Synthesis of New Chiral Phosphine Ligands and Their Applications in Asymmetric Catalysis

von

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Erklärung


Ehrenwörtliche Versicherung

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Parts of this Ph. D. thesis have been published:


To my parents
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1. General Introduction

Molecular chirality plays a key role in science and technology.\(^1\) Many organic compounds are chiral and many enantiomerically pure compounds are widely used in the preparation of cosmetics, flavours, pesticides, vitamins and pharmaceuticals.\(^2\) There are many examples which stress the necessity for preparing enantiomerically pure compounds. For example, the market for single enantiomer drugs in 1996 was $73 billion, which increased to $96 billion in 1998 and to $123 billion in 2000. The market for enantiopure materials continues to increase\(^3\); hence the search for efficient ways to access enantiomerically enriched compounds is still an active area of research to synthetic organic chemists.\(^4\)

To access enantiomerically pure compounds there are four main approaches.

1. Resolution of a racemic mixture
2. Synthesis from a chiral pool and synthesis using a chiral auxiliary\(^5\)
3. Synthesis using biocatalysts (enzymes, cell cultures and antibody)\(^6\)
4. Asymmetric catalysis using a man made chiral catalyst.

Among this variety of methods, asymmetric catalysis has proved to be an ideal method to prepare naturally and nonnaturally occurring chiral compounds in large quantities by using small amounts of chiral catalyst.

In the past three decades, many metal complexes using various chiral ligands have been found that catalyze various reactions with impressive enantioselectivities. However, despite the impressive progress in this area, the design of suitable chiral ligands for a particular application remains a formidable task.\(^7\) Hence the design of new chiral ligands for

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asymmetric catalysis is a highly active field of research\textsuperscript{8} that concentrates especially on chiral P,P and P,N-ligands, since this type of ligands plays a wide role in transition-metal-catalyzed asymmetric reactions.

1.1 Chiral P,P-ligands

The concept of $C_2$-symmetry in ligands was first introduced when Kagan developed the ligand DIOP.\textsuperscript{9} The main advantage of having a $C_2$-symmetrical axis in ligands is that it reduces the number of possible competing, diastereomeric transition states.\textsuperscript{10} In 1980, Noyori reported an axially chiral ligand, BINAP, which expanded the scope of transition-metal-catalyzed asymmetric hydrogenations.\textsuperscript{11,12} Since then many chiral P,P-ligands have been prepared and have played a successful role in transition-metal-catalyzed asymmetric reactions. BPPM\textsuperscript{13} (Achiwa), CHIRAPHOS\textsuperscript{14} (Bosnich), DuPHOS\textsuperscript{15} (Burk), BICP\textsuperscript{16} (Zhang), PHANEPHOS\textsuperscript{17} (Rossen), PENNPHOS\textsuperscript{18} (Zhang), BIPHEMP\textsuperscript{19} (Schönholzer), P-PHOS\textsuperscript{20} (Chan), SEGPHOS\textsuperscript{21} (Mikami) and TANGPHOS\textsuperscript{22} (Zhang) are some of the successful examples in this field (Figure 1).
These ligands were extensively employed in Rh-catalyzed asymmetric hydrogenation of enamides giving rise to the corresponding amino acid derivatives with high enantioselectivities (Scheme 1).\(^{23}\)

**Scheme 1.** Asymmetric hydrogenation of enamides using chiral diphosphine ligands

One of the outstanding industrial achievements using these chiral ligands in asymmetric catalysis is the widely known Takasago’s industrial synthesis of (−)-menthol (4) starting from myrcene. The crucial step is asymmetric isomerization of diethylgeranylamine (1) to 3-(R)-citronellal enamine (3) using the catalyst [(S)-BINAP]\(_2\)Ru\(^{+}\)ClO\(_4\)\(^-\) (2) (Scheme 2).\(^{24}\)

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1.1.1 Ferrocenyl P,P-ligands

Since the discovery of ferrocene in 1951,\(^{25}\) its fascinating sandwich structure has caught the attention of chemists as a potential platform for the preparation of new ligands for asymmetric catalysis.\(^{26}\) A very interesting structural feature in ferrocene chemistry is planar chirality. This means that compounds substituted at positions 1 and 2 with different groups are chiral because of the loss of plane of symmetry (Figure 2).

![Figure 2. Planar chirality in 1,2-disubstituted ferrocene](image)

The pioneering work of Ugi\(^{27}\) et al. on the \(C_2\)-functionalization of enantiopure \(N,N\)-dimethyl-1-ferrocenylethylamine, in which planar chirality was introduced into the ferrocene backbone using a diastereoselective \textit{ortho} lithiation with an appropriate chiral \textit{ortho}-directing group and subsequent \textit{in situ} trapping with an electrophile has become a standard methodology for the preparation of such compounds. In 1974 Hayashi reported the first example of a planar-chiral enantiopure ferrocenyl phosphate by introducing the ligand PPFA \((N,N\text{-dimethyl-1-[2-((diphenylphosphino)ferrocenyl]ethylamine})\).\(^{28}\) Its high reactivity was a

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landmark in the development of chiral ferrocene ligands for asymmetric catalysis. Josiphos,\textsuperscript{29} Taniaphos,\textsuperscript{30} Walphos\textsuperscript{31} and Bophoz\textsuperscript{32} are some successful examples (Figure 3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{chiral_ferrocenyl_ligands}
\caption{Chiral ferrocenyl P,P-ligands.}
\end{figure}

These ligands were successfully applied in Rh, Ru, Ir, and Pd-catalyzed asymmetric reactions providing high enantioselectivities and also noteworthy applications in industrial chemistry.\textsuperscript{26c} One of the intensive application to mention here is the preparation of (+)−Biotin (Lonza AG)\textsuperscript{33,34} and (S)-Metolachlor\textsuperscript{33} (Syngenta)\textsuperscript{33,35} using Josiphos by transition-metal-catalyzed hydrogenation reactions (Scheme 3).

Scheme 3. Industrial preparation of \((\rightarrow)-\text{Biotin}\) and \((S)-\text{Metolachlor}\)\(^{\circledast}\) using ferrocenyl P,P-ligand Josiphos.

Another very successful ferrocenyl ligand, reported by Knochel \textit{et al},\(^{30}\) which has found broad applications in transition-metal-catalyzed asymmetric catalysis, is Taniaphos (5). This ligand was prepared \textit{via} diastereoselective \textit{ortho}-lithiation using Ugi’s amine (Scheme 4).

Scheme 4. Preparation of Taniaphos
The second generation of Taniaphos was later prepared by replacing the dimethylamino group with a methoxy group at the α-position. This was prepared *via* diastereoselective *ortho*-lithiation using a sulfoxide (Scheme 5).³⁶

Scheme 5. Synthesis of second generation Taniaphos via sulfoxide approach

Taniaphos has been successfully applied in Rh and Ru-catalyzed hydrogenation of olefins, β-keto esters,³⁷ Cu-catalyzed 1,4-addition of cyclic and acyclic unsaturated ketones,³⁸ and aldol, Mannich-type reactions (Scheme 6).³⁹

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Scheme 6. Application of Taniaphos in asymmetric catalysis.

1.2 Chiral P,N-ligands

P,N-ligands are another important class in chiral ligands. To date, many P,N-ligands have been prepared and successfully applied in asymmetric catalysis. The success of these mixed donor ligands in metal-catalyzed asymmetric catalysis arises from the fact that they are a class of hemi labile ligands possessing a combination of hard and soft donor atoms. Therefore, the different features associated with each donor atom provide a unique reactivity to their metal complexes. Axially chiral aminophosphines such as Quinap, MAP, PINAP, Pyphos, phosphoryloxazolines such as PHOX, iminophosphine ligands such as VALAP and phosphinoarylpyridine ligands such as PINPHOS, CANPHOS, are representative examples of the variety of classes in this area (Figure 4).

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These chiral P,N-ligands have been successfully applied in Pd-catalyzed asymmetric alkylations\textsuperscript{52} and asymmetric Heck reactions,\textsuperscript{53} Rh-catalyzed asymmetric hydroboration reactions,\textsuperscript{54} Cu-catalyzed conjugated addition of dialkylzinc species to enones\textsuperscript{55} and Ir-catalyzed asymmetric hydrogenation reactions.\textsuperscript{56} Among these chiral P,N-ligands, phosphanyloxazolines (6) have proved to be the most efficient chiral ligands for metal-catalyzed asymmetric reactions. The syntheses of chiral phosphinoxazolines were reported independently, by Helmchen,\textsuperscript{57} Pfaltz,\textsuperscript{58} and Williams\textsuperscript{59}. The synthesis of PHOX ligands reported by Pfaltz \textit{et al.} is shown in scheme 7.

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1.2.1 Chiral Ferrocenyl P,N-ligands

Similar to the chiral ferrocenyl P,P-ligands, many chiral P,N-ligands based on the ferrocene backbone have been prepared and found successful applications in asymmetric catalysis. Ferrrocenyl oxazolinylphosphine (Fc-PHOX) its analogues, and PPFA-type ligands have proved to be the most successful ligands for asymmetric catalysis. Fc-PHOX ligands have been successfully applied in an amazing variety of enatioselective processes. Some of the successful applications to mention here are Pd-catalyzed asymmetric Heck reactions, Cu-catalyzed asymmetric 1,3-dipolar addition reactions, Ru and Ir-catalyzed hydrogenation reactions (Scheme 8).
2. Objectives

As shown in the previous section, Taniaphos and its analogues compounds are important ligands in asymmetric catalysis. To further explore this class of compounds, the main objectives of this work were firstly the development of new chiral P,P- or P,N-ligands based on the Taniaphos structure, and secondly to study their applications in transition-metal-catalyzed asymmetric reactions.

2.1 Ferrocenyl P,P-ligands

The first objective of this work was to prepare the new chiral ferrocenyl P,P-ligand 8 (Figure 5) in enantiomerically pure form and use this ligand in asymmetric catalysis.

2.2 Chiral Ferrocenyl P,N-ligand

Based on the progress in the synthesis of new chiral P,N-ligands and their successful applications in asymmetric catalysis, it was of interest to prepare chiral P,N-ligands based on the Taniaphos structure. The objectives of this work were to synthesize new chiral ferrocenyl P,N-ligands 9 and 10 (Figure 6) by replacing one of the phosphines by a N-donor group such as pyridine in Taniaphos and to test their efficiency in asymmetric catalysis.

2.3 Bis-ferrocenyl P,P-ligands

The third objective of this work was to prepare the new ferrocenyl ligand 11 (Figure 7), which bares structural similarities to Taniaphos and to apply this ligand in metal-catalyzed asymmetric reactions.
2.4. Chiral Paracyclophane P,P-ligands

The final objective was to synthesize new paracyclophane diphosphines of type 12, (Figure 8) bearing two different kinds of phosphines and test their efficiency in asymmetric catalysis.

![Figure 8. New paracyclophane diphosphines of type 12](image)

Results and Discussion

1. Synthesis of Planar Chiral Ferrocenyl P,P-ligand and their applications in asymmetric catalysis

1.1. Introduction

1.1.1 Chiral ferrocenyl ligands with planar chirality

In recent years many chiral ferrocenyl ligands have been prepared and have found broad applications in asymmetric catalysis. Many of the chiral ferrocenyl ligands developed, possess both planar and central chiralities, although there are some examples such as Fesulphos, MOPf and Taniaphos derivatives, showing only planar chirality. Fesulphos is a bidentate P,S-ligand and has been successfully applied in asymmetric catalysis. Whereas, Mopf (monophosphine) and Taniaphos derivative 5b (bisphosphine) have found limited applications in asymmetric catalysis due to the moderate selectivities observed (Scheme 9).

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Scheme 9. Applications of Fesulphos, MOPF and Taniaphos-derivative 5c in asymmetric catalysis.

In order to further explore planar chiral ferrocenyl ligands such as 5c, our goal was to prepare ligand 8 (Figure 9) and investigate its properties in asymmetric catalysis.

Figure 9. New chiral ferrocenyl ligand 8 for asymmetric catalysis

1.1.2. Synthesis of 1,2-disubstituted ferrocenes via diastereoselective ortho-metallation

Chiral 1,2-disubstituted ferrocenes have found much attention since these building blocks have emerged as a premiere structural ligand motif in metal-catalyzed asymmetric reactions.\(^6^7\) In 1970, Ugi reported the first example of diastereoselective ortho-lithiation on

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N,N-dimethylamino-1-ferrocenylethylamine using the \(N,N\)-dimethylamino group as an \textit{ortho-}directing group (Scheme 10).\(^{68}\)

\[
\begin{align*}
\text{Me} & \quad \text{NMe}_2 \\
\text{Fe} & \\
\downarrow & \\
\text{BuLi, THF, -78 \degree C} & \\
\text{PPh}_2\text{Cl} & \\
\text{Me} & \quad \text{NMe}_2 \\
\text{Fe} & \\
\end{align*}
\]

\textbf{Scheme 10.} Diastereoselective \textit{ortho-}lithiation on Ugi amine.

In addition to Ugi’s amine, a large number of other chiral \textit{ortho-}directing groups have been described such as sulfoxides,\(^{69}\) acetals,\(^{70}\) oxazolines,\(^{71}\) azepines,\(^{72}\) pyrrolidines,\(^{73}\) hydrazones,\(^{74}\) sulfoximines,\(^{75}\) imidazolines\(^{76}\) and phosphine oxides.\(^{77}\) Among these, the Ugi amine method, the oxazoline approach, and the sulfoxide approach are the most widely used strategies for the preparation of chiral 1,2-ferrocenes (Figure 10).

\[
\begin{align*}
\text{Fe} & \quad \text{NMe}_2 \\
\text{Fe} & \quad \text{O} \\
\text{Me} & \\
\text{Fe} & \quad \text{N} \quad \text{i-Pr} \\
\text{Fe} & \quad \text{R} \\
\text{Fe} & \quad \text{O} \\
\end{align*}
\]

\textbf{Figure 10.} Directing groups for the diastereoselective \textit{ortho-}lithiation on ferrocenes.

The Kagan sulfoxide approach has significantly enlarged the possibilities for preparing structurally diverse 1,2-substituted ferrocenes. The major advantage of this method is that, after a diastereoselective \textit{ortho-}lithiation and substitution, the sulfoxide group can be removed.

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by tert-butyllithium mediated C-S cleavage and the resulting ferrocenyllithium can be reacted with an electrophile (Scheme 11).\textsuperscript{78}

\textbf{Scheme 11.} Preparation of 1,2-disubstituted ferrocenes via Kagan sulfoxide approach

Ligand 8 could therefore be formed in enantiomerically pure form using Kagan’s sulfoxide as shown retrosynthetically in scheme 12.

\textbf{Scheme 12.} Synthetic approach to chiral ferrocenyl P,P-ligand 8

The diphosphine 8 can be prepared by the consecutive, one-pot exchange of bromine and sulfoxide on 16, followed by the addition of chlorodiphenylphosphine. Substrate 16 can be prepared via the diastereoselective lithiation of 14.

\textbf{1.2. Synthesis of Chiral Planar Ferrocenyl P,P-ligand 8}

\textbf{1.2.1. Diastereoselective ortho-lithiation}

The diastereoselective ortho-lithiation on the Kagan sulfoxide 14 using LDA proceeded with >98\% de. The resulting ferrocenyllithium was reacted with 15\textsuperscript{79} at -78 °C to furnish the corresponding ferrocenyl silane compound 16 in 93\% yield and 98\% de (Scheme 13).


\textsuperscript{79} Acemoglu, M. \textit{J. Lable Compd. Radiopharm.} 2002, 45, 361.
Treatment of 16 with \( t\)-BuLi (4.2 equiv) in THF at -78 °C, followed by the addition of chlorodiphenylphosphine led to a mixture of compounds that contained mono and disubstituted phosphines as well as the protolysis product (Scheme 14).

Scheme 13. Diasteroselective \textit{ortho}-lithiation of 14 and reaction with electrophile 15

\[ \text{Si} \quad \text{Br} \quad \text{SO}_{\text{Tol}} \quad \text{MeMe} \]
\[ \text{FeFe} \]
\[ 14:\text{>99\% ee} \]

\[ \text{Si} \quad \text{Cl} \quad \text{MeMe} \]
\[ \text{Br} \]
\[ 15: 1. \text{LDA (1.1 equiv), THF, -78 °C, 30 min} \]
\[ 2. \text{MeSiMeCl, -78 °C, 1 h; rt, 1 h} \]
\[ 16: 93\%; 98\% \text{ de} \]

Scheme 14. Exchange of sulfoxide and bromine using \( t\)-BuLi

1.2.2. Optimization for selective Sulfoxide-Lithium exchange

Since we are obtaining a complex mixture with the simultaneous exchange on 16 using \( t\)BuLi, we decided to perform a stepwise exchange of the sulfoxide and bromine. We screened some organomagnesium reagents and organolithium reagents for a selective exchange of the sulfoxide. For this study we have chosen the \((R_Fc,S)\)-(\(p\)-tolylsulfinyl)-2-bromoferrocene 17 as a test substrate. The bromoferrocene 17 can be synthesized via diastereoselective \textit{ortho}-lithiation of sulfoxide 14, followed by the addition of 1,1,2,2-tetrafluoro-1,2-dibromoethane (Scheme 15).

Scheme 15. Preparation of bromo-sulfoxide 17
With the test substrate in hand, we screened several organomagnesium and lithium reagents, the results are summarized in Table 1.

Table 1. Screening of organometallic reagents for a selective sulfoxide-lithium exchange on 17

<table>
<thead>
<tr>
<th>Entry</th>
<th>Organometallic reagent (RM)</th>
<th>Product (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>t-BuLi (2.2 equiv)</td>
<td>18a: −, 18b: −, 18c: 45</td>
</tr>
<tr>
<td>2</td>
<td>n-BuLi (1.1 equiv)</td>
<td>18a: −, 18b: 75, 18c: &lt;5</td>
</tr>
<tr>
<td>3</td>
<td>i-PrMgCl (1.1 equiv)</td>
<td>18a: 25, 18b: 5, 18c: Traces</td>
</tr>
<tr>
<td>4</td>
<td>PhMgCl (1.1 equiv)</td>
<td>18a: −, 18b: −, 18c: −</td>
</tr>
<tr>
<td>5</td>
<td>PhLi (1.1 equiv)</td>
<td>18a: 75, 18b: 4, 18c: &lt;1</td>
</tr>
</tbody>
</table>

<sup>a</sup>yields refers to the isolated products

Sulfoxide/lithium-exchange using t-BuLi (-78 °C, 10 min) on 17 led to complete exchange of both the bromine and the sulfoxide and gave product 18c in 90% yield (entry 1). Whereas, n-BuLi (-78 °C, 15 min) selectively exchanged the bromine, providing the product 18b in 75% yield (entry 2). Very poor exchange rate was observed with i-PrMgCl (-50 °C, 1 day), but, after long reaction times, we also observed the partial exchange of bromine (entry 3). No exchange (neither bromine nor sulfoxide) was observed with PhMgCl (entry 4). Exchange of sulfoxide using PhLi<sup>80</sup> (-78 °C, 10 min) proceeded selectively and afforded the desired product 18a in 75% yield. We also noticed a partial exchange of bromine and also traces of product 18c (entry 5).

Although exchange of the sulfoxide using PhLi proceeded selectively, the stability of the α-bromoferrocenyllithium species to racemization was unknown. Quenching of the ferrocenyllithium species 19 with diphenyldisulfide as an electrophile using various reaction times gave the ferrocenyl sulfide 20a in 30-72% yield. Measurement of the enantiopurity of the sulfone 21 formed via oxidation with m-CPBA gave an indication of the stability of bromo-lithium species 19 (Table 2).

Table 2. Verifying the configurational stability of α-bromoferrocenyllithium species 19

<table>
<thead>
<tr>
<th>Entry</th>
<th>Quenching the lithium species at $t$ (min)</th>
<th>Product 20a yield(%)$^a$</th>
<th>Product 21 yield(%)$^a$</th>
<th>ee(%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>72</td>
<td>90</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>70</td>
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<td>86</td>
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<td>3</td>
<td>15</td>
<td>66</td>
<td>90</td>
<td>64</td>
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<td>4</td>
<td>20</td>
<td>50</td>
<td>85</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>30</td>
<td>92</td>
<td>Rac</td>
</tr>
</tbody>
</table>

$^a$ isolated yield of analytically pure sample. $^b$ enantioselectivity was measured by chiral HPLC using a chiralcel OD-H column.

As the time before the bromo-lithium species was quenched with the electrophile was increased (5 to 60 min), the enantioselectivity of the desired product 21 dropped. It may be that 19 was undergoing a halogen dance$^{81}$ and thus led to racemization of the product. A possible disadvantage of this method is that the lithium species 19 must be quenched with very reactive electrophiles. To examine the scope of this method, the lithium species 19 was quenched with a variety of electrophiles to form 20a-e in 69-79% yield (Scheme 16). Compound 20c is an especially interesting building block for many cross-coupling reactions and can be accessed only by using this method.

Scheme 16. Preparation of bromoferrocenes of type 20 by the reaction of the lithium species 19 with various electrophiles.
Application of these findings to silyl ferrocene derivative 16, phenyllithium proved to be the appropriate reagent for the selective sulfoxide/lithium-exchange (Scheme 17). The sulfoxide/lithium-exchange on 16 using PhLi, followed by the addition of chlorodiphenylphosphine and in situ protection of the resulting phosphine with sulfur (S\textsubscript{8}, BuNH\textsubscript{2}), provided the thionophosphine compound 22 in 88% yield (Scheme 17).

Further, bromine/lithium-exchange on 22 using \textit{n}-BuLi, followed by reaction with chlorodiphenylphosphine and protection of the phosphine with sulfur, provided the air-stable diphosphine disulfide 24 in 89% yield. Deprotection of diphosphine disulfide 24 was smoothly accomplished using Raney-Ni\textsuperscript{82} in methanol, leading to the diphosphine 8 in 92% yield (Scheme 18).

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1.3. Applications in asymmetric catalysis

1.3.1. Rh-catalyzed hydrogenation of olefins

Explanation of the efficiency of this new chiral ferrocenyl P,P-ligand 8 in the Rh-catalyzed hydrogenation of α-acetamidocinnamate 25 to phenylalanine derivative 26 was conducted. Despite the hydrogenation reaction being quantitative, no selectivity was observed in the desired product 26 (Scheme 19).

\[
\text{Ph} \quad \text{CO}_2\text{Me} \quad \text{[Rh(nbd)$_2$]BF$_4$} \quad \text{Tol:MeOH (1:1)} \quad \text{H}_2, \text{10 bar, rt, 4 h} \quad \text{Ph} \quad \text{CO}_2\text{Me} \\
\text{NHAc} \quad \text{8} \quad \text{25} \quad \text{>95%; rac.} \quad \text{NHAc} \quad \text{26}
\]

Scheme 19. Application of 8 in Rh-catalyzed hydrogenation of 25

1.3.2. Pd-catalyzed asymmetric allylic alkylations

The application of 8 in Pd(0)-catalyzed allylic substitution reactions of racemic 1,3-diphenylprop-2-en-1-yl acetate (±)-27 with dimethylmalonate employing Trost’s procedure\textsuperscript{83} was investigated. [Pd(C$_3$H$_5$)Cl]$_2$ was used as the catalyst precursor in the presence of a mixture of dimethyl malonate, N,O-bis(trimethylsilyl)acetamide (BSA) and potassium acetate in CH$_2$Cl$_2$. Reaction at -20 °C using the ligand 8 provided the desired compound 28 in 90% yield and 30% ee (Scheme 20).

\[
\text{Ph} \quad \text{OAc} \quad \text{[Pd(C$_3$H$_5$)Cl]$_2$ (1 mol%) \quad 8 (2 mol%) \quad CH$_2$(CO$_2$Me)$_2$, KOAc (5 mol%) \quad BSA (3 equiv), CH$_2$Cl$_2$, -20 °C, 10 h \quad \text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
\text{Ph} \quad \text{27} \quad \text{28: 90%; 30% ee} \quad \text{Ph} \quad \text{Ph}
\]

Scheme 20. Pd-catalyzed allylic alkylation using ferrocenyl ligand 8

1.4. Conclusion

In conclusion, the synthesis of the chiral P,P-ligand 8 was achieved. We have shown that phenyllithium is the most efficient reagent for a selective sulfoxide/lithium-exchange on bromoferrocenyl sulfoxide 17. Furthermore, we have applied this methodology to the synthesis of various ferrocene derivatives of type 20. The ligand 8 was applied to Rh-

\textsuperscript{83} Trost, B. M.; Murphy, D. J. Organometallics 1985, 4, 1143.
catalyzed asymmetric hydrogenations and Pd-catalyzed allylic alkylations and very poor selectivities were observed. One of the possible reasons for the poor enantioselectivity using ligand 8 is that the C-Si bond is so long that the two donor phosphines are too far away from each other to form a favourable bite angle in the complex with the transition metal.


2.1 Introduction

Chiral P,N-ligands are one of the most important classes of chiral ligands because they have proved to be efficient in transition-metal-catalyzed asymmetric reactions, particularly in areas where $C_2$-symmetrical ligands failed. During the past two decades an increasing number of P,N-ligands and their catalysts were reported for a wide range of asymmetric reactions and improved the efficiency of existing processes. 2-Phosphinylphenyloxazoline ligands, one of the most successful chiral P,N-ligands, were reported by Pfaltz et al. These ligands have proved to be especially efficient in Ir-catalyzed asymmetric hydrogenation reactions of olefins (Scheme 21).

![Scheme 21. Asymmetric hydrogenation of olefins using Pflatz’s chiral phospineoxazoline ligand](image)

In addition to this Ir-catalyzed hydrogenation of olefins, Knochel et al. have demonstrated the iridium catalyzed hydrogenation of enamides such as 25 to amino acid derivatives 26 using a

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chiral terpene-derived P,N-ligand. This is of interest as it allows for the potential Ir-catalyzed formation of highly enantiomerically pure nonnatural α-amino acid derivatives, which have previously been extensively studied using Rh and Ru-catalysts (Scheme 22).

\[
\begin{align*}
\text{CO}_2\text{Me} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 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2.2. Synthesis of P,N-ligands 9 and 10

2.2.1 Synthesis of ferrocenyl ligands 9 and 10 with a pyridine ring as a N-donor

Initially we tried to synthesize the P,N-ligands 9-10 via a classical route. The phosphines 9a-b can be prepared by the deprotection of the corresponding sulfides. The phosphine sulfides can be prepared via the sulfoxide-lithium exchange of the corresponding ferrocenyl sulfoxide. The methyl ether can be prepared through the O-methylation of the corresponding alcohol which can be prepared by through the diastereoselective ortho-lithiation of the sulfoxide 14 (Scheme 24).

Thus, treating the Kagan sulfoxide 14 with LDA at -78 °C for 30 min, followed by the addition of 2-pyridinecarboxaldehyde, resulted in the alcohol 29 (Scheme 25). This alcohol was quite unstable at room temperature and turned black immediately after isolation.
Scheme 25. Preparation of pyridyl alcohol 29

Because we met the difficulties to isolate 29, we changed our synthetic pathway towards the P,N-ligands of type 9 and 10. Our new synthetic approach is outlined in the Scheme 26.

Scheme 26. Novel synthetic approach to the chiral ferrocenyl P,N-ligands 9-10

The phosphine sulfides 32a-33a and 32b-33b could be prepared by O-alkylation of the alcohols 31a-b. These alcohols can be synthesized through the sulfoxide-lithium exchange on 30, followed by the addition of the 2-pyridinecarboxaldehydes. Phosphine sulfide 30 can be prepared via the diastereoselective ortho-metallation of Kagan sulfoxide 14. Deprotection of phosphine sulfides 32a-33b will furnish chiral P,N-ligands 9-10.

The diastereoselective lithiation of 14 using LDA, followed by the addition of chlorodiphenylphosphine, led to an air sensitive phosphine, which was in situ protected with sulfur leading to the thianophosphinyl ferrocene 30 in 88% yield. Performance of a sulfoxide/lithium-exchange using phenyllithium, followed by the addition of 2-pyridinecarboxaldehyde, led to a 3:2 mixture of diastereomeric ferrocenyl alcohols 31a and 31b as 31 in 72% yield (Scheme 27).
Scheme 27. Preparation of pyridyl alcohol 31

This inseparable mixture of alcohols 31 was alkylated with MeI leading to the separable ferrocenyl methyl ethers 32a and 32b in 54% and 35% yield respectively (Scheme 28). In a similar manner, the alcohol mixture 31 was benzylated using KH and benzyl bromide, leading to separable benzyl ethers 33a and 33b in 56% and 36% yield respectively (Scheme 28).

Scheme 28. Preparation of protected ferrocenyl ligands 32a-33b

The stereochemistry of the two ferrocenyl ethers 32a and 32b at the α-centre was determined by X-ray analysis of the phosphine sulfide 32b as shown in figure 12.87

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87 a) For more details about atomic coordinates, bond lengths, bond angles Cambridge database number CCDC 627426.
The reduction of the phosphine sulfides 32a-33b was achieved smoothly with Raney-Ni in MeOH at 25 °C for 12 h, to furnish the air-stable chiral P,N-ligands 9a-10b in 82-88% yield (Scheme 29). These ligands are quite stable towards air.

Furthermore, we have prepared the ferrocenyl P,N-ligands of type 9c-d and 10c-d by changing the aromatic group on the phosphorus (Scheme 32). Thus, treating the sulfoxide 14
with LDA, followed by the addition of chlorobis(3,5-dimethylphenyl)phosphine, led to the sulfoxide 34 in 85% yield. Performing the sulfoxide-lithium exchange with PhLi, followed by the addition of 2-pyridinecarboxaldehyde, provided the mixture of diastereomeric alcohols 35 in 3:7 ratio ((R\textsubscript{Fc},S):(R\textsubscript{Fc},R)). On the other side, the diastereoselectivity of the alcohols changed to 1:1, when we performed the sulfoxide-lithium exchange using \textit{t}BuLi, followed by the addition of pyridine-2-carboxaldehyde (Scheme 30).

**Scheme 30. Preparation of ferrocenyl alcohol 35**

\[\text{O-alkylation of the alcohol mixture 35 using KH and CH}_3\text{I or PhCH}_2\text{Br led to the corresponding separable methyl ethers 36a (45%), 36b (44%) and benzyl ethers 37a (46%), 37b (44%) respectively (Scheme 31).}\]

**Scheme 31. Preparation of ferrocenyl ethers 36a-b and 37a-b**

Reduction of the phosphine sulfides 36a-b and 37a-b using Raney-Ni in methanol furnished the corresponding phosphine 9c-d and 10c-d in 80-90% yield (Scheme 32).
2.2.2. Synthesis of ferrocenyl P,N-ligands 9-10 with substituted pyridine as a N-donor

In addition, we directed our attention towards the preparation of chiral P,N-ligands having substituted pyridines as a N-donor group. We synthesized some 2-pyridine aldehydes with various substituents at the 6-position.

Treating 2,6-dibromopyridine with a fourfold excess of 2:1 PhMgCl-LiCl/CuCN mixture provided 6-phenyl-2-bromopyridine 39a in 82% yield. In a similar manner, reacting 2,6-dibromopyridine with tBuMgCl-LiCl, afforded 6-tbutyl-2-bromopyridine 39b in 68% yield. The bromine-lithium exchange on substrates 39a and 39b using nBuLi, followed by the addition of DMF, furnished the 2-pyridine aldehydes 40a and 40b in 43% and 82% yield, respectively (Scheme 33).89

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With the precursors in hands, we started our investigation towards the preparation of the new P,N-ligand derivatives of type 9 and 10 with substituted pyrdines as N-donors. Exchange of the sulfoxide on substrate 30 using PhLi at -78 °C, followed by the addition of 40a, led to the two diastereomeric alcohols 41a and 41b as an inseparable diastereomeric mixture 41 in 64% yield. The diastereomeric mixture 41 was treated with KH and CH₃I, to afford the readily separable methyl ethers 42a and 42b in 55% and 34% yield, respectively (Scheme 34).

Scheme 33. Synthesis of 6-substituted 2-pyridine aldehydes.

Scheme 34. Preparation of 6-phenylpyridyl-substituted P,N-ligands 42a-b.
The deprotection of the two phosphine sulfides 42a and 42b was performed using Raney-Ni in MeOH at room temperature overnight, furnishing the corresponding phosphines 9e and 9f in 80-84% yield (Scheme 35).

**Scheme 35.** Preparation of the chiral P,N-ligands 9e and 9f

Surprisingly, when we treated the ferrocenylsulfoxide 30 with PhLi at -78 °C, followed by the addition of 6-tbutyl-2-pyridinecarboxaldehyde 40b, we obtained the two diastereomeric alcohols 43a and 43b as separable compounds in 27% and 47% yield respectively (Scheme 35). Furthermore, the diastereoselectivity of the reaction was opposite to the other analogues 31a-b, 35a-b and 41a-b (Scheme 27 and 31). The (R_Fc,R) compound was obtained as the major diastereomeres and the (R_Fc,S)-compound as the minor one (Scheme 36). This change in the diastereoselectivity may be because of the sterical hindrance of the t-butyl group.

**Scheme 36.** Preparation of the phosphine sulfide 43a-b
Treating the two ferrocenyl alcohols 43a and 43b individually with KH and MeI or BnBr provided the corresponding methyl ethers 44a and 44b in 80% and 82% yield and benzyl ethers 45a-b in 85% yield respectively (Scheme 37). The stereochemistry of both diastereomers was deduced from their $^1$H, $^{13}$C NMR data when compared to that of compounds 32a and 32b.

![Scheme 37. Synthesis of phosphine sulfides 44a-b and 45a-b](image)

Desulfurization of the compounds 44a-b and 45a-b was smoothly accomplished using Raney-Ni in MeOH, furnishing the chiral phosphines 9g-h and 10e-f in 80-89% yield (Scheme 38). We then investigated the reduction of the phosphine sulfides of the ferrocenyl alcohols 43a and 43b. For this reason, we subjected the two ferrocenyl alcohols 43a-b under similar conditions (Raney-Ni, MeOH, rt, overnight) and obtained the corresponding phosphines 10g and 10h in 85% and 80% yields, respectively (Scheme 38).
2.3. Applications in asymmetric catalysis

For clarity, the structure of the chiral P,N-lignads 9a-h and 10a-h is depicted in Scheme 39.
Scheme 39. Overview of novel chiral P,N-ligands 9a-h and 10a-h

2.3.1. Pd-catalyzed asymmetric allylic alkylation

With the novel chiral ligands 9a-h and 10a-h in hand, we examined their applications in Pd(0)-catalyzed allylic substitution reactions of racemic 1,3-diphenylprop-2-en-1-yl acetate (±)-27 with dimethylmalonate, employing [Pd(C₅H₅)Cl]₂ as the catalyst precursor in the presence of a mixture of dimethylmalonate, N,O-bis(trimethylsilyl)acetamide (BSA), and potassium acetate in a solvent. The results are summarized in Table 3.

Table 3. Pd(0)-catalyzed asymmetric allylic substitution of 27 with dimethyl malonate.

<table>
<thead>
<tr>
<th>Entry</th>
<th>L*</th>
<th>Solvent</th>
<th>T[h]</th>
<th>Yield (%)*</th>
<th>ee&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-9a</td>
<td>THF</td>
<td>6</td>
<td>89</td>
<td>70(R)</td>
</tr>
<tr>
<td>2</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-9a</td>
<td>toluene</td>
<td>4</td>
<td>94</td>
<td>79(R)</td>
</tr>
<tr>
<td>3</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-9a</td>
<td>CH₂Cl₂</td>
<td>6</td>
<td>90</td>
<td>89(R)</td>
</tr>
<tr>
<td>4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-9a</td>
<td>CH₂Cl₂</td>
<td>12</td>
<td>90</td>
<td>97(R)</td>
</tr>
<tr>
<td>5</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-10a</td>
<td>CH₂Cl₂</td>
<td>6</td>
<td>90</td>
<td>82(R)</td>
</tr>
<tr>
<td>6</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-9c</td>
<td>CH₂Cl₂</td>
<td>6</td>
<td>91</td>
<td>89(R)</td>
</tr>
<tr>
<td>7</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-10c</td>
<td>CH₂Cl₂</td>
<td>6</td>
<td>87</td>
<td>85(R)</td>
</tr>
<tr>
<td>8</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-9b</td>
<td>CH₂Cl₂</td>
<td>8</td>
<td>69</td>
<td>25(S)</td>
</tr>
<tr>
<td>9</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-10b</td>
<td>CH₂Cl₂</td>
<td>8</td>
<td>60</td>
<td>20(S)</td>
</tr>
<tr>
<td>10</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-9d</td>
<td>CH₂Cl₂</td>
<td>8</td>
<td>65</td>
<td>25(S)</td>
</tr>
<tr>
<td>11</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-10d</td>
<td>CH₂Cl₂</td>
<td>8</td>
<td>55</td>
<td>28(S)</td>
</tr>
<tr>
<td>12</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-9e</td>
<td>CH₂Cl₂</td>
<td>10</td>
<td>90</td>
<td>78(R)</td>
</tr>
<tr>
<td>13</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-9f</td>
<td>CH₂Cl₂</td>
<td>10</td>
<td>85</td>
<td>30(S)</td>
</tr>
<tr>
<td>14</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-9g</td>
<td>CH₂Cl₂</td>
<td>1</td>
<td>73</td>
<td>65(R)</td>
</tr>
<tr>
<td>15</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-10e</td>
<td>CH₂Cl₂</td>
<td>1</td>
<td>75</td>
<td>64(R)</td>
</tr>
<tr>
<td>16</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,S)-10g</td>
<td>CH₂Cl₂</td>
<td>2</td>
<td>58</td>
<td>35(R)</td>
</tr>
<tr>
<td>17</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-9h</td>
<td>CH₂Cl₂</td>
<td>1</td>
<td>92</td>
<td>94(S)</td>
</tr>
<tr>
<td>18</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-10f</td>
<td>CH₂Cl₂</td>
<td>1</td>
<td>94</td>
<td>94(S)</td>
</tr>
<tr>
<td>19</td>
<td>(R&lt;sub&gt;Fc&lt;/sub&gt;,R)-10h</td>
<td>CH₂Cl₂</td>
<td>2</td>
<td>90</td>
<td>66(S)</td>
</tr>
</tbody>
</table>

* Isolated yields of analytically pure product.  Enantioselectivity was determined by HPLC using a chiralcel OD-H column.  Reaction was performed at -20 °C.
The results can be summarized as follows: high conversions and enantioselectivities were achieved in dichloromethane. Ligands bearing (S)-configuration at the α-centre, generally provided good reaction rates and enantioselectivities (entries 1-7 and 12). Exceptionally, in the case of P,N-ligands with a t-butyl group on the pyridine ring the (R)-isomers provided higher enantioselectivities compared to (S)-isomers (up to 94% ee; entries 14-19). The P,N-ligands bearing an alcohol group at the α-centre, such as 10g and 10h, provided mediocre results compared to the corresponding alkyl ethers 9g-h and 10g-h (entries 16 and 19). These results show the necessity of O-alkyl groups in creating a sterical environment capable of providing high enantioselectivities. The difference in the reactivity of both diastereomers (R_Fc,S) and (R_Fc,R), is clearly supporting the concept of substrate and catalyst matched and mismatched interactions.

2.3.2. Ir-catalyzed asymmetric hydrogenation of olefins

With encouraging results from the Pd(0)-catalyzed asymmetric allylic alkylation reactions with the P,N-ligands 9a-h and 10a-h, we then tested the efficiency of these new P,N-ligands in the Ir-catalyzed asymmetric hydrogenation of olefins.

Following, Pfaltz’s procedure,90 iridium complexes 46a-46g and 47a-47g were readily prepared by reacting a solution of [Ir(cod)Cl]_2 and the (R_Fc,S)-P,N-ligand or (R_Fc,R)-P,N-ligand in CH_2Cl_2 at room temperature for 1 h. The chloride ion was exchanged with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate using NaBARF in a biphasic CH_2Cl_2-H_2O system. The resulting orange BARF salts can be purified by silica gel column chromatography. These complexes were stable towards oxygen and moisture. The iridium-complexes 46a-g were prepared by using [Ir(cod)Cl]_2 and the (R_Fc,S)-P,N-ligand (Scheme 40 and Table 4)

---

Results and Discussion

Scheme 40. Preparation of iridium complexes 46a-g

Table 4. Preparation of Ir-catalysts 46a-g using the \((R_{\text{Fc}},S)\)-P,N-ligands.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>R</th>
<th>R'</th>
<th>R''</th>
<th>Yield</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9a</td>
<td>H</td>
<td>Me</td>
<td>Ph</td>
<td>90</td>
<td>46a</td>
</tr>
<tr>
<td>2</td>
<td>10a</td>
<td>H</td>
<td>Bn</td>
<td>Ph</td>
<td>90</td>
<td>46b</td>
</tr>
<tr>
<td>3</td>
<td>9c</td>
<td>H</td>
<td>Me</td>
<td>(3,5-dimethylphenyl)</td>
<td>92</td>
<td>46c</td>
</tr>
<tr>
<td>4</td>
<td>10c</td>
<td>H</td>
<td>Bn</td>
<td>(3,5-dimethylphenyl)</td>
<td>89</td>
<td>46d</td>
</tr>
<tr>
<td>5</td>
<td>9e</td>
<td>Ph</td>
<td>Me</td>
<td>Ph</td>
<td>82</td>
<td>46e</td>
</tr>
<tr>
<td>6</td>
<td>9g</td>
<td>tBu</td>
<td>Me</td>
<td>Ph</td>
<td>89</td>
<td>46f</td>
</tr>
<tr>
<td>7</td>
<td>10e</td>
<td>tBu</td>
<td>Bn</td>
<td>Ph</td>
<td>88</td>
<td>46g</td>
</tr>
</tbody>
</table>

*Isolated yield of analytically pure product.

Using the similar procedure mentioned above, iridium complexes 47a-g were prepared by using \((R_{\text{Fc}},R)\)-P,N-ligand (Scheme 41 and Table 5).

Scheme 41. Preparation of iridium complexes 47a-g
Table 5. Preparation of Ir-catalysts 46a-g using the (R\textsubscript{Fc},R)-P,N-ligands.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>R</th>
<th>R\textsuperscript{1}</th>
<th>R\textsuperscript{2}</th>
<th>Yield\textsuperscript{a}</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9b</td>
<td>H</td>
<td>Me</td>
<td>Ph</td>
<td>89</td>
<td>47a</td>
</tr>
<tr>
<td>2</td>
<td>10b</td>
<td>H</td>
<td>Bn</td>
<td>Ph</td>
<td>88</td>
<td>47b</td>
</tr>
<tr>
<td>3</td>
<td>9d</td>
<td>H</td>
<td>Me (3,5-dimethylphenyl)</td>
<td>93</td>
<td>47c</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10d</td>
<td>H</td>
<td>Bn (3,5-dimethylphenyl)</td>
<td>90</td>
<td>47d</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9f</td>
<td>Ph</td>
<td>Me</td>
<td>Ph</td>
<td>80</td>
<td>47e</td>
</tr>
<tr>
<td>6</td>
<td>9h</td>
<td>tBu</td>
<td>Me</td>
<td>Ph</td>
<td>88</td>
<td>47f</td>
</tr>
<tr>
<td>7</td>
<td>10f</td>
<td>tBu</td>
<td>Bn</td>
<td>Ph</td>
<td>80</td>
<td>47g</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Isolated yield of analytically pure product.

Applying these iridium complexes 46a-g and 47a-g in the asymmetric hydrogenation of olefin 48 gave disappointing results giving only traces of the product even at high hydrogen pressures and in different solvent systems (e.g. methanol, toluene, CH\textsubscript{2}Cl\textsubscript{2}, DMF etc) (Scheme 42).

![Scheme 42. Asymmetric hydrogenation of olefin 48 using the iridium complex 46a](image)

2.3.3. Ir-catalyzed asymmetric imine hydrogenation

Asymmetric synthesis of chiral amines is an important synthetic task since these structural units are widely used in pharmaceutical and agrochemical substances.\cite{a} Recently, the catalytic asymmetric hydrogenation of imines has drawn much attention since it proves to be one of the most efficient ways to form chiral amines. In the past decade, many efficient catalysts using different transition metals, such as Ti,\cite{92} Rh,\cite{93} and Ru\cite{94} were developed for the highly enantioselective imine hydrogenation. Although many efficient catalysts have been developed for the asymmetric imine hydrogenation, most of them were suitable only for


cyclic substrates. The reduction of acyclic imines with high enantioselectivities is still a major challenge in this field.\textsuperscript{95} Chiral iridium complexes based on P,P or P,N-ligands have been successfully applied as catalysts for the highly enantioselective hydrogenation of imines.\textsuperscript{96} One of the most notable examples was reported by Zhang \textit{et al.} in the hydrogenation of acyclic imines that gave up to 99% \textit{ee} using Ir/F-Binaphane catalysts.\textsuperscript{97} Furthermore, Bolm \textit{et al.} reported a highly enantioselective Ir-catalyzed hydrogenation of \textit{N}-aryl ketimines using sulfoximine ligands (P,N-ligands) with I\textsubscript{2} as an additive\textsuperscript{98} (Scheme 43).

Scheme 43. Ir-catalyzed asymmetric reduction of \textit{N}-aryl ketimines

We investigated the efficiency of the new iridium complexes \textit{46a-46g} and \textit{47a-47g} in asymmetric imine hydrogenation. For this purpose, \textit{N}-Phenylethylidene amine \textit{50a} was

---


\textsuperscript{98} Moessner, C.; Bolm, C. \textit{Angew. Chem. Int. Ed.} \textit{2005}, 44, 7564.
chosen as the test substrate and hydrogenation reaction was performed at 60 bar pressure using 1 mol% of 47a as the standard catalyst. The results are summarized in Table 6.

**Table 6.** Asymmetric hydrogenation of imine 50a using catalyst 47a and testing the effect of solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>ee(%) (^{b,c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene</td>
<td>96</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>CH(_2)Cl(_2)</td>
<td>55</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>MeOH</td>
<td>23</td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>Tol:MeOH (4:1)</td>
<td>72</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>Tol:MeOH (1:1)</td>
<td>63</td>
<td>56</td>
</tr>
<tr>
<td>6</td>
<td>Tol:MeOH (10:1)</td>
<td>80</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>Tol:iPrOH (4:1)</td>
<td>89</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>Tol:tBuOH (4:1)</td>
<td>63</td>
<td>56</td>
</tr>
</tbody>
</table>

\(^a\)Conversion was measured by chiral GC or by \(^1\)H NMR. \(^b\)Enantioselectivity was determined by chiral GC using a DEX-CB column. \(^c\)Configuration was assigned by comparing the literature values.

Hydrogenation of imine 50a in toluene provided the corresponding amine 51a in 96% conversion, but only in 11% ee (entry 1). We also noticed that very polar solvents (e.g. methanol) or less polar solvents (e.g. CH\(_2\)Cl\(_2\)) tremendously decreased the reaction rate and enantioselectivity (entries 2-3). Interestingly, performing the hydrogenation of imine 50a in a mixed solvent system such as toluene:methanol (4:1) showed a remarkable improvement in enantioselectivity from 11 to 67% ee but decreased the conversion of the amine 51a (entry 4). Increasing the portion of methanol in the solvent mixture of toluene/methanol or replacing the methanol by 2-propanol or \(t\)-butanol led to only mediocre conversions and poor
enantioselectivities of the amine 51a (entries 5-8). It turned out that a toluene:methanol (4:1) mixture only provided the improved selectivities in the hydrogenation of imine 50a.

For a systematic approach, we initially tested all the iridium complexes 47a-47g in the hydrogenation of imine 50a using the reaction conditions from the above screenings. We conducted the hydrogenation of 50a in toluene:methanol (4:1) at 60 bar pressure using the catalysts 47a-g (Table 7).

**Table 7.** Ir-catalyzed enantioselective hydrogenation of imine 50a using 47a-g

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv(%)</th>
<th>ee(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47a</td>
<td>72</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>47b</td>
<td>75</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>47c</td>
<td>70</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>47d</td>
<td>79</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>47e</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>47f</td>
<td>40</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>47g</td>
<td>34</td>
<td>18</td>
</tr>
</tbody>
</table>

*Conversion was measured by 'H-NMR analysis or by chiral GC.*
*Enantioselectivity was determined by chiral GC using a DEX-CB column.*
*Configuration was assigned by comparing the literature values.

Ir-complexes 47a-47d which have no substitution on the pyridine ring of the P,N-ligand provided better enantioselectivities and moderate conversions in the hydrogenation of imine 50a (entries 1-4). Ir-complexes 47e-47g with substitution on the pyridine ring of P,N-ligands provided poor conversions and selectivities (entries 5-7). Under similar conditions (toluene/methanol (4:1), H2, 60 bar, rt), we examined the efficiency of Ir-catalysts 46a-46g in the hydrogenation of imine 50a (Table 8).
Table 8. Ir-catalyzed enantioselective hydrogenation of imine 50a using 46a-g.

\[
\begin{array}{cccc}
\text{Entry} & \text{Catalyst} & \text{Conv(\%)}^a & \text{ee(\%)}^{b,c} \\
1 & 46a & 100 & 82 \\
2 & 46b & 100 & 82 \\
3 & 46c & 100 & 80 \\
4 & 46d & 100 & 80 \\
5 & 46e & 50 & 26 \\
6 & 46f & 21 & 6 \\
7 & 46g & 30 & 5 \\
\end{array}
\]

\(^a\) Conversion was measured by \(^1\)H-NMR analysis or by chiral GC.

\(^b\) Enantioselectivity was determined by chiral GC using a DEX-CB column.

\(^c\) Configuration was assigned by comparing the literature values

Ir-catalysts with (S)-configuration at the \(\alpha\)-center and no substitution on the pyridine ring of the P,N-ligand, provided improved results in the reduction of imine 50a. Reduction of imine 50a using the iridium catalysts 46a-d proceeded quantitatively and provided the amine 51a in 80-82\% ee (entries 1-4), whereas the Ir-catalysts 46e-f with substitutions on the pyridine ring of P,N-ligands provided low selectivities and conversions (entries 5-7).

To trace out the most efficient reaction conditions for the imine hydrogenation, we performed the hydrogenation of imine 50a using the catalyst 46a at low hydrogen pressures and low catalyst loadings (Table 9). Decreasing the hydrogen pressure from 60 to 10 bar didn’t effect the conversion; it rather improved the enantioselectivity of amine 51a from 82 to 84\% ee (entries 1-5). Hydrogenation at 1 bar hydrogen pressure resulted in long reaction timings (entry 5). Decreasing the catalyst loading from 1 mol\% to 0.5 mol\% increased the reaction time but retained the enantioselectivity at 84\% ee (entry 6). We observed a decrease in enantioselectivity when the catalyst loading was lower to 0.25 mol\% (entry 7).
Table 9. Effect of the catalyst loading and hydrogen pressure on the hydrogenation of imine 50a using the catalyst 46a

![Diagram](attachment:image.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst loading (mol %)</th>
<th>Pressure (bar)</th>
<th>Time [h]</th>
<th>Conversion [%]</th>
<th>ee(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>60</td>
<td>2</td>
<td>100</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>40</td>
<td>2</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>20</td>
<td>2</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>10</td>
<td>2</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1</td>
<td>21</td>
<td>75</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>10</td>
<td>3</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>7</td>
<td>0.25</td>
<td>10</td>
<td>12</td>
<td>100</td>
<td>80</td>
</tr>
</tbody>
</table>

*Conversion was measured by chiral GC or 1H NMR. **Enantioselectivity was determined by chiral GC using a DEX-CB column.

Among all catalysts 46a-g, 47a-g the iridium catalysts 46a, 46b, 46c and 46d provided better results under optimized conditions (toluene:MeOH (4:1), 10 bar H2, 2 h; 80-84% ee). In order to further improve this asymmetric imine hydrogenation, we performed the hydrogenation of various imines with different aryl substituents attached to the nitrogen atom of the imine, using the catalysts 46a-46b (Table 10). We noticed that reduction of imines with electron-rich aromatic groups on the imine nitrogen proceeded well and provided improved enantioselectivities (entries 2-6). Imines having ortho-substituted aromatic groups on the nitrogen atom gave mediocre conversions and enantioselectivities (entries 8-9). Interestingly,
the hydrogenation of the imine 52a (R = 3,5-dimethyl) gave the best results, providing the corresponding secondary amine (R)-53a\(^99\) in 93-94% ee (entry 10).

**Table 10.** Asymmetric hydrogenation of imines 50a-h and 52a using the Ir-complexes 46a and 46b

<table>
<thead>
<tr>
<th>Entry</th>
<th>Imine</th>
<th>R</th>
<th>Product</th>
<th>ee (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>L (1 mol %)</td>
<td>L = 46a</td>
<td>L = 46b</td>
</tr>
<tr>
<td>1</td>
<td>50a</td>
<td>H</td>
<td>51a</td>
<td>84(R)</td>
</tr>
<tr>
<td>2</td>
<td>50b</td>
<td>4-MeO</td>
<td>51b</td>
<td>88(R)</td>
</tr>
<tr>
<td>3</td>
<td>50c</td>
<td>4-Me</td>
<td>51c</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>50d</td>
<td>3,4-dioxymethylene</td>
<td>51d</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>50e</td>
<td>3,4,5-trimethoxy</td>
<td>51e</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>50f</td>
<td>3,4-dimethyl</td>
<td>51f</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>50g</td>
<td>3,4-dimethoxy</td>
<td>51g</td>
<td>81</td>
</tr>
<tr>
<td>8(^c)</td>
<td>50h</td>
<td>2,4-dimethyl</td>
<td>51h</td>
<td>83</td>
</tr>
<tr>
<td>9(^d)</td>
<td>50i</td>
<td>2-MeO</td>
<td>51i</td>
<td>54</td>
</tr>
<tr>
<td>10</td>
<td>52</td>
<td>3,5-dimethyl</td>
<td>53a</td>
<td>94(R)</td>
</tr>
</tbody>
</table>

\(^a\) In all cases full conversion was achieved in 2-4 h. \(^b\) Enantioselectivity was determined by HPLC (chiracel OD-H) or by GC using a chiral Dex-CB column. \(^c\) Reaction time is 10 h; isolated yield is 84%. \(^d\) Reaction time is 12 h; isolated yield is 50%.

To envisage the effect of functional groups on the imine hydrogenation, we investigated the hydrogenation on a series of imines of type 52 using the catalysts 46a and 46b (Table 11). Imines 52b-52h were smoothly reduced under the optimized conditions and provided the corresponding secondary amines 53b-53h in 84-94% ee (Table 9). Imines with electron donating groups (entries 2, 3, 4 and 7) provided better enantioselectivities compared to electron withdrawing groups (entry 5). Reduction of the imine 52h which was derived from

tetralone also proceeded well and the corresponding amine $53h$ was obtained in 84% ee (entry 8).

**Table 11.** Asymmetric hydrogenation of imines $52a$-$h$ using the Ir-complexes $46a$ and $47a$

![Diagram of reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Imine</th>
<th>R</th>
<th>$R^1$</th>
<th>Product$^a$</th>
<th>$ee(%)^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$L = 46a$</td>
<td>$L = 46b$</td>
</tr>
<tr>
<td>1</td>
<td>$52a$</td>
<td>H</td>
<td>Me</td>
<td>$53a$</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>$52b$</td>
<td>4-MeO</td>
<td>Me</td>
<td>$53b$</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>$52c$</td>
<td>4-Me</td>
<td>Me</td>
<td>$53c$</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>$52d$</td>
<td>3-OMe</td>
<td>Me</td>
<td>$53d$</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>$52e$</td>
<td>4-Cl</td>
<td>Me</td>
<td>$53e$</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>$52f$</td>
<td>4-Ph</td>
<td>Me</td>
<td>$53f$</td>
<td>88</td>
</tr>
<tr>
<td>7</td>
<td>$52g$</td>
<td>H</td>
<td>Et</td>
<td>$53g$</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td>$52h$</td>
<td>-(CH$_2$)$_3$-</td>
<td>Me</td>
<td>$53h$</td>
<td>84</td>
</tr>
</tbody>
</table>

$^a$In all cases full conversion was achieved. $^b$Enantioselectivity was determined by HPLC using a chiralcel OD-H column or by AD-column.

Although high enantioselectivities were achieved in the hydrogenation of imines of type $52$, the removal of the 3,5-dimethylphenyl group from the amine $53$ was difficult. In general, secondary amines with 4-methoxy or 2-methoxyphenyl on the nitrogen atom of the amine can be cleaved under practical conditions to provide chiral primary amines.\(^\text{100}\) Since the imines with $N$-(4-methoxyphenyl) group $50b$, $50e$, $50g$ and $N$-(2-methoxyphenyl) group $50i$ provided the corresponding amines in moderate enantioselectivities (entries 2; 5, 7, and 9 of Table 10), we searched for another substrate. We thought that $N$-aryl imine $56a$ with a 3,5-dimethyl-4-methoxyphenyl group on the imine nitrogen could also be the ideal substrate for the

deprotection to provide primary amines. Imine 56a was synthesized as showed in the following scheme (Scheme 44).

\[
\text{Me}_2\text{N} - \text{OMe} + \text{HNO}_3:\text{H}_2\text{SO}_4, \text{Ac}_2\text{O}, 0^\circ\text{C}, 2\text{~h;} 91\% \\
\text{N}_2\text{H}_4:\text{H}_2\text{O}, \text{FeCl}_3:6\text{H}_2\text{O}, \text{Charcoal, MeOH, 100}\%\text{C, 12}\text{~h;} 96\%
\]

Scheme 44. Synthesis of the imine 56a

To our delight, imine 56a could be smoothly reduced using the Ir-catalysts 46a and 46b, furnishing the corresponding secondary amine 57a in 92-94% ee. As we anticipated, deprotection of the 3,5-dimethyl-4-methoxyphenyl group on the amine 57a was accomplished by using cerium ammonium nitrate (CAN; Ce(NH$_4$)$_2$(NO$_3$)$_6$) in MeOH:H$_2$O (6:1), providing the chiral primary amine ($R$)-58 in 85% yield and 94% ee (Scheme 45).

\[
\text{Me}_2\text{N} - \text{OMe} + \text{L}^\star (1\text{~mol\%}), \text{H}_2, 10\text{~bar} \\
\text{ Tol:MeOH (4:1), 2~h, 25}^\circ\text{C} \\
\text{CAN (4 equiv), 25}^\circ\text{C} \\
\text{MeOH:H}_2\text{O (6:1), 12~h} \\
\]

85%; 94% ee

Scheme 45. Asymmetric hydrogenation of imine 56a using the Ir-catalysts 46a and 46b and subsequent deprotection to primary amine 58

To extend the scope of this asymmetric imine hydrogenation, we examined the reduction of various imines of type 56 using the Ir-catalysts 46a and 46b (Table 12). The results are summarized as follows. Both electron donating (entries 2, 3, 4, 7, 8, 12 and 13) and electron withdrawing substituents (entries 5, 6, 9, 10, 11 and 14) provided high enantioselectivities (80-94% ee; Table 10) in hydrogenation. Imines with electron withdrawing groups on the aromatic ring provided higher enantioselectivities compared to electron donating groups. Among the electron-rich imines, imines with meta- and ortho-substitution provided better enantioselectivities compared to para-substitution (entries 2, 4, 8 and 3, 7). Reduction of the
imine derived from tetralone \(56o\) provided the secondary amine in 84\% \(ee\), whereas the indanone derived imine \(56p\) provided the corresponding amine only in 70\% \(ee\).

### Table 12. Asymmetric hydrogenation of imines \(56a-p\) using the Ir-complex \(46a\) and \(46b\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Imine</th>
<th>Ar</th>
<th>R</th>
<th>Product</th>
<th>time ([h])</th>
<th>(ee(%)) (46a)</th>
<th>(46b)</th>
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<td>(56a)</td>
<td>Ph</td>
<td>Me</td>
<td>(57a)</td>
<td>2</td>
<td>94</td>
<td>92</td>
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<tr>
<td>2</td>
<td>(56b)</td>
<td>4-Me-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57b)</td>
<td>2</td>
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<td>85</td>
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<tr>
<td>3</td>
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<td>3-MeC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57c)</td>
<td>2</td>
<td>94</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
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<td>2-Me-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57d)</td>
<td>6</td>
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<td>94</td>
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<td>4-MeCO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57e)</td>
<td>4</td>
<td>94</td>
<td>92</td>
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<tr>
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<td>(57f)</td>
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<td>Me</td>
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<td>(56h)</td>
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<td>(57h)</td>
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<td>9</td>
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<td>(57i)</td>
<td>2</td>
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<td>91</td>
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<tr>
<td>10</td>
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<td>4-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57j)</td>
<td>4</td>
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<td>92</td>
</tr>
<tr>
<td>11</td>
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<td>3-Cl-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57k)</td>
<td>2</td>
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<td>90</td>
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<tr>
<td>12</td>
<td>(56l)</td>
<td>4-Ph-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57l)</td>
<td>2</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>13</td>
<td>(56m)</td>
<td>2-naphthyl</td>
<td>Me</td>
<td>(57m)</td>
<td>2</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>14</td>
<td>(56n)</td>
<td>3-CH&lt;sub&gt;3&lt;/sub&gt;CO-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>(57n)</td>
<td>2</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>15</td>
<td>(56o)</td>
<td>Ph</td>
<td>-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;-</td>
<td>(57o)</td>
<td>2</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>16&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(56p)</td>
<td>Ph</td>
<td>-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>(57p)</td>
<td>12</td>
<td>70</td>
<td>68</td>
</tr>
</tbody>
</table>

* Time to achieve full conversion. \(^b\) Enatioselectivity was determined by HPLC using chiral OD-H column or AD-column. \(^c\) Only 70\% conversion was achieved even after 12 h at rt.
The asymmetric imine hydrogenation with catalysts 46a and 46b can also be applied to various kinds of imines bearing a side-chain at the \( \alpha \)-position. Thus, imines 56q-s underwent a smooth hydrogenation and the respective secondary amines 57q-s were obtained in 92-95\% ee (Scheme 46).

\[
\text{Scheme 46. Reduction of imines 56q, 56r and 56s with side-chains at the} \ \alpha \text{-position using the catalysts 46a and 46b}
\]

Interestingly, reduction of the imine 56t bearing a remote keto group proceeded chemoselectively and quantitatively, yielding the corresponding amine 57t in 99\% ee (Scheme 47). No over-reduction of the ketone functionality was observed in this reaction.

\[
\text{Scheme 47. Chemoselective hydrogenation of imine 56t using the Ir-catalysts 46a and 46b}
\]

Deprotection of the functionalized amines of type 56 was also accomplished by using CAN to furnish the corresponding \((R)\)-primary amines in good yields (Scheme 48).
Furthermore, we extended this protocol to the asymmetric synthesis of chiral γ- and δ-lactams.\textsuperscript{101,102} Thus, the imines \textit{56u} and \textit{56v} bearing a remote ester group were subjected to the asymmetric hydrogenation, and after subsequent deprotection of the \textit{N}-aromatic group, the 5-phenyl-2-pyrrolidinone \textit{63} and 6-phenyl-2-piperidinone \textit{64} were obtained in 74\% yield, 92\% \textit{ee} and 78\% yield, 97\% \textit{ee} respectively (Scheme 49).

Scheme 49. Synthesis of γ- and δ-lactams \textit{63} and \textit{64}

Hydrogenation of disubstituted imines \textit{56w-γ} under optimized reaction conditions was then investigated (Scheme 50). Unlike the mono substituted imines, disubstituted imines with electron donating groups provided improved enantioselectivities compared to the electron withdrawing imine (Scheme 50).


Scheme 50. Hydrogenation of disubstituted imines 56w-y

2.4. Conclusion

In conclusion, the novel synthesis of P,N-ligands 9a-g and 10a-g in high yields was achieved. Their iridium complexes 46a-g and 47a-g were prepared and applied in asymmetric imine hydrogenation. Various N-arylketimines were reduced using the Ir-catalysts 46a and 46b in high conversions and enantioselectivities (up to 99% ee). We also described the synthesis of chiral primary amines and γ- and δ-lactams via this asymmetric imine hydrogenation.

3. Preparation of bis-ferrocenyl P,P ligands and their applications in asymmetric catalysis

3.1. Introduction

Although many chiral ferrocene ligands have been prepared for various transition-metal-catalyzed asymmetric reactions, only few ligands with two ferrocenyl groups (bis-ferrocenyl ligands) have been reported. Trap,\textsuperscript{103} Pigiphos,\textsuperscript{104} and Trost’s chiral pocket ligand\textsuperscript{105} are the only reported examples in this category. Among these bis-ferrocenyl P,P-ligands, ligand TRAP proved to be a very efficient ligand for asymmetric catalysis. Trap has been successfully applied in Rh-catalyzed asymmetric hydrogenation of indoles,\textsuperscript{106} and

hydrosilylation of prochiral ketones,\textsuperscript{107} and Rh and Pd-catalyzed asymmetric allylic alkylations\textsuperscript{108} (Scheme 51).

\begin{center}
\begin{tikzpicture}
  \node (a) [draw] {\[R \text{Fe} \text{Ph}_2 \text{PPh}_2 \text{Fe}\text{Ph-TRAP} \]};
  \node (b) [draw] {\[\text{Ts} \text{N} \text{Ts}\]};
  \node (c) [draw] {\[\text{H}_2, (50 \text{ atm}), \text{iPrOH}, 80 \text{ °C}\]};
  \node (d) [draw] {\[\text{Cs}_2\text{CO}_3 (10 \text{ mol\%})\]};
  \node (e) [draw] {\[\text{[Rh(\text{nbd})}_2\text{SbF}_6]/\text{Ph-TRAP (1 mol\%)}\]};
  \node (f) [draw] {\[\text{R} = (\text{CH}_2)_2\text{OTBS}: 94\%; 98\% \text{ ee}\]};
  \node (g) [draw] {\[\text{R} \text{N} \text{Ts} \]};
  \node (h) [draw] {\[\text{Ph-TRAP}\]};
  \node (i) [draw] {\[\text{Ph}\text{TRAP}\]};

\end{tikzpicture}
\end{center}

**Scheme 51.** Applications of Trap in asymmetric catalysis.

Based on this successful work, we decided to design a bis-ferrocenyl ligand for asymmetric catalysis. The ligand structure is shown in figure 13. The $\alpha$-carbon in the ligand structure is a chirotopic center.

\begin{center}
\begin{tikzpicture}
  \node (a) [draw] {\[\text{Ph}_2\text{P}\text{OMe}\text{Ph}\text{2P}\text{Ph}_2\text{P}\text{Fe}\text{Fe}\]};
  \node (b) [draw] {\[\text{Ph-TRAP}\]};

\end{tikzpicture}
\end{center}

**Figure 13.** Structure of new bis-ferrocenyl ligands 11

### 3.2. Synthesis of bis-ferrocenyl P,P-ligand 11

The synthetic approach for the ligand 11 is shown in the scheme 52. The bis-ferrocenyl phosphine 11 can be prepared through the reduction of the corresponding phosphine sulfides. The phosphine sulfides can be prepared via the sulfoxide-lithium exchange on 67, followed by the addition of chlorodiarylphosphines. The methyl ether can be prepared by $O$-methylation of the corresponding alcohol 66 which can be prepared via the diastereoselective ortho-lithiation of 14, followed by the addition of 65.


Scheme 52. Synthetic approach to the bis-ferrocenyl ligand 11

Diastereoselective ortho-lithiation on sulfoxide 14, followed by the addition of DMF, led to the aldehyde 65 in 80% yield. Addition of this aldehyde 65 to the lithiated species generated from the diastereoselective metatllation of 14, provided the bis-ferrocenyl alcohol 66 in 60% yield. O-methylation of 66 using KH and MeI led to the bis-ferrocenyl ether 67 in 85% yield (Scheme 53).

Scheme 53. Preparation of bis-ferrocenyl ether 67

Exchange of the sulfoxide using phenyllithium or tert-butyllithium, followed by the addition of chlorodiphenylphosphine led to an inseparable mixture of mono and disubstituted phosphines (Scheme 54).
Scheme 54. Performance of sulfoxide/lithium exchange on 67

Since compound 67 provided an inseparable mixture in the reaction with ClPPh₂ after the sulfoxide/lithium exchange, we changed our synthetic approach to ligand 11. Starting our synthesis from the sulfoxide 30, performance of sulfoxide-lithium exchange of 30 using PhLi, followed by the addition of DMF, furnished the ferrocenyl aldehyde 68 in 65% yield. Sulfoxide-lithium exchange on 30 using PhLi, followed by the addition of 68 led to the bis-ferrocenyl alcohol 69 in 55% yield (Scheme 55).

Scheme 55. Preparation of bis-ferrocenyl alcohol 69

We couldn’t accomplish the O-methylation of the alcohol 69 under any known reaction conditions. In addition, attempted deprotection on the bisphosphine sulfide 69 using Raney-Ni in MeOH resulted in no conversion (Scheme 56).

Scheme 56. Attempts to prepare the bis-ferrocenyl ether from 69
Keeping these problems from the above two synthetic approaches in mind, the following synthesis was attempted. Sulfoxide-lithium exchange on the substrate 30, followed by the addition of bromoferrocenyl aldehyde 20b, led to the bis-ferrocenyl alcohol 70 in 58% yield. O-methylation of 70 using KH and MeI led to the bis-ferrocenyl ether 71 in 84% yield (Scheme 57).

Scheme 57. Preparation of bis-ferrocenyl ether 71

The bromine-lithium exchange on 71 using n-BuLi, followed by the addition of chlorodiphenylphosphine or bis-2-furyl phosphine, gave the bis-ferrocenyl phosphine sulfides 72 and 73 in 76 and 80% yields, respectively (Scheme 58).

Scheme 58. Preparation of bis-ferrocenyl phosphine sulfides 72 and 73

Deprotection of the phosphine sulfides 72 and 73 using Raney-Ni in methanol provided the corresponding bisphosphines 11a-b in 76-80% yield, respectively (Scheme 59).

Scheme 59. Preparation of bis-ferrocenyl phosphines 11a and 11b
3.3 Applications in asymmetric catalysis

3.3.1 Rh-catalyzed hydrogenation of olefins

With the two bis-ferrocenyl ligands 11a-11b in hand, we applied them in Rh-catalyzed hydrogenation of \( \alpha \)-acetamidocinnamate 25 to yield the phenylalanine derivative 26. Hydrogenation of 25 using 11a proceeded quantitatively, but racemic product was obtained (Scheme 60).

![Scheme 60. Application of 11a in Rh-catalyzed hydrogenation of 25](image)

We also tested the efficiency of 11a in the Rh-catalyzed hydrogenation of dimethyl itaconate 74. The desired product 75 was obtained quantitatively but only in 18\% ee (Scheme 61).

![Scheme 61. Rh-catalyzed hydrogenation of dimethyl itaconate 75](image)

Application of ligand 11b in the above reactions resulted in no reactions.

3.3.2. Pd-catalyzed asymmetric allylic alkylation

We then examined the efficiency of new ferrocenyl ligand 11a in Pd(0)-catalyzed asymmetric alkylation on the racemic substrate 27 using dimethylmalonate as a nucleophile. We observed complete conversion in 5 minutes, however, a very low selectivity was achieved (Scheme 62).
Scheme 62. Asymmetric allylic alkylation using the ligand 11a

3.4. Conclusion

In conclusion, we prepared the new bis-ferrocenyl ligands 11 in good yields. Although the ligands formed very active catalysts, as shown by quantitative conversions and low reaction times, low enantioselectivities were observed.

4. Synthesis of new paracyclophane phosphines and their applications in asymmetric catalysis

4.1 Introduction

The [2,2]paracyclophane backbone serves as a powerful tool to develop new and efficient ligands for the asymmetric catalysis. The chiral [2,2]phanephos 13, a \( C_2 \) symmetric bisphosphine, is one of the most successful chiral ligands with a rigid paracyclophane backbone (Scheme 63). It has been efficiently used in Rh-catalyzed hydrogenation of dehydroamino acids,\(^\text{17}\) allylic acids,\(^\text{110}\) Ru-catalyzed hydrogenation of \( \beta \)-ketoesters,\(^\text{111}\) aromatic ketones\(^\text{112}\) and Pd-catalyzed amination reactions.\(^\text{113}\) The chiral \( C_2 \)-symmetrical phosphinites based on the paracyclophane backbone have also proved to be very efficient catalysts for Rh-catalyzed hydrogenation of \( N \)-acetyl dehydroamino acids and esters (Scheme 63).\(^\text{114}\)


Results and Discussion

\[
\begin{array}{c}
\text{CO}_2\text{Me} \quad \text{NHAc} \\
\text{Rh(nbd)}_2\text{BF}_4 (1\text{mol%}) \\
\text{L*}, \text{MeOH}, \text{rt}, \text{H}_2, 5 \text{bar} \\
\text{CO}_2\text{Me} \quad \text{NHAc}
\end{array}
\]

97-98% ee

\[\text{Phanephos}\]

\((R)-13a: \text{Ar} = \text{Ph}\)
\((R)-13b: \text{Ar} = 3,5-(\text{CH}_3)_2\text{-C}_6\text{H}_3\)

Scheme 63. Applications of \(C_2\)-symmetrical paracyclophane phosphines in asymmetric catalysis

Hems et al. prepared various non-\(C_2\)-symmetrical paracyclophane phosphines by introducing substituents on one of the aromatic ring of Phanephos 12. These ligands showed an indistinguishable performance to the original Phanephos 12 in Rh-catalyzed hydrogenation of dehydroamino acids and Ru-catalyzed hydrogenation of acetophenone (Scheme 63).\(^{115}\)

\[
\begin{array}{c}
\text{CO}_2\text{Me} \quad \text{NHAc} \\
\text{Rh(nbd)}_2\text{BF}_4 (1\text{mol%}) \\
\text{L*}, \text{MeOH}, \text{rt}, \text{H}_2, 5 \text{bar} \\
\text{CO}_2\text{Me} \quad \text{NHAc}
\end{array}
\]

97% ee

\[
\begin{array}{c}
\text{O} \\
\text{[L*RuCl}_2\text{(diamine)]} \\
\text{H}_2, 10 \text{bar}, \text{iPrOH} \\
25 \degree\text{C}, \text{tBuOK}, \text{s/c 10,000, 1 h} \\
\text{OH}
\end{array}
\]

99% ee

Scheme 63. Applications of non-\(C_2\)-symmetrical paracyclophane phosphines in Rh and Ru-catalyzed hydrogenation reactions

4.2 Synthesis of new paracyclophane phosphines

However, apart from this fascinating work, paracyclophane phosphines bearing two different kinds of aryl phosphines have not been synthesized until now. Our aims of this work were to synthesize the new diphosphines of type 12 based on the paracyclophane backbone and test their efficiency in asymmetric catalysis. This work also allows us to study the electronic properties of different phosphines to elucidate the effect of the phosphines on asymmetric catalysis. The new ligands structure is depicted in Figure 14.

![Figure 14. New paracyclophane phosphines of type 12](image)

The corresponding monometallation on chiral dibromide 76 using n-BuLi for 2 h at -78 °C, followed by the addition of chlorodiphenylphosphine led to an air sensitive diphenylphosphine derivative which was in situ protected with sulfur leading to the air stable phosphine sulfide 77 in 85% yield. Bromine/lithium-exchange on substrate 77 using n-BuLi at -78 °C for 1 h, followed by reaction with various chlorodiarylphosphines and in situ protection the resulting phosphine with sulfur, provided the bisphosphine sulfides 78a-78c in 50-86% yields. The deprotection of the phosphine sulfides was accomplished using Raney-Ni in MeOH (25 °C, 12 h) to obtain the diphosphines 12a-c in 20-66% yields (Scheme 65).  

116 a) For the preparation of the dibromide see the ref. (109) and for the preparation of racemic dibromide see b) Reich, H. J.; Cram, D. J. J. Am. Chem. Soc. 1969, 91, 3527.  
117 Ph. D thesis, Maud gayral, Oxford University.
Scheme 65. Preparation of new paracyclophane based ligands 12a-c.

In addition, we required also a mixed bisphosphine bearing an electron-rich aromatic group on the phosphorous such as 3,5-dimethylphenyl group. Thus, we prepared the diphosphine 12d, in the similar way to the synthesis as described in Scheme 65. The bromine-lithium exchange on substrate 77, using \( n \)-BuLi, followed by reaction with chlorobis(3,5-dimethylphenyl)phosphine and in situ protection with sulfur, provided the bisphosphinesulfide 78d in 86% yield. The deprotection of 78d was performed by using Raney-Ni in MeOH at room temperature, and provided the phosphine 12d in 92% yield (Scheme 66).

Scheme 66. Preparation of the paracyclophane phosphine 12d

4.3 Applications in asymmetric catalysis.

For clarity, the structure of chiral P,P-ligands 12a-d are shown in Scheme 67.
Scheme 67. Overview of new chiral paracyclophane based P,P-ligands 12a-d

4.3.1 Rh-catalyzed asymmetric hydrogenation reactions

Having these P,P-ligands in hand, we sought to investigate their efficiency in Rh-catalyzed asymmetric hydrogenation of N-acetyl methyl cinnamate 25. Since ligand 12a is very unstable and oxidized rapidly, we couldn’t apply this ligand in asymmetric catalysis. The ligands 12b-d gave mixed results in asymmetric hydrogenation of cinnamate 25. The ligand 12d proved to be efficient for the hydrogenation of 25 and gave the desired compound 26 in quantitative yield and 90% ee (Scheme 68).

Scheme 68. Rh-catalyzed hydrogenation of N-acetyl dehydroamino acids using the ligands 12b-d

Applying these ligands in Rh-catalyzed hydrogenation of dimethylitaconate, also resulted in moderate enantioselectivities (Scheme 69).
Scheme 69. Rh-catalyzed hydrogenation of dimethyl itaconate using the ligands 12c and 12d.

4.3.2 Ru-Catalyzed Hydrogenation of Prochiral Ketones

Enantiomerically pure alcohols serve as important intermediates in drug design. A direct approach to single enantiomer alcohols through catalytic reduction of ketones is most attractive, and various methods have been introduced.\textsuperscript{118} Owing to the inherent atom-economical nature of the hydrogenation reactions, hydrogenation of prochiral ketones is one of the most facile routes for generating single enantiomer alcohols. Recently, a groundbreaking discovery by Noyori and co-workers, found that phosphine-ruthenium-diamine complexes are very effective catalysts for the hydrogenation of ketones and aldehydes.\textsuperscript{119} Significantly, this method allowed the development of many efficient catalysts for highly enantioselective hydrogenation of a wide range of prochiral ketones.\textsuperscript{120} Thus, we sought to investigate the efficiency of these new ligands 12b-d in ruthenium catalyzed hydrogenation of prochiral ketones. We prepared various phosphine-ruthenium-diamine complexes 79a-c and


80a-c using chiral 1,2-diphenylethylenediamines. The ruthenium complexes were prepared analogous to the literature procedure. Heating a mixture of diphosphine 12b-d and [RuCl\(_2\)(C\(_6\)H\(_6\))]\(_2\) in toluene/DMF for 4 h at 115 °C, followed by the addition of chiral diamine and heating the mixture for 2 h at 115 °C provided the ruthenium complexes 79a-c and 80a-c in quantitative yields (Table 11). Catalysts 79a-c were prepared using (R,R)-1,2-diphenylethylenediamine, whereas the catalysts 80a-c were prepared by using (S,S)-1,2-diphenylethylenediamine.

**Table. 13** Preparation of Ru-complexes using the chiral diamine and the ligands 79a-c and 80a-c.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Ligand</th>
<th>Diamine(^a)</th>
<th>Product(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-F-C(_6)H(_4)</td>
<td>12b</td>
<td>(R,R)-DPEN</td>
<td>79a</td>
</tr>
<tr>
<td>2</td>
<td>4-F-C(_6)H(_4)</td>
<td>12b</td>
<td>(S,S)-DPEN</td>
<td>80a</td>
</tr>
<tr>
<td>3</td>
<td>3,5-(CF(_3))(_2)-C(_6)H(_3)</td>
<td>12c</td>
<td>(R,R)-DPEN</td>
<td>79b</td>
</tr>
<tr>
<td>4</td>
<td>3,5-(CF(_3))(_2)-C(_6)H(_3)</td>
<td>12c</td>
<td>(S,S)-DPEN</td>
<td>80b</td>
</tr>
<tr>
<td>5</td>
<td>3,5-(CH(_3))(_2)-C(_6)H(_3)</td>
<td>12d</td>
<td>(R,R)-DPEN</td>
<td>79c</td>
</tr>
<tr>
<td>6</td>
<td>3,5-(CH(_3))(_2)-C(_6)H(_3)</td>
<td>12d</td>
<td>(S,S)-DPEN</td>
<td>80c</td>
</tr>
</tbody>
</table>

\(^a\)DPEN = Diphenylethylenediamine. \(^b\)all product was obtained in quantitative yield.

We started our investigation on the ketone hydrogenation using the novel ruthenium complexes 79a-c and 80a-c and acetophenone as the model substrate under standard reaction conditions (i-PrOH solvent, 10 bar H\(_2\), t-BuOK/Ru : 25/1, 1.0-2.0 M solutions)\(^{120-121}\) (Table 14). Preliminary results indicate that the hydrogenation of acetophenone 81a using ruthenium complexes 79a-c led to poor conversions and enantioselectivities (entries 1-3). On the other hand the ruthenium complexes 80a-c provided better enantioselectivities in the hydrogenation of acetophenone 81a (entries 4-6). Among the ruthenium precatalysts 80a-c, catalyst 80c proved to be the most efficient catalyst for the asymmetric hydrogenation of acetophenone 81a and furnished the corresponding alcohol 82a in 97% ee (entry 6-10).
Table 14. Hydrogenation of acetophenone 81a using the ruthenium precatalysts 79a-80c.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>S/C</th>
<th>Time[h]</th>
<th>Conv(%)</th>
<th>ee&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>79a</td>
<td>500</td>
<td>12</td>
<td>45</td>
<td>14(S)</td>
</tr>
<tr>
<td>2</td>
<td>79b</td>
<td>500</td>
<td>12</td>
<td>54</td>
<td>22(S)</td>
</tr>
<tr>
<td>3</td>
<td>79c</td>
<td>500</td>
<td>12</td>
<td>55</td>
<td>25(S)</td>
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<td>4</td>
<td>80a</td>
<td>500</td>
<td>12</td>
<td>50</td>
<td>43(R)</td>
</tr>
<tr>
<td>5</td>
<td>80b</td>
<td>500</td>
<td>12</td>
<td>70</td>
<td>80(R)</td>
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<tr>
<td>6</td>
<td>80c</td>
<td>500</td>
<td>1</td>
<td>100</td>
<td>97(R)</td>
</tr>
<tr>
<td>7</td>
<td>80c</td>
<td>1000</td>
<td>1</td>
<td>100</td>
<td>97(R)</td>
</tr>
<tr>
<td>8</td>
<td>80c</td>
<td>2000</td>
<td>1</td>
<td>100</td>
<td>97(R)</td>
</tr>
<tr>
<td>9</td>
<td>80c</td>
<td>5000</td>
<td>1.5</td>
<td>100</td>
<td>97(R)</td>
</tr>
<tr>
<td>10</td>
<td>80c</td>
<td>1000</td>
<td>2</td>
<td>100</td>
<td>95(R)</td>
</tr>
</tbody>
</table>

<sup>a</sup> S/C: Substrate/Catalyst  
<sup>b</sup> Conversion was measured by chiral GC or by 1H-NMR.  
<sup>c</sup> Enantioselectivity was determined using chiral GC-DEX-CB column

These results indicated that the stereochemistry of the diamine played a major role in providing high conversions and enantioselectivities in ketone hydrogenation. The efficiency of this ruthenium-complex 80c in ketone hydrogenation was investigated by decreasing the catalyst loadings. Increasing the ratio of substrate/catalyst to 10000 provided the alcohol 82a in quantitative yield but diminished the enantioselectivity to 95% ee (entries 7-10 of Table 14).
Then we investigated the scope of ketone substrates for the asymmetric hydrogenation using the Ru-catalyst 80c. Various types of substituted acetophenones were reduced in high conversions providing the corresponding chiral alcohols in high enantioselectivities. The results are listed in Table 15.

**Table 15. Asymmetric hydrogenation of substituted acetophenones using the Ru-catalyst 80c**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time[h]</th>
<th>Product</th>
<th>ee(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\mathbf{81a}$</td>
<td>1</td>
<td>$\mathbf{82a}$</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>$\mathbf{81b}$</td>
<td>1.5</td>
<td>$\mathbf{82b}$</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>$\mathbf{81c}$</td>
<td>1</td>
<td>$\mathbf{82c}$</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>$\mathbf{81d}$</td>
<td>2</td>
<td>$\mathbf{82d}$</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>$\mathbf{81e}$</td>
<td>1.5</td>
<td>$\mathbf{82e}$</td>
<td>97</td>
</tr>
<tr>
<td>6</td>
<td>$\mathbf{81f}$</td>
<td>1.5</td>
<td>$\mathbf{82f}$</td>
<td>97</td>
</tr>
<tr>
<td>7</td>
<td>$\mathbf{81g}$</td>
<td>1</td>
<td>$\mathbf{82g}$</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>$\mathbf{81h}$</td>
<td>1</td>
<td>$\mathbf{82h}$</td>
<td>94</td>
</tr>
</tbody>
</table>
Reactions were performed with 1M solution of ketone in t-PrOH at S/C 2000/1 and t-BuOK (base/Ru = 25/1). In all cases full conversion was achieved. Enantiomeric excess was determined by chiral GC or chiral HPLC.

In order to further explore the substrate scope, we investigated the asymmetric hydrogenation of ketones bearing different types of side-chains at the α-position. Elongation of the side chain of the ketone from methyl to ethyl, n-butyl, n-pentyl or benzyl doesn’t affect the reactivity and provided the corresponding secondary alcohols in 90-97% ee (entries 1-4 of Table 16). Introducing branching at the α-position of the ketone led to long reaction times and poor selectivities (entry 5). Furthermore, we examined the chemoselective hydrogenation of α,β-unsaturated ketones of type 85a-b (entries 6-7; Table 16). Ketone 85a was smoothly reduced to afford the allylic alcohol 86a in 95% ee (entry 6) whereas the ketone 85b furnished the secondary alcohol 86b in 37% ee (entry 7). We also extended the hydrogenation of ketones using the Ru-catalyst 80c to hetero-aromatic ketones 87, 88 and 91 and obtained the corresponding alcohols in excellent enantioselectivities (entries 8-10; Table 16).

**Table 16.** Asymmetric hydrogenation of aryl and heteroaryl ketones using the Ru-catalyst 80c.¹
<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time[h]</th>
<th>Product$^b$</th>
<th>ee(%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="83a" alt="Substrate" /></td>
<td>1.5</td>
<td>84a</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td><img src="83b" alt="Substrate" /></td>
<td>1.5</td>
<td>84b</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td><img src="83c" alt="Substrate" /></td>
<td>1.5</td>
<td>84c</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td><img src="83d" alt="Substrate" /></td>
<td>2</td>
<td>84d</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td><img src="83e" alt="Substrate" /></td>
<td>5</td>
<td>84e</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td><img src="85a" alt="Substrate" /></td>
<td>1</td>
<td>86a</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td><img src="85b" alt="Substrate" /></td>
<td>2</td>
<td>86b</td>
<td>37</td>
</tr>
<tr>
<td>8</td>
<td><img src="87" alt="Substrate" /></td>
<td>3</td>
<td>88</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td><img src="89" alt="Substrate" /></td>
<td>2.5</td>
<td>90</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td><img src="91" alt="Substrate" /></td>
<td>4</td>
<td>92</td>
<td>92</td>
</tr>
</tbody>
</table>

$^a$ Reactions were performed with 1M solution of ketone in i-PrOH at S/C 2000/1 and t-BuOK (base/Ru = 25/1). $^b$ In all cases full conversion was achieved. $^c$ Enantiomeric excess was determined by chiral GC or chiral HPLC.

To broaden the application of this ruthenium catalyzed hydrogenation using the catalyst 80c, we performed the hydrogenation on disubstituted acetophenones 93a-d and obtained the respective alcohols 94a-d in good enantioselectivities. Reduction of the ketone 93d bearing
two methoxy groups on 3,4 positions of the aromatic ring was accomplished smoothly providing the alcohol $94d$ in 94% $ee$, which is a precursor for the synthesis of (−)-Salsolidine (Scheme 70).\textsuperscript{121}

\begin{center}
\includegraphics[width=\textwidth]{scheme70.png}
\end{center}

\textbf{Scheme 70.} Asymmetric hydrogenation of disubstituted acetophenone using the Ru-catalyst 80c

\section*{4.4. Conclusion}

In conclusion, we have synthesized new paracyclophane based diphosphine ligands 12a-d. By tuning the electronic properties of the phosphines, we were able to demonstrate the ligand 12d as the more efficient one for transition-metal catalyzed asymmetric reactions. The possible reason for the difference in the reactivity of the ligands 12c and 12d in asymmetric catalysis could be that the (3,5-trifluoromethylphenyl) group on the phosphine of the ligand 12c is an electron poor group. This may lead to an increase in the Lewis acidity on the transition metal, thereby decreasing the reactivity and selectivities in the asymmetric reactions. The ruthenium complex 80c which was derived from 12d and (S,S)-1,2-DPEN provided high enantioselectivities in hydrogenation of aromatic and hetero-aromatic ketones, quite comparable to the $C_2$-symmetrical dixylylphosphine 13b.

Summary and Outlook

5. Summary and Outlook

This work focused on the preparation of new chiral ligands and studies concerning their applications in asymmetric catalysis.

In the first project, we described the synthesis of a chiral planar ferrocenyl P,P-ligand 8 through the selective sulfoxide-lithium exchange. Performing the sulfoxide-lithium exchange on 1,2-bromo-ferrocenyl sulfoxide 17 using PhLi, followed by the addition of several electrophiles led to the bromo substituted 1,2-chiral ferrocenes of type 20 (Scheme 71).

\[
\begin{align*}
17 & \xrightarrow{\text{PhLi, Et₂O, 5 min, -78° C}} 19 \\
19 & \xrightarrow{E^+, -78° C, 30 min; \text{rt, 1-2 h}} 20a-e
\end{align*}
\]

\[
\begin{align*}
20a: E = \text{SPh} & \quad 72\% \\
20b: E = \text{CHO} & \quad 69\% \\
20c: E = \text{I} & \quad 70\% \\
20d: E = \text{SiMe₃} & \quad 70\% \\
20e: E = \text{P(S)Ph₂} & \quad 79\%
\end{align*}
\]

Scheme 71. Preparation of bromo ferrocenes of type 20 and chiral planar ferrocenyl ligand 8 through selective sulfoxide-lithium exchange using PhLi

The ferrocenyllithium species 19 was unstable and undergoes racemization for long reaction times. We extended this selective-sulfoxide lithium exchange to synthesize the chiral planar ferrocenyl P,P-ligand 8. This ligand gave poor enantioselectivities in Pd(0)-catalyzed asymmetric allylic alkylation (Scheme 72).
Scheme 72. Application of ferrocenyl P,P-ligand 8 in Pd(0)-catalyzed allylic alkylation

In the second project, the synthesis of various novel chiral P,N-ligands of type 9-10 was demonstrated. Various chiral P,N-ligands with or without substitutions on the pyridine ring were described (Figure 15).

Figure 15. New ferrocenyl P,N-ligands of type 9 and 10 for asymmetric catalysis.

The P,N-ligands of type 9 and 10 were synthesized via the diastereoselective ortho-lithiation of ferrocenyl sulfoxide 14 (Scheme 73).
Scheme 73. Synthesis of chiral ferrocenyl P,N-ligands 9a-b and 10a-b

The stereochemistry of the two ferrocenyl ethers 32a and 32b at the $\alpha$-center was determined by X-ray analysis of the phosphine sulfide 32b.

These chiral ferrocenyl P,N-ligands were applied successfully in Pd(0)-catalyzed asymmetric allylic alkylations of 27 and provided the desired product 28 in up to 97% ee (Scheme 74).

Scheme 74. Application of new P,N-ligands 9-10 in asymmetric allylic alkylations
Further, we applied these P,N-ligands 9a-g and 10a-g in Ir-catalyzed asymmetric hydrogenation of imines. The P,N-ligands 9a, 10a, 9c, and 9d were found to be efficient ligands for the iridium catalyzed imine hydrogenation under mild conditions. Iridium complexes based on these P,N-ligands 46a-d provided high enantioselectivities in the hydrogenation of various \( N-(3,5\text{-dimethyl-4-methoxy})\text{-phenyl-1-phenyl ethylidene amine\text{ of type 56}} \) that up to 99% \( ee \) (Scheme 75).

![Scheme 75. Hydrogenation of imine 56 using the Ir-catalysts 46a](image)

We also demonstrated the deprotection of \( N-(3,5\text{-dimethyl-4-methoxy})\text{-phenyl group on the amines of type 57} \) under practical conditions which lead to the various chiral primary amines and lactams (Scheme 76).

![Scheme 76. Deprotection of the amine 57](image)
Scheme 76. Deprotection of \(N\)-aromatic group and synthesis of chiral amines and lactams

In the third project we described the synthesis of bis-ferrocenyl ligands of type 11 and their applications in asymmetric catalysis (Figure 16). These ligands provided disappointing results in asymmetric hydrogenations and allylic alkylation.

![Figure 16. New bis-ferrocenyl P,P-ligands 11a and 11b](image)

In the final project we demonstrated the synthesis of new paracyclophane phosphines 12a-d (Figure 17).

![Figure 17. New paracyclophane based diphosphines 12a-d](image)

The ligand 12d was synthesized as outlined in the scheme 77.
Among these P,P-ligands 12a-d, ligand 12d proved to be an efficient ligand for Ru-catalyzed hydrogenation of various prochiral ketones (Scheme 78). The ruthenium-diamine complex 80c which was derived from ligand 12d provided high conversions and enantioselectivities in the hydrogenation of different aromatic and hetero-aromatic ketones up to 97% ee (Scheme 78).
Experimental Section

1. General conditions

All reactions were carried out with a magnetic stirring and, if air or moisture sensitive, in a flamed-dried glassware under a nitrogen or an argon atmosphere. The syringes which were used to transfer the reagents and the solvents were purged with nitrogen or argon prior to use.

Solvents

The solvents were dried according to standard methods by distillation over drying agents as stated below and were stored under argon or nitrogen. Dichloromethane and toluene were predried over calcium chloride and were distilled from calcium hydride. DMF was heated at reflux for 14 h over calcium hydride and was distilled. Diisopropylamine and i-PrOH were distilled from potassium hydride. Ethanol was treated with phthalic anhydride (25 g/L) and sodium, heated at reflux for 6 h and distilled. Methanol was treated with magnesium turnings (20 g/L), heated at reflux for 6 h and distilled. Tetrahydrofuran (THF) was continuously heated at reflux and freshly distilled from sodiumbenzophenone ketyl under nitrogen.

Reagents

Reagents of >98% purity were used as obtained.

n-Butyllithium was used as a solution in hexane.

t-Butyllithium was used as a solution in pentane.

**Lithium Diisopropylamine** was prepared by adding n-BuLi (1.5 M; 1.10 equiv.) to a 2.0 M solution of diisopropylamine (1.32 equiv.) in THF at -78 °C and then stirring at room temperature for 30 min. It was used, as it is in lithiation reactions.

**Phenyl lithium** was prepared by adding n-BuLi (1.5 M; 1.10 equiv.) to a 0.2 M solution of iodobenzene (1.0 equiv) in diethyl ether at 0 °C and then stirred at room temperature for 30 min. It was used, as it is in exchange and lithiation reactions.

The following reagents and substances were prepared according to the literature procedures:

- Sulfoxide ([14](#)), 1,3-Diphenyl-3-acetoxypropen ([27](#)), chloro dixylylphosphine,[123](#) bis 2-furlylphosphine,[124](#) and NaBARF[125](#)

**Content determination of organometallic reagents**

The organo lithium and organo magnesium solutions were titrated using the method of Paquette[126](#) and Knochel[127](#) prior to use.

Chromatography

Thin layer chromatography (TLC) was performed using aluminium plates covered with SiO2 (Merck 60, F-254). The chromatograms were developed under UV light and/or by treatment of the TLC plate with one of the solutions below followed by gentle heating with a heat gun:

- KMnO4 (0.3 g), K2CO3 (20 g) and KOH (0.3 g) in water (300 mL)

---

-Phosphormolybdic acid (5.0 g), Ce(SO$_4$)$_2$ (2.0 g) and conc. H$_2$SO$_4$ (12 mL) in water (230 mL)
Flash column chromatography was performed using SiO$_2$ 60 (0.040-0.063 mm; 230-400 mesh ASTM) or Al$_2$O$_3$ (grade III) from Merck. The diameters of the columns and the amount of silica gel were calculated according to the recommendations of W. C. Still.$^{128}$

### Analytical data

**Melting points** were uncorrected and measured on a Büchi B-540 apparatus.

**NMR** spectra were recorded on Brucker ARX 200, AC 300 or WH 400 instruments. Chemical shifts are reported as δ-values in ppm relative to the deuterated solvent peak: CDCl$_3$ (δH: 7.27, δC: 77.0) and Benzene-d$_6$ (δH: 7.16, δC: 128.0).

For the characterization of the observed signal multiplicities the following abbreviations were applied: s (singlet), d (doublet), dd (double doublet), t (triplet), dt (double triplet), m (multiplet), br (broad).

**Optical rotation values** were measured on the Perkin-Elmer 241 polarimeter.

**Infrared** spectra were recorded from 4000-400 cm$^{-1}$ on a Nicolet 510 FT-IR or a Perkin-Elmer 281 IR spectrometer. The absorption bands are reported in wave number (cm$^{-1}$). For the band characterization the following abbreviation were applied: br (broad), s (strong), m (medium), w (weak).

**Gas Chromatography (GC):** Hewlett-Packard 6890. Cjiral columns: Chirasil-Dex-CB (25 mm x 0.25 nm), Chirasil-L-val (25 m x 0.12 µm x 0.22 mm fused silica WCOT)). Carrier gas H$_2$.

**High Performance Liquid Chromatography (HPLC)** was performed using Gynkotec-HPLC with a diode-array UV-VIS detector. Chiral columns: OD-H, OD, OJ and AD (DiaceL Chemical Industries) with n-heptane/i-propanol as a mobile phase. Racemic compounds were used for optimizing the operating conditions for the resolution of the enantiomer and diastereomer peaks.

**Electron impact mass** (EI, 70 ev) specta were recorded on Finnigan MAT 95Q or Finnigan 90 instrument. High resolution mass spectra (HRMS) were recorded on the same instrument. The combination of gas chromatography with mass spectroscopic detection, a GC/MS from Hewlett-Packard HP 6890/MSD 5973 was used.

**Elemental Analysis** was carried out on a Heraeus CHN-Rapid-Elementanalyzer in the microanalytical laboratories of the Department für Chemie und Pharmazie, Ludwig-Maxmilians Universität München.

### 2. Typical Procedures

**Typical procedure for the diastereoselective ortho-lithiation of ferrocene 14 (TP 1)**

A 250 mL Schlenk flask under an argon atmosphere was charged with ferrocenyl sulfoxide 14 (5 mmol, 1.0 equiv.) in THF (50 mL) and added freshly prepared lithium diisopropylamine (2.0 M in THF; 2.75 mL; 1.1 equiv) at -78 °C. The reaction mixture was stirred at -78 °C for 30 min and then electrophile (1.10-1.20 equiv) was added. The reaction mixture was stirred at -78 °C for 1-1.5 h and then warm up to room temperature and stirred for 2 h. The reaction mixture was quenched with a saturated aqueous NH$_4$Cl solution (20 mL) and the aqueous layer was washed with Et$_2$O (4 x 25 mL). The combined organic extracts were washed with water, brine and then dried over MgSO$_4$. After evaporation of the solvents, the crude product was purified by column chromatography.

Typical procedure for the sulfoxide-lithium exchange on bromo ferrocenes of type 17 using PhLi (TP 2)

A 10 mL Schlenk flask under argon atmosphere, was charged with 1-bromo ferrocenyl sulfoxide 17 (1.0 mmol) was dissolved in THF (5.0 mL). This solution was added to a freshly prepared solution of phenyllithium (0.2 M in diethylether; 1.20 equiv) at -78 °C. After stirring the reaction mixture are -78 °C for 5 min, electrophile (1.10-1.20 equiv) was added and stirred for 30-45 min. Then the reaction mixture was warmed to room temperature and stirred for 1-2 h. Reaction mixture was quenched with saturated aqueous NH₄Cl solution (5 mL) and the aqueous layer was extracted with Et₂O (4 x 10 mL). The combined organic extracts were washed with water, brine and dried over MgSO₄. Evaporation of the solvents and purification by column chromatography afforded the desired bromoferrocenes of type 20.

Typical procedure for the preparation of ferrocenyl alcohols through the sulfoxide-lithium exchange (TP 3)

A Schlenk flask under an argon atmosphere was charged with ferrocenyl sulfoxide 30 or 34 (10 mmol, 1.0 equiv.) in THF and cooled to −78 °C. A solution of freshly prepared PhLi in ether (0.20 M in ether, 1.20 equiv.) was slowly added and the reaction mixture was stirred at −78 °C for 10 min. 2-Pyridinecarboxaldehyde (1.20 equiv) was added dropwise at −78 °C and reaction mixture was stirred for 1.5 h then at room temperature for 1.5 h-2 h. After quenching the reaction mixture with a saturated NH₄Cl solution (25 mL), the aqueous layer was extracted with diethyl ether (4 x 30 mL). The combined organic layers were washed with water, brine, dried over MgSO₄ and evaporated under reduced pressure. Purification of the residue by flash chromatography (silica gel, n-pentane:Et₂O 1:1) afforded the two diastereomeric alcohols as a separable or inseparable mixture.

Typical procedure for preparation of ferrocenyl ethers (TP 4):

A 50 mL Schlenk flask under an argon atmosphere was charged with KH (1 30 equiv) in THF and cooled to 0 °C. A solution of ferrocenyl alcohol (1.0 equiv) in THF was slowly added and the mixture was stirred at room temperature for 1 h. Methyliodide (1.20 equiv) or benzylbromide (1.20 equiv.) was then added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 10 min then at room temperature for 30 min. After quenching the reaction mixture with a saturated NH₄Cl solution, aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water, brine, dried over MgSO₄ and evaporated under reduced pressure. Crude product was purified by flash chromatography to furnish the ferrocenyl ethers as solids.

Typical procedure for the desulfurization of phosphine sulfides (TP 5).

An argon flushed 50 mL Schlenk flask was loaded with Raney Ni slurry (Raney Ni in water; (P,N-ligand: 10 equiv; P,P-ligand 25 equiv)). Raney Ni was washed with MeOH (4 x 15 mL). To this flask was then transferred a solution of the protected ligand in THF (2-4 mL), then added 25 mL MeOH and stirred at room temperature under argon atmosphere for 12 h (conversion was monitored by ³¹Pnmr). The reaction mixture was filtered under argon. The Raney Ni residue was washed with THF (4 x 10 mL). The combined filtrate was concentrated under reduced pressure to afford the pure product as a yellow solid and stored under argon.
Typical procedure for the preparation of ferrocenyl P,N-iridium complexes 46a-g and 47a-g (TP 6).

A 25 mL Schlenk flask under an argon atmosphere, was charged with P,N-ligand (0.50 mmol), [Ir(cod)Cl]$_2$ (0.25 mmol, 0.50 equiv.) in CH$_2$Cl$_2$ (5 mL) and stirred at room temperature for 1 h. NaBARF (0.75 mmol, 1.50 equiv.) was added followed by water (5 mL) and the resulting two-phase reaction mixture was stirred vigorously for 30 min. The separated aqueous layer was extracted with CH$_2$Cl$_2$ (4 × 15 mL). The combined organic extracts were washed with brine and dried over MgSO$_4$. The residue was purified by column chromatography (CH$_2$Cl$_2$ as an eluent) yielding the Ir-complexes as a bright orange solid.

Typical procedure for the preparation of N-arylimines (TP7).

A 250 mL round-bottomed flask was filled with a ketone (10.0 mmol), an amine (12.0 mmol) and molecular sieves (4 Å, 8 g) in toluene (60 mL). The reaction mixture was refluxed until full conversion was reached (conversion was monitored by GC). The reaction mixture was filtered through celite, solvent was evaporated and the crude product was further purified by column chromatography or vacuum distillation or recrystallization to afford the desired product.

Typical procedure for the Ir-catalyzed hydrogenation of the imines (TP 8):

A 10 mL Schlenk flask under an argon atmosphere was loaded with Ir-complex (0.005 mmol) and imine (0.5 mmol) in Toluene:MeOH (4:1). The mixture was stirred at room temperature for 10-15 min. Then the solution was transferred under argon to an autoclave which was equipped with a glass tube and a stirring bar. The autoclave was then purged three times with hydrogen (5 bar) and finally pressurized to 10 bar. The reaction mixture was stirred for the indicated period of time until full conversion was achieved. Then the hydrogen gas was released, evaporated the solvents and filtered through a short pad of silica gel. Conversion was checked by $^1$H-NMR/GC and enantioselectivity was determined using either Chiral GC or Chiral HPLC.

Typical procedure for the preparation of chiral primary amines and lactams (TP 9)

The secondary amine of type 57 (0.4 mmol) was dissolved in MeOH:H$_2$O (6:1; 21 mL) and cerium ammonium nitrate (CAN; 4 equiv; 1.6 mmol) was added at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for overnight. The reaction mixture was washed with CH$_2$Cl$_2$ (5 mL) and the aqueous layer was made alkaline using aqueous NaOH solution (2.0 M). The aqueous layer was washed with ethylacetate (4 x 15 mL) and the combined organic extracts were washed with water, brine, dried over MgSO$_4$ and concentrated in vacuo. Purification by chromatography afforded the primary amines and lactams.

Typical procedure for the preparation of ruthenium-diamine complexes 79a-c and 80a-c of paracyclophane phosphines (TP 10)

In a 10 mL Schlenk falso P,P-ligand (0.01 mmol) and [Ru(C$_6$H$_5$Cl)$_2$ (0.005 mmol) were dissolved in a mixture of toluene (2 mL) and DMF (1.5 mL) under an argon atmosphere. The mixture was heated at 115 °C for 4 h and then chiral diamine (0.01 mmol) was added and continued the stirring at 115 °C for 2 h. The reaction mixture was cooled to room temperature
and stirred for overnight. Evaporated the solvents under reduced pressure and the mixture was washed with CH₂Cl₂:Et₂O (1:1; 4 mL) under argon. Evaporation of the solvents, afforded the desired ruthenium-diamine complex of the paracyclophane phosphine (79a-c or 80a-c). These complexes are used in the ketone hydrogenation without any further purification.

**Typical procedure for the Ru-catalyzed hydrogenation of the ketones (TP 11)**

A 10 mL Schlenk flask was charged with the ruthenium precatalyst of type 79 or 80 (0.002 mmol) and ketone (4 mmol) and dry iPrOH (4 mL) under argon atmosphere. The mixture was stirred at room temperature for 15 min then transferred under argon to an autoclave which was equipped with a glass tube and a stirring bar. The autoclave was then purged three times with hydrogen (5 bar) and finally pressurized to 10 bar. The reaction mixture was stirred for the indicated period of time until full conversion was achieved. Then the hydrogen gas was released, evaporated the solvents and filtered through a short pad of silica gel. Conversion was checked by ¹H-NMR/GC and enantioselectivity was determined using either Chiral GC or Chiral HPLC.

**Typical procedure for the Pd(0)-catalyzed asymmetric alkylation on racemic 27 (TP 12)**

A 10 mL Schlenk flask was filled with ferrocenyl ligand (1.0 mol %), [Pd(C₃H₅)Cl]₂ (1.0 mg; 0.5 mol %) and CH₂Cl₂ (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 10 min. 3-Acetoxy-1,3-diphenyl-propene 27 (126 mg; 0.5 mmol), dimethylmalonate (0.2 mL; 1.5 mmol), N,O-bistrimethylsilylacetamide (305 mg; 1.5 mmol) and potassium acetate (0.5 mg; 1.0 mol%) were added successively. The reaction mixture was stirred for 1 h-12 h at room temperature. The reaction was quenched with saturated aqueous NH₄Cl (2 mL) and extracted with CH₂Cl₂ (4 x 10 mL). The organic phase was washed with water, brine, dried over Na₂SO₄ and concentrated in vacuo. Purification by flash chromatography yielded 28.

**Typical procedure for the Rh-catalyzed hydrogenations (TP 13)**

A 10 mL Schlenk flask was charged with the chiral ligand (1 mol %) and [Rh(nbd)₂]BF₄ (3.7 mg, 1 mol %) in toluene/methanol (5:1). Then added a solution of substrate 25 or 74 in methanol (4 mL) and stirred for 15 min at room temperature. The mixture was transferred to an autoclave which was equipped with a glass tube and a stirring bar. The autoclave was then purged three times with hydrogen (5 bar) and finally pressurized to the required pressure. The reaction mixture was stirred for the indicated period of time until full conversion was achieved. Then the hydrogen gas was released, evaporated the solvents and filtered through a short pad of silica gel, afforded the desired product 26 or 75. Conversion was checked by ¹H-NMR/GC and enantioselectivity was determined using either Chiral GC or HPLC.

3. Preparation of new planar chiral ferrocenyl P,P-ligand 8

(SFc, S)-[2-((2-Bromophenyl)dimethylsilyl)-ferrocen-1-yl]-p-tolylsulfoxide (16)
Prepared according to TP1 using sulfoxide 14 (1.62 g; 5.0 mmol), LDA (2.75 mL, 5.50 mmol; 1.10 equiv.), and 2-bromophenyldimethylchlorosilane 15 (1.50 g, 6.0 mmol; 1.2 equiv) as an electrophile. After the typical work-up, the crude product was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1), provided the desired compound (2.50 g, 4.65 mmol, 93 %) as a yellow solid.

**MP:** 146.5-148.5 °C

\[ [\alpha]_{D}^{20} = +20.1 \text{ (c = 0.2, acetone)} \]

\[ ^{1}H\text{-NMR (600 MHz, CDCl}_{3}\text{): } \delta = 7.59-7.58 \text{ (m, 2H), 7.45-7.44 \text{ (m, 2H), 7.27-7.24 \text{ (m, 3H), 7.17-7.15 \text{ (m, 2H), 4.56 \text{ (s, 1H), 4.46 \text{ (s, 1H), 4.35 \text{ (s, 1H), 4.24 \text{ (s, 5H), 2.41 \text{ (s, 3H), 1.04 \text{ (s, 3H), 0.79 \text{ (s, 3H ppm.}}}}}}}}\]

\[ ^{13}C\text{-NMR (150 MHz, CDCl}_{3}\text{): } \delta = 140.9, 139.6, 137.9, 132.4, 130.6, 130.0, 129.2, 126.3, 125.1, 78.7, 73.3, 71.6, 71.5, 70.1, 21.4, 0.74, -0.58 \text{ ppm.}}\]

**IR (KBr-Pressling):** \( \nu_{\text{max}} \text{(cm}^{-1}) = 3435 \text{ (br, s), 2920 \text{ (w), 1578 \text{ (w), 1411 \text{ (m), 1175 \text{ (m), 1048 \text{ (m), 810 \text{ (s), 757 \text{ (m).}}}}}}\]

**MS (70 eV, EI):** \( m/z \) (%) = 536 (M⁺, 68), 523 (47), 522 (100), 520 (90), 398 (11).

**HRMS (EI):** \( m/z \) calcd. for: \([C_{25}H_{25}79\text{BrFe}_{32}SSiO}] 535.9928, \text{ found: 535.9912.}\)

\((R_{Fc}, S)-[1\text{-Bromo-2-ferrocen-1-yl]}-p\text{-tolylsulfoxide (17)}\)

Prepared according to TP1 using sulfoxide 14 (1.62 g, 5.0 mmol), LDA (2.75 mL, 5.50 mmol; 1.10 equiv.), and 1,1,2,2-tetrafluorodibromothane (1.56 g; 6.0 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1), provided the desired compound (1.78 g, 4.41 mmol, 88 %) as a brown solid.

**MP:** 85.8-88.9 °C

\[ [\alpha]_{D}^{20} = +9.5 \text{ (c = 0.2, acetone)} \]

\[ ^{1}H\text{-NMR (300 MHz, C}_{6}D_{6}\text{): } \delta = 7.72-7.69 \text{ (m, 2H), 6.90-6.88 \text{ (m, 2H), 4.18 \text{ (dd, J = 1.3 Hz, 2.2 Hz, 1H), 4.05 \text{ (s, 5H), 3.85 \text{ (q, J = 1.3 Hz, 1H), 3.63 \text{ (t, J = 2.7 Hz, 1H), 1.98 \text{ (s, 3H ppm.}}}}}}\]

\[ ^{13}C\text{-NMR (75 MHz, C}_{6}D_{6}\text{): } \delta = 142.2, 140.7, 129.4, 125.5, 93.6, 77.5, 73.5, 72.5, 68.4, 68.2 \text{ ppm.}}\]

**IR (KBr-Pressling):** \( \nu_{\text{max}} \text{(cm}^{-1}) = 3436 \text{ (m), 3078 \text{ (w), 1641 \text{ (m), 1490 \text{ (w), 1191 \text{ (m), 1034 \text{ (s), 813 \text{ (m), 627 \text{ (nm.}}}}}}\]

**MS (70 eV, EI):** \( m/z \) (%) = 402 (M⁺, 100), 386 (14), 324 (19), 250 (57), 217 (57), 185 (31).

**HRMS (EI):** \( m/z \) calcd. for: \([C_{17}H_{15}79\text{BrFe}_{32}SO}] 401.9376, \text{ found: 401.9340.}\)

\((R_{Fc})-[2\text{-Bromo-2-ferrocen-1-yl]}-phenylsulfide (20a)\)
Prepared according to TP2, using sulfoxide 17 (403 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et₂O; 1.20 equiv) and diphenyldisulfide (262 mg; 1.20 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, n-pentane), provided the desired compound (269 mg, 0.72 mmol, 72 %) as a pale yellow solid.

**Experimental Section**

Prepared according to TP2, using sulfoxide 17 (403 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et₂O; 1.20 equiv) and diphenyldisulfide (262 mg; 1.20 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, n-pentane), provided the desired compound (269 mg, 0.72 mmol, 72 %) as a pale yellow solid.

**MP:** 66.7-67.0 °C

\[ [\alpha]_D^{20} = -6.0 \text{ (c = 0.2, acetone) } \]

**¹H-NMR (300 MHz, C₆D₆):** \( \delta = 7.23-7.22 \text{ (m, 2H), 6.98-6.93 \text{ (m, 2H), 6.86-6.81 \text{ (m, 1H), 4.34 \text{ (dd, J = 1.3 Hz, 2.6 Hz, 1H), 4.20 \text{ (dd, J = 1.7 Hz, 2.6 Hz, 1H), 4.04 \text{ (s, 5H), 3.77 \text{ (t, J = 2.6 Hz, 1H ppm.}}}} \]

**¹³C-NMR (75 MHz, C₆D₆):** \( \delta = 139.9, 129.0, 126.7, 125.5, 85.9, 77.9, 73.8, 72.5, 72.4, 68.7 \text{ ppm.} \)

**IR (KBr-Pressling):** \( \nu_{\text{max}} (\text{cm}^{-1}) = 3435 \text{ (s), 1627 \text{ (m), 1478 \text{ (m), 1394 \text{ (m), 1106 \text{ (w), 1024 \text{ (m), 1001 \text{ (m), 827 \text{ (m), 740 \text{ (m).}}}}}} \]

**MS (70 eV, EI):** \( m/z \text{ (%) = 372 (M⁺, 100), 292 (12), 258 (23), 203 (20), 171 (43).} \)

**HRMS (EI):** \( m/z \text{ calcd. for: } [C_{16}H_{13}^{79}BrFe^{32}S] 371.9271, \text{ found: 371.9273.} \)

**To a 50 mL round-bottomed flask was added ferroceny lsulfide 20a (186 mg; 0.5 mmol) and CH₂Cl₂ (10 mL). This solution was added slowly to a solution of mCPBA (345 mg, 2.0 mmol; 4.0 equiv) in CH₂Cl₂ (5 mL). After the addition the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with 2.0 M aqueous solution of NaHSO₃ (20 mL) and the aqueous layer was extracted with CH₂Cl₂ (4 x 10 mL). The combined organic extracts were washed with water, brine, dried over MgSO₄ and concentrated in vacum. The residue was purified by flash chromatography (silica gel, n-pentane), furnished the desired compound (190 mg, 0.47 mmol, 94 %) as a pale yellow solid.**

**MP:** 66.4-68.9 °C

\[ [\alpha]_D^{20} = -2.3 \text{ (c = 0.2, CH₂Cl₂) } \]

**¹H-NMR (300 MHz, C₆D₆):** \( \delta = 8.09-8.06 \text{ (m, 2H), 6.91-6.89 \text{ (m, 3H), 4.66 (dd, J = 1.7 Hz, 2.7 Hz, 1H), 4.33 (s, 5H), 4.12-4.11 \text{ (m, 1H), 3.67 (t, J = 2.9 Hz, 1H ppm.)}} \]

**¹³C-NMR (75 MHz, C₆D₆):** \( \delta = 143.2, 132.7, 128.9, 127.6, 89.3, 76.8, 74.6, 73.5, 70.0, 69.9 \text{ ppm.} \)

**IR (KBr-Pressling):** \( \nu_{\text{max}} (\text{cm}^{-1}) = 3436 \text{ (m), 1637 \text{ (w), 1445 \text{ (m), 1322 \text{ (s), 1200 \text{ (m), 1146 \text{ (s), 1088 \text{ (m), 938 \text{ (m), 724 \text{ (s), 612 \text{ (s).}}}}}} \]

**MS (70 eV, EI):** \( m/z \text{ (%) = 404 (M⁺, 62), 324 (100), 258 (5), 204 (28), 202 (25).} \)

**HRMS (EI):** \( m/z \text{ calcd. for: } [C_{16}H_{13}^{79}BrFe^{32}SO₂] 403.9169, \text{ found: 403.9149.} \)

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.3 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C);
t_r = 44.9 min [minor], t_r = 51.0 min [major]; 97% ee.

(R_Fe)-[2-Bromo-2-ferrocen-1-yl]-aldehyde (20b)

![Chemical Structure](image)

Prepared according to TP2, using sulfoxide 17 (403 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et_2O; 1.20 equiv), and DMF (1.0 mL; 1.30 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, n-pentane:Et_2O (10:1)), provided the desired compound (202 mg, 0.69 mmol, 69%) as a dark red oil.

[α]_D^{20} = −692 (c = 0.15, CH_2Cl_2)

^1H-NMR (300 MHz, C_6D_6): δ = 10.24 (s, 1H), 4.62 (s, 1H), 4.26 (s, 1H), 3.85 (s, 6H) ppm.

^13C-NMR (75 MHz, C_6D_6): δ = 191.4, 80.3, 76.5, 74.6, 72.2, 70.9, 66.8 ppm.

IR (neat): ν_max (cm⁻¹) = 3436 (w), 1681 (s), 1438 (m), 1224 (m), 987 (m), 828 (m), 749 (m).

MS (70 eV, EI): m/z (%) = 292 (M⁺, 66), 212 (100), 184 (33), 156 (4), 128 (51).

HRMS (EI): m/z calcd. for: [C_{11}H_9^2BrFeO] 291.9186, found: 291.9179.

(R_Fe)-[2-Bromo-2-ferrocen-1-yl]-Iodide (20c)

![Chemical Structure](image)

Prepared according to TP2, using sulfoxide 17 (403 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et_2O; 1.2 equiv), and I_2 (304 mg; 1.2 mmol; 1.2 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, n-pentane), provided the desired compound (274 mg, 0.70 mmol, 70%) as a pale yellow solid.

MP: 85.5-83.6 °C

[α]_D^{20} = −1.8 (c = 0.2, acetone)

^1H-NMR (600 MHz, C_6D_6): δ = 4.52 (s, 1H), 4.42 (s, 1H), 4.22 (s, 5H), 4.19 (s, 1H) ppm.

^13C-NMR (150 MHz, C_6D_6): δ = 84.5, 73.7, 73.6, 73.3, 69.6, 68.4 ppm.

IR (KBr-pressling): ν_max (cm⁻¹) = 2900 (w), 1690 (m), 1633 (s), 1569 (m), 1468 (m), 1312 (m), 1100 (m), 1028 (m), 845 (s), 779 (s).

MS (70 eV, EI): m/z (%) = 390 (M⁺, 100), 183 (17), 128 (74), 127 (12).

HRMS (EI): m/z calcd. for: [C_{10}H_8^79BrFeI] 389.8203, found: 389.8188.

(R_Fe)-[2-Bromo-2-ferrocen-1-yl]-trimethylsilane (20d)

![Chemical Structure](image)
Prepared according to TP2, using sulfoxide 17 (403 mg; 1.0 mmol), phenyllithium (6.0 mL; 0.2 M in Et₂O; 1.20 equiv), and trimethylchlorosilane (0.2 mL; 1.20 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, n-pentane), providing the desired compound (236 mg, 0.70 mmol, 70 %) as a pale yellow oil.

\[ \alpha \] D = \{-1.0 \text{ (c = 0.2, acetone)} \]

1H-NMR (300 MHz, C₆D₆): \( \delta = 4.41 \text{ (s, 1H)}, 4.40 \text{ (s, 1H)}, 4.18 \text{ (s, 5H)}, 4.17 \text{ (s, 1H)}, 0.21 \text{ (s, 9H)} \) ppm.

13C-NMR (75 MHz, C₆D₆): \( \delta = 82.5, 73.7, 73.0, 72.8, 67.6, 67.2, -0.2 \) ppm.

IR (neat): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 2910 \text{ (w)}, 1600 \text{ (w)}, 1558 \text{ (m)}, 1468 \text{ (m)}, 1229 \text{ (m)}, 1028 \text{ (m)}, 845 \text{ (s)}, 779 \text{ (s)}, 698 \text{ (m)} \).

MS (70 eV, EI): \( m/z \) (%) = 335 (M⁺, 100), 258 (77), 195 (14), 121 (25).

HRMS (EI): \( m/z \) calcd. for: [C₁₃H₁₇BrFeSi] 335.9632, found: 335.9640.

\((R\text{Fe})-[2\text{-Bromo-2-ferrocen-1-yl]}\text{-trimethylsilane (20e)}\)

Prepared according to TP2, using sulfoxide 17 (403 mg; 1.0 mmol), phenyllithium (6.0 mL; 0.2 M in Et₂O; 1.20 equiv). The reaction mixture was stirred at -78 °C for 5 min, and then ClPPh₂ (0.2 mL; 1.20 mmol; 1.20 equiv) was added as an electrophile. The reaction mixture was stirred 30 min at -78 °C and then at room temperature for 1 h. A solution of sulphur (320 mg; 10.0 equiv) in butylamine (1.0 mL) was added to the reaction mixture. Then reaction mixture was stirred at room temperature for 4-5 h and added saturated aqueous NH₄Cl solution (10 mL). The aqueous layer was extracted with Et₂O (4 x 15 mL) and the combined organic extracts were washed with HCl (2.0 M), water, brine, dried over MgSO₄, and concentrated in vacum. The crude product was purified by column chromatography (silica gel, n-pentane:Et₂O (10:1)), furnished the desired compound (380 mg, 0.79 mmol, 70 %) as a pale yellow solid.

MP: 125.5-123.6 °C

\[ \alpha \] D = \{-4.2 \text{ (c = 0.2, CH₂Cl₂)} \]

1H-NMR (300 MHz, C₆D₆): \( \delta = 7.64-7.54 \text{ (m, 4H)}, 7.15-7.10 \text{ (m, 6H)}, 4.64-4.62 \text{ (m, 1H)}, 4.54-4.53 \text{ (m, 1H)}, 4.42 \text{ (s, 5H)}, 4.29 \text{ (s, 1H)} \) ppm.

13C-NMR (75 MHz, C₆D₆): \( \delta = 134.6 \text{ (d, J = 87.1 Hz)}, 132.8 \text{ (d, J = 85.6 Hz)}, 131.4 \text{ (d, J = 11.0 Hz)}, 131.0 \text{ (d, J = 10.6 Hz)}, 129.2 \text{ (d, J = 2.9 Hz)}, 129.0 \text{ (d, J = 2.9 Hz)}, 127.6 \text{ (d, J = 12.7 Hz)}, 127.1 \text{ (d, J = 13.0 Hz)}, 82.8 \text{ (d, J = 10.1 Hz)}, 79.2 \text{ (d, J = 90.2 Hz)}, 78.2 \text{ (d, J = 10.8 Hz)}, 72.5 \text{ (d, J = 9.7 Hz)}, 72.0 \text{ (d, J = 7.6 Hz)}, 71.9 \) ppm.

IR (KBr-pressling): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 2914 \text{ (br, w)}, 1689 \text{ (w)}, 1646 \text{ (m)}, 1598 \text{ (m)}, 1219 \text{ (m)}, 1109 \text{ (m)}, 898 \text{ (s)}, 778 \text{ (s)}, 645 \text{ (s)} \).

MS (70 eV, EI): \( m/z \) (%) = 480 (M⁺, 12), 448 (100), 337 (64), 183 (30).

HRMS (EI): \( m/z \) calcd. for: [C₂₂H₁₈BrFeP³²S] 479.9400, found: 479.9412.

\((S\text{Fe})-[2\text{-((2-Bromophenyl)dimethylsilyl}]-1\text{-phosphinothiylferrocene (22)}\)
Prepared according to TP2, using sulfoxide 17 (538 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et₂O; 1.20 equiv). The reaction mixture was stirred at -78 °C for 10 min, and then ClPPh₂ (0.2 mL; 1.20 mmol; 1.2 equiv) was added as an electrophile. The reaction mixture was stirred 30 min at -78 °C and then at room temperature for 1 h. A solution of sulfur (320 mg; 10 equiv) in butylamine (1.0 mL) was added to the reaction mixture. Then reaction mixture was stirred at room temperature for 4-5 h and added saturated aqueous NH₄Cl solution (10 mL). The aqueous layer was extracted with Et₂O (4 x 15 mL) and the combined organic extracts were washed with HCl (2.0 M), water, brine, dried over MgSO₄, and concentrated in vacum. The crude product was purified by column chromatography (silica gel, n-pentane:Et₂O (8:1)), furnished the desired compound (542 mg, 0.88 mmol, 88%) as a yellow solid.

\[ \text{Prepared according to TP2, using sulfoxide 17 (270 mg; 0.5 mmol), phenyllithium (3 mL; 0.2 M in Et₂O; 1.20 equiv) and I}_2 (152 mg, 0.6 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, n-pentane), furnished the desired compound (234 mg, 0.45 mmol, 89%) as a yellow solid. \]

**Experimental Section**

**Prepared according to TP2, using sulfoxide 17 (538 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et₂O; 1.20 equiv). The reaction mixture was stirred at -78 °C for 10 min, and then ClPPh₂ (0.2 mL; 1.20 mmol; 1.2 equiv) was added as an electrophile. The reaction mixture was stirred 30 min at -78 °C and then at room temperature for 1 h. A solution of sulfur (320 mg; 10 equiv) in butylamine (1.0 mL) was added to the reaction mixture. Then reaction mixture was stirred at room temperature for 4-5 h and added saturated aqueous NH₄Cl solution (10 mL). The aqueous layer was extracted with Et₂O (4 x 15 mL) and the combined organic extracts were washed with HCl (2.0 M), water, brine, dried over MgSO₄, and concentrated in vacum. The crude product was purified by column chromatography (silica gel, n-pentane:Et₂O (8:1)), furnished the desired compound (542 mg, 0.88 mmol, 88%) as a yellow solid.**

**MP:** 121.4-122.8 °C

\[ \alpha \] \text{D}_{20} = +9.2 (c = 0.2, acetone)

\(^1\)H-NMR (300 MHz, CDCl₃): \( \delta = 7.99-7.94 \) (m, 2H), 7.75-7.69 (m, 2H), 7.58 (dd, \( J = 7.5 \) Hz, 1.8 Hz, 1H), 7.21 (d, \( J = 1.8 \) Hz, 1H), 7.02-6.99 (m, 3H), 6.92-6.90 (m, 4H), 6.70-6.66 (m, 1H), 4.40-4.39 (m, 1H), 4.27 (s, 5H), 4.10-4.09 (m, 1H), 3.92-3.91 (m, 1H), 1.00 (s, 3H), 0.86 (s, 3H) ppm.

\(^{13}\)C-NMR (75 MHz, CDCl₃): \( \delta = 140.8, 137.9, 135.7 \) (d, \( J = 16.0 \) Hz), 134.8 (d, \( J = 15.1 \) Hz), 132.9, 132.7 (d, \( J = 10.3 \) Hz), 132.3 (d, \( J = 10.5 \) Hz), 131.3, 130.9 (d, \( J = 3.1 \) Hz), 130.7, 128.1, 127.9 (d, \( J = 3.9 \) Hz), 127.8, 126.3, 82.8 (d, \( J = 12.8 \) Hz), 82.2 (d, \( J = 96.9 \) Hz), 78.3 (d, \( J = 14.4 \) Hz), 74.5 (d, \( J = 18.2 \) Hz), 72.1 (d, \( J = 9.7 \) Hz), 70.7, 1.9, 1.4 ppm.

\(^{31}\)P-NMR (81 MHz, CDCl₃): \( \delta = +41.33 \) ppm.

IR (KBr-Pressling): \( \nu_{\text{max}} (\text{cm}^{-1}) = 3435 \) (br, s), 2923 (w), 1628 (w), 1436 (w), 1101 (m), 811 (m), 717 (m), 616 (w).

MS (70 eV, EI): \( m/z \) (%) = 614 (M⁺, 63), 601 (18), 599 (17), 217 (100).

HRMS (EI): \( m/z \) calcd. for: \([C_{30}H_{28}BrFePSSi]^{613.9951}, \) found: 613.9950.

\((S_{\text{Fc}})-[2-((2-Bromophenyl)dimethylsilyl)]-1-iodo-ferrocene (23)\)

Prepared according to TP2, using sulfoxide 17 (270 mg; 0.5 mmol), phenyllithium (3 mL; 0.2 M in Et₂O; 1.20 equiv) and I₂ (152 mg, 0.6 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, n-pentane), furnished the desired compound (234 mg, 0.45 mmol, 89%) as a yellow solid.

**MP:** 110.0-112.4 °C

\[ \alpha \] \text{D}_{20} = +4.8 (c = 0.2, acetone)
**Experimental Section**

$^{1}$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.50-7.48 (m, 1H), 7.17-7.13 (m, 3H), 4.70 (q, $J = 1.3$ Hz, 1H), 4.38 (t, $J = 2.2$ Hz, 1H), 4.22 (s, 5H), 4.18 (dd, $J = 1.3$ Hz, 2.6 Hz, 1H), 0.98 (s, 3H), 0.72 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 139.7, 137.8, 132.6, 130.8, 126.2, 113.6, 88.7, 79.3, 73.6, 72.8, 72.7, 71.2, 1.0, 0.2 ppm.

IR (KBr-Pressling): $\nu_{\text{max}}$ (cm$^{-1}$) = 2920 (m), 1628 (w), 1599 (m), 1346 (w), 1001 (m), 811 (m), 707 (m).

MS (70 eV, EI): $m/z$ (%) = 524 (M$^+$, 90), 318 (20), 303 (25), 181 (100), 121 (68).

HRMS (EI): $m/z$ calcd. for: [C$_{18}$H$_{18}$BrFe$_{127}$Si] 523.8755, found: 523.8767.

$(S_{Fe})$-[2-(((2-Phosphiothioyl)phenyl))dimethylsilyl)-1- phosphinothioyl-ferrocene (24)

A 25 mL Schlenk flask was charged with phosphinesulfide 22 (616 mg; 1.0 mmol) and THF (5 mL) under argon atmosphere. nBuLi (1.6 M; 0.70 mL; 1.10 mmol) was added at -78 °C dropwise to the above solution and stirred the resulted lithium species for 15 min. CIPPh$_2$ (0.20 mL; 1.20 mmol; 1.20 equiv) was added as an electrophile and the reaction mixture was stirred 30 min at -78 °C and then at room temperature for 1 h. A solution of sulfur (320 mg; 10 equiv) in butylamine (1.0 mL) was added to the reaction mixture and the reaction mixture was stirred at room temperature for 4-5 h and added a saturated aqueous NH$_4$Cl solution (10 mL). The aqueous layer was extracted with Et$_2$O (4 x 15 mL) and the combined organic extracts were washed with HCl (2.0 M), water, brine, dried over MgSO$_4$, and concentrated in vacum. The crude product was purified by column chromatography (silica gel, n-pentane:Et$_2$O (6:1)), furnished the desired compound (670 mg, 0.89 mmol, 89%) as a yellow solid.

**MP:** 212.4-213.8 °C

$[\alpha]_D^{20} = +2.9$ (c = 0.2, acetone)

$^{1}$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.90-7.75 (m, 2H), 7.61-7.54 (m, 7H), 7.50-7.40 (m, 12H), 7.32-7.26 (m, 3H), 4.38-4.36 (m, 2H), 4.29 (s, 5H), 3.83-3.81 (m, 1H), 0.66 (s, 3H), 0.18 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 145.4 (d, $J = 18.3$ Hz), 140.0 (d, $J = 16.5$ Hz), 138.4 (d, $J = 87.5$ Hz), 135.4 (d, $J = 9.9$ Hz), 135.2 (d, $J = 87.3$ Hz), 134.8 (d, $J = 3.6$ Hz), 134.6 (d, $J = 87.5$ Hz), 134.3 (d, $J = 9.5$ Hz), 133.7 (d, $J = 3.1$ Hz), 132.5 (d, $J = 13.7$ Hz), 132.5 (d, $J = 10.1$ Hz), 132.4 (d, $J = 14.5$ Hz), 132.2 (d, $J = 10.5$ Hz), 128.1 (d, $J = 3.5$ Hz), 88.1 (d, $J = 87.6$ Hz), 81.2 (d, $J = 2.7$ Hz), 80.0 (d, $J = 2.9$ Hz), 71.6 (d, $J = 9.1$ Hz), 70.4, 70.2 (d ; $J = 8.9$ Hz), 4.6, 4.1 ppm

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta$ = +41.33 ppm.

IR (KBr-Pressling): $\nu_{\text{max}}$ (cm$^{-1}$) = 3430 (br, s), 2910 (m), 1500 (m), 1460 (m), 1219 (w), 1101 (m), 810 (m), 798 (m).

MS (70 eV, EI): $m/z$ (%) = 752 (M$^+$, 13), 689 (25), 688 (50), 687 (100), 656 (8).

HRMS (EI): $m/z$ calcd. for: [C$_{42}$H$_{38}$Fe$_2$P$_2$$_{32}$S$_2$Si] 752.1009, found: 752.1013.

$(S_{Fe})$-[2-(((2-Diphynlphosphiono)phenyl))dimethylsilyl)-1-diphenylphosphinoferrocene (8)
Prepared according to TP5, using the phosphinesulfide 24 (150 mg, 0.20 mmol) and Raney-Ni (765 mg, 13 mmol; 65.0 equiv.) in MeOH (25 mL). After evaporation of the solvent, the diphosphine (127 mg, 0.18 mmol; 92%) obtained as a yellow solid.

**MP:** 88.5-91.2 °C

\[ [\alpha]_D^{20} = +2.0 \ (c = 0.2, \text{acteone}) \]

**\(^{1}\)H-NMR (300 MHz, CDCl\(_3\)):** \(\delta = 7.90-7.75 \ (m, 2H), 7.61-7.54 \ (m, 7H), 7.50-7.40 \ (m, 12H), 7.32-7.26 \ (m, 3H), 4.38-4.36 \ (m, 2H), 4.29 \ (s, 5H), 3.83-3.81 \ (m, 1H), 0.66 \ (s, 3H), 0.18 \ (s, 3H) \ ppm.\)

**\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)):** \(\delta = 145.4 \ (d, J = 18.3 \ Hz), 140.0 \ (d, J = 16.5 \ Hz), 138.4 \ (d, J = 87.5 \ Hz), 135.4 \ (d, J = 9.9 \ Hz), 135.2 \ (d, J = 87.3 \ Hz), 134.8 \ (d, J = 3.6 \ Hz), 134.6 \ (d, J = 87.5 \ Hz), 134.3 \ (d, J = 9.5 \ Hz), 133.7 \ (d, J = 3.1 \ Hz), 132.51 \ (d, J = 13.7 \ Hz), 132.5 \ (d, J = 10.1 \ Hz), 132.4 \ (d, J = 14.5 \ Hz), 132.2 \ (d, J = 10.5 \ Hz), 128.1 \ (d, J = 3.5 \ Hz), 88.1 \ (d, J = 87.6 \ Hz), 81.2 \ (d, J = 2.7 \ Hz), 80.0 \ (d, J = 2.9 \ Hz), 71.6 \ (d, J = 9.1 \ Hz), 70.4, 70.2 \ (d, J = 8.9 \ Hz), 4.6, 4.1 \ ppm.\)

**\(^{31}\)P-NMR (81 MHz, CDCl\(_3\)):** \(\delta = -21.60, -10.61 \ ppm.\)

**IR (KBr-Pressling):** \(\nu_{\text{max}} \ (\text{cm}^{-1}) = 3430 \ (\text{br, s}), 2910 \ (\text{m}), 1500 \ (\text{m}), 1460 \ (\text{m}), 1219 \ (w), 1101 \ (m), 810 \ (m), 798 \ (m).\)

**MS (70 eV, EI):** \(m/z \ (%) = 688 \ (M^+, 13), 687 \ (25), 524 \ (100), 412 \ (45).\)

**HRMS (EI):** \(m/z \) calcd. for: \([C_{42}H_{38}FeP_{2}Si]\) 688.1567, found: 688.1573.

4. Preparation of new ferrocenyl P,N-ligands 9-10

\((S_{Fe})-1-((S)-p-\text{Toylsulfinyl})-2-(\text{diphenylphosphinothioyl}) \text{ ferrocene} (30):\)

Prepared according to the typical procedure TP1, using sulfoxide 14 (6.48 g, 20.0 mmol) in THF (200 mL) and LDA (11.0 mL; 22.0 mmol; 1.1 equiv.). The reaction mixture was stirred for 30 min at –78 °C and chloro diphenylphosphine (5.30 g, 24.0 mmol, 1.20 equiv.) was added slowly at –78 °C. The reaction mixture was stirred at –78 °C for 1.5 h then warmed to room temperature and stirred for 1.5 h. A solution of sulfur (1.92 g, 60.0 mmol, 3.0 equiv.) in butylamine (3 mL) was added to the reaction mixture at room temperature and stirred for 2-4 h (protection was monitored by \(^{31}\)P-NMR). After quenching the reaction mixture with a saturated NH\(_4\)Cl solution, aqueous layer was extracted with dichloromethane (4 × 100 mL). The combined organic layers were washed with 2N HCl, water, brine, dried over MgSO\(_4\) and evaporated under reduced pressure. Purification by flash chromatography (silica gel, n-
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pentane:Et₂O 1:1) of the residue provided the desired compound (9.50 g, 17.60 mmol, 88 %) as a pale brown solid.

**MP:** 120.3-121.3 °C  
[α]D²⁰ = −306 (c = 0.08, acetone).

**¹H-NMR (300 MHz, C₆D₆):** δ = 8.35-8.23 (m, 4H), 7.94 (d, J = 7.8 Hz, 2H) 7.24-7.15 (m, 6H) 6.92 (d, J = 7.5 Hz, 2H) 4.56-4.51 (m, 1H) 4.24-4.21 (m, 1H) 4.20 (s, 5H), 4.14-4.00 (m, 1H), 2.09 (s, 3H) ppm.

**¹³C-NMR (75 MHz, C₆D₆):** δ = 143.0, 141.6, 135.4 (d, J = 28.8 Hz), 134.2 (d, J = 28.2), 133.52 (d, J = 1.8 Hz), 132.1 (d, J = 3.5 Hz), 131.8 (d, J = 2.9 Hz), 129.7, 128.8 (d, J = 1.8 Hz), 128.6 (d, J = 7.6 Hz), 81.3, 80.0, 77.4 (d, J = 12.9 Hz), 72.5, 72.0 (d, J = 7.6 Hz), 71.9 (d, J = 10.0 Hz), 21.5 ppm.

**³¹P-NMR (81 MHz, C₆D₆):** δ = +42.45 ppm.

**IR(KBr):** υmax (cm⁻¹) = 3436 (br, s), 1630 (br, w), 1436 (w), 1041 (m), 717 (m).

**MS (70 eV, EI):** m/z (%) = 540 (M⁺, 26), 524 (22), 401 (100).

**HRMS (EI):** m/z calcld. for: [C₂₉H₂₅P₅6FeO₃²S₂] 540.0434, found: 540.0417

**Preparation of (R_Fc)-1-(Diphenylphosphinothioyl)-2-(α-hydroxypyridyl)methylferrocene (31):**

Prepared according to the typical procedure TP3, using ferrocenyl sulfoxide 30 (10.0 mmol, 5.40 g) in THF (10 mL), PhLi (0.20 M, 60 mM, 12.0 mmol, 1.20 equiv.) in diethylether, and 2-Pyridinecarboxaldehyde (2.30 mL, 24.0 mmol, 1.20 equiv.) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1) afforded the two diastereomeric alcohols 31a and 31b (3.69 g, 7.20 mmol, 72 %) as an inseparable mixture 31 in 6:4 ratio (by ³¹P-NMR).

**¹H-NMR (200 MHz, C₆D₆):** δ = 8.29-8.19 (m, 1H), 7.93-7.86 (m, 4H), 7.76-7.72 (m, 1H), 7.65-7.54 (m, 4H), 7.39-7.35 (m, 1H), 7.01-6.80 (m, 16H), 6.44-6.36 (m, 3H), 5.32 (d, J = 9.0 Hz, 1H), 4.96 (d, J = 6.0 Hz, 1H), 4.65 (s, 1H), 4.48 (s, 5H), 4.32 (s, 6H), 3.93-3.91 (m, 2H), 3.64-3.61 (m, 2H) ppm.

**³¹P-NMR (81 MHz, C₆D₆):** δ = +42.6 (minor, 40 %), +43.5 (major, 60%) ppm.

**Preparation of ferrocenyl methyl ethers 32a and 32b:**

Prepared according to the typical procedure TP4, using KH (104 mg, 2.60 mmol, 1.30 equiv.) in THF (4 mL), ferrocenyl alcohol 31 (dr 6:4, 1.01 g, 2.0 mmol) in THF (20 mL) and CH₃I (341 mg, 2.40 mmol, 1.20 equiv.). The reaction mixture was quenched with a saturated NH₄Cl solution (10 mL) and the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1) to furnish the two methyl ethers 32a (566 mg, 1.07 mmol, 54 %) and 32b (367 mg, 0.70 mmol, 35 %) yellow solids.
(RFe)-1-(Diphenylphosphinothioyl)-2-((S)-α-methoxypyridyl)methylferrocene (32a):

**MP:** 217.9-218.4 °C  
\([\alpha]_D^{20} = -25.8 (c = 0.22, \text{acetone}).

$^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta =$ 8.50-8.42 (m, 1H), 8.08-7.95 (m, 4H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.13-7.03 (m, 7H), 6.71-6.67 (m, 1H), 6.64 (s, 1H), 4.35 (s, 5H), 4.10-4.08 (m, 1H), 3.94 (dd, $J =$ 2.2 Hz, 4.0 Hz, 1H), 2.92 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, C$_6$D$_6$): $\delta =$ 161.4, 149.1, 136.4 (d, $J =$ 88.0 Hz), 135.7, 134.8 (d, $J =$ 87.0 Hz), 132.8 (d, $J =$ 4.7 Hz), 132.7 (d, $J =$ 4.7 Hz), 130.9 (d, $J =$ 2.9 Hz), 130.7 (d, $J =$ 2.9 Hz), 132.6, 127.9, 122.3, 122.2, 92.6 (d, $J =$ 11.8 Hz), 80.8, 75.8 (d, $J =$ 94.5 Hz), 75.5 (d, $J =$ 12.9 Hz), 72.9 (d, $J =$ 8.8 Hz), 71.7, 69.1 (d, $J =$ 10.5 Hz), 56.7 ppm.

$^{31}$P-NMR (81 MHz, C$_6$D$_6$): $\delta =$ +42.74 ppm.

IR(KBr): $\nu_{max}$ (cm$^{-1}$) = 3436 (br, s), 1630 (br, w), 1589 (s), 1436 (br, s), 3436 (m), 1099 (s), 819 (w), 715 (s), 502 (s).

MS (70 eV, EI): $m/z$ (%) = 523 (M$^+$, 28), 458 (68), 428 (100), 288 (14).

HRMS (EI): $m/z$ calcd. for: [C$_{29}$H$_{26}$P$_5$FeNO$_3$S]$^{523.0822}$, found: 523.0837

(\(R_{Fe}\))-1-(Diphenylphosphinothioyl)-2-(\(R\)-α-methoxypyridyl)methylferrocene (32b):

**MP:** 199.3-200.8 °C  
\([\alpha]_D^{20} = -21.7 (c = 0.18, \text{acetone}).

$^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta =$ 8.25-8.23 (m, 1H), 7.92-7.84 (m, 2H), 7.40-7.33 (m, 2H), 7.20-7.17 (m, 1H), 7.04-6.95 (m, 3H), 6.84-6.79 (m, 1H), 6.73-6.63 (m, 3H), 6.60 (s, 1H), 6.38-6.33 (m, 1H), 5.30 (dd, $J =$ 1.8 Hz, 4.0 Hz, 1H), 4.50 (s, 5H), 4.02 (dd, $J =$ 2.3 Hz, 4.0 Hz, 1H), 4.02 (dd, $J =$ 2.3 Hz, 4.0 Hz, 1H), 3.57 (dd, $J =$ 2.3 Hz, 4.0 Hz, 1H), 3.30 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, C$_6$D$_6$): $\delta =$ 160.0, 149.6, 135.6 (d, $J =$ 60.0 Hz), 134.8, 134.5 (d, $J =$ 60.0 Hz), 132.6 (d, $J =$ 10.6 Hz), 132.1 (d, $J =$ 10.6 Hz), 131.0 (d, $J =$ 2.9 Hz), 130.2 (d, $J =$ 2.9 Hz), 127.8, 127.6, 124.1, 121.9, 95.5 (d, $J =$ 11.8 Hz), 79.5, 74.4 (d, $J =$ 12.3 Hz), 73.3 (d, $J =$ 94.5 Hz), 72.4 (d, $J =$ 9.5 Hz), 71.4, 69.5 (d, $J =$ 10.2 Hz), 56.6 ppm.

$^{31}$P-NMR (81 MHz, C$_6$D$_6$): $\delta =$ +42.59 ppm.

IR(KBr): $\nu_{max}$ (cm$^{-1}$) = 3436 (br, s), 1588 (w), 1436 (s), 1158 (s), 1099 (s), 819 (m), 615 (s).

MS (70 eV, EI): $m/z$ (%) = 523 (M$^+$, 25), 458 (60), 428 (100), 426 (32).

HRMS (EI): $m/z$ calcd. for: [C$_{29}$H$_{26}$P$_5$FeNO$_3$S]$^{523.0822}$, found: 523.0837

Preparation of ferrocenyl benzyl ethers 33a and 33b:
Prepared according to the typical procedure TP4, using KH (104 mg, 2.60 mmol, 1.30 equiv.) in THF (4 mL), ferrocenyl alcohol 31 (dr 6:4, 1.01 g, 2.0 mmol) in THF (20 mL) and Benzyl bromide (411 mg, 2.40 mmol, 1.20 equiv). The reaction mixture was quenched with a saturated NH₄Cl solution (10 mL), the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1) to furnish the two benzyl ethers 33a (649 mg, 1.08 mmol, 54 %) and 33b (433 mg, 0.72 mmol, 36 %) as yellow solids.

(R₉Fc)-1-(Diphenylphosphinothioyl)-2-(((S)-α-benzyloxy)pyridyl)methylferrocene (33a):
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74.7 (d, J = 12.2 Hz), 72.9 (d, J = 94.5 Hz), 71.6 (d, J = 9.4 Hz), 71.3, 69.7 (d, J = 10.5 Hz) ppm.

$^{31}P$-NMR (81 MHz, C$_6$D$_6$): $\delta = +42.96$ ppm.

IR (KBr): $\nu_{\text{max}}$ (cm$^{-1}$) = 3435 (b, s), 1629 (b, w), 1436 (s), 1101 (s), 821 (m), 714 (s), 694 (s).

MS (70 eV, EI): m/z (%): 599 (M$^+$, 10), 534 (8), 429 (27), 428 (100), 427 (25)

HRMS (EI): m/z calcd. for: [C$_{35}$H$_{30}$P$_5$FeNO$_3$S] 599.1122, found: 599.1158

(R$_{Fe}$)-1-(Diphenylphosphino)-2-(((S)-α-methoxy)pyridyl)methylferrocene (9a):

Prepared according to TP5 from Raney-Ni (1.5 g, 24.0 mmol, 30 equiv.) and 32a (420 mg, 0.80 mmol) in MeOH (50 mL) and obtained as a yellow solid (331 mg, 0.67 mmol, 84%).

MP: 120.3-122.4 °C

[$\alpha$]$_D^{20}$ = +234 (c = 0.1, CH$_2$Cl$_2$)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 8.69-8.68$ (m, 1H), 7.75-7.69 (m, 2H), 7.63-7.51 (m, 4H), 7.39-7.38 (m, 2H), 7.30-7.22 (m, 5H), 5.49 (d, J = 3.3 Hz, 1H), 4.23-4.20 (m, 1H), 4.03 (s, 1H), 3.81 (s, 5H), 3.36 (s, 1H), 2.93 (s, 3H) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 160.6, 148.7, 135.2$ (d, J = 21.5 Hz), 132.4 (d, J = 18.3 Hz), 132.3, 130.8, 129.0, 128.7, 128.0 (d, J = 8.0 Hz), 127.63 (d, J = 6.5 Hz), 127.4, 122.6, 121.8, 95.6 (d, J = 24.0 Hz), 82.3, 73.8 (d, J = 9.5 Hz), 71.2, 70.5, 69.8, 69.2, 68.7 ppm.

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta = -21.17$ ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2920 (w), 1728 (w), 1586 (m), 1428 (s), 1126 (m), 1080 (s), 1105 (s), 748 (s), 698 (s).

MS (70 eV, EI): m/z (%): 491 (M$^+$, 39), 427 (28), 426 (100), 396 (32), 262 (30), 154 (37).

HRMS (EI): m/z calcd. for: [C$_{29}$H$_{26}$P$_5$FeNO] 491.1101, found: 491.1108

(R$_{Fe}$)-1-(Diphenylphosphino)-2-(((R)-α-methoxy)pyridyl)methylferrocene (9b):

Prepared according to TP4 from Raney-Ni (1.5 g, 24.0 mmol, 30 equiv.) and 32b (420 mg, 0.80 mmol) in MeOH (50 mL), and obtained as a yellow solid (325 mg, 0.66 mmol, 82%).

MP: 140.2-144.0 °C

[$\alpha$]$_D^{20}$ = +214 (c = 0.1, CH$_2$Cl$_2$)

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 8.07$ (m, 1H), 7.71-7.70 (m, 1H), 7.49 (br s, 2H), 7.33-7.28 (m, 3H), 7.12-6.94 (m, 4H), 6.79-6.76 (m, 3H), 5.39 (s, 1H), 4.66 (s, 1H), 4.31-4.26 (m, 1H), 4.10 (s, 5H), 3.65 (s, 1H), 3.34 (s, 3H) ppm.
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$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta = 160.3, 148.5, 139.1$ (d, $J = 9.2$ Hz), 137.5 (d, $J = 9.2$ Hz), 135.8, 135.0 (d, $J = 21.3$ Hz), 131.9 (d, $J = 18.5$ Hz), 128.9, 127.9 (d, $J = 8.0$ Hz), 127.5 (d, $J = 6.4$ Hz), 127.0, 122.0, 121.7, 92.9 (d, $J = 24.7$ Hz), 82.8 (d, $J = 9.8$ Hz), 76.5 (d, $J = 9.6$ Hz), 71.7 (d, $J = 4.2$ Hz), 70.0 (d, $J = 3.4$ Hz), 69.7, 68.7, 68.1 ppm.

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta = -21.25$ ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2928 (w), 1725 (w), 1586 (m), 1430 (m), 1162 (m), 1087 (s), 1104 (s), 816 (s), 744 (s), 698 (s).

MS (70 eV, EI): $m/z$ (%) = 491 (M$^+$, 47), 427 (28), 426 (100), 396 (37), 262 (38), 154 (50).

HRMS (EI): $m/z$ calcd. for: [C$_{29}$H$_{26}$P$_5$FeNO] 491.1101, found: 491.1110.

$^{(R,Fc)}$-1-(Diphenylphosphino)-2-(((S)-$\alpha$-benzyloxy)pyridyl))methylferrocene (10a):

Prepared according to TP4 from Raney-Ni (1.5 g, 24.0 mmol; 30 equiv.) and 33a (480 mg, 0.80 mmol) in MeOH (50 mL), and obtained as a yellow solid (402 mg, 0.71 mmol, 88%).

MP: 49.8-53.5 °C

[α]$_D^{20} = +230$ (c = 0.1, CH$_2$Cl$_2$)

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 8.71-8.70$ (m, 1H), 7.77-7.74 (m, 1H), 7.65-7.61 (m, 3H), 7.39-7.38 (m, 3H), 7.30-7.28 (m, 1H), 7.24-7.16 (m, 5H), 7.08 (t, $J = 7.3$ Hz, 1H), 7.02 (t, $J = 7.4$ Hz, 2H), 6.74-6.73 (m, 2H), 5.88 (s, 1H), 4.31 (d, $J = 10.9$ Hz, 1H), 4.26 (t, $J = 2.6$ Hz, 1H), 4.22 (s, 1H), 4.13 (d, $J = 10.9$ Hz, 1H), 3.90 (s, 1H), 3.83 (s, 5H) ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta = 160.7, 140.5$ (d, $J = 10.0$ Hz), 137.9 (d, $J = 10.2$ Hz), 137.6, 135.4 (d, $J = 22.0$ Hz), 132.4 (d, $J = 18.0$ Hz), 129.1, 128.4, 128.1 (d, $J = 1.7$ Hz), 128.0, 127.9, 127.8 (d, $J = 1.7$ Hz), 127.4, 127.4, 122.8, 122.3, 95.1 (d, $J = 26$ Hz), 76.5 (d, $J = 10.6$ Hz), 71.9 (d, $J = 4.5$ Hz), 71.7, 70.5, 70.49 (d, $J = 3.4$ Hz), 70.0, 69.8 ppm.

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta = -21.58$ ppm.

IR (KBr): $\nu_{\text{max}}$ (cm$^{-1}$) = 3054 (br, w), 2858 (br, w), 1587 (m), 1432 (m), 1047 (s), 817 (m), 739 (s), 690 (s).

MS (70 eV, EI): $m/z$ (%) = 567 (M$^+$, 38), 502 (87), 461 (57), 396 (100), 276 (33), 154 (34).

HRMS (EI): $m/z$ calcd. for: [C$_{35}$H$_{30}$P$_5$FeNO] 567.1414, found: 567.1389

$^{(R,Fc)}$-1-(Diphenylphosphino)-2-(((R)-$\alpha$-benzyloxy)pyridyl))methylferrocene (10b):

Prepared according to TP4 from Raney-Ni (1.5 g, 24.0 mmol; 30 equiv.) and 33b (482 mg, 0.80 mmol) in MeOH (50 mL), and obtained as a yellow solid (390 mg, 0.69 mmol, 86%).

MP: 58.0-60.2 °C

[α]$_D^{20} = +134$ (c = 0.1, CH$_2$Cl$_2$)
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**1H-NMR (400 MHz, CDCl₃):** δ = 8.05-8.03 (m, 1H), 7.51-7.42 (m, 4H), 7.39-7.27 (m, 7H), 7.20-7.18 (m, 1H), 7.04-7.01 (m, 1H), 6.95-6.91 (m, 2H), 6.79-6.71 (m, 3H), 5.71 (d, J = 2.1 Hz, 1H), 4.80-4.79 (m, 1H), 4.53 (d, J = 11.7 Hz, 1H), 4.45 (d, J = 11.7 Hz, 1H), 4.28 (t, J = 2.3 Hz, 1H), 4.05 (s, 5H), 3.70-3.69 (m, 1H) ppm.

**13C-NMR (100 MHz, CDCl₃):** δ = 160.7, 148.4, 139.3 (d, J = 9.2 Hz), 138.6, 137.6 (d, J = 9.6 Hz), 135.9, 135.2 (d, J = 21.3 Hz), 131.9 (d, J = 18.2 Hz), 128.9 (d, J = 0.8 Hz), 128.3, 127.9 (d, J = 7.8 Hz), 127.6, 127.5, 127.4 (d, J = 2.2 Hz), 127.0, 122.1, 121.8 (d, J = 1.5 Hz), 95.9 (d, J = 24.3 Hz), 80.7 (d, J = 7.3 Hz), 73.8 (d, J = 10.5 Hz), 71.3 (d, J = 4.8 Hz), 70.8, 69.9, 69.1, 69.0 (d, J = 4.5 Hz) ppm.

**31P-NMR (81 MHz, CDCl₃):** δ = -22.49 ppm.

**IR(KBr):** υ_max (cm⁻¹) = 3050 (w), 2860 (w), 1586 (m), 1432 (m), 1066 (m), 1026 (m), 815 (m), 738 (m), 692 (s), 614 (m).

**MS (70 eV, EI):** m/z (%) = 568 ([M+H]^+), 567 (M^+, 100), 502 (58), 461 (47), 385 (83), 276 (41), 212 (72).

**HRMS (EI):** m/z calcd. for: [C₃₅H₃₀P₅₆FeNO] 567.1414, found: 567.1436

**Preparation of (Rₓc)-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(α-hydroxypyridyl)methylferrocene (35):**

Prepared according to the typical procedure TP3, using ferrocenyl sulfoxide 35 (6.00 g, 10.0 mmol) in THF (10 mL), t-BuLi (1.50 M, 14.7 mL, 22.0 mmol, 2.20 equiv.), and 2-pyridinecarboxaldehyde (2.30 mL, 24.0 mmol, 1.20 equiv.) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1) to afford the two diastereomeric alcohols 35a and 35b (3.69 g, 6.50 mmol, 65 %) as an inseparable mixture 35 in 5:5 ratio by 31P-NMR.

**1H-NMR (200 MHz, C₆D₆):** δ = 8.29-8.19 (m, 1H), 7.93-7.86 (m, 4H), 7.76-7.72 (m, 1H), 7.65-7.54 (m, 4H), 7.39-7.35 (m, 1H), 7.01-6.80 (m, 16H), 6.44-6.36 (m, 3H), 5.32 (d, J = 9.0 Hz, 1H), 4.96 (d, J = 6.0 Hz, 1H), 4.65 (s, 1H), 4.48 (s, 5H), 4.32 (s, 6H), 3.93-3.91 (s, 2H), 3.64-3.61 (m, 2H) ppm.

**31P-NMR (81 MHz, C₆D₆):** δ = 43.09 (51 %), 43.83 (49 %).

**Preparation of ferrocenyl methyl ethers 36a and 36b:**

Prepared according to the typical procedure TP4, using KH (95 mg, 2.25 mmol, 1.50 equiv.) in THF (4 mL), ferrocenyl alcohol 35 (dr 5:5, 850 mg, 1.5 mmol) in THF (10 mL) and CH₃I (0.12 mL, 1.80 mmol, 1.20 equiv.). The reaction mixture was quenched with a saturated NH₄Cl solution (10 mL) and the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1) to furnish the two methyl ethers 36a (393 mg, 0.67 mmol, 45%) and 36b (256 mg, 0.66 mmol, 44%) as yellow solids.
(R_Fc)-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((S)-α-methoxy)pyridyl)methylferrocene (36b):

MP: 88 °C (sublimation)
[α]_D^20 = −25.8 (c = 0.22, acetone).

^1^H-NMR (400 MHz, C_6D_6): δ = 8.54-8.52 (m, 1H), 7.93-7.91 (m, 2H), 7.83-7.80 (m, 2H), 7.53 (tt, J = 1.0 Hz, 7.8 Hz, 1H), 7.12 (ddd, J = 1.9 Hz, 7.7 Hz, 1H), 6.78-6.77 (m, 2H), 6.68 (ddddd, J = 4.8 Hz, 7.4 Hz, 1H), 4.35 (s, 5H), 4.33-4.32 (m, 1H), 4.03-4.02 (m, 1H), 4.00-3.99 (m, 1H), 2.99 (s, 3H), 2.04 (s, 6H), 2.03 (s, 6H) ppm.

^13^C-NMR (100 MHz, C_6D_6): δ = 161.5, 149.2, 137.6 (d, J = 12.9 Hz), 137.4 (d, J = 13.0 Hz), 136.4 (d, J = 86.8 Hz), 135.7, 134.8 (d, J = 84.2 Hz), 132.9 (d, J = 3.0 Hz), 132.7 (d, J = 3.2 Hz), 130.7 (d, J = 10.5 Hz), 130.6 (d, J = 10.9 Hz), 122.5, 122.3, 92.5 (d, J = 11.4 Hz), 80.6, 76.3 (d, J = 93.6 Hz), 75.4 (d, J = 12.3 Hz), 73.1 (d, J = 8.9 Hz), 71.7, 69.2 (d, J = 10.3 Hz), 56.7, 21.15 (d, J = 0.8 Hz), 21.1 (d, J = 0.8 Hz) ppm.

^31^P-NMR (81 MHz, C_6D_6): δ = +42.31 ppm.

IR(KBr): ν_{max} (cm^{-1}) = 3635 (w), 2920 (m), 1587 (m), 1431 (m), 1073 (s), 846 (m), 689 (s), 670 (s).

MS (70 eV, EI): m/z (%) = 579 (M^+), 515 (27), 514 (80), 485 (31), 484 (100), 482 (22), 154 (17).

HRMS (EI): m/z calcd. for: [C_{33}H_{34}P_{56}FeNO_3^2S] 579.1448, found: 579.1457

(R_Fc)-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((R)-α-methoxy)pyridyl)methylferrocene (36b):

MP: 99.3-100.1 °C
[α]_D^20 = −21.7 (c = 0.18, acetone).

^1^H-NMR (400 MHz, C_6D_6): δ = 8.32-8.30 (m, 1H), 7.75-7.72 (m, 2H), 7.27 (tt, J = 1.0 Hz, 7.7 Hz, 1H), 7.14-7.12 (m, 2H), 6.74 (s, 1H), 6.66 (ddddd, J = 1.8 Hz, 7.7 Hz, 2H), 6.53 (s, 1H), 6.33 (ddddd, J = 1.3 Hz, 4.7 Hz, 7.5 Hz, 1H), 5.36-5.35 (m, 1H), 4.58 (s, 5H), 4.06-4.05 (m, 1H), 3.78-3.77 (m, 1H), 3.28 (s, 3H), 1.97 (s, 6H), 1.80 (s, 6H) ppm.

^13^C-NMR (100 MHz, C_6D_6): δ = 160.2, 149.5, 137.6 (d, J = 13.0 Hz), 137.3 (d, J = 13.3 Hz), 135.6 (d, J = 86.5 Hz), 134.8 (d, J = 84.8 Hz), 134.6, 132.9 (d, J = 3.2 Hz), 132.4 (d, J = 3.3 Hz), 130.5 (d, J = 10.7 Hz), 130.0 (d, J = 10.7 Hz), 124.3, 121.9, 95.4 (d, J = 11.5 Hz), 79.5, 74.6 (d, J = 12.1 Hz), 74.1 (d, J = 93.7 Hz), 72.4 (d, J = 9.2 Hz), 71.4, 69.3 (d, J = 10.4 Hz), 56.5, 21.1 (d, J = 0.8 Hz), 21.0 (d, J = 0.8 Hz) ppm.

^31^P-NMR (81 MHz, C_6D_6): δ = +42.31 ppm.
**Experimental Section**

**IR(KBr):** $v_{\text{max}}$ (cm$^{-1}$) = 3325 (w), 2918 (m), 1586 (m), 1467 (m), 1432 (m), 1122 (m), 1088 (m), 848 (m), 814 (m), 690 (s), 662 (s).

**MS (70 eV, EI):** $m/z$ (%) = 523 (M$^+$, 25), 458 (60), 428 (100), 426(32).

**HRMS (EI):** $m/z$ calcd. for: [C$_{33}$H$_{34}$P$_5$FeNO$_3$S] 579.1488, found: 579.1467

Preparation of ferrocenyl benzyl ethers 37a and 37b:

Prepared according to the typical procedure TP4, using KH (95 mg, 2.25 mmol, 1.50 equiv.) in THF (4 mL), ferrocenyl alcohol 35 (dr 5:5, 850 mg, 1.5 mmol) in THF (10 mL) and PhCH$_2$Br (312 mg, 1.80 mmol, 1.20 equiv.). The reaction mixture was quenched with a saturated NH$_4$Cl solution (10 mL) and the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et$_2$O 1:1) to furnish the two methyl ethers 37a (455 mg, 0.69 mmol, 46%) and 37b (435 mg, 0.66 mmol, 44%) yellow solids.

(R$_{Fe}$)-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((S)-α-benzylxy)pyridyl)methylferrocene (37a):

\[
\text{(R$_{Fe}$)-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((S)-α-benzylxy)pyridyl))methyl-ferrocene (37a):}
\]

**MP:** 222.6-223.9 °C

$[\alpha]_D^{20} = -10.8$ (c = 0.2, acetone).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 8.68$ (s, 1H), 7.67 (s, 1H), 7.58 (s, 1H), 7.41-6.66 (m, 10H), 6.63 (s, 2H), 6.47 (s, 1H), 4.31 (s, 1H), 4.18 (s, 2H), 4.05 (s, 5H), 3.89 (s, 1H), 3.75 (s, 1H), 2.28 (s, 6H), 2.09 (s, 6H), ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 149.3$, 138.5, 137.5 (d, $J = 13.0$ Hz), 136.2, 134.6 (d, $J = 89.2$ Hz), 133.7 (d, $J = 86.4$ Hz), 132.9, 130.1 (d, $J = 10.7$ Hz), 129.9 (d, $J = 11.6$ Hz), 127.8, 127.6, 126.8, 123.2, 122.8, 78.5, 75.3 (d, $J = 12.2$ Hz), 74.8 (d, $J = 95$ Hz), 73.2, 71.4, 71.1, 69.5 (d, $J = 11.2$ Hz), 21.5, 21.4 ppm

$^{31}$P-NMR (81 MHz, C$_6$D$_6$): $\delta = +43.10$ ppm.

**IR(KBr):** $v_{\text{max}}$ (cm$^{-1}$) = 3345 (br, w), 2917 (w), 1583 (m), 1437 (m), 1195 (m), 1051 (s), 848 (m), 690 (s), 675 (s).

**MS (70 eV, EI):** $m/z$ (%) = 655 (M$^+$, 45), 590 (11), 564 (17), 485 (30), 484 (100).

**HRMS (EI):** $m/z$ calcd. for: [C$_{39}$H$_{38}$P$_5$FeNO$_3$S] 655.1761, found: 655.1783

(R$_{Fe}$)-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((R)-α-benzylxy)pyridyl)methylferrocene (37b):

\[
\text{(R$_{Fe}$)-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((R)-α-benzylxy)pyridyl))methyl-ferrocene (37b):}
\]
Experimental Section

MP: 129.7-130.8 °C

$[\alpha]_D^{20} = -12.7$ (c = 0.2, acetone).

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 8.33 (brs, 1H) 7.36 (s, 2H), 7.23-7.19 (m, 6H), 7.12 (s, 1H), 7.02 (s, 1H), 6.98 (brs, 1H), 6.76 (s, 1H), 6.67 (m, 2H), 6.46 (s, 1H), 5.16 (brs, 1H), 4.50-4.42 (m, 2H), 4.27 (s, 6H), 3.53 (s, 1H), 2.25 (s, 6H), 2.01 (s, 6H), ppm.

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta$ = 148.9, 138.6, 137.7 (d, $J$ = 11.9 Hz), 137.3 (d, $J$ = 12.2 Hz), 134.0 (d, $J$ = 86.0 Hz), 133.3 (d, $J$ = 85.1 Hz), 133.2, 132.7, 129.9 (d, $J$ = 11.2 Hz), 129.6 (d, $J$ = 10.7 Hz), 128.5, 128.4, 127.7, 124.5, 76.8, 74.8 (d, $J$ = 12.1 Hz), 73.3 (d, $J$ = 92.1 Hz), 71.7, 71.2, 69.6 (d, $J$ = 12.0 Hz), 21.5 ppm.

$^{31}$P-NMR (81 MHz, C$_6$D$_6$): $\delta$ = +43.08 ppm.

IR(KBr): $\nu_{\text{max}}$ (cm$^{-1}$) = 3435 (b, s), 2912 (w), 1586 (m), 1433 (m), 1121 (m), 848 (m), 690 (s), 661 (s).

MS (70 eV, EI): $m/z$ (%) = 655 (M$^+$, 15), 485 (28), 484 (100), 483 (30), 154 (14).

HRMS (EI): $m/z$ calcd. for: [C$_{39}$H$_{38}$P$_5$FeNO$_3$S] 655.1761, found: 655.1758

(R$_{Fe}$)-1-Bis(3,5-dimethylphenylphosphino)-2-(((S)-$\alpha$-methoxy)pyridyl))methylferrocene (9c):

Prepared according to TP5 from Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and 36a (347 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (297 mg, 0.54 mmol, 90%).

MP: 112.3-113.2 °C

$[\alpha]_D^{20} = +16.2$ (c = 0.2, acetone)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 8.55-8.47 (m, 1H) 7.42-7.31 (m, 2H), 6.83-6.66 (m, 3H), 6.25-6.20 (s, 1H), 4.25-4.18 (m, 1H), 4.13 (s, 1H), 3.80 (s, 5H), 3.35 (s, 1H), 2.85 (s, 3H), 2.31 (s, 6H), 2.28 (s, 6H) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 161.2, 147.6, 133.5 (d, $J$ = 22.1 Hz), 132.0 (d, $J$ = 19.1 Hz), 131.1, 129.8, 129.0, 127.9, 127.2 (d, $J$ = 9.1 Hz), 126.6, 126.2 (d, $J$ = 6.7 Hz), 121.5, 120.2, 96.2 (d, $J$ = 25.2 Hz), 81.3, 71.8 (s, $J$ = 8.2 Hz), 71.2 (d, $J$ = 9.8 Hz), 71.0, 68.5 (d, $J$ = 6.7 Hz), 69.2, 68.7, 23.5, 21.7 ppm.

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta$ = -20.46 ppm.

IR(neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2911 (w), 1658 (w), 1522 (m), 1435 (s), 1246 (m), 1080 (s), 865 (s), 724 (s), 695 (s).

MS (70 eV, EI): $m/z$ (%) = 547 (M$^+$, 46), 482 (44), 480 (100), 260 (11).

HRMS (EI): $m/z$ calcd. for: [C$_{33}$H$_{34}$P$^{56}$FeNO] 547.1727, found: 547.1711

(R$_{Fe}$)-1-Bis(3,5-dimethylphenylphosphino)-2-(((R)-$\alpha$-methoxy)pyridyl))methylferrocene (9d):
Prepared according to TP4 from Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and 36b (347 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (286 mg, 0.49 mmol, 82%).

**MP:** 140.2-144.0 °C  
\([\alpha]_D^{20} = +22.1 \text{ (c = 0.2, acetone)}

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.11-8.07 \text{ (m, 1H)}, 7.75-7.72 \text{ (m, 1H)}, 6.91-6.80 \text{ (m, 3H)}, 6.77-6.72 \text{ (m, 1H)}, 6.21-6.19 \text{ (m, 4H)}, 5.40 \text{ (s, 1H)}, 4.85-4.80 \text{ (m, 1H)}, 4.43 \text{ (s, 1H)}, 4.05 \text{ (s, 5H)}, 3.65-3.59 \text{ (m, 1H)}, 2.91 \text{ (s, 3H)}, 2.32 \text{ (s, 6H)}, 2.26 \text{ (s, 6H)} \text{ ppm.}

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 161.0, 146.6, 133.5 \text{ (d, } J = 21.0 \text{ Hz)}, 133.2 \text{ (d, } J = 18.2 \text{ Hz)}, 132.1, 130.2, 130.0, 128.7 \text{ (d, } J = 9.5 \text{ Hz)}, 127.9, 126.0 \text{ (d, } J = 5.9 \text{ Hz)}, 124.2, 121.5, 121.2, 94.1 \text{ (d, } J = 25.0 \text{ Hz)}, 80.2, 71.8 \text{ (d, } J = 8.1 \text{ Hz)}, 71.6, 71.0 \text{ (d, } J = 8.8 \text{ Hz)}, 66.7, 68.2, 67.5, 24.2, 23.2 ppm.

\(^{31}\)P-NMR (81 MHz, CDCl\(_3\)): \(\delta = -20.25 \text{ ppm.}

IR(neat): \(\nu_{\text{max}} \text{ (cm}^{-1}) = 2982 \text{ (w), 1754 (w), 1628 (m), 1545 (m), 1368 (m), 1022 (m), 964 (s), 728 (s), 699 (s).}

MS (70 eV, EI): \(m/z \text{ (%) = 547 (M}^+\text{, 28), 482 (24), 480 (100), 365 (43), 260 (18).}

HRMS (EI): \(m/z \text{ calcd. for: } [C_{33}H_{34}P_{56}FeNO] 547.1727, \text{ found: } 547.1719.

\((R_Fc)-1\)-Bis(3,5-dimethylphenylphosphino)-2-(((S)-\(\alpha\)-benzyloxy)pyridyl)methylferrocene (10c):

Prepared according to TP4 from Raney-Ni (1.1 g, 18.0 mmol, 30 equiv.) and 37a (395 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (335 mg, 0.53 mmol, 89%).

**MP:** 69.1-70.5 °C  
\([\alpha]_D^{20} = +14.5 \text{ (c = 0.2, acetone)}

\(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.75-8.72 \text{ (m, 1H)}, 7.71-7.66 \text{ (m, 4H)}, 7.54-7.48 \text{ (m, 3H)}, 7.11-6.99 \text{ (m, 3H)}, 6.35-6.25 \text{ (m, 4H)}, 5.82-5.79 \text{ (m, 1H)}, 4.32-4.26 \text{ (m, 2H)}, 4.15 \text{ (s, 1H)}, 4.05-3.96 \text{ (m, 2H)}, 3.81 \text{ (s, 5H)}, 2.31 \text{ (s, 6H)}, 2.30 \text{ (s, 6H)} \text{ ppm.}

\(^{13}\)C-NMR (150 MHz, CDCl\(_3\)): \(\delta = 160.6, 141.0 \text{ (d, } J = 10.1 \text{ Hz)}, 138.2, 137.8 \text{ (d, } J = 22.1 \text{ Hz)}, 134.8 \text{ (d, } J = 10.2 \text{ Hz)}, 132.2, 130.6 \text{ (d, } J = 17.2 \text{ Hz)}, 128.4 \text{ (d, } J = 2.1 \text{ Hz)}, 128.2, 127.9, 127.5, 126.9, 126.4 \text{ (d, } J = 2.1 \text{ Hz)}, 126.1, 125.8, 122.7, 122.1, 96.2 \text{ (d, } J = 25.8 \text{ Hz)}, 75.9 \text{ (d, } J = 11.2 \text{ Hz)}, 72.8 \text{ (d, } J = 5.4 \text{ Hz)}, 71.8 \text{ (d, } J = 4.5 \text{ Hz)}, 71.0, 70.8, 70.2, 69.8, 23.9, 22.1 ppm.

\(^{31}\)P-NMR (81 MHz, CDCl\(_3\)): \(\delta = -21.46 \text{ ppm.}

IR(KBr): \(\nu_{\text{max}} \text{ (cm}^{-1}) = 3065 \text{ (br, w), 2926 (br, w), 1648 (m), 1444 (s), 1168 (s), 954 (m), 817 (m), 675 (s).}

MS (70 eV, EI): \(m/z \text{ (%) = 623 (M}^+\text{, 38), 558 (25), 452 (100), 260 (35).}

HRMS (EI): \(m/z \text{ calcd. for: } [C_{39}H_{38}P_{56}FeNO] 623.2040, \text{ found: } 623.2039\)
(\(R_F\))-1-Bis(3,5-dimethylphenylphosphino)-2-(((\(R\)-\(\alpha\)-benzyloxy)pyridyl))methylerrocene (10d):

\[
\begin{align*}
\text{Fe} & \quad \text{Xyl}2P \\
& \quad \text{OCH2Ph}
\end{align*}
\]

Prepared according to TP4 from Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and 33b (395 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (300 mg, 0.48 mmol, 80%).

MP: 55.6-60.9 °C

\([\alpha]_D^{20} = +14.3 \ (c = 0.2, \text{acetone})

\(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.45-8.41\ (m, 1H), 7.81-7.79\ (m, 2H), 7.65-7.60\ (m, 2H), 7.58-7.46\ (m, 4H), 7.10-6.90\ (m, 3H), 6.29-6.25\ (m, 3H), 5.64-5.60\ (m, 1H), 4.82-4.77\ (m, 2H), 4.34-4.31\ (m, 1H), 4.22-4.20\ (m, 1H), 3.98\ (s, 6H), 2.35\ (s, 6H), 2.33\ (s, 6H) ppm.

\(^{13}\)C-NMR (150 MHz, CDCl\(_3\)): \(\delta = 160.6, 145.2\ (d, J = 11.2 \text{ Hz}), 138.6\ (d, J = 10.5 \text{ Hz}), 137.9\ (d, J = 22.0 \text{ Hz}), 135.2\ (d, J = 10.8 \text{ Hz}), 132.2, 131.2\ (d, J = 16.9 \text{ Hz}), 128.4, 127.8\ (d, J = 2.3 \text{ Hz}), 126.8\ (d, J = 8.2 \text{ Hz}), 126.5, 126.0, 125.1\ (d, J = 2.4 \text{ Hz}), 125.9, 124.8, 122.1, 122.0, 95.4\ (d, J = 26.0 \text{ Hz}), 76.2\ (d, J = 13.0 \text{ Hz}), 74.0, 72.7\ (d, J = 4.4 \text{ Hz}), 71.0, 70.2, 69.8, 69.0, 24.2, 22.7 ppm.

\(^{31}\)P-NMR (81 MHz, CDCl\(_3\)): \(\delta = -22.49\ ppm.

IR(KBr): \(\nu_{\text{max}}\ (\text{cm}^{-1}) = 3065\ (w), 2925\ (w), 1646\ (m), 1538\ (m), 1026\ (s), 914\ (m), 862\ (m), 699\ (s), 672\ (m).

MS (70 eV, EI): \(m/z\ (%) = 623\ (M^+, 65), 558\ (11), 452\ (100), 260\ (35), 155\ (32).

HRMS (EI): \(m/z\ \text{calcd. for: } [C_{39}H_{38}P^{56}\text{FeNO}] 623.2040, \ \text{found: 623.2053}

2-Bromo-6-phenylpyridine 39a

Under an argon atmosphere, a 250 mL Schlenk flask was charged with CuCN (2.35 g, 26.2 mmol, 1.05 equiv) and THF (30 mL). This suspension was treated with a solution of PhMgCl-LiCl (32 mL, 1.65 M, 52.8 mmol, 2.1 equiv) at −78 °C. After 20 minutes stirring, 2,6-dibromopyridine 38 (5.92 g, 25 mmol, 1 equiv) in THF (30 mL) was slowly added. When the addition was completed, the reaction mixture was warmed up to room temperature and stirring for 12 h. The reaction mixture was quenched with an aqueous solution of NH\(_3\):NH\(_4\)Cl (6:4; 20 mL). Extracted the aqueous layer with Et\(_2\)O (4 x 30 mL), the combined organic layers were washed with water, brine and dried over MgSO\(_4\). Purification of the crude mixture was performed by flash chromatography (silica gel, n-pentan) and gave the desired product as a colourless oil (4.8 g, 20.5 mmol, 82%).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.95\ (m, 2H), 7.67\ (dd, J = 0.8 \text{ Hz}, 7.7 \text{ Hz}, 1H), 7.57\ (t, J = 7.7 \text{ Hz}, 1H), 7.49-7.38\ (m, 4H) ppm.
\[ ^{13}\text{C-NMR (75 MHz, CDCl}_3\] \): \( \delta = 158.5, 142.1, 138.9, 137.6, 129.6, 128.8, 126.9, 126.3, 118.9 \text{ ppm.} \]

IR (KBr): \( \nu_{\text{max}} (\text{cm}^{-1}) = 2850 (\text{w}), 1546 (\text{m}), 1429 (\text{m}), 1124 (\text{m}), 982 (\text{m}), 781 (\text{s}). \]

MS (70 eV, EI) \( m/z \) (%): 233 (M\(^+\)), 154 (100), 127 (36).

HRMS (EI): \( m/z \) calcd. for [C\(_{11}\)H\(_8\)N\(_7\)Br] 232.9840, found: 232.9843.

2-Bromo-6-\textit{tert}Butylpyridine 39a

Under an argon atmosphere, a 250 mL Schlenk flask was charged with CuCN (2.35 g, 26.2 mmol, 1.05 equiv) and THF (30 mL). This suspension was treated with a solution of \( \text{tBuMgCl-LiCl} \) (32 mL, 1.65 M, 52.8 mmol, 2.1 equiv) at –78 °C. After 20 minutes stirring, 2,6-dibromopyridine 38 (5.92 g, 25 mmol, 1 equiv) in THF (30 mL) was slowly added. When the addition was completed, the reaction mixture was warmed up to room temperature and stirring for 12 h. The reaction mixture was quenched with an aqueous solution of NH\(_3\):NH\(_4\)Cl (6:4; 20 mL). Extracted the aqueous layer with Et\(_2\)O (4 x 30 mL), the combined organic layers were washed with water, brine and dried over MgSO\(_4\). Purification of the crude mixture was performed by flash chromatography (silica gel, \( n\)-pentan) and gave the desired product as a colourless oil (17.8 mmol, 3.8 g, 68 %).

\[ ^1\text{H-NMR (300 MHz, CDCl}_3\] \): \( \delta = 7.43 \) (t, \( J = \text{7.7 Hz, 1H} \)), 7.26-7.23 (m, 2H), 1.33 (s, 9H) ppm.

\[ ^{13}\text{C-NMR (75 MHz, CDCl}_3\] \): \( \delta = 171.2, 141.2, 138.4, 124.9, 117.8, 37.6, 30.0 \text{ ppm.} \]

IR (KBr): \( \nu_{\text{max}} (\text{cm}^{-1}) = 2964 (\text{s}), 1580 (\text{s}), 1553 (\text{s}), 1398 (\text{s}), 1114 (\text{s}), 852 (\text{m}), 794 (\text{s}). \]

MS (70 eV, EI) \( m/z \) (%): 213 (M\(^+\)), 200 (99), 198 (100), 171 (18), 118 (14).

HRMS (EI): \( m/z \) calcd. for [C\(_9\)H\(_{12}\)N\(_7\)Br] 213.0153, found: 213.0142.

Preparation of 6-Phenyl-2-pyridylcarboxaldehyde 40a

A 100 mL Schlenk flask, under an argon atmosphere, was charged with 2-Bromo-6-phenylpyridine 39a (4.37 g, 18.6 mmol, 1 equiv) and THF (20 mL). The \( \text{nBuLi} \) (12.4 mL, 1.58 M, 19.5 mmol, 1.05 equiv) was added slowly to the above solution at –78 °C. After stirring for 15 minutes, DMF (2.2 mL, 27.9 mmol, 1.5 equiv) was slowly added and the reaction mixture was stirred for 2 hours at -78 °C before warming to room temperature. The reaction mixture was quenched at room temperature with an aqueous solution of NH\(_4\)Cl. The aqueous layer was extracted with Et\(_2\)O (4 x 10 mL) and the combined organic layers were washed with water, brine and dried over MgSO\(_4\). Evaporation of the solvent and purification of the crude mixture by flash chromatography (silica gel, \( n\)-pentan:Et\(_2\)O (10:1)), afforded the desired product as a colourless oil (15.8 mmol, 2.91 g, 85 %).
Experimental Section

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 10.17$ (s, 1H), 8.09-8.06 (m, 2H), 7.97-7.88 (m, 3H), 7.54-7.43 (m, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 193.9, 157.9, 152.7, 138.1, 137.8, 129.6, 128.9, 127.0, 124.4, 119.7$ ppm.

IR (KBr): $v_{\text{max}}$ (cm$^{-1}$) = 3401 (br, w), 2849 (w), 1071 (s), 1452 (m), 1027 (s), 1217 (s), 761 (s), 693 (m).

MS (70 eV, EI) $m/z$ (%) = 183 (M$^+$, 81), 154 (100), 127 (34), 77 (16).

HRMS (EI): $m/z$ calcd. for [C$_{12}$H$_9$NO] 183.0684, found: 183.0692.

Preparation of 6-tert-Butyl-2-pyridylcarboxaldehyde 40b

A 100 mL Schlenk flask, under an argon atmosphere, was charged with 2-Bromo-6-tert-butylpyridine 39b (3.3 g, 15.5 mmol, 1 equiv) and THF (20 mL). The nBuLi (10.3 mL, 1.58 M, 16.3 mmol, 1.05 equiv) was added slowly to the above solution at -78 °C. After stirring for 15 minutes, DMF (1.8 mL, 23.25 mmol, 1.5 equiv) was slowly added and the reaction mixture was stirred for 2 hours at -78 °C before warming to room temperature. The reaction mixture was quenched at room temperature with an aqueous solution of NH$_4$Cl. The aqueous layer was extracted with Et$_2$O (4 x 10 mL) and the combined organic layers were washed with water, brine and dried over MgSO$_4$. Evaporation of the solvent and purification of the crude mixture by flash chromatography (silica gel, n-pentan:Et$_2$O (10:1)), afforded the desired product as a colourless oil (13.2 mmol, 2.15 g, 85%).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 10.07$ (s, 1H), 7.77-7.76 (m, 2H), 7.57-7.44 (m, 1H), 1.40 (s, 9H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 194.5, 170.0, 151.9, 137.0, 123.4, 118.3, 37.6, 30.0$ ppm.

IR (KBr): $v_{\text{max}}$ (cm$^{-1}$) = 2961 (s), 1547 (s), 1502 (s), 1386 (s), 1114 (s), 830 (m), 760 (s).

MS (70 eV, EI) $m/z$ (%) = 163 (M$^+$, 34), 148 (100), 118 (12), 91 (5).

HRMS (EI): $m/z$ calcd. for [C$_{10}$H$_{13}$NO] 163.0997, found: 163.0976.

(R$_{\text{Fe}}$)-1-Diphenylphosphinothioloyl-2-[\(\alpha\)-hydroxy(6-phenylpyridyl)]-methylferrocene 41

Prepared according to the typical procedure TP3, using ferrocenyl sulfoxide 30 (10.0 mmol, 5.40 g) in THF (10 mL), PhLi (0.20 M, 60 mM, 12.0 mmol, 1.20 equiv.) in diethylether, and 6-phenyl-2-pyridinecarboxaldehyde 40a (2.20 g, 12.0 mmol, 1.1 equiv) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, n-
pentane:Et₂O 6:1 afforded the two diastereomeric alcohols 41a and 41b (3.79 g, 6.40 mmol, 64%) as an inseparable mixture 41 in 6:4 ratio (by ³¹P-NMR).

¹H-NMR (200 MHz, C₆D₆): δ = 8.04-7.96 (m, 2H), 7.93-7.75 (m, 6H), 7.69-7.63 (m, 2H), 7.58-7.47 (m, 3H), 7.26-7.13 (m, 6H), 7.04-6.93 (m, 9H), 6.82-6.72 (m, 10H), 6.37 (d, J = 11.0 Hz, 1H), 5.87 (d, J = 10.0 Hz, 1H), 4.76 (d, J = 6.0 Hz, 1H), 4.68-4.63 (m, 1H), 4.45 (s, 5H), 4.29 (s, 5H), 3.93-3.85 (m, 2H), 3.60-3.55 (m, 2H) ppm.

³¹P-NMR (81 MHz, C₆D₆): δ = +43.6 (60 %), +42.6 (40 %) ppm.

Preparation of ferrocenyl methyl ethers 42a and 42b
Prepared according to the typical procedure TP4, using KH (60 mg, 1.50 mmol, 1.50 equiv.) in THF (3 mL), ferrocenyl alcohol 41 (576 mg, 0.98 mmol, 1.0 equiv.) in THF (3 mL) and CH₃I (0.5 mL, 8.0 mmol, 8.0 equiv.). The reaction mixture was quenched with a saturated NH₄Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et₂O 6:1) to furnish the two methyl ethers 42a (322 mg, 0.54 mmol, 55 %) and 42b (198 mg, 0.33 mmol, 34 %) as yellow solids.

(R_Fc)-1-Diphenylphosphinothioyl-2-[(S)-α-methoxy(6-phenylpyridyl)]-methylferrocene 42a

MP: 141.2-143.8 °C
[α]D²⁰ = -28 (c = 0.3, CH₂Cl₂)
¹H-NMR (400 MHz, C₆D₆): δ = 8.25-8.23 (m, 2H), 8.08-7.98 (m, 4H), 7.45-7.19 (m, 5H), 7.07-7.04 (m, 7H), 6.70 (s, 1H), 4.31 (s, 5H), 4.20-4.18 (m, 1H), 3.89 (dd, J = 2.1 Hz, 4.0 Hz, 1H), 3.76-3.74 (m, 1H), 2.99 (s, 3H) ppm.

¹³C-NMR (100 MHz, C₆D₆): δ = 161.2, 156.6, 139.5, 136.9, 136.5 (d, J = 88.2 Hz), 134.8 (d, J = 84.6 Hz), 132.8 (d, J = 3.4 Hz), 132.7 (d, J = 3.7 Hz), 130.9 (d, J = 3.0 Hz), 130.7 (d, J = 3.8 Hz), 129.2, 129.0, 127.9, 127.2, 120.8, 118.8, 92.6 (d, J = 11.6 Hz), 81.0, 75.8 (d, J = 94.6 Hz), 75.5 (d, J = 12.3 Hz), 73.1 (d, J = 8.8 Hz), 71.6, 69.0 (d, J = 10.0 Hz), 56.8 ppm.

³¹P-NMR (81 MHz, C₆D₆): δ = +42.8 ppm.

IR (KBr): ν_max (cm⁻¹) = 3436 (m), 2925 (s), 1630 (w), 1446 (m), 1437 (m), 1101 (m), 759 (m), 693 (m).

MS (70 eV, EI) m/z (%) = 599 (M⁺, 100), 534 (22), 504 (100), 502 (16), 286 (16).

HRMS (EI): m/z calc. for [C₃₂H₃₂P⁶FeO₃²SN] 599.1135, found: 599.1129.

(R_Fc)-1-Diphenylphosphinothioyl-2-[(S)-α-methoxy(6-phenylpyridyl)]-methylferrocene 42b
Experimental Section

\begin{align*}
\text{MP:} & \quad 100-110 \degree C \\
[\alpha]_D^{20} & = -31 \text{ (c = 0.3, CH}_2\text{Cl}_2) \\
^1\text{H-NMR (400 MHz, C}_6\text{D}_6): & \quad \delta = 8.40-7.98 \text{ (m, 6H)}, 7.45-7.20 \text{ (m, 5H)}, 7.13-7.09 \text{ (m, 7H)}, 6.72 \text{ (s, 1H)}, 5.32-5.30 \text{ (m, 1H)}, 4.50 \text{ (s, 5H)}, 4.25-4.20 \text{ (m, 1H)}, 3.81-3.79 \text{ (m, 1H)}, 3.20 \text{ (s, 3H) ppm.} \\
^{13}\text{C-NMR (100 MHz, C}_6\text{D}_6): & \quad \delta = 162.4, 158.2, 140.5, 138.2, 137.2 \text{ (d, } J = 87.2 \text{ Hz), 135.2 (d, } J = 84.8 \text{ Hz), 133.2 (d, } J = 3.8 \text{ Hz), 132.9 (d, } J = 4.0 \text{ Hz), 132.6 (d, } J = 3.9 \text{ Hz), 131.4 (d, } J = 4.0 \text{ Hz), 129.2, 128.4, 121.2, 119.2, 93.0 (d, } J = 11.8 \text{ Hz), 81.5, 76.2 (d, } J = 95.0 \text{ Hz), 76.1 (d, } J = 13.2 \text{ Hz), 73.7 (d, } J = 9.0 \text{ Hz), 72.4, 69.2 (d, } J = 10.4 \text{ Hz), 61.2 \text{ ppm.} \\
^{31}\text{P-NMR (81 MHz, C}_6\text{D}_6): & \quad \delta = +41.2 \text{ ppm.} \\
\text{IR (KBr): } \nu_{\text{max}}(\text{cm}^{-1}) & = 3440 \text{ (m), 2900 (s), 1629 (w), 1446 (m), 1100 (m), 792 (m), 698 (s).} \\
\text{MS (70 eV, EI): } m/z & = 599 (M^+ +, 100), 532 (20), 504 (82), 502 (20), 286 (36). \\
\text{HRMS (EI): } m/z & \text{ calcd. for } [\text{C}_{32}\text{H}_{32}\text{P}_{56}\text{FeO}_{32}\text{SN}] 599.1135, \text{ found: 599.1130.} \\
\end{align*}

(R\text{Fe})-1-diphenylphosphino-2-[(S)-\alpha\text{-methoxy(6-phenylpyridyl)]methylferrocene} 9e

\begin{align*}
\text{MP:} & \quad 112-114 \degree C \\
[\alpha]_D^{20} & = -20 \text{ (c = 0.3, CH}_2\text{Cl}_2) \\
^1\text{H-NMR (400 MHz, C}_6\text{D}_6): & \quad \delta = 8.14-7.92 \text{ (m, 6H)}, 7.16-7.42 \text{ (m, 5H)}, 7.02-7.05 \text{ (m, 7H)}, 6.68 \text{ (s, 1H)}, 4.32 \text{ (s, 5H)}, 4.21-4.22 \text{ (m, 1H)}, 3.88-3.91 \text{ (m, 1H)}, 3.76-3.78 \text{ (m, 1H)}, 2.96 \text{ (s, 3H) ppm.} \\
^{13}\text{C-NMR (100 MHz, C}_6\text{D}_6): & \quad \delta = 157.2, 154.2, 137.2, 135.1, 134.5 \text{ (d, } J = 80.0 \text{ Hz), 132.8 (d, } J = 80.0 \text{ Hz), 131.4 (d, } J = 3.2 \text{ Hz), 130.7 (d, } J = 2.4 \text{ Hz), 129.4 \text{ (d, } J = 3.1 \text{ Hz), 129.2 (d, } J = 2.2 \text{ Hz), 128.4, 128.1, 126.8, 126.7, 126.5, 118.2, 116.8, 91.2 \text{ (d, } J = 10.4 \text{ Hz), 80.9, 74.6 (d, } J = 88 \text{ Hz), 74.5 \text{ (d, } J = 11.3 \text{ Hz), 72.8 (d, } J = 8.0 \text{ Hz), 70.8, 68.5 \text{ (d, } J = 10.8 \text{ Hz), 56.4 \text{ ppm.} \text{ IR (KBr): } \nu_{\text{max}}(\text{cm}^{-1}) & = 3421 \text{ (m), 2924 (s), 1572 (s), 1638 (m), 1512 (m), 1108 (m), 791 (m), 698 (m).} \\
\text{MS (70 eV, EI): } m/z & = 567 (M^+ +, 18), 534 (24), 504 (100), 501 (36). \\
\text{HRMS (EI): } m/z & \text{ calcd. for } [\text{C}_{35}\text{H}_{30}\text{P}_{56}\text{FeON}] 567.1414, \text{ found: 567.1428.} \\
\end{align*}
(R<sub>Fe</sub>)-1-diphenylphosphinothioyl-2-[(S)-<i>α</i>-hydroxy(6-phenylpyridyl)]-methylferrocene 43a

Prepared according to the typical procedure TP3, using ferrocenyl sulfoxide 30 (5.40 g, 10.0 mmol) in THF (10 mL), PhLi (0.20 M, 60 mL, 12.0 mmol, 1.20 equiv.) in diethylether, and 6-(<i>tert</i>-butyl)-2-pyridylcarbaldehyde 40b (1.98 g, 12.0 mmol, 1.20 equiv) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et<sub>2</sub>O 6:1) afforded the two diastereomeric alcohols 43a (1.54 g; 2.70 mmol, 27%) and 43b (2.67 g; 4.70 mmol, 47%) as yellow solids.

(R<sub>Fe</sub>)-1-Diphenylphosphinothioyl-2-[(S)-<i>α</i>-hydroxy(6-phenylpyridyl)]-methylferrocene 43a
Experimental Section

MP: 111-112 °C

[α]D$^{20}$ = -68.2 (c = 0.3, CH$_2$Cl$_2$)

$^1$H-NMR (400 MHz, C$_6$D$_6$): δ = 7.96-7.90 (m, 2H), 7.73-7.67 (m, 2H), 7.54-7.52 (m, 1H), 7.05-6.92 (m, 7H), 6.76 (dd, J = 0.8 Hz, 7.8 Hz, 1H), 6.47 (d, J = 9.2 Hz, 1H), 5.05 (d, J = 8.9 Hz, 1H), 4.51-4.49 (m, 1H), 4.26 (s, 5H), 3.95-3.94 (m, 1H), 3.70-3.69 (m, 1H), 1.34 (s, 9H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): δ = 167.4 161.6, 136.4, 135.8 (d, J = 87.4 Hz), 134.2 (d, J = 85.8 Hz), 132.8 (d, J = 10.8 Hz), 132.3 (d, J = 10.8 Hz), 131.2 (d, J = 3.1 Hz), 130.9 (d, J = 3.1 Hz), 128.1, 127.9, 118.9, 117.2, 97.1 (d, J = 11.8 Hz), 75.0 (d, J = 12.4 Hz), 74.2 (d, J = 9.2 Hz), 74.1 (d, J = 92.7 Hz), 71.7, 71.4, 69.5 (d, J = 10.2 Hz), 37.4, 30.3 ppm.

$^{31}$P-NMR (81 MHz, C$_6$D$_6$): δ = +43.6 ppm.

IR (KBr): ν$_{max}$ (cm$^{-1}$) = 3435 (br, s), 2956 (m), 1575 (m), 1437 (s), 1104 (s), 750.4 (s), 714 (s).

MS (70 eV, EI) m/z (%): 565 (M$^+$, 65), 501 (31), 500 (100), 482 (97), 210 (20).

HRMS (EI): m/z calcd. for [C$_{32}$H$_{32}$P$_5$FeO$_{32}$SN] 565.1292, found: 565.1301.

$(R$-Fc)-1-diphenylphosphophinothioyl-2-[(R)-α-hydroxy(6-tert-butlypyridyl)]methyl ferrocene 43b

Preparation of ferrocenyl methyl ethers 44a and 44b

$(R$:Fc)-1-Diphenylphosphophinothioyl-2-[(S)-α-methoxy(6-tert-butylypyridyl)]methyl ferrocene 44a
Prepared according to the typical procedure TP4, using KH (19 mg, 0.5 mmol, 1.5 equiv) in THF (1 mL), ferrocenyl alcohol 43a (170 mg, 0.30 mmol, 1.0 equiv) in THF (2 mL) and CH3I (0.1 mL, 1.6 mmol, 5.0 equiv). After quenching the reaction mixture with a saturated NH4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 10 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et2O 6:1) to furnish the methyl ether 44a (139 mg, 0.24 mmol, 80%) as a yellow solid.

**MP:** 196-198 °C  
**[α]D20** = -49 (c = 0.3, CH2Cl2)

1H-NMR (400 MHz, C6D6): δ = 8.07-7.97 (m, 4H), 7.38-7.36 (m, 1H), 7.23-7.19 (m, 1H), 7.06-7.04 (m, 6H), 6.99-6.97 (m, 1H), 6.52 (s, 1H), 4.35-4.33 (m, 1H), 4.32 (s, 5H), 3.95-3.94 (m, 1H), 3.77-3.75 (m, 1H), 2.92 (s, 3H), 1.43 (s, 9H) ppm.

13C-NMR (100 MHz, C6D6): δ = 168.7, 160.0, 136.5 (d, J = 88.2 Hz), 136.3, 134.9 (d, J = 85.0 Hz), 132.8 (d, J = 10.6 Hz), 132.7 (d, J = 10.7 Hz), 130.9 (d, J = 3.1 Hz), 130.6 (d, J = 3.1 Hz), 127.9, 127.7, 120.0, 117.9, 92.6 (d, J = 11.8 Hz), 81.0, 75.9 (d, J = 94.2 Hz), 75.5 (d, J = 12.4 Hz), 73.1 (d, J = 9.1 Hz), 71.5, 69.1 (d, J = 10.3 Hz), 56.5, 37.8, 30.6 ppm.

31P-NMR (81 MHz, C6D6): δ = +42.89 ppm.

IR (KBr): νmax (cm⁻¹) = 3436 (w), 2957 (m), 1575 (m), 1437 (s), 1162 (m), 1103 (s), 822 (m), 751 (m), 693 (s), 513 (m).

MS (70 eV, EI) m/z (%) = 580 ([M+H]+, 31), 579 (M+, 76), 564 (12), 514 (38), 485 (34), 484 (100), 482 (35).

HRMS (EI): m/z calcd. for [C33H34P56FeO32S] 579.1448, found: 579.1440.

(RFc)-1-Diphenylphosphphinothioyl-2-[(R)-α-methoxy(6-tert-butylpyridyl)methyl ferrocene 44b

Prepared according to the typical procedure TP4, using KH (30 mg, 1.25 mmol, 1.5 equiv) in THF (1.5 mL), ferrocenyl alcohol 43b (284 mg, 0.50 mmol, 1.0 equiv) in THF (2 mL) and CH3I (0.1 mL, 1.8 mmol, 3.5 equiv). After quenching the reaction mixture with a saturated NH4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et2O 6:1) to furnish the methyl ether 44b (239 mg, 0.41 mmol, 82%) as a yellow solid.
Experimental Section

**Preparation of ferrocenyl benzylethers 45a-b**

(RFc)-1-Diphenylphosphinothioyl-2-[(S)-α-benzylkoxy(6-tert-butylpyridyl)methyl]ferrocene 45a

Prepared according to the typical procedure TP4, using KH (19 mg, 0.5 mmol, 1.5 equiv) in THF (1 mL), ferrocenyl alcohol 43a (170 mg, 0.30 mmol, 1.0 equiv) in THF (2 mL) and PhCH2Br (260 mg, 1.6 mmol, 5.0 equiv). After quenching the reaction mixture with a saturated NH4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et2O 6:1) to furnish the benzyl ether 45a (169 mg, 0.25 mmol, 85%) as a yellow solid.

**MP:** 165.3-166.3 °C

[α]D20 = −85 (c = 0.2, acetone).
\[ ^1H\text{-NMR (400 MHz, } C_6D_6) : \delta = 8.05-7.91 (m, 4H), 7.46-7.45 (m, 1H), 7.05-6.78 (m, 14H), 4.68-4.61 (m, 1H), 4.39-4.38 (m, 1H), 4.31 (s, 5H), 4.18-4.12 (m, 1H), 3.98-3.96 (m, 1H), 3.89-3.78 (m, 1H), 1.46 (s, 9H) \text{ ppm.} \]

\[ ^{13}C\text{-NMR (100 MHz, } C_6D_6) : \delta = 168.2, 157.6, 139.7, 138.9, 135.0 (d, } J = 86.9 \text{ Hz), 134.8 (d, } J = 86.3 \text{ Hz), 134.0, 132.0 (d, } J = 10.8 \text{ Hz), 130.8 (d, } J = 10.8 \text{ Hz), 130.2 (d, } J = 10.8 \text{ Hz), 128.0, 127.9, 127.6 (d, } J = 12.7 \text{ Hz), 127.4 (d, } J = 11.4 \text{ Hz), 120.9, 117.1, 94.5 (d, } J = 11.7 \text{ Hz), 77.4, 74.0 (d, } J = 12.1 \text{ Hz), 73.2 (d, } J = 95.5 \text{ Hz), 72.6 (d, } J = 9.1 \text{ Hz), 70.9, 70.4, 69.5 (d, } J = 10.4 \text{ Hz), 37.4, 30.0 \text{ ppm.} \]

\[ ^{31}P\text{-NMR (81 MHz, } C_6D_6) : \delta = +42.71 \text{ ppm.} \]

\[ \text{IR (KBr-Pressling): } \nu_{\text{max}} (cm^{-1}) = 3436 (br, s), 2956 (w), 1629 (w), 1575 (m), 1479 (m), 1437 (m), 1103 (m), 1101 (s), 823 (m), 750 (m), 715 (m), 694 (m). \]

\[ \text{MS (70 eV, EI): } m/z (%) = 655 (M^{+}, 19), 565 (19), 564 (47), 485 (28), 484 (100). \]

\[ \text{HRMS (EI): } m/z \text{ calcd. for: } \left[ C_{39}H_{38}P_{56}FeO_{32}SN \right] 655.1761, \text{ found: 655.1742} \]

\[(R_{Fc})-1\text{-Diphenolphosphinoothioyl-2-[(R)-}\alpha\alpha\alpha\alpha\alpha\alpha\alpha\text{-benzyloxy(6-tert-butylpyridyl)methyl ferrocene 45b} \]

Prepared according to the typical procedure TP4, using KH (19 mg, 0.5 mmol, 1.5 equiv) in THF (1 mL), ferrocenyl alcohol 43b (170 mg, 0.30 mmol, 1.0 equiv) in THF (2 mL) and PhCHBr (260 mg, 1.6 mmol, 5.0 equiv). After quenching the reaction mixture with a saturated NH\textsubscript{4}Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, } n\text{-pentane:Et}_2O 6:1) to furnish the benzyl ether 45b (169 mg, 0.25 mmol, 85%) as a yellow solid.

\[ \text{MP: 181.0-181.9 }^\circ C \]

\[ [\alpha]_D^{20} = -80 (c = 0.2, \text{ acetone).} \]

\[ ^1H\text{-NMR (400 MHz, } C_6D_6) : \delta = 7.89-7.84 (m, 2H), 7.41 (d, } J = 7.2 \text{ Hz, 2H), 7.33-7.28 (m, 2H), 7.20 (t, } J = 7.7 \text{ Hz, 2H), 7.11-6.95 (m, 5H), 6.85-6.82 (m, 2H), 6.74-6.65 (m, 4H), 5.32-5.31 (m, 1H), 4.56 (d, } J = 11.2 \text{ Hz, 1H), 4.47 (d, } J = 11.4 \text{ Hz, 1H), 4.44 (s, 5H), 4.05-4.04 (m, 1H), 3.59-3.58 (m, 1H), 1.34 (s, 9H) \text{ ppm.} \]

\[ ^{13}C\text{-NMR (100 MHz, } C_6D_6) : \delta = 168.5, 158.5, 139.7, 139.6, 135.8 (d, } J = 86.8 \text{ Hz), 135.4, 134.7 (d, } J = 86.3 \text{ Hz), 132.6 (d, } J = 10.8 \text{ Hz), 132.0 (d, } J = 10.8 \text{ Hz), 130.9 (d, } J = 10.8 \text{ Hz), 130.1 (d, } J = 10.8 \text{ Hz), 128.4, 128.3, 127.8 (d, } J = 12.3 \text{ Hz), 127.6 (d, } J = 11.4 \text{ Hz), 121.3, 117.1, 95.5 (d, } J = 11.5 \text{ Hz), 77.6, 74.3 (d, } J = 12.1 \text{ Hz), 73.2 (d, } J = 94.5 \text{ Hz), 72.6 (d, } J = 9.1 \text{ Hz), 71.4, 70.9, 69.3 (d, } J = 10.3 \text{ Hz), 37.6, 30.3 \text{ ppm.} \]

\[ ^{31}P\text{-NMR (81 MHz, } C_6D_6) : \delta = +42.31 \text{ ppm.} \]

\[ \text{IR (KBr-Pressling): } \nu_{\text{max}} (cm^{-1}) = 3436 (br, s), 2956 (w), 1574 (m), 1160 (m), 1101 (s), 823 (m), 750 (m), 715 (m), 694 (m). \]

\[ \text{MS (70 eV, EI): } m/z (%) = 655 (M^{+}, 10), 485 (32), 484 (100), 483 (84), 427 (11). \]

\[ \text{HRMS (EI): } m/z \text{ calcd. for: } [C_{39}H_{38}P_{56}FeO_{32}SN] 655.1761, \text{ found: 655.1757} \]
(R_Fc)-1-Diphenylphosphino-2-[(S)-α-methoxy(6-tert-butylpyridyl)methylferrocene 9g

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{OCH}_3 \\
\text{Fe} & \\
\end{align*}
\]

Prepared according to the typical procedure TP5, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and 44a (232 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (175 mg, 0.32 mmol, 80%).

**MP:** 55-57 °C

\([\alpha]_D^{20} = +29 \text{ (c = 0.3, CH}_2\text{Cl}_2)\)

\(^1\text{H-NMR (400 MHz, C}_6\text{D}_6): \delta = 7.78-7.74 \text{ (m, 2H), 7.54-7.50 \text{ (m, 2H), 7.36-7.34 \text{ (m, 1H), 7.25-7.22 \text{ (m, 1H), 7.14-7.07 \text{ (m, 5H), 7.05-6.98 \text{ (m, 2H), 5.89 \text{ (d, J = 2.9 Hz, 1H), 4.20-4.19 \text{ (m, 1H), 4.08 \text{ (t, J = 2.6 Hz, 1H), 4.00 \text{ (s, 5H), 3.95-3.94 \text{ (m, 1H), 2.99 \text{ (s, 3H), 1.46 \text{ (s, 9H) ppm.}}}}}}}

\(^{13}\text{C-NMR (100 MHz, C}_6\text{D}_6): \delta = 168.4, 160.4, 141.6 \text{ (d, J = 10.9 Hz), 139.0 \text{ (d, J = 9.9 Hz), 136.4, 136.0 \text{ (d, J = 22.1 Hz), 132.9 \text{ (d, J = 18.2 Hz), 129.2, 128.3, 127.9, 127.5, 119.3, 117.9, 93.9 \text{ (d, J = 24.8 Hz), 83.7 \text{ (d, J = 8.8 Hz), 72.4 \text{ (d, J = 4.9 Hz), 70.9 \text{ (d, J = 3.9 Hz), 70.3, 69.7, 69.4 \text{ (d, J = 59.0 Hz), 56.5, 37.7, 30.6 ppm.}}}}}}

\text{IR (KBr): v}_{\text{max}} \text{ (cm}^{-1}) = 3436 \text{ (m), 2955 \text{ (m), 1576 \text{ (m), 1433 \text{ (m), 1085 \text{ (m), 820 \text{ (m), 742 \text{ (m), 696 \text{ (m), 489 \text{ (m).}}})}}}}

\text{MS (70 eV, EI) m/z} \text{ (%) = 548 ([M+H]^+ 38), 547 (M^+ 100), 532 (53), 395 (19), 347 (22), 210 (22).}

\text{HRMS (EI): m/z calcld. for [C}_{33}\text{H}_{34}\text{P}_{56}\text{FeON]} = 547.1727, \text{ found: 547.1719.}}

(R_Fc)-1-Diphenylphosphino-2-[(R)-α-methoxy(6-tert-butylpyridyl)methylferrocene 9h

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{OCH}_3 \\
\text{Fe} & \\
\end{align*}
\]

Prepared according to the typical procedure TP5, using Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and 44b (348 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (273 mg, 0.50 mmol, 83%).

**MP:** 142-144 °C

\([\alpha]_D^{20} = +21 \text{ (c = 0.3, CH}_2\text{Cl}_2)\)

\(^1\text{H-NMR (400 MHz, C}_6\text{D}_6): \delta = 7.66-7.61 \text{ (m, 2H), 7.10-7.07 \text{ (m, 4H), 7.04-7.00 \text{ (m, 1H), 6.87-6.73 \text{ (m, 6H), 5.70 \text{ (d, J = 2.1 Hz, 1H), 4.93-4.92 \text{ (m, 1H), 4.17 \text{ (s, 5H), 4.14-4.11 \text{ (m, 1H), 3.77-3.76 \text{ (m, 1H), 3.20 \text{ (s, 3H), 1.25 (s, 9H) ppm.}}}}}}}}

Experimental Section

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 168.0, 160.1, 141.0$ (d, $J = 11.7$ Hz), 139.1 (d, $J = 11.2$ Hz), 136.2, 135.8 (d, $J = 22.3$ Hz), 132.2 (d, $J = 17.6$ Hz), 129.1, 128.2, 127.7, 127.0, 119.2 (d, $J = 0.8$ Hz), 117.3, 97.0 (d, $J = 24.0$ Hz), 82.9 (d, $J = 8.0$ Hz), 74.8 (d, $J = 12.0$ Hz), 71.4 (d, $J = 4.9$ Hz), 70.3, 69.7, 69.4 (d, $J = 58.4$ Hz), 56.6, 37.4, 30.2 ppm.

$^{31}$P-NMR (81 MHz, C$_6$D$_6$): $\delta = -20.5$ ppm.

IR (KBr): $\nu_{\text{max}}$ (cm$^{-1}$) = 3436 (w), 2956 (m), 1574 (m), 1449 (m), 1156 (m), 1093 (s), 821 (m), 749 (m), 698 (m), 504 (m).

MS (70 eV, EI) $m/z$ (%): 548 ([M+H]$^+$, 40), 547 (M$^+$, 100), 532 (46), 394 (44), 332 (26), 210 (39).

HRMS (EI): $m/z$ calcd. for [C$_{33}$H$_{34}$P$_5$FeON] 547.1727, found: 547.1737.

(R$_{Fe}$)-1-Diphenylphosphino-2-[(S)-$\alpha$-benzylxylo(6-tert-butylpyridyl)methylferrocene 10e

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{OCH}_2\text{Ph} \\
\text{Fe} & \quad \text{Bu}
\end{align*}
\]

Prepared according to the typical procedure TP5, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and 45a (265 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (224 mg, 0.36 mmol, 89 %).

MP: 112.8-114.2 °C

[$\alpha$]$_D$ = +209 (c = 0.30, CH$_2$Cl$_2$).

$^{1}$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.76-7.62$ (m, 2H), 7.46-7.40 (m, 3H), 7.22 (t, $J = 7.7$ Hz, 1H), 7.12-7.11 (m, 3H), 7.01-6.97 (m, 7H), 6.82-6.80 (m, 2H), 6.20 (d, $J = 3.2$ Hz, 1H), 4.52-4.49 (m, 1H), 4.24-4.22 (m, 2H), 4.11 (t, $J = 2.2$ Hz, 1H), 3.99 (s, 6H), 1.48 (s, 9H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 168.4, 160.5, 141.4$ (d, $J = 10.3$ Hz), 139.1 (d, $J = 11.5$ Hz), 138.7, 136.5, 136.0 (d, $J = 22.3$ Hz), 133.0 (d, $J = 17.4$ Hz), 129.2 (d, $J = 0.8$ Hz), 128.4, 128.3, 128.1 (d, $J = 5.8$ Hz), 128.0, 127.5, 127.1, 119.7, 118.0, 93.7 (d, $J = 25.7$ Hz), 82.1 (d, $J = 8.9$ Hz), 77.3 (d, $J = 11.4$ Hz), 72.5 (d, $J = 5.3$ Hz), 71.6, 71.2 (d, $J = 3.8$ Hz), 70.3, 70.0, 37.8, 30.6 ppm.

$^{31}$P-NMR (81 MHz, C$_6$D$_6$): $\delta = -21.22$ ppm.

IR (KBr-Pressling): $\nu_{\text{max}}$ (cm$^{-1}$) = 3436 (br, m), 2956 (m), 1573 (m), 1452 (m), 1434 (m), 1087 (m), 1062 (m), 820 (m), 748 (s), 696 (s).

MS (70 eV, EI): $m/z$ (%): 623 (M$^+$, 30), 532 (19), 518 (34), 517 (100), 439 (13), 347 (13), 332 (51).

HRMS (EI): $m/z$ calcd. for [C$_{39}$H$_{38}$P$_5$FeON] 623.2040, found: 623.2021.

(R$_{Fe}$)-1-Diphenylphosphino-2-[(R)-$\alpha$-benzylxylo(6-tert-butylpyridyl)methylferrocene 10f

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{OCH}_2\text{Ph} \\
\text{Fe} & \quad \text{Bu}
\end{align*}
\]
Prepared according to the typical procedure TP5, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and 45b (265 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (212 mg, 0.34 mmol, 85%).

**MP:** 120.5-121.7 °C  
$[\alpha]_D^{20} = +105$ (c = 0.26, CH$_2$Cl$_2$).

**1H-NMR (400 MHz, C$_6$D$_6$):** δ = 7.65-7.60 (m, 2H), 7.46-7.44 (m, 2H), 7.24-7.20 (m, 2H), 7.14-7.10 (m, 6H), 6.85-6.74 (m, 6H), 5.97 (d, $J = 2.4$ Hz, 1H), 4.92-4.90 (m, 1H), 4.50 (s, 2H), 4.15-4.13 (m, 1H), 4.12 (s, 5H), 3.80-3.79 (m, 1H), 1.27 (s, 9H) ppm.

**13C-NMR (100 MHz, C$_6$D$_6$):** δ = 168.0, 160.3, 141.5 (d, $J = 12.0$ Hz), 139.4, 139.1 (d, $J = 11.5$ Hz), 136.3, 135.8 (d, $J = 22.1$ Hz), 136.7, 135.8 (d, $J = 17.6$ Hz), 129.1 (d, $J = 0.8$ Hz), 128.5, 128.2 (d, $J = 0.8$ Hz), 128.2, 127.8, 127.6, 127.0, 119.4, 117.4, 97.0 (d, $J = 27.4$ Hz), 81.0 (d, $J = 8.4$ Hz), 74.8 (d, $J = 12.6$ Hz), 71.4 (d, $J = 4.6$ Hz), 71.0, 70.4, 69.9 (d, $J = 4.2$ Hz), 69.7, 37.4, 30.2 ppm.

**31P-NMR (81 MHz, C$_6$D$_6$):** δ = -20.61 ppm.

**IR (KBr-Pressling):** $\nu_{max}$ (cm$^{-1}$) = 3436 (br, m), 2950 (m), 1585 (m), 1476 (m), 1434 (m), 1049 (m), 747 (m), 709 (m).

**MS (70 eV, EI):** m/z (%) = 623 (M$^+$, 96), 532 (44), 518 (38), 517 (100), 451 (41), 394 (41), 332 (84).

**HRMS (EI):** m/z calcd. for [C$_{39}$H$_{38}$P$_5$FeON] 623.2040, found: 623.2040

$(R_{Fe})$-1-Diphenylphosphino-2-[(S)-$\alpha$-hydroxy(6-tert-butylpyridyl)methylferrocene 10g

Prepared according to the typical procedure TP5, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and 43a (226 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (182 mg, 0.34 mmol, 85%).

**MP:** 98-100 °C  
$[\alpha]_D^{20} = -41.2$ (c = 0.3, CH$_2$Cl$_2$).

**1H-NMR (400 MHz, C$_6$D$_6$):** δ = 7.96-7.91 (m, 2H), 7.69-7.52 (m, 3H), 7.06-6.96 (m, 6H), 6.77-6.74 (m, 1H), 6.42 (s, 1H), 5.04 (s, 1H), 4.48-4.40 (m, 1H), 4.28 (s, 5H), 3.69-3.65 (m, 1H), 1.32 (s, 9H) ppm.

**13C-NMR (100 MHz, C$_6$D$_6$):** δ = 169.2, 161.2, 142.6 (d, $J = 10.9$ Hz), 140.1 (d, $J = 11.8$ Hz), 138.2, 137.1 (d, $J = 23.1$ Hz), 133.2 (d, $J = 20$ Hz), 130.1, 128.2, 127.4, 120.1 (d, $J = 1.1$ Hz), 116.9, 96.9 (d, $J = 25.2$ Hz), 83.1 (d, $J = 8.5$ Hz), 75.2 (d, $J = 12.2$ Hz), 71.7 (d, $J = 5.0$ Hz), 70.8, 70.1, 69.6 (d, $J = 58.2$ Hz), 37.2, 30.3 ppm.

**31P-NMR (81 MHz, C$_6$D$_6$):** δ = -20.0 ppm.

**IR (KBr):** $\nu_{max}$ (cm$^{-1}$) = 3436 (br, s), 2882 (s), 1572 (s), 1409 (s), 1112 (m), 747 (m), 698 (s).

**MS (70 eV, EI) m/z (%) =** 533 (M$^+$, 40), 501 (28), 500 (66), 482 (100).

**HRMS (EI):** m/z calcd. for [C$_{32}$H$_{32}$P$_5$FeON] 533.1571, found: 533.1578.
(R<sub>Fe</sub>)-1-Diphenylphosphino-2-[(R)-α-hydroxy(6-tert-butylpyridyl)methylferrocene 10h

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{OH} \\
\text{Fe} & \quad \text{fBu}
\end{align*}
\]

Prepared according to the typical procedure TP5, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and 43b (226 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (171 mg, 0.32 mmol, 80%).

**MP:** 101-104 °C  
[^{20}]{\alpha}_{D}^20 = -49.8 (c = 0.3, CH<sub>2</sub>Cl<sub>2</sub>)

**^1H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):** \(\delta = 7.95-7.91 (m, 2H), 7.70-7.61 (m, 2H), 7.08-7.00 (m, 6H), 6.91-6.88 (m, 2H), 6.75-6.70 (m, 2H), 5.14 (s, 1H), 4.69-4.67 (m, 1H), 4.20 (s, 5H), 3.96-3.90 (m, 1H), 3.62-3.60 (m, 1H), 1.20 (s, 9H) ppm.

**^13C-NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):** \(\delta = 168.8, 160.1, 141.5 (d, J = 12.1 Hz), 139.5 (d, J = 11.2 Hz), 135.9, 136.2 (d, J = 21.9 Hz), 132.4 (d, J = 18 Hz), 129.9, 128.5, 127.8, 127.2, 119.5 (d, J = 10 Hz), 116.8, 96.5 (d, J = 24.1 Hz), 82.5 (d, J = 8.0 Hz), 75.0 (d, J = 12.0 Hz), 71.5 (d, J = 4.9 Hz), 70.4, 69.5, 69.4 (d, J = 58.0 Hz), 37.4, 30.1 ppm.

**^31P-NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>):** \(\delta = -23.4\) ppm.

**IR (KBr):** \(\nu_{\text{max}} (\text{cm}^{-1}) = 3449 (\text{br, s}), 2990 (\text{m}), 1570 (\text{s}), 1400 (\text{s}), 1200 (\text{s}), 726 (\text{s}), 699 (\text{s}).

**MS (70 eV, EI) m/z (%):** 533 (M<sup>+</sup>, 30), 501 (32), 500 (48), 482 (100).

**HRMS (EI):** m/z calcd. for [C<sub>32</sub>H<sub>32</sub>P<sub>56</sub>FeON] 533.1571, found: 533.1577.

5. Preparation of iridium complexes 46a-g and 47a-g

Iridium complex (46a):

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{BARF} \\
\text{Fe} & \quad \text{BARF}
\end{align*}
\]

Prepared according to TP6 from P,N-ligand 9a (246 mg, 0.50 mmol), [Ir(cod)Cl]<sub>2</sub> (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) afforded the iridium complex 46a (746 mg, 90%) as a bright orange solid.
Iridium complex (47a):

Prepared according to TP6 from P,N-ligand 9b (246 mg, 0.50 mmol), [Ir(cod)Cl]2 (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH2Cl2) afforded the iridium complex 47a (736 mg, 89%) as a bright orange solid.

MP: 189.3-190.9 °C
\([\alpha]_D^{20} = +50 \, (c = 0.2, \text{CH}_2\text{Cl}_2)\)

\(^1\)H-NMR (400 MHz, CDCl3): \(\delta = 7.71-7.70 \, (m, 7H), 7.56-7.33 \, (m, 12H), 7.55-7.20 \, (m, 1H), 7.12-7.07 \, (m, 2H), 6.81 \, (s, 1H), 6.77-6.73 \, (m, 2H), 6.64-6.61 \, (m, 1H), 5.04-5.03 \, (m, 1H), 4.66-4.63 \, (m, 1H), 4.56-4.47 \, (m, 2H), 4.38 \, (s, 4H), 4.24-4.14 \, (m, 2H), 3.67-3.66 \, (m, 1H), 3.56 \, (s, 3H), 2.62-2.40 \, (m, 5H), 2.18-2.13 \, (m, 1H), 1.84-1.74 \, (m, 2H), 1.55 \, (s, 1H), 1.26 \, (s, 1H) \, ppm.

\(^13\)C-NMR (100 MHz, CDCl3): \(\delta = 161.8, 161.7 \, (q, J = 51.0 \, Hz), 149.2, 138.8, 134.5, 132.8 \, (d, J = 10.0 \, Hz), 131.9 \, (d, J = 2.6 \, Hz), 131.4, 131.3 \, (d, J = 11.3 \, Hz), 130.9, 130.7 \, (d, J = 2.4 \, Hz), 129.4 \, (d, J = 2.7 \, Hz), 129.0 \, (q, J = 2.9 \, Hz), 128.8 \, (d, J = 6.5 \, Hz), 128.7-128.0 \, (m, 128.6, 125.7 \, (d, J = 32.0 \, Hz), 125.0, 124.5, 123.2, 121.8, 120.5, 117.4, 92.8 \, (d, J = 13.3 \, Hz), 91.7 \, (d, J = 16.2 \, Hz), 88.6 \, (d, J = 11.6 \, Hz), 85.5 \, (d, J = 1.7 \, Hz), 73.2 \, (d, J = 1.9 \, Hz), 71.8 \, (d, J = 6.1 \, Hz), 71.2, 69.4 \, (d, J = 6.7 \, Hz), 67.4, 66.9, 60.6, 58.0, 35.1 \, (d, J = 4.0 \, Hz), 32.3 \, (d, J = 2.2 \, Hz), 31.0 \, (d, J = 2.3 \, Hz), 27.4 \, (d, J = 1.9 \, Hz) \, ppm.

\(^{31}\)P-NMR (81 MHz, CDCl3): \(\delta = +9.6 \, ppm\).
**IR (neat):** \( \nu_{\text{max}} (\text{cm}^{-1}) = 2925 \text{ (w)}, 1609 \text{ (w)}, 1353 \text{ (m)}, 1273 \text{ (s)}, 1156 \text{ (s)}, 1122 \text{ (s)}, 1095 \text{ (s)}, 887 \text{ (m)}, 838 \text{ (m)}, 715 \text{ (m)}, 668 \text{ (m)}. 

**MS (ESI):** 792 ([M+H]^{+}, 41), 792 (M^{+}, 100), 790 (65), 452 (11).

**HRMS (ESI):** \( m/z \) calcd. for: \([C_{37}H_{38}P_{56}FeNO_{193}]^{792.1670}\), found: 792.1639

Iridium complex (46b):

Prepared according to TP6 from P,N-ligand 10a (284 mg, 0.50 mmol), \([\text{Ir(COD)Cl}]_2\) (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, \( \text{CH}_2\text{Cl}_2 \)) provided the iridium complex 46b (780 mg, 90%) as a bright orange solid.

**MP:** 178.1-180.7 °C

\([\alpha]_D^{20} = +54 \text{ (c = 0.2, CH}_2\text{Cl}_2)\)

\(^1\text{H-NMR (400 MHz, CDCl}_3\): \( \delta = 8.77-8.75 \text{ (m, 1H)}, 8.13-8.09 \text{ (m, 2H)}, 8.03-8.02 \text{ (m, 1H)}, 7.96-7.92 \text{ (m, 1H)}, 7.78-7.72 \text{ (m, 8H)}, 7.61-7.60 \text{ (m, 3H)}, 7.52 \text{ (br, s, 3H)}, 7.48-7.44 \text{ (m, 1H)}, 7.41-7.34 \text{ (m, 8H)}, 6.95-6.87 \text{ (m, 3H)}, 5.05-5.04 \text{ (m, 1H)}, 4.87-4.86 \text{ (m, 2H)}, 4.51 \text{ (t, J = 2.6 Hz, 1H)}, 4.22-4.19 \text{ (m, 1H)}, 4.07 \text{ (t, J = 2.6 Hz, 1H)}, 3.98-3.97 \text{ (m, 1H)}, 3.13 \text{ (s, 4H)}, 2.52-2.48 \text{ (m, 2H)}, 2.35-2.29 \text{ (m, 1H)}, 2.09-2.00 \text{ (m, 2H)}, 1.79-1.75 \text{ (m, 1H)}, 1.57-1.52 \text{ (m, 3H)}, 1.23 \text{ (m, 2H) ppm.}

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\): \( \delta = 165.1, 161.7 \text{ (q, J = 50.1 Hz)}, 149.7, 136.4, 135.5 \text{ (d, J = 14.0 Hz)}, 134.8-134.7 \text{ (m)}, 133.4 \text{ (q, J = 360.1 Hz)}, 132.7 \text{ (d, J = 2.2 Hz)}, 130.8 \text{ (d, J = 2.6 Hz)}, 130.0 \text{ (d, J = 58.7 Hz)}, 129.2 \text{ (d, J = 11.0 Hz)}, 129.1 \text{ (q, J = 2.9 Hz)}, 128.9, 128.7 \text{ (q, J = 2.8 Hz)}, 128.6, 127.2, 126.1, 125.9, 123.8, 123.2, 120.5, 117.5-117.4 \text{ (m)}, 94.6 \text{ (d, J = 14.2 Hz)}, 94.0 \text{ (d, J = 6.8 Hz)}, 93.9, 78.6 \text{ (d, J = 1.8 Hz)}, 73.3 \text{ (d, J = 2.2 Hz)}, 72.3, 71.7 \text{ (d, J = 55.0 Hz)}, 70.4, 70.2 \text{ (q, J = 8.2 Hz)}, 67.0, 65.5, 35.7 \text{ (d, J = 4.5 Hz)}, 32.2 \text{ (d, J = 1.9 Hz)}, 28.7 \text{ (d, J = 2.1 Hz)}, 26.9 \text{ (d, J = 2.3 Hz) ppm).}

\(^{31}\text{P-NMR (81 MHz, CDCl}_3\): \( \delta = +9.6 \text{ ppm} \)

**IR (neat):** \( \nu_{\text{max}} (\text{cm}^{-1}) = 2927 \text{ (w)}, 1608 \text{ (w)}, 1353 \text{ (m)}, 1272 \text{ (s)}, 1117 \text{ (s)}, 1000 \text{ (w)}, 886 \text{ (m)}, 838 \text{ (m)}, 712 \text{ (m)}, 668 \text{ (m)}, 681 \text{ (m)}. 

**MS (ESI):** 869 ([M+H]^{+}, 44), 868 (M^{+}, 100), 866 (49), 584 (10), 391 (5).

**HRMS (ESI):** \( m/z \) calcd. for: \([C_{43}H_{42}P_{56}FeNO_{193}]^{868.1938}\), found: 868.1964

Iridium complex (47b):
Prepared according to TP6 from P,N-ligand 10b (284 mg, 0.5 mmol), [Ir(COD)Cl]2 (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Flash chromatographical purification (silica gel, CH2Cl2) provided the iridium complex 47 (763 mg, 88%) as a bright orange solid.

**MP:** 71.5-75.7 °C  
[α]D20 = +27 (c = 0.2, CH2Cl2)

**1H-NMR (400 MHz, CDCl3):** δ = 7.72-7.70 (m, 8H), 7.57-7.40 (m, 16H), 7.24-7.20 (m, 1H), 7.12-7.08 (m, 2H), 6.96 (s, 1H), 6.78-6.73 (m, 2H), 6.64-6.60 (m, 1H), 5.18-5.17 (m, 1H), 4.80-4.77 (m, 1H), 4.66-4.57 (m, 3H), 4.53-4.48 (m, 1H), 4.34 (s, 4H), 4.29-4.23 (m, 1H), 4.20-4.15 (m, 1H), 3.71-3.69 (m, 1H), 2.54-2.13 (m, 7H), 1.92-1.77 (m, 3H) ppm.

**13C-NMR (100 MHz, CDCl3):** δ = 161.8, 161.7 (q, J = 50.0 Hz), 149.3, 138.9, 136.4, 134.8 (br, s), 132.8 (d, J = 9.8 Hz), 131.9 (d, J = 2.5 Hz), 131.2 (d, J = 11.3 Hz), 131.26 (d, J = 54.0 Hz), 130.8 (d, J = 2.5 Hz), 129.4-129.3 (m), 129.1 (t, J = 3.0 Hz), 129.0, 128.9-128.7 (m), 128.5-128.4 (m), 127.5, 126.8 (q, J = 365.0 Hz), 125.9, 125.6, 123.2, 122.2, 117.5-117.4 (m), 93.4 (d, J = 13.0 Hz), 91.9 (d, J = 15.7 Hz), 88.7 (d, J = 12.1 Hz), 82.9, 73.2 (d, J = 1.4 Hz), 72.3, 71.7 (d, J = 6.3 Hz), 71.2, 69.8 (d, J = 7.2 Hz), 67.3, 66.7 (d, J = 5.0 Hz), 61.2, 34.5 (d, J = 3.5 Hz), 31.7 (d, J = 2.3 Hz), 31.6 (d, J = 2.3 Hz), 27.9 (d, J = 2.2 Hz) ppm.

**31P-NMR (81 MHz, CDCl3):** δ = +5.71 ppm.

**IR (neat):** νmax (cm⁻¹) = 2928 (w), 1609 (m), 1353 (m), 1273 (s), 1117 (s), 1001 (m), 839 (m), 669 (m), 682 (m).

**MS (ESI):** 869 ([M+H]+, 44), 868 (M+, 100), 866 (46), 584 (18).

**HRMS (ESI):** m/z calcd. for: [C43H42P56FeNO193Ir] 868.1938, found: 868.1948

**Iridium complex (46c):**

Prepared according to TP6 from P,N-ligand 9c (275 mg, 0.50 mmol), [Ir(cod)Cl]2 (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH2Cl2) afforded the iridium complex 46c (787 mg, 0.46 mmol; 92%) as a bright orange solid.

**MP:** 189.3-191.4 °C
\( [\alpha]_D^{20} = +60 \) (c = 0.2, CH\(_2\)Cl\(_2\))

\(^{1}H\)-NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.75-8.72 \) (m, 1H), 8.15-8.10 (m, 4H), 7.79-7.68 (m, 6H), 7.54-7.42 (m, 6H), 7.00-6.75 (m, 4H), 6.45-6.40 (m, 3H), 4.80-4.75 (m, 2H), 4.22-4.18 (m, 4H), 3.80-3.65 (m, 2H), 3.75 (s, 1H), 3.18 (s, 3H), 2.65-2.25 (m, 6H), 2.45 (s, 6H), 2.38 (s, 6H), 2.20-1.80 (m, 3H), 1.67-1.25 (m, 4H), ppm.

\(^{13}C\)-NMR (100 MHz, CDCl\(_3\)): \( \delta = 165.9, 162.7 \) (q, \( J = 54.2 \) Hz), 150.1, 135.2 (q, \( J = 290.7 \) Hz), 135.0, 134.8, 132.7 \( (d, J = 3.1 \) Hz), 130.8 \( (d, J = 3.1 \) Hz), 130.2 \( (d, J = 61.2 \) Hz), 129.2 \( (d, J = 11.2 \) Hz), 129.1 \( (q, J = 3.7 \) Hz), 128.7-128.6 \( (m, 125.2, 125.0, 123.6-121.0 \) (m), 116.8 \( (q, J = 3.6 \) Hz), 94.0-93.6 \( (m, 82.5 \) (d, \( J = 1.9 \) Hz), 73.5 \( (d, J = 2.3 \) Hz), 71.8 \( (d, J = 58.5 \) Hz), 70.4, 70.1 \( (d, J = 6.3 \) Hz), 70.0, 68.2, 66.2, 58.2, 36.5 \( (d, J = 3.8 \) Hz), 33.2 \( (d, J = 2.1 \) Hz), 28.9 \( (d, J = 2.1 \) Hz), 26.6 \( (d, J = 2.2 \) Hz), 25.4, 23.5 ppm.

\(^{31}P\)-NMR (81 MHz, CDCl\(_3\)): \( \delta = +9.2 \) ppm.

IR (neat): \( \nu_{max} (\text{cm}^{-1}) = 2945 \) (w), 1445 (w), 1345 (s), 1269 (m), 1156 (s), 1009 (s), 716 (m), 668 (s).

MS (FAB): 849 (\([\text{M}+\text{H}]^+\), 21), 848 (\(\text{M}^+\), 100), 782 (22).

HRMS (EI): \( m/z \text{ calcd. for: } [\text{C}_{41}\text{H}_{46}\text{PNO}^{193}\text{Ir}^{56}\text{Fe}]^{-} \): 848.2296, found 848.2292

Iridium complex (47c):

Prepared according to TP6 from P,N-ligand 9d (275 mg, 0.50 mmol), [Ir(cod)Cl]\(_2\) (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH\(_2\)Cl\(_2\)) afforded the iridium complex 47c (804 mg, 0.47 mmol; 93%) as a bright orange solid.

MP: 192.6-193.0 °C

\( [\alpha]_D^{20} = +61.0 \) (c = 0.2, CH\(_2\)Cl\(_2\))

\(^{1}H\)-NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.05-7.97 \) (m, 1H), 7.77-7.65 (m, 4H), 7.58-7.40 \( (m, 125.2, 125.0, 123.6-121.0 \) (m), 116.8 \( (q, J = 3.6 \) Hz), 94.0-93.6 \( (m, 82.5 \) (d, \( J = 1.9 \) Hz), 73.5 \( (d, J = 2.3 \) Hz), 71.8 \( (d, J = 58.5 \) Hz), 70.4, 70.1 \( (d, J = 6.3 \) Hz), 70.0, 68.2, 66.2, 58.2, 36.5 \( (d, J = 3.8 \) Hz), 33.2 \( (d, J = 2.1 \) Hz), 28.9 \( (d, J = 2.1 \) Hz), 26.6 \( (d, J = 2.2 \) Hz), 25.4, 23.5 ppm.

\(^{31}P\)-NMR (81 MHz, CDCl\(_3\)): \( \delta = +9.2 \) ppm.

IR (neat): \( \nu_{max} (\text{cm}^{-1}) = 3006 \) (w), 2825 (m), 1611 (w), 1345 (m), 1229 (s), 1198 (m), 1010 (s), 967 (m), 875 (m), 668 (m).

MS (FAB): 849 (\([\text{M}+\text{H}]^+\), 21), 848 (\(\text{M}^+\), 100), 782 (22).

HRMS (EI): \( m/z \text{ calcd. for: } [\text{C}_{41}\text{H}_{46}\text{PNO}^{193}\text{Ir}^{56}\text{Fe}]^{-} \): 848.2296, found 848.2292
Iridium complex (46d):

Prepared according to TP6 from P,N-ligand 10c (312 mg, 0.50 mmol), [Ir(cod)Cl]2 (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH2Cl2) provided the iridium complex 46d (796 mg, 0.45 mmol; 89%) as a bright orange solid.

MP: 188.2-190.1 °C
[α]D20 = +48.9 (c = 0.2, CH2Cl2)

1H-NMR (400 MHz, CDCl3): δ = 8.68-8.64 (m, 1H), 8.44-7.99 (m, 10H), 7.95-7.82 (m, 4H), 7.80-7.70 (m, 4H), 7.60-7.32 (m, 6H), 6.95-6.87 (m, 3H), 4.90-4.88 (m, 1H), 4.87-4.86 (m, 1H), 4.78-4.55 (m, 2H), 4.22-4.19 (m, 1H), 4.00-3.95 (m, 2H), 3.13 (s, 5H), 2.39 (s, 6H), 2.37 (s, 6H), 2.30-2.00 (m, 2H), 1.75-1.44 (m, 4H), 1.23 (s, 2H) ppm.

13C-NMR (100 MHz, CDCl3): δ = 165.0, 160.7 (q, J = 25.5 Hz), 150.1, 135.2, 135.0-134.0 (m), 133.2 (q, J = 287.0 Hz), 132.1 (d, J = 2.8 Hz), 131.8 (d, J = 2.6 Hz), 130.0 (d, J = 60.1 Hz), 129.5, 129.2 (q, J = 2.9 Hz), 128.9 (d, J = 11.2 Hz), 128.7 (q, J = 2.8 Hz), 128.2, 127.9, 126.8, 126.2, 124.2, 123.7, 121.2, 119.5-116.4 (m), 94.5 (d, J = 13.1 Hz), 93.8 (d, J = 7.0 Hz), 93.5, 78.6, 73.2 (d, J = 2.8 Hz), 72.1, 71.0 (d, J = 56.3 Hz), 70.8, 70.3 (q, J = 8.2 Hz), 69.2, 67.5, 35.7 (d, J = 2.9 Hz), 32.7 (d, J = 1.9 Hz), 28.6 (d, J = 2.7 Hz), 26.9 (d, J = 2.1 Hz), 23.3, 22.8 ppm.

31P-NMR (81 MHz, CDCl3): δ = +9.4 ppm

IR (neat): νmax (cm⁻¹) = 2918 (w), 1765 (m), 1644 (w), 1482 (m), 1399 (m), 1186 (s), 994 (w), 886 (m), 742 (s), 698 (s), 681 (s).

MS (ESI): 925 ([M+H]+, 64), 924 (M+, 100), 825 (19), 620 (10).

HRMS (ESI): m/z calcd. for: [C₄7H₅₈P₅6FeNO₁₉Ir] 924.2609, found: 924.2629

Iridium complex (47d):

Prepared according to TP6 from P,N-ligand 10d (312 mg, 0.50 mmol), [Ir(cod)Cl]2 (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH2Cl2) provided the iridium complex 47d (804 mg, 0.45 mmol; 90%) as a bright orange solid.
MP: 154.2-155.7 °C
\([\alpha]_D^{20} = +42.8 \text{ (c = 0.2, CH}_2\text{Cl}_2\)  
\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.08-8.01\) (m, 1H), 8.44-7.90 (m, 12H), 7.88-7.66 (m, 7H), 7.55-7.48 (m, 5H), 6.95-6.85 (m, 3H), 5.11-5.08 (m, 1H), 4.89-4.85 (m, 1H), 4.64 (s, 2H), 4.38-4.15 (m, 2H), 3.83 (s, 6H), 2.55-2.50 (m, 2H), 2.35 (s, 6H), 2.32 (s, 6H), 2.30-1.58 (m, 6H), 1.28-1.20 (m, 2H) ppm.
\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 161.4, 160.2\) (q, \(J = 54.1\) Hz), 149.2, 135.2-134.8 (m), 133.2 (q, \(J = 275.8\) Hz), 132.0 (d, \(J = 3.1\) Hz), 131.2 (d, \(J = 3.8\) Hz), 129.8 (d, \(J = 60.1\) Hz), 129.4, 128.9 (q, \(J = 3.2\) Hz), 128.9, 128.2 (q, \(J = 3.1\) Hz), 127.9 (d, \(J = 12.1\) Hz), 127.9-123.5 (m), 120.9-115.2 (m), 95.4 (d, \(J = 12.8\) Hz), 94.2 (d, \(J = 6.8\) Hz), 93.0, 78.6 (d, \(J = 2.2\) Hz), 73.0, 72.1, 71.0 (d, \(J = 58.1\) Hz), 70.9, 70.2 (q, \(J = 8.2\) Hz), 68.7, 67.2, 36.5 (d, \(J = 2.8\) Hz), 32.6 (d, \(J = 1.9\) Hz), 28.6 (d, \(J = 2.2\) Hz), 27.4 (d, \(J = 2.1\) Hz), 24.2, 23.8 ppm.
\(^{31}\)P-NMR (81 MHz, CDCl\(_3\)): \(\delta = +8.56\) ppm.
IR (neat): \(\nu_{\text{max}}\) (cm\(^{-1}\)) = 3008 (w), 1609 (m), 1425 (m), 1365 (s), 1135 (s), 981 (s), 839 (m), 785 (s), 670 (m), 654 (s).
MS (ESI): 925 ([M+H]\(^+\), 12), 924 (M\(^+\), 100), 825 (22), 620 (25).
HRMS (ESI): \(m/z\) calcd. for: [C\(_{47}\)H\(_{50}\)P\(_{56}\)FeNO\(_{193}\)Ir] \(924.2609\), found: 924.2608

Iridium complex (46e):

Prepared according to TP6 from P,N-ligand 9e (350 mg, 0.50 mmol), [Ir(cod)Cl\(_2\)] (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH\(_2\)Cl\(_2\)) afforded the iridium complex 46e (764 mg, 0.41 mmol; 82%) as a bright orange solid.

MP: 221.8-223.4 °C
\([\alpha]_D^{20} = +28.8 \text{ (c = 0.2, CH}_2\text{Cl}_2\)  
\(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.70-8.67\) (m, 1H), 8.11-7.88 (m, 8H), 7.81-7.55 (m, 10H), 7.45-7.33 (m, 11H), 6.95-6.82 (m, 1H), 4.96-4.90 (m, 1H), 4.45 (t, \(J = 2.2\) Hz, 1H), 4.11-4.00 (m, 3H), 3.79-3.68 (m, 3H), 3.21 (s. 5H), 2.67-2.29 (m, 5H), 2.15-1.81 (m, 2H), 1.68-1.27 (m, 3H) ppm.
\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 165.2, 160.9\) (q, \(J = 51.2\) Hz), 150.2, 135.0 (q, \(J = 278.9\) Hz), 135.0, 134.8 (d, \(J = 14.2\) Hz), 132.7, 130.8 (d, \(J = 2.8\) Hz), 130.2 (d, \(J = 55.4\) Hz), 129.2-127.8 (m), 126.2 (d, \(J = 11.4\) Hz), 125.0 (d, \(J = 2.8\) Hz), 123.8, 122.9, 121.2, 116.7 (q, \(J = 5.9\) Hz), 94.8-93.0 (m), 81.9, 73.0 (d, \(J = 2.8\) Hz), 71.2 (d, \(J = 56.2\) Hz), 70.2, 70.0 (d, \(J = 5.8\) Hz), 69.5 (d, \(J = 7.2\) Hz), 66.8, 64.3, 56.7, 36.2 (d, \(J = 4.1\) Hz), 33.8 (d, \(J = 3.1\) Hz), 28.5 (d, \(J = 1.8\) Hz), 26.6 (d, \(J = 2.2\) Hz) ppm.
\(^{31}\)P-NMR (81 MHz, CDCl\(_3\)): \(\delta = +9.7\) ppm.
IR (neat): \(\nu_{\text{max}}\) (cm\(^{-1}\)) = 2998 (w), 1465 (m), 1542 (m), 1268 (m), 1225 (s), 1165 (s), 1028 (s), 912 (m), 878 (m), 792 (m), 765 (m).
MS (ESI): 869 ([M+H]\(^+\), 2), 868 (M\(^+\), 100), 852 (18), 782 (15), 685 (22).
HRMS (ESI): m/z calcd. for: [C\textsubscript{43}H\textsubscript{42}PNO\textsuperscript{193}Ir\textsuperscript{56}Fe]: 868.1938, found 868.1922

Iridium complex (47e):

\[
\begin{array}{c}
\text{Ph}_2P
\end{array}
\]

Prepared according to TP6 from P,N-ligand 9f (350 mg, 0.50 mmol), [Ir(cod)Cl\textsubscript{2} (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH\textsubscript{2}Cl\textsubscript{2}) afforded the iridium complex 47e (745 mg, 0.40 mmol; 80%) as a bright orange solid.

MP: 199.0-201.2 °C
\([\alpha]_D^{20} = +24.3 \text{ (c = 0.2, CH}_{2}\text{Cl}_{2})\)

\(\text{H-NMR (400 MHz, CDCl}_3\):} \; \delta = 8.10-8.07 \text{ (m, 1H), 7.98-7.71 \text{ (m, 10H), 7.69-7.48 \text{ (m, 11H), 7.40-7.10 \text{ (m, 7H), 6.88-6.86 \text{ (m, 2H), 5.11-5.06 \text{ (m, 1H), 4.52-4.47 \text{ (m, 1H), 4.32-4.22 \text{ (m, 3H), 3.91-3.88 \text{ (m, 2H), 3.80-3.75 \text{ (m, 1H), 3.43 \text{ (s, 5H), 2.65-2.25 \text{ (m, 4H), 2.15-1.80 \text{ (m, 3H), 1.68-1.27 \text{ (m, 3H), ppm.}}}

1\text{C-NMR (100 MHz, CDCl}_3\):} \; \delta = 161.0, 160.0 \text{ (q, J = 52.7 Hz), 148.5, 134.3 \text{ (q, J = 282.1 Hz), 134.0, 134.2 \text{ (d, J = 14.6 Hz), 133.7 \text{ (d, J = 2.9 Hz), 133.3 \text{ (d, J = 11.4 Hz), 132.7-130.2 \text{ (m), 130.4-126.6 \text{ (m), 125.8 \text{ (d, J = 2.8 Hz), 125.0 \text{ (d, J = 10.8 Hz), 124.2, 123.2, 121.8, 118.2 \text{ (q, J = 6.1 Hz), 95.2-93.1 \text{ (m), 82.5 \text{ (d, J = 11.8 Hz), 73.0 \text{ (d, J = 2.8 Hz), 71.0 \text{ (d, J = 55.4 Hz), 70.8, 70.0 \text{ (d, J = 5.8 Hz), 69.4 \text{ (d, J = 6.7 Hz), 67.4, 65.8, 57.2, 37.4 \text{ (d, J = 3.8 Hz), 32.1 \text{ (d, J = 3.2 Hz), 28.5 \text{ (d, J = 1.9 Hz), 27.2 \text{ (d, J = 2.5 Hz) ppm.}}}

3\text{P-NMR (81 MHz, CDCl}_3\):} \; \delta = +9.6 \text{ ppm}}

IR (neat): \nu_{\text{max}} (\text{cm}^{-1}) = 3002 \text{ (br, w), 2999 \text{ (w), 1676 \text{ (w), 1556 \text{ (m), 1344 \text{ (m), 1298 \text{ (s), 1199 \text{ (s), 1009 \text{ (s), 965 \text{ (s), 898 \text{ (m), 856 \text{ (m), 695 \text{ (m).}}}

MS (ESI): 869 ([M+H]^+, 12), 868 (M^+, 100), 852 (11), 625 (22).

HRMS (ESI): m/z calcd. for: [C\textsubscript{43}H\textsubscript{42}PNO\textsuperscript{193}Ir\textsuperscript{56}Fe]: 868.1938, found 868.1935

Iridium complex (46f):

\[
\begin{array}{c}
\text{Ph}_2P
\end{array}
\]

Prepared according to TP6 from P,N-ligand 9g (302 mg, 0.50 mmol), [Ir(COD)Cl\textsubscript{2} (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash
Experimental Section

Chromatography (silica gel, CH$_2$Cl$_2$) provided the iridium complex 46f (790 mg, 0.45 mmol; 89%) as a bright orange solid.

**MP:** 128.1-129.7 °C

$[\alpha]_D^{20} = +63.4$ (c = 0.2, CH$_2$Cl$_2$

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 8.76-8.66$ (m, 2H), 8.24-8.05 (m, 3H), 7.98-7.75 (m, 9H), 7.60-7.54 (m, 6H), 7.40-7.32 (m, 4H), 6.95-6.87 (m, 3H), 5.00-4.88 (m, 3H), 4.50 (t, $J = 2.2$ Hz, 1H), 4.12-4.05 (m, 2H), 3.98-3.95 (m, 1H), 3.65-3.64 (m, 2H), 3.25 (s, 3H), 2.50-2.47 (m, 2H), 2.34-2.29 (m, 1H), 2.09-2.00 (m, 1H), 1.79-1.75 (m, 1H), 1.57-1.52 (m, 3H), 1.98 (s, 9H), 1.23 (m, 2H) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 166.2, 162.1$ (q, $J = 371.1$ Hz), 151.7, 138.2, 135.5 (d, $J = 14.0$ Hz), 135.0 (q, $J = 371.1$ Hz), 134.5-133.6 (m), 132.5 (t, $J = 2.1$ Hz), 130.8 (d, $J = 2.6$ Hz), 129.8 (d, $J = 57.6$ Hz), 129.2 (d, $J = 10.9$ Hz), 129.0, 128.8 (q, $J = 3.2$ Hz), 128.7 (q, $J = 2.8$ Hz), 128.2, 127.7, 126.2, 125.9-121.0 (m), 117.5-117.0 (m), 95.6 (d, $J = 14.0$ Hz), 94.2 (d, $J = 7.1$ Hz), 93.5, 78.8 (s), 73.0 (d, $J = 2.1$ Hz), 72.8, 71.0 (d, $J = 54.0$ Hz), 70.2, 70.0 (q, $J = 8.0$ Hz), 68.2, 66.5, 34.8 (d, $J = 5.2$ Hz), 31.0 (d, $J = 1.9$ Hz), 28.7 (d, $J = 2.1$ Hz), 26.9 (d, $J = 2.3$ Hz), 14.5, 11.8 ppm.

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta = +8.45$ ppm

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3008 (br, w), 2998 (w), 1665 (w), 1592 (m), 1156 (m), 1222 (s), 1177 (s), 980 (m), 886 (m), 728 (m), 662 (m).

**MS (ESI):** 849 ([M+H]$^+$, 40), 848 (M$^+$, 100), 820 (15), 657 (24).

**HRMS (ESI):** m/z calcd. for: [C$_{41}$H$_{46}$P$_5$FeNO$_{193}$Ir] 848.2283, found: 848.2275

Iridium complex (47f):

Prepared according to TP6 from P,N-ligand 9h (302 mg, 0.50 mmol), [Ir(COD)Cl]$_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH$_2$Cl$_2$) provided the iridium complex 47f (774 mg, 0.44 mmol; 88%) as a bright orange solid.

**MP:** 167.5-171.2 °C

$[\alpha]_D^{20} = +38.0$ (c = 0.2, CH$_2$Cl$_2$

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.65-7.68$ (m, 9H), 7.57-7.50 (m, 2H), 7.24-7.22 (m, 3H), 7.20-6.99 (m, 8H), 6.96 (s, 1H), 6.75-6.70 (m, 1H), 6.64-6.60 (m, 1H), 5.19-5.16 (m, 1H), 4.75-4.77 (m, 1H), 4.64-4.55 (m, 2H), 4.54-4.47 (m, 2H), 4.30 (s, 4H), 4.29-4.23 (m, 2H), 4.22-4.20 (m, 1H), 3.71-3.69 (m, 1H), 2.54-2.13 (m, 7H), 2.01 (s, 9H), 1.92-1.77 (m, 2H) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 161.8, 161.0$ (q, $J = 51.2$ Hz), 148.7, 139.2-136.4 (m), 134.5, 132.7 (d, $J = 10.2$ Hz), 131.9 (d, $J = 2.7$ Hz), 131.2 (d, $J = 52.2$ Hz), 131.0 (d, $J = 10.8$ Hz), 130.8 (d, $J = 2.5$ Hz), 129.4-129.0 (m), 128.9-128.7 (m), 128.5, 128.0, 128.2, 127.5, 126.8 (q, $J = 366.1$ Hz), 126.2, 125.2, 122.8, 122.2, 120.0-118.4 (m), 93.2 (d, $J = 12.2$ Hz), 92.1 (d, $J = 14.2$ Hz), 89.2 (d, $J = 11.7$ Hz), 82.0 (d, $J = 1.4$ Hz), 73.2, 72.3, 71.7 (d, $J = 6.8$ Hz).
Experimental Section

\( \text{N} \text{OBnPh}_2 \text{P} \text{Ir(COD)}^\dagger_{\text{tBu}} \text{FeBARF} \)

Prepared according to TP6 from P,N-ligand 10g (340 mg, 0.50 mmol), [Ir(COD)Cl]_2 (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH\(_2\)Cl\(_2\)) provided the iridium complex 46g (811 mg, 0.44 mmol, 88%) as a bright orange solid.

MP: 164.2-169.5 °C

\([\alpha]_{D}^{20} = +48.4 \quad \text{c} = 0.2, \text{CH}_2\text{Cl}_2\)

\( ^1\text{H-NMR (400 MHz, CDCl}_3\)): \(\delta = 8.88-8.82 \quad \text{(m, 2H), 8.15-8.00 \quad \text{(m, 4H), 7.95-7.82 \quad \text{(m, 6H),}}\)

\( 7.75-7.60 \quad \text{(m, 6H), 7.42-7.22 \quad \text{(m, 4H), 7.12-6.90 \quad \text{(m, 6H), 6.75-6.62 \quad \text{(m, 3H), 5.11-5.06 \quad \text{(m, 1H), 4.88-4.80 \quad \text{(m, 2H), 4.50-4.48 \quad \text{(m, 1H), 4.22 \quad \text{(s, 4H), 3.98-3.97 \quad \text{(m, 1H), 3.65-3.64 \quad \text{(m, 1H), 2.52-2.40 \quad \text{(m, 2H), 2.32-2.29 \quad \text{(m, 2H), 2.09-2.00 \quad \text{(m, 1H), 1.79-1.75 \quad \text{(m, 1H), 1.64 \quad \text{(s, 9H), 1.57-1.50 \quad \text{(m, 3H), 1.22 \quad \text{(m, 2H)} \text{ ppm.}})\)

\( ^{13}\text{C-NMR (100 MHz, CDCl}_3\)): \(\delta = 163.2, 160.6 \quad \text{(q, J = 50.1 Hz), 149.7, 136.4, 135.5 \quad \text{(d, J = 14.0 Hz), 134.8-134.7 \quad \text{(m, 133.4 \quad \text{(q, J = 360.1 Hz), 132.7 \quad \text{(d, J = 2.2 Hz), 130.8 \quad \text{(d, J = 2.6 Hz), 130.0 \quad \text{(d, J = 58.7 Hz), 129.2 \quad \text{(d, J = 11.0 Hz), 129.1 \quad \text{(q, J = 2.9 Hz), 128.9, 128.7 \quad \text{(q, J = 2.8 Hz), 128.6, 127.2, 126.1, 125.9, 123.8, 123.2, 120.5, 117.5-117.4 \quad \text{(m, 94.6 \quad \text{(d, J = 14.2 Hz), 94.0 \quad \text{(d, J = 6.8 Hz), 93.9, 78.6 \quad \text{(d, J = 1.8 Hz), 73.3 \quad \text{(d, J = 2.2 Hz), 72.3, 71.7 \quad \text{(d, J = 55.0 Hz), 70.4, 70.2 \quad \text{(q, J = 8.2 Hz), 67.0, 65.5, 35.7 \quad \text{(d, J = 4.5 Hz), 32.2 \quad \text{(d, J = 1.9 Hz), 28.7 \quad \text{(d, J = 2.1 Hz), 26.9 \quad \text{(d, J = 2.3 Hz), 16.5, 14.2 ppm.}})\)

\( ^{31}\text{P-NMR (81 MHz, CDCl}_3\)): \(\delta = +8.4 \text{ ppm.}})\)

\( \text{IR (neat): } v_{\max} (\text{cm}^{-1}) = 2914 (\text{w}), 1608 (\text{w}), 1574 (\text{m), 1275 (s), 1192 (s), 1024 (w), 925 (m), 886 (m), 768 (m), 681 (m).}}\)

\( \text{MS (ESI): } 925 ([M+H]^+, 11), 924 (M^+, 100), 902 (12), 789 (27), 584 (10).\)

\( \text{HRMS (ESI): } m/z \text{ calcd. for: [C}_{41}\text{H}_{46}\text{P}_{56}\text{FeNO}_{193}\text{Ir}] 925.2283, \text{ found: 924.2285} \)

Iridium complex (46g):

\( \text{Iridium complex (47g):} \)
Prepared according to TP6 from P,N-ligand 10f (340 mg, 0.50 mmol), [Ir(COD)Cl]₂ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Flash chromatographical purification (silica gel, CH₂Cl₂) provided the iridium complex 47g (740 mg, 0.40 mmol; 80%) as a bright orange solid.

**MP:** 122.5-128.7 °C

[α]D²₀ = +42.1 (c = 0.2, CH₂Cl₂)

**¹H-NMR (400 MHz, CDCl₃):** δ = 7.66-7.64 (m, 6H), 7.55-7.45 (m, 12H), 7.22-7.20 (m, 4H), 7.10-6.99 (m, 3H), 6.78-6.70 (m, 5H), 6.64-6.60 (m, 1H), 5.20-5.15 (m, 1H), 4.80-4.78 (m, 2H), 4.66-4.57 (m, 1H), 4.53-4.48 (m, 1H), 4.34 (s, 4H), 3.72-3.69 (m, 1H), 2.54-2.10 (m, 7H), 1.92-1.75 (m, 3H), 1.68 (s, 9H), 1.22 (m, 2H) ppm.

**¹³C-NMR (100 MHz, CDCl₃):** δ = 160.5, 160.0 (q, J = 50.0 Hz), 149.3, 138.9, 136.4, 134.8 (br, s), 132.8 (d, J = 9.8 Hz), 131.9 (d, J = 2.5 Hz), 131.27 (d, J = 11.3 Hz), 131.26 (d, J = 54.0 Hz), 130.8 (d, J = 2.5 Hz), 129.4-129.3 (m), 129.1 (t, J = 3.0 Hz), 129.0, 128.9-128.7 (m), 128.5-128.4 (m), 127.5, 126.8 (q, J = 365.0 Hz), 125.9, 125.6, 123.2, 122.2, 117.5-117.4 (m), 93.4 (d, J = 13.0 Hz), 91.9 (d, J = 15.7 Hz), 88.7 (d, J = 12.1 Hz), 82.9, 73.2 (d, J = 1.4 Hz), 72.3, 71.7 (d, J = 6.3 Hz), 71.2, 69.8 (d, J = 7.2 Hz), 67.3, 66.7 (d, J = 57.0 Hz), 61.2, 34.5 (d, J = 3.5 Hz), 31.7 (d, J = 2.3 Hz), 31.6 (d, J = 2.3 Hz), 27.9 (d, J = 2.2 Hz) 17.2, 15.3 ppm.

**³¹P-NMR (81 MHz, CDCl₃):** δ = +7.601 ppm.

**IR (neat):** νmax (cm⁻¹) = 3002 (br, w), 2999 (w), 1642 (m), 1554 (m), 1456 (m), 1275 (s), 1122 (s), 966 (m), 888 (m), 768 (m), 742 (m), 681 (m).

**MS (ESI):** 925 ([M+H]+, 21), 924 (M⁺, 100), 902 (16), 789 (30), 584 (11).

**HRMS (ESI):** m/z calcd. for: [C₄₇H₅₆P₅NₓEO1₉ₓIr] 924.2596, found: 924.2612

6. Synthesis of N-arylimines

**N-phenyl-1-phenylethylideneamine (50a)**

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and aniline (12.0 mmol, 1.12 g, 1.1 mL; 1.20 equiv.). Recrystallisation from n-pentane, afforded the desired imine (1.42 g, 7.30 mmol, 73%) as a yellow crystalline solid.

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**N-(4-methoxy)phenyl-1-phenylethylideneamine (50b)**

\[
\text{MP:} \quad 87.3-87.9 \, ^\circ\text{C}.
\]

\[
\text{\textsuperscript{1}H-NMR (300 MHz, CDCl}_3\text{):} \quad \delta = 7.98-7.95 (m, 2H), 7.45-7.43 (m, 3H), 6.91 (d, J = 8.9 \, \text{Hz}, 2H), 6.76 (d, J = 8.8 \, \text{Hz}, 2H), 3.80 (s, 3H), 2.30 (s, 3H) \, \text{ppm}.
\]

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 4-methoxy aniline (12.0 mmol, 1.48 g; 1.20 equiv.). Recrystallisation from n-pentane:EtOAc, afforded the desired imine (1.42 g, 6.29 mmol, 63%) as a yellow crystalline solid.

**N-(4-methyl)phenyl-1-phenylethylideneamine (50c)**

\[
\text{MP:} \quad 41-42 \, ^\circ\text{C}.
\]

\[
\text{\textsuperscript{1}H-NMR (300 MHz, CDCl}_3\text{):} \quad \delta = 7.98-7.96 (m, 2H), 7.49-7.44 (m, 3H), 7.16 (d, J = 8.0 \, \text{Hz}, 2H), 6.72 (d, J = 8.0 \, \text{Hz}, 2H), 2.35 (s, 3H), 2.20 (s, 3H) \, \text{ppm}.
\]

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 4-methyl aniline (12.0 mmol, 1.29 g; 1.20 equiv.). Recrystallisation from n-pentane:EtOAc, afforded the desired imine (1.57 g, 7.50 mmol, 75%) as a yellow solid.

**N-(3,4-Dioxymethylene)phenyl-1-phenylethylideneamine (50d)**

\[
\text{MP:} \quad 38-39 \, ^\circ\text{C}.
\]

\[
\text{\textsuperscript{1}H-NMR (300 MHz, CDCl}_3\text{):} \quad \delta = 7.98 (dd, J = 7.5 \, \text{Hz}, 2.1 \, \text{Hz}, 2H), 7.44-7.40 (m, 3H), 7.33 (t, J = 7.4 \, \text{Hz}, 2H), 7.08 (t, J = 7.4 \, \text{Hz}, 1H), 6.79 (d, J = 7.3 \, \text{Hz}, 2H), 2.18 (s, 3H) \, \text{ppm}.
\]

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4-dioxymethylene aniline (12.0 mmol, 1.65 g; 1.20 equiv.). Recrystallisation from MeOH, afforded the desired imine (1.82 g, 7.61 mmol, 76%) as a pale brown solid.

**MP:** 118.3-120.0 °C.

**$^1$H-NMR (300 MHz, CDCl$_3$):** $\delta = 7.96-7.93$ (m, 2H), 7.48-7.39 (m, 3H), 6.79 (d, $J = 8.1$ Hz, 1H), 6.37 (d, $J = 2.2$ Hz, 1H), 6.24 (dd, $J = 2.2$ Hz, 8.1 Hz, 1H), 5.90 (s, 2H), 2.26 (s, 3H) ppm.

**$^{13}$C-NMR (75 MHz, CDCl$_3$):** $\delta = 166.3$, 150.0, 146.0, 143.7, 139.4, 130.5, 128.4, 127.1, 111.8, 108.3, 101.6, 101.0, 17.4 ppm.

**IR (neat):** $\nu_{\text{max}}$ (cm$^{-1}$) = 3065 (w), 2889 (w), 1616 (m), 1481 (s), 1339 (m), 1240 (s), 1177 (s), 1031 (s), 938 (s), 848 (s).

**MS (70 eV, EI):** $m/z$ (%) = 239 (M$^+$, 57), 224 (100), 225 (15), 162 (8), 121 (9).

**HRMS (EI):** $m/z$ calcd. for: [C$_{15}$H$_{13}$NO$_2$] 239.0946, found: 239.0958.

N-(3,4,5-Trimethoxy)phenyl-1-phenylethylideneamine (50e)

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4,5-trimethoxy aniline (12.0 mmol, 2.20 g; 1.20 equiv.). Recrystallisation from $n$-pentane:EtOAc, afforded the desired imine (2.25 g, 7.89 mmol, 79%) as a yellow solid.

**MP:** 96.1-97.9 °C.

**$^1$H-NMR (300 MHz, CDCl$_3$):** $\delta = 7.97-7.94$ (m, 2H), 7.45-7.42 (m, 3H), 6.02 (s, 2H), 3.86 (s, 3H), 3.83 (s, 6H), 2.28 (s, 3H) ppm.

**$^{13}$C-NMR (75 MHz, CDCl$_3$):** $\delta = 166.0$, 153.6, 147.8, 139.2, 130.5, 128.5, 128.3, 127.1, 96.6, 61.0, 56.0, 17.4 ppm.

**IR (neat):** $\nu_{\text{max}}$ (cm$^{-1}$) = 3855 (w), 3752 (w), 2951 (w), 1636 (m), 1581 (s), 1496 (s), 1411 (s), 1233 (s), 1119 (s), 1011 (s), 768 (s), 696 (s).

**MS (70 eV, EI):** $m/z$ (%) = 285 (M$^+$, 66), 270 (100), 242 (3), 226 (3), 146 (3), 103 (5).

**HRMS (EI):** $m/z$ calcd. for: [C$_{17}$H$_{19}$NO$_3$] 285.1365, found: 285.1361.

N-(3,4-Dimethyl)phenyl-1-phenylethylidene amine (50f)

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4-dimethyl aniline (12.0 mmol, 1.45 g; 1.20 equiv.). Purification by vacuum distillation (160 °C, 0.1 mbar) afforded the desired imine (1.70 g, 7.58 mmol, 76%) as a yellow oil.
N-(3,4-Dimethoxy)phenyl-1-phenylethylideneamine (50g)

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4-dimethoxy aniline (12.0 mmol, 1.84 g; 1.20 equiv.). Recrystallisation from n-pentane:EtOAc, afforded the desired imine (1.91 g, 7.50 mmol, 75%) as a yellow solid.

**MP:** 91.6-92.6 °C.

**1H-NMR (300 MHz, CDCl3):** δ = 7.98-7.93 (m, 2H), 7.48-7.41 (m, 3H), 6.85 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 6.32 (dd, J = 2.7 Hz, 8.8 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.27 (s, 3H) ppm.

**13C-NMR (75 MHz, CDCl3):** δ = 166.0, 149.4, 145.2, 139.5, 133.0, 130.4, 128.3, 127.1, 111.7, 110.7, 104.3, 56.1, 55.8, 17.3 ppm.

**IR (neat):** νmax (cm⁻¹) = 3855 (w), 3075 (w), 2842 (w), 1700 (w), 1623 (m), 1576 (m), 1501 (s), 1228 (s), 1133 (s), 1024 (s), 856 (s), 770 (s), 704 (s).

**MS (70 eV, EI):** m/z (%) = 255 (M⁺, 97), 240 (100), 196 (3), 122 (4), 103 (4).

**HRMS (EI):** m/z calcd for: [C₁₆H₁₇NO₂] 255.1259, found: 255.1255.

N-(3,5-Dimethyl)phenyl-1-phenylethylideneamine (50h)

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 2,4-dimethyl aniline (12.0 mmol, 1.45 g, 1.48 mL; 1.20 equiv.). Purification by vacuum distillation (85 °C, 0.1 mbar), afforded the desired imine (1.75 g, 7.80 mmol, 78%) as a yellow oil.

**1H-NMR (300 MHz, CDCl3):** δ = 7.45-7.28 (m, 5H), 7.21-7.18 (m, 1H), 6.92 (s, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H) ppm.

**13C-NMR (75 MHz, CDCl3):** δ = 165.2, 150.5, 138.5, 132.1, 132.0, 130.3, 128.3, 127.1, 124.9, 117.0, 21.3, 17.4, 16.8 ppm.
**Experimental Section**

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2924 (w), 1682 (w), 1633 (s), 1589 (s), 1450 (m), 1274 (s), 1150 (m), 1029 (m), 845 (s), 763 (s), 672 (s).

MS (70 eV, EI): $m/z$ (%) = 223 ($M^+$, 44), 207 (88), 208 (100), 105 (25), 103 (9).

HRMS (EI): $m/z$ calcd. for: [C$_{16}$H$_{17}$N] 223.1361, found: 223.1371.

**N-(3,5-Dimethyl)phenyl-1-phenylethylideneamine (50i)**

![Chemical structure of N-(3,5-Dimethyl)phenyl-1-phenylethylideneamine (50i)]

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 2-methoxy aniline (12.0 mmol, 1.48 g; 1.20 equiv.). Purification by vacuum distillation (140 °C, 0.1 mbar), afforded the desired imine (1.58 g, 7.00 mmol, 70%) as a yellow solid.

**MP:** 42.4 °C

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.99-7.94 (m, 3H), 7.41-7.34 (m, 2H), 7.01 (dd, $J = 2.0$ Hz, 7.9 Hz, 1H), 6.93-6.85 (m, 2H), 6.77 (dd, $J = 2.0$ Hz, 7.7 Hz, 1H), 3.71 (s, 3H), 2.13 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 165.2, 151.5, 138.5, 133.1, 130.3, 128.3, 127.1, 124.9, 117.0, 21.3, 17.4 ppm.

**N-(3,5-Dimethyl)phenyl-1-(4-methoxylphenyl)ethylideneamine (52a)**

![Chemical structure of N-(3,5-Dimethyl)phenyl-1-(4-methoxylphenyl)ethylideneamine (52a)]

Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (1.72 g, 7.79 mmol, 78%) as a yellow oil.

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.98-7.95 (m, 2H), 7.49-7.43 (m, 3H), 6.73 (s, 1H), 6.43 (s, 2H), 2.32 (s, 6H), 2.24 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 165.2, 151.5, 138.5, 133.1, 130.3, 128.3, 127.1, 124.9, 117.0, 21.3, 17.4 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2915 (w), 1682 (w), 1633 (s), 1589 (s), 1450 (m), 1274 (s), 1150 (m), 1029 (m), 845 (s), 763 (s), 672 (s).

MS (70 eV, EI): $m/z$ (%) = 223 ($M^+$, 84), 208 (100), 105 (15), 103 (6), 77 (11).

HRMS (EI): $m/z$ calcd. for: [C$_{16}$H$_{17}$N] 223.1361, found: 223.1364.

**N-(3,5-Dimethyl)phenyl-1-(4-methoxyphenyl)ethylideneamine (52b)**

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Prepared according to TP7 from 4-methoxy acetophenone (10.0 mmol, 1.50 g) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by recrystallisation (n-pentane:MeOH), afforded the desired imine (1.90 g; 7.50 mmol, 75%) as a orange yellow solid.

**MP:** 62.3-64.6°C

**$^1$H-NMR (300 MHz, CDCl$_3$):** $\delta = 7.96-7.92$ (m, 2H), 6.96-6.91 (m, 2H), 6.72 (s, 1H), 6.43 (s, 2H), 3.85 (s, 3H), 2.30 (s, 6H), 2.21 (s, 3H) ppm.

**$^{13}$C-NMR (75 MHz, CDCl$_3$):** $\delta = 164.8, 161.7, 151.0, 138.9, 138.5, 129.0, 124.9, 117.4, 113.6, 55.4, 21.3, 17.2$ ppm.

**IR (neat):** $\nu_{\text{max}}$ (cm$^{-1}$) = 2915 (w), 1631 (s), 1592 (s), 1512 (m), 1365 (m), 1246 (s), 1171 (s), 1026 (s), 827 (s), 688 (s).

**MS (70 eV, EI):** $m/z$ (%) = 253 (M$^+$, 49), 239 (13), 238 (100), 105 (5).

**HRMS (EI):** $m/z$ calcd. for: [C$_{17}$H$_{19}$N] 253.1467 found: 253.1479.

$N$-(3,5-Dimethyl)phenyl-1-(4-methylphenyl)ethylideneamine (52c)

Prepared according to TP7 from 4-methylacetophenone (1.34 g; 1.33 mL, 10.0 mmol,) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (1.71 g; 7.20 mmol, 72%) as a yellow solid.

**MP:** 59.1-61.7 °C

**$^1$H-NMR (300 MHz, CDCl$_3$):** $\delta = 7.91-7.87$ (m, 2H), 7.29-7.27 (m, 2H), 6.75 (s, 1H), 6.50 (s, 2H), 2.43 (s, 3H), 2.33 (s, 6H), 2.25 (s, 3H) ppm.

**$^{13}$C-NMR (75 MHz, CDCl$_3$):** $\delta = 165.2, 151.3, 140.7, 138.5, 138.5, 129.0, 127.2, 124.9, 117.2, 26.5, 21.3, 17.3$ ppm.

**IR (neat):** $\nu_{\text{max}}$ (cm$^{-1}$) = 3029 (w), 1635 (s), 1588 (s), 1364 (s), 1272 (s), 1149 (m), 1031 (m), 841 (s), 810 (s), 736 (m), 688 (s).

**MS (70 eV, EI):** $m/z$ (%) = 237 (M$^+$, 64), 222 (100), 105 (8).

**HRMS (EI):** $m/z$ calcd. for: [C$_{17}$H$_{19}$N] 237.1517 found: 237.1522.

$N$-(3,5-Dimethyl)phenyl-1-(3-methoxyphenyl)ethylideneamine (52d)
Prepared according to TP7 from 3-methoxy acetophenone (10.0 mmol, 1.50 g, 1.38 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Recrystallisation of the crude product in methanol, afforded the desired imine (1.87 g; 7.40 mmol, 74%) as a yellow solid.

MP: 57.7-59.0 °C

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.59-7.57 (m, 1H), 7.51-7.48 (m, 1H), 7.34 (t, $J$ = 7.9 Hz, 1H), 7.01 (ddd, $J$ = 7.9 Hz, 2.6 Hz, 0.9 Hz, 1H), 6.73 (s, 1H), 6.43 (s, 2H), 3.87 (s, 3H), 2.31 (s, 6H), 2.23 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 165.0, 159.7, 151.4, 140.9, 139.0, 138.6, 129.2, 124.9, 119.8, 117.0, 111.8, 55.4, 21.3, 17.5 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3008 (w), 2910 (w), 1633 (s), 1277 (s), 1029 (s), 848 (s), 794 (s), 672 (s).

MS (70 eV, EI): m/z (%) = 253 (M$^+$, 66), 238 (100), 146 (5), 105 (6).

HRMS (EI): m/z calcd. for: [C$_{17}$H$_{19}$NO] 253.1467, found: 253.1469.

$\text{N}-(3,5\text{-dimethyl})\text{phenyl}-1-(4\text{-chlorophenyl})\text{ethylideneamine (52e)}$

Prepared according to TP7 from 4-chloro acetophenone (10.0 mmol, 1.54 g, 1.29 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (2.29 g; 8.90 mmol; 89%) as a pale yellow crystalline solid.

MP: 105.3-107.4 °C

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.91-7.88 (m, 2H), 7.42-7.38 (m, 2H), 6.73 (s, 1H), 6.40 (s, 2H), 2.31 (s, 3H), 2.19 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 163.8, 151.3, 138.6, 137.9, 136.5, 128.5, 125.0, 116.9, 21.3, 17.2 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2919 (br, w), 1635 (s), 1587 (s), 1399 (m), 1270 (m), 1152 (m), 1008 (s), 840 (s), 768 (s), 676 (s).

MS (70 eV, EI): m/z (%) = 259 (M$^+$, 22), 257 (63), 242 (100), 105 (22), 79 (10).

HRMS (EI): m/z calcd. for: [C$_{16}$H$_{16}$NCl] 257.0971, found: 257.0975.

$\text{N}-(3,5\text{-dimethyl})\text{phenyl}-1-(4\text{-phenylphenyl})\text{ethylideneamine (52f)}$
Prepared according to TP7 from 4-phenyl acetophenone (10.0 mmol, 1.96 g) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Recrystallisation of the crude product in \textit{n}-pentane, afforded the desired imine (1.95 g; 6.50 mmol, 65\%) as a pale yellow solid.

\textbf{MP:} 121.9-123.1 °C  
\textbf{\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}):} \( \delta = 8.07-8.02 \) (m, 2H), 7.70-7.64 (m, 4H), 7.49-7.44 (m, 3H), 6.75 (s, 1H), 6.45 (s, 2H), 2.33 (s, 6H), 2.28 (s, 3H) ppm.  
\textbf{\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}):} \( \delta = 164.8, 151.4, 143.1, 140.4, 138.3, 135.8, 128.8, 127.7, 127.6, 127.1, 127.0, 124.9, 117.1, 21.3, 17.4 \) ppm.  
\textbf{IR (neat):} \( \nu_{\text{max}} \) (cm\textsuperscript{-1}) = 3860 (w), 3747 (m), 3039 (br, w), 2915 (br, w), 1773 (w), 1625 (s), 1558 (s), 1548 (s), 1458 (s), 1398 (m), 1272 (m), 843 (s), 763 (s), 685 (s).  
\textbf{MS (70 eV, EI):} \( m/z \) (%) = 299 (M\textsuperscript{+}, 52), 284 (100), 152 (3), 105 (7).  
\textbf{HRMS (EI):} \( m/z \) calcd. for: [C\textsubscript{22}H\textsubscript{21}N] 299.1674, found: 299.1667.

\textbf{\textit{N-(3,5-Dimethyl)phenyl-1-phenylpropyldeneamine (52h)}}

Prepared according to TP7 from propiophenone (10.0 mmol, 1.34 g, 1.34 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (1.66 g; 7.00 mmol, 70\%) as a pale yellow oil.

\textbf{\textsuperscript{1}H-NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}):} \( \delta = 8.04-8.02 \) (m, 2H), 7.26-7.19 (m, 3H), 6.75 (s, 1H), 6.45 (s, 2H), 2.50 (q, \( J = 7.1 \) Hz, 2H), 2.31 (s, 6H), 0.89 (t, \( J = 7.1 \) Hz, 3H) ppm.  
\textbf{\textsuperscript{13}C-NMR (75 MHz, C\textsubscript{6}D\textsubscript{6}):} \( \delta = 165.1, 151.0, 138.2, 133.2, 130.4, 128.2, 127.6, 126.5, 117.4, 21.0, 17.2, 13.0 \) ppm.  
\textbf{IR (neat):} \( \nu_{\text{max}} \) (cm\textsuperscript{-1}) = 2920 (w), 1705 (m), 1600 (s), 1290 (s), 1029 (m), 848 (m), 795 (m), 699 (m).  
\textbf{MS (70 eV, EI):} \( m/z \) (%) = 237 (M\textsuperscript{+}, 25), 223 (100), 209 (90), 121 (70), 91 (19).  
\textbf{HRMS (EI):} \( m/z \) calcd. for: [C\textsubscript{17}H\textsubscript{19}N] 237.3395, found: 237.3404.

\textbf{\textit{N-(3,5-Dimethyl)phenyl-1-(1,2,3,4-tertahydro)naphthylideneamine (52h)}}
Prepared according to TP7 from α-tetralone (10.0 mmol, 1.46 g, 1.33 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Recrystallisation of the crude product (n-pentane:ethylacetate (10:1)), afforded the desired imine (1.79 g; 7.20 mmol, 72%) as a brown solid.

**MP:** 83.5-84.6 °C

**1H-NMR (300 MHz, CDCl3):** \(\delta = 8.33-8.30\) (m, 1H), 7.36 (ddd, \(J = 7.5\) Hz, 1.6 Hz, 1H), 7.31-7.26 (m, 1H), 7.20-7.18 (m, 1H), 6.70 (s, 1H), 6.40 (s, 2H), 2.90 (t, \(J = 6.2\) Hz, 2H), 2.54 (dd, \(J = 7.2\) Hz, 6.2 Hz, 2H), 2.30 (s, 6H), 1.96-1.87 (m, 2H) ppm.

**13C-NMR (75 MHz, CDCl3):** \(\delta = 165.4, 151.4, 141.3, 138.5, 133.8, 133.3, 130.6, 128.6, 126.4, 124.7, 117.1, 30.0, 29.9, 22.9, 21.3\) ppm.

**IR (neat):** \(v_{\text{max}}(\text{cm}^{-1}) = 2921\) (w), 1631 (s), 1588 (s), 1454 (m), 1290 (s), 1035 (m), 840 (s), 765 (s), 662 (s).

**MS (70 eV, EI):** \(m/z\) (%) = 249 (M+, 100), 221 (61), 121 (7), 105 (8), 77 (13).

**HRMS (EI):** \(m/z\) calcd. for: [C18H19N] 249.1517 found: 249.1513.

**Preparation of 2,6-Dimethyl-4-amino anisole (55)**

A 1.0 L flask was charged with 2,6-dimethyl-4-nitro anisole (180 mmol, 32.6 g), active charcoal (20%, 36.0 mmol, 434 mg), FeCl3·6H2O (10%, 18.0 mmol, 4.90 g), MeOH (500 mL) and refluxed. While the reaction mixture was refluxing, NH2NH2·H2O (1.8 mol, 57.5 g, 55.8 mL) was added slowly and continued stirring for overnight. Reaction mixture was cooled to room temperature, filtered and washed with MeOH (3 × 100 mL). Evaporated the filtrate under reduced pressure, filtered the residue through a short pad of silica gel and washed with ether to afford the amine in 96 % yield as a pale yellow crystalline solid.

**MP:** 62-64 °C

**1H-NMR (300 MHz, CDCl3):** \(\delta = 6.45-6.45\) (m, 2H), 4.02 (br, 2H, NH), 3.68 (s, 3H), 2.25-2.21 (m, 6H) ppm.

**13C-NMR (75 MHz, CDCl3):** \(\delta = 150.5, 140.9, 131.8, 116.1, 60.2, 16.3\) ppm.

**IR (neat):** \(v_{\text{max}}(\text{cm}^{-1}) = 3400\) (s), 2955 (m), 1623 (w), 1472 (m), 1212 (m), 1013 (s), 796 (m).

**MS (70 eV, EI):** \(m/z\) (%) = 151 (M+, 88), 137 (26), 136 (100), 108 (47), 93 (28).

**HRMS (EI):** \(m/z\) calcd. for: [C9H13NO] 151.0997, found 151.0999.

**N-(3,5-Dimethyl-4-methoxy)phenyl-1-phenylethlideneamine (56a)**
Prepared according to TP7 from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by vacuum distillation (140 °C, 0.1 mbar), afforded the desired imine (1.90 g, 7.50 mmol, 75%) as a yellow solid.

**MP:** 65.5-66.7 °C.

**1H-NMR (300 MHz, CDCl3):** \(\delta = 7.98-7.95\) (m, 2H) 7.46-7.43 (m, 3H), 6.48 (s, 2H), 3.70 (s, 3H), 2.28 (s, 6H), 2.27 (s, 3H) ppm.

**13C-NMR (75 MHz, CDCl3):** \(\delta = 164.6, 150.2, 140.4, 133.1, 130.6, 128.5, 128.4, 127.3, 119.8, 59.9, 17.5, 16.2\) ppm.

**IR (neat):** \(\nu_{\text{max}}\) (cm\(^{-1}\)) = 2945 (m), 2822 (w), 1686 (w), 1629 (s), 1471 (m), 1448 (s), 1278 (m), 1213 (s), 1007 (s), 874 (m), 766 (s), 692 (s).

**MS (70 eV, EI):** \(m/z\) (%) = 253 (M\(^+\), 32), 238 (100), 223 (2), 194 (2), 91 (10).

**HRMS (EI):** \(m/z\) calcd. for: \([\text{C}_{17}\text{H}_{19}\text{NO}]\) 253.1467, found: 253.1462.

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\[N-\text{(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methyl)phenylethylideneamine (56b)}\]

Prepared according to TP7 from 4-methyl acetophenone (1.34 g; 1.33 mL, 10.0 mmol,) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 20:1 (2% Et\(_3\)N) ), furnished the desired imine (1.85 g, 6.9 mmol, 69 %) as a yellow oil.

**1H-NMR (300 MHz, C\(_6\)D\(_6\)):** \(\delta = 8.02-7.99\) (m, 2H), 7.07-7.04 (m, 2H), 6.51 (s, 2H), 3.44 (s, 3H), 2.23 (s, 3H), 2.12 (s, 6H), 1.97 (s, 3H) ppm.

**13C-NMR (75 MHz, C\(_6\)D\(_6\)):** \(\delta = 164.0, 153.4, 148.4, 140.3, 137.6, 131.3, 129.1, 127.6, 119.9, 59.4, 21.2, 16.8, 16.3\) ppm.

**IR (neat):** \(\nu_{\text{max}}\) (cm\(^{-1}\)) = 2921 (br, w), 1631 (m), 1594 (m), 1477 (m), 1364 (m), 1275 (m), 1216 (s), 1182 (m), 1010 (s), 872 (m), 816 (s).

**MS (70 eV, EI):** \(m/z\) (%) = 267 (M\(^+\), 42), 253 (15), 252 (100), 119 (2), 117 (2).

**HRMS (EI):** \(m/z\) calcd. for: \([\text{C}_{18}\text{H}_{21}\text{NO}]\) 267.1623, found: 267.1631.

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\[N-\text{(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methyl)phenylethylideneamine (56c)}\]
Prepared according to TP7 from 3-methyl acetophenone (10.0 mmol, 1.34 g, 1.33 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 40:1 (2% Et₃N) ) afforded the desired imine (1.95 g, 7.29 mmol, 73%) as a yellow oil.

\[ ^1H-NMR \ (300 \text{ MHz, } C_6D_6): \delta = 7.99 (s, 1H), 7.84-7.81 (m, 1H), 7.18-7.16 (m, 1H), 7.07-7.04 (m, 1H), 6.52 (s, 2H), 3.43 (s, 3H), 2.24 (s, 6H), 2.17 (s, 3H), 1.97 (s, 3H) \text{ ppm.} \]

\[ ^{13}C-NMR \ (75 \text{ MHz, } C_6D_6): \delta = 164.3, 153.5, 148.3, 140.2, 137.8, 131.3, 131.2, 128.3, 128.2, 124.9, 119.9, 59.4, 21.4, 16.9, 16.3 \text{ ppm.} \]

IR (neat): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 2922 \text{ (w), } 1631 \text{ (m), } 1477 \text{ (m), } 1282 \text{ (m), } 1217 \text{ (s), } 1010 \text{ (m), } 875 \text{ (m), } 694 \text{ (s).} \)

MS (70 eV, EI): \( m/z \ (% ) = 267 \text{ (M}^+ \text{, 42), } 252 \text{ (100), } 133 \text{ (2), } 118 \text{ (4).} \)

HRMS (EI): \( m/z \text{ calcd. for: } [C_{18}H_{21}NO] 267.1623, \text{ found: } 267.1628. \)

\[ N-(3,5-\text{Dimethyl-4-methoxy})\text{-phenyl-1-(2-methylph enyl) ethylidene amine (56d)}: \]

Prepared according to TP7 from 2-methyl acetophenone (10.0 mmol, 1.34 g, 1.30 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 40:1 (2% Et₃N) ), afforded the desired imine (1.98 g, 7.40 mmol, 74%) as a yellow oil.

\[ ^1H-NMR \ (300 \text{ MHz, } CDCl_3): \delta = 7.33-7.30 \text{ (m, } 1H), 7.12-7.10 \text{ (m, } 2H), 6.87-6.86 \text{ (m, } 1H), 6.55 \text{ (s, } 2H), 3.44 \text{ (s, } 3H), 2.24 \text{ (s, } 6H), 2.06 \text{ (s, } 3H), 1.92 \text{ (s, } 3H) \text{ ppm.} \]

\[ ^{13}C-NMR \ (75 \text{ MHz, } CDCl_3): \delta = 168.1, 153.7, 148.0, 140.1, 135.9, 131.5, 129.6, 128.6, 127.8, 125.8, 119.5, 59.4, 29.2, 20.5, 16.3 \text{ ppm.} \]

IR (neat): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 2925 \text{ (w), } 1641 \text{ (m), } 1479 \text{ (s), } 1217 \text{ (s), } 1009 \text{ (s), } 871 \text{ (m), } 744 \text{ (s).} \)

MS (70 eV, EI): \( m/z \ (% ) = 268 \text{ ([M+H] }^+, 12), 267 \text{ (M}^+, 88), 252 \text{ (100), } 135 \text{ (15), } 130 \text{ (31), } 91 \text{ (56).} \)

HRMS (EI): \( m/z \text{ calcd. for: } [C_{18}H_{21}NO] 267.1623, \text{ found: } 267.1614. \)

\[ N-(3,5-\text{Dimethyl-4-methoxy})\text{-phenyl-1-(4-carbomethoxy)phenylethylideneamine (56e)} \]
Prepared according to TP7 from methyl 4-acetyl-benzoate (10.0 mmol, 1.78 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 40:1 (2% Et₃N)), provided the desired imine (2.33 g, 7.50 mmol, 75%) as a bright yellow solid.

**MP:** 90.0–92.4 °C.

**1H-NMR (300 MHz, C₆D₆):** δ = 8.21-8.19 (m, 2H), 7.97-7.95 (m, 2H), 6.46 (s, 2H), 3.52 (s, 3H), 3.43 (s, 3H), 2.20 (s, 6H), 1.84 (s, 3H) ppm.

**13C-NMR (75 MHz, C₆D₆):** δ = 166.4, 163.6, 153.8, 147.7, 143.8, 132.1, 131.4, 129.8, 127.5, 119.8, 59.4, 51.7, 16.8, 16.3 ppm.

**IR (neat):** ν_{max} (cm⁻¹) = 2955 (w), 1718 (s), 1437 (m), 1272 (s), 1112 (s), 1007 (s), 768 (s), 696 (s) ppm.

**MS (70 eV, EI):** m/z (%) = 311 (M⁺, 56), 296 (100), 132 (11).

**HRMS (EI):** m/z calcd. for: [C₁₉H₂₁NO₃] 311.1521, found: 311.1515.

*N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-trifluoromethyl)phenylethylideneamine (56f)*

Prepared according to TP7 from 4-trifluoromethyl acetophenone (10.0 mmol, 1.88 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by vacuum distillation (160 °C, 0.1 mbar), afforded the desired imine (2.70 g, 8.40 mmol, 84%) as a yellow oil.

**1H-NMR (300 MHz, CDCl₃):** δ = 7.98-7.95 (m, 2H), 7.46-7.43 (m, 2H), 6.48 (s, 2H), 3.70 (s, 3H), 2.28 (s, 6H), 2.27 (s, 3H) ppm.

**13C-NMR (75 MHz, CDCl₃):** δ = 164.0, 152.3, 146.7, 132.0 (q, J = 16.8 Hz), 131.3, 128.6, 127.5 (q, J = 283.3 Hz), 127.4, 125.2 (q, J = 3.6 Hz), 119.3, 59.9, 17.4, 16.2 ppm.

**IR (neat):** ν_{max} (cm⁻¹) = 2935 (br, w), 1633.2 (m), 1478 (m), 1326 (m), 1220 (s), 1124 (s), 1111 (s), 1011 (s), 843 (s), 605 (m) ppm.

**MS (70 eV, EI):** m/z (%) = 321 (M⁺, 48), 306 (100), 302 (2), 171 (2), 91 (5).

**HRMS (EI):** m/z calcd. for: [C₁₈H₁₈NF₃O] 321.1340, found: 321.1329.

*N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methoxy)phenylethylideneamine (56g)*
Prepared according to TP3 from 4-methoxy acetophenone (10.0 mmol, 1.50 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Recrystallisation from MeOH, afforded the desired imine (1.98 g, 6.99 mmol, 70%) as a yellow solid.

**MP**: 62.3-64.6 °C.

**$^1$H-NMR (400 MHz, C$_6$D$_6$)**: $\delta$ = 7.96-7.92 (m, 2H), 6.96-6.91 (m, 2H), 6.40 (s, 2H), 3.85 (s, 3H), 3.45 (s, 3H), 2.24 (s, 6H), 2.00 (s, 3H) ppm.

**$^{13}$C-NMR (100 MHz, C$_6$D$_6$)**: $\delta$ = 165.9, 160.8, 151.4, 145.6, 133.4, 129.4, 127.8, 120.6, 114.6, 55.9, 55.6, 16.6, 16.2 ppm.

**IR (neat)**: $\nu_{\text{max}}$ (cm$^{-1}$) = 2915 (w), 1631 (s), 1592 (s), 1512 (m), 1365 (m), 1246 (s), 1171 (s), 1026 (s), 827 (s), 688 (s).

**MS (70 eV, EI)**: $m/z$ (%) = 283 (M$^+$, 49), 268 (100), 105 (10).

**HRMS (EI)**: $m/z$ calcd. for: [C$_{18}$H$_{21}$NO$_2$] 283.1572, found: 283.1571.

$N$-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methoxy)phenylethylideneamine (56h)

Prepared according to TP7 from 3-methoxy acetophenone (10.0 mmol, 1.50 g, 1.38 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 20:1 (2% Et$_3$N)), furnished the desired imine (1.98 g, 7.0 mmol, 70%) as a yellow oil.

**$^1$H-NMR (400 MHz, C$_6$D$_6$)**: $\delta$ = 7.59-7.57 (m, 1H), 7.51-7.48 (m, 1H), 7.34 (t, $J$ = 7.9 Hz, 1H), 7.01 (dddd, $J$ = 0.9 Hz, 2.6 Hz, 7.9 Hz, 1H), 6.60 (s, 2H), 3.80 (s, 3H), 3.65 (s, 3H), 2.41 (s, 6H), 2.20 (s, 3H) ppm.

**$^{13}$C-NMR (100 MHz, C$_6$D$_6$)**: $\delta$ = 164.3, 153.5, 148.3, 140.2, 137.8, 131.3, 131.2, 128.3, 128.2, 124.9, 119.9, 60.1, 55.4, 17.2, 16.6 ppm.

**IR (neat)**: $\nu_{\text{max}}$ (cm$^{-1}$) = 3001 (w), 2910 (w), 1631 (s), 1592 (s), 1512 (m), 1365 (m), 1246 (s), 1171 (s), 1026 (s), 827 (s), 688 (s).

**MS (70 eV, EI)**: $m/z$ (%) = 283 (M$^+$, 59), 268 (100), 105 (11).

**HRMS (EI)**: $m/z$ calcd. for: [C$_{18}$H$_{21}$NO$_2$] 283.1572, found: 283.1584.

$N$-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propylidene amine (56i)

Prepared according to TP7 from 3-methoxy acetophenone (10.0 mmol, 1.50 g, 1.38 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 20:1 (2% Et$_3$N)), furnished the desired imine (1.98 g, 7.0 mmol, 70%) as a yellow oil.

**$^1$H-NMR (400 MHz, C$_6$D$_6$)**: $\delta$ = 7.59-7.57 (m, 1H), 7.51-7.48 (m, 1H), 7.34 (t, $J$ = 7.9 Hz, 1H), 7.01 (dddd, $J$ = 0.9 Hz, 2.6 Hz, 7.9 Hz, 1H), 6.60 (s, 2H), 3.80 (s, 3H), 3.65 (s, 3H), 2.41 (s, 6H), 2.20 (s, 3H) ppm.

**$^{13}$C-NMR (100 MHz, C$_6$D$_6$)**: $\delta$ = 164.3, 153.5, 148.3, 140.2, 137.8, 131.3, 131.2, 128.3, 128.2, 124.9, 119.9, 60.1, 55.4, 17.2, 16.6 ppm.

**IR (neat)**: $\nu_{\text{max}}$ (cm$^{-1}$) = 3001 (w), 2910 (w), 1631 (s), 1592 (s), 1512 (m), 1365 (m), 1246 (s), 1171 (s), 1026 (s), 827 (s), 688 (s).

**MS (70 eV, EI)**: $m/z$ (%) = 283 (M$^+$, 59), 268 (100), 105 (11).

**HRMS (EI)**: $m/z$ calcd. for: [C$_{18}$H$_{21}$NO$_2$] 283.1572, found: 283.1584.
Prepared according to TP7 from 3-fluoro acetophenone (10.0 mmol, 1.38 g, 1.23 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 40:1 (2% Et3N)), provided the desired imine (2.06 g, 7.59 mmol, 76%) as a yellow oil.

^{1}H-NMR (300 MHz, C$_6$D$_6$): $\delta$ = 7.84-7.79 (m, 1H), 7.65-7.62 (m, 1H), 7.00-6.84 (m, 2H), 6.44 (s, 2H), 3.43 (s, 3H), 2.22 (s, 6H), 1.81 (s, 3H) ppm.

^{13}C-NMR (75 MHz, C$_6$D$_6$): $\delta$ = 163.4 (d, $J$ = 245.0 Hz), 163.0 (d, $J$ = 3.0 Hz), 153.7, 147.6, 142.5 (d, $J$ = 7.5 Hz), 131.4, 129.9 (d, $J$ = 7.7 Hz), 123.1 (d, $J$ = 2.8 Hz), 119.8, 117.1 (d, $J$ = 22.0 Hz), 114.4 (d, $J$ = 23.0 Hz), 59.4, 16.7, 16.3 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2937 (br, w), 1691 (w), 1633 (m), 1585 (m), 1481 (m), 1440 (s), 1266 (s), 1217 (s), 1010 (m), 867 (s), 784 (s), 686 (s).

MS (70 eV, EI): $m/z$ (%) = 271 (M$^+$, 44), 256 (100), 120 (5).

HRMS (EI): $m/z$ calcd. for: [C$_{17}$H$_{18}$NFO] 271.1372, found: 271.1363.

N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-chloro)phenylethylideneamine (56j)

Prepared according to TP7 from 4-chloro acetophenone (10.0 mmol, 1.54 g, 1.29 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 40:1 (2% Et$_3$N)), afforded the desired imine (2.16 g, 7.51 mmol, 75%) as a yellow oil.

^{1}H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.90-7.87 (m, 2H), 7.44-7.37 (m, 2H), 6.40 (s, 2H), 3.70 (s, 2H), 2.27 (s, 6H), 2.20 (s, 3H) ppm.

^{13}C-NMR (75 MHz, CDCl$_3$): $\delta$ = 164.0, 153.1, 146.9, 138.0, 136.4, 131.2, 128.4, 119.4, 59.8, 17.2, 16.1 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2936 (br, w), 1633 (m), 1589 (m), 1477 (m), 1398 (w), 1272 (w), 1219 (s), 1091 (s), 1011 (s), 830 (s), 756 (m).

MS (70 eV, EI): $m/z$ (%) = 287 (M$^+$, 38), 274 (30), 272 (100), 91 (5).

HRMS (EI): $m/z$ calcd. for: [C$_{17}$H$_{18}$N$^{35}$ClO] 287.1077, found: 287.1078.

N-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-chloro)phenylethylideneamine (56k)
Prepared according to TP7 from 3-chloro acetophenone (10.0 mmol, 1.54 g, 1.29 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 40:1 (2% Et₃N)), afforded the desired imine (2.16 g, 7.51 mmol, 75%) as a yellow oil.

\[^1\text{H}-\text{NMR (300 MHz, CDCl}_3\text{):} \delta = 7.90-7.84 (m, 2H), 7.65-7.60 (m, 1H), 7.00-6.88 (m, 1H), 6.40 (s, 2H), 3.48 (s, 3H), 2.22 (s, 6H), 1.80 (s, 3H) \text{ppm.}\]

\[^{13}\text{C}-\text{NMR (75 MHz, CDCl}_3\text{):} \delta = 164.0, 152.8, 146.2, 138.1, 136.0, 130.4, 129.4, 129.0, 128.6, 126.2, 119.4, 59.6, 17.0, 16.1 \text{ppm.}\]

\(\text{IR (neat): } \nu_{\text{max}} (\text{cm}^{-1}) = 2912 \text{ (br, w), 1615 (m), 1509 (s), 1382 (m), 1272 (m), 1206 (m), 1091 (m), 868 (s), 790 (m), 698 (s).}\)

\(\text{MS (70 eV, EI): } m/z \text{ (%) = 287 (M}^+\text{, 30), 274 (55), 272 (100), 91 (15).}\)

\(\text{HRMS (EI): } m/z \text{ calcd. for: } [\text{C}_{17}\text{H}_{18}\text{N}_3\text{ClO}] 287.1077, \text{ found: 287.1066.}\)

N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-phenyl)phenylethylideneamine (56l)

Prepared according to TP7 from 4-phenyl acetophenone (10.0 mmol, 1.96 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Recrystallisation from n-pentane, afforded the desired imine (2.47 g, 7.50 mmol, 75%) as a yellow solid.

\(\text{MP: } 96.3-97.3 ^\circ \text{C}\)

\[^1\text{H}-\text{NMR (400 MHz, C}_6\text{D}_6\text{):} \delta = 8.12-8.09 (m, 2H), 7.55-7.53 (m, 2H), 7.51-7.48 (m, 2H), 7.25-7.18 (m, 3H), 6.55 (s, 2H), 3.45 (s, 3H), 2.26 (s, 6H), 2.00 (s, 3H) \text{ppm.}\]

\(^{13}\text{C}-\text{NMR (100 MHz, C}_6\text{D}_6\text{):} \delta = 163.9, 153.6, 148.2, 143.3, 140.9, 139.0, 131.4, 129.1, 128.1, 127.8, 127.5, 120.0, 59.4, 16.8, 16.4 \text{ppm.}\)

\(\text{IR (neat): } \nu_{\text{max}} (\text{cm}^{-1}) = 2929 \text{ (w), 1623 (m), 1595 (m), 1214 (s), 1066 (s), 870 (s), 765 (s), 693 (s).}\)

\(\text{MS (70 eV, EI): } m/z \text{ (%) = 329 (M}^+\text{, 52), 314 (100), 207 (6), 157 (5).}\)

\(\text{HRMS (EI): } m/z \text{ calcd. for: } [\text{C}_{23}\text{H}_{23}\text{NO}] 329.1780, \text{ found: 329.1765.}\)

N-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-naphthyl)ethylidene amine (56m)
1H-NMR (300 MHz, CDCl3): $\delta = 8.56$ (dd, $J = 1.8$ Hz, 8.8 Hz, 1H) 8.23-8.22 (m, 1H), 7.74-7.62 (m, 3H), 7.37-7.30 (m, 2H), 6.56 (s, 2H), 3.45 (s, 3H), 2.26 (s, 6H), 2.05 (s, 3H) ppm.

1H-NMR (300 MHz, CDCl3): $\delta = 8.13-8.08$ (m, 1H), 7.98-7.69 (m, 2H), 7.39-7.38 (m , 1H), 6.52 (s, 2H), 3.43 (s, 3H), 2.61 (s, 3H), 2.24 (s, 3H), 2.20 (s, 6H) ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2924 (w), 2912 (w), 1611 (m), 1497 (s), 1495 (s), 1388 (s), 1379 (s), 1267 (s), 1199 (s), 1030 (s), 971 (s), 764 (s).

MS (70 eV, EI): $m/z$ (%) = 304 ([M+H]$^+$, 11), 303 (M$^+$, 48), 288 (100), 151 (6).

HRMS (EI): $m/z$ calcd. for: [C$_{21}$H$_{21}$NO] 303.1623, found: 303.1622.

N-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro) naphthylidene amine (56o)

Prepared according to TP7 from 1,3-diacetyl benzene (10.0 mmol, 1.62 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 20:1 (2% Et$_3$N) ), furnished the desired imine (2.07 g, 7.0 mmol 70%) as a yellow oil.

1H-NMR (300 MHz, CDCl3): $\delta = 8.13-8.08$ (m, 1H), 7.98-7.69 (m, 2H), 7.39-7.38 (m, 1H), 6.52 (s, 2H), 3.43 (s, 3H), 2.61 (s, 3H), 2.24 (s, 3H), 2.20 (s, 6H) ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2924 (w), 1611 (m), 1497 (s), 1495 (s), 1388 (s), 1379 (s), 1267 (s), 1199 (s), 1030 (s), 971 (s), 764 (s).

MS (70 eV, EI): $m/z$ (%) = 305 (M$^+$, 78), 290 (100), 263 (29), 136 (30).

HRMS (EI): $m/z$ calcd. for: [C$_{19}$H$_{21}$NO$_2$] 295.1572, found: 295.1577.
Prepared according to TP7 from α-tetralone (10.0 mmol, 1.46 g, 1.33 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Recrystallisation from n-pentane:EtOAc, afforded the desired imine (1.79 g, 6.41 mmol, 64%) as a brown solid.

**MP:** 85.3-86.4 °C.

**1H-NMR (300 MHz, CDCl3):** δ = 8.32-8.29 (m, 1H), 7.35 (ddd, J = 7.5 Hz, 1.7 Hz, 1H), 7.30-7.27 (m, 1H), 7.20-7.16 (m, 1H), 6.46 (s, 2H), 3.70 (s, 3H), 2.89 (t, J = 6.2 Hz, 2 H), 2.58-2.54 (m, 2H), 2.27 (s, 6H), 1.93-1.87 (m, 2H) ppm.

**13C-NMR (75 MHz, CDCl3):** δ = 165.8, 153.0, 141.3, 133.8, 133.4, 131.2, 130.7, 128.7, 126.4, 119.7, 59.8, 30.0, 29.9, 23.0, 16.2 ppm.

**IR (neat):** νmax (cm⁻¹) = 2927 (m), 1625 (s), 1596 (m), 1453 (m), 1219 (s), 1004 (s), 872 (s), 766 (s).

**MS (70 eV, EI):** m/z (%) = 279 (M⁺, 48), 264 (100), 129 (8).

**HRMS (EI):** m/z calcd. for: [C₁₉H₂₁NO] 279.1623, found: 279.1634.

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N-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro) naphthylidene amine (56p)

Prepared according to TP7 from α-indanone (10.0 mmol, 1.38 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 20:1 (2% Et₃N)), furnished the desired imine (1.86 g, 7.00 mmol 70%) as a dark brown oil.

**1H-NMR (300 MHz, CDCl3):** δ = 8.28-8.19 (m, 1H), 7.35 (ddd, J = 7.4 Hz, 1.6 Hz, 1H), 7.28-7.25 (m, 1H), 7.11-7.10 (m, 1H), 6.42 (s, 2H), 3.68 (s, 3H), 2.89 (t, J = 6.2 Hz, 2H), 2.56 (t, J = 6.7 Hz, 2H), 2.24 (s, 6H), 1.93-1.87 (m, 2H) ppm.

**13C-NMR (75 MHz, CDCl3):** δ = 164.2, 152.0, 141.3, 133.2, 133.0, 131.4, 130.8, 128.2, 125.9, 120.0, 59.6, 30.6, 29.4, 16.2 ppm.

**IR (neat):** νmax (cm⁻¹) = 2907 (m), 1600 (s), 1575 (s), 1386 (m), 1112 (m), 1005 (m), 985 (m), 862 (s).

**MS (70 eV, EI):** m/z (%) = 265 (M⁺, 18), 250 (100), 129 (12), 116 (72).

**HRMS (EI):** m/z calcd. for: [C₁₉H₁₉NO] 265.1467, found: 265.1488.

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N-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propylidene amine (56q)
Prepared according to TP7 from propiophenone (10.0 mmol, 1.34 g, 1.34 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 80:1 (2% Et$_3$N) ), afforded the desired imine in (2.09 g, 7.81 mmol, 78%) as a yellow oil.

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 8.02-8.00$ (m, 2H), 7.24-7.19 (m, 3H), 6.53 (s, 2H), 3.43 (s, 3H), 2.52 (q, $J = 7.7$ Hz, 2H), 2.23 (s, 6H), 0.89 (t, $J = 7.7$ Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 169.4$, 153.4, 148.2, 138.6, 131.4, 130.2, 128.6, 128.0, 119.4, 59.4, 23.0, 16.4, 13.1 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2980 (w), 1705 (m), 1600 (s), 1220 (m), 1110 (m), 795 (m), 699 (m).

MS (70 eV, EI): m/z (%) = 267 (M$^+$, 75), 252 (100), 238 (99), 111 (20), 91 (29).

HRMS (EI): m/z calcd. for: [C$_{18}$H$_{21}$NO] 267.1623, found: 267.1629.

$N$-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl hexylidene amine (56r)

Prepared according to TP7 from n-hexanophenone (10.0 mmol, 1.76 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 100:1 (2% Et$_3$N) ), afforded the desired imine (2.23 g, 7.21 mmol, 72%) as a yellow oil.

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.27-7.25$ (m, 2H), 7.19-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.66 (s, 2H), 3.37 (s, 3H), 2.42-2.38 (m, 2H), 2.17 (s, 6H), 1.59-1.57 (m, 2H), 1.20-1.17 (m, 4H), 0.85 (t, $J = 7.7$ Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 169.5$, 153.6, 149.5, 144.0, 131.1, 128.7, 127.2, 126.7, 116.2, 59.5, 39.3, 32.1, 28.6, 22.9, 16.7, 15.3 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2990 (w), 1745 (m), 1600 (s), 1225 (m), 1010 (m), 699 (m).

MS (70 eV, EI): m/z (%) = 309 (M$^+$, 40), 294 (18), 253 (99), 238 (100), 151 (30).

HRMS (EI): m/z calcd. for: [C$_{21}$H$_{27}$NO] 309.2093, found: 309.2094.

$N$-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl hexylidene amine (56s)
Prepared according to TP7 from 1,3-diphenylpropiophenone (10.0 mmol, 2.54 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 100:1 (2% Et₃N)), afforded the desired imine (2.11 g, 7.41 mmol, 74%) as a yellow oil.

**1H-NMR (400 MHz, C₆D₆):** δ = 7.28-7.15 (m, 6H), 7.10-6.90 (m, 4H), 6.50 (s, 2H), 3.41 (s, 3H), 2.62-2.58 (m, 2H), 2.31-2.29 (m, 2H), 2.20 (s, 6H) ppm.

**13C-NMR (100 MHz, C₆D₆):** δ = 168.5, 164.4, 148.5, 144.0, 132.0, 131.1, 129.8, 129.4, 129.3, 128.6, 127.2, 126.7, 116.2, 59.5, 27.6, 22.9, 16.7 ppm.

**IR (neat):** νmax (cm⁻¹) = 2982 (w), 1815 (m), 1643 (s), 1460 (m), 1225 (m), 1125 (m), 814 (m), 765 (m), 699 (m).

**MS (70 eV, EI):** m/z (%) = 343 (M⁺, 20), 267 (40), 253 (19), 238 (100), 151 (10).

**HRMS (EI):** m/z calcd. for: [C₂₄H₂₅NO] 343.1936, found: 343.1954.

5-[(N-(3,5-Dimethyl-4-methoxy)phenyl)imino]-1,5-diphenylpentan-1-one (56t)

Prepared according to TP7 from 1,5-diphenyl-1,5-pentanediione (10.0 mmol, 2.52 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 4:1 (2% Et₃N)), provided the desired imine (2.70 g, 7.0 mmol, 70%) as a dark brown oil.

**1H-NMR (400 MHz, C₆D₆):** δ = 7.76-7.74 (m, 2H), 7.22-6.99 (m, 8H), 6.82 (s, 2H), 3.32 (s, 3H), 3.09-3.04 (m, 2H), 2.11 (s, 6H), 1.82-1.75 (m, 2H), 1.60-1.53 (m, 2H) ppm.

**13C-NMR (100 MHz, C₆D₆):** δ = 198.7, 161.7, 153.8, 149.5, 144.0, 137.5, 134.4, 132.7, 131.1, 130.7, 128.8, 128.2, 127.0, 114.0, 59.5, 38.6, 34.6, 23.8, 16.5 ppm.

**IR (neat):** νmax (cm⁻¹) = 3360 (m), 2949 (w), 1700 (m), 1680 (s), 1635 (m), 1189 (s), 1100 (s), 760 (s), 685 (s).

**MS (70 eV, EI):** m/z (%) = 385 (M⁺, 42), 280 (45), 266 (80), 253 (88), 238 (100).

**HRMS (EI):** m/z calcd. for: [C₂₆H₂₇NO₂] 385.2042, found: 385.2038.

Methyl 4-[(N-(3,5-dimethyl-4-methoxyphenyl)]imino]-4-phenylbutanoate (56u)
Prepared according to TP7 from methyl 3-benzoylpropionate (10.0 mmol, 1.92 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 5:1 (2% Et3N)), provided the desired imine (2.24 g, 6.89 mmol, 69%) as a dark brown oil.

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.19-7.17$ (m, 2H), 7.10-7.00 (m, 3H), 6.50 (s, 2H), 3.39 (s, 3H), 3.28 (s, 3H), $J = 6.4$ Hz, 2H), 2.52 (t, $J = 6.4$ Hz, 2H), 2.31-2.29 (m, 2H), 2.20 (s, 6H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 172.8$, 166.8, 153.6, 147.7, 138.3, 130.4, 128.7, 128.2, 127.9, 119.3, 59.4, 51.2, 33.4, 32.3, 16.3 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2950 (w), 1735 (s), 1686 (s), 1219 (s), 1165 (s), 1009 (m), 758 (s), 690 (s).

MS (70 eV, EI): $m/z$ (%) = 325 (M$^+$, 99), 310 (43), 266 (28), 250 (45), 238 (100).

HRMS (EI): $m/z$ calcd. for: [C$_{20}$H$_{23}$NO] 325.1678, found: 325.1662.

Methyl 5-[(N-(3,5-dimethyl-4-methoxyphenyl))imino]-5-phenylpentanoate (56v)

Prepared according to TP7 from methyl 4-benzoylbutanoate (10.0 mmol, 2.06 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; n-pentane:diethyl ether 5:1 (2% Et$_3$N)), provided the desired imine (2.37 g, 6.99 mmol, 70%) as a dark brown oil.

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.80-7.77$ (m, 2H), 7.13-7.03 (m, 3H), 6.90 (s, 2H), 3.32 (s, 3H), 3.28 (s, 3H), $J = 6.4$ Hz, 2H), 2.55 (t, $J = 6.4$ Hz, 2H), 2.23 (s, 6H), 2.17-2.13 (m, 2H), 2.00-1.94 (m, 2H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 173.1$, 167.0, 153.0, 145.9, 137.4, 132.7, 130.0, 128.5, 127.8, 120.2, 59.7, 50.9, 33.4, 33.0, 19.5, 18.6 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2945 (w), 1700 (s), 1686 (s), 1189 (s), 1165 (s), 798 (s), 650 (s).

MS (70 eV, EI): $m/z$ (%) = 339 (M$^+$, 60), 324 (25), 308 (27), 266 (65), 253 (55), 238 (100).

HRMS (EI): $m/z$ calcd. for: [C$_{21}$H$_{25}$NO$_3$] 339.1834, found: 339.1845.

N-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylideneamine (56W)
Prepared according to TP7 from 3,4-dichlorocetophenone (10.0 mmol, 1.89 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by recrystallisation from methanol provided the desired imine (2.29 g, 7.11 mmol, 71%) as a yellow oil.

$^1$H-NMR (400 MHz, $\text{C}_6\text{D}_6$): $\delta = 8.24$ (d, $J = 2.8$ Hz, 1H), 7.94 (dd, $J = 8.4$ Hz, 2.1 Hz, 1H), 7.09-7.01 (m, 1H), 6.60 (s, 2H), 3.51 (s, 3H), 2.27 (s, 6H), 2.05 (s, 3H) ppm.

$^{13}$C-NMR (100 MHz, $\text{C}_6\text{D}_6$): $\delta = 164.0, 148.5, 146.2, 140.1, 138.5, 135.2, 134.4, 128.3, 121.0, 120.1, 111.2, 59.4, 17.0, 16.7$ ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2925 (w), 1620 (w), 1562 (m), 1418 (s), 1366 (s), 1299 (m), 1007 (m), 808 (s), 712 (s).

MS (70 eV, EI): $m/z$ (%) = 321 (M$^+$, 25), 307 (10), 306 (100), 171 (27).

HRMS (EI): $m/z$ calcd. for: [C$_{17}$H$_{17}$ClNO] 321.0687, found: 313.1665.

$N$-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylideneamine (56x)

Prepared according to TP7 from 3,4-dimethoxyacetophenone (10.0 mmol, 1.80 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by recrystallisation from methanol provided the desired imine (2.23 g, 7.22 mmol, 72%) as a white solid.

MP: 115.9-117.1 $^\circ$C

$^1$H-NMR (400 MHz, $\text{C}_6\text{D}_6$): $\delta = 8.05$ (d, $J = 2.1$ Hz, 1H), 7.40 (dd, $J = 8.3$ Hz, 2.1 Hz, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.58 (s, 2H), 3.49 (s, 3H), 3.43 (s, 3H), 3.40 (s, 3H), 2.25 (s, 6H), 2.05 (s, 3H) ppm.

$^{13}$C-NMR (100 MHz, $\text{C}_6\text{D}_6$): $\delta = 163.5, 157.5, 152.3, 150.1, 148.5, 133.1, 131.4, 128.3, 121.0, 120.1, 110.8, 59.4, 55.44, 55.41, 16.7, 16.4$ ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2935 (w), 2959 (w), 1620 (w), 1594 (m), 1583 (s), 1510 (s), 1452 (m), 1414 (s), 1267 (s), 1217 (s), 1153 (s), 1018 (s), 867 (s), 765 (m).

MS (70 eV, EI): $m/z$ (%) = 314 ([M+H]$^+$, 12), 339 (M$^+$, 55), 299 (18), 298 (100), 268 (6).

HRMS (EI): $m/z$ calcd. for: [C$_{19}$H$_{23}$NO$_3$] 313.1678, found: 313.1665.

$N$-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylideneamine (56y)
Prepared according to **TP7** from 3,4-dimethylacetophenone (10.0 mmol, 1.48 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethylether 60:1 (2% Et₃N)), provided the desired imine (1.83 g, 6.50 mmol, 65%) as a yellow oil.

\[ ^1 \text{H-NMR (400 MHz, C}_6\text{D}_6\]): \delta = 7.38-7.22 (m, 2H), 6.91-6.82 (m, 1H), 6.61 (s, 2H), 3.40 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.25 (s, 6H), 2.05 (s, 3H) ppm.

\[ ^{13} \text{C-NMR (100 MHz, C}_6\text{D}_6\]): \delta = 163.0, 158.5, 150.3, 149.2, 148.5, 132.8, 131.9, 128.3, 121.0, 120.2, 111.2, 59.4, 17.4, 17.2, 16.7, 16.4 ppm.

\[ \text{IR (neat): } \nu_{\text{max}} (\text{cm}^{-1}) = 2912 (\text{w}), 1645 (\text{w}), 1600 (\text{m}), 1485 (\text{m}), 132.8, 131.9, 128.3, 121.0, 120.2, 111.2, 59.4, 17.4, 17.2, 16.7, 16.4 \text{ ppm}.\]

\[ \text{MS (70 eV, EI): } m/z (%) = 281 (M^+, 65), 266 (100), 265 (10), 151 (16), 146 (70).\]

\[ \text{HRMS (EI): } m/z \text{ calcd. for: } [\text{C}_{19}\text{H}_{23}\text{NO}] 281.1780, \text{ found: 281.1781.}\]

7. Asymmetric Hydrogenation of Imines

\((R)-\text{N-phenyl-1-phenyl ethyl amine (51a)}^{132}\)

Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50a** (98 mg; 0.50 mmol) and obtained as a yellow oil (95 mg, 0.48 mmol, 96%).

[\(\alpha\)]\(_D\)\(^{20} = -3.9 \) (c = 1.0, CHCl₃)

\[ ^1 \text{H-NMR (300 MHz, CDCl}_3\]): \delta = 7.36 (d, \( J = 7.4 \text{ Hz}, 2\text{H} \)), 7.33 (t, \( J = 8.1 \text{ Hz}, 2\text{H} \)), 7.22 (t, \( J = 7.4 \text{ Hz}, 1\text{H} \)), 7.06 (dd, \( J = 8.9 \text{ Hz}, 7.4 \text{ Hz}, 2\text{H} \)), 6.65 (t, \( J = 7.4 \text{ Hz}, 1\text{H} \)), 6.50 (d, \( J = 7.9 \text{ Hz}, 2\text{H} \)), 4.48 (q, \( J = 6.9 \text{ Hz}, 1\text{H} \)), 3.95 (br, NH), 1.50 (d, \( J = 7.1 \text{ Hz}, 3\text{H} \)) ppm.

The enantiomer ratio was determined by Chiral GC DEX-CB Column (100 °C (5 min), 5 °C/min 160 °C (50 min)); \( t_1 = 20.9 \text{ min} \) [minor], \( t_2 = 21.1 \text{ min} \) [major]; 84% ee.

\((R)-\text{N-(4-methoxy)phenyl-1-phenyl ethylidene amine (51b)}^{3}\)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50a (113 mg; 0.50 mmol) and obtained as a yellow oil (108 mg, 0.47 mmol, 95%).

\[ [\alpha]_D^{20} = +1.3 \text{ (c = 1.0, CHCl}_3\text{)} \]

$^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta$ = 7.21-7.10 (m, 4H), 7.05-7.00 (m, 1H), 6.69-6.64 (m, 2H), 6.73-6.72 (m, 2H), 4.17 (q, $J$ = 6.6 Hz, 1H), 3.54 (s, 3H), 3.31 (br, 1H, -NH), 1.13 (d, $J$ = 6.85 Hz, 3H) ppm.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 ml/min, heptane/iPrOH: 90/10, $\lambda$ = 215 nm, 25 °C); $t_r$ = 14.9 min [major], $t_r$ = 16.2 min [minor]; 88% ee.

$N$-(4-methyl)phenyl-1-phenyl ethyl amine (51c)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50c (105 mg; 0.50 mmol) and obtained as a yellow oil (100 mg, 0.48 mmol, 95%).

\[ [\alpha]_D^{20} = +48.2 \text{ (c = 1.0, CHCl}_3\text{)} \]

$^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta$ = 7.35-7.30 (m, 2H), 7.25-7.20 (m, 3H), 6.88 (d, $J$ = 8.0 Hz, 2H), 6.45 (d, $J$ = 8.0 Hz, 2H), 4.42 (q, $J$ = 6.7 Hz, 1H), 3.52 (br, NH), 2.20 (s, 3H), 1.52 (d, $J$ = 6.8 Hz, 3H) ppm.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 ml/min, heptane/iPrOH: 90/10, $\lambda$ = 215 nm, 25 °C); $t_r$ = 13.0 min [major], $t_r$ = 14.5 min [minor]; 85% ee.

$N$-(3,4,-Dioxymethylene)phenyl-1-phenyl ethyl amine (51d)

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Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50d (120 mg; 0.50 mmol) and obtained as a pale white solid. (111 mg, 0.46 mmol, 92%)

**MP:** 104.2-106.1 °C.

$[\alpha]_D^{20} = -11.4$ (c = 0.6, CH$_2$Cl$_2$)

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.34-7.12 (m, 5H), 6.50 (d, $J$ = 8.4 Hz, 1H), 6.10 (d, $J$ = 2.1 Hz, 1H), 5.91 (dd, $J$ = 2.1 Hz, 8.2 Hz, 1H), 5.72 (s, 2H), 4.31 (q, $J$ = 6.6 Hz, 1H), 1.43 (d, $J$ = 6.8 Hz, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 147.8, 144.2, 141.7, 139.6, 128.3, 126.7, 125.6, 108.1, 105.6, 100.2, 96.6, 54.6, 24.3 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3421 (m), 2956 (w), 1638 (w), 1519 (m), 1481 (s), 1352 (m), 1292 (m), 1204 (s), 1036 (s), 789 (m), 696 (s).

MS (70 eV, EI): $m/z$ (%) = 241 (M$^+$, 92), 226 (72), 137 (100), 105 (86), 79 (17).

HRMS (EI): $m/z$ calcd. for: [C$_{15}$H$_{15}$NO$_2$] 241.1103, found: 241.1084.

The enantiomer ratio was determined by Chiral GC DEX-CB Column (160 °C, const; 100 min); $t_r$ = 40.2 min [minor], $t_r$ = 41.0 min [major]; 90% ee.

$N$-(3,4,5-trimethoxy)phenyl-1-phenyl ethyl amine (51e)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50e (143 mg; 0.50 mmol) and obtained as a viscous oil. (135 mg, 0.47 mmol, 94%)

$[\alpha]_D^{20} = -30.2$ (c = 0.50, CH$_2$Cl$_2$)

$^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta$ = 7.18-7.17 (m, 1H), 7.11-7.10 (m, 3H), 7.02-6.98 (m, 1H), 5.64 (s, 2H), 4.18 (q, $J$ = 6.8 Hz, 1H), 3.75 (s, 3H), 3.47 (br, 1H, NH), 3.36 (s, 6H), 1.16 (d, $J$ = 6.7 Hz, 3H) ppm.

$^{13}$C-NMR (75 MHz, C$_6$D$_6$): $\delta$ = 154.7, 146.0, 144.2, 131.7, 128.8, 127.1, 126.1, 92.5, 60.7, 55.8, 54.1, 24.9 ppm.

IR (neat): $v_{\text{max}}$ (cm$^{-1}$) = 3376 (br, w), 2933 (w), 1609 (m), 1507 (m), 1420 (m), 1231 (s), 1117 (s), 1005 (m), 764 (m), 700 (s).

MS (70 eV, EI): $m/z$ (%) = 287 (M$^+$, 84), 272 (72), 182 (21), 168 (97), 105 (100).

HRMS (EI): $m/z$ calcd. for: [C$_{17}$H$_{21}$NO$_3$] 287.1521, found: 287.1498.

The enantiomer ratio was determined by HPLC using Chiralcel OJ column (flow rate 1.0 mL/min, heptane/iPrOH: 85/15, $\lambda$= 215 nm, 25 °C); $t_r$ = 44.2 min [major], $t_r$ = 55.2 min [minor]; 89% ee.

$N$-(3,4,-Dimethyl)phenyl-1-phenyl ethyl amine (51f)
Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50f (112 mg; 0.50 mmol) and obtained as a yellow oil (108 mg, 0.48 mmol, 92%) 

\[ \alpha \]_D^{20} = -20.9 (c = 1.0, CH2Cl2)  
^1\text{H}-\text{NMR} (400 MHz, \text{C}_6\text{D}_6): \delta = 7.17-7.16 (m, 1H), 7.10-7.06 (m, 3H), 7.00-6.96 (m, 1H), 6.80 (d, \text{J} = 8.8 Hz, 1H), 6.24-6.21 (m, 2H), 4.23 (q, \text{J} = 6.8 Hz, 1H), 3.40 (br, 1H, NH), 1.97 (s, 3H), 1.96 (s, 3H), 1.12 (d, \text{J} = 6.6 Hz, 3H) ppm.  
^13\text{C}-\text{NMR} (100 MHz, \text{C}_6\text{D}_6): \delta = 145.9, 145.8, 136.7, 130.3, 128.6, 126.8, 126.0, 124.9, 115.6, 112.3, 53.5, 18.7, 24.8, 20.0 ppm.

IR (neat): \( \nu_{\text{max}} \) (cm\(^{-1}\)) = 3406 (br, w), 2964 (m), 2920 (m), 1617 (s), 1500 (s), 1447 (m), 1317 (m), 801 (m), 698 (s). 

MS (70 eV, EI): m/z (%) = 225 (M⁺, 51), 210 (100), 121 (32), 120 (10), 106 (13), 105 (46). 
HRMS (EI): m/z calcd. for: [C\text{16}H\text{19}N] 225.1517, found: 225.1510. 

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, \( \lambda = 215 \) nm, 25 °C); \( t_r \) = 14.4 min [minor], \( t_r \) = 17.5 min [major]; 90% ee.

N-(3,4-Dimethoxy)phenyl-1-phenyl ethyl amine (51g)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50g (128 mg; 0.50 mmol) and obtained as a yellow oil (122 mg, 0.47 mmol, 95%) 

\[ \alpha \]_D^{20} = -34.2 (c = 0.55, CH2Cl2)  
^1\text{H}-\text{NMR} (400 MHz, \text{C}_6\text{D}_6): \delta = 7.19-7.18 (m, 1H), 7.12-7.08 (m, 3H), 7.02-6.98 (m, 1H), 6.52 (d, \text{J} = 8.7 Hz, 1H), 5.97 (d, \text{J} = 2.7 Hz, 1H), 5.93 (dd, \text{J} = 2.7 Hz, 8.6 Hz, 1H), 4.20 (br, 1H, NH), 4.17 (q, \text{J} = 6.6 Hz, 1H), 3.40 (s, 3H), 3.36 (s, 3H), 1.14 (d, \text{J} = 6.8 Hz, 3H) ppm.  
^13\text{C}-\text{NMR} (100 MHz, \text{C}_6\text{D}_6): \delta = 151.2, 146.0, 142.8, 142.5, 128.7, 126.9, 126.0, 115.3, 104.9, 100.6, 57.0, 55.4, 54.1, 24.9 ppm. 

IR (neat): \( \nu_{\text{max}} \) (cm\(^{-1}\)) = 3384 (m), 2961 (m), 2829 (m), 1617 (s), 1511 (s), 1448 (m), 1223 (s), 1165 (s), 1023 (m), 760 (m). 

MS (70 eV, EI): m/z (%) = 257 (M⁺, 100), 242 (73), 153 (20), 138 (43), 105 (54). 
HRMS (EI): m/z calcd. for: [C\text{16}H\text{19}NO\text{2}] 257.1416, found: 257.1415. 

The enantiomer ratio was determined by HPLC using Chiralcel OJ column (flow rate 1.0 mL/min, heptane/iPrOH: 85/15, \( \lambda = 215 \) nm, 25 °C); \( t_r \) = 34.5 min [minor], \( t_r \) = 39.5 min [major]; 81% ee.
N-(2,4-Dimethyl)phenyl-1-phenyl ethyl amine (51h)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50h (112 mg; 0.50 mmol) and obtained as a yellow oil (95 mg, 0.42 mmol, 84%)

$[\alpha]_D^{20} = -10.1$ (c = 0.40, CH$_2$Cl$_2$)

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.22$-7.18 (m, 2H), 7.16-7.06 (m, 3H), 6.45 (s, 2H), 6.16 (s, 1H), 4.17 (q, $J = 7.0$ Hz, 1H), 3.87 (brs, NH, 1H), 1.98 (s, 3H), 1.96 (s, 3H), 1.14 (d, $J = 7.0$ Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 145.4$, 142.6, 131.2, 129.5, 129.2, 128.5, 127.6, 126.4, 121.2, 54.5, 25.6, 24.9, 16.4 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3362 (m), 2928 (m), 1624 (m), 1500 (s), 1464 (m), 1165 (s), 1082 (m), 760 (m), 673 (s).

MS (70 eV, EI): $m/z$ (%) = 225 (M$^+$, 22), 210 (100), 121 (12), 105 (64).

HRMS (EI): $m/z$ calcd. for: [C$_{16}$H$_{19}$N] 225.1517, found: 225.1520.

The enantiomer ratio was determined by HPLC using Chiralcel OJ column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda = 215$ nm, 25 °C); $t_{\text{r}}$ = 10.3 min [minor], $t_{\text{r}}$ = 16.3 min [major]; 83% ee.

(R)-N-(2-Methoxy)phenyl-1-phenyl ethyl amine (51i)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 50i (114 mg; 0.50 mmol) and obtained as a yellow oil (57 mg, 0.25 mmol, 50%)

$[\alpha]_D^{20} = +4.2$ (c = 0.20, CH$_2$Cl$_2$)

$^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta = 7.37$ (d, $J = 7.7$ Hz, 2H), 7.30 (d, $J = 7.4$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 6.77 (d, $J = 7.9$ Hz, 1H), 6.65 (t, $J = 7.9$ Hz, 1H), 6.60 (t, $J = 7.8$ Hz, 1H), 6.35 (d, $J = 7.9$ Hz, 1H), 4.60 (brs, NH, 1H), 4.47 (q, $J = 6.7$ Hz, 1H), 3.88 (s, 3H), 1.57 (s, 3H) ppm.

The enantiomer ratio was determined by GC using Chiralsil DEX-CB column (100 °C (7 min) 5 °C/min 160 °C (60 min), const.); $t_{\text{r}}$ = 14.9 min [major], $t_{\text{r}}$ = 16.2 min [minor]; 54% ee.

(R)-N-(3,5-Dimethyl)phenyl-1-phenyl ethyl amine (53a)


Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52a (112 mg; 0.50 mmol) and obtained as a pale yellow oil (106 mg, 0.47 mmol, 94%).

\[ \alpha \]_D^20 = -12.8 (c = 0.5, CH_2Cl_2)

^1^H-NMR (300 MHz, C_6D_6): \( \delta = 7.25-7.23 \text{ (m, 2H)}, 7.18-7.13 \text{ (m, 2H)}, 7.08-7.06 \text{ (m, 1H)}, 6.37 \text{ (s, 1H)}, 6.16 \text{ (s, 2H)}, 4.32 \text{ (q, } J = 7.0 \text{ Hz, 1H)}, 3.71 \text{ (br, 1H, NH)}, 2.13 \text{ (s, 6H)}, 1.21 \text{ (d, } J = 7.1 \text{ Hz, 3H) ppm.}

^1^C-NMR (75 MHz, C_6D_6): \( \delta = 147.6, 145.8, 138.5, 128.8, 127.0, 126.1, 120.0, 112.0, 53.5, 24.8, 21.6 \text{ ppm.}

IR (neat): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 3406 \text{ (br, w)}, 2914 \text{ (w)}, 1597 \text{ (s)}, 1512 \text{ (m)}, 1336 \text{ (m)}, 1184 \text{ (m)}, 822 \text{ (m)}, 696 \text{ (m).}

MS (70 eV, EI): \( m/z \) (%) = 225 (M^+, 39), 210 (100), 121 (34), 120 (10), 105 (42).

HRMS (EI): \( m/z \) calcd. for: [C_{16}H_{19}N] 225.1517, found: 225.1511.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, \( \lambda = 215 \text{ nm, 25 °C); } t_r = 9.7 \text{ min [minor], } t_r = 11.0 \text{ min [major]; 94% ee.}

\((R)-N-(3,5,-Dimethyl)phenyl-1(4-methoxyphenyl)ethyl amine (53b)\)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52b (120 mg; 0.50 mmol) and obtained as a yellow oil (112 mg, 0.47 mmol, 94%).

\[ \alpha \]_D^20 = +10.8 (c = 0.5, CH_2Cl_2)

^1^H-NMR (300 MHz, C_6D_6): \( \delta = 7.29-7.23 \text{ (m, 2H)}, 6.91-6.85 \text{ (m, 2H)}, 6.47 \text{ (s, 1H)}, 6.28 \text{ (s, 2H)}, 4.90-4.40 \text{ (m, 1H)}, 3.63 \text{ (brs, 1H)}, 3.40 \text{ (s, 3H)}, 2.25 \text{ (s, 6H)}, 1.33 \text{ (d, } J = 6.6 \text{ Hz, 3H) ppm.}

^1^C-NMR (75 MHz, C_6D_6): \( \delta = 157.7, 146.6, 137.1, 136.5, 125.8, 118.4, 112.9, 110.6, 53.3, 51.5, 23.6, 20.3 \text{ ppm.}

IR (neat): \( \nu_{\text{max}} \text{ (cm}^{-1}) = 3390 \text{ (m)}, 2961 \text{ (w)}, 1602 \text{ (s)}, 1507 \text{ (s)}, 1341 \text{ 8s), 1029 \text{ (s)}, 825 \text{ (s).}

MS (70 eV, EI): \( m/z \) (%) = 255 (M^+, 16), 135 (100), 121 (11), 105 (8).

HRMS (EI): \( m/z \) calcd. for: [C_{17}H_{21}NO] 255.1618, found: 255.1609.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ = 215 nm, 25 °C); t_r = 13.9 min [minor], t_r = 15.7 min [major]; 94% ee.

\((R)-N-(3,5,-Dimethyl)phenyl-1(4-methylphenyl)ethyl amine (53c)\)

![Chemical structure of (R)-N-(3,5,-Dimethyl)phenyl-1(4-methylphenyl)ethyl amine (53c)]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52c (119 mg; 0.50 mmol) and obtained as a yellow oil (115 mg, 0.48 mmol, 96%).

\([\alpha]_D^{20} = +12.3 \, (c = 0.6, \text{CH}_2\text{Cl}_2)\)

\(^1\text{H}-\text{NMR (300 MHz, C}_6\text{D}_6\): \(\delta = 7.13 \, (d, J = 8.0 \, Hz, 2H), 6.95 \, (d, J = 7.7 \, Hz, 2H), 6.33 \, (s, 1H), 6.13 \, (s, 2H), 4.31 \, (q, J = 6.2 \, Hz, 1H), 3.50 \, (brs, 1H), 2.10 \, (s, 6H), 2.06 \, (s, 3H), 1.24 \, (d, J = 6.9 \, Hz, 3H) \, ppm.}

\(^{13}\text{C}-\text{NMR (75 MHz, C}_6\text{D}_6\): \(\delta = 147.8, 142.9, 138.3, 136.1, 129.4, 126.0, 119.6, 111.8, 53.1, 24.8, 21.5, 20.9 \, ppm.}

IR (neat): \(\nu_{\text{max}} \, (\text{cm}^{-1}) = 3395 \, (\text{br, w}), 2920 \, (\text{br, w}), 1597 \, (s), 1507 \, (m), 1473 \, (m), 1336 \, (m), 1184 \, (m), 1109 \, (w), 814 \, (s), 721 \, (w), 690 \, (m).}

MS (70 eV, EI): \(m/z \, (\%) = 239 \, (M^+, 89), 225 \, (14), 224 \, (100), 121 \, (48), 119 \, (72).}

HRMS (EI): \(m/z \, \text{calcd. for: [C}_{17}\text{H}_{21}\text{N}] = 239.1674, \, \text{found: 239.1678.}

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); t_r = 9.2 min [minor], t_r = 10.3 min [major]; 93% ee.

\((R)-N-(3,5,-Dimethyl)phenyl-1(3-methoxyphenyl)ethyl amine (53d)\)

![Chemical structure of (R)-N-(3,5,-Dimethyl)phenyl-1(3-methoxyphenyl)ethyl amine (53d)]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52d (127 mg; 0.50 mmol) and obtained as a pale yellow oil (121 mg, 0.47 mmol, 95%).

\([\alpha]_D^{20} = +10.5 \, (c = 0.5, \text{CH}_2\text{Cl}_2)\)

\(^1\text{H}-\text{NMR (300 MHz, C}_6\text{D}_6\): \(\delta = 7.07 \, (t, J = 8.0 \, Hz, 1H), 6.99-6.97 \, (m, 1H), 6.87-6.85 \, (m, 1H), 6.61 \, (dddt, J = 0.9 \, Hz, 2.7 \, Hz, 8.0 \, Hz, 1H), 6.32 \, (s, 1H), 6.13 \, (s, 2H), 4.33-4.25 \, (m, 1H), 3.50 \, (brs, 1H), 3.30 \, (s, 3H), 2.10 \, (s, 6H), 1.17 \, (d, J = 6.8 \, Hz, 3H) \, ppm.}

\(^{13}\text{C}-\text{NMR (75 MHz, C}_6\text{D}_6\): \(\delta = 160.5, 147.8, 147.7, 138.4, 129.7, 119.7, 118.3, 112.1, 112.0, 111.8, 54.5, 53.4, 24.8, 21.5 \, ppm.}

Experimental Section

IR (neat): \( \nu_{\text{max}} \) (cm\(^{-1}\)) = 3403 (br, w), 2918 (w), 1600 (s), 1335 (m), 1251 (s), 1043 (s), 820 (s), 690 (s).

MS (70 eV, EI): \( m/z \) (%): 255 (M\(^+\), 45), 240 (100), 135 (32), 121 (40), 105 (16), 91 (8).

HRMS (EI): \( m/z \) calcd. for: \([C_{17}H_{21}NO]\) 255.1623, found: 255.1624.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, \( \lambda = 215 \) nm, 25 °C); \( t_r = 17.4 \) min [minor], \( t_r = 19.9 \) min [major]; 94% ee.

\((R)-N-(3,5,-Dimethyl)phenyl-1(4-chlorophenyl)ethyl amine (53e)\)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52e (129 mg, 0.50 mmol) and obtained as a yellow crystalline solid (122 mg, 0.47 mmol, 94%).

MP: 44.2-46.4 °C
\([\alpha]_D^{20} = +8.0 \) (c = 0.6, CH\(_2\)Cl\(_2\))

\(^1\)H-NMR (300 MHz, C\(_6\)D\(_6\)): \( \delta \) = 7.07-7.03 (m, 2H), 6.91-6.86 (m, 2H), 6.33 (s, 1H), 6.04 (s, 2H), 4.12 (q, \( J = 6.6 \) Hz, 1H), 3.40 (brs, 1H), 2.10 (s, 6H), 1.02 (d, \( J = 6.6 \) Hz, 3H) ppm.

\(^{13}\)C-NMR (75 MHz, C\(_6\)D\(_6\)): \( \delta \) = 147.3, 144.3, 138.5, 132.5, 128.8, 127.4, 119.9, 111.8, 52.6, 24.6, 21.5 ppm.

IR (neat): \( \nu_{\text{max}} \) (cm\(^{-1}\)) = 3390 (m), 2853 (w), 1597 (m), 1486 (m), 1336 (m), 1207 (m), 1184 (m), 1086 (m), 1011 (m), 817 (s), 781 (m), 690 (m).

MS (70 eV, EI): \( m/z \) (%): 259 (M\(^+\), 73), 244 (100), 139 (42), 121 (58), 103 (21).

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, \( \lambda = 215 \) nm, 25 °C); \( t_r = 10.6 \) min [minor], \( t_r = 13.7 \) min [major]; 91% ee.

\((R)-N-(3,5,-Dimethyl)phenyl-1(4-phenylphenyl)ethyl amine (53f)\)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52f (150 mg; 0.50 mmol) and obtained as a yellow oil (142 mg, 0.47 mmol, 94%).

\([\alpha]_D^{20} = +8.0 \) (c = 0.6, CH\(_2\)Cl\(_2\))
$^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta$ = 7.44-7.39 (m, 3H), 7.26-7.22 (m, 1H), 7.20-7.05 (m, 5H), 6.30 (s, 1H), 6.20 (s, 2H), 4.35 (q, $J$ = 6.6 Hz, 1H), 3.50 (brs, 1H), 2.10 (s, 6H), 1.20 (d, $J$ = 6.6 Hz, 3H) ppm.

$^{13}$C-NMR (75 MHz, C$_6$D$_6$): $\delta$ = 147.8, 145.0, 141.5, 140.2, 138.6, 128.9, 127.7, 127.4, 127.3, 126.6, 120.0, 111.9, 53.1, 24.9, 21.7 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3392 (m), 2863 (w), 1590 (m), 1470 (s), 1330 (m), 1107 (m), 1100 (m), 1011 (m), 897 (s), 780 (m), 690 (m).

MS (70 eV, EI): $m/z$ (%) = 301 (M$^+$, 55), 286 (54), 181 (100), 165 (16), 121 (18).

HRMS (EI): $m/z$ calcd. for: [C$_{22}$H$_{23}$N] 301.1830, found: 301.1832.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda$= 215 nm, 25 °C); $t_r$ = 16.3 min [minor], $t_r$ = 13.6 min [major]; 88% ee.

$(R)$-N-(3,5,-Dimethyl)phenyl-1phenyl-propylamine (53g)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52g (119 mg; 0.50 mmol) and obtained as a brown oil (115 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +12.0 (c = 0.5, CH$_2$Cl$_2$)

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.28-7.20 (m, 2H), 7.18-7.05 (m, 3H), 6.25 (s, 1H), 6.16 (s, 2H), 4.31 (t, $J$ = 6.7 Hz, 1H), 3.71 (br, 1H, NH), 2.10 (s, 6H), 1.55-1.50 (m, 2H), 0.81 (t, $J$ = 7.4 Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta$ = 147.8, 145.8, 139.1, 128.7, 127.0, 126.7, 120.1, 112.7, 55.2, 25.0, 23.2, 21.2 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3390 (br, w), 2920 (m), 1600 (m), 1455 (m), 1120 (m), 1009 (s), 845 (m), 765 (m), 690 (s).

MS (70 eV, EI): $m/z$ (%) = 239 (M$^+$, 20), 210 (100), 165 (29), 121 (18).

HRMS (EI): $m/z$ calcd. for: [C$_{17}$H$_{21}$N] 239.1674, found: 239.1680.

The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda$= 215 nm, 25 °C); $t_r$ = 9.2 min [major], $t_r$ = 10.2 min [minor]; 94% ee.

$(R)$-N-(3,5,-Dimethyl)phenyl-1(1,2,3,4-dihydro)naphthylamine (53h)
Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 52h (125 mg; 0.50 mmol) and obtained as a brown oil (118 mg, 0.47 mmol, 94%).

\([\alpha]_D^{20} = +20.8 \text{ (c = 0.5, CH}_2\text{Cl}_2\)]

\(^1\text{H}-\text{NMR (300 MHz, C}_6\text{D}_6\): } \delta = 7.40-7.37 (m, 1H), 7.09-7.03 (m, 2H), 6.97-6.95 (m, 1H), 6.43 (s, 1H), 6.20 (s, 2H), 4.49-4.46 (m, 1H), 3.38-3.36 (m, 1H), 2.62-2.49 (m, 2H), 2.22 (s, 6H), 1.81-1.74 (m, 1H), 1.70-1.58 (m, 2H), 1.47-1.42 (m, 1H) ppm.

\(^{13}\text{C}-\text{NMR (75 MHz, C}_6\text{D}_6\): } \delta = 148.1, 138.9, 138.7, 137.6, 129.7, 129.1, 127.3, 126.3, 119.6, 111.4, 51.3, 29.6, 29.2, 21.7, 19.7 ppm.

IR (neat): \(\nu_{\text{max}} (\text{cm}^{-1}) = 3402 (\text{br, w}), 3019 (\text{m}), 2919 (\text{m}), 1595 (\text{s}), 1510 (\text{m}), 1447 (\text{m}), 1337 (\text{m}), 1183 (\text{m}), 817 (\text{s}), 742 (\text{s}), 689 (s)\).

MS (70 eV, EI): \(m/z (\%) = 251 (M^+, 63), 249 (12), 131 (70), 129 (12), 121 (100), 105 (6), 91 (17)\).

HRMS (EI): \(m/z \text{ calcd. for: } [\text{C}_{18}\text{H}_{21}\text{N}] 251.1674, \text{ found: } 251.1670\).

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, \(\lambda = 215 \text{ nm}, 25 \text{ °C}\)); \(t_r = 9.4 \text{ min [major]}, t_r = 10.3 \text{ min [minor]}; 84\% \text{ ee}\).

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl ethyl amine (57a)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56a (127 mg; 0.50 mmol) and obtained as a pale yellow solid (121 mg, 0.47 mmol, 95%).

\([\alpha]_D^{20} = -6.3 \text{ (c = 0.6, CH}_2\text{Cl}_2\)]

MP: 86.3 °C

\(^1\text{H}-\text{NMR (300 MHz, CDCl}_3\): } \delta = 7.39-7.29 (m, 4H), 7.25-7.22 (m, 1H), 6.21 (s, 2H), 4.41 (q, \(J = 6.7 \text{ Hz}, 1\text{H}), 3.62 (s, 3\text{H}), 2.15 (s, 6\text{H}), 1.49 (d, \(J = 6.7 \text{ Hz}, 3\text{H}) \text{ ppm.}

\(^{13}\text{C}-\text{NMR (75 MHz, CDCl}_3\): } \delta = 149.0, 145.2, 143.0, 131.2, 128.6, 126.8, 125.9, 113.6, 59.9, 54.1, 24.7, 16.2 ppm.

IR (neat): \(\nu_{\text{max}} (\text{cm}^{-1}) = 3381 (\text{m}), 2924 (\text{br, m}), 1609 (\text{m}), 1487 (\text{s}), 1190 (\text{s}), 1006 (\text{s}), 830 (\text{m}), 701 (\text{m})\).

MS (70 eV, EI): \(m/z (\%) = 255 (M^+, 100), 240 (87), 136 (77), 105 (98)\).

HRMS (EI): \(m/z \text{ calcd. for: } [\text{C}_{19}\text{H}_{21}\text{NO}] 255.1623, \text{ found: } 255.1627\).

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 1.0 mL/min, heptane/iPrOH: 80/20, \(\lambda = 215 \text{ nm}, 25 \text{ °C}\)); \(t_r = 6.4 \text{ min [minor]}, t_r = 7.6 \text{ min [major]}\; 94\% \text{ ee}\).

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methyl)phenyl ethyl amine (57b)
Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56b (134 mg; 0.50 mmol) and obtained as a viscous oil (128 mg, 0.47 mmol, 95%).

$\left[\alpha\right]_{D}^{20} = +3.8 \ (c = 0.6, \text{CH}_2\text{Cl}_2)$

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.19-7.15 \ (m, 2H), 7.00-6.97 \ (m, 2H), 6.17 \ (s, 2H), 4.29 \ (q, J = 6.6 \ Hz, 1H), 3.40 \ (br, 1H, NH), 3.38 \ (s, 3H), 2.09 \ (s, 6H), 2.12 \ (s, 3H), 1.23 \ (d, J = 6.7 Hz, 3H) \ ppm.$

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 149.5, 143.8, 143.1, 136.2, 131.0, 129.5, 126.1, 114.0, 59.5, 53.5, 25.0, 21.0, 16.5 \ ppm.$

IR (neat): $\nu_{\text{max}} \ (\text{cm}^{-1}) = 3392 \ (\text{br, w}), 2923 \ (w), 1608 \ (m), 1487 \ (m), 1340 \ (w), 1219 \ (s), 1135 \ (w), 1044 \ (m), 1009 \ (s), 835 \ (m), 815 \ (s).$

MS (70 eV, EI): $m/z \ (%) = 269 \ (\text{M}^+, 85), 253 \ (47), 151 \ (24), 136 \ (50), 119 \ (100).$

HRMS (EI): $m/z \ \text{calcd. for: } [\text{C}_{18}\text{H}_{23}\text{NO}]^+: 269.1780, \ \text{found: } 269.1783.$

The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, $\lambda = 215$ nm, 25 °C); $t_r = 11.4 \ \text{min [minor]}, t_r = 12.5 \ \text{min [major]; } 86\% \ \text{ee}.$

(R)–N-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methyl)phenyl ethyl amine (57c):

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56c (134 mg; 0.50 mmol) and obtained as a viscous yellow oil (129 mg, 0.48 mmol, 96%).

$\left[\alpha\right]_{D}^{20} = +4 \ (c = 0.6, \text{CH}_2\text{Cl}_2)$

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.12-7.10 \ (m, 2H), 6.90-6.88 \ (m, 1H), 6.18 \ (s, 2H), 4.29 \ (q, J = 6.9 \ Hz, 1H), 3.42 \ (br, 1H, NH), 3.37 \ (s, 3H), 2.17 \ (s, 6H), 2.11 \ (s, 3H), 1.23 \ (d, J = 6.9 Hz, 3H) \ ppm.$

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 149.5, 146.2, 143.8, 138.2, 131.1, 128.8, 127.8, 126.7, 123.3, 114.0, 59.5, 53.9, 25.1, 21.5, 16.5 \ ppm.$

IR (neat): $\nu_{\text{max}} \ (\text{cm}^{-1}) = 3396 \ (\text{br, w}), 2923 \ (w), 1607 \ (s), 1486 \ (s), 1222 \ (s), 1189 \ (m), 1009 \ (m), 835 \ (m), 784 \ (m).$

MS (70 eV, EI): $m/z \ (%) = 271 \ ([\text{M}+2\text{H}]^+, 9), 270 \ ([\text{M+H}]^+, 100), 213 \ (5).$

HRMS (EI): $m/z \ \text{calcd. for: } [\text{C}_{18}\text{H}_{24}\text{NO}]^+: 270.1858, \ \text{found: } 270.1846.$
The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); tᵣ₁ = 10.2 min [major], tᵣ₂ = 11.8 min [minor]; 94% ee.

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-methyl)phenyl ethyl amine (57d):

\[
\begin{align*}
&\text{OMe} \\
&\text{HN} \\
&\text{Me} \\
&\text{Me} \\
&\text{Me}
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56d (134 mg; 0.50 mmol) and obtained as a viscous yellow oil (128 mg, 0.47 mmol, 95%).

\([\alpha]_{D}^{20} = +1.8 \ (c = 0.6, \text{CH}_2\text{Cl}_2)\)

\(^1\text{H}-\text{NMR} (300 \text{ MHz, C}_6\text{D}_6): \delta = 7.41-7.39 \ (m, 1\text{H}), 7.10-7.05 \ (m, 1\text{H}), 7.03-7.01 \ (m, 2\text{H}), 6.09 \ (s, 2\text{H}), 4.50 \ (q, J = 6.7 \text{ Hz}, 1\text{H}), 3.37 \ (\text{brs}, 4\text{H}), 2.22 \ (s, 3\text{H}), 2.16 \ (s, 6\text{H}), 1.18 \ (d, J = 6.7 \text{ Hz}, 3\text{H}) \ \text{ppm.}\)

\(^13\text{C}-\text{NMR} (75 \text{ MHz, C}_6\text{D}_6): \delta = 149.5, 143.7, 143.5, 134.8, 131.1, 130.8, 126.9, 126.8, 125.1, 113.7, 59.5, 50.1, 22.7, 18.9, 16.5 \ \text{ppm.}\)

\(\text{IR (neat): } \nu_{\text{max}} (\text{cm}^{-1}) = 3406 \ (\text{br, w}), 2964 \ (\text{m}), 2920 \ (\text{m}), 1617 \ (\text{s}), 1500 \ (\text{s}), 1447 \ (\text{m}), 1317 \ (\text{m}), 801 \ (\text{m}), 698 \ (\text{s}).\)

\(\text{MS (70 eV, EI): } m/z \ (%) = 269 \ (M^+, 100), 254 \ (72), 151 \ (35), 136 \ (51), 119 \ (68), 91 \ (13).\)

\(\text{HRMS (EI): } m/z \ \text{calcd. for: } [\text{C}_{18}\text{H}_{23}\text{NO}] 269.1780, \ \text{found: } 269.1774.\)

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); tᵣ₁ = 13.9 min [major], tᵣ₂ = 15.7 min [minor]; 94% ee.

(R)-(++)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-carbomethoxy)phenyl ethyl amine (57e)

\[
\begin{align*}
&\text{OMe} \\
&\text{HN} \\
&\text{MeO}_2\text{C} \\
&\text{Me}
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56e (156 mg; 0.50 mmol) and obtained as a yellow solid (150 mg, 0.48 mmol, 96%).

\(\text{MP: } 113.7-115.2 \ \text{°C}\)

\([\alpha]_{D}^{20} = +23.3 \ (c = 0.6, \text{CH}_2\text{Cl}_2)\)
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 25.2 min [minor], t_r = 28.9 min [major]; 94% ee.

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-trifluoromethyl)phenyl ethyl amine (57f)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56f (161 mg; 0.50 mmol) and obtained as a yellow oil (155 mg, 0.48 mmol, 96%).

[α]_D^20 = +10.2 (c = 0.5, CH₂Cl₂)

1H-NMR (300 MHz, CDCl₃): δ = 7.57 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.20 (s, 2H), 4.45 (q, J = 6.7 Hz, 1H), 3.60 (s, 3H), 2.14 (s, 6H), 1.50 (d , J = 6.7 Hz, 3H) ppm.

13C-NMR (75 MHz, CDCl₃): δ = 149.4, 149.3, 142.3, 131.4, 129.6 (q, J = 32.3 Hz), 126.3, 125.6 (q, J = 3.8 Hz), 124.2 (q, J = 271.0 Hz), 113.8, 59.9, 54.1, 24.7, 16.2 ppm.

IR (neat): ν_max (cm⁻¹) = 3349 (m), 2966 (w), 1605 (m), 1488 (m), 1323 (s), 1222 (s), 1155 (s), 1062 (s), 835 (s), 607 (m).

MS (70 eV, EI): m/z (%) = 323 (M⁺, 100), 308 (77), 293 (11), 173 (33), 150 (21), 136 (4).

HRMS (EI): m/z calcd for: [C_{18}H_{20}F_{3}NO] 323.1497, found: 323.1481.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); t_r = 14.4 min [minor], t_r = 18.5 min [major]; 89% ee.

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methoxy)phenyl ethyl amine (57g)
Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56g (142 mg; 0.50 mmol) and obtained as a viscous yellow oil (136 mg, 0.48 mmol, 96%).

\[ \alpha \]_D^{20} = +6.4 (c = 0.5, CH_2Cl_2)

$^1$H-NMR (400 MHz, C_6D_6): \( \delta = 7.26-7.21 \) (m, 2H), 6.74-6.72 (m, 2H), 6.02 (s, 2H), 4.04 (q, \( J = 6.8 \) Hz, 1H), 3.85 (br, 1H, NH), 3.75 (s, 3H), 3.60 (s, 3H), 2.12 (s, 6H), 1.32 (d, \( J = 6.6 \) Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C_6D_6): \( \delta = 158.5, 151.6, 138.0, 136.4, 129.5, 122.4, 120.9, 114.1, 59.7, 55.2, 52.4, 24.9 \) ppm.

IR (neat): \( \nu_{\text{max}} \) (cm$^{-1}$) = 3406 (br, w), 2964 (m), 2920 (m), 1617 (s), 1500 (s), 1447 (m), 1317 (m), 801 (m), 698 (s).

MS (70 eV, EI): \( m/z \) (%) = 285 (M$^+$, 50), 270 (20), 151 (30), 135 (100).

HRMS (EI): \( m/z \) calcd. for: [C_{18}H_{23}NO_2]$^+$ = 285.1729, found: 285.1719.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, \( \lambda = 215 \) nm, 25 °C); \( t_r = 11.3 \) min [minor], \( t_r = 12.9 \) min [major]; 85% ee.

(R)$\rightarrow$N-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methoxy)phenyl ethyl amine (57h):

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56h (142 mg; 0.50 mmol) and obtained as a viscous oil (133 mg, 0.47 mmol, 94%).

\[ \alpha \]_D^{20} = -4.6 (c = 0.5, CH_2Cl_2)

$^1$H-NMR (400 MHz, C_6D_6): \( \delta = 7.23-7.11 \) (m, 1H), 6.98-6.71 (m, 2H), 6.67-6.60 (m, 1H), 6.10 (s, 2H), 4.04 (q, \( J = 7.1 \) Hz, 1H), 3.71 (br, 1H, NH), 3.66 (s, 3H), 3.46 (s, 3H), 2.10 (s, 6H), 1.46 (d, \( J = 7.0 \) Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C_6D_6): \( \delta = 158.1, 153.0, 138.2, 136.9, 130.1, 125.0, 122.4, 121.0, 113.9, 112.8, 59.2, 55.1, 53.8, 25.7 \) ppm.

IR (neat): \( \nu_{\text{max}} \) (cm$^{-1}$) = 3416 (br, w), 2954 (m), 2922 (m), 1607 (s), 1487 (s), 1319 (m), 801 (m), 689 (s).

MS (70 eV, EI): \( m/z \) (%) = 285 (M$^+$, 41), 270 (80), 151 (10), 135 (100).

HRMS (EI): \( m/z \) calcd. for: [C_{18}H_{23}NO_2]$^+$ = 285.1729, found: 285.1731.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, \( \lambda = 215 \) nm, 25 °C); \( t_r = 18.7 \) min [minor], \( t_r = 21.5 \) min [major]; 86% ee.

(R)$\rightarrow$N-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-fluoro)phenyl ethyl amine (57i)
Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56i (136 mg; 0.50 mmol) and obtained as a yellow oil (128 mg, 0.47 mmol, 94%).

\([\alpha]_D^{20} = -12\ (c = 0.6, \text{CH}_2\text{Cl}_2)\)

1H-NMR (400 MHz, C₆D₆): \(\delta = 7.03-7.00\ (m, 1H), 6.91-6.88\ (m, 2H), 6.72-6.67\ (m, 1H), 6.08\ (s, 2H), 4.14\ (q, J = 6.8\ Hz, 1H), 3.37\ (s, 3H), 3.28\ (br, 1H, NH), 2.16\ (s, 6H), 1.07\ (d, J = 6.8\ Hz, 3H)\) ppm.

13C-NMR (100 MHz, C₆D₆): \(\delta = 163.7\ (d, J = 245.5\ Hz), 149.7, 149.6\ (d, J = 6.1\ Hz), 143.4, 131.2, 130.3\ (d, J = 7.9\ Hz), 121.7\ (d, J = 2.6\ Hz), 113.9, 113.8\ (d, J = 21.3\ Hz), 113.0\ (d, J = 21.6\ Hz), 59.5, 53.4\ (d, J = 1.8\ Hz), 24.7, 16.5\ ppm.

IR (neat): \(\nu_{\max}\ (\text{cm}^{-1}) = 3389\ (\text{br, w}), 2927\ (\text{w}), 1608\ (\text{m}), 1485\ (\text{s}), 1222\ (\text{s}), 1009\ (\text{s}), 835\ (\text{m}), 784\ (\text{s}), 696\ (\text{s}).\)

MS (70 eV, EI): \(m/z\ (% = 275\ ([M+2H]^+), 7), 274\ ([M+H]^+), 100), 193\ (5).\)

HRMS (EI): \(m/z\) calcd. for: \([\text{C}_{17}\text{H}_{21}\text{NO}]^{+}\): 274.1607, found: 274.1595

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, \(\lambda = 215\ nm, 25^\circ\ C\)); \(t_r = 14.6\ min\) [minor], \(t_r = 18.0\ min\) [major]; 93% ee.

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-chloro)phenyl ethyl amine (57j)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56j (144 mg; 0.50 mmol) and obtained as a yellow oil (139 mg, 0.48 mmol, 96%).

\([\alpha]_D^{20} = +8.3\ (c = 0.6, \text{CH}_2\text{Cl}_2)\)

1H-NMR (400 MHz, C₆D₆): \(\delta = 7.13-7.08\ (m, 2H), 6.95-6.91\ (m, 2H), 6.07\ (s, 2H), 4.10\ (q, J = 6.6\ Hz, 1H), 3.38\ (s, 3H), 3.27\ (br, 1H, NH), 2.17\ (s, 6H), 1.06\ (d, J = 7.1\ Hz, 3H)\) ppm.

13C-NMR (100 MHz, C₆D₆): \(\delta = 149.7, 144.5, 143.4, 132.6, 131.2, 128.9, 127.5, 114.0, 59.5, 53.1, 24.8, 16.5\ ppm.

IR (neat): \(\nu_{\max}\ (\text{cm}^{-1}) = 2926\ (\text{w}), 1608\ (\text{m}), 1487\ (\text{s}), 1337\ (\text{w}), 1222\ (\text{s}), 1090\ (\text{m}), 1010\ (\text{s}), 825\ (\text{s}), 730\ (\text{m}), 695\ (\text{m}).\)

MS (70 eV, EI): \(m/z\ (% = 289\ (M^+, 87), 276\ (20), 274\ (69), 150\ (28), 139\ (100), 136\ (83).\)

HRMS (EI): \(m/z\) calcd. for: \([\text{C}_{17}\text{H}_{20}\text{N}^3\text{ClO}]^{+}\): 289.1233, found: 289.1227.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); \( t_\text{r} = 13.7 \text{ min} \) [minor], \( t_\text{r} = 17.1 \text{ min} \) [major]; 92% ee.

\((R)\)-\(N\)-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-chloro)phenyl ethyl amine (57k)

\[
\begin{align*}
\text{HN} & \quad \text{OMe} \\
\text{Cl} & \quad \text{Ph}
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56k (144 mg; 0.50 mmol) and obtained as a yellow oil (139 mg, 0.48 mmol, 96%).

\([\alpha]_D^{20} = +11.2 \ (c = 0.4, \text{CH}_2\text{Cl}_2)\)

\(^1\text{H}-\text{NMR} \ (400 \text{ MHz}, \text{C}_6\text{D}_6): \ \delta = 7.06-7.01 \ (m, 1H), 6.90-6.71 \ (m, 2H), 6.69-6.60 \ (m, 1H), 6.10 \ (s, 2H), 4.15 \ (q, \ J = 7.1 \text{ Hz}, 1H), 3.36 \ (s, 3H), 3.21 \ (br, 1H, NH), 2.11 \ (s, 6H), 1.04 \ (d, \ J = 6.9 \text{ Hz}, 3H) \text{ ppm.}\)

\(^{13}\text{C}-\text{NMR} \ (100 \text{ MHz}, \text{C}_6\text{D}_6): \ \delta = 151.2, 137.6, 136.4, 132.8, 130.9, 127.9, 127.4, 127.0, 125.9, 112.6, 59.6, 53.8, 25.4, 16.6 \text{ ppm.}\)

\text{IR (neat): } \nu_{\text{max}} \ (\text{cm}^{-1}) = 2926 \ (w), 1606 \ (s), 1412 \ (m), 1262 \ (s), 1191 \ (m), 1010 \ (s), 945 \ (s), 781 \ (m), 695 \ (m).\)

\text{MS (70 eV, EI): } m/z (%) = 289 (M^+, 61), 274 (32), 150 (22), 139 (100), 121 (26).

\text{HRMS (EI): } m/z \text{ calcld for: } [\text{C}_{17}\text{H}_{20}\text{N}_{35}\text{ClO}]^{289.1233}, \text{ found: } 289.1228.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); \( t_\text{r} = 14.2 \text{ min} \) [minor], \( t_\text{r} = 18.4 \text{ min} \) [major]; 90% ee.

\((R)\)-\(N\)-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-phenyl)phenyl ethyl amine (57l)

\[
\begin{align*}
\text{HN} & \quad \text{OMe} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56l (165 mg; 0.50 mmol) and obtained as a pale yellow powder (157 mg, 0.47 mmol, 95%).

MP: 156.2-157.9 °C
\([\alpha]_D^{20} = +48.7 \ (c = 0.6, \text{CH}_2\text{Cl}_2)\)
**Experimental Section**

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.47-7.43 (m, 4H), 7.31-7.27 (m, 2H), 7.21-7.17 (m, 2H), 7.13-7.09 (m, 1H), 6.20 (s, 2H), 4.34 (q, $J$ = 6.7 Hz, 1H), 3.43 (br, 1H, NH), 3.38 (s, 3H), 2.19 (s, 6H), 1.24 (d, $J$ = 6.7 Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta$ = 149.6, 145.2, 143.7, 141.5, 140.2, 131.2, 129.0, 127.7, 127.4, 127.3, 126.6, 114.0, 59.5, 53.5, 25.0, 16.5 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3354 (w), 2924 (w), 1604 (m), 1484 (s), 1217 (s), 998 (s), 827 (s), 767 (s).

MS (70 eV, EI): m/z (%) = 331 (M$^+$, 41), 316 (24), 181 (100), 165 (19), 151 (26), 136 (32).

HRMS (EI): m/z calcd. for: [C$_{23}$H$_{25}$NO] 331.1936, found: 331.1930.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda$ = 215 nm, 25 °C); $t_r$ = 17.5 min [minor], $t_r$ = 23.1 min [major]; 92% ee.

(R)$^{--\text{N-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-naphthyl) ethyl amine (57m)}}$

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56m (152 mg; 0.50 mmol) and obtained as a pale yellow oil (144 mg, 0.47 mmol, 94%).

$\alpha$$_D^{20}$ = −22.4 (c = 0.6, CH$_2$Cl$_2$)

$^1$H-NMR (600 MHz, C$_6$D$_6$): $\delta$ = 7.73 (s, 1H), 7.63-7.60 (m, 3H), 7.35 (dd, $J$ = 8.4 Hz, 1.6 Hz, 1H), 7.24-7.21 (m, 2H), 6.20 (s, 2H), 4.43 (q, $J$ = 6.7 Hz, 1H), 3.53 (br, NH, 1H), 3.35 (s, 3H), 2.14 (s, 6H), 1.27 (d, $J$ = 6.7 Hz, 3H) ppm.

$^{13}$C-NMR (150 MHz, C$_6$D$_6$): $\delta$ = 149.6, 143.8, 143.6, 134.2, 133.3, 131.2, 128.7, 128.1, 127.9, 126.2, 125.6, 124.8, 124.6, 114.0, 59.5, 54.0, 24.9, 16.5 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3405 (br, w), 2864 (m), 2910 (m), 1687 (s), 1510 (s), 1477 (m), 891 (m), 698 (s).

MS (70 eV, EI): m/z (%) = 305 (M$^+$, 56), 290 (30), 155 (100), 136 (35).

HRMS (EI): m/z calcd. for: [C$_{21}$H$_{23}$NO] 305.1780, found: 305.1785.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda$ = 215 nm, 25 °C); $t_r$ = 9.1 min [minor], $t_r$ = 10.2 min [major]; 92% ee.

(R)$^{--\text{N-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-acetyl)phenyl ethyl amine (57n)}}$

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56m (152 mg; 0.50 mmol) and obtained as a pale yellow oil (144 mg, 0.47 mmol, 94%).

$\alpha$$_D^{20}$ = −22.4 (c = 0.6, CH$_2$Cl$_2$)

$^1$H-NMR (600 MHz, C$_6$D$_6$): $\delta$ = 7.73 (s, 1H), 7.63-7.60 (m, 3H), 7.35 (dd, $J$ = 8.4 Hz, 1.6 Hz, 1H), 7.24-7.21 (m, 2H), 6.20 (s, 2H), 4.43 (q, $J$ = 6.7 Hz, 1H), 3.53 (br, NH, 1H), 3.35 (s, 3H), 2.14 (s, 6H), 1.27 (d, $J$ = 6.7 Hz, 3H) ppm.

$^{13}$C-NMR (150 MHz, C$_6$D$_6$): $\delta$ = 149.6, 143.8, 143.6, 134.2, 133.3, 131.2, 128.7, 128.1, 127.9, 126.2, 125.6, 124.8, 124.6, 114.0, 59.5, 54.0, 24.9, 16.5 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3405 (br, w), 2864 (m), 2910 (m), 1687 (s), 1510 (s), 1477 (m), 891 (m), 698 (s).

MS (70 eV, EI): m/z (%) = 305 (M$^+$, 56), 290 (30), 155 (100), 136 (35).

HRMS (EI): m/z calcd. for: [C$_{21}$H$_{23}$NO] 305.1780, found: 305.1785.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda$ = 215 nm, 25 °C); $t_r$ = 9.1 min [minor], $t_r$ = 10.2 min [major]; 92% ee.
Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56n (148 mg; 0.50 mmol) and obtained as a dark brown oil (138 mg, 0.46 mmol, 92%).

\[\alpha\]D = -14.8 (c = 0.50, CH2Cl2)

H-NMR (400 MHz, CD6): δ = 7.94-7.90 (m, 2H), 7.82-7.54 (m, 3H), 7.29-7.25 (m, 2H), 6.10 (s, 2H), 4.10 (q, J = 7.0 Hz, 1H), 3.54 (br, NH, 1H), 3.38 (s, 3H), 2.18 (s, 6H), 1.26 (d, J = 7.0 Hz, 3H) ppm.

C-NMR (100 MHz, CD6): δ = 196.5, 151.2, 137.6, 134.6, 131.5, 128.2, 127.4, 127.0, 126.8, 112.5, 59.4, 53.5, 26.5, 25.4, 16.6 ppm.

IR (neat): νmax (cm⁻¹) = 3405 (br, w), 2864 (m), 2910 (m), 1687 (s), 1510 (s), 1477 (m), 1297 (m), 891 (m), 698 (s).

MS (70 eV, EI): m/z (%) = 297 (M⁺, 100), 282 (91), 267 (10), 178 (13), 147 (85), 136 (90).

HRMS (EI): m/z calcd. for: [C19H23NO2] 297.1729, found: 297.1735.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); tᵣ = 17.2 min [minor], tᵣ = 19.5 min [major]; 80% ee.

(R)–N-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro)naphthyl amine (57n)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56o (139 mg; 0.50 mmol) and obtained as a brown oil (129 mg, 0.46 mmol, 92%).

\[\alpha\]D = +18.4 (c = 0.6, CH2Cl2)

H-NMR (400 MHz, CD6): δ = 7.44-7.42 (m, 1H), 7.10-7.06 (m, 2H), 6.98-6.95 (m, 1H), 6.20 (s, 2H), 4.46-4.39 (m, 1H), 3.50 (s, 3H), 3.23 (br, NH, 1H), 2.63-2.46 (m, 2H), 2.26 (s, 6H), 1.81-1.59 (m, 3H), 1.52-1.42 (m, 1H) ppm.

C-NMR (100 MHz, CD6): δ = 149.5, 144.0, 139.0, 137.5, 131.3, 129.7, 129.1, 127.3, 126.3, 113.6, 59.6, 51.8, 29.6, 29.1, 19.6, 16.5 ppm.

IR (neat): νmax (cm⁻¹) = 2929 (w), 1605 (m), 1487 (m), 1222 (s), 1010 (s), 835 (m), 742 (s).

MS (70 eV, EI): m/z (%) = 281 (M⁺, 62), 151 (46), 131 (100), 129 (12), 91 (18).

HRMS (EI): m/z calcd. for: [C19H23NO] 281.1780, found: 281.1780.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); tᵣ = 9.2 min [major], tᵣ = 10.2 min [minor]; 84% ee.

(R)–N-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro)naphthyl amine (57p)
Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56p (133 mg; 0.50 mmol) and obtained as a dark brown oil (73 mg, 0.27 mmol, 54%).

\[ \alpha_d^{20} = +4.9 \text{ (c = 0.4, CH}_2\text{Cl}_2) \]

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.46-7.43 (m, 1H), 7.10-6.99 (m, 3H), 6.20 (s, 2H), 4.44-4.40 (m, 1H), 3.52 (s, 3H), 3.23 (br, 1H, NH), 2.66-2.44 (m, 2H), 2.28 (s, 6H), 1.81-1.52 (m, 2H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta$ = 150.1, 144.2, 140.0, 137.5, 131.4, 129.9, 129.1, 127.3, 125.9, 112.6, 59.6, 51.8, 29.6, 19.6, 16.5 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2949 (w), 1622 (m), 1475 (s), 1298 (m), 1010 (m), 895 (m), 694 (m).

MS (70 eV, EI): $m/z$ (%) = 267 (M$^+$, 35), 165 (31), 131 (100), 129 (12), 91 (18).

HRMS (EI): $m/z$ calcd. for: [C$_{18}$H$_{21}$NO] 267.1623, found: 267.1630.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda$ = 215 nm, 25 °C); $t_r$ = 19.2 min [major], $t_r$ = 20.1 min [minor]; 70% ee.

(R)–N-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propyl amine (57q)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56q (134 mg; 0.50 mmol) and obtained as a pale yellow oil (129 mg, 0.48 mmol, 96%).

$\alpha_d^{20} = +2.0$ (c = 0.6, CH$_2$Cl$_2$)

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.18-7.17 (m, 1H), 7.13-7.09 (m, 3H), 7.02-6.98 (m, 1H), 6.10 (s, 2H), 4.04 (t, $J$ = 6.6 Hz, 1H), 3.43 (br, 1H, NH), 3.30 (s, 3H), 2.10 (s, 6H), 1.55-1.48 (m, 2H), 0.75 (t, $J$ = 7.4 Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta$ = 149.5, 144.8, 144.0, 131.1, 128.7, 127.0, 126.7, 114.0, 60.1, 59.5, 31.9, 16.5, 10.9 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3394 (br, w), 2930 (m), 1608 (m), 1487 (s), 1222 (s), 1009 (s), 835 (m), 750 (m), 698 (s).

MS (70 eV, EI): $m/z$ (%) = 269 (M$^+$, 21), 240 (100), 136 (9), 91 (15).

HRMS (EI): $m/z$ calcd. for: [C$_{19}$H$_{23}$NO] 269.1780, found: 269.1791.

The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, $\lambda$ = 215 nm, 25 °C); $t_r$ = 10.4 min [major], $t_r$ = 12.4 min [minor]; 94% ee.
Experimental Section

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl-hexylamine (57r)

\[
\begin{align*}
\text{HN} & \quad \text{OMe} \\
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56r (155 mg; 0.50 mmol) and obtained as a yellow oil (153 mg, 0.49 mmol, 98%).

\[
[a]_{D}^{20} = +2.4 \quad (c = 0.5, \text{CH}_2\text{Cl}_2)
\]

\( ^1\text{H-NMR (400 MHz, C}_6\text{D}_6\)): \( \delta = 7.24-7.22 \) (m, 2H), 7.14-7.12 (m, 2H), 7.04-7.00 (m, 1H), 6.18 (s, 2H), 4.18 (t, \( J = 7.1 \text{ Hz} \), 1H), 3.52 (br, NH), 3.34 (s, 3H), 2.14 (s, 6H), 1.58-1.52 (m, 2H), 1.32-1.15 (m, 6H), 0.82 (t, \( J = 7.0 \text{ Hz} \), 3H) ppm.

\( ^{13}\text{C-NMR (100 MHz, C}_6\text{D}_6\)): \( \delta = 149.5, 145.3, 144.0, 131.1, 128.7, 127.0, 126.7, 114.0, 59.5, 58.8, 39.3, 32.1, 26.4, 22.9, 16.5, 14.2 \) ppm.

IR (neat): \( \nu_{\text{max}} \) (cm\(^{-1}\)) = 2928 (m), 1608 (m), 1488 (s), 1222 (s), 1011 (m), 755 (s), 732 (m), 698 (s).

MS (70 eV, EI): m/z (%) = 327 (M\(^+\), 37), 241 (100), 226 (8), 117 (17).

HRMS (EI): m/z calcd. for: [C\(_{21}\)H\(_{29}\)NO] 311.2249, found: 311.2248.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, \( \lambda = 215 \text{ nm} \), 25 °C); \( t_r \) = 11.0 min [minor], \( t_r \) = 12.3 min [major]; 95% ee.

(R)-N-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl-hexylamine (57s)

\[
\begin{align*}
\text{HN} & \quad \text{Ph} \\
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56s (172 mg; 0.50 mmol) and obtained as a yellow oil (169 mg, 0.49 mmol, 98%).

\[
[a]_{D}^{20} = +6.9 \quad (c = 0.5, \text{CH}_2\text{Cl}_2)
\]

\( ^1\text{H-NMR (400 MHz, C}_6\text{D}_6\)): \( \delta = 7.44-7.14 \) (m, 6H), 7.00-6.82 (m, 4H), 6.18 (s, 2H), 4.16 (t, \( J = 7.1 \text{ Hz} \), 1H), 3.50 (br, NH), 3.43 (s, 3H), 2.80-2.69 (m, 2H), 2.34 (s, 6H), 2.12 (t, \( J = 7.0 \text{ Hz} \), 2H) ppm.

\( ^{13}\text{C-NMR (100 MHz, C}_6\text{D}_6\)): \( \delta = 149.5, 146.5, 145.3, 144.0, 138.2, 131.1, 130.3, 128.7, 127.0, 126.7, 125.4, 114.2, 59.5, 58.8, 26.4, 24.2, 16.5 \) ppm.

IR (neat): \( \nu_{\text{max}} \) (cm\(^{-1}\)) = 2918 (m), 1600 (m), 1425 (m), 1202 (s), 1142 (m), 864 (m), 698 (s).

MS (70 eV, EI): m/z (%) = 345 (M\(^+\), 41), 241 (100), 226 (22), 117 (71).

HRMS (EI): m/z calcd. for: [C\(_{24}\)H\(_{27}\)NO] 345.2093, found: 345.2081.
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ = 215 nm, 25 °C); t_r = 11.0 min [minor], t_r = 12.3 min [major]; 95% ee.

(R)-5-[(N-(3,5-Dimethyl-4-methoxy)phenyl)amino]-1,5-diphenylpentan-1-one (57t)

\[
\begin{align*}
\text{HN} & \quad \text{OMe} \\
\text{HN} & \quad \text{OMe} \\
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56t (193 mg; 0.50 mmol) and obtained as a dark brown oil (184 mg, 0.47 mmol, 95%).

\[\alpha]_D^{20} = \text{−11 (c = 0.4, CH}_2\text{Cl}_2\]

\[\begin{align*}
^1\text{H-NMR (400 MHz, C}_6\text{D}_6\text{)}: & \delta = 7.82-7.80 \text{ (m, 2H), 7.28-7.26 (m, 2H), 7.18-7.17 (m, 1H), 7.14-7.11 \text{ (m, 2H), 7.09-7.02 (m, 3H), 6.24 (s, 2H), 4.25 (t, } J = 6.7 \text{ Hz, 1H), 3.83 (br, NH), 3.37 \text{ (s, 3H), 2.48-2.46 (m, 2H), 2.17 (s, 6H), 1.87-1.81 (m, 1H), 1.68-1.59 \text{ (m, 3H) ppm.}} \\
^{13}\text{C-NMR (100 MHz, C}_6\text{D}_6\text{): } & \delta = 198.7, 149.5, 145.1, 144.0, 137.5, 132.7, 131.1, 128.8, 128.6, 128.2, 127.0, 126.7, 114.0, 59.5, 58.7, 58.6, 37.8, 21.0, 16.5 \text{ ppm.} \\
\text{IR (neat): } & \nu_{\text{max}} \text{ (cm}^{-1}) = 3010 \text{ (w), 1788 \text{ (m), 1685 \text{ (s), 1129 \text{ (m), 1155 \text{ (s), 1009 \text{ (m), 795 (m).}}} \\
\text{MS (70 eV, EI): } & m/z \text{ (%) = 389 ([M+2H]^+, 22), 388 ([M+H]^+, 100), 237 (15).} \\
\text{HRMS (EI): } & m/z \text{ calcd. for: } [C_{26}H_{30}NO_2]^+ = 388.2270, \text{ found: 388.2277.}
\end{align*}\]

The enantiomer ratio was determined by HPLC using a Chiralcel AD column (flow rate 0.2 mL/min, heptane/iPrOH: 80/20, λ = 215 nm, 25 °C); t_r = 57.0 min [major], t_r = 64.5 min [minor]; 99% ee.

(R)-Methyl 4-[(N-(3,5-dimethyl-4-methoxy)phenyl)amino]-4-phenyl butanoate (57u)

\[
\begin{align*}
\text{HN} & \quad \text{OMe} \\
\end{align*}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56u (163 mg; 0.50 mmol) and obtained as a brown oil (154 mg, 0.47 mmol, 94%).

\[\alpha]_D^{20} = +21 \text{ (c = 0.6, CH}_2\text{Cl}_2\]

\[\begin{align*}
^1\text{H-NMR (400 MHz, C}_6\text{D}_6\text{): } & \delta = 7.17 \text{ (s, 1H), 7.13-7.09 \text{ (m, 2H), 7.04-7.00 \text{ (m, 2H), 6.19 \text{ (s, 2H), 4.24 (t, } J = 6.8 \text{ Hz, 1H), 3.72 (br, NH), 3.35 \text{ (s, 3H), 3.30 \text{ (s, 3H), 2.80 (t, } J = 6.8 \text{ Hz, 1H), 2.53 (t, } J = 6.4 \text{ Hz, 1H), 2.21-2.16 \text{ (m, 2H), 2.15 (s, 6H) ppm.}} \\
\end{align*}\]
13C-NMR (100 MHz, C₆D₆): δ = 173.5, 149.6, 143.7, 132.8, 131.1, 128.8, 128.5, 126.6, 114.0, 59.4, 58.1, 51.1, 33.6, 31.1, 16.5 ppm.

IR (neat): v_{max} (cm⁻¹) = 3393 (br, w), 2949 (w), 1732 (s), 1488 (s), 1220 (s), 1162 (s), 1009 (s), 837 (m), 750 (s), 700 (s).

MS (70 eV, EI): m/z (%) = 327 (M⁺, 37), 241 (100), 226 (8), 117 (17).

HRMS (EI): m/z calcd. for: [C₂₀H₂₅NO₃] 327.1834, found: 327.1825.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 80/20, λ = 215 nm, 25 °C); t_r = 19.5 min [major], t_r = 25.3 min [minor]; 92% ee.

(R)-Methyl 5-[N-(3,5-dimethyl-4-methoxy)phenyl]amino]-4-phenyl pentanoate (57v)

\[
\begin{array}{c}
\text{OMe} \\
\text{HN} \\
\text{CO}_2\text{Me}
\end{array}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56v (170 mg; 0.50 mmol) and obtained as a yellow oil (164 mg, 0.48 mmol, 96%).

[α]_{D}^{20} = +8 (c = 0.6, CH₂Cl₂)

1H-NMR (400 MHz, C₆D₆): δ = 7.21-7.19 (m, 2H), 7.16-7.12 (m, 2H), 7.05-7.03 (m, 1H), 6.19 (s, 2H), 4.17 (t, J = 6.2 Hz, 1H) 3.62 (br, NH), 3.37 (s, 3H), 3.30 (s, 3H), 2.17 (s, 6H), 2.04-2.01 (m, 2H), 1.68-1.64 (m, 1H), 1.53-1.51 (m, 3H) ppm.

13C-NMR (100 MHz, C₆D₆): δ = 173.1, 149.5, 144.8, 143.8, 131.1, 128.7, 127.1, 126.6, 113.9, 59.5, 58.4, 50.9, 38.4, 33.6, 22.0, 16.5 ppm.

IR (neat): v_{max} (cm⁻¹) = 2949 (w), 1732 (s), 1684 (m), 1488 (m), 1222 (s), 1152 (m), 1010 (m), 753 (m), 700 (s).

MS (70 eV, EI): m/z (%) = 341 (M⁺, 100), 310 (13), 241 (45), 240 (46), 225 (18).


The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 80/20, λ = 215 nm, 25 °C); t_r = 16.1 min [minor], t_r = 17.3 min [major]; 98% ee.

N-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethyl)phenyl ethylamine (57w)

\[
\begin{array}{c}
\text{OMe} \\
\text{HN} \\
\text{Cl}
\end{array}
\]

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 57w (162 mg; 0.50 mmol) and obtained as a yellow oil (156 mg, 0.48 mmol, 96%)
Experimental Section

$[\alpha]_D^{20} = +18.2$ (c = 0.5, CH$_2$Cl$_2$)

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.51$-7.45 (m, 2H), 6.94 (s, 1H), 6.10 (s, 2H), 4.11 (q, $J = 6.8$ Hz, 1H), 3.88 (brs, NH, 1H), 3.43 (s, 3H), 2.22 (s, 6H), 2.00 (d, $J = 7.0$ Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 152.2$, 145.2, 140.5, 136.2, 135.2, 134.1, 132.2, 130.5, 125.2, 114.0, 56.6, 55.5, 16.7, 16.0 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2992 (w), 1664 (m), 1592 (m), 1433 (m), 1325 (m), 1212 (m), 1062 (s), 879 (s), 765 (m).

MS (70 eV, EI): m/z (%) = 323 ($M^+$, 59), 268 (19), 253 (100), 151 (16).

HRMS (EI): m/z calcd. for: [C$_{17}$H$_{19}$NOCl] 323.0844, found: 323.0852.

N-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylamine (57x)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56x (157 mg; 0.50 mmol) and obtained as a yellow oil (149 mg, 0.47 mmol, 94%)

$[\alpha]_D^{20} = +12.7$ (c = 0.5, CH$_2$Cl$_2$)

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta = 7.21$ (d, $J = 2.2$ Hz, 1H), 7.18 (d, $J = 8.3$ Hz, 1H), 7.10-7.05 (m, 1H), 6.11 (s, 2H), 4.25 (q, $J = 7.1$ Hz, 1H), 3.90 (brs, NH, 1H), 3.51 (s, 3H), 3.43 (s, 3H), 3.40 (s, 3H), 2.25 (s, 3H), 1.08 (d, $J = 6.9$ Hz, 3H) ppm.

$^{13}$C-NMR (100 MHz, C$_6$D$_6$): $\delta = 152.5$, 147.2, 145.2, 141.0, 135.6, 132.4, 126.2, 124.2, 120.4, 112.8, 56.8, 56.6, 56.3, 56.2, 23.7, 16.6 ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 2935 (w), 2959 (w), 1620 (w), 1594 (m), 1583 (s), 1510 (s), 1452 (m), 1414 (s), 1267 (s), 1217 (s), 1153 (s), 1018 (s), 867 (s), 765 (m).

MS (70 eV, EI): m/z (%) = 314 ([M+H]$^+$, 12), 339 (M$^+$, 55), 299 (18), 298 (100), 268 (6).

HRMS (EI): m/z calcd. for: [C$_{19}$H$_{25}$NO$_3$] 313.1678, found: 313.1665.

N-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethyl)phenyl ethylamine (57y)

Prepared according to the typical procedure TP8, using the iridium catalyst 46a (9.0 mg; 0.05 mmol) and imine 56y (140 mg; 0.50 mmol) and obtained as a yellow oil (134 mg, 0.47 mmol, 94%)

$[\alpha]_D^{20} = +4.5$ (c = 0.5, CH$_2$Cl$_2$)
**1H-NMR (400 MHz, C₆D₆):** δ = 7.22-7.18 (m, 1H), 7.10-7.06 (m, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.32 (s, 2H), 4.12 (q, J = 7.0 Hz, 1H), 3.85 (brs, NH, 1H), 3.42 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H), 2.25 (s, 6H), 1.00 (d, J = 7.0 Hz, 3H) ppm.

**13C-NMR (100 MHz, C₆D₆):** δ = 151.2, 140.2, 139.2, 135.4, 128.3, 124.2, 120.1, 111.2, 59.4, 55.2, 23.2, 21.5, 16.7, 16.4 ppm.

**IR (neat):** \( \nu_{\text{max}} (\text{cm}^{-1}) \) = 2912 (w), 1645 (w), 1585 (m), 1464 (m), 1398 (m), 1208 (m), 1118 (s), 1002 (s), 879 (s), 765 (m).

**MS (70 eV, EI):** \( m/z \) (%) = 283 (M⁺, 25), 268 (21), 253 (100), 151 (12).

**HRMS (EI):** \( m/z \) calcd. for: \[ C_{19}H_{25}NO \] 283.1936, found: 283.1665.

8. Synthesis of Chiral Primary Amines and Lactams

\((R)-\alpha\text{-methyl benzylamine (58)}^{136}\)

\[
\text{NH}_2
\]

Prepared according to the typical procedure TP9, using the chiral secondary amine 57a (102 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (42 mg; 0.34 mmol, 85%).

\([\alpha]_D^{20} = +28.9 \text{ (c = 1.0, CHCl}_3)\)

**1H-NMR (300 MHz, CDCl₃):** δ = 1.58 (d, J = 6.8 Hz, 3H), 1.68 (br, 2H), 4.25 (q, J = 6.8 Hz, 1H), 7.30-7.43 (m, 5H) ppm.

\((R)-\alpha\text{-methyl benzylamine (59)}^{137}\)

\[
\text{NH}_2
\]

Prepared according to the typical procedure TP9, using the chiral secondary amine 57j (116 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (51 mg; 0.33 mmol, 82%).

\([\alpha]_D^{20} = +18.9 \text{ (c = 1.0, CHCl}_3)\)

**1H-NMR (300 MHz, CDCl₃):** δ = 1.48 (d, J = 7.0 Hz, 3H), 1.62 (br, 2H), 4.21 (q, J = 6.9 Hz, 1H), 7.15-7.17 (m, 2H), 7.87-7.99 (m, 2H) ppm.

\((R)-\text{Methyl-4-(1-aminoethyl)benzoate ester (60)}^{138}\)

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Prepared according to the typical procedure TP9, using the chiral secondary amine 57e (126 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (63 mg; 0.35 mmol, 87%).

\[ \alpha \]_D^{20} = +21.9 (c = 1.0, CHCl₃)

^1^H-NMR (300 MHz, CDCl₃): δ = 7.99-7.87 (m, 2H), 7.17-7.15 (m, 2H), 4.20 (q, J = 6.9 Hz, 1H), 3.38 (s, 3H), 1.60 (br, 2H), 1.48 (d, J = 7.0 Hz, 3H) ppm.

^1^3^C-NMR (75 MHz, CDCl₃): δ = 166.8, 151.4, 129.1, 127.0, 126.1, 52.6, 51.8, 25.8 ppm.

MS (70 eV, EI): m/z (%) = 179 (M⁺, 18), 121 (20), 107 (18), 106 (100), 91 (2).

HRMS (EI): m/z calcd. for: [C₁₀H₁₃NO₂] 179.2158, found: 179.2165.

(R)-1-Phenyl-1-propylamine (61)

Prepared according to the typical procedure TP9, using the chiral secondary amine 57q (108 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (44 mg; 0.32 mmol, 80%).

^1^H-NMR (300 MHz, CDCl₃): 7.39-7.15 (m, 5H), 3.80 (t, J = 6.8 Hz, 1H), 1.75 (m, 2H), 1.60 (s, 2H), 0.88 (t, J = 7.1 Hz, 3H) ppm.

^1^3^C-NMR (75 MHz, CDCl₃): 144.2, 131.1, 127.0, 126.4, 55.0, 32.5, 12.5 ppm.

[\alpha]_D^{20} = +10.8 (c = 1.0, EtOH)

MS (70 eV, EI): m/z (%) = 135 (M⁺, 2), 121 (10), 106 (100), 91 (40).

HRMS (EI): m/z calcd. for: [C₉H₁₃N] 135.1048 found 135.1040

(R)-(+)

Prepared according to the typical procedure TP9, using the chiral secondary amine 57r (125 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a pale yellow oil (55 mg; 0.31 mmol, 78%).

[\alpha]_D^{20} = +4.8 (c = 1.6, EtOH)

^1^H-NMR (300 MHz, CDCl₃): 7.32-7.10 (m, 5H), 3.85 (t, J = 6.8 Hz, 1H), 1.80-1.00 (m, 10H), 0.84 (t, J = 7.0 Hz, 1H) ppm.

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): 144.0, 131.1, 127.0, 126.7, 55.1, 14.1, 38.5, 32.6, 27.1, 22.5 ppm.

**MS (70 eV, EI):** \(m/z\) (%) = 177 (M\(^+\), 5), 160 (6), 118 (12), 106 (100), 91 (36).

**HRMS (EI):** \(m/z\) calcd. for: \([C_{13}H_{19}N]^{-}\) 177.1517 found 177.1521

\((R)-5\)-Phenylpyrrolidin-2-one (63)\(^{140}\)

Prepared according to the typical procedure TP9, using the chiral secondary amine 57u (131 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a pale yellow oil (46 mg; 0.29 mmol, 72%).

\([\alpha]_D^{20}\) = +41.0 (c = 0.4, CH\(_2\)Cl\(_2\))

\(^{1}H\)-NMR (300 MHz, CDCl\(_3\)): \(\delta\) = 1.97-2.11 (m, 1H), 2.40-2.72 (m, 3H), 4.82 (t, \(J = 7.0\) Hz, 1H), 6.70 (brs, NH), 7.34-7.48 (m, 5H) ppm.

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta\) = 30.9, 31.4, 58.2, 125.8, 127.8, 128.9, 143.0, 178.9 ppm.

**MS (70 eV, EI):** \(m/z\) (%) = 161 (M\(^+\), 67), 117 (100), 104 (8), 77 (17).

**HRMS (EI):** \(m/z\) calcd. for: \([C_{10}H_{11}NO]^{-}\) 161.0841, found: 161.0843.

The enantiomer ratio was determined by Chiral GC using a Chiral DEX-CB column (100 °C (5), 5 °C/min to 160 °C (60) \(t_c\) = 36.7 min [major], \(t_m\) = 41.0 min [minor]; 92% ee.

\((R)-6\)-Phenylpiperidin-2-one (64)\(^{141}\)

Prepared according to the typical procedure TP9, using the chiral secondary amine 57v (137 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (55 mg; 0.31 mmol, 78%).

**MP:** 118-119 °C

\([\alpha]_D^{20}\) = +40.0 (c = 2.0, CHCl\(_3\))

\(^{1}H\)-NMR (400 MHz, C\(_6\)D\(_6\)): \(\delta\) = 1.19-1.27 (m, 2H), 1.42-1.48 (m, 2H), 2.04-2.11 (m, 1H), 2.15-2.22 (m, 1H), 3.94-3.97 (m, 1H), 6.80 (br, s, NH), 6.98-7.06 (m, 3H), 7.09-7.13 (m, 2H) ppm.

\(^{13}\)C-NMR (100 MHz, C\(_6\)D\(_6\)): \(\delta\) = 19.6, 31.2, 32.1, 57.3, 126.4, 127.5, 128.7, 143.7, 171.4 ppm.

**IR (neat):** \(\nu_{\text{max}}\) (cm\(^{-1}\)) = 3266 (br, w), 2955 (w), 1655 (s), 1623 (s), 1478 (s), 1355 (s), 1175 (m), 737 (s), 695 (s).


MS (70 eV, EI): m/z (%) = 176 ([M+H]^+, 12), 175 (M^+, 100), 119 (26), 106 (34), 98 (10), 77 (11).

HRMS (EI): m/z calcd. for: [C_{11}H_{13}NO] 175.0997 found 175.0989

The enantiomer ratio was determined by Chiral GC using a Chiral DEX-CB column (100 °C (5), 5 °C/min to 160 °C (60))

\[ t_r = 38.7 \text{ min [minor]}, t_r = 40.8 \text{ min [major]; } 97\% \text{ ee.} \]


\((S_{Fc}, S)-[2-(Formyl)-ferrocen-1-yl]-p-tolylsulfoxide (65)\)

\[
\begin{align*}
\text{CHO} & \quad \text{SOTol} \\
\text{Fe} & \quad \text{SOTol} \\
\end{align*}
\]

Prepared according to the TP1 using sulfoxide 14 (1.30 g; 4.0 mmol), THF (40 mL), LDA (2.2 mL, 4.4 mmol). The reaction mixture stirred at -78 °C for 30 min and added DMF (0.45 mL; 6.0 mmol; 1.5 equiv) as an electrophile and stirred for 1h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h before quenching with a Sat. NH$_4$Cl solution (20 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, n-pentane:Et$_2$O 1:1), provided the desired compound (1.13 g, 3.20 mmol, 80 %) as a red solid.

MP: 149.1-149.8 °C

[\alpha]_D^{20} = -188 (c = 0.1, acetone).

$^1$H-NMR (300 MHz, C$_6$D$_6$): δ = 11.05 (s, 1H), 7.47 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 4.81 (s, 1H), 4.34 (s, 1H), 4.17 (s, 5H), 3.98-3.97 (m, 1H), 1.89 (s, 3H) ppm.

$^{13}$C-NMR (75 MHz, C$_6$D$_6$): δ = 191.7, 144.4, 140.6, 129.9, 124.0, 98.5, 79.4, 73.8, 72.5, 71.7, 70.3, 21.0 ppm.

IR(KBr): $\nu_{max}$ (cm$^{-1}$) = 3436 (br, w), 3093 (w), 1673 (s), 1435 (m), 1227 (m), 1033 (s), 817 (m), 754 (m).

MS (70 eV, EI): m/z (%) = 352 (M^+, 100), 335 (21), 244 (54), 211 (20).

HRMS (EI): m/z calcd. for: [C$_{18}$H$_{16}$FeO$_2$S] 352.0220, found: 352.0211

\((S_{Fc})-1-[(S)-p-Tolylsulfinyl]-2-[\alpha-hydroxy-(2(S_{Fc})-1-[(S)-p-tolylsulfinyl])ferrocenyl]methy]ferrocene (66)\)

\[
\begin{align*}
\text{OH} & \quad \text{SOTol} \\
\text{Fe} & \quad \text{SOTol} \\
\end{align*}
\]

Prepared according to the TP1 using sulfoxide 14 (260 mg; 0.80 mmol), THF (8 mL), LDA (0.44 mL; 0.88 mmol, 1.1 equiv). The reaction mixture stirred at -78 °C for 30 min and added ferrocenyl aldehyde 65 (340 mg; 0.96 mmol; 1.2 equiv) as an electrophile and stirred for 1.5 h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h before quenching with a saturated aqueous NH$_4$Cl solution (15 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, Et$_2$O), provided the bisferrocenyl alcohol 66 (243 mg, 0.48 mmol, 60 %) as a yellow solid.
Experimental Section

**1H-NMR** (300 MHz, C$_6$D$_6$): $\delta$ = 8.26-8.24 (m, 2H), 7.95-7.92 (m, 2H), 7.11-7.04 (m, 4H), 6.01 (d, $J = 11.5$ Hz, 1H), 5.90 (d, $J = 11.5$ Hz, 1H), 4.94-4.90 (m, 2H), 4.20 (s, 5H), 4.09-4.06 (m, 1H), 3.99 (s, 5H), 3.89-3.80 (m, 2H), 3.77 -3.74 (m, 1H), 2.10 (s, 3H), 2.06 (s, 3H) ppm.

**13C-NMR** (75 MHz, C$_6$D$_6$): $\delta$ = 148.5, 147.2, 146.8, 145.4, 135.2, 134.7, 130.2, 127.8, 99.9, 99.0, 85.4, 84.7, 77.8, 76.2, 76.0, 74.5, 73.2, 72.4, 71.9, 71.2, 70.9, 24.2, 23.8 ppm.

**IR (KBr):** $\nu_{\text{max}}$ (cm$^{-1}$) = 3463 (br, w), 2793 (m), 1665 (m), 1598 (m), 1435 (m), 1389 (m), 1212 (m), 1063 (s), 817 (m), 754 (m).

**MS (70 eV, EI):** m/z (%) = 676 (M$^+$, 60), 659 (100), 324 (55), 211 (10).

**HRMS (EI):** m/z calcd. for: [C$_{35}$H$_{32}$S$_2$Fe$_2$O$_3$]$_6$76.0492, found: 676.0500

**Prepared according to the typical procedure TP4,** using KH (19 mg, 0.45 mmol, 1.50 equiv.) in THF (2.0 mL), bisferrocenyl alcohol 66 (203 mg, 0.3 mmol) in THF (1.0 mL) and CH$_3$I (135 mg; 0.05 mL, 0.90 mmol, 3.0 equiv). After quenching the reaction mixture with a saturated aqueous NH$_4$Cl solution (5 mL) and typical work-up, the residue was purified by flash chromatography (silica gel, Et$_2$O) to furnish the methyl ether 68 (176 mg, 0.26 mmol, 85%) as a yellow solid.

**MP:** 140.6-142.1 °C  
[a]$_D^{20}$ = −6.4 (c = 0.1, acetone).

1H-NMR (300 MHz, C$_6$D$_6$): $\delta$ = 8.16 (d, $J = 8.8$ Hz, 2H), 7.84 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 8.0$ Hz, 4H), 5.91 (s, 1H), 4.92-4.90 (m, 1H), 4.40-4.36 (m, 1H), 4.17 (s, 5H), 4.40-3.97 (m, 1H), 3.90 (s, 5H), 3.88-3.86 (m, 1H), 3.82-3.81 (m, 1H), 3.77-3.75 (m, 1H), 3.74 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H) ppm.

13C-NMR (75 MHz, C$_6$D$_6$): $\delta$ = 146.2, 144.2, 141.3, 141.1, 130.2, 130.1, 125.6, 124.2, 99.1, 98.8, 80.2, 79.4, 75.4, 74.8, 74.2, 72.5, 72.0, 71.9, 71.0, 70.2, 70.0, 59.7, 23.0, 21.2 ppm.

**IR (KBr):** $\nu_{\text{max}}$ (cm$^{-1}$) = 3436 (br, w), 3086 (w), 1632 (w), 1492 (w), 1108 (m), 1089 (s), 1039 (s), 813 (s).

**MS (70 eV, EI):** m/z (%) = 690 (M$^+$, 7), 628 (17), 625 (19), 507 (32), 506 (98), 384 (30), 383 (100).

**HRMS (EI):** m/z calcd. for: [C$_{36}$H$_{34}$$^{56}$Fe$_2$O$_3$S$_2$]$_6$90.0648, found: 690.0608

**Prepared according to the TP3 using sulfoxide 30 (1.62 g; 3.0 mmol), THF (40 mL), PhLi (18 mL, 3.6 mmol). The reaction mixture stirred at -78 °C for 10 min and added DMF (0.35 mL;
6.0 mmol; 1.5 equiv) as an electrophile and stirred for 1 h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h before quenching with a Sat. NH₄Cl solution (20 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, n-pentane:Et₂O 1:1), provided the desired compound (840 mg, 1.95 mmol, 65 %) as a red oil.

[α]D⁰ = +68.1 (c = 0.1, acetone).

H-NMR (300 MHz, C₆D₆): δ = 11.25 (s, 1H), 7.88-7.80 (m, 2H), 7.72-7.65 (m, 2H), 7.05-7.00 (m, 3H), 6.92-6.89 (m, 3H), 5.17-5.15 (m, 1H), 4.21 (s, 5H), 4.04-4.03 (m, 1H), 3.82-3.80 (m, 1H) ppm.

C-NMR (75 MHz, C₆D₆): δ = 193.4, 135.7 (d, J = 87.1 Hz), 133.9 (d, J = 85.6 Hz, 1H), 132.4 (d, J = 11.0 Hz), 132.0 (d, J = 10.6 Hz), 131.4 (d, J = 2.9 Hz), 131.4 (d, J = 2.9 Hz), 128.6 (d, J = 12.7 Hz), 128.1 (d, J = 13.0 Hz), 83.9 (d, J = 10.1 Hz), 80.2 (d, J = 90.2 Hz), 79.2 (d, J = 10.8 Hz), 72.8 (d, J = 9.7 Hz), 72.3 (d, J = 7.6 Hz), 72.0 ppm.

IR(neat): νmax (cm⁻¹) = 3436 (br, w), 2921 (w), 1664 (s), 1437 (m), 1243 (m), 1101 (m), 830 (w), 717 (m), 656 (m).

MS (70 eV, EI): m/z (%) = 430 (M⁺, 100), 402 (39), 365 (29), 338 (17), 337 (82).

HRMS (EI): m/z calcd. for: [C₂₃H₁₉₅₆FeOP₃₂S] 430.0244, found: 430.0239

(R₉C₉)-1-Diphenylphosphinothioyl-2-[α-hydroxy-((R₉C₉)-1-(diphenylphosphinothioyl))ferrocenyl]methylferrocene (69)

Prepared according to the TP3 using sulfoxide 30 (270 mg; 0.5 mmol), THF (5 mL), PhLi (3 mL; 0.6 mmol, 1.2 equiv). The reaction mixture stirred at -78 °C for 10 min and ferrocenylaldehyde 68 (259 mg; 0.6 mmol; 1.2 equiv) as an electrophile and stirred for 1.5 h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 2 h before quenching with a saturated aqueous NH₄Cl solution (10 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, n-pentane:Et₂O 10:1), provided the desired compound (230 mg, 0.28 mmol, 55 %) as a yellow solid.

MP: 281 °C (decomposed)
[α]D⁰ = +12 (c = 0.1, acetone).

H-NMR (400 MHz, C₆D₆): δ = 7.74-7.60 (m, 4H), 7.48-7.25 (m, 16H), 6.20 (d, J = 12.5 Hz, 1H), 5.81 (d, J = 11.5 Hz, 1H), 4.74-4.73 (m, 2H), 4.66-4.65 (m, 2H), 4.30 (s, 5H), 4.27 (s, 5H), 3.31-3.28 (m, 2H), 3.19-3.15 (m, 2H) ppm.

C-NMR (100 MHz, C₆D₆): δ = 139.1 (d, J = 86.8 Hz), 137.4 (d, J = 87.9 Hz), 137.3 (d, J = 86.3 Hz), 135.9 (d, J = 86.0 Hz), 133.7 (d, J = 10.9 Hz), 133.5 (d, J = 7.9 Hz), 132.6 (d, J = 8.0 Hz), 131.7 (d, J = 11.4 Hz), 131.2 (d, J = 2.8 Hz), 130.9 (d, J = 3.8 Hz), 130.0 (d, J = 2.9 Hz), 129.1 (d, J = 3.2 Hz), 128.9 (d, J = 9.9 Hz), 126.9 (d, J = 11.1 Hz), 98.6 (d, J = 13.2 Hz), 96.0 (d, J = 10.5 Hz), 76.9 (d, J = 13.1 Hz), 75.4 (d, J = 9.2 Hz), 75.0, 74.8 (d, J = 94.9 Hz), 73.7 (d, J = 11.2 Hz), 73.0 (d, J = 9.9 Hz), 72.9 (d, J = 9.8 Hz), 71.9 (d, J = 5.4 Hz), 71.8 (d, J = 92.8 Hz), 71.9, 71.2, 69.9 (d, J = 11.9 Hz), 69.1 (d, J = 10.6 Hz) ppm

IR (KBr-Pressling): νmax (cm⁻¹) = 3436 (br, s), 1619 (m), 1452 (m), 1338 (m), 1100 (m), 828 (m), 797 (m), 714 (m), 694 (m).

MS (70 eV, EI): m/z (%) = 832 (M⁺, 40), 817 (100), 695 (14), 445 (29).
HRMS (EI): m/z calcd. for: [C\textsubscript{18}H\textsubscript{16}\textsuperscript{56}FeO\textsubscript{2}\textsuperscript{32}S] 832.0538, found: 832.0530

(R\textsubscript{Fe})-1-Bromo-2-[\alpha-hydroxy-\((R\textsubscript{Fc})\)-1-(diphenylphosphinothioyl)] ferrocenyl)methyl-ferrocene (70)

Prepared according to the TP3 using sulfoxide 30 (1.10 g; 2.0 mmol), THF (10 mL), PhLi (11 mL; 2.2 mmol). The reaction mixture stirred at -78 °C for 10 min and added 1-bromo-2-ferrocenylcarboxaldehyde 20b (645 mg; 2.2 mmol; 1.2 equiv) as an electrophile and stirred for 1h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 2 h before quenching with a saturated aqueous NH\textsubscript{4}Cl solution (20 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, n-pentane:Et\textsubscript{2}O 8:1), provided the desired compound (807 mg, 1.16 mmol, 58%) as a yellow solid.

MP: 171-172.8 °C
\([\alpha]_D^{20} = +61.2 \text{ (c = 0.2, acetone).}

\textsuperscript{1}H-NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}): \delta = 7.74-7.60 (m, 4H), 7.48-7.25 (m, 16H), 6.20 (d, J = 12.5 Hz, 1H), 5.81 (d, J = 11.5 Hz, 1H), 4.74-4.73 (m, 2H), 4.66-4.65 (m, 2H), 4.30 (s, 5H), 4.27 (s, 5H), 3.31-3.28 (m, 2H), 3.19-3.15 (m, 2H) ppm.

\textsuperscript{13}C-NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}): \delta = 138.7 (d, J = 89.5 Hz), 136.4 (d, J = 85.2 Hz), 134.2 (d, J = 10.5 Hz), 134.0 (d, J = 10.7 Hz), 132.0 (d, J = 3.0 Hz), 131.4 (d, J = 2.8 Hz), 129.2 (d, J = 12.1 Hz), 128.5 (d, J = 13.1 Hz), 95.2 (d, J = 12.1 Hz), 91.4, 81.2, 77.2 (d, J = 12.2 Hz), 75.2 (d, J = 95.2 Hz), 73.8, 73.0 (d, J = 9.1 Hz), 72.1, 71.9, 70.5, 70.0 (d, J = 10.5 Hz), 67.2, 66.7 ppm.

\textsuperscript{31}P-NMR (81 MHz, C\textsubscript{6}D\textsubscript{6}): \delta = +43.19 ppm

IR (KBr-Pressling): \upsilon_{\text{max}} (cm\textsuperscript{-1}) = 3440 (br, w), 2972 (w), 1678 (m), 1629 (w), 1400 (m), 1378 (m), 1101 (s), 925 (s), 832 (s), 797 (s), 614 (s)

MS (70 eV, EI): m/z (%) = 694 (M\textsuperscript{+}, 100), 677 (70), 382 (10).

HRMS (EI): m/z calcd. for: [C\textsubscript{33}H\textsubscript{28}Fe\textsubscript{2}P\textsubscript{32}SO\textsubscript{79}Br] 693.9481, found: 693.9491.

(R\textsubscript{Fc})-1-Bromo-2-[\alpha-methoxy-\((R\textsubscript{Fe})\)-1-(diphenylphosphinothioyl)] ferrocenyl)methyl-ferrocene (71)

Prepared according to the typical procedure TP4, using KH (60 mg, 1.50 mmol, 1.50 equiv.) in THF (2 mL), ferrocenyl alcohol 70 (698 mg, 1.0 mmol) in THF (3 mL) and CH\textsubscript{3}I (215 mg; 0.1 mL, 1.50 mmol, 1.50 equiv.). After quenching the reaction mixture with a saturated NH\textsubscript{4}Cl and typical work-up, the residue was purified by flash chromatography (silica gel, n-pentane:Et\textsubscript{2}O 4:1) to furnish the methyl ether 71 (597 mg, 0.84 mmol, 84%) as a yellow solid.

MP: 181.6-182.6 °C
αD20 = +85 (c = 0.2, acetone).

**1H-NMR (400 MHz, C6D6):** δ = 8.07-7.98 (m, 4H), 7.06-7.03 (m, 6H), 6.43 (s, 1H), 4.33-4.29 (m, 2H), 4.20-4.19 (m, 1H), 4.09 (s, 5H), 3.99-3.97 (m, 1H), 3.88-3.87 (m, 2H), 3.12 (s, 3H) ppm.

**13C-NMR (100 MHz, C6D6):** δ = 136.5 (d, J = 86.8 Hz), 135.3 (d, J = 84.7 Hz), 132.8 (d, J = 10.7 Hz), 132.7 (d, J = 10.7 Hz), 130.9 (d, J = 2.8 Hz), 130.8 (d, J = 2.9 Hz), 127.93 (d, J = 12.1 Hz), 127.9 (d, J = 12.8 Hz), 94.3 (d, J = 11.9 Hz), 91.2, 79.1, 75.3 (d, J = 10.7 Hz), 74.5 (d, J = 94.2 Hz), 72.9, 72.8 (d, J = 8.5 Hz), 71.9, 71.4, 69.6, 69.3 (d, J = 10.5 Hz), 66.2, 65.7, 56.3 ppm

**31P-NMR (81 MHz, C6D6):** δ = +41.90 ppm.

**IR (KBr-Pressling):** v_max (cm⁻¹) = 3436 (br, s), 2930 (w), 1629 (w), 1436 (m), 1231 (m), 1101 (s), 823 (s), 717 (s), 694 (s)

**MS (70 eV, EI):** m/z (%) = 708 (M⁺, 100), 413 (20), 382 (60).

**HRMS (EI):** m/z calcd. for [C33H28Fe2P32SO79Br] 707.9637, found: 707.9613.

(RFc)-1-Diphenylphosphinothioyl-2-[αααα-methoxy-((RFc)-1-(diphenylphosphinothioyl)) ferrocenyl)methylferrocene (72)

A 25 mL Schlenk flask was charged with bisferrocenylether 71 (355 mg; 0.5 mmol) and THF (3 mL). The reaction mixture was cooled to -78 °C and nBuLi (1.6 M solution in pentane; 0.35 mL, 0.55 mmol, 1.1 equiv) and stirred for 15 min. Chlorodiphenylphosphine (168 mg; 0.15 mL, 0.75 mmol, 1.5 equiv) was added and at -78 °C and the reaction mixture was stirred for 1 h before warming to the room temperature. The reaction mixture was stirred at room temperature for 1 h and then sulfur (S₈; 160 mg; 5.0 mmol, 10 equiv) was added a solution in butylamine (2 mL) and the reaction mixture was stirred for 12 h at room temperature. Sat. NH₄Cl was added to the reaction mixture and the aqueous layer was extracted with diethylether (4 x 15 mL). The combined organic layers were washed with water, brine, dried over MgSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-pentane:Et₂O 4:1) to furnish bisphosphate sulfide 72 (323 mg, 0.38 mmol, 76%) as a yellow solid.

**MP:** 223.4-225.0 °C

[a]D20 = +57.6 (c = 0.2, acetone).

**1H-NMR (400 MHz, C6D6):** δ = 8.11-7.70 (m, 8H), 7.20-6.85 (m, 12H), 6.33 (s, 1H), 4.61-4.42 (m, 2H), 4.25 (s, 5H), 4.07 (s, 5H), 3.87 (s, 3H), 3.66-3.56 (m, 2H), 3.48-3.30 (m, 2H) ppm.

**13C-NMR (150 MHz, C6D6):** δ = 137.1 (d, J = 85.4 Hz), 136.4 (d, J = 85.3 Hz), 134.8 (d, J = 86.2 Hz), 132.8 (d, J = 10.6 Hz), 132.7 (d, J = 8.3 Hz), 132.6 (d, J = 8.0 Hz), 132.4 (d, J = 10.5 Hz), 130.95 (d, J = 3.6 Hz), 130.9 (d, J = 3.8 Hz), 130.44 (d, J = 3.6 Hz), 130.4 (d, J = 2.6 Hz), 128.3 (d, J = 9.6 Hz), 127.6 (d, J = 11.3 Hz), 98.6 (d, J = 12.9 Hz), 96.0 (d, J = 10.5 Hz), 75.9 (d, J = 12.9 Hz), 75.0 (d, J = 9.0 Hz), 74.9, 74.5 (d, J = 92.9 Hz), 73.7 (d, J = 12.2 Hz), 73.0 (d, J = 9.9 Hz), 72.6 (d, J = 9.8 Hz), 71.4 (d, J = 4.7 Hz), 71.1 (d, J = 98.8 Hz), 71.3, 71.2, 68.9 (d, J = 10.9 Hz), 68.1 (d, J = 10.6 Hz), 59.8 ppm

**31P-NMR (81 MHz, CDCl3):** δ = +43.98, +41.46 ppm.
**Experimental Section**

IR (KBr-Pressling): $v_{\text{max}}$ (cm$^{-1}$) = 3436 (br, s), 1629 (m), 1436 (m), 1101 (m), 1004 (m), 820 (m), 717 (m), 694 (m).

MS (70 eV, EI): $m/z$ (%) = 846 (M$^+$, 100), 782 (3), 695 (5), 630 (87), 445 (25), 324 (46).

HRMS (EI): $m/z$ calcd. for: [C$_{46}$H$_{40}$Fe$_2$P$_2$O$_3$S$_2$] 846.0695, found: 846.0668.

($R_Fc$)-1-Diphenylphosphinothioyl-2-[α-methoxy-((R_Fc)-1-(bis(2-furylphosphinothioyl)) ferrocenyl]methylferrocene (73)

A 25 mL Schlenk flask was charged with bisferrocenylether 71 (355 mg; 0.5 mmol) and THF (3 mL). The reaction mixture was cooled to -78 °C and $n$BuLi (1.6 M solution in pentane; 0.35 mL, 0.55 mmol, 1.1 equiv) and stirred for 15 min. Chlorobis(2-furyl)phosphine (152 mg; 0.75 mmol, 1.5 equiv) was added and at -78 °C and the reaction mixture was stirred for 1 h before warming to the room temperature. The reaction mixture was stirred at room temperature for 1 h and then sulfur (160 mg; 5.0 mmol, 10 equiv) was added a solution in butylamine (2 mL) and the reaction mixture was stirred for 12 h at room temperature. Sat. NH$_4$Cl was added to the reaction mixture and the aqueous layer was extracted with diethylether (4 x 15 mL). The combined organic layers were washed with water, brine, dried over MgSO$_4$ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-pentane:Et$_2$O 4:1) to furnish bisphsophne sulfide 73 (332 mg, 0.40 mmol, 80%) as a red solid.

MP: 206.9-207.6 °C

[$\alpha$]$_{D}^{20}$ = +35.8 (c = 0.2, acetone)

$^1$H-NMR (400 MHz, C$_6$D$_6$): $\delta$ = 8.01-7.98 (m, 2H), 7.86-7.82 (m, 2H), 7.25 (t, $J$ = 3.3 Hz, 1H), 7.13 (t, $J$ = 2.8 Hz, 1H), 7.08-7.01 (m, 8H), 6.41 (s, 1H), 5.93-5.91 (m, 2H), 4.56-4.52 (m, 3H), 4.39 (s, 5H), 4.12 (s, 5H), 3.83-3.82 (m, 1H), 3.76 (s, 3H), 3.71-3.70 (m, 1H), 3.54-3.53 (m, 1H) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 151.3 (d, $J$ = 98.0 Hz), 150.0 (d, $J$ = 92.2 Hz), 147.3 (d, $J$ = 7.0 Hz), 147.2 (d, $J$ = 7.0 Hz), 137.0 (d, $J$ = 85.0 Hz), 136.6 (d, $J$ = 87.8 Hz), 132.8 (d, $J$ = 8.1 Hz), 132.7 (d, $J$ = 8.4 Hz), 130.4 (d, $J$ = 2.8 Hz), 127.9 (d, $J$ = 2.8 Hz), 127.7 (d, $J$ = 13.2 Hz), 122.3 (d, $J$ = 13.3 Hz), 122.1 (d, $J$ = 11.4 Hz), 111.4 (d, $J$ = 9.1 Hz), 111.1 (d, $J$ = 9.5 Hz), 98.5 (d, $J$ = 15.6 Hz), 96.3 (d, $J$ = 10.3 Hz), 75.9 (d, $J$ = 13.5 Hz), 74.5 (d, $J$ = 92.8 Hz), 74.9 (d, $J$ = 92.7 Hz), 74.4 (d, $J$ = 9.3 Hz), 74.4, 73.3 (d, $J$ = 13.5 Hz), 72.3 (d, $J$ = 10.9 Hz), 71.48, 71.47, 69.7 (d, $J$ = 11.6 Hz), 68.4 (d, $J$ = 10.6 Hz), 59.4 ppm.

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta$ = +44.04, +10.81 ppm.

IR (KBr-Pressling): $v_{\text{max}}$ (cm$^{-1}$) = 3436 (br, s), 1613 (m), 1436 (m), 1158 (m), 1101 (m), 1003 (m), 757 (s), 691 (s), 658 (m).

MS (70 eV, ESI): $m/z$ (%) = 826 (M$^+$, 27), 795 (100), 645 (55), 397 (7).

HRMS (EI): $m/z$ calcd. for: [C$_{36}$H$_{36}$Fe$_2$P$_2$O$_3$S$_2$] 826.0280, found: 826.0293.

($R_Fc$)-1-Diphenylphosphinothioyl-2-[α-methoxy-((R_Fc)-1-(diphenylphosphino))ferrocenyl]methylferrocene (11a)
A 25 mL Schlenk flask was charged with bisferrocenylether 71 (355 mg; 0.5 mmol) and THF (3 mL). The reaction mixture was cooled to -78 °C and nBuLi (1.6 M solution in pentane; 0.35 mL, 0.55 mmol, 1.1 equiv) and stirred for 15 min. Chlorodiphenylphosphine (168 mg; 0.15 mL, 0.75 mmol, 1.5 equiv) was added and at -78 °C and the reaction mixture was stirred for 1 h before warming to the room temperature. The reaction mixture was stirred at room temperature for 1 h and then sulfur (S₈; 160 mg; 5.0 mmol, 10 equiv) was added a solution in butylamine (2 mL) and the reaction mixture was stirred for 12 h at room temperature. Sat. Nh₄Cl was added to the reaction mixture and the aqueous layer was extracted with diethylether (4 x 15 mL). The combined organic layers were washed with water, brine, dried over MgSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-pentane:E₂O 4:1) to furnish bisphosphone sulfide 72 (323 mg, 0.38 mmol, 76%) as a yellow solid.

**Physical properties:**
- **MP:** 123.0-124.0 °C
- **[α]Dᵢ²⁰:** +17.6 (c = 0.2, acetone)

**1H-NMR (400 MHz, C₆D₆):**
δ = 7.80-7.71 (m, 2H), 7.62-7.39 (m, 6H), 7.15-7.05 (m, 12H), 5.63-5.61 (m, 1H), 4.34-4.29 (m, 2H), 3.95-3.94 (m, 2H), 3.91 (s, 5H), 3.80 (s, 8H), 3.67-3.66 (m, 1H), 2.99-2.96 (m, 1H) ppm.

**13C-NMR (150 MHz, C₆D₆):**
δ = 139.1 (d, J = 13.0 Hz), 137.2 (d, J = 12.1 Hz), 137.0 (d, J = 2.1 Hz), 136.5 (d, J = 13.0 Hz), 134.8 (d, J = 22.1 Hz), 132.0 (d, J = 11.8 Hz), 129.6 (d, J = 11.2 Hz), 129.0 (d, J = 22.1 Hz), 128.9 (d, J = 5.5 Hz), 128.6 (d, J = 21.8 Hz), 127.4 (d, J = 6.2 Hz), 126.2 (d, J = 22.6 Hz), 126.0 (d, J = 3.2 Hz), 122.1 (d, J = 3.4 Hz), 111.6 (d, J = 10.2 Hz), 106.0 (d, J = 10.5 Hz), 74.5 (d, J = 24.2 Hz), 74.0 (d, J = 22.9 Hz), 73.9 (d, J = 13.1 Hz), 73.5 (d, J = 12.9 Hz), 72.7 (d, J = 13.1 Hz), 72.2 (d, J = 5.6 Hz), 72.0 (d, J = 6.0 Hz), 71.0 70.5 (d, J = 14.9 Hz), 69.7, 69.2, 67.3 (d, J = 5.9 Hz), 67.1 (d, J = 4.2 Hz), 57.6 ppm

**31P-NMR (81 MHz, CDCl₃):**
δ = -19.58 (d, J = 7.6 Hz), -23.95 (d, J = 6.9 Hz) ppm.

**IR (KBr-Pressling):**
υmax (cm⁻¹) = 3436 (br, s), 3068 (w), 1629 (m), 1434 (m), 1107 (m), 1002 (m), 742 (s), 698 (s).

**MS (70 eV, EI):** m/z (%) = 782 (M⁺, 14), 717 (15), 630 (90), 446 (30), 445 (100), 379 (8).

**HRMS (EI):** m/z calcld. for: [C₄₆H₄₀Fe₂O₅P₂] 782.1253, found: 782.1241.

(R₆Fc)-1-Diphenylphosphino-2-[α-methoxy-((R,Fc)-1-(bis(2-furylphosphino))ferroceny)methylferrocene (11b)

Prepared according to TP5, using bisferrocenylsulfide 73 (165 mg; 0.20 mmol) in THF (2 mL) and Raney-Ni (Raney Ni in water; 704 mg; 12 mmol, 60 equiv) in MeOH (25 mL) and obtained the desired product 11b (130 mg, 0.17 mmol, 85%) as a yellow solid.

**Physical properties:**
- **MP:** 126.3-129.0 °C
- **[α]Dᵢ²⁰:** +27.0 (c = 0.2, acetone)
**Experimental Section**

**1H-NMR (600 MHz, C₆D₆):** \( \delta = 7.64 \) (t, \( J = 7.6 \) Hz, 2H), 7.51 (t, \( J = 7.3 \) Hz, 2H), 7.27 (d, \( J = 5.9 \) Hz, 2H), 7.13-7.04 (m, 7H), 6.84 (s, 1H), 6.14 (s, 1H), 6.04 (s, 1H), 5.67 (t, \( J = 4.7 \) Hz, 1H), 5.00 (s, 1H), 4.56 (s, 1H), 4.53 (s, 1H), 4.29-4.25 (m, 1H), 4.08 (s, 5H), 4.06 (s, 1H), 3.79-3.77 (s, 1H), 3.57 (s, 5H), 3.15 (s, 3H) ppm.

**13C-NMR (150 MHz, CDCl₃):** \( \delta = 154.0 \) (d, \( J = 12.9 \) Hz), 153.4 (d, \( J = 11.8 \) Hz), 146.3 (d, \( J = 1.9 \) Hz), 140.6 (d, \( J = 11.8 \) Hz), 139.2 (d, \( J = 13.0 \) Hz), 135.3 (d, \( J = 21.1 \) Hz), 133.8 (d, \( J = 19.9 \) Hz), 128.7 (d, \( J = 6.0 \) Hz), 128.2 (d, \( J = 6.9 \) Hz), 128.0 (d, \( J = 21.2 \) Hz), 120.7 (d, \( J = 29.3 \) Hz), 120.7 (d, \( J = 3.4 \) Hz), 110.8 (d, \( J = 8.5 \) Hz), 110.7 (d, \( J = 6.5 \) Hz), 101.7 (d, \( J = 33.0 \) Hz), 97.2 (d, \( J = 24.3 \) Hz), 76.1 (d, \( J = 13.4 \) Hz), 74.3 (d, \( J = 12.9 \) Hz), 74.2 (d, \( J = 13.0 \) Hz), 73.0 (d, \( J = 6.0 \) Hz), 72.3 (d, \( J = 2.2 \) Hz), 70.4 (d, \( J = 6.0 \) Hz), 70.3, 70.2, 69.2 (d, \( J = 15.2 \) Hz), 68.5 (d, \( J = 5.6 \) Hz), 65.9, 57.3 ppm.

**31P-NMR (81 MHz, CDCl₃):** \( \delta = -10.07 \), -17.68 ppm.

**IR (KBr-Pressling):** \( \nu_{max} (\text{cm}^{-1}) = 3436 \) (br, s), 3050 (m), 1630 (w), 1434 (m), 1251 (m), 1001 (m), 807 (s), 742 (s).

**MS (70 eV, EI):** \( m/z \) (%) = 752 (M⁺, 13), 689 (25), 688 (50), 687 (100), 656 (8).

**HRMS (EI):** \( m/z \) calcd. for: \( [\text{C}_{42}\text{H}_{38}\text{FeP}_{2}\text{S}_{2}\text{Si}] \) 752.1009, found: 752.1013.

**IR (KBr-Pressling):** \( \nu_{max} (\text{cm}^{-1}) = 3436 \) (br, m), 2926 (m), 1434 (m), 1154 (w), 1108 (m), 1085 (s), 817 (m), 744 (s), 698 (m).

**MS (70 eV, EI):** \( m/z \) (%) = 762 (M⁺, 27), 610 (13), 446 (35), 445 (100), 425 (23).

**HRMS (EI):** \( m/z \) calcd. for: \( [\text{C}_{42}\text{H}_{36}\text{FeP}_{2}\text{O}_{3}] \) 762.0838, found: 762.0821.

**10. Synthesis of new paracyclophane based diphosphines**

(R)-4-Bromo-12-diphenylphosphinothioyl[2.2]paracyclop hane (77):

![Structural diagram of 12-diphenylphosphinothioyl[2.2]paracyclop hane](image)

Dibromide 76 (1.83 g; 5.0 mmol) and THF (15 mL) were added to a 50 mL Schlenk flask under argon atmosphere. nBuLi (1.5 M in pentane; 3.70 mL, 5.50 mmol) was added slowly to the above solution at -78 °C and stirred for 1 h. ClPPh₂ (1.33 g; 6.0 mmol, 1.20 equiv) was added and stirred for 1 h at -78 °C. The reaction mixture was warned to room temperature and stirred for 1.5 h. Sulfur (1.60 g; 50.0 mmol, 10 equiv) was added to the reaction mixture and stirred for overnight at room temperature. The reaction mixture was quenched with a saturated NH₄Cl solution (20 mL) and the aqueous layer was extracted with CH₂Cl₂ (4 x 30 mL). The combined organic layers were washed with water, brine, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by flash chromatography (silicagel, n-pentane:Et₂O (10:1)), afforded the desired compound as a white solid (2.14 g; 4.25 mmol, 85%).

**MP:** 148.1-148.9 °C

\([\alpha]_{D}^{20} = -22.9 \) (c = 0.4, CH₂Cl₂)

**1H-NMR (600 MHz, CDCl₃):** \( \delta = 7.83-7.71 \) (m, 5H), 7.48-7.35 (m, 6H), 6.65-6.53 (m, 5H), 3.60-3.49 (m, 2H), 3.39-3.35 (m, 1H), 3.01-2.97 (m, 1H), 2.90-2.71 (m, 4H) ppm.

**13C-NMR (150 MHz, CDCl₃):** \( \delta = 145.0 \) (d, \( J = 8.6 \) Hz), 141.6, 138.6 (d, \( J = 13.0 \) Hz), 138.2, 136.9 (d, \( J = 3.1 \) Hz), 136.3, 135.5 (d, \( J = 11.8 \) Hz), 134.6 (d, \( J = 86.2 \) Hz), 133.4, 132.9 (d, \( J = 10.6 \) Hz), 132.8 (d, \( J = 11.8 \) Hz), 132.2 (d, \( J = 84.6 \) Hz), 131.9 (d, \( J = 10.2 \) Hz), 131.3 (d, \( J = 3.1 \) Hz), 131.2 (d, \( J = 3.0 \) Hz), 131.1, 128.1 (d, \( J = 12.4 \) Hz), 128.0, (d, \( J = 12.4 \) Hz), 127.8 (d, \( J = 87.2 \) Hz), 127.2, 35.4, 34.7 (d, \( J = 4.9 \) Hz), 33.7 (d, \( J = 1.1 \) Hz), 31.92 ppm.
Experimental Section

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta = +40.44$ ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3440 (br, w), 2912 (w), 1629 (s), 1425 (m), 1325 (m), 1102 (m), 789 (s), 656 (s).

MS (70 eV, EI): m/z (%) = 504 (37), 502 (M$^+$, 34), 321 (18), 320 (100), 319 (16), 209 (10), 183 (11).

HRMS (EI): m/z calcd. for: [C$_{28}$H$_{24}$79BrP$_3$S] 502.0520, found: 502.0512

(R)-4-Bis(3,5-dimethylphenyl)phosphinothioyl-12-diphenylphosphinothioyl[2.2]paracyclophane (78d)

Monophosphine sulfide 77 (755 mg; 1.50 mmol) and THF (5 mL) were added to a 25 mL Schlenk flask under argon atmosphere. nBuLi (1.5 M in pentane; 1.2 mL, 1.70 mmol) was added slowly to the above solution at -78 °C and stirred for 2 h. Chlorobis(3,5-dimethylphenyl)phosphine (500 mg; 1.80 mmol, 1.20 equiv) was added and stirred for 1 h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 1.5 h. Sulfur (482 mg; 15.0 mmol, 10 equiv) was added to the reaction mixture and stirred for overnight at room temperature. The reaction mixture was quenched with a sat. NH$_4$Cl solution (10 mL) and the aqueous layer was extracted with CH$_2$Cl$_2$ (4 x 15 mL). The combined organic layers were washed with water, brine, over MgSO$_4$ and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, npentane:Et$_2$O (5:1)), afforded the desired compound as a white solid (910 mg; 1.30 mmol, 87%).

MP: 291 °C

$[\alpha]_D^{20} = +20.9$ (c = 0.4, CH$_2$Cl$_2$)

$^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.96-7.93$ (m, 2H), 7.73-7.69 (m, 2H), 7.51-7.47 (m, 5H), 7.33-7.31 (m, 4H), 7.26-7.23 (m, 2H), 7.10-7.08 (m, 2H), 7.02 (brs, 1H), 6.72-6.69 (m, 2H), 6.66-6.63 (m, 2H), 3.42-3.47 (m, 2H), 3.33-3.26 (m, 2H), 2.86-2.80 (m, 2H), 2.71-2.66 (m, 2H), 2.31 (s, 6H), 2.23 (s, 6H) ppm

$^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta = 144.93$ (d, $J = 13.3$ Hz), 139.4 (d, $J = 13.2$ Hz), 137.5 (d, $J = 13.2$ Hz), 136.6 (d, $J = 3.6$ Hz), 136.5 (d, $J = 3.7$ Hz), 136.1 (d, $J = 11.7$ Hz), 135.9 (d, $J = 12.3$ Hz), 135.7 (d, $J = 83.3$ Hz), 135.0 (d, $J = 83.8$ Hz), 134.7 (d, $J = 11.8$ Hz), 134.4 (d, $J = 12.0$ Hz), 133.2 (d, $J = 10.5$ Hz), 133.0 (d, $J = 3.1$ Hz) 132.7 (d, $J = 3.5$ Hz), 131.6 (d, $J = 10.3$ Hz), 131.5 (d, $J = 84.8$ Hz), 131.2 (d, $J = 84.8$ Hz), 131.1 (d, $J = 3.1$ Hz), 130.9 (d, $J = 10.1$ Hz), 130.9 (d, $J = 2.8$ Hz), 129.3 (d, $J = 10.1$ Hz), 127.9 (d, $J = 12.5$ Hz), 127.8 (d, $J = 87.7$ Hz), 127.8 (d, $J = 12.5$ Hz), 127.7 (d, $J = 88.7$ Hz), 35.4 (t, $J = 5.2$ Hz), 35.8 (d, $J = 16.0$ Hz), 21.8 (d, $J = 0.9$ Hz), 21.5 (d, $J = 0.9$ Hz) ppm

$^{31}$P-NMR (81 MHz, CDCl$_3$): $\delta = +38.71, +38.39$ ppm.

IR (neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3441 (br, w), 2785 (w), 1594 (m), 1447 (m), 1389 (m), 1101 (m), 874 (s), 725 (s), 696 (s).

MS (70 eV, EI): m/z (%) = 696 (M$^+$, 45), 521 (28), 320 (100), 309 (12), 183 (21).

HRMS (EI): m/z calcd. for: [C$_{44}$H$_{42}$P$_2$32S$_2$] 696.2203, found: 696.2211

(R)-4-Bis(3,5-dimethylphenyl)phosphino-12-diphenylphosphino[2.2]paracyclophane (12d):
Prepared according to TP5, by using bisphosphinesulfide 78d (698 mg; 1.0 mmol) and Raney-Ni (3.8 g; Raney-Ni in water) in MeOH (60 mL) and the bisphosphine 13d was obtained as a white solid (583 mg; 0.92 mmol, 92%).

**MP:** 211.0-212.2 °C  
$[\alpha]_{D}^{20} = -22.4$ (c = 0.4, CH$_2$Cl$_2$)  
$^1$H-NMR (600 MHz, CDCl$_3$): δ = 7.47-7.44 (m, 2H), 7.41-7.36 (m, 5H), 7.24-7.20 (m, 5H), 7.04-7.02 (m, 3H), 6.65-6.63 (m, 1H), 6.57-6.48 (m, 6H), 3.02-2.89 (m, 6H), 2.63-2.54 (m, 2H), 2.35 (s, 6H), 2.18 (s, 6H) ppm.  
$^{13}$C-NMR (150 MHz, CDCl$_3$): δ = 143.3 (d, $J = 14.7$ Hz), 143.1 (d, $J = 15.1$ Hz), 139.5 (d, $J = 12.1$ Hz), 139.4 (d, $J = 13.9$ Hz), 139.3 (d, $J = 6.1$ Hz), 138.9 (d, $J = 7.1$ Hz), 138.2 (d, $J = 12.2$ Hz), 138.1 (d, $J = 12.6$ Hz), 137.5 (d, $J = 17.5$ Hz), 137.4 (d, $J = 16.9$ Hz), 137.3 (d, $J = 7.9$ Hz), 137.2 (d, $J = 8.7$ Hz), 135.9 (d, $J = 0.9$ Hz), 135.7 (d, $J = 0.9$ Hz), 134.2 (d, $J = 6.8$ Hz), 134.1 (d, $J = 6.1$ Hz), 133.4 (d, $J = 22.8$ Hz), 133.3 (d, $J = 22.8$ Hz), 133.0 (d, $J = 20.4$ Hz), 132.7 (d, $J = 8.7$ Hz), 132.3 (d, $J = 6.8$ Hz), 131.3 (d, $J = 1.1$ Hz), 130.6 (d, $J = 20.9$ Hz), 130.3 (d, $J = 0.9$ Hz), 129.3 (d, $J = 0.8$ Hz), 128.5 (d, $J = 0.8$ Hz), 128.3 (d, $J = 22.7$ Hz), 128.2 (d, $J = 22.0$ Hz), 35.8 (d, $J = 18.7$ Hz), 35.7 (d, $J = 19.0$ Hz), 33.2 (d, $J = 2.6$ Hz), 33.0 (d, $J = 2.5$ Hz), 21.4, 21.2 ppm.  
$^{31}$P-NMR (81 MHz, CDCl$_3$): δ = 0.69, 0.03 ppm  
IR(neat): $\nu_{\text{max}}$ (cm$^{-1}$) = 3444 (br, w), 2019 (w), 1655 (s), 1450 (s), 1210 (s), 876 (s), 765 (m), 667 (m), 586 (m).  
MS (70 eV, EI): $m/z$ (%) = 632 ($M^+$, 14), 428 (32), 320 (100), 309 (11).  
HRMS (EI): $m/z$ calcd. for: [C$_{44}$H$_{42}$P$_2$] 632.2762, found: 632.2777  

11. Preparation of ruthenium-diamine complexes 79a-c and 80a-c

Prepartation of ruthenium-diamine complexes of 12b

Preparation of the ruthenium complex 79a:

Prepared according to TP10, using the ligand 12b (25 mg; 0.041 mmol; 1.0 equiv), [RuCl(C$_6$H$_5$)$_2$]$_2$ (9.4 mg; 0.021 mmol) and (S,S)-1,2-diphenylethylenediamine (8.9 mg; 0.041 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

$^1$H-NMR (200 MHz, CDCl$_3$): 8.45-7.82 (m, 21H), 7.32-6.44 (m, 13 H), 4.50-3.51 (m, 5H), 2.53-1.80 (m, 9H) ppm.
**Preparation of the ruthenium complex 80a:**

Prepared according to **TP10**, using the ligand 12b (25 mg; 0.041 mmol; 1.0 equiv), [RuCl(C₆H₆)₂] (9.4 mg; 0.021 mmol) and (S,S)-1,2-diphenylethylenediamine (8.9 mg; 0.041 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

**1H-NMR (200 MHz, CDCl₃):** 8.54-8.00 (m, 20H), 7.50-6.65 (m, 14H), 4.55-3.55 (m, 5H), 2.60-2.48 (m, 4H), 2.10-1.88 (m, 5H) ppm.

**31P-NMR (81 MHz, CDCl₃):** +43.65 (d, J = 25.0 Hz), +40.36 (d, J = 25.2 Hz) ppm.

**Preparation of ruthenium-diamine complexes of 12c**

**Preparation of the ruthenium complex 79c:**

Prepared according to **TP10**, using the ligand 12c (20 mg; 0.024 mmol; 1.0 equiv), [RuCl(C₆H₆)₂] (5.5 mg; 0.012 mmol) and (S,S)-1,2-diphenylethylenediamine (5.2 mg; 0.024 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

**1H-NMR (200 MHz, CDCl₃):** 8.55-8.08 (m, 12H), 8.00-7.95 (m, 4H), 7.75-6.60 (m, 14H), 6.60-6.51 (m, 2H), 4.48-4.30 (m, 2H), 2.85-2.46 (m, 6H), 1.81-1.64 (m, 6H) ppm.

**31P-NMR (81 MHz, CDCl₃):** +48.16 (d, J = 28.9 Hz), +45.79 (d, J = 27.0 Hz) ppm.

**Preparation of the ruthenium complex 80b:**

Prepared according to **TP10**, using the ligand 12c (20 mg; 0.024 mmol; 1.0 equiv), [RuCl(C₆H₆)₂] (5.5 mg; 0.012 mmol) and (S,S)-1,2-diphenylethylenediamine (5.2 mg; 0.024 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

**1H-NMR (200 MHz, CDCl₃):** 8.55-8.08 (m, 12H), 8.00-7.95 (m, 4H), 7.75-6.60 (m, 14H), 6.60-6.51 (m, 2H), 4.48-4.30 (m, 2H), 2.85-2.46 (m, 6H), 1.81-1.64 (m, 6H) ppm.

**31P-NMR (81 MHz, CDCl₃):** +48.16 (d, J = 28.9 Hz), +45.79 (d, J = 27.0 Hz) ppm.
Prepared according to TP10, using the ligand 12c (20 mg; 0.024 mmol; 1.0 equiv), [RuCl(C₆H₆)₂] (5.5 mg; 0.012 mmol) and (S,S)-1,2-diphenylethylenediamine (5.2 mg; 0.024 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

1H-NMR (200 MHz, CDCl₃): 8.68-7.98 (m, 16H), 7.80-6.90 (m, 14H), 6.66-6.54 (m, 2H), 4.55-4.38 (m, 2H), 3.01-2.67 (m, 4H), 2.60-2.55 (m, 2H), 2.00-1.60 (m, 6H) ppm.

31P-NMR (81 MHz, CDCl₃): +46.10 (d, J = 26.1 Hz), +43.20 (d, J = 26.2 Hz) ppm.

Preparation of ruthenium-diamine complexes of 12d

Preparation of the ruthenium complex 79c:

Prepared according to TP10, using the ligand 12d (50 mg; 0.07 mmol; 1.0 equiv), [RuCl(C₆H₆)₂] (16 mg; 0.035 mmol) and (R,R)-1,2-diphenylethylenediamine (15 mg; 0.07 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

1H-NMR (200 MHz, CDCl₃): 8.46-8.20 (m, 3H), 8.01-7.45 (m, 3H), 7.40-7.25 (m, 4H), 7.20-7.11 (m, 7H), 7.00-6.85 (m, 7H), 6.70-6.68 (m, 1H), 6.60-6.58 (m, 1H), 6.50-6.39 (m, 6H), 4.50-4.48 (m, 1H), 4.11-4.10 (m, 1H), 2.76-2.69 (m, 2H), 2.62-2.50 (m, 2H), 2.29 (s, 6H), 2.12 (s, 6H), 1.94-1.87 (m, 2H), 1.71-1.66 (m, 2H).

31P-NMR (81 MHz, CDCl₃): +48.16 (d, J = 28.9 Hz), +44.79 (d, J = 27.0 Hz) ppm.

Preparation of the ruthenium complex 80c:

Prepared according to TP10, using the ligand 12d (50 mg; 0.07 mmol; 1.0 equiv), [RuCl(C₆H₆)₂] (16 mg; 0.035 mmol) and (S,S)-1,2-diphenylethylenediamine (15 mg; 0.07 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

1H-NMR (200 MHz, CDCl₃): 8.36-8.34 (m, 2H), 8.30-8.26 (m, 1H), 8.10-8.05 (m, 1H), 8.00-7.92 (m, 1H), 7.40-7.25 (m, 4H), 7.20-7.10 (m, 8H), 7.05-6.90 (m, 7H), 6.76 (s, 1H), 6.60-6.54 (m, 2H), 6.47-6.36 (m, 5H), 4.50-4.48 (m, 1H), 4.19-4.12 (m, 1H), 2.86-2.70 (m, 2H), 2.60-2.55 (m, 2H), 2.23 (s, 6H), 2.02 (s, 6H), 1.95-1.86 (m, 2H), 1.71-1.66 (m, 2H) ppm.

31P-NMR (81 MHz, CDCl₃): +47.46 (d, J = 28.1 Hz), +44.19 (d, J = 27.1 Hz) ppm.
12. Asymmetric hydrogenation of ketones and olefins

(R)-1-Phenylethanol (82a):

\[
\text{\[
\begin{array}{c}
\text{OH} \\
\text{CH}_2
\end{array}
\]
}
\]

\([\alpha]_{D}^{20} = +40.4 \text{ (c = 1.0, CHCl}_3\text{)}\]
\(^1\text{H-NMR (300 MHz, CDCl}_3\text{): } \delta = 7.20-7.29 \text{ (m, 5H), 4.66 (q, J = 6.5 Hz, 1H), 2.80 (brs, 1H), 1.30 (d, J = 6.4 Hz, 1H) ppm.}\]
\(^1\text{C-NMR (75 MHz, CDCl}_3\text{):} \delta = 146.4, 128.8, 127.7, 125.9, 70.6, 25.6 \text{ ppm.}\]
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 30 °C/min 160 °C (30 min)); 8.5 min (R), 8.9 (S). 97% ee.

(R)-1-(4-Methoxyphenyl)ethanol (82b):

\[
\text{\[
\begin{array}{c}
\text{OH} \\
\text{MeO}
\end{array}
\]
}
\]

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 4-methoxy-acetophenone 81b (600 mg; 4.0 mmol) and obtained as colourless oil (584 mg; 3.84 mmol, 96%)

\([\alpha]_{D}^{20} = +43.6 \text{ (c = 1.0, CHCl}_3\text{)}\]
\(^1\text{H-NMR (300 MHz, CDCl}_3\text{): } \delta = 7.31-7.26 \text{ (m, 2H), 6.89-6.86 (m, 2H), 4.84 (q, J = 6.4Hz, 1H), 3.79 (s, 3H), 1.47 (d, J = 6.4 Hz, 3H), 1.83 (brs, 1H) ppm.}\]
\(^1\text{C-NMR (75 MHz, CDCl}_3\text{):} \delta = 159.0, 138.0, 126.6, 113.8, 69.9, 55.3, 25.0 \text{ ppm.}\]
Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (60 min), Const.); 26.0 min (R), 30.0 (S). 96% ee.

(R)-1-(3-Methylphenyl)ethanol (82c):

\[
\text{\[
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\]
}
\]

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3- methyl-acetophenone 81c (537 mg; 0.54 mL, 4.0 mmol) and obtained as colourless oil (523 mg; 3.84 mmol, 96%)

\([\alpha]_{D}^{20} = +64.2 \text{ (c= 1.0, CHCl}_3\text{)}\]
\(^1\text{H-NMR (300 MHz, CDCl}_3\text{): } \delta = 7.27-7.22 \text{ (m, 1H), 7.19-7.15 (m, 2H), 7.08 (d, J = 7.5 Hz, 1H), 4.85 (q, J = 6.5 Hz, 1H), 2.36 (s, 3H), 1.88 (s, 1H), 1.48 (d, J = 6.5 Hz, 3H) ppm.}\]
\(^1\text{C-NMR (75 MHz, CDCl}_3\text{):} \delta = 145.8, 138.1, 128.4, 128.2, 126.1, 122.4, 70.4, 25.1, 21.4 \text{ ppm.}\]
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 30 °C/min 160 °C (30 min)); 9.5 min (R), 9.7 (S). 97% ee.

(R)-1-(2-Methylphenyl)ethanol (82d):

![Structure](image)

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 81d (537 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (534 mg; 3.92 mmol, 98%)

\[ \alpha \]_D^20 = +48.2 (c = 1.0, CHCl_3)

¹H-NMR (300 MHz, CDCl_3): \( \delta = 7.52-7.49 \) (m, 1H), 7.26-7.21 (m, 1H), 7.19-7.13 (m, 2H), 5.12 (q, \( J = 6.4 \) Hz, 1H), 2.34 (s, 3H), 1.82 (s, 1H), 1.46 (d, \( J = 6.4 \) Hz, 3H) ppm.

¹³C-NMR (75 MHz, CDCl_3): \( \delta = 143.8, 134.2, 130.3, 127.1, 126.3, 124.4, 66.8, 23.9, 18.9 \) ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (30 min)); 20.1 min (R), 22.1 (S). 94% ee.

(R)-1-(3-Methoxyphenyl)ethanol (82e):

![Structure](image)

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3- methoxy-acetophenone 81e (601 mg; 0.55 mL, 4.0 mmol) and obtained as colourless oil (584 mg; 3.84 mmol, 96%)

\[ \alpha \]_D^20 = +54.8 (c = 1.0, CHCl_3)

¹H-NMR (300 MHz, CDCl_3): \( \delta = 7.29 \) (d, \( J = 8.2 \) Hz, 1H), 6.97-6.95 (m, 2H), 6.83 (dddd, \( J = 1.0 \) Hz, 2.6 Hz, 8.2 Hz, 1H), 4.88 (q, \( J = 6.5 \) Hz, 1H), 3.83 (s, 3H), 2.00 (brs, 1H), 1.50 (d, \( J = 6.5 \) Hz, 3H) ppm.

¹³C-NMR (75 MHz, CDCl_3): \( \delta = 159.7, 147.6, 129.5, 117.6, 112.8, 110.1, 70.3, 55.2, 25.1 \) ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (60) const; 29.8 min (R), 34.7 (S). 97% ee.

(R)-1-(3-Chlorophenyl)ethanol (82f):
Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3- chloro-acetophenone 81f (618 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (601 mg; 3.84 mmol, 96%) 

\[\alpha\]_D^20 = +42.4 (c = 1.0, CHCl_3) 

\[^1\text{H-NMR} (300\ \text{MHz, CDCl}_3): \delta = 7.37-7.36\ (m, 1H), 7.26-7.21\ (m, 3H), 4.89-4.82\ (m, 1H), 1.98\ (d, J = 3.5\ Hz, 1H), 1.47\ (d, J = 6.5\ Hz, 3H)\ ppm.\]

\[^{13}\text{C-NMR} (75\ \text{MHz, CDCl}_3): \delta = 147.8, 134.3, 129.7, 127.5, 125.6, 123.5, 69.8, 25.2\ ppm.\]

Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (10 min), 50 °C/min 160 °C (30 min)); 12.9 min (R), 13.2 (S). 97% ee.

(R)-1-(4-Chlorophenyl)ethanol (82g):

\[\alpha\]_D^20 = +26.8 (c = 1.0, CHCl_3) 

\[^1\text{H-NMR} (300\ \text{MHz, CDCl}_3): \delta = 7.30-7.28\ (m, 2H), 6.90-6.87\ (m, 2H), 4.82\ (q, J = 6.7\ Hz, 1H), 1.24\ (brs, 1H), 1.30\ (d, J = 6.8\ Hz, 3H)\ ppm.\]

\[^{13}\text{C-NMR} (75\ \text{MHz, CDCl}_3): \delta = 158.2, 136.5, 124.8, 112.1, 68.2, 24.5\ ppm.\]

Enantiomeric excess was determined by chiral GC using DEX-CB column (130 °C (60 min), Const.); 9.2 min (R), 10.7 (S). 96% ee.

(R)-1-(4-Trifluoromethylphenyl)ethanol (82h):

\[\alpha\]_D^20 = +34.9 (c = 1.0, CHCl_3) 

\[^1\text{H-NMR} (300\ \text{MHz, CDCl}_3): \delta = 7.61-7.59\ (m, 2H), 7.49-7.46\ (m, 2H), 4.98-4.91\ (m, 1H), 1.98\ (d, J = 3.3\ Hz, 1H), 1.49\ (d, J = 6.3\ Hz, 3H)\ ppm.\]

\[^{13}\text{C-NMR} (75\ \text{MHz, CDCl}_3): \delta = 149.7\ (q, J = 1.4\ Hz), 129.6\ (q, J = 32.3\ Hz), 125.6, 125.4\ (q, J = 3.9\ Hz), 124.1\ (q, J = 271.6\ Hz), 69.8, 25.4\ ppm.\]

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 30 °C/min 160 °C (30 min)); 9.3 min (R), 9.7 (S). 94% ee.

(R)-1-(3-Fluorophenyl)ethanol (82i):
Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3- fluoro-acetophenone 81i (552 mg; 0.49 mL, 4.0 mmol) and obtained as colourless oil (532 mg; 3.80 mmol, 95%)

\[ \alpha_d^{20} = +42.4 \ (c = 1.0, \text{CHCl}_3) \]

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.23-7.19 \) (m, 1H), 7.05-7.00 (m, 2H), 6.90-6.85 (m, 1H), 4.81 (q, \( J = 6.5 \) Hz, 1H), 1.96 (brs, 1H), 1.40 (d, \( J = 6.5 \) Hz, 3H) ppm.

\(^13\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 163.0 \) (d, \( J = 246.1 \) Hz), 148.5 (d, \( J = 6.4 \) Hz), 129.9 (d, \( J = 7.7 \) Hz), 120.9 (d, \( J = 2.6 \) Hz), 114.2 (d, \( J = 21.2 \) Hz), 112.3 (d, \( J = 21.2 \) Hz), 69.7 (d, \( J = 2.1 \) Hz), 25.2 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (10 min), 50 °C/min 160 °C (20 min)); 8.5 min (\( R \)), 10.1 (\( S \)). 96% ee.

\((R)\)-1-(1'-Naphtyl)ethanol (82j):

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 81j (681 mg; 0.61 mL, 4.0 mmol) and obtained as colourless oil (661 mg; 3.84 mmol, 96%)

\[ \alpha_d^{20} = +68.8 \ (c = 1.0, \text{CHCl}_3) \]

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 8.13-8.12 \) (m, 1H), 7.89-7.86 (m, 1H), 7.77 (d, \( J = 8.2 \) Hz, 1H), 7.67 (d, \( J = 7.2 \) Hz, 1H), 7.55-7.45 (m, 3H), 5.70-5.62 (m, 1H), 2.02 (d, \( J = 2.8 \) Hz, 1H), 1.67 (d, \( J = 6.57 \) Hz, 3H) ppm.

\(^13\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 141.3, 133.8, 130.2, 128.9, 127.9, 126.0, 125.6, 125.5, 123.1, 122.0, 67.1, 24.3 \) ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (115 °C (15 min), 15 °C/min 160 °C (60 min)); 26.8 min (\( S \)), 27.4 (\( R \)). 96% ee.

\((R)\)-1-(2'-Naphthyl)ethanol (82k):

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 1- naphthyl-acetophenone 81k (681 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (675 mg; 3.92 mmol, 98%)
Experimental Section

\[ \alpha_{D}^{20} = +60.4 \ (c = 1.0, \text{CHCl}_3) \]

\[^1\text{H}-\text{NMR} \ (300 \text{ MHz, CDCl}_3): \delta = 7.84-7.80 \ (m, \ 4\text{H}), 7.51-7.44 \ (m, \ 3\text{H}), 5.05 \ (q, J = 6.5 \text{ Hz, } 1\text{H}), 1.98 \ (\text{brs, } 1\text{H}), 1.58 \ (d, J = 6.2 \text{ Hz, } 3\text{H}) \ \text{ppm.} \]

\[^{13}\text{C}-\text{NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 143.2, \ 133.3, \ 132.9, \ 128.3, \ 127.9, \ 127.6, \ 126.1, \ 125.8, \ 123.8, \ 123.7, \ 70.5, \ 25.1 \ \text{ppm.} \]

Enantiomeric excess was determined by chiral GC using DEX-CB column (115 °C (15 min), 15 °C/min 160 °C (60 min)); 25.5 min (R), 26.3 (S). 97% ee.

(R)-1-(4-Phenylphenyl)ethanol (82l):

\[
\begin{align*}
\text{Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 4-phenyl-acetophenone 81l (785 mg; 4.0 mmol) and obtained as colourless oil (769 mg; 3.88 mmol, 97%)}
\end{align*}
\]

\[ \alpha_{D}^{20} = +51.0 \ (c = 1.0, \text{CHCl}_3) \]

\[^1\text{H}-\text{NMR} \ (300 \text{ MHz, CDCl}_3): \delta = 7.60-7.57 \ (m, \ 4\text{H}), 7.46-7.41 \ (m, \ 4\text{H}), 7.37-7.32 \ (m, \ 1\text{H}), 4.95 \ (q, J = 6.5 \text{ Hz, } 1\text{H}), 1.87 \ (\text{brs, } 1\text{H}), 1.54 \ (d, J = 6.5 \text{ Hz, } 3\text{H}) \ \text{ppm.} \]

\[^{13}\text{C}-\text{NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 144.8, \ 140.8, \ 140.4, \ 128.7, \ 127.2, \ 127.1, \ 125.8, \ 70.1, \ 25.1 \ \text{ppm.} \]

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 5 °C/min 160 °C (60 min)); 40.6 min (R), 42.7 (S). 94% ee.

(R)-1-Phenylpropanol (84a):

\[
\begin{align*}
\text{Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and propiophenone 83a (537 mg; 4.0 mL, 4.0 mmol) and obtained as colourless oil (523 mg; 3.84 mmol, 96%)}
\end{align*}
\]

\[ \alpha_{D}^{20} = +32.4 \ (c = 1.0, \text{CHCl}_3) \]

\[^1\text{H}-\text{NMR} \ (300 \text{ MHz, CDCl}_3): \delta = 7.36-7.26 \ (m, \ 5\text{H}), 4.60 \ (t, J = 6.5 \text{ Hz, } 1\text{H}), 1.94 \ (\text{brs, } 1\text{H}), 1.84-1.76 \ (m, \ 2\text{H}), 0.93 \ (t, J = 6.5 \text{ Hz, } 3\text{H}) \ \text{ppm.} \]

\[^{13}\text{C}-\text{NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 144.6, \ 128.4, \ 127.4, \ 125.9, \ 76.0, \ 31.9, \ 10.1 \ \text{ppm.} \]

Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (60 min), Const.); 11.9 min (R), 13.2 (S). 97% ee.

(R)-1-Phenylpentanol (84b):
Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 83b (649 mg; 0.66 mL, 4.0 mmol) and obtained as a colourless oil (624 mg; 3.80 mmol, 95%) 

\[ \alpha D^{20} = +28.9 \text{ (c = 1.0, CHCl}_3\rangle 

\text{H-NMR (300 MHz, CDCl}_3\rangle: \delta = 7.31-7.29 \text{ (m, 4H), 7.25-7.21} \text{ (m, 1H), 4.61 (t, J = 7.2 Hz, 1H), 1.84 (brs, 1H), 1.78-1.62 (m, 2H), 1.38-1.16 (m, 4H), 0.85 (t, J = 7.1 Hz, 3H) ppm.}

\text{C-NMR (75 MHz, CDCl}_3\rangle: \delta = 144.9, 128.4, 127.4, 125.9, 74.7, 38.8, 28.0, 22.6, 14.0 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (45)); 24.3 min (S), 24.4 (R). 97% ee.

(R)-1-Phenylhexanol (84c):

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 83c (713 mg; 4.0 mmol) and obtained as a colourless oil (714 mg; 3.84 mmol, 96%)

\[ \alpha D^{20} = +36.0 \text{ (c = 1.0, CHCl}_3\rangle 

\text{H-NMR (300 MHz, CDCl}_3\rangle: \delta = 7.34-7.24 \text{ (m, 5H), 4.63-4.62 (m, 1H), 1.86 (d, J = 3.1 Hz, 1H), 1.79-1.60 (m, 2H), 1.45-1.27 (m, 6H), 0.89-0.84 (m, 3H) ppm.}

\text{C-NMR (75 MHz, CDCl}_3\rangle: \delta = 145.0, 128.4, 127.4, 125.9, 74.5, 39.1, 31.7, 25.5, 22.5, 14.0 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (45)); 26.6 min (S), 26.7 (R). 94% ee.

(R)-1,3-Diphenylpropanol (84d):

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 83d (841 mg; 4.0 mmol) and obtained as colourless oil (815 mg; 3.84 mmol, 96%)

\[ \alpha D^{20} = +41.2 \text{ (c = 1.0, CHCl}_3\rangle 

\text{H-NMR (300 MHz, CDCl}_3\rangle: \delta = 7.36-7.19 \text{ (m, 10H), 4.72-4.66 (m, 1H), 2.20-1.98 (m, 2H), 1.90 (d, J = 3.6 Hz, 1H) ppm.}

\text{C-NMR (75 MHz, CDCl}_3\rangle: \delta = 144.5, 141.7, 128.5, 128.4, 128.3, 127.6, 125.9, 125.8, 73.9, 40.4, 32.0 ppm.
Enantiomeric excess was determined by chiral HPLC using a chiracel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 22.7 min [minor], t_r = 25.5 min [major]; 90% ee.

(R)-1-Phenyl-2-methylpropanol (84e):

\[
\text{\includegraphics[width=0.1\textwidth]{phenyl-methyl-propanol}}
\]

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 83e (593 mg; 0.60 mL, 4.0 mmol) and obtained as colourless oil (541 mg; 3.60 mmol, 90%)

\[\alpha\]_D\text{^20} = +12.8 (c = 1.0, CHCl_3)

\text{1H-NMR (300 MHz, CDCl}_3\text{): } \delta = 7.35-7.23 (m, 5H), 4.34 (d, J = 7.1 Hz, 1H), 1.98-1.89 (m, 2H), 0.99 (d, J = 7.0 Hz, 3H), 0.79 (d, J = 7.0 Hz, 3H) ppm.

\text{13C-NMR (75 MHz, CDCl}_3\text{): } \delta = 143.6, 128.1, 127.3, 126.5, 80.0, 35.2, 19.0, 18.2 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (30 min), 5 °C/min 160 °C (45)); 17.9 min (R), 18.6 (S). 38% ee.

(R)-(E)-4-Phenyl-3-buten-2-ol (86a):

\[
\text{\includegraphics[width=0.1\textwidth]{phenyl-butenol}}
\]

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 85a (585 mg; 4.0 mmol) and obtained as colourless oil (563 mg; 3.80 mmol, 90%)

\[\alpha\]_D\text{^20} = +36.8 (c=1.0, CHCl_3)

\text{1H-NMR (300 MHz, CDCl}_3\text{): } \delta = 7.41-7.30 (m, 4H), 7.28-7.22 (m, 1H), 6.58 (dd, J = 0.9 Hz, 15.9 Hz, 1H), 6.27 (dd, J = 6.4 Hz, 15.8 Hz, 1H), 4.55-4.46 (m, 1H), 1.71 (brs, 1H), 1.39 (d, J = 6.4 Hz, 3H) ppm.

\text{13C-NMR (75 MHz, CDCl}_3\text{): } \delta = 136.7, 133.5, 129.4, 128.5, 127.6, 126.4, 68.9, 23.4 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (115 °C (20 min), 5 °C/min 160 °C (30)); 18.8 min (R), 19.7 (S). 94% ee.

(R)-(E)-1,3-Diphenyl-2-propen-1-ol (86b):

\[
\text{\includegraphics[width=0.1\textwidth]{diphenyl-propenol}}
\]

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 85b (833 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (816 mg; 3.88 mmol, 98%)
[α]D \textsuperscript{20} = +2.0 (c = 1.0, CHCl\textsubscript{3})

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): δ = 7.46-7.21 (m, 10H), 6.69 (d, J = 0.9 Hz, 15.8 Hz, 1H), 6.38 (d, J = 6.4 Hz, 15.8 Hz, 1H), 5.38 (d, J = 6.4 Hz, 1H), 2.12 (brs, 1H) ppm.

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): δ = 142.7, 136.5, 131.5, 130.5, 128.6, 128.5, 127.8, 127.7, 126.6, 126.3, 75.1 ppm.

Enantiomeric excess was determined by chiral HPLC using a chiral OD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t\textsubscript{r} = 14.8 min [minor], t\textsubscript{r} = 19.1 min [major]; 37% ee.

(R)-1-(3-Pyridyl)ethanol (88):

\[
\begin{align*}
\text{OH} & \\
\text{N} & \\
\end{align*}
\]

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 87 (484 mg; 0.44 mL, 4.0 mmol) and obtained as colourless oil (483 mg; 3.92 mmol, 98%)

[α]D \textsuperscript{20} = +21.8 (c = 1.0, CHCl\textsubscript{3})

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): δ = 8.50-8.42 (m, 2H), 7.71 (tt, J = 7.9 Hz, 1.7 Hz, 1H), 7.27-7.23 (m, 1H), 4.91 (q, J = 6.6 Hz, 1H), 2.98 (brs, 1H), 1.49 (d, J = 6.5 Hz, 3H) ppm.

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): δ = 148.4, 147.2, 141.3, 133.3, 123.5, 67.8, 25.2 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (40 °C (15 min), 3 °C/min 160 °C (60 min)); 45.8 min (R), 46.8 (S). 96% ee.

(R)-1-(2-Thienyl)ethanol (90):

\[
\begin{align*}
\text{OH} & \\
\text{S} & \\
\end{align*}
\]

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 89 (505 mg; 0.43 mL, 4.0 mmol) and obtained as colourless oil (502 mg; 3.92 mmol, 98%)

[α]D \textsuperscript{20} = +16.4 (c = 1.0, CHCl\textsubscript{3})

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): δ = 7.22 (dd, J = 1.6 Hz, 4.6 Hz, 1H), 6.98-6.94 (m, 2H), 5.16-5.08 (m, 1H), 2.06 (brs, 1H), 1.59 (d, J = 6.4 Hz, 3H) ppm.

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}): δ = 149.8, 126.6, 124.4, 123.1, 66.2, 25.2 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (60 min)); 12.4 min (R), 14.5 (S). 92% ee.

(R)-1-Ferrocenylethanol (92):
Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone 91 (912 mg; 4.0 mmol) and obtained as colourless oil (865 mg; 3.76 mmol, 94%)

\[ [\alpha]_D^{20} = -30.2 \ (c = 1.0, \text{CHCl}_3) \]

$^1$H-NMR (300 MHz, CDCl$_3$): \( \delta = 4.58-4.50 \) (m, 1H), 4.22-4.20 (m, 2H), 4.18 (s, 5H), 4.15 (t, \( J = 1.9 \) Hz, 2H), 1.85 (d, \( J = 4.7 \) Hz, 1H), 1.43 (d, \( J = 6.3 \) Hz, 1H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): \( \delta = 94.5, 68.3, 67.9, 67.8, 66.1, 66.1, 65.6, 23.7 \) ppm.

Enantiomeric excess was determined by chiral HPLC using a chiracel OJ column (flow rate 0.6 mL/min, heptane/iPrOH: 95/5, \( \lambda = 215 \) nm, 25 °C); \( t_R = 34.8 \) min [major], \( t_R = 37.2 \) min [minor]; 94% ee.

1-(3', 4'-Dichlorophenyl)ethanol (94a)$^{142}$:

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3,4-dichloroacetophenone 93a (756 mg; 4.0 mmol) and obtained as colourless oil (745 mg; 3.92 mmol, 98%)

\[ [\alpha]_D^{20} = +35.8 \ (c = 1.0, \text{CHCl}_3) \]

$^1$H-NMR (300 MHz, CDCl$_3$): \( \delta = 7.45 \) (d, \( J = 2.1 \) Hz, 1H), 7.39 (d, \( J = 8.3 \) Hz, 1H), 7.18 (ddddd, \( J = 0.6 \) Hz, 2.1 Hz, 8.3 Hz, 1H), 4.84 (q, \( J = 6.5 \) Hz, 1H), 1.91 (brs, 1H), 1.45 (d, \( J = 6.6 \) Hz, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): \( \delta = 146.0, 132.5, 131.2, 130.4, 127.5, 124.7, 69.2, 25.3 \) ppm.

MS (70 eV, EI): \( m/z \) (%) = 190 (M$^+$, 35), 175 (100), 147 (47), 111 (70).

HRMS (EI): \( m/z \) calcd. for: [C$_8$H$_8$OCl$_2$] 189.9952, found: 189.9953

Enantiomeric excess was determined by chiral GC using DEX-CB column (160 °C (60 min), const.); 6.6 min (R), 7.1 (S). 97% ee.

1-(3', 4'-Dioxymethylene-phenyl)ethanol (94b)$^{143}$:
Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3,4-dioxymethyleneacetophenone 93b (657 mg; 4.0 mmol) and obtained as colourless oil (625 mg; 3.76 mmol, 94%)

\[ \alpha_D^20 = +42.6 \ (c = 1.0, \text{CHCl}_3) \]

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 6.87 (d, $J = 1.8$ Hz, 1H), 6.80 (dddd, $J = 0.5$ Hz, 1.8 Hz, 8.0 Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 5.92 (s, 2H), 6.80 (q, $J = 6.4$ Hz, 1H), 1.90 (brs, 1H), 1.44 (d, $J = 6.40$ Hz, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 147.7, 146.8, 139.9, 118.6, 108.0, 106.0, 100.9, 70.2, 25.1 ppm.

MS (70 eV, EI): $m/z$ (%) = 166 (M$^+$, 71), 151 (97), 148 (12), 123 (27), 93 (100).

HRMS (EI): $m/z$ calcd. for: [C$_9$H$_{10}$O$_3$] 166.0630, found: 166.0623

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 5 °C/min 160 °C (60)); 19.7 min (R), 20.1 (S). 90% ee.

1-(3', 4'-Dimethylphenyl)ethanol (94c)$^{144}$:

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3,4-dimethyl-acetophenone 93c (593 mg; 0.59 mL, 4.0 mmol) and obtained as colourless oil (583 mg; 3.88 mmol, 97%)

\[ \alpha_D^20 = +50.0 \ (c = 1.0, \text{CHCl}_3) \]

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.15 (brs, 1H), 7.12-7.09 (m, 2H), 4.84 (q, $J = 6.7$ Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.85 (brs, 1H), 1.48 (d, $J = 6.4$ Hz, 3H) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 143.3, 136.6, 135.7, 129.7, 126.7, 122.7, 70.2, 25.0, 19.8, 19.4 ppm.

MS (70 eV, EI): $m/z$ (%) = 150 (M$^+$, 43), 135 (82), 107 (100), 91 (49).

HRMS (EI): $m/z$ calcd. for: [C$_{10}$H$_{14}$O] 150.1045, found: 150.1035

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 5 °C/min 160 °C (60)); 15.4 min (R), 15.7 (S). 96% ee.

1-(3', 4'-Di´methoxyphenyl)ethanol (94d)$^{145}$:

Prepared according to the typical procedure TP11, using ruthenium catalysts 80c (2.1 mg; 0.002 mmol) and 3,4-dimethoxy-acetophenone 93d (721 mg; 4.0 mmol) and obtained as colourless oil (714 mg; 3.92 mmol, 98%)

\[ \alpha_D^20 = +49.6 \ (c = 1.0, \text{CDCl}_3) \]


\[ ^{145} \text{Zaitsev, A. B.; Adolfsson, H. Org. Lett. 2006, 8, 5129.} \]
H-NMR (300 MHz, CDCl₃): δ = 6.92 (d, J = 2.0 Hz, 1H), 6.87-6.86 (m, 1H), 6.83 (s, 1H), 4.86-4.79 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 1.86 (d, J = 2.2 Hz, 1H), 1.47 (d, J = 6.7 Hz, 3H) ppm.

C-NMR (75 MHz, CDCl₃): δ = 149.0, 148.3, 138.5, 117.5, 111.0, 108.6, 70.2, 55.9, 55.8, 25.0 ppm.

MS (70 eV, EI): m/z (%) = 182 (M⁺, 59), 167 (100), 139 (81), 124 (13).

HRMS (EI): m/z calcd. for: [C₁₀H₁₄O₃] 182.0943, found: 182.0923

Enantiomeric excess was determined by chiral GC using DEX-CB column (120 °C (120 min), const); 46.5 min (R), 50.5 (S). 94% ee.

Synthesis of trans-(S)-methyl2-carbomethoxy-3,5-diphenylpent-4-enolate (28)

Prepared according to TP12, using ligand 9h (3 mg, 0.0055 mmol) and 3-Acetoxy-1,3-diphenyl-propene 27 (126 mg; 0.5 mmol), dimethylmalonate (0.2 mL; 1.5 mmol) and (S)-28 obtained as a white solid (149 mg, 0.46 mmol; 92%).

MP: 94.1-94.8 °C

H-NMR (300 MHz, CDCl₃): δ = 7.25-7.00 (m, 10H), 6.40 (d, J = 15.8 Hz, 1H), 6.25 (dd, J = 15.8 Hz, 8.4 Hz, 1H), 4.15 (dd, J = 10.5, 8.8 Hz, 1H), 3.88 (d, J = 10.5 Hz, 1H), 3.55 (s, 3H), 3.45 (s, 3H) ppm.

C-NMR (75 MHz, CDCl₃): δ = 168.1, 167.5, 139.9, 136.0, 131.5, 129.1, 128.7, 128.1, 127.5, 127.3, 126.9, 126.3, 57.9, 52.8, 52.0, 49.1 ppm.

Enantiomeric excess was determined by chiral HPLC using a chiracel OD-H column (flow rate 0.6 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); tᵣ = 34.8 min (R), tᵣ = 37.2 min (S); 94% ee.

Synthesis of N-acetylphenylalaninmethylester (26)

Prepared according to TP13, using ligand 13d (6.4 mg, 0.0011 mmol) in MeOH (1 mL) and 2-acetamidoacrylicacidmethylester 25 (219 mg, 1.0 mmol) in MeOH (4 mL) at 5 bar H₂ pressure and obtained the desired compound 26 as colourless solid (211 mg, 0.95 mmol; 95%).

H-NMR (300 MHz, CDCl₃): δ = 7.32-7.17 (m, 3H), 7.13-7.04 (m, 2H), 6.06 (brs, 1H), 4.87 (brs, 1H), 3.70 (s, 3H), 3.20-3.00 (m, 2H), 1.97 (s, 3H) ppm.

C-NMR (75 MHz, CDCl₃): δ = 172.0, 169.7, 135.8, 129.2, 128.5, 127.0, 53.1, 52.3, 37.8, 23.2 ppm.

Enantiomeric excess was determined by GC using a chirilsil L-Val column (140 °C const); tᵣ = 11.6 min (R), tᵣ = 12.5 min (S); 90% ee.

Synthesis of 2-methylsuccinicaciddimethylester (75)

Prepared according to TP13, using ligand 13d (6.4 mg, 0.0011 mmol) in MeOH (1 mL) and 2-acetamidoacrylic acid methylester 74 (158 mg, 1.0 mmol) in MeOH (4 mL) at 5 bar H₂ pressure and obtained the desired compound 75 as colourless oil (144 mg, 0.90 mmol; 90%).

¹H-NMR (300 MHz, CDCl₃): δ = 3.66 (s, 3H), 3.64 (s, 3H), 2.99-2.85 (m, 1H), 2.74-2.65 (m, 1H), 2.40-2.38 (m, 1H), 1.20 (d, J = 7.1 Hz, 3H) ppm.

¹³C-NMR (75 MHz, CDCl₃): δ = 176.1, 172.7, 52.0, 51.8, 37.8, 36.1, 16.5 ppm.

Enantiomeric excess was determined by chiral HPLC using a chiracel OD-H column (flow rate 0.6 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); tᵣ = 34.8 min (R), tᵣ = 37.2 min (S); 60% ee.

13. Data for the x-ray crystallography analysis

**Crystallographic data of 4b:**

Empirical Formula : $\text{C}_{29}\text{H}_{26}\text{FeNOPS}$

Formular weight : 523.39

Temperature [°C] : 295 (2)K

Wavelength : 0.71073 Å

Crystal system : Monoclinic

Space group : $\text{P2}_1$

Unit cell dimensions :  
\[
\begin{align*}
a &= 9.0830 (18) \text{ Å} & \alpha &= 90 \text{ deg.} \\
b &= 9.7040 (18) \text{ Å} & \beta &= 102.60(3) \text{ deg.} \\
c &= 15.6420 (3) \text{ Å} & \gamma &= 90 \text{ deg.}
\end{align*}
\]

Volume : 1262.3 (5) Å$^3$

Z : 2

Density (calculated) : 1.377 Mg/m$^3$

Absorption coefficient : 0.766 mm$^{-1}$

F(000) : 544

Crystal size : 0.57 x 0.53 x 0.20 mm

Theta range for data collection: 2.60 to 26.30

Index ranges : -11≤h≤11, -11≤k≤11, -19≤l≤19

Reflections collected : 5121

Independent reflections : 4649

Absorption correction : Semi-empirical by psi-scan

Max no of parameters : 308

$R_1 (I>2\sigma(I))$ : 0.0363

$wR_2$ (all data) : 0.0975
goodness of fit : 1.099

14. ABBREVIATIONS

Ac acetyl
Ar aryl
Bn benzyl
br. Broad
brs Broadsinglet
BARF Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
calcd. Calculated
CAN Cerium Ammonium Nitrate
CH$_2$Cl$_2$ dichloromethane
COD 1,4-Cyclooctadiene
Conv. Conversion
d double
dec. decomposition
DMF $N,N$-dimethylformamide
$ee$ enantiomeric excess
equiv. equivalent
EI electron-impact
Et ethyl
FAB fast-atom bombardment
Fc Ferrocenyl
Fur 2-furyl
GC gas chromatography
h hour
HRMS high resolution mass spectroscopy
Hz Hertz
$n$-Bu $n$-butyl
$i$-Pr isopropyl
IR infra-red
$J$ coupling constant (NMR)
M molarity
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<th>Abbreviation</th>
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<tr>
<td>m</td>
<td>meta</td>
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<tr>
<td>m</td>
<td>multiplet</td>
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<td>minute</td>
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<td>Millilitre</td>
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<td>3,5-Dimethylphenyl (xylyl)</td>
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</table>
Curriculum Vitae

Name: Murthy Narasimha Cheemala
Date of Birth: April, 27th 1981
Nationality: Indian
Place of birth: Eluru, India
Marital status: Single
Mother language: Telugu. Other language: English (Fluent written and spoken)

Education

08/2003-present: Ph.D. student at the Ludwig-Maximilians-University, Munich, Germany under the guidance of Prof. Dr. Paul Knochel
Thesis title: “Synthesis of New Chiral Phosphine Ligands and Their Application in Asymmetric Catalysis”

2001-2003 Master of Science, Chemistry, University of Hyderabad, Hyderabad, India. Master thesis title “Synthesis of 1,1’-Binaphthyl Based Amines and Polyamines” Under the supervision of Prof. M. Periasamy, University of Hyderabad, India.

1998-2001 Bachelor of Science (Maths, Physics and Chemistry) at Sir. C. R. R. College, Eluru, Andhra Pradesh, India.


Publications


Conferences
