Supporting Information for

Ph_2Si-Bridged Constrained-Geometry Complexes of Hafnium and Titanium for Copolymerization of Ethylene and 1-Octene: An Experimental and Computational Comparison

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Experimental Part

General considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk or glovebox techniques. Dry toluene was obtained from a MB-SPS-800 solvent purification system, then distilled over Na/K alloy and stored over 3Å molecular sieves. Dry diethyl ether was obtained from a MB-SPS-800 solvent purification system and stored in a tank with Na and benzophenone. Heptane (99%) and deuterated benzene were distilled over CaH_2 and stored over 3Å molecular sieves. *tert*-Butylamine was dried over molecular sieves. 2,7-Di-*tert*-butyl-9*H*-fluorene was generously provided by TotalEnergies OneTech Belgium. Precursors **a**, **b** and proligands **1** and **2** were prepared using reported procedures,[1,2] and authenticated by NMR spectroscopy. Isopar G was passed through a column of alumina and stored in a Schlenk flask over 3Å molecular sieves. 1-Octene (99%) was stored in a Schlenk flask over 3Å molecular sieves. *N,N*-Dimethylanilinium tetrakis(pentafluorophenyl)borate was purchased from Strem. Other starting materials were purchased from Aldrich, Fluorochem, Acros or Strem and used as received.

Instruments and Measurements. NMR spectra of air- and moisture- sensitive compounds were recorded on Bruker AM-300, AM-400 spectrometers in Teflon-valved NMR tubes at room temperature. ^1H and ^{13}C chemical shifts are reported in ppm *vs.* $SiMe_4$ (0.00), as determined by reference to the residual solvent signals or using hexamethyldisiloxane (*vide infra*). Coupling constants are given in Hertz.

$^{13}C\{^1H\}$ NMR analyses of ethylene/1-octene copolymer samples were run in the research center of TotalEnergies OneTech Belgium on a AM-500 Bruker spectrometer equipped with a high temperature 10 mm cryoprobe using the following conditions: the sample was prepared by dissolving a sufficient amount of polymer in 1,2,4-trichlorobenzene (TCB, 99 %, spectroscopic grade) at 130 °C and periodic shaking up to homogenize the sample, followed by addition of C_6D_6 (spectroscopic grade) and a minor amount of hexamethyldisiloxane (HMDS, 99.5+ %) as internal standard (δ 2.03 ppm). To give an example, ca. 600 mg of polymer were dissolved in 2.0 mL of TCB, followed by addition of 0.5 mL of C_6D_6 and 2 to 3 drops of HMDS. The characteristic signals from the incorporated 1-octene sequences were assigned using the reported protocol.[3]

Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations.

DSC measurements were performed on a SETARAM Instrumentation DSC 131 differential scanning calorimeter, under a continuous flow of helium and using aluminum capsules, at a heating rate of 10 °C/min. First and second runs were recorded after cooling to 30 °C. The melting temperatures reported in tables correspond to the second run.

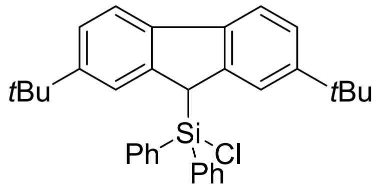
SEC analyses of ethylene/1-octene copolymer samples were carried out in TCB at 135 °C in the research center of TotalEnergies OneTech Belgium, using polystyrene standards for universal calibration.

The density of the polyolefin was measured according to the method of standard ISO 1183-1:2012 method A at a temperature of 23 °C (weight of displaced fluid (Buoyancy) at 23 °C in isopropanol).

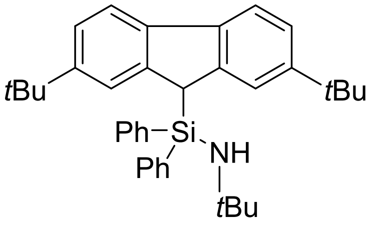
General polymerization procedure. Bench polymerization experiments (Table 2) were performed in a 100 mL high-pressure stainless-steel reactor equipped with a stirring bar and externally heated with a heating tile. The reactor was purged twice (vacuum-argon cycles) and charged with Isopar G, 1-octene and TIBAL. The system was thermally equilibrated at the desired temperature for minimum 1 h. Then, under argon, a mixture of catalyst precursor, coactivator (Turner's reagent, *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate) and trisisobutylaluminum (TIBAL) in toluene (ca. 2 mL) was added by syringe. The monomer pressure was increased to (35) bar (kept constant by means of a regulator) and the reaction mixture was stirred for 30 min. The polymerization was stopped by venting the reactor and quenching with methanol (ca. 1 mL). The polymer was precipitated from methanol (ca. 800 mL) and 35 wt% aqueous HCl (ca. 2 mL) was added to dissolve possible (co)catalyst residues. The polymer was separated by filtration, washed with methanol (ca. 200 mL) and dried under reduced pressure overnight at 60 °C in the oven.

Larger-scale ethylene-1-octene copolymerization experiments in the presence of H_2 (Table 3) were conducted in a 1 L high pressure stainless-steel, mechanically stirred reactor, following the above procedure.

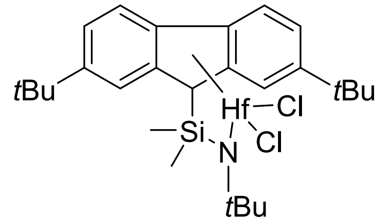
Synthesis and characterization of proligands and complexes



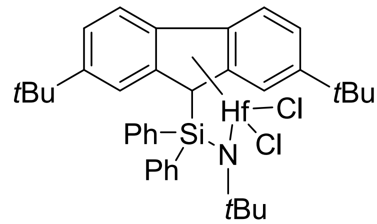
Intermediate b.[2] *n*BuLi (4.0 mL of a 2.5 M solution in hexane, 10.0 mmol, 1.1 equiv) was added dropwise at 0 °C to a solution of 2,7-di-*tert*-butyl-9*H*-fluorene (2.54 g, 9.12 mmol, 1.0 equiv) in diethyl ether (40 mL). The reaction mixture was stirred overnight. The solution of the lithium salt in diethyl ether was added at –78 °C to a solution of Ph_2SiCl_2 (2.65 mL, 12.77 mmol, 1.4 equiv) in diethyl ether (5 mL), and the suspension was stirred for 1 day at room temperature. The solution was filtrated to remove LiCl. After removal of the solvent in vacuum, additional washing of the solid residue with *n*-heptane (8 mL) and drying, **b** was obtained as an off-white solid (3.52 g, 78%). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 7.66 (d, *J* = 8.0, 3H, Haro), 7.52 (m, 2H), 7.44–7.40 (m, 4H, Haro), 7.34 (dd, *J* = 8.1, 1.4, 2H, Haro), 7.06–7.00 (m, 5H) (Flu and Ph), 4.50 (s, 1H, CH), 1.24 (s, 18H, *t*Bu).



Proligand 2.[2] An oven-dried Schlenk flask was cooled under vacuum and filled with argon. *tert*-Butylamine (0.74 mL, 7.0 mmol, 1.0 equiv) was transferred into the flask and dissolved in a 1:1 *v/v* mixture of *n*-heptane and diethyl ether (5 mL). The flask was cooled to –78 °C and *n*BuLi (2.9 mL of a 2.4 M solution in hexane, 7.0 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred at ca. –30 °C for 30 min. A white suspension formed. A solution of **b** (3.47 g, 7.0 mmol, 1.0 equiv) in diethyl ether (45 mL) was added dropwise via syringe over a period of 45 min at –30 °C. The reaction mixture was stirred at room temperature for 3 days. The solution was filtered from LiCl and evaporated under vacuum. The solid residue was washed with a minimal amount of heptane to give **2** as a white solid (2.79 g, 75%). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 7.60 (d, J = 8.0, 2H, Haro), 7.56 (dd, J = 7.5 and 1.8, 4H, Haro), 7.52 (br s, 2H, Haro), 7.34 (dd, J = 8.0 and 1.5, 2H, Haro), 7.21–7.17 (m, 3H, Haro), 7.14 (m, 3H, Haro), 4.36 (s, 1H, C*H*), 1.35 (s, 18H, *t*Bu), 1.08 (s, 9H, *t*Bu).

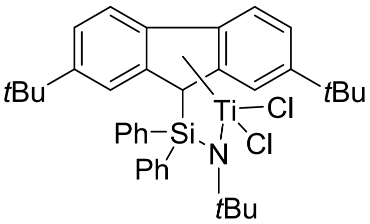


1-HfCl$_2$.[2] To a solution of proligand **1** (0.600 g, 1.48 mmol, 1.0 equiv) in Et$_2$O (15 mL) was added *n*BuLi (1.30 mL of a 2.5 M solution in hexanes, 3.18 mmol, 2.1 equiv) at –20 °C under stirring. After stirring overnight at room temperature, the solution was evaporated and anhydrous HfCl$_4$ (0.51 g, 1.59 mmol) was added to the residue. Diethyl ether (18 mL) was added to the flask at –78 °C, and the reaction mixture was stirred at room temperature for 3 days. The reaction mixture was evaporated to dryness and toluene (15 mL) was added. After filtration and evaporation, the solid residue was washed with *n*-heptane (6 mL) and dried in vacuum to give **1-HfCl$_2$** as a light-yellow solid (0.47 g, 48%). ^{1}H NMR (400 MHz, chloroform-d_3, 25 °C): δ 8.05 (d, J = 8.9, 2H, Flu), 7.83 (s, 2H, Flu), 7.53 (dd, J = 8.8, 1.6, 2H, Flu), 1.38 (s, 18H, *t*Bu), 1.25 (s, 9H, N*t*Bu), 0.99 (s, 6H, SiMe$_2$). ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6, 25 °C): δ 152.80, 135.95, 125.24, 123.86, 123.13, 120.74 (Flu), 74.6 (C-9, Flu), 55.14 (*C*(CH$_3$), *t*Bu), 35.34 (*C*(CH$_3$), *t*Bu), 33.89 (C(*C*H$_3$), *t*Bu), 31.04 (C(*C*H$_3$), *t*Bu), 6.22 (SiMe$_2$). Single crystals suitable for X-ray diffraction studies were grown from a benzene solution at room temperature.



2-HfCl$_2$. Using a protocol similar to that described above for the synthesis of **1-HfCl$_2$**, complex **2-HfCl$_2$** was prepared from proligand **2** (0.700 g, 1.32 mmol, 1.0 equiv), *n*BuLi (1.18 mL of a 2.4 M solution in hexanes, 2.84 mmol, 2.15 equiv) and HfCl$_4$ (0.43 g, 1.35 mmol, 1.0 equiv) and isolated as a light-orange solid (0.45 g, 44%). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 8.10 (br s, 4H, Haro), 7.80 (d, J = 8.8, 2H, Haro), 7.47 (s, 2H, Haro), 7.39 (d, J = 9.8, 2H, Haro), 7.33–7.25 (m, 6H, Haro) (Ph and Flu), 1.48

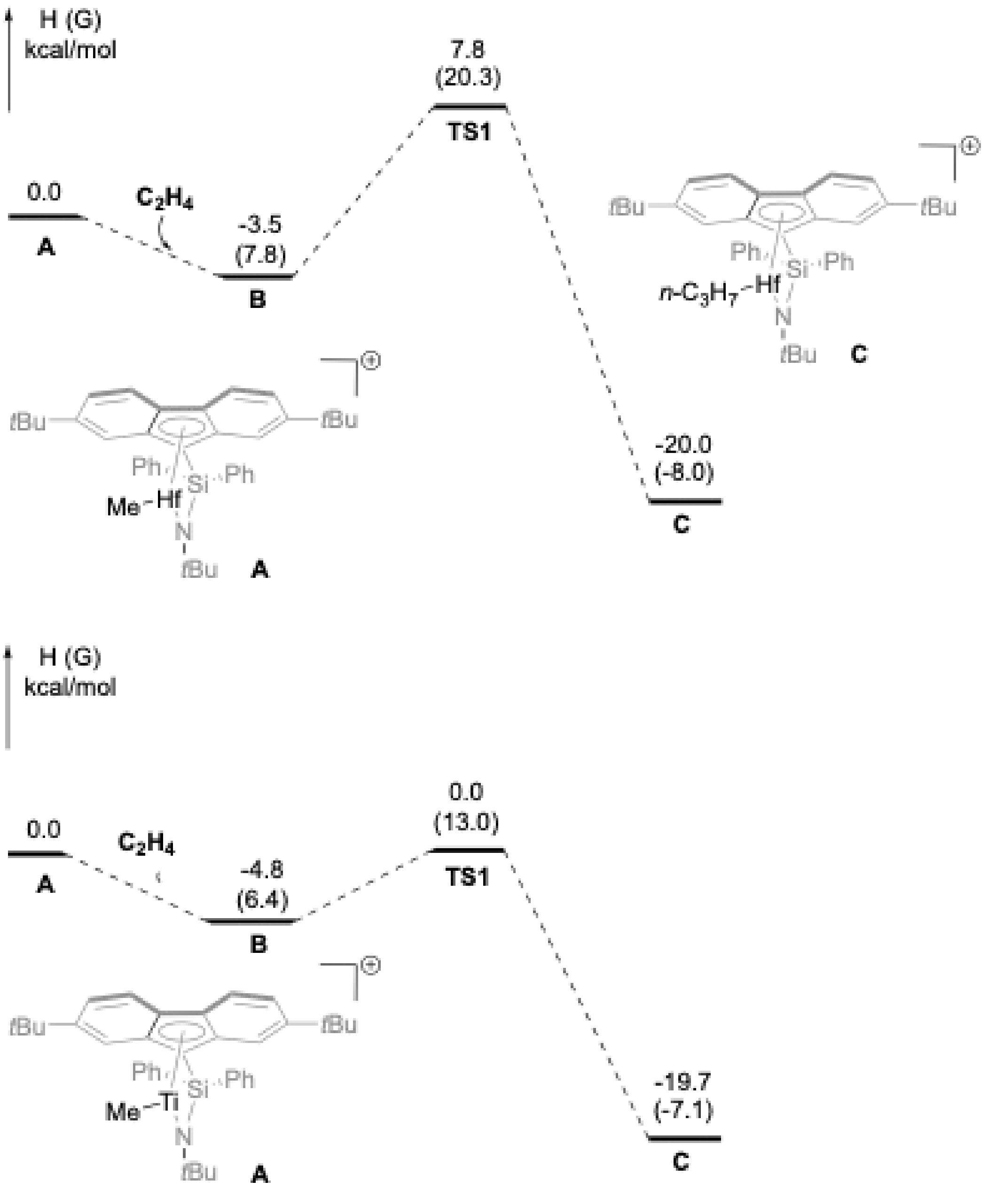
(s, 9H, *t*Bu), 1.17 (s, 18H, *t*Bu). $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 25 °C): δ 152.54, 137.36, 136.77, 135.67, 130.40, 128.49, 125.51, 123.61, 122.23 (Ph and Flu), 73.6 (C-9, Flu), 54.96 (*C*(CH$_3$), *t*Bu), 35.29 (*C*(CH$_3$), *t*Bu), 34.52 (C(*C*H$_3$), *t*Bu), 30.96 (C(*C*H$_3$), *t*Bu). Anal. Calcd for $C_{37}H_{43}NSiHfCl_2$: C, 57.03; H, 5.56; N, 1.80. Found: C, 56.89; H, 5.64; N, 1.71. Single crystals suitable for X-ray diffraction studies were grown from a benzene solution at room temperature.



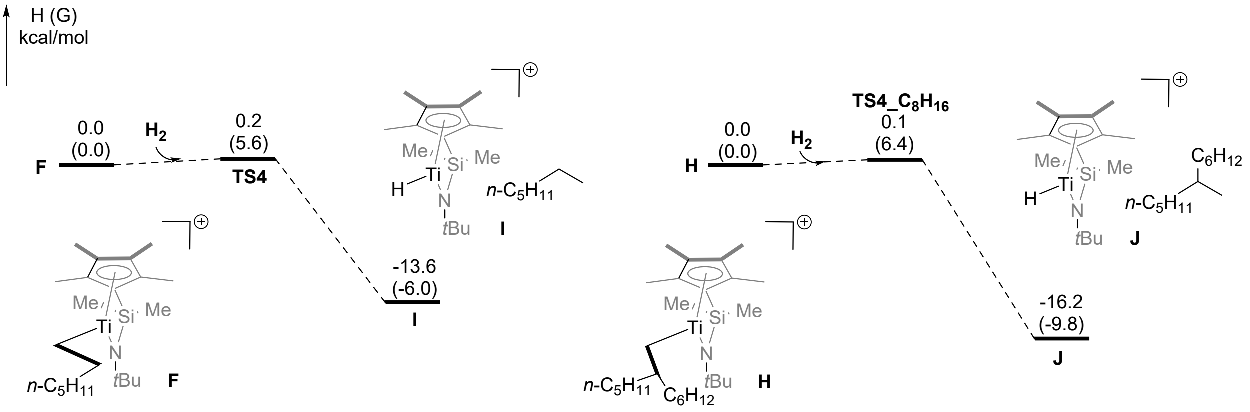
2-TiCl₂. To a solution of proligand **2** (1.11 g, 2.09 mmol) in Et$_2$O (40 mL) was added *n*BuLi (1.67 mL of a 2.5 M solution in hexanes, 4.17 mmol, 2.0 equiv) at −20 °C with stirring. After stirring for 2 days, the solvent was removed under reduced pressure and TiCl$_4$(THF)$_2$ (0.699 g, 2.11 mmol, 1.0 equiv) was added. *n*-Hexane (40 mL) was vacuum-transferred at −80 °C, and the reaction mixture, protected from light with aluminum foil, was stirred at room temperature for 4 days. The resulting solution was filtered to remove the precipitate, which was washed with *n*-heptane (10 mL). The combined filtrates were evaporated, and the resulting solid was dried to give **2-TiCl₂** as a dark violet powder (0.986 g, 77%). Recrystallization of this material from *n*-heptane (15 mL) afforded crystals of **2-TiCl₂** (0.080 g, 6%). ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 8.06 (m, 4H), 7.71 (d, $J = 9.4$, 2H), 7.51–7.47 (m, 4H), 7.29–7.24 (m, 6H) (Ph and Flu), 1.53 (s, 9H, *t*Bu), 1.16 (s, 18H, *t*Bu).$^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 25 °C): δ 152.63, 136.91, 135.82, 135.17, 131.11, 130.76, 128.60, 125.60, 123.76 (Ph and Flu), 94.1 (C-9, Flu), 61.85 (*C*(CH$_3$), *t*Bu), 35.27 (*C*(CH$_3$), *t*Bu), 33.24 (C(*C*H$_3$), *t*Bu), 30.83 (C(*C*H$_3$), *t*Bu). Anal. Calcd for $C_{37}H_{43}NSiTiCl_2$: C, 68.52; H, 6.68; N, 2.16. Found: C, 68.70; H, 6.72; N, 2.05. Single crystals of **2-TiCl₂** suitable for X-ray diffraction studies were grown from a benzene solution at room temperature.

Crystal structure determination of 1-HfCl₂, 2-HfCl₂ and 2-TiCl₂. Diffraction data were collected at 150 K with a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, [MoKα] radiation (λ = 0.71073 Å, multilayer monochromator). The structure was solved by dual-space algorithm using the SHELXT program,[4] and then refined with full-matrix least-squares methods based on F2 (SHELXL).[5] For **2-HfCl₂** and **2-TiCl₂**, the contribution of the disordered solvent molecules to the calculated structure factors was estimated following the BYPASS algorithm,[6] implemented as the SQUEEZE option in PLATON.[7] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. Crystal data and details of data collection and structure refinement for the different compounds are given in Table S1. Crystal data, details of data collection and structure refinement for all compounds (CCDC 2497781–2497783) can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details. All calculations were carried out with the Gaussian 09 suite of programs,[8] employing B3PW91[9,10] functional, and using a standard split valence basis set def2-SVP.[11] Solvation energies were evaluated by a self-consistent reaction field (SCRF) approach based on accurate numerical solutions of the Poisson-Boltzmann equation by using the SMD solvation model.[12] Toluene was used as solvent. All geometries were optimized without any symmetry restriction and the nature of the extrema was verified by analytical frequency calculations. The calculation of electronic energies and enthalpies of the extrema of the potential energy surface (minima and transition states) were performed at the same level of theory as the geometry optimizations. Enthalpy (or free enthalpy values for ion-pair reorganization) were obtained at T = 298 K within the harmonic approximation using the methos of Castro *et al.*[13] IRC calculations were performed to confirm the connections of the optimized transition states.



Scheme S1. Energy profile computed for the first ethylene coordination/insertion step for [{Ph$_2$Si(2,7-*t*Bu$_2$Flu)N*t*Bu}M−Me]$^+$ (**A**) (energies in kcal.mol^{-1} relative to **A**): (top) M = Hf; (bottom) M = Ti



Scheme S2. Energy profile computed for the transfer-to-hydrogen step for [{$Me_2Si(Me_4Cp)NtBu$}M−R]$^+$ (**3-TiCl$_3$**): (left) after ethylene insertion, R = *n*-C_7H_{15}; (right) after 1-octene insertion, R = *n*-$C_7H_{15}(2\text{-}C_6H_{12})$; energies in kcal.mol^{-1} relative to **F** and **H**, respectively.

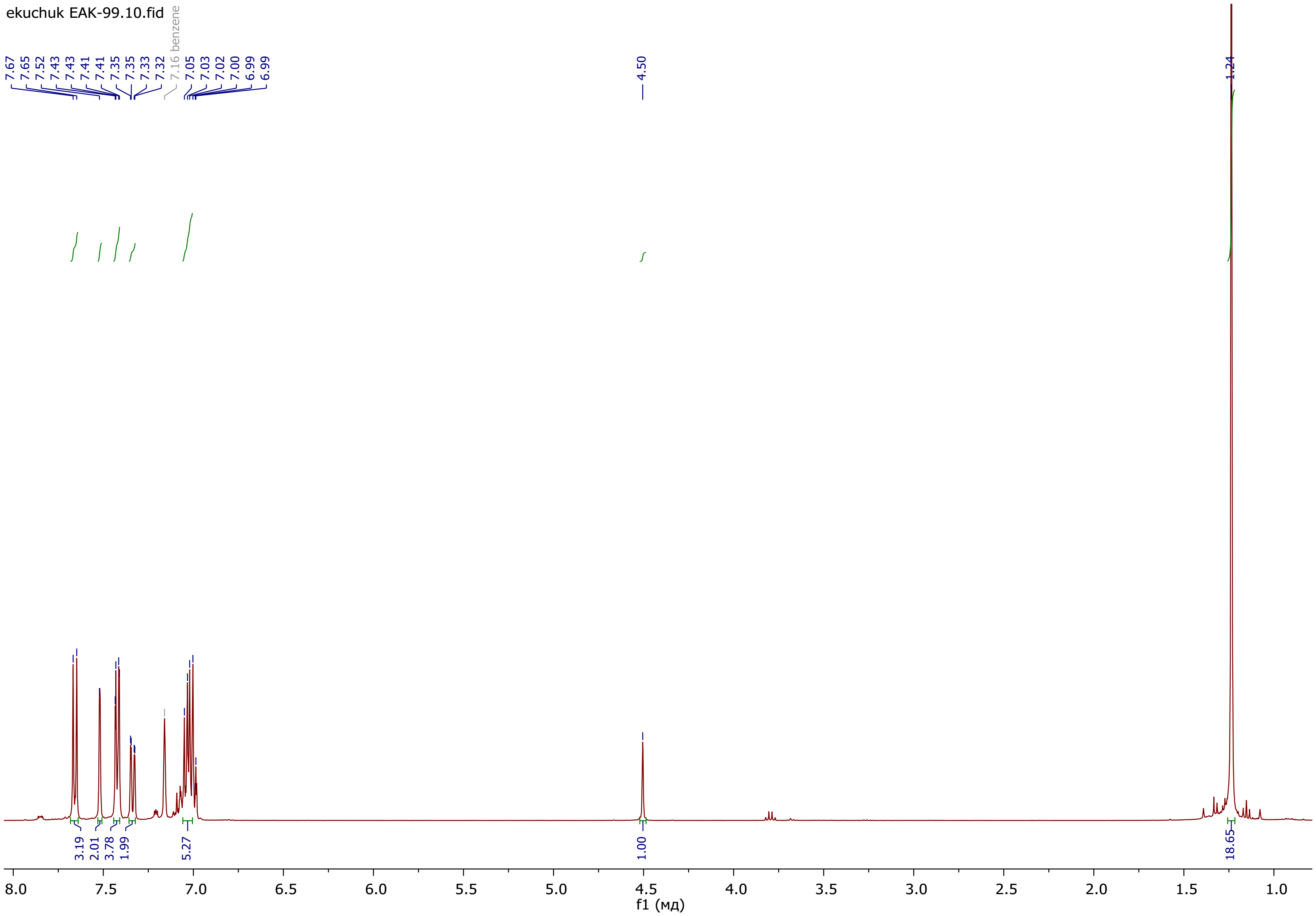


Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of precursor **b**.

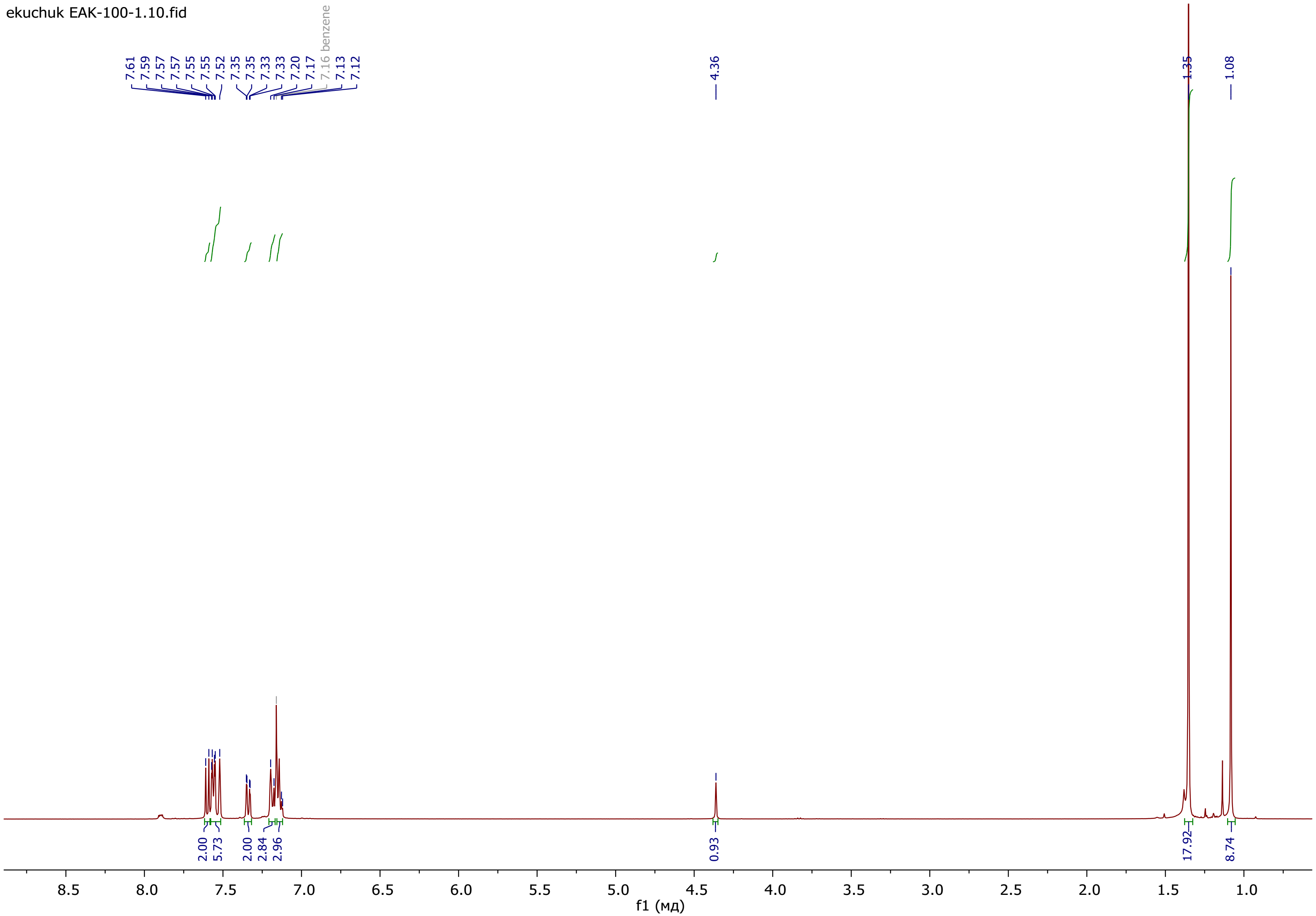


Figure S2. ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of proligand **2**.

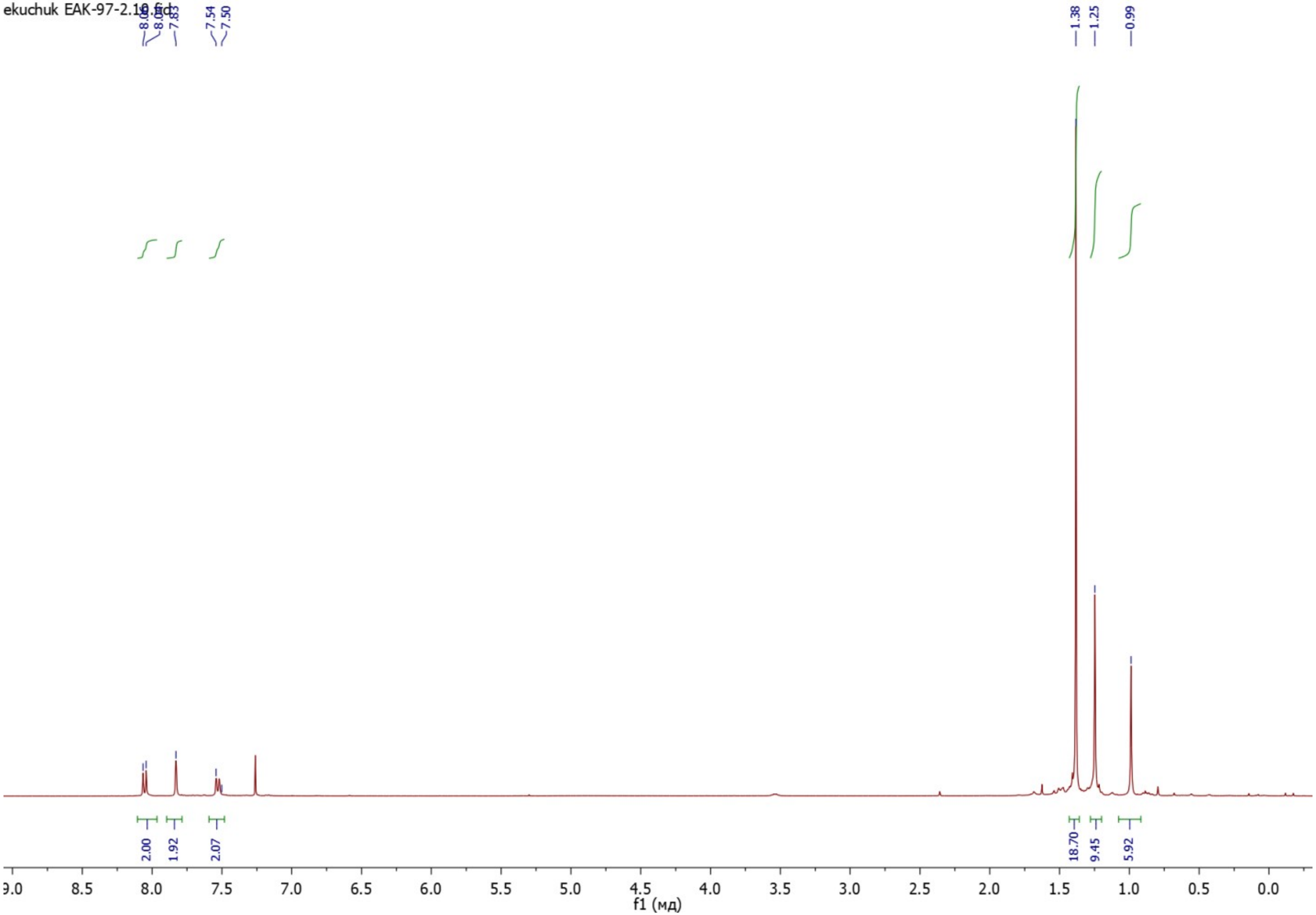


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of complex **1-HfCl$_2$**.

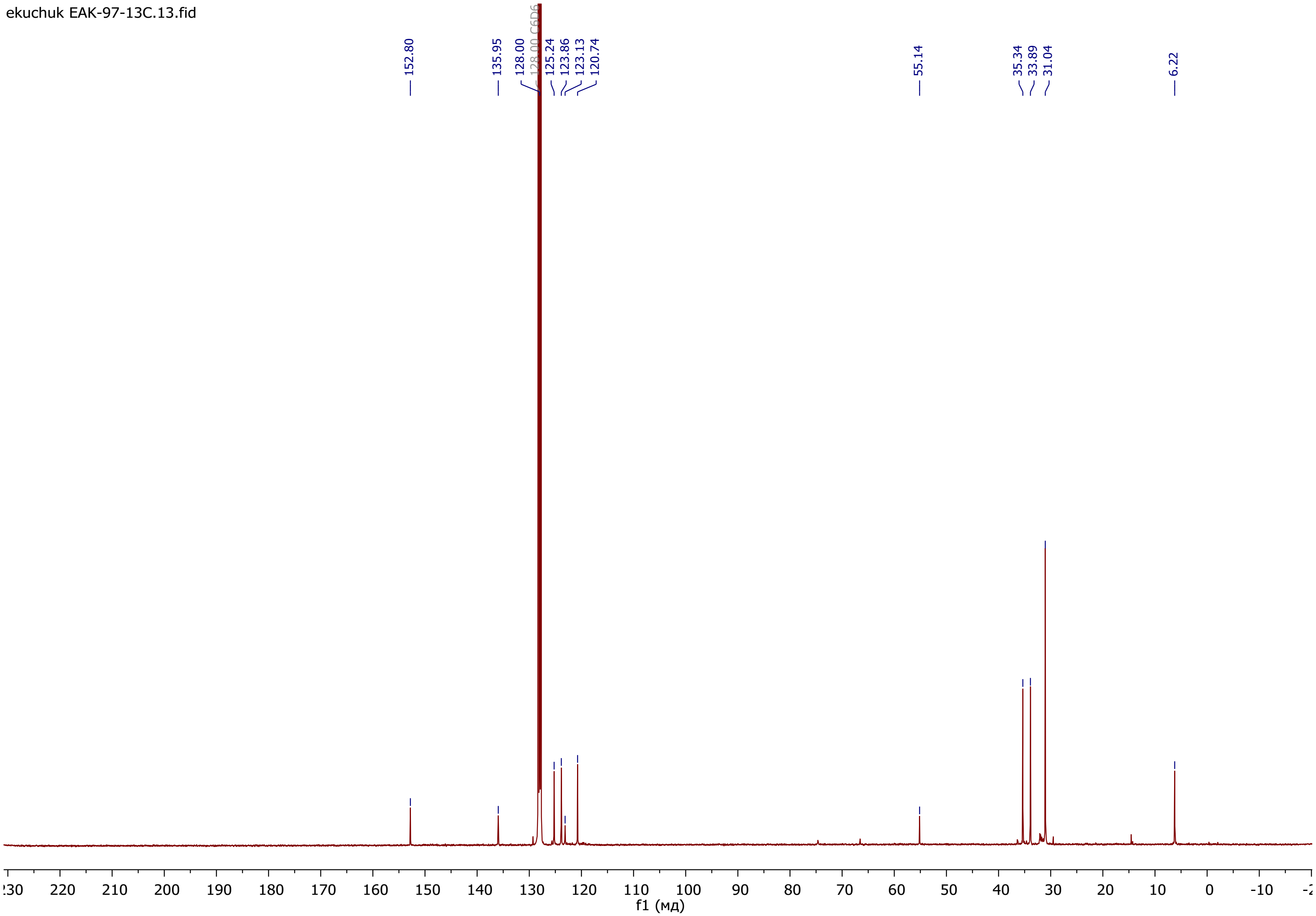


Figure S4. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6, 25 °C) of complex **1-HfCl$_2$**.

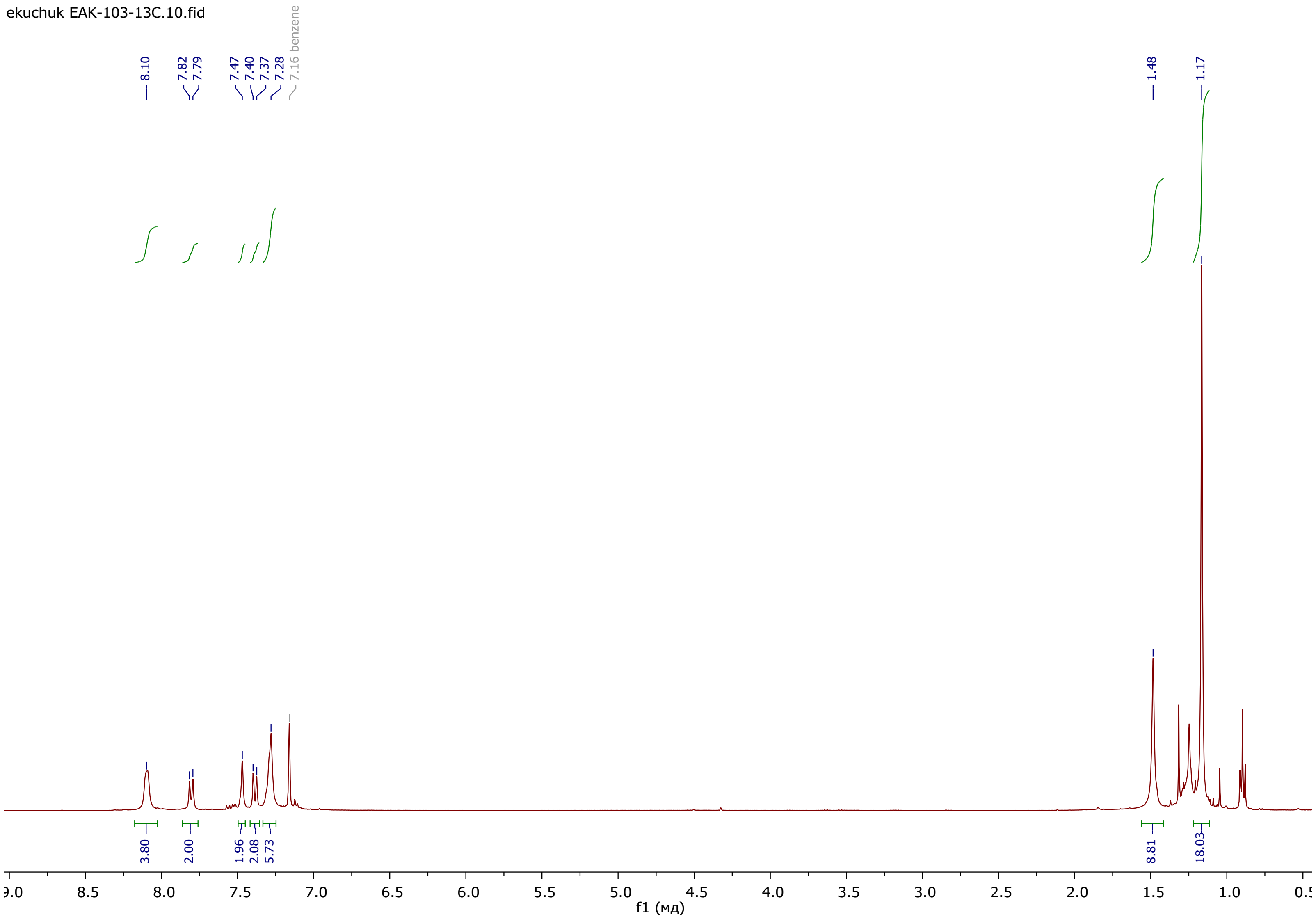


Figure S5. ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of complex **2-HfCl$_2$**.

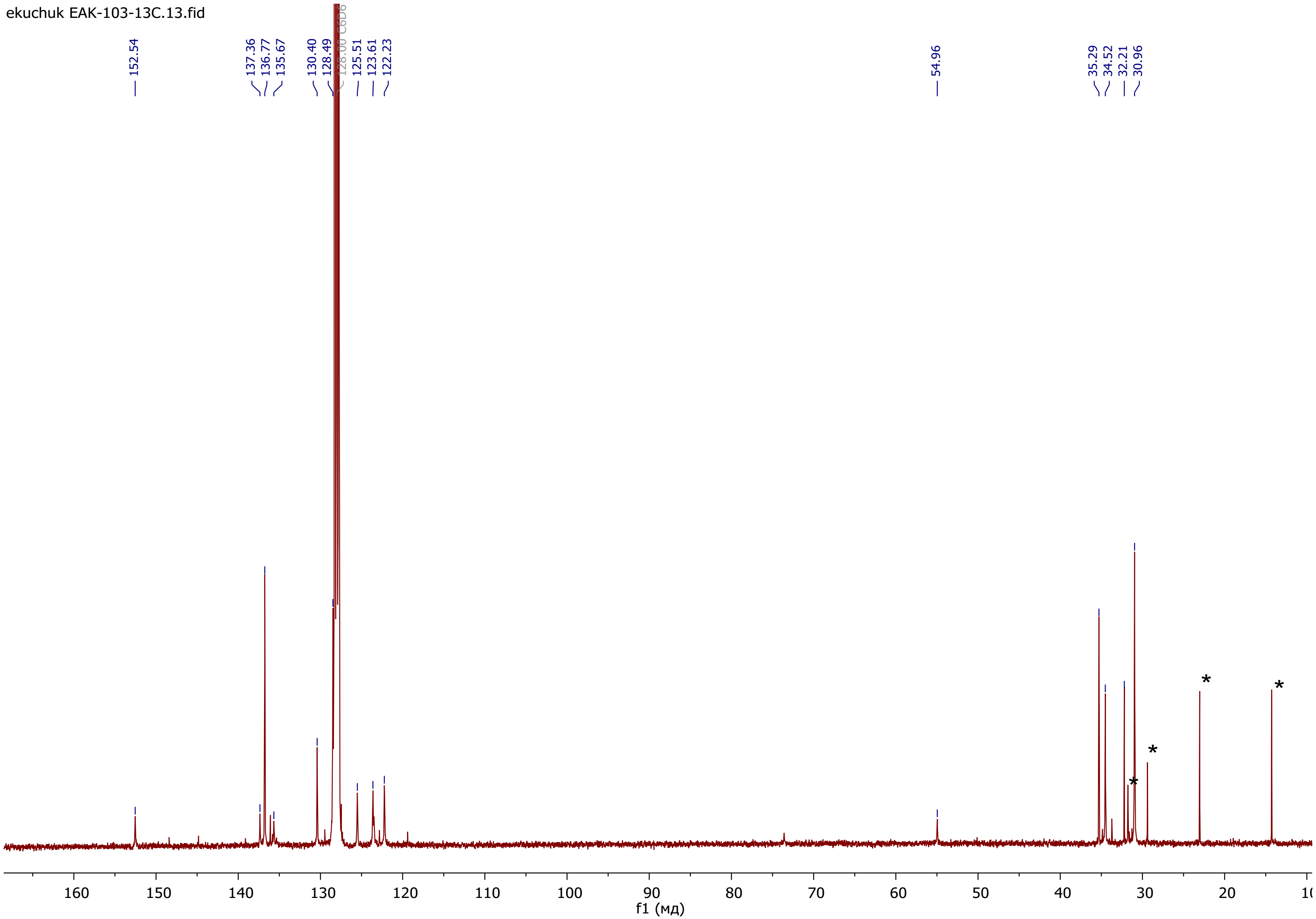


Figure S6. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6, 25 °C) of complex **2-HfCl$_2$**. *stands for residual signals of heptane

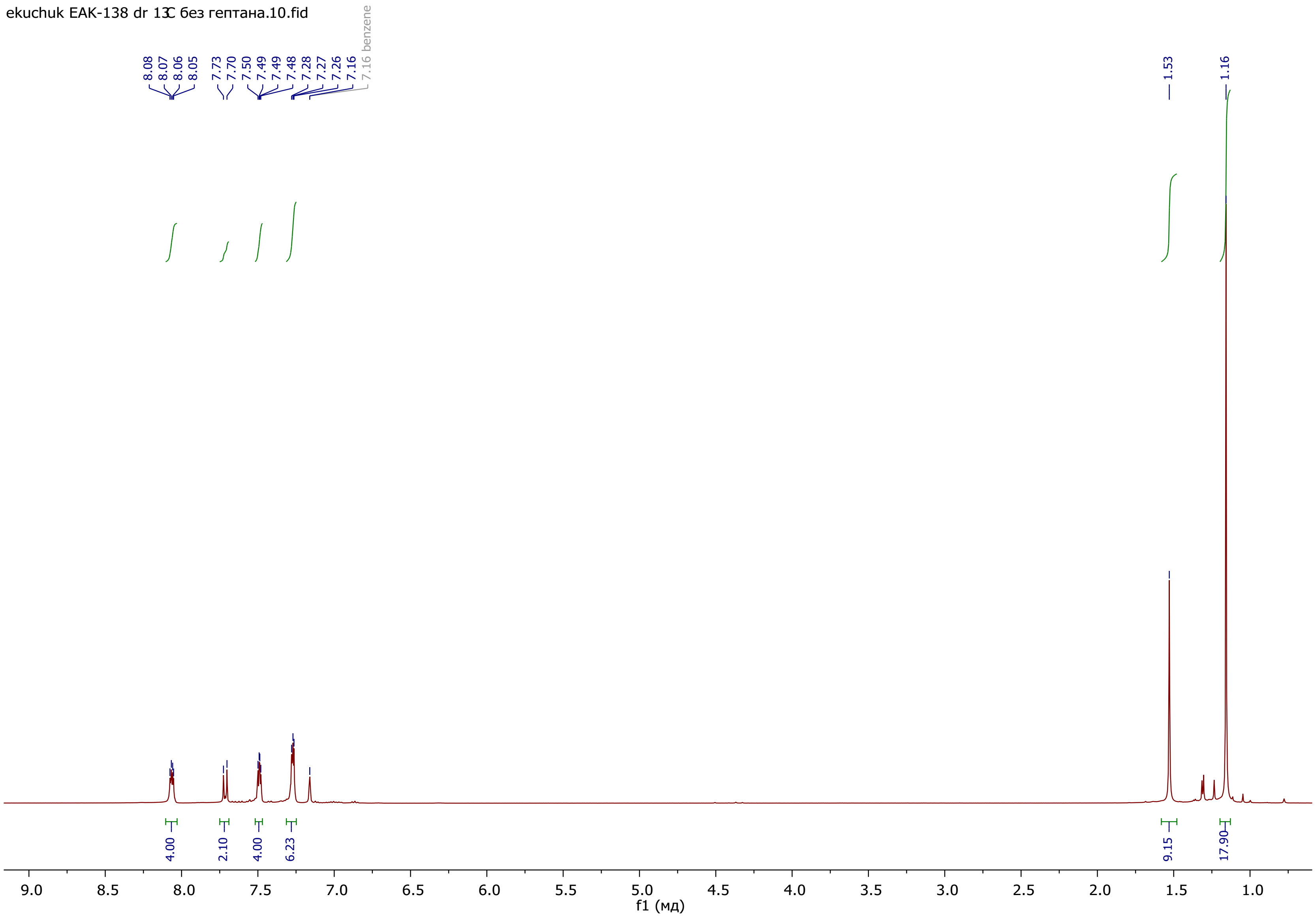


Figure S7. ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of complex **2-TiCl$_2$**.

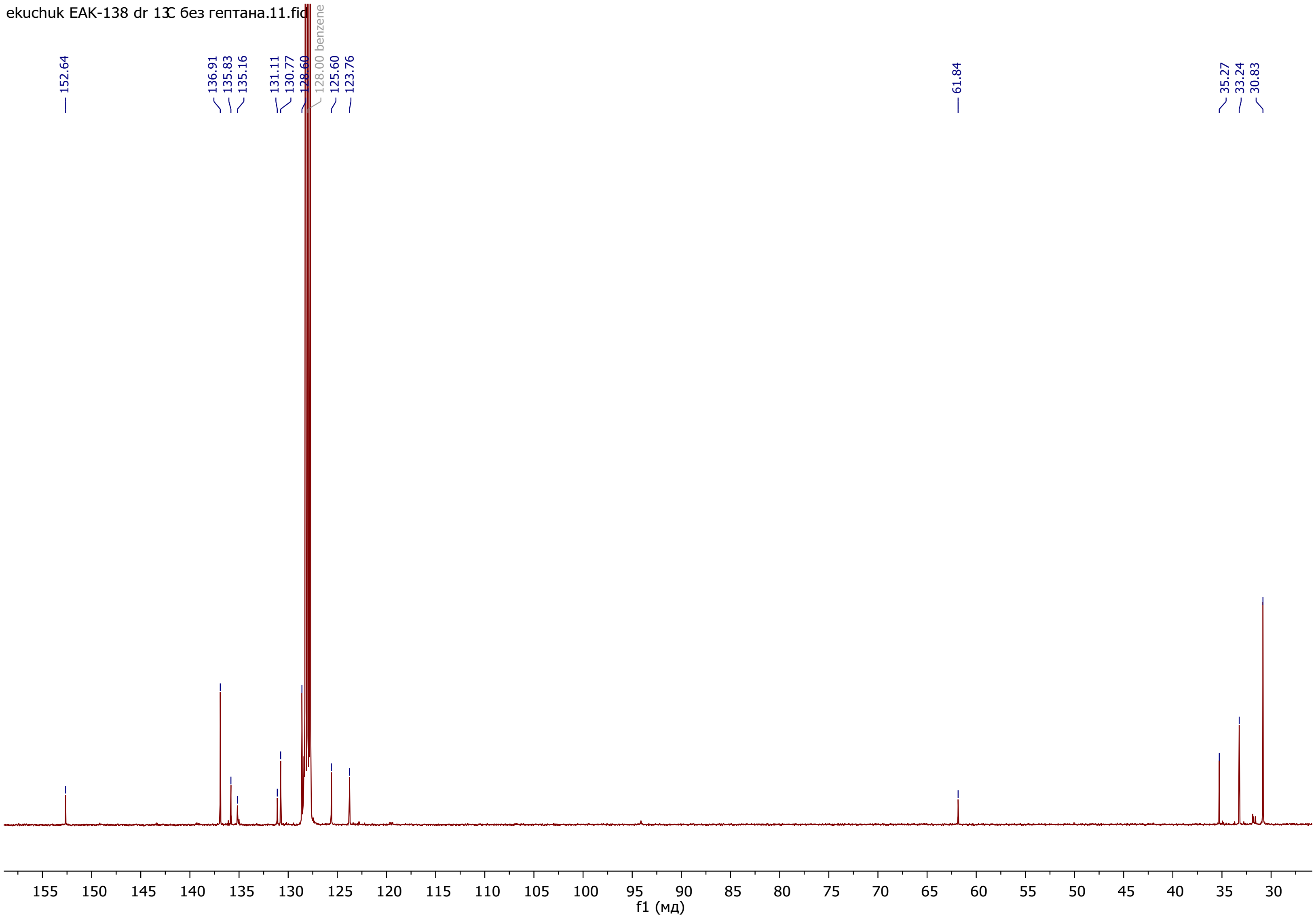


Figure S8. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6, 25 °C) of complex **2-TiCl$_2$**.

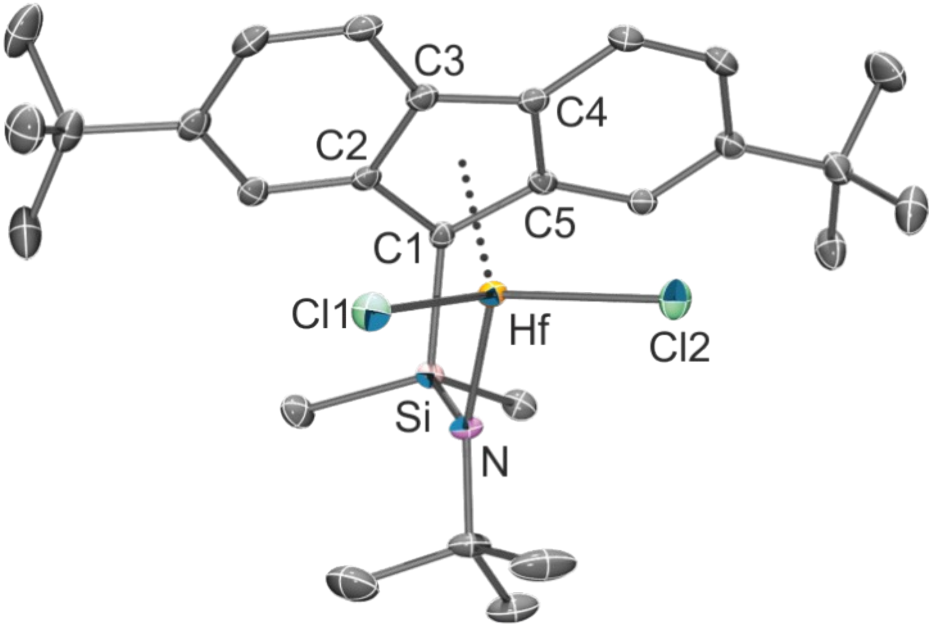


Figure S9. ORTEP representation of the solid-state molecular structure of **1-HfCl$_2$** (H atoms omitted for clarity; ellipsoids drawn at the 50% probability level).

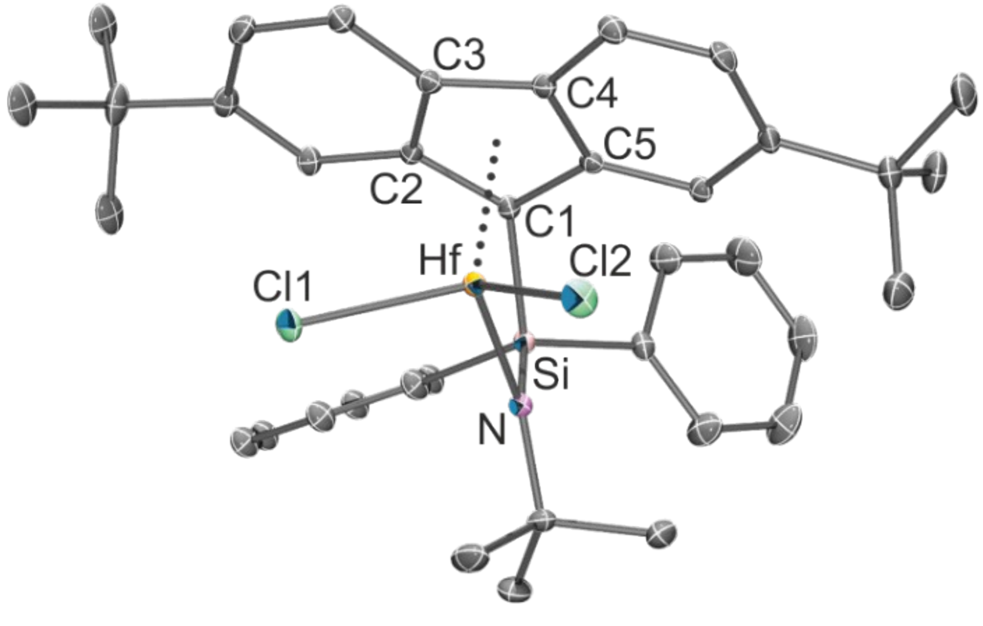


Figure S10. ORTEP representation of the solid-state molecular structure of **2-HfCl$_2$·(C$_6$H$_6$)** (H atoms omitted for clarity; ellipsoids drawn at the 50% probability level).

Table S1. Summary of Crystal and Refinement Data for Complexes **1-HfCl$_2$, 2-HfCl$_2$** and **2-TiCl$_2$·(C$_6$H$_6$).**

Complexes	**1-HfCl$_2$**	**2-HfCl$_2$·(C$_6$H$_6$)**	**2-TiCl$_2$·(C$_6$H$_6$)**
Empirical formula	$C_{27}H_{39}Cl_2HfNSi$	$C_{43}H_{49}Cl_2HfNSi$	$C_{37}H_{43}Cl_2NSiTi \cdot C_6H_6$
Formula weight	655.07	857.31	726.72
Temperature, K	150 (2)	150 (2)	150 (2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	P 2$_1$/c	P -1	P -1
a, Å	13.1859(14)	9.6214(10)	9.5821(9)
b, Å	20.6732(19)	10.8140(11)	10.7801(11)
c, Å	22.013(3)	19.814(2)	19.711(2)
β, deg	104.640(4)	85.156(4)	84.843(4)
Volume, Å^3	5805.8(11)	1959.9(3)	1935.6(3)
Z	8	2	2
Density (calc.), Mg/m^3	1.499	1.453	1.247
Absorption coefficient, mm^{-1}	3.833	2.858	0.421
Crystal size, mm^3	0.250 × 0.130 × 0.100	0.150 × 0.070 × 0.070	0.460 × 0.150 × 0.130
Reflections collected	64401/13220	30817/8940	30548/8844
Reflections [I>2σ]	11631	8353	7848
Max. and min. transmission	0.682; 0.557	0.819; 0.747	0.947; 0.879
Data / restraints / parameters	13220/0/599	8940/74/421	8844/0/475
Final R indices [I>2σ(I)]	0.0252	0.0209	0.0338
R indices (all data)	0.0316	0.0237	0.0397
Goodness-of-fit on F^2	1.100	1.035	1.039
Largest diff. peak, e.Å^{-3}	–0.520, 0.895	–0.836, 0.937	–0.352, 0.356

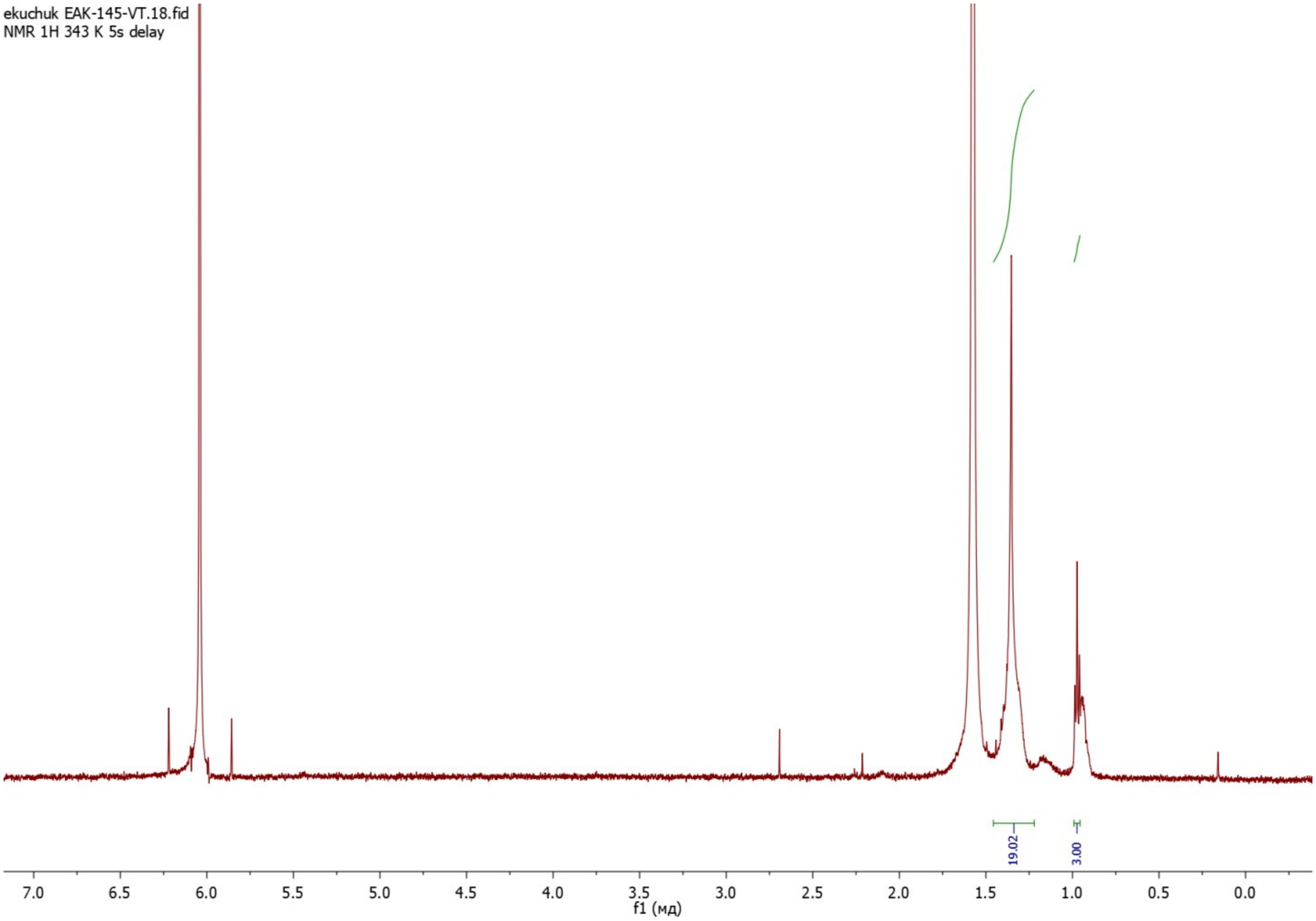


Figure S11. ^{1}H NMR spectrum (500 MHz, tetrachloroethane-d_2, 70 °C) of an ethylene/1-octene copolymer obtained with **2-TiCl$_2$** (Table 2, entry 10).

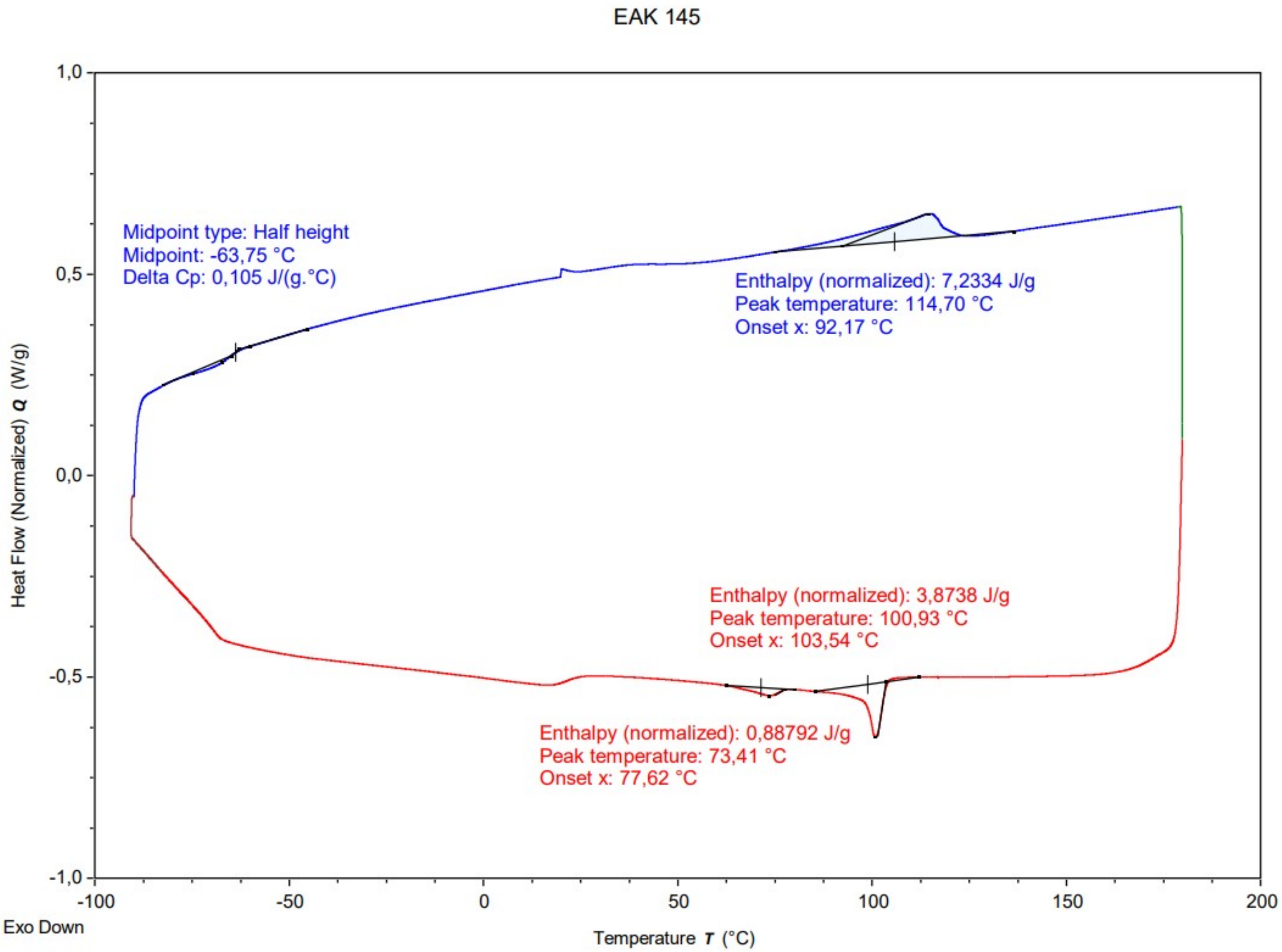


Figure S12. DSC trace for an ethylene/1-octene copolymer obtained with **2-TiCl$_2$** (Table 2, entry 10).

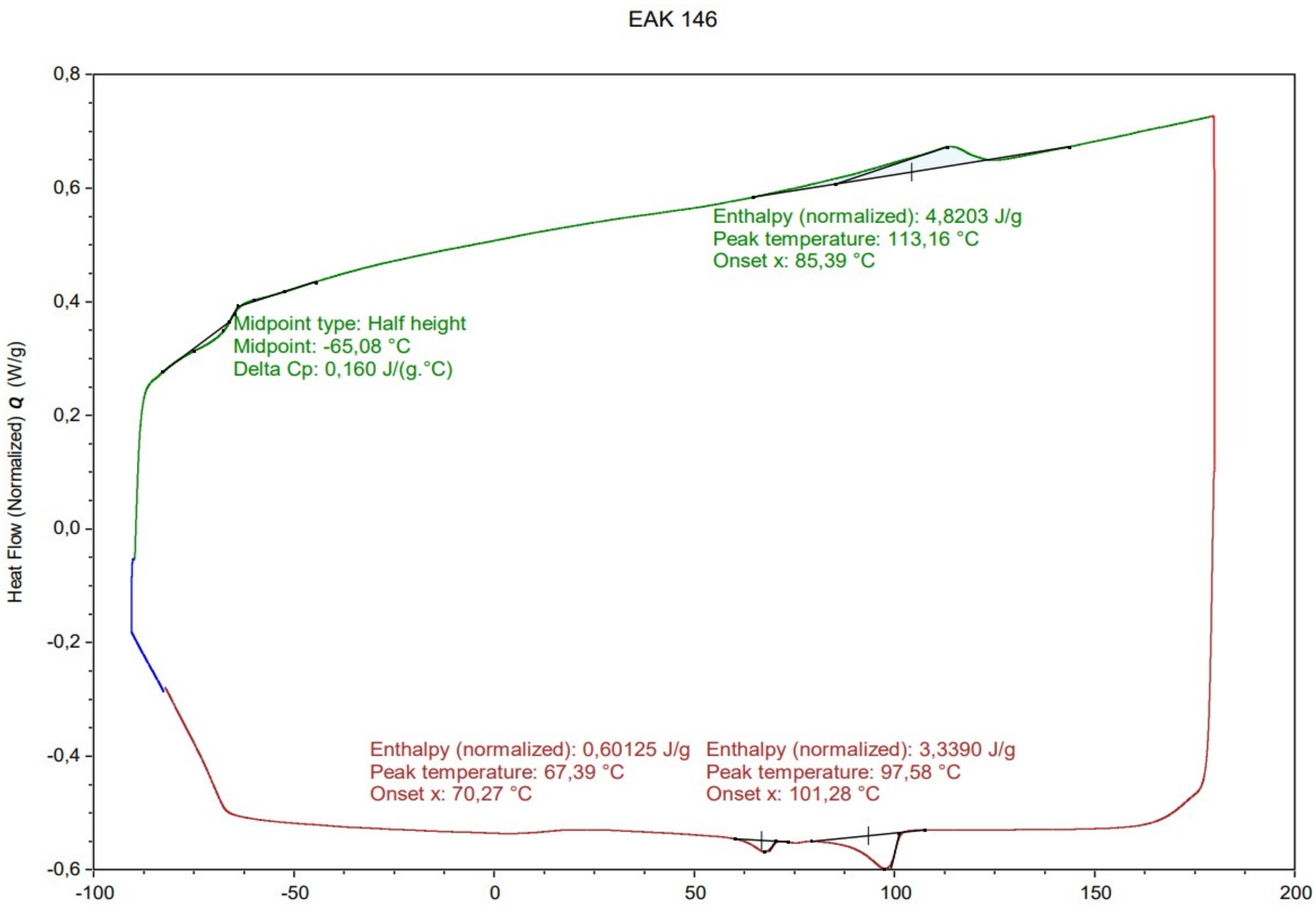


Figure S13. DSC trace for an ethylene/1-octene copolymer obtained with **2-TiCl$_2$** (Table 2, entry 8).

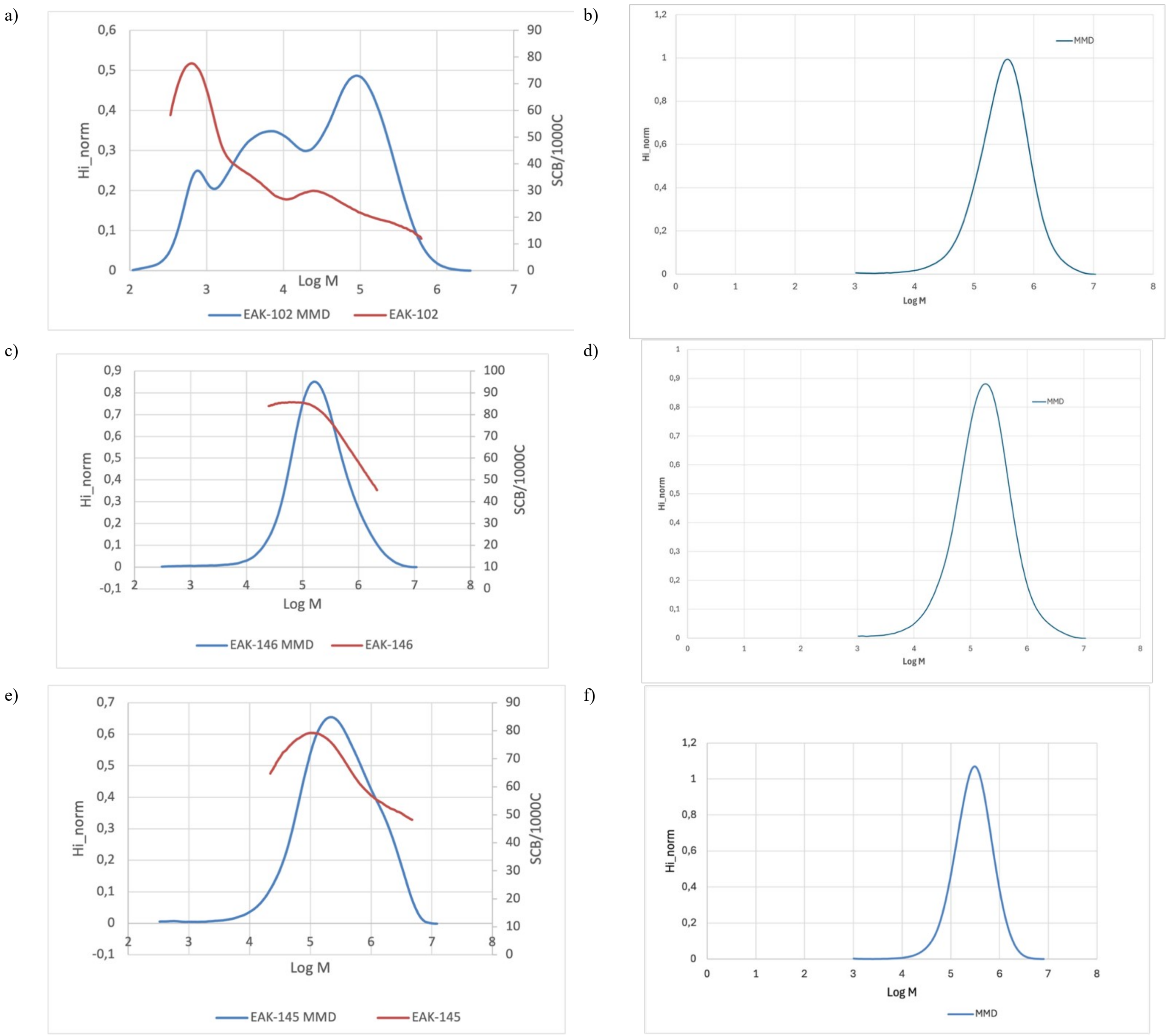


Figure S14. SEC traces for ethylene/1-octene copolymers obtained with **2-TiCl$_2$**: (a) Table 2, entry 3; (b) entry 7; (c) entry 8; (d) entry 9; (e) entry 10; (f) Table 3, entry 2.

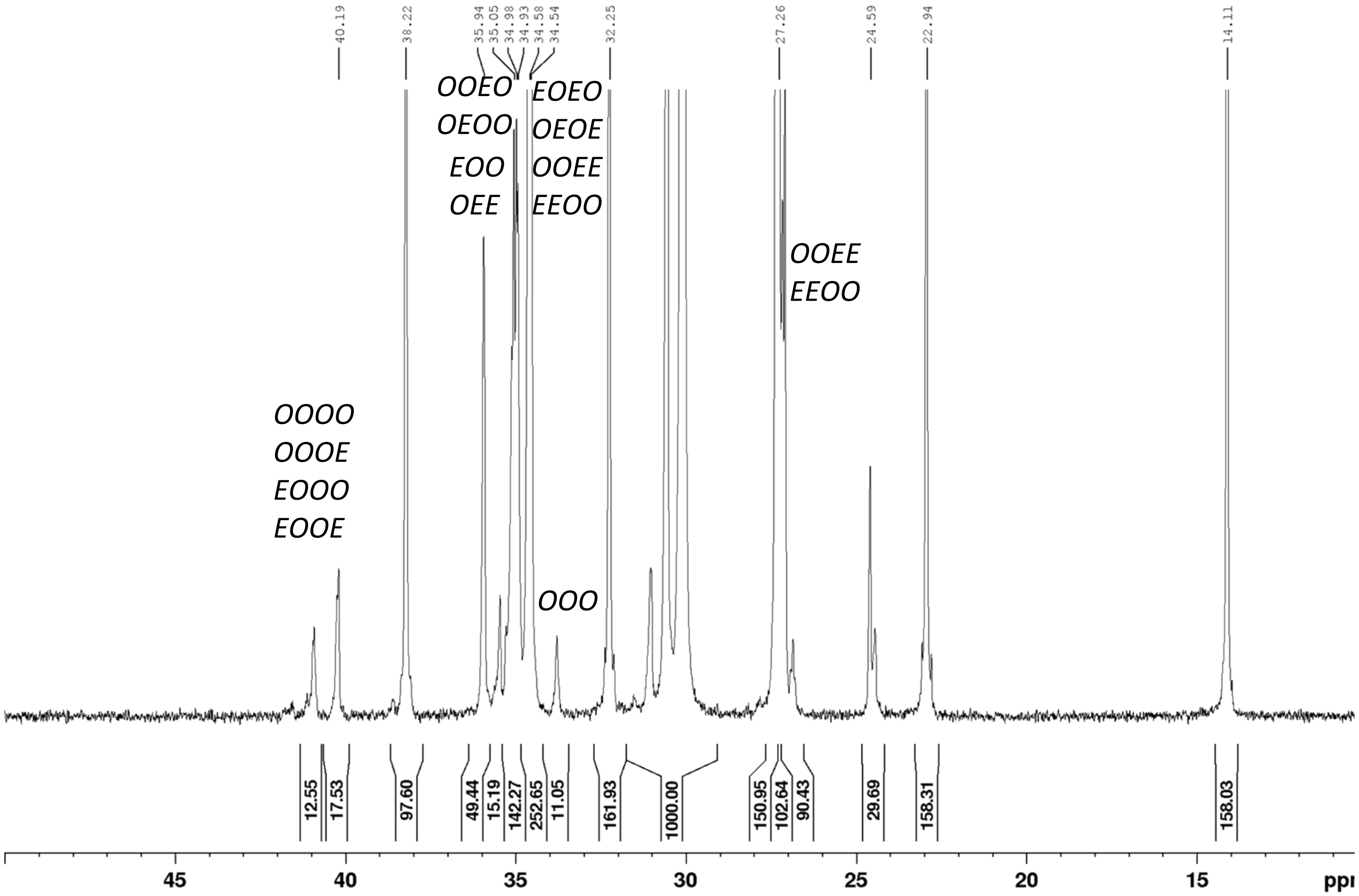


Figure S15. Aliphatic region of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 135 °C, C_6D_6/1,2,4-trichlorobenzene 1:9 *v/v*) of an ethylene-1-octene copolymer prepared with **2-TiCl$_2$** (Table 3, entry 2).

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