

Supporting Information

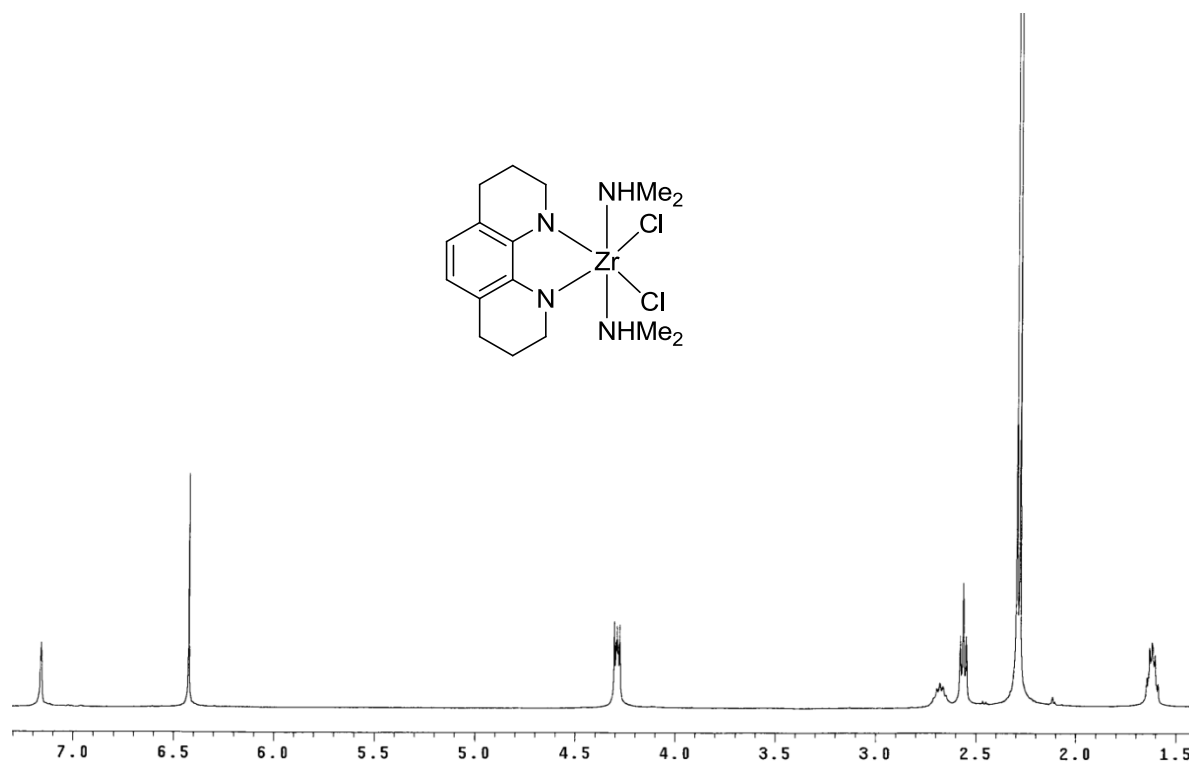
Preparation of octahydro- and tetrahydro- [1,10]phenanthroline zirconium and hafnium complexes for olefin polymerization

Eun Yeong Hwang,^a Geun Ho Park,^a Chun Sun Lee,^a Yi Young Kang,^b Junseong Lee,^b and

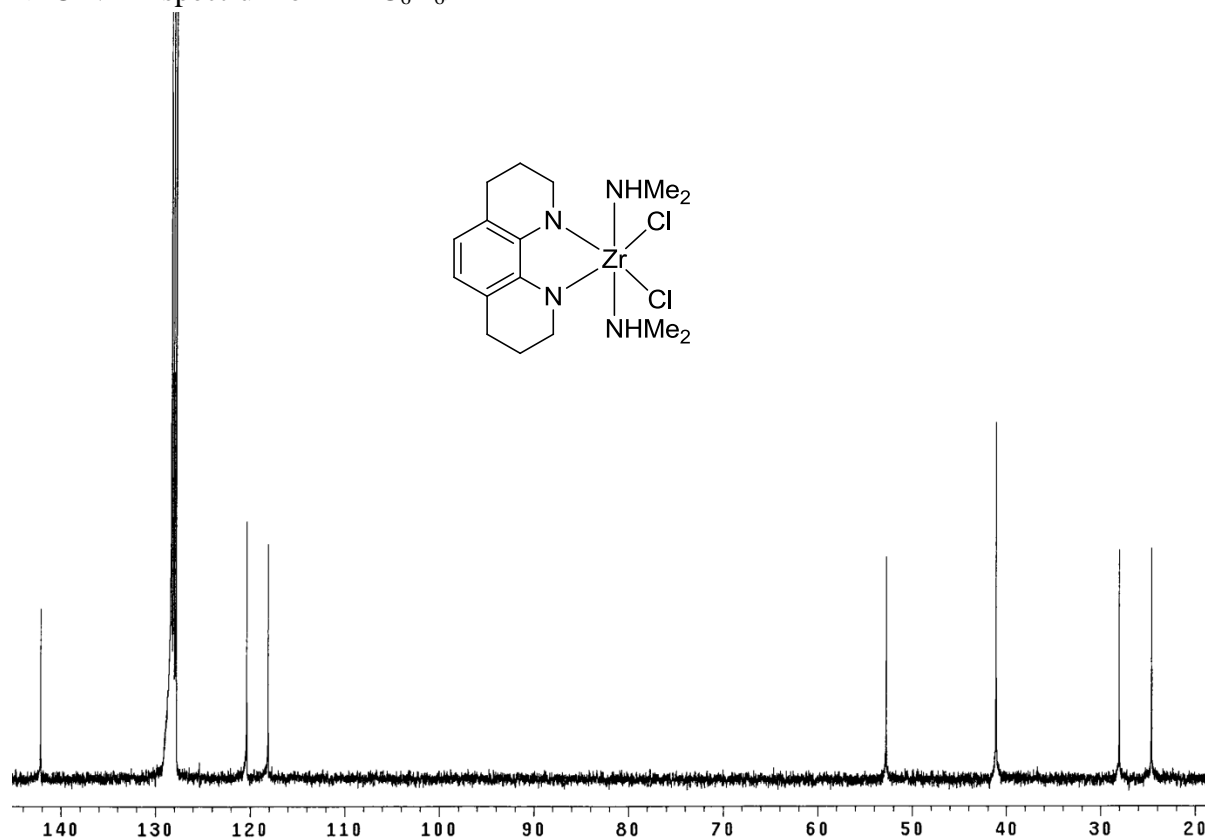
Bun Yeoul Lee^{a}*

^aDepartment of Molecular Science and Technology, Ajou University, Suwon 443-749, South Korea; ^bDepartment of Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 500-757, Korea; Email: bunyeoul@ajou.ac.kr; Tel: 82-31-219-1844

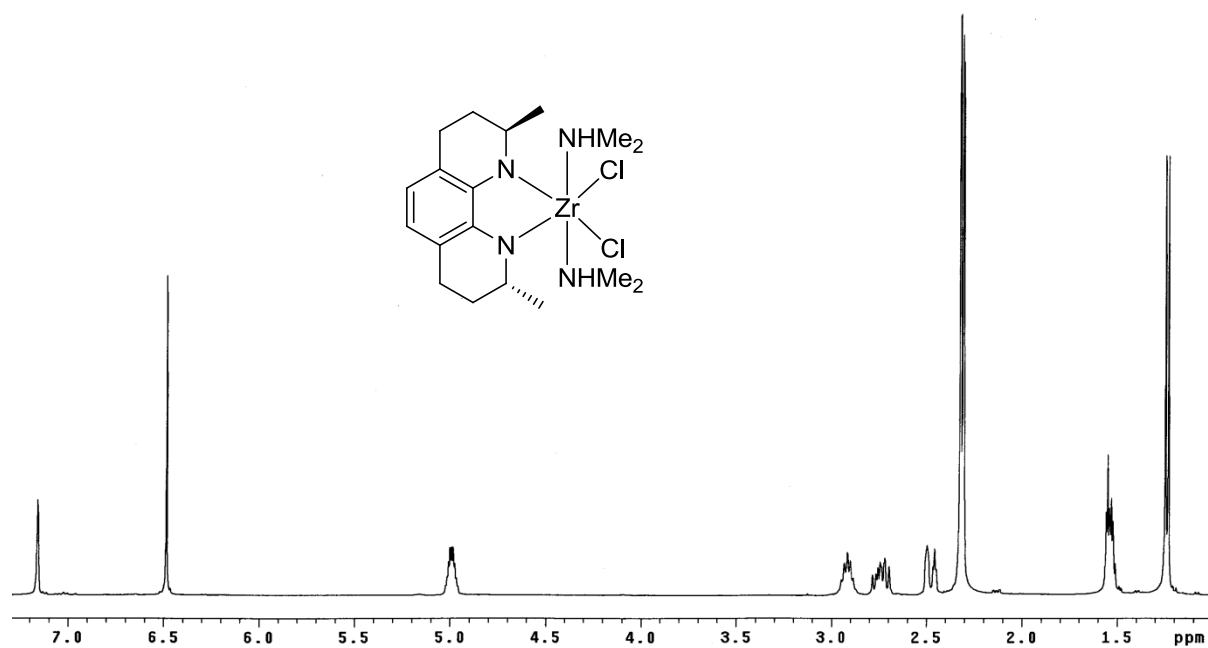
^1H NMR spectrum of **4** in C_6D_6



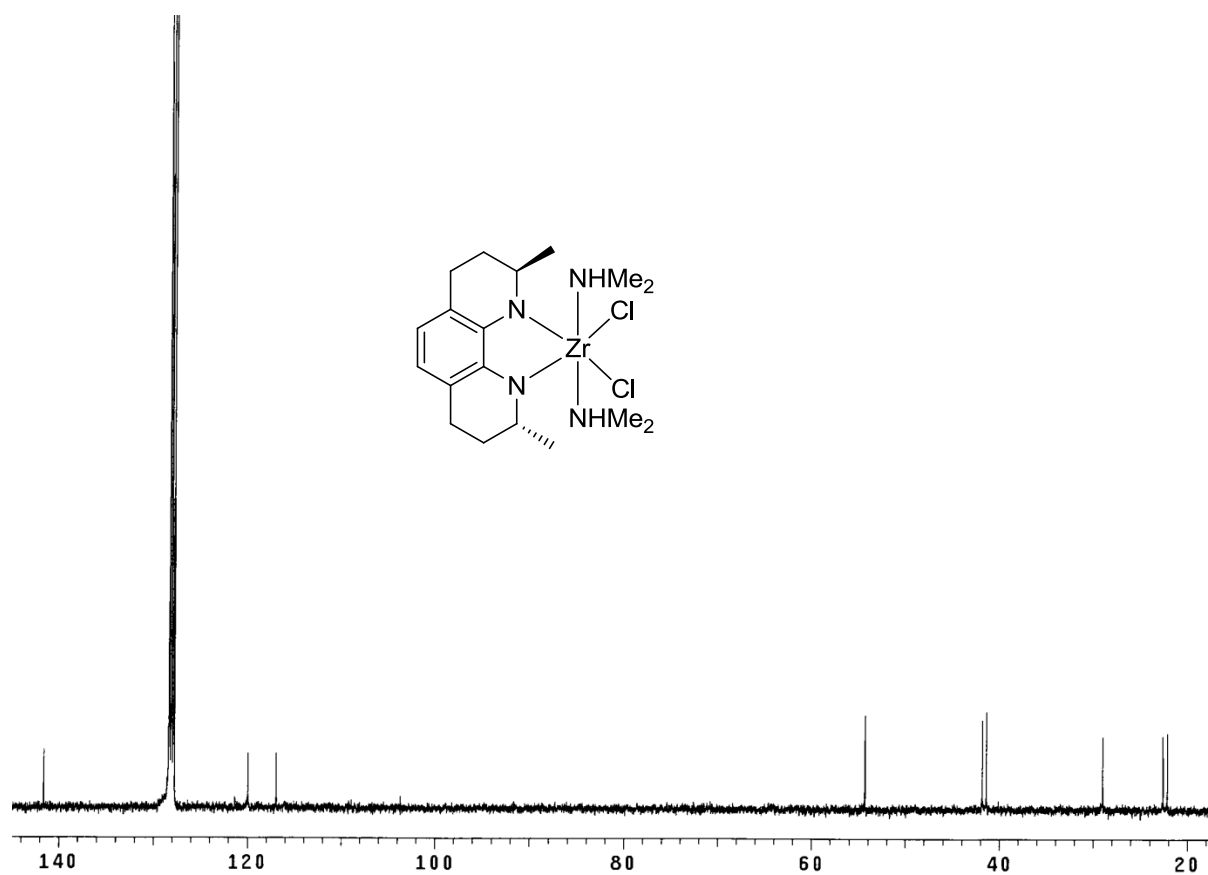
^{13}C NMR spectrum of **4** in C_6D_6



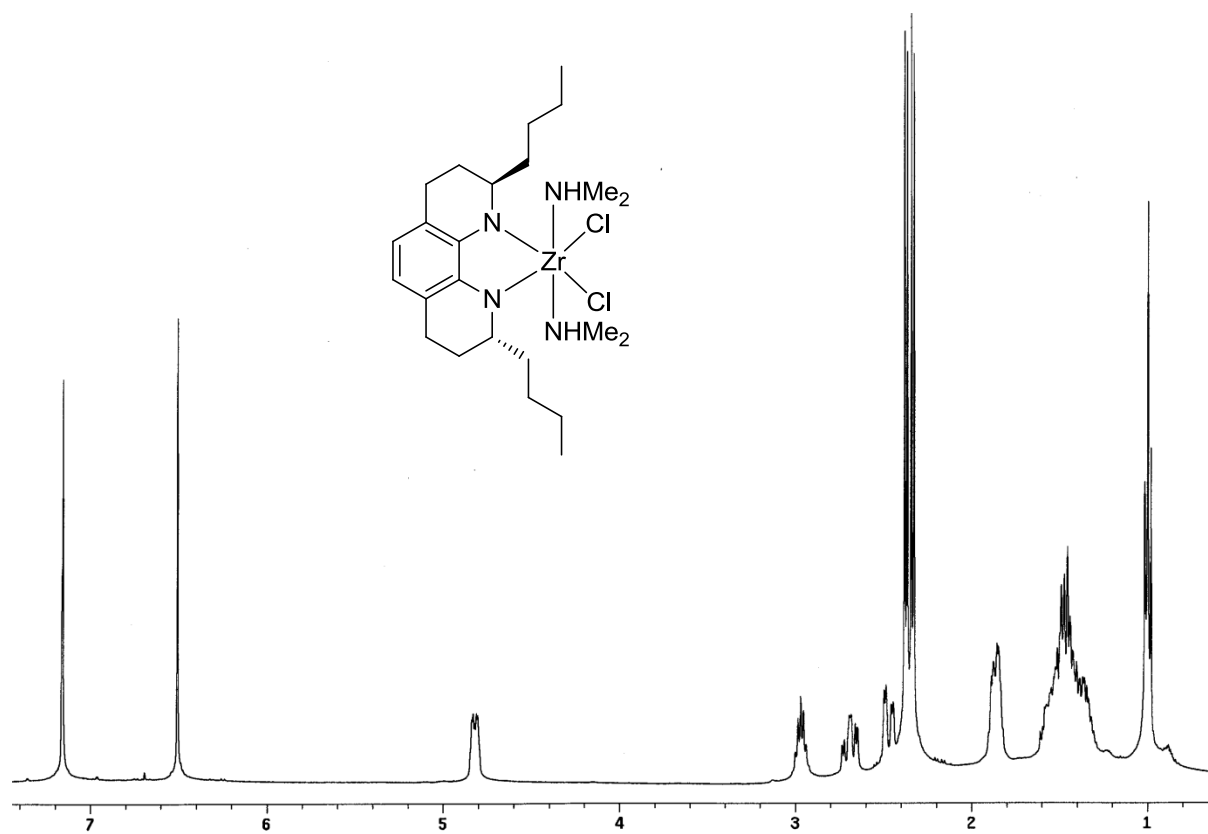
^1H NMR spectrum of **5** in C_6D_6



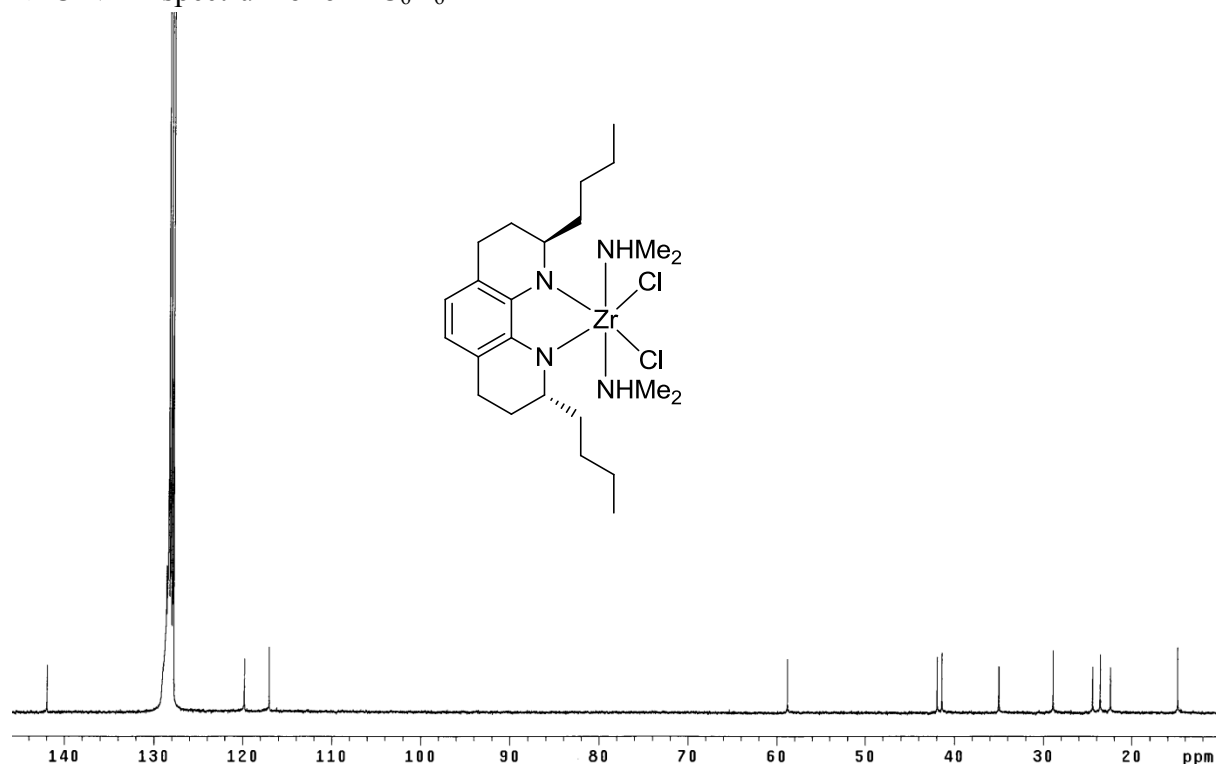
^{13}C NMR spectrum of **5** in C_6D_6



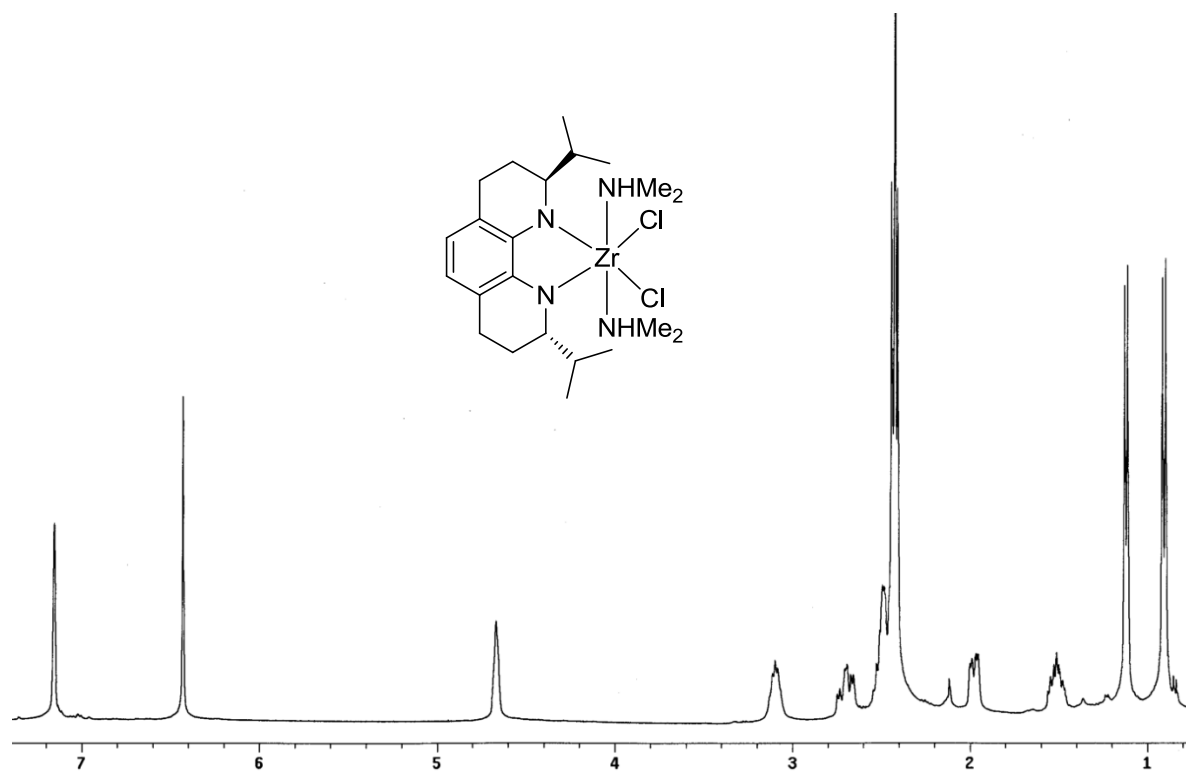
^1H NMR spectrum of **6** in C_6D_6



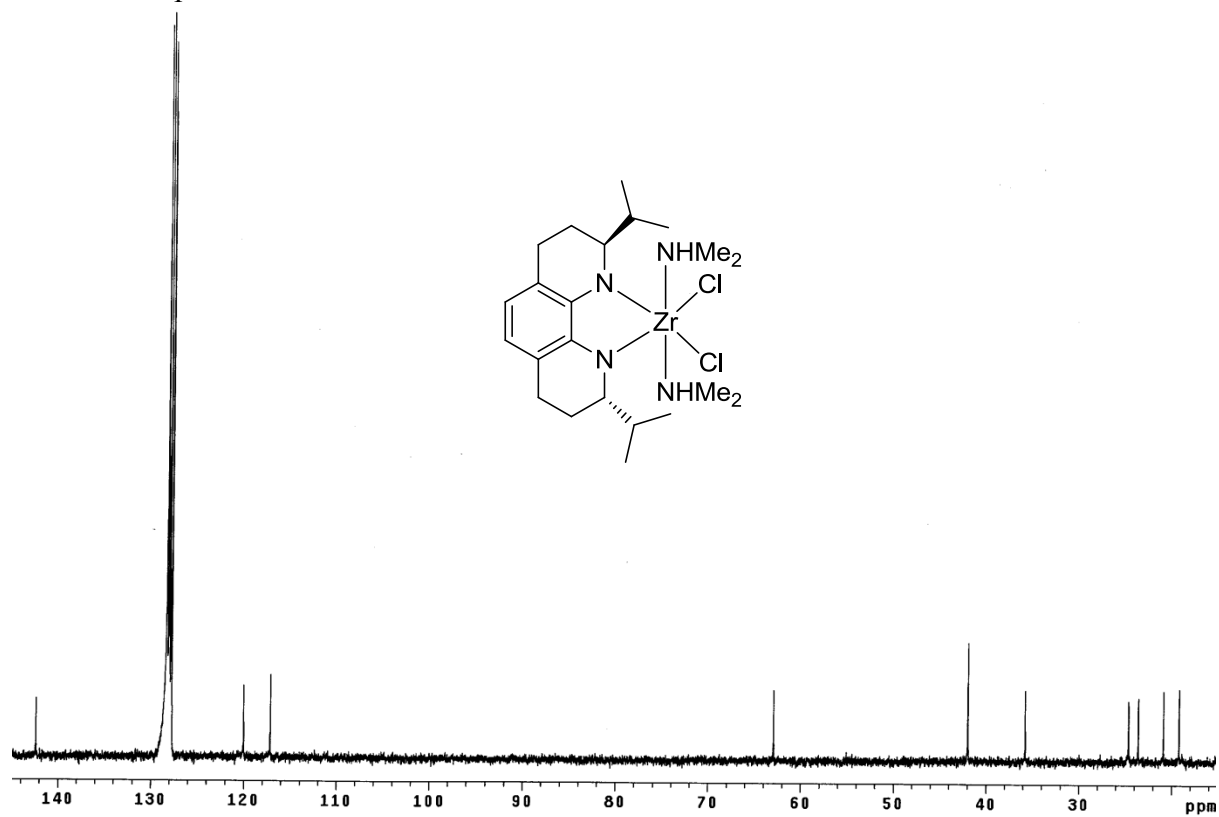
^{13}C NMR spectrum of **6** in C_6D_6



^1H NMR spectrum of **7** in C_6D_6



^{13}C NMR spectrum of **7** in C_6D_6

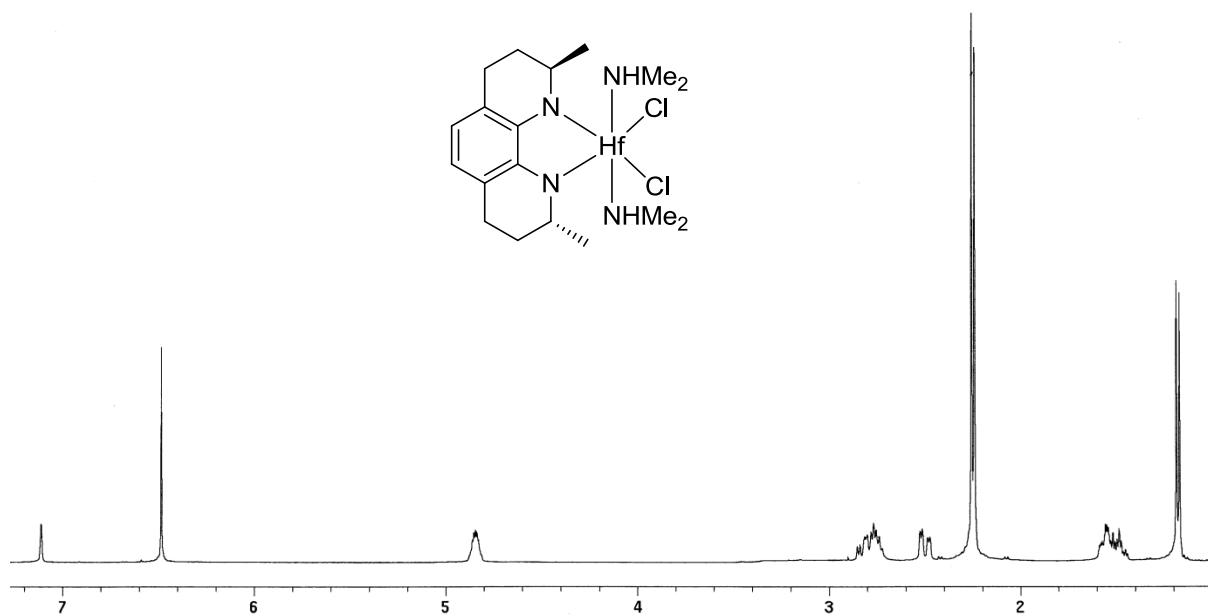


Chemical structure of the complex is shown above the spectrum. The complex consists of a hafnium (Hf) center coordinated by two dimethylamino groups (NHMe₂) and two chlorine atoms (Cl). The hafnium center is also coordinated by a ligand derived from a 1,2,3,4-tetrahydronaphthalene derivative, which is shown as a fused ring system with two nitrogen atoms (N) coordinated to the hafnium center.

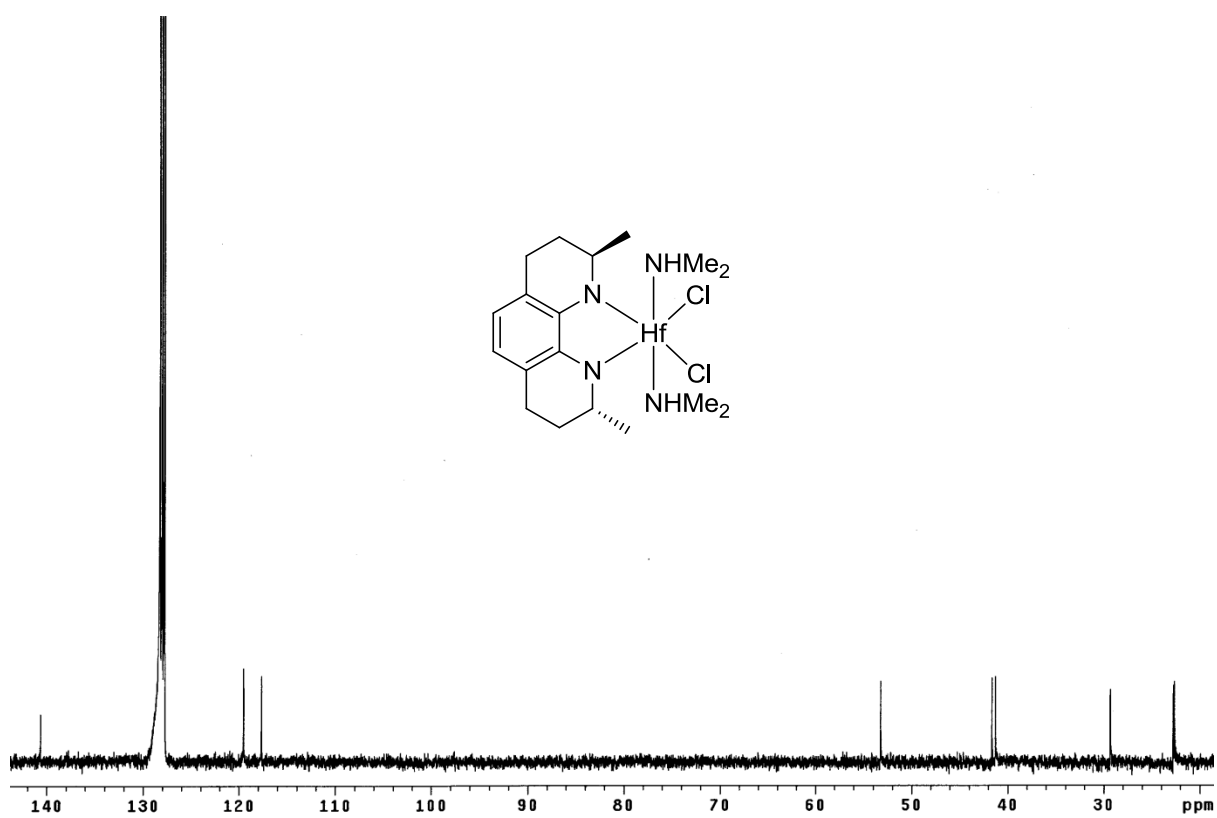
Chemical structure of the complex is shown above the spectrum. The complex consists of a hafnium (Hf) center coordinated by two dimethylamino groups (NHMe₂) and two chlorine atoms (Cl). The hafnium center is also coordinated by a ligand derived from a 1,2,3,4-tetrahydronaphthalene derivative, which is shown as a fused ring system with two nitrogen atoms (N) coordinated to the hafnium center.

[illegible]

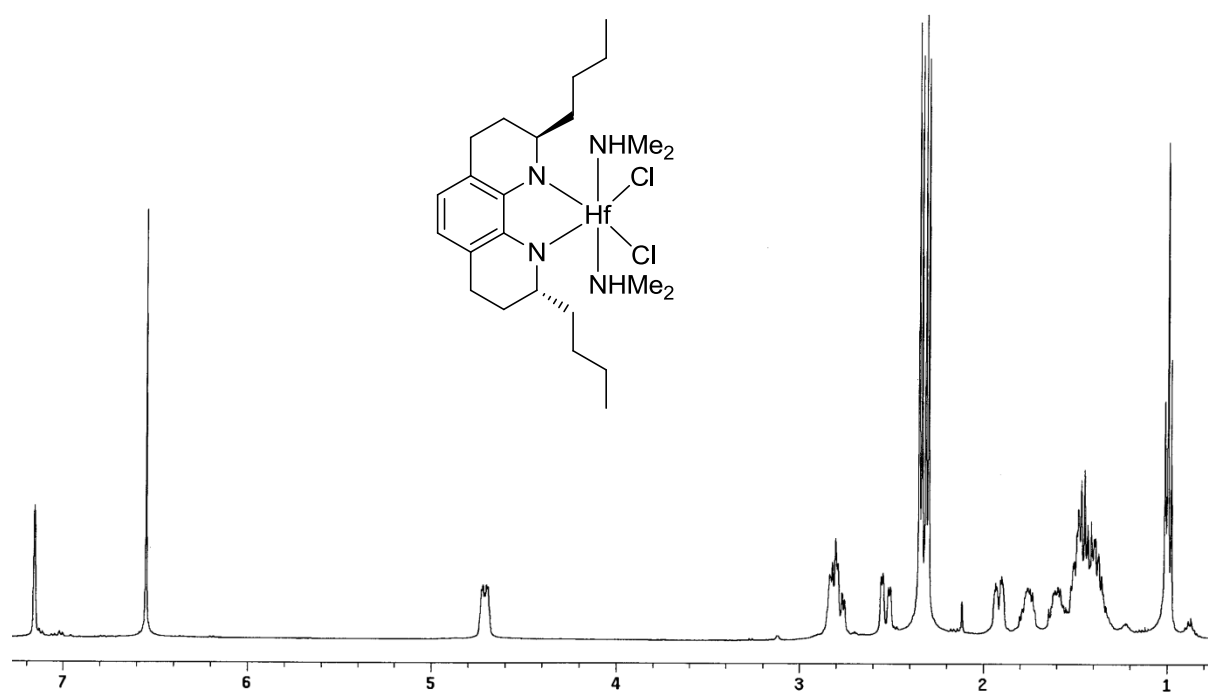
^1H NMR spectrum of **9** in C_6D_6



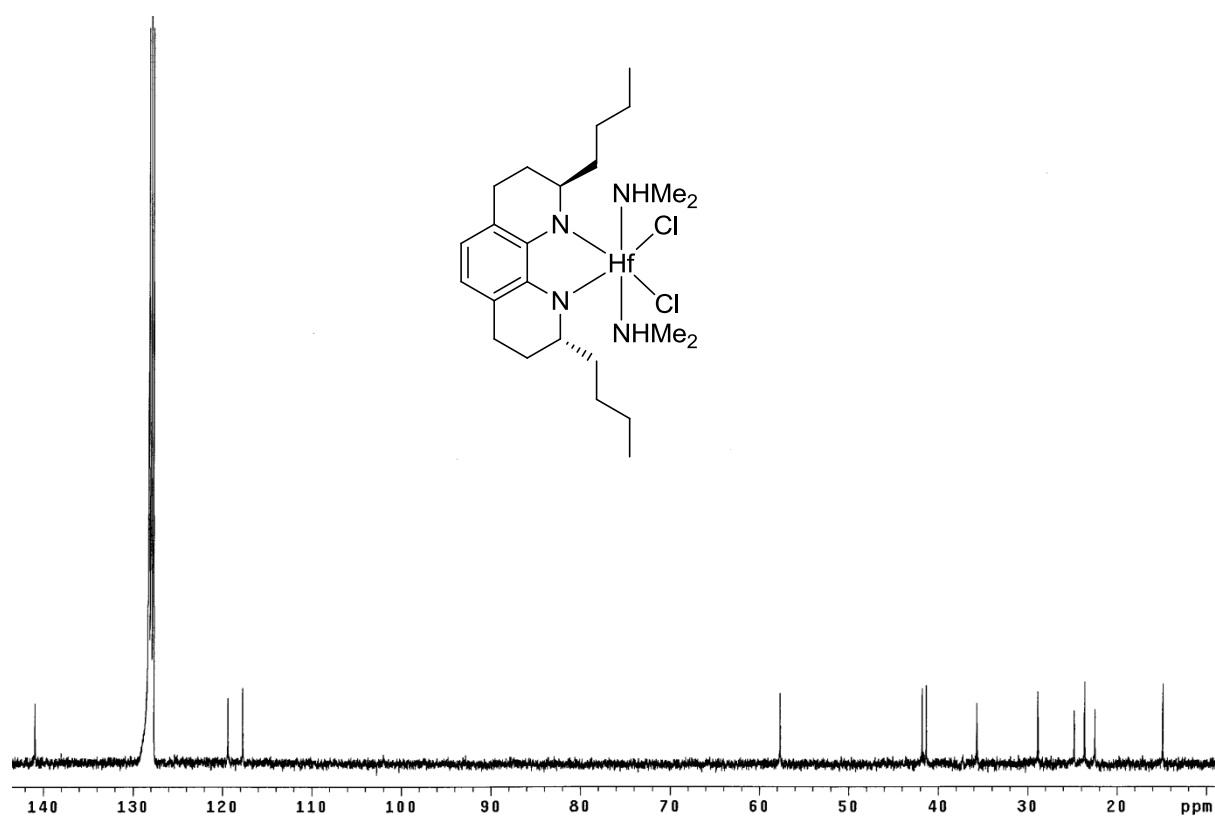
^{13}C NMR spectrum of **9** in C_6D_6



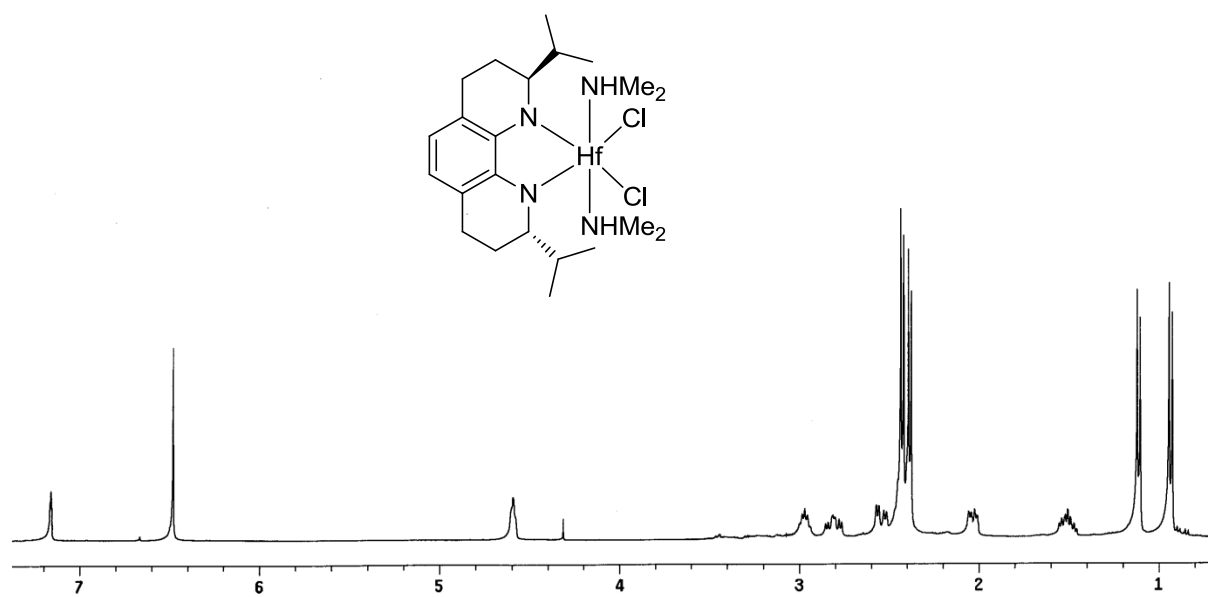
^1H NMR spectrum of **10** in C_6D_6



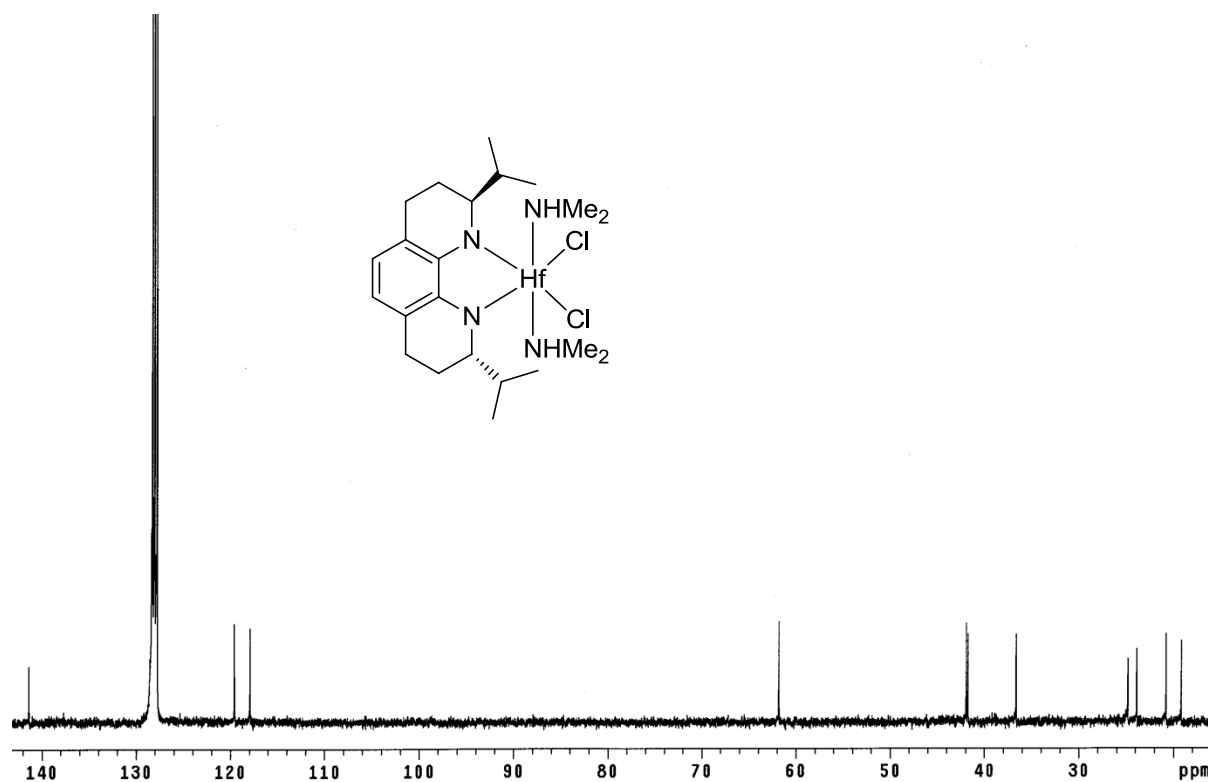
^{13}C NMR spectrum of **10** in C_6D_6



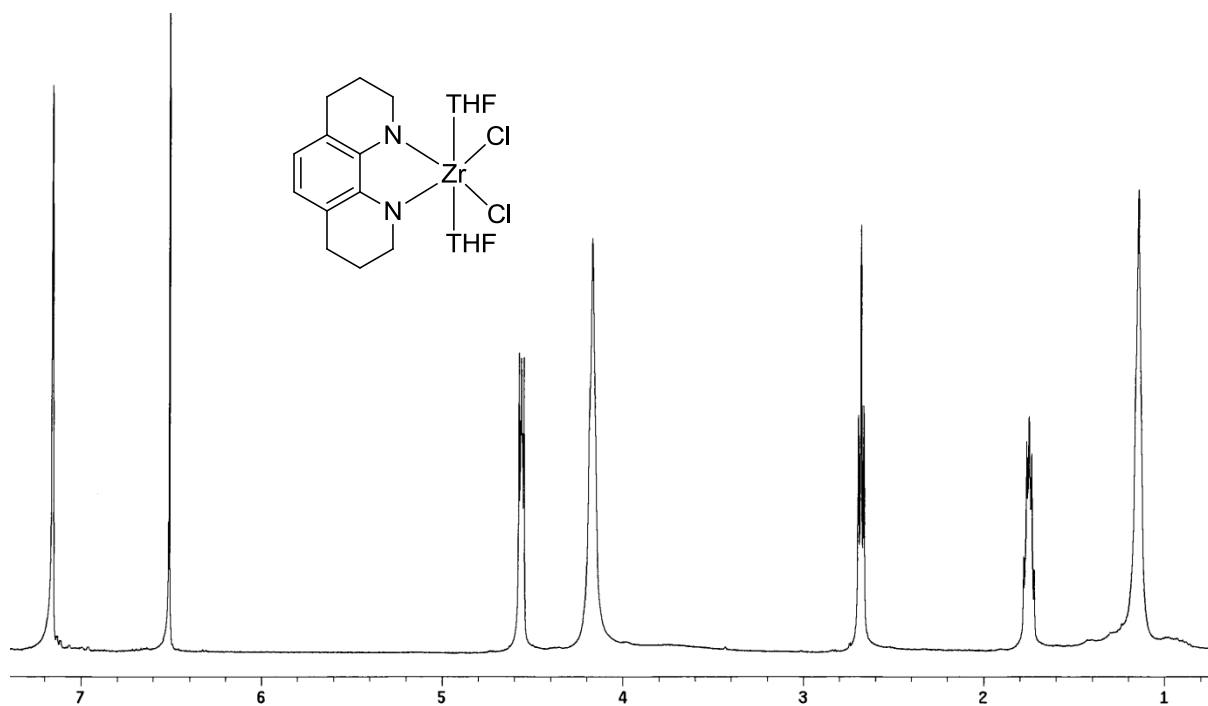
^1H NMR spectrum of **11** in C_6D_6



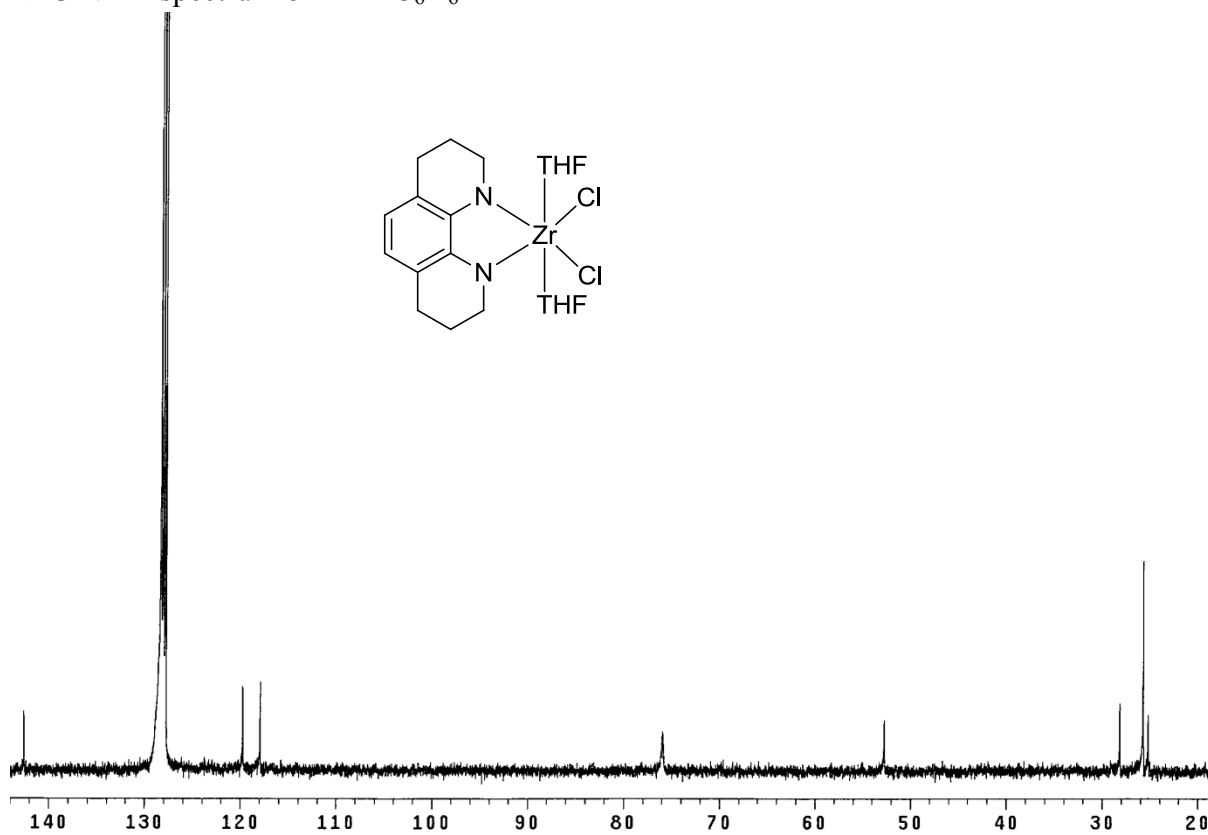
^{13}C NMR spectrum of **11** in C_6D_6



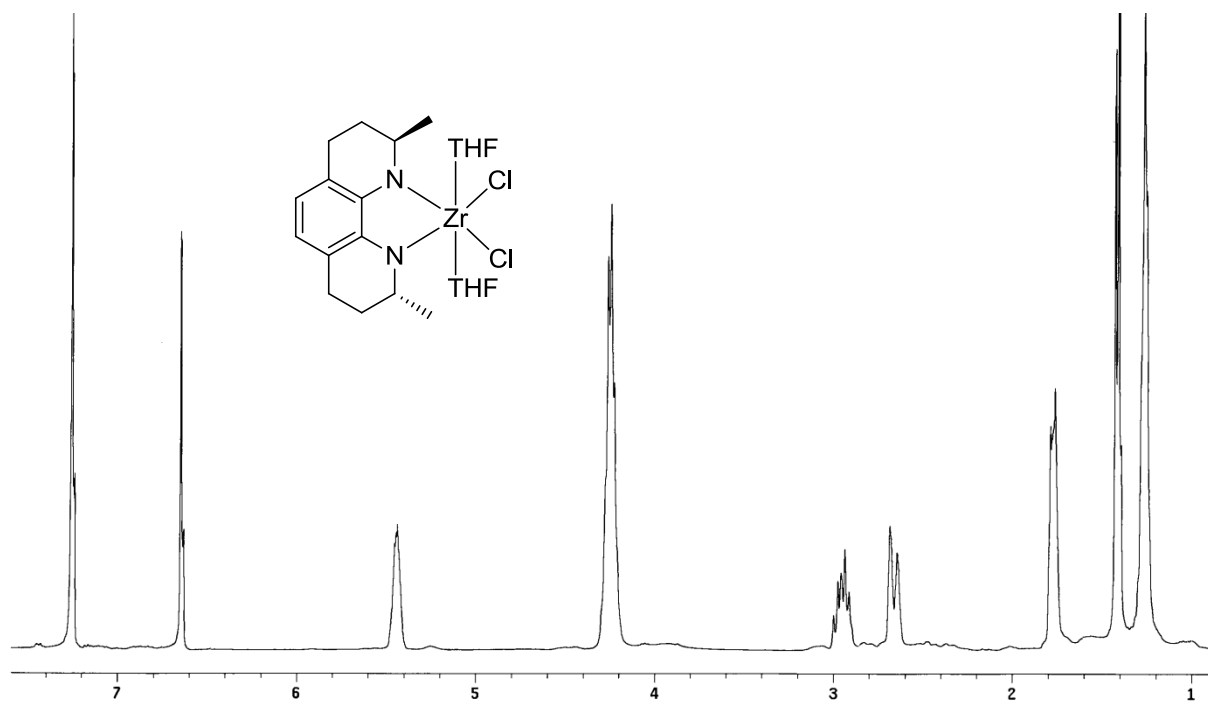
^1H NMR spectrum of **12** in C_6D_6



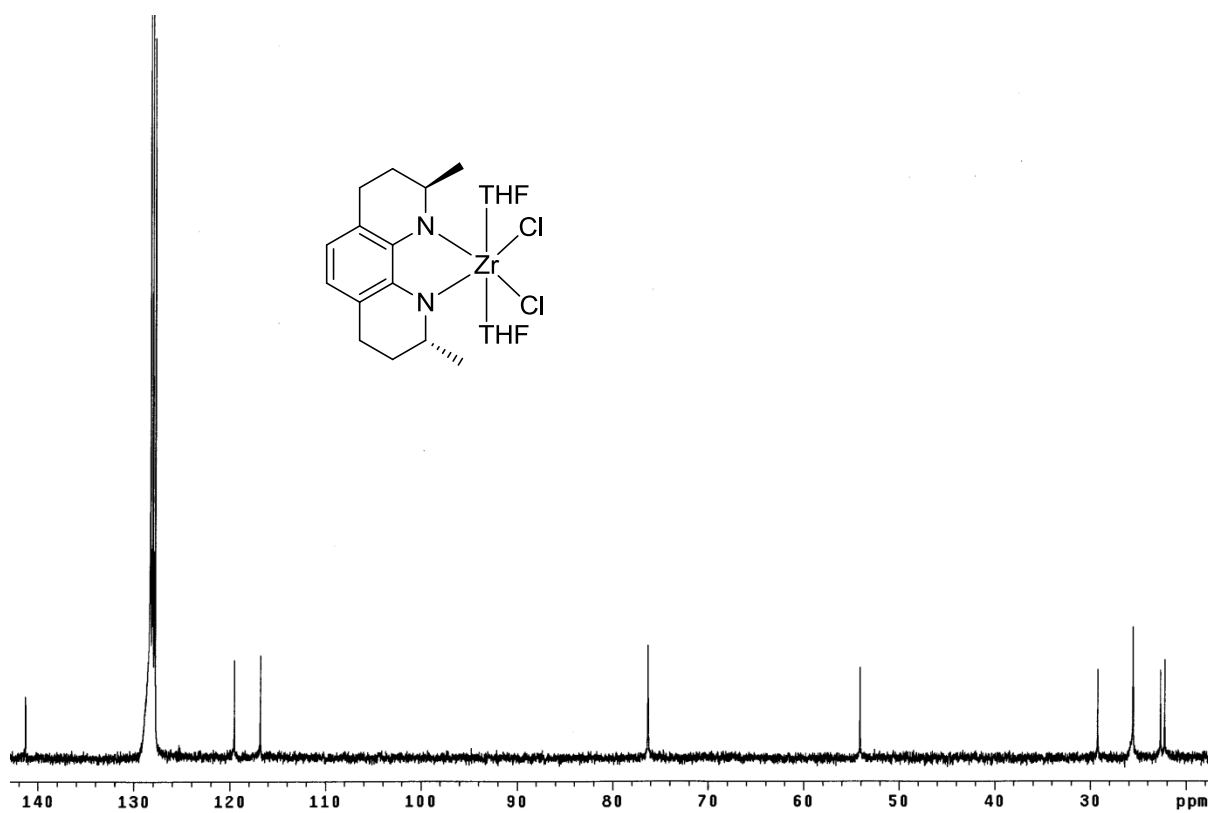
^{13}C NMR spectrum of **12** in C_6D_6



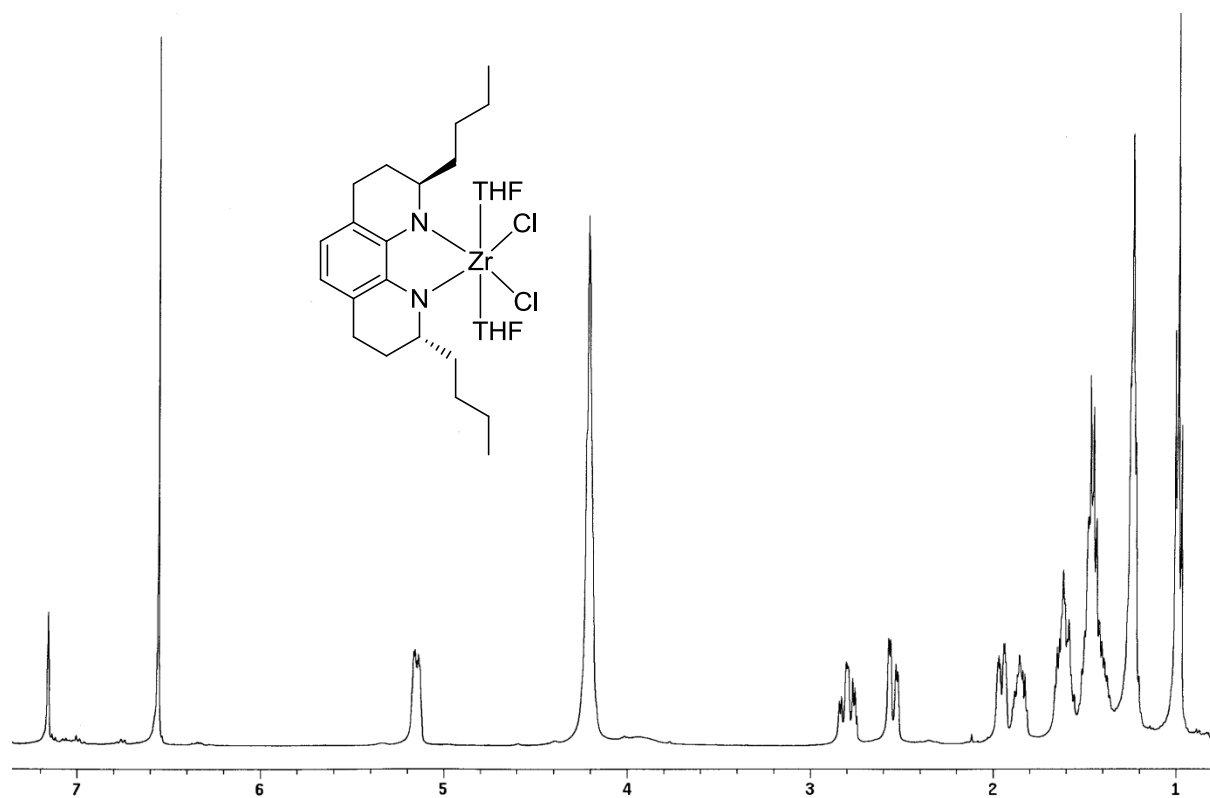
^1H NMR spectrum of **13** in C_6D_6



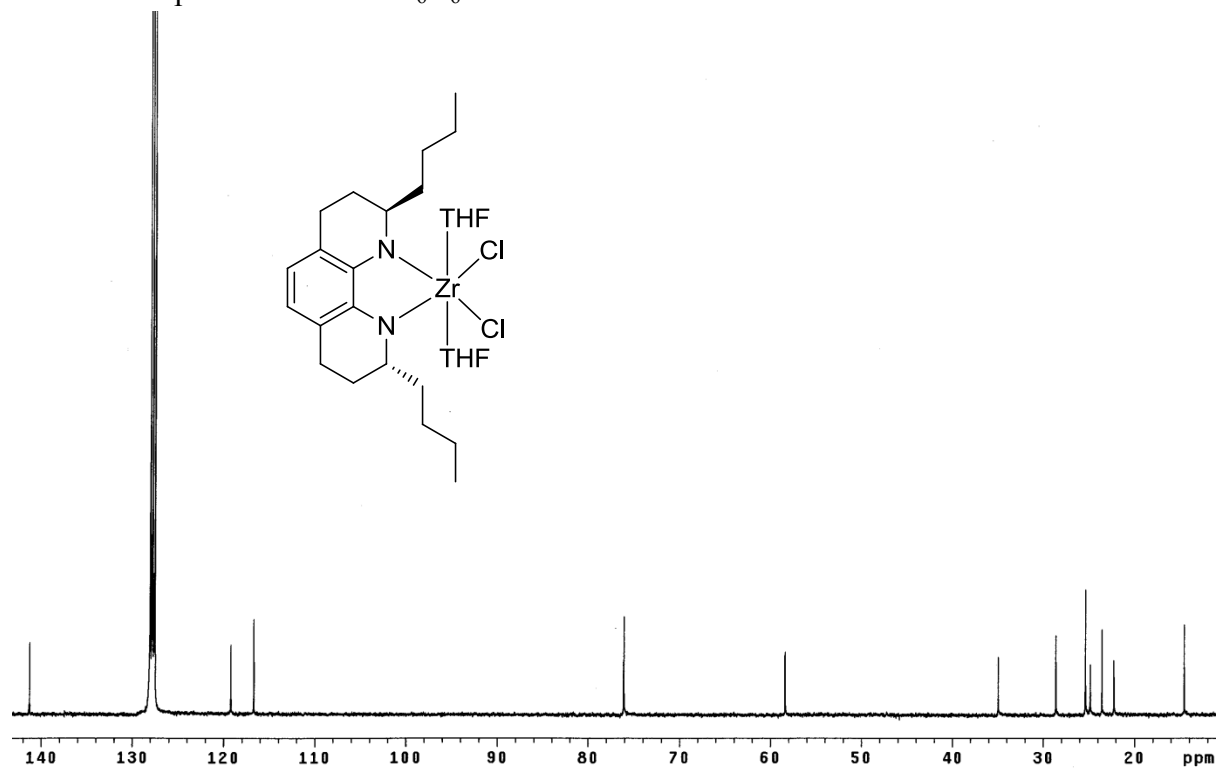
^{13}C NMR spectrum of **13** in C_6D_6



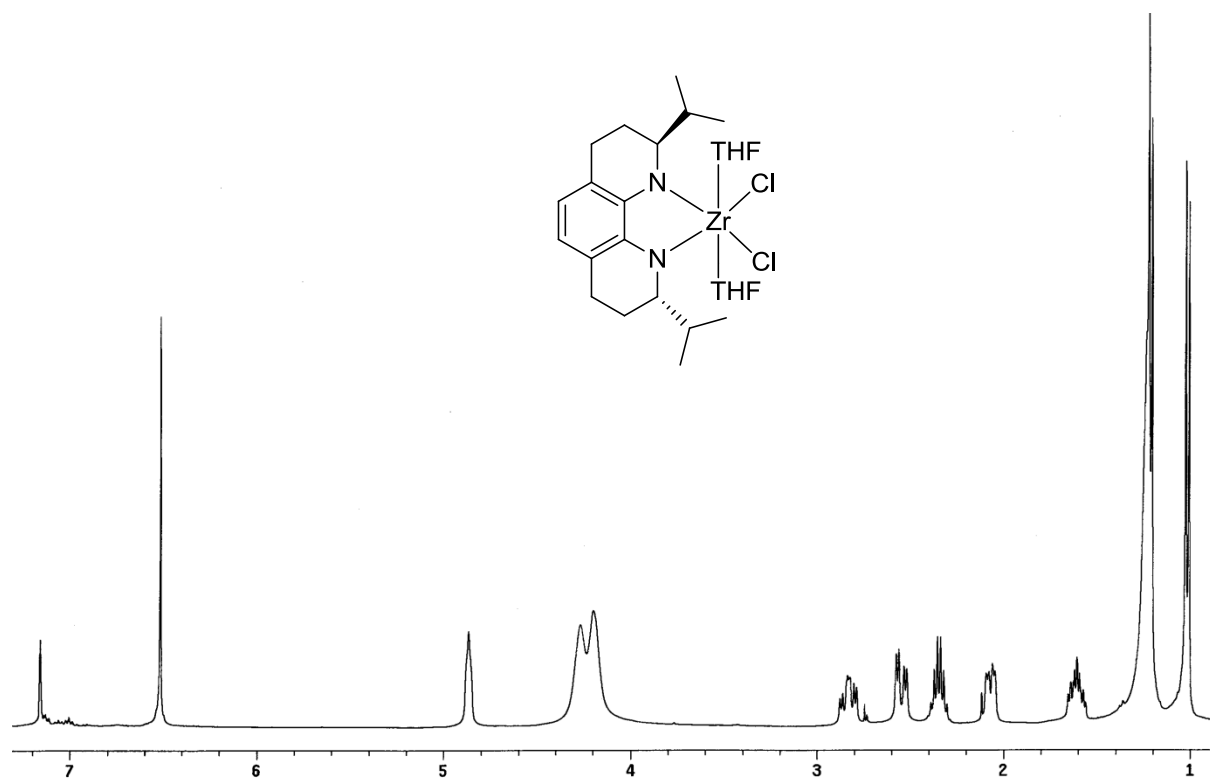
^1H NMR spectrum of **14** in C_6D_6



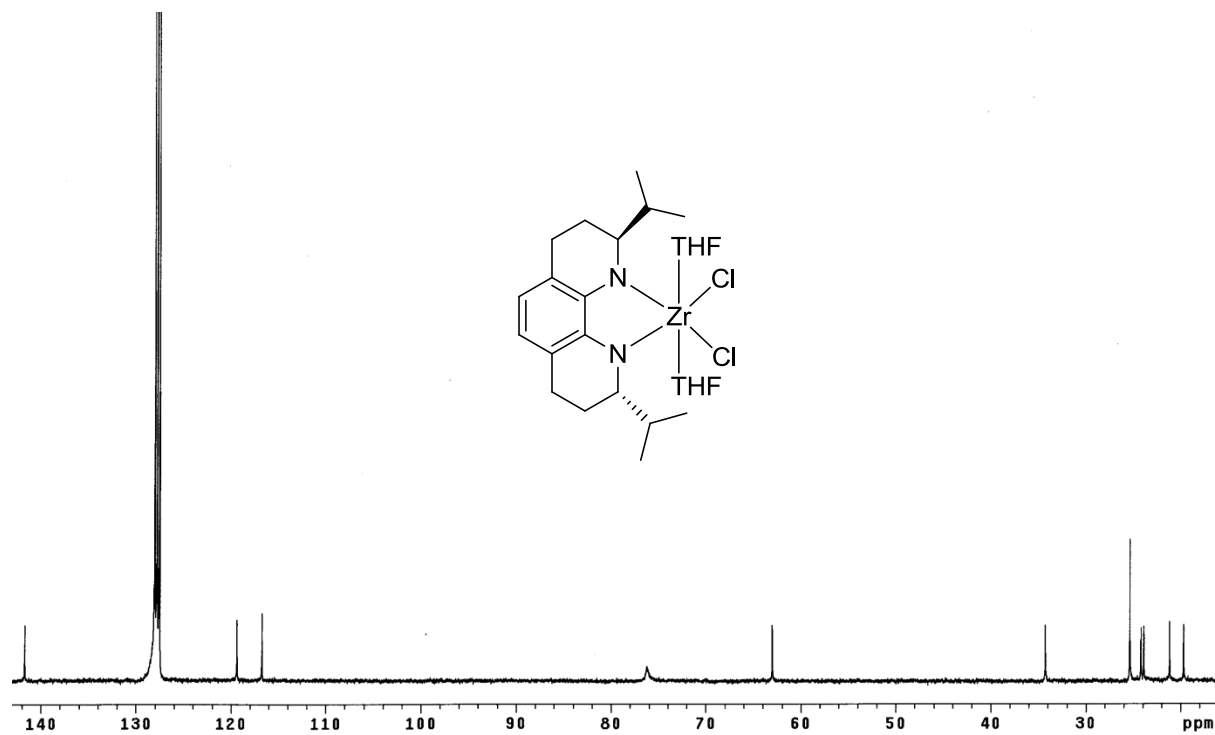
^{13}C NMR spectrum of **14** in C_6D_6



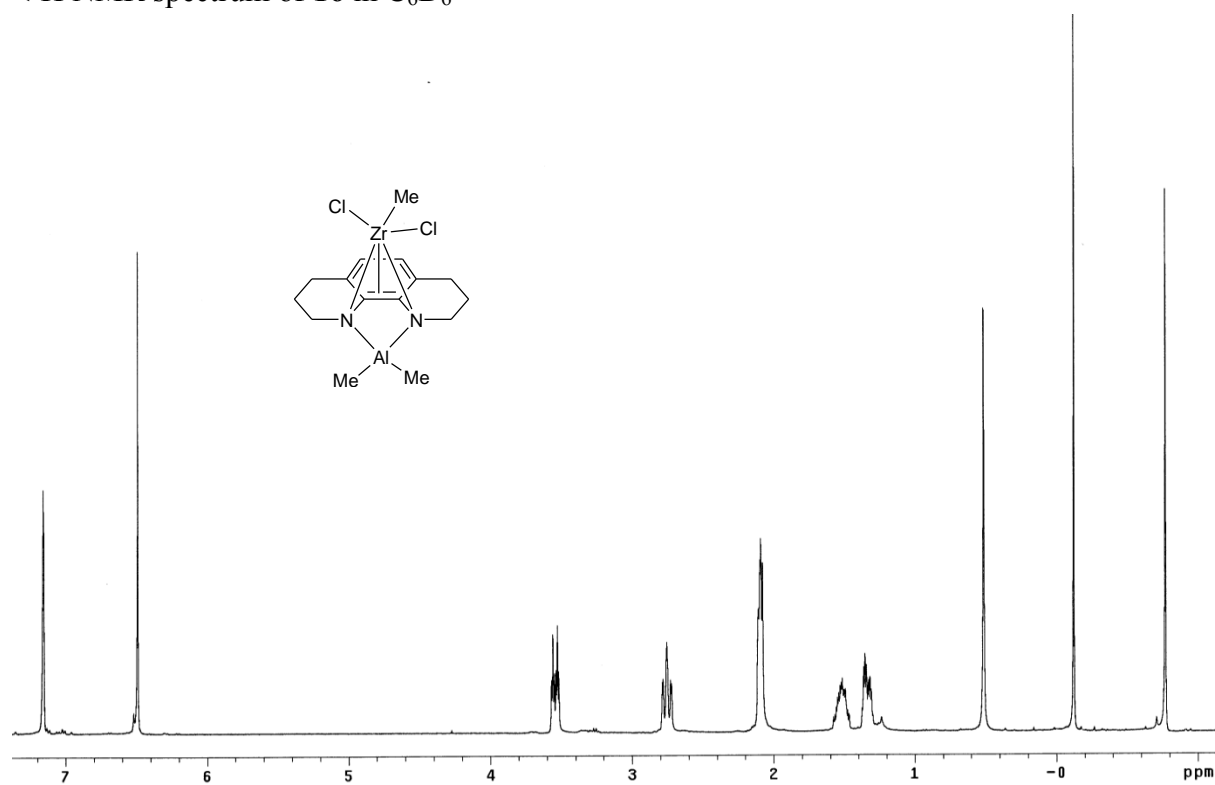
^1H NMR spectrum of **15** in C_6D_6



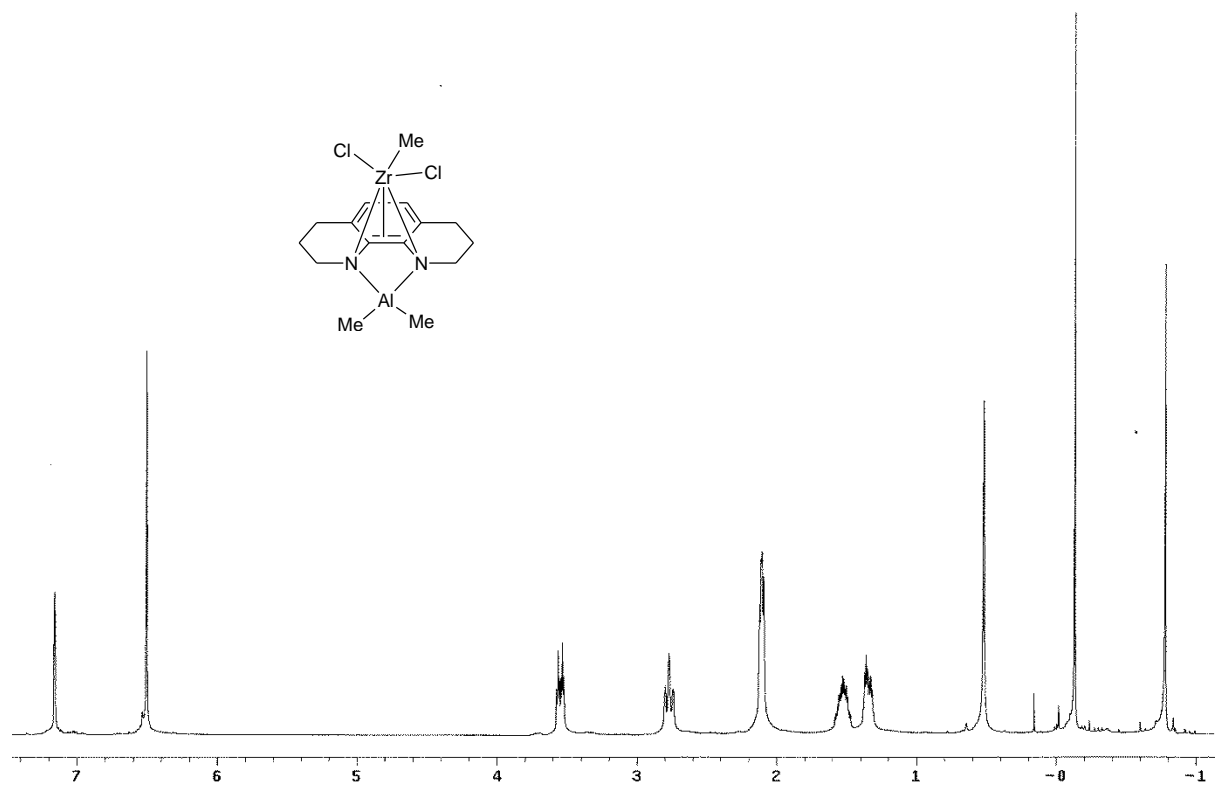
^{13}C NMR spectrum of **15** in C_6D_6



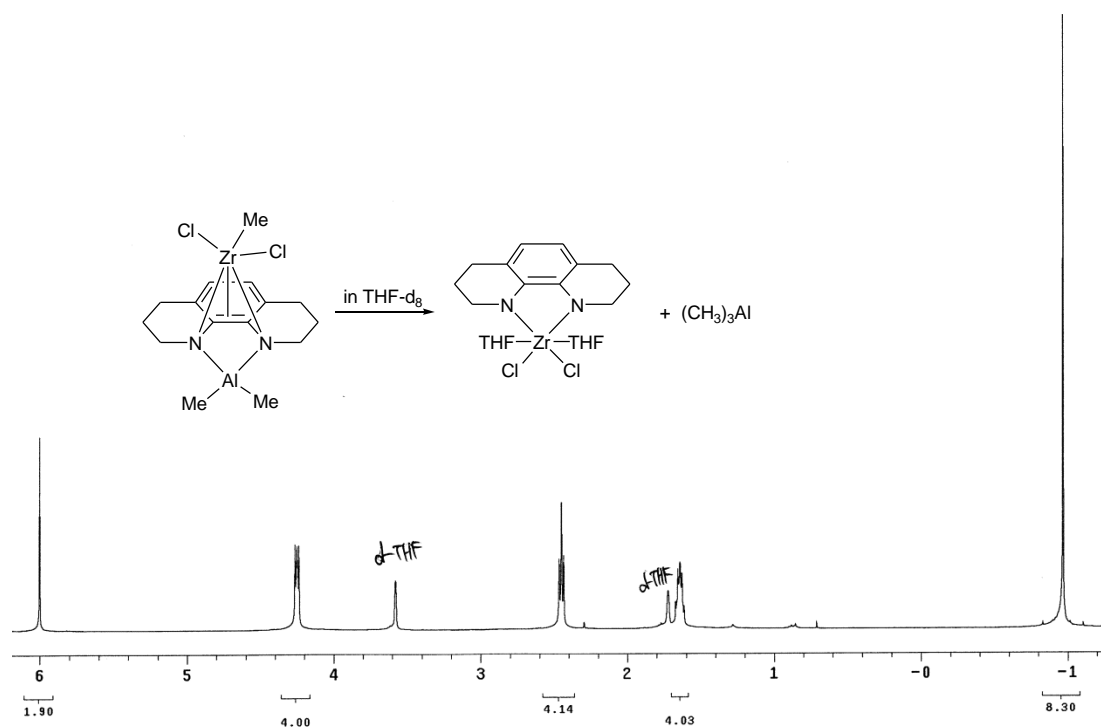
^1H NMR spectrum of **16** in C_6D_6



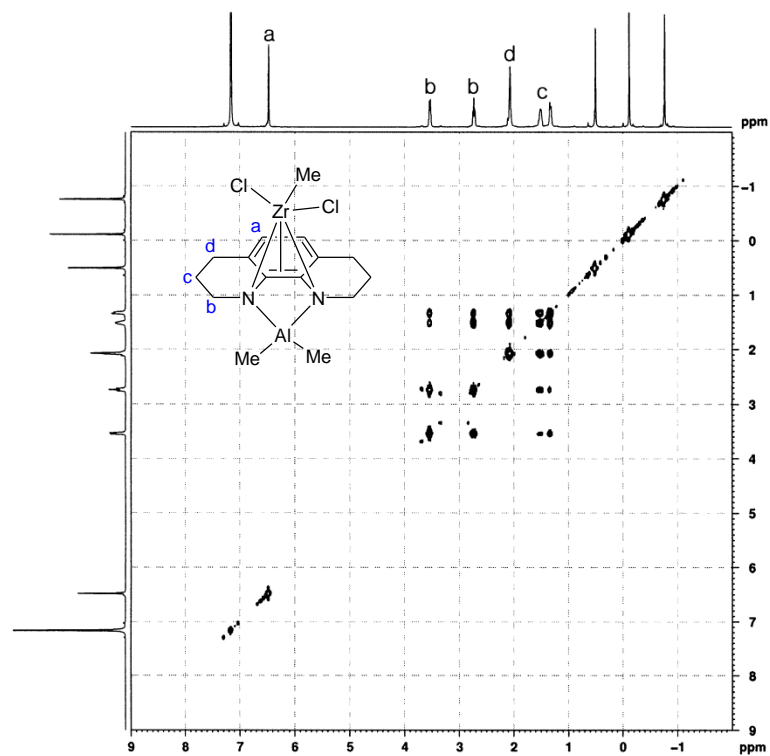
^1H NMR spectrum of **16** in C_6D_6 after heating at 80 °C for 3 hours



< ^1H NMR spectrum of **16** in THF-d_8 : The spectrum showed that **16** reconverted to **12** in THF .>

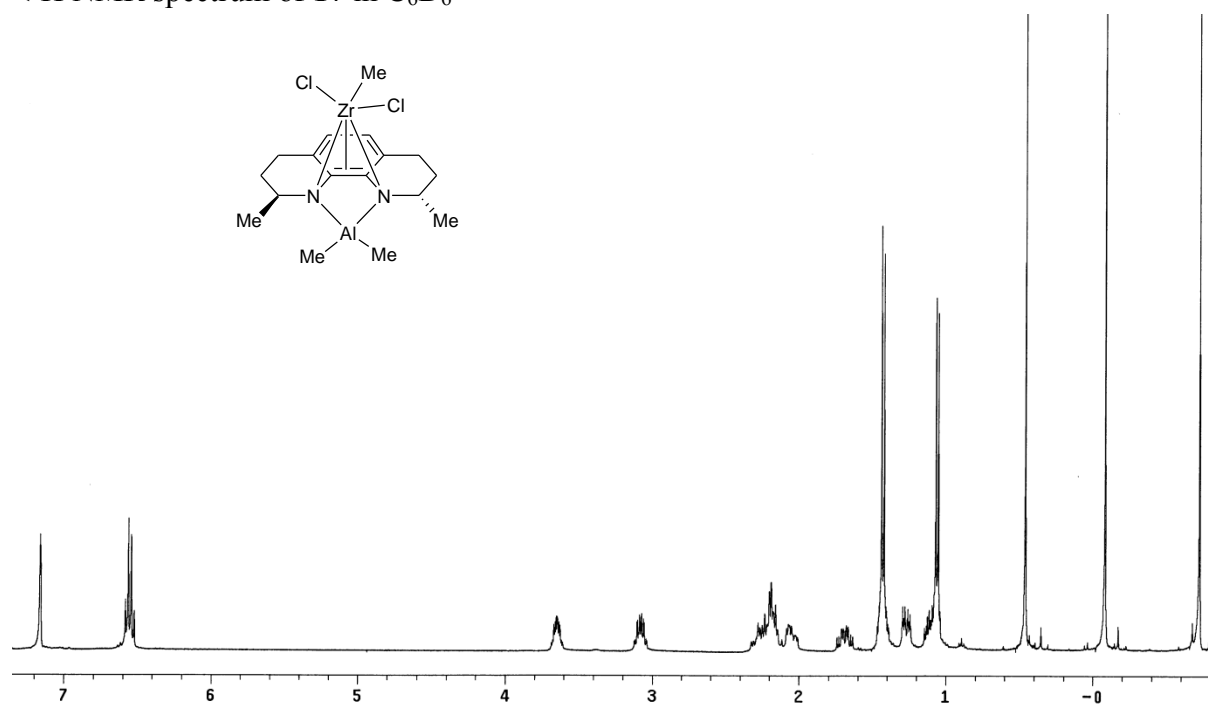


< ^1H - ^1H COSY NMR spectrum of **16** and signal assignment>

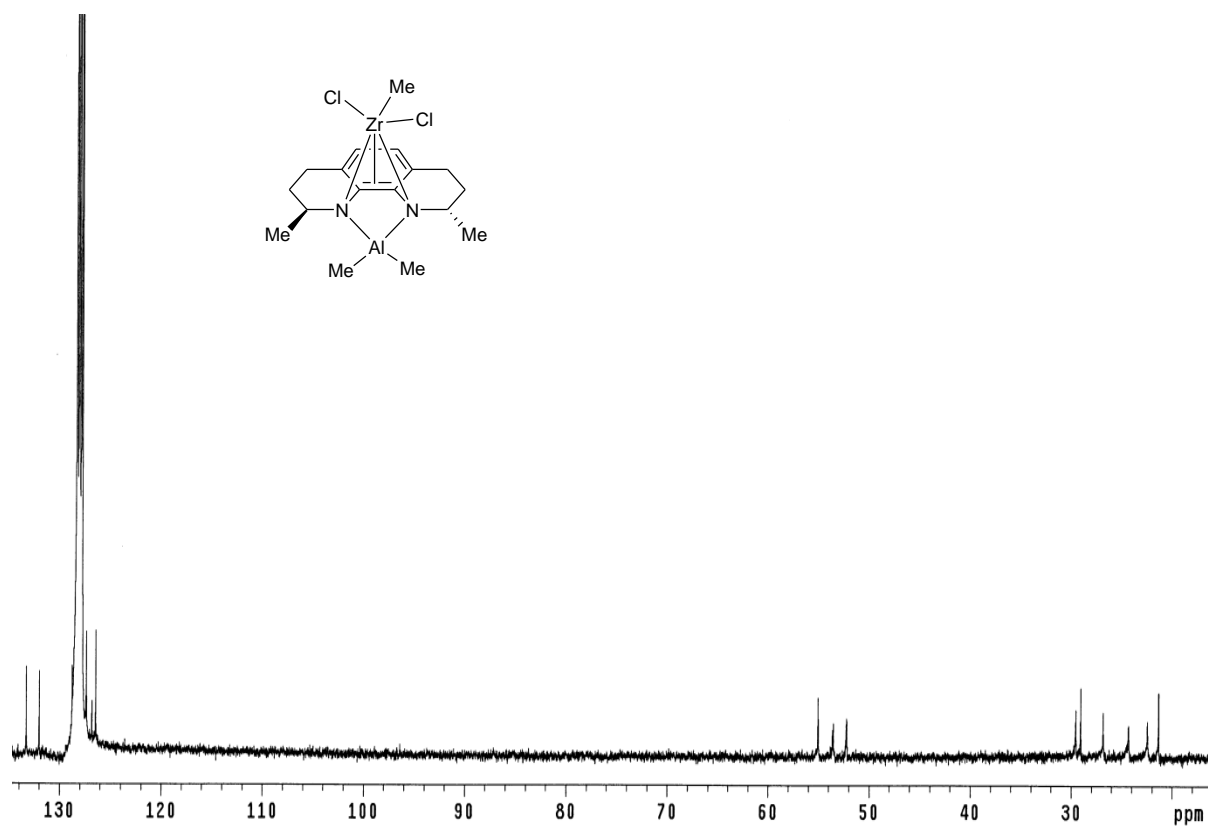


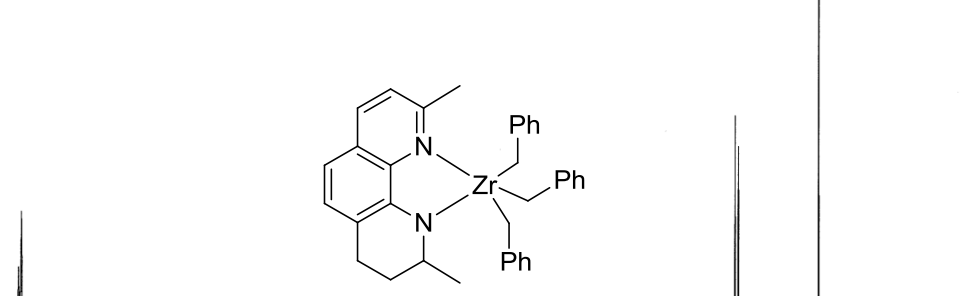
The figure displays a ^{13}C NMR spectrum of a zirconium complex. The x-axis represents the chemical shift in ppm, ranging from 0 to 130. The spectrum shows a large, sharp peak at approximately 130 ppm, a smaller peak at approximately 125 ppm, and several smaller peaks in the aliphatic region between 20 and 40 ppm. An inset shows the chemical structure of the complex, which is a zirconium (Zr) complex coordinated by two chlorine (Cl) atoms and two methyl (Me) groups, and a ligand consisting of two nitrogen (N) atoms and two methyl (Me) groups, all coordinated to a central aluminum (Al) atom.

^1H NMR spectrum of **17** in C_6D_6



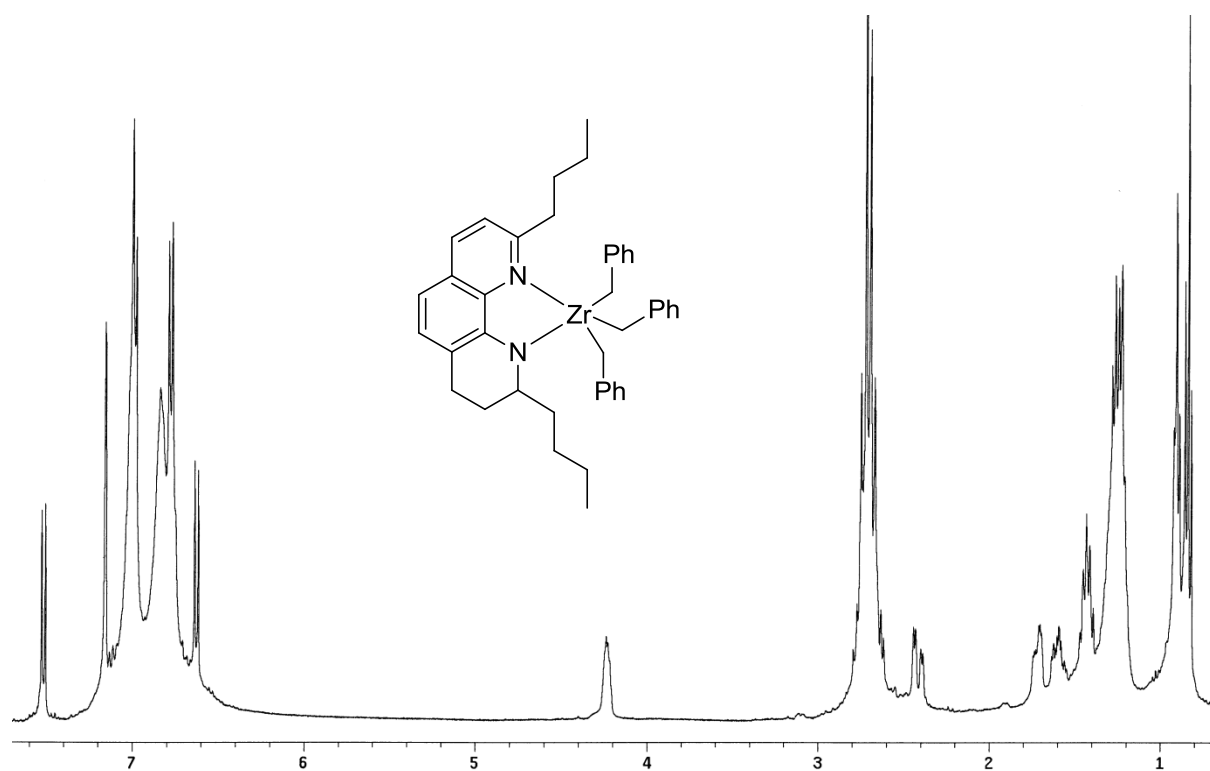
^{13}C NMR Spectrum of **17** in C_6D_6



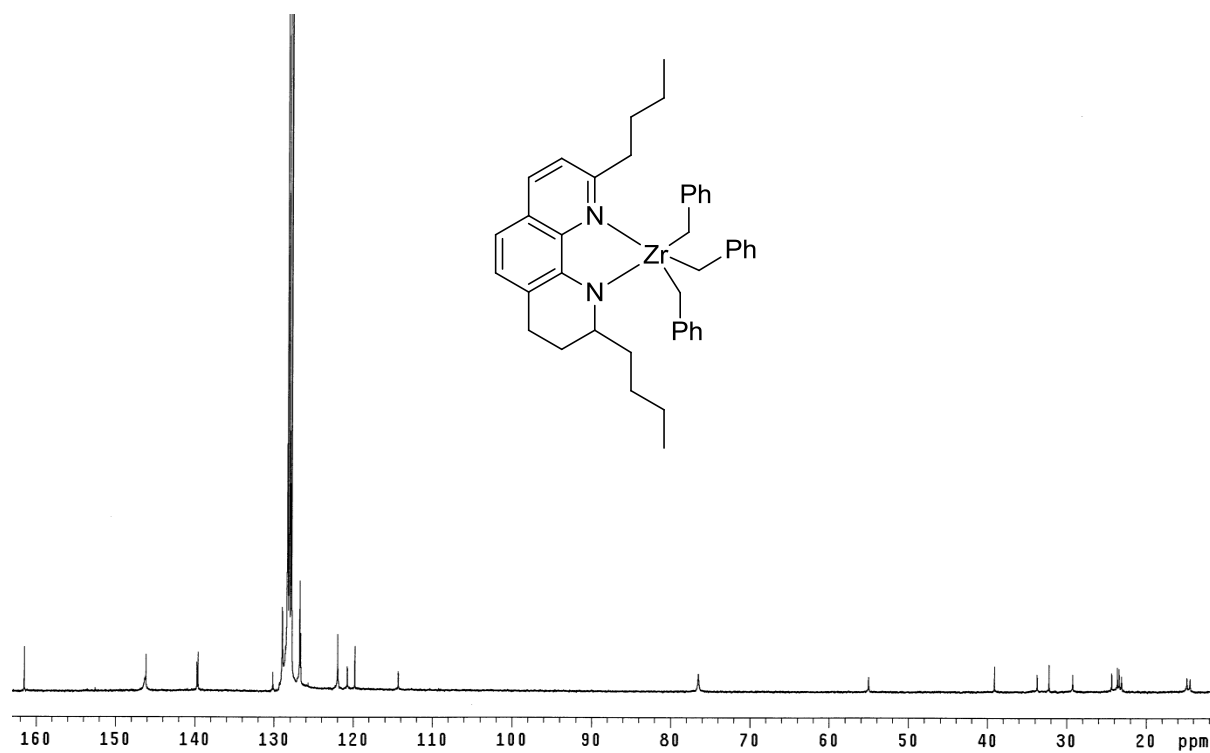

Cc1ccc2c(c1)nc(Cc3ccccc3)nc2Cc4ccccc4

[illegible]

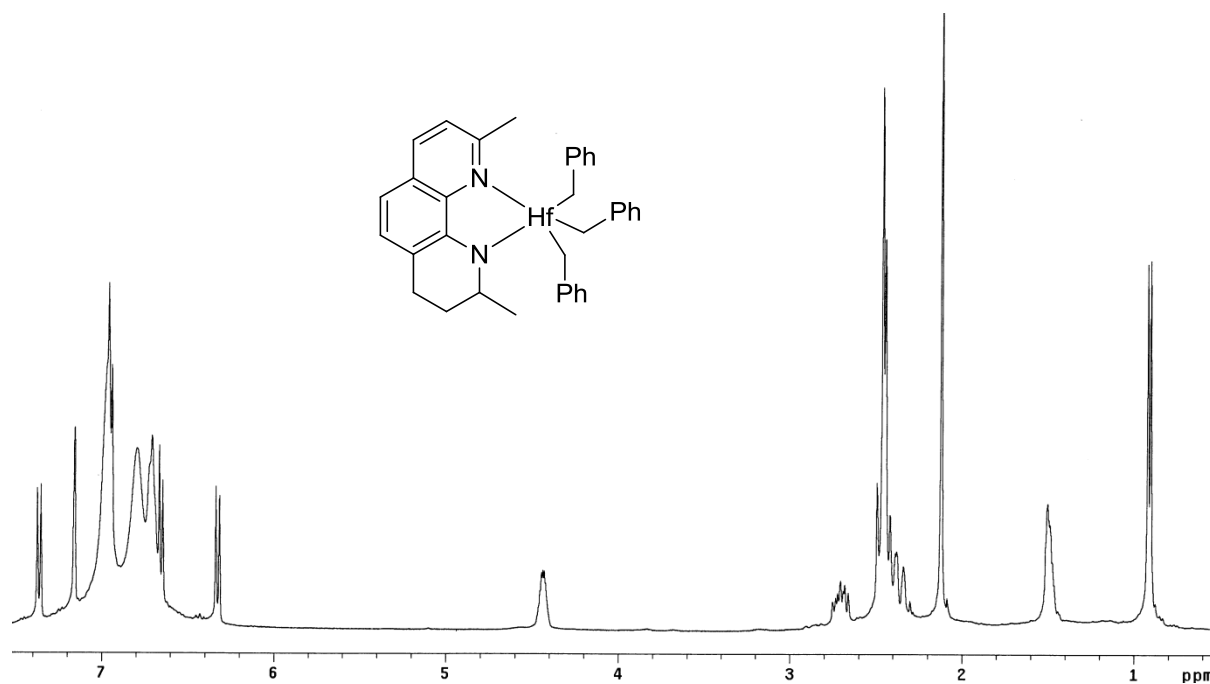
< ^1H NMR spectrum of **19** in C_6D_6 >



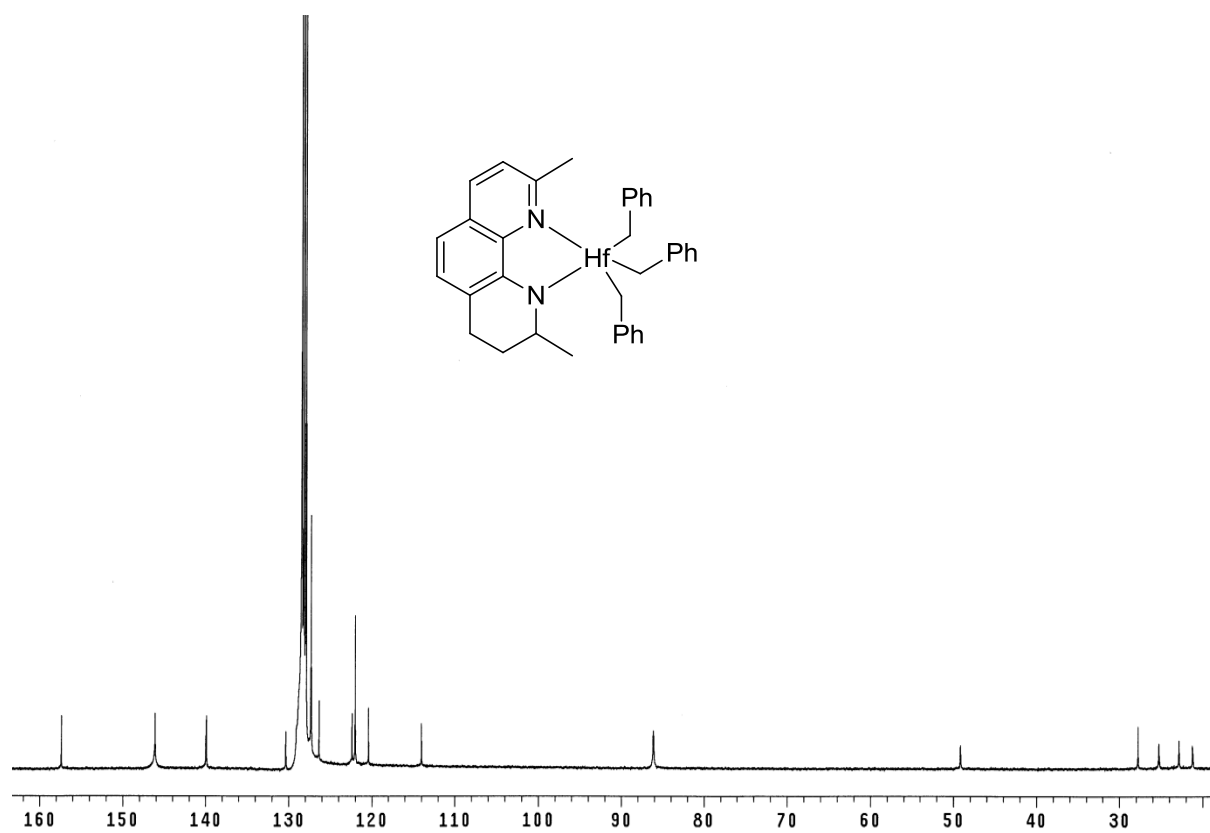
< ^{13}C NMR Spectrum of **19** in C_6D_6 >



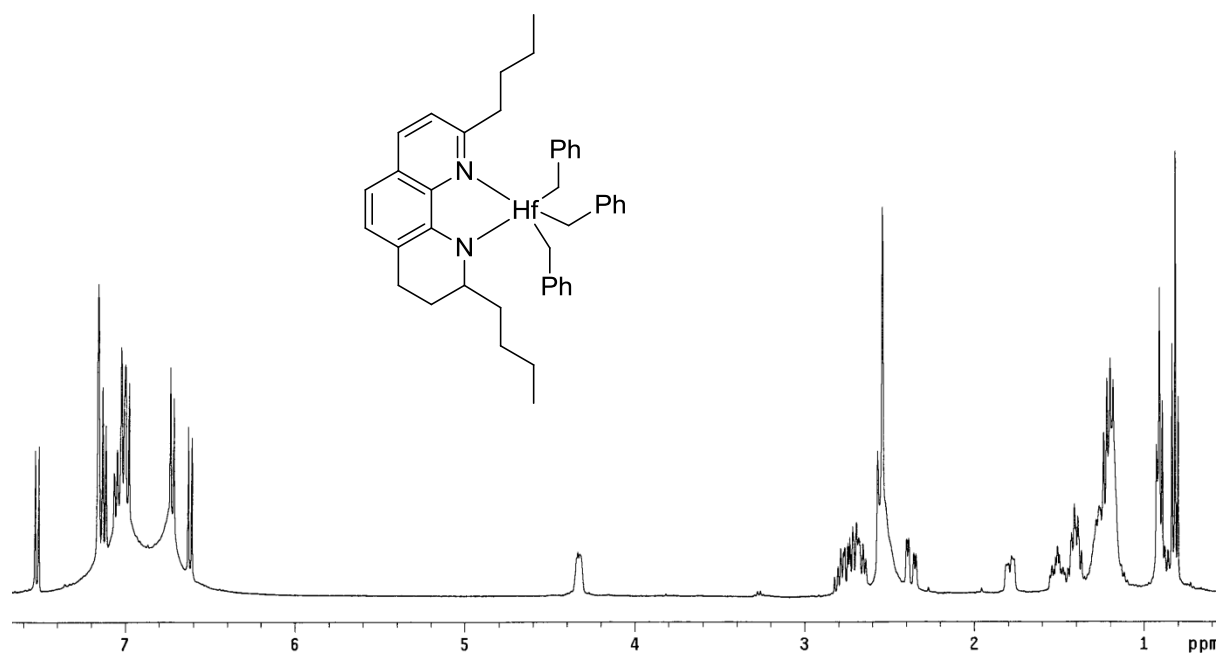
^1H NMR spectrum of **20** in C_6D_6



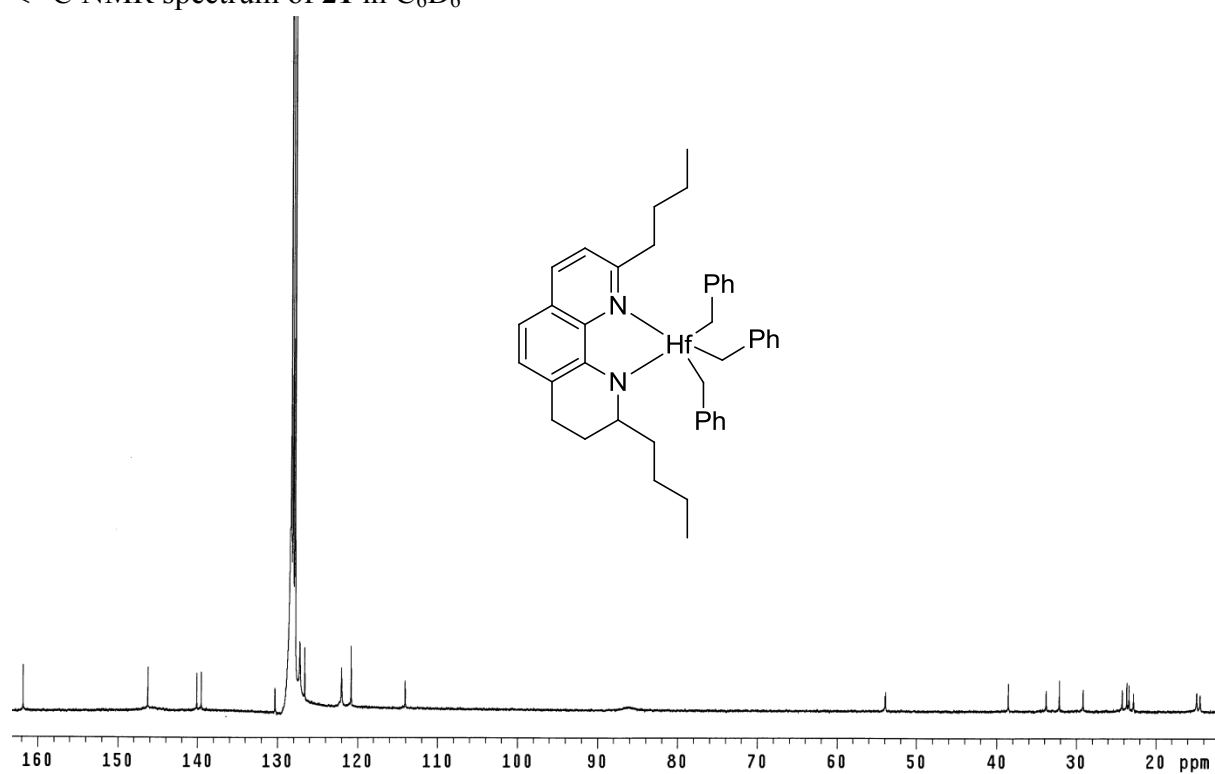
^{13}C NMR spectrum of **20** in C_6D_6



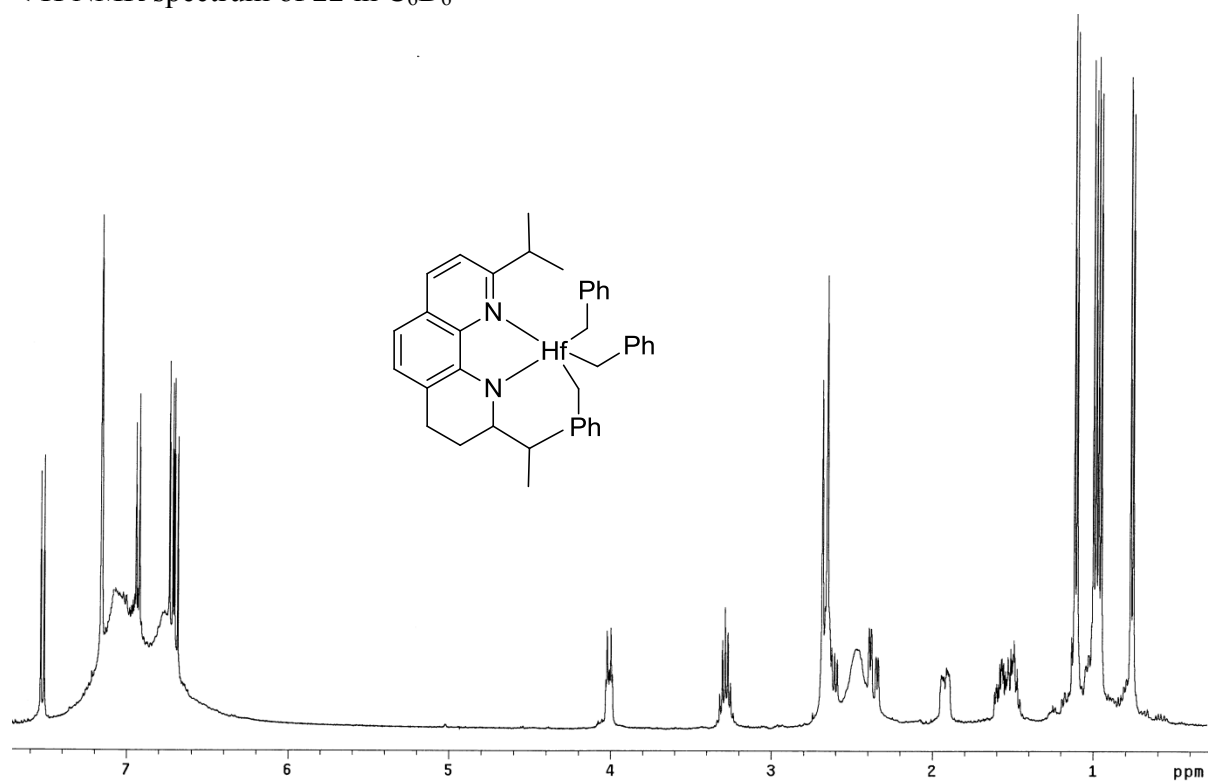
^1H NMR spectrum of **21** in C_6D_6



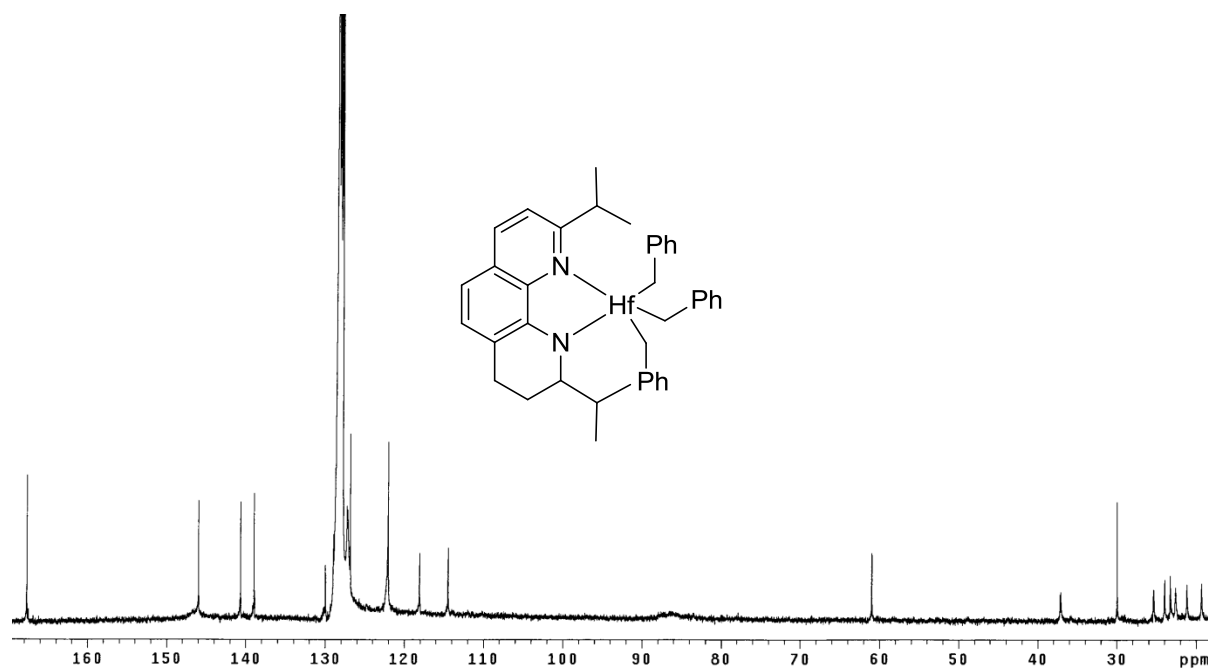
^{13}C NMR spectrum of **21** in C_6D_6



^1H NMR spectrum of **22** in C_6D_6

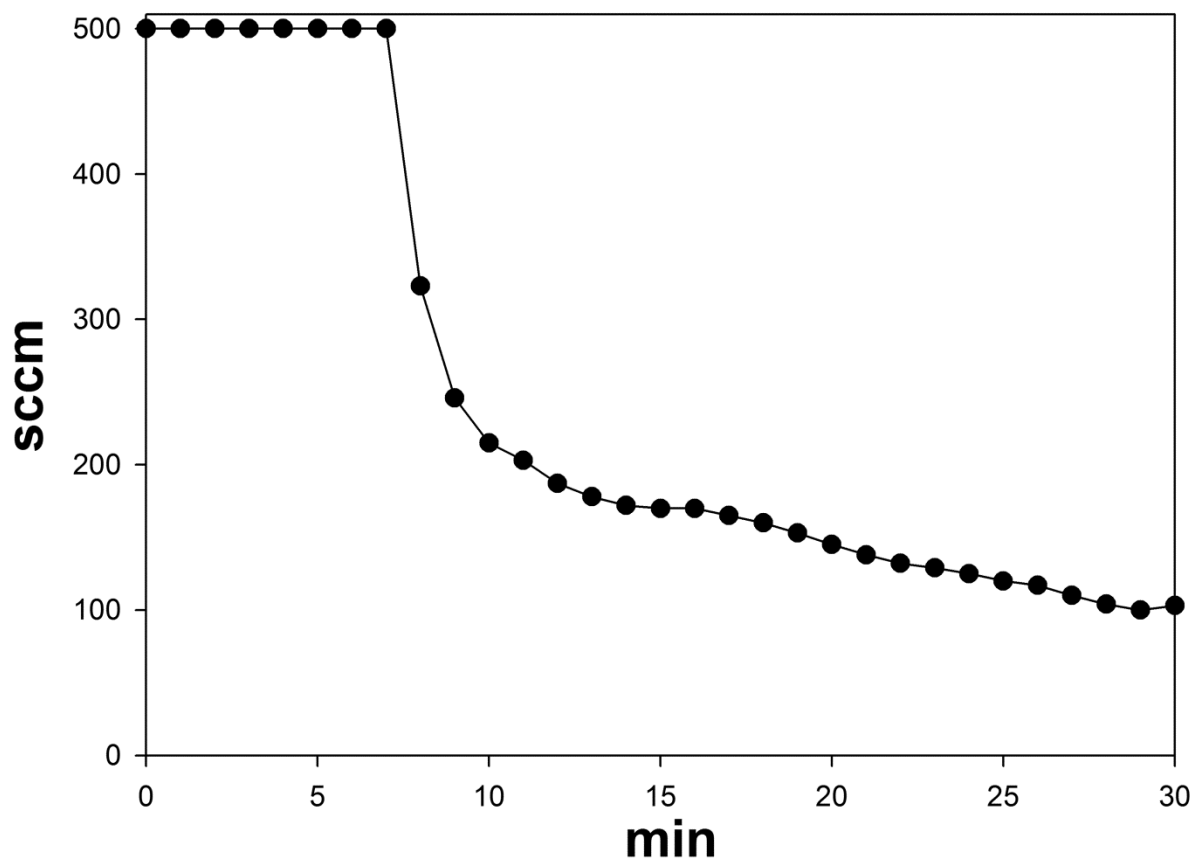


^{13}C NMR spectrum of **22** in C_6D_6

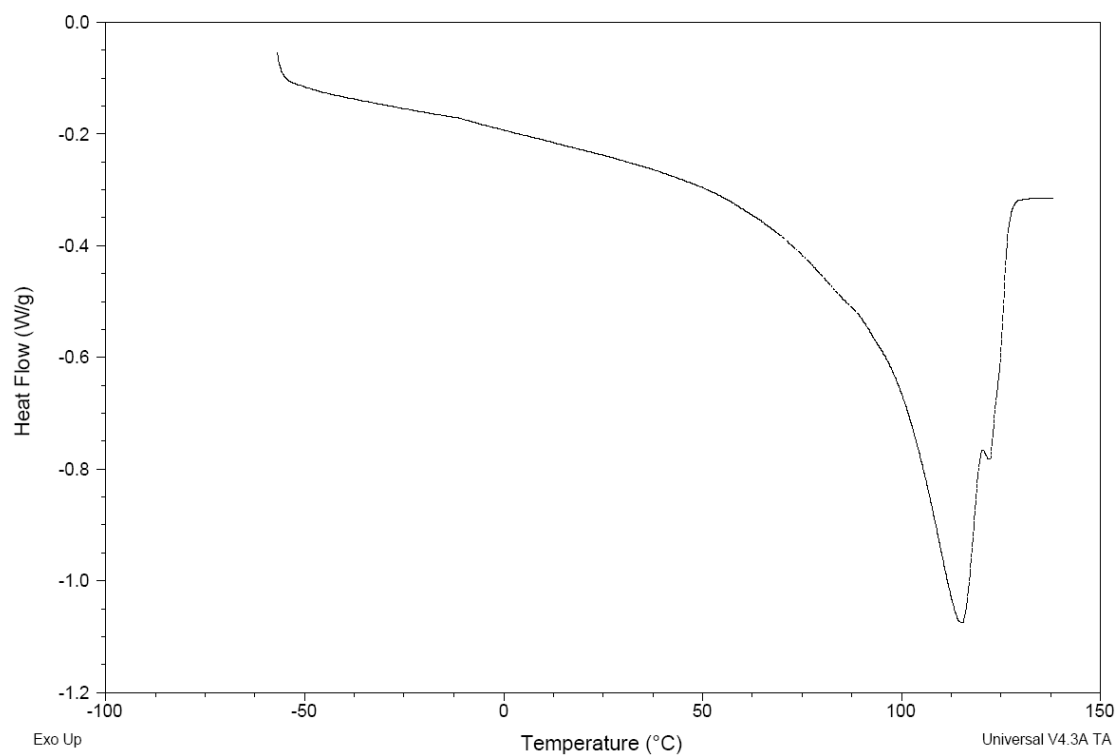


<Ethylene consumption rate versus time>

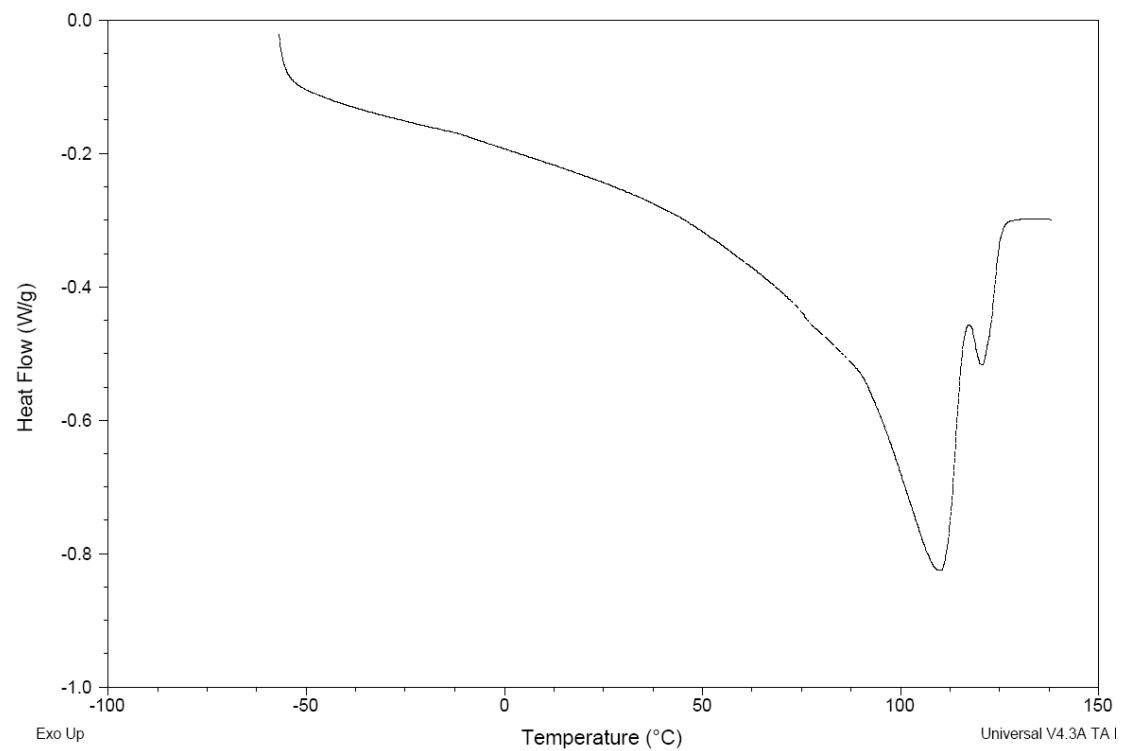
Polymerization conditions: **16** (1.5 μmol), MMAO (4.5 mmol), methylcyclohexane (40 mL), in the absence of 1-octene, 100 °C, ethylene (28–30 bar)



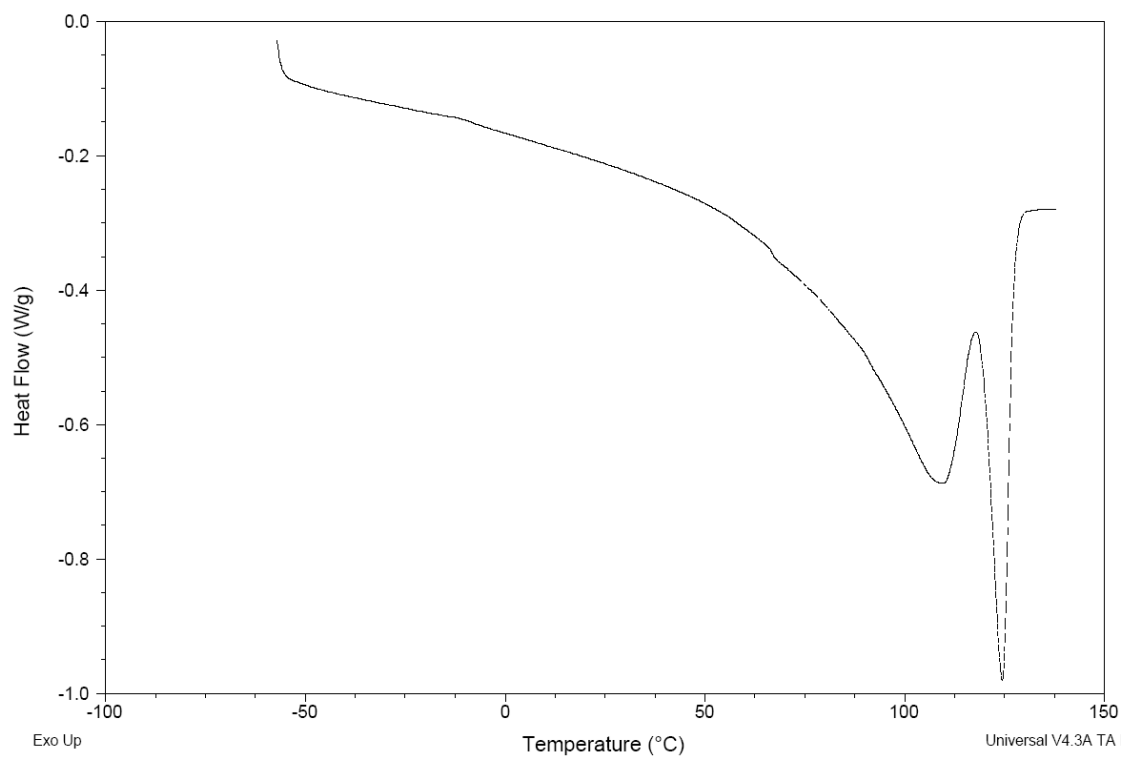
< DSC curve for the polymer generated with **4**>



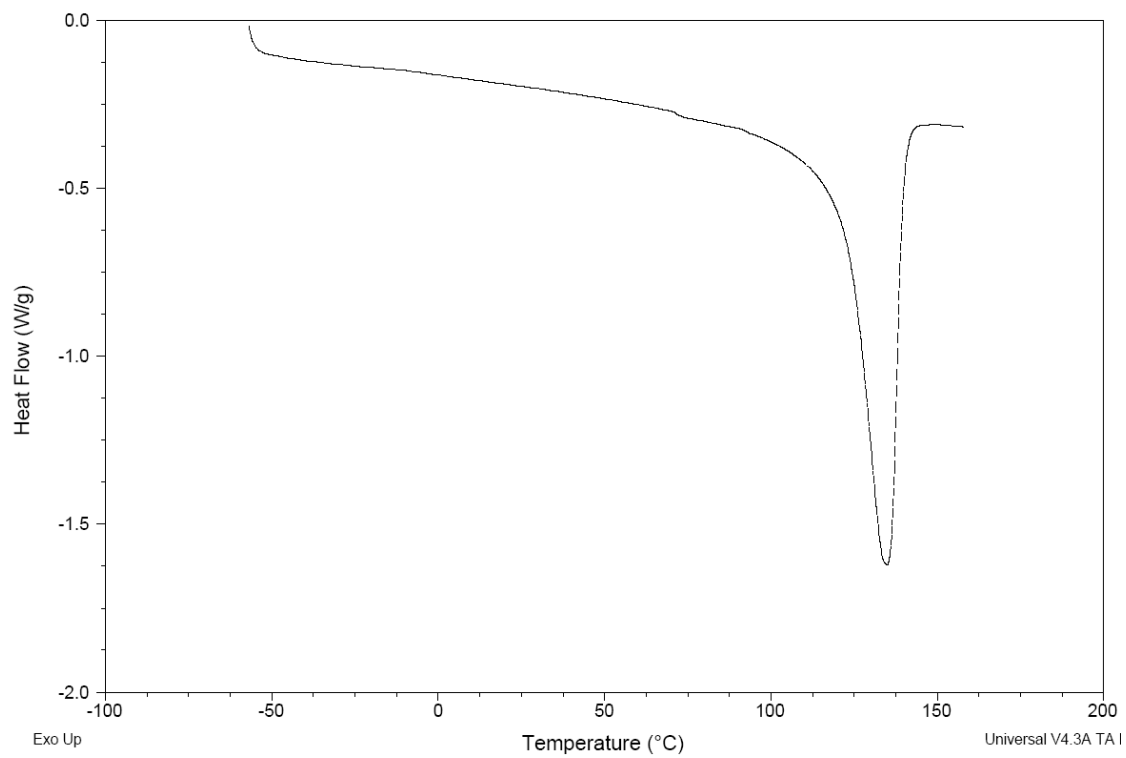
< DSC curve for the polymer generated with **5**>



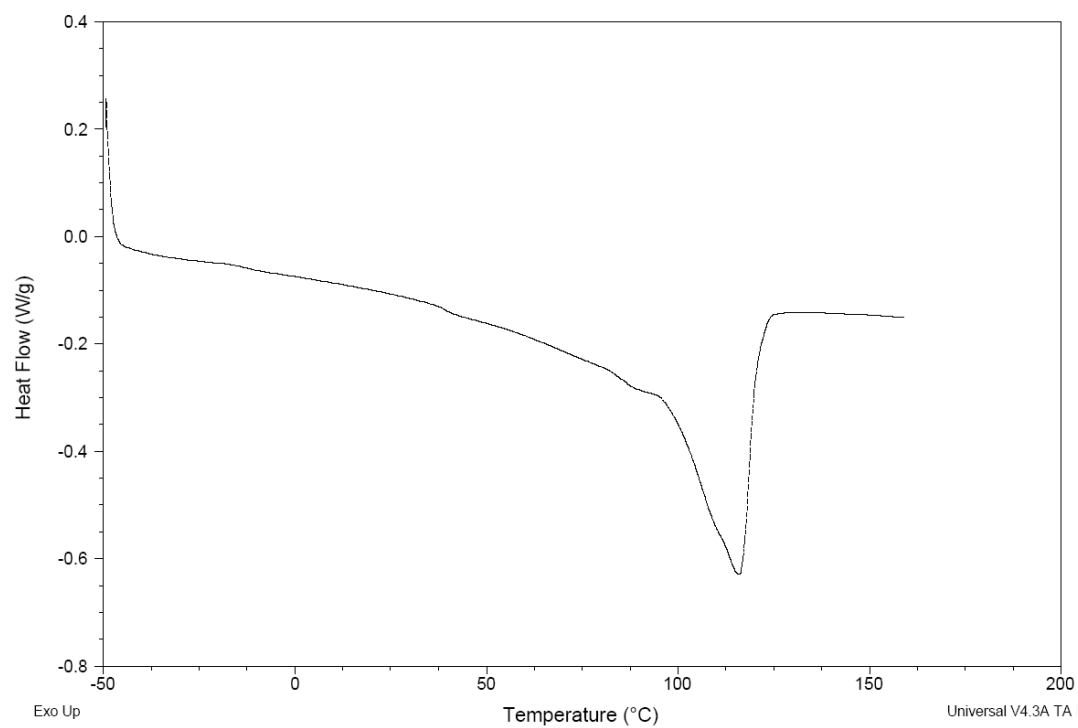
< DSC curve for the polymer generated with **6**>



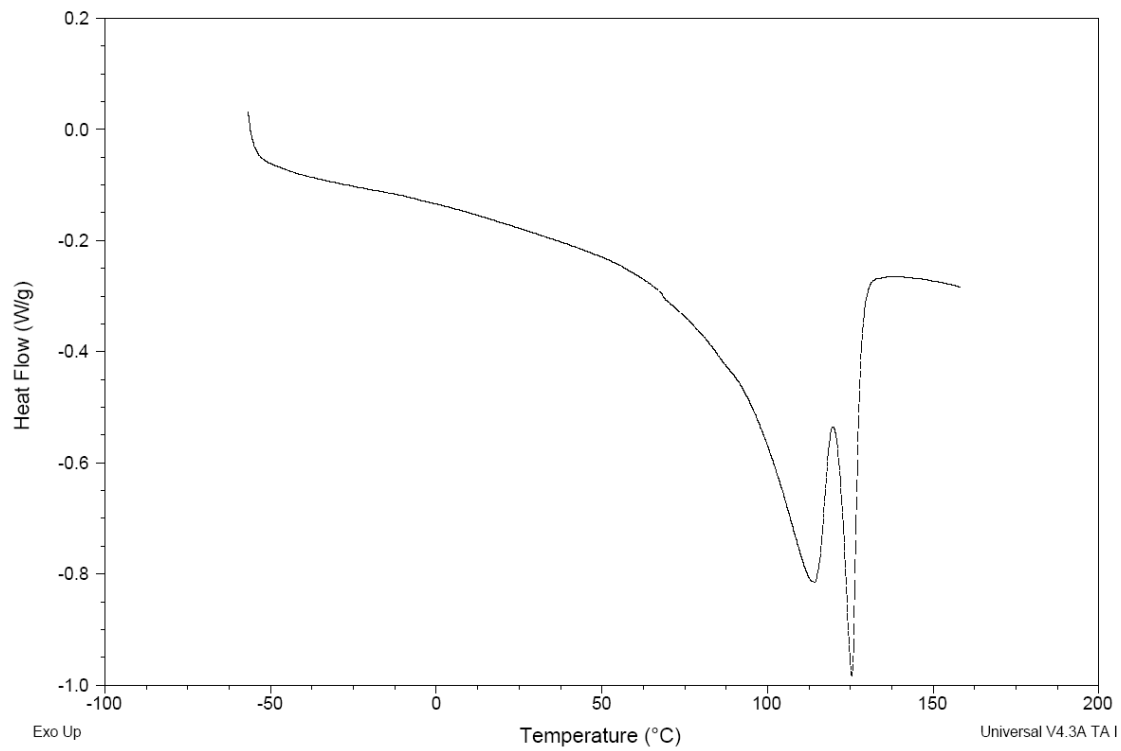
< DSC curve the polymer generated with **7**>



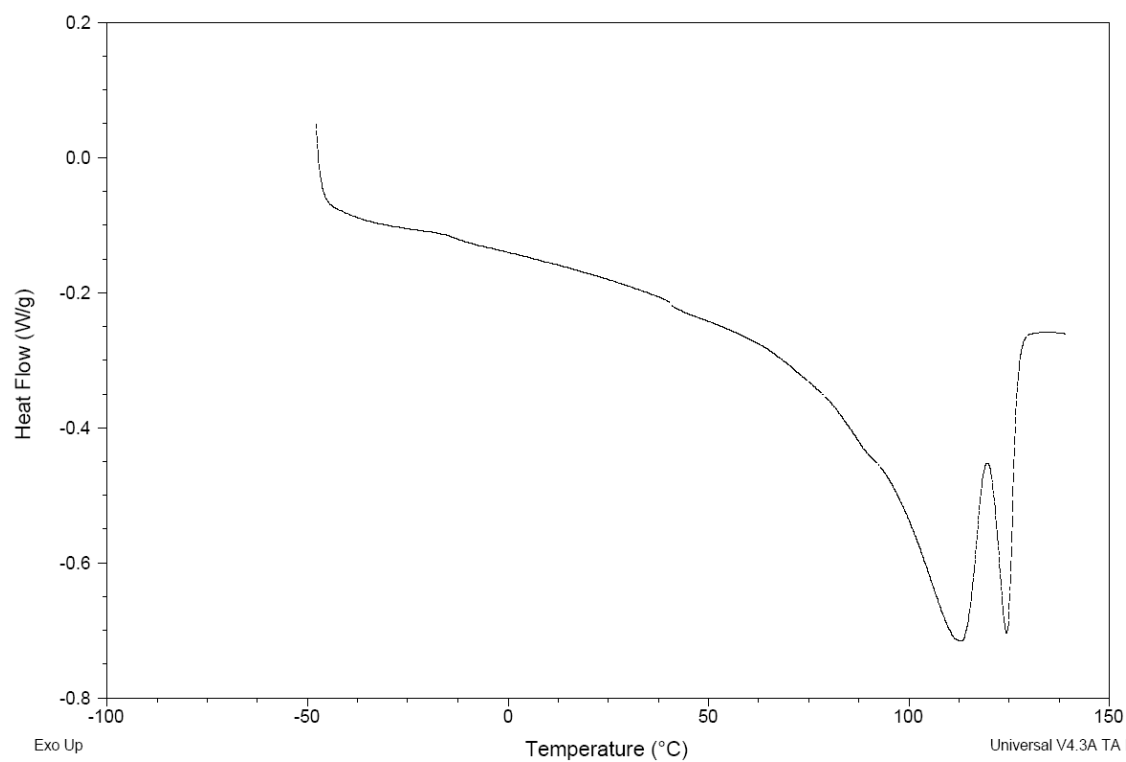
< DSC curve for the polymer generated with **12**>



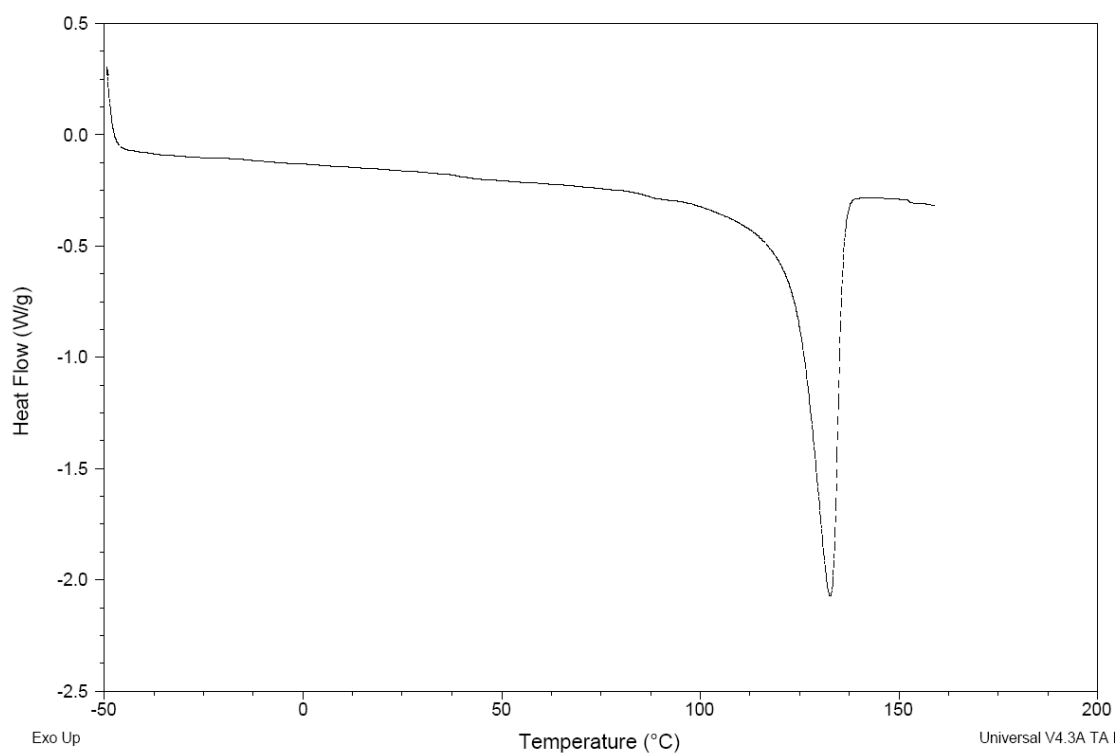
< DSC curve for the polymer generated with **13**>



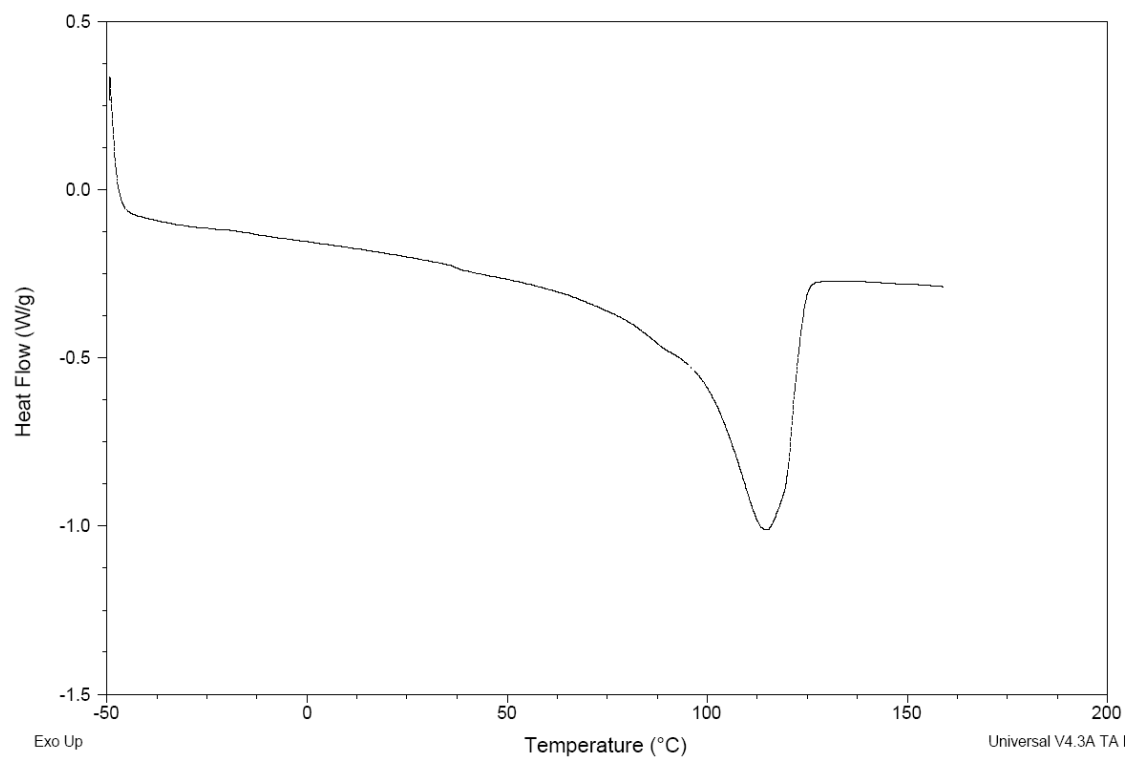
< DSC curve for the polymer generated with **14**>



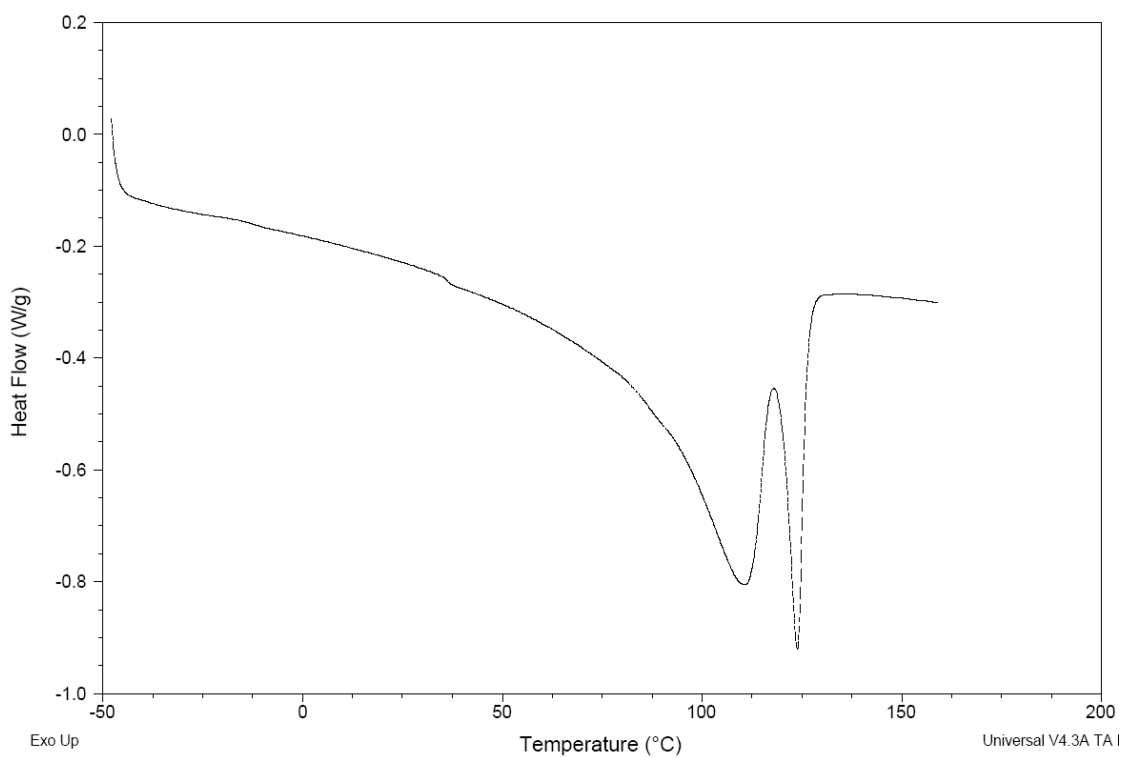
< DSC curve for the polymer generated with **15**>



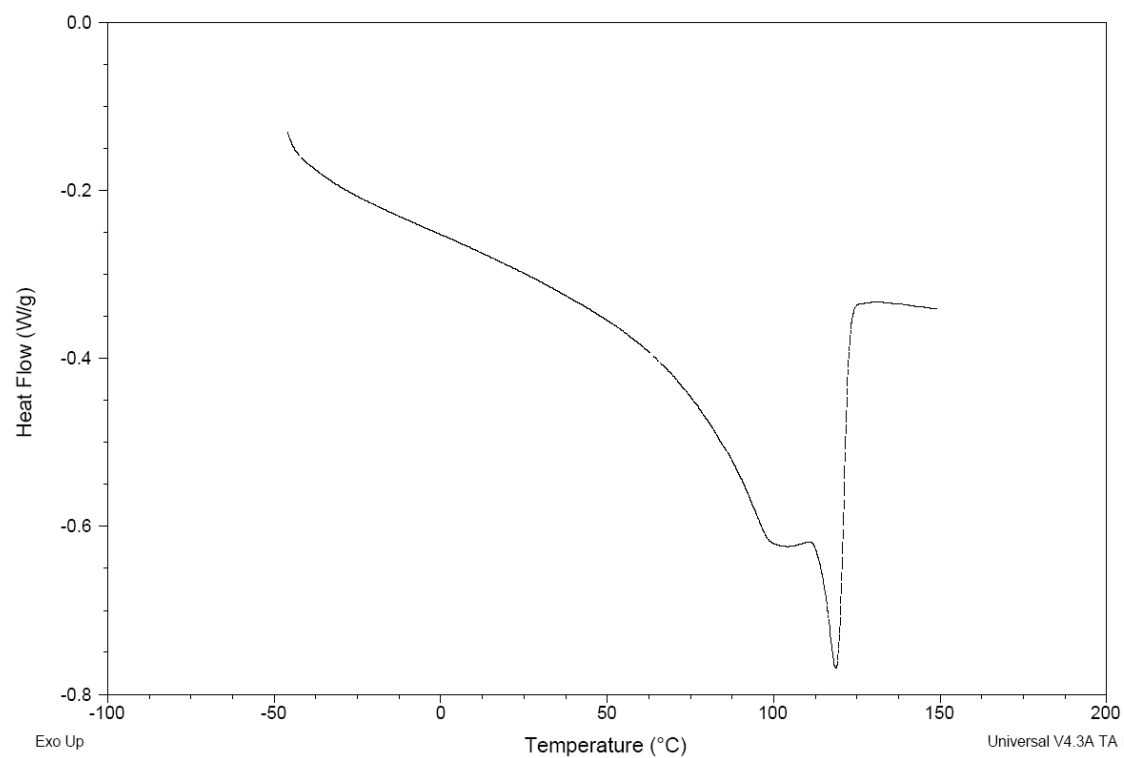
< DSC curve for the polymer generated with **16**>



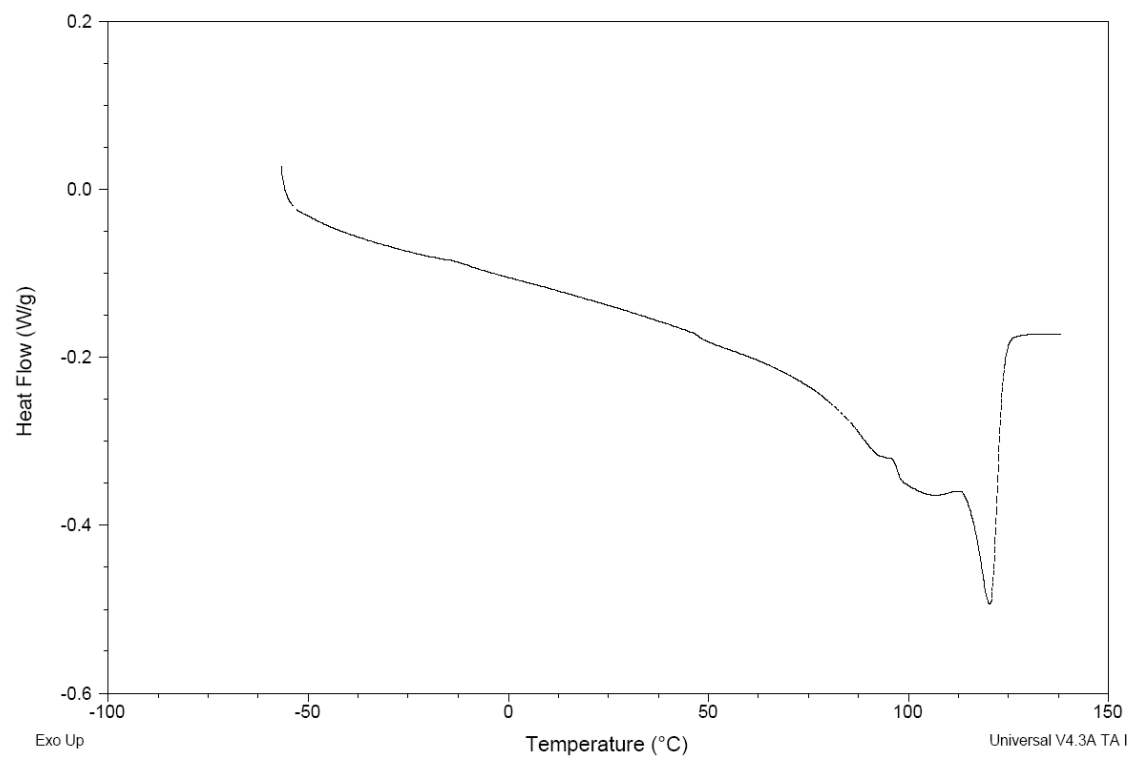
< DSC curve for the polymer generated with **17**>



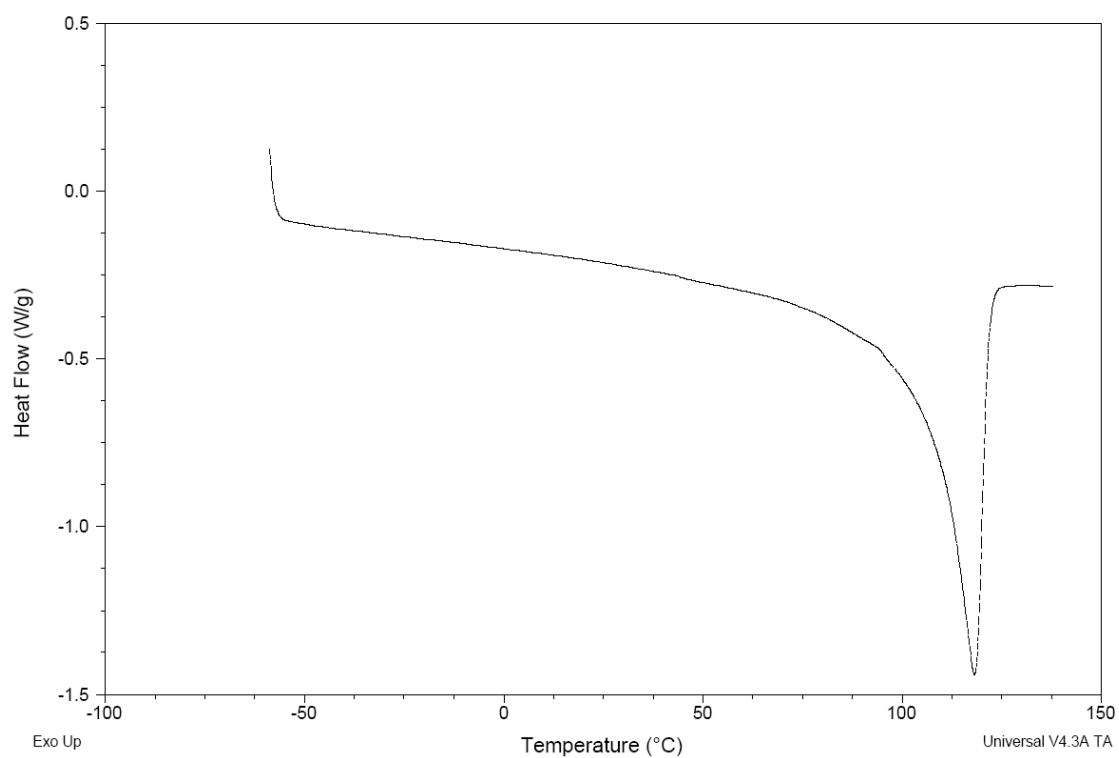
< DSC curve for the polymer generated with **18**>



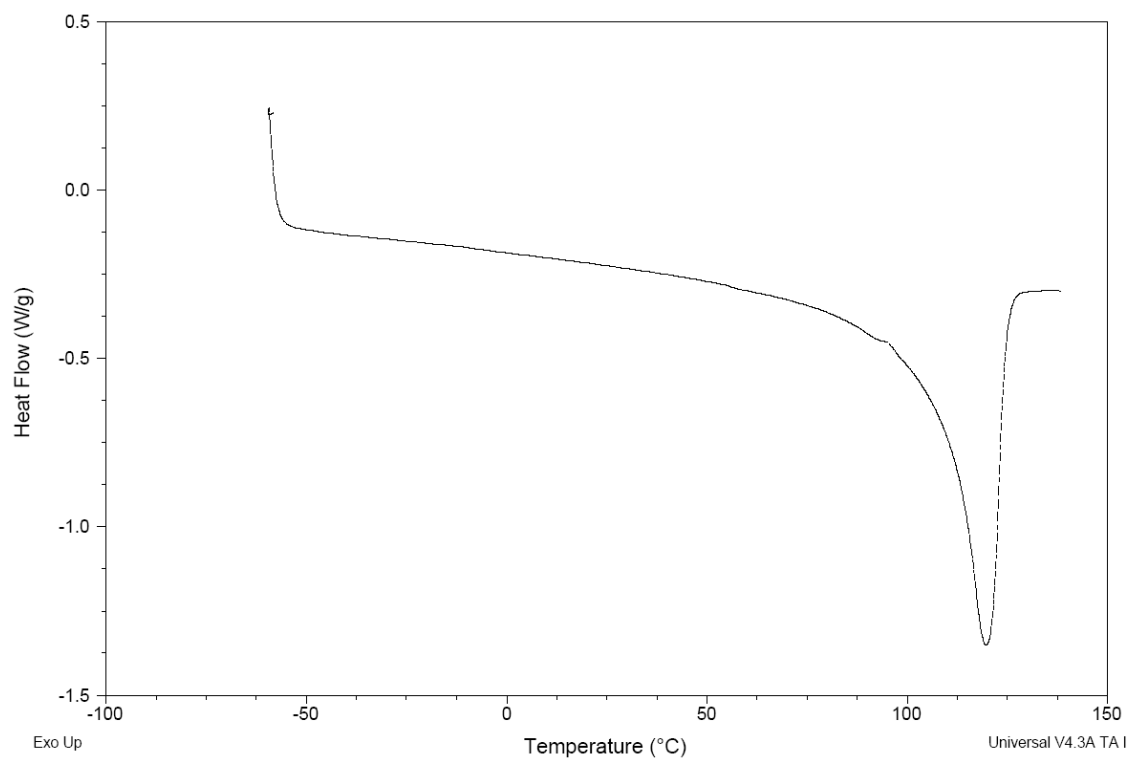
< DSC curve for the polymer generated with **19**>



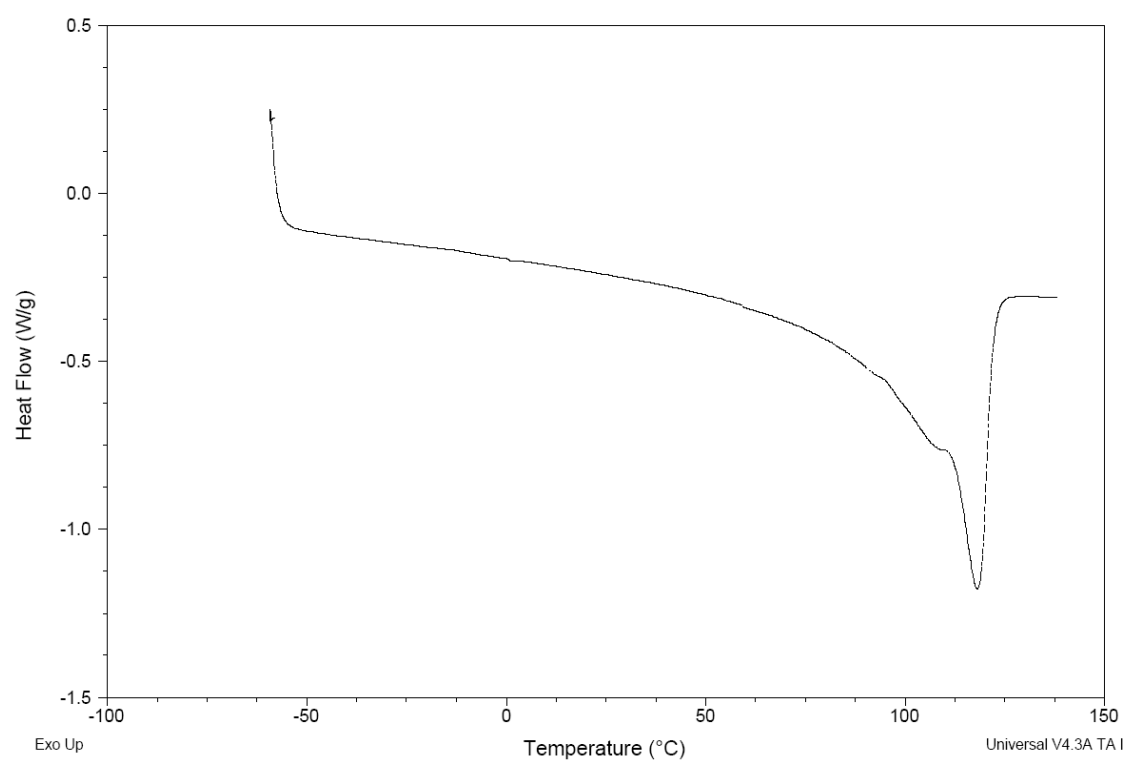
< DSC curve for the polymer generated with **20**>



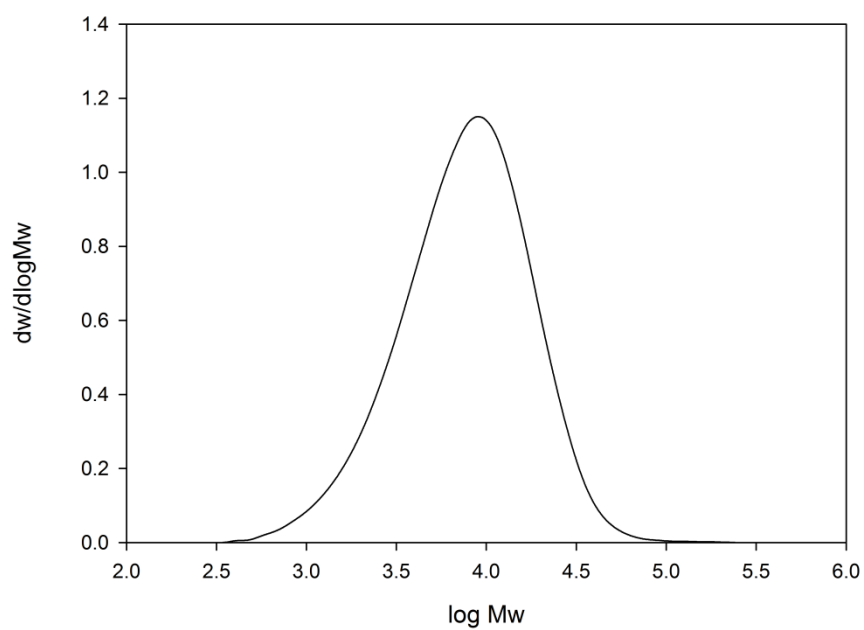
< DSC curve for the polymer generated with **21**>



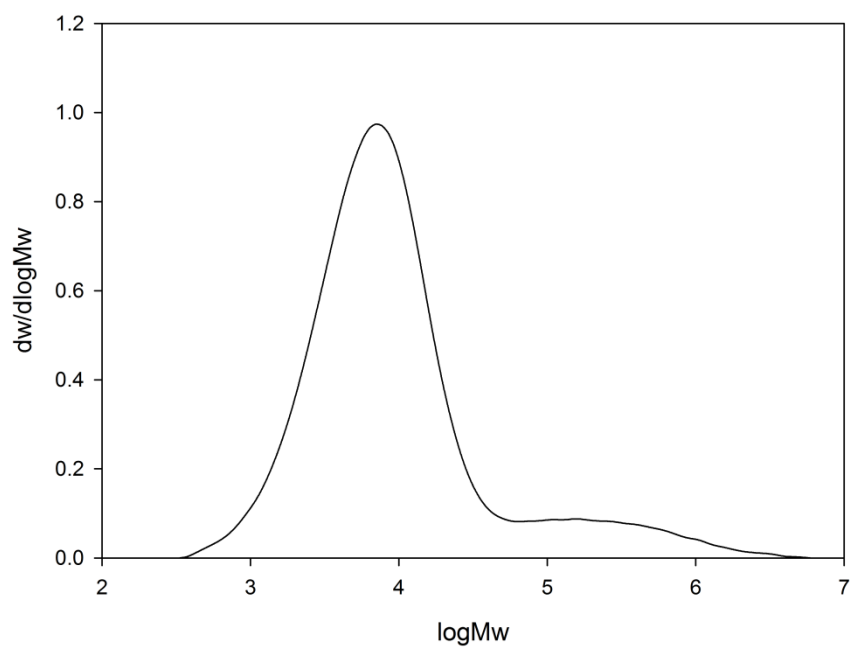
< DSC curve for the polymer generated with **22**>



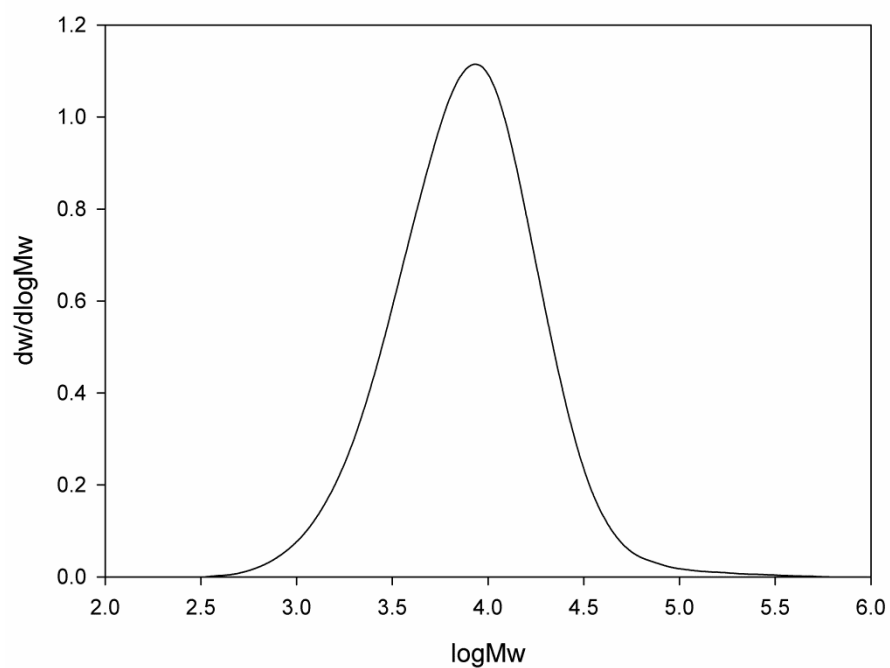
< GPC curve for the polymer generated with **12** (entry 6 in Table 1)>



< GPC curve for the polymer generated with **13** (entry 7 in Table 1)>



< GPC curve for the polymer generated with **16** (entry 10 in Table 1)>



< GPC curve for the polymer generated with **17** (entry 11 in Table 1)>

