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In-depth ^{27}Al NMR investigation of $Al(C_6F_5)_3$ and its complexes with Lewis bases

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1. General information

All reagents were purchased from Acros, Aldrich or ABCR and used without further purification. Hexane, toluene, benzene were distilled over Na-benzophenone ketyl anion-radical and stored over 4Å Linde type molecular sieves. C_6D_6 was vacuum transferred from potassium metal and stored over 4Å Linde type molecular sieves in a high-quality glovebox (O_2, H_2O < 1 ppm) free of donor solvent vapors. All reactions outside a glovebox were carried out under argon atmosphere using standard Schlenk technique. ^{1}H, ^{19}F, ^{13}C, ^{31}P, ^{27}Al NMR were recorded on Bruker AVANCE III HD 300 spectrometer (300.1, 282.4, 75.5, 121.5, 78.2 MHz, respectively) in dry C_6D_6. Chemical shifts in C_6D_6 were measured relative to residual C_6D_5H (δ = 7.16 ppm) for ^{1}H or C_6D_6 (δ = 128.06 ppm) for ^{13}C. Chemical shifts for ^{19}F are relative to external $CFCl_3$ in $CDCl_3$ sample (δ = 0 ppm).

2. Experimental procedures

2.1. Synthesis of $Al(C_6F_5)_3 \cdot 0.5$toluene

Published procedure of E. Y.-X. Chen *et al*. (S. Feng, G. R. Roof and E. Y.-X. Chen, *Organometallics*, 2002, **21**, 832–839) was used. In a high-quality glovebox (O_2, H_2O < 1 ppm) free of donor solvent vapors, a Schlenk tube was charged with $B(C_6F_5)_3$ (491 mg, 0.96 mmol), sealed with glass stopper, and removed outside the glovebox. On a Schlenk line, absolute toluene (1.0 mL) and absolute *n*-hexane (3.0 mL) were added. To the resulted suspension, a 2.0 M solution of $AlMe_3$ in *n*-hexane (0.48 mL, 0.96 mmol) was added dropwise. During $AlMe_3$ addition all solids gradually dissolved. The obtained solution was left without stirring while being opened to an argon line. White crystalline solids precipitated out in 2–3 hours. After that the Schlenk tube was placed to a freezer (–18°C) and left there overnight, then connected to a Schlenk line, and the mother liquor was decanted by Pasteur pipette. The residual solids were washed with absolute *n*-hexane 3 times, dried under high vacuum, and transferred to a glovebox. Product $Al(C_6F_5)_3 \cdot 0.5$toluene was obtained as a white crystalline solid (325 mg, 64% yield).

^{1}H NMR (300.1 MHz, C_6D_6) δ: 7.16–7.10 (m, ca. 2H), 7.09–7.03 (m, ca. 1H), 7.03–6.97 (m, ca. 1H) (a mixture of partially deuterated toluenes), 2.10 (s, 3H, CH_3). **^{19}F NMR (282.4 MHz, C_6D_6) δ:** –122.8 to –123.1 (m, 2F), –150.8 (tt, *J* = 20.2, 3.0 Hz, 1F), –160.5 to –160.8 (m, 2F). **$^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6) δ:** 151.8–147.8 (m, CF in C_6F_5), 144.4–140.3 (m, CF in C_6F_5), 138.4–138.0 (m, C in partially deuterated toluenes), 139.3–135.1 (m, CF in C_6F_5), 129.7–129.3 (m, CH/CD in partially deuterated toluenes), 128.9–128.5 (m, CH/CD in partially deuterated toluenes, overlapped with C_6D_6), 125.6–125.1 (m, CH/CD in partially deuterated

toluenes), 111.5 (br. t, J = 45 Hz, Al-*C*), 21.5–21.1 (m, CH_3 in partially deuterated toluenes). **^{27}Al NMR (78.2 MHz, C_6D_6) δ:** 134±2 ($W_{1/2}$ 12 kHz).

2.2. NMR investigations of $Al(C_6F_5)_3$·complexes with Lewis bases

2.2.1. Preparation of $Al(C_6F_5)_3$·complexes

In a high-quality glovebox (O_2, H_2O < 1 ppm) free of donor solvent vapors, NMR tube was charged with $Al(C_6F_5)_3$ (20–25 mg), dissolved in absolute C_6D_6 (0.50 mL) and sealed with septum. Outside the glovebox, appropriate Lewis base (3 equiv. of pyridine, 2,6-lutidine, $P(OEt)_3$, MeCN, Me_2S or 30 equiv. of THF) was added *via* microsyringe.

2.2.2. High-quality ^{27}Al NMR spectra acquisition and processing

High-quality ^{27}Al NMR spectra were recorded on "Bruker AVANCE III HD 300 MHz" spectrometer (^{27}Al, 78.2 MHz), and "Bruker AVANCE III WB 400 MHz" spectrometers (^{27}Al, 104.3 MHz), equipped with solid-state 1 kW AVANCE III electronic unit with high-speed response (<0.1 μsec) for the possibility of recording wideline signals >10–20 kHz with extremely short T_2 relaxation times to avoid signal loss in solution. ^{27}Al chemical shift scale sets by Bruker instrument automatically using ^{2}H lock channel (or the field was set manually using the same ^{1}H solvent signal) with compensation of magnetic susceptibility for different samples, normalized to external aluminum aqua cation water solution standard ($[Al(H_2O)_6]^{3+}$, 0 ppm). ^{27}Al spectra were recorded using single-pulse sequence, with a dwell time of not more than 1.0–1.5 μsec (corresponding to the spectral width ~4000–4500 ppm or ~350–450 kHz), with long acquisition time (typical 0.8 sec) and long recycle delay (typical 0.7 sec) to get the clearest signal without any losses, including for narrow signals of high-symmetrical aluminum and aluminum glass signal with slow T_1 relaxation in solid state. Typical T_2 relaxation times (equivalent to FID length) of studied aluminum samples in solution are very short (0.2–1.0 msec), while T_1 relaxation times can be much longer, especially for solid state aluminum signal from glass. T_1 relaxation times can reach more than 200-300 msec, and therefore require long delays in the sum of more than a 1 sec in order to avoid signal losses during the accumulation process. Correct accumulation of the solid-state glass signal is very important for further processing of the spectra and for obtaining the final clear difference spectra. Since aluminum ^{27}Al has a very good sensitivity in NMR, typical summary recording time of ^{27}Al spectra is from 4.5 min (176 scans) to 33 min (1280 scans), which is sufficient to obtain a clear signal from ~10 mg (or more) of the aluminum complex in 0.6 mL solution. If necessary, the recording time can be increased for more complex cases. The signal width of the target ^{27}Al signals ~10–20 kHz does not require high power radiofrequency field, so

standard hard 90° ^{27}Al pulses of 8–12 μsec long (30–50 W) were used. Further processing of the spectra involves subtracting the glass spectrum from the raw data of the sample to obtain difference aluminum ^{27}Al spectra containing a pure target ^{27}Al signal, and this can be done both with the direct FID processing and with the processed spectra after the Fourier transform (the result will be identical), using the standard Bruker Topspin software (usually 3 and 4 versions). The required subtraction accuracy and the quality of signal acquisition from the glass depend on the intensity and width of the aluminum ^{27}Al target signal. However, it is very important to take into account that in many cases, in order to obtain a pure aluminum ^{27}Al signal from the target complex, which does not contain any perturbations from the glass, all manipulations should be carried out with high accuracy. So, both ^{27}Al raw data sets for processing (sample and glass without sample) should be received from exactly the same NMR tube under exactly the same acquisition parameters, with very precise setting of shimming to compensate for magnetic inhomogeneity, temperature control, compensation of magnetic susceptibility of the sample, and chemical shift scale calibration, that in sum afforded a very good and clear spectrum. Ideally, the same solvent should be used for both target sample and blank glass sample. Determination of chemical shift and signal width ($W_{1/2}$) has some peculiarities compared to usual NMR, the most correct chemical shift and width parameters of the recorded signal will be obtained by line shape simulation that could be easily performed using standard TopSpin software package ("solid line shape analysis" program package ("SOLA") in Bruker TopSpin software, usually 3 and 4 versions), using "Gauss/Lorentz" model for simulation. Other details and a detailed description of the ^{27}Al approach can be also found in the main text of the article.

2.2.3. NMR data of Al(C$_6$F$_5$)$_3$·complexes

Al(C$_6$F$_5$)$_3$·Pyridine complex

^{1}H NMR (300.1 MHz, C$_6$D$_6$) δ: 8.43 (dt, *J* = 4.6, 1.7 Hz, 1H, CH in Pyridine), 6.98 (tt, *J* = 7.9, 1.8 Hz, 1H, CH in Pyridine), 6.65 (ddd, *J* = 7.6, 4.5, 1.5 Hz, 1H, CH in Pyridine), 2.12 (s, 3H, CH_3 in partially deuterated toluenes) *[Coordinated and non-coordinated pyridines are in a fast exchange and give one set of signals]*. **^{19}F NMR (282.4 MHz, C$_6$D$_6$) δ:** –121.7 to –121.9 (m, 2F), –151.6 (tt, *J* = 20.0, 2.7 Hz, 1F), –160.8 to –161.1 (m, 2F). **^{13}C{^{1}H} NMR (75.4 MHz, C$_6$D$_6$) δ:** 152.8–148.9 (m, CF in C_6F_5), 149.8 (s, CH in Pyridine), 144.8–140.7 (m, CF in C_6F_5), 139.8–135.7 (m, CF in C_6F_5), 137.6 (s, CH in Pyridine), 124.5 (s, CH in Pyridine), 114.4–112.6 (m, Al-*C*), 21.8–21.5 (m, CH_3 in partially deuterated toluenes), (C,CH/CD in partially deuterated toluenes are overlapped with the other signals) *[Coordinated and non-coordinated*

pyridines are in a fast exchange and give one set of signals]. **^{27}Al NMR (78.2 MHz, C_6D_6) δ:** 127±1 ($W_{1/2}$ 4.0 kHz).

$Al(C_6F_5)_3$·2,6-Lutidine complex

^{1}H NMR (300.1 MHz, C_6D_6) δ: 7.14–7.09 (m, partially deuterated toluenes, overlapped with the other signals), 7.07–6.98 (m, 1H, free Lutidine), 6.73–6.64 (m, 1H, coordinated Lutidine), 6.61–6.55 (m, 2H, free Lutidine), 6.21–6.14 (m, 2H, coordinated Lutidine), 2.41 (s, 3H, CH_3 in free Lutidine), 2.25 (s, 3H, CH_3 in coordinated Lutidine), 2.12 (s, 3H, CH_3 in partially deuterated toluenes). **^{19}F NMR (282.4 MHz, C_6D_6) δ:** –122.6 to –122.9 (m, 2F), –152.1 to –152.6 (m, 1F), –160.7 to –161.2 (m, 2F). **^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6) δ:** 160.2 (s, C in Lutidine), 158.0 (s, C in Lutidine), 151.9–147.9 (m, CF in C_6F_5), 144.1–140.0 (m, CF in C_6F_5), 142.1 (s, CH in coordinated Lutidine), 139.5–135.3 (m, CF in C_6F_5), 136.1 (s, CH in free Lutidine), 129.3 (s, CH in toluene), 128.6 (s, CH in toluene), 125.7 (s, CH in toluene), 125.4 (s, CH in free Lutidine), 119.9 (s, Ch in coordinated Lutidine), 24.5 (s, CH_3 in free Lutidine), 24.2 (s, CH_3 in coordinated Lutidine), 21.4 (s, CH_3 in partially deuterated toluenes) (Al-C missed due to low intensity). **^{27}Al NMR (78.2 MHz, C_6D_6) δ:** 117±1 ($W_{1/2}$ 3.6 kHz).

$Al(C_6F_5)_3$·MeCN complex

^{1}H NMR (300.1 MHz, C_6D_6) δ: 7.13– .08 (m, CH in partially deuterated toluene), 7.07–6.97 (m, CH in partially deuterated toluene), 2.11 (s, 3H, CH_3 in partially deuterated toluenes), 0.56–0.49 (m, 3H, CH_3CN, mixture of coordinated and free). **^{19}F NMR (282.4 MHz, C_6D_6) δ:** –123.2 to –123.6 (m, 2F), –152.9 to –153.6 (m), 1F, –161.4 to –162.1 (m, 2F). **^{27}Al NMR (78.2 MHz, C_6D_6) δ:** 86±5 ($W_{1/2}$ 12 kHz).

$Al(C_6F_5)_3$·THF complex

^{1}H NMR (300.1 MHz, C_6D_6) δ: 7.14–7.06 (m, CH in partially deuterated toluene), 7.06–6.96 (m, CH in partially deuterated toluene), 3.59–3.49 (m, 4H, THF), 2.11 (s, 3H, CH_3 in partially deuterated toluenes), 1.50–1.39 (m, 4H, THF) *[Coordinated and non-coordinated THF are in a fast exchange and give one set of signals]*. **^{19}F NMR (282.4 MHz, C_6D_6) δ:** –122.8 to –123.1 (m, 2F), –151.9 (t, J = 19.5 Hz, 1F), –161.1 to –161.4 (m, 2F). **^{27}Al NMR (78.2 MHz, C_6D_6) δ:** 129±2 ($W_{1/2}$ 4.5 kHz).

$Al(C_6F_5)_3 \cdot Me_2S$ complex

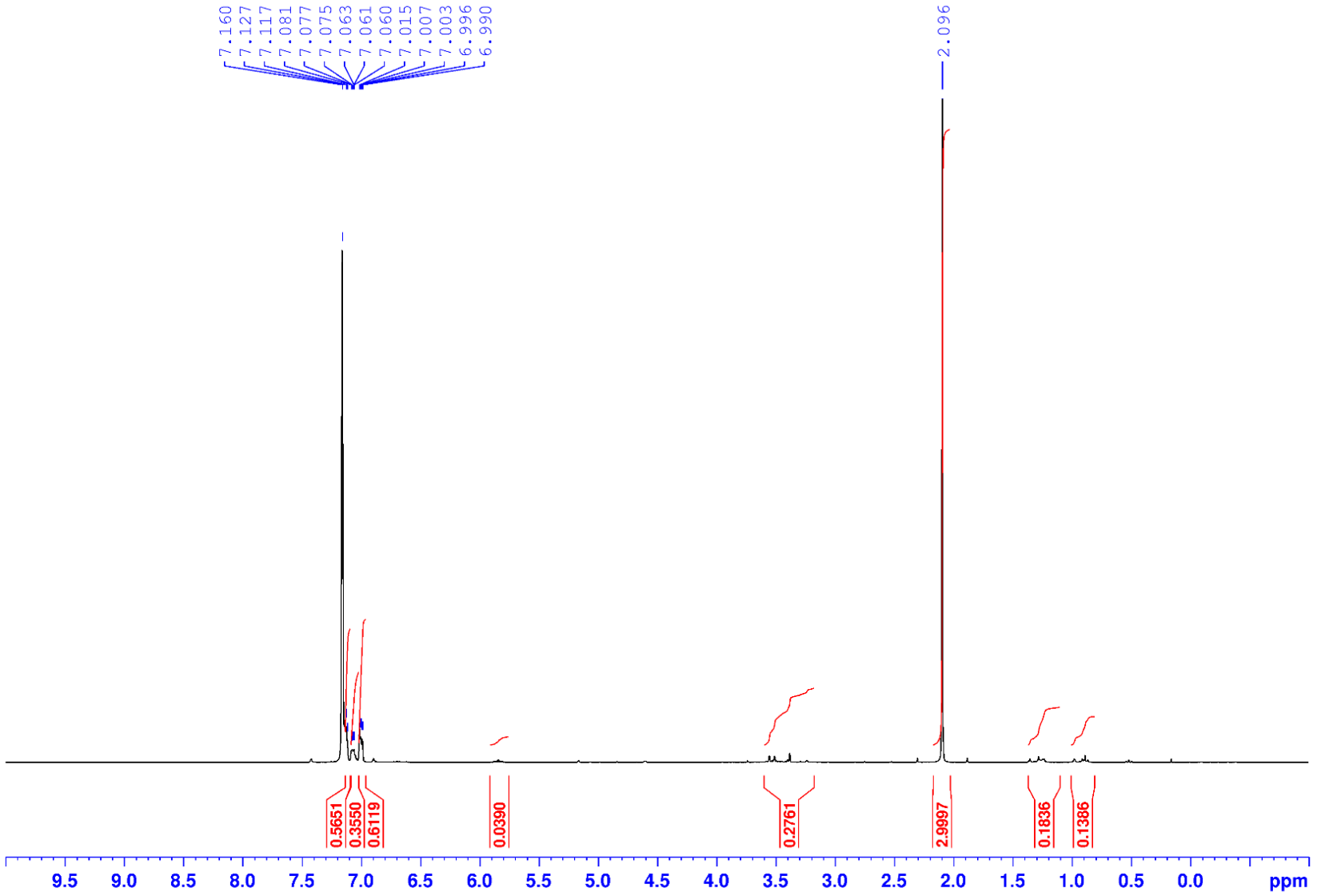
^{1}H NMR (300.1 MHz, C_6D_6) δ: 7.14–7.08 (m, CH in partially deuterated toluene), 7.07–6.97 (m, CH in partially deuterated toluene), 2.11 (s, 3H, CH_3 in partially deuterated toluenes), 1.57–1.51 (m, 6H, Me_2S, mixture of coordinated and free). **^{19}F NMR (282.4 MHz, C_6D_6) δ:** –121.5 to –121.7 (m, 2F), –150.2 (t, J = 19.8 Hz, 1F), –160.0 to –160.4 (m, 2F). **^{27}Al NMR (78.2 MHz, C_6D_6) δ:** 135±2 ($W_{1/2}$ 5.5 kHz).

$Al(C_6F_5)_3 \cdot P(OEt)_3$ complex

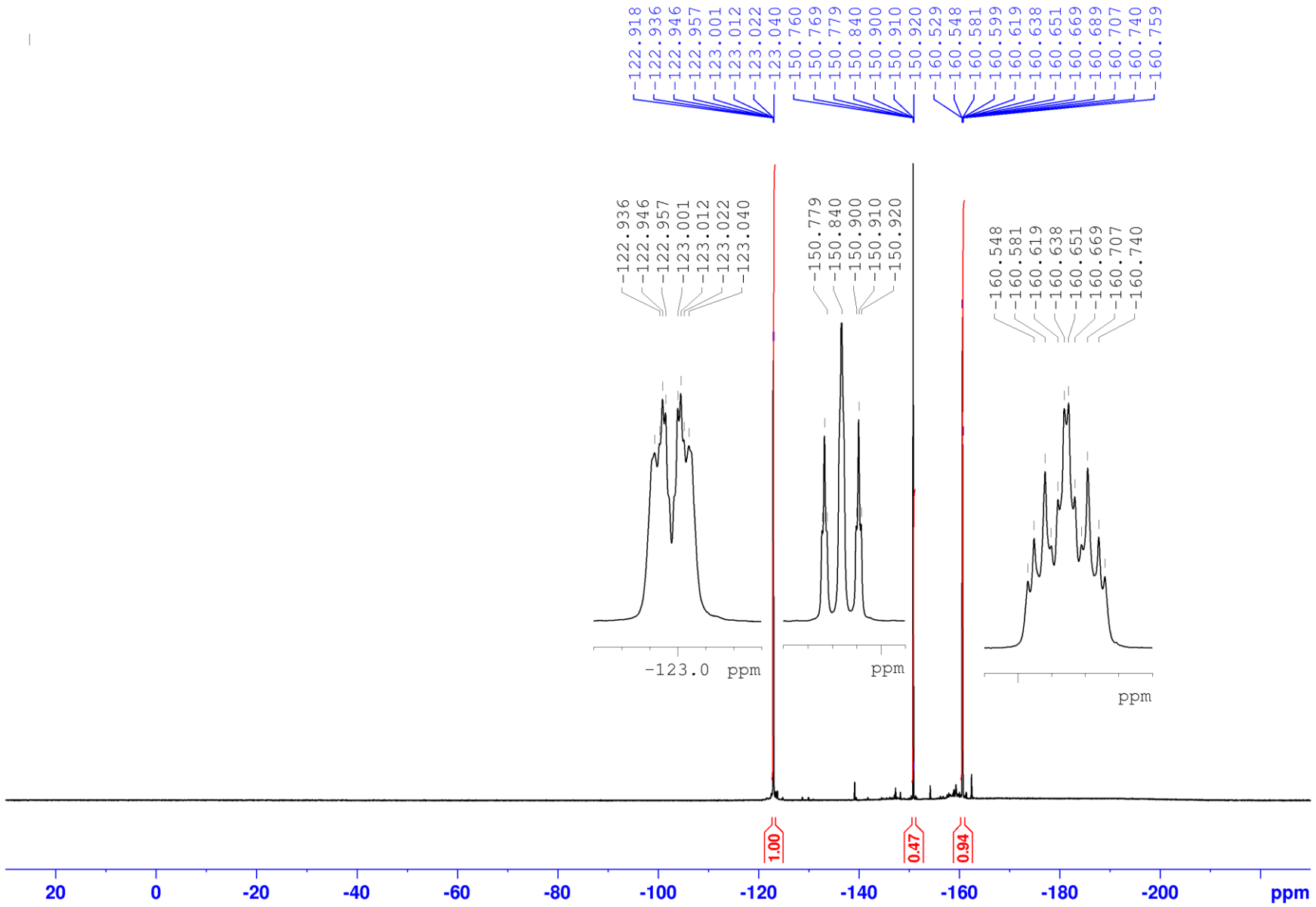
^{1}H NMR (300.1 MHz, C_6D_6) δ: 7.14–7.07 (m, CH in partially deuterated toluene), 7.07–6.96 (m, CH in partially deuterated toluene), 3.78 (dq, J = 8.0, 7.1 Hz, 6H, CH_2 in $P(OEt)_3$), 2.11 (s, 3H, CH_3 in partially deuterated toluenes), 1.09 (t, J = 7.0 Hz, 9H, CH_3 in $P(OEt)_3$) *[Coordinated and non-coordinated $P(OEt)_3$ are in a fast exchange and give one set of signals]*. **^{19}F NMR (282.4 MHz, C_6D_6) δ:** *[in ^{19}F NMR spectra several types of C_6F_5-groups are presented that could be attributed to different complexes existing in dynamic equilibrium]* –123.4 to –123.7 (m, 2F, complex 1), –123.7 to –123.9 (m, 2F, complex 2), –153.0 (t, J = 19.7 Hz, complex 2), –153.2 (t, J = 19.6 Hz, complex 1), –161.4 – -161.9 (m, 2F, both complexes). **^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6) δ:** 138.6 (s) *[Coordinated and non-coordinated $P(OEt)_3$ are in a fast exchange and give one set of signals]*. **^{27}Al NMR (78.2 MHz, C_6D_6) δ:** 110±2 ($W_{1/2}$ 4.0 kHz).

3. Copies of ^{1}H, ^{19}F, ^{13}C, ^{27}Al-NMR spectra and 2D correlations

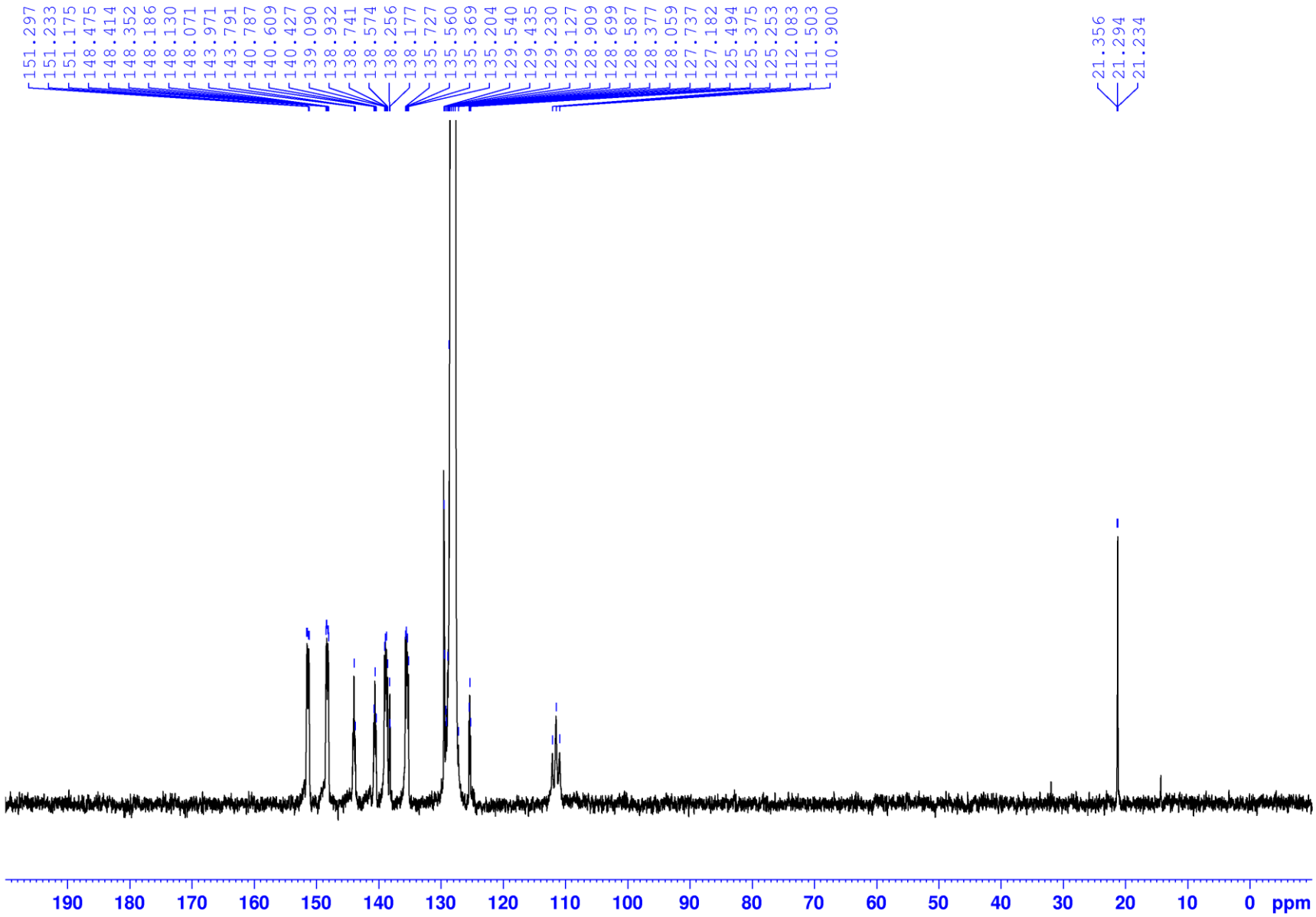
^{1}H NMR (300.1 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot 0.5$toluene



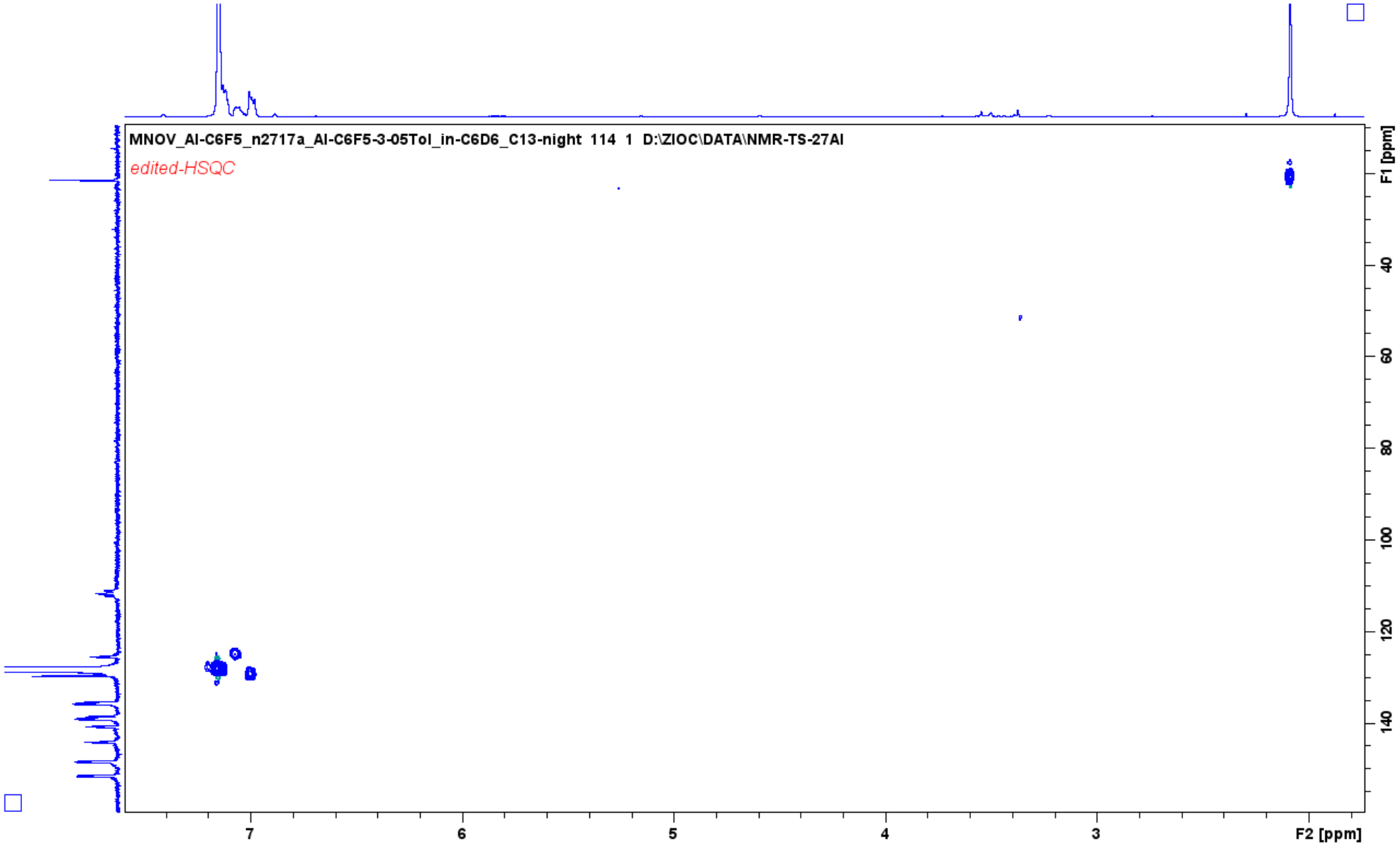
^{19}F NMR (282.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot 0.5$toluene



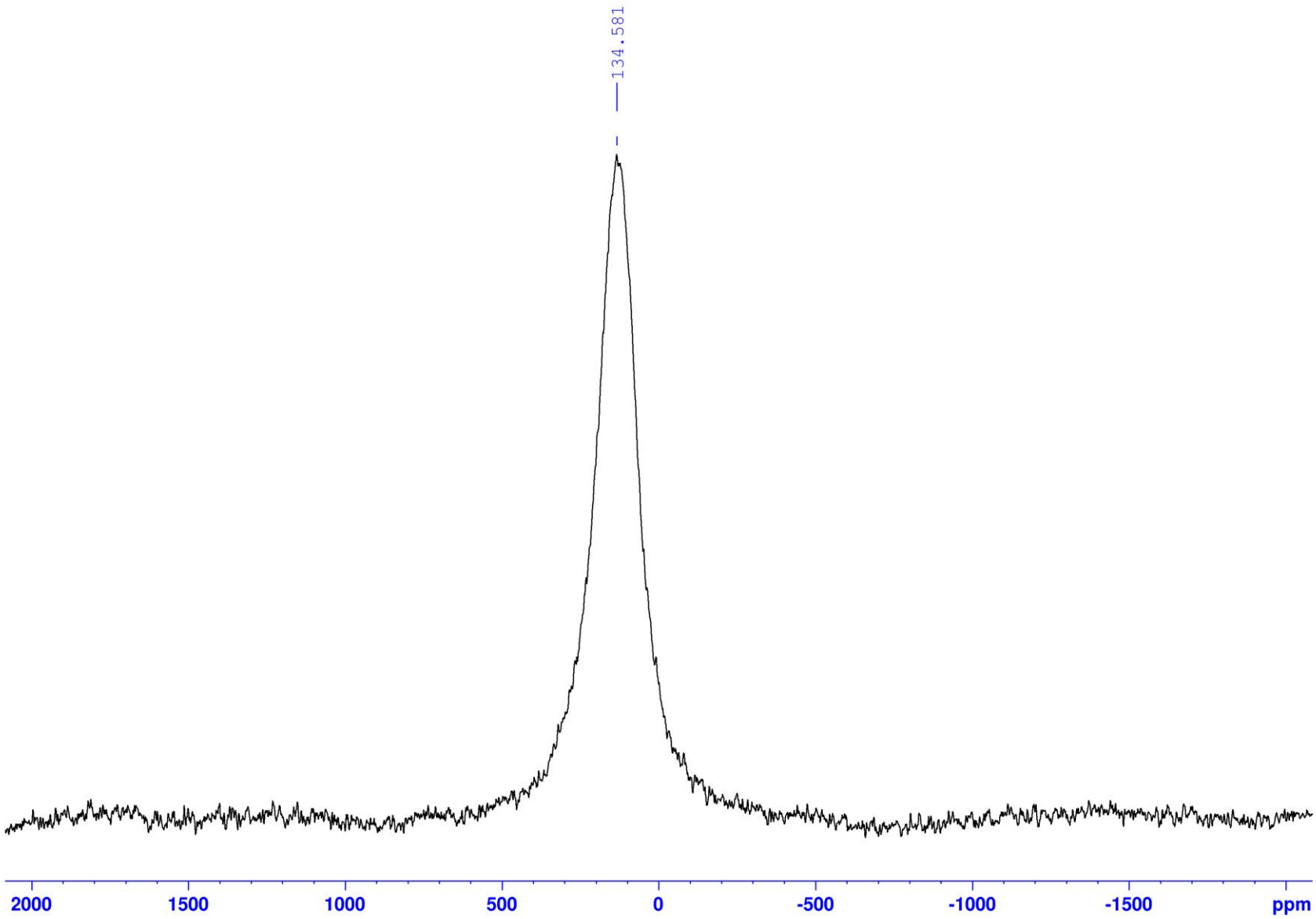
$^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot 0.5$toluene



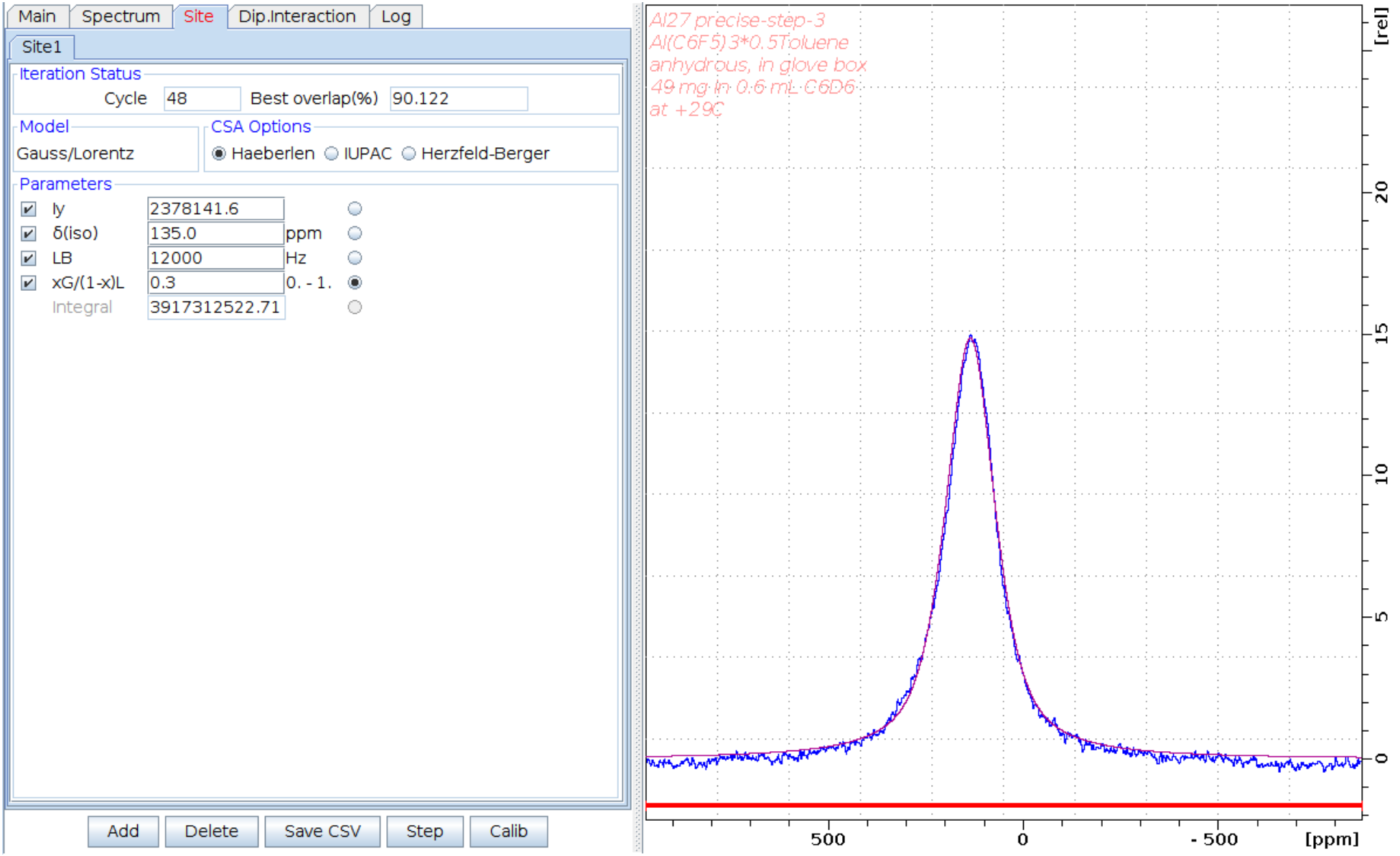
{^{1}H,^{13}C}-edited HSQC (C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot 0.5$toluene



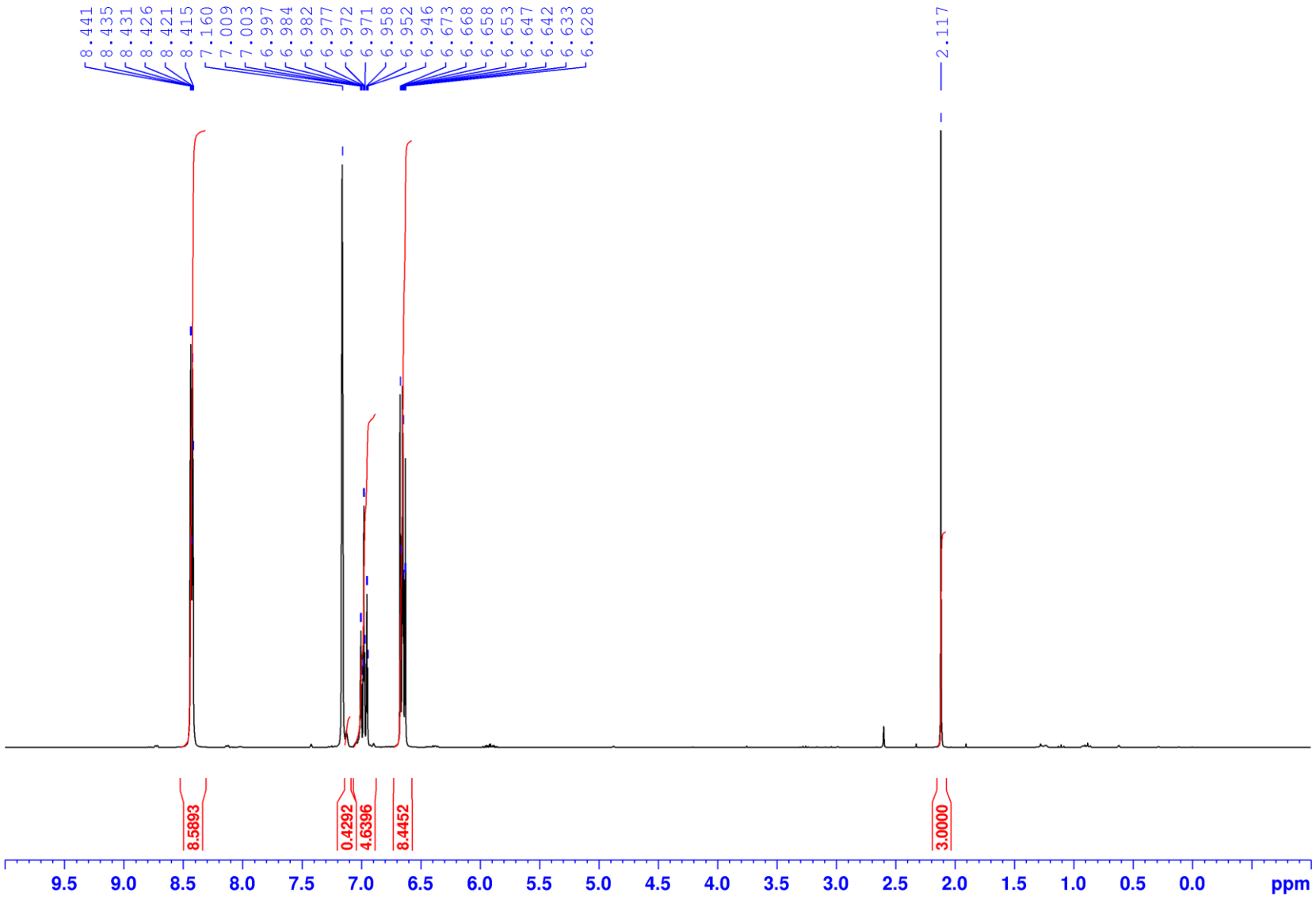
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot 0.5$toluene



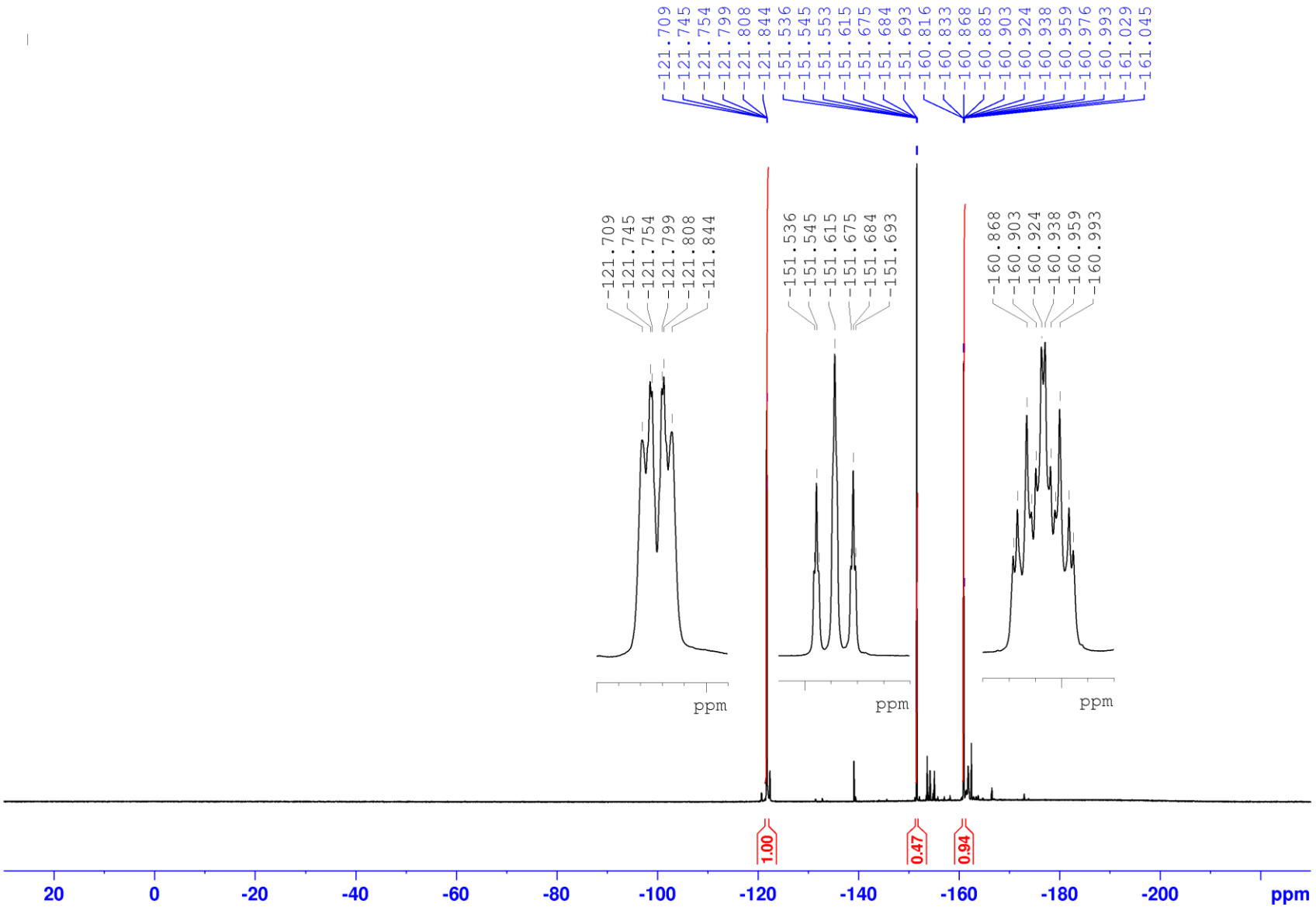
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot 0.5$toluene — Line shape analysis



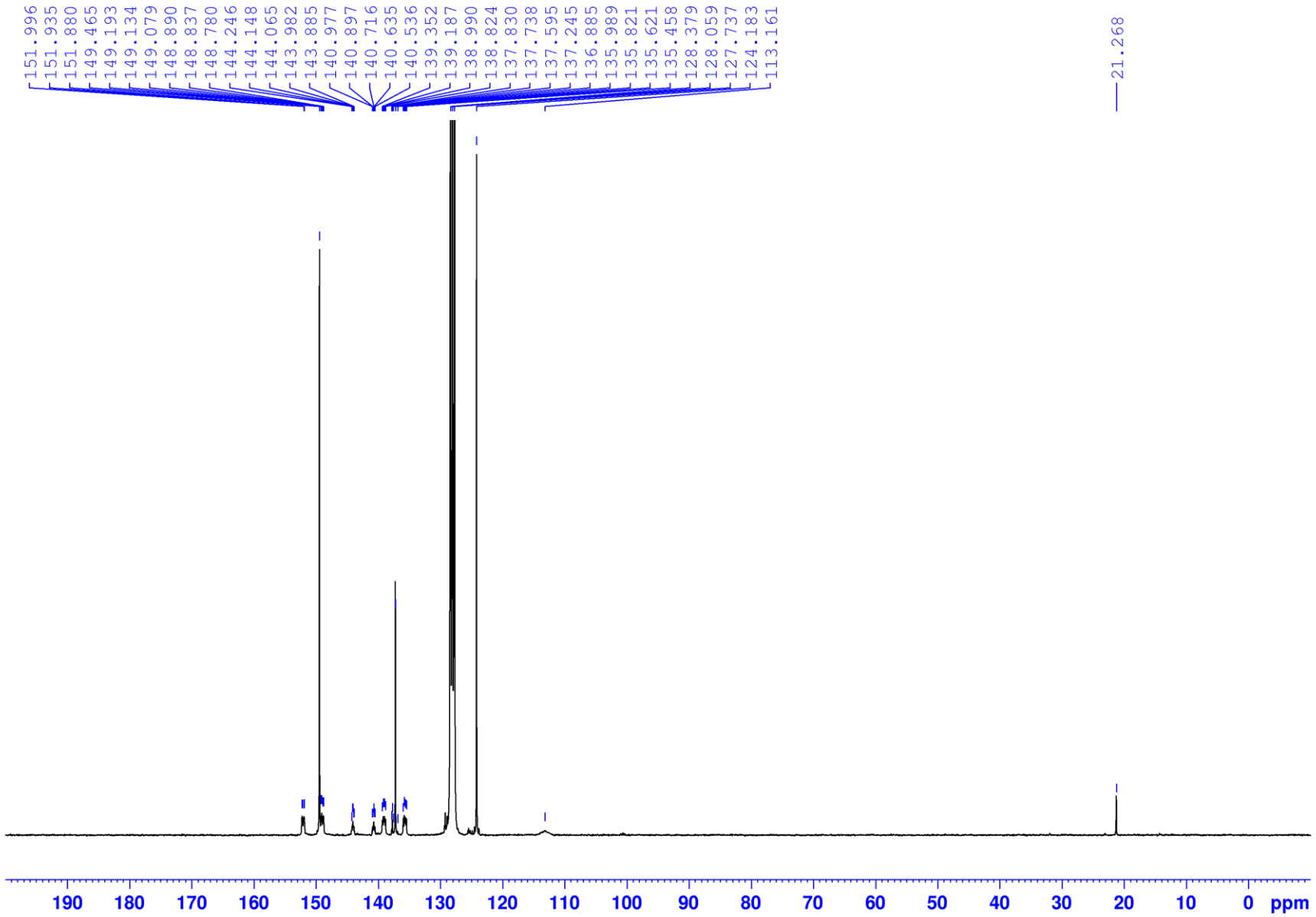
^{1}H NMR (300.1 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·Pyridine complex



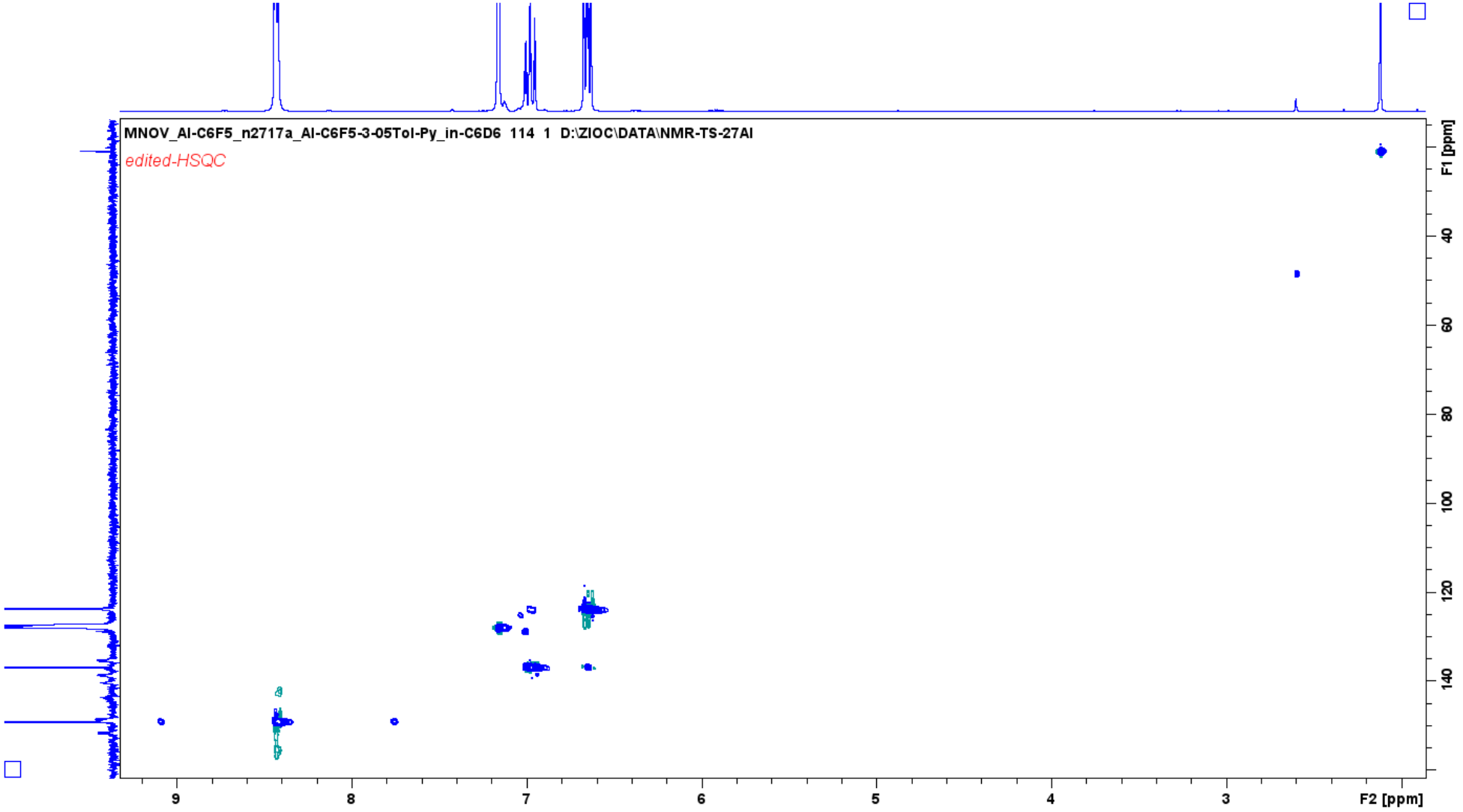
^{19}F NMR (282.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·Pyridine complex



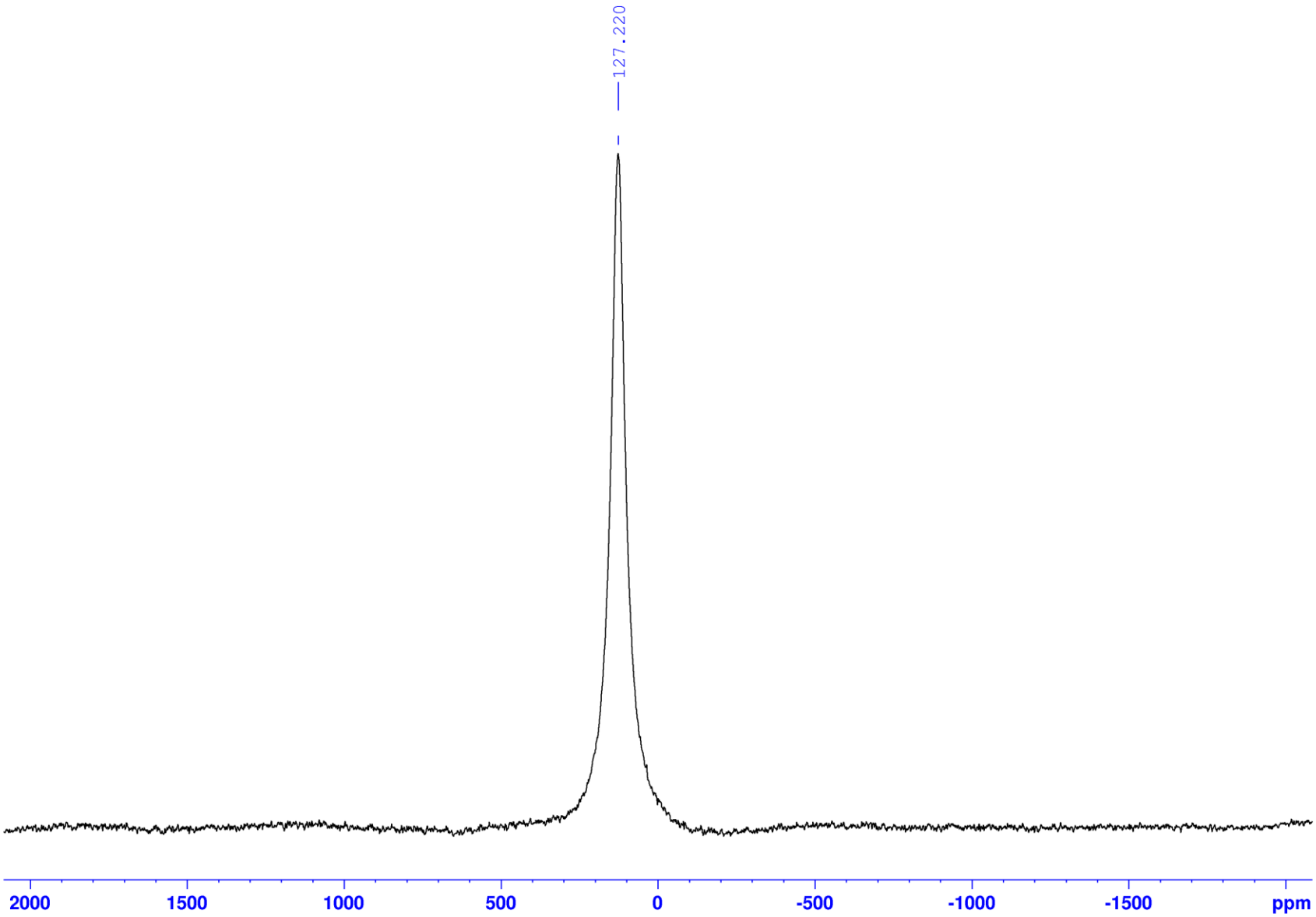
$^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·Pyridine complex



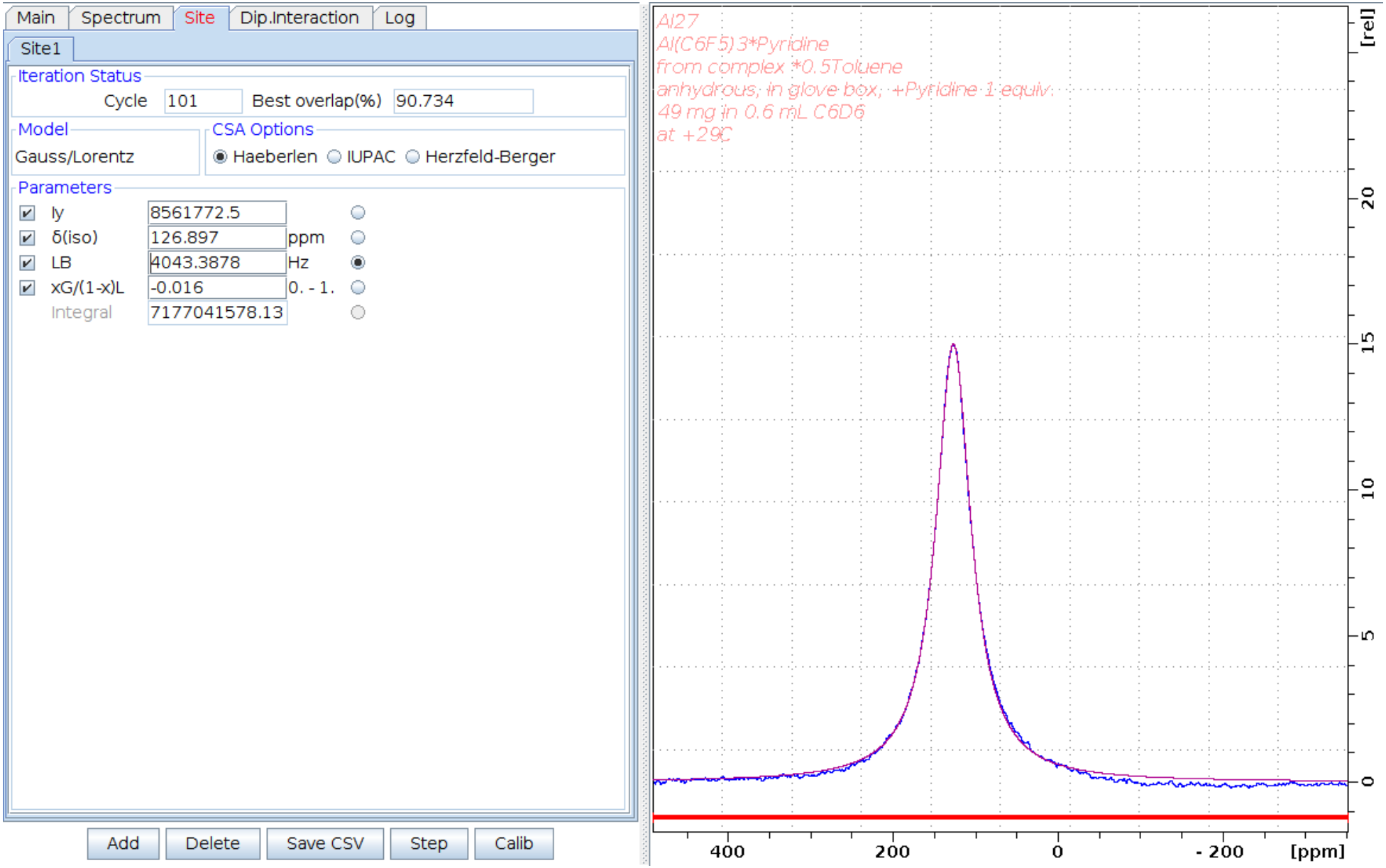
{^{1}H,^{13}C}-edited HSQC (C_6D_6, 298 K) of $Al(C_6F_5)_3$·Pyridine complex



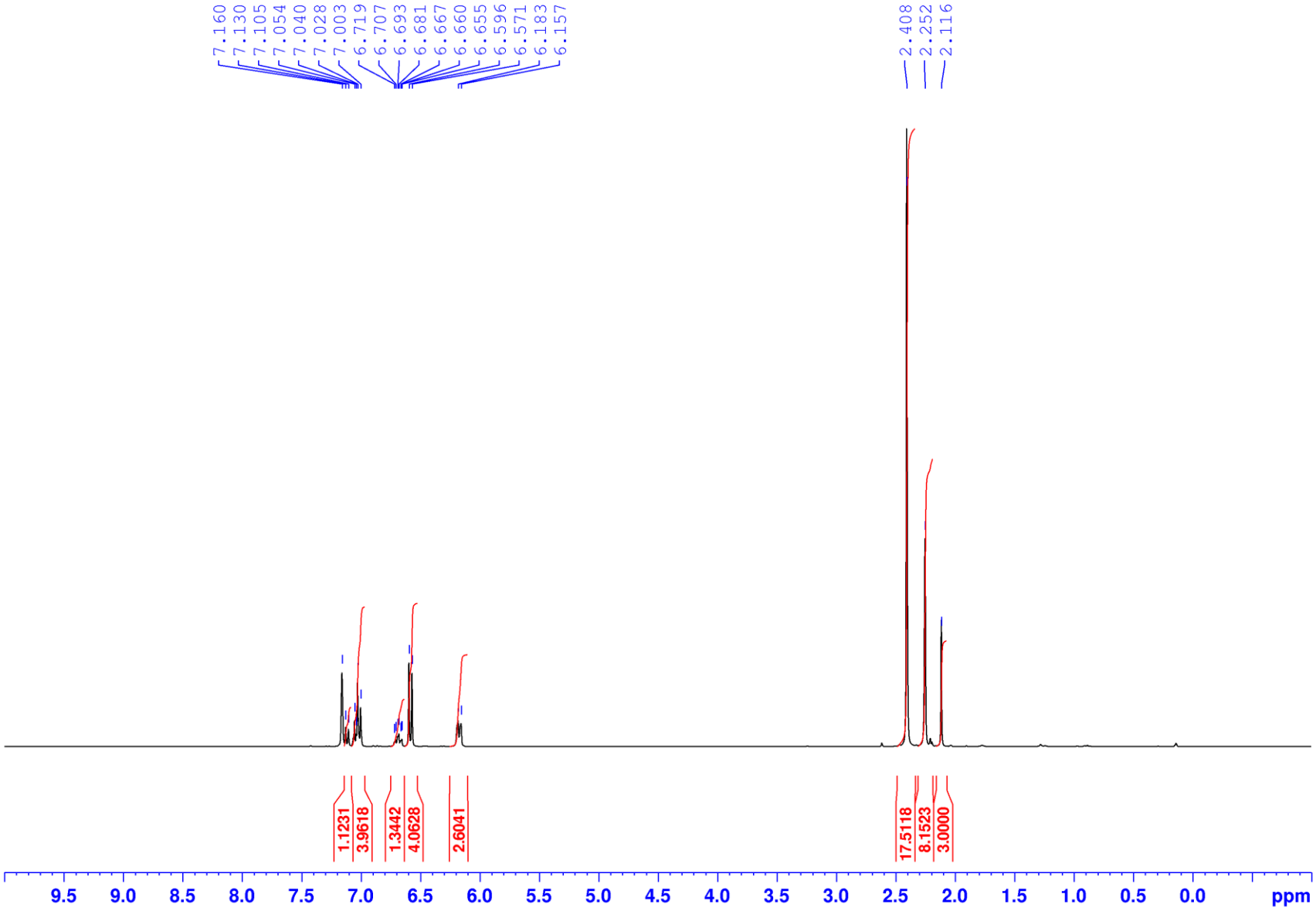
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·Pyridine complex



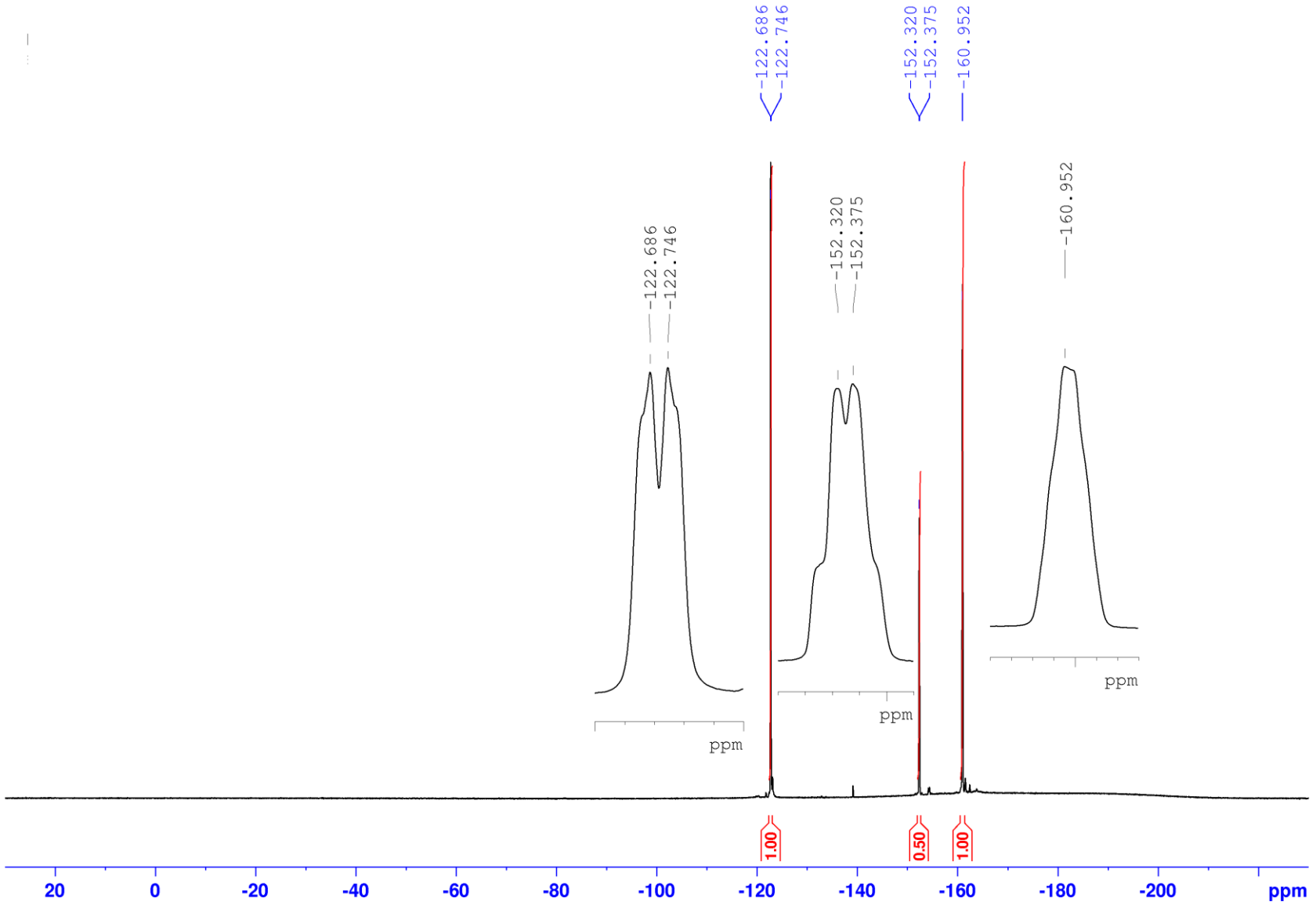
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·Pyridine complex — Line shape analysis



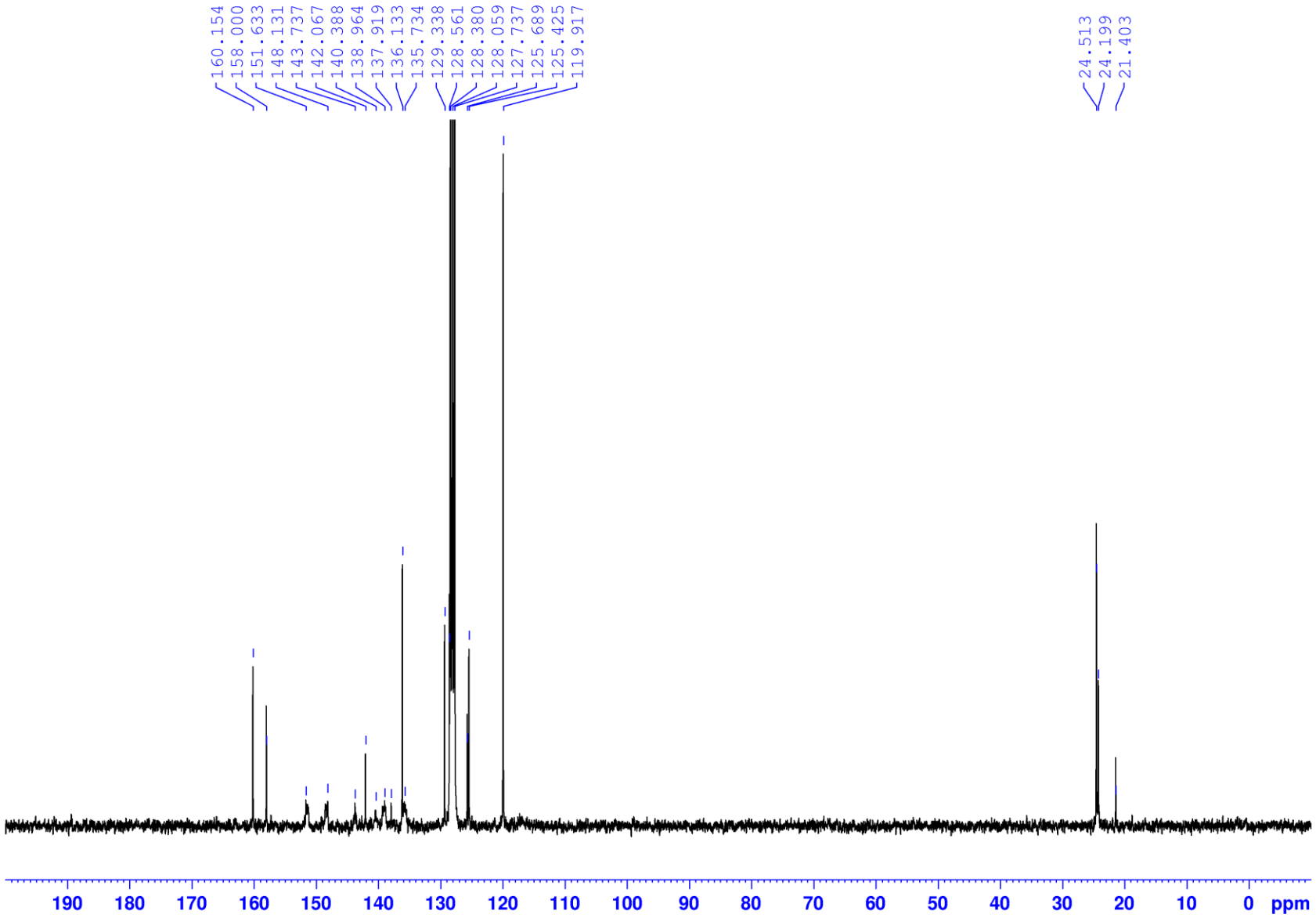
^{1}H NMR (300.1 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·2,6-Lutidine complex



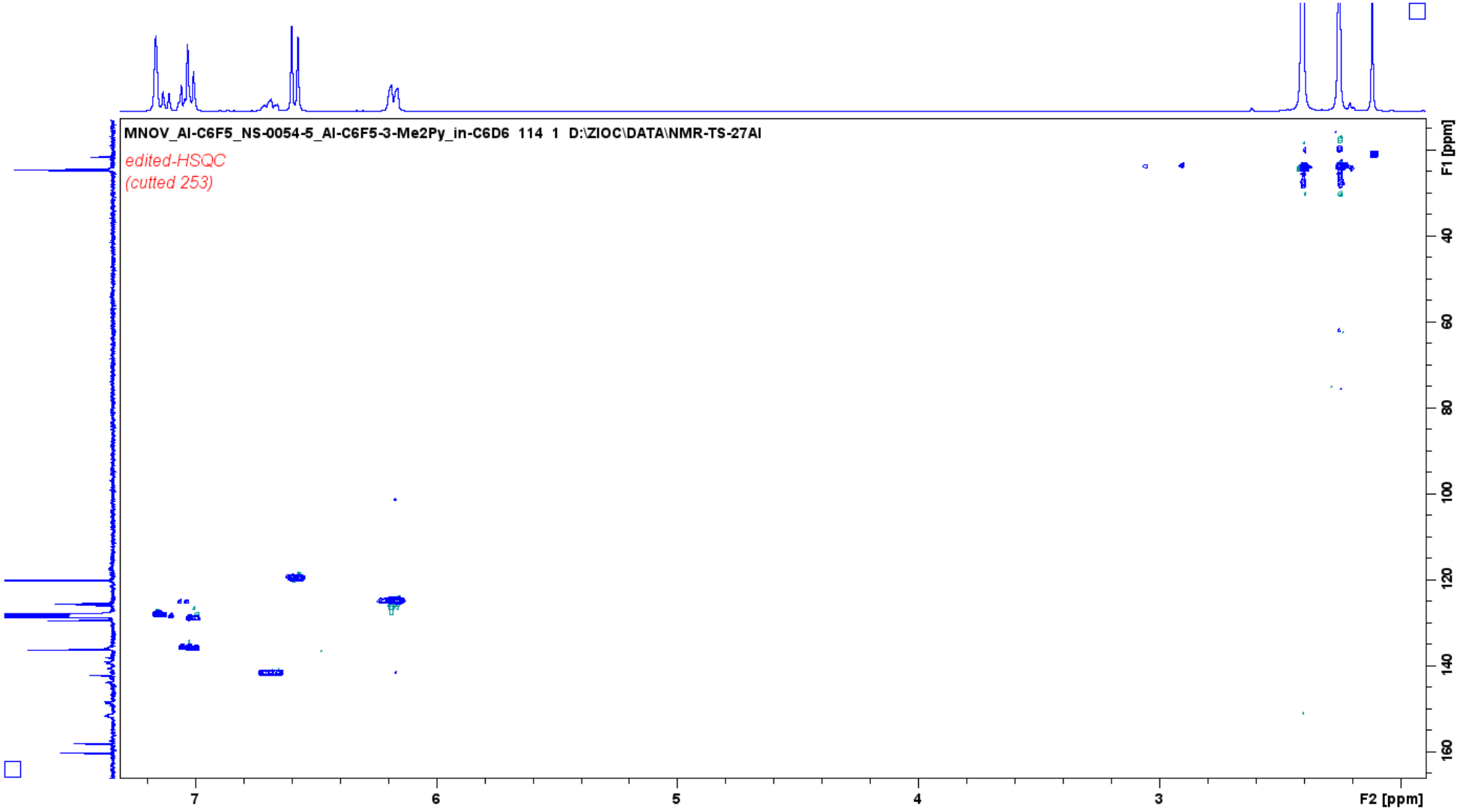
^{19}F NMR (282.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·2,6-Lutidine complex



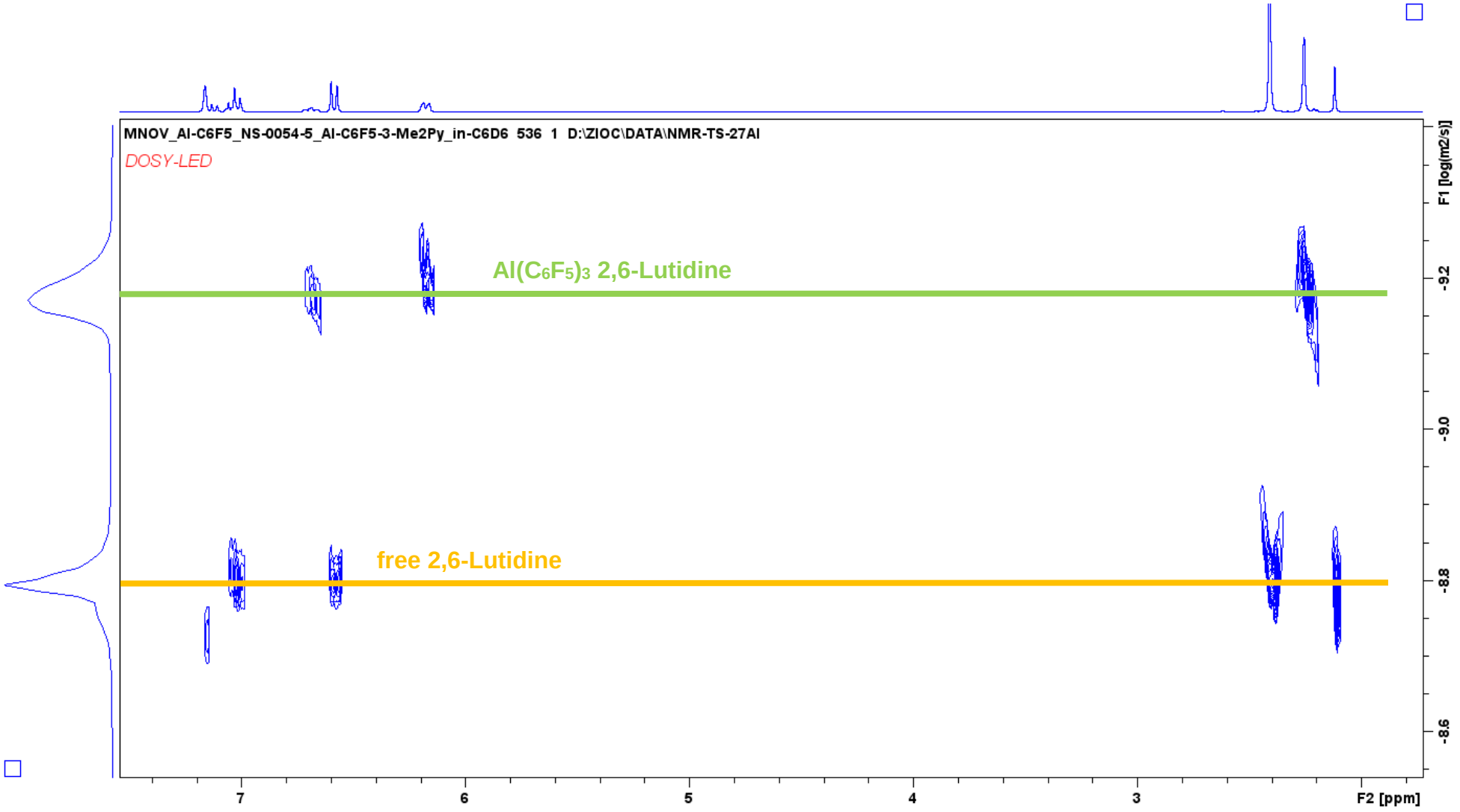
$^{13}C\{^{1}H\}$ NMR (75.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot$2,6-Lutidine complex



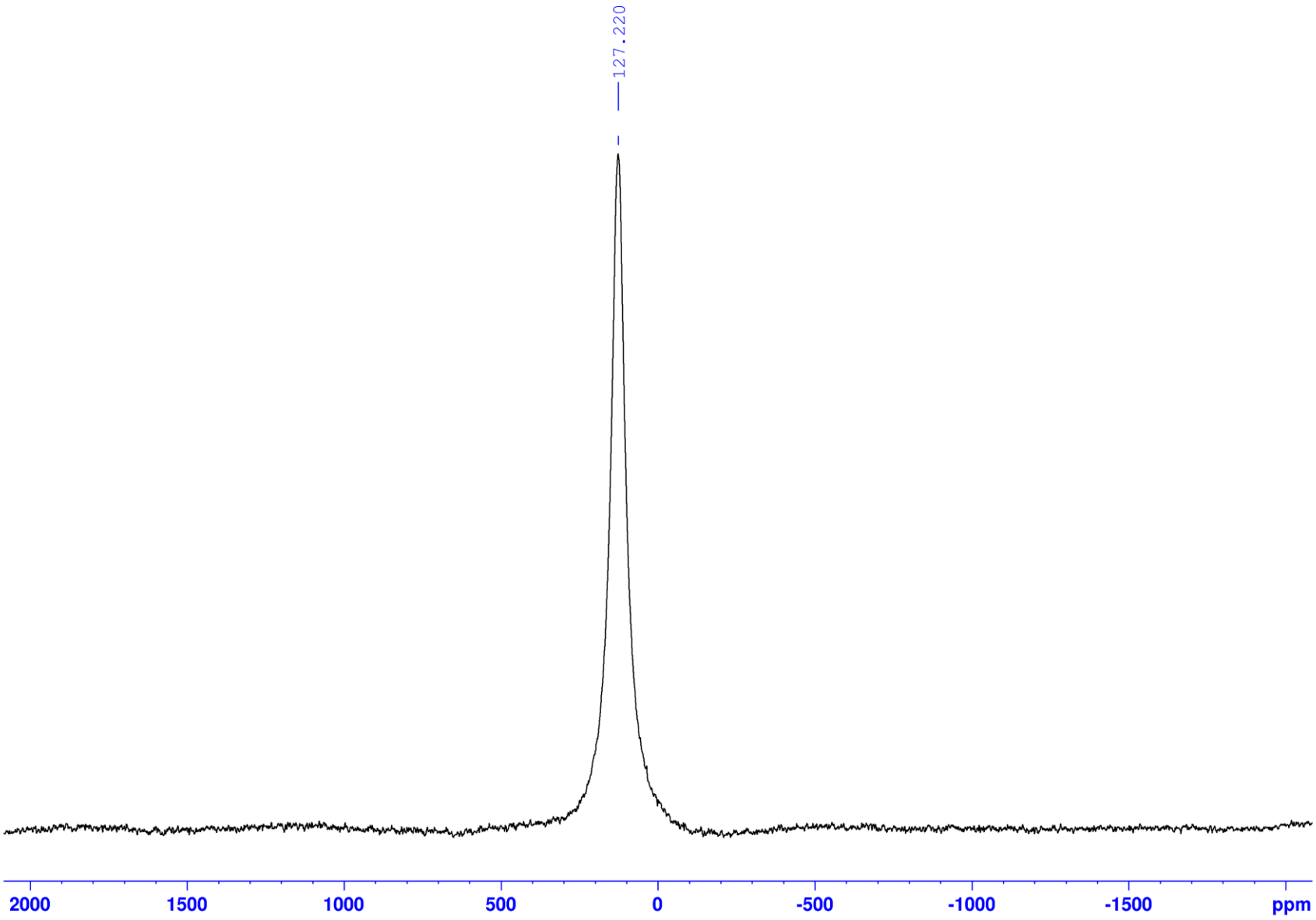
{^{1}H,^{13}C}-edited HSQC (C_6D_6, 298 K) of $Al(C_6F_5)_3$·2,6-Lutidine complex



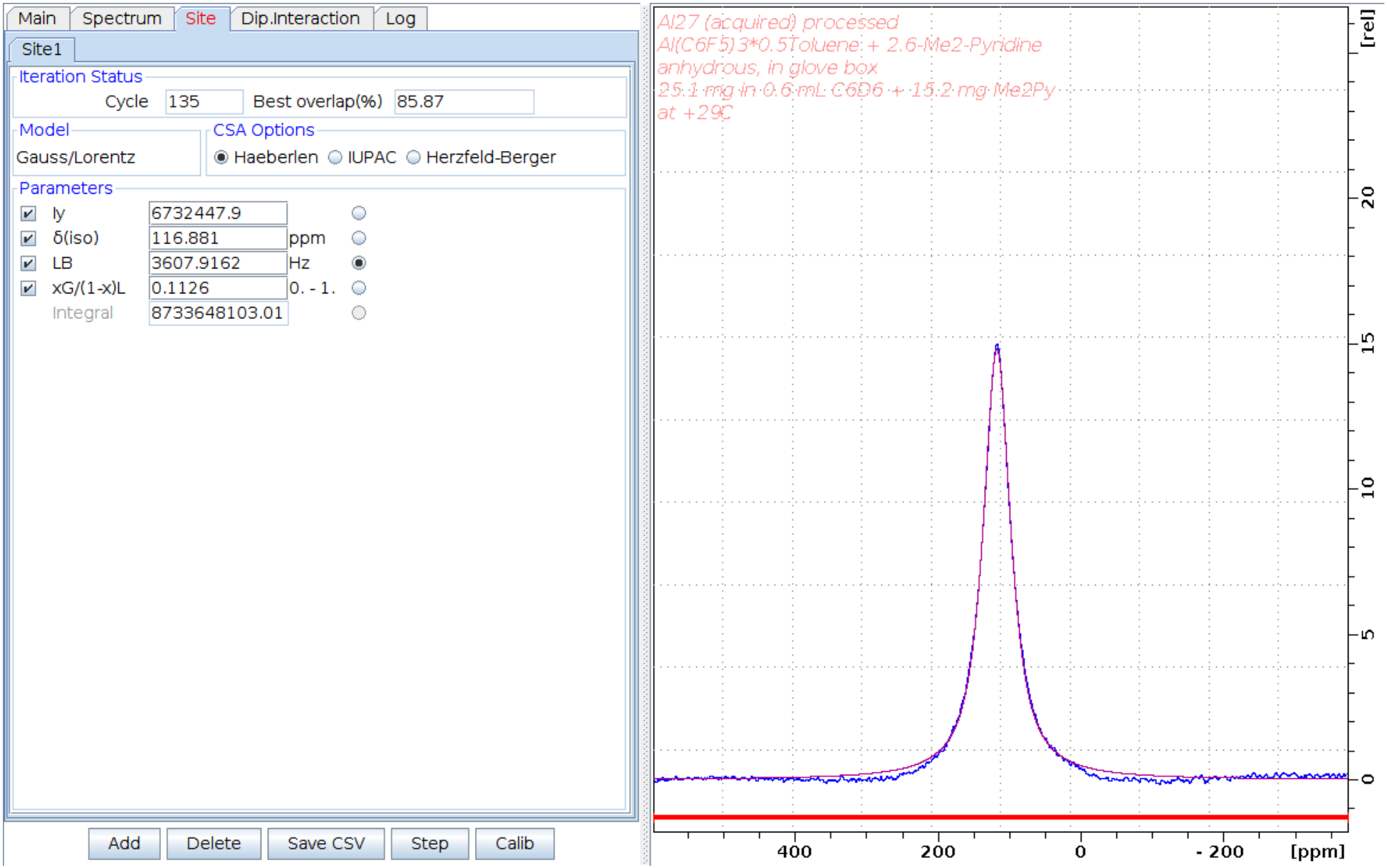
{^{1}H}-DOSY (C_6D_6, 298 K) of $Al(C_6F_5)_3$·2,6-Lutidine complex



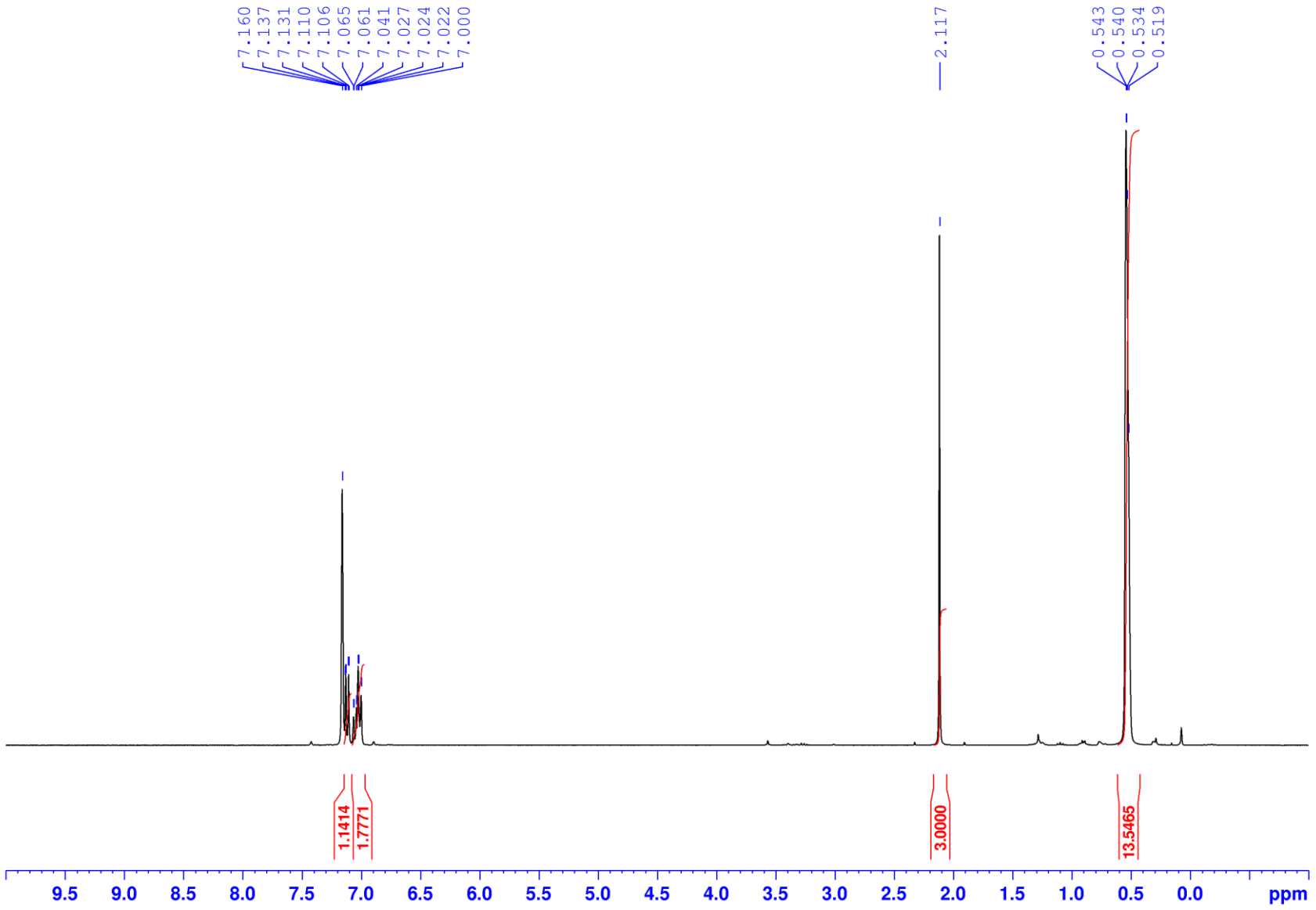
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·2,6-Lutidine complex



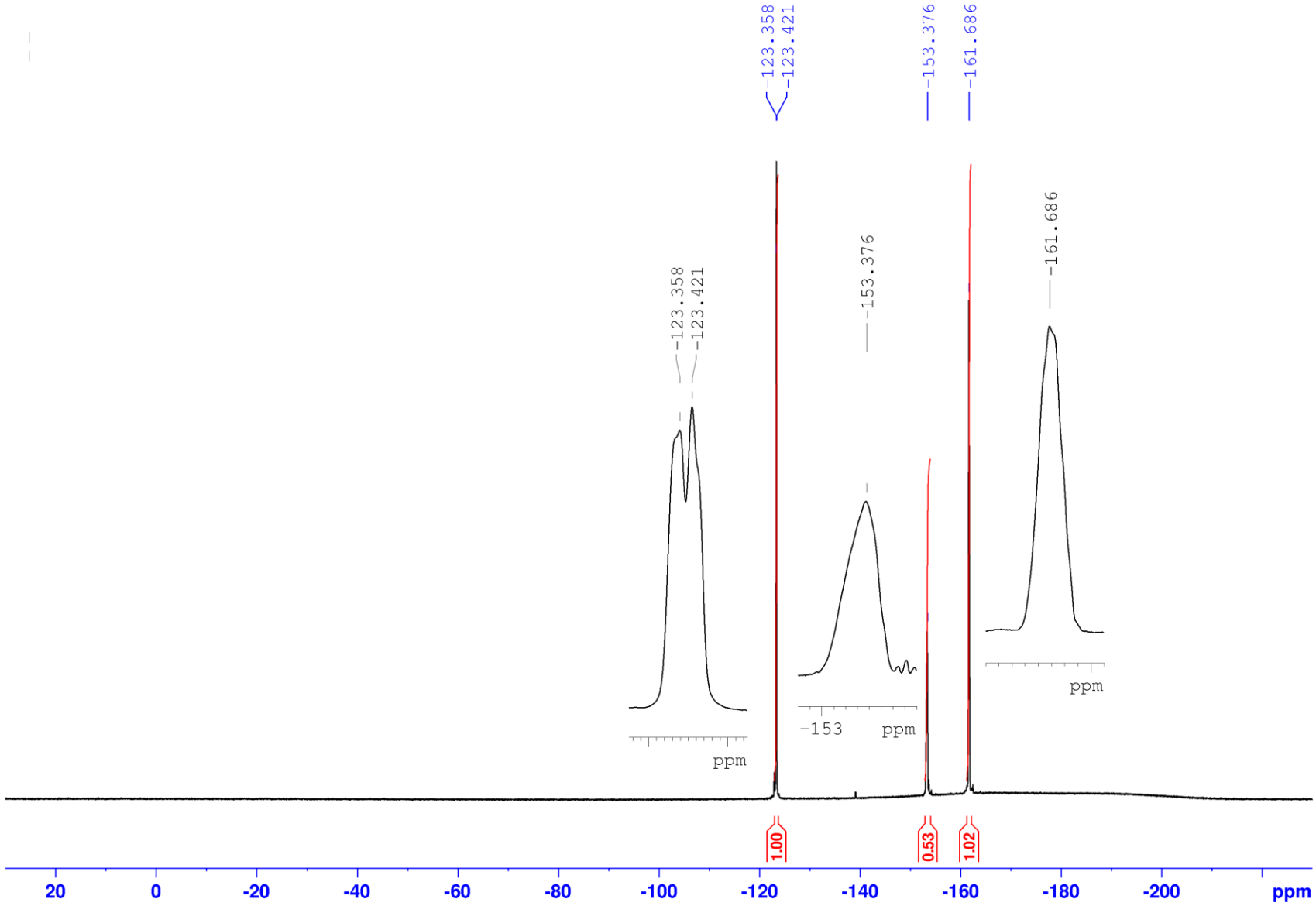
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·2,6-Lutidine complex — Line shape analysis



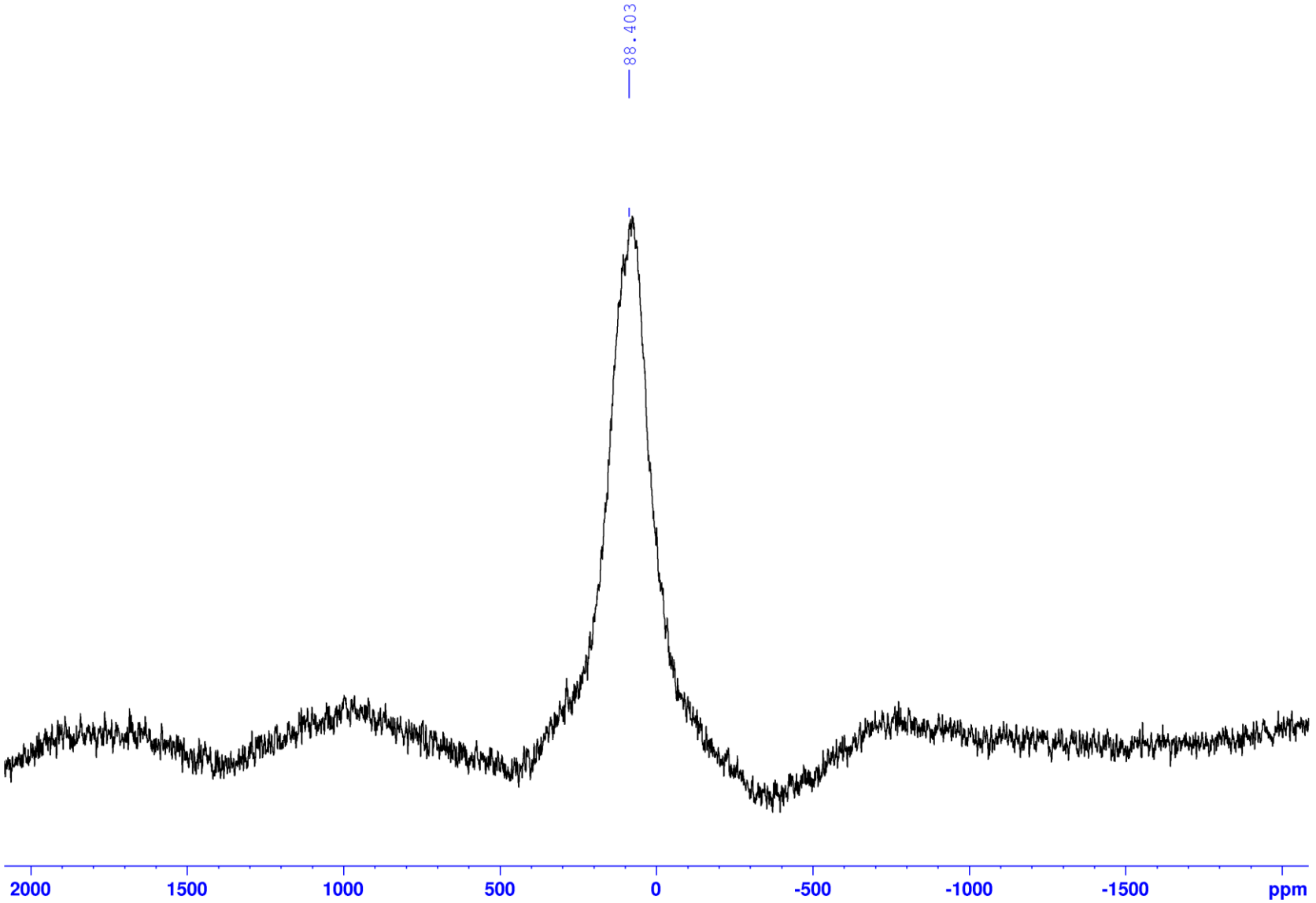
^{1}H NMR (300.1 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3$·MeCN complex



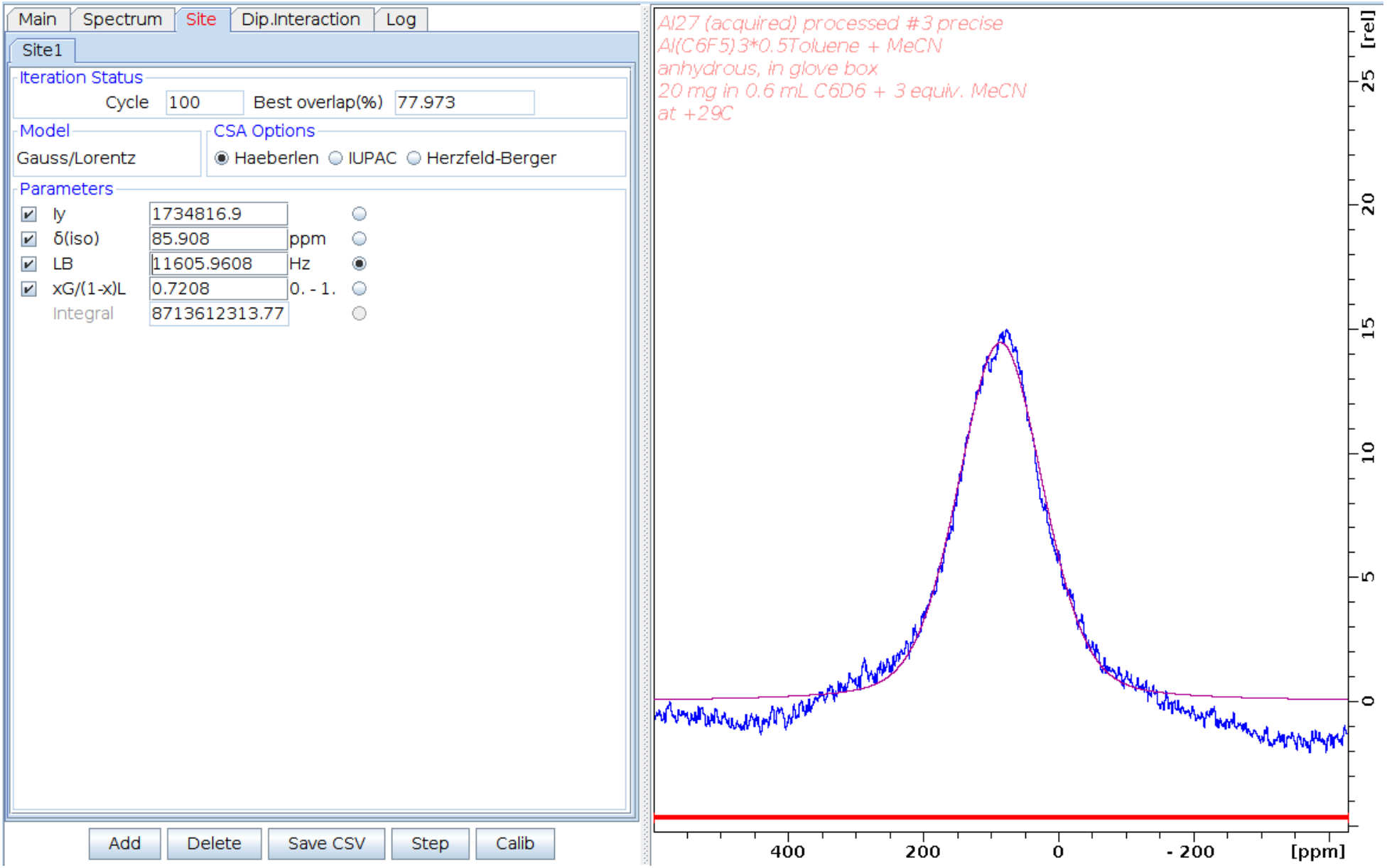
^{19}F NMR (282.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot MeCN$ complex



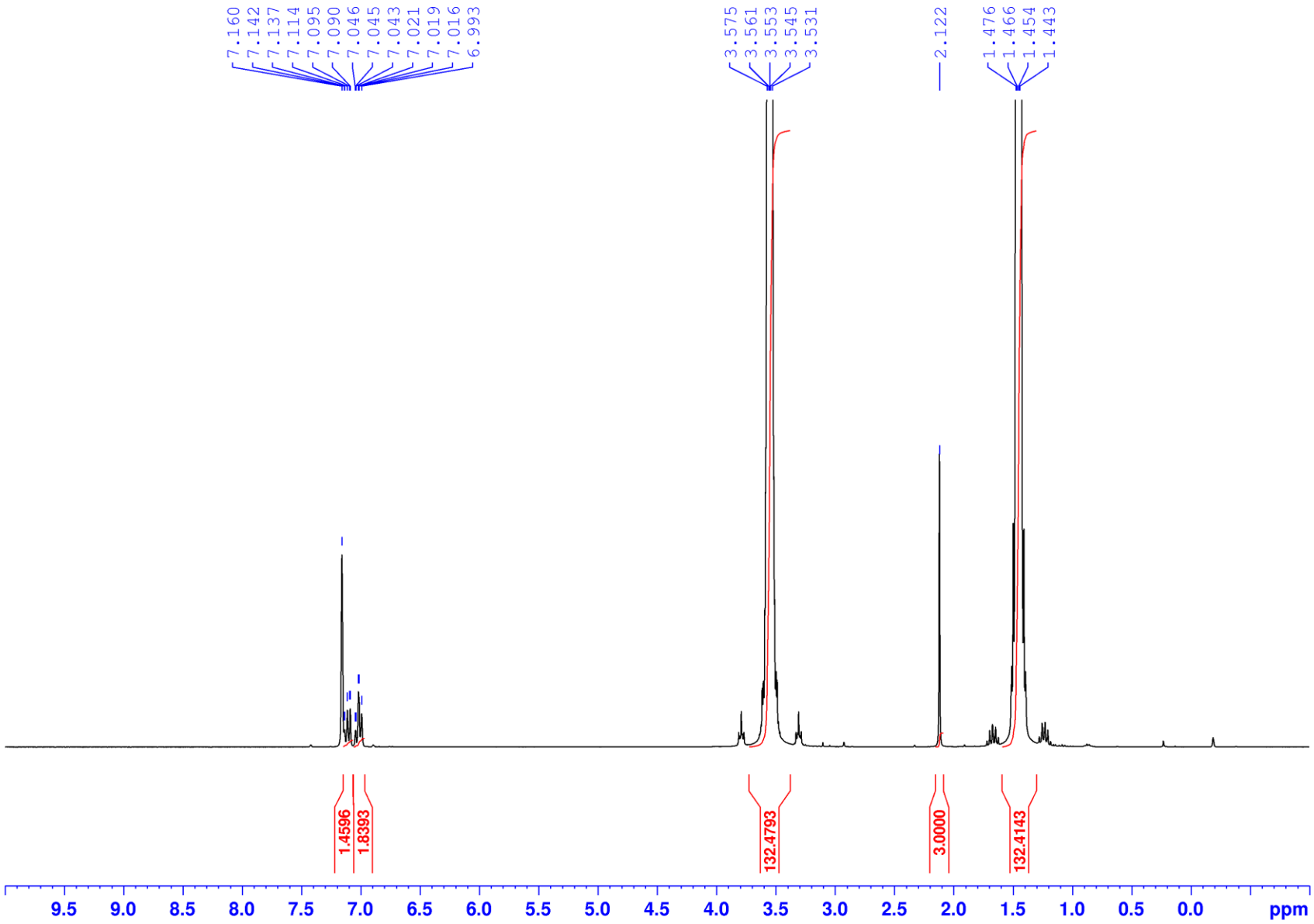
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot MeCN$ complex



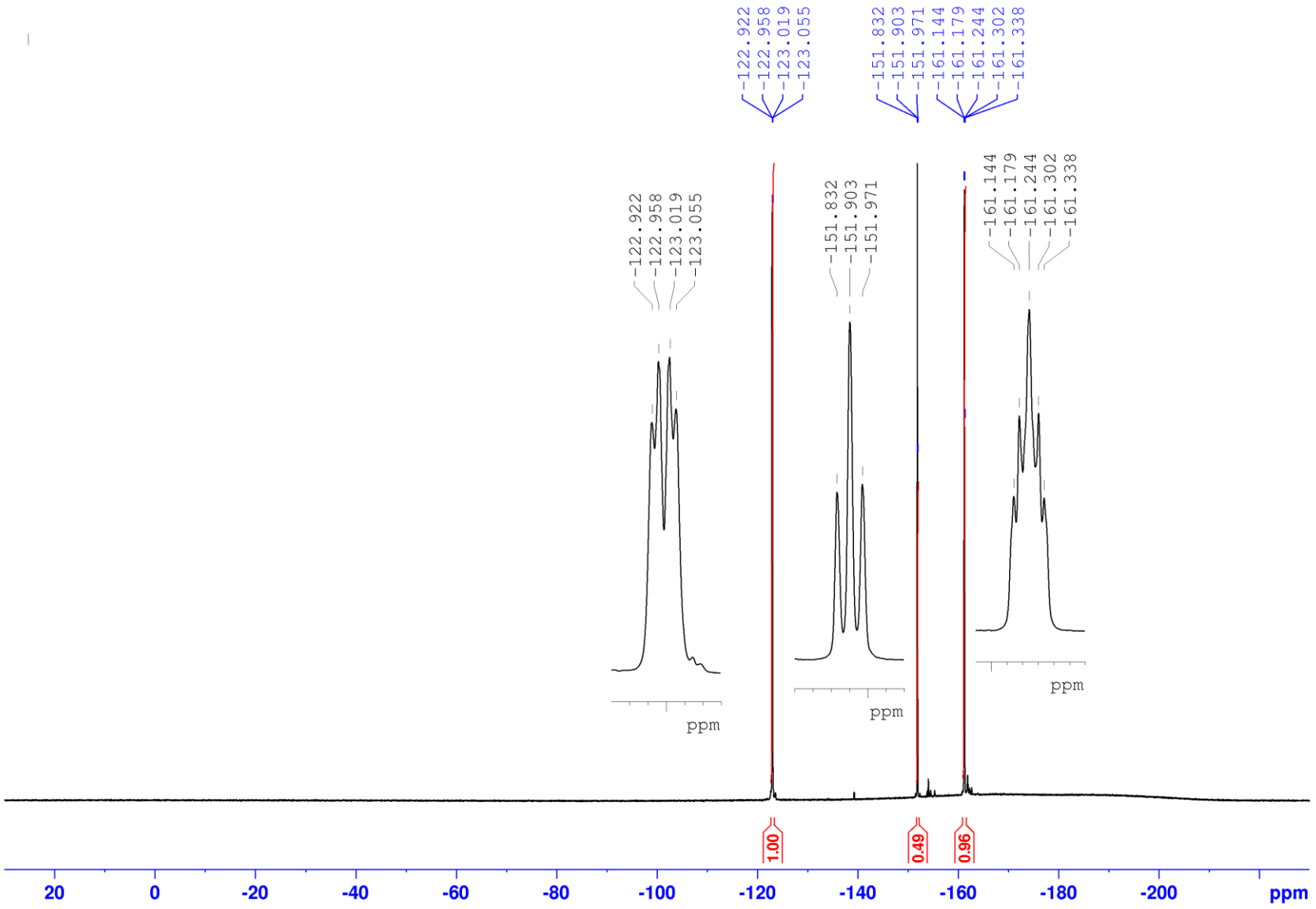
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot MeCN$ complex — Line shape analysis



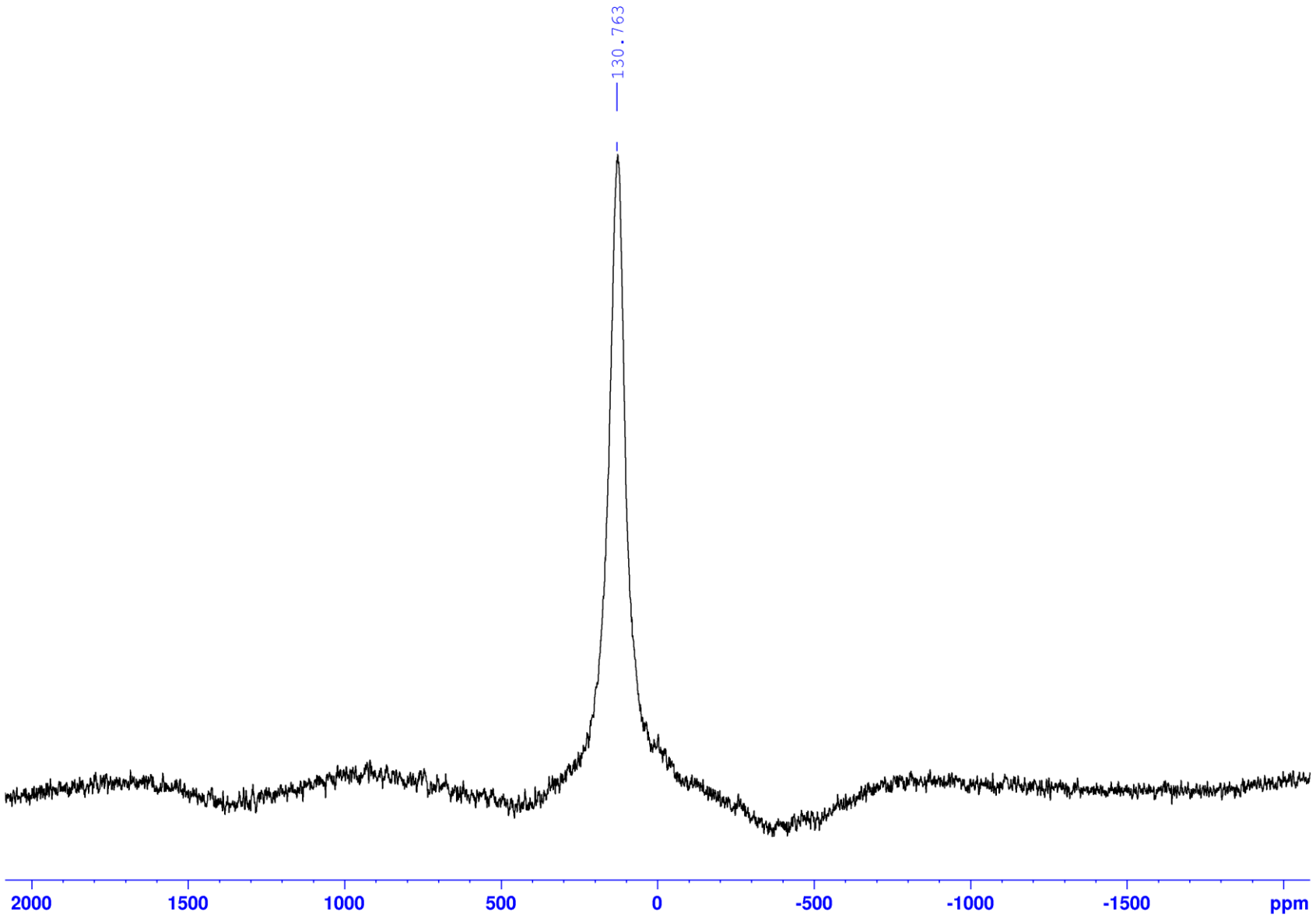
^{1}H NMR (300.1 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot THF$ complex



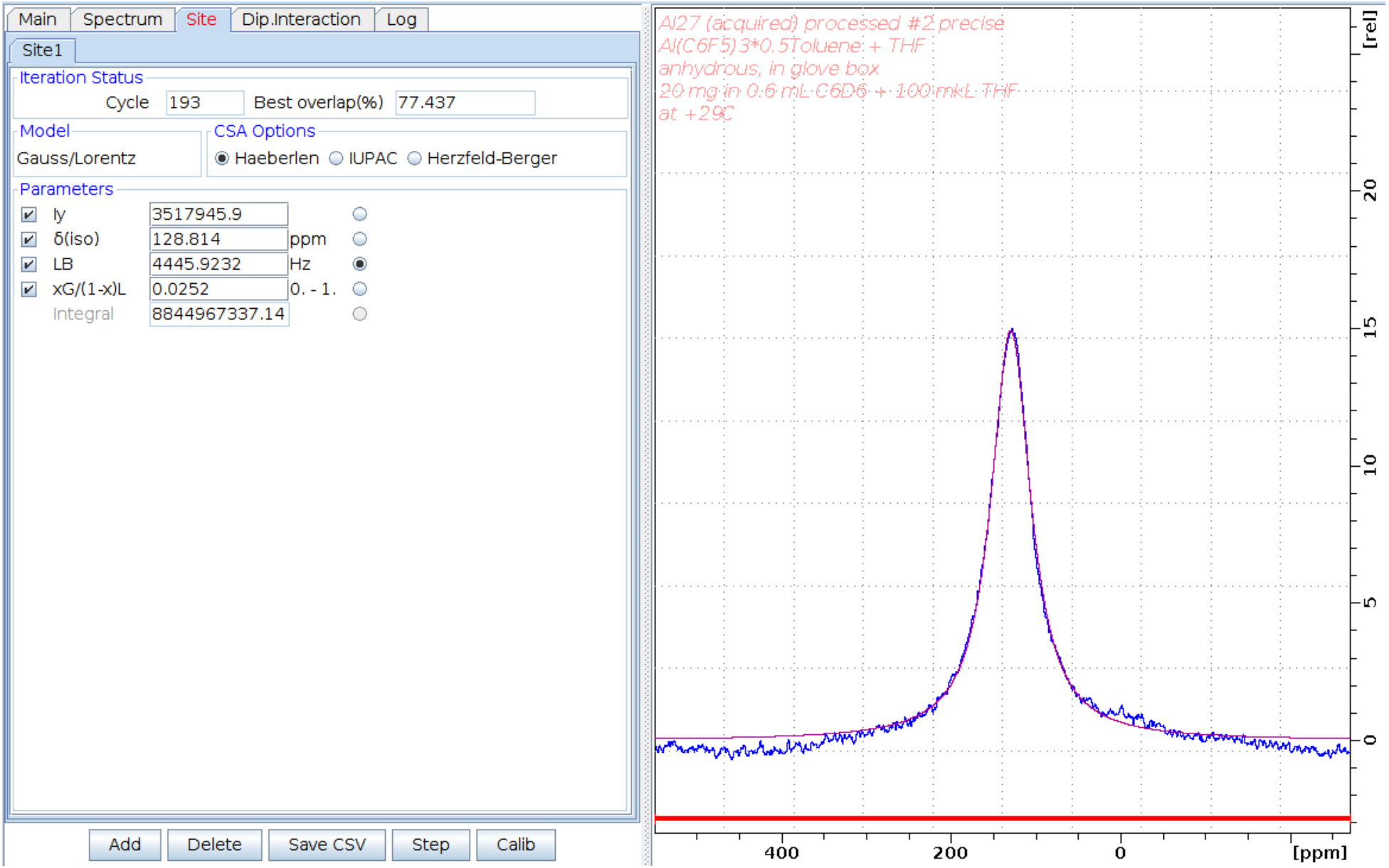
^{19}F NMR (282.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot THF$ complex



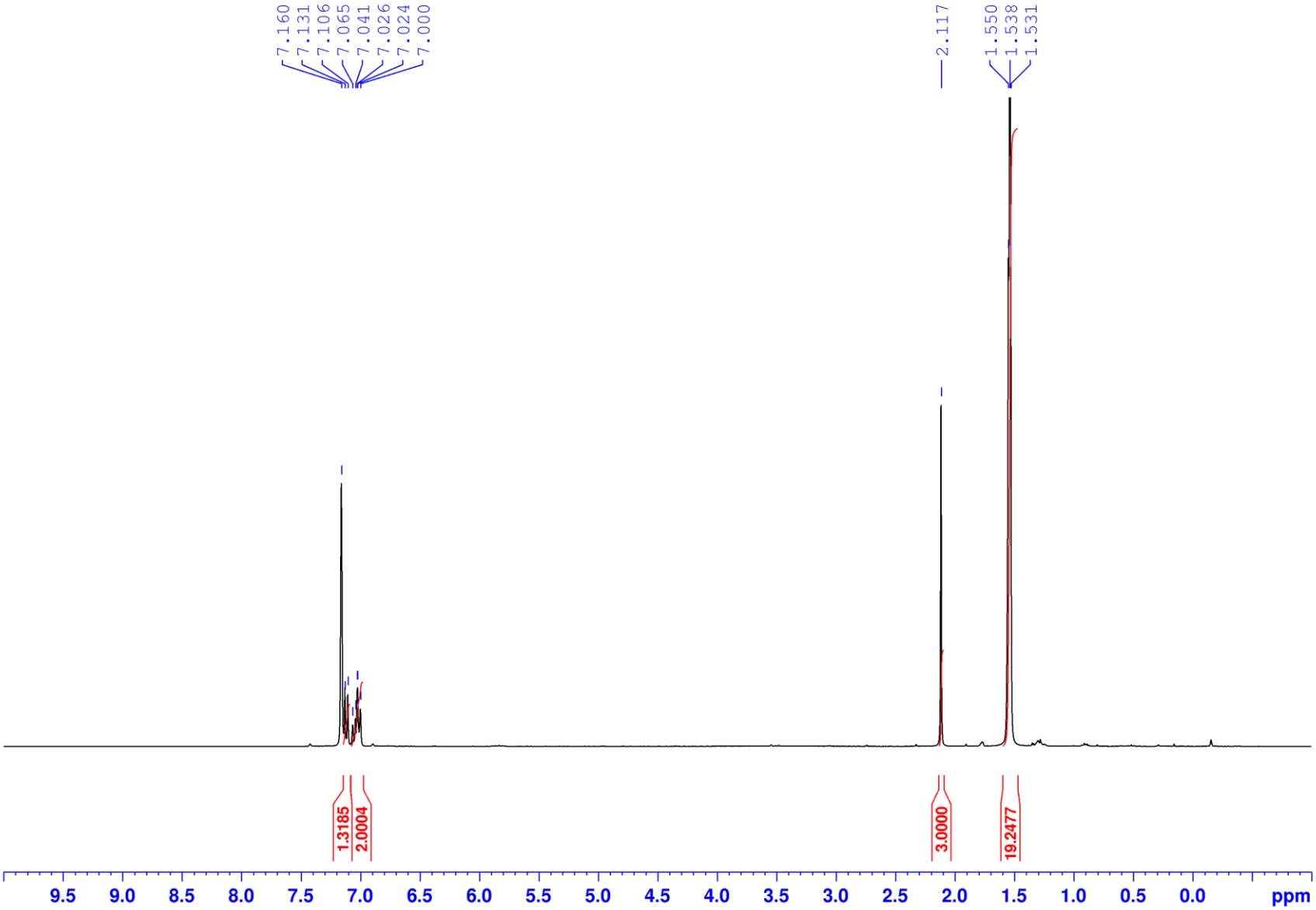
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot THF$ complex



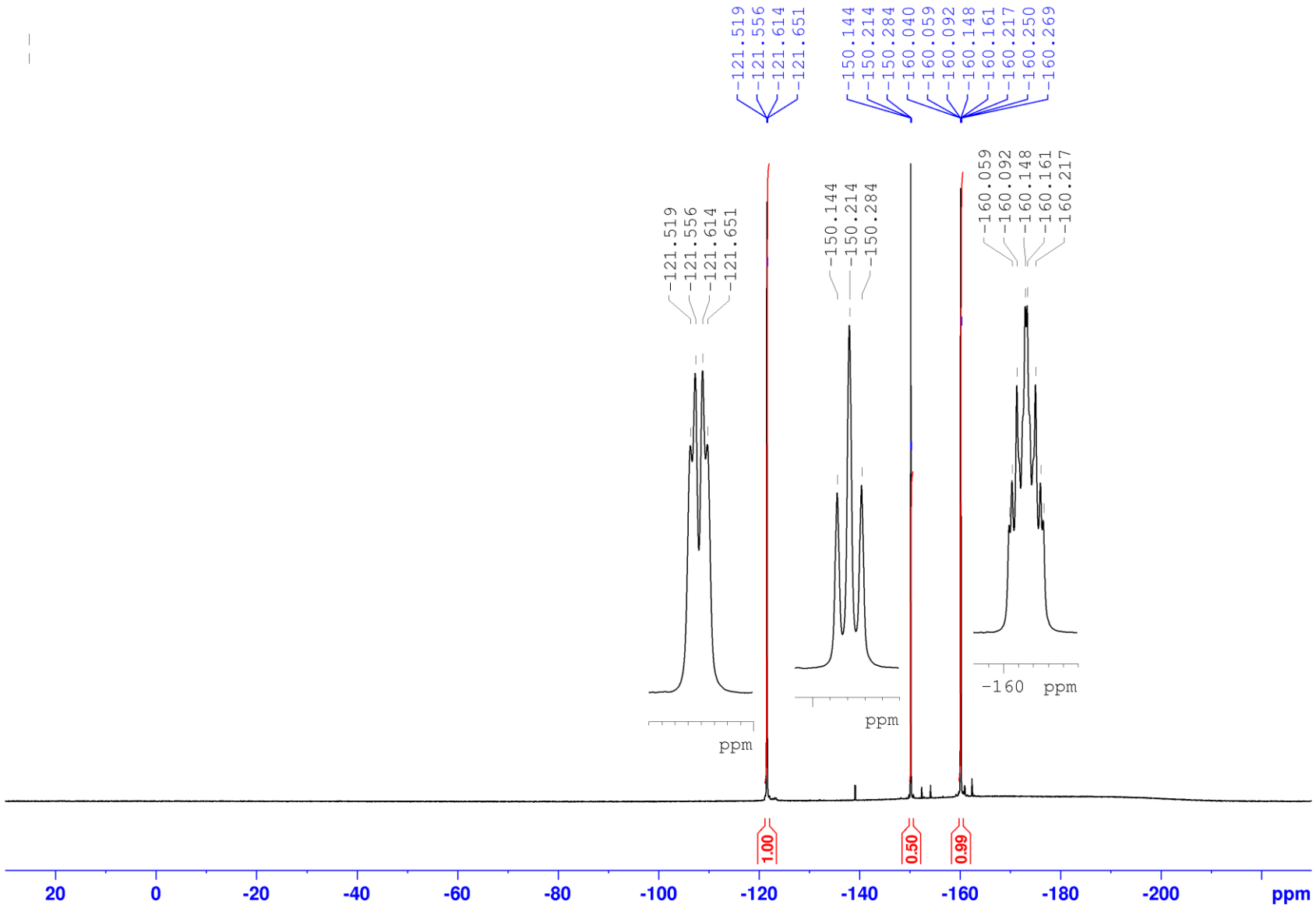
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot THF$ complex — Line shape analysis



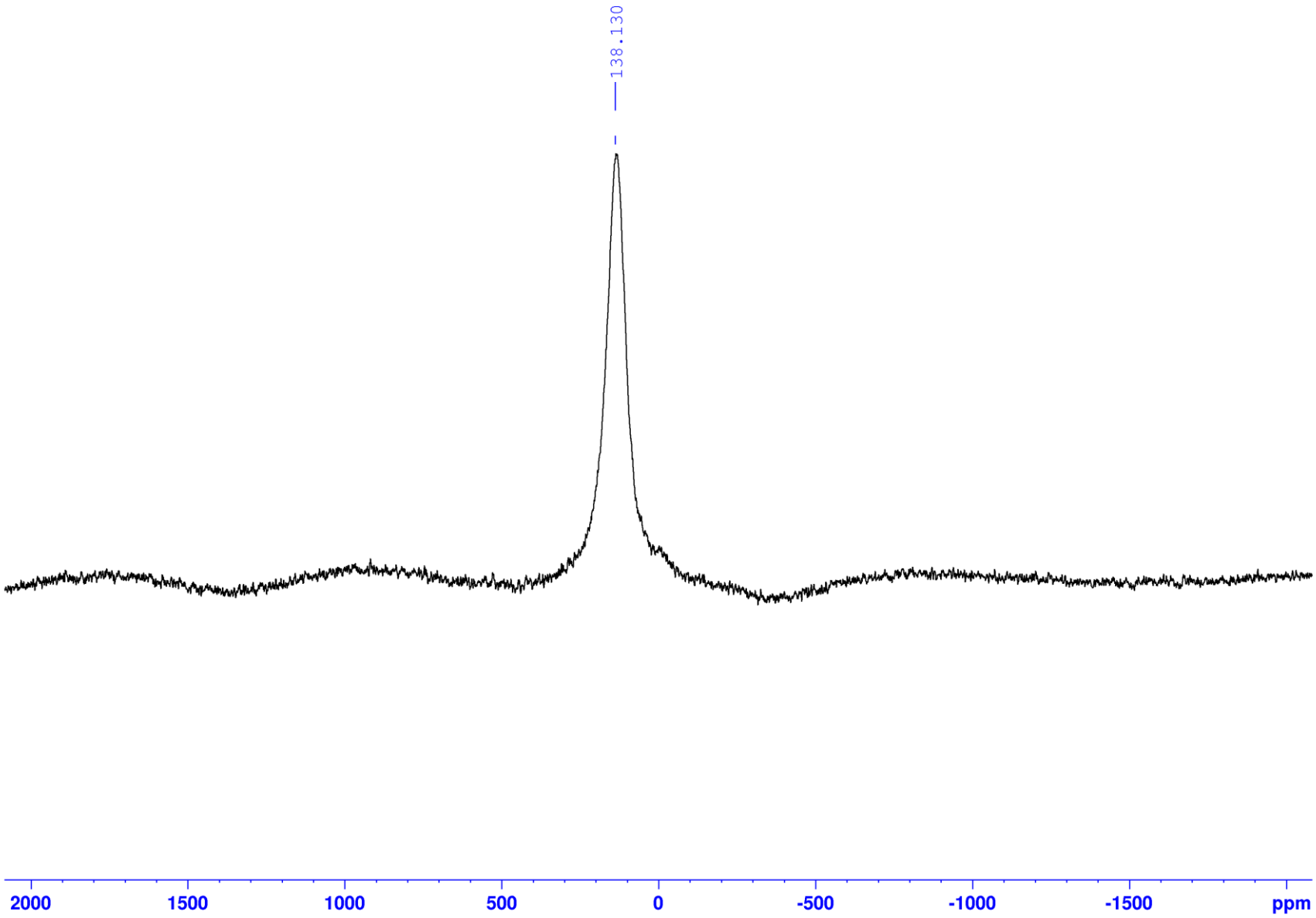
^{1}H NMR (300.1 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot Me_2S$ complex



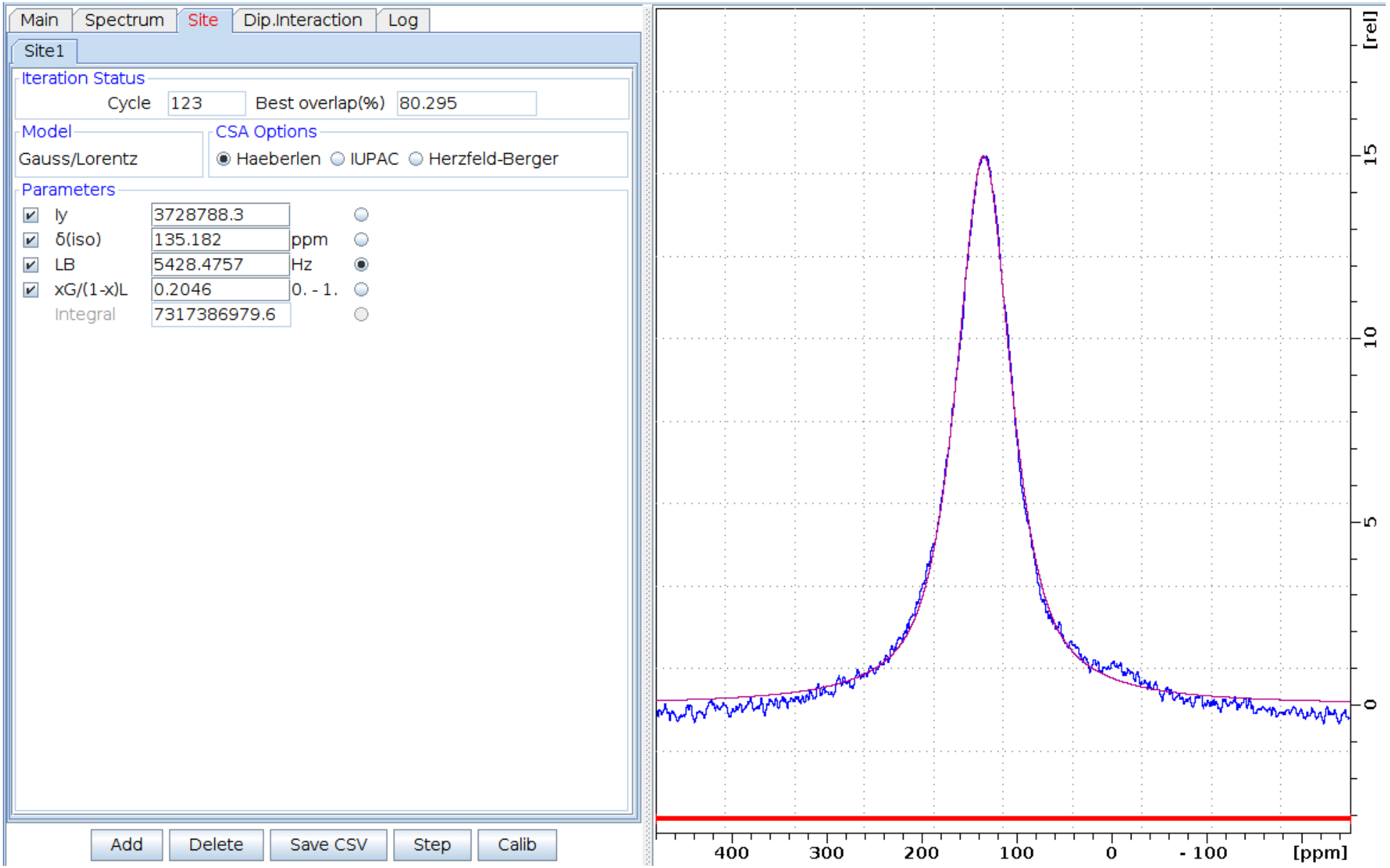
^{19}F NMR (282.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot Me_2S$ complex



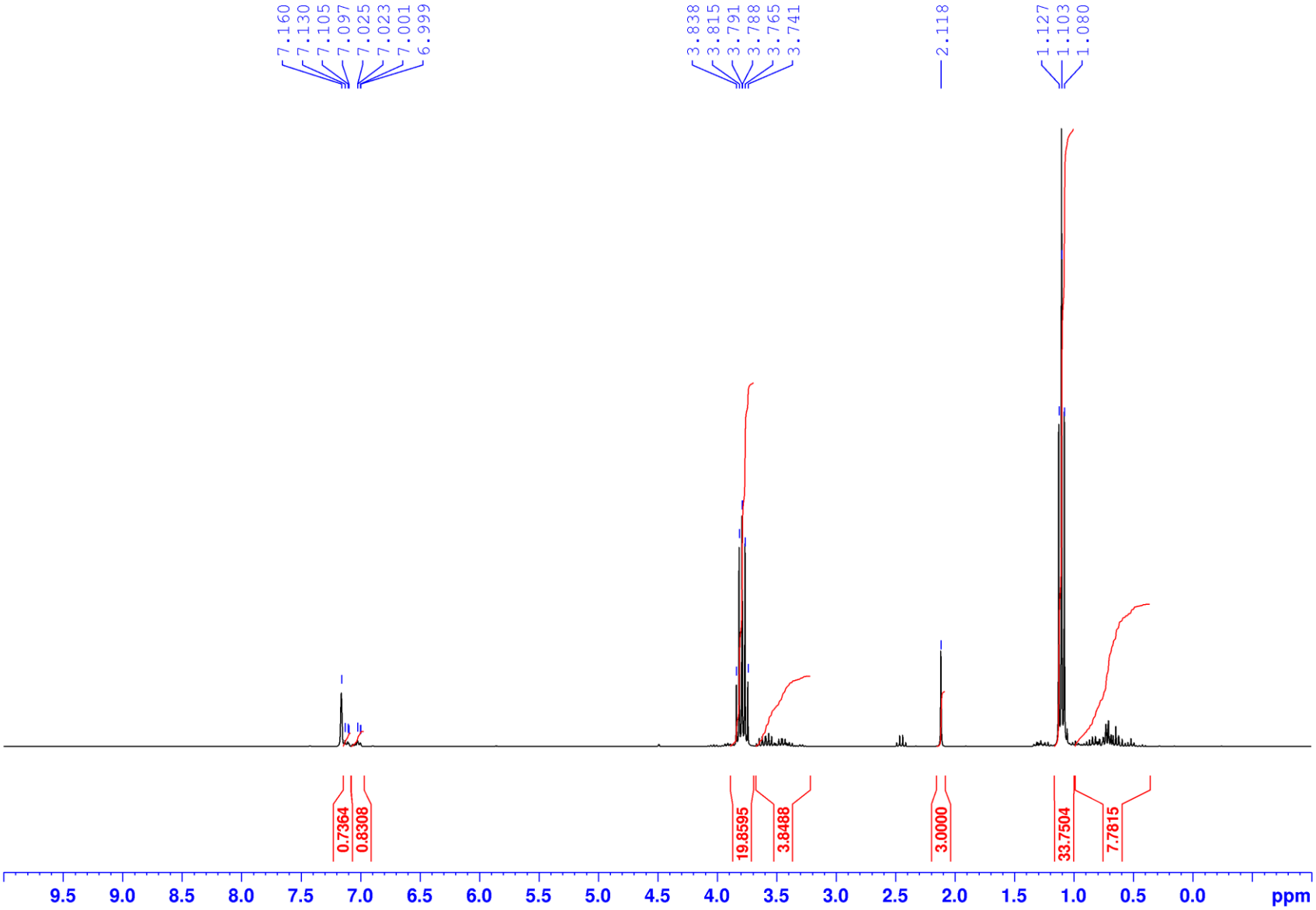
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot Me_2S$ complex



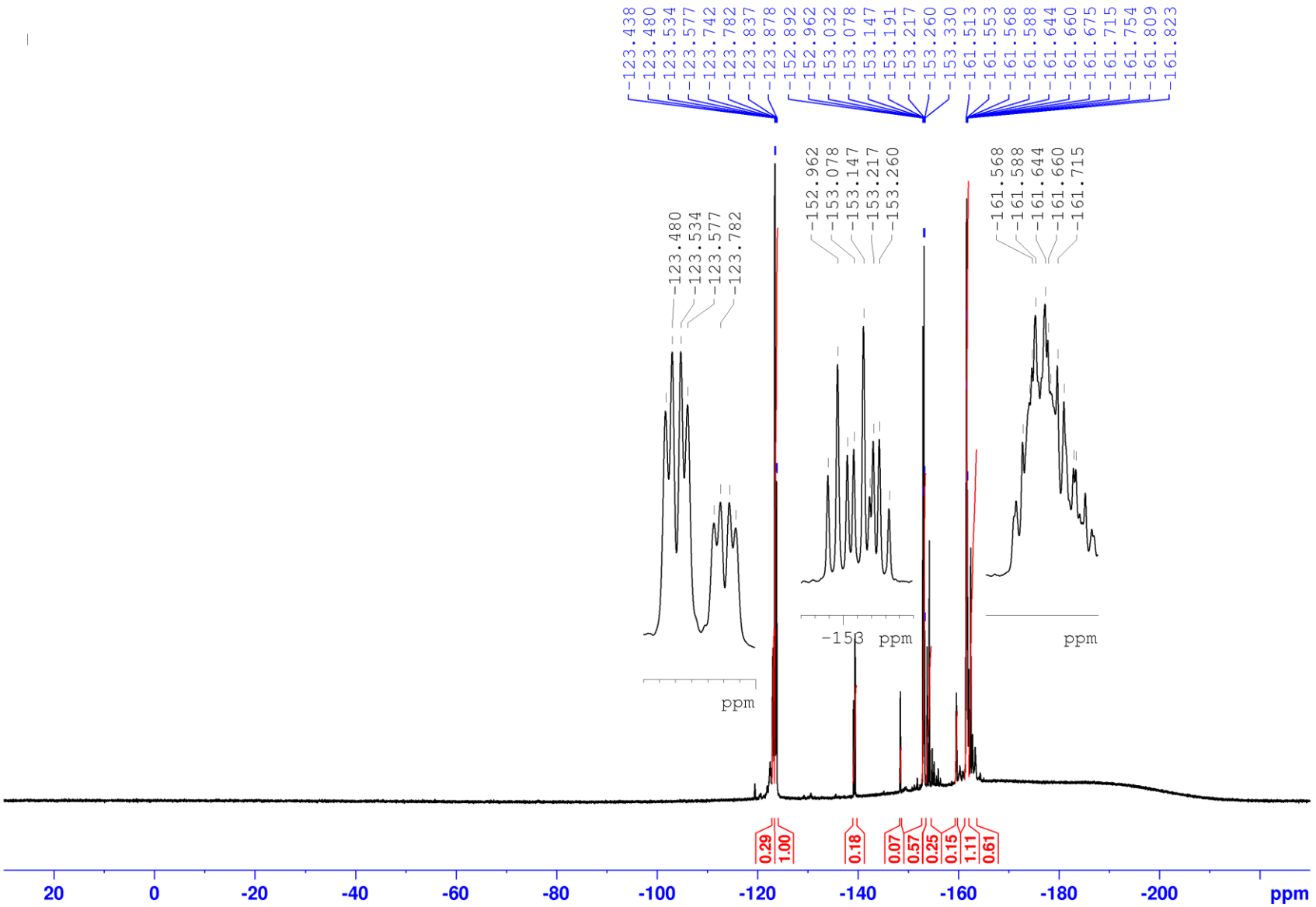
^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot Me_2S$ complex — Line shape analysis



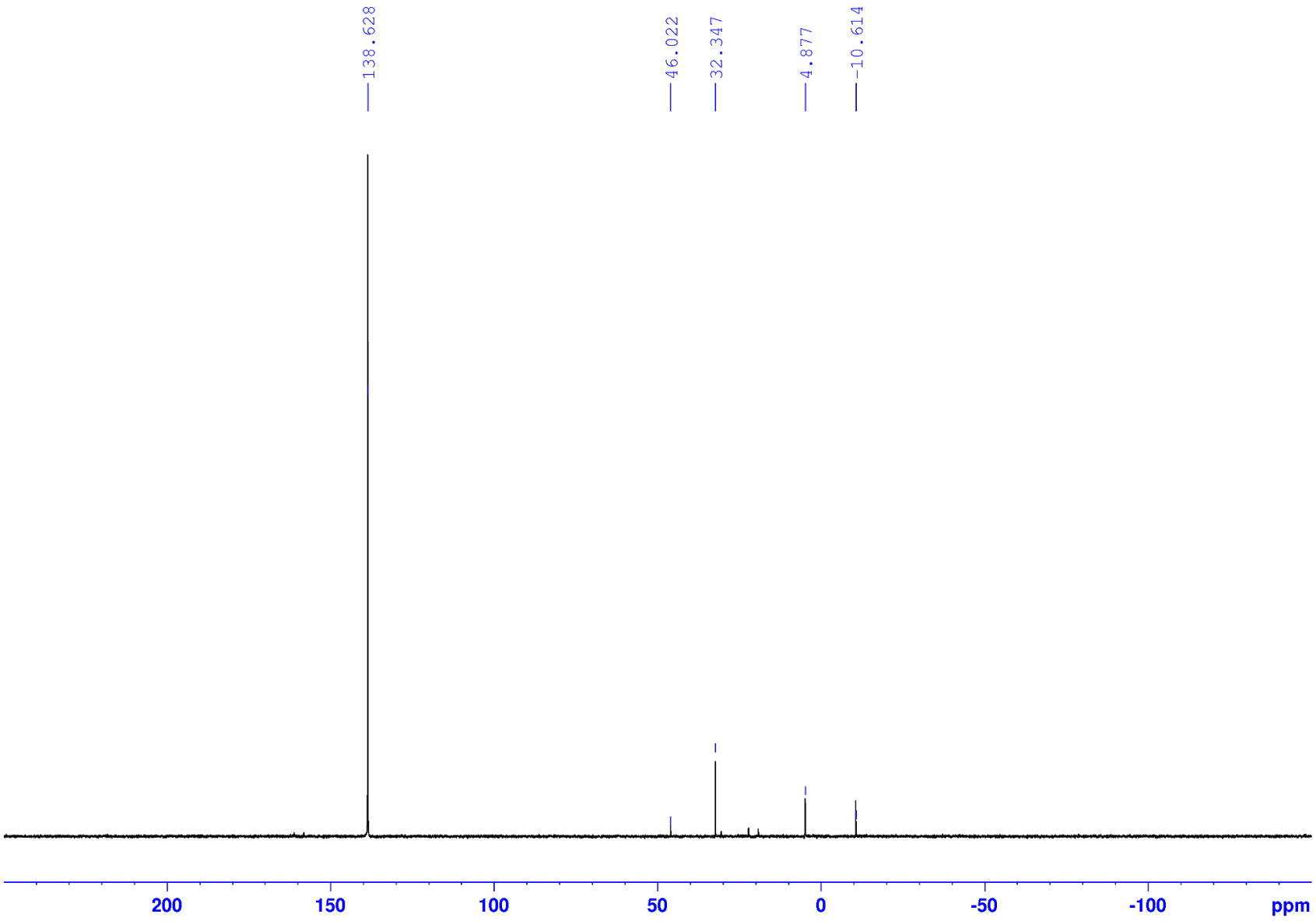
^{1}H NMR (300.1 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot P(OEt)_3$ complex



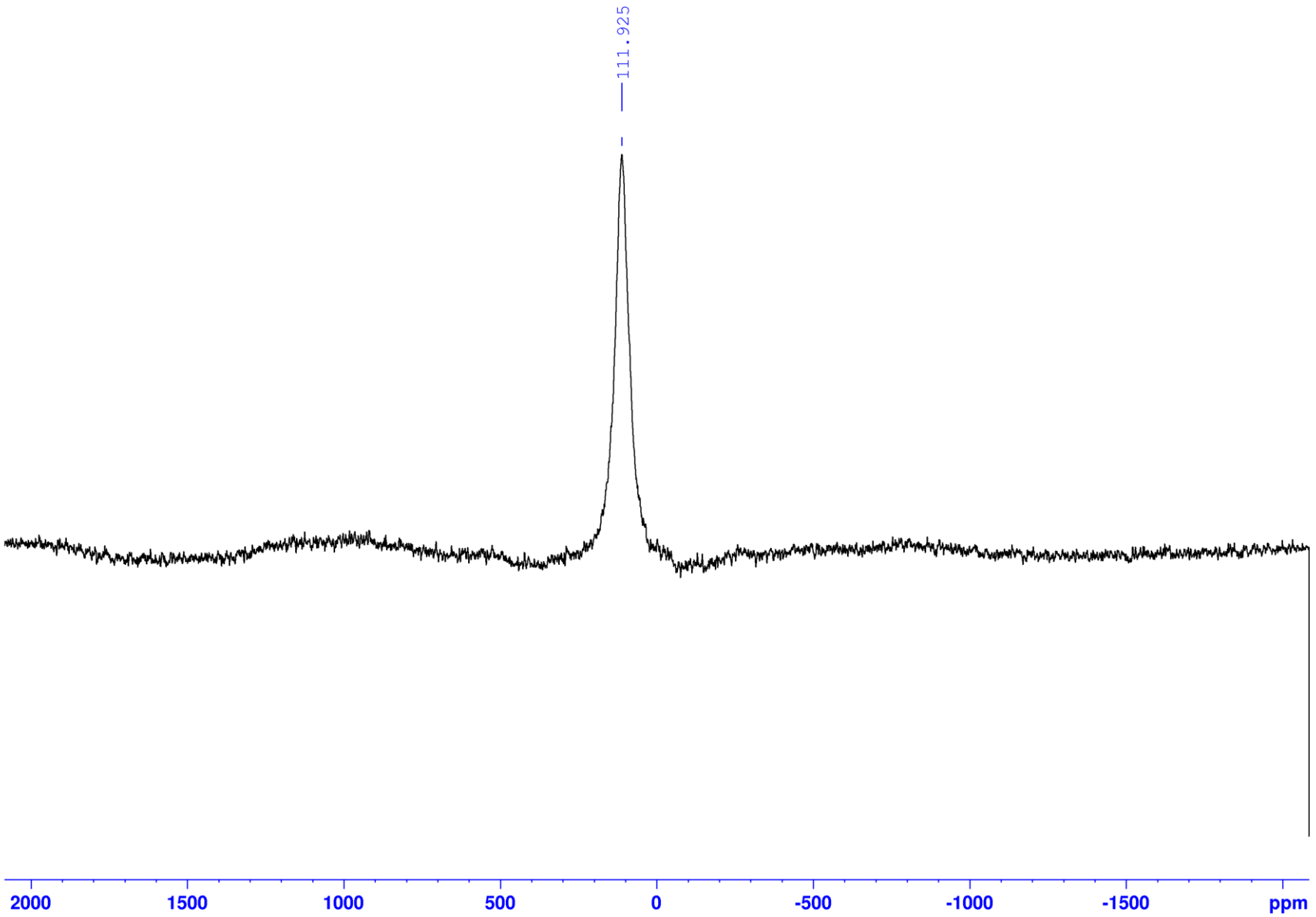
^{19}F NMR (282.4 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot P(OEt)_3$ complex



$^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot P(OEt)_3$ complex



^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot P(OEt)_3$ complex



^{27}Al NMR (78.2 MHz, C_6D_6, 298 K) of $Al(C_6F_5)_3 \cdot P(OEt)_3$ complex — Line shape analysis