Asymmetric Synthesis of Hetero-Bimetallic Planar
Chiral Ferrocene Pallada-/Platinacycles and their
Application to Enantioselective Aza-Claisen
Rearrangements

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           [η^5-(4'R,5''R)-(S)p)-2-(2''-4'',5''-dihydro-4'',5''-diphenyl-1''-tosyl-1''H-imidazolyl)cyclopentadienyl, 1''-C, 3''-N]-platinum(II)-iron(II)] ([FBIPP-Cl]_2) ........................................... 11
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\{\text{acetonitrile-}\{\eta^5-(4''''R,5''''R)-(1''-S_R)-2''-(2''''-4'''',5''''-dihydro-4'''',5''''-diphenyl-1''''-tosyl-1''''H-imidazolyl)cyclopentadienyl, \kappa \text{Cl'}, \kappa \text{N3'}-\text{heptafluorobutyrate-platinum(II)}\}\}\text{-iron(II) (FBIPP-O}_2\text{CC}_3\text{F}_7\}\}

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1. Experimental

All reactions were performed in oven dried (150 °C) glassware under a positive pressure of nitrogen and were magnetically stirred. For all reactions liquids and solutions were added via syringe and septa. For catalysis all glassware used (also for catalyst activation and preparation of stem solutions) was washed intensively with demineralized water to remove all remaining chloride. Methanol and benzene were stored in crown-capped bottles under argon over 4 Å molecular sieves. Acetonitrile, tetrahydrofuran (THF) and dichloromethane (DCM) were purified by distillation and subsequently by a solvent purification system. n-Hexane (HPLC grade), iso-propanol (HPLC grade), absolute ethanol, chloroform (>99%) and n-pentane (UV quality) were used as purchased. For work-up procedures and column chromatography technical grade solvents (diethyl ether, petrol ether and ethyl acetate) were purified by distillation prior to use. Solvents were mostly removed at room temperature (in special cases at a heating bath temperature of 40 °C) and 600 – 10 mbar pressure by rotary evaporation. Non-volatile compounds were dried in vacuo at 0.1 mbar. [FBIP-Cl]$_2$[1] was prepared according to literature procedures.

Yields refer to chromatographically purified compounds and are calculated in mol% of the used starting material. For thin layer chromatography (TLC), silica gel plates from Merck (silica gel 60 F$_{254}$) were used. Visualization occurred by fluorescence quenching under UV light and/or by staining with KMnO$_4$ / NaOH. Purification by flash-chromatography was performed on silica gel 0.040 – 0.063 mm provided by Merck, using a forced flow of eluent at 0.2-0.4 bar pressure.

NMR-spectra were recorded at 21 °C on spectrometers operating at 500 or 300 MHz (1H), 125 or 75 MHz (13C) and 235 MHz (19F). Deuterated solvents were used as purchased and are stated for the corresponding compound characterizations after the corresponding frequency. Chemical shifts are referred in terms of ppm and J-coupling constants are given in Hz. Abbreviations for multiplicities are as follows: s (singulet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), b (broad signal). IR-spectra were recorded by the IR service of the Universität Stuttgart on a spectrometer with an ATR unit. Aggregation state of the sample is stated in parentheses, signals are given by wavenumbers (cm$^{-1}$). Optical rotation was measured on a polarimeter operating at the sodium D line with a 100 mm path cell length. Melting points were measured in open glass capillaries and are uncorrected. Mass spectra were obtained from the MS service of the Universität Stuttgart. The ionisation method is stated in parentheses. Microanalyses were performed by the analytical service of the Universität Stuttgart. Single crystal X-ray analyses were performed by Dr. Wolfgang Frey (Universität Stuttgart). Enantiomeric excesses (ee’s) were determined by high performance liquid chromatography (HPLC). The applied method is given in the description of the respective product.
1.1 General Procedures (GPs)

1.1.1 GP for the Deprotection of the Rearrangement Products (GP2)[1]

![Chemical structure]

A solution of NaOEt (5.75 equiv.) in EtOH (1M) was added to the respective substrate at room temperature and the resulting mixture was warmed to 54 °C and stirred for 18 h. After cooling to room temperature saturated NH₄Cl (aq) (1.0 mL/100 mg) and DCM (1.0 mL/100 mg) were added and the phases were separated. The aqueous phase was extracted with DCM (3x 2.0 mL/100 mg). The combined organic phases were dried over Na₂SO₄. The solvent was subsequently removed in vacuo and the crude product was purified by column chromatography.

1.2 Catalytic Asymmetric Aza-Claisen Rearrangement

1.2.1 (S)-2,2,2-Trifluoro-4-(1-propylallyl)-4-methoxyphenyl)-N-(4-methoxyphenyl)acetamide (S)-5a

![Chemical structure]

Table 1, #2: According to GP1, precatalyst amount: 0.5 mol%, reaction time: 72 h, reaction temperature: 20 °C, yield: 94%, ee: 97%.

Table 1, #6: According to GP1, precatalyst amount: 0.05 mol%, reaction time: 72 h, reaction temperature: 55 °C, yield: 99%, ee: 98%.

C₁₅H₁₈F₃NO₂. MW: 301.30 g /mol. ¹H-NMR (300 MHz, CDCl₃): δ = 7.12-7.00 (m, 2H, o-CH), 6.94-6.83 (m, 2H, m-CH), 5.63-5.49 (m, 1H, HC=CH₂), 5.25 (d, J = 17.2, 1H, trans=HC=CH₂), 5.20 (d, J = 10.2, 1H, cis=HC=CH₂), 5.08-4.97 (m, 1H, HC(N)), 3.85 (s, 3H, OCH₃), 1.66-1.45 (m, 2H, CH₂-CH₂-CH₂), 1.47-1.28 (m, 2H, CH₂=CH₂-CH₂), 0.93 (t, J = 7.3, 3H, CH₃-CH₂-CH₂). ¹³C-NMR (75 MHz, CDCl₃): 160.0 (ºC), 157.0 (q, J_C-F = 34 Hz, C=O), 135.6 (HC=CH₂), 132.0 (o-CH), 131.2 (o-CH), 128.2 (ºC-N), 119.5 (HC=CH₂), 116.7 (q, J_C-F = 286 Hz, CF₃), 113.9 (m-CH), 113.8 (m-CH), 60.8 (HC(N)), 55.6 (OCH₃), 33.9 (HC=CH₂-CH₂-CH₂), 19.6 (HC=CH₂-CH₂-CH₂).
All the other obtained analytical data are in accordance with the literature.\textsuperscript{[1]}

1.2.2 (S)-2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-(1-\textit{iso}-butylallyl)acetamide (S)-5b

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{s5b.png}
\caption{(S)-5b}
\end{figure}

Table 1, \#8: According to \textbf{GP1}, precatalyst amount: 1.5 mol\%, reaction time: 72 h, reaction temperature: 20 °C, yield: 87\%, \textit{ee}: 99\%.

Table 1, \#10: According to \textbf{GP1}, precatalyst amount: 0.1 mol\%, reaction time: 72 h, reaction temperature: 55 °C, yield: 62\%, \textit{ee}: 98\%.

Table 1, \#11: According to \textbf{GP1}, precatalyst amount: 0.2 mol\%, reaction time: 72 h, reaction temperature: 55 °C, yield: 99\%, \textit{ee}: 98\%.

\textbf{C}_{16}\textbf{H}_{26}\textbf{F}_{3}\textbf{NO}_{2}, \textbf{MW}: 315.33 g /mol. \textbf{\textit{1}}\textbf{H-NMR (300 MHz, CDCl}_{3})*: \delta = 7.11-6.96 (m, 2H, \textit{o}-CH), 6.90-6.81 (m, 2H, \textit{m}-CH), 5.62-5.46 (m, 1H, HC=CH\textsubscript{2}), 5.30-5.05 (m, 3H, \textit{\textit{i}}\textbf{Bu}-C(N)H-CH=CH\textsubscript{2}), 3.81 (s, 3H, OCH\textsubscript{3}), 1.64-1.20 (m, 3H, (N)(CH-CH\textsubscript{2}-CH(CH\textsubscript{3})\textsubscript{2}), 0.91 (dd, \textit{J}_{1} = 6.4, \textit{J}_{2} = 2.3, 6H, (CH\textsubscript{3})\textsubscript{2}).

All the other obtained analytical data are in accordance with the literature.\textsuperscript{[1]}

1.2.3 (S)-2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-(1-methylallyl)acetamide (S)-5c

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{s5c.png}
\caption{(S)-5c}
\end{figure}

Table 1, \#13: According to \textbf{GP1}, precatalyst amount: 0.1 mol\%, reaction time: 48 h, reaction temperature: 55 °C, yield: 78\%, \textit{ee}: 88\%. 
1.2.4 (S)-2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-(5-phenylpent-1-en-3-yl)acetamide (S)-5d

Table 1, #15: According to GP1, precatalyst amount: 1.0 mol%, reaction time: 72 h, reaction temperature: 20 °C, yield: 83%, ee: 95%.

Table 1, #17: According to GP1, precatalyst amount: 0.2 mol%, reaction time: 72 h, reaction temperature: 55 °C, yield: 98%, ee: 95%.

1.2.5 (R)-N-(1-(Benzyloxy)-2-methylbut-3-en-2-yl)-2,2,2-trifluoro-N-(4-methoxyphenyl)acetamide (R)-5e
Table 1, #19: According to GP1, precatalyst ([FBIP-Cl]₂) amount: 2.0 mol%, reaction time: 72 h, reaction temperature: 55 °C, yield: 94%, ee: 80%.

Table 1, #19: According to GP1, precatalyst amount: 2.0 mol%, reaction time: 72 h, reaction temperature: 55 °C, yield: 94%, ee: 87%.

C₂₁H₂₂F₃NO₃, MW: 393.40 g/mol. ¹H-NMR (300 MHz, CDCl₃): δ = 7.41-7.09 (m, 7H, arom. H, o-CH), 6.85-6.77 (m, 2H, m-CH), 6.21-6.09 (m, 1H, H=C=CH₂), 5.21-5.09 (m, 2H, H=C=CH₂), 4.58-4.45 (m, 2H, Ph-CH₂-O), 4.17 (d, J = 9.4, 1H, BnOCH₂), 3.82 (s, 3H, OCH₃), 3.65 (d, J = 9.4, 1H, BnOCH₂), 1.21 (s, 3H, CH₃).

All the other obtained analytical data are in accordance with the literature.¹¹

1.3 Deprotection

1.3.1 (S)-N-(4-Methoxyphenyl)-3-amino-1-hexene from allylic amide (S)-6a

Application of GP2 furnished the deacylated product 6a in 99% ee. Enantiomeric excess was determined by HPLC (Chiralcel OD-H, n-hexane/i-PrOH 99.8:0.2, 0.8 mL/min, 250 nm). All the other obtained analytical data are in accordance with the literature.¹¹

1.3.2 (S)-N-(4-Methoxyphenyl)-3-amino-5-methyl-1-hexene from allylic amide (S)-6b
Application of GP2 furnished the deacylated product 6b in 99% ee. Enantiomeric excess was determined by HPLC (Chiralcel OD-H, n-hexane/i-PrOH 99.5:0.5, 0.8 mL/min, 250 nm). All the other obtained analytical data are in accordance with the literature.\cite{1}

1.3.3 (S)-N-(4-Methoxyphenyl)-3-amino-1-butane from allylic amide (S)-6c

Application of GP2 furnished the deacylated product 6c in 88% ee. Enantiomeric excess was determined by HPLC (Chiralcel OD-H, n-hexane/i-PrOH 99.8:0.2, 0.8 mL/min, 250 nm). All the other obtained analytical data are in accordance with the literature.\cite{1}

1.3.4 (S)-4-Methoxy-N-(5-phenylpent-1-en-3-yl)aniline (S)-6d

Application of GP2 furnished the deacylated product 6d in 95% ee. Enantiomeric excess was determined by HPLC (Chiralcel OD-H, n-hexane/i-PrOH 98.2:1.8, 0.8 mL/min, 210 nm). All the other obtained analytical data are in accordance with the literature.\cite{1}

1.4 Mechanistic studies
ESI-MS of a mixture of the activated catalyst and (Z)-(Z)-Hex-2-en-1-yl 2,2,2-trifluoro-N-(4-methoxyphenyl)acetimidate after 3h identified a species where the substrate was coordinated to the catalyst:

**MS (ESI) m/z:** 1706.2 (18%, [M – OTs + ((Z)-(Z)-Hex-2-en-1-yl 2,2,2-trifluoro-N-(4-methoxyphenyl)acetimidate)]


**HRMS (ESI) m/z:** calc. for [M – OTs + ((Z)-(Z)-Hex-2-en-1-yl 2,2,2-trifluoro-N-(4-methoxyphenyl)acetimidate)]$^+$: 1706.2259; found: 1706.2271.

### 2. References

3. NMR spectra

3.1 trans-\(N,N\)-µ-[(1S)-2-[(4R,5R)-1-(4-Tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1H-imidazol-2-yl-κN3]-1'-'[(4R,5R)-1-(4-tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1H-imidazol-2-yl-κN3]-1-ferrocene-κC1]-chloroplatinum(II) (1) and Bis-[(1S)-2-[(4R,5R)-1-(4-tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1H-imidazol-2-yl-κN3]-1'-'[(4R,5R)-1-(4-tolylsulfonyl)-4,5-dihydro-4,5-diphenyl-1H-imidazol-2-yl]-1-ferrocene-κC1]-µ-dichlorodiplatinum(II) (12)[2]
3.2 Bis-\{[µ-chloro-\{(η⁵-(4''R,5''R)-(S⁰)-2-(2''-4',5'-dihydro-4',5'-diphenyl-1''-tosyl-1''H-imidazolyl)cyclopentadienyl, 1'-C, 3'-M]-palladium(II)}-\}([µ-chloro-
\{(η⁵-(4''R,5''R)-(S⁰)-2-(2''-4',5'-dihydro-4',5'-diphenyl-1''-tosyl-1''H-imidazolyl)cyclopentadienyl, 1'-C, 3'-M]-platinum(II)}-iron(II)}) ([FBIPP-Cl]₂)
3.3 \{\text{Acetonitrile-}[\eta^5-(4''R,5''R)-(1'-S_\text{R})-2''-(2''''-4''',5''''-dihydro-4''',5''''-diphenyl-1''''-tosyl-1''''H-imidazolyl)cyclopentadienyl, }\kappa \text{C}1, \kappa \text{N3}-\text{heptafluorobutyrate-palladium(II)}\}\cdot \{\text{acetonitrile-}[\eta^5-(4''''R,5''''R)-(1'-S_\text{R})-2''''-(2''''''-4''''',5''''''-dihydro-4''''',5''''''-diphenyl-1''''''-tosyl-1''''''H-imidazolyl)cyclopentadienyl, }\kappa \text{C}1', \kappa \text{N3}-\text{heptafluorobutyrate-platinum(II)}\}\cdot \text{iron(II)} (\text{FBIPP-O}_2\text{CC}_3\text{F}_7)\}
HPLC’s for Compounds 6a – 6d and 5e
**Compound:**

```
\[
  \begin{align*}
  \text{MeO} & \quad \text{NH} \\
  \text{Pr} & \quad (\text{ee} = 98\%)
  \end{align*}
\]
```

**Column:** Chiralpak OD-H  
**Method:** n-Hexane/i-PrOH (99.8/0.2), 0.8 ml/min, 250 nm

### UV Results

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**Nearly racemic reference:**

```
\[
  \begin{align*}
  \text{MeO} & \quad \text{NH} \\
  \text{Pr} & \quad \text{Pr}
  \end{align*}
\]
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### UV Results

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Compound: 

\[
\begin{align*}
\text{NH} & \\
\text{MeO} &
\end{align*}
\]

6b (ee = 99%)

Column: Chiralpak OD-H
Method: \(\text{n-Hexane/PrOH (99.5/0.5), 0.8 ml/min, 250 nm}\)

UV Results

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UV Results

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Compound:

\[
\begin{align*}
\text{MeO} & - \text{NH} - \text{MeO}^6c \\
\text{Me} & \quad (\theta = 88\%)
\end{align*}
\]

Column: Chiralpak OD-H
Method: \(\alpha\)-Hexane/\(t\)-PrOH (99.8/0.2), 0.8 ml/min, 250 nm

UV Results

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Compound:

\[
\text{MeO-} \quad \begin{array}{c}
\text{6d} \\
\text{(ee = 95\%)}
\end{array} \\
\text{NH} \\
\text{Ph}
\]

Column: Chiralpak OD-H

Method: \(\text{n-Hexane/i-PrOH (98.2/1.8), 0.8 ml/min, 250 nm}\)

UV Results

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</tbody>
</table>
Compound:

\[
\begin{array}{c}
\text{MeO} \\
\text{BnO} \\
\end{array}
\] \quad \text{CF}_3

\text{(ee = 87%)}

Column: Chiralpak AD-H
Method: \(\alpha\)-Hexane/i-PrOH (99.8/0.2), 0.8 ml/min, 210 nm

**UV Results**

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Height</th>
<th>Area</th>
<th>Area Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.513</td>
<td>117539</td>
<td>7700378</td>
<td>93.353</td>
</tr>
<tr>
<td>25.977</td>
<td>5874</td>
<td>548253</td>
<td>6.647</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td>123413</td>
<td>8248631</td>
</tr>
</tbody>
</table>

**Nearly racemic reference:**

**UV Results**

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Height</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.493</td>
<td>267872</td>
<td>18036873</td>
<td>51.40</td>
</tr>
<tr>
<td>25.463</td>
<td>176616</td>
<td>17053662</td>
<td>48.60</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td>444481</td>
<td>35098535</td>
</tr>
</tbody>
</table>