

Supporting Information
**Highly Efficient Ru(II)-Alkylidene Based Hoveyda-Grubbs Catalysts for Ring-
Closing Metathesis Reactions**

Mariam Y. Al-Enezi, Elizabeth John, Yehia A. Ibrahim and Nouria A. Al-Awadi*

**Chemistry Department, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait.*

Email: na.nabaq.kw@gmail.com

Table of Contents

NMR Spectra.....	2-22
Mass spectra.....	22-30
Deconvoluted HRMS (ESI)	30-39
Single Crystal X-ray Diffraction Studies of the Ru complexes 7a , 7b & 7c	40-42

NMR spectra

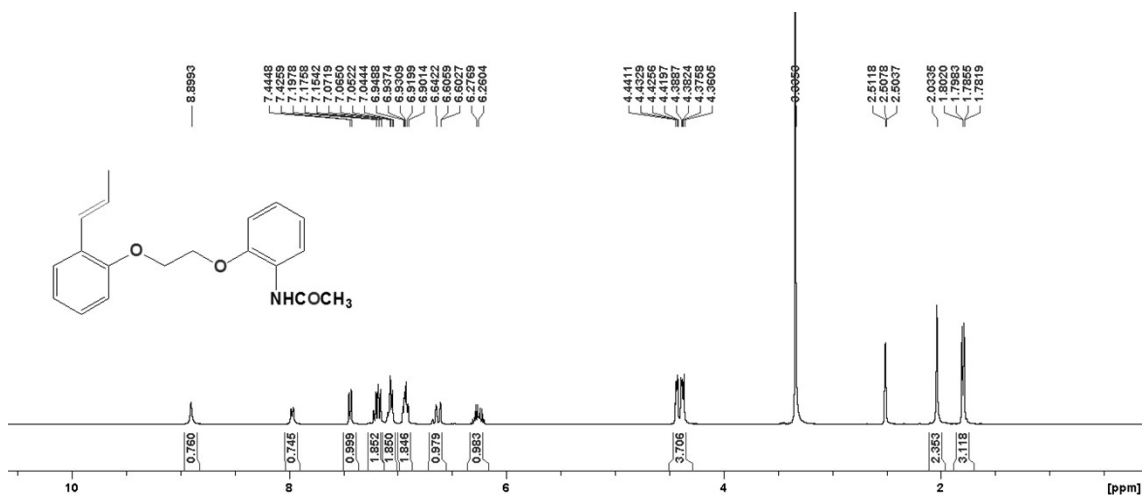


Figure S1. ¹H-NMR spectrum of 6a in DMSO-d₆ at 25 °C.

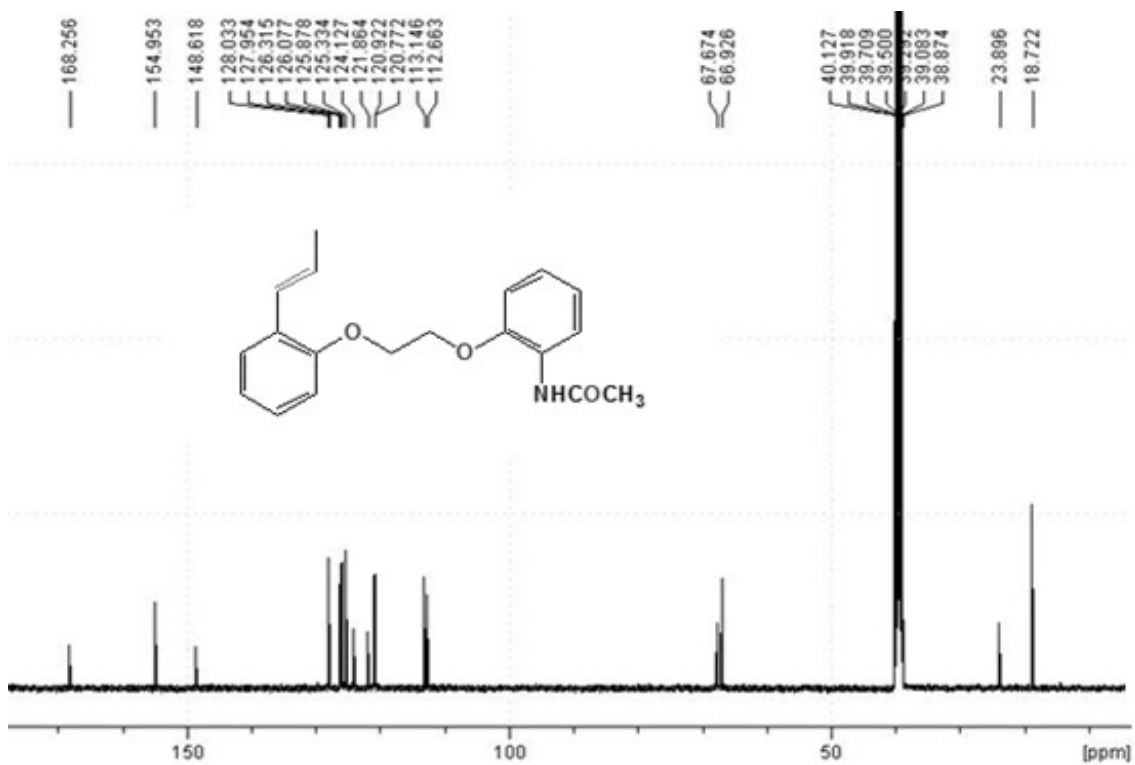
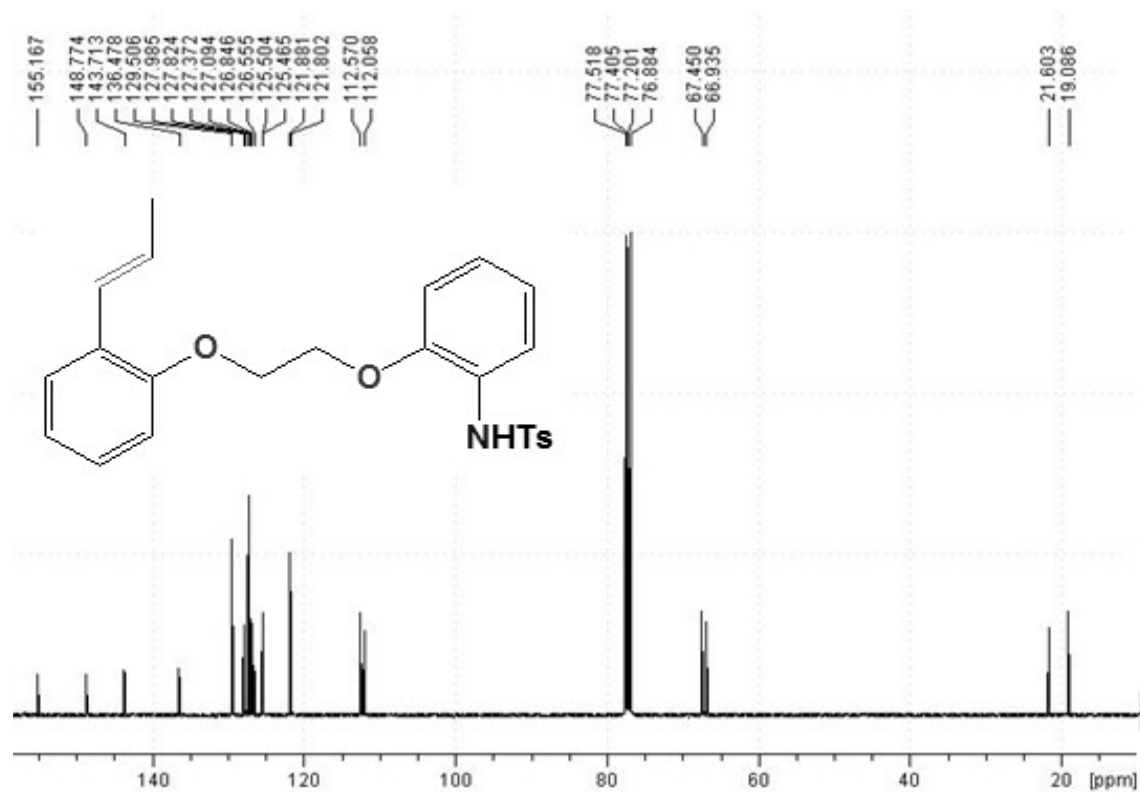
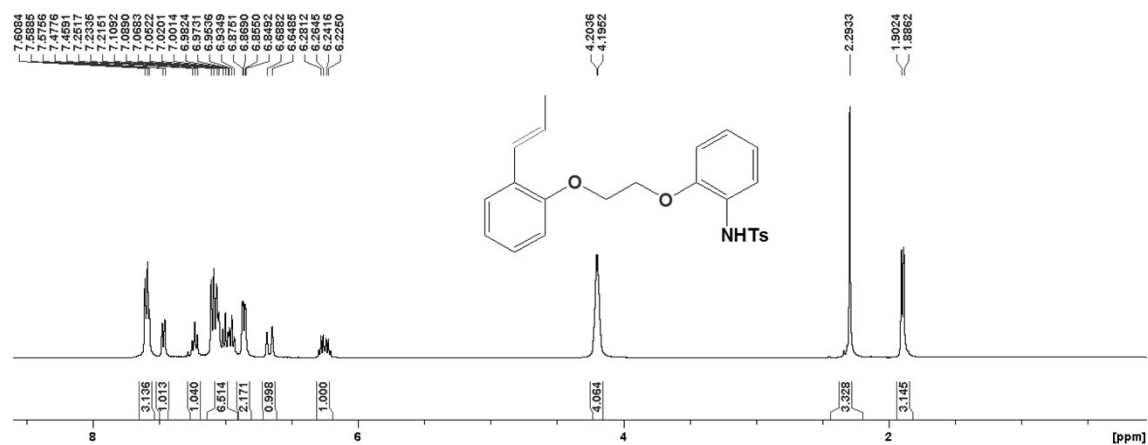


Figure S2. ¹³C-NMR spectrum of 6a in DMSO-d₆ at 25 °C.



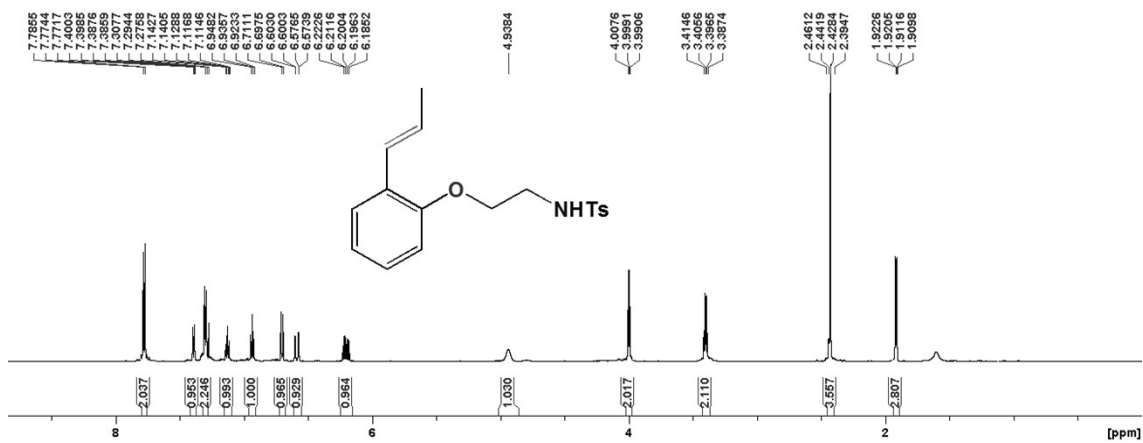


Figure S5. ¹H-NMR spectrum of **6c** in CDCl₃ at 25 °C.

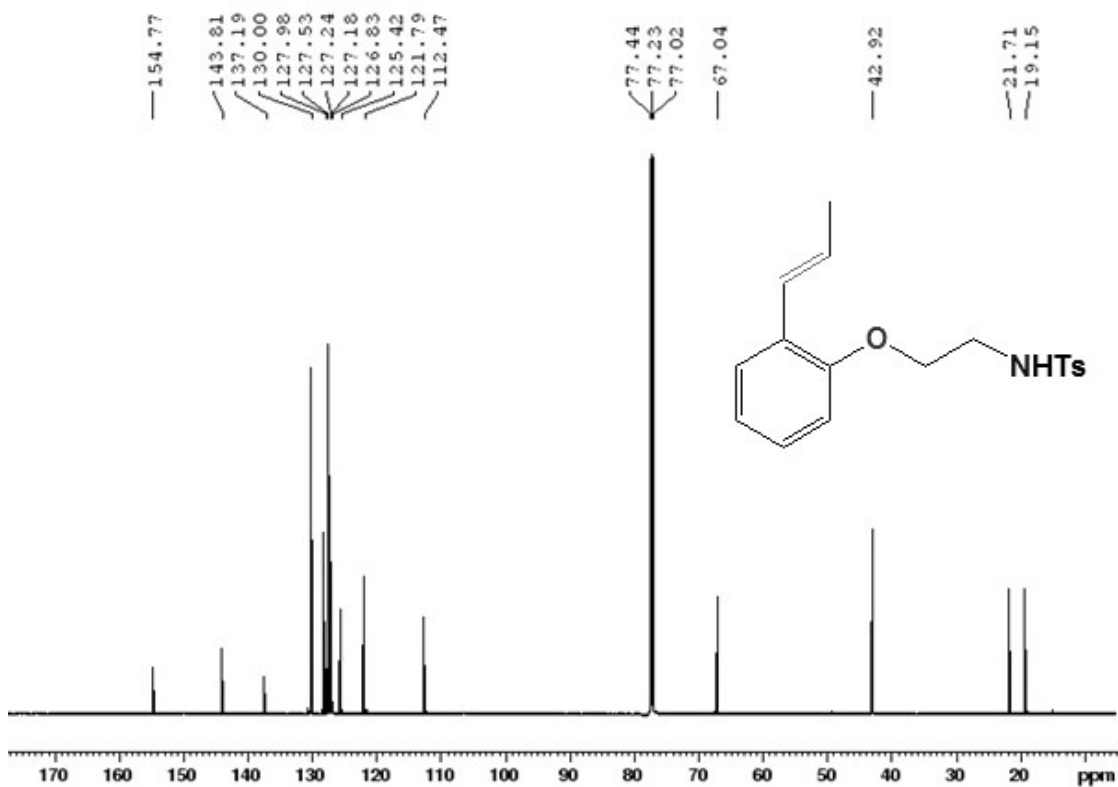


Figure S6. ¹³C-NMR spectrum of **6c** in CDCl₃ at 25 °C.

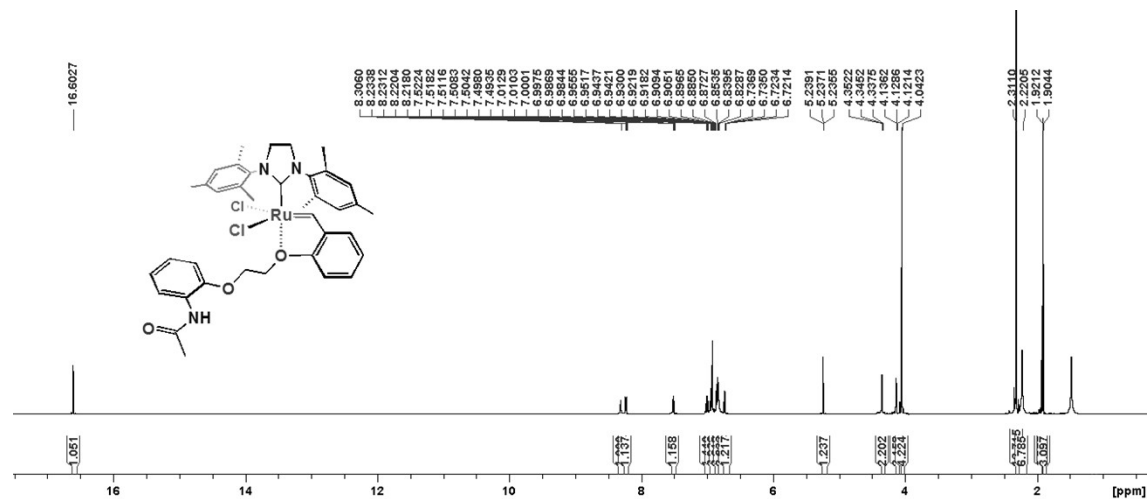


Figure S7. ¹H-NMR spectrum of **7a** in CD₂Cl₂ at 25 °C.

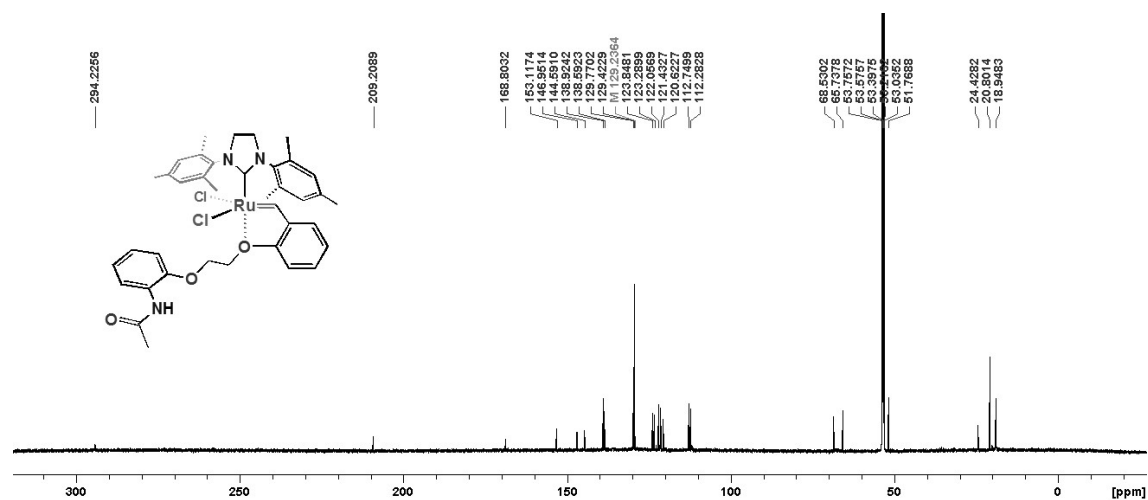


Figure S8. ¹³C-NMR spectrum of **7a** in CD₂Cl₂ at 25 °C.

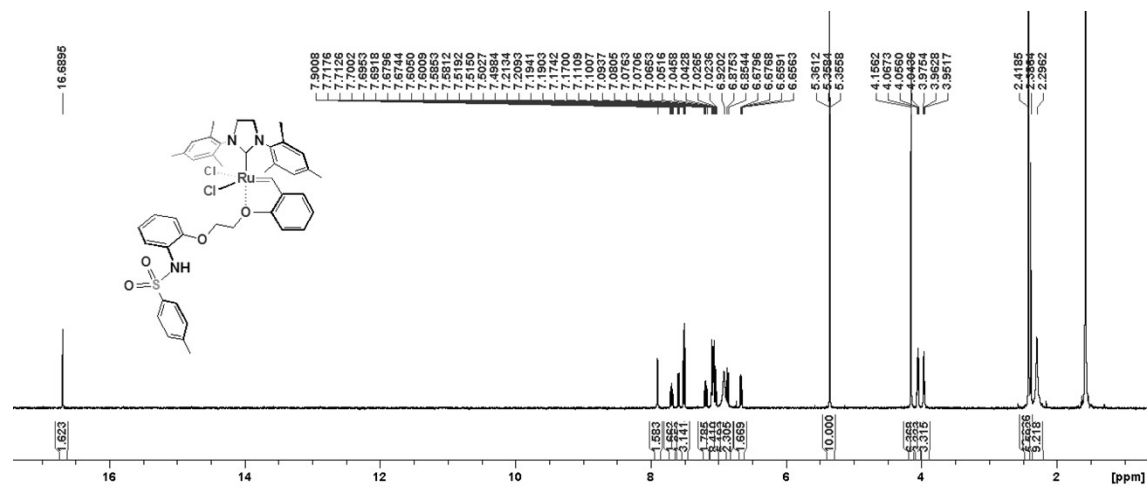


Figure S9. $^1\text{H-NMR}$ spectrum of **7b** in CD_2Cl_2 at $25\text{ }^\circ\text{C}$.

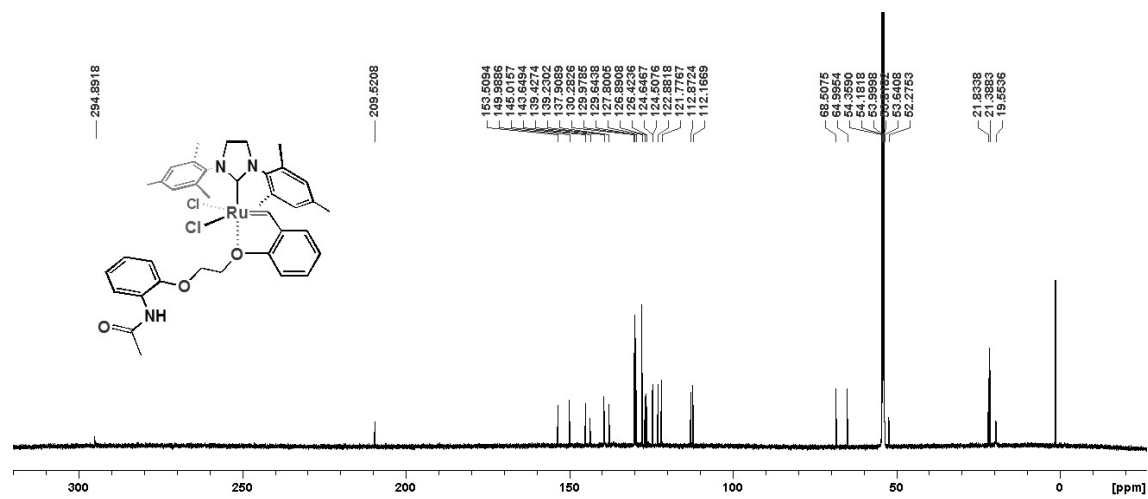


Figure S10. $^{13}\text{C-NMR}$ spectrum of **7b** in CD_2Cl_2 at $25\text{ }^\circ\text{C}$.

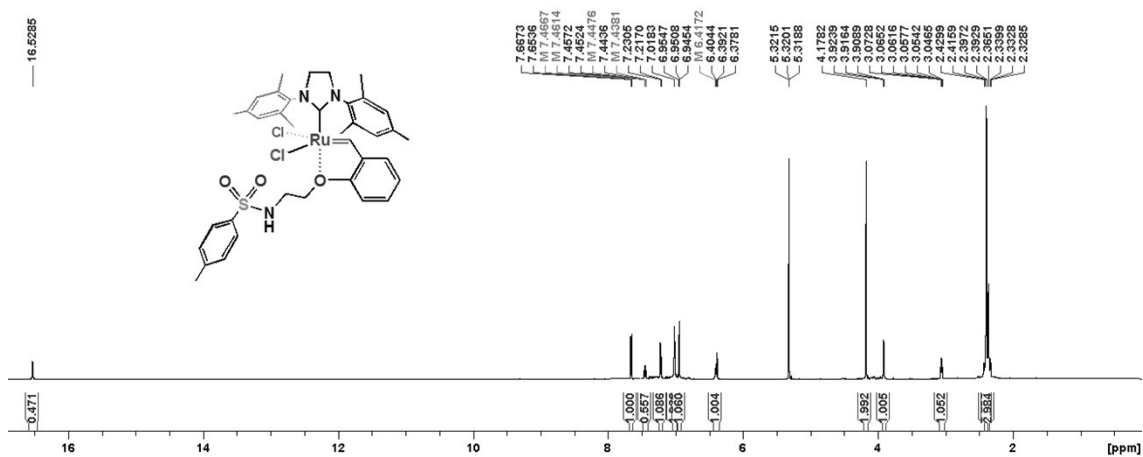


Figure S11. ¹H-NMR spectrum of **7c** in CD₂Cl₂ at 25 °C.

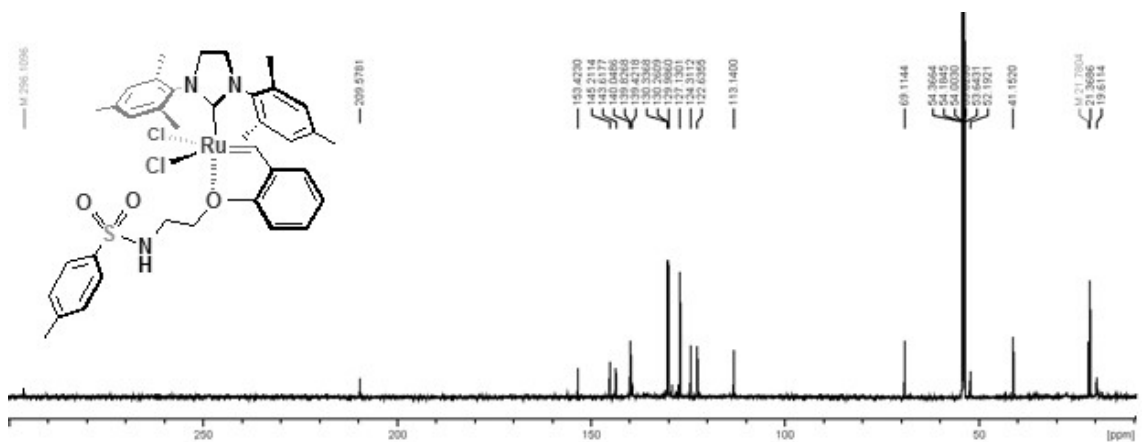


Figure S12. ¹³C-NMR spectrum of **7c** in CD₂Cl₂ at 25 °C.

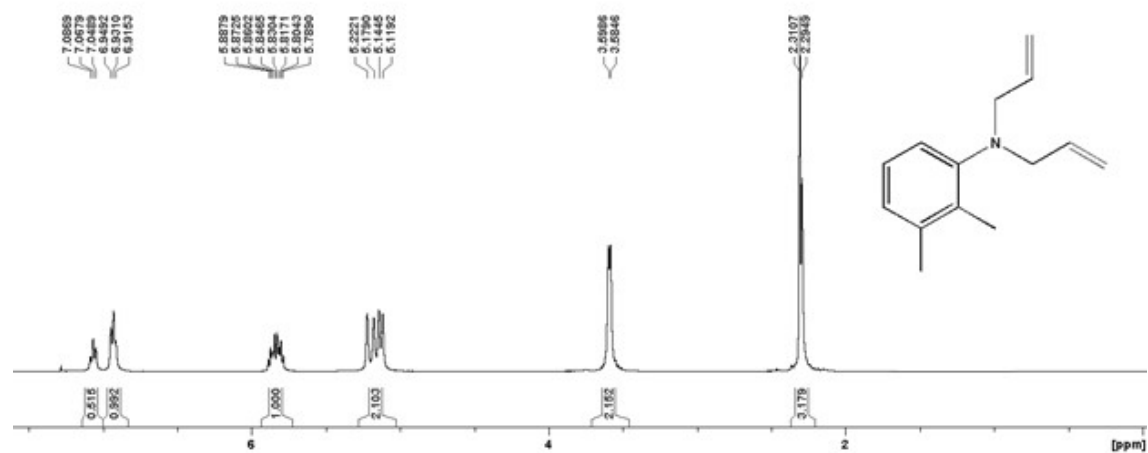


Figure S13. $^1\text{H-NMR}$ spectrum of **8i** in CDCl_3 at $25\text{ }^\circ\text{C}$.

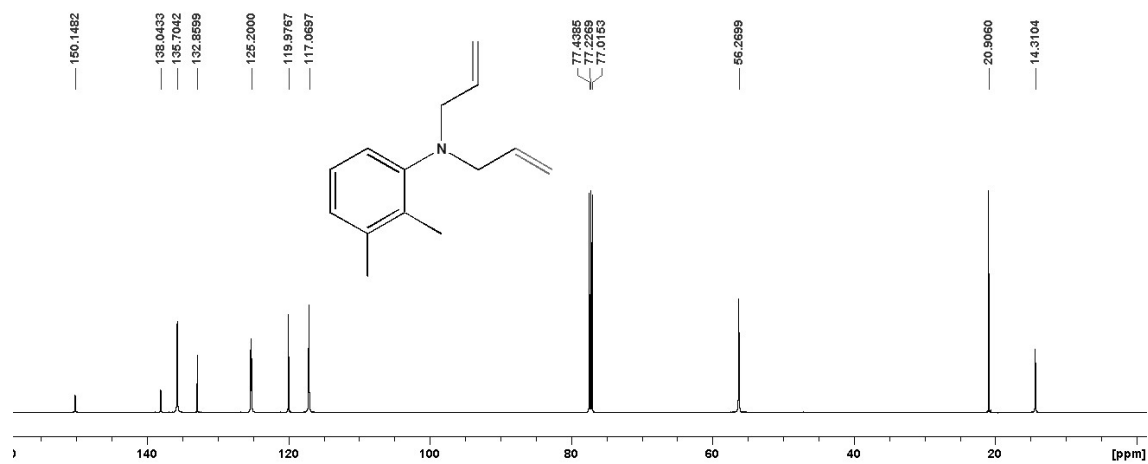


Figure S14. $^{13}\text{C-NMR}$ spectrum of **8i** in CDCl_3 at $25\text{ }^\circ\text{C}$.

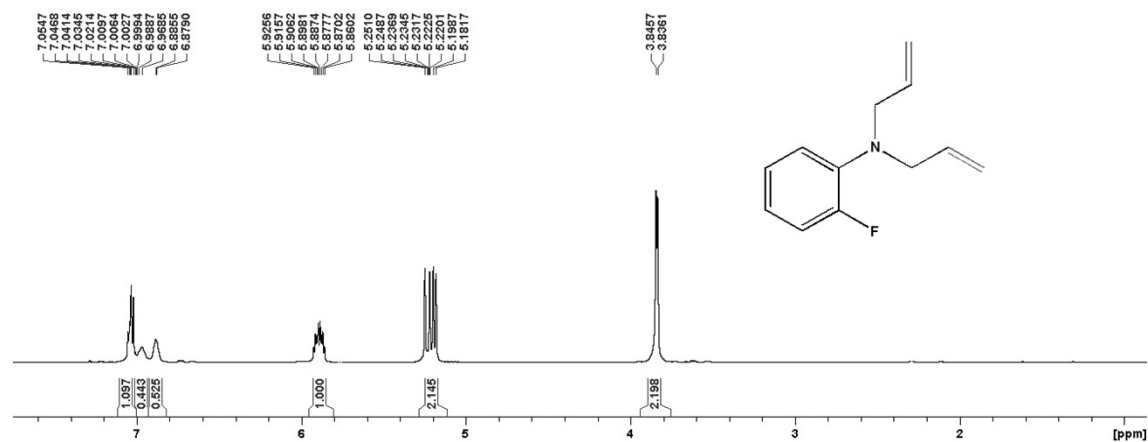


Figure S15. ¹H-NMR spectrum of **8k** in CDCl₃ at 25 °C.

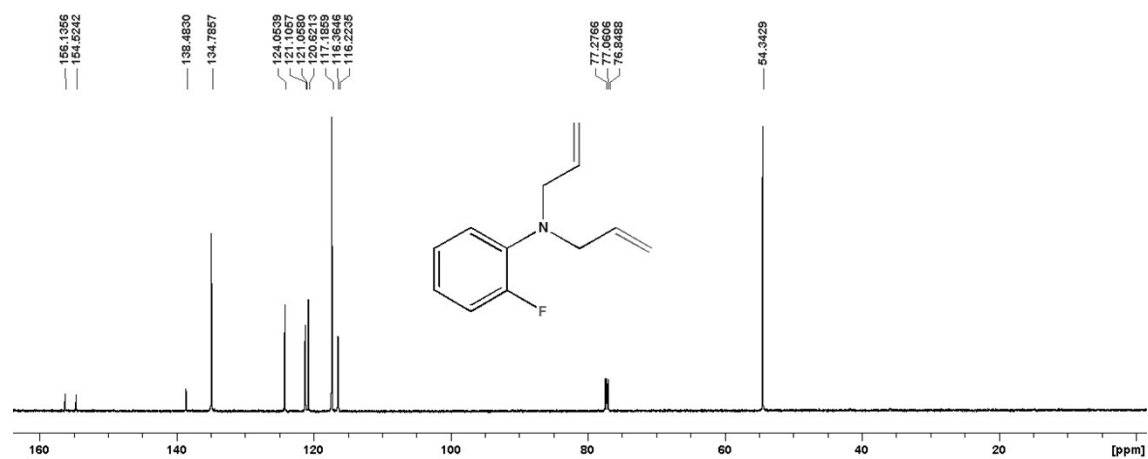


Figure S16. ¹³C-NMR spectrum of **8k** in CDCl₃ at 25 °C.

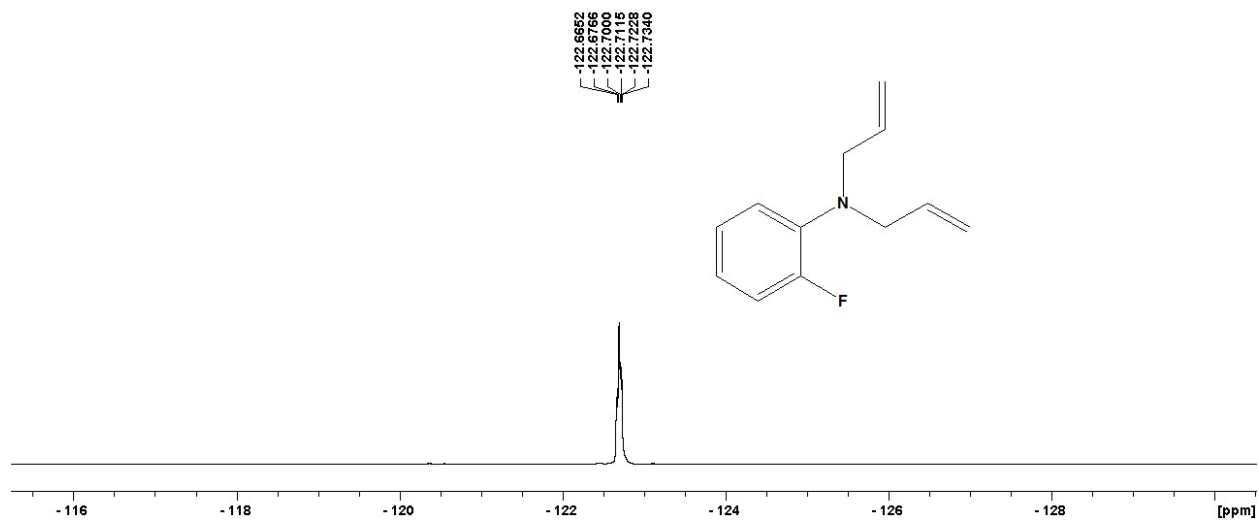


Figure S17. ¹⁹F NMR spectrum of **8k** in CDCl₃ at 25 °C.

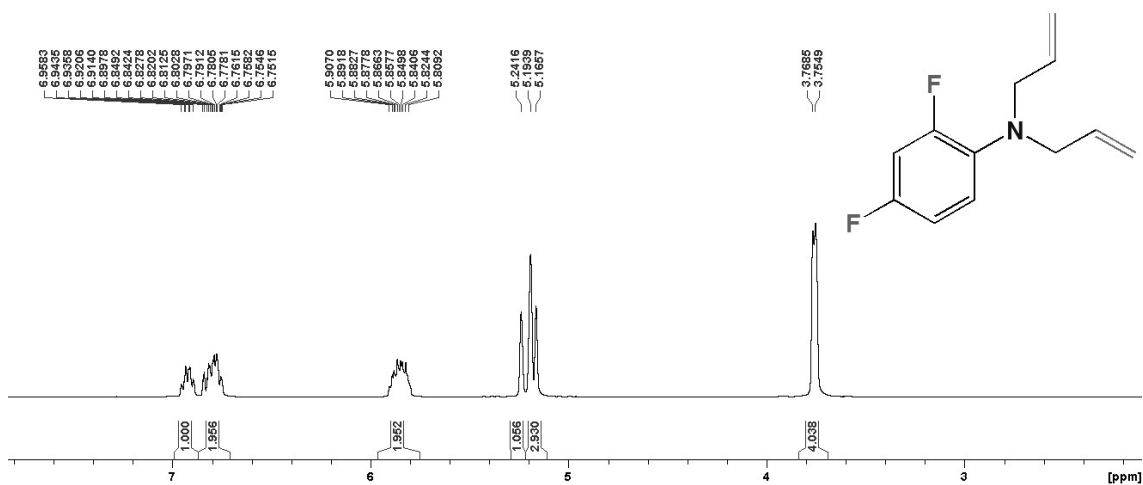


Figure S18. ¹H-NMR spectrum of **8o** in CDCl₃ at 25 °C.

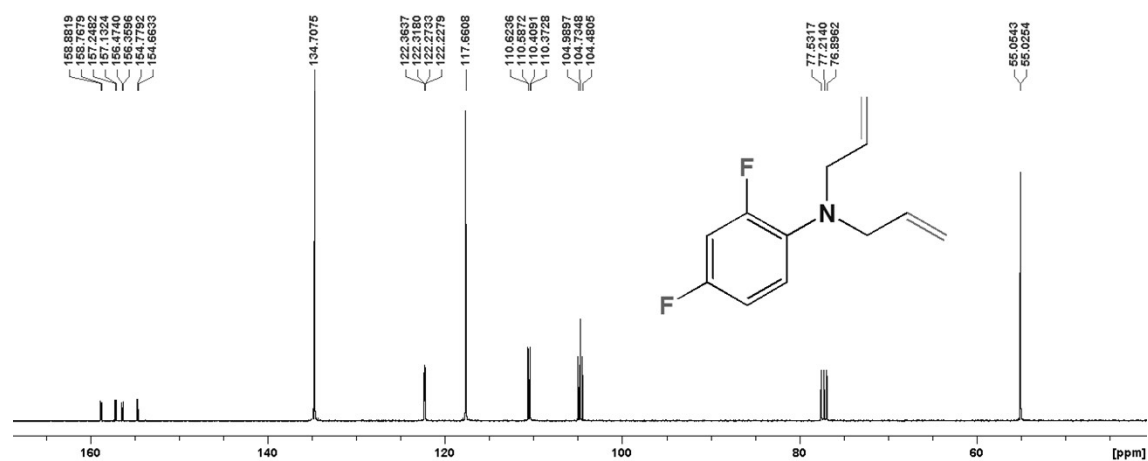


Figure S19. ^{13}C -NMR spectrum of **8o** in CDCl_3 at $25\text{ }^\circ\text{C}$.

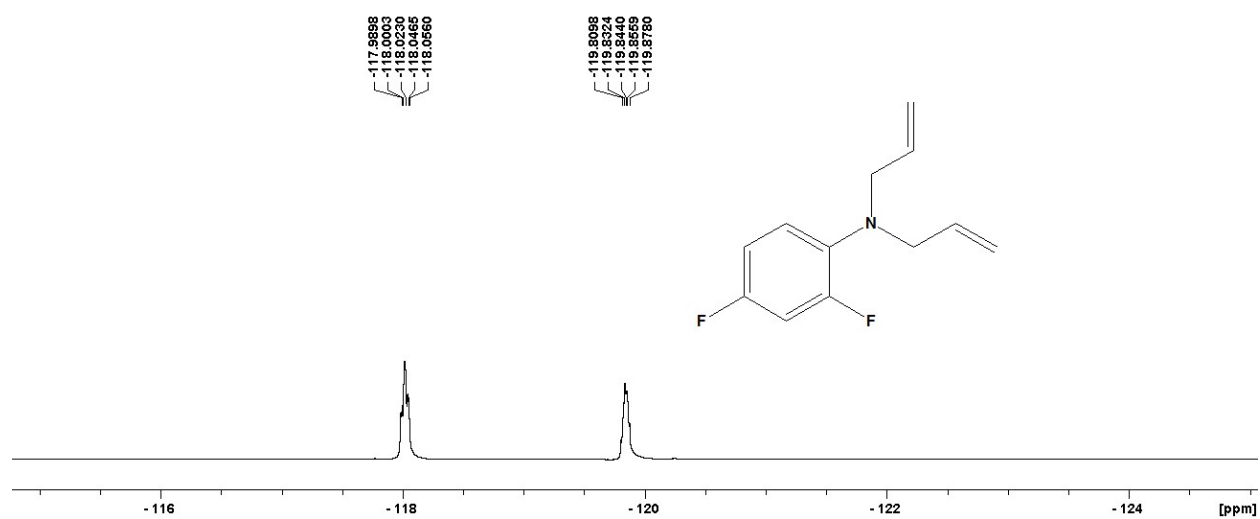


Figure S20. ^{19}F NMR spectrum of **8o** in CDCl_3 at $25\text{ }^\circ\text{C}$.

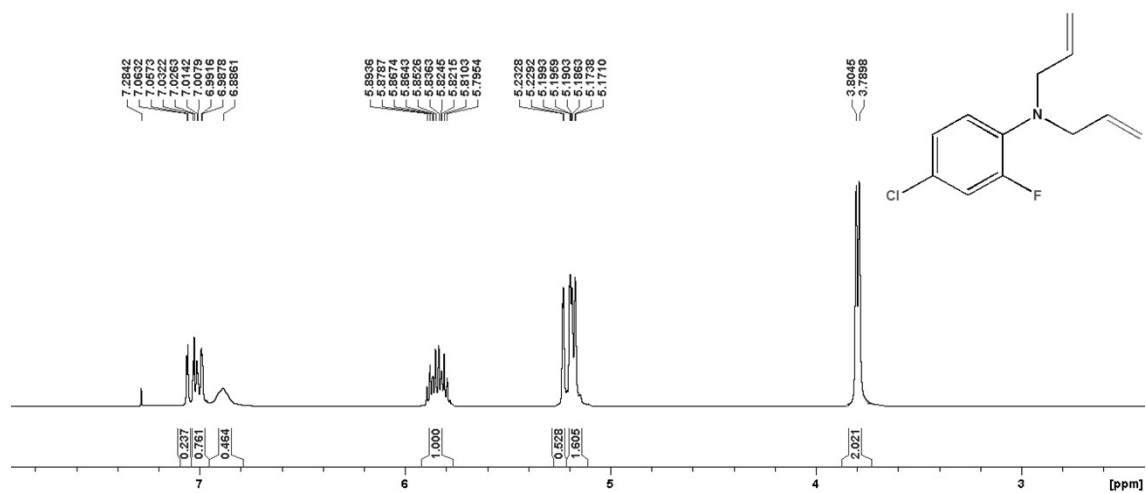


Figure S21. $^1\text{H-NMR}$ spectrum of **8q** in CDCl_3 at $25\text{ }^\circ\text{C}$.

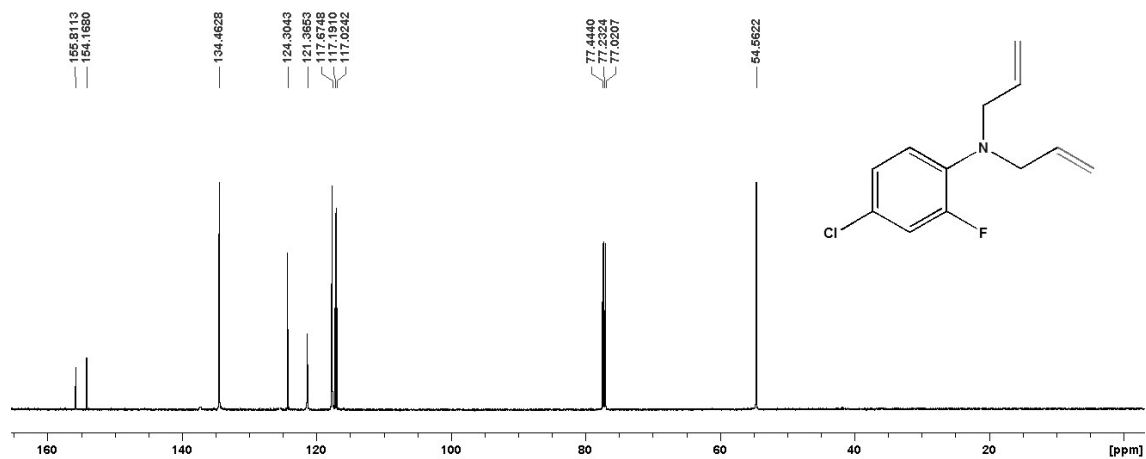


Figure S22. $^{13}\text{C-NMR}$ spectrum of **8q** in CDCl_3 at $25\text{ }^\circ\text{C}$.

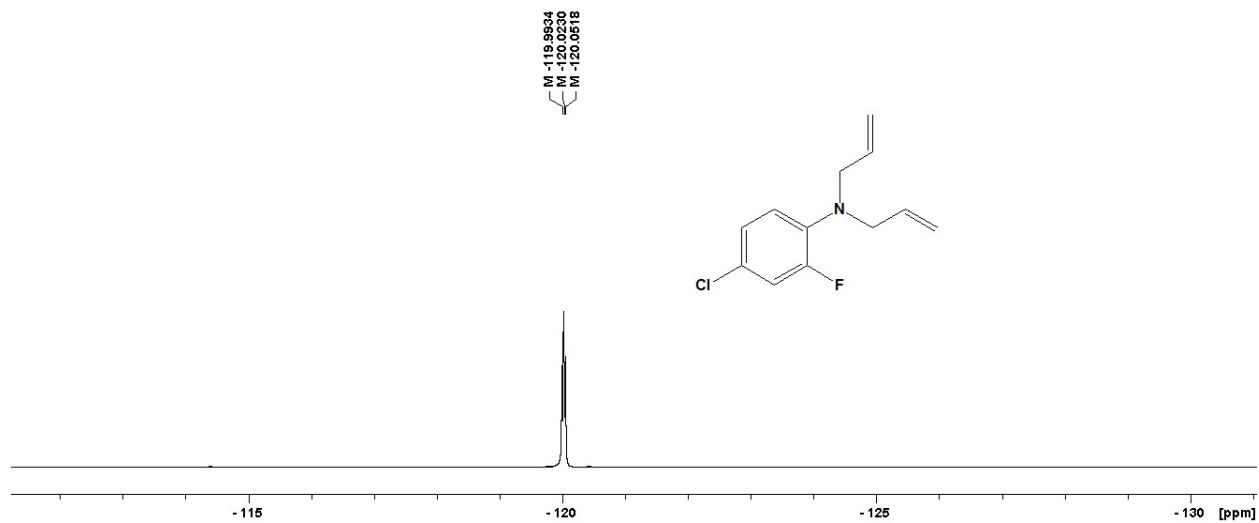


Figure S23. ¹⁹F NMR spectrum of **8q** in CDCl₃ at 25 °C.

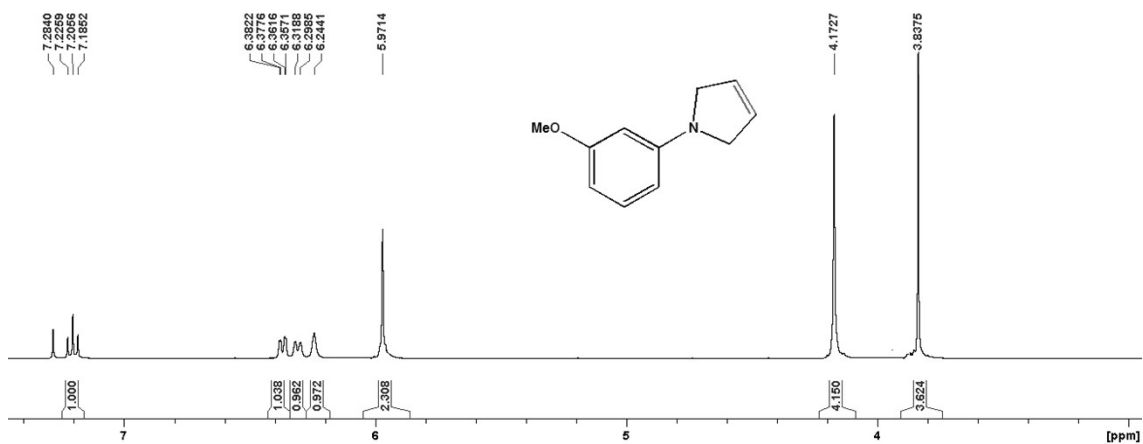


Figure S24. ¹H-NMR spectrum of **9f** in CDCl₃ at 25 °C.

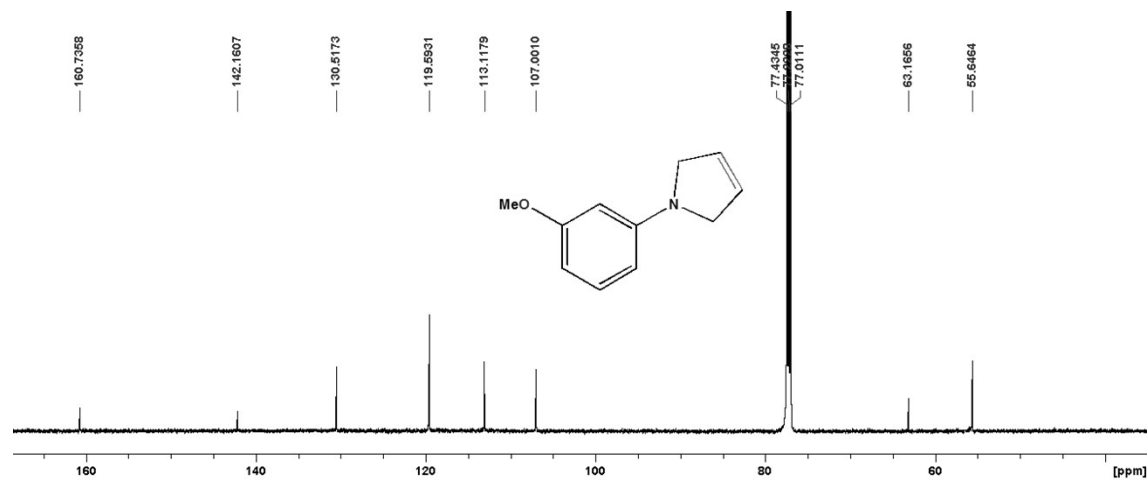


Figure S25. ¹³C-NMR spectrum of **9f** in CDCl₃ at 25 °C.

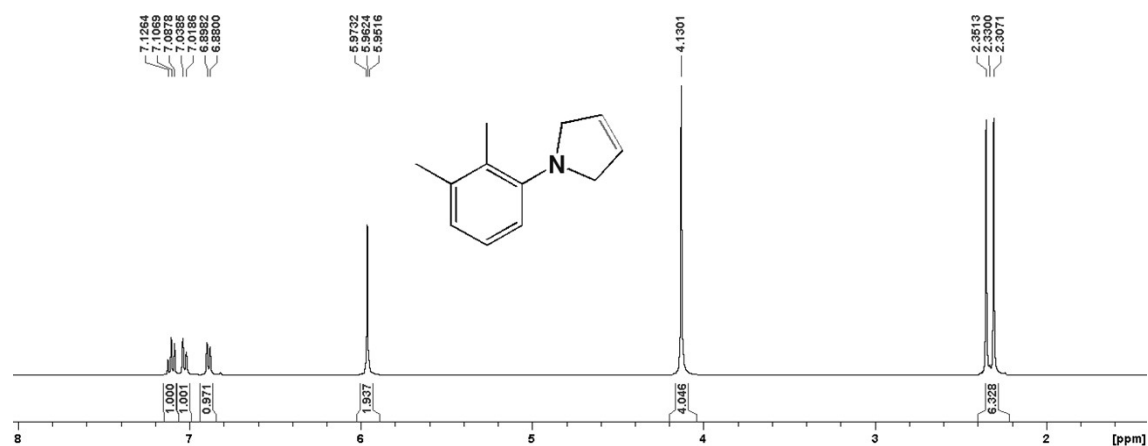


Figure S26. ¹H-NMR spectrum of **9i** in CDCl₃ at 25 °C.

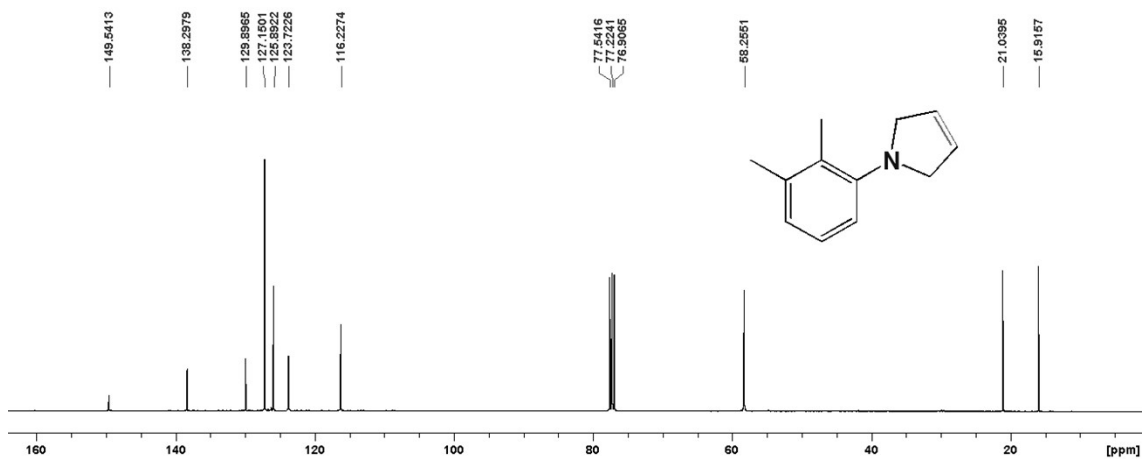


Figure S27. ^{13}C -NMR spectrum of **9i** in CDCl_3 at $25\text{ }^\circ\text{C}$.

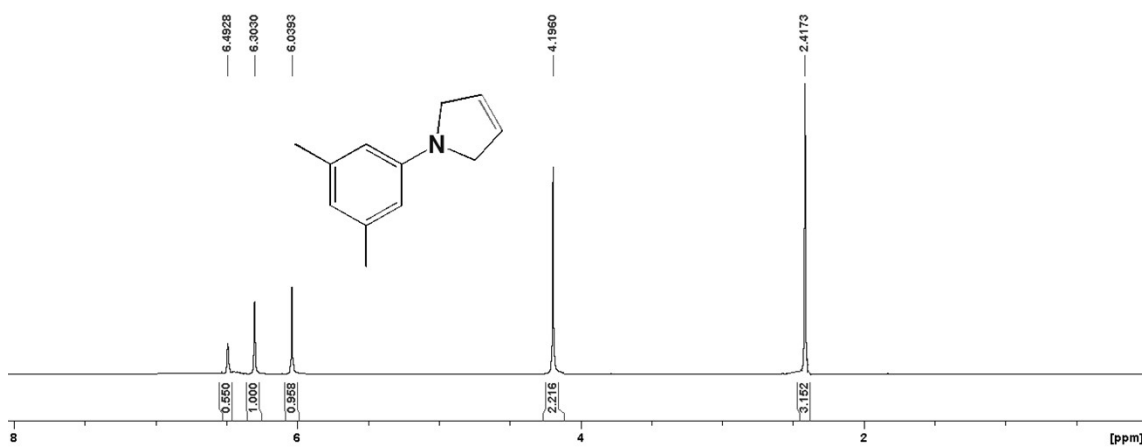


Figure S28. ^1H -NMR spectrum of **9j** in CDCl_3 at $25\text{ }^\circ\text{C}$.

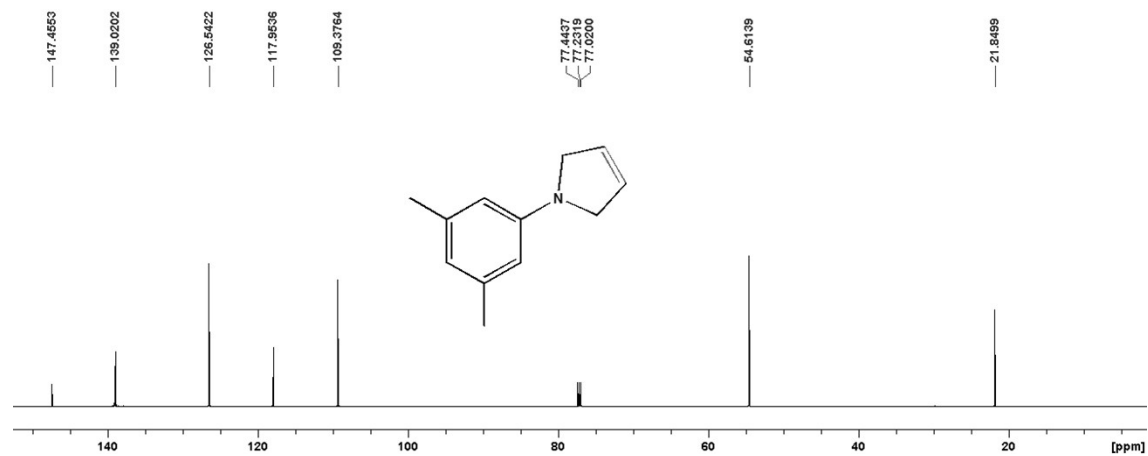


Figure S29. $^{13}\text{C-NMR}$ spectrum of 9j in CDCl_3 at $25\text{ }^\circ\text{C}$.

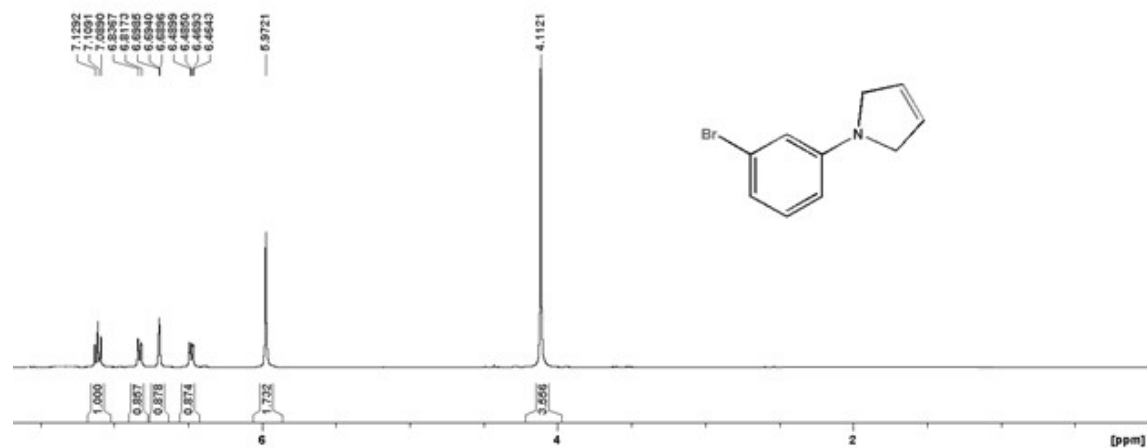


Figure S30. $^1\text{H-NMR}$ spectrum of 9l in CDCl_3 at $25\text{ }^\circ\text{C}$.

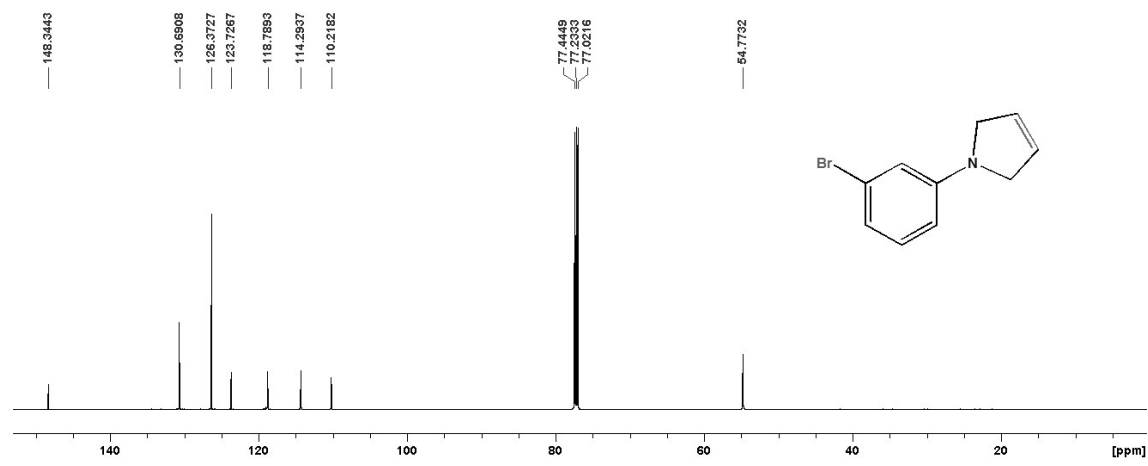


Figure S31. ^{13}C -NMR spectrum of **9l** in CDCl_3 at $25\text{ }^\circ\text{C}$.

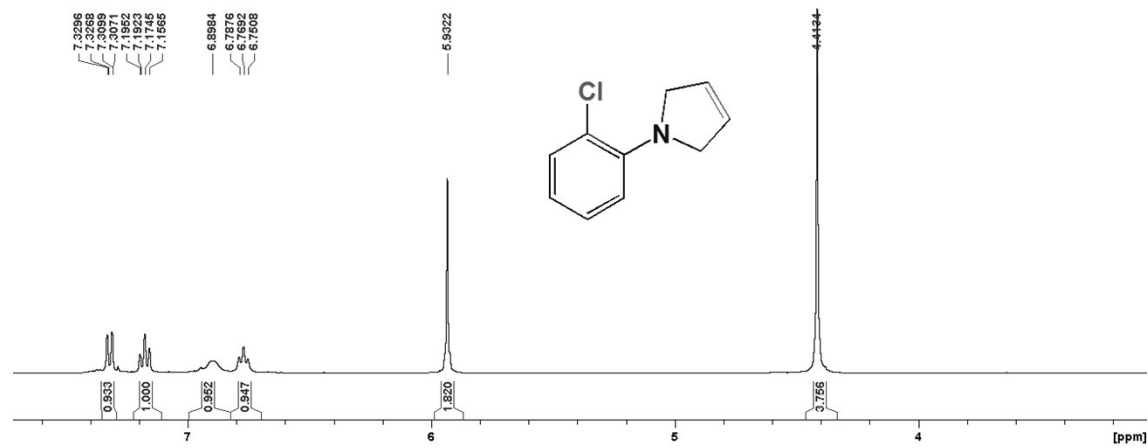


Figure S32. ^1H -NMR spectrum of **9m** in CDCl_3 at $25\text{ }^\circ\text{C}$.

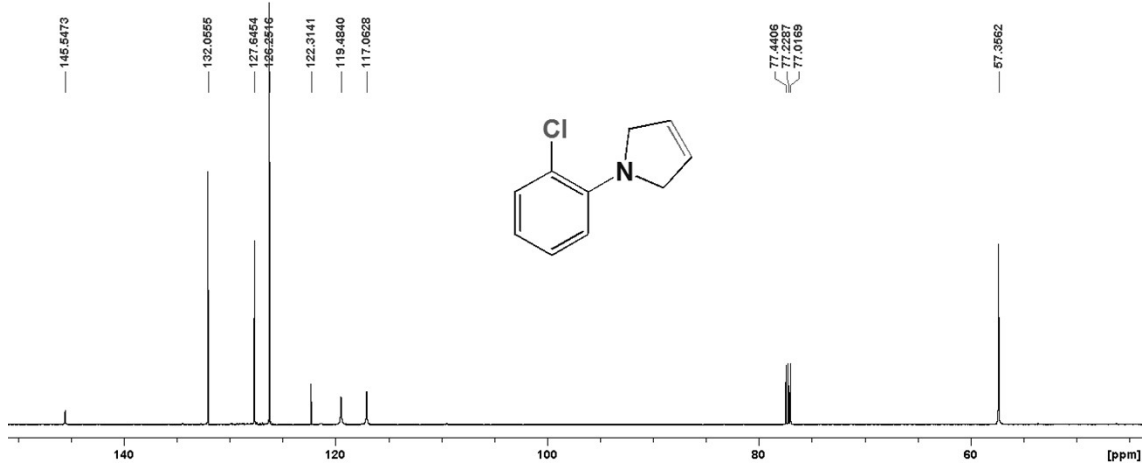


Figure S33. ^{13}C -NMR spectrum of **9m** in CDCl_3 at 25 $^\circ\text{C}$.

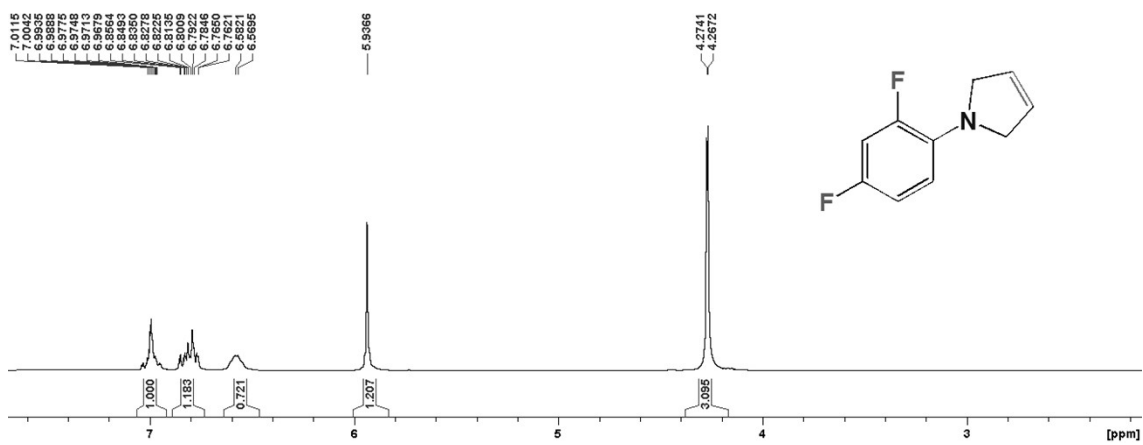


Figure S34. ^1H -NMR spectrum of **9o** in CDCl_3 at 25 $^\circ\text{C}$.

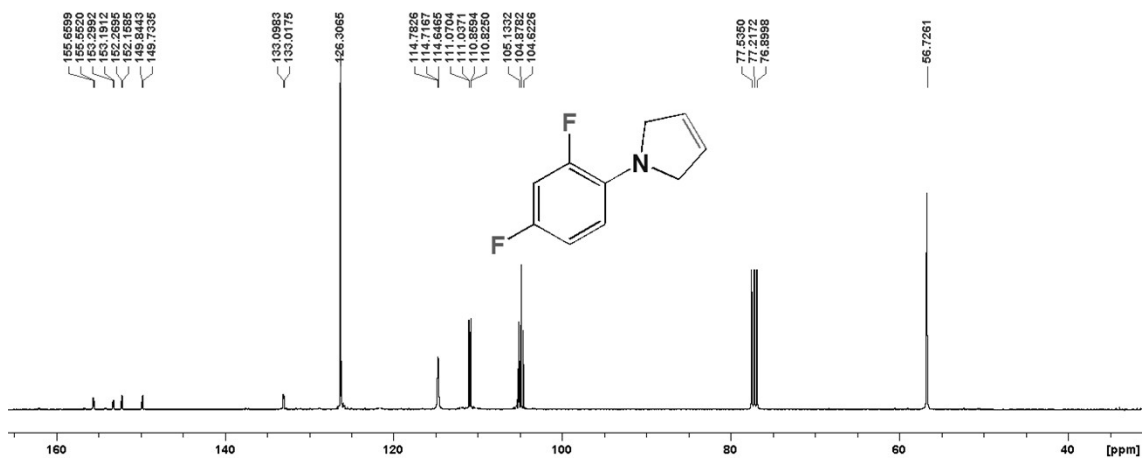


Figure S35. ¹³C-NMR spectrum of **9o** in CDCl₃ at 25 °C.

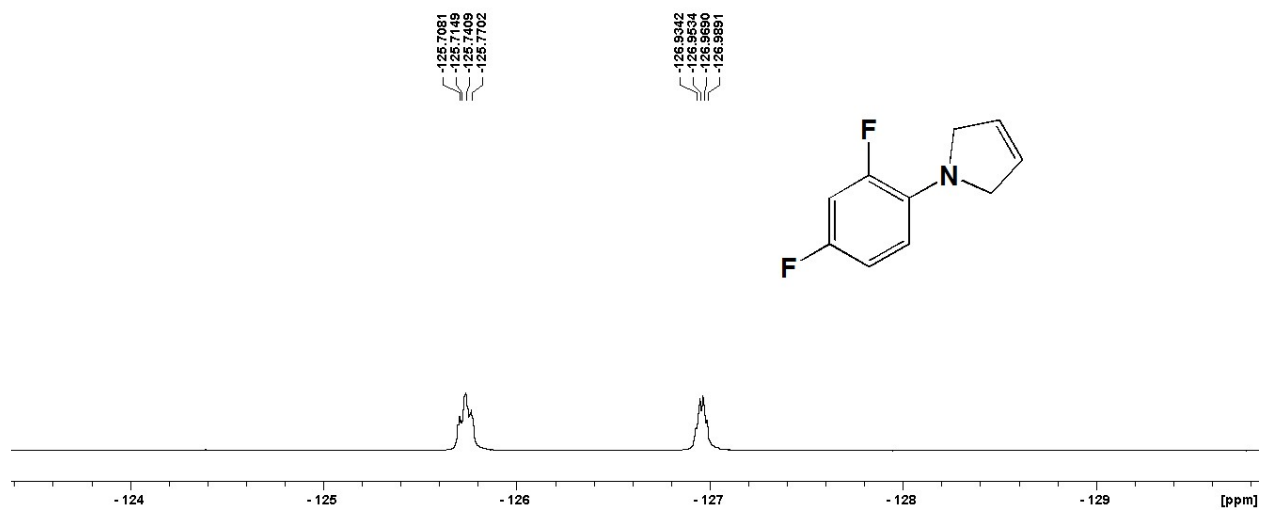
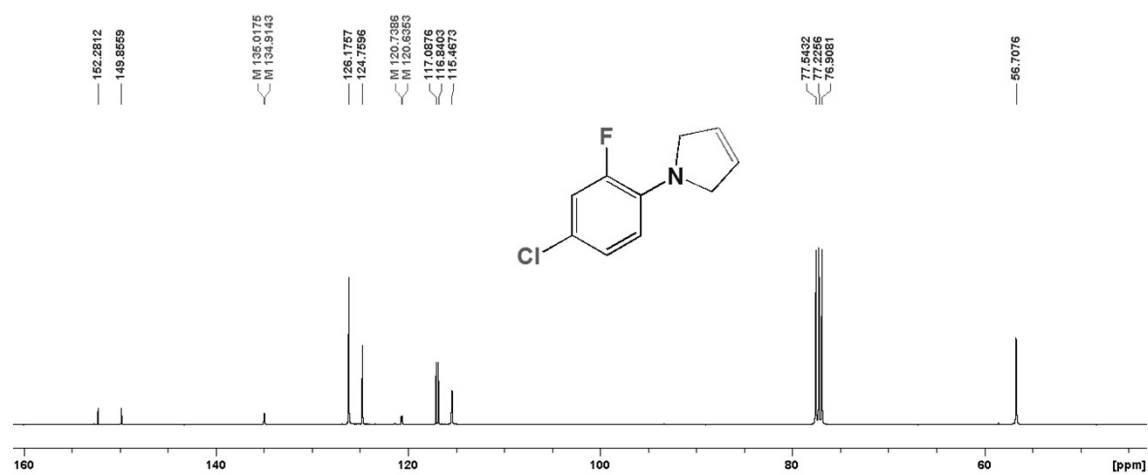
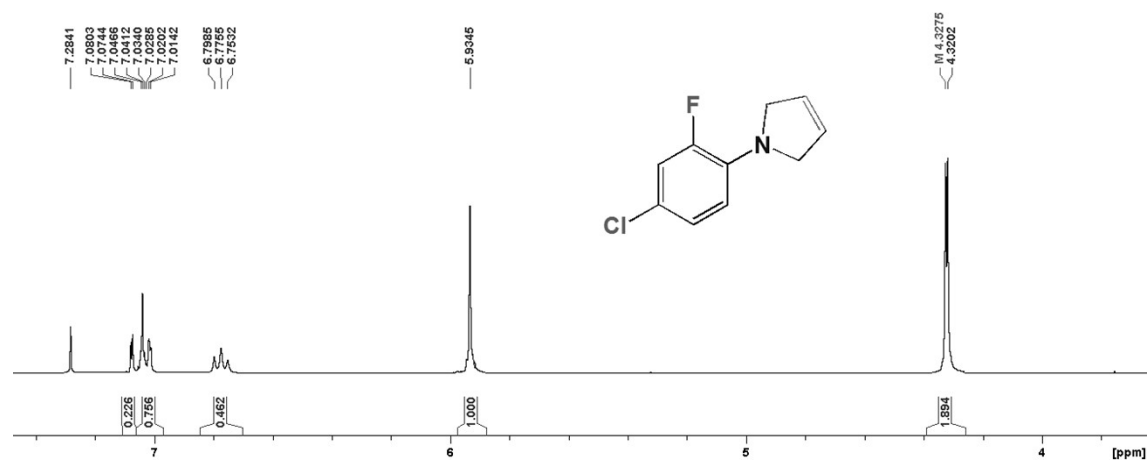


Figure S36. ¹⁹F NMR spectrum of **9o** in CDCl₃ at 25 °C.



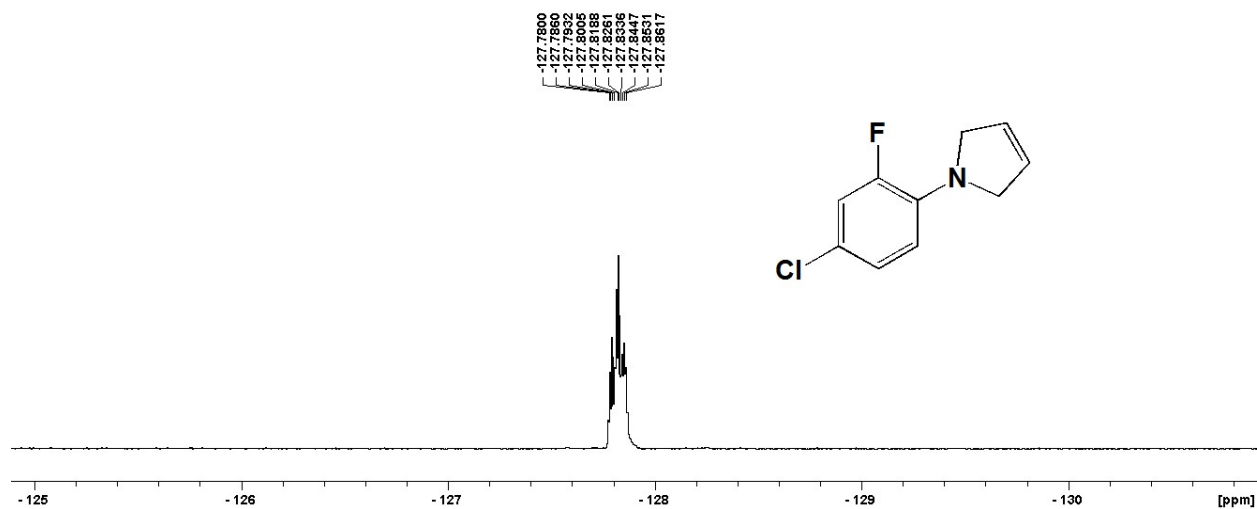


Figure S39. ^{19}F NMR spectrum of **9q** in CDCl_3 at $25\text{ }^\circ\text{C}$.

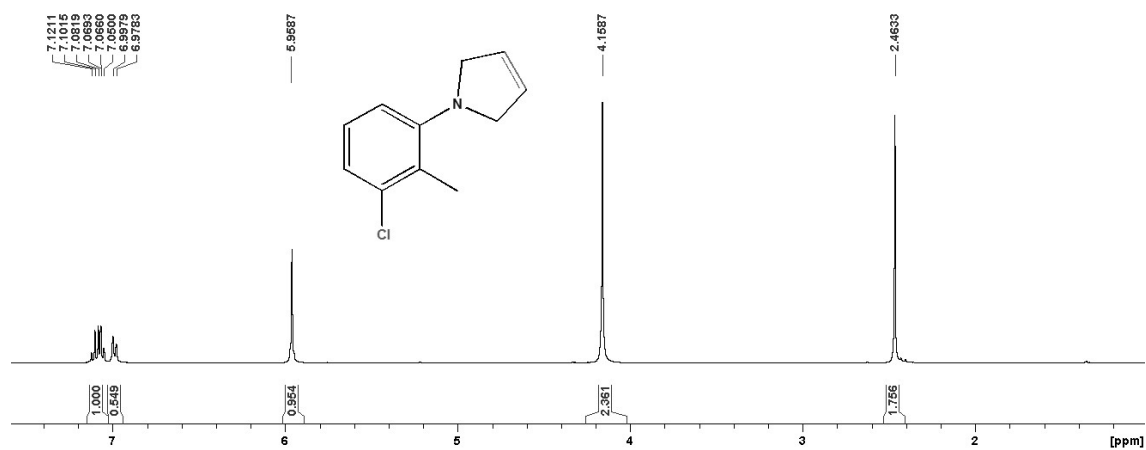


Figure S40. ^1H -NMR spectrum of **9r** in CDCl_3 at $25\text{ }^\circ\text{C}$.

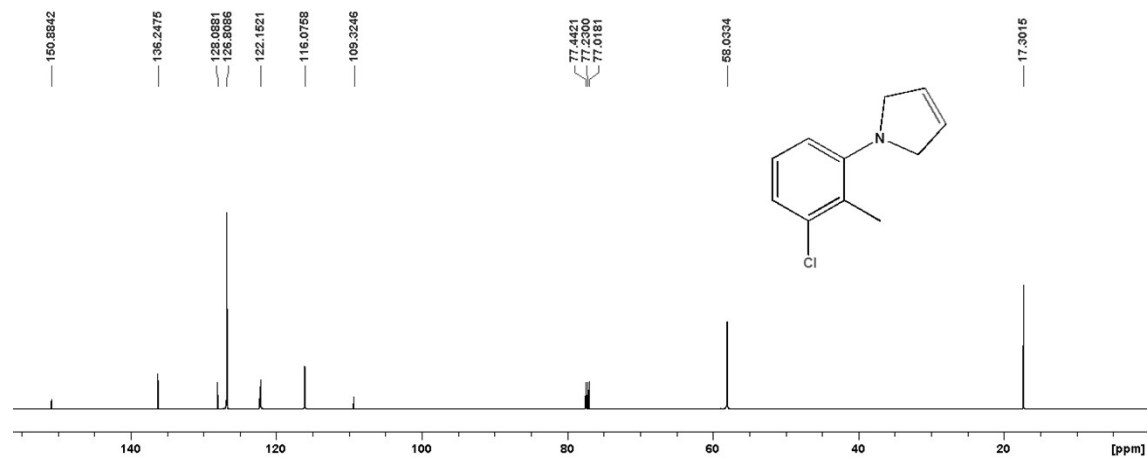


Figure S41. ^{13}C -NMR spectrum of **9r** in CDCl_3 at $25\text{ }^\circ\text{C}$.

Mass spectra

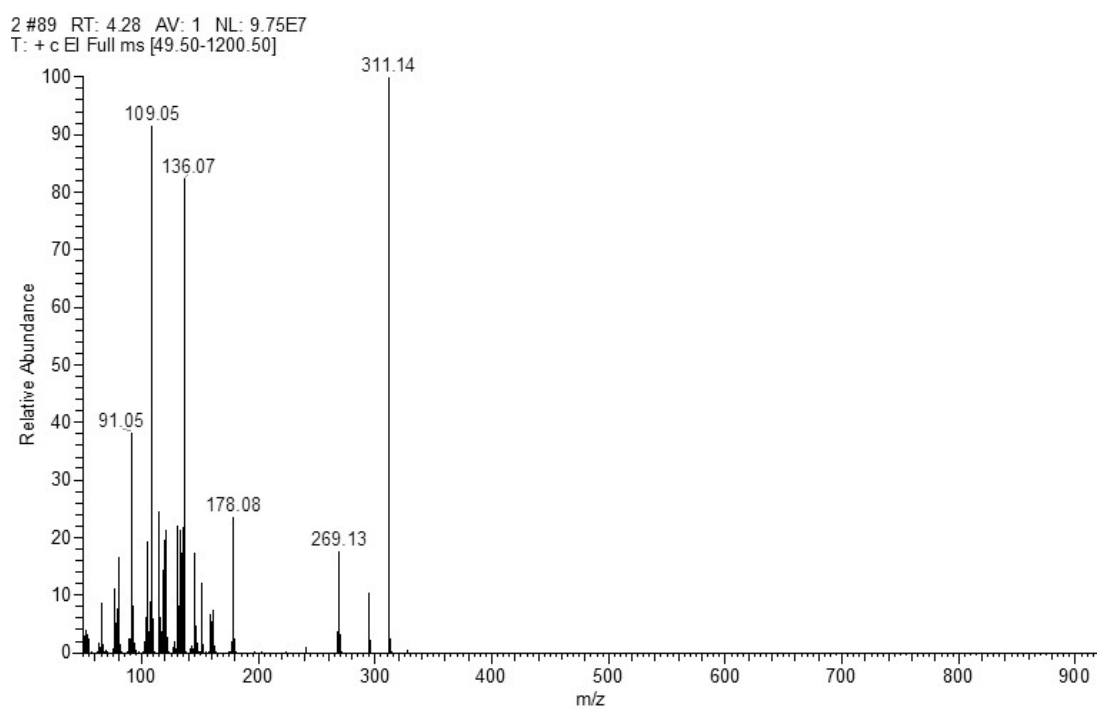


Figure S42. EI spectrum of **6a**.

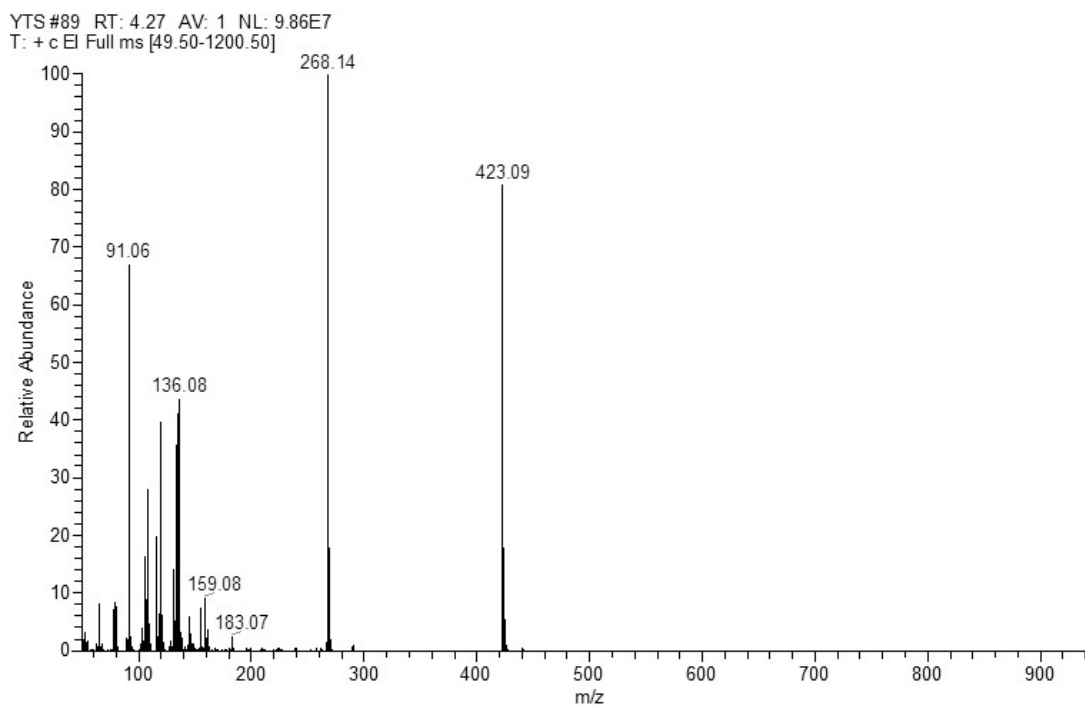


Figure S43. EI spectrum of 6b.

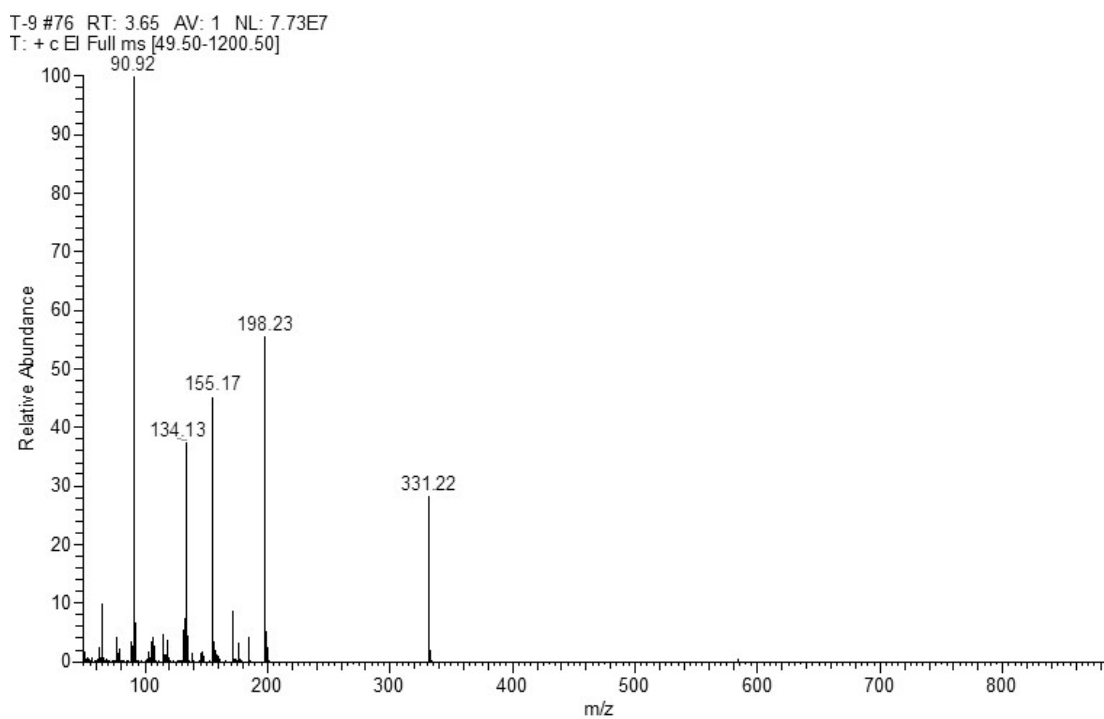


Figure S44. EI spectrum of 6c.

PLC #193 RT: 8.59 AV: 1 NL: 3.72E7
T: + c EI Full ms [49.50-1000.50]

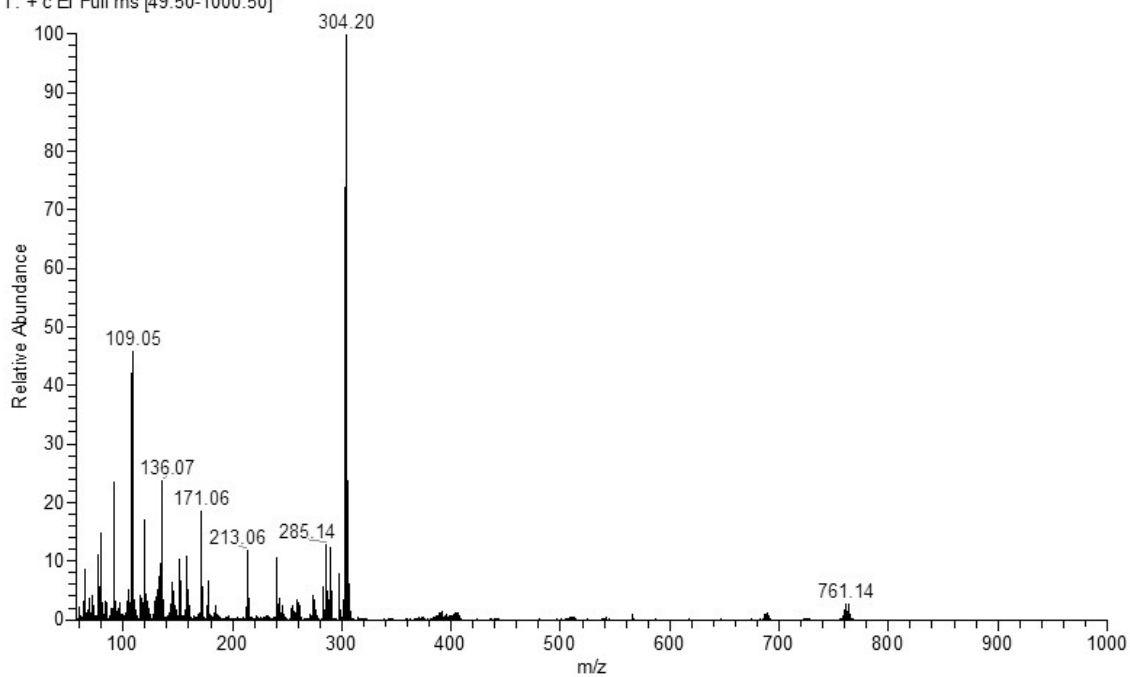


Figure S45. EI spectrum of 7a.

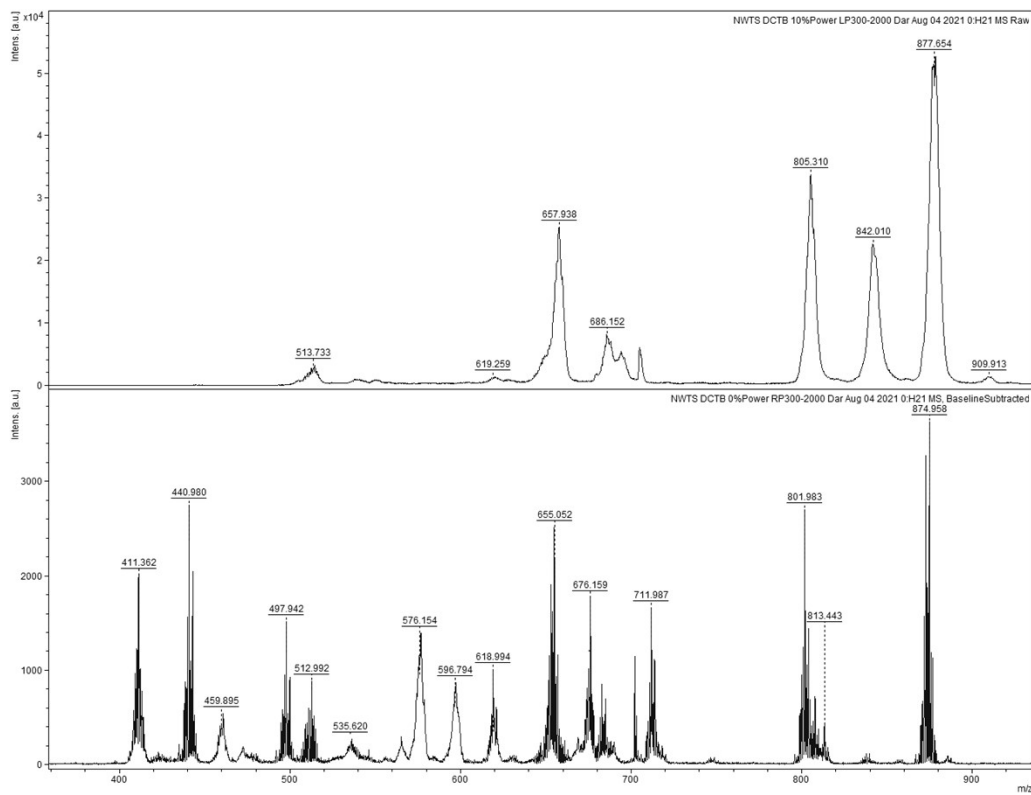


Figure S46. MALDI-MS spectrum of 7b.

BG FAB-782-re #16-20 RT: 0.67-0.84 AV: 5 NL: 2.49E6
T: + c FAB Full ms [49.50-900.50]

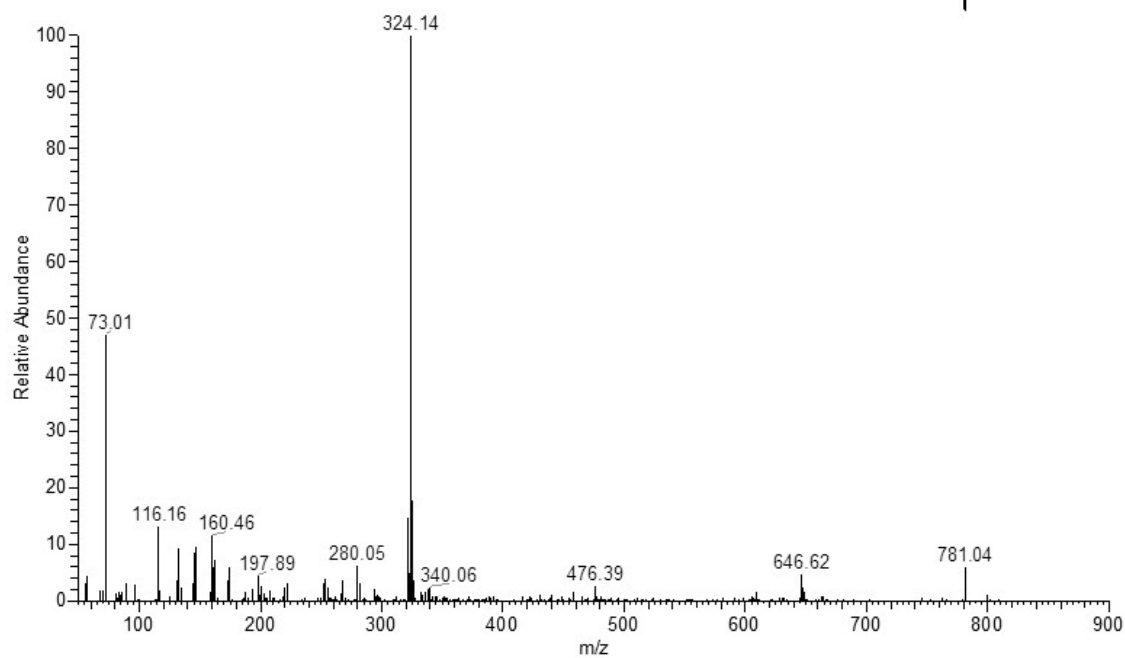


Figure S47. FAB-MS spectrum of 7c.

2-3diMe #11 RT: 0.49 AV: 1 NL: 9.66E7
T: + c EI Full ms [49.50-1200.50]

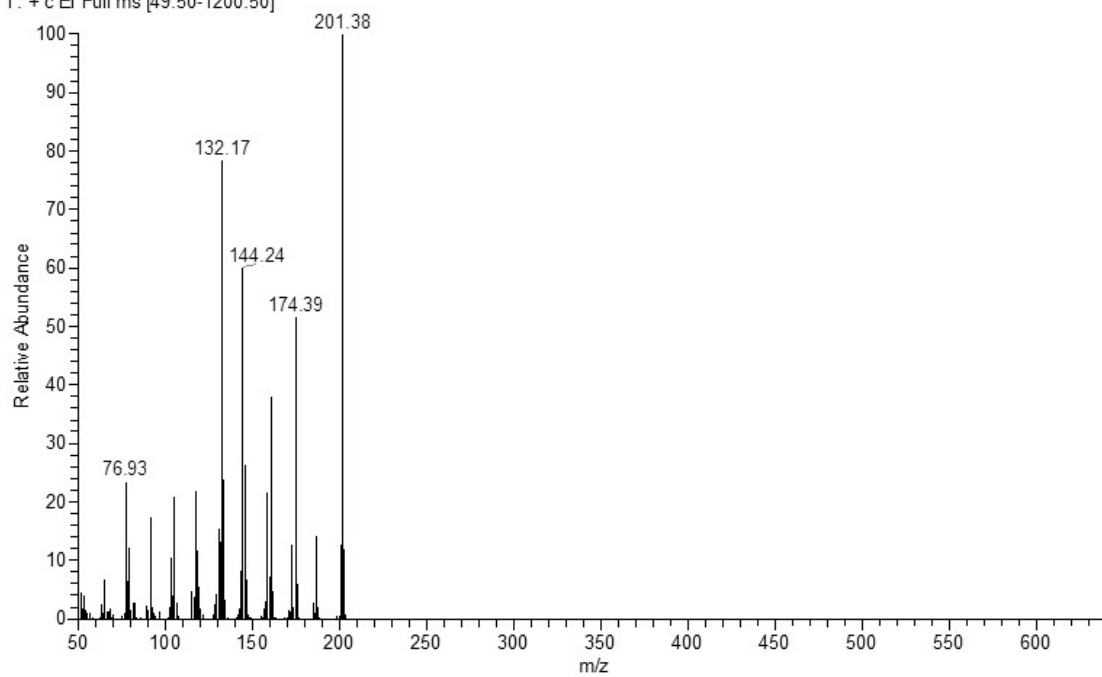


Figure S48. EI spectrum of 8i.

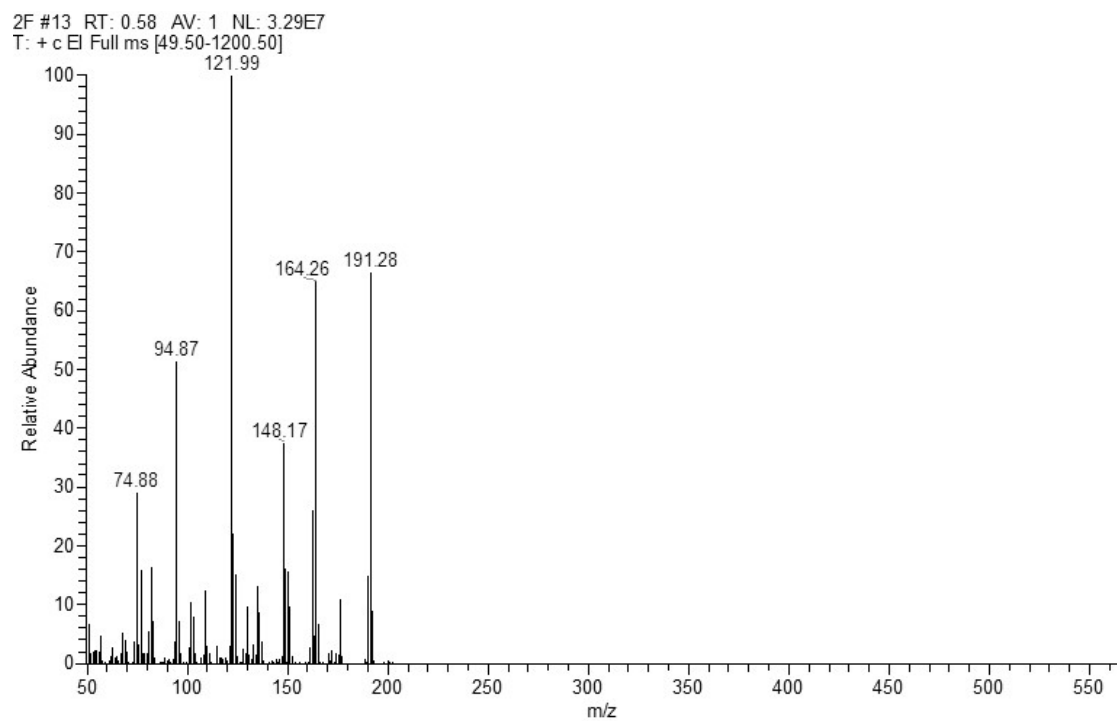


Figure S49. EI spectrum of 8k.

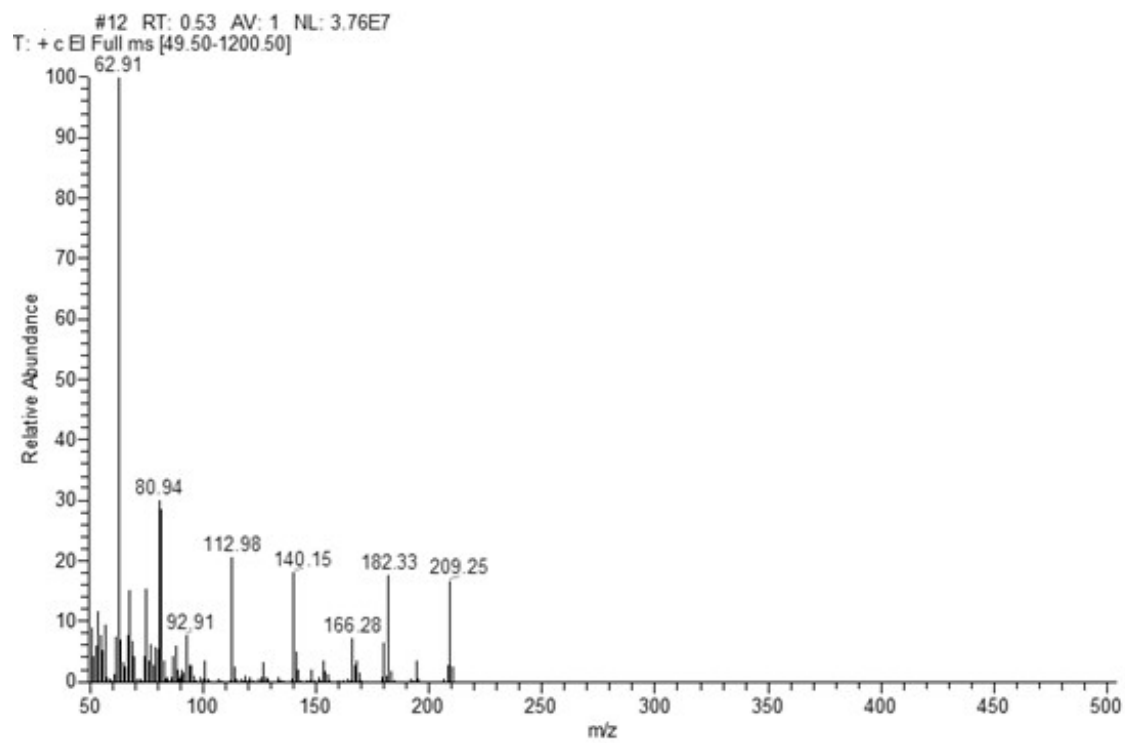


Figure S50. EI spectrum of 8o.

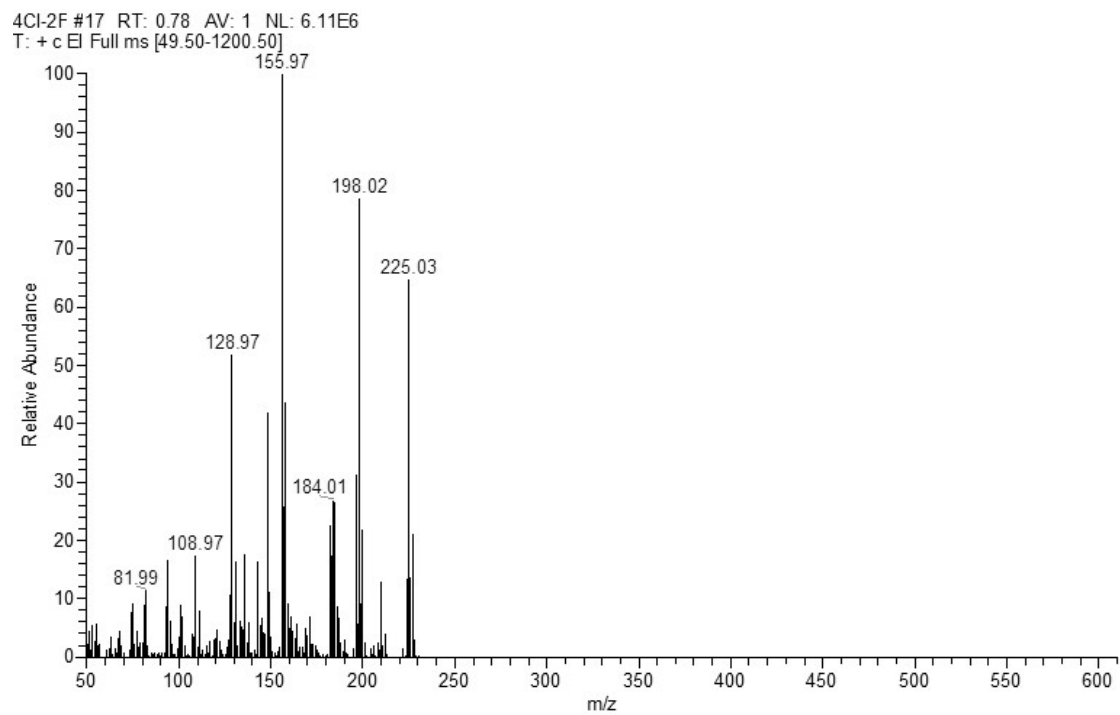


Figure S51. EI spectrum of 8q.

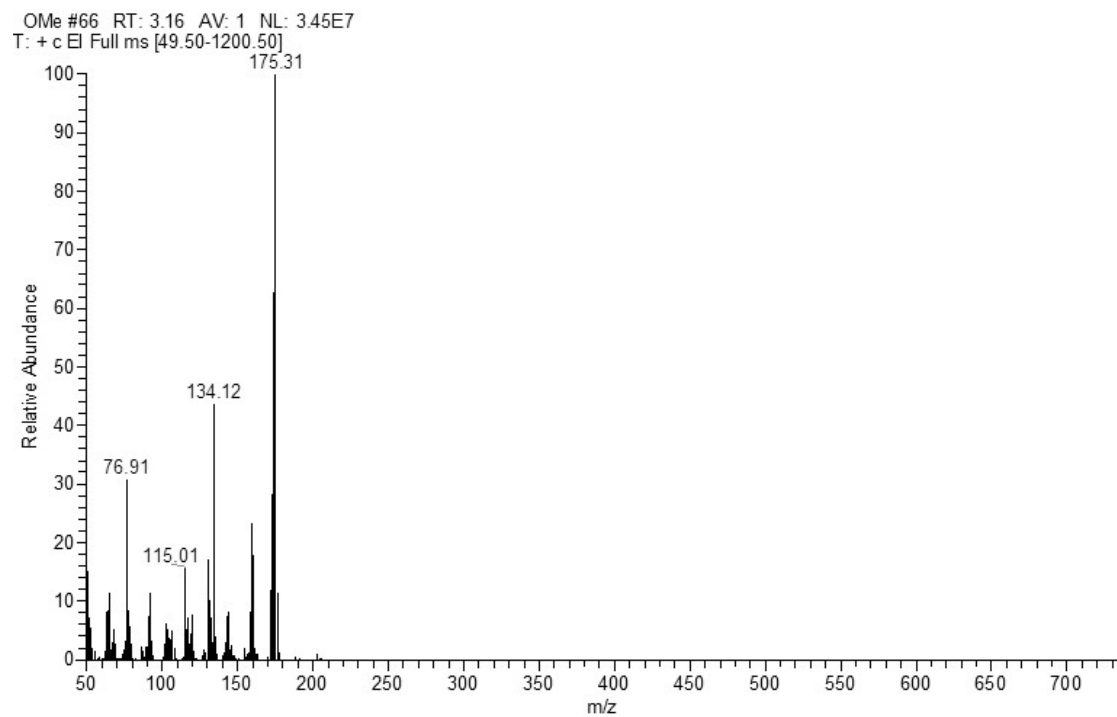


Figure S52. EI spectrum of 9f.

2.3M1 #21 RT: 0.97 AV: 1 NL: 4.87E7
T: + c EI Full ms [49.50-1200.50]

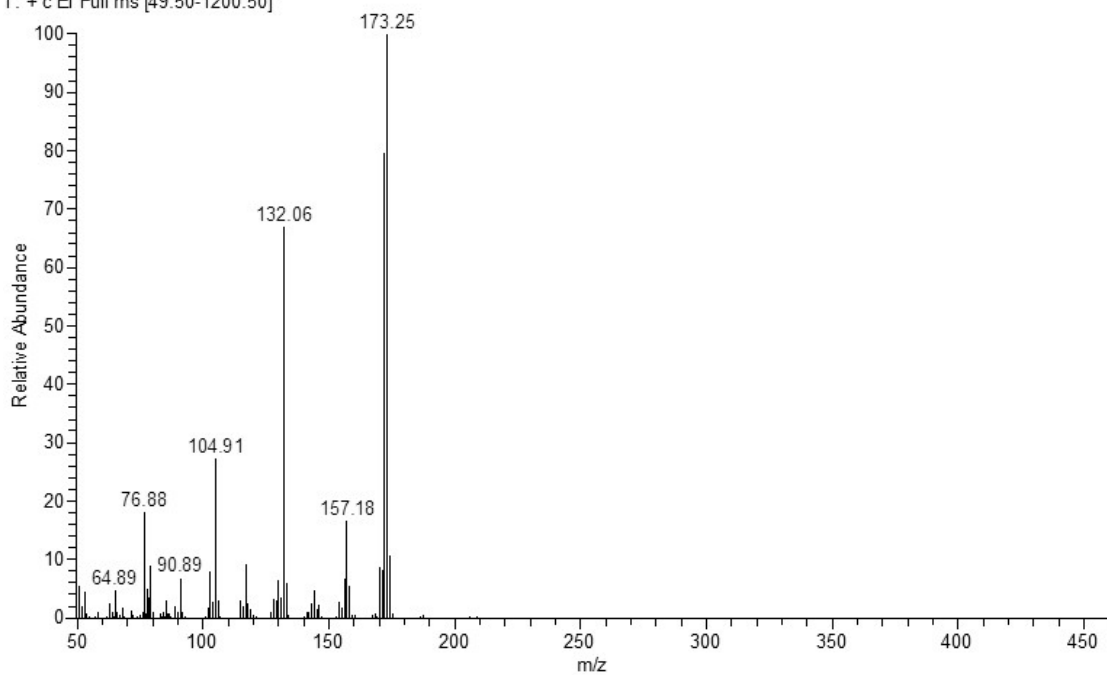


Figure S53. EI spectrum of 9i.

3.5-pdtVpure #12 RT: 0.54 AV: 1 NL: 6.64E6
T: + c EI Full ms [49.50-1200.50]

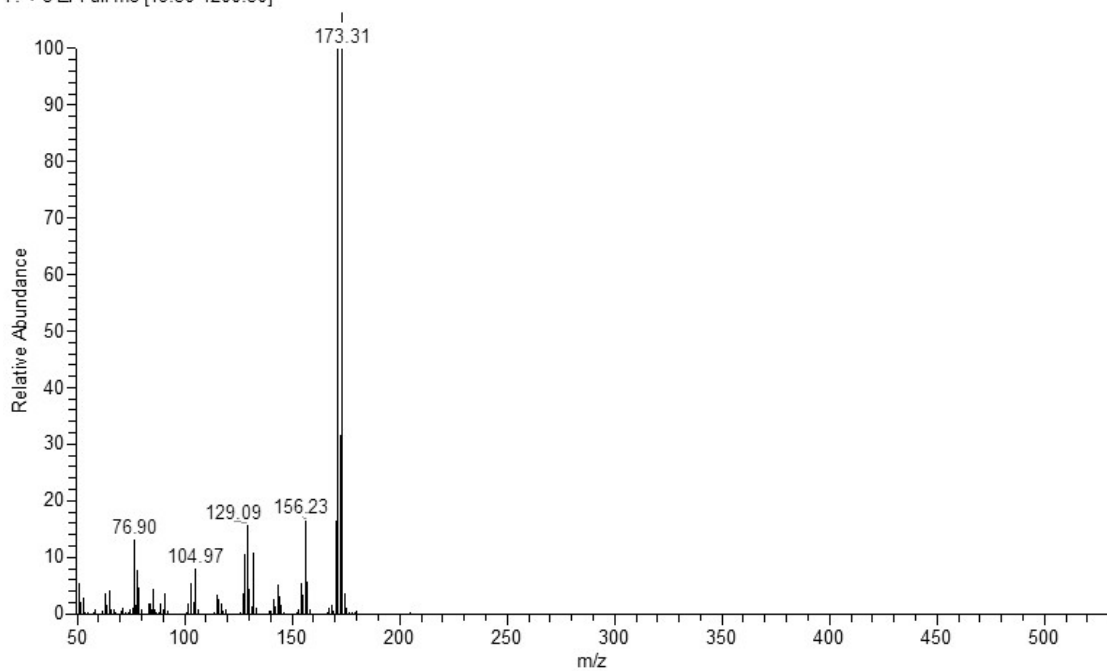


Figure S54. EI spectrum of 9j.

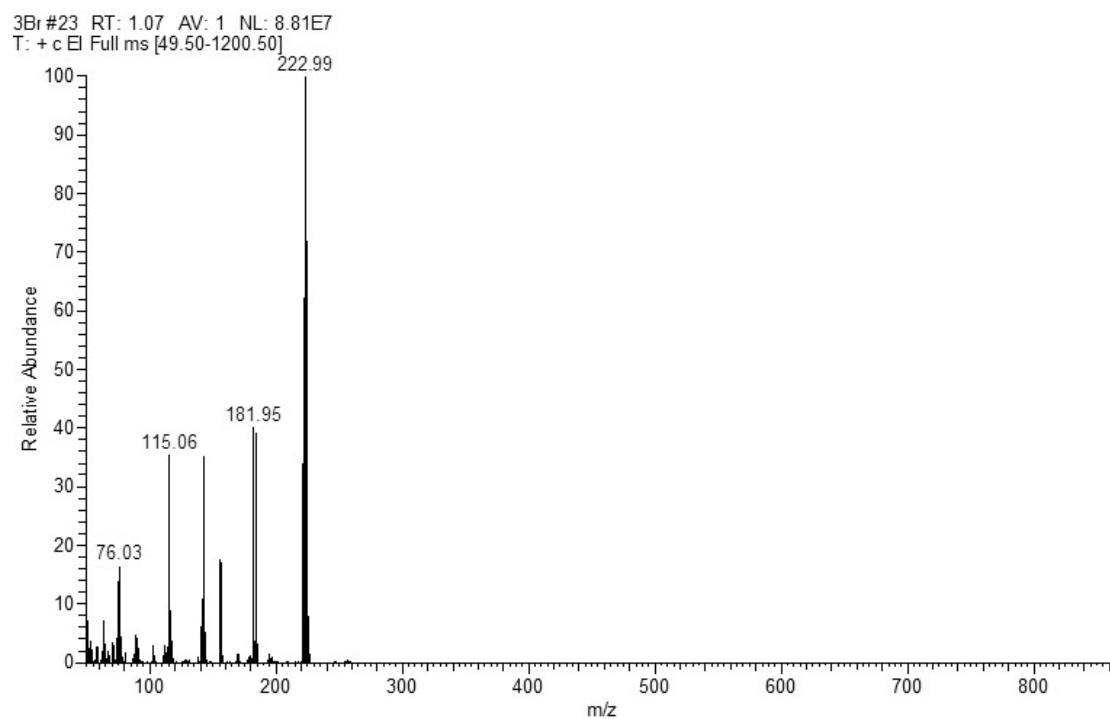


Figure S55. EI spectrum of 9l.

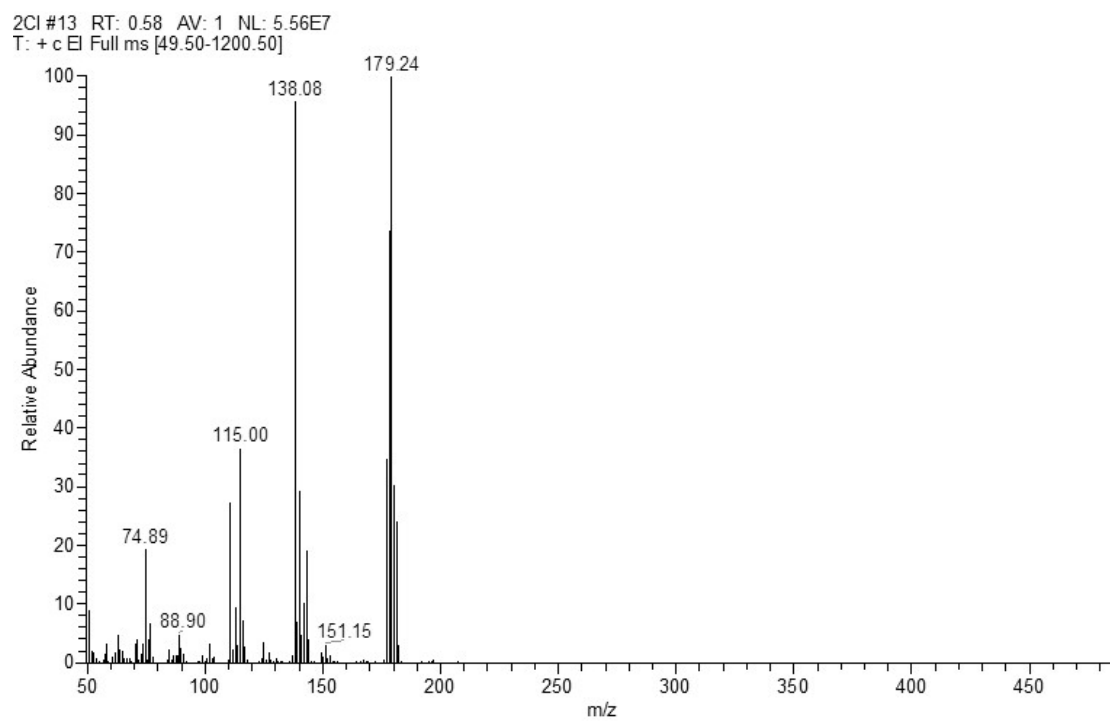


Figure S56. EI spectrum of 9m.

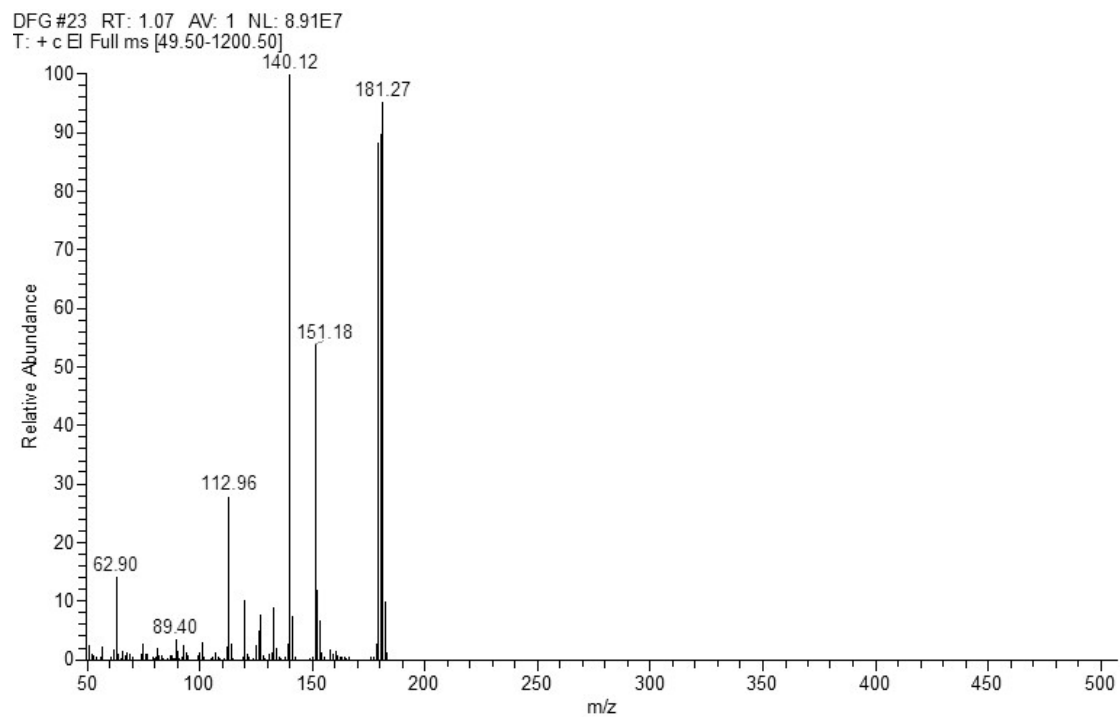


Figure S57. EI spectrum of 9o.

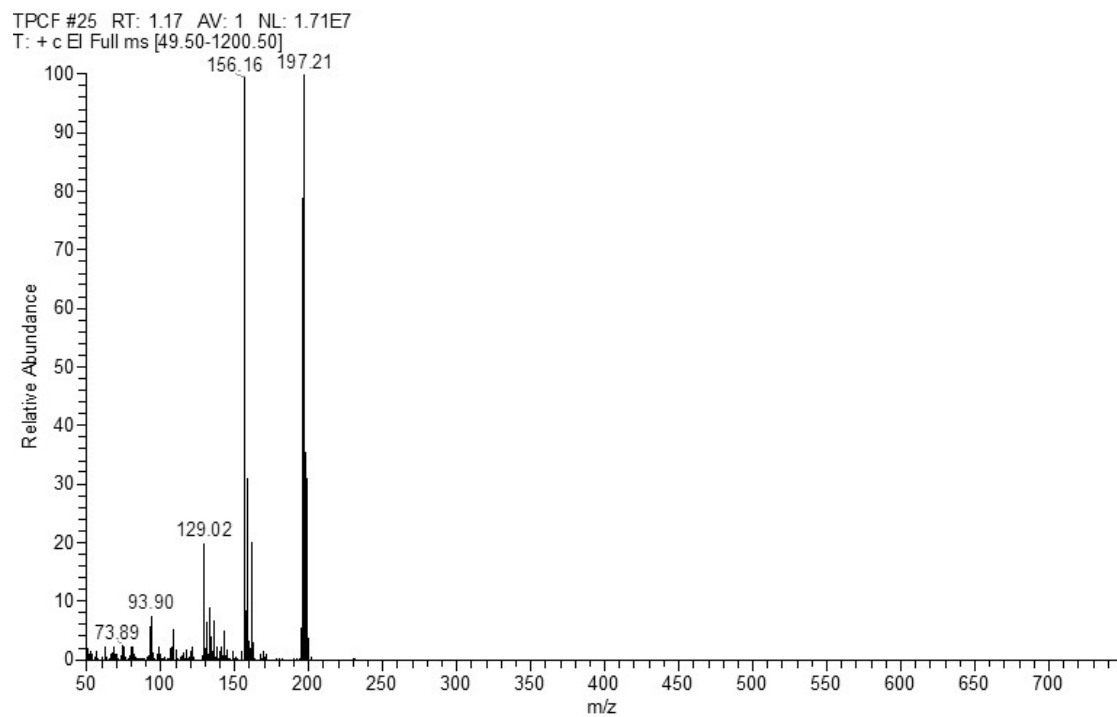


Figure S58. EI spectrum of 9q.

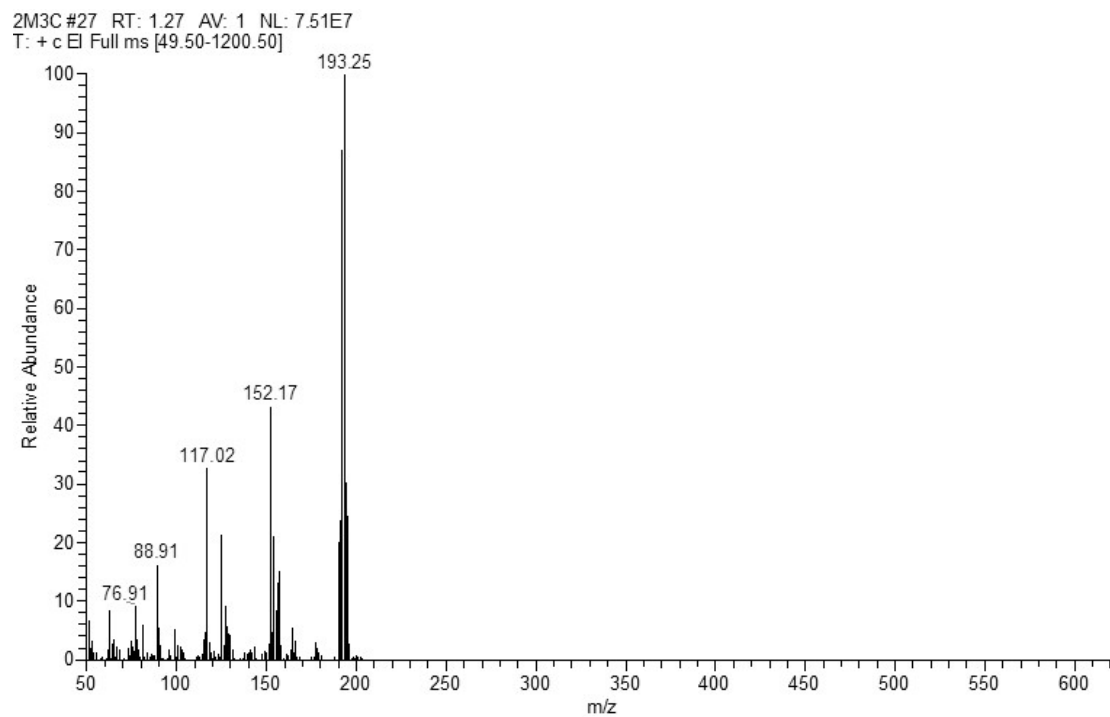


Figure S59. EI spectrum of 9r.

Deconvoluted HRMS (ESI)

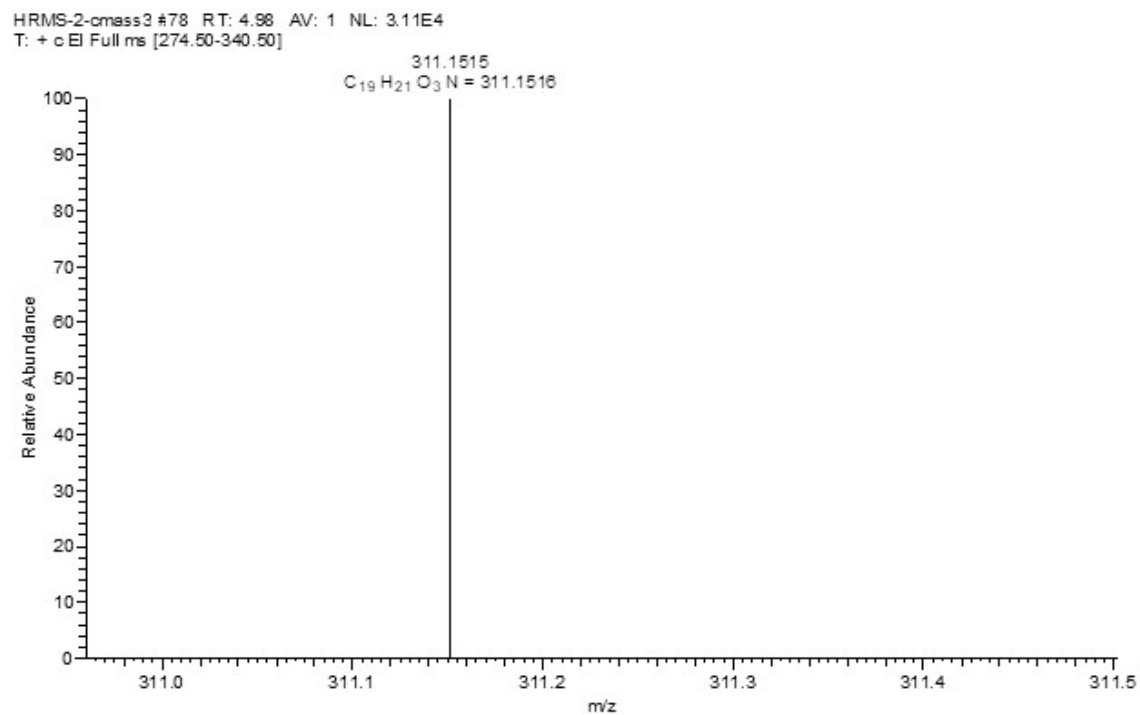


Figure S60. HRMS spectrum of 6a.

HRMS-4TS-cmass1 #15 RT: 4.53 AV: 1 NL: 2.27E4
T: + c EI Full ms [389.50-450.50]

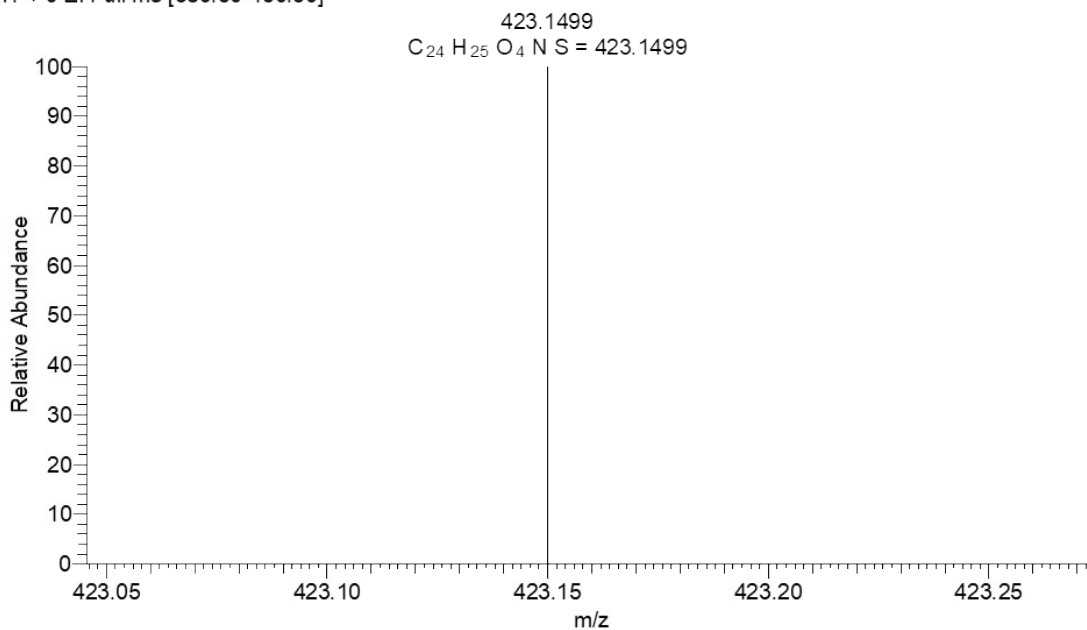


Figure S61. HRMS spectrum of 6b.

HRMS-T9-cmass1 #6 RT: 3.37 AV: 1 NL: 2.51E4
T: + c EI Full ms [299.50-360.50]

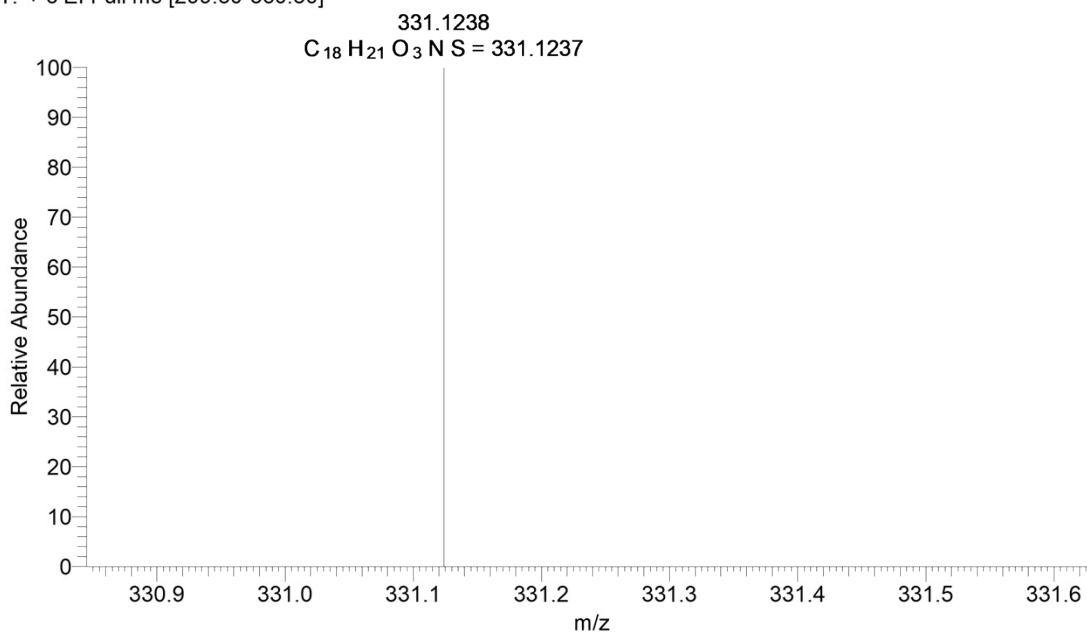


Figure S62. HRMS spectrum of 6c.

HRMS-PLC-c1 #31 RT: 7.57 AV: 1 NL: 1.79E3
T: + c EI Full ms [739.50-800.50]

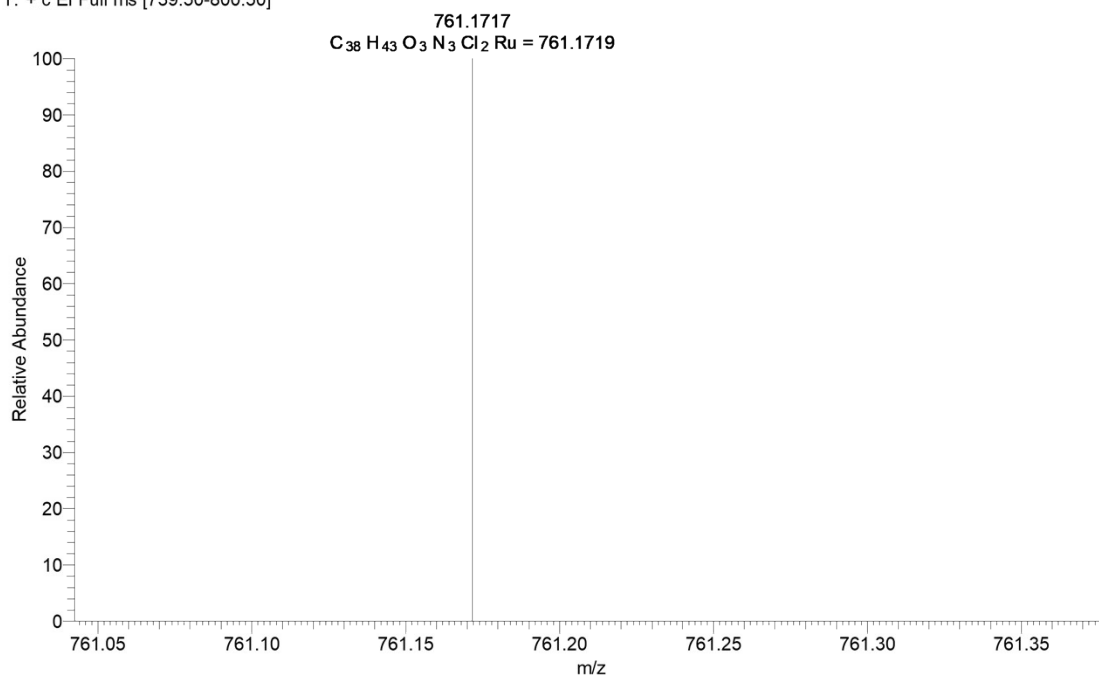


Figure S63. HRMS spectrum of **7a**.

HRMS-TS2-cmass2 #175 RT: 10.18 AV: 1 NL: 1.44E2
T: + c EI Full ms [719.50-820.50]

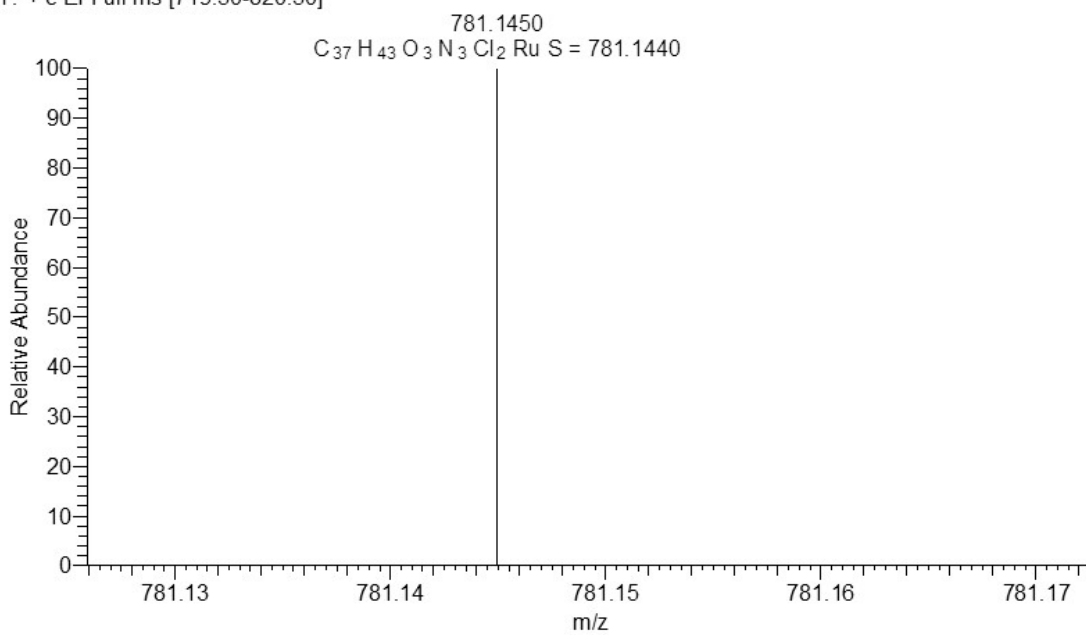


Figure S64. HRMS spectrum of **7c**.

HRMS-2,3Dime-cmass1 #25-27 RT: 1.55-1.67 AV: 3 NL: 1.51E5
T: + c EI Full ms [169.50-220.50]

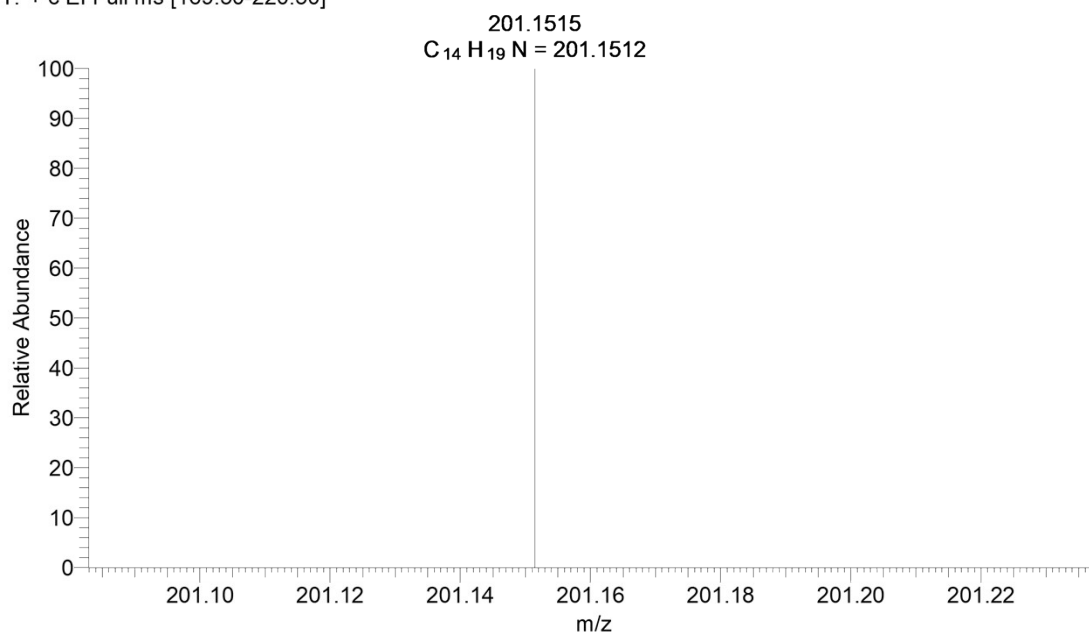


Figure S65. HRMS spectrum of **8i**.

HRMS-2F_210802123320-cmass1 #19-22 RT: 1.76-1.98 AV: 4 NL: 2.25E4
T: + c EI Full ms [159.50-220.50]

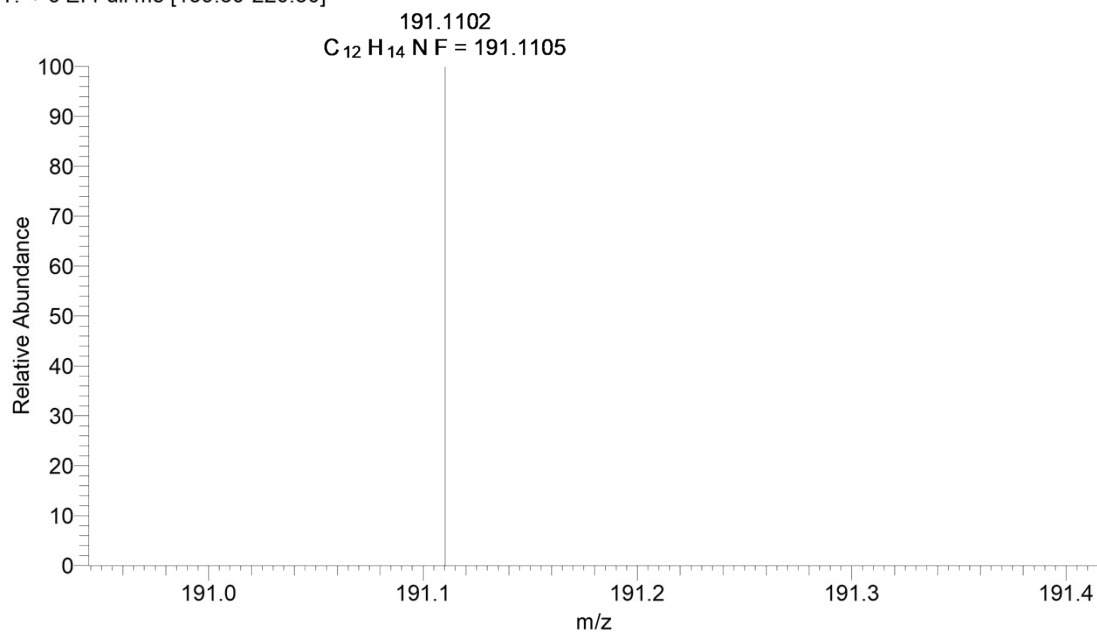


Figure S66. HRMS spectrum of **8k**.

HRMS-24F-cmass1 #10-12 RT: 0.75-0.89 AV: 3 NL: 4.38E5
T: + c EI Full ms [169.50-235.50]

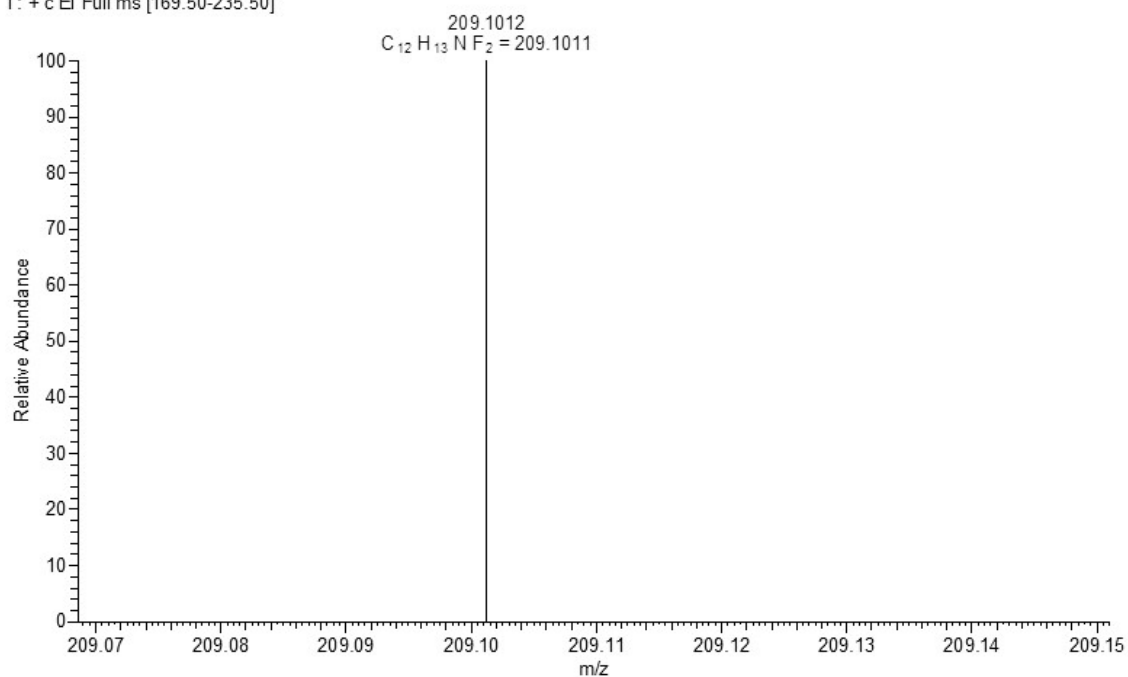


Figure S67. HRMS spectrum of **8o**.

HRMS-4C2Fst-cmass1 #26 RT: 2.03 AV: 1 NL: 4.31E5
T: + c EI Full ms [189.50-250.50]

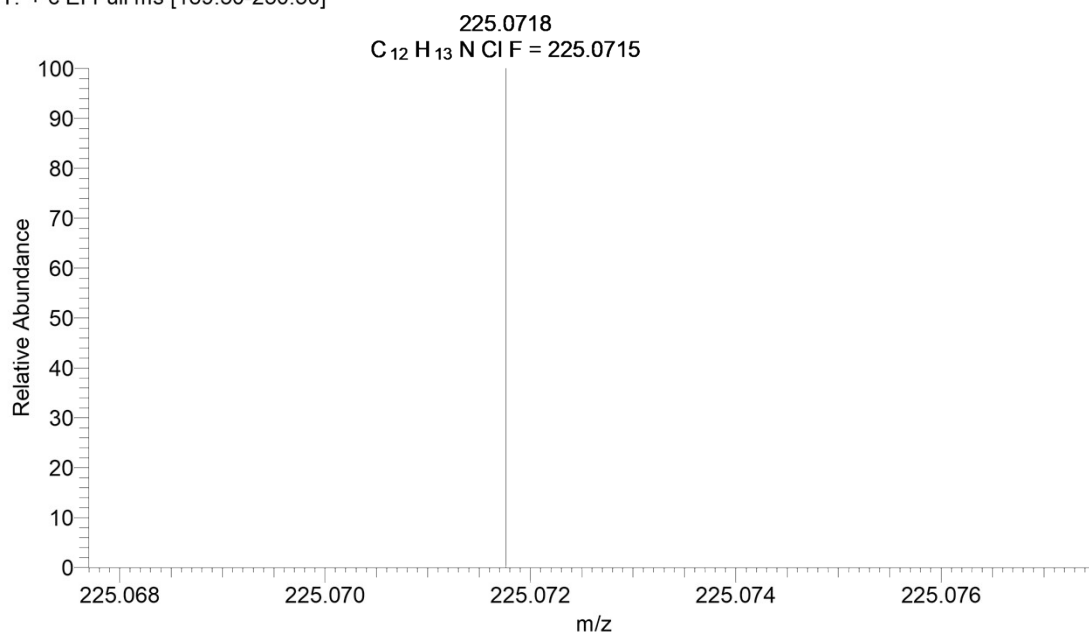


Figure S68. HRMS spectrum of **8q**.

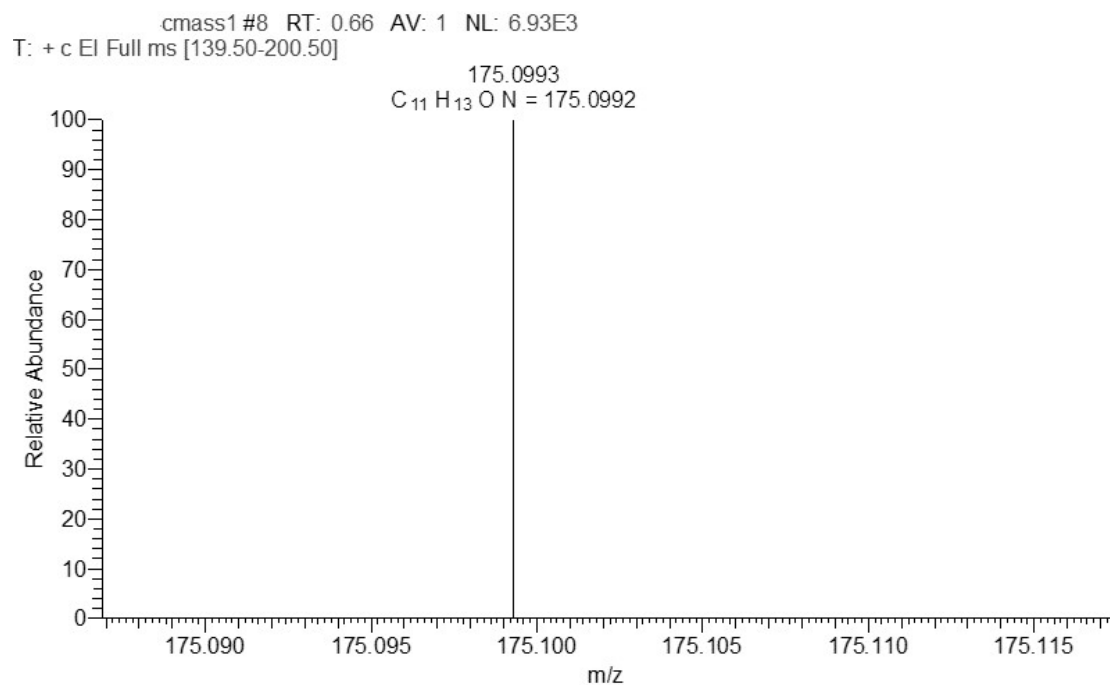


Figure S69. HRMS spectrum of **9f**.

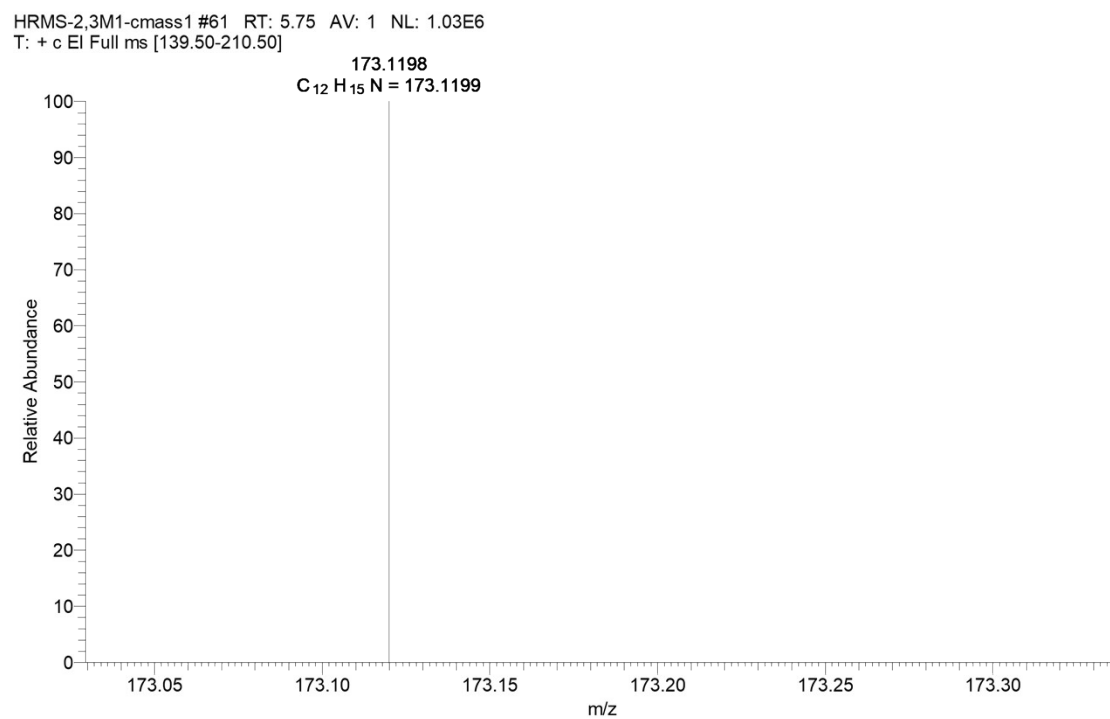


Figure S70. HRMS spectrum of **9i**.

HRMS-3,5pdt-cmass1 #61 RT: 5.75 AV: 1 NL: 1.03E6
T: + c EI Full ms [139.50-210.50]

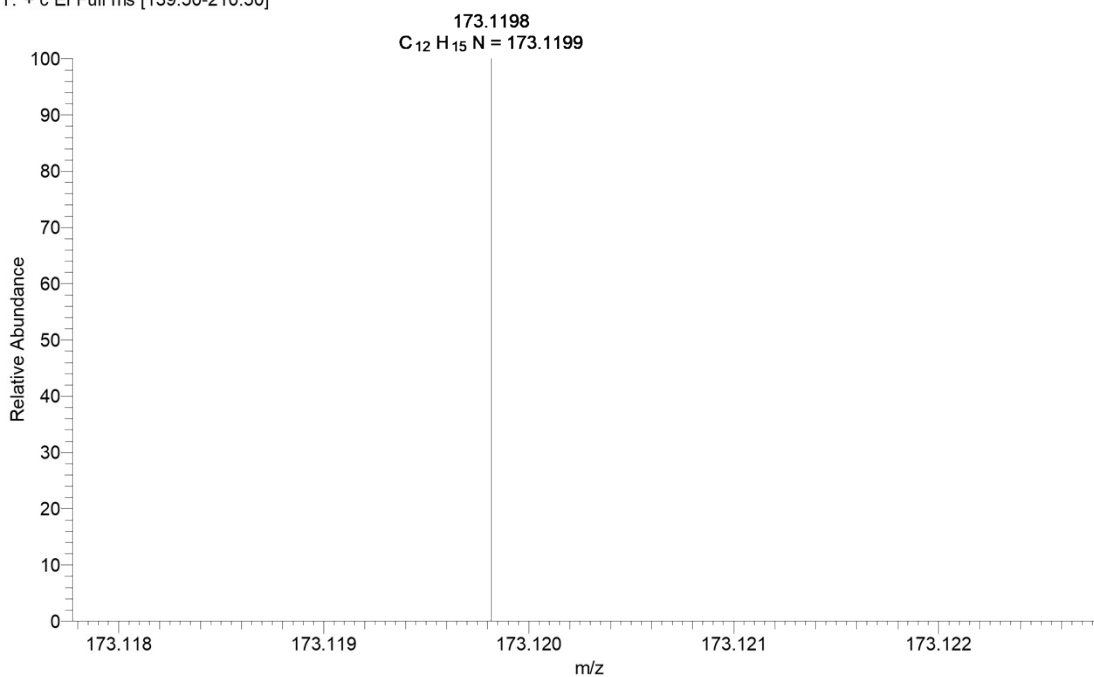


Figure S71. HRMS spectrum of **9j**.

HRMS-3Brpdt-cmass1 #61-62 RT: 4.48-4.55 AV: 2 NL: 4.91E4
T: + c EI Full ms [189.50-260.50]

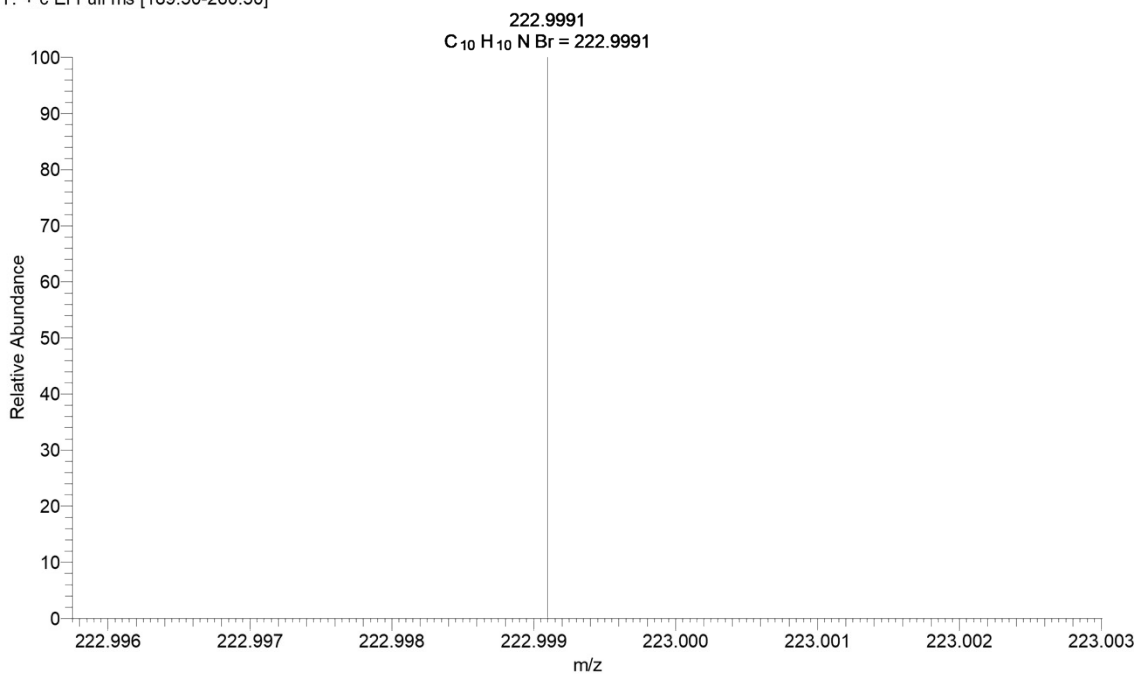


Figure S72. HRMS spectrum of **9i**.

HRMS-2ClPdt-cmass1 #21 RT: 2.23 AV: 1 NL: 1.34E6
T: + c EI Full ms [139.50-210.50]

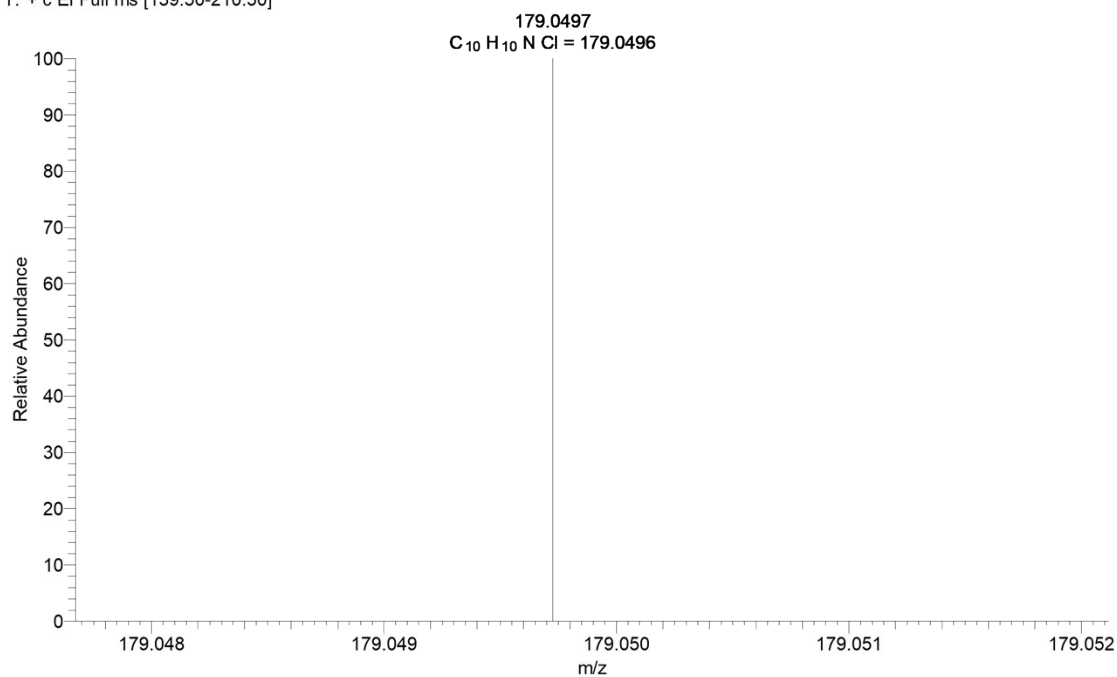


Figure S73. HRMS spectrum of **9m**.

HRMS-DFG-cmass1 #119 RT: 10.35 AV: 1 NL: 5.25E3
T: + c EI Full ms [149.50-220.50]

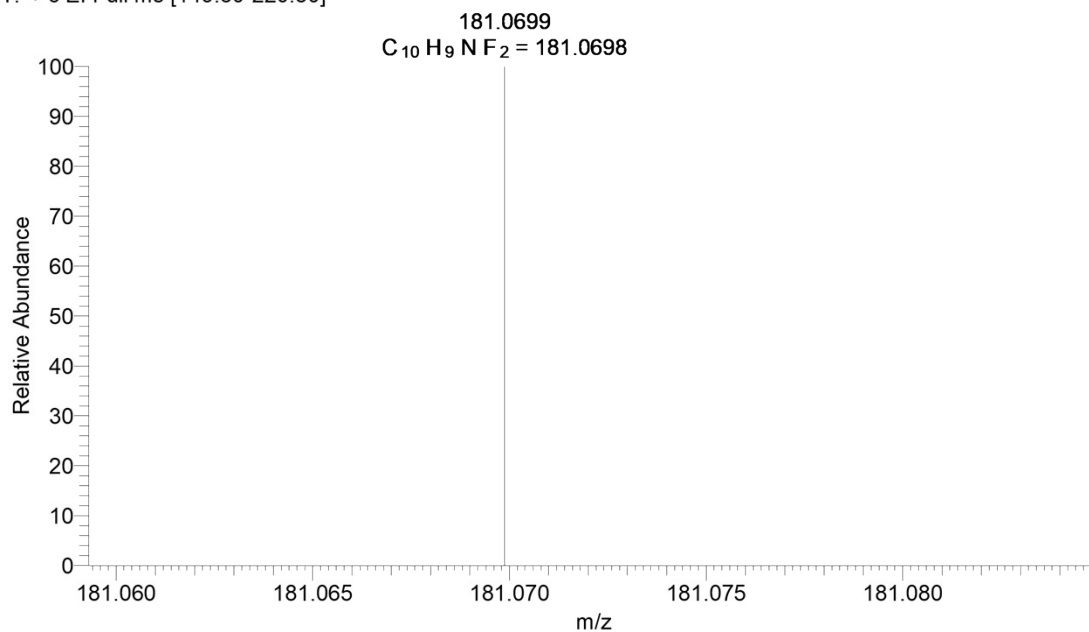


Figure S74. HRMS spectrum of **9o**.

HRMS-4C2F-cmass1 #29 RT: 2.05 AV: 1 NL: 1.26E5
T: + c EI Full ms [159.50-220.50]

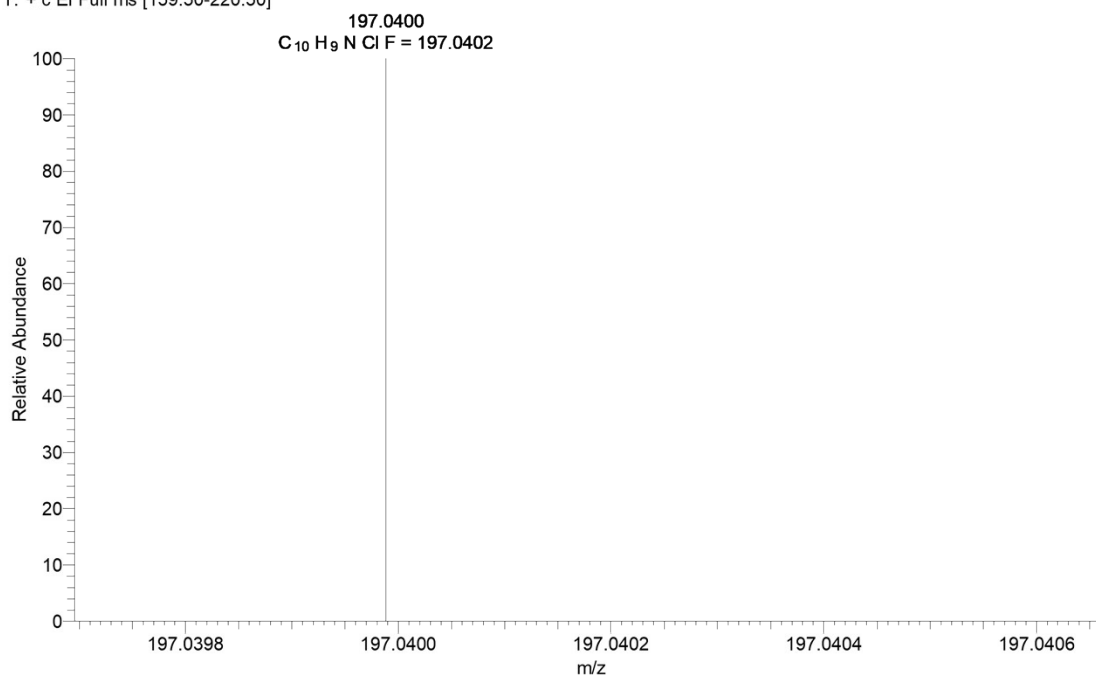


Figure S70. HRMS spectrum of **9q**.

HRMS-2M3C-cmass1 #72-88 RT: 5.42-6.59 AV: 17 NL: 4.18E5
T: + c EI Full ms [159.50-220.50]

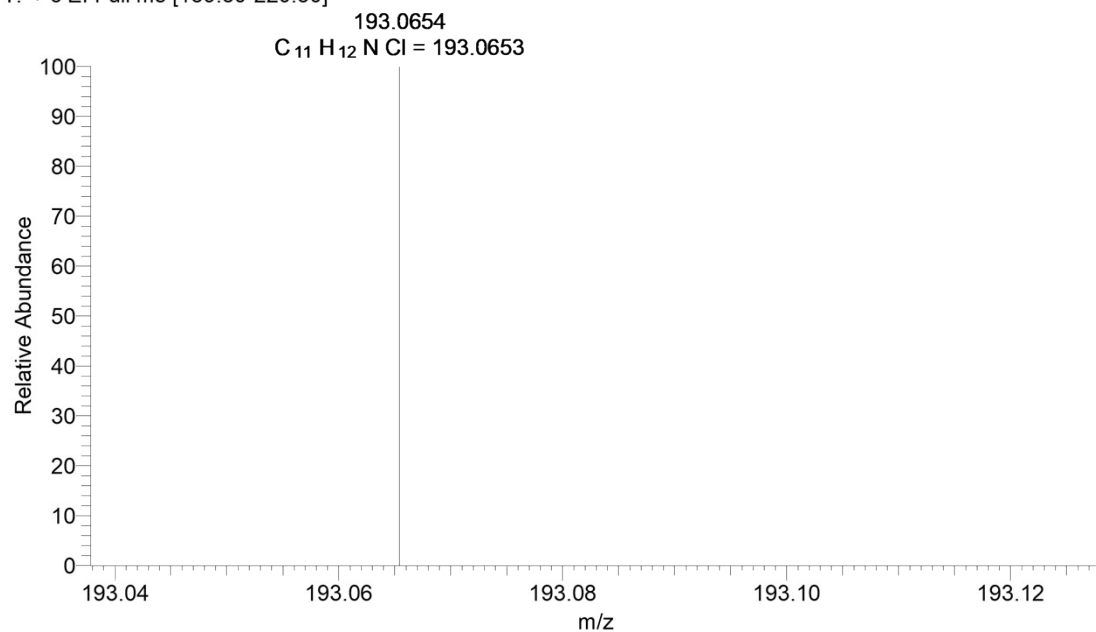


Figure S71. HRMS spectrum of **9r**.

Single Crystal X-ray diffraction study of the Ru complexes **7a**, **7b** & **7c**

Single crystals of **7a**, **7b** & **7c** were grown by solvent diffusion method. The single crystal data collection of **7a** and **7c** were made on Bruker X8 prospector diffractometer by Cu-K α . The reflection frames were then integrated with the Bruker SAINT Software package using a narrow-frame algorithm; the structures were solved using the Bruker SHELXTL Software Package. The single crystal data collection of **7b** was made on Rigaku Rapid II diffractometer by Mo-K α . This structure was then solved by 'crystalstructure' software package. Finally, all structures were refined using SHELXL-2017/1. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the riding model. The crystal structures (thermal ellipsoid representation) of **7a**, **7b** & **7c** are given in **Figure S72-S74** and their various crystallographic data including crystal nature, data collection strategy and refinement parameters are summarized in the **Table S1**.

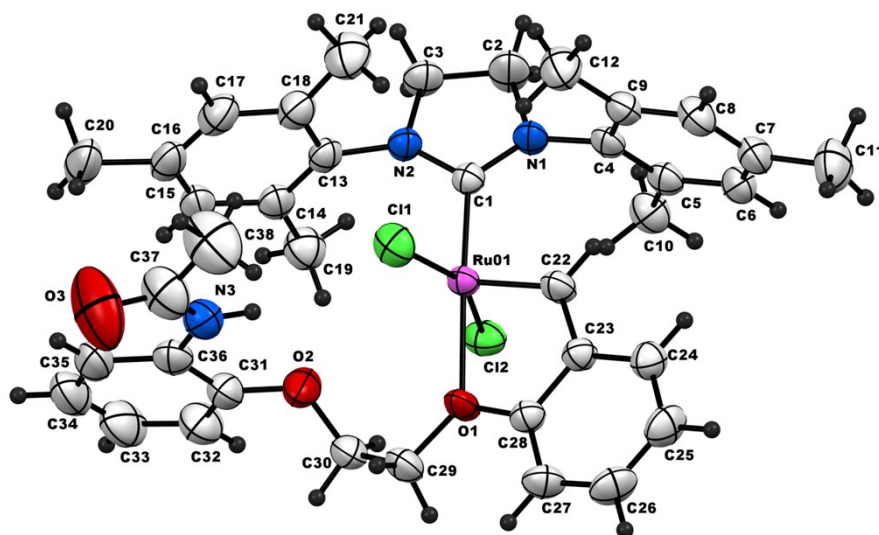


Figure S72. crystal structure (thermal ellipsoid representation; 50% probability) of **7a**.

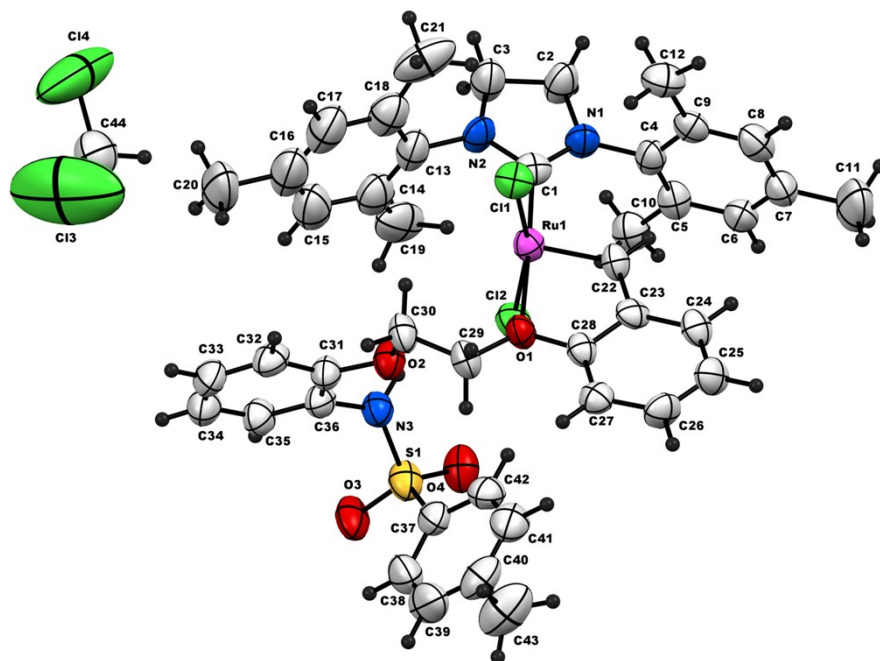


Figure S73. crystal structure (thermal ellipsoid representation; 50% probability) of 7b.

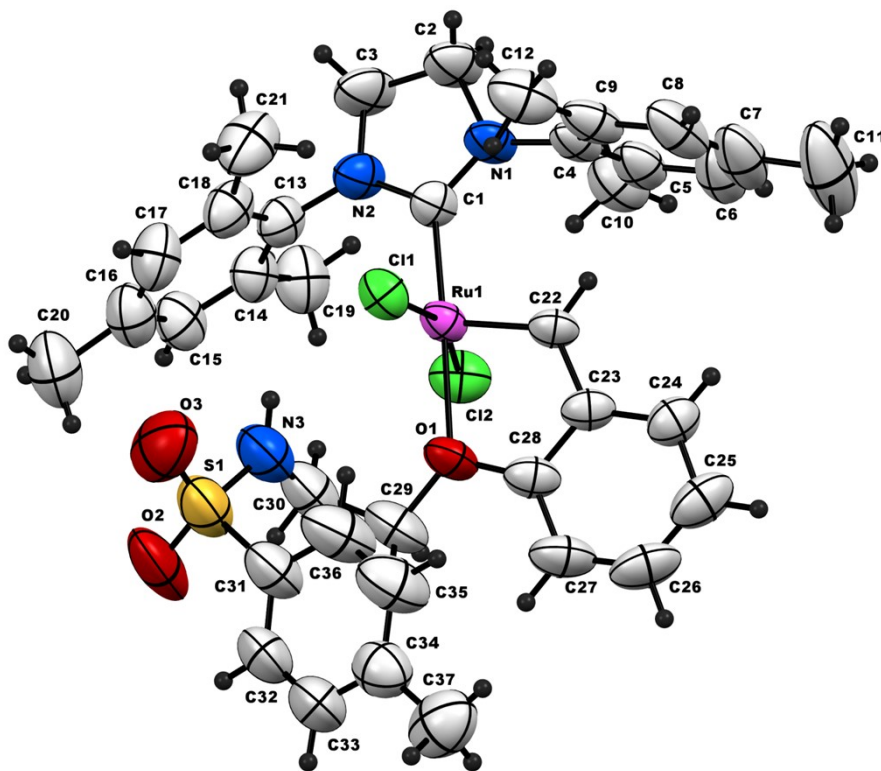


Figure S74. crystal structure (thermal ellipsoid representation; 50% probability) of 7c.

Table S1. Summary on the nature and various crystallographic parameters of **7a**, **7b** & **7c**.

Crystal sample	7a	7b	7c
Chemical formula	C ₃₈ H ₄₃ Cl ₂ N ₃ O ₃ Ru	C ₄₄ H ₄₉ Cl ₄ N ₃ O ₄ RuS	C ₃₇ H ₄₃ Cl ₂ N ₃ O ₃ RuS
M_r	761.72	958.79	781.77
Crystal system, space group	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Trigonal, <i>R</i> -3 :H
Temperature (K)	296	150	150
a, b, c (Å)	8.8611 (4), 10.6837 (5), 19.3949 (10)	12.038 (10), 14.886 (12), 24.180 (19)	28.6420 (5), 24.4463 (9)
α, β, γ (°)	74.511 (2), 87.898 (2), 89.558 (2)	90, 91.36 (3), 90	90, 90, 120
V (Å ³)	1768.22 (15)	4332 (6)	17368.0 (9)
Z	2	4	18
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	5.30	0.70	5.36
Crystal size (mm)	0.21 × 0.20 × 0.08	0.10 × 0.05 × 0.04	0.18 × 0.14 × 0.12
Diffractometer	Bruker APEX-II CCD	Rigaku R-AXIS RAPID	Bruker APEX-II CCD
Absorption correction	Multi-scan	Multi-scan	Multi-scan
	SADABS2016/2 - Bruker AXS area detector scaling and absorption correction	ABSCOR (Rigaku, 1995)	SADABS2016/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.220, 0.495	0.379, 0.972	0.45, 0.57
No. of measured, independent & observed [$I > 2\sigma(I)$] reflections	37958, 6204, 5934	24863, 7781, 3493	61572, 6025, 4870
R_{int}	0.040	0.171	0.067
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.595	0.602	0.598
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.069, 1.09	0.077, 0.214, 0.96	0.053, 0.151, 1.03
No. of reflections	6204	7781	6025
No. of parameters	431	515	431
H-atom treatment	Constrained	Constrained	Constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.40, -0.29	1.01, -0.75	0.74, -0.51