Electronic Supplementary Material (ESI) for ChemComm.


**Supplementary Information**

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

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## Part I. General information

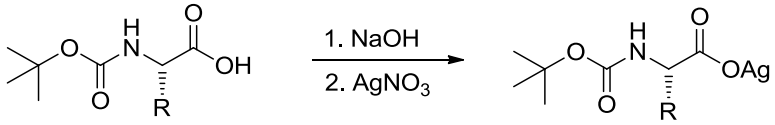
All reagents were of grade quality, purchased commercially from Sigma-Aldrich, Alfa-Aesar or Fluka and used without further purification. All solvents were dried and distilled prior to use. Purification by column chromatography was performed on Davisil grade chromatographic silica media 60 Å (35-75 $\mu$m, 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, 8$\mu$m, 150x4.5 mm and a PDA detector. Specific rotations were measured by using ADP410 Polarimeter at wavelength $\lambda$=589nm and sample concentration "*c*" has units of g/100ml.

[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

## Part II. Synthesis

### Synthesis of silver carboxylate salts

### General procedure[2]




Boc-protected amino acid (1.4eq, 0.5gr) was added to a stirring solution of aqueous NaOH (1.2eq in 1ml $H_2O$). The mixture was left to stir at r.t for 15 min and an aqueous solution of $AgNO_3$ (1.0eq in 1ml $H_2O$) 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 $H_2O$ (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), $AgNO_3$ (0.35gr, 2.0mmol). White solid (0.51gr, 1.8mmol), 88%. $^1$H-NMR (500 MHz, DMSO-$d_6$, 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), $AgNO_3$ (0.32gr, 1.9mmol). White solid (0.38gr, 1.3mmol) 68%. $^1$H-NMR (500 MHz, DMSO-$d_6$, 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. $AgNO_3$ (0.267gr, 1.57mmol). White solid (0.442gr, 1.31mmol) 83%. $^1$H-NMR (400 MHz, DMSO-$d_6$, 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).

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[2] K. Endo and R. H. Grubbs, *J. Am. Chem. Soc.*, 2011, **133**, 8525.

**Boc-Phenylalanine silver salt**

Boc-Phe (0.50gr, 1.88mmol), NaOH (64.4mg, 1.62mmol), $AgNO_3$ (0.229gr, 1.35mmol). White solid (0.437gr, 1.17mmol) 87%. $^1$H-NMR (400 MHz, DMSO-$d_6$, 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**

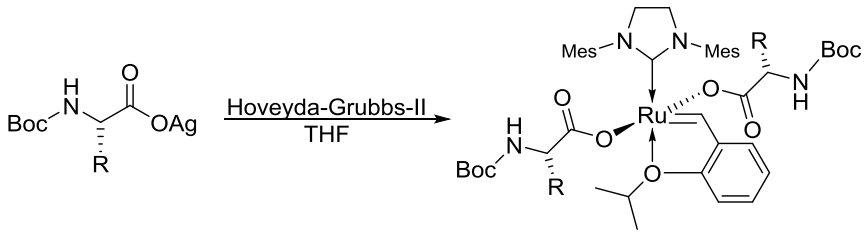
Boc-Val (0.50gr, 2.30mmol), NaOH (78.8mg, 1.97mmol), $AgNO_3$ (0.279gr, 1.64mmol). White solid (0.254gr, 0.752mmol) 48%. $^1$H-NMR (400 MHz, DMSO-$d_6$, ppm): δ 6.06 (bs, 1H), 3.74 (m, 1H), 2.02 (m, 1H), 1.37 (s, 9H), 0.834 (d, J = 6.8 Hz, 3H), 0.804 (d, J = 6.8 Hz, 3H).

**Boc-D-Alanine silver salt**

Boc-Ala (0.30gr, 1.59mmol), NaOH (55.6mg, 1.39mmol), $AgNO_3$ (0.198gr, 1.16mmol). White solid (0.17gr, 0.58mmol) 50%. $^1$H-NMR (500 MHz, DMSO-$d_6$, 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 2$^{nd}$ 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%. $^{1}$H-NMR (500 MHz, $C_6D_6$, ppm): δ 17.99 (s, 1H), 7.47 (dd, J = 7.5, 1.5 Hz, 1H), 7.02 (ddd, 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, 4H), 2.29 (s, 12H), 2.22 (s, 6H), 1.42 (s, 18H), 0.85 (d, J = 6.0, 6H). $^{13}$C-NMR (100 MHz, $C_6D_6$, ppm): δ 304.5, 206.2, 174.7, 155.5, 154.7, 143.9, 138.0, 137.7, 137.2, 129.6, 123.3, 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 $C_{45}H_{62}N_4O_9Ru$: 904.3564, found 904.3546. $[\alpha]_D^{25}$: 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%. $^{1}$H-NMR (500 MHz, $C_6D_6$, 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 = 7.5 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). $^{13}$C-NMR (100 MHz, $C_6D_6$, 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 [$C_{47}H_{65}N_4O_9Ru$]: 931.3790, found 931.3818. $[\alpha]_D^{25}$: +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%. $^{1}$H-NMR (500 MHz, $C_6D_6$, 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). $^{13}$C-NMR (100 MHz, $C_6D_6$, 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 [$C_{53}H_{77}N_4O_9Ru$]: 1015.4733, found 1015.4729; $[\alpha]_D^{25}$: -18.2 (*c* = 1.10, toluene).

**Complex Ru-F**

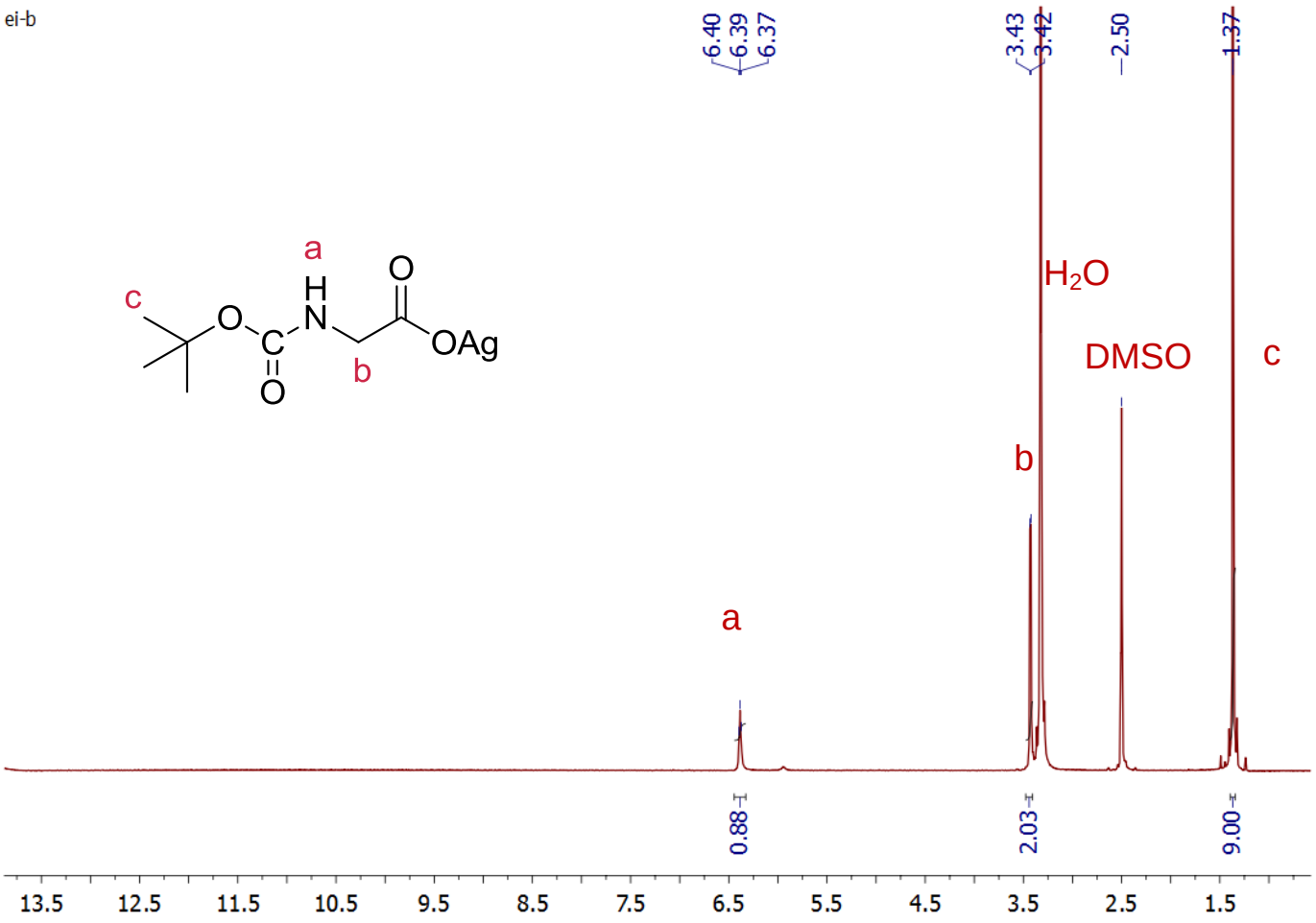
Hoveyda-Grubbs 2nd generation (20mg, 0.0319mmol) in dry THF (1.3ml), Boc-Phe silver salt (24.9mg, 0.0670mmol). 29.8mg, 0.0275mmol, 87%. $^1$H-NMR (500 MHz, $C_6D_6$, ppm): δ 17.70 (s, 1H), 7.36 (d, J = 7.0 Hz, 1H), 7.14-6.90 (m, 15H), 6.79 (t, J = 7.4 Hz, 1H), 6.28 (d, J = 8.0 Hz, 1H), 5.33 (dd, J = 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). $^{13}$C-NMR (100 MHz, $C_6D_6$, ppm): δ 307.6, 212.4, 175.9, 175.0, 155.4, 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 [$C_{59}H_{73}N_4O_9Ru$]: 1083.4431, found 1083.4416. $[\alpha]_D^{25}$: -37.5 (*c* = 1.07, toluene).

**Complex Ru-DA**

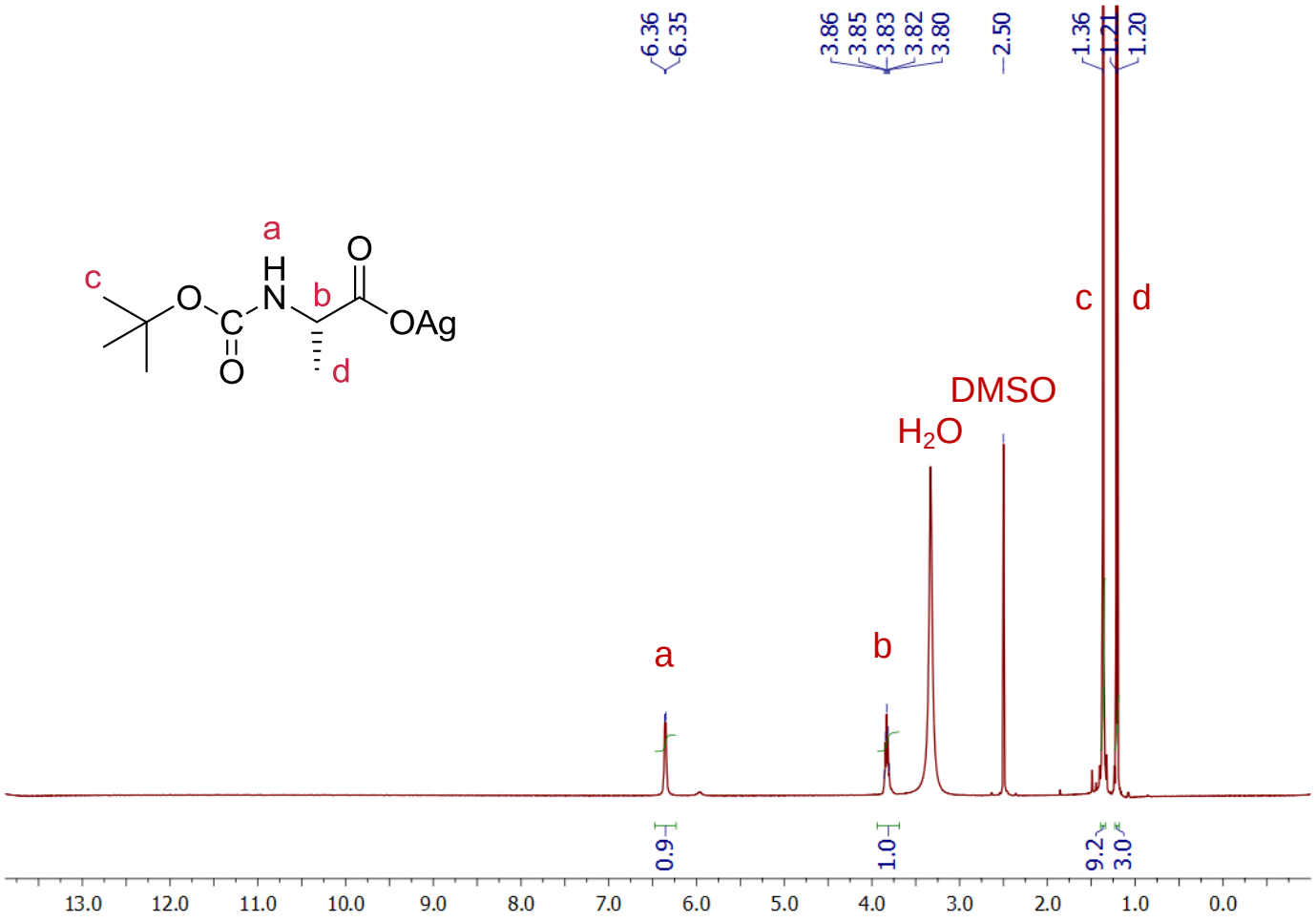
Hoveyda-Grubbs 2nd generation (50mg, 0.0798mmol) in dry THF (1.3ml), Boc-Ala silver salt (49.6mg, 0.168mmol). 58.3mg, 0.0625mmol, 78%. $^1$H-NMR (500 MHz, $C_6D_6$, ppm): δ 17.6 (s, 1H), 7.31 (dd, J = 7.5, 1.0 Hz, 1H), 6.99-6.91 (m, 5H), 6.73 (t, J = 7.5 Hz, 1H), 6.20 (d, J = 8.5 Hz, 1H), 5.67 (d, J = 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). $^{13}$C-NMR (100 MHz, $C_6D_6$, 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 [$C_{47}H_{65}N_4O_9Ru$]: 931.3790, found 931.3822; $[\alpha]_D^{22}$: -38.5 (*c* = 1.04, toluene).

## Part III. NMR spectra

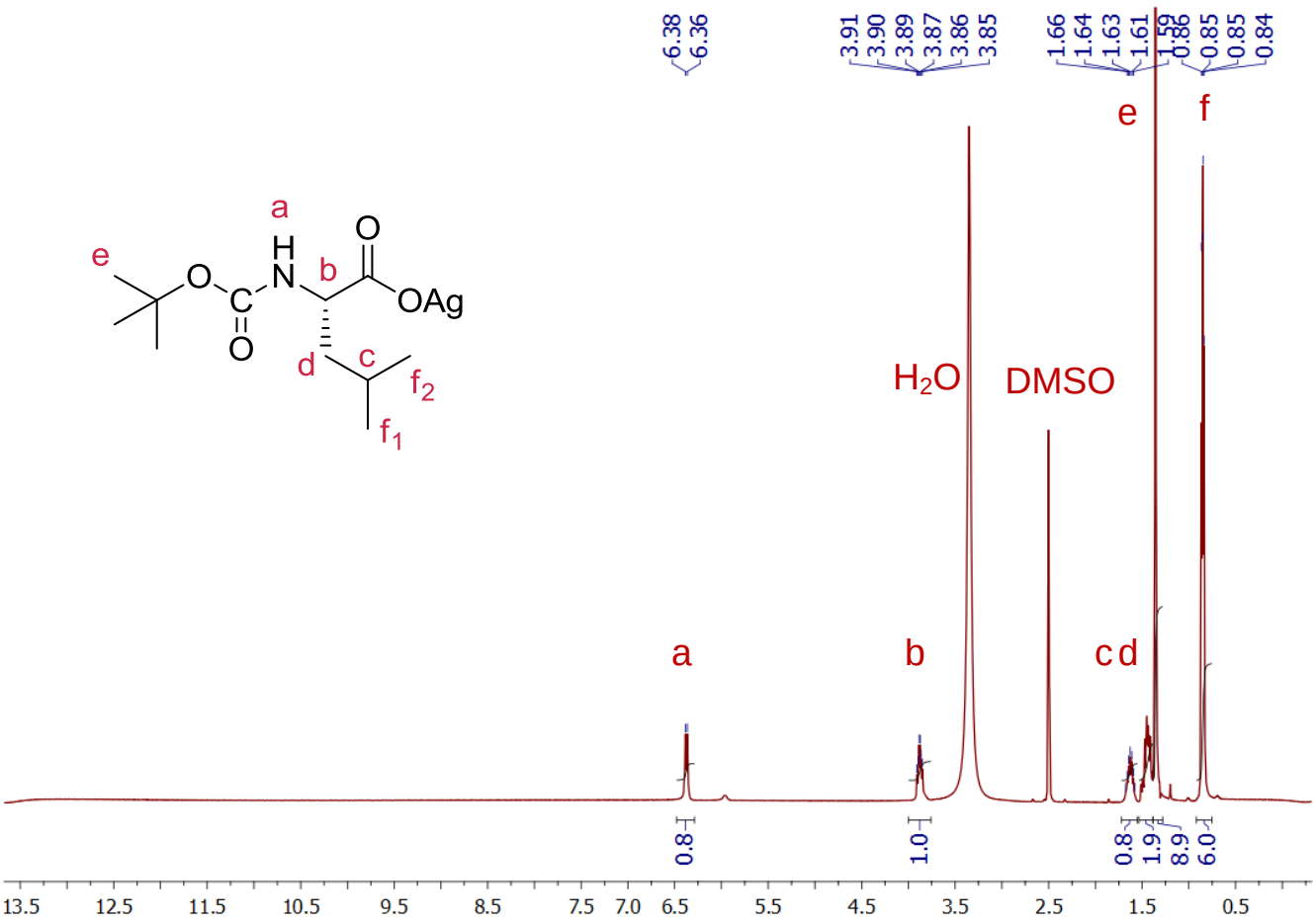
### Boc-Glycine silver salt



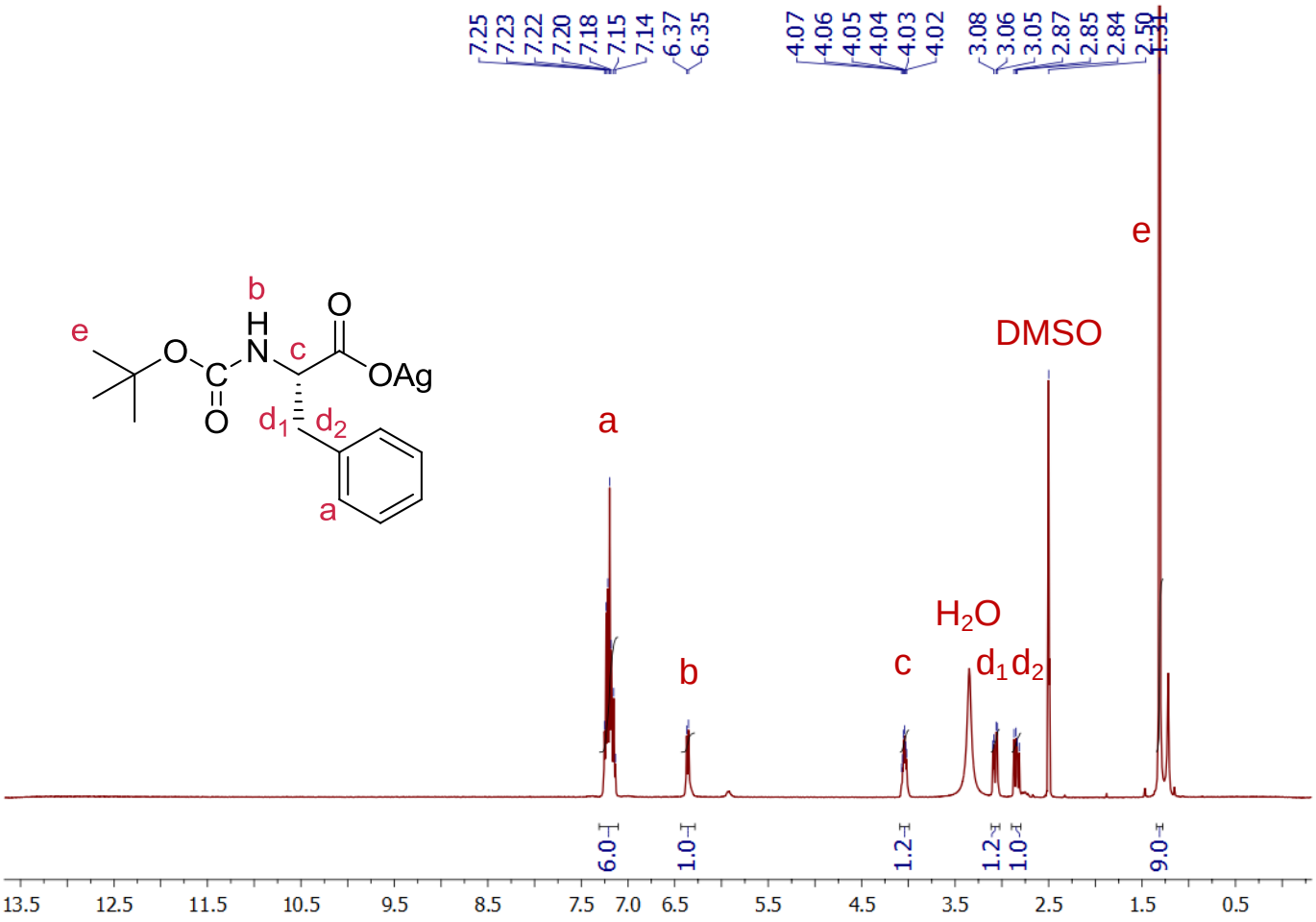
**Boc-Alanine silver salt**



**Boc-Leucine silver salt**



**Boc-Phenylalanine silver salt**



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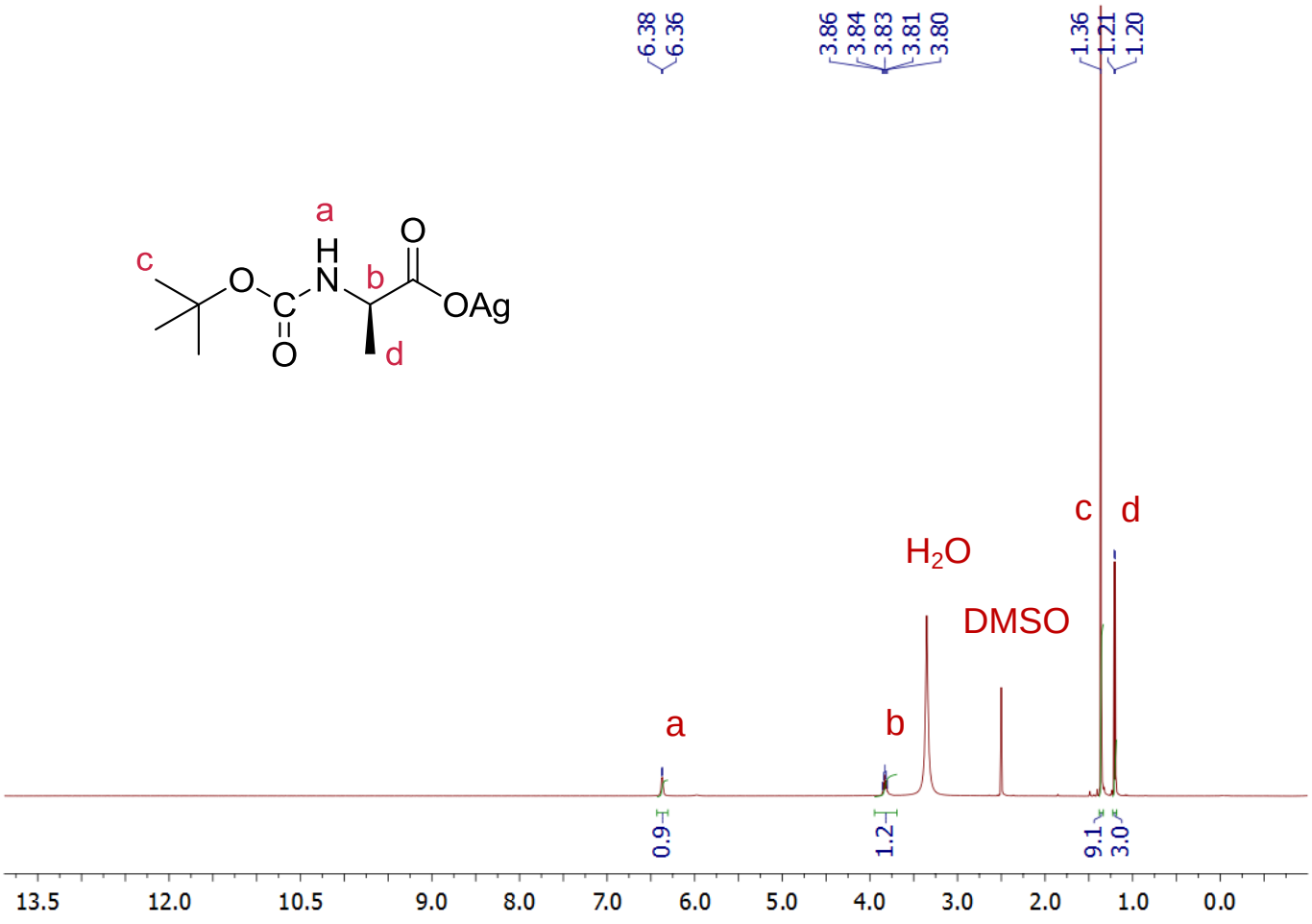
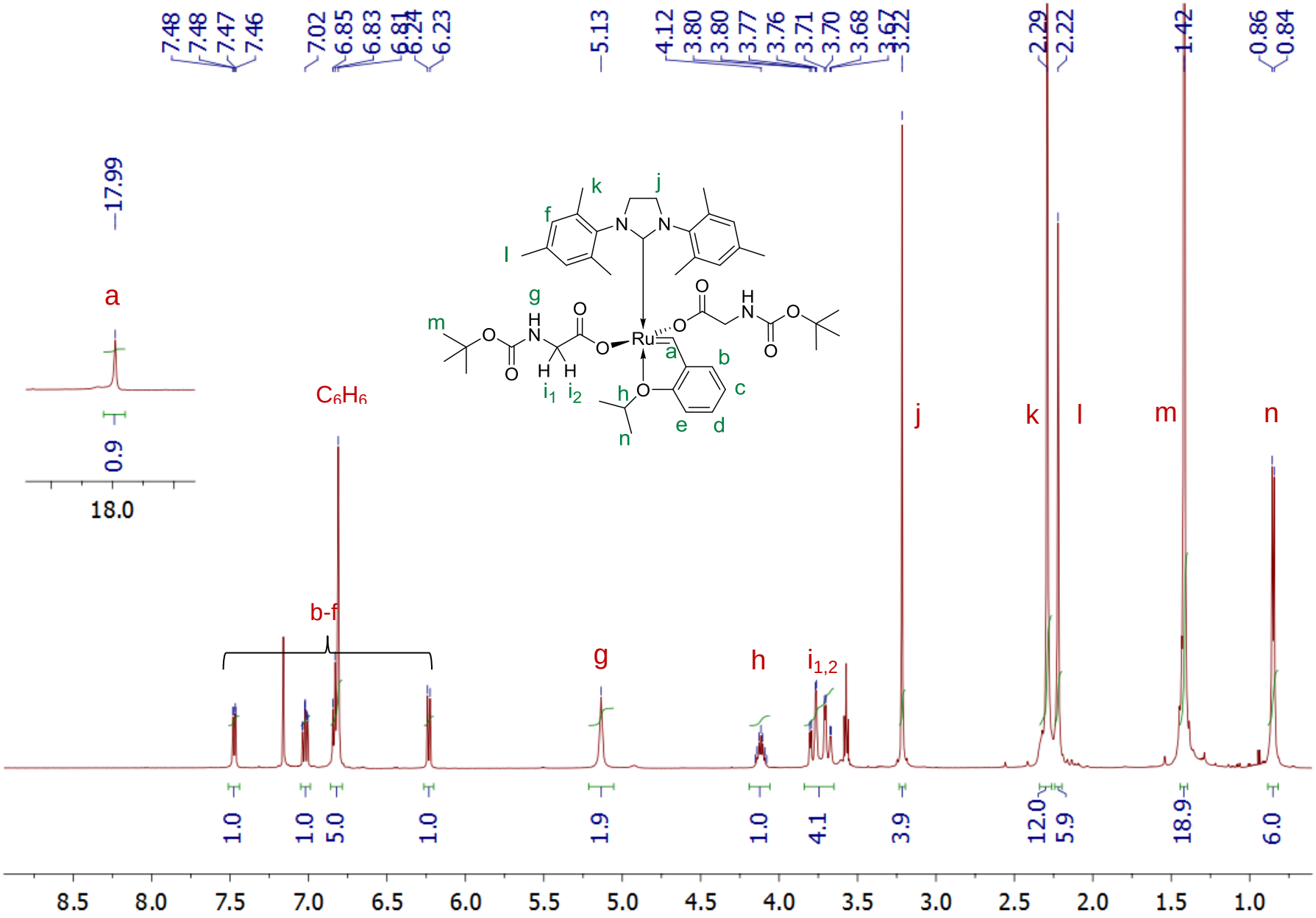


**Complex Ru-G**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3.76
3.71
3.70
3.68
3.67
3.22
2.29
2.22
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0.84
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C6H6
b-f
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h
i1,2
j
k
l
m
n
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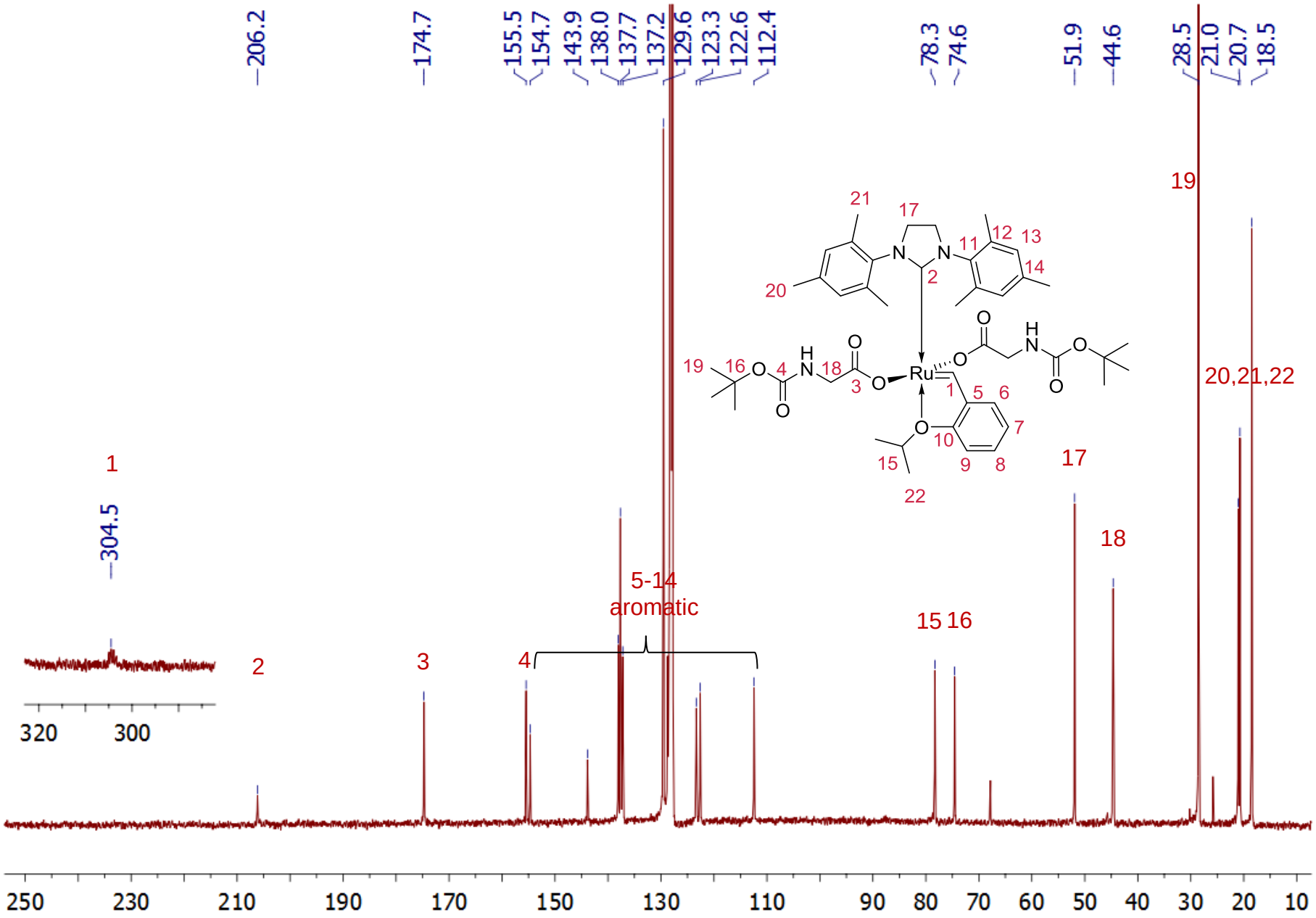
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74.6
51.9
44.6
28.5
21.0
20.7
18.5
304.5
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3
4
5-14
aromatic
15 16
17
18
19
20,21,22
320
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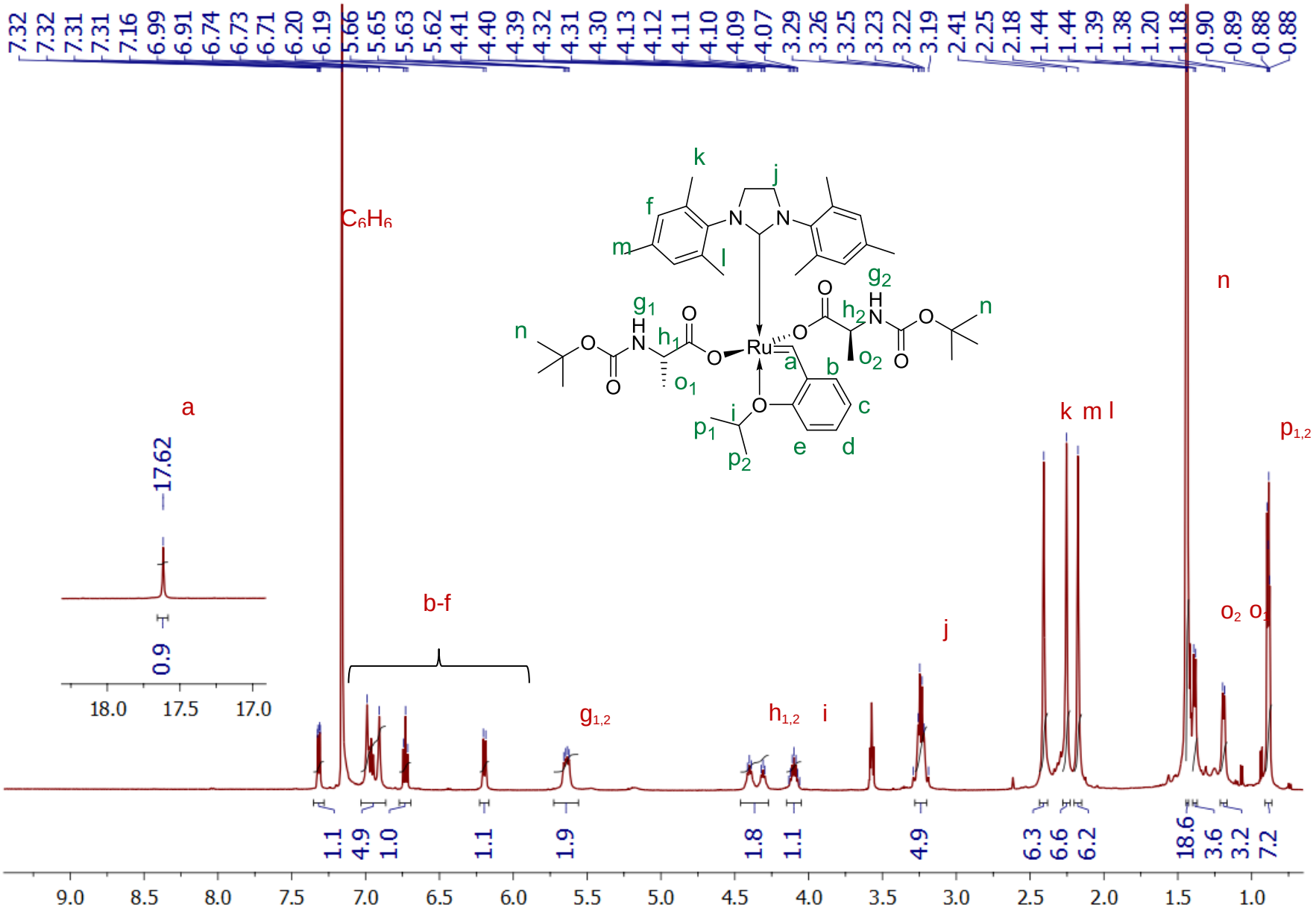
10

**Complex Ru-A**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b-f
g1,2
h1,2
i
j
k m l
n
o2 o1
p1,2
1.1 4.9 1.0 1.1 1.9 1.8 1.1 4.9 6.3 6.6 6.2 18.6 3.6 3.2 7.2
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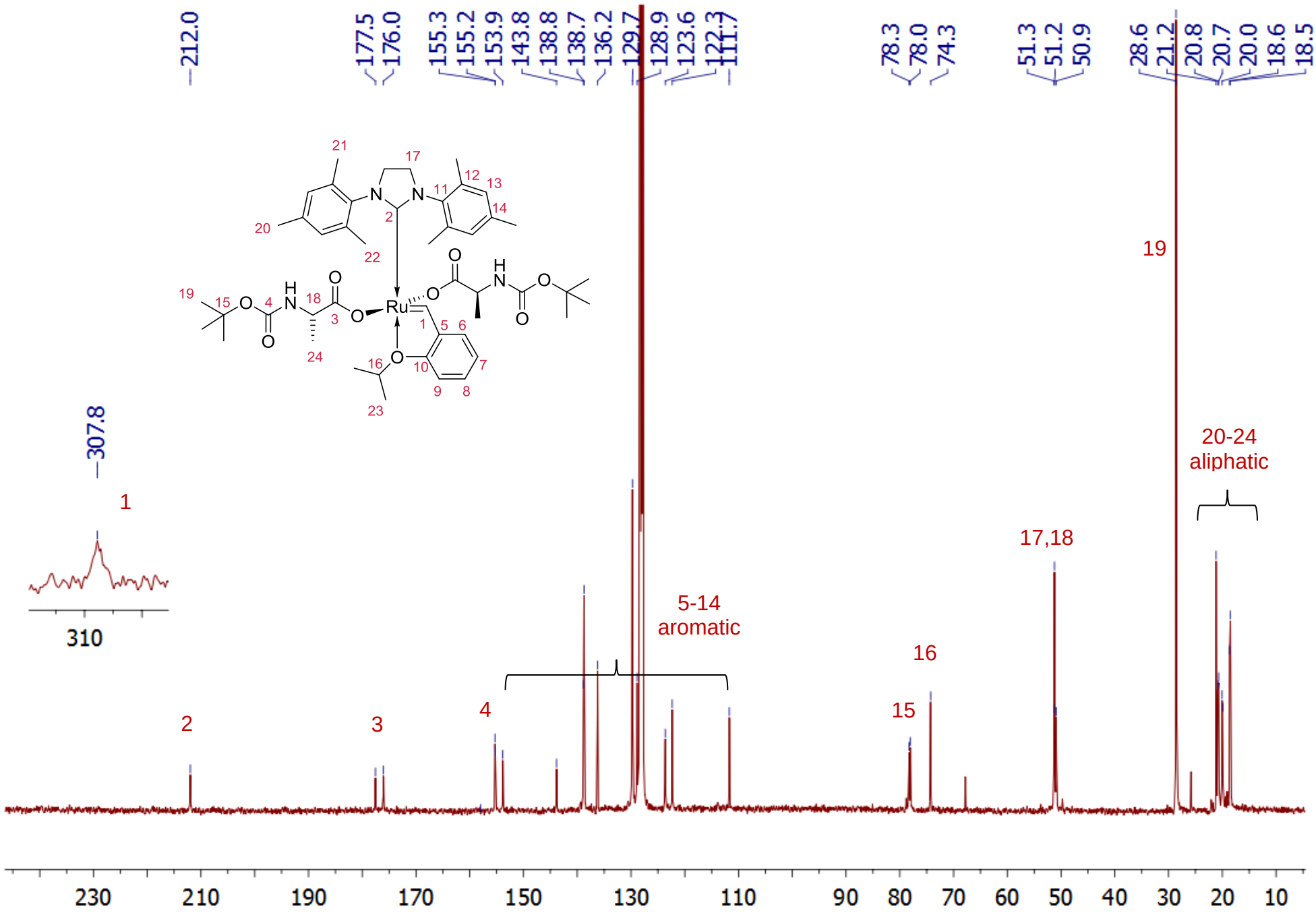
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20-24
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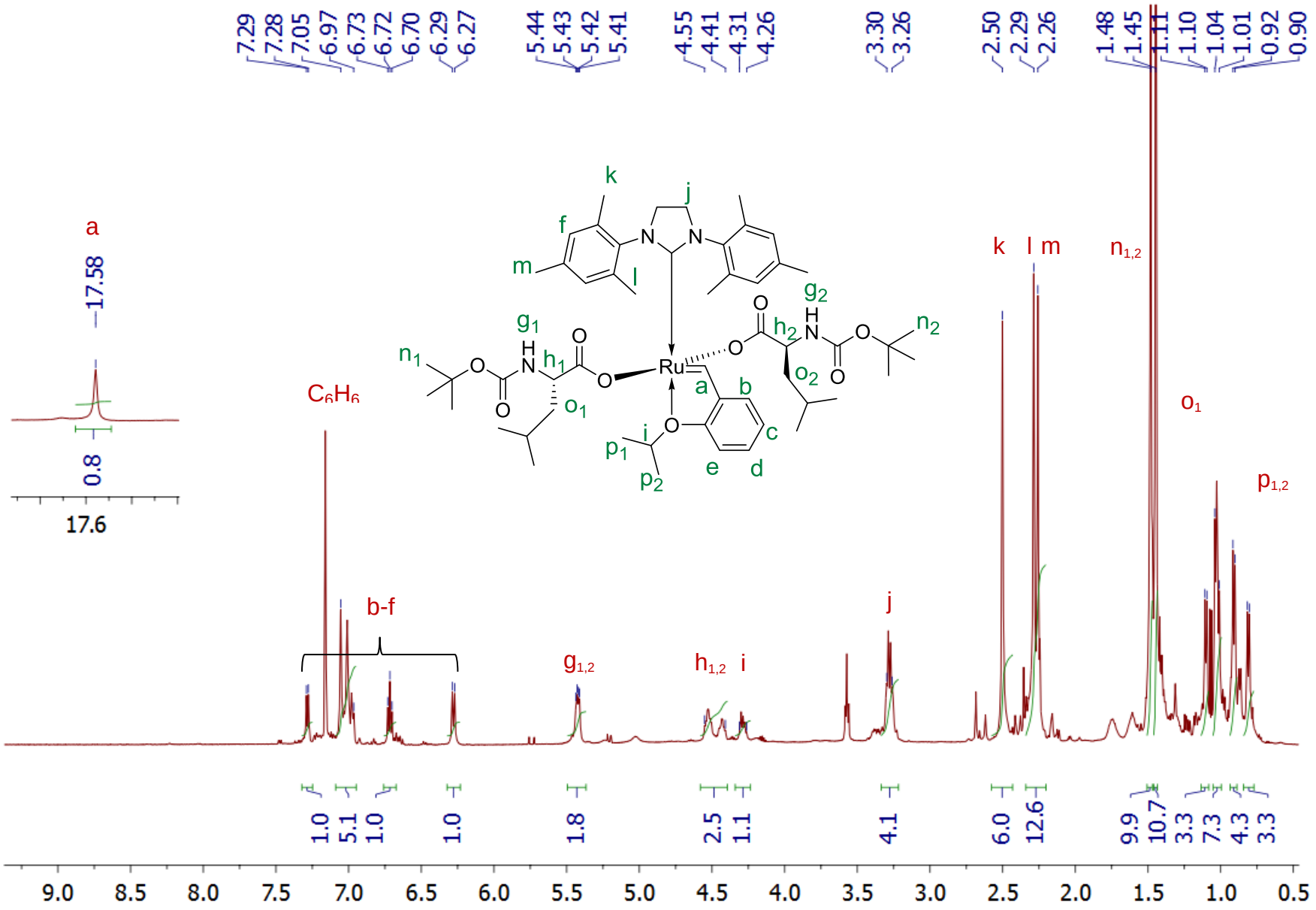
**Complex Ru-L**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i
j
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l m
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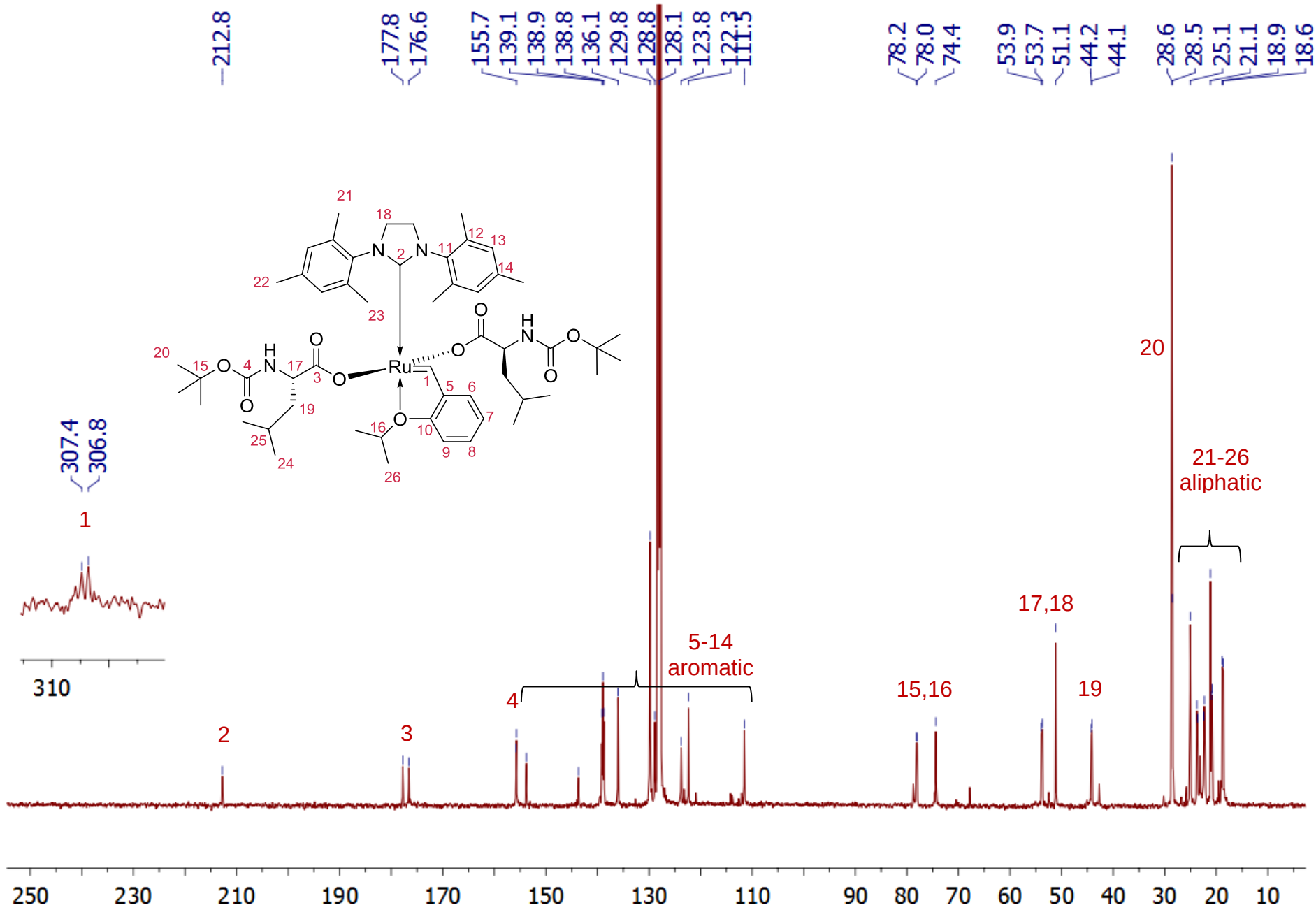
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122.3
111.5
78.2
78.0
74.4
53.9
53.7
51.1
44.2
44.1
28.6
28.5
25.1
21.1
18.9
18.6
307.4
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19
20
21-26
aliphatic
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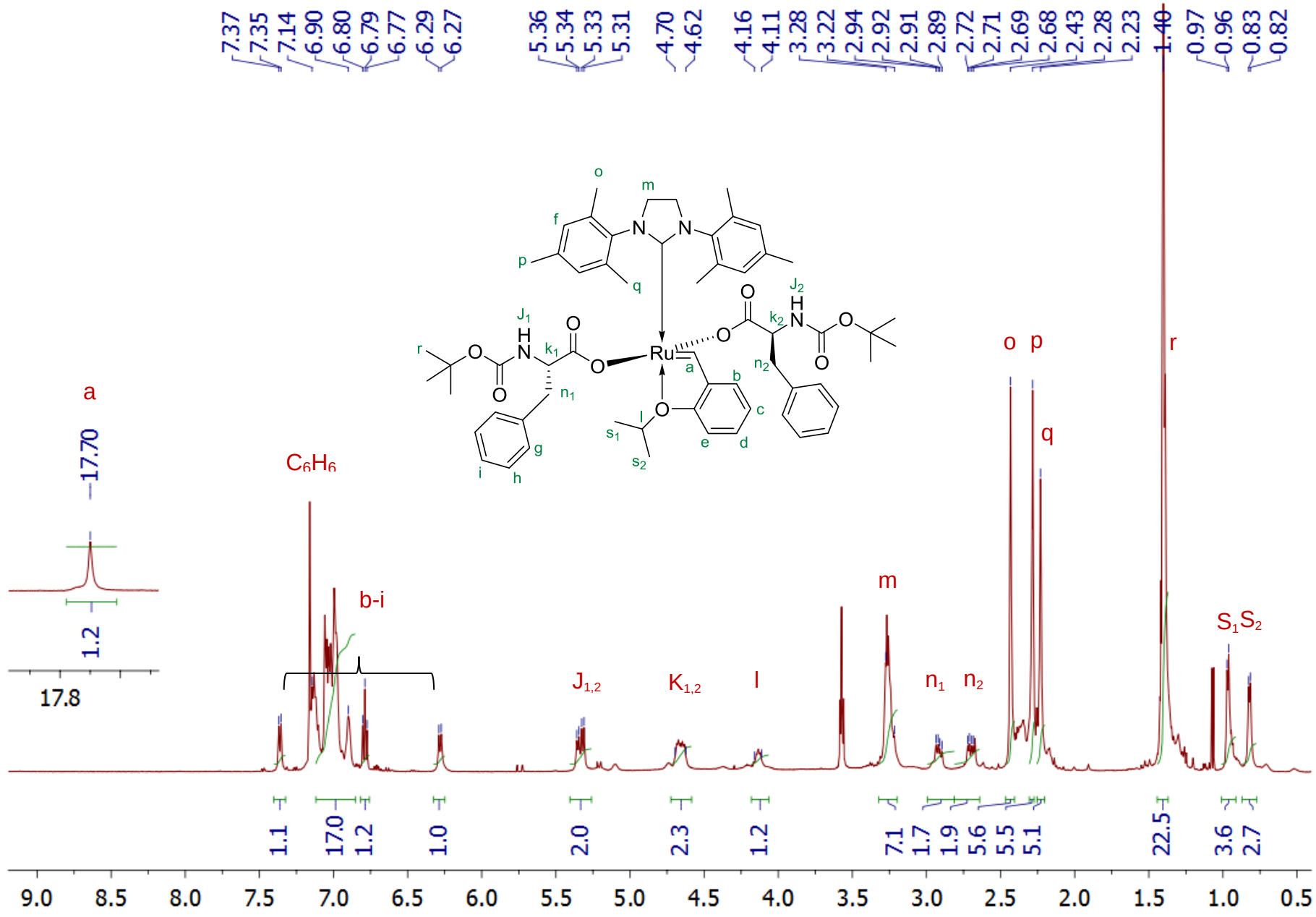
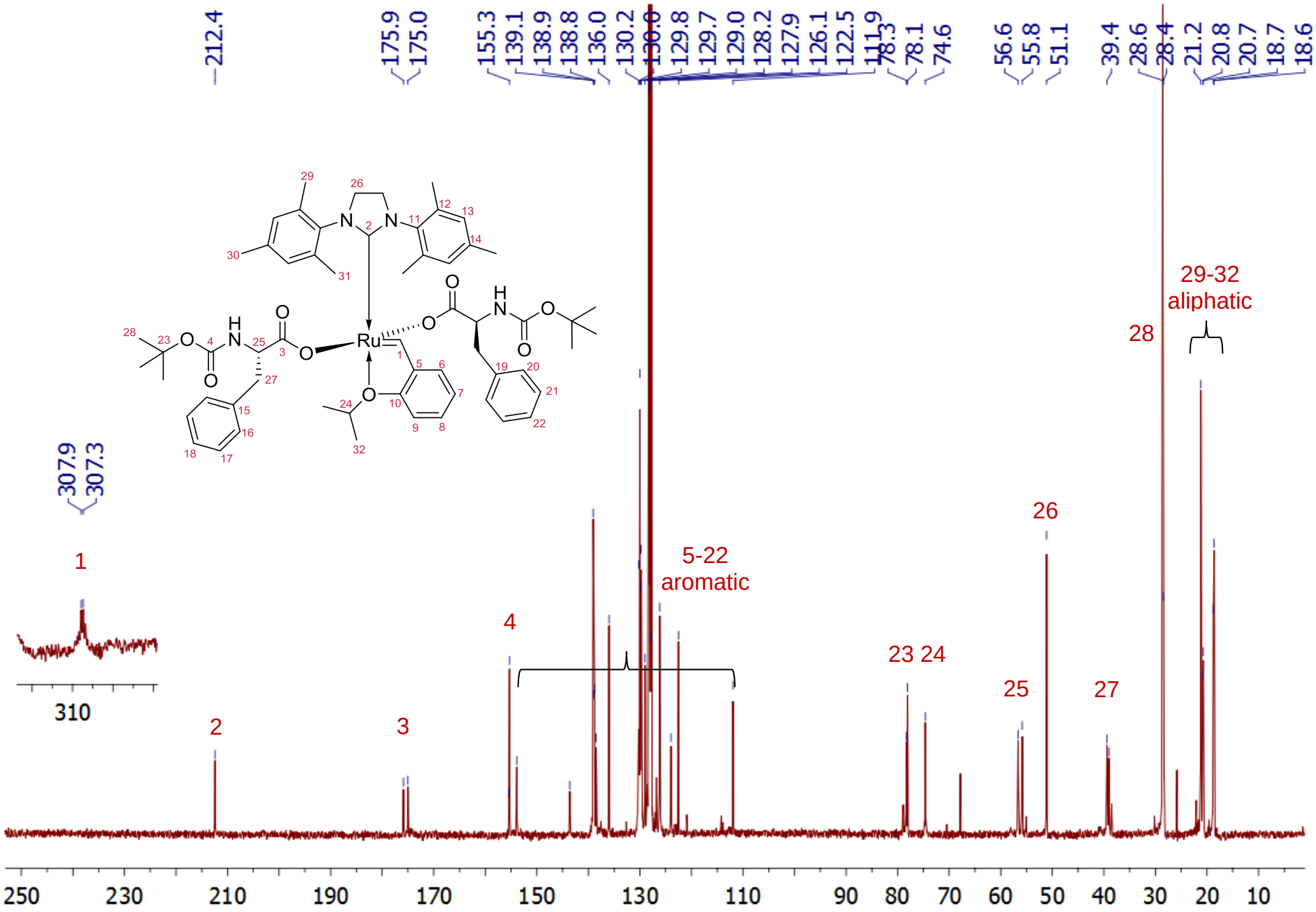
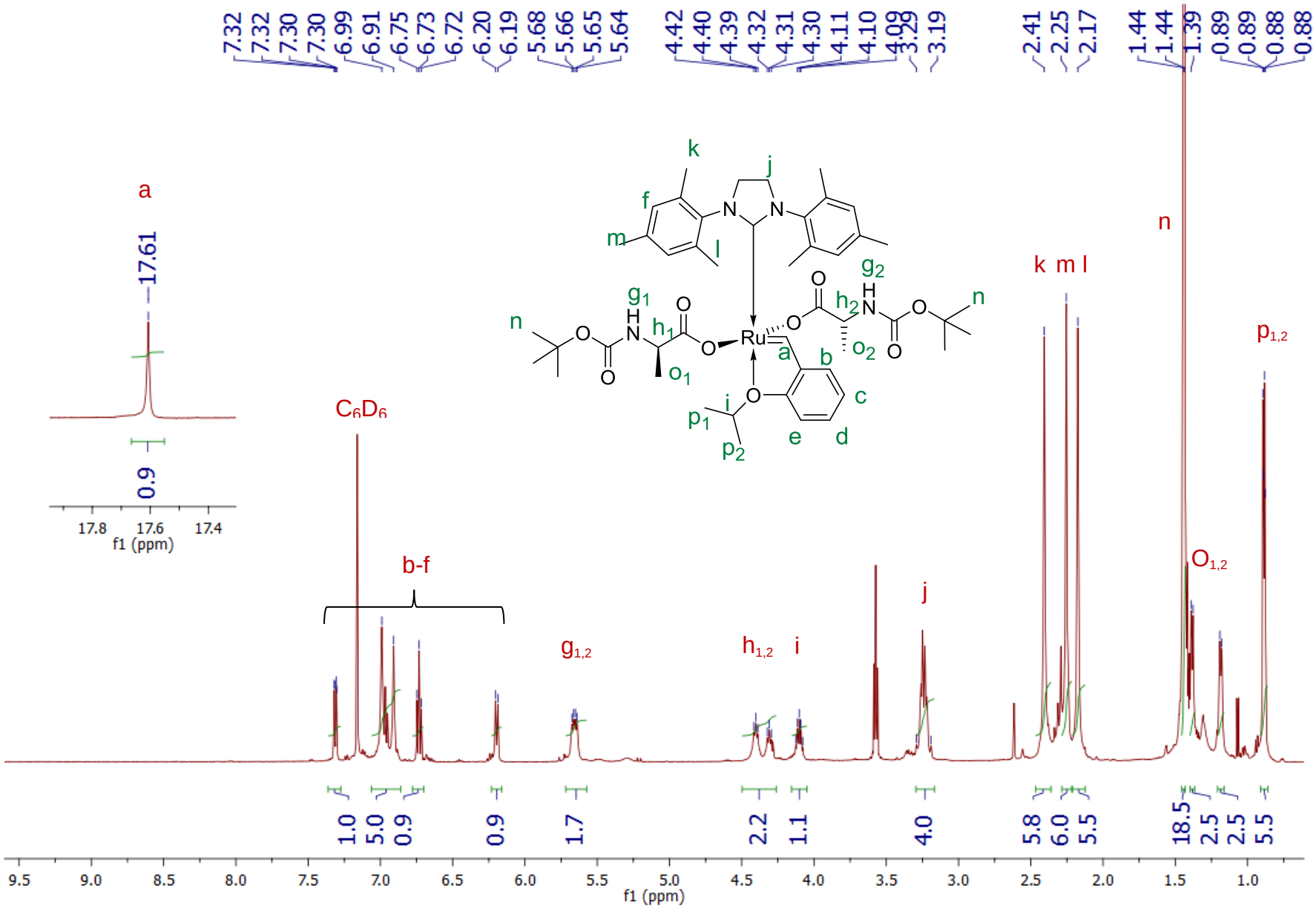
10

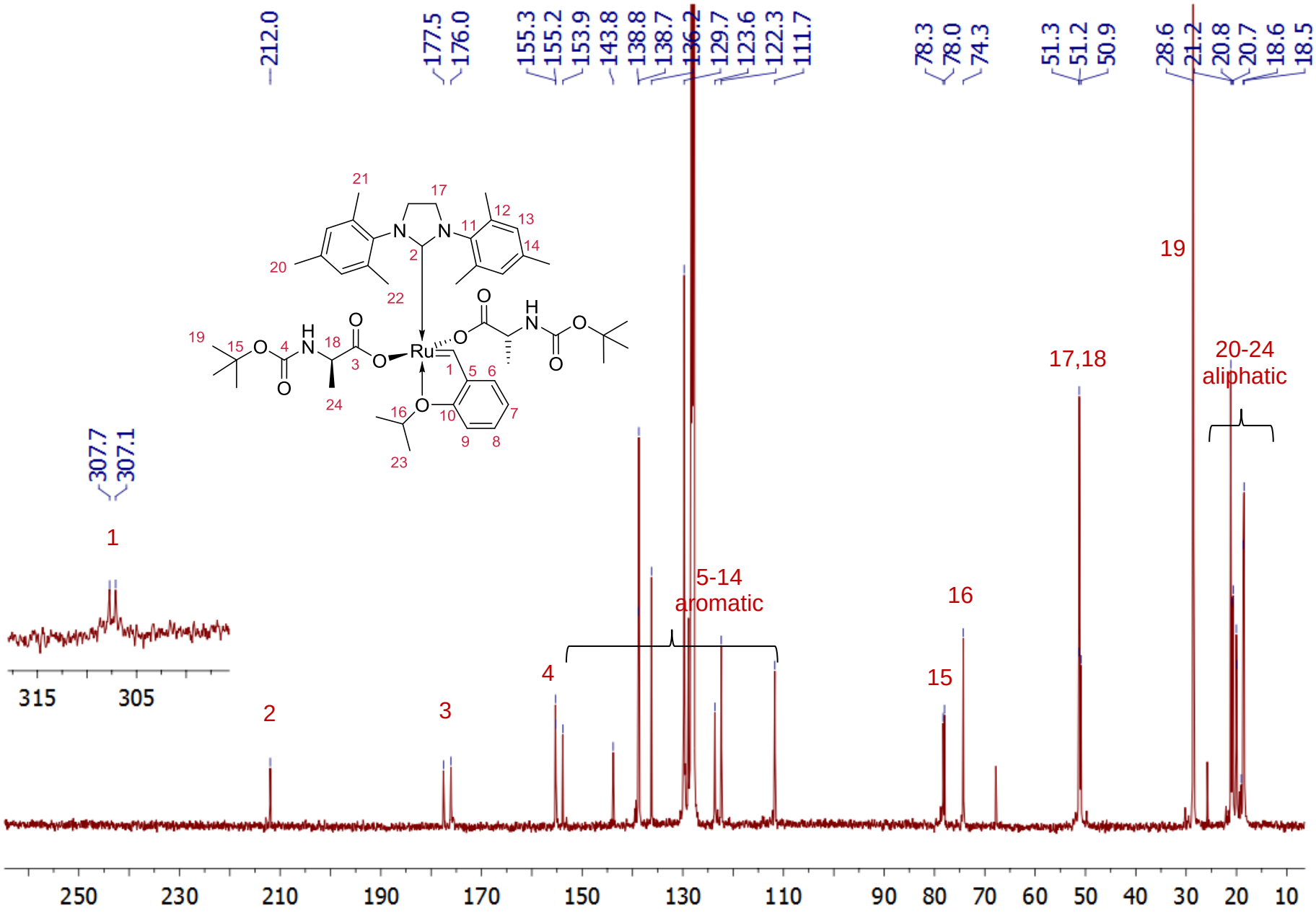
**Complex Ru-F**


7.37
7.35
7.14
6.90
6.80
6.79
6.77
6.29
6.27
5.36
5.34
5.33
5.31
4.70
4.62
4.16
4.11
3.28
3.22
2.94
2.92
2.91
2.89
2.72
2.71
2.69
2.68
2.43
2.28
2.23
1.40
0.97
0.96
0.83
0.82
a
17.70
1.2
17.8
C6H6
b-i
J1,2
K1,2
l
m
n1
n2
o
p
q
r
S1S2
1.1
17.0
1.2
1.0
2.0
2.3
1.2
7.1
1.7
1.9
5.6
5.5
5.1
22.5
3.6
2.7
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


212.4
175.9
175.0
155.3
139.1
138.9
138.8
136.0
130.2
130.0
129.8
129.7
129.0
128.2
127.9
126.1
122.5
111.9
78.3
78.1
74.6
56.6
55.8
51.1
39.4
28.6
28.4
21.2
20.8
20.7
18.7
18.6
307.9
307.3
1
310
2
3
4
5-22
aromatic
23 24
25
26
27
28
29-32
aliphatic
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10

**Complex Ru-DA**




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
18.6
18.5
307.7
307.1
1
2
3
4
5-14
aromatic
15
16
17,18
19
20-24
aliphatic
315
305
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10

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.

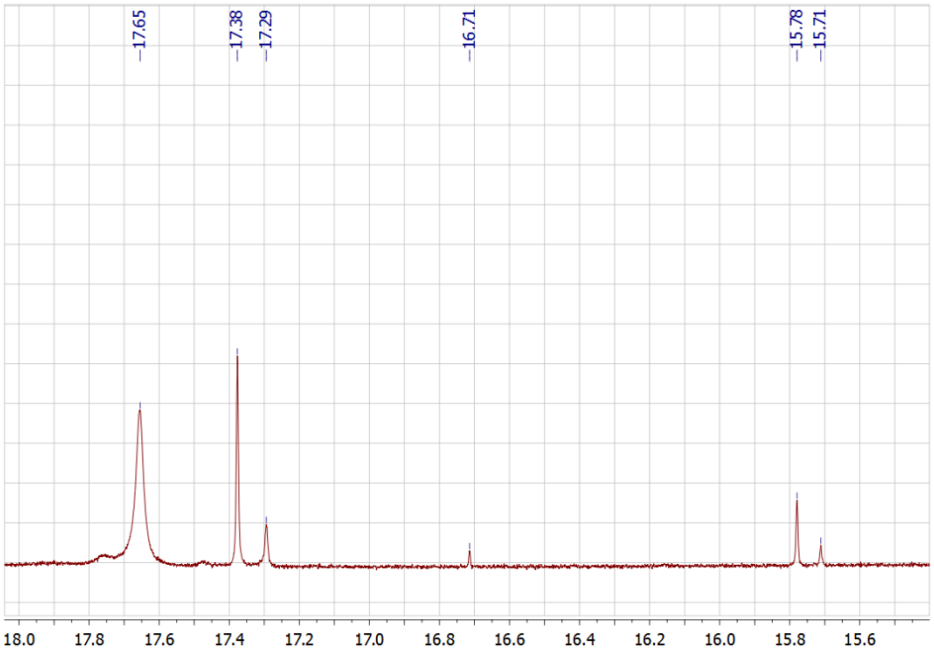



**Figure 1**. Synthesis with Boc-valine silver salt.

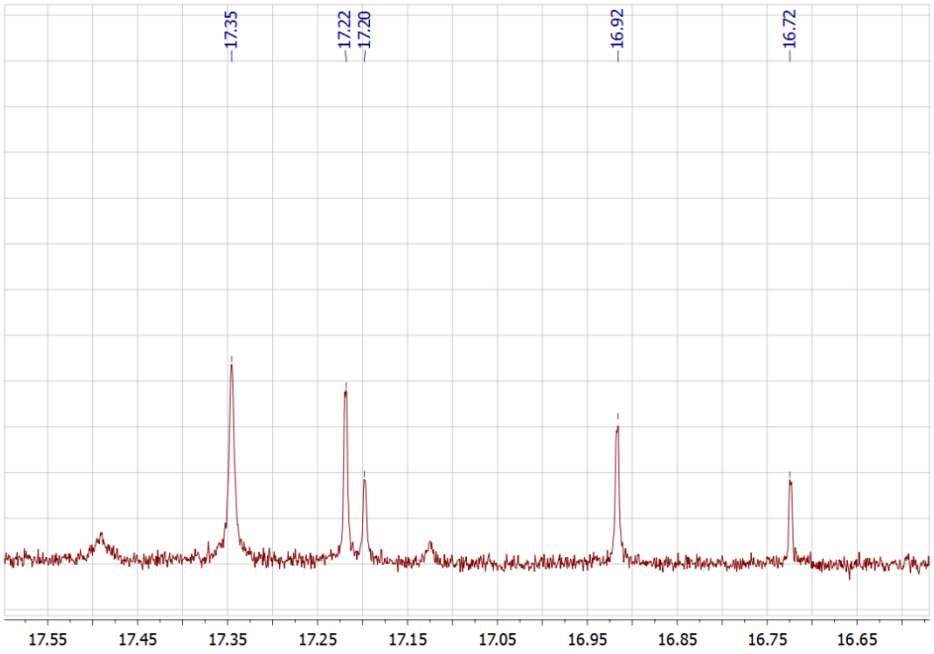
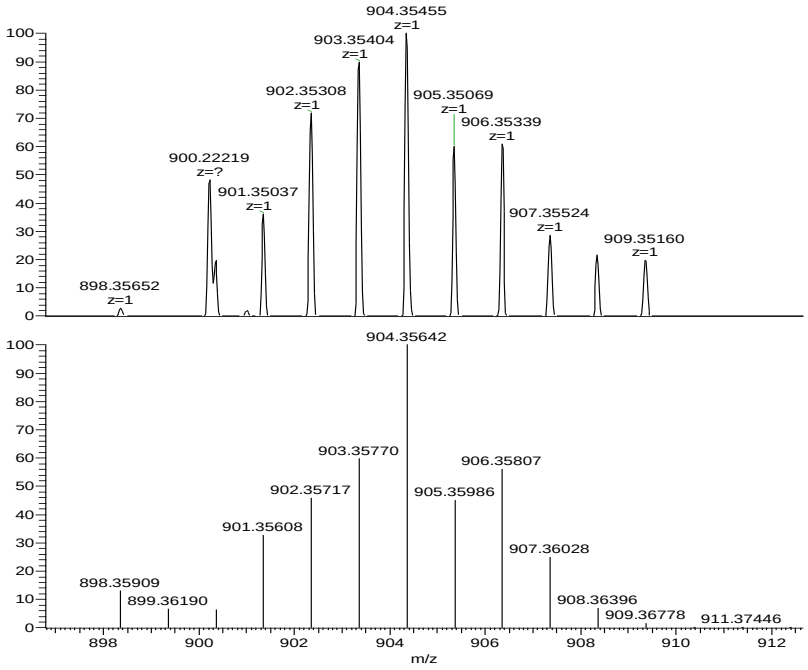


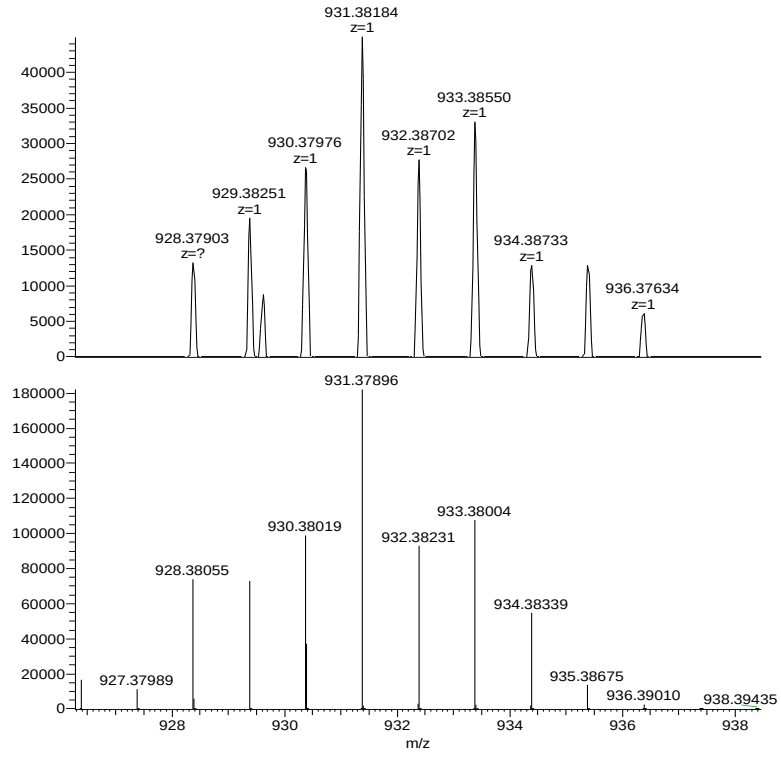

**Figure 2**. Synthesis with Boc-proline silver salt.

# Part IV. HR-MS data

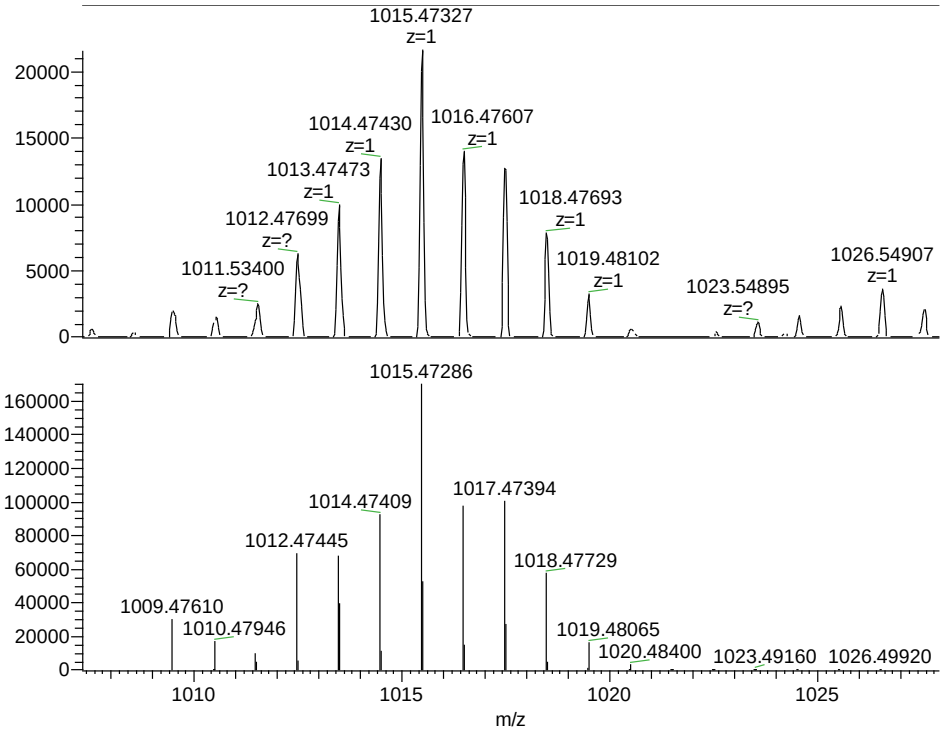
## Complex Ru-G



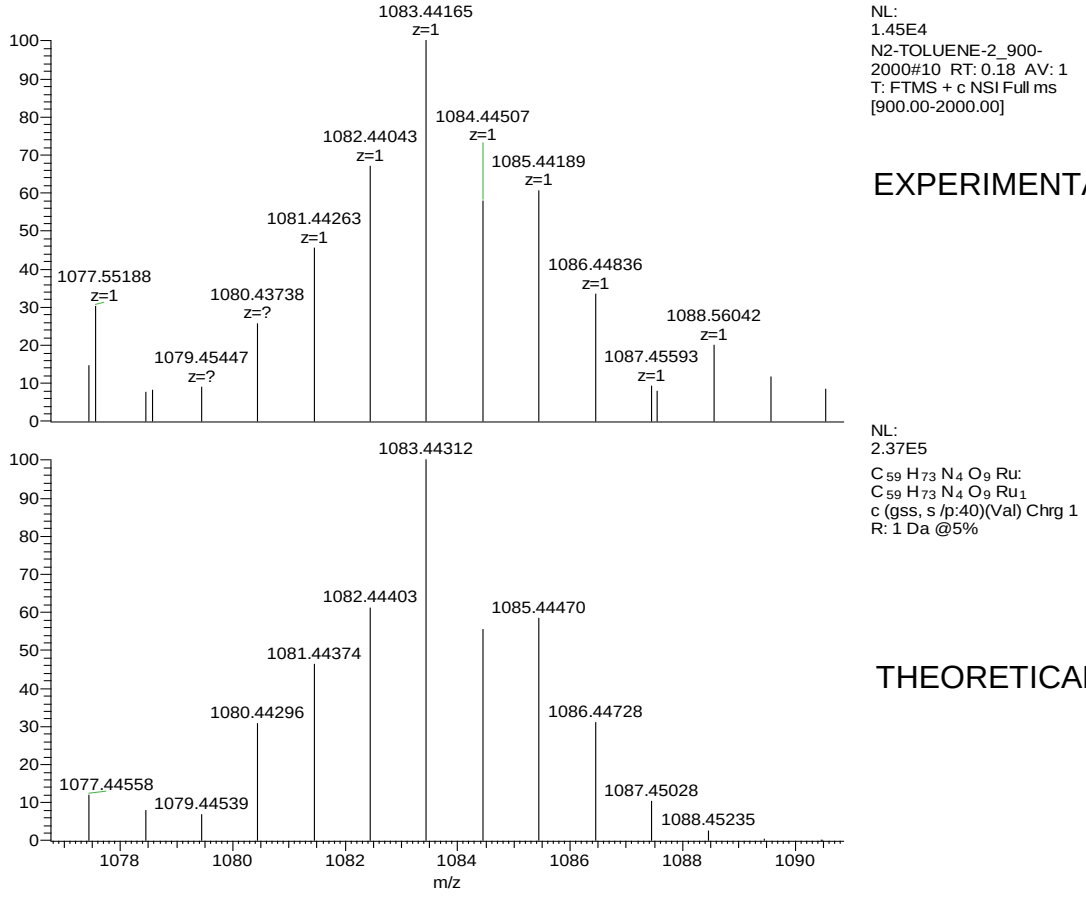

## Complex Ru-A



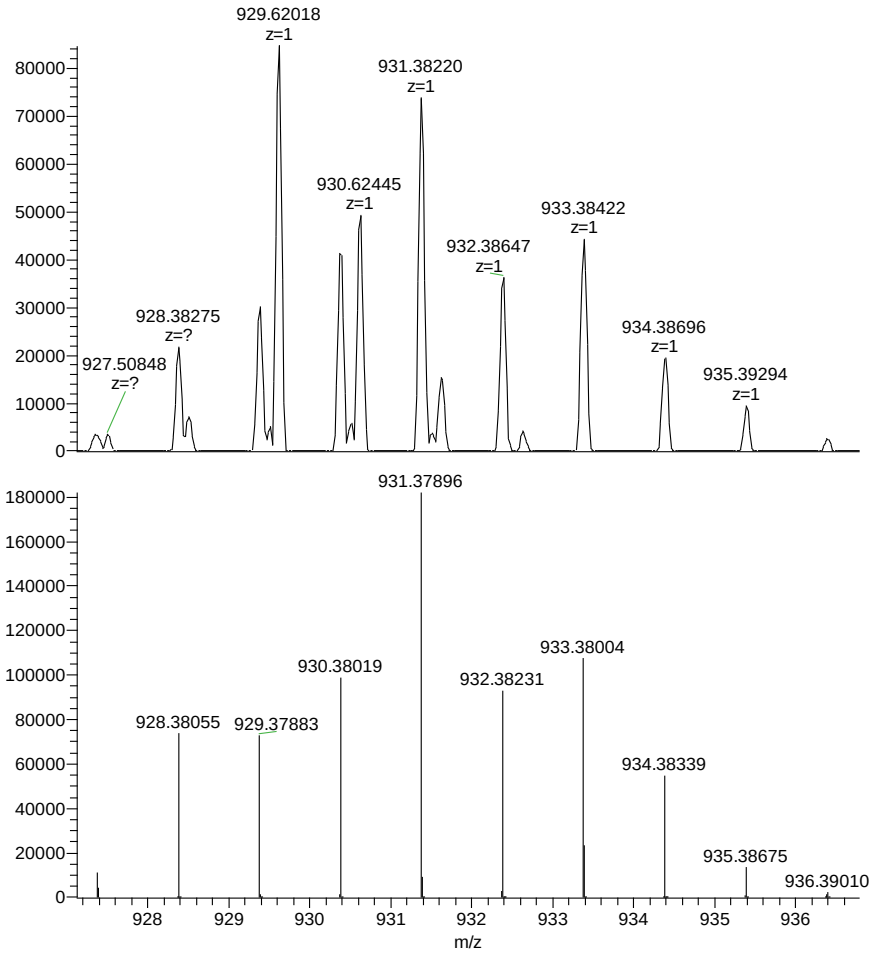
## Complex Ru-L




## Complex Ru-F



## Complex Ru-DA



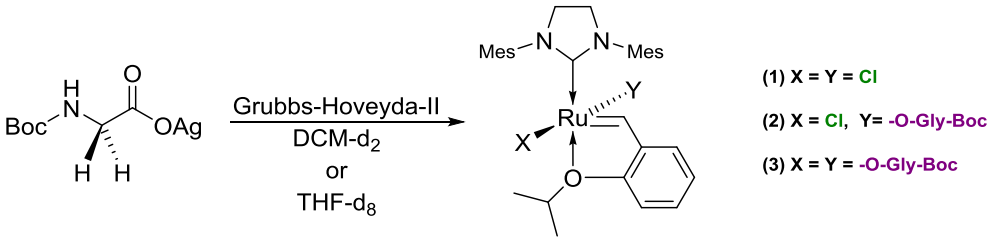
## Part V. X-Ray data

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.

| | |
|---|---|
| Chemical formula | $C_{90}H_{124}N_8O_{18}Ru_2$ |
| Formula weight | 1808.11 |
| Temperature (K) | 110 |
| Crystal system | Triclinic |
| Space group | P -1 |
| *a* (Å) | 16.0973(18) |
| *b* (Å) | 18.0969(19) |
| *c* (Å) | 20.125(2) |
| *α* (°) | 90.430 |
| *β* (°) | 113.250 |
| *γ* (°) | 99.817 |
| *V* (Å$^3$) | 5289.5(10) |
| *Z* | 2 |
| *ρ* (g cm$^{-3}$) | 1.135 |
| *μ* (mm$^{-1}$) | 0.345 |
| *F*(000) | 1904.0 |
| Radiation | MoKα |
| Wavelength | 0.71073 |
| *hkl* range | $h \leq 19$ |
| | $k \leq 21$ |
| | $l \leq 23$ |
| No. of reflections | 10863 |
| No. of parameters | 1091 |
| *w* $R_2$ | 0.2245 |

## Part VI. Synthesis of Ru-G in DCM

Synthesis of **Ru-G**, as specified in the general procedure, in DCM-$d_2$, was followed by $^1$H-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-$d_8$ was followed by $^1$H-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-$d_2$. 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 Blechert[4] and co-workers and Braddock and co-workers.[5]




**Scheme 1**. Synthesis of Ru-G starting from Grubbs-Hoveyda 2$^{nd}$ generation

[3] (a) M. Kim, M. –S. Eum, M. Y. Jin, K. –W. Jun, C. W. Lee, K. A. Kuen, C. H. Kim and C. S. Chin, *J. Organomet. Chem.*, 2004, **689**, 3535; (b) S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda , *J. Am. Chem. Soc.*, 2000, **122**, 8168.

[4] K. Vehlow, S. Maechling, K. Köhler and S. Blechert, *Tetrahedron Lett.*, 2006, **47**, 8617.

[5] K. Tanaka, V. P. W. Böhm, D. Chadwick, M. Roeper and D. C. Braddock, *Organometallics*, 2006, **25**, 5696.

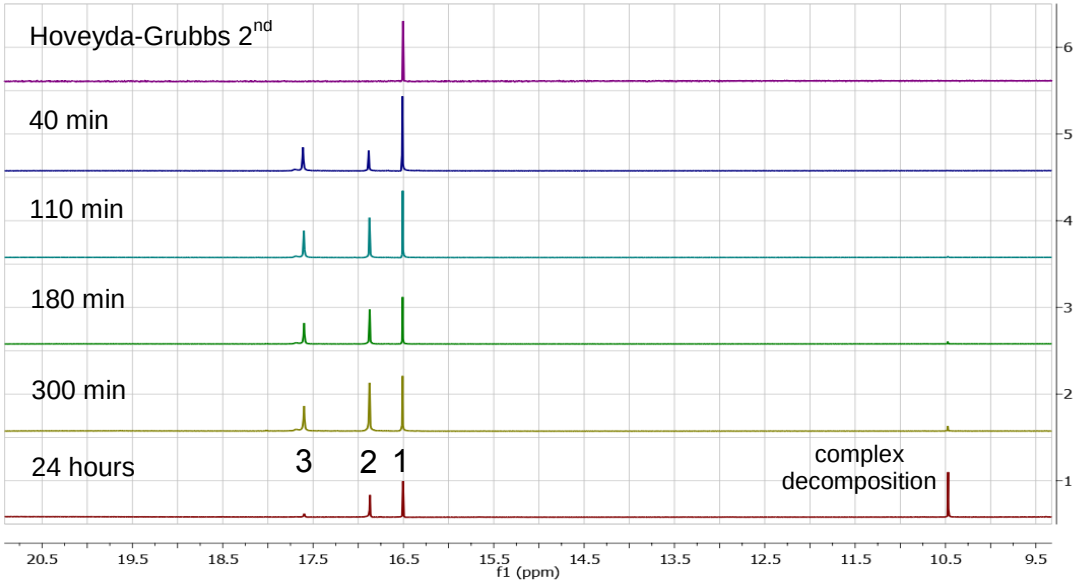



**Figure 3.** Reaction progress for the synthesis of **Ru-G** in DCM-$d_2$

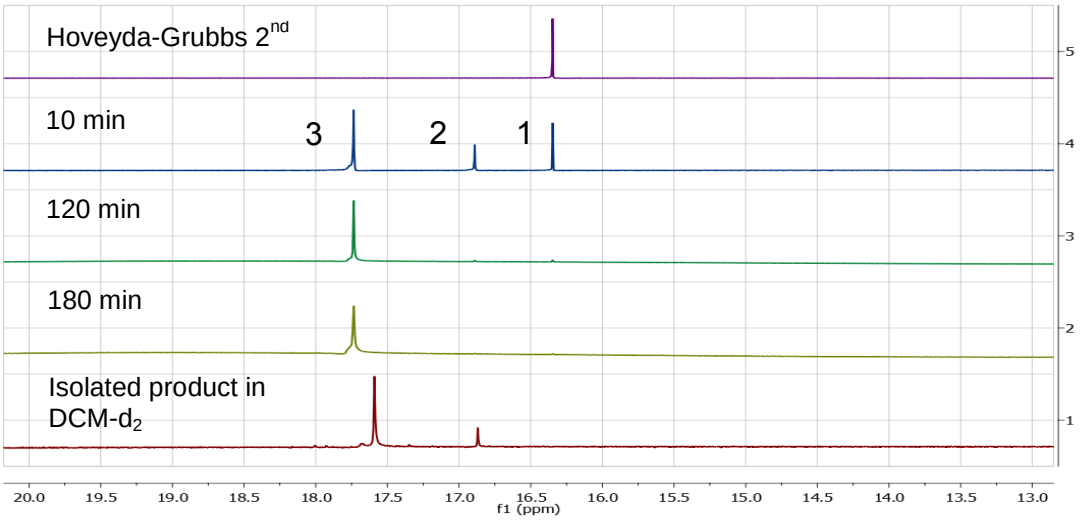
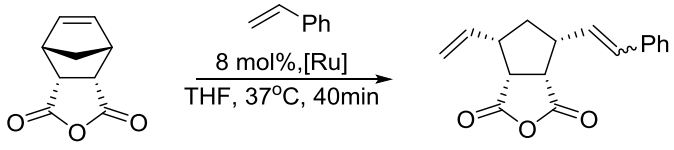



**Figure 4**. Reaction progress for the synthesis of **Ru-G** in THF-$d_8$

## 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]

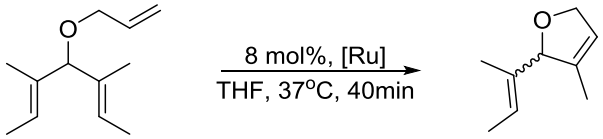



**1** **3**

To a solution of **1** (20.0mg, 0.122mmol) and styrene (136mg, 1.31mmol) in THF (1.5ml), complex **Ru-A** (8.9mg, 9.55μmol, 7.8mol%) in dry THF (0.5ml), (0.056M) was added in the glovebox and the mixture was left to stir at 37ºC for 2 hours. Reaction was quenched with ethyl vinyl ether. The solvent was evaporated and the crude was purified by flash chromatography with 50% $Et_2O$/pentane to obtain product **3**. Conversions were monitored by GC-MS and *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]




**2** **4**

To triene **2** (9.7mg, 0.054mmol) complex **Ru-A** (4 mg, 4.3μmol, 8.0mol%) in dry THF (1.0ml, 0.056M) was added in the glovebox and the mixture was left to stir at 37ºC for 2 hours. Reaction was quenched with ethyl vinyl ether. The solvent was evaporated and the crude was purified by flash chromatography with 5% $Et_2O$/pentane to obtain product **4**. Conversions were monitored by GC-MS and *ee* was determined by HPLC.

---

[6] J. J. Van Veldhuizen, S. B. Garber, J. S. Kingsbury and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2002, **124**, 4954.

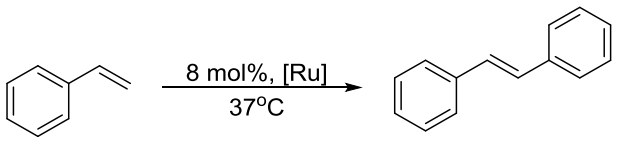
[7] T. W. Funk, J. M. Berlin and R. H. Grubbs, *J. Am. Chem. Soc.*, 2006, **128**, 1840.

Data for ARCM under different conditions:

| entry | catalyst | temperature (°C) | solvent | additive[a] | conversion [%] | *ee* [%] |
|---|---|---|---|---|---|---|
| 1 | Hoveyda-Grubbs II[b] | 37 | THF | - | 100 | 0 |
| 2 | **Ru-G** | 37 | THF | - | 83 | 0 |
| 3 | **Ru-F**[c] | 37 | THF | - | 93 | 0 |
| 4 | **Ru-L** | 37 | THF | - | 100 | 12 |
| 5 | **Ru-A** | 37 | THF | - | 100 | 20 |
| 6 | **Ru-A** | 0 | THF | - | 15 | 27 |
| 7 | **Ru-DA** | 37 | THF | - | 100 | 20 |
| 8 | **Ru-DA** | 0 | THF | - | 10 | 28 |
| 9 | **Ru-A** | 37 | THF | Ala-OAg | 89[d] | 34 |
| 10 | **Ru-A** | 37 | benzene | - | 92[d] | 44 |
| 11 | **Ru-A** | 37 | benzene | Ala-OAg | 63[d] | 56 |
| 12 | **Ru-A** | 37 | benzene/hexane 1:1 | Ala-OAg | 0 | n.a. |
| 13 | **Ru-A** | 37 | benzene/hexane 2:1 | Ala-OAg | 0 | n.a. |

ARCM conditions as specified in the general procedure. [a]40mol% in respect to **Ru-A** [b]2.5 mol% [c]7.0 mol% [d]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 37ºC. Reaction was quenched with ethyl vinyl ether. Conversions and *E*/*Z* ratio were monitored by GC-MS.

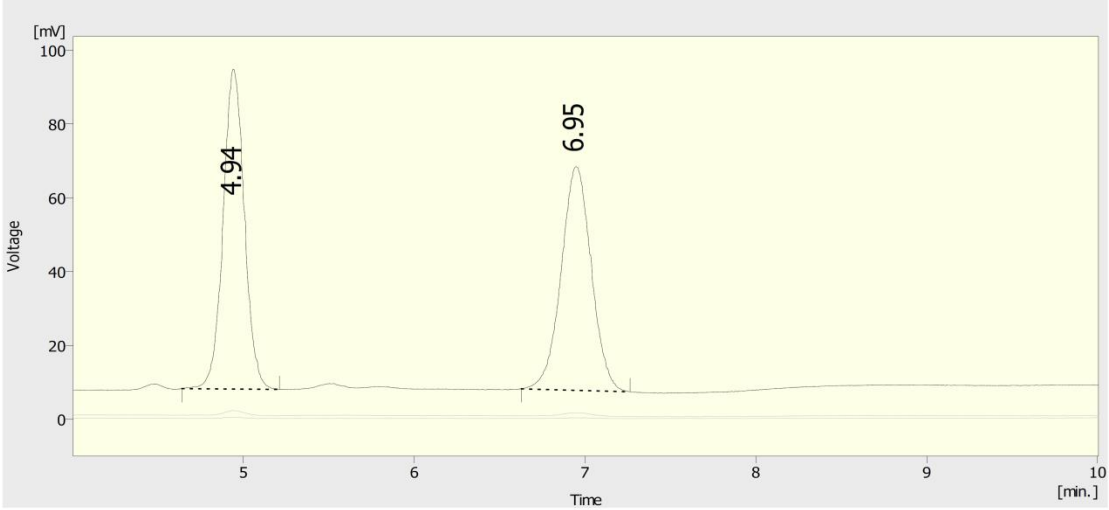
Data for CM under different conditions:

| entry | catalyst | solvent | t (hours) | additive[a] | conversion [%] | *E*:Z |
|---|---|---|---|---|---|---|
| 1 | Hoveyda-Grubbs II[b] | benzene | 24 | - | 87 | 1:0 |
| 2 | **Ru-A** | THF | 24 | Ala-OAg | 36 | 1:0 |
| 3 | **Ru-A** | benzene | 48 | Ala-OAg | 38 | 1:0 |

CM conditions as specified in the general procedure. [a]40mol% in respect to **Ru-A** [b]2.5 mol%.

## Part VIII. Chiral HPLC data

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

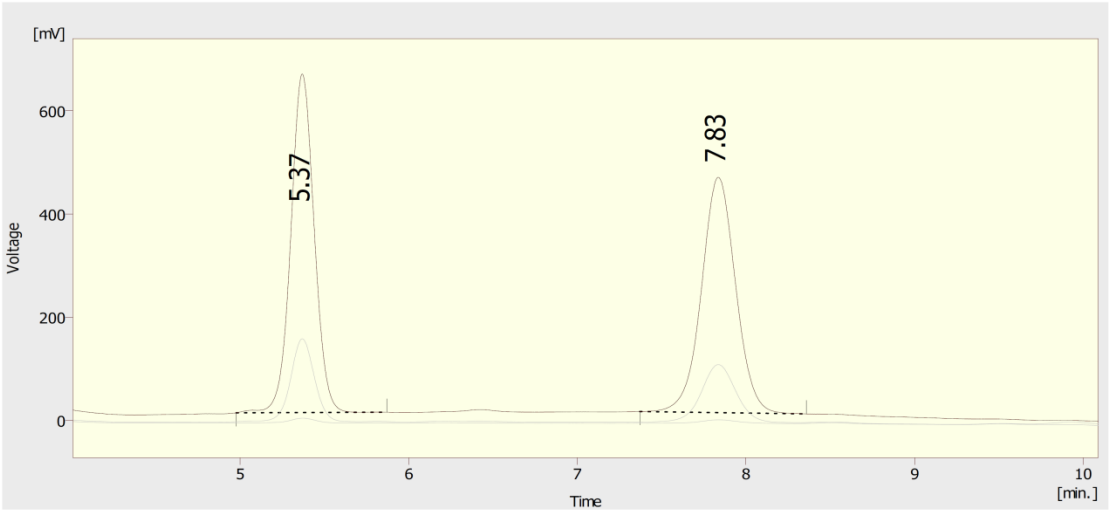



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\EI-292-1-2ul - Channel 2)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.943 | 750.766 | 86.681 | 50.2 | 58.8 | 0.14 | 885 | |
| 2 | 6.947 | 745.530 | 60.621 | 49.8 | 41.2 | 0.19 | 922 | |
| | Total | 1496.296 | 147.303 | 100.0 | 100.0 | | | |

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

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

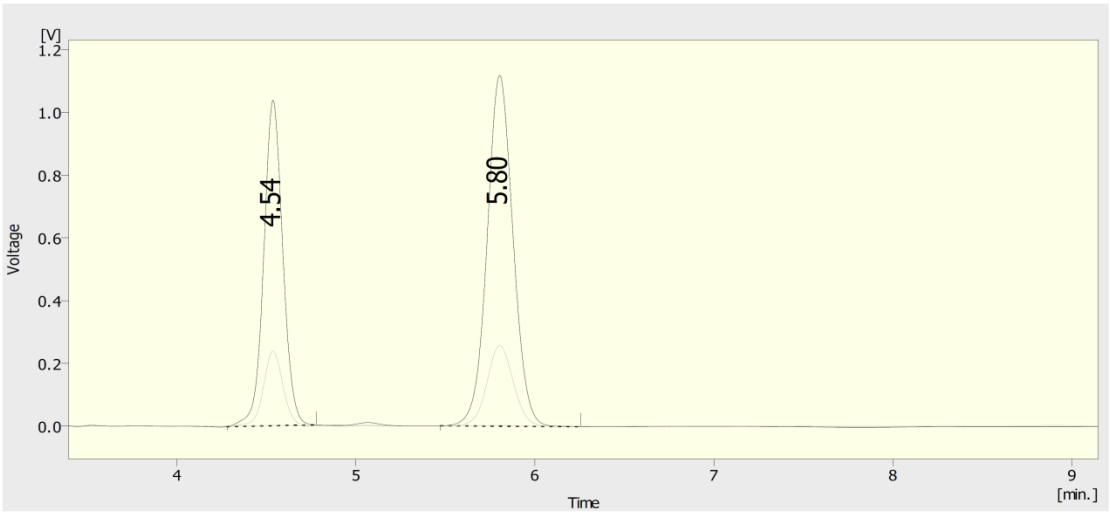



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\EI-299-1 - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 5.367 | 6345.328 | 656.047 | 49.6 | 59.0 | 0.15 | 863 | |
| 2 | 7.833 | 6436.968 | 456.059 | 50.4 | 41.0 | 0.22 | 863 | |
| | Total | 12782.296 | 1112.106 | 100.0 | 100.0 | | | |

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

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

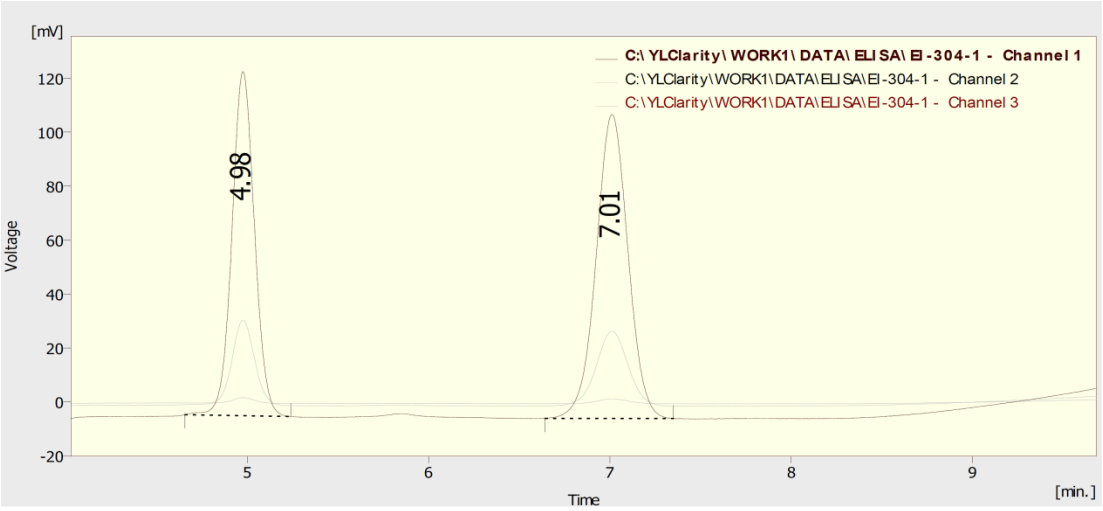



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-340-1-f5-b - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.537 | 1781.147 | 237.850 | 40.2 | 48.1 | 0.12 | 773 | |
| 2 | 5.803 | 2645.113 | 256.453 | 59.8 | 51.9 | 0.16 | 555 | |
| | Total | 4426.260 | 494.303 | 100.0 | 100.0 | | | |

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

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

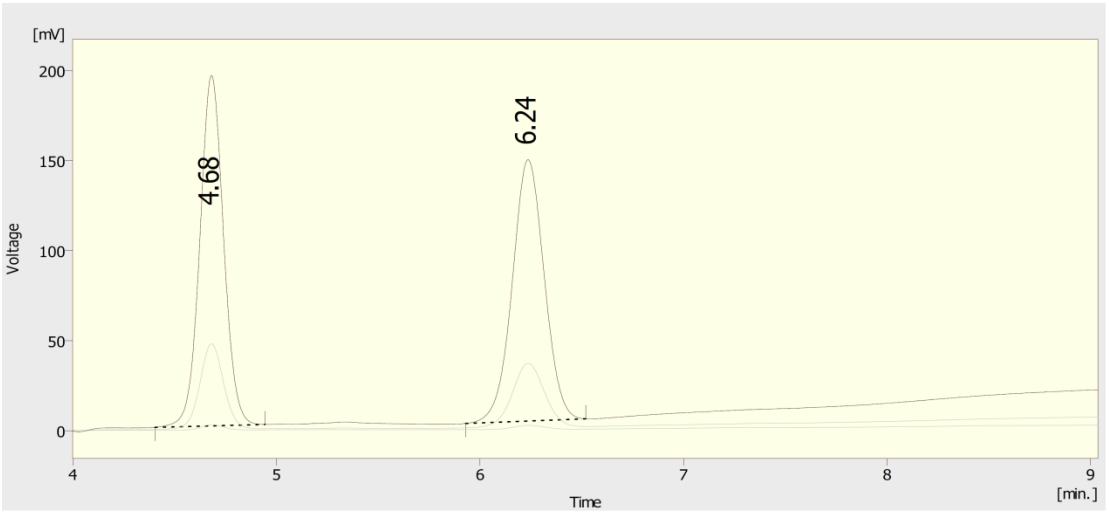



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\EI-304-1 - Channel 2)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.977 | 267.614 | 31.252 | 44.2 | 53.1 | 0.14 | 870 | |
| 2 | 7.010 | 337.252 | 27.655 | 55.8 | 46.9 | 0.19 | 864 | |
| | Total | 604.866 | 58.907 | 100.0 | 100.0 | | | |

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 12% *ee*.

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

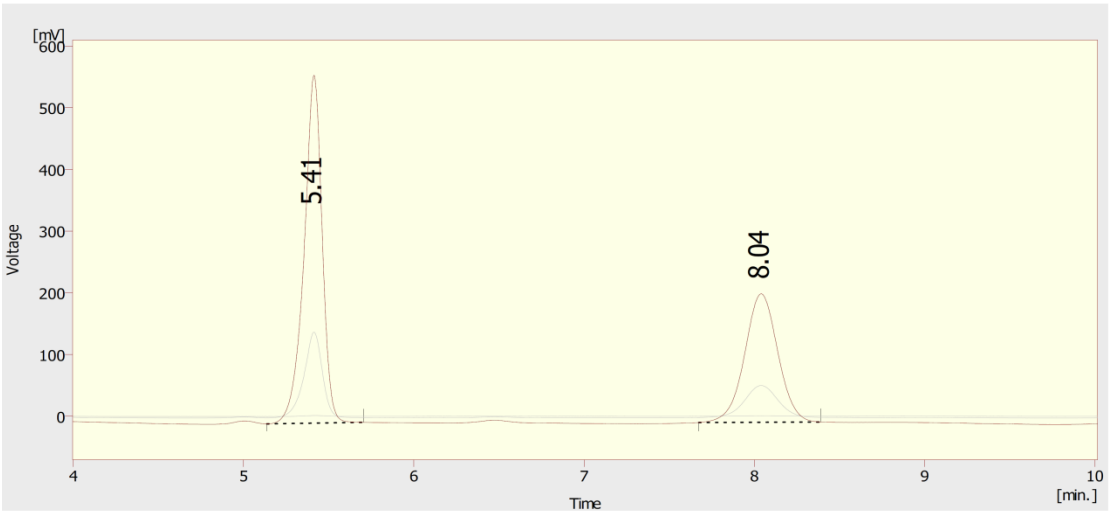



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\EI-300-1-2ul - Channel 2)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.680 | 379.959 | 47.185 | 49.9 | 57.3 | 0.13 | 747 | |
| 2 | 6.237 | 380.778 | 35.208 | 50.1 | 42.7 | 0.17 | 783 | |
| | Total | 760.737 | 82.393 | 100.0 | 100.0 | | | |

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

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

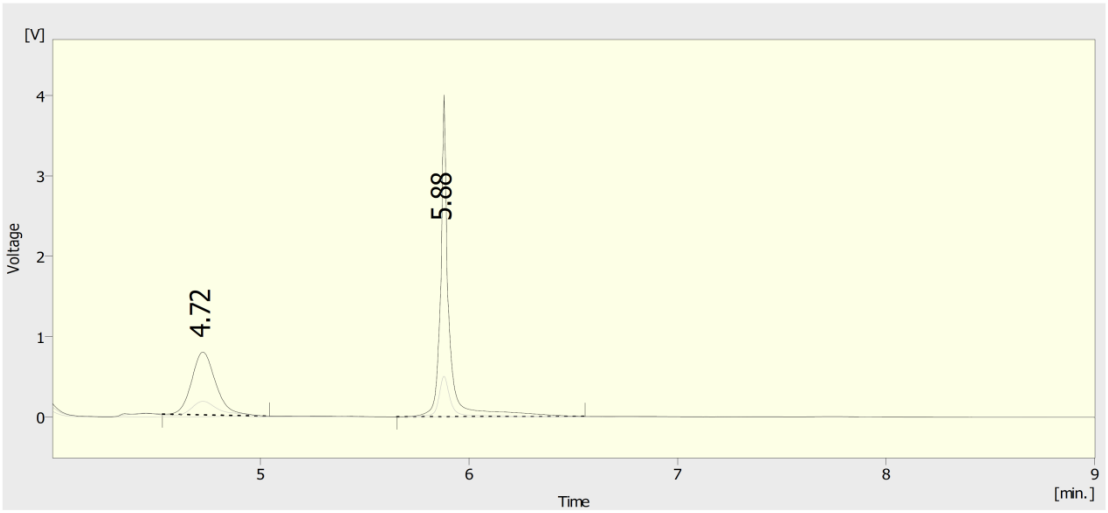



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-337-1-f6-b - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 5.413 | 1027.110 | 138.262 | 60.0 | 73.0 | 0.11 | 813 | |
| 2 | 8.040 | 683.447 | 51.257 | 40.0 | 27.0 | 0.21 | 932 | |
| | Total | 1710.557 | 189.519 | 100.0 | 100.0 | | | |

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

ARCM product received by **Ru-A** at 0°C:

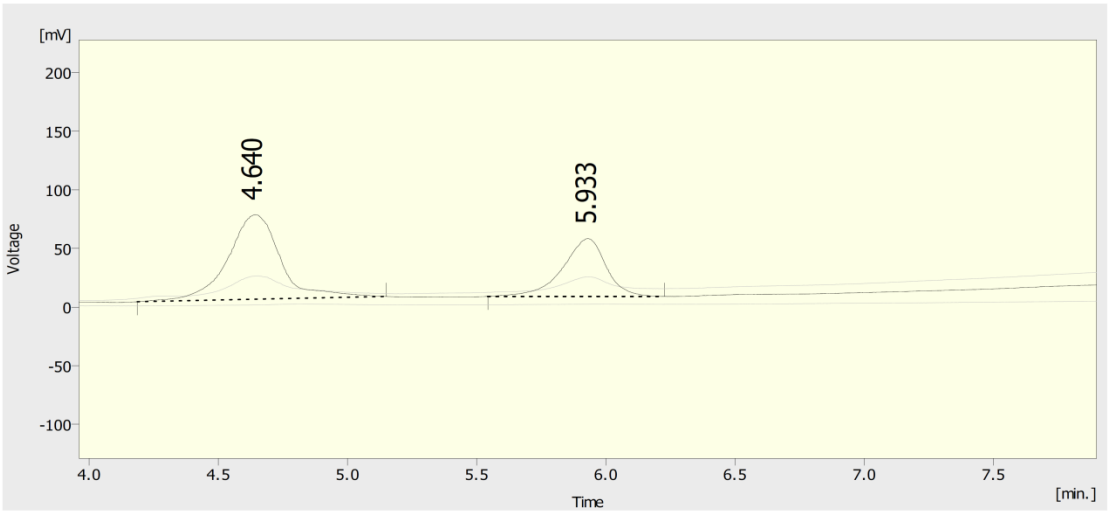



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-342-t1-b - Channel 3)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.723 | 6295.909 | 781.446 | 36.7 | 16.3 | 0.12 | 669 | |
| 2 | 5.880 | 10842.524 | 4003.505 | 63.3 | 83.7 | 0.03 | 437 | |
| | Total | 17138.434 | 4784.951 | 100.0 | 100.0 | | | |

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

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

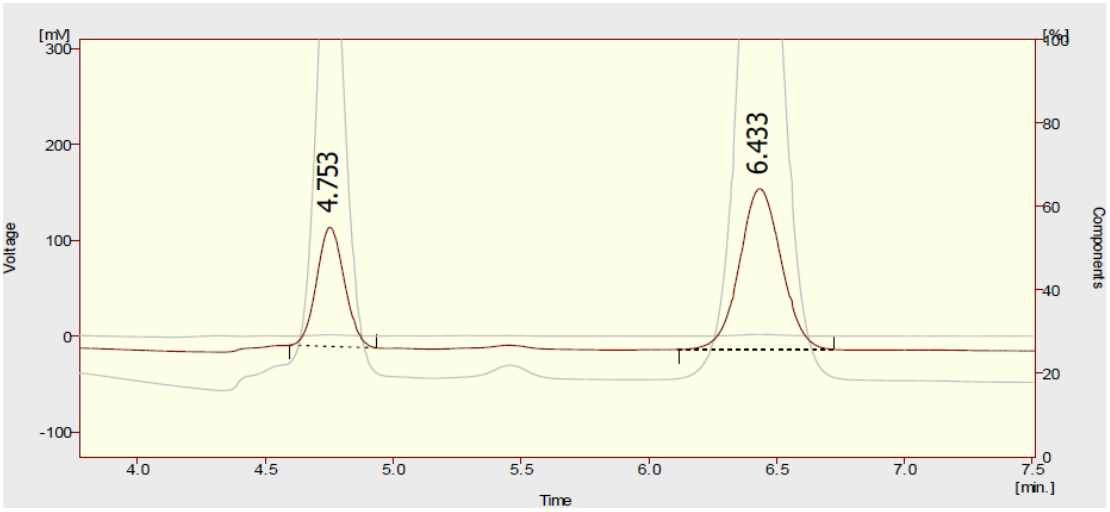



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-333-t1-c - Channel 3)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.640 | 1021.624 | 72.116 | 63.9 | 59.4 | 0.21 | 841 | |
| 2 | 5.933 | 577.307 | 49.305 | 36.1 | 40.6 | 0.17 | 863 | |
| | Total | 1598.931 | 121.421 | 100.0 | 100.0 | | | |

Conditions: 210nm, hexane/isopropanol 98:2, flow, 0.6ml/min, 28% *ee*.

ARCM product received by **Ru-A** with excess Boc-Ala silver salt:

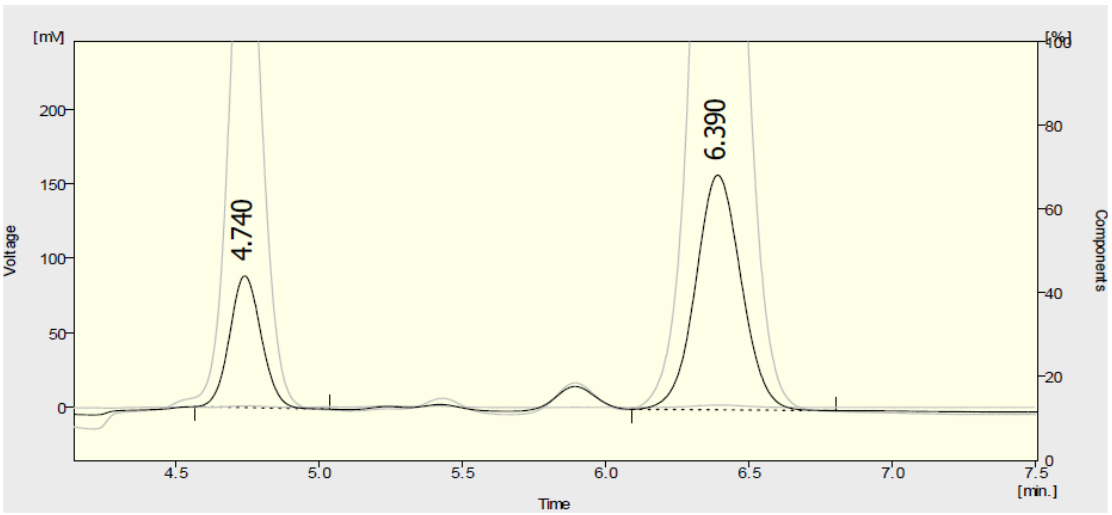



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-356-B-1-f9-20ul - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.753 | 940.365 | 124.130 | 33.0 | 42.5 | 0.12 | 858 | |
| 2 | 6.433 | 1912.390 | 167.684 | 67.0 | 57.5 | 0.18 | 872 | |
| | Total | 2852.755 | 291.814 | 100.0 | 100.0 | | | |

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

ARCM product received by **Ru-A** in benzene:

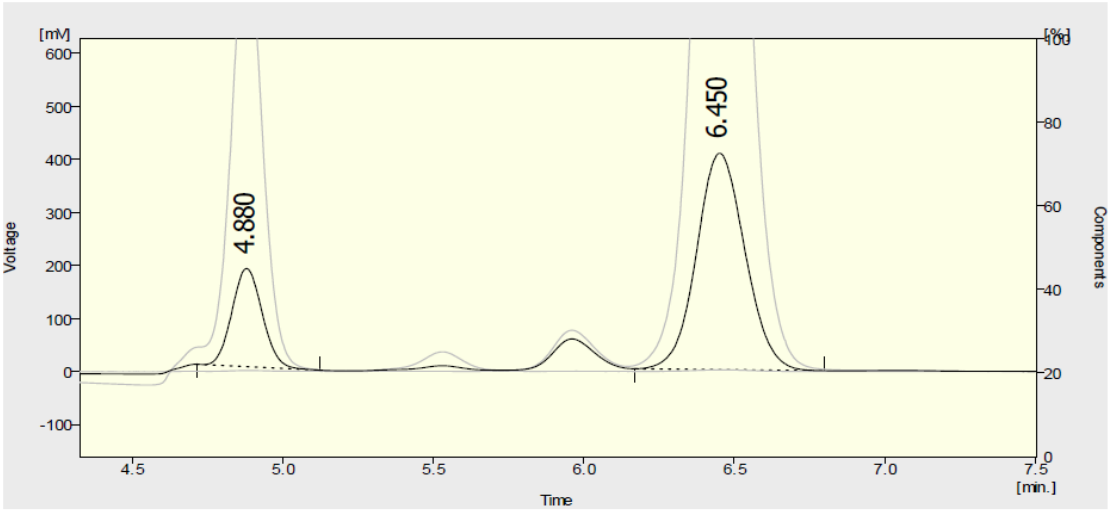



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-359-1-f8-b - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.740 | 681.048 | 88.423 | 28.0 | 35.9 | 0.12 | 846 | |
| 2 | 6.390 | 1754.348 | 157.633 | 72.0 | 64.1 | 0.18 | 849 | |
| | Total | 2435.396 | 246.056 | 100.0 | 100.0 | | | |

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:

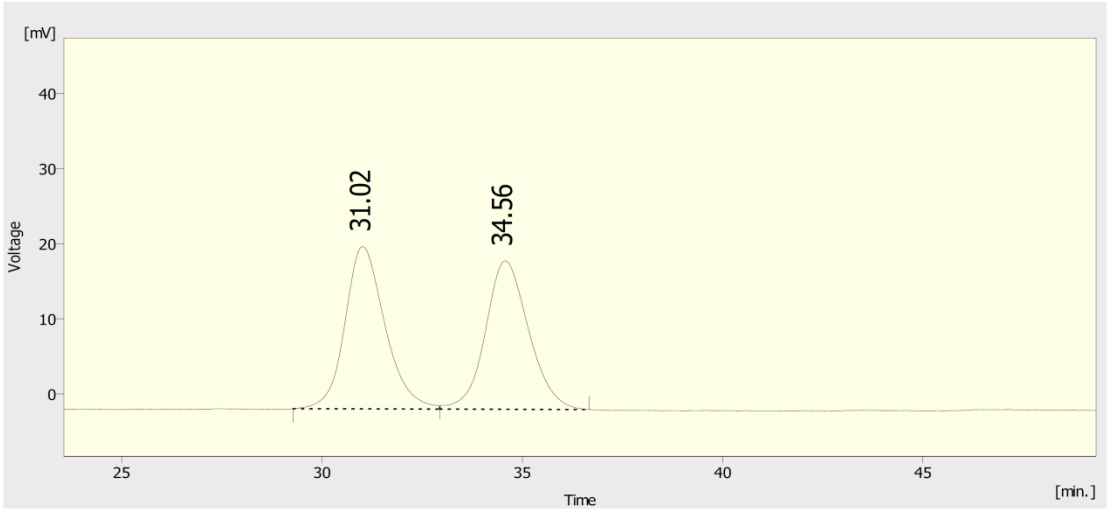



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-360-1-f8 - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.880 | 1298.816 | 185.295 | 22.1 | 31.2 | 0.11 | 816 | |
| 2 | 6.450 | 4574.577 | 408.080 | 77.9 | 68.8 | 0.18 | 829 | |
| | Total | 5873.393 | 593.375 | 100.0 | 100.0 | | | |

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

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

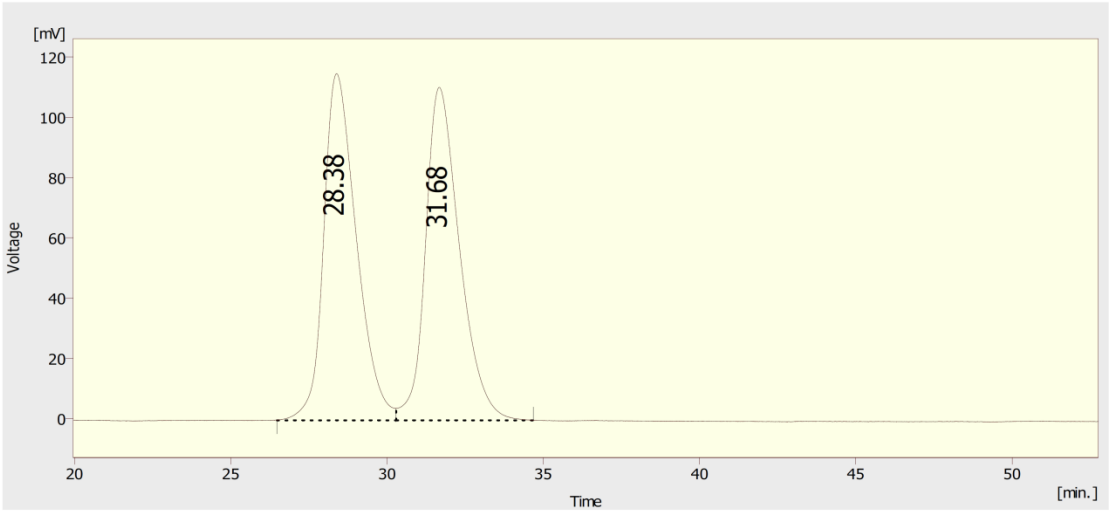



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\EI-296-1-b-2ul - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 31.020 | 1502.532 | 21.659 | 50.3 | 52.3 | 1.08 | 454 | |
| 2 | 34.560 | 1482.722 | 19.780 | 49.7 | 47.7 | 1.20 | 596 | |
| | Total | 2985.254 | 41.439 | 100.0 | 100.0 | | | |

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

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

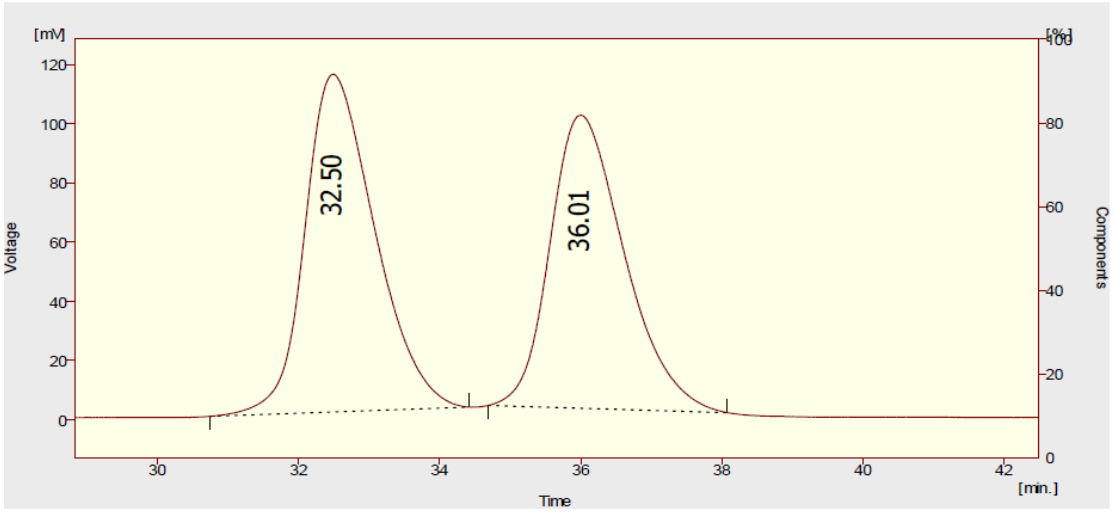



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\EI-301-1-f15-20 - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 28.380 | 8366.730 | 115.108 | 50.0 | 51.0 | 1.10 | 637 | |
| 2 | 31.677 | 8379.103 | 110.546 | 50.0 | 49.0 | 1.13 | 601 | |
| | Total | 16745.832 | 225.654 | 100.0 | 100.0 | | | |

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

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

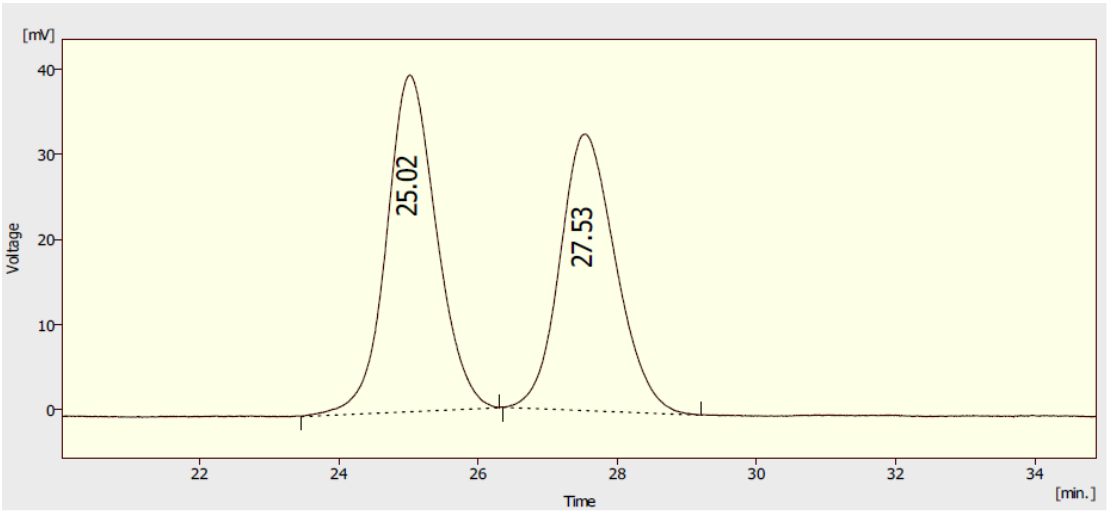



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\EI-319-2-f20-8per - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 32.497 | 7852.563 | 114.123 | 52.0 | 53.5 | 1.06 | 946 | |
| 2 | 36.007 | 7261.169 | 99.120 | 48.0 | 46.5 | 1.12 | 972 | |
| | Total | 15113.731 | 213.242 | 100.0 | 100.0 | | | |

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

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

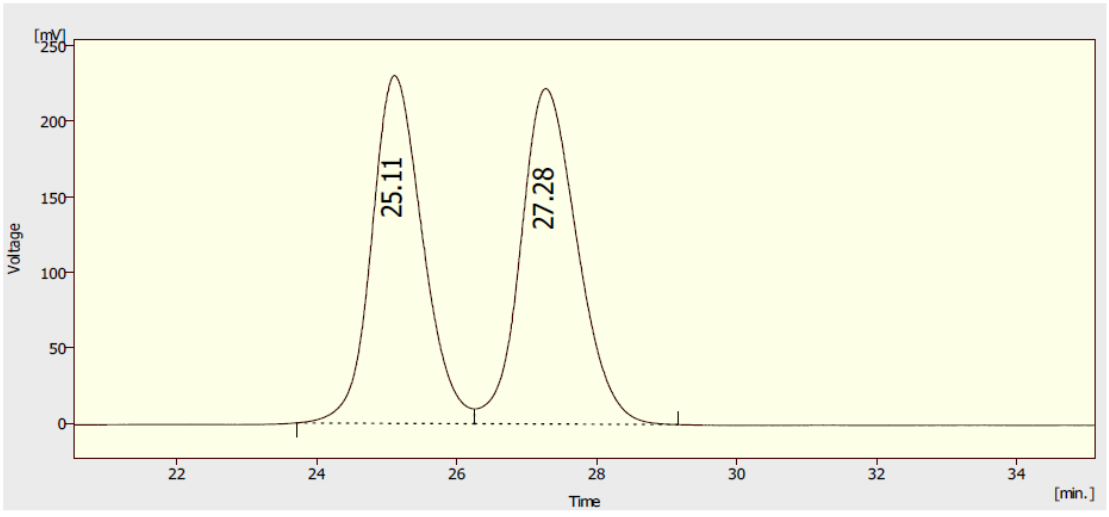



*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-302-1-f11-16-8per - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 25.017 | 1978.851 | 39.573 | 52.2 | 54.9 | 0.76 | 994 | |
| 2 | 27.530 | 1813.239 | 32.491 | 47.8 | 45.1 | 0.86 | 997 | |
| | Total | 3792.090 | 72.064 | 100.0 | 100.0 | | | |

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

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



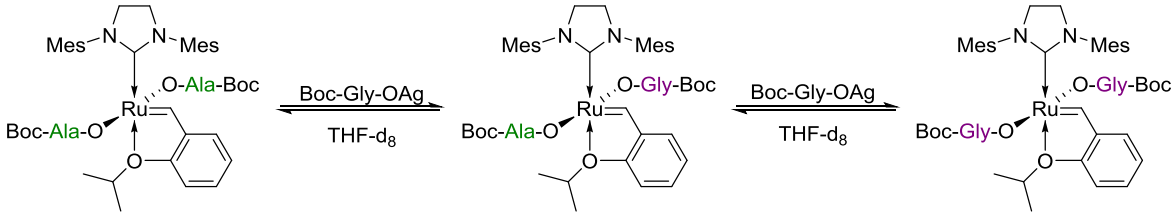

*Result Table (Uncal - C:\YLClarity\WORK1\DATA\ELISA\ei-334-1-f10 - Channel 1)*

| | Reten. Time [min] | Area [mV.s] | Height [mV] | Area [%] | Height [%] | W05 [min] | Peak Purity [-] | Compound Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 25.110 | 11639.336 | 230.376 | 48.2 | 50.9 | 0.78 | 651 | |
| 2 | 27.277 | 12489.667 | 222.047 | 51.8 | 49.1 | 0.86 | 660 | |
| | Total | 24129.003 | 452.422 | 100.0 | 100.0 | | | |

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

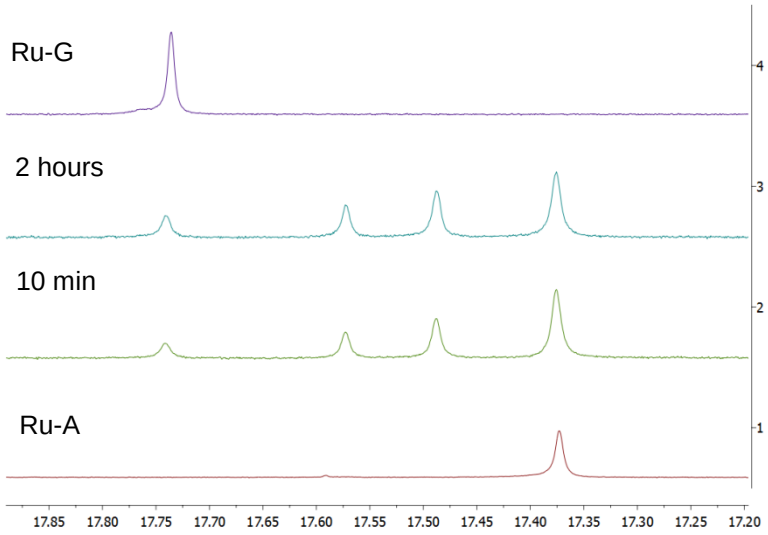
## Part IX. $^{1}$H-NMR data of anionic ligand exchange

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




**Ru-A** **Ru-G**

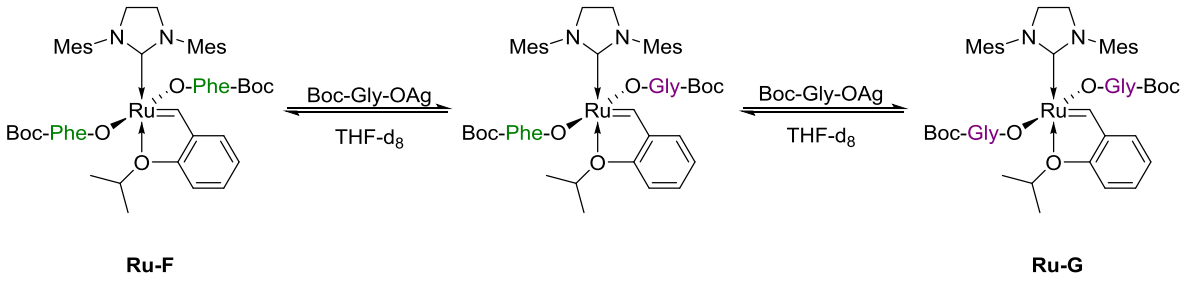
In the glove box, **Ru-A** complex (6.45mg, 6.92µmol, 1.0eq) in THF-$d_8$ (0.2ml) was added to an NMR-tube charged with Boc-Gly-OAg (4.20mg, 1.49x$10^{-5}$ mol, 2.1eq) in THF-$d_8$ (0.3ml). Reaction was followed by $^{1}$H-NMR (400MHz).




Ratio of carbene peaks:

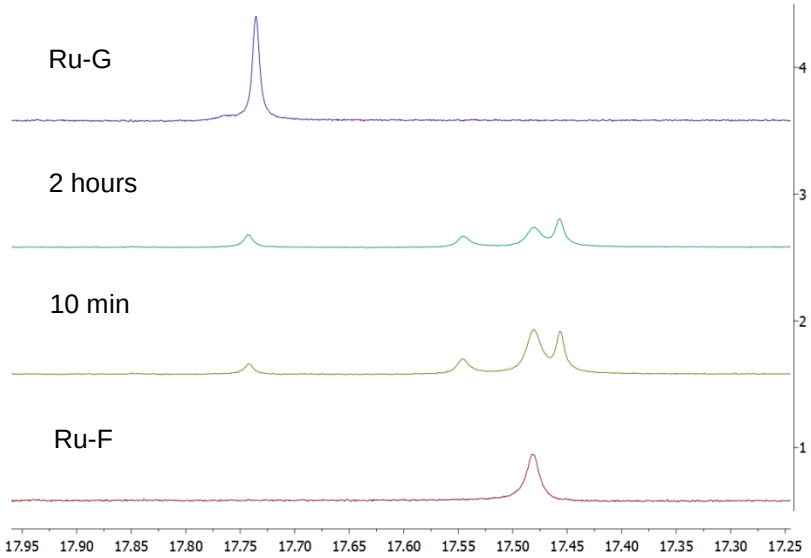
| | **Ru-A** 17.37ppm | - 17.57ppm | - 17.49ppm | **Ru-G** 17.74ppm |
|---|---|---|---|---|
| 10 min | 1.00 | 0.52 | 0.30 | 0.18 |
| 2 hours | 1.00 | 0.63 | 0.40 | 0.29 |

Ligand exchange for **Ru-F** with Boc-Glycine silver salt




**Ru-F** **Ru-G**

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-$d_8$ (1.0ml). Reaction was followed by $^{1}$H-NMR (400MHz).




Ratio of carbene peaks:

| | **Ru-F** 17.48ppm | - 17.46ppm | - 17.55ppm | **Ru-G** 17.74ppm |
|---|---|---|---|---|
| 10 min | 1.00 | 0.70 | 0.31 | 0.13 |
| 2 hours | 1.00 | 1.12 | 0.51 | 0.43 |

After 2 hours the amount of the original Ru complex according to the $^{1}$H-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.