

## **Appendix A. Supporting Information**

### **Ruthenium indenylidene complexes bearing bis(*N*-Alkyl/*N'*-Mesityl)-sided heterocyclic carbene ligands**

## **Приложение А. Вспомогательная информация**

### **Инденилиденовые комплексы рутения, содержащие бис(*N*-алкил/*N'*-мезитил) гетероциклические карбеновые лиганды**

#### **GENERAL INFORMATION**

Unless otherwise stated, all reactions were carried out under an argon atmosphere using the Schlenk technique. Solvents were dried and freshly distilled before use, such as dichloromethane by  $\text{CaH}_2$ , toluene by sodium, and benzophenone indicator. Solvents *n*-hexane, *n*-pentane, ethyl acetate, dichloromethane, methanol, and toluene were purchased from Fiers.  $\text{RuCl}_2(3\text{-phenyl-1indenylidene})(\text{PCy}_3)_2$  (**6**) was obtained from GMCX (China). Penten-3-ol, hepten-3-ol and 2-cyclohexen-1-ol, *cis,cis*-cycloocta-1,5-diene (**8**), potassium tert-butoxide ( $\text{KO}t\text{Bu}$ ) diethyl diallyl malonate (**9**) and potassium bis(trimethylsilyl)amide (KHMDS), were purchased from Sigma Aldrich. 1-mesityl-3-methyl-4,5-dihydro-imidazolium chloride (**5a**) and 1-mesityl-3-cyclohexyl-4,5-dihydro-imidazolium chloride (**5b**) were prepared according to previously reported procedures [1, 2]. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Across Organics.

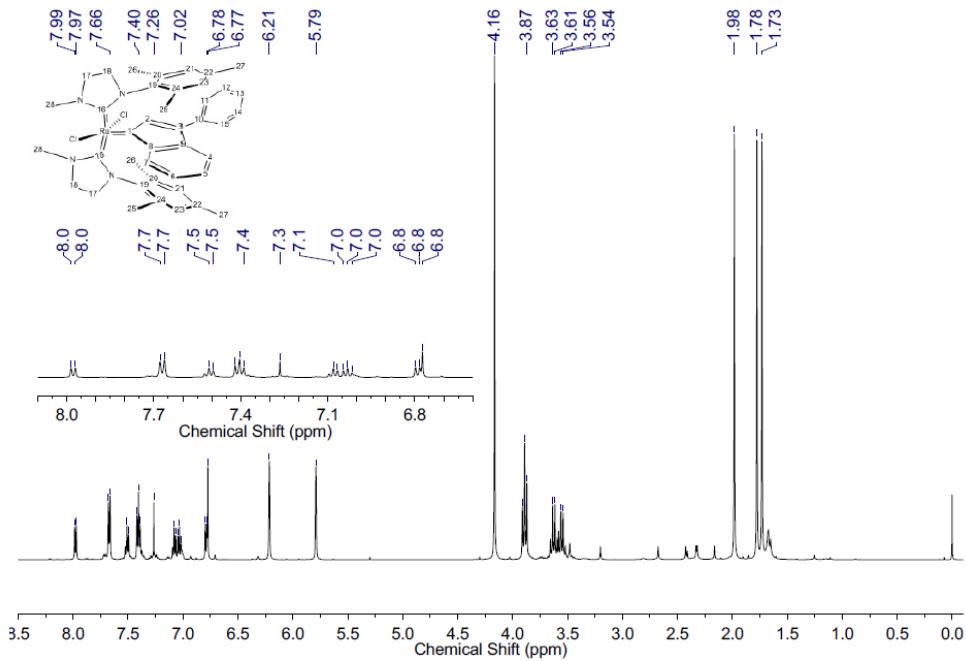
$^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{31}\text{P}$ -NMR, and 2D-NMR spectra were recorded on Bruker 300 MHz and 500 MHz spectrometers. Chemical shifts are listed in ppm from tetramethylsilane with the residual solvent resonance as an internal standard ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or external  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ).

Diffuse Reflectance Infrared Fourier transform spectroscopy (DRIFTS) measurements were recorded on a Thermo Nicolet 6700 FTIR spectrometer equipped with an  $\text{N}_2$  cooled MCT-A (mercury-cadmium-tellurium) detector and a KBr beam splitter. Elemental analyses were performed on a CHNS-O analyzer from Inter-Science. Single crystal X-ray diffraction data were collected using an Agilent Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using Cu- $\text{K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) and  $\omega$  scans. All images were interpreted and integrated with the program CrysAlisPro (Agilent Technologies)<sup>1</sup>. Using Olex-2 [3], the structures were solved by direct methods using the ShelXS structure solution program and refined by full-matrix least-squares on  $F^2$  using the ShelXL program [4]. Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms in the riding mode and isotropic temperature factors were fixed at 1.2 times  $U(\text{eq})$  of the parent atoms (1.5 times for methyl groups).

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<sup>1</sup>CrysAlisPro, Agilent Technologies: Version 1.171.36.34.

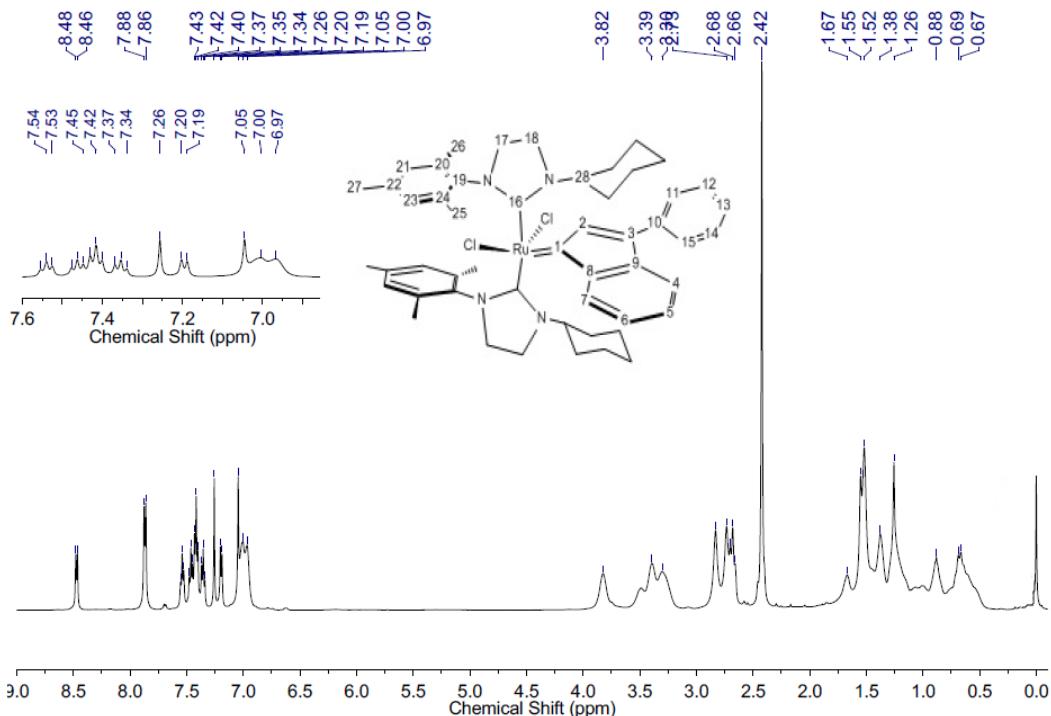
**RuCl<sub>2</sub>bis(1-mesityl-3-methylimidazolidin-2-ylidene)(3-phenyl-1-indenyldene) (7a)**



**Fig. S1.** <sup>1</sup>H-NMR spectrum of 7a in CDCl<sub>3</sub>

**Рис. S1.** Спектр <sup>1</sup>Н-ЯМР соединения 7а в CDCl<sub>3</sub>

**RuCl<sub>2</sub>bis(1-cyclohexyl-3-mesitylimidazolidin-2-ylidene)(3-phenylinden-1-ylidene) (7b)**



**Fig. S2.** <sup>1</sup>H-NMR spectrum of 7b in CDCl<sub>3</sub>

**Рис. S2.** Спектр <sup>1</sup>Н-ЯМР соединения 7б в CDCl<sub>3</sub>

*Single-crystal X-ray diffraction analysis.* Crystal data for compound **7a**. CCDC 1830901, C<sub>41</sub>H<sub>46</sub>N<sub>4</sub>Cl<sub>2</sub>Ru, M = 766.79, triclinic, space group P-1 (No. 2), a = 9.8123(6) Å, b = 11.1346(8) Å, c = 18.2094(9) Å, α = 88.320(5)°, β = 85.219(5)°, γ = 65.454(7)°, V = 1803.4(2) Å<sup>3</sup>, Z = 2, T = 100 K, ρ<sub>calc</sub> = 1.412 g cm<sup>-3</sup>, μ(Cu-Kα) = 5.149 mm<sup>-1</sup>, F(000) = 796, 20129 reflections measured, 6339 unique (*R*<sub>int</sub> = 0.1159) which were used in all calculations. The final *R*1 was 0.0587 (I > 2σ (I)) and wR2 was 0.1433 (all data).

Crystal data for compound **7b**. CCDC 1049432, C<sub>51</sub>H<sub>62</sub>N<sub>4</sub>Cl<sub>2</sub>Ru, M = 903.02, monoclinic, space group P2<sub>1</sub>/c (No. 14), a = 22.6954(6) Å, b = 15.7051(5) Å, c = 12.8872(3) Å, β = 92.902(2)°, V = 4587.5(2) Å<sup>3</sup>, Z = 4, T = 100 K, ρ<sub>calc</sub> = 1.307 g cm<sup>-3</sup>, μ(Cu-Kα) = 4.124 mm<sup>-1</sup>, F(000) = 1896, 37921 reflections measured, 9508 unique (*R*<sub>int</sub> = 0.0876) which were used in all calculations. The final *R*1 was 0.0472 (I > 2σ (I)) and wR2 was 0.1241 (all data).

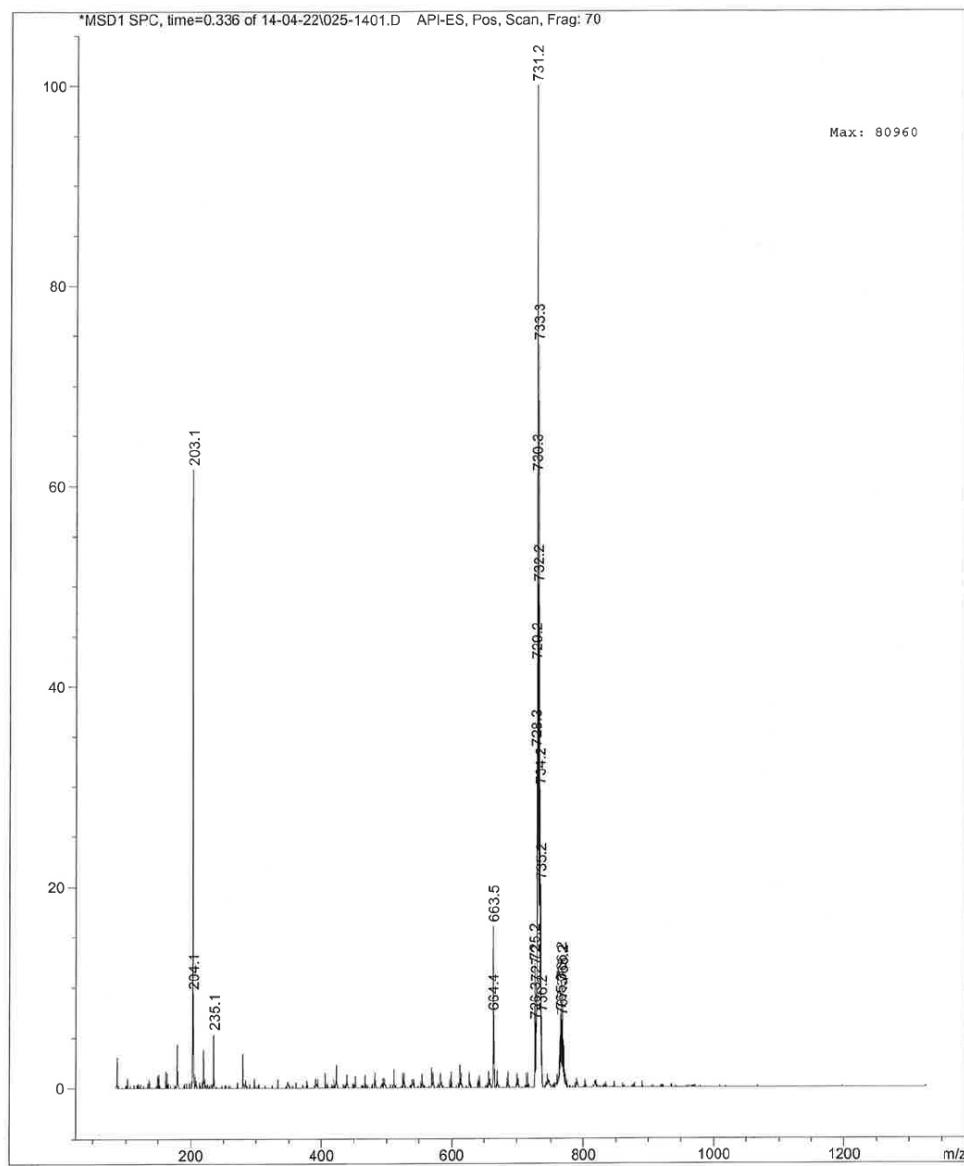
*Applied procedure for the ROMP of cis,cis-cycloocta-1,5-diene [5–7].* For example, 0.05 mol% catalyst loading: 4.07 μmol of the complex was dissolved in 1 mL toluene-d8. An NMR-tube was charged with *cis,cis*-cycloocta-1,5-diene (0.1 mL, 0.81 mmol), toluene-d8 (0.5 mL) and complex solution (0.1 mL). The NMR tube was then closed, and the temperature was raised to 80 °C. The conversion was determined by integrating the olefinic <sup>1</sup>H NMR signals of the formed polymer and the consumed monomer.

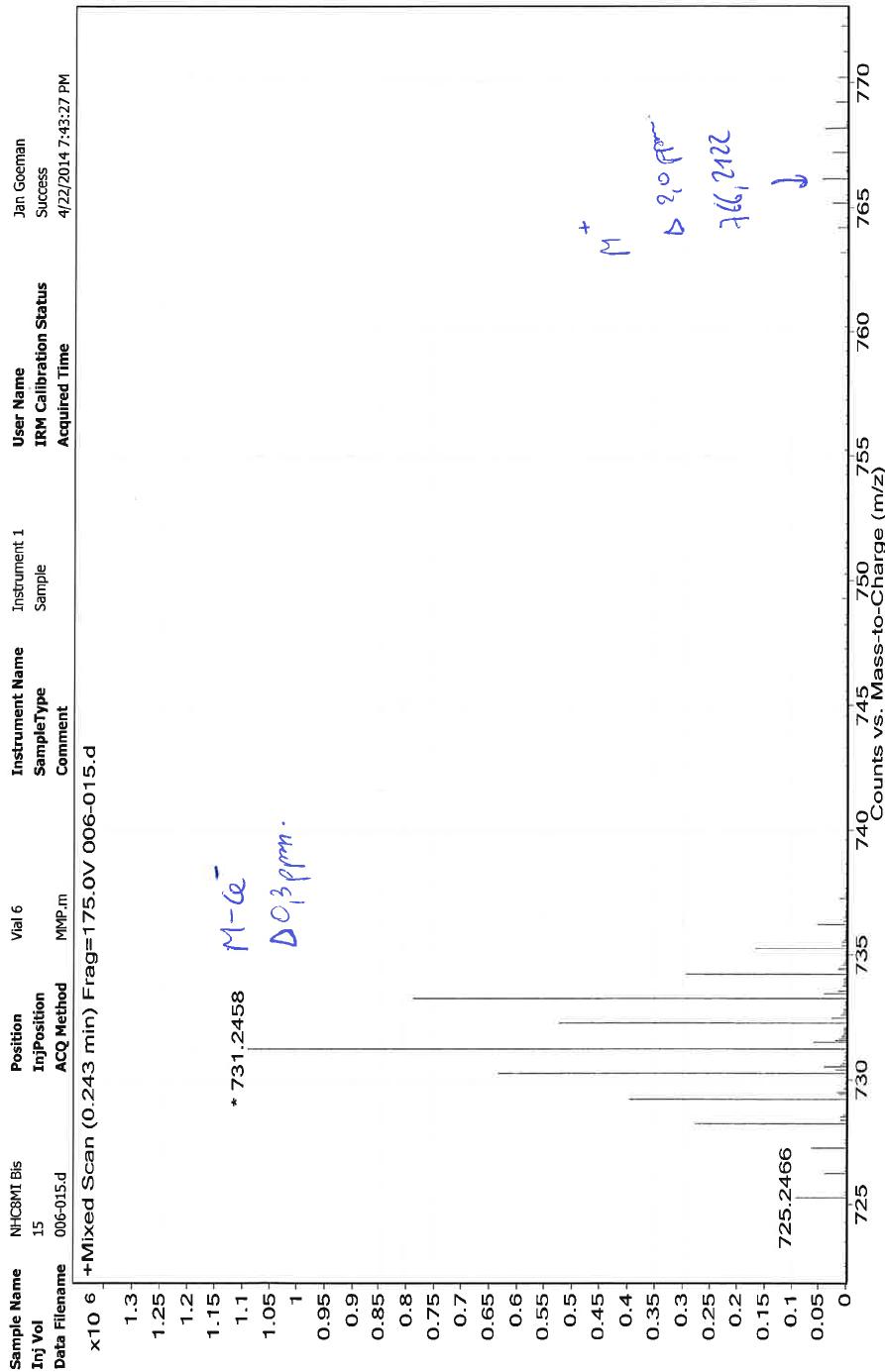
*Applied procedure for the RCM of diethyl diallyl malonate [5–7].* For example, 0.5 mol% catalyst loading: 2.7 μmol of the complex in NMR tube was dissolved in 0.3 mL of toluene-*d*8 and left for 2 minutes before adding 0.13 mL (0.54 mmol) of diethyl diallyl malonate. The NMR tube was then closed, and the temperature was raised to 80 °C. The conversion was monitored by integrating the allylic methylene peaks in the <sup>1</sup>H NMR spectrum of the diethyl diallyl malonate and the product.

*Applied procedure for isomerization of allylic alcohols.* An NMR-tube was charged with 2.5 μmol (5 mol%) of catalyst and dissolved in 0.5 mL CDCl<sub>3</sub>. 0.05 mmol of the substrate and 2.5 μmol (5 mol%) of KO*t*Bu were then added. The NMR tube was closed, and the temperature was kept at r.t. or at 80 °C. The conversion was determined by integrating the <sup>1</sup>H-NMR signals of the consumed alcohol (5.68 ppm) and the formed carbonyl compound (1.86 ppm).

## ESI-MS spectra of compound 7a

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Inj Volume : 5  $\mu$ l  
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Flow injectie analyse  
sequentie per vial  
ES positive mode  
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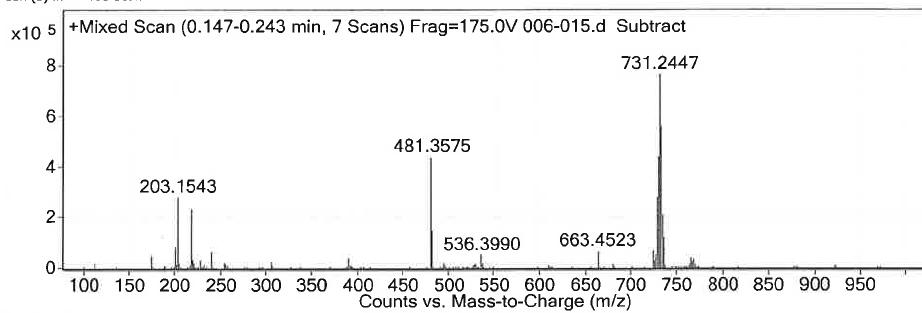


## Qualitative Analysis Report

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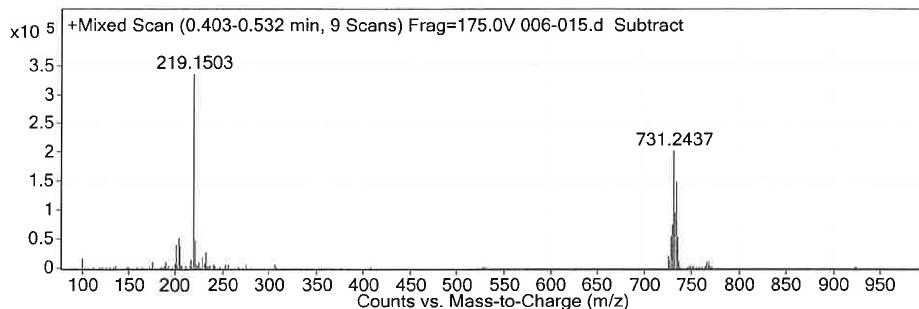


### Peak List

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219.1499	230072.5
240.1746	65319.2
481.3575	437149.7
482.3607	145949.4
536.399	48802.1
663.4523	63710.9
725.2461	66982.4
727.2447	49550
728.245	198620.3
729.2448	280342.2
730.2451	438978.3
731.2447	765359.4
731.4773	42843.3
732.2457	368402.8
733.2443	557327.3
734.2465	205075.8
735.2438	119817
736.245	39263.7

Spectrum Source  
Peak (2) in "+ TIC Scan"

### Qualitative Analysis Report

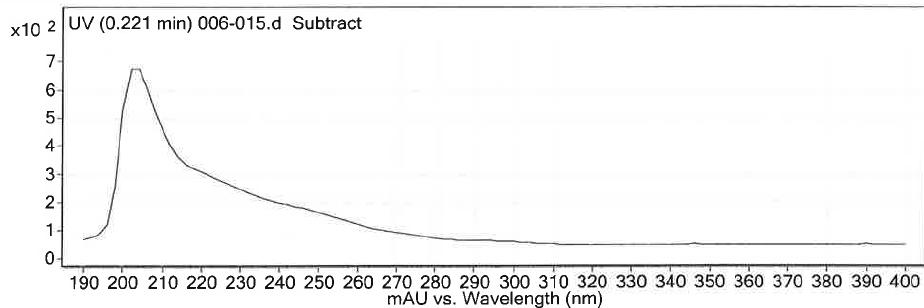


Peak List

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205.1334	37771.2
219.1503	335461.7
220.1529	47464.7
220.1777	17671.7
221.1644	44639.4
228.1746	17653.2
233.1284	25519
725.2458	19289.6
728.2444	53835.9
729.2439	74829
730.2442	116808.1
731.2437	202561.5
732.2449	96997.6
733.2434	148758.2
734.2457	54814.3
735.2432	32898.5

Spectrum Source

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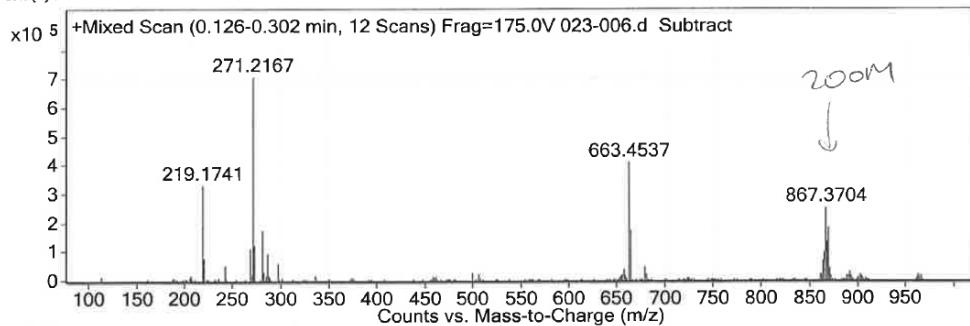
ESI-MS spectra of compound 7b

Qualitative Analysis Report

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User Spectra

Spectrum Source  
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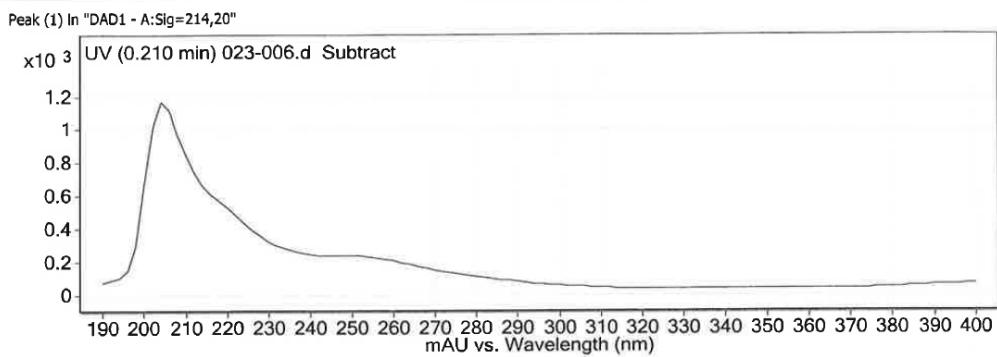
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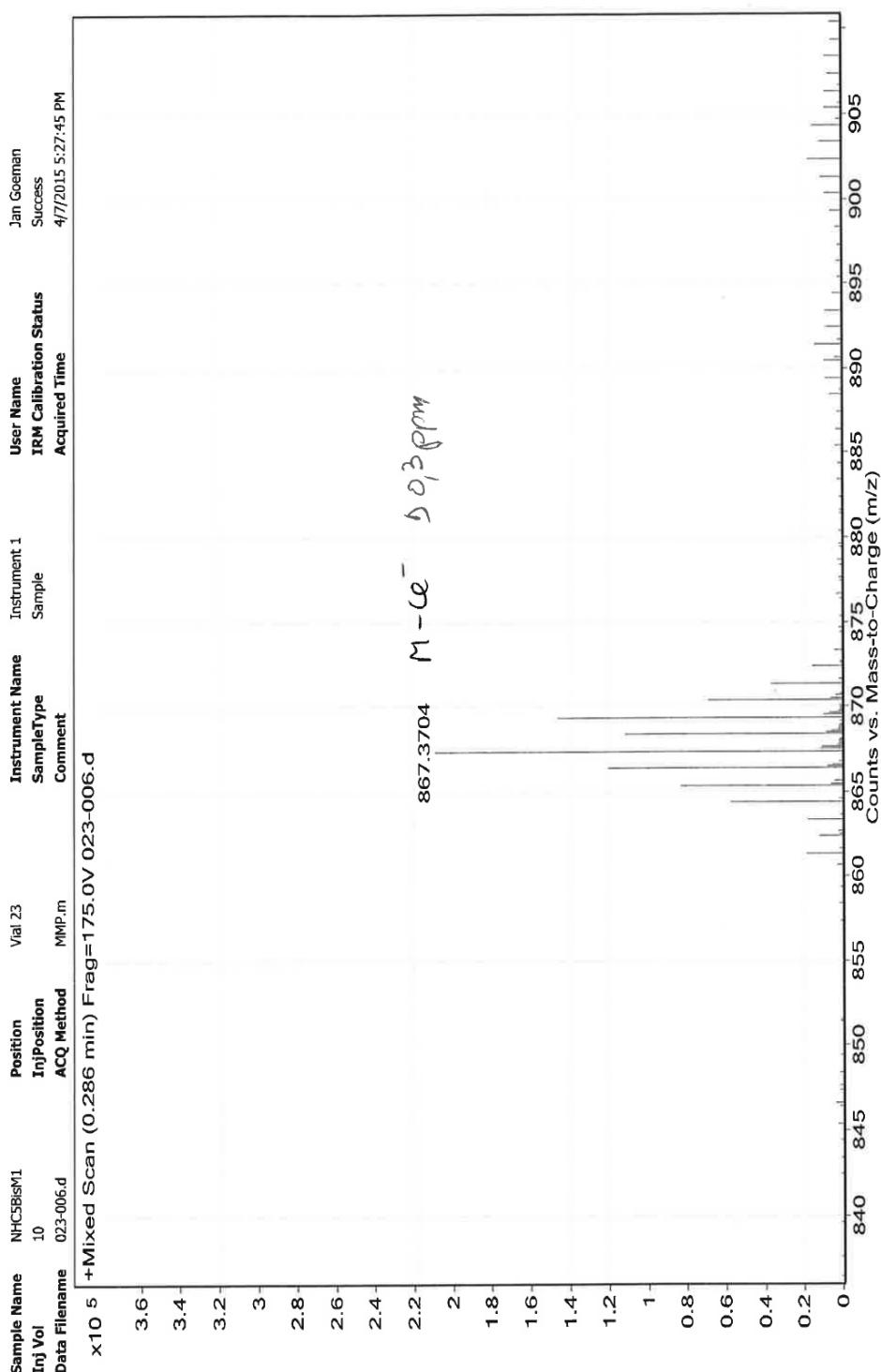
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269.2008	111933.8
271.2167	706316.6
271.365	37206.3
272.2196	123737.9
281.2389	171228.1
287.2114	94971.8
297.2338	58016.5
657.3289	36547.8
663.4537	407919.8
664.4568	175307.3
665.4602	37443
680.4795	46726
864.3705	66283.3
865.37	98490.1
866.371	143246.4
867.3704	250545.9
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870.373	80065.8
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Spectrum Source

### Qualitative Analysis Report

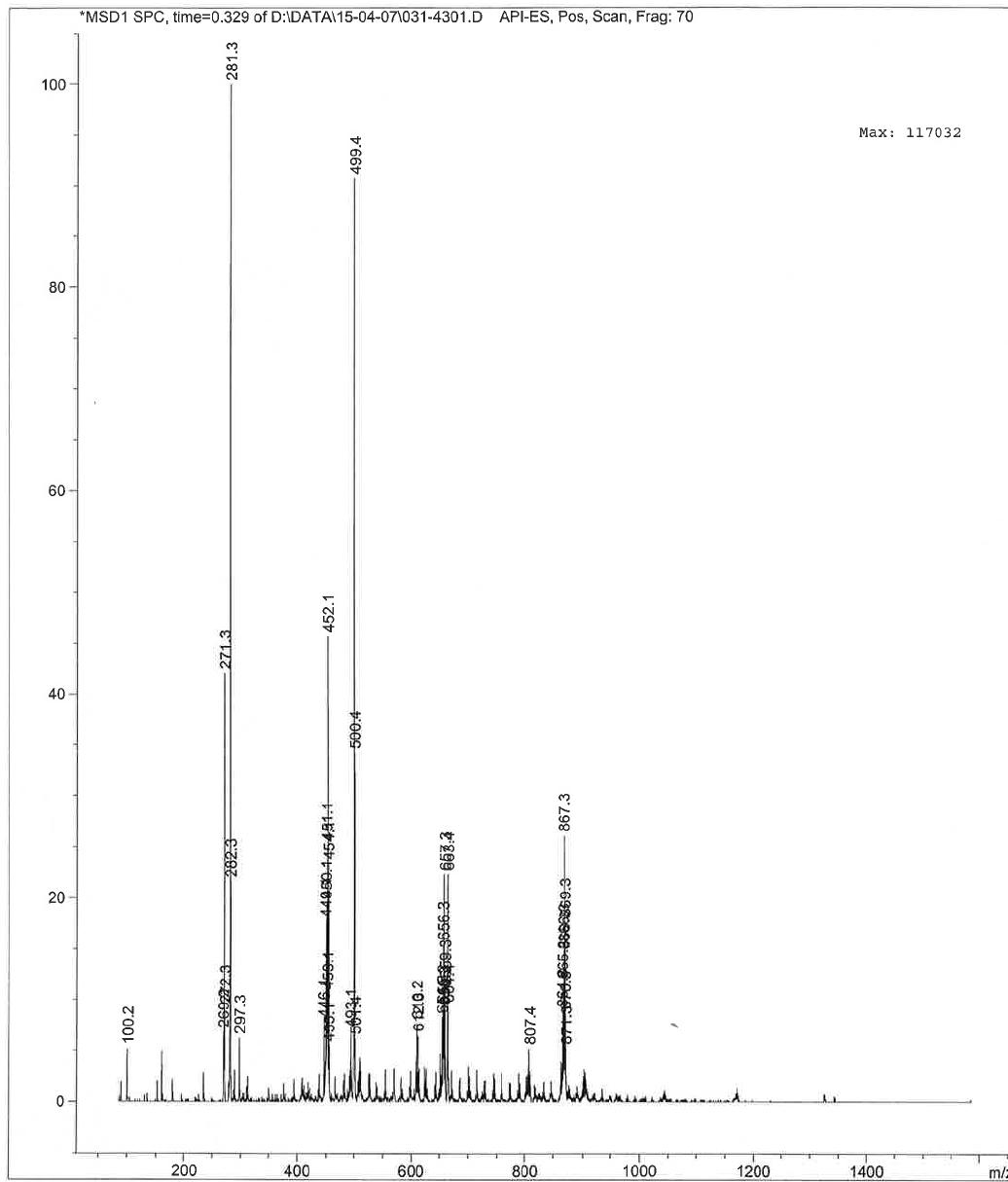
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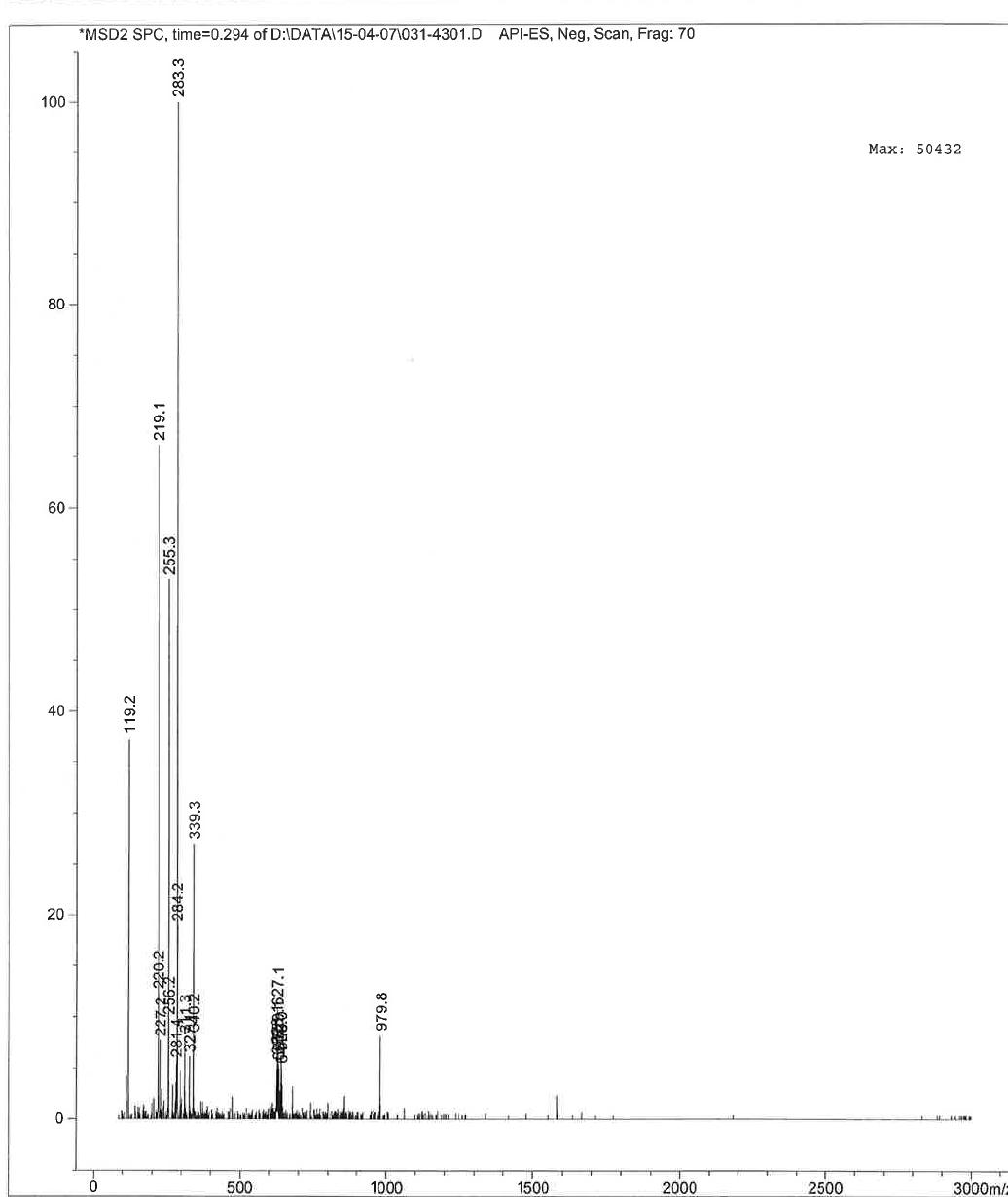
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Method Info     : Flow Injectie Analyse
                  ESI source, positive and negative mode
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#### REFERENCES

1. Ledoux N., Allaert B., Pattyn S., Mierde H. V., Vercaemst C., Verpoort F. *N,N'-dialkyl- and N-alkyl-N-mesityl-substituted N-heterocyclic carbenes as ligands in grubbs catalysts.* *Chemistry – A European Journal.* 2006;12(17):4654-4661. <https://doi.org/10.1002/chem.200600064>.
2. Ledoux N., Allaert B., Linden A., Van Der Voort P., Verpoort F. Bis-coordination of *N*-(alkyl)-*N'*-(2,6-diisopropylphenyl) heterocyclic carbenes to Grubbs catalysts. *Organometallics.* 2007;26(4):1052-1056. <https://doi.org/10.1021/om060937u>.
3. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. J. *OLEX2: a complete structure solution, refinement and analysis program.* *Journal of Applied Crystallography.* 2009;42:339-341. <https://doi.org/10.1107/S0021889808042726>.
4. Sheldrick G. M. *SHELX Version 2014/6. Acta Crystallographica.* 2008;A64:112-122. <https://doi.org/10.1107/S0108767307043930>.
5. Ritter T., Hejl A., Wenzel A. G., Funk T. W., Grubbs R. H. A standard system of characterization for olefin metathesis catalysts. *Organometallics.* 2006;25(24):5740-5745. <https://doi.org/10.1021/om060520o>.
6. Monsaert S., Drozdak R., Dragutan V., Dragutan I., Verpoort F. Indenyliidene-ruthenium complexes bearing saturated N-heterocyclic carbenes: synthesis and catalytic investigation in olefin metathesis reactions. *European Journal of Inorganic Chemistry.* 2008;(3):432-440. <https://doi.org/10.1002/ejic.200700879>.
7. Sauvage X., Zaragoza G., Demonceau A., Delaude L. Mixed isobutylphobane/N-heterocyclic carbene ruthenium-indenyliidene complexes: synthesis and catalytic evaluation in olefin metathesis reactions. *Advanced Synthesis and Catalysis.* 2010;352(11-12):1934-1948. <https://doi.org/10.1002/adsc.201000207>.