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Homogeneous Catalytic Ring-expansion of Aziridines: Methodology for the Facile and Atom-economical Synthesis of Heterocyclic Small Molecules

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ABSTRACT

Homogeneous Catalytic Ring-expansion of Aziridines: Methodology for the Facile and Atom-economical Synthesis of Heterocyclic Small Molecules

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The [(salen)CrCl + LB] catalyst system was found to be a highly active catalyst system for the [aziridine + CO_2] coupling reaction, and exhibited a marked preference for the formation of 5-substituted oxazolidinone product, especially in the absence of cocatalyst. The activity of this catalyst system is optimized by modifying the cocatalyst and tuning the reaction conditions to facilitate the conversion of a wide variety of substituted aziridines into oxazolidinones under mild reaction conditions.

An investigation of the [(salen)CrCl + LB]-catalyzed [aziridine + CO_2] coupling reaction was very instructive. A Hammett plot of aziridine substituents and a series of DFT ground-state calculations both intimated a transition state having cationic character. However, several experiments showed convincingly that a carbocation does not exist during the course of the catalyzed [aziridine + CO_2] coupling reaction. Opposite-face ligand attachment was studied as well, both using experiment and DFT calculations, and give a rationale for the observed selectivity differences between many of the Lewis bases used as cocatalysts. Finally, a transition state calculation has shown the energetic difference between the two product regioisomers.

Expanding the (salen)CrCl-catalyzed [aziridine + CO_2] coupling reaction to include the [aziridine + isocyanate] coupling has opened this methodology to produce a series of imidazolidinones. Optimization of the [aziridine + isocyanate] coupling reaction has shown that, in contrast to the [aziridine + CO_2] and [epoxide + CO_2] coupling, a Lewis basic cocatalyst does

not improve either the rate or the selectivity of the ring-expansion. Rather, it hinders the reaction rate. Further optimization of the reaction conditions have produced a coupling methodology that is amenable to a wide range of aziridines and isocyanates.

Finally, the conversion of aziridines and organic carbonyls to form oxazolidines were attempted. While the (salen)CrCl catalyst was not capable of facilitating this transformation, another Lewis acid, $Sc(OTf)_3$ was active in this role. Upon an investigations of reaction parameters including ligand additive, temperature, concentration, and substrate effects, conditions useful for the conversion of both aldehydes and ketones to *N*-tosyl oxazolidines were formed.

Thesis Advisor: Professor SonBinh T. Nguyen

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Chapter 1

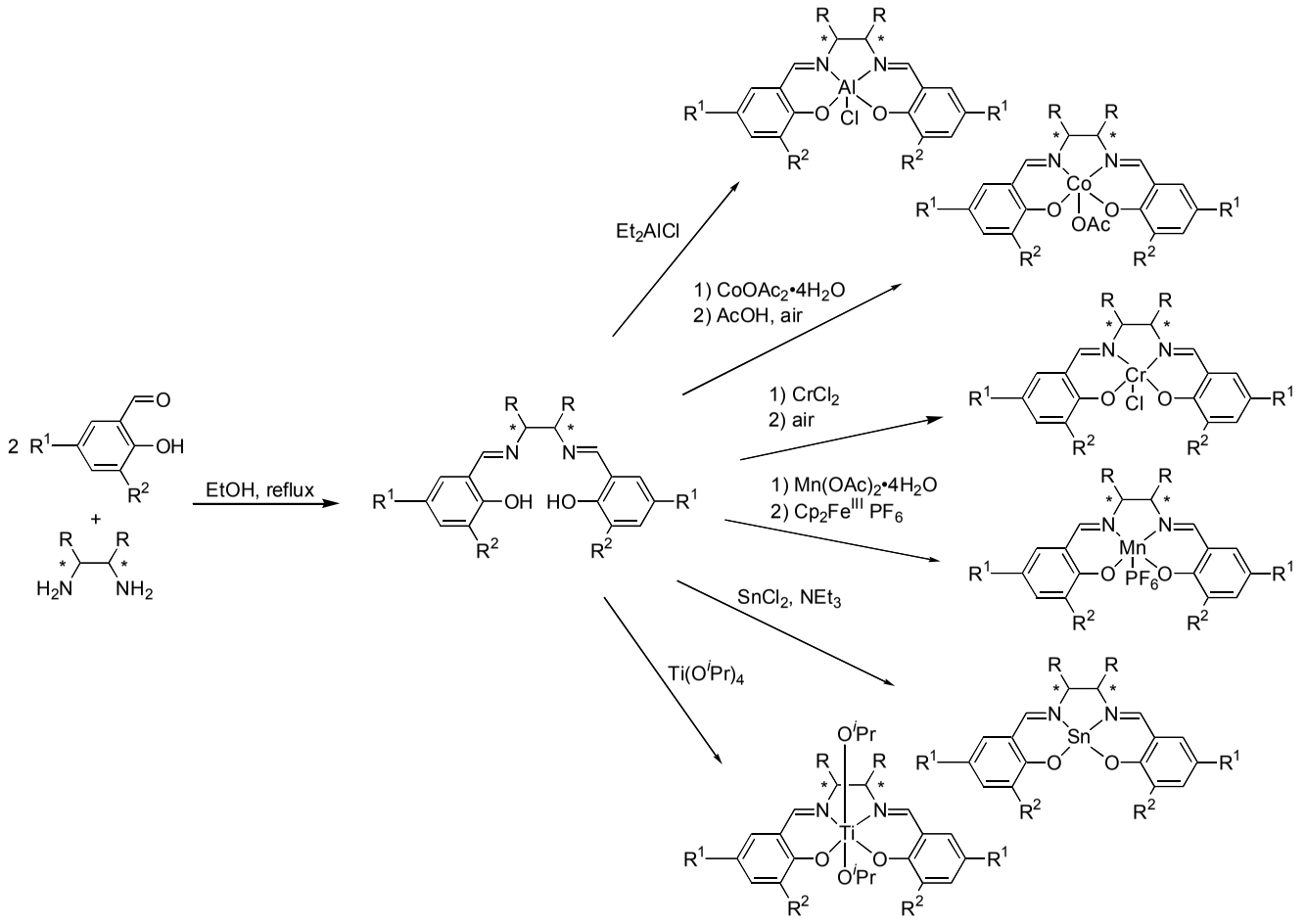
Introduction to Catalytic [Strained Ring + Heterocumulene] Cycloaddition by (Salen)metal Complexes

Portions of this chapter appear as a review in *Adv. Synth. Catal.*

1.1. Introduction

The coupling of heterocumulenes, most commonly carbon dioxide, to strained 3-membered rings such as epoxides and aziridines has garnered significant attention in recent years as an attractive route to a variety of heteroatom-containing fine chemicals and polymers.[1-4] From the catalysis viewpoint, this strategy offers many possibilities for controlling both the outcome of the reaction (small molecules or polymers) and its regiochemistry via manipulation of either the nature of the catalyst or reaction conditions. While a variety of homogeneous catalysts have been developed for these transformations,[5-12] we focus this thesis introduction specifically on the use of (salen)metal[13] catalysts due to their demonstrated high catalytic activity and efficiency in organic transformations,[14] the facile modular syntheses and tunability of the salen ligand environment (Scheme 1.1), and the large amount of recently available mechanistic information for a wide range of (salen)metal-catalyzed [strained ring + heterocumulene] couplings. Additionally, the well-known stereochemical control exhibited by chiral (salen)metal complexes in catalysis makes them attractive candidates for further development in making these processes asymmetric, either in directed enantioselective catalysis or in a kinetic resolution fashion.

Scheme 1.1. Facile syntheses of salen ligands (left) and their metallation[15-19] (right) to give a number of (salen)metal complexes.

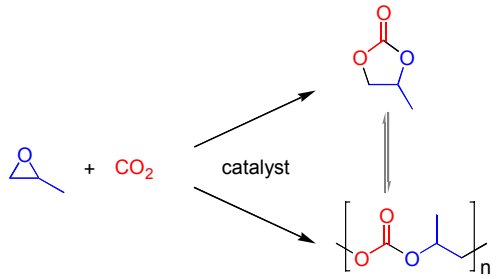


1.2. [Epoxide + CO_2] Coupling

Given the limited fossil fuel reserves on earth, the use of CO_2 as a carbon source in the production of fine chemicals and materials has been a long-standing challenge for chemists. CO_2, while generally a stable, unreactive compound, is ubiquitous in the atmosphere as a byproduct from sundry natural and industrial processes and thus is readily available for use as a chemical feedstock. One process that has attracted much recent attention is the coupling of CO_2 with epoxides (Scheme 1.2) to produce organic carbonates, which have numerous consumer and industrial uses. While the recycling of CO_2 generated from large-scale industrial processes would certainly be helpful in the management of carbon, any implication that the aforementioned [epoxide + CO_2] coupling could make a significant dent in the overall global emission of CO_2 is probably over-optimistic. If all of the world's production of ethylene and propylene oxide—the two epoxides produced on the largest scale (EO = 14.7 million metric tons[20] and PO = 5.8 million metric tons[21])—were diverted for use in the formation of organic carbonates via coupling with CO_2, only 19 million metric tons of CO_2 would be consumed per year. As the current estimated world output of CO_2 is about 6.4 *billion* metric tons annually,[22] CO_2 sequestration via organic carbonate formation would at best reduce the world's CO_2 output by only 0.3% per annum, notwithstanding the fact that most of the EO and PO produced currently are used in polyols and glycols syntheses. Rather, the main value of making organic carbonates via catalytic CO_2 sequestration lies in its atom-economic advantages over other competing technologies: not only that all atoms in the starting materials end up in the product, there is no chemical waste due to the use of additional reagents (such as bases in phosgene-diol copolymerizations[23]) or side products (such as methanol in condensation processes[23]). Another attractive feature of the direct coupling of CO_2 and epoxides to form organic and polymeric carbonates is the potential ability

to control the stereochemistry in the final products. Both of these factors have contributed to a rising interest in [epoxide + CO_2] coupling chemistry over the last two decades (Figure 1.1).

Scheme 1.2. A general scheme for [epoxide + CO_2] coupling to form either cyclic carbonates (top) or polymeric carbonates (bottom)



Although the direct coupling of CO_2 and epoxides to form both polymeric and cyclic carbonates is practiced commercially as in the syntheses of poly(ethylene carbonate) (PEC), poly(propylene carbonate) (PPC),[3] ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC),[24] CO_2 fixation in this manner is an energy-intensive process. Despite the thermodynamic favorability for these reactions (-54.0 kJ/mol for [PO + CO_2] → PC[10]), their high activation barriers (67.6 kJ/mol and 100.5 kJ/mol for PPC and PC formation, respectively), even in the presence of a (salen)CrCl complex, necessitate increased pressure. Additionally, as purification of the desired organic carbonates from side products and unreacted epoxides is also energetically expensive, much effort during the last two decades has been focused on the development of ever more selective and efficient catalysts for facilitating the [epoxide + CO_2] coupling under milder conditions.

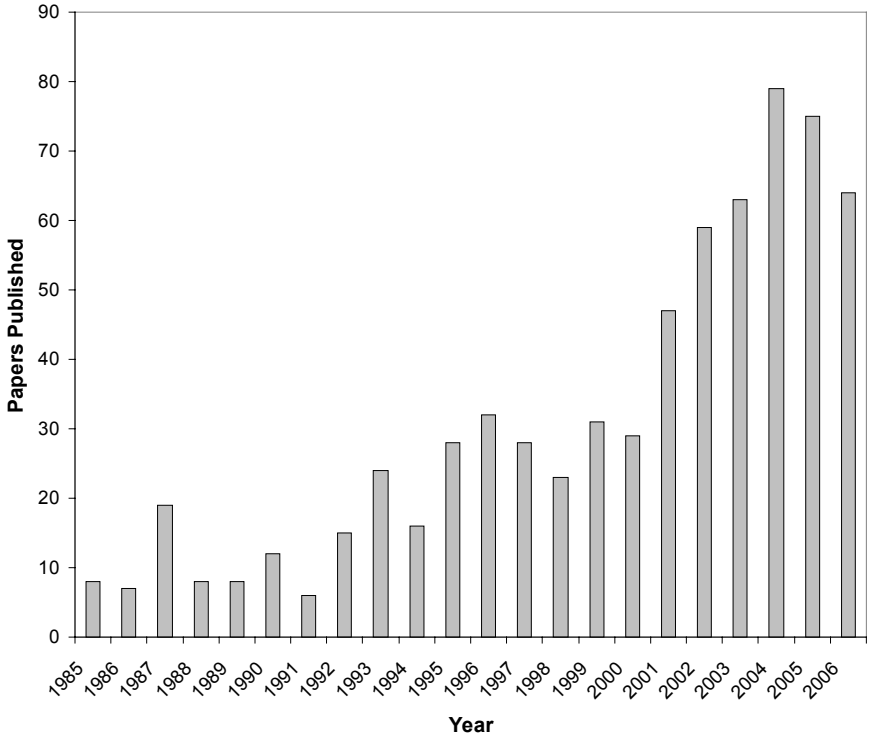


Figure 1.1. A histogram plot of the number of articles published during the January 1985-December 2006 period on the [epoxide + CO_2] coupling. This figure was generated using a SciFinder search and the search terms <"epoxide or oxirane" and "CO_2 or carbon dioxide" and "carbonate">.

It is important to note three additional caveats concerning any practical processes underlying Scheme 1.2. First, while there is a world market for organic carbonates (the world production of cyclic carbonates is about 60,000 metric tons[24]) that demand is stable and not likely to expand significantly. The majority of cyclic carbonates are used as solvents for selected polymers and resins as well as solvents and plasticizers in the personal care and cosmetics industry.[25] We note in passing that as solvents, cyclic carbonates have the advantage of being safe for human contact, being poorly absorbed through the skin[25] and readily biodegradable.[26]

Second, the market scope for polycarbonates is quite narrow and the syntheses of large numbers of these materials still must be accomplished using traditional methods due to the inability of the reactions in Scheme 1.2 to provide the desirable structures. The global polycarbonates sold in 2002 (2.8 million tons, worth more than US$ 5 billion[27,28]), consisted of a small variety of engineering polymers, the vast majority being poly(bisphenol A)carbonate, which is made from the condensation copolymerization of a diol with either phosgene or a phosgene surrogate, rather than by the ring-opening processes described in Scheme 1.2.[27,29] While PEC and PPC have recently been marketed for a few selected applications,[3] their market share is very limited. They may have increased economic impact, however, if they can be produced inexpensively from EO and PO.

Third, at present the CO_2 used for the synthesis of organic carbonates is still employed in a pure, highly pressurized form, having been extracted, purified, and concentrated from the waste gases produced during electricity generation, petroleum production/cracking, or fertilizer synthesis.[30] As this purification/concentration of CO_2 is an energetically intensive process, one of the challenges in catalyst development for CO_2 utilization would be a system that can employ CO_2 at low concentration and in the presence of impurities.[29]

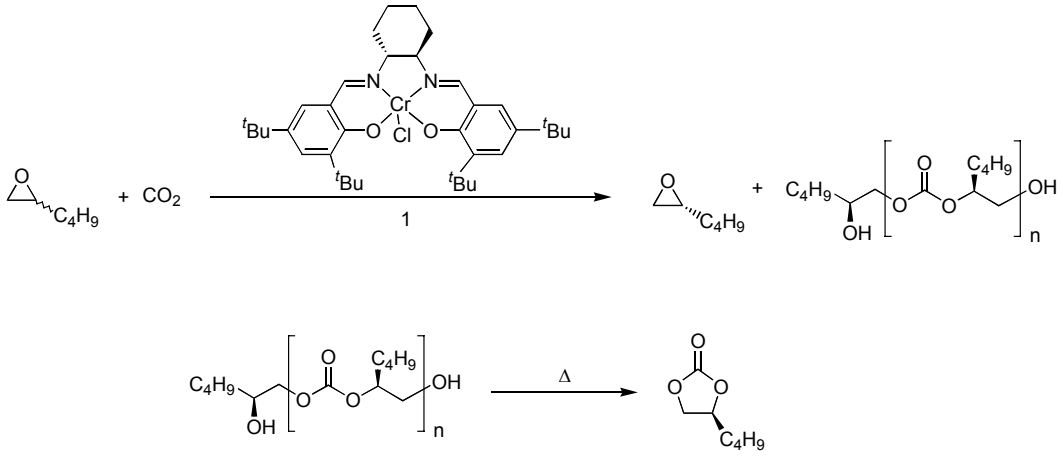
1.3. (Salen)Cr^{III} and (Salen)Co^{III}

The use of (salen)Cr^{III} as a catalyst for the [epoxide + CO_2] coupling was first documented by Jacobsen et al.[31] as an example in a 1999 patent for the nucleophilic kinetic resolution of epoxides (Scheme 1.3). The Jacobsen group disclosed very briefly the formation of chiral polycarbonates from racemic 1-hexene oxide by stereoselectively coupling one enantiomer of the epoxide with CO_2 (at a pressure of only 1 atm) in the *sole* presence of a chiral (salen)Cr^{III} catalyst. This reaction can be viewed as a straightforward activation of the epoxide by the

Lewis-acidic Cr^{III} center for subsequent ring opening, the latter step possiby by a second (salen)CrCl moiety. Upon heating, the polycarbonate product decomposed into enantiomerically enriched cyclic carbonate. While it was not clear from the patent example that the (salen)Cr^{III} catalyst was actually involved in this decomposition step, its occurrence hinted a potential common origin for the formation of both cyclic and polymeric products and the possibility that the catalytic outcome can be changed by simple manipulation of reaction conditions.

Indeed, Kruper and Dellar have previously shown that (porphyrin)Cr^{III} complexes can catalyze the coupling of epoxides and CO_2 to form both polymeric and cyclic carbonates, whose proportions could be manipulated by changing the reaction temperature.[32] Interestingly, these researchers showed that the presence of *N*,*N*-dimethylaminopyridine (DMAP) is critical in promoting the (porphyrin)Cr-catalyzed [epoxide + CO_2] coupling, suggesting a strong synergistic behavior between the porphyrin Lewis acid (LA) and the DMAP Lewis base (LB). Similar LB-dependence has subsequently been observed for the (salen)Co^{III}-catalyzed [epoxide + CO_2] coupling by many groups (*vide infra*),[33-38] suggesting a common operating mechanism where the Lewis-acidic metal complex serves to activate the epoxide for ring-opening by a subsequent nucleophile. We note that Jacobsen et al., in their extensive study of the (salen)Cr^{III}- and (salen)Co^{III}-catalyzed nucleophilic ring-opening of epoxides, have proposed similar mechanisms of action where the nucleophile is actually ligated to a second (salen)metal complex.[39] In this section, we will consider both (salen)Cr^{III}- and (salen)Co^{III}-catalyzed [epoxide + CO_2] couplings together in light of the well-understood analogy between these two complexes and the similar trends in their reactivity.

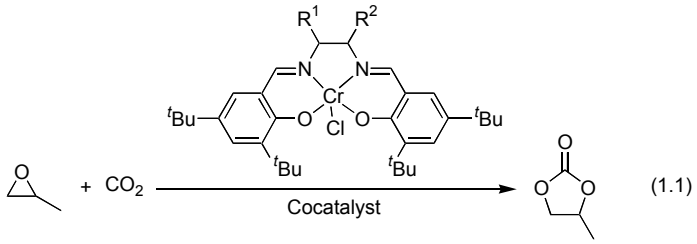
Scheme 1.3. The chiral resolution of racemic hexene oxide by CO_2, as catalyzed by an enantiomerically pure (salen)Cr^{III} catalyst, and subsequent formation of enantiomerically enriched hexene carbonate. Adapted from reference 31.



1.3.1. (Salen)Cr^{III} and (Salen)Co^{III} Catalysts for Cyclic Carbonate Synthesis

In 2001, our research group employed a wide range of (salen)CrCl complexes together with DMAP to catalyze the highly efficient conversion of a variety of epoxides to the corresponding cyclic carbonates (eq 1.1).[40] Significant improvements in catalyst activity over the (salen)CrCl alone or the analogous [(porphyrin)CrCl + DMAP] system were observed under mild reaction conditions. Motivated by the Jacobsen bimetallic model,[41] Paddock et al proposed a simple (salen)CrCl-activation of the epoxide for eventual ring-opening at the least-substituted position by a putative nucleophilic CO_2 moiety coordinated to a [(DMAP)(salen)Cr] complex. Although the activation of CO_2 by nucleophiles has been proposed to explain the rate improvements in cyclic carbonate synthesis catalyzed by metal salts under high CO_2 pressure,[42] it has not been verified to date. As we elaborate on this issue below, it is sufficient to note at this point that we subsequently postulated the existence of a $DMAP^+$-CO_2^- nucleophile[33,34] and the Darenbourgh group has proposed a $DMAP^+$-C(O)O-$(CH_2)_2$-O^- cocatalyst. Mechanistic details notwithstanding, the [(salen)M + LB] catalyst system opens up a range of new opportunities for

low-pressure catalytic regimes in which changes in catalyst structure and reaction conditions can be made to favor formation of cyclic carbonates over polymers[35] or vice versa, especially because harsher conditions were needed for the reaction to proceed in the absence of LB cocatalyst (*vide infra*).



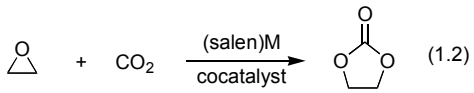
(1.1)

Shortly after the report by Paddock et al., Lu and coworkers examined a variety of (salen)metal catalysts for the [epoxide + CO_2] coupling in supercritical CO_2 ($scCO_2$) and concluded that both (salen)CrCl and (salen)Co^{II} catalysts are also active in the presence of cocatalytic amounts of tetralkylammonium salts (Table 1.1).[43] In contrast, Lewis bases such as *N*-methylimidazole (NMI) are inactive as cocatalysts under the same conditions. The reasons behind the activity enhancement induced by soluble halide salts will be reconciled with those for Lewis bases later in this review.

Since it has been shown earlier that the [epoxide + CO_2] coupling is enhanced in the presence of LB cocatalysts in organic media,[40] the solubility of the NMI LB in $scCO_2$ vs those for the halide salts in $scCO_2$ is a parameter that must be addressed. The solubilities of the (salen)metal complexes in $scCO_2$ must also be considered, as this solvent is not known to reliably dissolve polar organic molecules.[43] (Indeed, the Darensbourg group has observed that (salen)Cr^{III} complexes containing 4-*t*butyl groups are not soluble in CO_2-enriched organic media.[44]) Finally, amine LBs like imidazole can reversibly form zwitterionic, insoluble complexes with the electrophilic CO_2.[45] Under the conditions that Lu et al. described (4 MPa CO_2 and 110 °C),[43] the

formation of such a complex, if not reversible, may remove the cocatalyst from reaction and slow down the reaction rate. Such a situation was intimated by Paddock et al. upon observing that the TOF (turnover frequency, TOF = moles of product per mole of catalyst per hour) for reaction 1.1 decreases with increasing CO_2 pressure in the presence of DMAP (above 50 psig, at 75 °C[46]). Nevertheless, Lu's work indicates that the addition of [LA + halide] is a third possibility for catalyzing the [epoxide + CO_2] coupling in addition to the LA-only[31] and the [LA + LB][32,40] strategies.

Table 1.1. Comparison of *N*-methylimidazole (NMI)- and Bu_4NBr-cocatalyzed coupling of EO and CO_2 in the presence of (salen)Cr^{III} and (salen)Co^{II} complexes. Adapted from reference 43.



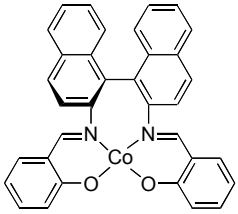
(1.2)

entry	cocatalyst	M	# equiv.	TOF(h^{-1})
1	none	Co	0	0
2	none	Cr	0	0
3	Bu_4NBr	none	1	78
4	NMI	Cr	1	<5
5	NMI	Co	1	<5
6	Bu_4NBr	Cr	1	2140
7	Bu_4NBr	Co	1	1320

Reaction conditions: (salen)M/cocatalyst/EO molar ratio: 1/1/5000, 110 ºC, 1 h, 15-16 MPa.

The [(salen)Co^{II} + LB] strategy was also employed by Shen et al., who showed that complex **2**, although inactive in the absence of a LB cocatalyst, would achieve TOF in the [PO + CO_2] coupling to form PC upon the addition of a LB.[47] Interestingly, although **2** possesses a chiral

binapthyldiamino backbone, an insignificant enantiomeric excess (ee) was observed in the kinetic resolution of PO, possibly because the reaction must be carried out at a high temperature (80 °C) to achieve reasonable rates. While the (salen)Co systems later employed by Paddock et al.[33] and Lu et al.[48] (*vide infra*) were both capable of greater enantioselectivity (selectivity factors[49] (*s* of 4.8 and 6.4, respectively), Chen et al. measured their *s* factors at room temperature and with (salen)Co^{II} complexes, which are much less active than the Co^{III} analogs. Indeed, Paddock et al. demonstrated a substantial rate increase in the (porphyrin)Co^{III}Cl-catalyzed [epoxide + CO_2] coupling, almost two orders of magnitude over that for the corresponding (porphyrin)Co^{II} catalysis.[34,46] The handling of the (salen)Co^{II} complex under conventional laboratory conditions has been shown to easily allow for conversion of the catalyst center to Co^{III} unless atmospheric oxidants are rigorously excluded.[46]

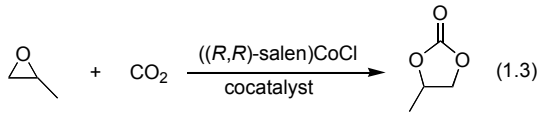


2

In 2004, Paddock et al. reported a systematic study of Lewis base cocatalysts in the presence of a (salen)Co^{III}Cl catalyst (Table 1.2).[33] Although reaction 1.3 proceeds very slowly in the absence of cocatalyst, its rate increases substantially upon the addition of a LB. Among the LBs investigated (Table 1.2, cf. entries 2-5), pyridine and triethylamine were both markedly less reactive than the more nucleophilic NMI, while DMAP was found to be the most active due to its high nucleophilicity. These observations suggest a nucleophilic-type ring-opening step by the LB in the mechanism of the [LA + LB]-catalyzed [epoxide + CO_2] coupling (Scheme 1.4, C). If no nucleophilic cocatalyst is available, the epoxide could be ring-opened using the dissociated

axial anion from the Lewis acid catalyst (Scheme 1.4, A, B, or F). If an external nucleophile in the form of either a LB additive or halide anion is available, this species can independently open the coordinated epoxide (Scheme 1.4, C and D). The halide initiation processes could also occur through a bimetallic route (Scheme 1.4, E), similar to the well-known Jacobsen bimetallic mechanism for the kinetic resolution of racemic epoxide by azide nucleophiles.[39] These initiation steps will be discussed in further detail in section 1.4.2.

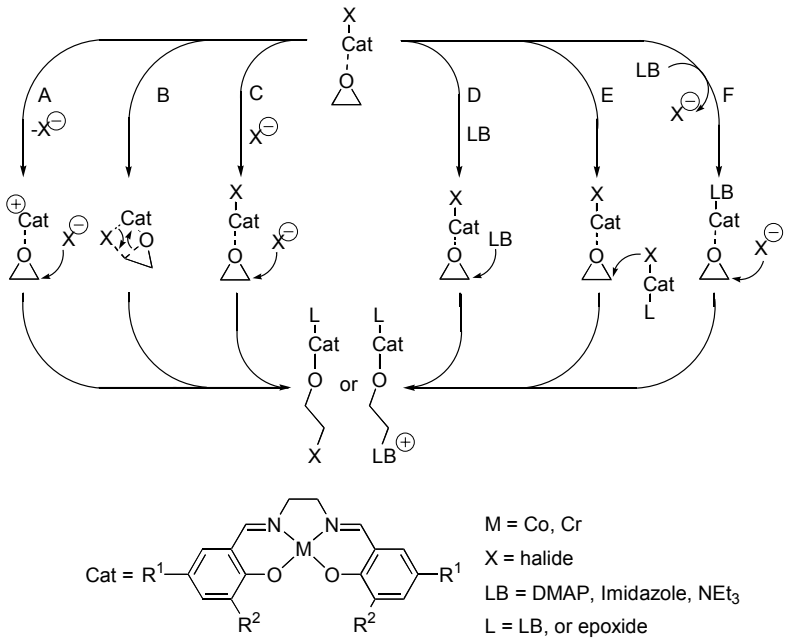
Table 1.2. Activity of (salen)CoCl for the coupling of propylene oxide and CO_2 to form propylene carbonate in the presence of Lewis basic cocatalysts. Adapted from reference 33.



entry	cocatalyst	# equiv	TON	TOF(h^{-1})
1	none	0	20	0.5
2	NMI	2	422	506
3	Pyridine	2	452	25
4	Triethylamine	2	395	99
5	DMAP	1	452	603
6	DMAP	2	400	1200
7	DMAP	4	497	993
8	DMAP	8	464	697

Reaction conditions: catalyst (1 equiv. 0.066 mol% of ((*R*,*R*)-salen)CoCl). Lewis base (2 equiv, 0.132 mol %, propylene oxide (1500 equiv, 3.5 mL), CO_2 (300 psig), CH_2Cl_2 (0.5 mL), DMAP = 4-(*N,N*-dimethylamino)pyridine, NMI = *N*-methylimidazole.

Scheme 1.4. Potential initiation steps for the ring-opening of the Lewis acid-coordinated epoxide.



1.3.2. Kinetic Resolution

As mentioned above, the initial disclosure of the (salen)metal-catalyzed [epoxide + CO_2] coupling in the 1999 patent by Jacobsen et al. outlined a kinetic resolution of racemic hexene oxide by (*R,R*)-(salcy)CrX complex.[31] Thus it is not surprising that the combined use of chiral (salcy)Co(OTs) (salcy = *N*,*N*'-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexanediamine) with an active ionic cocatalyst, would lead to the resolution of racemic PO via coupling with carbon dioxide.[48,49] In the presence of 2 equivalents of Bu_4NCl, this kinetic resolution afforded a maximum selectivity factor of 6 at room temperature.[50,51] While not directly comparable due to the differences in CO_2 pressure, the resolution selectivities for the analogous polymer synthesis (PPC) reported recently by the Lu group have generally been much smaller than 6 (1.9-4.7) even at room temperature.[50,51] Given that the resolution measurements for the polymer were carried out via thermal degradation[51] and should give comparable value as that for cyclic carbonate,[46]

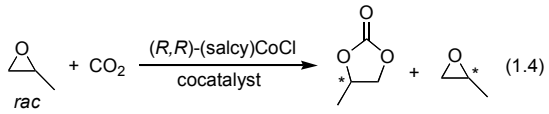
this is somewhat puzzling and points toward a need for careful experimentation and standardization in selectivity evaluation whenever polymer degradation is concerned.

Paddock et al. has investigated the chiral resolution of PO using the enantiopure [(salcy)Co(Cl) + LB] cocatalyst system.[33,49] In contrast, when chiral DMAP-type Lewis bases were used as cocatalysts (Table 1.3) there was little enantioselectivity observed. clearly indicating that the chiral induction observed in the PC product was primarily influenced by the chirality of the salen ligand.[33] Because the chirality of the LB cocatalyst does not significantly impact the stereochemical outcome of the epoxide ring-opening, it is very likely that the key to chiral selection is the pre-coordination and activation of the epoxide isomer matched to the chiral Lewis acid (Figure 1.2). The cocatalyst could then react preferentially to this coordinated PO isomer in the ring-opening step, leading to the observed enantioselectivity. In this model, increasing the *size* of the LB would increase the resolution selectivity in this system by forcing the activated complex to interact with the chiral salen ligand, thus enhancing stereospecificity, as was indeed observed.[33] This size dependence on the amine-LB stands in stark contrast to the observation by Lu's group for the enantiopure [(salcy)Co(Cl) + halide] system where resolution selectivity in both PC and PPC syntheses increases as the size of the anion decreases from I^- to Cl^-.[48,50,51]

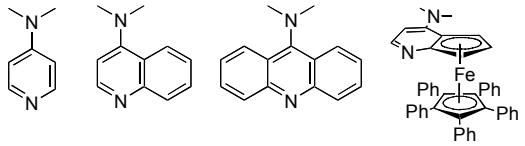
When DMAQ, one of the most selective LBs in reaction 1.4, was applied to the synthesis of PPC from racemic PO, Paddock et al. observed a resolution selectivity factor of 5 in the presence of chirally pure (salcy)CoCl, consistent with the values reported for earlier PC synthesis,[33] as to be expected.[35] While differences in reaction conditions prevent the direct comparison of this selectivity to early values reported by Lu and coworkers for the [(salcy)CoOTs + halide]-catalyzed PC[48] and PPC[50] syntheses, recent reports[33,35] implicate LB usage as a more promising

strategy for maximizing resolution selectivity. Indeed, the bulky LB cocatalyst 7-methyl-1,5,7-triazabicylo[4.4.0]dec-5-ene (MTBD), a sterically similar nucleophile to DMAQ, exhibits improved resolution selectivity (s = 5.5-5.7) in comparison to halide cocatalyst (s = 2.9 for I to 4.6 for F) when employed in the synthesis of PPC.[51]

Table 1.3. Kinetic resolution of racemic propylene oxide by enantioselective reaction with (*R,R*)-(salcy)CoCl. Adapted from reference 33.



entry	cocatalyst	temp (^{o}C)	time (h)	Selectivity (s)
1	DMAP	100	0.33	1.8
2	DMAP	50	8	2.8
3	DMAP	rt	48	3.0
4	DMAP*	rt	4.5	4.8
5	DMAP*	3	50	5.6
6	DMAQ	rt	15	4.6
7	DMAA	rt	37	4.7



DMAP DMAQ DMAA DMAP*

Reaction conditions: (*R,R*)-(salcy)CoCl (1 equiv, 0.066 mol%). Lewis base (2 equiv, 0.132 mol %, propylene oxide (1500 equiv, 3.5 mL), CO_2 (300 psig), CH_2Cl_2 0.5 mL.

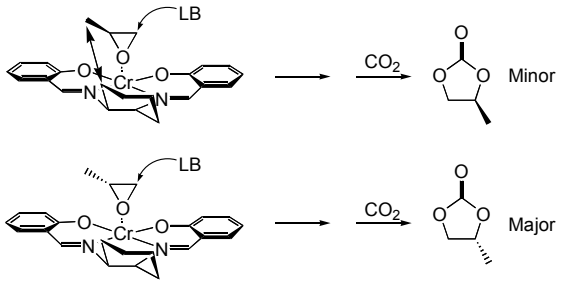


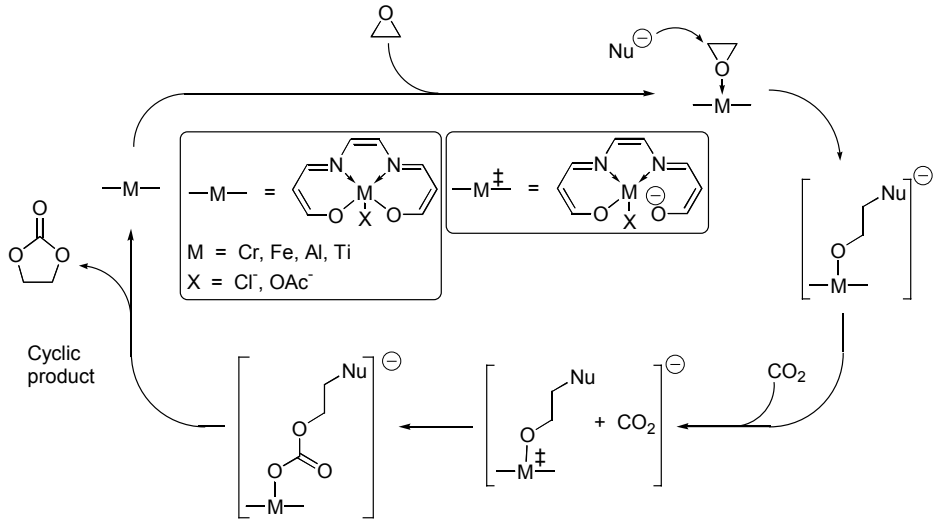
Figure 1.2. Different steric interactions between the chiral salen ligand and the pendant methyl group of the two propylene oxide enantiomers allow for the kinetic resolution of racemic PO. The top intermediate is more sterically hindered and should be less prevalent in a reaction, leading to the observed selectivity.

1.4. A General Mechanistic Model?

1.4.1. Computational Investigation

The mechanism of the (salen)metal-catalyzed coupling of CO_2 and epoxides has been examined both energetically and geometrically, using density functional theory (DFT).[52] Based on the experimental models proposed by Inoue, Kuran, Jacobsen, and Darensbourg (*vide supra*), among others, Luinstra et al. proposed a series of elementary steps for the [epoxide + CO_2] coupling (Scheme 1.5), and then examined those steps computationally for a wide range of (salen)metal complexes.[52] Upon coordination of epoxide to the (salen)metal site, the resulting activated epoxide can undergo an exothermic ring-opening via an external nucleophile at the more substituted position, which may be either a LB cocatalyst, an anion, or the anionic ligand from a second (salen)metal complex. The resulting alkoxide intermediate undergoes insertion of CO_2 into the metal—O bond. This results in the direct formation of an organic carbonate, which will then take one of two pathways: propagation as a polycarbonate chain or ring-closing to a small cyclic carbonate. The former pathway, where another epoxide inserts into the carbonate-metal bond, is generally favored at low temperature and high CO_2 pressure.

Scheme 1.5. DFT investigation of (salen)metal-catalyzed [EO + CO_2] coupling reactions, which form either ethylene carbonate EC (A) or polyethylene carbonate PEC (B). For computational simplicity, only truncated (salen)metal complexes were used. Adapted from reference 52.



As expected from our discussion thus far, a reasonable first step in the mechanism for the [epoxide + CO_2] coupling may involve the coordination of a molecule of epoxide to the LA catalyst. Mechanistically, Luinstra et al. suggested, through a DFT investigation, that this coordination occurs at the vacant site (opposite that of the chloride anion) of a (salen)CrCl complex. This step has no activation barrier and is thermodynamically favorable based on DFT calculations.[52] Mirroring the [(salen)CrX + halide] catalyst system (see section 1.3), the subsequent nucleophilic ring-opening of this coordinated EO with a free acetate nucleophile (Scheme 1.5) is significantly exothermic with a very low reaction barrier (Table 1.4). We note with interest that this epoxide ring-opening was found computationally to have an increased activation barrier when DMAP was used as the external nucleophile instead of acetate. However, the propagation rate for the (salen)CrCl-catalyzed [epoxide + CO_2] copolymerization has been experimentally observed to increase significantly upon the addition of DMAP.[53] This

disparity in the observed and theoretical reaction rates suggests that DMAP may not act as a simple nucleophile. Given that halide addition is also known to increase the rate of the [epoxide + CO_2] coupling,[53] it is more likely that the initiation in the case of the [(salen)Cr + DMAP] follows the model proposed by the Chisholm group for (TPP)AlX-catalyzed [epoxide + CO_2] copolymerization (*vide supra*).[37] Instead of initial epoxide coordination to the vacant site of (salen)CrX, DMAP preferentially coordinates to the opposite face of X, labilizes it, and allows for more facile coordination of the epoxide substrate to the cationic (DMAP)(salen)Cr complex. Subsequent nucleophilic attack by the free anion then initiates the coupling of CO_2.

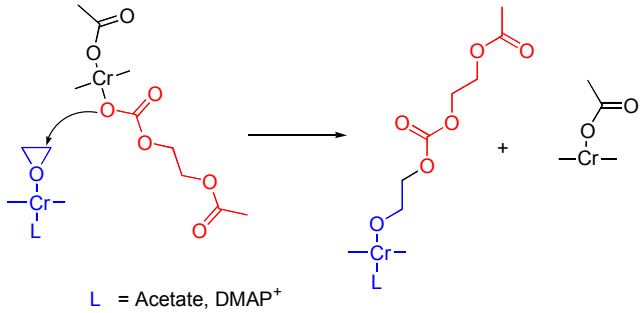
Curiously, the insertion of CO_2 into the resulting Cr-O or Al-O bond was found computationally to require a pre-dissociation of one of the phenoxy groups from the salen ligand framework to provide an open coordination site *cis* to the initiated alkoxide (Scheme 1.5). Once dissociation has occurred, the insertion has a very low activation barrier (5 kJ/mol), readily generates a (salen)metal carbonate intermediate that can subsequently coordinate EO for the propagation step. However, a low-energy pathway for a subsequent *syn* insertion of coordinated EO into the Cr-carbonate bond on the same (salen)Cr center (i.e. intramolecular insertion at a putative (EO)(salen)Cr(carbonate) complex) could not be found computationally. Instead, propagation was proposed to occur via a bimetallic mechanism where a (salen)metal-carbonate complex delivers its nucleophilic carbonate moiety to an activated epoxide that has been coordinated to another (salen)Cr center (eq 1.5). This proposal is similar to a model proposed to explain the syndiotacticity observed by the Coates group in the *rac*-(salcy)Co^{III}Br-catalyzed alternating copolymerization of [*rac*-PO + CO_2] (see section 1.3.2). Interestingly, the calculated activation barrier for the first step of the propagation, the ring-opening of the epoxide by the metal-carbonate species, drops significantly for an EO—[(salen)Cr—DMAP]$^+$ intermediate

when compared to that of the parent EO—[(salen)Cr(acetate)] complex (Table 1.5), again consistent with reported experimental data.[9,11,53]

Table 1.4. Calculated activation barriers for the acetate-induced ring-opening of EO coordinated to various (salen)MCl complexes. Adapted from reference 52.

M	Cr^{III}	Ti^{III}	Al^{III}	Fe^{III}	Co^{III}
$\Delta E^{\ddagger}$ [kJ/mol]	2	5	5	12	29
ΔE [kJ/mol]	-123	-129	-119	-115	-83

Table 1.5. Proposed model for the (salen)Cr—carbonate-induced ring-opening of an EO moiety coordinated to (salen)Cr(acetate) and cationic (salen)M-DMAP complexes. Adapted from reference 52.



L = Acetate, $DMAP^{+}$

	Ring-opening of (L)(salen)Cr(EO) by (OAc)(salen)Cr(carbonate)	
L =	Acetate	DMAP
$\Delta E^{\ddagger}$ [kJ/mol]	51	27
ΔE [kJ/mol]	8	-70

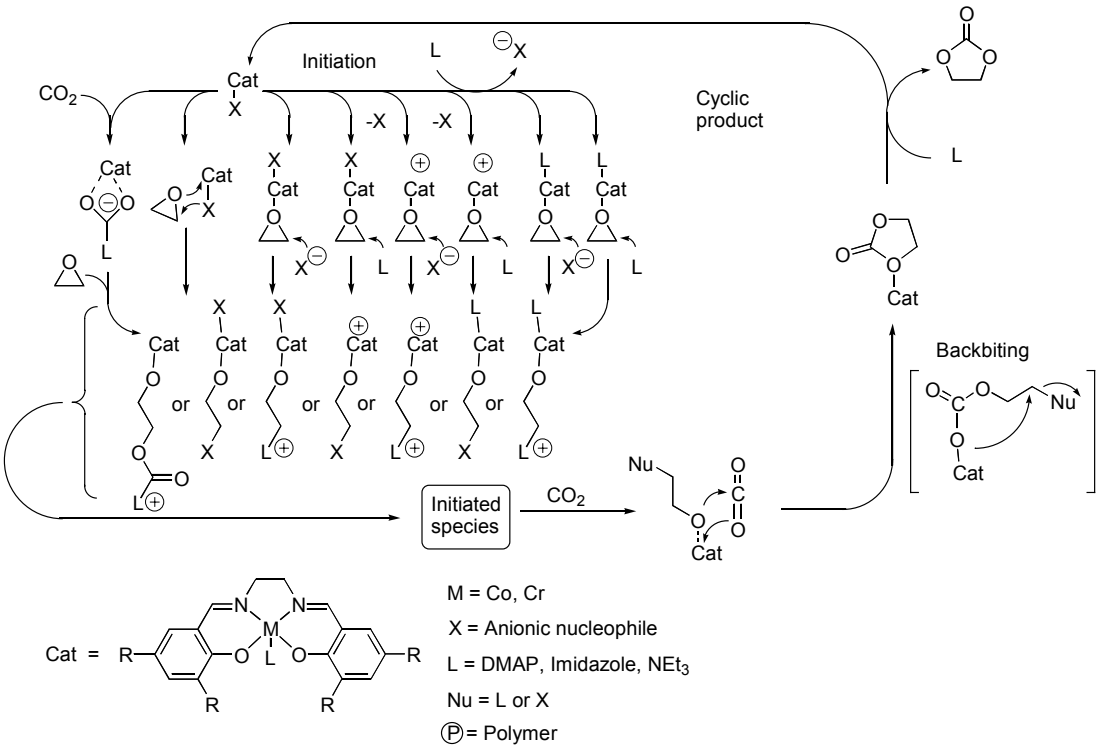
1.4.2. General Mechanism

That the mechanisms of the (salen)AlX-, (salen)CrX-, and (salen)CoX-catalyzed [epoxide + CO_2] couplings have many similarities allows for the beginning formulation of a standard, unifying mechanistic model for these reactions (Scheme 1.6). In all cases examined to date, the first step invariably involves the ring-opening of a coordinated epoxide by a nucleophilic species such as halides, amines, phosphines, a LB zwitterion, or the axial ligand of another metal

complex. This is often facilitated by the coordination of either a LB or an anionic ligand to the opposite face of the catalyst. Subsequent insertion of CO_2 into the resulting metal-alkoxide bond can occur either directly or after dissociation of one of the salen-phenoxide bonds.[52] In either case, a metal—carbonate species is formed.

If the reaction leans toward the formation of cyclic carbonate (often favored by high temperature or lower CO_2 pressure[10]), subsequent ring-closure of the coordinated α-carbonate-ω-nucleophile species would result in the elimination of the cocatalytic nucleophile and formation of the cyclic species. Displacement of this product by a new epoxide molecule allows for the start of another catalytic cycle.

Scheme 1.6. A general mechanistic model for the (salen)metal-catalyzed coupling of CO_2 and epoxides to form poly- or cyclic carbonates.

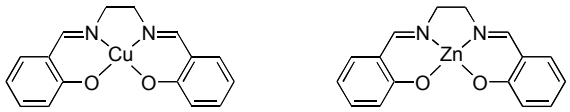


In contrast, propagation in the formation of polycarbonate occurs via insertion of an epoxide comonomer into the newly formed (salen)metal—carbonate complex. This step can proceed by either a direct insertion of the epoxide into the Cr—OC(O)OR bond or by a cooperative bimetallic epoxide ring-opening (equation 1.5), where an epoxide activated by coordination to a (salen)metal complex is ring-opened by a coordinated nucleophilic carbonate molecule delivered by a (salen)Cr—OC(O)OR complex. This latter mechanism is essentially a chain transfer and has recently garnered significant support.[38,52]

Whether a bimetallic mechanism operates in the steady state of the (salen)metal-catalyzed [epoxide + CO_2] coupling has been a subject of debate. While some doubts has been raised in the past[9] about the feasibility of such a bimetallic scheme, as initially proposed[40] based on the Jacobsen-Katsuki model, recent evidence suggests that it cannot be discounted. Luinstra et al.

were not able to model a low-energy, monometallic pathway for the direct insertion of epoxides into a Cr—OC(O)OR bond and found a bimetallic mode of action instead.[52] Further, Coates et al. have presented significant evidence for a bimetallic chain-transfer-type propagation in their discussion of polycarbonate tacticity and regiochemistry (see sections 1.3.2.2 and 1.3.2.3).[38]

Given the general model in Scheme 1.6, it is not surprising that (salen)metal complexes **9-12** were found to be inactive for the [epoxide + CO_2] coupling.[19] That the catalyst center must stabilize an axial anionic propagating species suggests that these complexes, being neutral and stable inside the salen framework, would be ineffective as catalysts.



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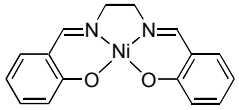
(10)



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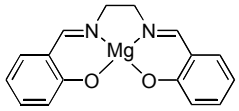

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1.5. Other Strained-Ring/Heterocycle Coupling

While there are a multitude of potential combinations of heterocumulenes and strained ring systems that could theoretically undergo the (salen)metal-catalyzed coupling, they have not been thoroughly explored. For example, a strategy similar to the [epoxide + CO_2] coupling can be devised for the syntheses of five-membered nitrogen-containing heterocycles such as oxazolidinones and imidazolidinones. Such a methodology would provide a direct and versatile route towards the syntheses of these biologically active compounds and potentially many others that are found in Nature. In theory, the synthesis of oxazolidinones could be accomplished in at least two ways, via either nitrogen-containing strained rings (such as aziridines) or nitrogen-

containing heterocumulenes (like isocyanates), both of which are readily available. These strategies may allow easy access to a plethora of biologically active oxazolidinones. Indeed, oxazolidinone-based antibiotics constitute the first new class of synthetic antibacterials developed in the last fifty years[54-56] with excellent activity in the treatment of antibiotic-resistant infections.[57-61]

That [aziridine + CO_2] or [epoxide + isocyanate] couplings have not been widely investigated as [epoxide + CO_2] coupling can be attributed to the higher Lewis-basicity of the nitrogen moiety in aziridines. In the presence of a Lewis acid catalyst, potential [LA + LB] interactions may lead to the poisoning of the catalyst and slow down the reaction. Surprisingly, a comparison of the reaction enthalpies for the [epoxide + CO_2], [aziridine + CO_2], and [epoxide + isocyanate] couplings (Figure 1.3) reveals that the more-studied [epoxide + CO_2] systems has a *much smaller* driving force than the other two combinations.[62-66] When the epoxide substrate is changed to an aziridine, formation of the oxazolidinone product is ~50 kJ/mol more favorable than that for the carbonate analog. If the heterocumulene was further changed into an isocyanate, the driving force for the reaction is ~200 kJ/mol more exothermic.

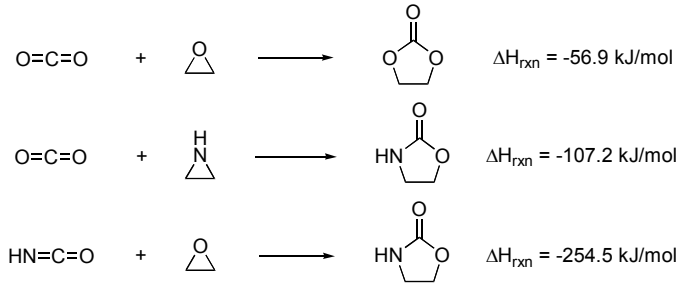


Figure 1.3. Reaction enthalpies for the cyclic coupling of two different strained rings and two different heterocumulenes. Formation enthalpies obtained from references 62-66.

It should be apparent that the [aziridine + CO_2] and [epoxide + isocyanate] couplings are inherently more complex than the analogous [epoxide + CO_2] coupling. In the case of a monosubstituted epoxide and CO_2, the two potential cyclic carbonate products are indistinguishable, regardless of whether the epoxide opens via the more- or less-substituted C—O bond (Figure 1.4). However, for the analogous [aziridine + CO_2] and [epoxide + isocyanate] couplings, the presence of the nitrogen allows for a differentiation of the two different products, depending on the regioselectivity of the ring-opening. This poses an additional challenge for control over regioselectivity in the oxazolidinone products and makes fine-tuning of the catalyst and reaction conditions even more difficult.

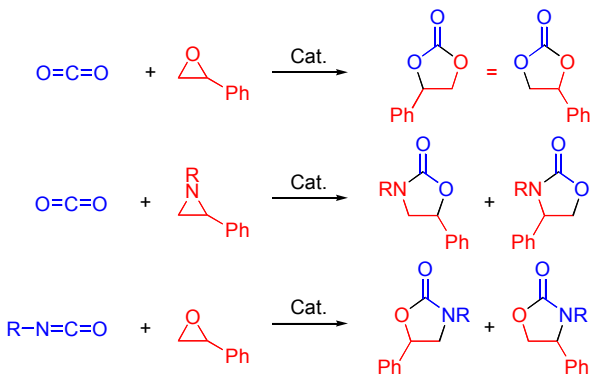


Figure 1.4. The coupling of CO_2 and epoxides leads to the formation of one product while the [aziridine + CO_2] and [epoxide + isocyanate] couplings can give two isomeric species.

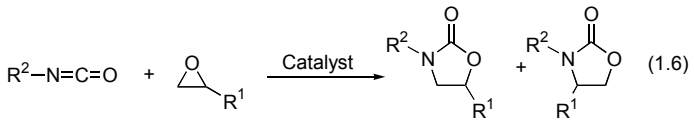
1.5.1. The (Salen)Cr^{III}-Catalyzed Coupling of Epoxides and Isocyanates to Form Oxazolidinones.

An alternative synthesis for oxazolidinones can be envisioned through the [epoxide + isocyanate] coupling of (eq 1.6).[67-72] This reaction has recently been demonstrated for the [(salen)Cr + LB] catalyst system by Paddock[46] who showed it to be general for a variety of both epoxides and isocyanates. Because isocyanates are subject to trimerization in the presence of LB during thermal activation, extensive optimization must be carried out to minimize this side reaction. This objective was achieved in nonpolar solvents with the use of soft, bulky LB cocatalysts such as phosphine oxides or weakly nucleophilic LB such as 4-CF_3-pyridine.

Paddock suggested a mechanism for reaction 1.6 (Scheme 1.7) that is analogous to the general model proposed for the [epoxide + CO_2] coupling (*vide supra*). Initial coordination of the epoxide activates it for subsequent ring-opening by a chloride anion, either free or coordinated. Incorporation of the isocyanate proceeds via insertion into the (salen)Cr—alkoxide bond, giving

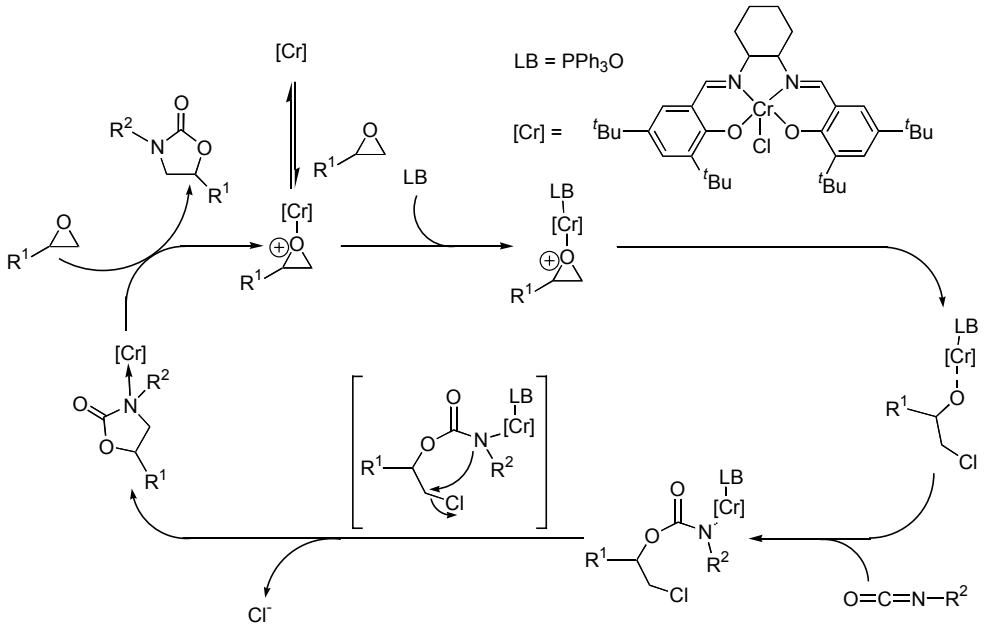
the corresponding metal-bound carbamate, which collapses upon itself, expels the chloride nucleophile, and forms the oxazolidinone. Displacement of this product by another epoxide molecule then continues the cycle.

As shown in Figure 1.4, two different regioisomers can result from eq 1.1. For the majority of epoxides, ring-opening occurred only at the least-substituted C-O bond, producing exclusively the 5-substituted isomer. (In contrast, the (salen)Cr-catalyzed [aziridine + CO_2] coupling (see Chapter 2) opened the aziridine ring at the *more* substituted N—C bond, also giving the 5-substituted oxazolidinone as the major product). The opening of the coordinated epoxide in the [epoxide + isocyanate] coupling is thus more reminiscent of a nucleophilic-type ring-opening. Only in the case of a phenyl substituted epoxide does a significant amount of the 4-substituted oxazolidinone form. This observed selectivity was probably due to stabilization of the more-substituted C—O bond in styrene oxide upon Lewis acid coordination, which allowed for attack at the more-substituted site, leading to formation of the opposite regioisomer as a side product.



(1.6)

Scheme 1.7. Proposed mechanism for the [(salen)CrCl + LB]-catalyzed [epoxide + isocyanate] coupling to form 5-substituted oxazolidinones. Adapted from reference 46.



1.6. Outlook for Catalytic Cycloaddition/Coupling in Synthetic Chemistry

The utility of (salen)metal catalysts for the formation of both cyclic carbonates and polycarbonates from CO_2 and epoxide has been amply demonstrated through a large number of investigations. By varying simple reaction conditions such as temperature, pressure, and cocatalytic additive, the reaction outcome can be changed to favor the production of polymeric or cyclic products with impressive chemoselectivity and excellent stereoselectivity. As numerous strained three-membered rings and heterocumulenes are readily available, this strategy holds the promise for easy access to a wide range of hetero-substituted polymers and cyclic molecules. Because the mechanism of the (salen)metal-catalyzed [epoxide + CO_2] couplings have been clarified by many elegant and thought provoking mechanistic studies, a ready extension of the known catalysis into the directed study of similar systems should be possible.

Further mechanistic studies will aid in the development of ever more versatile catalyst systems for [strained ring + heterocumulene] couplings. In particular, the stereoelectronic tuning of (salen)metal complexes and their modification with cocatalysts can allow for a ready manipulation of the underpinning mode of reactivity to include new substrates, yielding a plethora of high value heteroatom-containing products.

Although the (salen)metal-catalyzed [strained ring + heterocumulene] coupling is still a nascent field with more papers being published each year, accurate evaluation of progress has been quite difficult due to the wide range of reaction parameters, catalyst types, and substrate classes. While we have attempted to summarize the progress made in this exciting research area and present a mechanistic consensus whenever possible, it is clear that concerted efforts to systematize research directions must be made before the vigorous activities in the field dilute its significant potential. In particular, future studies in this area must be cognizant that multicomponent catalyst systems, such as those presented herein, will require extensive standardization of reaction parameters if accurate and physically meaningful data are to be obtained. The larger the number of variables, the more tightly they must be regulated so that the effect of each reaction parameter can be evaluated accurately. For instance, system homogeneity and catalyst solubility in non-conventional solvents—supercritical media, or solvents under high CO_2 pressure—must be carefully maintained throughout the reaction. Additionally, the nature of catalyst components in reaction media (such as LB in $scCO_2$) must be carefully evaluated. Thus far, several challenges remain unaddressed:

1. The use of both LB and halide cocatalysts have been widespread, but there has not been a direct and thorough comparison between these two classes of cocatalysts under the same conditions. Such a contrast would greatly benefit further catalyst development.

2. With LB additives, there is always the potential for forming zwitterionic complexes between CO_2 and other heterocumulenes, which may also act as a cocatalyst. Further investigation into the formation of these complexes and their effect on the overall [strained ring + heterocumulene] coupling reactions are needed.
3. As other more Lewis basic heteroatom-containing substrates are being investigated, it becomes increasingly pertinent to consider issues associated with Lewis-basic substrates on both the (salen)metal catalyst and the cocatalytic environment beyond the immediate reacting group (for example, aziridine substrates can also act as LB cocatalysts, and isocyanates can form trimers in the presence of LBs).
4. Factors controlling the regioselectivity of the strained heterocycle ring-opening must be completely understood before catalyst systems can be designed with tunable chemo- and stereoselectivity. While aziridines favor ring-opening at the more-substituted C—N bond in coupling with CO_2, it is not clear if this is general for all [aziridine + heterocumulene] coupling. In the same vein, although epoxides have long been believed to undergo coupling with CO_2 via the opening of the less-substituted C—O bond, there is no guarantee that this is always the case. Mechanistic studies that explain these ring-opening selectivities and the difference between aziridine and epoxide would be very informative in the design of selective catalysts for these synthetic transformations.
5. While the nature of the ligand *trans* to the active face of the (salen)metal catalyst has been investigated on a limited scale for [epoxide + CO_2] coupling reactions, a more comprehensive and thorough investigation of the effect of cocatalyst (*N*-heterocyclic LB, phosphine-containing LB, and halide ligands) will be of fundamental importance, both in understanding the mechanism and in the development of more active catalyst systems.

This study could then be extended to include the *trans* effect as it relates to other heteroatom-containing strained ring and heterocumulene substrates.

6. Additionally, the partitioning of reaction paths as a function of the cocatalyst is still poorly understood. While it is known that both the *trans* effect and cocatalyst nucleophilicity influence the reaction selectivity (cyclic, alternating copolymer, or homopolymer product), a clear delineation of their respective contributions would be invaluable for reaction design.

We are confident that there are practical improvements yet to be made in the [strained ring + heterocumulene] couplings: more active catalyst systems, milder reaction conditions, broader substrate scopes with higher selectivity. While great potential exists to make these atom efficient coupling methodologies applicable to mainstream and industrial processes, the first challenge lies in the thorough understanding of the reaction mechanisms, and many variables must be considered when attempting to modify and improve previous studies. Thus, researchers coming into this field should strive to exploit known mechanistic hypotheses with periodic trends in substrate selection rather than blindly combining catalysts and starting materials under a myriad of conditions until a chance mixture fortuitously yields positive results.

1.7. Thesis Overview

Chapter Two of this thesis outlines the [(salen)Cr + LB]-catalyzed [aziridine + CO_2] coupling to selectively form 5-substitued oxazolidinones. Reaction conditions were varied and optimized to give high selectivity and short reaction times for these valuable molecules.

Chapter Three details a mechanistic study of the [aziridine + CO_2] coupling reaction including an extended analysis of the mechanism proposed in Chapter Two by way of a Hammett plot, the

use of DFT calculations, kinetics, and the synthesis of a model for the putative intermediate (salen)Cr—NR_2.

In Chapter Four, the [(salen)Cr + LB]-catalyzed [aziridine + CO_2] coupling methodology is expanded to include the [aziridine + isocyanate] coupling to selectively form imidazolidinones. Optimization of this reaction has revealed a variety of reaction trends, including the first [strained-ring + heterocumulene] reaction that is *hindered* by the addition of a LB cocatalyst.

The fifth and final chapter of this thesis describes the investigation and optimization of the $Sc(OTf)_3$-catalyzed coupling of aziridines with aldehydes and ketones, yielding oxazolidines.

Chapter 2

[(Salen)CrCl + DMAP] Catalyst System for the Coupling of Aziridines and CO_2 to Form Oxazolidinones

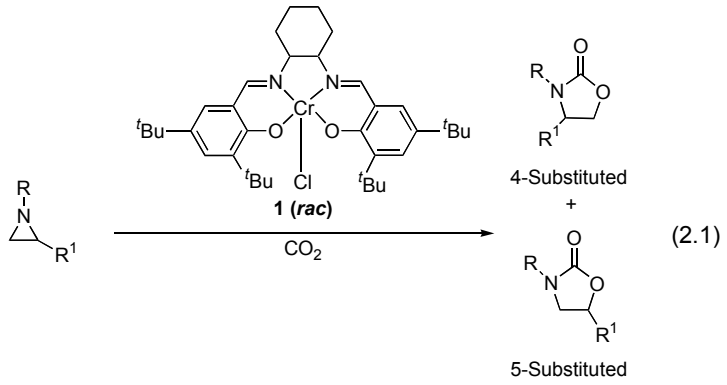
Portions of this chapter have appeared in:

Miller, A. W.; Nguyen, S. T. *Org. Lett.* **2004**; 6(14), 2301-2304.

2.1. Introduction

A number of 5-substituted oxazolidinones have been shown to have high potency as antibacterial agents, and are widely used in the pharmaceutical industry.[1-8] Chiral oxazolidinones also have utility in organic synthesis as chiral synthons and auxilliaries.[9,10] An attractive route to these valuable compounds is the [2+3] coupling between aziridines and CO_2 (eq 2.1), as the variety of multiply substituted aziridines presents the chemist with an abundance of synthetic precursors. Additionally, the chemical fixation of CO_2 is a desirable reaction as it is an inexpensive and abundant C_1 feedstock.

Previous research into the aziridine/CO_2 coupling reaction has employed several catalyst systems—lithium iodide,[11] tin, ammonium, and antimony salts,[12] and nickel complexes[13]—albeit with limited success. Reaction 2.1 has also been carried out with iodine catalysts in supercritical CO_2.[14] While the results were promising, these methods suffer from the use of high pressure or low selectivity and multiple product isomers.



(2.1)

In 2001, Paddock et al. reported the use of the [(salen)Cr^{III} + DMAP] catalyst system in the fixation of CO_2 with epoxides to form carbonates.[15] In this chapter, I describe the extension of this catalytic system to aziridines (eq 2.1). In contrast to the majority of reported catalysts, this [(salen)Cr^{III} + DMAP] catalyst system consistently gives 5-substituted oxazolidinones (with

selectivity as high as 40:1) for a wide range of substrates. The good selectivity and high activity of the (salen)Cr^{III} catalyst is the best to date. The opening of the aziridine ring at the most substituted carbon is a behavior that is reminiscent of the classical electrophilic ring-opening of three-membered heterocycles.[16]

2.2. Optimization

In contrast with the analogous epoxide/CO_2 coupling,[15] reaction 2.2 does not require a co-catalyst to proceed. The presence of a slight excess of Lewis base (LB) co-catalyst does improve the TOF in CH_2Cl_2. However, a greater than twofold excess of LB leads to a slight decrease in catalyst activity (Figure 2.1). Less basic LBs showed lower activity, as did bulkier bases (Table 2.1). Of the five LBs studied, DMAP exhibits the highest activity.

Interestingly, the percentage of 5-substituted oxazolidinone product is strongly dependent on the catalyst/cocatalyst ratio. As the concentration of cocatalyst decreases, the proportion of the 5-substituted isomer increases (Figure 2.2). For *N*-^{n}propyl-2-phenylaziridine, reaction 2.1 turns over slowly and affords an 8:1 ratio of the 5- to 4-substituted products when the co-catalyst/catalyst ratio is 2. In the absence of DMAP co-catalyst, a 40:1 selectivity was observed favoring 5-phenyl-N-^{n}propyloxazolidinone.

The activity of our catalyst system is strongly dependent on the solvent used in the reaction (Figure 2.3). Toluene and benzene do not facilitate fast reaction rates while DME worked reasonably well. However, dichloromethane (DCM) affords the highest TOF.

(2.2)

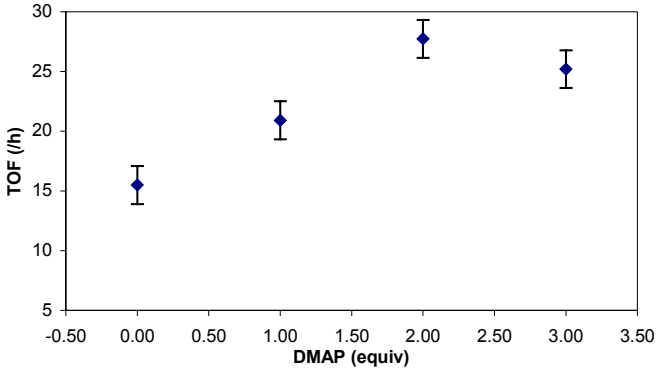


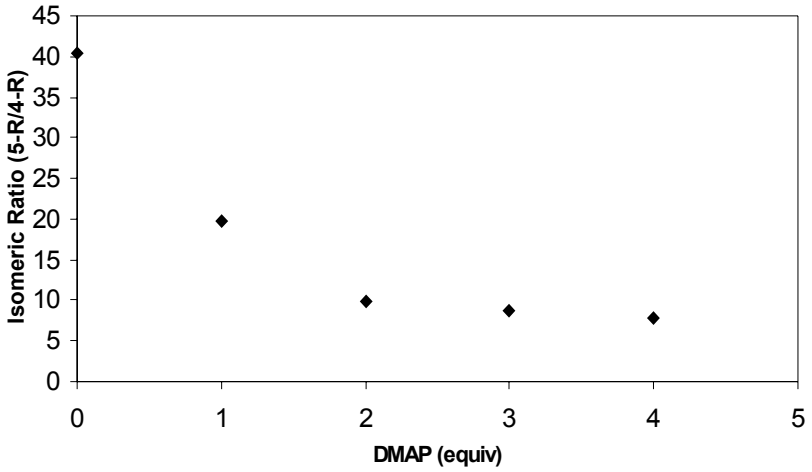
Figure 2.1. Activity of (salen)Cr^{III}/DMAP as a function of DMAP concentration in the reaction of CO_2 and *N*-^{n}propyl-2-phenylaziridine. Reaction conditions: catalyst (12.6 mg, 0.02 mmol), 400 psig CO_2, *N*-^{n}propyl-2-phenylaziridine (0.322 g, 2 mmol, 100 equiv), CH_2Cl_2 (3.7 mL), 100 ^{o}C, 120 min.

Table 2.1. Activity of [(Salen)Cr^{III} + LB] Catalyst System in the Reaction of CO_2 and *N*-^{n}propyl-2-phenylaziridine.

entry	Lewis base	TOF[a] (hr^{-1})
s	*N*,*N*-Dimethyl-4-aminopyridine (DMAP)	27
2	Triethylamine	20
3	Triphenylphosphine oxide	20
4	Pyridine	11
5	Imidazole	23

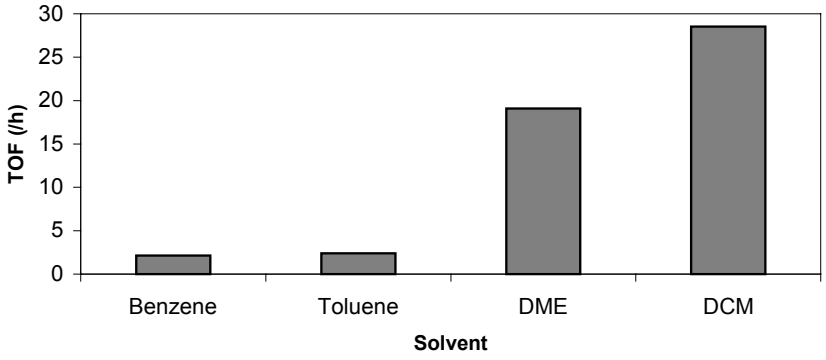
Reaction conditions: catalyst (12.6 mg, 0.02 mmol), co-catalyst (2 equiv), *N*-^{n}propyl-2-phenylaziridine (0.322 g, 2 mmol, 100 equiv), CO_2 (400 psig), CH_2Cl_2 (3.7 mL), 100 ^{o}C, 120 min. [a]TOF determined using GC yields

Figure 2.2. Ratio of 5-substituted to 4-substituted isomers in the reaction of CO_2 and *N*-^{n}propyl 2-phenylaziridine as a function of DMAP concentration.



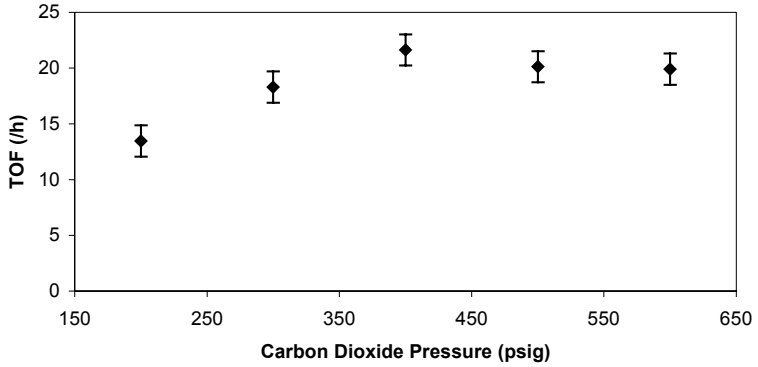
Reaction conditions: catalyst (13.37 mg, 0.023 mmol) *N*-^{n}propyl-2-phenylaziridine (2 mmol, 100 equiv), CO_2 (400 psig), CH_2Cl_2 (3.7 mL), 100 ^{o}C, 120 min.

Figure 2.3. Activity of the (salen)Cr^{III}/DMAP catalyst as a function of solvent in the reaction of CO_2 and *N*-^{n}propyl-2-phenylaziridine.



Reaction conditions: catalyst (12.6 mg, 0.02 mmol), DMAP (2 equiv), *N*-^{n}propyl-2-phenylaziridine (0.322 g, 2 mmol, 100 equiv), solvent (3.7 mL), 400 psig CO_2, 100 ^{o}C, 120 min.

Figure 2.4. Activity of the (salen)Cr^{III}/DMAP catalyst system as a function of CO_2 pressure in the reaction of CO_2 and *N*-^{n}propyl-2-phenylaziridine.

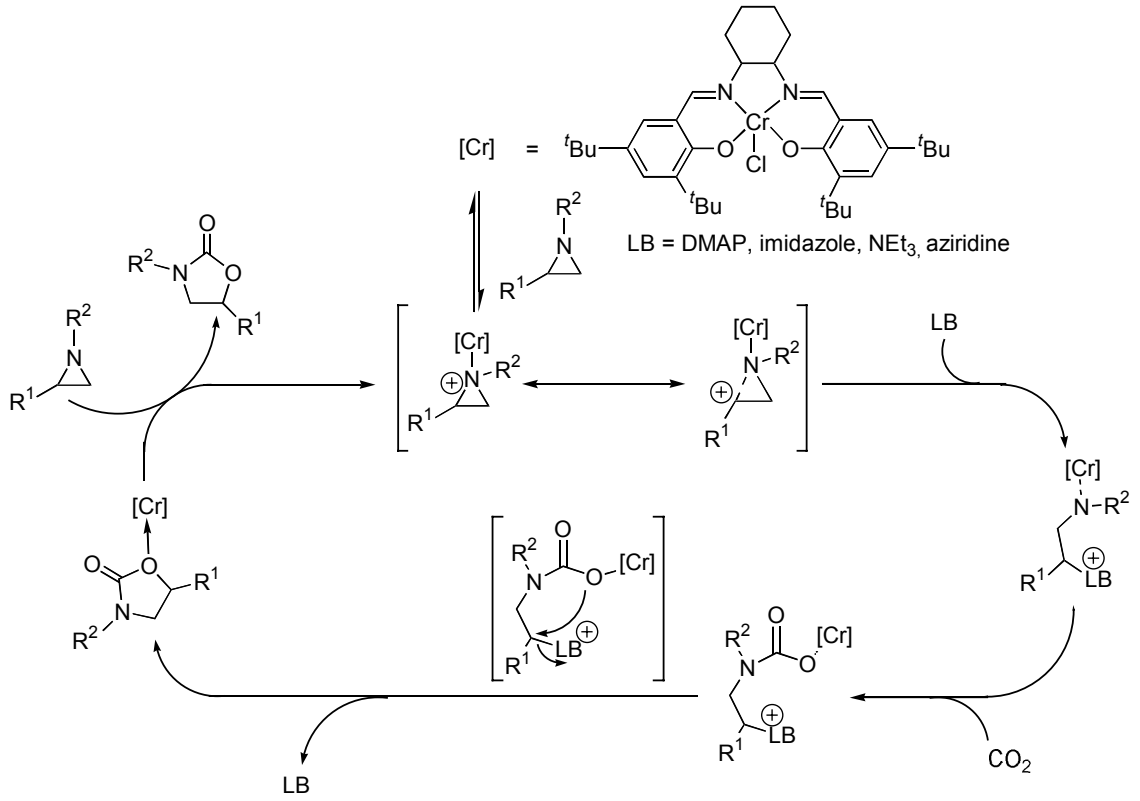


Reaction conditions: catalyst (12.6 mg, 0.02 mmol), DMAP (2 equiv), *N*-^{n}propyl-2-phenylaziridine (0.322 g, 2 mmol, 100 equiv), CH_2Cl_2 (3.7 mL), 400 psig CO_2, 100 ^{o}C, 60 min.

2.3. Proposed Mechanism

The results above can be explained by a mechanism in which the aziridine is first activated by coordination to the Lewis-acidic (salen)Cr^{III} center, resulting in the formation of a partially cationic nitrogen (Scheme 2.1). This is followed by the nucleophilic ring-opening of the aziridine by the LB co-catalyst at the more substituted carbon to give an ionic intermediate. The presence of too much LB would inhibit the reaction due to the competitive coordination of the LB to the Lewis-acidic Cr site.

Scheme 2.1. A proposed mechanism for the [(salen)Cr^{III} + DMAP]-catalyzed [aziridine + CO_2] coupling.



Scheme 2.1 can also be used to rationalize the dependence of reaction rate on CO_2 pressure. As in the case of the [epoxide + CO_2] coupling chemistry,[15] the reaction yield increases as a function of increasing pressure up to a certain point and then slowly drops off (Figure 2.4). We postulate that, at high CO_2 pressures, the amount of available DMAP for catalysis is reduced due to its reaction with CO_2 to form a zwitterionic complex, which is not active as a cocatalyst.[17]

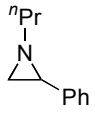
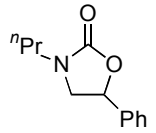
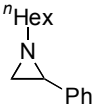
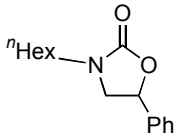
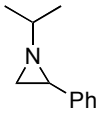
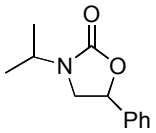
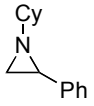
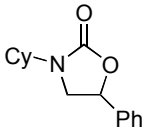
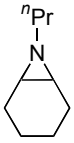
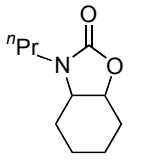
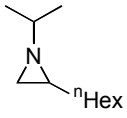
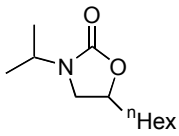
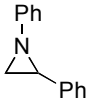
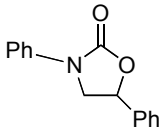
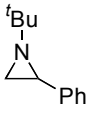
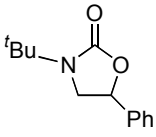
Further, the mechanism shown in Scheme 2.1 explains catalytic activity in the absence of a co-catalyst. Since the aziridine is itself a LB (pK_b = 6.14),[18] it may act as its own co-catalyst. However, DMAP (pK_b = 4.3)[18] is still the more effective cocatalyst under our reaction conditions.

2.4. Aziridine Substrate Scope

Under optimized conditions, the [(salen)Cr^{III} + DMAP] catalyst system is an active catalyst for the [aziridine + CO_2] coupling reaction. Substrates were primarily varied as to their *N*-substitution, however 1,2-disubstituted aziridines also show good yield (albeit at longer reaction times, Table 2.2, cf entries 1 and 5), as do 1,2,3-trisubstituted aziridines (Table 2.2, entry 5).

Trends in substrate reactivity show that increasing the steric hindrance of the *N*-substitution leads to a large decrease in reaction rate (Table 2.2, cf entries 1, 2, 3, 4, and 8), consistent with our proposed mechanism, where bulky aziridines are expected to coordinate poorly to the (salen)Cr^{III} center, slowing their conversion to products. Phenyl substitution at the 2-position also seems to increase the reaction rate relative to alkyl substitutions (Table 2.2, cf entries 3 and 6).

Table 2.2. Substrate scope of the [(salen)Cr^{III} + DMAP] catalyst system in the reaction of CO_2 and *N*-substituted aziridines.[19]

entry	substrate	time (h)	major product		minor product (%)[e]	isolated yield (%)[f]
			structure	(%)[e]		
1		5		90	10	93
1a*		14		94	2.3	90
2		8		87[b]	11	91
3		12		92	3	86
4		16		97[b]	2	91
5		18		94	NA[d]	92
6		20		92	7	93
7		28		89[c]	0	82
8		120[a]		92	2	89

Reaction conditions: catalyst (12.6 mg, 0.02 mmol), DMAP (2 equiv), substrate (2 mmol, 100 equiv), CH_2Cl_2 (3.7 mL), 400 psig CO_2, 100 °C, *no cocatalyst used in this reaction. [a]5 mol% catalyst. [b]Isomers can be separated by recrystallization from hexanes. [c]Remainder is 1,2,4,5,-tetraphenyl-1,4-piperazine formed from the dimerization of aziridine. [d]All *cis* as determined by ^{1}H NMR spectroscopy. [e]GC yields. [f]Mixture of isomers.

2.5. Conclusion

In conclusion, [(salen)Cr^{III} + DMAP] is an excellent catalyst system for the [aziridine + CO_2] coupling to form 5-substituted oxazolidinones selectively. Previous catalytic syntheses of oxazolidinones via the coupling of aziridines and CO_2 have only been possible using less reactive catalysts that give multiple product isomers. This is the first catalyst system to give a high excess of the 5-substituted isomer over the 4-substituted one, along with high catalyst activity. Recent investigations into the antibiotic properties of oxazolidinones show that the 5-substituted oxazolidinone comprises the active isomer. These include linezolid,[4] ranbezolid,[2] DuP-721 and DuP-105,[7] and AZD2563.[8] These fully synthetic compounds show great antibacterial potential for widespread use against *Staphylococci*, *Pneumococci*, and *Enterococci* bacteria, many of which are resistant to traditional antibiotics.[4] While the work presented herein does not directly contribute to the synthesis of the chiral 5-(*S)*-substituted oxazolidinone isomers which have exhibited antibacterial properties, our strategies suggest an atom-economic pathway towards the synthesis of such compounds, especially when the chirality of the 5-position can be controlled.

2.6. Experimental

General Information. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova 500 (499.570 MHz for ^{1}H, 125.631 MHz for ^{13}C) or a Mercury 400 (400.168 MHz for ^{1}H, 100.631 MHz for ^{13}C) spectrometer. NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and integration). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. IR spectra were collected on a Nicolet 5PC

instrument and analyzed using PC-IR software. High-resolution electron-impact mass spectra (HREIMS) were obtained from the Analytical Services Laboratory, Northwestern University (Evanston, IL). Elemental analyses were provided by Atlantic Microlab, Inc. (Norcross, GA). GC analyses of oxazolidinone products were carried out on a Hewlett Packard 5890A gas chromatograph equipped with FID detector and a 30-m HP-5 capillary column with 0.32-mm inner diameter and 0.25-mm film thickness was used. Temperature program: intitial time = 0 min., initial temperature = 60 $^{\circ}$C, rate = 20 $^{\circ}$C/min; final time = 2.5 min., final temperature = 250 $^{\circ}$C.

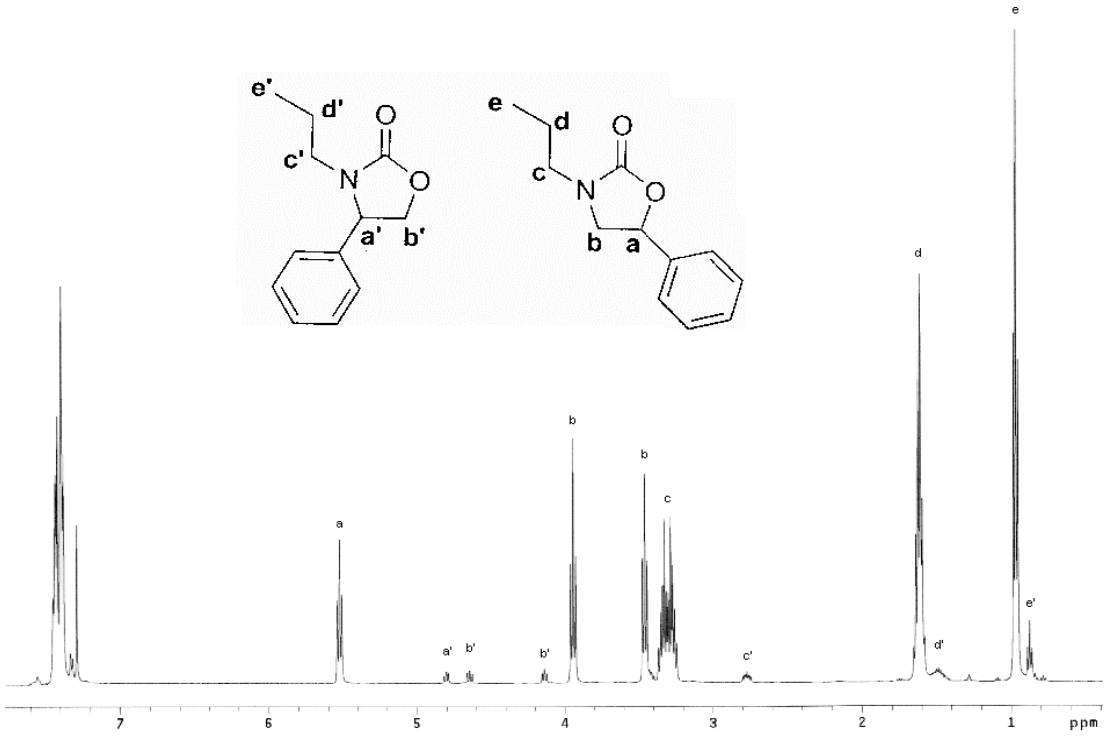
Materials. Catalyst was synthesized according to published procedures.[21,22] Racemic diaminocyclohexane was obtained from Aldrich. Solvents used were purchased from either Fischer Chemical or Aldrich Chemical. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. All other reagents were purchased from the Aldrich Chemical Company and used without further purification, unless otherwise noted. Aziridines and β-amino alcohol precursors were synthesized using published procedures.[23] Data are available for 3,5-diphenyloxazolidinone.[24] Analytical data for the following compounds have not been reported and were confirmed by us.

General Experimental Procedure. On the bench top, a 45-mL Parr high pressure reactor equipped with a magnetic stir bar was charged with catalyst **1** (12.6 mg, 2 x 10^{-5} mol), DMAP (4.9 mg, 4 x 10^{-5} mol), and a solution of the aziridine (2 mmol) in CH_2Cl_2 (4 mL, 0.5 M solution). Finally, undecane (100 μl, 0.474 mmol, internal standard) was placed in the reactor. The reactor was sealed and placed under constant CO_2 pressure for 5 minutes to allow equilibration, the CO_2 valve was closed, and the reactor was placed in a magnetically stirred 100

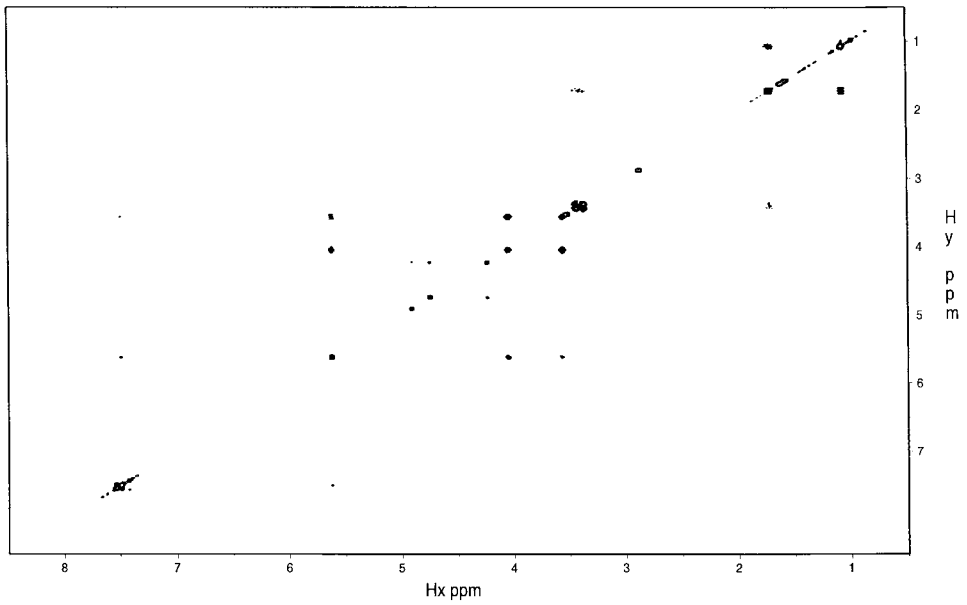
°C oil bath. After 2 h the reactor was removed from the oil bath, quickly cooled in running cold tap water, and vented to a hood. A small aliquot was then removed from the solution for GC analysis. (The catalyst was removed by eluting the aliquot in CH_2Cl_2 (20 mL) through a solvent-wet silica plug which was doped with triethylamine (100 μL) before introduction of the aliquot. Yield was determined via GC using peak areas and undecane internal standard.). Further purification by column chromatography over neutral alumina, (150 mesh, 58Å, hexanes:ethyl acetate 60:40) gave analytically pure oxazolidinone product (mixture of 4- and 5-substituted isomers).

***N*-^{n}propyl-5-phenyloxazolidinone.** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.97 (t, 3H, propyl C*H*$_3$, ^3J = 7.0 Hz), 1.63 (q, 2H, propyl C*H*$_2$, ^3J = 7.0 Hz), 3.29 (m, 2H, propyl N-C*H*$_2$), 3.47 (t, 1H, N-C*H*$_2$, ^3J = 8.0 Hz), 3.94 (t, 1H, N-C*H*$_2$, ^3J = 8.5 Hz), 5.53 (t, 1H, O-C*H*, ^3J = 8.0 Hz), 7.40 (m, 5H, arom-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.3 (propyl *C*H$_3$), 20.8 (propyl *C*H$_2$), 45.9 (propyl *C*H$_2$), 52.2 (N-*C*H$_2$), 74.5 (O-*C*H), 125.7 (*Cm*), 128.9 (*Co*), 129.0 (*Cp*), 139.2 (*Ci*), 158.2 (*C*=O). FTIR (CH_2Cl_2): ν_{CO} 1752.55 cm^{-1}. Anal.: Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82; Found: C, 70.15, H, 7.38, N, 6.87. HREIMS: Calcd for $C_{12}H_{15}NO_2$: 205.1097, Found: 205.1097.

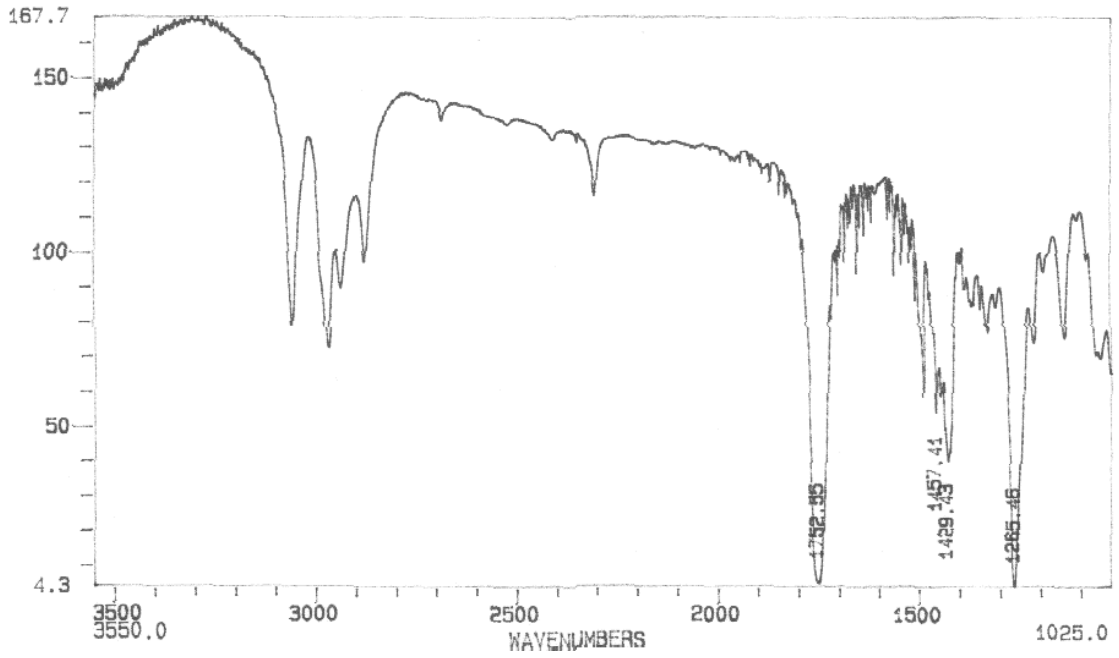
Figure 2.5. A) The ^{1}H NMR spectrum of *N*-propyl-5-phenyloxazolidinone. There is a small amount of the 4-substituted isomer in this sample.



B) The NOESY spectrum of *N*-propyl-5-phenyloxazolidinone.



C) The FT-IR Spectrum of *N*-^{n}propyl-5-phenyloxazolidinone.



***N*-^{n}hexyl-5-phenyloxazolidinone**. A yellow solid (mp 31.0-31.9 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.86 (t, 3H, ^{n}hexyl CH_3, ^{3}J = 6.0 Hz), 1.28 (m, 6H, ^{n}hexyl CH_2), 1.53 (m, 2H, ^{n}hexyl

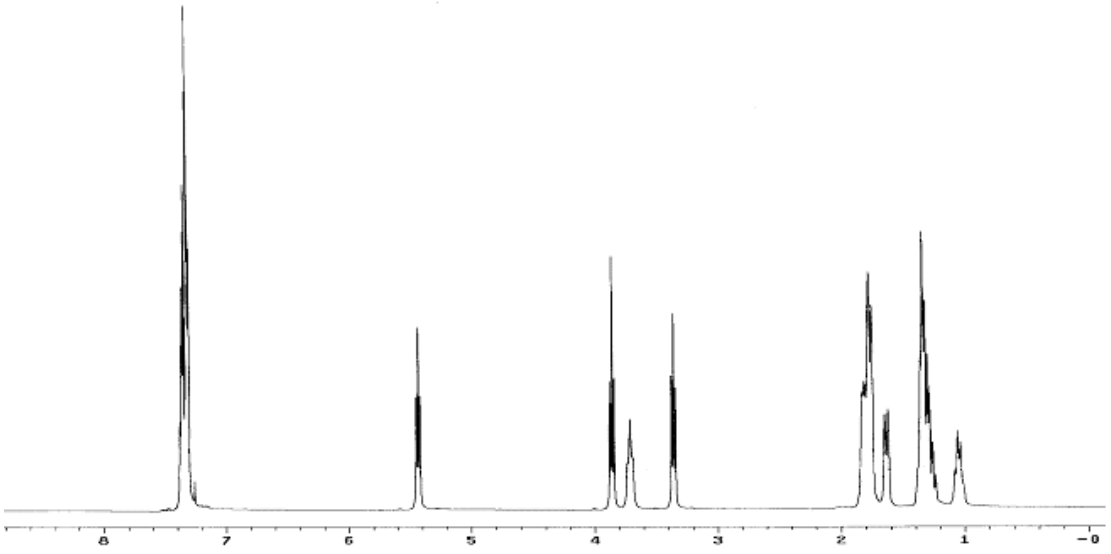
C*H*$_2$), 3.28 (m, 2H, N-C*H*$_2$), 3.41 (dd, 1H, N-C*H*$_2$, ^3J = 8.0 Hz), 3.90 (dd, 1H, N-C*H*$_2$, ^3J = 9.0 Hz), 5.47 (t, 1H, O-C*H*$_2$, ^3J = 8.0 Hz), 7.35 (m, 5H, arom *H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 14.2 (^{n}hexyl *C*H$_3$), 22.8 (^{n}hexyl *C*H$_2$), 26.5 (^{n}hexyl *C*H$_2$), 27.5 (^{n}hexyl *C*H$_2$), 31.6 (^{n}hexyl *C*H$_2$), 44.4 (^{n}hexyl *C*H$_2$), 52.4 (N-*C*H$_2$), 74.5 (O-*C*H), 125.7 (*Cm*), 129.0 (*Co*), 129.1 (*Cp*), 139.2 (*Ci*), 158.2 (*C*=O). Anal.: Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66; Found: C, 72.58, H, 8.63, N, 5.82. HREIMS: Calcd. for $C_{15}H_{19}NO_2$: 247.1567; Found: 247.1566.

***N*-^{i}propyl-5-phenyloxazolidinone.** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.10 (d, 3H, isopropyl C*H*$_3$, ^3J = 7.0 Hz), 1.15 (d, 3H, ^{i}propyl C*H*$_3$, ^3J = 7.0 Hz), 3.30 (dd, 1H, N-C*H*$_2$, ^3J = 8.0 Hz), 3.82 (t, 1H, N-C*H*$_2$, ^3J = 8.5 Hz), 4.10 (m, 1H, N-C*H*), 5.41 (dd, 1H, O-C*H*, ^3J = 8 Hz), 7.30 (m, 5H, arom-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 19.7 (^{i}propyl *C*H$_3$), 20.2 (^{i}propyl *C*H$_3$), 45.1 (^{i}propyl *C*H), 47.6 (N-*C*H$_2$), 74.7 (O-*C*H), 125.7 (*Cm*), 128.9 (*Co*), 129.1 (*Cp*), 139.2 (*Ci*), 157.4 (*C*=O). Anal.: Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82; Found: C, 70.20, H, 7.48, N, 6.67. HREIMS: Calcd. for $C_{12}H_{15}NO_2$: 205.1097; Found: 205.1095.

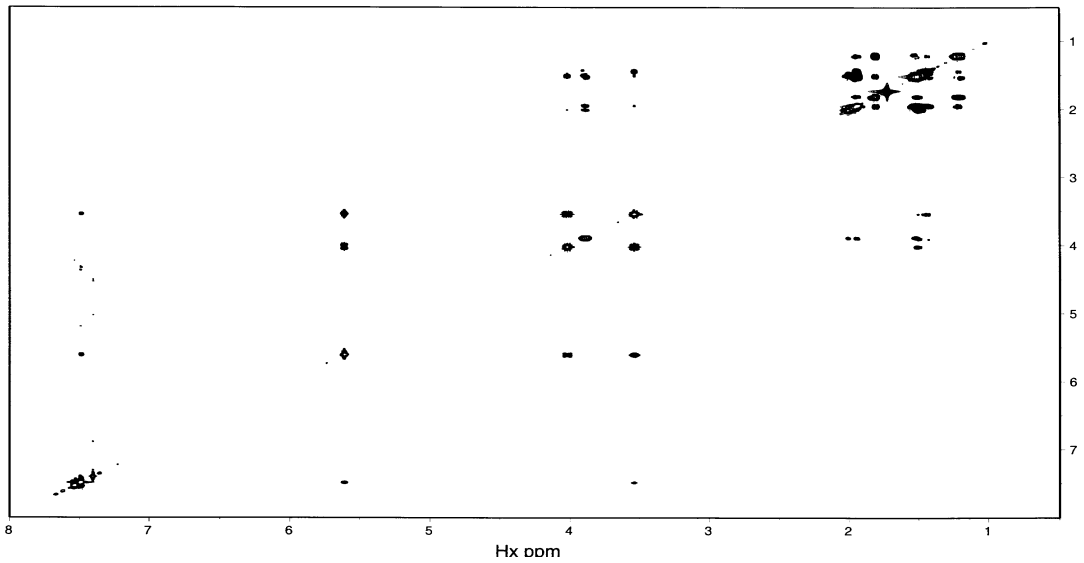
***N*-^{c}hexyl-5-phenyloxazolidinone.** An off-white solid (mp 97.3-98.0 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.06 (m, 1H, ^{c}hexyl *H*), 1.34 (m, 4H, ^{c}hexyl *H*), 1.62 (m, 1H, ^{c}hexyl *H*), 1.78 (m, 4H, ^{c}hexyl *H*), 3.36 (dd, 1H, N-C*H*$_2$), 3.71 (m, 1H, N-C*H*), 3.86 (t, 1H, N-C*H*$_2$, ^3J = 8.5 Hz), 5.43 (dd, 1H, O-C*H*, ^3J = 8.0 Hz), 7.32 (m, 5H, arom *H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 25.5 (^{c}hexyl *C*H$_2$), 25.5 (^{c}hexyl *C*H$_2$), 25.6 (^{c}hexyl *C*H$_2$), 30.3 (^{c}hexyl *C*H$_2$), 30.8 (^{c}hexyl *C*H$_2$), 48.5 (N-*C*H$_2$), 52.8 (N-*C*H), 74.8 (O-*C*H), 125.7 (*Cm*), 128.9 (*Co*), 129.1 (*Cp*), 139.3 (*Ci*), 157.5

(*C*=O). Anal.: Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71; Found: C, 73.41, H, 7.82, N, 5.68. HREIMS: Calcd. for $C_{15}H_{19}NO_2$: 245.1410; Found: 245.1409.

Figure 2.6. A) The ^{1}H NMR spectrum of *N*-^{c}hexyl-5-phenyloxazolidinone.



B) The NOESY spectrum of *N*-^{c}hexyl-5-phenyloxazolidinone.



***N*-^{n}propyl-hexahydrobenzooxazolidinone:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.76 (t, 3H, propyl CH_3, ^{3}J = 7.0 Hz), 1.17 (m, 1H, ^{c}hexyl), 1.33 (m, 3H, ^{c}hexyl), 1.37 (m, 2H, propyl CH_2), 1.63 (m, 1H, ^{c}hexyl), 1.72 (m, 3H, ^{c}hexyl), 2.80 (m, 1H, N-CH_2), 3.21 (m, 1H, N-CH_2), 3.53 (m, 1H, N-C*H*), 4.32 (m, 1H, O-C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.3 (propyl *C*H_3), 19.7 (propyl *C*H_2), 19.9 (^{c}hexyl), 21.1 (^{c}hexyl), 25.7 (^{c}hexyl), 27.0 (^{c}hexyl), 43.4 (N-*C*H_2), 54.2 (N-*C*H), 73.4 (O-*C*H), 159.0 (*C*=O). Anal.: Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64; Found: C, 65.36, H, 9.46, N, 7.60. HREIMS: Calcd. for $C_{10}H_{17}NO_2$: 183.1254; Found: 183.1249.

***N*-^{i}propyl-5-hexyloxazolidinone**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 (t, 3H, ^{n}hexyl CH_3, ^{3}J = 6.8 Hz), δ 1.06 (d, 6H, isopropyl CH_3, ^{3}J = 4.8 Hz), 1.18 (m, 8H, ^{n}hex $^{2\text{-}5}$CH_2) 1.51 (m, 1H, ^{n}hexyl ^{1}CH_2), 1.61 (m, 1H, ^{n}hexyl ^{1}CH_2) 2.98 (dd, 1H, N-CH_2, ^{3}J = 7.2 Hz), 3.45 (t, 1H, N-CH_2, ^{3}J = 8.4 Hz), 3.98 (m, 1H, N-C*H*), 4.37 (m, 1H, O-C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 14.3 (^{n}hexyl *C*H_3), 19.7 (^{i}propyl *C*H_3), 20.1 (^{i}propyl *C*H_3), 22.7 (^{n}hexyl *C*H_2), 24.7 (^{n}hexyl *C*H_2), 29.1 (^{n}hexyl *C*H_2), 31.8 (^{n}hexyl *C*H_2), 35.3 (^{n}hexyl *C*H_2), 44.7 (^{i}propyl *C*H), 45.1 (N-*C*H_2), 73.8 (O-*C*H), 157.5 (*C*=O). Anal.: Calcd for $C_{12}H_{23}NO_2$: C, 67.57; H, 10.87; N, 6.57; Found: C, 67.48, H, 10.96, N, 6.56. HREIMS: Calcd for $C_{12}H_{23}NO_2$: 213.1723; Found: 213.1726.

***N*-^{t}butyl-5-phenyloxazolidinone** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.41 (s, 9H, ^{t}Butyl CH_3), 3.46 (t, 1H, N-CH_2, ^{3}J = 8.5 Hz), 3.96 (t, 1H, N-CH_2, ^{3}J = 8.5 Hz), 5.38 (t, 1H, O-C*H*, ^{3}J = 8.0 Hz), 7.36 (m, 5H, arom-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 27.6 (^{t}Butyl *C*H_3), 51.3 (N-*C*H_2), 53.8 (^{t}Butyl *C*), 73.8 (O-*C*H), 125.8 (C_m), 128.9 (C_o), 129.1 (C_p), 139.2 (*Ci*), 157.0 (*C*=O).

Anal.: Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39; Found: C, 71.25, H, 7.91, N, 6.37.

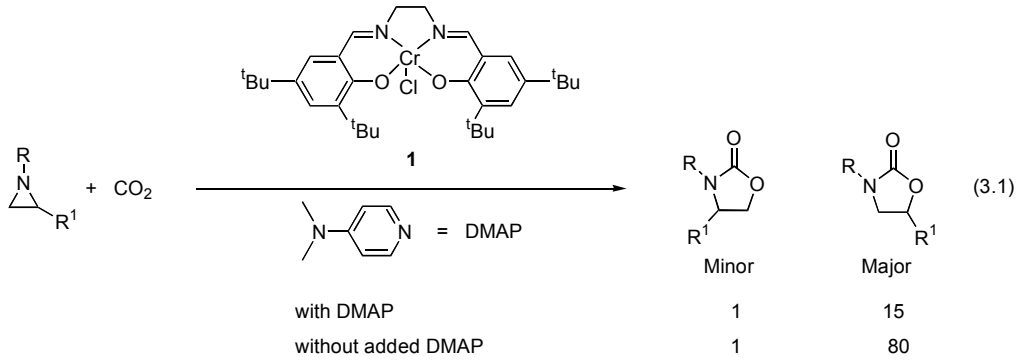
HREIMS: Calcd. for $C_{13}H_{17}NO_2$: 219.1254; Found: 219.1252.

Chapter 3

Experimental and DFT Study of the Mechanism for the [(Salen)Chromium^{III} + LB]-Catalyzed [Aziridine + CO_2] Coupling to Form 5-Substituted Oxazolidinones

3.1. Introduction

In Chapter Two we detailed the use of the [(salen)$Cr^{III}Cl$ + DMAP] catalyst system in the conversion of a range of aziridine substrates into 5-substituted oxazolidinones under mild conditions with selectivity up to 40:1 (eq 1).[1] Surprisingly, the (salen)$Cr^{III}Cl$ complex is also active for this reaction in the absence of DMAP with selectivity as high as 80:1 (reaction 3.1), in stark contrast to the analogous epoxide/CO_2 coupling where Lewis base additive does not greatly affect the isomer ratios.[2] Intrigued by this observation, and interested in the utility of the reaction shown in equation 3.1, we investigate the mechanism of the [(salen)$Cr^{III}Cl$ + DMAP]-catalyzed [aziridine + CO_2] coupling to selectively form 5-substituted oxazolidinones using both DFT calculations and experiments to better understand the parameters that govern its reactivity and selectivity.



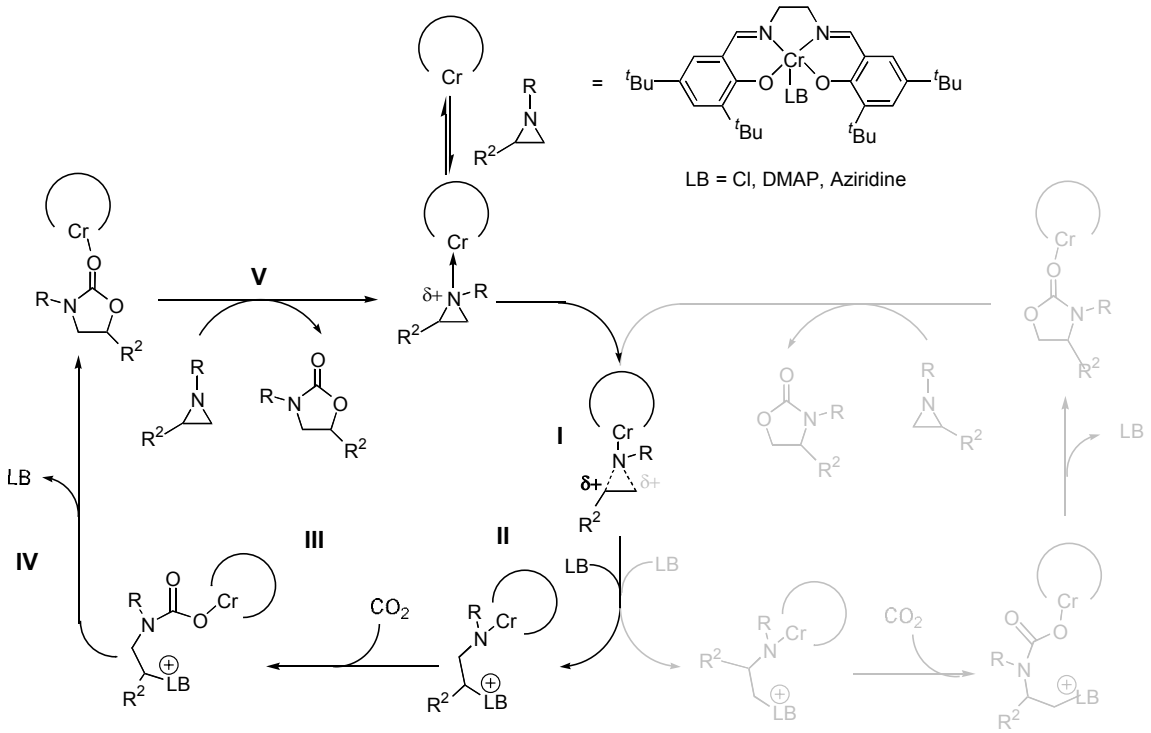
(3.1)

3.2. Proposed Mechanism

We proposed a mechanism for reaction 3.1 in Chapter Two in which the aziridine substrate first coordinates to the Lewis acidic chromium center of catalyst **1**.[1] This results in the polarization of the more substituted N—C^2 bond of the aziridine ring (Scheme 3.1, **I**), which is subsequently opened by a Lewis base (Scheme 3.1, **II**). CO_2 then inserts into the N-Cr bond (Scheme 3.1, **III**), a process that may be facilitated by the backside coordination of the extra

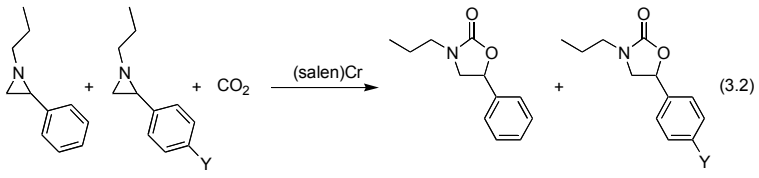
Lewis base.[3-7] Ring-closing occurs between one of the CO_2 oxygens and the β-carbon of the ring-opened aziridine, displacing the Lewis base (Scheme 3.1, **IV**). The newly formed oxazolidinone is then displaced by another aziridine molecule, and the cycle continues (Scheme 3.1, **V**). These mechanistic steps were proposed based on literature precedents and optimization data for reaction 3.1: First, the reaction rate decreases with increasingly bulky *N*-substitution on the aziridine substrate. Second, the reaction rate increases with more polar solvents (polar solvents stabilize N—C bond polarization). Third, the addition of a Lewis base cocatalyst increases the reaction rate. Finally, extremely high CO_2 pressure slows the reaction rate.

Scheme 3.1. Proposed mechanism for the (salen)Cr^{III}-catalyzed coupling of aziridine and CO_2 to form oxazolidinone. The bold-faced δ+ on the more substituted carbon in the right-hand resonance form in I denotes a larger positive charge development there in comparison to that on the methylene group (lighter δ+)



3.3. Hammett Plot.

Since the first step in Scheme 3.1 includes the activation of the aziridine ring and the possible formation of an ionic transition state, a Hammett-type investigation would shed light on the extent of charge development in this ring-opening process (Scheme 3.1, **I**). To this end, we examined the competitive reaction of several *p*-substituted *N*-^{n}propyl-2-arylaziridines with CO_2 against the parent *N*-^{n}propyl-2-phenylaziridine in the presence of the (salen)$Cr^{III}Cl$/DMAP catalyst. The ratio of oxazolidinone products from the two aziridines were then plotted against the Hammett σ_{+p} value[8] to give a line whose slope is $\rho = -1.28$ (0.99 correlation factor, Figure 3.1).[9] This negative ρ suggests the presence of cationic character in the aziridine ring-opening step and supports our hypothesis that the aziridine N—C^2 bond becomes polarized upon coordination to the Lewis acidic Cr center (*vide supra*).[10] Further, the linear correlation of the isomer ratio of the products as a function of σ_{+p} (Figure 3.2) offers evidence for the strong influence of substrate electronic effects on product selectivity (Scheme 3.1, right cycle vs. left).



(3.2)

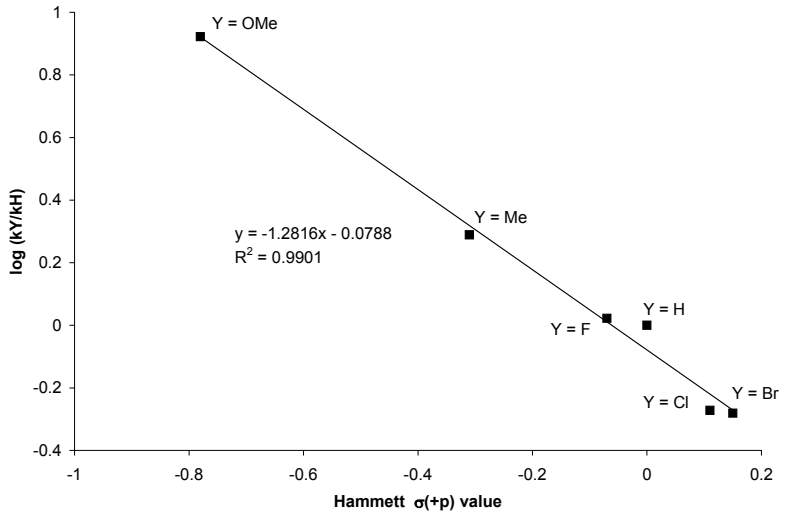


Figure 3.1. A Hammett competition experiment showing a decrease in reaction rate as more electron-withdrawing substituents are placed on the aziridine substrate. Reaction conditions: *N*-^{n}propyl-2-phenylaziridine (0.322g, 2 mmol) and *N*-^{n}propyl-2-(*para*-substituted)phenylaziridine (2 mmol), (salen)CrCl catalyst (12.6 mg, 0.02 mmol), 400 psig CO_2, CH_2Cl_2 (3.7 mL), rt, run to about 10% conversion.

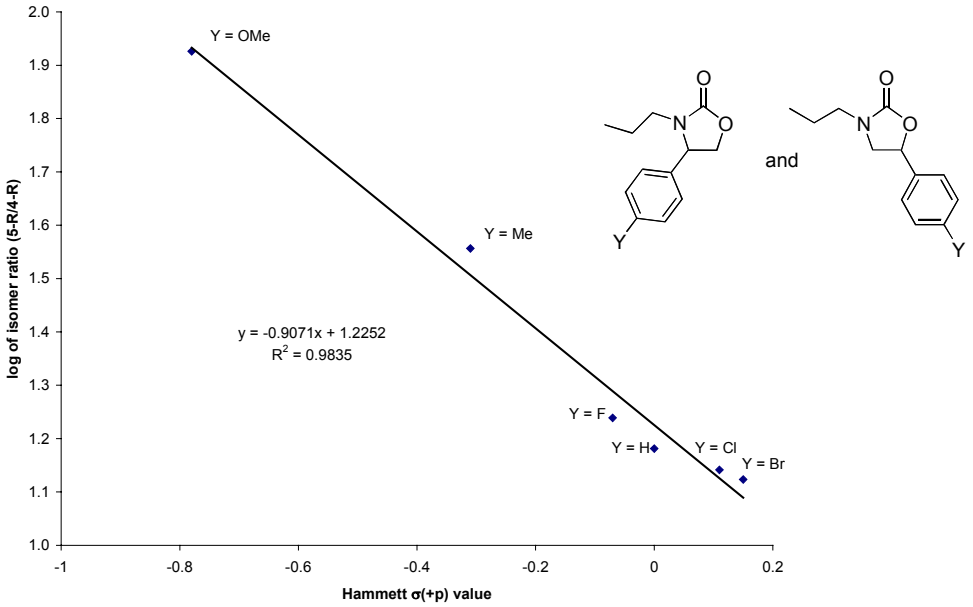


Figure 3.2. Plot of the decrease in reaction selectivity as more electron-withdrawing substituents are placed on the aziridine substrate, from 80:1 with the most electron-donating subsitutent (OMe) to 13:1 with the most electron-withdrawing substituent (Br). Reaction conditions: *N*-^{n}propyl-2-phenylaziridine (0.322g, 2 mmol), *N*-^{n}propyl-2-(*para*-substituted)phenylaziridine (2 mmol), (salen)CrCl catalyst (12.6 mg, 0.02 mmol), 400 psig CO_2, CH_2Cl_2 (3.7 mL), rt, run to about 15% conversion.

That aziridines possessing more electron-donating substituents react faster and give higher product selectivity than the parent *N*-^{n}propyl-2-phenylaziridine could be a consequence of a lengthening of the N—C^2 bond upon coordination to the Cr center, resulting in preferential ring-opening at this site (Scheme 3.1, **I**). The difference in N—C^2 bond lengthening between the *para*-substituted phenylaziridine and its parent should be observable via DFT computations. Indeed, a plot of calculated bond length vs Hammett σ_{+p} value for both coordinated and free aziridines (Figure 3.3) showed further agreement with the trend suggested by the experimentally derived plot shown in Figure 3.1. The notable lengthening of the N—C^2 bond compared to the N—C^3 one in the presence of the (salen)Cr Lewis acid as the electron density at C^2 increases clearly suggests a catalyst-induced increasing selectivity for the 5-substituted oxazolidinones.

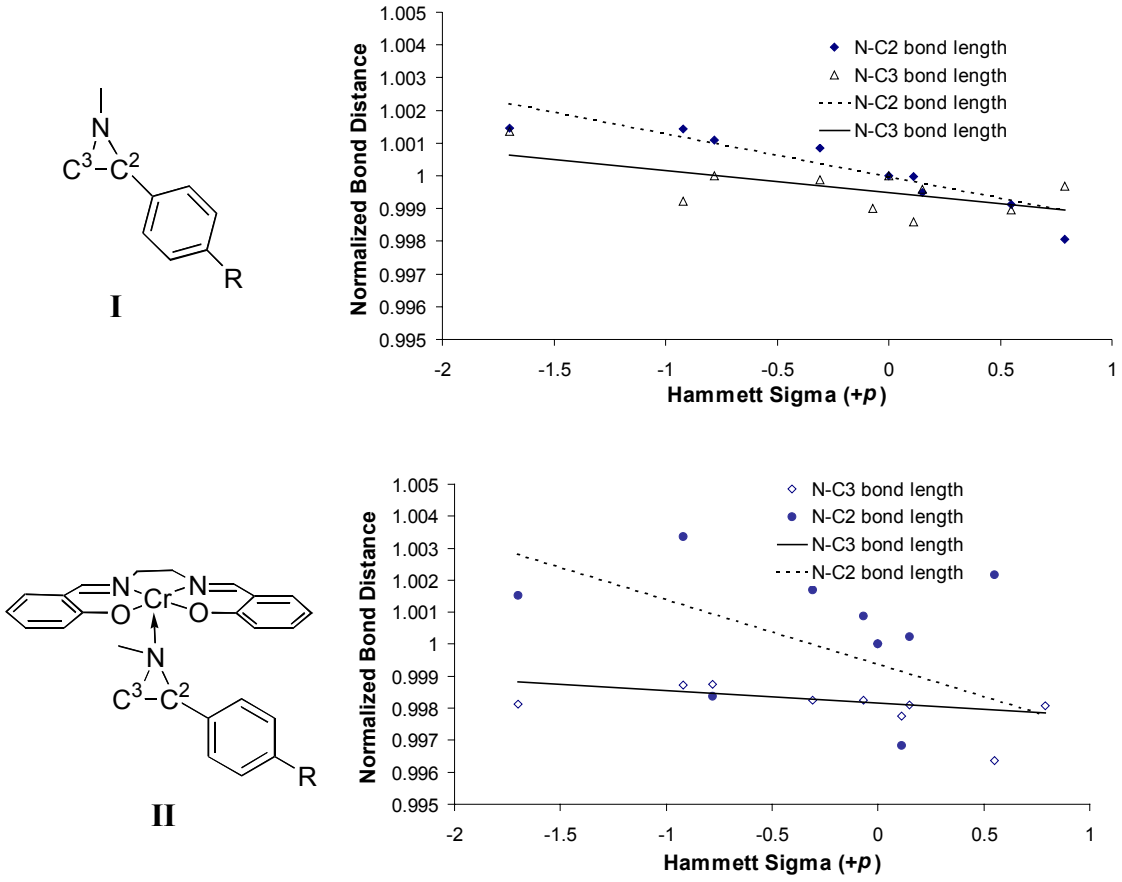


Figure 3.3. Geometry optimization of aziridine substrates (**I**) uncoordinated and (**II**) coordinated to a truncated (salen)Cr center. Conformational geometries were optimized using DFT as implemented by the Q-Chem software package, using EDF1/6-31+G(d) basis set.

3.4. Thermodynamic Stability and Transition State Calculations

Thermodynamic stability alone cannot explain the experimentally-observed selectivity for the 5-substituted product in the presence of the (salen)Cr catalyst. Computationally, 5-aryl oxazolidinone is roughly 3.1 kcal/mole more stable than the 4-aryl oxazolidinone, regardless of the nature of the *p*-substituents on the aryl ring,[11] which suggests that the selectivity of reaction

3.1 is not a product-based ground state effect (Figure 3.4.). Hence, the increased selectivity obtained with electron-donating substrates may be a product of a stabilized transition state rather than a thermodynamic difference.

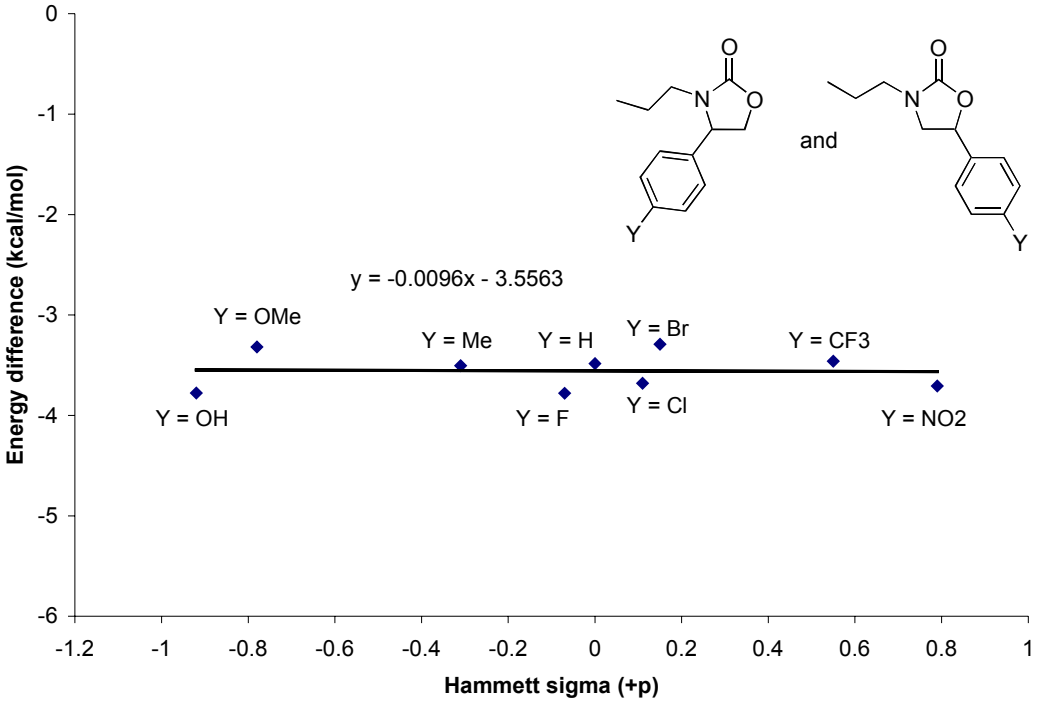


Figure 3.4. A comparison of the difference in energies of 5- and 4-substituted isomers in the ground-state energies of substituted uncoordinated aziridines reveals steady energy differences between 4- and 5-substituted oxazolidinones. Conformational geometries were optimized using DFT as implemented by the Q-chem software package, utilizing B3LYP exchange, 6-311+G(d) basis set.[12]

Because the determination of the overall reaction thermodynamics did not appear to have an impact on the regioselectivity of reaction 3.1, we surmised that the selectivity differences observed experimentally between various substrates arose as a result of the energy of the expected rate limiting transition state (TS). We explored the TS energy with DFT calculations using the truncated (salen)CrCl complex, and an abbreviated aziridine substrate (Figure 3.5).

The transition state calculations revealed a marginal energy difference of 1.6 kcal/mol between the transition state of the nucleophilic attack of the PMe_3 (other nucleophiles were used as well, though they failed to converge to a reasonable transition state) on the more-substituted side of a coordinated aziridine (giving the 5-substituted oxazolidinone) vs the less-substituted side of the aziridine (giving the 4-substituted oxazolidinone). While this calculated energy difference may be of the correct magnitude to support the observed selectivity, it is within the experimental error for the computational model and cannot be used alone.[12-14] However, because the two transition structures are so closely related, the 1.6 kcal/mol energy difference is relatively physically meaningful.

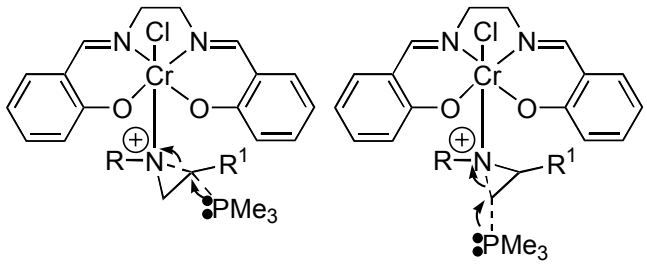
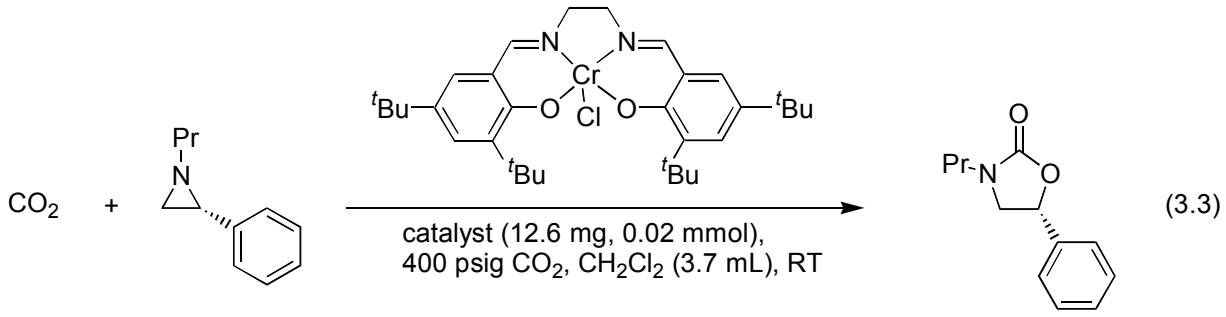


Figure 3.5. Comparison between the nucleophilic attack by PMe_3 at the more substituted (left) and less-substituted (right) sites on a Cr(salen)-coordinated aziridine.

3.5. Potential for Racemization of Chiral Aziridines?

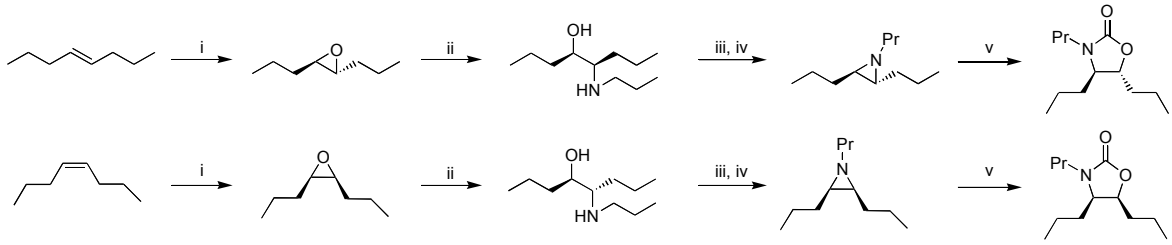
The mechanism shown in Scheme 3.1 suggests a potential carbocation intermediate at C^2 prior to (or during) attack by the Lewis base, which would lead to a potential scrambling of the stereochemistry of a coordinated chiral aziridine. This scrambling would be propagated through the reaction, readily apparent in the oxazolidinone products due to the double-inversion inherent in our proposed mechanism (Scheme 3.1, steps II and IV). However, stirring (*R*)-*N*-^{n}propyl 2-phenylaziridine with the achiral catalyst **1** under optimized reaction conditions led to no

observable racemization. Further, treatment of this mixture with CO_2 using our standard oxazolidinone synthesis conditions (eq 3.3), no racemization occurred for either the substrate or products, suggesting an insignificant contribution from the ionic resonance form. Additionally, the products of the coupling between CO_2 and pure samples of either *cis* or *trans* isomers of *N*-^{n}propyl 2,3-dipropylaziridine retain their respective diastereopurity as verified by ^{1}H NMR spectroscopy. Hence, while a polarization of the N—C^{2} bond may exist and is enhanced by electron-donating substituents as well as by activation by the Lewis-acidic chromium center (*vide supra*), a true, planar carbocation intermediate does not exist.



(3.3)

Scheme 3.2. Synthesis of precursors for the double-inversion experiment. Reaction conditions: i) *m*CPBA (1.2 equiv), $CHCl_3$, 18 h. ii) ^{n}propylamine (3.5 equiv), 100 °C, neat, 18 h. iii) Br_2, PPh_3, CH_3CN, 0 °C, 1 h. iv) triethylamine, rt. 1 h. v) (salen)CrCl catalyst (1 mol%), 400 psig CO_2, rt, 24h



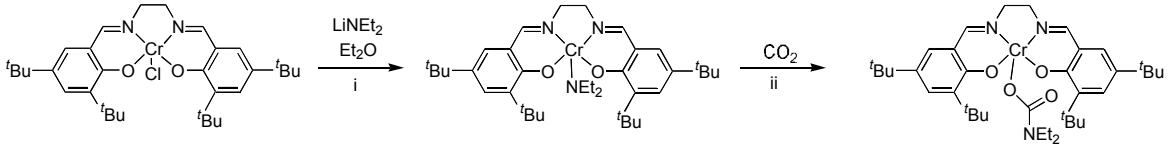
3.6. Experimental Observation of Carbon Dioxide Insertion into Cr—N Bond

Although the insertion of CO_2 into chromium-alkoxide bonds has been postulated and observed spectroscopically by several groups,[15,16] the analogous step for insertion into the

(salen)Cr-NR_2 bond (Scheme 3.3) has only been suggested once. Additionally, convincing experimental evidence for the existence of either this intermediate or the parent Cr-NR_2 complex has not been demonstrated. To this end, we synthesized the (salen)Cr-NEt_2 analogue of the chromium amide intermediate shown in Scheme 3.3, step ii and investigate the insertion of CO_2 into its Cr-N bond (Scheme 3.3).

Treatment of the parent (salen)Cr-Cl with $LiNEt_2$ in Et_2O yielded the hexanes-soluble (salen)Cr-NEt_2 product, which is characterized by IR (Figure 3.6). The imine stretch for (salen)Cr-NEt_2 is 1720 cm^{-1}, not significantly different from that of the parent (salen)Cr-Cl (1620 cm^{-1}). Its ESIMS spectrum shows a diminutive parent peak at 614.6 Da indicative of a $[(salen)Cr\text{-}NEt_2)H]^+$ moiety with matched isotopic pattern. Additionally, we were pleased to observe that Cr-NEt_2 is not as reactive as $LiNEt_2$. As a comparison, when $LiNEt_2$ was combined with dry CH_2Cl_2 at ambient temperature under an inert atmosphere, a vigorous release of gas was observed, and the color of the mixture changed from yellow to brown. However, dissolving Cr-NEt_2 resulted in no apparent reaction.

Scheme 3.3. Synthesis of (salen)Cr amide as a model intermediate analogue, and insertion of carbon dioxide into Cr-N bond. i) (salen)CrCl (203 mg, 0.35 mmol) and $LiNEt_2$ (27 mg 0.34 mmol) in diethyl ether (100 mL), 24 h, rt. ii) (salen)CrNEt_2 (102 mg, 0.20 mmol) in CH_2Cl_2 (4 mL) under CO_2 pressure (400 psig) heated to 100 °C for 30 min.



(Salen)Cr-NEt_2 can insert CO_2 to yield the corresponding chromium carbamate, observable by IR analysis (Figure 3.6). The IR spectrum of the product (salen)Cr($OC(O)NEt_2$) exhibited a new peak at 1720 cm^{-1}, corresponding well to the carbonyl stretching frequency in known linear organic carbamates.[17] The imine stretch (1620 cm^{-1}) is similar to that observed for (Salen)Cr-

NEt_2 (*vide supra*). As expected, (salen)Cr($OC(O)NEt_2$) readily decarboxylates under vacuum when left at ambient temperature, as shown by IR spectroscopy and mass-balance experiments. Table 3.1 lists the mass data for a sample of (salen)Cr-NEt_2 that has been subjected to a few carboxylation/decarboxylation cycles. The macroscopic weight of this sample increases upon carboxylation and readily decreases under low pressure conditions. After the third cycle, the observed decrease in the mass of the sample was accompanied by a change in the UV-visible spectrum of the product, indicating some decomposition of the resulting (salen)Cr complex.

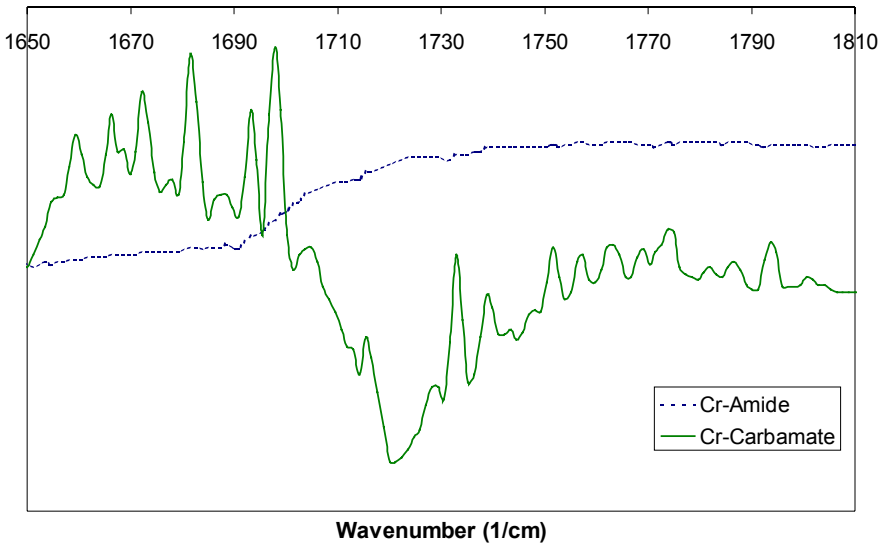


Figure 3.6. IR spectra of (salen)CrNEt_2 and (salen)Cr$OC(O)NEt_2$, showing a new peak at 1720 cm^{-1} after reaction with CO_2. This is the first observation of CO_2 insertion into a Cr-N bond.

Table 3.1. Typical weight data for the reversible incorporation of CO_2 into the (salen)Cr^{III} complex.

Cycle	Initial mass (mg)	Δ_m	Final mass (mg)	Yield (%)
1	113.9	8.0	121.9	95.8
1	121.9	-7.7	114.2	
2	114.2	7.5	121.7	93.4
2	121.7	-7.3	114.4	
3	114.4	6.3	120.7	81.5
3	120.7	-6.0	114.7	

Reaction conditions: (Salen)Cr^{III} complex was dissolved in CH_2Cl_2 (0.5 M solution), placed in a stainless steel reactor, and pressurized with CO_2 to 400 psig, and heated at 100 °C for 30 min. Reaction was then cooled, CH_2Cl_2 was evaporated, and the sample weighed to give the post-reaction "Initial mass". After vacuum line for 2h, the sample was reweighed, and the mass recorded as the "Final mass".

To further observe the mass loss during CO_2 release decomposition, thermogravimetric analysis (TGA) was performed on two samples of the (salen)Cr complexes. TGA of the (salen)$CrNEt_2$ (Figure 3.7, top curve) and (salen)$CrOC(O)NEt_2$ (Figure 3.7, bottom curve) show generally similar shapes overall, the major difference being a substantial initial mass lost during early heating. Between room temperature and about 90 °C, approximately 4% of the total mass is lost from the (salen)$CrOC(O)NEt_2$ sample. The 4% weight loss corresponds to ~50% of the expected weight loss if 100% of the (salen)$CrOC(O)NEt_2$ decomposed to 100% (salen)Cr(NEt_2). Practically speaking, between initially isolating the (salen)$CrOC(O)NEt_2$, removing the solvent, walking to the TGA instrument, preparing the sample and actually collecting the data required ~20 minutes, and thus it is not unexpected that fast decomposition may have decreased the mass prematurely.

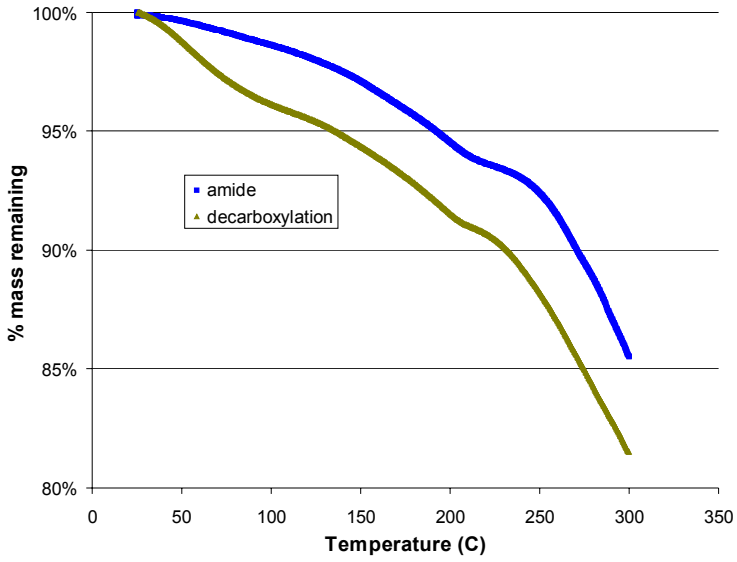


Figure 3.7. TGA experiment: (salen)Cr(NEt_2), (as synthesized, top trace) and (salen)CrOC(O)NEt_2 (immediately following isolation, bottom trace). TGA conditions: air, 20 °C min^{-1}.

3.7. Kinetic Experiments

The coordination as a Lewis basic ligand to the opposite site of the (salen)Cr center has been suggested to activate the CO_2 insertion step.[3-7] Variation of DMAP concentration over the experimentally applicable range for reaction 3.1 (from 0-2 equivalents with respect to catalyst, when competitive inhibition by DMAP is not significant[1]) reveals that the rate law is indeed second order with respect to DMAP (Figure 3.8), further supporting the dual role of DMAP as both the activator and the nucleophile.

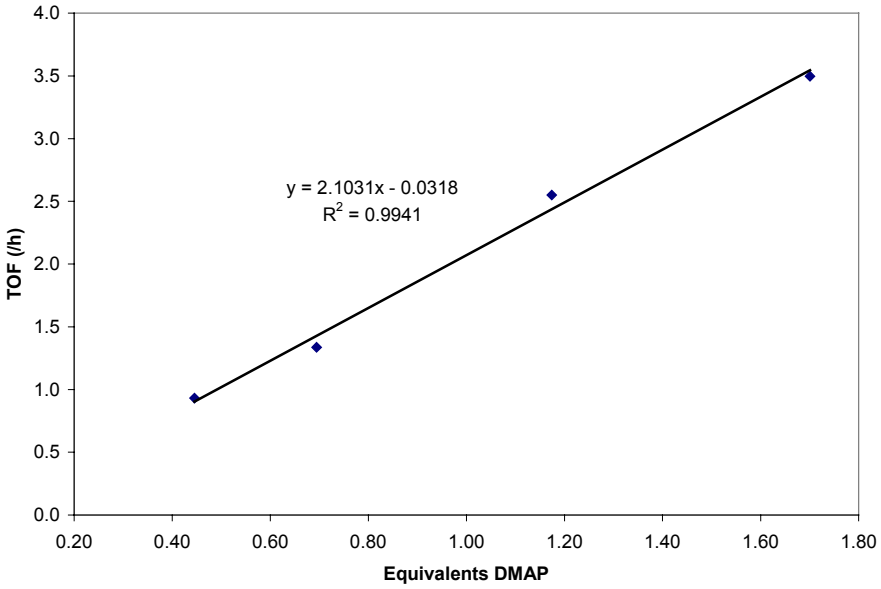


Figure 3.8. Kinetic plot of the reaction between *N*-^{n}propyl-2-phenylaziridine and CO_2 catalyzed by (salen)$Cr^{III}Cl$ in the presence of varying amounts of DMAP cocatalyst. Reaction conditions: *N*-^{n}propyl-2-phenylaziridine (0.322g, 2 mmol), (salen)CrCl catalyst (12.6 mg, 0.02 mmol), DMAP cocatalyst (varying amounts: 0.45 to 1.70 equiv with respect to catalyst) 400 psig CO_2, CH_2Cl_2 (3.7 mL), rt, 24 h.

To further verify the dual role of DMAP, we varied the concentration of aziridine in the presence of two equivalents of DMAP as cocatalyst. We were gratified to observe a first-order aziridine dependence in the presence of DMAP (Figure 3.9, left). However, in the absence of DMAP, reaction 3.1 exhibits third-order rate dependence on the concentration of aziridine (Figure 3.9, right). Assuming that the aziridine ring-opening is the rate-limiting step, this observation is consistent with a three-fold role of aziridine as proposed in our mechanism (Scheme 3.1, **II**) when there is no DMAP cocatalyst: aziridine coordinates to one face of the (salen)Cr catalyst, acts as substrate, and acts as the nucleophile to open the coordinated aziridine substrate. The moderate Lewis basicity of aziridine (pK_b = 6.14)[18] has been invoked to explain catalytic activity in the absence of DMAP (eq 3.1).[1] the kinetics of the (salen)Cr^{III}/DMAP

catalyzed coupling of *N*-tosyl-aziridines with CO_2 were also attempted in order to minimize the ability of the aziridine to act as its own LB, however the as substrates in kinetically monitored these reactions, however the *N*-tosyl-aziridines were not reactive under the reaction conditions.

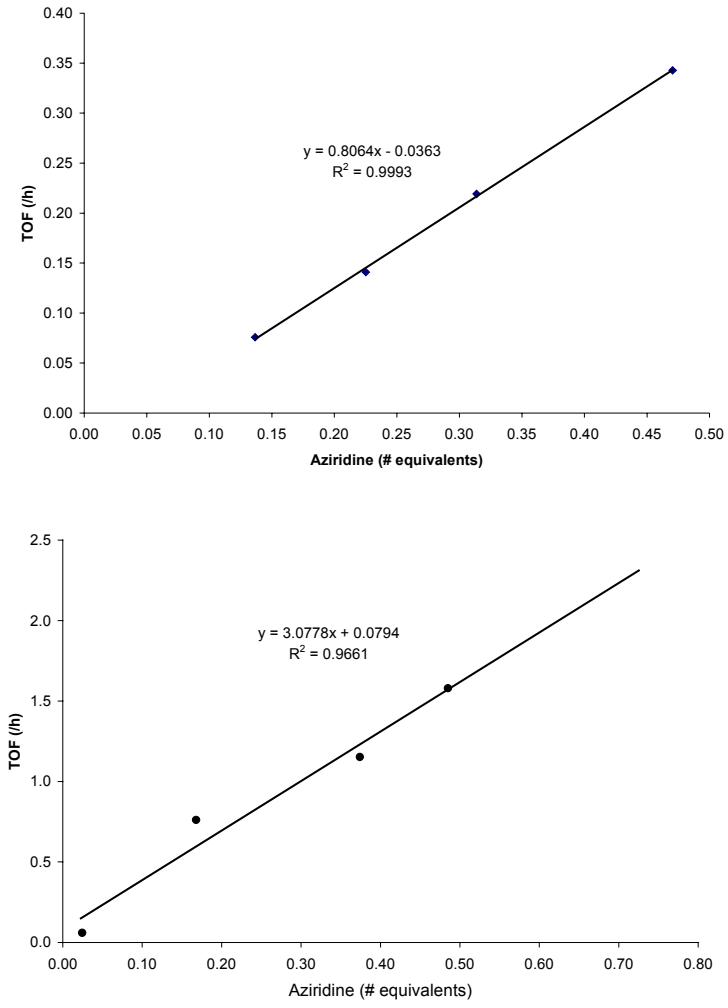


Figure 3.9. Kinetic plots of the reaction between *N*-^{n}propyl-2-phenylaziridine and CO_2 catalyzed by (salen)$Cr^{III}Cl$. General reaction conditions: *N*-^{n}propyl-2-phenylaziridine (varying amounts, between 0.088g and 0.228g; 0.55 mmol to 1.42 mmol), catalyst (5.8mg, 0.01 mmol from standard solution), 400 psig CO_2, CH_2Cl_2 (1.8 mL), rt, 24 h. *Top*: in the presence of 2 equiv of DMAP cocatalyst (2.45 mg, 0.02 mmol from standard solution). *Bottom*: in the absence of DMAP cocatalyst.

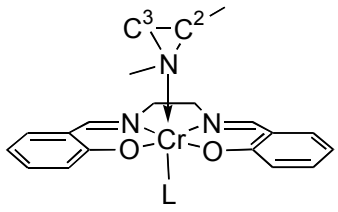
3.8. *Trans* Ligand Effects

The role that DMAP plays as the nucleophile in opening the coordinated aziridine substrate is quite subtle. That the experimental selectivity favors the ring-opening on the more substituted side of the aziridine ring suggests a mechanism that diverges from the analogous [epoxide + CO_2] coupling.[2,4,6] Rather than a simple nucleophilic ring-opening that is governed by sterics, the Lewis base-induced ring-opening resembles an electrophilic mechanism that favors the more substituted N—C^2 bond. As such, increasing the nucleophilicity of the Lewis base cocatalyst is expected to modulate the selectivity of reaction 3.1 (Table 3.2), with more Lewis basic cocatalyst being less selective. In addition, changing the coordinating ability of the solvent results in a subtle change in isomer ratio (Table 3.2). Coordinating solvents such as THF and DME are sigma donors that can compete with the DMAP Lewis base cocatalysts for binding to the Lewis acidic (salen)Cr center, negatively influencing the selectivity. In contrast, CH_3CN and aziridine gave rise to higher selectivity, potentially due to the higher concentration of these molecules in solution (MeCN was a solvent, and the aziridine substrate was present in 100-fold excess initially in the reaction solution).

Given the above observations, it is reasonable to suggest that a connection also exists between the nature of a ligand coordinated to one face of the (salen)Cr center and the bond lengths of the strained aziridine ring coordinated to the opposite face. For example, DMAP is expected to compete more effectively against the less Lewis basic (and more bulky) aziridine substrate in coordination to the (salen)Cr center, better facilitating the aziridine ring-opening. Competition between the DMAP cocatalyst and aziridine, which can act as LB itself in reaction, has been shown to result in a significant change in selectivity for reaction 3.1.[1]

Our *ab initio* computational calculations (*vide infra*) do indeed offer additional support for the hypothesis that coordination of the Lewis basic additives to the (salen)Cr center do make a significant difference in the bond length of coordinated aziridines, and thereby in the isomer ratio of oxazolidinone products. A geometry-optimized comparative evaluation of several *trans*-(L)(salen)Cr(aziridine) complexes (**2**) reveals that the aziridine N—C^2 bond length increases significantly over the N—C^3 bond length when a strongly coordinating Lewis base such as DMAP or imidazole is coordinated to the opposite site of the (salen) Cr center (Table 3.2). Less coordinating LBs, such as pyridine, PPh_3O, and the aziridine substrate tend to preferentially lengthen the N—C^2 bond over the N—C^3 bond by a factor between 2.8-5. This results in an increase in experimental selectivity from 16:1 (for *trans* ligand L = Cl^-) to 21:1 (for L = PPh_3O), 32:1 (for L = pyridine), and 40:1 (for L = aziridine) (Table 3.2). When the *trans* ligand is changed to acetonitrile or THF, however, the trend breaks down, and the calculated bond lengthening does not correspond well with the observed selectivity. This difference can probably be attributed to the experimental use of these "ligands" as solvents, as opposed to the other Lewis basic cocatalysts, which were used only at twice the concentration of catalyst.

Table 3.2. Comparison between calculated N—C^2 and N—C^3 bond-lengths and the experimentally observed selectivity differences in the (salen)CrCl-catalyzed [aziridine + CO_2] coupling reaction



2

L = DMAP, Cl^-, CH_3CN, aziridine, imidazole, PPh_3O, pyridine, THF

entry	*Trans* ligand (L)	Cr-N	N—C^2 [a]	N—C^3 [a]	Experimental Selectivity[b]
1	*Cl*	*2.345*	*1.523 (0)*	*1.483 (0)*	*16*[c,d]
	Appropriate Lewis base cocatalyst (2 equiv) was added[c]				
2	DMAP	2.373	1.530 (0.007)	1.483 (0)	24
3	Imidazole	2.272	1.537 (0.014)	1.484 (0.001)	20
4	Pyridine	2.285	1.536 (0.013)	1.491 (0.008)	32
	Coordinating substrate serves as the Lewis base, no other cocatalyst added				
5	Aziridine	2.311	1.536 (0.013)	1.489 (0.006)	40[c]
	Two equivalents of DMAP cocatalyst was added[c]				
6	MeCN				35[e]
7	DME				27
8	THF				9

Reaction conditions: *N*-^{n}propyl-2-phenylaziridine (0.322g, 2 mmol), (salen)CrCl catalyst (12.6 mg, 0.02 mmol), 400 psig CO_2, solvent (3.7 mL), rt, reaction was run to about 15% conversion. Conformational geometries were optimized for *N*-^{n}propyl-2-phenylaziridine using DFT as implemented by the Q-Chem software package, using EDF1/6-31+G(d). [a]parentheses denote deviation from L = Cl (entry 1). [b]Ratio of 5-substituted vs. 4-substituted aziridines. [c]CH_2Cl_2 used as solvent. [d]Additional NBu_4Cl (25 mol%) was added to the reaction. [e]Using MeCN as solvent also resulted in the formation of a substantial amount of aziridine dimer (1,4 piperazine) byproduct.

3.9. Conclusion

Analysis of the mode of action of the [(salen)CrCl + LB]-catalyzed [aziridine + CO_2] coupling has helped to clarify some important aspects of this coupling reaction. We have shown via a Hammett study that the electronic properties of the substrate have a substantial effect on both the reactivity and regioselectivity of the [aziridine + CO_2] coupling as displayed through cationic character in the transition state. This has been corroborated through the use of DFT ground-state calculations. Transition-state calculations have also suggested a rationale for the observed preference for the production of 5-substituted over 4-substituted oxazolidinones. Additionally, the reaction of chiral and *meso* aziridines has shown that the cationic character does not extend to a stabilized ring-opened aziridine cation, which would racemize during the course of a reaction, but maintains the ee during the course of the reaction. Kinetics have supported the previously understood role of the LB in the reaction and have intimated the importance of a ligand coordinated to the *trans*-face of the (salen)Cr catalyst to facilitate reaction. Finally the synthesis of a reactive intermediate analogue has shown that the CO_2 insertion step indeed takes place.

3.10. Experimental Section.

Computational Methods. Calculations were carried out using the Q-Chem software package (Q-Chem Inc., Shadyside, PA),[19] versions 2.1 and 3.0, running on a Linux PC cluster at Northwestern University or an OS-X G5 cluster at Binghamton University, respectively. Molecular geometries for ground-state species were optimized using the EDF1 hybrid functional[20] and 6-31+G(d) basis set. All structures were verified to be minima or transition states by vibrational analysis. As (salen)Cr^{III} can potentially be in both doublet and quartet spin

states,[33] we have carried out several calculations on both of these spin states. In all cases, the quartet configuration was observed to give the lowest ground state energy, and thus it was used in all of the ground-state calculations. Unscaled zero-point energies at EDF1/3-21G level of theory were used for subsequent energetic calculations.

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (499.570 MHz for ^{1}H, 125.631 MHz for ^{13}C) spectrometer. NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and integration. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. Assignment of NMR spectra are made using ACD Labs software version 4.02 (Advanced Chemistry Development, Inc., Toronto, Canada). IR spectra were collected on a Nicolet 5PC instrument and analyzed using Nicolet's PC-IR software. Elemental analyses were provided by Atlantic Microlab, Inc. (Norcross, GA). GC-MS experiments were carried out on an Agilent Technologies 6890N gas chromatograph-mass spectrometer equipped with a 30 m HP-5 capillary column (0.32-mm inner diameter and 0.25-mm film thickness) and Agilent's MSD ChemStation software version D.01.02 build 16. Temperature program: intitial time = 2 min., initial temperature = 60 $^{\circ}$C, rate = 20 $^{\circ}$C/min; final time = 12 min., final temperature = 250 $^{\circ}$C. GC analyses of oxazolidinone products were carried out on a Hewlett-Packard 5890A gas chromatograph equipped with an FID detector and a 30 m HP-5 capillary column (0.32-mm inner diameter and 0.25-mm film thickness). Temperature program: intitial time = 0 min., initial temperature = 60 $^{\circ}$C, rate = 20 $^{\circ}$C/min; final time = 2.5 min., final temperature = 250 $^{\circ}$C.

Materials. Catalyst **1**[2,26] and the aziridine precursors were synthesized according to published procedures.[27] Synthetic reagents (Aldrich Chemical), solvents for the catalytic reactions (Fischer

Chemical or Aldrich Chemical), and deuterated solvents (Cambridge Isotope Laboratories) were obtained from commercial sources and used as received. Diethyl ether for the IR study was dried over alumina and Q5 catalyst via the Dow-Grubbs solvent system[28] and installed by Glass Contours, Inc. (Laguna Beach, CA). Except for *N*-^{n}propyl-5-phenyloxazolidinone,[1] the remaining oxazolidinones have not been made and their analytical data have been fully reported herein.

Procedure for Obtaining Hammett Data. On the bench top, a 45-mL Parr high-pressure reactor equipped with a magnetic stir bar was charged with catalyst **1** (12.6 mg, 2 x 10^{-5} mol). A *para*-substituted *N*-^{n}propyl-2-phenylaziridine (2 mmol) was then taken up in a gas-tight syringe, followed by enough CH_2Cl_2 to fill the 1-mL volume in the syringe (approximately 0.7 mL), and added to the reactor. The syringe was subsequently rinsed with CH_2Cl_2 (1 mL), and the rinse was also added to the reactor to ensure incorporation of all of the substrate. This process was repeated with *N*-^{n}propyl-2-phenylaziridine (0.322g, 2 mmol) to give a final 4-mL solution of both aziridines in CH_2Cl_2 (0.5 M solution in each aziridine). Finally, undecane (100 μL, 0.474 mmol, internal standard) was placed in the reactor, which was subsequently sealed and placed under constant CO_2 pressure (400 psig) for 10 minutes to allow equilibration. The CO_2 valve was then closed, and the reactor was placed on a magnetic stirring plate. After a desired period, the reactor was carefully vented inside a fume hood and a small aliquot was then removed from the solution for GC analysis. The catalyst was removed from this aliquot by elution with CH_2Cl_2 (20 mL) through a wet-packed silica plug (15 mm x 5 mm), which was prepared with 5 vol% triethylamine in CH_2Cl_2. Reactivity ratio was determined via GC using peak areas and undecane internal standard.

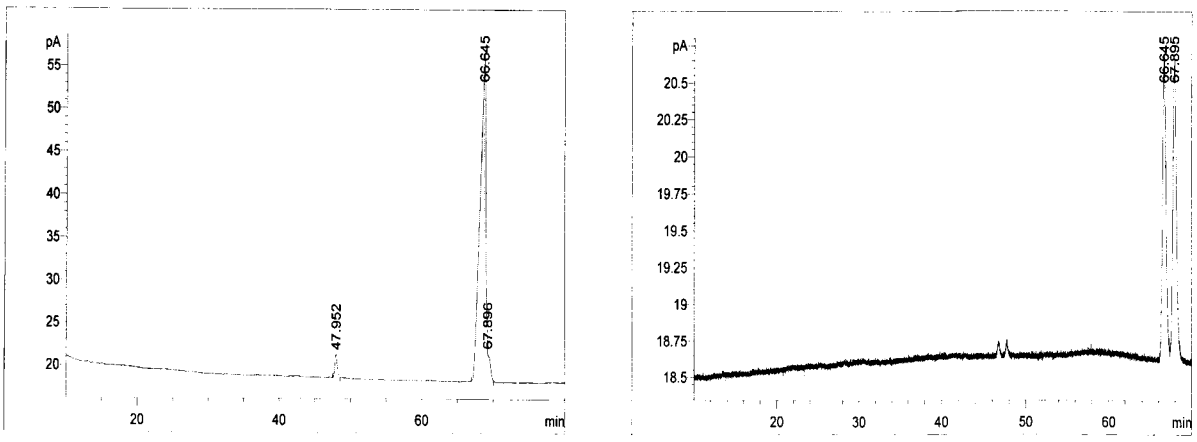


Figure 3.10. Chiral gas chromatography traces of the (*rac*-salen)CrCl-catalyzed coupling of (*R*)-*N*-^{n}propyl 2-phenylaziridine with CO_2 (left) showed single enantiomers of both the starting material, (*R*)-*N*-^{n}propyl 2-phenylaziridine (rt 47.95 min) and the product *N*-^{n}propyl-5-phenyloxazolidinone (rt 66.65 min). The coupling of *rac*-*N*-^{n}propyl 2-phenylaziridine with CO_2 under the same conditions gave a racemic mixture of the expected products (right).

***N*-^{n}propyl-5-(*p*-tolyl)oxazolidinone.** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.95 (t, 3H, propyl C*H*$_3$, ^{3}J = 7.0 Hz), 1.60 (m, 2H, propyl C*H*$_2$), 2.37 (s, 3H, methyl C*H*$_3$), 3.28 (m, 2H, propyl N-C*H*$_2$), 3.43 (t, 1H, N-C*H*$_2$, ^{3}J = 8.0 Hz), 3.90 (t, 1H, N-C*H*$_2$, ^{3}J = 8.5 Hz), 5.46 (t, 1H, O-C*H*, ^{3}J = 8.0 Hz), 7.24 (m, 5H, arom-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.3 (propyl *C*H$_3$), 20.9 (propyl *C*H$_2$), 21.4 (tosyl *C*H$_3$), 46.1 (propyl *C*H$_2$), 52.4 (N-*C*H$_2$), 74.6 (O-*C*H), 125.8 (*C*$_m$), 129.8 (*C*$_o$), 136.1 (C$_p$), 138.9 (C$_i$), 158.3 (*C*=O). FTIR (thin film): ν_{CO} 1753 cm^{-1}. Anal.: Calcd. for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39; Found: C, 71.24, H, 7.85, N, 6.38. GC-MS(EI): Calcd. for $C_{13}H_{17}NO_2$: 219.1, Found: 219.2.

***N*-^{n}propyl-5-(*p*-methoxyphenyl)oxazolidinone.** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.95 (t, 3H, propyl C*H*$_3$, ^{3}J = 7.0 Hz), 1.59 (m, 2H, propyl C*H*$_2$), 3.28 (m, 2H, propyl N-C*H*$_2$), 3.45 (t, 1H, N-

C*H*$_2$, ^3J = 8.0 Hz), 3.73 (s, 3H, OC*H*$_3$), 3.92 (t, 1H, N-C*H*$_2$, ^3J = 8.5 Hz), 5.44 (t, 1H, O-C*H*, ^3J = 8.0 Hz), 7.20 (m, 5H, arom-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 11.3 (propyl *C*H$_3$), 20.9 (propyl *C*H$_2$), 46.1 (propyl *C*H$_2$), 52.4 (N-*C*H$_2$), 55.1 (methoxy *C*H$_3$), 75.2 (O-*C*H), 112.7 (*C*$_m$), 127.4 (*C*$_o$), 131.1 (*C*$_i$), 156.4 (*C*=O), 158.7 (*C*$_p$). FTIR (thin film): ν_{CO} 1756 cm^{-1}. Anal.: Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95; Found: C, 66.43, H, 7.03, N, 5.78. GCMS(EI): Calcd. for $C_{13}H_{17}NO_3$: 235.3, Found: 235.2.

***N*-*n*propyl-5-(*p*-chlorophenyl)oxazolidinone.** ^1H NMR ($CDCl_3$, 500 MHz): δ 0.95 (t, 3H, propyl C*H*$_3$, ^3J = 7.0 Hz), 1.59 (m, 2H, propyl C*H*$_2$), 3.28 (m, 2H, propyl N-C*H*$_2$), 3.40 (t, 1H, N-C*H*$_2$, ^3J = 8.0 Hz), 3.93 (t, 1H, N-C*H*$_2$, ^3J = 8.5 Hz), 5.48 (t, 1H, O-C*H*, ^3J = 8.0 Hz), 7.35 (m, 5H, arom-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 11.3 (propyl *C*H$_3$), 20.9 (propyl *C*H$_2$), 46.1 (propyl *C*H$_2$), 52.3 (N-*C*H$_2$), 73.8 (O-*C*H), 127.1 (*C*$_m$), 129.4 (*C*$_o$), 134.9 (*C*$_p$), 137.7 (*C*$_i$), 158.0 (*C*=O). FTIR (thin film): ν_{CO} 1753 cm^{-1}. Anal.: Calcd. for $C_{12}H_{14}ClNO_2$: C, 60.13; H, 5.89; N, 5.84; Cl, 14.79; Found: C, 60.33; H, 5.88; N, 5.78; Cl, 14.84. GCMS(EI): Calcd. for $C_{12}H_{14}ClNO_2$: 239.1, Found: 239.2.

***N*-*n*propyl-5-(*p*-fluorophenyl)oxazolidinone.** ^1H NMR ($CDCl_3$, 500 MHz): δ 0.94 (t, 3H, propyl C*H*$_3$, ^3J = 7.0 Hz), 1.59 (m, 2H, propyl C*H*$_2$), 3.28 (m, 2H, propyl N-C*H*$_2$), 3.40 (t, 1H, N-C*H*$_2$, ^3J = 8.0 Hz), 3.90 (t, 1H, N-C*H*$_2$, ^3J = 8.5 Hz), 5.48 (t, 1H, O-C*H*, ^3J = 8.0 Hz), 7.20 (m, 5H, arom-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 11.3 (propyl *C*H$_3$), 20.9 (propyl *C*H$_2$), 46.0 (propyl *C*H$_2$), 52.4 (N-*C*H$_2$), 74.0 (O-*C*H), 116.1 (*C*$_m$, ^1J = 21.5 Hz), 127.7 (*C*$_o$), 134.9 (*C*$_p$), 158.0 (*C*=O), 163.0 (*C*$_i$, ^1J = 253.5 Hz),. FTIR (thin film): ν_{CO} 1751 cm^{-1}. Anal.: Calcd. for

$C_{12}H_{14}FNO_2$: C, 64.56; H, 6.32; N, 6.27; F, 8.51; Found: C, 64.57; H, 6.31; N, 6.27; F, 8.41. GCMS(EI): Calcd. for $C_{12}H_{14}FNO_2$: 223.1, Found: 223.2.

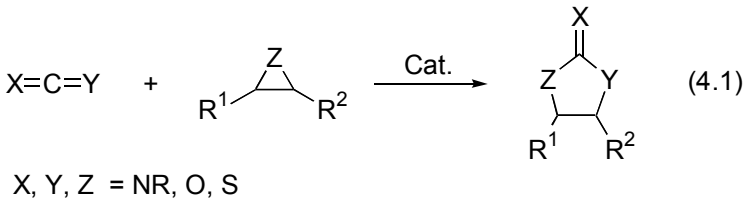
***N*-*n*propyl-5-(*p*-bromophenyl)oxazolidinone.** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.95 (t, 3H, propyl C*H*$_3$, ^3J = 7.0 Hz), 1.59 (m, 2H, propyl C*H*$_2$), 3.28 (m, 2H, propyl N-C*H*$_2$), 3.39 (t, 1H, N-C*H*$_2$, ^3J = 8.0 Hz), 3.93 (t, 1H, N-C*H*$_2$, ^3J = 8.5 Hz), 5.47 (t, 1H, O-C*H*, ^3J = 8.0 Hz), 7.41 (m, 4H, arom-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 127.4 (C_m), 132.3 (C_o), 138.2 (C_p), 138.2 (C_i), 158.0 (*C*=O). FTIR (thin film): ν_{CO} 1750 cm^{-1}. Anal.: Calcd. for $C_{12}H_{14}BrNO_2$: C, 50.72; H, 4.97; N, 4.93; Br, 28.12; Found: C, 50.75; H, 4.96; N, 4.94; Br, 28.13. GCMS(EI): Calcd. for $C_{12}H_{14}BrNO_2$: 283.0, Found: 283.1.

Chapter 4

Optimization of the (Salen)Chromium^{III}-Catalyzed Coupling of Isocyanates with Aziridines to form Imidazolidinones

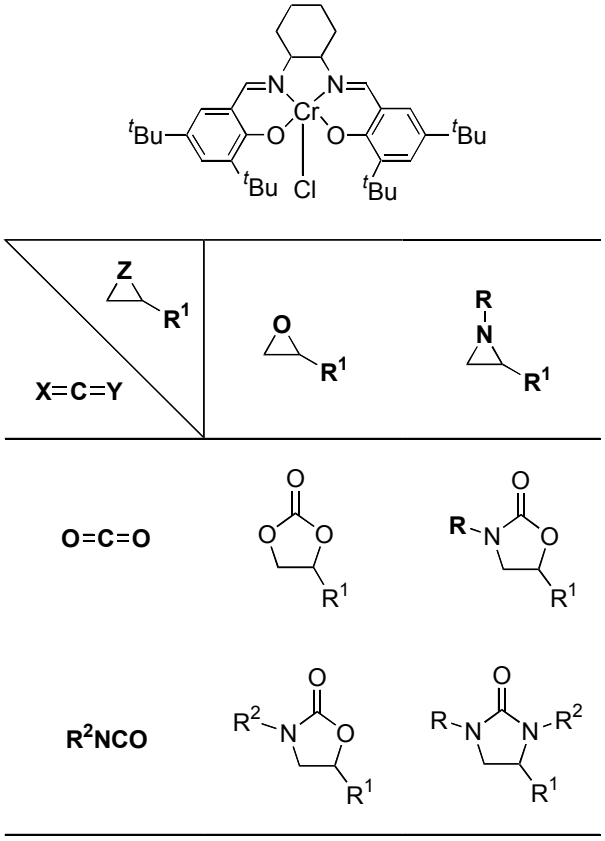
4.1. Introduction

The coupling of strained rings (such as epoxides, aziridines and episulfides) with heterocumulenes (such as carbon dioxide, carbon disulfide, isocyanates, or isothiocyanates) (eq 4.1) is an atom-economical route to a variety of highly substituted 1,3-heterocyclic systems. This synthetic route is made particularly attractive due to the variety of both strained rings and heterocumulenes available to the organic chemist as well as the broad utility of the coupling products, which have utility as synthons and chemical intermediates in organic synthesis[1-6] and have potency as pharmaceutical applications.[6-11]



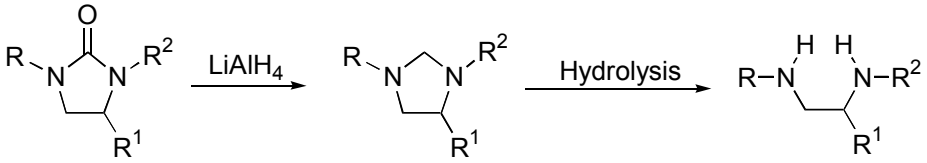
Previous research in the Nguyen laboratory[12-14] and elsewhere[15,16] has demonstrated that the coupling strategy depicted in eq 4.1 can be facilitated through the use of a (salen)Cr^{III} catalyst, often in concert with a LB cocatalyst. This catalyst system is highly efficient for [epoxide + CO_2],[14-16] [epoxide + isocyanate],[14] and [aziridine + CO_2][12] coupling reactions (leading to the formation of cyclic carbonates, oxazolidinones, and oxazolidinones, respectively (Scheme 4.1)). In this chapter, we have expand it to include [aziridine + isocyanate] coupling (eq 4.2). In principle, the [aziridine + isocyanate] coupling will allow ready access to the full spectrum of N- and O-containing 1,3-heterocycles (Scheme 4.1).

Scheme 4.1. The (salen)CrCl-catalyzed coupling of a variety of *N*- and *O*-containing 3-membered rings and heterocumulenes results in the formation of a range of heterocyclic products.

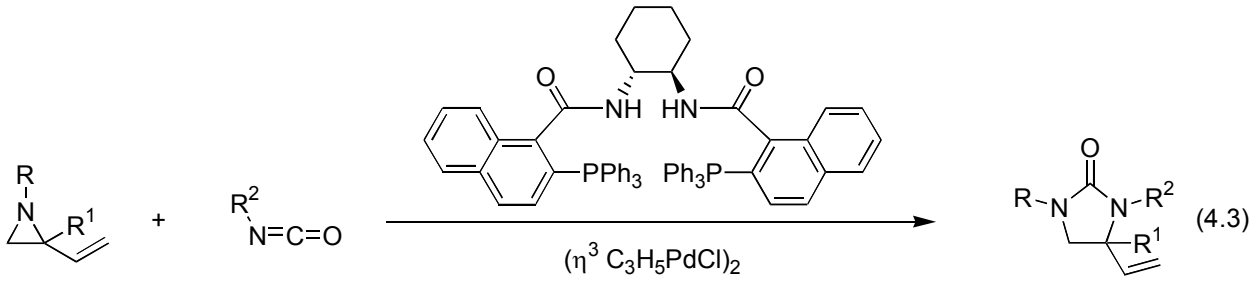


Imidazolidinones are useful in a range of synthetic applications, including chiral auxiliaries[1,3-5,17-20] and protecting groups.[21] When decarbonylated, imidazolidinones give access to vicinal 1,2-diamines (Scheme 4.2), which are present in a large number of fine chemicals and biologically active molecules,[8,9,22] as well as peptides,[23-25] antibiotics,[26] and anticancer agents.[7,27] For more details regarding the utility of 1,2 diamines, readers are referred to an excellent review by Lucet et al.[28] Further, imidazolidinones have been investigated in herbicidal,[29] antiviral,[11] and drug-delivery applications, the latter of which utilize the enzymatic decomposition of imidazolidinones to unmask the prodrug.[6,10,30,31]).

Scheme 4.2. The decarbonylation of imidazolidinone to give vicinal 1,2-diamines.[21]



A variety of catalysts have been developed to facilitate the [aziridine + isocyanate] coupling, including Pd,[21,32-34] Ni,[35] $MgBr_2$,[36] and TMSCl.[36] While some of these systems provide reasonably good yield and selectivity, none is without drawbacks. Pd-based catalytic systems require 2-10 mol% of a relatively expensive metal, and are limited to 2-vinylaziridines (eq 4.3). NiI_2, while less expensive, requires a high reaction temperature for activity. $MgBr_2$ and TMSCl are less expensive, but require air- and moisture-free conditions for catalyst stability.



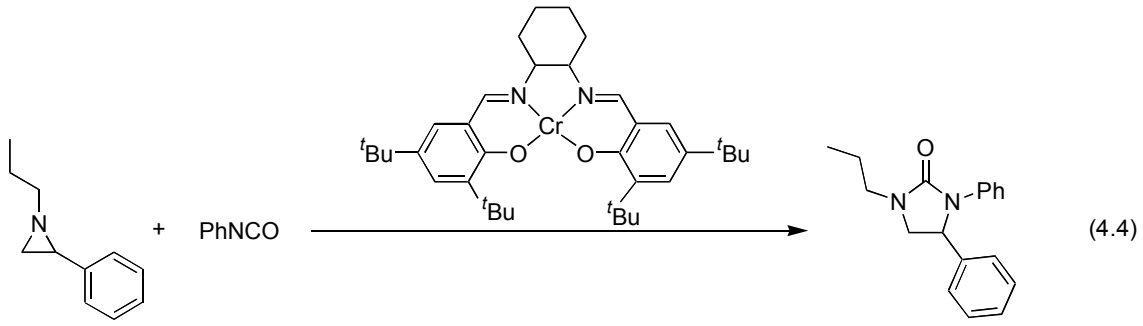
(4.3)

At this time there is no known selective, air- and moisture-stable catalyst for the [aziridine + isocyanate] coupling. Such a catalyst would be of great importance in the synthesis of these useful molecules. Herein we detail our investigation into the use of the (salen)CrCl catalyst in the formation of imidazolidinones via the [aziridine + isocyanate] coupling reaction.

4.2. Use of Lewis Base Cocatalyst

To determine the initial feasibility of our system, the coupling of *N*-propyl-2-phenylaziridine with phenyl isocyanate to give *N*-phenyl-*N'*-propyl-5-phenylimidazolidin-2-one was investigated

(eq 4.4). The reaction was catalyzed by 5 mol% (salen)CrCl in CH_2Cl_2 at ambient temperature. We initially chose *N*,*N*-dimethylaminopyridine (DMAP) as a cocatalyst, due to the rate increase we observed in the [(salen)CrCl + DMAP]-catalyzed [aziridine + CO_2] coupling reaction (for details see Chapters 2 and 3). We were pleased to observe that these initial conditions resulted in the formation of a substantial amount of the desired imidazolidinone product, albeit at a somewhat sluggish reaction rate (TOF = ~1/h).



(4.4)

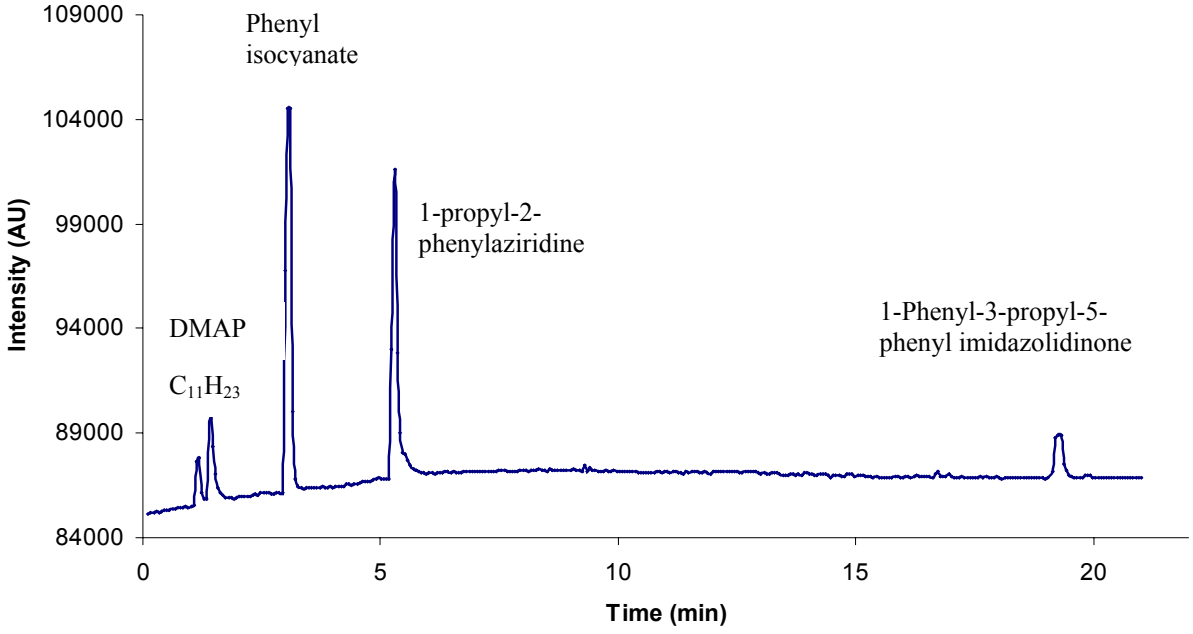


Figure 4.1. A representative gas chromatograph trace taken early in reaction 4.4 (approximately 10% conversion).

Previous literature reports[37,38] and research from our laboratory[14] have shown that low yields in reactions involving isocyanates could be due to the trimerization of the starting material (eq 4.5). A literature search revealed that the trimerization of isocyanates can be facilitated by tertiary amines. Thus, as we investigated the effects of various LB cocatalysts on the reaction rate, we were attentive to the formation of trimerization side-products.

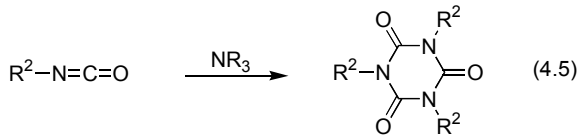
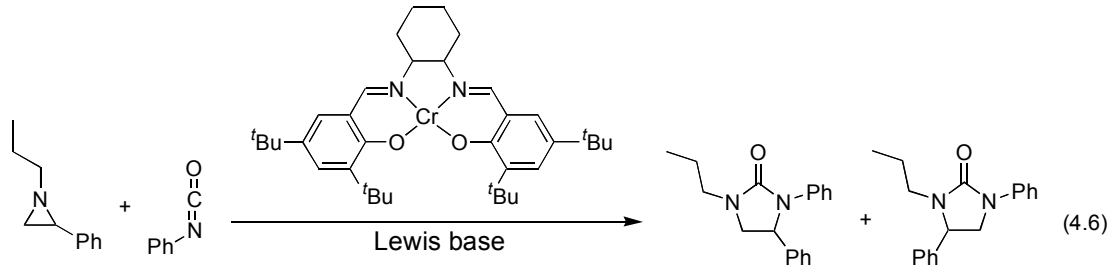


Table 4.1. Effects of various Lewis bases on the [(salen)CrCl + LB]-catalyzed coupling of *N*-propyl-2-phenylaziridine with phenyl isocyanate.



Entry	Lewis base	TOF[a] (h^{-1})	Selectivity major/minor
1	*N*,*N*-Dimethyl-4-aminopyridine (DMAP)	1	10.9
2	Triphenylphosphine	6	10.3
3	Triphenylphosphine oxide	6	10.3
4	Diisopropylethylamine (DIPEA)	5	11.1
5	Pyridine	5	10.6
6	*N*-Methylimidazole (NMI)	2	11.9
7	None	6	10.5

Reaction conditions: catalyst (3.1 mg, 0.02 mmol), cocatalyst (2 equiv), *N*-propyl-2-phenylaziridine (0.081 g, 0.5 mmol, 100 equiv), phenyl isocyanate (0.060 g, 0.5 mmol, 120 equiv), CH_2Cl_2 (0.9 mL), 60 °C, 5 h. [a]TOF determined using GC yields

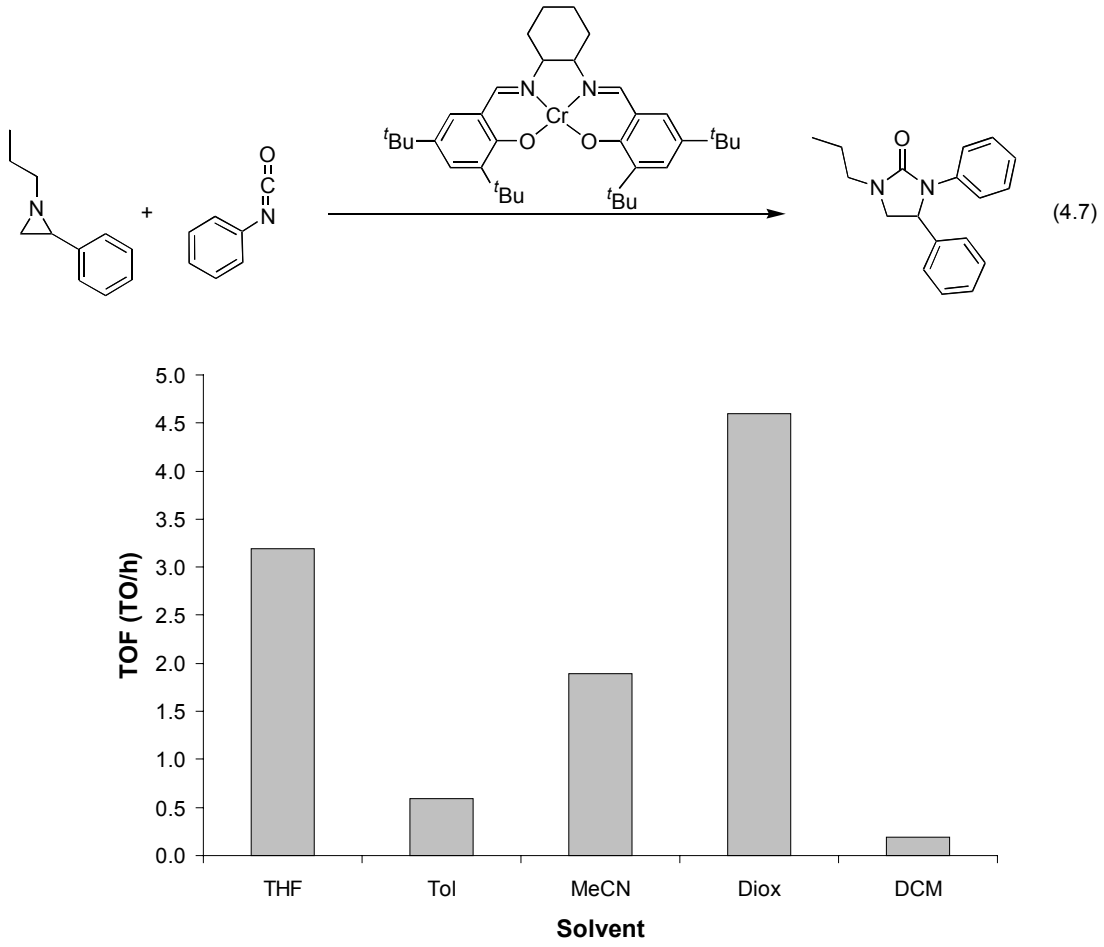
Our results indicate that the basicity and coordination strength of the Lewis-basic additives have a substantial inhibitory effect on the observed reaction rate. Strongly coordinating *N*-heterocyclic additive such as DMAP and NMI give the most marked TOF decrease of all LBs tested, reducing the reaction rate from 6 TO/h for the non-cocatalyzed reaction to 1 and 2 TO/h for DMAP and NMI, respectively (Table 4.1, cf. entries 1 and 6 to entry 7). More bulky or less nucleophilic cocatalysts such as DIPEA and pyridine, respectively, are less capable of coordinating to the (salen)Cr center, leading to a decrease in the rate, although is less severely than that listed above: from 6 TO/h to 5 TO/h (Table 4.1, cf. entries 4 and 5 to entry 7). Phosphine-containing additives were the least inhibitive to the reaction, reducing the reaction rate only marginally, (Table 4.1, cf. entries 2 and 3 to entry 7). These are most likely due to competitive coordination to the Lewis acidic Cr metal center between the LB additive and the aziridine substrate. The most highly coordinating LBs, those that are very basic and structurally unhindered slow the reaction down most, while those that are either bulkier or less basic (and thus less able to coordinate) do not result in as dramatic a rate decrease. As expected, the "softer" PPh_3 and $O{=}PPh_3$ do not coordinate well to the "hard" Cr center and show little effect on the TOF. That the addition of the LBs shown in Table 4.1 show no favorable cocatalytic activity (observable either by an increase in reaction rate, or an increase in selectivity) led us to exclude the use of LB additives in future reactions.

4.3. Solvent Effects

The solvent used in reaction 4.7 was varied to include toluene, 1,4-dioxane, CH_2Cl_2, THF, and acetonitrile. A comparison of solvent polarity revealed subtle trends in reaction rate. When reaction 4.7 was carried out in CH_2Cl_2, a moderately polar, weakly coordinating solvent, the

reaction rate was the slowest observed, yet it was comparable to that in toluene, a nonpolar, noncoordinating solvent. A comparison between reactions carried out in toluene and 1,4-dioxane, both nonpolar solvents showed a dramatic rate different with the reaction rate in toluene being slower than that in the coordinating solvent dioxane. Other coordinating, polar solvents such as THF and acetonitrile both showed intermediate reaction rates to those discussed above. For the [aziridine + isocyanate] system at hand, the solvent coordinating ability of the solvent seems to have more influence on the reaction rate than the solvent polarity. These solvent trends are somewhat different than those observed by Paddock in his [epoxide + isocyanate] system,[14] in which nonpolar solvents led to the greatest rate enhancement. These results led us to employ the solvent 1,4-dioxane in subsequent reactions.

Figure 4.2. Activity of (salen)CrCl catalyst as a function of solvent in the reaction of and *N*-propyl-2-phenylaziridine.

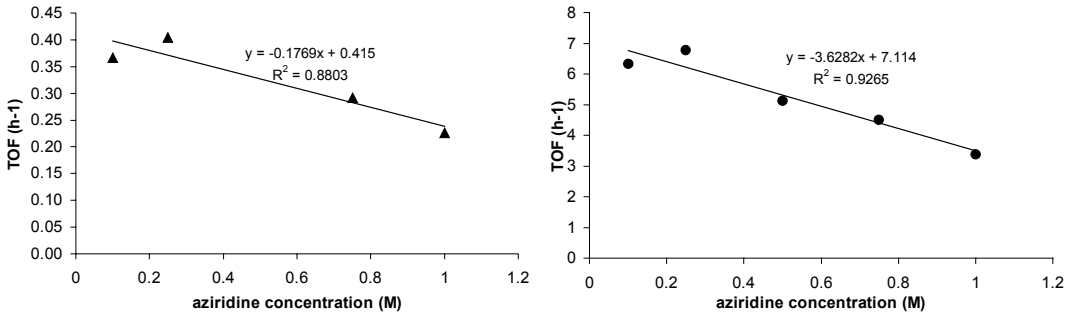


Reaction conditions: catalyst (3.1 mg, 0.02 mmol), *N*-propyl-2-phenylaziridine (0.081 g, 0.5 mmol, 100 equiv), phenyl isocyanate (0.060 g, 0.5 mmol, 120 equiv), solvent (0.9 mL), 25 ^{o}C, 18 h.

4.4. Aziridine Concentration

Not surprisingly considering the effect of LBs on the reaction rate, the effect of aziridine concentration has a marked effect of overall reaction rate. A series of reactions at different aziridine concentrations were performed to investigate this at both ambient temperature (Figure 4.3A) and 60 ^{o}C (Figure 4.3B).

Figure 4.3. Activity of (salen)CrCl catalyst as a function of aziridine concentration in the reaction between *N*-propyl-2-phenylaziridine and phenyl isocyanate: (A, left) carried out at ambient temperature and (B, right) at 60 ^{o}C.

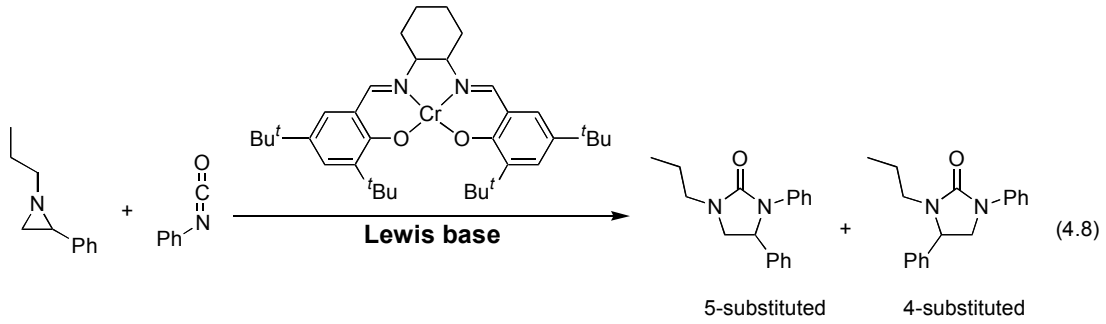


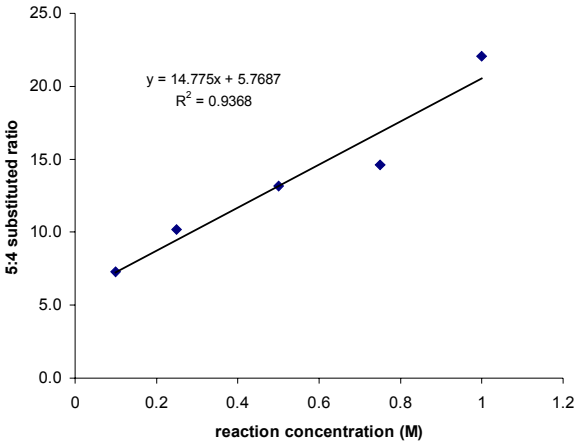
Reaction conditions: catalyst (3.1 mg, 0.02 mmol), *N*-propyl-2-phenylaziridine (0.081 g, 0.5 mmol, 100 equiv), phenyl isocyanate (0.060 g, 0.5 mmol, 120 equiv), 25 ^{o}C or 60 ^{o}C, 14 h for reaction at rt or 4 h for reaction at 60 ^{o}C.

The negative slopes of the plots shown in Figure 4.3 suggest an inhibitory effect by the aziridine substrate. Considering the Lewis-basic nature of the aziridine and rate decrease observed through the use of LB additives (*vide supra*), the most likely reason for the rate decrease upon increasing aziridine concentration is the competitive coordination of aziridine substrates with the Lewis-acidic Cr center, that inhibit subsequent coordination and reaction by the isocyanate substrate.

By plotting the selectivity for reaction 4.8 under varying aziridine concentration, a linear correlation between aziridine concentration and product selectivity (Figure 4.4) can be observed. At increased aziridine concentration, the selectivity of reactions was enhanced, although reaction rate was inhibited. These results may be interpreted as evidence for the aziridine acting as a cocatalyst in this reaction (See Chapter 2).

Figure 4.4. Selectivity in the (salen)Cr^{III}-catalyzed coupling of phenyl isocyanate and *N*-propyl-2-phenylaziridine.



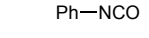
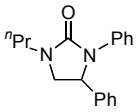
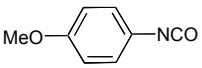
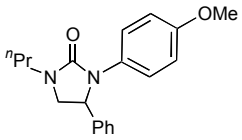
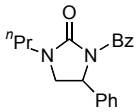
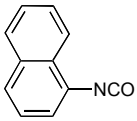
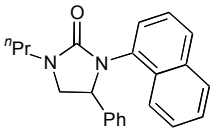
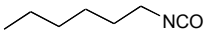


4.5. Substrate Scope

4.5.1. Isocyanate Substrate Scope

An exploration into the range of isocyanate substrates compatible with (salen)CrCl-catalyzed coupling with aziridines reveals interesting trends in scope (Table 4.2).

Table 4.2. Substrate scope of the (salen)CrCl catalyst in the reaction of *N*-^{n}propyl-2-phenylaziridine and isocyanates.

Entry	Aziridine	Isocyanate	Product	Yield (%)[a]
1				92
2				91
3				64
4				93
5			NA	0
6			NA	0

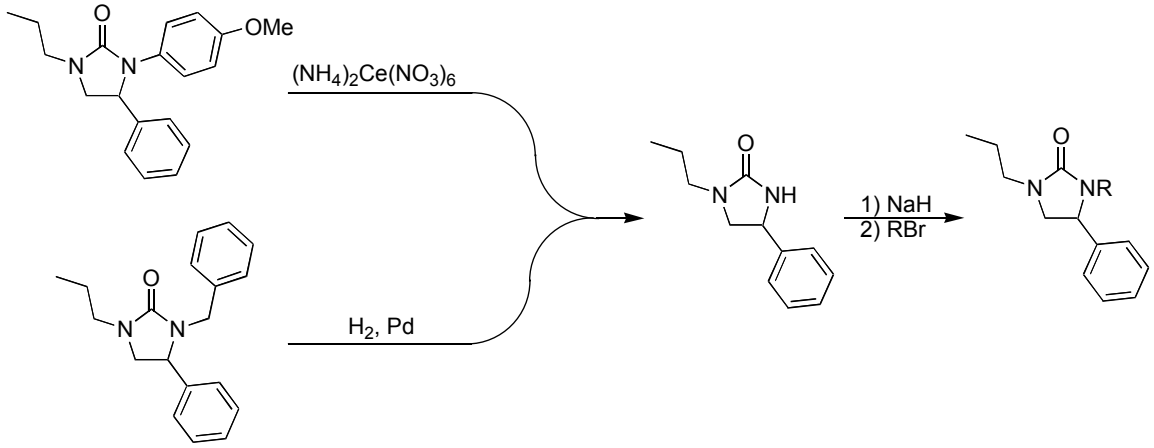
Reaction conditions: catalyst (3.1 mg, 0.02 mmol), *N*-propyl-2-phenylaziridine (2 mmol, 100 equiv) isocyanate (2.4 mmol, 120 equiv slight excess due to the anticipated loss via formation of isocyanate trimer), 1,4 dioxane (3.7 mL), 60 ^{o}C. In all cases, isomers can be readily separated by column chromatography (60:40 v:v hexanes:ethyl acetate eluent). [a]Isolated yields, both isomers.

Under our optimized conditions ((salen)CrCl catalyst (1 equiv), *N*-propyl-2-phenylaziridine (100 equiv), Phenyl isocyanate (120 equiv), 1,4-dioxane (0.25M in aziridine), 60 ^{o}C, 12 h), the (salen)CrCl catalyst was found to be effective for both aryl- and benzyl-substituted isocyanates, but not alkyl isocyanates (Table 4.2, entries 5 and 6). This limitation in substrate scope was similar to that observed by Paddock in the analogous [(salen)CrCl + PPh_3O]-catalyzed [epoxide

+ isocyanate] coupling reaction,[14] and is attributed to the higher reactivity of alkyl isocyanates, which quickly condense to form trimers in solution. Aromatic or benzyl substituents on the isocyanate, however, allowed for facile conversion to the imidazolidinone with no appreciable formation of side products.

Because alkyl isocyanates were unproductive under our employed conditions, we were interested in the use of isocyanates whose *N*-substitution could be replaced with an alkyl group after coupling as an alternative route to other alkyl-substituted imidazolidinones. To this end, we chose to incorporate benzyl isocyanate (which can be subsequently removed by reduction[39]) and *para*-methoxyphenyl isocyanate (which can be removed via oxidation with ceric ammonium nitrate[40,41]) with *N*-alkyl aziridines (Table 4.2, entries 2 and 3). Removal of either the benzyl or *p*-methoxyphenyl group (Scheme 4.3) followed by alkylation of the newly deprotected nitrogen would give access to a wide range of substituted imidazolidinones and expand the usefulness of our [aziridine + isocyanate] coupling methodology.

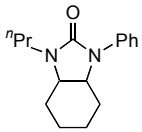
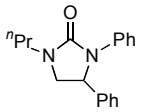
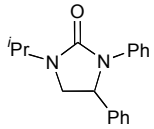
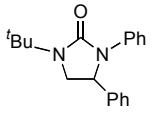
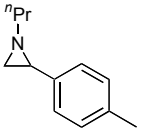
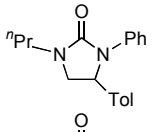
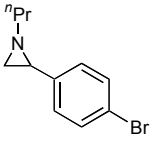
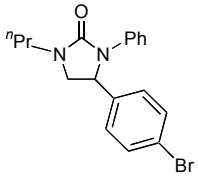
Scheme 4.3. Deprotection[39,40,41] and subsequent substitution reaction[41] of imidazolidinones.



4.5.2. Aziridine Substrate Scope

We further investigated the aziridine substrate scope in the (salen)CrCl-catalyzed [aziridine + isocyanate] coupling (Table 4.3) using our optimized conditions (*vide supra*). Starting material employed included both aromatic and aliphatic aziridines, as well as aziridines containing electron-donating and -withdrawing functionality. The effect of steric bulk around the aziridine nitrogen were also explored by implementing ^{n}Pr, ^{i}Pr, and ^{t}Bu substituents.

Table 4.3. Substrate scope of (salen)CrCl-catalyzed coupling of phenylisocyanate and aziridines.

entry	aziridine	isocyanate	product	yield (%)[a]
1		Ph—NCO		91
2		Ph—NCO		92
3		Ph—NCO		86
4		Ph—NCO		82
5		Ph—NCO		89
6		Ph—NCO		85
7		Ph—NCO	NA	0
8		Ph—NCO	NA	0
9		Ph—NCO	NA	0

Reaction conditions: catalyst (3.1 mg, 0.02 mmol), aziridine (2 mmol, 100 equiv), phenylisocyanate (2.4 mmol, 120 equiv), 1,4-dioxane (3.7 mL), 60 ^{o}C, isomers can be readily separated by column chromatography (hexanes: ethyl acetate 60:40 v:v eluent). [a]Isolated yield of a mixture of isomers.

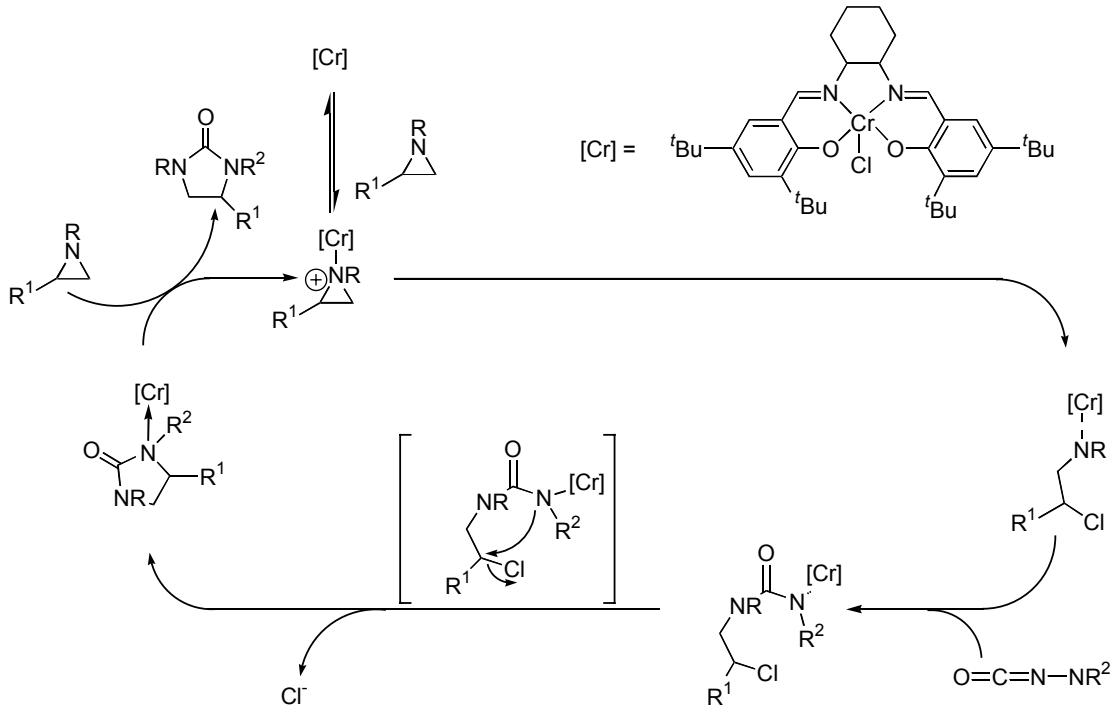
The *N*-substitutuent on the aziridine plays a dramatic role in its reactivity in the (salen)CrCl-catalyzed [aziridine + isocyanate] couplings. Both *N*-H aziridines and *N*-tosyl aziridines were unreactive under the conditions employed (Table 4.3 entries 7, 8, and 9). *N*-H aziridines are less

hindered, and are likely to coordinate too tightly to the Cr center and do not allow isocyanate insertion, preventing catalytic turnover (*vide infra*). On the other hand, the nitrogen of the *N*-tosyl aziridine is poorly coordinating and cannot undergo the initial catalytic activation (*vide infra*). To circumvent this problem and obtain *N*-tosyl-imidazolidinones, judicious choice of *N*-substitution can allow for deprotection and tosylation (or other *N*-protection) can be readily undertaken after formation of the imidazolidinone.[39,40,41]

4.6. Proposed Mechanism

In proposing a mechanism for the (salen)CrCl-catalyzed [aziridine + isocyanate] coupling we borrowed from the mechanism proposed by Paddock for the analogous [(salen)CrCl + PPh_3O]-catalyzed [epoxide + isocyanate] coupling reaction.[14] As mentioned above, both systems exhibit similar reactivity notwithstanding the subtle effect of LB additive (Paddock's system showed no activity in the absence of Lewis basic cocatalyst[14] and ours works best when the aziridine itself acts as cocatalyst at low concentrations). For the (salen)CrCl-catalyzed [aziridine + isocyanate] coupling, we postulate that activation of the aziridine is accomplished via coordination to the (salen)Cr catalyst. Ring-opening of the aziridine then occurs primarily via nucleophilic attack from the chloride anion at the more-substituted N—C bond, in agreement with the stability of the analogous carbocation. Subsequent insertion of the isocyanate into the Cr-N bond gives the (salen)Cr-coordinated urea, which then expels the chloride and closes the 5-membered ring, to form the imidazolidinone. The product imidazolidinone remains coordinated to the Cr until it is displaced by a new aziridine substrate.

Scheme 4.4. Proposed mechanism for the (salen)CrCl-catalyzed [aziridine + isocyanate] coupling reaction.



For analogous [(salen)metal + LB]-catalyzed [strained ring + heterocumulene] coupling reactions a LB additive is beneficial, or in some cases necessary, for activity. Such a LB may not be beneficial to our system due to the presence of a large aziridine substrate in solution, competing for access to the Lewis-acidic Cr center. As isocyanates are not strongly coordinating, it is likely that LB additives or excess substrate would compete for empty coordination sites on the catalyst.

4.7. Conclusion

We have successfully shown that the (salen)CrCl catalyst is highly active in the [aziridine + isocyanate] coupling when aromatic or benzyl isocyanates are used with either alkyl- or aryl-aziridines. The resulting 5-membered ring products, imidazolidinones, are potentially useful as intermediates in the synthesis of fine chemicals (for example, as masked 1,2-diamines), antiviral pharmaceuticals, and chiral auxiliaries, as well as in drug delivery applications. In contrast to

other [strained ring + heterocumulene] reactions, the addition of a LB additive improves neither the reaction rate, yield, or selectivity in [aziridine + isocyanate] couplings. Under our optimized reaction conditions (60 ºC, no cocatalyst, 1,4-dioxane as solvent, 0.25 M concentration in aziridine), this methodology is applicable to a variety of aromatic and benzyl-substituted isocyanates, as well as multiply-substituted alkyl and aryl aziridines.

4.8. Experimental

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (499.570 MHz for ^{1}H, 125.631 MHz for ^{13}C) spectrometer. NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and integration). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. IR spectra were collected on a Nicolet 5PC instrument and analyzed using PC-IR software. Elemental analyses were provided by Atlantic Microlab, Inc. (Norcross, GA). GC-MS analyses of imidazolidinone products were carried out on an Hewlett-Packard 5890A gas chromatograph equipped with an Hewlett-Packard 5973 mass selective detector and a 30-m HP-5 capillary column (0.32-mm inner diameter and 0.25-mm film thickness). Temp program: intitial time = 0 min, initial temperature = 60 $^{\circ}C$, rate = 20 $^{\circ}C$/min; final time = 2.5 min, final temperature = 250 $^{\circ}C$.

Materials. Catalyst was synthesized according to published procedures.[13,42] Solvents used were purchased from either Fischer Chemical or Aldrich Chemical. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and used without further purification. All other reagents were purchased from the Aldrich Chemical Company and used without further purification, unless

otherwise noted. Aziridines and β-amino alcohol precursors were synthesized using published procedures.[43]

General Experimental Procedure. On the bench top, an oven-dried 4-mL vial equipped with a magnetic stir bar was charged with catalyst **1** (3.1 mg, 2 x 10^{-5} mol), isocyanate (0.6 mmol), and a solution of the aziridine (0.5 mmol) in 1,4 dioxane (2 mL, 0.25 M solution). Finally, undecane (50 µl, 0.237 mmol, internal standard) was placed in the vial, which was then sealed and placed in a magnetically stirred 60 °C oil bath. After 12 h the reactor was removed from the oil bath, and a small aliquot was removed from the solution for GC-MS analysis. (The catalyst was removed by eluting the aliquot with CH_2Cl_2 (20 mL) through a solvent-wet silica plug (5 mm x 20 mm) which was pre-doped with triethylamine (100 µL). Percent yield was determined via GC using peak areas in comparison to the undecane internal standard.) Further purification by column chromatography over triethylamine-doped silica, (150 mesh, 58Å, hexanes:ethyl acetate 60:40) gave analytically pure imidazolidinone product. Analytical data for the following compounds has not been reported elsewhere:

1-*N*-benzyl-3-*N*-^{n}propyl-5-phenylimidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.03 (t, 3H, propyl CH_3, ^3J = 7.5 Hz), 1.67 (m, 2H, propyl CH_2), 3.49 (m, 3H, propyl CH_2 and one of C$^4H_2$), 3.86 (t, 1H, one of C$^4H_2$ ^3J = 8.0 Hz), 4.50 (m, 2H, benzyl CH_2), 5.50 (t, 1H, C^5H, ^3J = 7.0 Hz), 7.00 (t, 2H, *N*-benzyl-H_m), 7.15 (m, 2H, *N*-benzyl-H_o), 7.29 (m, 2H, C-phenyl-*H*), 7.44 (m, 4H, aromatic-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.9 (propyl *C*H_3), 20.7 (propyl *C*H_2), 46.1 (benzyl-*C*), 47.2 (*C*$^4H_2$), 53.2 (propyl *C*H_2), 77.5 (*C*^{5}H), 122.0 (*N*-benzyl-C_m), 124.1 (*N*-benzyl-C_o), 126.4 (C-phenyl-C_m), 129.2 (C-phenyl-C_p), 129.3 (C-phenyl-C_o), 129.7 (*N*-benzyl-C_i), 138.0 (C-phenyl-C_i), 148.8 (*N*-benzyl-C_p), 153.5 (*C*=O). FTIR (CH_2Cl_2): ν_{CO} 1701

cm^{-1}. Anal.: Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52; Found: C, 77.90, H, 7.77, N, 9.46. EIMS: Calcd for $C_{19}H_{22}N_2O$: 294.2, Found: 294.1.

1-*N*-napthyl-3-*N*-*n*propyl-5-phenylimidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.09 (t, 3H, propyl C*H*$_3$, ^3J = 7.5 Hz), 1.80 (m, 2H, propyl C*H*$_2$), 3.54 (m, 1H, one of C^4*H*$_2$), 3.69 (m, 2H, C*H*$_2$), 4.00 (t, 1H, one of C^4*H*$_2$), 5.53 (t, 1H, C^5*H*, ^3J = 7.0 Hz), 7.31 (m, 4H, *N*-napthyl-*H*$_m$), 7.45 (m, 3H, *N*- napthyl-*H*), 7.80 (m, 2H, *N*-aromatic-*H*), 8.25 (m, 2H, *N*-aromatic-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.7 (propyl *C*H$_3$), 20.9 (propyl *C*H$_2$), 47.2 (*C*^{4}H$_2$), 53.7 (propyl *C*H$_2$), 77.3 (*C*^{5}H), 118.0 (aromatic-*C*), 122.0 (aromatic-*C*), 124.9 (aromatic-*C*), 125.7 (aromatic-*C*), 126.0 (aromatic-*C*), 126.3 (aromatic-*C*), 127.9 (aromatic-*C*), 128.9 (aromatic-*C*), 129.0 (aromatic-*C*), 129.4 (aromatic-*C*), 130.0 (aromatic-*C*), 134.6 (*N*-napthyl-*C*$_i$), 139.2 (C-phenyl-*C*$_i$), 144.6 (*N*-phenyl-*C*$_p$), 153.0 (*C*=O). FTIR (CH_2Cl_2): ν_{CO} 1701 cm^{-1}. Anal.: Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.84; Found: C, 80.21, H, 6.85, N, 8.76. EIMS: Calcd for $C_{22}H_{22}N_2O$: 330.2, Found: 330.2.

1-*N*-phenyl-3-*N*-*n*propyl-4,5-cyclohexyl-imidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.00 (t, 3H, propyl C*H*$_3$, ^3J = 7.5 Hz), 1.64 (m, 2H, propyl C*H*$_2$,), 1.20-1.95 (m, 8H, cyclohexyl C*H*$_2$), 3.08 (m, 1H, C^5*H*$_2$), 3.65 (m, 1H, C^4*H*$_2$), 4.50 (t, 1H, C^5*H*, ^3J = 5.0 Hz), 6.98 (m, 1H, *N*-phenyl-*H*), 7.10 (m, 2H, *N*-phenyl-*H*), 7.27 (m, 2H, C-phenyl-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.7 (propyl *C*H$_3$), 20.6 (cyclohexyl *C*H$_2$), 20.9 (propyl *C*H$_2$), 25.7 (cyclohexyl *C*H$_2$), 27.4 (cyclohexyl *C*H$_2$), 44.3 (propyl *N*-*C*H$_2$), 54.8 (cyclohexyl *C*H$_2$), 66.1 (*C*^{5}H$_2$), 75.6 (*C*^{4}H), 122.0 (*N*-phenyl-*C*$_p$), 123.9 (*N*-phenyl-*C*$_o$), 128.7 (*N*-phenyl-*C*$_m$), 148.3 (*N*-phenyl-*C*$_i$), 154.2

(*C*=O). FTIR (CH_2Cl_2): ν_{CO} 1701 cm^{-1}. Anal.: Calcd for $C_{16}H_{22}N_2O$: C, 74.38; H, 8.58; N, 10.84; Found: C, 74.85, H, 8.83, N, 10.70. EIMS: Calcd for $C_{16}H_{22}N_2O$: 258.2, Found: 258.2.

1-*N*-phenyl-3-*N*-^{n}propyl-5-phenylimidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.01 (t, 3H, propyl CH_3, ^3J = 7.5 Hz), 1.70 (m, 2H, propyl CH_2, ^3J = 7.0 Hz), 3.43 (m, 3H, propyl CH_2 and one of C^4H_2), 3.90 (t, 1H, one of C^4H_2 ^3J = 8.0 Hz), 5.50 (t, 1H, C^5H, ^3J = 7.0 Hz), 6.95 (t, 2H, *N*-phenyl-H_m), 7.15 (m, 2H, *N*-phenyl-H_o), 7.24 (m, 2H, C-phenyl-*H*), 7.40 (m, 4H, C-phenyl-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.6 (propyl CH_3), 20.9 (propyl CH_2), 47.1 (C^4H_2), 53.6 (propyl CH_2), 77.1 (C^5H), 122.2 (*N*-phenyl-C_m), 123.9 (*N*-phenyl-C_o), 126.1 (C-phenyl-C_m), 128.7 (C-phenyl-C_p), 129.0 (C-phenyl-C_o), 129.1 (*N*-phenyl-C_i), 139.2 (C-phenyl-C_i), 148.0 (*N*-phenyl-C_p), 153.1 (*C*=O). FTIR (CH_2Cl_2): ν_{CO} 1701 cm^{-1}. Anal.: Calcd for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99; Found: C, 77.46, H, 7.53, N, 9.51. EIMS: Calcd for $C_{18}H_{20}N_2O$: 280.2, Found: 280.2.

1-*N*-phenyl-3-*N*-^{n}propyl-5-(*p*-tolyl)imidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.01 (t, 3H, propyl CH_3, ^3J = 7.0 Hz), 1.67 (m, 2H, propyl CH_2, ^3J = 7.0 Hz), 2.38 (s, 3H, tolyl CH_3), 3.44 (m, 2H, propyl *N*-CH_2), 3.49 (m, 1H, C^4H_2), 3.89 (t, 1H, C^4H_2 ^3J = 8.5 Hz), 5.48 (t, 1H, C^5H, ^3J = 7.0 Hz), 6.96 (t, 1H, phenyl-*H*) 7.22 (m, 8H, aromatic-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.8 (propyl CH_3), 20.9 (propyl CH_2), 21.5 (tolyl CH_3), 47.2 (C^4H_2), 53.5 (propyl CH_2), 77.5 (C^5H), 122.1 (phenyl-C_p), 124.0 (phenyl-C_m), 126.2 (tolyl-C_o), 128.8 (phenyl-C_o), 129.8 (tolyl-C_m), 136.3 (phenyl-C_i), 138.9 (tolyl-C_i), 148.3 (tolyl-C_p), 153.3 (*C*=O). FTIR

(CH_2Cl_2): ν_{CO} 1702 cm^{-1}. Anal.: Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52; Found: C, 77.56, H, 7.48, N, 9.38. EIMS: Calcd for $C_{19}H_{22}N_2O$: 294.2, Found: 294.2.

1-*N*-(*p*-methoxy)phenyl-3-*N*-^{n}propyl-5-phenylimidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.00 (t, 3H, propyl CH_3, ^3J = 7.0 Hz), 1.68 (m, 2H, propyl CH_2, ^3J = 7.0 Hz), 3.39 (m, 2H, propyl CH_2), 3.39 (m, 1H, C$^4H_2$), 3.77 (s, 3H, propyl O-CH_3), 3.88 (t, 1H, C$^4H_2$), 5.48 (t, 1H, C^5H, ^3J = 7.0 Hz), 6.80 (m, 2H, *N*-phenyl-H_m), 7.08 (m, 2H, *N*-phenyl-H_o), 7.22 (m, 5H, C-phenyl-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.7 (propyl CH$_3$), 20.9 (propyl CH$_2$), 47.2 (C^4H$_2$), 53.6 (propyl CH$_2$), 55.7 (O-CH$_3$), 77.4 (C^5H), 114.1 (*N*-phenyl-C_m), 124.5 (*N*-phenyl-C_o), 126.1 (C-phenyl-C_m), 128.9 (C-phenyl-C_p), 129.1 (C-phenyl-C_o), 139.3 (*N*-phenyl-C_i), 141.2 (C-phenyl-C_i), 153.0 (*N*-phenyl-C_p), 155.0 (C=O). FTIR (CH_2Cl_2): ν_{CO} 1701 cm^{-1}. Anal.: Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64; Found: C, 74.24, H, 7.76, N, 8.21. EIMS: Calcd for $C_{20}H_{24}N_2O_2$: 310.2, Found: 310.2.

1-*N*-phenyl-3-*N*-^{t}butyl-5-phenyl-imidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.52 (s, 6H, ^{t}butyl 2-CH_3), 1.57 (s, 3H, ^{t}butyl -CH_3), 3.42 (t, 1H, C$^4H_2$, ^3J = 8.0 Hz), 3.92 (t, 1H, C$^4H_2$ ^3J = 7.5 Hz), 5.35 (t, 1H, C^5H, ^3J = 7.5 Hz), 6.93 (d, 1H, phenyl-*H* ^3J = 7.0 Hz), 7.10 (d, 1H, phenyl-*H* ^3J = 7.0 Hz), 7.30 (m, 8H, phenyl-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 27.4 (^{t}butyl CH$_3$), 52.2 (C^4H$_2$), 54.1 (^{t}butyl CCH$_3$), 76.2 (C^5H), 121.8 (*N*-phenyl-C_p), 123.8 (C-phenyl-C_p), 126.0 (C-phenyl-C_o), 128.7 (C-phenyl-C_m), 128.8 (*N*-phenyl-C_o), 129.0 (*N*-phenyl-C_m), 139.5 (*N*-phenyl-C_i), 148.5 (C-phenyl-C_i), 150.9 (C=O). FTIR (CH_2Cl_2): ν_{CO} 1701 cm^{-1}.

Anal.: Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52; Found: C, 77.66, H, 7.40, N, 9.36. EIMS: Calcd for $C_{19}H_{22}N_2O$: 294.4, Found: 294.2.

1-*N*-phenyl-3-*N*-^{i}propyl-5-phenyl-imidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.26 (dd, 6H, ^{i}propyl 2-C*H*$_3$), 3.37 (t, 1H, C^4*H*$_2$ ^3J = 7.5 Hz), 3.84 (t, 1H, C^4*H*$_2$ ^3J = 7.0 Hz), 4.42 (m, 1H, ^{i}propyl C*H*), 5.48 (t, 1H, C^5*H*, ^3J = 7.0 Hz), 6.96 (d, 1H, *N*-phenyl-*H*$_p$), 7.15 (d, 1H, C-phenyl-*H*$_p$), 7.40 (m, 8H, aromatic-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 20.0 (^{i}propyl *C*H$_3$), 45.2 (^{i}propyl *C*H), 48.2 (*C*^{4}H$_2$), 77.5 (*C*^{5}H), 122.1 (*N*-phenyl-*C*$_p$), 123.9 (C-phenyl-*C*$_m$), 126.0 (C-phenyl-*C*$_o$), 128.7 (*N*-phenyl-*C*$_o$), 128.9 (C-phenyl-*C*$_p$), 129.1 (*N*-phenyl-*C*$_m$), 139.4 (*N*-phenyl-*C*$_i$), 148.3 (C-phenyl-*C*$_i$), 152.2 (*C*=O). FTIR (CH_2Cl_2): ν_{CO} 1701 cm^{-1}. Anal.: Calcd for $C_{18}H_{22}N_2O$: C, 77.10; H, 7.19; N, 9.99; Found: C, 77.27, H, 7.30, N, 9.83. EIMS: Calcd for $C_{18}H_{22}N_2O$: 280.4, Found: 280.2.

1-*N*-phenyl-3-*N*-^{n}propyl-5-(*p*-bromophenyl)imidazolidinone. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.00 (t, 3H, propyl C*H*$_3$, ^3J = 7.5 Hz), 1.67 (m, 2H, propyl C*H*$_2$, ^3J = 7.5 Hz), 3.41 (m, 3H, propyl *N*-C*H*$_2$ and one of C^4*H*$_2$), 3.89 (t, 1H, one of C^4*H*$_2$ ^3J = 8.5 Hz), 5.44 (t, 1H, C^5*H*, ^3J = 7.5 Hz), 6.97 (t, 1H, *N*-phenyl-*Hp* ^3J = 7.5 Hz) 7.10 (m, 2H, aromatic-*H*), 7.25 (m, 6H, aromatic-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.8 (propyl *C*H$_3$), 20.9 (propyl *C*H$_2$), 47.1 (*C*^{4}H$_2$), 53.5 (propyl *C*H$_2$), 76.7 (*C*^{5}H), 122.3 (*N*-phenyl-*C*$_p$), 122.9 (C-phenyl-*C*$_p$), 123.8 (C-phenyl-*C*$_o$), 127.8 (*N*-phenyl-*C*$_o$), 128.8 (C-phenyl-*C*$_m$), 132.2 (*N*-phenyl-*C*$_m$), 138.3 (*N*-phenyl-*C*$_i$), 148.0 (C-phenyl-*C*$_i$), 152.7 (*C*=O). FTIR (CH_2Cl_2): ν_{CO} 1701 cm^{-1}. Anal.: Calcd for $C_{18}H_{19}BrN_2O$: C,

60.18; H, 5.33; N, 7.80; Found: C, 60.16, H, 5.47, N, 7.74. EIMS: Calcd for $C_{18}H_{19}BrN_2O$: 359.3, Found: 359.2.

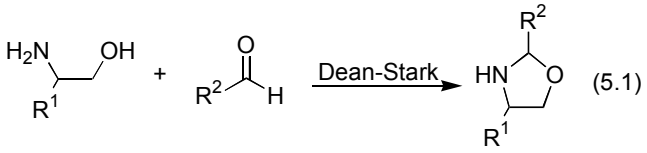
Chapter 5

Synthesis of Oxazolidines via the $Sc(OTf)_3$-Catalyzed Coupling of Aziridines and Organic Carbonyls

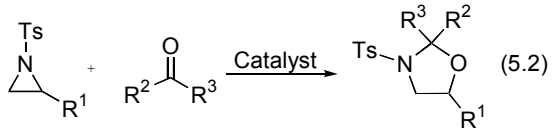
5.1. Introduction

Oxazolidines are a useful class of compounds that are common in natural products, active as pharmaceutical prodrugs (as they can be considered masked amino alcohols[1-4]) and useful as chiral auxiliaries[5-7] and synthetic intermediates.[8-10] Further, oxazolidines can be readily transformed into oxazolines,[11] which, when used as ligands of metal complexes, are capable of facilitating enantioselective catalysis such as hydrosilylation, reductive aldol reaction, and the asymmetric ring opening of meso epoxides.[12,13]

Classically, oxazolidines are synthesized by coupling β-amino alcohols with aldehydes under Dean-Stark conditions (Eq 5.1), which requires high temperatures to drive the reaction to completion.[10,14] An attractive alternative to Dean-Stark-type conditions is the direct coupling of aziridines and carbonyl compounds (Eq. 5.2). [Aziridine + carbonyl] coupling methodology represents an atom-economical methodology and offers several distinct advantages over the traditional conditions when an appropriate catalyst is used. On one hand, with an appropriate catalyst, the heat required for the reaction to go to completion could be reduced allowing temperature-sensitive reactants to be used. By lowering the activation energy of the reaction, such a catalyst may also allow the substrate scope to be expanded to include the coupling of aziridines with both aldehydes and ketones, giving rise to oxazolidines containing both tertiary- and quaternary carbon centers (eq. 5.2). In contrast to Dean-Stark type coupling scheme, which can be reversible due to residual water that may exist with the reactants in solution (eq. 5.1), the reaction shown in equation 5.2 is driven forward by the release of ring strain, and water is not produced as a byproduct, so the reaction is less reversible. Finally, the commercial and synthetic availability of a variety of aldehydes and ketones as well as aziridines offers a vast number of potential products available from this transformation.



To date, the only literature report of successful oxazolidine syntheses via the coupling of aziridines and carbonyl-containing compounds has been limited to the reaction of aldehydes and secondary aziridines. Due in part to the absence of catalyst, the previously reported reaction was performed at high temperatures and required long reaction times of up to 36 h. Additionally, only aliphatic aldehydes were readily coupled to form oxazolidine products.[15] Herein, we report a more general method for the synthesis of oxazolidines via the $Sc(OTf)_3$-catalyzed coupling of aziridines and organic carbonyls. We further demonstrate that this methodology is applicable to a range of substrates, and propose a mechanism for this transformation.

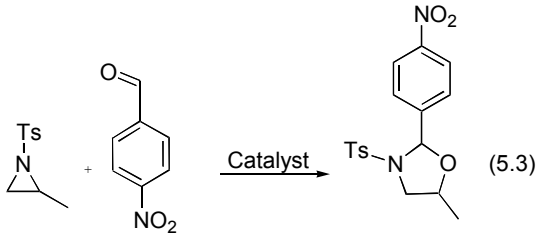


5.2. Lewis Acid Catalyst Screening

N-Tosyl aziridines and *p*-nitrobenzaldehyde were initially chosen as test substrates (Eq 5.3) and reaction parameters optimized. Initial catalyst screening reactions were conducted at room temperature with 10% catalyst loading on test substrates. We were pleased to find that several metals facilitated the transformation, but it was noted that scandium triflate stood out as the most active, yielding the fastest rate observed thus far (Table 5.1). We attribute the observed activity of the $Sc(OTf)_3$ complex to the high Lewis-acidity of the scandium, combined with the high lability of the triflate counterions. In comparson, $Ti(OiPr)_4$, and $TiCl_4$, (Table 5.1 entries 5 and 7), both strongly Lewis acidic, but with less labile anions, were much less catalytically active. Several metal chlorides also showed some substrate activation, including $SnCl_4$, $AlCl_3$ and $TiCl_4$

(Table 5.1 entries 3-5), suggesting that the nature of the anions has some effect on the metal activity in the coupling. The use of the triflate anion alone, however, gave no observable reactivity, supporting the role of the LA in the reaction.

Table 5.1. Activity of metal complexes in the coupling of *N*-tosylmethylazridine and *p*-nitrobenzaldehyde



(5.3)

Entry	Catalyst	Yield[a] (%)
1	(salen)Zn	0
2	(salen)Cr	0
3	$SnCl_4$	<10
4	$AlCl_3$	<10
5	$TiCl_4$	<10
6	$ZrCl_2$	0
7	$Ti(O^iPr)_4$	0
8	$Sc(OTf)_3$	50
9	HOTf	0
10	None	0

[a]% Determined using GC-MS. Reaction Conditions: catalyst (30 mg, 1 equiv), *N*-tosyl-2-methylaziridine (107 mg, 8 equiv), *p*-nitrobenzaldehyde (75 mg, 8 equiv); CH_2Cl_2 (1 M aziridine), 25 °C, 16 h.

5.3. Solvent

The nature of the solvent used in the reaction had a substantial effect on the reaction rate. Methylene chloride, a polar and noncoordinating solvent resulted in the fastest reaction rate. Reactions carried out in nonpolar aromatic solvents such as benzene and toluene not only showed diminished rates relative to methylene chloride but also facilitated the formation of

additional side products. The slow reaction rate may be due in part to the limited solubility of the starting materials in benzene and toluene. Acetonitrile, a polar coordinating solvent, allowed little product formation, due to competition for access to the Lewis acidic metal center. THF, another coordinating solvent, was not compatible with the $Sc(OTf)_3$ and gave a viscous polymer quickly, inhibiting formation of the desired product. With respect to reaction concentration, we found that the highest rate was observed when the reaction was carried out at a one molar concentration in aziridine due to solubility limits.

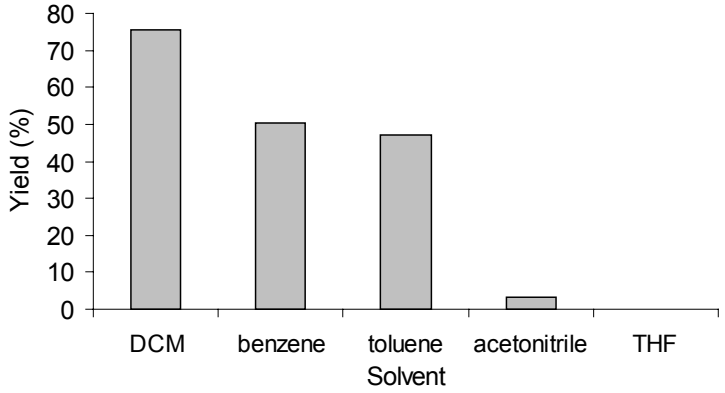


Figure 5.1. Solvent optimization. reaction conditions; $Sc(OTf)_3$ catalyst (50 mg, 100 mmol; 1 equiv), *N*-tosyl-2-methylaziridine (214 mg, 10 equiv), *p*-nitrobenzaldehyde (180 mg, 12 equiv), solvent (1M in aziridine), 40 °C, 16 h.

We believe that the increased reaction rates observed when polar, non-coordinating solvents such as methylene chloride were used indicates that a polar solvent stabilizes an ionic reaction intermediate. Because methylene chloride is weakly coordinating, it is unlikely to compete for access to the Lewis-acidic center (*vide infra*). Toluene and benzene are unable to stabilize the ionic intermediates, and coordinating solvents such as acetonitrile compete with the carbonyl-containing substrates for coordination to the LA. To obtain optimal results with this [aziridine + carbonyl] coupling reaction, the solvent chosen must have sufficient polarity to stabilize

transition states while not competing with the aziridine substrate for coordination to the $Sc(OTf)_3$ catalyst.

5.4. Ligand

Previous investigation into the use of $Sc(OTf)_3$ as a catalyst has suggested that the addition of coordinating ligands, including BINOL[16] can result in a substantial increase in regio- and stereoselectivity.[17,18] As such, we were interested to determine what effect, if any, coordinating ligands would have on the catalytic rate enhancement we had already observed. The addition of hydroxyl-containing additives, napthol, BINOL, and *tert*-butanol (Table 5.2, entries 1-3) resulted in a marginal decrease in TOF—while the addition of amine-containing additives substantially decreased the reaction rate (Table 5.2, entries 4 and 5). Under these conditions the selectivity of the reaction increased slightly, although in all cases the observed selectivity gains were accompanied by a substantial decrease in reactivity. Because reaction yields were negatively affected by coordinating ligands, and the selectivity increase was very marginal, their use was abandoned to simplify reaction parameters.

Entry	Additive	TOF (h^{-1})
1	Napthol	0.7
2	(*R*)-BINOL	1.2
3	^{t}Butyl alcohol	1.4
4	DMAP	0.1
5	DIPEA	0.0
6	None	1.4

Table 5.2. Comparison of turnover frequency of $Sc(OTf)_3$ in the presence of coordinating or Lewis-basic additives. Reaction conditions: catalyst (50 mg, 1 equiv), ligand (1 equiv), *N*-tosyl-2-methylaziridine (214 mmol, 10 equiv), *p*-nitrobenzaldehyde (180 mg, 12 equiv), methylene chloride (1M in aziridine), 40 °C, 16 h.

While the addition of coordinating alcohol ligands does not appreciably increase the reaction selectivity, and in some cases substantially slows the catalytic turnover, we suspected that the reaction rate may be increased by increasing the relative concentration of the carbonyl substrate (Figure 5.2). This is indeed the case: increasing the concentration of the organic carbonyl from one to two equivalents with respect to the aziridine substrate lead to a nearly three-fold reaction rate increase. In contrast, when two equivalents of aziridine are used relative to carbonyl substrate, the reaction rate actually *decreased* (Figure 5.2).

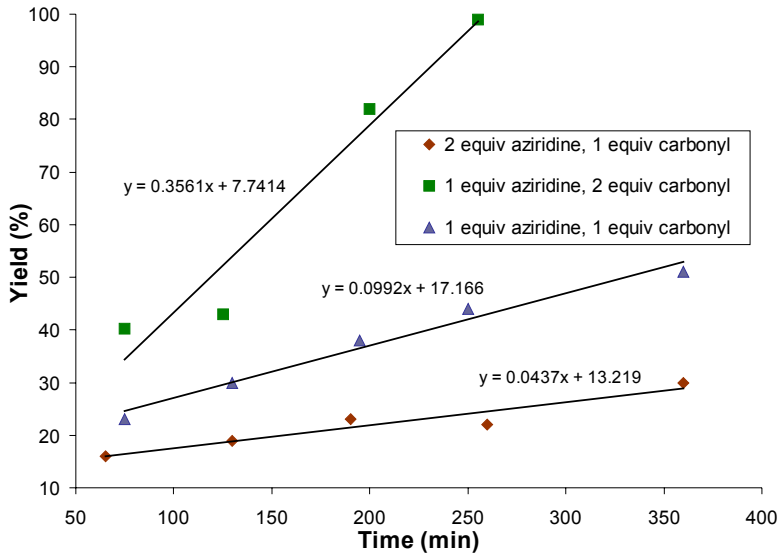


Figure 5.2. Comparison of reaction rates as a function of substrate equivalent in the reaction of *N*-tosyl methylaziridine and *p*-nitrobenzaldehyde. Reaction Conditions: catalyst (50 mg, 1 equiv), *N*-tosyl-2-methylaziridine (214 mg, 10 equiv or 428 mg, 20 equiv), *p*-nitrobenzaldehyde (150 mg, 10 equiv or 300 mg, 20 equiv, 1M in methylene chloride), 40 °C, 16 h.

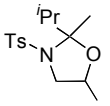
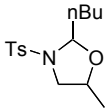
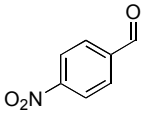
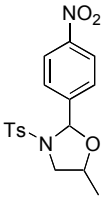
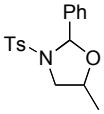
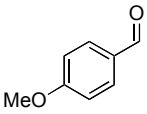
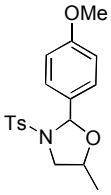
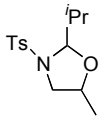
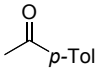
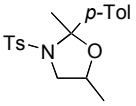
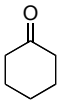
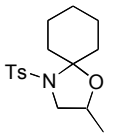
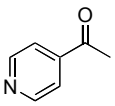
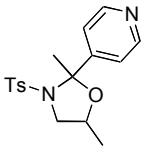
5.5. Substrate Scope

Following optimization of solvent and relative amounts of substrate, the substrate scope of the $Sc(OTf)_3$-catalyzed [aziridine + carbonyl] coupling was explored. The optimized reaction conditions are as follows: $Sc(OTf)_3$ catalyst (1 equiv), carbonyl substrate (20 equiv) and

aziridine (10 equiv, 1M in methylene chloride). These conditions are applicable to aldehydes and ketones, including those containing electron-donating and electron-withdrawing groups (Table 5.3, entries 3, 5, 7, 8) and carbonyl compounds containing linear and branched alkanes (Table 5.3, entries 1, 2, 4, 6). To the best of our knowledge, this is the first example where ketones can be efficiently be coupled to an aziridine to afford an oxazolidine. Previous literature reported[15] [aziridine + ketone] coupling to form the corresponding oxazolidine resulted in less than 5% product formation, while our [*N*-tosyl-2-methylaziridine + cyclohexanone] coupling affords an 84% yield of oxazolidine product. Incorporation of ketones in this coupling chemistry is particularly attractive in that it allows the formation of a quaternary carbon at the 2-position of the oxazolidine, something that has not been achieved successfully using similar methodology.

While our optimized conditions are compatible with a range of aldehydes and ketones, the scope of aziridine substrates was not expanded beyond *N*-tosyl aziridines. In our hands, *N*-alkyl and secondary aziridines were found to be inactive, likely due to the competitive coordination against the carbonyl substrate, similar to that with *N*-containing Lewis basic additives and coordinating solvents.

Table 5.3. Substrate scope of the $Sc(OTf)_3$-catalyzed coupling of aziridines and carbonyls. Reaction conditions: catalyst (50 mg, 1 equiv), *N*-tosyl-2-methylaziridine (214 mmol; 10 equiv, 1M in methylene chloride), *p*-nitrobenzaldehyde (300 mg, 20 equiv), 40 °C, 16 h.

entry	carbonyl	product	reaction time (h)	yield (%)
1			24	77
2			6	86
3			4	89
4			16	82
5			16	91
6			16	72
7			24	68
8			18	83
9			48	0

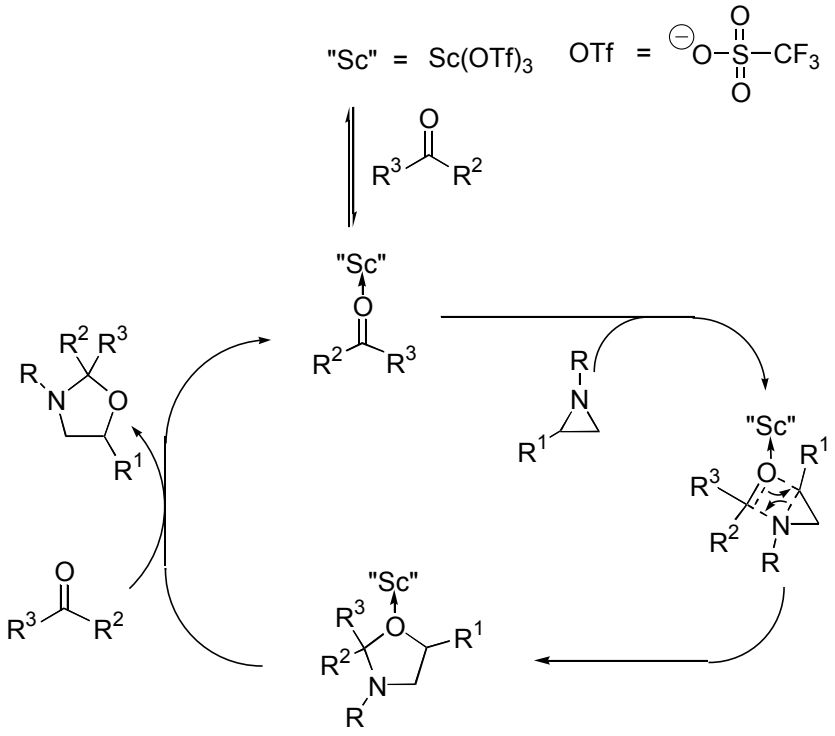
5.6. Mechanism

Although a systematic investigation of the mode of action of the $Sc(OTf)_3$-catalyzed coupling of aziridines and organic carbonyls has not been undertaken, we propose a mechanism based on optimization data (Scheme 5.1). Initial coordination of the ketone or aldehyde to the metal center results in an activated carbonyl ready for coupling to the aziridine, via a [2 + 2]-like concerted transition state, giving the product as a coordinated oxazolidine (Scheme 5.1).

The four-electron [$2\pi + 2\sigma$] cycloaddition step, affords a five-membered oxazolidine ring following ring expansion. This concerted one-step mechanism is driven forward by the release of ring-strain from the newly opened aziridine. Following ring expansion, the loosely coordinated oxazolidine can readily be displaced by the ketone substrate to facilitate catalytic turnover.

An alternative mechanism can be described in which, following carbonyl coordination to the Lewis acidic Sc center, the carbonyl carbon undergoes nucleophilic attack by the Lewis basic aziridine nitrogen. We believe that this is a less likely route than the concerted pathway shown in Scheme 5.1 because the sulfonamide is only weakly nucleophilic, and such an attack may be unlikely.

Scheme 5.1. Proposed mechanism for the coupling aziridines and organic carbonyls by the $Sc(OTf)_3$ catalyst.



Reaction 5.2 favors polar noncoordinatng solvents such as methylene chloride. Benzene and toluene, both nonpolar solvents are most likely unable to stabilize polar transition states, and afford intermediate reaction rates. The most polar solvent tested, acetonitrile, also gave low reactivity, presumeably due to its strong coordination to the scandium metal. This [solvent + Lewis acid] interaction inhibits carbonyl coordination and greatly reduces catalytic activity.

5.7. Conclusion

We have demonstrated the scandium triflate-catalyzed [aziridines + carbonyl] coupling is a viable path toward the synthesis of functionalized oxazolidines. Reactions were optimally carried out at 10% catalyst loading in refluxing methylene chloride. A 2:1 ratio of organic

carbonyl : aziridine, the reaction can be completed in as little as four hours. The unreacted equivalent of ketone or aldehyde can be recovered from the reaction mixture by either distillation or column chromatography. Our [aziridine + carbonyl] coupling can be carried out effectively under benchtop conditions and is not negatively influenced by oxygen in the reaction media, and further, is general for a wide range of aldehydes and ketones.

5.8. Experimental

General. All reactions were carried out under air atmosphere unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded either on a Varian Mercury 400 FT-NMR spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or an Inova-500 FT-NMR (500 MHz for ^{1}H, 120 MHz for ^{13}C). ^{1}H NMR data are reported as follows: chemical shift (multiplicity (b = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and peak assignments. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ), while peak assignments are made with the aid of ACD Laboratories software (Toronto, Canada). Combined gas chromatography-mass spectrometry (GC-MS) data were obtained on an Agilent 6890N gas chromatograph coupled to an Agilent 5973N mass spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 instrument equipped with an HP-5 column (30-m length, 0.32-mm inner diameter and 0.25-mm film thickness) temperature program: hold at 60 °C for 2 min. heat 20 °C/min for 12 min., then hold at 300 °C for 6 min.

All flash-chromatography was carried out using a 3-cm inner-diameter column containing a 40-cm plug of silica gel (230-400 mesh, Sorbent Technologies) that was doped with triethylamine and under a positive pressure of nitrogen, unless otherwise noted. All plug

columns were carried out using a standard pipette packed with 5 mm of silica gel that was doped with triethylamine. Elemental analysis was performed by Atlantic Microlab, Inc (Norcross, GA).

Materials. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. All other reagents were purchased from Aldrich and used without further purification.

Synthesis of *N*-tosyl-2-methylaziridine. Adapted from published procedures.[19] To a 250-mL round-bottom flask equipped with a magnetic stir bar was added aqueous KOH (10% w/w, 50 mL) and 2-methylaziridine (5.025 g, 87.6 mmol). This mixture was cooled down in an ice bath while stirring before tosyl chloride (17.00 g, 89.0 mmol) was added as a solid. The resulting mixture was stirred inside the ice bath for 30 minutes before being warmed on the bench top to ambient temperature and allowed to stir overnight, during which time a white precipitate formed. The precipitate was filtered and washed with cold water (2 x 15 mL). The crude white product was recrystallized in hexanes at 0 °C. Isolated crystals were then filtered and dried under reduced pressure to yield a white solid (10.45 g, 49.5 mmol, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (d, 3H, -C*H*$_3$), 2.04 (d, 1H, -C*H*$_2$), 2.46 (s, 3H, aromatic-C*H*$_3$), 2.63 (d, 1H -C*H*$_2$), 2.84 (s, 1H, C*H*), 7.38 (d, 2H, aromatic-*H*), 7.87 (d, 2H, aromatic-*H*).[19]

General Procedure for the Synthesis and Purification of Oxazolidines. To a 20-mL scintillation vial equipped with a magnetic stir bar was charged scandium triflate (0.1 mmol), methylene chloride (2 mL), the organic carbonyl (2 mmol), and the aziridine (1 mmol). The reaction vial was then capped and brought to reflux in an oil bath. After an allotted time (4-24 h, depending on the substrate), the reaction was removed from the oil bath and the cooled solution was passed through a plug of triethylamine-doped silica gel with methylene chloride eluent (20

mL) to removed the catalyst. The resulting yellow liquid was concentrated on a rotary evaporator and purified by column chromatography over silica (50:50 v/v methylene chloride:hexanes).

***N*-toluenesulfonyl-2-isopropyl-2-methyl-5-methyl oxazolidine.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (d, 3H, -C*H*$_3$), 1.14 (d, 1H, methyl –C*H*$_3$), 1.59 (s, 6H, isopropyl -C*H*$_3$), 2.42 (s, 3H, aromatic -C*H*$_3$), 2.78 (m, 1H, isopropyl -C*H*), 3.02 (m, 1H, -C*H*$_2$), 3.58 (s, 1H, -C*H*$_2$), 3.95 (m, 1H, -C*H*), 7.31 (d, 2H, aromatic-*H*), 7.74 (d, 2H, aromatic-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz):. δ 17.0 (isopropyl-*C*H$_3$), 17.7 (C^5-*C*H$_3$), 21.8 (tosyl-*C*H$_3$), 23.8 (C^2-*C*H$_3$), 36.8 (isopropyl-*C*H), 50.3 (*C*^{4}H$_2$), 71.0 (*C*^{5}H), 102.5 (*C*^{2}), 127.3 (tosyl-*C*$_m$), 130.0 (tosyl-*C*$_o$), 136.9 (tosyl-*C*$_i$), 143.8 (tosyl-*C*$_p$). Anal.: Calcd. for $C_{15}H_{23}NO_3S$: C, 60.58; H, 7.79; N, 4.71. Found: C, 60.91, H, 8.02, N, 4.50. EIMS: Calcd. for $C_{15}H_{23}NO_3S$: 297.1, Found: 296.2.

***N*-toluenesulfonyl-2-isopropyl -5-methyl oxazolidine.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (d, 3H, -C*H*$_3$), 1.02 (d, 3H, -CH$_3$-aromatic), 1.14 (d, 3H, -C*H*$_3$), 2.03 (m, 1H, -C*H*), 2.46 (s, 6H, -C*H*$_3$), 2.86 (t, 1H, -C*H*), 3.79 (dd, 2H, C*H*$_2$), 4.95 (s, 1H, -C*H*), 7.35 (d, 2H, aromatic-*H*), 7.76 (d, 2H, aromatic-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz):. δ 15.8 (isopropyl-*C*H$_3$), 17.9 (C^5-*C*H$_3$), 21.8 (tosyl-*C*H$_3$), 34.0 (isopropyl-*C*H), 53.8 (*C*^{4}H$_2$), 73.1 (*C*^{5}H), 95.8 (*C*^{2}), 127.9 (tosyl-*C*$_m$), 130.2 (tosyl-*C*$_o$), 135.4 (tosyl-*C*$_i$), 144.3 (tosyl-*C*$_p$). Anal.: Calcd. for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.47; N, 4.94. Found: C, 59.69 H, 7.68, N, 4.73. EIMS: Calcd. for $C_{14}H_{21}NO_3S$: 283.1, Found: 283.2.

***N*-toluenesulfonyl-2-propyl-5-methyl oxazolidine.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (t, 3H, -C*H*$_3$), 1.15 (d, 3H, -CH_3), 1.42 (m, 2H, -C*H*$_2$), 1.58 (m, 2H, -C*H*$_2$), 2.46 (s, 3H, -CH_3-aromatic), 2.91 (t, 1H, -C*H*), 3.66 (dd, 1H, C*H*$_2$), 4.29 (m, 1H, -C*H*$_2$), 5.05 (s, 1H, -C*H*) 7.35 (d, 2H, aromatic-*H*), 7.76 (d, 2H, aromatic-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.3 (propyl-*C*H_3), 18.0 (C^5-*C*H_3), 22.8 (tosyl-*C*H_3), 26.1 (propyl-*C*H_2), 36.3 (propyl-*C*H_2), 53.5 (*C*^{4}H$_2$), 73.3 (*C*^{5}H), 91.9 (*C*^{2}H), 128.1 (tosyl-*C*$_m$), 130.2 (tosyl-*C*$_o$), 135.2(tosyl-*C*$_i$), 144.3(tosyl-*C*$_p$). Anal.: Calcd. for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.47; N, 4.94. Found: C, 59.58, H, 7.69, N, 4.74. EIMS: Calcd. for $C_{14}H_{21}NO_3S$: 283.1, Found: 283.1.

***N*-toluenesulfonyl-2-spiro-cyclohexyl-5-methyl oxazolidine.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (d, 3H, -C*H*$_3$), 1.49 (m, 2H, -C*H*$_2$-), 1.55 (m, 4H, -C*H*$_2$-), 1.60 (m, 2H, -C*H*$_2$-), 1.79 (m, 2H, -C*H*$_2$-), 2.83 (m, 1H, -C*H*), 3.59 (m, 1H, -C*H*$_2$), 4.13 (m, 1H, -C*H*$_2$), 7.26 (d, 2H, aromatic-*H*), 7.71 (m, 2H, aromatic-H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.3 (C^5-*C*H_3), 21.7 (tosyl-*C*H_3), 23.7 (cyclohexyl-*C*H_2), 23.8 (cyclohexyl-*C*H_2), 24.8 (cyclohexyl-*C*H_2), 35.4 (cyclohexyl-*C*H_2), 36.5 (cyclohexyl-*C*H_2), 53.6 (*C*^{4}H$_2$), 70.5 (*C*^{5}H), 99.0 (*C*^{2}), 127.5 (tosyl-*C*$_m$), 129.7 (tosyl-*C*$_o$), 138.2 (tosyl-*C*$_i$), 143.3 (tosyl-*C*$_p$). Anal.: Calcd. for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53. Found: C, 62.48, H, 7.68, N, 4.22. EIMS: Calcd. for $C_{16}H_{23}NO_3S$: 309.1, Found: 309.1.

***N*-toluenesulfonyl-2-(4-nitrophenyl)-5-methyl oxazolidine.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (d, 3H, -C*H*$_3$), 1.23 (m, 2H, -C*H*$_3$), 1.58 (s, 3H, -C*H*$_3$-aromatic), 2.47 (d, 2H, -C*H*), 2.99 (m, 1H, -C*H*), 3.60 (m, 1H, -C*H*), 3.87 (m, 1H, -C*H*$_2$), 4.11 (m, 1H, -C*H*$_2$), 6.17 (s, 1H, -C*H*), 7.34 (dd, 2H, aromatic-*H*), 7.77 (m, 4H, aromatic-H), 8.24 (d, 2H, aromatic-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.3 (C^5-*C*H_3), 21.4 (tosyl-*C*H_3), 53.0 (*C*^{4}H$_2$), 75.0 (*C*^{5}H), 90.4 (*C*^{2}H),

123.8 (tosyl-C_m), 127.9 (C^2-phenyl-C_m), 128.1 (tolyl-C_m), 130.3 (tosyl-C_o), 135.0 (tosyl-C_i), 145.0 (C^2-phenyl-C_i), 146.1 (tosyl-C_p), 148.4 (C^2-phenyl-C_p). Anal.: Calcd. for $C_{17}H_{18}N_2O_5S$: C, 56.34; H, 5.01; N, 7.73. Found: C, 56.74, H, 5.22, N, 7.66. EIMS: Calcd. for $C_{17}H_{18}N_2O_5S$: 362.1, Found: 362.2.

***N*-toluenesulfonyl-2-(4-methylphenyl)-2-methyl-5-methyl oxazolidine.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (d, 2H, -C*H*$_3$), 1.92 (s, 3H, -C*H*$_3$ quaternary), 2.37 (s, 3H, -C*H*$_3$ *para*), 2.46 (s, 3H, -C*H*$_3$ *para*), 3.12 (t, 1H, -C*H*$_2$), 3.62 (m, 1H, -C*H*$_2$), 4.01 (m, 1H, -C*H*), 7.19 (d, 2H, aromatic-*H*), 7.35 (d, 2H, aromatic-*H*), 7.56 (d, 2H, aromatic-*H*), 7.78 (d, 2H, aromatic-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.4 (C^5-*C*H$_3$), 21.3 (C^2-phenyl-*C*H$_3$), 21.8 (tosyl-*C*H$_3$), 27.0 (C^2-*C*H$_3$), 54.8 (C^4H$_2$), 70.6 (C^5H), 99.1 (C^2), 126.3 (tosyl-C_m), 127.8 (tolyl-C_o), 129.1 (tosyl-C_o), 129.8 (tolyl-C_m), 137.6 (tolyl-C_p), 138.0 (tosyl-C_i), 140.8 (tolyl-C_i), 143.6 (tosyl-C_p). Anal.: Calcd. for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 66.12, H, 6.83, N, 3.95. EIMS: Calcd. for $C_{19}H_{23}NO_3S$: 345.1, Found: 345.2.

N-toluenesulfonyl-2-(4-methoxyphenyl)-5-methyl oxazolidine. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59 (d, 3H, -C*H*$_3$), 2.46 (s, 3H, C*H*$_3$-aromatic), 3.00 (m, 1H, -C*H*), 3.64 (m, 1H, -C*H*$_2$), 3.83 (s, 3H, -OC*H*$_3$), 4.14 (m, 1H, -C*H*$_2$), 6.03 (3, 1H, C^2*H*), 6.89 (d, 2H, aromatic-*H*), 7.32 (m, 4H, aromatic-*H*), 7.48 (m, 2H, aromatic-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.9 (C^5-*C*H$_3$), 21.9 (tosyl-*C*H$_3$), 47.6 (O-*C*H$_3$), 53.8 (C^4H$_2$), 71.1 (C^5H), 98.0 (C^2), 117.8 (C^2-phenyl-C_m), 126.0 (tosyl-C_m), 127.7 (C^2-phenyl-C_o), 129.1 (tosyl-C_o), 129.8 (C^2-phenyl-C_i), 136.0 (tosyl-C_i), 143.6 (tosyl-C_p), 155.9 (C^2-phenyl-C_p). Anal.: Calcd. for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09; N, 4.03. Found: C, 62.56, H, 6.26, N, 4.00. EIMS: Calcd. for $C_{18}H_{21}NO_4S$: 347.1, Found: 347.1.

***N*-toluenesulfonyl-2-phenyl-5-methyl oxazolidine.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66 (d, 3H, -C*H*$_3$), 2.45 (s, 3H, -C*H*$_3$-aromatic), 3.13 (m, 1H, -C*H*$_2$), 3.65 (m, 2H, -C*H*$_2$), 6.31 (s, 1H, -C*H*), 7.32 (d, 2H, aromatic-*H*), 7.37 (d, 4H, aromatic-*H*), 7.79 (d, 2H, aromatic-*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.0 (C^5-*C*H_3), 21.9 (tosyl-*C*H_3), 52.4 (*C*$^4H_2$), 75.1 (*C*^{5}H), 101.3 (*C*^{2}), 126.0 (tosyl-*C*$_m$), 127.7 (C^2-phenyl-*C*$_o$), 127.9 (C^2-phenyl-*C*$_m$), 128.4 (tosyl-*C*$_o$), 129.7 (C^2-phenyl-*C*$_i$), 136.0 (tosyl-*C*$_i$), 137.0 (C^2-phenyl-*C*$_p$), 143.6 (tosyl-*C*$_p$). Anal.: Calcd. for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.70, H, 6.51, N, 4.06. EIMS: Calcd. for $C_{17}H_{19}NO_3S$: 317.1, Found: 317.1.

Chapter 6

Epilogue

6.1. [(Salen)CrCl) + LB]-Catalyzed [Aziridine + Heterocumulene] Coupling

In summary, I will discuss the chemical implications of the major scientific points presented in this thesis and recommend venues for further discovery.

The majority of this thesis (Chapters 2, 3, and 4) deals with the discovery and mechanistic investigation of [aziridine + heterocumulene] coupling reactions. I have shown that [epoxide + CO_2] coupling methodology can readily be extended to both [aziridine + CO_2] coupling as well as [aziridine + RNCO] coupling. These contributions have brought to light several interesting trends in chemical reactivity (Table 6.1), some of which offer themselves as potentially fruitful areas for future research.

Table 6.1. Reaction variables for [strained ring + heterocumulene] coupling reactions

Variable	CO_2 + 	CO_2 + 	RNCO + 	RNCO + 
LB cocatalyst	required	enhances rate	enhances rate	inhibits rate
Solvent	polar, noncoord.	polar, noncoord.	nonpolar, coord.	nonpolar, coord.
Optimal CO_2 pressure	low (50 psig)	moderate (400 psig)	N/A	N/A
Selectivity	N/A	[Lewis base]	nd	[Lewis base]

Perhaps the most interesting across-the-board trend was found through the role of the LB in the four reactions shown in Table 6.1. The addition of a LB cocatalyst was necessary for the coupling of epoxides and CO_2, however in the case of either the [aziridine + CO_2] or [epoxide + RNCO] coupling, it is simply a rate-enhancer. As we have shown in Chapter 4, in the case of [aziridine + RNCO] coupling, the addition of a cocatalytic amount of LB actually *inhibits* the

reaction rate. While we have made some progress in understanding the roles of the aziridine in this reaction. We also do not yet fully understand all the effects that isocyanates have on the overall reaction rate. A further investigation into these effects would be most interesting. The role of CO_2 pressure on reaction rate and the parameters that affect reaction selectivity are also poorly understood. Though there is limited data regarding the trends shown in Table 6.1, much remains to be investigated. One potential path to a further understanding of these nascent trends is via a mechanistic study, probing the kinetics of nitrogen-containing heterocumulene addition, CO_2 uptake, and selectivity with LB addition.

Additional studies can probe whether the (salen)CrCl catalyst is compatible with other substrates, such as carbodiimides, isothiocyanates, or episulfides. These substrates would allow the possible expansion of the trends shown in Table 6.1, and extend the utility of the [strained ring + hetercumulene] coupling to produce broader access to useful 5-membered heterocycles.

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Chapter 1

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APPENDIX A

Computational Ground-State Geometry Structures (in 3-dimentional Cartesian coordinates (Å)):

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-N,N-dimethylaminophenyl)aziridine)
71

C	-3.496773	-0.040817	0.500188
C	-2.835432	-0.394852	-0.690929
C	-3.617183	-1.002599	-1.688857
C	-4.979333	-1.251693	-1.516079
C	-5.642019	-0.910458	-0.308754
C	-4.853343	-0.293141	0.699696
C	-1.412858	0.000041	-0.927045
C	-0.514273	-0.703708	-1.873467
N	-0.203566	-0.784206	-0.428657
C	-0.496285	-2.098234	0.208320
C	0.405075	-3.251480	-0.240540
C	0.040550	-4.560434	0.474206
N	-6.996375	-1.163884	-0.123507
Cr	1.659652	0.502005	0.170011
Cl	3.477598	1.863706	0.630754
N	2.297419	-0.680779	1.688085
C	1.894003	-0.180836	3.012001
C	0.562169	0.569432	2.876794
N	0.605774	1.378953	1.658359
C	0.153548	2.604344	1.651019
C	0.138372	3.479785	0.513860
C	0.542239	3.046937	-0.804356
C	0.440859	3.991506	-1.864791
C	-0.004159	5.287414	-1.640040
C	-0.385850	5.714952	-0.348235
C	-0.317148	4.812368	0.702257
O	0.951801	1.831620	-1.074892
C	3.262314	-1.561602	1.612223
C	3.921007	-1.992701	0.414499
C	4.950246	-2.966742	0.536213
C	5.637825	-3.445842	-0.567118
C	5.296482	-2.954268	-1.848833
C	4.298558	-2.003974	-2.010362
C	3.579554	-1.480109	-0.895783
O	2.640439	-0.598429	-1.110244
H	0.372621	1.185069	3.770755
H	1.805828	-0.999254	3.745222
H	0.746073	3.662422	-2.857266
H	4.039775	-1.619278	-2.996279
H	-0.724859	6.736689	-0.179872
H	6.430106	-4.184811	-0.449157
H	-0.262636	-0.154381	2.786577
H	2.669903	0.517711	3.359126
H	3.629818	-2.006144	2.547951
H	-0.251038	3.014547	2.587075
H	5.201791	-3.332228	1.534517
H	5.827299	-3.324536	-2.727575
H	-0.610880	5.123152	1.707561
H	-0.054134	5.986317	-2.477421
H	-1.227103	1.064750	-0.815625
H	0.201457	-0.135480	-2.463686
H	-0.871409	-1.624938	-2.333223
H	-3.165992	-1.262852	-2.646657
H	-2.938808	0.457426	1.294055
H	-5.301848	0.012680	1.641402
H	-5.526291	-1.701953	-2.340216
H	-1.544313	-2.375105	0.018849
H	-0.397457	-1.954193	1.293032
H	1.454292	-3.003081	-0.053234
H	0.310085	-3.395597	-1.327154
H	0.683742	-5.383027	0.132093
H	-1.003256	-4.853048	0.282286
H	0.165090	-4.477706	1.564728
C	-7.671307	-0.631010	1.050077
C	-7.808402	-1.568281	-1.262086
H	-8.836117	-1.742954	-0.927671
H	-7.829815	-0.804201	-2.061842
H	-7.439876	-2.508737	-1.696629
H	-8.722085	-0.936483	1.031283
H	-7.227755	-1.031293	1.973378
H	-7.635571	0.473207	1.099612

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-hydroxyphenyl)aziridine)
64

C	-3.770278	-1.133398	0.641106
C	-3.070955	-1.330191	-0.565064
C	-3.592392	-2.275874	-1.469641
C	-4.745016	-3.010500	-1.182328
C	-5.412593	-2.811142	0.034461
C	-4.922329	-1.861874	0.946595
C	-1.863260	-0.499110	-0.863196
C	-0.867100	-0.837904	-1.906747
N	-0.441451	-0.916091	-0.490481
C	-0.286108	-2.289554	0.076750
C	0.743917	-3.183389	-0.622733
C	0.870691	-4.545794	0.073843
O	-6.540337	-3.557203	0.273470
Cr	1.002039	0.799296	0.139261
Cl	2.431330	2.547009	0.662046
N	1.834553	-0.206630	1.686481
C	1.288504	0.203723	2.989978
C	-0.176386	0.624452	2.811898
N	-0.290322	1.406133	1.579579
C	-1.019707	2.488706	1.533436
C	-1.221074	3.311013	0.374513
C	-0.677168	2.978232	-0.923531
C	-0.996155	3.844475	-2.008645
C	-1.787487	4.970666	-1.829149
C	-2.310495	5.300984	-0.558281

C	-2.026475	4.473332	0.516786
O	0.052583	1.914948	-1.157383
C	2.977323	-0.843690	1.650045
C	3.770966	-1.090837	0.482502
C	4.995208	-1.795404	0.647661
C	5.838882	-2.053468	-0.420921
C	5.466517	-1.602586	-1.708821
C	4.281571	-0.909627	-1.911642
C	3.392112	-0.625453	-0.834078
O	2.281453	0.013553	-1.086308
H	-0.520568	1.194811	3.689797
H	1.375823	-0.601184	3.737872
H	-0.583179	3.595881	-2.985664
H	3.999220	-0.550503	-2.900592
H	-2.926849	6.190071	-0.426805
H	6.776008	-2.589465	-0.271953
H	-0.814142	-0.269607	2.723430
H	1.868112	1.071026	3.339400
H	3.396270	-1.204337	2.600143
H	-1.534448	2.806849	2.451694
H	5.270970	-2.126705	1.651341
H	6.125891	-1.793317	-2.557904
H	-2.420376	4.713636	1.507015
H	-2.003108	5.614275	-2.684262
H	-1.999389	0.561082	-0.663934
H	-0.404448	-0.034266	-2.475490
H	-0.961565	-1.785887	-2.435743
H	-3.105264	-2.435798	-2.431185
H	-3.412664	-0.391265	1.355604
H	-5.439339	-1.690254	1.893853
H	-5.137857	-3.734662	-1.895409
H	-1.259076	-2.801960	0.077131
H	0.002453	-2.154317	1.126603
H	1.720367	-2.690749	-0.647883
H	0.450752	-3.343248	-1.670472
H	1.627382	-5.166037	-0.425999
H	-0.078090	-5.102677	0.060763
H	1.178735	-4.435432	1.124071
H	-6.920402	-3.285401	1.128124

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-methoxyphenyl)aziridine)
67

C	4.847737	-2.792392	0.563063
C	3.802299	-1.836710	0.430941
C	3.466694	-1.327989	-0.882671
C	4.207337	-1.838175	-1.989563
C	5.217334	-2.773806	-1.818184
C	5.553687	-3.260450	-0.533250
C	3.122962	-1.420238	1.622113
N	2.126522	-0.574126	1.685223
C	1.694793	-0.076215	3.000282
C	0.320945	0.589570	2.851199
N	0.315798	1.380044	1.618629
C	-0.246037	2.558298	1.581544
C	-0.322596	3.411354	0.429677
C	0.160275	3.009160	-0.872071
C	-0.002421	3.930534	-1.945726
C	-0.599612	5.168877	-1.752399
C	-1.068834	5.563121	-0.479035
C	-0.929552	4.686522	0.586044
O	0.696308	1.838899	-1.118872
Cr	1.449019	0.568725	0.154846
O	2.517775	-0.459009	-1.108201
N	-0.363729	-0.823785	-0.439387
C	-0.583304	-2.157760	0.187816
C	0.348459	-3.265330	-0.313109
C	0.027326	-4.613048	0.347590
C	-1.613713	-0.076201	-0.875177
C	-0.738230	-0.740941	-1.869777
C	-3.013547	-0.509799	-0.568172
C	-3.841229	-1.102477	-1.533744
C	-5.189232	-1.392592	-1.274847
C	-5.737079	-1.090890	-0.017786
C	-4.920771	-0.497378	0.965548
C	-3.589423	-0.206555	0.684064
O	-7.035301	-1.321054	0.351382
Cl	3.156771	2.053343	0.640596
H	0.091115	1.207646	3.733682
H	1.654743	-0.884920	3.748311
H	0.367068	3.627014	-2.924378
H	3.952839	-1.457226	-2.978015
H	-1.531720	6.539354	-0.337371
H	6.355577	-3.987648	-0.407586
H	-0.456590	-0.185994	2.771935
H	2.426481	0.675063	3.332395
H	3.497415	-1.847756	2.562913
H	-0.700603	2.945576	2.504200
H	5.094377	-3.154564	1.563799
H	5.761971	-3.136334	-2.691704
H	-1.284003	4.974516	1.578320
H	-0.701624	5.849970	-2.599623
H	-1.462557	0.993242	-0.759766
H	-0.071090	-0.142373	-2.486839
H	-1.088272	-1.669247	-2.321399
H	-3.444850	-1.324185	-2.524807
H	-2.982009	0.276238	1.449433
H	-5.354498	-0.258150	1.935956
H	-5.792748	-1.838934	-2.061715
H	-1.625316	-2.474317	0.028092
H	-0.453856	-2.027031	1.271053
H	1.392645	-2.996151	-0.123676
H	0.248513	-3.366917	-1.404251
H	0.686605	-5.403178	-0.037849
H	-1.011219	-4.923381	0.155046
H	0.163813	-4.576716	1.439378
C	-7.947201	-1.815640	-0.629019
H	-8.913955	-1.885628	-0.119958
H	-8.031358	-1.121940	-1.480429
H	-7.651551	-2.812669	-0.990388

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-methylphenyl)aziridine)
66

C	4.830556	-2.222564	0.588320
C	3.675623	-1.405563	0.438769
C	3.321185	-0.911893	-0.875009
C	4.156419	-1.294928	-1.966012
C	5.270786	-2.099968	-1.778405
C	5.624640	-2.570591	-0.492296

C	2.922264	-1.090996	1.616432
N	1.833081	-0.365926	1.665752
C	1.332633	0.079559	2.976378
C	-0.090277	0.631615	2.810092
N	-0.148612	1.417862	1.576125
C	-0.787124	2.556548	1.533622
C	-0.925027	3.393662	0.375670
C	-0.419181	3.015564	-0.924879
C	-0.663008	3.906540	-2.008898
C	-1.350513	5.098337	-1.825533
C	-1.836293	5.472732	-0.552170
C	-1.623900	4.622282	0.521995
O	0.216095	1.893836	-1.160252
Cr	1.075654	0.710931	0.129703
O	2.277936	-0.162797	-1.114255
N	-0.535653	-0.881285	-0.479196
C	-0.516865	-2.250016	0.116970
C	0.411433	-3.259613	-0.568544
C	0.440674	-4.589903	0.198724
C	-1.904101	-0.320848	-0.853172
C	-0.957663	-0.788404	-1.894920
C	-3.187927	-1.023733	-0.532834
C	-3.815228	-1.901125	-1.434168
C	-5.024413	-2.529904	-1.111334
C	-5.655328	-2.311733	0.123610
C	-5.039875	-1.412304	1.016431
C	-3.837243	-0.779153	0.693738
C	-6.947837	-3.007249	0.484784
Cl	2.631040	2.350126	0.643522
H	-0.375071	1.232032	3.689328
H	1.347156	-0.738466	3.715170
H	-0.277493	3.621541	-2.987085
H	3.889378	-0.922348	-2.954282
H	-2.369100	6.413908	-0.418646
H	6.507866	-3.193759	-0.354171
H	-0.804575	-0.202996	2.729550
H	1.991007	0.885658	3.332934
H	3.320284	-1.487314	2.561350
H	-1.267087	2.918125	2.454366
H	5.090488	-2.573712	1.589452
H	5.887721	-2.367977	-2.638466
H	-1.989652	4.897023	1.514023
H	-1.512060	5.758549	-2.679954
H	-1.926146	0.752031	-0.672860
H	-0.412607	-0.056640	-2.487744
H	-1.166967	-1.732042	-2.396579
H	-3.369167	-2.090214	-2.410352
H	-3.396580	-0.077337	1.402916
H	-5.510438	-1.201681	1.978989
H	-5.482967	-3.200404	-1.840974
H	-1.535744	-2.661357	0.136520
H	-0.206033	-2.127203	1.161515
H	1.426331	-2.856859	-0.646315
H	0.071113	-3.446008	-1.597432
H	1.111697	-5.309781	-0.290385
H	-0.557202	-5.050234	0.255335
H	0.801227	-4.451108	1.228664
H	-7.361239	-3.555157	-0.371485
H	-6.796365	-3.730347	1.301194
H	-7.710198	-2.291726	0.825813

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-fluorophenyl)aziridine)
63

C	-3.621988	2.225375	1.521588
C	-3.093894	1.310326	0.591790
C	-3.783446	1.134065	-0.624898
C	-4.939345	1.861449	-0.923770
C	-5.412767	2.772807	0.020156
C	-4.779885	2.962419	1.246153
C	-1.874424	0.486411	0.873818
C	-0.871541	0.823078	1.913525
N	-0.464076	0.921661	0.493946
C	-0.341933	2.310385	-0.034993
C	0.819362	3.132961	0.531439
C	0.754969	4.590801	0.051121
Cr	1.003623	-0.788652	-0.156596
Cl	2.438662	-2.524933	-0.682179
N	-0.283208	-1.388648	-1.602504
C	-1.007926	-2.474989	-1.565825
C	-1.209899	-3.304974	-0.412212
C	-0.672963	-2.977006	0.889891
C	-0.995728	-3.847377	1.970249
C	-1.784131	-4.974374	1.782600
C	-2.299361	-5.301019	0.507695
C	-2.011770	-4.468777	-0.562903
O	0.054253	-1.913255	1.131134
C	-0.172989	-0.593952	-2.827108
C	1.287960	-0.156545	-3.000190
N	1.836303	0.231762	-1.689912
C	2.989276	0.850859	-1.647102
C	3.783546	1.079594	-0.476114
C	3.391688	0.618595	0.838303
C	4.277347	0.892296	1.921428
C	5.470631	1.572806	1.725730
C	5.855647	2.020031	0.440173
C	5.016208	1.771402	-0.633814
O	2.271084	-0.006164	1.083130
H	-0.511205	-1.158288	-3.711127
H	1.364476	0.665789	-3.729776
H	-0.588151	-3.601683	2.950283
H	3.985218	0.536036	2.908561
H	-2.913309	-6.190752	0.369742
H	6.799089	2.546527	0.297593
H	-0.819541	0.293113	-2.731056
H	1.874513	-1.009446	-3.372311
H	3.414355	1.213639	-2.593530
H	-1.519124	-2.789013	-2.487400
H	5.300279	2.102300	-1.635253
H	6.126775	1.756799	2.578785
H	-2.400513	-4.706331	-1.555733
H	-2.003316	-5.621271	2.634289
H	-2.004757	-0.572968	0.666207
H	-0.399682	0.015668	2.468651
H	-0.966462	1.766560	2.451897
H	-3.136737	2.363342	2.487069
H	-3.414643	0.410131	-1.351873
H	-5.468430	1.729882	-1.866645
H	-5.186872	3.668883	1.968240
F	-6.538034	3.489635	-0.260585
H	-1.279031	2.857405	0.146590
H	-0.238723	2.225389	-1.124783

H	1.777240	2.696238	0.235547
H	0.793622	3.109545	1.630961
H	1.612061	5.161260	0.433574
H	-0.160678	5.093090	0.395127
H	0.778673	4.655422	-1.046989

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-phenylaziridine)
63

H	-0.908293	0.803878	3.711056
C	-0.412395	0.369997	2.828529
C	1.112683	0.434381	2.985110
H	1.455377	-0.310740	3.721361
N	-0.791229	1.066749	1.597640
C	-1.849124	1.832482	1.561093
C	-2.330186	2.539818	0.408268
C	-1.712651	2.416486	-0.892539
C	-2.303534	3.133086	-1.971717
C	-3.430163	3.922486	-1.785302
C	-4.033675	4.044935	-0.513473
C	-3.483068	3.357774	0.557490
O	-0.673941	1.654664	-1.135514
Cr	0.603154	0.906108	0.139214
O	2.054390	0.554869	-1.107160
C	3.311727	0.295615	-0.873136
C	3.841650	-0.008098	0.438858
C	5.227004	-0.299083	0.580393
C	6.087790	-0.303437	-0.505562
C	5.568460	-0.007496	-1.788078
C	4.224300	0.282581	-1.968524
H	-1.830837	3.044897	-2.949344
C	3.029594	-0.006548	1.619153
N	1.742163	0.225206	1.670090
H	3.825100	0.525106	-2.952971
N	-0.253760	-1.193098	-0.458427
C	0.221453	-2.450677	0.188048
C	1.582158	-2.954346	-0.299824
C	1.941930	-4.308338	0.329706
C	-1.702170	-1.196046	-0.928354
C	-0.587367	-1.327103	-1.896973
C	-2.679231	-2.281510	-0.593168
C	-3.392247	-2.206949	0.620064
C	-4.353612	-3.165752	0.952536
C	-4.633862	-4.215689	0.067109
C	-3.947210	-4.292835	-1.150079
C	-2.978953	-3.333529	-1.477046
Cl	1.378450	3.023720	0.651160
H	-4.914778	4.671359	-0.376173
H	7.146950	-0.522844	-0.373681
H	-0.732310	-0.681204	2.748605
H	1.399567	1.434333	3.343242
H	3.556706	-0.194253	2.565684
H	-2.433174	1.950293	2.485856
H	5.610644	-0.515610	1.580367
H	6.236164	0.001709	-2.651841
H	-3.937945	3.440901	1.546903
H	-3.851646	4.458904	-2.637021
H	-2.118568	-0.196347	-0.841322
H	-0.315643	-0.472210	-2.513209
H	-0.385463	-2.302261	-2.340834
H	-2.467065	-3.398035	-2.436810
H	-3.192631	-1.383535	1.305900
H	-4.891055	-3.089568	1.898907
H	-4.168640	-5.096010	-1.854225
H	-5.387567	-4.962240	0.320498
H	-0.526194	-3.243449	0.037099
H	0.262652	-2.252415	1.266923
H	2.367852	-2.227858	-0.070137
H	1.570253	-3.057223	-1.394689
H	2.927392	-4.648077	-0.017698
H	1.211477	-5.088016	0.067464
H	1.982748	-4.248562	1.428023

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-chlorophenyl)aziridine)
63

C	3.661623	-1.233762	1.934876
C	2.975093	-0.576949	0.898941
C	3.692287	-0.271301	-0.274721
C	5.036648	-0.624661	-0.424492
C	5.688676	-1.286237	0.623758
C	5.009073	-1.589049	1.807992
C	1.566800	-0.095117	1.071228
C	0.579071	-0.740832	1.969485
N	0.344872	-0.799267	0.509851
C	0.581956	-2.132575	-0.113593
C	-0.412569	-3.223880	0.295051
C	-0.093111	-4.558219	-0.394248
Cr	-1.406145	0.651905	-0.210880
Cl	-3.057199	2.163336	-0.783014
N	-0.228413	1.385878	-1.682097
C	0.356732	2.553392	-1.674306
C	0.439679	3.438307	-0.546288
C	-0.065724	3.084314	0.760017
C	0.109910	4.027305	1.811641
C	0.737512	5.246290	1.592264
C	1.224819	5.596455	0.312929
C	1.075495	4.695535	-0.730410
O	-0.635426	1.934692	1.030922
C	-0.233271	0.553058	-2.886305
C	-1.616440	-0.096485	-3.034907
N	-2.089728	-0.524728	-1.708513
C	-3.114768	-1.335357	-1.630492
C	-3.819952	-1.691237	-0.434298
C	-3.489148	-1.143196	0.864217
C	-4.247733	-1.602058	1.981079
C	-5.271810	-2.526031	1.832264
C	-5.606710	-3.048279	0.561027
C	-4.883579	-2.629862	-0.544181
O	-2.530119	-0.279610	1.069219
H	0.019595	1.134614	-3.787229
H	-1.571537	-0.942023	-3.740307
H	-0.274944	3.757401	2.794328
H	-3.995247	-1.191446	2.958146
H	1.709974	6.558503	0.149947
H	-6.420241	-3.765252	0.452741
H	0.530950	-0.230947	-2.768356
H	-2.326425	0.647078	-3.425863
H	-3.488933	-1.785339	-2.560844
H	0.826712	2.904529	-2.603958

H	-5.128544	-3.021654	-1.534053
H	-5.829781	-2.850677	2.712377
H	1.443310	4.951020	-1.726653
H	0.849146	5.946693	2.422311
H	1.466162	0.980660	0.958277
H	-0.128497	-0.128278	2.524556
H	0.854184	-1.683374	2.443580
H	3.150626	-1.455305	2.871249
H	3.195056	0.257660	-1.087557
H	5.575027	-0.379540	-1.338831
H	5.526407	-2.086662	2.626006
Cl	7.377771	-1.735049	0.462464
H	1.598778	-2.479943	0.124359
H	0.542115	-1.985414	-1.201329
H	-1.435939	-2.916549	0.055710
H	-0.380696	-3.365526	1.385551
H	-0.804636	-5.335887	-0.083956
H	0.918052	-4.913787	-0.144050
H	-0.152915	-4.476132	-1.490139

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-bromophenyl)aziridine)
63

C	3.394615	-1.093509	1.525137
C	2.621281	-0.231686	0.726090
C	3.251931	0.385394	-0.372454
C	4.593588	0.142725	-0.681476
C	5.330267	-0.728537	0.129006
C	4.741184	-1.346583	1.236077
C	1.195908	0.111088	1.025054
C	0.330761	-0.612466	1.987307
N	0.010575	-0.716860	0.546154
C	0.334484	-2.025800	-0.093696
C	-0.457138	-3.227722	0.431818
C	-0.071985	-4.515025	-0.312504
Cr	-1.867509	0.527916	-0.127035
Cl	-3.701953	1.800669	-0.713436
N	-0.768704	1.441874	-1.559363
C	-0.397075	2.694864	-1.542100
C	-0.476443	3.569655	-0.406726
C	-0.892916	3.108187	0.897776
C	-0.878030	4.048849	1.965290
C	-0.503555	5.370029	1.760295
C	-0.109824	5.826250	0.482045
C	-0.094018	4.928037	-0.574579
O	-1.236939	1.867696	1.150358
C	-0.616659	0.626417	-2.765461
C	-1.894632	-0.202242	-2.966729
N	-2.357135	-0.698828	-1.660448
C	-3.278543	-1.628366	-1.624372
C	-3.995490	-2.063898	-0.461352
C	-3.770833	-1.502458	0.853644
C	-4.559297	-2.009125	1.928121
C	-5.511927	-2.996843	1.724960
C	-5.732515	-3.545646	0.440150
C	-4.977891	-3.079873	-0.624645
O	-2.873273	-0.588492	1.110537
H	-0.413035	1.243127	-3.655734
H	-1.712512	-1.028213	-3.673268
H	-1.193826	3.695440	2.945995
H	-4.394024	-1.577343	2.914737
H	0.172662	6.867300	0.328571
H	-6.489441	-4.314749	0.288994
H	0.242583	-0.046865	-2.621010
H	-2.683615	0.441033	-3.384534
H	-3.562908	-2.109124	-2.571549
H	0.022263	3.126459	-2.462047
H	-5.140008	-3.488387	-1.624429
H	-6.103213	-3.349991	2.571753
H	0.212576	5.263259	-1.567885
H	-0.520616	6.065535	2.601652
H	0.973331	1.168676	0.911415
H	-0.391623	-0.047729	2.573548
H	0.709291	-1.516021	2.463750
H	2.957093	-1.565885	2.403379
H	2.689239	1.085096	-0.991413
H	5.058056	0.632371	-1.534747
H	5.323895	-2.008511	1.874774
Br	7.182679	-1.060804	-0.264404
H	1.408738	-2.236153	0.010475
H	0.137695	-1.904781	-1.166091
H	-1.531864	-3.047849	0.329285
H	-0.266659	-3.360901	1.506945
H	-0.647093	-5.370499	0.066598
H	0.995763	-4.752852	-0.192229
H	-0.273483	-4.435975	-1.391404

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-trifluoromethylphenyl)aziridine)
66

C	4.834470	-3.175806	0.485214
C	3.903532	-2.104167	0.389144
C	3.672042	-1.481105	-0.895890
C	4.389567	-1.997038	-2.014591
C	5.285958	-3.047348	-1.878971
C	5.521076	-3.649604	-0.621177
C	3.242273	-1.681089	1.588729
N	2.352153	-0.726064	1.683938
C	1.935012	-0.265978	3.018955
C	0.658299	0.575925	2.882071
N	0.781857	1.426014	1.696636
C	0.407544	2.677578	1.729584
C	0.464488	3.593880	0.626106
C	0.867329	3.186072	-0.699044
C	0.836334	4.167348	-1.728440
C	0.455810	5.477211	-1.467287
C	0.073986	5.880711	-0.168066
C	0.076594	4.941785	0.852562
O	1.214173	1.957323	-1.002132
Cr	1.857361	0.567714	0.211421
O	2.832989	-0.497958	-1.088707
N	-0.022653	-0.679687	-0.527198
C	-0.393536	-1.964773	0.141739
C	0.273839	-3.229306	-0.416345
C	-0.070371	-4.460576	0.435746
C	-1.161734	0.145167	-1.119545
C	-0.224297	-0.605808	-1.988899
C	-2.607429	-0.187991	-0.936745
C	-3.278663	-1.184198	-1.668817
C	-4.640505	-1.435101	-1.475371

C	-5.366652	-0.689988	-0.536858
C	-4.718983	0.321453	0.190306
C	-3.360407	0.564976	-0.011818
C	-6.846342	-0.920964	-0.347237
Cl	3.705584	1.801343	0.822061
H	0.487656	1.169140	3.794573
H	1.770310	-1.112218	3.705319
H	1.142951	3.855294	-2.726044
H	4.217442	-1.522718	-2.980354
H	-0.214412	6.912692	0.029075
H	6.234834	-4.467131	-0.522617
H	-0.211853	-0.084870	2.745798
H	2.742536	0.358672	3.429367
H	3.539042	-2.201628	2.510469
H	0.006580	3.075189	2.672641
H	5.008574	-3.625002	1.465689
H	5.820788	-3.409199	-2.758795
H	-0.217657	5.235206	1.862784
H	0.459592	6.205710	-2.280581
H	-0.943167	1.203454	-1.007104
H	0.550839	-0.062050	-2.525168
H	-0.571677	-1.513370	-2.479935
H	-2.746745	-1.767286	-2.419045
H	-2.876203	1.363762	0.549143
H	-5.272532	0.916795	0.915386
H	-5.131557	-2.212850	-2.057206
H	-1.483928	-2.101158	0.113345
H	-0.116662	-1.848264	1.195666
H	1.361575	-3.105140	-0.459196
H	-0.059298	-3.406167	-1.449178
H	0.422811	-5.357522	0.038289
H	-1.152828	-4.656159	0.452924
H	0.260838	-4.333942	1.476797
F	-7.245774	-2.146848	-0.792616
F	-7.218493	-0.835066	0.965513
F	-7.596532	0.006349	-1.023810

Truncated Salen(Cr)Cl-(*N*-^{n}propyl-2-(*p*-nitrophenyl)aziridine)
65

C	5.046606	-2.678307	0.369973
C	3.964181	-1.758501	0.288483
C	3.488811	-1.338902	-1.012515
C	4.138781	-1.885144	-2.156742
C	5.191541	-2.780423	-2.033832
C	5.658253	-3.188876	-0.762831
C	3.396978	-1.284083	1.515779
N	2.387446	-0.458241	1.630695
C	2.073564	0.104117	2.953657
C	0.691728	0.767560	2.900028
N	0.579585	1.495643	1.634123
C	0.029874	2.679524	1.591171
C	-0.120521	3.489196	0.416956
C	0.228999	3.022634	-0.905406
C	-0.004077	3.908026	-1.995392
C	-0.530173	5.178037	-1.795704
C	-0.856800	5.639564	-0.500753
C	-0.656129	4.795198	0.579923
O	0.705353	1.823739	-1.148620
C	1.575977	0.610024	0.110015
O	2.491262	-0.512259	-1.191700
N	-0.298006	-0.861159	-0.340323
C	-0.550996	-2.108701	0.432856
C	0.455025	-3.233163	0.172724
C	0.157722	-4.465458	1.038880
C	-1.514840	-0.178136	-0.923166
C	-0.591983	-0.952345	-1.787906
C	-2.926924	-0.581463	-0.623633
C	-3.707833	-1.290604	-1.556674
C	-5.050754	-1.583197	-1.304036
C	-5.617477	-1.164243	-0.096957
C	-4.873602	-0.449855	0.849990
C	-3.538486	-0.155799	0.573354
N	-7.039419	-1.468070	0.179405
C	3.322933	2.090934	0.329672
H	0.550946	1.434182	3.765841
H	2.105142	-0.667810	3.739621
H	0.261423	3.559564	-2.992811
H	3.785213	-1.558800	-3.133981
H	-1.255916	6.642617	-0.354114
H	6.490081	-3.887282	-0.676649
H	-0.097571	-0.000393	2.939780
H	2.828330	0.871410	3.182057
H	3.873261	-1.645722	2.437776
H	-0.344779	3.112431	2.529419
H	5.397745	-2.979856	1.359086
H	5.668040	-3.170013	-2.934565
H	-0.903549	5.131116	1.589567
H	-0.688433	5.830934	-2.656048
H	-1.372308	0.899993	-0.938327
H	0.110729	-0.422210	-2.427229
H	-0.911801	-1.928283	-2.155968
H	-3.270170	-1.600347	-2.504500
H	-2.959891	0.418561	1.296415
H	-5.343341	-0.128084	1.775679
H	-5.657559	-2.117599	-2.031369
H	-1.563006	-2.487651	0.220479
H	-0.533611	-1.832209	1.495652
H	1.472828	-2.882755	0.368991
H	0.422986	-3.518612	-0.888730
H	0.879124	-5.267594	0.831028
H	-0.849563	-4.864949	0.848739
H	0.224103	-4.229310	2.111253
O	-7.675054	-2.088444	-0.686192
O	-7.512003	-1.082220	1.259547

N-^{n}propyl-2-(4-dimethylaminophenyl)aziridine
35

C	0.025675	-0.607498	0.179751
C	-0.431617	0.688826	0.468143
C	-1.784994	1.022687	0.392547
C	-2.763983	0.060790	0.032438
C	-2.295141	-1.239658	-0.284872
C	-0.937136	-1.555848	-0.203223
N	-4.125754	0.371119	0.006909
C	1.468634	-0.983273	0.258424
N	2.486824	0.070704	0.339512
C	3.684315	-0.096454	-0.487816
C	4.838193	0.784847	0.004486

C	6.083422	0.692063	-0.885630
C	2.327164	-0.821613	1.485315
H	1.730989	-1.857597	-0.350333
H	3.093778	-1.584727	1.664928
H	1.908245	-0.368973	2.386296
H	3.410355	0.190572	-1.515219
H	4.009633	-1.157946	-0.524125
H	4.486457	1.826404	0.050325
H	5.097990	0.500104	1.036369
H	6.472746	-0.335870	-0.932257
H	6.890614	1.333739	-0.504942
H	0.294675	1.457886	0.730972
H	-0.623522	-2.571544	-0.455354
H	-2.988926	-2.016423	-0.595901
H	-2.072071	2.047892	0.613246
H	5.865823	1.011254	-1.915800
C	-5.054305	-0.545790	-0.636795
C	-4.544906	1.756789	0.147184
H	-6.072045	-0.153612	-0.536175
H	-4.844632	-0.686934	-1.714462
H	-5.034131	-1.533192	-0.153253
H	-5.638989	1.795685	0.183773
H	-4.171972	2.183670	1.088424
H	-4.203886	2.404096	-0.683619

N-^{n}propyl-2-(4-hydroxyphenyl)aziridine
28

C	0.840818	-0.436941	0.006323
C	1.206081	0.890103	-0.285902
C	2.538001	1.306085	-0.221463
C	3.539852	0.391786	0.136215
C	3.196209	-0.935807	0.433518
C	1.856964	-1.337124	0.369307
O	4.836160	0.856966	0.182802
C	-0.576922	-0.908010	-0.063189
N	-1.647726	0.056684	-0.323415
C	-2.872518	-0.078076	0.471189
C	-4.063586	0.615537	-0.198984
C	-5.342074	0.529851	0.645084
C	-1.384587	-0.965615	-1.333429
H	-0.813277	-1.710088	0.647220
H	-2.096928	-1.792608	-1.435470
H	-0.951207	-0.607008	-2.269062
H	-2.676092	0.384655	1.450546
H	-3.122553	-1.143126	0.661621
H	-3.798987	1.668032	-0.381123
H	-4.236630	0.162270	-1.187515
H	-5.654092	-0.514110	0.800121
H	-6.176738	1.055199	0.160523
H	0.427585	1.603343	-0.555090
H	1.604706	-2.372179	0.608652
H	3.969021	-1.654027	0.718662
H	2.814294	2.336819	-0.442403
H	-5.196767	0.982563	1.637599
H	5.430216	0.121146	0.415843

N-^{n}propyl-2-(4-methoxyphenyl)aziridine
31

C	-0.375720	-0.423899	0.071220
C	-0.745160	0.901777	0.372252
C	-2.077849	1.307593	0.319510
C	-3.086912	0.392589	-0.034438
C	-2.737595	-0.933005	-0.340821
C	-1.391585	-1.322722	-0.286051
O	-4.366189	0.893518	-0.053882
C	1.043608	-0.890136	0.125503
N	2.121399	0.084790	0.315875
C	3.324844	-0.086539	-0.503318
C	4.539731	0.609472	0.121031
C	5.801317	0.474980	-0.741902
C	1.885861	-0.894109	1.374326
H	1.262181	-1.720582	-0.557370
H	2.600011	-1.717378	1.492748
H	1.477652	-0.496619	2.305566
H	3.111288	0.352172	-1.489991
H	3.557241	-1.159440	-0.670718
H	4.295453	1.671655	0.273199
H	4.723590	0.185911	1.120648
H	6.094933	-0.578366	-0.865585
H	6.651842	1.004064	-0.290346
H	0.030849	1.619445	0.637115
H	-1.137215	-2.355900	-0.532281
H	-3.490415	-1.665880	-0.624227
H	-2.358821	2.335906	0.546500
H	5.644591	0.895315	-1.746797
C	-5.435261	0.004595	-0.363862
H	-6.346773	0.609048	-0.303537
H	-5.339911	-0.408452	-1.380628
H	-5.494997	-0.820738	0.364176

N-^{n}propyl-2-(4-methylphenyl)aziridine
30

C	0.811084	-0.447631	-0.017688
C	1.190503	0.868492	-0.337113
C	2.530229	1.262072	-0.265082
C	3.541549	0.363372	0.123758
C	3.156130	-0.950560	0.439227
C	1.815556	-1.349137	0.372184
C	4.986604	0.803715	0.204659
C	-0.610283	-0.906652	-0.082356
N	-1.677770	0.067144	-0.327240
C	-2.897701	-0.069774	0.474398
C	-4.091404	0.631001	-0.183776
C	-5.364896	0.541676	0.667420
C	-1.426103	-0.946054	-1.348063
H	-0.846728	-1.714360	0.621356
H	-2.141796	-1.769625	-1.454131
H	-0.995360	-0.581014	-2.282395
H	-2.693742	0.386297	1.455269
H	-3.149120	-1.135372	0.659719
H	-3.825913	1.684284	-0.359993
H	-4.271111	0.184975	-1.174392
H	-5.677832	-0.502813	0.816805
H	-6.201483	1.072207	0.191975
H	0.421640	1.584457	-0.626928
H	1.549675	-2.376475	0.630723

H	3.912762	-1.674973	0.747246
H	2.794149	2.292987	-0.511487
H	-5.212392	0.986808	1.662305
H	5.641375	-0.020255	0.517944
H	5.354144	1.169981	-0.765766
H	5.117979	1.623752	0.927703

N-^{n}propyl-2-(*p*-fluorophenyl)aziridine
27

C	2.545932	-1.304793	0.215277
C	3.518699	-0.374118	-0.144939
C	3.203529	0.949682	-0.447257
C	1.862224	1.344341	-0.380310
C	0.850104	0.437962	-0.014162
C	1.210582	-0.889220	0.279600
C	-0.568066	0.907761	0.057635
N	-1.636472	-0.058363	0.320714
C	-2.864733	0.079329	-0.469584
C	-4.053868	-0.615508	0.202344
C	-5.335253	-0.522758	-0.636733
C	-1.369348	0.961082	1.331893
H	-0.805470	1.711285	-0.650292
H	-2.080437	1.788170	1.439418
H	-0.930260	0.600857	2.264169
H	-2.671416	-0.380247	-1.450908
H	-3.114058	1.145070	-0.655329
H	-3.790763	-1.669448	0.378101
H	-4.222512	-0.166781	1.193648
H	-5.646102	0.522574	-0.784336
H	-6.168813	-1.049451	-0.151918
H	0.430899	-1.600759	0.549071
H	1.603183	2.377538	-0.618896
H	3.990957	1.647585	-0.728754
H	2.832616	-2.332176	0.436030
F	4.825883	-0.772492	-0.203829
H	-5.194461	-0.970015	-1.632276

N-^{n}propyl-2-phenylaziridine
27

H	-0.279656	1.692418	-0.511511
C	-0.083498	0.821062	0.125320
C	-0.872752	0.815204	1.408397
N	-1.206384	-0.100125	0.322482
H	-1.534391	1.669860	1.591422
H	-0.446769	0.357749	2.303412
C	-2.426787	0.176835	-0.442422
H	-2.262028	-0.204381	-1.461543
H	-2.616893	1.267550	-0.530716
C	-3.652185	-0.507716	0.173889
H	-3.443368	-1.584489	0.263769
H	-3.799963	-0.132058	1.198308
C	-4.926601	-0.283359	-0.651635
H	-5.183540	0.784652	-0.716385
H	-5.785940	-0.802644	-0.205544
C	1.305508	0.283709	-0.003592
C	3.958887	-0.655078	-0.244081
C	1.621935	-1.053469	0.297680
C	2.337087	1.140218	-0.430493
C	3.653171	0.677883	-0.548738
C	2.937509	-1.517248	0.177738
H	0.823947	-1.726353	0.610520
H	2.107555	2.179644	-0.674665
H	4.438501	1.358095	-0.882391
H	3.164539	-2.559228	0.409949
H	4.982342	-1.019728	-0.338902
H	-4.808197	-0.658839	-1.679159

N-^{n}propyl-2-(*p*-chlorophenyl)aziridine
27

C	-0.785807	-0.746576	-0.304857
C	-2.132107	-1.123685	-0.263875
C	-3.098181	-0.182278	0.108191
C	-2.731681	1.126345	0.443244
C	-1.379803	1.485744	0.399236
C	-0.388907	0.561325	0.022558
Cl	-4.791982	-0.651163	0.150020
C	1.044308	0.983739	-0.029625
C	1.849843	1.030566	-1.302333
N	2.072699	-0.018396	-0.313273
C	3.308068	0.038479	0.475897
C	4.448100	-0.722079	-0.210701
C	5.729287	-0.747755	0.632378
H	1.308703	1.764080	0.694445
H	2.592131	1.832325	-1.390805
H	1.397318	0.709473	-2.242656
H	3.089906	-0.419847	1.452614
H	3.623294	1.085061	0.671529
H	4.110150	-1.749032	-0.415064
H	4.652417	-0.260737	-1.189634
H	6.110090	0.267234	0.822102
H	6.527035	-1.310484	0.127896
H	-0.025252	-1.475595	-0.582436
H	-1.097162	2.506363	0.664205
H	-3.490187	1.851807	0.734319
H	-2.428562	-2.140500	-0.516245
H	5.555467	-1.223737	1.609465

N-^{n}propyl-2-(*p*-bromophenyl)aziridine
27

C	1.472993	-0.892836	0.381050
C	2.369516	0.067809	-0.100823
C	1.915572	1.319627	-0.530639
C	0.547256	1.604468	-0.470359
C	-0.376776	0.659203	0.009048
C	0.107030	-0.590767	0.432879
C	-1.828025	1.009182	0.061123
N	-2.815170	-0.040981	0.324214
C	-4.043528	-0.023548	-0.478707
C	-5.162004	-0.833680	0.186058
C	-6.430433	-0.900341	-0.673937
C	-2.646014	1.004942	1.326009
H	-2.122397	1.783302	-0.657938
H	-3.420782	1.775055	1.417409
H	-2.187658	0.693151	2.266817
H	-3.796370	-0.463471	-1.456953

H	-4.395658	1.012549	-0.668299
H	-4.788572	-1.849210	0.385592
H	-5.396971	-0.390142	1.166395
H	-6.844363	0.101178	-0.865670
H	-7.214480	-1.492588	-0.181935
H	-0.600951	-1.340562	0.784909
H	0.196167	2.580026	-0.811258
H	2.615469	2.061408	-0.910908
H	1.832600	-1.866585	0.707963
Br	4.242752	-0.326767	-0.194795
H	-6.227672	-1.366545	-1.650218

N-^{n}propyl-2-(*p*-trifluoromethylphenyl)aziridine
30

C	-0.303427	0.626327	-0.001089
C	0.136641	-0.670917	0.311846
C	1.495349	-0.997296	0.263726
C	2.440558	-0.027490	-0.100933
C	2.012365	1.272311	-0.418914
C	0.654118	1.589775	-0.370386
C	3.914694	-0.337476	-0.106855
C	-1.747918	1.002962	0.053753
N	-2.749422	-0.033983	0.309911
C	-3.984655	0.011158	-0.481782
C	-5.110036	-0.783552	0.190053
C	-6.388781	-0.821775	-0.656229
C	-2.557811	0.994664	1.324693
H	-2.030453	1.793434	-0.652069
H	-3.318305	1.776723	1.431067
H	-2.098420	0.663185	2.258044
H	-3.754882	-0.426361	-1.465183
H	-4.319802	1.054449	-0.660647
H	-4.752263	-1.806741	0.378855
H	-5.325910	-0.342323	1.175719
H	-6.787875	0.188216	-0.834366
H	-7.176859	-1.405130	-0.160181
H	-0.600469	-1.427045	0.578741
H	0.333471	2.601181	-0.625624
H	2.737012	2.033163	-0.706503
H	1.816357	-2.009203	0.504419
H	-6.204706	-1.282760	-1.638552
F	4.549474	0.190636	-1.199172
F	4.549186	0.189000	0.992438
F	4.181360	-1.675282	-0.103469

N-^{n}propyl-2-(*p*-nitrophenyl)aziridine
29

C	-0.105985	-0.599651	0.074653
C	-0.522224	0.718241	0.344832
C	-1.868792	1.073736	0.262783
C	-2.810729	0.098912	-0.088273
C	-2.428291	-1.220587	-0.359245
C	-1.077217	-1.558521	-0.275793
N	-4.235279	0.470690	-0.183080
C	1.330022	-0.995333	0.147567
N	2.347402	0.044235	0.324277
C	3.569198	-0.070174	-0.481512
C	4.714474	0.754984	0.115226
C	5.978907	0.718572	-0.752285
C	2.156076	-0.909948	1.407363
H	1.594894	-1.836043	-0.504533
H	2.905711	-1.695229	1.557247
H	1.710878	-0.512261	2.321226
H	3.326568	0.302381	-1.488118
H	3.886102	-1.127797	-0.594150
H	4.371664	1.793228	0.238036
H	4.943257	0.381352	1.125506
H	6.358786	-0.307176	-0.871520
H	6.783575	1.319174	-0.306422
H	0.227613	1.465590	0.599735
H	-0.771375	-2.583097	-0.492969
H	-3.179673	-1.957546	-0.632021
H	-2.195870	2.091752	0.459810
H	5.785635	1.119710	-1.758512
O	-5.046256	-0.414308	-0.502116
O	-4.543308	1.648960	0.060007

N-^{n}propyl-4-(*p*-hydroxyphenyl)oxazolidinone
31

C	-3.340752	-0.695199	0.608680
C	-3.571512	-0.446997	-0.749668
C	-2.604260	0.232500	-1.507126
C	-1.413127	0.655423	-0.909691
C	-1.173065	0.407357	0.456109
C	-2.147895	-0.266948	1.208786
C	0.114418	0.901445	1.109908
C	0.410793	2.395447	0.778659
O	1.259371	2.345888	-0.440671
C	1.938408	1.083449	-0.413467
N	1.347708	0.296576	0.561737
O	2.872066	0.802737	-1.160826
C	1.787999	-1.099653	0.750600
C	1.280696	-2.069076	-0.343241
C	1.796110	-3.504662	-0.104045
H	0.979765	2.869481	1.590601
H	0.065530	0.746512	2.195710
H	2.887139	-1.085373	0.730508
H	1.463426	-1.429165	1.746987
H	1.646369	-1.693694	-1.309029
H	0.184138	-2.056264	-0.362363
H	2.895670	-3.528612	-0.088785
H	1.453088	-4.175597	-0.904329
H	1.428420	-3.902315	0.853635
H	-1.979010	-0.457720	2.267771
H	-0.665577	1.196761	-1.482907
H	-2.780511	0.435789	-2.561242
H	-4.087959	-1.217388	1.202482
O	-4.765691	-0.868702	-1.346410
H	-0.493377	2.962018	0.545525
H	-5.303100	-1.307214	-0.701655

N-^{n}propyl-5-(*p*-hydroxyphenyl)oxazolidinone
31

C	-4.046842	1.119689	-0.531431
C	-4.406840	0.702507	0.758435
C	-3.535222	-0.113021	1.493822
C	-2.306458	-0.506052	0.949953
C	-1.941363	-0.084891	-0.339274
C	-2.821552	0.722630	-1.079615
C	-0.609196	-0.479396	-0.932491
O	-0.047164	-1.650462	-0.208871
C	1.371160	-1.480856	-0.122326
N	1.681575	-0.205855	-0.562246
C	0.490362	0.622593	-0.778785
O	2.130124	-2.364636	0.266694
C	3.062176	0.292608	-0.506102
C	3.361573	1.198493	0.713464
C	4.854869	1.596411	0.741462
H	-0.716193	-0.757069	-1.991619
H	0.269810	1.271620	0.081797
H	0.575584	1.230179	-1.688889
H	3.690119	-0.606559	-0.451403
H	3.289587	0.829365	-1.440490
H	3.101469	0.646535	1.628773
H	2.736814	2.102991	0.674458
H	5.487362	0.697926	0.779543
H	5.079472	2.213092	1.622645
H	5.125357	2.169789	-0.158126
H	-2.553478	1.035553	-2.087655
H	-1.634714	-1.160530	1.495281
H	-3.817661	-0.450916	2.488777
H	-4.723279	1.742348	-1.112088
O	-5.638820	1.086923	1.301066
H	-6.101188	1.631842	0.679706

N-^{n}propyl-4-(*p*-methoxyphenyl)oxazolidinone

34

C	-3.340752	-0.695199	0.608680
C	-3.571512	-0.446997	-0.749668
C	-2.604260	0.232500	-1.507126
C	-1.413127	0.655423	-0.909691
C	-1.173065	0.407357	0.456109
C	-2.147895	-0.266948	1.208786
C	0.114418	0.901445	1.109908
C	0.410793	2.395447	0.778659
O	1.259371	2.345888	-0.440671
C	1.938408	1.083449	-0.413467
N	1.347708	0.296576	0.561737
O	2.872066	0.802737	-1.160826
C	1.787999	-1.099653	0.750600
C	1.280696	-2.069076	-0.343241
C	1.796110	-3.504662	-0.104045
H	0.979765	2.869481	1.590601
H	0.065530	0.746512	2.195710
H	2.887139	-1.085373	0.730508
H	1.463426	-1.429165	1.746987
H	1.646369	-1.693694	-1.309029
H	0.184138	-2.056264	-0.362363
H	2.895670	-3.528612	-0.088785
H	1.453088	-4.175597	-0.904329
H	1.428420	-3.902315	0.853635
H	-1.979010	-0.457720	2.267771
H	-0.665577	1.196761	-1.482907
H	-2.780511	0.435789	-2.561242
H	-4.087959	-1.217388	1.202482
O	-4.765691	-0.868702	-1.346410
H	-0.493377	2.962018	0.545525
C	-5.560171	-1.516977	-0.393235
H	-6.489072	-1.845003	-0.857415
H	-5.025161	-2.380923	-0.001722
H	-5.784272	-0.829270	0.420865

N-^{n}propyl-5-(*p*-methoxyphenyl)oxazolidinone

34

C	-4.046842	1.119689	-0.531431
C	-4.406840	0.702507	0.758435
C	-3.535222	-0.113021	1.493822
C	-2.306458	-0.506052	0.949953
C	-1.941363	-0.084891	-0.339274
C	-2.821552	0.722630	-1.079615
C	-0.609196	-0.479396	-0.932491
O	-0.047164	-1.650462	-0.208871
C	1.371160	-1.480856	-0.122326
N	1.681575	-0.205855	-0.562246
C	0.490362	0.622593	-0.778785
O	2.130124	-2.364636	0.266694
C	3.062176	0.292608	-0.506102
C	3.361573	1.198493	0.713464
C	4.854869	1.596411	0.741462
H	-0.716193	-0.757069	-1.991619
H	0.269810	1.271620	0.081797
H	0.575584	1.230179	-1.688889
H	3.690119	-0.606559	-0.451403
H	3.289587	0.829365	-1.440490
H	3.101469	0.646535	1.628773
H	2.736814	2.102991	0.674458
H	5.487362	0.697926	0.779543
H	5.079472	2.213092	1.622645
H	5.125357	2.169789	-0.158126
H	-2.553478	1.035553	-2.087655
H	-1.634714	-1.160530	1.495281
H	-3.817661	-0.450916	2.488777
H	-4.723279	1.742348	-1.112088
O	-5.638820	1.086923	1.301066
C	-6.322362	1.892505	0.382476

H	-7.280667	2.191526	0.804566
H	-5.728809	2.779319	0.165276
H	-6.489310	1.333298	-0.536946

N-^{n}propyl-4-(*p*-methylphenyl)oxazolidinone
33

C	-3.340752	-0.695199	0.608680
C	-3.571512	-0.446997	-0.749668
C	-2.604260	0.232500	-1.507126
C	-1.413127	0.655423	-0.909691
C	-1.173065	0.407357	0.456109
C	-2.147895	-0.266948	1.208786
C	0.114418	0.901445	1.109908
C	0.410793	2.395447	0.778659
O	1.259371	2.345888	-0.440671
C	1.938408	1.083449	-0.413467
N	1.347708	0.296576	0.561737
O	2.872066	0.802737	-1.160826
C	1.787999	-1.099653	0.750600
C	1.280696	-2.069076	-0.343241
C	1.796110	-3.504662	-0.104045
H	0.979765	2.869481	1.590601
H	0.065530	0.746512	2.195710
H	2.887139	-1.085373	0.730508
H	1.463426	-1.429165	1.746987
H	1.646369	-1.693694	-1.309029
H	0.184138	-2.056264	-0.362363
H	2.895670	-3.528612	-0.088785
H	1.453088	-4.175597	-0.904329
H	1.428420	-3.902315	0.853635
H	-1.979010	-0.457720	2.267771
H	-0.665577	1.196761	-1.482907
H	-2.780511	0.435789	-2.561242
H	-4.087959	-1.217388	1.202482
C	-4.808341	-0.883763	-1.367722
H	-0.493377	2.962018	0.545525
H	-5.426332	-1.388028	-0.626288
H	-5.343351	-0.019817	-1.759235
H	-4.584239	-1.571470	-2.181822

N-^{n}propyl-5-(*p*-methylphenyl)oxazolidinone
33

C	-4.046842	1.119689	-0.531431
C	-4.406840	0.702507	0.758435
C	-3.535222	-0.113021	1.493822
C	-2.306458	-0.506052	0.949953
C	-1.941363	-0.084891	-0.339274
C	-2.821552	0.722630	-1.079615
C	-0.609196	-0.479396	-0.932491
O	-0.047164	-1.650462	-0.208871
C	1.371160	-1.480856	-0.122326
N	1.681575	-0.205855	-0.562246
C	0.490362	0.622593	-0.778785
O	2.130124	-2.364636	0.266694
C	3.062176	0.292608	-0.506102
C	3.361573	1.198493	0.713464
C	4.854869	1.596411	0.741462
H	-0.716193	-0.757069	-1.991619
H	0.269810	1.271620	0.081797
H	0.575584	1.230179	-1.688889
H	3.690119	-0.606559	-0.451403
H	3.289587	0.829365	-1.440490
H	3.101469	0.646535	1.628773
H	2.736814	2.102991	0.674458
H	5.487362	0.697926	0.779543
H	5.079472	2.213092	1.622645
H	5.125357	2.169789	-0.158126
H	-2.553478	1.035553	-2.087655
H	-1.634714	-1.160530	1.495281
H	-3.817661	-0.450916	2.488777
H	-4.723279	1.742348	-1.112088
C	-5.682819	1.100653	1.320446
H	-6.214518	1.727280	0.605914
H	-6.276373	0.213839	1.537646
H	-5.515872	1.659860	2.239868

N-^{n}propyl-4-(*p*-fluorophenyl)oxazolidinone
30

C	-3.340752	-0.695199	0.608680
C	-3.571512	-0.446997	-0.749668
C	-2.604260	0.232500	-1.507126
C	-1.413127	0.655423	-0.909691
C	-1.173065	0.407357	0.456109
C	-2.147895	-0.266948	1.208786
C	0.114418	0.901445	1.109908
C	0.410793	2.395447	0.778659
O	1.259371	2.345888	-0.440671
C	1.938408	1.083449	-0.413467
N	1.347708	0.296576	0.561737
O	2.872066	0.802737	-1.160826
C	1.787999	-1.099653	0.750600
C	1.280696	-2.069076	-0.343241
C	1.796110	-3.504662	-0.104045
H	0.979765	2.869481	1.590601
H	0.065530	0.746512	2.195710
H	2.887139	-1.085373	0.730508
H	1.463426	-1.429165	1.746987
H	1.646369	-1.693694	-1.309029
H	0.184138	-2.056264	-0.362363
H	2.895670	-3.528612	-0.088785
H	1.453088	-4.175597	-0.904329
H	1.428420	-3.902315	0.853635
H	-1.979010	-0.457720	2.267771
H	-0.665577	1.196761	-1.482907
H	-2.780511	0.435789	-2.561242
H	-4.087959	-1.217388	1.202482
F	-4.499545	-0.774717	-1.213414
H	-0.493377	2.962018	0.545525

N-^{n}propyl-5-(*p*-fluorophenyl)oxazolidinone
30

C	-4.046842	1.119689	-0.531431
C	-4.406840	0.702507	0.758435
C	-3.535222	-0.113021	1.493822
C	-2.306458	-0.506052	0.949953
C	-1.941363	-0.084891	-0.339274
C	-2.821552	0.722630	-1.079615
C	-0.609196	-0.479396	-0.932491
O	-0.047164	-1.650462	-0.208871
C	1.371160	-1.480856	-0.122326
N	1.681575	-0.205855	-0.562246
C	0.490362	0.622593	-0.778785
O	2.130124	-2.364636	0.266694
C	3.062176	0.292608	-0.506102
C	3.361573	1.198493	0.713464
C	4.854869	1.596411	0.741462
H	-0.716193	-0.757069	-1.991619
H	0.269810	1.271620	0.081797
H	0.575584	1.230179	-1.688889
H	3.690119	-0.606559	-0.451403
H	3.289587	0.829365	-1.440490
H	3.101469	0.646535	1.628773
H	2.736814	2.102991	0.674458
H	5.487362	0.697926	0.779543
H	5.079472	2.213092	1.622645
H	5.125357	2.169789	-0.158126
H	-2.553478	1.035553	-2.087655
H	-1.634714	-1.160530	1.495281
H	-3.817661	-0.450916	2.488777
H	-4.723279	1.742348	-1.112088
F	-5.364189	1.001230	1.180104

N-^{n}propyl-4-(phenyl)oxazolidinone
30

C	1.938408	1.083449	-0.413467
O	1.259371	2.345888	-0.440671
C	0.410793	2.395447	0.778659
C	0.114418	0.901445	1.109908
N	1.347708	0.296576	0.561737
H	0.979765	2.869481	1.590601
H	0.065530	0.746512	2.195710
C	1.787999	-1.099653	0.750600
H	2.887139	-1.085373	0.730508
H	1.463426	-1.429165	1.746987
C	1.280696	-2.069076	-0.343241
H	1.646369	-1.693694	-1.309029
H	0.184138	-2.056264	-0.362363
C	1.796110	-3.504662	-0.104045
H	2.895670	-3.528612	-0.088785
H	1.453088	-4.175597	-0.904329
H	1.428420	-3.902315	0.853635
C	-1.173065	0.407357	0.456109
C	-3.571512	-0.446997	-0.749668
C	-2.147895	-0.266948	1.208786
C	-1.413127	0.655423	-0.909691
C	-2.604260	0.232500	-1.507126
C	-3.340752	-0.695199	0.608680
H	-1.979010	-0.457720	2.267771
H	-0.665577	1.196761	-1.482907
H	-2.780511	0.435789	-2.561242
H	-4.087959	-1.217388	1.202482
H	-4.499545	-0.774717	-1.213414
O	2.872066	0.802737	-1.160826
H	-0.493377	2.962018	0.545525

N-^{n}propyl-5-(phenyl)oxazolidinone
30

C	1.371160	-1.480856	-0.122325
O	-0.047164	-1.650462	-0.208871
C	-0.609196	-0.479396	-0.932491
C	0.490362	0.622593	-0.778785
N	1.681575	-0.205855	-0.562245
H	-0.716193	-0.757069	-1.991619
H	0.269810	1.271620	0.081797
H	0.575585	1.230179	-1.688889
C	3.062176	0.292608	-0.506101
H	3.690119	-0.606559	-0.451402
H	3.289588	0.829364	-1.440489
C	3.361573	1.198493	0.713465
H	3.101469	0.646535	1.628774
H	2.736814	2.102991	0.674459
C	4.854869	1.596411	0.741463
H	5.487362	0.697925	0.779544
H	5.079472	2.213091	1.622646
H	5.125358	2.169788	-0.158125
C	-1.941363	-0.084891	-0.339274
C	-4.406840	0.702507	0.758435
C	-2.821552	0.722630	-1.079615
C	-2.306458	-0.506052	0.949953
C	-3.535222	-0.113021	1.493822
C	-4.046842	1.119689	-0.531431
H	-2.553478	1.035553	-2.087655
H	-1.634714	-1.160530	1.495281
H	-3.817661	-0.450916	2.488777
H	-4.723279	1.742348	-1.112088
H	-5.364189	1.001230	1.180104
O	2.130124	-2.364636	0.266695

N-^{n}propyl-4-(*p*-chlorophenyl)oxazolidinone
30

C	-3.340752	-0.695199	0.608680
C	-3.571512	-0.446997	-0.749668
C	-2.604260	0.232500	-1.507126
C	-1.413127	0.655423	-0.909691
C	-1.173065	0.407357	0.456109
C	-2.147895	-0.266948	1.208786
C	0.114418	0.901445	1.109908
C	0.410793	2.395447	0.778659
O	1.259371	2.345888	-0.440671

C	1.938408	1.083449	-0.413467
N	1.347708	0.296576	0.561737
O	2.872066	0.802737	-1.160826
C	1.787999	-1.099653	0.750600
C	1.280696	-2.069076	-0.343241
C	1.796110	-3.504662	-0.104045
H	0.979765	2.869481	1.590601
H	0.065530	0.746512	2.195710
H	2.887139	-1.085373	0.730508
H	1.463426	-1.429165	1.746987
H	1.646369	-1.693694	-1.309029
H	0.184138	-2.056264	-0.362363
H	2.895670	-3.528612	-0.088785
H	1.453088	-4.175597	-0.904329
H	1.428420	-3.902315	0.853635
H	-1.979010	-0.457720	2.267771
H	-0.665577	1.196761	-1.482907
H	-2.780511	0.435789	-2.561242
H	-4.087959	-1.217388	1.202482
Cl	-4.499545	-0.774717	-1.213414
H	-0.493377	2.962018	0.545525

N-^{n}propyl-5-(*p*-chlorophenyl)oxazolidinone
30

C	-4.046842	1.119689	-0.531431
C	-4.406840	0.702507	0.758435
C	-3.535222	-0.113021	1.493822
C	-2.306458	-0.506052	0.949953
C	-1.941363	-0.084891	-0.339274
C	-2.821552	0.722630	-1.079615
C	-0.609196	-0.479396	-0.932491
O	-0.047164	-1.650462	-0.208871
C	1.371160	-1.480856	-0.122326
N	1.681575	-0.205855	-0.562246
C	0.490362	0.622593	-0.778785
O	2.130124	-2.364636	0.266694
C	3.062176	0.292608	-0.506102
C	3.361573	1.198493	0.713464
C	4.854869	1.596411	0.741462
H	-0.716193	-0.757069	-1.991619
H	0.269810	1.271620	0.081797
H	0.575584	1.230179	-1.688889
H	3.690119	-0.606559	-0.451403
H	3.289587	0.829365	-1.440490
H	3.101469	0.646535	1.628773
H	2.736814	2.102991	0.674458
H	5.487362	0.697926	0.779543
H	5.079472	2.213092	1.622645
H	5.125357	2.169789	-0.158126
H	-2.553478	1.035553	-2.087655
H	-1.634714	-1.160530	1.495281
H	-3.817661	-0.450916	2.488777
H	-4.723279	1.742348	-1.112088
Cl	-5.364189	1.001230	1.180104

N-^{n}propyl-4-(*p*-bromophenyl)oxazolidinone
30

C	-3.340752	-0.695199	0.608680
C	-3.571512	-0.446997	-0.749668
C	-2.604260	0.232500	-1.507126
C	-1.413127	0.655423	-0.909691
C	-1.173065	0.407357	0.456109
C	-2.147895	-0.266948	1.208786
C	0.114418	0.901445	1.109908
C	0.410793	2.395447	0.778659
O	1.259371	2.345888	-0.440671
C	1.938408	1.083449	-0.413467
N	1.347708	0.296576	0.561737
O	2.872066	0.802737	-1.160826
C	1.787999	-1.099653	0.750600
C	1.280696	-2.069076	-0.343241
C	1.796110	-3.504662	-0.104045
H	0.979765	2.869481	1.590601
H	0.065530	0.746512	2.195710
H	2.887139	-1.085373	0.730508
H	1.463426	-1.429165	1.746987
H	1.646369	-1.693694	-1.309029
H	0.184138	-2.056264	-0.362363
H	2.895670	-3.528612	-0.088785
H	1.453088	-4.175597	-0.904329
H	1.428420	-3.902315	0.853635
H	-1.979010	-0.457720	2.267771
H	-0.665577	1.196761	-1.482907
H	-2.780511	0.435789	-2.561242
H	-4.087959	-1.217388	1.202482
Br	-4.936288	-0.928946	-1.431658
H	-0.493377	2.962018	0.545525

N-^{n}propyl-5-(*p*-bromophenyl)oxazolidinone
30

C	-4.046842	1.119689	-0.531431
C	-4.406840	0.702507	0.758435
C	-3.535222	-0.113021	1.493822
C	-2.306458	-0.506052	0.949953
C	-1.941363	-0.084891	-0.339274
C	-2.821552	0.722630	-1.079615
C	-0.609196	-0.479396	-0.932491
O	-0.047164	-1.650462	-0.208871
C	1.371160	-1.480856	-0.122326
N	1.681575	-0.205855	-0.562246
C	0.490362	0.622593	-0.778785
O	2.130124	-2.364636	0.266694
C	3.062176	0.292608	-0.506102
C	3.361573	1.198493	0.713464
C	4.854869	1.596411	0.741462
H	-0.716193	-0.757069	-1.991619
H	0.269810	1.271620	0.081797
H	0.575584	1.230179	-1.688889
H	3.690119	-0.606559	-0.451403
H	3.289587	0.829365	-1.440490
H	3.101469	0.646535	1.628773
H	2.736814	2.102991	0.674458
H	5.487362	0.697926	0.779543
H	5.079472	2.213092	1.622645
H	5.125357	2.169789	-0.158126
H	-2.553478	1.035553	-2.087655

H -1.634714 -1.160530 1.495281
H -3.817661 -0.450916 2.488777
H -4.723279 1.742348 -1.112088
Br -5.726819 1.114382 1.339826

N-^{n}propyl-4-(*p*-nitrophenyl)oxazolidinone
32

C -3.340752 -0.695199 0.608680
C -3.571512 -0.446997 -0.749668
C -2.604260 0.232500 -1.507126
C -1.413127 0.655423 -0.909691
C -1.173065 0.407357 0.456109
C -2.147895 -0.266948 1.208786
C 0.114418 0.901445 1.109908
C 0.410793 2.395447 0.778659
O 1.259371 2.345888 -0.440671
C 1.938408 1.083449 -0.413467
N 1.347708 0.296576 0.561737
O 2.872066 0.802737 -1.160826
C 1.787999 -1.099653 0.750600
C 1.280696 -2.069076 -0.343241
C 1.796110 -3.504662 -0.104045
H 0.979765 2.869481 1.590601
H 0.065530 0.746512 2.195710
H 2.887139 -1.085373 0.730508
H 1.463426 -1.429165 1.746987
H 1.646369 -1.693694 -1.309029
H 0.184138 -2.056264 -0.362363
H 2.895670 -3.528612 -0.088785
H 1.453088 -4.175597 -0.904329
H 1.428420 -3.902315 0.853635
H -1.979010 -0.457720 2.267771
H -0.665577 1.196761 -1.482907
H -2.780511 0.435789 -2.561242
H -4.087959 -1.217388 1.202482
N -4.799811 -0.880751 -1.363459
H -0.493377 2.962018 0.545525
O -5.597162 -1.461652 -0.662828
O -4.951586 -0.634992 -2.538477

N-^{n}propyl-5-(*p*-nitrophenyl)oxazolidinone
32

C -4.046842 1.119689 -0.531431
C -4.406840 0.702507 0.758435
C -3.535222 -0.113021 1.493822
C -2.306458 -0.506052 0.949953
C -1.941363 -0.084891 -0.339274
C -2.821552 0.722630 -1.079615
C -0.609196 -0.479396 -0.932491
O -0.047164 -1.650462 -0.208871
C 1.371160 -1.480856 -0.122326
N 1.681575 -0.205855 -0.562246
C 0.490362 0.622593 -0.778785
O 2.130124 -2.364636 0.266694
C 3.062176 0.292608 -0.506102
C 3.361573 1.198493 0.713464
C 4.854869 1.596411 0.741462
H -0.716193 -0.757069 -1.991619
H 0.269810 1.271620 0.081797
H 0.575584 1.230179 -1.688889
H 3.690119 -0.606559 -0.451403
H 3.289587 0.829365 -1.440490
H 3.101469 0.646535 1.628773
H 2.736814 2.102991 0.674458
H 5.487362 0.697926 0.779543
H 5.079472 2.213092 1.622645
H 5.125357 2.169789 -0.158126
H -2.553478 1.035553 -2.087655
H -1.634714 -1.160530 1.495281
H -3.817661 -0.450916 2.488777
H -4.723279 1.742348 -1.112088
N -5.674020 1.097907 1.316570
O -6.385834 1.802155 0.637265
O -5.941386 0.699150 2.427249

Trans ligand Geometries

CH_3CN–Truncated Salen(Cr)–*N*-^{n}propyl-2-phenylaziridine
68

C -1.766264 3.622648 -1.759408
C -1.302514 2.740562 -0.748042
C -1.086254 3.282671 0.571620
C -1.344970 4.661141 0.812213
C -1.805648 5.496494 -0.192396
C -2.011385 4.963576 -1.484442
C -0.597496 2.489706 1.659611
N -0.367040 1.200978 1.625090
Cr -0.851248 -0.039542 0.104004
N -2.875083 0.219072 0.568866
C -4.031510 0.348228 0.625509
O -1.068589 1.481682 -1.062166
C 0.125232 0.502339 2.817783
C -0.634608 -0.823649 2.944891
N -0.806397 -1.413975 1.602692
C -1.186635 -2.668256 1.507995
C -1.615666 -3.335053 0.316441
C -1.940414 -4.720277 0.405966
C -2.391468 -5.430075 -0.693408
C -2.537941 -4.759524 -1.929656
C -2.237648 -3.409419 -2.057330
C -1.764125 -2.653953 -0.950576
O -1.472842 -1.385802 -1.134550
N 1.224929 -0.389118 -0.593575
C 2.278526 -1.155294 0.224686
C 3.743284 -0.847848 0.232959
C 4.295818 -0.227000 1.372066
C 5.665029 0.040967 1.457362
C 6.515643 -0.318310 0.403477
C 5.986418 -0.956658 -0.723892
C 4.614487 -1.223818 -0.806457
C 1.752671 0.566088 -1.625052
C 2.244222 1.904121 -1.071784

C	2.766219	2.811968	-2.195619
C	1.544843	-1.811381	-0.881947
H	1.982825	3.034543	-2.933348
H	3.610400	2.351689	-2.728007
H	3.118210	3.767948	-1.785598
H	3.045127	1.724750	-0.343664
H	1.433388	2.412876	-0.541122
H	2.578502	0.081548	-2.163350
H	0.938123	0.717397	-2.342760
H	2.044187	-1.995794	-1.832689
H	0.771410	-2.533787	-0.645469
H	1.886001	-1.372546	1.216573
H	4.235237	-1.745859	-1.683098
H	6.642733	-1.257236	-1.540789
H	7.584686	-0.114878	0.468123
H	6.069323	0.522065	2.347741
H	3.645248	0.049163	2.203349
H	-2.346563	-2.894143	-3.010937
H	-2.895829	-5.308870	-2.801158
H	-2.632025	-6.488584	-0.608026
H	-1.829339	-5.220189	1.369824
H	-1.197694	-3.268488	2.428573
H	-0.113458	-1.514275	3.626130
H	-1.632538	-0.628461	3.366897
H	-0.001635	1.111857	3.725797
H	1.199952	0.311635	2.696128
H	-0.400956	3.019654	2.600993
H	-1.174929	5.056347	1.815526
H	-2.002231	6.548807	0.007712
H	-2.369254	5.613050	-2.284645
H	-1.922322	3.215740	-2.757775
C	-5.476910	0.496925	0.668432
H	-5.934758	-0.383713	1.137560
H	-5.753670	1.392628	1.239930
H	-5.866050	0.595224	-0.353986

THF—Truncated Salen(Cr)—*N*-^{n}propyl-2-phenylaziridine
75

C	0.881318	-4.598536	-0.945193
C	0.439576	-3.267159	-0.701705
C	0.032414	-2.888971	0.628255
C	0.074131	-3.880933	1.642750
C	0.509094	-5.171962	1.366225
C	0.919784	-5.543786	0.066559
C	0.390931	-2.360102	-1.807859
N	-0.012847	-1.112490	-1.765226
C	-0.007897	-0.306486	-2.996836
C	-1.145445	0.717745	-2.926118
N	-1.248879	1.236132	-1.549921
C	-1.866624	2.376244	-1.342534
C	-2.212699	2.922521	-0.063605
C	-2.019489	2.194377	1.170053
C	-2.438555	2.812679	2.377998
C	-3.014129	4.077154	2.375352
C	-3.199883	4.795316	1.171957
C	-2.805305	4.217968	-0.022821
O	-1.500683	0.985913	1.226419
C	-0.702386	-0.119152	-0.135187
O	-2.759235	-0.981840	-0.573788
C	-3.040827	-2.417907	-0.575579
C	-4.555824	-2.559298	-0.831101
O	-0.378703	-1.675803	0.943588
N	1.216735	0.831696	0.424513
C	1.862386	0.309803	1.679105
C	2.769214	-0.907925	1.503733
C	3.382652	-1.333018	2.846158
C	2.122722	1.572263	-0.569682
C	1.219201	2.315325	0.336865
C	3.617199	1.612835	-0.527217
C	4.340385	2.440097	0.351543
C	5.738670	2.496306	0.295352
C	6.439863	1.732457	-0.645059
C	5.731954	0.915075	-1.536545
C	4.336330	0.861345	-1.479577
C	-3.970827	-0.346790	-0.064299
C	-5.098825	-1.110963	-0.749208
H	2.608943	-1.578953	3.587252
H	4.012698	-0.538621	3.271498
H	4.015166	-2.221643	2.717169
H	3.570702	-0.670848	0.794978
H	2.206719	-1.742815	1.078424
H	2.450270	1.124205	2.125627
H	1.036374	0.091857	2.365934
H	1.626863	2.829875	1.205125
H	0.331003	2.781114	-0.071478
H	1.740179	1.433873	-1.578388
H	3.821621	3.066663	1.076293
H	6.276744	3.149978	0.982666
H	7.527811	1.784441	-0.693326
H	6.265109	0.327384	-2.284423
H	3.797743	0.228507	-2.187250
H	-2.303304	2.256968	3.305292
H	-3.331220	4.519456	3.320542
H	-3.653027	5.785043	1.185163
H	-2.945213	4.758276	-0.960911
H	-2.163305	2.968047	-2.219147
H	-0.981152	1.529770	-3.650699
H	-2.096019	0.225866	-3.179803
H	-0.116010	-0.939048	-3.890835
H	0.959035	0.210472	-3.078932
H	0.708608	-2.763832	-2.778440
H	1.188108	-4.869048	-1.957225
H	1.257136	-6.558884	-0.136832
H	0.533338	-5.908518	2.171006
H	-0.237375	-3.593511	2.645853
H	-3.994771	-0.453362	1.030537
H	-3.916944	0.712358	-0.322062
H	-6.039548	-1.039095	-0.189723
H	-5.273164	-0.705252	-1.754408
H	-5.011076	-3.204120	-0.069254
H	-4.764978	-3.007447	-1.809679
H	-2.747214	-2.826950	0.398248
H	-2.415336	-2.856166	-1.357110

N-^{n}propyl-2-phenylaziridine—Truncated Salen(Cr)—*N*-^{n}propyl-2-phenylaziridine
89

C	5.792623	-1.376017	1.903797
C	6.945509	-0.657328	1.559338

C	6.821984	0.556416	0.873814
C	5.555140	1.042718	0.526453
C	4.389812	0.323370	0.853379
C	4.527987	-0.887034	1.560370
C	3.025266	0.865992	0.552327
C	2.781307	1.852730	-0.521450
N	2.209406	0.489215	-0.693642
C	2.937241	-0.320130	-1.722937
C	2.874925	0.228949	-3.154028
C	3.609287	-0.689165	-4.143069
Cr	0.000361	0.064014	-0.166202
N	-2.147678	-0.420881	0.705557
C	-2.711470	0.545759	1.702333
C	-3.355429	1.793546	1.099027
C	-3.937762	2.706905	2.187541
N	-0.760315	1.100790	-1.716412
C	-0.841991	2.405220	-1.811243
C	-0.489447	3.345632	-0.789038
C	-0.092941	2.937836	0.537778
C	0.175201	3.954232	1.491041
C	0.067909	5.299941	1.155645
C	-0.309281	5.702818	-0.144236
C	-0.586711	4.732187	-1.093250
O	0.030812	1.673816	0.900572
H	-0.389769	6.759477	-0.393969
H	0.473419	3.646811	2.492407
N	-0.153347	-1.472950	-1.472956
C	0.203036	-2.719942	-1.259699
C	0.730505	-3.250347	-0.040575
C	0.937837	-2.437504	1.137369
C	1.402563	-3.084507	2.314575
C	1.670963	-4.447859	2.328406
C	1.490031	-5.240919	1.171981
C	1.023007	-4.643618	0.014248
O	0.696401	-1.145788	1.176143
H	1.706376	-6.307856	1.195284
H	1.529230	-2.475647	3.209175
C	-1.328706	0.258369	-2.779106
C	-0.594681	-1.089659	-2.829401
H	-1.247602	-1.862263	-3.263140
C	-3.167164	-1.332997	0.010848
C	-4.656320	-1.184390	0.076866
C	-5.417920	-1.594891	1.187363
C	-6.814151	-1.487153	1.181772
C	-7.478773	-0.976216	0.061322
C	-6.737574	-0.583572	-1.060852
C	-5.343585	-0.692383	-1.051550
C	-2.319364	-1.833895	1.117150
H	0.288411	-1.011477	-3.476222
H	0.282758	6.055192	1.913065
H	-0.887580	5.024175	-2.100809
H	0.862658	-5.246883	-0.881409
H	2.027579	-4.911125	3.249018
H	-1.237332	2.832286	-2.742470
H	0.086215	-3.433381	-2.086907
H	-2.810367	-1.584011	-0.985927
H	-1.505791	-2.511764	0.892070
H	-2.759267	-1.982049	2.102858
H	-4.931082	-2.024050	2.061302
H	-4.783936	-0.386618	-1.936564
H	-7.243467	-0.195644	-1.944864
H	-7.381025	-1.816128	2.052788
H	-8.565852	-0.893318	0.057181
H	-3.461627	0.025509	2.315724
H	-1.882896	0.817769	2.367508
H	-4.156595	1.500619	0.408662
H	-2.615802	2.346254	0.511757
H	-4.732392	2.200617	2.754128
H	-4.376721	3.608752	1.740865
H	-3.169383	3.032376	2.902895
H	2.084335	2.669781	-0.373270
H	3.602112	2.087396	-1.197831
H	2.356314	0.917387	1.409595
H	3.639461	-1.448337	1.842470
H	5.482990	2.003747	0.017247
H	7.709839	1.133393	0.613897
H	5.876772	-2.317397	2.447749
H	7.930674	-1.035062	1.833318
H	2.534589	-1.336252	-1.680218
H	3.992154	-0.393135	-1.426717
H	3.333170	1.227487	-3.192034
H	1.836803	0.367473	-3.481590
H	3.166418	-1.695087	-4.175776
H	4.668364	-0.805128	-3.873560
H	3.570245	-0.275437	-5.159365
H	-1.279039	0.757515	-3.758647
H	-2.390216	0.094974	-2.549022

Cl–Truncated Salen(Cr)–*N*-^{n}propyl-2-phenylaziridine
63

H	-0.908293	0.803878	3.711056
C	-0.412395	0.369997	2.828529
C	1.112683	0.434381	2.985110
H	1.455377	-0.310740	3.721361
N	-0.791229	1.066749	1.597640
C	-1.849124	1.832482	1.561093
C	-2.330186	2.539818	0.408268
C	-1.712651	2.416486	-0.892539
C	-2.303534	3.133086	-1.971717
C	-3.430163	3.922486	-1.785302
C	-4.033675	4.044935	-0.513473
C	-3.483068	3.357774	0.557490
O	-0.673941	1.654664	-1.135514
Cr	0.603154	0.906108	0.139214
O	2.054390	0.554869	-1.107160
C	3.311727	0.295615	-0.873136
C	3.841650	-0.008098	0.438858
C	5.227004	-0.299083	0.580393
C	6.087790	-0.303437	-0.505562
C	5.568460	-0.007496	-1.788078
C	4.224300	0.282581	-1.968524
H	-1.830837	3.044897	-2.949344
C	3.029594	-0.006548	1.619153
N	1.742163	0.225206	1.670090
H	3.825100	0.525106	-2.952971
N	-0.253760	-1.193098	-0.458427
C	0.221453	-2.450677	0.188048
C	1.582158	-2.954346	-0.299824
C	1.941930	-4.308338	0.329706
C	-1.702170	-1.196046	-0.928354
C	-0.587367	-1.327103	-1.896973

C	-2.679231	-2.281510	-0.593168
C	-3.392247	-2.206949	0.620064
C	-4.353612	-3.165752	0.952536
C	-4.633862	-4.215689	0.067109
C	-3.947210	-4.292835	-1.150079
C	-2.978953	-3.333529	-1.477046
Cl	1.378450	3.023720	0.651160
H	-4.914778	4.671359	-0.376173
H	7.146950	-0.522844	-0.373681
H	-0.732310	-0.681204	2.748605
H	1.399567	1.434333	3.343242
H	3.556706	-0.194253	2.565684
H	-2.433174	1.950293	2.485856
H	5.610644	-0.515610	1.580367
H	6.236164	0.001709	-2.651841
H	-3.937945	3.440901	1.546903
H	-3.851646	4.458904	-2.637021
H	-2.118568	-0.196347	-0.841322
H	-0.315643	-0.472210	-2.513209
H	-0.385463	-2.302261	-2.340834
H	-2.467065	-3.398035	-2.436810
H	-3.192631	-1.383535	1.305900
H	-4.891055	-3.089568	1.898907
H	-4.168640	-5.096010	-1.854225
H	-5.387567	-4.962240	0.320498
H	-0.526194	-3.243449	0.037099
H	0.262652	-2.252415	1.266923
H	2.367852	-2.227858	-0.070137
H	1.570253	-3.057223	-1.394689
H	2.927392	-4.648077	-0.017698
H	1.211477	-5.088016	0.067464
H	1.982748	-4.248562	1.428023

DMAP–Truncated Salen(Cr)–*N*-^{n}propyl-2-phenylaziridine
81

C	-0.645650	-4.907814	0.051531
C	-0.522396	-3.489368	-0.002485
C	-0.559925	-2.821467	-1.286942
C	-0.729130	-3.625814	-2.446388
C	-0.853217	-5.005580	-2.349838
C	-0.806351	-5.662324	-1.098251
C	-0.404430	-2.769555	1.232155
N	-0.269909	-1.470745	1.353397
C	-0.370639	-0.851802	2.686412
C	0.394504	0.475801	2.673237
N	0.122553	1.165138	1.402213
C	0.131959	2.475003	1.361304
C	-0.063086	3.277156	0.190869
C	-0.226841	2.700641	-1.125082
C	-0.408448	3.591925	-2.217121
C	-0.410009	4.968547	-2.029067
C	-0.239672	5.535539	-0.745142
C	-0.072589	4.693907	0.341550
O	-0.201246	1.406593	-1.359346
Cr	-0.207945	-0.095621	-0.143419
O	-0.443507	-1.521060	-1.431070
N	2.115679	-0.398172	-0.515285
C	2.773389	0.539376	-1.478146
C	3.196501	1.886652	-0.891275
C	3.775883	2.810214	-1.972929
C	3.033138	-1.107610	0.482420
C	2.514264	-1.812651	-0.711321
C	4.471705	-0.776421	0.733293
C	4.807232	-0.093088	1.920064
C	6.136147	0.203028	2.233963
C	7.164093	-0.188771	1.366162
C	6.850252	-0.887990	0.194924
C	5.517429	-1.183989	-0.115774
N	-2.324417	0.073891	0.080291
C	-2.951340	1.257047	0.316595
C	-4.314375	1.394329	0.515588
C	-5.164666	0.252630	0.475892
C	-4.504106	-0.980199	0.211882
C	-3.135172	-1.014661	0.019951
N	-6.510543	0.328512	0.671787
H	-0.241071	6.616819	-0.614186
H	-0.535031	3.159464	-3.208934
H	-0.904466	-6.745511	-1.040532
H	-0.760133	-3.120371	-3.410647
H	0.011315	-1.520654	3.473418
H	0.117034	1.097925	3.538206
H	1.473595	0.279307	2.739940
H	-1.434839	-0.662253	2.893897
H	-0.538806	5.622449	-2.892814
H	0.055501	5.110978	1.342442
H	-0.614701	-5.396829	1.026676
H	-0.987974	-5.593477	-3.259018
H	0.301533	3.016595	2.301209
H	-0.457794	-3.367001	2.153065
H	-2.658016	-1.963922	-0.193210
H	-5.049354	-1.916493	0.141645
H	-4.706689	2.392015	0.690134
H	2.483747	-1.306869	1.401532
H	1.735271	-2.553301	-0.583420
H	3.181725	-2.006296	-1.550317
H	5.303178	-1.755650	-1.017633
H	4.017430	0.208790	2.609584
H	6.370730	0.735743	3.156052
H	7.645415	-1.215163	-0.475602
H	8.202387	0.038523	1.607811
H	3.658843	0.050836	-1.908989
H	2.050074	0.682815	-2.289655
H	3.948903	1.728459	-0.109041
H	2.341407	2.373437	-0.413561
H	4.657674	2.363610	-2.453925
H	4.089896	3.767759	-1.535739
H	3.039185	3.028597	-2.758081
H	-2.325092	2.141902	0.345782
C	-7.332340	-0.880103	0.600801
C	-7.150422	1.620708	0.924195
H	-8.221364	1.467997	1.078742
H	-6.743667	2.096099	1.828480
H	-7.021821	2.305460	0.072426
H	-8.376826	-0.613143	0.777001
H	-7.264495	-1.354726	-0.389501
H	-7.035912	-1.612401	1.366701

Imidazole–Truncated Salen(Cr)–*N*-^{n}propyl-2-phenylaziridine
71

C	-4.497376	0.280172	1.410885
C	-3.943305	0.889410	0.266204
C	-4.815402	1.261396	-0.774154
C	-6.188093	0.999696	-0.687860
C	-6.718397	0.371970	0.444941
C	-5.867599	0.018308	1.500488
C	-2.476003	1.185911	0.253064
C	-1.746466	1.852700	-0.849759
N	-1.430598	0.427576	-0.579955
C	-1.969129	-0.514352	-1.614630
C	-2.451404	-1.856648	-1.063438
C	-2.984875	-2.763591	-2.182241
Cr	0.712836	0.057931	0.076901
O	1.257516	1.457836	-1.146483
C	1.547042	2.721976	-0.927607
C	1.434647	3.355859	0.366250
C	1.764831	4.736065	0.499215
C	2.185266	5.487631	-0.584500
C	2.286553	4.865967	-1.849868
C	1.979073	3.521927	-2.019869
C	1.012810	2.655705	1.541164
N	0.644442	1.396152	1.607917
C	0.407280	0.800058	2.936528
C	-0.297843	-0.552899	2.764731
N	0.240989	-1.215714	1.571067
C	0.428492	-2.513140	1.559487
C	0.903404	-3.277594	0.447213
C	1.103008	-2.701028	-0.862382
C	1.546490	-3.563524	-1.900739
C	1.788367	-4.910960	-1.662019
C	1.596722	-5.476570	-0.380914
C	1.154280	-4.664599	0.649483
O	0.865197	-1.436756	-1.143170
N	2.803500	-0.234503	0.422673
C	3.744625	-0.068716	-0.581803
C	3.470845	-0.654600	1.497387
N	4.794583	-0.756092	1.218188
C	4.989562	-0.389251	-0.099215
H	-2.210818	-2.980756	-2.931245
H	-3.838045	-2.305365	-2.701875
H	-3.327460	-3.722448	-1.770641
H	-3.243217	-1.682554	-0.323812
H	-1.631232	-2.363014	-0.544739
H	-2.800633	-0.028506	-2.143373
H	-1.160825	-0.661069	-2.340146
H	-2.254039	2.053794	-1.792997
H	-0.969227	2.569504	-0.609058
H	-2.079090	1.389061	1.246204
H	-4.435874	1.775987	-1.654993
H	-6.844315	1.296520	-1.506263
H	-7.788091	0.172779	0.512496
H	-6.272589	-0.453888	2.395340
H	-3.846899	0.009589	2.244351
H	2.053067	3.047801	-2.997786
H	2.614230	5.448966	-2.711506
H	2.432824	6.541327	-0.465879
H	1.682781	5.197715	1.484741
H	1.009304	3.240591	2.471586
H	-0.186813	1.468791	3.578602
H	1.378381	0.652652	3.434037
H	-0.172861	-1.175058	3.665096
H	-1.375649	-0.397361	2.621174
H	0.202739	-3.071028	2.478490
H	0.993233	-5.082860	1.645027
H	1.789721	-6.534828	-0.210829
H	2.132047	-5.542031	-2.482840
H	1.690885	-3.135266	-2.891817
H	3.456734	0.259145	-1.571006
H	5.968356	-0.387965	-0.561567
H	5.516038	-1.049410	1.869228
H	3.045126	-0.910018	2.457648

PPh_3O—Truncated Salen(Cr)—*N*-^{n}propyl-2-phenylaziridine
97

C	-6.136912	-1.201894	0.698403
C	-5.266592	-0.847578	-0.341327
C	-5.781266	-0.139288	-1.440790
C	-7.124158	0.229258	-1.488985
C	-7.978719	-0.114639	-0.437064
C	-7.484015	-0.834811	0.650806
C	-3.826735	-1.227474	-0.352932
C	-3.119256	-1.867310	0.794537
N	-2.749077	-0.424208	0.458226
C	-3.305766	0.577543	1.454763
C	-3.775785	1.882697	0.799998
C	-4.280642	2.864098	1.881193
Cr	-0.758060	-0.094327	-0.195326
O	-0.164164	-1.450083	1.022973
C	0.052023	-2.749059	0.875030
C	-0.186272	-3.455752	-0.353688
C	0.035086	-4.856301	-0.420018
C	0.489425	-5.560821	0.674153
C	0.744885	-4.865318	1.877054
C	0.534347	-3.504354	1.973905
C	-0.579399	-2.771460	-1.549400
N	-0.875916	-1.502295	-1.645637
C	-0.992783	-0.894869	-3.011950
C	-1.824286	0.390559	-2.891057
N	-1.318291	1.121974	-1.697716
C	-1.143280	2.411684	-1.748774
C	-0.669692	3.239954	-0.681279
C	-0.397245	2.725287	0.627407
C	0.045504	3.646387	1.606420
C	0.224824	4.985263	1.312107
C	-0.038674	5.487505	0.021584
C	-0.484286	4.618930	-0.951943
O	-0.570420	1.443959	0.964179
O	1.096358	0.201829	-0.799671
H	-3.473888	3.121252	2.576826
H	-5.105971	2.422907	2.451179
H	-4.640389	3.789514	1.420823
H	-4.578134	1.662184	0.091166
H	-2.945564	2.333513	0.258375
H	-4.142706	0.120591	1.990740
H	-2.492140	0.782232	2.152426
H	-3.640130	-1.987140	1.736366
H	-2.362377	-2.606934	0.588692
H	-3.439173	-1.487561	-1.329869
H	-5.776063	-1.781336	1.539183
H	-8.146059	-1.117673	1.460372

H	-9.023552	0.168916	-0.471052
H	-7.505907	0.776105	-2.342701
H	-5.118869	0.124079	-2.259805
H	0.733706	-2.969529	2.893229
H	1.112476	-5.409833	2.739368
H	0.653825	-6.628703	0.615600
H	-0.158706	-5.367557	-1.358106
H	-0.597331	-3.380184	-2.458982
H	-1.442292	-1.599609	-3.720548
H	0.018635	-0.637662	-3.340914
H	-1.732849	1.000969	-3.796944
H	-2.879104	0.149611	-2.732689
H	-1.380588	2.932601	-2.681329
H	-0.704096	4.984076	-1.950756
H	0.102897	6.537859	-0.196261
H	0.572397	5.659256	2.086672
H	0.247300	3.266366	2.599459
P	2.594838	0.094347	-0.181764
C	3.403574	1.738085	-0.404089
C	2.769033	-0.335234	1.607053
C	3.585722	-1.141731	-1.131686
C	3.857101	-1.111107	2.024910
C	4.034064	-1.379735	3.383480
C	3.123680	-0.882585	4.318520
C	2.035375	-0.114836	3.894411
C	1.853757	0.164321	2.540166
H	4.553622	-1.514534	1.300327
H	4.876953	-1.978999	3.706625
H	3.262118	-1.093807	5.372117
H	1.324230	0.266548	4.617818
H	0.991505	0.729476	2.205070
C	4.599724	-0.713573	-1.993256
C	5.320869	-1.651843	-2.735123
C	5.026511	-3.011486	-2.617372
C	4.010910	-3.437705	-1.755766
C	3.288018	-2.506155	-1.011329
H	4.826554	0.341932	-2.078503
H	6.111224	-1.320956	-3.397869
H	5.589027	-3.737775	-3.191163
H	3.784311	-4.492292	-1.656787
H	2.506522	-2.842683	-0.340709
C	4.489440	2.104919	0.397437
C	5.089382	3.350641	0.214582
C	4.597526	4.226424	-0.757135
C	3.505250	3.859089	-1.547085
C	2.905273	2.611726	-1.373693
H	4.852445	1.432037	1.165571
H	5.930178	3.640328	0.833321
H	5.059490	5.197122	-0.891955
H	3.116624	4.546225	-2.288654
H	2.046653	2.317001	-1.963295

Pyridine–Truncated Salen(Cr)–*N*-″propyl-2-phenylaziridine
73

C	-3.029577	-3.935182	-0.850915
C	-4.353756	-3.522639	-1.022674
C	-4.660685	-2.178123	-0.793294
C	-3.641554	-1.302527	-0.415710
N	-2.354128	-1.690576	-0.259171
C	-2.069059	-2.996810	-0.473706
C	-0.735993	-0.267783	0.140230
N	1.000048	1.206646	0.326303
C	1.770997	1.298728	1.609900
C	1.365304	2.455013	2.534680
C	1.951971	2.297563	3.944810
N	-1.842662	0.678512	1.550325
C	-2.690437	1.659365	1352798
C	-3.017228	2.247934	0.087682
C	-2.414666	1.814144	-1.149684
C	-2.834200	2.446461	-2.349897
C	-3.786248	3.459663	-2.333140
C	-4.372691	3.892531	-1.122788
C	-3.990073	3.287491	0.063082
O	-1.491236	0.875322	-1.218270
H	-5.115589	4.689115	-1.123084
H	-2.384853	2.109548	-3.283041
N	-0.217826	-1.419964	1.727325
C	0.713089	-2.343404	1.766739
C	1.514732	-2.769667	0.659592
C	1.284713	-2.292005	-0.684685
C	2.027635	-2.893655	-1.736433
C	2.979857	-3.871662	-1.476053
C	3.236898	-4.311268	-0.157556
C	2.502790	-3.770686	0.885198
O	0.404596	-1.360872	-0.984932
H	3.990642	-5.073795	0.033128
H	1.829410	-2.558539	-2.753832
C	-1.604390	0.202711	2.925092
C	-1.124655	-1.250221	2.872655
H	-0.640817	-1.537322	3.818622
C	1.790143	1.412924	-0.975051
C	3.281830	1.564380	-1.025530
C	3.878871	2.833423	-1.149821
C	5.266851	2.965625	-1.284290
C	6.082867	1.828159	-1.290547
C	5.500380	0.559181	-1.171745
C	4.113797	0.427881	-1.047433
C	0.907178	2.475574	-0.451884
H	-1.988003	-1.917354	2.725670
H	-0.833752	0.832553	3.388430
H	2.673461	-4.114240	1.906911
H	3.534075	-4.306364	-2.308685
H	-4.086192	3.924365	-3.273154
H	-4.433328	3.610890	1.006551
H	-3.213436	2.068939	2.227200
H	0.873764	-2.868441	2.718650
H	1.369168	0.781126	-1.756160
H	-0.043975	2.666840	-0.935151
H	1.366233	3.344990	0.012607
H	3.256515	3.727947	-1.168581
H	3.673754	-0.564450	-0.978143
H	6.127508	-0.332753	-1.185186
H	5.706121	3.958004	-1.388824
H	7.163403	1.927958	-1.398240
H	1.629859	0.337143	2.115108
H	2.840866	1.378904	1.379677
H	0.269560	2.532550	2.588454
H	1.713608	3.409143	2.115142
H	1.586979	1.385783	4.438156
H	1.677697	3.151259	4.579031
H	3.050179	2.244779	3.922984

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H  -1.035459 -3.296104  -0.343021      H  -5.126317 -4.229590  -1.325073
H  -3.858769 -0.254321  -0.237549      H  -2.513308  0.284406   3.539373
H  -5.674928 -1.799289  -0.908774
H  -2.729705 -4.969558  -1.012781
```

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PUBLICATIONS

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2. Miller, A. W.; Goyal, S; Nguyen, S. T. "*Sc (OTf)$_3$-Catalyzed Synthesis of Substituted Oxazolidines from Aldehydes and Aziridines*", manuscript in preparation.

3. Miller, A. W.; Arnold, F. P.; Nguyen, S. T. "*A Mechanistic Study of the (Salen)Chromium^{III}/DMAP-catalyzed Formation of 5-Substituted Oxazolidinones from Carbon Dioxide and Aziridines*", submitted to *J. Am. Chem. Soc.*

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