CH_2), 1.87-1.83 (m, 1H, CH_2), 1.70-1.60 (m, 3H, CH_2CH_2), 1.43-1.33 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.5, 136.2, 128.9, 128.3, 128.0, 79.2, 59.6, 46.7, 34.0, 30.5, 22.2 ppm; IR (neat): υ_{max} = 1731 cm^{-1}; MS (ESI): calcd. for $C_{13}H_{16}NO_2$ $(MH)^+$ 218.1176, found 218.1175, 240.0993 $[M+Na]^+$.

3-Benzylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (2p).[31] Analytical TLC on silica gel, 2:3 EtOAc/petroleum ether, R_f = 0.40; pale yellow liquid; yield 72% (83 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.27 (m, 5H, ArH), 4.77 (d *J* = 14.8 Hz, 1H, NCH_2), 4.45 (q *J* = 5.2 Hz, 1H, CHO), 4.05 (d *J* = 15.2 Hz, 1H, NCH_2), 3.48 (q *J* = 5.6 Hz, 1H, CHN), 1.94-1.86 (m, 1H, CH_2), 1.77-1.69 (m, 2H, CH_2), 1.57-1.37 (m, 4H, 2xCH_2), 1.24-1.18 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0, 136.4, 128.8, 128.2, 127.9, 73.5, 53.6, 45.8, 27.0, 25.4, 19.7, 19.6 ppm; IR (neat): υ_{max} = 1741 cm^{-1}; MS (ESI): calcd. for $C_{14}H_{18}NO_2$ $(MH)^+$ 232.1332, found 232.1332, 254.1150 $[M+Na]^+$.

3-(4-Nitrobenzylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (2q). Analytical TLC on silica gel, 2:3 EtOAc/petroleum ether, R_f = 0.25; colourless solid; yield 86% (119 mg); M.p 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d *J* = 8.8 Hz, 2H, ArH), 7.48 (d *J* = 8.8 Hz, 2H, ArH), 4.77 (d *J* = 16.0 Hz, 1H, NCH_2), 4.52 (q *J* = 5.6 Hz, 1H, CHO), 4.24 (d *J* = 16.0 Hz, 1H, NCH_2), 3.54 (q *J* = 6.4 Hz, 1H, CHN), 1.95-1.89 (m, 1H, CH_2), 1.82-1.74 (m, 2H, CH_2), 1.57-1.40 (m, 4H, 2xCH_2), 1.28-1.22 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.1, 147.7, 144.2, 128.8, 124.1, 73.8, 54.3, 45.5, 27.0, 25.6, 19.8, 19.6 ppm; IR (neat): υ_{max} = 1742 cm^{-1}; MS (ESI): calcd. for $[C_{14}H_{17}N_2O_4]^+$ 277.1183, found 277.1180, 299.1001 $[M+Na]^+$.

5-(Hydroxymethyl)-3-(3-methylphenyl)oxazolidin-2-one (toloxatone) (2r).[34] Analytical TLC on silica gel, 3:2 EtOAc/petroleum ether, R_f = 0.09; white solid; yield 70% (72 mg); M.p 78–79 °C (lit.[34] 75–76 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (s, 1H, ArH), 7.31 (d *J* = 8.4 Hz, 1H, ArH), 7.24 (t *J* = 8.0 Hz, 1H, ArH), 6.96 (d *J* = 7.6 Hz, 1H, ArH), 4.74-4.68 (m, 1H, CHN), 4.03-3.92 (m, 3H, CH_2N, CH_2OH), 3.76-3.70 (m, 1H, CH_2OH), 2.80 (t *J* = 6.8 Hz, 1H, OH), 2.35 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 139.2, 138.1, 129.0, 125.2, 119.3, 115.6, 73.1, 62.9, 46.6, 21.8 ppm; IR (neat): υ_{max} = 3481, 2912, 1722, 1419, 1233 cm^{-1}; MS (ESI): calcd. for $C_{11}H_{14}NO_3$ $(MH)^+$ 208.0968, found 208.0968, 230.0788 $[M+Na]^+$.

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Keywords: Aluminium catalysis • aziridines • carbon dioxide fixation • oxazolidinones • Schiff bases

[1] a) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709–1742; b) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933–5947; c) B. Yu, L.-N. He, *ChemSusChem* **2015**, *8*, 52–62; d) *New and Future Developments in Catalysis, Activation of Carbon Dioxide* (Ed.: S. L. Suib), Elsevier B. V. **2013**; e) *Carbon Dioxide Utilization: Closing the Carbon Cycle* (Ed.: P. Styring, E. A. Quadrelli and K. Armstrong), Elsevier B. V., **2014**; f) D. T. Allen, C. Tran, E. Zeitler, *ACS Sustainable Chem. Eng.* **2019**, *7*, 3702−3709.

[2] M. North, *ChemSusChem* **2019**, *12*, 1763–1765

[3] For examples see: a) D. J. Diekema, R. N. Jones, *Drugs* **2000**, *59*, 7–16; b) S. Lemaire, P. M. Tulkens, F. Van Bambeke, *Antimicrob. Agents Chemother.* **2010**, *54*, 2540–2548; c) K. Michalska, E. Bednarek, E. Gruba, K. Lewandowska, M. Mizera, J. Cielecka-Piontek, *Chem. Cent. J.* **2017**, *11*, 82; d) T. Niemi, T. Repo, *Eur. J. Org. Chem.* **2019**, 1180–1188.

[4] S. G. Davies, A. M. Fletcher, P. M. Roberts, J. E. Thomson, *Org. Biomol. Chem.* **2019**, *17*, 1322–1335.

[5] C. Phung, R. M. Ulrich, M. Ibrahim, N. T. G. Tighe, D. L. Lieberman, A. R. Pinhas, *Green Chem.* **2011**, *1*, 3224–3229.

[6] X.-Y. Dou, L.-N. He, Z.-Z. Yang, J.-L. Wang, *Synlett* **2010**, 2159–2163.

[7] a) M. T. Hancock, A. R. Pinhas, *Tetrahedron Lett.* **2003**, *44*, 5457–5460; b) A. Sudo, Y. Morioka, E. Koizumi, F. Sanda, T. Endo, *Tetrahedron Lett.* **2003**, *44*, 7889–7891; c) A. Sudo, Y. Morioka, F. Sanda, T. Endo, *Tetrahedron Lett.* **2004**, *45*, 1363–1365; d) Y. Wu, L.-N. He, Y. Du, J.-Q. Wang, C.-X. Miao, W. Li, *Tetrahedron* **2009**, *65*, 6204–6210; e) H. Matsuda, A. Ninagawa, H. Hasegawa, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2717–2718; f) Y. Wu, G. Liu, *Tetrahedron Lett.* **2011**, *52*, 6450–6452.

[8] a) A. W. Miller, S. T. Nguyen, *Org. Lett.* **2004**, *6*, 2301–2304; b) W.-M. Ren, Y. Liu, X-B. Lu, *J. Org. Chem.* **2014**, *79*, 9771–9777; c) D. Adhikari, A. W. Miller, M.-H. Baik, S. T. Nguyen, *Chem. Sci.* **2015**, *6*, 1293–1300; d) S. Arayachukiat, P. Yingcharoen, S. V.C. Vummaleti, L. Cavallo, A. Poater, V. D'Elia, *Mol. Catal.* **2017**, *443*, 280–285; e) Y. Xie, C. Lu, B. Zhao, Q. Wang, Y. Yao, *J. Org. Chem.* **2019**, *84*, 1951–1958.

[9] a) T. Y. Ma, S. Z. Qiao, *ACS Catal.* **2014**, *4*, 3847–3855; b) X.-Z. Lin, Z.-Z. Yang, L.-N. He, Z.-Y. Yuan, *Green Chem.* **2015**, *17*, 795–798.

[10] a) H. Xu, X.-F. Liu, C.-S. Cao, B. Zhao, P. Cheng, L.-N. He, *Adv. Sci.* **2016**, *3*, 1600048; b) X. Wang, W.-Y. Gao, Z. Niu, L. Wojtas, J. A. Perman, Y.-S. Chen, Z. Li, B. Aguila, S. Ma, *Chem. Commun.* **2018**, *54*, 1170–1173; c) C.-S. Cao, Y. Shi, H. Xu, B. Zhao, *Dalton Trans.* **2018**, *47*, 4545–4553.

[11] a) C. Phung, A. R. Pinhas, *Tetrahedron Lett.* **2010**, *51*, 4552–4554; b) Z.-Z. Yang, L.-N. He, S.-Y. Peng, A.-H. Liu, *Green Chem.* **2010**, *12*, 1850–1854; c) Z.-Z. Yang, Y.-N. Li, Y.-Y. Wei, L.-N. He, *Green Chem.* **2011**, *13*, 2351–2353; d) H. Zhou, G.-X. Wang, W.-Z. Zhang, X.B. Lu, *ACSCatal.* **2015**, *5*, 6773–6779.

[12] H. Kawanami, Y. Ikushima, *Tetrahedron Lett.* **2002**, *43*, 3841–3844.

[13] a) H.-F. Jiang, J.-W. Ye, C.-R. Qi, L.-B. Huang, *Tetrahedron Lett.* **2010**, *51*, 928–932; b) X.-Y. Dou, L.-N. He, Z.-Z. Yang, *Synth. Commun.* **2012**, *42*, 62–74.

[14] a) J. Seayad, A. M. Seayad, J. K. P. Ng, C. L. L. Chai, *ChemCatChem* **2012**, *4*, 774–777; b) A. Ueno, Y. Kayaki, T. Ikariya, *Green Chem.* **2013**, *15*, 425–430; c) V. B. Saptal, B. M. Bhanage, *ChemSusChem* **2016**, *9*, 1980–1985; d) A.-H. Liu, Y.-L. Dang, H. Zhou, J.-J. Zhang, X-B. Lu, *ChemCatChem* **2018**, *10*, 2686–2692.

[15] a) Y. Du, Y. Wu, A.-H. Liu, L.-N. He, *J. Org. Chem.* **2008**, *73*, 4709–4712; b) C. Qi, J. Ye, W. Zeng, H. Jiang, *Adv. Synth. Catal.* **2010**, *352*, 1925–1933; c) R. A. Watile, D. B. Bagal, K. M. Deshmukh, K. P. Dhake, B. M. Bhanage, *J. Mol. Catal A.* **2011**, *351*, 196–203; d) A. C. Kathalikkattil, J. Tharun, R. Roshan, H.-G. Soek, D.-W. Park, *App. Catal. A.* **2012**, *447-448*, 107–114; e) R. A. Watile, B. M. Bhanage, *Indian J. Chem. A.* **2012**, *51*, 1354–1360. (f) V. Saptal, D. B. Shinde, R. Banerjee, B. M. Bhanage, *Catal. Sci. Technol.* **2016**, *6*, 6152–6158.

[16] See supporting information.

[17] For examples see: a) D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North, R. S. Rojas, *ChemCatChem* **2018**, *10*, 2271–2277; b) S. A. Kuznetsova, Y. A. Rulev, V. A. Larionov, A. F. Smol'yakov, Y. V. Zubavichus, V. I. Maleev, H. Li, M. North, A. S. Saghyan, Y. N. Belokon, *ChemCatChem* **2019**, *11*, 511–519; c) P. A. Carvalho, J. W. Comerford, K. J. Lamb, M. North, P. S. Reiss, *Adv. Syn. Catal.* **2019**, *361*, 345–354; d) X. Wu, C. Chen, Z. Guo, M. North, A. C. Whitwood, *ACSCatal.* **2019**, *9*, 1895–1906.

[18] W. Clegg, R. W. Harrington, M. North, P. A. Villuendas, *J. Org. Chem.* **2010**, *75*, 6201–6207.

[19] J. A. Castro-Osma, M. North, X. Wu, *Chem. Eur. J.* **2016**, *22*, 2100–2107.

[20] X. Wu, M. North, *ChemSusChem* **2017**, *10*, 74–78.

[21] a) K. J. Shaw, J. R. Luly, H. Rapoport, *J. Org. Chem.* **1985**, *50*, 4515–4523; b) C. Anaya de Parrodi, V. Vázquez, L. Quintero, E. Juaristi, *Synth. Commun.* **2001**, *31*, 3295–3302; c) C. Miniejew, F. Outurquin, X. Pannecoucke, *Org. Biomol. Chem.* **2004**, *2*, 1575–1576; d) D.

Stephens, Y. Zhang, M. Cormier, G. Chavez, H. Arman, O. V. Larionov, *Chem. Commun.* **2013**, *49*, 6558–6560; e) T. J. Senter, M. C. O'Reilly, K. M. Chong, G. A. Sulikowski, C. W. Lindsley, *Tetrahedron Lett.* **2015**, *56*, 1276–1279.

[22] CCDC 189567 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road,386 Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

[23] For previous syntheses of toloxatone see: a) S. Cacchi, G. Fabrizi, A. Goggiamani, *Heterocycles* **2003**, *61*, 505–512; b) B. Mallesham, B. M. Rajesh, P. Rajamohan Reddy, D. Srinivas, S. Trehan, *Org. Lett.* **2003**, *5*, 963–965; c) J. Li, Y. Zhang, Y. Jiang, D. Ma, *Tetrahedron Lett.* **2012**, *53*, 3981–3983; d) W. Mahy, P. K. Plucinski, C. G. Frost, *Org. Lett.* **2014**, *16*, 5020–5023; e) J. Rintjema, R. Epping, G. Fiorani, E. Martín, E. C. Escudero-Adán, A. W. Kleij, *Angew. Chem. Int. Ed.* **2016**, *55*, 3972–3976; f) Y. Toda, S. Gomyou, S. Tanaka, Y. Komiyama, A. Kikuchi, H. Suga, *Org. Lett.* **2017**, *19*, 5786–5789; g) W. Paisuwan, T. Chantra, P. Rashatasakhon, M. Sukwattanasinitt, A. Ajavakom, *Tetrahedron* **2017**, *73*, 3363–3367; h) Y. Lee, J. Choi, H. Kim, *Org. Lett.* **2018**, *20*, 5036–5039; i) W. Yi, X.-X. Fang, Q.-Y. Liu, G.-Q. Liu, *Eur. J. Org. Chem.* **2018**, 6671–6681.

[24] J. A. Castro-Osma, M. North, W. K. Offermans, W. Leitner, T. E. Müller, *ChemSusChem* **2016**, *9*, 791–794.

[25] A. Williams Free Energy Relationships in Organic and Bio-organic Chemistry; RSC: Cambridge, **2003**.

[26] CrysAlisPro, Oxford Diffraction Ltd. Version 1.171.34.41

[27] Empirical Absorption Correction Using Spherical Harmonics, Implemented in SCALE3 ABSPACK Scaling Algorithm Within CrysAlisPro Software, Oxford Diffraction Ltd. Version 1.171.34.40

[28] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, **2009**, *42*, 339–341.

[29] Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst*. **2015**, *A71*, 3–8.

[30] Sheldrick, G. M. A Short History of SHELX. *Acta Cryst.* **2008**, *A64*, 112–122.

[31] A. Baba, K. Seki, H. Matsuda, *J. Org. Chem.* **1991**, *56*, 2684–2688.

[32] M. Lv, P. Wang, D. Yuan, Y. Yao, *ChemCatChem* **2017**, *9*, 4451–4455.

[33] J. Sepúlveda-Arques, T. Armero-Alarte, A. Acero-Alarcón, E. Zaballos-García, B. Y. Solesio, J. E. Carrera, *Tetrahedron* **1996**, *52*, 2097–2102.

[34] W. Paisuwan, T. Chantra, P. Rashatasakhon, M. Sukwattanasinitt, A. Ajavakom, *Tetrahedron* **2017**, *73*, 3363–3367.

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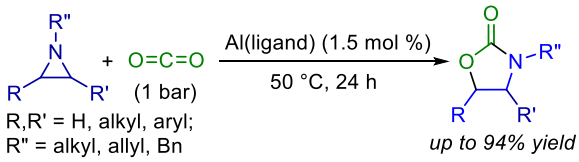

R,R' = H, alkyl, aryl;
R" = alkyl, allyl, Bn

up to 94% yield

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- solvent-free
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The synthesis of oxazolidinones by the coupling of CO_2 with aziridines catalysed by an aluminium complex is reported. Oxazolidinones are obtained in good to high yields, The process is scalable, the catalyst can be reisolated and reused and the chemistry has been applied to the synthesis of the antidepressant, toloxatone.

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Synthesis of Oxazolidinones using Carbon Dioxide as a C-1 Building Block and an Aluminium-based Catalyst