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Vanadium^{V}(salen) catalysed synthesis of oxazolidinones from epoxides and isocyanates

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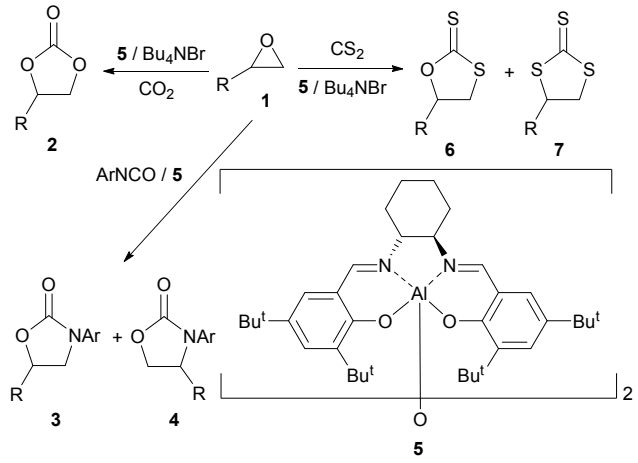
The combination of a vanadium^{V}(salen) complex V^{+}O(salen) $EtOSO_3^-$ and tetrabutylammonium bromide forms a highly active catalyst system for the reaction between epoxides and isocyanates leading to oxazolidinones. The reaction conditions were optimized and the optimal conditions (80 °C in toluene for 5 hours with 2 mol% of vanadium catalyst and 2 mol% of tetrabutylammonium bromide cocatalyst) applied to eight epoxides and six aromatic isocyanates, giving 18 oxazolidinones with conversions of 34–98% and isolated chemical yields of the major regioisomer of 23–89%.

Introduction

The reaction of epoxides **1** with heterocumulenes can lead to a range of five–membered ring heterocycles, some of which are shown in Scheme 1. The area is currently dominated by the synthesis of cyclic carbonates **2** from epoxides and carbon dioxide,[1] but the reaction of epoxides with isocyanates to form oxazolidinones **3/4** is also of significant interest as oxazolidinones are components of pharmaceuticals[2] and useful synthetic intermediates.[3] Catalysts based on ammonium salts,[4] lanthanide salts,[5] lithium halides,[6] magnesium halides,[7] tetraphenylantimony iodide[8] and trialkyltin halides.[9] have previously been reported for the synthesis of oxazolidinones from epoxides and isocyanates.[10]

We have reported that bimetallic aluminium(salen) complex **5**[11] would catalyse the formation of cyclic carbonates **2** from epoxides **1** and carbon dioxide,[12] the formation of di– and tri–thiocarbonates **6** and **7** from epoxides and carbon disulphide[13] and the synthesis of oxazolidinones **3/4** from epoxides and isocyanates[14] (Scheme 1). Whilst complex **5** displayed high activity at room temperature for the synthesis of cyclic carbonates, it was less active for the synthesis of thiocarbonates and oxazolidinones; reactions requiring higher catalyst loadings (5 mol%) and reaction temperatures (50–90 °C). A mechanistic study[15] revealed that thiocarbonate and oxazolidinone synthesis catalysed by complex **5** had higher enthalpies of activation and less negative entropies of activation than cyclic carbonate synthesis. Therefore, we aimed to develop more active catalysts for the reaction between epoxides and carbon disulphide or isocyanates based on using more Lewis acidic metals to lower the enthalpy of activation. This led to the discovery that a bimetallic titanium(salen) complex was a highly active catalyst for the synthesis of thiocarbonates[16] **6/7** and in this paper we report the development of a vanadium^{V}(salen) complex for the synthesis of oxazolidinones **3/4**.

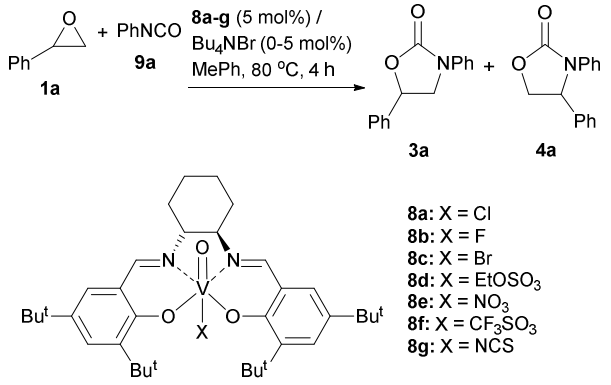


Scheme 1. Synthesis of heterocycles using catalyst **5**

Results and discussion

Vanadium^{V}(salen) complexes **8a–g** have previously been developed as highly enantioselective catalysts for asymmetric cyanohydrin synthesis,[17,18] asymmetric Strecker reactions[19] and asymmetric Michael additions of cyanide to nitroalkenes.[20] The catalytic activity of complexes **8a–g** was found to vary significantly depending upon the nature of the counterion with the highest catalytic activity observed with the least Lewis acidic complex (**8g**) and the lowest catalytic activity observed with the most Lewis acidic complexes (**8d,f**). Therefore, complexes **8a–g** were screened as catalysts for the synthesis of oxazolidinones **3a/4a** from styrene oxide **1a** and phenylisocyanate **9a** as shown in Scheme 2. When catalysed by aluminium(salen) complex **5**, some of the reactions shown in Scheme 1 require the use of tetrabutylammonium bromide as a cocatalyst. Therefore, the screening of vanadium^{V}(salen) complexes **8a–g** was carried out both with and without the use

of an equimolar amount of tetrabutylammonium bromide as a cocatalyst and the results are presented in Table 1.



Scheme 2. Screening of vanadium^{V}(salen) complexes for oxazolidinone **3a/4a** synthesis.

Table 1. Use of complexes **8a–g** as catalysts for the synthesis of oxazolidinones **3a/4a**.[a]

Entry	Complex	Conversion (%)[b,c]	Conversion (%)[c,d]
1	**8a**	26 (1:1.7)	42 (1:2.7)
2	**8b**	14 (1:1.3)	55 (1:2.7)
3	**8c**	18 (1:1.4)	61 (1:2.4)
4	**8d**	12 (1:1.3)	90 (1:2.8)
5	**8e**	56 (1:1.5)	77 (1:2.9)
6	**8f**	10 (1:1.3)	90 (1:3.5)
7	**8g**	47 (1:1.4)	44 (1:1.7)

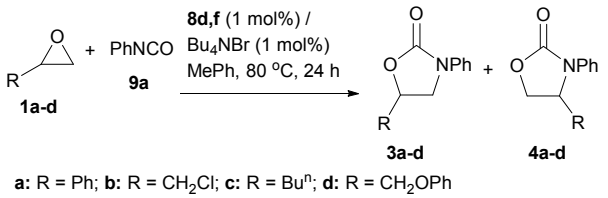
[a] Reaction conditions: 5 mol% catalyst, 0 or 5 mol% Bu_4NBr, toluene, 80 °C, 4 hours. Conversions determined by ^1H NMR analysis of the reaction mixture. [b] Without the use of Bu_4NBr as cocatalyst. [c] Figure in brackets is the ratio of **3a:4a**. [d] With the use of Bu_4NBr as cocatalyst.

All of complexes **8a–g** displayed some catalytic activity even in the absence of tetrabutylammonium bromide, with the nitrate (**8e**) and isothiocyanate (**8g**) complexes being the most active catalysts (Table 1, entries 5 and 7). However, the level of catalytic activity was modest, with at most 56% conversion being obtained. The addition of tetrabutylammonium bromide as a cocatalyst substantially improved the conversion in all cases except for the reaction catalysed by complex **8g** (Table 1, entry 7). Under these conditions, complexes **8d** and **8f** both gave 90% conversion of styrene oxide into oxazolidiones **3a/4a** (Table 1, entries 4 and 6).

The tetrabutylammonium bromide could perform at least two functions in these reactions: it could ring–open the epoxide, and it could react with the vanadium complexes to form complex **8c** in situ. However, the catalytic activity of complex **8c** was significantly increased by the addition of tetrabutylammonium bromide (Table 1, entry 3) and the activity of complexes **8d–f** with tetrabutylammonium bromide were higher than that of complex **8c** with tetrabutylammonium bromide (Table 1, entries 3–6). These results suggest that the principal role of the tetrabutylammonium bromide is to provide a good nucleophile (which can subsequently also be a good leaving group) to ring–open the epoxide. The two complexes which displayed the highest catalytic activity (**8d,f**) were those in which the counterion is a sulphate or sulphonate group. Park and coworkers have recently presented evidence that sulphonate anions can activate carbon dioxide during cyclic carbonate synthesis by formation of a mixed anhydride[21] and a similar activation of the isocyanate in our system would account for the high catalytic activity displayed by complexes **8d,f**. Thus the most active catalysts would be capable of activating both the epoxide (and/or the ring–opened bromo–alkoxide) and the isocyanate within the catalytic cycle.

To investigate the importance of the tetrabutylammonium anion, reactions were carried out under the conditions specified in Table 1, with complex **8d** and tetrabutylammonium fluoride, chloride or iodide as cocatalyst. The use of tetrabutylammonium fluoride as cocatalyst resulted in no conversion occurring, whilst a tetrabutylammonium chloride cocatalyst gave 41% conversion to a 1:1.6 ratio of **3a/4a**. When tetrabutylammonium iodide was used as cocatalyst, a conversion of 87% was obtained to a 1:1.8 ratio of **3a/4a**. These results highlight the importance of a good nucleophile / leaving group in the tetrabutylammonium salt and confirm that tetrabutylammonium bromide is the optimal cocatalyst both in terms of conversion and **3a/4a** ratio.

Styrene oxide is known to be an unusual substrate for epoxide ring–opening reactions as the phenyl ring favours ring–opening at the secondary carbon atom, thus giving oxazolidinone **4a** as the major product. Therefore, the two most active catalysts **8d** and **8f** were screened with epoxides **1a–d** to investigate the generality of the oxazolidinone synthesis (Scheme 3). Epoxides **1b–d** were chosen to include an unfunctionalized aliphatic substrate and two functionalized epoxides. These reactions were carried out using just 1 mol% of vanadium complex and tetrabutylammonium bromide, giving the results shown in Table 2.



Scheme 3. Screening of vanadium^{V}(salen) complexes **8d,f** for oxazolidinone **3a–d/4a–d** synthesis.

Table 2. Use of complexes **8d,f** as catalysts for the synthesis of oxazolidinones **3a–d/4a–d**.[a]

Entry	Complex	Epoxide	Conversion (%)[b]
1	**8d**	**1a**	90 (1:2.8)
2	**8d**	**1b**	52 (1:0)
3	**8d**	**1c**	41 (2.3:1)
4	**8d**	**1d**	58 (1:0)
5	**8f**	**1a**	90 (1:3.5)
6	**8f**	**1b**	42 (1:0)
7	**8f**	**1c**	24 (2.3:1)
8	**8f**	**1d**	49 (1:0)

[a] Reaction conditions: 1 mol% catalyst, 1 mol% Bu_4NBr, toluene, 80 °C, 24 hours. Conversions determined by ^1H NMR analysis of the reaction mixture. [b] Figure in brackets is the ratio of **6:7**.

Styrene oxide **1a** was still an excellent substrate for both catalysts under these conditions (Table 2, entries 1 and 5). The aliphatic epoxides gave lower conversions, but in each case, complex **8d** was found to be a more effective catalyst than complex **8f**. Therefore, subsequent reaction optimization experiments focussed on the use of complex **8d** with epoxides **1b–d**. Experiments were carried out to optimize the reaction time, amount of catalyst **8d**, amount of tetrabutylammonium bromide and the concentration of substrates **1** and **9a**. The results of this study are shown in Table 3.

Table 3. Influence of catalyst loading and substrate concentrations in the synthesis of oxazolidiones **3a–d/4a–d** catalysed by complex **8d**.[a]

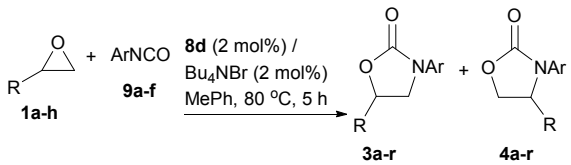
Entry	Epoxide (conc M)	**8d** (mol%)	Time (h)	Conversion (%)[b]
1	**1b** (1.67)	0.5	24	51 (1:0)
2	**1b** (1.67)	0.5	48	51 (1:0)
3	**1c** (1.67)	0.5	24	16 (4:1)
4	**1c** (1.67)	0.5	48	16 (4:1)
5	**1d** (1.67)	0.5	24	46 (1:0)
6	**1d** (1.67)	0.5	48	46 (1:0)
7	**1b** (1.67)	1.0	24	52 (1:0)
8	**1c** (1.67)	1.0	24	41 (2.33:1)
9	**1d** (1.67)	1.0	24	58 (1:0)
10	**1b** (1.67)	2.0	24	54 (1:0)
11	**1c** (1.67)	2.0	24	45 (2:1)
12	**1d** (1.67)	2.0	24	70 (1:0)
13	**1b** (1.67)	4.0	24	56 (1:0)
14	**1c** (1.67)	4.0	24	53 (1.9:1)
15	**1d** (1.67)	4.0	24	81 (1:0)
16	**1b** (0.84)	2.0	24	70 (1:0)
17	**1c** (0.84)	2.0	24	45 (2.4:1)
18	**1d** (0.84)	2.0	24	93 (1:0)
19	**1b** (0.42)	2.0	24	58 (1:0)
20	**1c** (0.42)	2.0	24	41 (2.4:1)
21	**1d** (0.42)	2.0	24	74 (1:0)
22[c]	**1b** (1.67)	1.0	24	48 (1:0)
23[c]	**1c** (1.67)	1.0	24	31 (3.1:1)
24[c]	**1d** (1.67)	1.0	24	47 (1:0)

[a] Reaction conditions: same concentration of Bu_4NBr as complex **8d**, same concentration of **9a** as **1** unless stated otherwise, toluene, 80 °C. Conversions determined by ^1H NMR analysis of the reaction mixture. [b] Figure in brackets is the ratio of **3:4**. [c] 1.2 equivalents of isocyanate **9a** used.

The effect of varying the concentration of catalyst **8d** (and tetrabutylammonium bromide) was found to be substrate dependent. Thus, for epichlorohydrin **1b**, the conversion only increased from 51 to 56% as the catalyst concentration increased from 0.5 to 4 mol% (Table 3, entries 1,7,10 and 13). However, for epoxides **1c** and **1d** the effect of catalyst concentration was much more pronounced: from 16 to 53% conversion for epoxide **1c** (Table 3, entries 2,8,11 and 14) and from 46 to 81% conversion for epoxide **1d** (Table 3, entries 3,9,12 and 15). The influence of reaction time was also investigated for reactions catalysed by 0.5 mol% of complex **8d** by leaving reactions for either 24 or 48 hours. However, for all three substrates exactly the same conversion was observed after 24 and 48 hours (Table 3, entries 1–6). Reactions involving 1-hexene oxide **1c** were found to be insensitive to the substrate concentration (Table 3, entries 11,17 and 20), whereas reactions involving substrates **1b** and **1d** were much more concentration dependent (Table 3, entries 10,16,19 and 12,18,21). In each case the optimal conversion was found at a substrate concentration of 0.84 M (Table 3, entries 16–18).

During these reactions, diphenyl urea was identified as a by-product arising from reaction between isocyanate **9a** and adventitious water. This (rather than catalyst deactivation) was found to be the reason why the conversion did not increase when the reaction time increased from 24–48 hours. In an attempt to minimise the effect of this side reaction, reactions were carried out using 1.2 equivalents of isocyanate **9a**, however, for all three substrates this resulted in a lower conversion than when exactly one equivalent of isocyanate was used (Table 3, entries 7–9 and 22–24).

Thus, the optimal conditions were determined to be the use of 2 mol% of catalyst **8d** and tetrabutylammonium bromide with equimolar amounts of epoxide and isocyanate at a substrate concentration of 0.84 M at 80 °C in toluene. Although the reactions shown in Table 3 were all run for at least 24 hours, further control experiments showed that the conversion did not increase after a reaction time of just five hours. Thus, these conditions were taken as standard and applied to reactions involving eight epoxides (**1a–h**) and six isocyanates (**9a–f**) as shown in Scheme 4. These reactions were all worked up and the major isomer of the oxazolidinone (**3a–r** or **4a-r**) isolated by flash chromatography. The results are given in Table 4.



1. a: R = Ph; **b:** R = CH_2Cl; **c:** R = Bu^n; **d:** R = CH_2OPh; **e:** R = Me; **f:** R = Et; **g:** R = Oct^n; **h:** R = CH_2OH

9. a: Ar = Ph; **b:** Ar = 4-FC_6H_4; **c:** Ar = 4-ClC_6H_4; **d:** Ar = 4-BrC_6H_4; **e:** Ar = 4-$MeOC_6H_4$; **f:** Ar = 4-MeC_6H_4.

3:4. a: R = Ar = Ph; **b:** R = CH_2Cl, Ar = Ph; **c:** R = Bu^n, Ar = Ph; **d:** R = CH_2OPh, Ar = Ph; **e:** R = Me, Ar = Ph; **f:** R = Et, Ar = Ph; **g:** R = Oct^n, Ar = Ph; **h:** R = CH_2OH; **i:** R = Ph, Ar = 4-FC_6H_4; **j:** R = Ph, Ar = 4-ClC_6H_4; **k:** R = Ph, Ar = 4-BrC_6H_4; **l:** R = Ph, Ar = 4-$MeOC_6H_4$; **m:** R = Ph, Ar = 4-MeC_6H_4; **n:** R = CH_2Cl, Ar = 4-FC_6H_4; **o:** R = CH_2Cl, Ar = 4-ClC_6H_4; **p:** R = CH_2Cl, Ar = 4-BrC_6H_4; **q:** R = CH_2Cl, Ar = 4-$MeOC_6H_4$; **r:** R = CH_2Cl, Ar = 4-MeC_6H_4;

Scheme 4. Synthesis of oxazolidinones **3a–r/4a–r**.

Epoxides bearing an aliphatic sidechain (**1c,f,g**) were found to be the worst substrates under these reaction conditions, giving the lowest conversions and isolated yields of 3,5–oxazolidinones **3c,f,g** (Table 4, entries 3,6,7). In contrast substrates with aromatic or functionalised sidechains gave much better conversions and isolated yields (Table 4, entries 1,2,4). Glycidol **1h** was also a reasonably good substrate, showing that the alcohol does not inhibit the reaction by coordinating to the vanadium ion (Table 4, entry 8). For styrene oxide **1a** and glycidol **1h**, the 3,4–oxazolidinone **4a,h** was the major isomer of the product whilst for all other substrates, the 3,5–isomer was the major product. The 3,5–isomer arises from

ring–opening of the epoxide at its terminal end and is the normal product of these reactions. The electron–rich aromatic ring of styrene oxide diverts the ring–opening to the methine carbon and for glycidol, the reaction is known to follow a different pathway in which the isocyanate first reacts with the alcohol to form a urethane, which then intramolecularly ring–opens the epoxide to form an oxazolidinone, leading to the formation of the 3,4–isomer.[22] The reactions of epichlorohydrin **1b** and 3–phenoxypropylene oxide **1d** were notable for being completely regioselective (Table 4, entries 2 and 4).

Table 4. Synthesis of oxazolidinones **3a–r/4a–r** catalysed by complex **8d**.[a]

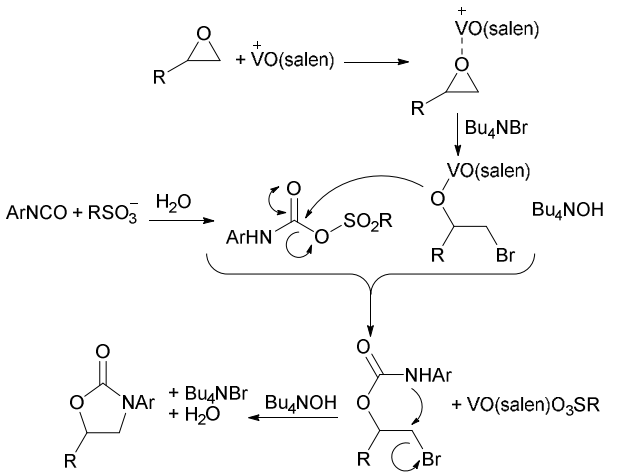
Entry	Epoxide	Isocyanate	Conversion (%)[b]	Product (%)[c]
1	**1a**	**9a**	98 (1:2.5)	**4a** (64)
2	**1b**	**9a**	70 (1:0)	**3b** (68)
3	**1c**	**9a**	46 (2.4:1)	**3c** (29)
4	**1d**	**9a**	93 (1:0)	**3d** (89)
5	**1e**	**9a**	83 (4.0:1)	**3e** (60)
6	**1f**	**9a**	52 (3.0:1)	**3f** (36)
7	**1g**	**9a**	46 (3.0:1)	**3g** (31)
8	**1h**	**9a**	72 (1:3.2)	**4h** (49)
9	**1a**	**9b**	68 (1:2.2)	**4i** (41)
10	**1a**	**9c**	40 (1:1.9)	**4j** (25)
11	**1a**	**9d**	40 (1:2.1)	**4k** (23)
12	**1a**	**9e**	65 (1:2.6)	**4l** (41)
13	**1a**	**9f**	76 (1:2.1)	**4m** (47)
14	**1b**	**9b**	52 (1:0)	**3n** (44)
15	**1b**	**9c**	34 (1:0)	**3o** (30)
16	**1b**	**9d**	41 (1:0)	**3p** (40)
17	**1b**	**9e**	63 (1:0)	**3q** (58)
18	**1b**	**9f**	71 (1:0)	**3r** (69)

[a] Reaction conditions: 2 mol% of **8d** and Bu_4NBr, [**1**] = [**9**] = 0.84 M, toluene, 80 ºC, 5 hours. Conversions determined by ^1H NMR analysis of the reaction mixture. [b] Figure in brackets is the ratio of **3:4**. [c] Figure in brackets is the isolated chemical yield of the purified major regioisomer.

Styrene oxide **1a** and epichlorohydrin **1b** were then selected as representative epoxides leading to the 3,4– and 3,5–oxazolidinones respectively, and each was reacted with five substituted aromatic isocyanates (Table 4, entries 9–18). In both cases, isocyanates bearing electronically neutral (Table 4, entries 9 and 14) or electron–donating substituents (Table 4, entries 12,13,17) gave better conversions and isolated yields than isocyanates bearing electron–withdrawing substituents (Table 4, entries 10,11,15,16). This may indicate that ring closure to form the oxazolidinone ring is the rate determining step of the mechanism as this would be favoured by an electron–rich substituent on the nitrogen atom. In all cases, the regiochemistry seen using phenyisocyanate was mirrored with the substituted aromatic isocyanates showing that this is determined by the nature of the epoxide and is not significantly affected by the isocyanate. The reactions of epichlorohydrin **1b** were again completely regioselective (Table 4, entries 14–18). Attempts to use aliphatic isocyanates or disubstituted epoxides were unsuccessful.

To investigate the reaction mechanism, attempts were made to study the reaction kinetics. However, initial experiments indicated that catalyst decomposition was occurring during the reactions which prevented meaningful kinetic data from being acquired. Never the less, based on our previous work[12–15] and the results of Park,[21] a possible mechanism is shown in Scheme 5. The epoxide is first activated by coordination to the positively charged vanadium^V ion and then ring–opened by bromide provided by the teatrabutylammonium bromide counterion. Meanwhile, the sulphate or sulphonate counterion of the vanadium catalyst reacts with the isocyanate and adventitious water to form a mixed anhydride. Nucleophilic attack of the vanadium coordinated alkoxide on the carbonyl of the mixed anhydride then leads to an acyclic bromocarbamate and regeneration of the vanadium catalyst. The bromoalkoxide can finally cyclize to the oxazolidinone (in what appears to be the rate determining step), regenerating the tetrabutylammonium bromide and adventitious water. For vanadium^V(salen) complexes which do not have a sulphate or sulphonate counterion, this mechanism can be modified to have the vanadium coordinated alkoxide undergo nucleophilic attack on the unactivated isocyanate, thus explaining why such complexes are still catalytically active, but less active than catalysts which do have a sulphate or sulphonate counterion.

Epoxides **1a–h** were all used as racemates, so even though complexes **8** are chiral no asymmetric induction was expected in reactions which progressed to high conversion and none of oxazolidinones **3/4a-r** displayed any optical activity. This is consistent with previous work using aluminium based catalyst **5**.[14]



Scheme 5. Possible mechanism for the formation of oxazolidinones.

Conclusions

Vanadium^V complex **8d** and tetrabutylammonium bromide form a highly active catalyst system for the synthesis of oxazolidinones from epoxides and aromatic isocyanates. Compared to the previously reported[14] use of bimetallic aluminium(salen) complex **5**, the catalyst loading can be reduced from 5 mol% (10 mol% of metal ions) to 2 mol% and the reaction time reduced from 24 to 5 hours. Another difference between the two systems is that the vanadium based catalyst requires the use of tetrabutylammonium bromide as a cocatalyst, whilst tetrabutylammonium bromide inhibited reactions catalysed by complex **5**. The reaction mechanism

appears to involve cooperative Lewis acid activation of the epoxide and nucleophilic activation of the epoxide.

Acknowledgements
The authors thank EPSRC for a studentship to CB.

Experimental

Catalysts **8a–g** were prepared as previously reported.[18] All other compounds were commercially available and used as supplied. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 ^{o}C on a Bruker Avance300 spectrometer operating at 300 or 75 MHz, respectively, or on a JEOL400 spectrometer operating at 400 or 100 MHz, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane. Infrared spectra were recorded at room temperature on a Varian 800 FT-IR Scimitar series spectrometer, measuring specific absorbance intensities as: broad (br), strong (s), medium (m), or weak (w). Melting points were determined on a Stuart SMP3 system.

General procedure for the synthesis of oxazolidinones 3a–r/4a–r.

To a stirred solution of complex **8a–g** (8.4–41.8 μmol) and a cocatalyst (8.4–41.8 μmol) in toluene (0.5–2 ml) was added an epoxide **1a–h** (0.835 mmol) and isocyanate **9a–f** (0.835 mmol). The reaction was then heated to 80 °C and stirred for 5–48 hours. 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 regioisomeric oxazolidinones was determined by ^{1}H NMR spectroscopy, then the residue was purified as described for each compound below. The major isomers of **3a–r/4a–r** are all known compounds and the spectroscopic data matched those reported in the literature.[9,14]

Data for 4a: Obtained as a white solid after purification by flash chromatography using CH_2Cl_2:hexane (85:15) as solvent. mp 128–129 ^{o}C (lit.[14] 128–129 °C); υ_{max}(ATR) 3065, 2981, 2889, 1750, 1705, 1596 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.5–7.2 (9H, m, ArH), 7.10 (1H, t *J* 7.4 Hz, ArH), 5.42 (1H, dd *J* 8.8, 6.0 Hz, CH), 4.81 (1H, t *J* 8.7 Hz, CH_2), 4.22 (1H, dd *J* 8.6, 6.0 Hz, CH_2); 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.

Data for 3b: Obtained as a white solid after washing with Et_2O. mp 104–105 ^{o}C (lit.[7] 104–105 °C); υ_{max}(ATR) 3040, 2981, 2917, 1734, 1599 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6–7.3 (4H, m, ArH), 7.17 (1H, t *J* 7.4, 1.1 Hz, ArH), 4.88 (1H, dddd, *J* 8.7, 6.5, 5.6, 4.1 Hz, CH), 4.17 (1H, t, *J* 8.9 Hz, CH_2N), 3.96 (1H, dd, *J* 9.1, 5.7 Hz, CH_2N), 3.79 (1H, dd *J* 11.6, 4.2 Hz, CH_2Cl), 3.74 (1H, dd *J* 11.6, 6.6 Hz, CH_2Cl); δ_C(75 MHz, $CDCl_3$) 153.9, 138.0, 129.1, 124.4, 118.6, 70.9, 48.3, 44.5.

Data for 3c: Obtained as a cream coloured solid after purification by flash chromatography using CH_2Cl_2:hexane (75:25) as solvent. mp 62–63 ^{o}C (lit.[14] 65–66 °C); υ_{max}(ATR) 3064, 2981, 2930, 2880, 1741, 1703, 1597 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.56 (2H, dd *J* 8.7, 1.0 Hz, ArH), 7.39 (2H, t *J* 8.7 Hz, ArH), 7.14 (1H, tt *J* 7.4, 1.2 Hz, ArH), 4.7–4.5 (1H, m, CH), 4.09 (1H, t *J* 8.5 Hz, CH_2N), 3.66 (1H, dd *J* 8.8, 7.2 Hz, CH_2N), 2.0–1.8 (1H, m, CH_2), 1.8–1.7 (1H, m, CH_2), 1.6–1.3 (4H, m, CH_2CH_2Me), 0.96 (3H, t *J* 7.2 Hz, CH_3); 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.

Data for 3d: Obtained as a white solid after washing with Et_2O. mp 139–140 ^{o}C (lit.[14] 139–140 °C); υ_{max}(ATR) 3043, 2940, 1736, 1598 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.60 (2H, d *J* 7.7 Hz, ArH), 7.41 (2H, t *J* 8.5 Hz, ArH), 7.33 (2H, t *J* 7.3 Hz, ArH), 7.18 (1H, t *J* 7.3 Hz, ArH), 7.02 (1H, t *J* 7.3 Hz, ArH), 6.93 (2H, d *J* 7.6 Hz, ArH), 5.0–4.9 (1H, m, CH), 4.3–4.1 (3H, m, CH_2O + CH_2N), 4.06 (1H, dd *J* 8.9, 5.9 Hz, CH_2N); 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.

Data for 3e: Obtained as a white solid after purification by flash chromatography using CH_2Cl_2:hexane (75:25) as solvent. mp 78–80 ^{o}C (lit.[14] 79–82 °C); υ_{max}(ATR) 3036, 2981, 2884, 1740, 1670, 1599 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.51 (2H, dd *J* 8.7, 1.0 Hz, ArH), 7.36 (2H, t *J* 8.1 Hz, ArH), 7.11 (1H, t *J* 7.4 Hz, ArH), 4.8–4.6 (1H, m, CH), 4.09 (1H, t *J* 8.5 Hz, CH_2), 3.60 (1H, dd *J* 8.9, 7.1 Hz, CH_2), 1.51 (3H, d *J* 6.3 Hz, CH_3); δ_C(75 MHz, $CDCl_3$) 154.9, 138.6, 129.1, 124.1, 118.5, 69.5, 52.1, 20.7.

Data for 3f:[9] Obtained as a colourless oil after purification by flash chromatography using CH_2Cl_2:hexane (75:25) as solvent. υ_{max}(ATR) 3038, 2970, 1738, 1703, 1597 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.57 (2H, dd *J* 7.4, 1.0 Hz, ArH), 7.38 (2H, t *J* 8.7 Hz, ArH), 7.13 (1H, t *J* 7.4 Hz, ArH), 4.7–4.5 (1H, m, CH), 4.07 (1H, t *J* 8.6 Hz, CH_2), 3.65 (1H, dd *J* 8.8, 7.1 Hz, CH_2), 2.0–1.7 (2H, m, $MeCH_2$), 1.07 (3H, t *J* 7.5, CH_3); δ_C(75 MHz, $CDCl_3$) 154.89, 138.28, 128.91, 123.78, 118.02, 74.04, 49.94, 27.90, 8.66.

Data for 3g: Obtained as a beige coloured solid after purification by flash chromatography using CH_2Cl_2:hexane (75:25) as solvent. mp 71–72 ^{o}C (lit.[14] 70–71 °C); υ_{max}(ATR) 2981, 2889, 1706, 1594 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6–7.5 (2H, m, ArH), 7.5–7.3 (2H, m, ArH), 7.14 (1H, tt *J* 7.3, 1.2 Hz, ArH), 4.7–4.6 (1H, m, CH), 4.07 (1H, t *J* 8.5 Hz, CH_2N), 3.64 (1H, dd *J* 8.7, 7.2 Hz, CH_2N), 2.0–1.8 (1H, m, CH_2), 1.8–1.6 (1H, m, CH_2), 1.6–1.2 (12H, m, $(CH_2)_6Me$), 0.87 (3H, t *J* 6.9 Hz, CH_3); 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.

Data for 4h: Obtained as a white solid after purification by flash chromatography using CH_2Cl_2 as solvent. mp 110–112 ^{o}C (lit.[14] 109–111 °C); υ_{max}(ATR) 3271, 3137, 3082, 2981, 2889, 1737, 1599 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.5–7.2 (4H, m, ArH), 7.1–6.9 (2H, m, ArH + OH), 4.58 (1H, dd *J* 12.2, 2.9 Hz, CH_2O), 3.97 (1H, dd *J* 12.2, 6.5 Hz, CH_2O), 3.29 (1H, ddt *J* 6.7, 4.1, 2.7 Hz, CHN), 2.89 (1H, t *J* 4.4 Hz, CH_2O), 2.71 (1H, dd *J* 4.9, 2.6 Hz, CH_2O); δ_C(75 MHz, $CDCl_3$) 153.1, 137.7, 129.1, 123.8, 119.1, 65.8, 49.5, 44.6.

Data for 4i: Obtained as a cream coloured solid after purification by flash chromatography using CH_2Cl_2:hexane (85:15) as solvent. mp 91–92 ^{o}C (lit.[14] 94–97 °C); υ_{max}(ATR) 2981, 2889, 1744, 1710, 1509 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.4–7.2 (7H, m, ArH), 6.95 (2H, dd *J* 9.2, 8.3 Hz, ArH), 5.36 (1H, dd *J* 8.8, 6.3 Hz, CH), 4.78 (1H, t *J* 8.7 Hz, CH_2), 4.21 (1H, dd *J* 8.7, 6.3 Hz, CH_2); 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), 116.3, 115.8 (d *J* 22 Hz), 69.8, 61.3.

Data for 4j: Obtained as a white solid after purification by flash chromatography using CH_2Cl_2:hexane (85:15) as solvent. mp 123–

125 °C (lit.[14] 126–128 °C); υ_{max}(ATR) 3040, 2960, 1737, 1700, 1597 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.5–7.0 (9H, m, ArH), 5.35 (1H, dd *J* 8.7, 6.1 Hz, ArH), 4.77 (1H, t *J* 8.7 Hz, CH_2), 4.20 (1H, dd, *J* 8.5, 6.0 Hz, CH_2); 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.

Data for 4k: Obtained as a yellow solid after purification by flash chromatography using CH_2Cl_2:hexane (85:15) as solvent. mp 136–137 °C (lit.[14] 134–137 °C); υ_{max}(ATR) 2981, 2909, 1735, 1601 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.4–7.0 (9H, m, ArH), 5.29 (1H, dd *J* 8.7, 6.0 Hz, CH), 4.71 (1H, t *J* 8.7 Hz, CH_2), 4.13 (1H, dd, *J* 8.6, 6.0 Hz, CH_2); 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.

Data for 4l: Obtained as a cream coloured solid after purification by flash chromatography using CH_2Cl_2:hexane (85:15) as solvent. mp 103–105 °C (lit.[14] 105–107 °C); υ_{max}(ATR) 2923, 1734 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.5–7.3 (7H, m, ArH), 6.90 (2H, d *J* 8.4 Hz, ArH), 5.62 (1H, t *J* 8.4 Hz, CH), 4.34 (1H, t *J* 8.8 Hz, CH_2), 3.92 (1H, t *J* 8.7 Hz, CH_2), 3.79 (3H, s, OCH_3); 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.

Data for 4m: Obtained as a cream coloured solid after purification by flash chromatography using CH_2Cl_2:hexane (85:15) as solvent. mp 104–106 °C (lit.[14] 105–107 °C); υ_{max}(ATR) 3040, 2982, 2915, 1738, 1601 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.6–7.2 (7H, m, ArH), 7.06 (2H, d *J* 8.3 Hz, ArH), 5.38 (1H, dd *J* 8.9, 6.2 Hz, CH), 4.74 (1H, t *J* 8.7 Hz, CH_2), 4.17 (1H, dd *J* 8.5, 6.0 Hz, CH_2), 2.25 (3H, s, $ArCH_3$); 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.

Data for 3n: Obtained as a white solid after washing with Et_2O. mp 105–106 °C (lit.[14] 101–104 °C); υ_{max}(ATR) 2982, 2908, 1735 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.52 (2H, dd *J* 9.2, 4.6 Hz, ArH), 7.10 (2H, dd *J* 9.2, 8.2 Hz, ArH), 5.0–4.8 (1H, m, CH), 4.18 (1H, t *J* 9.0 Hz, NCH_2), 3.97 (1H, dd *J* 9.1, 5.7 Hz, NCH_2), 3.84 (1H, dd *J* 11.6, 7.4 Hz, CH_2Cl), 3.77 (1H, dd *J* 11.6, 6.4 Hz, CH_2Cl); 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.

Data for 3o: Obtained as a white solid after washing with Et_2O. mp 128–129 °C (lit.[14] 130–133 °C); υ_{max}(ATR) 3040, 2907, 1737, 1598 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.47 (2H, d *J* 9.0 Hz, ArH), 7.32 (2H, d *J* 9.0 Hz, ArH), 4.9–4.8 (1H, m, CH), 4.13 (1H, t *J* 8.9 Hz, NCH_2), 3.91 (1H, dd *J* 9.1, 6.0 Hz, NCH_2), 3.78 (1H, dd *J* 11.6, 4.3 Hz, CH_2Cl), 3.74 (1H, dd *J* 11.7, 6.2 Hz, CH_2Cl); δ_C(75 MHz, $CDCl_3$) 153.7, 136.5, 129.6, 129.0, 119.6, 71.0, 48.1, 44.6.

Data for 3p: Obtained as a white solid after washing with Et_2O. mp 126–127 °C (lit.[23] 125–127 °C); υ_{max}(ATR) 3080, 2981, 2890, 1734, 1637 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.52 (2H, d *J* 9.1 Hz, ArH), 7.47 (2H, d *J* 9.1 Hz, ArH), 5.0–4.8 (1H, m, CH), 4.17 (1H, t *J* 9.0 Hz, NCH_2), 3.96 (1H, dd *J* 9.1, 5.7 Hz, NCH_2), 3.83 (1H, dd *J* 11.6, 4.2 Hz, CH_2Cl), 3.75 (1H, dd *J* 11.6, 6.4 Hz, CH_2Cl); δ_C(75 MHz, $CDCl_3$) 153.6, 137.0, 132.0, 119.9, 117.2, 70.9, 48.0, 44.5.

Data for 3q: Obtained as a white solid after washing with Et_2O. mp 103–105 °C (lit.[14] 105–107 °C); υ_{max}(ATR) 3030, 2973, 2904, 2841, 1731, 1598 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.46 (2H, d *J* 9.1 Hz, ArH), 6.94 (2H, d *J* 9.1 Hz, ArH), 4.82 (1H, dq *J* 8.8, 5.2 Hz, CH), 4.16 (1H, t *J* 9.0 Hz, NCH_2), 3.95 (1H, dd *J* 9.1, 5.7 Hz, NCH_2), 3.78 (3H, s, OCH_3), 3.9–3.7 (2H, m, CH_2Cl); δ_C(75 MHz, $CDCl_3$) 156.7, 154.1, 131.1, 120.6, 114.4, 70.9, 55.5, 48.7, 44.7.

Data for 3r: Obtained as a cream coloured solid after washing with Et_2O. mp 101–103 °C (lit.[14] 104–107 °C); υ_{max}(ATR) 3025, 2909, 1733, 1616 cm^{-1}; δ_H(300 MHz, $CDCl_3$) 7.44 (2H, d *J* 8.5 Hz, ArH), 7.21 (2H, d *J* 8.1 Hz, ArH), 4.86 (1H, dddd, *J* 8.7, 6.6, 5.7, 4.2 Hz, CH), 4.17 (1H, t *J* 9.0 Hz, NCH_2), 3.96 (1H, dd, *J* 9.2, 5.7 Hz, NCH_2), 3.81 (1H, dd, *J* 11.6, 4.2 Hz, CH_2Cl), 3.75 (1H, dd, *J* 11.5, 6.6 Hz, CH_2Cl), 2.36 (3H, s, $ArCH_3$); δ_C(75 MHz, $CDCl_3$) 154.0, 135.6, 134.3, 129.7, 118.8, 71.0, 48.6, 44.5, 20.7.

Notes and references

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