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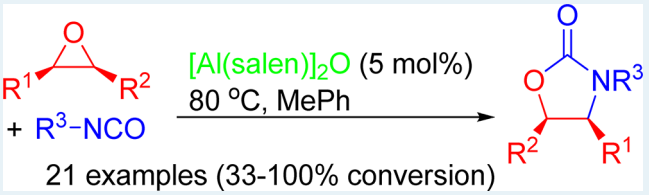
Bimetallic Aluminum(salen) Catalyzed Synthesis of Oxazolidinones from Epoxides and Isocyanates

Thilo Baronsky, Christopher Beattie, Ross W. Harrington, Reyhan Irfan, Michael North,* Javier G. Osende, and Carl Young

School of Chemistry and University Research Centre in Catalysis and Intensified Processing, Newcastle University, Bedson Building, Newcastle upon Tyne, NE1 7RU, U.K.

Supporting Information

ABSTRACT: The bimetallic aluminum(salen) complex [Al(salen)]$_2$O is shown to catalyze the synthesis of oxazolidinones from epoxides and isocyanates. The reaction is demonstrated to proceed with overall retention of epoxide stereochemistry, and both aromatic and aliphatic isocyanates can be used as substrates. In contrast to the corresponding reactions between epoxides and carbon dioxide or carbon disulfide which are also catalyzed by [Al(salen)]$_2$O, no cocatalyst is needed in the reactions with isocyanates. A mechanism is proposed which involves breaking and reforming of the Al−O−Al unit during the catalytic cycle, and this is supported by results obtained using monometallic catalysts.



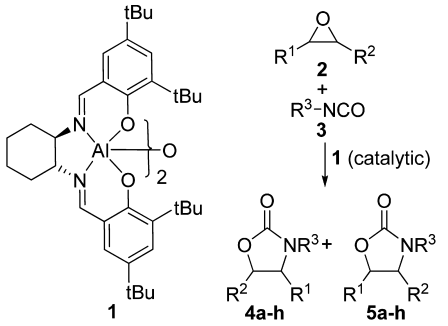
KEYWORDS: *oxazolidinone, aluminum, salen, epoxide, isocyanate*

INTRODUCTION

Aluminum(salen) complex **1** was first introduced by Jacobsen as a catalyst for asymmetric Michael additions.[1−7] The same complex was subsequently shown by Zhu to catalyze Passerini-type reactions,[8] and we have previously shown that complex **1** will catalyze: the asymmetric addition of trimethylsilyl cyanide to aldehydes;[9,10] the synthesis of cyclic carbonates from epoxides and carbon dioxide;[11−15] and the synthesis of di- or trithiocarbonates from epoxides and carbon disulfide.[16,17] Both of the latter two reactions involve the reaction between an epoxide and a heterocumulene. We therefore decided to investigate the use of complex **1** to catalyze the reaction between epoxides and isocyanates leading to oxazolidinones as shown in Scheme 1. Oxazolidinones are of medicinal chemistry interest in their own right[18−26] and are also useful synthetic intermediates, for example, as precursors of β-aminoalcohols.[27] Related mononuclear, aluminum(salen) complexes have also been used for cyclic carbonate synthesis[28] and polycarbonate synthesis by direct reaction of carbon dioxide with epoxides,[29] oxetanes,[30] or ring-opening polymerization of cyclic carbonates.[31]

The reaction shown in Scheme 1 has previous been shown to be catalyzed by species including: ammonium salts,[32] lanthanide salts,[33−35] lithium halides,[36−40] magnesium halides,[41] tetraphenylantimony iodide,[42−44] and trialkyltin halides.[45−48] However, both the regiochemistry (formation of **4** versus **5**) and stereochemistry of the reaction (retention or inversion of epoxide **2** stereochemistry) should be controlled, and the reaction should accommodate a wide range of epoxides **2** and isocyanates **3**. In this respect it is notable that previous work has largely been restricted to mono-substituted epoxides and arylisocyanates and has often employed toxic catalysts. In contrast, complex **1** is derived from an abundant, inexpensive, and relatively non-toxic metal. There is only one previous example of an aluminum catalyst for the synthesis of oxazolidinones from epoxides and isocyanates and that involved the use of aluminum trichloride in refluxing DMF.[49] Oxazolidinones have also been prepared by related chemistry involving the reaction between epoxides and ethyl carbamate catalyzed by a cobalt(salen) complex.[50]

Scheme 1. Synthesis of Oxazolidinones Using Catalyst 1



a: R^1=Ph, R^2=H, R^3=Ph; **b:** R^1=Me, R^2=H, R^3=Ph; **c:** R^1=CH_2Cl, R^2=H, R^3=Ph; **d:** R^1=^{n}Bu, R^2=H, R^3=Ph; **e:** R^1=^{n}Oct, R^2=H, R^3=Ph; **f:** R^1=CH_2OPh, R^2=H, R^3=Ph; **g:** R^1=CH_2OH, R^2=H, R^3=Ph; **h:** R^1-R^2=$(CH_2)_4$, R^3=Ph

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RESULTS AND DISCUSSION

Screening studies were carried out using equimolar amounts of styrene oxide and phenyl isocyanate under various conditions with the results being shown in Table 1. Initial experiments were based around the use of 2.5 mol % of complex **1** and tetrabutylammonium bromide as a cocatalyst in the absence of a solvent, conditions which were optimal for the addition of carbon dioxide to epoxides.[11−15] However, at room temperature this resulted in no reaction occurring (Table 1, entry 1) and even at 80 °C, only 18% conversion of styrene oxide into oxazolidinone **5a** was observed (Table 1, entry 2). Increasing the catalyst loadings to 5 mol % (Table 1, entry 3) was not beneficial, and further increase of the reaction temperature to 120 °C resulted in decomposition (Table 1, entry 4).

Table 1. Reaction of Styrene Oxide with Phenylisocyanate

entry	**1**[a]	Bu_4NBr[a]	solv.	*t* (h)	*T* (°C)	conv. (%)[b]	**4a:5a**[b]
1	2.5	2.5		18	18	0	
2	2.5	2.5		18	80	18	0:1
3	5	5		18	80	17	0:1
4	5	5		18	120	0	
5	0	0		18	80	0	
6	2.5	0		20	80	50	1.5:1
7	0	2.5		20	80	37	1:1.8
8	5	0		20	80	68	1.4:1
9	5	0		40	80	85	1.4:1
10	2.5	0	EC[c]	20	80	59	1.3:1
11	5	0	DCB[d]	20	80	64	1.9:1
12	5	0	DCB[d]	40	80	72	1.8:1
13	5	0	MePh	24	80	100	1.9:1

[a]mol %. [b]Conversion of epoxide **2** into **4a**+**5a** and ratio of **4a**:**5a** determined by ^{1}H NMR spectroscopy of the reaction mixture. [c]EC = ethylene carbonate. [d]DCB = 1,2-dichlorobenzene.

Control experiments at 80 °C proved to be informative. In the absence of catalyst **1** or tetrabutylammonium bromide, no reaction occurred (Table 1, entry 5). Both complex **1** and tetrabutylammonium bromide were found to be catalytically active in their own right (Table 1, entries 6 and 7), but catalyzed the preferential formation of opposite regioisomers of oxazolidinones **4**/**5a**. Furthermore, comparison of Table 1, entries 2,6 and 7 shows that complex **1** and tetrabutylammonium bromide actually inhibit each others catalytic activity, a result which is in marked contrast to the reactions of epoxides with carbon dioxide and carbon disulfide where a cooperative effect between these two catalytic species was observed.[11−17]

Subsequent reaction optimization experiments therefore focused on the use of complex **1** alone, and by increasing the catalyst loading to 5 mol %, the conversion could be increased to 68% after 20 h (Table 1, entry 8) or 85% after 40 h (Table 1, entry 9). Finally, the influence of a solvent was investigated through the use of three high boiling point solvents with very different polarities. Ethylene carbonate is a green polar aprotic solvent which can be used as a replacement for dimethylformamide (DMF) and dimethylsulfoxide (DMSO).[51−53] It gave only a slight improvement in conversion compared to solvent free conditions (compare Table 1, entries 6 and 10). The chlorinated solvent 1,2-dichlorobenzene of intermediate polarity gave no improvement in conversion, but a minor increase in regioselectivity compared to the use of no solvent (compare Table 1, entries 8 and 9 with 11 and 12). Finally, the use of a nonpolar solvent, toluene proved to be optimal, giving 100% conversion of styrene oxide into a 2:1 ratio of oxazolidinones **4a** and **5a** after a reaction time of 24 h (Table 1, entry 13).

The conditions of Table 1, entry 13 were taken as optimal and applied to seven other epoxides to give oxazolidinones **4b**−**h** and **5b**−**h** as detailed in Table 2. The results in entries 2−6 of Table 2 show that styrene oxide was exceptional in giving 3,4-isomer **4a** as the major product since the 3,5−isomer of oxazolidinones **4**/**5b**−**f** was the major product with other monosubstituted epoxides. Thus, in general, epoxide ring-opening occurs at the less hindered carbon atom, but for styrene oxide, this sterically driven trend is overridden by the electronic preference for ring-opening to occur at the benzylic position.[54] All of the reactions proceeded readily beyond 50%, and no kinetic resolution of the racemic epoxides occurred, consistent with previous results obtained for cyclic carbonate synthesis using catalyst **1**.[11−15]

Table 2. Reaction of Epoxides with Phenylisocyanate

		epoxide **2**			
entry	**1** (mol %)	R^1	R^2	conv. (%)[a]	**4**:**5**[b]
1	5	Ph	H	100	1.9:1 (61, 32)
2	5	Me	H	100	1:10 (0, 48)
3	5	CH_2Cl	H	100	0:1 (82)
4	5	^{n}Bu	H	100	1:6.1 (12, 62)
5	5	^{n}Oct	H	91	1:6.6 (13, 65)
6	5	CH_2OPh	H	100	0:1 (94)
7	5	CH_2OH	H	71	1:0 (62)
8[c]	10	$(CH_2)_4$		63	(44)

[a]Conversion of epoxide **2** into **4**+**5** determined by ^{1}H NMR spectroscopy of the reaction mixture. [b]Ratio of **4**:**5** determined by ^{1}H NMR spectroscopy prior to chromatographic separation. Figures in brackets are isolated chemical yields after separation by column chromatography. [c]Reaction time 48 h.

Glycidol also underwent epoxide ring-opening selectively at the more hindered carbon atom (Table 2, entry 7). However, it is well-known[55−59] that this epoxide reacts with isocyanates by a different mechanism in which the isocyanate first reacts with the alcohol to form an intermediate carbamate which then reacts intramolecularly with the epoxide to form 3,4-oxazolidinone **4g**. Notably however, this mechanism is known to require a base (sodium hydride[55,56] or triethylamine[58,59] are commonly used), and this was the first indication that complex **1** might have significant basicity, presumably associated with its bridging oxygen atom.

Cyclohexene oxide also underwent reaction, to form oxazolidinone **4h**. In this case, the amount of catalyst was increased to 10 mol % and the reaction time extended to 48 h (Table 2, entry 8) to ensure that a good yield of compound **4h** was obtained as a single diastereomer by NMR spectroscopy. Crystals of compound **4h** suitable for X-ray analysis were grown from diethyl ether, and the resulting crystal structure (Figure 1) clearly showed that the two rings were *cis*-fused to one another. Both the *cis*-[60,61] and *trans*-isomers[62] of compound **4h** are known compounds, and the formation of *cis*-fused product was unexpected as it implies that the conversion of cyclohexene oxide into oxazolidinone **4h** occurs by a double inversion mechanism. Such a mechanism and stereochemical outcome has previously been observed during the reaction of 1,2-disubstituted epoxides with carbon dioxide catalyzed by complex **1** and tetrabutylammonium bromide.[63] In this case, the epoxide initially undergoes ring-opening by bromide to

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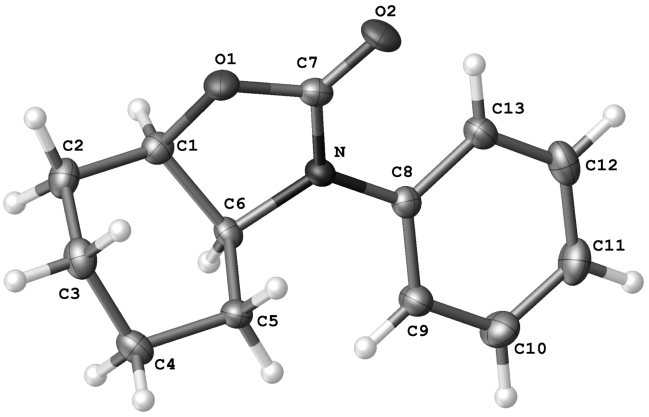
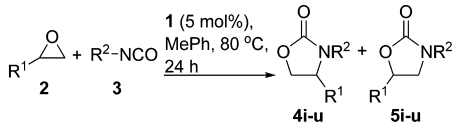


Figure 1. X-ray structure of compound **4h**.

form an aluminum bound bromo alkoxide which can react with carbon dioxide to form an aluminum bound bromo carbonate which can then undergo ring closure, eliminating the bromide to form the cyclic carbonate product.[12,13] However, for the synthesis of oxazolidinone **4h**, no tetrabutylammonium bromide or other nucleophilic cocatalyst was present, so the formation of a *trans*-fused product was anticipated as had been observed for the reaction between cyclohexene oxide and carbon disulfide catalyzed by complex **1** and tributylamine.[16,17]

Having shown that the synthesis was compatible with a range of epoxides, its compatibility with various isocyanates was investigated. Styrene oxide and epichlorohydrin were selected as representative examples of aromatic and aliphatic epoxides, and they were each reacted with six aromatic isocyanates to give oxazolidinones **4**/**5i**−**t** as shown in Scheme 2. The results are

Scheme 2. Synthesis of Oxazolidinones 4/5i−t



i: R^1=Ph, R^2=4-$O_2NC_6H_4$; **j**: R^1=Ph, R^2=4-$MeOC_6H_4$;
k: R^1=Ph, R^2=4-MeC_6H_4; **l**: R^1=Ph, R^2=4-FC_6H_4;
m: R^1=Ph, R^2=4-ClC_6H_4;**n**: R^1=Ph, R^2=4-BrC_6H_4;
o: R^1=CH_2Cl, R^2=4-$O_2NC_6H_4$; **p**: R^1=CH_2Cl,
R^2=4-$MeOC_6H_4$; **q**: R^1=CH_2Cl, R^2=4-MeC_6H_4;
r: R^1=CH_2Cl, R^2=4-FC_6H_4; **s**: R^1=CH_2Cl, R^2=4-ClC_6H_4;
t: R^1=CH_2Cl, R^2=4-BrC_6H_4; **u**: R^1=CH_2Cl, R^2=Cy

presented in Table 3. For reactions involving styrene oxide, the 3,4-oxazolidinone (**4i**−**n**) was always the major product formed in around a 2:1 ratio relative to 3,5-oxazolidinone **5i**−**n** (Table 3, entries 1−6). In contrast, for reactions involving epichlorohydrin, only the 3,5-oxazolidinone (**5o**−**t**) was formed from any of the isocyanates (Table 3, entries 7−12). The electronic properties of the isocyanate affected the yield of oxazolidinones **4**/**5i**−**t** with the highest yields obtained using electron-rich isocyanates (Table 3, entries 2−4 and 8−10) while electron deficient isocyanates gave lower yields and the 4-nitrophenylisocyanate gave particularly low yields with both epoxides (Table 3, entries 1 and 7). The reaction was not restricted to aromatic isocyanates as shown by the formation of product **5u** from epichlorohydrin and cyclohexylisocyanate (Table 3, entry 13).

In view of the moderate yields obtained with electron deficient isocyanates, the effect of nucleophilic cocatalysts was investigated in the hope that that the cocatalyst might be able

Table 3. Reaction of Epoxides with Aromatic Isocyanates[a]

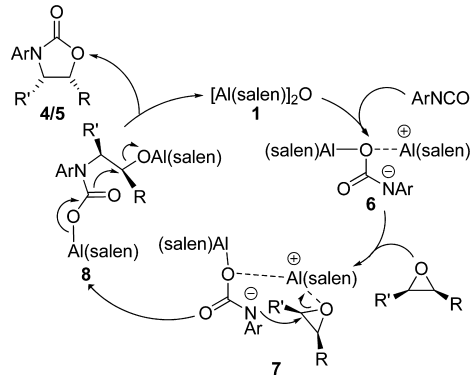
entry	epoxide **2**, R^1	isocyanate **3**, R^2	conv. (%)[b]	**4**:**5**[c]
1	Ph	4-$O_2NC_6H_4$	34	2.8:1 (14, 6)
2	Ph	4-$MeOC_6H_4$	62	1.8:1 (38, 17)
3	Ph	4-MeC_6H_4	69	1.9:1 (38, 7)
4	Ph	4-FC_6H_4	68	2.2:1 (40, 22)
5	Ph	4-ClC_6H_4	38	3.5:1 (28, 8)
6	Ph	4-BrC_6H_4	39	2.5:1 (27, 11)
7	CH_2Cl	4-$O_2NC_6H_4$	41	0:1 (36)
8	CH_2Cl	4-$MeOC_6H_4$	88	0:1 (80)
9	CH_2Cl	4-MeC_6H_4	100	0:1 (89)
10	CH_2Cl	4-FC_6H_4	79	0:1 (44)
11	CH_2Cl	4-ClC_6H_4	46	0:1 (43)
12	CH_2Cl	4-BrC_6H_4	40	0:1 (40)
13	CH_2Cl	Cy	33	0:1 (21)

[a]All reactions carried out at 80 °C in toluene for 24 h using 5 mol % of catalyst **1**. [b]Conversion of epoxide **2** into **4**+**5** determined by ^{1}H NMR spectroscopy of the reaction mixture. [c]Ratio of **4**:**5** determined by ^{1}H NMR spectroscopy. Figures in brackets are isolated chemical yields after separation by column chromatography.

to react with the isocyanate, converting it into a more reactive acylating agent. The reaction between styrene oxide and 4-chlorophenylisocyanate was selected as a test reaction. However, triethylamine, *N*,*N*-dimethylaminopyridine, triphenylphosphine, triphenylphsophine oxide, pyridine *N*-oxide, hexamethylphosphoramide, and trimethylammonium oxide were all found to be catalytically inactive in their own right and acted as inhibitors of reactions when used with complex **1**.

A catalytic cycle which accounts for the observed regio- and stereochemistry is shown in Scheme 3. In this mechanism, the

Scheme 3. Proposed Catalytic Cycle



Lewis-basic bridging oxygen of complex **1** first reacts with the isocyanate to form adduct **6**. This increases the Lewis acidity of the aluminum ions, one of which can coordinate to the epoxide, forming adduct **7** in which the epoxide ring is activated toward ring-opening. In most cases for monosubstituted epoxides, the epoxide ring-opening occurs at the terminal carbon by an S_N2 type mechanism (and hence with inversion of configuration in the case of cyclohexene oxide). However, in the case of styrene oxide the electronic stabilization available from the aromatic ring favors ring-opening at the benzylic position. In either case, ring-opening forms adduct **8** in which the bimetallic Al−O−Al unit within the catalyst has been broken. Ring closure of adduct **8** as shown involves a second substitution reaction which will proceed with inversion of configuration and forms oxazolidinones **4**/**5** as well as reforming bimetallic catalyst **1**.

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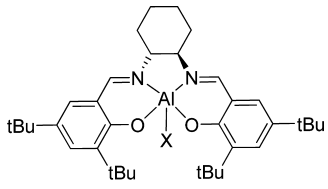
The mechanism shown in Scheme 3 requires that the catalyst initially possesses an Al−X−Al unit, but that this is capable of being broken during the catalytic cycle. To investigate this, the use of the monometallic aluminum(salen) complexes[17] **9**−**11** (Figure 2) as catalysts for the reaction between phenyl-



9: X=Et; **10**: X=OEt; **11**: X=Cl

Figure 2. Monometallic aluminum(salen) complexes **9**−**11**.

isocyanate and styrene oxide, 1-decene oxide or 3-chloropropylene oxide to form oxazolidinones **4**/**5a,c,e** was investigated with the results being presented in Table 4.

Table 4. Oxazolidinone Synthesis Using Monometallic Complexes 9−11[a]

epoxide **2**, R^1	catalyst[b]			
	9	**10**	**11**	**1**
Ph	0	0	53 (2.4:1 **4a:5a**)	100 (1.9:1 **4a:5a**)
^{n}Oct	6 (all **5e**)	7 (all **5e**)	35 (1:5.4 **4e:5e**)	91 (1:6.6 **4e:5e**)
$ClCH_2$	57 (all **5c**)	49 (all **5c**)	66 (all **5c**)	100 (all **5c**)

[a]All reactions carried out at 80 °C in toluene for 24 h using 5 mol % of catalyst. [b]Conversion of epoxide **2** into **4**+**5** and in brackets, ratio of **4**:**5** determined by ^{1}H NMR spectroscopy of the reaction mixture.

Monomometallic complexes **9** and **10** had essentially no catalytic activity for the synthesis of oxazolidinones **4**/**5a,e**. However, chloride containing complex **11** was catalytically active, had about half the activity of complex **1**, and gave a similar **4**:**5** ratio to complex **1**. In all cases, 5 mol % of catalyst was used, but since complex **1** is bimetallic it contains twice as many aluminum(salen) units as complex **11**. This may account for the difference in catalytic activity between complexes **1** and **11**. It is known that chlorine can bridge between aluminum atoms,[64−71] which would result in the formation of oligomeric species analogous to complex **1** and provide the bimetallic assembly required for the mechanism shown in Scheme 3. In contrast, this is not possible for complex **9** and sterically retarded in complex **10**.

In contrast, all of the monometallic complexes catalyzed the addition of phenylisocyanate to 3-chloropropylene oxide, and all displayed a level of catalytic activity which was about half that displayed by complex **1** (Table 4). It appears that 3-chloropropylene oxide can act as a source of chloride during the reactions and that this can convert monometallic complexes **9** and **10** into chloro complex **11**. The chloride may be generated by nucleophilic substitution using either the ethoxide ligand present in complex **10** or the adventitious moisture in the reactions.

CONCLUSIONS

Bimetallic aluminum(salen) complex **1** catalyzes the synthesis of oxazolidinones from epoxides and aromatic or aliphatic isocyanates. In contrast to the corresponding reactions between epoxides and either carbon dioxide or carbon disulfide which are also catalyzed by complex **1**, no cocatalyst is needed for the reaction with isocyanates, and cocatalysts including tetrabutylammonium bromide were found to inhibit the reaction. Compared to previously reported catalysts for the synthesis of oxazolidinones from epoxides and isocyanates,[32−49] the use of complex **1** allows the use of aliphatic as well as aromatic isocyanates. Reactions can be carried out at lower temperatures than literature procedures which require the use of refluxing DMF,[39] refluxing xylene,[37] or a sealed system at 200 °C.[32] The use of highly toxic catalysts based on tin[45−48] and/or antimony[42−44,46] is avoided as is the use of lanthanide based catalysts.[33,34] Finally, only 5 mol % catalyst is required compared with the 10 mol %[42−44,46] or even 50 mol %[41] required by some other catalyst systems.

Use of cyclohexene oxide as substrate resulted in the exclusive formation of *cis*-fused oxazolidinone **4h**, the structure of which was proven by X-ray crystallography. This is the same stereochemistry as seen in the reaction between epoxides and carbon dioxide catalyzed by complex **1**, but the opposite stereochemistry to that seen in the reaction between epoxides and carbon disulfide catalyzed by complex **1**. The stereochemistry of compound **4h** implies that the reaction mechanism involves a double inversion of configuration. Additional mechanistic studies to elucidate the catalytic cycle and provide a coherent mechanistic analysis for the reactions between epoxides and heterocumulenes catalyzed by complex **1** are underway and will be reported in due course.

EXPERIMENTAL SECTION

General Procedures. ^{1}H NMR spectra were recorded at 400 or 300 MHz, ^{13}C NMR spectra were recorded at 100 or 75 MHz, and ^{19}F NMR spectra were recorded at 376 MHz. All spectra were recorded at ambient temperature. ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent peak, ^{19}F NMR spectra were externally referenced to $CFCl_3$. For ^{1}H NMR spectra, multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), or a combination of these. GCMS were recorded on a FactorFour (VF-5 ms) capillary column (30 m × 0.25 mm) with helium as the carrier gas. The conditions used were as follows: initial temperature 60 °C, hold at initial temperature for 3 min, then ramp rate 15 °C/min to 270 °C; hold at final temperature for 5 min. For the first 3.50 min, the eluent was routed away from the mass detector. Subsequently, the detector was operated in full EI or CI scan mode.

General Procedure for the Synthesis of Oxazolidinones. To a stirred solution of complex **1** (0−0.087 mmol) and a cocatalyst (0−0.087 mmol) in toluene (2 mL) was added an epoxide (0.874 mmol) and isocyanate (0.874 mmol). The reaction was then heated to 80 °C and stirred for 18−48 h. The reaction was cooled to room temperature and solvent removed in vacuo. CH_2Cl_2 (5 mL) was added to the residue and the mixture filtered through silica, washing with additional CH_2Cl_2 (5 mL), and the solvent was removed in vacuo. The conversion and ratio of regioisiomeric oxazolidinones was determined by ^{1}H NMR spectroscopy; then the residue was purified as described for each compound below.

3,4-Diphenyloxazolidin-2-one[72] **4a.** Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4a** (0.128 g, 61%) as a white solid. mp 128−130 °C (lit.[61] 128−129 °C); υ_{max}(ATR) 3065, 2976, 1744 cm^{-1}; δ_H(300 MHz,

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$CDCl_3$) 7.5−7.2 (9H, m), 7.10 (1H, tt *J* 7.4, 1.3 Hz), 5.43 (1H, dd *J* 8.8, 6.0 Hz), 4.80 (1H, t *J* 8.7 Hz), 4.22 (1H, dd *J* 8.6, 6.0 Hz); δ_C(75 MHz, $CDCl_3$) 155.8, 138.6, 137.3, 129.3, 128.9, 128.8, 126.3, 124.7, 121.0, 69.8, 60.9; GCMS T_R 15.76 min; *m*/*z*(CI) 240 (MH^+, 100), 195 (50).

3,5-Diphenyloxazolidin-2-one[72] 5a. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5a** (0.067 g, 32%) as a white solid. mp 76−78 °C (lit.[61] 78−79 °C); υ_{max}(ATR) 3062, 2975, 1734 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.3 (9H, m), 7.16 (1H, tt *J* 7.4, 1.1 Hz), 5.66 (1H, dd, *J* 8.8, 7.6 Hz), 4.40 (1H, t *J* 8.8 Hz), 3.98 (1H, dd *J* 8.9, 7.6 Hz); δ_C(75 MHz, $CDCl_3$) 154.7, 138.4, 138.3, 129.1, 129.0, 125.7, 124.2, 118.6, 74.1, 52.8; GCMS T_R 16.33 min; *m*/*z*(CI) 240 (MH^+, 100), 194 (80).

3-Phenyl-5-methyloxazolidin-2-one[32] 5b. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5b** (0.074 g, 48%) as a white solid. mp 79−82 °C (lit.[32] 79−82 °C); υ_{max}(ATR) 3036, 2938, 2877, 1742 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.54 (2H, d *J* 8.7 Hz), 7.38 (2H, t *J* 8.1 Hz), 7.14 (1H, t *J* 7.4 Hz), 4.80 (1H, sex *J* 6.5 Hz), 4.13 (1H, t *J* 8.5 Hz), 3.63 (1H, dd *J* 8.9, 7.1 Hz), 1.54 (3H, d *J* 6.3 Hz); δ_C(75 MHz, $CDCl_3$) 154.9, 138.6, 129.1, 124.1, 118.5, 69.5, 52.1, 20.7; *m*/*z*(ESI) 200 ($M+Na^+$, 100), 178 (MH^+, 30).

3-Phenyl-5-chloromethyloxazolidin-2-one[41] 5c. Purification by washing with hexane and Et_2O gave compound **5c** (0.221 g, 82%) as a white solid. mp 101−103 °C (lit.[41] 104−105 °C); υ_{max}(ATR) 3065, 2962, 1735 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.3 (4H, m), 7.17 (1H, tt *J* 7.4, 1.1 Hz), 4.88 (1H, dddd, *J* 8.7, 6.5, 5.6, 4.1 Hz), 4.19 (1H, t, *J* 8.9 Hz, 1H), 3.98 (1H, dd, *J* 9.1, 5.7 Hz), 3.75 (1H, dd *J* 11.6, 6.6 Hz); δ_C(75 MHz, $CDCl_3$) 153.9, 138.0, 129.1, 124.4, 118.6, 70.9, 48.3, 44.5; GCMS T_R 13.87 min; *m*/*z*(CI) 214 ($M(^{37}Cl)H^+$, 30); 212 ($M(^{35}Cl)H^+$, 100), 132 (72).

3-Phenyl-4-butyloxazolidin-2-one 4d. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4d** (0.045 g, 12%) as a cream colored solid. mp 122−123 °C; υ_{max}(ATR) 3064, 2954, 1740 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.3 (4H, m), 7.20 (1H, tt *J* 6.9, 1.7 Hz), 4.52 (1H, t *J* 8.4 Hz), 4.5−4.3 (1H, m), 4.13 (1H, dd *J* 8.3, 5.2 Hz), 1.8−1.6 (1H, m), 1.6−1.5 (1H, m), 1.4−1.1 (4H, m), 0.88 (3H, t *J* 6.7 Hz); δ_C(75 MHz, $CDCl_3$) 155.7, 137.1, 128.5, 125.2, 122.1, 66.9, 56.5, 31.7, 26.1, 22.4, 13.7; *m*/*z*(ESI) 461 ($2M+Na^+$, 100), 242 ($M+Na^+$, 20), 220 (MH^+, 5); Found (ESI) 220.1331, $C_{13}H_{18}NO_2$ (MH^+) requires 220.1338.

3-Phenyl-5-butyloxazolidin-2-one[19] 5d. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5d** (0.227 g, 62%) as a cream colored solid. mp 65−66 °C; υ_{max}(ATR) 2958, 2927, 2872, 1737 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.5 (2H, m), 7.5−7.3 (2H, m), 7.15 (1H, tt *J* 7.4, 1.2 Hz), 4.7−4.6 (1H, m), 4.10 (1H, t *J* 8.5 Hz), 3.68 (1H, dd *J* 8.8, 7.2 Hz), 2.0−1.8 (1H, m), 1.8−1.6 (1H, m), 1.6−1.3 (4H, m), 0.96 (3H, t *J* 7.2 Hz); δ_C(75 MHz, $CDCl_3$) 154.9, 138.7, 129.0, 124.0, 118.4, 73.1, 50.7, 34.8, 26.7, 22.4, 13.8; *m*/*z*(ESI) 461 ($2M+Na^+$, 100), 242 ($M+Na^+$, 20), 220 (MH^+, 5).

3-Phenyl-4-octyloxazolidin-2-one 4e. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4e** (0.06 g, 13%) as a yellow oil; υ_{max}(ATR) 3180, 3056, 1706 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.3 (3H, m), 7.3−7.1 (2H, m), 4.55 (1H, t *J* 8.4 Hz), 4.5−4.3 (1H, m), 4.15 (1H, dd *J* = 8.3, 5.3 Hz), 1.8−1.7 (1H, m), 1.7−1.5 (1H, m), 1.4−1.2 (12H, m), 0.88 (3H, t *J* 6.2 Hz); δ_C(75 MHz, $CDCl_3$) 155.7, 137.1, 129.2, 125.2, 122.1, 66.9, 56.5, 32.0, 31.7, 29.3, 29.2, 29.0, 23.9, 22.5, 13.9; *m*/*z*(ESI) 573 ($2M+Na^+$, 100), 298 ($M+Na^+$, 95), 276 (MH^+, 10); Found (ESI) 276.1958, $C_{17}H_{26}NO_2$ (MH^+) requires 276.1964.

3-Phenyl-5-octyloxazolidin-2-one[73] 5e. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5d** (0.300 g, 65%) as a beige colored solid. mp 70−71 °C (lit.[73] 69−70 °C); υ_{max}(ATR) 2917, 2850, 1721 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.5 (2H, m), 7.5−7.3 (2H, m), 7.14 (1H, tt *J* 7.3, 1.2 Hz), 4.7−4.6 (1H, m), 4.08 (1H, t *J* 8.5 Hz), 3.66 (1H, dd *J* 8.7, 7.2 Hz), 2.0−1.8 (1H, m), 1.8−1.6 (1H, m), 1.6−1.2 (12H, m), 0.89 (3H, t *J* 6.9 Hz); δ_C(75 MHz, $CDCl_3$) 154.9, 138.7, 129.0, 123.9, 118.4, 73.1, 50.7, 35.1, 31.8, 29.4, 29.3, 29.1, 24.6, 22.6, 13.9; *m*/*z*(ESI) 573 ($2M+Na^+$, 100), 298 ($M+Na^+$, 95), 276 (MH^+, 10).

3-Phenyl-5-phenoxymethyloxazolidin-2-one[41,43] 5f. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5f** (0.420 g, 94%) as a white solid. mp 139−140 °C (lit.[41,43] 138−139 °C); υ_{max}(ATR) 3061, 2960, 1737 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.60 (2H, d *J* 7.7 Hz), 7.41 (2H, t *J* 8.5 Hz), 7.33 (2H, t *J* 7.3 Hz), 7.18 (1H, t *J* 7.3 Hz), 7.02 (1H, t *J* 7.3 Hz), 6.93 (2H, d *J* 7.6 Hz), 5.1−4.9 (1H, m), 4.3−4.2 (3H, m), 4.10 (1H, dd *J* 8.9, 5.9 Hz); δ_C(75 MHz, $CDCl_3$) 158.3, 154.3, 138.4, 129.7, 129.1, 124.3, 122.0, 118.6, 115.0, 70.5, 68.4, 47.7; *m*/*z*(ESI) 561 ($2M+Na^+$, 100), 292 ($M+Na^+$, 100), 270 (MH^+, 10).

3-Phenyl-4-hydroxymethyloxazolidin-2-one[57] 4g. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4g** (0.201 g, 62%) as a white solid. mp 109−111 °C (lit.[57] 112−115 °C); υ_{max}(ATR) 3271, 1737 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.5−7.2 (4H, m), 7.10 (1H, tt *J* 7.2, 1.4 Hz), 6.76 (1H, br s), 4.57 (1H, dd *J* 12.2, 2.9 Hz), 4.00 (1H, dd *J* 12.2, 6.5 Hz), 3.29 (1H, ddt *J* 6.7, 4.1, 2.7 Hz), 2.90 (1H, t *J* 4.4 Hz), 2.71 (1H, dd *J* 4.9, 2.6 Hz); δ_C(75 MHz, $CDCl_3$) 153.1, 137.7, 129.1, 123.8, 119.1, 65.8, 49.5, 44.6; *m*/*z*(ESI) 409 ($2M+Na^+$, 100), 216 ($M+Na^+$, 35).

***Cis*-3-Phenylhexahydrobenzooxazolidin-2-one[60,61] 4h.** Purification by crystallization from Et_2O gave compound **4h** (0.160 g, 44%) as a white solid. mp 88−89 °C (lit.[45] 93−94 °C); υ_{max}(ATR) 3065, 2936, 2864, 1734 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.4 (2H, m), 7.4−7.3 (2H, m), 7.16 (1H, tt *J* 7.3, 1.2 Hz), 4.69 (1H, dt *J* 6.5, 4.4 Hz), 4.28 (1H, q *J* 6.3 Hz), 2.2−2.1 (1H, m), 2.1−2.0 (1H, m), 1.9−1.7 (1H, m), 1.7−1.5 (4H, m), 1.4−1.2 (1H, m); δ_C(75 MHz, $CDCl_3$) 155.8, 137.5, 129.1, 124.7, 121.3, 73.2, 56.1, 26.7, 26.1, 19.9, 19.1; *m*/*z*(ESI) 457 ($2M+Na^+$, 100), 240 ($M+Na^+$, 32), 218 (MH^+, 5). X-ray data is given in the Supporting Information.

3-(4-Nitrophenyl)-4-phenyloxazolidin-2-one 4i. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4i** (0.026 g, 14%) as a yellow syrup. υ_{max}(ATR) 3033, 2883, 1773 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 8.01 (2H, d *J* 9.0 Hz), 7.52 (2H, d *J* 9.1 Hz), 7.4−7.2 (5H, m), 5.35 (1H, dd *J* 8.7, 5.4 Hz), 4.74 (1H, t *J* 8.6 Hz), 4.15 (1H, dd *J* 8.7, 5.5 Hz); δ_C(75 MHz, $CDCl_3$) 155.0, 143.0, 137.6, 129.8, 129.4, 125.9, 125.6, 124.6, 119.6, 69.9, 60.5; GCMS T_R 18.72 min; *m*/*z*(EI) 284 (M^+, 100), 225 (25), 179 (20), 149 (40), 91 (30); Found (ESI) 285.0883, $C_{15}H_{13}N_2O_4$ (MH^+) requires 285.0875.

3-(4-Nitrophenyl)-5-phenyloxazolidin-2-one 5i. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5i** (0.016 g, 9%) as a yellow solid. mp 151−153 °C; υ_{max}(ATR) 3050, 2917, 1743 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 8.25 (2H, d *J* 9.3 Hz), 7.74 (2H, d *J* 9.3 Hz), 7.5−7.4 (5H, m), 5.72 (1H, dd *J* 8.7, 7.5 Hz), 4.48 (1H, t *J* 8.9 Hz), 4.04 (1H, dd *J* 9.1, 7.5 Hz); δ_C(75 MHz, $CDCl_3$) 154.0, 143.8, 137.4, 129.5, 129.2, 125.8, 125.6, 124.9, 117.7, 74.3, 52.4; *m*/*z*(ESI) 307 ($M+Na^+$,

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100), 285 (MH^+, 50), 259 (70); Found (ESI) 285.0887, $C_{15}H_{13}N_2O_4$ (MH^+) requires 285.0875.

3-(4-Methoxyphenyl)-4-phenyloxazolidin-2-one[74] 4j. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4j** (0.089 g, 38%) as a cream colored solid. mp 131−133 °C (lit.[57] 137−138 °C); υ_{max}(ATR) 2923, 1734 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.3−7.1 (7H, m), 6.68 (2H, d *J* 9.1 Hz), 5.22 (1H, dd *J* 8.8, 6.4 Hz), 4.66 (1H, t *J* 8.7 Hz), 4.09 (1H, dd *J* 8.6, 6.4 Hz), 3.61 (3H, s); δ_C(75 MHz, $CDCl_3$) 157.0, 156.2, 138.5, 130.2, 129.2, 128.7, 126.5, 123.3, 114.3, 69.6, 61.4, 55.3; GCMS T_R 18.15 min; *m*/*z*(EI) 269 (M^+, 100), 224 (25).

3-(4-Methoxyphenyl)-5-phenyloxazolidin-2-one[75] 5j. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5j** (0.040 g, 17%) as a cream colored solid. mp 105−107 °C; υ_{max}(ATR) 2925, 2853, 1738 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.5−7.3 (7H, m), 6.91 (2H, d *J* 9.1 Hz), 5.62 (1H, dd *J* 8.7, 7.5 Hz), 4.34 (1H, t *J* 8.8 Hz), 3.94 (1H, dd *J* 8.8, 7.5 Hz), 3.80 (3H, s); δ_C(75 MHz, $CDCl_3$) 156.8, 155.0, 138.5, 131.6, 129.0, 125.7, 120.6, 114.5, 74.0, 55.6, 53.3; GCMS T_R 17.05 min; *m*/*z*(EI) 269 (M^+, 100).

3-(4-Methylphenyl)-4-phenyloxazolidin-2-one[39] 4k. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4k** (0.089 g, 38%) as a cream colored solid. mp 105−107 °C (lit.[39] 107−109 °C); υ_{max}(ATR) 3036, 2971, 1741 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.4−7.2 (7H, m), 7.08 (2H, d *J* 8.3 Hz), 5.39 (1H, dd *J* 8.9, 6.2 Hz), 4.77 (1H, t *J* 8.7 Hz), 4.19 (1H, dd *J* 8.5, 6.0 Hz), 2.27 (3H, s); δ_C(75 MHz, $CDCl_3$) 155.9, 138.6, 134.7, 134.4, 129.4, 129.2, 128.6, 126.2, 121.2, 69.7, 60.9, 20.6; GCMS T_R 16.21 min; *m*/*z*(EI) 253 (M^+, 100).

3-(4-Methylphenyl)-5-phenyloxazolidin-2-one[39] 5k. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5k** (0.015 g, 7%) as a cream colored solid. mp 98−100 °C (lit.[39] 95−97 °C); υ_{max}(ATR) 2963, 1734 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.5−7.4 (7H, m), 7.19 (2H, d *J* 8.1 Hz), 5.63 (1H, t *J* 8.1 Hz), 4.36 (1H, t *J* 8.8 Hz), 3.95 (1H, dd, *J* 9.0, 7.6 Hz), 2.34 (3H, s); δ_C(100 MHz, $CDCl_3$) 154.8, 138.2, 135.6, 133.8, 129.6, 129.0, 128.9, 125.6, 118.4, 74.0, 52.8, 20.7; GCMS T_R 16.93 min; *m*/*z*(EI) 253 (M^+, 35), 208 (100), 118 (65), 91 (35).

3-(4-Fluorophenyl)-4-phenyloxazolidin-2-one 4l. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4l** (0.091 g, 40%) as a cream colored solid. mp 94−97 °C; υ_{max}(ATR) 2976, 1737 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.4−7.2 (7H, m),), 6.94 (2H, dd *J* 9.2, 8.3 Hz), 5.34 (1H, dd *J* 8.8, 6.3 Hz), 4.78 (1H, t *J* 8.7 Hz), 4.21 (1H, dd *J* 8.7, 6.3 Hz); δ_C(75 MHz, $CDCl_3$) 159.9 (d *J* 243 Hz), 156.0, 138.2, 130.3, 129.5, 126.4, 123.1 (d *J* 8 Hz), 115.8 (d *J* 22 Hz), 69.8, 61.3; δ_F($CDCl_3$) −117.2 (s); GCMS T_R 15.48 min; *m*/*z*(EI) 257 (M^+, 100); Found (ESI) 258.0908, $C_{15}H_{13}NO_2F$ (MH^+) requires 258.0930.

3-(4-Fluorophenyl)-5-phenyloxazolidin-2-one 5l. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5l** (0.044 g, 22%) as a cream colored solid. mp 78−81 °C; υ_{max}(ATR) 3026, 2976, 1726 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.53 (2H, dd *J* 9.1, 4.6 Hz), 7.5−7.4 (5H, m), 7.09 (2H, dd *J* 9.3, 8.1 Hz), 5.66 (1H, t *J* 8.2 Hz), 4.37 (1H, t *J* 8.8 Hz), 3.96 (1H, dd *J* 8.9, 7.6 Hz); δ_C(100 MHz, $CDCl_3$) 159.3 (d *J* 243 Hz), 154.8, 137.9, 134.2, 129.2, 129.1, 125.6, 120.1 (d *J* 7 Hz), 115.8 (d *J* 23 Hz), 74.0, 53.0; δ_F($CDCl_3$) −118.2 (s); GCMS T_R 16.26 min; *m*/*z*(CI) 258 (MH^+, 100), 213 (60); Found (ESI) 258.0915, $C_{15}H_{13}NO_2F$ (MH^+) requires 258.0930.

3-(4-Chlorophenyl)-4-phenyloxazolidin-2-one[76,77] 4m. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4m** (0.058 g, 28%) as a white solid. mp 126−128 °C (lit.[76] 131 °C); υ_{max}(ATR) 3030, 2967, 2908, 1736 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.4−7.1 (9H, m), 5.30 (1H, dd *J* 8.7, 6.1 Hz), 4.73 (1H, t *J* 8.7 Hz), 4.15 (1H, dd, *J* 8.5, 6.0 Hz); δ_C(100 MHz, $CDCl_3$) 155.7, 137.7, 135.5, 129.8, 129.4, 129.0, 128.9, 126.1, 121.8, 69.7, 60.5; *m*/*z*(ESI) 298 (M-(^{37}Cl)+Na^+, 30), 296 (M(^{35}Cl)+Na^+, 100).

3-(4-Chlorophenyl)-5-phenyloxazolidin-2-one 5m. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5m** (0.017 g, 8%) as a white solid. mp 113−117 °C; υ_{max}(ATR) 2922, 1750 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6−7.3 (9H, m), 5.67 (1H, t *J* 8.1 Hz), 4.38 (1H, t *J* 8.8 Hz), 3.95 (1H, dd, *J* 9.0, 7.5 Hz); δ_C(100 MHz, $CDCl_3$) 147.3, 137.8, 136.7, 129.7, 129.2, 129.1, 129.0, 125.6, 119.4, 74.0, 52.6; *m*/*z*(ESI) 298 (M(^{37}Cl)+Na^+, 30), 296 (M(^{35}Cl)+Na^+, 100); Found (ESI) 274.0620, $C_{15}H_{13}NO_2{}^{35}Cl$ (MH^+) requires 274.0635.

3-(4-Bromophenyl)-4-phenyloxazolidin-2-one 4n. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **4n** (0.075 g, 27%) as a yellow solid. mp 134−137 °C; υ_{max}(ATR) 3010, 2922, 1739 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.4−7.2 (9H, m), 5.33 (1H, dd *J* 8.7, 6.0 Hz), 4.75 (1H, t *J* 8.7 Hz), 4.17 (1H, dd, *J* 8.6, 6.0 Hz); δ_C(75 MHz, $CDCl_3$) 155.5, 138.1, 136.5, 131.9, 129.5, 129.0, 126.2, 122.4, 117.7, 69.8, 60.8; GCMS T_R 17.47 min; *m*/*z*(CI) 319 (M(^{81}Br)H^+, 100), 317 (M(^{79}Br)H^+, 95); Found (ESI) 318.0112, $C_{15}H_{13}NO_2{}^{79}Br$ (MH^+) requires 318.0130.

3-(4-Bromophenyl)-5-phenyloxazolidin-2-one[75] 5n. Purification by flash chromatography (CH_2Cl_2:EtOAc 98:2) gave compound **5n** (0.030 g, 11%) as a yellow solid. mp 100−103 °C; υ_{max}(ATR) 2963, 1745 cm^{-1}; δ_H(400 MHz, $CDCl_3$) 7.7−7.4 (9H, m), 5.66 (1H, t *J* 7.9 Hz), 4.37 (1H, t *J* 8.8 Hz), 3.95 (1H, dd, *J* 8.8, 7.5 Hz); δ_C(100 MHz, $CDCl_3$) 154.4, 138.0, 137.5, 132.1, 129.2, 129.1, 125.6, 119.9, 117.1, 74.1, 52.6; GCMS T_R 18.46 min; *m*/*z*(CI) 319 (M(^{81}Br)H^+, 70), 317 (M(^{79}Br)H^+, 70), 274 (100), 272 (75).

3-(4-Nitrophenyl)-5-chloromethyloxazolidin-2-one[41,78] 5o. Purification by washing with hexane and Et_2O gave compound **5o** (0.021 g, 6%) as a yellow solid. mp 157−160 °C (lit.[74] 155−157 °C); υ_{max}(ATR) 3138, 1756 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 8.28 (2H, d *J* 9.3 Hz), 7.76 (2H, d *J* 9.3 Hz), 5.1−4.9 (1H, m), 4.26 (1H, t *J* 9.1 Hz), 4.05 (1H, dd *J* 9.2, 5.7 Hz), 3.9−3.8 (2H, m); δ_C(75 MHz, $CDCl_3$) 153.2, 143.9, 143.4, 125.0, 117.7, 71.1, 48.0, 44.4; GCMS T_R 17.29 min; *m*/*z*(EI) 258 (M(^{37}Cl)$^+$, 25), 256 (M(^{35}Cl)$^+$, 75), 177 (100).

3-(4-Methoxyphenyl)-5-chloromethyloxazolidin-2-one[79] 5p. Purification by washing with hexane and Et_2O gave compound **5p** (0.250 g, 80%) as a white solid. mp 105−107 °C (lit.[75] 105−106 °C); υ_{max}(ATR) 3020, 2970, 1731 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.41 (2H, d *J* 9.1 Hz), 6.89 (2H, d *J* 9.1 Hz), 4.82 (1H, dq *J* 8.8, 5.2 Hz), 4.09 (1H, t *J* 9.0 Hz), 3.87 (1H, dd *J* 9.1, 5.7 Hz), 3.78 (3H, s), 3.74 (2H, d *J* 5.1); δ_C(75 MHz, $CDCl_3$) 156.7, 154.1, 131.1, 120.6, 114.4, 70.9, 55.5, 48.7, 44.7; GCMS T_R 15.58 min; *m*/*z*(CI) 244 (M(^{37}Cl)H^+, 25), 242 (M(^{35}Cl)H^+, 75), 161 (100), 120 (25).

3-(4-Methylphenyl)-5-chloromethyloxazolidin-2-one 5q. Purification by washing with hexane and Et_2O gave compound **5q** (0.129 g, 45%) as a cream colored solid. mp 104−107 °C; υ_{max}(ATR) 3033, 2963, 2920, 1734 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.43 (2H, d *J* 8.5 Hz), 7.20 (2H, d *J* 8.1 Hz), 4.86 (1H, dddd, *J* 8.7, 6.6, 5.7, 4.2 Hz), 4.16 (1H, t *J* 9.0 Hz), 3.95 (1H, dd, *J* 9.2, 5.7 Hz), 3.80 (1H, dd, *J* 11.6, 4.2 Hz), 3.74

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(1H, dd, *J* 11.5, 6.6 Hz), 2.34 (3H, s); δ_C(75 MHz, $CDCl_3$) 154.0, 135.6, 134.3, 129.7, 118.8, 71.0, 48.6, 44.5, 20.7; GCMS T_R 14.59 min; *m*/*z*(CI) 228 ($M(^{37}Cl)H^+$, 7), 226 ($M(^{35}Cl)H^+$, 20), 146 (100), 118 (45), 91 (35); Found (ESI) 226.0627, $C_{11}H_{13}NO_2{}^{35}Cl$ (MH^+) requires 226.0635.

3-(4-Fluorophenyl)-5-chloromethyloxazolidin-2-one 5r. Purification by washing with hexane and Et_2O gave compound **5r** (0.128 g, 44%) as a white solid. mp 101−104 °C; υ_{max}(ATR) 2946, 1737 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.48 (2H, dd *J* 9.2, 4.6 Hz), 7.05 (2H, dd *J* 9.2, 8.2 Hz), 5.0−4.8 (1H, m), 4.13 (1H, t *J* 9.0 Hz), 3.91 (1H, dd *J* 9.1, 5.7 Hz), 3.76 (2H, d *J* 5.0 Hz); δ_C(75 MHz, $CDCl_3$) 160.9, 154.0, 133.8 (d *J* 5.2 Hz), 120.2, 115.7 (d *J* 22.3 Hz), 70.4, 48.1, 44.7; δ_F($CDCl_3$) −117.4 (s); GCMS T_R 13.90 min; *m*/*z*(CI) 232 ($M(^{37}Cl)H^+$, 7), 230 ($M(^{35}Cl)H^+$, 20), 150 (100), 122 (75), 95 (35); Found (ESI) 230.0376, $C_{10}H_{10}NO_2F^{35}Cl$ (MH^+) requires 230.0384.

3-(4-Chlorophenyl)-5-chloromethyloxazolidin-2-one[41] 5s. Purification by washing with hexane and Et_2O gave compound **5s** (0.216 g, 40%) as a white solid. mp 130−133 °C (lit.[41] 131−133 °C); υ_{max}(ATR) 2938, 1738 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.49 (2H, d *J* 9.0 Hz), 7.33 (2H, d *J* 9.0 Hz), 5.0−4.8 (1H, m), 4.14 (1H, t *J* 9.0 Hz), 3.93 (1H, dd *J* 9.1, 5.6 Hz), 3.8−3.7 (2H, m); δ_C(75 MHz, $CDCl_3$) 153.7, 136.5, 129.6, 129.0, 119.6, 71.0, 48.1, 44.6; GCMS T_R 15.34 min; *m*/*z*(CI) 250 ($M(2\times{}^{37}Cl)H^+$, 6), 248 ($M(^{35}Cl+^{37}Cl)H^+$, 50), 246 ($M(2\times{}^{35}Cl)H^+$, 80), 166 (100), 130 (50), 63 (30).

3-(4-Bromophenyl)-5-chloromethyloxazolidin-2-one[80] 5t. Purification by washing with hexane and Et_2O gave compound **5t** (0.147 g, 40%) as a white solid. mp 125−128 °C (lit.[76] 125−127 °C); υ_{max}(ATR) 2961, 1733 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.48 (2H, d *J* 9.1 Hz), 7.42 (2H, d *J* 9.1 Hz), 5.0−4.8 (1H, m), 4.13 (1H, t *J* 9.0 Hz), 3.91 (1H, dd *J* 9.1, 5.7 Hz), 3.8−3.7 (2H, m); δ_C(75 MHz, $CDCl_3$) 153.6, 137.0, 132.0, 119.9, 117.2, 70.9, 48.0, 44.5; GCMS T_R 16.27 min; *m*/*z*(EI) 293 ($M(^{81}Br+^{37}Cl)H^+$, 10), 291 ($M(^{81}Br+^{35}Cl$ or $^{79}Br+^{37}Cl)H^+$, 100), 289 ($M(^{79}Br+^{35}Cl)H^+$, 80), 210 (25), 130 (25).

3-Cyclohexyl-5-chloromethyloxazolidin-2-one 5u. Purification by washing with hexane and Et_2O gave compound **5u** (0.040 g, 21%) as a white solid. mp 94−97 °C; υ_{max}(ATR) 2930, 2856, 1729 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 4.8−4.6 (1H, m), 3.8−3.6 (4H, m), 3.42 (1H, dd *J* 9.0, 5.6 Hz), 1.9−1.7 (4H, m), 1.7−1.6 (1H, m), 1.5−1.3 (4H, m), 1.2−1.0 (1H, m); δ_C(75 MHz, $CDCl_3$) 156.3, 71.6, 52.9, 44.7, 44.0, 30.4, 30.3, 25.4; *m*/*z*(ESI) 220 ($M(^{37}Cl)H^+$, 35), 218 ($M(^{35}Cl)H^+$, 35); Found (ESI) 218.0929, $C_{10}H_{17}NO_2{}^{35}Cl$ (MH^+) requires 218.0948.

■ ASSOCIATED CONTENT

Supporting Information

^1H, ^{13}C, and ^{19}F NMR spectra of oxazolidinones **4**/**5a**−**u**. X-ray data for compound **4h**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Michael.north@ncl.ac.uk.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

Salen, (1*R*,2*R*)-*N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)cyclohexane-1,2-diamine

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