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Synthesis of Oxazolidinones from Epoxides and Isocyanates Catalysed by Aluminium Heteroscorpionate Complexes

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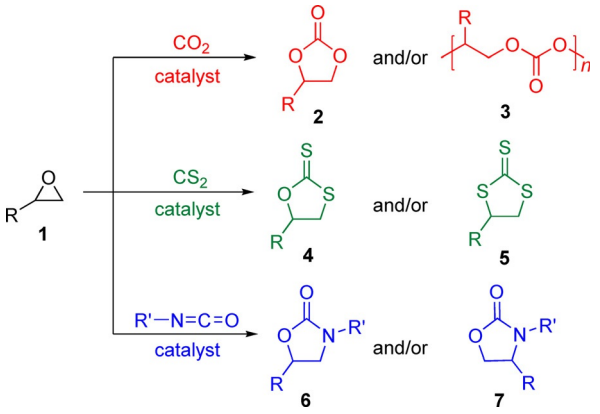
The combination of an aluminium(heteroscorpionate) complex and tetrabutylammonium bromide acts as a highly efficient catalyst system for the synthesis of oxazolidinones from epoxides and isocyanates. Twenty two complexes were tested derived from a range of bispyrazole ligands and containing 1–3 aluminium atoms per complex. The optimal catalyst was found to be a bimetallic complex of a thioacetamidate ligand. Under the optimal reaction conditions (80 °C in toluene for 24 h using 5 mol% of both aluminium catalyst and tetrabutylammonium bromide co-catalyst), six epoxides were reacted with six aromatic isocyanates, giving 25 oxazolidinones in moderate to excellent yields showing broad substrate scope. The regiochemistry of the reaction (to produce 3,4- or 3,5-oxazolidinones) is controlled by the substrate with epoxide ring opening occurring preferentially at the less hindered end of the epoxide unless a substituent on the epoxide can stabilise a positive charge.

Introduction

Epoxides **1** are particularly useful substrates in organic synthesis as many are commercially available and a number of procedures have been developed for the production of enantiomerically pure epoxides.[1] They have been widely used as building blocks for the synthesis of either cyclic or polycarbonates **2**, **3**,[2] cyclic dithiocarbonates **4** and trithiocarbonates **5**,[3] and oxazolidinones **6** and **7**[4] by reaction with carbon dioxide, carbon disulfide and isocyanates, respectively (Scheme 1).

Oxazolidinones find important applications in medicinal chemistry,[5] as chemical intermediates[6] and as chiral auxiliaries.[7] Many catalysts have been reported for the synthesis of oxazolidinones from epoxides and isocyanates since Speranza and Peppel published the first work in 1958;[4a] including ammonium salts, lanthanide salts, lithium halides, magnesium halides, tetraphenylantimony iodide, trialkyltin halides and metal complexes.[4] An important aspect of the reaction is its regioselectivity, which determines the **6**:**7** ratio.



Scheme 1. Synthesis of five-membered heterocycles by the reaction between epoxides and heterocumulenes.

We have previously reported that bimetallic aluminium(salen) complex **8** (Figure 1) is an active catalyst for the reaction of epoxides with carbon dioxide,[4t,8] carbon disulfide[3q,r,4t] and isocyanates.[4q,t] For the synthesis of oxazolidinones, the optimal conditions were 5 mol% of catalyst at 80 °C for 24 h in a non-polar solvent such as toluene. The catalyst was shown to be active for a range of mono- and disubstituted epoxides with aromatic isocyanates, giving good to excellent yields of oxazolidinones. Vanadium(salen) complex **9** in combination with tetrabutylammonium bromide was also shown to be an

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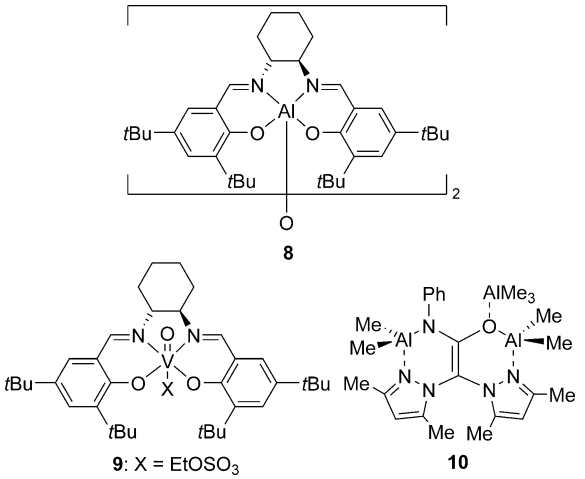


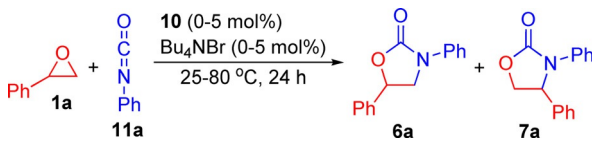
Figure 1. Catalysts for oxazolidinone and cyclic carbonate synthesis.

effective catalyst for the synthesis of oxazolidinones from epoxides and aromatic isocyanates.[4s] This catalyst also showed a broad scope and was applied to eight epoxides and six aromatic isocyanates giving the oxazolidinone products in yields of up to 89% of the major regioisomer.

Whilst salen complexes often give active catalysts in reactions involving ring opening of epoxides,[9] the tetradentate nature of the salen ligand restricts the opportunities to vary the coordination number and geometry around the metal ion(s). Therefore, we have been interested in exploring the use of other types of ligand to allow a wider range of metal complex geometries to be investigated. Recently, we reported cyclic carbonate synthesis from epoxides and carbon dioxide using aluminium heteroscorpionate complexes as catalysts.[10] A combination of trimetallic complex **10** and tetrabutylammonium bromide was shown to be the third most active aluminium catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide at ambient temperature and one bar carbon dioxide pressure.[10b] Herein, we report the use of a range of mono-, bi- and trimetallic scorpionate-based aluminium complexes as catalysts for the production of oxazolidinones from epoxides and isocyanates.

Results and Discussion

For initial studies on the reaction between epoxides and isocyanates, styrene oxide **1a** and phenylisocyanate **11a** were used as test substrates in a 1:1 ratio (Scheme 2). Complex **10** was as the lead catalyst as it was the most active aluminium scorpionate catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide[10b] and the results obtained are



Scheme 2. Reaction of styrene oxide **1a** and phenylisocyanate **11a**.

Table 1. Optimisation of reaction conditions for the reaction of styrene oxide **1a** with phenylisocyanate **11a** catalysed by complex **10**.

Entry	**10** [mol%]	Bu_4NBr [mol%]	Solvent	*T* [°C]	Conv. [%][a]	**6a**:**7a**[a]
1	5	5	–	25	5	1:1.4
2	5	5	–	50	16	1:1.8
3	5	5	–	80	0	–
4	5	5	toluene	80	100	1:1.3
5	5	–	toluene	80	20	1:3.0
6	–	5	toluene	80	25	1:3.8
7	5	5	DMC[b]	80	60	1:1.7
8	10	10	DMC[b]	80	62	1:1.6
9	5	5	DEC[c]	80	9	0:1
10	5	5	EC[d]	80	40	1:1.3
11	5	5	PC[e]	80	26	1:3.1
12	5	5	EtOAc	80	14	1:1.8
13	5	5	*p*-cymene	80	0	–
14[f]	5	5	EC[d]	80	41	1:1.5
15[g]	5	5	EC[d]	80	44	1:1.5
16[f]	5	5	PC[e]	80	45	1:1.2
17[g]	5	5	PC[e]	80	28	1:1.6

[a] Conversion of epoxide **1a** into **6a** + **7a** and ratio of **6a**:**7a** determined by ^{1}H NMR spectroscopy of the unpurified reaction mixture. [b] Dimethyl carbonate. [c] Diethyl carbonate. [d] Ethylene carbonate. [e] Propylene carbonate. [f] 1.2 equivalents of phenylisocyanate used. [g] 3.0 equivalents of phenylisocyanate used.

shown in Table 1. Initial conditions were based on the use of 5 mol% of complex **10** and tetrabutylammonium bromide as a co-catalyst for 24 h under solvent-free conditions, which were optimal for the reaction of carbon dioxide and epoxides.[10b] However, conversions were very low for reactions performed at 25–80 °C (Table 1, entries 1–3) because of the solidification of the reaction mixture within two hours. This suggested that a solvent was required to increase the conversion to the oxazolidinone products.

Toluene was initially selected as a solvent for the reaction as it has previously been shown to be a suitable solvent for oxazolidinone synthesis.[4q,t] The use of toluene had a beneficial effect on the reaction, enabling quantitative conversion of styrene oxide into a 1:1.3 ratio of oxazolidinones **6a** and **7a** in 24 h when 5 mol% of both complex **10** and tetrabutylammonium bromide were used as the catalyst system (Table 1, entry 4). Control experiments showed that under these conditions, complex **10** or tetrabutylammonium bromide alone had only low catalytic activity, giving 20% and 25% conversion into oxazolidinones **6a** and **7a** with a ratio of 1:3.0 and 1:3.8, respectively (entries 5, 6). This suggests that a nucleophile is needed to ring-open the epoxide coordinated to an aluminium of complex **10**.

A range of greener solvents was also investigated (Table 1, entries 7–13), but none could match the conversion obtained using toluene as solvent. Dimethyl (DMC) and diethyl carbonate (DEC) have previously been used as green replacements for toluene.[11] However, whilst DMC gave promising results (entry 7), the conversion was still lower than that obtained in toluene and could not be improved by doubling the catalyst concentrations (entry 8). Ethylene (EC) and propylene carbonate (PC) are hygroscopic and are polar aprotic solvents[12] and

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they, like DMC, gave moderate conversions (entries 10, 11). Thus, the amount of phenylisocyanate used was increased to 1.2 or 3.0 equivalents relative to styrene oxide to investigate if the low conversions were caused by hydrolysis of the phenylisocyanate. However, no significant increase in conversion was observed (entries 14–17). Therefore, toluene was used for further studies.

The structure of the catalyst was next varied and 21 additional complexes were tested (Figure 2), including:

1) complexes **12**–**18**: Mononuclear alkyl aluminium complexes supported by one scorpionate ligand.[13]
2) complexes **19**–**20**: Mononuclear phenoxide aluminium complexes supported by one scorpionate ligand.[13]
3) complexes **21**–**26**: Mononuclear alkyl aluminium complexes containing two scorpionate ligands.[14]
4) complexes **27**–**29**: Binuclear alkyl aluminium complexes containing one scorpionate ligand.[15]
5) complexes **30**–**32**: Trinuclear alkyl aluminium complexes containing one scorpionate ligand.[15]

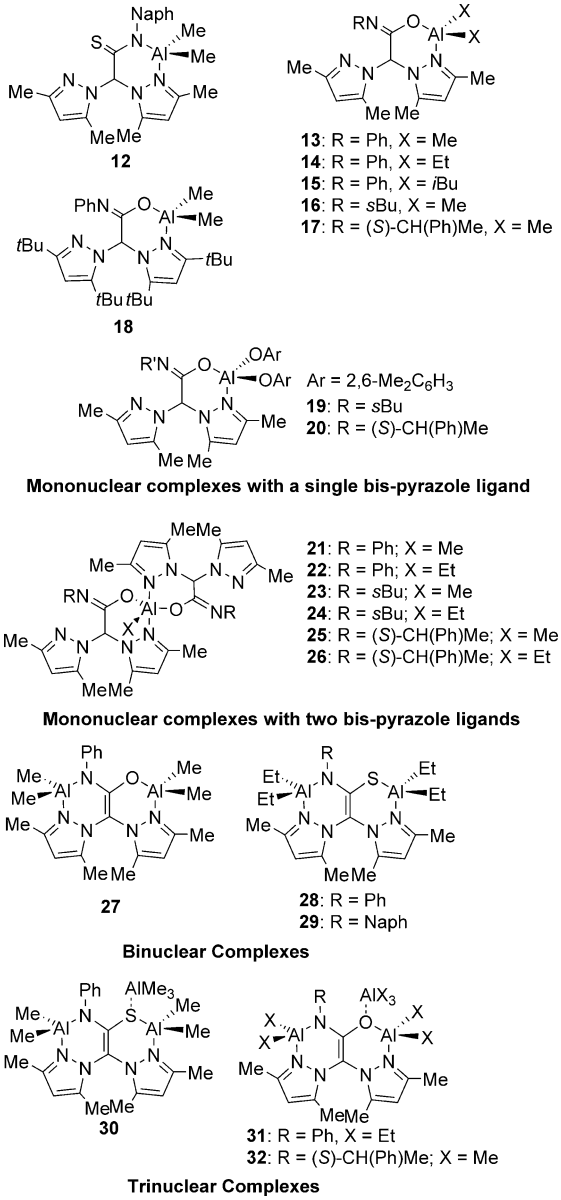

Figure 2. Complexes **12**–**32**.

Complexes **12**–**32** were tested for the reaction of styrene oxide **1a** with phenylisocyanate **11a** to produce oxazolidinones **6a**:**7a** in toluene at 80 °C for 24 h using 5 mol% of complexes **12**–**32** and tetrabutylammonium bromide. The results are shown in Table 2.

Table 2. Use of complexes **12**–**32** as catalysts for the synthesis of oxazolidinones **6a**:**7a**.[a]

Entry	Catalyst	Conversion [%][b]	**6a**:**7a**
1	**12**	0	–
2	**13**	14	1:2.0
3	**14**	22	1:1.8
4	**15**	36	1:1.3
5	**16**	24	1:3.3
6	**17**	0	–
7	**18**	31	2.2:1
8	**19**	56	1:1.2
9	**20**	0	–
10	**21**	0	–
11	**22**	18	4:1
12	**23**	22	2.6:1
13	**24**	77	1.6:1
14	**25**	0	–
15	**26**	0	–
16	**27**	52	1:1.3
17	**28**	100	1:1.5
18	**29**	0	–
19	**30**	16	1:10
20	**31**	36	1:1.4
21	**32**	72	1:1.2

[a] Reactions performed at 80 °C for 24 h with 5 mol% of catalyst **12**–**32** and 5 mol% of tetrabutylammonium bromide. [b] Conversion of epoxide **1a** into **6a**+**7a** and ratio of **6a**:**7a** determined by ^{1}H NMR spectroscopy of the unpurified reaction mixture.

Mononuclear acetamidate complexes **13**–**17** displayed moderate levels of catalytic activity under the optimal reaction conditions (Table 2, entries 2–6). In contrast, mononuclear thioacetamidate complex **12** displayed no catalytic activity at all (entry 1), suggesting higher Lewis acidity of aluminium in complexes **13**–**17** than in complex **12**, probably because of the more electron-withdrawing effect of acetamidate than thioacetamidate ligands. The effect of the alkyl ligand attached to aluminium was investigated (entries 2–4) and it was found that Me > Et > *t*Bu, a trend that is consistent with the decrease in the lability of the Al–C bond. By replacing the methyl group on the pyrazole ring by a *tert*-butyl group, the conversion increased from 14% to 31% (entries 2 and 7), showing that encumbered substituents on the pyrazoles improves the catalytic performance. Complex **18** also changed the regiochemistry of the oxazolidinone synthesis, favouring the formation of the 3,5-isomer **6a** (entry 7). Changing the alkyl groups in complex **16** to phenoxy groups in complex **19** had a beneficial effect on the catalytic activity of the complex (entries 5 and 8).

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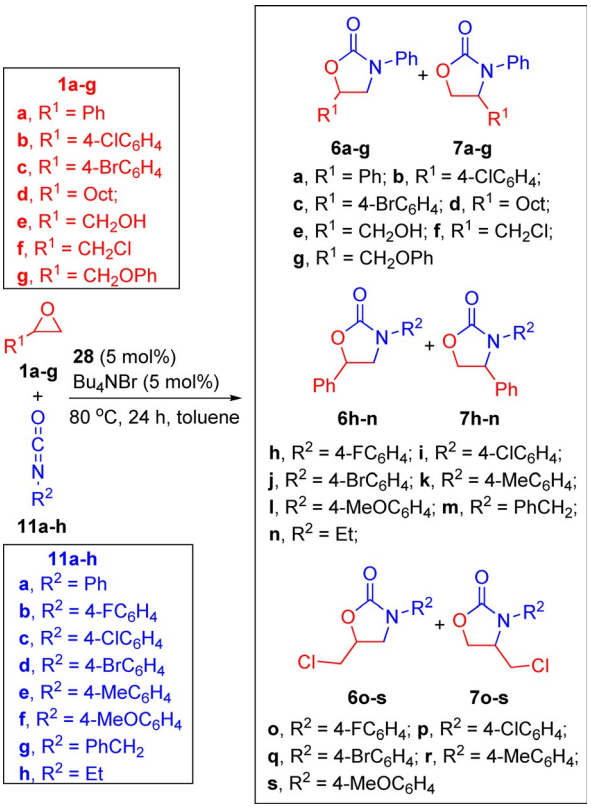
Monoaluminium complexes **21**–**26** supported by two bidentate bispyrazole ligands displayed no to good catalytic activity (Table 2, entries 10–15). In general, these complexes showed lower catalytic activity, probably because the metal centre is too sterically hindered by the two scorpionate ligands. The complexes in this class that were active (**22**–**24**) also showed inverted regiochemistry, favouring the formation of 3,5-isomer **6a** (entries 11–13).

Bimetallic complex **28** showed excellent catalytic activity, giving complete conversion of styrene oxide **1a** into oxazolidinones **6a**:**7a** under optimal reaction conditions (Table 2, entry 17) highlighting the importance of a second aluminium. This finding was confirmed when comparing the results obtained for complexes **13** and **27** (entries 2 and 16). However, the nature of the substituent on the nitrogen of the thioacetamidate was critical as changing the phenyl group to a naphthyl group resulted in dramatic decrease in catalytic activity (entry 18). Finally, trimetallic complexes **30**–**32** showed moderate to good catalytic activity for the synthesis of oxazolidinones **6a**:**7a** (entries 19–21). However, these complexes were not as active as trimetallic complex **10**, which gave 100% conversion of styrene oxide **1a** into **6a**:**7a**.

The results obtained with catalysts **10**, **12**–**32** cannot be explained just on the basis of the number of aluminium centres in the catalysts. Thus, the two most active catalysts (**10** and **28**) are trimetallic and bimetallic, respectively. Complexes **27** and **10** also differ only by the presence of a third aluminium in complex **10**, yet this doubles the catalytic activity. Rather, the results suggest that the three-dimensional orientation of two or more Lewis acidic aluminium centres is important for optimal activity, a result which is indicative of cooperative catalysis involving two aluminium centres activating both components of the reaction. Most of catalysts **10**, **12**–**32** had no significant effect on the regiochemistry of the reaction, exhibiting a slight preference for the formation of 3,4-isomer **7a**. However, sterically hindered mononuclear complexes **18** and **22**–**24** did have an effect on the reaction regiochemistry, giving 3,5-isomer **6a** as the major product, though with very low conversions except for complex **24**, which unfortunately gave the lowest regioselectivity (entry 13).

Amongst the aluminium catalysts studied, catalysts **10** and **28** gave quantitative conversions to the oxazolidinone products **6a**:**7a** in a 1:1.3 and 1:1.5, ratio respectively. As complex **28** gave a slightly higher **6a**:**7a** ratio, is more stable and easier to synthesise, we determined that complex **28** was the optimal catalyst for this transformation. Therefore, we investigated the synthesis of a range of oxazolidinones using 5 mol% of catalyst **28** and 5 mol% of tetrabutylammonium bromide in toluene at 80 °C for 24 h (Scheme 3) and the results are shown in Table 3.

If aromatic epoxides **1b** and **1c** containing an electron-withdrawing group in the *para*-position were used as substrates (Table 3, entries 2, 3), excellent conversions were achieved though the **6b**,**c**:**7b**,**c** ratio decreased from 1:1.5 to 1:1. This is caused by the electron-withdrawing groups destabilizing the benzylic carbocation favouring the formation of the 3,4-isomer **6b**,**c**. Unfunctionalised aliphatic epoxide **1d** gave 85% conversion, with the 3,5-isomer **7d** as the major product (entry 4). Glycidol **1e** was found not to be a good substrate for this reaction because the alcohol functionality can react with the alkyl groups and hydrolyse catalyst **28** (entry 5). In contrast, functionalised aliphatic epoxides epichlorohydrin **1f** and 3-phenoxypropylene oxide **1g** were excellent substrates, giving 100% conversion and 100% regioselectivity to the 3,5-isomer **6f**–**g** (entries 6, 7). These results are consistent with the nucleophilic attack of the bromide taking place at the less hindered carbon atom of an aliphatic epoxide by an S_N2 type mechanism, but in some cases, also at the more hindered carbon atom by a mechanism with some S_N1 character. Relative to 1-decene oxide **1d** with a simple alkyl substituent, the presence of electronegative groups (as in epoxides **1f** and **1g**) disfavours the S_N1 type reaction, whilst aromatic groups favour the S_N1 type process to an extent that depends on how electron-rich the aromatic ring is (epoxides **1a**–**c**).[16]



Scheme 3. Synthesis of oxazolidinones **6a**–**s**/**7a**–**s**.

Styrene oxide **1a** and epichlorohydrin **1f** were selected as representative aromatic and aliphatic epoxides respectively for the synthesis of a wider range of oxazolidinones. These epoxides were reacted with five substituted aromatic isocyanates **11b**–**f** and two aliphatic isocyanates **11g**,**h** and the results are shown in Table 3, entries 8–21. Catalyst **28** was found to be highly active for the synthesis of oxazolidinones if aromatic isocyanates **11b**–**f** were used, achieving good to excellent conversions and isolated yields (entries 8–12 and 15–19). However, no conversion was obtained if aliphatic isocyanates **11g**,**h** were used (entries 13, 14 and 20, 21), indicating that the reac-

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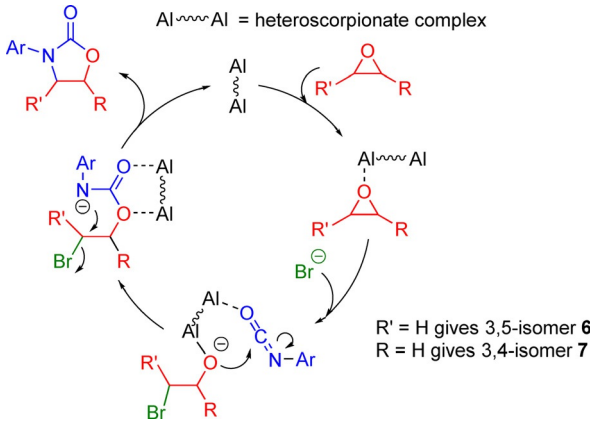
Table 3. Synthesis of oxazolidinones **6a–s/7a–s** catalysed by complex **28**.[a]

Entry	Epoxide	Isocyanate	Conv. [%][b]	Yield [%][c]	**6a:7a**
1	**1a** (R^1 = Ph)	**11a** (R^2 = Ph)	100	96	1:1.5
2	**1b** (R^1 = 4-ClC_6H_4)	**11a** (R^2 = Ph)	100	75	1:1
3	**1c** (R^1 = 4-BrC_6H_4)	**11a** (R^2 = Ph)	100	73	1:1
4	**1d** (R^1 = Oct)	**11a** (R^2 = Ph)	85	67	3.2:1
5	**1e** (R^1 = CH_2OH)	**11a** (R^2 = Ph)	0		–
6	**1f** (R^1 = CH_2Cl)	**11a** (R^2 = Ph)	100	97	1:0
7	**1g**(R^1 = CH_2OPh)	**11a** (R^2 = Ph)	100	93	1:0
8	**1a** (R^1 = Ph)	**11b** (R^2 = 4-FC_6H_4)	100	79	1:1.2
9	**1a** (R^1 = Ph)	**11c** (R^2 = 4-ClC_6H_4)	100	86	1:1.3
10	**1a** (R^1 = Ph)	**11d** (R^2 = 4-BrC_6H_4)	69	62	1:1.4
11	**1a** (R^1 = Ph)	**11e** (R^2 = 4-MeC_6H_4)	91	73	1:1.4
12	**1a** (R^1 = Ph)	**11f** (R^2 = 4-MeOC_6H_4)	88	65	1:1.3
13	**1a** (R^1 = Ph)	**11g** (R^2 = CH_2Ph)	0	–	–
14	**1a** (R^1 = Ph)	**11h** (R^2 = Et)	0	–	–
15	**1f** (R^1 = CH_2Cl)	**11b** (R^2 = 4-FC_6H_4)	71	67	1:0
16	**1f** (R^1 = CH_2Cl)	**11c** (R^2 = 4-ClC_6H_4)	82	81	1:0
17	**1f** (R^1 = CH_2Cl)	**11d** (R^2 = 4-BrC_6H_4)	100	79	1:0
18	**1f** (R^1 = CH_2Cl)	**11e** (R^2 = 4-MeC_6H_4)	100	81	1:0
19	**1f** (R^1 = CH_2Cl)	**11f** (R^2 = 4-MeOC_6H_4)	100	78	1:0
20	**1f** (R^1 = CH_2Cl)	**11g** (R^2 = CH_2Ph)	0	–	–
21	**1f** (R^1 = CH_2Cl)	**11h** (R^2 = Et)	0	–	–

[a] Reactions performed at 80 °C for 24 h with 5 mol% of catalyst **28** and 5 mol% of tetrabutylammonium bromide. [b] Conversion of epoxide **1a–g** into **6a–s**+**7a–s** and ratio of **6a–s**:**7a–s** determined by ^{1}H NMR spectroscopy of the unpurified reaction mixture. [c] Yield of isolated oxazolidinone.

tion is restricted to aromatic isocyanates. As presented in Table 3 and consistent with the analysis presented above, if styrene oxide **1a** was used as substrate and reacted with aromatic isocyanates, 3,4-oxazolidinones **7h–l** were the major products formed in a 1:1.2 to 1:1.4 ratio relative to the 3,5-isomer **6h–l**. However, if epichlorohydrin **1f** was reacted with aromatic isocyanates, the reaction was completely regioselective for the formation of the 3,5-oxazolidinone products **6o–r**.

Based on the need for a co-catalyst, the higher reactivity of polymetallic complexes and previous results for the synthesis of cyclic carbonates catalysed by acetamidate and thioacetamidate scorpionate aluminium complexes,[10] we propose the mechanism shown in Scheme 4. First, the epoxide is activated by coordination to one of the aluminium centres. Then, the bromide anion provided by the tetrabutylammonium bromide ring-opens the coordinated epoxide to form a halo-alkoxide. The isocyanate can be activated by a second aluminium centre (if present in the catalyst) and is inserted into the aluminium–oxygen bond to afford a carbamate, which can ring-close to give the oxazolidinone and regenerate the tetrabutylammonium bromide and the aluminium complex. The formation of regioisomer **6** or **7** is determined by the regiochemistry of the initial epoxide ring opening by bromide, which in turn is determined by the nature of the substituent attached to the epoxide rather than by the nature of the catalyst except if the catalyst contains only sterically hindered aluminiums.



Scheme 4. Possible mechanism for the synthesis of oxazolidinones catalysed by heteroscorpionate aluminium complexes.

Conclusions

Bimetallic scorpionate aluminium complex **28** catalyses the synthesis of oxazolidinones from epoxides and aromatic isocyanates. Compared to our previously reported bimetallic aluminium(salen) catalyst **8**, tetrabutylammonium bromide is required as a co-catalyst whilst this was shown to inhibit oxazolidinone formation catalysed by complex **8**.[4q] The reaction mechanism seems to involve a dual Lewis acid activation of the epoxide and the isocyanate by aluminium complex **28** and a nucleophilic attack of the bromide predominantly at the less hindered carbon atom of the epoxide.

Compared to the previously reported catalysts for this reaction,[4a,c,d] the combination of complex **28** and tetrabutylammonium bromide allows reactions to be conducted at lower temperatures. Only 5 mol% of catalyst loading is needed to achieve good to excellent yields compared to previous catalyst systems in which up to 50 mol% was required.[4f,h–j,p] The regiochemistry of the reaction is controlled by the substrate on the

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basis of carbenium ion stability rather than the catalyst as the same regiochemical trends have been observed with previously reported metal(salen)-based catalysts[4q,s,t] and the complexes reported in this paper. Complex **28** is derived from aluminium, which is inexpensive and an Earth-crust abundant metal,[17] avoiding the use of highly toxic catalysts[4f–l] and expensive lanthanide-based catalysts.[4u,18] The largest remaining challenge in enhancing the sustainability of this reaction is the use of toxic isocyanates. Future work should focus on using alternative reagents such as carbamates or on the in situ generation of isocyanates from non-toxic precursors such as amines and carbon dioxide.

Experimental Section

Commercially available chemicals (Alfa, Aldrich, Fluka) were used as received and all reactions were performed in dry glassware. Heteroscorpionate ligands and aluminium complexes **10** and **12--32** were prepared as reported previously.[13–15] ^{1}H and ^{13}C NMR spectra were recorded on a Jeol Oxford 400 spectrometer at resonance frequencies of 400 and 100 MHz, respectively. All spectra were recorded at ambient temperature and were referenced to the residual solvent peak. Mass spectrometry was performed by the University of York mass spectrometry service using electrospray ionisation (ESI). Melting points were determined using a Stuart SMP3 apparatus. Infrared spectra were recorded on a Bruker Vertex 70 instrument equipped with "Specac" Golden Gate Single Reflection Diamond ATR accessories.

General procedure for oxazolidinone synthesis

Epoxide **1a–g** (0.874 mmol) and isocyanate **11a–h** (0.874 mmol) were added to solution of catalyst **10**, **12–32** (0.044 mmol) and Bu_4NBr (14 mg, 0.044 mmol) in dry toluene (1.5 mL). The resulting mixture was stirred at 80 °C for 24 h. After being allowed to cool to RT, toluene was removed in vacuo to give the crude oxazolidinone products. The conversion of epoxide to oxazolidinone was then determined by ^{1}H NMR spectroscopy of the crude mixture. The products were purified by flash chromatography to give compounds **6/7a–s**.

3,5-Diphenyloxazolidin-2-one (**6a**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (5:1), then hexane–EtOAc (3:1). (80 mg, 38%). M.p. 80–82 °C (lit. 79–82 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.56$ (2H, d, J 7.8 Hz, ArH), 7.46–7.35 (7H, m, ArH), 7.15 (1H, t, J 7.4 Hz, ArH), 5.64 (1H, dd, J 8.6, 7.6 Hz, CHO), 4.38 (1H, t, J 8.8 Hz, CH_2N), 3.96 ppm (1H, dd, J 8.9, 7.6 Hz, CH_2N). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 154.8$, 138.2, 138.2, 129.2, 129.1, 125.8, 124.3, 118.4, 74.1, 52.8 ppm. Mass spec. (ESI+): calcd. m/z 240.1019 $[C_{15}H_{13}NO_2+H]^+$; found: 240.1015. calcd. m/z 262.0838 $[C_{15}H_{13}NO_2+Na]^+$; found: 262.0838. IR Neat: $\tilde{\nu} = 1745.2$ cm^{-1}.

3,4-Diphenyloxazolidin-2-one (**7a**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (5:1), then hexane–EtOAc (3:1) (121 mg, 58%). M.p. 77–79 °C (lit. 76–78 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.50$–7.20 (9H, m, ArH), 7.10 (1H, t, J 7.4 Hz, ArH), 5.43 (1H, dd, J 8.7, 6.0 Hz, CHN), 4.80 (1H, t, J 8.7 Hz, CH_2O), 4.23 ppm (1H, dd, J 8.6, 6.0 Hz, CH_2O). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 155.8$, 138.6, 137.3, 129.4, 128.9, 128.8, 126.3, 124.7, 121.0, 69.8, 60.9 ppm. Mass spec. (ESI+): calcd. m/z 240.1019 $[C_{15}H_{13}NO_2+H]^+$; found: 240.1015. calcd. m/z 262.0838 $[C_{15}H_{13}NO_2+Na]^+$; found: 262.0838. IR Neat: $\tilde{\nu} = 1741.3$ cm^{-1}.

3-Phenyl-5-(4-chlorophenyl)-oxazolidin-2-one (**6b**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of CH_2Cl_2–hexane (4:1) (90 mg, 38%). M.p. 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.54$ (2H, d, J 7.9 Hz, ArH), 7.45–7.35 (6H, m, ArH), 7.16 (1H, td, J 7.4, 0.9 Hz, ArH), 5.64 (1H, t, J 8.2 Hz, CHO), 4.39 (1H, t, J 8.9 Hz, CH_2N), 3.93 ppm (1H, dd, J 8.9, 7.5 Hz, CH_2N). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 154.4$, 137.9, 136.6, 135.1, 129.3, 129.1, 127.1, 124.3, 118.3, 73.3, 52.6 ppm. Mass spec. (ESI+): calcd. m/z 274.0629 $[C_{15}H_{12}ClNO_2+H]^+$; found: 274.0636. Calcd. m/z 296.0449 $[C_{15}H_{12}ClNO_2+Na]^+$; found: 296.0449. IR Neat: $\tilde{\nu} = 1733.4$ cm^{-1}.

3-Phenyl-4-(4-chlorophenyl)-oxazolidin-2-one (**7b**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of CH_2Cl_2–hexane (4:1) (90 mg, 38%). M.p. 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.40$–7.20 (8H, m, ArH), 7.12–7.02 (1H, m, ArH), 5.37 (1H, dd, J 8.7, 6.0 Hz, CHN), 4.76 (1H, dd, J 9.3 8.2 Hz, CH_2O), 4.15 ppm (1H, dd, J 8.7, 6.0 Hz, CH_2O). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 155.8$, 136.8, 136.8, 134.9, 129.7, 129.1, 127.7, 125.0, 120.9, 69.6, 60.2 ppm. Mass spec. (ESI+): calcd. m/z 274.0629 $[C_{15}H_{12}ClNO_2+H]^+$; found: 274.0636. Calcd. m/z 296.0449 $[C_{15}H_{12}ClNO_2+Na]^+$; found: 296.0449. IR Neat: $\tilde{\nu} =$ 1733.4 cm^{-1}.

3-Phenyl-5-(4-bromophenyl)-oxazolidin-2-one (**6c**): Obtained as a white solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (7:1), then hexane–EtOAc (4:1), then hexane–EtOAc (3:1), (100 mg, 36%). M.p 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.60$–7.50 (4H, m, ArH), 7.45–7.35 (2H, m, ArH), 7.35–7.30 (2H, m, ArH), 7.20–7.10 (1H, m, ArH), 5.60 (1H, t, J 8.2 Hz, CHO), 4.39 (1H, t, J 8.9 Hz, CH_2N), 3.92 ppm (1H, dd, J 8.9, 7.5 Hz, CH_2N). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 155.4$, 137.9, 137.2, 132.2, 129.2, 127.3, 124.4 123.2, 118.3, 73.3, 52.5 ppm. Mass spec. (ESI+): calcd. m/z 339.9944 $[C_{15}H_{12}BrNO_2+Na]^+$; found: 339.9937. IR Neat: $\tilde{\nu} = 1725.5$ cm^{-1}.

3-Phenyl-4-(4-bromophenyl)-oxazolidin-2-one (**7c**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (7:1), then hexane–EtOAc (4:1), then hexane-EtOAc (3:1), (103 mg, 37%). M.p. 156–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.49$ (2H, d, J 8.4 Hz, ArH), 7.40–7.35 (2H, m, ArH), 7.30–7.25 (2H, m, ArH), 7.19 (2H, d, J 8.4, ArH), 7.10 (1H, t, J 7.4, ArH), 5.37 (1H, dd, J 8.7, 6.0 Hz, CHN), 4.78 (1H, t, J 8.7 Hz, CH_2O), 4.17 ppm (1H, dd, J 8.7, 6.0 Hz, CH_2O). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 155.4$, 136.9, 132.3, 128.9, 128.7, 127.6 124.6, 122.6, 120.5, 69.2, 59.8 ppm. Mass spec. (ESI+): calcd. m/z 339.9944 $[C_{15}H_{12}BrNO_2+Na]^+$; found: 339.9937. IR Neat: $\tilde{\nu} = 1745.2$ cm^{-1}.

3-Phenyl-5-octyloxazolidin-2-one (**6d**): Obtained as a white solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (123 mg, 51%). M.p. 71–73 °C (lit. 70–71 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.54$ (2H, d, J 8.9 Hz, ArH), 7.37 (2H, t J 8.1 Hz, ArH), 7.13 (1H, t, J 7.4 Hz, ArH), 4.64 (1H, m, CHO), 4.08 (1H, t, J 8.5 Hz, CH_2N), 3.66 (1H, dd, J 8.6, 7.2 Hz, CH_2N), 1.90–1.60 (2H, m, CH_2), 1.45–1.15 (12H, m, $6\times CH_2$), 0.95–0.75 ppm (3H, m, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): $\delta =$ 155.3, 138.7, 129.3, 124.2, 118.5, 73.4, 50.8, 35.4, 32.1, 29.7, 29.6, 29.5, 24.9, 22.9, 14.4 ppm. Mass spec. (ESI+): calcd. m/z 276.1958 $[C_{17}H_{25}NO_2+H]^+$; found: 276.1960. Calcd. m/z 298.1778 $[C_{17}H_{25}NO_2+Na]^+$; found: 298.1771. IR Neat: $\tilde{\nu} = 1716.6$ cm^{-1}.

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3-Phenyl-4-octyloxazolidin-2-one (**7d**): Obtained as a pale yellow oil after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (39 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.60–7.30 (3H, m, ArH), 7.25–7.15 (2H, m, ArH), 4.56 (1H, t, *J* 8.4 Hz, CHN), 4.50–4.35 (1H, m, CH_2O), 4.16 (1H, dd, *J* 8.3, 5.3 Hz, CH_2O), 1.85–1.45 (2H, m, CH_2), 1.45–1.15 (12H, m, 6× CH_2), 0.88 ppm (3H, t, *J* 6.5 Hz, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.7, 137.0, 129.2, 125.2, 122.1, 66.9, 56.5, 32.0, 31.7, 29.3, 29.2, 29.0, 24.0, 22.5, 13.9 ppm. Mass spec. (ESI+): calcd. *m/z* 276.1958 $[C_{17}H_{25}NO_2+H]^+$; found: 276.1955. Calcd. *m/z* 298.1778 $[C_{17}H_{25}NO_2+Na]^+$; found: 298.1781. IR Neat: $\tilde{\nu}$ = 1723 cm^{-1}.

3-Phenyl-5-chloromethyloxazolidin-2-one (**6f**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (2:1) (179 mg, 97%). M.p. 108–110 °C (lit. 101–103 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.60–7.50 (2H, m, ArH), 7.45–7.35 (2H, m, ArH), 7.16 (1H, tt, *J* 7.4, 1.0 Hz, ArH), 4.95–4.80 (1H, m, CHO), 4.17 (1H, t, *J* 9.0, Hz, CH_2N), 3.96 (1H, dd, *J* 9.2, 5.7 Hz, CH_2N), 3.79 (1H, dd, *J* 11.6, 4.1 CH_2Cl), 3.74 ppm (1H, dd, *J* 11.6, 6.5, CH_2Cl). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 153.9, 137.8, 129.1, 124.4, 118.3, 70.8, 48.1, 44.5 ppm. Mass spec. (ESI+): calcd. *m/z* 234.0292 $[C_{10}H_{10}ClNO_2+Na]^+$; found: 234.0298. IR Neat: $\tilde{\nu}$ = 1727.9 cm^{-1}.

3-Phenyl-5-phenoxymethyloxazolidin-2-one (**6g**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (3:1), then hexane–EtOAc (2:1) (218 mg, 93%). M.p. 138–141 °C (lit. 139–140 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.60 (2H, d, *J* 7.9 Hz, ArH), 7.42 (2H, t, *J* 8.02 Hz, ArH), 7.31 (2H, d, *J* 8.5 Hz, ArH), 7.18 (1H, t, *J* 7.4 Hz, ArH), 7.02 (1H, t, *J* 7.3 Hz, ArH), 6.93 (2H, d, *J* 7.9 Hz, ArH), 5.10–4.90 (1H, m, CHO), 4.35–4.20 (3H, m, CH_2O+CH_2N), 4.10 ppm (1H, dd, *J* 8.9, 6.0 Hz, CH_2N). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 158.3, 154.3, 138.4, 129.7, 129.1, 124.3, 122.0, 118.6, 115.0, 70.5, 68.4, 47.7 ppm. Mass spec. (ESI+): calcd. *m/z* 292.0944 $[C_{16}H_{15}NO_3+Na]^+$; found: 292.0949. IR Neat: $\tilde{\nu}$ = 1731.9 cm^{-1}.

3-(4-Fluorophenyl)-5-phenyloxazolidin-2-one (**6h**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (7:1), then hexane–EtOAc (5:1) (81 mg, 36%). M.p. 78–80 °C (lit. 78–81 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.55–7.40 (7H, m, ArH), 7.08 (2H, m, ArH), 5.65 (1H, dd, *J* 8.6, 7.6 Hz, CHO), 4.37 (1H, t, *J* 8.8 Hz, CH_2N), 3.95 ppm (1H, dd, *J* 8.6, 7.6 Hz, CH_2N). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 159.4 (d, *J* 244 Hz), 154.8, 137.9, 134.2, 129.2, 129.1, 125.6, 120.1 (d, *J* 8 Hz), 115.8 (d, *J* 23 Hz), 74.0, 53.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ = −118.25 ppm (s). Mass spec. (ESI+): calcd. *m/z* 258.0925 $[C_{15}H_{12}FNO_2+H]^+$; found: 280.0749. calcd. *m/z* 280.0744 $[C_{15}H_{12}FNO_2+Na]^+$; found: 280.0749. IR Neat: $\tilde{\nu}$ = 1732.1 cm^{-1}.

3-(4-Fluorophenyl)-4-phenyloxazolidin-2-one (**7h**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (7:1), then hexane–EtOAc (5:1) (97 mg, 43%). M.p. 95–97 °C (lit. 94–97 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.4–7.25 (7H, m, ArH), 6.93 (2H, m, ArH), 5.33 (1H, dd, *J* 8.8, 6.3 Hz, CHN), 4.77 (1H, t, *J* 8.7 Hz, CH_2O), 4.20 ppm (1H, dd, *J* 8.7, 6.3 Hz, CH_2O). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 161.5, 155.9, 138.2, 133.3, 129.5, 129.0, 126.4, 123.1 (d, *J* 8 Hz), 115.7 (d, *J* 23 Hz), 69.7, 61.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ = −117.01 ppm (s). Mass spec. (ESI+): calcd. *m/z* 258.0925 $[C_{15}H_{12}FNO_2+H]^+$; found: 280.0749. calcd. *m/z* 280.0744 $[C_{15}H_{12}FNO_2+Na]^+$; found: 280.0749. IR Neat: $\tilde{\nu}$ = 1732.1 cm^{-1}.

3-(4-Chlorophenyl)-5-phenyloxazolidin-2-one (**6i**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (89 mg, 37%). M.p. 115–119 °C (lit. 113–117 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.55–7.25 (9H, m, ArH), 5.66 (1H, dd, *J* 8.5, 7.8 Hz, CHO), 4.37 (1H, t, *J* 8.8 Hz, CH_2N), 3.95 ppm (1H, dd, *J* 8.8, 7.6 Hz, CH_2N). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.8, 138.1, 137.0, 129.7, 129.5, 129.4, 125.9, 119.7, 74.3, 52.9 ppm. Mass spec. (ESI+): calcd. *m/z* 274.0629 $[C_{15}H_{12}ClNO_2+H]^+$; found: 274.0629. calcd. *m/z* 296.0449 $[C_{15}H_{12}ClNO_2+Na]^+$; found: 296.0449. IR Neat: $\tilde{\nu}$ = 1735.9 cm^{-1}.

3-(4-Chlorophenyl)-4-phenyloxazolidin-2-one (**7i**): Obtained as a pale orange solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (116 mg, 49%). M.p. 125–128 (lit. 126–128 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.50–7.30 (9H, m, ArH), 5.36 (1H, dd, *J* 8.7, 6.2 Hz, CHN), 4.79 (1H, t, *J* 8.7 Hz, CH_2O), 4.21 ppm (1H, dd, *J* 8.7, 6.1 Hz, CH_2O). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.7, 137.7, 135.5, 129.8, 129.4, 129.0, 128.9, 126.2, 121.8, 69.7, 60.5 ppm. Mass spec. (ESI+): calcd. *m/z* 274.0629 $[C_{15}H_{12}ClNO_2+H]^+$; found: 274.0629. calcd. *m/z* 296.0449 $[C_{15}H_{12}ClNO_2+Na]^+$; found: 296.0449. IR Neat: $\tilde{\nu}$ = 1728.2 cm^{-1}.

3-(4-Bromophenyl)-5-phenyloxazolidin-2-one (**6j**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (72 mg, 26%). M.p. 101–105 °C (lit. 100–103 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.70–7.30 (9H, m, ArH), 5.64 (1H, t, *J* 8.5 Hz, CHO), 4.36 (1H, t, *J* 8.8 Hz, CH_2N), 3.94 ppm (1H, dd, *J* 8.8, 7.6 Hz, CH_2N). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.4, 137.9, 137.2, 132.7, 132.1, 130.0, 129.2, 129.1, 125.6, 119.7, 74.0, 52.6 ppm. Mass spec. (ESI+): calcd. *m/z* 318.0124 $[C_{15}H_{12}BrNO_2+H]^+$; found: 318.0125. calcd. *m/z* 339.9944 $[C_{15}H_{12}BrNO_2+Na]^+$; found: 339.9941. IR Neat: $\tilde{\nu}$ = 1749 cm^{-1}.

3-(4-Bromophenyl)-4-phenyloxazolidin-2-one (**7j**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (101 mg, 36%). M.p. 132–135 °C (lit. 134–137 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.50–7.30 (9H, m, ArH), 5.35 (1H, dd, *J* 8.7, 6.0 Hz, CHN), 4.77 (1H, t, *J* 8.7 Hz, CH_2O), 4.19 ppm (1H, dd, *J* 8.6, 6.0 Hz, CH_2O). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.6, 137.7, 136.1, 131.9, 129.5, 129.0, 126.1, 122.1, 117.6, 69.7, 60.5 ppm. Mass spec. (ESI+): calcd. *m/z* 318.0124 $[C_{15}H_{12}BrNO_2+H]^+$; found: 318.0130. calcd. *m/z* 339.9944 $[C_{15}H_{12}BrNO_2+Na]^+$; found: 339.9944. IR Neat: $\tilde{\nu}$ = 1742 cm^{-1}.

3-(4-Methylphenyl)-5-phenyloxazolidin-2-one (**6k**): Obtained as a white solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (68 mg, 31%). M.p. 96–98 °C (lit. 98–100 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.50–7.35 (6H, m, ArH), 7.18 (2H, d, *J* 8.4 Hz, ArH), 5.63 (1H, t, *J* 8.1 Hz, CHO), 4.36 (1H, t, *J* 8.8 Hz, CH_2N), 3.94 (1H, dd, *J* 8.8, 7.6 Hz, CH_2N), 2.34 ppm (3H, s, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.8, 138.2, 135.6, 133.9, 129.6, 129.0, 129.0, 125.7, 118.4, 74.0, 52.9, 20.7 ppm. Mass spec. (ESI+): calcd. *m/z* 254.1176 $[C_{16}H_{15}NO_2+H]^+$; found: 254.1168. calcd. *m/z* 276.0995 $[C_{16}H_{15}NO_2+Na]^+$; found: 279.0991. IR Neat: $\tilde{\nu}$ = 1735 cm^{-1}.

3-(4-Methylphenyl)-4-phenyloxazolidin-2-one (**7k**): Obtained as a white solid after purification by flash chromatography using a solvent system of hexane–EtOAc (9:1) (95 mg, 43%). M.p. 106–108 °C (lit. 105–107 °C).[4q] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.40–7.20 (6H, m, ArH), 7.05 (2H, d, *J* 8.7 Hz, ArH), 5.36 (1H, dd, *J* 8.8, 6.2 Hz, CHN), 4.76 (1H, t, *J* 8.7 Hz, CH_2O), 4.25–4.15 (1H, m, CH_2O), 2.25 ppm (3H, s, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, 298 K): δ =

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156.0, 138.3, 134.5, 134.4, 129.5, 129.3, 128.7, 126.3, 121.1, 69.8, 60.8, 20.7 ppm. Mass spec. (ESI+): calcd. *m/z* 276.0995 $[C_{16}H_{15}NO_2+Na]^+$; found: 279.1005. IR Neat: $\tilde{\nu}=1739\ cm^{-1}$.

3-(4-Methoxyphenyl)-5-phenyloxazolidin-2-one (**6l**): Obtained as a pale orange solid after purification by flash chromatography using a solvent system of hexane:EtOAc (5:1) (66 mg, 28%). M.p. 100–102 °C (lit. 105–107 °C).[4q] ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta=$ 7.50–7.35 (7H, m, ArH), 6.97–6.87 (2H, m, ArH), 5.63 (1H, dd, *J* 8.6, 7.6 Hz, CHO), 4.35 (1H, t, *J* 8.8 Hz, CH_2N), 3.94 (1H, dd, *J* 8.8, 7.6 Hz, CH_2N), 3.80 ppm (3H, s, OCH_3). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 298 K): $\delta=$156.4, 155.0, 138.2, 131.2, 129.0, 128.9, 125.6, 120.5, 114.2, 73.9, 55.4, 53.1 ppm. Mass spec. (ESI+): calcd. *m/z* 270.1125 $[C_{16}H_{15}NO_3+H]^+$; found: 270.1124. calcd. *m/z* 292.0944 $[C_{16}H_{15}ClNO_2+Na]^+$; found: 292.0944. IR Neat: $\tilde{\nu}=1732.1\ cm^{-1}$.

3-(4-Methoxyphenyl)-4-phenyloxazolidin-2-one (**7l**): Obtained as a pale orange solid after purification by flash chromatography using a solvent system of hexane–EtOAc (5:1) (86 mg, 37%). M.p. 134–136 °C (lit. 137–138 °C).[4q] ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta=$ 7.30–7.12 (7H, m, ArH), 6.74 (2H, d, *J* 9.2 Hz, ArH), 5.26 (1H, dd, *J* 8.7, 6.4 Hz, CHN), 4.72 (1H, t, *J* 8.7 Hz, CH_2O), 4.16 (1H, dd, *J* 8.7, 6.4 Hz, CH_2O), 3.67 ppm (3H, s, OCH_3). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 298 K): $\delta=$156.8, 156.4, 138.2, 129.8, 129.2, 128.8, 126.5, 123.3, 114.2, 69.7, 61.4, 55.3 ppm. Mass spec. (ESI+): calcd. *m/z* 270.1125 $[C_{16}H_{15}NO_3+H]^+$; found: 270.1124. calcd. *m/z* 292.0944 $[C_{16}H_{15}ClNO_2+Na]^+$; found: 292.0944. IR Neat: $\tilde{\nu}=1739.8\ cm^{-1}$.

3-(4-Fluorophenyl)-5-chloromethyloxazolidin-2-one (**6o**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (5:1) (125 mg, 67%). M.p. 102–105 °C (lit. 101–104 °C).[4q] ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta=$7.50 (2H, dd *J* 9.2, 4.6 Hz, ArH), 7.08 (2H, dd *J* 9.1, 8.3 Hz, ArH), 5.0–4.8 (1H, m, CHO), 4.15 (1H, t *J* 8.9 Hz, CH_2N), 3.94 (1H, dd *J* 9.1, 5.7 Hz, CH_2N), 3.80 (1H, dd *J* 11.6, 4.1 Hz, CH_2Cl), 3.75 ppm (1H, dd *J* 11.6, 6.6 Hz, CH_2Cl). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 298 K) 159.5 (d, *J* 244.5 Hz), 154.0, 133.9 (d, *J* 3.2 Hz), 120.2 (d, *J* 8.1 Hz), 115.9 (d, *J* 22.6 Hz), 70.8, 48.4, 44.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): $\delta=-116.96$ ppm (s). Mass spec. (ESI+): calcd. *m/z* 230.0379 $[C_{10}H_9ClFNO_2+H]^+$; found: 230.0371. calcd. *m/z* 252.0198 $[C_{10}H_9ClFNO_2+Na]^+$; found: 252.0195. IR Neat: $\tilde{\nu}=$ 1740 cm^{-1}.

3-(4-Chlorophenyl)-5-chloromethyloxazolidin-2-one (**6p**): Obtained as an orange solid after purification by flash chromatography using a solvent system of hexane–EtOAc (1:1) (174 mg, 81%). M.p. 129–132 °C (lit. 130–133 °C).[4q] ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta=$7.51–7.45 (2H, m, ArH), 7.36–7.30 (2H, m, ArH), 4.95–4.85 (1H, m, CHO), 4.15 (1H, t, *J* 8.9 Hz, CH_2N), 3.95 (1H, dd, *J* 9.1, 5.7 Hz, CH_2N), 3.80 (1H, dd *J* 12.3, 4.6 Hz, CH_2Cl), 3.76 ppm (1H, dd *J* 12.2, 6.8 Hz, CH_2Cl). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 298 K): $\delta=$ 153.7, 136.5, 129.6, 129.0, 119.6, 70.9, 48.1, 44.6 ppm. Mass spec. (ESI+): calcd. *m/z* 267.9903 $[C_{10}H_9Cl_2NO_2+Na]^+$; found: 267.9900. IR Neat: $\tilde{\nu}=1741.3\ cm^{-1}$.

3-(4-Bromophenyl)-5-chloromethyloxazolidin-2-one (**6q**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of first hexane–EtOAc (3:1), then hexane–EtOAc (2:1) (200 mg, 79%). M.p. 126–128 °C (lit. 125–128 °C).[4q] ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta=$7.53–7.43 (4H, m, ArH), 4.95–4.85 (1H, m, CHO), 4.15 (1H, t, *J* 8.94 Hz, CH_2N), 3.94 (1H, dd, *J* 9.1, 5.6 Hz, CH_2N), 3.80 (1H, dd *J* 13.0, 5.4 Hz, CH_2Cl), 3.75 ppm (1H, dd *J* 12.9, 7.8 Hz, CH_2Cl). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 298 K): $\delta=$ 153.6, 136.9, 132.6, 119.7, 117.2, 70.8, 48.0, 44.5 ppm. Mass spec. (ESI+): calcd. *m/z* 311.9397 $[C_{10}H_9BrClNO_2+Na]^+$; found: 311.9395. IR Neat: $\tilde{\nu}=1732.1\ cm^{-1}$.

3-(4-Methylphenyl)-5-chloromethyloxazolidin-2-one (**6r**): Obtained as a pale yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (3:1) (160 mg, 81%). M.p. 104–106 °C (lit. 104–107 °C).[4q] ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta=$7.42 (2H, d *J* 8.5 Hz), 7.18 (2H, d *J* 8.3 Hz), 4.95–4.77 (1H, m, CHO), 4.14 (1H, t *J* 9.0 Hz, CH_2N), 3.93 (1H, dd, *J* 9.2, 5.7 Hz, CH_2N), 3.79 (1H, dd, *J* 11.6, 4.1 Hz, CH_2Cl), 3.73 (1H, dd, *J* 11.6, 6.7 Hz, CH_2Cl), 2.32 ppm (3H, s, CH_3). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 298 K): $\delta=$154.0, 135.6, 134.1, 129.6, 118.5, 70.8, 48.3, 44.5, 20.7 ppm. Mass spec. (ESI+): calcd. *m/z* 226.0629 $[C_{11}H_{12}ClNO_2+H]^+$; found: 226.0619. calcd. *m/z* 248.0449 $[C_{11}H_{12}ClNO_2+Na]^+$; found: 248.0448. IR Neat: $\tilde{\nu}=1732\ cm^{-1}$.

3-(4-Methoxyphenyl)-5-chloromethyloxazolidin-2-one (**6s**): Obtained as a yellow solid after purification by flash chromatography using a solvent system of hexane–EtOAc (3:1) (165 mg, 78%). M.p. 106–108 °C (lit. 105–106 °C).[4q] ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta=$ 7.42 (2H, d, *J* 9.1 Hz, ArH), 6.91 (2H, d, *J* 9.1 Hz, ArH), 4.9–4.8 (1H, m, CHO), 4.12 (1H, t, *J* 8.9 Hz, CH_2N), 3.91 (1H, dd, *J* 9.1, 5.7 Hz, CH_2N), 3.79 (3H, s, OCH_3), 3.78–3.73 ppm (2H, m, CH_2Cl). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 298 K): $\delta=$156.6, 154.2, 130.8, 120.4, 114.4, 70.8, 55.5, 48.6, 44.6 ppm. Mass spec. (ESI+): calcd. *m/z* 242.0578 $[C_{11}H_{12}ClNO_3+H]^+$; found: 242.0575. calcd. *m/z* 264.0398 $[C_{11}H_{12}ClNO_3+Na]^+$; found: 264.0397. IR Neat: $\tilde{\nu}=1728.2\ cm^{-1}$.

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