Multidentate Di-N-heterocyclic carbene ligands for transition metal catalyzed hydrogenation reactions
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Chapter 6

Synthesis of Chiral BINAM-based di-tzNHC Complexes and Application in Rh Catalyzed Enantioselective Hydrosilylation

Abstract

Despite the prolific use of (di-)NHC complexes in homogeneous catalysis, there are relatively few reports of their successful application in asymmetric transformations. In this chapter the atropisomeric binaphthyl backbone is combined with readily accessible 1,2,3-triazolylidene groups to obtain a strongly electron-donating \( C_2 \)-symmetric ligand. The target ligand was efficiently synthesized in a three step synthesis with an overall yield of 91% starting from commercially available starting materials. The corresponding di-NHC silver(I), palladium(II), rhodium(I) and iridium(I) complexes were synthesized and characterized. The Rh(I) complex 5 was applied in the catalytic asymmetric hydrosilylation of ketones, providing good conversions at catalyst loadings as low as 0.2 mol% and giving chiral inductions of up to 51% ee.

6.1. Introduction

Enantioselective catalysis is one of the key areas in homogeneous catalysis. It enables the production of chiral molecules, needed for many purposes, mostly bio-related applications. Most catalytic enantioselective reactions are facilitated by well-defined metal complexes bearing chiral ligands. In contrast to the successful application of a wide range of chiral phosphorus-based ligands for a variety of enantioselective transformations, efforts to induce chirality by means of chiral N-heterocyclic carbene (NHC) ligands have met with only limited attention and success. This is remarkable considering the continued popularity of NHCs in homogeneous catalysis. The relatively few transition metal complexes of chiral (di-) NHCs applied in enantioselective transformations have been described in recent reviews\(^1\)–\(^4\) and some general strategies in ligand design have been put forward, that are depicted in Figure 1.\(^4\)

As the imidazole ring itself is inherently planar, the most convenient way of introducing chirality in these ligands is via the incorporation of chiral substituents either at the nitrogen atoms or on the backbone of the NHC (Figure 1, A and B). The latter approach was, amongst others, suitable for Ru catalysts active in ring-closing metathesis.\(^6\) Although good results were achieved with such catalysts, the general design for these types of ligands proved to be ineffective. This has been attributed to the dynamic nature of the N-substituents on an NHC: the nitrogen substituents can rotate freely and rotation is also possible around the M-C\(_{\text{NHC}}\) bond. This causes the chiral space to be ill-defined, which hampers adequate chiral induction during transfer of relevant reactant moieties to coordinated substrates.\(^3\) Incorporation of chiral auxiliaries or stereogenic centers in the remote locations on the backbone often results in poor chiral induction at the metal center.\(^7\) Therefore, very large substituents are required to ensure efficient chiral definition using these approaches.\(^3,7\)
As has been argued throughout this thesis, bidentate ligands provide more rigid (chiral) environments around the metal center compared to their monodentate analogues.\textsuperscript{8,9} Several such chiral bidentate ligands consist of an NHC donor in combination with another hetero-atom donor.\textsuperscript{10–17} An example of such a ‘hybrid’ system is Burgess’ oxazoline functionalized NHC iridium hydrogenation catalyst (Figure 1, C).\textsuperscript{18} This system is active in the hydrogenation of unfunctionalized alkenes under 1 bar of H\textsubscript{2} with excellent enantiomeric excesses (ee). Furthermore, the group of Bellemin and Gade reported a similar NHC-oxazoline rhodium complex that catalyzed hydrosilylation of even the challenging dialkyl ketones enantioselectively.\textsuperscript{19}

Lastly, chelated di-NHC catalysts have been used for enantioselective transformations (Figure 1, D).\textsuperscript{11–16,20} In particular, the catalysts reported by Shi et al. have been successfully employed in several reactions.\textsuperscript{21–34} High ee's were obtained in a range of catalytic reactions, including hydrosilylation of ketones and esters, addition of arylboronic acids to N-Boc imines\textsuperscript{37,38} and umpolung allylation aldehydes with cyclohexenyl acetate.\textsuperscript{39}

Inspired by this $C_2$-symmetric system, we set out to combine the success of the atropisomeric binaphthyl backbone with the straightforward synthetic (“click” chemistry-based) routes available for 1,2,3-triazolylidines.\textsuperscript{40,41} This could allow for the development of a modular toolbox of chiral di-NHC ligands based on this motif. The superior donor-strength of triazolylidenes over imidazole-2-ylidenes might prove critical in the pursuit of successful enantioselective catalysis where oxidative addition reactivity is rate-limiting. Here, we describe the synthesis and coordination chemistry of the first chiral di(1,2,3-triazolylidene) ligand (Figure 1, box), based on 2,2'-diamino-1,1'-binaphthalene (BINAM) as well as its application in Rh-catalyzed hydrosilylation of ketones.

### 6.2. Synthesis of $C_2$-symmetric di-tzNHC Ligand

To warrant the most efficient chiral induction, the triazoles are introduced directly at the 2 and 2' positions of the binaphthyl moiety, closest to the atropisomeric center. We decided to connect the triazole to the binaphthyl unit through the nitrogen atoms as the commercially available enantiopure BINAM is easily converted into the corresponding bis-azide via nucleophilic aromatic substitution. Besides, this route has the advantage of extending the scope of viable substituents to include alkyl groups at the heterocycle without having to use hazardous alkyl azides.

The desired ligand 3 could be synthesized from commercially available chiral (R)-BINAM, which was first reacted with tert-butyl nitrite, to generate the diazonium intermediate and subsequently with trimethylsilyl azide to obtain bis-azide 1 in 96% yield (Scheme 1). Substitution of the diazonium fragment proceeds via an $S_N\textsubscript{1,2}$-
mechanism, generating a carbocation, which may decrease the steric interaction between the 2 and 2’ positions of the binaphthyl system and might consequently lead to racemization. To suppress this process, the (R)-2,2’-diamino-1,1’-binaphthalene solution was cooled to -15 °C prior to the addition of both reagents. Analysis using chiral high-performance liquid chromatography (HPLC) indicated that the enantiomeric excess of the product 1 was >99% ((R)-enantiomer).

The formation of the desired bis-azide was confirmed using 1H NMR, 13C NMR, infrared (IR) spectroscopy and high resolution mass spectrometry (HR-MS). Most indicative for the formation of the product was the disappearance of the signals around 3500 cm\(^{-1}\) in the IR spectrum, ascribed to the amine functionality, and the appearance of a sharp peak at 2098 cm\(^{-1}\), characteristic of the azide group.

Bis-azide (R)-1 was reacted with an alkyne to afford bis-triazole (R)-2 via a copper catalyzed ‘click’-reaction (Scheme 1). An aromatic acetylene was selected for this [3+2] cycloaddition, because aromatic groups stabilize the NHC formed in the corresponding complexes. After screening several solvent systems, performing the reaction in an acetonitrile/water mixture (4:1) and in the presence of triethylamine resulted in 95% yield of (R)-2 after column chromatography. Interestingly, the intermediate product containing only one triazole ring and one azide moiety was neither isolated nor observed by 1H NMR spectroscopy. This implies that the second ‘click’ reaction is much faster than the first reaction, which might be
caused by ligation of the copper catalyst to the initially formed triazole, resulting in a favorable proximity effect for the conversion of the remaining azide.\textsuperscript{42}

Lastly, the desired ligand, bis-triazolium salt (R)-3, was obtained by methylation of (R)-2 (Scheme 1). Methyl iodide is most often used for methylation of NHCs. However, we previously noted (see previous chapters) that methyl iodide is generally not nucleophilic enough to effectively methylelate a triazole ring in high yields.\textsuperscript{43} Therefore, methyl triflate was applied in this step, leading to (R)-3 in quantitative yield after evaporation of the excess reagent. The triazolium salt was identified in the \textsuperscript{1}H NMR spectrum by a substantial downfield shift of the triazole peak to 8.71 ppm compared to (R)-2 ($\Delta \delta = 0.62$ ppm) and the appearance of a signal at 4.04 ppm for the methyl groups. A small downfield shift of the triazolylidenium carbon atom was also observed by $^{13}$C NMR spectroscopy.

Overall, ligand precursor (R)-3 could be synthesized in three steps starting from the commercially available bis-amino precursor with an overall yield of 91%. The synthetic route is deemed quite efficient, while still allowing facile ligand modification. The (S)-enantiomer was also successfully synthesized using the same route with similar results.

\subsection*{6.3. Chiral di-tzNHC Complexes}

\textit{Synthesis and characterization of chiral di-tzNHC Ag(I) complex}

Silver complex 4 was synthesized in a similar fashion as di-NHC silver complexes described in Chapters 2 and 3 (Scheme 2), by stirring the ligand with Ag$_2$O in acetonitrile at room temperature. To drive the reaction to completion 4 Å molecular sieves were added to the reaction mixture.

\begin{equation}
\text{Scheme 2: Synthesis of silver(I) complex (R)-4.}
\end{equation}

The formation of silver (I) complex (R)-4 was confirmed by the disappearance of the hydrogen signal of the triazolium ring in the \textsuperscript{1}H NMR spectrum. The protons of the ligand were observed in pairs of equivalent protons in the \textsuperscript{1}H NMR spectrum, indicating that the complex is still C\textsubscript{2}-symmetric. The exact mass of the parent ion obtained from HR-CSI-MS suggests a dimeric structure for this complex,
(corresponding to a $[\text{M}_2\text{L}_2\cdot\text{2OTf}]^{2+}$ fragment). Unfortunately, no single crystals suitable for X-ray diffraction have been obtained to support this assumption.

A pair of doublets was observed in the $^{13}$C NMR spectrum at characteristic carbene shifts ($\delta = 167.2$ ppm, $J_{107\text{AgC}} = 171.2$ Hz and $J_{109\text{AgC}} = 197.5$ Hz).

These well resolved Ag-C$_{\text{NHC}}$ couplings indicate a strong bond between the metal and the carbene in solution. Attempts to transmetalate complex (R)-4 to e.g. palladium(II) were unsuccessful, which is likely due to this strong Ag-C bond. Therefore, we turned to a direct deprotonation route to obtain other chiral di-tzNHC metal complexes.

**Synthesis and characterization of chiral di-tzNHC Ir(I), Rh(I) and Rh(III) complexes**

Rhodium(I) 1,5-cyclooctadiene (cod) complex (R)-5 was synthesized via direct deprotonation of the ligand with KOTBu in the presence of half a molar equivalent of [Rh(cod)Cl]$_2$ (Scheme 3). The resulting complex was purified using column chromatography with regular silica and non-dried solvents, leading to an isolated yield of 80%, which illustrates the high stability of the complex towards water and aerobic conditions. The $^1$H NMR spectrum of (R)-5 indicated $C_2$-symmetry, as each signal must be assigned to two equivalent protons for the ligand as well as the cod fragment. Coupling of the rhodium with the carbene carbon is observed at 173.2 ppm ($J_{\text{RhC}} = 50.9$ Hz) in the $^{13}$C NMR spectrum, which is in accordance with the shifts and coupling constants found in rhodium di-tzNHC and aryl-linked NHC-tzNHC complexes (Chapter 4). ESI HR-MS detection of the correct mass (minus the triflate anion) confirmed the formation of the desired mononuclear species. In contrast to Shi et al., we did not observe the formation of dinuclear species, which explains the lower yield (25%) in their case.

![Scheme 3: Synthesis of rhodium(I)- and iridium(I)(cod) complexes (R)-5 and (R)-6.](image)

Iridium complex (R)-6 was prepared using the same procedure as for (R)-5, using the corresponding [Ir(cod)Cl]$_2$ precursor (Scheme 3). Full conversion of the ligand was observed after three hours. The isolated yield for the desired complex after
regular column chromatography is significantly lower (21%) than for the analogous rhodium complex \((R)-5\). This may indicate that the iridium species is inherently less stable than the rhodium species or more sensitive under the chosen work-up conditions. Again, the formation of the desired \(C_2\)-symmetric Ir(I) complex was confirmed by \(^1\text{H}\) and \(^{13}\text{C}\) NMR and HR-MS analysis. The NHC carbon peak was observed at 170.7 ppm in the \(^{13}\text{C}\) NMR spectrum. This value is quite low field compared to the tzNHC peak of the \([\text{Ir(tzNHC-CH}_2\text{-tzNHC)}\text{(cod)}]\)X complex from Chapter 4 (162.5 ppm), which can be attributed to the slightly electron withdrawing binaphthyl linker.

To assess the electron-donating capabilities of the novel di-tzNHC ligand, Rh(I) carbonyl complex \((R)-7\) was synthesized by stirring complex \((R)-5\) under 5 bar of syngas pressure (Scheme 4). Characterization of the resulting complex revealed the formation of the desired species with preservation of the \(C_2\)-symmetry. Two doublets are observed in the \(^{13}\text{C}\) NMR spectrum at 185.5 ppm \((J_{\text{RhC}} = 56.8 \text{ Hz})\) and 161.8 ppm \((J_{\text{RhC}} = 43.7 \text{ Hz})\) that correspond to the carbonyl carbon and tzNHC-carbon, respectively. The rhodium-carbon coupling constant is smaller than was observed in complex \((R)-5\), which is attributed to the presence of the strongly \(\pi\)-accepting CO ligands.

![Scheme 4: Synthesis of Rh(I) carbonyl complex (R)-7 and Rh(III) complex (R)-8. The possible (symmetric and asymmetric) isomers of 8 are represented in the box.](image-url)
Chapter 6

The IR adsorption spectrum of (R)-7 showed two adsorption bands ($\nu_{CO} = 2066$ cm$^{-1}$ and 2005 cm$^{-1}$) for the carbonyl ligands, which is in line with the frequencies found for the ligands described in Chapter 4 ($2075 < \nu_{CO} < 2005$ cm$^{-1}$). Furthermore, these values correspond to strong electron-donating properties for the di-tzNHC (R)-3 ligand compared to BINAP (2,2’-bis(diphenylphosphino)-1,1’-binaphthyl; $\nu_{CO} = 2094$ and 2048 cm$^{-1}$)

chiral di-imidazolylidene and di-benzimidazolylidene ligands ($2086 < \nu_{CO} < 2011$ cm$^{-1}$)

and the “i-bitz” ligand ($2076 < \nu_{CO} < 2019$ cm$^{-1}$).

The rhodium(III) complexes reported as (pre)catalysts by Shi’s group contain two iodido ligands as well as an $\kappa^2$-acetato ligand.$^{35}$ When following the reported synthetic procedure to prepare the analogous complex (R)-8, i.e. stirring the ligand with [Rh(cod)Cl]$_2$, 2 equivalents of KI and excess NaOAc under reflux in acetonitrile,$^{49,50}$ no product was obtained. A protocol to oxidize an Ir(I) di-NHC complex of Miecznikowski and Crabtree$^{53}$ did result in the desired rhodium(III) complex (R)-8 (Scheme 3). This complex was purified using column chromatography, showing that also this rhodium complex is stable under aerobic conditions. The $^1$H NMR spectrum indicated that the isolated complex exists as a mixture of isomers. Assuming that the ligand will only coordinate in a cis-fashion, occupying two coordination sites in the equatorial plane of the complex, there are two possibilities for coordination of the acetate group: i) at the two remaining sites in the equatorial plane, leading to the symmetric isomer, or ii) an equatorial-apical coordination mode, yielding the asymmetric isomer (box, Scheme 4). The $^1$H NMR spectrum is consistent with the presence of one $C_2$-symmetric and one asymmetric isomer. HR-MS showed data corresponding to the parent complex, minus either the acetate or one iodine ligand.

**Synthesis and characterization of chiral di-tzNHC palladium(II) complex**

Palladium complex (R)-9 was synthesized using the protocol described in Chapter 2 and 3, by stirring ligand (R)-3 with KOTBu and half a molar equivalent of [Pd($\eta^3$-C$_3$H$_5$)Cl]$_2$ (Scheme 5). Full conversion of (R)-3 was observed within two hours.

![Scheme 5: Synthesis of palladium(II) complex (R)-9.](image-url)
The palladium complex \((R)-9\) was obtained in quantitative yields after isolation using column chromatography with regular silica and solvents, indicating the stability of this complex. The complex can be stored under nitrogen for several months and even in solvents exposed to oxygen for several weeks without decomposition. NMR spectroscopy revealed that the introduction of the allyl group breaks the symmetry of the complex, leading to a non-symmetric complex. The protons of the allyl moiety are observed as three separate signals in the \(^1\)H NMR spectrum while all ligand hydrogens give rise to distinctive signals. The presence of two carbene carbon signals at 163.2 and 164.4 ppm in the \(^{13}\)C NMR spectrum confirmed the loss of \(C_2\)-symmetry in this complex.

In summary, Ag(I), Pd(II), Ir(I) and Rh(I) complexes of ligand \((R)-3\) were successfully synthesized and characterized using NMR and HR-MS. The complexes were stable enough to be purified using regular column chromatography and most complexes were obtained in high yields. They have been tested for enantioselective catalysis as will be described in the next section.

6.4. Catalytic Application of Chiral di-tzNHC Complexes

The strong electron-donating properties of NHC ligands make them very suitable ligands for transformations in which oxidative addition is the key (slow) step, such as in hydrogenation, hydrosilylation and allylic alkylation processes. All these transformations are also amenable to asymmetric catalysis when using prochiral substrates and are therefore ideal cases to evaluate the novel di-triazolylidene ligand, as will be described in this paragraph.

Initially, we tested palladium(II) complex \((R)-9\) in the asymmetric allylic alkylation reaction of 1,3-diphenylprop-3-enyl acetate and dimethyl malonate, but no conversion was noted at room temperature. This might be caused by an inhibiting effect of the strongly coordinated allyl ligand, preventing formation of an active Pd species.

Rh(I) catalyst \((R)-5\) was also tested in the hydrogenation of methyl Z-2-acetamido-3-phenylacrylate under 25 bar hydrogen pressure at 40 °C overnight, which resulted in only minor conversion to the racemic product. Rh complex \((R)-5\) and Ir complex \((R)-6\) were active in the transfer hydrogenation of acetophenone in isopropanol in the presence of catalytic amount of base. Full conversion of the starting material was observed after stirring at 80 °C overnight. Unfortunately, chiral HPLC analysis revealed that a racemic mixture of the product was formed under these conditions.

Rhodium catalyzed enantioselective hydrosilylation of ketones

Enantioselective hydrosilylation of ketones is a valuable reaction to produce chiral silyl ethers or secondary alcohols after hydrolysis. The conditions required for this
reaction are milder than for most hydrogenations\textsuperscript{52} and the bulky nature of silanes compared to H\textsubscript{2} may lead to improved chiral induction. Complexes based on various metals,\textsuperscript{53-57} with rhodium as prime example,\textsuperscript{10,17,35,58} are known to facilitate hydrosilylation.

The group of Shi reported very efficient hydrosilylation reactions of prochiral ketones using a Rh(III) complex with a chiral bidentate di-benzimidazolylidene ligand.\textsuperscript{35,36} Given the resemblance of ligand 3 to these systems, we decided to probe the activity of complex (R)-5 for this application. Acetophenone was chosen as the benchmark substrate using similar reaction conditions as reported by Shi: stirring the substrate (c = 0.25 mmol/L) with 2 mol\% catalyst, 2 equivalents of H\textsubscript{2}SiPh\textsubscript{2} for 24 hours at room temperature followed by hydrolysis with HCl. A solvent screening indicated that THF was the best solvent for our system. Varying the temperature had no beneficial effect. The results of the complexes in the hydrosilylation at different catalyst loadings are depicted in Table 1.

**Table 1:** Results of the hydrosilylation of acetophenone catalyzed by (R)-5 and (R)-8.

<table>
<thead>
<tr>
<th>Catalyst loading</th>
<th>T (°C)</th>
<th>Conv. (Yield)\textsuperscript{a}</th>
<th>ee\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1% of (R)-5</td>
<td>25</td>
<td>33% (17%)</td>
</tr>
<tr>
<td>2</td>
<td>0.2% of (R)-5</td>
<td>25</td>
<td>78% (78%)</td>
</tr>
<tr>
<td>4</td>
<td>1.1% of (R)-5</td>
<td>25</td>
<td>90% (90%)</td>
</tr>
<tr>
<td>5</td>
<td>2.0% of (R)-5</td>
<td>25</td>
<td>92% (78%)</td>
</tr>
<tr>
<td>6</td>
<td>2.0% of (R)-8</td>
<td>25</td>
<td>42% (13%)</td>
</tr>
<tr>
<td>7\textsuperscript{c}</td>
<td>2.0% of Shi’s catalyst</td>
<td>15</td>
<td>87% (87%)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Determined by GC analysis using para-xylene as an internal standard.

\textsuperscript{b} determined by chiral GC

\textsuperscript{c} values reported by Shi et al.\textsuperscript{35}

We were able to decrease catalyst loadings significantly to 0.2 mol\% without loss of enantiomeric excess (ee) and little loss in conversion (Table 1, entry 2). Shi reported reactions with a catalyst loading of 1 mol\% leading to 77\% yield after 48 hours.

\textsuperscript{*}The observed yields (after hydrolysis) were at times significantly lower than the conversion while several signals of high-boiling compounds were also detected in GC results. This indicates that the hydrolysis step is not very reproducible.
similar to the results achieved at 0.2 mol% catalyst loading with complex (R)-5 after 24 hours (entry 2). The increased activity in our case might be caused by the electron-donating properties of the ligand. The enantioselectivity on the other hand, was significantly lower for our system compared to Shi, yet higher than the imidazolylidene-naphthoxy Rh(I) complex of Crabtree et al.

Surprisingly, complex 8, which is more closely related to the pre-catalyst of Shi, proved less active in the hydrosilylation reaction under the same conditions and a racemic mixture of 1-phenylethanol was observed (entry 6). Therefore, we assume that the difference in ee between the benzimidazolylidene and triazolylidene complexes is caused by steric effects (vide infra).

We performed a small substrate screening including bulky substrates and substrates with various electronic properties to obtain insight in the catalyst performance (Table 2). This screening showed higher conversions for more electron-rich ketones, while adding an electron-withdrawing group on the phenyl ring led to slightly reduced conversion. The 4-bromoacetophenone (entry 2) was converted with similar ee as acetophenone.

Table 2: Substrate scope of hydrosilylation of aryl alkyl ketones catalyzed by (R)-5.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Conv. (Yield)</th>
<th>ee</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>92%(78%)</td>
<td>26%</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>79%(78%)</td>
<td>32%</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>100%(0%)</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>iPr</td>
<td>100%(100%)</td>
<td>51%</td>
</tr>
</tbody>
</table>

a) Determined by GC analysis using para-xylene as an internal standard b) Determined by chiral GC c) Determined by chiral HPLC.

The hydrosilylation of 4-methoxyacetophenone (Table 2, entry 3) resulted in full conversion of the starting compound, but no traces of the product could be observed in the GC. This might be explained by the nature of the substrate, as the methoxy group might not be stable under the catalytic conditions in the presence of the highly oxophilic silicon species. The conversion of phenyl isopropyl ketone (entry 4) gave significantly better results in terms of ee than for the reaction with
acetophenone. The higher enantioselectivity obtained with this sterically congested ketone indicates that increasing the steric bulk around the triazolylidenes aids the transfer of chirality in this reaction. This bulkiness could be introduced in the side groups on the triazolylidene (in the direct vicinity of the metal centre). Another possibility is the introduction of groups at the 2 and 2’ positions on the binaphthyl backbone that may decrease rotational freedom of the triazolylidene moieties, yielding an even more rigid complex and possibly enhanced chiral definition.

6.5. Conclusion
A new chiral \( C_2 \)-symmetric di-1,2,3-triazolylidene ligand with a binaphthyl backbone was successfully obtained via an efficient three-step synthesis from commercially available starting materials in 91% overall yield. Silver(I), palladium(II), iridium(I) and rhodium(I) complexes were synthesized and characterized using multinuclear NMR spectroscopy and mass spectrometry. The complexes were stable enough to be purified by column chromatography and most complexes were obtained in high yields. Rhodium complex \((R)-7\) allowed for the assessment of the electron-donating properties of the ligands and the \( \nu_{\text{avg}}(\text{CO}) \) observed was lower than for similar di-imidazol-2-ylidene complexes, indicating stronger electron-donating properties of the new ligand.

Rhodium(I) complex \((R)-5\) was successfully applied in the asymmetric hydrosilylation of prochiral ketones. Good yields were obtained at catalyst loadings as low as 0.2 mol%, indicating the increased activity of complex \((R)-5\) compared to the complexes reported by Shi.\(^{35}\) Chirality was efficiently transferred onto various aryl ketone substrates. Furthermore, we observed increased enantioselectivity when bulkier substrates were used. This indicates that using even bulkier substrates may lead to higher ee while modification of the ligand may allow for effective transfer of chirality to smaller substrates.

Because of the combination of interesting electronic properties and the straightforward synthetic route, chiral 1,2,3-triazolylidene-based ligands are deemed very interesting subjects for further research. The possibilities in design and diversity of side-groups of (chiral) tzNHCs has barely been explored, and the before-mentioned benefits promise future applications for this type of ligands in asymmetric catalysis.

6.6. Experimental Section
All experiments were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were freshly distilled under an argon atmosphere from sodium benzophenoneketyl (toluene, THF, pentane and diethyl ether) and from CaH\(_2\) (DCM and MeCN). Acetophenone was vacuum-distilled and stored over 4 Å molecular sieves under a
nitrogen atmosphere. NMR spectra were recorded on either a Bruker AV400 MHz, Bruker DRX300 MHz, Varian Mercury 300 MHz, Bruker IMC500 MHz. $^1$H-$^1$H COSY and/or $^1$H-$^{13}$C HSQC NMR spectroscopy was used to assign the peaks of several compounds. Thin layer chromatography was carried out using Merck aluminium TLC sheets (Silica gel 60 F254). Column chromatography was carried out using Screening Devices 60-200 μm (60 Å pore size) silica gel and using technical grade solvents. HR-MS was performed on a Bruker MicrOTOF-Q machine in ESI mode. IR spectra were recorded on a Bruker Alpha-PFT-IR spectrometer.

GC analyses for determination of conversions and yields were performed with a Thermo Scientific Trace GC Ultra system with a Restek RTX®-200 (30 meters, 0.25 mmID) capillary column with a split injection method, using p-xylene as an internal standard. Determination of the ee of the products formed using HPLC was carried out using a Shimadzu LC-10AT VP with a Chiralcel OD-H column (0.9 mL/min flowrate, heptane/isopropanol=95/5) except for acetoephone. The products of the acetoephone hydrosilylation were analysed using chiral GC using a Supelco β-dex 225 column (30m x 0.25mm, 92° C to 95 °C with a ramp 0.1°C per minute, holding at 95°C for 10 minutes).

The ligand synthesis starting from both BINAM enantiomers from racemic BINAM. The results of the synthesis of the (R)-ligand are reported, as all complexes were synthesized using the (R)-ligand. It was found that using starting from (S)-BINAM or (+/-)-BINAM did not have a significant effect on any of the ligand synthesis steps.

1. A solution of 1,1'-binaphthyl-2,2'-diamine (280 mg, 0.98 mmol, 1.0 equiv.) in MeCN (7.5 mL) was cooled to 0 °C, after which tert-butyl nitrite (305 mg, 2.95 mmol, 3.0 equiv.) was added. To this solution trimethylsilyl azide (272 mg, 2.36 mmol, 2,4 equiv.) was added, upon which the color changed from brown to a bright red solution.

$^1$H NMR (CDCl$_3$) δ 8.08 (d, J$_{HH}$ = 8.8 Hz, 2H, Ar-C$_H$), 7.95 (d, J$_{HH}$ = 8.1 Hz, 2H, Ar-Ch), 7.53 (d, J$_{HH}$ = 8.8 Hz, 2H, Ar-Ch), 7.47 (dd, J$_{HH}$ = 8.2 Hz, J$_{HH}$ = 6.9 Hz, J$_{HH}$ = 1.2 Hz, 2H, Ar-Ch), 7.33 (dd, J$_{HH}$ = 8.4 Hz, J$_{HH}$ = 6.9 Hz, J$_{HH}$ = 1.3 Hz, 2H, Ar-Ch), 7.08 (d, J$_{HH}$ = 8.5 Hz, 2H, Ar-Ch); $^{13}$C NMR (CDCl$_3$) δ 153.0 (Ar-C$_q$), 136.0 (Ar-C$_q$), 133.5 (Ar-C$_q$), 130.9 (Ar-C$_q$), 130.4 (Ar-Ch), 128.3 (Ar-Ch), 127.4 (Ar-Ch), 125.6 (Ar-Ch), 125.5 (Ar-Ch), 117.2 (Ar-Ch). HR-MS (ESI) for C$_{20}$H$_{12}$N$_6$: m/z calculated 336.1123, [M]$^+$, observed 336.1122. IR: 2098, 2042, 1285, 801, 743 cm$^{-1}$.

2. To a solution of 2,2'-diazido-1,1'-binaphthalene (212 mg, 0.63 mmol, 1.0 equiv.) in MeCN:H$_2$O (4:1, 10 mL) was added copper(II)sulfate pentahydrate (11 mg, 0.063 mmol, 0.1 equiv.), sodium ascorbate (63
mg, 0.32 mmol, 0.5 equiv.), p-tolyl acetylene (146 mg, 1.26 mmol, 2.0 equiv.) and triethyl amine (32 mg, 0.32 mmol, 0.5 equiv.). The resulting red mixture was stirred for 60 hours at 50 °C. The MeCN and triethylamine were removed in vacuo and the product was purified using column chromatography (SiO$_2$, PE : EtOAc = 4:1 → 1:1) yield the product (340 mg, 0.60 mmol, 95% yield) as an orange oil. $^1$H NMR (CDCl$_3$) $\delta$ 8.09 (d, $^3$J$_{HH} = 8.7$ Hz, 2H, Ar-CH), 7.96 (d, $^3$J$_{HH} = 8.2$ Hz, 2H, Ar-CH), 7.55 (ddd, $^3$J$_{HH} = 8.1$ Hz, 2H, Ar-CH), 7.47 (d, $^3$J$_{HH} = 1.5$ Hz, 2H, Ar-CH), 7.13 (d, $^3$J$_{HH} = 1.2$ Hz, 2H, Ar-CH), 7.35 (d, $^3$J$_{HH} = 8.6$ Hz, 2H, Ar-CH), 7.41 (ddd, $^3$J$_{HH} = 8.3$ Hz, 2H, Ar-CH), 6.33 (s, 6H, Tol-CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$ 147.3 (Ar-C$_q$), 138.1 (Ar-C$_q$), 134.8 (Ar-C$_q$), 133.4 (Ar-C$_q$), 132.6 (Ar-C$_q$), 130.9 (tz-C), 129.5 (Tol-C), 128.6 (Ar-C), 128.2 (Ar-C), 128.0 (Ar-C), 127.8 (Ar-C), 127.4 (Ar-C), 126.4 (Ar-C), 125.7 (Tol-C), 123.4 (Ar-C), 121.1 (Ar-C), 21.5 (Ar-CH)$_3$. HR-MS (ESI) for C$_{38}$H$_{29}$N$_6$: m/z calculated 569.2448, [MH]$^+$, observed 569.2451.

(S) or (R)-2,2'-bis-(3-methyl-4-(p-tolyl)-1,2,3-triazolium)-1,1'-binaphthyl triflate; (S)- or (R)-3. Under inert conditions 2,2'-bis(4-(p-toly)-1H-1,2,3-triazol-1-yl)-1,1'-binaphthalene (282 mg, 0.50 mmol, 1.0 equiv.) was dissolved in dried DCM (10 mL) and the solution was cooled to -78 °C. Methylene triflate (156 mg, 1.375 mmol, 2.75 equiv.) was added quickly, which resulted in a cloudy discharge above the solution. After stirring for 15 minutes the mixture was allowed to heat up to room temperature and stirred for 12 hours, after which the mixture was concentrated in vacuo yielding the product as an orange-brown solid (456 mg, 0.50 mmol, quantitative yield). $^1$H NMR (CDCl$_3$) $\delta$ 7.91 (s, 2H, tz-CH), 7.81 (d, $^3$J$_{HH} = 6.6$ Hz, 2H, Ar-CH), 8.15-8.20 (m, 4H, Ar-CH), 7.77 (ddd, $^3$J$_{HH} = 8.2$ Hz, 7.0 Hz, 1.0 Hz, 2H, Ar-CH), 7.59 (ddd, $^3$J$_{HH} = 8.4$ Hz, 7.0 Hz, 1.1 Hz, 2H, Ar-CH), 7.33-7.40 (m, 8H, Ar-CH), 4.04 (s, 6H, N-CH$_3$), 2.42 (s, 6H, Tol-CH$_3$); $^{13}$C NMR (CDCl$_3$) $\delta$ 144.5 (Ar-C$_q$), 143.5 (Ar-C$_q$), 134.7 (Ar-C$_q$), 133.1 (triazole-CH), 133.0 (Ar-C$_q$), 132.9 (Ar-C$_q$), 130.7 (Tol-CH), 130.0 (Ar-C), 129.8 (Tol-CH), 129.8 (Ar-C), 129.6 (Ar-C), 127.3 (Ar-C), 127.0 (Ar-C), 123.1 (Ar-C), 118.7 (Ar-C), 39.4 (N-CH$_3$), 21.8 (Tol-CH$_3$). HR-MS (ESI) for C$_{38}$H$_{29}$N$_6$: m/z calculated 299.1422, [M-2OTf]$^+$, observed 299.1423.

Bis([(R)2,2'-bis-(3-methyl-4-(p-tolyl)-1,2,3-triazol-5-ylidene)-1,1'-binaphthyl] silver(I) triflate; (R)-4. Under inert conditions (R)-3 (198.0 mg, 0.22 mmol, 1.0 equiv.) and Ag$_2$O (203.4 mg, 0.88 mmol, 4.0 equiv.) were added to a Schlenk, after which 4Å molsieves were added followed by dry MeCN (15 mL). The mixture was stirred in the dark at 50 °C for 48h, after which the mixture was filtered over Celite and concentrated in vacuo yielding the product as an off-white solid (269.4 mg, quantitative yield). $^1$H NMR (CD$_2$Cl$_2$) $\delta$ 7.56 (d, $^3$J$_{HH} = 8.8$ Hz, 8H, Ar-CH), 7.37 (d, $^3$J$_{HH} = 8.2$ Hz, 4H, Ar-CH), 7.22-7.27 (m, 4H, Ar-CH), 6.99-7.13 (m, 20H, Ar-CH/Tol-CH), 6.35 (d, $^3$J$_{HH} = 8.7$ Hz, 4H, Ar-CH), 3.96
(s, 12H, N-CH$_3$), 2.73 (s, 12H, Tol-CH$_3$); $^{13}$C NMR (acetone-$d_6$) $\delta$ 167.2 (d, $^{1}$J$_{C-H}$ = 171.2 Hz, $^{1}$J$_{Cag07}$ = 197.5 Hz, C$_{tznHC}$) 141.2 (Ar-C$_q$), 138.0 (Ar-C$_q$), 133.7 (Ar-C$_q$), 131.3 (Ar-C$_q$), 130.3 (Ar-CH), 130.6 (Ar-CH) 128.4 (Ar-CH), 128.2 (Ar-CH), 127.8 (Ar-C$_q$), 127.1 (Ar-CH), 127.0 (Ar-CH), 126.8 (Ar-C$_q$), 126.1 (Ar-CH), 37.9 (triazole-CH$_3$), 21.6 (toly-CH$_3$). HR-MS (ESI) for C$_{80}$H$_{64}$Ag$_2$N$_{12}$C$_{13}$F$_3$SO$_3$: m/z calculated 1557.3008, [M-OTf]$^+$, observed 1557.3601 and for C$_{80}$H$_{64}$Ag$_2$N$_{12}$: m/z calculated 703.1739, [M-2OTf]$^+$, observed 703.1740.

((R)-2,2'-bis(3-methyl-4-(p-toly)-1,2,3-triazol-5-ylidene)-1,1'-binaphthyl)
$\eta^4$-cyclooctadiene iridium(I) triflate; (R)-5. Under inert conditions a solution of (R)-3 (102 mg, 0.11 mmol, 1.0 equiv.), [Rh(cod)Cl]$_2$ (28.1 mg, 0.06 mmol, 0.5 equiv.) and KOtBu (49.4 mg, 0.44 mmol, 4.0 equiv.) in THF (10 mL) was stirred for 3 hours at room temperature, after which the solution was filtered over Celite and concentrated in vacuo. Purification using column chromatography (SiO$_2$, DCM:acetone=3:1) yielded the product as an orange solid (83.7 mg, 0.055 mmol, 80% yield). $^{1}$H NMR (CD$_2$Cl$_2$) $\delta$ 8.20 (d, $^{3}$J$_{HH}$ = 8.6 Hz, 2H, Ar-CH), 8.01 (d, $^{3}$J$_{HH}$ = 8.6 Hz, 2H, Ar-CH), 7.95 (d, $^{3}$J$_{HH}$ = 8.2 Hz, 2H, Ar-CH), 7.58-7.63 (m, 2H, Ar-CH), 7.50-7.55 (m, 2H, Ar-CH), 7.45 (s, 2H, Ar-CH), 7.35-7.43 (m, 8H, Tol-CH), 4.77 (m, 2H, cod-CH), 3.13 (s, 6H, N-CH$_3$), 2.71-2.79 (m, 2H, cod-CH), 2.47 (s, 6H, CH$_3$), 2.20-2.35 (m, 2H, cod-CH$_2$), 1.95-2.02 (m, 2H, cod-CH$_2$), 1.14-1.26 (m, 2H, cod-CH$_2$), 0.79-0.89 (m, 2H, cod-CH$_2$); $^{13}$C NMR (CD$_2$Cl$_2$) $\delta$ 173.2 (d, $^{1}$J$_{CRR}$ = 50.9 Hz, C$_{tznHC}$) 140.8 (Ar-C$_q$), 137.8 (Ar-C$_q$), 133.8 (Ar-C$_q$), 132.3 (Ar-C$_q$), 131.9 (Ar-C$_q$), 131.1 (Ar-C$_q$), 130.3 (Ar-CH), 129.7 (Ar-CH), 129.0 (Ar-CH), 128.5 (Ar-CH), 128.3 (Ar-CH), 127.9 (Ar-CH), 127.8 (Ar-CH), 126.0 (Ar-CH), 126.3 (Ar-CH), 92.5 (d, $^{3}$J$_{CRR}$ = 9.0, cod-CH), 86.7 (d, $^{3}$J$_{CRR}$ = 7.5 Hz, cod-CH), 36.6 (N-CH$_3$), 36.0 (cod-CH$_2$), 26.6 (cod-CH$_2$), 21.6 (tol-CH$_3$). HR-MS (ESI) for C$_{80}$H$_{64}$RhN$_6$ calculated m/z 807.2682 [M-OTf]$^+$, observed 807.2682.

((R)-2,2'-bis(3-methyl-4-(p-toly)-1,2,3-triazol-5-ylidene)-1,1'-binaphthyl)
$\eta^4$-cyclooctadiene iridium(I) triflate; (R)-6. Under inert conditions a solution of (R)-3 (98.5 mg, 0.11 mmol, 1.0 equiv.), [Ir(cod)Cl]$_2$ (36.8 mg, 0.055 mmol, 0.5 equiv.) and KOtBu (25 mg, 0.22 mmol, 2.0 equiv.) in dry THF (4 mL) was stirred for 3 hours at room temperature, after which the solution was purified using column chromatography (SiO$_2$, DCM:acetone=1:1) yielding the product (24 mg, 0.023 mmol, 21% yield) as a red solid. $^{1}$H NMR (acetone-$d_6$) $\delta$ 8.36 (d, $^{3}$J$_{HH}$ = 8.6 Hz, 2H, Ar-H), 8.23 (d, $^{3}$J$_{HH}$ = 8.6 Hz, 2H, Ar-H), 8.07 (d, $^{3}$J$_{HH}$ = 7.3 Hz, 2H, Ar-H), 7.59-7.70 (m, 4H, Ar-H), 7.55 (d, $^{3}$J$_{HH}$ = 7.9 Hz, 4H, tol-H), 7.44 (d, $^{3}$J$_{HH}$ = 8.1 Hz, 2H, Ar-H), 7.36 (d, $^{3}$J$_{HH}$ = 7.9 Hz, 4H, tol-H 4.57-4.61 (m, 2H, cod-CH), 3.28 (s, 6H, NCH$_3$), 2.42 (s, 6H, Ar-CH$_3$), 2.16-2.25 (m, 2H, cod-CH), 1.70-1.78 (m, 2H, cod-CH$_2$), 0.87-0.99 (m, 4H, cod-CH$_2$), 0.67-0.77 (m, 2H, cod-CH$_2$); $^{13}$C NMR (acetone-$d_6$) $\delta$ 170.7 (C$_{tznHC}$), 145.7 (Ar-C$_q$), 138.8 (Ar-C$_q$), 137.1 (Ar-C$_q$), 133.7 (Ar-C$_q$), 131.7 (Ar-C$_q$), 131.4 (Ar-C$_q$), 131.0 (Ar-C$_q$), 130.1 (Tol-CH), 128.9 (tol-CH), 128.2 (Ar-CH), 128.0 (Ar-CH), 127.6 (Ar-CH), 127.0 (Ar-CH), 125.6 (Ar-CH), 122.5 (Ar-CH), 79.4 (cod-CH), 70.9 (cod-CH), 37.0 (N-CH$_3$), 129.
(R)-2,2'-bis(3-methyl-4-(p-tolyl)-1H-1,2,3-triazol-5-ylidene)-1,1'-binaphthylene)dicarbonyl rhodium(I) triflate; (R)-7. Rh(I) complex (R)-5 (approx. 100 mg) was dissolved in DCM (4 mL) and pressurized in an autoclave at 10 bar of syngas. After evaporation of the volatiles a sample of the product was taken for analysis (no yield was determined). 1H NMR (CD$_2$Cl$_2$) δ 8.23 (d, $^3$J$_{HH}$ = 8.2 Hz, 2H, Ar-CH), 8.00 (d, $^3$J$_{HH}$ = 8.3 Hz, 2H, Ar-CH), 7.91 (d, $^3$J$_{HH}$ = 8.6 Hz, 2H, Ar-CH), 7.54-7.69 (m, 6H, Ar-CH), 7.32 (d, $^3$J$_{HH}$ = 7.9 Hz, 4H, Tol-CH), 7.16 (d, $^3$J$_{HH}$ = 7.9 Hz, 4H, Tol-CH), 3.41 (s, 6H, N-CH$_2$Tol). HR-MS (ESI) for C$_{44}$H$_{44}$IrN$_6$: m/z calculated 755.1642, [M-OTf]$^-$, observed 755.1642.

(R)-2,2'-bis(3-methyl-4-(p-tolyl)-1H-1,2,3-triazol-5-ylidene)-1,1'-binaphthylene)diodo acetato rhodium(III) triflate; (R)-8. Under inert conditions rhodium complex 12 (106.6 mg, 0.11 mmol, 1.0 equiv.), I$_2$ (100.6 mg, 0.334 mmol, 3.0 equiv.) and NaOAc (62.0 mg, 0.55 mmol, 5.0 equiv.) were dissolved in dry MeCN and stirred at room temperature over night, after which the product was purified using column chromatography (SiO$_2$, Hexane:DCM=1:1 for the elution of excess iodine, DCM:acetone=1:1 for product elution) yielding the product as a red solid (no yield determined). 1H NMR (CD$_2$Cl$_2$) δ 8.67 (d, $^3$J$_{HH}$ = 8.7 Hz, 1H, Ar-CH), 8.56 (d, $^3$J$_{HH}$ = 8.7 Hz, 1H, Ar-CH), 8.43 (d, $^3$J$_{HH}$ = 8.7 Hz, 2H, Ar-CH), 8.27 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H, Ar-CH), 7.51-7.67 (m, 6H, Ar-CH), 7.33-7.42 (m, 6H, Ar-CH/Tol-CH), 6.90-7.17 (m, 20H, Ar-CH/Tol-CH), 6.46 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, Ar-CH), 6.03 (d, $^3$J$_{HH}$ = 7.4 Hz, 1H, Ar-CH), 3.21 (s, 6H, N-CH$_3$), 2.88 (s, 3H, N-CH$_3$), 2.84 (s, 3H, N-CH$_3$), 2.39 (s, 6H, Tol-CH$_3$), 2.34 (s, 3H, Tol-CH$_3$), 2.30 (s, 3H, Tol-CH$_3$); 13C NMR (CD$_2$Cl$_2$) δ 146.2 (Ar-C$_q$), 139.8 (Ar-C$_q$), 137.9 (Ar-C$_q$), 134.0 (Ar-C$_q$), 133.0 (Ar-C$_q$), 131.8 (Ar-C$_q$), 130.8 (Ar-C$_q$), 128.4 (Tol-CH), 128.2 (Ar-CH), 128.1 (tol-CH), 127.6 (Ar-CH), 127.2 (Ar-CH), 126.9 (Ar-CH), 123.9 (Ar-CH), 37.1 (N-CH$_3$), 21.7 (Tol-CH$_3$). HR-MS (ESI) for C$_{44}$H$_{48}$IrO$_2$Rh: m/z calculated 1011.9966 [M$^+$], observed 1012.0030.
temperature, after which the solution was purified using column chromatography (SiO$_2$, DCM:acetone=1:1) yielding the product (96.0 mg, 0.11 mmol, quantitative yield) as a yellow solid. $^1$H NMR (CD$_2$Cl$_2$) $\delta$ 8.25 (d, $^3$J$_{HH}$ = 8.6 Hz, 1H, Ar-CH$_2$), 8.14 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H, Ar-CH$_2$), 7.99 (d, $^3$J$_{HH}$ = 8.3 Hz, 1H, Ar-CH$_2$), 7.89-7.94 (m, 2H, Ar-CH$_2$), 7.78 (d, $^3$J$_{HH}$ = 8.9 Hz, 1H, Ar-CH$_2$), 7.49-7.65 (m, 6H, Ar-CH$_2$), 7.19-7.22 (m, 4H, Tol-CH$_2$), 6.89-6.92 (m, 4H, Tol-CH$_2$), 4.45-4.59 (m, 1H, allyl-CH$_2$), 3.46 (s, 3H, N-CH$_3$), 3.41 (s, 3H, N-CH$_3$), 2.36-2.38 (m, 1H, allyl-CH$_2$), 2.10-2.05 (m, 1H, allyl-CH$_2$), 1.28-1.36 (m, 2H, allyl-CH$_2$);

$^{13}$C NMR (CD$_2$Cl$_2$) $\delta$ 164.4 (C$_{tzNHC}$), 163.2 (C$_{tzNHC}$), 147.4 (Ar-$C_q$), 147.3 (Ar-$C_q$), 140.5 (Ar-$C_q$), 140.4 (Ar-$C_q$), 136.9 (Ar-$C_q$), 136.7 (Ar-$C_q$), 133.7 (Ar-$C_q$), 133.5 (Ar-$C_q$), 131.4 (Ar-$C_q$), 131.1 (Ar-$C_q$), 131.1 (Ar-$C_q$), 130.6 (Ar-CH$_2$), 130.5 (Ar-CH$_2$), 129.8 (Tol-CH$_2$), 129.4 (Tol-CH$_2$), 129.2 (Ar-CH$_2$), 129.2 (Ar-CH$_2$), 128.0 (Ar-CH$_2$), 127.3 (Ar-CH$_2$), 125.0 (Ar-$C_q$), 124.9 (Ar-$C_q$), 122.5 (Ar-CH$_2$), 122.4 (Ar-CH$_2$), 117.9 (allyl-CH$_2$), 63.0 (allyl-CH$_2$), 58.9 (allyl-CH$_2$), 36.4 (N-CH$_2$), 36.1 (N-CH$_2$), 21.1 (CH$_3$). HR-MS (ESI) for C$_{43}$H$_{37}$PdN$_6$: m/z calculated 743.2115 [M-OTf$^+$], observed 743.2130.

**Rhodium catalyzed hydrosilylation.** In a dried Schlecko flask equipped with a magnetic stirrer, the rhodium catalyst (0.1-2 mol%, weighed in a small aluminium weighing vessel) was dissolved in dry THF (2 mL), after which the substrate (62 $\mu$L, 0.5 mmol), $p$-xylene (61 $\mu$L, 0.5 mmol) and diphenylsilane (139 $\mu$L, 0.75 mmol) were added. After stirring for 24 hours at the desired temperature, water (2 mL) and 2M HCl (1 mL) were added, the product was extracted using diethyl ether (2 x 10 mL) and the resulting solution was used for GC and HPLC analysis.

**Palladium catalyzed asymmetric allylic alkylation.** In a dried Schlenk flask equipped with a magnetic stirrer, the palladium catalyst (0.01 equiv., weighed using a small aluminium weighing vessel), 1,3-diphenylprop-3-enyl acetate (1.0 equiv.), dimethyl malonate (3.0 equiv.), bis-trimethylsilyl acetamide (3.0 equiv.) KOAc (0.1 equiv.) and $p$-xylene (1.0 equiv.) were dissolved in DCM (1.0 equivalent at 0.1 M) and the mixture was stirred at room temperature for 5 hours. After this, a saturated solution of NH$_4$Cl (5 times initial V$_{solv}$) was added and the mixture was extracted with diethyl ether (2 x 10 mL) and the resulting solution was used for GC and HPLC analysis.

**Rhodium catalyzed hydrogenation of alkenes.** In an autoclave (150 mL) with six inserts glass GC vials were placed with a septum cap, pierced by a small needle, containing a magnetic stirrer, the rhodium catalyst (0.01 equivalents, weighed in a small aluminium weighing vessel) and the substrate (1.0 equivalents, weighed in a small aluminium weighing vessel) dissolved in DCM (1.0 equivalent at a concentration of 1.0 M). The autoclave was flushed three times with hydrogen (up to 25 bar) and subsequently filled to 25 bar and stirred overnight at 40 °C. The crude sample was filtered over silica and tested for conversion.

**Rhodium catalyzed transfer hydrogenation of acetophenone.** In a dried Schlecko flask equipped with a magnetic stirrer, the rhodium catalyst (0.01 equiv., weighed using a small aluminium weighing vessel) and KOTBu (0.1 equiv., weighed using a small aluminium weighing vessel)
were dissolved in a degassed stock of substrate and internal standard in isopropanol (0.1 M solution of acetophenone and p-xylene in isopropanol). The mixture was stirred at 80 °C overnight, after which the crude sample was analyzed.

6.7 References

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