Supporting Information for

Synthesis, Mass-Spectrometric Characterization and Polymerization Studies of Group 4 Dinuclear Bis(metallocene) Complexes

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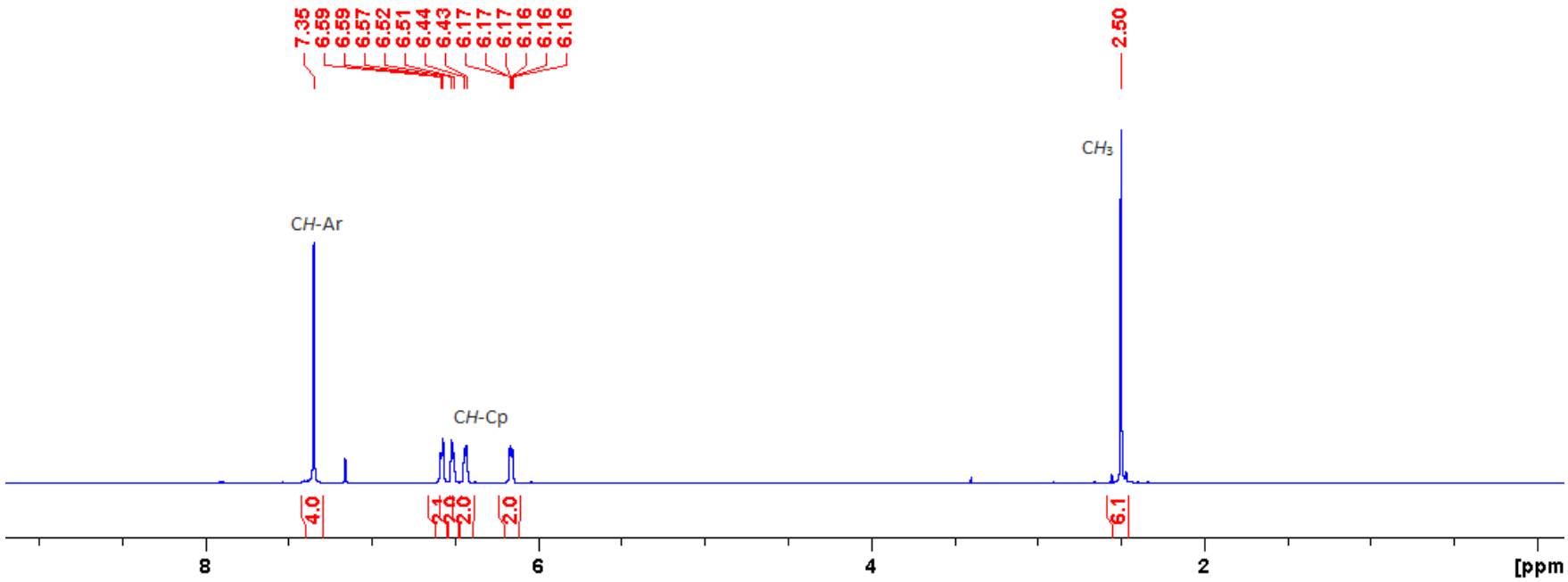
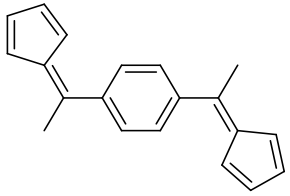
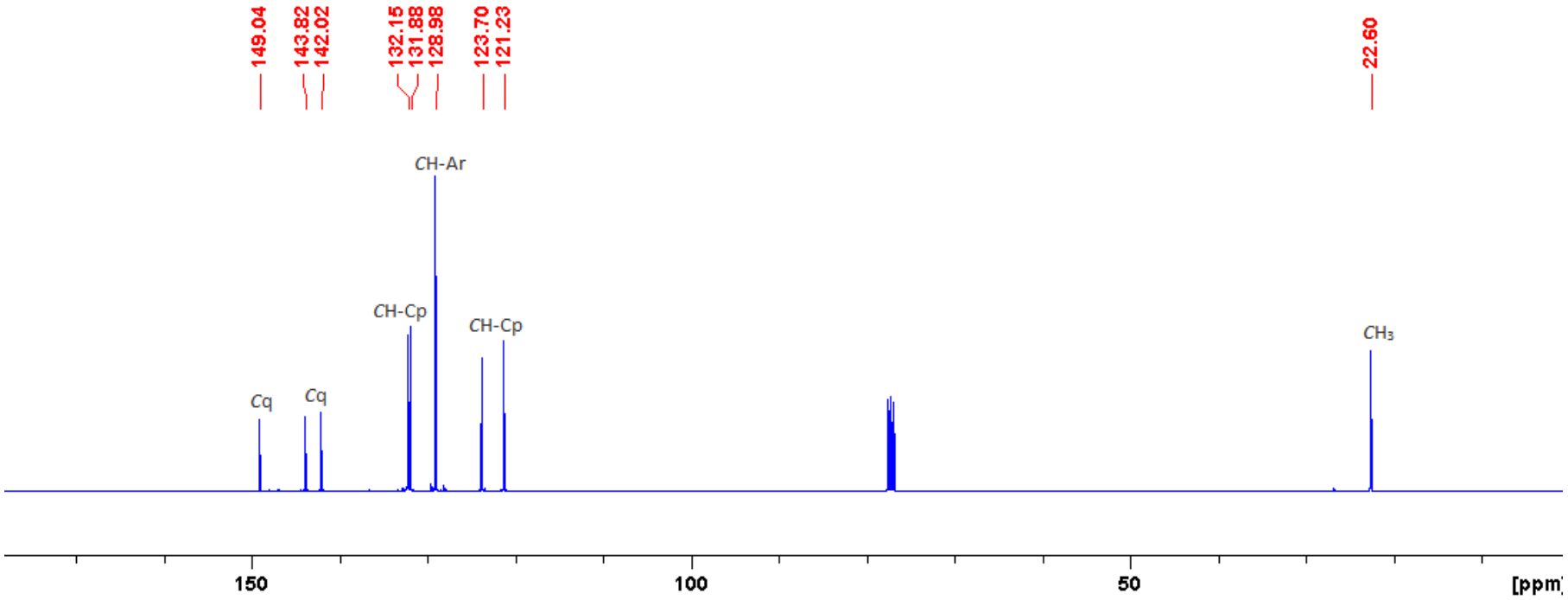


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **1a**. jfc-gs190-1

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128.98
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121.23
22.60
CH-Ar
CH-Cp
CH-Cp
Cq
Cq
CH3
150
100
50
[ppm]

Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **1a**.

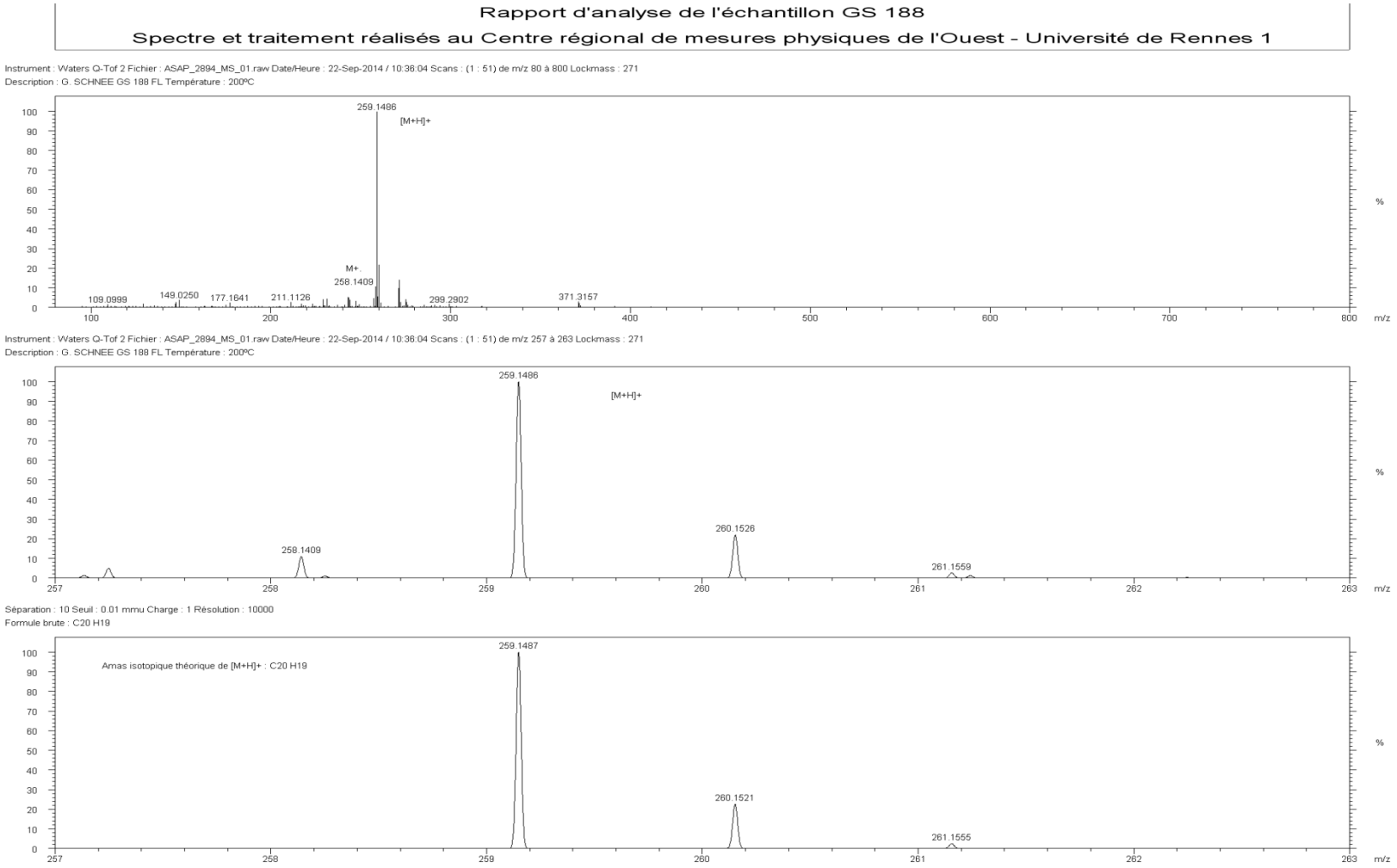


Figure S3. ASAP mass spectrum of **1a**.

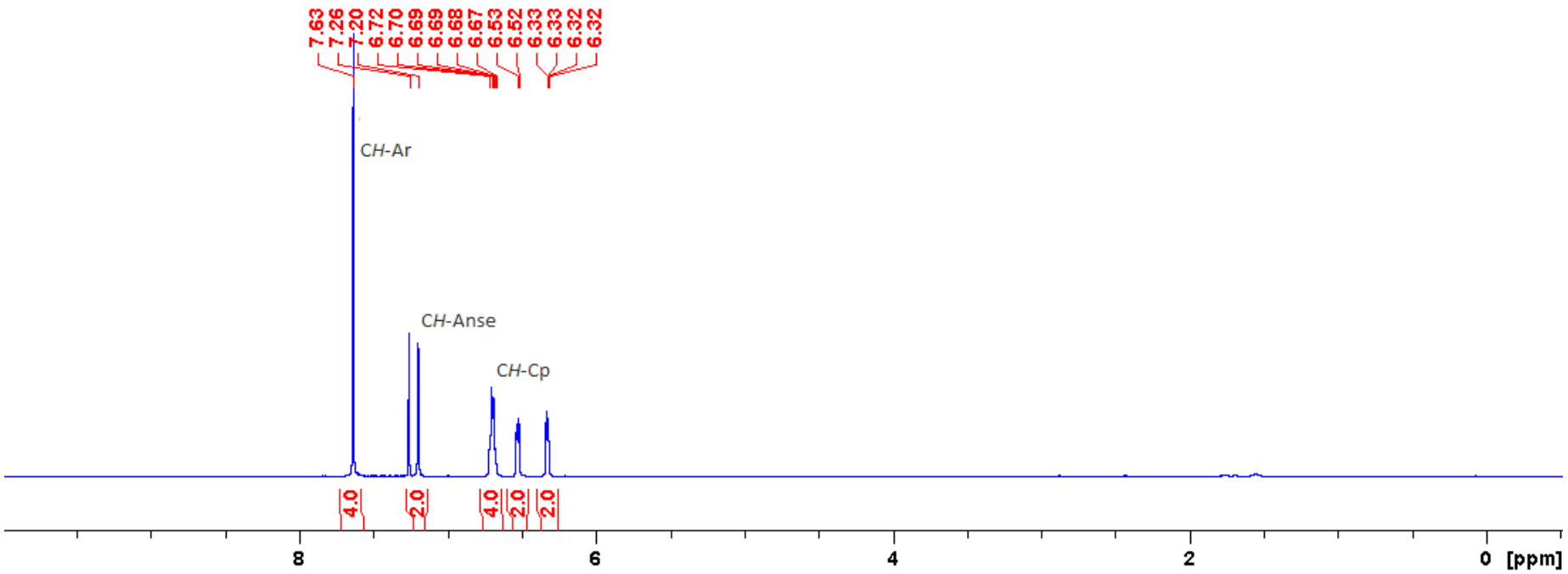
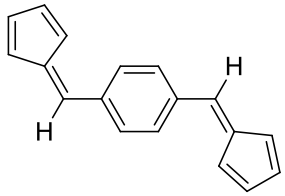


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **1b**.



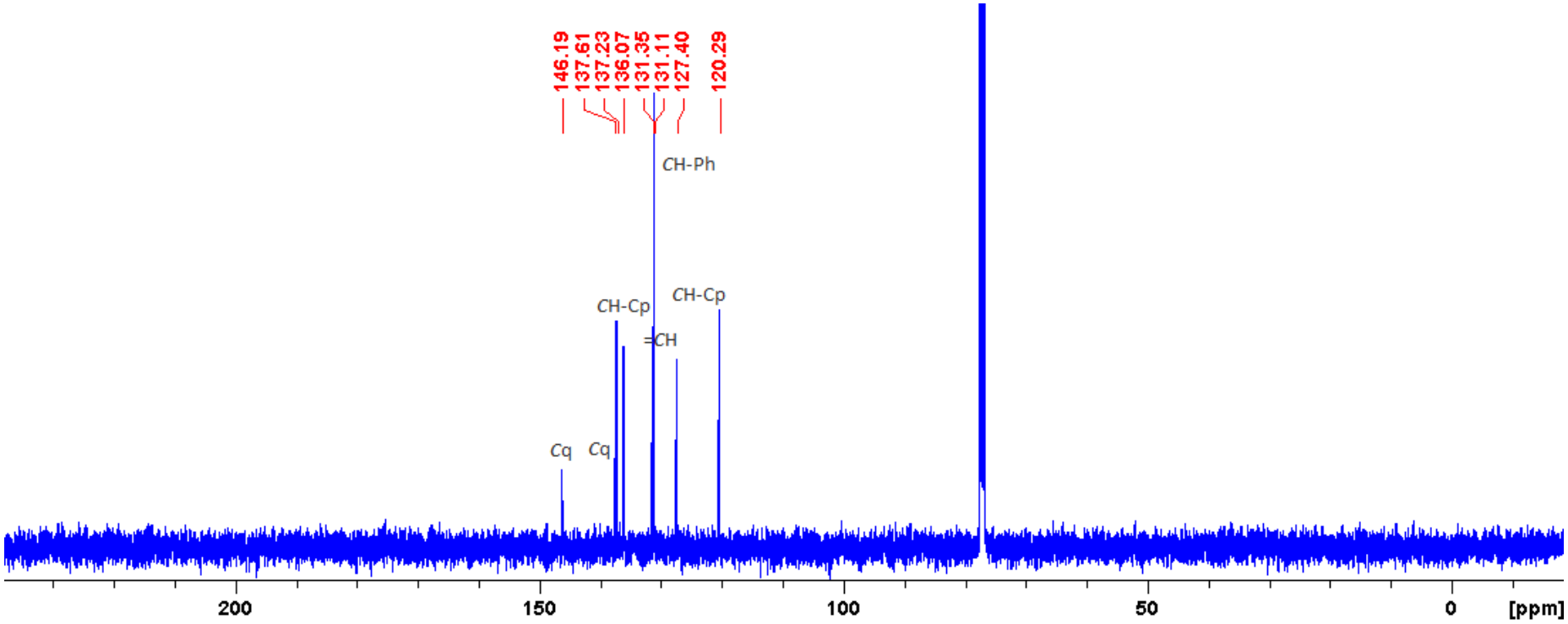


Figure S5. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **1b**.

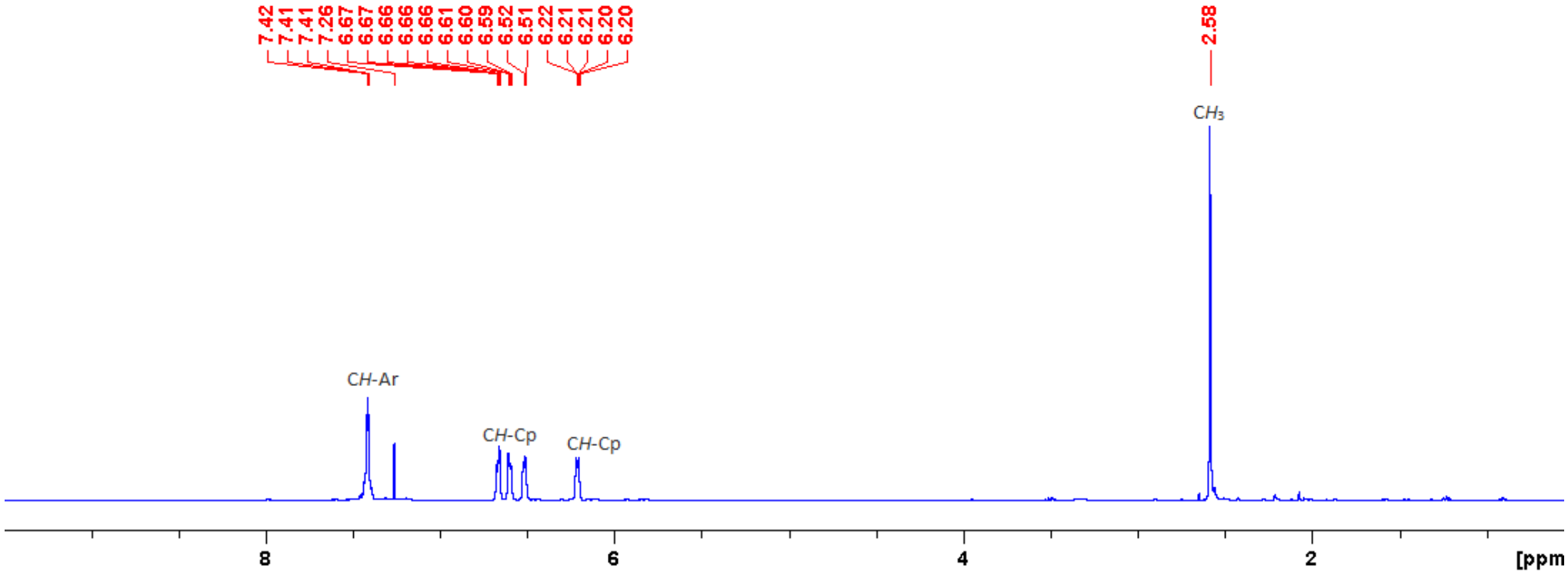
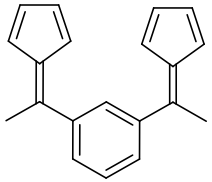


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **1c**.



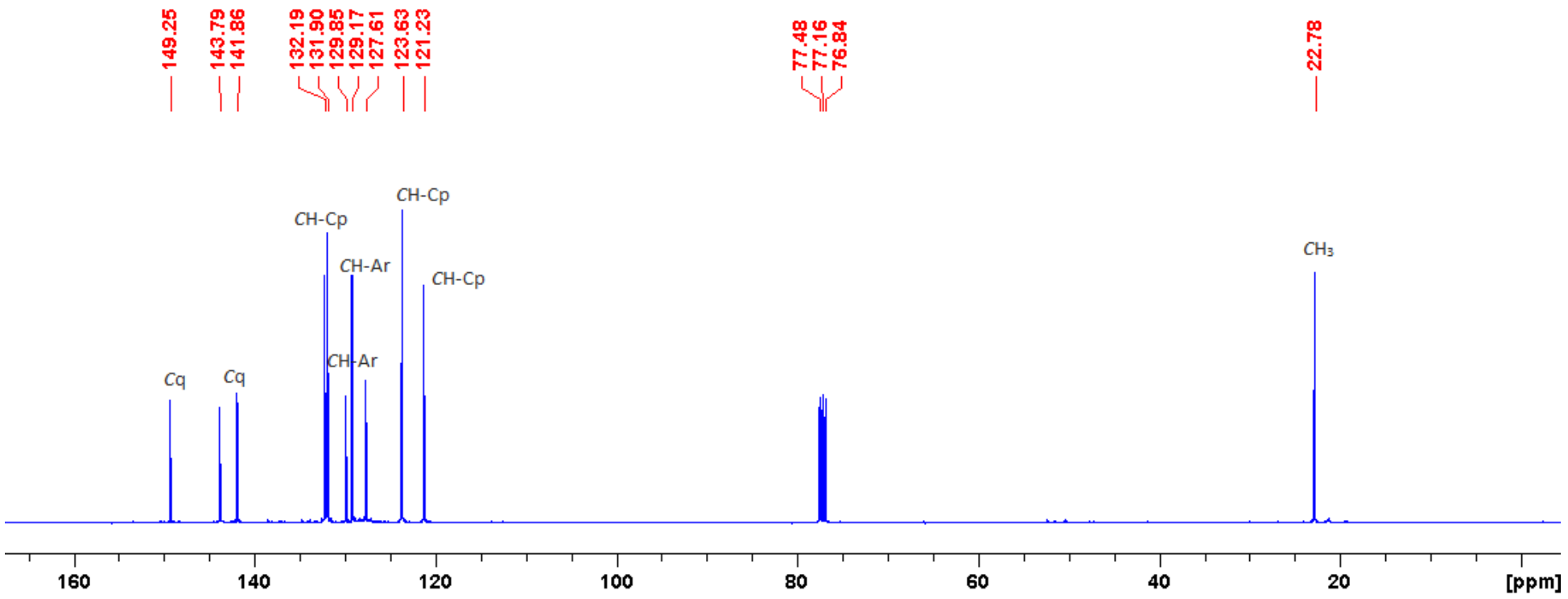


Figure S7. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **1c**.

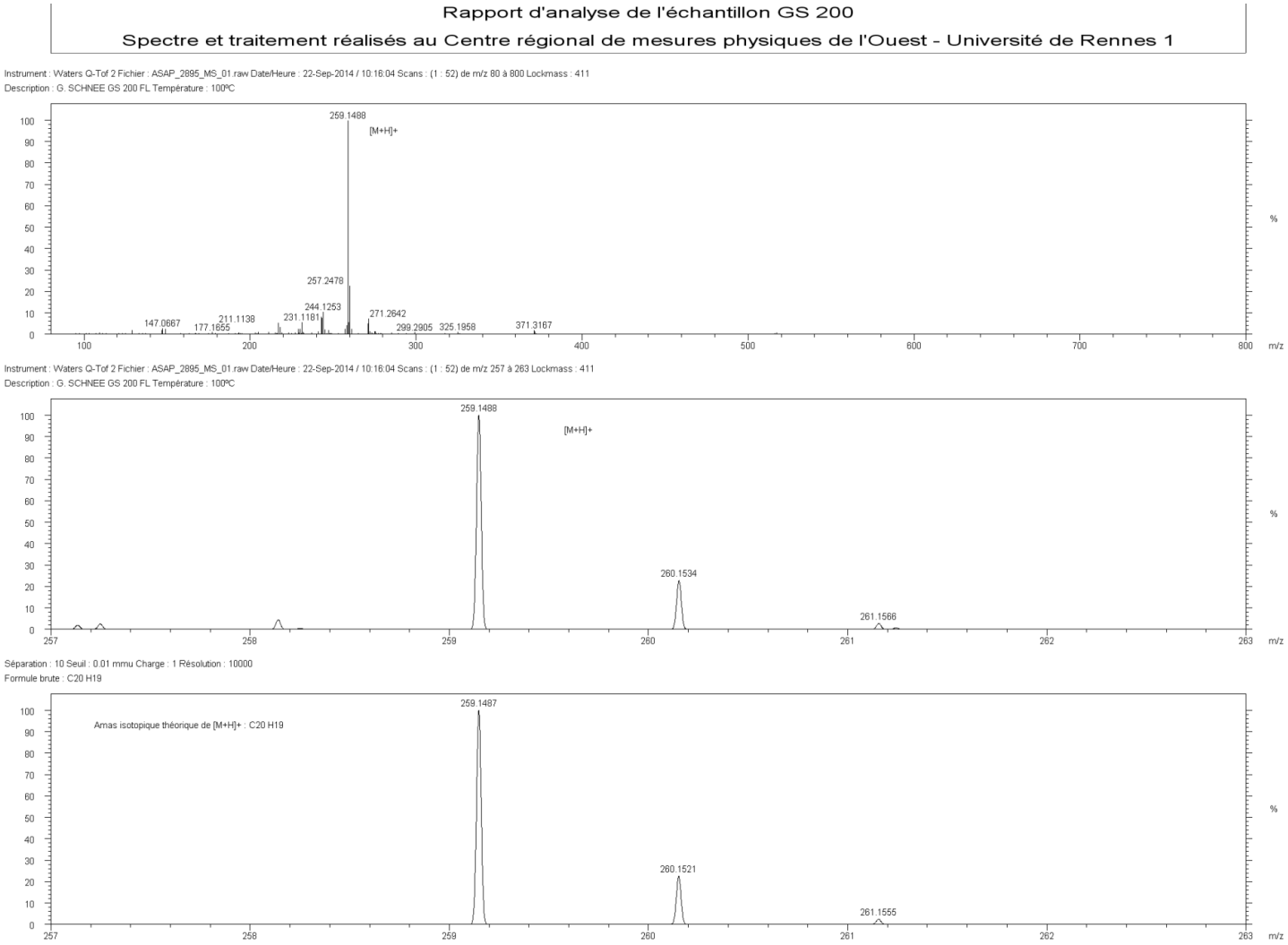


Figure S8. ASAP Mass spectrum of **1c**.

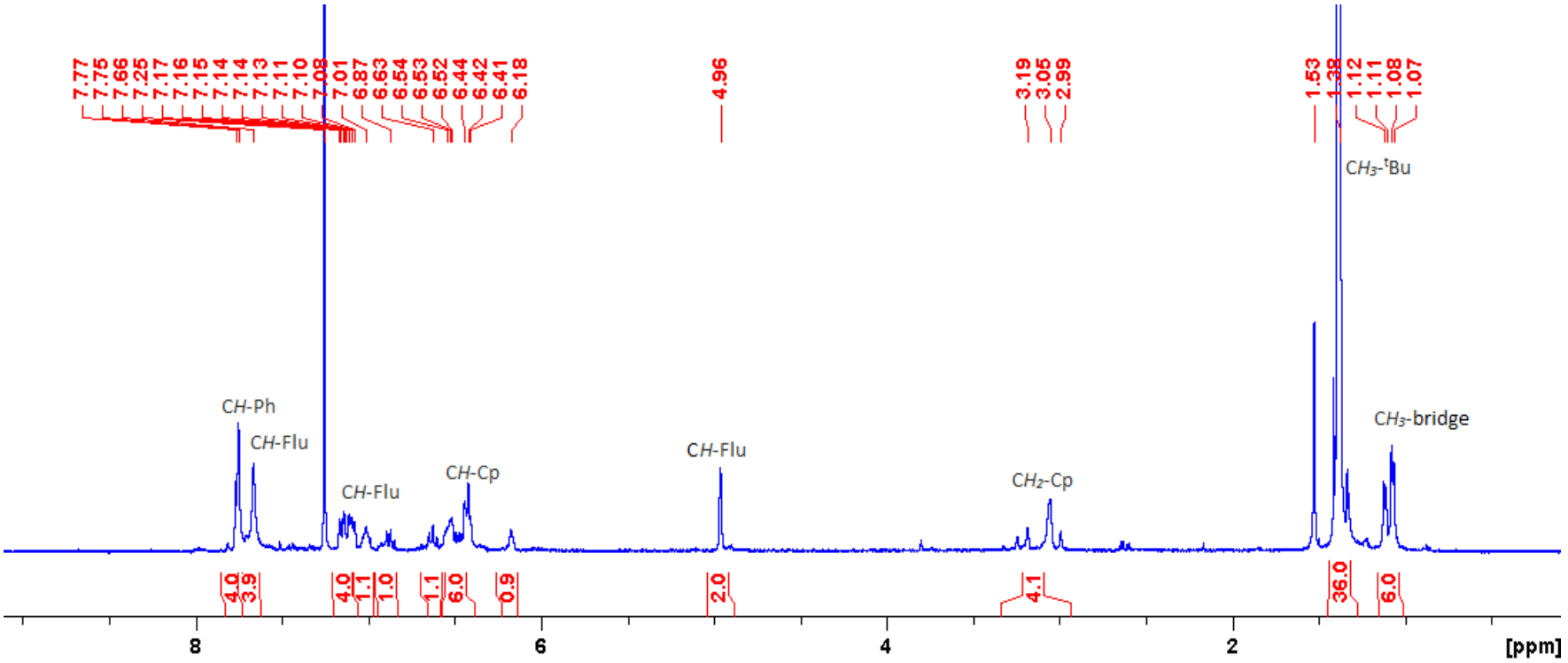
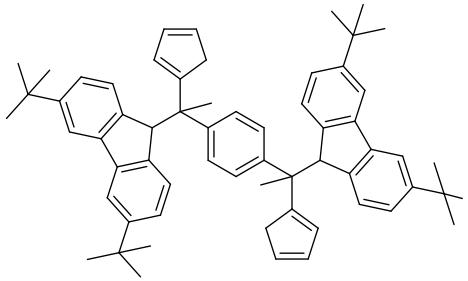


Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **2a**.



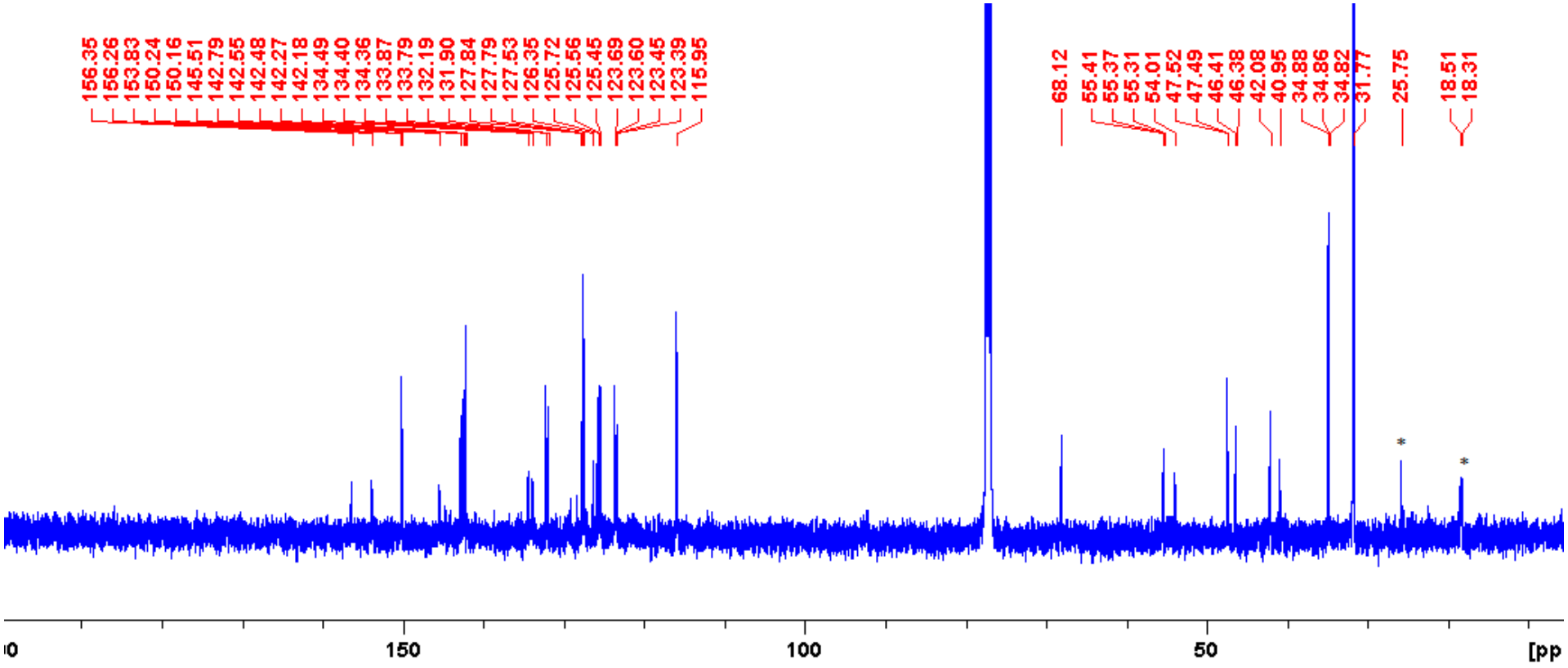


Figure S10. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **2a**. (* stand for residual solvent peaks)

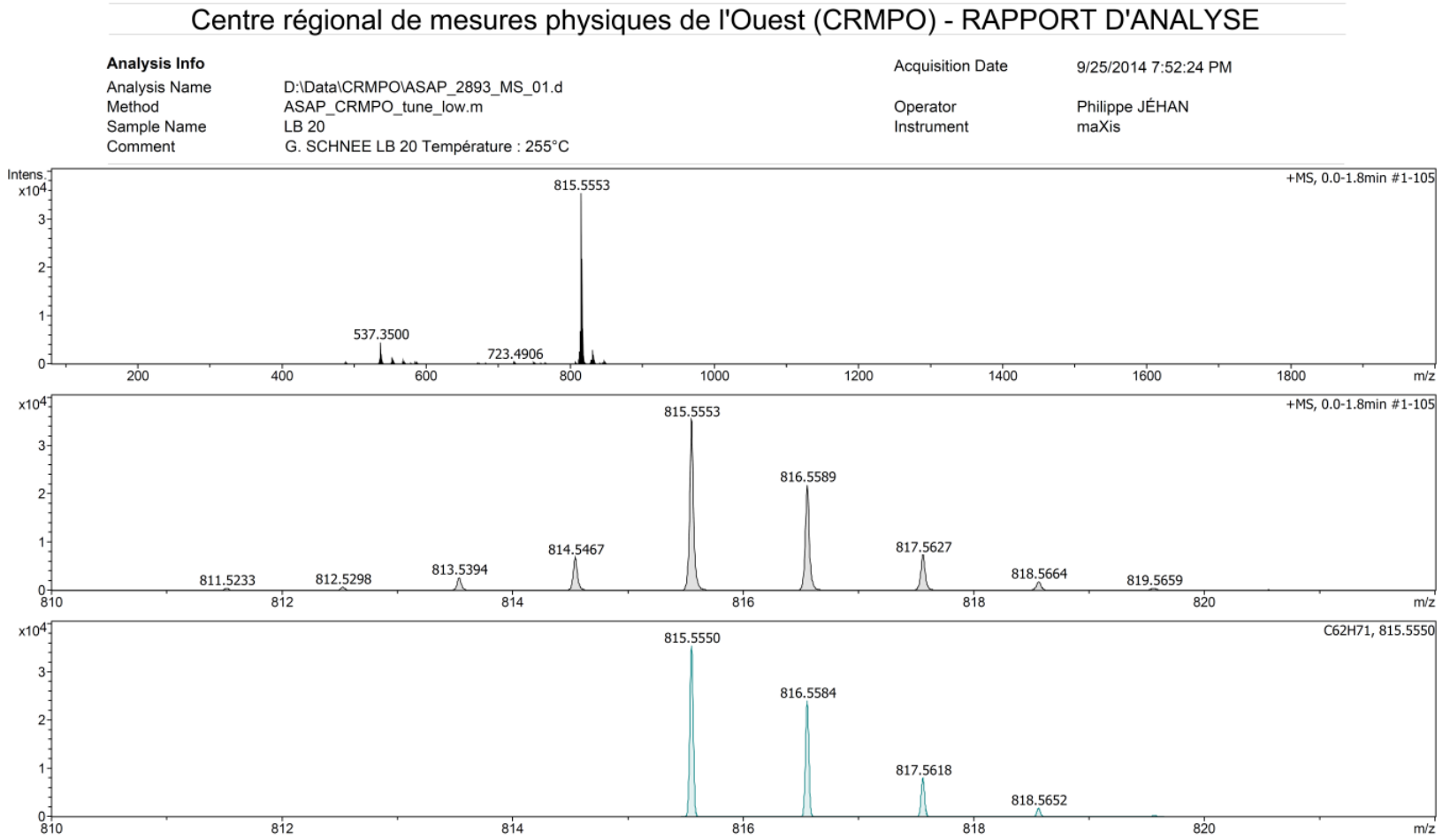


Figure S11. ASAP mass spectrum of **2a**.

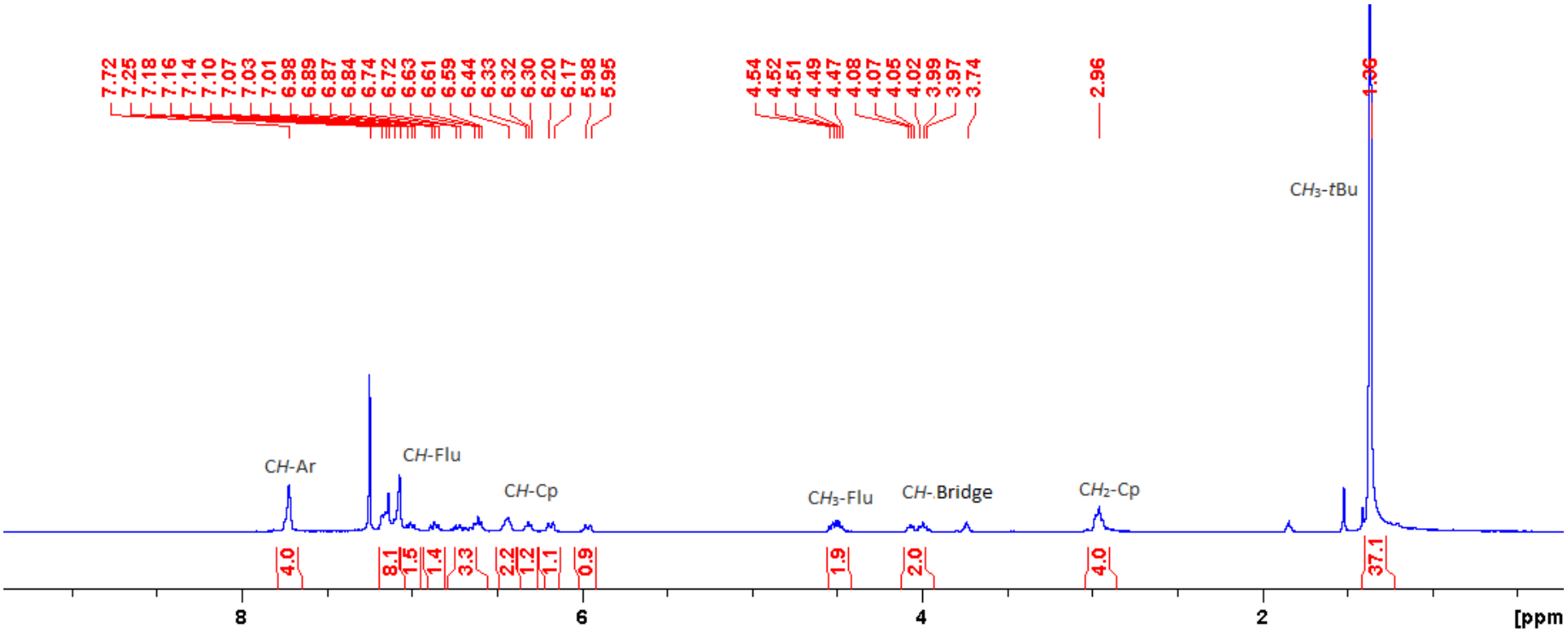
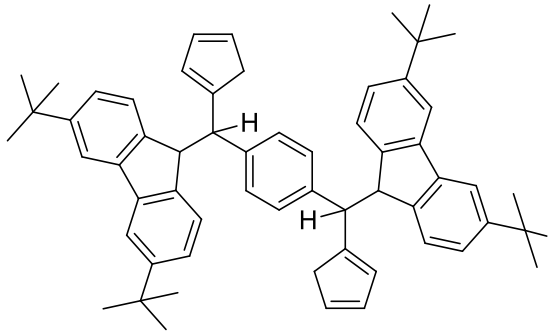


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **2b**.



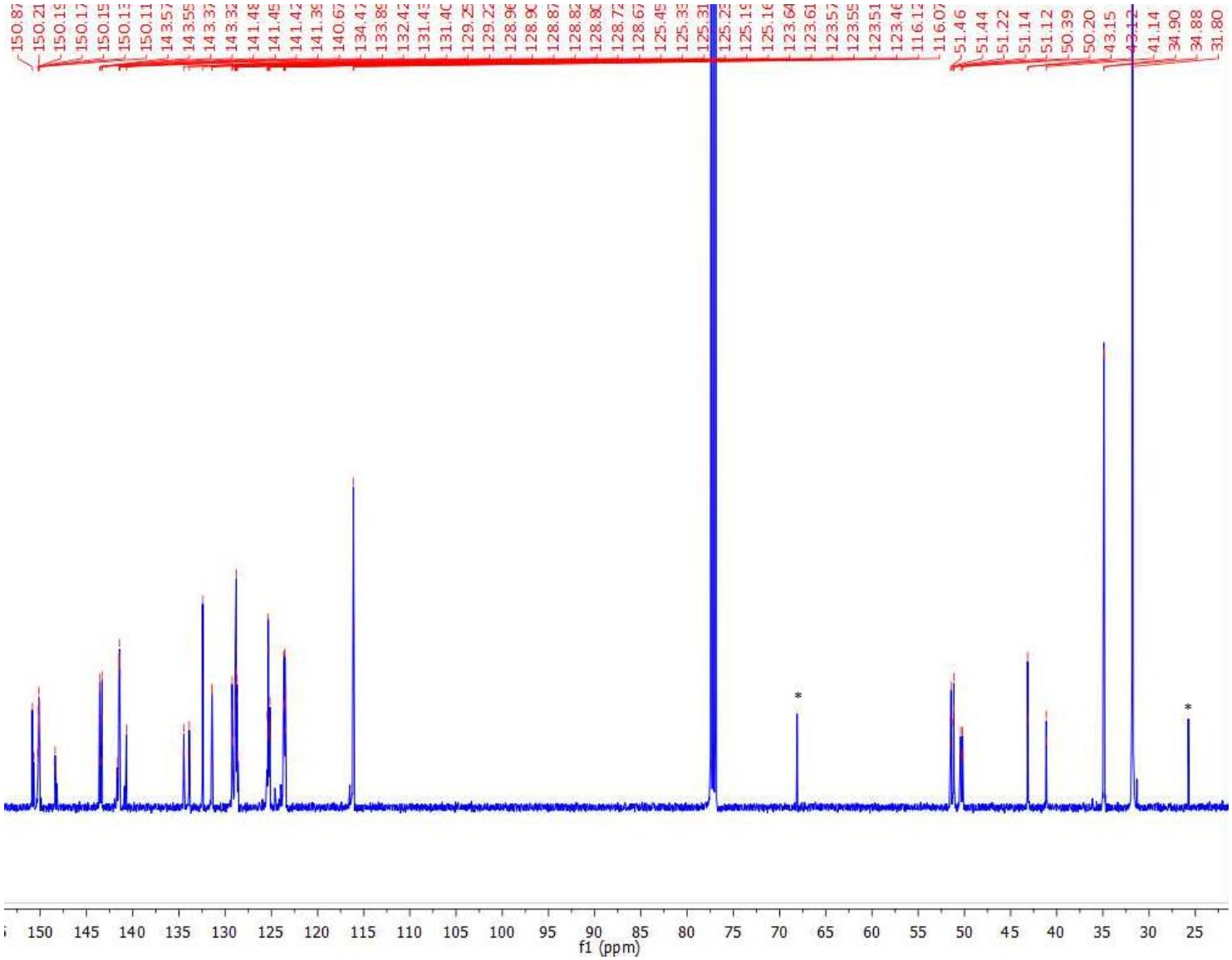


Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **2b**. (* stand for residual solvent peaks)

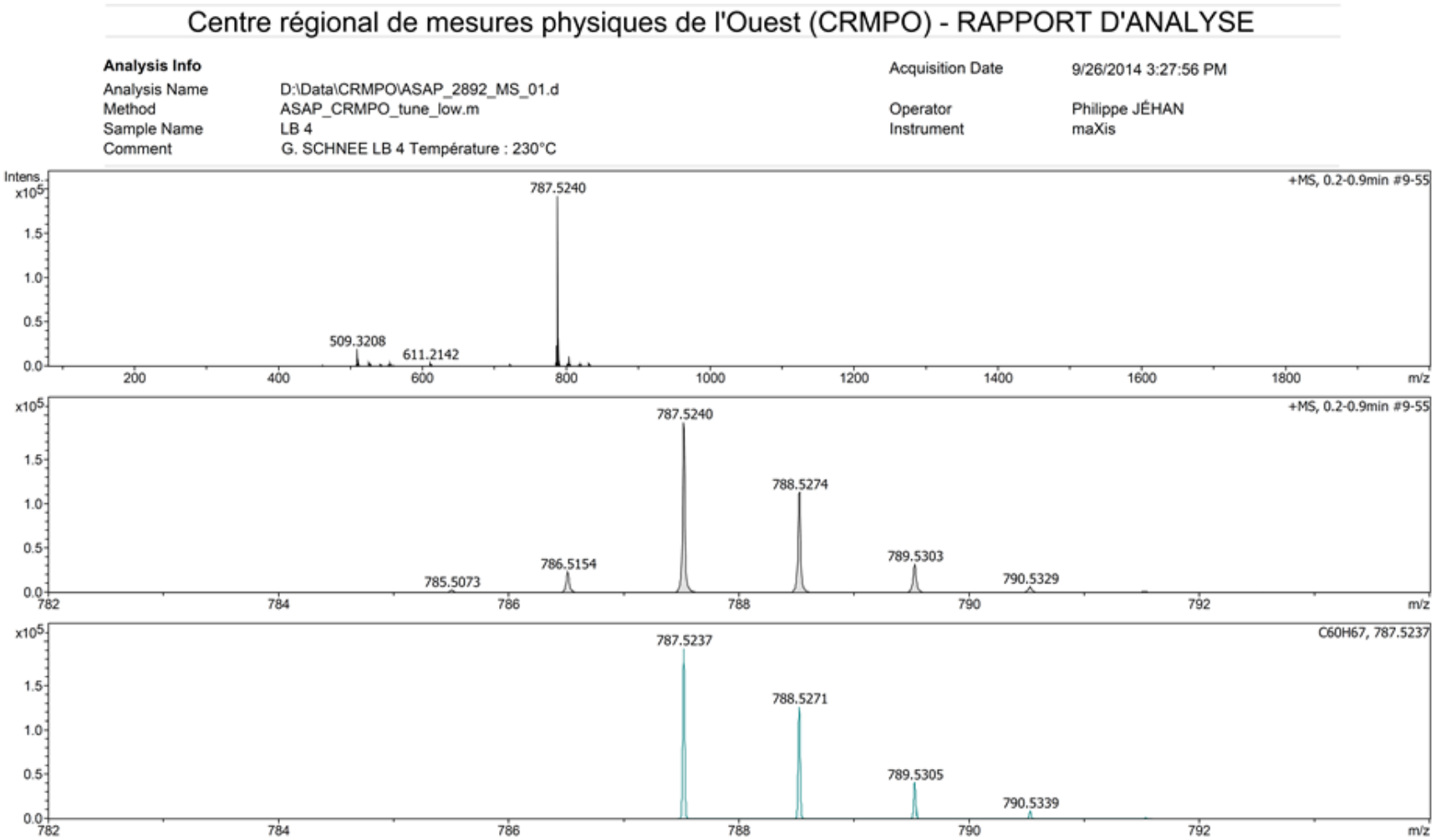


Figure S14. ASAP mass spectrum of **2b**.

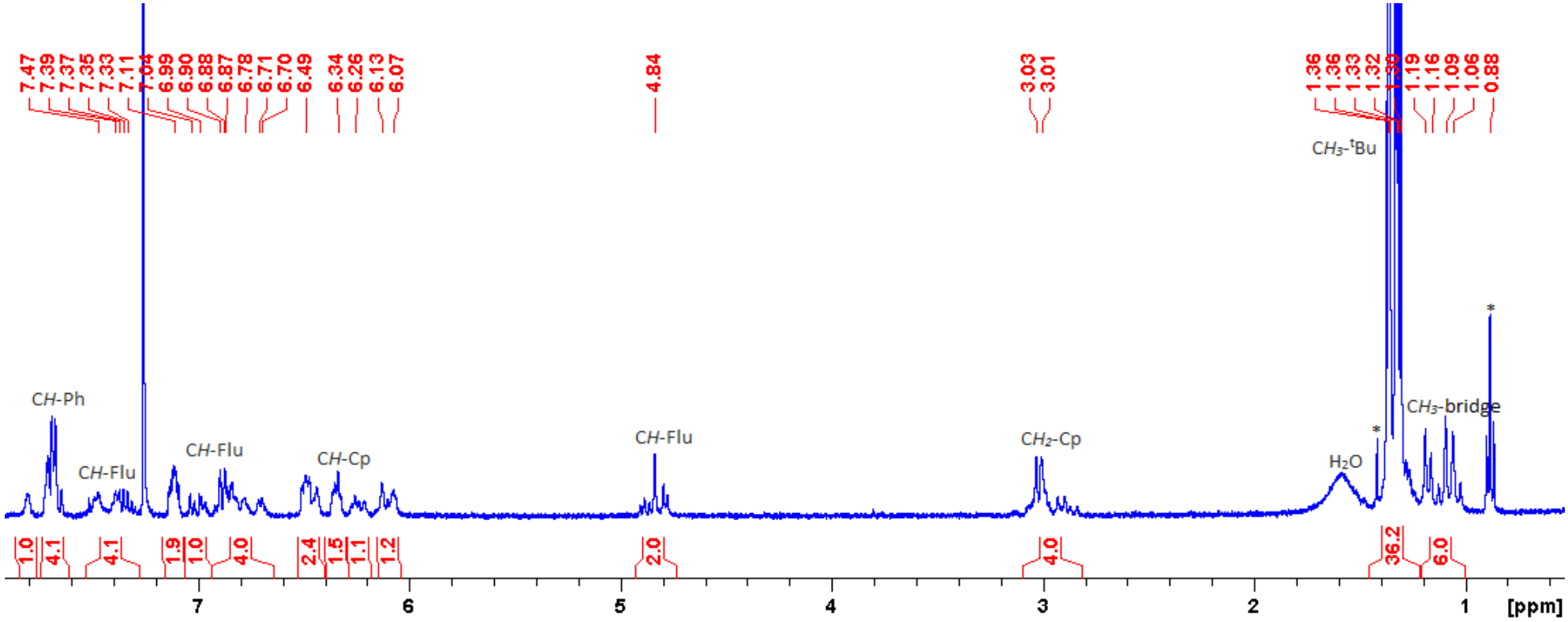


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 25 °C) of **2c**. (* stands for residual solvent peak)

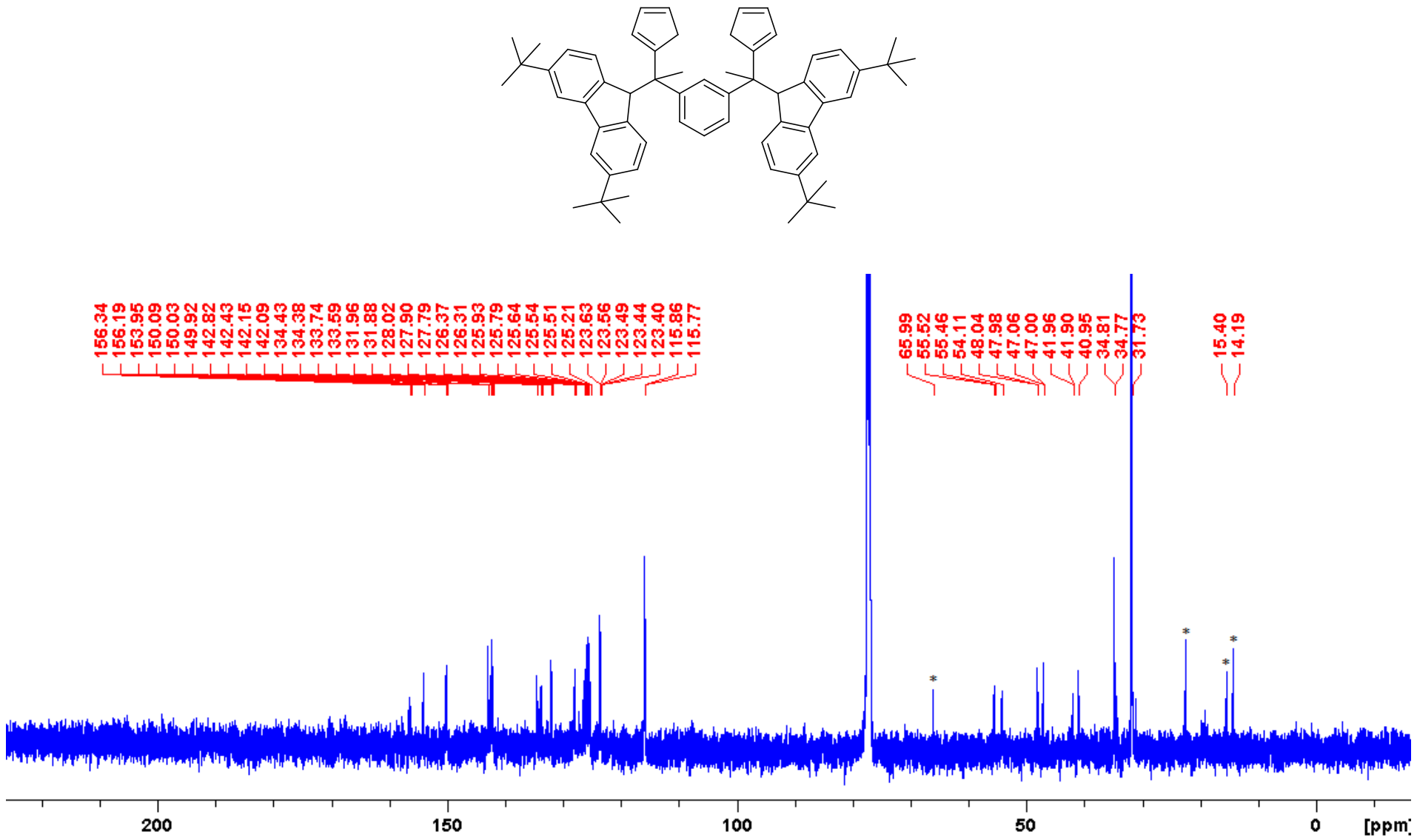


Figure S16. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **2c**. (* stand for residual solvent peaks)

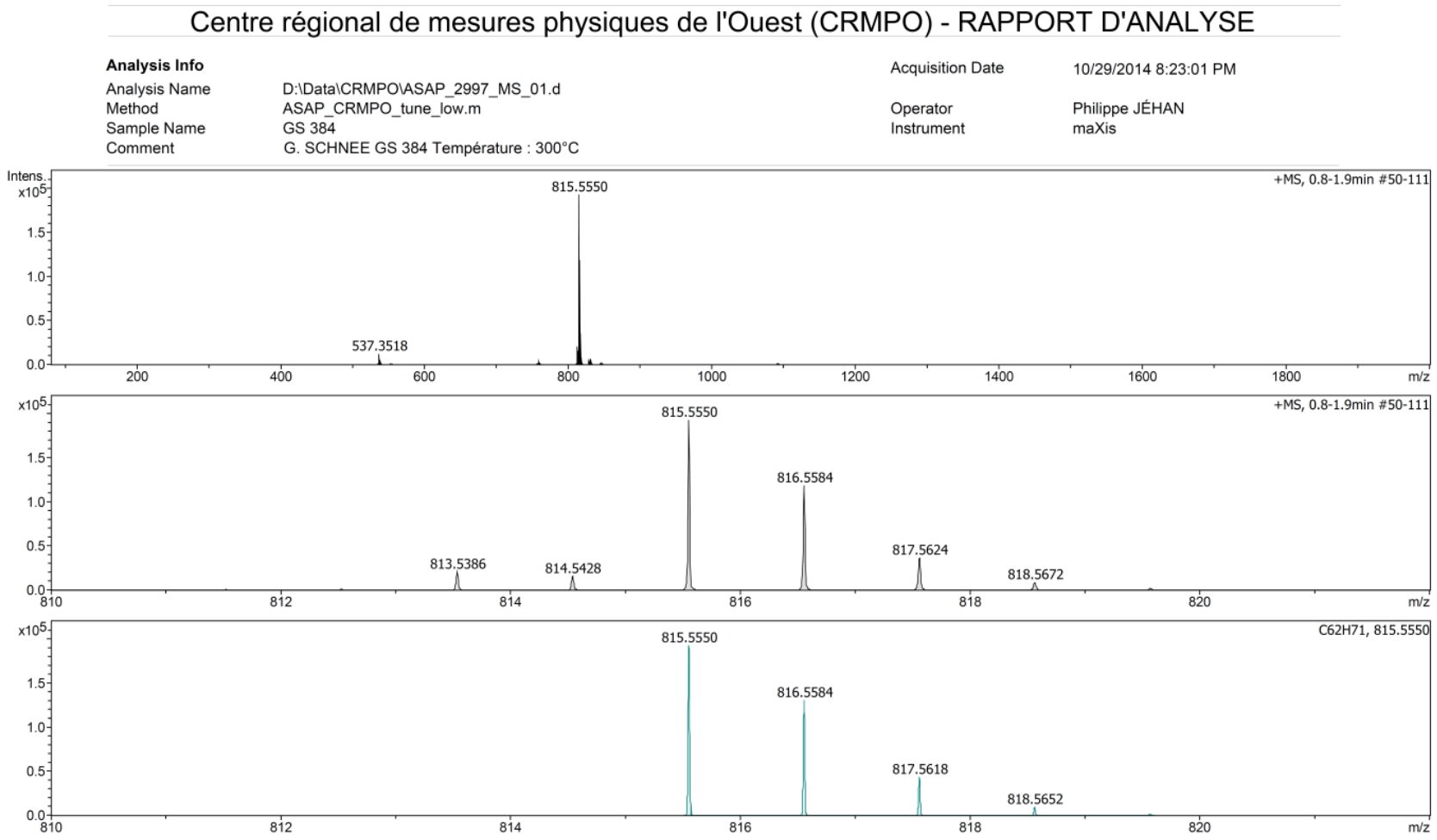


Figure S17. ASAP mass spectrum of **2c**.

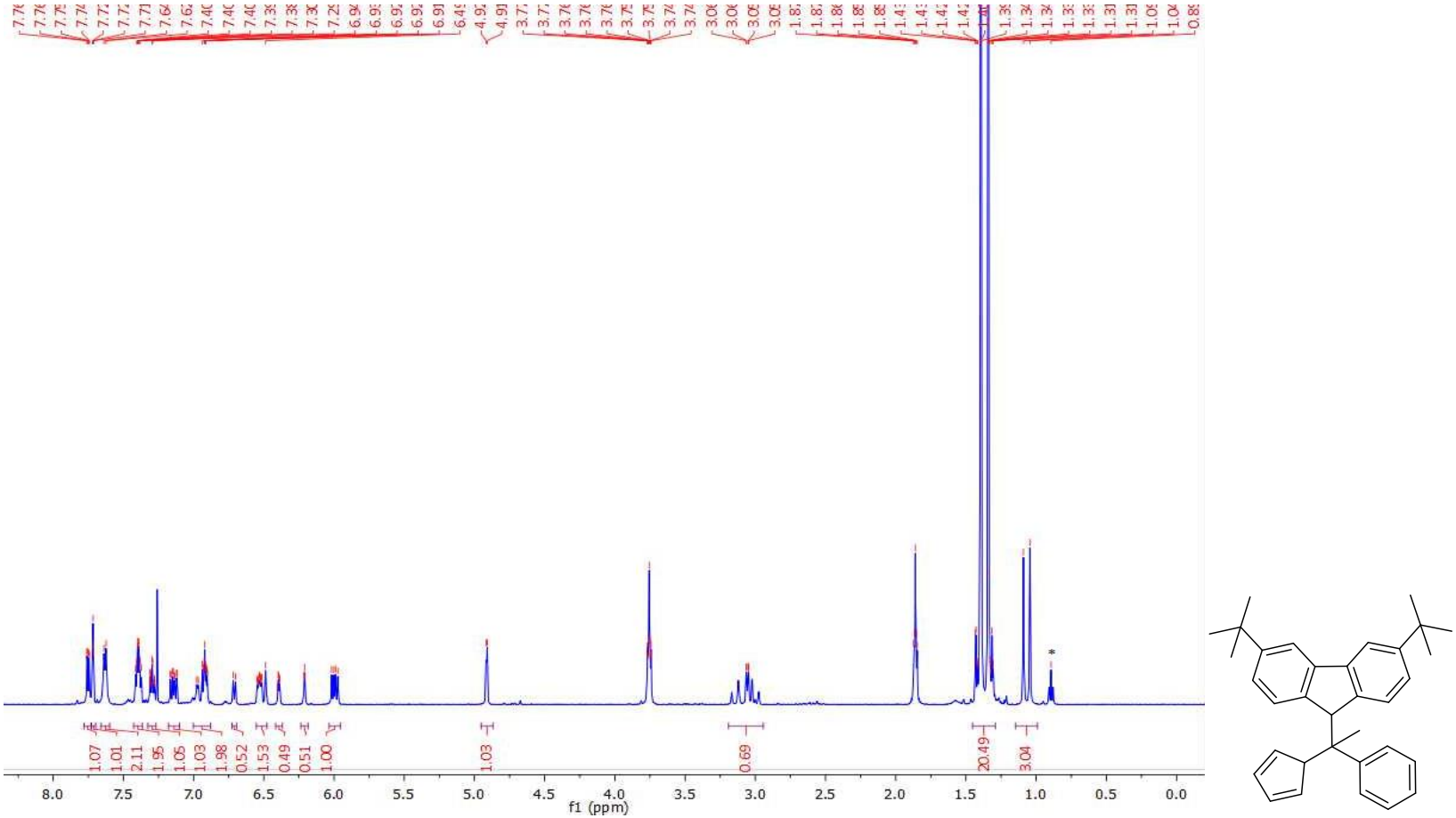


Figure S18. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 25 °C) of **2a'**. (*residual solvent peak)

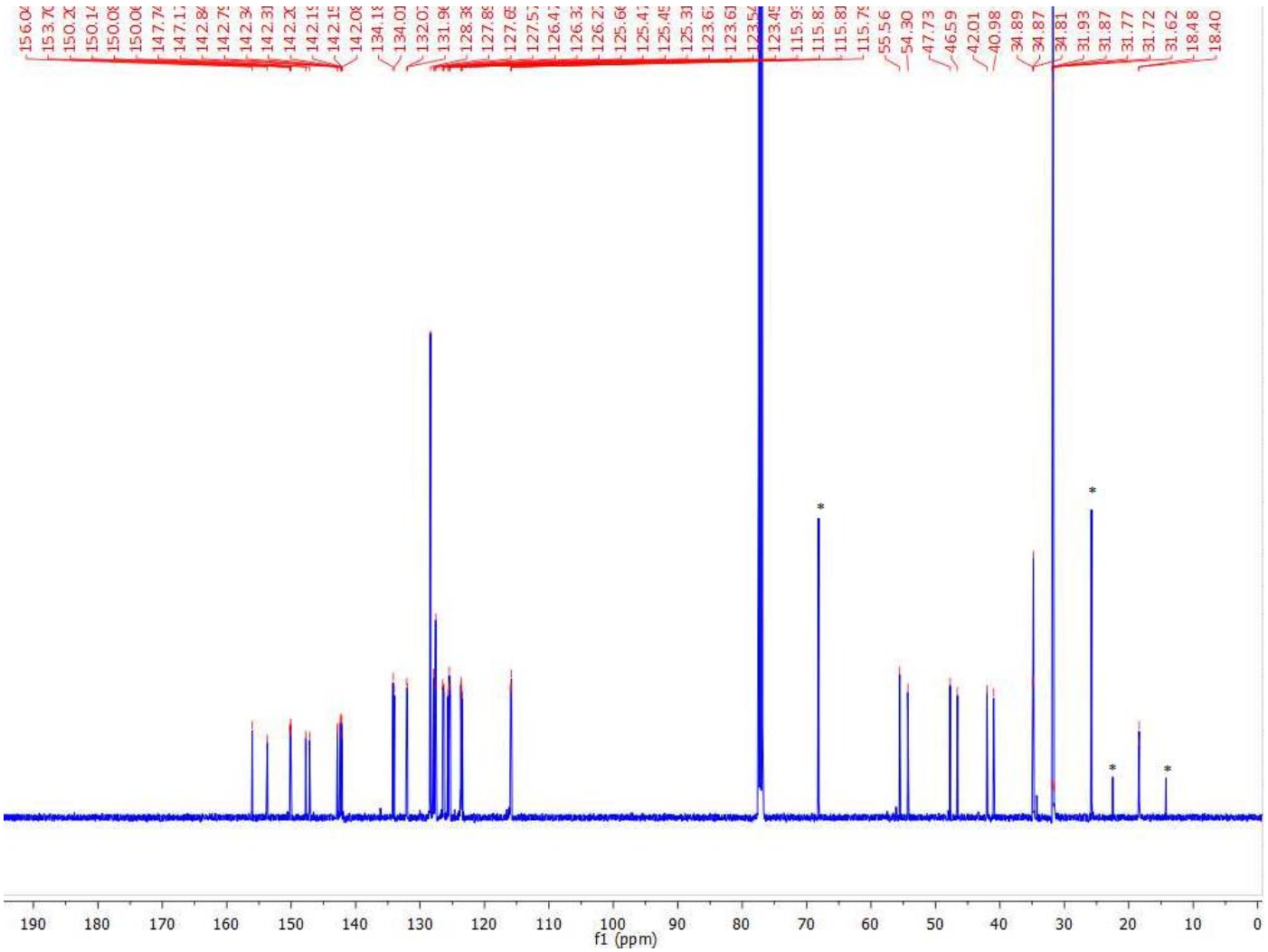


Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **2a'**. (*residual solvent peak)

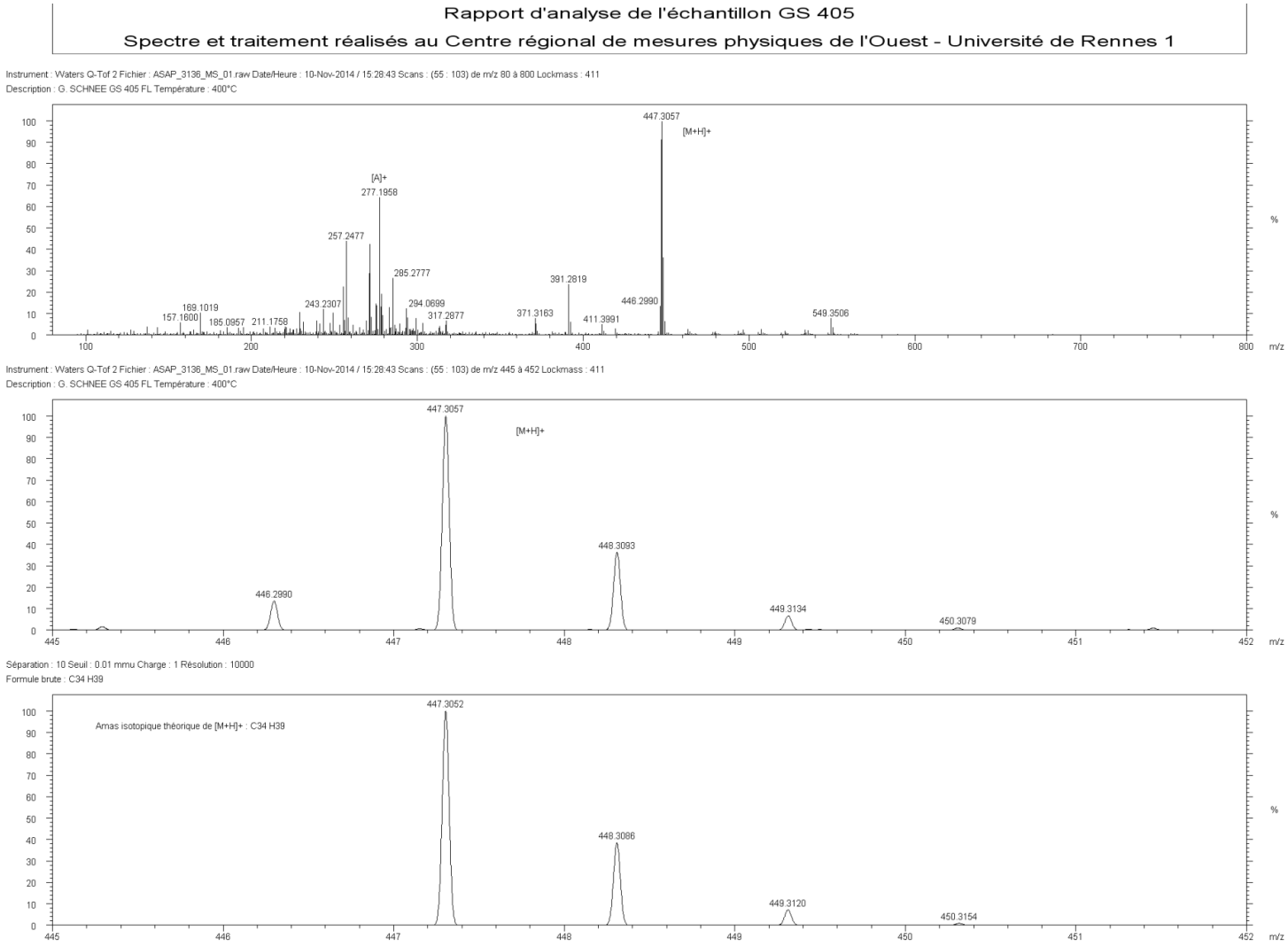


Figure S20. ASAP mass spectrum of **2a'**.

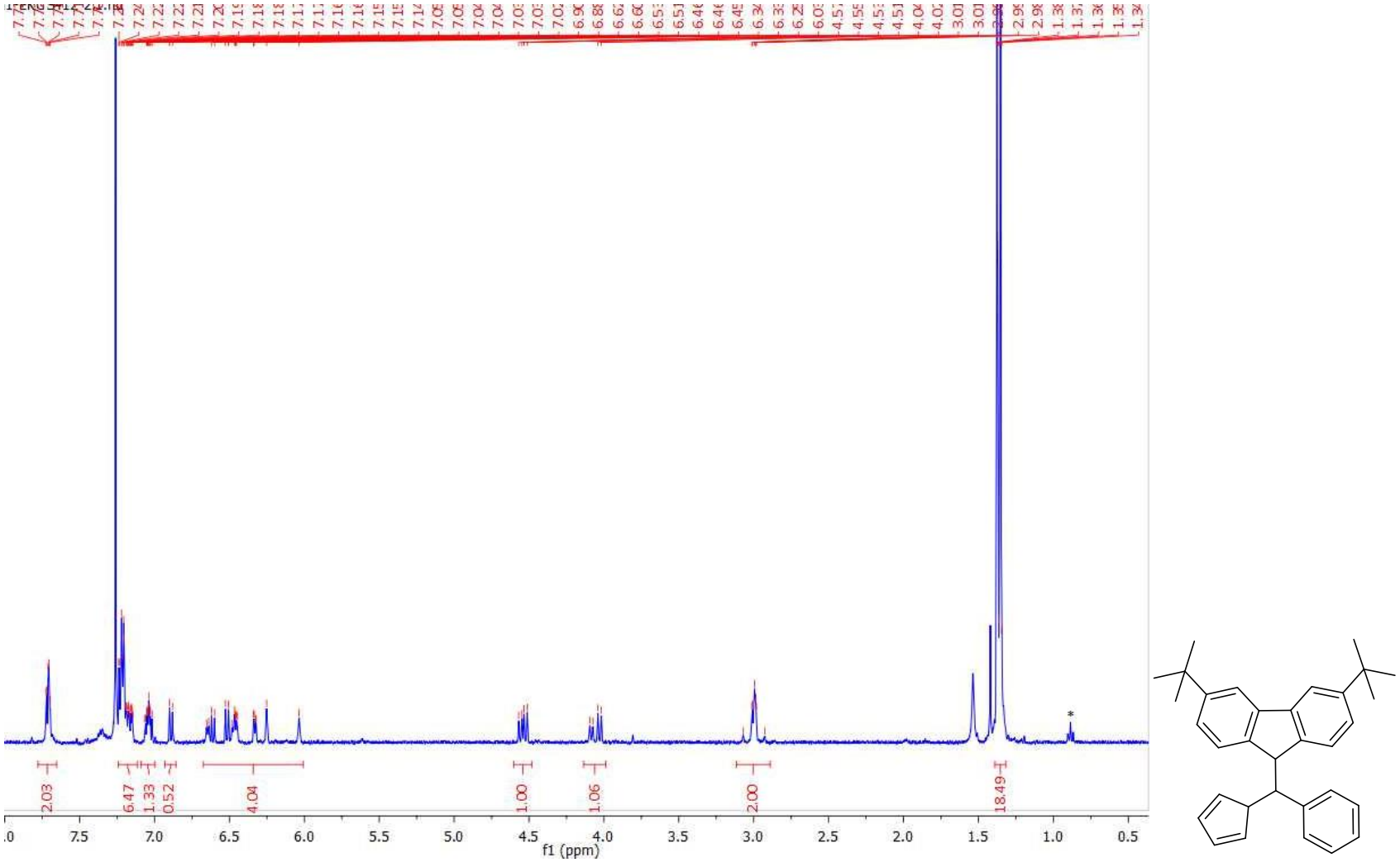


Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **2b'**. (*stands for residual solvent peak)

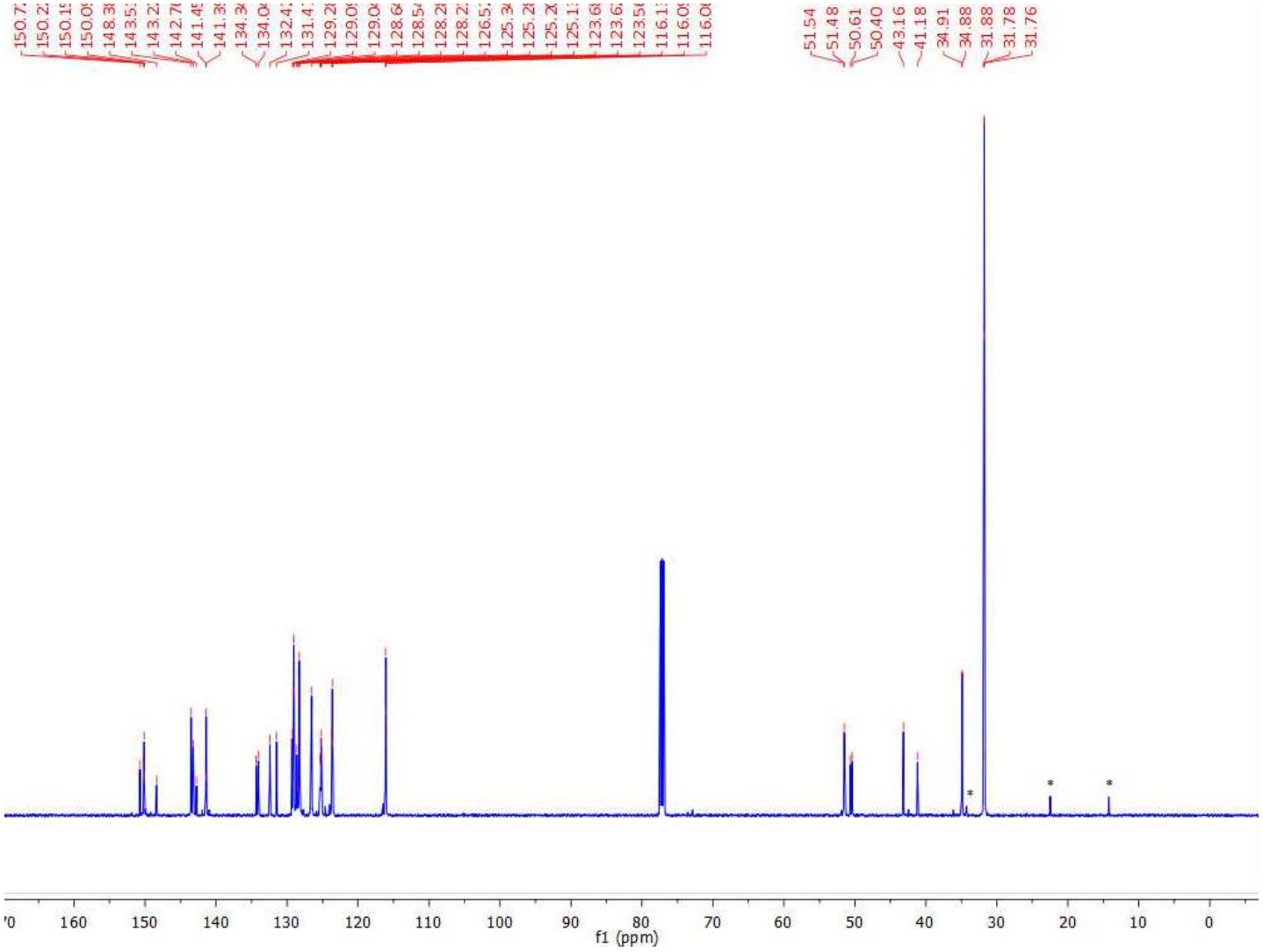


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 25 °C) of **2b'**. (*stand for residual solvent peak)

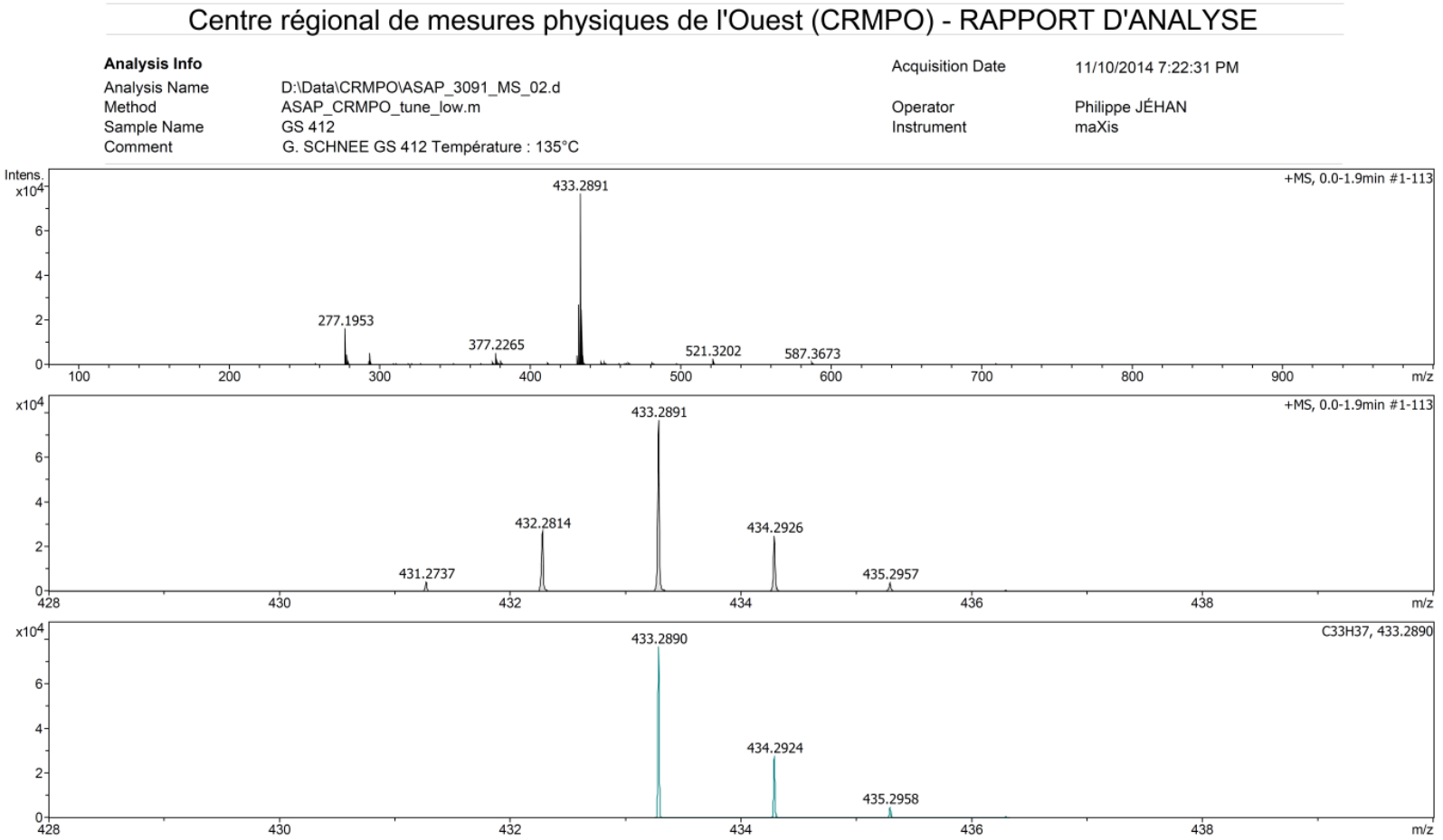


Figure S23. ASAP mass spectrum of **2b'**.

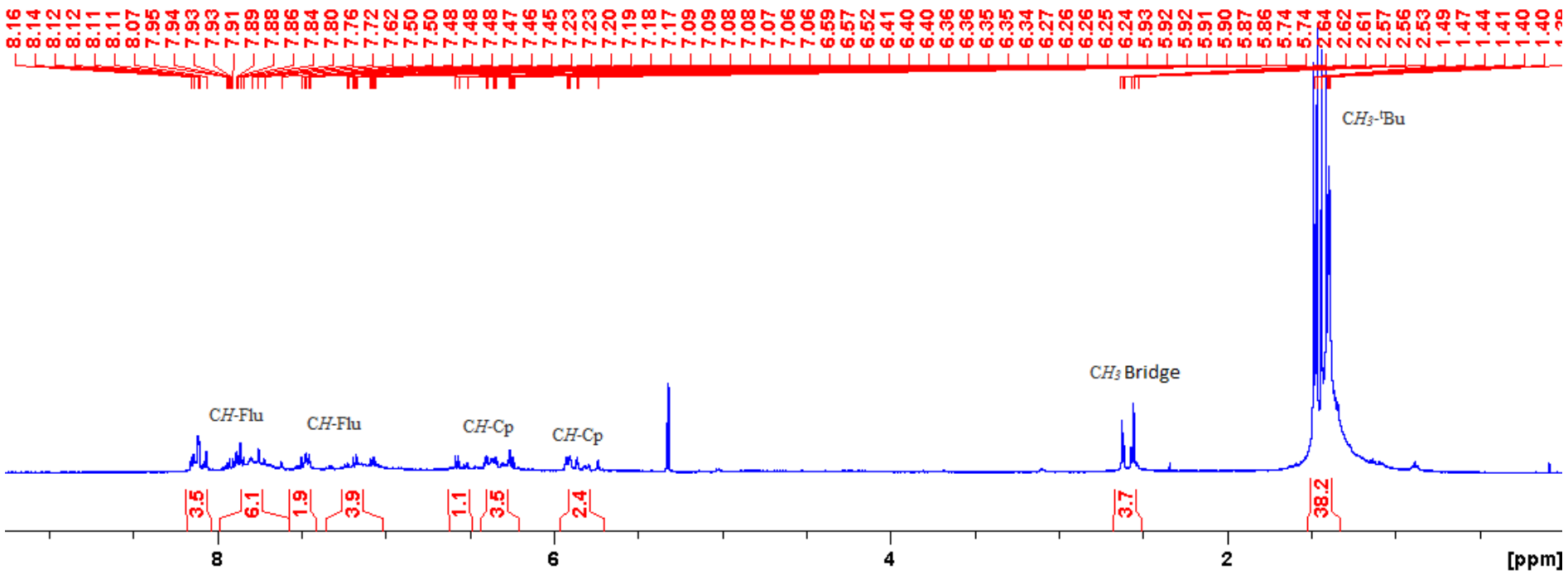
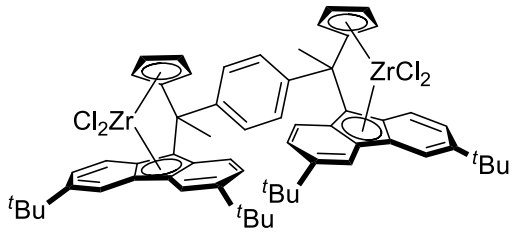


Figure S24. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, 25 °C) of **3a-Zr$_2$**.



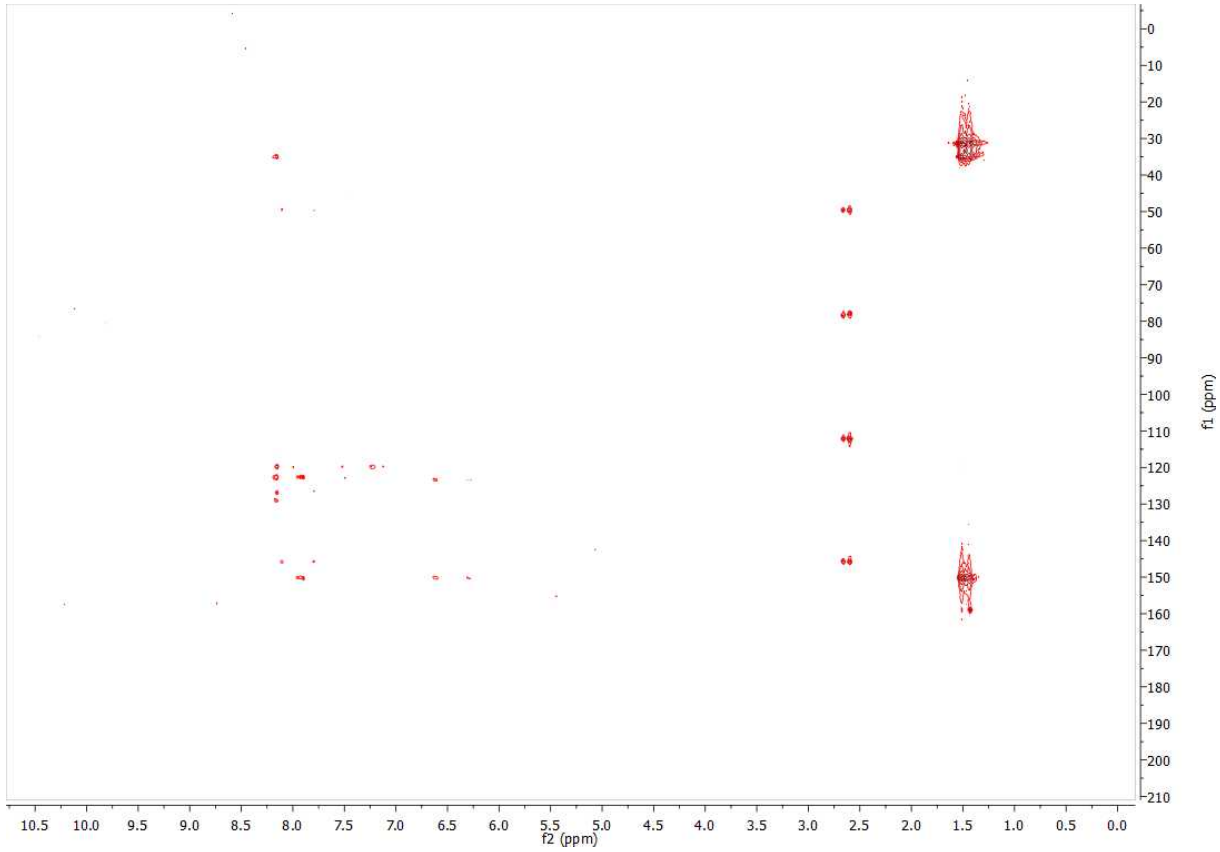


Figure S25. HMBC spectrum (CD_2Cl_2, 500 MHz, 25 °C) of **3a-Zr$_2$**.

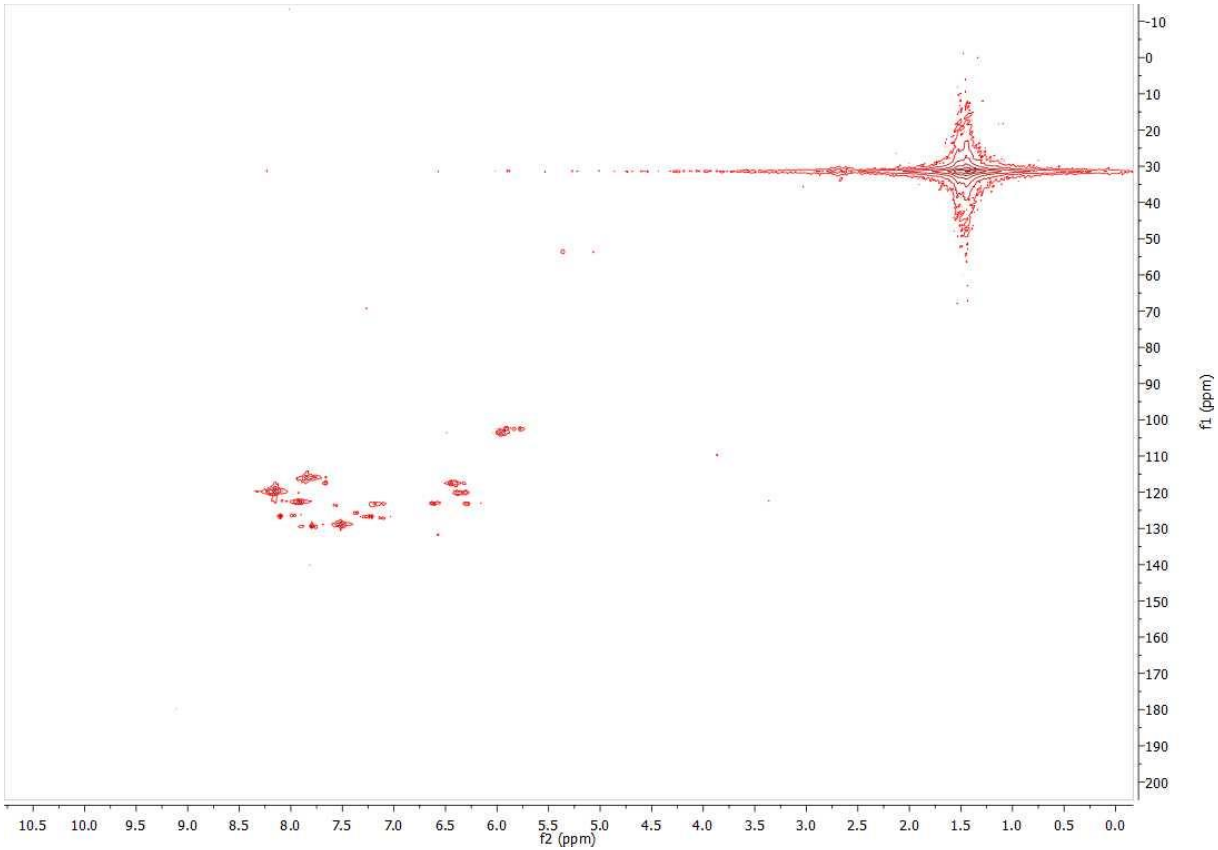


Figure S26. HSQC spectrum (CD_2Cl_2, 500 MHz, 25 °C) of **3a-Zr$_2$**.

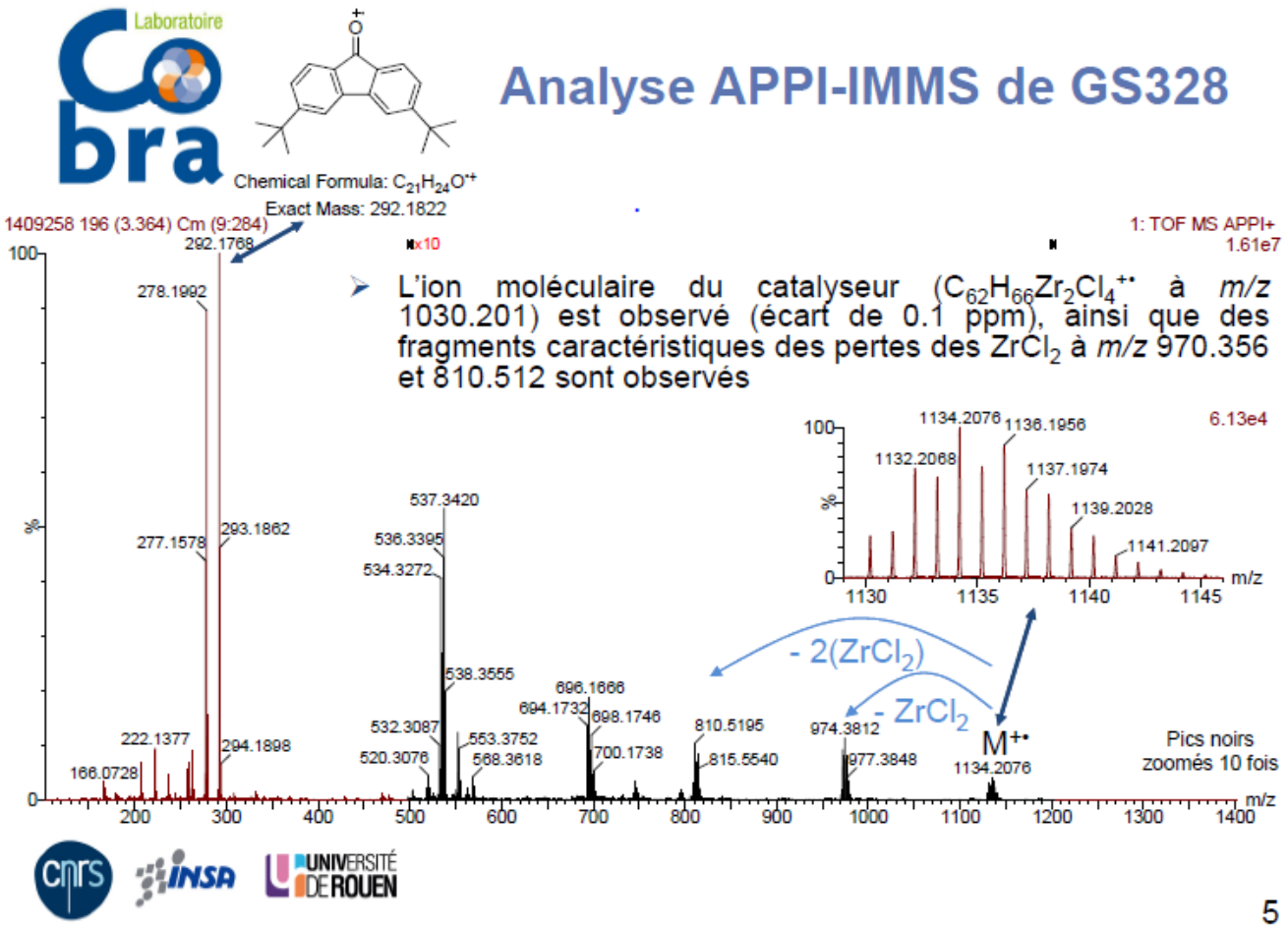


Figure S27. APPI-IMMS of **3a-Zr$_2$**.

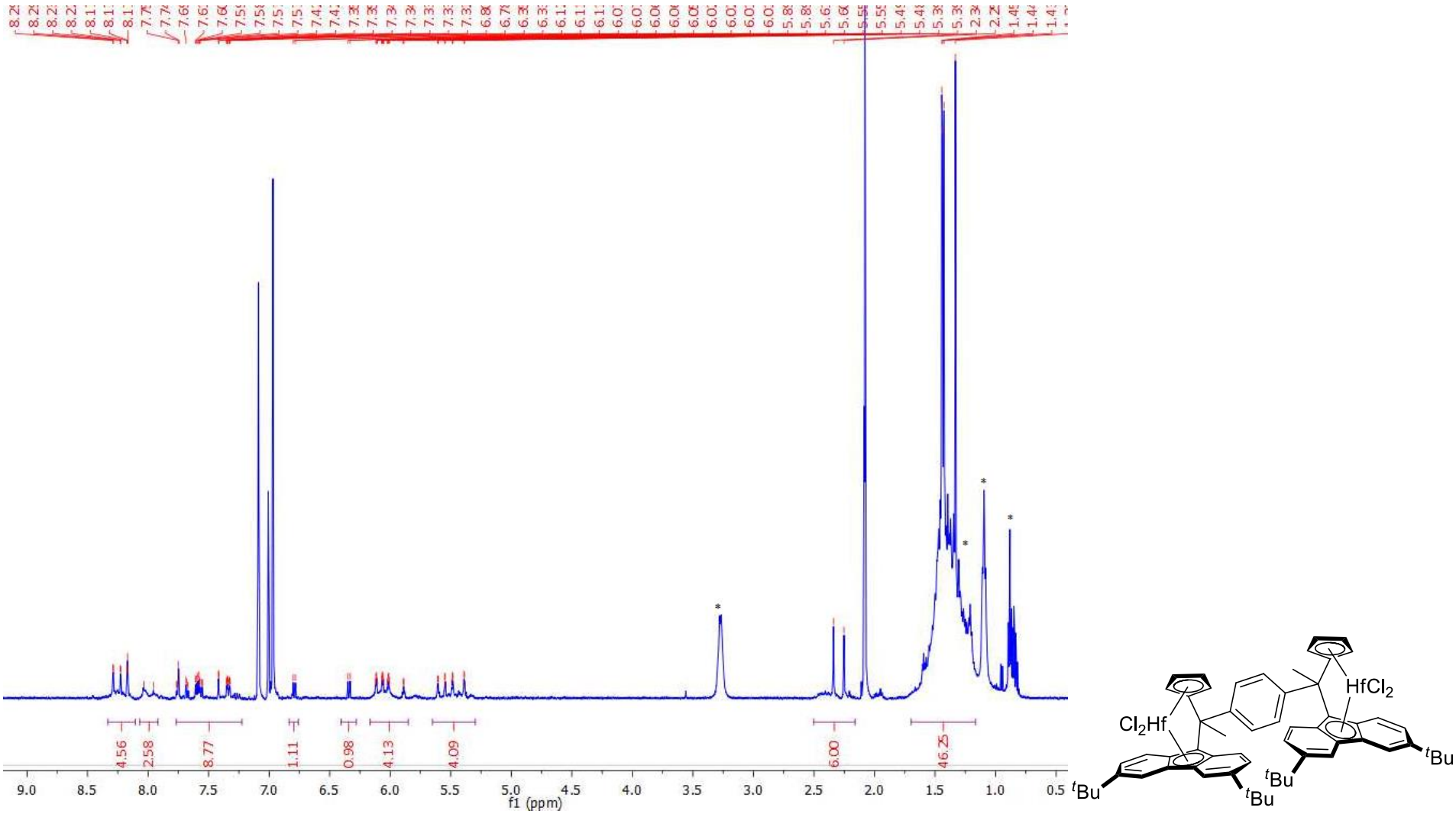


Figure S28. ^{1}H NMR spectrum (toluene-d_8, 500 MHz, 25 °C) of **3a-Hf$_2$**. (* stand for residual solvent peaks)

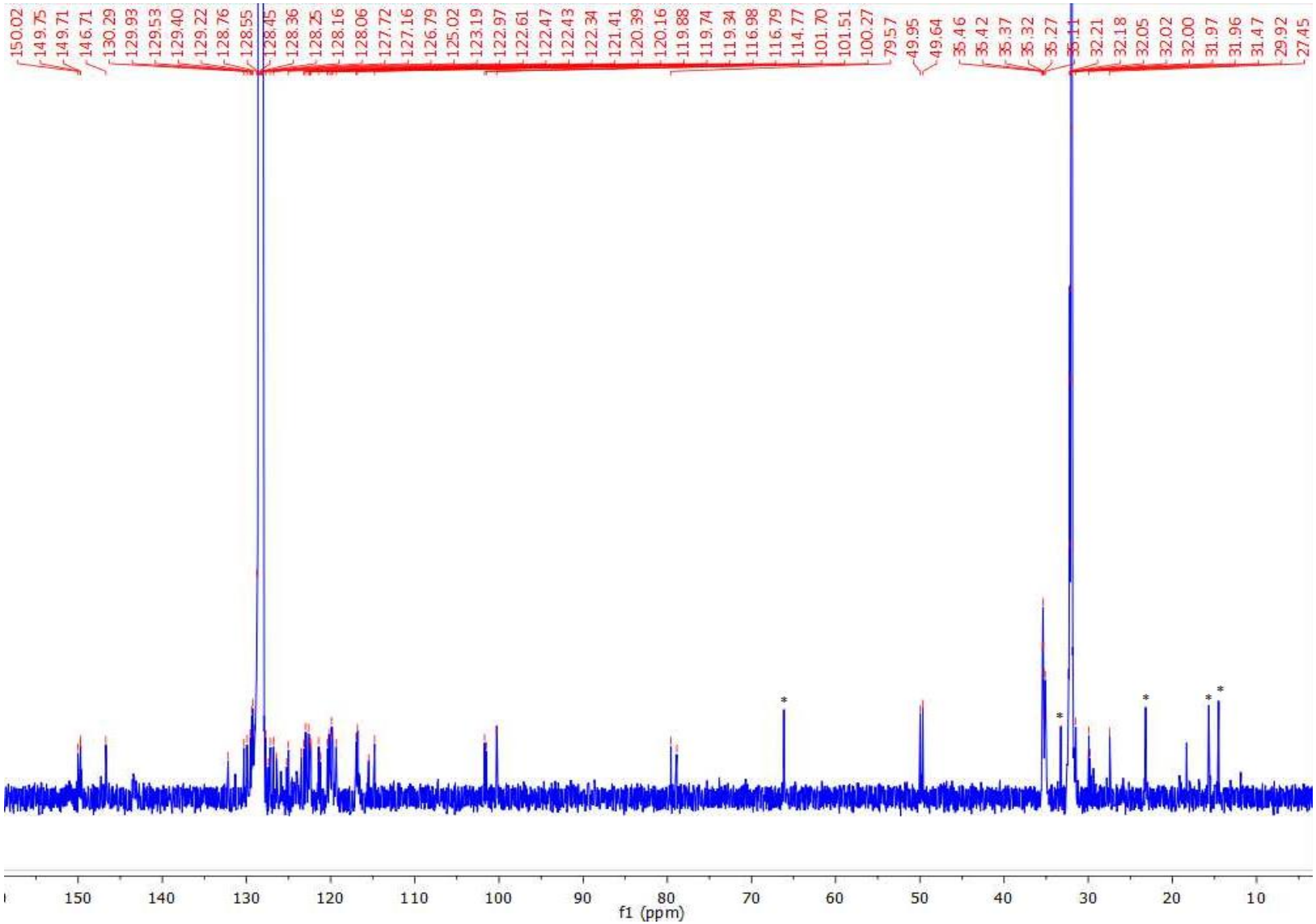


Figure S29. ^{13}C NMR spectrum (C_6D_6, 125 MHz, 25 °C) of **3a-Hf$_2$**. (*residual solvent peak)

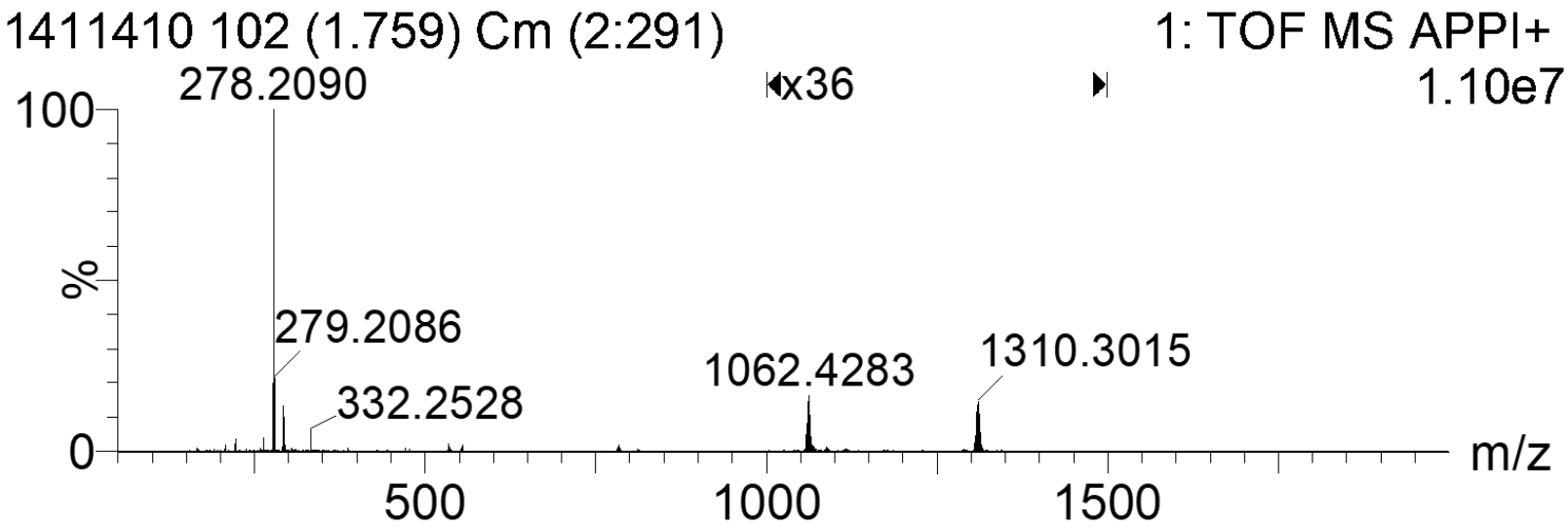


Figure S30. APPI-IMMS of **3a-Hf$_2$**.

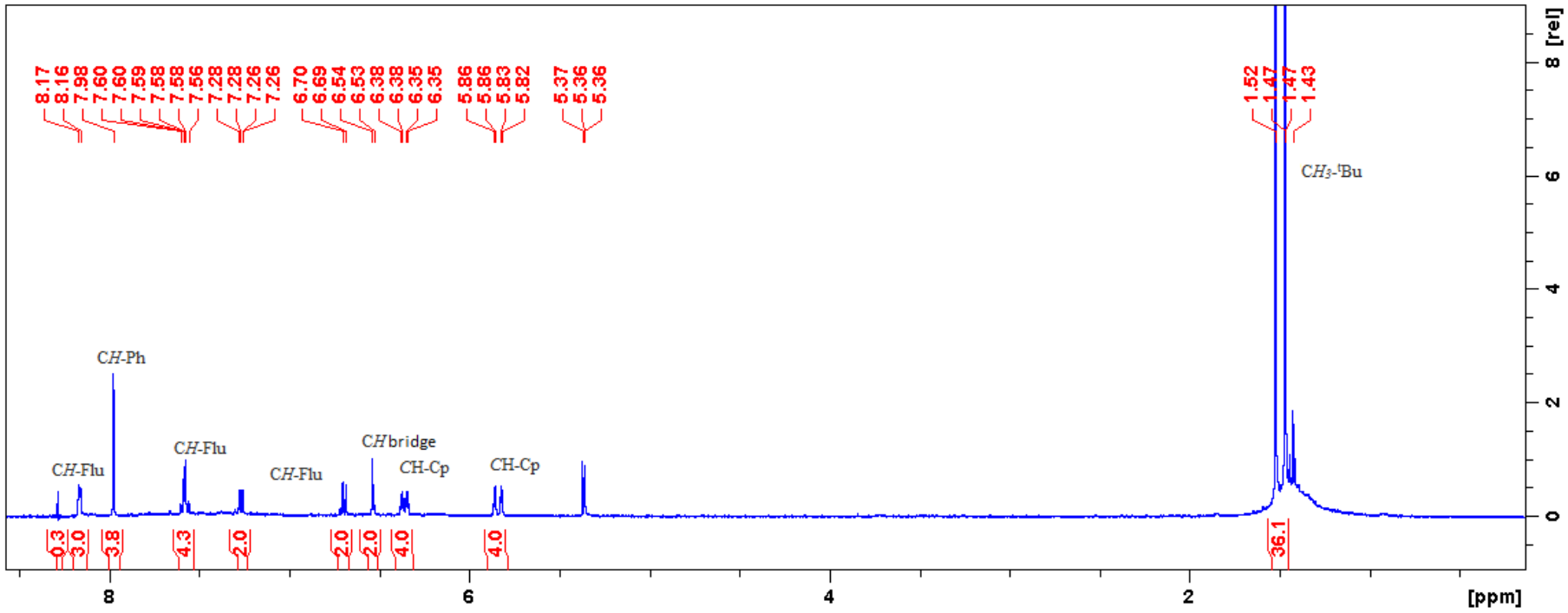
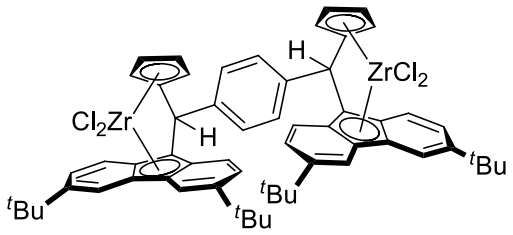


Figure S31. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, 25 °C) of **3b-Zr$_2$.**



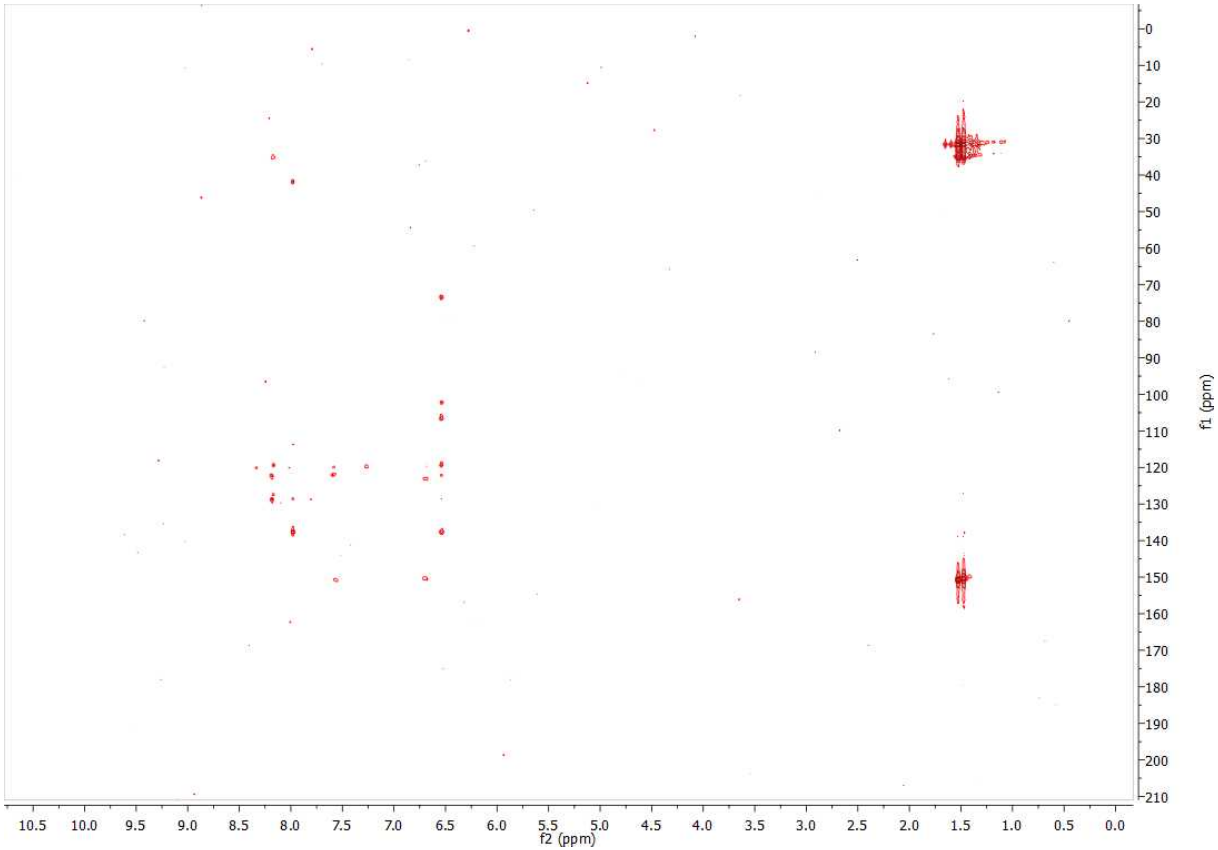


Figure S32. HMBC spectrum (CD_2Cl_2, 500 MHz, 25 °C) of **3b-Zr$_2$**.

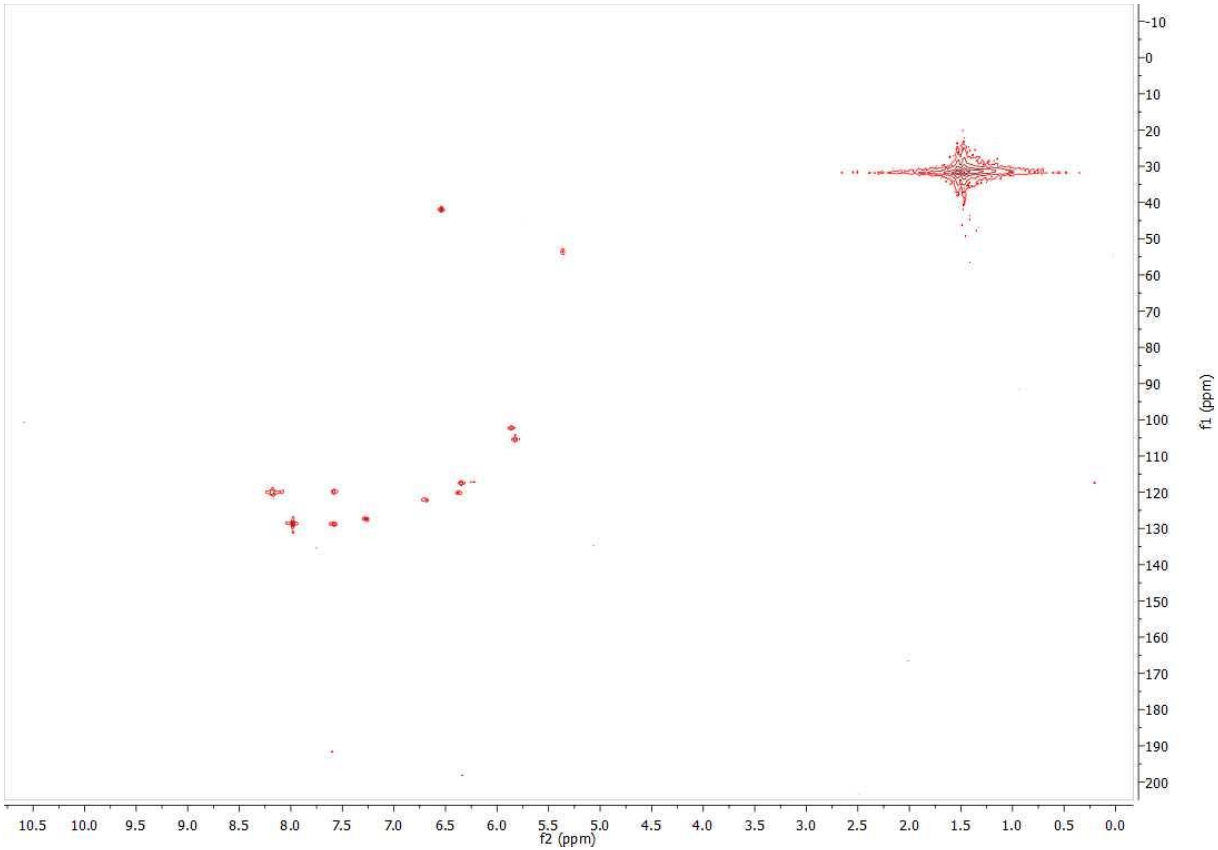


Figure S33. HSQC spectrum (CD_2Cl_2, 500 MHz, 25 °C) of **3b-Zr_2**.

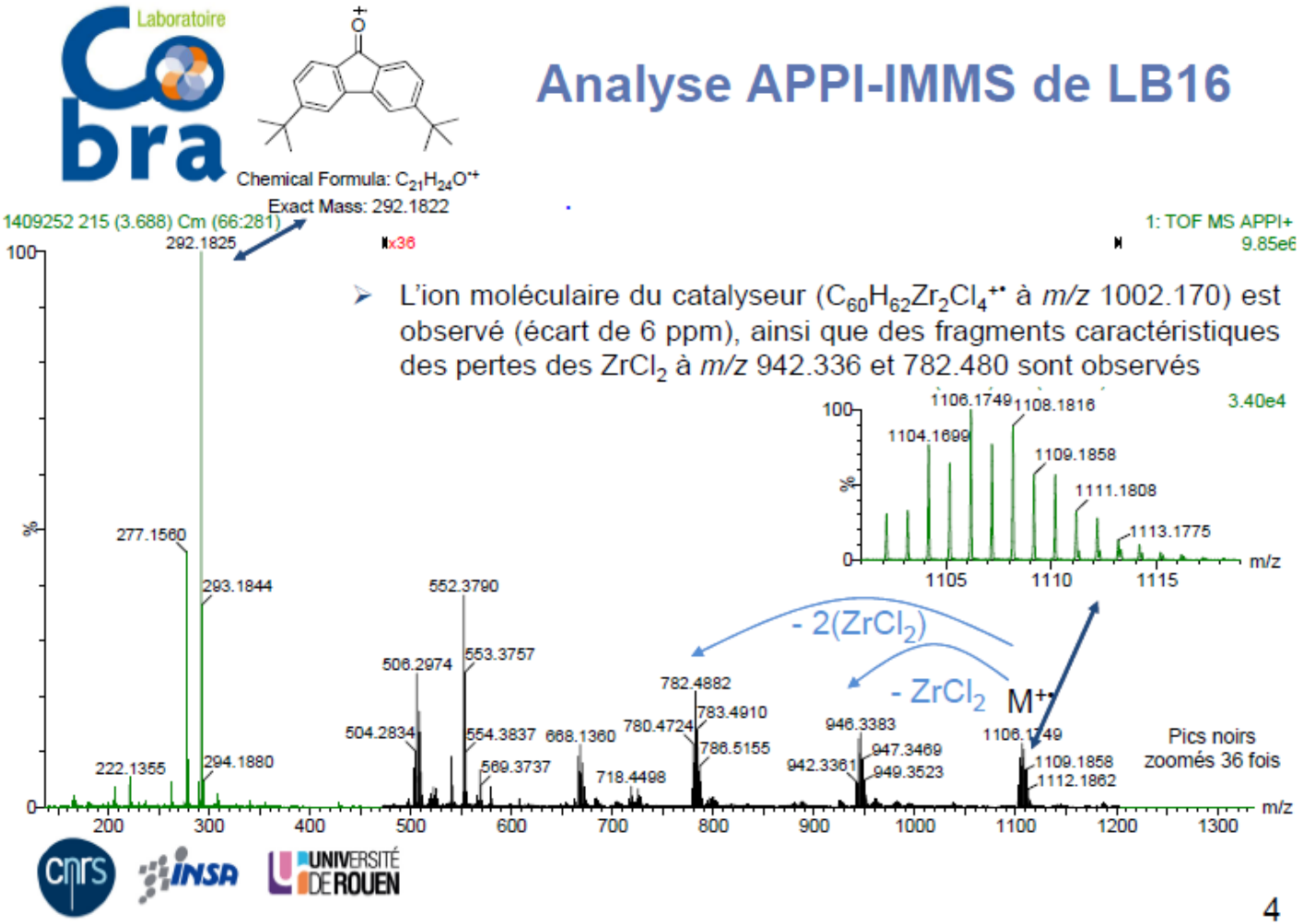


Figure S34. APPI-IMMS of **3b-Zr_2**.

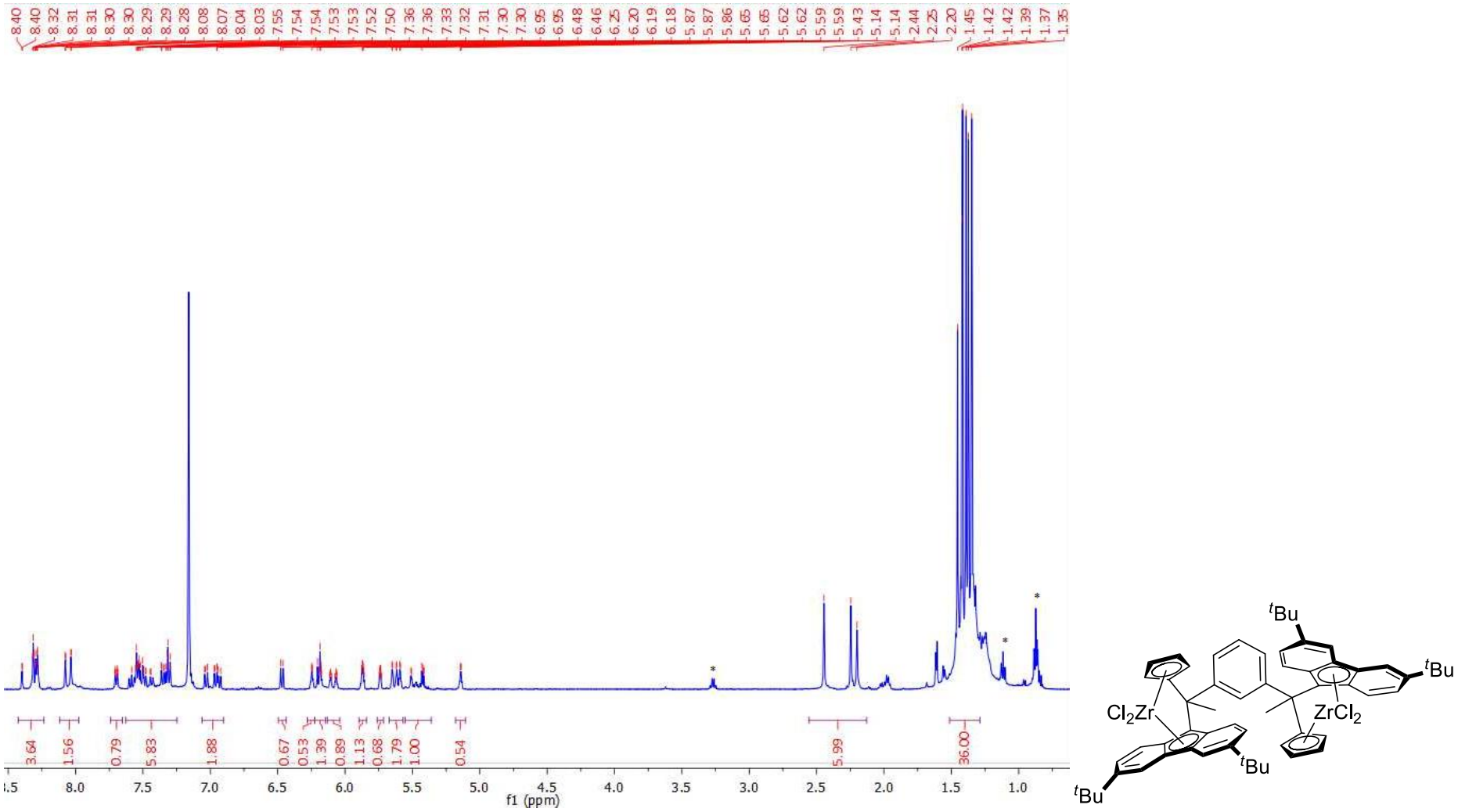


Figure S35. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of **3c-Zr$_2$**. (* stand for residual solvent peaks)

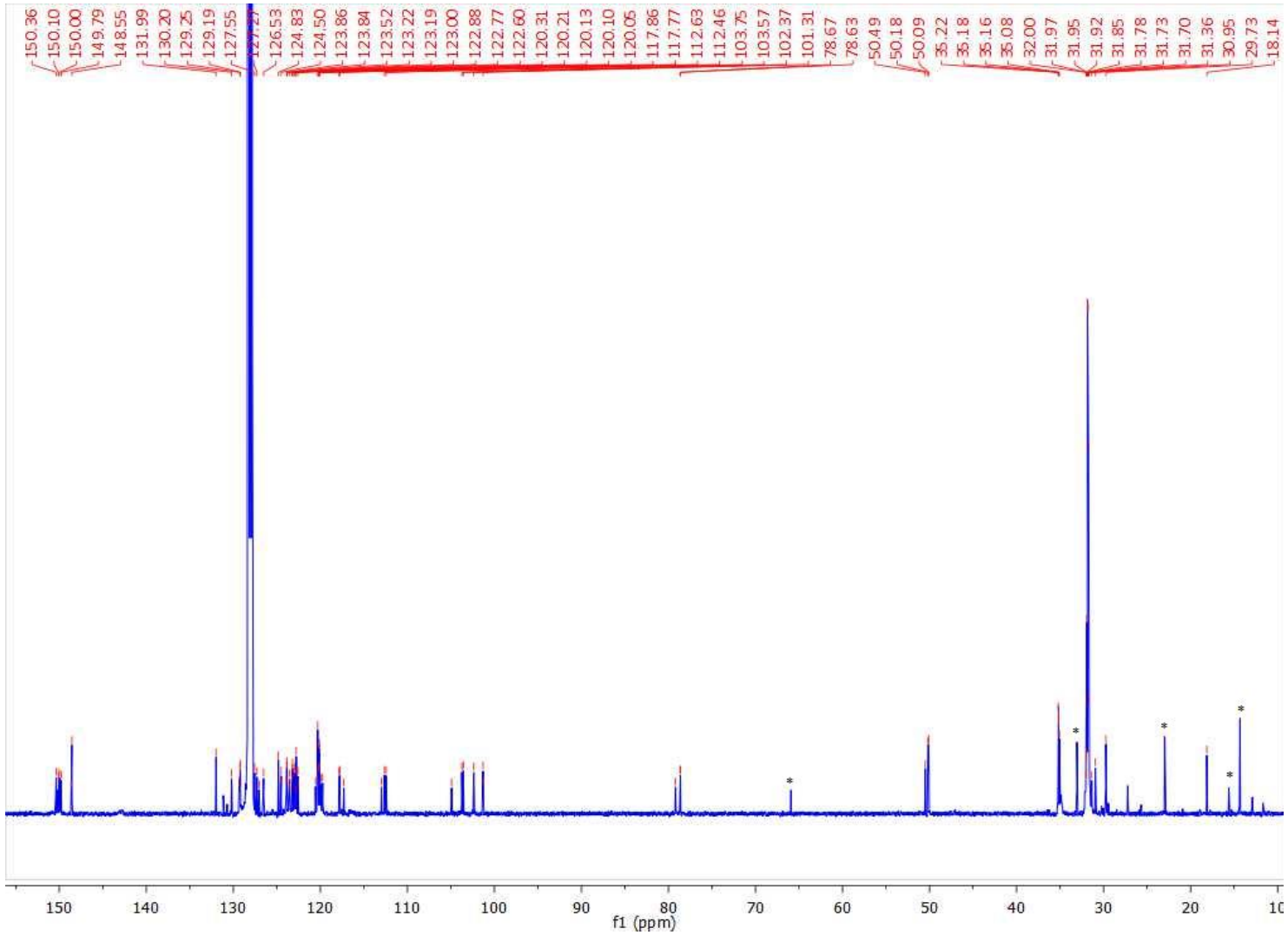


Figure S36. ^{13}C NMR spectrum (C_6D_6, 125 MHz, 25 °C) of **3c-Zr$_2$**. (*residual solvent peak)

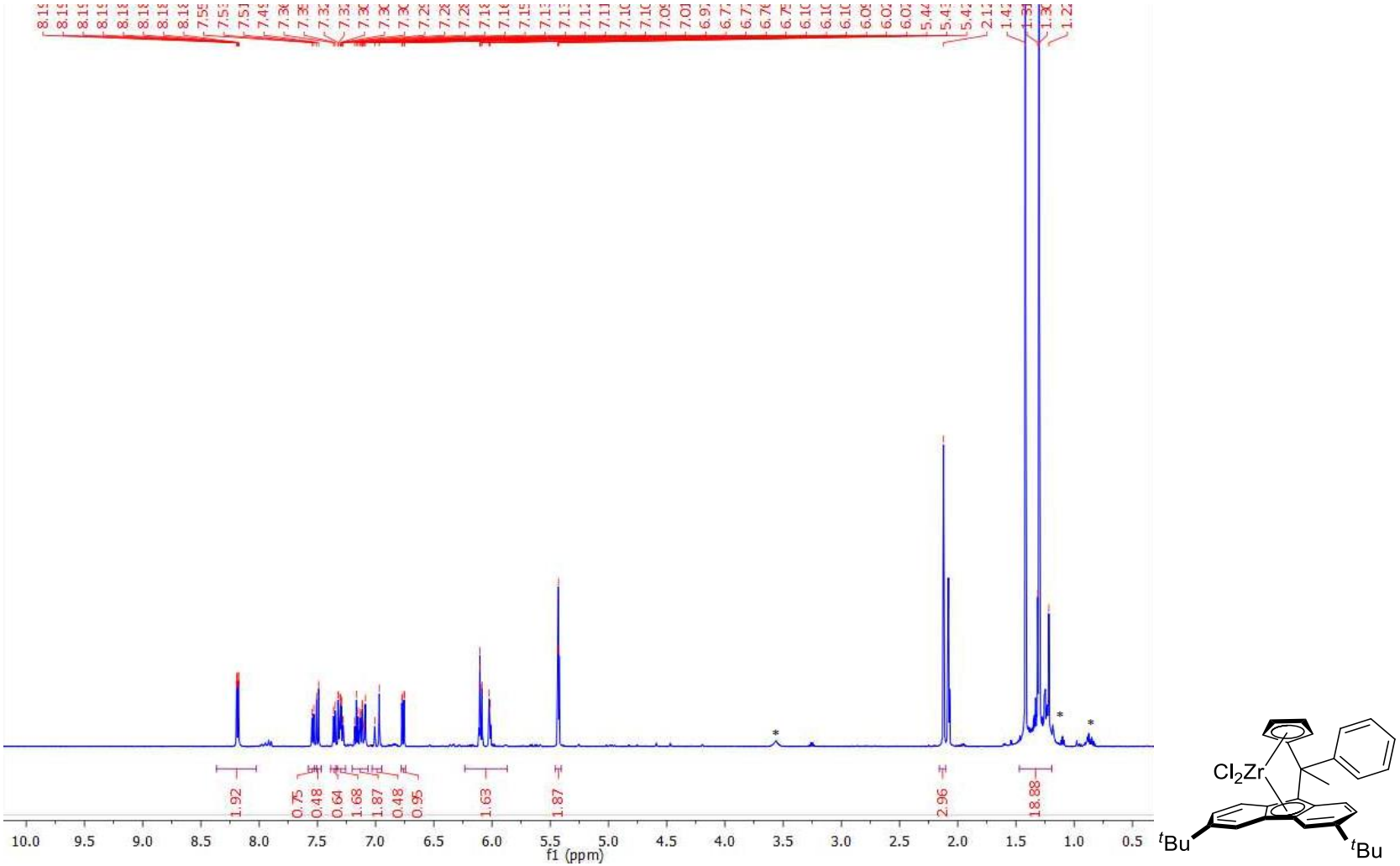


Figure S37. ^{1}H NMR spectrum (toluene-d_8, 500 MHz, 25 °C) of **3a'-Zr**. (* stand for residual solvent peaks)

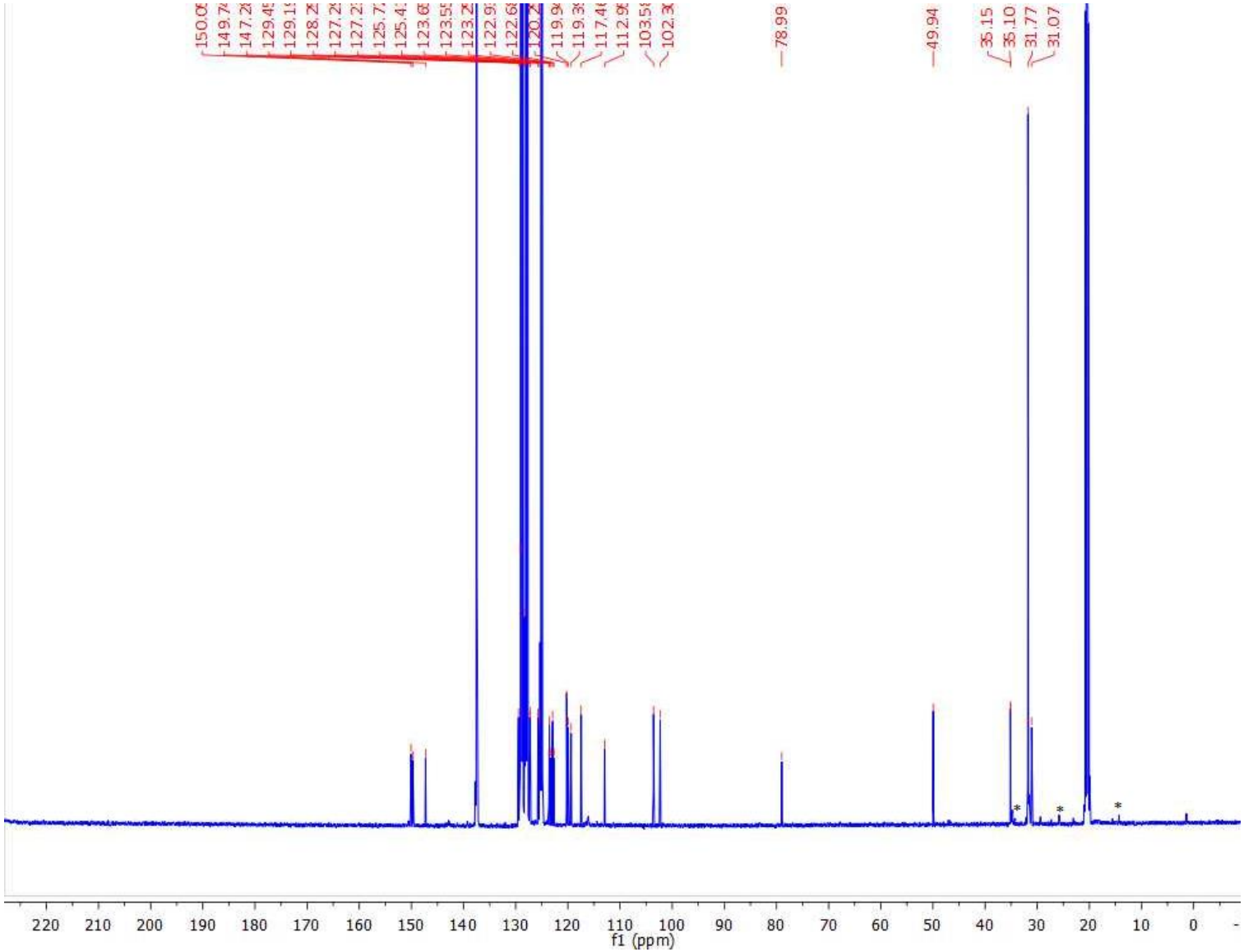


Figure S38. ^{13}C NMR spectrum (toluene-d_8, 125 MHz, 25 °C) of **3a'-Zr**. (* stand for residual solvent peaks)

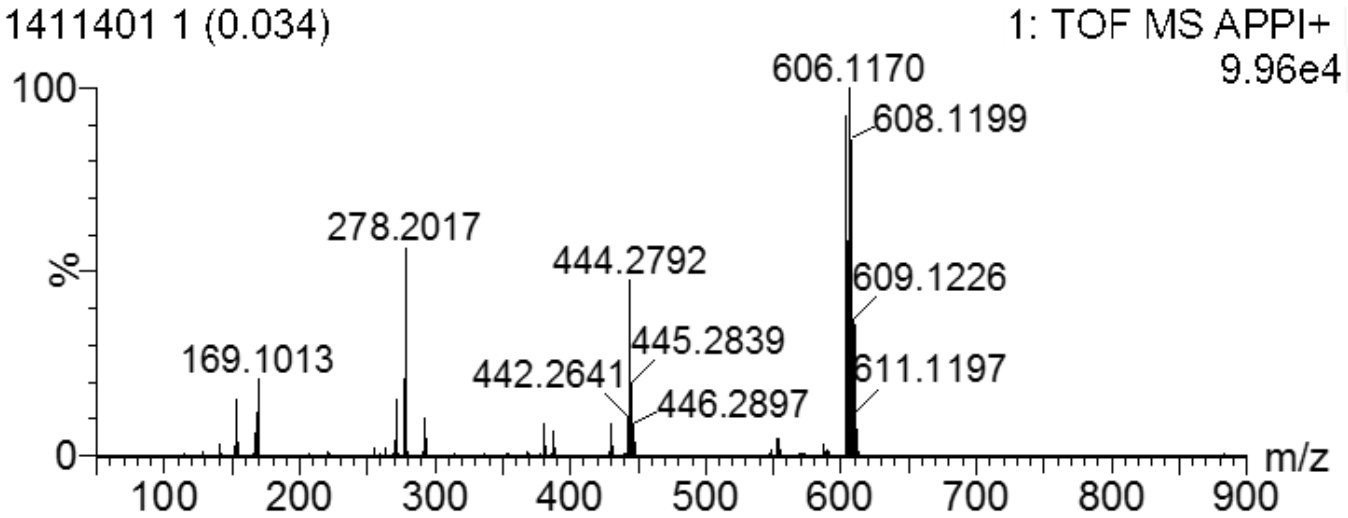


Figure S39. APPI-IMMS of **3a'-Zr**.

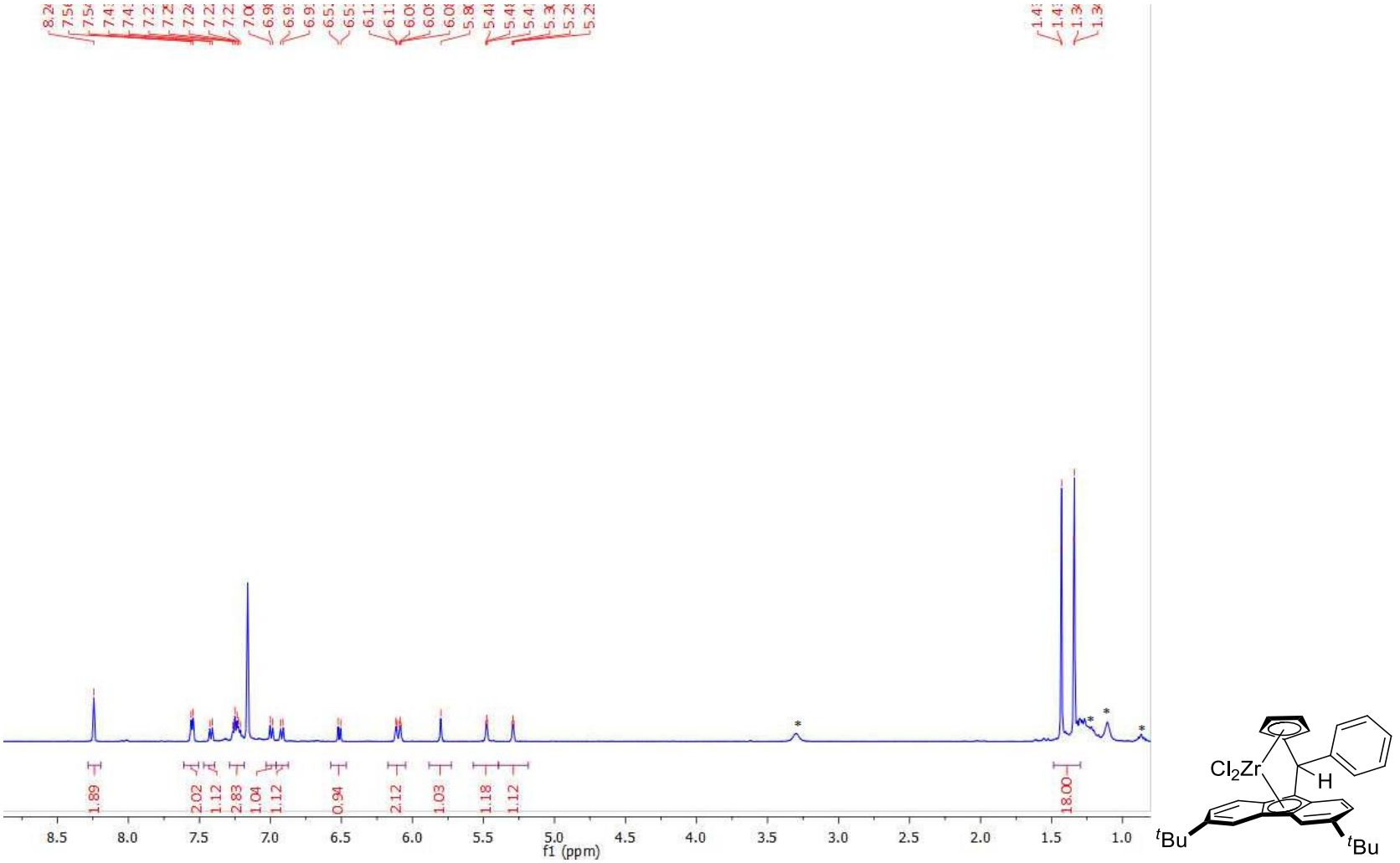


Figure S40. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of **3b'-Zr**. (*residual solvent peak)

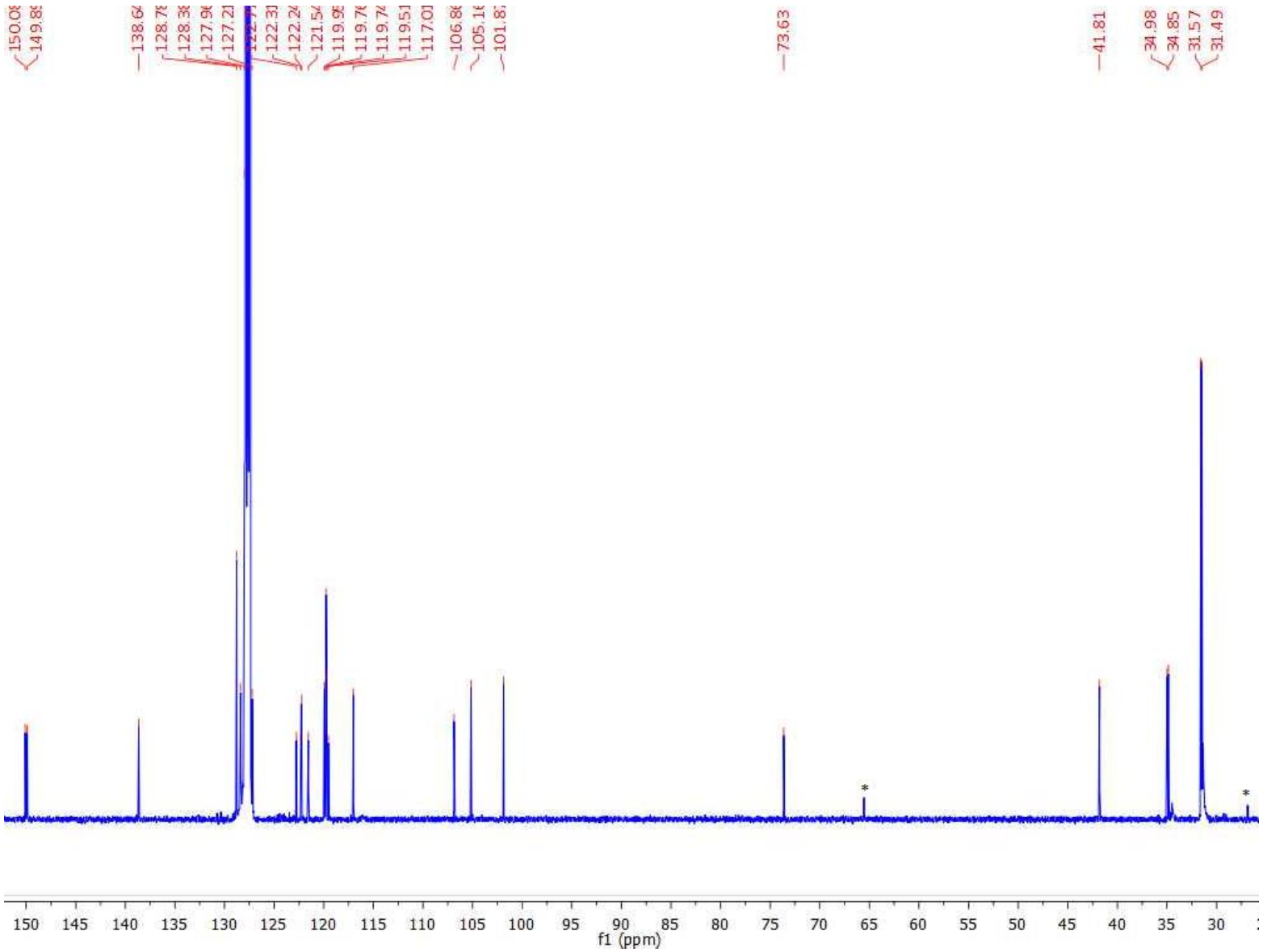


Figure S41. ^{13}C NMR spectrum (C_6D_6, 125 MHz, 25 °C) of **3b'-Zr**. (*residual solvent peak)

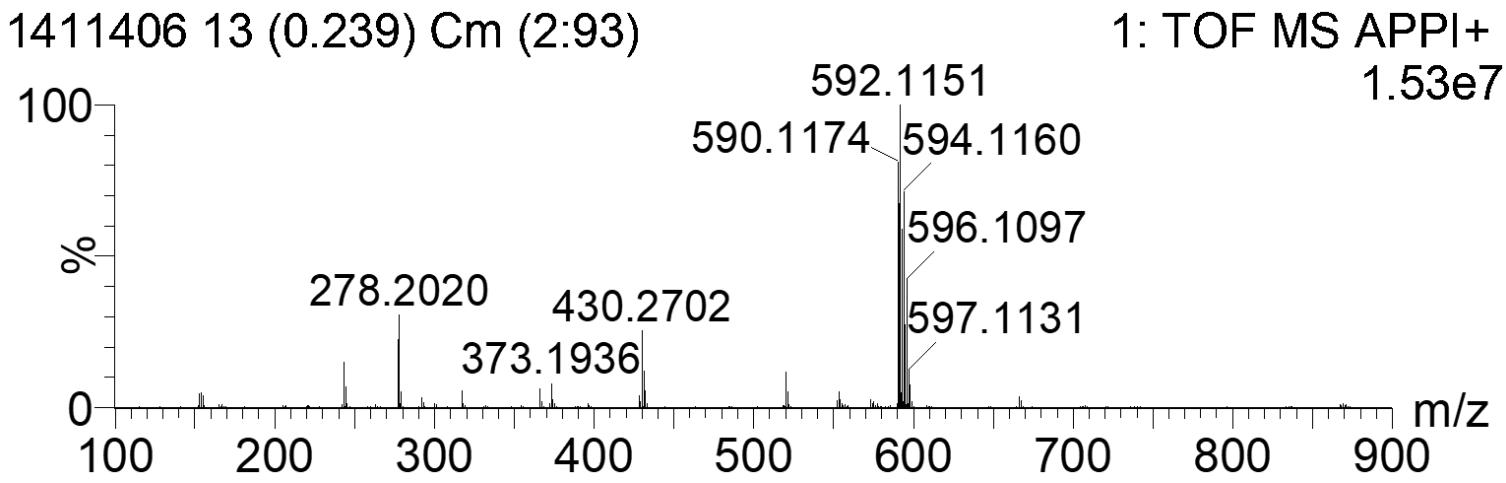


Figure S42. APPI-IMMS of **3b'-Zr**.

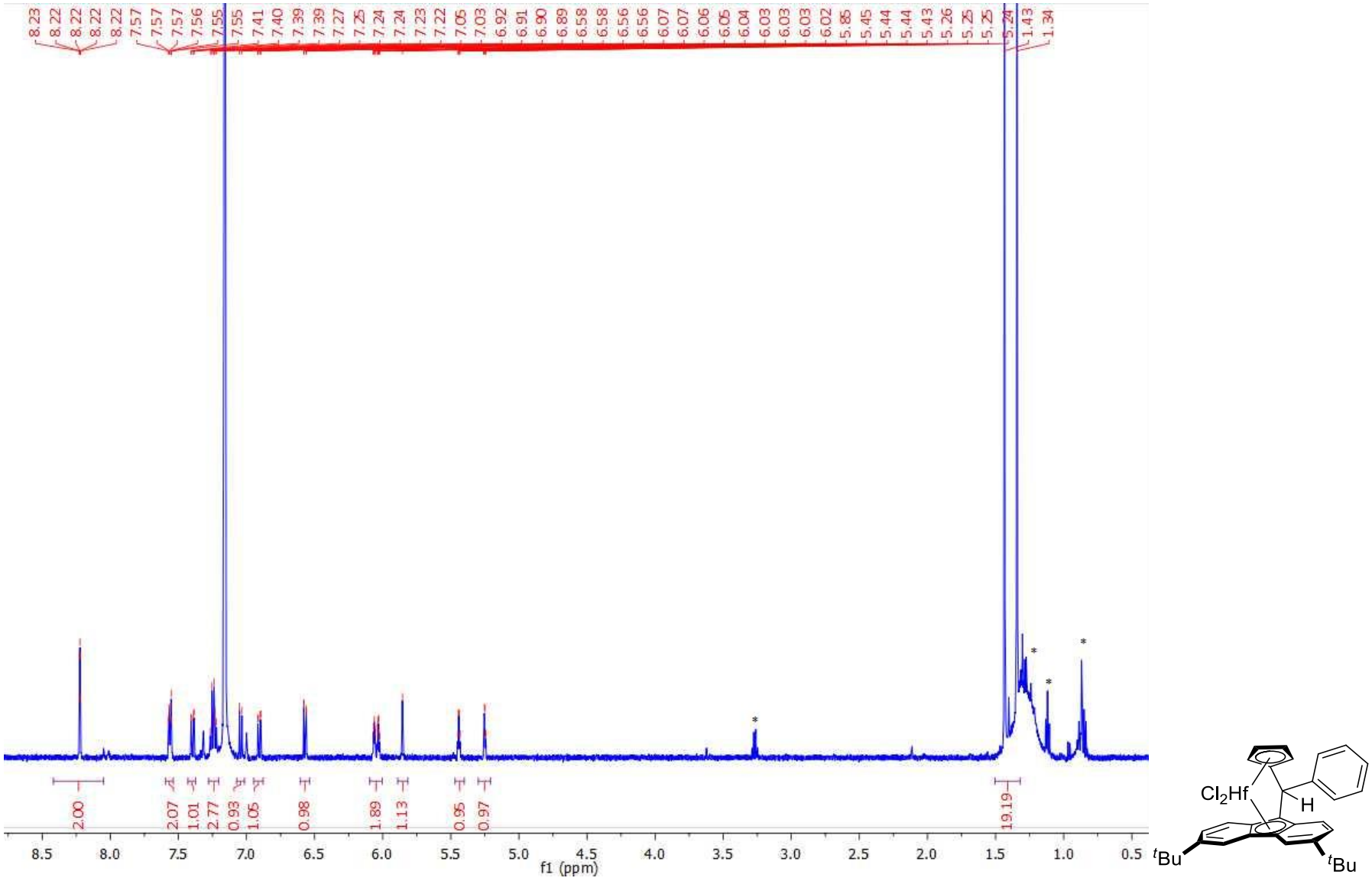


Figure S43. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of **3b'-Hf**. (* stand for residual solvent peaks)

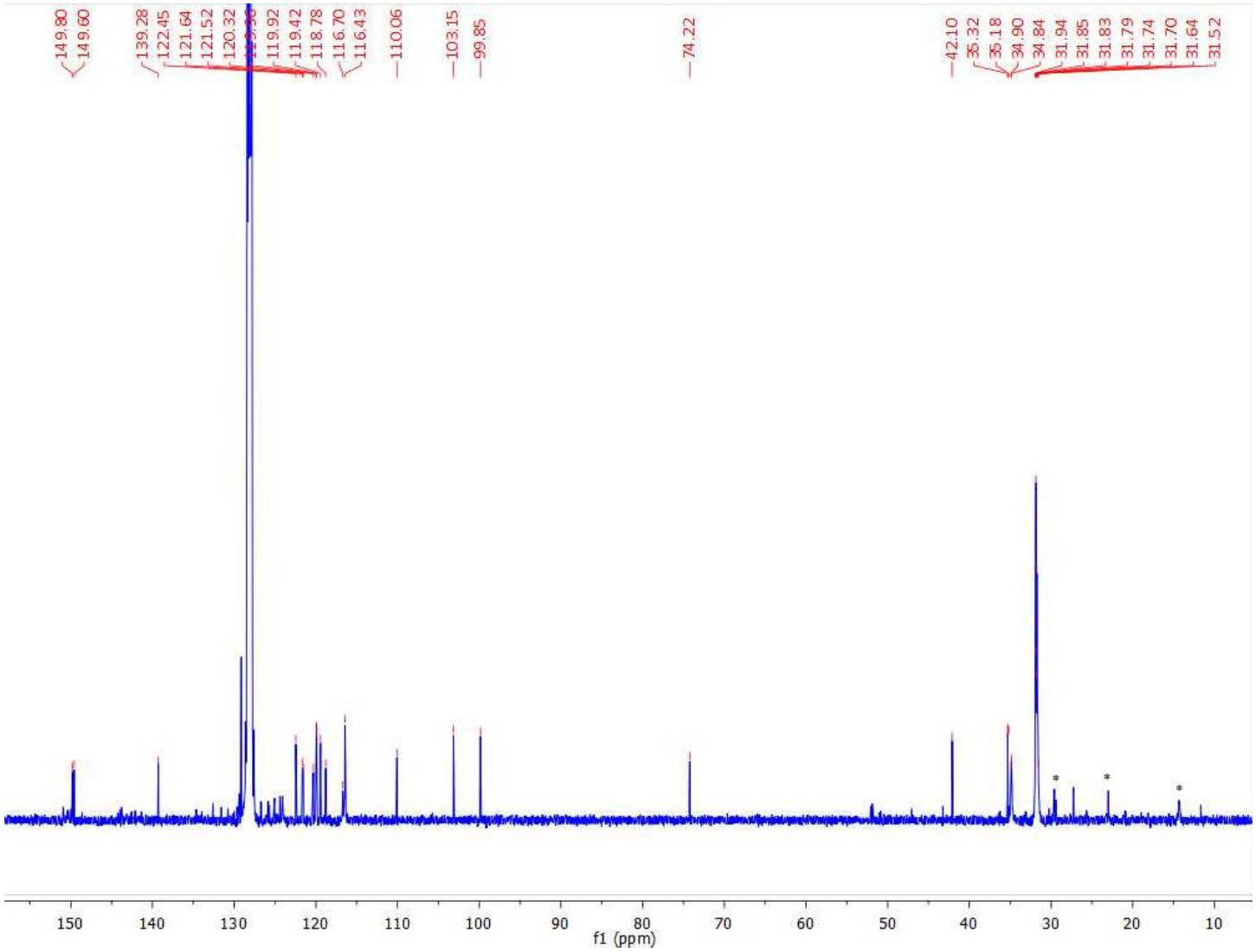


Figure S44. ^{13}C NMR spectrum (C_6D_6, 125 MHz, 25 °C) of **3b'-Hf**. (*residual solvent peak)

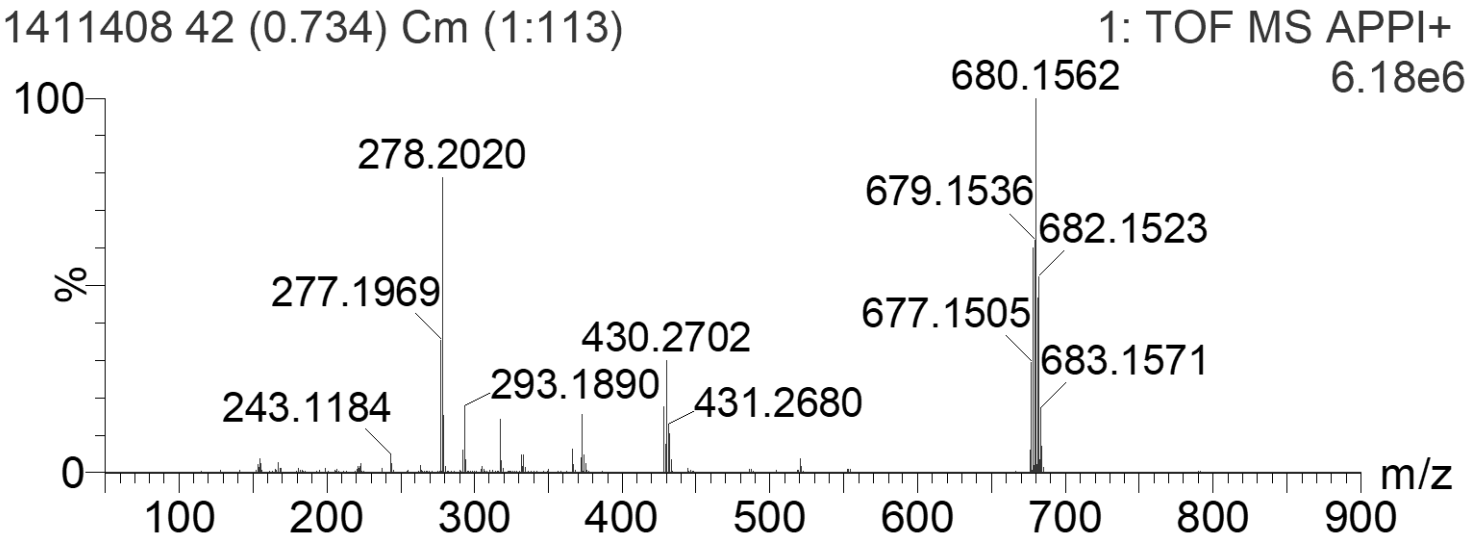


Figure S45. APPI-IMMS of **3b'-Hf**.

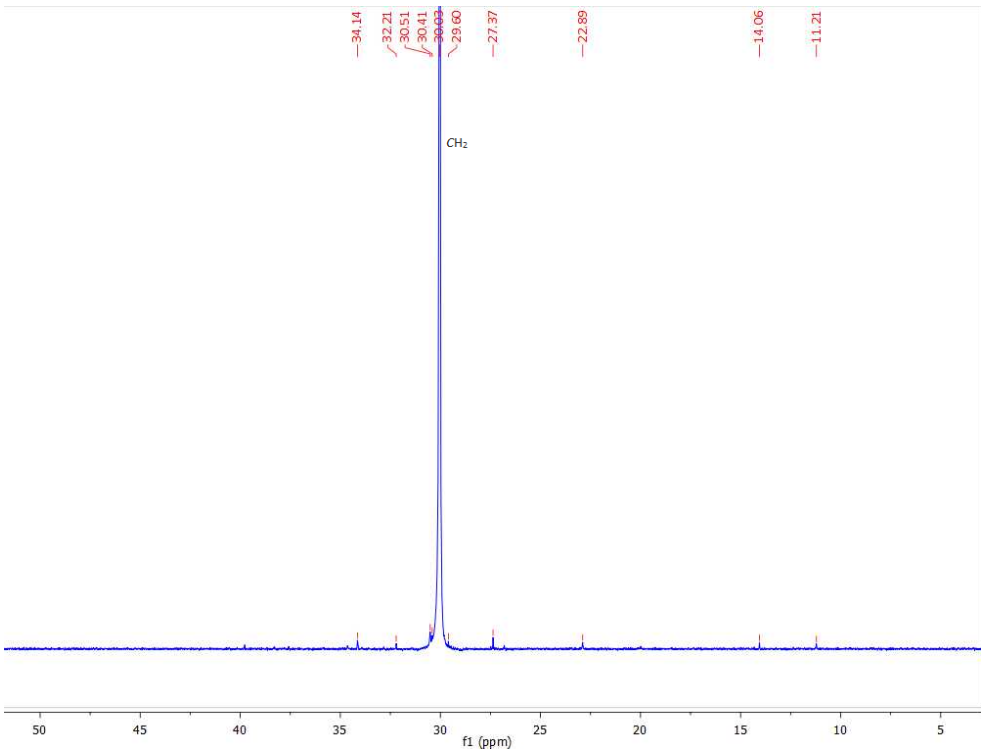


Figure S46. ^{13}C NMR spectrum ($C_6D_3Cl_3$, 500 MHz, 100 °C) of PE (Table 1, run 1).

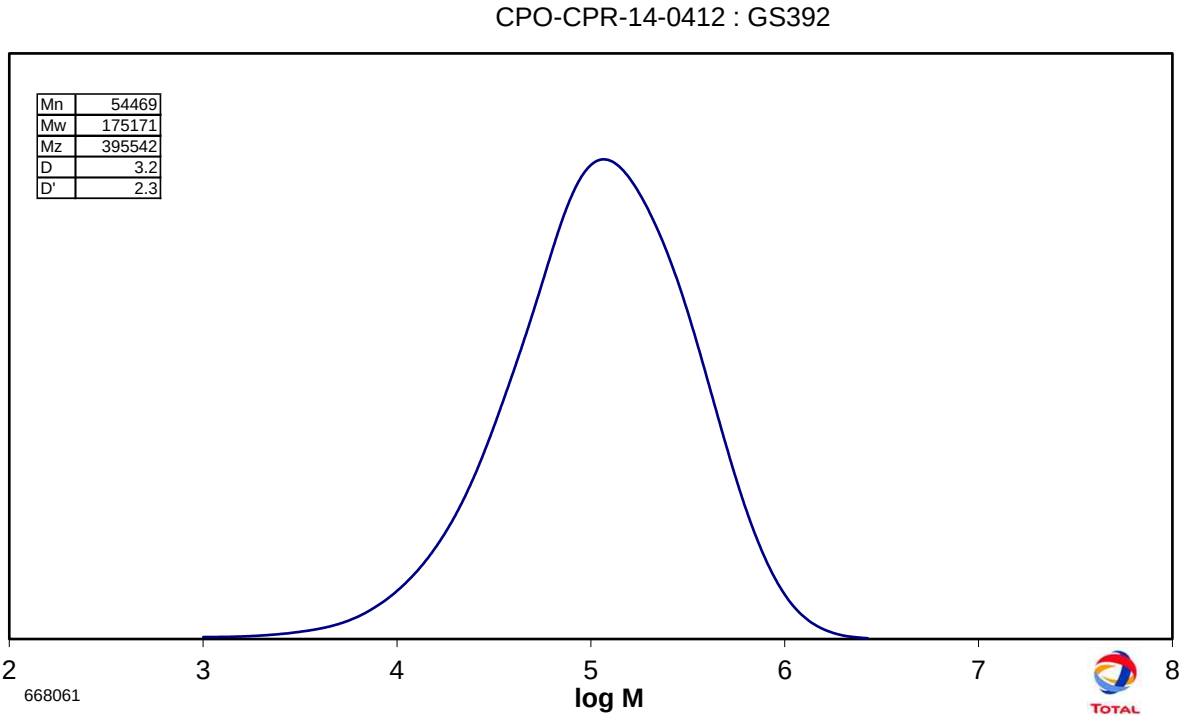


Figure S47. GPC trace of PE (Table 1, run 1) obtained with **3a-Zr$_2$**.

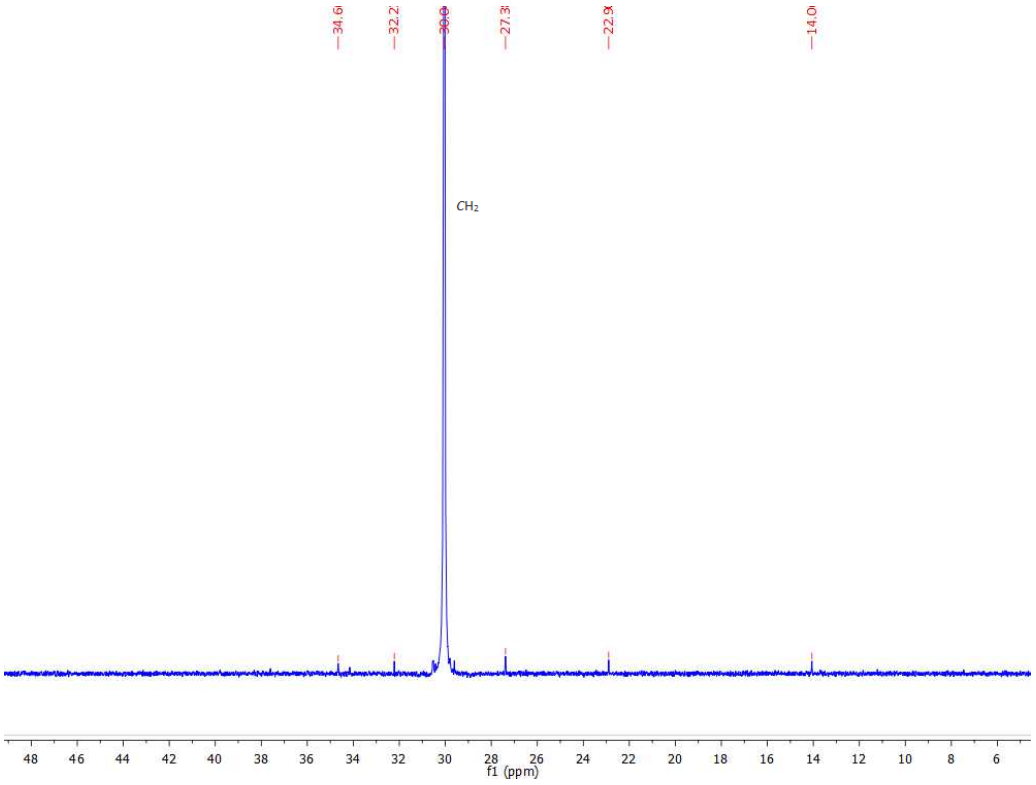


Figure S48. ^{13}C NMR spectrum ($C_6D_3Cl_3$, 500 MHz, 100 °C) of PE (Table 1, run 3).

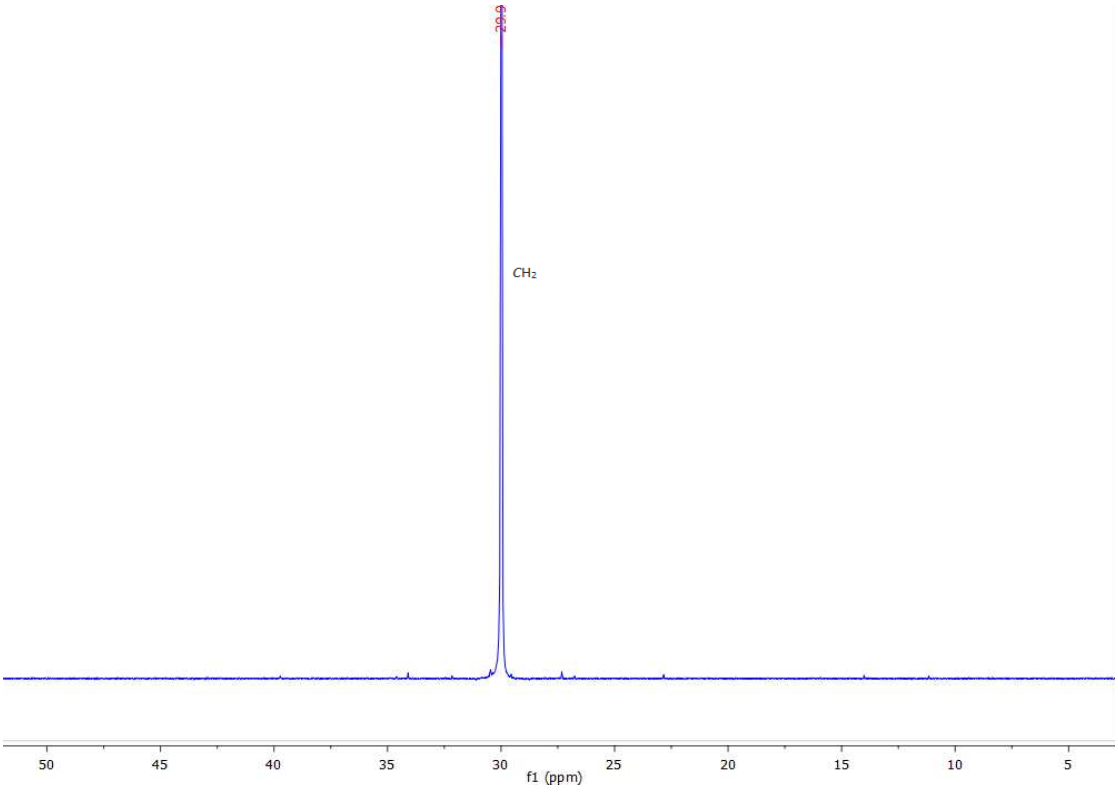


Figure S49. ^{13}C NMR spectrum ($C_6D_3Cl_3$, 500 MHz, 100 °C) of PE (Table 1, run 5).

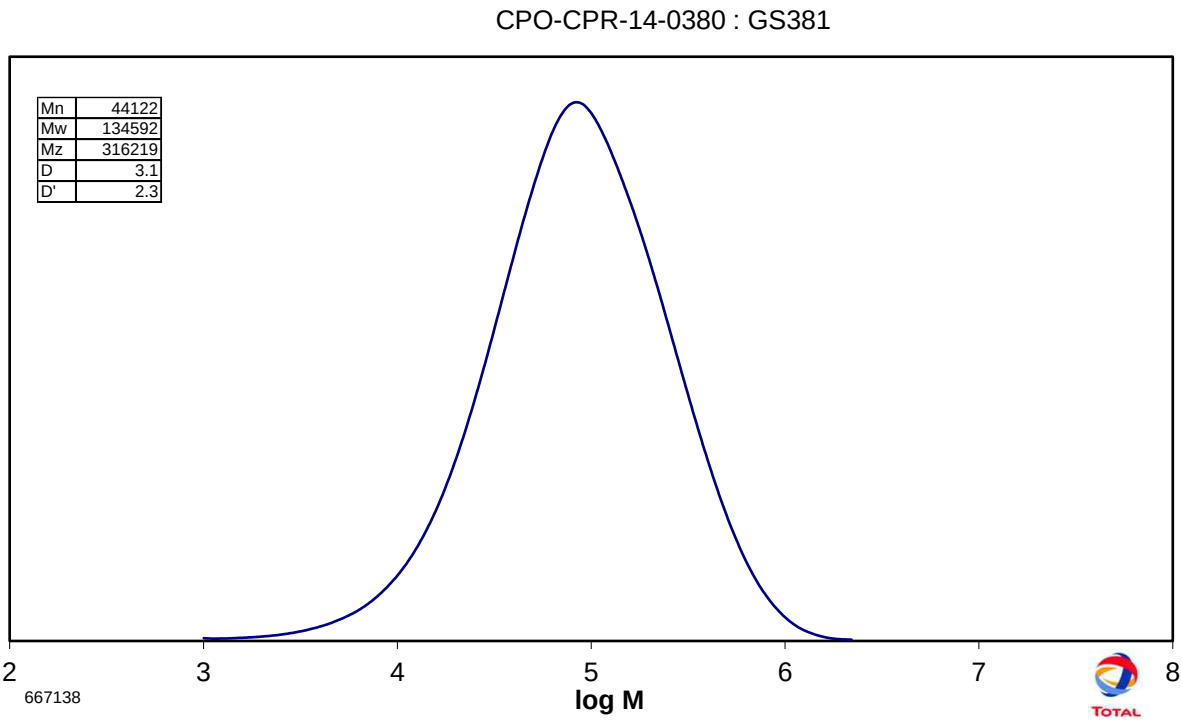


Figure S50. GPC trace of PE (Table 1, run 5) obtained with **3b-Zr_2**.

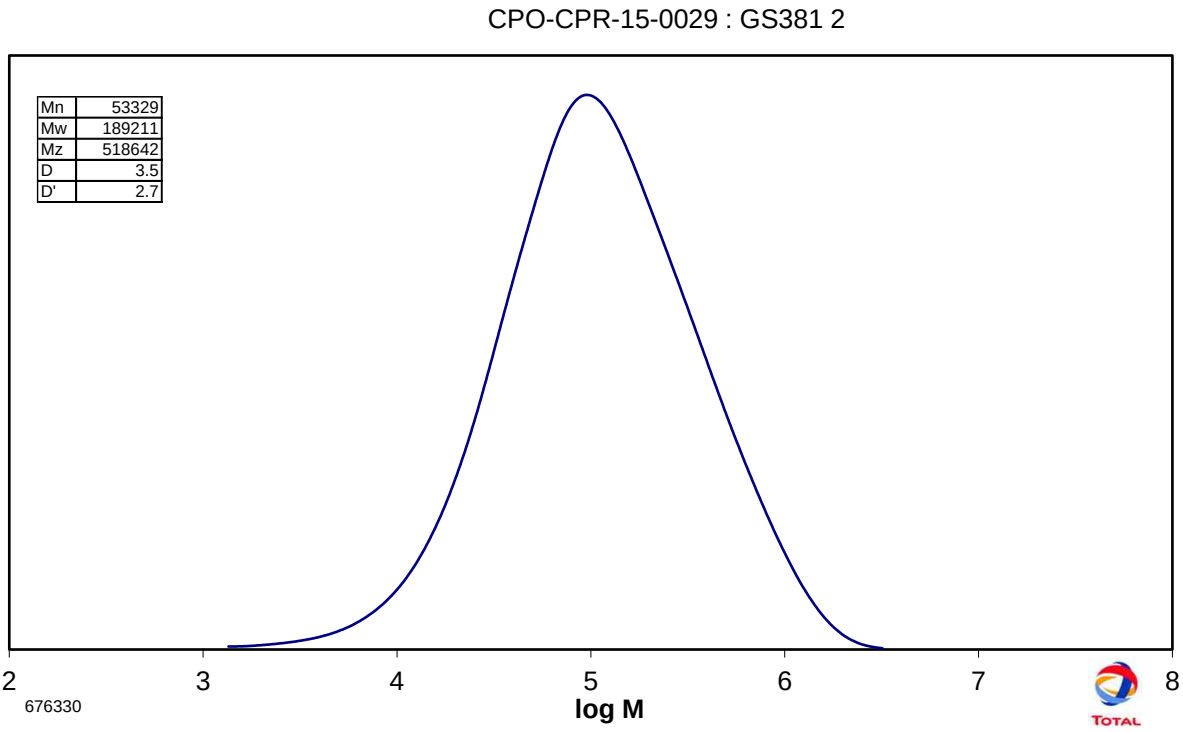


Figure S51. GPC trace of PE (Table 1, run 6) obtained with **3b-Zr_2**.

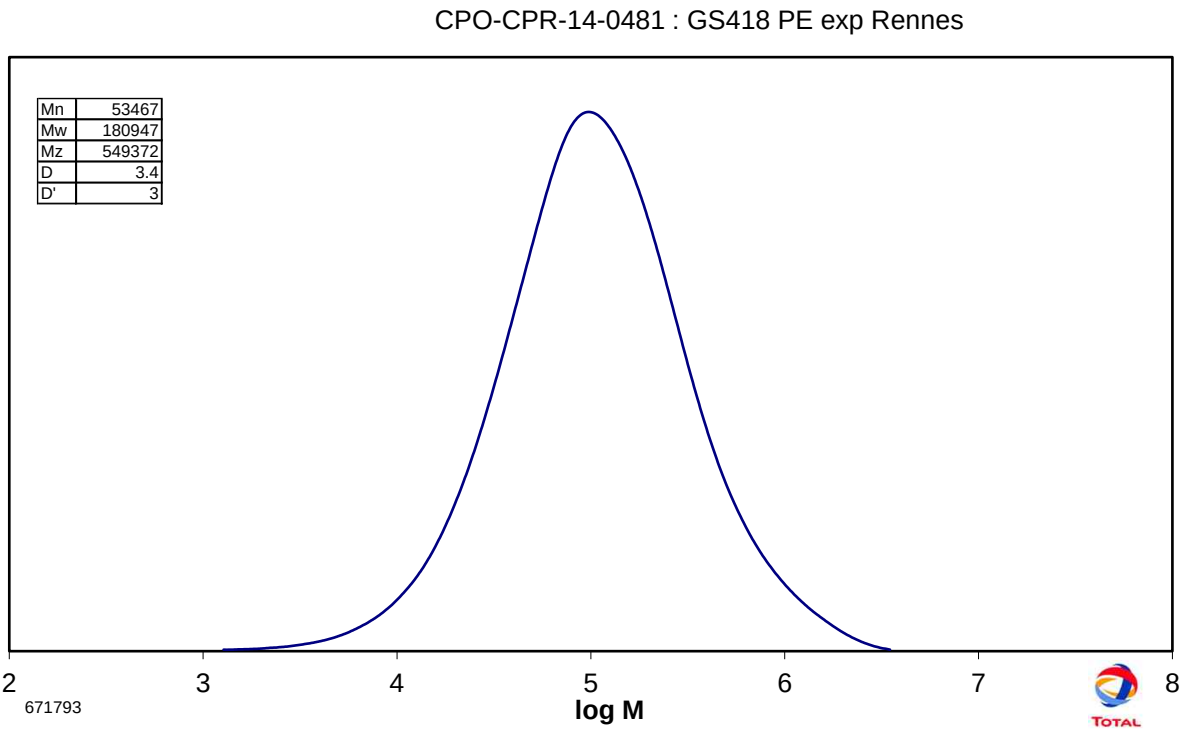


Figure S52. GPC trace of PE (Table 1, run 7) obtained with **3b'-Zr**.

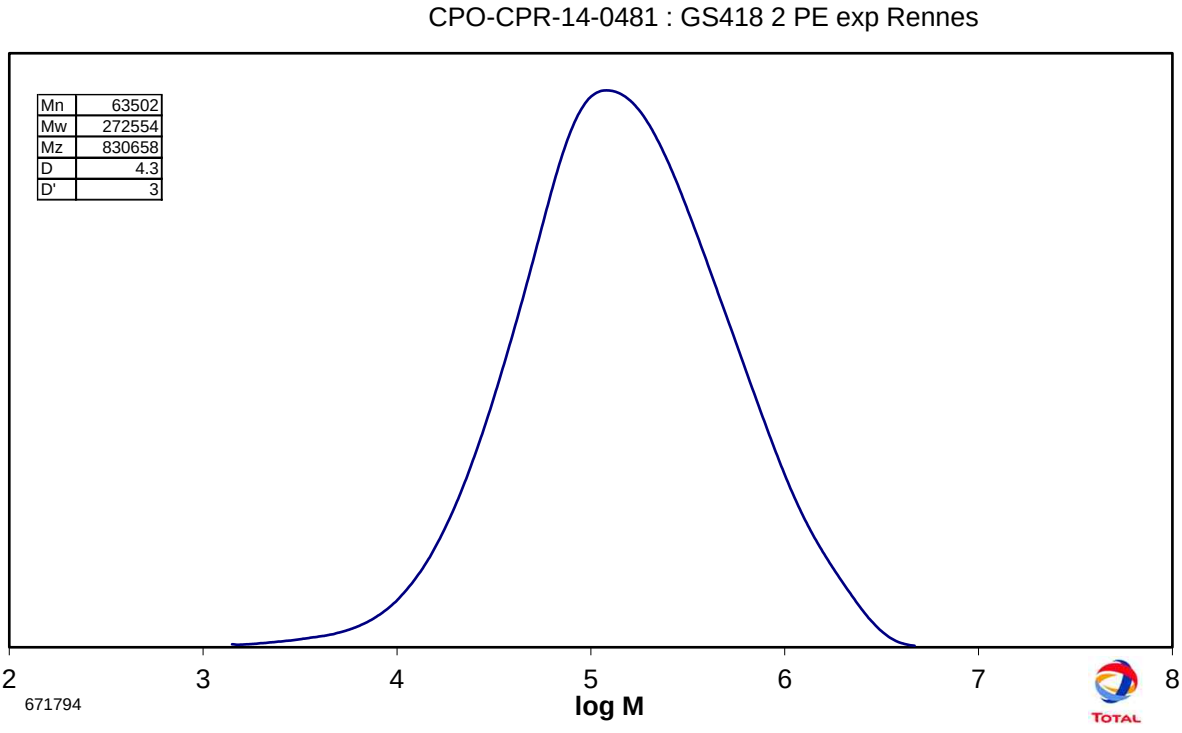


Figure S53. GPC trace of PE (Table 1, run 8) obtained with **3b'-Zr**.

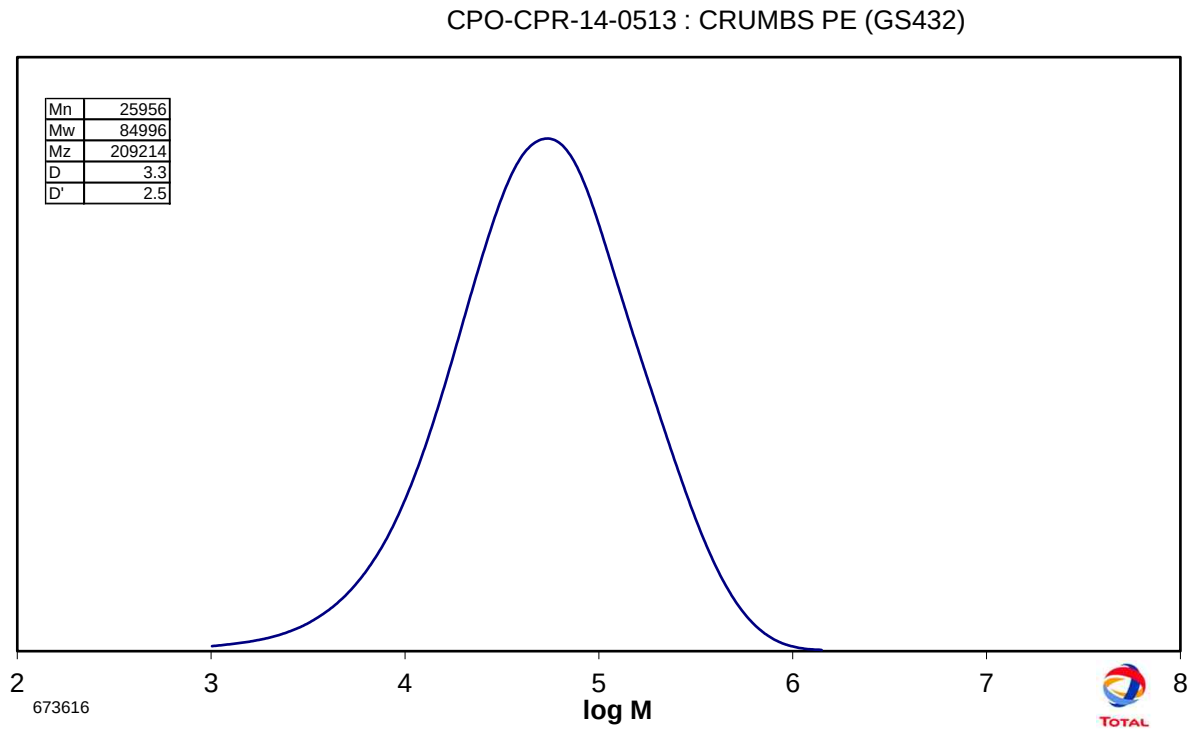


Figure S54. GPC trace of PE (Table 1, run 9) obtained with **3c-Zr$_2$**.

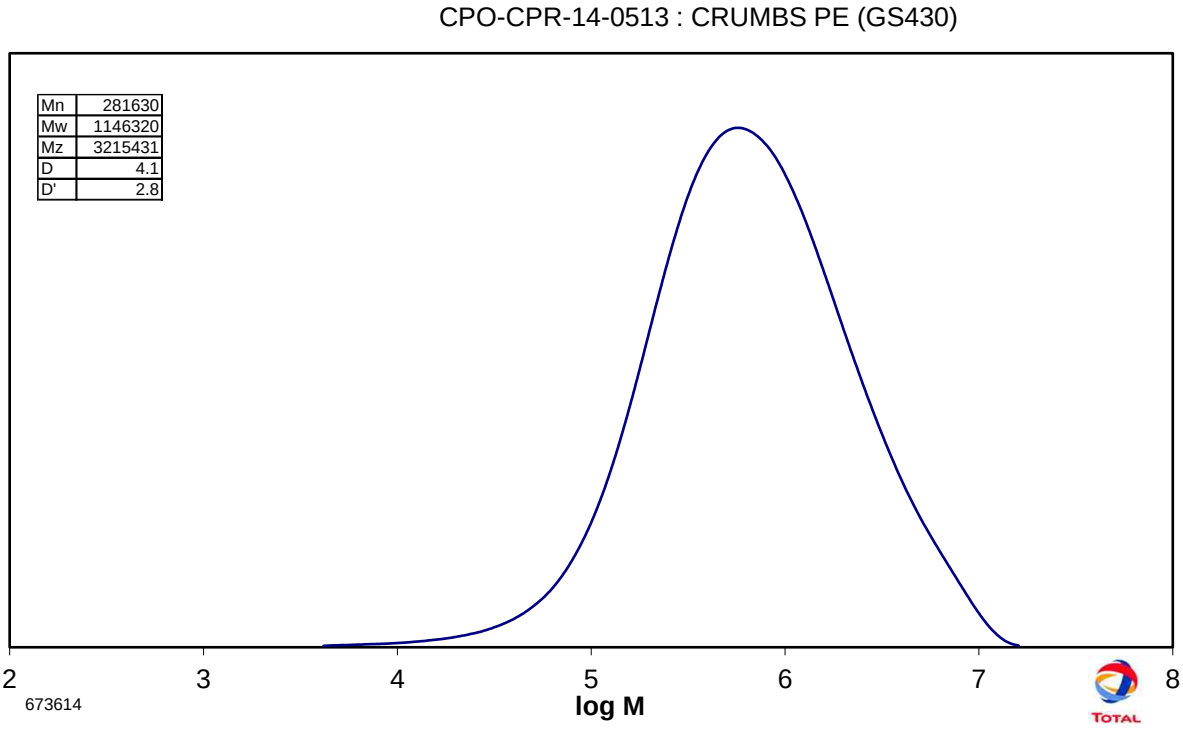


Figure S55. GPC trace of PE (Table 1, run 12) obtained with **3b'-Hf**.

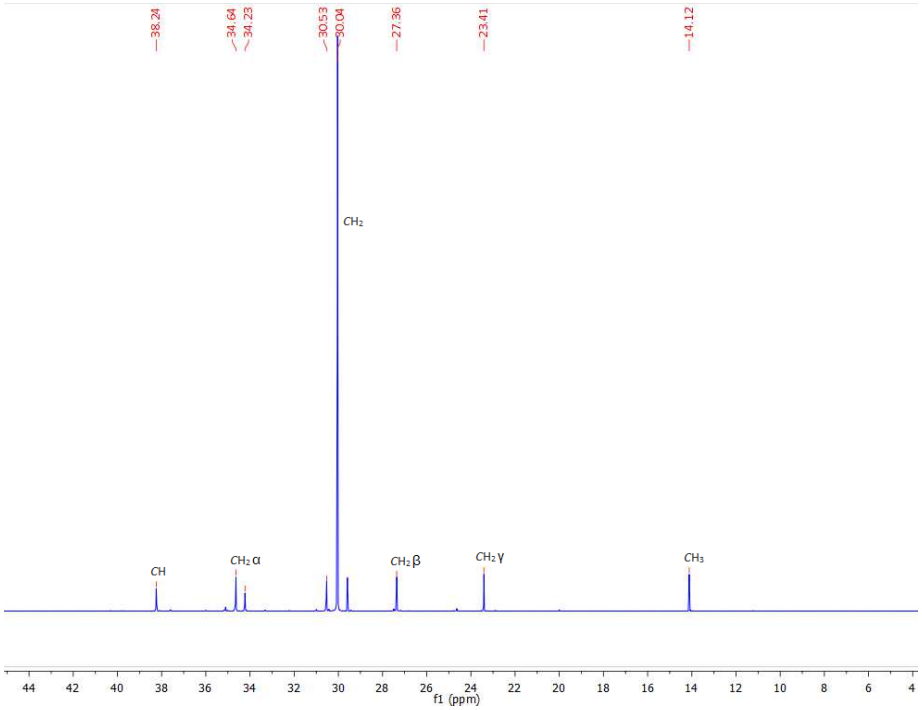


Figure S56. ^{13}C NMR spectrum ($C_6D_3Cl_3$, 500 MHz, 100 °C) of PE/PHex (Table 2, run 1).

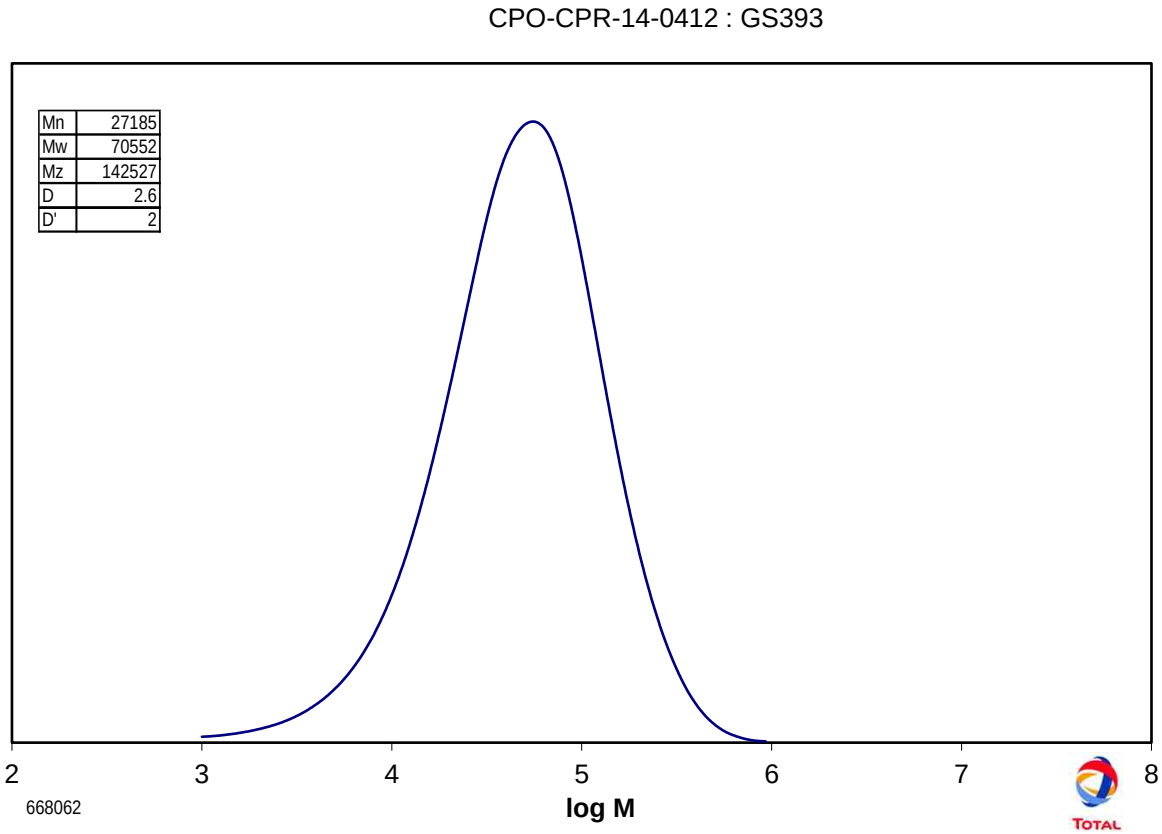


Figure S57. GPC trace of PE/PHex (Table 2, run 1) obtained with **3a-Zr$_2$**.

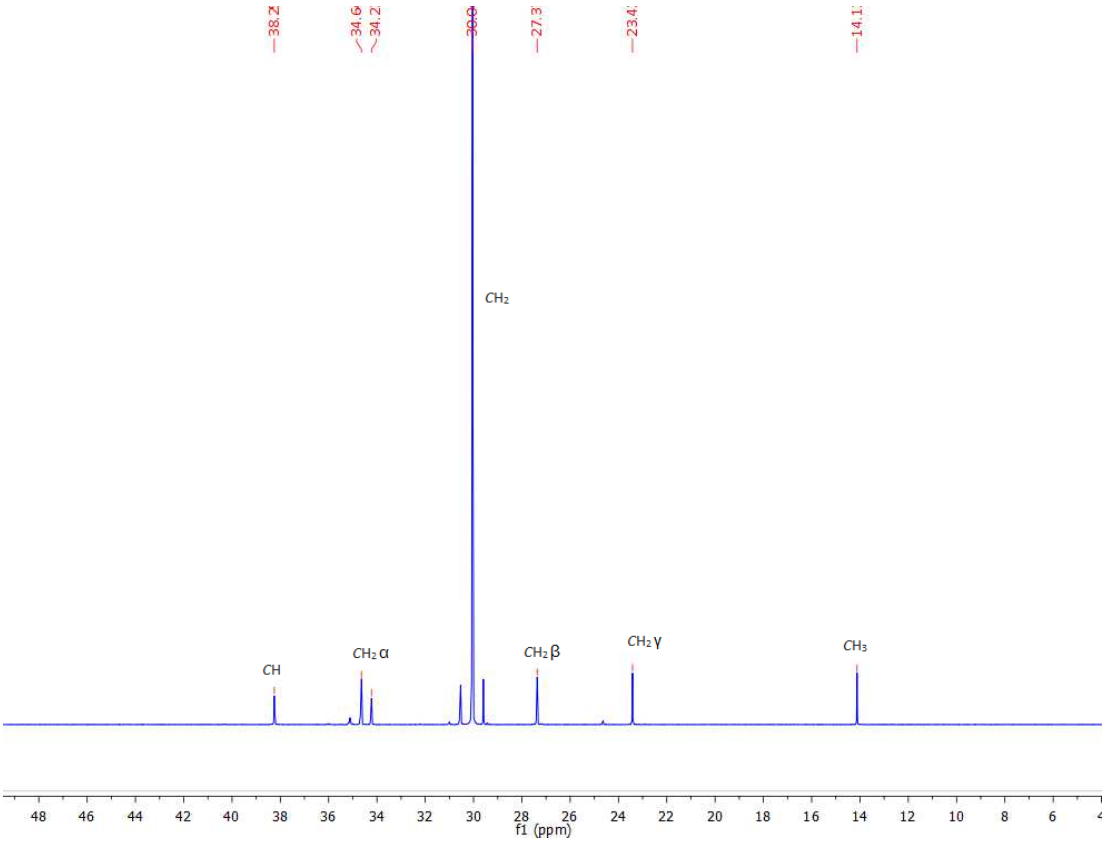


Figure S58. ^{13}C NMR spectrum ($C_6D_3Cl_3$, 500 MHz, 100 °C) of PE/PHex (Table 2, run 4).

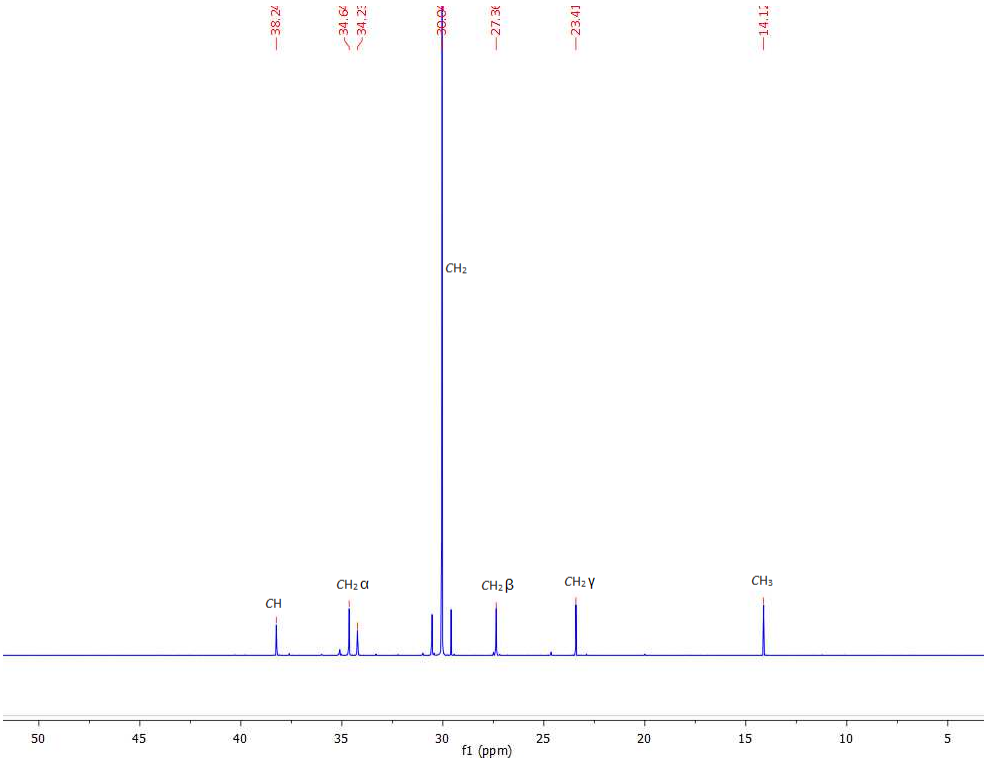


Figure S59. ^{13}C NMR spectrum ($C_6D_3Cl_3$, 500 MHz, 100 °C) of PE/PHex (Table 2, run 5).

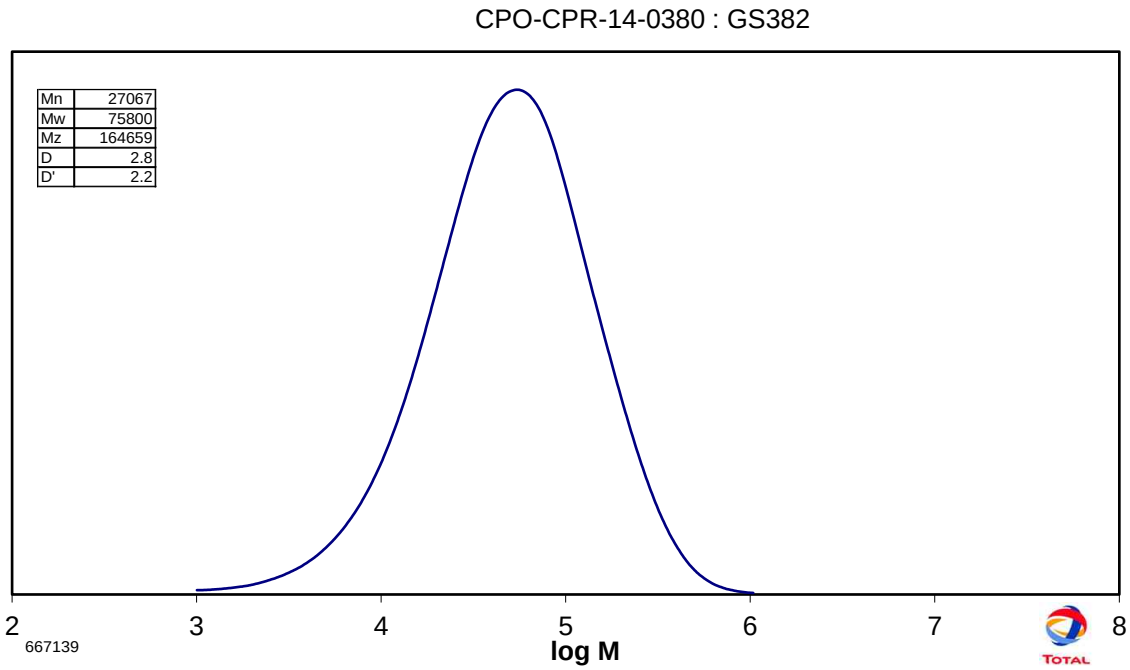


Figure S60. GPC trace of PE/PHex (Table 2, run 5) obtained with **3b-Zr$_2$**.

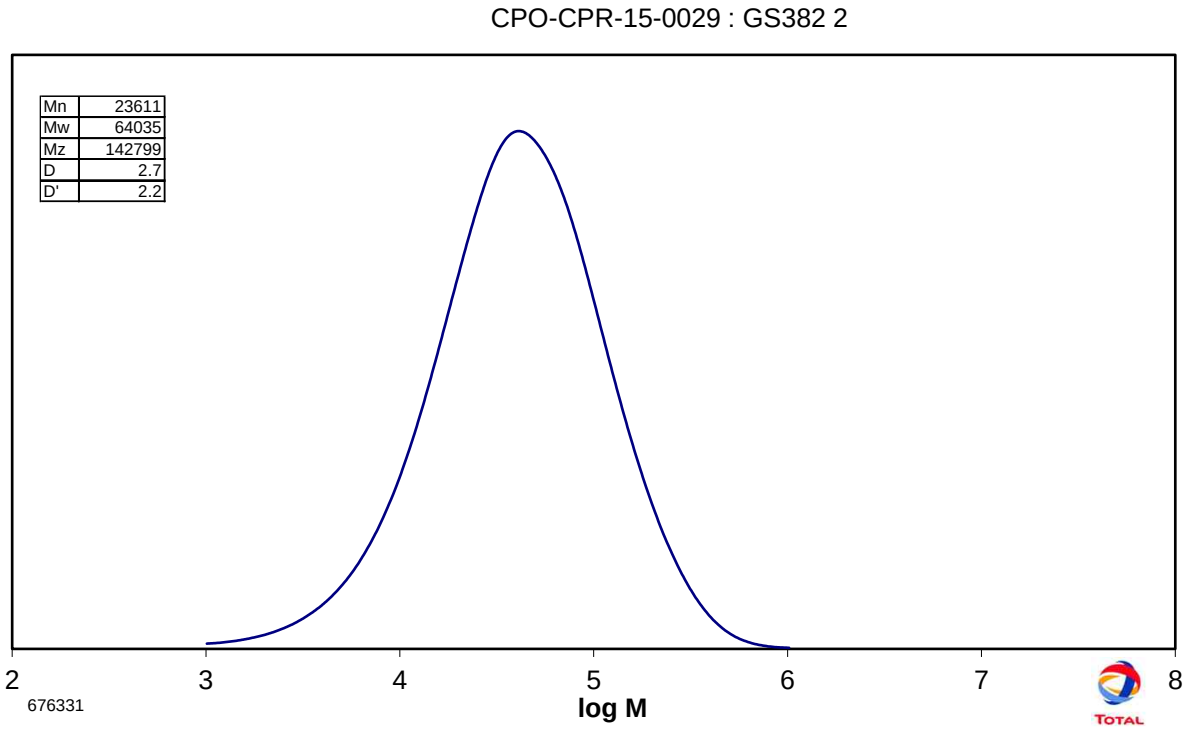


Figure S61. GPC trace of PE/PHex (Table 2, run 6) obtained with **3b-Zr$_2$**.

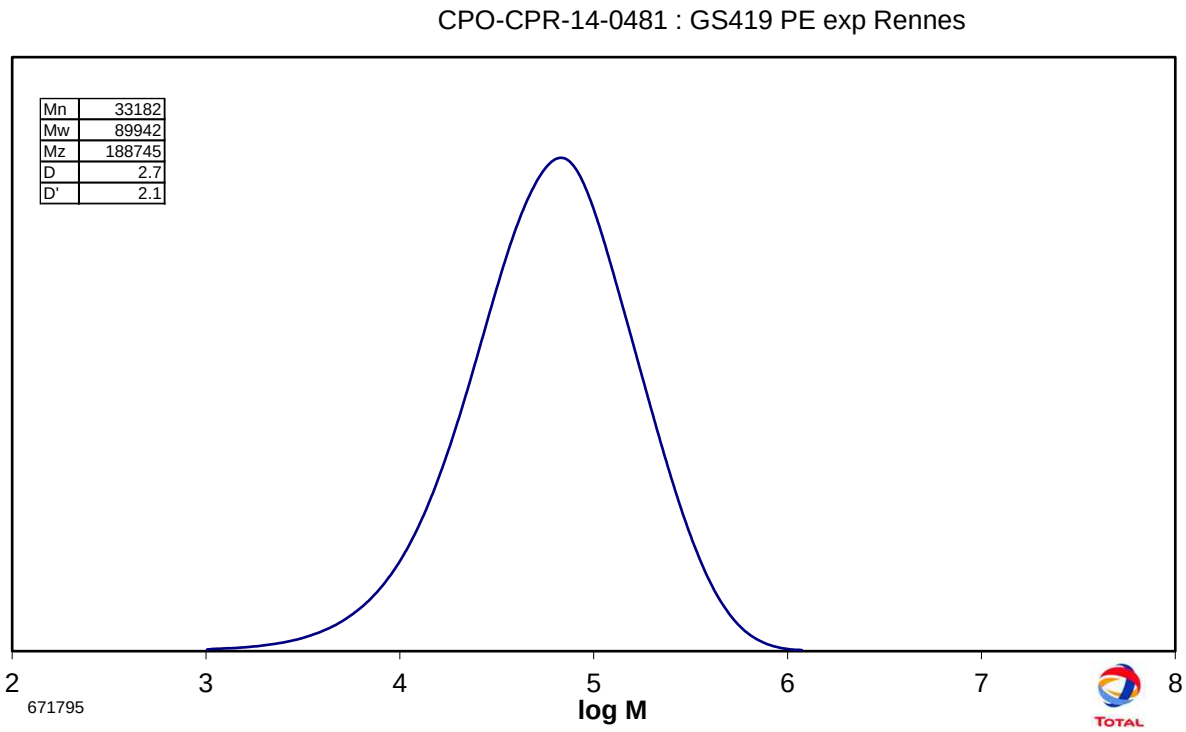


Figure S62. GPC trace of PE/PHex (Table 2, run 7) obtained with **3b'-Zr**.

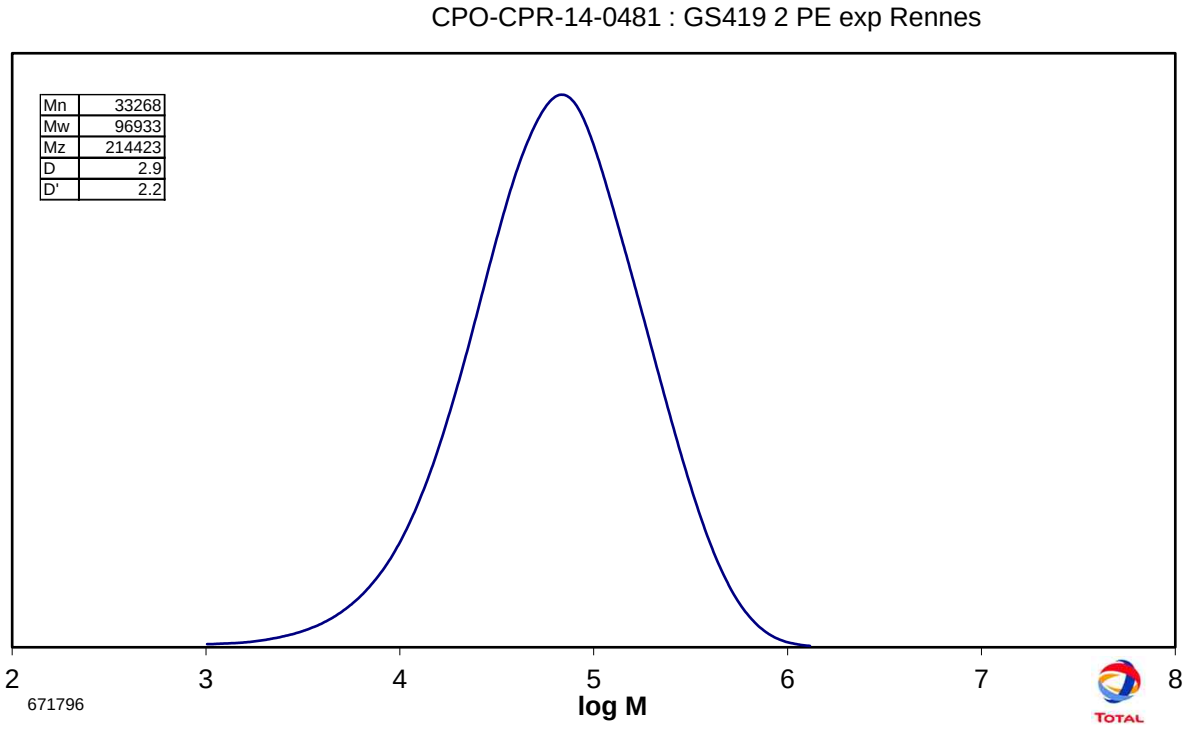


Figure S63. GPC trace of PE/PHex (Table 2, run 8) obtained with **3b'-Zr**.

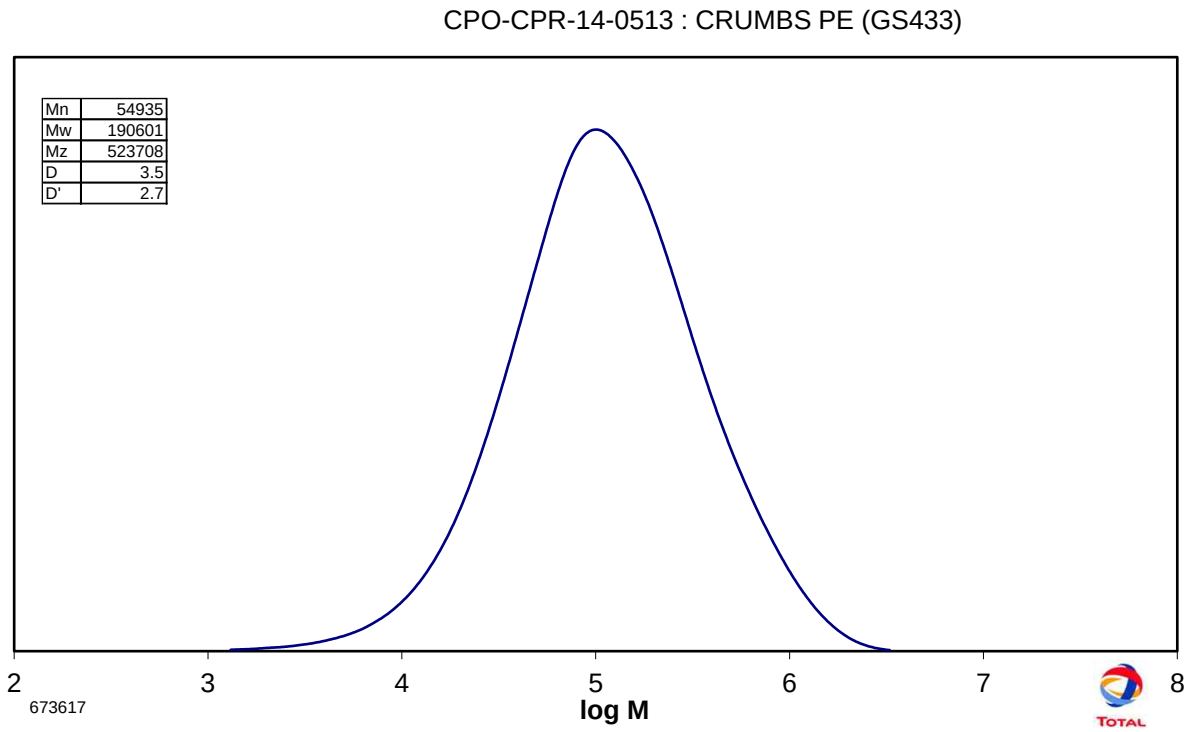


Figure S64. GPC trace of PE/PHex (Table 2, run 9) obtained with **3c-Zr$_2$**.

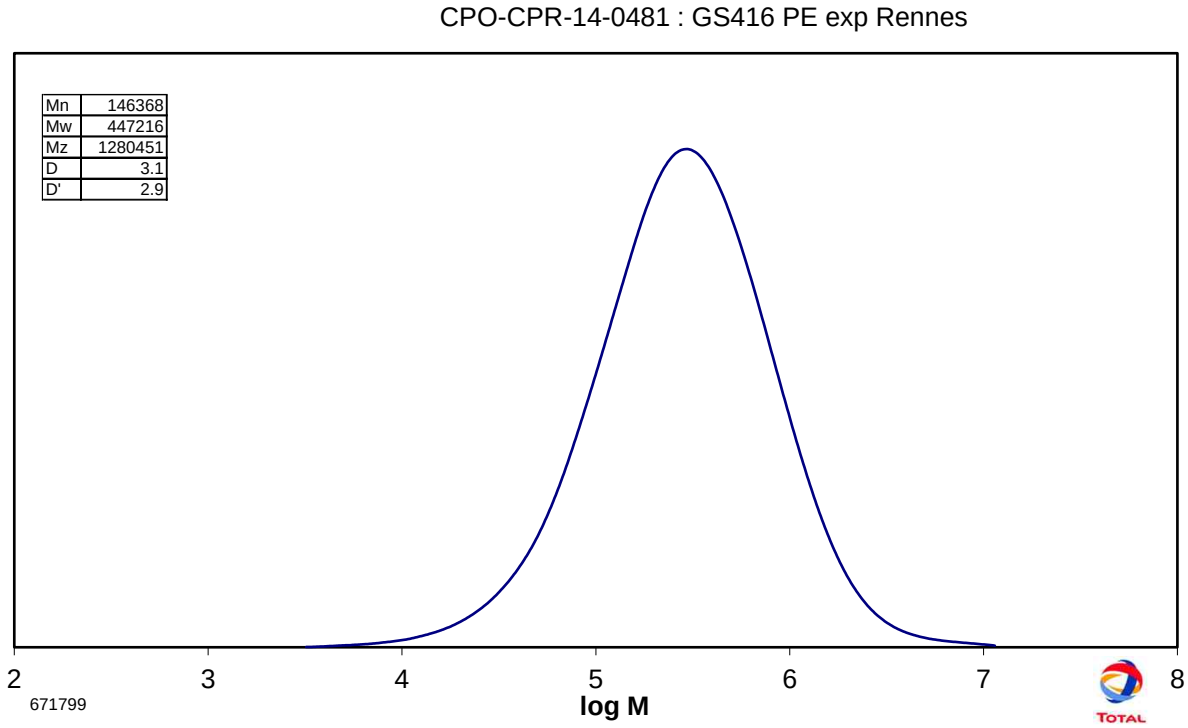


Figure S65. GPC trace of PE/PHex (Table 2, run 10) obtained with **3a-Hf$_2$**.

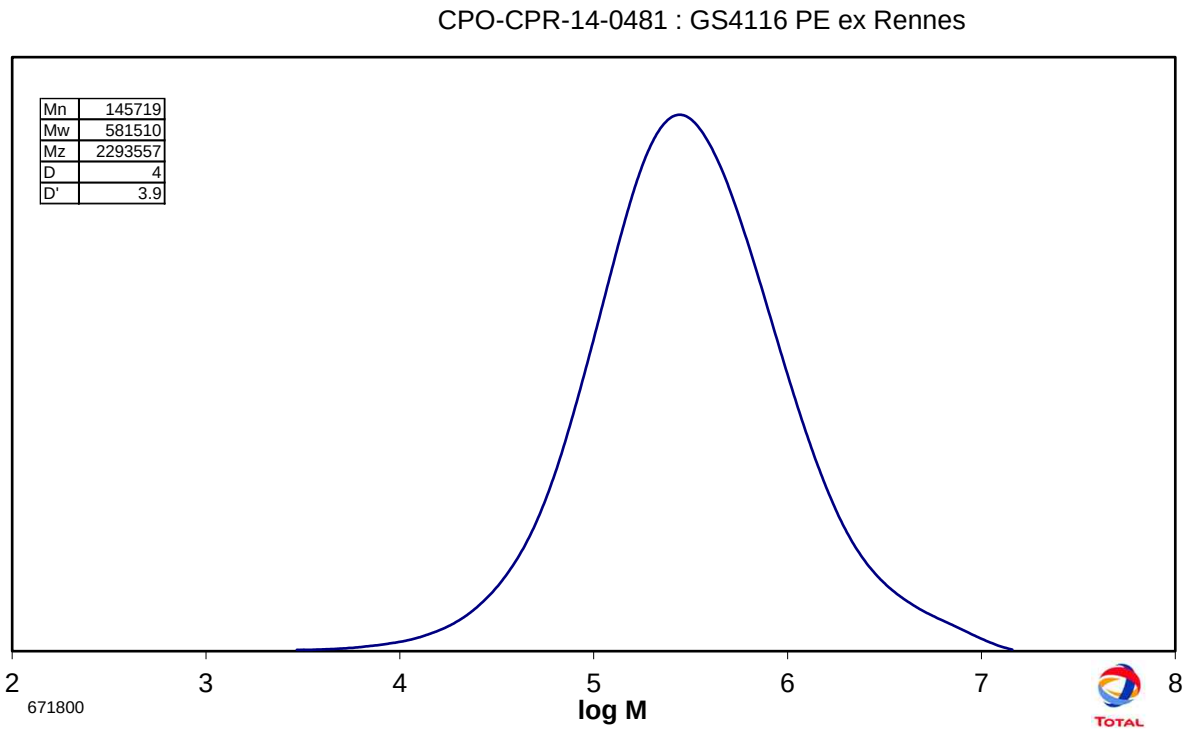


Figure S66. GPC trace of PE/PHex (Table 2, run 11) obtained with **3a-Hf$_2$.**

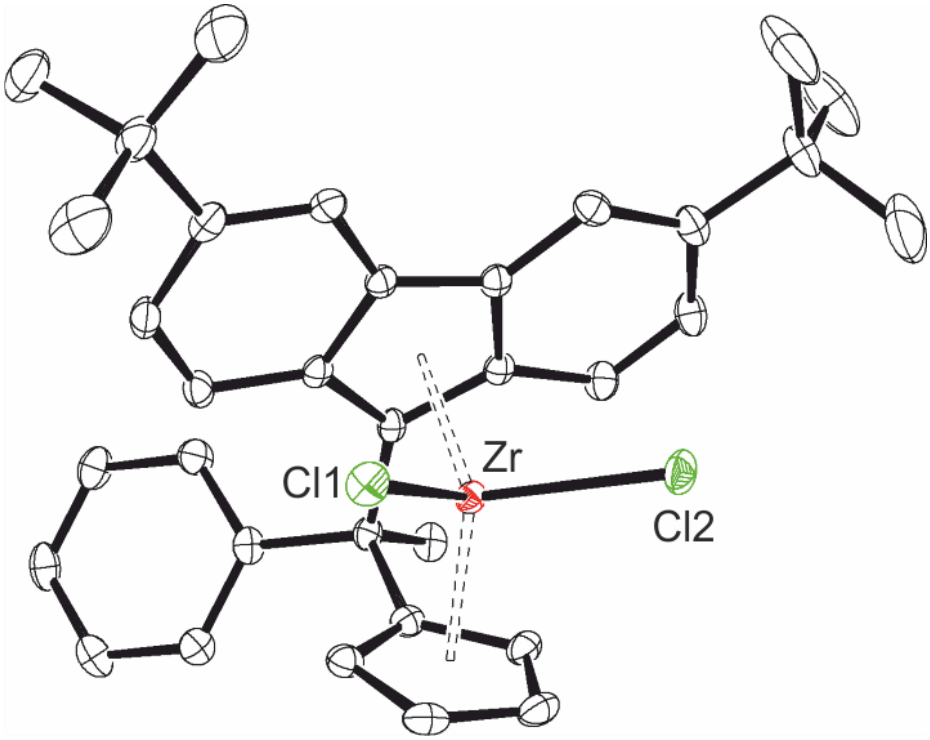


Figure S67. Molecular structure of **3a'-Zr** (ellipsoids drawn at the 50% probability level; all hydrogen atoms are omitted for clarity).

Table S1. Summary of Crystal and Refinement Data for Compound **3a'-Zr**.

	3a-Zr
Empirical formula	C_{34} H_{36} Cl_2 Zr
Formula weight	606.75
Temperature, *K*	150(2)
Wavelength, Å	0.71073
Crystal system	orthorhombic
space group	*P c c n*
a, Å	15.8912(19)
b, Å	31.664(4)
c, Å	11.9600(13)
β, deg	90
Volume, $Å^3$	6018.0(12)
Z	8
Calculated density, $g.cm^{-3}$	1.339
Absorption coefficient, mm^{-1}	0.564
Crystal size, mm	0.46 x 0.21 x 0.11
no. of rflns collected	91512
no. of indep rflns	6899 [R(int) = 0.0457]
Max. and min. transmission	0.940 and 0.886
Data / restraints / parameters	6899 / 0 / 341
Final *R* indices [I>2σ]	$R1^a$ = 0.025, $wR2^b$ = 0.0573
R indices (all data)	$R1^a$ = 0.0321, $wR2^b$ = 0.0613
Goodness-of-fit on F^2	1.064
Largest diff. peak and hole, $e.Å^{-3}$	0.343 and -0.316