Epimeric Pyrroloimidazolone Auxiliaries in the Diastereoselective Synthesis of
Chiral $N$-Ferrocenyl/$N$-Phenyl Ligands and Arene-Chromium Tricarbonyl
Complexes

by

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ABSTRACT

This thesis describes the synthesis and use of an \( N \)-based L-proline derived chiral auxiliary/directing group for selective synthesis of planar chiral and central chiral products. A series of planar chiral ferrocenes were prepared, and converted to chloroimidazoliums and complexed to palladium via oxidative addition. In addition to this, a centrally chiral Ir(I) catalyst was prepared for the purpose of evaluating the importance of planar chirality for the induction of enantioselectivity in the Ir(I) catalyzed hydrogenations of 2-substituted quinolines. A lower enantioselectivity was observed, allowing the conclusion that planar chirality does contribute to the enantioselectivity. The pyrroloimidazolone directing group used to induce high diastereoselectivity in ferrocene lithiations (>95:5 dr) has been applied (with minor modifications) towards the diastereoselective lithiation of \( \eta^6 \)-arene chromium tricarbonyl complexes. The \textit{anti}-epimer of the pyrroloimidazolone auxiliary undergoes pro-\( R \) lithiation in >95:5 dr. The \textit{syn}-epimer of this auxiliary undergoes pro-\( S \) lithiation in >95:5 dr. The origin of selectivity is believed to be caused by a conformational bias exerted by the \( O \)-group. The selectivity of lithiations, and stereochemistry of all the products has been confirmed by a combination of X-ray analysis, transmetalation and deuteration experiments and by the preparation and comparison of solely planar chiral enantiomers.
To my family
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ABBREVIATIONS

ArCr(CO)₃ arene chromium tricarbonyl complex
Bu butyl
COD 1,5-cyclooctadiene
Cp cyclopentadienyl
DMF N,N-dimethyl formamide
DoM directed ortho-metalation
dr diastereomeric ratio
DIBAL-H diisobutylaluminum hydride
equiv equivalents
E⁺ electrophile
er enantiomeric ratio
h hours
HPLC high pressure liquid chromatography
i- iso
IR infrared
LDA lithium diisopropylamide
LTMP lithium 2,2,6,6-tetramethyl piperidide
min minute
n- normal
NHC N-heterocyclic carbene
NMR nuclear magnetic resonance
o ortho
p para
quant. quantitative
Ph phenyl
Pr propyl
rt room temperature
s secondary
t tertiary
TBAF tetrabutylammonium fluoride
TES triethylsilyl
TESCl chlorotriethylsilane
TFA trifluoroacetic acid
THF tetrahydrofuran
TLC thin layer chromatography
TMS trimethylsilyl
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
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<tr>
<td>TMCDA</td>
<td>$N,N',N,N''$-tetramethy-1,2diaminocyclohexane</td>
</tr>
<tr>
<td>TMEDA</td>
<td>$N,N,N',N''$-tetramethylene diamine</td>
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1. Introduction

Many of the complex molecules produced by living organisms such as proteins, nucleic acids and carbohydrates are produced as a single enantiomer and/or diastereomer in high selectivity. In some cases chemists are able to selectively synthesize single enantiomers/diastereomers, but for the most part our arsenal of asymmetric strategies is still limited. A multitude of enantioselective methods have been developed by chemists to address the selective synthesis of chiral molecules. The focus of research in the Metallinos group can be divided into two categories: the development of new asymmetric transformations and, more often than not applying these transformations towards the development of new previously inaccessible chiral ligands for asymmetric catalysis. Recent efforts are focused on the development of \(N\)-based chiral auxiliaries for diastereoselective lithiations of prochiral ferrocenes. The most recent advancements were the development of an epimeric pyroloimidazolone directing group for highly diastereoselective lithiation of ferrocenes, providing access to both planar chiral enantiomers of 1,2-substituted aminoferrocenes. This strategy was then applied to the synthesis of unusual chiral imidazolylidene (NHC) ligands which, when complexed to Ir(I), are capable of hydrogenating quinolines under relatively low pressures of hydrogen (5 atm) with good to high enantioselectivity.

The first part of this thesis will discuss an application of this recently reported methodology towards the synthesis of planar chiral \(N\)-substituted ferrocenyl imidazolylidene and imidazolylidene ligands with the intent of preparing enantiopure bidentate ligands for the preparation of metal complexes to use in asymmetric catalysis. The utility of the pyroloimidazolone directing group was then extended to the synthesis of planar chiral \(N\)-
substituted η⁶-arene chromium tricarbonely complexes. Last, the importance of the planar chirality of the aforementioned Ir(I) complexes³ will be studied by preparing solely centrally chiral analogues and testing their induction of enantioselectivity in the hydrogenations of previously studied substrates.
1.1 Planar Chirality

Chirality is a mathematical property of asymmetry. The word chiral is derived from the Greek word for hand (kheir) which was the first observation of chirality. Chirality exists when an object is distinguishable from its mirror image. The simplest example of this is the relationship between one's hands (Figure 1), which perfectly describes the relationship between two enantiomeric molecules.

![Mirror Plane](image)

**Figure 1.** The chirality of hands and molecules.

Chirality is assigned using the Cahn-Ingold-Prelog system, which is based on assigning priority of substituents based on a combination of the atomic number and to a lesser extent the molecular weight of substituents. Within the field of chemistry there are sub-classes of chirality used to describe different types of asymmetry depending on the dimensions in which it is asymmetric. Apart from central chirality, axial and planar chirality may be used to describe elements of chirality for molecules with sp- and sp$^2$-hybridized atoms. Axial chirality exists in a molecule that does not
have a stereogenic centre, but possesses an axis of chirality like those shown in Figure 2. The most common form of axial chirality exists in biaryl ring systems (1), where free-rotation around the C$_{Ar1}$-C$_{Ar2}$ bond is restricted. This type of chirality is also observed in polysubstituted allenes (2); here, the central carbon atom is sp-hybridized.

![Figure 2. Axially chiral polysubstituted allenes and ortho-substituted biaryls.](image)

Planar chirality exists in cyclic systems in which there is a clearly defined inequivalence between the two faces of the ring. This is easily explained using metal-arene complexes as an example. In these compounds one face is haptically bound to a metal (Figure 3). For organometallics such as ferrocene, the Schlögl convention, which follows similar rules to the Cahn-Ingold-Prelog system, may be used to assign absolute stereochemistry. Chirality is assigned by looking at the molecule from a top-view of the disubstituted ring, and assigning priority based on atomic number (and size) as shown in Figure 3. If A > B, then a counterclockwise priority is assigned and denoted as $S_P$ indicating that the configuration is S, and the type of chirality is planar. When more than one element of chirality exists within a molecule, the priority order is central > axial > planar > helicity.
Two chemically identical compounds that possess one stereogenic centre that are opposite in their stereochemical assignment are referred to as enantiomers and appear as mirror images of one another. A molecule may possess multiple stereogenic centres or axes/planes of chirality. Molecules which possess one or more elements of chirality in their stereochemical assignment (but are not mirror images) are diastereomers. For example, tartaric acid contains two stereogenic centres and may exist as two unique diastereomers (Figure 4). The structures with stereochemical assignments $1R,2R$ (5) and $1S,2S$ (8) are mirror images of one another, and are therefore enantiomers. Compounds with the stereochemical assignments $1S,2R$ (7) and $1R,2S$ (6) appear to be enantiomers, but because both chiral centres contain the same groups, these compounds are equivalent, and referred to as meso compounds. The number of stereoisomers that can exist for a chiral molecule depends on the number of individual stereogenic components within the molecule and can be calculated using the equation $2^n$, where $n$ is the number of stereogenic centres or planar/axial elements of chirality in the molecule. This equation does not take into account the equivalence of meso-structures.
Chiral compounds exhibit the ability to rotate plane-polarized light. This observation was made more than 200 years ago by French physicist François Jean Dominique Arago, who noted that compounds that possess structures which are mirror images of one another rotate plane polarized light in equal magnitudes, but in opposing directions. Since this observation, the specific rotation of chiral molecules has been used as a physical constant for chiral molecules. The specific rotation can be defined as the direction and number of degrees by which plane polarized light has been displaced per unit distance-concentration product as the light passes through a sample of compound in solution. In the equation (Figure 5), $\alpha$ is the magnitude of displacement in degrees, $l$ is the path length of the sample measured in decimeters, and $\rho$ is the density (concentration of analyte) of the solution in g/mL. The superscript in the equation indicates the temperature at which the measurement was taken while the subscript D refers to wavelength of light used to obtain the measurement; D stands for the sodium D line which is 589 nm. Though always expressed as degree ($^\circ$) with clockwise rotation denoted as $+$, and counterclockwise rotation denoted as $-$, the true units of specific rotation are: °L/dm(g). It is customary to report the wavelength of light used

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**Figure 4.** Isomers of tartaric acid.
and the temperature under which the measurement was made. Factors affecting the measured optical rotation include: enantiomeric/diastereomeric purity, solvent used, wavelength used, temperature of the sample at the time of measurement, length of the cell, and the concentration of the analyte studied. There exists no linear relationship between these parameters and any comparisons made are only valid when all the parameters are identical to those first reported in the literature. The instrument used to measure the specific rotation of a sample is called a polarimeter. Although the equation for specific rotation implies a linear relationship between rotation and analyte concentration, this is not always the case as non-linear effects can occur in specific rotation measurements.\textsuperscript{9}

\[
[\alpha]_D^{20} = \frac{\alpha}{l \times c}
\]

**Figure 5.** Equation for the calculation of specific rotations.

All chiral molecules rotate plane polarized light, but it is still possible for some enantiopure molecules to possess a specific rotation of zero.

### 1.2 Metal-Arene Complexes

A metal-arene complex is a compound which contains a transition metal bound through neutral or anionic haptic bonds to one or two aromatic rings.\textsuperscript{10} There are two main categories of metal-arene complexes: sandwich compounds, and half-sandwich compounds. Representative examples of common metal arene compounds are shown in Figure 6. Sandwich compounds, which contain a metal atom haptically bound between two aromatic rings, can additionally be sub-categorized as either bent sandwich compounds, which contain additional ligands, or regular flat
sandwich compounds. Half-sandwich compounds contain a metal atom bound by a single aromatic ring and can contain one or more additional ligands coordinated in a linear fashion. Half-sandwich compounds with three additional ligands are commonly referred to as “piano stool complexes” because they adopt a morphology that resembles a three-legged stool. Metal arene complexes with more diverse structures have been reported but do not easily fit into these categories.

<table>
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<tr>
<th>Metal Arene Complexes</th>
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<tr>
<td>Sandwich compounds</td>
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**Figure 6.** Representative examples of metal-arene complexes.

The aromatic rings may be neutral (benzene) or anionic (cycopentadienyl) and many oxidation states of metals are also observed with 0, +2 and +4 being the most common. Metal-arene compounds can be formed with a variety of transition metals and aromatic compounds. Sandwich compounds containing the formula \( [\eta^5\text{C}_5\text{H}_5\text{M}] \) are referred to as metallocenes. These compounds generally contain a metal atom in the +2 oxidation state and are haptically bound by
two anionic cyclopentadienide rings. The first metallocene to be characterized was ferrocene, which contains a Fe$^{2+}$ atom in the centre.$^{12}$

### 1.2.1 Ferrocene

The structure of bis(cyclopentadienyl)iron(II), or ferrocene (10) was initially unclear and thought to consist of two σ-bonded Cp rings attached to a Fe$^{2+}$ (9), as shown in Figure 7.

![Diagram showing initial and correct structures of ferrocene](image)

**Figure 7.** Initial (left) and correct (right) structures of ferrocene.

Ferrocene was discovered simultaneously in 1951 by two independent research groups: Keally and Pauson$^{11}$ (Duquesne University) and Miller, Tabboth and Tremaine (British Oxygen Company).$^{12}$ The correct structure was determined the next year by Woodward and Wilkinson$^{13}$ and Fischer and Pfab$^{14}$ who were later awarded the 1973 Nobel prize in Chemistry for their contributions towards the study of metallocenes. The evidence that led to the determination of the correct structure (10) was the observation that all ten C-H bonds in the molecule were equivalent, leading to the correct assumption that the rings are aromatic and bound to the metal through haptic bonds.
Ferrocene is the oldest known and most widely studied organometallic compound. The discovery of ferrocene is credited with having caused the rapid growth and emergence of organometallic chemistry as a separate discipline. The bonding of ferrocene, as mentioned previously, is haptic through the two cyclopentadienide rings. The six electron pairs donated to the central metal by the Cp rings fill the six d² sp³ hybrid orbitals of the ferrocene, rendering it with a stable 18 electron configuration. Ferrocenes are electron-rich aromatics because of the formal negative charges resonating on the cyclopentadienyl rings. As a result, these compounds undergo electrophilic aromatic substitution three million times faster than benzene, but do not undergo nucleophilic aromatic substitution. They are stable to strong bases and reducing agents, but decompose in the presence of many strong oxidizing agents such as halogens, and nitric acid. It is for this reason that indirect methods such as mercuration or lithiation/substitution must be used to incorporate certain heteroatoms onto a Cp ring.

Lithiation is the most commonly used method for the preparation of substituted ferrocenes. The isolation of monosubstituted ferrocenes via lithiation is not always a simple endeavour due to their tendency to undergo metalation on both Cp rings. Fortunately, procedures have been developed for the preparation of both monolithio- and 1,1'-dilithioferrocene. In 1990, Kagan reported a procedure for the preparation of monolithioferrocene using t-BuLi with a short lithiation period (15 min), achieving nearly quantitative yields (up to 98%) of monosubstituted products. Methods for the isolation of lithioferrocene have been described by Bildstein who, using the procedure established by Kagan for the preparation of monolithioferrocene, showed the intermediate can be precipitated and isolated using anhydrous Schlenk filtration techniques. On the other hand, 1,1'-dilithioferrocene can be obtained exclusively with the use of N,N,N',N'-tetramethylethylenediamine (TMEDA) in combination with n-BuLi in hexane.
convenient method for monosubstitution of ferrocene with electrophiles was reported by Mueller-Westerhoff who employed Schlosser's base ($t$-BuLi/$t$-BuOK), which allows for an *in-situ* electrophile quench.\(^{22}\)

The major applications of ferrocenes in industry are as ligands. The thermostability and oxygen-tolerance of ferrocene make it a good ligand choice for reactions that require harsh conditions. In addition to stability, the ease of rotation between the upper and lower rings allows flexibility, reducing steric strain. A popular ferrocene ligand, $[1,1'$-*bis*(diphenylphosphino)ferrocene] (dpf) was first reported in the 1960’s and is still widely used today in a number of palladium-catalyzed reactions.\(^{23}\) Some widely used ferrocene ligands are the planar chiral PhTrap\(^{24}\) (55), Josiphos\(^{25}\) (56), and Xyliphos\(^{26}\) (57) ligands (Figure 10). The syntheses and applications of these ligands will be discussed in detail in Section 1.3.2. (*vide infra*).

There are a number of other fields in which ferrocene has found niche uses. Ferrocene derivatives have found applications in the fuel industry as “anti-knock” agents, and are known to be much safer than leaded alternatives.\(^{27}\) Certain ferrocenium salts have also been shown to possess anticancer and antimalarial activity.\(^{28}\) In the early 2000’s, a ferrocenyl analogue of Tamoxifen was used as an experimental drug to treat breast cancer.\(^{29}\) In materials chemistry, the degradation of ferrocene has found application in the production of carbon nanotubes.\(^{30}\) The polymerization of vinylferrocene produces the ferrocene analogue of polystyrene which has been studied as a conductive polymer.\(^{31}\) Owing to the ease of its crystallization, ferrocene is also sometimes used as an auxiliary to induce the crystallization of otherwise non-solid compounds for the purpose of determining absolute stereochemistry by the heavy atom method in X-ray diffraction of single crystals.
1.2.2 Arene-Chromium Tricarbonyl Complexes

Arene chromium tricarbonyl complexes have the general formula \((\eta^5\text{-C}_5\text{H}_5)\text{ML}_3\) or \((\eta^6\text{-C}_6\text{H}_6)\text{ML}_3\), where \(\eta\) refers to the number of carbons equally participating in the haptic bonds to the metal and ligands L are not required to be equivalent. In \((\eta^5\text{-C}_5\text{H}_5)\text{ML}_3\) compounds there is an anionic donor ligand with a haptic bond to the metal, whereas in \((\eta^6\text{-C}_6\text{H}_6)\text{ML}_3\) this haptic ligand is a neutral donor. This class of compounds also falls under a broader category of compounds called half-sandwich compounds, which is used to describe any haptic metal-arene that is bound to a single aromatic ring. The first "piano stool" complex characterized and studied was \((\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3\) (11) (Figure 8) reported by Fischer and Öfele in 1957. This compound was first prepared by carbonylation of bis(benzene)chromium.\(^{32}\) The crystal structure was determined two years later by Corradine and Allegra.\(^{33}\) Since then, a number of syntheses of these types of compounds have been reported, all of which involve variations of the original procedure.\(^{34}\) Methods for complexation include refluxing the arene with metals of the type \(\text{M(CO)}_6\), or via transfer reactions, in which the pre-complexed \(\text{Cr(CO)}_3\) is transferred from one aromatic ring to another which contains a higher electron density. This second type of transfer reaction can be thought of as nucleophilic substitution, in which the more electron-rich ring system functions as the better nucleophile. Typical transfer reagents for this type of reaction include naphthalene-\(\text{Cr(CO)}_3\) and \(\text{L}_3\text{Cr(CO)}_3\) where L is a labile ligand such as acetonitrile, ammonia or pyridine.
Despite the existence of arene-metal-tricarbonyl complexes containing a wide range of metals and ligands (L), only complexes based on an \((\eta^6-C_6H_6)Cr(CO)_3\) formulation will be discussed here and will be referred to as ArCr(CO)\(_3\). In general, the industrial applications of ArCr(CO)\(_3\) are somewhat limited. They are mainly used as catalysts for the large-scale preparation of substituted pyridines,\(^{35}\) and as anti-knock agents in the petroleum industry.\(^{36}\) In academic applications, they have been used as ligand scaffolds in transition-metal catalyzed reactions and as electrophilic arene equivalents to which nucleophiles may be added via S\(_{N}\)Ar chemistry, owing to their electron deficiency.\(^{37}\)

Typically, ArCr(CO)\(_3\) are bright yellow in colour due to their strong absorption in the low 400 nm region of the electromagnetic spectrum. Compounds of the formula \((\eta^6-C_6H_6)Cr(CO)_3\) have an octahedral coordination geometry. In terms of valence bond theory, the six electron pairs donated to the central metal by the ligands fill the six d\(^2\) sp\(^3\) hybrid orbitals of the chromium\(^0\) atom, rendering it an 18 electron complex. Three of these pairs of electrons are donated by the arene and the remaining pairs by the carbon monoxide molecules. Overlap of the full non-bonding d orbitals of the chromium atom with the empty anti-bonding orbitals of ligands decreases the overall electron density on the metal atom, contributing to the instability of these compounds.\(^{38}\)
The unique reactivity of ArCr(CO)₃ complexes arises from the overall net electron withdrawing nature of the chromium and carbon monoxide ligands. The Cr(CO)₃ moiety has an electron withdrawing effect similar to that of a nitro group. This diminishment of electron density of the aromatic ring has two major effects on the overall properties of the molecule. The first effect is the observation of enhanced acidity (lowered pKₐ) of the aromatic protons. Upon complexation, the pKₐ of an unsubstituted benzene ring drops from approximately 43 to 35. This enhanced acidity allows for the deprotonation of the complexed aromatics by a number of bases including alkyllithiums, and metal-amides. The second effect observed is an increased propensity of these molecules to undergo nucleophilic aromatic substitution (SₐNₐr) and nucleophilic aromatic addition with nucleophiles. Under normal conditions the electron cloud of the uncomplexed benzene ring acts as a deterrent to nucleophilic additions by anions, and instead favours deprotonation. Depending on both the size and pKₐ of the base used, and the size and properties of substituents already present on the aromatic ring, different reactivities are observed.

**Scheme 1.** Reactivity of anions with benzene(chromium) tricarbonyl.
In general, metalated compounds whose conjugate acids have a pKₐ above 35, with the exception of t-BuLi, tend to act as bases towards benzene chromium tricarbonyl. Metalated compounds with a lower pKₐ (22-34), such as enolates, allylic and heteroatom-stabilized anions tend to act as nucleophiles. A summary of the reactivities of many bases/nucleophiles is provided in Scheme 1. The reactivity of certain anions can in some cases be selectively modified to act as either a base or a nucleophile with the use of additives such as hexamethylphosphoramide (HMPA) or dimethylpyrimidone (DMPU).
In the late 1970’s, Semmelhack et al. undertook a thorough investigation of the reactivities of these compounds towards metalation and nucleophilic addition. Comprehensive summaries of the reactivities of various mono- and di-substituted \((\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3\) complexes towards metalating reagents and nucleophiles (Schemes 1 and 2) have been reported.\(^{44}\) In the decades since,
the utility of these compounds have been demonstrated through the preparation of optically pure synthons for the asymmetric synthesis of complex molecules and natural products such as (−)-lausubine, 11-epi-helioporin B, (+)- and (−)-acetoxytubipofuran, korupensamine and aklavinone.

![Scheme 3. Stereoselective synthesis of AB-ring system of aklavinone.](attachment:Scheme_3.png)

Uemura’s synthesis of aklavinone (Scheme 3) is an example of the types of stereoselective transformations that are possible with ArCr(CO)₃. The naphthalene derivative 18 first undergoes nucleophilic addition from above the plane of the complexed ring. The anion resulting from this addition then stereoselectively adds to a coordinated carbon monoxide ligand from below the plane of the ring. The acyl anion generated is then trapped with methyl iodide providing a methyl ketone (19). In one pot, a 1,2-trans substitution pattern was generated using the planar chirality imparted by the complexation to chromium(tricarbonyl).

### 1.3 Synthesis and Applications of Planar Chiral Ferrocenes and η⁶-Arene Chromium Tricarbonyl Complexes

The most convenient method of functionalizing metal-arene complexes is by metalation with strong bases followed by substitution with electrophilic reagents. The range of the pKₐ values
of the aromatic C-H bonds in metal arene complexes is between 33-40 (this is based on the capacity of such compounds to be deprotonated by metalating reagents such as LDA with a pKₐ of approximately 34).⁵¹,⁵² This property allows them to be deprotonated by most commercially available bases. The methods of preparing optically active metal-arene complexes by metalation can be classified into two categories that involve the use of either chiral metalating reagents (enantioselective), or chiral directing groups/auxiliaries (diastereoselective).

1.3.1 Enantioselective Lithiation

The use of chiral metalating reagents for the desymmetrization of prochiral metal-arenes was and perhaps still is the most efficient method for the generation of planar chirality in this class of compounds. Directed enantioselective ortho-metalation was independently developed by a number of research groups such as Kündig⁵³, Simpkins⁵⁴ and Uemura.⁵⁵ Among the metal-arenes most easily desymmetrized are those bearing heteroatom substituents. Many heteroatom substituted ArCr(CO)₃ and ferrocenes undergo ortho-metalation by chiral lithium amide bases (Figure 9), resulting in poor to excellent enantiomeric ratios (75:25 to 97:3), upon quenching with suitable electrophiles.⁵⁶
Arguably the simplest, most widely known and used chiral lithium amide base is the “Simpkins base” (21), named after Nigel Simpkins who first demonstrated its use.\textsuperscript{41} While desymmetrization of ArCr(CO)\textsubscript{3} was possible by this method, these bases were for the most part ineffective at introducing high levels of enantioselectivity in ferrocenes (Scheme 4). Despite the high yields, only phosphinyl ferrocenes underwent desymmetrization (up to 75:25 er) by these bases.\textsuperscript{57}
Scheme 4. Enantioselective lithiation-substitution of metal-arenes

with Simpkin’s base.41,58

Uemura and coworkers have demonstrated that enantioselective lateral lithiation of prochiral methylene groups of ArCr(CO)₃ compounds is possible with chiral lithium amide bases (Scheme 5), providing products in high yields and with up to 97:3 er.58 This was demonstrated in his synthesis of atropoisomeric benzamides and anilides from prochiral starting materials. Using Simpkin’s base (21), both planar and axial chirality may be introduced in high yields and enantiomeric ratios (up to 99:1).59

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20
Scheme 5. Enantiotopic lateral lithiation of prochiral anilides with chiral amide bases inducing planar and axial chirality.\textsuperscript{59}

Chirality can also be imparted to prochiral substrates via lithiation with achiral bases if chiral ligands are added to the reaction mixture. This approach effectively creates a chiral base upon complexation. These chiral additives commonly contain appropriate chelating atoms such as oxygen, or more commonly, nitrogen.\textsuperscript{60} The use of chiral additives towards the asymmetric lithiation of metal arenes was the first ever attempted enantioselective lithiation. In 1970, Nozaki showed that (−)-sparteine-mediated lithiation of isopropylferrocene resulted in mixtures of products with minor optical activity (52:48 er).\textsuperscript{61} Since then, Widdowson and coworkers have demonstrated that high levels of enantiopurity (up to 96:4 er) are observed in the products of heteroatom-substituted ArCr(CO)\textsubscript{3} complexes subjected to the same conditions.\textsuperscript{62} The limitations of chiral amide bases, and chiral additives to effectively induce enantioselectivity in ferrocene lithiation left a major gap in the asymmetric methodology of ferrocenes that wasn’t revisited for two decades.

In the latter part of the 20\textsuperscript{th} century, inspired by Beak\textsuperscript{63} and Hoppe,\textsuperscript{64} Snieckus demonstrated that (−)-sparteine-mediated directed ortho-metalation of \(\text{N,N-diisopropylferrocenecarboxamide}\) (35) proceeded with high levels of enantioselectivity (Scheme
The major increase in selectivity compared to the results obtained by Nozaki may be attributed to the coordinating capability of the heteroatom directing group present on the ring. A more facially-selective chiral intermediate is formed upon coordination of (−)-sparteine (37) to the lithiated intermediate. In essence, the major difference between the results of Nozaki and Snieckus was that Nozaki studied asymmetric ortho-metallation while Snieckus investigated asymmetric directed ortho- metallation (DoM). A not widely known fact from Nozaki’s original publication was that diastereoselectivity was observed in lithiations of ferrocenes bearing chiral nitrogen containing substituents. The presence of heteroatoms with coordination capability within the substrates has an observable effect on the enantioselectivity of lithiations. This observation is known as the complex-induced proximity effect, which aims to explain the differences in reactivity of lithiated compounds.

Scheme 6. (−)-Sparteine-mediated lithiation of N,N-diisopropyl ferrocenecarboxamide and electrophile quench.

(−)-Sparteine (37) is a natural product of the alkaloid class of compounds and is derived from leguminous flowers such as the Scotch Broom. Many efforts have been made towards its...
total synthesis and many have been successful. Despite this, and its natural abundance, the stoichiometric use of complex natural products for the induction of enantioselectivity in lithiations is not considered sustainable. This urged further studies into use of chiral diamines as asymmetric catalysts for lithiation, which fortunately revealed that other synthetically derived chiral diamines could be used for the induction of chirality.\textsuperscript{68} Uemura demonstrated the use of chiral 1,2-cyclohexyldiamines to induce up to 90:10 er in the lithiation-substitution of \(N,N\)-dimethylaminoferroocene, but with low overall yields (5-49\%).\textsuperscript{69} The next advancement in this area was done by Metallinos, who expanded upon the results of Kessar\textsuperscript{70}, Harmata\textsuperscript{71}, Vedejs\textsuperscript{72}, and Simpkins\textsuperscript{73} who demonstrated the ease with which certain BF\textsubscript{3}- or BH\textsubscript{3}-coordinated tertiary amines underwent sp\textsuperscript{3}-lithiation α to nitrogen. Applying this approach to the directed orthometalation of dimethylaminoferroocene (38), 1,2-disubstituted products were obtained in higher yields than had been previously reported (up to 93\%). In conjunction with the BF\textsubscript{3} activation of dimethylaminoferroocene (38), the use of chiral diamines, both natural and synthetically derived, was also studied (Scheme 7). The use of (−)-sparteine (37) had very little influence on the selectivity of the deprotonation by isopropyllithium, but much greater selectivity was observed with the use of synthetically derived chiral cyclohexyldiamines (40 and 43, up to 90:10 er). Even more useful was the observation that the lithiation selectivity could be reversed with the use of the enantiomer of the chiral diamine ligand. Using this method, a rare class of enantio-enriched 1-amino-2-phosplinoferrocene ligands (45) was synthesized and coordinated to various metals (Pd, Pt, Ir). Each of these compounds was then investigated as ligands in asymmetric transition metal-catalyzed reactions for their activity and induction of selectivity.\textsuperscript{74} The stereochemistry of 42 and 45 was confirmed by X-ray crystallography. While this method provided access to enantiopure planar chiral aminoferroccenes after recrystallization, not all products were easily crystallized. The
lack of manipulability of the tertiary amine to a different functional group limited the utility of the products.

**Scheme 7.** Lithiation of BF$_3$-activated aminoferrocenes with diaminocyclohexane ligands/i-PrLi.

1.3.2 Diastereoselective Lithiation

1.3.2.1 Diastereoselective Lithiation of Ferrocenes

The most widely studied method of stereoselective planar chiral induction in metal arene compounds involves diastereoselective lithiation with chiral directing groups or auxiliaries. This method relies on pre-existing chirality in the molecule to differentiate the two diastereotopic "ortho-" or neighbouring protons. Coordination of heteroatoms in the directing group to the base results in diastereoselective formation of lithiated intermediates. Chiral carbon-$_7^{75}$, phosphorous-$_7^{76}$
and sulphur-based$^{77}$ directing groups have been reported as viable auxiliaries for the diastereoselective lithiation of ferroenes (Scheme 8).

![Diagram of diastereoselective lithiation of ferrocene and examples of selected chiral directing groups](image)

**Scheme 8.** Diastereoselective lithiation of ferrocene and examples of selected chiral directing groups.

The first diastereoselective lithiation of pro-planar chiral substrates was reported by Nozaki in the late 1960’s.$^{62}$ In this, he reported that lithiation of a chiral piperidinyl ferrocene (49, Scheme 8) followed by electrophile quench gave 2-substituted products in low yields, but in high
diastereomeric ratio (up to 93:7 dr). However, the diastereoselectivity of this substrate was called into question shortly after by Ugi, who upon repetition of these experiments was unable to achieve the reported selectivity.\textsuperscript{78}

The next and perhaps simplest reported chiral auxiliary \textit{N,N}-dimethylferrocenyl-\textit{\textalpha}-ethylamine (48) was developed by Ugi in the 1960s.\textsuperscript{76\textit{c}} Resolution of racemates with (R)-(+)\textsuperscript{-}tartaric acid provided both enantiopure substrates. This strategy involved the directed ortho-lithiation of \textit{N,N}-dimethylferrocenyl-\textit{\textalpha}-ethylamine (48, Scheme 9). The origin of selectivity in this reaction is thought to arise from a conformational bias induced by steric repulsion of the \textit{\textalpha}-methyl group with the lower Cp-ring of the ferrocene core (Scheme 9). In the most stable conformation, (52\textit{a}) the methyl group would be oriented above the plane of the ring to minimize steric interaction with the lower unsubstituted Cp ring. In this conformation, the nitrogen coordinates to the alkyllithium delivering it to the pro-\textit{R}\textsubscript{p} hydrogen atom, resulting in selective deprotonation. Opposite stereoselectivity is observed in the lithiation of the enantiomer, which also provides planar chiral products in up to 96:4 dr.

\textbf{Scheme 9.} Proposed origin of lithiation selectivity of Ugi’s amine.\textsuperscript{76\textit{c}}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme9.png}
\caption{Proposed origin of lithiation selectivity of Ugi’s amine.\textsuperscript{76\textit{c}}}
\end{figure}
The attractive feature of Ugi’s amine (48) is that the substituted products can undergo further manipulations. For example, stereoselective \( S_N1 \) reactions occur with retention of stereochemistry, by substitution of the dimethylamino group with other nucleophiles. This methodology is used for the large-scale preparation of planar chiral ferrocene compounds which are used as ligands in metal-catalyzed reactions. The most commonly prepared ligands are those mentioned previously: diphosphinylferrocenes such as PhTRAP (55), JosiPhos (56) and Xyliphos (57), shown in Figure 10.\(^7\)

![Chemical structures of PhTRAP, JosiPhos, and Xyliphos](image)

**Figure 10.** Commercially important planar chiral ferrocene ligands derived from Ugi’s amine.

The largest scale application of a ferrocene containing compound is in the synthesis of Metolachlor, an active ingredient in the herbicide Dual.\(^8\) A cationic iridium complex of 57 is employed as a hydrogenation catalyst in the late-stage reduction of an intermediate in the synthesis of Metolachlor. This catalyst possesses very high activity, allowing it to be used at low loadings (1 \( \times 10^{-7} \) mol%). Metolachlor is produced in quantities >20 000 tonnes per year; low catalyst loadings makes this method viable for such large scales.
Reported independently by a number of groups, ferrocenes bearing chiral oxazolines (47) have also been shown to undergo diastereoselective lithiation with high selectivity. This directing group is thought to induce selective deprotonation by means of a steric interaction with the alkyl group of the alkyllithium reagent and the R-group substituent on the oxazoline. The extent of diastereoselectivity depends on the size of the base used. Directing groups that undergo selective deprotonation which exhibit dependence on the bases used have been referred to as "under base control" (Scheme 10).

![Scheme 10. Proposed origin of lithiation selectivity of Kagan's oxazoline.](image)

A survey of all the chiral directing groups used for diastereoselective lithiations of ferrocene-containing compounds revealed that there are no N-based chiral directing groups in which the nitrogen is attached directly to the Cp ring. The lack of ferrocenyl N-based directing groups is not surprising due to the difficulty associated with introducing nitrogen onto a Cp ring (Scheme 11).
The first method of preparing chiral aminoferrocenes was established by Togni in 1981, where he employed a lengthy synthesis comprised of multiple functional group conversions.\textsuperscript{82} Beginning with Kagan’s acetal (46), diastereoselective lithiation followed by electrophile quench with methyl iodide provided the planar chiral ferrocene (61), which was then subjected to acid-hydrolysis of the acetal providing the ferrocenyl aldehyde (62). This aldehyde was then oxidized to an ester (63), hydrolyzed (64), converted to an acyl azide (65), and then subjected to Curtius rearrangement conditions to provide the Cp-nitrogen bond (66). This provided the first method for the synthesis of planar chiral ferrocenes in which the imidazolium moiety was bound directly to the Cp ring (68). While this method did provide access to planar chiral aminoferrocenes that were amenable to further manipulation, the number of steps required to access these compounds made this methodology unappealing.

\textbf{Scheme 11.} Togni’s synthesis of planar chiral aminoferrocenes using Kagan’s acetal.\textsuperscript{83}
Togni was determined to find a convenient method by which these compounds could be prepared. His next route made use of Ugi’s amine (48) to induce planar chirality by sequential lithiation and quench with CO₂. Hoffman elimination of the resulting amine, followed by a Curtius rearrangement of an acyl azide, addition of nucleophiles across the alkene, and reduction of the N-benzyl group provided a planar chiral aminophosphine ligand. The number of steps required to prepare planar chiral aminoferroenes highlighted the need for additional methods.

In the late 1990’s Salter employed a method for the introduction of a nitrogen ferrocene bond by lithiation of a ferrocenyl oxazoline (47) and electrophile quench with N₂O₄, followed by hydrolysis of the oxazoline and Pt-catalyzed reduction of the photosensitive nitroferrocene. While feasible, there is little that can be done with the resulting aminoacid (ester). The ability to convert the directing group to a heteroatom or other functional group would impart utility to this method, unfortunately it is not applicable to non-carbon based directing groups.

While Ugi’s amine is amenable to further manipulations, additional "traceless" directing groups (those which can be completely removed from the final products) are desired. In this regard, only Kagan’s sulfoxides (51) are removeable. Treatment of these sulfoxides with t-BuLi affords lithium-sulfoxide exchange resulting in a lithioferrocene which can then quenched with additional electrophiles. This method is very useful for the preparation of planar chiral ferrocenes, given that the initial functional group substituted onto the ring is stable to organolithium reagents.

Previous work in the Metallinos group has focused on developing new chiral N-based auxiliaries for diastereoselective lithiation of ferrocenes. The feasibility of this type of directing group was established when ferrocenyl phthalimidines (71) underwent diastereoselective lithiation in excess of 95:5 dr (Scheme 12). This auxiliary, albeit in racemic form, could be cleaved to
aminoferrocenes in principle by oxidation back to the phthalimide and treatment with hydrazine. The substrates were prepared racemically by an Ullman coupling of iodoferrocene (78) and phthalimidine to produce 69, followed by reduction and silylation of the hemiaminal (70) affording racemic starting materials (71). When treated with LDA with an in-situ electrophile quench with TMSCl, a 2-substituted compound was obtained as the major product (72), in addition to an inseparable mixture of regioisomers and disubstituted products. The key observation of this result was that the 2-substituted product (72) appeared to be a single diastereomer by $^1$H and $^{13}$C NMR spectroscopy. What this meant was that each enantiomer underwent diastereoselective lithiation with $\geq 95:5$ diastereoselectivity. This was promising because if this result could be observed with an optically pure starting material, a new N-based chiral auxiliary had been discovered.

Scheme 12. Diastereoselective lithiation of phthalimidines.\textsuperscript{75}
Based on previous work done in our lab on diastereoselective sp$^3$ ortho-lithiation of L-proline derived imidazolone 75 (Scheme 13),$^{85}$ and the current need for a homochiral imide, an L-proline derived hydantoin (79) was chosen as a starting material. Thus, L-proline hydantoin (79), prepared by condensation of KOCN with L-proline (77), followed by recrystallization of the crude product from water (Scheme 14). L-proline hydantoin (79) was then coupled to iodoferrocene (78) using a modified Ullman procedure using DMSO as solvent to give ferrocenyl hydantoin 80.$^{2a}$ Stepwise hydrosilylation of 80 with Cp$_2$ZrHCl (Schwartz reagent) followed by trapping of the zirconium alkoxide with TESCl gave (syn-81). Lithiation of syn-81 with t-BuLi followed by electrophile quench with various electrophiles (Scheme 15) gave planar chiral products in >95:5 dr via deprotonation of the pro-$S_p$ hydrogen atom.$^{2a}$ The 95:5 dr observed is comparable to what was observed with other directing groups such as Ugi’s amine (48), oxazolines (47), or acetals (46), (Scheme 8). This method represented the first example of a chiral $N$-based directing group used for the diastereoselective lithiation of ferrocene.$^{2a}$ Further studies of the lithiation behavior revealed that the selectivity of the deprotonation was not sensitive to the size of the base used, implying that the selectivity was not under base control. The selectivity of the deprotonation was established by obtaining a crystal structure from an X-ray diffraction of a single crystal of boronic acid derivative.

**Scheme 13.** Diastereoselective lithiation of L-proline derived imidazolones.
The structure revealed that the lithiation was selective for deprotonation of the pro-$S_p$ hydrogen atom. The origin of selectivity in the lithiation of syn-$81$ was then studied. Based on the results of other chiral directing groups used in diastereoselective lithiations of ferrocene, it can be generalized that the origin of selectivity of directing groups with stereocentres $\alpha$ to the ferrocene core arises through steric interactions of the directing group with the lower Cp ring (Cp ring control, *vide supra*). Directing groups with stereocentres farther away from the ferrocene core ($\gamma$ or beyond) usually operate by steric influences of the substrate with the base (base control) because steric interactions with the lower Cp ring at such distances are generally negligible (*vide supra*).

Scheme 14. Synthesis of L-proline derived pyrroloimidazolidine auxiliary.
To determine by which mode this directing group operated, the β-epimer was synthesized. It was reasoned that if the directing group operated by Cp-ring control, a reversal of lithiation selectivity would be observed.\textsuperscript{2b} The \textit{anti}-epimer was prepared by reduction of ferrocenyl hydantoin (80) with Schwartz’s reagent. The isolated configurationally unstable hemiaminal (83) mixture was then treated with \textit{n}-BuLi followed by silylation, affording a nearly 1:1 mixture of \textit{syn}- and \textit{anti}- epimers (81), which were separable by flash column chromatography (Scheme 16).\textsuperscript{2b} As was anticipated, lithiation of \textit{anti}-81 with \textit{t}-BuLi followed by electrophile quench gave products (84\textit{a-c}) that were single diastereomers (≥ 95:5 dr by \textit{¹}H and \textit{¹³}C NMR spectroscopy). Importantly, the products 84\textit{a-c} possessed the opposite planar chirality \textit{via} deprotonation of the pro-\textit{R} hydrogen of the Cp ring.
The reversal of lithiation selectivity was confirmed by single-crystal X-ray diffraction of the anti-derived methyl derivative (84a). Further evidence of the preferred orientations of the urea carbonyls in both syn- and anti-81 was obtained by nOe experiments. Irradiation of the methine at \( \delta 5.44 \) for the syn-81 produced a 1.0% nOe for a Cp hydrogen at \( \delta 4.30 \). What this meant was that the hydrogen located at the \( \beta \)-stereocentre was close to the pro-R hydrogen atom on the Cp ring. Therefore, the doublet at \( \delta 4.80 \) was tentatively assigned at the pro-S<sub>P</sub> hydrogen of the Cp ring. In the case of anti-81, the doublet at \( \delta 5.41 \) was tentatively assigned as the pro-R<sub>P</sub> hydrogen. This was assigned based on an nOe of 0.6% upon irradiation of the methine at \( \delta 5.41 \). Lithiation and deuteration of both epimers confirmed this assignment as both of these signals are completely diminished in the \(^1\text{H}\) NMR spectra of the deuterated epimers.
Scheme 17. Comparison of imidazolone antipodes derived from *syn* and *anti* epimers.$^{2^b}$

The stereochemistry of the products was confirmed by acid catalyzed elimination of the silanol to give solely planar chiral products (Scheme 17). The products obtained had opposite specific rotations, thus were shown to be enantiomers.
1.3.2.2 Diastereoselective Lithiation of $\eta^6$-Arene Chromium Tricarbonyl Complexes

Thus far, chiral carbon- and sulphur-based directing groups have been reported for the induction of planar chirality in ArCr(CO)$_3$ by diastereoselective lithiation. Of these, $\alpha$-ethylamines$^{86}$ (86), aminals$^{87}$ (87), chiral acetals$^{88}$ (88), and sulfoxides$^{89}$ (89) are prime examples (Figure 11).

**Figure 11.** Chiral directing groups used in diastereoselective lithiations of arene-chromium tricarbonyl complexes.

The methodology developed by Ugi (chiral $\alpha$-ethylamines, Scheme 9) was later applied towards the diastereoselective lithiation of ArCr(CO)$_3$, in which even higher levels of diastereoselectivity were observed (99:1 dr).$^{87}$ It has been established that the lithiation selectivity of ArCr(CO)$_3$ with chiral centres $\alpha$ to the aryl ring operates under the same principle as proposed for ferrocenes, i.e., that selectivity arises from avoidance of steric interactions with the CO ligands instead of the Cp ring (Cp ring control). ArCr(CO)$_3$ derived from $\alpha$-ethylamines (86) can also be further manipulated via $S_N1$ chemistry. Salzer has demonstrated that treatment with chloroethylchloroformate of ArCr(CO)$_3$ bearing $\alpha$-ethylamines results in substitution of the dimethylamine by a chlorine atom with retention of stereochemistry (Scheme 18).$^{90}$ This chloride may be nucleophilically displaced in an $S_N1$ fashion by other nucleophiles with the use of TIPF$_6$. $^{91}$
This method was used for the preparation of Hasiphos\textsuperscript{91} (92) and Daniphos\textsuperscript{92} (93), ArCr(CO)\textsubscript{3} analogues of the ferrocenyl diphosphine ligands. These ligands were shown to be useful for asymmetric induction in a number of transition metal-catalyzed reactions such as Suzuki-Miyaura couplings, allylic alkylations\textsuperscript{93} and Heck reactions, among many others.\textsuperscript{94}

\begin{center}
\begin{tikzpicture}
  \node (a) at (0,0) {\textbf{Scheme 18.} Conversion of \(\alpha\)-ethylamines to other functional groups and ligands.}\textsuperscript{91-93}

  \begin{itemize}
    \item 1. chloromethyl chloroformate
    \item 2. \(\text{TiPF}_6\)
    \item 3. Nu-H
  \end{itemize}

  \begin{itemize}
    \item Hasiphos 92
    \item Daniphos 93
  \end{itemize}

  \begin{tikzpicture}
    \node (a) at (0,0) {OC\textsuperscript{2}Cr(CO)\textsubscript{3}E E NMe\textsubscript{2} 1. chloromethyl chloroformate \rightarrow OC\textsuperscript{2}Cr(CO)\textsubscript{3}E Nu};
    \node (b) at (2,0) {OC\textsuperscript{2}Cr(CO)\textsubscript{3}E PPh\textsubscript{2} OMe};
    \node (c) at (4,0) {OC\textsuperscript{2}Cr(CO)\textsubscript{3}E PPh\textsubscript{2} PPh\textsubscript{2}};
    \node (d) at (0,-2) {\text{t-But}};
  \end{tikzpicture}
\end{center}

ArCr(CO)\textsubscript{3} analogues of chiral auxiliaries used for diastereoselective lithiations of ferrocene have been developed based on chiral acetics,\textsuperscript{95} chiral sulfoxides\textsuperscript{96} derived from Ellman’s reagent, oxazolines,\textsuperscript{97} aminals,\textsuperscript{98} sulfoximines,\textsuperscript{99} hydrazones,\textsuperscript{100} and imidazolines.\textsuperscript{101} Some of these auxiliaries are sensitive to the steric demands of the bases used for lithiation, while some are not. In ferrocene lithiations, the directing groups which exhibit sensitivity to the bases used are referred to as under base control, whereas the reactions which are unaffected by the size of the base are referred to as under Cp-ring control. As previously explained, classical substrates such as Ugi’s amine (48) operate under Cp ring control (Scheme 9). Since there is no direct analogy for
diastereoselective lithiations of ArCr(CO)₃, the terms “substrate” or “carbonyl control” will tentatively be assigned for directing groups whose selectivity is not sensitive to the base used (analogous to Cp ring control). Some of these auxiliaries allow for further manipulation of the directing group, while some are permanently present in the final products. It should also be noted that thus far, no N-based directing groups have been reported for diastereoselective lithiation of ArCr(CO)₃.

### 1.3.3 Applications of Planar Chiral Ferrocenes as Ligands for Asymmetric Transition-Metal Catalyzed Reactions

When the diphenylmethanol adduct 82c was treated with acid an unexpected tetracyclic product (94) was obtained in which the alcohol had intramolecularly added to the intermediate iminium ion (Scheme 19).³ Both syn- and anti-derived adducts (82c plus its diastereomer) underwent annulation, the stereochemistry of the products was assigned using the coupling constants of the methine proton at the acetal-aminal juncture and nOe experiments. This compound was then converted to an NHC ligand by the methods shown in Scheme 19. This NHC was then trapped with [Ir(COD)Cl]₂ providing 95. Treatment of this compound with PPh₃ then gave cationic Ir-complex 96a. Following the same synthetic route, 96b was prepared from anti-81.¹⁰²

Based on the work by Crabtree and coworkers who employed imidazolylidenes as ligands for the Ir-catalyzed hydrogenation of 2-substituted quinolines,¹⁰³ chiral imidazolylidene ligands have been of particular interest to the Metallinos group. The use of imidazolylidene ligands dramatically increases the reactivity of the Ir-catalysts towards hydrogenation, allowing for high conversions at low H₂ pressures (as low as 1 atm), with sterically demanding substrates converting at slightly higher pressures (5 atm).¹⁰⁴
The chiral Ir-complexes 96a-b were tested for their activity as hydrogenation catalysts under similar conditions reported by Crabtree (Scheme 20).\textsuperscript{103} After optimization of the conditions, and the hydrogenation of numerous 2- and 2,6-disubstituted quinolones, it was found that \textit{syn}-derived complex 96a was capable of hydrogenating quinolines under 5 atm of H\textsubscript{2} at 1 mol % catalyst loading with up to 90:10 er and good overall yields (25-94%).\textsuperscript{3} \textit{Anti}-derived complex 96b was found to give high overall conversions but with low enantioselectivities (73:27 er), and only at high pressures of H\textsubscript{2} (45 atm). Analogues of Ir-complex 96a-b were synthesized by changing the carbonyl electrophiles during the lithiation step. An analogue incorporating benzaldehyde as the electrophile gave an annulated compound upon cyclization with a \textit{syn}-stereochemical relationship in the ligand framework, similar to the \textit{anti}-derived 96b. Under the optimized conditions, this analogue gave good conversion of 2-methylquinoline (88%) but with poor enantioselectivity (59:41 er).\textsuperscript{105}
Based on the results of the 2-methylquinoline hydrogenations with complexes 96a-b, it may be inferred that an anti-stereochemical relationship of the ligand backbone is favourable for inducing high enantioselectivity. What is unclear is the role that the planar chiral ferrocene moiety plays in the low pressure reactivity and selectivity of the hydrogenation. This anti-relationship in the imidazolylidene ligand backbone is present in a number of commercially available chiral catalysts.
The first enantioselective Grubbs ring closing metathesis catalyst 99 (Figure 12) bears a 4,5-diphenyl-anti-configured imidazolylidene ligand.\textsuperscript{106} In Grubbs’ first report of this catalyst, he mentioned that the anti-substituted backbone was effective at transferring chiral information from the backbone to the metal centre by means of a “gearing effect” imparted on the mono-ortho-substituted aryl rings. In this ligand, the ortho-substituted aryl groups orient themselves into an anti-anti-configuration with respect to the 4,5-trans-diphenyl substituents, thereby relaying the chiral information to the metal centre.\textsuperscript{107} While this gearing effect may not be present in rigid systems such as the annulated Ir-complexes 96a-b, the anti-configuration of the imidazolylidene ligand may play an important role in the transfer of chiral information to the substrates.

With multiple sites and elements of chirality within ligands 96a-b it can be difficult to pinpoint which stereocentre(s) are responsible for the observed enantioselectivity. With regards to central chirality, both syn- and anti-configured imidazolylidene ligands showed catalytic activity, but only the anti-configured ligand 96a demonstrated good enantioselectivity.\textsuperscript{3} The element of planar chirality may be too far away from the metal centre to impart any chiral information. In addition to that, and the variance in reactivity observed with different phosphines, a bidentate ligand with a
phosphine bound directly to the Cp ring was sought.\textsuperscript{107} In this bidentate ligand, the element of planar chirality would be closer to the metal centre and may impart this chiral information, thereby increasing the enantioselectivity.

In the initial attempts at substituting the ferrocene with a phosphine by lithiation-quench, spontaneous oxidation of the resulting ferrocenylphosphine was observed (Scheme 21).\textsuperscript{108} To circumvent this problem, a less electron rich phosphine bearing electron-withdrawing trifluoromethyl groups was prepared by the methods reported by Casalnuovo.\textsuperscript{109} Unfortunately, every attempt at the oxidation of the aminal bearing this phosphine with various oxidizing agents did not provide the desired imidazolium salt. Despite the presence of electron withdrawing groups, the nucleophilic nature of arylphosphines (which is exploited in their use as ligands) was likely the reason for which this method was not working.

\begin{center}
\textbf{Scheme 21.} Attempted synthesis of phosphino imidazolones from \textit{syn-81}.\textsuperscript{110}
\end{center}

Another attempt at the synthesis of a bidentate phosphine-NHC ligand was attempted by lithiation of the annulated urea (Scheme 22). Lithiation of 100 proceeds by coordination of the urea oxygen to the alkyllithium base resulting in \textit{ortho}-substitution upon electrophile quench providing the trisubstituted planar chiral ferrocene 101. To avoid the reaction of nucleophilic phosphines with
DIBAL-H, iodine was first installed. After reduction by DIBAL-H, 102 was subjected to metal halogen exchange with $n$-BuLi providing 103. Unfortunately, these arylphosphines are incompatible with the highly electrophilic oxidants required to oxidize the aminal, resulting in phosphonium adducts instead of imidazolylidenes. The use of phosphines with electron withdrawing groups, or protecting groups resulted in either partial recovery or decomposition of the starting materials.

Scheme 22. Attempted synthesis/coordination of bidentate phosphine-NHC ligand.

The efforts towards a bidentate ligand were not abandoned. Instead, a more robust imidazolium ligand was sought, based on the work of Debono et al.\textsuperscript{110} Racemic and planar chiral phosphine-imidazolylidene ligands (105) were prepared by the Ugi method (lithiation of 48) and coordinated to Pd-sources (Scheme 23).\textsuperscript{112} It was the first report of a planar chiral Pd-imidazolylidene complex to be used as a catalyst in asymmetric Suzuki-Miyaura couplings. The bidentate complexes 106
and 107 contain a 7-member coordination ring. These compounds all displayed moderate activity in Suzuki-Miyaura couplings of arylbromide and boronic acids with yields of up to 87%. When used for asymmetric couplings of 2-substituted napthylboronic acids and halides, good conversions (up to 95%) but poor enantioselectivities (≤ 71:29 er) were observed.\textsuperscript{112}

**Scheme 23.** Synthesis of Pd-complexes bearing bidentate planar chiral ligands.\textsuperscript{112}

Secondary ureas may be converted to NHCs by an indirect method by first preparing a chloroimidazolium species.\textsuperscript{113} Treatment of the resulting chloroimidazolium with \textit{t}-BuLi effects a metal-chlorine exchange providing the NHC, which can be trapped by electrophilic metals or other reagents (or it can be protonated). This methodology has previously been used by our group for the preparation of chiral imidazolylidenes\textsuperscript{111} and guanidines\textsuperscript{86} derived from the same L-proline hydantoin (79) starting material.
Chlorination of ureas can be accomplished by a number of reagents including oxalyl chloride, thionyl chloride, and chlorophosphorous reagents (PCl$_3$, PCl$_5$, POCl$_3$). Depending on the substrate, the product may be prone to nucleophilic addition (or rehydration by water). Chloroimidazoliniums derived from saturated imidazolines are more susceptible to nucleophilic attack. This reactivity has been used for the preparation of guanidines. Stabilized chloroimidazoliums are those derived from unsaturated imidazolones, which are stabilized by the aromatic imidazolium ring. These compounds are not as susceptible to nucleophilic attack and are stable to moisture.

In addition to NHCs, phosphines are usually the second ligand of choice in catalytic systems because of their strong electron donating properties. Though popular, phosphines are not the only atom capable of ligation to metals for the purpose of catalyst development. Nitrogen, oxygen, sulphur, and selenium are also able coordinate to metals and many of such complexes are also catalytically active. Bidentate coordination complexes with ligands bearing imidazolylidenes and additional nitrogen, oxygen or sulphur atoms have been shown in some cases to possess similar catalytic activity as their phosphorus-containing analogues. For reviews on sulfur-functionalized imidazolylidene ligands refer to references; for reviews on bidentate imidazolylidene ligands and complexes thereof please see references.

Planar chiral thioether ligands have also been prepared and studied as ligands for asymmetric catalysis. The Fesulphos complex (108, Figure 13) contains a planar chiral ferrocene ligand with P-, S- functionality derived from Kagan’s sulfoxide (51). Standard lithiation-substitution followed by electrophile quench with chlorophosphines provided the planar chirality after which the sulfoxide was reduced by silane. The Fesulphos ligand has been used in asymmetric allylic alkylation reactions and displayed moderate to good enantioselectivities (70:30...
to 95:5 er). In addition, ThioclickFerrophos (109), which is also derived from Ugi’s amine (48), displays similar catalytic activity.

Bidentate planar chiral ferrocene ligands with both thioether-imidazolylidene and phosphine-imidazolylidene functionalities have been prepared and coordinated to palladium, rhodium and iridium (Figure 13). Using the approach developed by Ugi, planar chirality was installed via deprotonation-substitution. Quaternization of the tertiary amine followed by displacement by imidazole generated the desired ligands, which were then coordinated to both palladium (110), iridium (111), and rhodium (112 and 113). Complexes 111 and 113 displayed no catalytic activity in asymmetric hydrogenations of numerous substrates. Rhodium complex 112 displayed poor activity and enantioselectivity in the hydrogenation of dimethyl itaconate (44% yield, 59:41 er).

Figure 13. Planar chiral S- and P- imidazolylidene coordination complexes of Pd, Ir, and Rh.
2. Objectives:

The aims of the current work can be split into three goals, all of which are related through the use of the L-proline derived pyrroloimidazolone directing group.

1. The first goal is to prepare solely planar chiral unsaturated imidazolylidene ligands bearing heteroatom substituents (85), and after conversion to imidazolylidenes (114), coordinate them to Pd or Ir, with the aim of preparing catalysts bearing bidentate ligands (115, Scheme 24). Pd-complexes will be tested as catalysts for asymmetric Suzuki-Miyaura couplings to determine the extent of chiral induction in the axially-chiral products formed. Iridium complexes will be used for asymmetric hydrogenations of 2- and 2,6-substituted quinolines to determine the extent of chiral induction and the low-pressure activity of the catalysts.

![Scheme 24. Proposed synthesis of bidentate planar chiral transition-metal complexes.](image)

2. The second goal is to investigate the importance of planar chirality in the Ir-catalysts used for asymmetric hydrogenations of 2- and 2,6-substituted quinolines. The two iridium complexes previously investigated (96a,b) are pseudo-enantiomers, sharing only one chiral centre with the same configuration, the γ centre derived from L-proline. By preparing an N-phenyl analogue
(anti-121) of iridium complex 96a, (Scheme 25) and using it to hydrogenate previously studied quinoline substrates, the extent of chiral induction imparted by the planar chirality will be inferred.

Scheme 25. Proposed synthesis of N-phenyl Ir(I) analogue (121).

3. The final goal is to expand the utility of the epimeric imidazolone directing group towards the diastereoselective lithiation-substitution of η⁶-arene chromium tricarbonyl complexes (ArCr(CO)₃), with the aim of preparing planar chiral products in high diasteromeric ratios. It is
hoped that a reversal of lithiation selectivity, as was observed when the β-stereocentre was epimerized in the ferrocene series,\textsuperscript{2b} will result in a similar reversal of lithiation selectivity in ArCr(CO)\textsubscript{3} complexes (Scheme 26).

Scheme 26. Proposed diastereoselective lithiation-substitution of η\textsuperscript{6}-arene chromium tricarbonyl compounds with L-proline derived chiral auxiliaries.
3. Results and Discussion

3.1 Planar Chiral N-Substituted Ferrocenyl Imidazolones: Imidazolylidene Ligands and Coordination Chemistry

The first set of reactions studied was the chlorination/oxidation of planar chiral ferrocenyl imidazolones. The synthesis of these compounds began with the synthesis of iodoferrocene (78), via an in-situ lithiation-electrophile quench with elemental iodine. This method is an improvement on the previously reported synthesis of iodoferrocene which required the isolation of the pyrophoric intermediate lithio-ferrocene.\textsuperscript{21} Thus, iodoferrocene may be prepared by a modification of the procedure reported by Mueller and Westerhoff, quenching with elementa\textsuperscript{121} by lithiation of ferrocene in the presence of substoichiometric amounts of \textit{t}-BuLi/KO\textit{t}-Bu followed by quench with iodine. This procedure provides a mixture containing a small amount of ferrocene which need not be removed by chromatographic means.\textsuperscript{108} The yield can then be determined using \textsuperscript{1}H NMR spectroscopy integration ratios to obtain a molar ratio of FcI : Fc, which can then be converted to masses using the total mass of the product mixture.

The coupling of iodoferrocene (78) to L-proline hydantoin (79) is then accomplished using a Cu\textsubscript{2}O-mediated procedure which is a combination of two procedures reported by Bildstein\textsuperscript{21} and Sato.\textsuperscript{122} Reduction of 80 using Schwartz’s reagent (Cp\textsubscript{2}ZrHCl) and \textit{in-situ} protection of the resulting hemiaminal alkoxide provided syn-81 after recrystallization. Diastereoselective lithiation of syn-81 followed by electrophile quench with chlorophosphines and disulfides (dimethyl disulfide and diphenyl disulfide) gave products 82 in good yields and high diastereomeric purity (Scheme 27). Subsequent treatment of 82 with TsOH in CHCl\textsubscript{3} at reflux led to planar-chiral
imidazolones 85b-g in good yields, as established previously in our group.\textsuperscript{2b} \textit{Syn-81} also underwent elimination under these conditions, providing achiral imidazolone 85g in good yield.

\begin{center}
\begin{tabular}{c|c|c|c}
82 & E\textsuperscript{*} & yield (%) & 85 & yield (%) \\
\hline
b & 1,2-diodoethane & 87 & I & b & 94 \\
f & dimethyl disulfide & 95 & SMe & c & 88 \\
l & diphenyl disulfide & 94 & SPh & d & 94 \\
j & Cl(P(Ar\textsubscript{1})\textsubscript{2}) & 79 & P(Ar\textsubscript{1})\textsubscript{2} & e & 86 \\
k & Cl(P(Ar\textsubscript{2})\textsubscript{2}) & 68 & P(Ar\textsubscript{2})\textsubscript{2} & f & 83 \\
- & n/a\textsuperscript{*} & - & H & g & 88 \\
\hline
\end{tabular}
\end{center}
\textsuperscript{* unsubstituted (\textit{syn-81})}

\textbf{Scheme 27.} Diastereoselective lithiation of \textit{syn-81} and elimination to solely planar chiral imidazolones.

With planar-chiral imidazolones in hand, attempts were then made to convert them to bidentate imidazolylidene ligands. Initial studies of the chlorination were first performed on unsubstituted imidazolone 85g (E = H). There are multiple reagents reported to chlorinate ureas such SOCl\textsubscript{2}, oxalyl chloride, PCl\textsubscript{3}, and POCl\textsubscript{3} among a few others.\textsuperscript{114} A previously established procedure using POCl\textsubscript{3} was chosen as a starting point.\textsuperscript{103} After scanning variables such as temperature, solvent, reaction time and chlorinating reagent, it was found that neat POCl\textsubscript{3} under
mild heating (50 °C) gave the cleanest conversion to the corresponding chloroimidazolium salts. Isolation of the cationic chloroimidazolium salt was accomplished by salt metathesis with KPF₆, and precipitation of the resulting salt in a cold Et₂O/ hexane solution. Once the product was confirmed, the chlorination of imidazolones 85b-g was carried out (Scheme 28).

![Scheme 28. Chlorination/oxidation of imidazolones with POCl₃.](image)

All the ureas except the phosphines (85e and 85f) gave the desired chloroimidazolium salts 124a-d. Multiple attempts at the chlorination of phosphines using POCl₃ and the aforementioned reagents resulted in the consumption of starting material and the isolation of an intractable black solid upon precipitation. ³¹P NMR spectroscopy revealed the presence of multiple phosphine containing compounds, none of which could be isolated or characterized. While no product was isolated, it is suspected that an addition reaction between the triarylphosphine and POCl₃ had occurred.¹²³

Chloroimidazolium salts may be converted to imidazolyldienes by two methods: oxidative addition to a low-valent metal centre¹¹⁵ or metal-halogen exchange with two equivalents of
A procedure for the oxidative addition of chloroimidazolium salts to a Pd$^{0}$ source reported by Furstner was attempted first.$^{115}$

For ease of preparation, the first compound studied was the achiral chloroimidazolium salt $124a$. Reflux of the chloroimidazolium salt with tetrakis(triphenylphosphine)palladium$^{0}$ (Pd(PPh$_3$)$_4$) in CH$_2$Cl$_2$ under inert atmosphere provided, after crystallization of the crude reaction mixture, Pd-complex $125a$ as bright yellow crystals in 78% yield (Scheme 29). TLC analysis could not be used to follow the course of the reaction because of the ionic nature of the starting materials and products. When the oxidative addition procedure was established for $124a$, experiments were carried out on both the thiomet and thiophenyl derivatives ($124b,c$). Upon crystallization of the crude reaction mixtures, the reaction that contained thioether $125b$ gave bright yellow powdery crystals that were confirmed by X-ray analysis to be the oxidative addition product. Unfortunately, despite being a potentially bidentate ligand, the sulphur atom in $125b$ was not bound to the Pd atom. This result was not entirely unexpected as it is known that phosphines are better ligands than sulphur atoms.$^{125}$ The rationale used was that an intramolecular donor might have had a chance to

![Scheme 29. Oxidative addition of chloroimidazolium salts to Pd(PPh$_3$)$_4$.](image)
displace the phosphine, but this was not the case and cationic imidazolylidene-Pd complex 125b was obtained instead (Figure 14). The crystal structure of complex 125b shows an overall square planar coordination geometry at palladium with the chlorine atom *trans* to the pyrroloimidazolylidene ligand. The ligand is monodentate with $R_p$ absolute configuration of the ferrocene moiety. The triphenylphosphines are in slightly different chemical environments, an observation that is consistent with the nonequivalency of the phosphines atoms by $^{31}$P NMR spectroscopy.

**Figure 14.** ORTEP plot of 125b with 30% probability ellipsoids. Hydrogen atoms, PF$_6^-$ counterion, and 2 CHCl$_3$ of crystallization omitted for clarity.
Despite the monodentate coordination of the ligand to the metal of 125b, it was still potentially a viable catalyst for asymmetric Suzuki-Miyaura reactions.\textsuperscript{113} Under the conditions reported by Debo\-no et al.,\textsuperscript{113} 125b was tested as a catalyst for the coupling of 1-bromo-2-methyl naphthalene (126) and 1-naphthyl boronic acid (127). The product of the reaction (128) would bear axial chirality, resulting from a hindered rotation around the newly formed Ar-Ar bond. While no optically pure sample was available for comparison, a calibration curve (Figure 15) was prepared using specific rotations and % ee measurements (measured by chiral HPLC) reported by Hayashi in the late 1980s.\textsuperscript{126}

\begin{equation}
\begin{array}{c}
\text{126} \quad \text{Br} \\
\text{Me} \\
\text{127} \quad \text{B(OH)}_2 \\
\end{array}
\begin{array}{c}
\text{1 mol\% 125b} \\
\text{K}_2\text{CO}_3, \text{toluene,} \\
70 \degree \text{C}, 24 \text{ h} \\
(68\%) \\
\end{array}
\begin{array}{c}
\text{128} \\
\end{array}
\end{equation}

\textbf{Scheme 30.} Suzuki-Miyaura coupling with Pd complex 125b.

From this calibration curve a regression line was obtained with an \(R^2\) value of 0.9993. The sample prepared using complex 125b was found to have a specific rotation of −5.63 (c 1.0, CHCl\(_3\)). Using the equation of the regression line, the calculated ee was found to be 14\% or 57:43 er. Based on the calculated rotation value it was determined that the overall selectivity of Pd-complex 125b in the Suzuki-Miyaura coupling was very low. In the ORTEP plot (Figure 14) the nitrogen-ferrocene bond is rotated so that the planar chiral Cp ring is not near the Pd centre. This
orientation may not allow for chiral information to be transferred to the reaction centre during catalysis. Methods of preparing binap 128 in excesses of 95:5 er have been reported, many of which are discussed in Hayashis's report. Additional substrates would have been investigated had an enantiomeric ratio of at least 75:25 been observed. However, discouraged by these results, no further substrates were studied.

The pursuit of planar-chiral bidentate Pd- complexes was not abandoned. It was reasoned that if non-phosphine containing Pd-sources were used then a more labile ligand could be intramolecularly displaced by the sulphur atom. Unfortunately, the tendency of palladium to undergo oxidative addition is dramatically enhanced by strongly donating ligands such as alkyl phosphines, or by very polarized C-X bonds within the substrate (where X can be a halogen, a carbon atom, a proton or a triflate, among other groups). The cationic nature of the imidazolium ring may polarize the C-Cl bond sufficiently that another phosphine-free Pd$^0$ could undergo
Figure 15. Calibration curve of specific rotation vs. ee of 2-Me-1,1'-BINAP

and calculation of er.

oxidative addition. Two additional palladium sources were investigated: (dba)$_2$Pd$^0$ and (CH$_3$CN)$_4$Pd$^0$. No evidence of complex or crystal formation was observed in either case. It was decided that another method of generating the imidazolylidene was required.

Established in the late 1930s independently by both Wittig$^{128}$ and Gillman$^{129}$ was a method of metathesis between an organolithium and an organohalide. In this reaction, treatment of alkyl, vinyl, allylic or aryl-halides with alkyllithium reagents results in the exchange of the halogen for the lithium atom. While the mechanism of exchange is still debated, it is believed to proceed through S$_N$2-like addition of the anion to the halogen and displacement of the alkyl, vinyl, allylic or aryllithium species.$^{130}$ Though this is a reversible process, as long as the newly generated lithium species is less basic than the orginal lithium species, the reaction under most conditions
will proceed in the forward direction. This method has been applied to haloimidazoliums (129) and has been shown to generate the imidazolyldiene (130) in solution.\textsuperscript{114, 125} The imidazolyldiene can then be coordinated \textit{in-situ} to an electrophilic metal (132) or can be protonated providing an imidazolium salt (131, Scheme 31).

\begin{center}
\includegraphics{scheme31}
\end{center}

\textbf{Scheme 31.} Metal-halogen exchange of chloroimidazolium salts by \textit{t}-BuLi followed by trapping of the imidazolyldiene with electrophiles.\textsuperscript{125}

The oxidative addition approach, which may provide the coordinated imidazolyldiene directly, was not giving the desired product so a step-wise approach was taken. This step-wise ylidene deprotonation-coordination approach, which does not proceed \textit{via} oxidation addition, allows the use of metal salts in higher oxidation states, so that non-phosphine containing Pd-sources can be used. THF was used as the solvent in all cases for solubility reasons and compatibility with alkyllithium reagents. Treatment of chloroimidazolium salt 124b with \textit{t}-BuLi followed by quenching with electrophilic metals (Pd, Ir, Rh) in all cases yielded no isolable
products (Scheme 32). Attempts to isolate materials by column chromatography and/or crystallization of the crude or Celite filtered reaction mixtures gave no recognizable products. In most cases, a black solid was collected from the reaction mixture upon attempts to precipitate products. This black solid was insoluble in all common organic solvents, leading to the conclusion that it may have been Pd$^0$. Investigation of the reaction mixtures soon after addition of the Pd-source revealed the same insoluble black material.

Despite no isolation of desired products, the failure of these reactions may be attributed to the coordination step. That is, the imidazolylidene is formed, but coordination to the metal is not occurring, possibly due to insolvability of the metal complexes at low temperatures, or decomposition of the metal complexes before coordination can take place. It is also possible that

<table>
<thead>
<tr>
<th>entry</th>
<th>complex</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh(COD)Cl$_2^*$</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>PdCl$_2$</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>PdCl$_2$(CH$_3$CN)$_2$</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>PdCl$_2$(PPh$_3$)$_2$</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>[PdCl(allyl)$_2^*$</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>[Ir(COD)Cl]$^2*$</td>
<td>No</td>
</tr>
</tbody>
</table>

$^*$0.55 equiv

**Scheme 32.** Attempts to generate and trap imidazolylidenes with various metals.
coordination does take place, but isolation of the products is the issue. Formation of the imidazolylidene was proven by subsequent conversion of the chloroimidazolium salts 124b-c to imidazolium salts 134a-b by protonation of the generated imidazolylidene (Scheme 33).

![Scheme 33](image)

Scheme 33. Reduction of chloroimidazoliums by t-BuLi.

Following the procedure by Debono et al. for the preparation of bidentate phosphine-imidazolylidene complexes of palladium, 113 134a was treated with either KOt-Bu or NaH in CH3CN in the presence of Pd(CH3CN)2Cl2 under reflux (Scheme 34). After refluxing for 16 hours a new yellow coloured spot appeared on the TLC of the reaction mixture. Column chromatography of the reaction mixture in 90/5/5 CH2Cl2/MeOH/acetone provided a yellow solid in low quantity (~22%). 1H NMR revealed the same signals present in the starting material, minus the C3 imidazolium proton which would be absent in the desired product. Since coordination to the metal provided no new proton signals, the identity of the isolated material could not be verified. Low- and high- resolution mass spectrometry revealed a molecular ion peak with a mass of 526.41 amu, while the desired product would have a mass of 515.57 amu. No fragments were observed at the expected mass.
Attempts to recrystallize the material for the purpose of single crystal X-ray diffraction led to the eventual decomposition of the material. Attempts to repeat the experiment were not successful. Many conditions, including variations of the Pd-source, base and solvent were attempted but no products were isolated.

### 3.2 A Biferrocene Ligand Precursor

Focus then changed to the development of a C₂-symmetric bidentate imidazolylidene ligand. Bis-NHC ligands have been reported to impart a number of unique properties to the metal complexes thereof. Among these properties are an observed trend of high thermostability and high catalytic performance in challenging reactions such as alkane dehydrogenation. Imidazolylidene
ligands are known to be stronger σ-donors than phosphine ligands and the effect of two imidazolylidenes coordinated to a single metal can be additive.\textsuperscript{132} An Ullmann homocoupling of imidazolone 85c was performed (Scheme 35) using a slight excess of copper bronze, and DMSO as the solvent. The desired C\textsubscript{2}-symmetric biferrocene 136 was obtained in 21\% yield, with partial recovery of deiodinated imidazolone 85g. Unfortunately, upon treatment of the product with POCI\textsubscript{3}, decomposition of starting material was observed with no isolation of the desired product.

### 3.3 Attempts Towards Annulated Bidentate Imidazolinyldene Ligands and their Coordination Complexes

It was previously established that ferrocenyI phosphines are incompatible with Ph\textsubscript{3}CBF\textsubscript{4}, resulting in phosphonium adducts.\textsuperscript{108} From the attempted chlorination/oxidation of phosphino and thioether imidazolones 85b and 85d, it is likely that phosphines, even those with electron

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**Scheme 35.** Ullman coupling of imidazolone 85c and attempted chlorination with POC1\textsubscript{3}.
withdrawing groups, are too nucleophilic to be compatible with these electrophilic reagents. The thioether imidazolones underwent chlorination with ease, suggesting that they may be stable towards oxidation of the aminal by Ph$_3$CBF$_4$. Following the procedure previously established for the synthesis of aminal 102, a metal-halogen exchange was used to install a thiomethyl ether upon electrophile quench (Scheme 36). Treatment of aminal 138 with Ph$_3$CBF$_4$ resulted in complete consumption of the starting material.

Attempts were made to isolate the product by anhydrous precipitation techniques but the identity of the material could not be confirmed. This was most likely because of the instability of imidazolinium, or its tendency to rehydrate by the addition of water. To further study the oxidation, experiments were carried out in a Schlenk-NMR tube in acetone-d$_6$ in the hope of observing evidence that the oxidation had taken place. If the sulphur atom had been oxidized by the reagent,
it was expected that the chemical shift (δ) of thiomethyl-singlet shown in Figure 16 would be downfield with respect to the chemical shift of the starting material 138 in acetone-d6 (2.37 ppm, s, 3H). In addition, the diastereotopic aminal protons indicated on the top spectrum at 4.34 ppm (d, 1H, J = 6.8 Hz) and 3.94 ppm (d, 1H, J = 6.8 Hz) would still be present. The resulting crude NMR spectrum (Figure 16, bottom) showed minimal displacement of the thiomethyl singlet, disappearance of the diastereotopic aminal protons, and a new 1H singlet at 9.22 ppm indicated in red. While not directly comparable, the chemical shift of the C2 protons of the imidazoliums 134 was approximately 9.2 ppm. Two attempts to trap this intermediate were made (Scheme 36). In the first attempt [Ir(COD)Cl]2 dimer was used as the electrophile, and in the second attempt (CH3CN)2PdCl2 was used. In both cases, slight excess of KOr-Bu was employed to generate the ylidene by deprotonation of the imidazolinium at low temperature but no products were observed. 1H NMR spectroscopy suggested that the oxidation had taken place, implying that the deprotonation/coordination step was problematic. Repetition of this experiment under glovebox conditions is likely required for isolation of the imidazolinylidene (139) or complexes bearing this ligand.
Figure 16. $^1$H NMR spectrum of aminal 138 before (top) and after (bottom) treatment with Ph$_3$CBF$_4$ (400 MHz, 298 K, acetone-d$_6$)
3.4 Chiral Annulated N-Phenyl NHCs Derived From L-Proline Hydantoin

To determine the importance of planar chirality in iridium complex 96a, a non planar chiral analogue was required. The synthesis of the N-phenyl analogue (116) was undertaken by acid-catalyzed condensation of phenyl isocyanate with L-proline (Scheme 37). Crystallization of the product from the reaction mixture gave 141 in high yield (95%) and enantiomeric purity (>95:5 er). Treatment of 141 with Cp₂ZrHCl followed by *in-situ* silylation provided the analogous lithiation substrate 116 in good yields and diastereomeric purity (>95:5 dr). The product was obtained in better diastereomeric ratio (>95:5 dr) than the ferrocenyl analogue, which was fortunate because the product was obtained as an oil, thus rendering crystallization impossible. While the lithiation-substitution reaction itself would impart no planar chirality in the molecule, it was expected to proceed via coordination of the urea to the alkyllithium base resulting in ortho-substituted products upon electrophile quench as was seen in the ferrocene analogue.² Many lithiation conditions were investigated including the use of different alkyllithium bases, equivalents of bases, solvents, and diamine additives (Scheme 38).¹³³

![Scheme 37. Preparation of N-phenyl analogue of syn-81.](image-url)
Scheme 38. Attempted lithiations of N-phenyl analogue 116.

Close examination of the preceding experiments revealed that the major product in all cases was the achiral elimination product 143. This result suggested that the methine on the exo-face of the fused-ring system α to the nitrogen was prone to abstraction with concurrent loss of TESO⁻ (Figure 17). The near anti-periplanar configuration of the α to nitrogen methine and the TESO group in 116 may have enhanced the ease of this elimination.

Figure 17. Elimination of the stereodetermining β-silyloxy group.
To solve this problem it was reasoned that preparation of an alkoxy analogue with anti-stereochemistry would be less prone to E2-type anti-periplanar elimination. This modification would also impart the added benefit of a more basic alkoxide upon elimination, thereby inhibiting elimination of the leaving group under metalation conditions. Based on the results of an early experiment I performed investigating further manipulations of the imidazolone directing group in the ferrocene series, a method for substitution at the β-chiral centre with oxygen-based nucleophiles was chosen. Under acidic conditions in the absence of nucleophiles, compounds bearing the triethylsilane group undergo elimination providing achiral imidazolones.\(^{2b}\) This method was previously used to prepare planar-chiral enantiomers, which were used to prove the diastereoselectivity of the imidazolone directing group in ferrocene lithiation.\(^{2b}\) Attempts to eliminate the triethylosilyloxy moiety of the diphenylmethanol adduct 85c under acidic conditions resulted in an intramolecular nucleophilic substitution of the directing group by the alcohol group.\(^3\) This result is what led to the eventual transformation of the imidazolone directing group into the imidazolyldene ligands. Later experiments used non-nucleophile containing starting materials, but instead a nucleophilic solvent (MeOH) resulted in the isolation of a single product (144) with an anti-configuration in good yield (Scheme 39).
Scheme 39. Acid-catalyzed substitution at the β-stereocentre by nucleophilic alcohols.

For the N-phenyl series, an alcohol with a similar A-value to the triethylsilyloxy group was desired. A-values are a system used to determine the most stable orientations of atoms within a molecule.\textsuperscript{134} It is also used to compare the volume of space occupied by different functional groups in order to compare steric bulk. The origin of selectivity in the lithiation of \textbf{81} is due to unfavourable steric interactions between the triethylsilyloxy group and the lower Cp ring (Cp control).\textsuperscript{2b} To achieve a similar lithiation selectivity, a functional group which could impart a similar steric bulk to the pyrroloimidazolone was necessary. In the end, isopropanol was chosen as the nucleophile because it possesses a similar A-value to that of the triethylsilyloxy group. The A-value of the isopropyloxy (Oi-Pr) group is 2.15, and while there is no measured A-value for a triethylsilyloxy (OEt\text{SiEt}_3) group, trimethylsilyloxy (OEt\text{SiMe}_3) has a value of 0.74, and an isopentyl group (CH\text{2C(CH}_3)_3) has a value of 2.\textsuperscript{135} The A-value of the triethylsilyloxy moiety can be approximated somewhere between that of the trimethylsilyloxy and isopentyl groups in the range of 0.74 < A_{\text{OSiEt}_3} < 2.
The acid catalyzed substitution reaction was applied to the 116 and a similar substitution product (anti-145) was obtained in low yield, along with the eliminated imidazolone 143 (Scheme 39). However, this route was low yielding, and not efficient due to the sacrificial use of the silane group. Instead, this method was applied to the hemiaminal 146 obtained after Schwartz reduction of hydantoin 141 (Scheme 40). Initially, the isolation of this intermediate was arduous owing to the water-solubility of the product and the need to use water for the work-up procedure. Very low yields were obtained (30-40%) due to the aqueous work-up involved. Modifications of the work-up procedure allowed this compound to be obtained in higher yields (Scheme 40). Instead of aqueous work-up/ extraction after the reaction was complete as shown by TLC, a small amount of a sat. NaHCO₃ solution was added to the reaction mixture and stirred for 5 minutes. To this was then added dry silica gel and the solvent was removed under reduced pressure. This silica was then filtered in a fritted funnel eluting with 50:50 EtOAc/hexanes, providing 146 in good yield and purity. Compound 146 was then submitted to the acetalization conditions (Scheme 40). Three products were observed: the expected anti-145, and the elimination product 143, but this time a syn-epimer (syn-145) was also observed. This result suggests that under acidic conditions an iminium intermediate is formed, and is then quenched by predominant nucleophilic addition from the exo-face of the fused ring system and minor addition from the endo-face.
With the desired lithiation substrates in hand, both epimers were subjected to the lithiation conditions established with ferrocenes 81 and quenched with benzophenone. Though both expected products were formed (147), they were obtained in low yields with complete recovery of starting material. Optimization revealed that a higher temperature during lithiation was all that was required for complete lithiation of the starting materials (Scheme 41). Despite these not being asymmetric lithiations, it was established that ortho-substituted products could be prepared in good yields.

Scheme 40. Preparation of the epimeric isopropoxy-imidazolones anti and syn-145.
Scheme 41. Ortho-lithiation of isopropoxy-modified imidazolones anti and syn-145.

Following the same methodology used to prepare Ir-catalysts 96, these compounds were then subjected to acid-induced annulation. Under the conditions shown in Scheme 19, both products (118) were formed in less than 4 minutes and in excellent yields (Scheme 42). In both cases a single product was isolated, which by $^1$H and $^{13}$C NMR spectroscopy appears to be a single diastereomer. The reaction proceeds through an iminium intermediate, and cyclizes through addition of the alcohol to the iminium with inversion of stereochemistry. The stereochemistry of the products were determined by the coupling constants of the methine hydrogen atom located on the hemiaminal carbon. Compounds 118 bearing syn-stereochemistry at the methine give a doublet with coupling constants of 6.8 Hz. Compounds bearing anti-stereochemistry give a doublet with a coupling constant of 1.6 Hz because of the near-90° angle between the methine and the neighbouring proton. As a side note, syn-118 undergoes lithiation with t-BuLi to provide ortho-substituted products via coordination of the urea to t-BuLi, as is seen in the annulated ferrocenyl urea 100. Only one experiment was performed, quenching with ClPPh$_2$ providing the
arylphosphine in 83% yield. This product was prepared to show that ortho-lithiation of syn-118 was possible. The product does not serve as a NHC precursor because the methods by which the urea may be converted to a NHC ligand are not compatible with phosphines. Anti-118 was then treated with DIBAL-H using a cosolvent system of THF/CH₂Cl₂ to allow for a more concentrated reaction mixture, leading to faster conversion (Scheme 43).

Despite the inherent instability of these compounds, aminal anti-119 was isolable by column chromatography in 95% yield and recrystallized in acetone. Anti-119 was then treated with tritylium tetrafluoroborate in THF at −78 °C and stirred for 5 hours; to this solution was then added KOrBu and [Ir(COD)Cl]₂. Treatment of the intermediate imidazolinium with KOrBu generated the imidazolylidene, which was immediately trapped with [Ir(COD)Cl]₂ providing anti-120 which was isolated by column chromatography in 34% over two steps (Scheme 43). The neutral complex was
then treated with one equivalent of PPh₃. The initially yellow solution turned red immediately upon addition of the PPh₃ solution. After 3h, TLC analysis revealed that the starting material had been consumed, at which time the solvent was removed under reduced pressure and salt metathesis was performed using a KPF₆ solution in CH₃CN. After 1 h, the solvent was removed and the red solid was treated with pentane, affording a bright red powdery solid which was collected on a Hirsch funnel, providing anti-121 in 97% yield. ¹H NMR spectroscopy of both the neutral and cationic Ir complexes revealed a doublet appearing much further upfield than is generally seen with aromatic protons (9.64 ppm in the neutral complex, and 9.10 ppm in th cationic complex. ¹H-¹³C HSQC experiments of the neutral complex showed that this signal corresponds to the proton ortho- to the imidazolylidene nitrogen of the disubstituted phenyl ring. Upon comparing the ¹H NMR spectrum of the ferrocenyl analogue (96a), an unusually high chemical shift was also observed for the

Scheme 43. Conversion of annulated urea to cationic Ir-complex anti-121.
neighbouring Cp proton. The crystal structure of 96a revealed that this proton is oriented towards the apical position of the square planar Ir atom, and it is therefore believed to be deshielded by the electron cloud of the Ir atom. If this is the case, then a decrease in electron density at the metal should shield this proton to some extent. Upon treatment with triphenyl phosphine, rendering the Ir cationic, a downfield shift from 9.64 ppm to 9.09 ppm was observed. This suggests that this proton is interacting with the metal in some way. Further experiments, which add electron density to the metal are required to make a definitive statement. From this observation arises two additional questions: (1) to what extent is this proton affected by the electron density of the metal; and (2) is it possible that this proton may undergo C-H activation? If this is possible, the installation of nucleophiles at this position may provide a new method of preparing bidentate complexes.

With the desired catalyst in hand, we then performed hydrogenations on substrates which gave the best results when using the ferrocene analogue 96a. 2-Methylquinoline (97a) and 6-fluoro-2-methylquinoline (97b) were subjected to hydrogenation under the same conditions used previously.\(^3\) Low conversions at 5 atm of pressure necessitated the need to apply higher pressures of H\(_2\) (45 atm) for conversions (Scheme 44). This indicates that the N-phenyl analogue is less reactive than the ferrocene containing catalysts. In the ferrocene containing catalysts, the anionic nature of the cyclopentadienide ring may contribute to an overall higher electron density on the Ir atom compared to the phenyl analogue because the nitrogen on the phenyl ring can donate electron density into the ring and not just to the ylidene. However, the lower reactivity of catalyst 121 cannot exclusively be explained by a lower electron density at the Ir centre. In 2008 Nolan et al. studied the electronic and steric parameters of a number of imidazolylidene and imidazolinylidene ligands by comparing the CO stretch frequencies of carbonylated Ir-complexes bearing these imidazolylidene ligands.\(^{137}\) By comparing these frequencies they were able to correlate the amount
of $d \rightarrow \pi^*$ (imidazolylidene) back donation of the metal and the $d \rightarrow \pi^*$ (CO). Assuming that the extent of $d \rightarrow \pi^*$ (imidazolylidene) back donation is directly related to the overall electron density on the metal they were able to compare the donating capacity of each imidazolylidene ligand. What they observed was that the overall reactivity of these complexes was not proportional to the electron density on the metal, suggesting that other factors, such as sterics, play a more important role.\textsuperscript{135}

![Scheme 44. Asymmetric hydrogenation of quinolines with catalyst anti-114.](image)

Under these conditions quinolines 97a-b were both converted to their tetrahydroquinoline derivatives in 98a-b in 72\% and 80\% yields respectively. CSP HPLC analysis (CHIRALCEL OD-H column, eluting with 2:94:4 EtOAc/hexanes/Et$_3$N) determined that the major product in both cases was the ($S$)-configured enantiomer, the same result as obtained with ferrocene analogue 96a. The enantiomeric ratio of the products was determined to be 65:35 and 71:29 for tetrahydroquinoline and 6-fluorotetrahydroquinoline, respectively. These results suggest that the planar chirality of 96a is important for inducing high enantioselectivity in hydrogenations of
substrates of this type. It has been postulated that hydrogenations with ylidene-Ir complexes proceed via an outer-sphere mechanism. What this means is that each species remains separate and intact before, during and after the reaction has taken place. While it is sometimes possible to explain the selectivity by invoking hydrogen bonding, this is not always possible or obvious. From these results, it is evident that to achieve higher enantioselectivity additional derivatives or analogues of the planar chiral Ir-complex (96a) should be investigated.

3.5 Selective Synthesis of Enantiomeric η⁶-Arene Chromium Tricarbonyl Complexes with Epimeric Pyrroloimidazolones

Disubstituted ArCr(CO)₃ possess planar chirality just like ferrocenes. Chemical reactions of both ferrocenes and ArCr(CO)₃ in many cases occur selectively by approach of reaction partners from above or below the plane of the aromatic rings so as to avoid steric interactions with other parts of the molecule. Examples of this include stereoretentetive S_N₁ reactions of both Ugi’s amine¹³⁷ and chiral α-chloroethyl substituted ArCr(CO)₃⁹¹ and directed nucleophilic additions by nucleophiles to ArCr(CO)₃.⁴⁷-⁵¹ Thus far, many of the stereoselective transformations possible with ferrocenes have analogous transformations with ArCr(CO)₃, such as those just mentioned. The diastereoselective lithiation of both Ugi’s amine and ArCr(CO)₃ bearing the same α-ethylamine group are believed to undergo selective lithiation by this same priniciple (Cp control and substrate/carbonyl control).⁸⁷ Given that the epimeric pyrroloimidazolone directing group on ferrocenes induce selective lithiation of the pro-R or pro-S positions of the Cp ring,²ᵇ it should also be possible to differentiate the pro-chiral ortho- positions of ArCr(CO)₃.

Since it was established that isopropoxy-modified imidazolones ¹⁴⁵ were stable to lithiation conditions, methods for the complexation of these compounds to chromium were sought. After
trying a few different methods for the complexation of aromatics to Cr(CO)$_6$, including refluxing$^{138}$ or exposure of the two reagents to UV light in high-boiling hydrocarbons, it was concluded that solubility of the arenes in these solvents was too low even at elevated temperatures. In the early 1990s, Hudeček et al. observed that with the use of esters and ketones as cosolvents the rates of complexation of arenes to Cr(CO)$_6$ could be dramatically enhanced.$^{139}$ Particularly, $n$-BuOAc was found to be the best cosolvent for the preparation of ArCr(CO)$_3$. In the original procedure by Hudeček, he reports results using decalin as the solvent. It was decided that decalin (bp 190 °C) was not necessary and instead octane (bp 125 °C) was used (Scheme 45). The use of $n$-BuOAc improved the solubility of the starting material and enhanced the rate of reaction. The stoichiometric ratio of ligand to Cr(CO)$_6$ in most reported syntheses of these compounds is quite high at around 4:1; a near stoichiometric ratio with a slight excess of Cr(CO)$_6$ (1.1 equiv) provided products in good yields. The products (148) of the reaction were bright yellow in colour, so to some extent the progress of the reaction could be followed colourimetrically. The reaction was stopped once evidence of decomposition was observed (insoluble black particles). Both products were obtained as thick yellow oils but could be crystallized in a number of oxygen containing solvents (acetone, EtOAc, Et$_2$O, EtOH). It was found that these compounds slowly decompose if left in oxygenated solutions for extended periods of time. $^1$H NMR results are best when taken in degassed NMR solvents.
Lithiation of *anti*-148 under the same conditions as ferrocene 81 (using 2.2 equiv *t*-BuLi), followed by quench with iodomethane, gave 149a as a single diastereomer according to NMR spectroscopy, indicating that the product had been formed in >95:5 dr. Further optimization of the reaction revealed that only 1.5 equivalents of base was necessary for high conversion of products (Scheme 46).
Scheme 46. Electrophile scope for the lithiation of anti-145.

<table>
<thead>
<tr>
<th>149a-j</th>
<th>E⁺</th>
<th>E</th>
<th>yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Mel</td>
<td>Me</td>
<td>93</td>
</tr>
<tr>
<td>b</td>
<td>Ph₂CO</td>
<td>Ph₂C(OH)</td>
<td>83</td>
</tr>
<tr>
<td>c</td>
<td>DMF</td>
<td>CHO</td>
<td>85</td>
</tr>
<tr>
<td>d</td>
<td>PhNCO</td>
<td>CONHPH</td>
<td>94</td>
</tr>
<tr>
<td>e</td>
<td>Me₃SiCl</td>
<td>SiMe₃</td>
<td>83</td>
</tr>
<tr>
<td>f</td>
<td>Ph₂PCl</td>
<td>PPh₂</td>
<td>81</td>
</tr>
<tr>
<td>g</td>
<td>(SMe)₂</td>
<td>SMe</td>
<td>86</td>
</tr>
<tr>
<td>h</td>
<td>1,1,2,2-EtBr₄</td>
<td>Br</td>
<td>94</td>
</tr>
<tr>
<td>i</td>
<td>Me₃SnCl</td>
<td>SnMe₃</td>
<td>70</td>
</tr>
<tr>
<td>j</td>
<td>methanol-d₄</td>
<td>D</td>
<td>88</td>
</tr>
</tbody>
</table>

With good initial results, the task of proving that all the products obtained possess the same relative stereochemistry was undertaken. Repetition of this experiment and quenching with several other carbon and heteroatom electrophiles gave ortho-substituted products in equally good yields and levels of diastereomeric purity (Scheme 46). No evidence of additional diastereomers was observed by TLC or NMR spectroscopy. That the lithiation-substitution of anti-145 proceeded with high levels of diastereomeric selectivity was undeniable, however the absolute stereochemistry of the product was yet to be proven. Single-crystal X-ray diffraction of sulfide 149g confirmed that the pro-\( R_p \) aryl hydrogen had been deprotonated during lithiation (Figure 18), which matches the lithiation stereochemistry observed for ferrocene anti-81.²ᵇ
To prove that the anion of *anti*-145 has configurational stability, and that all the products obtained from the lithiation of *anti*-145 have the same relative stereochemistry, a transmetalation experiment with stannane 149i was performed (Scheme 47). Stannane 149i was treated with *n*-BuLi at −78 °C in THF for 1 hr and quenched with dimethyldisulfide. The sulfide product obtained from the transmetalation was physically (melting point and R<sub>f</sub>) and spectroscopically (H and C<sup>13</sup>NMR, specific rotation) identical to sulfide 149g, obtained by direct lithiation of *anti*-145. Since an identical product was formed indirectly by transmetalation, this result proves that the stannane
derivative also possesses the same relative stereochemistry as 149g obtained by direct lithiation-quench. Furthermore it can be tentatively stated that all the products derived from lithiation of anti-145 possess the same relative stereochemistry.\textsuperscript{140}

![Scheme 47. Transmetalation of stannane 149i.](image)

Attention was then turned to syn-145. If products with opposite planar chirality could be obtained in equally high levels of diastereomeric purity then it could be concluded that the imidazolone directing group is also applicable towards the diastereoselective lithiation-substitution of N-substituted $\eta^6$-arene chromium tricarbonyl compounds providing both planar-chiral products. Under the same conditions as the anti-epimer, syn-145 underwent lithiation-substitution in equally high yields and levels of diastereomeric purity. Again, repetition of this experiment and quenching with several other carbon and heteroatom electrophiles gave ortho-substituted products in equally good levels of diastereomeric purity (Scheme 48).
The highly diastereoselective nature of the deprotonation step was investigated in deuteration experiments by quenching the reaction mixture with methanol-d₄ to give 149j and 150f. A comparison of the ¹H NMR spectra of starting material and products revealed selective loss of one of the aryl hydrogen atoms (Figures 19 and 20). In both starting materials the signal that was lost upon deuteration was the most downfield signal (indicated with a red arrow), which appeared as a doublet in both cases. This was the exact same observation made from deuteration experiments with the ferrocenyl epimers. This proves that the pro-R₁ ortho-proton is the most deshielded proton in anti-145. This is believed to be caused by its close proximity to the urea oxygen in the minimum energy state, as was previously established with the ferrocene analogues.

Though the absolute stereochemistry of anti-derived products (149a-j) can be assigned with confidence, the absolute stereochemistry of the syn-derived products (150a-f) could not yet be assigned. To prove the stereochemistry of the syn-derived products, they were then subjected to
Figure 19. $^1$H NMR spectra of anti-148 (top) and deuterated 149j (top) (400 MHz, 298 K, acetone-d$_6$)
Figure 20. $^1$H NMR spectra of syn-148 (top) and deuterated 150f (bottom) (400 MHz, 298 K, acetone-d$_6$)
acid-induced elimination of the L-proline derived central chirality providing solely planar-chiral products. Upon elimination of the methyl and thiomethyl adducts of both series (149a, 149g, and 150a, 150d) two sets of planar chiral enantiomers would be obtained (Scheme 49). As anticipated, products 151a/ent-151a, and 151b/ent-151b had equal but opposite specific rotations, thus verifying that the pro-$S_p$ hydrogen of syn-148 had been selectively removed during lithiation with \textit{t}-BuLi.

\textbf{Scheme 49.} Preparation of planar-chiral enantiomers.

Now that it had been proven that both planar chiral products were accessible by lithiation, attempts were then made to increase the ratio of the \textit{syn} : \textit{anti} -alkoxy-modified epimers. The acid catalyzed substitution reaction was then attempted with ethanol, a smaller more nucleophilic alcohol. Under the same conditions as before, using EtOH the reaction was complete in under 5
min with full conversion of starting material (Scheme 50). No elimination byproduct was observed, but the ratio of syn- to anti- was for the most part unchanged (15:85 as opposed to 15:65). The ethoxy products obtained (syn- and anti-152) were more easily separated by chromatography than their isopropoxy counterparts. The syn-epimer co-eluted with an unknown impurity and required multiple recrystallizations. Complexation of anti-152 with Cr(CO)$_6$ was then performed under the same conditions as before, providing anti-153 in 42% yield. The reaction did not go to completion because evidence of decomposition was observed after 16 h, at which point the reaction was suspended. The product was obtained as a bright yellow solid and was shown to be a single diastereomer by NMR.

![Scheme 50. Synthesis and of ethoxy modified piano stool complexes.](image)

To gain more insight into the selectivity of the directing group, anti-153 was then subjected to lithiation with both $n$-BuLi and $t$-BuLi, quenching with dimethyl disulfide (Scheme 51). Both reactions yielded the same thioether adduct 154 in 63% and 96% yields, respectively. These results
suggest that the size of the $O$-alkyl group has little to no effect on the diastereoselectivity of the lithiation. The difference in yields is in accordance with previous optimization reactions which revealed that $t$-BuLi is the ideal base for lithiating these compounds. The relative stereochemistry of thioether 154 is tentatively assigned to be the same as all the products derived from the lithiation of the isopropoxy congener anti-145.

**Scheme 51.** Lithiation of anti-142 by $n$-BuLi and $t$-BuLi.
4. Conclusions and Future Work

A cationic Pd-complex (125b) of a planar chiral ferrocene ligand bearing a pyrrolomimidazolylidene has been prepared by oxidative addition to Pd(PPh$_3$)$_4$. Xray analysis reveals a mondentate complex coordinated to the palladium through the imidazolylidene. Although a bidentate complex was desired, it was established that sulfur atoms are stable towards treatment with POCl$_3$. Ferrocenyl phsophines were not stable to these conditions, resulting in the decomposition of starting materials. If thioether donor atoms are used, non-phosphine containing Pd$^0$ sources are required to obtain bidentate complexes because intramolecular thioethers are not capable of displacing phosphine ligands. Towards this end, Pd$^0$ sources with strong electron donating ligands are required to facilitate oxidative addition, and yet must be labile enough to be displaced by heteroatoms such as thioethers. Methods for the conversion of 2-chloroimidazolium species to imidazolium species has also been established by treatment with n-BuLi, followed by protonation by water. In the future, methods of installing phosphines are necessary after conversion of the urea to chloroimidazolium. A double metal-halogen exchange approach may give the desired product (Scheme 52). Treatment of 85c with POCl$_3$ followed by addition of n-BuLi and quench with chlorophosphines and electrophilic metals should be investigated. After treatment with n-BuLi a ferrocenyl anion and the imidazolylidene should be produced (155). The anion could then be quenched with chlorophosphines, and while nucleophilic, the imidazolylidene is unlikely to react with the chlorophosphine because it is a neutral donor. The imidazolylidene could then be trapped by addition of electrophilic metals.
Two new arene chromium tricarbonyl complexes (145) bearing epimeric imidazolone directing groups have been prepared and shown to undergo diastereoselective lithiation in excess of 95:5 dr. Compounds with syn- and anti- stereochemistries undergo lithiation with opposite selectivity leading to planar chiral enantiomers (151 and ent-151) upon treatment with acid. Anti- configured imidazolones undergo deprotonation of pro-R hydrogen atom and syn- undergoes pro-S deprotonation. The size of the O-alkyl group has little to no effect on the stereoselectivity of the lithiations. The stereochemistry of the products was proven by a combination of X-ray analysis, transmetalation and deuteration experiments. These results are in accordance with previously reported results obtained with ferrocene. In future, two additional aspects of this chemistry should be explored. Efforts towards maximizing the yield of syn-configured products should be made. A possible method for this would be an in-situ electrophile quench of the zirconium
alkoxide generated from the Schwartz reagent with a suitable electrophile other than TESCl. Experiments showing that the size of the $O$-group has little to no effect on the selectivity of the lithiations suggest that larger $O$-groups should not be a problem. The second aspect is the removal of the chiral auxiliary to provide planar chiral ArCr(CO)$_3$ of aniline derivatives. While this method is capable of providing planar chiral products in high diastereomeric ratios, the utility of the products is limited until methods for removal of the auxiliary are established. Removal of the auxiliary from the ferrocene containing compounds was accomplished by base catalyzed removal of the silane, reduction of the heminal (aldehyde equivalent) by NaBH$_4$ and hydrolysis of the urea by refluxing in KOH. To achieve this, the use of an alcohol with a masked reactivity must be used. If the trimethylsilylalcohol shown in Scheme 53 is used as the initial $O$-group, after lithiation, treatment of the products with $F^-$ sources such as TBAF should provide the hemiaminal which can then be removed by the methods previously reported and discussed.$^{85}$

Scheme 53. A proposed method for the removal of the pyrroloimidazolone auxiliary.
Additional aspects of the N-phenyl Ir complex that require further experimentation include the synthesis and evaluation of the complex derived from the annulated aminal with syn-stereochemistry in the backbone (syn-121). While the ferrocene analogue did not provide high enantioselectivity, only experimentation will reveal if the same trend will be observed. In addition, treatment of the neutral Ir-complexes with anionic nucleophiles such as MeLi, which would result in an increase of electron density at the Ir atom, should be investigated. If a further deshielding of the upfield doublet is observed then this methodology may provide access to C-H activation products, possibly providing access to bidentate complexes after installation of nucleophilic atoms.

5. Experimental

General. All reagents were purchased from Aldrich, Fisher Scientific, Acros, Strem or Oakwood chemicals and used as received unless otherwise indicated. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone ketyl under an atmosphere of nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All alkyllithiums were titrated against N-benzylbenzamide to a blue endpoint. All reactions were performed under nitrogen or argon in flame- or oven-dried glassware using syringe-septum cap techniques unless otherwise indicated. All reactions were run in round-bottom flasks with magnetic stir bars unless otherwise noted. The size/volume of the glassware used in all reactions was dictated by the amount of solvent required, such that each reaction vessel was no more than half-full. TLC was performed on silica gel. Column chromatography was performed on silica gel 60 (70-230 mesh). Schwartz’s reagent was prepared according to a literature procedure. NMR spectra were obtained at room temperature, unless otherwise stated, on a Bruker Avance 300, 400 or 600 MHz instrument and are
referred to the residual proton signal of the deuterated solvent for $^1$H spectra, and to the carbon multiplet of the deuterated solvent for $^{13}$C spectra according to published values. FT-IR spectra were obtained on Bruker ALPHA platinum ATR spectrometer as neat materials. Specific rotations of diastereomerically and enantiomerically pure materials were measured on a Rudolph Research Autopol III automatic polarimeter. Mass spectra were obtained on a Micromass GCT spectrometer. Combustion analyses were performed by Atlantic Microlab Inc., Norcross, GA, USA. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

$(+)	ext{-}2-[(2S,\text{-}Thiophenyl)\text{-}ferrocenyl]-1R\text{-}triethylsilyloxy\text{-}7aS\text{-}hexahydropyrrolo[1,2\text{\text{-}c}]\text{imidazol-3-one}]$ (82i). A solution of syn-81 (500 mg, 1.13 mmol) in THF (15 mL) at $\text{-}78 \degree \text{C}$ was treated with $\text{t\text{-}BuLi}$ (2.1 mL, 1.25 M, 2.49 mmol). After 30 min, phenyl disulfide (617 mg, 0.93 mmol) in THF (5 mL) was added via cannula, and the reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (70:30 hexane/EtOAc $R_f = 0.31$) gave 82i (620 mg, 95%) as a red oil; $[\alpha]_D^{20}$ +43.7 (c 1.0, acetone); IR (ATR, oil) $\nu_{\text{max}}$ 2953, 2875, 1713, 1475, 1402, 1087 cm$^{-1}$; 7.14 (d, 2H, $J = 6 \text{ Hz}$), 7.11 (t, 1H, $J = 6 \text{ Hz}$), 7.04 (t, 1H, $J = 6 \text{ Hz}$), 5.55 (d, 1H, $J = 6.8 \text{ Hz}$), 4.42 (s, 1H), 4.38 (s, 5H), 4.18 (s, 1H), 3.81 (q, 1H, $J = 7.2 \text{ Hz}$), 3.72 (td, 1H, $J = 7.2, 4.4 \text{ Hz}$), 3.15-3.09 (m, 1H), 1.92-1.89 (m, 1H), 1.80-1.73 (m, 2H), 1.65-1.60 (m, 1H), 0.86 (t, 9H, $J = 8 \text{ Hz}$), 0.56 (q, 6H, $J = 8 \text{ Hz}$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.9, 140.0, 128.24, 128.23, 125.1, 94.9, 83.0, 77.3, 71.2, 66.4, 65.5, 62.5, 46.7, 25.5, 25.3, 6.8, 4.8; EI-MS [m/z (%)] 548 (M$^+$, 87), 94.
(+)-2-[2R-(4-bis(Trifluoromethyl)diphenylphosphino)ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-3-one (82j). To a solution of syn-81 (760 mg, 1.00 mmol) in CHCl₃ (30 mL) was added p-toluenesulfonic acid (760 mg, 4.0 mmol). The solution was heated to reflux and stirred for approximately 20 min. The acid was neutralized by addition of a sat. aq. NaHCO₃ solution (10 mL). The reaction mixture was extracted with EtOAc (3 x 10 mL). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (EtOAc:Et₃N 99/1, R_f = 0.34) provided 82j (501 mg, 79%) as a yellow glassy solid; [α]²⁰ D +101.2 (c 0.5, CHCl₃); IR (ATR, solid) ν_max 3087, 2974, 2909, 2881, 1735, 1475, 1319, 1057 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.63 (m, 4H), 7.47 (d, 2H, J = 7.6 Hz), 7.28-7.24 (m, 3H), 6.56 (s, 1H), 5.06 (s, 1H), 4.37 (t, 1H, J = 2.0 Hz), 4.15 (s, 5H), 3.66-3.57 (m, 3H), 2.74-2.62 (m, 2H), 2.39-2.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 150.14, 143.2 (d, 1C, J ¹³C-³¹P = 13.0 Hz), 141.5 (d, 1C, J ¹³C-³¹P = 13.0 Hz), 135.4 (d, 1C, J ¹³C-³¹P = 13.0 Hz), 132.3 (d, 1C, J ¹³C-³¹P = 13.0 Hz), 131.7 (d, 1C, J ¹³C-³¹P = 13.0 Hz) 130.3 ((d, 1C, J ¹³C-³¹P = 33.0 Hz), 126.3, 125.4 (d, 1C, J ¹³C-³¹P = 15.0 Hz), 125.2 (d, 1C, J ¹³C-³¹P = 4.0 Hz), 125.1 (d, 1C, J ¹³C-³¹P = 3.0 Hz), 124.9 (d, 1C, J ¹³C-³¹P = 6.0 Hz), 122.6 (d, 1C, J ¹³C-³¹P = 15.0 Hz), 104.9 (d, 1C, J ¹³C-³¹P = 9.0 Hz), 98.9 (q, 1C, J ¹³C-¹⁹F = 13.0 Hz), 70.6, 70.5, 70.4, 68.7, 68.67, 68.4, 67.7, 67.6, 42.3, 27.8, 22.8; ³¹P NMR
(+)-2-[2S<sub>p</sub>-(Thiophenyl)ferrocenyl]-2,5,6,7-tetra-hydropyrrolo[1,2-c]imidazol-3-one (85d). To a solution of 82i (613 mg, 1.12 mmol) in CHCl<sub>3</sub> (10 mL) was added p-toluenesulfonic acid (850 mg, 4.47 mmol). The solution was heated to reflux and stirred for approximately 30 min. The acid was neutralized by addition of a sat. aq. NaHCO<sub>3</sub> solution (10 mL). The reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 acetone/hexanes R<sub>f</sub> = 0.25) provided 85d (440 mg, 94%) as a yellow solid which can be recrystallized from EtOAc to provide small, yellow cuboidal crystals; mp 165 °C (EtOAc); [α]<sub>D</sub><sup>20</sup> +23.2 (c 0.6, acetone); IR (ATR, solid) ν<sub>max</sub> 3367, 3156, 3091, 2980, 2901, 2887, 1682, 1635, 1477, 1080 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18 (t, 2H, J = 7.2 Hz), 7.08-7.02 (m, 3H), 6.63 (s, 1H), 5.20 (s, 1H), 4.38 (s, 1H), 4.36 (s, 1H), 4.35 (s, 1H), 3.73 (m, 2H), 2.78-2.63 (m, 2H) 2.38 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.63, 139.8, 128.7, 125.8, 125.7, 125.0, 103.9, 97.1, 72.2, 70.7, 68.3, 68.0, 66.5, 41.8, 27.6, 22.3; EI-MS [m/z (%)] 416(M<sup>+</sup>, 100), 351(18), 308(17), 243(15), 229(11), 171(6), 110(11), 56(8); HR-MS (EI) calcd. for C<sub>22</sub>H<sub>20</sub>FeN<sub>2</sub>OS: 416.0646; found: 416.0640.
(+)-2-[2S\textsubscript{p}-(4-bis(Trifluoromethyl)diphenylphosphino)-2,5,6,7-tetra-hydropyrrolo[1,2-c]imidazol-3-one (85\text{e}). To a solution of 82\text{j} (613 mg, 1.12 mmol) in CHCl\textsubscript{3} (10 mL) was added p-toluenesulfonic acid (850 mg, 4.47 mmol). The solution was heated to reflux and stirred for approximately 30 min. The acid was neutralized by addition of a sat. aq. NaHCO\textsubscript{3} solution (10 mL). The reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. Flash column chromatography (EtOAc:Et\textsubscript{3}N 99/1, R\text{f} = 0.34) provided 85\text{e} (501 mg, 79\%) as a yellow glassy solid; [\alpha]\textsubscript{D}\textsuperscript{20} = +101.2 (c 0.5, CHCl\textsubscript{3}); IR (ATR, solid) \text{\nu}_{\text{max}} 3087, 2974, 2909, 2881, 1735, 1475, 1319, 1057 cm\textsuperscript{-1}; ¹H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.68-7.63 (m, 4H), 7.47 (d, 2H, \textit{J} = 7.6 Hz), 7.28-7.24 (m, 3H), 6.56 (s, 1H), 5.06 (s, 1H), 4.37 (t, 1H, \textit{J} = 2.0 Hz), 4.15 (s, 5H), 3.66-3.57 (m, 3H), 2.74-2.62 (m, 2H), 2.39-2.29 (m, 2H); ¹³C NMR (100 MHz, CDCl\textsubscript{3}) \delta 150.14, 143.2 (d, 1C, \textit{J}¹³C-³¹P = 13.0 Hz), 141.5 (d, 1C, \textit{J}¹³C-³¹P = 13.0 Hz), 135.4 (d, 1C, \textit{J}¹³C-³¹P = 13.0 Hz), 132.3 (d, 1C, \textit{J}¹³C-³¹P = 13.0 Hz), 131.7 (d, 1C, \textit{J}¹³C-³¹P = 13.0 Hz) 130.3 ((d, 1C, \textit{J}¹³C-³¹P = 33.0 Hz), 126.3, 125.4 (d, 1C, \textit{J}¹³C-³¹P = 15.0 Hz), 125.2 (d, 1C, \textit{J}¹³C-³¹P = 4.0 Hz), 125.1 (d, 1C, \textit{J}¹³C-³¹P = 3.0 Hz), 124.9 (d, 1C, \textit{J}¹³C-³¹P = 6.0 Hz), 122.6 (d, 1C, \textit{J}¹³C-³¹P = 15.0 Hz), 104.9 (d, 1C, \textit{J}¹³C-³¹P = 9.0 Hz), 98.9 (q, 1C, \textit{J}¹³C-¹⁹F = 13.0 Hz), 70.6, 70.5, 70.4, 68.7, 68.67, 68.4, 67.6, 67.7, 42.3, 27.8, 22.8; ³¹P NMR (162 MHz, CDCl\textsubscript{3}) \delta -21.62; EI-MS \text{[m/z (\%)]} 628 (M\textsuperscript{+}, 100), 563 (23), 483 (17), 387 (44), 368 (16), 217 (4); HR-MS (EI) calcd. for C\textsubscript{30}H\textsubscript{23}FeN\textsubscript{2}PF\textsubscript{6}: 628.0802, found 628.0811.
[3-Chloro-2-ferrocenyl-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-4-ium] hexafluorophosphate (124a). A mixture of imidazolone 85h (100 mg, 0.32 mmol) in neat POCl₃ (0.5 mL, 5.36 mmol) was heated at 50 °C for 16 hours. The resulting solution progressively changed from orange to black during this period. After cooling to room temperature, the volatiles were removed under high vacuum. The black residue was dissolved in CH₂Cl₂ (10 mL) and treated with a sat. solution of KPF₆ in H₂O/MeOH (2 mL). The mixture was stirred for 15 min at room temperature resulting in a colour change from black to deep red. Water was added (10 mL) resulting in a biphasic mixture from which the organic layer was isolated, washed with water, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was taken up in CH₂Cl₂ (2 mL) and added to an ice-cooled Et₂O solution in an ice bath. The precipitate was collected by Hirsch funnel filtration and washed with cold Et₂O to give a gold/beige powder 124a (134 mg, 89%); mp 220 °C (Et₂O); IR (ATR, solid) ν max 3169, 3104, 3089, 2957, 1710, 1623, 1525, 831, cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 7.91 (s, 1H), 4.93 (s, 2H), 4.49 (m, 9H), 3.19 (t, 2H, J = 7.6 Hz), 2.81(quintet, 2H, J =7.2 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 139.3, 127.0, 118.2, 92.4, 70.5, 67.6, 64.8, 48.4, 27.2, 23.6; ³¹P NMR (162 MHz, acetone-d₆) δ -144.3 (sept, 1P, J = 706 Hz); EI-MS [m/z (%)] 327 (M⁺, 77), 307 (9), 206 (11), 154 (27), 136 (28), 107 (21), 77 (20), 69 (100), 50 (22); HR-MS (FAB) calcd. for C₁₆H₁₆ClFeN₂⁺: 327.0346, found 327.0358.
(+)-[3-Chloro-2-[(2S)-thiomethyl]ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-4-
ium]hexafluorophosphate (124b). A mixture of imidazolone 85b (147 mg, 0.42 mmol) in neat POCl$_3$ (0.5 mL, 5.36 mmol) was heated at 50 °C for 16 hours. The resulting solution progressively changed from orange to black during this period. After cooling to room temperature, the volatiles were removed under high vacuum. The black residue was dissolved in CH$_2$Cl$_2$ (10 mL) and treated with a sat. solution of KPF$_6$ in H$_2$O/MeOH (2 mL). The mixture was stirred for 15 min at room temperature resulting in a colour change from black to deep red. Water was added (10 mL) resulting in a biphasic mixture from which the organic layer was isolated, washed with water, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude product was taken up in CH$_2$Cl$_2$ (2 mL) and added to an ice-cooled Et$_2$O solution in an ice bath. The precipitate was collected by Hirsch funnel filtration and washed with cold Et$_2$O to give a gold/beige powder 124b (161 mg, 77%) as a gold/beige powder; mp 96 °C (Et$_2$O); [$\alpha$]$^D_{D}$$^{\circ}$ +30.2 (c 1.0, CHCl$_3$); IR (ATR, solid) $\nu_{\text{max}}$ 3152, 2977, 2923, 2875, 2858, 2851, 1650, 1537, 827 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 8.04 (s, 1H), 4.96 (s, 1H), 4.75 (s, 1H), 4.61 (bs, 7H), 3.23 (s, 2H), 2.80 (s, 2H), 2.21 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.4, 128.1, 120.2, 93.9, 79.1, 72.3, 72.0, 68.1, 67.4, 48.6, 27.2, 24.0, 20.9; ESI-MS [m/z (%)] 373 (M$^+$, 100), 217 (5); HR-MS (ESI) calcd for C$_{17}$H$_{18}$N$_2$SClFe: 373.0229; found: 373.0222.
(+)[3-Chloro-2-[(2Sp-thiophenyl)ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-4-ylium]hexafluorophosphate (124c). A mixture of imidazolone 85d (100 mg, 0.24 mmol) in neat POCl₃ (0.5 mL, 5.36 mmol) was heated at 50 °C for 16 hours. The resulting solution progressively changed from orange to black during this period. After cooling to room temperature, the volatiles were removed under high vacuum. The black residue was dissolved in CH₂Cl₂ (10 mL) and treated with a sat. solution of KPF₆ in H₂O/MeOH (2 mL). The mixture was stirred for 15 min at room temperature resulting in a colour change from black to deep red. Water was added (10 mL) resulting in a biphasic mixture from which the organic layer was isolated, washed with water, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was taken up in CH₂Cl₂ (2 mL) and added to an ice-cooled Et₂O solution in an ice bath. The precipitate was collected by Hirsch funnel filtration and washed with cold Et₂O to give a gold/beige powder 124c (101 mg, 73%) as a gold/beige powder; mp >230 °C (Et₂O); [α]D⁺²⁰° +28.0 (c 1.0, CHCl₃); IR (ATR, solid) v_max 3154, 2967, 2919, 2873, 2858, 1608, 1547, 824 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 8.10 (s, 1H), 7.25 (t, 2H, J = 6.8 Hz), 7.18 (t, 1H, J = 6.8 Hz), 7.04 (d, 2H, J = 7.2 Hz), 5.14 (s, 1H), 4.88 (s, 1H), 4.82 (t, 1H, J = 2.8 Hz), 4.61 (s, 5H), 4.42-4.29 (m, 2H), 3.23 (t, 2H, J = 7.6 Hz), 2.79 (quin, 2H, J = 7.2 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 138.7, 137.3, 129.1, 128.7, 127.5, 126.4, 120.8, 95.4, 74.8, 74.2, 72.2, 69.2, 68.4, 48.5, 27.2, 23.5; ³¹P NMR (162 MHz, acetone-d₆) δ -144.3 (sept, 1P, J = 706 Hz); ³¹P NMR (162 MHz, acetone-d₆) δ -144.3 (sept, 1P, J = 706 Hz); ESI-MS [m/z (%)] 435 (M⁺, 100), 433 (8), 241 (5), 157 (5); HR-MS (ESI) calcd for C₂₂H₂₀N₂SClFe: 435.0385; found: 435.0396.
(-)[3-Chloro-2-[(2Rp-iodo)ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-4-iyum]hexafluorophosphate (124d) A mixture of imidazolone 85c (472 mg, 1.09 mmol) in neat POCl₃ (0.5 mL, 5.36 mmol) was heated at 50 °C for 16 hours. The resulting solution progressively changed from orange to black during this period. After cooling to room temperature, the volatiles were removed under high vacuum. The black residue was dissolved in CH₂Cl₂ (10 mL) and treated with a sat. solution of KPF₆ in H₂O/MeOH (2 mL). The mixture was stirred for 15 min at room temperature resulting in a colour change from black to deep red. Water was added (10 mL) resulting in a biphasic mixture from which the organic layer was isolated, washed with water, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was taken up in CH₂Cl₂ (2 mL) and added to an ice-cooled Et₂O solution in an ice bath. The precipitate was collected by Hirsch funnel filtration and washed with cold Et₂O to give a gold/beige powder 124d (474 mg, 73%) was obtained as an iridescent brown powder; mp >220 °C (Et₂O); [α]D₂⁰ −46.8 (c 0.5, CHCl₃); IR (ATR, solid) νmax 3181, 3108, 2921, 2852, 1701, 1614, 1524, 1487, 1225, 1109, 828 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 8.10 (s, 1H), 4.94 (s, 1H), 4.87 (s, 1H), 4.70 (s, 1H), 4.53 (m, 7H), 3.28 (s, 2H), 2.79 (s, 2H); ¹³C NMR (100 MHz, acetone) δ 139.0, 129.4, 120.6, 95.5, 74.8, 73.3, 69.2, 67.3, 48.9, 37.3, 27.3, 23.8; ³¹P NMR (162 MHz, acetone-d₆) δ -144.3 (sept, 1P, J = 706 Hz); FAB-MS [m/z (%)] 453 (M⁺, 63), 332(15), 149 (22), 123 (54), 111 (63), 109 (100); HR-MS (FAB) calcd. for C₁₆H₁₅ClFeIN₂⁺: 452.9318, found 452.9297.
1-[Ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-3-ylidine-[trans-(bis(triphenylphosphine))]palladium(II)chloride(hexafluorophosphate) (125a). A solution of 124a (60 mg, 0.13 mmol) and Pd(PPh₃)₄ (147 mg, 0.13 mmol) in CH₂Cl₂ (3.0 mL) was refluxed for 16 h. After cooling the solution was filtered through celite, evaporated to dryness and allowed to crystallize in CHCl₃/pentane producing 125a as bright yellow powdery crystals (76 mg, 62%); mp 193-195 °C (CHCl₃); IR (ATR, solid) νₓ max 3076, 3056, 1702, 1618, 1586, 1573, 1498, 1481, 1435, 1413, 1388, 1185, 1159, 832, 690, 491, 424 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 7.49-7.44 (m, 7H), 7.31-7.29 (m, 23 H), 7.18 (s, 1H), 5.91 (s, 1H), 4.83 (s, 1H), 4.53 (q, 1H, J = 11.6 Hz), 4.45 (s, 1H), 4.3 (s, 5H), 4.28 (s, 1H), 4.20 (q, 1H, J = 11.6 Hz), 2.99-2.91 (m, 1H), 2.72-2.60 (m, 2H), 2.56-2.50 (m, 1H); ¹³C NMR (100 MHz, acetone-d₆) δ 139.4, 134.8, 134.7, 134.2, 133.5, 131.8, 131.4, 130.9, 129.7, 129.3, 130.0, 128.9, 128.4, 128.3, 117.8, 117.7, 97.3, 70.0, 69.7, 68.0, 67.2, 66.1, 64.4, 47.6, 27.1, 22.3; ³¹P NMR (162 MHz, acetone-d₆) δ 30.3 (s, 1P), 20.8 (s, 1P) -144.2 (sept, 1P, J = 708 Hz); FAB-MS [m/z (%)] 957 (M⁺, 100), 956 (66), 695 (32), 538 (41), 293 (51), 154 (90), 137 (58); HR-MS (FAB) calcd. for C₅₂H₄₆ClFeN₂P₂Pd: 955.1210, found 955.1373.

(+)-(2-[(2R_p-Thiomethyl)ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-3-ylidine-[trans-(bis(triphenylphosphine))]palladium(II)chloride(hexafluorophosphate) (125b). A solution of 124b (150 mg, 0.29 mmol) and Pd(PPh₃)₄ (334 mg, 0.13 mmol) in CH₂Cl₂ (25 mL) was refluxed for 16 h. After cooling the solution was filtered through celite, evaporated to dryness and allowed to crystallize in CHCl₃/pentane producing 125b as bright yellow powdery crystals (246 mg, 67%); mp >230 °C (CHCl₃); [α]D²⁰ +25.1 (c 1.0, CHCl₃); X-ray diffraction data.
was collected on single yellow crystal (0.300 x 0.190 x 0.090 mm$^3$) obtained by crystallization in CHCl$_3$/pentane: C$_{53}$H$_{48}$N$_2$PdFeClSP$_2$: M = 1388.34, orthorhombic, P2$_1$2$_1$2$_1$, a = 11.2517(5) Å, b = 16.424(1) Å, c = 31.1181(18) Å, V = 5750.6(5) Å$^3$, α = 90°, β = 90°, γ = 90°, Z = 4, D$_c$ = 1.604 g/cm$^3$, F(000) = 2800, T = 147(2) K; 30535 data were collected. The structure was solved by Direct Methods (SHELXTL) and refined by full-matrix least squares on F$^2$ resulting in final R, R$_w$, and GOF [for 13109 data with F > 2σ(F)] of 0.0444, 0.0697 and 0.980 respectively. Flack parameter = -0.011(13); IR (ATR, solid) $\nu_{max}$ 3054, 1708, 1480, 1362 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) δ 7.73 (s, 1H), 7.68-7.41 (m, 3H), 5.41 (s, 1H), 4.53 (s, 1H), 4.42 (t, 1H, $J = 2.8$ Hz), 4.17 (s, 5H), 3.18-3.12 (m, 1H), 3.03-2.97 (m, 1H), 2.36 (t, 2H, $J = 7.2$ Hz), 1.89 (s, 3H), 1.57 (quin, 2H, $J = 7.6$ Hz); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ 140.6, 134.2, 134.1, 131.7, 131.2, 129.2, 129.1, 128.7, 128.6, 120.5, 95.3, 79.0, 78.3, 71.3, 70.4, 66.1, 65.9, 46.8, 25.9, 22.3, 18.7; $^{31}$P NMR (162 MHz, acetone-d$_6$) δ 30.1 (s, 1P), 20.6 (s, 1P) -144.5 (sept, 1P, $J = 708$ Hz); ESI-MS$[m/z \%]$ 1095 (M$^+\%$, 100), 1003 (18), 833 (82), 743 (17), 659 (6), 389 (48), 263 (23); HR-MS (ESI) calcd for C$_{53}$H$_{48}$N$_2$PdFeClSP$_2$: 1003.1086; found: 1003.1126. Anal. Calcd for C$_{53}$H$_{48}$N$_2$PdFeF$_6$ClSP$_3$·CHCl$_3$: C, 55.37; H, 4.21. Found: C, 55.60; H, 4.33.

(+)-[2-[(2R$_p$-thiomethyl)ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-4-ium]hexafluorophosphate (134a). A solution of 124b (175 mg, 0.34 mmol) in THF (8 mL) at −78 °C was treated with t-BuLi (0.88 mL, 0.77 M, 0.67 mmol). After 1 hour water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The residue is then dissolved in CH$_2$Cl$_2$ (2 mL) and this solution is added dropwise to a cold solution of Et$_2$O in a tared flask within an ice bath. The resulting solution is put into the freezer for 16 hours, after decanting the colourless
solution and washing with cold Et_2O the residue is dried under reduced pressure to give **134a** (130 mg, 80%) as a brown residue; mp 128 °C (Et_2O); [\(\alpha\)]\(_D\)^{20} +31.6 (c 1.0, CHCl_3); IR (ATR, solid) \(\nu_{\text{max}}\) 3162, 2980, 2924, 1702, 1608, 1547, 824 cm\(^{-1}\); \(^1\)H NMR (400 MHz, acetone-d\(_6\)) \(\delta\) 9.33 (s, 1H), 7.77 (s, 1H), 4.99 (s, 1H), 4.69 (s, 1H), 4.54 (bs, 3H), 4.43 (s, 5H), 3.16 (s, 2H), 2.80 (s, 2H), 2.23 (s, 3H); \(^{13}\)C NMR (100 MHz, acetone-d\(_6\)) \(\delta\) 139.5, 131.6, 116.7, 94.6, 72.9, 72.0, 67.3, 65.8, 30.9, 27.8, 23.0, 21.2; \(^{31}\)P NMR (162 MHz, acetone-d\(_6\)) \(\delta\) -144.5 (sept, 1P, \(J = 708\) Hz), ESI-MS\([m/z (\%)\]373(18), 339 (M\(^+\), 100); HR-MS (ESI) calcd for C\(_{17}\)H\(_{19}\)N\(_2\)FeS: 339.0613; found: 339.0601.

\(+\)-[2-[(2\(R_p\)-Thiophenyl)ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-4-ium]hexafluorophosphate (134b). A solution of **124c** (352 mg, 0.60 mmol) in THF (15 mL) at \(-78\) ° C was treated with \(t\)-BuLi (2.4 mL, 0.50 M, 1.2 mmol). After 1 hour water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The residue is then dissolved in CH\(_2\)Cl\(_2\) (2 mL) and this solution is added dropwise to a cold solution of Et\(_2\)O in a tared flask within an ice bath. The resulting solution is put into the freezer for 16 hours, after decanting the colourless solution and washing with cold Et\(_2\)O the residue is dried under reduced pressure to give **134b** (277 mg, 85%) as a brown oily residue; [\(\alpha\)]\(_D\)^{20} +30.3 (c 1.0, CHCl_3); IR (ATR, oil) \(\nu_{\text{max}}\) 3150, 2966, 1696, 1608, 1477, 825 cm\(^{-1}\); \(^1\)H NMR (400 MHz, acetone-d\(_6\)) \(\delta\) 9.24 (s, 1H), 7.59 (s, 1H), 7.23 (t, 2H, \(J = 7.6\) Hz), 7.14 (t, 1H, \(J = 7.6\) Hz), 7.03 (d, 2H, \(J = 7.6\) Hz), 5.17 (s, 1H), 4.77 (s, 1H), 4.72 (s, 1H), 4.53 (s, 5H), 4.45 (t, 2H, \(J = 6.8\) Hz), 3.05 (t, 2H, \(J = 7.2\) Hz), 2.70 (t, 2H, \(J = 7.2\) Hz), \(^{13}\)C NMR (100 MHz, acetone-d\(_6\)) \(\delta\) 139.7, 138.0, 132.5, 129.2, 126.5, 126.1, 117.1, 96.1, 74.8, 72.3,
72.1, 68.5, 67.5, 48.5, 27.6, 22.5; $^{31}$P NMR (162 MHz, acetone-$d_6$) $\delta$ -144.3 (sept, 1P, $J = 708$ Hz), ESI-MS[$m/z$ (%)] 401 (M$^+$, 100); HR-MS (ESI) calcd for C$_{22}$H$_{21}$N$_2$FeS: 401.0769; found: 401.0768.

2-[2R$_p$-(bis)Ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-c]imidazol-3-one (136). To a stirred solution of 85c (200 mg, 0.46 mmol) in DMSO (3.5 mL) was added copper bronze (35 mg, 0.55 mmol) and heated at 50 °C for 8 hours. To the resulting dark solution was added water (10 mL) and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash chromatography (Acetone: MeOH 95/5 $R_f = 0.17$) gave 136 (52 mg, 18%) as a bright red solid which was recrystallized from acetone to give bright red cuboidal crystals; mp >230 °C (acetone); IR (ATR, solid) $\nu$$_{max}$ 3142, 3088, 2970, 2953, 2897, 2853, 1696, 1643, 1522, 1483, 1403, 1080 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.87 (s, 2H), 5.01 (s, 2H), 4.53 (s, 2H), 4.22 (s, 2H), 4.14 (s, 10H), 3.66-3.62 (m, 2H), 3.46-3.40 (m, 2H), 2.75-2.69 (m, 2H), 2.58-2.52 (m, 2H), 2.34 (t, 4H, $J = 7.2$ Hz); $^{13}$C NMR (100 MHz, acetone) $\delta$ 149.4 (s, 2C), 126.0 (s, 2C), 103.9 (s, 2C), 93.8 (s, 2C), 73.7 (s, 2C), 70.5 (s, 10C), 69.2 (s, 2C), 66.7 (s, 2C), 64.9 (s, 2C), 42.2 (s, 2C), 27.9 (s, 2C), 22.6 (s, 2C); EI-MS [$m/z$ (%)] 614 (M$^+$, 32), 549 (100), 547 (54), 427 (17), 274 (33), 194 (4), 56 (5); HR-MS (EI) calcd for C$_{32}$H$_{30}$Fe$_2$N$_4$O$_2$: 614.1068, found 614.1061.
(+)-2-[2Sp-1-(Thiomethyl)-5,5-diphenyl-ferrocenyl][6aS,6bS]-6a,6b,7,8,9,11-hexahydro-5H-pyrrolo[1',2':3,4]imidazo[5,1-b][1,3]oxazine (138). A solution of aminal 102 (139 mg, 0.23 mmol) in THF (10 mL) at −78 °C was treated with n-BuLi (0.15 mL, 2.42 M, 0.35 mmol). After 30 min, dimethyl disulfide (0.05 mL, 0.46 mmol) was added via syringe, and the reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na2SO4, filtered and concentrated under reduced pressure. Flash column chromatography (90:10 CH2Cl2/acetone Rf = 0.27) gave 138 (77 mg, 73%) as a yellow oil; [α]D20 +201.8 (c 1.0, CHCl3); IR (ATR, oil) νmax 3088, 3059, 2960, 2938, 2917, 2864, 2838, 1599, 1491, 987 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.69 (d, 2H, J = 7.2 Hz), 7.48 (t, 2H, J = 7.2 Hz), 7.38 (t, 1H, J = 7.2 Hz), 7.14-7.12 (m, 3H), 6.95-6.93 (m, 2H), 4.96 (s, 1H), 4.34 (d, 1H), 4.24 (d, 1H, J = 2.0 Hz), 3.94-3.92 (m, 2H), 3.89-3.88 (m, 1H), 3.69 (s, 5H), 3.34 (m, 1H), 2.99-2.97 (m, 1H), 2.38 (s, 3H), 2.32 (m, 1H), 1.96-1.92 (m, 1H), 1.89-1.87 (m, 2H); 13C NMR (100 MHz, CHCl3) δ 147.3, 145.8, 127.7, 127.6, 127.3, 127.2, 126.5, 91.6, 82.5, 81.2, 73.0, 71.5, 69.9, 68.5, 63.9, 56.1, 30.6, 26.7, 20.7; EI-MS[m/z (%)] 522 (M+, 100), 439 (30), 330 (17), 121 (4), 83 (21); HR-MS (EI) calcd for C30H30N2OFeS: 542.1428; found: 542.1427.

(–)-(S)-2-Phenyltetrahydro-1H-pyrrolo[1,2-c]imidazole-1,3(2H)-dione (141). A solution of L-proline (1.00 g, 8.68 mmol) and phenylisocyanate (0.95 mL, 8.68 mmol) in THF (20 mL) was heated to reflux for 3 hours. Aqueous HCl (10 mL, 8 M) was added and the mixture was left to reflux for an additional 16 hours. Once cooled to room temperature, 20 mL of CH2Cl2 was added and the solution was neutralized with an
excess of saturated NaHCO₃ in water. The organic extract was washed with water, brine, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (35:65 EtOAc/hexane Rᵢ = 0.25) gave 141 (1.74 g, 93%) as a colorless solid that was recrystallized from EtOAc to give colourless needle crystals mp 147-149 °C (EtOAc); [α]ᵢD²⁰ −49.2 (c 1.0, CHCl₃); IR (ATR, solid) νmax 3463, 2969, 2360, 1708, 1494, 1353 cm⁻¹; ¹H (400 MHz, CDCl₃) δ 7.4-7.3 (m, 4H), 4.3-4.2 (m, 1H), 3.85-3.76 (m, 1H), 3.39-3.33 (m, 1H), 2.38-2.34 (m, 1H), 2.39-2.34 (m, 2H), 1.93-1.83 (m, 1H), 1.56 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 140.7, 128.7, 126.5, 125.9, 82.1, 62.3, 45.6, 26.45, 25.1, 6.5, 4.6; EI-MS [m/z (%)] 216 (M⁺ 100), 188 (17), 119 (31), 91 (4); HR-MS (EI) calcd. for C₁₂H₁₃N₂O₂: 216.0899; found: 216.0895.

(−)-(1R,7aS)-2-phenyl-1-((triethylsilyl)oxy)tetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one (116). To a foil-wrapped flask containing 141 (2.00 g, 9.26 mmol) and Cp₂ZrHCl (Schwartz’s reagent, 2.90 g, 11.1 mmol) was added warm THF (20 mL) and the mixture was allowed to stir for 15 min. Imidazole (1.45 g, 21.3 mmol) and 4-dimethylaminopyridine (102 mg, 0.83 mmol) were added by temporarily removing the septum and adding the solids. Chlorotriethylsilane (1.53 mL, 12.0 mmol) was then added by syringe. The solution was left to stir at room temperature for 16 hours, diluted with Et₂O (20 mL) and water (10 mL), and stirred for a further 10 min. The organic phase was then filtered through Celite, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (silica gel, 30:70 EtOAc/ hexanes Rᵢ = 0.23) gave 116 (757 mg, 89%) as a colourless oil; [α]ᵢD²⁰ −66.2 (c 0.95, acetone); IR (ATR, solid) νmax 3061, 3042, 2952, 2901, 2876, 1705, 1599, 1500, 1402, 1106, 1035 cm⁻¹; ¹H (400 MHz, CDCl₃) δ 7.39-7.32 (m, 4H), 5.65 (d, 1H, J = 6.4 Hz), 4.00 (q, 1H, J = 7.2 Hz), 3.70-3.67 (m, 1H), 3.20-3.14 (m, 1H), 2.07-2.00 (m, 2H), 1.93-1.91 (m, 1H), 1.79-1.77 (m, 1H), 0.79 (t, 9H, J = 8.0 Hz), 0.49-0.34 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 137.7, 128.8, 126.1, 126.0, 82.2, 62.0, 46.0, 26.5,
25.1, 6.6, 4.6; El-MS (m/z[%]) 332 (M⁺, 61), 303 (74), 259 (19), 201 (56), 184 (50), 146 (42), 93 (100), 76 (91), 74 (90); HR-MS (El) calcd. for C₁₈H₂₈N₂O₂Si: 332.1920; found: 332.1921.

2-Phenyl-6,7-dihydro-2H-pyrrolo[1,2-c]imidazol-3(5H)-one (143). To a solution of 116 (200 mg, 0.69 mmol) in CH₂Cl₂ (10 mL) was added p-toluenesulfonic acid (261 mg, 1.37 mmol). The solution was stirred for 20 min at room temperature and the acid was then quenched by the addition of a saturated aqueous NaHCO₃ solution (20 mL). The reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (EtOAc Rf = 0.30) gave 143 (117 mg, 85%) as colorless solid that was recrystallized from Et₂O to colorless needles; mp 163 °C (Et₂O); IR (ATR, solid) νmax 3118, 3063, 3047, 2986, 2965, 2945, 2889. 1673, 1639, 1595, 1503, 1420, 1345 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.58 (d, 2H, J = 10.4 Hz), 7.39 (t, 2H, J = 10.0 Hz), 7.19 (t, 1H, J = 10.0 Hz), 6.27 (s, 1H), 3.77 (t, 2H, J = 9.2 Hz), 2.78 (t, 2H, J = 9.6 Hz), 2.46 (quin, 2H, J = 9.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 138.0, 129.1, 127.7, 125.3, 121.5, 101.4, 42.6, 27.9, 22.9; El-MS [m/z (%)] 200 (M⁺, 100), 171 (89), 157 (11), 127 (5), 104 (8); HR-MS (El) calcd. for C₁₂H₁₄N₂O: 200.0944; found: 200.0934.

(–)-2-Ferrocenyl-1S-methoxy-7aS-hexahydropyrrolo[1,2-c]imidazol-3-one (144). To a solution of syn-81 (100 mg, 0.23 mmol) in MeOH (2 mL) was added p-toluenesulfonic acid (173 mg, 0.9 mmol). The solution was stirred for 4 min. The acid was neutralized by addition of a sat. aq. NaHCO₃ solution (10 mL). The reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (74:25:1 hexanes/EtOAc/Et₃N, Rf = 0.24) gave 133 (68 mg, 88%) as a
yellow solid which was recrystallized from EtOAc providing yellow needle shaped crystals; mp 122 °C (EtOAc); $[\alpha]_D^{20} = -45.9$ (c 1.7, CHCl$_3$); IR (ATR, solid) $\nu_{\text{max}}$ 2991, 2952, 2873, 2830, 1706, 1498, 1458, 1068 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.20 (s, 1H), 5.02 (s, 1H), 4.50 (s, 1H), 4.18 (s, 5H), 4.07 (s, 1H), 4.02 (s, 1H), 3.72 (q, 1H, $J = 8.0$ Hz), 3.52 (q, 1H, $J = 8.0$ Hz), 3.29 (s, 3H), 3.17-3.11 (m, 1H), 2.13-2.07 (m, 2H), 2.04-2.03 (m, 1H), 1.30 (quin, 1H, $J = 9.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.0, 89.3, 69.0, 64.6, 64.4, 62.1, 61.7, 59.1, 50.1, 45.6, 29.2, 24.8; EI-MS [m/z (%)] 340 (M$^+$, 100), 308 (26), 243 (64), 227 (51), 121 (11), 56 (9); HR-MS (EI) calcd for C$_{17}$H$_{20}$N$_2$O$_2$Fe: 340.0874; found: 340.0888.

$(-$)-(1R,7aS)-1-Hydroxy-2-phenyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one (146). To a foil-wrapped flask containing 141 (2.0 g, 9.26 mmol) and Cp$_2$ZrHCl (Schwartz’s reagent, 2.90 g, 11.1 mmol) was added warm THF (20 mL) and the mixture was allowed to stir for 15 min. A sat. aqueous NaHCO$_3$ solution (4 mL) and dry silica (2 g) was then added to flask and the mixture was stirred for a further 5 min. This slurry was then evaporated to dryness under reduced pressure. Flash chromatography (50:50 EtOAc/hexane $R_f = 0.30$) gave 146 (1.76 g, 87%) as a colorless solid that was recrystallized from EtOH, EtOAc or Et$_2$O to give colourless needles; mp 177-179 °C (EtOAc); $[\alpha]_D^{20} = -35.0$ (c 0.8, MeOH); IR (ATR, solid) $\nu_{\text{max}}$ 3251, 3108, 3080, 3066, 3047, 2978, 2961, 2939, 2909, 2875, 1659, 1597, 1416, 1328, 1292, 1088, 1067 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 7.73 (d, 2H, $J = 10.8$ Hz), 7.33 (t, 2H, $J = 10.8$ Hz), 7.07 (t, 1H, $J = 10.8$ Hz), 5.73 (d, 1H, $J = 10.0$ Hz), 5.53 (d, 1H, $J = 10.8$ Hz), 3.67-3.55 (m, 2H), 3.10-3.02 (m, 1H), 2.12-2.10 (m, 1H), 1.98-1.86 (m, 2H), 1.46-1.39 (p, 1H, $J = 12.4$ Hz); $^{13}$C NMR (100 MHz, acetone-d$_6$) $\delta$ 160.3, 139.3, 128.4, 123.0, 120.1, 82.2, 66.1, 45.2, 28.3, 24.5; EI-MS [m/z (%)] 200 (M$^+$, 100), 218 (51), 171 (90), 146 (18), 119 (14), 93 (22), 77 (28), 70 (27), 51 (9); HR-MS (EI) calcd. for C$_{12}$H$_{14}$N$_2$O$_2$: 218.1055; found 218.1059.
(+)-(1S,7aS)-1-Isopropoxy-2-phenyltetrahydro-1\textit{H}-pyrrolo[1,2-\textit{c}]imidazol-3(2\textit{H})-one \textit{(anti-145)} and (−)-(1\textit{R},7aS)-1-isopropoxy-2-phenyltetrahydro-1\textit{H}-pyrrolo[1,2-\textit{c}]imidazol-3(2\textit{H})-one \textit{(syn-145)}. To a stirred solution of hemiaminal 146 (300 mg, 1.39 mmol) in \textit{i}-PrOH (5 mL) and CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added \textit{p}-toluenesulfonic acid (264 mg, 1.39 mmol). After stirring for 30 minutes at room temperature, the acid was neutralized with sat. aq. NaHCO\textsubscript{3} solution (20 mL) and the reaction mixture was extracted with EtOAc (15 mL). The organic extract was washed with water, brin, dried over anhyd Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. Flash column chromatography (35:65 EtOAc/hexane \textit{R}_f = 0.30) gave, sequentially, \textit{anti-145} (235 mg, 65 \%) and \textit{syn-145} (55 mg, 15\%, \textit{R}_f = 0.23) both of which were recrystallized from either EtOH, EtOAc or Et\textsubscript{2}O to colorless needles.

\textit{(anti-145). mp 100-101 °C (EtOH); [\alpha]_D^20 +23.2 (c 0.6, acetone); IR (ATR, solid) \nu_{\text{max}} 3061, 3044, 2969, 2933, 2906, 1687, 1597, 1499, 1456, 1410, 1396, 1278, 1040 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz acetone-d\textsubscript{6}) \delta 7.63 (d, 2\textit{H}, \textit{J} = 7.6 Hz), 7.34 (t, 2\textit{H}, \textit{J} = 8.0 Hz), 7.08 (t, 1\textit{H}, \textit{J} = 8.0 Hz), 5.58 (s, 1\textit{H}), 3.97-3.86 (m, 1\textit{H}), 3.64-3.59 (m, 2\textit{H}), 3.09-3.03 (m, 1\textit{H}) 2.15-2.06 (m, 1\textit{H}) 1.96-1.85 (m, 2\textit{H}), 1.49-1.41 (s, 1\textit{H}, \textit{J} = 9.2 Hz), 1.107 (d, 6\textit{H}, \textit{J} = 6.0 Hz); \textsuperscript{13}C NMR (100 MHz, acetone-d\textsubscript{6}) \delta 161, 139.7, 128.7, 123.9, 121.2, 87.6, 69.4, 64.5, 45.6, 24.8, 23.1, 22.5; EI-MS [m/z (%)] 260 (M\textsuperscript{+}, 60) 217 (57), 201 (79), 146 (46), 121 (56), 70 (100); HR-MS (EI) calcd. for C\textsubscript{15}H\textsubscript{20}N\textsubscript{2}O\textsubscript{2}: 260.1525; found 260.1523.

(syn-145). mp 76-77 °C (Et\textsubscript{2}O); [\alpha]_D^20 -102.2 (c 1.0, acetone); IR (ATR, solid) \nu_{\text{max}} 3051, 2971, 2953, 2875, 1679, 1500, 1486, 1454, 1416, 1160cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, acetone-d\textsubscript{6}) \delta 7.57-7.55 (d, 2\textit{H}, \textit{J} = 8.0 Hz), 7.35-7.31 (t, 2\textit{H}, \textit{J} = 8.0 Hz), 7.13-7.09 (t, 1\textit{H}, \textit{J} = 8.0 Hz), 5.66-5.64 (d, 1\textit{H}, \textit{J} = 6.8 Hz), 4.09-4.08 (q, 1\textit{H}, \textit{J} = 6.0 Hz), 3.79-3.77 (m, 1\textit{H}), 3.54-3.49 (m, 1\textit{H}), 3.08-3.03 (m, 1\textit{H}) 2.02-1.85 (m, 4\textit{H}), 1.55-
1.40 (d, 3H, J = 6.0 Hz), 1.04-1.02 (d, 3H, J = 6.0 Hz); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ 158.5, 139.4, 128.3, 124.0, 122.5, 85.8, 71.2, 60.7, 45.4, 25.9, 25.5, 22.4, 21.4; EI-MS [m/z (%)] 260 (M$^+$, 62), 217 (45), 201 (57), 146 (38), 121 (49), 119 (26), 77 (29), 70 (100); HR-MS (EI) calcd. for C$_{15}$H$_{20}$N$_2$O$_2$: 260.1525; found 260.1528.

(−)-(1$S$,7$a$S)-2-(2-(Hydroxydiphenylmethyl)phenyl)-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one (anti-147). A solution of anti-145 (500 mg, 1.92 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (2.8 mL, 1.5 M, 4.20 mmol). The solution turned yellow upon addition and progressively darkened to red. After 15 min the reaction mixture was warmed to −40 °C by switching cold baths, and stirred at that temperature for an additional 15 min. A solution of benzophenone (734 mg, 4.03 mmol) in THF (10 mL) was added by cannula. The solution turned green upon addition of the electrophile, and the reaction was then allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexane R$_f$ = 0.46) gave anti-147 (757 mg, 89%) as a colorless oil that crystallized upon standing; mp 120-122 °C (EtOAc/hexane); [α]$^20_D$ = −16.8 (c 1.2, acetone); IR (ATR, solid) ν$_{max}$ 3325, 3058, 3023, 2971, 2894, 2877, 1679, 1417, 1327, 1261, 1054 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) : δ 7.50 (d, 1H, J = 8.0 Hz), 7.44-7.36 (m, 7H), 7.32-7.23 (m, 5H), 6.78 (d, 1H, J = 8.0 Hz) 6.015 (d, 1H, J = 4.0 Hz), 3.89 (s, 1H), 3.50-3.44 (m, 1H) 3.39-3.33 (m, 2H), 2.95-2.88 (m, 1H), 1.79-1.69 (m, 2H), 1.64-1.56 (m, 1H), 1.01 – 0.97 (m, 6H), 0.62- 0.57 (s, 1H, J = 4.0 Hz); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ 164.3, 148.9, 147.2, 146.9, 135.5, 134.7, 130.6, 128.4, 128.2, 128.1, 127.9, 127.6, 126.9, 126.9, 126.7, 88.8, 80.6, 71.1, 66.0, 45.5, 27.3, 24.8, 22.0, 21.8; EI-MS
m/z (%) 442 (M⁺, 7), 382 (54), 349 (23), 260 (30), 201 (51), 121 (36), 105 (68), 77 (53), 70 (100); HR-MS (EI) calcd. for C₂₈H₃₀N₂O₃: 442.2251; found 442.2256.

(--)-1(R,7aS)-2-(2-(Hydroxydiphenylmethyl)phenyl)-1-isopropoytetahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one  (syn-147). A solution of syn-145 (170 mg, 0.65 mmol) in THF (5 mL) at −78 °C was treated with t-BuLi (0.90 mL, 1.45 M, 1.31 mmol). The solution turned yellow initially and progressively darkened to red. After 15 min the reaction mixture was warmed to −40 °C bath by switching cold baths, and stirred at that temperature for an additional 15 min. A solution of benzophenone (263 mg, 1.44 mmol) in THF (3 mL) was added by cannula. The solution turned green upon addition of the electrophile, and the reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was then added and the mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexanes Rf = 0.40) gave syn-147 (174 mg, 60%) as a colorless oil that was recrystallized from acetone/hexane to cuboidal crystals; mp 151-153 °C (acetone/hexane); [α]D²⁰ −114.3 (c 1.0, acetone); IR (ATR, solid) νmax 3303, 3089, 3067, 3028, 2968, 2930, 2909, 2875, 1958, 1945, 1882, 1848, 1666, 1450, 1084 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 7.55-7.24 (m, 13H), 6.94 (d, 1H, J = 8.0 Hz), 5.59 (s, 1H), 3.78 (d, 1H, J = 6.8 Hz), 3.38-3.35 (m, 1H), 3.28-3.20 (m, 2H), 2.95 (quin, 1H, J = 4.4 Hz), 1.88-1.81 (m, 3H), 1.63-1.60 (m, 1H), 0.96 (t, 6H, 6.4 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 161.6, 148.7, 146.7, 146.5, 135.9, 133.9, 130.3, 128.1, 128.0, 127.8, 127.5, 127.47, 126.6, 26.55, 86.7, 80.3, 71.2, 61.6, 45.0, 26.3, 24.9, 21.7, 21.5; EI-MS [m/z (%)] 382 (M⁺, 100), 442 (5), 349 (50), 305 (31) 285 (59), 256 (61), 217 (26), 201 (27), 164 (26), 104 (24); HR-MS (EI) calcd for C₂₈H₃₀N₂O₃: 442.2256; found: 442.2233.
(+)-(6aR,6bS)-5,5-Diphenyl-6b,7,8,9-tetrahydro-5H-benzo[d]pyrrolo[1',2':3,4]imidazo[5,1-b][1,3]oxazin-11(6aH)-one (syn-118). To a solution of anti-147 (145 mg, 0.33 mmol) in CHCl₃ (15 mL) was added p-toluenesulfonic acid (250 mg, 1.3 mmol) and stirred for 4 min. The acid was neutralized by addition of a sat. aq. NaHCO₃ solution (10 mL). The reaction mixture was extracted with EtOAc (15 mL). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 hexanes/EtOAc, Rf = 0.50) gave syn-118 (123 mg, 97%) as a white solid which was recrystallized from Et₂O providing needle shaped crystals; mp 187-189 °C (Et₂O); [α]D²⁰ + 391.3 (c 1.0, acetone); IR (ATR, solid) νmax 3059, 3033, 2947, 2931, 2894, 1710, 1601, 1490, 1403 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 7.90 (dd, 1H, J = 8.4, 1.2 Hz), 7.46-7.41 (m, 3H), 7.32-7.26 (m, 6H), 7.22-7.19 (m, 2H), 6.99 (td, 1H, J = 8.4, 1.2 Hz), 6.89 (dd, 1H, J = 6.4, 1.2 Hz), 5.23 (d, 1H, J = 6.8 Hz), 4.01 (q, 1H, J = 6.8 Hz), 3.73 (dt, 1H, J = 5.6, 1.6 Hz), 3.09 (dt, 1H, J = 5.6, 1.2 Hz), 2.29-2.24 (m, 1H), 2.04-1.98 (m, 1H), 1.97-1.93 (m, 2H); ¹³C NMR (100 MHz, acetone-d₆) δ 159.1, 146.5, 143.8, 134.9, 129.6, 129.2, 128.3, 128.2, 127.8, 127.5, 127.4, 127.3, 122.0, 120.7, 85.1, 78.5, 59.3, 45.5, 25.8, 24.2; EI-MS[m/z (%)] 382 (M⁺, 100), 305 (41), 285 (32), 284 (21), 256 (35), 254 (17), 165 (22), 105 (44), 77 (12), 70 (36); HR-MS (EI) calcd for: C₂₅H₂₂N₂O₂: 382.1676; found: 382.1692.

(+)-(6aR,6bS)-1-(diphenylphosphino)-5,5-diphenyl-6b,7,8,9-tetrahydro-5H-benzo[d]pyrrolo[1',2':3,4]imidazo[5,1-b][1,3]oxazin-11(6aH)-one (syn-118b). A solution of syn-118 (382 mg, 1.00 mmol) in THF (15 mL) at −78 °C was treated with t-BuLi (1.42 mL, 1.55 M, 2.20 mmol). After 30 min, chlorodiphenyl...
phosphine (0.44 mL, 2.40 mmol) was added by syringe, and the reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (80:18:2 hexane/EtOAc/CH$_2$Cl$_2$ R$_f$ = 0.34) gave 118b (470 mg, 83%) as a white oily residue; [α]$_{D}^{20}$ +372.5 (c 1, acetone); IR (ATR, oil) ν$_{max}$ 3054, 2035, 2978, 2952, 2887, 1722, 1572, 1432, 695 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) δ 7.52-7.48 (m, 2H), 7.42-7.41 (m, 3H), 7.36-7.25 (m, 11H), 7.20-7.11 (m, 5H), 7.09-7.06 (m, 1H), 6.93 (d, 1H, $J$ = 7.6 Hz), 5.03 (d, 2H, $J$ = 5.6 Hz), 3.72 (quin, 1H, $J$ = 5.6 Hz), 3.05-3.01 (m, 1H), 2.34-2.30 (m, 1H), 1.98-1.94 (m, 2H), 1.85-1.83 (m, 1H); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ 160.8, 146.4, 143.8, 139.8 (d, 1C, $J$$_{^{13}$C-$^{31}$P} = 16.0 Hz), 139.6, 139.3, 138.7 (d, 1C, $J$$_{^{13}$C-$^{31}$P} = 14.0 Hz), 135.2, 134.4 (d, 1C, $J$$_{^{13}$C-$^{31}$P} = 17.0 Hz), 133.4 (d, 1C, $J$$_{^{13}$C-$^{31}$P} = 18.0 Hz), 132.9 (d, 1C, $J$$_{^{13}$C-$^{31}$P} = 17.0 Hz), 130.8, 130.6 (d, 1C, $J$$_{^{13}$C-$^{31}$P} = 0.5 Hz), 129.1, 128.3, 128.26, 128.1, 128.0, 127.9, 127.6, 124.2; $^{31}$P NMR (162 MHz, acetone-d$_6$) δ -16.31(s, 1P); EI-MS[m/z (%)] 566 (M$^+$, 61), 490 (33), 489 (100), 469 (44), 392 (17), 362 (12), 104 (5); HR-MS (EI) cald for: C$_{37}$H$_{31}$N$_2$O$_2$P: 566.2118; found: 566.2129.

(−)-(6aS,6bS)-5,5-Diphenyl-6b,7,8,9-tetrahydro-5H-benzo[d]pyrrolo[1′,2′:3,4]imidazo[5,1-b][1,3]oxazin-11(6aH)-one (anti-118). To a solution of syn-136 (275 mg, 0.62 mmol) in CH$_2$Cl$_2$ (10 mL) was added p-toluenesulfonic acid (235 mg, 1.24 mmol) and stirred for 2 min. The acid was neutralized by addition of a sat. aq. NaHCO$_3$ solution (10 mL). The reaction mixture was extracted with EtOAc (15 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated.
under reduced pressure. Flash column chromatography (50:50 hexanes/EtOAc, R\text{f} = 0.70) gave \textit{anti-118} (123 mg, 96\%) as a white solid which was recrystallized from EtOAc/CH\textsubscript{2}Cl\textsubscript{2}/hexanes providing needle shaped crystals; mp >230 °C (EtOAc/CH\textsubscript{2}Cl\textsubscript{2}/hexanes); [\alpha]\textsubscript{D}\textsuperscript{20} = −467.4 ° (c 1.0, CH\textsubscript{2}Cl\textsubscript{2}); IR (ATR, solid) \nu\text{max} 3057, 3033, 2971, 2898, 1716, 1601, 1489, 1307 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, acetone-d\textsubscript{6}) δ 8.07 (dd, 1H, J = 8.0, 0.8 Hz), 7.44-7.41 (3H, m), 7.34-7.25 (m, 6H), 7.20-7.18 (m, 2H), 7.03 (t, 1H, J = 6.8 Hz), 6.89 (dd, 1H, J = 6.8, 1.2 Hz), 5.04 (d, 1H, J = 1.6 Hz), 3.84-3.80 (m, 1H), 3.62-3.56 (m, 1H), 3.18-3.11 (m, 1H), 2.02-1.90 (m, 3H) m 1.43-1.38 (m, 1H); \textsuperscript{13}C NMR (100 MHz, acetone-d\textsubscript{6}) δ 159.1, 146.4, 143.7, 134.6, 129.8, 129.2, 128.3, 128.25, 128.2, 128.14, 127.8, 127.54, 127.5, 122.4, 120.3, 85.4, 81.7, 62.5, 45.5, 28.1, 25.18; EI-MS[m/z (%)] 382 (M\textsuperscript{+}, 100), 313 (12), 285 (68), 256 (49), 132 (43), 85 (64), 83 (94), 69 (30); HR-MS (EI) calcd for: C\textsubscript{25}H\textsubscript{22}N\textsubscript{2}O\textsubscript{2}: 382.1676; found: 382.1672.

\textit{(--)(6aS,6bS)-5,5-diphenyl-6a,6b,7,8,9,11-hexahydro-5H-benzo[d]pyrrolo[1',2':3,4]imidazo[5,1-b][1,3]oxazine (anti-119).} To a solution of \textit{(anti-118)} (202 mg, 0.53 mmol) in THF (4 mL) and CH\textsubscript{2}Cl\textsubscript{2} (2 mL) at −78 °C was added dropwise a solution of DIBAL-H in hexane (2.18 mL, 2.11 mmol, 0.97 M). The cold bath was removed and the solution was allowed to warm to room temperature (\textit{ca.} 25 min) and stirred for an additional hour. To the solution was then added a sat. aq. solution of Rochelle’s salt, diluted with EtOAc (10 mL) and stirred for an additional ten minutes. The reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 hexanes/EtOAc, R\text{f} = 0.24) gave \textit{anti-119} (185 mg, 95\%) as a white solid.
which was recrystallized from acetone to give colourless needle shaped crystals; mp 168-170 °C (acetone); $[\alpha]_D^{20} = -384.6 \degree$ (c 1.0, CH$_2$Cl$_2$); IR (ATR, solid) $v_{\text{max}}$ 3082, 3060, 3025, 2966, 2911, 2879, 2829, 2815, 1601, 1575, 1485, 1449, 1320 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 7.41-7.37 (m, 3H), 7.31-7.29 (m, 2H), 7.26-7.22 (m, 3H), 7.17-7.13 (m, 3H), 6.90 (d, 1H, J = 8.0 Hz), 6.74-6.72 (d, 2H, J = 3.6 Hz), 4.59 (d, 1H, J = 7.6 Hz), 4.38 (d, 1H, J = 3.2 Hz), 4.28 (d, 1H, J = 7.6 Hz), 3.65 (q, 1H, J = 4.0 Hz), 3.11 (q, 1H, J = 4.0 Hz), 2.73-2.71 (m, 1H), 2.09-2.07 (m, 1H), 1.75-1.63 (m, 3H); $^{13}$C NMR (100 MHz, acetone-d$_6$) $\delta$ 147.1, 144.4, 141.8, 129.6, 129.0, 128.3, 128.2, 128.0, 127.8, 127.7, 127.5, 127.1, 118.8, 87.5, 84.4, 74.6, 70.7, 54.7, 28.7, 25.3; EI-MS [m/z (%)] 368 (8), 356 (7), 270 (14), 255 (11), 194 (19), 132 (13), 85 (28), 83 (100), 82 (8); HR-MS (EI) calcd for: C$_{25}$H$_{24}$N$_2$O: 368.1833; found: 368.1877.

**120a and 120b.** A solution of *anti-119* (95 mg, 0.26 mmol) and tritylium tetrafluoroborate (94 mg, 0.28 mmol) in CH$_2$Cl$_2$ (2 mL) was stirred in a Schlenk flask at room temperature covered from light. After 5 h, solvent was removed in vacuo and the crude solid was washed with dry diethyl ether (3 x 5 mL) and dried in vacuo. To this was added Ir(μ-Cl)(COD)$_2$ (87 mg, 0.13 mmol) and degassed THF (7 mL) in glovebox. The solution was cooled to −78 °C and with increased flow of argon, KOTBu (32 mg, 0.29 mmol) was added at −78 °C. After 1 h, the cold bath was removed and the volatiles were removed under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 2:8 EtOAc/hexanes, R$_f$ = 0.45 and 0.21) afforded 120a (60 mg, 34%) and 113b (24 mg, 12%).
(-)-Chloro[\eta^4-1,5-cyclooctadiene]2-(6aS,6bS)-5,5-diphenyl-6a,6b,7,8,9,11-hexahydro-5H-
coordination isomer; mp >230 °C (acetone); [\alpha_\text{D}^0] = -213.63 ° (c 0.5, CHCl_3);
IR (ATR, solid) \nu_{\text{max}} 3069, 3063, 3022, 2960, 2944, 2884, 2862, 2855, 2846,
1610, 1558, 1440, 1366, 755, 694; \textsuperscript{1}H NMR (600 MHz, CDCl_3) \delta 9.64 (d, 1H,
J = 8.4 Hz), 7.36-7.27 (m, 4H), 7.25-7.24 (m, 5H), 7.15 (d, 2H, J = 2.4 Hz), 7.08 (t, 1H, J =
8.4 Hz), 6.82 (d, 1H, J = 8.4 Hz), 5.15 (d, 1H, J = 3.0 Hz), 4.85 (dt, 1H, J = 6.2, 4.8 Hz), 4.71-4.65
(m, 2H), 4.00-3.99 (m, 1H), 3.63-3.59 (m, 1H), 3.33 (t, 1H, J = 6.2 Hz), 2.62-2.61 (m, 1H), 2.32-
2.29 (m, 1H), 2.25-2.15 (m, 3H), 1.97-193 (m, 2H), 1.82-1.76 (m, 4H), 1.46-1.39 (m, 2H); \textsuperscript{13}C
NMR (150 MHz, CDCl_3) \delta 210.6, 146.0, 143.1, 135.4, 129.6, 129.5, 128.6, 128.4, 128.2, 128.0,
127.7, 127.3, 123.8, 123.7, 86.7, 86.3, 86.25, 86.1, 69.5, 56.1, 51.1, 46.8, 34.1, 32.6, 29.6, 29.0,
27.7, 25.1, EI-MS[m/z (%)] 667 (M^+-Cl, 100), 665 (83), 663 (25), 591 (6), 320 (9); HR-MS (FAB)
calcd for C\textsubscript{33}H\textsubscript{30}ON\textsubscript{2}Ir: 663.1982; found : 663.1969 NOTE: compound unstable, easily loses Cl
and 4H atoms. ESI at two different voltages: 128.5 V and 241.0 V shows this compound loses 4
additional H atoms. Anal. Calcd for C\textsubscript{33}H\textsubscript{30}ON\textsubscript{2}Ir: C, 56.44; H, 4.88. Found: C, 56.70; H, 5.06.

MINOR: [\alpha_\text{D}^0] = -163.82 ° (c 0.5, CHCl_3); IR (ATR, solid) \nu_{\text{max}} 3060, 3044, 3022, 2961, 2946,
2920, 2885, 2835, 1714, 1704, 1599, 1327, 750, 699 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl_3) \delta 10.00
(d, 1H, J = 8.4 Hz), 7.47-7.37 (m, 4H), 7.33-7.28 (m, 5H), 7.17-7.15 (m, 2H), 7.00 (t, 1H, J = 8.0
Hz), 6.80 (dd, 1H, J = 8.4 Hz 7.6, 1.2 Hz), 5.28 (d, 1H, J = 7.6 Hz), 4.68-4.66 (m, 1H), 4.61-4.59
(m, 1H), 4.33-4.25 (m, 2H), 3.75-3.68 (m, 1H), 2.33-2.11 (m, 9H), 1.90-1.87 (m, 1H), 1.76-1.72
(m, 2H), 1.57 (quint, 2H, J = 7.2 Hz); \textsuperscript{13}C NMR was not legible; EI-MS[m/z (%)] 667 (M^+-Cl,
100), 665 (95), 664 (13), 663 (35); HR-MS (FAB) calcd for: C\textsubscript{33}H\textsubscript{30}ON\textsubscript{2}Ir: 663.1982; found :
663.1931. NOTE: compound unstable, easily loses Cl and 4H atoms. ESI at two different voltages:
128.5 V and 241.0 V shows this compound loses 4 additional H atoms, after the Cl is lost. Anal.
Calcd for C₃₃H₃₀ON₂Ir: C, 56.44; H, 4.88. Found: C, 56.65; H, 5.59. Sample's identity still cannot be assigned with confidence.

\[\text{(-)-}\eta^4\text{-1,5-cyclooctadiene][triphenylphosphine]2-(6aS,6bS)-5,5-diphenyl-6a,6b,7,8,9,11-hexahydro-5H-benzo[d]pyrrolo[1',2':3,4]imidazo-2-ylidene} \text{iridium hexafluorophosphate (121).} \]

To a solution of 120a (44 mg, 0.06 mmol) in CH₂Cl₂ (1 mL) was added a solution of triphenylphosphine (16 mg, 0.06 mmol) in CH₂Cl₂ (1 mL) and resulting red solution was stirred for 3 h at room temperature and then concentrated. The residue was dissolved in minimum amount of CH₃CN and KPF₆ (15 mg, 0.08 mmol) in CH₃CN was added and stirred at room temperature for another hour, passed through Celite and washed with CH₂Cl₂. Volatiles were removed under reduced pressure and resulting red solid was triturated with pentane to afford 121 as red crystalline solid (68 mg, 97%). mp 189-190 °C; [\alpha]D²⁰ = -261.15 ° (c 0.5, CHCl₃); IR (ATR, solid) \(v_{\text{max}}\) 3058, 2953, 2883, 1731, 1601, 1573, 1236, 1092, 832, 695 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 9.10 (d, 1H, \(J = 8.0\) Hz), 7.47-7.41 (m, 8H), 7.36-7.31 (m, 9H), 7.30-7.23 (m, 7H), 7.15-7.11 (m, 3H), 6.91 (d, 1H, \(J = 8.0\) Hz), 4.99 (quint, 1H, \(J = 3.2\) Hz), 4.58 (d, 1H, \(J = 7.2\) Hz), 4.13-4.01 (m, 4H), 3.82 (t, 1H, \(J = 8.8\) Hz), 3.36 (q, 1H, \(J = 11.2\) Hz), 2.65-2.61 (m, 1H), 2.42-2.39 (m, 1H), 2.28-2.25 (m, 1H), 2.17-2.04 (m, 6H), 1.79-1.75 (m, 2H), 0.31 (quint, 1H, \(J = 8.4\) Hz), \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 201.6 (d, 1C, \(J_{^{13}\text{C}-^{31}\text{P}} = 8.0\) Hz), 145.0, 143.0, 134.3, 133.8, 132.3, 132.2, 131.6, 131.2, 130.7, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 123.8, 121.0, 91.3, 91.2, 88.3, 86.4, 83.3, 81.8, 69.7, 46.7, 32.2, 31.4, 30.5, 30.2, 27.0, 26.0; ESI-MS \([m/z (%)]\) 929 (M⁺, 100), 407 (8), 267 (4); HR-MS (FAB) calcd for C₅₁H₄₉ON₂IrP: 929.3206; found: 929.3205. Anal. Calcd for C₅₁H₄₉F₆IrN₂OP₂: C, 57.03; H, 4.60. Found: C, 54.68; H, 4.81. Compound likely failed CH analysis because chromatography could not be used for isolation, it was precipitated out of solution.
(S)-2-Methyl-1,2,3,4-tetrahydroquinoline (98a). A solution of 2-methyl quinoline 97a (0.07 mL, 0.51 mmol), triphenyl phosphine (1 mg, 1 mol%) and iridium catalyst 121 (6 mg, 1 mol%) in toluene (2 mL) in a vial was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 45 atm, and the mixture was stirred for 72 h at room temperature. The solvent was removed under reduced pressure and the crude reaction mixture was passed through a plug of silica gel, eluting with 2:94:4 EtOAc/hexanes/Et3N to give 98a (54 mg, 72%) as colorless oil; $[\alpha]_D^{20} = -42$ (c 1.25, CHCl₃) [lit $^{143}$ (R)-98a $[\alpha]_D^{20} = +84$ (c 0.2, CHCl₃, 99% ee)]. CSP HPLC analysis (Chiralcel OD-H; eluent: 98:2 hexanes/i-PrOH, 0.5 mL/min) determined 65:35 er, 30% ee [tR(minor) = 12.91 min, tR(major) = 14.78 min]; $^1$H NMR (400 MHz, CDCl₃) δ 7.01-6.97 (m, 2H), 6.63 (t, 1H, $J = 7.6$ Hz), 6.51-6.48 (m, 1H), 3.45-3.39 (m, 1H), 2.90-2.71 (m, 2H), 1.99-1.91 (m, 1H), 1.68-1.55 (m, 1H), 1.23 (d, 3H, $J = 6.3$ Hz); $^{13}$C NMR (100 MHz, CDCl₃) δ 144.7, 129.2, 126.6, 121.0, 116.9, 113.9, 47.1, 30.0, 26.5, 22.5.

(S)-6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (98b). A solution of 6-fluoro-2-methyl quinoline 97b (81 mg, 0.51 mmol), triphenyl phosphine (1 mg, 1 mol%) and iridium catalyst 121 (6 mg, 1 mol%) in toluene (2 mL) in a vial was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 45 atm, and the mixture was stirred for 72 h at room temperature. The solvent was removed under reduced pressure and the crude reaction mixture was passed through a plug of silica gel, eluting with 2:94:4 EtOAc/hexanes/Et3N to give 92b (66 mg, 80%) as a white solid; $[\alpha]_D^{20} = -37$ (c 2.55, CHCl₃), [lit $^{122}$ (R)-92b + 80 (c 0.2, CHCl₃, 98% ee)]; CSP HPLC analysis (Chiralcel OD-H;
eluent: 98:2 hexanes/i-PrOH, 0.5 mL/min) determined 71 : 29 er, 42% ee [tR(minor) = 11.84 min, tR(major) = 14.63 min]; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 6.71-6.65 (m, 2H), 6.43-6.38 (m, 1H), 3.40-3.32 (bm, 2H), 2.83 2.67 (m, 2H), 1.95-1.88 (m, 1H), 1.63-1.50 (m, 1H), 1.21 (d, 3H, J = 6.3 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 157.0, 153.9, 140.9, 122.5, 122.4, 115.5, 115.2, 114.7, 114.6, 113.3, 113.0, 47.3, 29.8, 26.7, 22.4.

\(+\)-Tricarbonyl[(1S,7aS)-1-isopropoxy-2-phenyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (anti-148). A solution of anti-145 (500 mg, 1.92 mmol), Cr(CO)\(_6\) (465 mg, 2.11 mmol) and n-BuOAc (1.77 mL, 13.4 mmol) in octane (13 mL) was heated in a round bottomed flask equipped under nitrogen at 145 °C for 24 hours. The sublimed solids were mechanically pushed back into the solution periodically using a needle for the first 8 hours. The reaction mixture was cooled to room temperature, filtered through Celite with EtOAc, and concentrated under reduced pressure. Flash column chromatography (70:20:10 CH\(_2\)Cl\(_2\)/EtOAc/hexane R\(_f\) = 0.25) gave anti-148 (608 mg, 80%) as a bright yellow oil that crystallizes upon standing; mp 171-174 °C (Et\(_2\)O/hexane); [\(\alpha\)]\(^{20}\)D +37.7 (c 1.0, acetone); IR (ATR, solid) \(v_{\text{max}}\) 3121, 2973, 2933, 2902, 2880, 1952, 1855, 1710, 1529, 1466, 1381, 1070 cm\(^{-1}\); \(^1\)H NMR (400 MHz, acetone-d\(_6\)) δ 6.687 (dd, 1H, J = 6.8, 2.8 Hz), 5.87 (t, 2H, J = 6.4 Hz), 5.74 (d, 1H, J = 6.0 Hz), 5.37 (s, 1H), 5.28 (t, 1H, J = 6.0 Hz), 4.08 (sept, 1H, J = 6.4 Hz), 3.66-3.61 (m, 2H), 3.09 (td, 1H, J = 4.4, 2.0 Hz), 2.14 (quin, 1H, J = 6.4 Hz), 1.97-1.91 (m, 2H), 1.29 (d, 3H, J = 6.4 Hz), 1.205 (d, 3H, J = 6.4 Hz); \(^{13}\)C NMR (100 MHz, acetone-d\(_6\)) δ 234.2, 159.7, 120.7, 95.8, 95.7, 88.4, 86.7, 84.1, 82.4, 69.0, 63.6, 34.4, 27.9, 24.3, 23.0, 22.1; EI-MS [m/z (%)] 396 (M\(^+\), 25), 340 (65), 313 (56), 312 (95), 260 (38), 253 (77), 252 (100), 201 (84), 200 (45), 77 (47), 70 (70), 52 (57); HR-MS (EI) calcd. for C\(_{18}\)H\(_{20}\)CrN\(_2\)O\(_5\): 396.0772; found 396.0781. Anal. Calcd for C\(_{18}\)H\(_{20}\)CrN\(_2\)O\(_5\): C, 54.55; H, 5.09. Found: C, 54.56; H, 5.12.
(+)-Tricarbonyl[(1S,7aS)-1-isopropoxy-2-phenyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (syn-148). A solution of syn-145 (500 mg, 1.92 mmol), Cr(CO)\textsubscript{6} (465 mg, 2.11 mmol) and \textit{n}-BuOAc (1.77 mL, 13.4 mmol) in octane (13 mL) was heated in a round bottomed under nitrogen at 145 °C for 24 hours. The sublimed solids were mechanically pushed back into solution periodically using a needle for the first 8 hours. The reaction mixture was cooled to room temperature, filtered through Celite with EtOAc, and concentrated under reduced pressure. Flash column chromatography (80:10:10 CH\textsubscript{2}Cl\textsubscript{2}/EtOAc/hexane \(R_f = 0.40\)) gave syn-148 (602 mg, 78%) as a bright yellow solid that was recrystallized from Et\textsubscript{2}O/hexane to bright yellow crystals; mp 163-165 °C (Et\textsubscript{2}O/hexane); [\(\alpha\)]\textsubscript{D}\textsuperscript{20} = −135.6 (c 1.0, acetone); IR (ATR, solid) \(\nu_{\text{max}}\) 3126, 3102, 2980, 2915, 2891, 2860, 1972, 1951, 1878, 1839, 1700, 1529, 1469, 1090 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, acetone-d\textsubscript{6}) \(\delta\) 6.40 (d, 1H, \(J = 6.0\) Hz), 5.85 (t, 2h, \(J = 6.8\) Hz), 5.74 (d, 1H, \(J = 8.4\) Hz), 5.495 (d, 1H, \(J = 6.8\) Hz), 5.28 (t, 1H, \(J = 6.0\) Hz), 4.11 (q, 1H, \(J = 2.4\) Hz), 4.01 (sept, 1H, \(J = 6.0\) Hz), 3.44 (q, 1H, \(J = 6.8\) Hz), 3.14-3.11 (m, 1H), 2.09-2.07 (m, 1H), 2.00-1.89 (m, 3H), 1.32 (d, 3H, \(J = 6.0\) Hz), 1.24 (d, 3H, \(J = 6.0\) Hz); \textsuperscript{13}C NMR (100 MHz, acetone-d\textsubscript{6}) \(\delta\) 234.1, 156.6, 121.2, 95.5, 95.4, 88.5, 85.2, 82.3, 70.8, 60.9, 44.4, 25.9, 25.6, 22.5, 21.2; FAB-MS [m/z (%)] 419 (M+Na, 100) 397 (M+H, 28), 337 (12), 306 (4), 283 (10), 261 (11) 252 (100), 201 (4); HR-MS (EI) calcd. for C\textsubscript{18}H\textsubscript{21}CrN\textsubscript{2}O\textsubscript{5}: 397.0850; found 397.0855. Anal. Calcd for C\textsubscript{18}H\textsubscript{20}CrN\textsubscript{2}O\textsubscript{5}: C, 54.55; H, 5.09. Found: C, 54.59; H, 5.08.

(–)-Tricarbonyl[(1S,7aS)-2-(2R\textsubscript{p}-(methyl)-\(\eta^6\)-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149a). A solution of anti-148 (163 mg, 0.41 mmol) in THF (10 mL) at −78 °C was treated with \(t\)-BuLi (0.39 mL, 1.57 M, 0.62 mmol). After 30 min, methyl iodide (0.70 mmol) was added by syringe, and the reaction was allowed to
warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexane R$_f$ = 0.46) gave 149a (168 mg, 93%) as a bright yellow oil; [\(\alpha\)]$^D_{19}$ +86.3 (c 1.0, acetone); IR (ATR, solid) $\nu_{\text{max}}$ 3085, 2972, 2935, 2902, 1952, 1854, 1710, 1462, 1376, 1029 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 5.90 (d, 1H, $J$ = 6.4 Hz), 5.71 (t, 1H, $J$ = 6.0 Hz), 5.56 (d, 1H, $J$ = 6.0 Hz), 5.52 (t, 1H, $J$ = 6.4 Hz), 5.11 (s, 1H), 4.05 (sept, 1H, $J$ = 6.4 Hz), 3.65-3.59 (m, 2H), 3.08-3.03 (m, 1H), 2.18-1.25 (m, 1H), 2.11 (s, 3H), 2.00-1.88 (m, 2H), 1.48 (quin, 1H, $J$ = 6.0 Hz); $^{13}$C NMR (100 MHz, acetone-d$_6$) $\delta$ 233.7, 160.7, 113.5, 112.7, 95.3, 94.8, 93.2, 90.9, 90.6, 70.3, 65.4, 45.9, 27.5, 24.8, 22.7, 22.0, 18.0; EI-MS [m/z (%)] 410 (M$^+$, 2), 354 (20), 326 (67), 231 (52), 135 (43), 91 (32), 70 (85); HR-MS (FAB) calcd. for C$_{19}$H$_{22}$CrN$_2$O$_5$: 411.1007; found 411.1016.

(–)-Tricarbonyl[(1S,7aS)-2-(2R$_p$-(hydroxydiphenylmethyl)-η$^6$-phenyl)-1-isopropoxy tetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149b). A solution of anti-148 (126 mg, 0.32 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.31 mL, 1.57 M, 0.48 mmol). After 30 min, a solution of benzophenone (99 mg, 0.54 mmol) in THF (2 mL) was added by cannula, and the reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexane R$_f$ = 0.23) gave 149b (154 mg, 83%) as a yellow powdery solid; mp 183-185 °C (THF); [\(\alpha\)]$^D_{19}$ −36.9 (c 1.0, THF); IR (ATR, solid) $\nu_{\text{max}}$ 3200, 2970, 2926, 2873, 2854, 1957, 1875, 1682, 1489, 1444, 1421, 1376, 1036 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 10.86, (s, 1H), 7.33-7.23 (m, 10H), 6.30 (s, 1H), 5.62-5.60 (m,
(−)-Tricarbonyl[(1S,7aS)-2-(2R−(formyl)-η⁶-phenyl)-1-isopropanoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149c). A solution of anti-148 (162 mg, 0.41 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.40 mL, 1.56 M, 0.61 mmol). After 30 min, dimethylformamide (0.06 mL, 0.73 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (70:10:20 CH₂Cl₂:EtOAc:hexanes Rₚ = 0.15) gave 149c (148 mg, 85%) as a bright red solid which was recrystallized from EtOAc to bright red powdery crystals; mp 158-160 °C (EtOAc/hexane); [α]Dº = 330.9 (c 1.0, acetone); IR (ATR, solid) νmax 3102, 2977, 2941, 2898, 2878, 2878, 1974, 1963, 1914, 1873, 1707, 1688, 1522, 1379, 1028 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 9.36 (s, 1H), 6.28 (d, 1H, J = 6.0 Hz), 6.15 (t, 1H, J = 5.6 Hz), 6.03 (d, 1H, J = 6.4 Hz), 5.66 (t, 1H, J = 6.8 Hz), 5.41 (s, 1H), 4.09 (sept, 1H, J = 6.0 Hz), 3.75-3.64 (m, 2H), 3.14 (dt, 1H, J = 5.6 Hz, 1.6 Hz), 2.19-2.10 (m, 2H), 1.98-1.97 (m, 1H), 1.55 (quin, 1H, J = 5.2 Hz), 1.35 (d, 3H, J = 6.0 Hz), 1.28 (d, 3H, J = 6.0 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 231.8, 183.9, 161.3, 119.4, 97.7, 96.0, 92.9, 90.3, 88.4, 85.6, 69.6, 65.3, 45.9, 24.9, 22.7, 21.4; ESI-MS [m/z (%)] 447 (M+Na, 100), 365 (38), 311
(32), 283 (23), 261 (7), 229 (13), 202 (2); HR-MS (FAB) calcd. for C_{19}H_{21}CrN_{2}O_{6}: 425.0799; found 425.0766. Anal. Calcd for C_{19}H_{20}CrN_{2}O_{6}: C, 53.78; H, 4.71. Found: C, 53.60; H, 4.7.

(--)-Tricarbonyl[(1S,7aS)-2-(2Rp-(N-phenylcarboxamido)-\(\eta^6\)-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149d). A solution of anti-148 (167 mg, 0.42 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.40 mL, 1.57 M, 0.63 mmol). After 30 min, phenyl isocyanate (0.08 mL, 0.72 mmol) was added by syringe, which turned the reaction mixture red. The reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na_{2}SO_{4}, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexane R_{f} = 0.18) gave 149d (216 mg, 88%) as a bright yellow solid that was recrystallized from EtOAc to bright yellow needles; mp 140 °C (EtOAc/hexane); [\alpha]_{D}^{20} \sim 43.5 (c 1, acetone); IR (ATR, solid) \nu_{\text{max}} 3116, 3098, 3079, 2971, 2924, 2897, 1956, 1868, 1715, 1461, 1432, 1376, 1362, 1028 cm\(^{-1}\); \textsuperscript{1}H NMR (400 MHz, acetone-d_{6}) \delta 9.51 (bs, 1H), 7.68 (d, 2H, J = 8.0 Hz), 7.30 (t, 2H, J = 7.6 Hz), 7.08 (t, 1H, J = 7.2 Hz), 6.07 (d, 1H, J = 6.4 Hz), 5.87 (d, 1H, J = 6.4 Hz), 5.74 (t, 1H, J = 6.4 Hz), 5.61 (t, 1H, J = 6.4 Hz), 5.37 (s, 1H), 4.09 (sept, 1H, J = 6.0 Hz), 3.63 (t, 1H, J = 6.8 Hz), 3.46 (t, 1H, J = 4.0 Hz), 2.96-2.95 (m, 1H), 2.08-2.07 (m, 1H), 1.95-1.81 (m, 3H), 1.31 (d, 3H, J = 6.4 Hz), 1.27 (d, 3H, J = 6.4 Hz); \textsuperscript{13}C NMR (100 MHz, acetone-d_{6}) \delta 232.4, 162.2, 161.0, 139.2, 128.5, 123.8, 119.8, 114.2, 107.5, 92.9, 92.2, 91.5, 90.5, 90.2, 70.2, 65.6, 59.7, 45.8, 27.4, 24.7, 22.8, 21.8; ESI-MS [m/z (\%)] 538 (M+Na, 22), 456 (100), 402 (6), 320 (44), 227 (11); HR-MS (FAB) calcd. for C_{23}H_{25}CrN_{3}O_{6}Na: 538.1041; found 538.1055.
(--)-Tricarbonyl[(1S,7aS)-2-(2S\textsubscript{p}-(trimethylsilyl)-\eta\textsuperscript{6}-phenyl)-1-isopropoxytetrahydro-1\textsubscript{H}-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149e). A solution of anti-148 (190 mg, 0.48 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.46 mL, 1.56 M, 0.72 mmol). After 30 min, chlorotrimethylsilane (0.10 mL, 0.82 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. Flash column chromatography (70:25:5 CH\textsubscript{2}Cl\textsubscript{2}/hexane/EtOAc R\textsubscript{f} = 0.26) gave 149e (186 mg, 83%) as a bright yellow solid that was recrystallized from Et\textsubscript{2}O/hexane to bright yellow needles; mp 162 °C (decomp), (EtOAc/hexane); [\alpha]\textsubscript{D}\textsuperscript{20} = −27.9 (c 1.0, acetone); IR (ATR, solid) \nu\textsubscript{max} 3122, 3099, 2967, 2944, 2894, 2880, 1959, 1912, 1704, 1505, 1461, 1021 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, acetone-d\textsubscript{6}) \delta 5.97 (d, 1H, J = 5.6 Hz), 5.89 (t, 1H, J = 5.6 Hz), 5.745 (d, 1H, J = 4.8 Hz), 5.57 (t, 1H, J = 4.8 Hz), 5.24 (s, 1H), 4.05 (m, 1H), 3.64-3.60 (m, 2H), 3.12 (m, 1H), 2.14 (m, 1H), 1.99 (m, 1H), 1.58 (m, 1H), 1.32 (d, 3H, J = 4.8 Hz), 1.25 (d, 3H, J = 4.8 Hz), −0.31 (s, 9H); \textsuperscript{13}C NMR (100 MHz, acetone-d\textsubscript{6}) \delta 234.0, 160.9, 120.3, 104.3, 100.8, 95.6, 92.8, 92.1, 89.4, 70.3, 65.9, 44.9, 27.1, 24.9, 22.7, 21.6, −0.2; ESI-MS [m/z (%)] 491 (M+H, 100), 469 (30), 409 (4), 355 (7), 333 (4); HR-MS (FAB) calcd. for C\textsubscript{21}H\textsubscript{29}CrN\textsubscript{2}O\textsubscript{6}: 469.1245; found 469.1221.

(--)-Tricarbonyl[(1S,7aS)-2-(2S\textsubscript{p}-(diphenylphosphino)-\eta\textsuperscript{6}-phenyl)-1-isopropoxytetrahydro-1\textsubscript{H}-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149f). A solution of anti-148 (400 mg, 1.01 mmol) in THF (15 mL) at −78 °C was treated with t-BuLi (1.50 mL, 1.55 M, 1.50 mmol). After 30 min, chlorodiphenylphosphine (0.36 mL, 1.50 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added
and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexane Rₑ = 0.28) gave 149f (470 mg, 81%) as a bright yellow oil; [α]ᵢ²⁰ −242.3 (c 1.0, acetone); IR (ATR, solid) νₓₓ × 3055, 2971, 2934, 2896, 2874, 1959, 1871, 1713, 1571, 1423, 1027 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 7.42–7.38 (m, 10H), 5.79–5.76 (m, 2H), 5.66 (t, 1H, J = 5.6 Hz), 5.57 (d, 1H, J = 2.0 Hz), 4.95 (d, 1H, J = 6.4 Hz), 4.17 (sept, 1H, J = 6.0 Hz), 3.58 (t, 1H, J = 6.0 Hz), 2.97 (q, 1H, J = 6.4 Hz), 2.85-2.81 (m, 1H), 1.70-1.62 (m, 3H), 1.35 (d, 3H, J = 6.0 Hz), 1.26 (d, 3H, J = 6.0 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 232.78, 232.75, 162.3, 135.2, 135.1, 134.9, 134.87, 134.7, 134.7, 133.7, 133.5, 131.0, 129.8, 128.8, 128.7, 128.6, 128.4, 128.37, 128.2, 128.16, 118.4, 118.2, 107.7, 107.5, 97.7, 96.43, 96.40, 94.0, 93.3, 88.8, 88.7, 69.5, 65.5, 45.9, 26.9, 26.89, 24.5, 22.9, 22.1; ESI-MS [m/z (%)] 603 (M+Na, 13), 581 (M+H, 100), 537 (13), 483 (12), 445 (26), 401 (68), 387 (22), 359 (5); HR-MS (FAB) calcd. for C₃₀H₃₀CrN₂O₅P: 581.1292; found 581.1340.

(--)-Tricarbonyl[(1S,7aS)-2-(2Sₚ-(thiomethyl)-η⁶-phenyl)-1-isoproxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149g). A solution of anti-148 (137 mg, 0.34 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.29 mL, 1.55 M, 0.48 mmol). After 30 min, dimethyl disulfide (0.07 mL, 0.52 mmol) was added by syringe, and the reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexane Rₑ = 0.20) gave 149g (150 mg, 86%) as a bright yellow solid that was recrystallized from Et₂O/hexane to bright yellow needles; mp 165 °C (decomp), (EtOAc/hexane); [α]ᵢ²⁰ −239.5 (c 1.0, acetone); X-ray diffraction data was
collected on single yellow crystal (0.230 x 0.110 x 0.070 mm³), obtained by crystallization from Et₂O/hexanes: \( \text{C}_{19}\text{H}_{22}\text{CrN}_2\text{O}_5\text{S}: M = 442.44 \), orthorhombic, \( P2_12_12_1 \), \( a = 8.1257(5) \) Å, \( b = 8.1602(5) \) Å, \( c = 30.1139(19) \) Å, \( V = 1996.8(2) \) Å³, \( \alpha = 90^\circ \), \( \beta = 90^\circ \), \( \gamma = 90^\circ \), \( Z = 4 \), \( D_c = 1.472 \) g/cm³, \( F(000) = 920 \), \( T = 147(2) \) K; 40891 data were collected. The structure was solved by Direct Methods (SHELXTL) and refined by full-matrix least squares on \( F^2 \) resulting in final \( R \), \( R_w \) and \( GOF \) [for 4612 data with \( F > 2\sigma(F) \)] of 0.0233, 0.0592 , and 1.086 respectively, Flack parameter = 0.003(4); IR (ATR, solid) \( \nu_{\text{max}} \) 3079, 2972, 2925, 2898, 1956, 1866, 1714, 1462, 1432, 1028 cm⁻¹; \(^1\)H NMR (400 MHz, acetone-d₆) \( \delta \) 5.94 (d, 1H, \( J = 6.4 \) Hz), 5.82 (t, 1H, \( J = 6.4 \) Hz), 5.63 (d, 1H, \( J = 6.4 \) Hz), 5.46 (t, 1H, \( J = 6.0 \) Hz), 5.14 (s, 1H), 4.10 (sept, 1H, \( J = 6.0 \) Hz), 3.66-3.60 (m, 2H), 3.06-3.03 (m, 1H), 2.43 (s, 3H), 2.14-2.11 (m, 1H), 1.99-1.90 (m, 2H), 1.64 (quin, 1H, \( J = 10.0 \) Hz), 1.313 (d, 3H, \( J = 6.0 \) Hz), 1.247 (d, 3H, \( J = 6.0 \) Hz); \(^{13}\)C NMR (100 MHz, acetone-d₆) \( \delta \) 233.2, 161.3, 119.9, 112.4, 97.2, 95.1, 90.0, 88.9, 88.1, 69.8, 65.5, 45.9, 27.4, 24.8, 22.8, 21.9, 15.5; ESI-MS [m/z (%)] 465(M+Na, 24), 443 (M+H, 57), 383 (100); HR-MS (FAB) calcd. for \( \text{C}_{19}\text{H}_{22}\text{CrN}_2\text{O}_5\text{S}+\text{Na} \): 465.0547; found 465.0511. Anal. Calcd for \( \text{C}_{19}\text{H}_{22}\text{CrN}_2\text{O}_5\text{S} \): C,51.58; H, 5.01. Found: C, 51.23; H, 5.00.

\((-\text{Tricarbonyl}}[(1S,7aS)-2-(2R_p-(bromo)-\eta^6{-}\text{phenyl})-1-isopropoxytetrahydro-1H-pyrrolo}[1,2-c]imidazol-3(2H)-one]chromium(0) (149h)\) A solution of anti-148 (160 mg, 0.40 mmol) in THF (7 mL) at −78 °C was treated with \( t-\text{BuLi} \) (0.62 mL, 0.97 M, 0.60 mmol). After 30 min, 1,1,2,2-tetrabromoethane (0.08 mL, 0.69 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexanes \( R_f = 0.25 \)) gave 149h (148 mg, 85%) as a bright yellow solid which was
recrystallized from EtOAc to bright yellow crystals; mp 116-118 °C (EtOAc/hexane); $[\alpha]_D^{20} +61.2$
(c 0.85, acetone); IR (ATR, solid) $\nu_{\text{max}}$ 3082, 2971, 2936, 2899, 2879, 1963, 1874, 1712, 1504, 1029, 616 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 5.98 (d, 1H, $J = 6.4$ Hz), 5.95 (d, 1H, $J = 6.4$ Hz), 5.84 (t, 1H, $J = 6.0$ Hz), 5.50 (t, 1H, $J = 6.4$ Hz), 5.18 (s, 1), 4.08 (sept, 1H, $J = 6.0$), 3.68-3.59 (m, 2H), 3.09-3.02 (m, 1H), 2.18-2.13 (m, 1H), 2.01-1.96 (m, 1H), 1.92-1.89 (m, 1H), 1.62 (quin, 1H, $J = 9.6$ Hz), 1.30 (d, 3H, $J = 6.0$ Hz), 1.25 (d, 3H, $J = 6.0$ Hz); $^{13}$C NMR (150 MHz, acetone-d$_6$) $\delta$ 232.2, 160.8, 111.0, 103.6, 97.0, 95.7, 94.0, 90.3, 89.6, 69.9, 65.3, 45.8, 27.6, 24.7, 22.7, 21.8; ESI-MS [\text{m/z} (\%)] 498 (M$+$Na, 100), 496 (M$+$Na, 98), 363 (62), 265 (7); HR-MS (FAB+) calcd for C$_{18}$H$_{20}$BrCrN$_2$O$_5$: 474.9955; found: 474.9915.

(−)-Tricarbonyl[(1$S$,7a$S$)-2-[(2S$_p$-(trimethylstannyl))-η$^6$-phenyl]-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2$H$)-one]chromium(0) (149i). A solution of anti-148 (261 mg, 0.66 mmol) in THF (10 mL) at −78 °C was treated with $t$-BuLi (0.65 mL, 1.52 M, 0.99 mmol). After 30 min, chlorotrimethylstannane (1.12 mL, 1.12 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (80:10:10 hexane/CH$_2$Cl$_2$/EtOAc $R_f = 0.23$) gave 149i (263 mg, 70%) as a bright yellow solid that was recrystallized from EtOAc to bright yellow needles; mp 180 °C (EtOAc/hexane); $[\alpha]_D^{20} -81.9$ (c 1.02, acetone); IR (ATR, solid) $\nu_{\text{max}}$ 3104, 2972, 2920, 2892, 2361, 2342, 2361, 2342, 1951, 1882, 1859, 1696, 1500, 1460, 1375, 1033 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 6.05 (s, 1H), 5.82 (s, 1H), 5.66 (s, 1H), 5.47 (s, 1H), 5.31 (s, 1H), 4.03 (s, 1H), 3.64 (s, 2H), 3.12 (s, 1H), 2.07 (m, 1H), 1.99 (m, 1H), 1.52 (m, 1H), 1.31 (s, 3H), 1.25 (s, 3H), 128.
0.29 (s, 1H); $^{13}$C NMR (100 MHz, acetone-$d_6$) δ 234.5, 160.6, 122.6, 103.1, 102.4, 95.1, 92.8, 88.5, 87.9, 69.6, 65.1, 44.7, 27.1, 24.6, 22.6, 21.6, −5.9; $^{119}$Sn NMR (149 MHz, acetone-$d_6$) δ −13.7; ESI -MS [m/z (%)] 583 (M+Na, 100), 561 (8), 508 (7), 447 (43), 339 (5); HR-MS (FAB) calcd. for C$_{21}$H$_{28}$CrN$_2$O$_5$Sn: 561.0498; found 561.0504.

(+-)Tricarbonyl[(1S,7aS)-2-(2R$^p$-deutero)-$\eta^6$-phenyl]-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (149j). A solution of anti-148 (167 mg, 0.42 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.40 mL, 1.56 M, 0.63 mmol). After 30 min, methanol-$d_4$ (0.05 mL, mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (75:25 hexane/EtOAc $R_f = 0.20$) gave 149j (148 mg, 88%) as a bright yellow oil; [α]$_D^{20}$ +35.4 (c 1.3, acetone); IR (ATR, solid) $\nu_{\text{max}}$ 2970, 2931, 2874, 1954, 1859, 1714, 1521, 1381, 1040 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-$d_6$) δ 5.87 (s, 2H), 5.74 (bs, 1H), 5.37 (s, 1H) 5.28 (s, 1H), 4.08 (bs, 1H) 3.64 (bs, 2H), 3.09 (bs, 1H), 2.13-2.09 (m, 1H), 1.97-1.91 (m, 2H), 1.45 (t, 1H, $J = 9.6$ Hz), 1.288 (d, 3H, $J = 3.2$ Hz), 1.235 (d, 3H, $J = 3.6$ Hz); $^{13}$C NMR (100 MHz, acetone-$d_6$) δ 234.2, 159.7, 120.6, 95.7, 95.68, 88.4, 86.7, 83.9 (t, $J_{13^c-^2H} = 28.2$ Hz), 82.4, 69.0, 63.6, 45.4, 27.9, 24.3, 23.0, 22.1; ESI-MS [m/z (%)] 420 (M+Na, 100), 398 (M+H, 7), 338 (14), 284 (10), 262 (8), 202 (6); HR-MS (FAB) calcd. for C$_{18}$H$_{20}$DCrN$_2$O$_5$: 398.0913; found 398.0944.
(+-)Tricarbonyl[(1R,7aS)-2-(2S_p-(methyl)-eta^6-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo
[1,2-c]imidazol-3(2H)-one]chromium(0) (150a). A solution of syn-
148 (203 mg, 0.51 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.53 mL, 1.45 M, 0.77 mmol). After 30 min, methyl iodide (0.05 mL, 0.87 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na_2SO_4, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 hexane/EtOAc R_f = 0.32) gave 150a (183 mg, 87%) as a bright yellow solid that was crystallized from Et_2O/hexane to yellow powdery crystals; mp 146-148 °C (Et_2O/hexane); [alpha]_D^20 +86.9 (c 1.0, acetone); IR (ATR, solid) v_max 3093, 3073, 2973 2937, 2900, 1946, 1891, 1845, 1713, 1528, 1482, 1460, 1380, 1089 cm^-1; ^1H NMR (400 MHz, acetone-d_6) δ 5.89 (d, 1H, J = 6.8 Hz), 5.63-5.62 (m, 2H), 5.50 (t, 1H, J = 4.8 Hz), 5.29 (d, 1H, J = 6.4 Hz), 4.21 (q, 1H, J = 7.2 Hz), 4.04-4.00 (m, 1H), 3.41-3.36 (m, 1H), 3.12-3.07 (m, 1H), 2.12 (s, 3H), 2.00-1.88 (m, 4H), 1.285 (d, 3H, J = 5.6 Hz), 1.217 (d, 3H, J = 5.6 Hz); ^13C NMR (100 MHz, acetone-d_6) δ 233.9, 157.7, 111.7, 94.2, 94.0, 92.6, 91.4, 89.2, 89.1, 71.0, 62.1, 44.8, 26.44, 25.5, 22.35, 21.68, 17.9; ESI-MS [m/z (%)] 449 (M+K, 10), 433 (M+Na, 100), 411 (M+H, 13), 351 (6), 297 (18), 275 (6), 203 (4); HRMS (FAB+) calcd for C_{19}H_{22}CrN_2O_5+H: 411.1007; found: 411.0973.

(+-)Tricarbonyl[(1R,7aS)-2-(2S_p-(formyl)-eta^6-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo
[1,2-c]imidazol-3(2H)-one]chromium(0) (150b). A solution of syn-
148 (203 mg, 0.51 mmol) in THF (10 mL) at −78 °C was treated with t-
BuLi (0.50 mL, 1.50 M, 0.76 mmol). After 30 min, dimethylformamide (0.07 mL, 0.86 mmol) was added by syringe, and the reaction was
allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (70:20:10 CH₂Cl₂/hexane/EtOAc Rᵣ = 0.19) gave 139b (202 mg, 94%) as a bright red solid that was recrystallized from EtOAc/hexane; mp 146-148 °C (EtOAc/hexane); [α]₀° +195.0 (c 1.0, acetone); IR (ATR, solid) νₘₐₓ 3121, 3084, 2971, 2933, 2898, 1971, 1910, 1879, 1708, 1680, 1520, 1074 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 9.47 (s, 1H), 6.28 (d, 1H, J = 5.6 Hz), 6.17 (bt, 1H), 5.88 (d, 1H, J = 6.0 Hz), 5.61-5.60 (m, 2H), 4.30-4.28 (m, 2H, J = 6.4 Hz), 3.99 (t, 1H, J = 5.2 Hz), 3.40-3.38 (m, 1H, J = 8.0 Hz), 3.18 (m, 1H), 2.12-2.10 (m, 1H), 2.00-1.99 (m, 2H), 1.353 (d, 3H, J = 5.2 Hz), 1.27 (d, 3H, J = 5.2 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 231.9, 184.2, 157.7, 121.3, 96.5, 96.3, 93.2, 89.4, 87.5, 84.0, 70.7, 62.1, 44.1, 26.5, 25.1, 22.2, 21.0; ESI-MS [m/z (%)] 870 (2M+Na, 8), 447(M+Na, 100), 381(23), 311(9), 284(3), 229(3); HRMS (FAB+) calcd for C₁₉H₂₀CrN₂O₆+H: 425.0799; found 425.0767. Anal. Calcd for C₁₉H₂₀CrN₂O₆: C, 53.78; H, 4.71. Found: C, 53.84; H, 4.73.

(+)-Tricarbonyl[(1R,7aS)-2-(2S,R-(N-phenylcarboxamido)-η⁶-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (150c). A solution of of syn-148 (217 mg, 0.55 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.55 mL, 1.50 M, 0.82 mmol). After 30 min, phenyl isocyanate (0.10 mL, 0.93 mmol) was added by syringe, and the reaction mixture was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 hexane/EtOAc Rᵣ = 0.24) gave 150c (256 mg, 91%) as a bright yellow solid; mp 151-152 °C; [α]₀° +196.1 (c 1.0, acetone); IR (ATR, solid) νₘₐₓ
3292, 3273, 3076, 2969, 2978, 2894, 2881, 1967, 1879, 1709, 1685, 1063 cm⁻¹; ¹HNMR (400 MHz, acetone-d₆) δ 9.45 (s, 1H), 7.65 (dd, 2H, J = 8.8, 1.2 Hz), 7.34-7.30 (m, 2H), 7.09 (t, 1H, J = 7.2 Hz), 5.99 (dd, 1H, J = 6.4, 1.2 Hz), 5.92 (dd, 1H, J = 6.4, 1.2 Hz), 5.71 (td, 1H, J = 6.4, 1.2 Hz), 5.67-5.65 (m, 2H), 4.19 (q, 1H, J = 6.8 Hz), 3.93 (sept, 1H, J = 6.0 Hz), 3.16-3.10 (m, 1H), 2.96-2.93 (m, 1H), 1.92-1.80 (m, 3H), 1.75-1.71 (m, 1H), 1.24 (d, 3H, J = 6.0 Hz), 1.18 (d, 3H, J = 6.0 Hz); ¹³CNMR (100 MHz, acetone-d₆) δ 232.2, 162.1, 157.5, 138.9, 128.6, 123.8, 119.6, 105.3, 92.8, 92.7, 91.5, 90.5, 89.1, 72.1, 61.3, 45.1, 26.1, 25.0, 22.2, 21.5; ESI-MS [m/z (%)] 538 (M+Na, 100), 456 (14), 425 (2), 402 (38), 320 (4), 203 (3); HRMS (FAB+) calcd. for C₂₅H₂₅CRN₃O₆+H: 516.1221; found: 516.1173.

(+)-Tricarbonyl[(1R,7aS)-2-(2Rp-(thiomethyl)-η⁶-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (150d). A solution of syn-148 (154 mg, 0.39 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.38 mL, 1.55 M, 0.58 mmol). After 30 min, dimethyl disulfide (0.06 mL, 0.67 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (ca. 25 min). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 hexane/EtOAc Rᵣ = 0.24) gave 150d (161 mg, 94%) as a bright yellow solid that was recrystallized from EtOAc/hexane to bright yellow needles; mp 154-155 °C (EtOAc/hexane); [α]D²⁰ +94.7 (c 1.0, acetone); IR (ATR, solid) νmax 3098, 2977, 2959, 2892, 2869, 1956, 1873, 1713, 1511, 1068, 1011 cm⁻¹; ¹HNMR (400 MHz, acetone-d₆) δ 5.95 (dd, 1H, J = 6.4, 0.8 Hz), 5.72 (dt, 2H, J = 6.4, 0.8 Hz), 5.55 (td, 1H, J = 6.4, 0.8 Hz), 5.29 (d, 1H, J = 6.4 Hz), 4.20 (q, 1H, J = 6.4 Hz), 4.09 (sept, 1H, J = 6.4 Hz), 3.37 (dt, 1H, J = 6.4, 2.8 Hz), 3.12-3.07 (m, 1H), 2.43 (s, 3H), 2.02-1.88 (m, 3H), 1.32 (d, 3H, J = 6.4 Hz), 1.22 (d, H, J = 6.4 Hz); ¹³CNMR (100
MHz, acetone-d$_6$) δ 233.4, 158.1, 118.1, 115.8, 93.9, 93.6, 90.8, 90.4, 88.5, 70.9, 62.3, 44.7, 26.4, 25.6, 22.4, 21.8, 16.3; ESI-MS [m/z (%)] 465 (M+Na, 100), 443 (M+H, 20), 383 (20), 329 (4); HR-MS (FAB+) calcd. for C$_{19}$H$_{22}$CrN$_2$O$_5$S: 443.0727; found 398.0720. Anal. Calcd for C$_{19}$H$_{22}$CrN$_2$O$_5$S: C, 51.58; H, 5.01. Found: C, 51.61; H, 5.04.

(−)-Tricarbonyl[(1R,7aS)-2-(2S$_p$-(bromo)-η$^6$-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (150e). A solution of syn-148 (182 mg, 0.46 mmol) in THF (6 mL) at −78 °C was treated with t-BuLi (0.72 mL, 0.96 M, 0.69 mmol). After 30 min, 1,1,2,2-tetrabromoethane (0.09 mL, 0.78 mmol) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexanes R$_f$ = 0.20) gave 150e (181 mg, 83%) as a bright yellow solid which was recrystallized from EtOAc to bright yellow crystals; mp 140-142 °C (EtOAc/hexane); [α]$_D$ +71.1 (c 0.94, acetone); IR (ATR, solid) $_\nu$$_{max}$ 3084, 2978, 2893, 1666, 1893, 1713, 1429, 658 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) δ 6.04 (d, 1H, $J$ = 6.4 Hz), 5.93 (d, 1H, $J$ = 6.4 Hz), 5.74 (t, 1H, $J$ = 6.4 Hz), 5.57 (t, 1H, $J$ = 6.4 Hz), 5.34 (d, 1H, $J$ = 6.4 Hz), 4.22 (q, 1H, $J$ = 6.0 Hz), 4.08-4.02 (q, 1H, $J$ = 6.0 Hz), 3.42-3.38 (m, 1H), 3.12-3.07 (m, 1H), 2.02-1.90 (m, 4H), 1.30 (d, 3H, $J$ = 6.0 Hz), 1.23 (d, 3H, $J$ = 6.0 Hz); $^{13}$C NMR (150 MHz, acetone-d$_6$) δ 232.4, 157.7, 113.9, 101.9, 95.7, 94.2, 94.0, 90.9, 88.6, 71.1, 62.3, 44.9, 26.3, 25.6, 22.4, 21.7; ESI-MS [m/z (%)] 499 (M+Na, 83), 497 (M+Na, 81), 477 (M+H, 48), 475 (M+H, 56), 363 (90), 361 (100), 341 (76), 339 (71), 283 (19); HR-MS (ESI) calcd. for C$_{18}$H$_{20}$CrN$_2$O$_5$: 474.9973; found 474.9955.
(-)-Tricarbonyl[(1R,7aS)-2-(2Sp-(deutero)-η⁶-phenyl)-1-isopropoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (150f). A solution of syn-148 (86 mg, 0.22 mmol) in THF (10 mL) at −78 °C was treated with t-BuLi (0.22 mL, 1.50 M, 0.32 mmol). After 30 min, methanol-d₄ (0.05 mL) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine and dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 hexane/EtOAc Rf = 0.24) gave 150f (74 mg, 86%) as a bright yellow crystalline solid; mp 155-156 °C (CH₂Cl₂/hexane); [α]D⁰ –131.8 (c 1.0, acetone); IR (ATR, solid) νmax 3121, 3101, 2980, 2959, 2892, 2631, 1952, 1877, 1845, 1701, 1524, 1454, 1084, 1018 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 5.85-5.83 (m, 2H), 5.73 (d, 1H, J = 7.2 Hz), 5.50 (d, 1H, J = 6.8 Hz), 5.28 (t, 1H, J = 6.4 Hz), 4.11 (dt, 1H, J = 6.8, 2.4 Hz), 4.01 (sept, 1H, J = 6.0 Hz), 3.44 (dt, 1H, J = 7.6 Hz), 3.14 (m, 1H), 2.13-2.09 (m, 1H), 2.01-1.84 (m, 3H), 1.26 (d, 3H, J = 6.0 Hz), 1.24 (d, 3H, J = 6.0 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 234.2, 156.6, 121.2, 95.5, 95.4, 88.4, 85.2, 85.0 (t, J₁⁺C₂⁻H = 27.2 Hz), 82.2, 70.8, 60.9, 44.4, 25.9, 25.6, 22.5, 21.2; ESI-MS [m/z (%)] 420 (M+Na 100), 398 (M+H, 4), 384 (4), 362 (6), 284 (8), 243 (4), 202 (13), 184 (10), 140 (3); HR-MS (FAB+) calcd. for C₁₈H₁₉DCrN₂O₅+H: 398.0913; found: 398.0929.

(-)-Tricarbonyl[(2Rₚ-(methyl)-η⁶-phenyl)-6,7-dihydro-2H-pyrrolo[1,2-c]imidazol-3(5H)-one]chromium(0) (151a). To a solution of 149a (90 mg, 0.22 mmol) in CH₂Cl₂ (6 mL) was added p-toluenesulfonic acid (83 mg, 0.44 mmol). The solution was stirred at reflux for approximately 3-5 min. The acid was neutralized by addition of a sat. aq. NaHCO₃ solution (10 mL). The reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water,
brine, dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (EtOAc $R_f = 0.08$) gave 151a (66 mg, 86%) as a yellow oil; $[\alpha]_D^{20} = -131.6$ (c 1.0, acetone); IR (ATR, solid) $\nu_{\text{max}}$ 3139, 3101, 3068, 2980, 2953, 2904, 2886, 1950, 1857, 1680, 1630, 1404 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 6.17 (s, 1H), 5.895 (d, 1H, $J = 6.4$ Hz), 5.77 (t, 1H, $J = 6.0$ Hz), 5.62 (d, 1H, $J = 6.4$ Hz), 5.53 (t, 1H, $J = 6.0$ Hz), 3.65 (t, 2H, $J = 6.8$ Hz), 2.80 (t, 2H, $J = 6.8$ Hz), 2.46 (t, 2H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, acetone-$d_6$) $\delta$ 233.2, 149.4, 128.0, 112.3, 111.0 104.4, 95.8, 95.5, 93.2, 89.9, 42.1, 27.6, 22.4, 17.5; ESI-MS [m/z (%)] 723 (2M+K, 4), 373(M+Na, 92), 351(M+H, 17), 251 (6), 237 (100), 215 (56); HR-MS (FAB+) calcd. for C$_{16}$H$_{14}$CrN$_2$O$_4$+H: 351.0431; found: 351.0450.

(+)-Tricarbonyl[2$S_p$-(methyl)-$\eta^6$-phenyl]-6,7-dihydro-2H-pyrrolo[1,2-c]imidazol-3(5H)-one](chromium(0) (ent-151a). To a solution of 150a (115 mg, 0.28 mmol) in CH$_2$Cl$_2$ (6 mL) was added p-toluenesulfonic acid (106 mg, 0.56 mmol).

The solution was stirred at reflux for approximately 3-5 min. The acid was neutralized by the addition of a sat. aq. NaHCO$_3$ solution (10 mL). The reaction mixture was then extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (EtOAc $R_f = 0.17$) gave ent-151a (76 mg, 77%) as a yellow oil; $[\alpha]_D^{20} = +133.2$ (c 1.0, acetone); IR (ATR, solid) $\nu_{\text{max}}$ 3138, 4000, 3068, 2979, 2960, 2929, 2903, 1954, 1863, 1683, 1631, 1529, 1405 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 6.15 (s, 1H), 5.88 (d, 1H, $J = 6.8$ Hz), 5.76 (t, 1H $J = 6.8$ Hz, 5.60 (d, 1H, $J = 6.8$ Hz, 5.52 (t, 1H, $J = 6.0$ Hz), 3.64 (t, 2H, $J = 6.8$ Hz), 2.78 (t, 2H, $J = 6.8$ Hz), 2.44 (t, 2H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, acetone-$d_6$) $\delta$ 233.2, 149.3, 128.0, 112.3, 111.0, 104.4, 95.8, 95.5, 93.2, 89.8, 42.1, 27.6, 22.4, 17.5; ESI-MS [m/z (%)] 389 (M+K, 4), 373 (M+Na,
100, 351 (M+H, 18), 237 (40), 215 (23); HR-MS (FAB+) calcd. for C_{16}H_{14}CrN_{2}O_{4}+H: 351.0431; found: 351.0411.

(--)-Tricarbonyl[(2S_\text{p}-(thiomethyl)-\eta^6-phenyl)-6,7-dihydro-2H-pyrrolo[1,2-c]imidazol-3(5H)-one]chromium(0) (151b). To a solution of 149g (115 mg, 0.28 mmol) in CH_2Cl_2 (6 mL) was added p-toluenesulfonic acid (106 mg, 0.56 mmol). The solution was stirred at reflux for approximately 3-5 min. The acid was neutralized by the addition of a sat. aq. NaHCO_3 solution (10 mL). The reaction mixture was then extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na_2SO_4, filtered and concentrated under reduced pressure. Flash column chromatography (silica gel, 30:70 acetone/EtOAc R_f = 0.17) gave 151b (51 mg, 78%) as a yellow oil; \([\alpha]_D^{20} = -174.7 (c 0.75, \text{acetone})\); IR (ATR, solid) \nu_{\text{max}} 3438, 3153, 3079, 2982, 2965, 2924, 1955, 1866, 1682, 1634, 1512, 1406 cm\(^{-1}\); \(^1\)H NMR (400 MHz, acetone-\text{d}_6) \delta 6.19 (s, 1H), 6.08 (d, 1H, \(J = 6.8 \text{ Hz}\)), 5.86 (t, 1H, \(J = 6.4 \text{ Hz}\)), 5.73 (d, 1H, \(J = 6.4 \text{ Hz}\)), 5.47 (t, 1H, \(J = 6.4 \text{ Hz}\)), 3.64 (t, 2H, \(J = 6.8 \text{ Hz}\)), 2.78 (t, 2H, \(J = 6.8 \text{ Hz}\)), 2.49 (s, 3H), 2.44 (t, 2H, \(J = 6.8 \text{ Hz}\)); \(^{13}\)C NMR (100 MHz, acetone-\text{d}_6) \delta 232.8, 149.4, 127.1, 116.3, 110.1, 105.2, 97.9, 95.0, 88.6, 88.0, 42.1, 27.6, 22.3, 14.8; ESI-MS [m/z (%)] 381(25), 320(12), 269(100), 247(39), 227(4); HR-MS (FAB+) calcd. for C_{16}H_{14}CrN_{2}O_{4}S+H: 383.0152; found: 383.0152.
(+)-Tricarbonyl[(2Rp-(thiomethyl)-η^6-phenyl)-6,7-dihydro-2H-pyrrolo[1,2-c]imidazol-3(5H)-one]chromium(0) (ent-151b). To a solution of 149d (48 mg, 0.11 mmol) in CH₂Cl₂ (5 mL) was added p-toluenesulfonic acid (41 mg, 0.22 mmol). The solution was stirred at reflux for approximately 3-5 min. The acid was neutralized by the addition of a sat. aq. NaHCO₃ solution (10 mL). The reaction mixture was then extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (EtOAc R_f = 0.17) gave ent-151b (39 mg, 94%) as a yellow oil; [α]_D^20 +179.6 (c 1.0, acetone); IR (ATR, solid) ν max 3153, 3080, 2981, 2964, 2923, 1955, 1866, 1676, 1634, 1408 cm⁻¹; ^1H NMR (400 MHz, acetone-d₆) δ 6.19 (s, 1H), 6.08 (d, 1H, J = 5.6 Hz), 5.85 (t, 1H, J = 6.4 Hz), 5.732 (d, 1H, J = 5.6 Hz), 5.47 (dt, 1H, J = 6.4, 0.8 Hz), 3.64 (t, 2H, J = 6.8 Hz), 2.78 (t, 2H, J = 6.8 Hz), 2.49 (s, 3H), 2.45 (t, 2H, J = 6.8 Hz); ^13C NMR (100 MHz, acetone-d₆) δ 232.8, 149.4, 127.1, 116.3, 105.2, 97.8, 95.0, 88.6, 88.0, 42.1, 27.6, 22.3, 14.8; ESI-MS [m/z (%)] 421 (M+K, 5), 405 (M+Na, 99), 383 (M+H, 18), 285 (7), 269 (100), 247 (34), 212 (5); HR-MS (FAB+) calcd. for C₁₆H₁₄CrN₂O₄S+H: 383.0152; found: 383.0186.

(−)-(1S,7aS)-1-ethoxy-2-phenyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one (anti-152) and (−)-(1R,7aS)-1-ethoxy-2-phenyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one (syn-152). To a stirred solution of hemiaminal 146 (1.07 g, 4.89 mmol) in EtOH (10 mL) and CH₂Cl₂ (10 mL) was added p-toluenesulfonic acid (1.74 g, 9.17 mmol). After stirring for 5 minutes at room temperature, the acid was neutralized with sat. aq. NaHCO₃ solution (20 mL) and the reaction mixture was extracted with EtOAc (15 mL). The organic extract was washed with water,
brine, dried over anhyd Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Flash column chromatography (30:70 EtOAc/hexane R$_f$ = 0.32) gave, sequentially, $\textit{anti}$-$\textbf{152}$ (1010 mg, 84 %) and $\textit{syn}$-$\textbf{152}$ (195 mg, 16%, R$_f$ = 0.23).

($\textit{anti}$-$\textbf{152}$); thick colourless oil; [α]$_D^{20}$ = −9.7 (c 0.98, acetone); IR (ATR, solid) ν$_{\max}$ 2971, 2930, 2900, 2874, 1707, 1603, 1391, 1040 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) δ 7.68 (d, 2H, $J$ = 8.0 Hz), 7.33 (t, 2H, $J$ = 8.0 Hz), 7.08 (t, 1H, $J$ = 7.2 Hz), 5.54 (s, 1H), 3.65-3.50 (m, 4H), 3.08 (dt, 1H, $J$ = 9.2, 4.1 Hz), 2.09-2.07 (m, 1H), 1.96-1.90 (m, 2H), 1.43 (pent, 1H, $J$ = 9.2 Hz), 1.12 (t, 3H, $J$ = 7.2 Hz); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ 160.7, 139.4, 128.5, 123.4, 120.1, 87.7, 62.6, 59.7, 45.4, 28.3, 24.4, 14.6; EI-MS[\textit{m/z} (%)] 246 (M$^+$, 100), 217 (17), 201 (95), 171 (67), 149 (29), 121 (56), 105 (15), 77 (48), 70 (34); HR-MS (EI) calcd for C$_{14}$H$_{18}$N$_2$O$_2$: 246.1368; found: 246.1359.

($\textit{syn}$-$\textbf{152}$). colourless crystals; mp 81-83 °C; [α]$_D^{20}$ = −99.8 (c 1.0, acetone); IR (ATR, solid) ν$_{\max}$ 2973, 2928, 2879, 1775, 1704, 1597, 1397, 2088 cm$^{-1}$; $^1$H NMR (400 MHz, acetone-d$_6$) δ 7.61 (d, 2H, $J$ = 8.0 Hz), 7.34 (t, 2H, $J$ = 6.0 Hz), 7.08 (t, 1H, $J$ = 7.2 Hz), 5.49 (d, 1H, $J$ = 6.4 Hz), 4.12-4.10 (q, 1H, $J$ = 6.8Hz), 3.67-3.52 (m, 2H), 3.50-3.47 (m, 1H), 3.11-3.07 (m, 1H), 2.02-1.94 (m, 4H), 1.16 (t, 3H, $J$ = 6.8 Hz); EI-MS[\textit{m/z} (%)] 246 (M$^+$, 38), 216 (54), 173 (21), 171 (40), 119 (100), 104 (18), 77 (39), 70 (24); HR-MS (EI) calcd for C$_{14}$H$_{18}$N$_2$O$_2$: 246.1368; found: 246.1357.

(+)-Tricarbonyl[(1S,7aS)-1-ethoxy-2-phenyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) ($\textbf{153}$). A solution of $\textit{anti}$-$\textbf{152}$ (500 mg, 2.03 mmol), Cr(CO)$_6$ (490 mg, 2.23 mmol) and n-BuOAc (1.87 mL, 14.2 mmol) in octane (14 mL) was heated in a round bottomed flask equipped under nitrogen at 145 °C for 24 hours. The sublimed solids were mechanically pushed back into the
solution periodically using a needle for the first 8 hours. The reaction mixture was cooled to room temperature, filtered through Celite with EtOAc, and concentrated under reduced pressure. Flash column chromatography (70:20:10 CH₂Cl₂/EtOAc/hexane Rₚ = 0.45) gave 153 (328 mg, 42%) as a bright yellow oil that crystallizes upon standing; mp 183-185 °C (EtOAc); [α]D²⁰ +54.8 (c 1.0, acetone); IR (ATR, solid) νmax 3121, 2984, 2944, 2897, 2877, 1938, 1876, 1843, 1713, 1529 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 6.70 (d, 1H, J = 7.2 Hz), 5.88-5.84 (m, 3H), 5.35 (s, 1H), 5.28 (t, 1H, J = 4.8 Hz), 3.70-3.59 (m, 4H), 3.13-3.07 (m, 1H), 2.13-2.08 (m, 1), 1.98-1.89 (m, 2H), 1.45 (pent, 1H, J = 6.8 Hz), 1.23 (t, 3H, J = 6.8 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ 234.2, 159.8, 120.6, 95.7, 95.6, 88.6, 87.2, 83.9, 82.3, 62.0, 59.4, 45.4, 28.2, 24.3, 14.5; ESI-MS [m/z (%)] 405 (M⁺ + Na, 100), 383 (M⁺ + H, 13), 337 (19), 269 (8), 247 (5), 201 (5); HR-MS (FAB) calcd for C₁₇H₁₉O₅CrN₂: 383.0694; found: 383.0685.

(+)-Tricarbonyl[(1S,7aS)-2-(2R(S)-(thiomethyl)-η⁶-phenyl)-1-ethoxytetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-one]chromium(0) (154). A solution of 153 (143 mg, 0.37 mmol) in THF (3 mL) at −78 °C was treated with t-BuLi (0.35 mL, 1.65 M, 0.56 mmol). After 30 min, dimethylsulfide (0.06 mL) was added by syringe, and the reaction was allowed to warm to room temperature (ca. 25 min). Water (10 mL) was added and the reaction mixture was extracted with EtOAc (10 mL). The organic extract was washed with water, brine, dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography (50:50 EtOAc/hexane Rₚ = 0.36) gave 143 (151 mg, 96%) as a bright yellow oil; [α]D²⁰ +163.3 (c 1.0, acetone); IR (ATR, solid) νmax 3086, 2974, 2928, 2898, 2879, 1952, 1859, 1705, 1431, 1390 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ 5.94-
5.89 (m, 2H), 5.54 (d, 1H, $J = 6.0$ Hz), 5.36 (t, 1H, $J = 6.4$ Hz), 5.07 (s, 1H), 3.70-3.59 (m, 4H), 3.07-3.03 (m, 1H), 2.45 (s, 3H), 2.11-2.07 (m, 1H), 1.99-1.92 (m, 2H), 1.64 (pent, 1H, $J = 6.8$ Hz), 1.28 (t, 3H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, acetone-6) δ 232.9, 161.5, 121.0, 109.1, 99.7, 96.3, 90.8, 87.4, 86.0, 63.6, 60.8, 45.8, 27.9, 24.7, 14.6, 14.5; ESI-MS [$m/z$ (%)] 451 (M$^+$ + Na, 100), 388 (9), 315 (43), 247 (7), 150 (13); HR-MS (FAB) calcd for C$_{18}$H$_{21}$O$_5$CrN$_2$S: 429.0571; found: 429.0582.
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7. Vita

Cody Wilson-Konderka was born in Welland, ON, Canada, on June 12, 1990. After graduating from high school, he attended Brock University, where he obtained his BSc degree (2014) in biochemistry in the lab of Dr. Costa Metallinos. He continued at towards his M. Sc. of Chemistry at Brock University under the supervision of Dr. Costa Metallinos.

List of Publications:


4. Wilson-Konderka, C., Lough, A. J., Metallinos, C., "(+)-trans-Chlorido{2-[(R_\text{p})-2-(methylsulfanyl)ferrocenyl]-2,5,6,7-tetrahydropyrrolo[1,2-\text{c}]imidazol-3-ylidene}bis(triphenylphosphane-\kappa P)palladium(II) hexafluoridophosphate dichloroform disolvate"