

Supporting Information for

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

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Figure S1. ^1H NMR spectrum of **1a**.

Figure S2. ^{13}C NMR spectrum of **1a**.

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

Figure S4. ^1H NMR spectrum of **1b**.

Figure S5. ^{13}C NMR spectrum of **1b**.

Figure S6. ^1H NMR spectrum of **1c**.

Figure S7. ^{13}C NMR spectrum of **1c**.

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

Figure S9. ^1H NMR spectrum of **2a**.

Figure S10. ^{13}C NMR spectrum of **2a**.

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

Figure S12. ^1H NMR spectrum of **2b**.

Figure S13. ^{13}C NMR spectrum of **2b**.

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

Figure S15. ^1H NMR spectrum of **2c**.

Figure S16. ^{13}C NMR spectrum of **2c**.

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

Figure S18. ^1H NMR spectrum of **2a'**.

Figure S19. ^{13}C NMR spectrum of **2a'**.

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

Figure S21. ^1H NMR spectrum of **2b'**.

Figure S22. ^{13}C NMR spectrum of **2b'**.

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

Figure S24. ^1H NMR spectrum of **3a-Zr₂**.

Figure S25. HMBC spectrum of **3a-Zr₂**.

Figure S26. HSQC spectrum of **3a-Zr₂**.

Figure S27. APPI-IMMS of **3a-Zr₂**.

Figure S28. ^1H NMR spectrum of **3a-Hf₂**.

Figure S29. ^{13}C NMR spectrum of **3a-Hf₂**.

Figure S30. APPI-IMMS of **3a-Hf₂**.

Figure S31. ^1H NMR spectrum of **3b-Zr₂**.

Figure S32. HMBC spectrum of **3b-Zr₂**.

Figure S33. HSQC spectrum of **3b-Zr₂**.

Figure S34. APPI-IMMS of **3b-Zr₂**.

Figure S35. ^1H NMR spectrum of **3c-Zr₂**.

Figure S36. ^{13}C NMR spectrum of **3c-Zr₂**.

Figure S37. ^1H NMR spectrum of **3a'-Zr**.

Figure S38. ^{13}C NMR spectrum of **3a'-Zr**.

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

Figure S40. ^1H NMR spectrum of **3b'-Zr**.

Figure S41. ^{13}C NMR spectrum of **3b'-Zr**.

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

Figure S43. ^1H NMR spectrum of **3b'-Hf**.

Figure S44. ^{13}C NMR spectrum of **3b'-Hf**.

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

Figure S46. ^{13}C NMR spectrum of PE (Table 1, run 1).

Figure S47. GPC trace of PE (Table 1, run 1) obtained with **3a-Zr₂**.

Figure S48. ^{13}C NMR spectrum of PE (Table 1, run 3).

Figure S49. ^{13}C NMR spectrum of PE (Table 1, run 5).

Figure S50. GPC trace of PE (Table 1, run 5) obtained with **3b-Zr₂**.

Figure S51. GPC trace of PE (Table 1, run 6) obtained with **3b-Zr₂**.

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-Zr₂**.

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

Figure S57. GPC trace of PE/PHex (Table 2, run 1) obtained with **3a-Zr₂**.

Figure S58. ^{13}C NMR spectrum of PE/PHex (Table 2, run 4).

Figure S59. ^{13}C NMR spectrum of PE/PHex (Table 2, run 5).

Figure S60. GPC trace of PE/PHex (Table 2, run 5) obtained with **3b-Zr₂**.

Figure S61. GPC trace of PE/PHex (Table 2, run 6) obtained with **3b-Zr₂**.

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-Zr₂**.

Figure S65. GPC trace of PE/PHex (Table 2, run 10) obtained with **3a-Hf₂**.

Figure S66. GPC trace of PE/PHex (Table 2, run 11) obtained with **3a-Hf₂**.

Figure S67. Molecular structure of **3a'-Zr**.

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

Figure S68. DFT-optimized structures of C_s -symmetric and C_i -symmetric isomers of **3a-Zr₂**.

Figure S69. DFT-optimized structures of C_s -symmetric and C_i -symmetric isomers of **3c-Zr₂**.

Cartesian coordinates

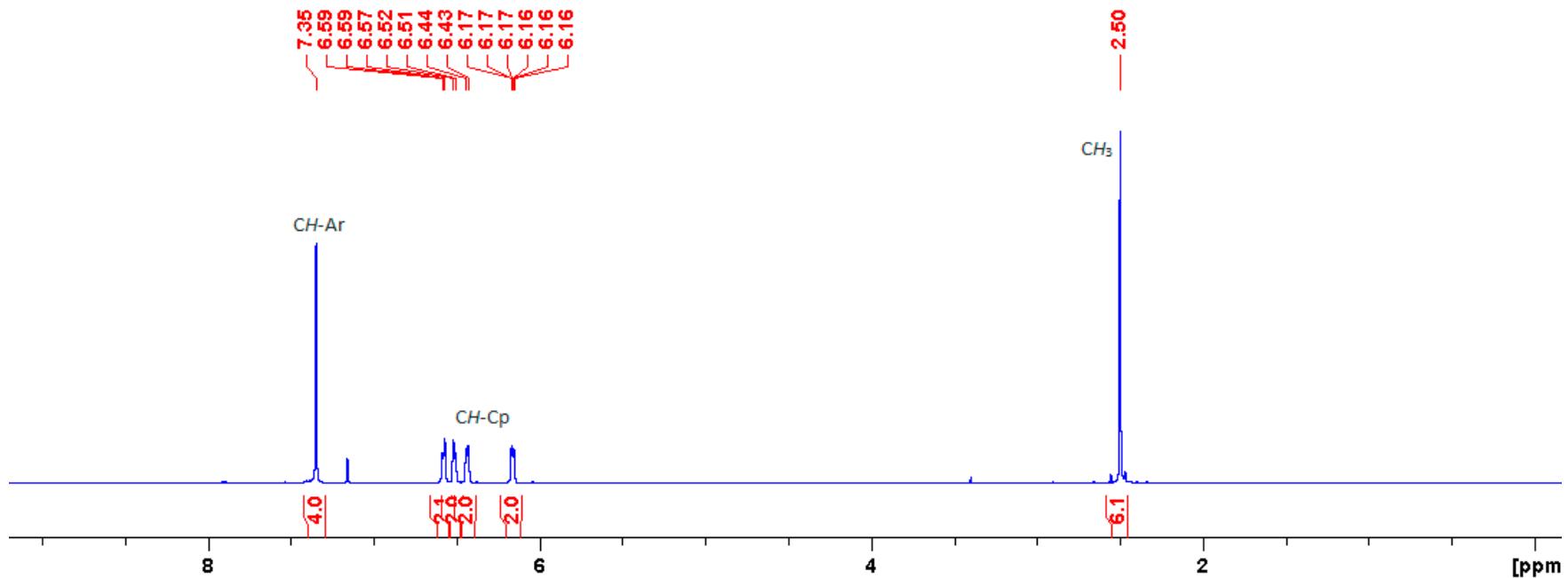
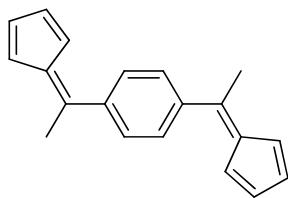


Figure S1. ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of **1a**. jfc-gs190-1



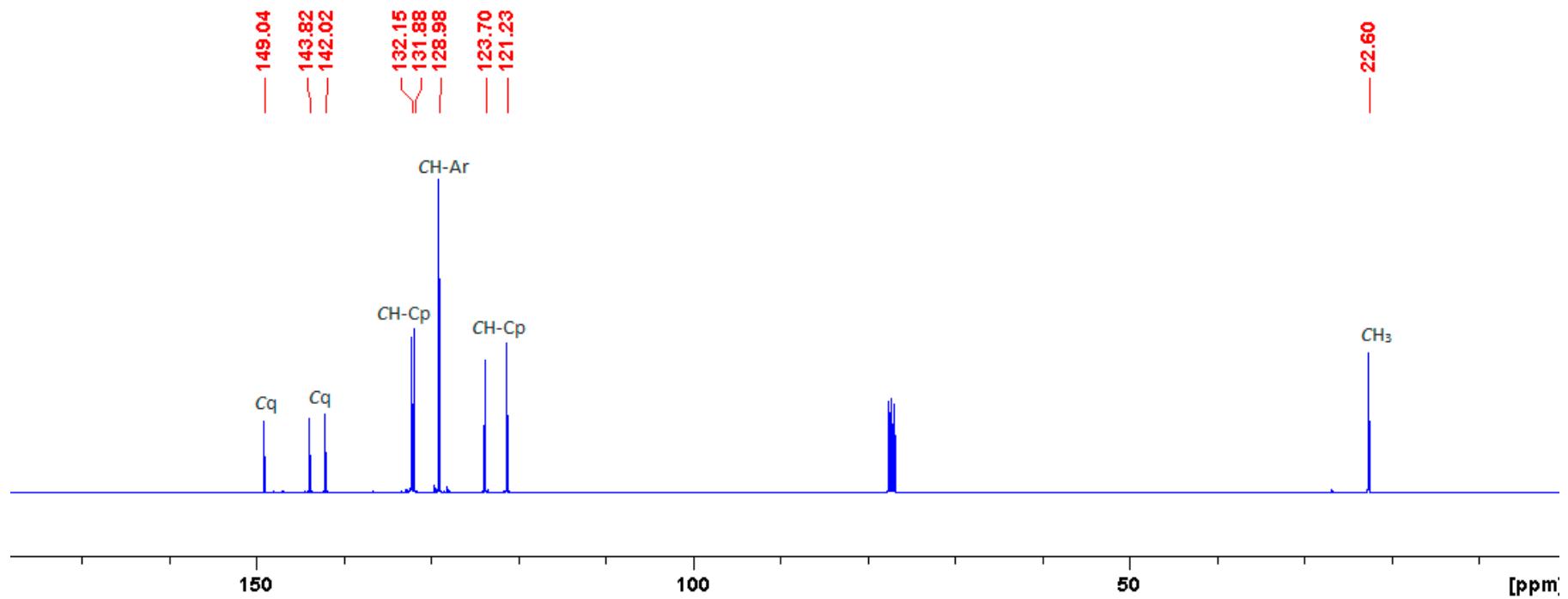


Figure S2. ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 25 °C) of **1a**.

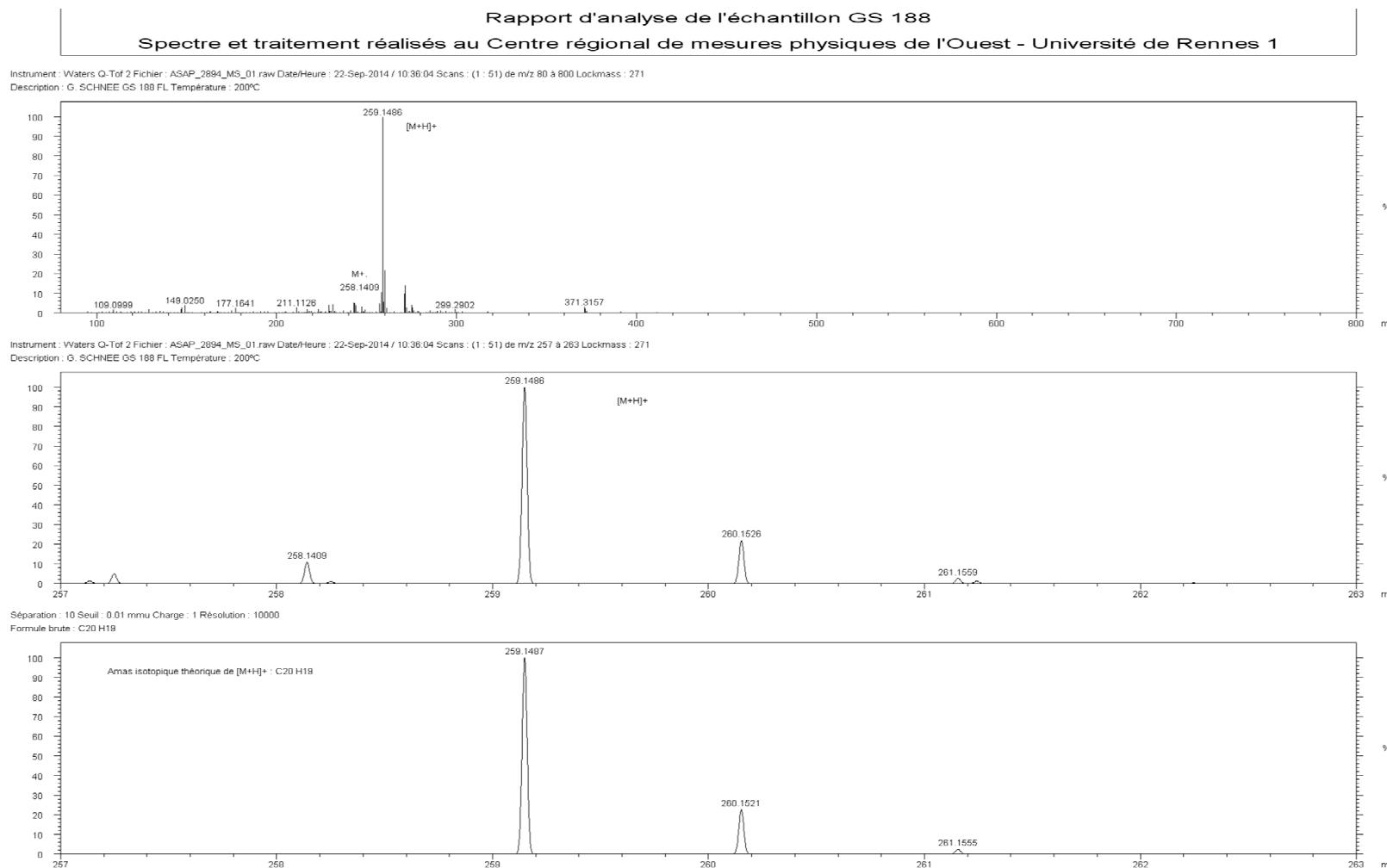


Figure S3. ASAP mass spectrum of **1a**.