Electronic Supplementary Material (ESI) for Dalton Transactions.

A Ruthenium Racemization Catalyst for Synthesis of Primary Amines from Secondary Amines: Catalysis and Deactivation

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General Considerations

All work was carried out under standard Schlenk conditions under argon; all solvents were dried, degassed and purged with Ar prior to use. All used glassware was pre-dried at 120°C and heated with a heat gun while purged with Ar prior to use. Chemicals were purchased from Sigma-Aldrich and Strem and were used as received. All reactions were performed in a magnetically stirred home-made stainless steel autoclave equipped with manometer, temperature controller and sampling unit (50μL samples). The reactions were all performed in triplo, and these results where within an experimental error. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded on a Bruker Avance 400 MHz with broad band inverse detection probe and a Bruker Avance 500 MHz with dual channel cryo probe optimized for $^{13}C/^{1}H$ (DCH). Chemical shifts are reported in ppm using TetraMethylSilane (TMS) as reference. All NMR experiments have been performed under inert atmosphere is airtight Wilmad Young NMR quartz tubes. GC-analyses were performed on a Shimadzu GC-2010 equipped with an Ultra-2 column. Ammonia of purity grade N4.7 was used and was introduced to the autoclaves using a Bronkhorst liquiFlow mass-flow controller (MFC). FT-IR spectra were recorded *in situ* on a Shimadzu 8300 equipped with a home-made autoclave with a built-in ZnS path length window.

Synthesis

Synthesis of 1,2,3,4,5-Pentaphenylcyclopentadiene:[1]

A three-neck round-bottom flask was charged with magnesium turnings (0.513 g, 20 mmol) and THF (5 ml). A solution of PhBr (3.807 g, 23 mmol) in THF (20 ml) was added drop wise into the stirring solution. This mixture was stirred for one hour and a solution of 2,3,4,5-tetraphenylcyclopentadienone (5.049 g, 13 mmol) in THF (20 ml) was added via a dropping funnel. 10 ml of extra THF were necessary to wash all 2,3,4,5-tetraphenylcyclopentadienone back into the mixture. After 2.25 h of stirring, $LiAlH_4$ (1.45 g, 35 mmol) was added in portions. After two more hours, the reaction was quenched using NH_4Cl (18.6g, 0.35mol) in H_2O which had been prepared in the meanwhile. Following that, the mixture was transferred into a separation funnel and dichloromethane was added. After five washes the organic layer was dried over $MgSO_4$. After filtration the solvent was removed in vacuum. The product was obtained as a pale white-yellow powder. NMR. ^{1}H NMR (298 K, 400 MHz, $CDCl_3$, δ=ppm): 7.23 (t, 2H, Ph), 7.22 (d, 2H, Ph), 7.17 (m, 8H, Ph), 7.12 (d, 1H, Ph), 7.05 (m, 8H, Ph), 7.00 (m, 4H, Ph) 5.08 (s, 1H, Cp). ^{13}C NMR (298 K, 100.6 MHz, $CDCl_3$): 144.02, 136.16, 135.82, 130.13, 129.03, 128.57, 127.69, 126.96.

Synthesis of (η^5-CpPh5) $Ru(CO)_2H$:[1]

1,2,3,4,5-pentaphenylcyclopentadiene (2 g, 4.4 mmol) and [$Ru_3(CO)_{12}$] (1 g, 1.56 mmol) were put in a 50 ml Schlenk tube and flushed with Ar. Afterwards, decane (12 ml) and toluene (6 ml) were added and the mixture was heated for 2.5 days at 160°C. After cooling to room temperature it was washed with pentane and dried in vacuum. The obtained powder was of dark brown colour. ^{1}H NMR (298 K, 400 MHz, $CDCl_3$, δ=ppm): 7.23 (t, 10H, Ph), 7.13 (t, 10H, Ph), 7.05 (d, 5H, Ph), -9.84 (s, 1H, RuH). ^{13}C NMR (298 K, 100.6 MHz, $CDCl_3$): 196.89 (CO), 132.16, 129.54, 128.36, 127.82, 106.46 .IR (cm^{-1}): 2009, 1952 (CO).

Synthesis of (η^5-$CpPh_5$)$Ru(CO)_2Cl$:[1]

1,2,3,4,5-pentaphenylcyclopentadiene (0.27 g, 0.6 mmol) and [$Ru_3(CO)_{12}$] (0.143 g, 0.22 mmol) were put in a 20 ml Schlenk tube and flushed with argon. Afterwards decane (1.6 ml) and toluene (0.82 ml) were

added and the mixture was heated for 2.5 days at 160°C. After cooling to room temperature $CHCl_3$ (2 ml) was added and the mixture was heated to 160°C for 1.25 h. After cooling to room temperature it was washed with pentane and dried in vacuum. The obtained powder was yellow. ^{1}H NMR (298 K, 400 MHz, $CDCl_3$, δ=ppm): 7.23 (t, 10H, Ph), 7.13 (t, 10H, Ph), 7.07 (d, 5H, Ph). ^{13}C NMR (298 K, 100.6 MHz, $CDCl_3$): 196.92 (CO), 132.20, 129.59, 128.40, 127.85, 106.50. ESI-MS: 639.1709 (M+H).

Synthesis of (η^5-$CpPh_5$)Ru(CO)(PPh_3)Cl:[2]

A Schlenk tube was charged with (η^5-$CpPh_5$) $Ru(CO)_2Cl$ (103 mg) and PPh_3 (49 mg). Dichloromethane (2.5 ml) was added as solvent. Trimethylamine-N-oxide (23.5 mg) was dissolved in acetonitrile (1 ml) in another Schlenk tube. The acetonitrile solution was slowly added to the dichloromethane solution and the mixture was stirred for 15 minutes at room temperature. The colour changed from yellow via orange to dark red during the addition. The mixture was filtered over silica employing dichloromethane as solvent. A red powder was obtained after evaporating the solvents. ^{1}H NMR (298 K, 300 MHz, $CDCl_3$, δ=ppm): 7.48 (t, 6H, Ph), 7.34 (t, 3H, Ph), 7.16 (t, 6H, Ph), 7.11 (t, 5H, Ph), 6.92 (t, 10H, Ph), 6.81 (d, 10H, Ph). ^{13}C NMR (298 K, 100.6 MHz, $CDCl_3$): 132.38, 127.93, 127.27, 127.17. ^{31}P NMR (298K, 161.9 MHz, $CDCl_3$): 39.08. ESI-MS: 575.1061 (M-Cl-PPh_3).

Catalysis

General procedure for the splitting of secondary amines:

A 75 ml stainless-steel autoclave is charged with 2 mol% of complex and purged with Ar. Secondary amine and t-amylalcohol were added via syringe. The autoclave is closed and liquid NH_3 was added via a mass flow controller (MFC). The mixture was heated to 170°C for the 23.5 h time.

Table S1: Catalyst screening

Complex	Time (h)	NH_3 (mL), eq	Conversion (%)	Primary Amine (%)[c]	Primary Amine Selectivity (%)[c]
1	24	5, 120	81.5±5	76.5±4	94
2[a]	24	5, 120	22.5±2	22.5±2	100
3	24	5, 120	26.5±2	25.0±2	94
1+KO^{t}Bu	23.75	15, 120	0	0	0
1	21	0.5, 12	54±3	53±3	98
2	21	0.5, 12	13±1	11±1	85
3	21.5	0.5, 12	68.5±4	62±3	90
1+KO^{t}Bu	21.5	0.5, 12	23.5±2	23.5±2	100

Complex (2 mol%), dicyclohexylamine (1.5 mmol), tert-amyl alcohol (3 mL), NH_3(l), 170°C. a) 0.75 mL MTBE as co-solvent. b) 2 mol% KO^{t}Bu added. c) standard deviation over 3 experiments.

Table S2: Ammonia Excess Screening

Entry	Time (h)	NH_3 (mL), eq	Conversion (%)[c]	Primary Amine (%)[c]
1	23.5	5, 120	81.5±5	76.5±4
2	21	2.5, 60	82.5±3	78±2
3	23.5	5, 40	61	58.5±3
4	24	2.5, 20	51±3	47.5±2
5	21	0.5, 12	54±3	53±2
6	23.5	0.5, 4	16.5±1	15.5±1

Complex **1** (2 mol%), dicyclohexylamine (1.5 mmol), tert-amyl alcohol (3 mL), NH_3(l), 170°C. a) 0.75 mL MTBE as co-solvent. b) 2 mol% KO^{t}Bu added. c) standard deviation over 3 experiments.

Table S3: Screening of complex 3

Entry	Time (h)	NH_3(eq)	Conversion (%)[a]	Primary Amine (%)[a]
1	24	4	15±1	6±1
2	21.5	12	68.5±3	62±2
3	23	20	29±2	27.5±2
4	23	60	26±2	26±2
5	24	120	26.5±2	25.0±2

Complex **3** (2 mol%), dicyclohexylamine (1.5 mmol), tert-amyl alcohol (3 mL), NH_3(l), 170°C. a) standard deviation over 3 experiments.

Table S4: Effect of the base at different amounts of ammonia

Entry	Time	NH_3 (mL), eq	Conversion (%)[a]	Primary Amine (%)[a]
1	23.5	0.5, 4	42±3	39.5±4
2	21.5	0.5, 12	23.5±2	23.5±2
3	24	2.5, 20	63.5±1	58±2
4	23.5	5, 40	18±1	17±1
5	23.75	7.5, 60	6.5±1	6.5±1
6	23.75	15, 120	0	0

Complex **1** (2 mol%, 0.03 mmol), dicyclohexylamine (1.5 mmol), KO^{t}Bu (2 mol%, 0.03 mmol) tert-amyl alcohol (3 mL), NH_3(l), 170°C. a) standard deviation over 3 experiments.

Table S5: Reaction temperature of 150ºC in the splitting of dicyclohexylamine

Entry	Time	NH_3 (mL), eq	Conversion (%)[a]	Primary Amine (%)[a]
1	16	2.5, 20	26±2	22±2
2	24	5, 120	41±3	39±3

Complex **1** (2 mol%, 0.03 mmol), dicyclohexylamine (1.5 mmol), KO^{t}Bu (2 mol%, 0.03 mmol) tert-amyl alcohol (3 mL), NH_3(l), 150°C. a) standard deviation over 3 experiments.

Spectroscopy

Procedure for the NMR reactions:

*Reaction of complex **1** with cyclohexylamine:*

Into a Wilmad-Young NMR tube, complex **1** (0.073 mmol, 46.6 mg) was weighed and dissolved in $CDCl_3$. ^{1}H and ^{13}C NMR spectra were recorded and after that, 10 eq. cyclohexylamine (0.73 mmol, 63 µL) were added. Again, both ^{1}H and ^{13}C NMR were recorded and the mixture was left at room temperature for 18h. After this time, both ^{1}H and ^{13}C were recorded. The mixture was heated to 60ºC for 1 h.

*Reaction of complex **1** with secondary amine and primary amine:*

In a Wilmad-Young NMR tube, complex **1** (0.09 mmol, 32.7 mg) was weighed and dissolved in $CDCl_3$. ^1H and ^{13}C NMR spectra were recorded and after that, 10 eq. dicyclohexylamine (0.5 mmol, 99.4 μL) were added. Again, both ^1H and ^{13}C NMR were recorded and the mixture was heated to 60ºC for 4h. Spectra were recorded again and the mixture was continued to heat at 60ºC for 4 days. ^1H and ^{13}C NMR revealed no change.

*Reaction of complex **1** with ammonia and cyclohexylamine:*
In a 15 mL stainless steel autoclave, complex **1** (0.09 mmol, 57 mg) was placed. $CDCl_3$ was added to dissolve the mixture and NH_3 (2.5 mL, 90 mmol) was subsequently added via a Mass Flow controller. The autoclave was closed and heated to 170ºC for 1.45 h. After cooling to room temperature, the resulting mixture was transferred to a Wilmad-Young NMR tube and ^1H and ^{13}C NMR were recorded. After that, 10 eq. cyclohexylamine (0.9 mmol, 89 mg, 0.1 mL) were added. Again, both ^1H and ^{13}C NMR were recorded and the mixture was left at room temperature for 18h. After this time, both ^1H and ^{13}C were recorded.

*Reaction of complex **3** with cyclohexylamine:*
In a Wilmad-Young NMR tube, complex **3** (0.05 mmol, 39.1 mg) was weighed and dissolved in $CDCl_3$. ^1H and ^{13}C NMR spectra were recorded and after that, 11.4 eq. cyclohexylamine (65 μL, 0.57 mmol) were added. Both ^1H and ^{13}C NMR were recorded and the mixture was left at room temperature for 18h. After this time, both ^1H and ^{13}C NMR were recorded. The mixture was heated to 90ºC for 6 h. Again, both ^1H and ^{13}C NMR were recorded. The mixture was heated again to 90ºC for 2 days before recording the spectra again.

In situ FT-IR monitoring
In a home-made stainless steel autoclave equipped with a ZnS path length cell, 6 mL $CHCl_3$ (dry degassed) was placed and a background was recorded for further use. At the same time, complex **1** (0.1 mmol, 63.8 mg) was weighed into a Schlenk tube and dissolved in dry degassed $CHCl_3$. The autoclave was emptied and dried before purging it with Ar again. The solution of complex **1** was transferred to the autoclave and a spectrum was recorded again. After this, cyclohexylamine (1 mmol, 115 μL) was added and the autoclave was sealed and heated to 40ºC. Spectra were recorded with 15 minutes time intervals.

NMR spectroscopy

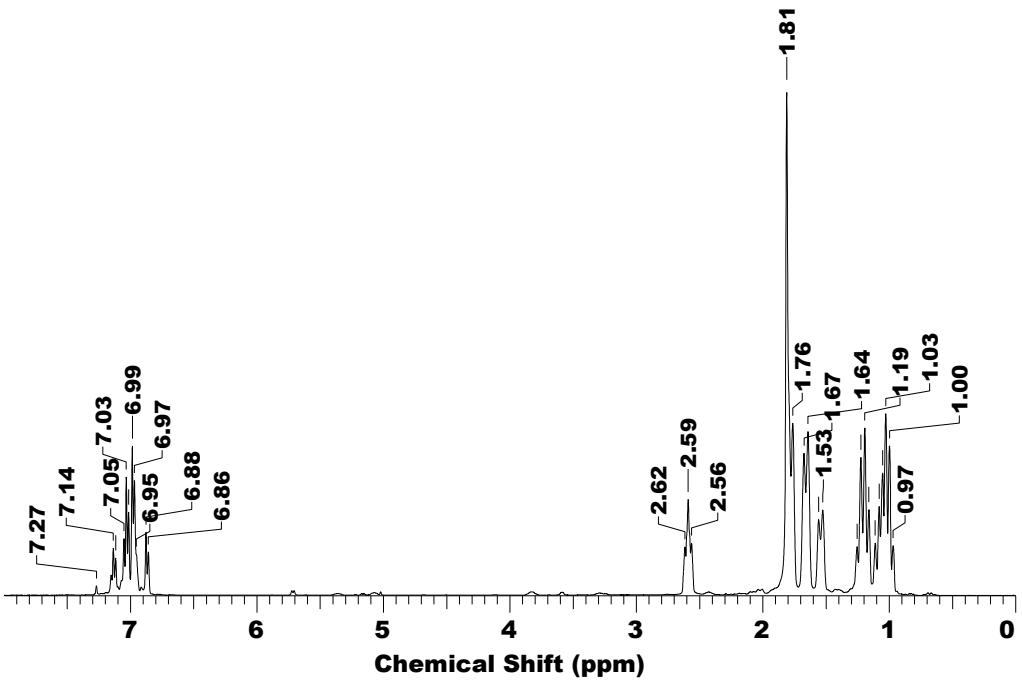


Figure S1: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K) of complex 1 with 10 eq. of cyclohexylamine immediately after the addition. The peak at 1,81ppm resembles the free amine

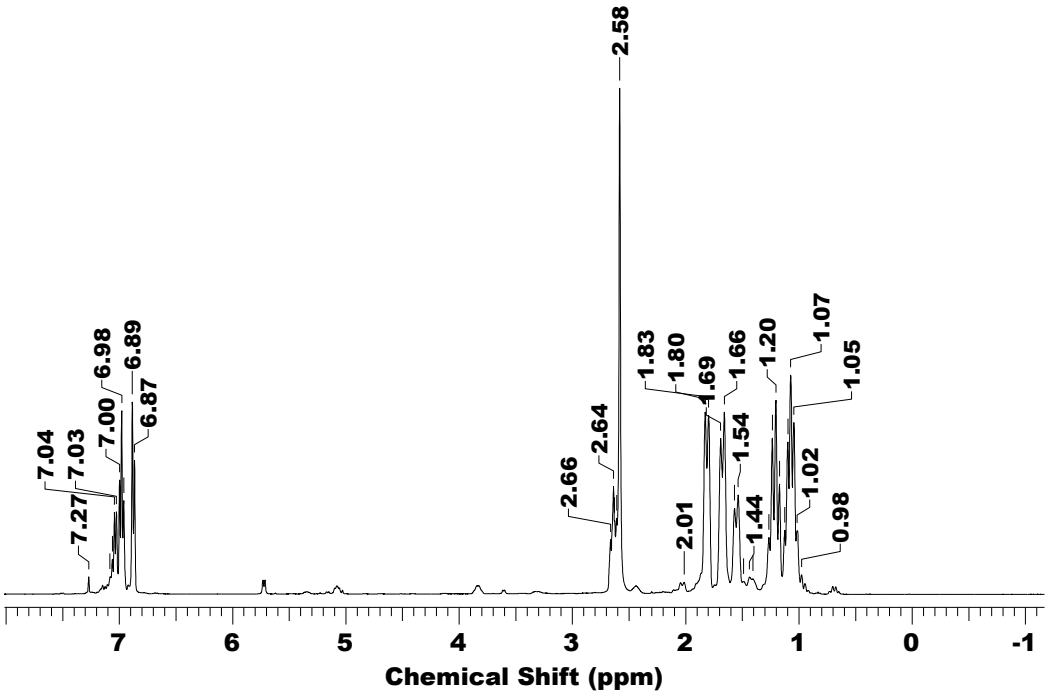


Figure S2: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K) of complex 1 with 10 eq. of cyclohexylamine after 18 h at r.t.. The peak originated form 2.09 ppm is now shifted completely to 2.58 ppm.

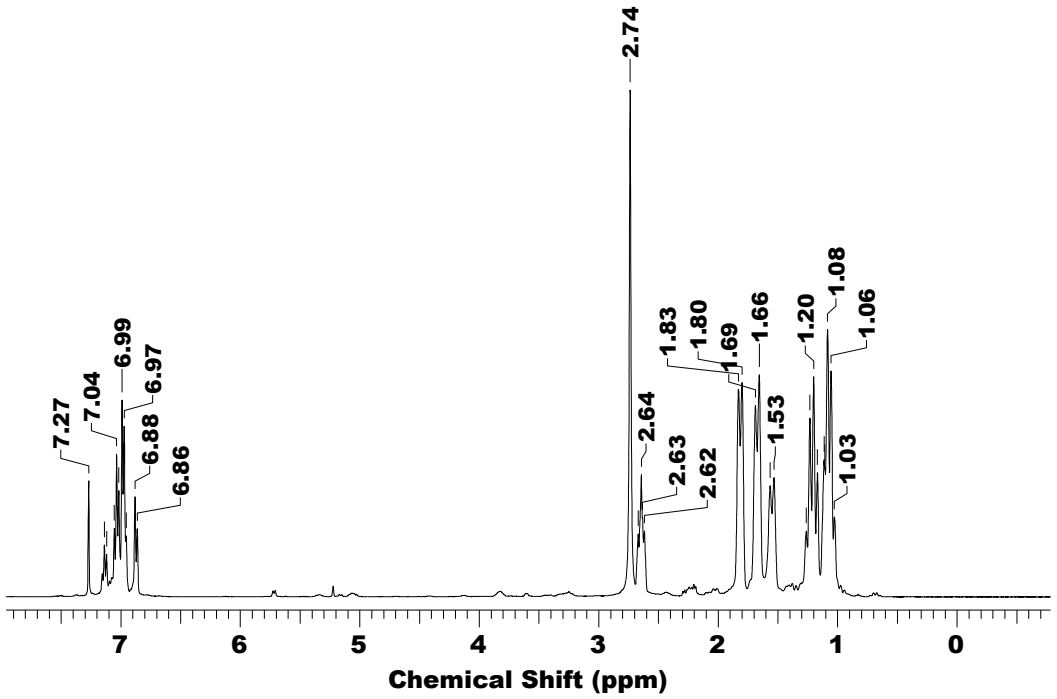


Figure S3: ^{1}H NMR ($CDCl_3$, 400 MHz, 298K) of complex 1 with 10 eq. of cyclohexylamine after 18 h at r.t. followed by 1 h at 60°C. The peak originated form 2.58 ppm is now shifted completely to 2.74 ppm.

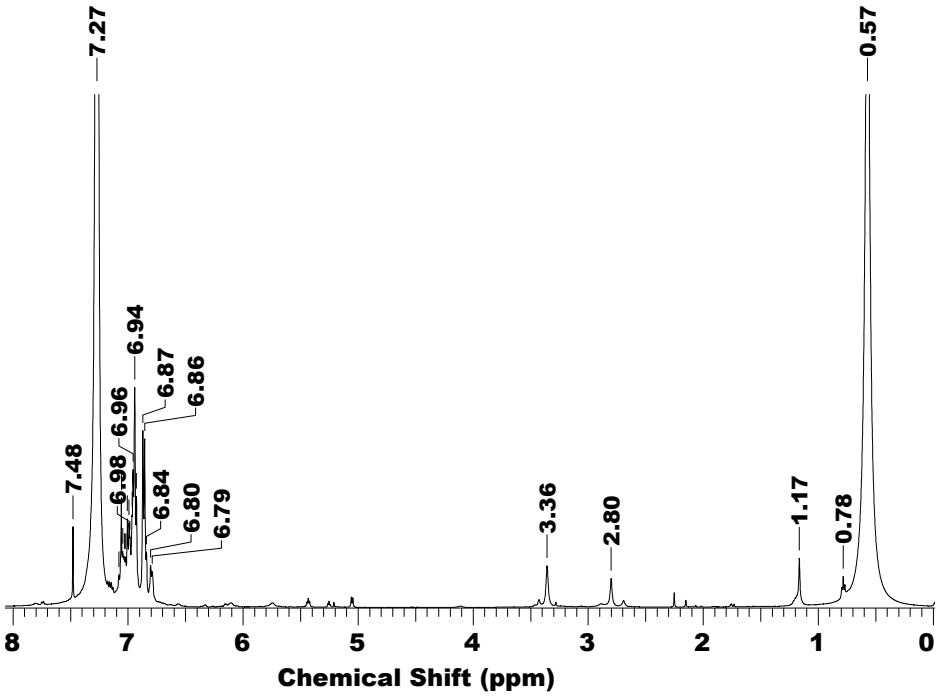


Figure S4: ^{1}H (500 MHz, $CDCl_3$, 298K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) after the reaction with NH_3 (170°C, 1.45 h, $CDCl_3$). The peak at 0.57 ppm is free NH_3; coordinated NH_3 can be found at 3.36 and 2.80 ppm.

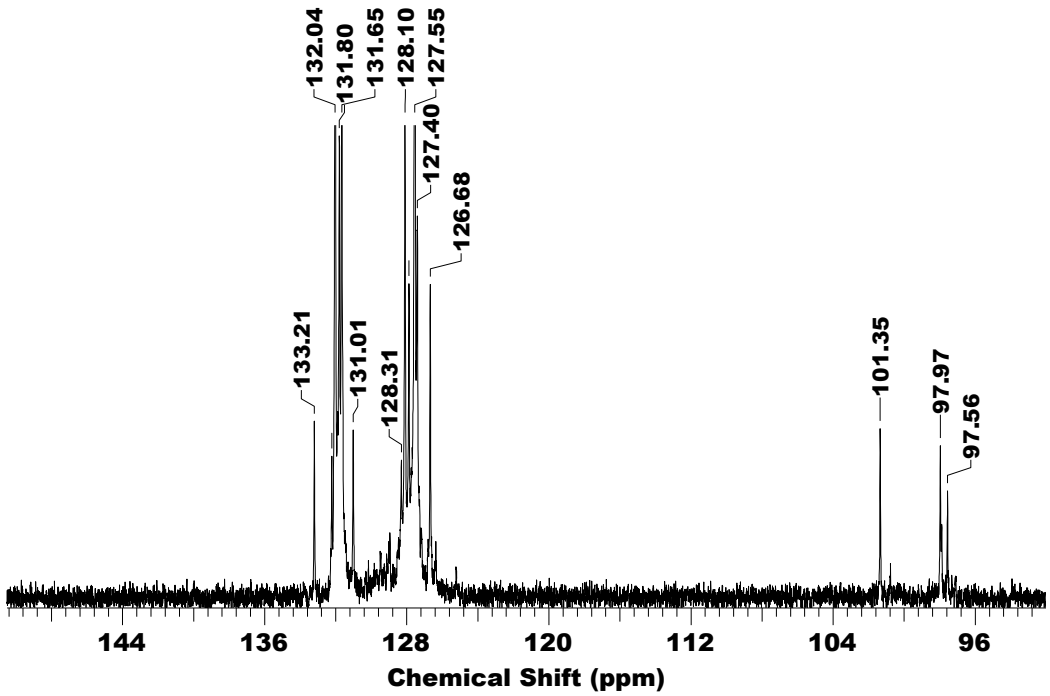


Figure S5: ^{13}C NMR (125.73 MHz, $CDCl_3$. 298 K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) after the reaction with NH_3 followed by addition of 10 eq. n-hexylamine at r.t..

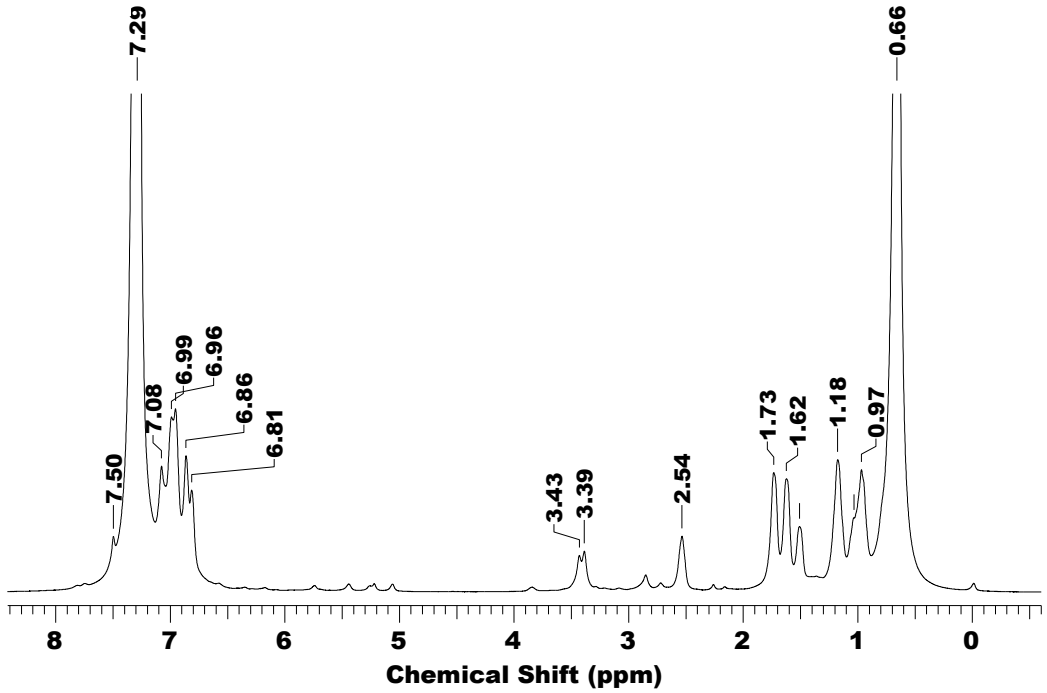


Figure S6: ^{1}H (500 MHz, $CDCl_3$, 298K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) after the reaction with NH_3 followed by the addition of 10 eq. cyclohexylamine. The peak at 0.66 ppm is free NH_3; coordinated cyclohexylamine can be found at 2.54 ppm.

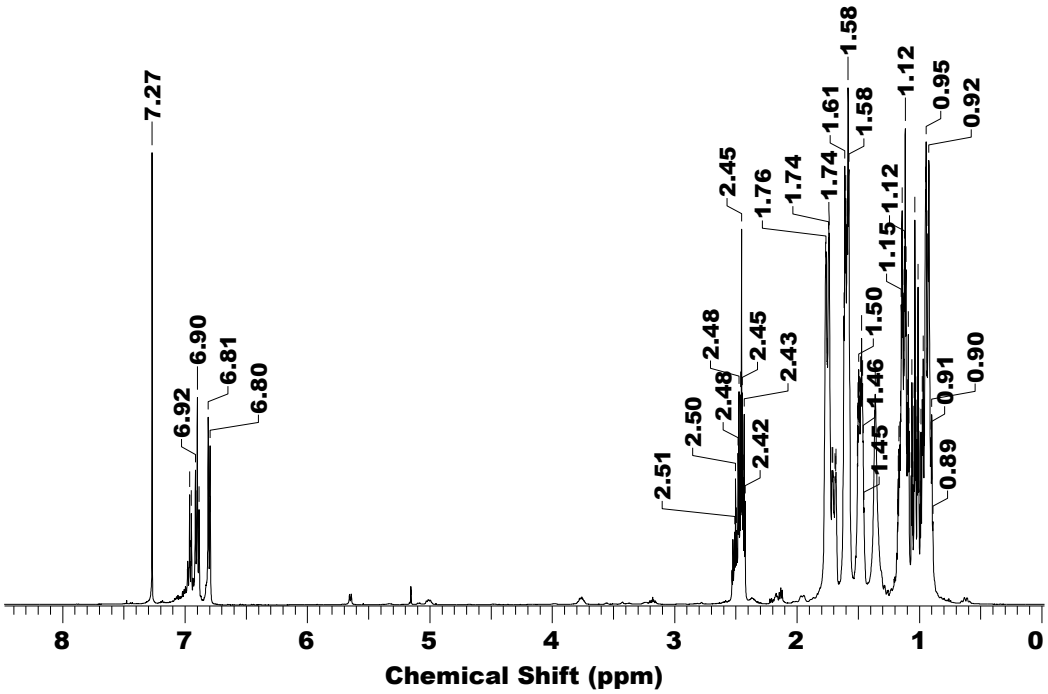


Figure S7: ^{1}H (500 MHz, $CDCl_3$, 298K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) immediately after the addition of 10 eq. dicyclohexylamine.

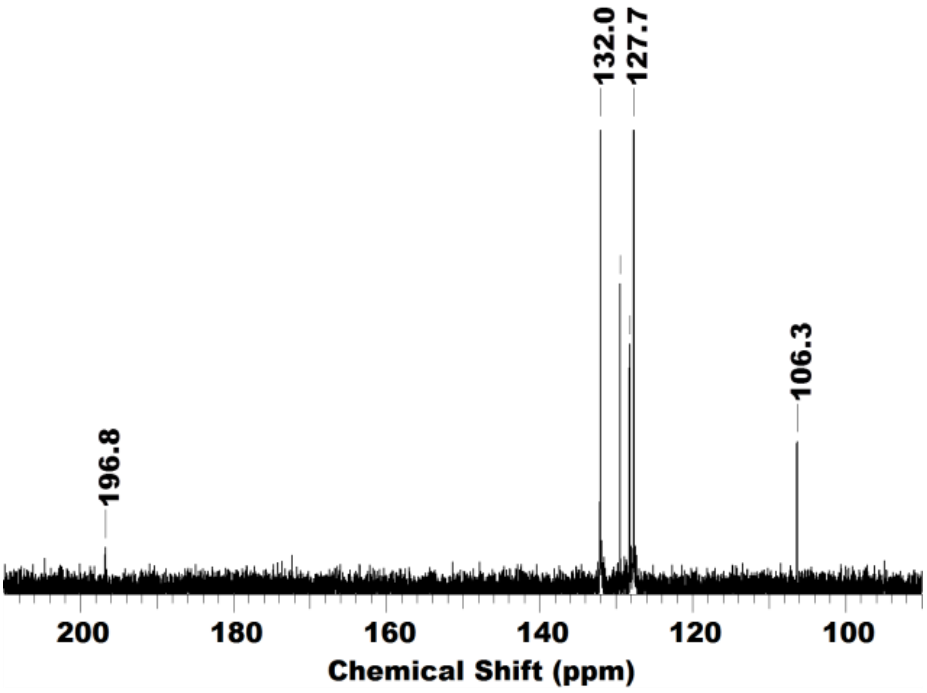


Figure S8: ^{13}C NMR (125.73 MHz, $CDCl_3$) spectrum of $Ru(CpPh_5)(CO)_2Cl$ with 10 eq. dicyclohexylamine after 18 h at r.t..

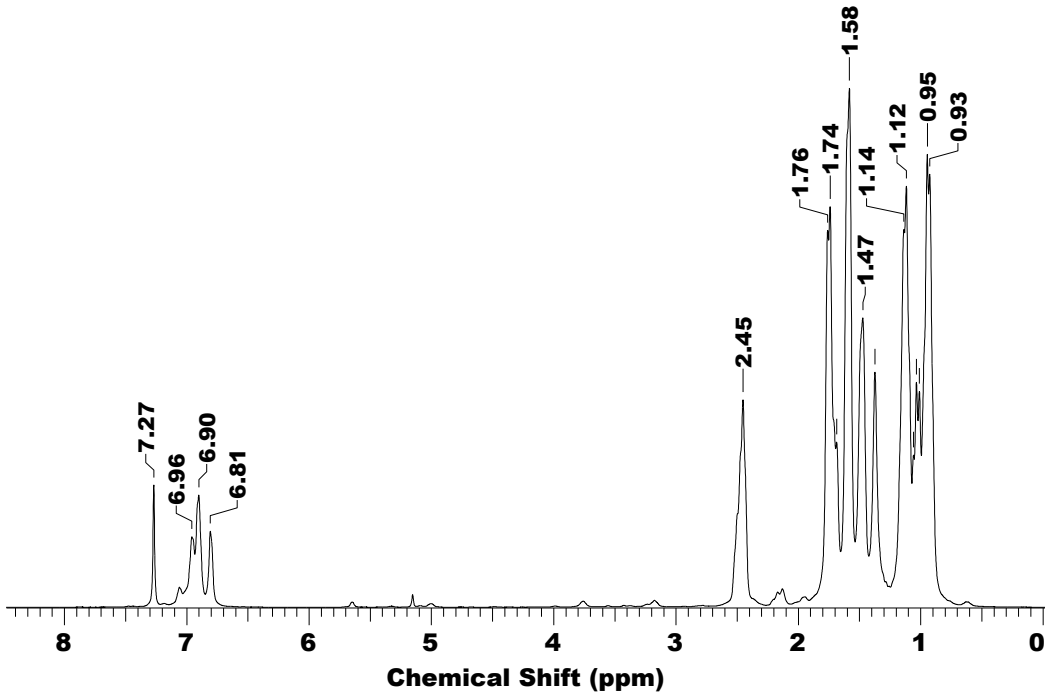


Figure S9: ^{1}H (500 MHz, $CDCl_3$, 298K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) after the addition of 10 eq. dicyclohexylamine and heated to 60°C for 4 h.

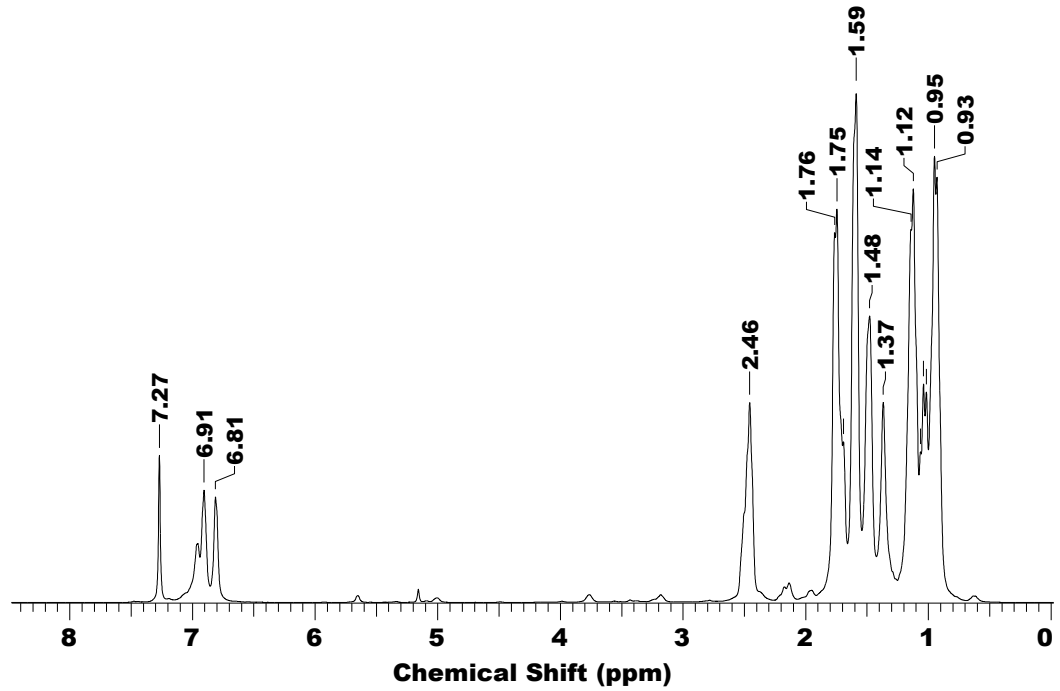


Figure S10: ^{1}H (500 MHz, $CDCl_3$, 298K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) after the addition of 10 eq. dicyclohexylamine and heated to 60°C for 4 days.

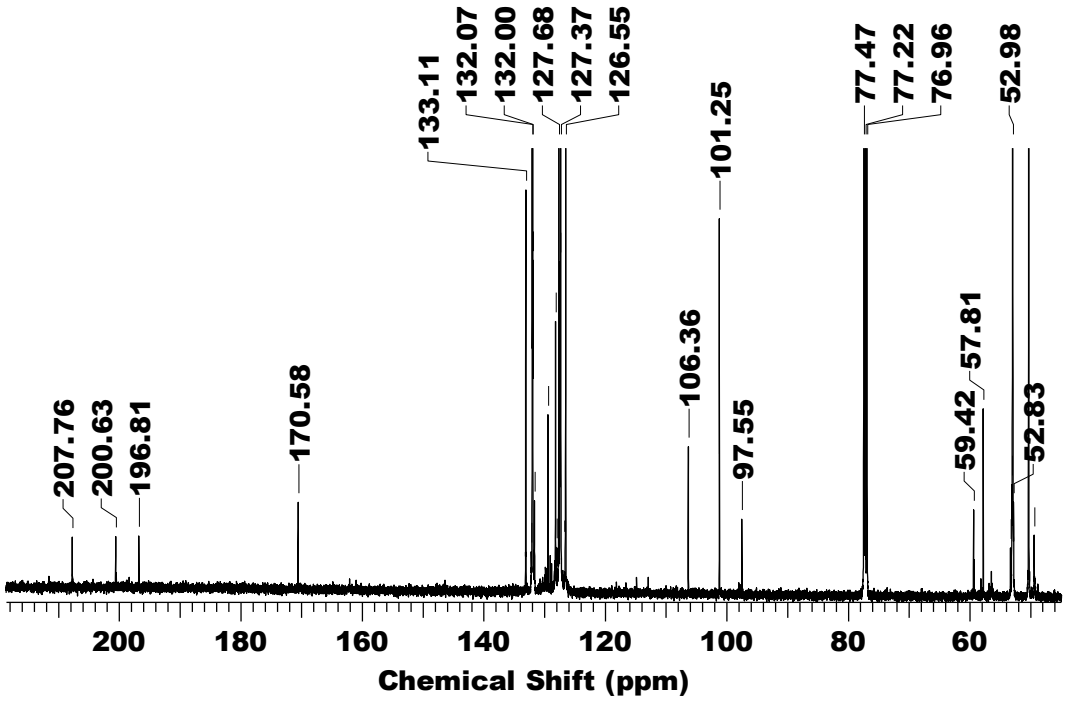


Figure S11: ^{13}C NMR (125.73 MHz, $CDCl_3$, 298 K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) with 10 eq. cyclohexylamine after 4 h at 60°C.

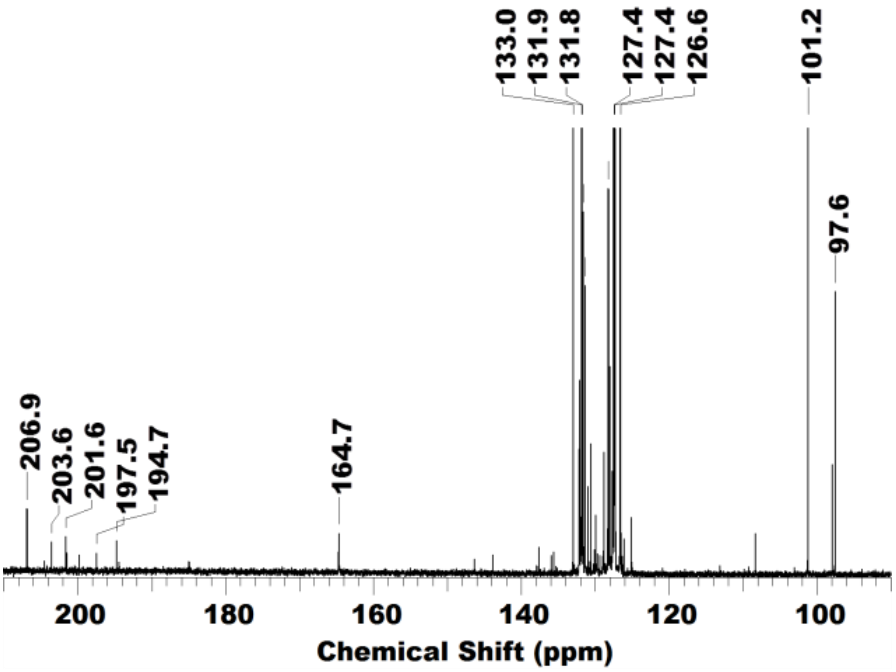


Figure S12: ^{13}C NMR (125.73 MHz, $CDCl_3$, 298 K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) with 10 eq. n-hexylamine after 6 h at 90°C.

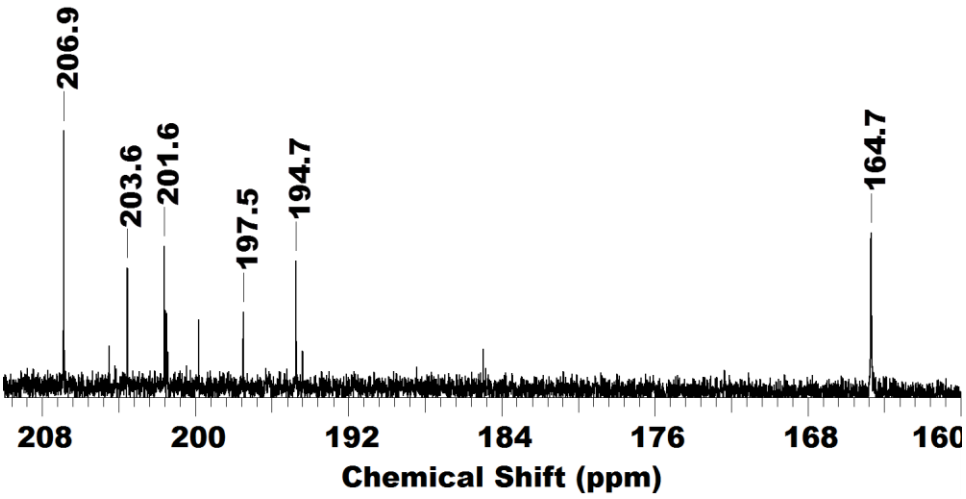


Figure S13: ^{13}C NMR (125.73 MHz, $CDCl_3$. 298 K) spectrum of $Ru(CpPh_5)(CO)_2Cl$ (1) with 10 eq. n-hexylamine after 6h at 90°C (zoomed carbonyl region).

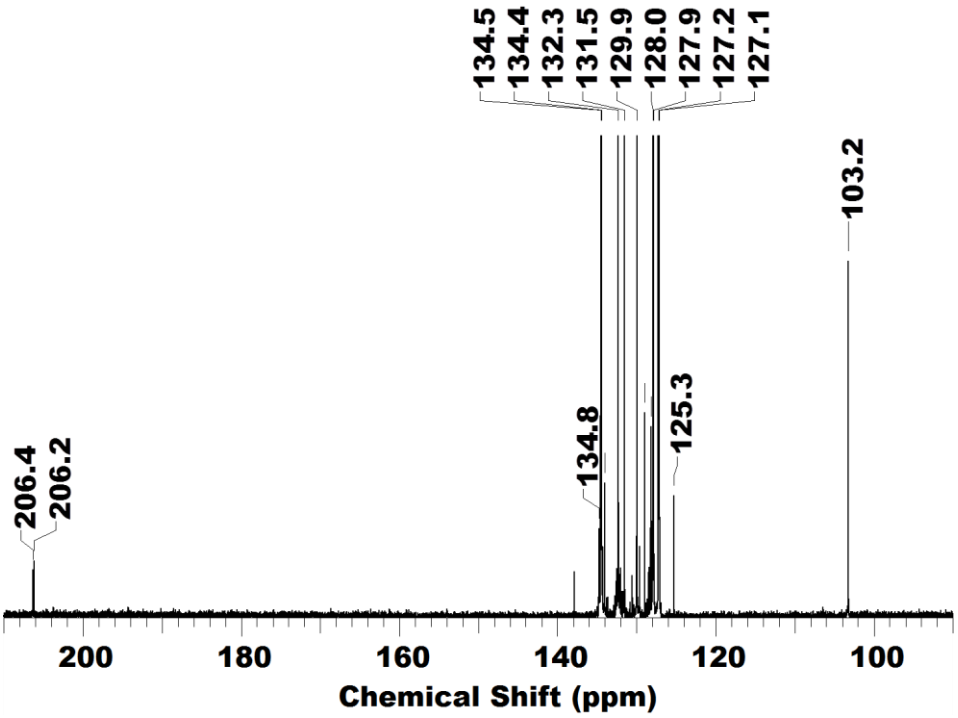


Figure S14: ^{13}C NMR (125.7 MHz, 298 K, $CDCl_3$, 298 K) spectrum of $Ru(CpPh_5)(CO)(PPh_3)Cl$ (3). J_{CP}=25.8 Hz.

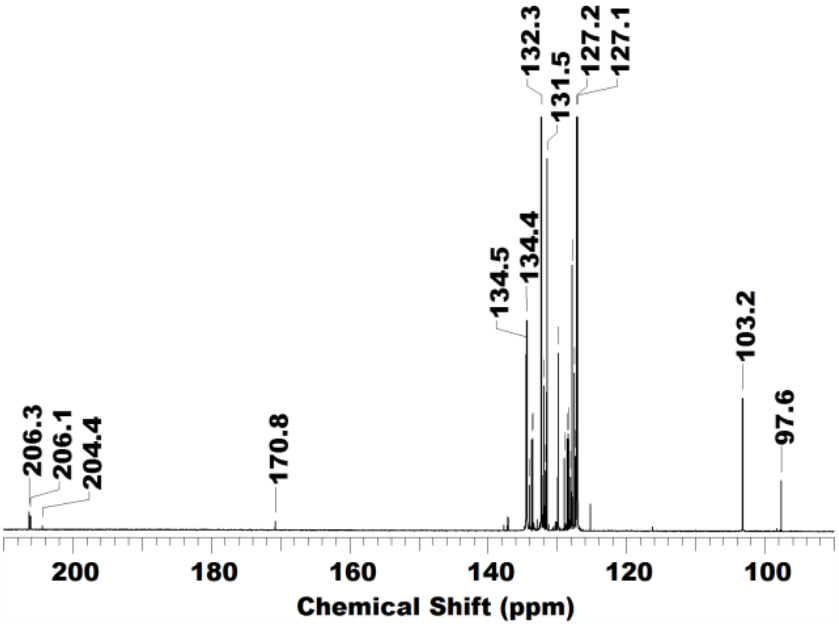


Figure S15: ^{13}C NMR (125.73 MHz, $CDCl_3$, 298 K) spectrum of 3 with 10 eq. cyclohexylamine after 6 h at 90°C.

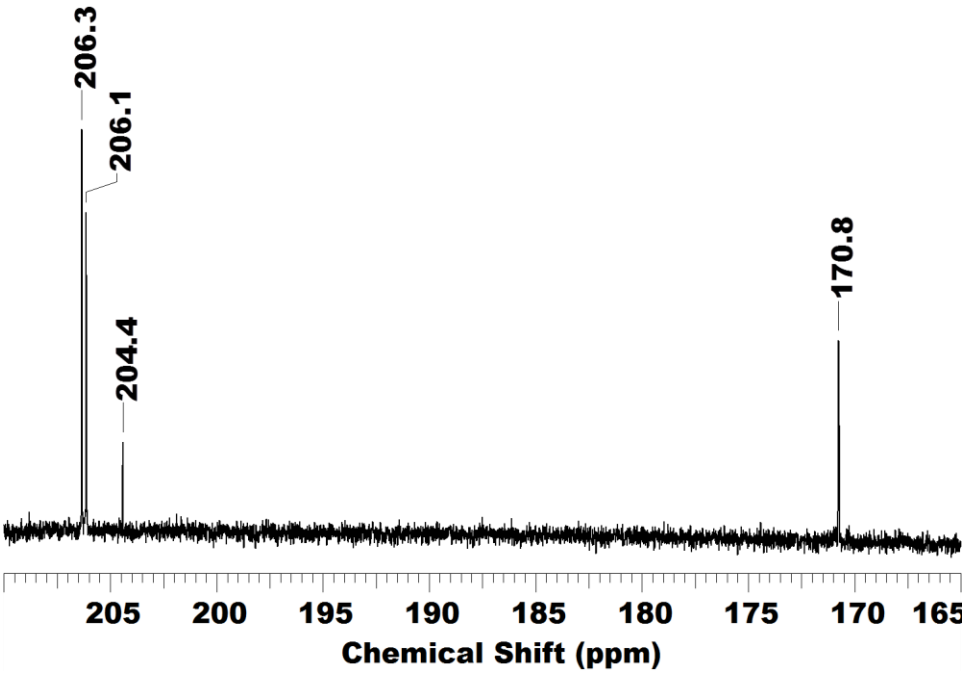


Figure S16: ^{13}C NMR (125.73 MHz, $CDCl_3$, 298 K) spectrum of 3 with 10 eq. cyclohexylamine after 2 days at 90°C (zoomed carbonyl region).

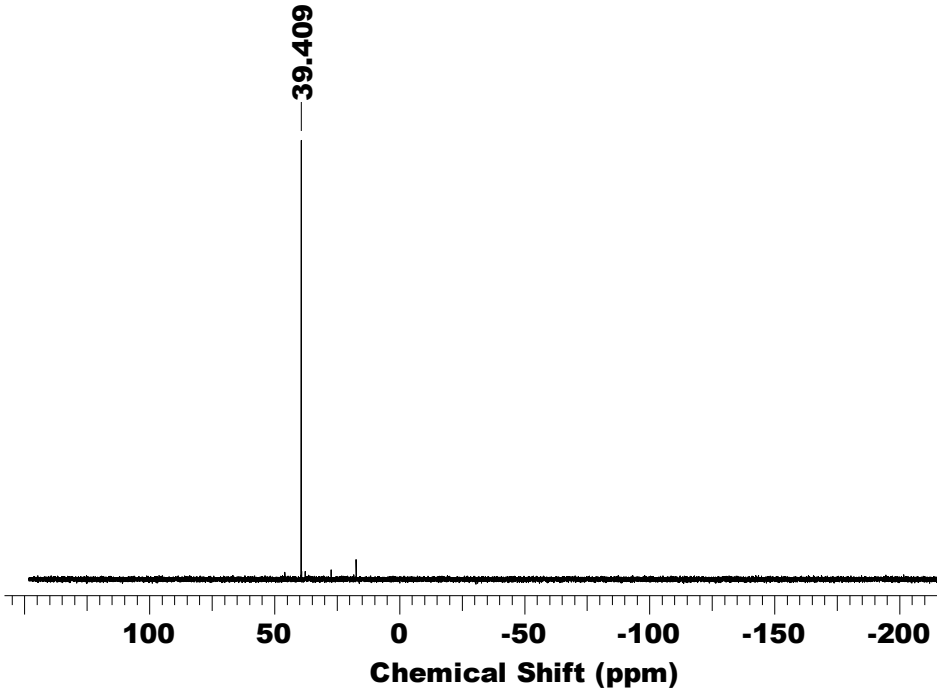


Figure S17: ^{31}P NMR (168 MHz, $CDCl_3$, 298 K) spectrum of 3 without additives.

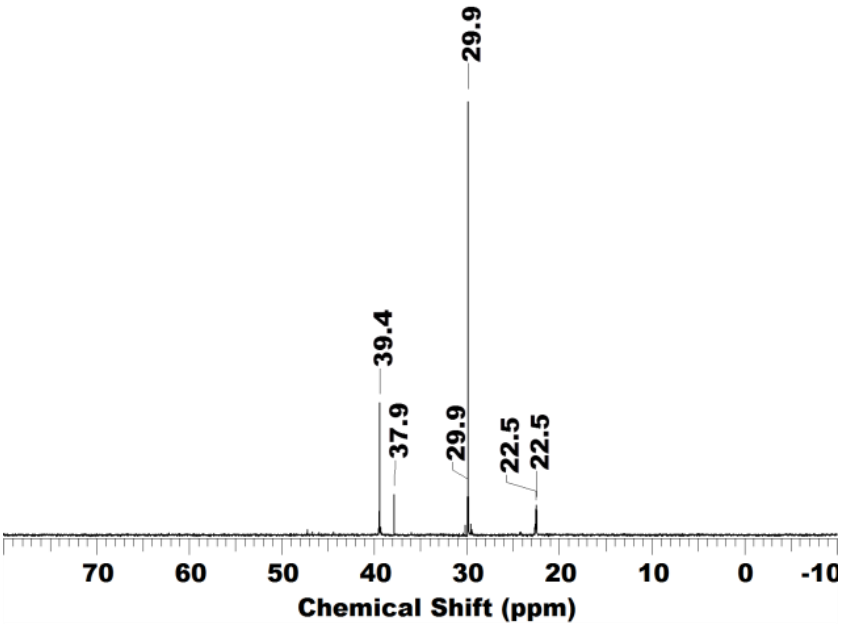


Figure S18: ^{31}P NMR (168 MHz, $CDCl_3$, 298 K) spectrum of 3 with 10 eq. cyclohexylamine after 2 days at 90°C.

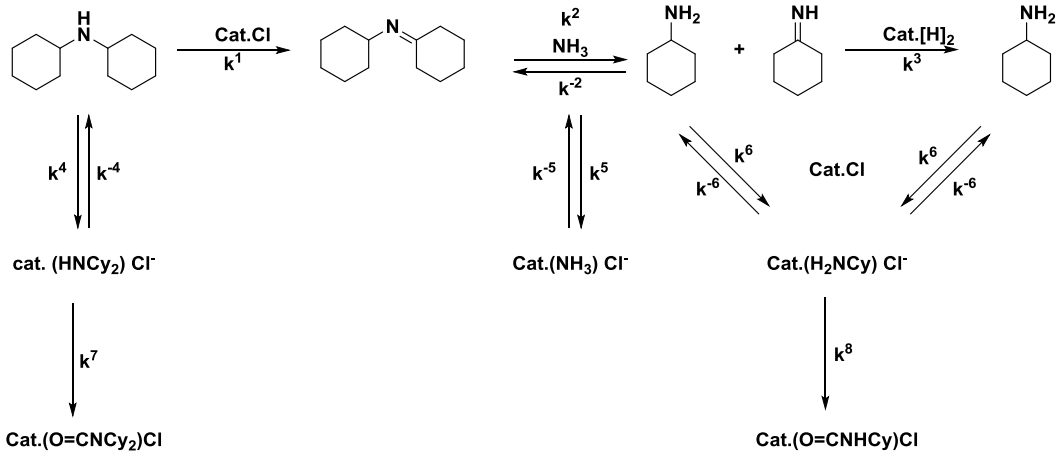
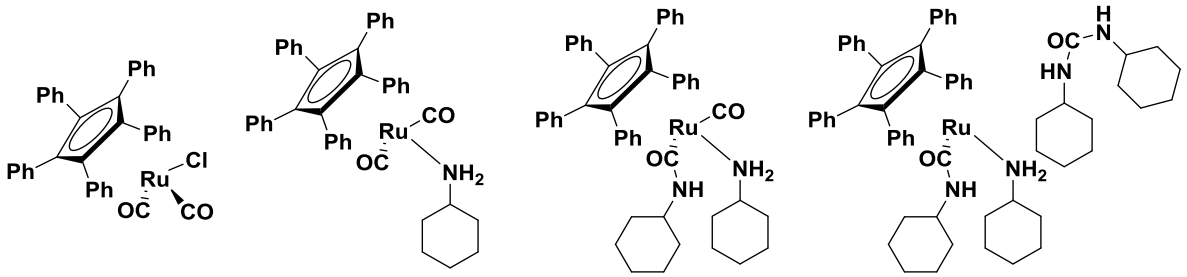


Figure S19: Equilibria in the splitting of dicyclohexylamine, including catalyst deactivation.

Mass spectrometry

*With complex **1**:*

Complex **1** (164 mg, 0.257 mmol) + 40 eq. cyclohexylamine (1.18 mL, 10.28 mmol) heated to 130ºC overnight in t-amylalcohol (5 mL). The solvent from the resulting mixture was evaporated and the remaining powder was subjected to ESI-MS.



1 **5** **6** **7**

Table S5: ESI-MS data obtained from complex 1 with 40 equiv. cyclohexylamine, heated to 130ºC for 16 h.

Entry	Mass found	Corresponding complex
1	1424	2x**6**-2Cyclohexylamine+Na
2	1269	**6**+**1**-3CO+2Na-Cyclohexylamine-Cl
3	1185	2x**1**-2CO-Cl
4	1147	2x**1**-Cl-3CO+Na/ **6**-CO+ RuHCl+K+Cyclohexylamine+Cyclohexylimine (dehydrogenation)
5	1048	**6**-CO+RuHCl+K+Cyclohexylimine
6	993	**7**-H_2 (imine formation)
7	949	**6**-CO-Cylohexylamine+ RuHCl+K+Cyclohexylimine
8	914	**6**-CO-Cylohexylamine+ RuH+K+Cyclohexylimine
9	855	**xx**
10	818	**6**-CO-Cylohexylamine+ RuHCl+K+H
11	773	**6**+H-CO/ **5**-CO+Cyclohexylamine
12	756	**xx**-Cyclohexylamine
13	702	**5**
14	639	**1**

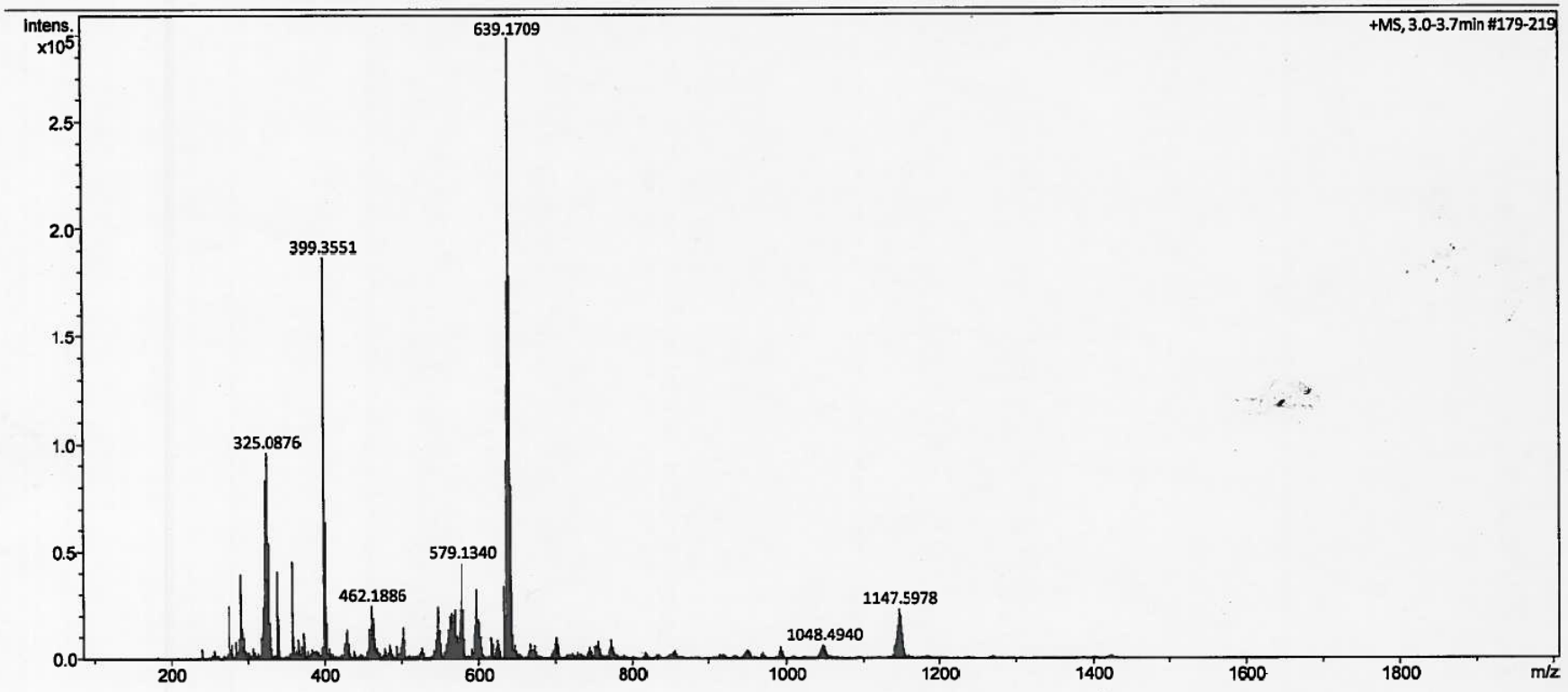
Display Report

Analysis Info

Analysis Name	D:\Data\Alans Data April2014\280414 Dennis Pingen 1058DP14.d	Acquisition Date	4/28/2014 11:52:23 AM
Method	240414ALANstune_low.m	Operator	Bruker UK
Sample Name	Dennis Pingen 1058DP14	Instrument	micrOTOF 8213750.10408
Comment	Dennis Pingen 1058DP14		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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Analysis Info

Analysis Name	D:\Data\Alans Data April2014\280414 Dennis Pingen 1058DP14.d	Acquisition Date	4/28/2014 11:52:23 AM
Method	240414ALANstune_low.m	Operator	Bruker UK
Sample Name	Dennis Pingen 1058DP14	Instrument	micrOTOF 8213750.10408
Comment	Dennis Pingen 1058DP14		

Acquisition Parameter

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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
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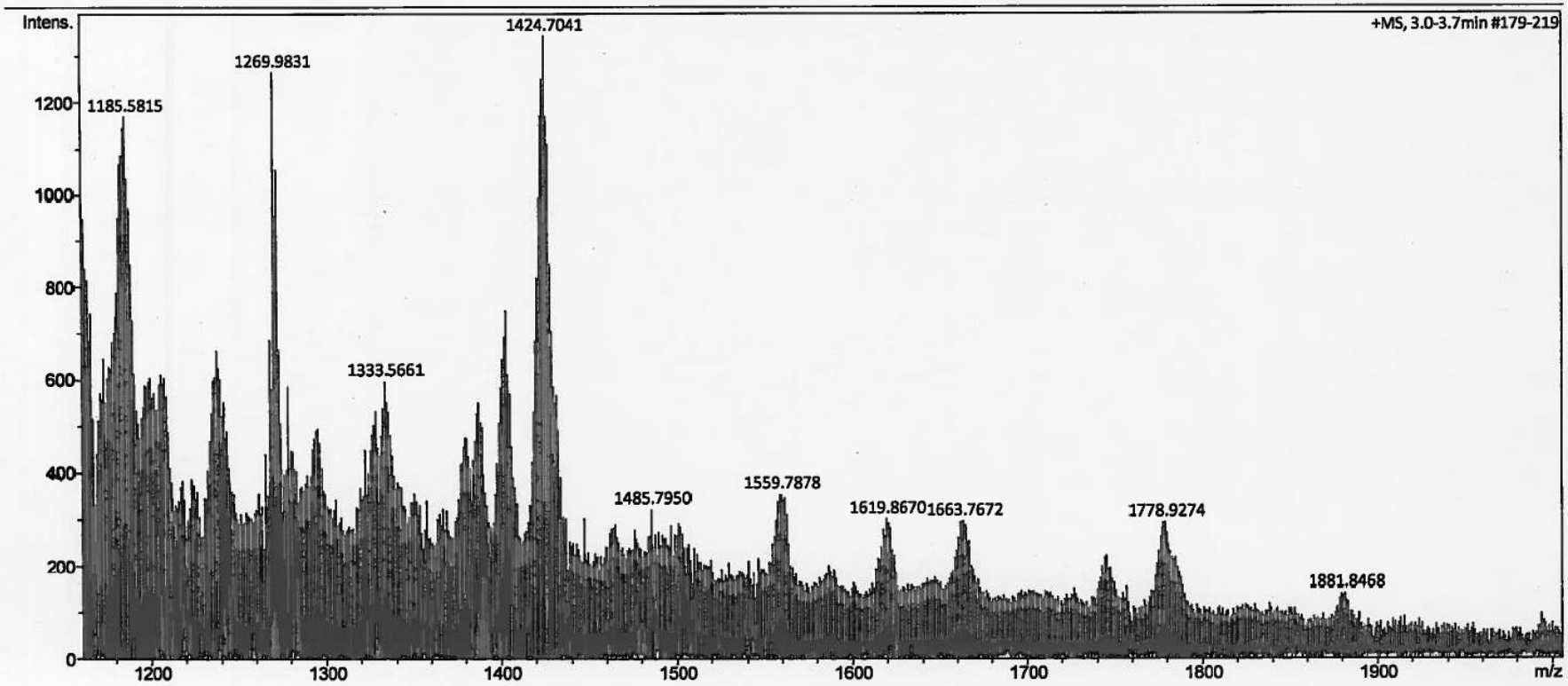

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Analysis Info		Acquisition Date	4/28/2014 11:52:23 AM
Analysis Name	D:\Data\Alans Data April2014\280414 Dennis Pingen 1058DP14.d		
Method	240414ALANstune_low.m	Operator	Bruker UK
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Comment	Dennis Pingen 1058DP14		

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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
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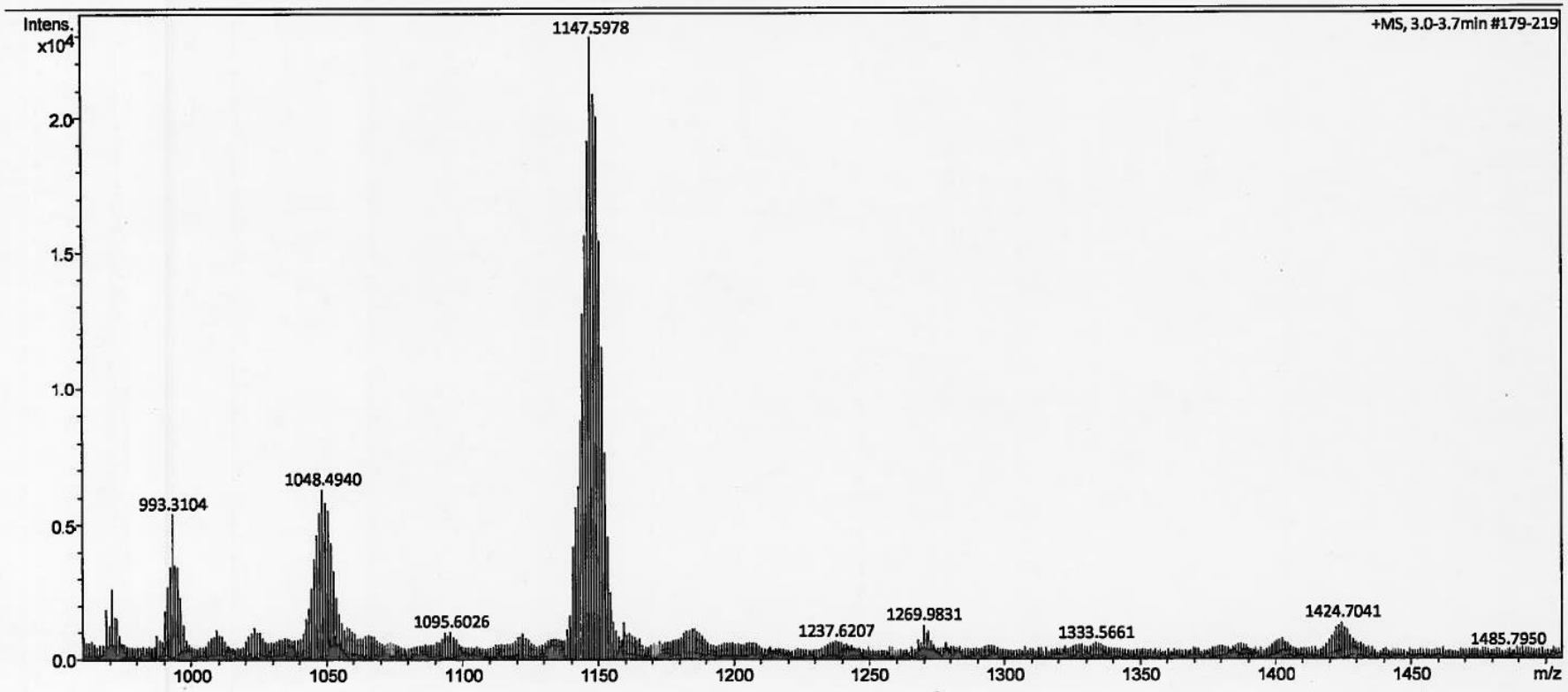

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Analysis Info

Analysis Name	D:\Data\Alans Data April2014\280414 Dennis Pingen 1058DP14.d	Acquisition Date	4/28/2014 11:52:23 AM
Method	240414ALANstune_low.m	Operator	Bruker UK
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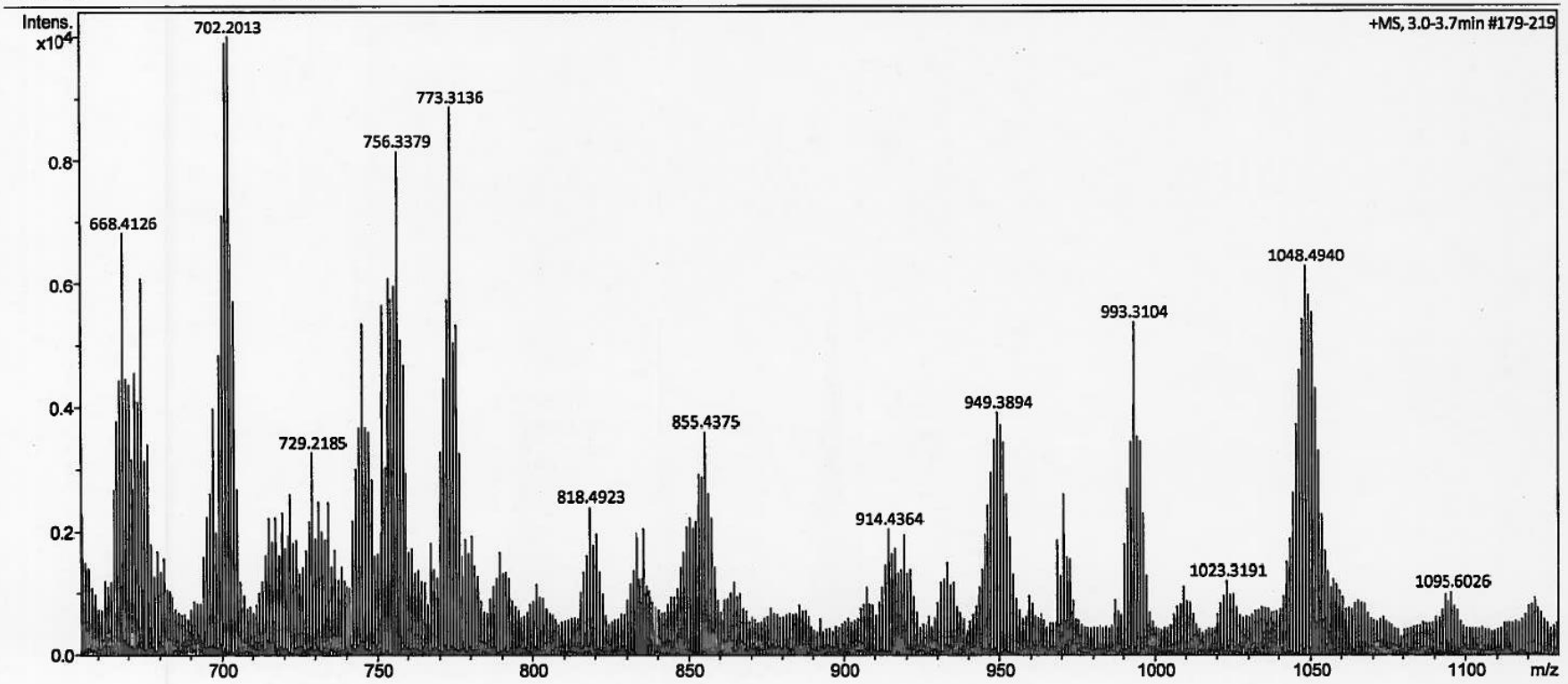
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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Analysis Info		Acquisition Date	4/28/2014 11:52:23 AM
Analysis Name	D:\Data\Alans Data April2014\280414 Dennis Pingen 1058DP14.d		
Method	240414ALANstune_low.m	Operator	Bruker UK
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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
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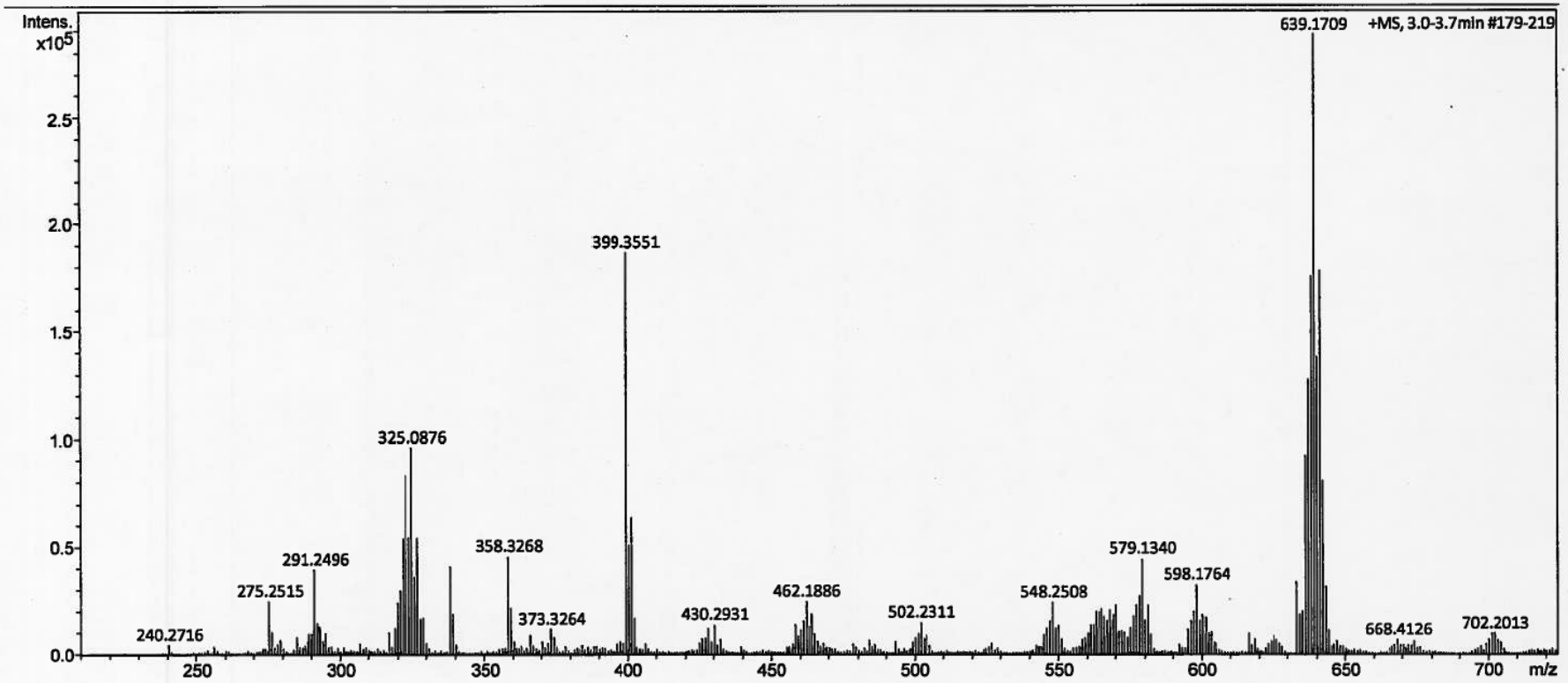
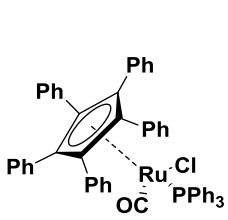


*With complex **3**:*

Complex **3** (63.8 mg, 0.1 mmol) was heated to 100ºC in $CHCl_3$ (8 mL) in an autoclave in the presence of 10 equiv cyclohexylamine (115 µL, 0.57 mmol). After evaporation of the solvent, the resulting mixture was subjected to ESI-MS.



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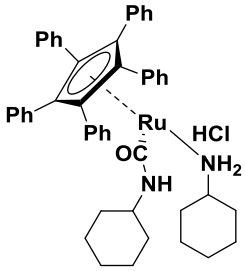

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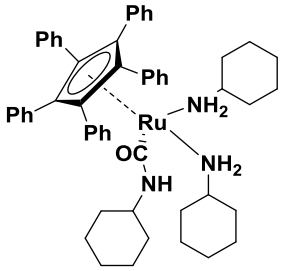

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Table S6: ESI-MS analysis from the mixture of complex 3 with 10 equiv. cyclohexylamine heated to 90ºC for 4 days.

Entry	Mass found	Corresponding complex
1	356	Ru(2x carbamoyl)+2H
2	547	**Ru(CpPh$_5$)**
3	575	**3**-Cl-[PPh_3]
4	765	**9** – COCyclohexylamine –2H_2 (imines)
5	793	**8** – HCl + Na –2H
6	809	**8** + H/ **3**-Cl-CO
7	874	**3** + 2H / **9** + 3H
8	1094	**Ru$_2$(CpPh$_5$)$_2$**
9	1120	
10	1229	
11	1257	**3**+**9**-[PPh_3]-2xCyclohexylamine-CO
12	1285	**3**+**9**-[PPh_3]-2xCyclohexylamine
13	1305	
14	1313	2x**3**+Cyclohexylamine+Na+K-2Cl
15	1338	2x**8** – 2xCOCyclohexylamine -2Cl + 2Na
16	1366	2x**8** – COCyclohexylamine, Cyclohexylamine –2Cl + 2Na
17	1394	2x**8** – 2Cyclohexylamine –2Cl + 2Na
18	1493	2x**8** – Cyclohexylamine –2Cl + 2Na

Display Report

Analysis Info

Analysis Name	D:\Data\Alans Data March 2014\260314 Dennis Pingen 1017DP14.d	Acquisition Date	3/26/2014 1:49:01 PM
Method	160913alanstune_low.m	Operator	Bruker UK
Sample Name	Dennis Pingen 1017DP14	Instrument	micrOTOF 8213750.10408
Comment	Dennis Pingen 1017DP14		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
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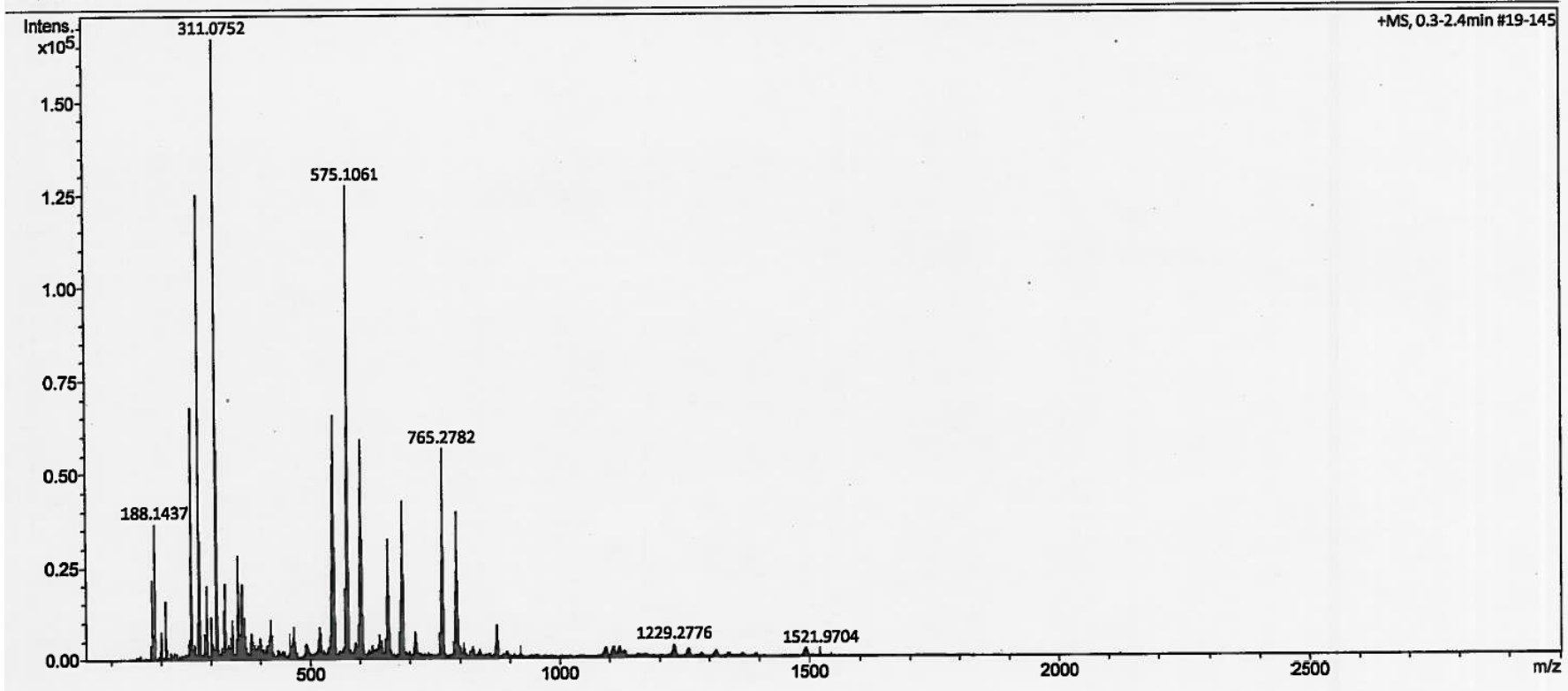

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Analysis Info

Analysis Name	D:\Data\Alans Data March 2014\260314 Dennis Pingen 1017DP14.d	Acquisition Date	3/26/2014 1:49:01 PM
Method	160913alanstune_low.m	Operator	Bruker UK
Sample Name	Dennis Pingen 1017DP14	Instrument	micrOTOF 8213750.10408
Comment	Dennis Pingen 1017DP14		

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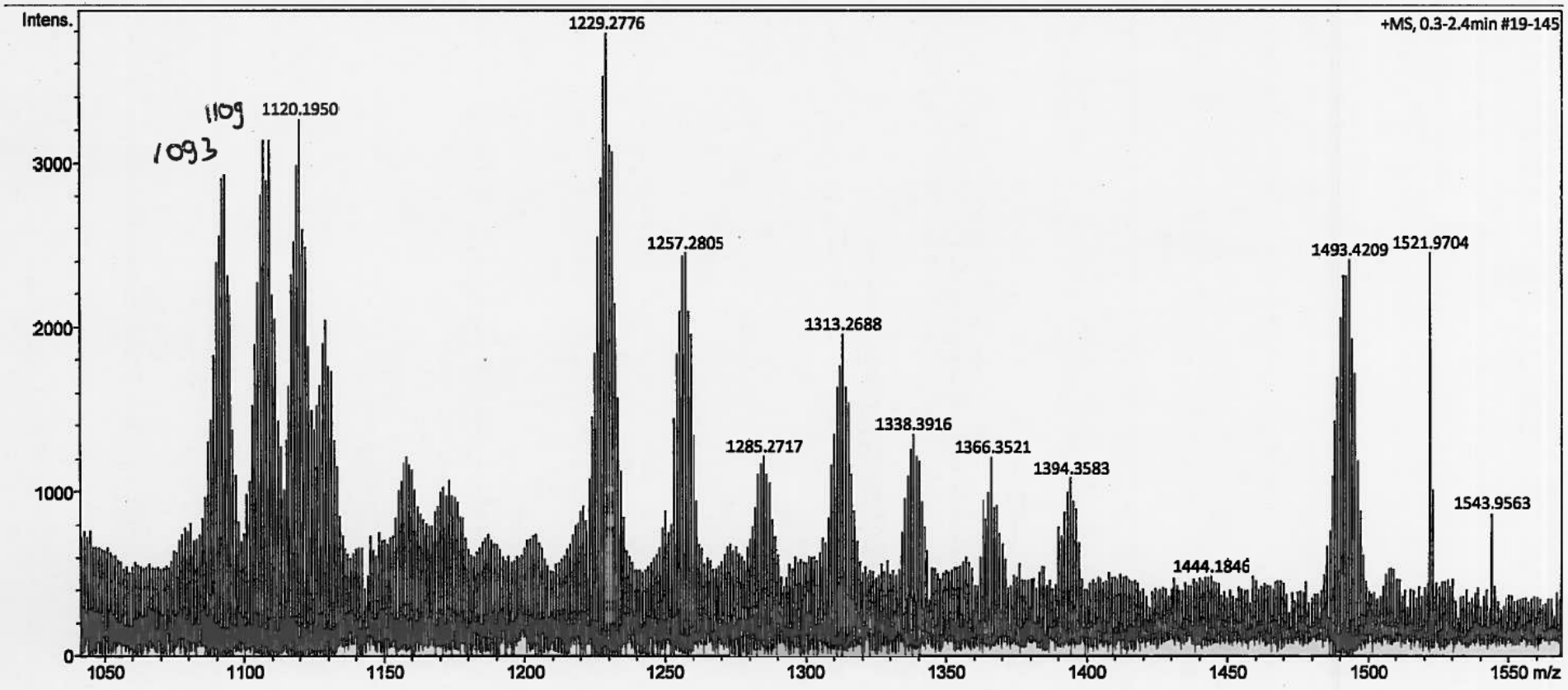

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Analysis Info

Analysis Name	D:\Data\Alans Data March 2014\260314 Dennis Pingen 1017DP14.d	Acquisition Date	3/26/2014 1:49:01 PM
Method	160913alanstune_low.m	Operator	Bruker UK
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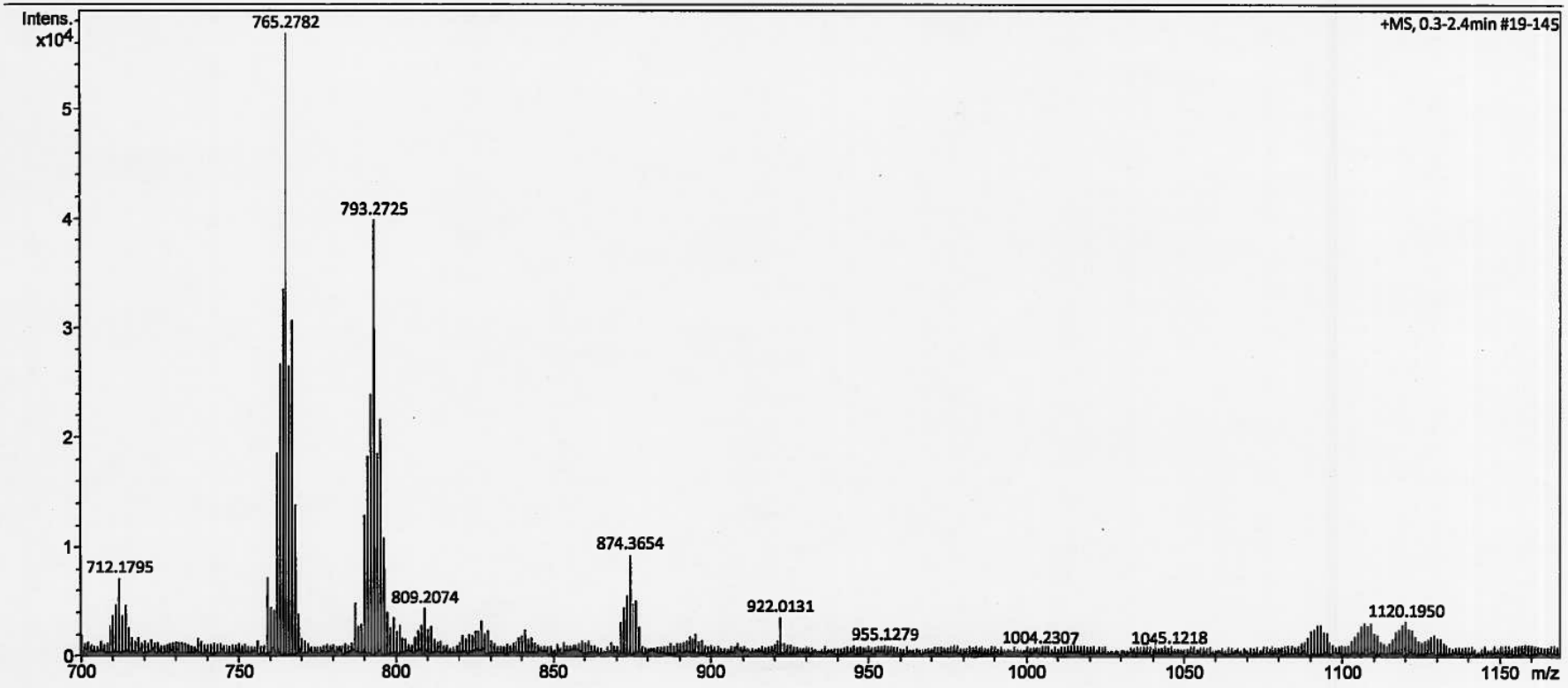

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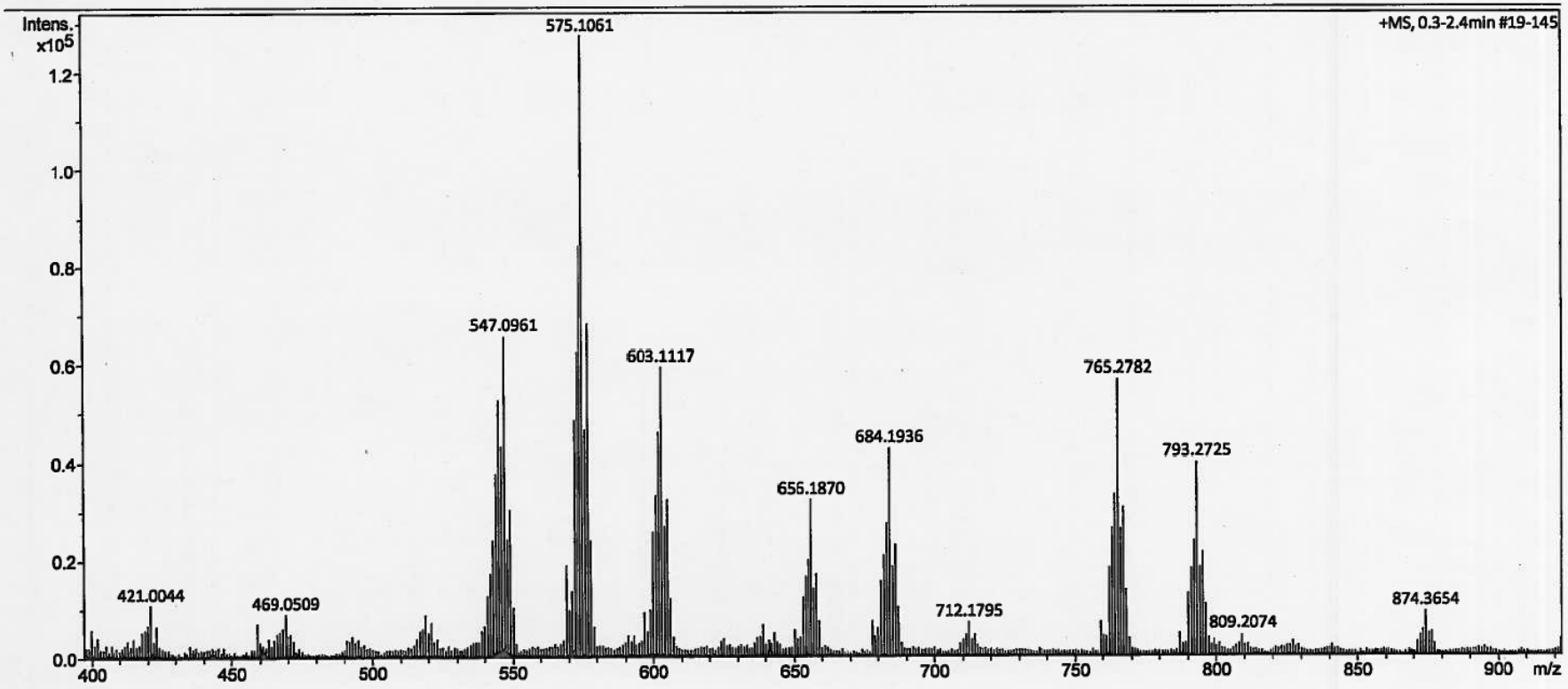

GC-Analysis

Yields of the catalytic runs have been determined by the area of the GC signal. The retention times of the reaction outcome were compared with the retention times of the neat components. Response factors for cyclohexylamine, dicyclohexylamine and dicyclohexylimine were determined and used in the calculation.

GC Method Details:
Amine Alkylation / Higher Start-Fast Pure Components

Injection Mode / ratio:	Split / 100
Temperature:	270°C
Carrier Gas:	He
Flow Controle Mode:	Pressure
Pressure:	121.0 kPa
Total Flow:	144.0 mL/min
Column Flow:	0.70 mL/min
Liner Velocity:	25.8 cm/sec
Column type:	Ultra-2 serial Nr.: US8649351H
Column length:	25 m, 0.33 μm film thickness, 0.20 mm inner diameter
Column Max. Temp. :	310°C
Pressure program:	121.0 -> 164.0 @ 1.8 kPa/min 164.0 hold 15 min
Temperature program:	80°C -> 270°C @ 8°C/min 270 hold 15 min

References

[1] B. Martín-Matute, M. Edin, K. Bogár, B. Kaynak, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2005**, *127*, 8817-8825.

[2] S.-B. Ko, B. Baburaj, M.-J. Kim, J. Park, *J. Org. Chem.* **2007**, *72*, 6860-6864.