Enantiomerically Pure Planar Chiral N-Oxazolidinoyl Diene Tricarbonyl Iron(0) Complexes: Their Synthesis and Functionalization

A thesis presented by
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Finally, I would like to thank all my friends and family here at Swarthmore and back at home. Their unwavering support still baffles me.
**List of Common Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>Ar</td>
<td>either aryl or argon, depending on context</td>
</tr>
<tr>
<td>bda</td>
<td>benzylideneacetone</td>
</tr>
<tr>
<td>Bn</td>
<td>benzyl</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>brine</td>
<td>saturated aqueous NaCl solution</td>
</tr>
<tr>
<td>CAN</td>
<td>ceric ammonium nitrate</td>
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<tr>
<td>cat.</td>
<td>Catalyst</td>
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<tr>
<td>CSA</td>
<td>camphorsulfonic acid</td>
</tr>
<tr>
<td>DCC</td>
<td>(N,N')-dicyclohexylcarbodiimide</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DIAD</td>
<td>diisopropyl azodicarboxylate</td>
</tr>
<tr>
<td>DIBAL</td>
<td>diisobutylaluminum hydride</td>
</tr>
<tr>
<td>DMAP</td>
<td>dimethyl amino pyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>(N,N)-dimethyl formamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>d.r.</td>
<td>diastereoisomeric ratio</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>EVE</td>
<td>ethyl vinyl ether</td>
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<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
</tr>
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<td>iPe₂</td>
<td>diisopinocampheyl</td>
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$i$-Pr  
isopropyl
IR  
infrared
LDA  
lithium di $i$-propylamine
Me  
methyl
MHz  
megahertz
$n$-Bu/Bu  
n-Butyl
NIS  
$N$-iodosuccinimide
NMR  
nuclear magnetic resonance
Ph  
phenyl
ppm  
parts per million
PPTS  
pyridinium $p$-toluenesulfonate
TBAF  
tetra-$n$-butylammonium fluoride
TBDPS  
tert-butyldiphenylsilyl
TEOC  
2-(trimethylsilyl)ethyl carbamate
THF  
tetrahydrofuran
TLC  
thin layer chromatography
TsOH  
$para$-toluene sulfonic acid
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Introduction

As organic chemistry was developing during the last century, it was largely focused on developing successful synthetic pathways to intrinsically complicated molecules. Often, when the targets where chiral, racemic mixtures were produced. Although subsequent separation of the different enantiomers, typically via resolution, would lead to the desired enantiomerically pure product, the method was inefficient given its maximum output of a given enantiomer was only 50%. There was a push to design methodologies that offered one-pot reaction sequences where many transformations could be executed with control over the molecule’s absolute stereochemistry. This led to the development of more streamlined synthetic methods, where substrates or reagents would dictate the introduction of new stereocenters, and produce the non-racemic products in ever-improved ratios. These methods are collectively known as asymmetric syntheses. Today, there are several general approaches used to selectively synthesize one enantiomeric form of a molecule. These include the direct use of well-known chiral pool starting materials (amino acids, carbohydrates, small natural products), the use of chiral auxiliaries as temporarily installed stereodirecting moieties, the use of chiral stoichiometric reagents, and the use of chiral catalysts.

Chiral pool materials are readily available, naturally occurring enantiopure substances that are often used as starting materials in asymmetric synthetic pathways. For
instance, in just one case of the many that could be cited, Ma et al used the chiral pool member (S)-citronellal to install a specific stereocenter in the macromolecular backbone of natural product Leucosceptroid A (Figure 1).\(^1\)

![Figure. Introduction of one stereocenter using a starting material from the chiral pool.](image)

Chiral pool members can also be used to direct the formation of new stereocenters. In the same paper describing the total synthesis of Leucosceptroid A, Ma uses a derivative of D-mannitol, another starting material from the chiral pool, to synthesize an aldehyde that will undergo a stereoselective nucleophilic addition, in order to install a second stereocenter A (Figure 2).

![Figure. Introduction of one stereocenter using a starting material from the chiral pool.](image)
Figure 2. (R)-2,2-Dimethyl-1,3-dioxolane-4-carbaldehyde 1 used for the diastereoselective introduction of an alkoxy group (Stereocenter A).

This reaction shows a classic use of Felkin-Ahn nucleophilic addition, where the stereochemistry of the starting material (in this case, carbaldehyde 1) dictates the stereochemical outcome via substrate control. Felkin and Ahn reported that a chiral center α to a carbonyl group can direct the diastereoselective addition of nucleophiles. They noted that either the largest or most electronegative substituent α to the carbonyl had to be placed antiperiplanar to the carbonyl group, in a staggered transition state, in order to avoid the torsional strain present in the partially eclipsed transition state or in order to maximize favorable orbital interactions between the nucleophile and the carbonyl (Figure 3).

Figure 3. Transition state for the acetylide ion nucleophilic attack on the aldehyde.

The introduction of that stereocenter A is used later on in the synthesis, in an intermediary step involving a ring closure where yet another stereocenter is introduced, guided by our previous stereocenter A (Figure 4).
Chiral auxiliaries are structural units that are temporarily incorporated into a molecule in order to control the stereochemical outcome of a synthesis via substrate control, and are often derived from the chiral pool. A privileged chiral auxiliary, and perhaps the one most commonly employed in synthesis today, is the Evans oxazolidinone. It is used as part of a strategy to enantioselectively prepare, on one hand, stereocenters α to a carbonyl in alkylation reactions; and on the other hand, stereocenters α and β to a carbonyl in aldol reactions. The auxiliary, exemplified by X and Y (Figure 5) is now commercially available, but was initially prepared from an amino acid. Typically, the derived amino alcohol is carbonylated and the chiral, non-racemic heterocyclic oxazolidinone is acylated to produce an imide (or N-acyloxazolidinone). The imide is then used in alkylation or aldol reactions, and the chirality present on the oxazolidinone ring controls the diastereoselectivity of the reaction via substrate control. The oxazolidinone is easily removed (thus, the term auxiliary is used), and produces a
carbonyl compound with high degrees of enantiomeric purity. For example, Dias et al used this method to synthesize (-)-pironetin (Figure 5 and 6). 5

Figure 5. Pironetin as synthesized by Dias via oxazolidinone auxiliaries. All stereocenters shown were introduced using aldol reactions. (Bn = CH₂Ph).

The aldol reactions are typically carried out by conversion of the N-acyloxazolidinone into the corresponding boron enolate, which reacts with the electrophilic aldehyde in a cyclic transition state known as the Zimmerman-Traxler transition state. In this example, and as summarized in Figure 6, the process was used iteratively, affording all six stereocenters in pironetin with excellent stereocontrol.
Figure 6. Repeated Aldol reactions used in the total synthesis of Pironetin.

Figure 7 depicts the transition state for these aldol reactions. The positioning of the oxazolidinone ring substituents "on top" of the Zimmerman-Traxler chair is what dictates which face of the aldehyde is preferred. In the favored case, the benzyl group points away from the chair, and thus does not have any unfavorable diaxial interactions with the aldehyde's substituents. This is possible when the boron enolate attacks the aldehyde from the "back" or si face.
Figure 7. Transition state depicting the Z-boron enolate attacking either the *si* (left) or *re* (right) face of the aldehyde. The *si* attack is preferred. Obtained from Evans.  

As the examples show, using materials from or derived from the chiral pool allows for the diastereoselective formation of new stereocenters via substrate control. While these materials, such as the family of oxazolidinones described above, are effective tools in synthesis, there are inherent disadvantages to using them. Not only is there a limitation of substrates available from the chiral pool, there is also the addition of steps for introduction and removal of the auxiliary into a synthetic pathway. An alternative strategy to the synthesis of chiral non-racemic products is the use of chiral stoichiometric reagents. An example is the Brown allylation of aldehydes. This process uses an allylborane equipped with two Lpc ligands, derived from either the (+) or the (-)-α-pinene, to diastereoselectively add an allyl group to an aldehyde. Roush used this in his total synthesis of (+)-superstolide A (Figure 8).
Figure 8. Brown allylation of an aldehyde as part of the synthesis of (+)-Superstolide A

The reaction proceeds through a Zimmerman-Traxler transition state where the R group of the aldehyde lies equatorially, as shown in Figure 9. However, depending on whether the (+) or (-) borane reagent is used, the re or si face of the aldehyde is attacked. In the case presented, the (-)-Ipc2 borane reagent is used and the si face of the aldehyde is attacked. The aldehyde’s facial selectivity depends on the minimization of steric interactions between the allyl group, the aldehyde substituent, and the Ipc2 ligands on the borane reagent.\textsuperscript{8}
The use of chiral reagents such as \( \text{Ipc}_2\text{B-allyl} \) have some advantages over the auxiliary approach, such as fewer steps required in the synthetic pathway. However, unlike the auxiliary, the source of chirality is typically not recovered. Furthermore, there is still an inherent inefficiency where the enantiocontrolling agent is used in equimolar ratio to the substrate. The more efficient, elegant and preferred route is that of catalytic asymmetric synthesis. The origins of the stereodirecting catalysts are varied; they can be “simple” organic molecules such as prolines or peptides; they can stem from metalloid elements such as boron; or they can contain transition metal elements, such as ruthenium, copper or rhodium. One of the first efficient transition-metal mediated (ruthenium) hydrogenation of \( \beta \)-ketoesters was developed by Noyori, and the Nobel Prize in 2001 was awarded to him for this important discovery.\(^{10}\) Trost \textit{et al} used this as part of their synthesis of (\(-\))-ushikulide A (Figure 11).\(^{11}\)
Figure 11. Ruthenium catalyzed asymmetric hydrogenation of a β-ketoester.

Figure 12. Transition state for the asymmetric hydrogenation. Methanol is used in the reaction as a proton source to form the oxonium ion that will then be reduced to the alcohol. Transition state obtained from Noyori.12

Although asymmetric catalysis is the more elegant route, the availability and cost of the required catalysts can be prohibitive. Accordingly, the use of simple but efficient stoichiometric stereodirecting groups remains a useful approach. The use of planar chiral
organometallic molecules has proven to be an alternate strategy for asymmetric synthesis, either as catalysts for asymmetric reactions, or as scaffolds used to stereoselectively modify the organic ligands of the metal complex, which are often coordinated as \( \pi \)-systems. A lot of work has been done on using stoichiometric amounts of these organometallic scaffolds in order to stereoselectively synthesize molecules. Chromium, molybdenum, and iron planar chiral scaffolds are of particular interest for total syntheses.

Kündig et al used a planar chiral \([\eta^6\text{-arene}]\text{Cr(CO)}_3\) complex for the total synthesis of (-)-lasubine(I).\(^{13}\) They were able to diastereoselectively coordinate the \( \eta^6 \)-arene ring to the chromium complex with a diastereomeric excess of 84\%, using a method developed by Alexakis.\(^{14}\) The chiral aminal shown in Figure 13, derived from chiral pool component L-(+)-tartaric acid, controlled the facial selectivity of the complexation of the Cr(CO)\(_3\) fragment. The position of the chromium tricarbonyl unit then dictated, via substrate control, the stereochemical outcome of an aza-Diels Alder cycloaddition.
Figure 13. Pathway to stereoselective aza-Diels Alder cycloaddition via a chromium tricarbonyl arene complex. Transition state shown. Obtained from Kundig.\textsuperscript{12}

The diastereoselectivity for this cycloaddition is of 100:0; the modest yields were attributed to the steric hindrance of the trimethylsilyl group in the diene approach. As the transition state shows, the diene approaches from the top face of the imine (\textit{st}-face), which also corresponds to an approach (\textit{anti}) to the chromium tricarbonyl unit, which essentially blocks off the entire bottom face of the molecule.

The position of the Cr(CO)\textsubscript{3} unit then also played a role in enabling a diastereoselective radical cyclization (Figure 14).

Figure 14. Diastereoselective radical cyclization using chromium Cr(CO)\textsubscript{3} arene.
For the reaction in Figure 14, a single diastereomer in 90% yield was obtained. It was proposed that the high selectivity was caused by the preferred intramolecular addition to the enone’s *re* face, where the alkyl chain would not interact with the chromium tricarbonyl unit. Thus Kündig successfully used this chromium scaffold to synthesize a bicyclic system with 3 stereocenters, 2 of which were induced by the facial stereochemistry of the metal fragment.

![Figure 15](image)

Figure 15. Stereocenters with * were induced via proximal chirality of the chromium complex.

Similarly, Liebeskind developed enantiomerically pure molybdenum scaffolds, such as [(η³-dihydropyridinyl)MoTp(CO)₂], to use in total syntheses such as that of (-)-indolizidine 209B (Figure 16).¹⁵ Starting from ethyl *N*-benzyl-*N*-acetylamide, Libeskind obtained the acetal 1a with an enantiomeric excess greater than 99.5%. Subsequent complexation of the molybdenum atom proceeded to give a π-allyl complex, where the molybdenum metal added *anti* to the acetate leaving group. The complex then underwent regioselective, subsequent methoxy abstractions and nucleophilic additions to
give complex 1b, where the molybdenum moiety dictated the anti addition of the methoxy groups. Subsequent modification of the side chains and removal of the metal unit led to compound 1c. Hydrogenation using a Pd/C catalyst and subsequent intramolecular cyclization led to the desired natural product (-)-indolizidine 209B.

![Chemical diagram](image)

Figure 16. Synthesis of (-)-indolizidine 209B. Two of the three stereocenters (*) shown were induced by the molybdenum complex.

Just like in the previous examples, planar chiral iron tricarbonyl scaffolds can be used to diastereoselectively synthesize a variety of molecules. Originally, iron tricarbonyl diene complexes were used to protect the diene system. Later, these units were used as stereodirecting groups. However, unlike chromium- and molybdenum-based systems, iron is less expensive and more environmentally benign, making it a more suitable metal to use in stoichiometric substrate controlled reactions. An example of this chemistry used in the context of total synthesis is that of Roush et al, where an ($\eta^4$-diene)Fe(CO)$_3$
complex was used in the synthesis of ikarugamycin (Figure 17).\textsuperscript{18} Beginning with the meso compound \textbf{1d}, an asymmetric crotylboration was performed, producing a homoallylic alcohol with excellent enantioselectivity (> 98%). Grignard addition of a vinyl group to the alkylidene malonate derived from this compound introduced additional stereochemistry with a high diastereoselectivity of 97:3.

\begin{center}
\includegraphics[width=\textwidth]{Figure_17.png}
\end{center}

\textbf{Figure 17.} Use of planar chiral iron tricarbonyl scaffold in the enantioselective synthesis of ikarugamycin.

As the preceding examples reveal, it is clear that planar chiral \(\pi\)-complexes serve as effective tools for stereoselective synthesis. However, accessing these in enantiomerically pure form is not always efficient. For instance, some of the examples shown here rely on inefficient resolution methods – a highly effective approach would be diastereoselective complexation. A significant step towards the use of diastereoselective
complexation to prepare iron tricarbonyl diene complexes was that taken by Pearson in 1994. Chiral auxiliaries positioned adjacent to the diene were effective in distinguishing the diastereotopic diene faces (Figure 18).

![Diagram](image)

<table>
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<th>Dienamide side chain</th>
<th>Reaction conditions</th>
<th>Combined yield</th>
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<td>Et₂O, reflux</td>
<td>95</td>
<td>4.6:1</td>
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<tr>
<td>Xa</td>
<td>BDA, Fe(CO)₅, Et₂O, reflux</td>
<td>74</td>
<td>2.2:1</td>
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<tr>
<td>Xb</td>
<td>Et₂O, reflux</td>
<td>46</td>
<td>1.5:1</td>
</tr>
<tr>
<td>Xc</td>
<td>Et₂O, reflux</td>
<td>78</td>
<td>2:1</td>
</tr>
</tbody>
</table>

Figure 18. Diastereoselective complexation of dienamides. Obtained from Pearson.

The Paley laboratory’s contribution to this field has centered on the discovery of other auxiliaries that might be used for the diastereoselective complexation of pure planar chiral diene complexes. Importantly, an emphasis has been on subsequent modification of the organic ligand, with an eye for creative use of the auxiliary following demetallation. Initially, it was shown that diastereoselective complexation of an iron tricarbonyl moiety was possible on a series of enantiopure sulfinyl dienes. Using 1,3-allylic strain, appropriate location of the sulfoxide group along the periphery of the diene was essential in order to maximize the complexation diastereoselectivities. The 3,4-disubstituted-(Z)-1-sulfinyl dienes were determined to have the best diastereoisomeric ratios (Figure 19), and
were used for the construction of large carbocyclic rings via ring closing metathesis, or to perform couplings or spiroketalizations (Figure 20).20, 21

![Diagram of ring closing metathesis](image)

Figure 19. Determination of effect diene substitution has on the complexation diastereoselectivities for introduction of an iron tricarbonyl unit. Obtained from Paley.22

![Reactions](image)

Figure 20. a. Use of iron scaffold for ring closing metathesis leading to an 8 membered carbocyclic ring. b. Use of iron scaffold for pinacol coupling. c. Use of iron scaffold for spiroketalization. Obtained from the Paley lab.21
The substituents on the diene periphery of these (Z)-1-sulfinyldiene iron(0) tricarbonyl complexes have undergone a variety of transformations: allylations, acetylations, ring closing metathesis, nucleophilic additions, etc. However, there were a few drawbacks to the use of the sulfoxide auxiliary. The yields to prepare the dienes were modest – the Stille reaction was particularly capricious, probably because of the polarized nature of the sulfoxide oxygen atom. In addition, the Paley lab saw modest complexation diastereoselectivities (4:1 – 6:1) and experienced difficulties removing the auxiliary at the end of sequences - the reactions to do so either failed or resulted in complicated mixtures. Thus, the research began to make a pivot towards the use of other auxiliaries. It wasn’t until Movassaghi published a paper showing the synthesis of a N-carbamoyldiene that an approach to such compounds, using Evans chiral oxazolidinone auxiliaries, became feasible.\textsuperscript{23}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure21.png}
\caption{N-carbamoyldiene obtained from Movassaghi.\textsuperscript{23}}
\end{figure}

The oxazolidinone used by Movassaghi was achiral, but it was simple to imagine the chiral version attached to the diene system. The synthesis of complicated, functionalized chiral N-oxazolidinoyldienes, and/or their suitability for diastereoselective complexations was then unknown.
The goal of the research presented in this thesis has been to determine the 
substrate scope and the extent of the synthetic manipulations available on 
enantiomerically pure planar chiral N-oxazolidinoyl diene tricarbonyl iron(0) complexes 
(Figure 22). The results described here serve to extend preliminary work carried out by 
previous student researchers in the Paley laboratory. Their results will be described in the 
next section of this thesis.

![Figure 22. Available sites R1, R2 for group installation and modification.](image-url)
Results and Discussion

As mentioned earlier, we want to use the oxazolidinoyl iron tricarbonyl diene scaffolds for the diastereoselective synthesis of molecules. In order to do so, we want to be able to control the selective synthesis of the diene unit by manipulating the R₁ and R₂ side chains (Figure 1), and to be able to observe diverse functionalization of the side chains using useful synthetic handles, such as esters, amides, ketones or aldehydes. These goals are the product of observations made on experiments conducted by some of my predecessors. In order to give a comprehensive explanation of how my research fits in the general timeline, a brief summary of previous results will now be presented.

![Molecular template of interest for the iron tricarbonyl diene scaffold.](image)

Previously in the Paley laboratory, Nathaniel Erskine was the first to show that the synthesis of these oxazolidinoyl iron tricarbonyl diene molecules was possible (Scheme 1). He was able to synthesize compound 3 with a 6.7:1 complexation diastereoisomeric ratio, though at this stage of the group’s progress in this area, the yield was quite poor - therefore, the diastereoisomeric ratio reported should not be assumed to be accurate.
Compound 3 was not a solid, so it was not possible to obtain a crystal structure that would have shown the correct stereochemical assignment. Notice how Erskine introduced two protected alcohols at the R<sub>1</sub> and R<sub>2</sub> positions. One of the major goals of the Paley lab was to have a group, specifically at those positions, that has the oxidation state of an aldehyde. There are several ways to do so: one is to start with the oxidation state of a carboxylic acid and then do a reduction; another is to start with the aldehyde or ketone itself; and finally, one can start with the oxidation state of an alcohol and then oxidize it. Earlier work showed that having a ketone at the R<sub>2</sub> position was not a viable option: the Stille and complexation reactions did not give clean products in high yields. Accordingly, Erskine tried to have an alcohol available for future oxidation, but found that to be problematic. Instead of obtaining desired alcohol deprotection or Stille product, he obtained either a six membered ring amide (6) or a lactone derivative (8), products of intermolecular reactions (Schemes 2 and 3).
Scheme 2. Intramolecular formation of a cyclic amide.

Scheme 3. Intramolecular lactone formation.

Several years later, another member of the Paley lab, Alice Wong, moved away from using the morpholine amide at the R₃ position and shifted to the more-easily transformed ester (Scheme 4). Not only was she able to synthesize the iron tricarbonyl diene complex 11, she was also able to obtain its crystal structure (Figure 2). From the crystal structure, the stereochemical assignment was finally made, showing that the iron tricarbonyl unit is anti relative to the isopropyl group.
Scheme 4. Synthesis of the ester iron tricarbonyl diene scaffold.

Figure 2. Crystal structure of the N-oxazolidinoyl diene tricarbonyl iron (0) complex 11.
Left: major product (resolution not good enough to show hydrogen atoms). Right: minor product (hydrogen atoms shown).

There are a few noteworthy points to be made from these structures. In the major product’s structure (left), the methyl at the R₂ position is lying in the plane of the diene. In contrast, in the minor structure, it seems that same methyl is distorted to point out of the plane of the diene, possibly in order to avoid non-bonding interactions with one of the methyl groups on the oxazolidinone isopropyl group. This steric interaction could be highly important in determining the diastereoisomeric outcome of the reaction. In addition to the non-bonding interactions between the methyl at R₂ and the isopropyl...
group, we could also envision that interactions between any group at \( R_2 \) and any group at \( R_1 \) would limit the possible conformations at \( R_2 \). The combination of the \( R_1/R_2 \) and \( R_2/\text{oxazolidinone} \) non-bonding interactions could enhance the iron complexation facial bias, enhancing the diastereoselective ratios. Furthermore, we notice that in both the major and the minor product, it seems that the oxazolidinone carbonyl is lying on the same face as the metal atom—perhaps the oxygen atom is having some electrostatic interaction with the iron atom. This could be another conformational factor in determining the reaction diastereoselectivity.

After solving the crystal structure, Wong attempted to reduce the ester group. Though several reactions were explored, complicated mixtures were obtained. The goal of obtaining an aldehyde adjacent to the iron tricarbonyl diene complex, for further diastereoselective transformations, remained elusive. As a strategy to prepare an aldehyde at \( R_1 \), the Paley lab had attempted, on one hand, to introduce the oxidation state of a carboxylic acid, and on the other hand, to oxidize an alcohol to provide the targeted aldehyde. Neither had worked. Of course, the aldehyde itself was not compatible with any of the reactions to be used in this sequence of steps (the cuprate addition, the Stille coupling, the iron tricarbonyl complexation). The notion of using a protected aldehyde was not yet envisioned. Conceivably, one could have a dithioacetal, which has the oxidation state of an aldehyde, at the \( R_1 \) position; however, synthesizing the alkynyl dithioacetal starting material is not possible. An alkynyl diethylacetal was in fact possible to prepare, but proved too unstable during the stannylcupration of the alkyne. Thus, a more stable cyclic acetal was targeted. Julia Murphy, another of my predecessors,
attempted to use a dioxolane ring at R\textsubscript{1}. From her work, we saw the successful conversion of alkynyl acetals, specifically dioxolanes, to the corresponding vinylstannane via \textit{syn}-stannylcupration, with a very high degree of regioselectivity (Scheme 5). This, at last, led to an approach to the desired iron tricarbonyl dienal complexes with an aldehyde oxidation state at R\textsubscript{1}.

![Scheme 5](image)

Scheme 5. \textit{Syn}-stannylcupration of 12 with a 14:1 degree of regioselectivity

The vinyl stannane 13 was converted to the iron tricarbonyl complex 14 (Scheme 6). The acetal was manipulated, as had been hoped, to introduce an additional stereocenter. As shown in Scheme 6, the aldehyde was revealed by hydrolysis; subsequent Knoevenagel condensation with Meldrum’s acid gave an alkylidene malonate. Conjugate addition to this compound gave 16 with perfect diastereoselectivity.

![Scheme 6](image)

Scheme 6. Functionalization of the dioxolane ring.
The combination of Erskine, Wong and Murphy’s research was pivotal in two ways: on one hand, they determined that using a cyclic acetal at the R1 position was, so far, the only successful pathway to further manipulation, and on the other hand, that the molecular interactions between the R2 and the oxazolidinone isopropyl group could potentially affect the iron complexation diastereoselectivities. Despite the promising results, we had yet to observe diastereoselective ratios greater than 7:1 or obtain data on the possible synthetic manipulations of the acetal group.

This is where my story starts. My research initially focused on ameliorating the iron complexation diastereoselectivities by enhancing the non-bonding interactions on the diene via a careful balancing of the steric at the R1 and R2 positions. In addition, we wanted to observe possible functionalization of the diene system via manipulation of the side chains. The results will be presented in the given order.

**Complexation Diastereoselectivities**

As part of the lab’s exploration of this chemistry, the scope of substrates that could be prepared, and the complexation diastereoselectivities, needed to be determined. Concurrent work in the lab suggested improved selectivities when the dioxolane was replaced by the large 1,3-dioxane unit. We wanted to observe if the introduction of the dioxane at R1 affected the diastereoisomeric ratios via R1/R2 interactions, and consequently started the research with one of the smallest substrates available at R2: a methyl group (Scheme 7). Commercially available diethyl acetal 17 was converted into 31
the more stable dioxane by the method of Graham et al.\textsuperscript{24} This compound then underwent regioselective stannylicupration, with 70% yield and 13:1 regioisomeric ratio, to afford vinyl stannane 18. The likely origin of the stannylicupration regioselectivity is shown in Figure 3.

Scheme 7. Obtaining the methyl iron tricarbonyl diene scaffold.

Figure 3. Likely origin of the regioselectivity observed for the stannylicupration of 17.

The approach to prepare the iron tricarbonyl diene complex 18 was identical to that taken by all my predecessors in the Paley laboratory, and relied on a Stille coupling to form a sigma bond between the vinyl carbon atoms in order to prepare the diene (Scheme 8).
Scheme 8. Retrosynthetic analysis of the Stille coupling.

An approach to the synthesis of the l-oxazolidinoyl vinyl stannane was not evident until Stahl demonstrated that a palladium catalyzed vinylation of a chiral oxazolidinone was possible (Scheme 9). The cross coupling between the nitrogen nucleophile (from the oxazolidinone) and the butylvinyl ether, the alkene source, was possible and favored because of the nitrogen atom’s greater nucleophilicity. The vinyl oxazolidinone produced in this way was stannylated using the method of Hegedus. The other partner of the Stille, the vinyl iodide, was easily prepared from vinyl stannane using NIS, a well-known and highly preceded reaction.

Scheme 9. Synthesis of the l-oxazolidinoyl vinyl stannane for the Stille reaction. The first reaction derived from Stahl’s work. The second reaction was derived from Hegedus’ work.

We performed the coupling of the vinyl oxazolidinone and the iodoalkene via a modified Stille reaction based on the work Fürstner did. The Fürstner method uses two salts, CuTC (copper(1) thiophene-2-carboxylate) and (Ph$_2$PO$_2$)(NBu$_4$), to improve the coupling reaction’s yields. Fürstner uses the copper salt as a co-catalyst: the copper
replaces the tin group on the vinyl oxazolidinone partner, increasing the molecule’s nucleophilicity. This species can then perform the transmetallation with the vinyl-iodo-palladium(II) complex after the oxidative addition of the palladium catalyst with the vinyl iodide more readily. The phosphinate acts as a tin scavenger by binding with tin halide to form a tributylstannyl diphenyl phosphinate salt (Bu$_3$SnO$_2$PPh$_2$) that precipitates out of solution, driving the reaction to completion. Instead of using two salts, the Paley lab showed that the reaction can occur using CuO$_2$PPh$_2$ alone, and obtained excellent yields of up to 99%. The diastereoselective complexation of the iron tricarbonyl unit to the diene to produce 19 occurred with yields near 66% and with a disappointing diastereoisomeric ratio of 3:1.

The methyl in itself is a relatively small group, whose non-bonding interactions with the oxazolidinone isopropyl group are relatively minor, which would explain the rather small diastereoselective ratios. Having apparently established the lowest expected complexation diastereoselectivity using the methyl group as the R$_2$ substituent, we next sought to explore other substrates. Figure 4 summarizes our findings. The remainder of this thesis describes the synthesis of these complexes, as well as detailing the transformations performed on them.

![Figure 4. Families of iron tricarbonyl diene scaffolds: yields and diastereoselective ratios shown.](image-url)
Overall the results we obtained were very promising. The Stille and complexation reaction yields were overall better (ranged from 55-75 to 70-99%) than what we saw with the sulfoxide series, probably because of the difference between the electron donating nature of the oxazolidinone and the electron withdrawing nature of the sulfoxide. The better iron complexation yields were probably a result of using Fe$_2$(CO)$_9$ over (bda)Fe(CO)$_3$. Not only were the yields better, but Fe$_2$(CO)$_9$ is more practical to use since it is commercially available, while (bda)Fe(CO)$_3$ has to be synthesized. We also noticed better separation of the products and byproducts using Fe$_2$(CO)$_9$.

Most importantly, as shown in Figure 4, we also noticed that, generally, as the $R_2$ side chain increases in size, so do the diastereoselective ratios. This corroborates the assumptions we made once Wong’s crystal structure was resolved.

\[
R_2 = \text{Methyl}
\]

As described earlier, a main focus of this research was to use the planar chirality of the iron tricarbonyl diene unit to influence the selectivity in the creation of new stereocenters. To access that, in this case where $R_2$ was the methyl group, we wanted to use conjugate additions on an alkylidene malonate to diastereoselectively introduce a stereocenter alpha to the diene. Roush used the same method in his total synthesis of ikarugamycin. Upon addition, we wanted to observe if ring closure via Diels Alder was possible. Scheme 10 was the proposed pathway to this.

Removal of the 1,3-dioxane ring, followed by the conversion to the alkylidene malonate and subsequent conjugate addition would introduce the double bond necessary for the Diels Alder. Removal of the alkylidene malonate moiety via decarboxylation and concomitant alkylidination, decomplexation of the iron and intramolecular Diels Alder would lead to the bicyclic system 26 (transition state shown). The terminal alkene obtained using Eschenmoser’s salt should not react in a Diels Alder reaction – it would have to form a very unstable cyclopropane ring. As laid out, the first step was to hydrolyze the dioxane ring.

**Hydrolysis of the 1,3-dioxane ring**

To install the alkylidene malonate, we had to hydrolyze the 1,3-dioxane ring back to the aldehyde form using “acidic” conditions. We initially used CSA in a 5:1 THF and water solution, and obtained relatively high yields of 72% of aldehyde 26. Unfortunately, the reaction had to be stirred for over 4 days. To improve the reaction time, we
transitioned to using an acetone and water solution, which resulted in slightly better yields in only 24 hours. Modification of the ratio between the acetone and water led to very minor changes in the yields (Scheme 11).

Scheme 11. Hydrolysis of the dioxane to the aldehyde.

I was able to successfully add the alkylidene malonate unit via Knoevenagel reaction and conduct the conjugate addition at the position adjacent to the iron tricarbonyl diene unit with perfect diastereoselectivity of 100:0 (Scheme 12). Unfortunately, the yields for the Meldrum’s reaction were inexplicably low (20%) on a large scale.

Scheme 12. Diastereoselective conjugate addition to the alkylidene malonate.
After obtaining compound 21, the next step in the synthesis was to remove the alkylidene malonate for a future Diels Alder reaction. This step revealed itself to be one of the most challenging goals in the synthesis.

Removal of the alkylidene malonate unit

Scheme 13. Removal of the alkylidene malonate.

The initial attempt to remove the alkylidene malonate was via decarboxylation and subsequent esterification via pathway A (Scheme 13). Unfortunately, a complicated mixture was obtained with no indication that the desired ester was present. We suspect that the elevated temperature required for the reaction led to decomposition. This was the
first indication we had that the oxazolidinoyl diene complexes were more thermally labile than the sulfoxide-containing counterparts.

Next, a hydrosilylation of the cyclic malonate (pathway B) using a method developed by Frost on cyclic malonates attached to aliphatic groups was attempted.\textsuperscript{29} We obtained a complicated mixture that was not easily separable, but were able to obtain the desired aldehyde. The amount of product was too low to allow us to accurately determine a yield, but it was enough to do some chemistry on the aldehyde (Scheme 14). I was able to reduce the aldehyde to an alcohol and install a silyl-protecting group, although the amounts were too small to be quantified. Subsequent demetalation was unsuccessful.

Scheme 14. Transformations required to attempt and intermolecular Diels Alder reaction.

I then tried to manipulate 21 using a method developed by Tsukamoto for the one-pot synthesis of alpha-substituted acrylate esters (pathway C).\textsuperscript{30} In this transformation, gentle heating in an alcohol solvent leads to loss of acetone and decarboxylation at the malonate derivative. Presumably, an enol intermediate is formed and is trapped using Eschenmoser’s salt to afford the acrylate ester. The reaction was successful: without the
presence of acid, we were able to trap the ester after the decarboxylation and install the alkylidine group with 74% yield.

The synthesis of compound 24 via pathway C was facile. We then wondered if we could mimic the reaction conditions, without the presence of the Eschenmoser’s salt, and have just the decarboxylation occur, without the alkylidination, in order to simply obtain the corresponding ester. At 65 °C, with or without pyridinium p-toluenesulfonate, we saw cleavage of the oxazolidinone moiety (path D). We then lowered the reaction temperature to 45 °C, and without the presence of acid, obtained β-dicarbonyl 29. Although no modification of the compound was done, it is conceivable that differentiation of the ester and the carboxylic acid could be used in future steps for decarboxylation.

Diels Alder Attempts

Having obtained one successful product where the alkylidene malonate was removed, we attempted the Diels Alder reaction after demetalation (Scheme 15). Unfortunately, the reaction did not go forward, possibly because the vinyl group alpha to the ester is sterically hindering the reaction.
Scheme 15. Attempted Diels Alder.

We then tried another Diels Alder reaction with the malonate still present in the molecule (Scheme 16). We modified the terminal alkene via cross metathesis to insert an electron withdrawing group (an ester). The ester would hopefully make the dienophile more electron deficient and promote the Diels Alder reaction. Unfortunately, that was not the case. Again, we believe that the malonate creates too much steric hindrance for the cycloaddition to occur.

In summary, we were able to introduce a stereocenter adjacent to the diene and to obtain a single diastereomer. However, the difficulties affiliated with the removal of the malonate and with the Diels Alder reaction prompted us to find other methods to produce macrocyclic rings, which will be discussed in other sections. Again, to allow for functionalization, the introduction of reactive functional groups such as a carbonyl is important. Having observed the chemistry possible on the iron tricarbonyl diene scaffold with the methyl group at R₂, we then wanted to introduce a group that could undergo nucleophilic attack upon oxidation: an alcohol.

\[ R₂ = \text{CH}_2\text{CH}_2\text{OTBDPS} \]

We attempted to synthesize the iron tricarbonyl diene complex where the R₂ group was an ethyl chain bearing a terminal protected alcohol (Scheme 17).

Scheme 17. Approaches to obtain the vinyliodide-Stille partner.
Stannylcupration to afford the required vinyl stannane 36 proceeded with high yields and with a regioisomeric ratio of 12:1. The difficulty came after subsequent deprotection of the alcohol group: we obtained a complicated mixture of products that did not allow us to cleanly separate the desired homoallylic alcohol. On the other hand, reversing the sequence order by starting with the replacement of the tributylstannane unit with an iodide atom, and removal of the alcohol-protecting silyl group afforded clean alcohol 39. A Swern oxidation was attempted on this alcohol, but the reaction failed.

From this sequence, we were able to obtain interesting products 38 and 39. The homoallylic alcohol 39 was used later on for a Mitsunobu reaction (see Scheme 21). The vinyl iodide group 38 was used to synthesize complex 20 (Scheme 18). Notable here is the improved diastereoselectivity of the complexation with the larger R₂ side chain in place of the methyl group.


As mentioned earlier, we were looking for ways to create macrocycles that did not involve using an alkylidene malonate and doing a Diels Alder reaction. Ring closing metathesis seemed the logical next step to the sequence (Scheme 19).
Scheme 19. Proposed pathway to prepare a cyclooctene ring via ring closing metathesis.

Silyl ether 20 was successfully deprotected to afford the alcohol, and it was oxidized to aldehyde 40 with 98% yield (Scheme 20). However, subsequent allylation of the alcohol failed and resulted in complicated mixtures.

Scheme 20. Allylation of the aldehyde at the R2 position.
In pathway 3A, the products obtained suggested those of an intramolecular reaction – perhaps the boron lewis acid coordinated not only to the aldehyde, but also to the acetal, which caused the intramolecular reaction. In pathway 3B, the products were not clean enough to observe anything of consequence.

**Carbamate**

In the interest of varied structural motifs, we wanted to try to modify the alcohol on the R2 side chain. Murphy previously showed that an N-carbamoyl sulfonamide could be incorporated in a vinyl iodide Stille coupling partner that also possessed the dioxolane. I emulated the same chemistry with the dioxane ring at the R1 position (Scheme 21).

![Scheme 21. Synthesis of the carbamate iron tricarbonyl diene scaffold.](image)

Starting from alcohol 39, obtained from the homoallylic alcohol family mentioned earlier, displacement of the alcohol via a Mitsunobu reaction occurred with a 85% yield.
Subsequent coupling to the oxazolidinoyl vinyl stannane occurred with excellent yields of 94%. The complexation to the Fe(CO)₃ iron fragment gave complex 21 with a 75% yield and a diastereoisomeric ratio greater than 15:1. This ratio represents the most selective complexation observed to date in our laboratory. This was very exciting, and confirmed that the bulkiness of that side chain did indeed affect the diastereoselective ratios.

Deprotection of the carbamate group left an available hydrogen that could undergo a palladium-catalyzed vinylation - the same reaction we use to synthesize the N-vinyl oxazolidinoyl (Stahl method, see Scheme 9). Addition of that double bond could be used in future cross metathesis to synthesize azepane motifs. Indeed, the reaction proceeded with a 76% yield, representing, by far, the most complicated substrate this reaction has been successfully performed on. However, attempted hydrolysis of the acetal led instead to de-vinylation - this corresponds to nothing more than the hydrolysis of an enamine.

Because of time constraints, we did not take this chemistry further. In order to access the azepane, one would need to hydrolyze the acetal before N-deprotection and N-vinylation. This will be a future project in the Paley laboratory.

\[ R_2 = \text{CH}_2\text{CH}_2\text{CO}_2\text{Et} \]

We next considered whether an ester could be incorporated in the \( R_2 \) side chain. Initially, access to the ester was attempted via oxidation of the corresponding alcohol (derived from alkynyl acetal 45, Scheme 22).
Scheme 22. Attempted synthesis of the Ester Stille partner.

In analogy to the sequence described in Scheme 17, alkynyl acetal 45 was readily prepared. After stannylecupration, the silyl ether was removed. While oxidation to the aldehyde was successful, further oxidation via the Pinnick method was not. Our presumption is that the vinyl stannane functional group is not robust enough to survive these conditions.

Instead of obtaining the ester via oxidation of an alcohol or aldehyde, we tried to start the synthesis using a carboxylic acid as a starting material (Scheme 23). After the conversion from the carboxylic acid to the ester, which occurred with 83% yield, the same route was used as described for similar substrates we had prepared. Diastereoselective complexation of the iron tricarbonyl to the diene occurred with 81% yield and d.r. of 8:1.
Scheme 23. Synthesis of the ester iron tricarbonyl diene scaffold.

Again, because of time constraints, we were not able to take this chemistry further. However, the successful synthesis of the iron tricarbonyl diene complex with the presence of the ester was a promising preliminary result.

**$S_N2'$ reaction**

As mentioned previously, the overarching theme of this research is to diastereoselectively introduce new stereocenters, and the problems we encountered with the malonate pushed us to find new chemistry that could do this. Accordingly, we devised a pathway where an $S_N2'$ reaction on an allylic leaving group would introduce a new stereocenter and leave an open terminal alkene for future ring closure, via either ring closing metathesis or Diels Alder (Scheme 24).
Scheme 24. Proposed sequence to access a ring closing metathesis substrate proceeding through a $S_N2'$ reaction.

Using leftover starting material from an earlier sequence (Scheme 22, product 44), we obtained the iron tricarbonyl diene complex with a diastereoisomeric ratio of 7.8:1 (Scheme 25). I then hydrolyzed the acetal and added a vinyl group via Grignard addition. Subsequent isomerization, via a 1,3 transposition of the hydroxyl using a rhenium catalyst developed by Osborn, was successful.\textsuperscript{31} We attempted to make the allylic alcohol a better leaving group (product 55), but the reaction failed. Again, due to time constrains, this chemistry was not pursued further. Certainly other leaving groups can be considered as a future student prepares for carrying out the desired $S_N2'$ reaction.

Scheme 25. Formation of an allylic alcohol on the R$_1$ side chain.
Conclusion

Broadly, the goal of this research was to observe the scope of the molecules we could make, how effective the syntheses were, and what the broader outcomes were. One objective of this research was to observe how oxazolidinoyl iron tricarbonyl diene scaffolds could be used for the diastereoselective synthesis of molecules. To determine the substrate scope, we wanted to manipulate the group functionalization at the R₁ and R₂ side chain. We were able to incorporate the desired aldehyde both at the R₁ and the R₂ position, although subsequent manipulation was only successful at the R₁ side chain. In addition to the aldehyde, we observed the successful incorporation of alcohol (protected and de-protected), ester, amide, vinyl and many other functional groups.

Another objective of this research was to determine how effective the production of these molecules were, which involved looking at reaction yields, but most importantly, the diastereoselectivity of complexation and nucleophilic addition reactions. The yields for the Stille and complexation reactions, when the chiral auxiliary was the Evans oxazolidinone, were higher than those seen in the sulfoxide series (70-99% versus 55-75%). To observe what affected the complexation diastereomeric ratios, we wanted to manipulate the selective synthesis of the diene unit by modifying the size of the R₁ and R₂ side chains. In the first chapter of this thesis, the iron complexation diastereoselectivities were shown to increase as the size of the R₂ side chain increased. This corroborates the assumptions we made when the crystal structure for the oxazolidinoyl iron tricarbonyl diene system was resolved: it seems that in order to avoid non-bonding interactions between the R₂ side chain and the oxazolidinone isopropyl
group, the R₂ side chain is distorted out of the diene’s plane, which restricts its available conformations and thus enhances the complexation facial bias. All nucleophilic addition reactions on the oxazolidinoyl iron tricarbonyl diene complexes were perfect (100:0). The last objective of this research, and just like in any research, is to observe what we can do with this chemistry. Although several attempts were made on producing macrocyclic rings through Diels Alder reactions, none were successful. Despite this, we were able to determine a few viable synthetic routes to natural structural motifs.
References


12477-12487.


**2001**, *42* (15), 2923-2925; Iwata, C.; Fujita, M.; Hattori, K.; Uchida, S.; Imanishi, T.,


8126-8127.


Experimental Section

All reactions were carried out on a Schlenk line under argon atmosphere. The solvents used in these methods were all anhydrous unless otherwise noted. THF, tolyene, and dichloromethane solvents were purchased from J.T. Baker and kept in an anhydrous solvent dispenser. When being utilized, the collection flasks for these solvents were either purged with alternating evacuation and argon flow, or sufficiently dried in glassware oven. Upon collection, the solvents were run through a neutral alumina/copper(II) oxide columns. All other liquids were measured and transferred using gastight syringes or cannulas, and all solids were weighed using an analytical balance. All air-sensitive reagents were stored under inert nitrogen atmosphere in a glovebox.

All crude products were purified by flash column chromatography using Merck 200-400 silica gel as the solid phase, and mixtures of hexanes, ethyl acetate as eluents (with or without either triethylamine or formic acid). Compounds with limited solubility in these solvents were loaded onto the column using either toluene or chloroform.

Thin layer chromatography was carried out using uniplate 150 micron precoated glass plates purchased from Analtech. Visualization of product spots was done using ultraviolet light, vanillin dip, and/or permanganate dip. Products were characterized by NMR using a Bruker Ascend 400 MHz NMR with autosample (400 MHz for $^1$H, 100 MHz for $^{13}$C). Fourier transform IR spectra were taken using a DigiLab Excalibur Series spectrometer at 4 cm$^{-1}$ resolution. Rotational analysis was carried out using a Jasco P-2000 series polarimeter. HRMS was perfomed by the Mass Spectrometry Facility in the Department of Chemistry at the University of California at Riverside.
Stannyl vinyl oxazolidinone 1a:

(4S)-(-)-4-Isopropyl-2-oxazolidinone

(1.00 g, 7.74 mmol, 1.0 eq) and (dpp)Pd(OTFA)$_2$ (256 mg, 0.385 mmol, 0.05 eq) were placed in a flask open to the air. Butyl vinyl ether (10.0 mL, 77.4 mmol, 10 eq) was added and the flask was placed in a 75 °C oil bath. After stirring for 4.5 hr it was removed, cooled to room temperature, and the reaction mixture was directly loaded onto a column and chromatographed (silica, 4:1 hexanes/EtOAc) to afford the N-vinyl oxazolidinone as a white solid (1.082 g, 90%).

NOTE: the product sublimed while on the vacuum line for prolonged periods. After chromatography, fractions were combined and concentrated and the product – often an oil at this stage - was suspended in hexanes and then this was concentrated on the rotary evaporator. This process was repeated a second time to afford the product as a white solid that was placed on the vacuum line for no more than one minute.

2,2,6,6-Tetramethylpiperidine (2.24 mL, 13.27 mmol, 1.3 eq) was dissolved in THF (8.7 mL) in a flame-dried Schlenk flask under argon. The solution was cooled to 0 °C and n-BuLi (1.6 M in hexanes, 8.0 mL, 12.76 mmol, 1.25 eq) was added dropwise via syringe. The reaction was stirred for 30 min at 0 °C. Meanwhile, in a separate flask under argon, the vinyl oxazolidinone (1.584 g, 10.21 mmol, 1 eq) was dissolved in THF (25 mL) and this solution was cooled to -78 °C. Bu$_3$SnCl (3.05 mL, 11.23 mmol, 1.1 eq) was added to this solution, and after than the LiTMP solution was added via cannula. After stirring at -78 °C for 15 min, the bath was removed and the solution was allowed to warm to room temperature. The solution was diluted with Et$_2$O (100 mL) and this was washed with H$_2$O (2 x 40 mL), brine (1 x 40 mL), dried (MgSO$_4$), filtered, and concentrated using the
rotary evaporator. The residue was chromatographed (silica, 9:1 hexanes/EtOAc containing 1% NEt₃) to afford stannyl vinyl oxazolidinone 1a as a clear oil (3.942 g, 87%). Spectroscopic data matched those previously reported for this compound.

![Diagram of the reaction](image)

General Procedure for Preparation of N-Oxazolidinoyl Diene Iron(0) Tricarbonyl Complexes. In the glove box, Fe₂(CO)₉ (3.5 eq) was added to a Schlenk flask equipped with a stir bar. The flask was sealed with a cap and brought out of the glove box. In the fume hood, under an argon atmosphere, the cap was removed and replaced with a septum. A toluene solution (0.1 M relative to the diene) of the N-oxazolidinoyl diene 8a-i (1 eq) was added directly to the Fe₂(CO)₉ via cannula. The flask was again sealed with a cap and was then placed in a 35 °C oil bath for 20-22 hr. Upon completion of this reaction period, the flask was removed from the oil bath and the contents were cooled to room temperature. The reaction mixture was then filtered through a pad of silica on a glass-fritted filter (the silica was loaded as a slurry with EtOAc containing 2% NEt₃) using EtOAc containing 2% NEt₃ to rinse the flask and silica pad. The filtrate was collected and concentrated using a rotary evaporator [Caution: the rotary evaporator should be in the fumehood, and care should be taken to dispose of the contents of the collection flask, which contain iron carbonyls]. The green-colored residue is chromatographed on a short column to remove the bulk of the green color (assumed to be Fe₂(CO)₁₂) (silica, 1:1 hexanes/CH₂Cl₂ containing 1% NEt₃ until the color has eluted, then 100% EtOAc to collect the diastereomeric complexes). After concentration of the fractions containing the diastereomeric complexes, using the rotary evaporator...
evaporator, the diastereomer ratio was determined by $^1$H NMR integration. A second, more careful, chromatography (silica, hexanes/EtOAc mixtures) provided the major N-oxazolidinoyl diene iron(0) tricarbonyl complex 9a-i (except for 9b, which was purified by recrystallization).
R₂ = methyl

Alkynyl acetal 17a: 1,1-dithoxy-2-butyne (2.065 g, 14.52 mmol, 1.0 eq) was dissolved in CH₂Cl₂ (15.5 mL) under an argon atmosphere. 2,2-Dimethyl-1,3-propanediol (7.56 g, 72.6 mmol, 5 eq) and indium(III) triflate (327 mg, 0.581 mmol, 0.04 eq) were successively added. After stirring at room temperature overnight, the solution was loaded onto a column of basic alumina and was then eluted with hexanes. The solvent containing the eluted product was removed via careful distillation using a Vigreux column; the residue was purified by bulb-to-bulb distillation at ambient pressure (100-125 °C) give the alkynyl acetal 17a as a clear liquid of adequate purity for use in the next step (1.708 g, 76%). ¹H NMR (400 MHz) δ 0.84 (s, 3H), 1.12 (s, 3H), 1.90 (s, 3H), 3.44 (d, J = 11.6 Hz, 2H), 3.71 (d, J = 11.6 Hz, 2H), 5.21 (s, 1H); ¹³C NMR (100 MHz) δ 14.13, 22.11, 22.66, 31.59, 74.44, 75.98, 82.48, 90.92; IR see RQ-I-15 642.7, 783.0, 853.4, 895.7, 927.9, 960.3, 984.2, 1014.7, 1030.3, 1094.1, 1138.7, 1173.3, 1216.9, 1231.8, 1258.1, 1310.1, 1334.4, 1363.5, 1389.7, 1471.3, 1711.5, 2256.2, 2744.1, 2869, 2956.6 cm⁻¹; HRMS (M+H⁺) calculated for C₉H₁₃O₂: 153.0910, found 153.0912.
Vinyl stannane 17b: Bis(tributyltin) (12.3 mL, 24.4 mmol, 2.2 eq) was dissolved in THF (65 mL) under an argon atmosphere; the solution was cooled to -78 °C. n-BuLi (1.6 M in hexanes, 14.5 mL, 23.3 mmol, 2.1 eq) was added dropwise via syringe, and the bath temperature was warmed to -40 °C. After the reaction mixture was stirred at that temperature for 30 min, the bath was recooled to -78 °C and CuCN (1.984 g, 22.16 mmol, 2.0 eq) was added at once. The bath was again warmed to -40 °C and the reaction mixture was stirred at that temperature for 45 min, during which time an orange-yellow solution formed. The bath was again recooled to -78 °C, and anhydrous MeOH (0.673 mL, 16.62 mmol, 1.5 eq) was added dropwise via syringe. To this solution was then added, via cannula, a THF (28 mL) solution of alkynyl acetal 17a (1.708 g, 11.08 mmol, 1.0 eq). The reaction mixture was allowed to warm to a temperature of -25 °C over the next 3.5 hr, at which time it was quenched with an aqueous solution of saturated NH₄Cl/NH₄OH (9:1, total used: 65 mL). Upon warming to room temperature this was transferred to a separatory funnel with EtOAc (190 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 75 mL). The combined organics were then washed with brine (2 x 60 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The crude oil was purified via column chromatography (silica, hexanes containing 3% NEt₃) to afford vinyl stannane 17b (as a mixture of regioisomers) as a clear oil (3.46 g, 70%). ¹H NMR (peaks from major regioisomer; 400 MHz) δ 0.76 (s, 3H), 0.82-0.99 (m, 15H), 1.24 (s, 3H), 1.25-1.33 (m, 6H), 1.38-1.54 (m, 6H), 1.97 (d with tin satellites, 3H, J = 1.9 Hz, J_{Sn-H} = 22 Hz), 3.52 (d, 2H, J = 6.8 Hz), 3.66 (dd, 2H, J = 10, 1.8 Hz), 5.19 (d with tin satellites, 1H, J = 5.9 Hz, J_{Sn-H} = 3.7 Hz), 5.64 (dq with tin satellites, 1H, J = 5.9, 1.8 Hz, J_{Sn-H} = 35
\( \text{^{13}C NMR (100 MHz) } \delta \ 9.1 \text{ (with tin satellites, } J_{\text{Sn-C}} = 162 \text{ Hz), 13.66, 13.73, 20.3, 22.0, 23.1, 27.4 \text{ (with tin satellites, } J_{\text{Sn-C}} = 28 \text{ Hz), 29.1 \text{ with tin satellites, } J_{\text{Sn-C}} = 9.7 \text{ Hz), 30.1, 77.3, 97.2 \text{ (with tin satellites, } J_{\text{Sn-C}} = 33 \text{ Hz), 136.3 \text{ (with tin satellites, } J_{\text{Sn-C}} = 14 \text{ Hz), 147.3; IR see RQ-I-2 668.3, 931.1, 983.9, 1016.3, 1079.3, 1113.7, 1146.1, 1377.7, 1464.5, 2847.0, 2870.8, 2926.5, 2955.2 \text{ cm}^{-1}; HRMS (M+H\text{)} \text{ calculated for } C_{21}H_{43}O_2^{120}\text{Sn: } 447.2280, \text{ found } 447.2292.}
Oxazolidinoyl diene 18b: Vinyl stannane 18 (3.46 g, 7.77 mmol, 1 eq), as a mixture of regioisomers, was dissolved in CH$_2$Cl$_2$ (80 mL) under an argon atmosphere and this solution was cooled to 0 °C. NIS (2.10 g, 9.32 mmol, 1.2 eq) was added all at once, and the reaction mixture was stirred for 3 hr at 0 °C. At that time, saturated aqueous NaHCO$_3$ (40 mL) and saturated aqueous Na$_2$S$_2$O$_3$ (40 mL) were added; the mixture was transferred to a separatory funnel using Et$_2$O (300 mL). The layers were separated and the organic layer was washed with brine (2 x 40 mL), dried (MgSO$_4$), filtered, and concentrated using the rotary evaporator. A $^1$H NMR spectrum of the unpurified material revealed a regioisomeric ratio of ca. 11:1. The residue was chromatographed (silica, 40:1 hexanes/EtOAc containing 0.5% NEt$_3$) to afford the isomerically pure vinyl iodide (1.955 g, 88%) as a clear oil. [NOTE: due to potentially volatility of this compound flasks containing the compound were only briefly connected to the vacuum manifold]. $^1$H NMR (400 MHz) δ 0.74 (s, 3H), 1.20 (s, 3H), 2.51 (dd, 3H, $J = 1.5, 0.2$ Hz), 3.48 (br dd, 2H, $J = 11.3, 0.8$ Hz), 3.64 (dt, 2H, $J = 11.3, 1.4$ Hz), 5.03 (dd, 1H, $J = 6.0, 0.2$ Hz), 6.27 (dq, 1H, $J = 6.0, 1.5$ Hz); $^{13}$C NMR (100 MHz) δ 21.9, 22.9, 29.2, 30.1, 77.2, 97.9, 102.12, 138.0. The data matched those reported for this compound, prepared through a different route, by Burke et al. (Science, 347, 1221-1226, 2015).

Stannyl vinyl oxazolidinone 1a (3.23 g, 7.27 mmol, 1 eq) was weighed into a one-dram vial; this vial, along with a Schlenk flask equipped with a stir bar containing the vinyl iodide prepared above (2.05 g, 7.27 mmol, 1 eq), were brought into the glove box. In the glove box, portions of DMF were used to dissolve 1a and then transfer it by disposable pipette into the flask containing the vinyl iodide. The vial and pipette were repeatedly
rinsed with DMF (total used: 34 mL to dissolve the reactants). Pd(PPh₃)₄ (840 mg, 0.727 mmol, 0.1 eq) and copper diphenylphosphinate (2.35 g, 8.36 mmol, 1.15 eq) were added at the same time and the reaction was stirred for 18.5 hr. In the fumehood, the reaction mixture was then filtered through a pad of silica on a glass-fritted filter (the silica was loaded as a slurry with EtOAc) using EtOAc (ca. 150 ml) to rinse the flask and silica pad. The filtrate was concentrated using the rotary evaporator and then re-dissolved in Et₂O (300 mL) and transferred to a separatory funnel. The solution was washed with H₂O (2 x 60 mL), brine (2 x 60 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 2:1 hexanes/EtOAc) to afford oxazolidinoyl diene 18b (2.26 g, 100 % yield) as a clear oil. ¹H NMR (400 MHz) δ 0.76 (s, 3H), 0.86 (d, 3H, J = 7.0 Hz), 0.90 (d, 3H, J = 6.8 Hz), 1.22 (s, 3H), 1.90 (s, 3H), 1.92 (partially obscured m, 1H), 3.52 (dd, 2H, J = 11.4, 7.3 Hz), 3.65 (ddd, 2H, J = 11.4, 5.6, 2.7 Hz), 3.91 (m, 1H), 4.15 (dd, 1H, J = 9.0, 4.6 Hz), 4.35 (t, 1H, J = 9.0 Hz), 5.15 (d, 1H, J = 5.8 Hz), 5.28 (s, 1H), 5.49 (s, 1H), 5.66 (d, 1H, J = 5.8 Hz); ¹³C NMR (100 MHz) δ 14.5, 15.1, 17.8, 22.0, 23.0, 28.8, 30.1, 60.2, 62.9, 98.7, 113.6, 126.5, 135.5, 142.4, 156.7; IR See RQ-62, 34 666.0, 754.3, 930.9, 967.8, 984.6, 1024.0, 1055.2, 1088.0, 1123.6, 1152.7, 1179.2, 1222.9, 1310.3, 1337.6, 1393.3, 1468.6, 1613.6, 1755.2, 2871.3, 2958.1, 3506.4 cm⁻¹; 18b was not stable enough to be submitted for HRMS.
N-Oxazolidinoyl Diene Iron(0) Tricarbonyl Complex 19. Prepared according to the general procedure, using diene 18b (1.109 g, 3.584 mmol, 1 eq) and Fe₂(CO)₉ (4.56 g, 12.55 mmol, 3.5 eq) in toluene (36 mL). The diastereomer ratio was established to be 3:1, and chromatographies (silica, 5:1 hexanes/EtOAc) afforded the major complex 19 (907.5 mg, 56%) as a yellow oil. The minor complex (320.9 mg, 20%) was also obtained. Major diastereomer: ¹H NMR (400 MHz) δ 0.21 (d, 1H, J = 3.5 Hz), 0.57 (d, 1H, J = 6.6 Hz), 0.73 (s, 3H), 0.92 (d, 3H, J = 7.1 Hz), 0.94 (d, 3H, J = 6.8 Hz), 1.21 (s, 3H), 1.75 (d, 1H, J = 3.4 Hz), 2.10 (s, 3H), 2.32 (m, 1H), 3.45 (d, 1H, J = 10.9 Hz), 3.50 (d, 1H, J = 10.8 Hz), 3.65 (m, 2H), 3.96 (m, 1H), 4.15 (dd, 1H, J = 9.0, 4.9 Hz), 4.32 (t, 1H, J = 9.0 Hz), 4.40 (d, 1H, J = 6.6 Hz); ¹³C NMR (100 MHz) δ 13.9, 14.3, 18.1, 21.8, 23.1, 28.4, 29.9, 34.8, 56.8, 61.6, 63.5, 77.5, 100.7, 102.2, 102.6, 156.1; IR. Minor diastereomer: ¹H NMR (400 MHz) δ 0.35 (d, 1H, J = 3.7 Hz), 0.61 (d, 1H, J = 6.9 Hz), 0.73 (s, 3H), 0.94 (d, 3H, J = 7.0 Hz), 0.98 (d, 3H, J = 6.8 Hz), 1.21 (s, 3H), 1.80 (d, 1H, J = 3.8 Hz), 2.14 (s, 3H), 2.24 (m, 1H), 3.45 (d, 1H, J = 11.0 Hz), 3.50 (d, 1H, J = 10.9 Hz), 3.65 (m, 2H), 4.13 (m, 2H), 4.31 (m, 1H), 4.38 (d, 1H, J = 6.9 Hz); ¹³C NMR (100 MHz) δ 14.5, 15.4, 18.1, 21.8, 23.1, 28.8, 29.9, 36.9, 56.0, 62.8, 64.8, 77.4, 77.6, 98.6, 102.7, 102.9, 155.1; IR see RQ-21, 37.568.7, 595.5, 621.3, 660.7, 692.4, 770.7, 788.6, 820.9, 862.7, 929.1, 964.5, 981.2, 1012.7, 1035.6, 1057.0, 1088.1, 1105.1, 1171.3, 1217.0, 1324.6, 1374.8, 1394.1, 1406.6, 1426.0, 1464.4, 1558.5, 1737.7, 1749.9, 1963.3, 2048.6, 2845.7, 2956.6 cm⁻¹. HRMS (M+Na⁺) calculated for C₂₀H₂₇NO₅Na⁵⁶Fe: 472.1029, found 472.1018.
Aldehyde Diene Iron Tricarbonyl Complex 26. Complex 19 (0.908 g, 2.02 mmol, 1 eq) was dissolved in a 5:1 solution of THF:H₂O (23 mL). CSA was added (0.1642 g, 0.707 mmol, 0.35 eq). The reaction was stirred for four days. It was then transferred to a separatory funnel using EtOAc (140 mL) and washed with saturated NaHCO₃ (40 mL). The aqueous layer was then further extracted with EtOAc (40 mL). The combined organic layers were washed with a saturated brine solution (40 mL), then dried with MgSO₄, filtered and concentrated in vacuo. The resulting yellow oil was purified via column chromatography (silica gel, hexane/EtOAC, 3:1 to 2:1) to afford aldehyde 26 as a yellow foam (0.530 g, 72%). ¹H NMR (400 MHz) δ 0.75 (d, 1H, J = 4.0 Hz), 0.81 (d, 1H, J = 6.0 Hz), 0.90 (q, 6H), 2.19 (d, 1H, J = 4.0 Hz), 4.07 (m, 1H), 4.20 (m, 1H), 4.37 (t, 1H). ¹³C NMR (100 MHz) δ 13.77, 14.98, 17.98, 28.92, 37.41, 54.44, 61.86, 63.50, 101.10, 104.85, 156.01, 195.94; IR See RQ-I-6 565.1, 593.7, 614.4, 678.4, 764.4, 973.2, 990.1, 1012.5, 1039.0, 1055.9, 1089.6, 1151.7, 1172.0, 1213.4, 1258.6, 1326.9, 1381.3, 1404.5, 1425.6, 1487.8, 1667.9, 1739.3, 1758.0, 1975.7, 2010.4, 2060.4, 2850.1, 2919.8, 2965.1 cm⁻¹. HRMS (M+Na⁺) calculated for C₁₅H₁₀NO₆Na⁶²Fe: 364.15, found 364.0478.
Alkylidene Malonate 19b. Complex 26 (40.7 mg, 0.112 mmol, 1 eq) was dissolved in pyridine (1.2 mL) under argon atmosphere. Meldrum’s Acid (16.2 mg, 0.112 mmol, 1 eq) was added. After 72 hours, the dark brown solution was transferred to a separatory funnel with EtOAc (40 mL) and then washed with a saturated solution of CuSO₄ (2 x 10 mL). The combined organic layers were washed with saturated brine solution (2 x 10 mL), then dried with MgSO₄, filtered and concentrated in vacuo. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAC, 2:1) to afford 19b (42 mg, 77%) as an orange foam. ¹H NMR (400 MHz) δ 0.98 (d, 6H, J = 5.2 Hz), 1.381 (s, 1H), 1.72 (d, 7H, J = 10.4 Hz), 2.28 (s, 3H), 2.38 (d, 2H, J = 2.8 Hz), 2.80 (d, 1H, J = 12 Hz), 4.10 (d, 1H), 4.21 (d, 1H), 4.40 (t, 1H), 8.00 (d, 1 H, J = 12 Hz). ¹³C NMR (100 MHz) δ 13.82, 14.20, 14.84, 18.01, 27.51, 27.77, 28.87, 29.70, 37.92, 52.32, 61.94, 63.56, 103.31, 104.58, 105.86, 109.30, 155.97, 161.43, 162.76, 163.35; IR See RQ-I-81 558.8, 589.6, 612.8, 645.6, 672.7, 703.2, 727.2, 756.6, 771.2, 792.9, 890.4, 927.5, 971.1, 998.2, 1020.0, 1052.7, 1094.7, 1119.6, 1187.0, 1205.5, 1224.2, 1275.2, 1327.4, 1349.5 1394.8, 1465.6, 1568.5, 1707.2, 1740.4, 1984.9, 2005.5, 2060.6, 2923.1 cm⁻¹. HRMS (M+Na⁺) calculated for C₂₁H₃₅NO₅Na⁵⁸Fe: 512.26, found 512.0614.
Malonate 23. Alkyldene Malonate 19b (40 mg, 0.0919 mmol, 1 eq) was dissolved in THF (2.1 mL) under an argon atmosphere. The solution was brought to –78 °C. The pentenyl MgBr (0.5 M solution in THF, 0.327 mL, 0.164 mmol, 2 eq) was added dropwise. The solution was stirred at -78 °C for three hours, after which it was brought to – 25 °C to be quenched with saturated NH₄Cl (10 mL). After letting warm up to room temperature, it was transferred to a separatory funnel with EtOAc (30 mL). The organic layer was extracted, and washed with saturated brine solution (10 mL), then dried with MgSO₄, filtered and concentrated in vacuo. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAC, 2:1) to afford 23 (34 mg, 73%) as an oil. ¹H NMR (400 MHz) δ 0.32 (d, 1 H, 3.6 Hz), 0.95 (d, 6H), 1.2 (m, 2.7 H), 1.39 (m, 1H), 1.45 (m, 1H), 1.60 (m, 3H), 1.79 (s, 3H), 1.87 (s, 3h), 1.89 (m, 1H), 2.10 (m, 2H), 2.17 (s, 3H), 2.34 (m, 1H), 2.81 (m, 1H), 3.81 (d, 1H), 4.07 (m, 1H), 4.19 (m, 1H), 4.36 (t, 1H), 4.94 (m, 2H), 5.7 (m, 1H). ¹³C NMR (100 MHz) δ 14.02, 14.46, 17.94, 26.63, 27.26, 28.18, 28.74, 32.57, 33.85, 35.33, 39.29, 61.86, 63.23, 65.97, 102.59, 102.74, 105.07, 115.02, 138.00, 156.03, 164.09, 164.77; IR See RQ-I-84 755.5, 910.5, 1011.7, 1058.8, 1209.5, 1296.9, 1394.6, 1640.7, 1753.8, 1994.8, 2049.4, 2925.4 cm⁻¹. HRMS (M+Na⁺) calculated for C₂₆H₃₃NO₃Na⁶⁶Fe: 582.39, found 581.1397.
Alkylidene Ester 24. Malonate 23 (32.9 mg, 0.0588 mmol, 1 eq) was dissolved in methanol (1.9 mL) under and argon atmosphere. Eschenmosers’ salt (32.6 mg, 0.176 mmol, 3 eq) was added all at once. The solution was refluxed at 65 °C for 24 hours. The methanol was then removed using the rotary evaporator. The leftover brown oil was transferred to a separatory funnel with EtOAc (20 mL) and washed with NaHCO₃ (8 mL). The aqueous layer was then extracted with EtOAc (10 mL). The combined organics were washed with saturated brine solution (10 mL), then dried with MgSO₄, filtered and concentrated in vacuo. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1) to afford 24 (32.9 mg, 74%) as an oil. 

\[ \text{\textsuperscript{1}H NMR (400 MHz)} \delta 0.15 \text{ (d, 1H)}, 0.96 \text{ (m, 6H)}, 1.26 \text{ (m, 4H)}, 1.55 \text{ (m, 1H)}, 1.65 \text{ (m, 1H)}, 1.86 \text{ (m, 1H)} 2.0 \text{ (m, 2H)}, 2.11 \text{ (s, 3H)}, 2.32 \text{ (m, 1H)}, 2.49 \text{ (m, 1H)}, 3.77 \text{ (s, 3H)}, 3.98 \text{ (m, 1H)}, 4.18 \text{ (m, 1H)}, 4.33 \text{ (t, 1H)}, 4.93 \text{ (m, 2H)}, 5.61 \text{ (d, 1H, J = 1.2 Hz)}, 5.77 \text{ (m, 1H)}, 6.27 \text{ (s, 1H)}. \]

\[ \text{\textsuperscript{13}C NMR (100 MHz)} \delta 13.78, 13.97, 17.99, 27.30, 28.62, 29.70, 33.37, 33.87, 34.82, 51.76, 61.86, 63.15, 64.94, 101.95, 102.23, 114.74, 126.57, 138.46, 142.00, 156.30, 166.63. \]
Silyl-protected alcohol 30. A 3:2 solution of phenylsilane to triethylamine was made in THF (5 mL). The malonate 23 (0.0259 g, 0.0463 mmol, 1 eq) was dissolved in that solution (0.278 mL) under an argon atmosphere. The reaction was stirred at room temperature for 2 hours, after which it was quenched with water (0.045 mL). The solution was transferred to a separatory funnel using diethyl ether (5 mL) and washed with water (2 x 5 mL). The organic layer was washed with saturated brine solution (5 mL), then dried with MgSO₄, filtered and concentrated \textit{in vacuo}. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAC, 3:1) to afford 30 as an oil (yield not determined). ¹H NMR (400 MHz) δ 0.11 (d, 1H), 0.61 (d, 1H), 0.91 (m, 6H), 1.30 (m, 1.5 H), 1.81 (d, 1H), 2.05 (m, 2.4 H), 2.15 (m, 3.6 H), 2.6 (two separate doublets seen, 0.6 H), 2.8 (two separate doublets seen, 0.3H), 2.95 (m, 1H), 4.2 (m, 1H), 4.35 (t, 1H), 5.0 (m, 1.8H), 5.6 (m, 1H), 7.5 (complicated peaks), 9.84 (s, 0.8H).

The oil (yield undetermined, assumed 0.0463 mmol, 1 eq) was then dissolved in THF (0.5 mL) at 0 °C. NaBH₄ (0.88 mg, 0.0232 mmol, 0.5 eq) was then added. The ice bath was removed. After 1 hour, the reaction was quenched with 3 drops of 1M HCl. The solution was transferred to a separatory funnel with EtOAc (25 mL) then washed with 1M HCl (5 mL). The organic layer was washed with saturated brine solution (3 x 5 mL). The pH was determined to be neutral. The solution was then dried with MgSO₄, filtered and concentrated \textit{in vacuo}. The resulting oil was purified via column chromatography.
(silica gel, hexane/EtOAC, 3:1) to afford an oil (yield undeterminable). $^1$H NMR (400 MHz, not clean) $\delta$ 0.070 (d, 1H), 0.60 (d, 1H), 0.96 (m, 5.5 H), 1.24 (m, 2 H), 1.4 (m), 1.77 (m, 2.7H), 1.90 (m, 1H), 2.05 (s, 3H), 2.31 (m, 1H), 3.79 (m, 2H), 4.0 (m, 1H), 4.21 (m, 1H), 4.43 (t, 1H), 5.0 (m, 2H), 5.8 (m, 1H).

Then, the product (assume 0.0463 mmol, 1 eq), was dissolved in THF (0.5 mL) under an argon atmosphere. Imidazole (0.008 g, 0.1158 mmol, 2.5 eq) was added, after which DPSCI (d 1.074, 0.0142 mL, 0.0556 mmol, 1.2 eq) was added dropwise. The reaction was stirred at room temperature for 24 hours, after which it was quenched with saturated NH$_3$Cl (1 mL). The solution was transferred to a separatory funnel using diethyl ether (5 mL). The aqueous layer was extracted with Et$_2$O (2 x 5 mL). The combined organics were washed with saturated brine solution (7 mL), then dried with MgSO$_4$, filtered and concentrated in vacuo. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAC, 5:1) to afford the silyl-protected alcohol 30 (yield undeterminable). $^1$H NMR (400 MHz, not clean) $\delta$ 0.58 (d, 1H), 1.4 (m, 4H), 3.7 (m, 2H), 3.96 (m, 1H), 4.2 (m, 1H), 4.3 (t, 1H), 4.9 (m, 2H), 5.7 (1H), 7.35 (m, 6H), 7.7 (m, 4H). Some peaks were present but their integration could not be determined.
β-diester 29. Malonate 23 (12 mg, 0.021 mmol, 1 eq) was dissolved in ethanol (0.6 mL) under an argon atmosphere. The reaction was stirred at 45 °C for 6 hours. The ethanol was removed using a rotary evaporator. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAC, 1.5:1 with 0.5% formic acid) to afford 29 as an oil (yield not measurable). \(^1\)H NMR (400 MHz) \(\delta\) 0.084 (d, 0.62H), 0.209 (d, 0.39H), 0.88 (m, 1.6H), 0.97 (m, 5.4 H), 1.33 (m, 5.5H), 1.40 (m, 2.6 H), 1.55 (m, 1.4H), 1.75 (m, 1.2H), 1.89 (m, 1.1H), 2.05 (m, 2H), 2.15 (m, 2.7H), 2.4 (several peaks inseparable, 2.2H), 3.75 (dd, 1H), 4.05 (m, 1H), 4.5 (m, 3.8H), 5.0 (m, 1.9 H), 5.75 (m, 1H).

N-Oxazolidinoyl Diene 32. Alkylidene ester 24 (21.2 mg, 0.0423 mmol, 1 eq) was transferred to a schlenk flask under an argon atmosphere. Triethylamine N-oxide (21.8 mg, 0.423 mmol, 10 eq) was added to the flask. The two compounds were dissolved in toluene (0.40 mL) and stirred at room temperature for 4 hours. The toluene was removed using a rotary evaporator, and the crude oil was directly purified via column chromatography (silica gel, hexane/EtOAC, 2:1) to afford the demetallated diene 32 (yield undeterminable). \(^1\)H NMR (400 MHz) \(\delta\) 0.85 (dd, 6H), 1.35 (m, 2H), 1.45 (m, 2H), 1.63 (m, 3H), 1.82 (s, 3H), 1.87 (m, 1H), 2.05 (m, 2H), 3.5 (m, 1H), 3.74 (s, 3H), 3.82 (m, 1H), 4.13 (m, 1H), 4.32 (t, 1H), 2.9 (m, 2H), 5.2 (s, 1H), 5.3 (s, 1H), 5.56 (dd, 1H), 5.61 (s, 1H), 5.75 (m, 1H), 6.18 (s, 1H). \(^13\)C NMR (100 MHz) \(\delta\)
Vinylic ester malonate 23f. Malonate 23 (23.4 mg, 0.0418 mmol, 1 eq) was dissolved in CH₂Cl₂ in an argon atmosphere. Ethyl acrylate (22.8 mL, 0.209 mmol, 5 eq) was added. The solution was subsequently freezed and thawed (x3), after which the 2nd generation Grubbs catalyst was added (0.4 mg, 0.0004 mmol, 0.01 eq). The solution was stirred at 40 °C for 2.5 hours. The CH₂Cl₂ was removed via rotary evaporator, after which the crude product was directly purified via column chromatography (silica gel, hexane/EtOAC, 3:1) to afford 23f (23.9 mg, 92%). ¹H NMR (400 MHz) δ 0.34 (d, 1H, J = 3.6 Hz), 0.86 (m, 1H), 0.96 (dd, 6H), 1.25 (m, 6H), 1.39 (m, 2H), 1.6 (m, 4H), 1.80 (s, 3H), 1.85 (m, 4H), 2.19 (m, 4H), 2.31 (m, 1H), 2.80 (m, 1H), 3.81 (t, 1H), 4.09 (m, 1H), 4.1 (m, 2H), 4.40 (t, 1H), 5.80 (dt, 1H), 6.88 (dt, 1H).

N-Oxazolidinoyl Diene 33. Vinyl ester malonate 23f (23.9 mg, 0.0384 mmol, 1 eq) was transferred to a schlenk flask under an argon atmosphere. Triethylamine N-oxide (28.8 mg, 0.384 mmol, 10 eq) was added to the flask. The two compounds were dissolved in toluene (0.40 mL) and stirred at room temperature for 4 hours. The toluene was removed using a rotary evaporator, and the crude oil was directly purified via column chromatography (silica gel,
hexane/EtOAC, 2:1 to 1:1) to afford the demetallated diene 33 (yield undeterminable). $^1$H NMR (400 MHz, not clean) δ 0.85 (dd, 7.7H), 1.27 (m, 6H), 1.74 (m, 5H), 1.88 (3H), 2.19 (m, 1.6H), 3.5 (m, 1.7H), 3.8 (m, 1H), 4.15 (m, 2.9 H), 4.35 (t, 1H), 5.21 (s, 0.8H), 5.34 (s, 0.8H), 5.82 (m, 1.7 H), 6.93 (m, 1H).
\[ R_2 = \text{CH}_2\text{CH}_2\text{OTBDPS} \]

**Alkynyl Acetal 35a:** 4-(t-Butyldiphenylsilyloxy)-1-butyne (1.76 g, 5.71 mmol, 1.0 eq) was dissolved in triethylorthoformate (50 mL) under an argon atmosphere. ZnI\(_2\) (1.82 g, 5.71 mmol, 1.0 eq) was added in one portion; the flask was sealed and placed in a 110 °C oil bath. After 24 hr the flask was removed from the bath, cooled to room temperature, and was fitted with a short-path distillation apparatus and connected to the vacuum manifold. With a receiving flask placed in a -78 °C cooling bath, the solvent was removed under reduced pressure (1-2 mm Hg). The residue was chromatographed (silica, 40:1 hexanes/EtOAc containing 1% NEt\(_3\)) to afford alkynyl acetal 35a as a clear oil (1.963 g, 84%). \(^1\)H NMR (400 MHz) \(\delta\) 1.04 (s, 9H), 1.21 (t, 6H, \(J = 7.2\) Hz), 2.50 (td, 2H, \(J = 6.8, 1.6\) Hz), 3.55 (m, 2H), 3.70 (m, 2H), 3.77 (t, 2H, \(J = 6.8\) Hz), 5.21 (t, 1H, \(J = 1.6\) Hz), 7.40 (m, 6H), 7.67 (m, 4H); \(^1^3\)C NMR (100 MHz) \(\delta\) 15.1, 19.2, 22.8, 26.8, 60.6, 62.1, 76.2, 83.3, 91.4, 127.7, 129.7, 133.5, 135.6; IR (neat) 3071, 3049, 2974, 2931, 2884, 2858, 1112, 1053, 702, cm\(^{-1}\); 35a was not stable enough to be submitted for HRMS.
Alkynyl Acetal 35b: Alkynyl Acetal 35a (1.963 g, 4.78 mmol, 1.0 eq) was dissolved in CH₂Cl₂ (5.9 mL) under an argon atmosphere. 2,2-Dimethyl-1,3-propanediol (2.49 g, 23.9 mmol, 5 eq) and indium(III) triflate (107 mg, 0.191 mmol, 0.04 eq) were successively added. After stirring at room temperature overnight, the solution was loaded onto a column of basic alumina and was then eluted with 19:1 hexanes/EtOAc. Concentration of the fractions containing the product afforded alkynyl acetal 35b as a clear oil (1.864 g, 92%). \( ^1H \) NMR (400 MHz) δ 0.85 (s, 3H), 1.04 (s, 9H), 1.08 (s, 3H), 2.53 (td, 2H, J = 7.2, 1.6 Hz), 3.42 (d, 2H, J = 11.6 Hz), 3.72 (d, 2H, J = 11.6 Hz), 3.79 (t, 2H, J = 7.2 Hz), 5.22 (br s, 1H), 7.36-7.45 (m, 6H), 7.65 (m, 4H); \( ^13C \) NMR (100 MHz) δ 19.2, 22.1, 22.67, 22.69, 26.8, 30.3, 62.0, 75.7, 76.2, 83.5, 90.7, 127.7, 129.7, 133.4, 135.5; IR 613.3, 701.9, 739.1, 823.4, 932.1, 985.2, 1013.4, 1087.5, 1110.9, 1143.7, 1215.6, 1231.0, 1361.9, 1377.8, 1427.8, 1463.8, 2855.7, 2928.8, 2955.2, 3049.5, 3070.9; HRMS (M+H⁺) calculated for C₂₆H₃₅O₃Si: 423.2350, found 423.2353.

Vinyl Stannane 36: Bis(tributyltin) (4.90 mL, 9.70 mmol, 2.2 eq) was dissolved in THF (60 mL) under an argon atmosphere; the solution was cooled to -78 °C. \( n \)-BuLi (1.6 M in hexanes, 5.79 mL, 9.26 mmol, 2.1 eq) was added dropwise via syringe, and the bath temperature was warmed to -40 °C. After the reaction mixture was stirred at that temperature for 30 min, the bath was recooled to -78 °C and CuCN (790 mg, 8.82 mmol, 2.0 eq) was added at once. The bath was again warmed to -40 °C and the reaction mixture was stirred at
that temperature for 45 min, during which time an orange-yellow solution formed. The bath was again recooled to -78 °C, and anhydrous MeOH (0.268 mL, 6.62 mmol, 1.5 eq) was added dropwise via syringe. To this solution was then added, via cannula, a THF (20 mL) solution of alkynyl acetal 35b (1.864 g, 4.41 mmol, 1.0 eq). The reaction mixture was allowed to warm to a temperature of -25 °C over the next 3.5 hr, at which time it was quenched with an aqueous solution of saturated NH₄Cl/NH₄OH (9:1, total used: 40 mL). Upon warming to room temperature this was transferred to a separatory funnel with EtOAc (75 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 40 mL). The combined organics were then washed with brine (2 x 40 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The crude oil was purified via column chromatography (silica, hexanes containing 3% NEt₃) to afford vinyl stannane 36 (as a mixture of regioisomers) as a clear oil (2.90 g, 92%). ¹H NMR (peaks from major regioisomer; 400 MHz) δ 0.71 (s, 3H), 0.75-0.87 (m, 15H), 1.05 (s, 9H), 1.19 (s, 3H), 1.20-1.30 (m, 6H), 1.35-1.43 (m, 6H), 2.65 (m with tin satellites, 2H), 3.36 (d, 2H, J = 10.4 Hz), 3.56 (d, 2H, J = 10.4 Hz), 3.61 (t, 2H, J = 8.0 Hz), 5.02 (d with tin satellites, 1H, J = 6.0 Hz, J_Sn-H = 33 Hz), 7.36-7.43 (m, 6H), 7.67 (m, 4H); ¹³C NMR (peaks from major regioisomer; 100 MHz) δ 9.6 (with tin satellites, J_Sn-C = 158 Hz), 13.7, 19.2, 22.0, 22.7, 26.9, 27.4 (with tin satellites, J_Sn-C = 30 Hz), 29.0 (with tin satellites, J_Sn-C = 9.0 Hz), 30.0, 37.8, 63.6, 97.2, 127.6, 127.7, 129.55, 129.61, 134.0, 135.6, 138.6, 147.3; IR see RQ-I-23 613.3, 701.9, 739.1, 823.4, 932.1, 985.2, 1012.4, 1087.5, 1110.9, 1143.7, 1215.6, 1231.0, 1361.9, 1377.8, 1427.8, 1463.8, 2855.7, 2928.8, 2955.2, 3049.5, 3070.9 cm⁻¹; HRMS (M+Na⁺) calculated for C₃₈H₆₂O₃NaSi¹²⁰Sn: 737.3382, found 737.3366.
Oxazolidinocyl Diene 38a: Vinyl stannane 36 (2.90 g, 4.06 mmol, 1 eq), as a mixture of regioisomers, was dissolved in CH$_2$Cl$_2$ (40 mL) under an argon atmosphere and this solution was cooled to 0 °C. NIS (1.01 g, 4.47 mmol, 1.1 eq) was added all at once, and the reaction mixture was stirred for 2 hr at 0 °C. At that time, saturated aqueous NaHCO$_3$ (40 mL) and saturated aqueous Na$_2$S$_2$O$_3$ (40 mL) were added; the mixture was transferred to a separatory funnel using EtOAc (120 mL). The layers were separated and the organic layer was washed with brine (40 mL), dried (MgSO$_4$), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 40:1 hexanes/EtOAc containing 1% NEt$_3$) to afford the isomerically pure vinyl iodide (1.98 g, 88%) as a clear oil. $^1$H NMR (400 MHz) δ 0.72 (s, 3H), 1.05 (s, 9H), 1.18 (s, 3H), 2.76 (t, 2H, $J = 6.4$ Hz), 3.37 (d, 2H, $J = 10.6$ Hz), 3.57 (d, 2H, $J = 10.0$ Hz), 3.78 (t, 2H, $J = 6.4$ Hz), 5.03 (d, 1H, $J = 6.0$ Hz), 6.38 (d, 1H, $J = 5.9$ Hz), 7.38-7.44 (m, 6H), 7.67 (m, 4H); $^{13}$C NMR (100 MHz) δ 19.2, 21.9, 22.9, 26.9, 30.0, 43.5, 62.2, 98.1, 105.9, 127.7, 129.7, 133.5, 135.7, 140.2; IR see RQ-I-51-11 613.8, 642.6, 701.8, 738.2, 789.6, 823.1, 921.1, 933.4, 985.9, 1013.0, 1028.2, 1104.9, 1137.6, 1189.1, 1215.2, 1231.0, 1262.7, 1309.1, 1332.6, 1362.4, 1389.6, 1427.7, 1471.2, 1589.3, 1643.4, 2856.2, 2954.7, 3048.4, 3070.3; HRMS (M+K') calculated for C$_{26}$H$_{35}$O$_3$SiK: 589.1032, found 589.1030.

Stannyl vinyl oxazolidinone 1a (1.60 g, 3.60 mmol, 1 eq) was weighed into a one-dram vial; this vial, along with a Schlenk flask equipped with a stir bar containing the vinyl iodide prepared above (1.98 g, 3.60 mmol, 1 eq), were brought into the glove box.
In the glove box, portions of DMF were used to dissolve 1a and then transfer it by disposable pipette into the flask containing the vinyl iodide. The vial and pipette were repeatedly rinsed with DMF (total used: 18 mL to dissolve the reactants). Pd(PPh₃)₄ (416 mg, 0.360 mmol, 0.1 eq) and copper diphenylphosphinate (1.01 g, 3.60 mmol, 1.0 eq) were added at the same time and the reaction was stirred for 21 hr. In the fumehood, the reaction mixture was then filtered through a pad of silica on a glass-fritted filter (the silica was loaded as a slurry with EtOAc) using EtOAc (ca. 100 mL) to rinse the flask and silica pad. The filtrate was concentrated using the rotary evaporator and then re-dissolved in Et₂O (200 mL) and transferred to a separatory funnel. The solution was washed with H₂O (2 x 60 mL), brine (1 x 60 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 5:1 to 4:1 hexanes/EtOAc) to afford oxazolidinoyl diene 38a (1.871 g, 90 % yield) as a thick pale yellow oil. ¹H NMR (400 MHz) δ 0.70 (s, 3H), 0.78 (d, 3H, J = 7.0 Hz), 0.83 (d, 3H, J = 6.8 Hz), 1.05 (s, 9H), 1.17 (s, 3H), 1.83 (m, 1H), 2.45 (m, 1H), 2.66 (m, 1H), 3.27 (d, 1H, J = 11.0 Hz), 3.33 (d, 1H, J = 10.9 Hz), 3.52 (m, 2H), 3.74 (m, 2H), 3.81 (dt, 1H, J = 8.6, 3.8 Hz), 4.09 (dd, 1H, J = 8.6, 4.1 Hz), 4.24 (app t, 1H, 9.0, 8.8 Hz), 5.00 (d, 1H, J = 6.3 Hz), 5.22 (s, 1H), 5.29 (s, 1H), 5.68 (d, 1H, J = 6.2 Hz), 7.36-7.43 (m, 6H), 7.67 (m, 4H); ¹³C NMR (100 MHz) δ 14.3, 17.8, 19.7, 22.0, 23.0, 26.9, 28.8, 30.0, 32.5, 59.9, 62.59, 62.62, 76.99, 77.03, 98.3, 113.4, 127.75, 127.77, 128.9, 129.7, 133.7, 133.8, 135.60, 135.62, 136.5, 141.1, 156.4; IR See RQ-1-55 613.1, 688.0, 703.7, 740.9, 803.4, 823.2, 930.9, 985.3, 1012.3, 1032.3, 1089.6, 1110.2, 1153.8, 1177.3, 1233.2, 1310.0, 1326.3, 1391.7, 1427.7, 1471.7, 1589.0, 1612.5, 1762.4, 2341.6, 2359.8, 2856.6, 2957.3, 3048.3, 3070.6 cm⁻¹. 38a was not stable enough to be submitted for HRMS.
**N-Oxazolidinoyl Diene Iron(0) Tricarbonyl Complex 20.**

Prepared according to the general procedure, using diene 38a (1.87 g, 3.24 mmol, 1 eq) and Fe$_2$(CO)$_9$ (4.12 g, 11.30 mmol, 3.5 eq) in toluene (31 mL). The diastereomer ratio was established to be 7.5:1, with an overall yield of 1.95 g (84%); chromatography (silica, 7:1 hexanes/EtOAc) afforded the major complex 20 (1.72 g, 74%) as a pale yellow foam. $^1$H NMR (400 MHz) δ 0.25 (d, 1H, $J = 3.4$ Hz), 0.43 (d, 1H, $J = 5.2$ Hz), 0.62 (d, 3H, $J = 7.0$ Hz), 0.70 (s, 3H), 0.81 (d, 3H, $J = 6.8$ Hz), 1.06 (s, 9H), 1.18 (s, 3H), 1.66 (d, 1H, $J = 3.4$ Hz), 2.20 (m, 1H), 2.68 (collapsed dt/app pentent, 1H, $J = 14.2$, 6.6 Hz), 2.87 (collapsed dt/app pentent, 1H, $J = 14.2$, 7.0 Hz), 3.32 (d, 1H, $J = 11.0$ Hz), 3.37 (d, 1H, $J = 11.1$ Hz), 3.49 (dd, 1H, $J = 11.0$, 2.6 Hz), 3.60 (m, 2H), 3.80 (app t, 1H, $J = 8.9$ Hz), 3.87-4.00 (m, 3H), 4.49 (d, 1H, $J = 5.2$ Hz), 7.34-7.46 (m, 6H), 7.66 (m, 4H); $^{13}$C NMR (100 MHz) δ 13.5, 17.6, 19.3, 21.8, 23.1, 26.9, 28.7, 29.8, 31.7, 36.7, 57.2, 61.0, 63.5, 64.1, 76.99, 77.2 99.9, 101.1, 101.3, 127.7, 127.8, 129.77, 129.82, 133.48, 133.54, 135.5, 135.6, 156.1; IR RQ-I-60 564.1, 578.3, 601.4, 628.4, 661.9, 688.2, 701.2, 743.8, 786.8, 822.8, 920.0, 974.4, 989.9, 1013.9, 1057.4, 1103.6, 1154.9, 1205.4, 1326.2, 1392.6, 1426.8, 1463.4, 1589.1, 1755.1, 2967.4, 2052.1, 2856.1, 2957.1 cm$^{-1}$; HRMS (M+Na$^+$) calculated for C$_{37}$H$_{45}$NO$_6$NaSi$^{56}$Fe: 740.2313, found 740.2293.
Hydroxy Dioxolane Diene Iron Complex 20a. Diene iron complex 20 (0.4774 g, 0.6652 mmol, 1 eq) was dissolved in THF (7.2 mL). TBAF (1.0 M in THF, 0.80 mL, 0.7982 mmol, 1.2 eq) was added dropwise to a flask open to air. After 24 hours, the solution was transferred to a separatory funnel using EtOAc (40 mL) and washed with saturated NaHCO₃ (10 mL). The organic layer was washed with saturated brine solution (10 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 1:1.5 hexanes/EtOAc) to afford 20a (0.2794 g, 88%) as a clear oil. ¹H NMR (400 MHz) δ 0.39 (d, 1H, J = 3.2 Hz), 0.52 (d, 1H, H = 6.8 Hz), 0.73 (s, 3H), 0.92 (t, 6H), 1.18 (s, 3H), 1.75 (d, 1H), 2.4 (2 peaks, m, 2H), 2.95 (m, 1H), 3.23 (s, 1H), 3.5 (dd, 2H), 3.65 (t, 2H), 3.79 (m, 1H), 4.05 (m, 2H), 4.15 (m, 1H), 4.30 (t, 1H), 4.39 (d, 1H, J = 6.8 Hz). ¹³C NMR (100 MHz) δ 13.57, 17.92, 21.73, 23.00, 29.04, 29.87, 31.34, 37.50, 56.01, 61.53, 62.11, 64.46, 99.99, 101.76, 102.35, 156.20; IR see RQ-I-69 561.1, 591.0, 604.6, 629.5, 662.9, 976.5, 1015.7, 1056.1, 1075.6, 1219.0, 1726.7, 1971.3, 2047.9, 2872.2, 2957.4, 3476.9 cm⁻¹; HRMS (M+Na⁺) calculated for C₂₁H₂₈NO₆NaSi⁵⁶Fe: 501.31, found 502.1135.

Aldehyde Dioxolane Diene Iron Complex 40. Alcohol 20a (58.6 mg, 0.122 mmol, 1 eq) was dissolved in CH₂Cl₂ (1.6 mL) under an argon atmosphere. In a separate flask, DIPEA (0.085 mL, 0.489 mmol, 4 eq) was dissolved in DMSO (0.31 mL). The DMSO and amine solution was transferred to the alcohol solution via cannula. The total solution was cooled to -40 °C. The SO₃.pyridine (55.1 mg, 0.367
mmol, 3 eq) was added. The solution was warmed to 0 °C and stirred at that temperature for 2 hours. The reaction was quenched with saturated NaHCO₃ (4 mL) and brought to room temperature. The solution was then transferred to a separatory funnel with EtOAc (18 mL). The organic layer was washed with water (2 x 4 mL) and then brine (4 mL). The organic layer was then dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 3:1 hexanes/EtOAc) to afford 40 (57.4 mg, 98%) as a pale yellow oil. ¹H NMR (400 MHz) δ 0.36 (d, 1H, J = 3.2 Hz), 0.50 (d, 1H, J = 5.6 Hz), 0.72 (s, 3H), 0.90 (dd, 6H), 1.18 (s, 3H), 1.80 (d, 1H, J = 3.2 Hz), 2.37 (t, 1H), 3.42 (m, 2H), 3.6 (m, 3H), 3.73 (dd, 1H), 3.95 (m, 1H), 4.13 (m, 1H), 4.21 (t, 1H), 4.39 (d, 1H, J = 5.2 Hz). ¹³C NMR (100 MHz) δ 13.65, 17.95, 21.81, 23.11, 28.99, 29.93, 36.65, 43.56, 55.77, 61.95, 63.79, 93.43, 101.62, 103.34, 156.10, 198.51; IR see RQ-1-79 591.1, 661.2, 1036.9, 1226.0, 1390.7, 1708.3, 1745.4, 1926.5, 1958.3, 1983.5, 2047.3, 2869.2, 2965.7 cm⁻¹; HRMS (M+Na⁺) data not obtained yet.
R₂ = sulfonamide

Oxazolidinoyl diene 21: The vinyl iodide required for 21 was derived from vinyl stannane 36; its preparation was described above (see synthesis of oxazolidinoyl diene 38a).

The vinyl iodide (148 mg, 0.270 mmol, 1 eq) was dissolved in THF (2.9 mL); TBAF (1.0 M solution in THF, 0.32 mL, 0.32 mmol, 1.2 eq) was added dropwise via syringe. After 16 hr, the solution was diluted with EtOAc (20 mL) and this was washed with saturated aqueous NaHCO₃ (7 mL), brine (7 mL), dried (MgSO₄), filtered, and concentrated using a rotary evaporator. The residue was chromatographed (silica, 5:1 hexanes/EtOAc) to afford the alcohol (54.8 mg, 65%) as a clear oil. ¹H NMR (400 MHz) δ 0.74 (s, 3H), 1.22 (s, 3H), 2.37 (br s, 1H), 2.81 (t, 2H, J = 5.9 Hz), 3.50 (dd, 2H, J = 11.3, 0.8), 3.65 (dd, 2H, J = 10.0, 1.4 Hz), 3.74 (br t, 2H, J = 5.4 Hz), 5.05 (d, 1H, J = 5.5 Hz), 6.48 (d, 1H, J = 5.5 Hz); ¹³C NMR (100 MHz) δ 21.8, 22.9, 30.0, 43.7, 60.1, 77.2, 98.0, 106.7, 140.8; IR (neat) see RQ-I-42 642.8, 930.9, 984.0, 1024.2, 1066.1, 1100.7, 1136.1, 1191.3, 1216.0, 1231.9, 1278.9, 1309.9, 1391.1, 1469.4, 1640.8, 2850.4, 2954.7, 3416.3 cm⁻¹; HRMS (M+Na⁺) calculated for C₁₀H₁₇O₃NaI: 335.0115, found 335.0113.
The alcohol prepared above (54.8 mg, 0.176 mmol, 1 eq) was dissolved under an argon atmosphere in THF (1.8 mL), and to this solution was added PPh₃ (92.1 mg, 0.351 mmol, 2 eq) and the N-TEOC-protected p-tolylsulfonamide (66.5 mg, 0.211 mmol, 1.2 eq). The mixture was cooled to 0 °C, and DIAD (0.061 mL, 0.316 mmol, 1.8 eq) was added dropwise via syringe. The bath was removed and the reaction was stirred at room temperature for 16.5 hr. The solvent was removed using the rotary evaporator and the residue was chromatographed (silica, 12:1 hexanes/EtOAc) to afford the sulfonamide (90.6 mg, 85%) as a clear oil. \(^1\)H NMR (400 MHz) δ 0.72 (s, 3H), 0.99 (m, 2H), 1.19 (s, 3H), 2.43 (s, 3H), 3.00 (m, 2H), 3.54 (d, 2H, J = 11.1 Hz), 3.63 (d, 2H, J = 11.2 Hz), 3.96 (m, 2H), 4.17 (m, 2H), 5.14 (d, 1H, J = 5.8 Hz), 6.40 (d, 1H, J = 5.8 Hz), 7.31 (d, 2H, J = 8.3 Hz), 7.83 (d, 2H, J = 8.3 Hz); \(^13\)C NMR (100 MHz) δ -1.7, 17.4, 21.6, 21.8, 22.9, 30.0, 41.4, 46.1, 66.1, 77.1, 97.8, 102.8, 128.2, 129.3, 136.4, 140.7, 144.6, 152.2; IR see RQ-I-65 581.7, 652.8, 672.4, 703.8, 753.7, 814.6, 883.9, 860.6, 920.0, 932.7, 985.3, 1013.6, 1043.5, 1091.2, 1140.5, 1170.1, 1185.7, 1213.3, 1250.4, 1307.6, 1359.8, 1389.5, 1453.7, 1494.6, 1597.1, 1641.5, 1731.9, 2850.6, 2903.5, 2955.1 cm\(^{-1}\); HRMS (M+Na\(^+\)) calculated for C\(_{23}\)H\(_{36}\)NO\(_6\)NaSiSI: 632.0970, found 632.0959.

Stannyl vinyl oxazolidinone 1a (64.9 mg, 0.146 mmol, 1 eq) was weighed into a one-dram vial; this vial, along with a Schlenk flask equipped with a stir bar containing the sulfonamido vinyl iodide prepared above (89.0 mg, 0.146 mmol, 1 eq), were brought into the glove box. In the glove box, portions of DMF were used to dissolve 1a and then transfer it by disposable pipette into the flask containing the vinyl iodide. The vial and pipette were repeatedly rinsed with DMF (total used: 0.75 mL to dissolve the reactants).
Pd(PPh₃)₄ (17 mg, 0.0146 mmol, 0.1 eq) and copper diphenylphosphinate (47.1 mg, 0.168 mmol, 1.15 eq) were added at the same time and the reaction was stirred for 19 hr. In the fumehood, the reaction mixture was then filtered through a pad of silica on a glass-fritted filter (the silica was loaded as a slurry with EtOAc) using EtOAc (ca. 30 ml) to rinse the flask and silica pad. The filtrate was concentrated using the rotary evaporator and then re-dissolved in Et₂O (35 mL) and transferred to a separatory funnel. The solution was washed with H₂O (2 x 8 mL), brine (1 x 8 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 4:1 to 3:1 hexanes/EtOAc) to afford oxazolidinoyl diene 8i (87.7 mg, 94% yield) as a white solid.

'H NMR (400 MHz) δ 0.0 (s, 9H), 0.74 (s, 3H), 0.87 (d, 3H, J = 7.0 Hz), 0.90 (d, 3H, J = 6.8 Hz), 0.96 (m, 2H), 1.23 (s, 3H), 1.89 (m, 1H), 2.43 (s, 3H), 2.77 (m, 1H), 3.64 (m, 4H), 3.86 (m, 3H), 4.17 (m, 3H), 4.38 (t, 1H, J = 8.9 Hz), 5.31 (d, 1H, J = 6.2 Hz), 5.37 (s, 1H), 5.76 (s, 1H), 5.79 (d, 1H, J = 6.2 Hz), 7.31 (d, 2H, J = 8.2 Hz), 7.82 (d, 2H, J = 8.2 Hz); ¹³C NMR (100 MHz) δ -1.7, 14.6, 17.6, 17.8, 21.7, 22.0, 23.1, 29.1, 30.1, 30.3, 46.5, 60.3, 63.0, 66.2, 77.2, 77.3, 98.3, 115.0, 128.2, 129.1, 129.4, 135.9, 136.5, 140.8, 144.6, 152.4, 156.6; IR see RQ-I-70 563.1, 578.0, 630.8, 857.8, 1055.7, 1091.6, 1165.9, 1391.5, 1597.9, 1673.3, 1728.6, 1755.0, 1975.8, 2050.6, 2342.6, 2359.2, 2955.5 cm⁻¹; the diene was not stable enough to be submitted for HRMS.

Prepared according to the general procedure, from the diene (87.7 mg, 0.1377 mmol, 1 eq) and Fe₂(CO)₉ (175.3 mg, 0.4820 mmol, 3.5 eq) in toluene (1.4 mL). The diastereomer ratio was established to be at least 15:1, and chromatography (silica, 5:1 hexanes/EtOAc containing 1% NEt₃) afforded the complex (as a diastereomeric mixture)
21 (80.7 mg, 75%) as a light yellow foam. $^1$H NMR (peaks from major diastereomer; 400 MHz) $\delta$ 0.01 (s, 9H), 0.34 (d, 1H, $J = 3.4$ Hz), 0.52 (d, 1H, $J = 6.4$ Hz), 0.71 (s, 3H), 0.94 (m, 9H), 1.21 (s, 3H), 1.74 (d, 1H, $J = 3.3$ Hz), 2.40 (m, 1H), 2.44 (s, 3H), 2.70 (m, 1H), 2.94 (m, 1H), 3.48 (d, 1H, $J = 10.8$ Hz), 3.63 (m, 3H), 3.89 (m, 1H), 4.14 (m, 4H), 4.37 (m, 1H), 4.56 (m, 2H), 7.33 (d, 2H, $J = 8.0$ Hz), 7.82 (m, 2H, $J = 8.4$ Hz); $^{13}$C NMR (peaks from major diastereomer; 100 MHz) $\delta$ -1.6, 13.7, 17.6, 18.0, 21.6, 21.8, 23.1, 28.8, 29.2, 29.9, 46.5, 56.6, 61.4, 64.6, 66.3, 77.4, 101.3, 128.4, 129.4, 136.6, 144.7, 152.2; IR see RQ-73 666.2, 813.7, 972.3, 1036.2, 1061.2, 1093.2, 1171.3, 1216.5, 1277.4, 1393.5, 1454.9, 1597.8, 1754.9, 1995.5, 2057.5, 2872.0, 2958.3, 3019.4 cm$^{-1}$; HRMS (M+Na$^+$) calculated for $C_{34}H_{48}N_2O_{11}$NaSiS$^{56}$Fe: 799.1990, found 799.2026.

**Sulfonimide Diene Iron Tricarbonyl 21a.** The TEOC-protected sulphonamide 21 (62.1 mg, 0.0799 mmol, 1 eq) was dissolved in THF (1 mL). TBAF (0.096 mL, 1.2 eq) was added. The reaction was stirred for 21 hours, after which it was diluted with EtOAc (25 mL). The solution was washed with saturated NaHCO$_3$ (8 mL). The separated organic layer was washed with saturated brine solution (8 mL), then dried (MgSO$_4$), filtered and concentrated *in vacuo*. The resulting oil was purified via column chromatography (silica gel, 2.5:1 hexanes/EtOAc) to afford the deprotected sulfonamide 21a (49.8 mg, 99%). $^1$H NMR (400 MHz) $\delta$ 0.22 (d, 1H, $J = 3.6$ Hz), 0.39 (d, 1H, $J = 7.2$ Hz), 0.74 (s, 3H), 0.89 (dd, 6H), 1.20 (s, 3H), 1.71 (d, 1H, $J = 3.6$ Hz), 2.25 (m, 1H), 2.35 (m, 1H), 2.42 (s, 3H), 2.93 (m, 1H), 3.10 (m, 1H), 3.30 (m, 1H), 3.45 (m, 2H), 3.65 (m, 2H), 2.75 (m, 1H), 4.13 (m, 1H), 4.33 (m, 2H), 6.20 (m, 1H), 7.27 (m,
2H), 7.70 (m, 2H). $^{13}$C NMR (100 MHz) δ 13.49, 14.20, 17.81, 21.08, 21.51, 21.73, 23.05, 27.44, 29.15, 29.86, 37.47, 42.39, 55.48, 60.42, 61.62, 64.11, 101.96, 102.06, 127.12, 139.60, 136.98, 143.25, 156.01; IR see RQ-I-74 595.3, 629.4, 662.0, 988.9, 1013.5, 1057.7, 1102.7, 1156.4, 1209.3, 1324.6, 1394.2, 1455.4, 1599.4, 1750.7, 1969.1, 2053.2, 2958.0, 3242.6 cm$^{-1}$; HRMS (M+Na$^+$) calculated for C$_{28}$H$_{36}$N$_2$O$_6$NaS$^{56}$Fe: calculated 655.51, found 655.1383.

Sulfonamide Diene Iron Tricarbonyl 42. Compound 21a

(46.1 mg, 0.0729 mmol, 1 eq) was dissolved in butyl vinyl ether (0.5 mL, 50 eq). DppPd(OTFA)$_2$ (4.8 mg, 7.3 μmol, 0.1 eq) was added. The reaction was stirred at 75 °C for 3.5 hours. The solvent was removed via rotary evaporator. The residue was chromatographed (silica, 4:1 hexanes/EtOAc) to afford 42 (36.7 mg, 76% yield). $^1$H NMR (400 MHz) δ 0.36 (d, 1H, J = 3.2 Hz), 0.49 (br, 1H), 0.70 (m, 3H), 0.94 (dd, 6H), 1.18 (s, 3H), 1.60 (m, 1H), 2.41 (s, 4H), 2.58 (m, 1H) 2.90 (m, 1H), 3.43 (m, 2H), 3.10 (m, 3H), 3.30 (m, 1H), 4.1 (m, 2H), 4.40 (m, 3H), 4.6 (m, 1H), 6.85 (m, 1H), 7.28 (m, 2H), 7.65 (m, 2H). $^{13}$C NMR (100 MHz) δ 13.62, 18.09, 21.56, 21.81, 23.02, 27.15, 28.94, 29.84, 44.87, 61.59, 64.21, 93.38, 101.88, 126.89, 129.90, 132.24, 135.83, 143.97.
\[ R_2 = \text{CH}_2\text{CH}_2\text{CH}_2 \text{OTBDPS} \]

**Alkynyl acetal 44a:** 5-(t-Butyldiphenylsilyloxy)-1-pentyne (2.74 g, 8.50 mmol, 1.0 eq) was dissolved in triethylorthofomate (50 mL) under an argon atmosphere. ZnI₂ (2.71 g, 8.50 mmol, 1.0 eq) was added in one portion; the flask was sealed and placed in a 110 °C oil bath. After 24 hr the flask was removed from the bath, cooled to room temperature, and was fitted with a short-path distillation apparatus and connected to the vacuum manifold. With a receiving flask placed in a -78 °C cooling bath, the solvent was removed under reduced pressure (1-2 mm Hg). The residue was chromatographed (silica, 40:1 hexanes/EtOAc containing 1% NEt₃) to afford alkynyl acetal 44a as a clear oil (3.30 g, 92%). ¹H NMR (400 MHz) δ 1.04 (s, 9H), 1.22 (t, 6H, J = 7.1 Hz), 1.78 (m, 2H), 2.40 (td, 2H, J = 7.2, 1.5 Hz), 3.55 (m, 2H), 3.71 (m, 4H), 5.24 (t, 1H, J = 1.5 Hz), 7.40 (m, 6H), 7.65 (m, 4H); ¹³C NMR (100 MHz) δ 15.1, 15.2, 19.2, 26.8, 31.2, 60.6, 62.4, 75.8, 86.1, 91.4, 127.6, 129.6, 133.8, 135.5; 44a was not stable enough to be submitted for HRMS.

**Alkynyl acetal 45:** Alkynyl acetal 44a (3.03 g, 7.78 mmol assumed, 1.0 eq) was dissolved in CH₂Cl₂ (10.0 mL) under an argon atmosphere. 2,2-Dimethyl-1,3-propanediol (4.05 g, 38.89 mmol, 5 eq) and indium(III) triflate (175 mg, 0.311 mmol, 0.04 eq) were successively added. After stirring at room temperature for 24 hr, the solution was loaded onto a column of basic alumina and was then eluted with 19:1 hexanes/EtOAc. Concentration
of the fractions containing the product afforded alkynyl acetal 45 as a clear oil (3.016 g, 89%). \(^1\)H NMR (400 MHz) \(\delta\) 0.86 (s, 3H), 1.04 (s, 9H), 1.10 (s, 3H), 1.79 (m, 2H), 2.42 (td, 2H, \(J = 7.6, 1.6\) Hz), 3.43 (d, 2H, \(J = 11.6\) Hz), 3.72 (m, 4H), 3.82 (m, 4H), 5.23 (s, 1H), 7.35-7.44 (m, 6H), 7.65 (m, 4H); \(^13\)C NMR (100 MHz) \(\delta\) 15.2, 19.2, 22.2, 22.8, 26.8, 30.3, 31.2, 62.4, 75.2, 75.8, 86.5, 90.9, 127.6, 129.6, 133.8, 135.6; HRMS (M+H\(^+\)) calculated for C\(_{23}\)H\(_{37}\)O\(_3\)Si: 437.2507, found 437.2515.

Vinyl stannane 45a Bis(tributyltin) (6.73 mL, 15.19 mmol, 2.2 eq) was dissolved in THF (60 mL) under an argon atmosphere; the solution was cooled to -78 °C. n-BuLi (1.6 \(M\) in hexanes, 9.07 mL, 14.50 mmol, 2.1 eq) was added dropwise via syringe, and the bath temperature was warmed to -40 °C. After the reaction mixture was stirred at that temperature for 30 min, the bath was recooled to -78 °C and CuCN (1.24 g, 13.81 mmol, 2.0 eq) was added at once. The bath was again warmed to -40 °C and the reaction mixture was stirred at that temperature for 45 min, during which time an orange-yellow solution formed. The bath was again recooled to -78 °C, and anhydrous MeOH (0.420 mL, 10.36 mmol, 1.5 eq) was added dropwise via syringe. To this solution was then added, via cannula, a THF (20 mL) solution of alkynyl acetal 45 (3.016 g, 6.907 mmol, 1.0 eq). The reaction mixture was allowed to warm to a temperature of -25 °C over the next 3.5 hr, at which time it was quenched with an aqueous solution of saturated NH\(_4\)Cl/NH\(_4\)OH (9:1, total used: 60 mL). Upon warming to room temperature this was transferred to a separatory funnel with EtOAc (75 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 40 mL). The combined organics were then washed with brine.
(2 x 40 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The crude oil was purified via column chromatography (silica, hexanes containing 3% NEt₃) to afford vinyl stannane 45a (as a mixture of regioisomers) as a clear oil (4.49 g, 89%).

1H NMR (peaks from major regioisomer; 400 MHz) δ 0.69 (s, 3H), 0.75-0.87 (m, 15H), 1.08 (s, 9H), 1.22 (s, 3H), 1.24-1.36 (m, 6H), 1.42-1.50 (m, 6H), 1.59 (m, 2H), 2.48 (m, 2H), 3.43 (d, 2H, J = 11.2 Hz), 3.60 (d, 2H, J = 11.2 Hz), 3.67 (t, 2H, J = 6.0 Hz), 5.18 (d with tin satellites, 1H, J = 6.0 Hz, J_{Sn-H} = 3.8 Hz); 5.64 (d with tin satellites, 1H, J = 6.0 Hz, J_{Sn-H} = 34 Hz), 7.36-7.45 (m, 6H), 7.65-7.68 (m, 4H); 13C NMR (peaks from major regioisomer; 100 MHz) δ 9.8 (with tin satellites, J_{Sn-C} = 165 Hz), 13.7, 19.2, 22.2, 23.1, 27.1, 27.4 (with tin satellites, J_{Sn-C} = 29 Hz), 29.1 (with tin satellites, J_{Sn-C} = 9.6 Hz), 30.3, 30.9, 33.3, 63.6, 77.2, 97.2, 127.6, 129.6, 134.0, 135.6, 136.6, 152.2; HRMS (M+Na⁺) calculated for C₃₉H₆₄O₃NaSi₁₂°Sn: 751.3539, found 751.3556.

**Alcohol Vinyl Stannane 45b.** Protected alcohol 45a (0.81 g, 1.113 mmol, 1 eq) was dissolved in THF (12 mL). TBAF (1.22 mL, 1.22 mmol, 1.1 eq) was added dropwise to a flask open to air. The reaction was stirred for 16 hours. It was then diluted with EtOAc (50 mL). The solution was washed with saturated NaHCO₃ (25 mL). The organic layer was then washed with saturated brine solution (25 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The crude oil was purified via column chromatography (silica, 9:1 hexanes/EtOAc with 1% NEt₃) to afford alcohol vinyl stannane 45b as a clear oil (yield undetermined, regioisomeric ratio undetermined). 1H NMR (400 MHz) δ 0.72
(m, 4H), 0.89 (m, 20H), 1.21 (m, 1H), 1.27 (m, 1H), 1.35 (m, 3 H), 1.45 (m, 9H), 1.65 (m, 2.6H), 2.39 (m, 1H), 2.45 (m, 1H), 3.5 (m, 7H), 5.20 (m, 1H), 5.65 (m, 1H).

Aldehyde Dioxolane Diene Iron Complex 46. Alcohol 45b

(0.1737 g, 0.3550 mmol, 1 eq) was dissolved in CH₂Cl₂ (4.6 mL) under an argon atmosphere. In a separate flask, DIPEA (0.247 mL, 1.42 mmol, 4 eq) was dissolved in DMSO (0.9 mL). The DMSO and amine solution was transferred to the alcohol solution via cannula. The total solution was cooled to -40 °C. The SO₃.pyridine (160 mg, 1.07 mmol, 3 eq) was added. The solution was warmed to 0 °C and stirred at that temperature for 2 hours. The reaction was quenched with saturated NaHCO₃ (7 mL) and brought to room temperature. The solution was then transferred to a separatory funnel with EtOAc (25 mL). The organic layer was washed with water (2 x 7 mL) and then brine (7 mL). The organic layer was then dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 9:1 hexanes/EtOAc with 1% NEt₃) to afford 46 (157.2 mg, 91%) as a pale yellow oil. ¹H NMR (400 MHz) δ 0.71 (m, 3H), 0.85 (m, 15 H), 1.19 (s, 1H), 1.22 (s, 2H), 1.31 (m, 7H), 1.49 (m, 6H), 5.15 (m, 1H), 5.65 (m, 1H), 9.75 (t, 1H).
Alkynyl acetal 48b: Ethyl 4-pentynoate (1.86 g, 14.74 mmol, 1.0 eq) was dissolved in triethylorthoformate (50 mL) under an argon atmosphere. ZnI₂ (4.706 g, 14.74 mmol, 1.0 eq) was added in one portion; the flask was sealed and placed in a 110 °C oil bath. After 20 hr the flask was removed from the bath, cooled to room temperature, and was fitted with a short-path distillation apparatus and connected to the vacuum manifold. With a receiving flask placed in a -78 °C cooling bath, the solvent was removed under reduced pressure (1-2 mm Hg). The residue was chromatographed (silica, 9:1 hexanes/EtOAc containing 0.5% NEt₃) to afford alkynyl acetal 48b as a clear oil (2.795 g, 82%). ¹H NMR (400 MHz) δ 1.23 (t, 6H, J = 7.2 Hz), 1.27 (t, 3H, J = 7.2 Hz), 2.56 (br m, 4H), 3.56 (m, 2H), 3.73 (m, 2H), 4.15 (q, 2H, J = 7.2 Hz), 5.24 (d, 1H, J = 1.6 Hz); ¹³C NMR (100 MHz) δ 14.2, 14.6, 15.1, 33.2, 60.65, 60.71, 84.3, 91.3, 171.7.

Alkynal Acetal 49. Acetal 48b (2.7952 g, 12.24 mmol, 1.0 eq) was dissolved in CH₂Cl₂ (16 mL) under an argon atmosphere. 2,2-Dimethyl-1,3-propanediol (6.376 g, 61.22 mmol, 5 eq) and indium(III) triflate (275.3 mg, 0.490 mmol, 0.04 eq) were successively added. After stirring at room temperature overnight, the solution was loaded onto a column of basic alumina and was then eluted with hexanes. The solvent containing the eluted product was removed via careful distillation using a Vigreux column; the residue was purified by bulb-to-bulb distillation at ambient pressure (100-125 °C) give the alkynyl acetal 49 as a clear liquid of adequate purity for use in the next step (2.763 g).
94%). ¹H NMR (400 MHz) δ 0.86 (s, 3H), 1.10 (s, 3H), 1.26 (t, 3H), 2.56 (m, 4H), 3.43 (d, J = 11.6 Hz, 2H), 3.72 (d, J = 11.6 Hz, 2H), 4.14 (q, 2H), 5.25 (s, 1H). ¹³C NMR (100 MHz) δ 14.19, 14.48, 22.16, 22.70, 30.34, 33.02, 60.74, 75.67, 75.73, 84.72, 90.66, 171.66.

**Vinyl stannane 49a**: Bis(tributyltin) (0.24 mL, 0.4806 mmol, 2.2 eq) was dissolved in THF (3 mL) under an argon atmosphere; the solution was cooled to -78 °C. *n*-BuLi (1.6 M in hexanes, 0.29 mL, 0.4588 mmol, 2.1 eq) was added dropwise via syringe, and the bath temperature was warmed to -40 °C. After the reaction mixture was stirred at that temperature for 30 min, the bath was recooled to -78 °C and CuCN (0.039 g, 0.437 mmol, 2.0 eq) was added at once. The bath was again warmed to -40 °C and the reaction mixture was stirred at that temperature for 45 min, during which time an orange-yellow solution formed. The bath was again recooled to -78 °C, and anhydrous MeOH (0.013 mL, 0.33 mmol, 1.5 eq) was added dropwise via syringe. To this solution was then added, via cannula, a THF (1 mL) solution of alkynyl acetal 49 (52.5 mg, 0.218 mmol, 1.0 eq). The reaction mixture was allowed to warm to a temperature of -25 °C over the next 3.5 hr, at which time it was quenched with an aqueous solution of saturated NH₄Cl/NH₄OH (9:1, total used: 5 mL). Upon warming to room temperature this was transferred to a separatory funnel with EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organics were then washed with brine (2 x 10 mL), dried (MgSO₄), filtered, and concentrated using the
rotary evaporator. The crude oil was purified via column chromatography (silica, 19:1 hexanes/EtOAc containing 2% NEt₃) to afford vinyl stannane 49a (as a mixture of regioisomers) as a clear oil (87.2 mg, 73%). ¹H NMR (peaks from major regioisomer; 400 MHz) δ 0.76 (s, 3H), 0.82-0.99 (m, 17H), 1.23-1.37 (m, 14H), 1.45 (m, 6H), 1.69 (s, 3H), 2.33 (m, 2H), 2.65 (m, 2H, with tin satellites), 3.55-3.65 (m, 5H), 4.13 (m, 2H, with tin satellites), 5.15 (m, 1H, with tin satellites), 5.65 (m, 1H, with tin satellites). ¹³C NMR (100 MHz) δ 9.69, 10.32, 13.65, 13.73, 14.23, 22.00, 23.07, 27.11, 27.40, 29.02, 29.61, 30.07, 34.73, 60.42, 97.16, 137.80, 150.30, 173.00; IR see RQ-I-56 932.1, 985.1, 1015.9, 1099.9, 1162.4, 1140.4, 1231.6, 1376.2, 1418.7, 1464.3, 1737.0, 2359.9, 2849.2, 2870.9, 2926.7, 2955.6 cm⁻¹; HRMS (M+Na⁺) calculated for C₃₅H₄₆O₄NaSn²⁰: calculated 555.37, found 555.2467.

Oxazolidinocyl diene 50a: Vinyl stannane 49a (0.0872 g, 0.164 mmol, 1 eq), as a mixture of regioisomers, was dissolved in CH₂Cl₂ (1.7 mL) under an argon atmosphere and this solution was cooled to 0 °C. NIS (0.044 g, 0.197 mmol, 1.2 eq) was added all at once, and the reaction mixture was stirred for 3 hr at 0 °C. At that time, saturated aqueous NaHCO₃ (5 mL) and saturated aqueous Na₂S₂O₃ (5 mL) were added; the mixture was transferred to a separatory funnel using Et₂O (30 mL). The layers were separated and the organic layer was washed with brine (2 x 5 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 10:1 hexanes/EtOAc containing 1% NEt₃) to afford the isomerically pure vinyl iodide (31.9
mg, 53%) as a clear oil. [NOTE: due to potentially volatility of this compound flasks containing the compound were only briefly connected to the vacuum manifold]. $^1$H NMR (400 MHz) δ 0.74 (s, 3H), 1.20 (s, 3H), 1.27 (t, 3H), 2.55 (m, 2H), 2.79 (m, 2H), 3.51 (dd, 2H), 3.61 (dd, 2H), 4.14 (q, 2H), 5.11 (d, 1H), 6.32 (q, 1H); $^{13}$C NMR (100 MHz) δ 14.20, 21.85, 22.89, 30.02, 34.13, 35.48, 60.69, 97.93, 108.24, 139.39, 172.00.

Stannyl vinyl oxazolidinone 1a (38.5 mg, 0.0866 mmol, 1 eq) was weighed into a one-dram vial; this vial, along with a Schlenk flask equipped with a stir bar containing the vinyl iodide prepared above (31.9 mg, 0.0866 mmol, 1 eq), were brought into the glove box. In the glove box, portions of DMF were used to dissolve 1a and then transfer it by disposable pipette into the flask containing the vinyl iodide. The vial and pipette were repeatedly rinsed with DMF (total used: 0.5 mL to dissolve the reactants). Pd(PPh$_3$)$_4$ (10 mg, 0.009 mmol, 0.1 eq) and copper diphenylphosphinate (28.0 mg, 0.10 mmol, 1.15 eq) were added at the same time and the reaction was stirred for 19 hr. In the fumehood, the reaction mixture was then filtered through a pad of silica on a glass-fritted filter (the silica was loaded as a slurry with EtOAc) using EtOAc (ca. 50 ml) to rinse the flask and silica pad. The filtrate was concentrated using the rotary evaporator and then re-dissolved in Et$_2$O (30 mL) and transferred to a separatory funnel. The solution was washed with H$_2$O (2 x 5 mL), brine (2 x 5 mL), dried (MgSO$_4$), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 2:1 hexanes/EtOAc) to afford oxazolidinocyl diene 50a (0.034 g, 99 % yield) as a clear oil.

$^1$H NMR (400 MHz) δ 0.75 (s, 3H), 0.88 (m, 6H), 1.24 (m, 6H), 1.93 (m, 1H), 2.43 (m, 3H), 2.73 (m, 1H), 3.51 (dd, 2H), 3.26 (d, 2H), 3.82 (m, 1H), 4.11 (m, 3H), 4.31 (t, 1H), 5.17 (d, 1H, J = 6 Hz), 5.31 (s, 1H), 5.43 (s, 1H), 5.71 (d, 1H, J = 6 Hz). $^{13}$C NMR (100 MHz) δ 14.20, 21.85, 22.89, 30.02, 34.13, 35.48, 60.69, 97.93, 108.24, 139.39, 172.00.
N-Oxazolidinoyl Diene Iron(0) Tricarbonyl Complex 22.

Prepared according to the general procedure, using diene 50a (0.034 g, 0.086 mmol, 1 eq) and Fe₂(CO)₉ (0.1095 g, 0.301 mmol, 3.5 eq) in toluene (0.86 mL). The diastereomer ratio was established to be 8:1, and chromatographies (silica, 4:1 hexanes/EtOAc) afforded the major complex 22 (37.3 mg, 81%) as a yellow oil. The minor complex was also obtained. Mixture of diastereoisomers: ¹H NMR (400 MHz) δ 0.29 (d, 0.8H), 0.39 (d, 0.1H), 0.49 (d, 0.8H), 0.55 (0.1H), 0.72 (s, 3H), 0.94 (m, 5H), 1.05 (m, 0.8H), 1.20 (s, 3H), 1.26 (m, 3H), 1.72 (d, 0.9H), 1.82 (d, 0.1H), 2.43 (m, 0.8H), 2.59 (m, 2H), 2.73-2.91 (m, 2H), 3.10 (m, 0.1H), 3.45 (t, 2H), 3.61 (m, 2H), 2.91 (m, 0.9H), 4.10-4.20 (m, 3H), 4.30-4.50 (m, 2H). ¹³C NMR (100 MHz) δ 13.69, 14.23, 15.68, 18.05, 19.00, 21.80, 23.10, 24.21, 24.36, 29.07, 29.81, 29.84, 29.97, 34.75, 36.13, 37.72, 55.51, 56.28, 60.57, 60.69, 61.75, 63.31, 64.22, 65.42, 100.52, 101.77, 101.97, 102.11, 103.49, 156.51, 172.35, 172.41; IR see RQ-1-72 601.6, 1013.5, 1099.6, 1161.6, 1206.4, 1392.9, 1729.0, 1751.3, 1967.1, 2051.3, 2961.7 cm⁻¹. HRMS (M+Na⁺) calculated for C₂₉H₃₅O₉NaFe: calculated 558.37, found 558.1397.
Oxazolidinoyl diene 51a:  Vinyl stannane 45a (3.10 g, 4.26 mmol, 1 eq), as a mixture of regioisomers, was dissolved in CH$_2$Cl$_2$ (40 mL) under an argon atmosphere and this solution was cooled to 0 °C. NIS (1.15 g, 5.11 mmol, 1.2 eq) was added all at once, and the reaction mixture was stirred for 2.5 hr at 0 °C. At that time, saturated aqueous NaHCO$_3$ (20 mL) and saturated aqueous Na$_2$S$_2$O$_3$ (20 mL) were added; the mixture was transferred to a separatory funnel using EtOAc (150 mL). The layers were separated and the organic layer was washed with brine (20 mL), dried (MgSO$_4$), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 40:1 hexanes/EtOAc containing 0.5% NEt$_3$) to afford the isomerically pure vinyl iodide (1.955 g, 88%) as a clear oil.  $^1$H NMR (400 MHz) $\delta$ 0.65 (s, 3H), 1.06 (s, 9H), 1.17 (s, 3H), 1.77 (m, 2H), 2.65 (t, 2H, $J = 7.4$ Hz), 3.36 (d, 2H, $J = 11.2$ Hz), 3.56 (d, 2H, $J = 11.2$ Hz), 3.70 (t, 2H, $J = 5.8$ Hz), 5.09 (d, 1H, $J = 6.0$ Hz), 6.32 (d, 1H, $J = 6.0$ Hz), 7.36-7.43 (m, 6H), 7.66 (m, 4H); $^{13}$C NMR (100 MHz) $\delta$ 19.3, 21.8, 22.9, 27.0, 29.9, 32.3, 36.7, 62.2, 97.8, 111.0, 127.7, 129.7, 133.8, 135.5, 138.4; See MY-9, RSP-XXIV-2, SC-23. HRMS (M+Na$^+$) calculated for C$_{27}$H$_{37}$O$_3$NaSiI: 587.1449, found 587.1434.

Stannyl vinyl oxazolidinone 1a (1.54 g, 3.46 mmol, 1 eq) was weighed into a one-dram vial; this vial, along with a Schlenk flask equipped with a stir bar containing the vinyl iodide prepared above (1.955 g, 3.46 mmol, 1 eq), were brought into the glove box. In the glove box, portions of DMF were used to dissolve 1a and then transfer it by disposable pipette into the flask containing the vinyl iodide. The vial and pipette were
repeatedly rinsed with DMF (total used: 17.5 mL to dissolve the reactants). Pd(PPh₃)₄ (400 mg, 0.346 mmol, 0.1 eq) and copper diphenylphosphinate (1.12 g, 3.98 mmol, 1.15 eq) were added at the same time and the reaction was stirred for 18.5 hr. In the fumehood, the reaction mixture was then filtered through a pad of silica on a glass-fritted filter (the silica was loaded as a slurry with EtOAc) using EtOAc (ca. 100 ml) to rinse the flask and silica pad. The filtrate was concentrated using the rotary evaporator and then re-dissolved in Et₂O (175 mL) and transferred to a separatory funnel. The solution was washed with H₂O (2 x 75 mL), brine (1 x 75 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 4:1 to 3:1 to 2.5:1 hexanes/EtOAc) to afford oxazolidinoyl diene 51a (2.05 g, 94 % yield) as a thick pale yellow oil. ¹H NMR (400 MHz) δ 0.68 (s, 3H), 0.85 (d, 3H, J = 7.2 Hz), 0.88 (d, 3H, J = 6.8 Hz), 1.08 (s, 9H), 1.20 (s, 3H); 51a was not stable enough to be submitted for HRMS.

![TBDPSO](image)

Aldehyde (20 mg, 0.031 mmol, 1 eq) was dissolved in THF (0.3 mL) and cooled to -78 °C. Vinyl MgBr (1.0 M in THF, 0.034 mL, 0.034 mmol, 1.1 eq) was added dropwise. The solution was stirred for 2.5 hours at -78 °C, after which it was quenched with saturated NaHCl₄ (5 mL). The solution was brought to room temperature, and transferred to a separatory funnel with EtOAc (20 mL). The organic layer was washed with saturated brine solution (5 mL), dried (MgSO₄), filtered, and concentrated using the rotary evaporator. The residue was chromatographed (silica, 5:1
hexanes/EtOAc) to afford allylic alcohol 53 (15.7 mg, 75%) as a clear oil. An $^1$H NMR (400 MHz) of the un-chromatographed residue was taken but is not clean enough to be reported.

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\text{TBDPSO} \quad \begin{array}{c}
\text{O}_3\text{ReOSiPh}_3 \quad (0.2 \text{ mg, } 0.0005 \text{ mmol, } 0.02 \text{ eq) was dissolved in THF (0.1 mL). In a separate flask, allylic alcohol 53 (15.7 mg, 0.022 mmol, 1 eq) was dissolved in THF (0.1 mL) and cooled to 0 } \degree \text{C. The allylic alcohol solution was then transferred via cannula to the rhenium catalysts solution and stirred for 30 minutes at 0 } \degree \text{C. The solution was quenched with one drop of NEt}_3, \text{ and the solvent was removed using a rotary evaporator. Chromatography (silica, 5:1 hexanes/EtOAc) afforded the isomerized allylic alchol 54 (8.9 mg, 57%). $^1$H NMR (400 MHz) $\delta$ 0.49 (d, 1H, $J = 3.6$ Hz), 0.85 (m, 6H), 1.05 (m, 8H), 1.15-1.4 (m, 7H), 1.75 (d, 1H, $J= 3.7$ Hz), 1.73 (m, 2H), 2.30 (m, 1H), 2.53 (m, 1H), 2.65 (m, 1H), 3.58 (m, 2H), 3.80 (m, 1H), 4.01 (m, 3H), 5.75 (m, 2H), 7.35 (m, 6H), 7.60 (m, 4H). $^{13}$C NMR (100 MHz) $\delta$ 10.96, 13.1a, 14.06, 18.03, 19.22, 22.98, 23.72, 25.54, 26.87, 28.82, 28.91, 29.37, 29.20, 30.34, 33.43, 35.20, 38.71, 57.87, 61.45, 63.50, 63.60, 64.11, 68.15, 101.34, 127.73, 127.76, 128.80, 129.75, 129.78, 130.51, 130.89, 131.02, 133.55, 133.70, 135.50, 156.27.} \ende