New Enantioselective Lewis Acid Catalysts

Mustafa Guzel

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To the Graduate School:

This thesis entitled "New Enantioselective Lewis Acid Catalysts" and written by Mustafa GUZEL is presented to the Graduate School of Clemson University. I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Chemistry.

Thesis Advisor

We have reviewed this thesis and recommend its acceptance:

R. Karl Dieter

Accepted for the Graduate School:
NEW ENANTIOSELECTIVE LEWIS ACID CATALYSTS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Chemistry

by
Mustafa GUZEL
December 1996
NEW EVOLUTIONARY LIPID
WORM CATALYSIS

A Thesis
Presented to
the Graduate School of
Carnegie University

To Parnel Peckham
on the Recognition of the
Materia in Science
Commend

in

Materia Medica
December 1990
ABSTRACT

Recently, many organic chemists have been ultimately interested in research in the synthesis of enantiomerically pure organics which are useful to synthesis of biologically active agents and prodrug substances. In the past decades, the new concepts in catalyst design unexpectedly explored the direction of natural product synthesis. In many cases, using enantioselective catalysts are the most suitable and efficient method into enantiopure systems.

The evolutionary development of enantioselective catalysts which operate on the same principle is a testimony not only to progress in asymmetric induction but to the potential that the π stacking phenomenon offers. In many cases attractive interactions between the catalyst aryl and substrate vinyl groups have been implicated on the basis of π stacking effects. Thus it is assumed that the secondary interactions play a key role, since the secondary coordination mode (aryl-vinyl π stack) will be most effective with substrates where the enal/enone π acidity compliments the catalyst aryl π basicity.

The basis for most of these catalytic enantioselective reactions involves formation of a chiral metallocyclic Lewis acid from a chiral catalyst precursor and a suitable organometallic species. Thus a traditional method to coordinate the substrate to the catalyst has been to employ a Lewis acidic metal center to chelate [σ] the substrate via a carbonyl group, into an asymmetric environment. Subsequent asymmetric additions to the substrate would then be influenced by local steric bulk of the catalyst. Such coordination locks the reactant into a chiral environment where steric and/or electronic effects prejudice
approach of an incoming reactant to make formation of one enantiomer more favorable than the other.

The metallocyclic systems envisaged have been sourced from enantiopure diols and \( \eta^6 \) arene chromium tricarbonyl group as a key stereodirective element. Complexation with a \( \text{Cr(CO)}_3 \) group provides a temporary and powerful means of polarity inversion for aromatic rings and can lead to interesting synthetic applications. The chiral Lewis acid would be utilized in the enantioselective catalysis of carbon-carbon bond forming reactions, based on rational mechanistic principles. Therefore it was desired to develop a novel family of chiral controller ligands which could utilize the stereodirective and dipole attractive effects inherent to arene chromium tricarbonyl complexes. The tricarbonyl arene chromium(0) moiety has a number of distinct advantages associated with it, and would seem particularly well suited to incorporation into a chiral catalyst.

Chromium tricarbonyl complexes of several chiral diol catalyst precursors were produced and used to compare the enantioselectivity of the complexed catalysts versus the noncomplexed catalysts. The catalyst precursors were reacted with Diels-Alder reactants to mediate enantioselective cycloadditions. Based on the results of this research, it has been determined that the chromium tricarbonyl functionality has an influential effect on the enantioselectivity of the reactions studied. In the case of Diels-Alder cycloaddition reactions, complexation of the catalysts led to increases of up to 30% in enantiomeric excess.
DEDICATION

This work is dedicated to my lovely wife, my mother and other family members whose encouragement and extreme support have been very great for me. I would like to dedicate it also to all "Golden Times" heroes and companions. Very special thanks to my lovely wife and my colleagues especially to Brant Chapman for helping me to get through this thesis.
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CHAPTER I
INTRODUCTION TO ENANTIOSELECTIVE CATALYSTS ARENE
CHROMIUM TRICARBONYL COMPLEXES

Introduction
The rapid evolution of enantioselective catalysis has resulted in many systems capable of mediating asymmetric carbon-carbon bond forming reactions with extremely high selectivity. Over the past few years a number of new developments have emerged, particularly with regard to catalyst-substrate coordination. A traditional method to coordinate the substrate to the catalyst has been to employ a Lewis acidic metal center to chelate [\(\sigma\)] the substrate via a carbonyl group, into an asymmetric environment. Subsequent asymmetric additions to the substrate will then be influenced by local steric bulk of the catalyst. More recently, reports of dual point binding catalysts have emerged, where conjugated substrates engage in primary coordination to a Lewis acidic site via a carbonyl group, with additional stabilization achieved via overlap of a substrate vinyl group with an aryl group present in the catalyst. The vinyl group can then be subject to enantioselective addition, stereoselectivity a function of the relative stereochemistry of the catalyst-substrate architecture (Figure 1).

Figure 1. A dual point binding enantioselective catalyst (An enal or enone coordinates to a Lewis acidic, e.g. a chiral metallocycle. Secondary interaction of its vinyl group of the catalyst leads to a preferentially stabilized transition state).
In many cases, attractive interactions between the catalyst aryl and substrate vinyl groups have been implicated on the basis of π stacking effects.\(^3\) Examples of successful catalysts which operate under this regime include the Yamamoto acyloxyboronate 2,\(^4\) and the Corey oxazaborolidine 3\(^5\), both shown as a 1:1 complex with a coordinated enal. In a similar vein, the highly selective chloroborane catalysts reported by Hawkins e.g. 4,\(^6\) foster secondary interactions with the catalyst aryl group via dipole induced-dipole attractions with the ester function of the (acrylate) substrates.

While these systems offer potential for application in a number of crucial areas, they also expose some of the typical limitations of present day state of the art catalysts. The Yamamoto acyloxyboronate for example gives very poor product e.e. for [4+2] additions if β substituted acroleins are used as dienophiles, and the Corey oxazaborolidine catalysts work best with esoteric dienophiles such as 2-bromoacrolein, where an s-cis dienophile orientation is enforced. Thus a major limitation of such systems is often their substrate specificity and broad application of the catalyst is often not possible. Since it is assumed that the secondary interactions play a key role, this is unsurprising, since the secondary coordination mode (aryl-vinyl π stack) will be most effective with substrates where the enal/ enone π acidity *compliments* the catalyst aryl π basicity. While tuning of the Lewis acidic σ coordination site of such dual point substrate binding catalysts is easily accomplished, via metal ligand variation, fine tuning of the catalyst aryl-substrate vinyl π stacking interactions is not generally possible, without drastically changing the catalyst architecture. In addition to obtaining a firmer understanding of the π stacking phenomenon in the context of catalyst
design, we believe the effective modulation of catalyst π electron density to be a crucial factor in the logical development of dual point binding catalysts, since in its absence, such catalysts will have severely restricted application.

**Objective**

Based on literature precedent and on independent observations from this laboratory, the work proposed herein is centered around the development and refinement of π–π attractive catalyst systems, by means of tuning the π basicity of the arene, specifically by preparation of mixed arene metal carbonyl complexes. Our intent was to initially focus heavily on mixed ligand arene dicarbonyl chromium derivatives of facially resolved complexes, Figure 2. (R=alkoxy). By screening a range of derivatives X, a range of (catalyst) arene π basicities could then be created easily (vide infra).

![Diagram of π Attractive interactions](image)

**Figure 2. π Attractive interactions**

**Technical Considerations**

In order to be successful in the design of new enantioselective catalysts, a number of technical considerations must be taken into account. They are briefly discussed, and serve as background to our ultimate design strategy.

**Axial chirality of chromium(0)carbonyl complexes.** Axial chirality is inherent to ortho and meta disubstituted arene chromium tricarbonyl complexes, and conventional CIP notations are applied, assigning the chromium tripod highest priority e.g. face resolved
complexes 6 and 7, which bear an enantiomeric relationship. Several procedures are available to achieve facial resolution of such complexes (e.g. R₁=CHO, R₂=MeO)

typically requiring diastereomer resolution, enzymatic resolution, or more recently enantio(facial)selective complexation. Additionally, diastereoselective complexation can be employed if R₁ or R₂ bears a non-racemic chiral center, subsequent chromatographic (diastereomer) purification of tricarbonyl chromium complexes then being possible. Optically pure arene chromium carbonyl complexes are typically crystalline, hence a large number of structural studies of these complexes have been reported. From these, and related theoretical calculations, the preferred conformation that the tricarbonyl chromium tripod occupies has been determined. As expected, for unsubstituted arene chromium tricarbonyl complexes, a staggered aryl C-C / Cr-CO orientation is preferred, as shown in 8. Mono and bis substituted tricarbonylchromium complexes however may indeed adopt an orientation where one or more of the carbonyl groups will eclipse ring substituents, particularly where the substituents are electron releasing (e.g. MeO).

Variation of arene σ and π donor ability using mixed ligand η₆ arene complexes. The tuning of arene σ/π orbital density of arene chromium carbonyl complexes has long been established, most notably from studies involving the ionization of mixed ligand chromium complexed benzoic acids 9. In this study, acidity proved a function of donor / acceptor effects of the arene metal carbonyl system. As expected, the low pKa of tricarbonyl chromium complexed benzoic acid is a function of the net withdrawing ability of the tricarbonyl groups. Replacement of just one of these ligands however has a profound
effect on acidity of the complex. Thus a dicarbonyl monontriphenyolphosphino complex has an even higher pKa than benzoic acid itself, a consequence of the strong back donor ability of the phosphine, making the arene a net electron donor. Similar results were obtained in our laboratories with the aniline mustard agents, as shown in the preliminary results section. These effects however, were designed to impact on the \( \sigma \) basicity of the arene, whereas for the purpose of this study, variation in \( \pi \) basicity is desirable. MO theory of arene chromium carbonyl complexes, in combination with photoelectron spectroscopy and ionization potential data, reveals major changes in both the \( \sigma \) and \( \pi \) bonding occur on arene complexation. In one photoelectron spectroscopy study, the aromatic \( \pi \)-type orbitals in benzene chromium tricarbonyl were shown to be approx. 1.06 eV (2nd IP) lower in energy than in the uncomplexed state (1st IP). Hoffmann has attributed the major MO interactions between \( \text{Cr(CO)}_3 \) and benzene to be via the 1e-\( \epsilon_{2u} \) and 2e-\( \epsilon_{1g} \) fragment orbitals. Ring substituents will interact with the \( \pi \) orbitals of the complexed arene and typical \( \pi \) donor substituents [\( \text{NEt}_2, \text{NH}_2, \text{OMe}, \text{F, Me} \)] induce \( \pi \) symmetry interactions with the complex, and can be monitored by lowered (CO) infrared carbonyl stretching frequencies. Unsurprisingly therefore, charge - transfer absorption bands have been reported between substituted arene chromium tricarbonyl complexes and other arenes. Toluene chromium tricarbonyl is reported to form a complex with tetracyanoethylene, and an x-ray structure of the 1:1 complex of anisole chromium tricarbonyl with 1,3,5 trinitrobenzene has been reported. Of interest is that the two aryl rings are stacked at 3.4 A, ideal for a through space \( \pi \) stacking interaction.
A measurable contribution to arene $\pi$ orbital density is also likely on (chromium) ligand replacement, and preliminary results obtained with 8-phenylmenthol acrylates do indeed support this notion.\textsuperscript{10} Assuming the same correlation of ligand-chromium donor / acceptor ability exists in our designed catalysts as did with the aniline mustard agents, it will only be necessary to prepare functionalized mixed dicarbonyl chromium complexed arenes of type \textbf{10}, where arene $\pi$ basicity / acidity can be varied by a single ligand $(X)$ exchange. The inclusion of $\pi$ donor ring substituents in selected catalysts will merely mandate estimation and calculation of overall arene $\pi$ density, and appropriate choice of ligand $X$.\textsuperscript{20} Ligand substitution of arene chromium tricarbonyl complexes is a well established process, and a range of substituted arene chromium dicarbonyl derivatives can be prepared by conventional photolytic methods.\textsuperscript{20,21}

\begin{center}
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\end{center}

\textbf{Prior art in substrate-catalyst $\pi$-stacking.} Since the introduction of 8-phenylmenthol as a chiral auxiliary for Diels-Alder cycloadditions, general interest in '$\pi$ stacking' to stabilize a variety of asymmetric transition state assemblies has been intense.\textsuperscript{3} The phenomenon has been invoked extensively, and approximates the close association of two unsaturated systems leading to stabilization, at a distance of 3.3-3.5Å.\textsuperscript{3} Following on from the early studies by Corey, Whitesell suggested that a through space electronic interaction between the glyoxylate group and the aryl ring of 8-phenylmenthol derived \textbf{11} existed, on the basis of fluorescence quenching.\textsuperscript{22}
In seminal studies by Evans involving enantioselective cycloadditions to crotonate derivatives of chiral oxazolidinones, best selectivities were obtained using the benzyl oxazolidinones shown in 12, with selectivity falling off sharply with alkyl oxazolidinones. This anomaly however was not observed in control reactions involving alkylation of related acyl enolates, instead following a trend based purely on steric bulk of the oxazolidinone substituent. This prompted further studies on substituted benzyl oxazolidinone derivatives, and the findings firmly supported the notion that some attractive or stabilizing effect between the vinyl group and arene existed in the case of 32 (p. 12), in agreement with the studies of Whitesell. A survey of the literature reveals a multitude of studies where \( \pi \) stacking has been invoked to explain anomalous behaviour in asymmetric processes, involving chiral auxiliaries, and, more recently, enantioselective catalysts, including those illustrated in 2-4. The \( \pi \) stacking of an arene chromium carbonyl complex with a substrate has even been reported. In the stoichiometric asymmetric [3+2] addition of various alkenes to chiral aryl nitrones, the authors noted high levels of asymmetric induction and facial selectivity using arene chromium carbonyl complexed nitrones, and postulated that the alkene substituents (aryl shown) engaged in stacking with the polarized lower face of the controller, as shown in 13.
Reports of substrate π stacking with enantioselective catalysts however have largely been confined to Diels-Alder reactions, where the dienophile is stabilized by an arene-vinyl π stack, including those depicted in 2-4 in the introduction. In the catalyst-crotonaldehyde complex 2, the existence of π stacking was supported by NOE measurements, which identified the vinyl portion of the substrate, engaged in a π stack with the aryl group at a distance of 3.4 Å. In the case of the Corey catalyst 3, experimental evidence supported the notion that the dienophile sits preferentially s-cis and at a distance of 3.3 Å above the indole ring. The π stacking involved served to block the lower face of the enal to cycloaddition with cyclopentadiene. The enantioselectivity of the reaction dropped from 200:1 to a mere 7:1 on replacement of the β indolylmethylene group with a β napthylmethylene group, a presumed consequence of the diminished π basicity of the arene (donor). Very recently, π stacking effects have been invoked to explain anomalous results obtained with designed host-guest complexes. Thus it is likely that the fundamental study proposed herein will shed light on many important areas of organic chemistry, both in emerging and maturing fields alike.

Research Plan

Figure 3 shows the essential design features for our approach to an efficient, versatile and tunable catalyst assembly. A σ basic enal or enone coordinates to a Lewis acidic center, which is harnessed in a chiral environment, and is attached to an arene. The molecular architecture for the catalyst system is such that the substrate (enal / enone) vinyl group is positioned at approximately 3.3-3.5 Å parallel to the arene, ideally situated to foster π-π attractive interactions.
The arene is derivitized as a η6 arene chromium system, allowing, via ligand (X) variation, the π basicity to be tuned to match the π acidity of the vinyl group of the coordinated substrate. The lower face of the vinyl group is thus shielded to attack, and the coordination of the enal/enone is a function of the proximal steric constraints of the catalyst, including the arene ring substituents, which in turn will be influenced by the metal carbonyl tripod. Thus an incoming reactant (e.g. Diels-Alder diene) will approach with a rigorously defined vector, giving rise to highly selective addition. The magnitude of the π basicity of the arene will be a function of the electron density at the chromium center. The choice of an η6 arene chromium based system for the catalyst is further supported by the inherent axial chirality that face resolved arene (0) metal complexes provide, allowing ultimate development of a powerful new line of multifunctional catalysts.

**Catalyst Design 1: Strategy**

Our initial plan was to prepare a series of metallo-1,3-dioxolanes 15, suitably substituted as the corresponding chromium carbonyl complexes. The most readily available enantiopure diols for use in this study were determined to be m disubstituted arene 16 the 1-naphthalene diol 17 and 2-naphthalene diol 18.
We wished to adopt a unified strategy for the synthesis of all of the desired metallodioxolane complexes, and opted for the route outlined in Scheme 1. Mixed carbonyl complexes 19 would be formed via photolysis of tricarbonyl complexes 20, available in turn via complexation of arene diols 21. This route was attractive because it could capitalize on the Sharpless type asymmetric dihydroxylation sequence to introduce the diol function, and the required asymmetric center. All that would be required would be the requisite vinyl arenes 22, which in turn could be prepared via Wittig methodology from the appropriate arene carboxaldehyde.
Scheme 1. Unified strategy for preparation of mixed ligand metallodioxolanes

Catalyst Design 2: m-Anisyl Dioxolanes

We firstly began preparation of meta anisaldehyde derived diols 16. According meta anisaldehyde 23 was protected as the cyclic acetal 24 and subjected to complexation to give 25 (Scheme 2). Since deprotection of the cyclic acetal using conventional conditions led to decomplexation, we elected to transketalize to give dimethoxy acetal 26, which was deprotected to give aldehyde 27. Baker's yeast reduction was then performed, 25 to give a aldehyde 28 and alcohol 29.
Scheme 2. Resolution of m-anisaldehyde chromium(0) tricarbonyl via Baker’s Yeast

We had planned to perform a Wittig reaction on 28, then subject this to asymmetric dihydroxylation. Due to the poor optical yield obtained with the yeast reduction, we investigated an alternate strategy to the diol as shown in Scheme 3.
Anisaldehyde was converted to alkene 30, then Sharpless dihydroxylation performed\textsuperscript{26} immediately to give 31. To test the hypothesis behind catalyst design, this diol was then converted to titanium metallocycle 32, and its catalytic behavior investigated. Problems were encountered obtaining reproducible results, that stemmed from the closure reaction, which required extensive heating. Under these conditions, decomplexation became a competing reaction. We elected to pursue bromoborane metallocycles following this, and are described in the later section.

It was eventually decided to use diol 31 as a building block for the subsequent chromium(0) carbonyl complexes. Accordingly, it was bis protected, either as the TMS (33) or TBS ethers (37) as shown in Scheme 4. Complexation was then performed to give either 34 or 38 respectively, isolated initially as 4:1 diastereomeric mixtures. Diastereomer separation was achieved using silica gel chromatography, to give protected complexes 35/36 and 39/40. Unfortunately, assignment of stereochemistry was not possible, as X-ray quality crystals could not be obtained.
Scheme 4. Protection and separation of m-anisaldehyde derived chromium(0) tricarbonyls

It was later found that it is possible to complex diol 31 directly, circumventing the need for protecting groups (Scheme 5). Complex 41 was obtained in moderate yield, and converted into metallocycle 42 using standard conditions. In an effort to improve the overall yield of arene complexes, diol 31 was also converted into cyclic acetal 43 (Scheme 6).
Scheme 5. Preparation of m-anisaldehyde chromium(0)tricarbonyl derived metallodioxolane

Scheme 6. Protection and deprotection of m-anisaldehyde derived arene chromium(0)tricarbonyls

Complexation now gave a higher yield of the diastereomers 44 and 46 which were separable chromatographically. Deprotection\textsuperscript{28,29,30} however proved less efficient than desired, resulting in only moderate yields of the complexes 45 and 47, ready for metallocycle formation. Ligand substitution of the complexes 44 and 46 was achieved using photolytic conditions (Scheme 7). Photolysis in the presence of triphenyl phosphine gave moderate yields of mixed complexes 48 and 51 respectively.
Scheme 7. Protection, photolysis and deprotection of m-anisaldehyde derived arene chromium(0) tricarbonyls

Ligand substitution was also attempted on the resolved trialkylsilyl protected diol complexes 52 and 54 (Scheme 8). These TMS derivatives were prepared from diols 45 and 47 respectively, and photolyzed to give mixed phosphine complexes 53 and 55 respectively. Deprotection in this series was far more efficient, giving complexes 49 and 51 respectively (Scheme 8).
Scheme 8 Protection, photolysis and deprotection of m-anisaldehyde derived arene chromium(0) tricarbonyls

Catalysis Using Metallodioxolanes

The primary objective was to prepare enantioselective Diels-Alder catalysts. Due to the problems encountered forming the titanium metallocycles, all of the diol precursors
were converted\textsuperscript{32,33} with the exceptional of last two diol precursors $49$ and $51$, which are ongoing at the time of writing, into the corresponding bromoboranes using bromoborane dimethyl sulfide complex (Scheme 9). The metalallocyclic catalysts were used to catalyze the cycloaddition of acrolein with cyclopentadiene (Scheme 10), with the exo-endomixture of products separated, and subjected to europium shift analysis.

Scheme 9. 

$m$-Anisaldehyde based enantioselective Lewis acid catalysts
Scheme 10. Enantioselective Lewis acid catalysts in Diels-Alder reactions

The results are presented in Table 1, and show a trend based on steric bulk of the catalyst framework. The proposed catalyst transition-state assembly is depicted in Figure 4.

<table>
<thead>
<tr>
<th>CATALYSTS</th>
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<tr>
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<tr>
<td>E</td>
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</table>

Table 1. Enantioselective catalytic Diels-Alder reactions

Figure 4. Proposed transition-state assembly of Lewis acid catalyst
Catalyst Design 3: 1-Naphthyl Dioxolanes

In an effort to prepare complexes 18, we commenced from 1-naphthaldehyde, which was subjected to Wittig protocol and then Sharpless dihydroxylation to give diol 61 in (Scheme 11). A portion of the diol was converted to the bis TMS ether 64, which was then complexed to give a mixture of 65 and 66. The remainder was subjected to direct complexation, which gave diols 62 and 63 respectively.

Scheme 11. Preparation 1-naphthaldehyde derived arene chromium(0) tricarbonyls

The recovered yields for the reactions in Scheme 11 were somewhat disappointing, so an additional protection strategy was investigated. Accordingly, diol 61 was converted to TBS ether 67, and subjected to complexation to give a mixture of 68 and 69 (Scheme 12).
Scheme 12. Protection and deprotection of 1-naphthylaldehyde derived arene chromium (0) tricarbonyls

Deprotection of these ethers was possible using TBAF, giving diols 62 and 63 respectively. Application of these diols in enantioselective catalysis, and preparation of mixed ligand analogs in ongoing at the time of writing.

**Catalyst Design 4: 2-Naphthyl Dioxolanes**

For the preparation of catalyst precursors 17, 2-naphthaldehyde 70 was similarly subjected to Wittig reaction to give 71, then asymmetric dihydroxylation to give 72 (Scheme 13). In a manner analogous to that described above in Schemes 11 and 12, two independent routes to diols 73 and 74 were explored (Schemes 13 and 14), and additionally, trimethylsilyl ethers 76 and 77 were prepared (Scheme 13). Application of the diols in enantioselective catalysis, and preparation of mixed ligand analogs in ongoing at the time of writing.
Scheme 13. Preparation of 2-naphthylaldehyde derived arene chromium(0) tricarboxyls

Scheme 14. Protection and deprotection of 2-naphthylaldehyde derived arene chromium (0) tricarboxyls
Appendix: Preparation of Racemic diols

For subsequent HPLC analysis, racemic standards of the described diols were synthesized\textsuperscript{34} according to the protocols outlined in Scheme 15. Styrene 30 was processed to diol 81, which was additionally converted\textsuperscript{27} to acetal 82. Similarly naphthyl styrenes 60 and 73 were processed to diols 83 and 85 respectively, together with their acetal derivatives 84 and 86 (Scheme 15). Separation of the enantiomers was conducted using a Diacel chiral column, either the OD or OJ version.

Scheme 15. Preparation and protection of racemic diols
CHAPTER II

EXPERIMENTAL PROCEDURES

General Information

Infrared spectra were obtained as neat films between salt plates or as potassium bromide pellets using a Nicolet Model 510 spectrometer and were reported in reciprocal centimeters (cm\(^{-1}\)), \(^1\)H and \(^13\)C NMR spectra were obtained using a Bruker Model AC300. Both \(^1\)H and \(^13\)C data were presented in parts per million (ppm) (\(\delta\)) down field relative to tetramethylsilane as internal standard, or in the absence of TMS the spectrum was referenced to the NMR solvent used (especially CDCl\(_3\), C\(_6\)D\(_6\), CD\(_3\)COCD\(_3\)). The \(^1\)H NMR data were tabulated in the order: multiplicity, number of protons and the coupling constant (Hz). Mass spectral analyses were performed on a Hewlett-Packard 5985 Gas Chromatography / Mass Spectrometer at 70 eV (direct insertion) and the data were tabulated as m/e (intensity expressed as percent of base peak). Column Chromatography was typically carried out on Merck flash grade silica gel using Hexane-Ether, Hexane-Ethyl Acetate mixtures. TLC was carried out using glass backed plates coated with Merch Kieselgel F254. Optical rotations were obtained in the indicated solvents (usually Chloroform) using a Horiba Model SEPA-200 High Sensitive Polarimeter. Enantiomeric excesses were determined using ISCO model 2350 HPLC pump, V\(^4\) Absorbance detector, and a Hewlett-Packard Series II Integrator. Separation of enantiomers was achieved by elution with Hexane-Isopropyl alcohol mixtures on Chiralcel OD or OJ HPLC columns at a detector wavelength of 254 nm. Racemic mixtures of the compounds studied were
prepared by conventional methods, and were used to determine proper eluent composition, column resolution and integrator function. Ether, THF and n-Butyl ether were distilled from sodium benzophenone ketyl. Hexane, benzene and methanol were distilled from calcium hydride. Dichloromethane was distilled from phosphorus pentoxide before use. DMF was dried by stirring with barium oxide for 12 hours at room temperature, followed by distillation from alumina at reduced pressure. Solvents used for complexations were deoxygenated by three cycles of freezing under vacuum, purging with nitrogen gas and thawing. Hexacarbonyl chromium was purchased from Strem Chemicals and used as supplied. Baker’s Yeast was purchased from any grocery store. All other reagents were purchased from Aldrich Chemical Company and used as supplied. 2-Methyl acrolein and cyclopentadiene were distilled from calcium hydride prior to use. All handling of air and moisture sensitive reagents was conducted under dry nitrogen atmosphere using needles and cannula were dried in an oven at 150 °C for at least 12 hours and the tips were flame dried immediately prior to use. Syringes were either dried in an oven at 150 °C for 12 hours and allowed to cool down in a dessicator, or dried in an evacuated drying pistol for 12 hours and used immediately upon removal. Reactions were stirred with Teflon coated magnetic stir bars unless other wise indicated. Experiments were monitored by thin layer chromatography or 1H NMR as described. Solvents were removed in vacuo using a Bucher rotary evaporator at 25 mm Hg. Commercial solvents and reagents were used without further purification with the exceptions.
General Complexation Procedure

The arene and hexacarbonyl chromium (typically 1.0/2.0 molar ratio) were placed in a flame dried, round bottomed flask fitted with a reflux condenser. The contents were evacuated and purged with dry nitrogen three times. A 10/1 mixture of butyl ether/THF solution is cannulated into the flask and the contents were deoxygenated with three cycles of freezing, purging, pulling vacuum and allowing to warm up by liquid nitrogen.

The solution was refluxed under nitrogen gas at 140 °C until the onset of decomplexation, generally between 20 and 30 hours, which was followed by TLC with using cannula. The mixture was allowed to cool down to the room temperature, and filtered through a plug of a silica to remove inorganic decomplexation products, and the solvent was evaporated and removed under vacuum.

The care was taken to ensure that all of the green inorganic decomplexation products are removed prior to solvent removal since they often cause spontaneous decomplexation of the products. The crude product was separated by column chromatography, using Hexane/Ether or Hexane/EtOAc solvent mixtures in order to get both diastereomers. All of the diastereomers were kept with benzene solution in the fridge after taking spectral data to not allow for decomplexation.
Resolution and Determination of m-Anisaldehyde Chromium(0) Tricarbonyl Complexes Via Baker’s Yeast

Preparation of protected (with ethylene glycol) m-anisaldehyde. To a solution of dried benzene (165 ml) m-anisaldehyde (3.147 gr., 23.11 mmol) and p-toluene sulfonic acid (0.440 gr., 2.311 mmol) were added to the flask fitted with Dean-Stark Trap condenser. Then ethylene glycol (1.72 gr., 27.73 mmol) was added to flask and the mixture was refluxed at 150 °C for 48 hours. The color changed from reddish brown through orange during the reflux. The reaction was followed by TLC then the solvent was evaporated. The crude mixture was dissolved in Ethyl acetate (100 ml) and washed with water (100 ml) three times, solvent was evaporated. The crude product was columned with 70/30 Hexane/Ether eluent and the column chromatography yielded the protected m-anisaldehyde as an orange oil (3.98 gr., 95%). $^1$H NMR (300 MHz, CDCl$_3$) δ : 7.10-7.08 (d, 1H, 6 Hz), 6.89-6.87 (d, 1H, 6 Hz), 6.87-6.85 (d, 1H, 6 Hz), 6.70 (s, 1H), 5.60 (s, 1H), 3.92-3.90 (d, 2H, 6 Hz), 3.85-3.83 (d, 2H, 6 Hz), and 3.78 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ : 159.6, 136.9, 129.3, 119.7, 115.9, 111.9, 106.4, 61.9, 55.1, and 30.7.
Preparation of protected m-anisaldehyde chromium(0) tricarbonyl. Protected m-anisaldehyde (2.0014 gr., 11.11 mmol) was reacted with chromium hexacarbonyl (4.894 gr., 22.22 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex 95 a 100 percent of one (less polar diastereomer) 1-R ethylene glycoxy m-anisaldehyde chromium(0) tricarbonyl as an orange color crystals (2.9 gr., 82%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 5.64 (s, 1H), 5.55-5.51 (t, 1H, 12 Hz), 5.26 (s, 1H), 5.10-5.08 (d, 1H, 6 Hz), 5.04-5.02 (d, 1H, 6 Hz), 4.14-4.10 (d, 2H, 12 Hz), 4.05-4.01 (d, 2H, 12 Hz), and 3.73 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 159.6, 139.4, 129.4, 118.7, 115.0, 111.4, 103.4, 65.2, 55.2, and 29.6. IR (neat) 2961.7, 2893.6, 1974.5, 1889.4, 1719.1, 1591.5, 1472.3, 1276.6, 1097.9, 1046.8, 953.2, and 791.5 cm$^{-1}$. 

![Chemical Structures](image.png)
Deprotection of m-anisaldehyde chromium(0) tricarbonyl. Protected m-anisaldehyde chromium(0) tricarbonyl complex (1.20 gr., 3.798 mmol) and tosulic acid (0.360 gr., 1.899 mmol were added to the methanol solution (50 ml), the mixture was stirred at R.T. for 70 minutes. The reaction was followed by TLC. Evaporation of the solvent gave the quantitative yield of Dimethyl acetal m-anisaldehyde chromium(0) tricarbonyl (1.108 gr., 91%) as an orange powder then continued the next reaction. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 5.57 (s, 1H), 5.30-5.28 (d, 2H, 6 Hz), 5.07-5.05 (d, 2H, 6 Hz), 3.72 (s, 3H), and 3.39 (s, 6H).
Preparation of m-anisaldehyde chromium(0) tricarbonyl. Dimethylacetal m-anisaldehyde chromium(0) tricarbonyl (0.800 gr., 2.51 mmol) was selectively hydrolyzed by stirring in a mixture of chloroform (40 ml) TFA (20 ml) and water (20 ml) (2/1/1 ratio) at 0 °C for 120 minutes. The reaction was followed by TLC. The mixture was extracted with EtOAc (100 ml) and washed with saturated NaHCO₃ two times then washed with water (50 ml). The organic extracts was separated and evaporation of the solvent gave a quantitative yield of m-anisaldehyde chromium(0) tricarbonyl as a yellow crystals (0.550 gr., 80%). ¹H NMR (300 MHz, CDCl₃) δ: 9.58 (s, 1H), 5.46-5.44 (d, 1H, 6 Hz), 5.34-5.32 (d, 1H, 6 Hz), 5.13 (s, 1H), 4.96-4.93 (t, 1H, 9 Hz), 3.87 (s, 3H), and 3.77 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 223.2, 143.5, 113.3, 94.9, 83.8, 63.2, 55.6, and 29.6. IR (neat) 3080.9, 3046.8, 1991.5, 1914.9, 1821.3, 1489.4, and 1038.3 cm⁻¹.
Resolution of m-anisaldehyde chromium(0) tricarbonyl via Baker’s Yeast. The Baker’s yeast (10 gr.) was prepared by centrifuging and washing in the small test tubes with water (300 ml H₂O). After removing of the water yeast was poured into a round bottomed flask. Glucose (2.5 gr.) was added to yeast, the mixture was stirred at R.T. for 30 minutes then m-anisaldehyde chromium(0) tricarbonyl racemic mixture (0.232 gr., 0.85 mmol), and ethanol (10 ml) were added to the reaction mixture, then stirred at R.T. for 30 minutes more. The mixture was extracted with EtOAc (100 ml) and washed with water (50 ml) three times. After evaporation of the solvent and column chromatography with hexane/ether (70/30) of the crude mixture gave a quantitative yield of each racemates (50/50) as stated one aldehyde and other one alcohol (0.175 gr., 75%). The product 28 was found to be in the ¹H NMR (300 MHz, CDCl₃) δ : 9.56 (s, 1H), 5.56-5.54 (d, 1H, 6 Hz), 5.22 (s, 1H), 5.11-5.09 (d, 1H, 6 Hz), 4.93 (s, 1H), and 3.72 (s, 3H). IR (neat) 2944.7, 2255.3, 1974.5, 1906.4, 1480.9, 1293.6, 1097.9, 927.7, and 731.9 cm⁻¹. The product 29 was found to be alcohol ¹H NMR (300 MHz, CDCl₃) δ : 5.60 (s, 1H), 5.23 (s, 1H), 5.11-5.09 (d, 1H, 6 Hz), 4.93 (s, 1H), 4.56-4.54 (d, 2H, 6 Hz) and 3.73 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ : 223.2, 143.5, 113.3, 94.9, 83.8, 63.2, 55.6, and 29.6. IR
m-Methoxy styrene. To a solution of PPh₃, CH₃Br (21.14 gr. 59.18 mmol) in THF (150 ml) in the round bottomed flask was added n-butyl lithium (19.57 ml, 2.52 M in hexane) drop wise and was stirred at R.T. for 4 hours then m-anisaldehyde (6.0 ml, 49.31 mmol) was added to the flask, and continued stirring at R.T. for 48 hours, the reaction was followed by TLC every 6 hours. The solution was removed and filtered with EtOAc (300 ml) then the solvent was evaporated. The crude was columned by using hexane/ether (95/5 to 70/30) eluent and the column chromatography yielded m-methoxy styrene (5.649 gr., 85%) as a colorless oil. $^1$H NMR (300 MHz, CDCl₃) $\delta$: 7.28 - 7.23 (t, 1H, 15 Hz), 7.05 - 7.00 (t, 1H, 15 Hz), 6.85 - 6.81 (d, 1H, 12 Hz), 6.74 - 6.69 (t, 1H, 15 Hz), 5.81 - 5.78 (d, 1H, 9 Hz), 5.29 - 5.25 (d, 1H, 12 Hz), 4.17 - 4.10 (q, 1H, 21 Hz), and 3.85 (s, 3H). $^{13}$C NMR (75 MHz, CDCl₃) $\delta$: 137.6, 135.8, 134.8, 128.4, 126.9, 128.3, 125.3, 112.3, and 21.3.
S-1,2 - Dihydroxy (m-methoxy phenyl) ethylene. To a solution of t-BuOH (160 ml) and H₂O (160 ml) in the round bottomed flask, AD-mix-α (15.65 gr.) was added and stirred for a while at R.T. After observing two layers, m-methoxy styrene (1.50 gr., 11.18 mmol) was added to the solution at 0 °C and was stirred vigorously at 0 °C for 9 hours. The reaction was followed by TLC, then Na₂SO₃ (16.77 gr.) was added to the reaction mixture and allowed to warm up to the R.T., stirred for more 1 hour, the solution was washed with EtOAc (300 ml) and organic extracts were combined and filtered with EtOAc (100 ml). Solvent evaporation afforded S-1,2, -dihydroxy(m-methoxy) styrene as a colorless oil (1.87 gr., 99%). ¹H NMR (300 MHz, CDCl₃) δ : 7.25-7.21 (t, 1H, 12 Hz), 6.93-6.91 (d, 1H, 6 Hz), 6.89-6.87 (d, 1H, 6 Hz), 6.83-6.80 (t, 1H, 9 Hz), 4.75-4.73 (d, 1H, 6 Hz), 4.31 (s, 1H), 4.01 (s, 1H), and 3.78 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ : 138.7, 137.8, 129.0, 128.5, 126.5, 125.3, 37.7, 32.1, and 21.2. IR (neat) 3412.8 (br), 3097.9, 3046.8, 1812.8, 1480.9, and 1029.8 cm⁻¹. MS (m/e) 208 (M⁺, 100%). [α]D= +71.8 (c=0.5, CHCl₃).
S-1,2, -di(trimethylsilyloxy) m-methoxy styrene. In the round bottomed flask, S-1,2-(dihydroxy) m-methoxy styrene (0.468 gr., 2.78 mmol) and imidazole (1.89 gr., 27.8 mmol) were added together in the presence of DMF (2 ml) as a solvent, TMS-Cl (1.41 ml, 11.13 mmol) was added via syringe to the reaction mixture and was stirred at R.T. for 48 hours, was followed by TLC. The solution was poured over iced 1% HCl (50 ml) and washed with EtOAc (50 ml) and extracted with EtOAc (50 ml) then washed quickly with iced saturated NaHCO₃ (50 ml) and iced saturated NaCl (50 ml). The organic extracts were combined and evaporation of the solvent and column chromatography (95/5 to 70/30) hexane/ether) afforded S-1,2, -di(trimethylsilyloxy) m-methoxy styrene (0.797, 91.8%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ : 7.25-7.21 (t, 1H, 12 Hz), 6.95-6.93 (d, 2H, 6 Hz), 6.83-6.81 (d, 1H, 6 Hz), 4.74-4.71 (t, 1H, 9 Hz), 3.88 (s, 3H), 3.64-3.62 (d, 2H, 6 Hz), and 0.14-0.08 (d, 18H, 18 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 138.7, 137.8, 129.0, 128.5, 126.5, 125.3, 37.7, 32.1, 21.9, 21.2, and 11.1. [α]₀⁺=+47.07 (c=0.5, CHCl₃).
Preparation of S-1,2, -di(t-butyl dimethylsilyloxy) m-methoxy styrene. In the round bottomed flask, S-1,2, -dihydroxy m-methoxy styrene (0.357 gr., 2.12 mmol) and imidazole (1.302 gr., 19.72 mmol) were added together in the presence of DMF (1 ml) as a solvent, then TBS-Cl (0.960 gr., 6.37 mmol) was added to the reaction mixture which was stirred at R.T. for 49 hours, followed by TLC. The solution was poured over iced 1% HCl (50 ml) and washed with EtOAc (50 ml) then extracted with EtOAc (50 ml), washed quickly with iced saturated NaHCl (50 ml) and iced saturated NaCl (50 ml). The organic extracts were combined and evaporation of the solvent and column chromatography (95/5 to 60/40) hexane/ether) afforded S-1,2, -di(t- butyl dimethylsilyloxy) m-methoxy styrene (0.763 gr., 90.6%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ : 7.20-7.17 (t, 1H, 9 Hz), 6.95-6.93 (d, 2H, 6 Hz), 6.78-6.76 (d, 1H, 6 Hz), 4.71-4.68 (t, 1H, 9 Hz), 3.85 (s, 3H), 0.86- 0.79 (d, 18H, 21 Hz), and 0.15 - 0.07 (d, 12H, 24 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) δ : 138.7, 137.8, 129.0, 128.5, 126.5, 125.3, 37.7, 32.1, 21.9, 21.2, 11.1, 0.25 and 0.02. [α]$_D$ = +69.8 (c=0.5, CHCl$_3$).
S-1,2, -dihydroxy m-methoxy styrene chromium(0) tricarbonyl. S-1,2, -dihydroxy m-methoxy styrene (0.490 gr., 2.914 mmol) was reacted with chromium hexacarbonyl (1.282 gr., 5.83 mmol) following the general complexation procedure (section 3-2) giving a quantitative yield of arene complex as a 90/10 mixture of the two possible diastereomers which were then separated by silica gel chromatography. The more polar chromatography fraction was found to be 1-S, S, -1,2, -dihydroxy m-methoxy styrene tricarbonyl chromium(0) (0.412 gr., 46.5%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) : 6.92 (s, 1H), 5.60-5.57 (t, 1H, 9 Hz), 5.42 (s, 1H), 5.09 (s, 1H), 5.05 (s, 1H), 4.79 (s, 1H), 4.53 (s, 1H), and 3.70 (s, 3H). \(^1\)\(^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) : 232.2, 128.3, 113.8, 94.9, 83.8, 82.9, 72.8, 67.8, and 55.7. IR (neat) 3438.3 (br), 3097.9, 3038.3, 2340.4, 1983.0, 1897.9, 1812.8, 1480.9, and 1038.3 cm\(^{-1}\). \([\alpha]_D^0 = +142.9\) (c= 0.5, CHCl\(_3\)). The less polar chromatography fraction was found to be in IR (neat) 3387.2 (br), 2944.7, 1966.0, 1872.3, 1548.9, 1472.3, 1276.6, and 1038.3 cm\(^{-1}\). \([\alpha]_D^0 = +31.9\) (c= 0.5, CHCl\(_3\)).
S-1,2, -di(trimethylsilyloxy) m-methoxy styrene chromium(0) tricarbonyl. S-1,2, -di (trimethylsilyloxy) m-methoxy styrene (0.312 gr., 1.00 mmol) was reacted with chromium hexacarbonyl (0.550 gr., 2.50 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as a 50/50 mixture of the two possible diastereomers which were then separated by silica gel flash column chromatography. The less polar chromatography fraction (35) was found to be the 1-R,S diastereomer (0.316 gr., 70.5%). ^1H NMR (300 MHz, CDCl3) δ: 5.32 (s, 1H), 5.20-5.18 (d, 1H, 6 Hz), 5.13 (s, 1H), 5.03-5.01 (d, 1H, 6 Hz), 4.56-4.54 (d, 1H, 6 Hz), 3.70 (s, 3H), 3.54 (s, 1H), 3.40 (s, 1H), 0.19 (s, 6H), and 0.01 (s, 6H). ^13C NMR(75 MHz, CDCl3) δ: 233.5, 133.9, 129.6, 127.2, 125.3, 118.3, 113.3, 84.1, 71.5, 55.2, 26.5, and 25.9. IR (neat) 3659.6 (br), 3089.3, 3038.4, 1966.0, 1897.9, 1821.3, 1489.4, 1251.1, 1038.3, 851.1, and 689.4 cm⁻¹. MS (m/e) 448 (M⁺, 46.5%). [α]D+ = +98.5 (c=0.5, CHCl₃). The more polar fraction (36) was found to be in IR (neat) 3472.3 (br), 3089.4, 3038.3, 2323.4, 1974.5, 1897.9, 1821.3, 1480.9 4, 1123.4, 1038.3, and 680.9 cm⁻¹. [α]D+ = +60.9 (c= 0.5, CHCl₃).
S-1,2, -di(t-butyl dimethylsilyloxy) m-methoxy styrene chromium(0) tricarbonyl.

S-1,2, -di(t-butyl dimethylsilyloxy) m-methoxy styrene (0.561 gr., 1.42 mmol) was reacted with chromium hexacarbonyl (0.779 gr., 3.54 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as a 70/30 mixture of the two possible diastereomers which were then separated by silica gel flash column chromatography. The less polar chromatography fraction (39) was found to be the 1-R,S diastereomer (0.526 gr., 69.8%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 5.32 (s, 1H), 5.20-5.18 (d, 1H, 6 Hz), 5.13 (s, 1H), 5.03-5.01 (d, 1H, 6 Hz), 4.56-4.54 (d, 1H, 6 Hz), 3.70 (s, 3H), 3.54 (s, 1H), 3.40 (s, 1H), 0.97 (s, 9H), 0.87 (s, 9H), 0.19 (s, 6H), and 0.01 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 232.9, 134.2, 129.4, 127.8, 126.8, 118.3, 113.3, 83.7.
72.3, 55.2, 26.5, 25.9, 0.26, and 0.12. IR (neat) 3446.8 (br), 3106.4, 3038.3, 1966.0, 1897.9, 1829.8, 1480.9, 1038.3, and 680.9 cm⁻¹. [α]D = +99.1 (c = 0.5, CHCl₃). The more polar fraction (40) was found to be in IR (neat) 3106.4, 3038.3, 1966.0, 1889.4, 1821.3, 1489.4, 1046.8, and 689.4 cm⁻¹. [α]D = +33.5 (c = 0.5, CHCl₃).

Preparation of S-1,2-dioxy m-methoxy styrene titanium chloride (catalyst A). In the vacuum two neck flask S-1,2-dihydroxy m-methoxy styrene (0.504 gr., 3.0 mmol) was dissolved in azeotropically distilled toluene (2 ml), then to solution toluene (2 ml) was added and azeotropically distilled, procedure applied until 6 ml toluene was used. Titanium di(isopropoxy) chloride (6 ml., 0.5 M in toluene solution), was refluxed at 60 °C for 3 hours under nitrogen atmosphere. The crude reaction mixture was allowed to cool down to the R.T., continued to next reaction. Due to continuity of the next reaction, no spectral data were taken.
Use of S-1,2, -dioxy m-methoxy styrene titanium chloride as a catalyst in Diels-Alder reaction. To catalysis solution (0.885 gr., 3.0 mmol), methylene chloride (8 ml) was added and cooled to -80 °C with acetone bath. The cyclopentadiene (0.8 ml) and 2-methyl acrolein (0.210 gr., 3.0 mmol) (both freshly distilled) were added to the reaction mixture rapidly by syringe. The mixture was stirred at -80 °C for 22 hours, allowed to warm up to the R.T. and quenched with saturated NaHCO₃ (0.5 ml) and Et₃N (0.5 ml). The crude reaction mixture was then filtered with methylene chloride (50 ml) and the solvent was evaporated at 0°C. After using Europium (III) Chiral Shift Reagent in NMR enantiomeric excess was calculated as follows: $^1$H NMR(300 MHz, CDCl₃) $\delta$: exo 11.142, $\delta$: endo 11.181, exo/endo 1.76/1, ee = (0.9223-0.5244) / (0.9223+ 0.5244) =27.52% ee.
Preparation of 1-R,S-1,2-dioxy m-methoxy styrene chromium(0) tricarbonyltitanium chloride (catalyst B). In the vacuum two neck flask 1R, S-1,2-dihydroxy m-methoxy styrene chromium(0) tricarbonyl (0.692 gr., 2.276 mmol) was dissolved in toluene (3.0 ml). The solvent was azeotropically distilled and added 3 ml more repeating azeotropic distillation, then titanium di(isopropoxy) chloride (4.55 ml in 0.5 M toluene solution) was added to the flask. The reaction mixture was refluxed at 60 °C for 90 minutes under nitrogen atmosphere. When added titanium di(isopropoxy) chloride, the color of reaction mixture changed from light green to black. Then the crude reaction mixture was allowed to cool down to the R.T., and continued to next reaction. Due to continuity of the next reaction, no spectral data were taken.
The use of 1-R, S-1,2, -dioxy m-methoxy styrene chromium(0) tricarbonyl titanium chloride as a catalyst in Diels-Alder reaction. To catalysis solution (0.958 gr., 2.275 mmol) methylene chloride (10 ml) was added and cooled to -80 °C with acetone bath. Freshly distilled cyclopentadiene (0.8 ml) and 2-methyl acrolein (0.188 ml, 2.275 mmol) were added to the solution by syringe. The mixture was stirred at -80 °C for 20 hours. The mixture was allowed to warm up to the R.T. and quenched with saturated NaHCO₃ (0.8 ml) and Et₃N (0.8 ml). The crude mixture was then filtered with methylene chloride (50 ml), the solvent was evaporated at 0°C. After using Europium (III) Chiral Shift Reagents enantiomeric excess was calculated as follows: \( ^1H \text{NMR (300 MHz, CDCl}_3) \delta : \text{exo: 17.0431, } \delta : \text{endo: 17.1435, } \text{exo/endo 2.73/1, } \text{ee} = (7.962-2.914) / (7.962+2.914) = 46.4\% \text{ ee.} \)
Preparation of 1-Naphthaldehyde Derived Arene Chromium Tricarbonyls

**Preparation of 1-vinyl naphthalene.** The following experimental procedure is typical as Wittig Reaction. To a solution of Wittig reagent, PPh₃CH₂Br (47.35 gr., 132.54 mmol) in THF (400 ml) in the round bottomed flask fitted with condenser was added n-BuLi (42.32 ml, 2.61 M in hexane) drop wise and was stirred at R.T. for 4 hours then 1-Naphthylaldehyde (15 ml, 110.45 mmol) to the flask via syringe and refluxed at 65 °C for 40 hours. The reaction was followed by TLC and the crude was removed and filtered with EtOAc (500 ml) then solvent was evaporated. The product was separated by using flash vacuum column with 90/10 hexane/methylene chloride eluent yielding 1-vinyl naphthalene as a light yellow oil (15.928 gr., 94%). ¹H NMR (300 MHz, CDCl₃) δ : 7.97-7.95 (d, 1H, 6 Hz), 7.84-7.80 (q, 2H, 12 Hz), 7.65 - 7.57 (d, 1H, 24 Hz), 7.37 - 7.28 (q, 4H, 27 Hz), 5.65 - 5.58 (d, 1H, 21 Hz), and 5.29 - 5.22 (d, 1H, 21 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 135.3, 133.6, 130.4, 128.9, 128.0, 126.2, 125.6, 122.7, 109.5, 92.7, 75.2, and 72.8. IR (neat) 3097.9, 3046.8, 1966.0, 1821.3, 1489.4, 1038.3, and 680.9 cm⁻¹.
Preparation of S,1,2,-dihydroxy naphthyl ethylene via asymmetric dihydroxylation reaction. The following experimental procedure is typical: To a 1/1 solution of t-BuOH (150 ml) and H₂O (150 ml) in the round bottomed flask, AD-mix-α (27.32 gr.) was added and stirred for a while at R.T. until observing two layers, 1-vinyl naphthalene (3.0086 gr., 19.51 mmol) was added to the solution at 0 °C and the mixture was stirred vigorously at 0 °C for 22 hours. Na₂SO₃ (29.26 gr.) was added to the solution while stirring at 0 °C. The mixture was allowed to warm up to the R.T., stirred at R.T. for 60 minutes, and washed with EtOAc (300 ml) and organic extracts were combined and filtered with EtOAc (100 ml). Evaporation of solvent and column chromatography of the crude with 60/40 EtOAc/hexane eluent afforded the S-1,2,-dihydroxy naphthyl ethylene as a white powder (3.216 gr., 88%). ¹H NMR (300 MHz, CDCl₃) δ: 8.04-8.02 (d, 1H, 6 Hz), 7.88-7.78 (q, 2H, 30 Hz), 7.69-7.67 (d, 1H, 6 Hz), 7.47-7.41 (d, 3H, 18 Hz), 5.63-5.60 (d, 1H, 9 Hz), 3.96-3.94 (d, 1H, 6 Hz), and 3.79-3.74 (t, 1H, 15 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 133.2, 129.6, 129.0, 128.3, 127.4, 126.2, 125.4, 121.3, 112.4, 109.6, 91.3, and 74.6. IR (neat) 3251.1 (br), 3097.9, 3038.3, 2323.4, 1966.0, 1829.8, 1489.4, 1029.8, 783.0, and 672.3. MS (m/e) 229 (M⁺, 100%). [α]D = + 45.63 (c=0.5, CHCl₃)
Preparation of S-1,2, -di(trimethylsilyloxy) naphthylethylene. The following experimental procedure is typical: In the round bottomed flask, S-1,2, -dihydroxy naphthylethylene (0.993 gr, 5.28 mmol) and imidazole (2.88 gr., 42.24 mmol) were added together in the presence of DMF (4 ml) as a solvent, TMS-Cl (2.01 ml, 15.84 mmol) was added to the reaction mixture via syringe and the mixture was followed by TLC. Then the solution was poured over iced 1% HCl (100 ml) and washed with EtOAc (100 ml) and extracted with EtOAc (150 ml), washed quickly with iced saturated NaHCO₃ (50 ml) and iced saturated NaCl (50 ml). Extraction and evaporation of the solvent was subjected to the column. Column chromatography (90/10 to 50/50 hexane/EtOAc) yielded S-1,2 -di (trimethyl silyloxy) naphthylethylene as a colorless oil (1.526 gr., 87%). ¹H NMR (300 MHz, CDCl₃) δ : 8.17-8.15 (d, 1H, 6 Hz), 7.88-7.86 (d, 1H, 6 Hz), 7.80 - 7.73 (q, 2H, 21 Hz), 7.56-7.47 (m, 4H, 27 Hz), 5.54-5.51 (t, 1H, 9 Hz), 3.86-3.86 (d, 1H, 6 Hz), 3.73-3.71 (d, 1H, 6 Hz), and 0.16-0.09 (d, 18H, 21 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 135.3, 133.6, 130.4, 128.9, 128.0, 126.2, 125.6, 122.7, 121.5, 109.5, 70.9, 26.5, and 25.8. MS (m/e) 332 (M⁺, 2.33%) [α]D = +61.81 (c=0.5, CHCl₃).
Preparation of S-1,2, -di(trimethylsilyloxy) naphthylethylene chromium(0) tricarbonyl. S-1,2, -di(trimethylsilyloxy) naphthylethylene (1.033 gr., 3.11 mmol) was reacted with chromium hexacarbonyl (1.711 gr., 7.78 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as a 70/30 mixture of the two possible diastereomers which were then separated by silica gel chromatography by using 95/5 hexane/ether eluent. The less polar chromatography fraction was found to be 1-R, S-1,2 di(trimethylsilyloxy) naphthylethylene (0.384 gr., 40%) as a red powder. ¹H NMR (300 MHz, CDCl₃) δ : 7.43-7.41 (d, 1H, 6 Hz), 7.36-7.28 (m, 3H, 24 Hz), 6.24-6.22 (d, 1H, 6 Hz), 6.12-6.10 (d, 1H, 6 Hz), 5.58-5.55 (t, 1H, 9 Hz), 5.53-5.47 (m, 2H, 18 Hz), 4.16-4.13 (q, 1H, 9 Hz), and 1.00-0.83 (d, 18H, 51 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 232.5, 130.3, 129.0, 128.5, 126.4, 125.0, 104.4, 93.2, 91.3, 88.0, 73.1, 69.3, 1.1, and 0.6. IR (neat) 3421.3 (br), 1974.5, 1897.9, 1625.5, 1259.6, 1131.9, and 851.1 cm⁻¹. [α]D = +304.2 (c= 0.5, CHCl₃).
Preparation of S-1,2, -di(t-butyl dimethyl silyloxy) naphthylethylene. The following experimental is typical: In the round bottomed flask; S-1,2, -dihydroxy naphthylethylene (1.238 gr., 6.58 mmol) and imidazole (4.48 gr., 65.85 mmol) were added together in the presence of DMF (2 ml) as a solvent, TBS-Cl (3.34 ml, 26.34 mmol) was added to the reaction mixture via syringe and the mixture was stirred at R.T. for 64 hours, following by TLC. The solution was poured over iced 1% HCl (100 ml) and washed with EtOAc (100 ml) and extracted with EtOAc (50 ml) then washed quickly with iced saturated NaHCO₃ (50 ml) and iced saturated NaCl (50 ml). The organic extracts were combined and the solvent was evaporated. Column chromatography (90/10 to 60/40 hexane/EtOAc) yielded. S-1,2 di(t-butyl dimethylsilyloxy) naphthylethylene as a colorless oil (1.955 gr., 74.4%). ¹H NMR (300 MHz, CDCl₃) δ: 7.97-7.78 (m, 4H, 57 Hz), 7.51-7.44 (m, 3H, 21 Hz), 4.88-4.85 (t, 1H, 9 Hz), 3.76-3.70 (d, 1H, 18 Hz), 3.65-3.60 (d, 1H, 15 Hz), 0.93-0.85 (d, 18H, 24 Hz), and 0.07-(-0.03) (d, 12H, 30 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 130.3, 129.0, 128.4, 128.1, 126.4, 125.0, 113.2, 93.1, 92.0, 91.4, 71.7, 69.3, 26.3, 25.6, 1.1, and 0.6. [α]DB = +78.9 (c= 0.5, CHCl₃).
Preparation of S-1,2, -di(t-butyl dimethylsilyloxy) naphthylethylene chromium(0) tricarbonyl. S-1,2, -di(t-butyl dimethylsilyloxy) naphthylethylene (0.650 gr., 1.56 mmol) was reacted with chromium hexacarbonyl (0.859 gr., 3.90 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as a 80/20 mixture of the two possible diastereomers which were then separated by silica gel chromatography by using 98/2 hexane/ether eluent. The less polar chromatography fraction was found to be 1-R, S-1,2 di (t-butyldimethylsilyloxy) naphthylethylene (0.522 gr., and 0.131 gr. for each diastereomer, 76%). $^1$H NMR (300 MHz, CDCl₃) δ : 7.58-7.56 (d, 1H, 6 Hz), 7.44-7.38 (m, 2H, 12 Hz), 6.38-6.36 (d, 1H, 6 Hz), 6.11-6.09 (d, 1H, 6 Hz), 5.53-5.45 (d, 2H, 24 Hz), 5.29 - 5.24 (d, 2H, 15 Hz), 0.89-0.78 (d, 18H, 33 Hz), and 0.06 - (-0.01) (d, 12H, 21 Hz). $^{13}$C NMR (75 MHz, CDCl₃) δ : 232.4, 130.2, 129.0, 128.5, 128.1, 126.4, 125.0, 104.7, 93.1, 92.0, 71.7, 69.3, 26.3, 25.6, 1.0, and 0.6. IR (neat) 3412.8 (br), 3097.9, 3038.3, 1966.0, 1897.9, 1829.8, 1480.9, 1251.1, 1038.3, and 680.9 cm⁻¹. [α]⁺ = +98.8 (c = 0.5, CHCl₃).
Deprotection reactions of 1-R and 1-S - S-1,2 di(t-butyl dimethylsilyloxy) naphthylethylene chromium(0) tricarbonyls. Both the more polar diastereomer and the less polar the diastereomer of arene complexes were placed into separate round bottomed flasks (0.119 gr., 0.215 mmol and 0.64 gr., 0.011 mmol respectively) then TBAF (0.312 ml, 1.078 mmol and 0.017 ml, 0.058 mmol respectively) were added to the flasks, the reaction mixtures were stirred at R.T. for 30 minutes. The crude mixtures were filtered with 70/30 EtOAc/hexane. After evaporation of the solvent of each diastereomers, extremely fast decomplexation was observed during the work up of each reaction. \(^1\)H NMR (300 MHz, CDCl\(_3\)) and \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) show fast decomplexation products but not deprotection products. Both unpredicted products were kept in the fridge dissolving in methylene chloride/hexane mixture in order to regrow crystals.
Preparation of S-1,2 dihydroxy naphthylethylene chromium(0) tricarbonyl. S-1,2,-dihydroxy naphthylethylene (2.053 gr., 12.10 mmol) was reacted with chromium hexacarbonyl (4.00 gr., 18.16 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as totally the more polar diastereomer which was separated from starting material by column chromatography using 70/30 hexane/EtOAc eluent. The chromatography fraction was found to be 1-S, S-1,2 dihydroxy naphthylethylene as a red powder (1.432 gr., 40%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) : 7.51 (s, 1H), 7.37 (s, 2H), 6.14 (s, 1H), 5.72-5.68 (d, 2H, 12 Hz), 5.52 (s, 1H), 5.32 (s, 1H), 5.21-5.19 (d, 1H, 6 Hz), and 4.00 (s, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) : 232.4, 131.2, 129.6, 128.8, 128.2, 127.2, 93.6, 92.0, 91.4, 88.0, 71.8, and 69.2. IR (neat) 3676.6, 3097.9, 3046.8, 1974.5, 1906.4, 1821.3, 1497.9, 1038.3, and 672.3. 

\([\alpha] = +73.6 \text{ (c= 0.5, CHCl}_3\text{)}.\)
Preparation of 2-Naphthaldehyde Derived Arene Chromium Tri-carbonyls

Preparation of 2-vinyl naphthalene. The following experimental procedure is typical as Wittig Reaction: To a solution of Wittig reagent, PPh₃CH₃Br (17.41 gr., 48.75 mmol) in THF (400 ml) in the round bottomed flask fitted with condenser was added n-BuLi (16.12 ml, 2.52 M in hexane) drop wise and was stirred at R.T. for 4 hours then 2-Naphthylaldehyde (6.343 gr., 40.61 mmol) to the flask via syringe and refluxed at 65 °C for 51 hours. The reaction was followed by TLC and the crude was removed and filtered with EtOAc (500 ml) then solvent was evaporated. The product was separated by using flash vacuum column with 70/30 hexane/methylene chloride eluent yielding 2-vinyl naphthalene as a white powder (5.98 gr., 95.5%). \(^1\)H NMR (300 MHz, CDCl₃) \(\delta\) : 7.82-7.76 (q, 4H, 18 Hz), 7.66-7.63 (d, 1H, 9 Hz), 7.48-7.44 (d, 2H, 12 Hz), 6.92-6.89 (q, 1H, 9 Hz), 5.91 - 5.87 (d, 1H, 12 Hz), and 5.36-5.33 (d, 1H, 9 Hz). \(^13\)C NMR (75 MHz, CDCl₃) \(\delta\) : 138.5, 135.0, 132.0, 131.8, 128.4, 127.7, 127.4, 126.7, 126.3, 125.7, 92.5, and 70.5.
Preparation of S,1,2, -dihydroxy 2-naphthyl ethylene via asymmetric dihydroxylution reaction. The following experimental procedure is typical: To a 1/1 solution of t-BuOH (80 ml) and H₂O (80 ml) in the round bottomed flask, AD-mix-α (18.16 gr.) was added and stirred for a while at R.T. until observing two layers, 2-vinyl naphthalene (2.00 gr., 12.97 mmol) was added to the solution at 0 °C and the mixture was stirred vigorously at 0 °C for 26 hours. Na₂SO₃ (20.00 gr.) was added to the solution while stirring at 0 °C. The mixture was allowed to warm up to the R.T., stirred at R.T. for 60 minutes, and washed with EtOAc (200 ml) and organic extracts were combined and filtered with EtOAc (100 ml). Evaporation of solvent and column chromatography of the crude with 60/40 EtOAc/hexane eluent afforded the S-1,2 -dihydroxy 2-naphthyl ethylene as a white powder (1.552 gr., 64%). ¹H NMR (300 MHz, CDCl₃) δ : 7.86-7.82 (d, 4H, 12 Hz), 7.50 -7.45 (t, 3H, 15 Hz), 5.02-4.99 (t, 1H, 9 Hz), 3.86-3.84 (d, 1H, 6 Hz), and 3.77-3.75 (d, 1H, 6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 137.2, 134.7, 131.9, 129.7, 128.3, 127.5, 127.1, 126.5, 126.0, 125.2, 47.9, and 35.9. IR (neat) 3208.5 (br), 1523.4, 1072.3, 1021.3, and 774.5. MS (m/e) 229 (M⁺, 100%). [α] = +8.32 (c = 0.5, CH₃OH).
Preparation of S-1,2, -di(trimethylsilyloxy) 2-naphthylethylene. The following experimental procedure is typical: In the round bottomed flask, S-1,2, -dihydroxy 2-naphthylethylene (1.238 gr., 6.58 mmol) and imidazole (4.48 gr., 65.85 mmol) were added together in the presence of DMF (2 ml) as a solvent, TMS-Cl (3.34 ml, 26.34 mmol) was added to the reaction mixture via syringe and the mixture was followed by TLC. Then the solution was poured over iced 1% HCl (100 ml) and washed with EtOAc (100 ml) and extracted with EtOAc (150 ml), washed quickly with iced saturated NaHCO₃ (50 ml) and iced saturated NaCl (50 ml). Extraction and evaporation of the solvent was subjected to the column. Column chromatography (90/10 to 50/50 hexane/EtOAc) yielded S-1,2, -di(trimethyl silyloxy) 2-naphthylethylene as a colorless oil (1.955 gr., 79%). ¹H NMR (300 MHz, CDCl₃) δ: 7.89-7.83 (d, 4H, 18 Hz), 7.55-7.48 (t, 3H, 21 Hz), 4.93-4.91 (t, 1H, 6 Hz), 3.76-3.74 (d, 1H, 6 Hz), 3.73-3.71 (d, 1H, 6 Hz), and 0.17 - 0.09 (d, 18H, 24 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 138.0, 135.0, 134.7, 131.9, 128.4, 127.4, 127.1, 126.5, 125.2, 123.3, 35.3, 31.6, 0.04, and 0.5. IR (neat) 3463.8 (br), 3063.8, 2961.7, 1974.5, 1659.6, 1251.1, 1157.4, 868.1, and 834.0 cm⁻¹. MS (m/e) 332 (M⁺, 2.32%).

[α]_D = +103.3 (c = 0.5, CHCl₃).
Preparation of S-1,2, -di(trimethylsilyloxy) 2-naphthylethylene chromium(0)

tricarbonyl. S-1,2, -di(trimethylsilyloxy) 2-naphthylethylene (1.424 gr., 4.29 mmol) was reacted with chromium hexacarbonyl (2.359 gr., 10.72 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as a 80/20 mixture of the two possible diastereomers which were then separated by silica gel chromatography by using 95/5 hexane/ether eluent. The less polar chromatography fraction was found to be 1-R, S-1,2 di(trimethylsilyloxy) 2-naphthylethylene (1.246 gr., 62%) as a red powder. ¹H NMR (300 MHz, CDCl₃) δ: 7.83 (s, 1H), 7.48-7.44 (d, 2H, 12 Hz), 6.11 (s, 1H), 5.50-5.47 (s, 2H, 9 Hz), 5.34 (s, 1H), 4.73 (s, 2H), 3.63- 3.54 (d, 2H, 21 Hz), and 0.28 - 0.10 (s, 18H, 54 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 233.4, 129.4, 129.1, 128.5, 128.2, 126.7, 125.4, 112.3, 96.3, 74.3, 45.6, 27.3, 0.04, and (-0.5). IR (neat) 3106.4, 3055.3, 1983.0, 1906.4, 1821.3, 1480.9, 1055.3, and 680.9 cm⁻¹. [α]₀ = +63.2 (c= 0.5, CHCl₃). The more polar chromatography fraction was found to be in IR (neat) 3106.4, 3055.3, 1966.0, 1821.3, 1489.4, 1038.3, and 680.9 cm⁻¹. [α]₀ = +39.9 (c= 0.5, CHCl₃).
Preparation of S-1,2, -di(t-butyl dimethylsilyloxy) 2-naphthyl ethylene. The following experimental is typical: In the round-bottomed flask, S-1,2, -dihydroxy 2-naphthylethylene (0.743 g, 3.95 mmol) and imidazole (1.787 g, 11.86 mmol) were added together in the presence of DMF (2 ml) as a solvent, TBS-Cl (1.787 ml, 11.86 mmol) was added to the reaction mixture via syringe and the mixture was stirred at R.T. for 64 hours, following by TLC. The solution was poured over iced 1% HCl (100 ml) and washed with EtOAc (100 ml) and extracted with EtOAc (50 ml) then washed quickly with iced saturated NaHCO₃ (50 ml) and iced saturated NaCl (50 ml). The organic extracts were combined and the solvent was evaporated. Column chromatography (90/10 to 60/40 hexane/EtOAc) yielded S-1,2, -di(t-butyldimethylsilyl oxy) 2-naphthylethylene as a colorless oil (1.247 g, 75.9%). 

\[ \text{[1H NMR (300 MHz, CDCl₃)] } \delta : 8.16-8.13 (d, 1H, 9 Hz), 7.95-7.93 (d, 1H, 6 Hz), 7.86-7.84 (d, 1H, 6 Hz), 7.76-7.74 (d, 1H, 6 Hz), 7.51-7.44 (q, 3H, 21 Hz), 5.49-5.46 (t, 1H, 9 Hz), 3.81-3.72 (d, 2H, 27 Hz), 0.96-0.84 (d, 18H, 36 Hz), and 0.03-(-0.07) (q, 12H, 30 Hz). \]

\[ \text{[13C NMR (75 MHz, CDCl₃)] } 136.3, 134.7, 131.6, 129.4, 128.7, 128.1, 126.8, 125.3, 124.4, 46.3, 34.6, 26.5, 23.3, 0.09, and 0.03. \]

IR (neat) 3097.9, 3038.3, 1957.4, 1821.3, 1497.9, 1046.8, and 672.3. \[ [\alpha]_D^0 = +56.4 \ (c= 0.5, \text{CHCl}_3) \]
Preparation of S-1,2, -di(t-butyldimethylsilyloxy) 2-naphthyl ethylene chromium(0) tricarbonyl. S-1,2, -di(t-butyldimethylsilyloxy) 2-naphthylethylene (0.928 gr., 2.34 mmol) was reacted with chromium hexacarbonyl (1.288 gr., 5.85 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as a 60/40 mixture of the two possible diastereomers which were then separated by silica gel chromatography by using 95/5 hexane/ether eluent. The less polar chromatography fraction was found to be 1-R, S-1,2, -di (t-butyldimethylsilyloxy) 2-naphthylethylene (0.767 gr., for each diastereomer, 62.3%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.85 (s, 2H), 7.49 (s, 2H), 6.43 (s, 1H), 5.64 (s, 1H), 5.00 (s, 2H), 3.85-3.81 (d, 2H, 12 Hz), 1.31-1.25 (d, 18H, 18 Hz), and 0.17-0.05 (s, 12H, 36 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 232.4, 130.2, 129.0, 128.5, 128.1, 126.4, 125.0, 104.7, 93.1, 92.0, 71.7, 69.3, 26.3, 25.6, 1.0, and 0.6. $[\alpha]_D = +86.7$ (c = 0.5, CHCl$_3$).
Deprotection reactions of 1-R and 1,S, S-1,2 di(t-butyldimethyl silyloxy) 2-naphthylethylene chromium(0) tricarbonyls. Both the more polar diastereomer and the less polar the diastereomer of arene complexes were placed into separate round bottomed flasks (0.180 gr., 0.325 mmol and 0.214 gr., 0.388 mmol respectively) then TBAF (0.472 ml, 1.625 mmol and 0.507 ml, 1.94 mmol respectively) was added to the flasks, the reaction mixtures were stirred at R.T. for 30 minutes. The crude mixtures were filtered with 80/20 EtOAc/hexane. After evaporation of the solvent for both diastereomers, extremely fast decomplexation was observed during the work up of each reaction. $^1$H NMR (300 MHz, CDCl$_3$) and $^{13}$C NMR (75 MHz, CDCl$_3$) show fast decomplexation products but not deprotection products. Both unpredicted products were kept in the fridge dissolving in methylene chloride/hexane mixture in order to regrow crystals.
Preparation of S-1,2 dihydroxy 2-naphthylethylene chromium(0) tricarbonyl. S-1,2, -dihydroxy 2-naphthylethylene (1.087 gr., 5.77 mmol) was reacted with chromium hexacarbonyl (2.542 gr., 11.55 mmol) following the general complexation procedure (section 3.2) giving a quantitative yield of arene complex as totally the more polar diastereomer which was separated from starting material by column chromatography using 70/30 hexane/EtOAc eluent. During the work up of reaction, unexpectedly fast decomplexation and ligand exchange with benzene chromium(O) tricarbonyl was observed. The chromatography fraction was found to be 1-S, S-1,2, dihydroxy 2-naphthylethylene in very low yield as a red powder (0.374 gr., 20%). $^1$H NMR and $^{13}$C NMR spectrums show benzene chromium(0) tricarbonyl as the major product.
Reactions of m-Anisaldehyde Derived Arene Chromium Tricarbonyls

Preparation of protected S-1,2, -dihydroxy (m-methoxy) phenyl ethylene with 2,2, -dimethoxy propane. The following reaction procedure is typical: S-1,2, -dihydroxy (m-methoxy) phenyl ethylene (1.725 gr., 10.54 mmol), 2,2, -dimethoxy propane (1.89 ml, 15.39 mmol) and catalytic amount of tosulic acid (0.195 gr., 1.026 mmol) were added together in the round bottomed flask, in the presence of DMF (51.3 ml, 0.2 M in hexane) as a solvent. The solution was then stirred at R.T. for 24 hours, following by TLC. The mixture was washed with EtOAc (100 ml) and extracted with 1% HCl (50 ml) three times, the solvent was evaporated. The column chromatography of the crude mixture yielded title product as a colorless oil (1.598 gr., 75%). [α]D = +47.07 (c=0.5, CHCl3). 1H NMR (300 MHz, CDCl3) δ: 7.29-7.26 (d, 1H, 9 Hz), 6.93 (s, 2H), 6.83-6.81 (d, 1H, 6 Hz), 5.05-5.02 (t, 1H, 9 Hz), 4.32-4.27 (t, 1H, 15 Hz), 3.82 (s, 3H), 3.73-3.67 (t, 1H, 18 Hz), and 1.61-1.48 (d, 6H, 39 Hz). 13C NMR (75 MHz, CDCl3) δ: 139.7, 137.4, 128.5, 127.8, 127.4, 127.1, 126.5, 125.1, 45.2, 44.8, 27.1, and 22.6.
Preparation of protected S-1,2, -dihydroxy (m-methoxy) styrene chromium(0) carbonyl. S-1,2 di(isopropyloxy) (m-methoxy) styrene (2.843 gr., 13.66 mmol) was reacted with chromium hexacarbonyl (6.009 gr., 27.32 mmol) following the general complexation reaction procedure (section 3.2) giving a quantitative yield of arene complex as a 10/90 mixture of the two possible diastereomers which were then separated by column chromatography by using 98/2 hexane/ether eluent (2.198 gr., 47%). The less polar chromatography fraction was found to be as Top-diastereomer (0.220 gr.). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ : 7.36 (s, 2H), 5.56 (s, 1H), 5.29 (s, 1H), 5.07 (s, 2H), 4.82 (s, 1H), 3.86 (s, 3H), and 1.51-1.44 (d, 6H, 21 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ : 232.4, 130.3, 128.5, 127.4, 126.8, 125.3, 124.8, 60.6, 46.4, 43.6, 26.9, and 24.3. IR (neat) 3429.8 (br), 2936.2, 2366.0, 1985.5, 1893.5, and 1668.1 cm$^{-1}$ [\(\alpha\)]$_{D}$ = +60.7 (c = 0.5, CHCl$_3$). The more polar chromatography fraction was found to be as Bottom-diastereomer (1.978 gr.). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ : 7.31 (s, 2H), 5.56 (s, 1H), 5.29 (s, 1H), 5.08 (s, 2H), 4.54 (s, 1H), 3.71 (s, 3H), and 1.51-1.44 (s, 6H, 21 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ : 232.4, 129.8, 128.3, 127.9, 126.3, 125.4, 123.7, 60.8, 46.2, 43.9, 26.5, and 23.2. IR (neat) 3446.8 (br), 1974.5, 1880.9, 1651.1, 1548.9, 1463.8, 1259.6, 1166.0, 1021.3, and 842.6 cm$^{-1}$. [\(\alpha\)]$_{D}$ = +19.9 (c = 0.5, CHCl$_3$).
Photolysis of 1, S, S-1, 2, -dimethyl acetal (m-methoxy) styrene chromium(0) tricarbonyl. The following reaction procedure typical: To the quartz test tube triphenyl phosphine (0.617 gr., 2.35 mmol) was added and the more polar diastereomer, 1-S, S-1,2, -dimethyl acetal (m-methoxy) styrene chromium(0) tricarbonyl (0.081 gr., 0.235 mmol) was dissolved in distilled benzene (5 ml), added to the quartz tube. The mixture was deoxygenated under nitrogen atmosphere for 10 minutes, then with argon filled balloon, was placed to the photolysis oven. The solution was photolized for 4 hours. Evaporation of the solvent and the column chromatography with 95/5 hexane/ether eluent afforded 1- S, S-1,2, -dimethylacetal (m-methoxy) styrene chromium(0) dicarbonyl triphenyl phosphine as a yellow powder (0.062 gr., 45.6%). $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ : 7.15-7.03 (s, 15H, 36 Hz), 5.72 (s, 1H), 4.86 (s, 1H), 4.51-4.49 (d, 1H, 6 Hz), 4.36 (s, 1H), 4.14-4.10 (d, 2H, 12 Hz), 4.02 (s, 1H), 3.18-3.14 (s, 3H, 12 Hz) and 1.44-1.36 (d, 6H, 24 Hz).
Photolysis of 1,R, S-1,2, -dimethyl acetal (m-methoxy) styrene chromium(0) tricarbonyl. To the quartz test tube PPh₃ (0.114 gr., 0.436 mmol) was added and the less polar diastereomer, 1-R, S-1,2, -dimethyl acetal (m-methoxy) styrene chromium(0) tricarbonyl (0.015 gr., 0.0436 mmol) was dissolved in distilled benzene (5 ml), added to the quartz tube. The mixture was deoxygenated under nitrogen atmosphere for 10 minutes, then with argon filled balloon, was placed to the photolysis oven. The solution was photolized for 4 hours. Evaporation of the solvent and the column chromatography with 98/2 hexane/ether eluent afforded 1,R, S-1,2, -dimethylacetal (m-methoxy) styrene chromium(0) dicarbonyl triphenyl phosphine (0.018 gr., 71%). \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)) \(\delta\) : 7.14- 7.01 (s, 15H, 39 Hz), 5.72 (s, 1H), 4.85 (s, 1H), 4.51-4.49 (d, 1H, 6 Hz), 4.36 (s, 1H), 4.14 (d, 2H), 4.02 (s, 1H), and 3.15-3.11 (s, 3H, 12 Hz)
Photolysis of 1,R, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium(0) tricarbonyl. To the quartz test tube PPh₃ (0.679 gr., 2.59 mmol) was added and the less polar diastereomer, 1-R, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium(0) tricarbonyl (0.116 gr., 0.259 mmol) was dissolved in distilled benzene (3 ml), added to the quartz tube. The mixture was deoxygenated under nitrogen atmosphere for 10 minutes, then with argon filled balloon, was placed to the photolysis oven. The solution was photolized for 4 hours. Evaporation of the solvent and the column chromatography with 95/5 hexane/ether eluent afforded 1,R, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium(0) dicarbonyl triphenyl phosphine (0.095 gr., 53.6%). ¹H NMR (300 MHz, C₆D₆) δ: 7.15-7.03 (s, 15H, 36 Hz), 5.72 (s, 1H), 5.16 (s, 1H), 4.74-4.70 (d, 2H, 12 Hz), 4.44 (s, 1H), 3.84 (s, 1H), 3.75 (s, 1H), 3.61-3.53 (s, 3H, 24 Hz), and 0.25-0.01 (d, 18H, 72 Hz).
Photolysis of 1, S, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium(0) tricarbonyl. To the quartz test tube PPh₃ (0.226 gr., 0.863 mmol) was added and the more polar diastereomer, 1-S, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium(0) tricarbonyl (0.039 gr., 0.087 mmol) was dissolved in distilled benzene (2 ml), added to the quartz tube. The mixture was deoxygenated under nitrogen atmosphere for 10 minutes, then with argon filled balloon, was placed to the photolysis oven. The solution was photolized for 4 hours. Evaporation of the solvent and the column chromatography with 95/5 hexane/ether eluent afforded 1,R, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium(0) dicarbonyl triphenyl phosphine (0.033 gr., 55.9%). ¹H NMR (300 MHz, C₆D₆) δ: 7.15-7.04 (s, 15H, 33 Hz), 5.19 (s, 1H), 4.86 (s, 1H), 4.76 (s, 1H), 4.51 (s, 1H), 4.31-4.27 (br, 1H, 12 Hz), 4.14- 4.12 (d, 1H, 6 Hz), 4.05-4.03 (d, 1H, 6 Hz), 3.18-3.14 (s, 3H, 12 Hz), and 0.21-0.06 (d, 18H, 45 Hz).
Deprotection of 1,R, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium (0) dicarboxyl triphenyl phosphine. The less polar diastereomer of 1,R, S-1,2, -di (trimethylsilyloxy) (m-methoxy) styrene chromium(0) dicarboxyl triphenyl phosphine (0.026 gr., 0.038 mmol) was dissolved in distilled MeOH (2 ml) under nitrogen atmosphere and to the solution potassium carbonate (0.500 gr., 3.617 mmol) was added, the mixture was stirred at R.T. for 20 minutes. Filtration through a small plug silica gel with EtOAc (50 ml) afforded the title product as a yellow powder (0.020 gr., 100%). $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$: 7.15-7.03 (s, 15H, 36 Hz), 5.52 (s, 1H), 4.86 (s, 1H), 4.50-4.47 (d, 1H, 9 Hz), 4.27-4.24 (d, 1H, 9 Hz), 4.04 (s, 1H), 3.82 (s, 1H), 3.48 (s, 1H), and 3.17-3.13 (s, 3H, 12 Hz). $^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta$: 232.4, 133.3, 133.0, 132.6, 129.4, 128.7, 127.3, 126.9, 29.8, 26.5, and 25.3. IR (neat) 3429.8, 2927.7, 2366.0, 1889.4, 1838.3, 1736.2, 1438.3, and 1251.1 cm$^{-1}$. MS (m/e) 538 (M$^+$, 8.05%). $[\alpha]_D^{20}$ = +39.8 (c=0.5, CH$_3$OH).
Deprotection of 1, S-1,2, -di(trimethylsilyloxy) (m-methoxy) styrene chromium (0) dicarbonyl triphenyl phosphine. The more polar diastereomer of 1,S, S-1,2, -di (trimethylsilyloxy) (m-methoxy) styrene chromium(0) dicarbonyl triphenyl phosphine (0.033 gr., 0.048 mmol) was dissolved in distilled MeOH (2 ml) under nitrogen atmosphere and to the solution potassium carbonate (0.500 gr., 3.62 mmol) was added, the mixture was stirred at R.T. for 30 minutes. Filtration through a small plug silica gel with EtOAc (50 ml) afforded the title product as a yellow powder (0.024 gr., 92.3%). MS (m/e) 538 (M⁺, 8.05%). ¹H NMR (300 MHz, C₆D₆) δ : 7.15-7.02 (s, 15H, 39 Hz), 5.51 (s, 1H), 4.83 (s, 1H), 4.50-4.48 (d, 1H, 6 Hz), 4.27-4.24 (d, 1H, 9 Hz), 4.04 (s, 1H), 3.86 (s, 1H), 3.44 (s, 1H), and 3.19-3.15 (s, 3H, 12 Hz). ¹³C NMR (75 MHz, C₆D₆) δ : 233.7, 133.1, 133.0, 132.3, 128.7, 128.6, 128.0, 127.6, 127.4, 29.8, 26.5, and 25.3. IR (neat) 3455.3, 2927.7, 2851.1, 1889.4, 1829.8, 1736.2, 1608.5, 1438.3, 1063.8, 748.9, and 706.4 cm⁻¹. MS (m/e) 538 (M⁺, 10.76%). [α]_D = +178.6 (c=0.5, CH₃OH ).
Preparation of racemic Diol’s and Racemic Protected Diol’s of Discussed Olefins for HPLC

Preparation of racemic 1,2-di-hydroxy (m-methoxy) styrene  To a round bottomed flask, m-methoxy styrene (0.268 gr., 2.0 mmol) was placed with NMO (Methyl Morpholine - N-oxide) (0.235 gr., 2.0 mmol) in the presence of 2/5/10 ratio t-BuOH (0.4 ml), acetone (1 ml), water (2 ml) mixture as a solvent, then OsO$_4$ (1.56 mgr., 6.29x10$^{-3}$ mmol) was added to the flask. The reaction mixture was stirred at R.T. for 24 hours following by TLC. After adding 1 gr. of sodium hydrosulfite (Na$_2$S$_2$O$_4$), the reaction mixture was washed with EtOAc (50 ml) and extracted with saturated NaCl (50 ml), filtered through a small plug of silica gel with EtOAc (50 ml). Solvent evaporation and column chromatography with 70/30 hexane/EtOAc afforded the title product as a colorless oil (0.175 gr., 52%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ : 7.25-7.22 (t, 1H, 9 Hz), 6.93-6.91 (d, 1H, 6 Hz), 6.89-6.86 (d, 1H, 9 Hz), 6.83-6.80 (t, 1H, 9 Hz), 4.75-4.72 (d, 1H, 9 Hz), 4.31 (s, 1H), 4.01 (s, 1H), and 3.78-3.74 (s, 3H, 12 Hz).
Preparation of racemic 1,2,-dihydroxy 1-naphthyl ethylene. To a round bottomed flask, 1-naphthyl ethylene (0.200 gr., 1.297 mmol) was placed with NMO (Methyl Morpholine - N - oxide) (0.153 gr., 1.297 mmol) in the presence of 2/5/10 ratio t-BuOH (0.08 ml), acetone (0.2 ml), water (0.5 ml) mixture as a solvent, then OsO₄ (1.0 mgr., 3.85x10⁻³ mmol) was added to the flask. The reaction mixture was stirred at R.T. for 28 hours following by TLC. After adding 1 gr. of sodium hydrosulfite (Na₂S₂O₄), the reaction mixture was washed with EtOAc (50 ml) and extracted with saturated NaCl (50 ml), then filtered through a small plug of silica gel with EtOAc (50 ml). Solvent evaporation and column chromatography with 70/30 hexane/EtOAc yielded the title product as a white powder (0.152 gr., 62%). ¹H NMR (300 MHz, CDCl₃) δ : 8.04-8.01 (d, 1H, 9 Hz), 7.88-7.78 (q, 2H, 30 Hz), 7.69-7.66 (d, 1H, 9 Hz), 7.47-7.42 (d, 3H, 15 Hz), 5.63-5.60 (d, 1H, 9 Hz), 3.96-3.94 (d, 1H, 6 Hz), and 3.81-3.77 (t, 1H, 12 Hz).
Preparation of racemic 1,2-dihydroxy 2-naphthyl ethylene. To a round bottomed flask, 2-naphthyl ethylene (0.200 gr., 1.297 mmol) was placed with NMO (Methyl Morpholine - N - oxide) (0.153 gr., 1.297 mmol) in the presence of 2/5/10 ratio t-BuOH (0.08 ml), acetone (0.2 ml), water (0.5 ml) mixture as a solvent, then OsO₄ (1.0 mgr., 3.85x10⁻³ mmol) was added to the flask. The reaction mixture was stirred at R.T. for 28 hours following by TLC. After adding 1 gr. of sodium hydrosulfite (Na₂S₂O₄), the reaction mixture was removed and washed with EtOAc (50 ml). Solvent evaporation and column chromatography with 70/30 hexane/EtOAc yielded the title product as a white powder (0.216 gr., 88%). ¹H NMR (300 MHz, CDCl₃) δ : 7.84-7.72 (s, 4H, 24 Hz), 7.48-7.41 (s, 3H, 21 Hz), 5.01 (s, 1H), 3.84-3.81 (d, 1H, 9 Hz), and 3.77-3.75 (d, 1H, 6 Hz).
Preparation of racemic 1,2-\(-\)dimethylacetal (m-methoxy) styrene. To a round
bottomed flask, catalytic amount of tosulic acid (5.2 mgr., \(2.74 \times 10^{-2}\) mmol) and 1,2,
-dihydroxy (m-methoxy) styrene (0.046 gr., 0.274 mmol) were placed together in the
presence of DMF (2 ml, 0.2 M in hexane), 2,2-\(-\)dimethoxy propane (0.050 ml, 0.410
mmol) was added to the solution and the mixture was stirred at R.T. for 24 hours, washed
with EtOAc (50 ml) and extracted with 1% HCl three times. The organic extracts were
combined and the solvent was evaporated. Column chromatography of the crude mixture
with 70/30 hexane/ether eluent afforded the title product as a colorless oil (0.044 gr.,
77%). \(^1\)H NMR (300 MHz, \(\text{CDCl}_3\)) \(\delta\) : 7.37-7.29 (s, 2H, 24 Hz), 6.94 (s, 1H), 6.85-6.82
(d, 1H, 9 Hz), 5.08-5.03 (t, 1H, 15 Hz), 4.32-4.27 (t, 1H, 15 Hz), 3.81-3.73 (s, 3H, 24
Hz), 3.70-3.67 (t, 1H, 9 Hz), and 1.55-1.48 (d, 6H, 21 Hz). \(^1\)\(^3\)C NMR (75 MHz, \(\text{CDCl}_3\))
\(\delta\) : 128.9, 127.1, 125.7, 122.5, 117.7, 108.7, 87.5, 60.5, 48.3, 35.6, 27.5, and 13.6.
Preparation of racemic 1,2, -dimethylacetal 1-naphthyl ethylene. To a round bottomed flask, catalytic amount of tosulic acid (3 mgr., $1.75 \times 10^{-2}$ mmol), 1,2, -dihydroxy 1-naphthyl ethylene (0.033 gr., 0.175 mmol) were placed together in the presence of DMF (0.875 ml, 0.2 M in hexane) under nitrogen atmosphere. Then to the solution 2,2, -dimethoxy propane (0.032 ml, 0.263 mmol) was added and the mixture was stirred at R.T. for 24 hours, washed with EtOAc (50 ml) and extracted with 1% HCl three times. The organic extracts were combined and the solvent was evaporated. Column chromatography with 70/30 hexane/ether eluent afforded the title product as a white powder (0.040 gr., 100%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.90-7.82 (s, 2H, 24 Hz), 7.82-7.75 (t, 2H, 21 Hz), 7.53-7.47 (d, 3H, 18 Hz), 5.87-5.82 (t, 1H, 15 Hz), 4.66-4.61 (t, 1H, 15 Hz), 3.83-3.78 (t, 1H, 15 Hz), and 1.65-1.53 (d, 6H, 24 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 135.2, 133.5, 128.8, 128.2, 128.0, 126.1, 122.6, 109.4, 75.2, 70.8, 26.4, and 25.7.
Preparation of racemic 1,2, -dimethylacetal 2-naphthyl ethylene. To a round bottomed flask, catalytic amount of tosolic acid (3 mgr., 1.57x10^-2 mmol), 1,2, -dihydroxy 2-naphthylethylene (0.030 gr., 0.157 mmol) were placed together in the presence of DMF (0.784 ml, 0.2 M in hexane) under nitrogen atmosphere 2,2, -dimethoxy propane (0.029 ml, 0.235 mmol) was added to the solution and the mixture was stirred at R.T. for 24 hours, washed with EtOAc (50 ml) and extracted with 1% HCl three times. The organic extracts were combined and the solvent was evaporated. Column chromatography with 70/30 hexane/ether eluent afforded the title product as a white powder (0.036 gr., 86%).

\[ ^1H \text{ NMR (300 MHz, CDCl}_3) \delta : 7.85-7.75 \text{ (d, 4H, 30 Hz), 7.63-7.59} \text{ (s, 1H, 12 Hz), 7.51-7.40} \text{ (d, 2H, 33 Hz), 5.67-5.63} \text{ (t, 1H, 12 Hz), 4.15-4.11} \text{ (d, 1H, 12 Hz), 3.77-3.75} \text{ (d, 1H, 6 Hz), and 2.13-2.00} \text{ (d, 6H, 39 Hz).} \]

\[ ^{13}C \text{ NMR (75 MHz, CDCl}_3) \delta : 137.5, 134.7, 132.0, 131.8, 128.4, 127.7, 127.4, 127.1, 126.7, 125.2, 47.9, 35.9, 25.8, \text{ and 21.2.} \]
Preparation of S-1,2, -dioxy (m-methoxy) styrene bromoborane (catalyst C). To a solution of 31 S-1,2, -dihydroxy m-methoxy styrene (0.0526 gr., 0.328 mmol) in the flask dissolved in anhydrous dichloromethane (2 ml) was added with a syringe at -80 °C of BH$_2$Br.DMS (0.313 ml, 0.313 mmol in 1 M solution of dichloromethane). The mixture was allowed to warm up slowly to R.T. by stirring. The reaction was followed by TLC. After removing of volatile components in vacuo continued to next reaction. Due to continuity of the next reaction no spectral data were taken.
Preparation of 1, R, S-1,2, -dioxy (m-methoxy) styrene chromium(0) tricarbonyl bromoborane (catalyst D). To a solution of 45 S-1,2, -dihydroxy m-methoxy styrene chromium(0) tricarbonyl (0.057 gr., 0.188 mmol) in the flask dissolved in anhydrous dichloromethane (2.5 ml) was added with a syringe at -80 °C of BH2Br.DMS (0.282 ml, 0.282 mmol in 1 M solution of dichloromethane). The mixture was allowed to warm up slowly to R.T. by stirring. The reaction was followed by TLC. After removing of volatile components in vacuo continued to next reaction. Due to continuity of the next reaction no spectral data were taken.
Preparation of 1, S, S-1,2, -dihydroxy (m-methoxy) styrene chromium(0) tricarbonyl bromoborane (catalyst E). To a solution of 47 S-1,2, -dihydroxy m-methoxy styrene chromium(0) tricarbonyl (0.073 gr., 0.240 mmol) in the flask dissolved in anhydrous dichloromethane (2.5 ml) was added with a syringe at -80 °C of BH₂Br.DMS (0.360 ml, 0.360 mmol in 1 M solution of dichloromethane). The mixture was allowed to warm up slowly to R.T. by stirring. The reaction was followed by TLC. After removing of volatile components in vacuo continued to next reaction. Due to continuity of the next reaction no spectral data were taken.
Use of S-1,2, -dioxy (m-methoxy) styrene bromoborane as a catalyst in Diels-Alder reaction. To catalysis solution (0.080 gr., 0.313 mmol), dissolved in methylene chloride (3 ml) cooled to -80 °C with acetone bath, cyclopentadiene (0.412 ml, 6.24 mmol) and 2-methyl acrolein (0.260 ml, 3.146 mmol) (both freshly distilled) were added to the reaction mixture rapidly by syringe. The mixture was stirred at -80 °C for 22 hours, following by TLC, and allowed to warm up to the R.T. and quenched with saturated NaHCO₃ two times (20 ml) then extracted with methylene chloride (10 ml). The crude reaction mixture was then filtered with methylene chloride (50 ml) and the solvent was evaporated at 0 °C. Column chromatography with silica gel by using 90/10 hexane/ether eluent afforded the products (0.425 gr., 99%). After using Europium (III) Chiral Shift Reagent in NMR the racemic mixture of exo and endo products were observed. $^1$H NMR (300 MHz, CDCl₃) $\delta$: exo 11.702, $\delta$: endo 11.932, exo/endo 1.48/1, ee = (0.1742 - 0.1179) / (0.1742 + 0.1179) = 19.4% ee
The use of 1-R, S-1,2, -dioxy m-methoxy styrene chromium(0) tricarbonyl bromoborane (catalyst D) in Diels-Alder reaction. To catalysis solution (0.074 gr., 0.187 mmol), dissolved in methylene chloride (2 ml) was added and cooled to -80 °C with acetone bath. The cyclopentadiene (0.247 ml, 3.74 mmol) and 2-methyl acrolein (0.155 ml, 1.87 mmol) (both freshly distilled) were added to the reaction mixture rapidly by syringe. The mixture was stirred at -80 °C for 18 hours, and allowed to warm up to R.T. and quenched with saturated NaHCO₃ (20 ml), and extracted with methylene chloride (10 ml). The crude reaction mixture was then filtered with methylene chloride (50 ml) and the solvent was evaporated at 0 °C. Column chromatography with silica gel by using 90/10 hexane/ether eluent afforded the products (0.266 gr., 99%). After using Europium (III) Chiral Shift Reagent in NMR enantiomeric excess was calculated as follows: ¹H NMR (300 MHz, CDCl₃) δ : exo 10.7385, endo 10.7734, exo/endo 1.80/1, ee= (2.671-1.485) / (2.671+1.485) = 28.5% ee.
The use of 1-S, S-1,2, -dioxy m-methoxy styrene chromium(0) tricarbonyl titanium chloride as a catalyst in Diels-Alder reaction. To catalysis solution (0.094 gr., 0.240 mmol), dissolved in methylene chloride (2 ml) was added and cooled to -80 °C with acetone bath. The cyclopentadiene (0.317 ml, 4.80 mmol) and 2-methyl acrolein (0.198 ml, 2.40 mmol) (both freshly distilled) were added to the reaction mixture rapidly by syringe. The mixture was stirred at -80 °C for 18 hours, and allowed to warm up to R.T. and quenched with saturated NaHCO₃ (20 ml), and extracted with methylene chloride (10 ml). The crude reaction mixture was then filtered with methylene chloride (50 ml) and the solvent was evaporated at 0 °C. Column chromatography with silica gel by using 90/10 hexane/ether eluent afforded the products (0.271 gr., 83%). After using Europium (III) Chiral Shift Reagent in NMR enantiomeric excess was calculated as follows: \(^1\)H NMR (300 MHz, CDCl₃) \(\delta\): exo 12.0443, endo 12.1138, exo/endo 1.50/1, ee = (3.1165-2.0717) / (3.1165+2.0717) = 20.1% ee.
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nm  | Nanometer
NMR | Nuclear magnetic resonance spectroscopy
Ph  | Phenyl
ppm | Part per million
R.T. | Room temperature
q   | Quartet
s   | Singlet
t   | Triplet
TBAF | Tetra butyl ammonium fluoride
TBS-Cl | t-Butyl dimethyl silyl chloride
THF | Tetrahydofuran
TLC | Thin layer chromatography
TMS-Cl | Trimethyl silyl chloride
TsOH | Tosulic acid
REFERENCES


17. Nonlinear Substituent Interactions and the Electron Richness of Substituted (η\textsubscript{6}-Arene)Cr(CO)\textsubscript{3} Complexes As Measured by IR and \textsuperscript{13}C NMR Spectroscopy and Cyclic Voltammetry: Role of π-Donor and π-Acceptor Interactions; Hunter, A. D.; Mozol, V.; Tsai, S. D.; Organometallics, 1992, 11, 2251.


21. In addition, the increase in arene basicity on addition of π donor groups e.g. methoxy is often relatively minor [benzoic acid pKa= 4.2; o methoxy benzoic acid pKa= 4.1; p methoxy benzoic acid pKa= 4.5]. Mixed ligand η\textsubscript{6} arene chromium carbonyl complexes however, often have a more pronounced effect [HOOCC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{3} pKa= 4.77; HOOCC\textsubscript{6}H\textsubscript{5}Cr(CO)\textsubscript{2}PPh\textsubscript{3} pKa= 6.15 both relative to control substrate HOOCC\textsubscript{6}H\textsubscript{5} pKa= 5.68 under these conditions] and additionally, catalyst architecture will generally be preserved.


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