Supplementary Information

Amino Acids as Chiral Anionic Ligands for Ruthenium Based Asymmetric Olefin Metathesis

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Part I. General information

All reagents were of grade quality, purchased commercially from Sigma-Aldrich, Alfa-Aesar or Fluka and used without further purification. All solvents were dried and distilled prior to use. Purification by column chromatography was performed on Davisil grade chromatographic silica media 60 Å (35-75 µm, 220-440 mesh). TLC analyses were performed using Merck precoated silica gel (0.2mm) aluminum (backed) sheets. NMR spectra were recorded on Bruker DPX_400 or DMX_500 instruments; chemical shifts, given in ppm, are relative to the residual solvent peak.¹ HR-MS data were obtained using a thermoscientific LTQU XL Orbitrap HR-MS equipped with APCI (atmospheric-pressure chemical ionization). Gas chromatography data were obtained using an Agilent 6850 GC equipped with an Agilent 5973 MSD working under standard conditions and an Agilent HP5-MS column. HPLC chiral analyses were performed using Young lin 9100 system equipped with a Reprosil column Chiral-NR, 8µm, 150x4.5 mm and a PDA detector. Specific rotations were measured by using ADP410 Polarimeter at wavelength λ=589nm and sample concentration “c” has units of g/100ml.

Part II. Synthesis

Synthesis of silver carboxylate salts

General procedure

Boc-protected amino acid (1.4eq, 0.5gr) was added to a stirring solution of aqueous NaOH (1.2eq in 1ml H₂O). The mixture was left to stir at r.t for 15 min and an aqueous solution of AgNO₃ (1.0eq in 1ml H₂O) was added dropwise in the dark. White precipitate immediately appeared and after stirring for 15 min at r.t the mixture was filtered and washed with H₂O (1ml x 3), MeOH (1ml x 3) and hexane (1ml x 3). Drying under high vacuum yielded silver carboxylate salts as white solids.

Boc-Glycine silver salt

Boc-Gly (0.50gr, 2.8mmol), NaOH (98mg, 2.4mmol), AgNO₃ (0.35gr, 2.0mmol). White solid (0.51gr, 1.8mmol), 88%. ¹H-NMR (500 MHz, DMSO-d₆, ppm): δ 6.38 (t, J = 5.0 Hz, 1H), 3.43 (d, J = 5.0 Hz, 2H), 1.37 (s, 9H).

Boc-Alanine silver salt

Boc-Ala (0.50gr, 2.6mmol), NaOH (90.6mg, 2.3mmol), AgNO₃ (0.32gr, 1.9mmol). White solid (0.38gr, 1.3mmol) 68%. ¹H-NMR (500 MHz, DMSO-d₆, ppm): δ 6.36 (d, J = 7.0 Hz, 1H), 3.83 (dq, J = 7.5, 7.0 Hz, 2H), 1.36 (s, 9H), 1.21 (d, J = 7.5 Hz, 3H).

Boc-Leucine silver salt

Boc-Leu (0.50gr, 2.2mmol), NaOH (74.6mg, 1.85mmol), MeOH (~0.5ml) was added to increase solubility of un-reacted acid. AgNO₃ (0.267gr, 1.57mmol). White solid (0.442gr, 1.31mmol) 83%. ¹H-NMR (400 MHz, DMSO-d₆, ppm): δ 6.37 (d, J = 8.4 Hz, 1H), 3.88 (ddd, J = 8.8, 8.4, 5.3 Hz, 1H), 1.63 (m, 1H), 1.45 (m, 2H), 1.36 (s, 9H) 0.856 (d, J = 6.8 Hz, 3H), 0.846 (d, J = 6.4, Hz, 3H).

Boc-Phenylalanine silver salt

Boc-Phe (0.50gr, 1.88mmol), NaOH (64.4mg, 1.62mmol), AgNO₃ (0.229gr, 1.35mmol). White solid (0.437gr, 1.17mmol) 87%. ¹H-NMR (400 MHz, DMSO-d₆, ppm): δ 7.25 – 7.14 (m, 5H), 6.36 (d, J = 8.0 Hz, 1H), 4.05 (ddd, J = 8.4, 8.0, 4.4 Hz, 1H), 3.07 (dd, J = 13.6, 4.4 Hz, 1H), 2.84 (dd, J = 13.6, 8.4 Hz, 1H), 1.31 (s, 9H).

Boc-Valine silver salt

Boc-Val (0.50gr, 2.30mmol), NaOH (78.8mg, 1.97mmol), AgNO₃ (0.279gr, 1.64mmol). White solid (0.254gr, 0.752mmol) 48%. ¹H-NMR (400 MHz, DMSO-d₆, ppm): δ 6.06 (bs, 1H), 3.74 (m, 1H), 2.02 (m, 1H), 1.37 (s, 9H), 0.834 (d, J = 6.8 Hz, 3H), 0.804 (d, J = 6.8 Hz, 3H).

Boc-D-Alanine silver salt

Boc-Ala (0.30gr, 1.59mmol), NaOH (55.6mg, 1.39mmol), AgNO₃ (0.198gr, 1.16mmol). White solid (0.17gr, 0.58mmol) 50%. ¹H-NMR (500 MHz, DMSO-d₆, ppm): δ 6.37 (d, J = 7.5 Hz, 1H), 3.83 (dq, J = 7.5, 7.0 Hz, 2H), 1.36 (s, 9H), 1.20 (d, J = 7.0 Hz, 3H).

Synthesis of ruthenium complexes

General procedure

A solution of commercially available Hoveyda-Grubbs 2nd generation (1.0eq, 50.0 mg, 0.0798mmol) in dry THF (1.3ml) is added at once to Boc-protected amino acid silver salt (2.1eq) in the glovebox at the dark. The solution is left to stir at 37°C. After 3 hours silver chloride is filtered out and solvent evaporated to yield deep purple solid.
Complex Ru-G

Hoveyda-Grubbs 2nd generation (20.0mg, 0.0319mmol) in dry THF (0.7ml), Boc-Gly silver salt (18.9mg, 0.0670mmol). 27.1mg, 0.030mmol, 94%. ¹H-NMR (500 MHz, C₆D₆, ppm): δ 17.99 (s, 1H), 7.47 (dd, J = 7.5, 1.5 Hz, 1H), 7.02 (dd, J = 8.0, 7.5, 1.5 1H), 6.83 (t, J = 7.0 Hz, 1H), 6.81 (s, 4H), 6.23 (d, J = 8.5 Hz, 1H), 5.14 (bs, 2H), 4.12 (sep, J = 6.0, 1H), 3.80-3.67 (m, 4H), 3.22 (s, 3H), 2.29 (s, 12H), 2.22 (s, 6H), 1.42 (s, 18H), 0.85 (d, J = 6.0, 6H). ¹³C-NMR (100 MHz, C₆D₆, ppm): δ 304.5, 206.2, 174.7, 155.5, 154.7, 143.9, 139.0, 137.7, 137.2, 129.6, 122.6, 112.4, 78.3, 74.6, 51.9, 44.6, 28.5, 21.0, 20.7, 18.5. HRMS m/z calc. for C₄₅H₆₂N₄O₉Ru: 904.3564, found 904.3546. [α]D²⁵: 0.00 (c = 1.03, toluene).

Complex Ru-A

Hoveyda-Grubbs 2nd generation (50.0mg, 0.0798mmol) in dry THF (1.3ml), Boc-Ala silver salt (49.6mg, 0.168mmol). 71.0mg, 0.076mmol, 95%. ¹H-NMR (500 MHz, C₆D₆, ppm): δ 17.6 (s, 1H), 7.32 (dd, J = 7.5, 1.5 Hz, 1H), 6.99-6.91 (m, 5H), 6.73 (t, J = 7.0 Hz, 1H), 6.19 (d, J = 8.0 Hz, 1H), 5.65 (d, J = 6.5 Hz, 1H), 5.63 (d, J = 6.5 Hz, 1H), 4.35 (m, 2H), 4.10 (sep, J = 6.0, 1H), 3.26-3.19 (m, 4H), 2.41 (s, 6H), 2.25 (s, 6H), 2.18 (s, 6H), 1.443 (s, 9H), 1.437 (s, 9H), 1.38 (d, J = 6.5 Hz, 3H), 1.19 (d, J = 6.5 Hz, 3H), 0.890 (d, J = 6.0 Hz, 3H), 0.883 (d, J = 6.0 Hz, 3H). ¹³C-NMR (100 MHz, C₆D₆, ppm): δ 307.4, 212.0, 177.5, 176.0, 155.3, 155.2, 153.9, 143.8, 138.8, 138.7, 136.2, 129.7, 123.6, 122.3, 111.7, 78.3, 78.0, 74.3, 51.3, 51.2, 50.9, 28.6, 21.2, 20.8, 20.7, 20.0, 19.9, 18.6, 18.5. HRMS m/z calc. for [C₄₇H₆₅N₄O₉Ru]: 931.3790, found 931.3818. [α]D²⁵: +38.3 (c = 1.04, toluene).

Complex Ru-L

Hoveyda-Grubbs 2nd generation (20mg, 0.0319mmol) in dry THF (1.0 ml), Boc-Leu silver salt (22.7mg, 0.0670mmol). 25.3mg, 0.0249mmol, 77%. ¹H-NMR (500 MHz, C₆D₆, ppm): δ 17.58 (s, 1H), 7.28 (d, J = 7.0, 1H), 7.05-6.96 (m, 5H), 6.72 (t, J = 7.5 Hz ,1H), 6.28 (d, J = 8.5 Hz, 1H), 5.42 (dd, J = 8.4, 3.7 Hz, 2H), 4.55-4.41 (m, 2H), 4.31-4.26 (m, 1H), 3.30-3.26 (m, 4H), 2.50 (s, 6H), 2.29 (s, 6H), 2.26 (s, 6H), 1.48 (s, 9H), 1.45 (s, 9H), 1.10 (d, J = 6.5 Hz, 3H), 1.04-1.01 (m, 6H), 0.909 (d, J = 7.0 Hz, 3H), 0.810 (d, J = 7.0 Hz, 3H). ¹³C-NMR (100 MHz, C₆D₆, ppm): δ 307.1, 212.8,
177.8, 176.6, 155.8, 155.7, 153.8, 143.7, 139.1, 138.9, 138.8, 136.1, 129.8, 123.8, 122.3, 111.5, 78.2, 78.0, 74.4, 53.9, 53.7, 51.1, 44.2, 44.1, 28.6, 28.5, 25.1, 23.8, 23.6, 22.5, 22.3, 21.1, 20.9, 20.8, 18.9, 18.6. HRMS m/z calc. for [C_{55}H_{77}N_{4}O_{9}Ru]: 1015.4733, found 1015.4729; [α]_{D}^{25}: -18.2 (c = 1.10, toluene).

Complex Ru-F

Hoveyda-Grubbs 2nd generation (20mg, 0.0319mmol) in dry THF (1.3ml), Boc-Phe silver salt (24.9mg, 0.0670mmol). 29.8mg, 0.0275mmol, 87%. \(^1\)H-NMR (500 MHz, C\(_6\)D\(_6\), ppm): δ 17.70 (s, 1H), 7.36 (d, J = 7.0 Hz, 1H), 7.14-6.90 (m, 15H), 6.79 (t, J = 7.4 Hz, 1H), 6.28 (d, J = 8.0 Hz, 1H), 5.33 (dd, J = 16.9, 7.7 Hz, 2H), 4.70-4.62 (m, 2H), 4.16-4.11 (m, 1H), 3.28-3.22 (m, 4H), 2.92 (dd, J = 13.5, 7.0 Hz, 2H), 2.70 (dd, J = 13.5, 6.0 Hz, 2H), 2.43 (s, 6H), 2.28 (s, 6H), 2.23 (s, 6H), 1.40 (s, 18H), 0.967 (d, J = 6.0, 3H), 0.822 (d, J = 5.5, 3H). \(^1^3\)C-NMR (100 MHz, C\(_6\)D\(_6\), ppm): δ 307.4, 212.0, 175.9, 175.0, 155.3, 153.9, 143.6, 139.1, 138.9, 138.8, 138.5, 136.0, 130.2, 130.0, 129.8, 129.7, 129.0, 128.2, 127.9, 126.1, 124.0, 122.5, 111.9, 78.3, 78.1, 56.6, 55.8, 51.1, 39.4, 39.0, 28.6, 28.4, 21.2, 20.8, 20.7, 18.7, 18.6. HRMS m/z calc. for [C_{59}H_{73}N_{4}O_{9}Ru]: 1083.4431, found 1083.4416. [α]_{D}^{25}: -37.5 (c = 1.07, toluene).

Complex Ru-DA

Hoveyda-Grubbs 2nd generation (50mg, 0.0798mmol) in dry THF (1.3ml), Boc-Ala silver salt (49.6mg, 0.168mmol). 58.3mg, 0.0625mmol, 78%. \(^1\)H-NMR (500 MHz, C\(_6\)D\(_6\), ppm): δ 17.6 (s, 1H), 7.31 (dd, J = 7.5, 1.0 Hz, 1H), 6.99-6.91 (m, 5H), 6.73 (t, J = 7.5 Hz, 1H), 6.20 (d, J = 8.5 Hz, 1H), 5.67 (d, J = 6.0 Hz, 1H), 5.64 (d, J = 6.5 Hz, 1H), 4.36 (m, 2H), 4.10 (sep, J = 6.0, 1H), 3.29-3.19 (m, 4H), 2.41 (s, 6H), 2.25 (s, 6H), 2.18 (s, 6H), 1.443 (s, 9H), 1.436 (s, 9H), 1.38 (d, J = 7.0 Hz, 3H), 1.19 (d, J = 6.5 Hz, 3H), 0.890 (d, J = 6.0 Hz, 3H), 0.884 (d, J = 6.0 Hz, 3H). \(^1^3\)C-NMR (100 MHz, C\(_6\)D\(_6\), ppm): δ 307.4, 212.0, 177.5, 176.0, 155.3, 155.2, 153.9, 143.8, 138.8, 138.7, 136.2, 129.7, 123.6, 122.3, 111.7, 78.3, 78.0, 74.3, 51.3, 51.2, 50.9, 28.6, 21.2, 20.8, 20.7, 20.0, 19.9, 18.6, 18.5. HRMS m/z calc. for [C_{47}H_{65}N_{4}O_{9}Ru]: 931.3790, found 931.3822; [α]_{D}^{22}: -38.5 (c = 1.04, toluene).
Part III. NMR spectra

Boc-Glycine silver salt
Boc-Alanine silver salt
Boc-Leucine silver salt

O
H
O
OAg

H2O
DMSO

1.0

0.5

13.5

12.5

11.5

10.5

10.0

9.5

9.0

8.5

8.0

7.5

7.0

6.5

6.0

5.5

5.0

4.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0.0
Boc-Phenylalanine silver salt
Boc-D-Alanine silver salt

![Chemical structure of Boc-D-Alanine silver salt]
Complex Ru-A

C₆H₆
Complex Ru-F
Complex Ru-DA
Any attempt to synthesize complexes bearing Boc-valine or Boc-proline as anionic ligands were unsuccessful. The $^1$H-NMRs (400MHz) of the reaction crudes disclosed a mixture of carbenes.

**Figure 1.** Synthesis with Boc-valine silver salt.

**Figure 2.** Synthesis with Boc-proline silver salt.
Part IV. HR-MS data

Complex Ru-G

Complex Ru-A
Complex Ru-DA

![Graph showing experimental and theoretical mass spectra]

**EXPERIMENTAL**

- NL: 8.46E4
- sample2_toluene_400-1050
- RT: 0.31
- AV: 1 T: FTMS + p
- NSI Full ms
- [400.00-1050.00]

**THEORETICAL**

- NL: 1.82E5
- C_{47}H_{65}O_{9}N_{4}Ru
- C_{47}H_{65}O_{9}N_{4}Ru_{1}
- pa Chrg 1
Part V. X-Ray data

Crystals of Ru-G suitable for x-ray diffraction were grown by slow diffusion of pentane into ether solution of the complex. CIF files are attached separately.

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Part VI. Synthesis of Ru-G in DCM

Synthesis of Ru-G, as specified in the general procedure, in DCM-d2, was followed by ¹H-NMR (500MHz) (Figure 3). Inspection of the benzylidene shift showed that after 5 hours the reaction does not complete and after 24 hours the complex decomposes as indicated by the 2-isopropoxybenzaldehyde peak of the decomposition product.³ Synthesis of Ru-G as specified in the general procedure in THF-d₈ was followed by ¹H-NMR (500MHz) as well (Figure 4). As can be seen, the reaction is complete after only 3 hours, yielding a single carbene peak of the desired product 3. Subsequently, a sample from the isolated product was taken to the NMR in DCM-d₂. Disproportionation of the di-substituted complex 3 to the mono-substituted complex 2 was observed. This indicates that DCM is not a suitable solvent for the synthesis of the chiral complexes as it facilitates a degenerate ligand exchange of the anionic ligands, in accordance with previous work by Blechert⁴ and co-workers and Braddock and co-workers.⁵

Scheme 1. Synthesis of Ru-G starting from Grubbs-Hoveyda 2nd generation

Figure 3. Reaction progress for the synthesis of Ru-G in DCM-d$_2$

Figure 4. Reaction progress for the synthesis of Ru-G in THF-d$_8$
Part VII. Catalytic activity tests

General procedure of AROCM of 1

Substrate 1 was prepared according to literature; product 3 is a known compound.\(^6\)

\[
\begin{array}{c}
\text{O} \quad \text{Ph} \\
8 \text{mol\%}[\text{Ru}] \\
\text{THF, } 37^\circ\text{C, 40min} \\
\end{array}
\begin{array}{c}
\text{O} \\
\text{2} \\
\end{array} 
\xrightarrow{\text{Ph}}
\begin{array}{c}
\text{O} \quad \text{Ph} \\
\text{3} \\
\end{array}
\]

To a solution of 1 (20.0mg, 0.122mmol) and styrene (136mg, 1.31mmol) in THF (1.5ml), complex Ru-A (8.9mg, 9.55\mu\text{mol}, 7.8mol\%) in dry THF (0.5ml), (0.056M) was added in the glovebox and the mixture was left to stir at 37\(^\circ\)C for 2 hours. Reaction was quenched with ethyl vinyl ether. The solvent was evaporated and the crude was purified by flash chromatography with 50\% Et\(_2\)O/pentane to obtain product 3. Conversions were monitored by GC-MS and \textit{ee} was determined by HPLC.

General procedure of ARCM of 2

Substrate 2 was prepared according to literature; product 4 is a known compound.\(^7\)

\[
\begin{array}{c}
\text{O} \\
\text{2} \\
\end{array} 
\xrightarrow{8 \text{mol\%}[\text{Ru}] \\
\text{THF, } 37^\circ\text{C, 40min} \\
\text{O} \quad \text{2} \\
\end{array} 
\]

To triene 2 (9.7mg, 0.054mmol) complex Ru-A (4 mg, 4.3\mu\text{mol}, 8.0mol\%) in dry THF (1.0ml, 0.056M) was added in the glovebox and the mixture was left to stir at 37\(^\circ\)C for 2 hours. Reaction was quenched with ethyl vinyl ether. The solvent was evaporated and the crude was purified by flash chromatography with 5\% Et\(_2\)O/pentane to obtain product 4. Conversions were monitored by GC-MS and \textit{ee} was determined by HPLC.


Data for ARCM under different conditions:

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<th>ee [%]</th>
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<td>Ru-G</td>
<td>37</td>
<td>THF</td>
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ARCM conditions as specified in the general procedure. <sup>a</sup>40mol% in respect to Ru-A<sup>b</sup> 2.5 mol% <sup>c</sup>7.0 mol% <sup>d</sup>accompanied by cycloisomerization products.
General procedure of CM of styrene

To a solution of styrene (12.5µl, 0.11mmol) in dry solvent (1.0ml), complex Ru-A (8 mg, 8.6µmol, 7.8mol%) in dry solvent (1.0ml, 0.056M) was added in the glovebox and the mixture was left to stir at 37°C. Reaction was quenched with ethyl vinyl ether. Conversions and E/Z ratio were monitored by GC-MS.

Data for CM under different conditions:

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>solvent</th>
<th>t (hours)</th>
<th>additive&lt;sup&gt;a&lt;/sup&gt;</th>
<th>conversion [%]</th>
<th>E:Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hoveyda-Grubbs II&lt;sup&gt;b&lt;/sup&gt;</td>
<td>benzene</td>
<td>24</td>
<td>-</td>
<td>87</td>
<td>1:0</td>
</tr>
<tr>
<td>2</td>
<td>Ru-A</td>
<td>THF</td>
<td>24</td>
<td>Ala-OAg</td>
<td>36</td>
<td>1:0</td>
</tr>
<tr>
<td>3</td>
<td>Ru-A</td>
<td>benzene</td>
<td>48</td>
<td>Ala-OAg</td>
<td>38</td>
<td>1:0</td>
</tr>
</tbody>
</table>

CM conditions as specified in the general procedure. <sup>a</sup>40mol% in respect to Ru-A <sup>b</sup>2.5 mol%.
Part VIII. Chiral HPLC data

ARCM promoted by Hoveyda-Grubbs-II:

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 0% ee.

ARCM product received by Ru-G:

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 0% ee.
ARCM product received by Ru-A:

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 20% ee.

ARCM product received by Ru-L:

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 12% ee.
ARCM product received by **Ru-F**:  

![Graph](Image)

<table>
<thead>
<tr>
<th>Reten. Time [min]</th>
<th>Area [mV·s]</th>
<th>Height [mV]</th>
<th>Area [%]</th>
<th>Height [%]</th>
<th>W05 [min]</th>
<th>Peak Purity [-]</th>
<th>Compound Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.68</td>
<td>370.950</td>
<td>47.165</td>
<td>49.9</td>
<td>57.3</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.237</td>
<td>380.778</td>
<td>35.208</td>
<td>50.1</td>
<td>42.7</td>
<td>0.17</td>
<td>747</td>
</tr>
<tr>
<td>Total</td>
<td>760.737</td>
<td>82.393</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 0% ee.

ARCM product received by **Ru-DA**:  

![Graph](Image)

<table>
<thead>
<tr>
<th>Reten. Time [min]</th>
<th>Area [mV·s]</th>
<th>Height [mV]</th>
<th>Area [%]</th>
<th>Height [%]</th>
<th>W05 [min]</th>
<th>Peak Purity [-]</th>
<th>Compound Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.414</td>
<td>1027.115</td>
<td>126.262</td>
<td>60.0</td>
<td>73.0</td>
<td>0.11</td>
<td>813</td>
</tr>
<tr>
<td>2</td>
<td>8.040</td>
<td>685.497</td>
<td>51.237</td>
<td>40.0</td>
<td>27.0</td>
<td>0.21</td>
<td>932</td>
</tr>
<tr>
<td>Total</td>
<td>1712.557</td>
<td>177.499</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 20% ee.
ARCM product received by Ru-A at 0°C:

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 27% ee.

ARCM product received by Ru-DA at 0°C:

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 28% ee.
ARCM product received by Ru-A with excess Boc-Ala silver salt:

Conditions: 220nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 34% ee.

ARCM product received by Ru-A in benzene:

Conditions: 220nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 44% ee.
ARCM product received by **Ru-A** in benzene with excess Boc-Ala silver salt:

Conditions: 220nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 56% ee.

AROCM promoted by **Hoveyda-Grubbs-II**:

Conditions: 254nm, hexane/isopropanol 92:8, flow, 0.75ml/min, 0% ee.
AROCM product received by Ru-G:

Conditions: 254nm, hexane/isopropanol 92:8, flow, 0.75ml/min, 0% ee.

AROCM product received by Ru-A:

Conditions: 254nm, hexane/isopropanol 92:8, flow, 0.75ml/min, 4% ee.
AROCM product received by **Ru-F**:

![Graph showing chromatogram](image)

Conditions: 254nm, hexane/isopropanol 92:8, flow, 0.75ml/min, 4% ee.

AROCM product received by **Ru-DA**:

![Graph showing chromatogram](image)

Conditions: 254nm, hexane/isopropanol 92:8, flow, 0.75ml/min, 4% ee.
Part IX. $^1$H-NMR data of anionic ligand exchange

Ligand exchange for Ru-A with Boc-Glycine silver salt

In the glove box, Ru-A complex (6.45mg, 6.92µmol, 1.0eq) in THF-d$_8$ (0.2ml) was added to an NMR-tube charged with Boc-Gly-OAg (4.20mg, 1.49x10$^{-5}$ mol, 2.1eq) in THF-d$_8$ (0.3ml). Reaction was followed by $^1$H-NMR (400MHz).

Ratio of carbene peaks:

<table>
<thead>
<tr>
<th></th>
<th>Ru-A</th>
<th>-</th>
<th>-</th>
<th>Ru-G</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>17.37ppm</td>
<td>17.57ppm</td>
<td>17.49ppm</td>
<td>17.74ppm</td>
</tr>
<tr>
<td>2 hours</td>
<td>1.00</td>
<td>0.52</td>
<td>0.30</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.63</td>
<td>0.40</td>
<td>0.29</td>
</tr>
</tbody>
</table>
Ligand exchange for **Ru-F** with Boc-Glycine silver salt

In the glove box, Boc-Gly-OAg (8.40mg, 2.97x10⁻⁵ mol, 2.1eq) was added to an NMR-tube charged with **Ru-F** complex (15.1mg, 1.39x10⁻⁵ mol, 1.0eq) and THF-d₈ (1.0ml). Reaction was followed by ¹H-NMR (400MHz).

<table>
<thead>
<tr>
<th></th>
<th><strong>Ru-F</strong></th>
<th>-</th>
<th>-</th>
<th><strong>Ru-G</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>17.48ppm</td>
<td>17.46ppm</td>
<td>17.55ppm</td>
<td>17.74ppm</td>
</tr>
<tr>
<td>2 hours</td>
<td>1.00</td>
<td>0.70</td>
<td>0.31</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.12</td>
<td>0.51</td>
<td>0.43</td>
</tr>
</tbody>
</table>

After 2 hours the amount of the original Ru complex according to the ¹H-NMR (400MHz) benzylidene signal in the **Ru-F** experiment is less than the amount of original Ru complex in **Ru-A** when Boc-glycine was added in both cases.