Supporting Information

Synthesis of phenoxyimino Hf benzyl complexes and their activation towards olefin polymerization

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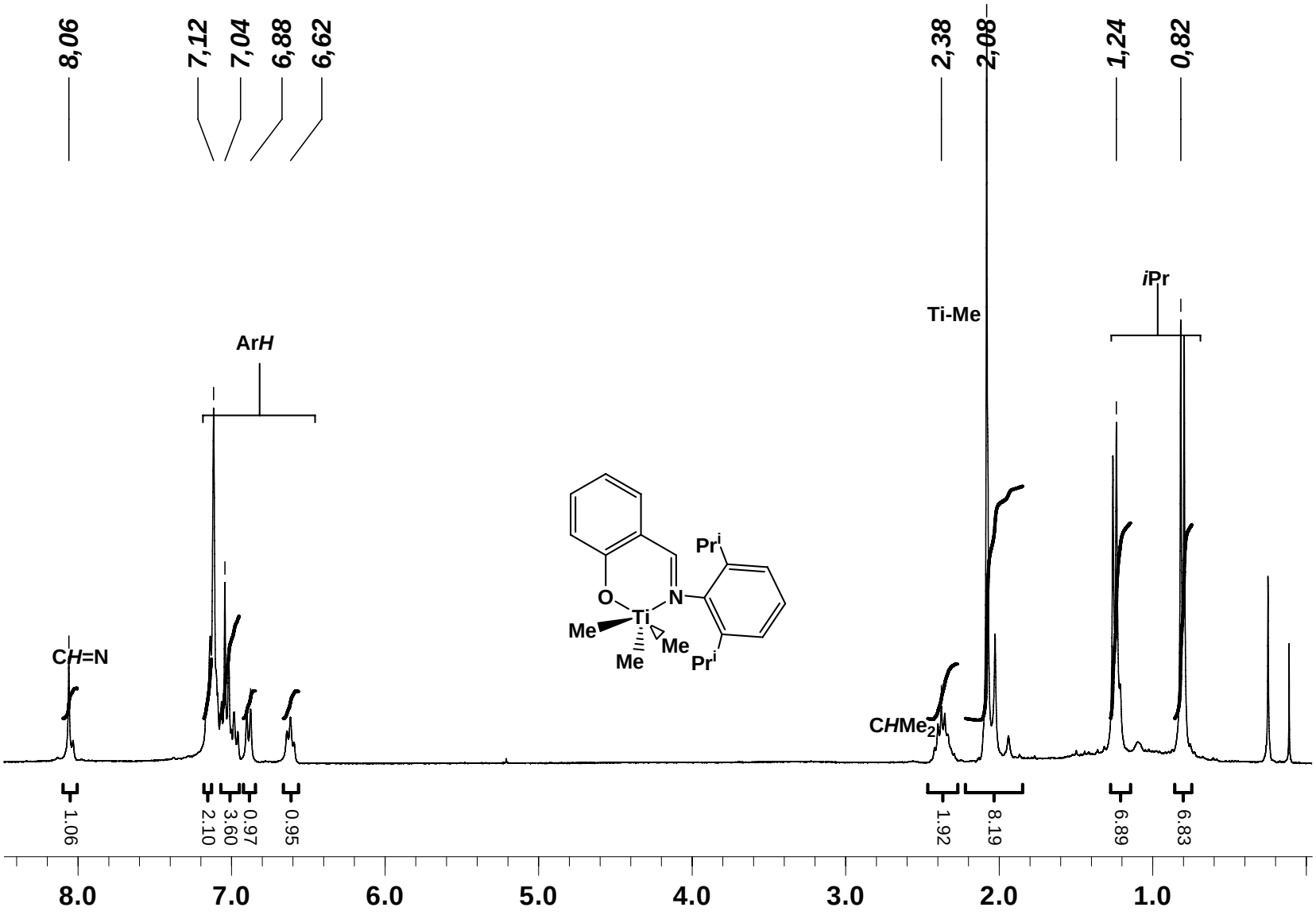
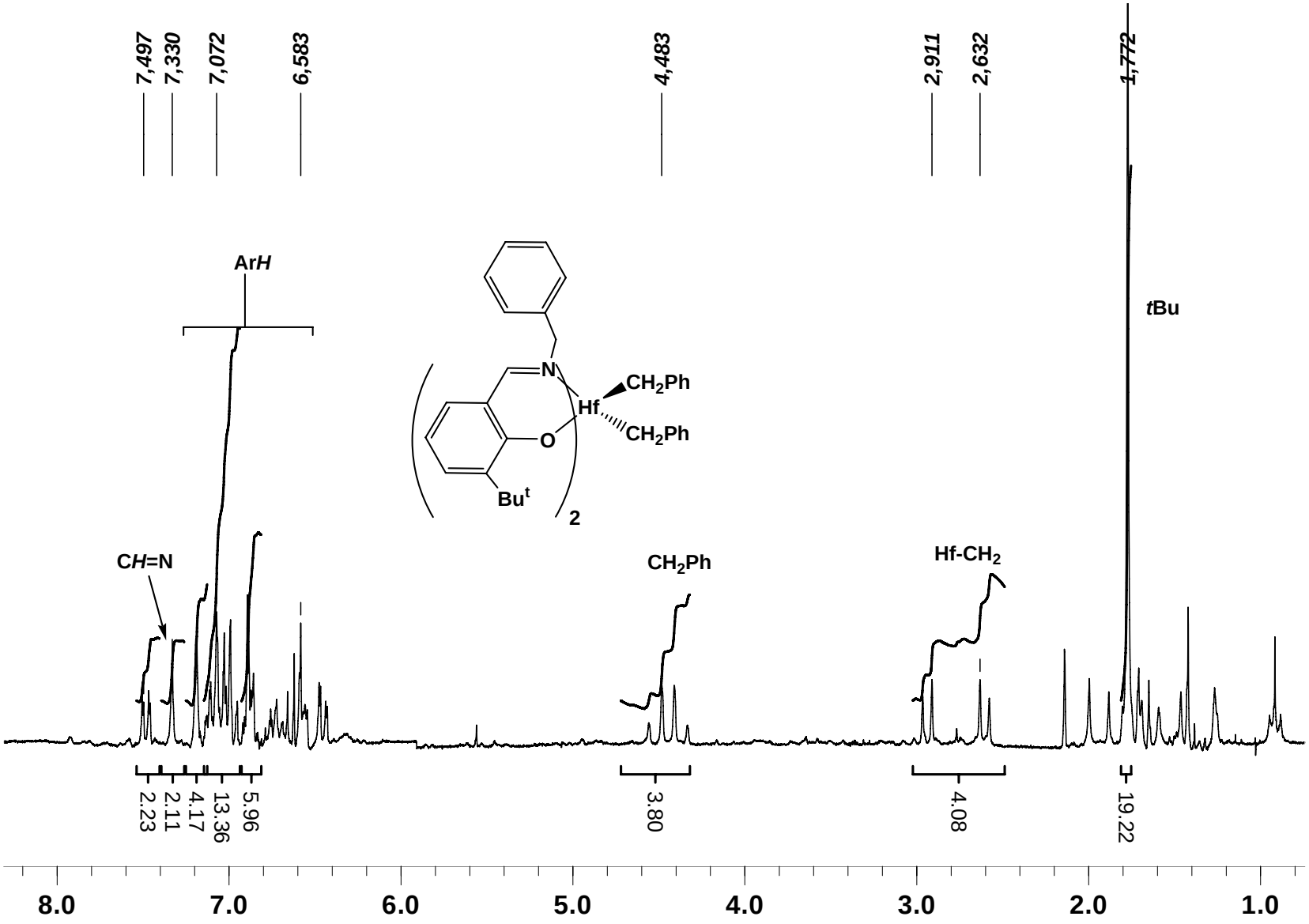
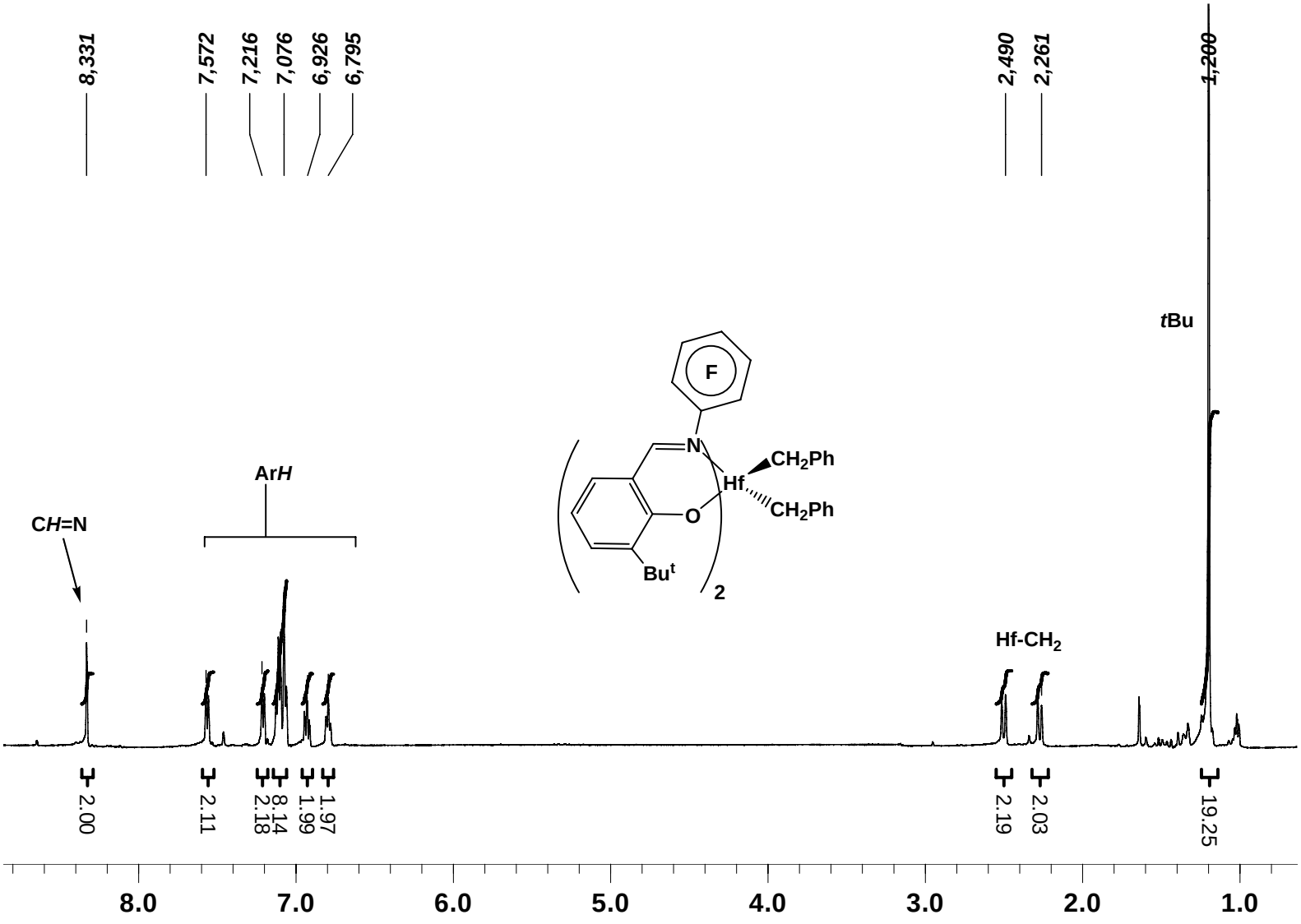
1. ^{1}H NMR spectrum of compound $LTiMe_3$ (L – 2,6-di-*i*-propylphenylaldiminato)



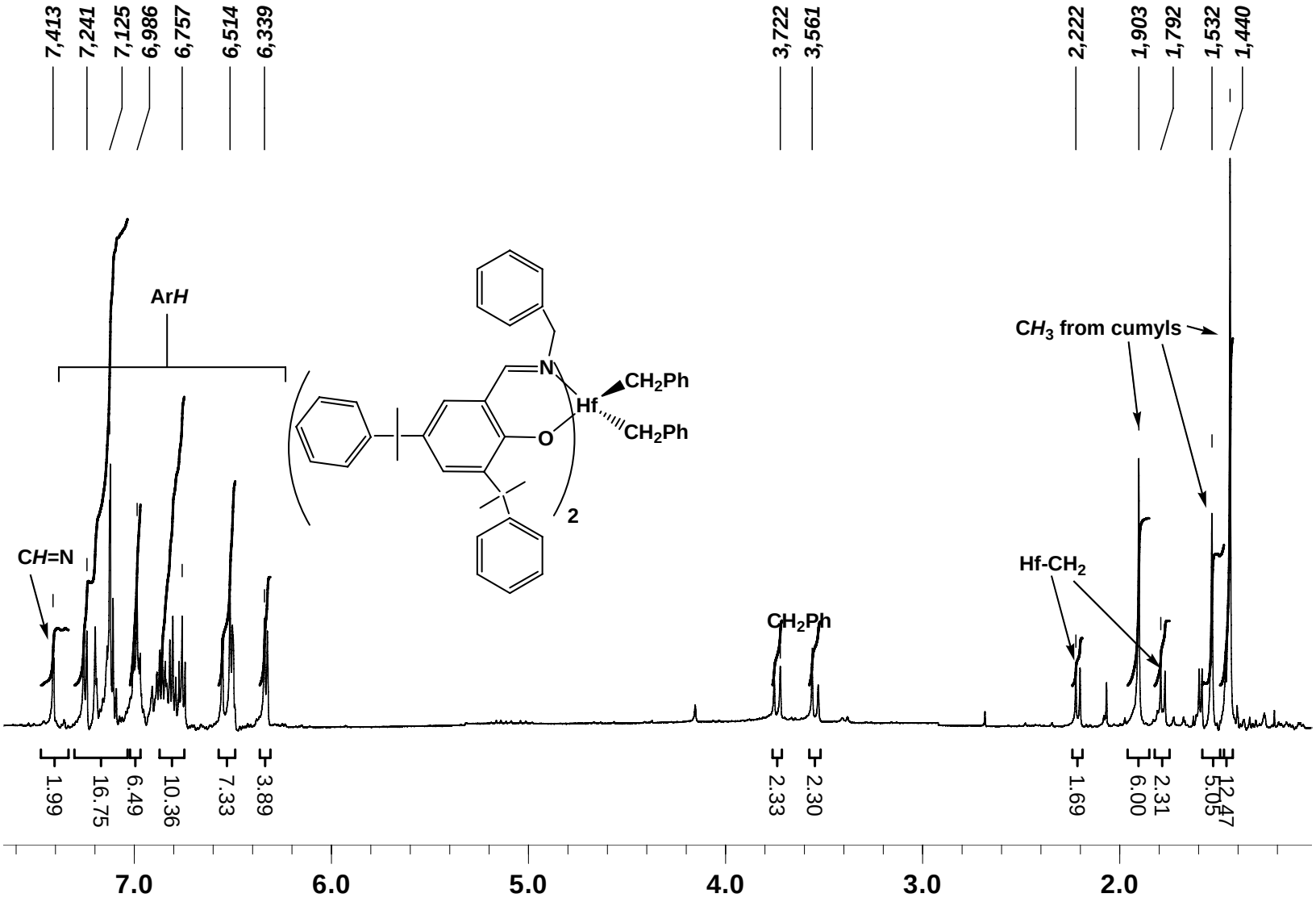
2. ^{1}H NMR spectrum of compound **9**



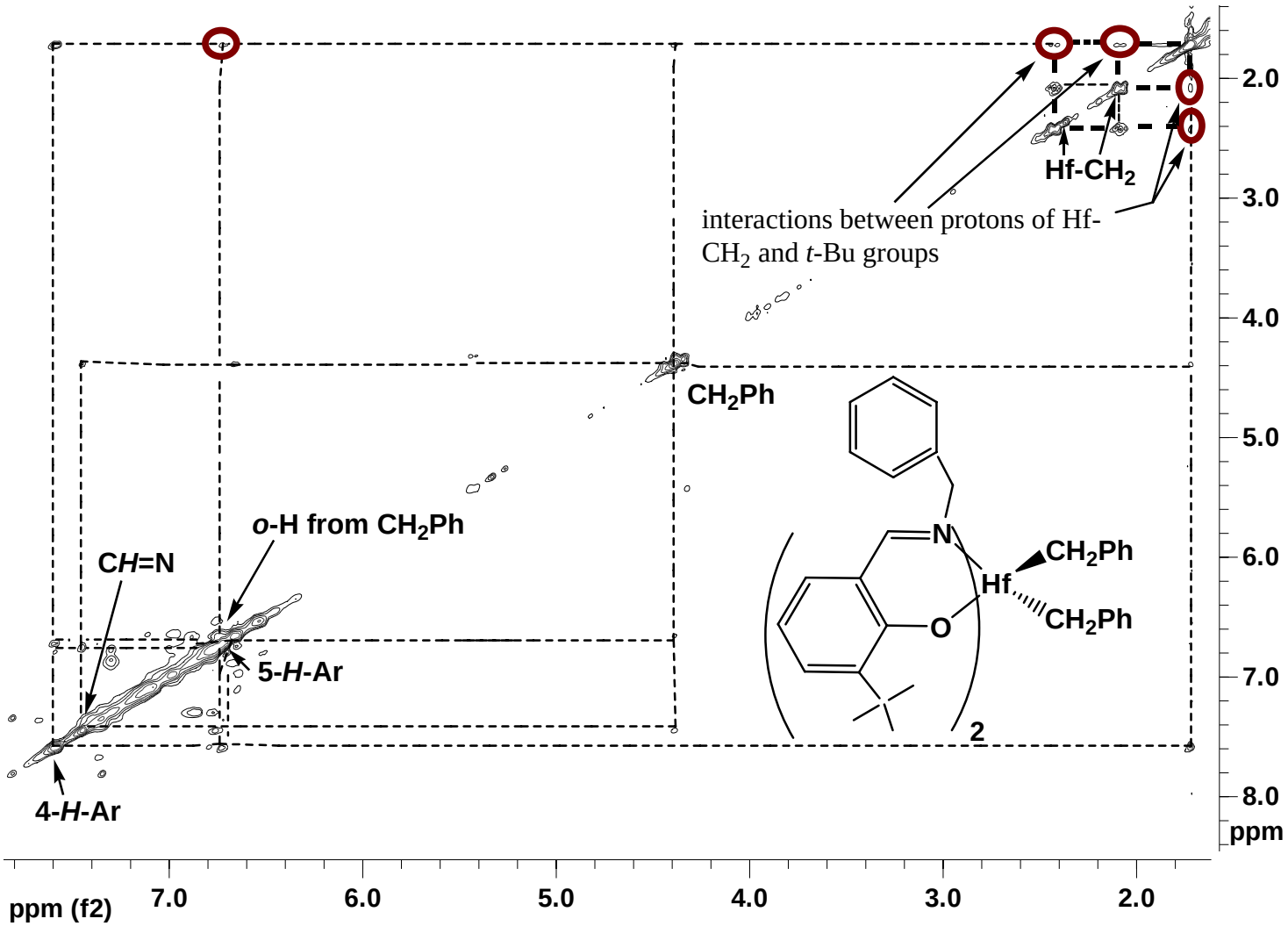
3. ^{1}H NMR spectrum of compound **11**



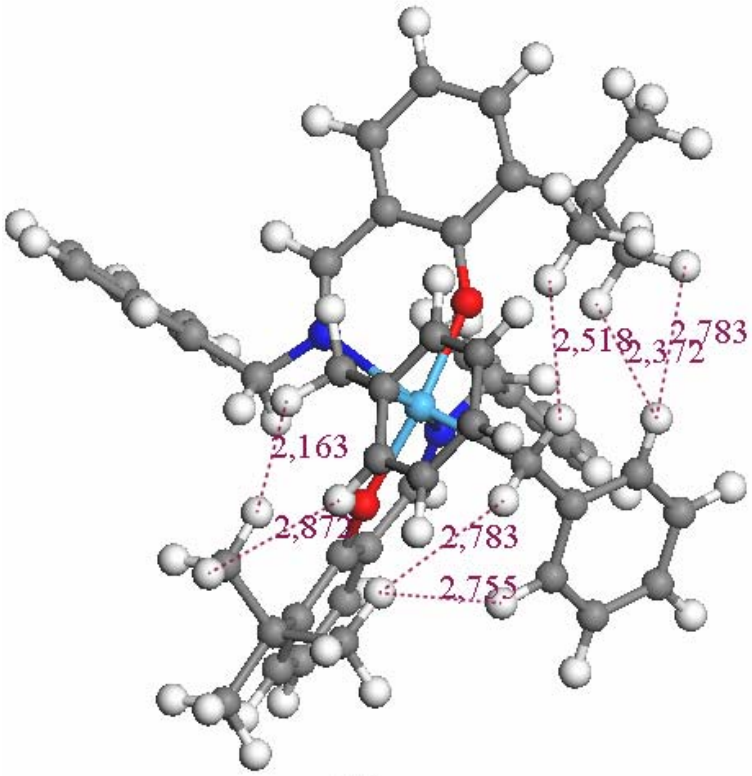
4. ^{1}H NMR spectrum of compound **10**



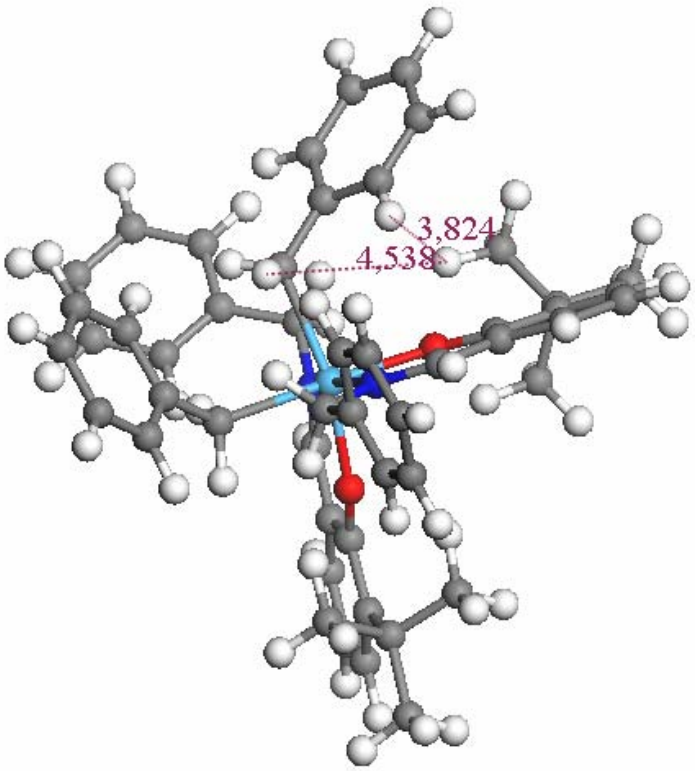
5. 2D NOESY NMR spectrum of compound **9**.



6. Structures of *cis*- and *trans*-isomers of **9** (the distances in Å between *ortho*- and methylene protons of Hf-CH_2Ph groups and *t*-Bu groups are shown).

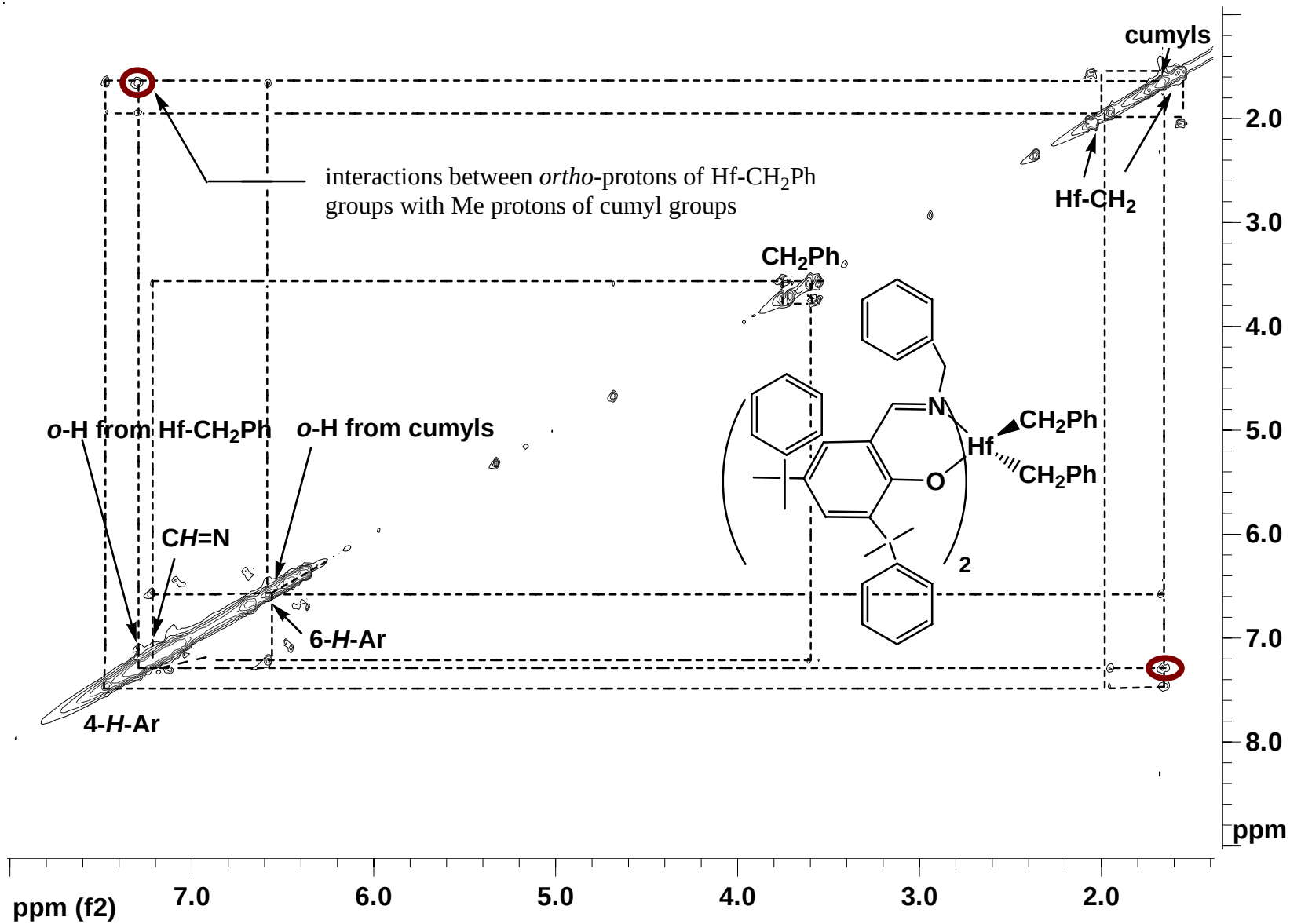


cis

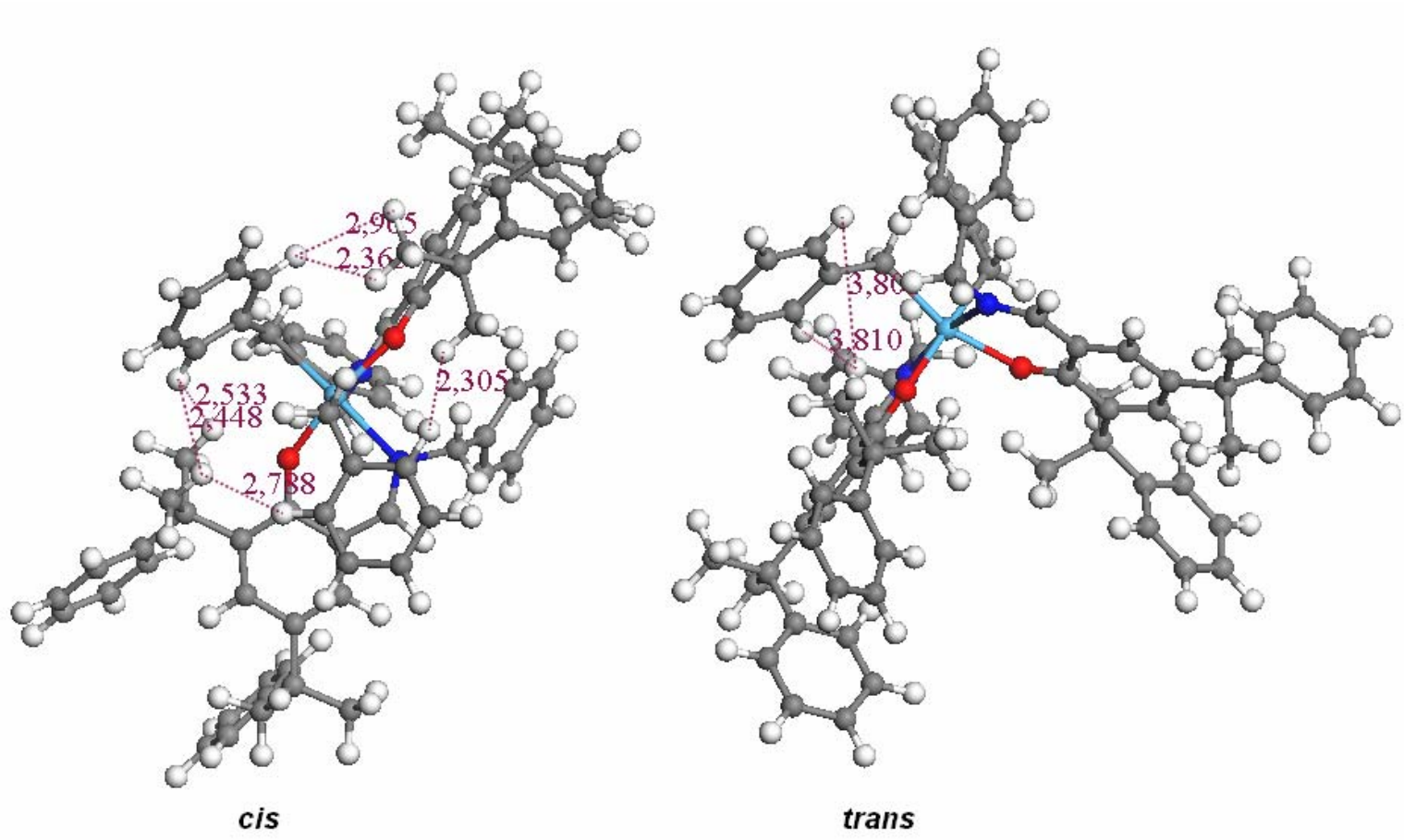


trans

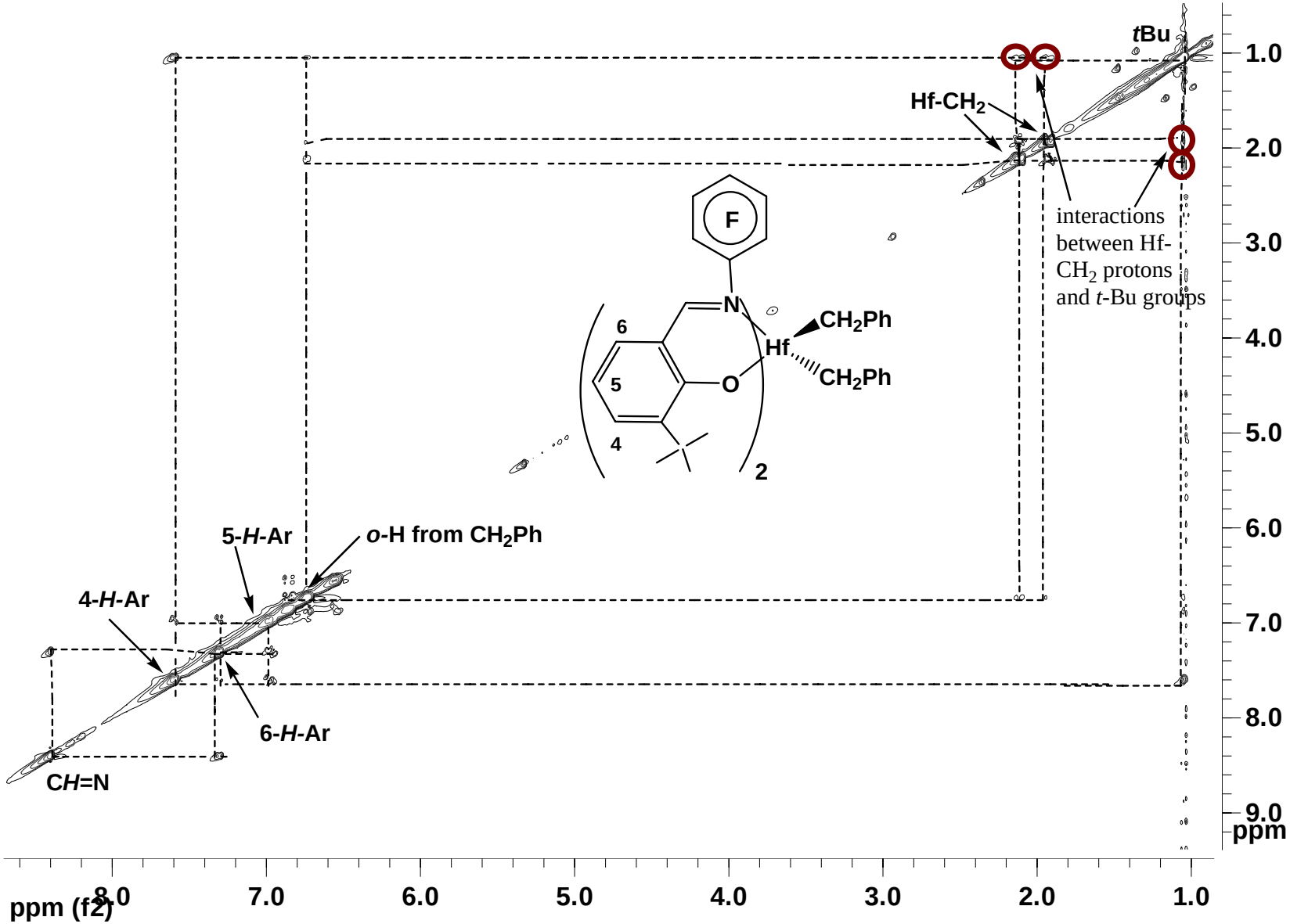
7. 2D NOESY NMR spectrum of compound **10**.



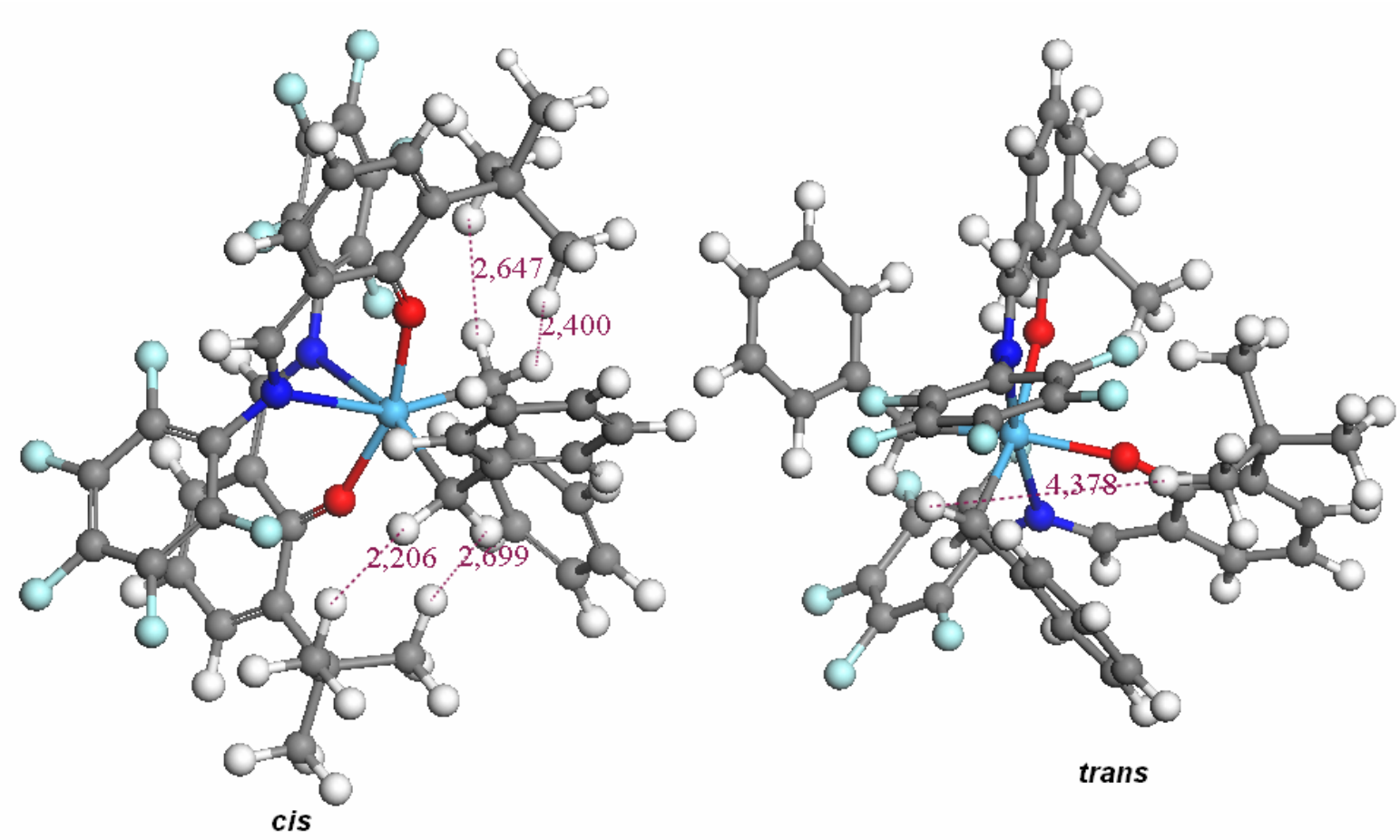
8. Structures of *cis*- and *trans*-isomers of **10** (the distances in Å between *ortho*-protons of Hf-CH_2Ph groups and Me protons from cumyl groups are shown).



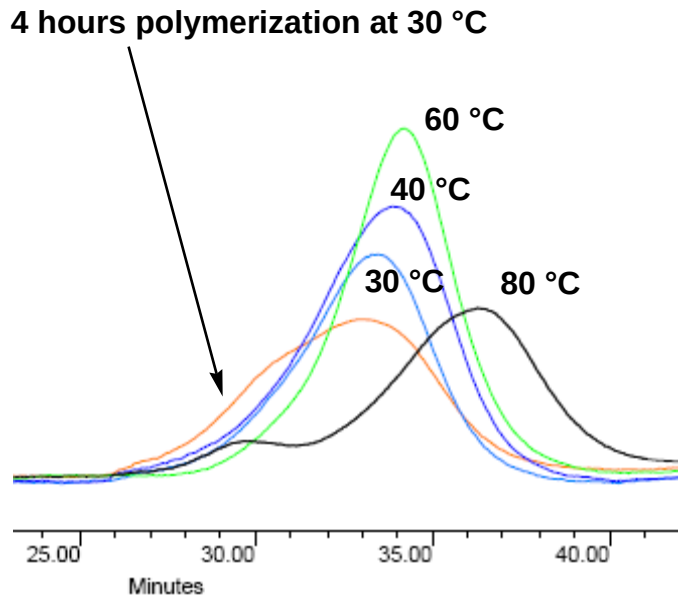
9. 2D NOESY NMR spectrum of compound **11**.



10. Structures of *cis*- and *trans*-isomers of **11** (the distances in Å between methylene protons of Hf-CH_2Ph groups and *t*-Bu groups are shown).

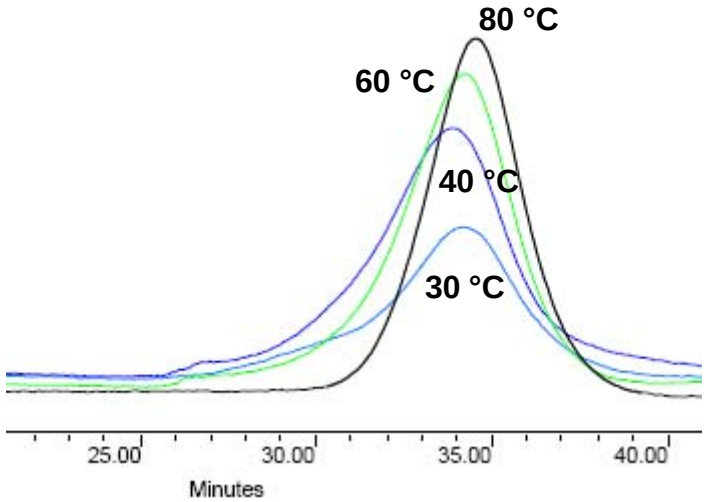


11. GPC of the polyethene produced with complex **5** at different polymerization temperatures. Conditions: Hf/MAO = 2000:1, toluene 200 ml, ethene pressure 4 bar.



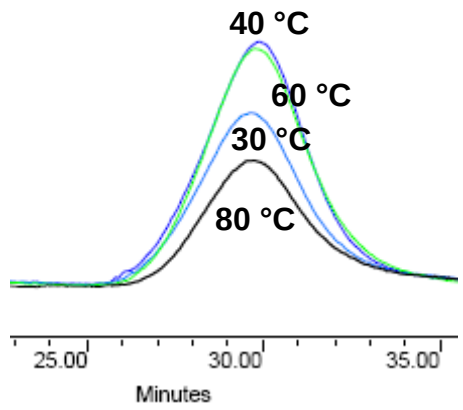
	Mn	Mw	Mz	MP	Polydispersity
	10310	226937	2811106	13916	22.010297
	37794	159648	564836	64174	4.224136
	45715	436567	3724275	81419	9.549835
	68461	422924	2522860	110066	6.177551
	74252	663662	3306218	167914	8.937918

12. GPC of the polyethene produced with complex **6** at different polymerization temperatures. Conditions: Hf/MAO = 2000:1, toluene 200 ml, ethene pressure 4 bar.



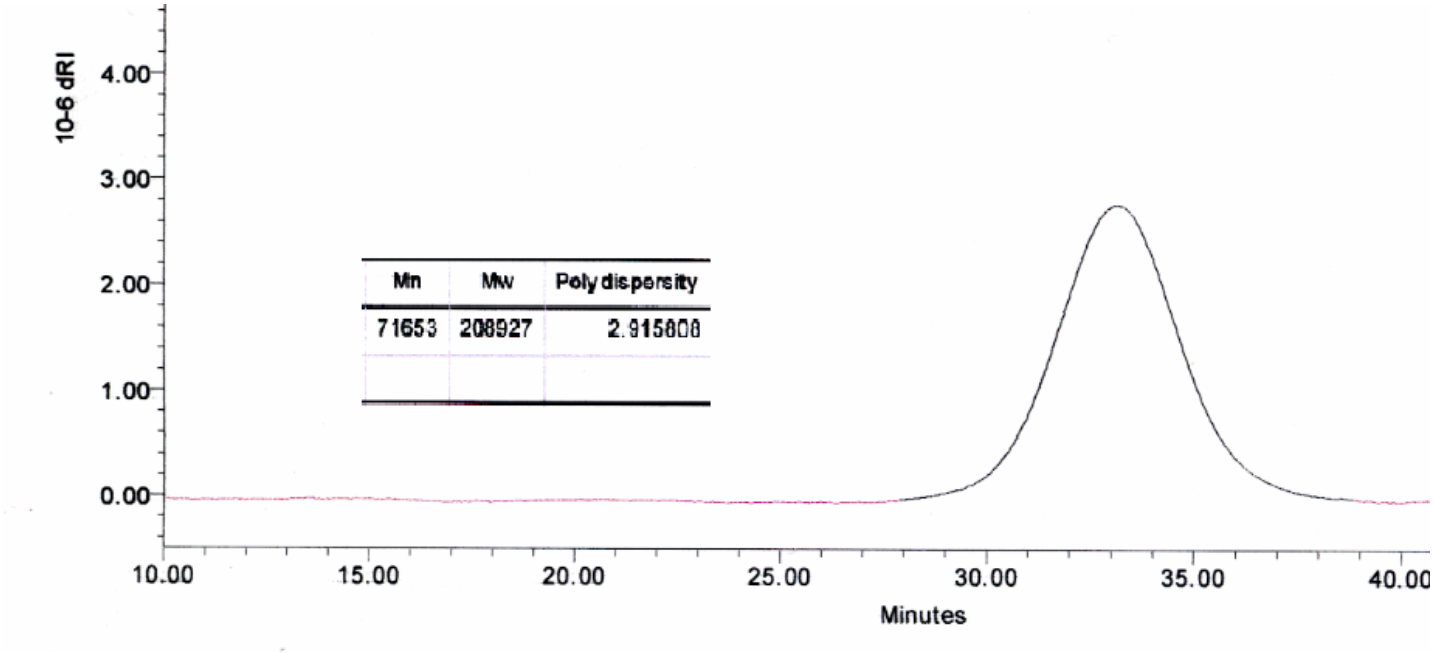
	Mn	Mw	Mz	MP	Polydispersity
	31273	81480	180060	51168	2.605436
	44820	273047	2894303	63135	6.092112
	58730	381980	3253757	80535	6.503961
	39790	296711	1639276	65518	7.456970

13. GPC of the polyethene produced with complex **8** at different polymerization temperatures. Conditions: Hf/MAO = 2000:1, toluene 200 ml, ethene pressure 4 bar.

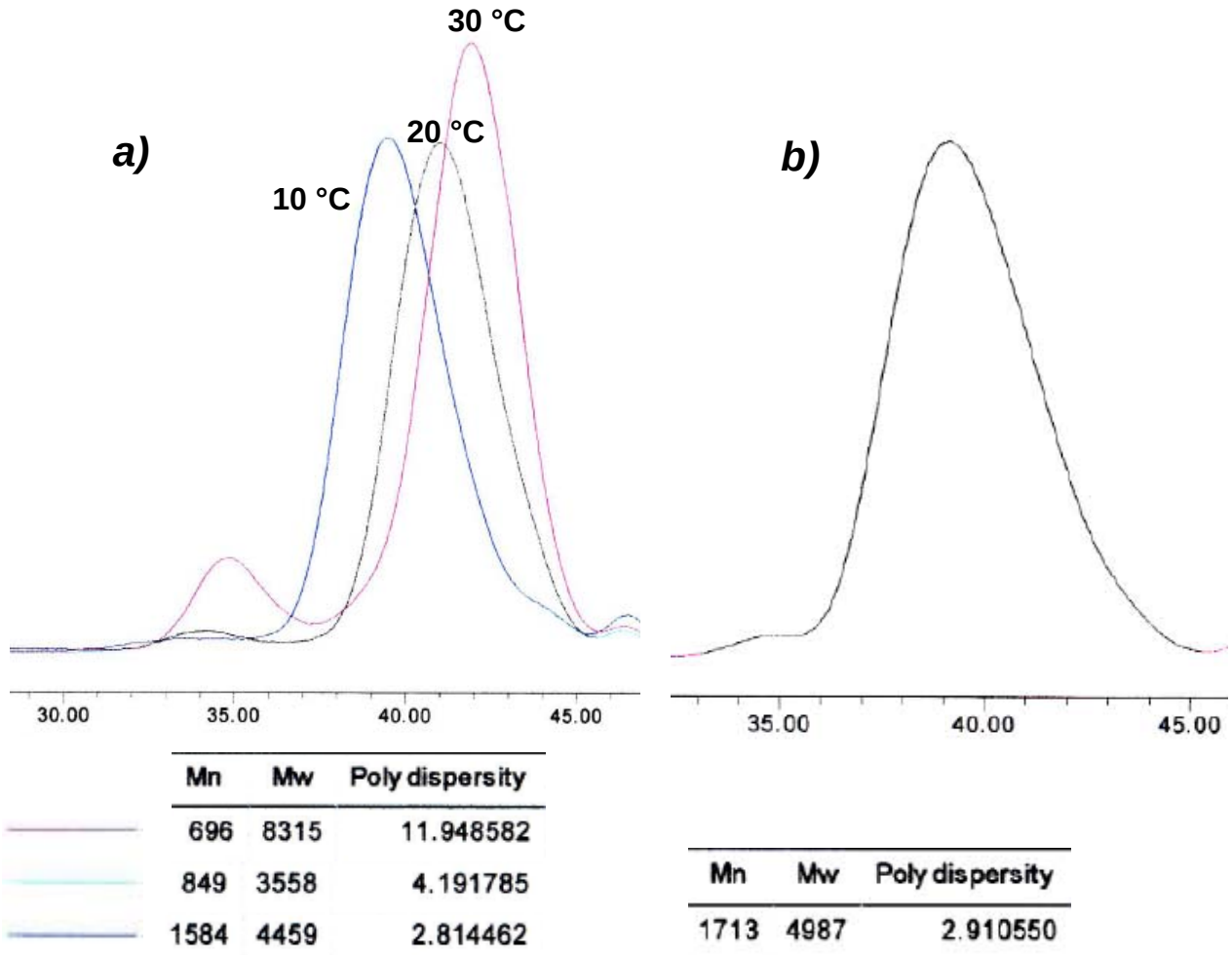


	Mn	Mw	Mz	MP	Polydispersity
	393635	1555530	3036483	1272736	3.951702
	645683	1685548	3836493	1241596	2.610489
	796971	1792092	3896811	1149368	2.248629
	709442	1876354	3917444	1338136	2.644831

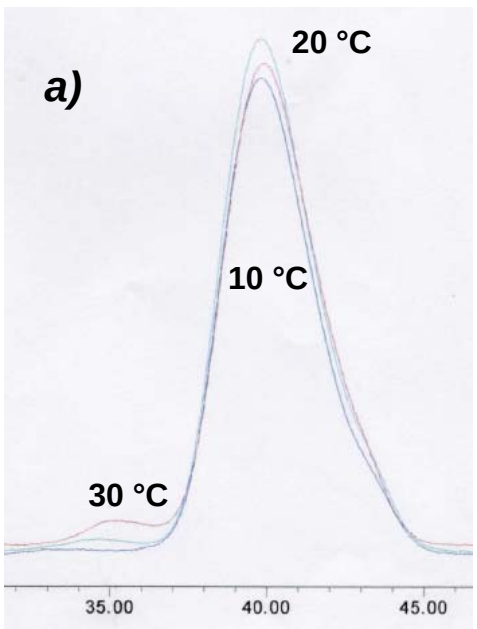
14. GPC of the polyethene produced with complex **11**. Conditions: Hf/MAO = 2000:1, toluene 200 ml, ethene pressure 4 bar, polymerization temperature 30 °C.

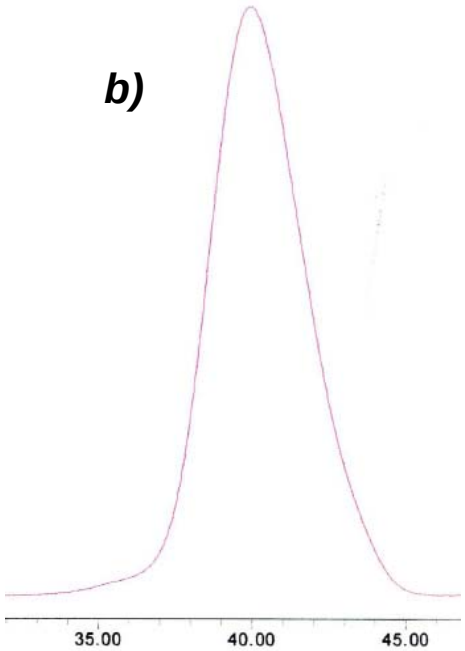


15. a) GPC of the polypropylene produced with complex **7** at different polymerization temperatures. Conditions: Hf/MAO = 2000:1, toluene 200 ml, propene pressure 6 bar. b) GPC of the polypropylene produced with complex **11**. Conditions: Hf/MAO = 2000:1, toluene 200 ml, propene pressure 6 bar.



16. a) GPC of the polypropylene produced with complex **8** at different polymerization temperatures. Conditions: Hf/MAO = 2000:1, toluene 200 ml, propene pressure 6 bar. b) GPC of the polypropylene produced with complex **12**. Conditions: Hf/MAO = 2000:1, toluene 200 ml, propene pressure 6 bar.

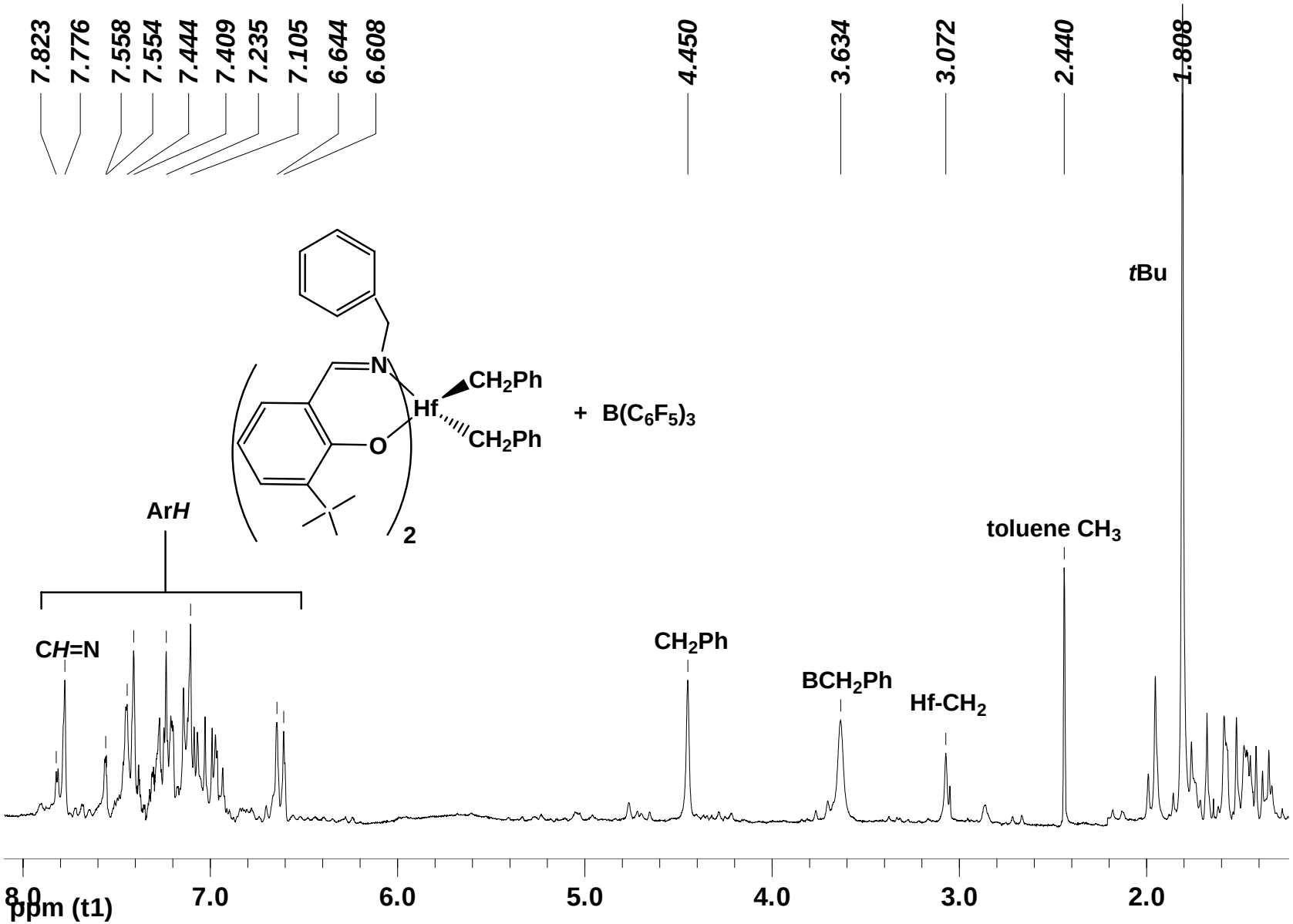




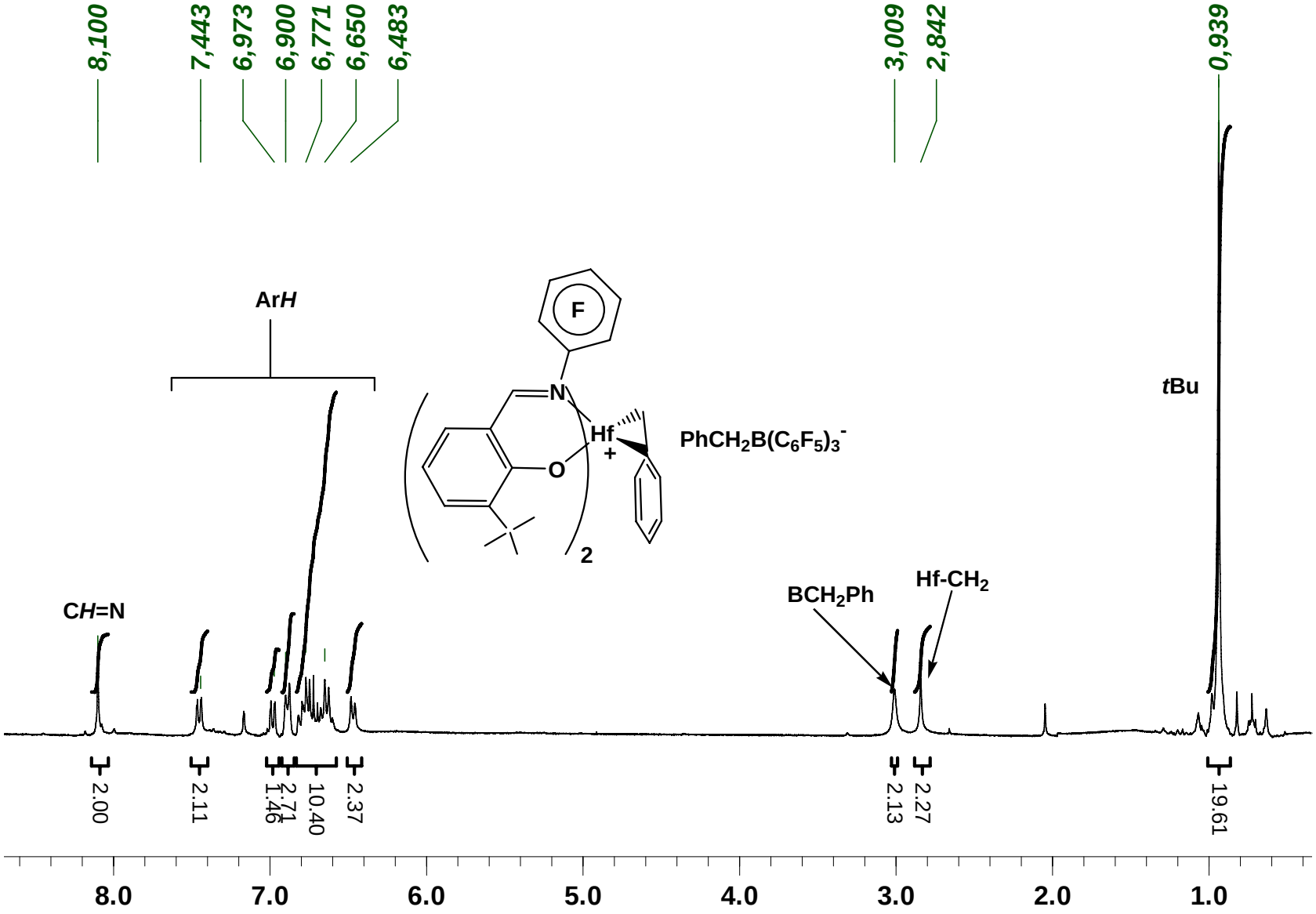
Mn	Mw	Poly dispersity
1303	3479	2.669943
1278	3415	2.672465
1272	2418	1.900934

Mn	Mw	Poly dispersity
1287	2813	2.186039

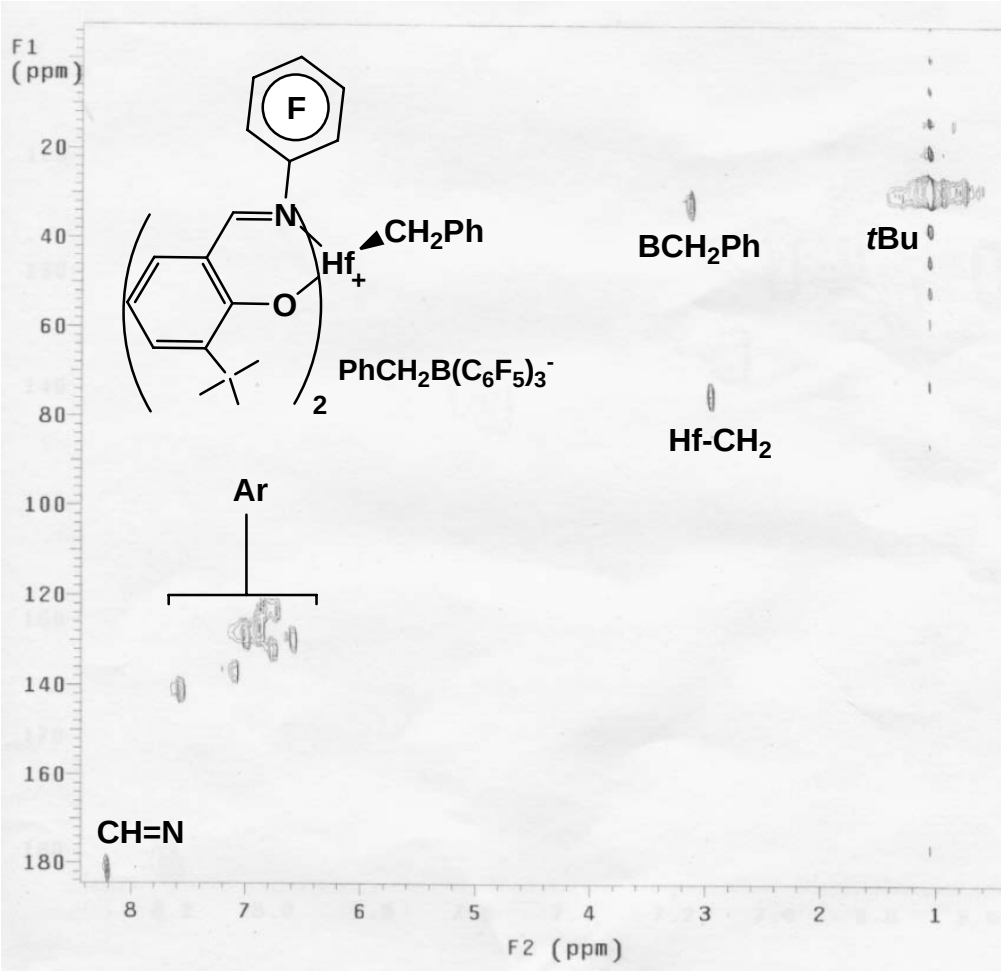
17. ^{1}H NMR spectrum of products from reaction of **9** and $B(C_6F_5)_3$.



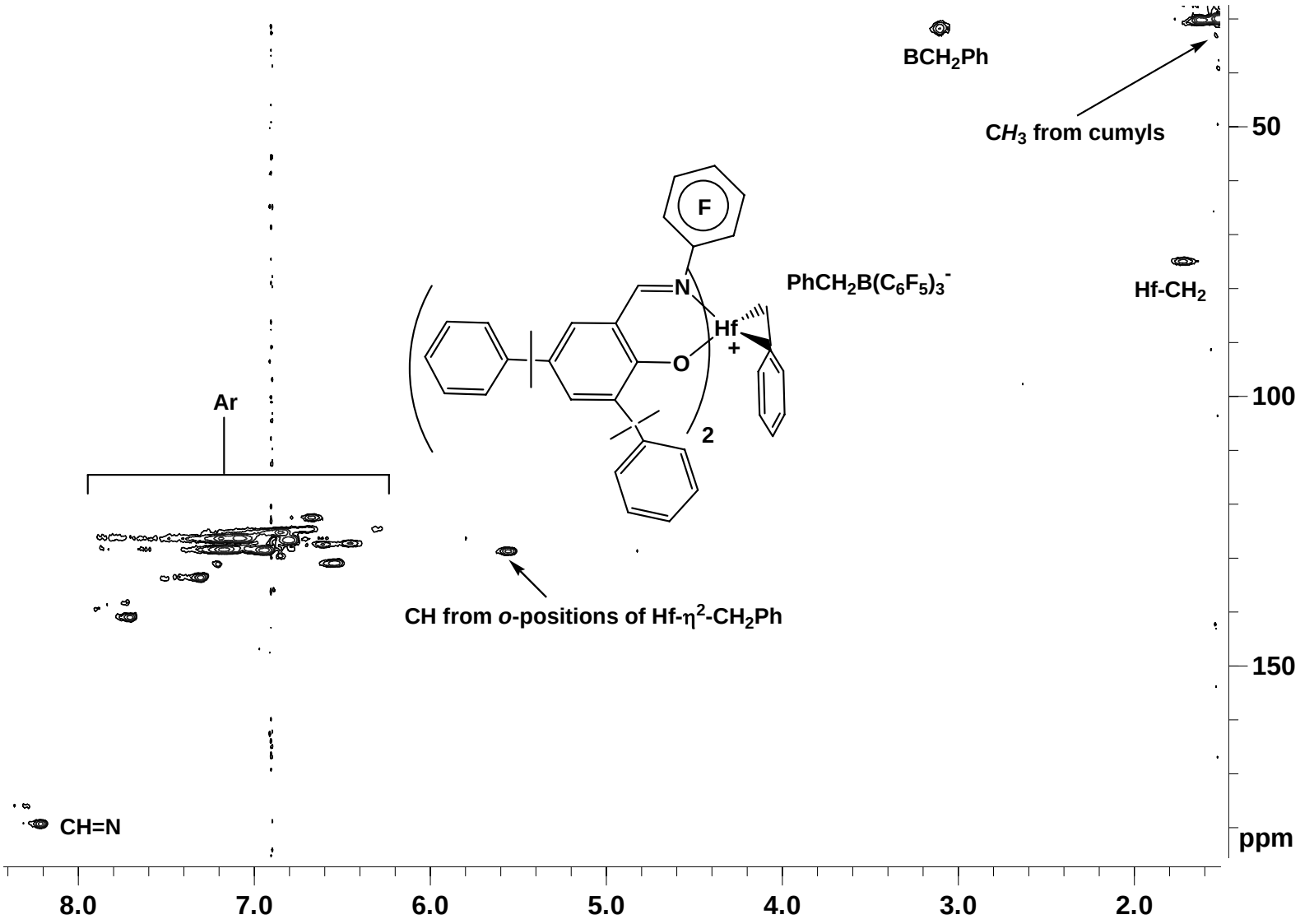
18. ^{1}H NMR spectrum of compound **14**



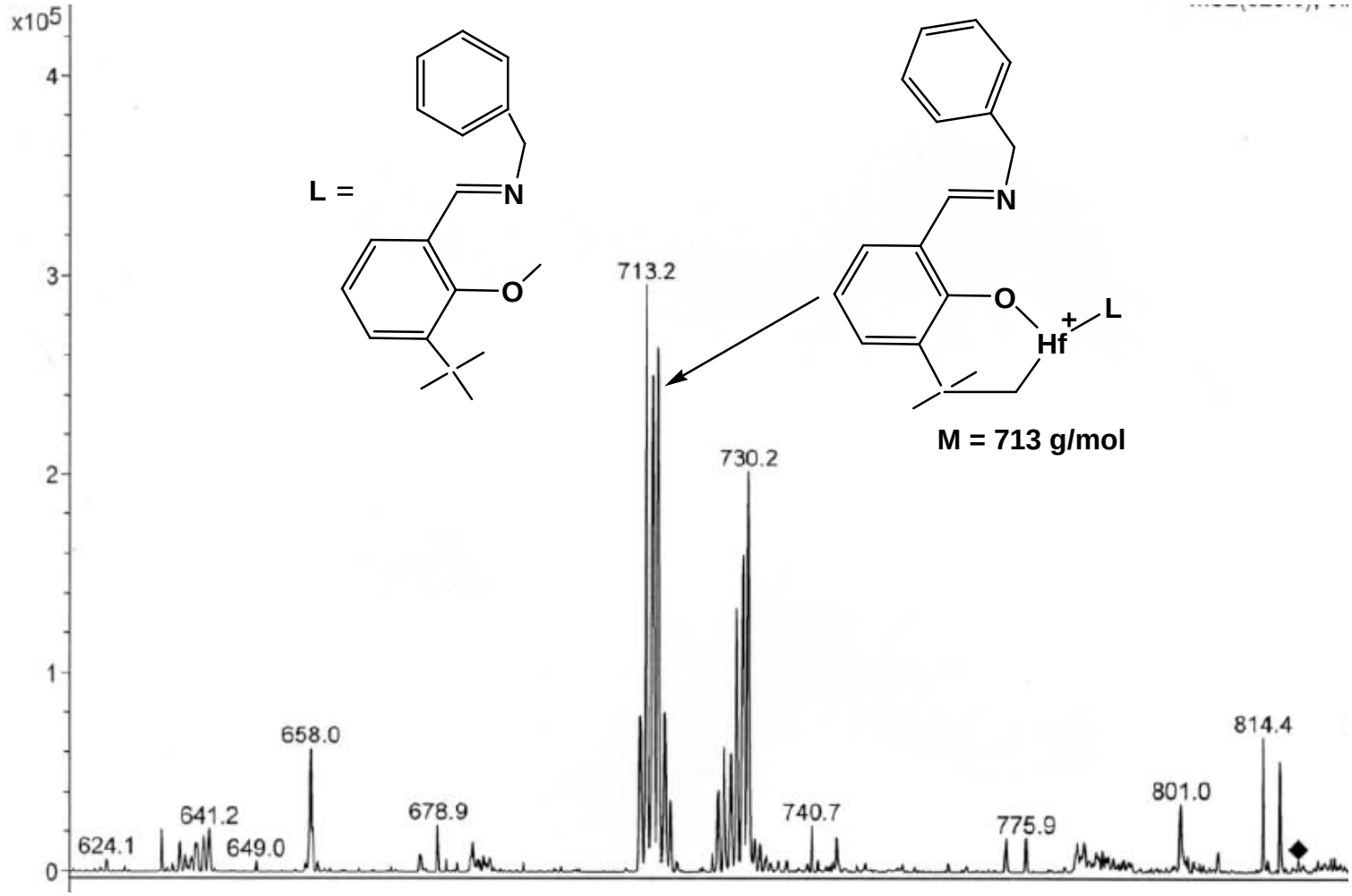
19. HETCOR 2D-COSY spectrum of compound **14**.



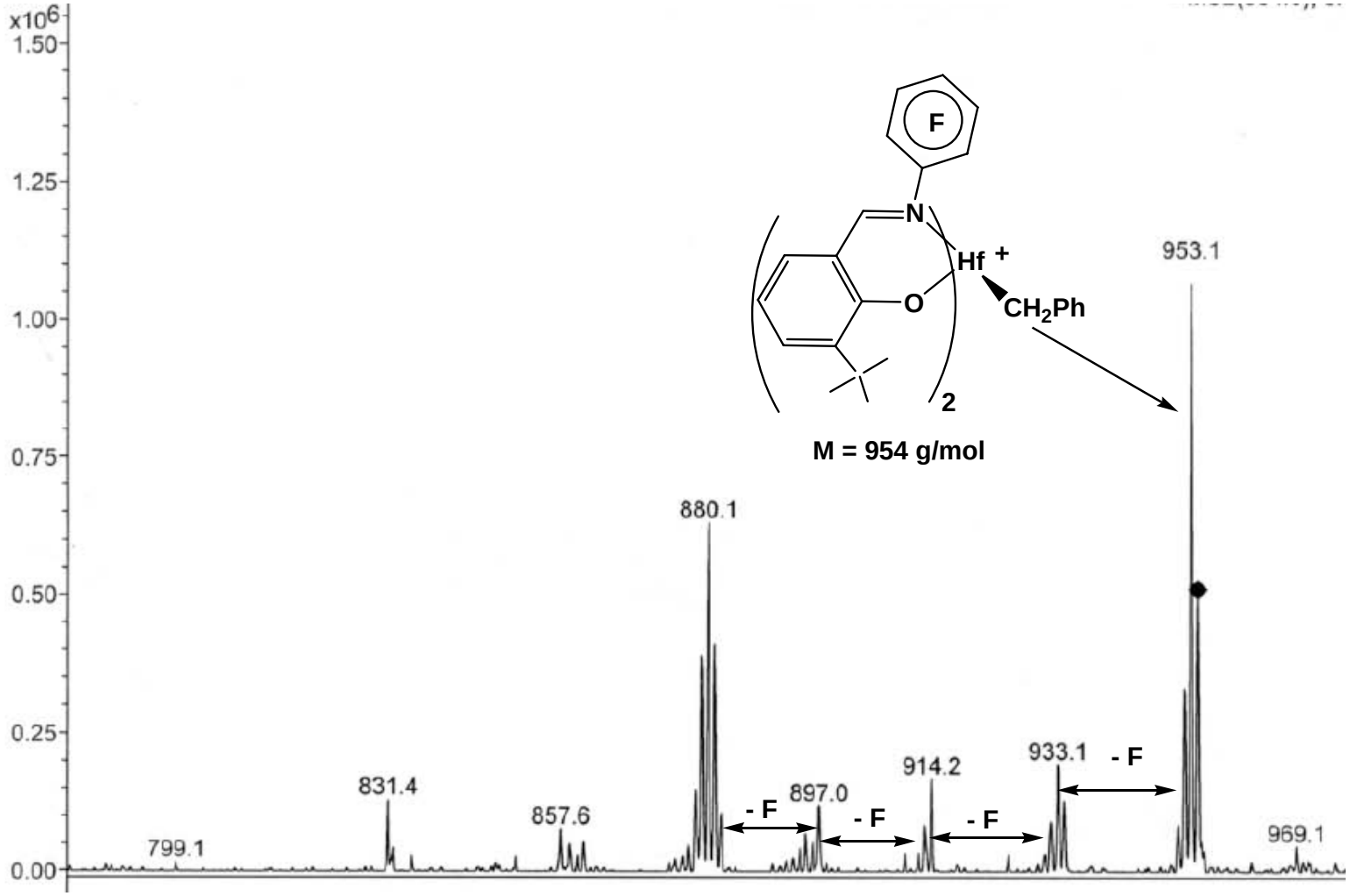
20. HETCOR 2D-COSY spectrum of compound **15**.



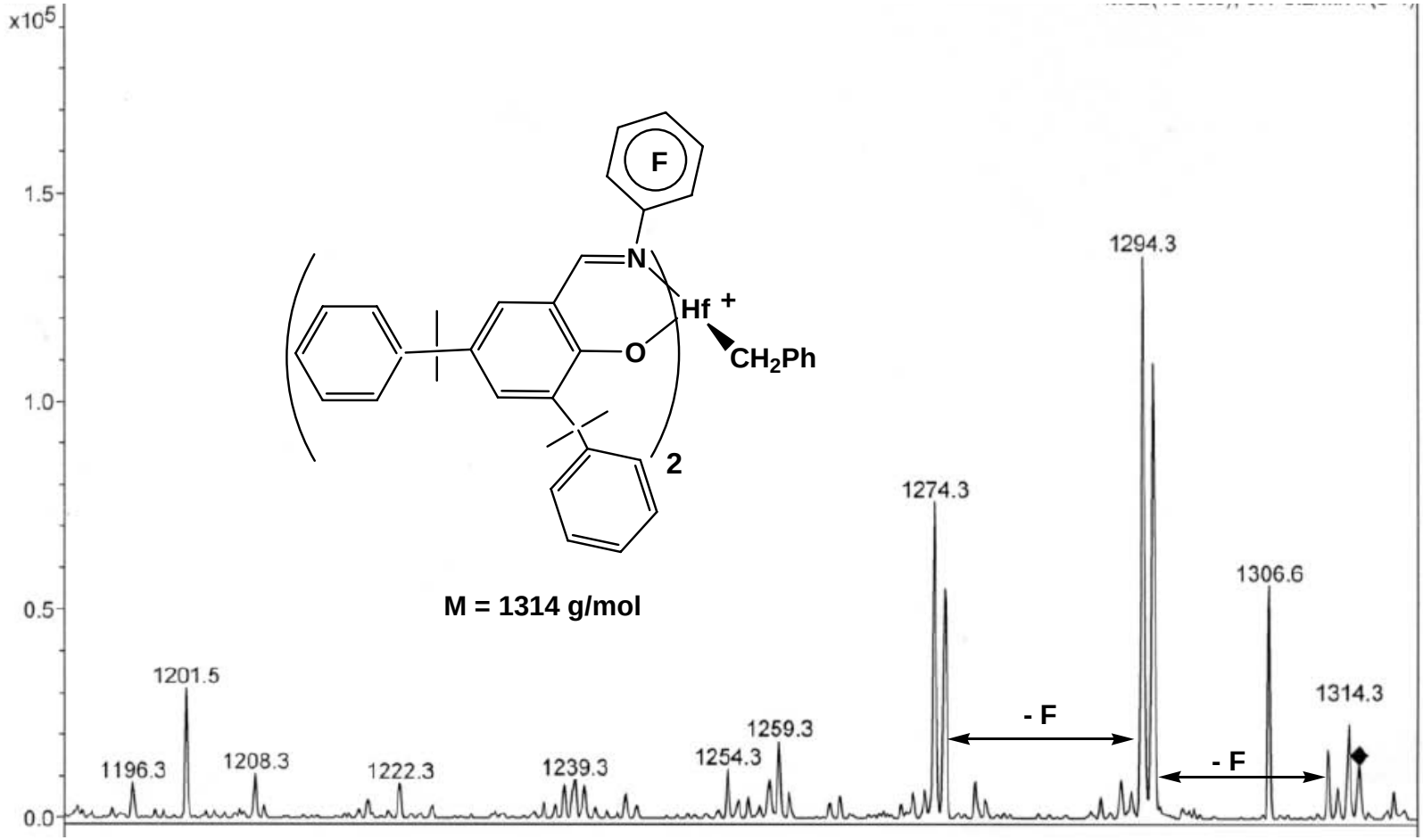
21. ESI-MS spectrum of reaction of complex **9** with $B(C_6F_5)_3$



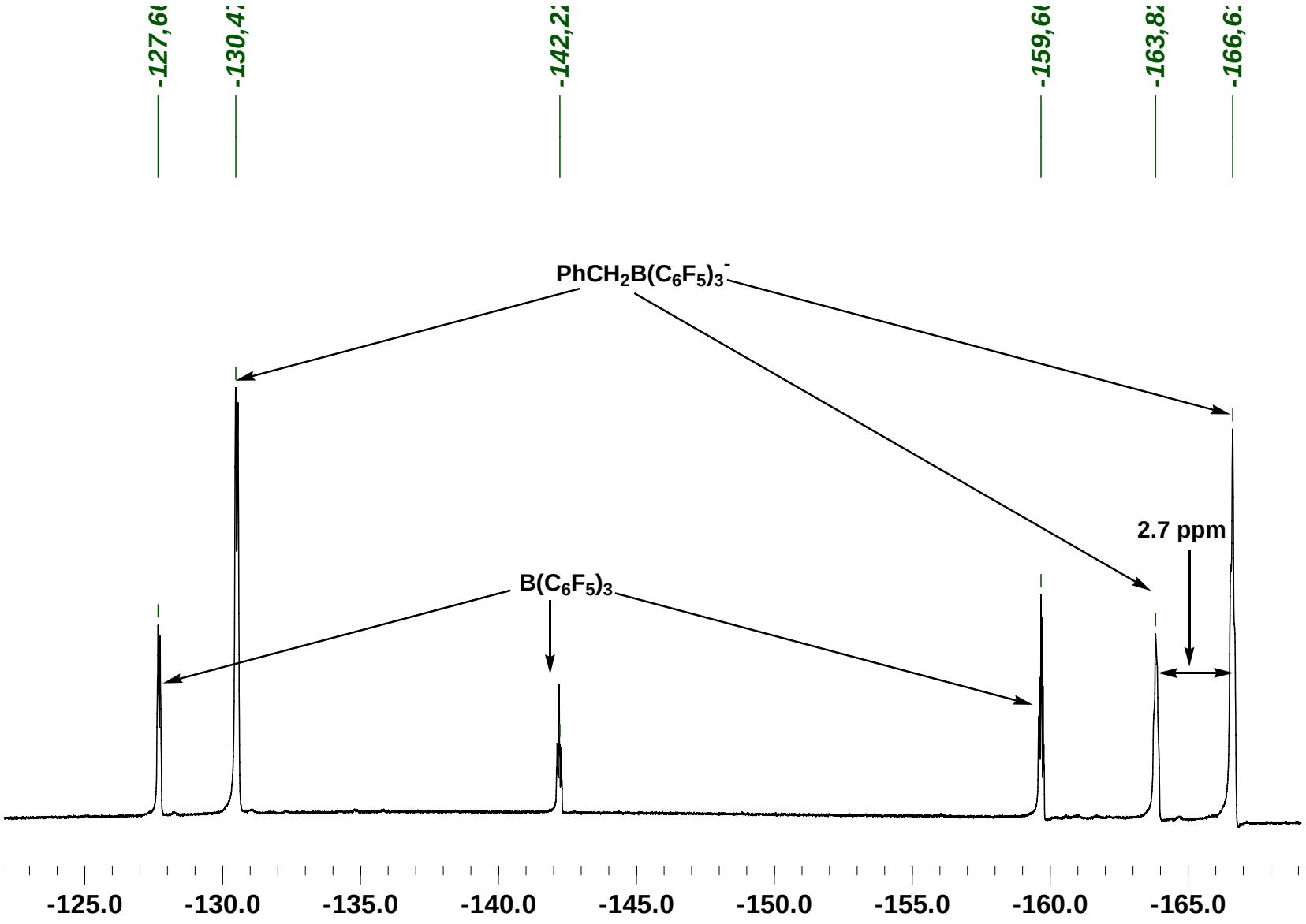
22. ESI-MS spectrum of complex **14**.



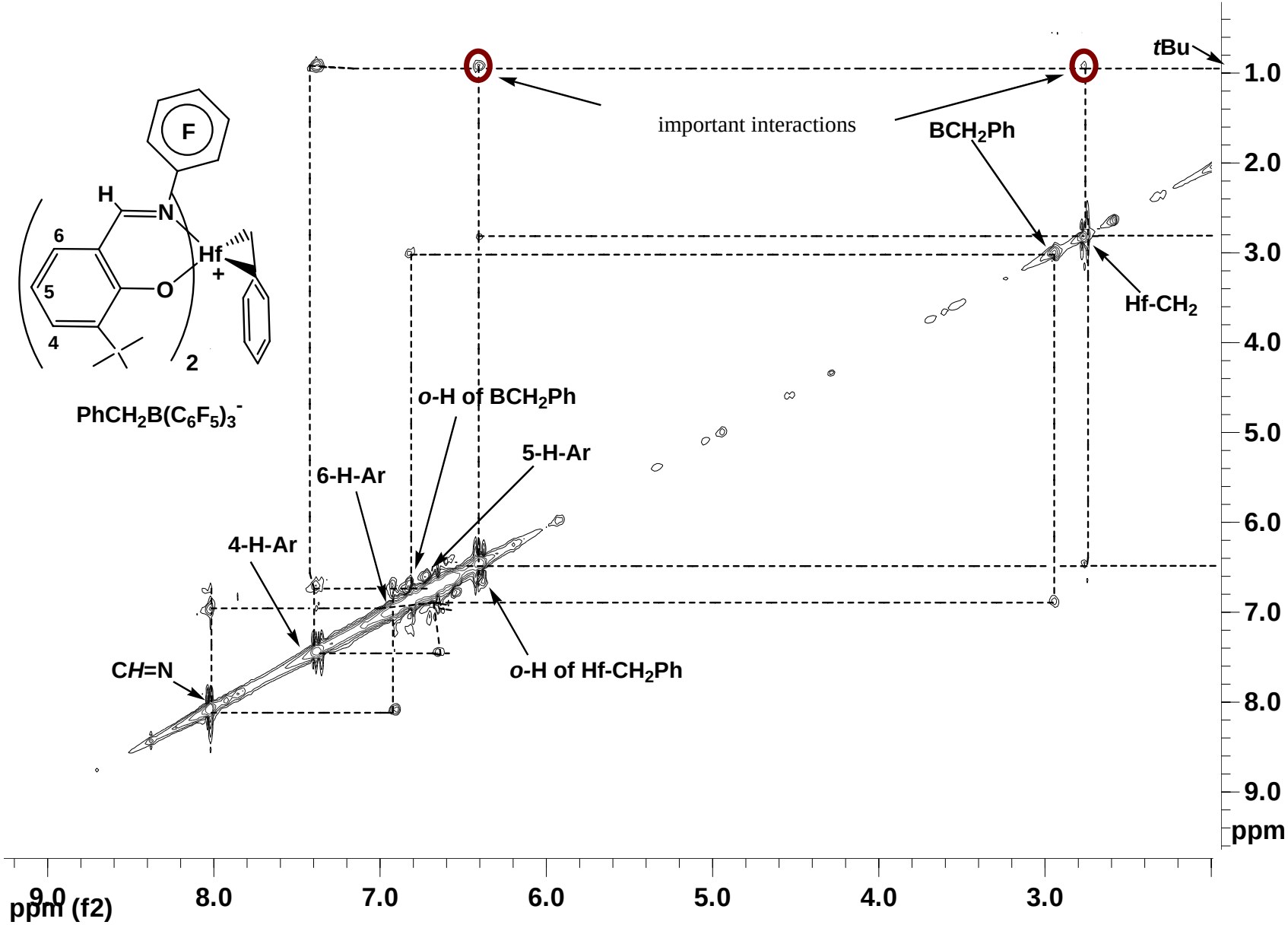
23. ESI-MS spectrum of complex **15**.



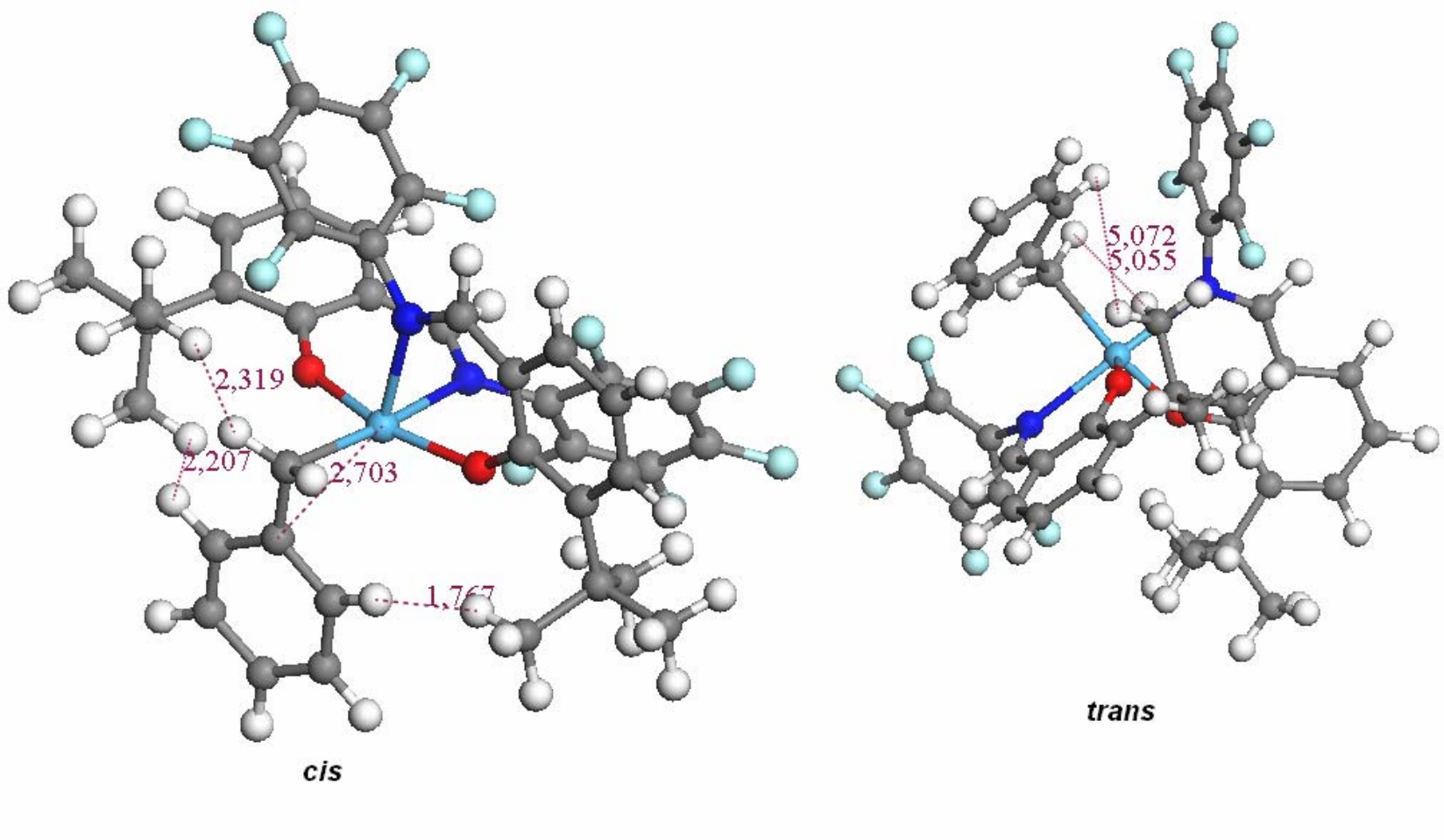
24. ^{19}F NMR spectrum of compound **10**/$B(C_6F_5)_3$.



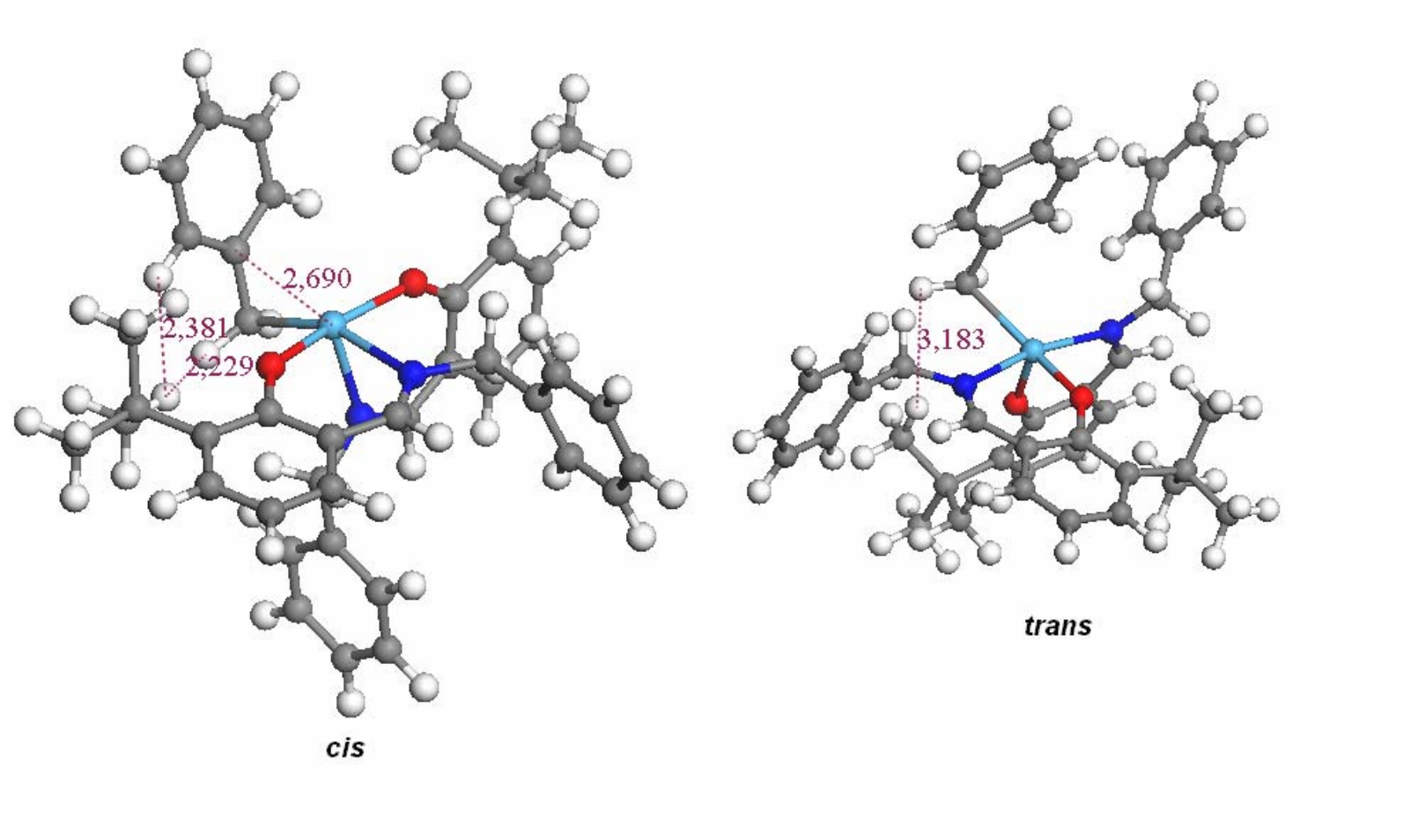
25. 2D NOESY NMR spectrum of compound **14**.


F
H
N
6
Hf
+
5
O
4
2
PhCH2B(C6F5)3-
important interactions
tBu
BCH2Ph
Hf-CH2
o-H of BCH2Ph
5-H-Ar
6-H-Ar
4-H-Ar
CH=N
o-H of Hf-CH2Ph
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f2)

26. Calculated with ADF program structures of *cis*- and *trans*-**14** with shown distances (Å) between Hf and C_{ipso}; between methylene and *ortho*-protons from Hf-CH_2Ph groups and protons of *t*-Bu groups.



27. Calculated with ADF program structures of *cis*- and *trans*-**9**/B(C_6F_5)$_3$ with shown distances (Å) between Hf and C_{ipso}; between methylene and *ortho*-protons from Hf-CH_2Ph groups and protons of *t*-Bu groups..

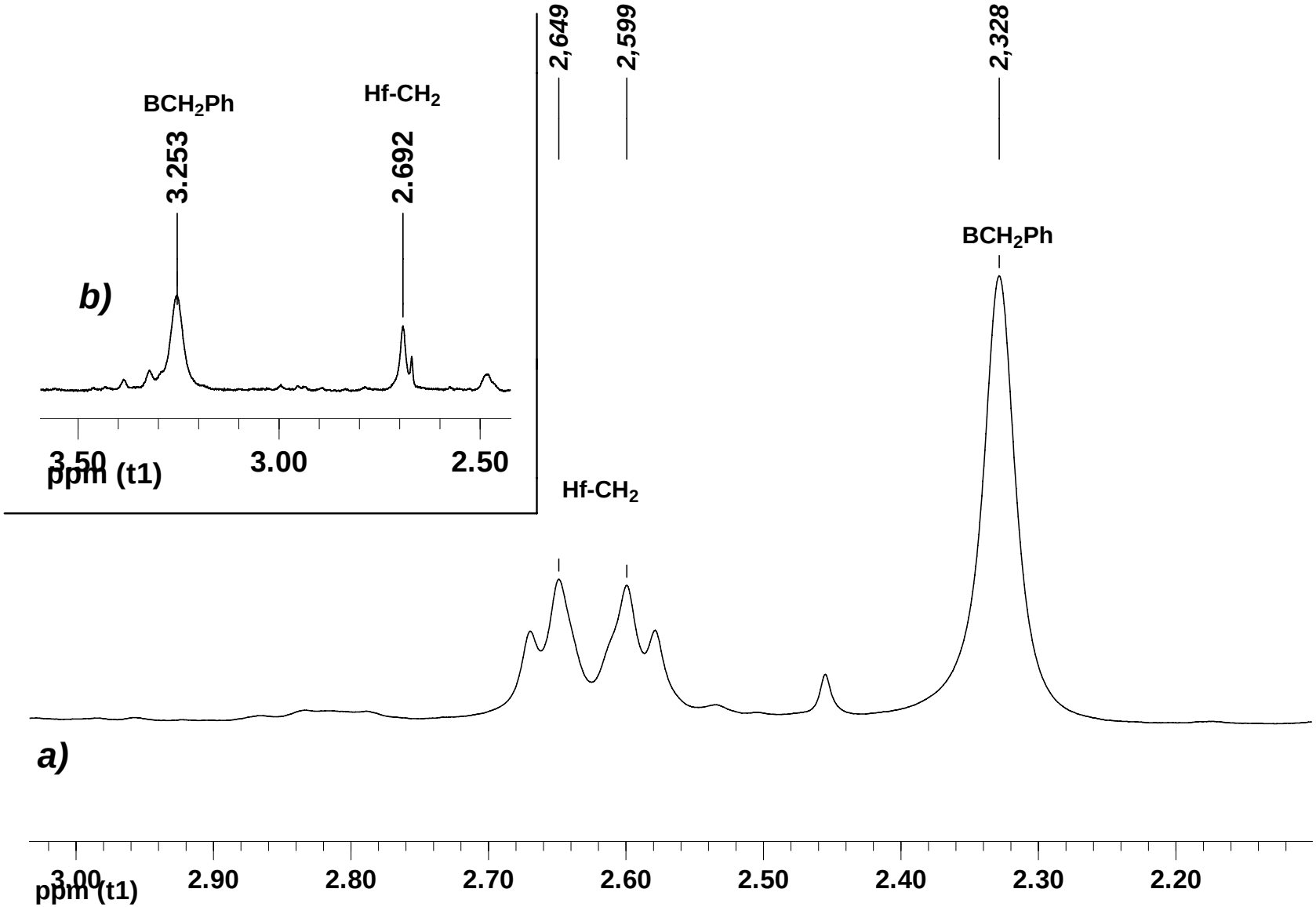


28. Relative to *trans* isomer energies of isomeric structures for bis(phenoxyimino) Hf dibenzyl complexes and for the corresponding monobenzyl cationic species calculated with Turbomole 5.8 and ADF 2005.01 computation software.

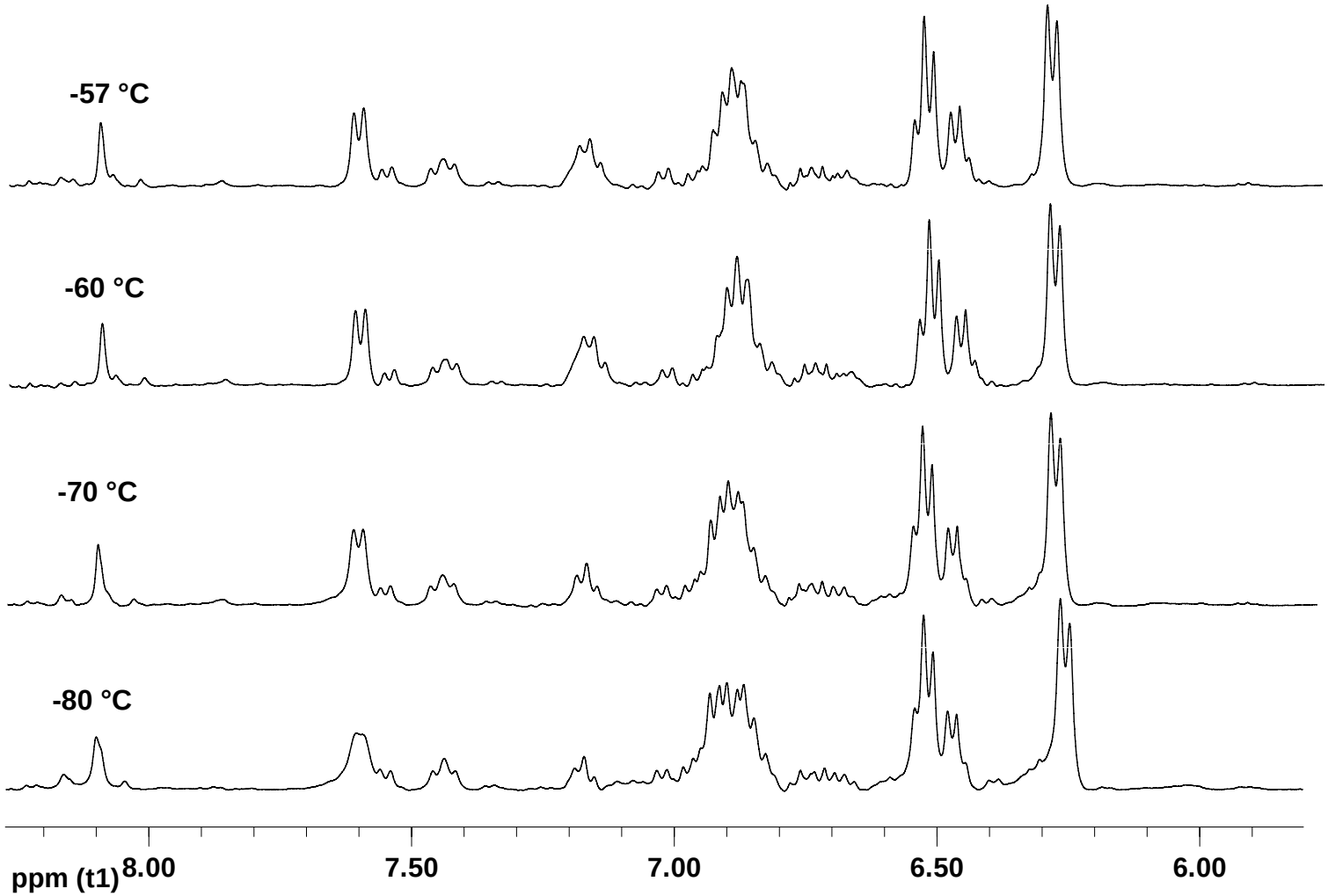
complex	E_r(*cis*), kJ/mol	E_r(*ciscis*), kJ/mol	E_r(*trans*), kJ/mol
9	-35.1	-14.0	0
	-35.0[a]	-8.7[a]	0[a]
9/$B(C_6F_5)_3$	-8.1	-7.7	0
10	-21.6	-17.2	0
10/$B(C_6F_5)_3$	-8.3	-3	0
11	-32.3	0	0
14	-34.5	-36.0	0
12	-50.9	-26.5	0
15	-19.6	0	0

[a]Calculated with ADF2005.01 program.

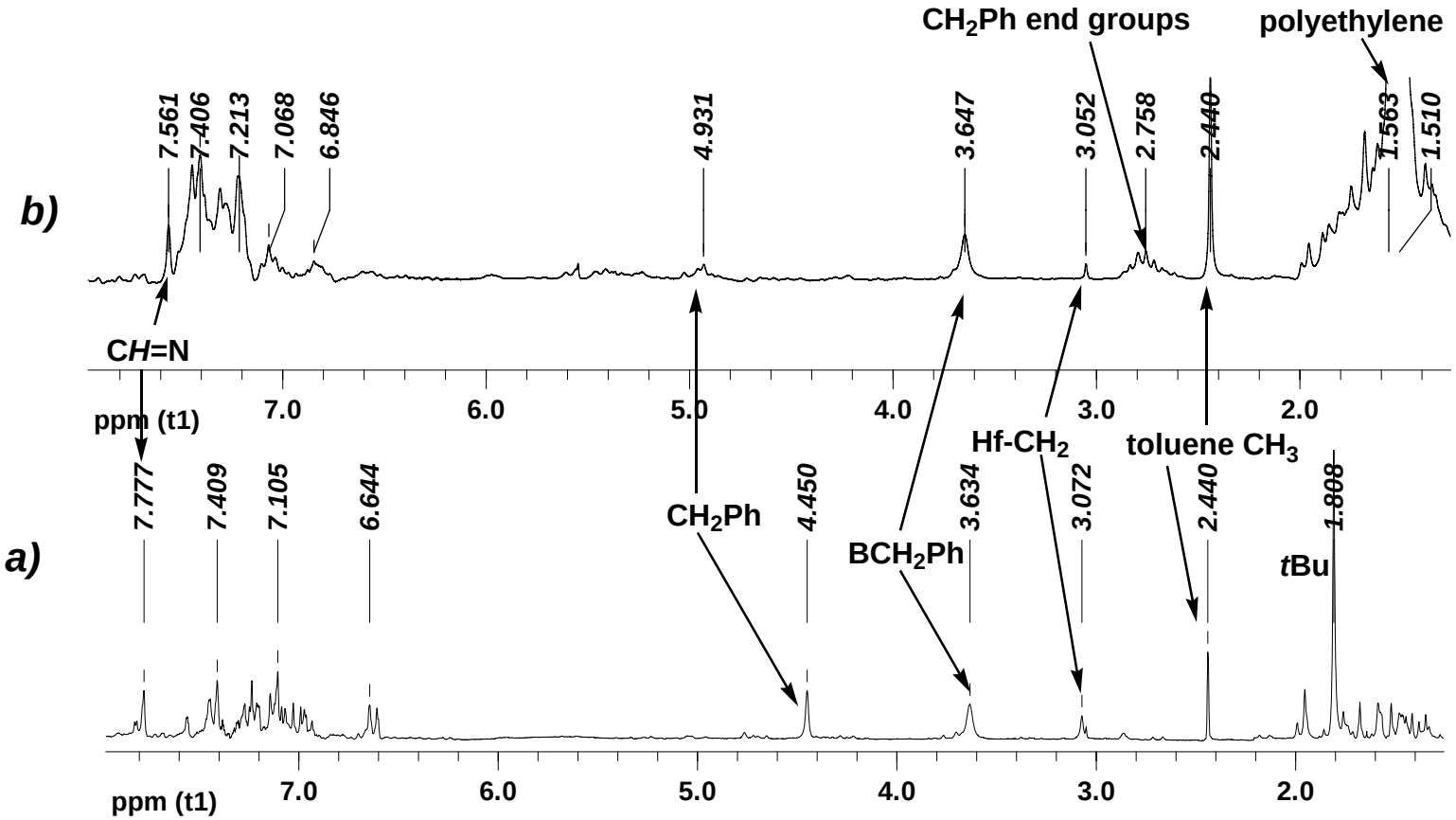
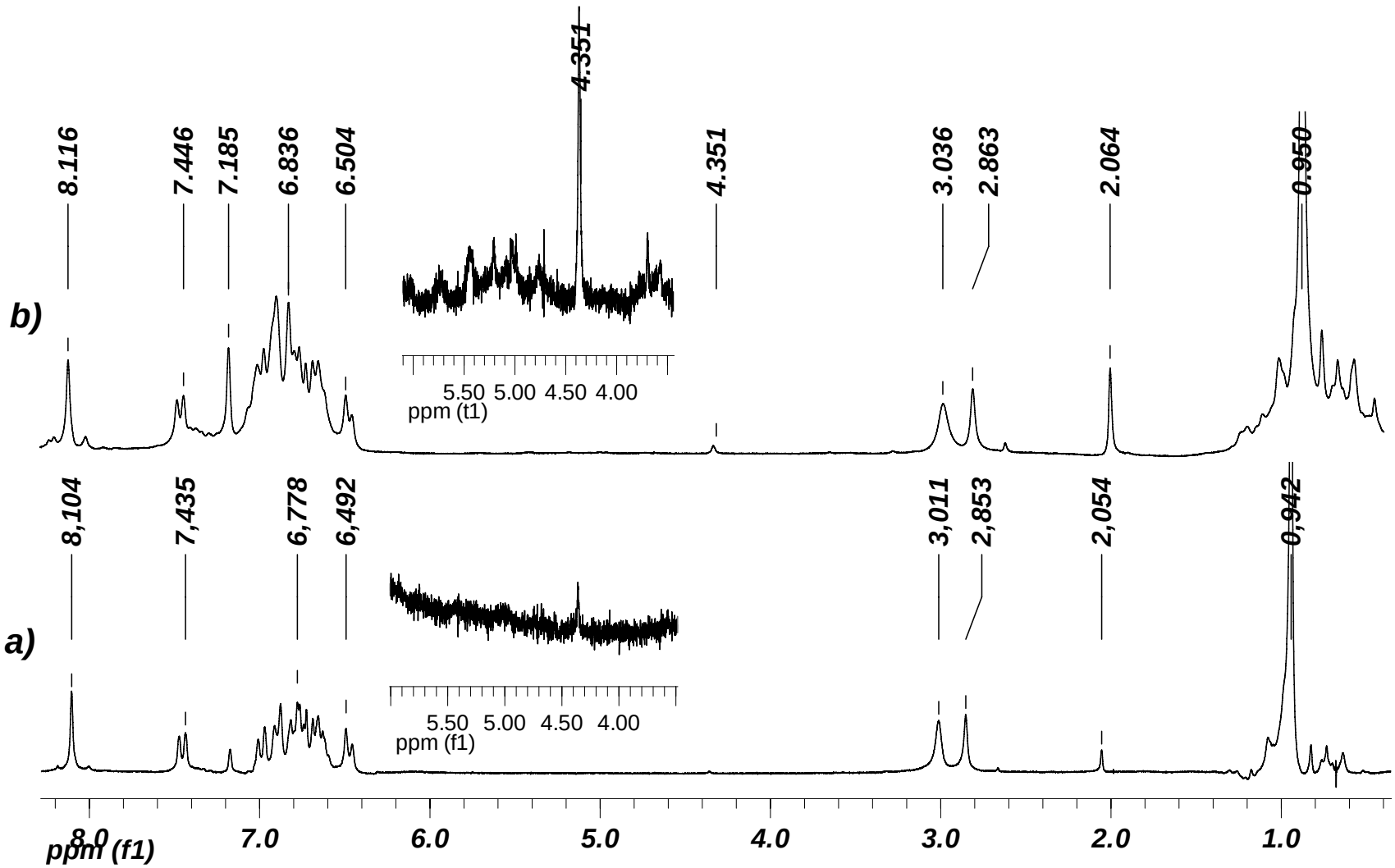
29. ^{1}H NMR spectrum of compound **9**/$B(C_6F_5)_3$: a) solvent: CD_2Cl_2, T = -80 °C; b) solvent: C_6D_5Br, T = 27 °C.



30. Dynamic NMR of compound **14** (area of aromatic and imino protons). Solvent: CD_2Cl_2



31. Ethene polymerization with **9**/B(C_6F_5)$_3$ in C_6D_5Br in NMR tube: a) before addition of ethylene. b) after 10 minutes of ethene bubbling.



32. Ethene polymerization with **14** in C_6D_5Br in NMR tube: a) before addition of ethene. b) after 30 seconds of ethene bubbling.