Supporting Information

# Towards a Practical Perfluoroalkylation of (Hetero)Arenes using Cobalt Nanocatalysts and Perfluoroalkyl Bromides

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## 1. General comments

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under an argon atmosphere. All chemicals were purchased from *Aldrich*, *TCI*, *Alfa*, or *ABCR* and used without further purification. Acetone was dried over molsieves 4Å and was freezed out to remove oxygen before using. All perfluoroalkylation reactions were set up under argon in 10 mL thick-walled screw cap vial or in a 50 mL autoclave (PARR Instrument Company). Multiplets of NMR were assigned as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), br.s (broad singlet), and m (multiplet).

## 2. Analytical methods

$^{1}$H NMR spectra were recorded using Bruker AV300 (300 MHZ for 1H), Bruker AV400 (400 MHz for 1H) and Fourier 300 (300 MHZ for $^{1}$H) spectrometers. $^{19}$F NMR spectra were obtained at 282 MHz. Conversions and yields of perfluoroalkylation reactions were determined by 19 F NMR using either 1,4-difluorobenzene or 1,2-difluorobenzene as internal standard. For quantitative $^{19}$F NMR a puls delay of 30s are required. NMR chemical shifts are reported in parts per million (ppm) downfield from TMS and were referenced to the residual proton resonance and the natural abundance. All measurements were carried out at room temperature unless otherwise stated.

High resolution mass spectra were recorded on a MAT 95XP ThermoFisher Mass Spectrometer using Electrospray Ionization mode.

XRD pattern of the materials were recorded on a PANalytical X'Pert Pro diffractometer in reflection mode with Cu Kα radiation (λ=1.5406 Å) and a silicon strip detector (X'Celerator).

The XPS measurements were performed on an ESCALAB 220iXL (ThermoFischer Scientific) with monochromated Al Kα radiation (E = 1486.6 eV). Samples are prepared on a stainless-steel holder with conductive double-sided adhesive carbon tape. The electron binding energies were obtained with charge compensation using a flood electron source and referenced to the C1s peak assuming sp2 carbon as main component at 284.0 eV. For quantitative analysis the peaks were deconvoluted with Gaussian-Lorentzian curves using the software Unifit 2020, the peak areas were divided by the transmission function of the spectrometer and the element specific sensitivity factor of Scofield.[1]

Scanning transmission electron microscopy (STEM) measurements were performed at 80kV with a probe aberration-corrected JEM-ARM200F (microscope: JEOL, Japan; corrector: CEOS, Germany) using annular bright field (ABF) and high angle annular dark field (HAADF) detectors. The microscope is equipped with a JED-2300 (JEOL) energy-dispersive x-ray-spectrometer (EDXS) and an Enfinium ER electron energy loss spectrometer (EELS, Gatan, USA) for chemical analysis. The sample was deposed on a holey carbon supported Cu-grid (mesh 300) without any pretreatment and transferred to the microscope.

## 3. General procedures

### 3.1 Catalyst preparation

In a representative procedure for the preparation of 3% Co@N/C-800 (**Cat2**), $Co(OAc)_2{\cdot}4H_2O$ (0.5 mmol, 124.5 mg) and 1,10-phenanthroline (1.0 mmol, 180.2 mg) were solved in 50 mL ethanol for 30 minutes at room temperature. Next, carbon powder (689.7 mg, VULCAN® XC72R, Cabot Corporation Prod. Code XVC72R; CAS No. 1333-86-4) was added and the whole reaction mixture was refluxed for 4 hours. After cooling the reaction mixture to room temperature the ethanol was

removed in high vacuum and the remaining solid was dried at 60 °C for 12 hours. The catalyst was grinded to a fine powder and was transferred into a ceramic crucible and placed in an evacuated (5 mbar) and argon flushed oven. The oven was heated to 800 °C (25 °C per minute), and held at 800 °C for 2 hours under argon atmosphere. Next, the oven was switched off and cooled to room temperature. Argon was constantly passed through the oven during the whole process. Elemental analysis of **Cat2** (wt%)**:** C = 92.28, H = 0.20, N = 2.70, Co = 3.05, O = 1.32

**3.2 Synthesis protocol for the cobalt catalyzed perfluoroalkylation of (hetero)arenes**

In a representative procedure, to a 10 mL thick-walled screw cap vial with a magnetically stirring bar $Cs_2CO_3$ (1 mmol, 325.8 mg) and cobalt catalayst **Cat2** (10 mol% [Co], 200.0 mg) was added. The Vial was transferred into a schlenk chamber and evacuated and refilled with argon 3 times. Under argon atmosphere (hetero)arene substrate (10 mmol) was added. Additionally perfluorohexyl bromide (1 mmol, 213 µL) was introduced and the screw cap vial was closed. The closed vial was transferred into an aluminum block and heated while stirring for 24 h at 130 °C. Thereafter, the reaction mixture was cooled down with ice and diluted with 5ml diethylether. The suspension was centrifuged for 15min at 30000 RPM. The solution was decanted and the solid was washed 3 further times with diethylether. The etheric solutions were combined, an aliquot for the quantitative $^{19}F$ NMR and GCMS was taken and the solvent was evaporated under mild vacuum. The residue was purified by combi flash chromatography with pentane/ethyl acetate. For determining the yield 0.2 mmol 1,4-difluororbenzene was added as the standard and directly a $^{19}F$ NMR in $CDCl_3$ was recorded.

**3.3 Synthesis protocol for the cobalt catalyzed trifluoromethylation of (hetero)arenes**

In a 50 mL autoclave, **Cat2** (10 mol% [Co], 400 mg) and $Cs_2CO_3$ (1 mmol, 651.6 mg) were added. Next, 2 mmol (hetero)arene and 4 mL acetone were added. The autoclave was pressurized with the full pressure (ca. 12 bar) of the $CF_3Br$ bottle. Then the autoclave was heated to 130 °C with an aluminum block for 48 h.

**3.4 Synthesis protocol for the trifluoromethylation of acetophenone and recycling of the catalyst**

In a 100 mL round Schlenk, 20 mL acetone and 12 mmol acetophenone were freezed to remove oxygen. Next, in a 100 mL autoclave with mechanical stirrer from Parr Instrument **Cat2** (10 mol% [Co], 2.04 g) and $Cs_2CO_3$ (1.5 equiv, 18 mmol, 5.9 g) were added and under argon stream the acetone solution was transferred to the autoclave via a syringe. The autoclave is closed and spilled 5 min with argon and weighted. The $CF_3Br$ bottle was connected to the autoclave and the full pressure was given for 3 minutes. After weighting again ca. 26 g (174 mmol) of $CF_3Br$ was in the autoclave. The reaction was carried out at 130 °C for 48 h. After cooling to room temperature the black reaction solution was quantitatively filled in a 250 mL flask and the liquid phase was evaporated and condensed in another 250 mL flask. The black residue was suspended with water, filtrated and washed with water and $CH_2Cl_2$. After drying the catalyst can be reused up to 6 times. Next, the condensed colorless liquid is reduced on the rotavapor and was filled into a 20 mL volumetric flask for quantitative measurement. 0.4 ml was taken in a NMR tube, 20 µL 1,2-difluorobenzol was used as an internal standard and the tube was filled to 0.7 mL with $CDCl_3$. The quantitative $^{19}F$ NMR (Figure S1) was carried out with a puls delay of 30 s. The conversion was determined with GC by taking 1 mL of the stock solution and mixing it with 70.7 mg hexadecane.

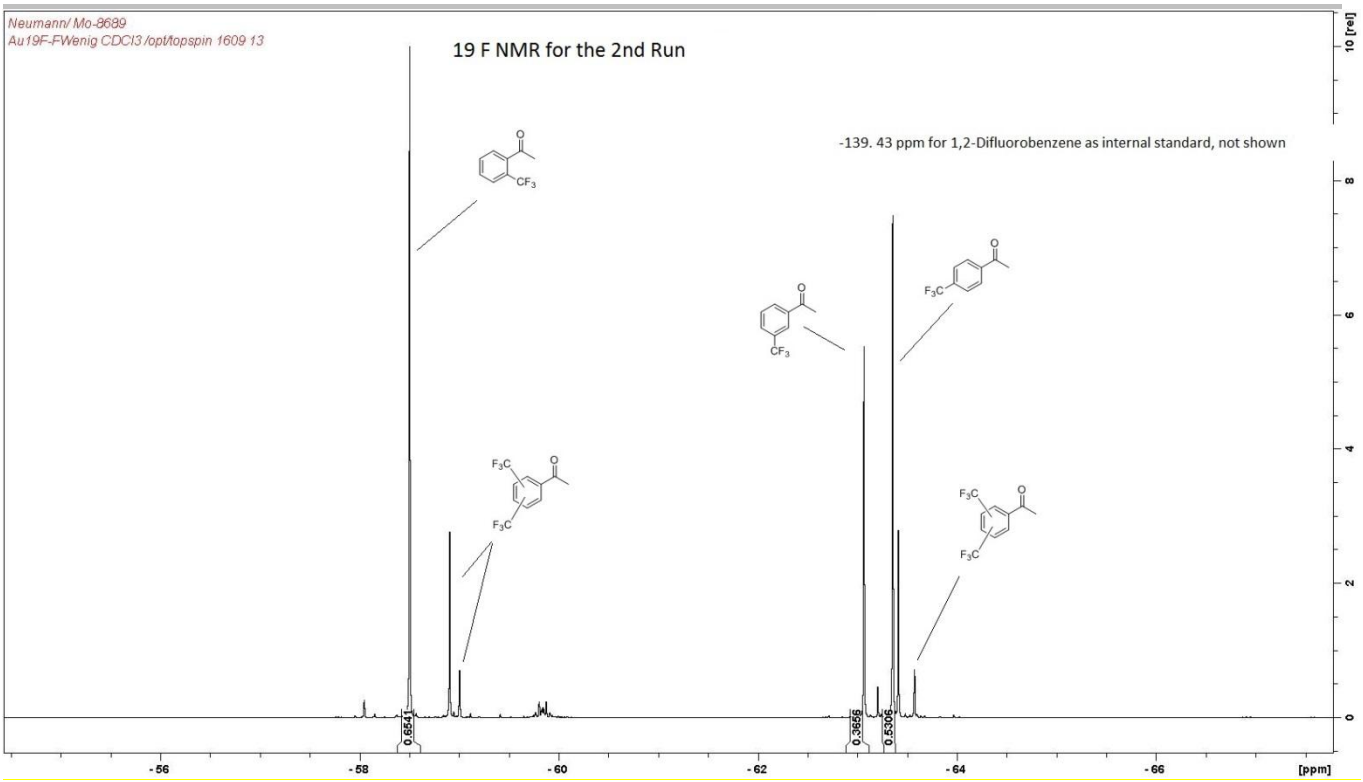



**Figure S1.** The quantitative $^{19}F$ NMR for determining the yield of trifluoromethylation of acetophenone.

### 3.5 An Example for the Evaluation of a typical $^{19}F$ NMR

The $^{19}F$ NMR spectrum gives full information with regard to yield, conversion, loss of fluorine and reduced sideproduct ($R_FH$). (Figure S2) Since the chemical shift of the -$CF_3$ group is identical for all products and educt the total amount of fluorine can be determined. Interestingly after each reaction some amount of the fluorine is missing. We envisioned that a part of the fluorine chain was decomposed into gaseous fragments, which are released during the opening of the reaction vessel. As an example of the calculations, cording to the 19F NMR, we calculated 43% yield, 88% conversion, 23% loss of fluorine and 11% reduced sideproduct for the perfluorohexylation of 4-picoline using **Cat1** as the catalyst.

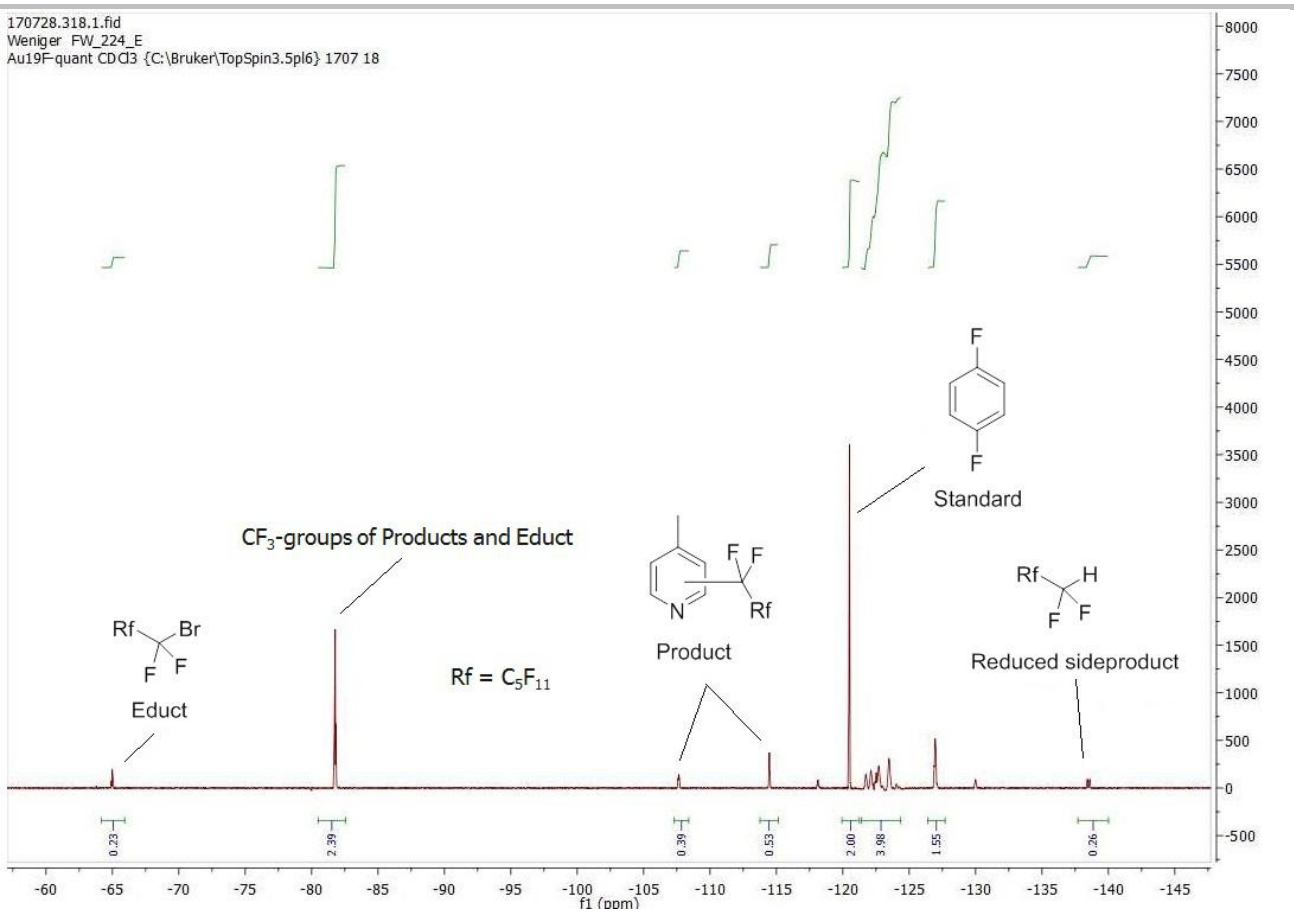



**Figure S2**. An Example for the Evaluation of a typical $^{19}F$ NMR.

## 4. Catalyst characterization

### 4.1 Powder X-ray Diffraction

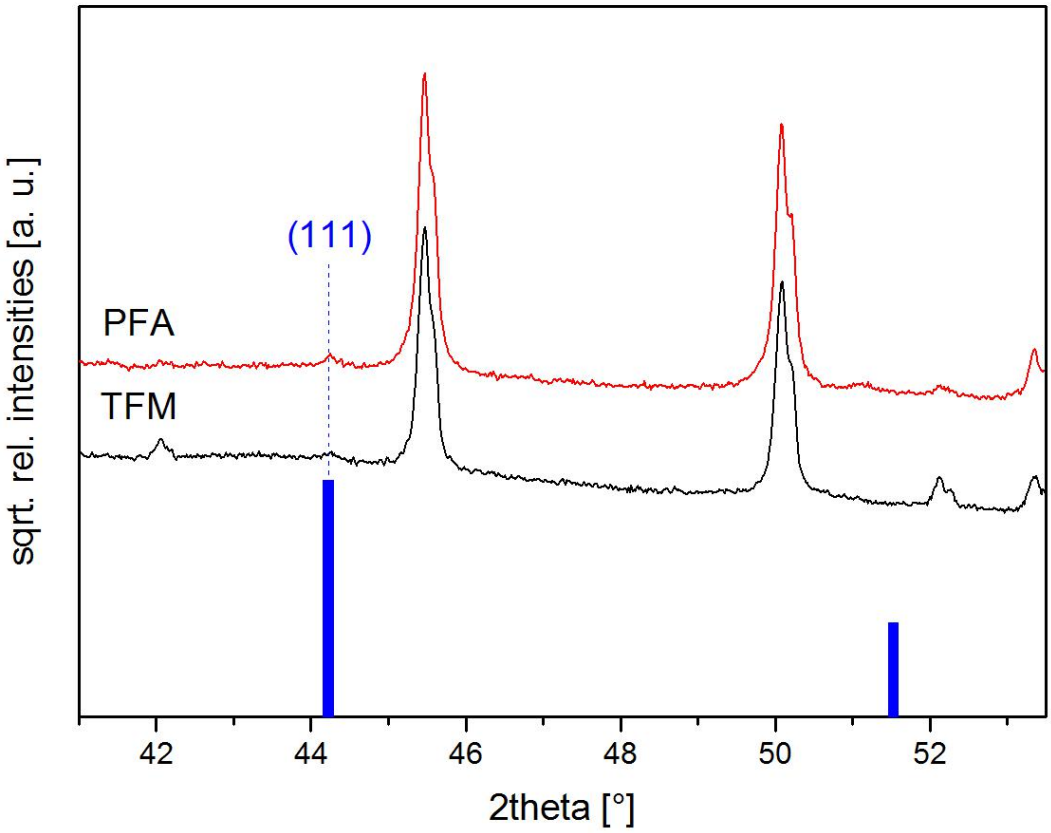



**Figure S3**. Detailed representation of the powder diffraction pattern of the catalyst after the 6th recycling step and reference peak positions of metallic Co (pdf 00-015-0806, ICDD, 2016). The diffraction peak at 44.22° 2theta can be indexed as (111) Brag reflex of the cubic modification of metallic cobalt.

### 4.2 X-ray photoelectron spectroscopy

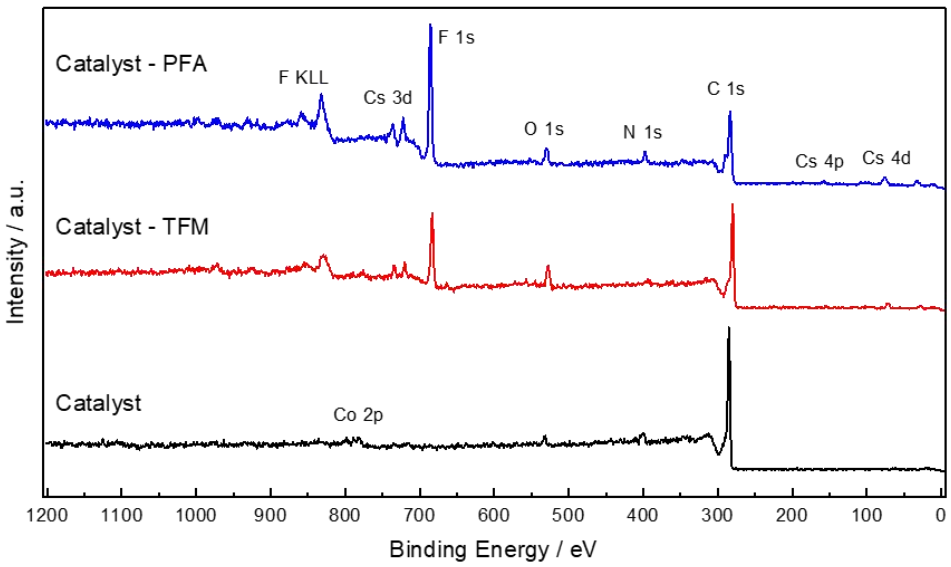



**Figure S4**. XPS survey spectra of the fresh and recycled catalyst after the 6th recycling of trifluoromethylation (TFM) and perfluoroalkylation (PFA). Whereas the fresh catalyst only shows signals for carbon, nitrogen, oxygen and cobalt, fluorine and cesium are clearly visible for both recycled catalysts.

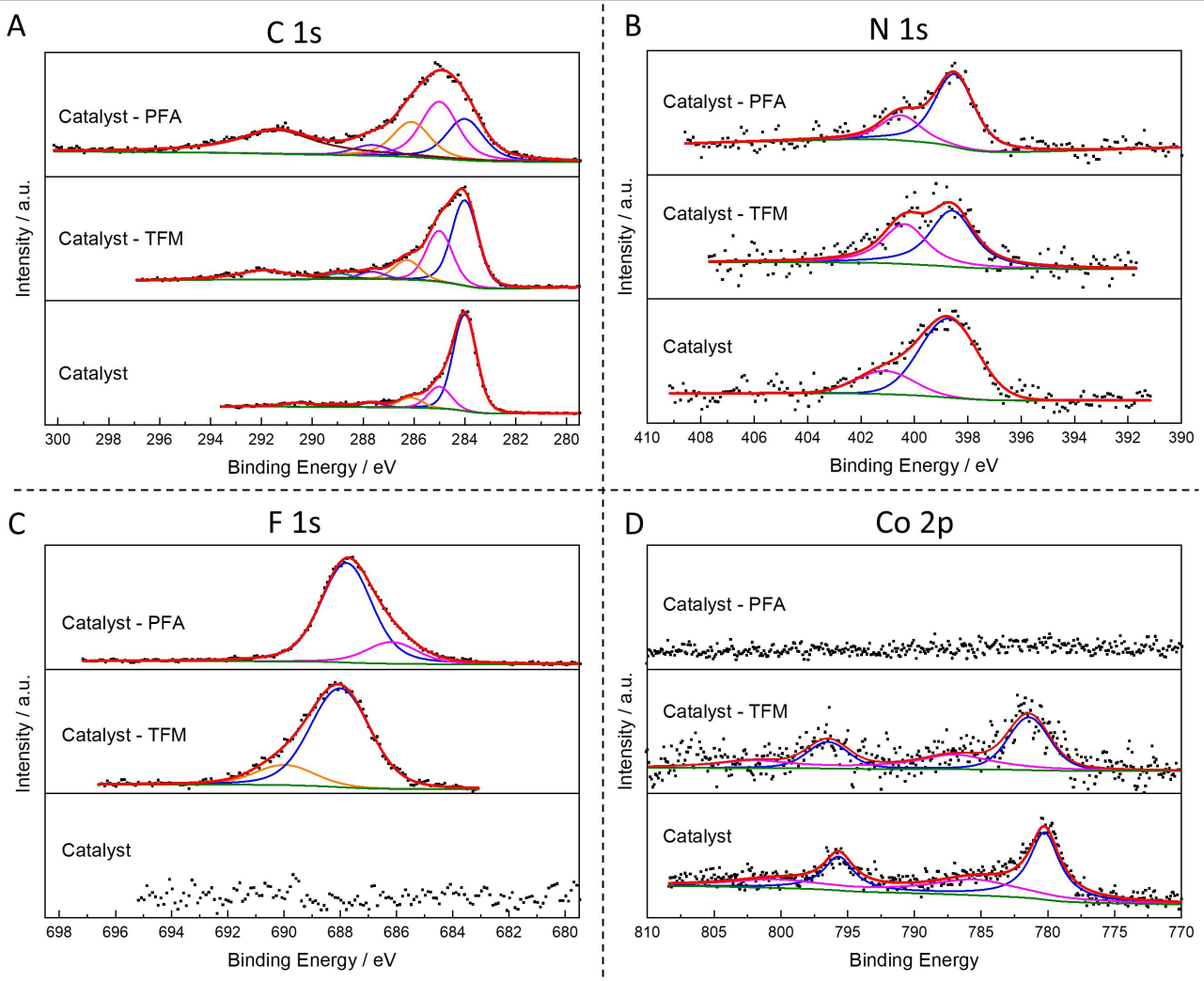



**Figure S5**. XP spectra of the fresh and recycled catalyst after the 6th cycle of trifluoromethylation (TFM) and perfluoroalkylation (PFA). A) The C 1s spectra of the fresh catalyst shows mainly C-C and C-C/C-H bonds at 248.0 eV and 248.8 eV whereas the spectra of the recycled materials clearly depict the formation of C-O/C-OH functionalities between 286 eV and 289 eV. A broad feature at about 292 eV binding energy indicates the formation of $CF_2$ at the surface. B) The N 1s region can be deconvoluted with two signals at 398.6 eV and 400.6 eV which are characteristic for pyridinic and pyrrolic nitrogen.[1] D) The F 1s spectra of the recycled catalysts show one main component at 688 eV characteristic for organic fluorine groups. In the fresh catalyst no F can be found. D) Co 2p region of the fresh and recycled catalyst. Only in the fresh catalyst and after trifluoromethylation cobalt can be found with a binding energy of about 780 eV characteristic for oxidic cobalt (probably Co3O4 as main component when considering the satellite structures).[2]

### 4.3. Additional STEM data

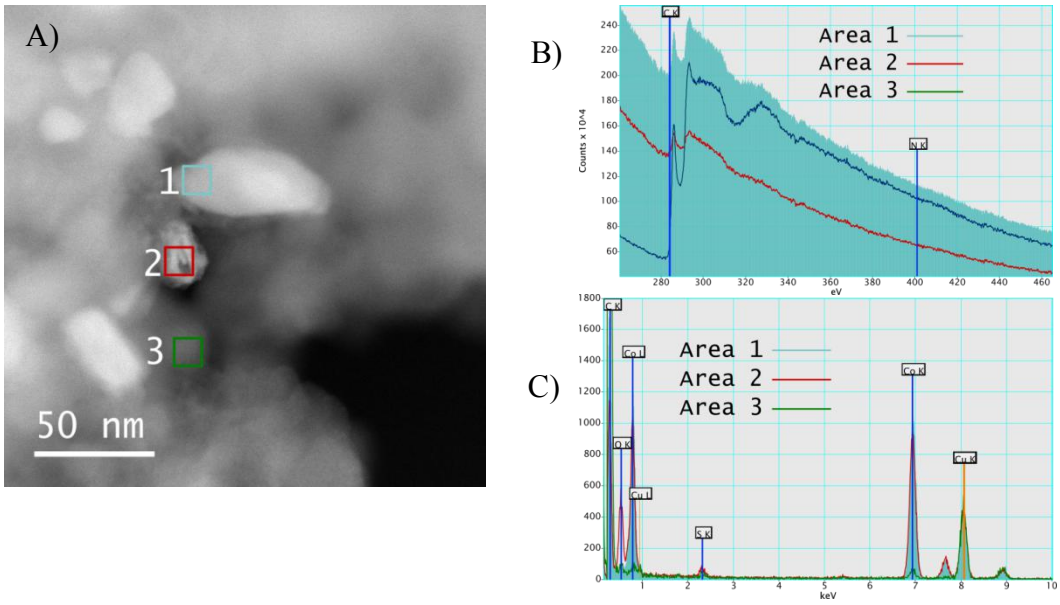



**Figure S6**. Fresh catalyst: A) ADF image with regions marked from which spectra were extracted from the spectrum imaging dataset. B) EELS data shows the similarity of the C and N content in all three areas whereas in C) the EDXS data shows the different composition of the particles in area 1 (metal Co) and 2 (Co oxide). Also, in area 3 there is Co present although not in the form of a particle but probably in a finely distributed manner.

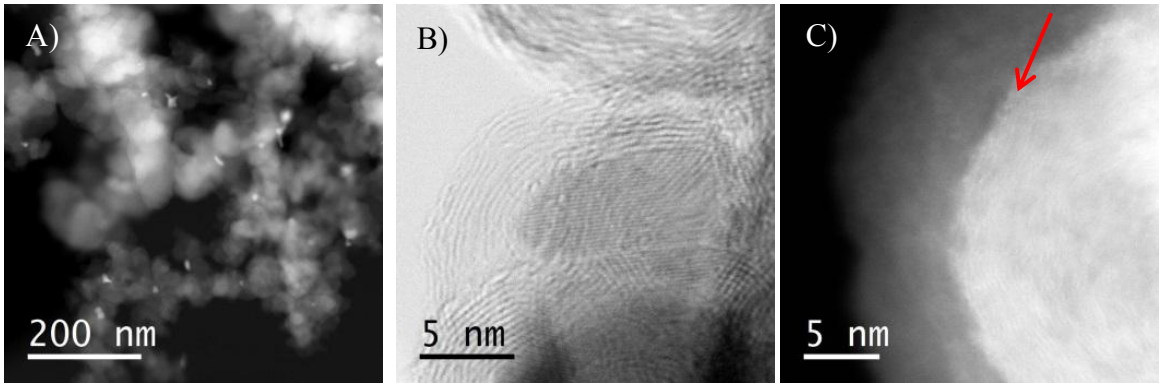



**Figure S7.** Fresh catalyst: A) HAADF-STEM image showing the general morphology with Co particles lighting up as bright particles compared to support. B) ABF-STEM image of a Co particle surrounded by graphitic carbon. C) HAADF-STEM images with high magnification showing dots on the surface of carbon support particle (bright onion like structure) possibly indicating a distributed Co phase.

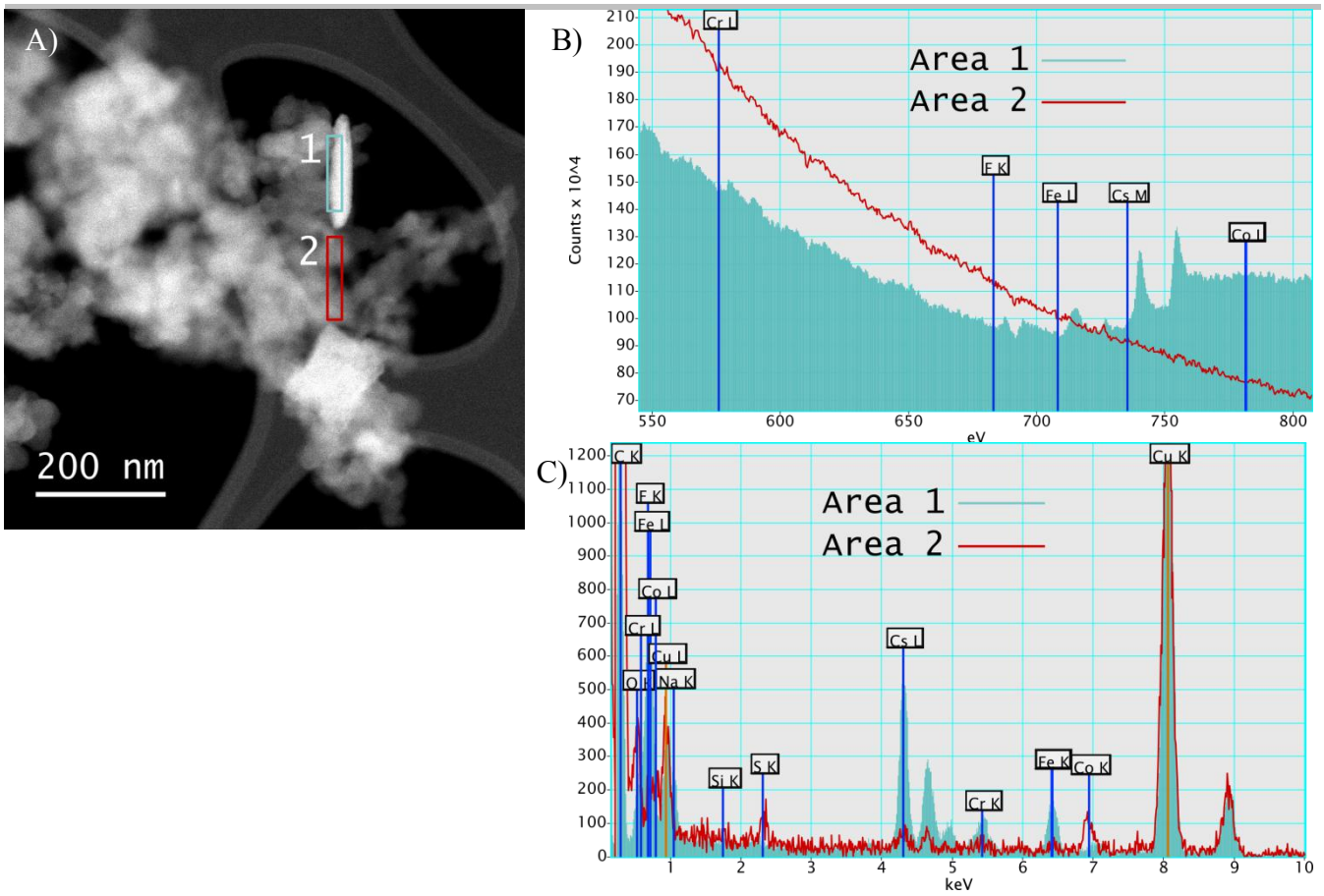



**Figure S8.** Catalyst TFM: A) ADF-STEM image with marked areas from which EELS and EDX spectra were extracted from the spectrum imaging dataset. B) Detail of the EELS data showing the presence of Cr, Fe, Cs and F in the bright particle in area 1 while Co content is negligible. This is also verified by EDX (C) data, which in contrast show the presence of a small amount of Co in area 2, indicating a prevalence of the distributed Co phase in the recycled catalyst.

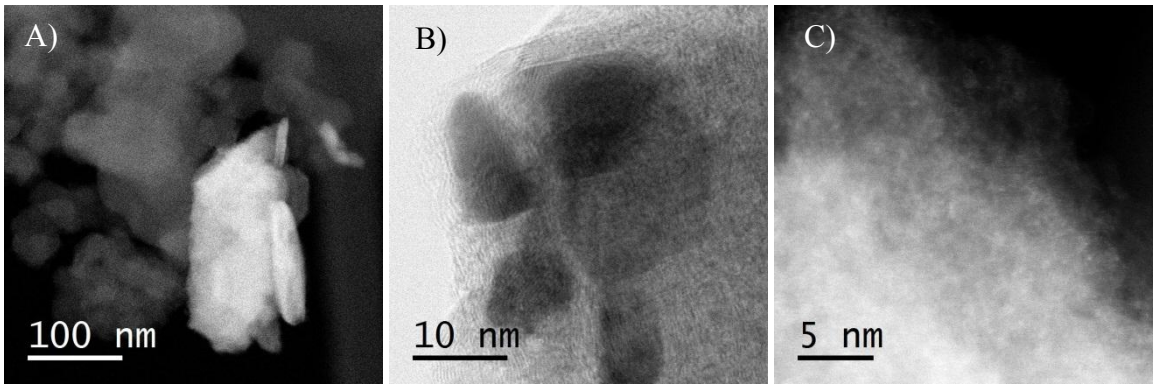



**Figure S9.** Catalyst TFM: A) HAADF-STEM images showing a larger Cs, F, Fe and Cr containing particle, B) ABF-STEM image of the graphitic shell of Co particles comparable to the fresh sample and C) HAADF-STEM image showing more pronounced dots in a carbon matrix probably indicating a distributed Cs containing phase.

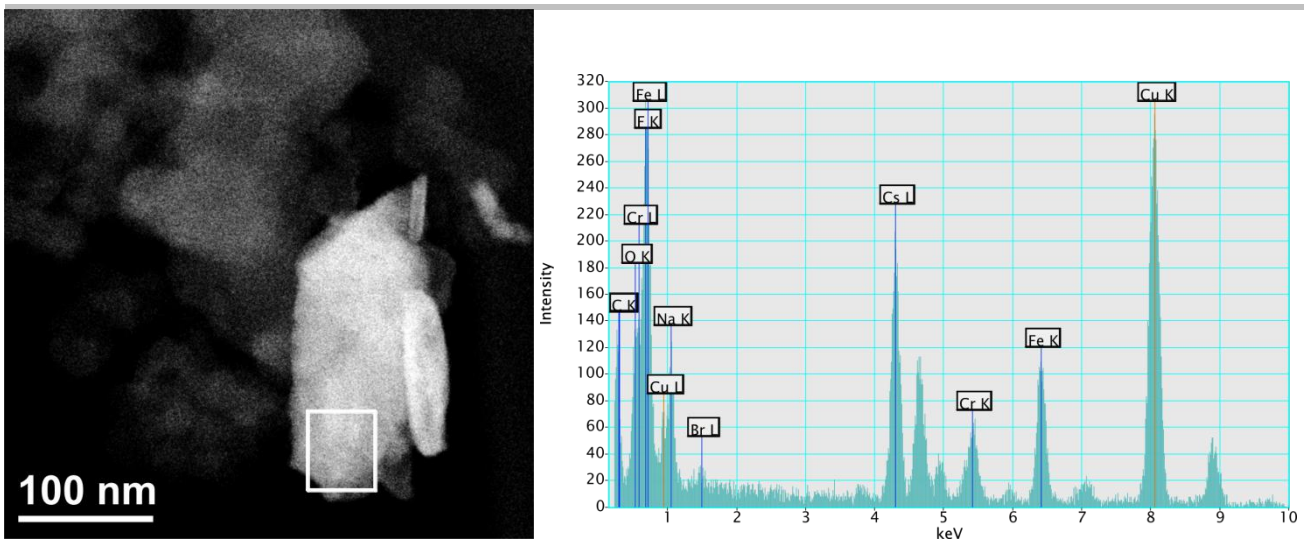



**Figure S10.** Catalyst TFM: HAADF-STEM image with region marked from which the EDX spectrum stems. This spectrum indicates the element composition of the large particle, consisting of F, O, Cr, Fe, Cs.

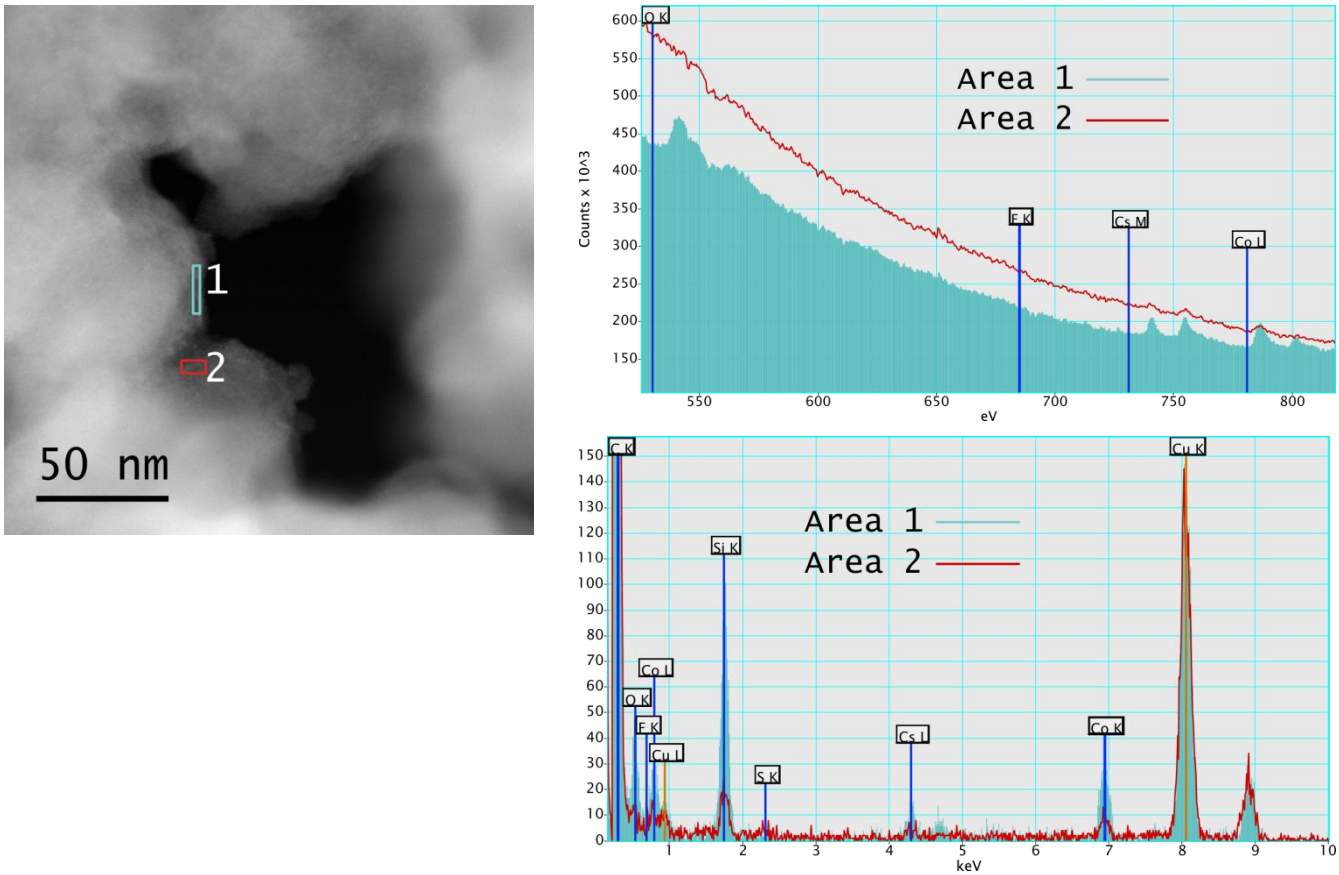



**Figure S11.** Catalyst-PFA: A) ADF-STEM image with marked areas from which EELS and EDX spectra were extracted from the spectrum imaging dataset. B) Detail of the EELS data showing the presence of Cs and Co in the bright part close to the surface in area 1. In addition, the corresponding EDX (C) data shows the strong presence of Si in area 1. In contrast, area 2 contains much less Si, Co and Cs although it is still present, while F seems to negligible in both areas.

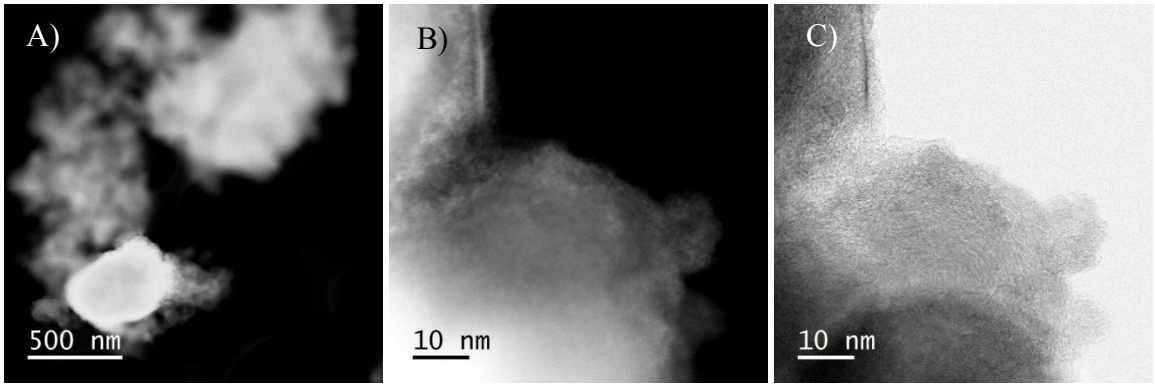



**Figure S12.** Catalyst-PFA: A) HAADF-STEM image of a large Cs, F and Si containing particle attached to the Vulcan support, B) HAADF-STEM image showing a close up of the area used in SZ1 with the bright parts on the surface of the support particles indicating the presence of Cs, C) ABF-STEM image corresponding to B).

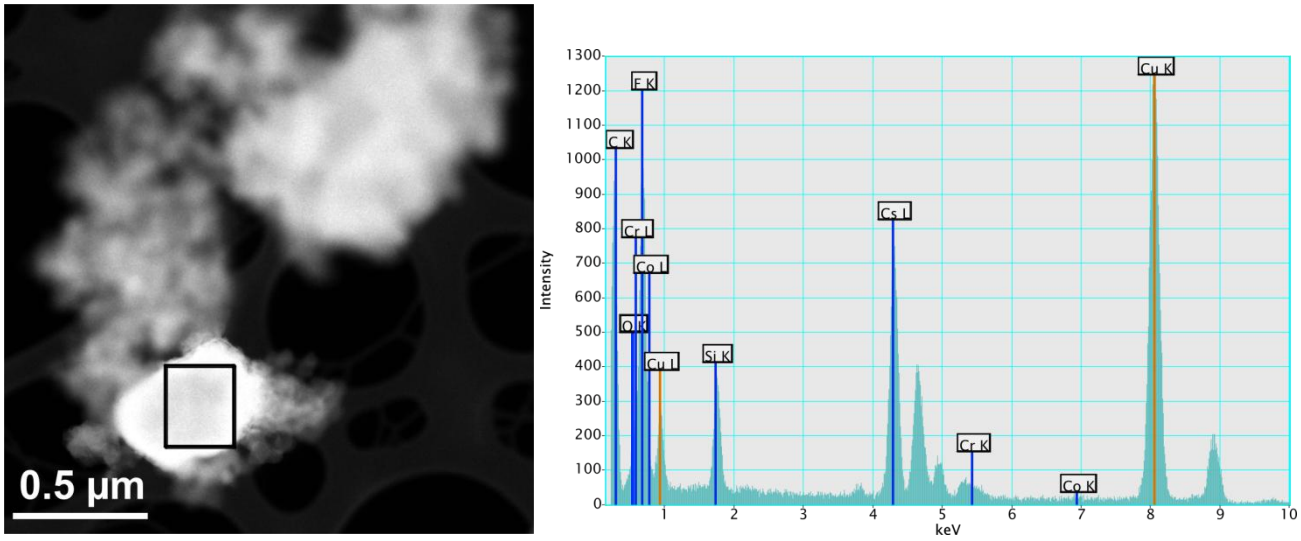
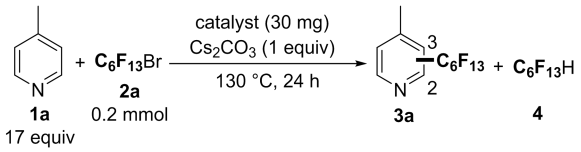



**Figure S13.** Catalyst-PFA: HAADF-STEM image with region marked from which the EDX spectrum stems. The spectrum indicates the element composition of the large particle, mainly consisting of F, O, Si and Cs.

## 5. Ancillary experimental data

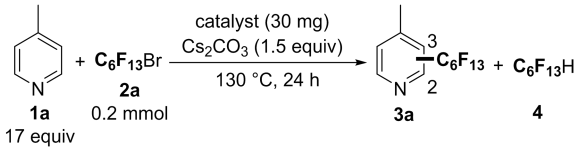
**Table S1**. Perfluorohexylation of 4-picoline with different cobalt catalysts prepared from different cobalt precursors.




| entry | cobalt precursor | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|
| 1 | $Co(OAc)_2{\cdot}4H_2O$ | 82 | 30 | 37 | 7 | 38 |
| 2 | $CoCl_2{\cdot}6H_2O$ | 64 | 6 | 9 | 3 | 55 |
| 3 | $CoSO_4{\cdot}7H_2O$ | 62 | 5 | 8 | 8 | 54 |
| 4 | $Co(NO_3)_2{\cdot}6H_2O$ | 62 | 4 | 7 | 4 | 55 |

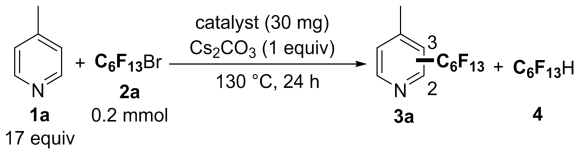
| | | | | | | |
|---|---|---|---|---|---|---|
| 5 | $Co_3(PO_4)_2$ | 60 | 3 | 5 | 3 | 55 |

**Table S2**. Perfluorohexylation of 4-picoline with different cobalt catalysts prepared using different supports.




| entry | support | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|
| 1 | $\alpha$-$Al_2O_3$ | 47 | 0 | 0 | 5 | 42 |
| 2 | $SnO_2$ | 47 | 0 | 0 | 5 | 37 |
| 3 | BN | 48 | 0 | 0 | 5 | 41 |
| 4 | $B_2O_3$ | 43 | 0 | 0 | 4 | 37 |
| 5 | MgO | 49 | 4 | 8 | 7 | 36 |
| 6 | ZrO | 43 | 0 | 0 | 5 | 37 |
| 7 | $CeO_2$ | 45 | 0 | 0 | 5 | 37 |
| 8 | $TiO_2$ (anatase) | 57 | 7 | 12 | 7 | 41 |
| 9 | $V_2O_5$ | 46 | 0 | 0 | 4 | 41 |
| 10 | $SiO_2$ | 41 | 0 | 0 | 4 | 35 |
| 11 | ZnO | 56 | 8 | 14 | 9 | 36 |

**Table S3**. Perfluorohexylation of 4-picoline with acid-washed cobalt catalysts.

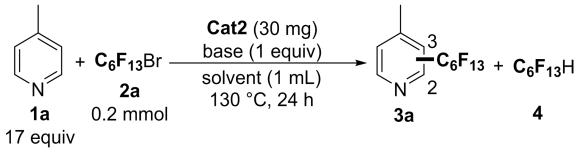



| entry | catalyst | cobalt precursor | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|---|
| 1 | Co@N/C | $Co(OAc)_2{\cdot}4H_2O$ | 67 | 20 | 30 | 10 | 33 |
| 2 | Co@N/C | $CoCl_2{\cdot}6H_2O$ | 64 | 18 | 28 | 9 | 34 |
| 3 | Co@N/C | $CoSO_4{\cdot}7H_2O$ | 55 | 11 | 20 | 8 | 32 |
| 4 | Co@N/C | $Co(NO_3)_2{\cdot}6H_2O$ | 56 | 13 | 23 | 9 | 31 |
| 5 | Co@N/C | $Co_3(PO_4)_2$ | 47 | 8 | 17 | 9 | 28 |
| 6 | Co@N/MS4Å | $Co(OAc)_2{\cdot}4H_2O$ | 41 | 4 | 10 | 5 | 33 |
| 7 | Co@/TiO2 (rutile) | $Co(OAc)_2{\cdot}4H_2O$ | 44 | 0 | 0 | 6 | 38 |
| 8 | Co@N/$\alpha$-$Al_2O_3$ | $Co(OAc)_2{\cdot}4H_2O$ | 46 | 0 | 0 | 6 | 42 |
| 9 | Co@N/SnO | $Co(OAc)_2{\cdot}4H_2O$ | 46 | 0 | 0 | 5 | 41 |
| 10 | Co@N/BN | $Co(OAc)_2{\cdot}4H_2O$ | 43 | 0 | 0 | 5 | 37 |
| 11 | Co@N/$B_2O_3$ | $Co(OAc)_2{\cdot}4H_2O$ | 46 | 2 | 4 | 5 | 39 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 12 | Co@/ZrO | $Co(OAc)_2{\cdot}4H_2O$ | 49 | 0 | 0 | 4 | 43 |
| 13 | $Co@/CeO_2$ | $Co(OAc)_2{\cdot}4H_2O$ | 54 | 5 | 10 | 5 | 42 |
| 14 | Co@/BC | $Co(OAc)_2{\cdot}4H_2O$ | 48 | 0 | 0 | 4 | 40 |
| 15 | Co@/TiO2 (anatas) | $Co(OAc)_2{\cdot}4H_2O$ | 52 | 3 | 5 | 5 | 43 |
| 16 | $Co@/V_2O_5$ | $Co(OAc)_2{\cdot}4H_2O$ | 64 | 10 | 16 | 11 | 39 |
| 17 | $Co@/SiO_2$ | $Co(OAc)_2{\cdot}4H_2O$ | 42 | 0 | 0 | 3 | 37 |

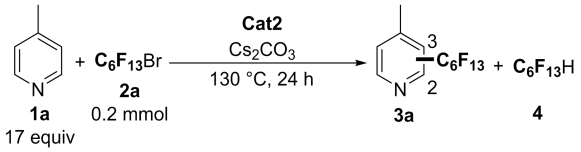
Reaction conditions: Catalysts were washed with 0.5 M $H_2SO_4$ for 8h at 80°C after preparation. Yields and conversions were determined by $^{19}F$ NMR with 1,4-difluorobenzene as standard.

**Table S4**. Cobalt-catalyzed perfluorohexylation of 4-picoline in different solvents.




| entry | solvent | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|
| 1 | heptane | 97 | 2 | 2 | 78 | 8 |
| 2 | cyclohexane | 100 | 1 | 1 | 81 | 10 |
| 3 | perfluorhexane | 100 | 0 | 0 | 25 | - |
| 4 | $CH_3CN$ | 100 | 9 | 9 | 44 | 28 |
| 5 | acetone | 95 | 21 | 22 | 36 | 26 |
| 6 | DMSO | 95 | 0 | 0 | 29 | 52 |
| 7 | $CH_2Cl_2$ | 19 | 0 | 0 | 0 | 17 |
| 8 | $CHCl_3$ | 13 | 0 | 0 | 0 | 12 |
| 9 | DCE | 30 | 0 | 0 | 0 | 27 |
| 10 | $CH_2Cl_2/H_2O$ (3:1) | 37 | 1 | 3 | 1 | 30 |
| 11 | EtOAc | 79 | 10 | 13 | 46 | 15 |
| 12 | DMA | 100 | 3 | 3 | 51 | 35 |

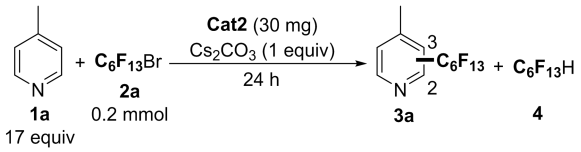
**Table S5**. Cobalt-catalyzed perfluorohexylation of 4-picoline with different amount of catalyst and base.




| entry | amount of **Cat2** | amount of $Cs_2CO_3$ | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|---|
| 1 | 40 mg | 0 | 38 | 12 | 32 | 19 | 3 |
| 2 | 40 mg | 1 equiv | 100 | 47 | 47 | 41 | 9 |
| 3 | 40 mg | 2 equiv | 100 | 41 | 41 | 49 | 5 |
| 4 | 20 mg | 2 equiv | 93 | 27 | 29 | 54 | 8 |

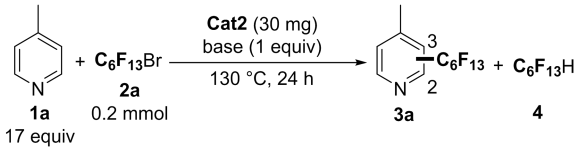
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 5 | 20 mg | 1 equiv | 88 | 27 | 31 | 51 | 6 |
| 6 | 5 mg | 1 equiv | 52 | <5 | 10 | 47 | 3 |

**Table S6**. Cobalt-catalyzed perfluorohexylation of 4-picoline at different temperatures.



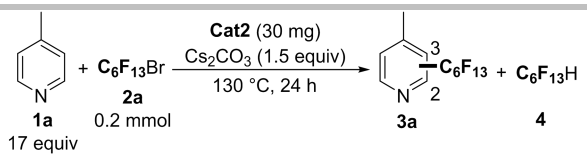

| entry | temperature | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|
| 1 | 90 °C | 39 | 0 | 0 | 0 | 37 |
| 2 | 100 °C | 40 | 0 | 0 | 0 | 38 |
| 3 | 110 °C | 42 | 2 | 5 | 3 | 36 |
| 4 | 120 °C | 67 | 22 | 33 | 7 | 34 |
| 5 | 130 °C | 99 | 46 | 46 | 5 | 39 |
| 6 | 140 °C | 100 | 44 | 44 | 6 | 45 |

**Table S7**. Cobalt-catalyzed perfluorohexylation of 4-picoline at different temperatures.



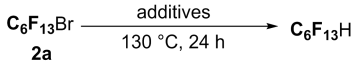

| entry | base | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|
| 1 | No base | 38 | 13 | 34 | 3 | 19 |
| 2 | $Cs_2CO_3$ | 100 | 60 | 60 | 12 | 22 |
| 3 | $K_2CO_3$ | 87 | 49 | 56 | 8 | 22 |
| 4 | $KHCO_3$ | 78 | 48 | 61 | 8 | 11 |
| 5 | KOAc | 69 | 35 | 51 | 6 | 16 |
| 6 | $K_3PO_4$ | 83 | 51 | 61 | 8 | 14 |
| 7 | $K_2HPO_4$ | 63 | 31 | 49 | 5 | 19 |
| 8 | KOH | 87 | 47 | 54 | 13 | 22 |
| 9 | $Mg(OH)_2$ | 40 | 13 | 33 | 3 | 22 |
| 10 | $HNEt_2$ | 92 | 18 | 20 | 24 | 36 |
| 11 | $NEt_3$ | 99 | 10 | 10 | 42 | 31 |
| 12 | DBU | 100 | 11 | 11 | 42 | 31 |

**Table S8**. Cobalt-catalyzed perfluorohexylation of 4-picoline with different additives.




| entry | additive | conversion of **2a** / % | yield of **3a** / % | selectivity of **3a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|---|---|
| 1 | 10 mol% ($n$-Bu)$_4$NBr | 100 | 33 | 33 | 30 | 27 |
| 2 | 15 mol% $PPh_3$ | 100 | 45 | 45 | 23 | 25 |
| 3 | 1 equiv $PPh_3$ | 100 | 37 | 37 | 9 | 28 |
| 4 | 1 equiv LiCl | 92 | 47 | 51 | 13 | 27 |
| 5 | 1 equiv LiBr | 78 | 30 | 38 | 20 | 27 |
| 6 | 1 equiv Zn (dust) | 95 | 30 | 32 | 20 | 40 |

**Table S9**. Degradation of perfluoroalkyl reagent.

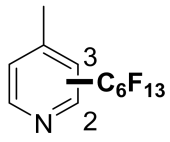



| entry | additives | conversion of **2a** / % | yield of **4** / % | loss of **2a** / % |
|---|---|---|---|---|
| 1 | $C_6F_{13}Br$ | 25 | 0 | 25 |
| 2 | $C_6F_{13}Br$ + $Cs_2CO_3$ | 27 | 0 | 26 |
| 3 | $C_6F_{13}Br$ + $Cs_2CO_3$ + **Cat2** | 43 | 0 | 42 |
| 4 | $C_6F_{13}Br$ + **Cat2** | 41 | 0 | 41 |

## 6. Characterization data

### 6.1 Perfluoroalkylated (hetero)arenes

Notes: For the $^{13}C$ NMR (F coupled), peaks for the C of perfluoroalkyl chain and C adjacent to perfluoroalkyl chain (in most cases) are too broad to be assigned (not shown in the following data).

**3a**, 


**2- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.62 (d, J = 5.1Hz, -Py, 1H), 7.51 (s -Py, 1H), 7.31 (d, J = 5.6 Hz, 1H, -Py), 2.46 (m, 3H, $CH_3$).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.37 (tt, J = 9.9 Hz, J = 2.3 Hz, 3F, $CF_3$), -113.60 (t, J = 14.0 Hz, 2F, ArCF2), -121.15, -121.42, -122.37, -125.73 (m, 8F, CF2, chain).

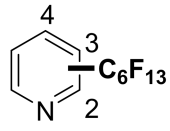
**HRMS (ESI):** m/z$^+$calcd for $C_{12}H_6F_{13}N$ $(M+H)^+$ 412.03654; found 412.03651.

**3- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.70 (s, 1H, py), 8.62 (d, J = 4.7Hz, 1H, py), 7.32 (d, J = 4.7 Hz, 1H, py), 2.51 (m, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.35 (tt, J = 10.0 Hz and J = 2.2 Hz, 3F, CF3), -106.64 (pseudo t, J = 15.4 Hz, 2F, ArCF2), -120.64, -121.22, -122.32, -125.69 (m, 8F, CF2, chain).

**HRMS (ESI):** m/z$^+$calcd for $C_{12}H_6F_{13}N$ $(M+H)^+$ 412.03654; found 412.03659.

**3b**, 


**2- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.79 (d, J = 4.4 Hz, 1H, py), 7.91 (t, J = 8.2Hz, 1H, py), 7.71 (d, J = 8.2 Hz, 1H, py), 7.52 (m, 1H, py).

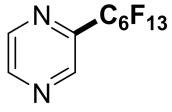
**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.9 Hz and J = 2.3 Hz, 3F, CF3), -113.7 (pseudo t, J = 13.6 Hz, 2F, pyCF2), -121.2, -121.5, -122.4, -125.7 (m, 8F, CF2, chain).

**HRMS (ESI):** m/z$^+$calcd for $C_{11}H_4F_{13}N$ $(M+H)^+$ 398.02089; found 398.02073.

**3- isomer:**

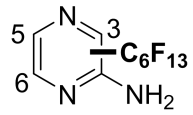
**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.85 (m, 2H, py), 7.92 (d, J = 8.3Hz, 1H, py), 7.48 (m, 1H, py).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.9 Hz and J = 2.3 Hz, 3F, CF3), -111.2 (t, J = 15.5 Hz, 2F, pyCF2), -121.0, -121.5, -122.4, -125.7 (m, 8F, CF2, chain).

**3c**, 


**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.97 (d, J = 41.5 Hz, 1H, pyz), 8.83 (m, 1H, pyz), 8.76 (m, 1H, pyz).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (m, 3F, CF3), -114.3 (t, J = 12.6 Hz, 2F, pyzCF2), -121.1 - -121.5, -122.4, -125.8 (m, 8F, CF2 chain).

**3d**, 


**3- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.20 (d, J = 2.2 Hz, 1H, pyz), 8.06 (d, J = 2.2Hz, 1H, pyz), 5.15 (s,2H, NH2).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.9 Hz and J = 2.3 Hz, 3F, CF3), -122.5 (t, J = 14.2 Hz, 2F, pyzCF2), -121.1, -121.5, -122.4, -125.7 m, (8F, CF2, chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 152.77, 146.01, 133.73.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+):146.05, 133.76.

**HRMS (ESI):** m/z$^+$calcd for $C_{10}H_4F_{13}N_3$ $(M+H)^+$ 414.02704; found 414.02639

**5- isomer:**

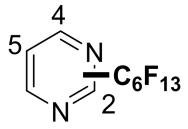
**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.31 (d, J = 1.4 Hz, 1H, pyz), 8.04 (d, J = 1.4 Hz, 1H, pyz), 5.03 (s,2H, NH2).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.9 Hz and J = 2.3 Hz, 3F, CF3), -113.3 (tt, J = 13.4 Hz, J = 2.9 Hz. 2F, pyzCF2), -121.2, -121.8, -122.4, -125.7 (m, 8F, CF2, chain).

**6- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 8.25 (s, 1H, pyz), 8.16 (s, 1H, pyz), 4.90 (s,2H, NH2).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.9 Hz and J = 2.3 Hz, 3F, CF3), -114.7 (t, J = 13.5 Hz, 2F, pyzCF2), -121.2, -121.5, -122.3, -125.7 (m, 8F, CF2, chain).




**3e,**

**2- isomer:**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 8.95 (d, J = 4.8 Hz, 2H, pyz), 7.53 (t, J = 4.8 Hz, 1H, pyz).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (m, 3F, CF3), -114.5 (t, J = 12.9 Hz, 2F, pyzCF2), -121.0, -122.6 (m 6F, CF2), -125.8 (m, 2F, CF2).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 157.87, 123.00.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 157.89, 123.02.

**HRMS (EI, 70 eV):** m/z$^{+}$calcd for $C_{10}H_3F_{13}N$ $(M)^{+}$ 398.00831; found 398.00832

**4- isomer:**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 9.43 (s, 1H, pyz), 9.03 (d, J = 4.9Hz, 1H, pyz), 7.70 (dd, J = 4.9 Hz, J = 1.4 Hz, 1H, pyz).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (t, J = 9.8 Hz 3F, CF3), -115.6 (t, J = 13.2 Hz, 2F, pyzCF2), -121.0, -121.4, -122.4, -125.8 (m, 8F, CF2, chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 159.10, 158.96, 119.08 (t, *J* = 4.3 Hz).

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 159.13, 158.99, 119.11 (t, *J* = 4.2 Hz).

**HRMS (EI, 70 eV):** m/z$^{+}$calcd for $C_{10}H_3F_{13}N$ $(M)^{+}$ 398.00831; found 398.00832

**5- isomer:**

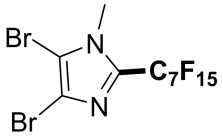
**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 9.45 (s, 1H, pyz), 8.96 (s,2H, pyz).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (m, 3F, CF3), -112.1 (t, J = 12.9 Hz, 2F, pyzCF2), -120.9, -121.4, -122.4, -125.7 (m, 8F, CF2, chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 161.50, 155.37 (t, *J* = 6.2 Hz).

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 161.53, 155.40 (t, *J* = 6.3 Hz).

**HRMS (EI, 70 eV):** m/z$^{+}$calcd for $C_{10}H_3F_{13}N$ $(M)^{+}$ 398.00831; found 398.00832

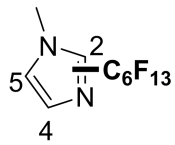



**3f,**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 3.79 (s, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.1 Hz, 3F, CF3), -108.2 (t, J = 14.4 Hz, 2F, imCF2), -120.5, -120.9, -121.5, -122.3, 125.7 (m, 10F, CF2 chain).

**HRMS (ESI):** m/z$^{+}$calcd for $C_{11}H_3Br_2F_{15}N_2$ $(M+H)^{+}$ 608.84761; found 608.84737




**3g,**

**2- isomer:**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** 7.13 (m, 1H, im), 7.00 (m, 1H, im), 3.79 (s, 3H, CH3).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 129.39, 125.58, 34.47.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 129.40, 125.61, 34.49.

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.6 (m, 3F, CF3), -107.8 (m, 2F, imCF2), -121.1, -121.3, -122.5, -125.9 (m 8F, CF2, chain).

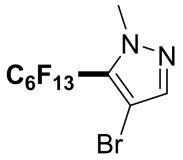
**HRMS (EI, 70 eV):** $C_{10}H_5F_{13}N_2$ 401.03179; found 401.03168.

**5- isomer:**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.52 (s,1H, im), 7.38 (s, 1H, im), 3.70 (s, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.8 (m, 3F, CF3), -105.9 (m, 2F, imCF2), -121.0, -121.5, -122.7, -126.1 (m 8F, CF2, chain).

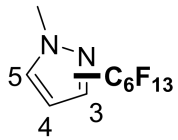
**HRMS (EI, 70 eV):** $C_{10}H_5F_{13}N_2$ 401.03179; found 401.03154

**3h**, 


**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.52 (t, J = 0.9 Hz, 1H, pz), 4.00 (t, J = 1.9 Hz, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.9 Hz, J = 2.3 Hz, 3F, CF3), -107.4 (t, J = 13.5 Hz, 2F, pzCF2), -120.9, -121.5, -122.3, -125.7 (m, 8F, CF2 chain).

**GCMS (EI, 70 eV) *m*:*z* (relative intensity):** 411 and 409 ($M^+$-$CF_3$, 1 and 1), 211 and 209 ($M^+$-$C_5F_{11}$, 97 and 100).

**3i,** 


**3- isomer:**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.44 (s, 1H, pz), 6.53 (d, J = 2.1 Hz, 1H, pz), 3.99 (s, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.7 Hz, J = 2.4 Hz, 3F, CF3), -109.2 (t, J = 13.7 Hz, 2F, pzCF2), -121.2, -122.2, -122.5, -125.7 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 131.48, 106.25, 39.62.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 131.52, 106.28, 39.65.

**HRMS (ESI):** m/z$^+$calcd for $C_{10}H_5F_{13}N_2$ $(M+H)^+$ 401.03179; found 401.03114.

**4- isomer:**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.67 (s, 1H, pz), 7.62 (s, 1H, pz), 3.96 (s, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (t, J = 9.1 Hz, 3F, CF3), -104.1 (t, J = 14.3 Hz, 2F, pzCF2), -121.1, -122.3, -122.5, -125.7 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 137.98 (t, *J* = 4.5 Hz), 130.18 (t, *J* = 4.9 Hz), 39.42.

**HRMS (ESI):** m/z$^+$calcd for $C_{10}H_5F_{13}N_2$ $(M+H)^+$ 401.03179; found 401.03137.

**5- isomer:**

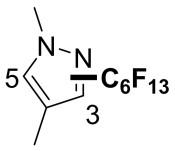
**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.52 (m, 1H, pz), 6.61 (d, J = 2.0 Hz, 1H, pz), 4.0 (s, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (t, J = 10.0 Hz, 3F, CF3), -106.7 (t, J = 14.7 Hz, 2F, pzCF2), -120.9, -121.3, -122.4, -125.7 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 138.50, 109.91, 39.02.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 138.53, 109.94, 39.04.

**HRMS (ESI):** m/z$^+$calcd for $C_{10}H_5F_{13}N_2$ $(M+H)^+$ 401.03179; found 401.03135.




**3j,**

**3- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 7.22 (s, 1H, pz), 3.89 (s, 3H, NCH3), 2.12 (s, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (t, J = 10.0 Hz, 3F, CF3), -108.9 (t, J = 14.1 Hz, 2F, pzCF2), -121.3, -131.8, -122.4, -125.7 (8F, $CF_2$ chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 131.17, 117.72, 39.41, 8.37.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 131.20, 39.44, 8.40.

**5- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 7.33 (s, 1H, pz), 3.94 (t, J = 1.7 Hz, 3H, NCH3), 2.14 (t, J = 2.3 Hz, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (t, J = 10.1 Hz, 3F, CF3), -107.3 (t, J = 14.2 Hz, 2F, pzCF2), -121.6 (4F, CF2 chain), -122.4, -125.8 (m, 4F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 139.84, 121.32, 39.51, 9.00.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 139.86, 39.50, 9.03.


**3k,**

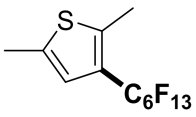
**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 6.75 (pseudo t, J = 2.2 Hz, 1H, pyrrole), 6.75 (m, 1H, pyrrole), 6.16 (pseudo t, J = 3.5 Hz, 1H, pyrrole), 3.72 (s, 3H CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.8 Hz, J = 2.3 Hz, 3F, CF3), -104.1 (t, J = 13.6 Hz, 2F, pyrroleCF2), -120.6, -121.3, -122.4, -125.8 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 128.15, 114.54 (t, *J* = 5.4 Hz), 107.93, 35.83.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 128.15, 114.53 (t, *J* = 5.4 Hz), 107.93, 35.83 (p, *J* = 3.4 Hz).

**GCMS (EI, 70 eV) *m*:*z* (relative intensity):** 399 ($M^+$, 29), 380 (11), 130 (100).




**3l,**

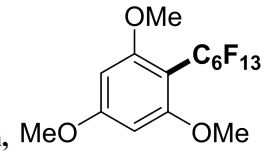
**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 6.67 (s,1H, thiophene), 2.47 (m,3H, CH3), 2.40 (s, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 10.0 Hz, J = 2.3 Hz, 3F, CF3), -105.4 (t, J = 14.3 Hz, 2F, thiopheneCF2), -121.5, -121.7, -122.4, -125.8 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 141.43 (t, *J* = 4.1 Hz), 136.80, 124.59 (t, *J* = 5.3 Hz), 14.89, 13.82.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 124.61 (t, *J* = 5.5 Hz), 14.91, 13.84.

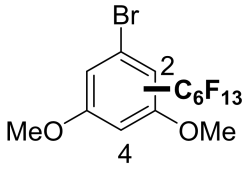
**HRMS (EI, 70 eV):**430.00554; found 430.00395

**3m,** 


**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 6.14 (s, 2H, arom), 3.84 (s, 3H, CH3), 3.80 (s, 6H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.9 Hz, J = 2.3 Hz, 3F, CF3), -102.3 (t, J = 14.3 Hz, 2F, CF2mesitylene), -121.8 (m, 4F, CF2 chain), -122.3, -125.7 (m, 4F, CF2 chain).

**HRMS (ESI):** [M+H]+ calcd for $C_{15}H_{11}F_{13}O_3$, 487.05734; found, 487.05704.

**3n,** 


**2- isomer:**

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 6.86 (d, J = 2.4 Hz, 1H, arene), 6.47 (m, 1H, arene), 3.80 (s,3H, OCH3), 3.81 (s, 3H, OCH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 10.1 Hz, J = 2.7 Hz, 3F, CF3), -100.6 (t, J = 15.8 Hz, 2F, CF2aryl), -119.9, -121.7, -122.3, -125.7 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 162.67, 161.98 (t, *J* = 1.7 Hz), 123.64 (t, *J* = 3.7 Hz), 112.93, 99.40, 56.51, 55.70.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 112.93, 99.41, 56.51, 55.70.

**HRMS (ESI)**: m/z$^+$calcd for $C_{14}H_8BrF_{13}O_2$ $(M+H)^+$ 534.95729; found 534.95671

**4- isomer:**

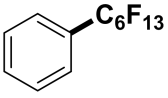
**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 6.78 (s, 2H, arene), 3.83 (s,6H, OCH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.8 Hz, J = 2.4 Hz, 3F, CF3), -103.3 (t, J = 14.6 Hz, 2F, CF2aryl), -121.7, -121.8, -122.3, -125.8 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 160.83 (t, *J* = 2.0 Hz), 127.62, 109.00, 56.66.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 109.03, 56.70.

**HRMS (EI, 70 eV):**533.94946; found 533.94946

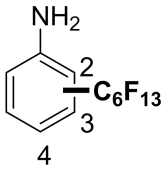
**3o,** 


**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 7.64-754 (m, 3H, benzene), 7.54-7.46 (m, 2H, benzene).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.7 (tt, J = 9.9 Hz, J = 2.3 Hz, 3F, CF3), -110.6 (t, J = 14.9 Hz, 2F, CF2benzene), -121.3, -121.7, -122.6, -125.9 (m, 8F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 131.92, 128.60, 126.84 (t, *J* = 6.7 Hz).

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 131.88 (t, *J* = 1.5 Hz), 128.56, 126.80 (t, *J* = 6.6 Hz).



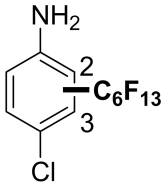

**3p,**

**2- isomer:**

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.31 (m, 2H, aniline), 6.80 (m, 1H, aniline), 6.71 (d, J = 6.9 Hz, 1H, aniline), 4.22 (s, 2H, NH2).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (tt, J = 9.8 Hz, J = 2.3 Hz, 3F, CF3), -108.1 (t, J = 15.1 Hz, 2F, CF2aniline), -121.3, -121.5, -122.3, -125.7 (m, 8F, CF2 chain).

**GCMS (EI, 70eV) *m*:*z* (relative intensity):** 411 ($M^+$, 50), 392 (19), 342 (6), 173 (6), 142 (100).




**3q,**

**2- isomer:**

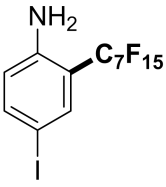
**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.28 (m,1H, arene), 7.26-7.19 (m, 1H, arene), 6.65 (d, J = 8.6 Hz, 1H, arene), 4.24 (s, 2H, NH2).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.4 (t, J = 9.9 Hz, 3F, CF3), -108.6 (t, J = 14.8 Hz, 2F, areneCF2), -121.4 (m, 4F, CF2 chain), -122.4, -125.7, (m, 4F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 144.47, 133.06, 128.42 (t, *J* = 9.1 Hz), 122.52, 119.07.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 133.08, 128.45 (t, *J* = 9.1 Hz), 119.09.

**HRMS (ESI):** m/z$^+$calcd for $C_{12}H_5ClF_{13}N$ $(M+H)^+$ 445.99757; found 445.99763.




**3r,**

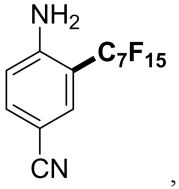
**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 7.56 (m, 1H, aniline), 7.52 (dm, J = 8.6 Hz, 1H, aniline), 6.49 (d, J = 8.6 Hz, 1H, aniline), 4.25 (broad s, 2H, NH2).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.8 (tt, J = 10.0 Hz, 2.4 Hz, 3F, CF3), -108.9 (t, J = 14.9 Hz, 2F, CF2aniline), -121.5, -121.8, -121.9 (m, 6F, CF2 chain), -122.7, -126.1 (m, 4F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 145.48, 141.50, 137.05 (t, *J* = 9.0 Hz), 119.70.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 141.50, 137.06 (t, *J* = 9.1 Hz), 119.71.

**HRMS (ESI)**: m/z$^+$ calcd for $C_{13}H_5F_{15}IN$ $(M+H)^+$587.92999; found 587.92919.




**3s,** , white solid

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 7.60 (d, J = 2.1 Hz, 1H, arene), 7.51 (dd, J = 8.3 Hz, J = 1.8 Hz, 1H, arene), 6.74 (d, J = 8.3 Hz, 1H, arene), 4.79 (s, 2H, NH2).

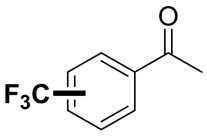
**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -80.8 (t, J = 10.1 Hz, 3F, CF3), -109.4 (t, J = 13.7 Hz, 2F, arylCF2), -121.5 -121.9, -122.7, -126.1 (m, 10F, CF2 chain).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 149.13, 136.04, 134.11 (t, *J* = 9.0 Hz), 118.56, 117.82, 100.38.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 136.05, 134.13 (t, *J* = 8.8 Hz), 117.84.

**HRMS (EI, 70 eV):** [M+H]+ calcd for $C_{14}H_5F_{15}N_2$ 487.0286; found 487.0282.

**6.2 Trifluoromethylated heteroarenes**




**5a**,

**2- isomer:**

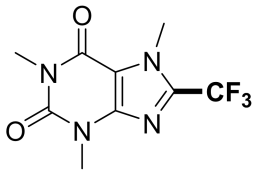
**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -62.1 (s, 3F, CF3)

**3- isomer:**

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -63.1 (s, 3F, CF3)

**4- isomer:**

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -63.3 (s, 3F, CF3)




**5b,**

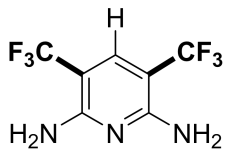
**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 4.14 (pseudo q, *J* = 1.3 Hz, 3H, CH3), 3.57 (s, 3H, CH3), 3.40 (s, 3H, CH3).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -62.3 (s, 3F, CF3).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 155.40, 151.27, 146.46, 119.94, 116.34, 33.15 (q, *J* = 2.0 Hz), 29.85, 28.15.

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 33.18 (q, *J* = 1.9 Hz), 29.89, 28.19.

**HRMS (EI):** [M+H]+ calcd for $C_9H_9F_3N_4O_2$, 263.07504; found, 263.07522.




**6c**,

**$^1$H NMR (300 MHz, $CDCl_3$):** δ = 7.69 (s, arene), 5.13 (s,4H, NH2).

**$^{19}$F NMR (282 MHz, $CDCl_3$):** δ = -62.1 (s, 3F, CF3).

**$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 156.51, 135.82, 129.72 – 119.00 (q, *J* = 267.9 Hz), 98.51 – 97.18 (q, *J* = 33.4 Hz).

**$^{13}$C NMR Dept135 (75 MHz, $CDCl_3$):** δ = (+): 135.86 (hept, *J* = 4.6 Hz).

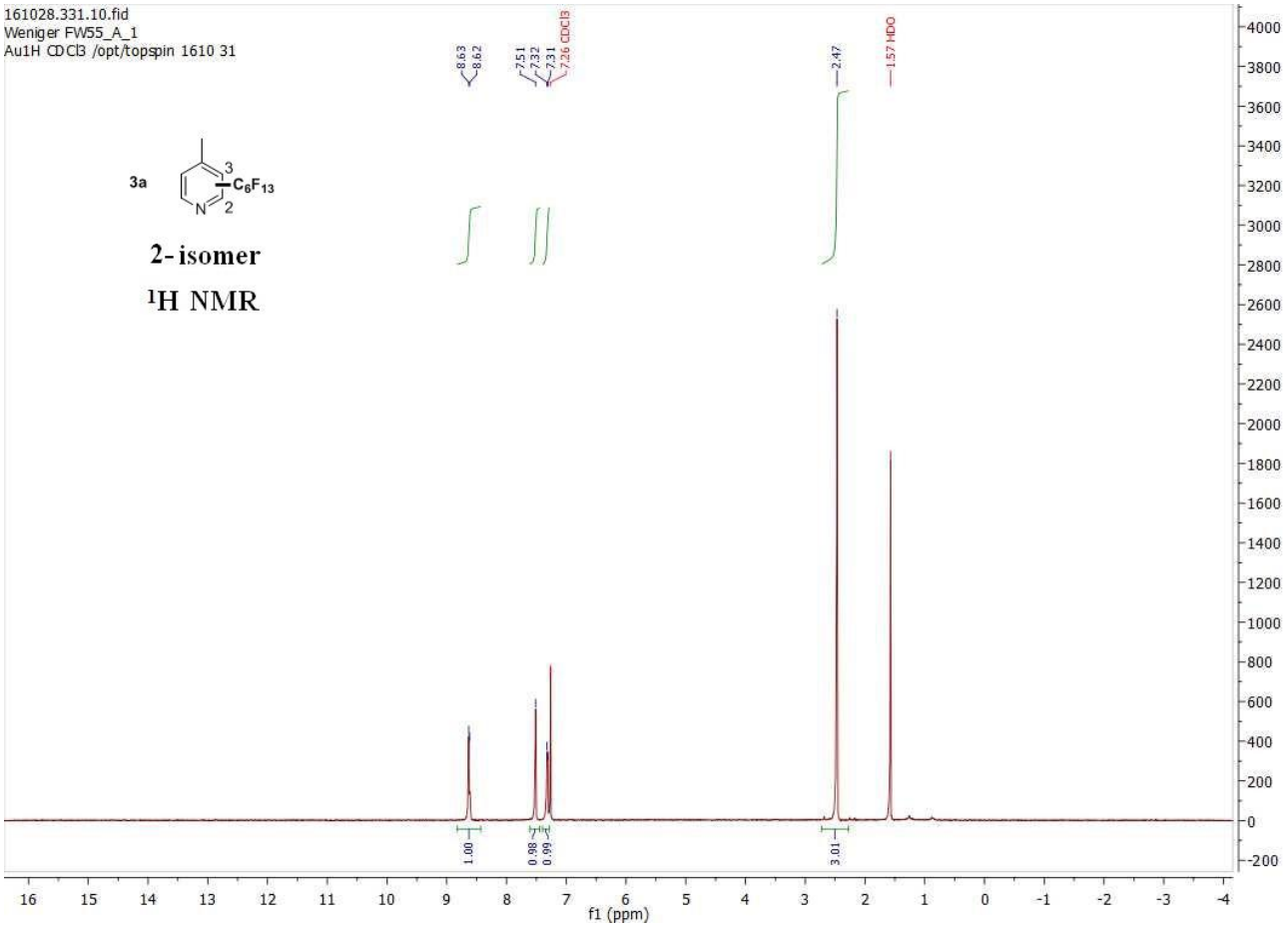
**MS (EI, 70 eV):** m/z (%) = 245 (100) M+, 226 (28), 198 (43).

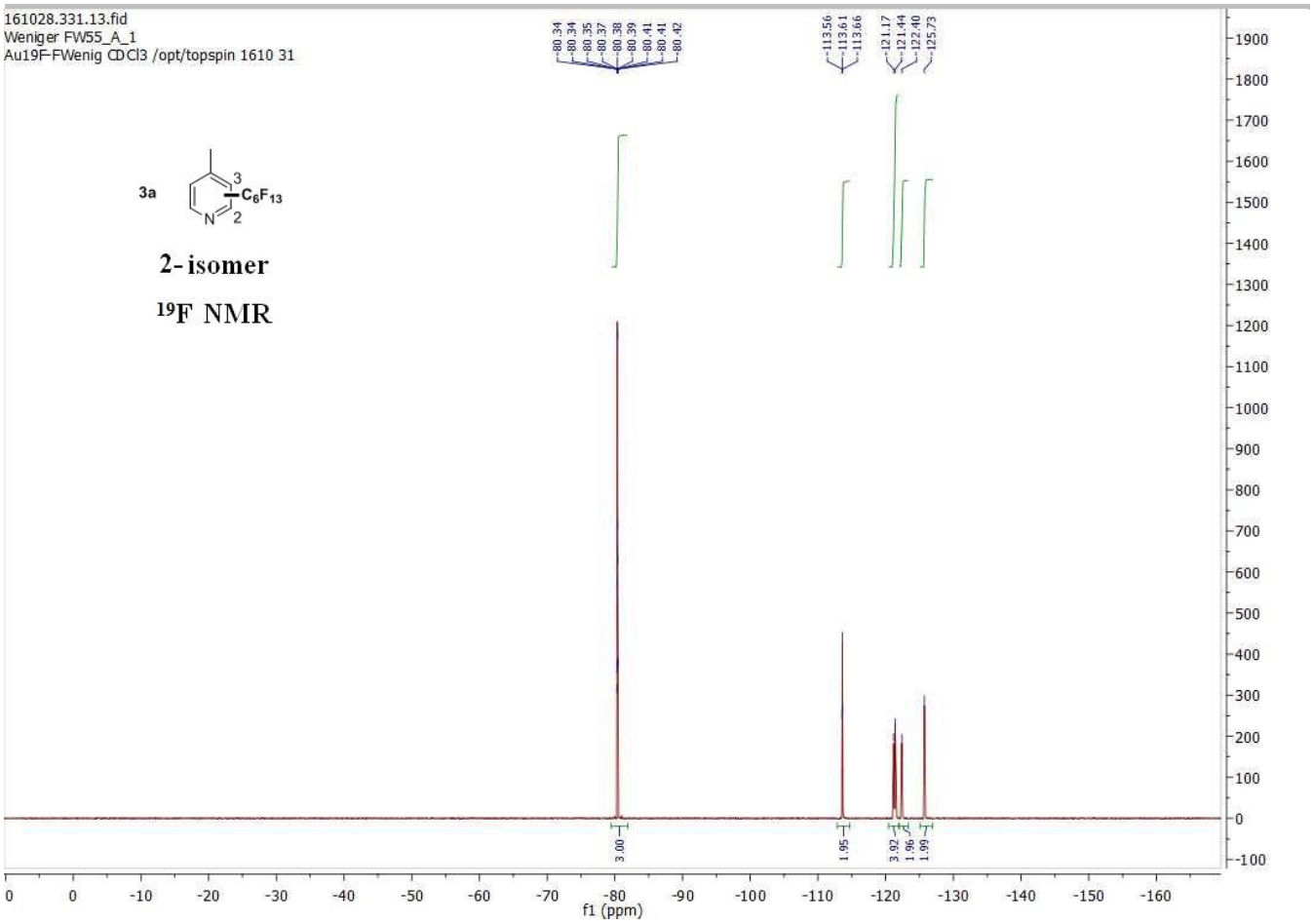
## 7. References

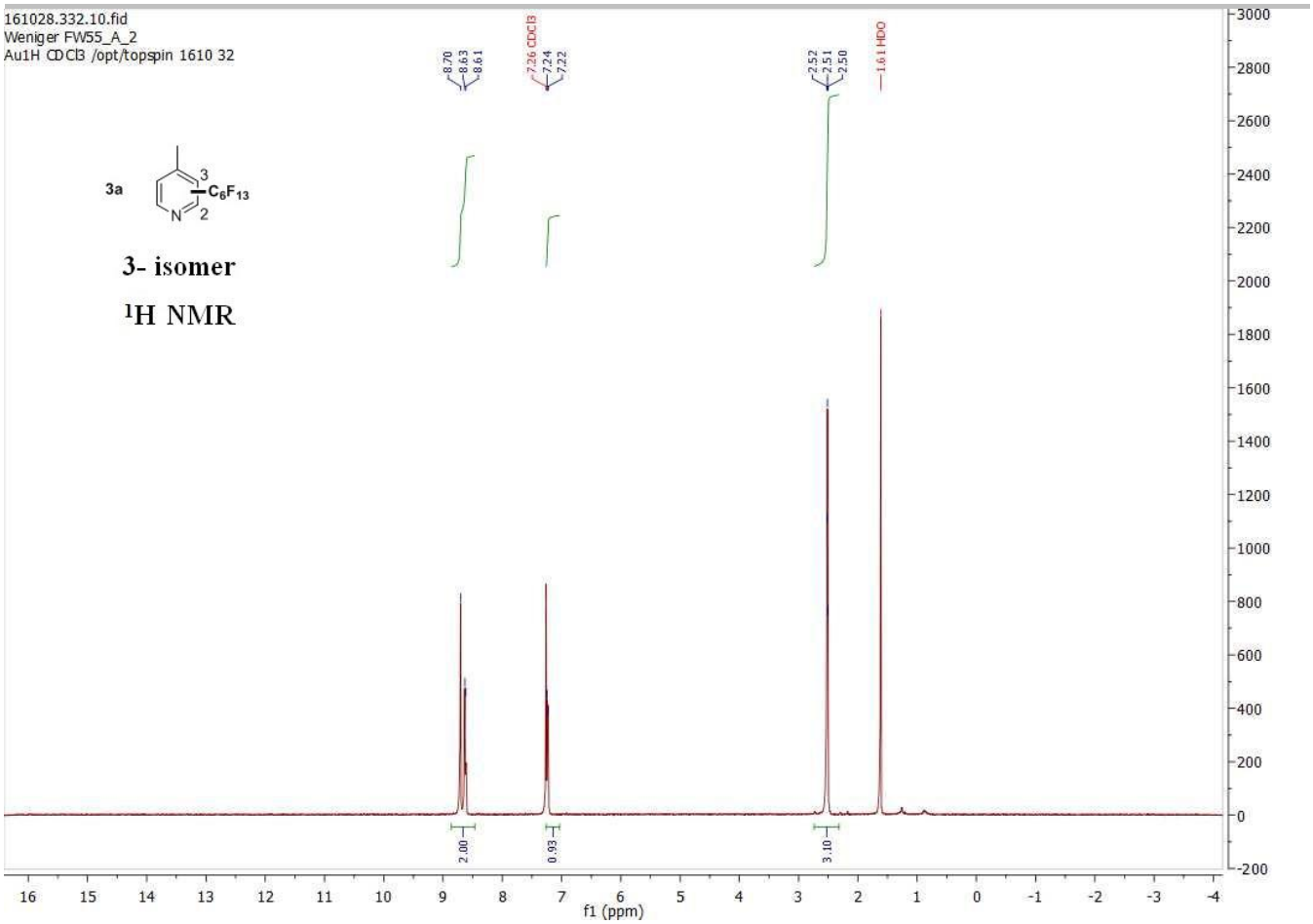

1. J. H. Scofield, *J. Electron. Spectrosc. Relat. Phenom.*, 1976, **8**, 129-137.
2. (a) B. J. Matsoso, K. Ranganathan, B. K. Mutuma, T. Lerotholi, G. Jones and N. J. Coville, *RSC Adv.*, 2016, **6**, 106914-106920; (b) F. Jaouen, J. Herranz, M. Lefevre, J.-P. Dodelet, U. I. Kramm, I. Herrmann, P. Bogdanoff, J. Maruyama, T. Nagaoka and A. Garsuch, *ACS Appl. Mater. Interfaces*, 2009, **1**, 1623-1639.
3. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717-2730.


## 8. Spectra

### 8.1 Perfluoroalkylated (hetero)arenes




161028.331.13.fid
Weniger FW55_A_1
Au19F-FWenig CDCl3 /opt/topspin 1610 31
3a
2-isomer
19F NMR
f1 (ppm)


161028.332.10.fid
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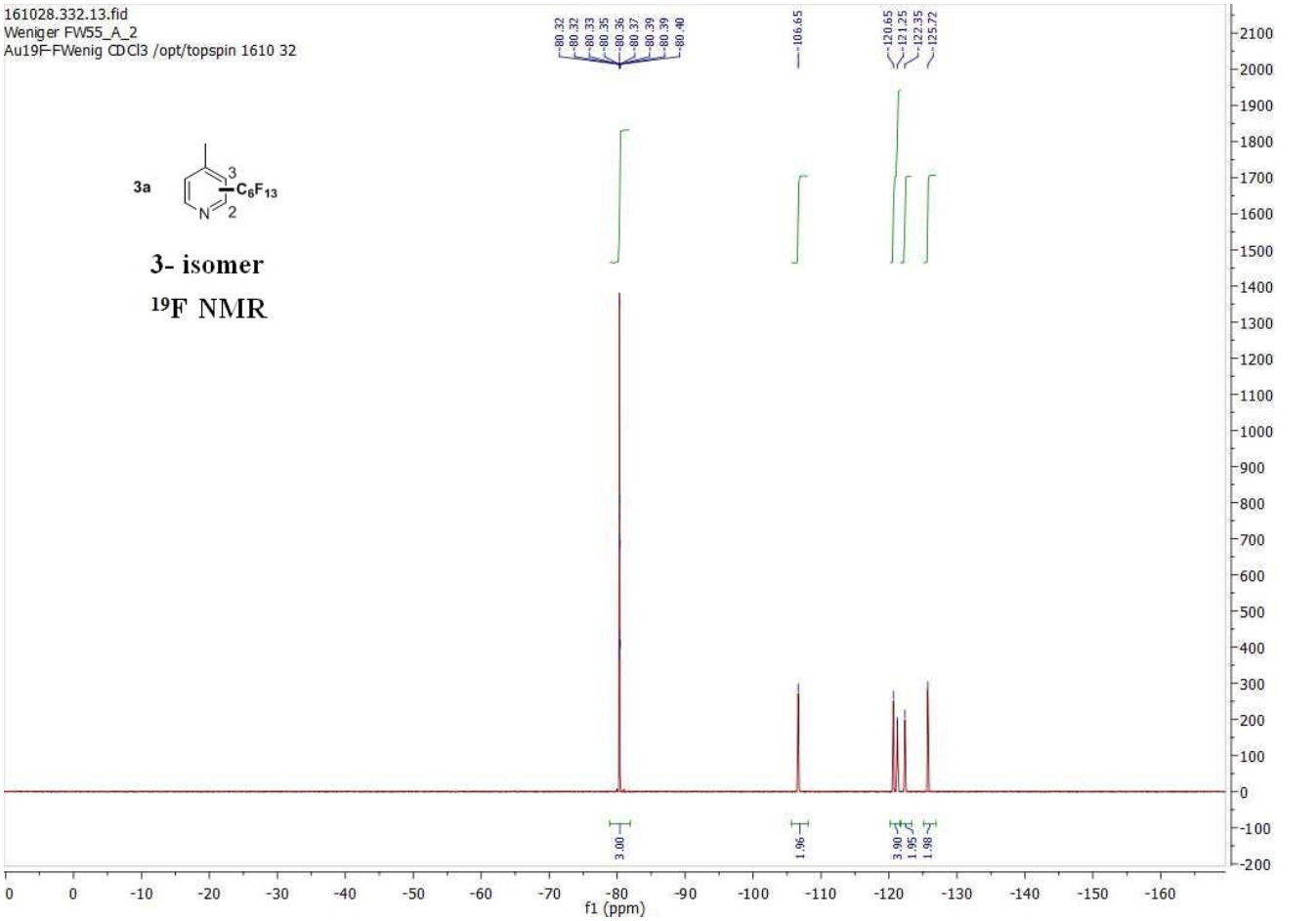
Au1H CDCl3 /opt/topspin 1610 32
8.70
8.63
8.61
7.26 CDCl3
7.24
7.22
2.52
2.51
2.50
1.61 HDO
3a
3
2
N
C6F13
3- isomer
1H NMR
2.00
0.93
3.10
f1 (ppm)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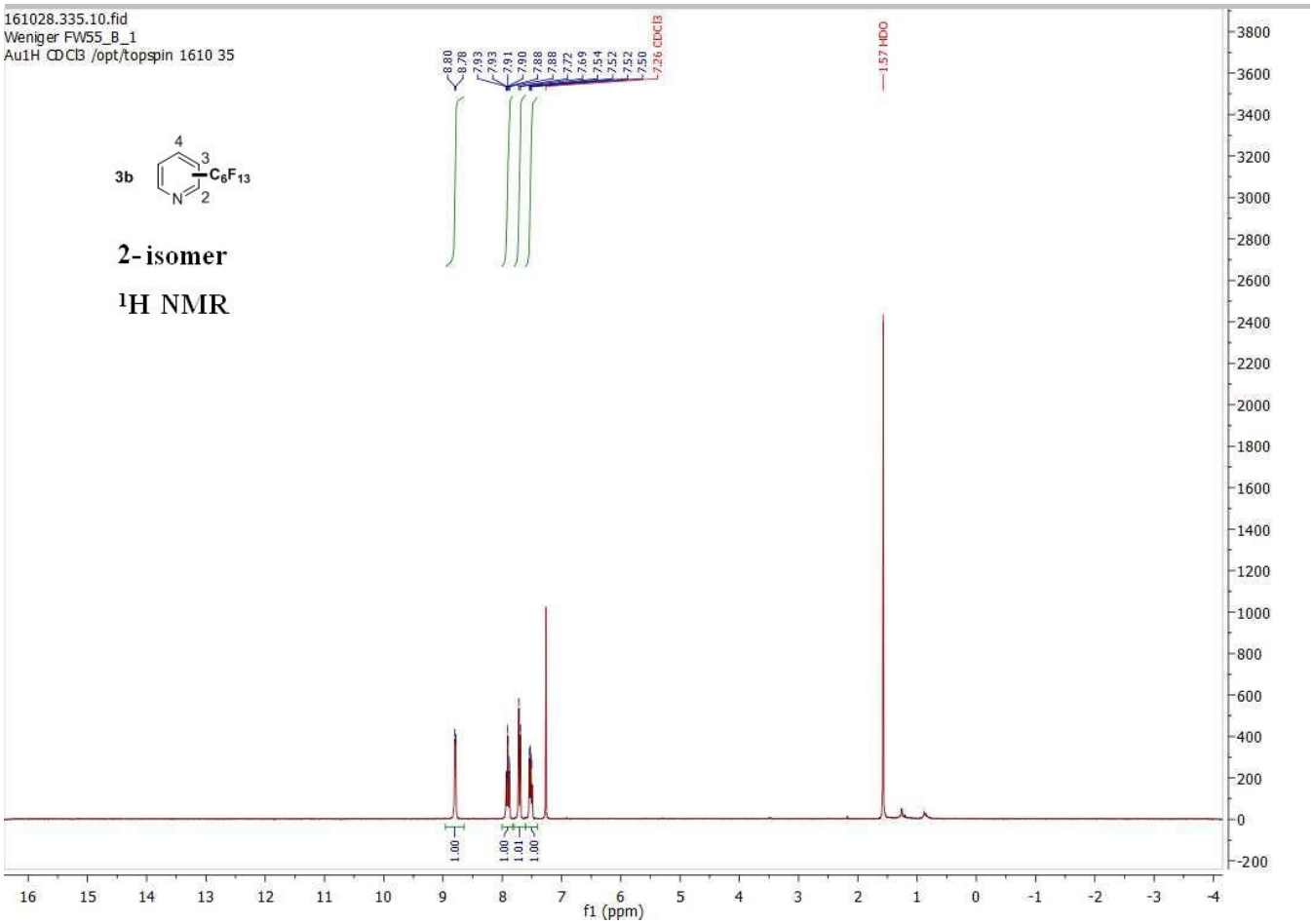
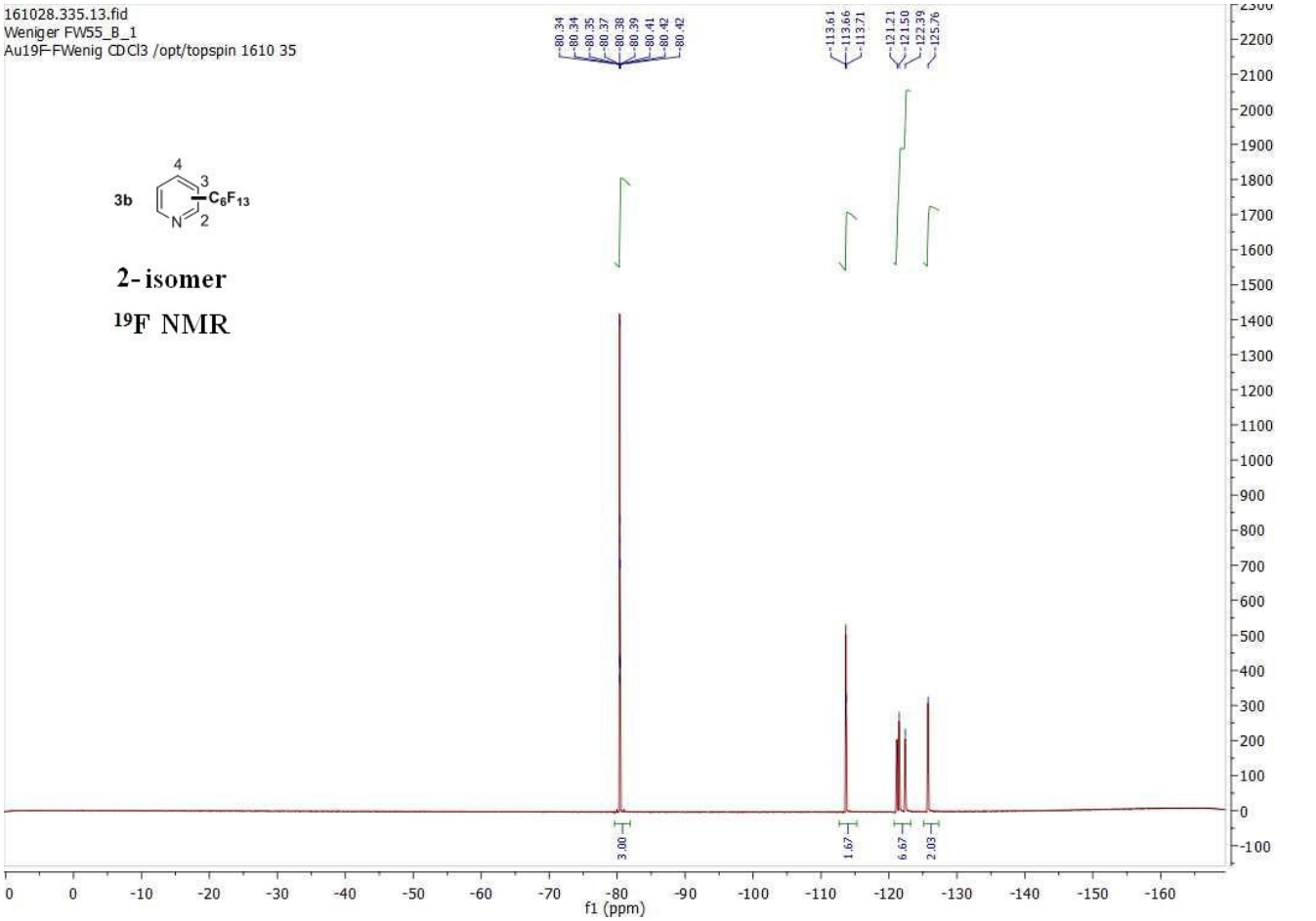
Au19F-FWenig CDCl3 /opt/topspin 1610 32
-80.32
-80.32
-80.33
-80.35
-80.36
-80.37
-80.39
-80.39
-80.40
-106.65
-120.65
-121.25
-122.35
-125.72
3a
3
2
N
C6F13
3- isomer
19F NMR
3.00
1.96
3.90
1.95
1.98
f1 (ppm)


161028.335.10.fid
Weniger FW55_B_1
Au1H CDCl3 /opt/topspin 1610 35
3b
$C_6F_{13}$
2-isomer
$^1$H NMR
f1 (ppm)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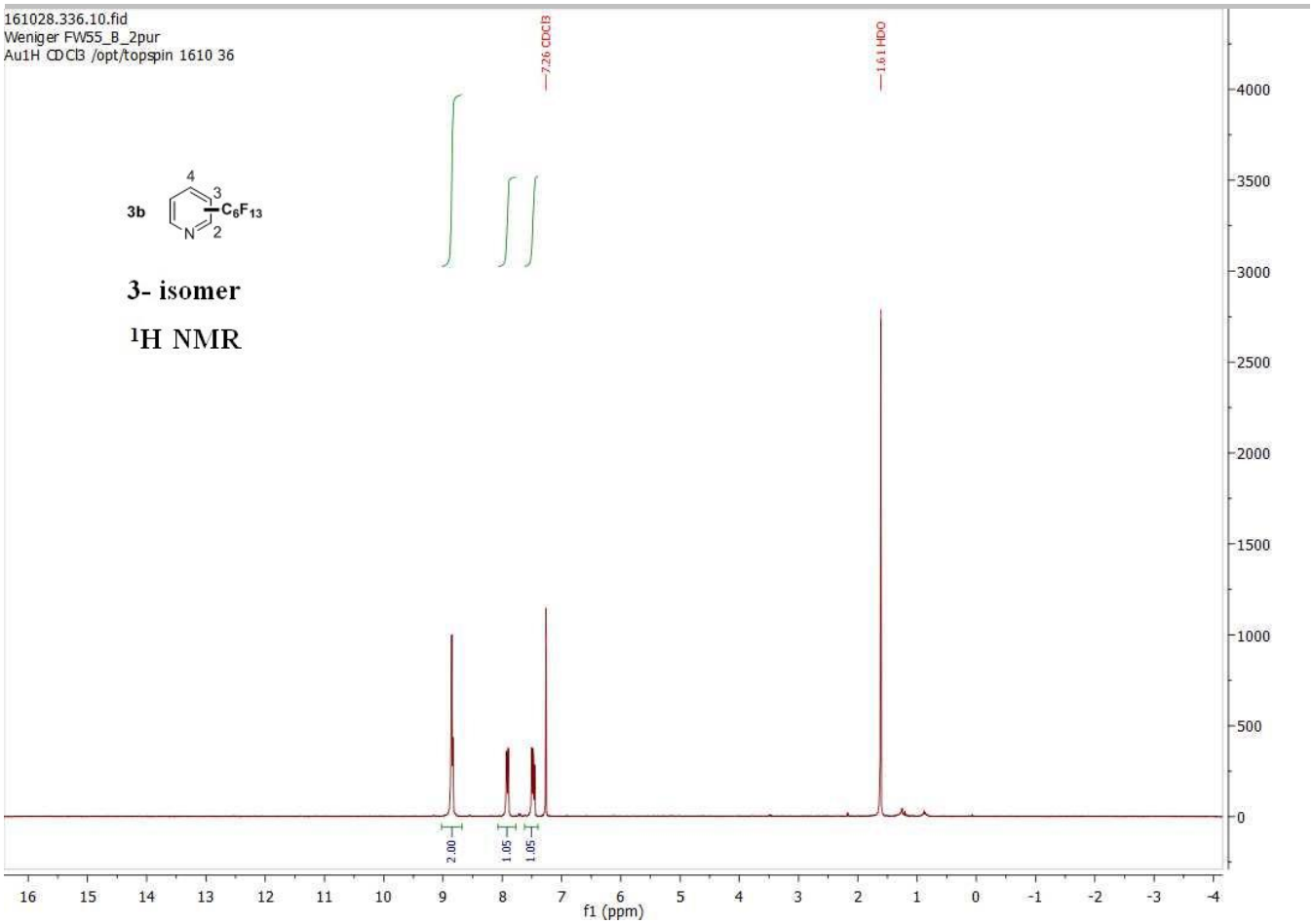
Au19F-FWenig CDCl3 /opt/topspin 1610 35
3b
$C_6F_{13}$
2-isomer
$^{19}$F NMR
f1 (ppm)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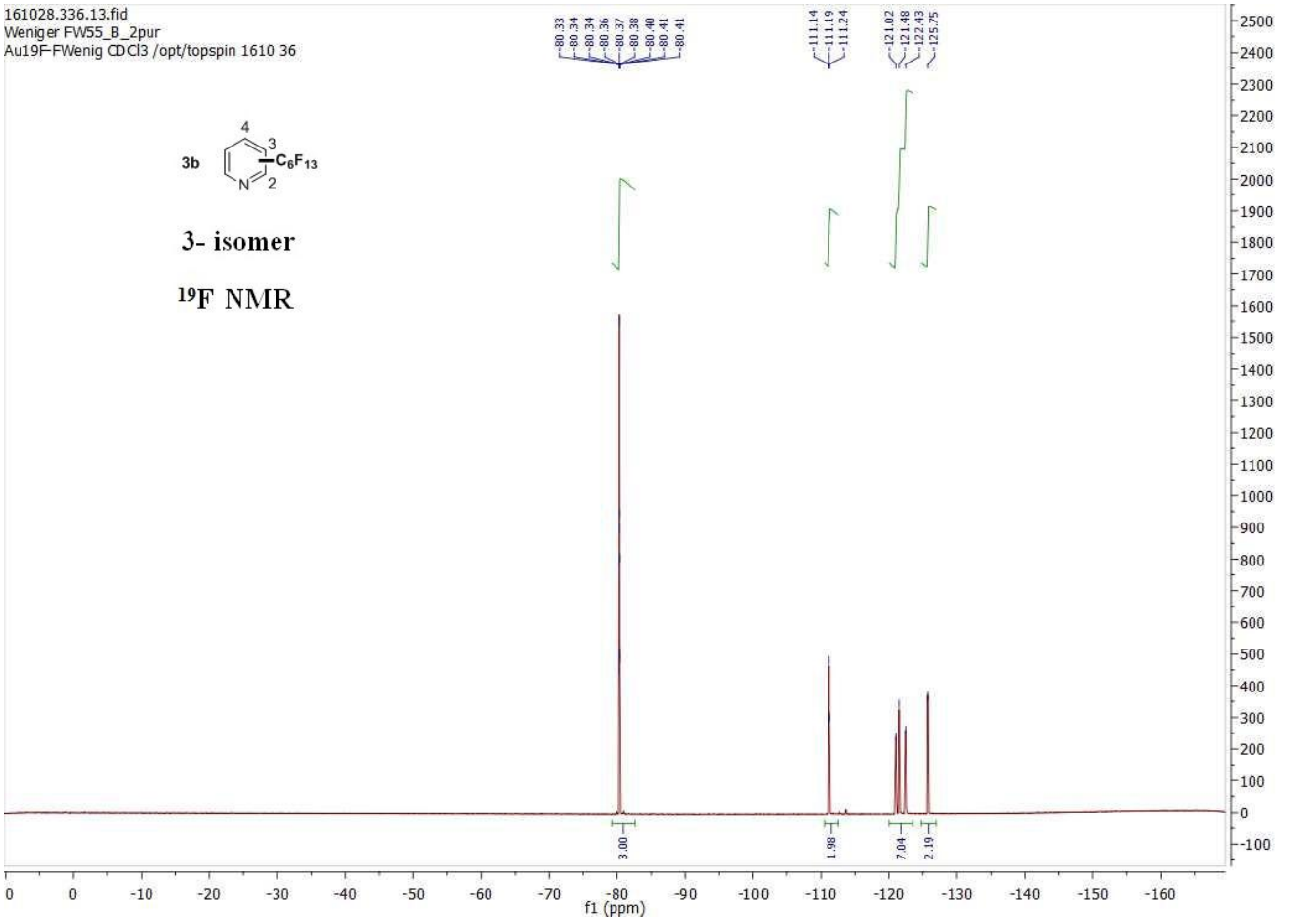
Weniger FW55_B_2pur
Au1H CDCl3 /opt/topspin 1610 36
7.26 CDCl3
1.61 HDO
3b
3- isomer
1H NMR
2.00
1.05
1.05
f1 (ppm)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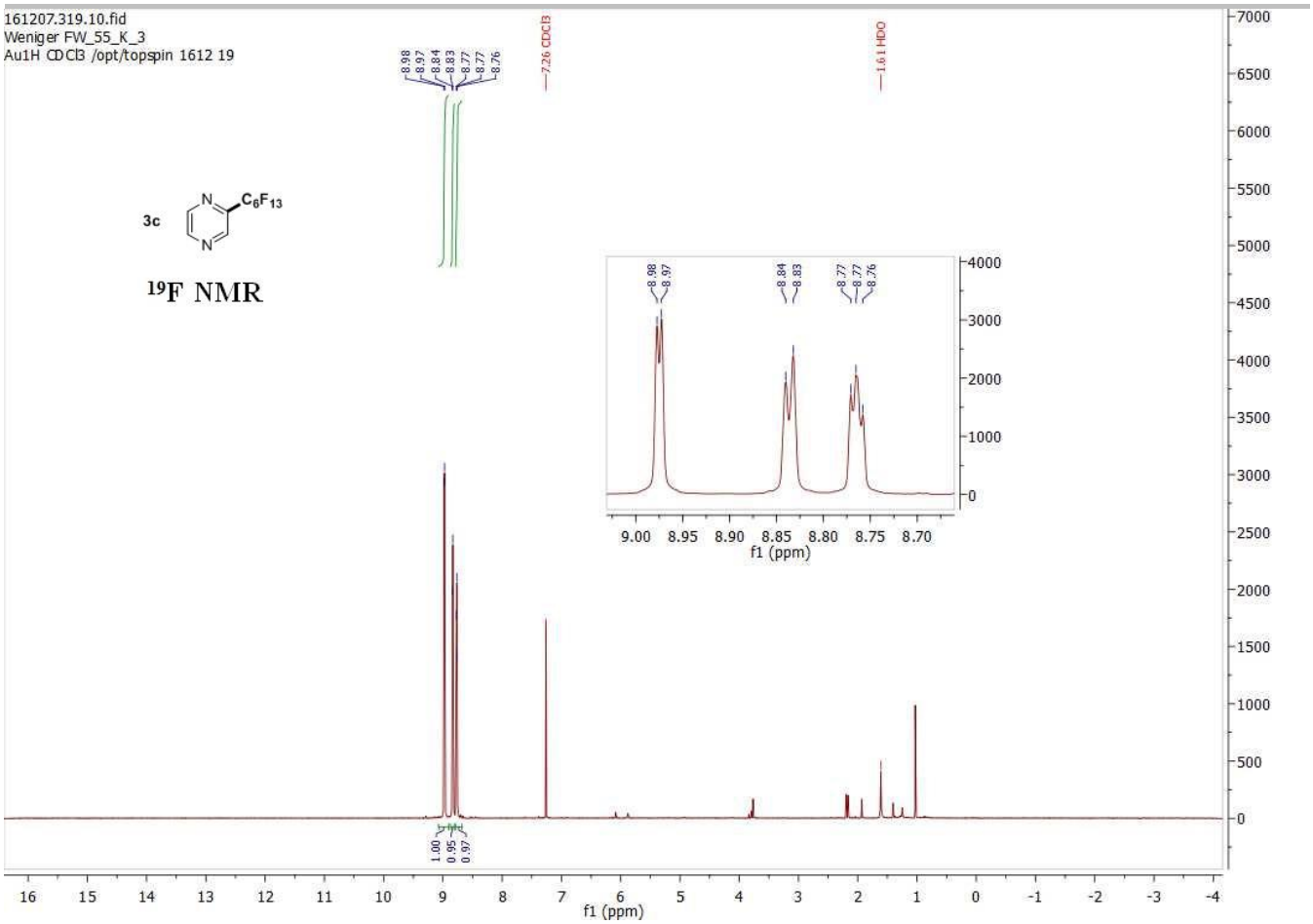
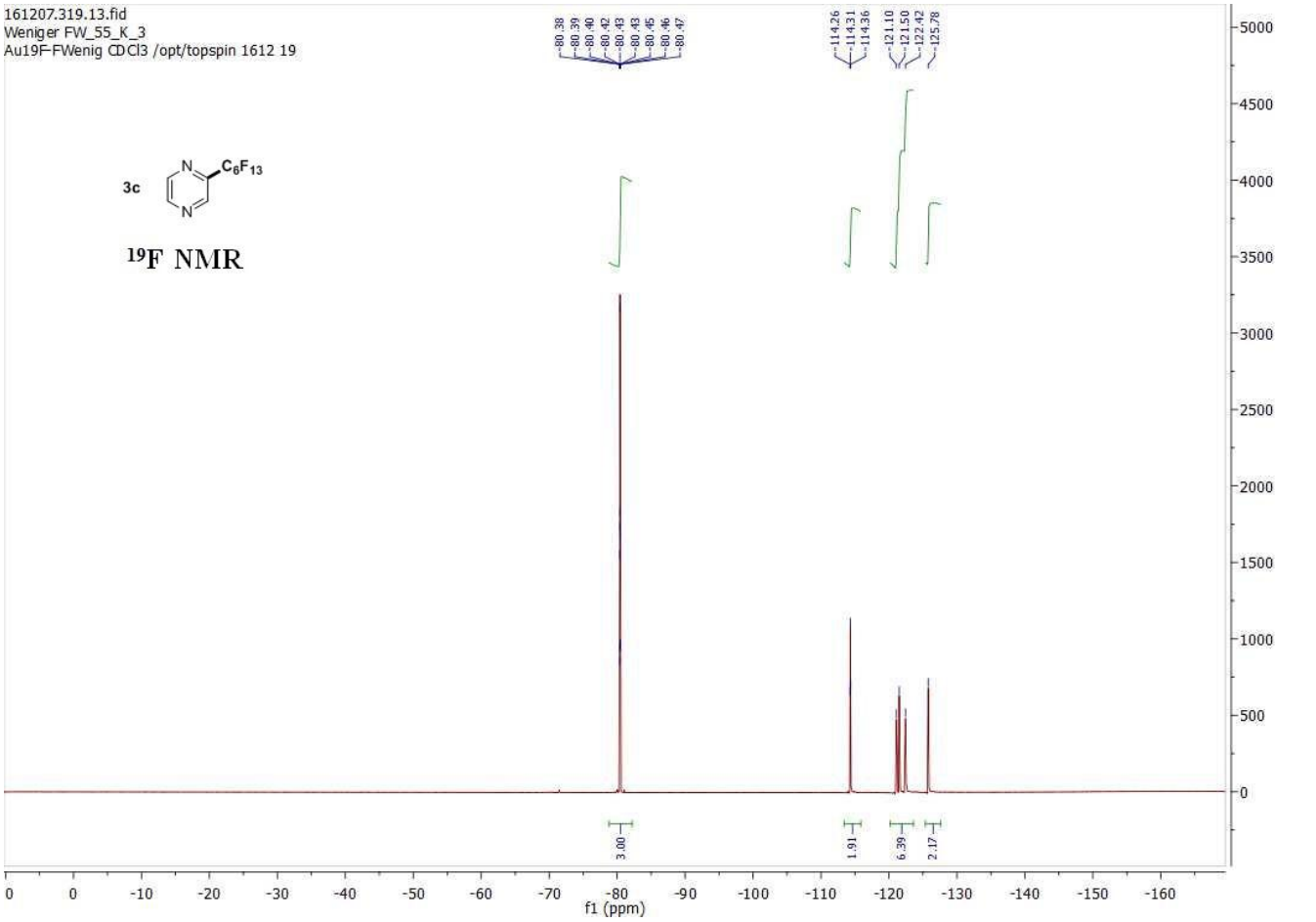
-80.33
-80.34
-80.34
-80.36
-80.37
-80.38
-80.40
-80.41
-80.41
-111.14
-111.19
-111.24
-121.02
-121.48
-122.43
-125.75
3b
3- isomer
19F NMR
3.00
1.98
7.04
2.19
f1 (ppm)


161207.319.10.fid
Weniger FW_55_K_3
Au1H CDCl3 /opt/topspin 1612 19
3c
$C_6F_{13}$
$^{19}$F NMR
f1 (ppm)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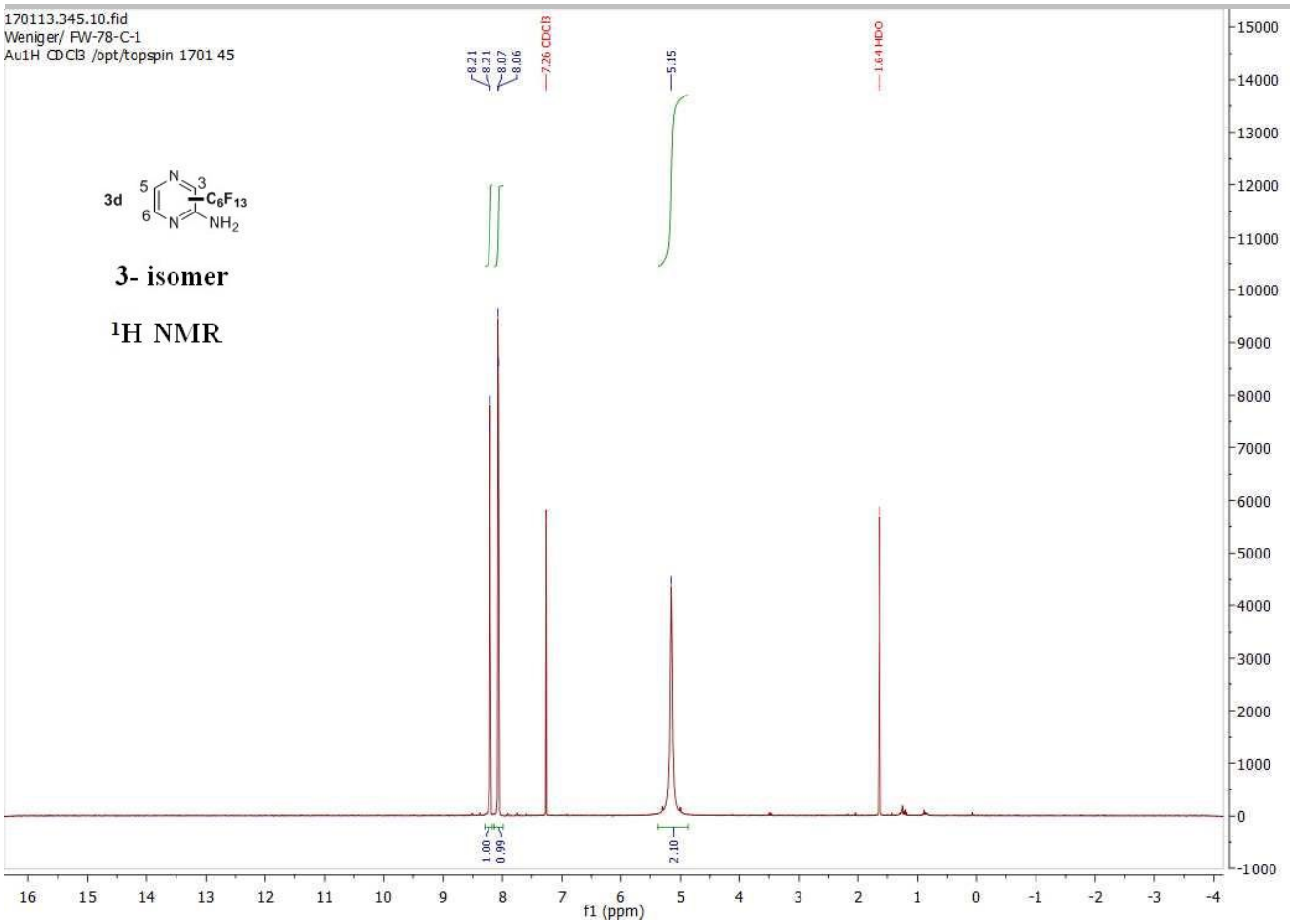
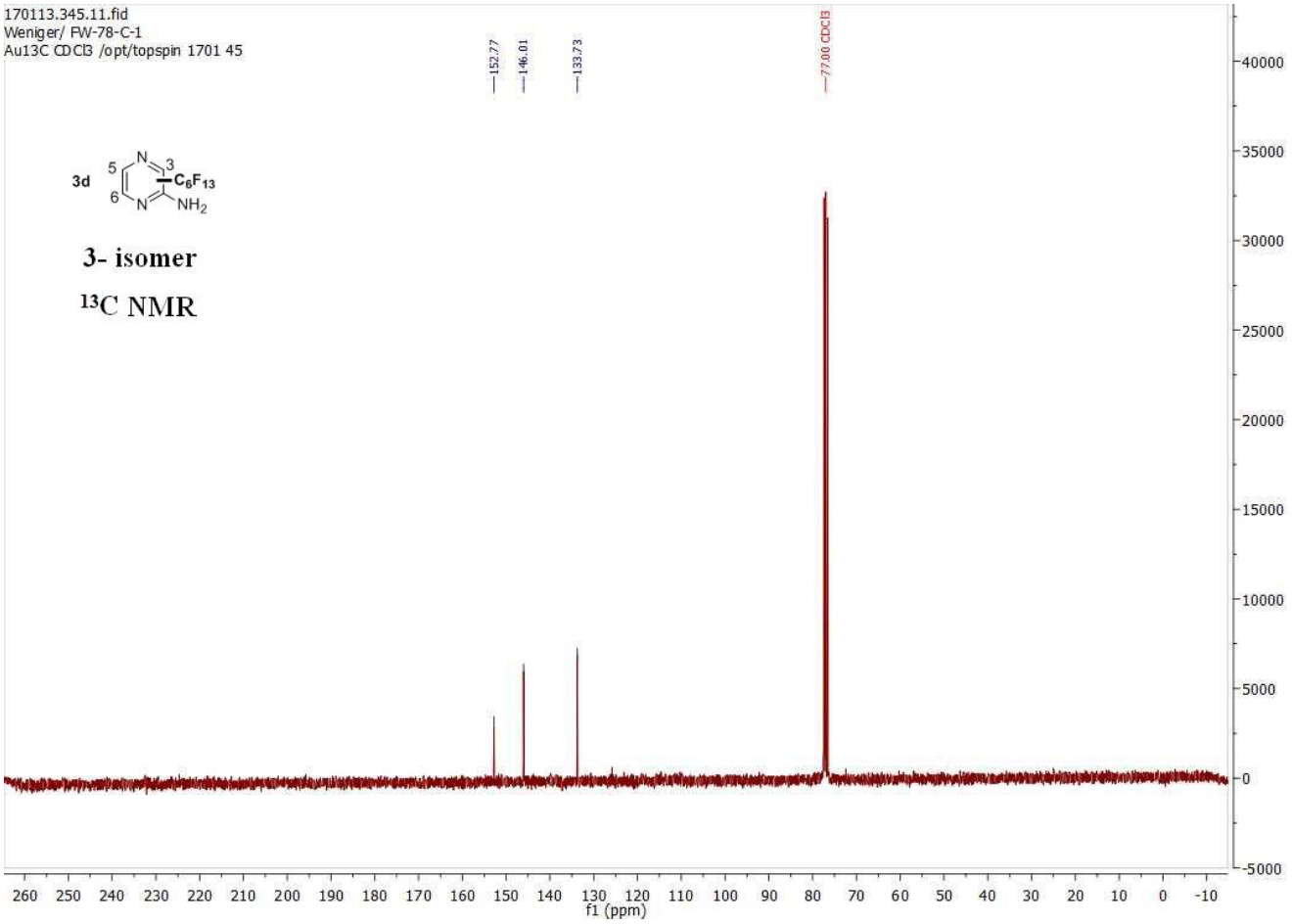
Au19F-FWenig CDCl3 /opt/topspin 1612 19
3c
$C_6F_{13}$
$^{19}$F NMR
f1 (ppm)


170113.345.10.fid
Weniger/ FW-78-C-1
Au1H CDCl3 /opt/topspin 1701 45
8.21
8.21
8.07
8.06
7.26 CDCl3
5.15
1.64 HDO
3d
3- isomer
1H NMR
1.00
0.99
2.10
f1 (ppm)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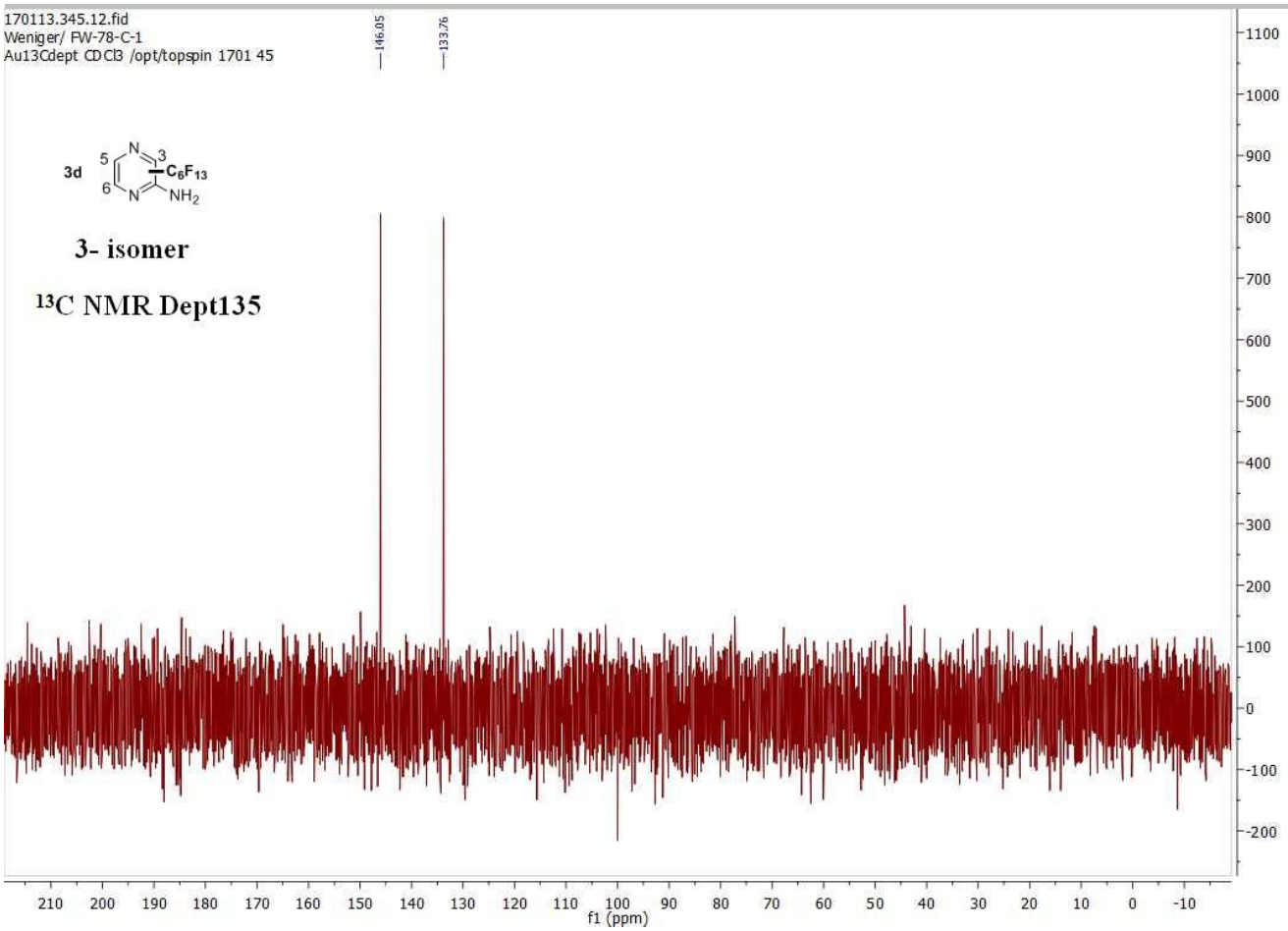
146.01
133.73
77.00 CDCl3
3d
3- isomer
13C NMR
f1 (ppm)


170113.345.12.fid
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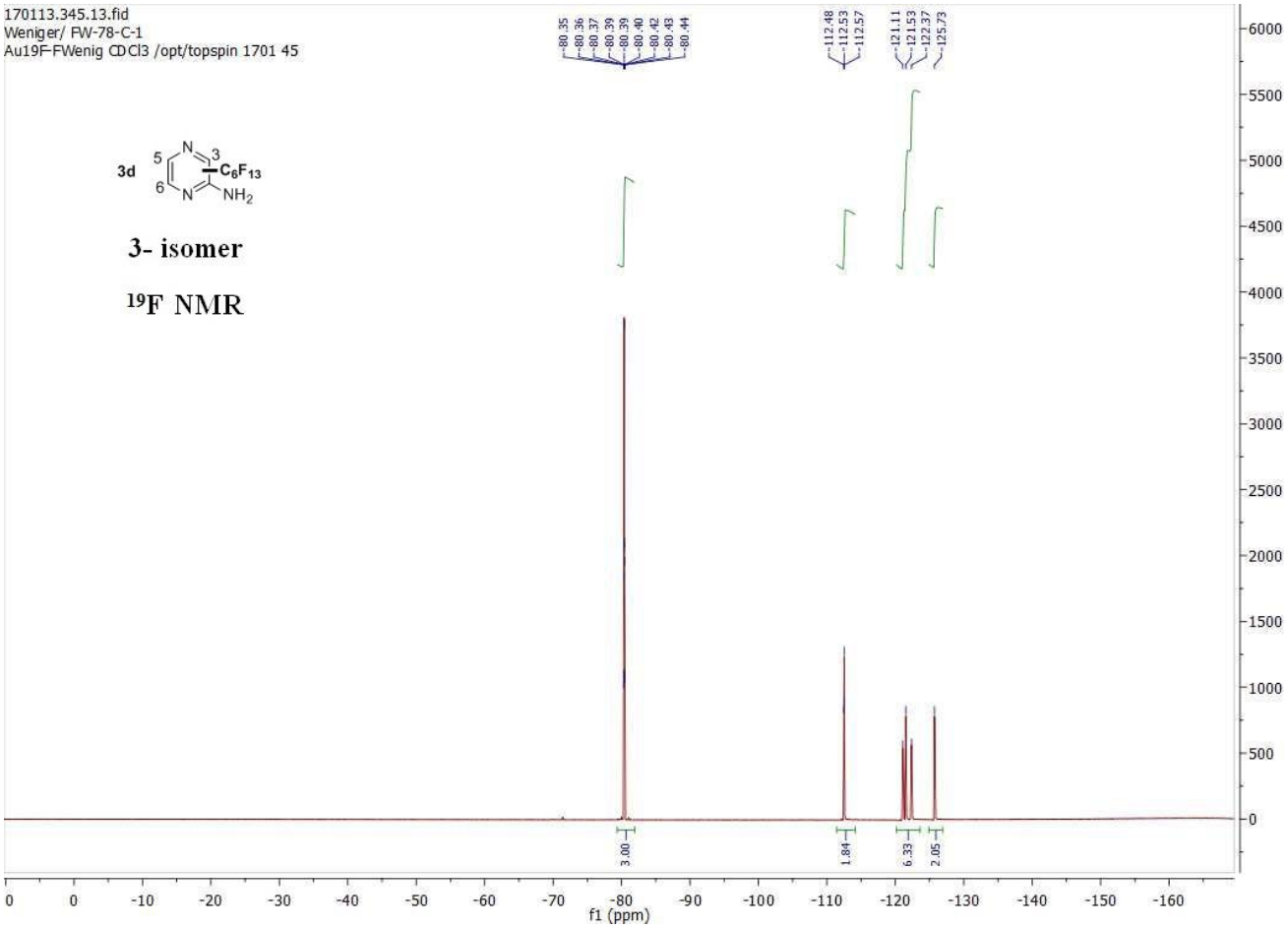
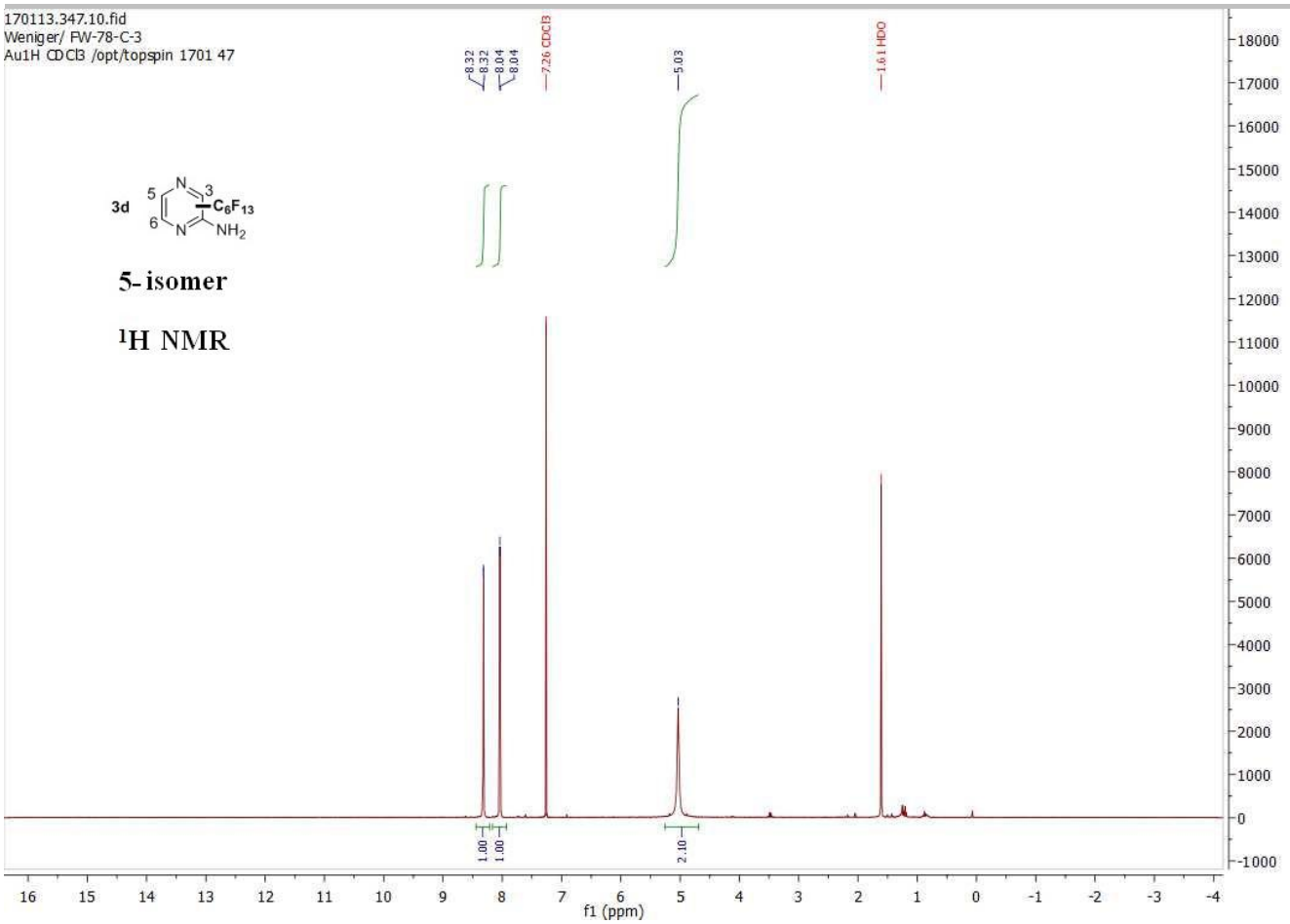
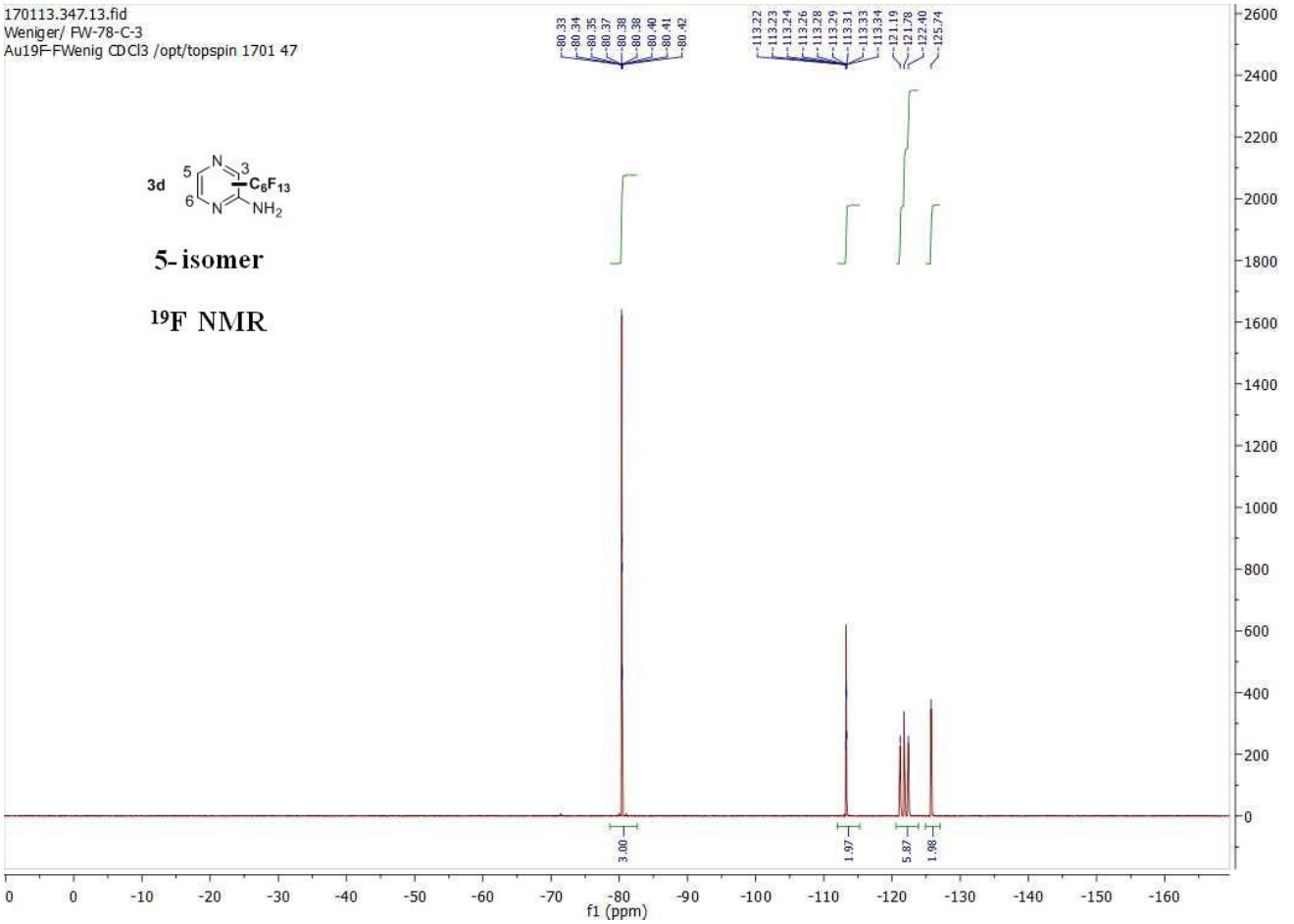
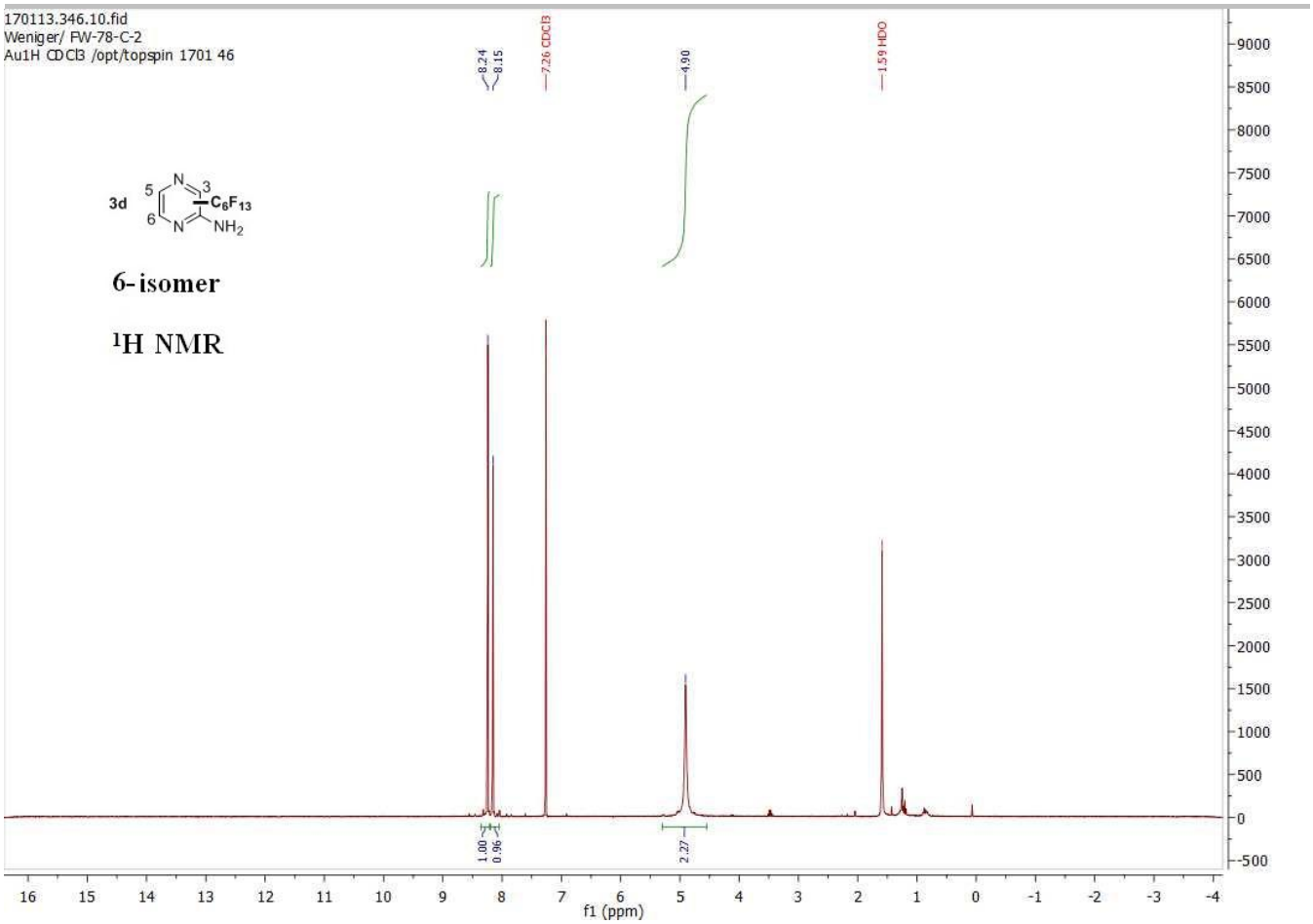
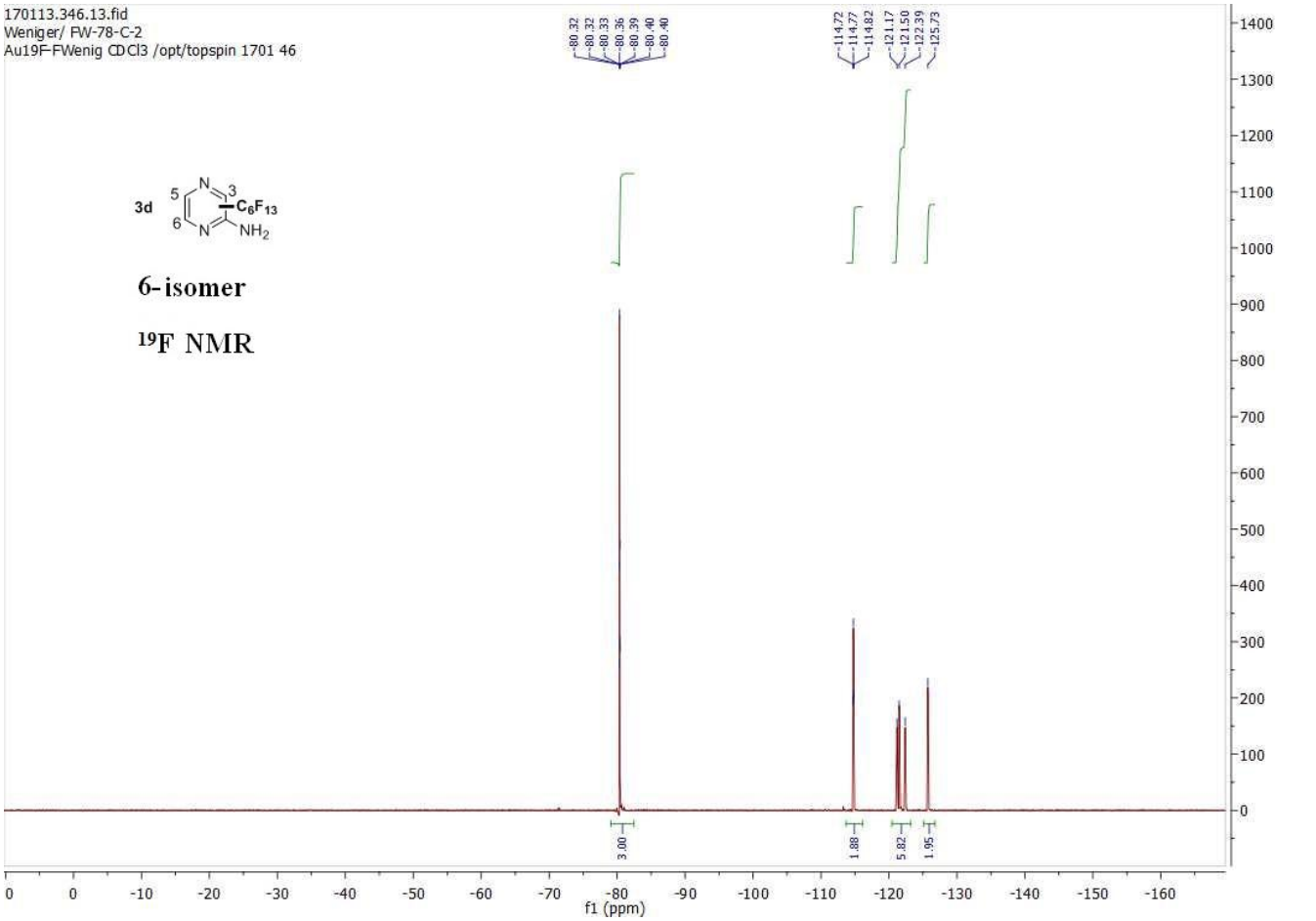
146.05
133.76
3d
3- isomer
13C NMR Dept135
f1 (ppm)


170113.345.13.fid
Weniger/ FW-78-C-1
Au19F-FWenig CDCl3 /opt/topspin 1701 45
3d
3- isomer
19F NMR
f1 (ppm)


170113.347.10.fid
Weniger/ FW-78-C-3
Au1H CDCl3 /opt/topspin 1701 47
8.32
8.32
8.04
8.04
7.26 CDCl3
5.03
1.61 HDO
3d
5-isomer
1H NMR
1.00
1.00
2.10
f1 (ppm)


170113.347.13.fid
Weniger/ FW-78-C-3
Au19F-FWenig CDCl3 /opt/topspin 1701 47
3d
5-isomer
19F NMR
3.00
1.97
5.87
1.98
f1 (ppm)


170113.346.10.fid
Weniger/ FW-78-C-2
Au1H CDCl3 /opt/topspin 1701 46
8.24
8.15
7.26 CDCl3
4.90
1.59 HDO
3d
$C_6F_{13}$
$NH_2$
6-isomer
$^1$H NMR
1.00
0.96
2.27
f1 (ppm)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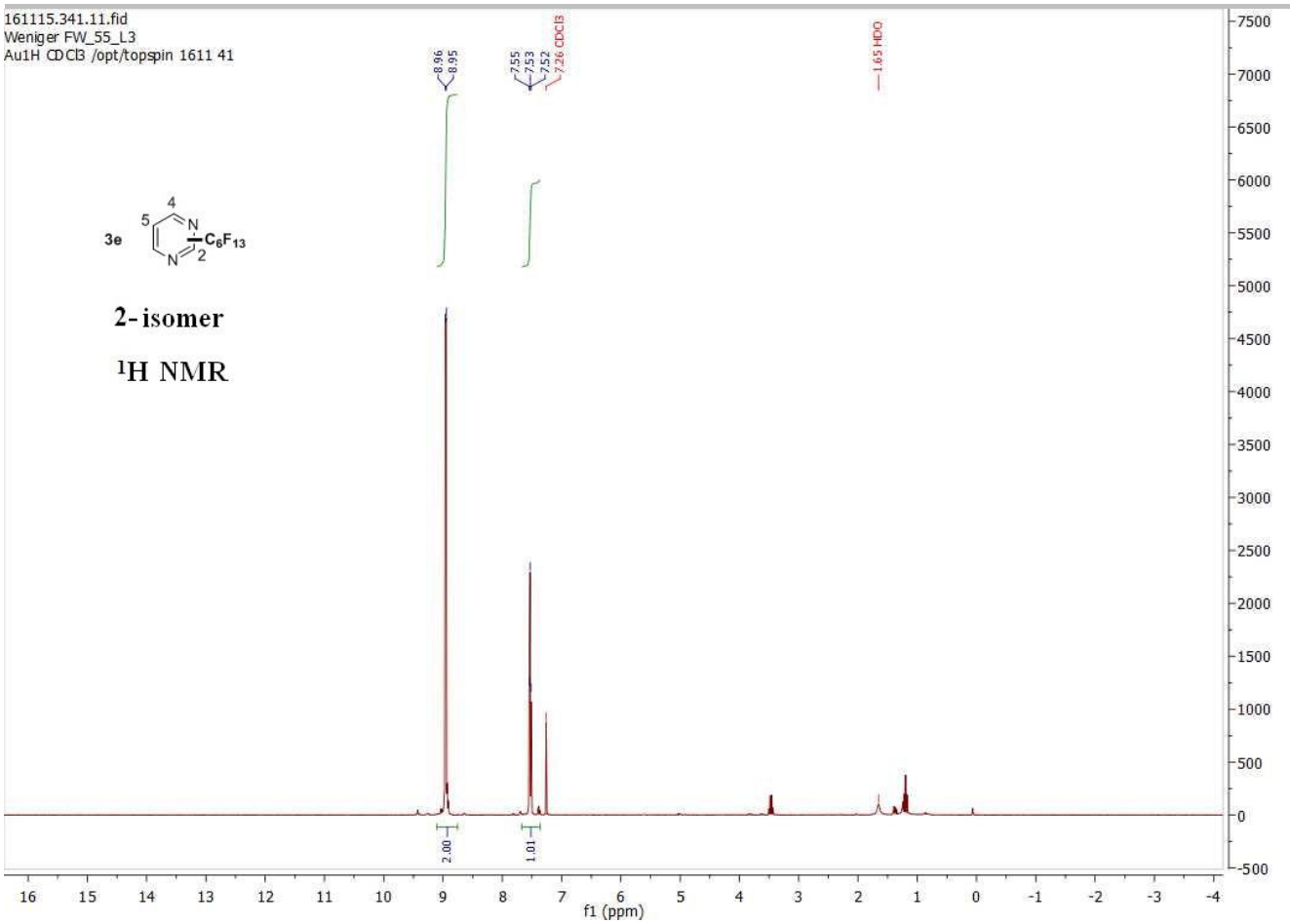
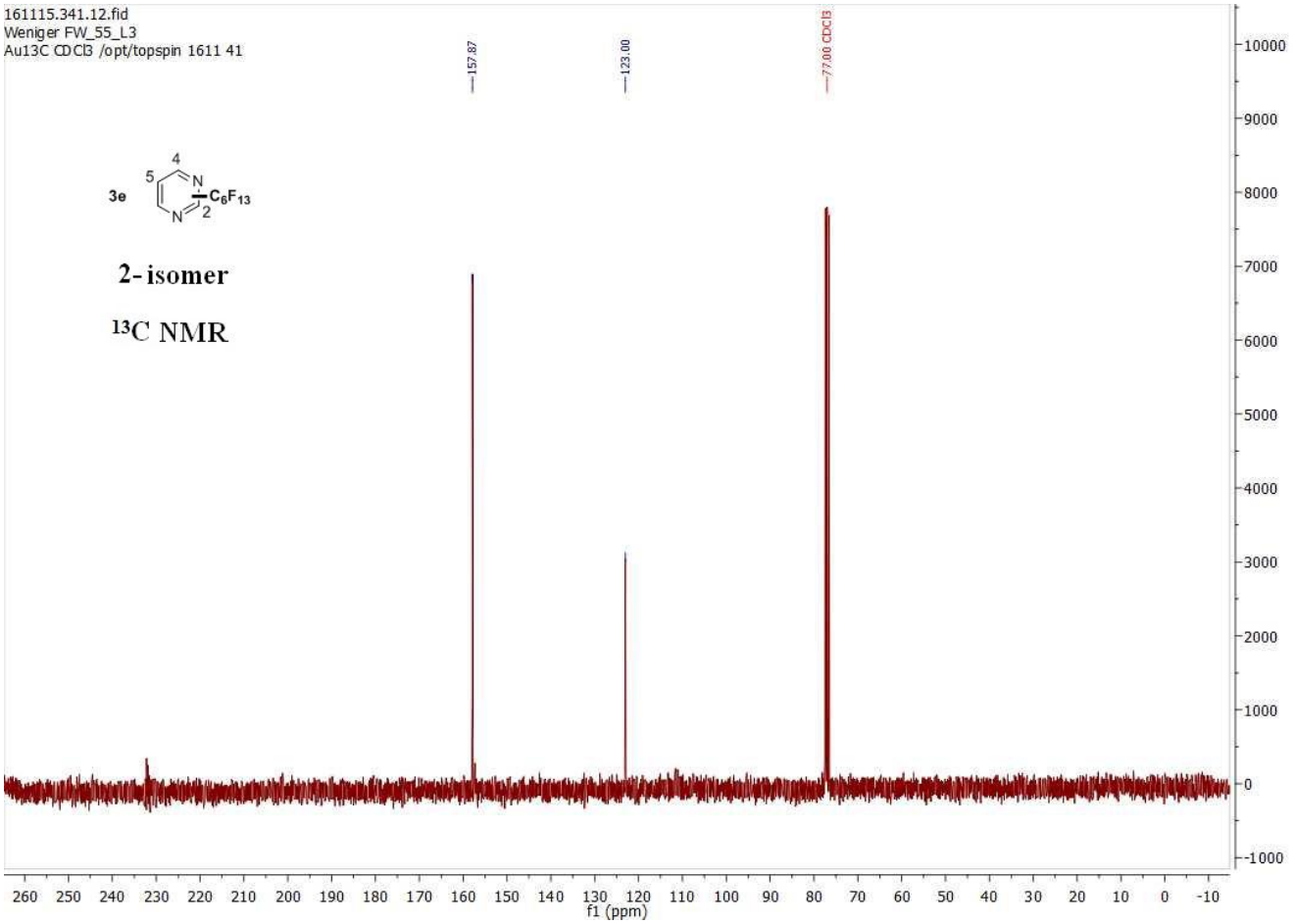
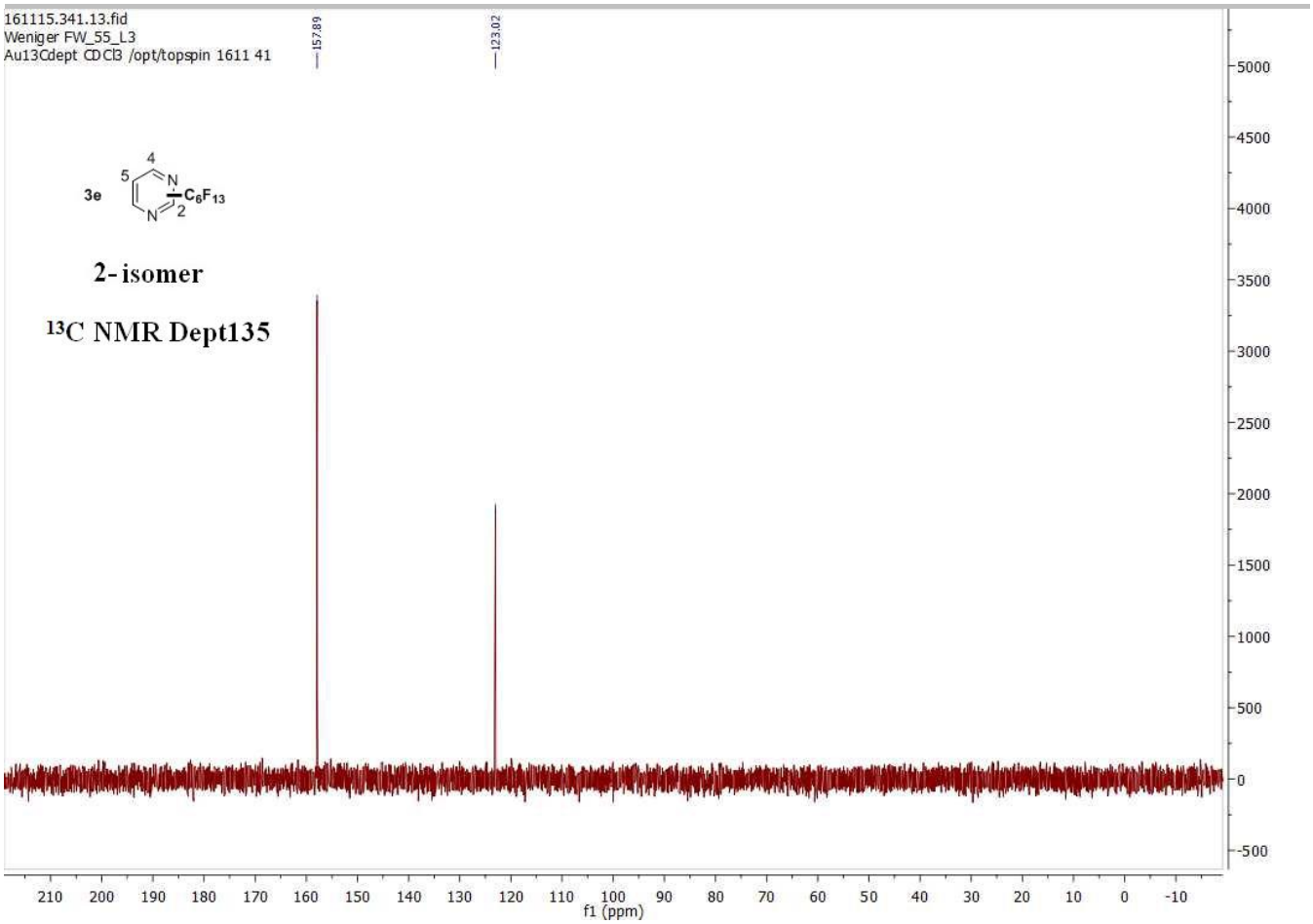
Weniger/ FW-78-C-2
Au19F-FWenig CDCl3 /opt/topspin 1701 46
-80.32
-80.32
-80.33
-80.36
-80.39
-80.40
-80.40
-114.72
-114.77
-114.82
-121.17
-121.50
-122.39
-125.73
3d
$C_6F_{13}$
$NH_2$
6-isomer
$^{19}$F NMR
3.00
1.88
5.82
1.95
f1 (ppm)


161115.341.11.fid
Weniger FW_55_L3
Au1H CDCl3 /opt/topspin 1611 41
8.96
8.95
7.55
7.53
7.52
7.26 CDCl3
1.65 HDO
3e
2-isomer
1H NMR
2.00
1.01
f1 (ppm)


161115.341.12.fid
Weniger FW_55_L3
Au13C CDCl3 /opt/topspin 1611 41
157.87
123.00
77.00 CDCl3
3e
2-isomer
13C NMR
f1 (ppm)


161115.341.13.fid
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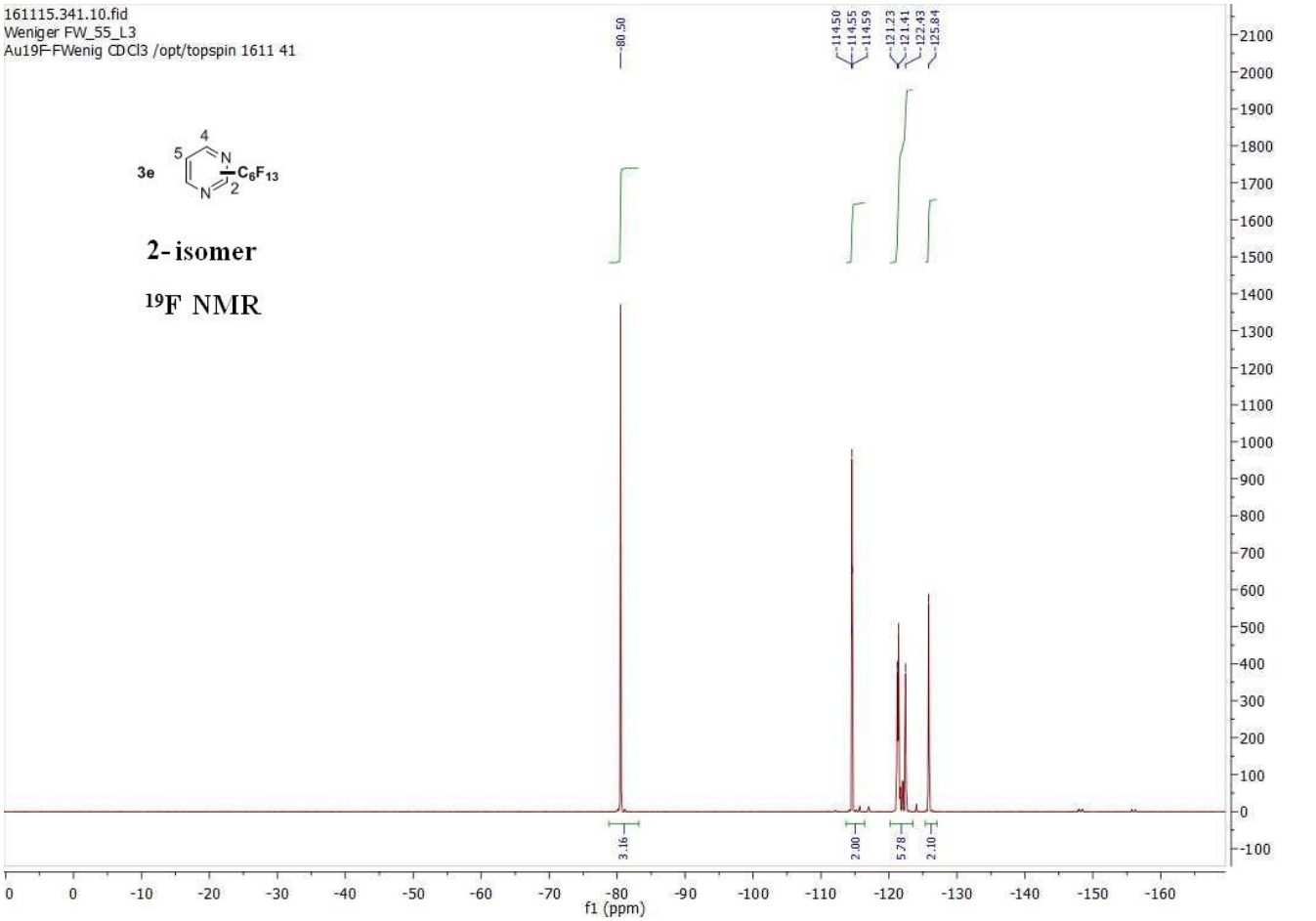
Au13Cdept CDCl3 /opt/topspin 1611 41
157.89
123.02
3e
2- isomer
13C NMR Dept135
f1 (ppm)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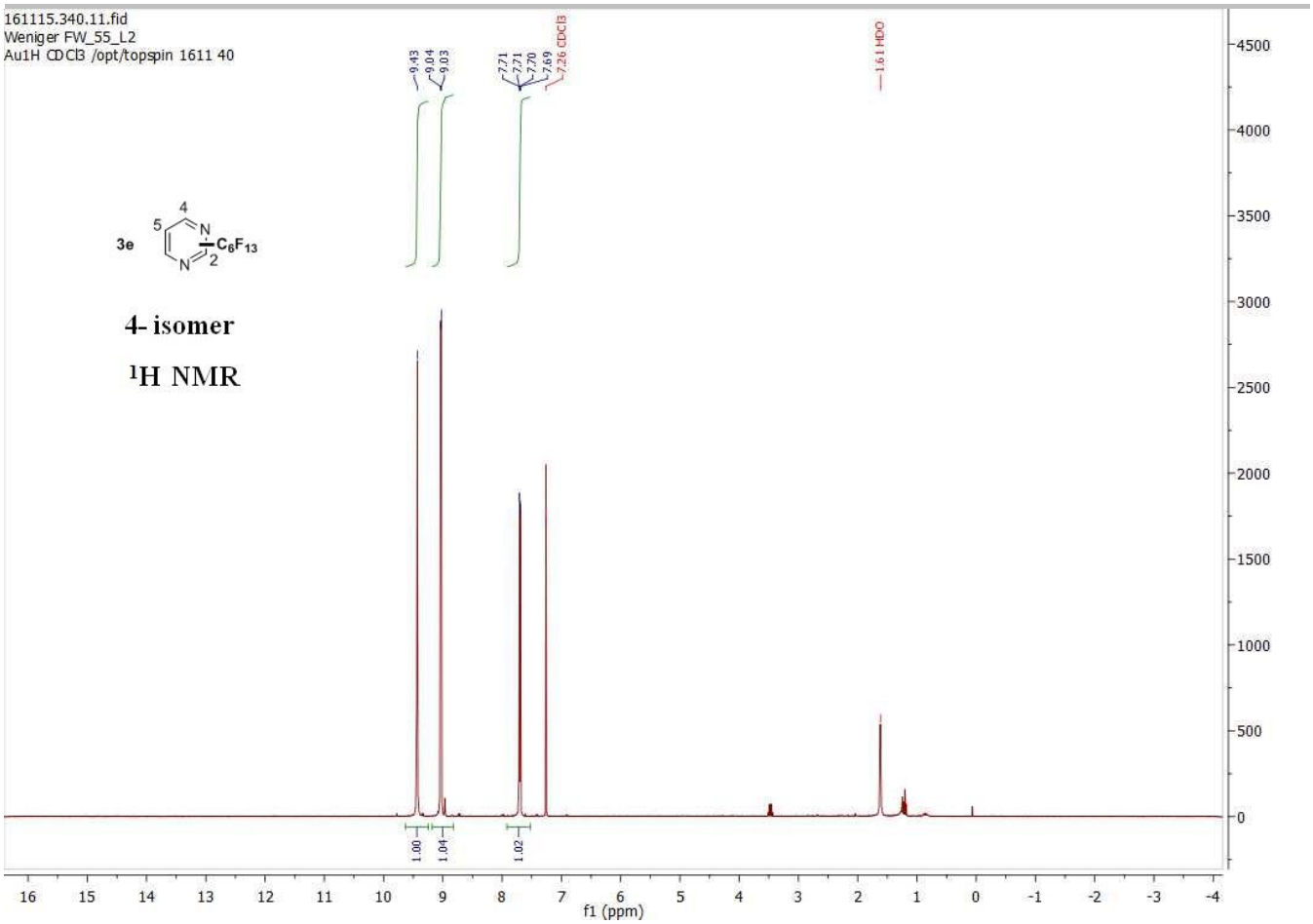
Au19F-FWenig CDCl3 /opt/topspin 1611 41
-80.50
-114.50
-114.55
-114.59
-121.23
-121.41
-122.43
-125.84
3e
2- isomer
19F NMR
3.16
2.00
5.78
2.10
f1 (ppm)


161115.340.11.fid
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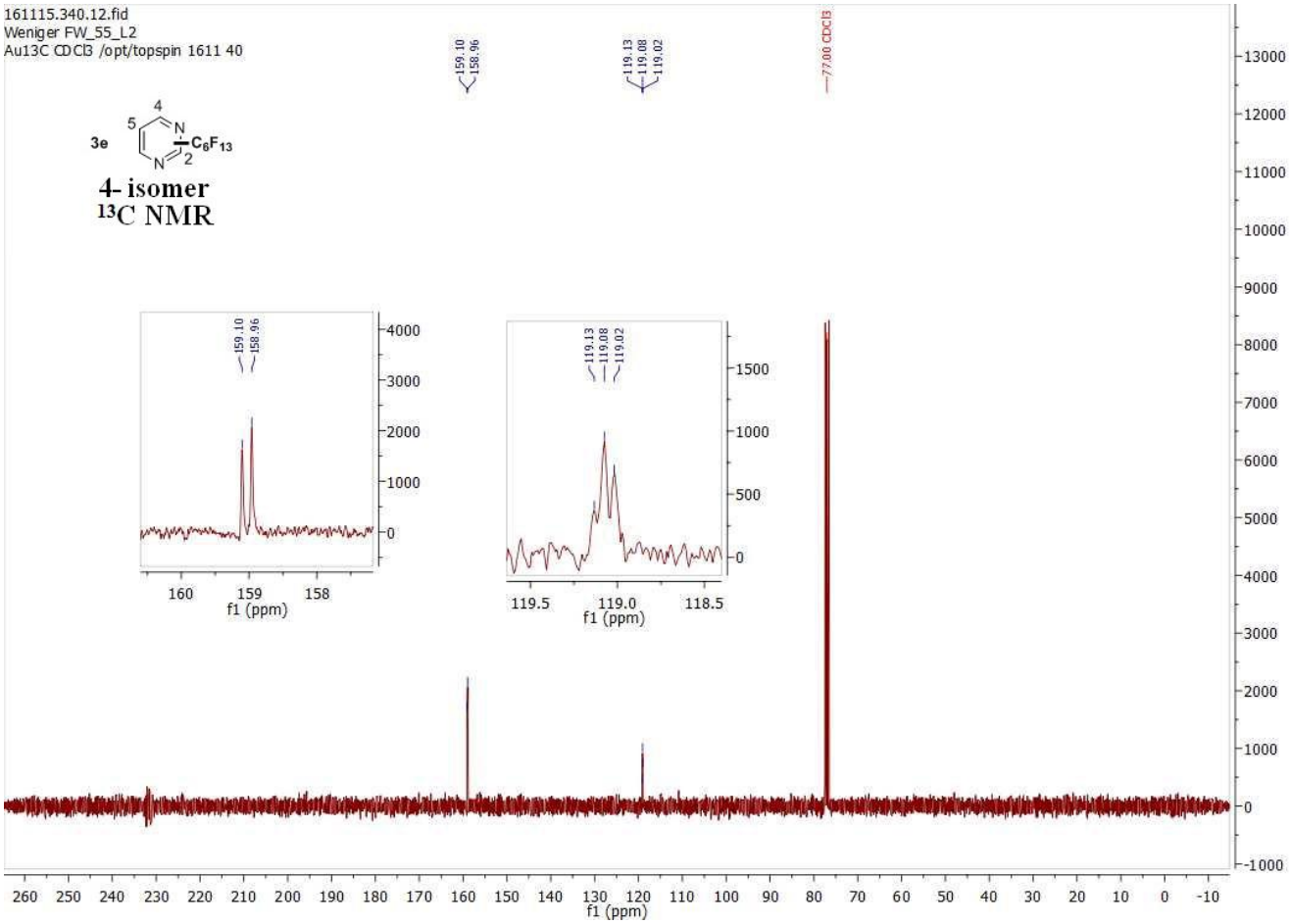
Au1H CDCl3 /opt/topspin 1611 40
9.43
9.04
9.03
7.71
7.71
7.70
7.69
7.26 CDCl3
1.61 HDO
3e
4- isomer
1H NMR
1.00
1.04
1.02
f1 (ppm)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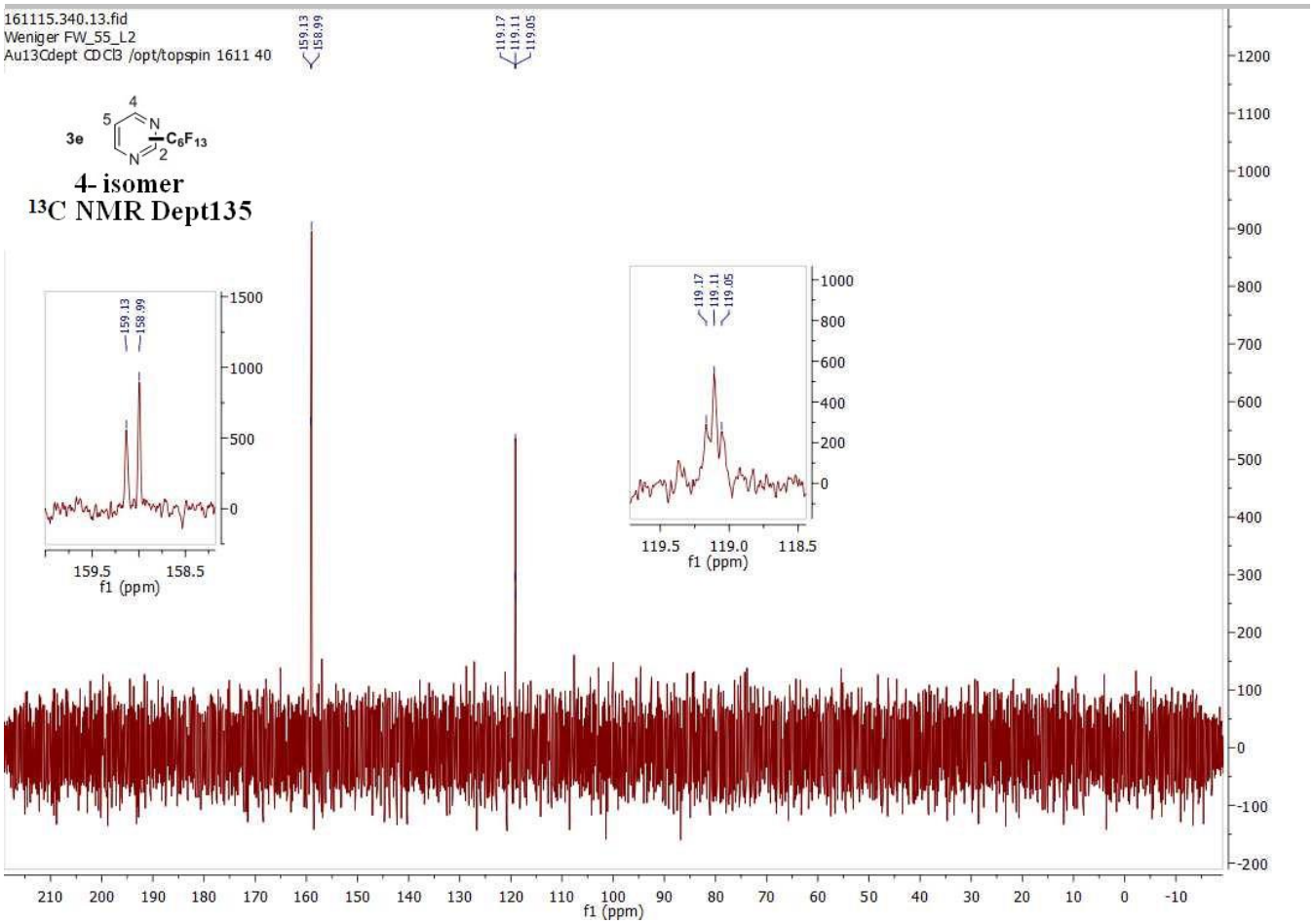
Au13C CDCl3 /opt/topspin 1611 40
159.10
158.96
119.13
119.08
119.02
77.00 CDCl3
3e
4- isomer
13C NMR
f1 (ppm)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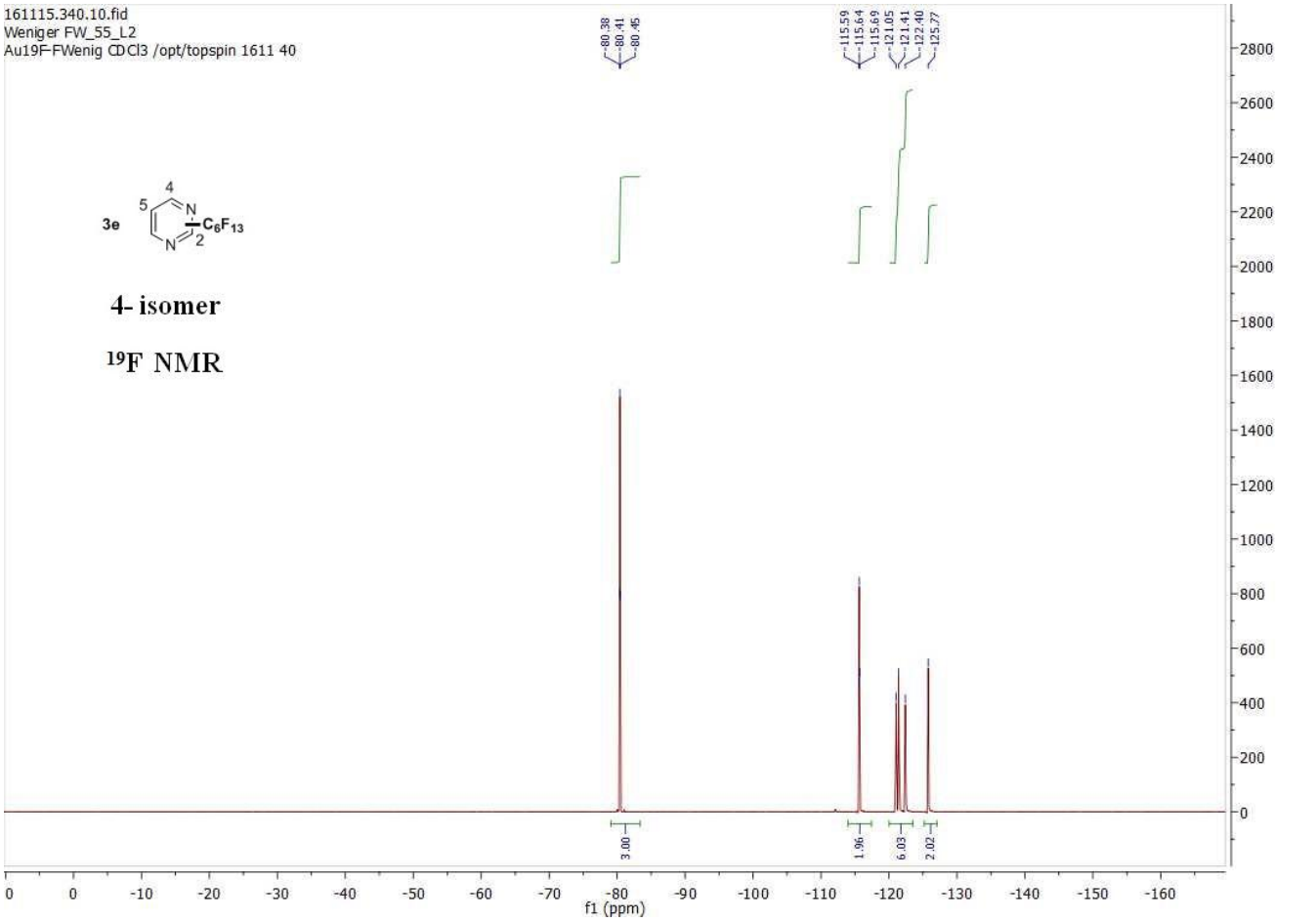
Au13Cdept CDCl3 /opt/topspin 1611 40
159.13
158.99
119.17
119.11
119.05
3e
4- isomer
13C NMR Dept135
f1 (ppm)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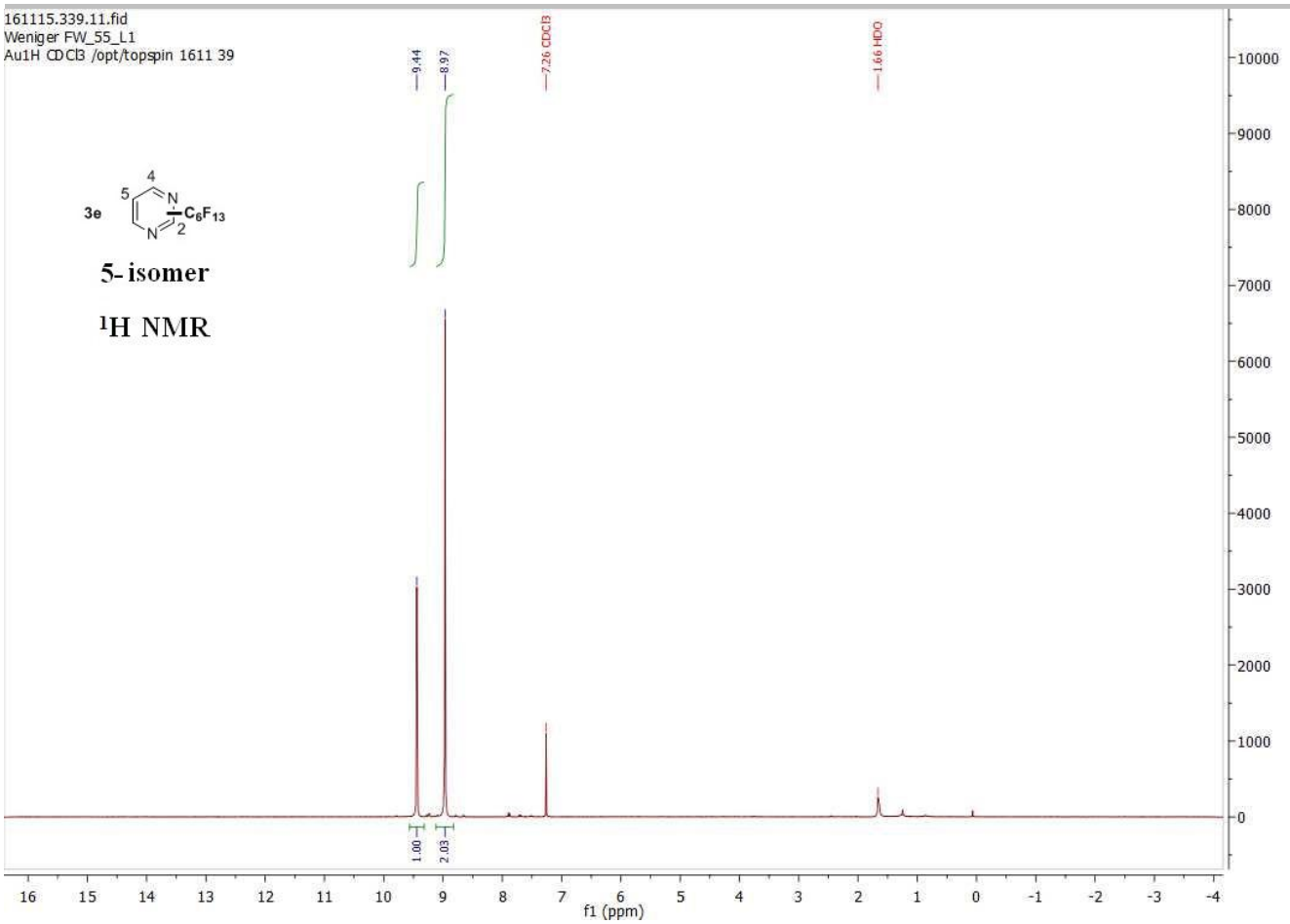
Au19F-FWenig CDCl3 /opt/topspin 1611 40
-80.38
-80.41
-80.45
-115.59
-115.64
-115.69
-121.05
-121.41
-122.40
-125.77
3e
4- isomer
19F NMR
3.00
1.96
6.03
2.02
f1 (ppm)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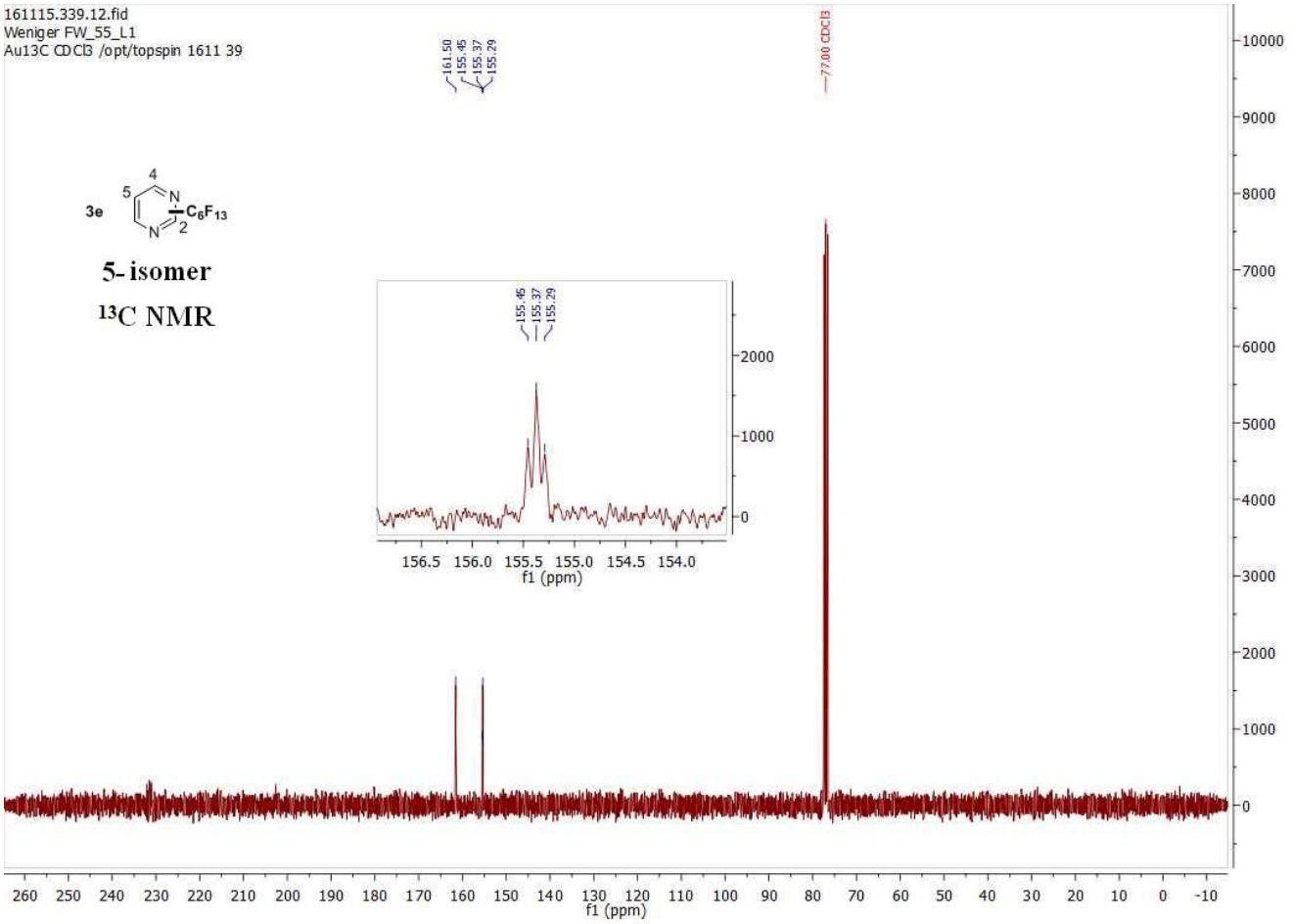
Au1H CDCl3 /opt/topspin 1611 39
9.44
8.97
7.26 CDCl3
1.66 HDO
3e
5-isomer
1H NMR
1.00
2.03
f1 (ppm)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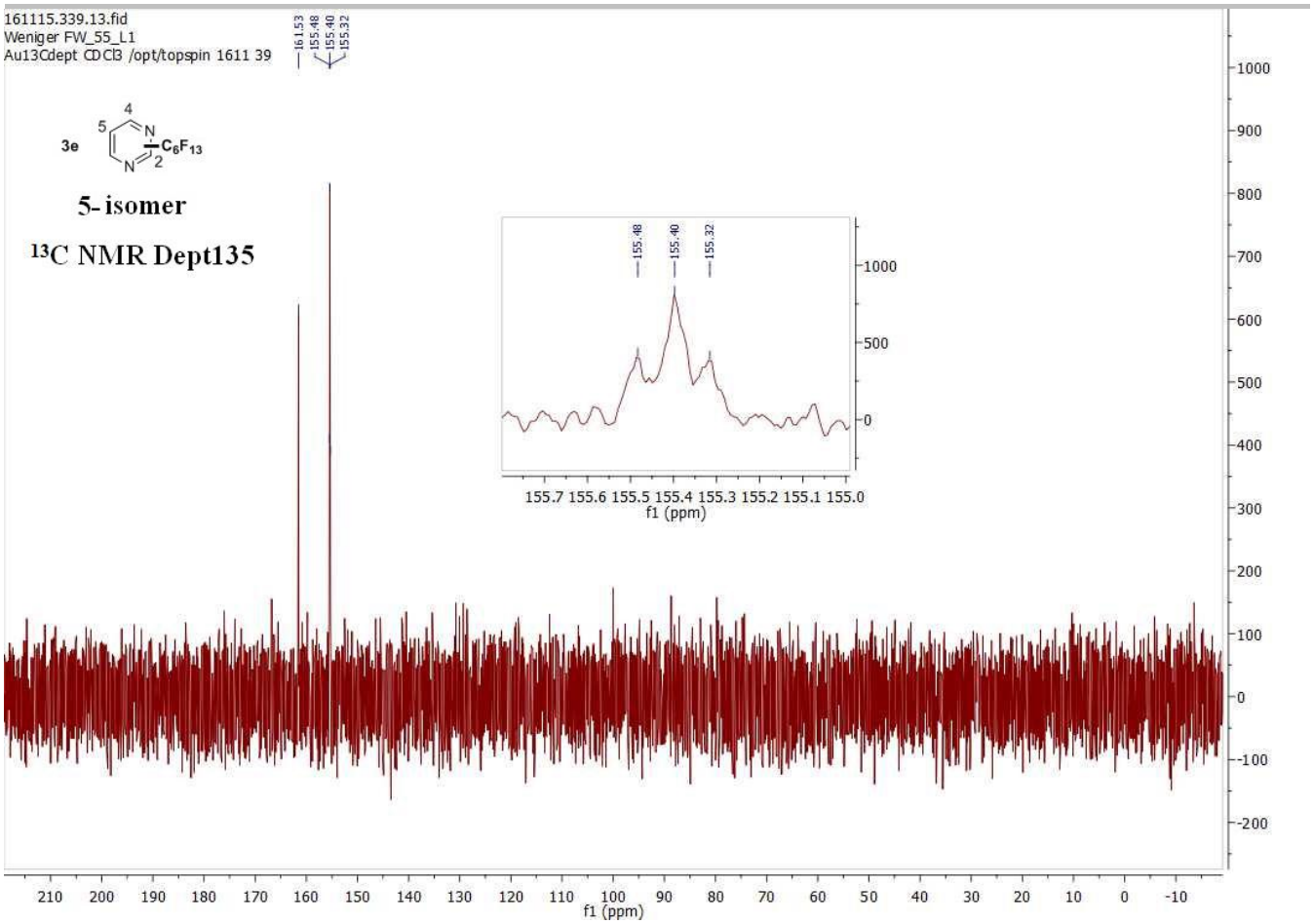
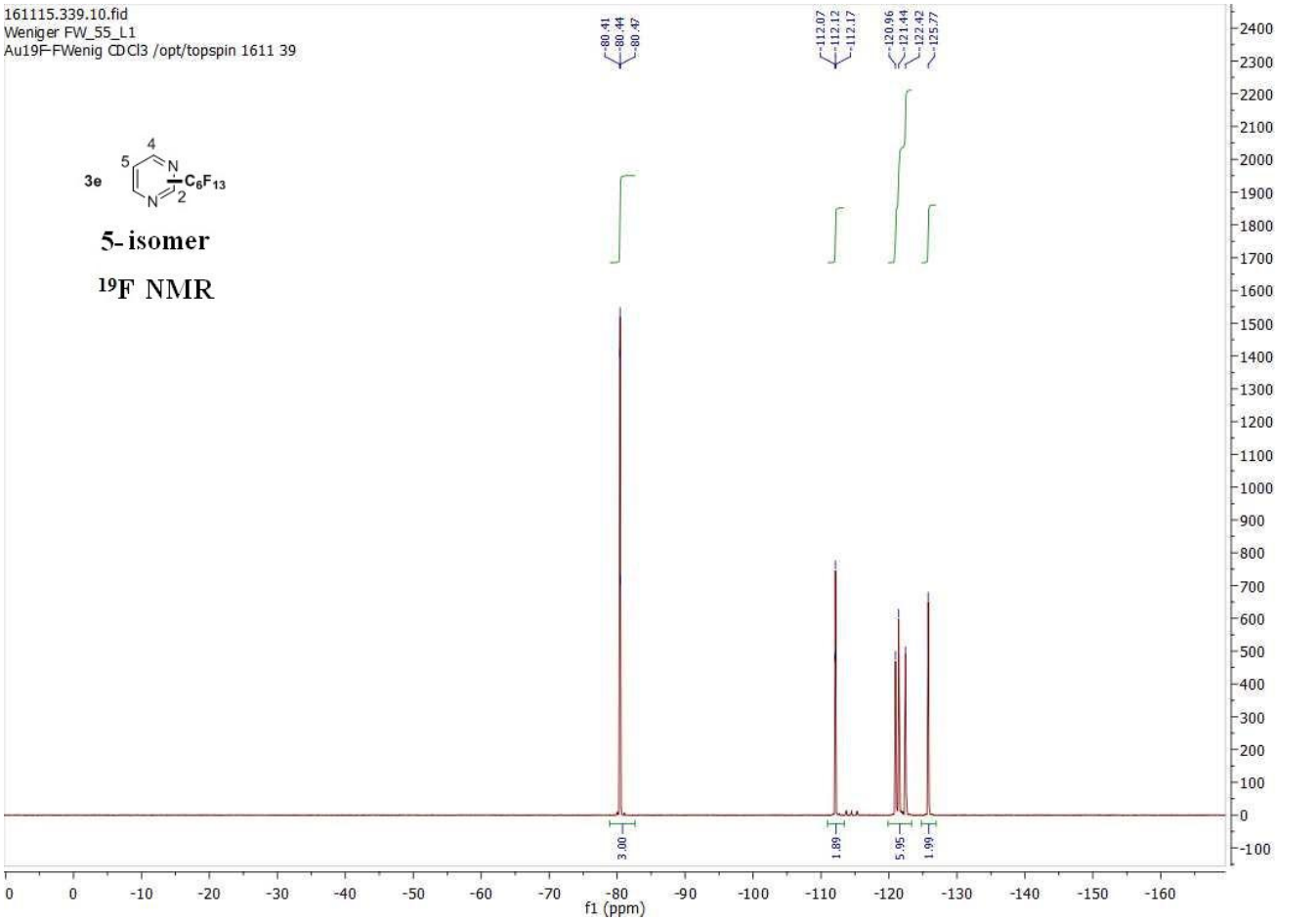
Au13C CDCl3 /opt/topspin 1611 39
161.50
155.45
155.37
155.29
77.00 CDCl3
3e
5-isomer
13C NMR
f1 (ppm)


161115.339.13.fid
Weniger FW_55_L1
Au13Cdept CDCl3 /opt/topspin 1611 39
161.53
155.48
155.40
155.32
3e
5-isomer
13C NMR Dept135
155.48
155.40
155.32
155.7 155.6 155.5 155.4 155.3 155.2 155.1 155.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


161115.339.10.fid
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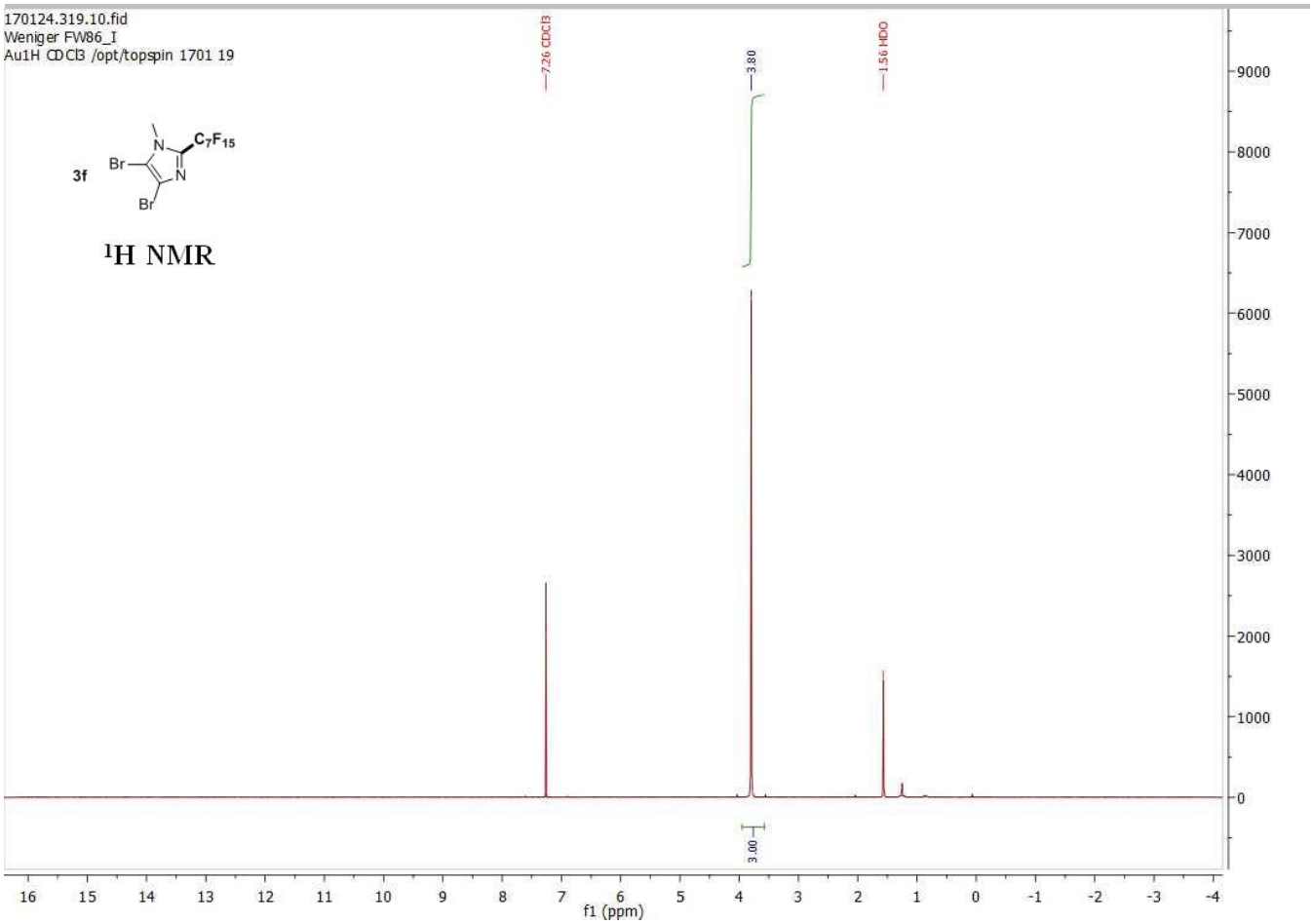
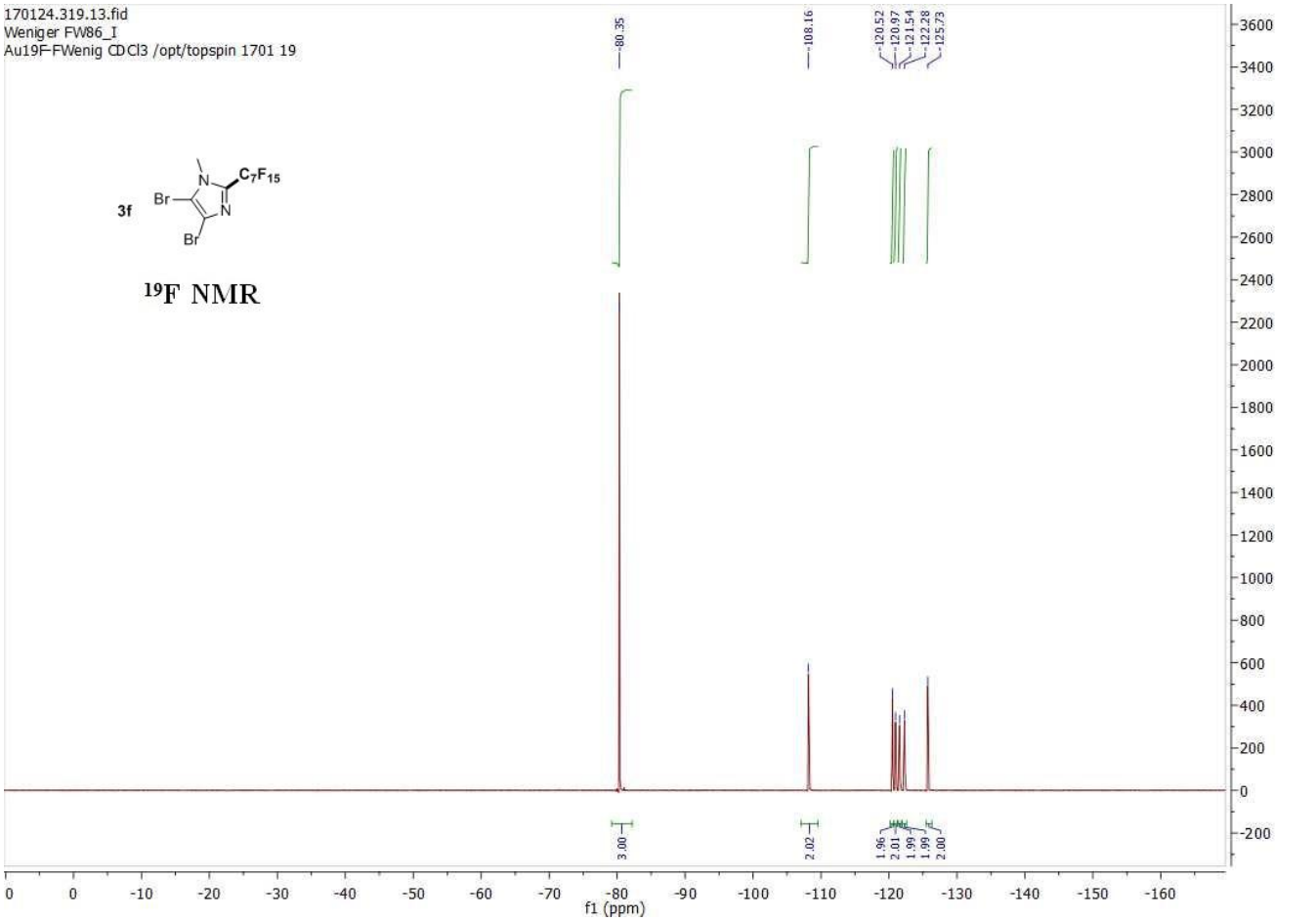
Au19F-FWenig CDCl3 /opt/topspin 1611 39
-80.41
-80.44
-80.47
-112.07
-112.12
-112.17
-120.96
-121.44
-122.42
-125.77
3e
5-isomer
19F NMR
3.00
1.89
5.95
1.99
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


170124.319.10.fid
Weniger FW86_I
Au1H CDCl3 /opt/topspin 1701 19
7.26 CDCl3
3.80
1.56 HDO
3f
Br
Br
N
N
C7F15
1H NMR
3.00
f1 (ppm)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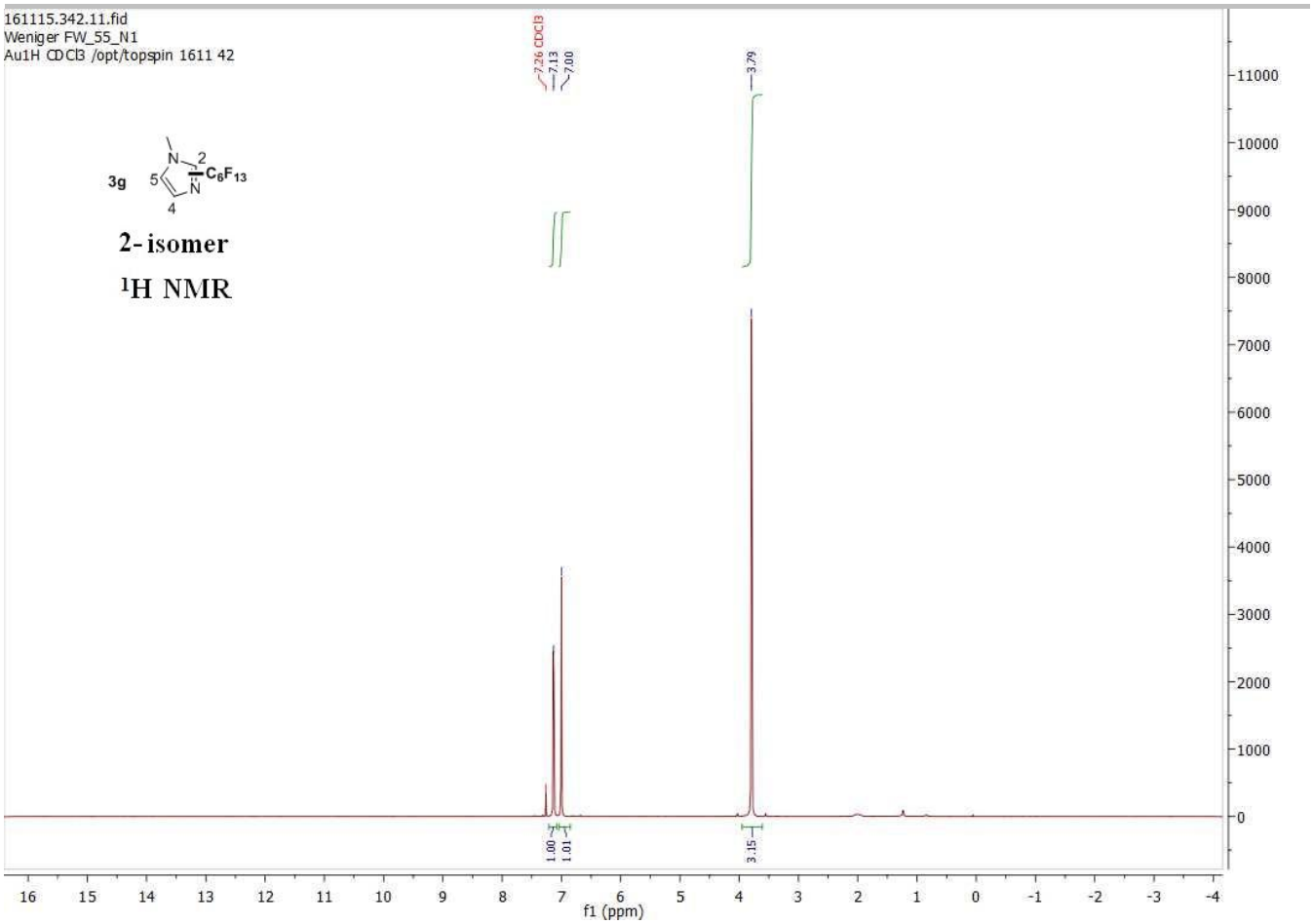
Au19F-FWenig CDCl3 /opt/topspin 1701 19
-80.35
-108.16
-120.52
-120.97
-121.54
-122.28
-125.73
3f
Br
Br
N
N
C7F15
19F NMR
3.00
2.02
1.96
2.01
1.99
1.99
2.00
f1 (ppm)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Au1H CDCl3 /opt/topspin 1611 42
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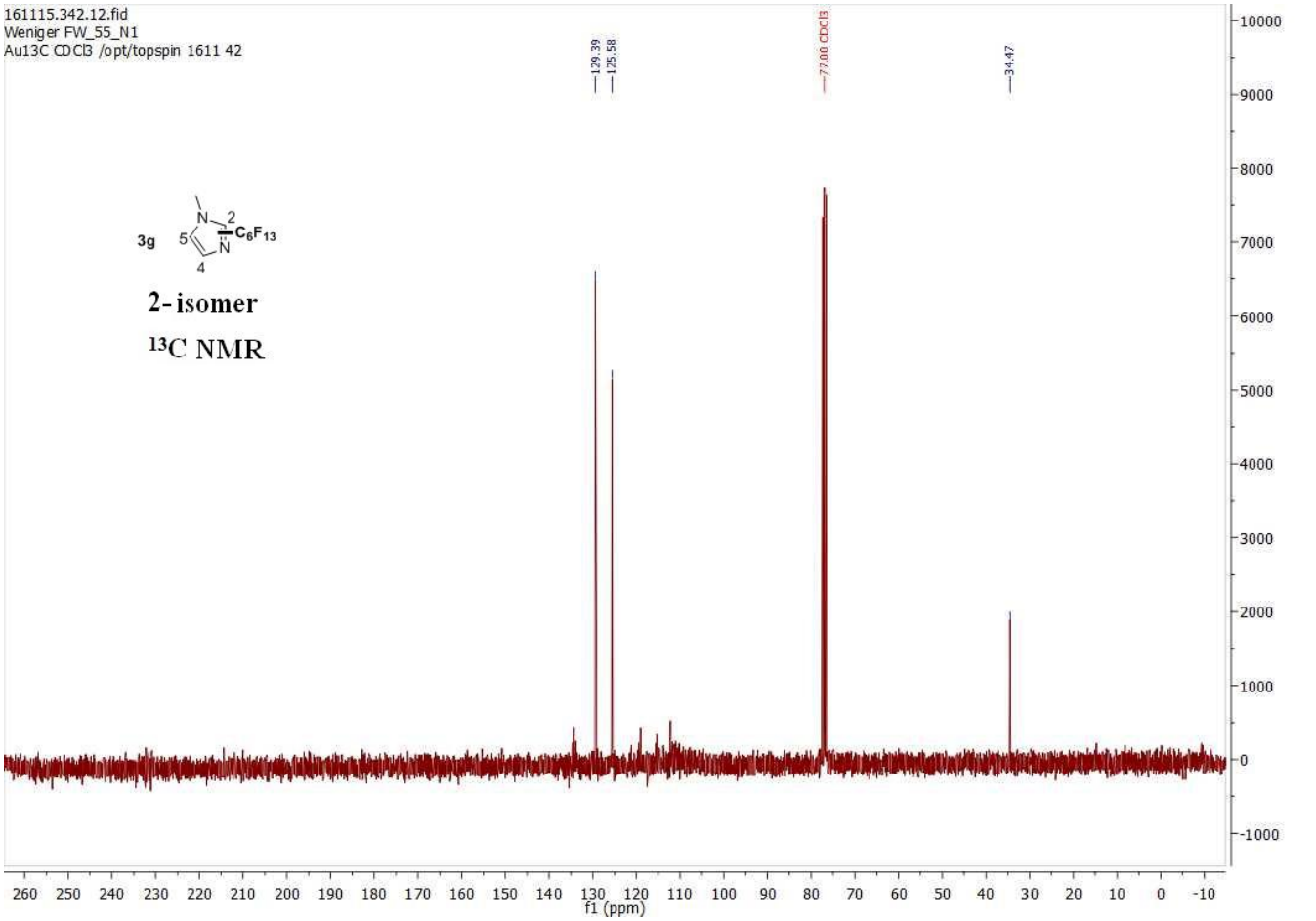
7.13
7.00
3.79
3g
2-isomer
1H NMR
1.00
1.01
3.15
f1 (ppm)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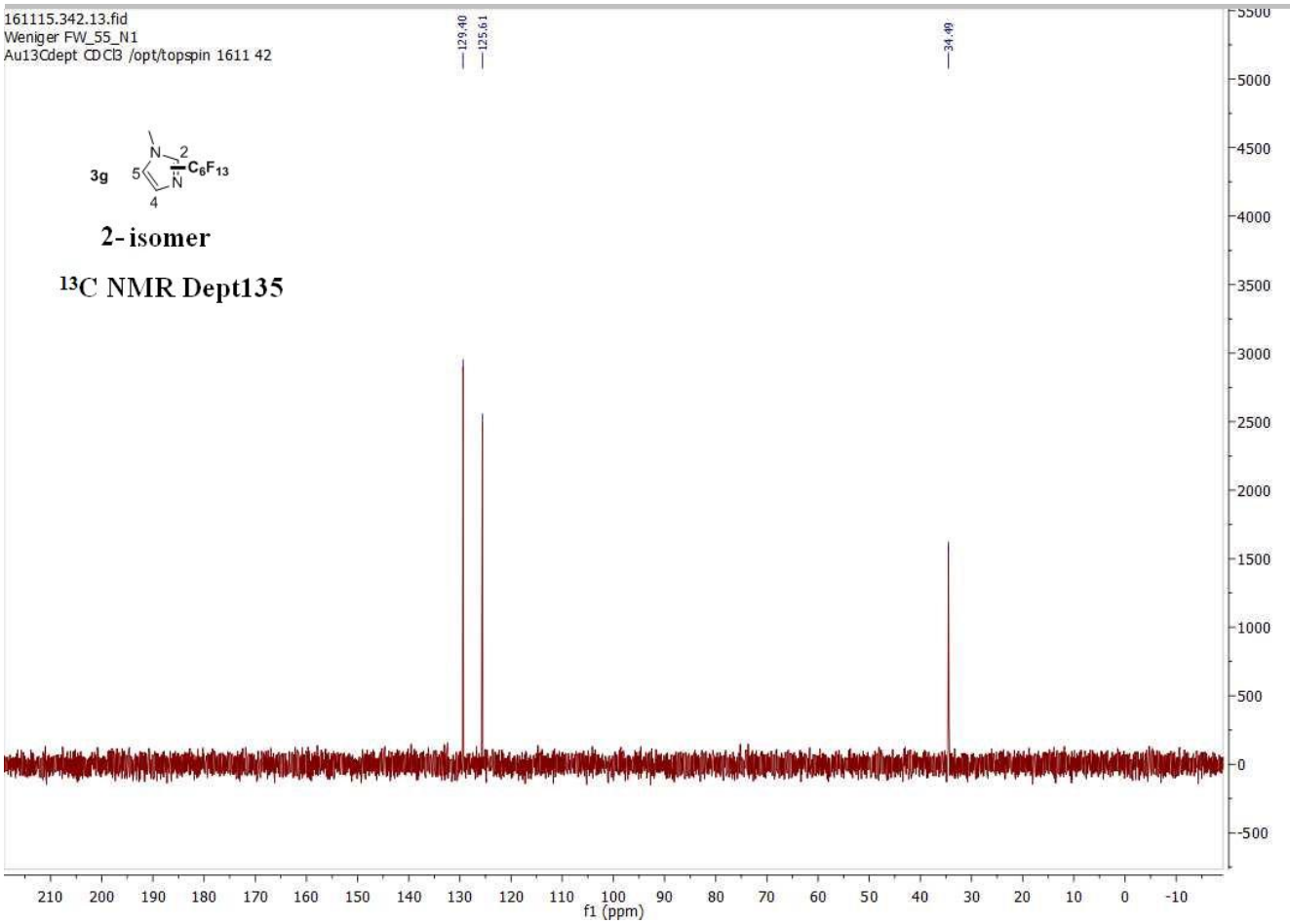
Au13C CDCl3 /opt/topspin 1611 42
129.39
125.58
77.00 CDCl3
34.47
3g
2-isomer
13C NMR
f1 (ppm)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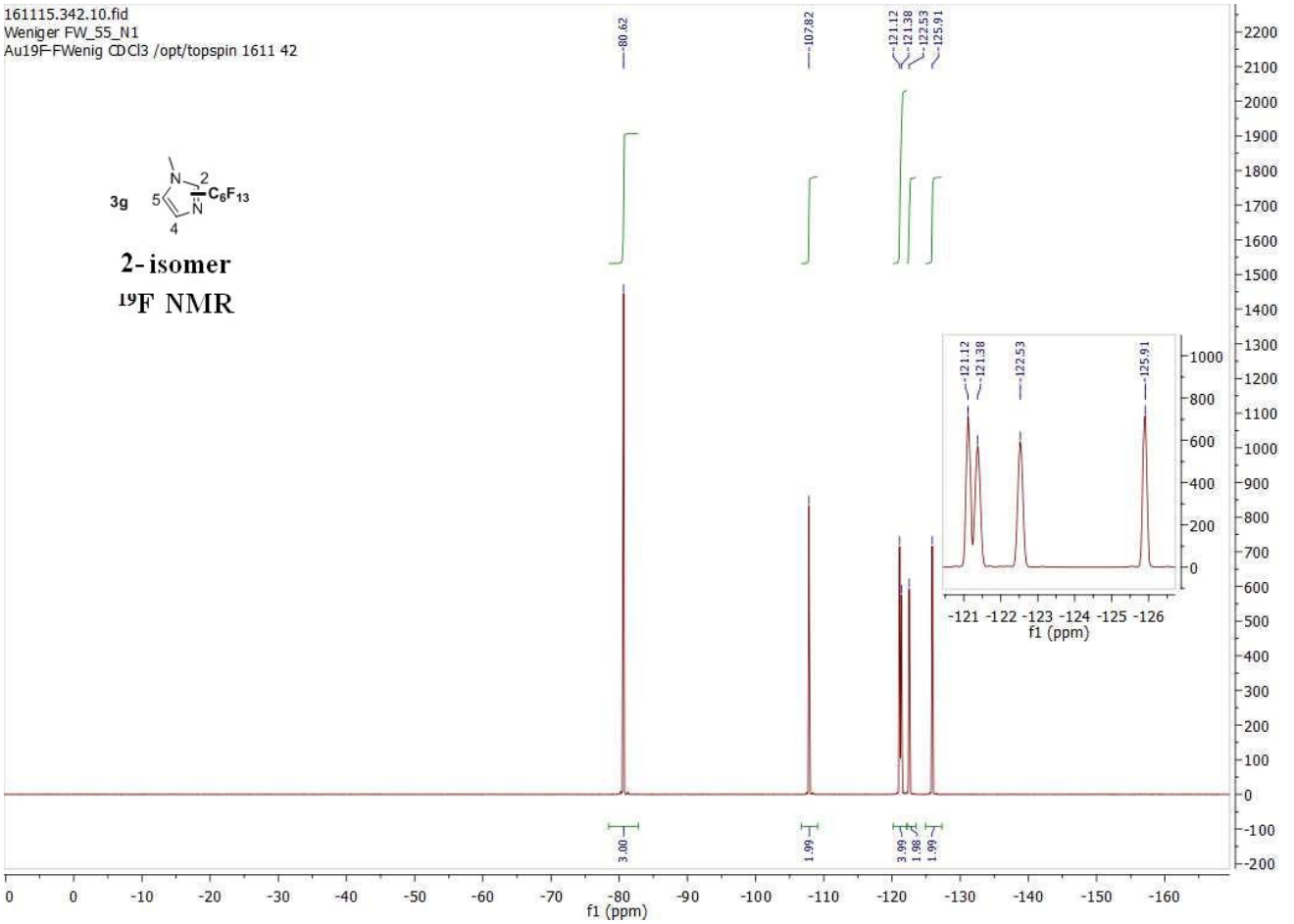
Au13Cdept CDCl3 /opt/topspin 1611 42
129.40
125.61
34.49
3g
2-isomer
13C NMR Dept135
f1 (ppm)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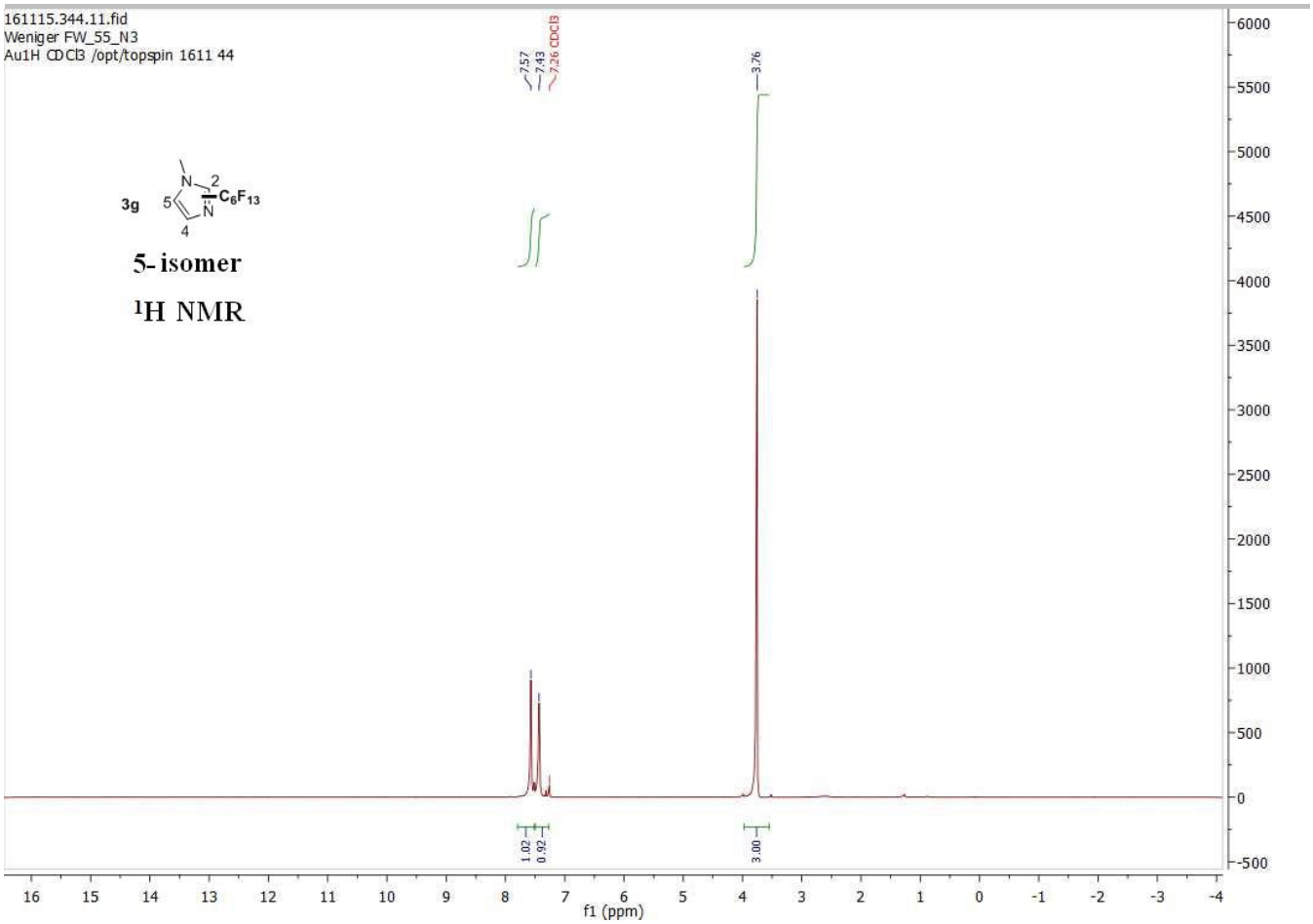
Au19F-FWenig CDCl3 /opt/topspin 1611 42
-80.62
-107.82
-121.12
-121.38
-122.53
-125.91
3g
2-isomer
19F NMR
3.00
1.99
3.99
1.98
1.99
f1 (ppm)


161115.344.11.fid
Weniger FW_55_N3
Au1H CDCl3 /opt/topspin 1611 44
7.57
7.43
7.26 CDCl3
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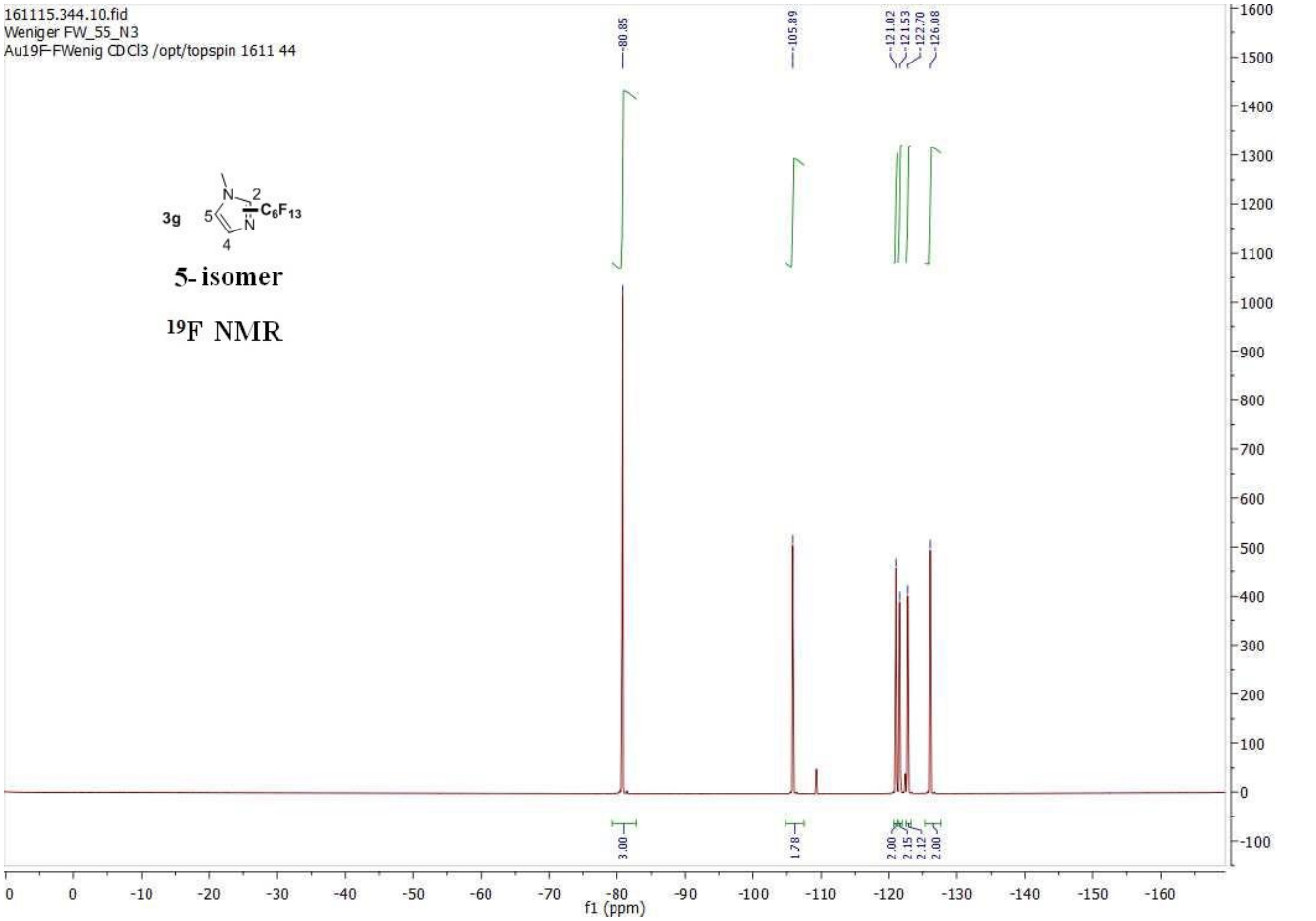
3g
5-isomer
1H NMR
1.02
0.92
3.00
f1 (ppm)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Au19F-FWenig CDCl3 /opt/topspin 1611 44
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-105.89
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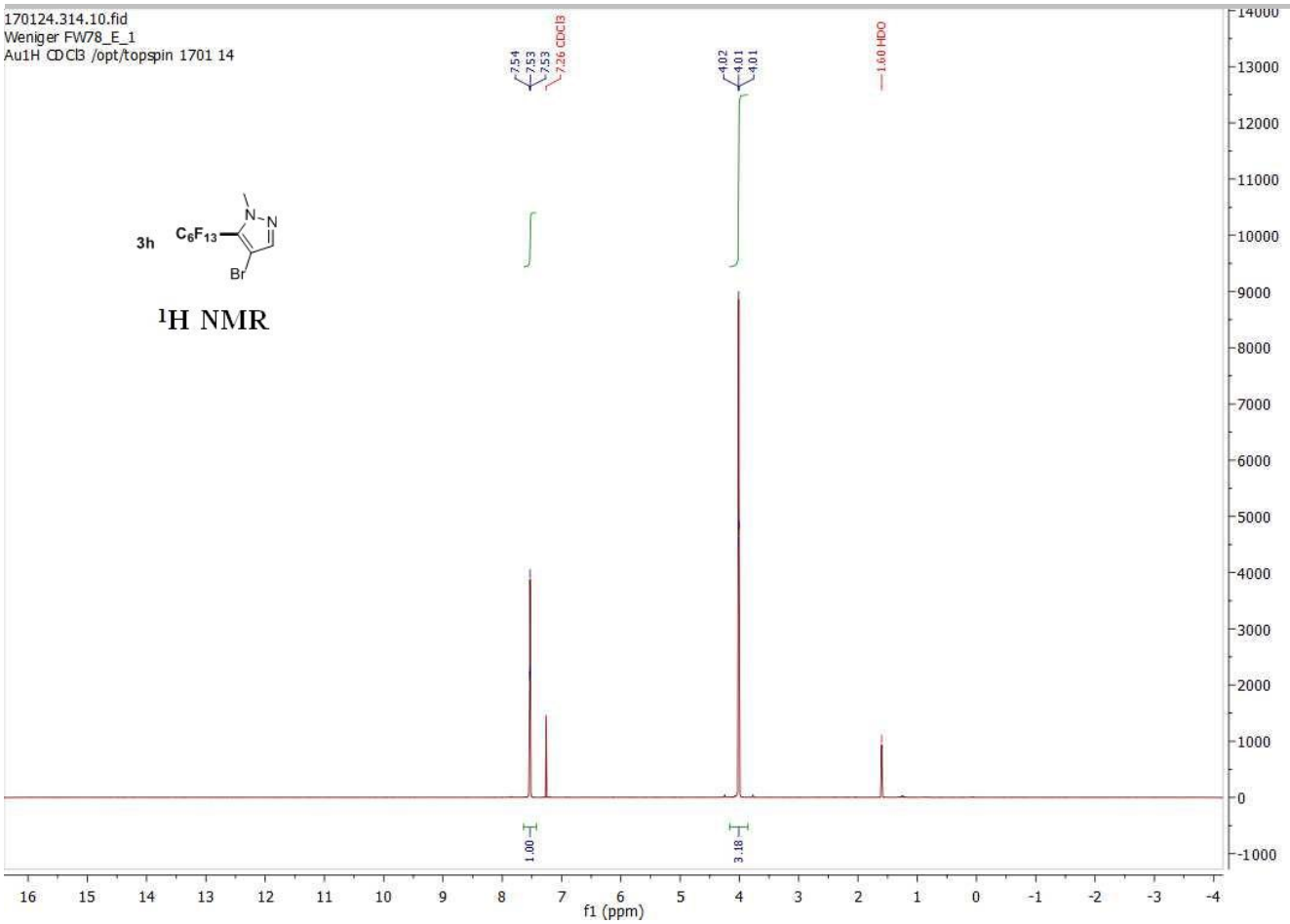
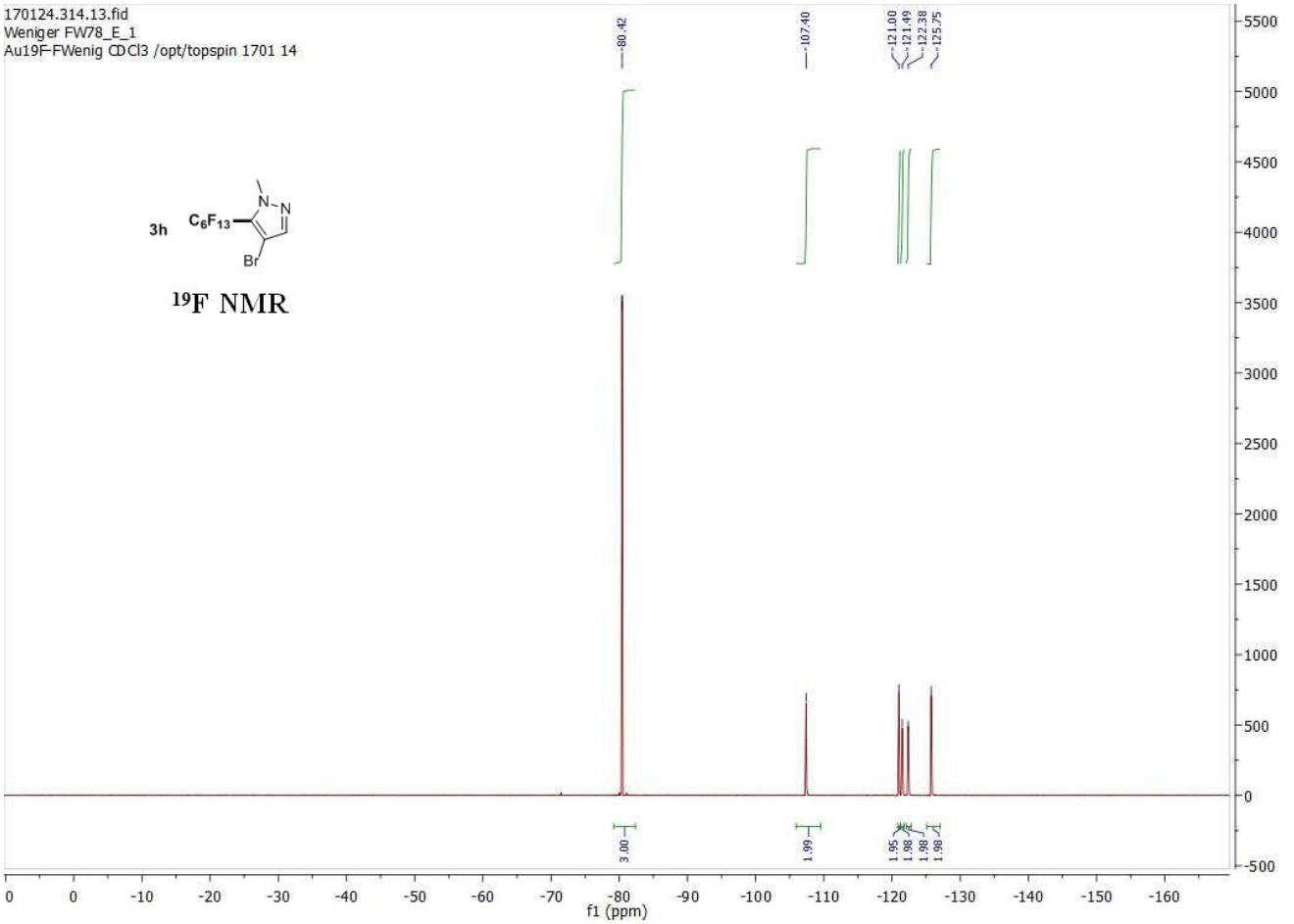
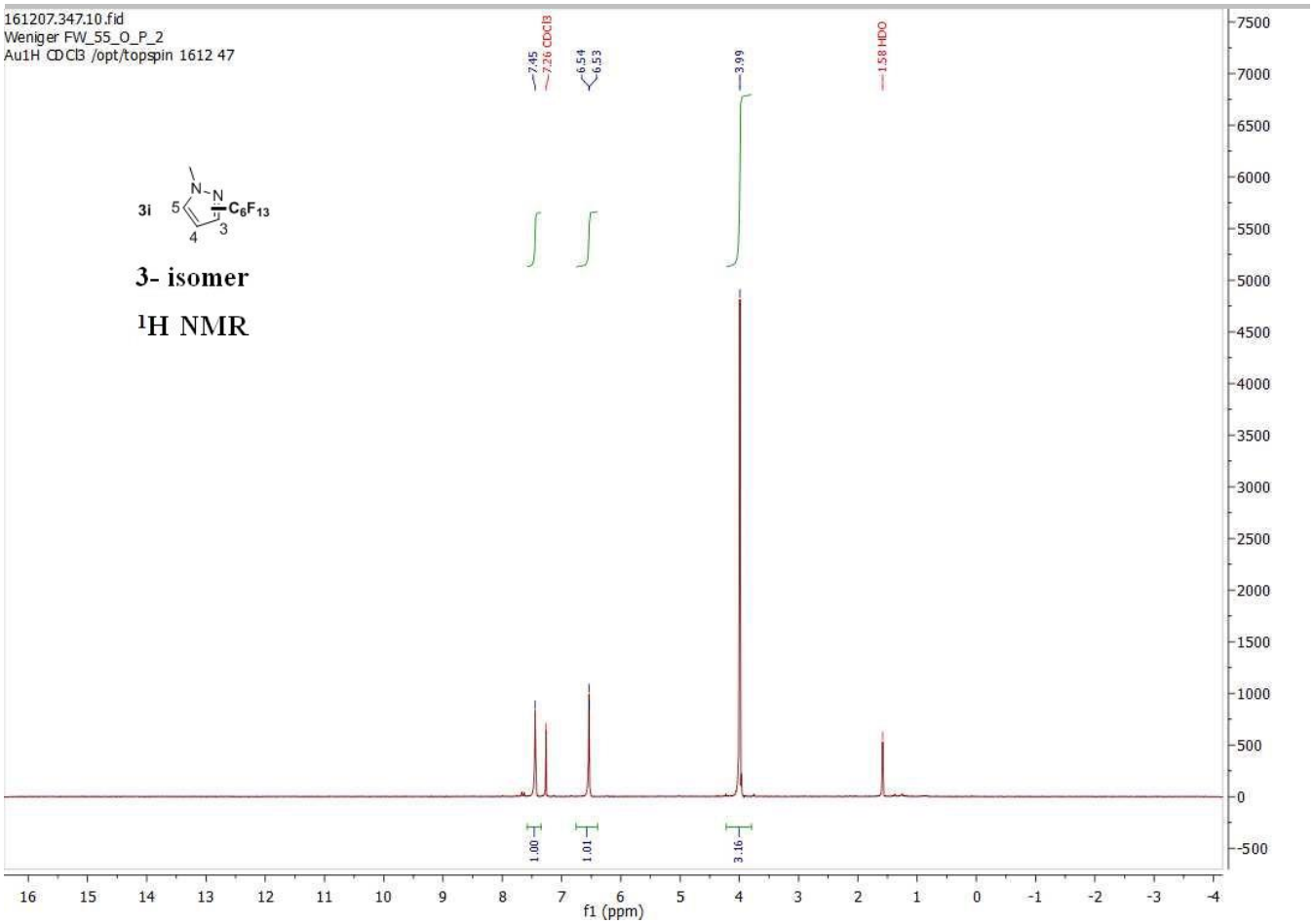
-121.53
-122.70
-126.08
3g
5-isomer
19F NMR
3.00
1.78
2.00
2.15
2.12
2.00
f1 (ppm)




$^{1}$H NMR




$^{19}$F NMR


161207.347.10.fid
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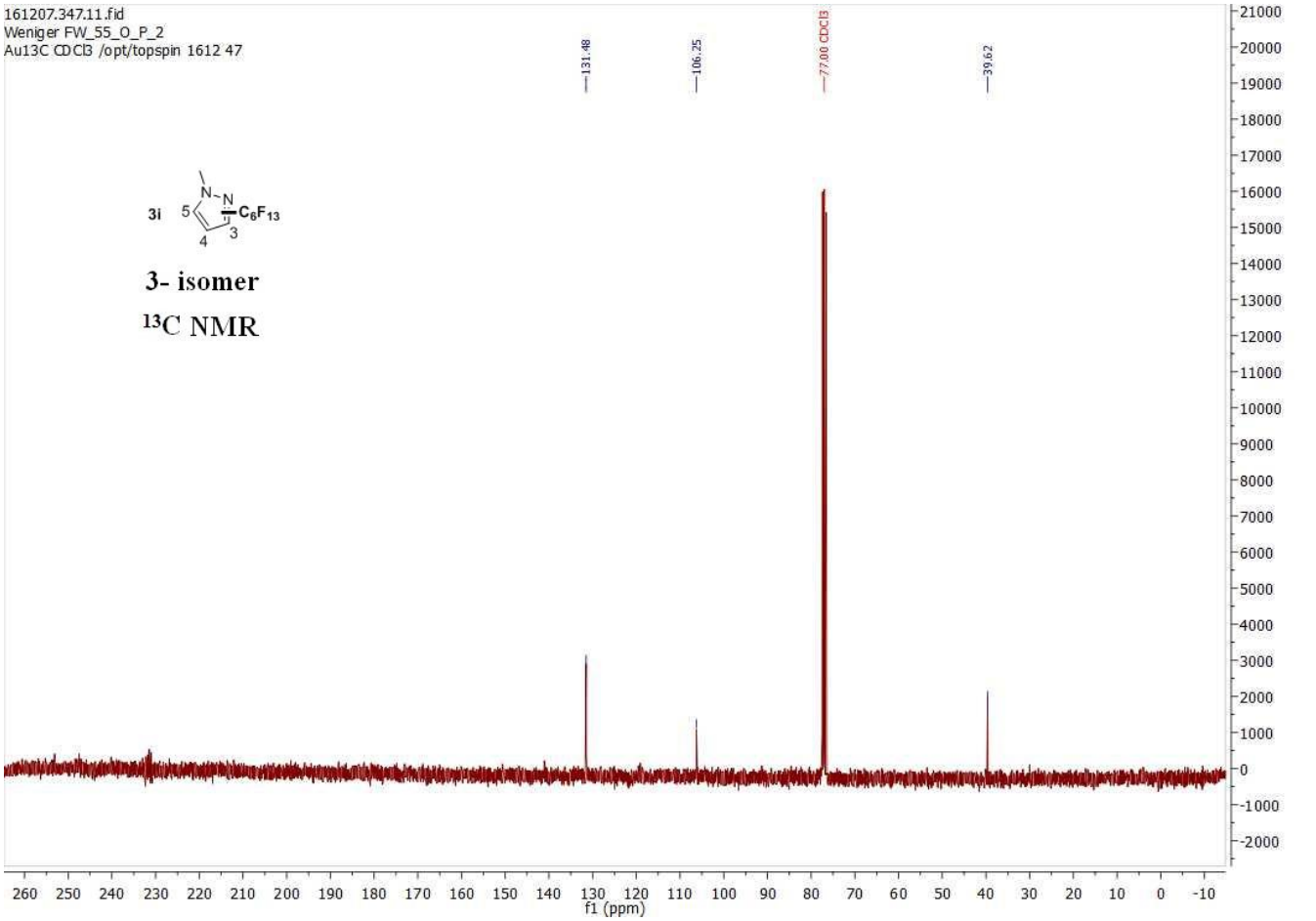
Au1H CDCl3 /opt/topspin 1612 47
7.45
7.26 CDCl3
6.54
6.53
3.99
1.58 HDO
3i
C6F13
3- isomer
1H NMR
1.00
1.01
3.16
f1 (ppm)


161207.347.11.fid
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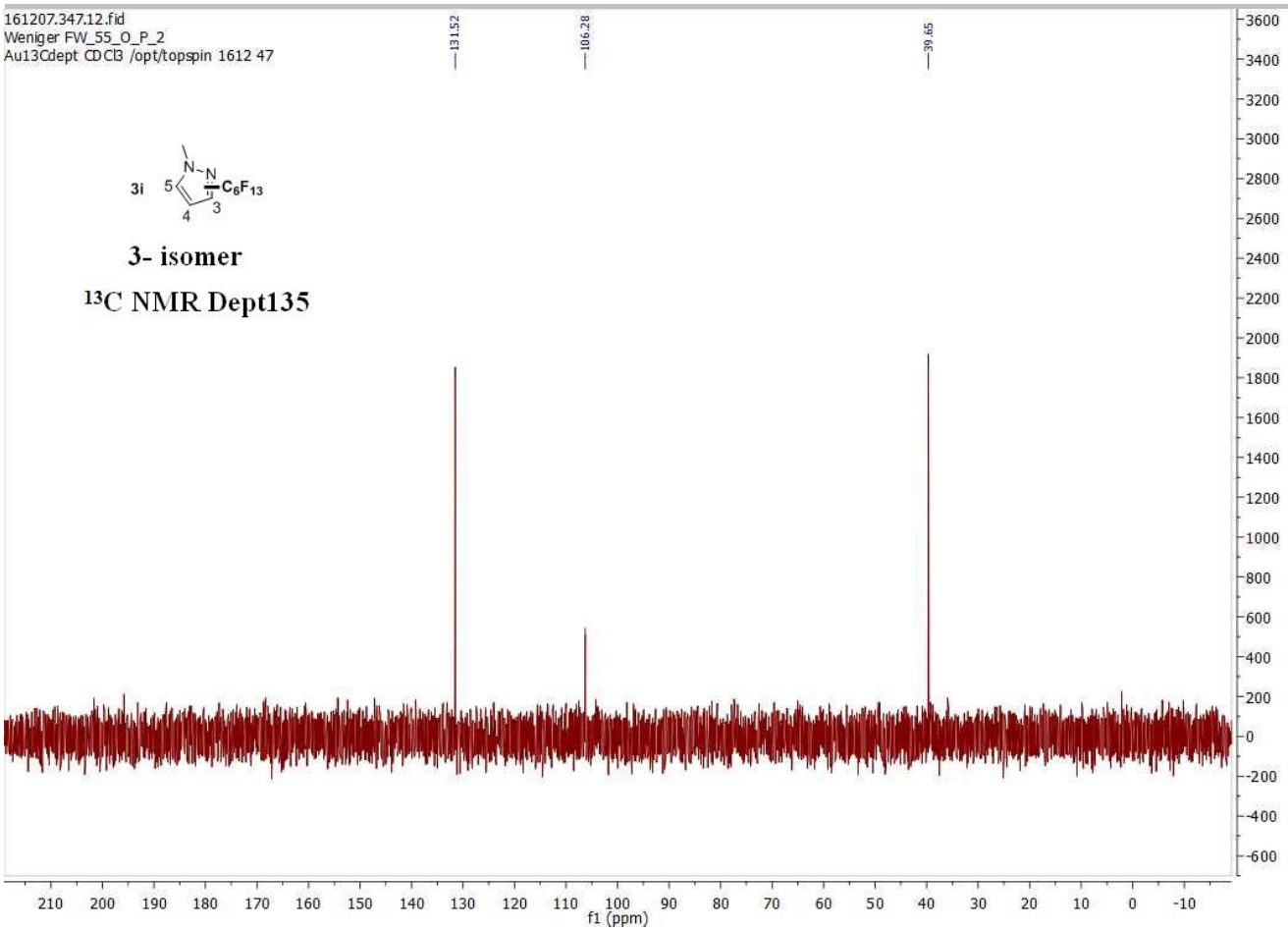
Au13C CDCl3 /opt/topspin 1612 47
131.48
106.25
77.00 CDCl3
39.62
3i
C6F13
3- isomer
13C NMR
f1 (ppm)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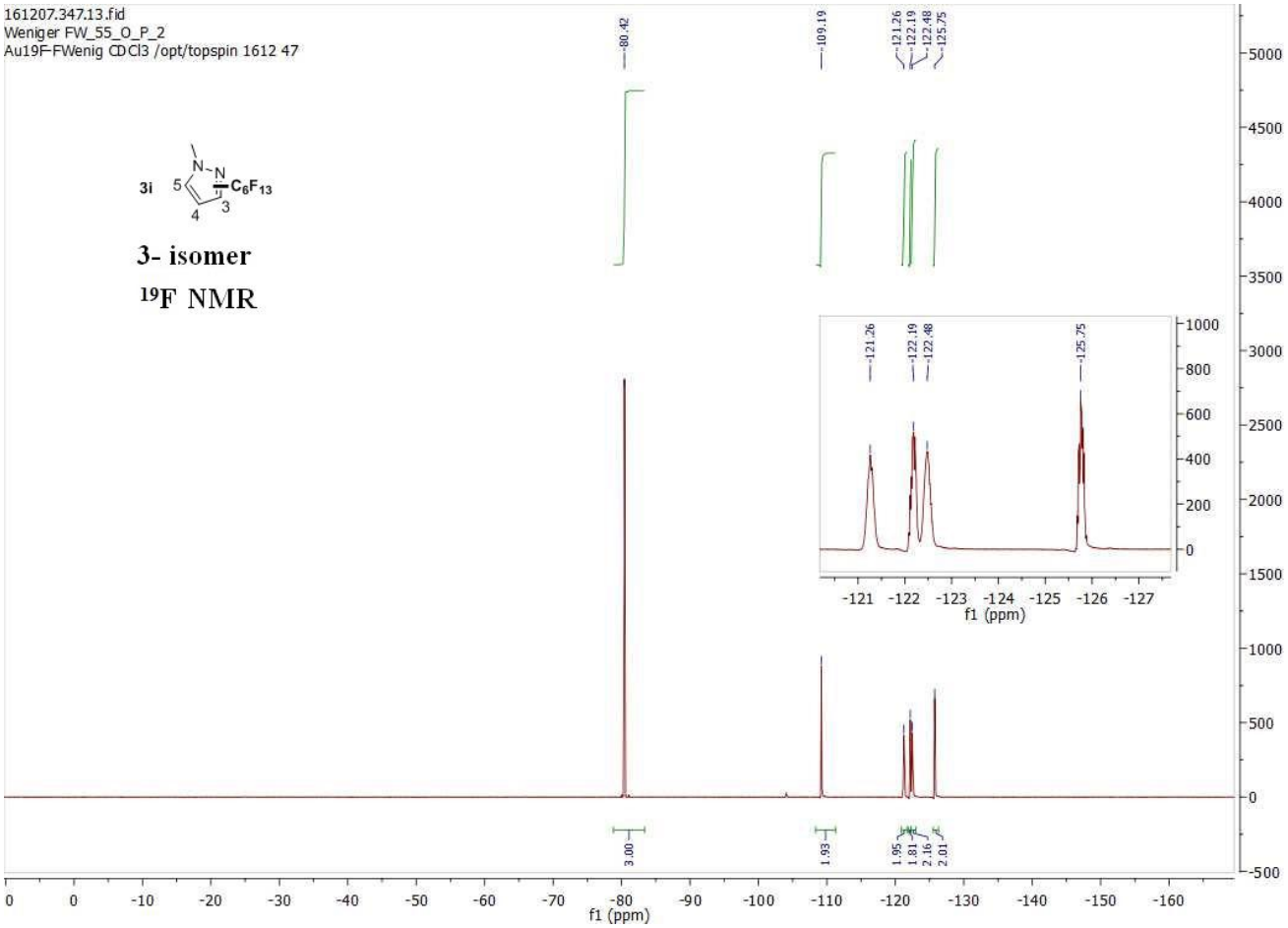
131.52
106.28
39.65
3i
3- isomer
13C NMR Dept135
f1 (ppm)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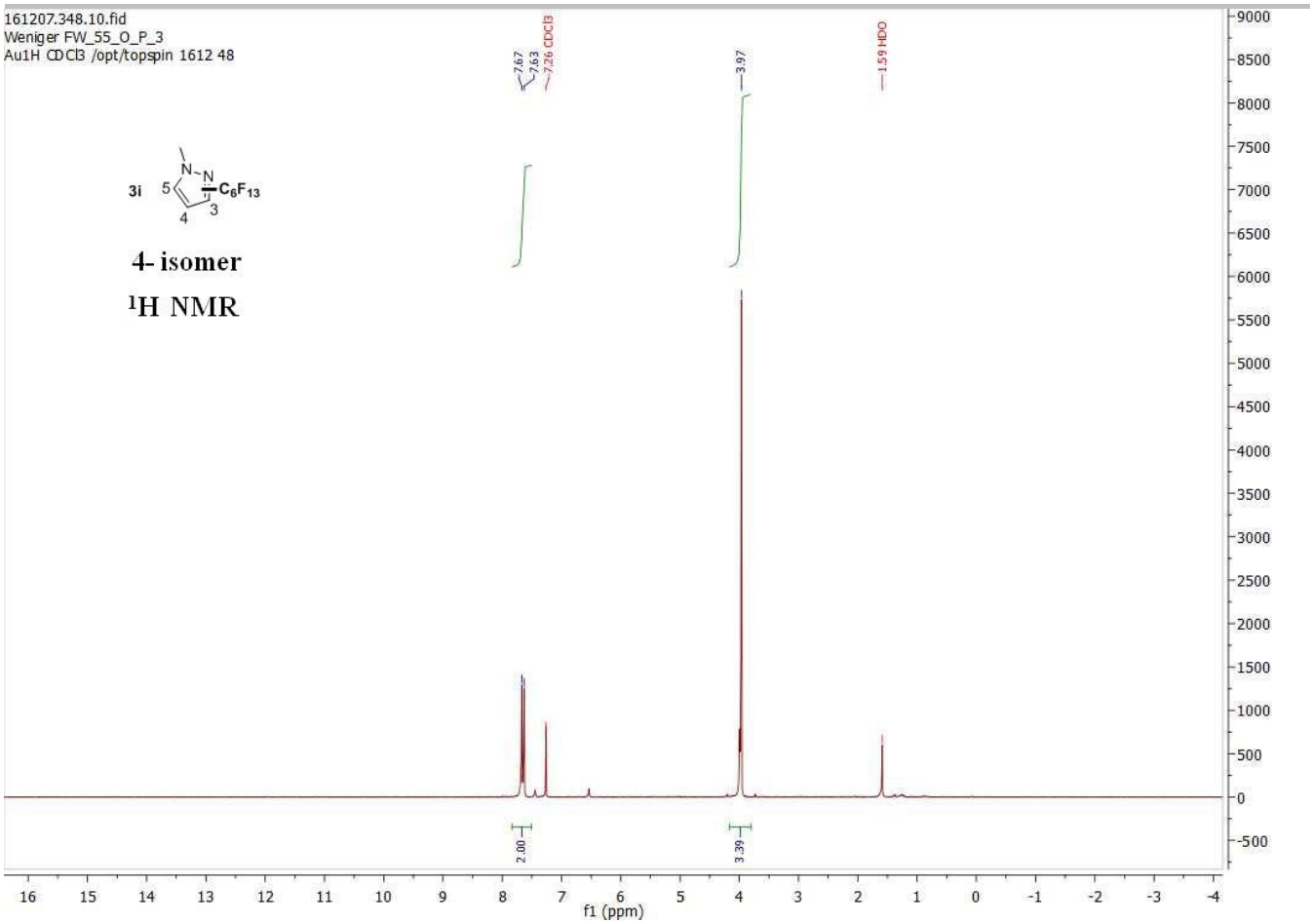
Au19F-FWenig CDCl3 /opt/topspin 1612 47
-80.42
-109.19
-121.26
-122.19
-122.48
-125.75
3i
3- isomer
19F NMR
3.00
1.93
1.95
1.81
2.16
2.01
f1 (ppm)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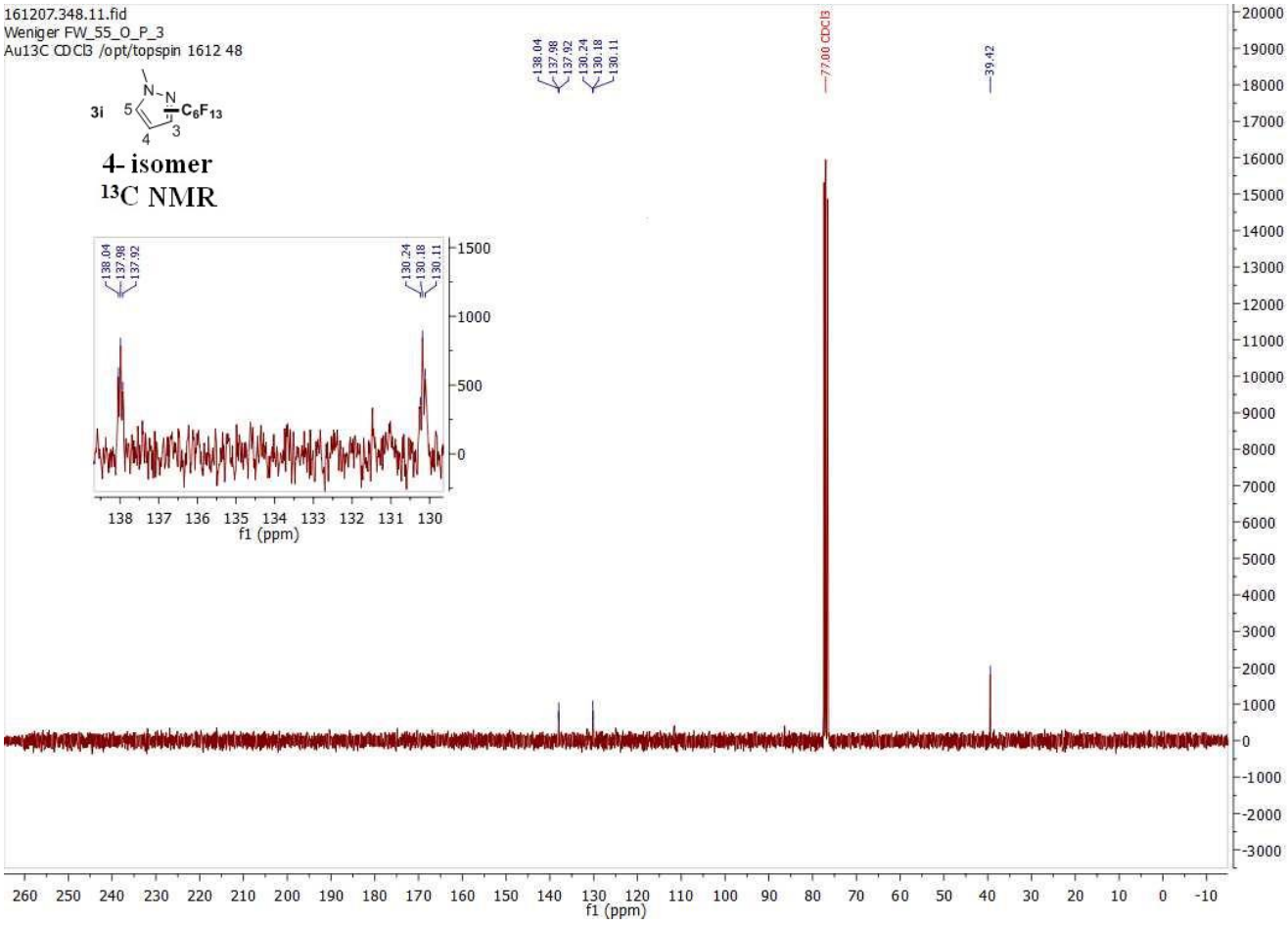
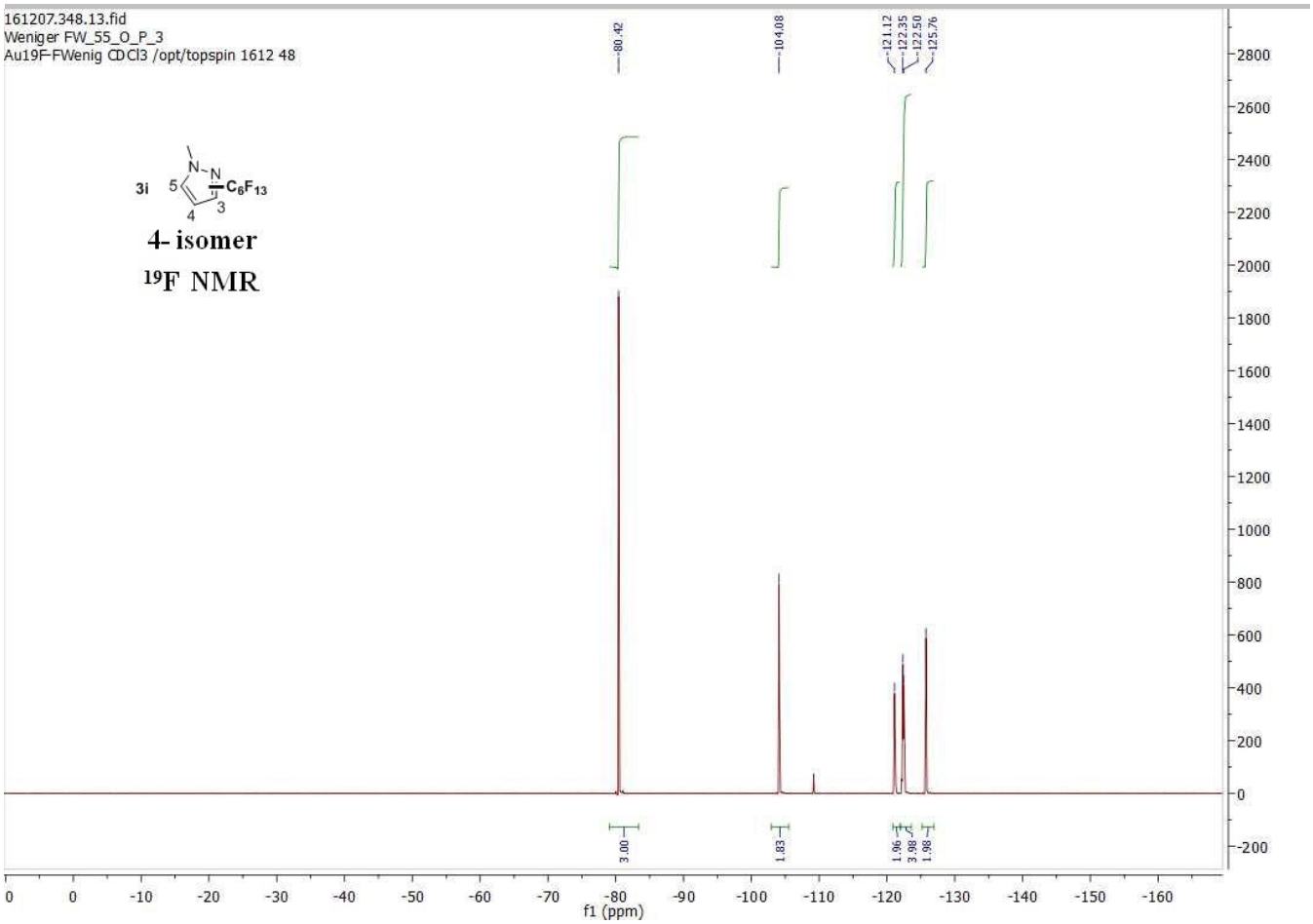
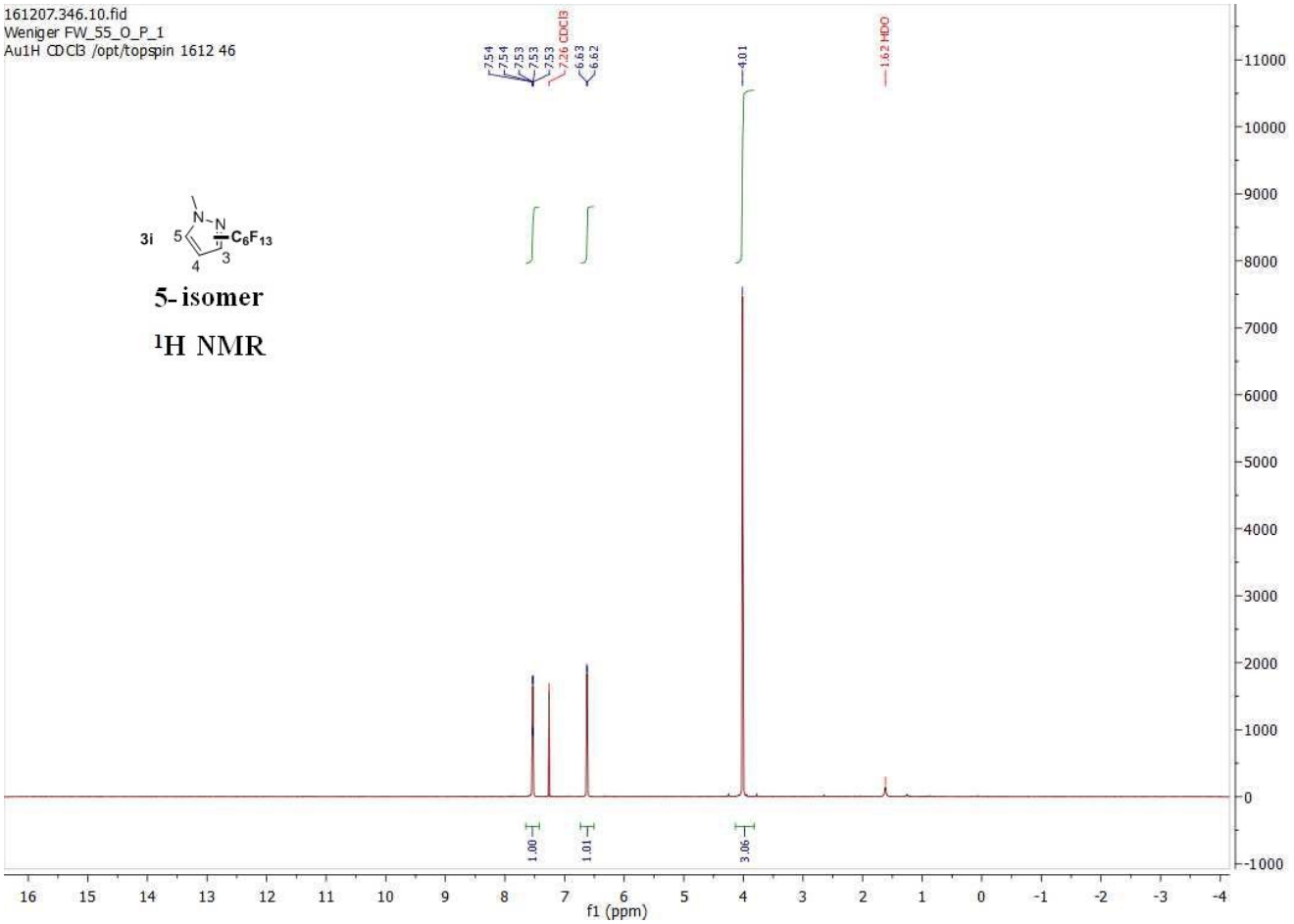
Au1H CDCl3 /opt/topspin 1612 48
7.67
7.63
7.26 CDCl3
3.97
1.59 HDO
3i
4- isomer
1H NMR
2.00
3.39
f1 (ppm)


161207.348.11.fid
Weniger FW_55_O_P_3
Au13C CDCl3 /opt/topspin 1612 48
138.04
137.98
137.92
130.24
130.18
130.11
77.00 CDCl3
39.42
3i
4- isomer
13C NMR
f1 (ppm)


161207.348.13.fid
Weniger FW_55_O_P_3
Au19F-FWenig CDCl3 /opt/topspin 1612 48
-80.42
-104.08
-121.12
-122.35
-122.50
-125.76
3i
4- isomer
19F NMR
3.00
1.83
1.96
3.98
1.98
f1 (ppm)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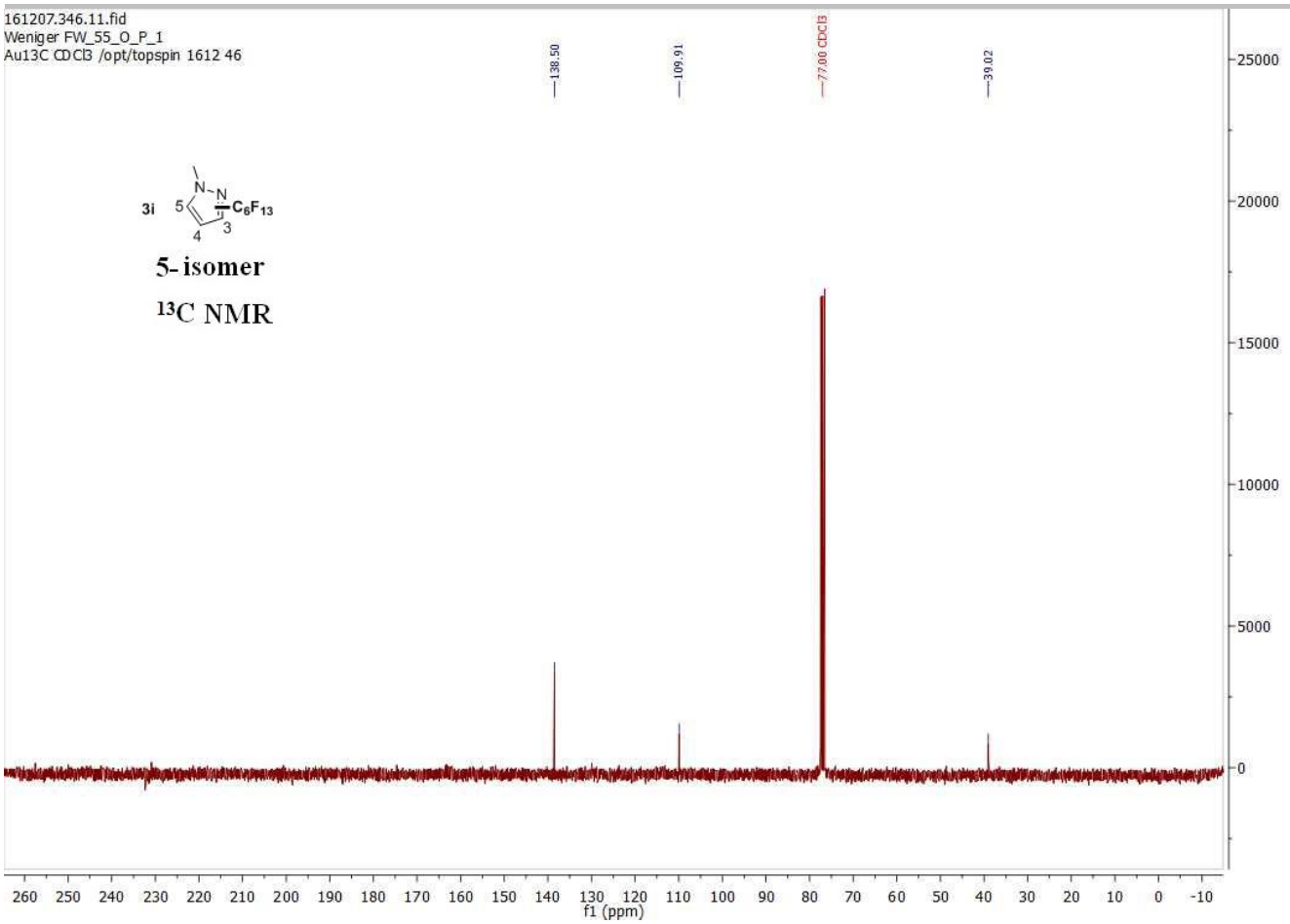
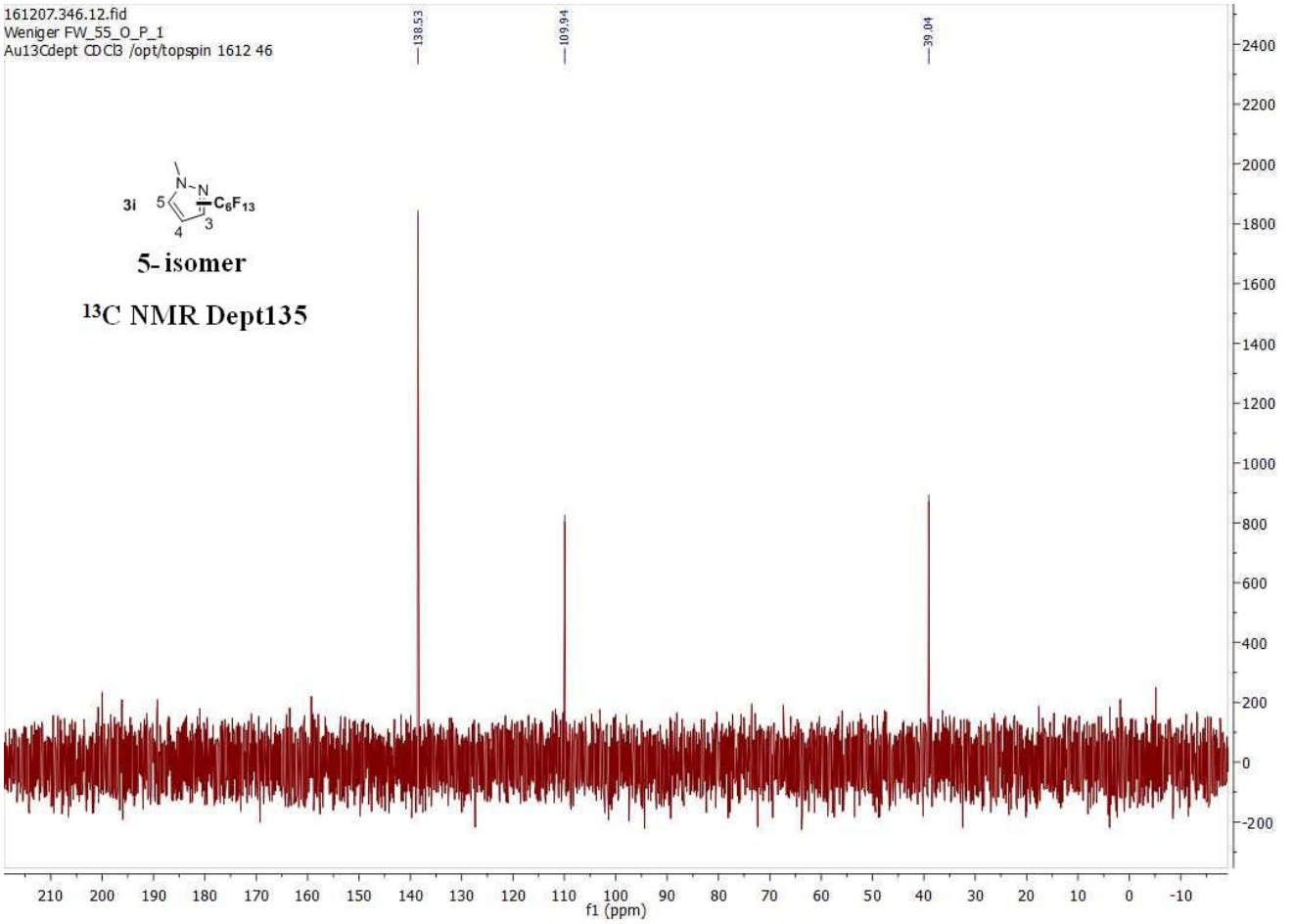
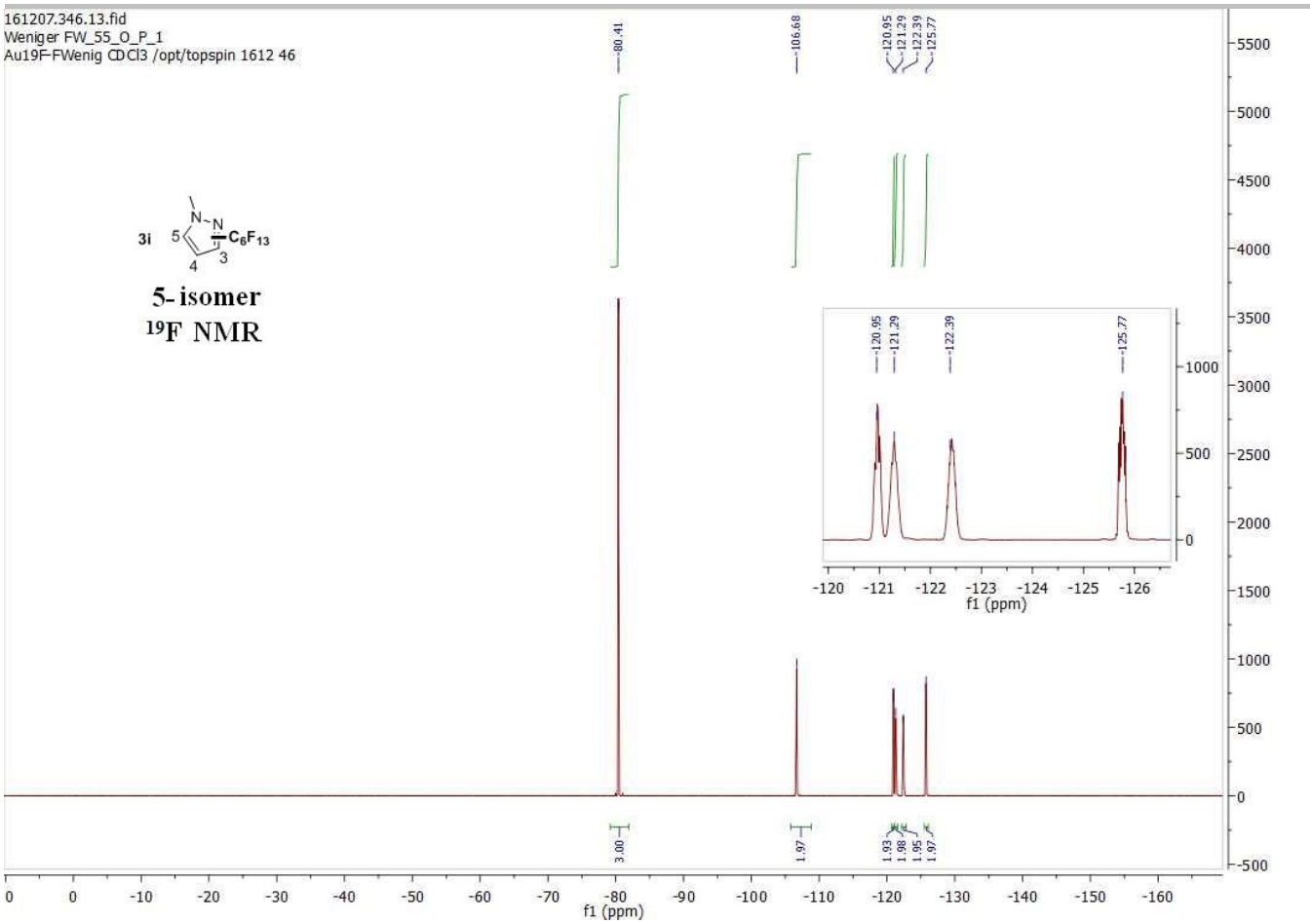
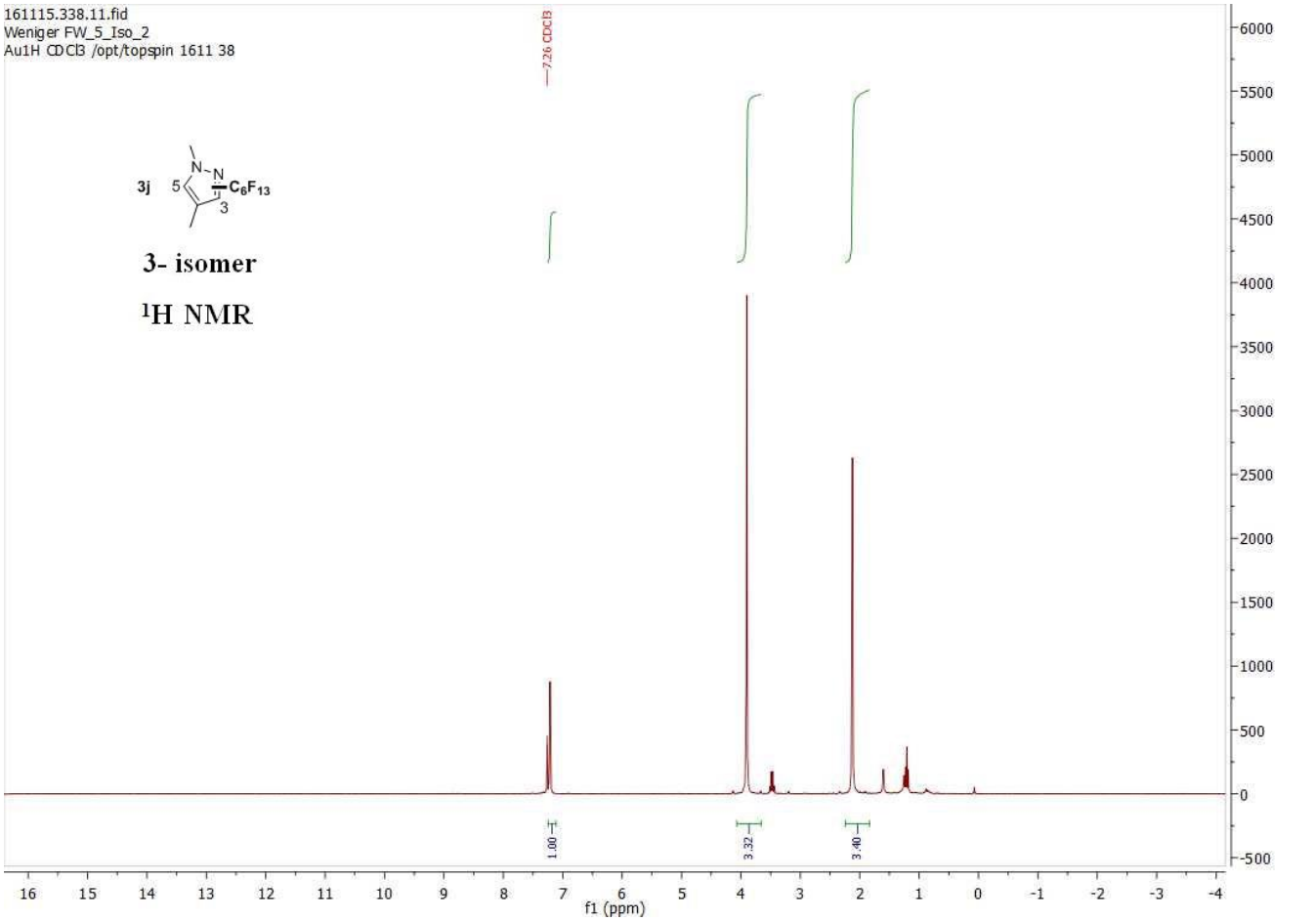
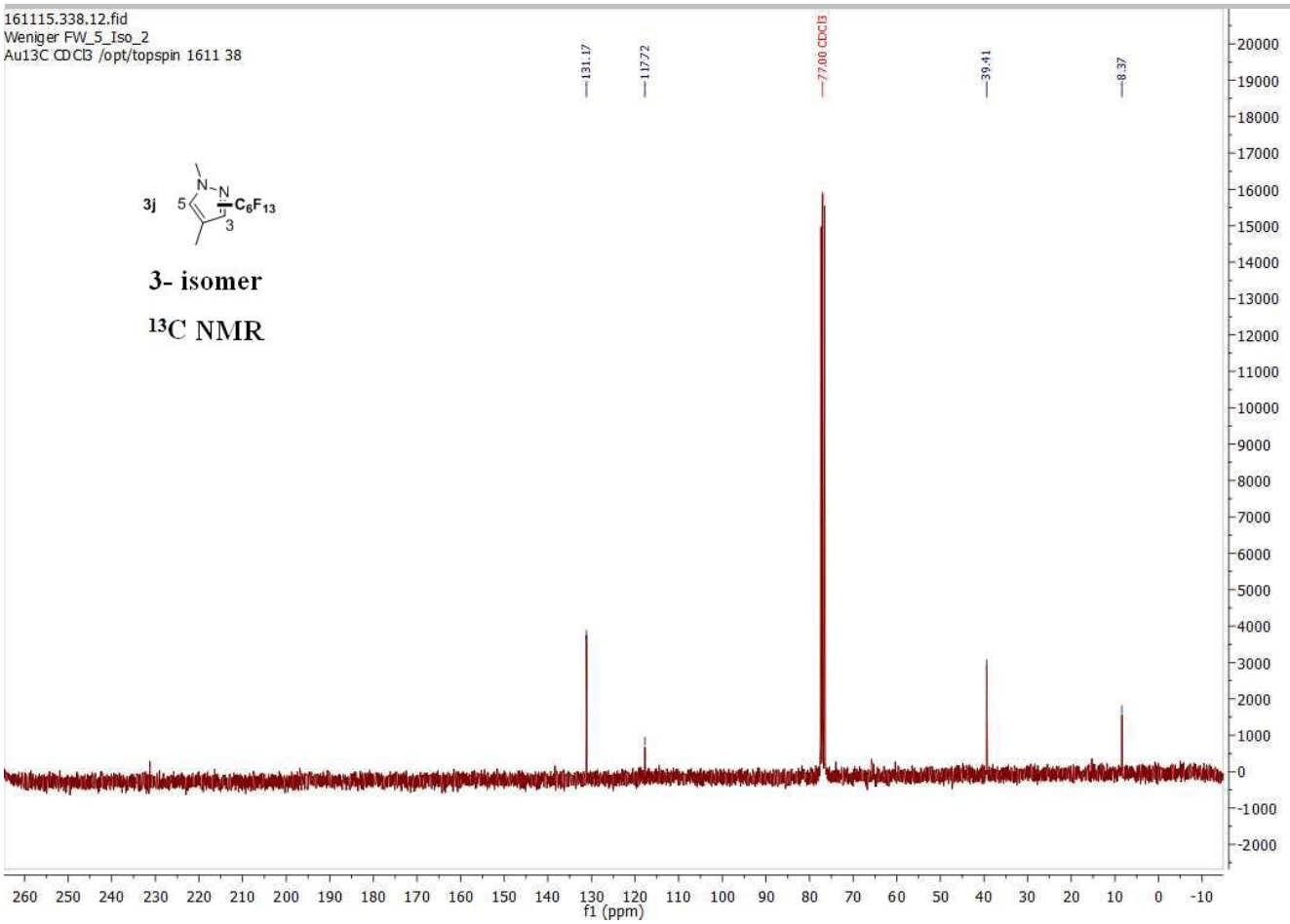
Weniger FW_55_O_P_1
Au1H CDCl3 /opt/topspin 1612 46
7.54
7.54
7.53
7.53
7.26 CDCl3
6.63
6.62
4.01
1.62 HDO
3i
5- isomer
1H NMR
1.00
1.01
3.06
f1 (ppm)


161207.346.11.fid
Weniger FW_55_O_P_1
Au13C CDCl3 /opt/topspin 1612 46
138.50
109.91
77.00 CDCl3
39.02
3i
5-isomer
13C NMR
f1 (ppm)


161207.346.12.fid
Weniger FW_55_O_P_1
Au13Cdept CDCl3 /opt/topspin 1612 46
138.53
109.94
39.04
3i
5-isomer
13C NMR Dept135
f1 (ppm)


161207.346.13.fid
Weniger FW_55_O_P_1
Au19F-FWenig CDCl3 /opt/topspin 1612 46
-80.41
-106.68
-120.95
-121.29
-122.39
-125.77
3i
5
4
3
$C_6F_{13}$
5- isomer
$^{19}$F NMR
f1 (ppm)


161115.338.11.fid
Weniger FW_5_Iso_2
Au1H CDCl3 /opt/topspin 1611 38
7.26 CDCl3
3j
5
3
$C_6F_{13}$
3- isomer
$^{1}$H NMR
1.00
3.32
3.40
f1 (ppm)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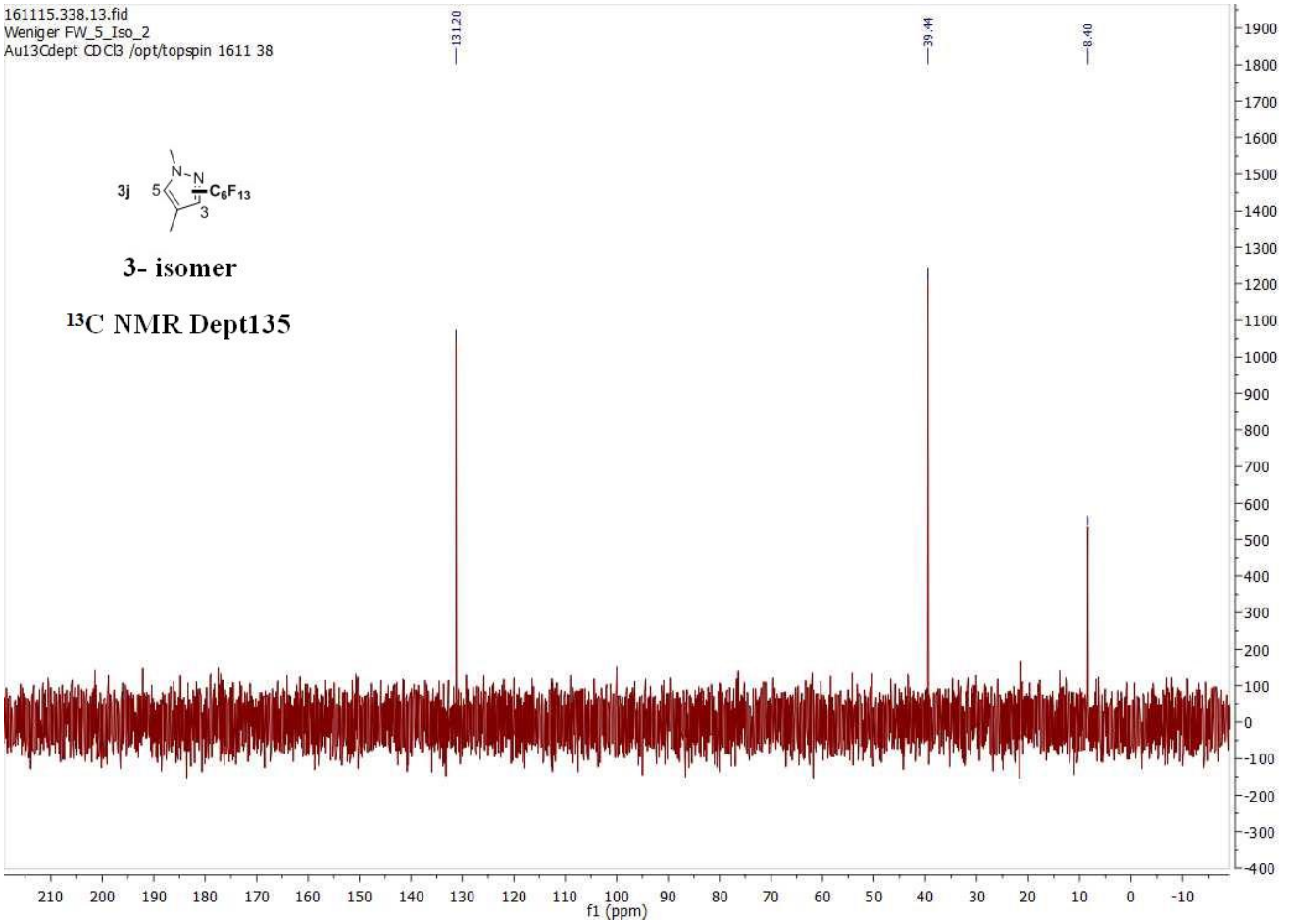
Au13C CDCl3 /opt/topspin 1611 38
131.17
117.72
77.00 CDCl3
39.41
8.37
3j
3- isomer
13C NMR
f1 (ppm)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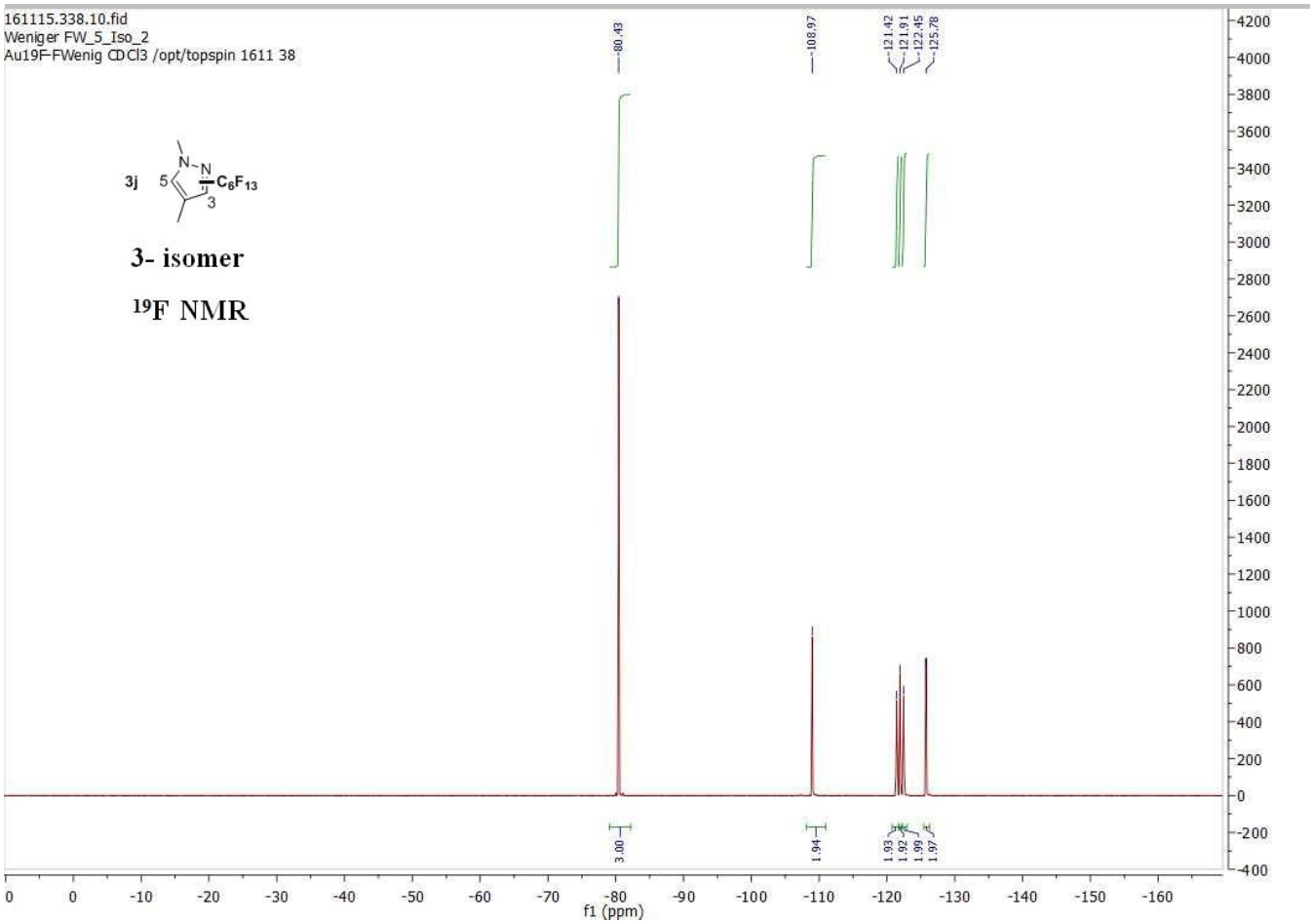
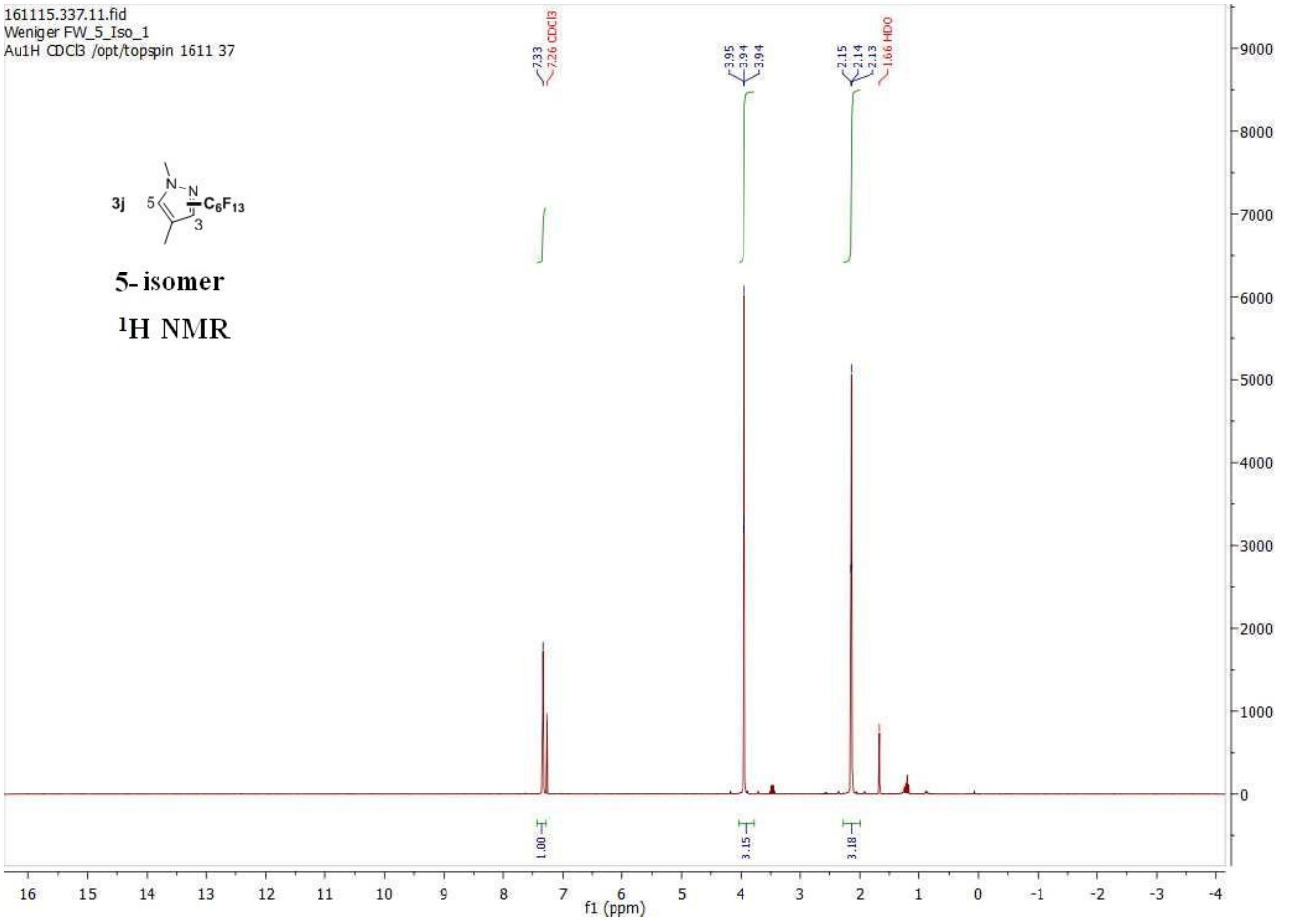
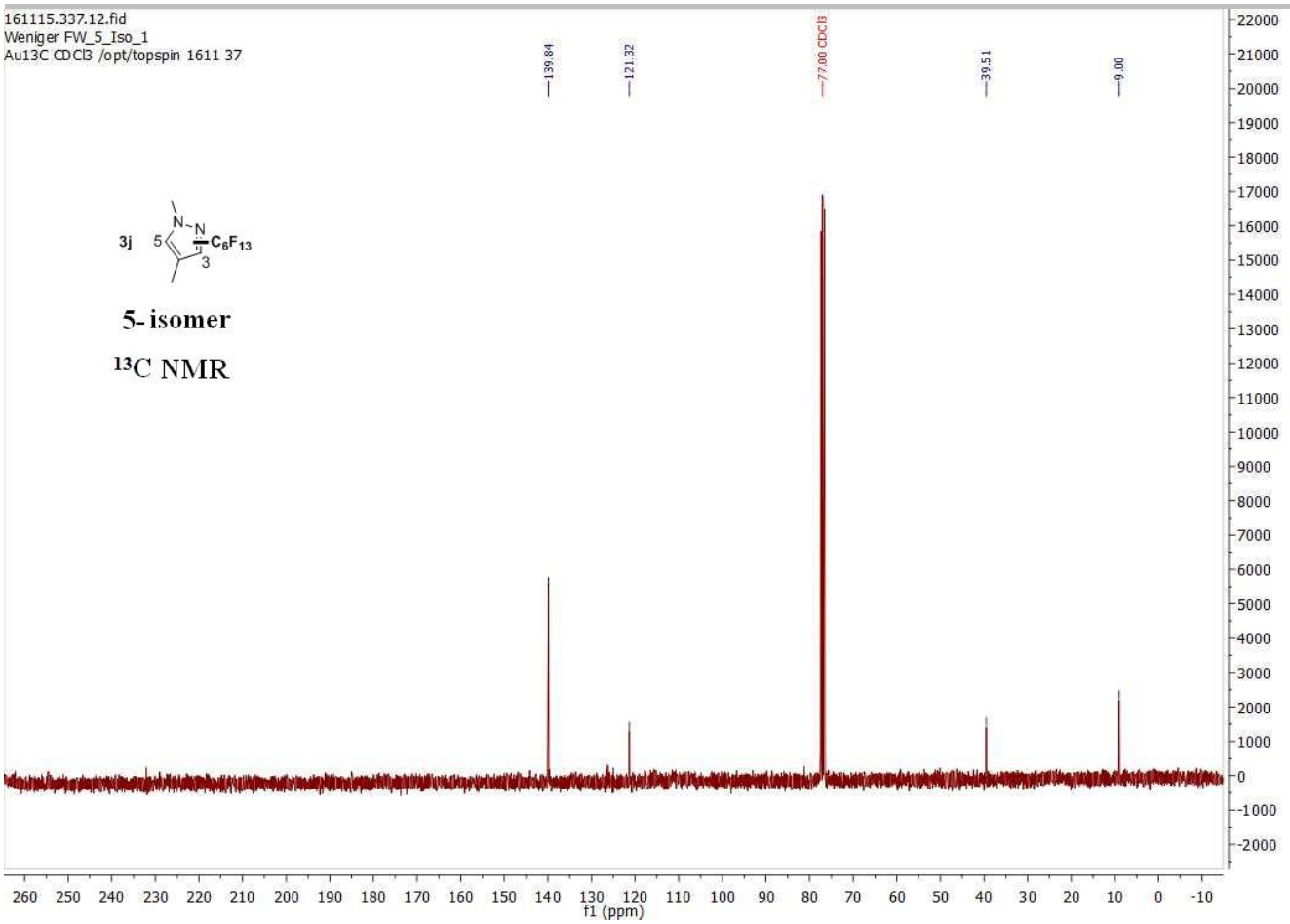
Weniger FW_5_Iso_2
Au13Cdept CDCl3 /opt/topspin 1611 38
131.20
39.44
8.40
3j
3- isomer
13C NMR Dept135
f1 (ppm)


161115.338.10.fid
Weniger FW_5_Iso_2
Au19F-FWenig CDCl3 /opt/topspin 1611 38
-80.43
-108.97
-121.42
-121.91
-122.45
-125.78
3j
3- isomer
19F NMR
3.00
1.94
1.93
1.92
1.99
1.97
f1 (ppm)


161115.337.11.fid
Weniger FW_5_Iso_1
Au1H CDCl3 /opt/topspin 1611 37
7.33
7.26 CDCl3
3.95
3.94
3.94
2.15
2.14
2.13
1.66 HDO
3j
5- isomer
1H NMR
1.00
3.15
3.18
f1 (ppm)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Weniger FW_5_Iso_1
Au13C CDCl3 /opt/topspin 1611 37
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121.32
77.00 CDCl3
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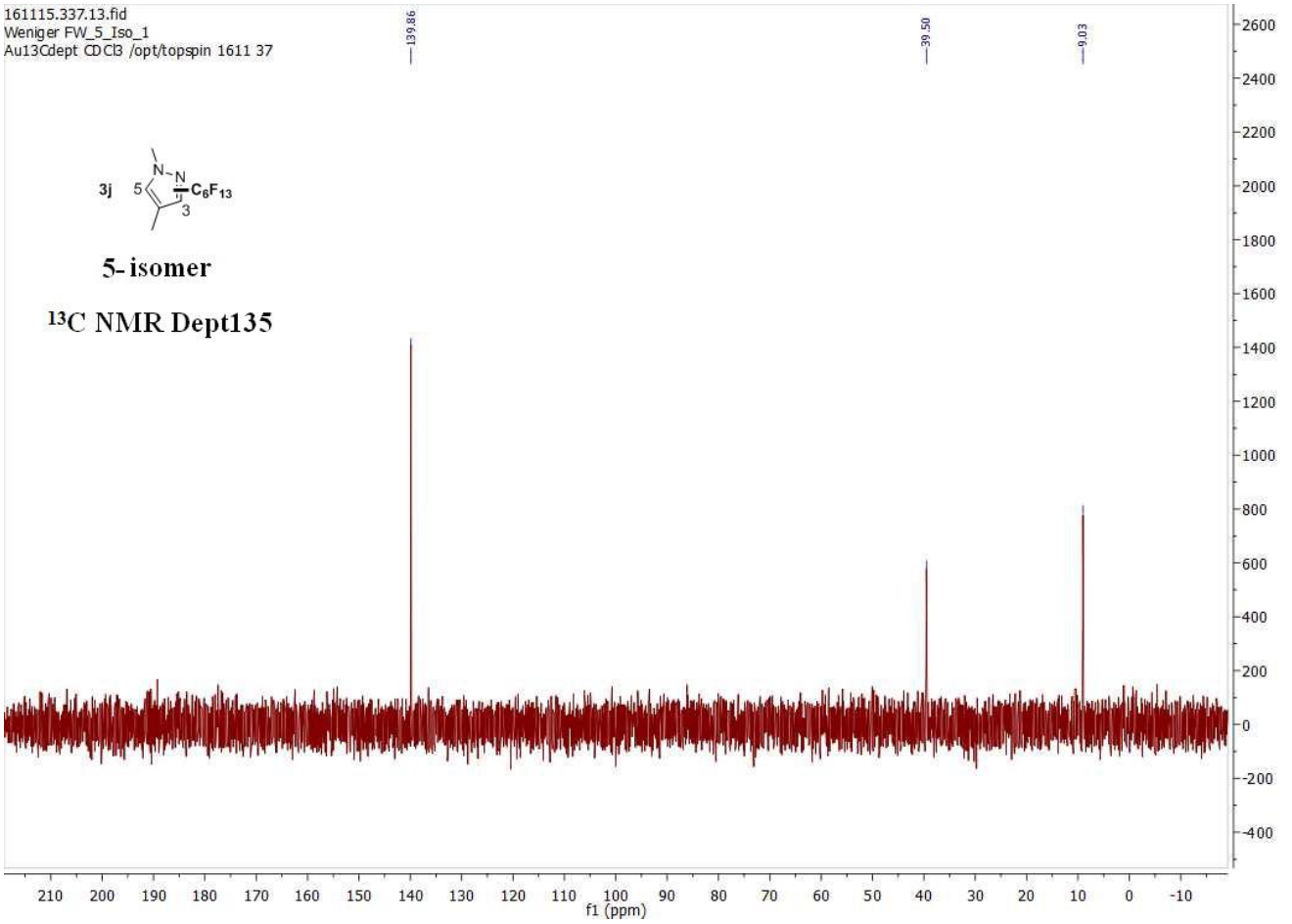
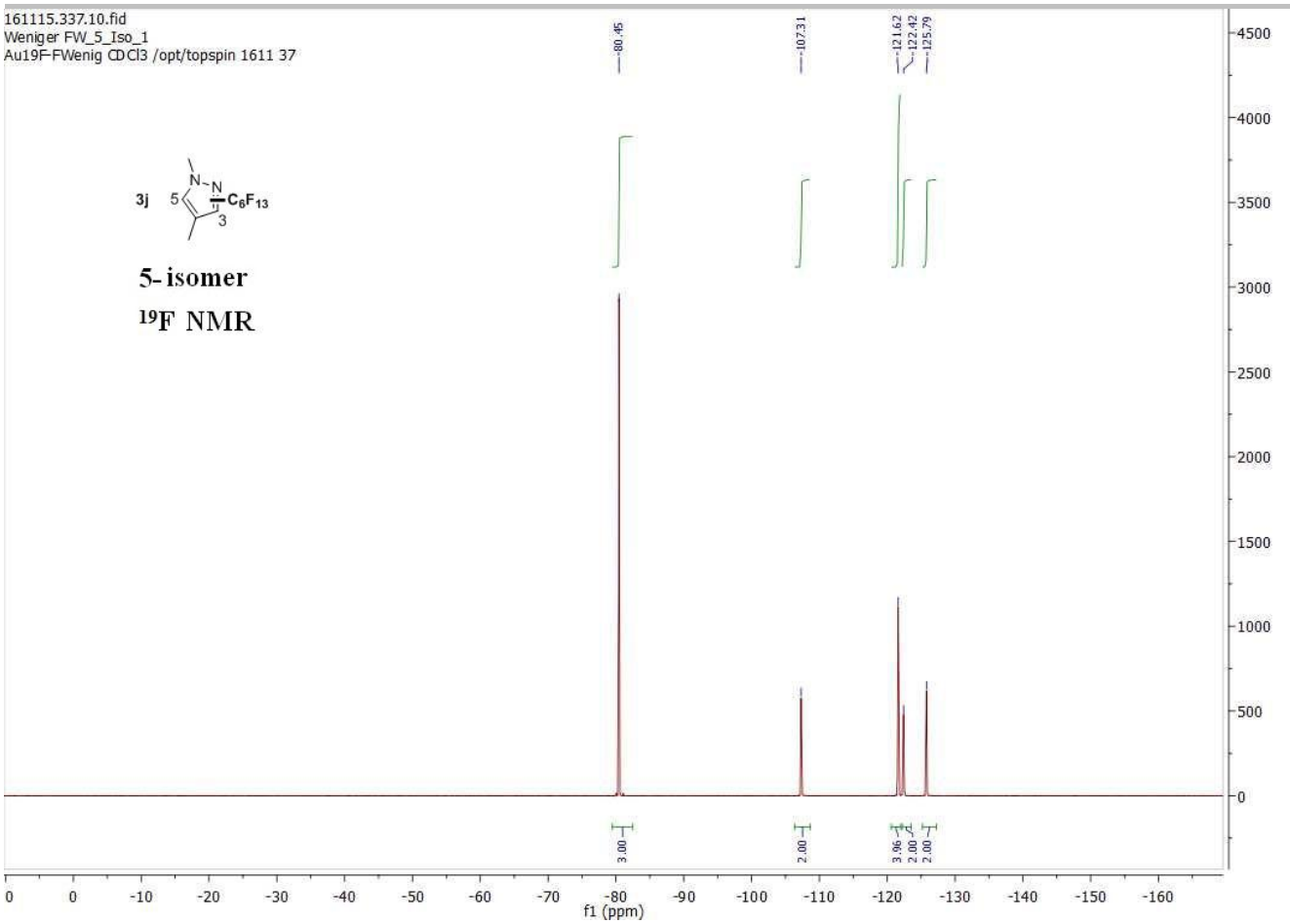
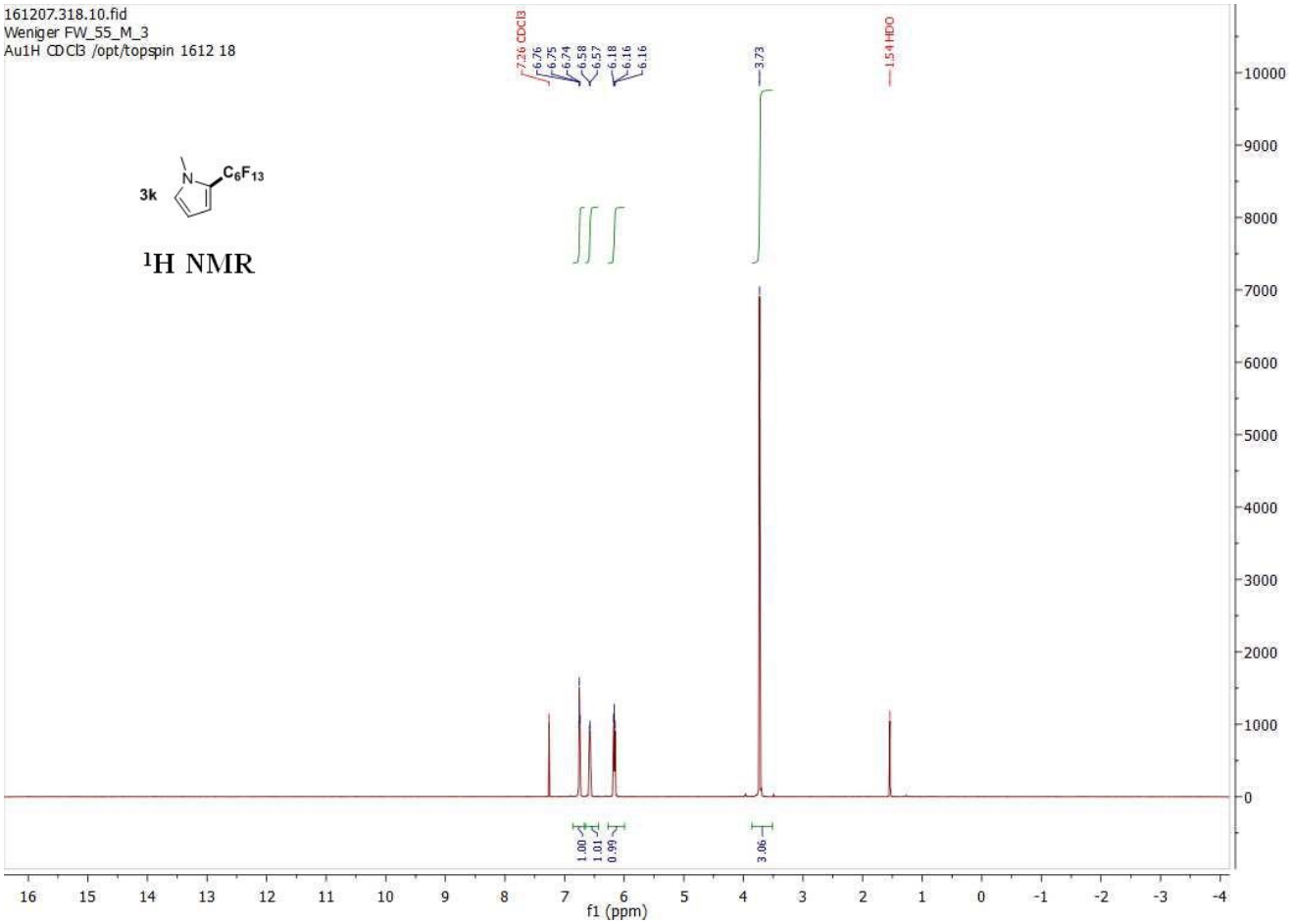
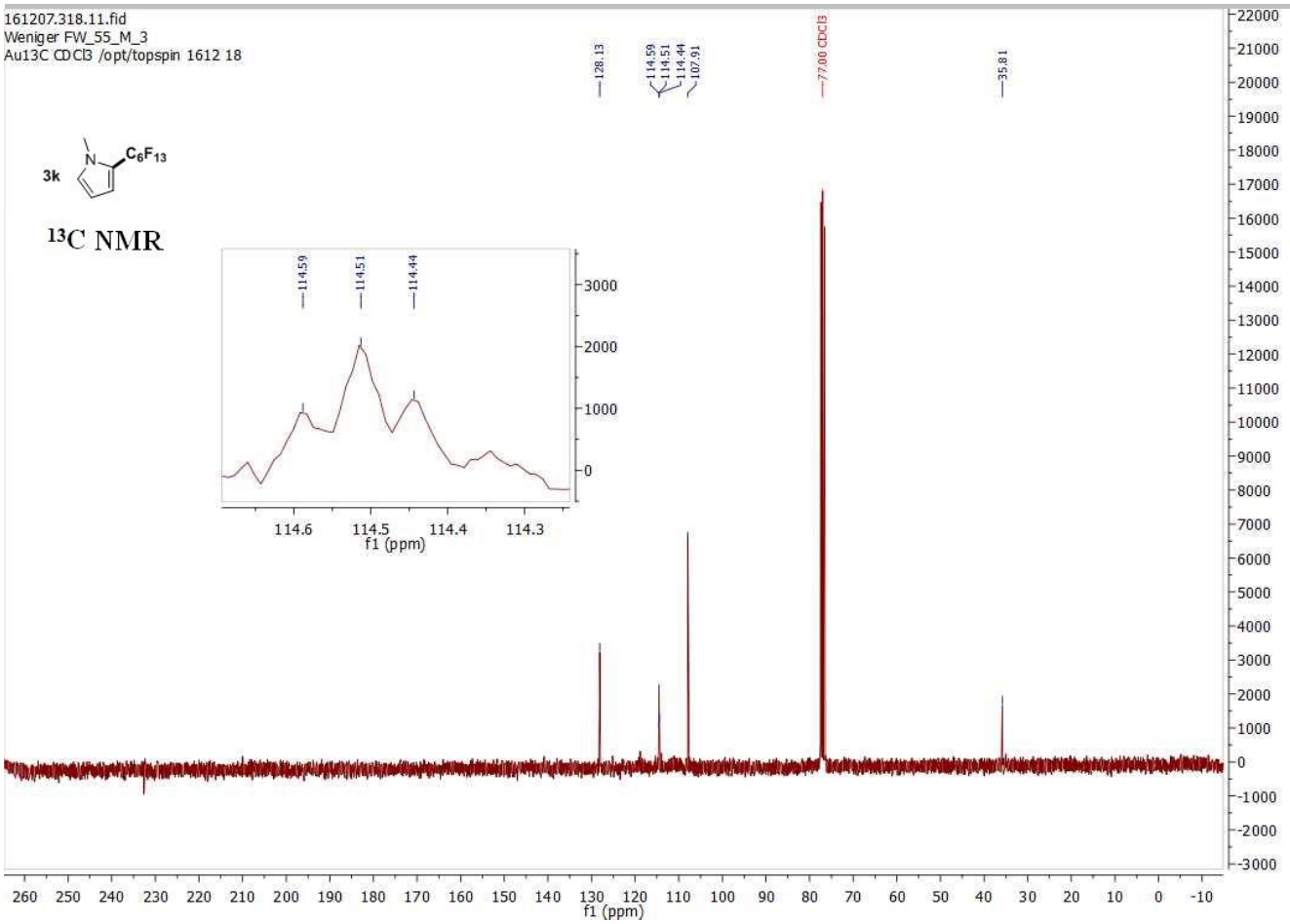
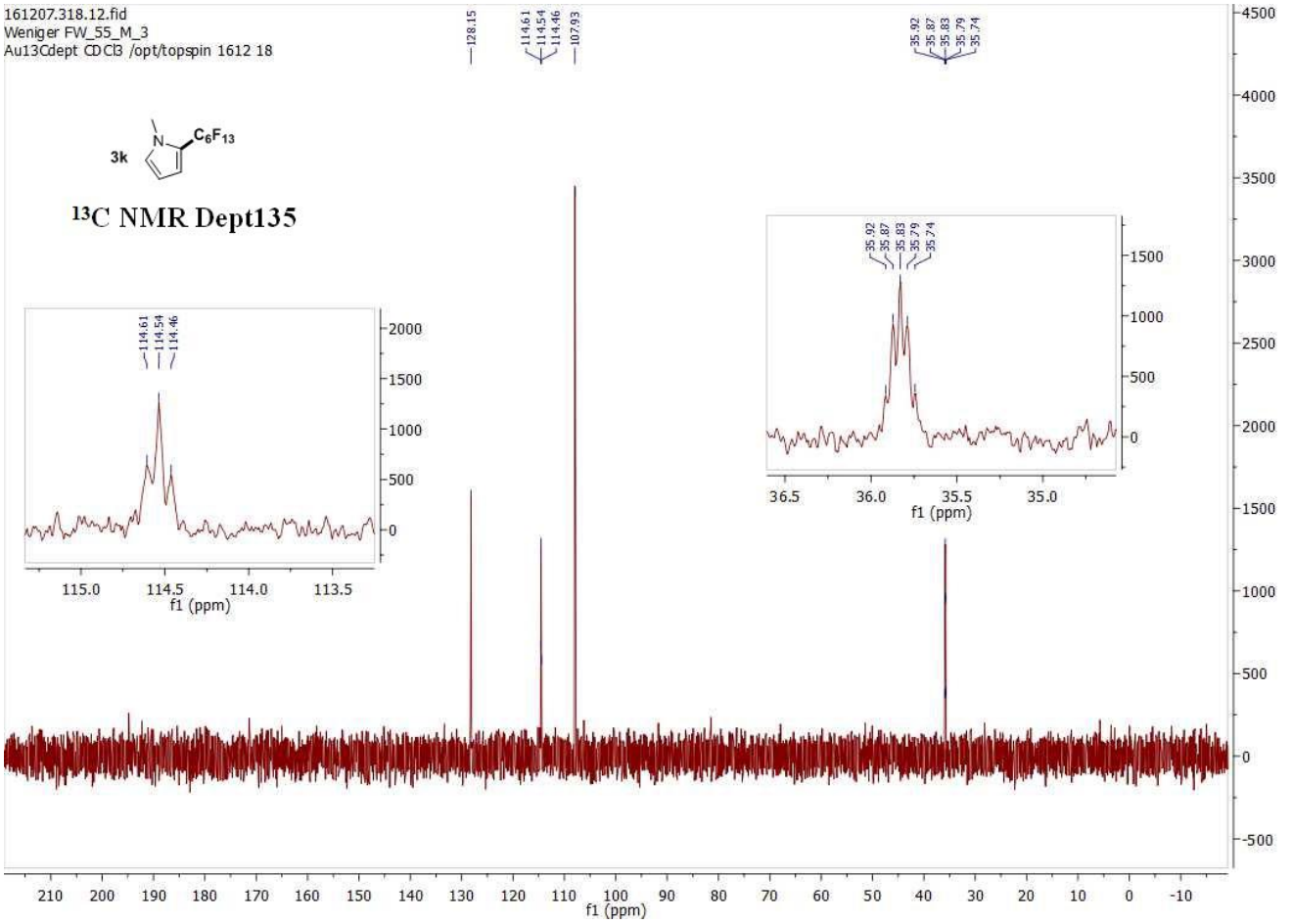
9.00
3j
5-isomer
13C NMR
f1 (ppm)

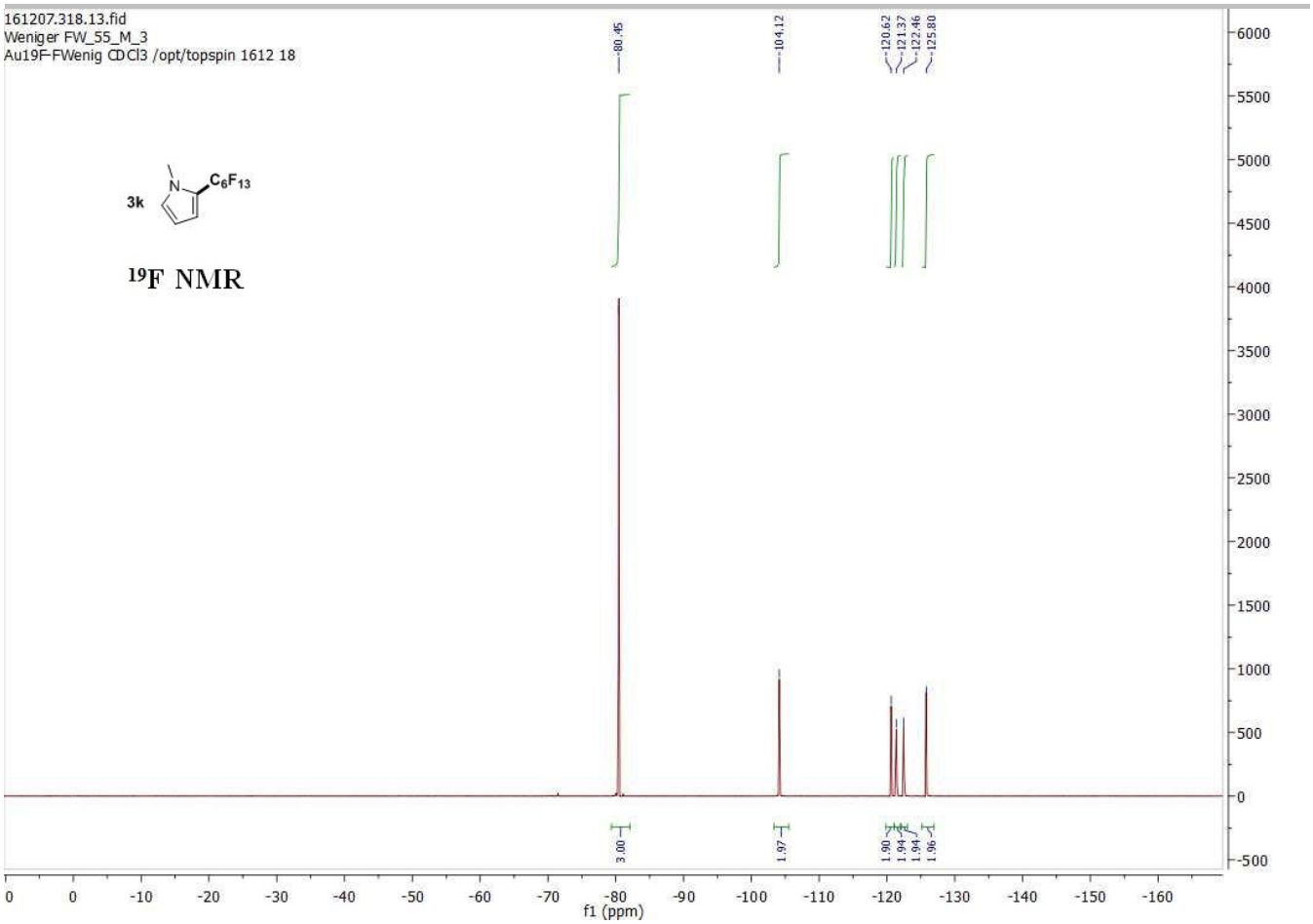

161115.337.13.fid
Weniger FW_5_Iso_1
Au13Cdept CDCl3 /opt/topspin 1611 37
139.86
39.50
9.03
3j
5-isomer
13C NMR Dept135
f1 (ppm)

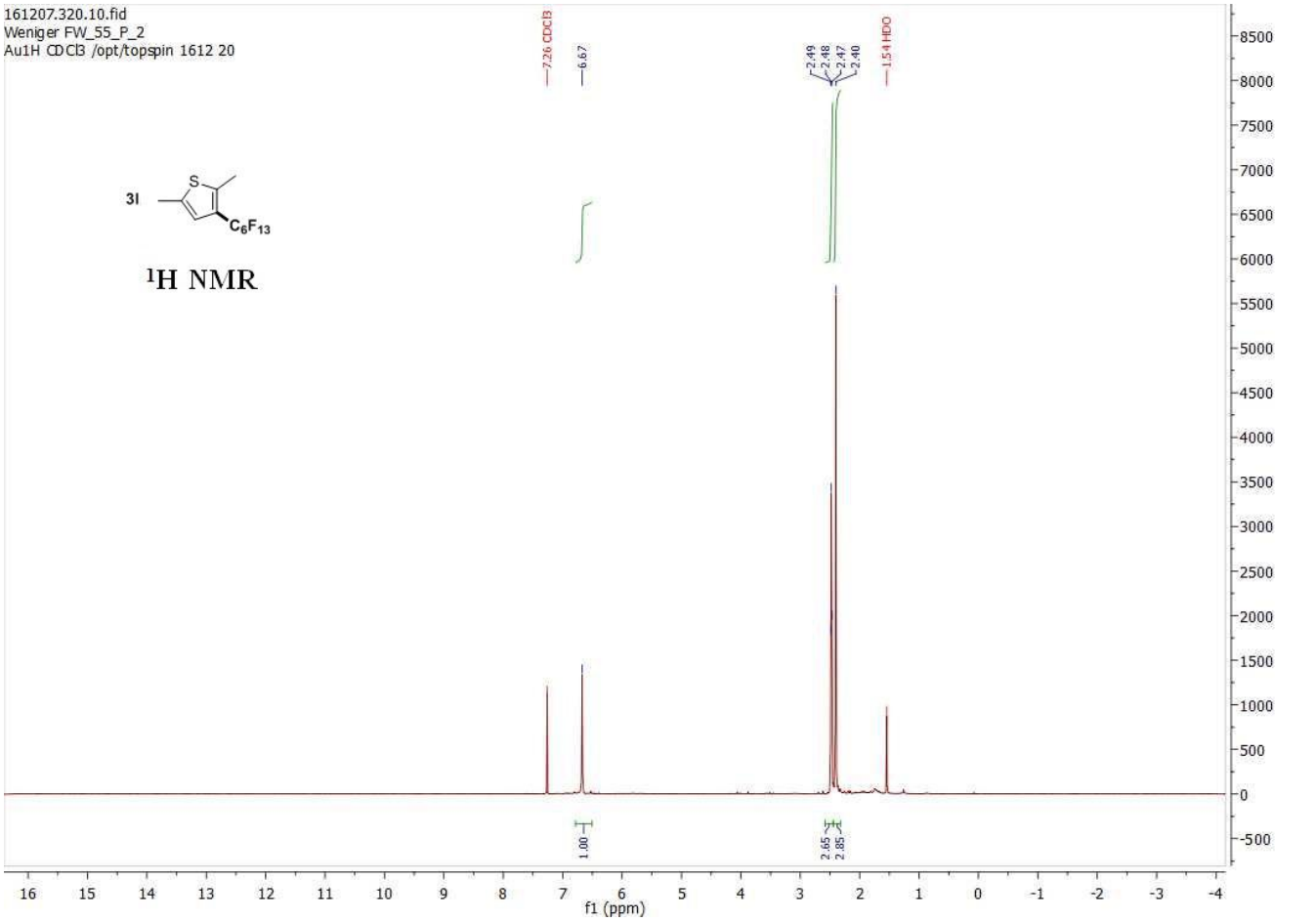

161115.337.10.fid
Weniger FW_5_Iso_1
Au19F-FWenig CDCl3 /opt/topspin 1611 37
-80.45
-107.31
-121.62
-122.42
-125.79
3j
5-isomer
19F NMR
3.00
2.00
3.96
2.00
2.00
f1 (ppm)

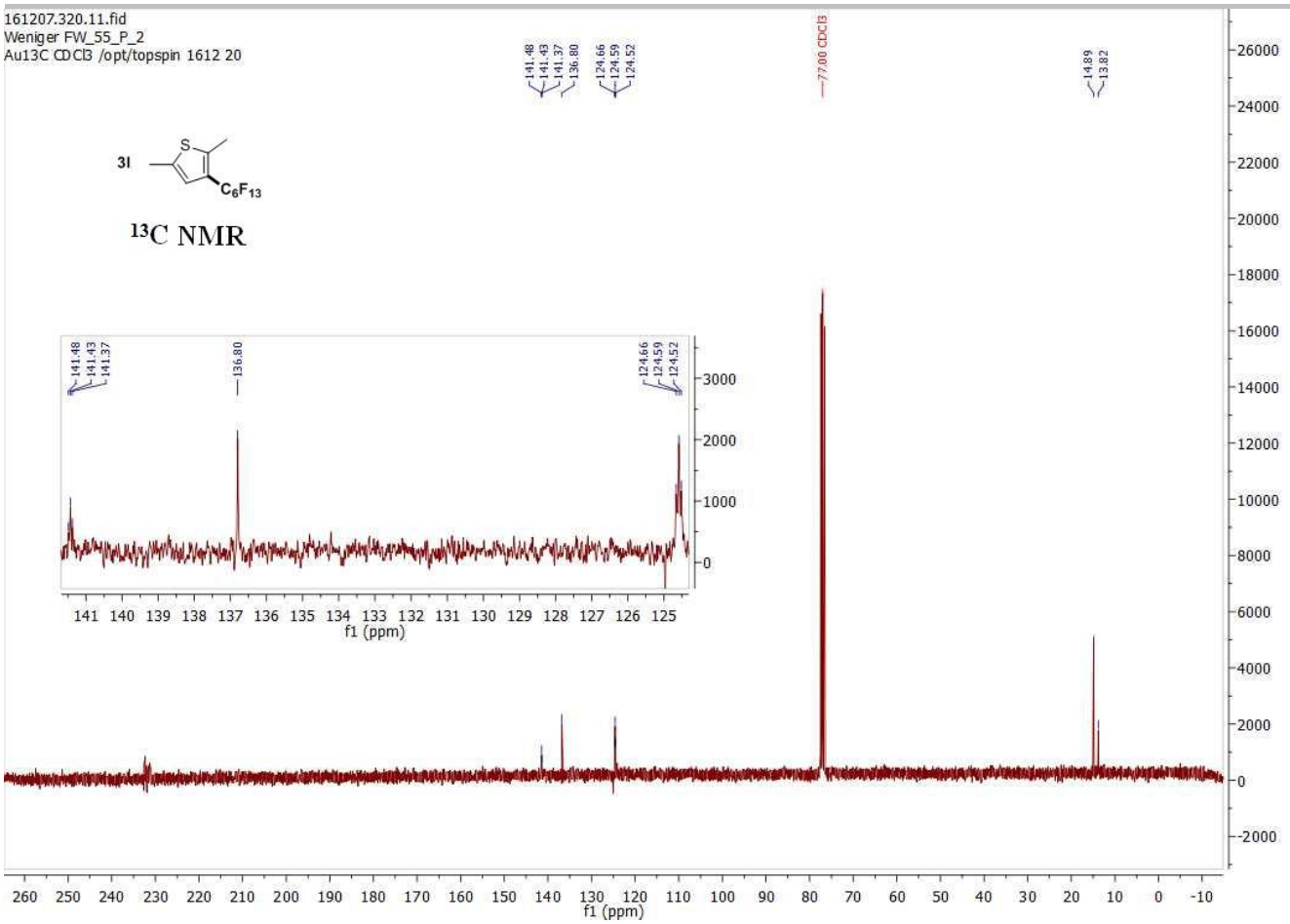

161207.318.10.fid
Weniger FW_55_M_3
Au1H CDCl3 /opt/topspin 1612 18
7.26 CDCl3
6.76
6.75
6.74
6.58
6.57
6.18
6.16
6.16
3.73
1.54 HDO
3k
1H NMR
1.00
1.01
0.99
3.06
f1 (ppm)

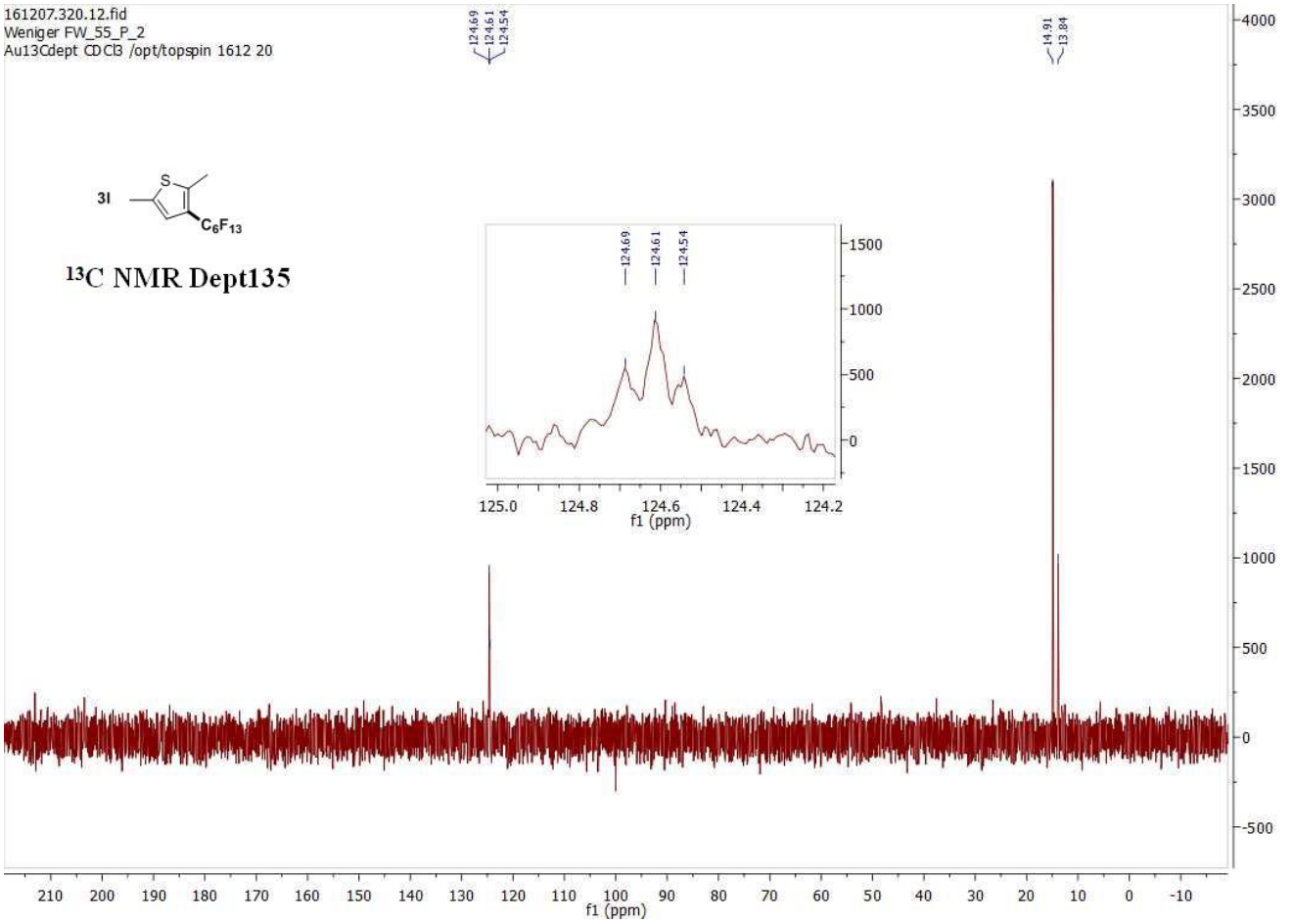

161207.318.11.fid
Weniger FW_55_M_3
Au13C CDCl3 /opt/topspin 1612 18
128.13
114.59
114.51
114.44
107.91
77.00 CDCl3
35.81
3k
$C_6F_{13}$
$^{13}$C NMR
114.59
114.51
114.44
f1 (ppm)
f1 (ppm)

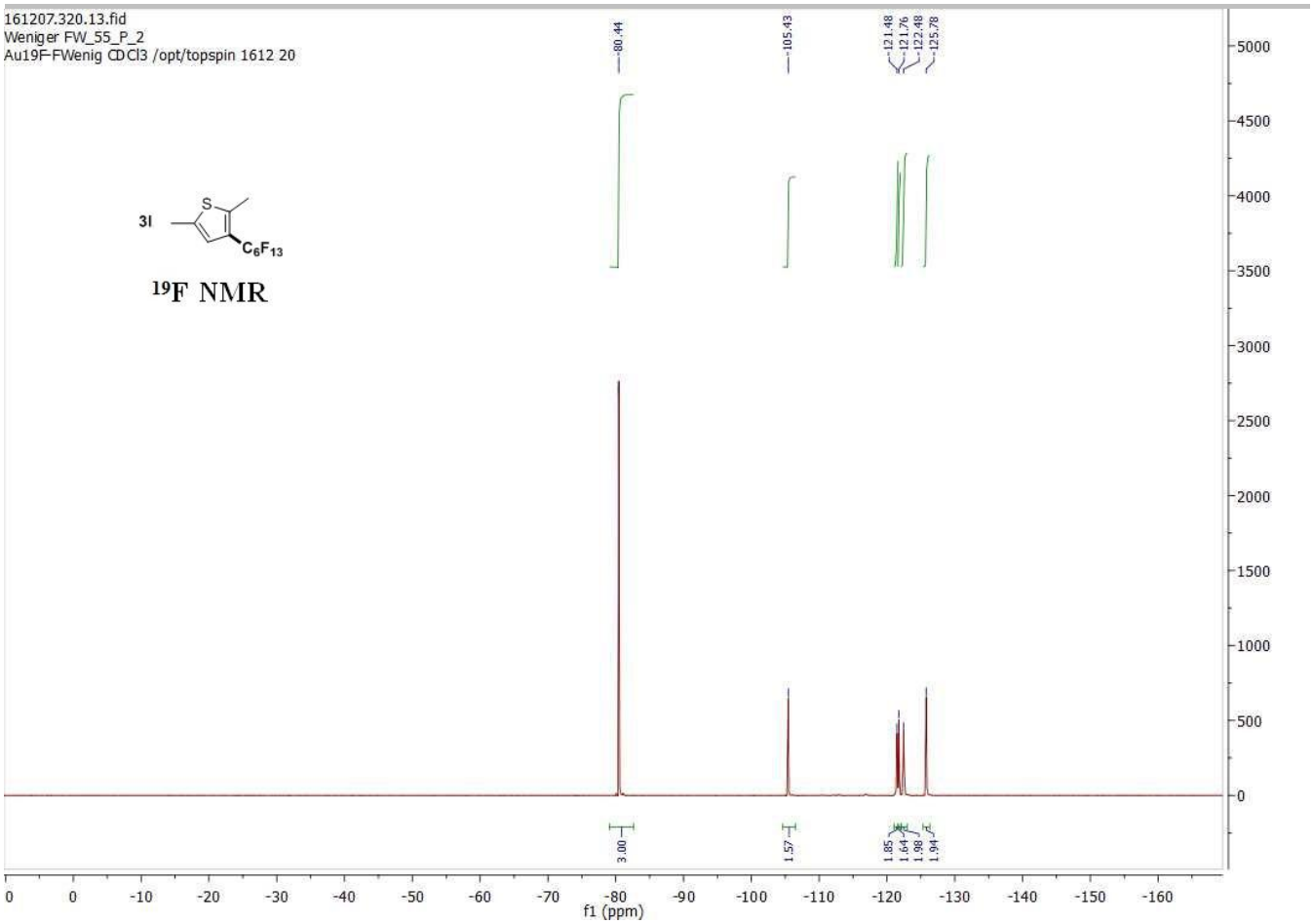

161207.318.12.fid
Weniger FW_55_M_3
Au13Cdept CDCl3 /opt/topspin 1612 18
128.15
114.61
114.54
114.46
107.93
35.92
35.87
35.83
35.79
35.74
3k
$C_6F_{13}$
$^{13}$C NMR Dept135
114.61
114.54
114.46
35.92
35.87
35.83
35.79
35.74
f1 (ppm)
f1 (ppm)
f1 (ppm)

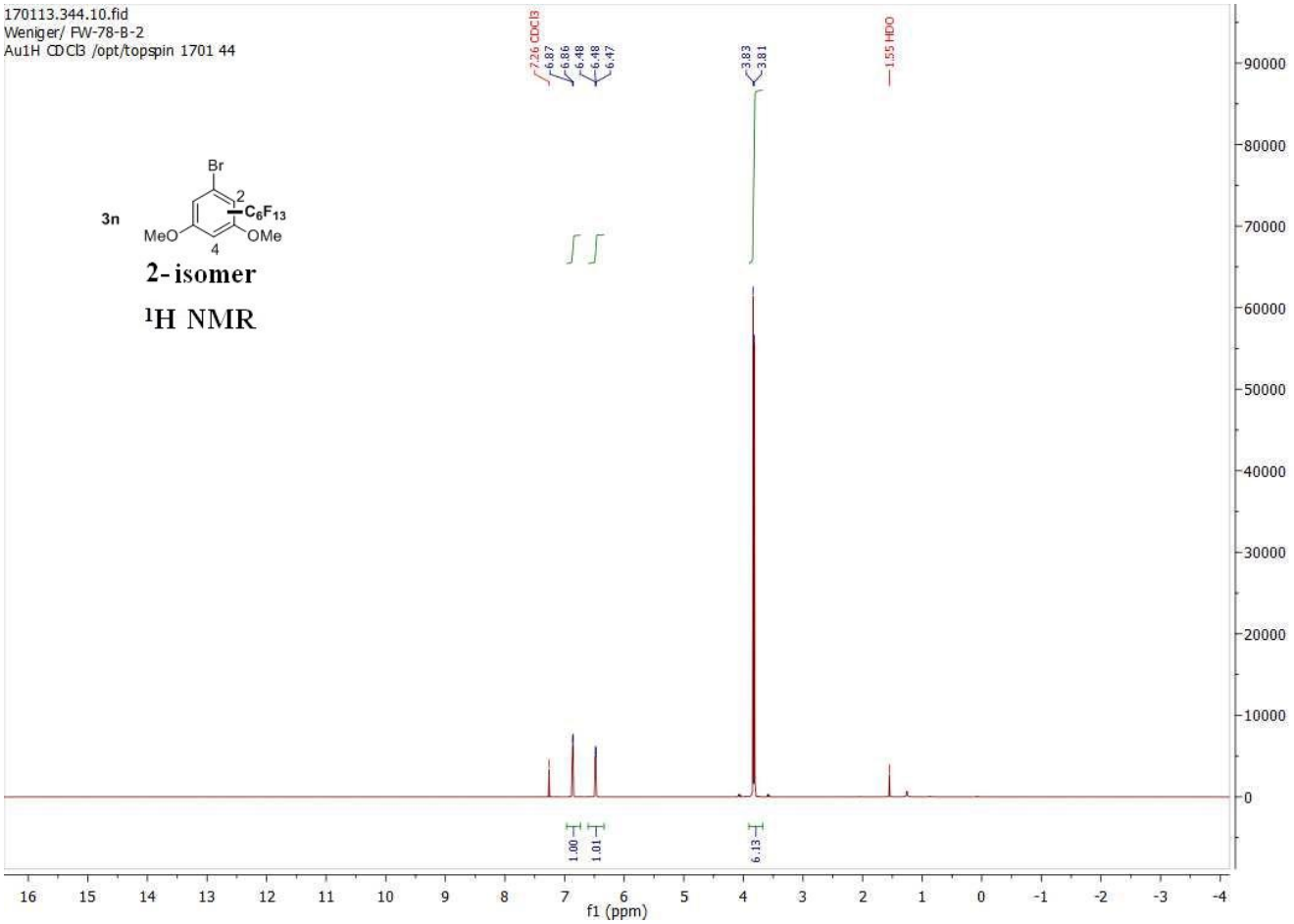

161207.318.13.fid
Weniger FW_55_M_3
Au19F-FWenig CDCl3 /opt/topspin 1612 18
-80.45
-104.12
-120.62
-121.37
-122.46
-125.80
3k
$C_6F_{13}$
$^{19}$F NMR
3.00
1.97
1.90
1.94
1.94
1.96
f1 (ppm)

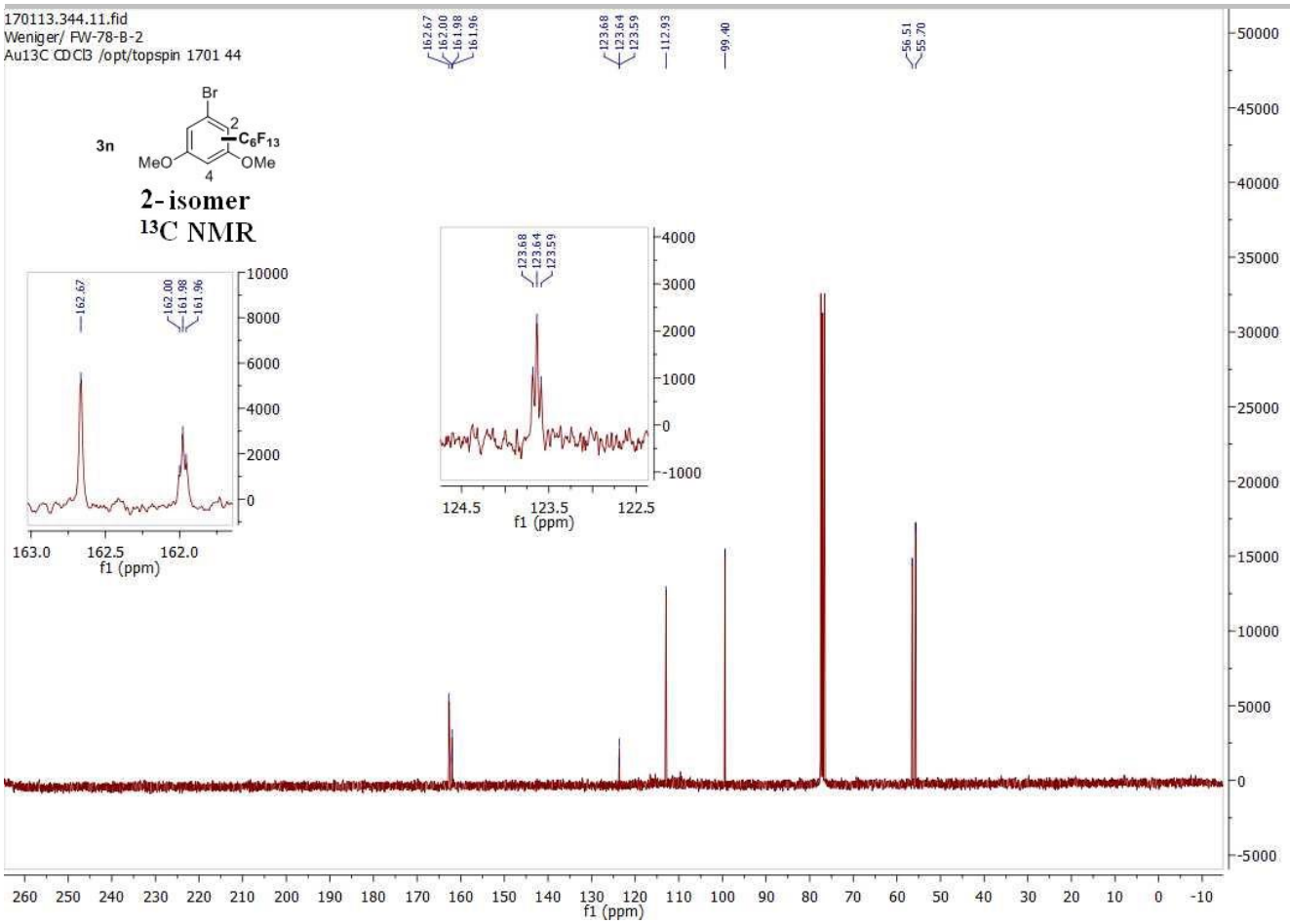

161207.320.10.fid
Weniger FW_55_P_2
Au1H CDCl3 /opt/topspin 1612 20
7.26 CDCl3
6.67
2.49
2.48
2.47
2.40
1.54 HDO
3l
$C_6F_{13}$
$^{1}$H NMR
1.00
2.65
2.85
f1 (ppm)

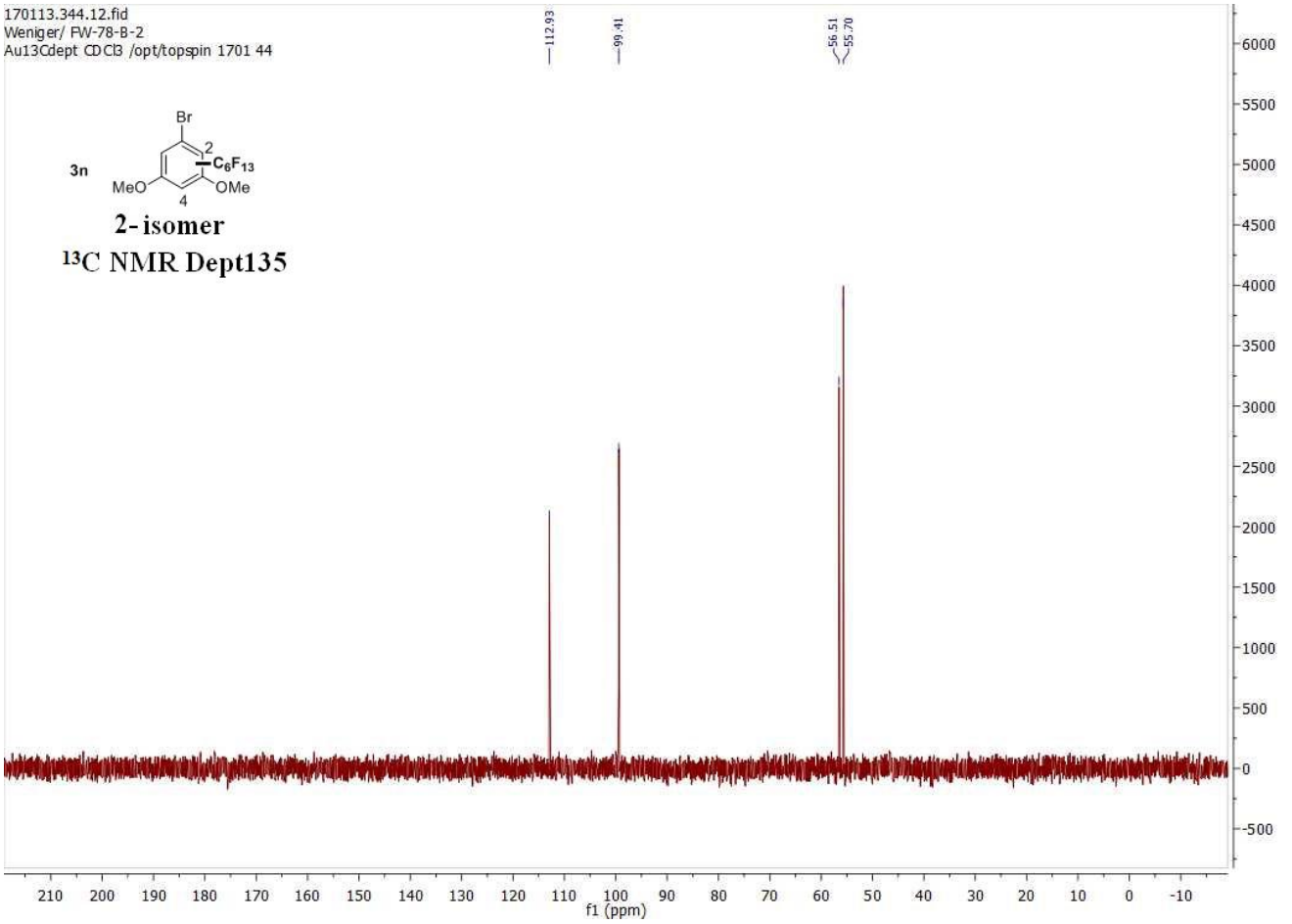

161207.320.11.fid
Weniger FW_55_P_2
Au13C CDCl3 /opt/topspin 1612 20
141.48
141.43
141.37
136.80
124.66
124.59
124.52
77.00 CDCl3
14.89
13.82
3l
$C_6F_{13}$
$^{13}$C NMR
f1 (ppm)


161207.320.12.fid
Weniger FW_55_P_2
Au13Cdept CDCl3 /opt/topspin 1612 20
124.69
124.61
124.54
14.91
13.84
3l
$C_6F_{13}$
$^{13}$C NMR Dept135
f1 (ppm)


161207.320.13.fid
Weniger FW_55_P_2
Au19F-FWenig CDCl3 /opt/topspin 1612 20
-80.44
-105.43
-121.48
-121.76
-122.48
-125.78
3l
$C_6F_{13}$
$^{19}$F NMR
3.00
1.57
1.85
1.64
1.98
1.94
f1 (ppm)


170113.344.10.fid
Weniger/ FW-78-B-2
Au1H CDCl3 /opt/topspin 1701 44
7.26 CDCl3
6.87
6.86
6.48
6.48
6.47
3.83
3.81
1.55 HDO
3n
Br
$C_6F_{13}$
MeO
OMe
2-isomer
$^1$H NMR
1.00
1.01
6.13
f1 (ppm)


170113.344.11.fid
Weniger/ FW-78-B-2
Au13C CDCl3 /opt/topspin 1701 44
3n
2-isomer
13C NMR
f1 (ppm)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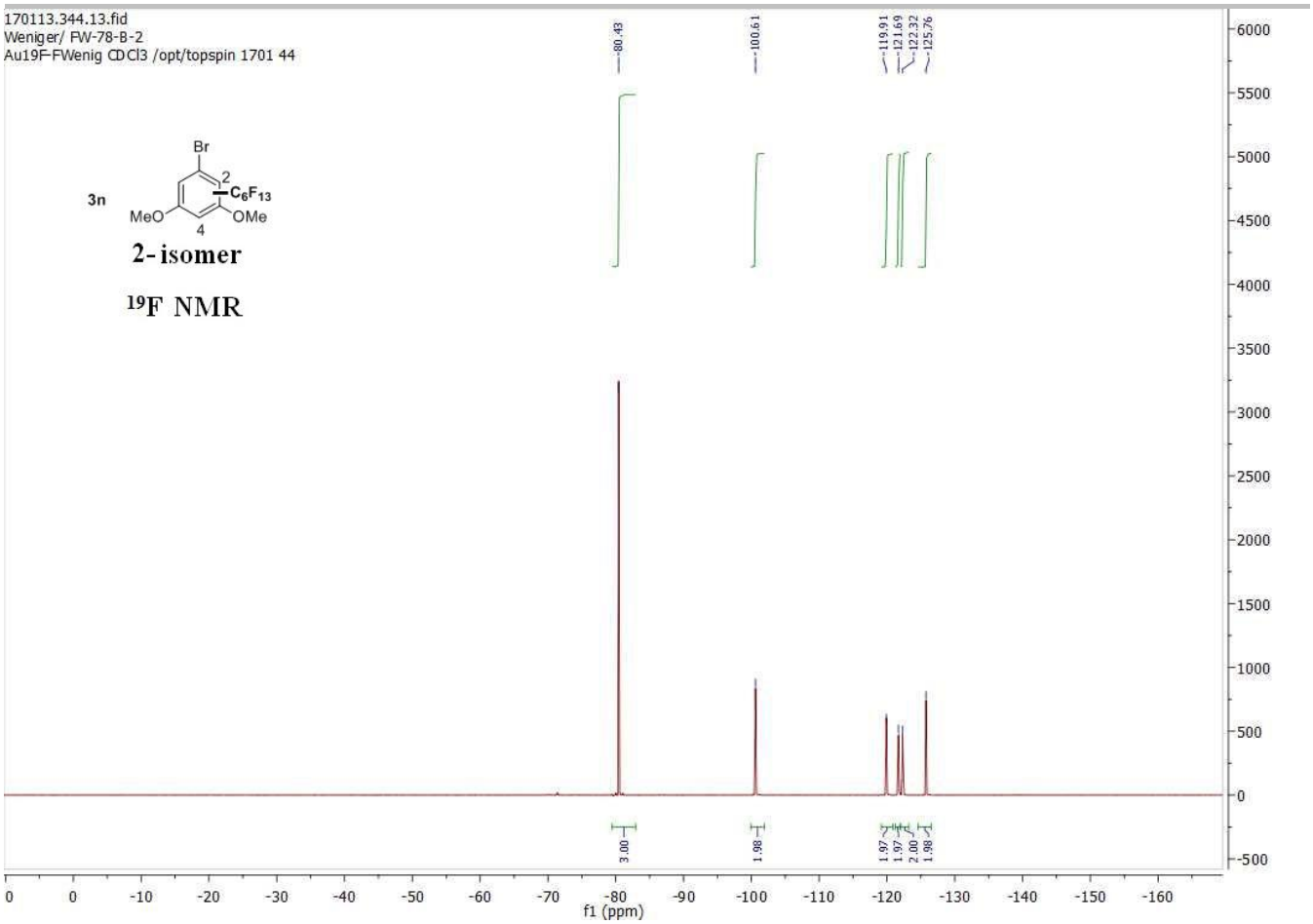
Weniger/ FW-78-B-2
Au13Cdept CDCl3 /opt/topspin 1701 44
3n
2-isomer
13C NMR Dept135
f1 (ppm)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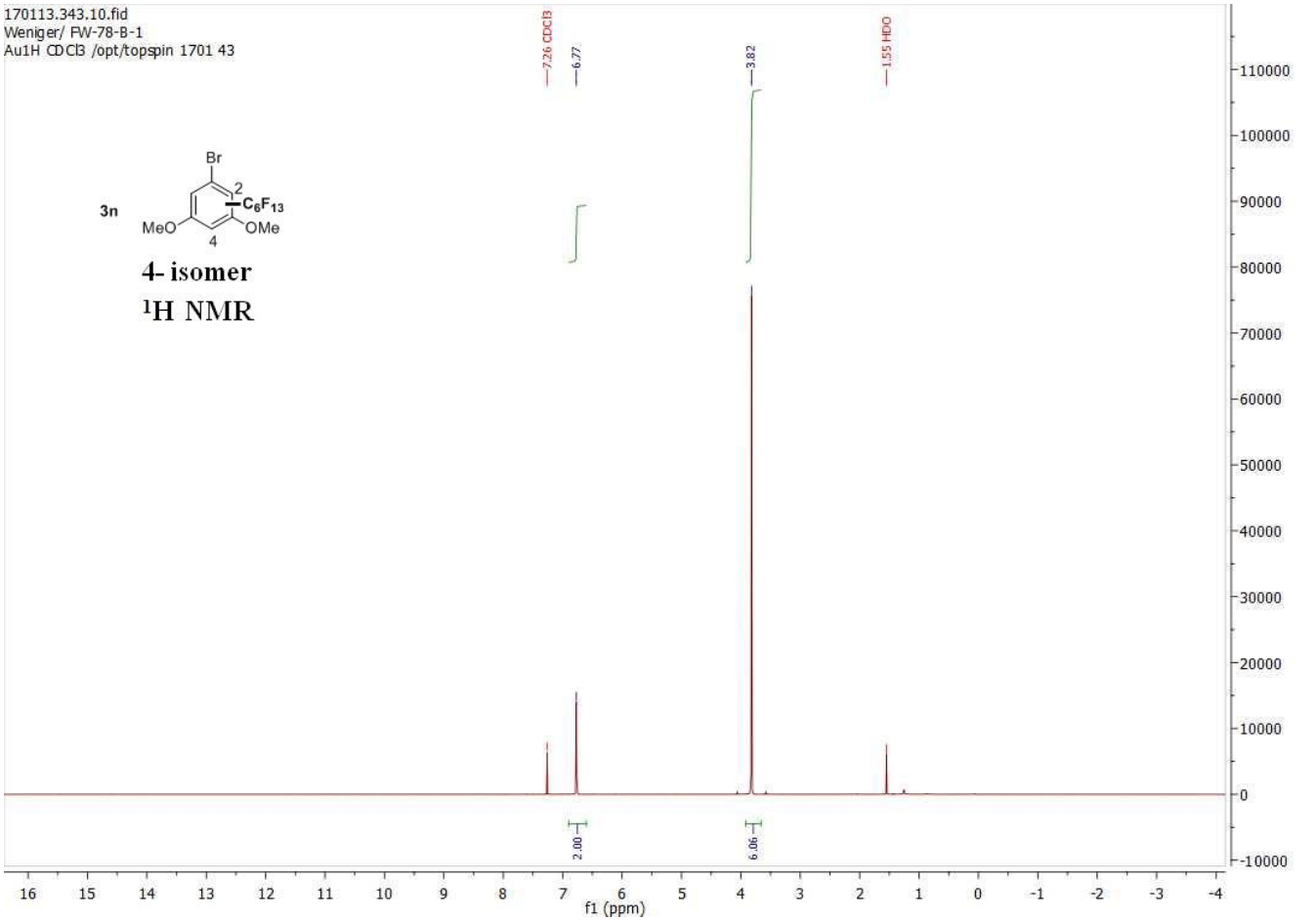
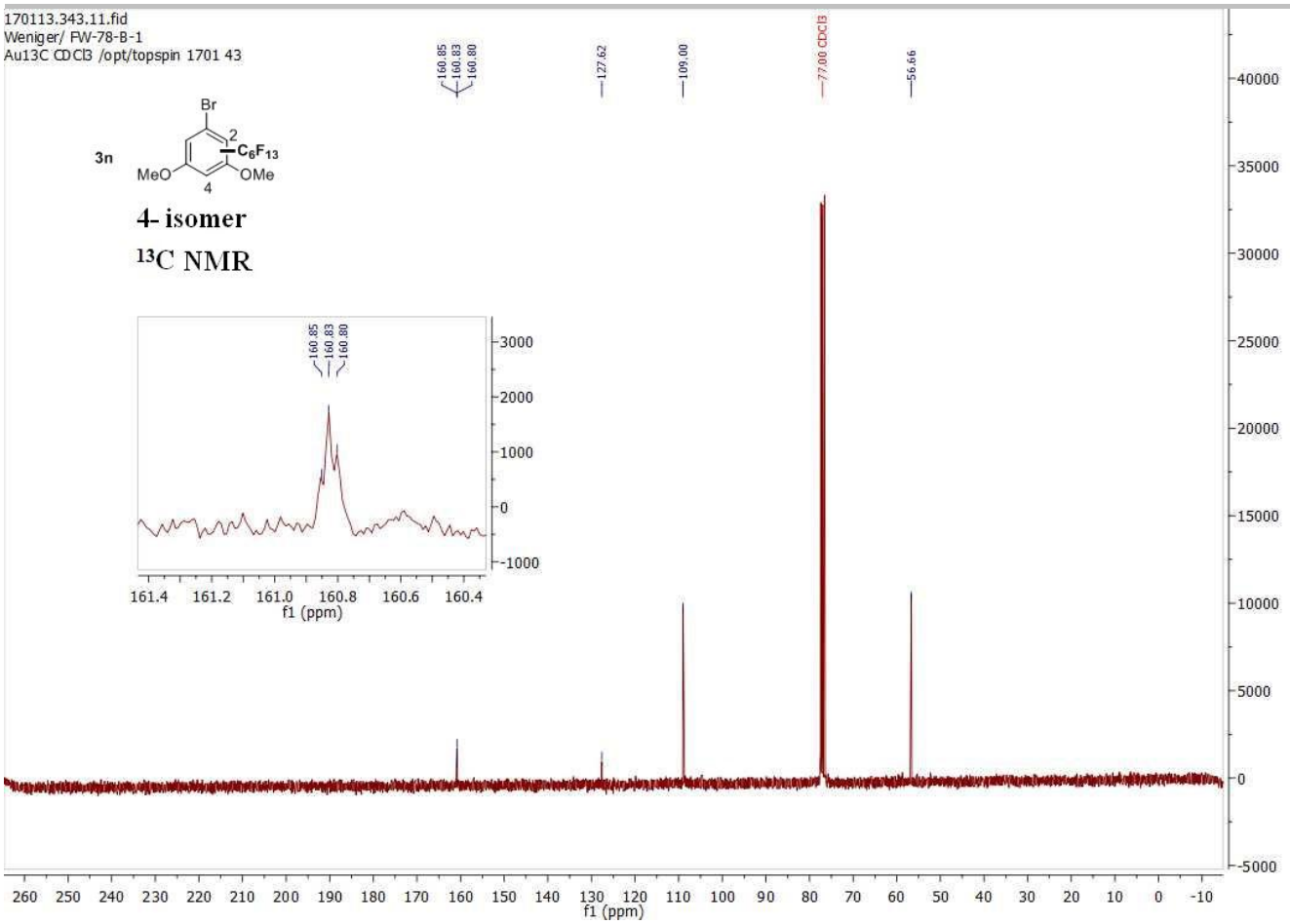
Au19F-FWenig CDCl3 /opt/topspin 1701 44
-80.43
-100.61
-119.91
-121.69
-122.32
-125.76
3n
Br
2
C6F13
MeO
OMe
4
2-isomer
19F NMR
3.00
1.98
1.97
1.97
2.00
1.98
f1 (ppm)


170113.343.10.fid
Weniger/ FW-78-B-1
Au1H CDCl3 /opt/topspin 1701 43
7.26 CDCl3
6.77
3.82
1.55 HDO
3n
Br
2
C6F13
MeO
OMe
4
4-isomer
1H NMR
2.00
6.06
f1 (ppm)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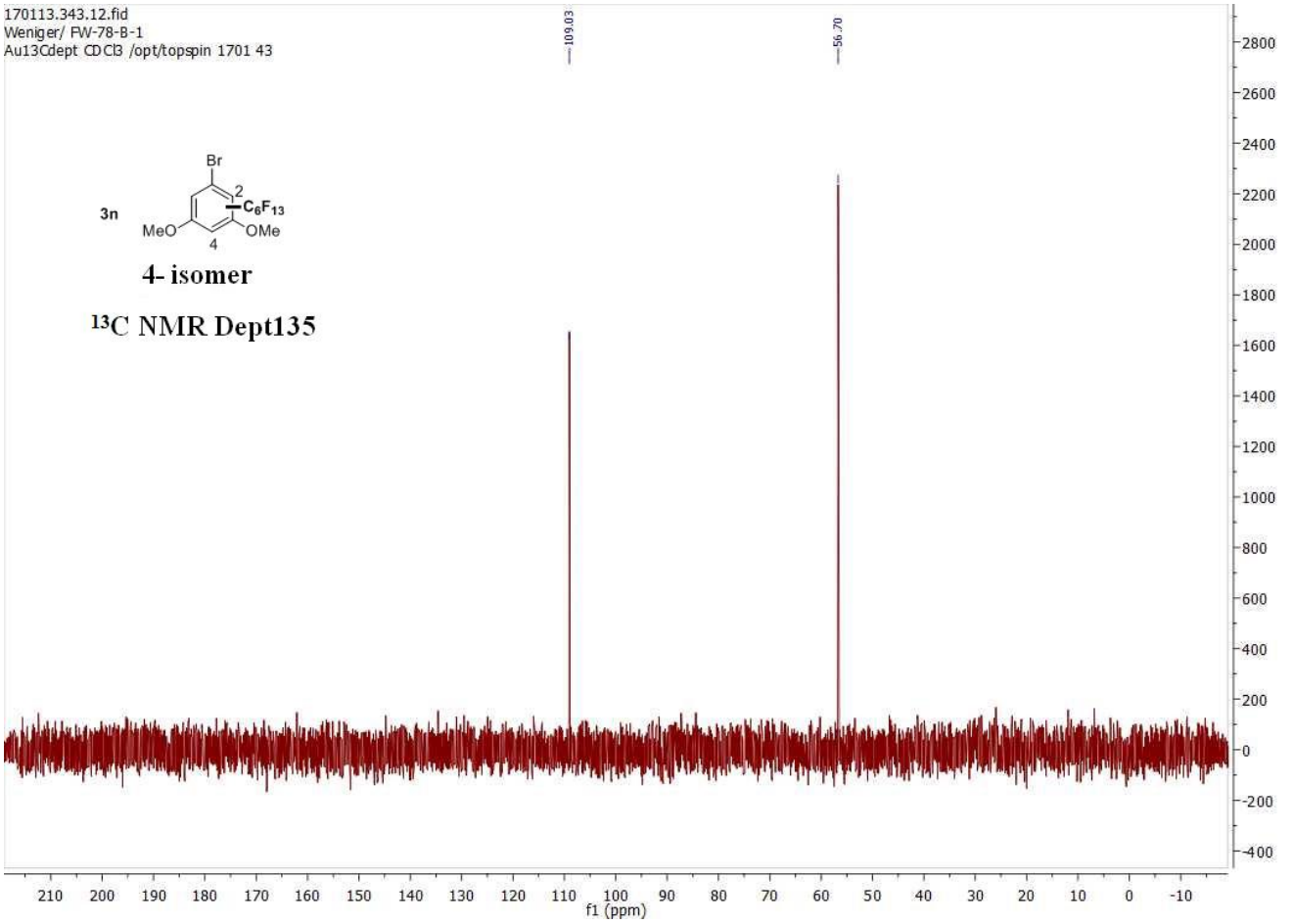
Weniger/ FW-78-B-1
Au13C CDCl3 /opt/topspin 1701 43
160.85
160.83
160.80
127.62
109.00
77.00 CDCl3
56.66
Br
2
C6F13
MeO
OMe
4
3n
4- isomer
13C NMR
f1 (ppm)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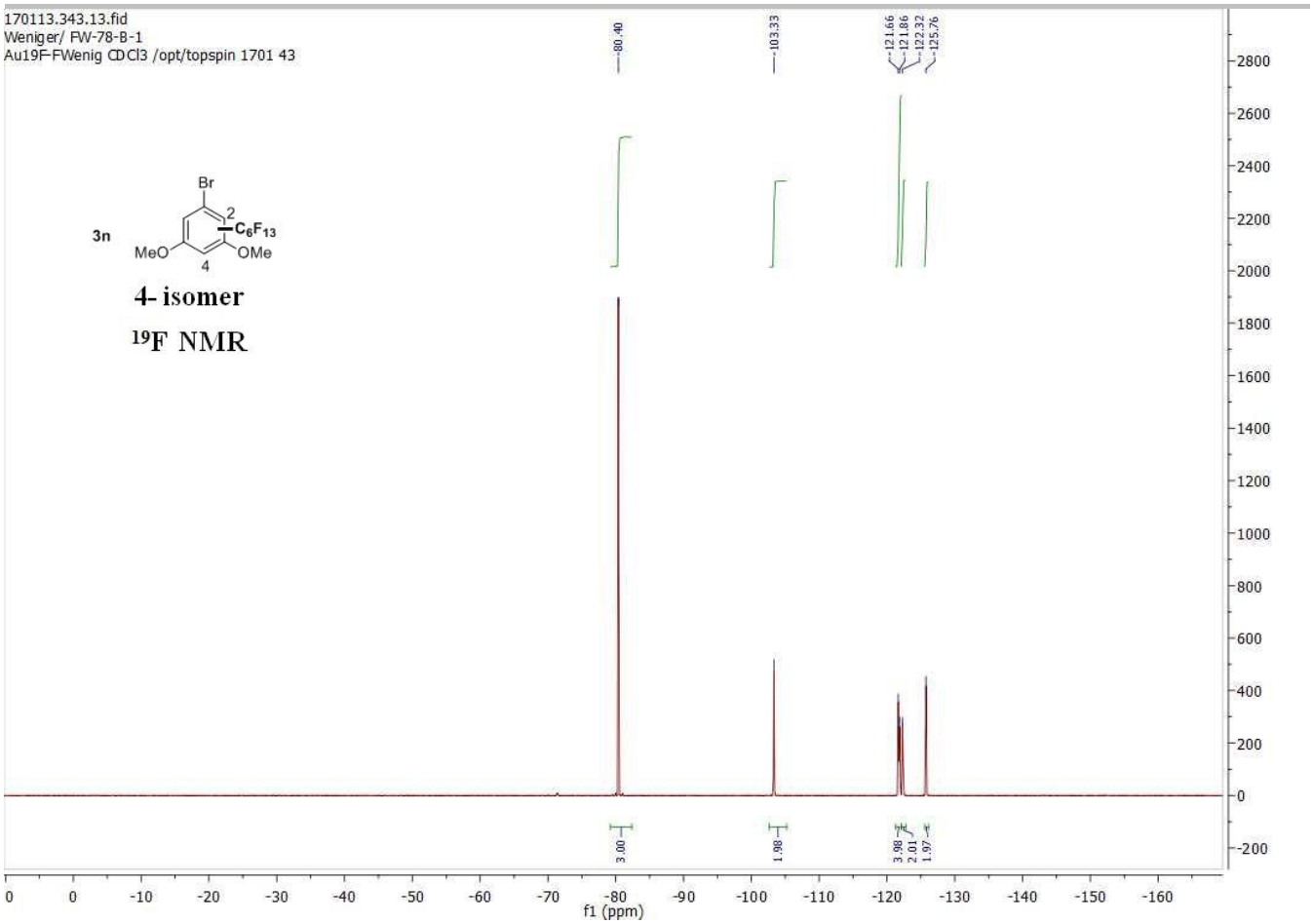
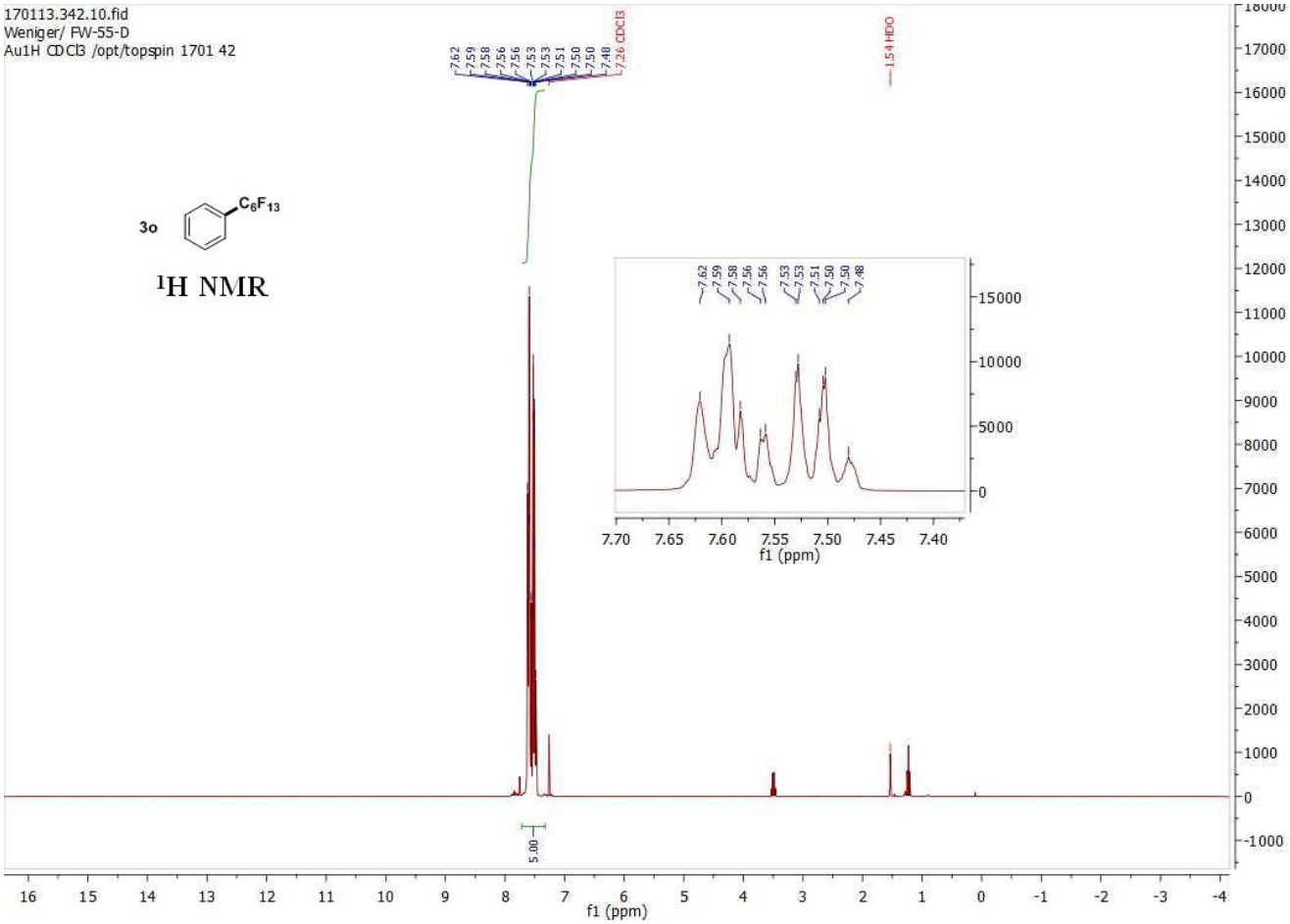
Weniger/ FW-78-B-1
Au13Cdept CDCl3 /opt/topspin 1701 43
109.03
56.70
Br
2
C6F13
MeO
OMe
4
3n
4- isomer
13C NMR Dept135
f1 (ppm)


170113.343.13.fid
Weniger/ FW-78-B-1
Au19F-FWenig CDCl3 /opt/topspin 1701 43
-80.40
-103.33
-121.66
-121.86
-122.32
-125.76
3n
Br
2
C6F13
MeO
OMe
4
4- isomer
19F NMR
3.00
1.98
3.98
2.01
1.97
f1 (ppm)


170113.342.10.fid
Weniger/ FW-55-D
Au1H CDCl3 /opt/topspin 1701 42
7.62
7.59
7.58
7.56
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7.26 CDCl3
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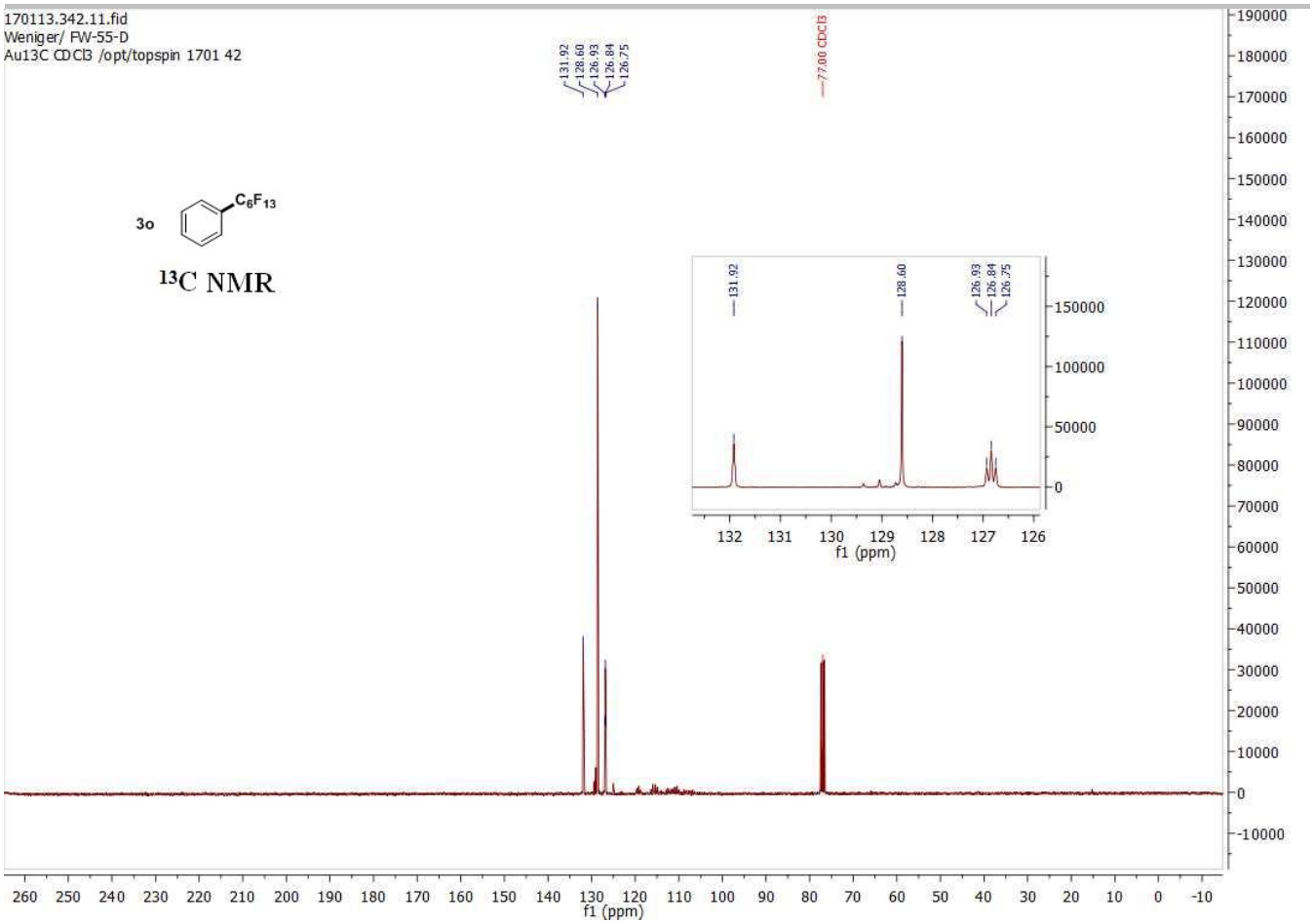
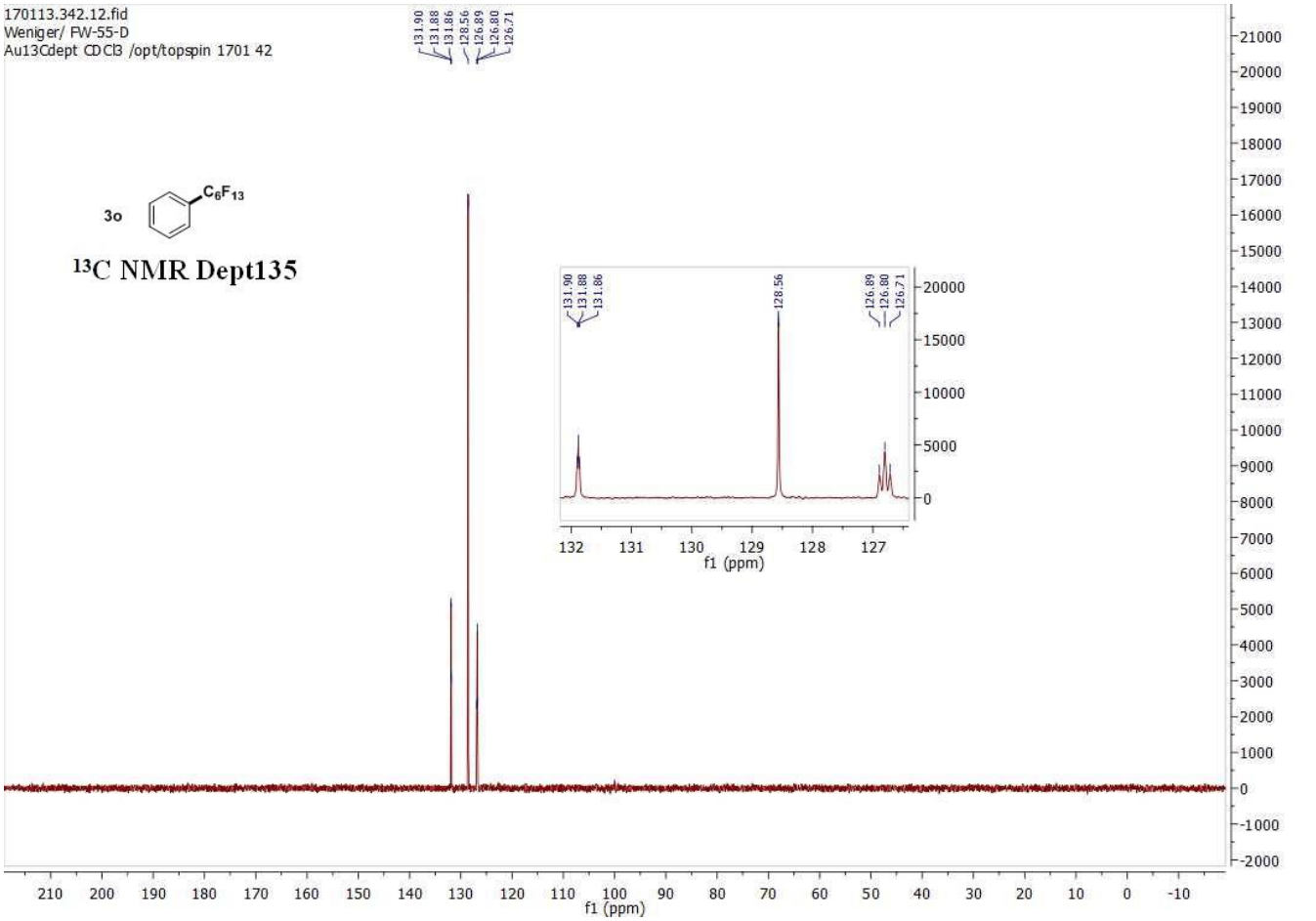
3o
C6F13
1H NMR
5.00
f1 (ppm)


170113.342.11.fid
Weniger/ FW-55-D
Au13C CDCl3 /opt/topspin 1701 42
131.92
128.60
126.93
126.84
126.75
77.00 CDCl3
3o
$C_6F_{13}$
$^{13}$C NMR
f1 (ppm)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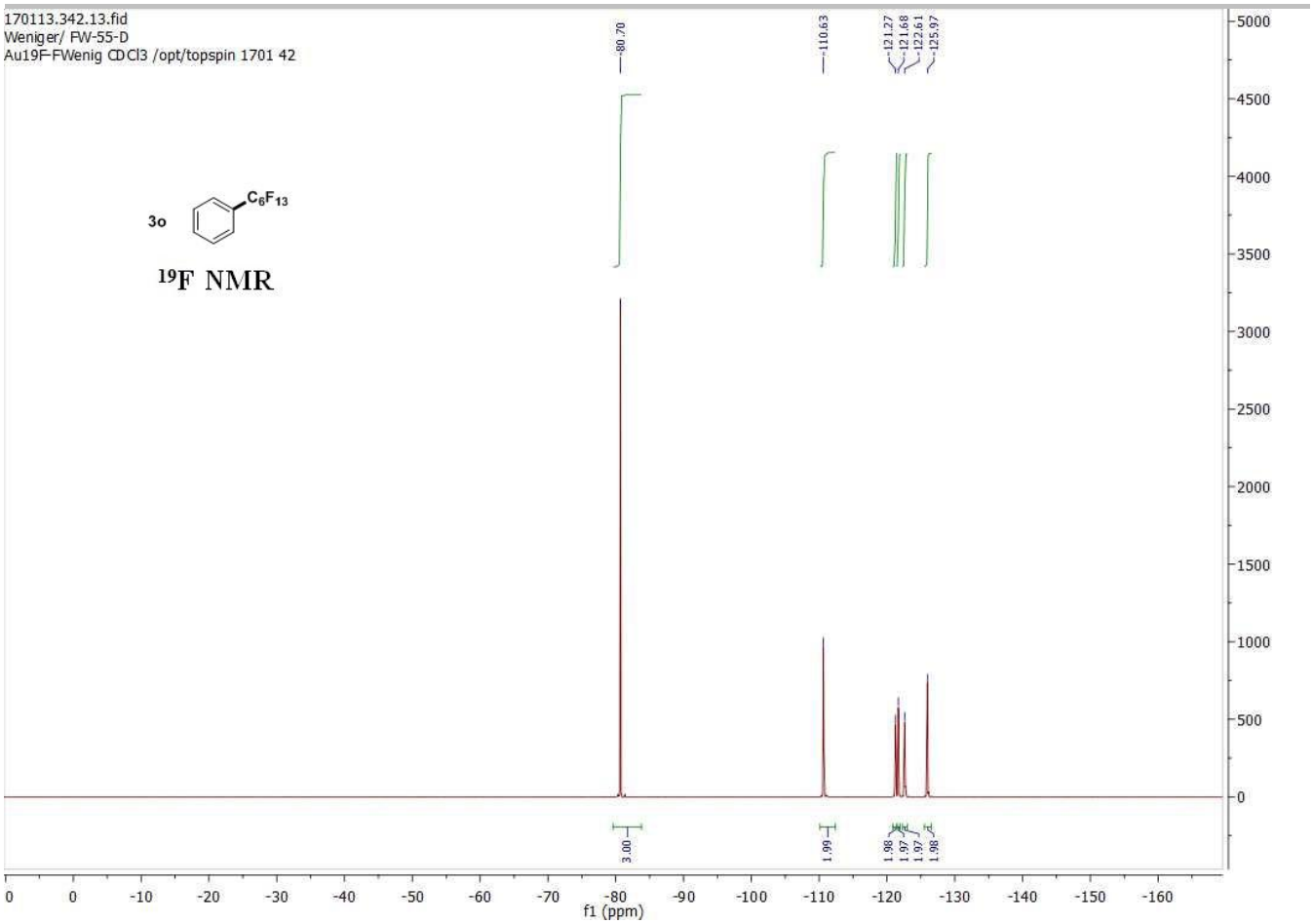
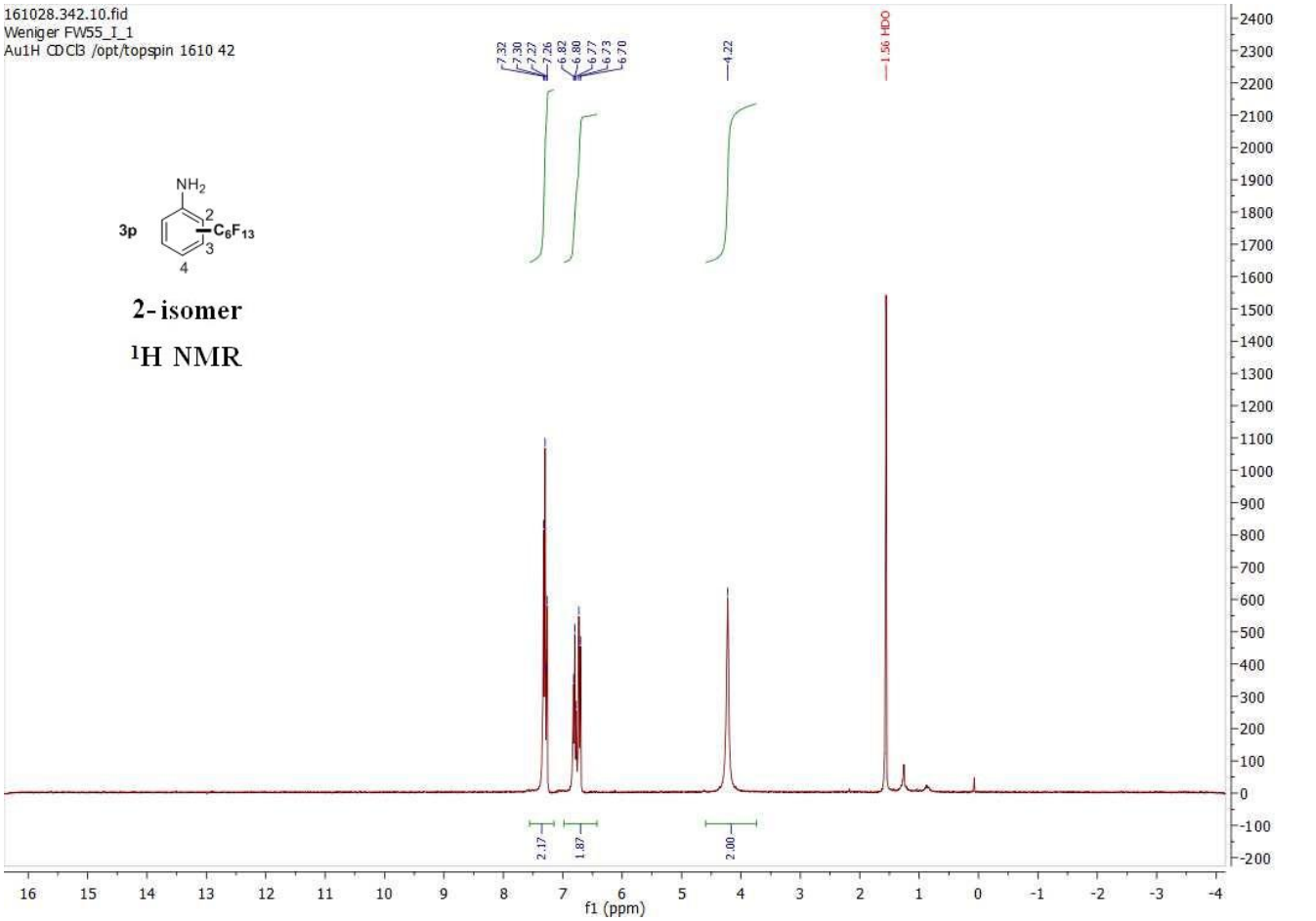
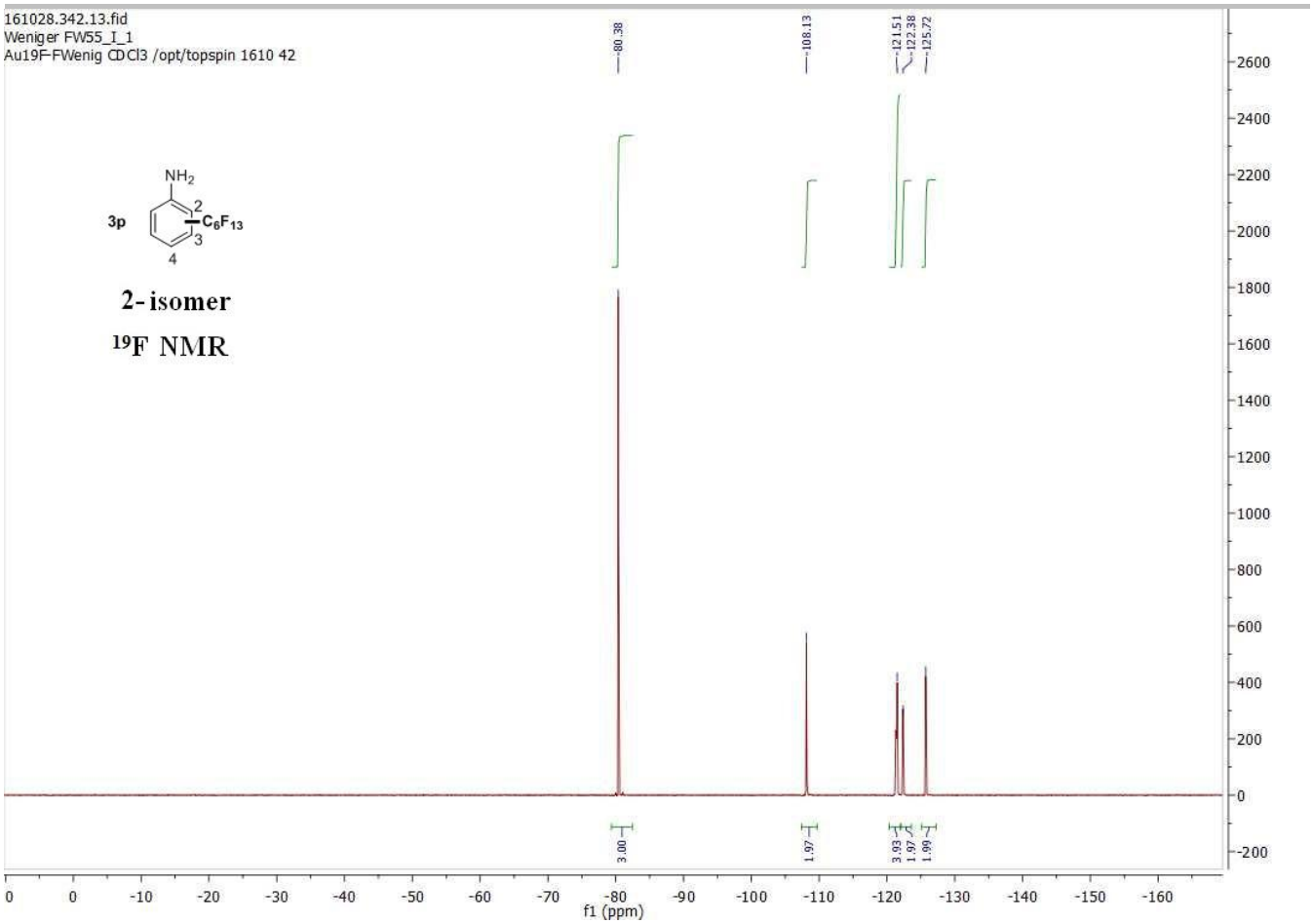
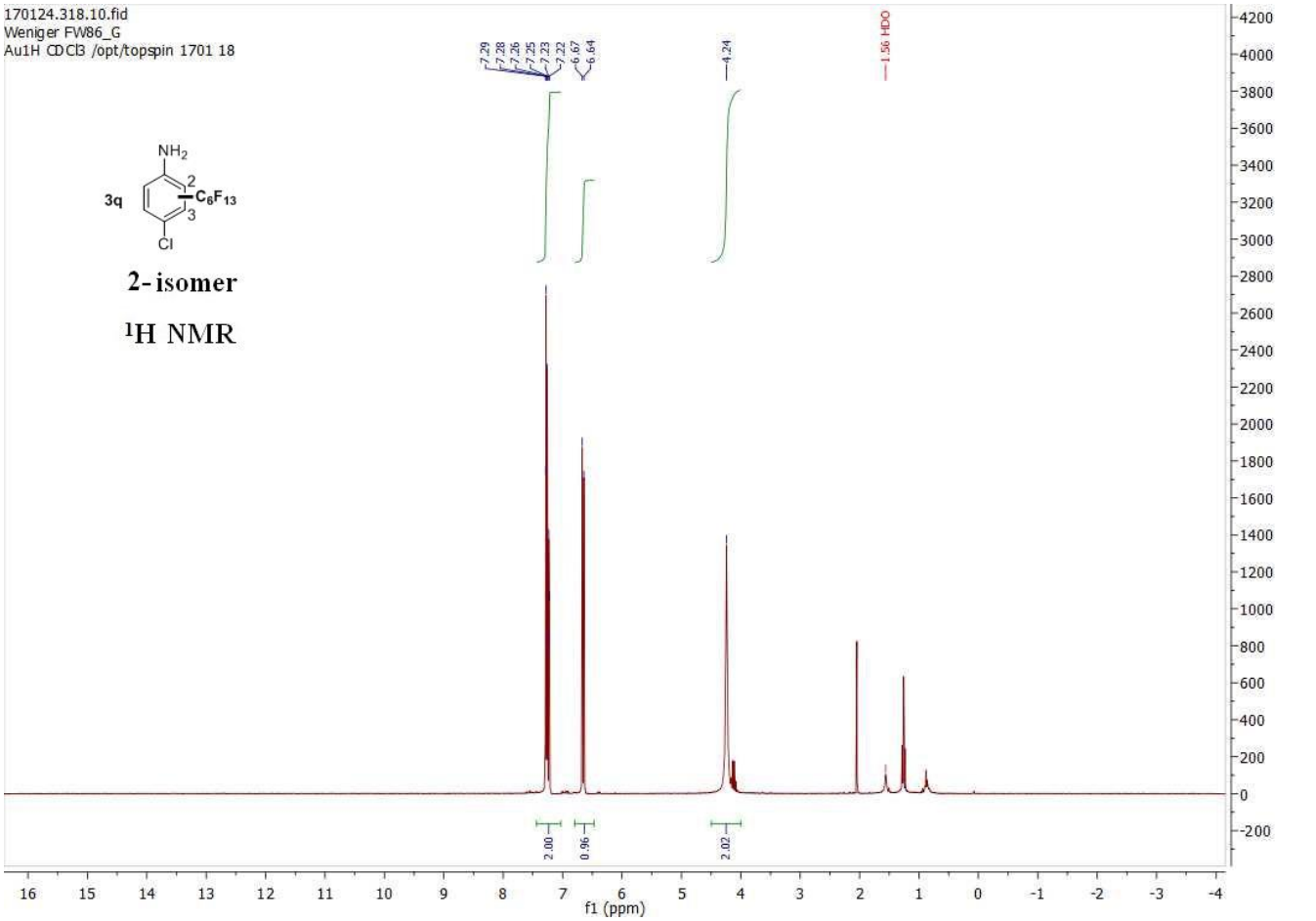
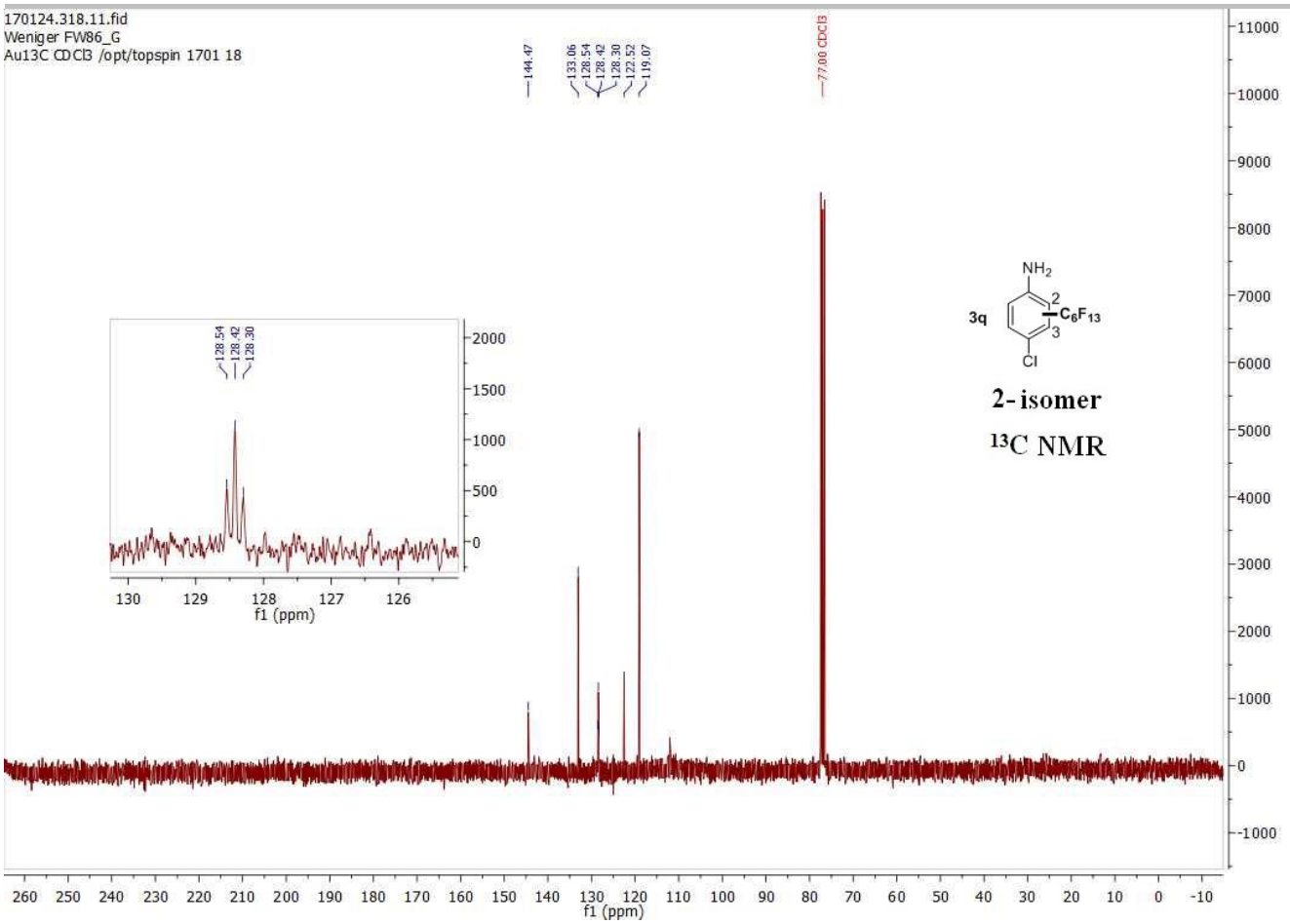
Weniger/ FW-55-D
Au13Cdept CDCl3 /opt/topspin 1701 42
131.90
131.88
131.86
128.56
126.89
126.80
126.71
3o
$C_6F_{13}$
$^{13}$C NMR Dept135
f1 (ppm)

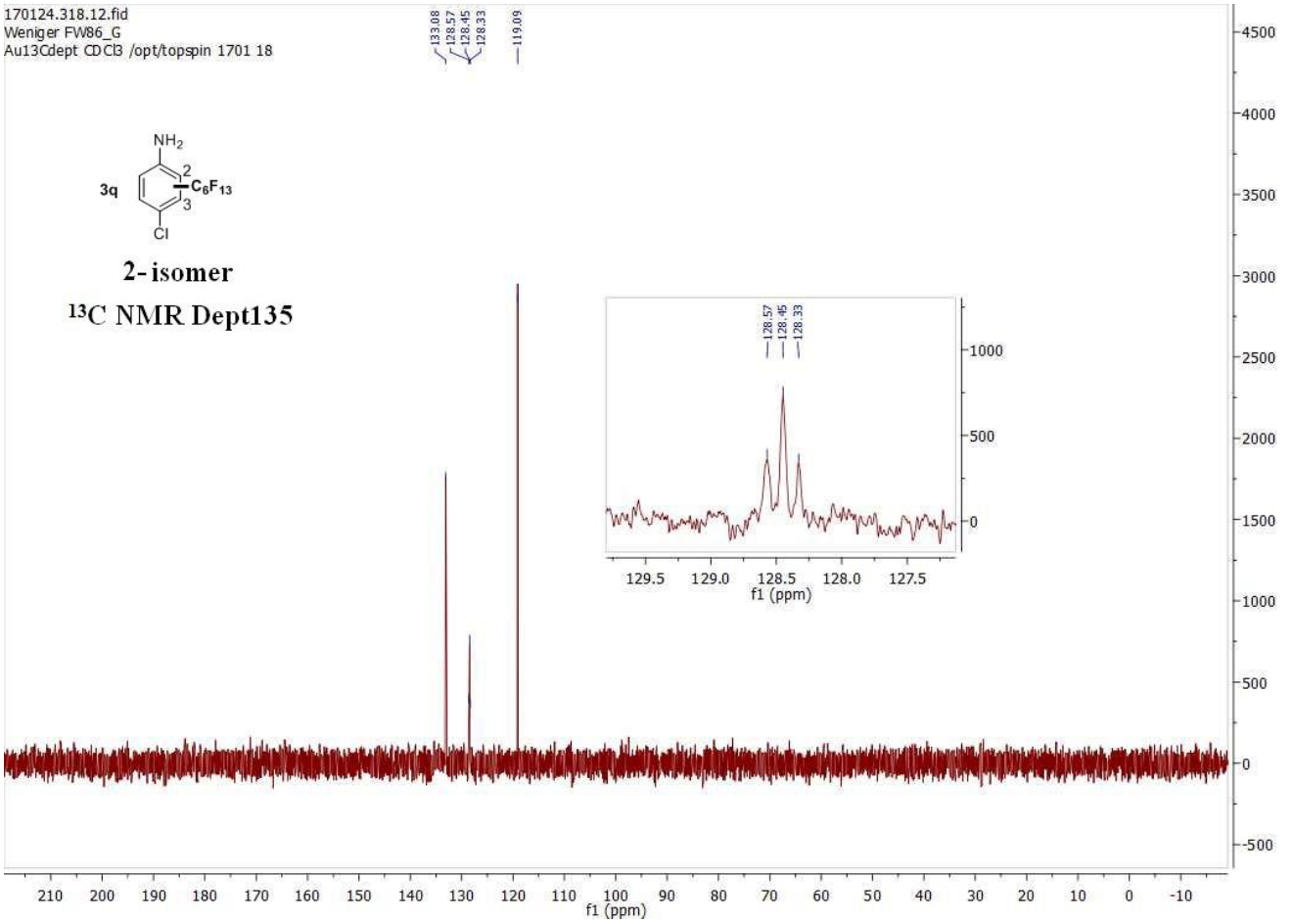

170113.342.13.fid
Weniger/ FW-55-D
Au19F-FWenig CDCl3 /opt/topspin 1701 42
-80.70
-110.63
-121.27
-121.68
-122.61
-125.97
3o
$C_6F_{13}$
$^{19}$F NMR
3.00
1.99
1.98
1.97
1.97
1.98
f1 (ppm)

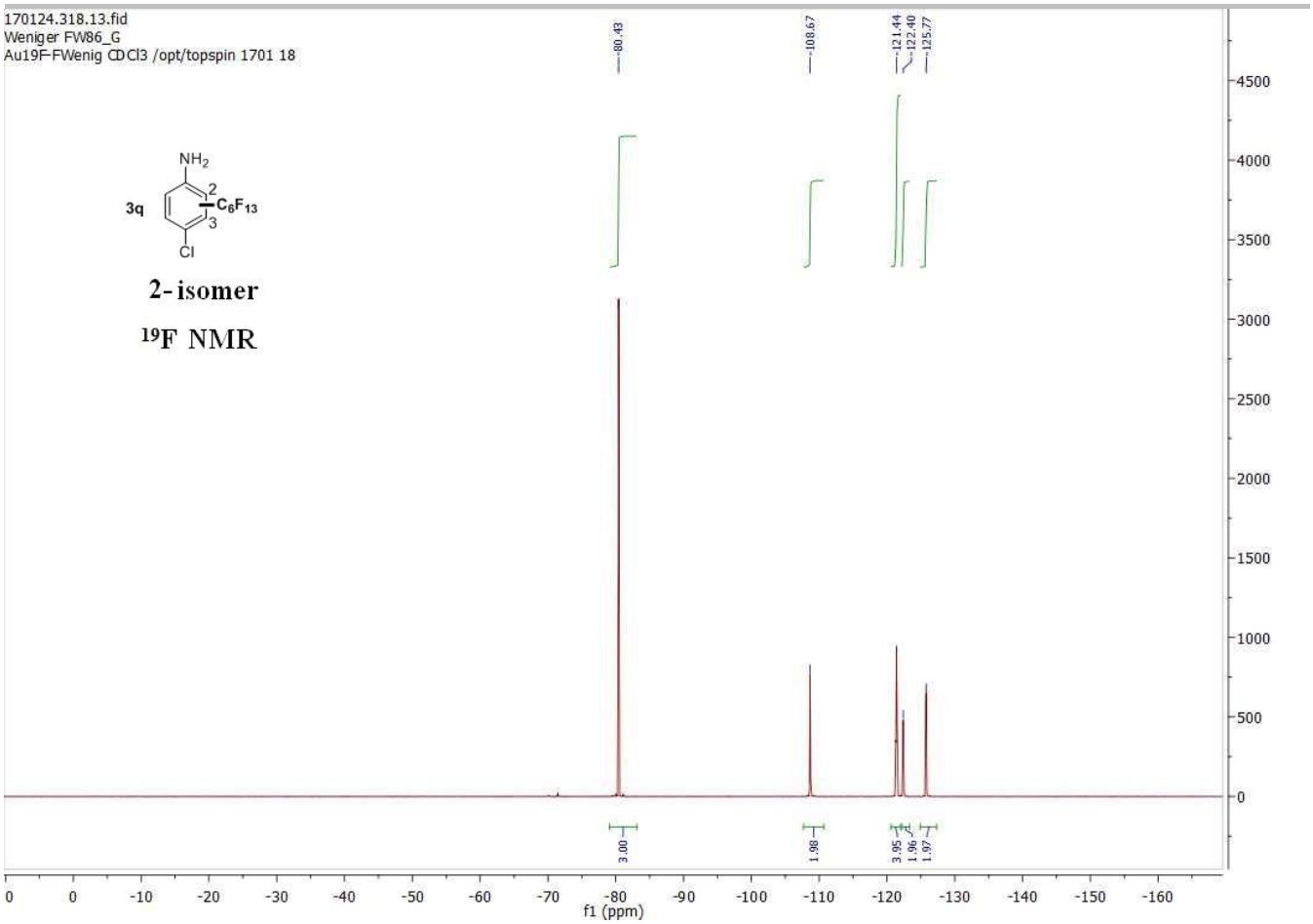

161028.342.10.fid
Weniger FW55_1_1
Au1H CDCl3 /opt/topspin 1610 42
7.32
7.30
7.27
7.26
6.82
6.80
6.77
6.73
6.70
4.22
1.56 HDO
3p
$NH_2$
$C_6F_{13}$
2-isomer
$^1$H NMR
2.17
1.87
2.00
f1 (ppm)

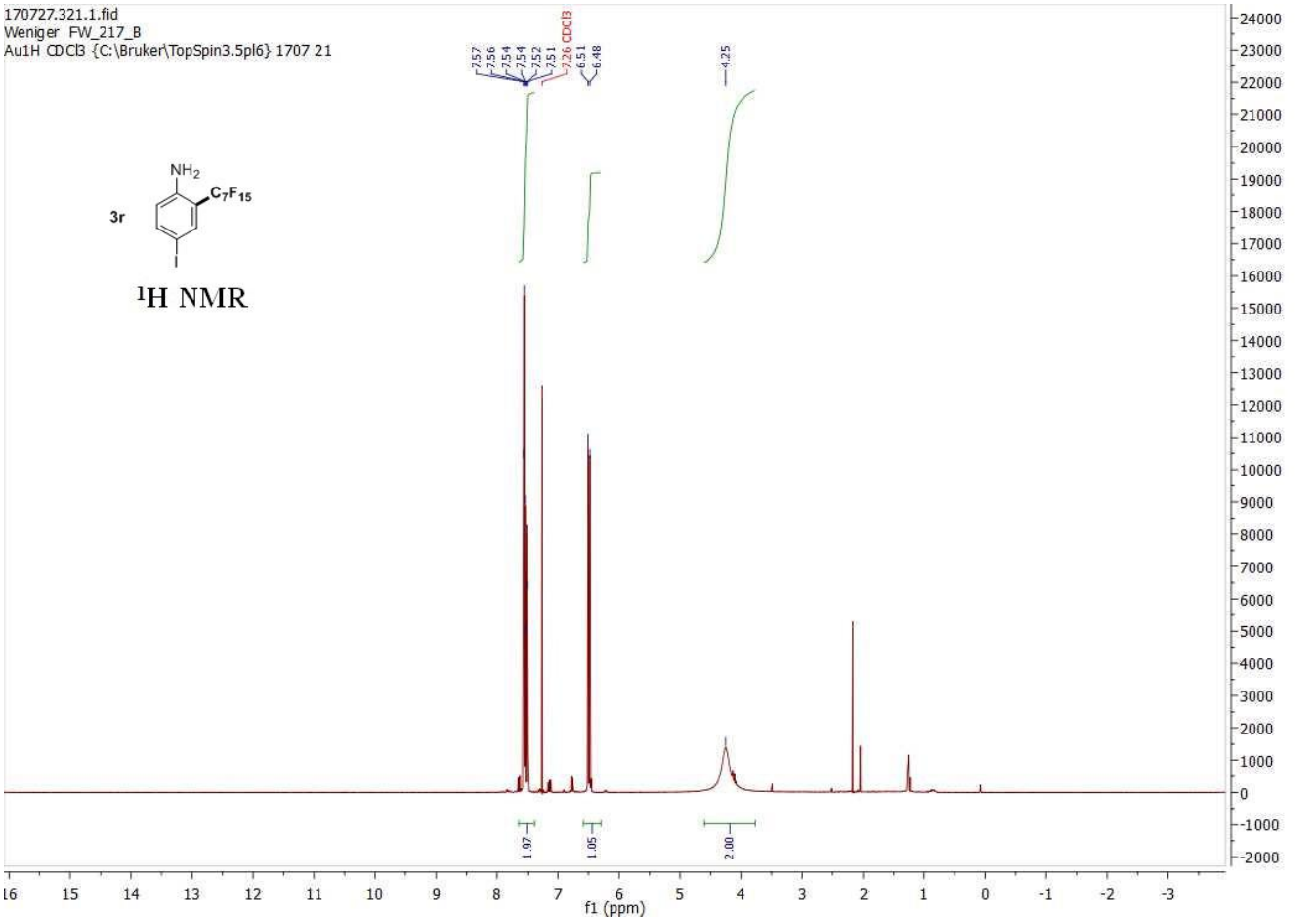

161028.342.13.fid
Weniger FW55_I_1
Au19F-FWenig CDCl3 /opt/topspin 1610 42
-80.38
-108.13
-121.51
-122.38
-125.72
3p
2-isomer
19F NMR
3.00
1.97
3.93
1.97
1.99
f1 (ppm)

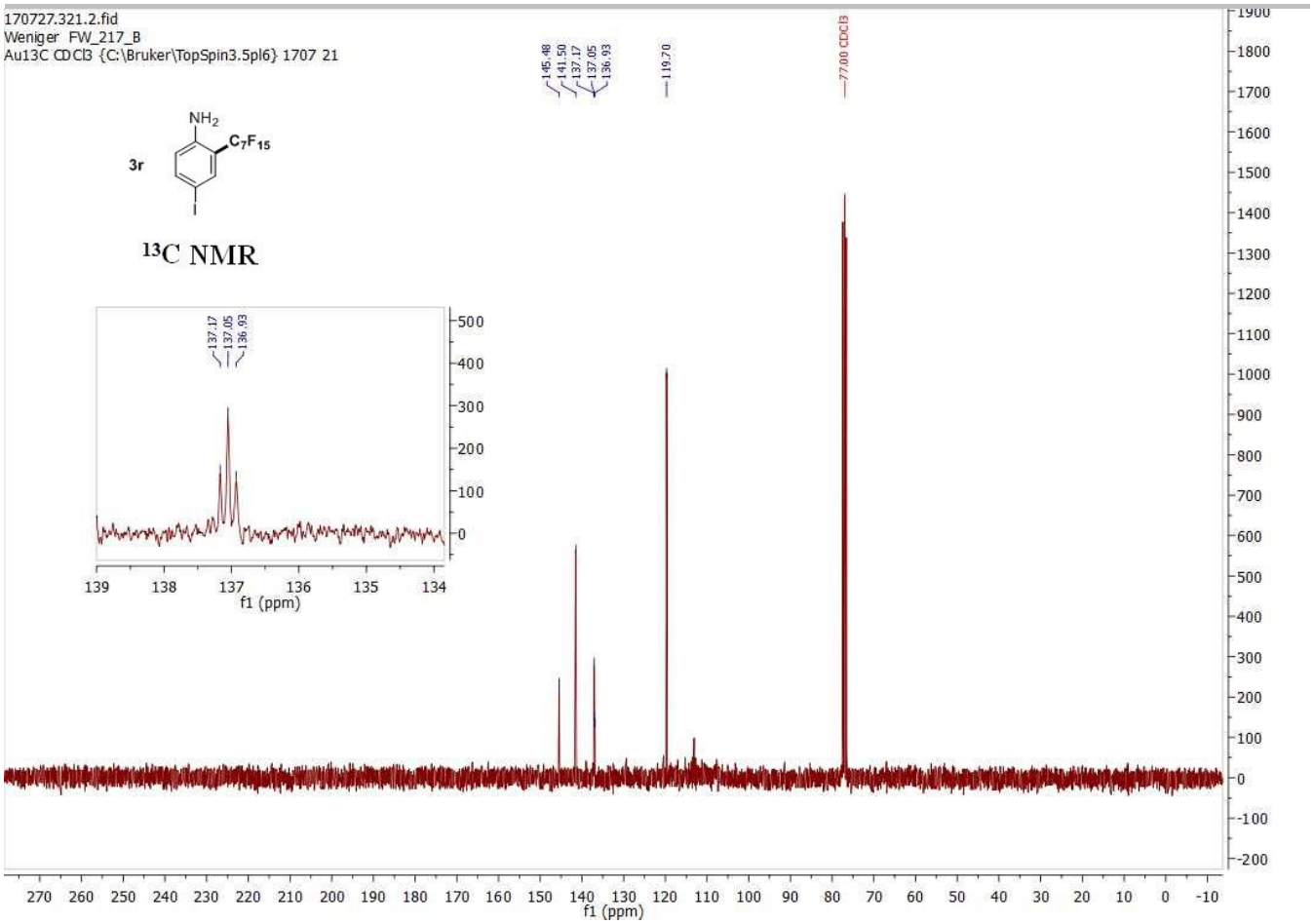

170124.318.10.fid
Weniger FW86_G
Au1H CDCl3 /opt/topspin 1701 18
7.29
7.28
7.26
7.25
7.23
7.22
6.67
6.64
4.24
1.56 HDO
3q
2-isomer
1H NMR
2.00
0.96
2.02
f1 (ppm)

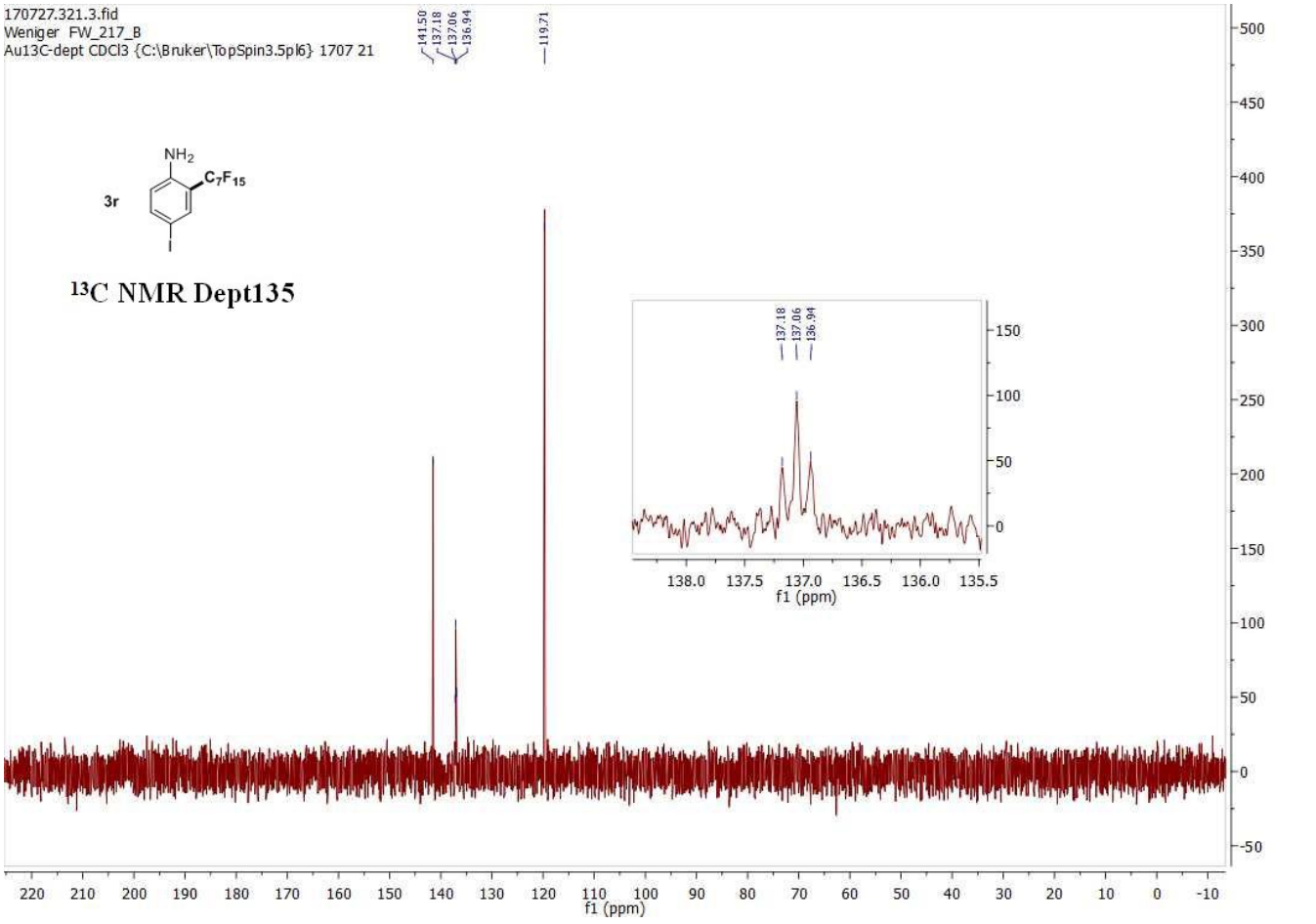

170124.318.11.fid
Weniger FW86_G
Au13C CDCl3 /opt/topspin 1701 18
144.47
133.06
128.54
128.42
128.30
122.52
119.07
77.00 CDCl3
3q
NH2
C6F13
Cl
2-isomer
13C NMR
f1 (ppm)

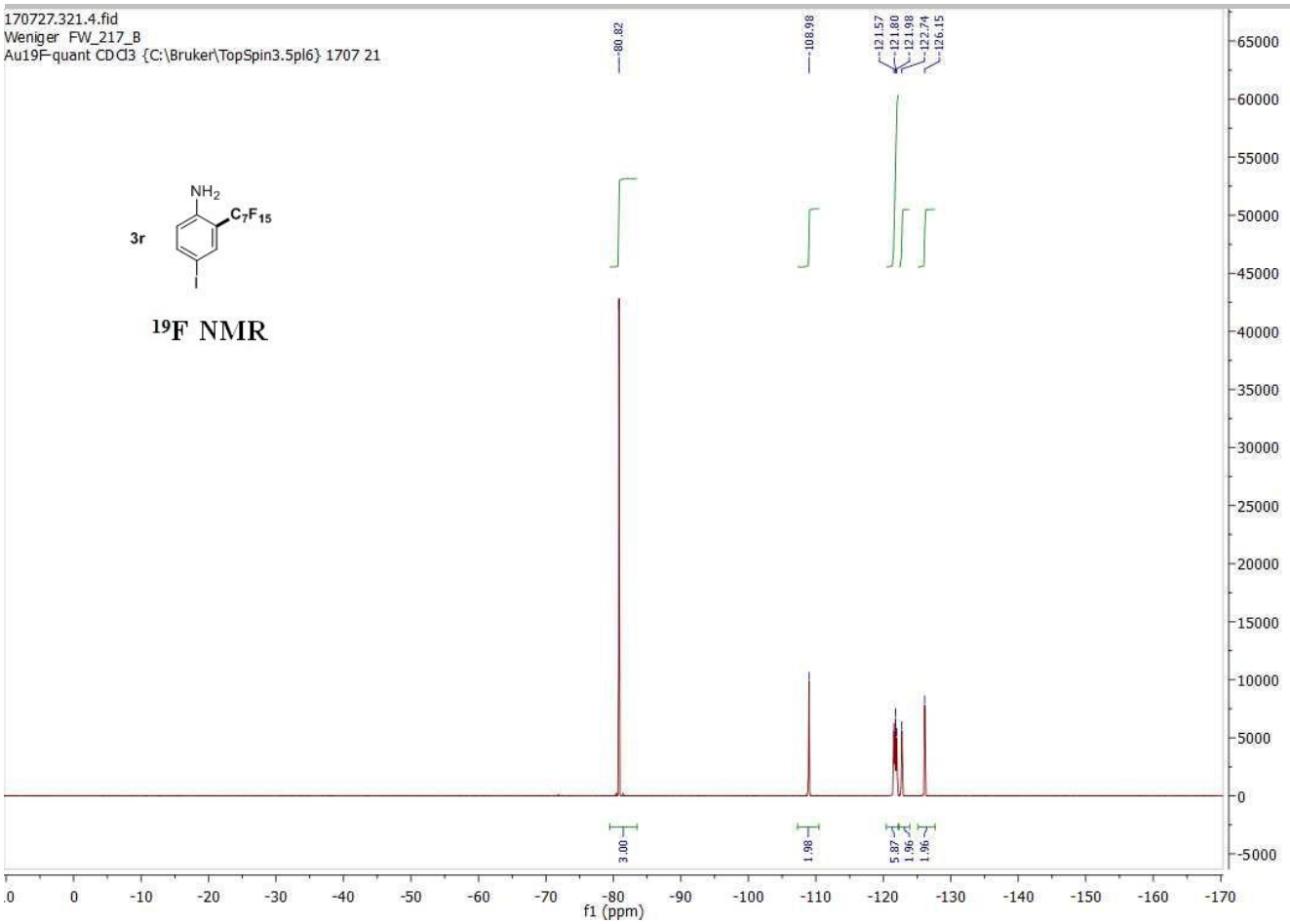

170124.318.12.fid
Weniger FW86_G
Au13Cdept CDCl3 /opt/topspin 1701 18
133.08
128.57
128.45
128.33
119.09
3q
NH2
C6F13
Cl
2-isomer
13C NMR Dept135
f1 (ppm)

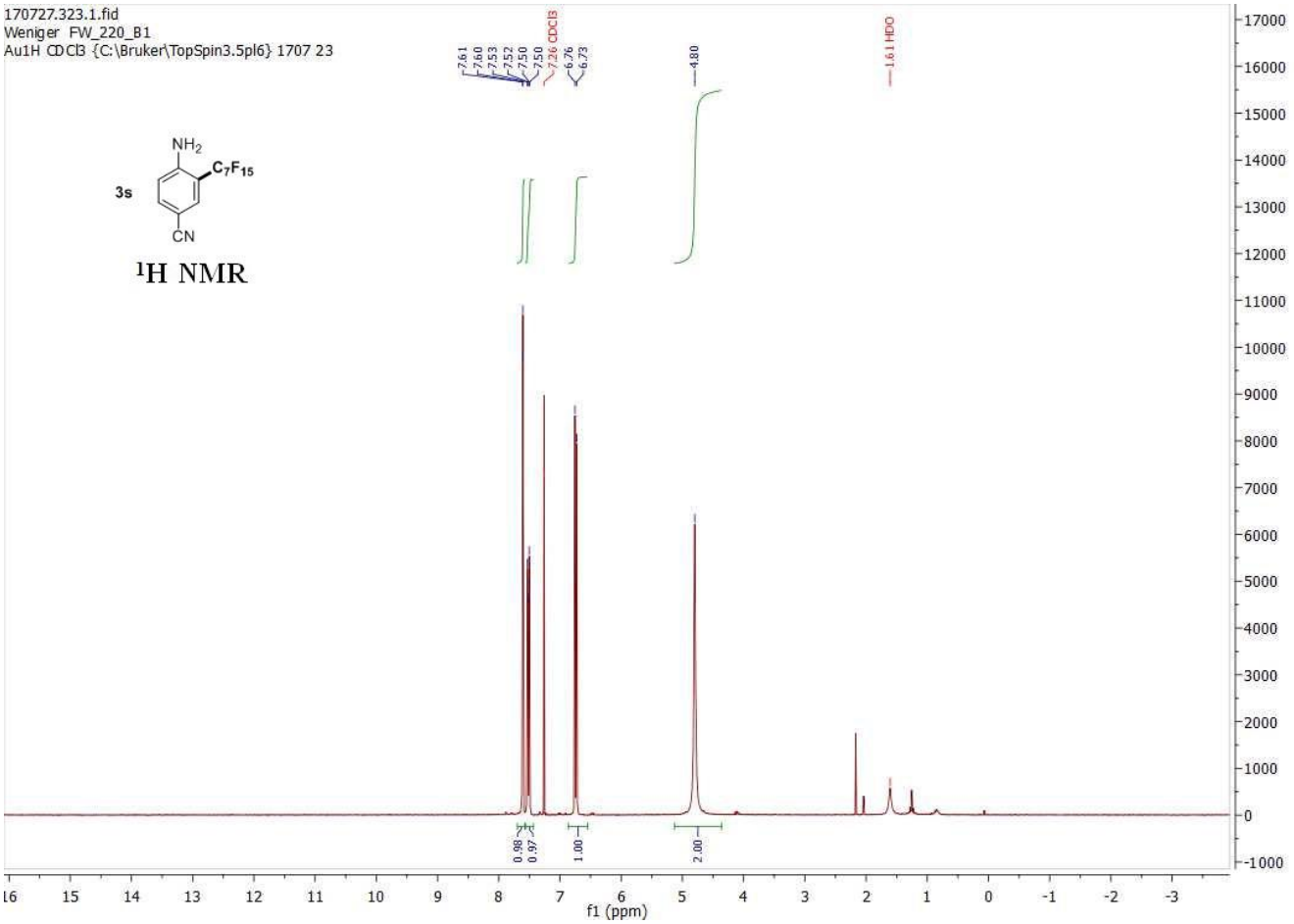

170124.318.13.fid
Weniger FW86_G
Au19F-FWenig CDCl3 /opt/topspin 1701 18
-80.43
-108.67
-121.44
-122.40
-125.77
3q
2-isomer
19F NMR
3.00
1.98
3.95
1.96
1.97
f1 (ppm)

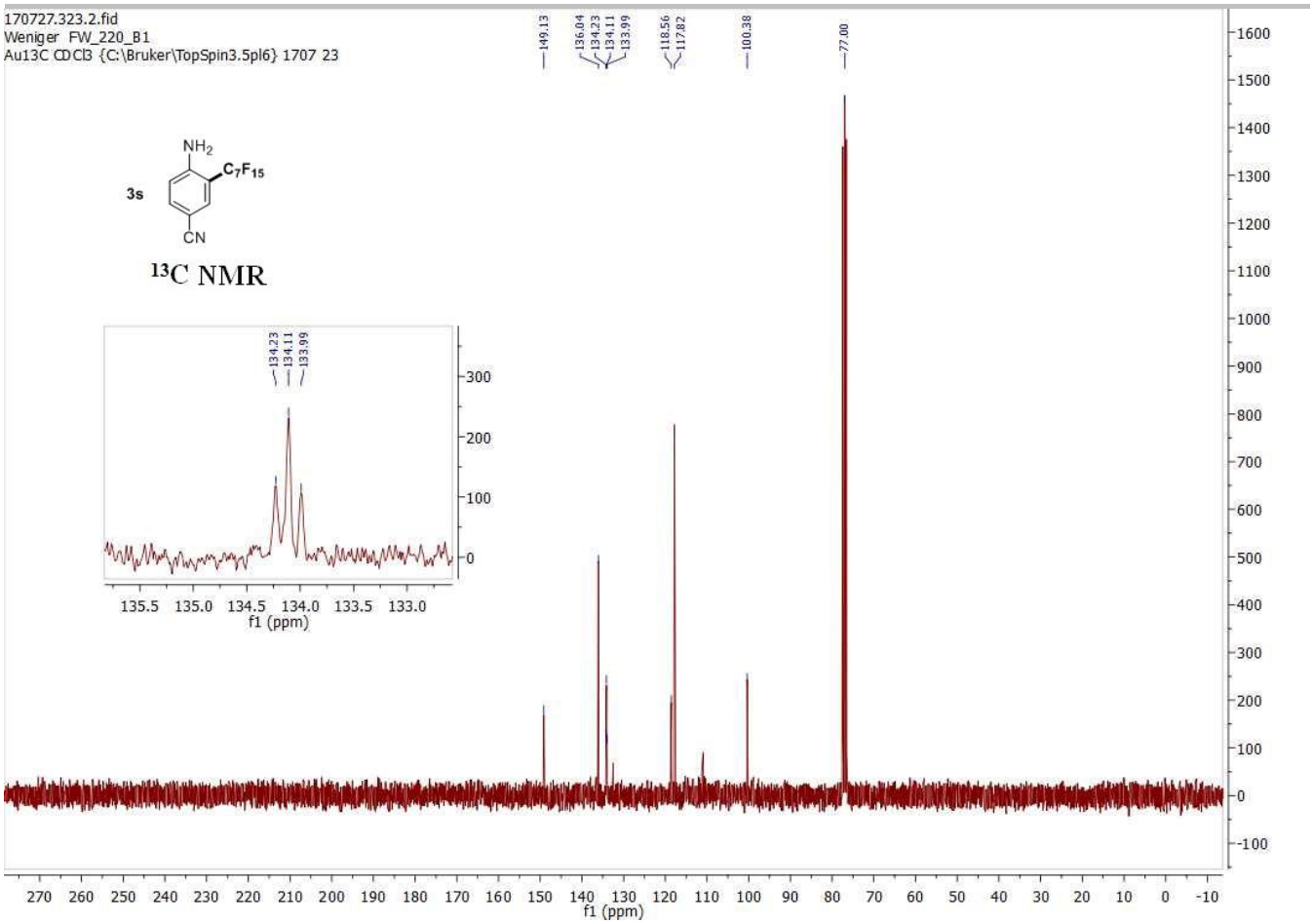

170727.321.1.fid
Weniger FW_217_B
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 21
7.57
7.56
7.54
7.54
7.52
7.51
7.26 CDCl3
6.51
6.48
4.25
3r
1H NMR
1.97
1.05
2.00
f1 (ppm)

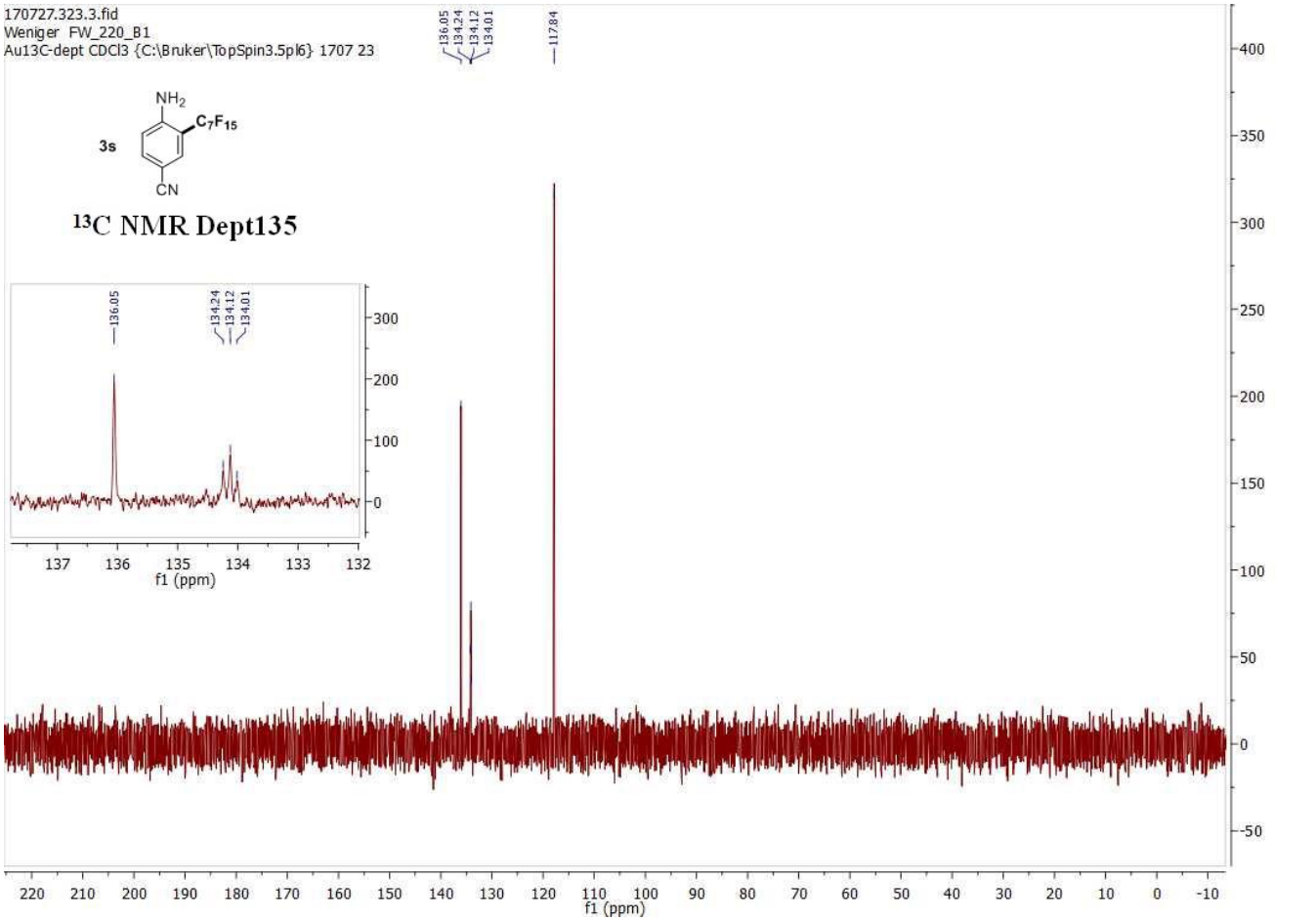

170727.321.2.fid
Weniger FW_217_B
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 21
145.48
141.50
137.17
137.05
136.93
119.70
77.00 CDCl3
NH2
C7F15
I
3r
13C NMR
137.17
137.05
136.93
f1 (ppm)
f1 (ppm)

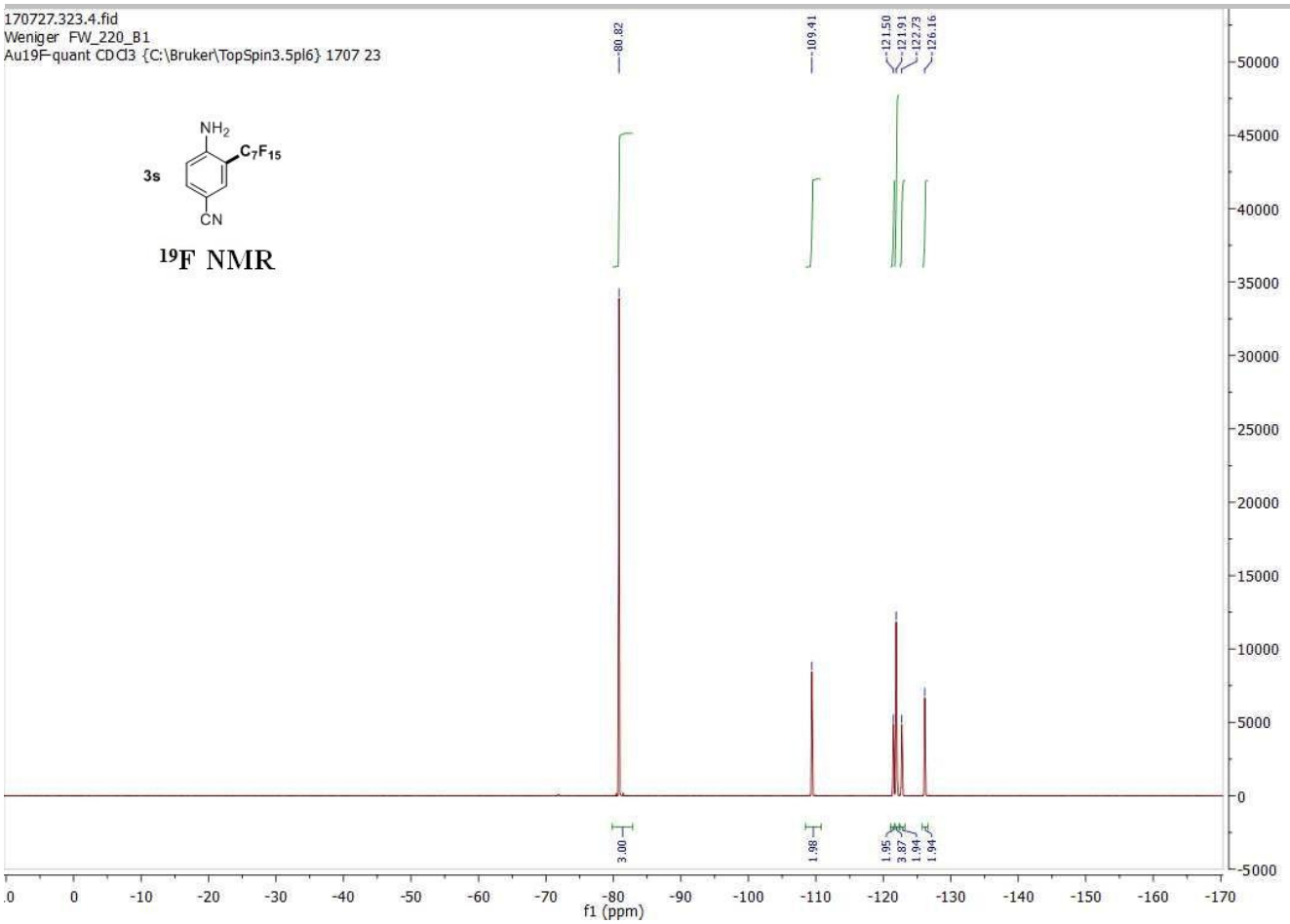

170727.321.3.fid
Weniger FW_217_B
Au13C-dept CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 21
141.50
137.18
137.06
136.94
119.71
NH2
C7F15
I
3r
13C NMR Dept135
137.18
137.06
136.94
f1 (ppm)
f1 (ppm)


170727.321.4.fid
Weniger FW_217_B
Au19F-quant CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 21
-80.82
-108.98
-121.57
-121.80
-121.98
-122.74
-126.15
3r
NH2
C7F15
I
19F NMR
3.00
1.98
5.87
1.96
1.96
f1 (ppm)

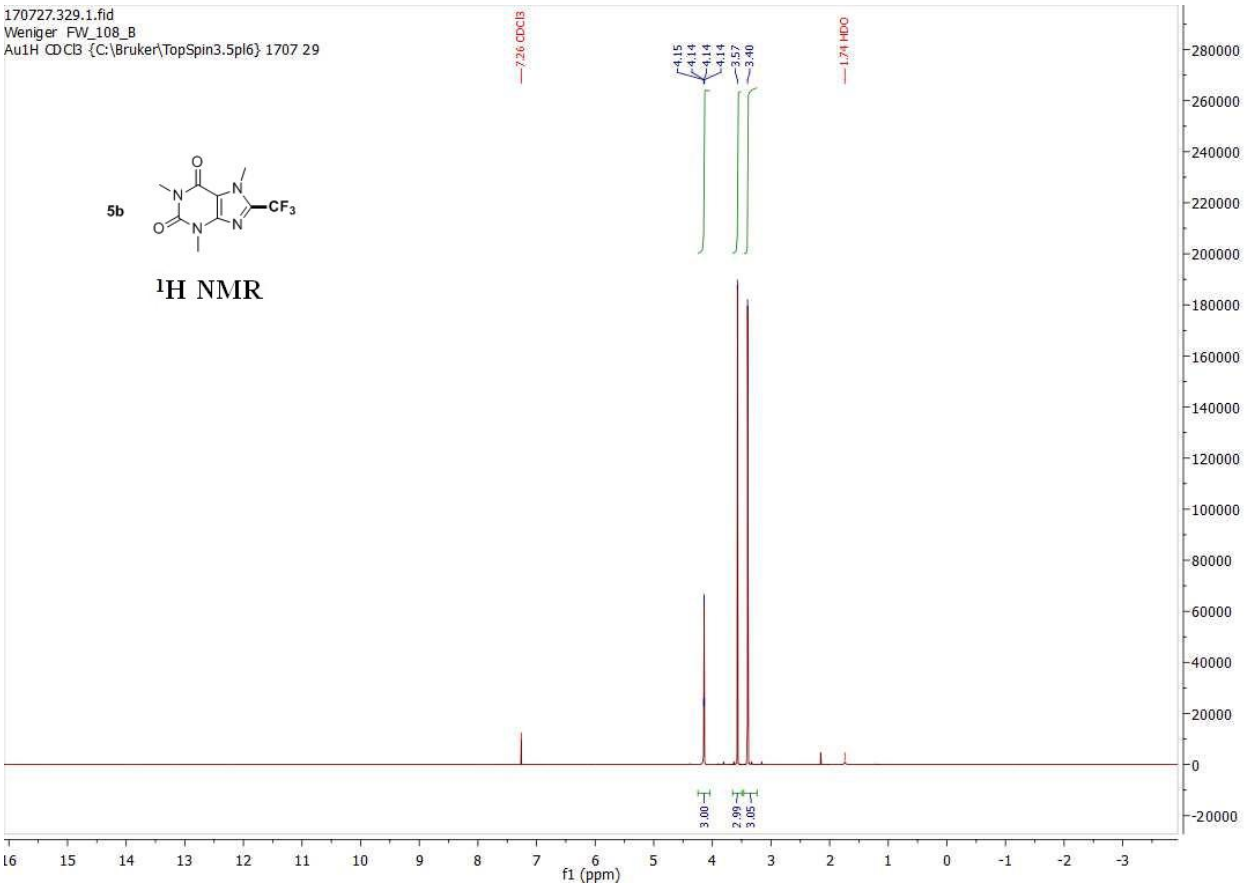

170727.323.1.fid
Weniger FW_220_B1
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 23
7.61
7.60
7.53
7.52
7.50
7.26 CDCl3
6.76
6.73
4.80
1.61 HDO
3s
NH2
C7F15
CN
1H NMR
0.98
0.97
1.00
2.00
f1 (ppm)

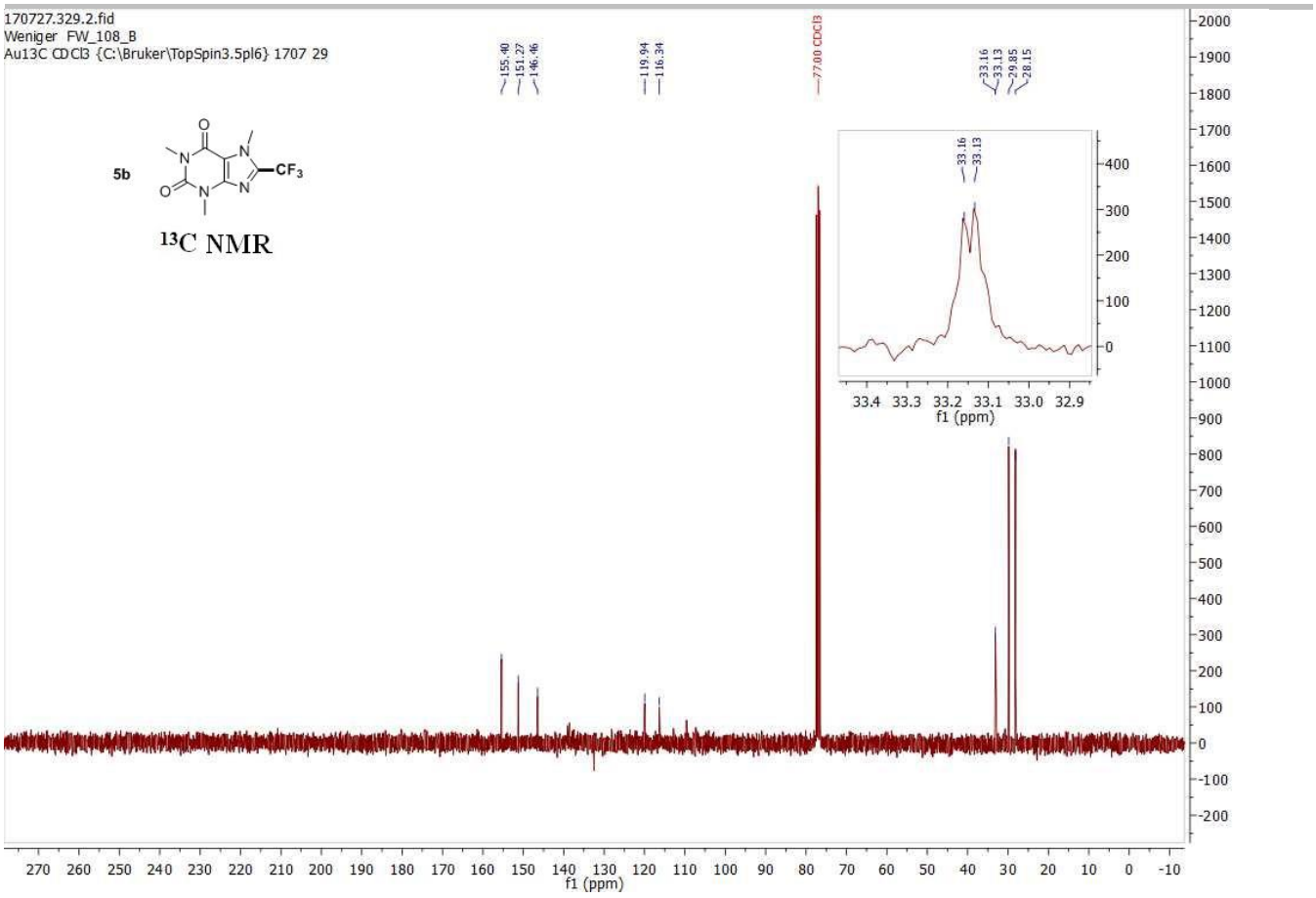

170727.323.2.fid
Weniger FW_220_B1
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 23
149.13
136.04
134.23
134.11
133.99
118.56
117.82
100.38
77.00
NH2
C7F15
CN
3s
13C NMR
134.23
134.11
133.99
135.5 135.0 134.5 134.0 133.5 133.0
f1 (ppm)
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

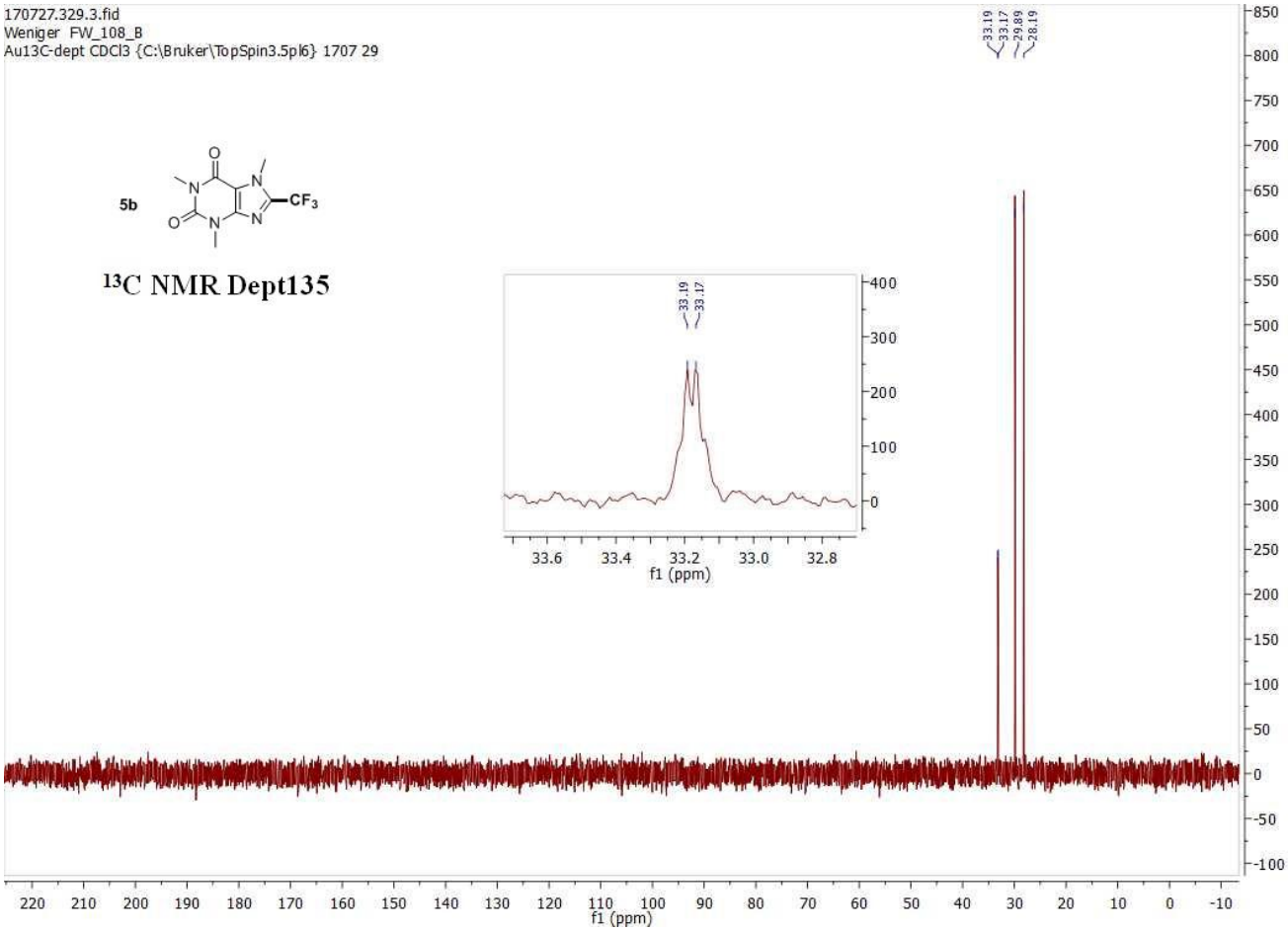

170727.323.3.fid
Weniger FW_220_B1
Au13C-dept CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 23
136.05
134.24
134.12
134.01
117.84
NH2
C7F15
CN
3s
13C NMR Dept135
136.05
134.24
134.12
134.01
137 136 135 134 133 132
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

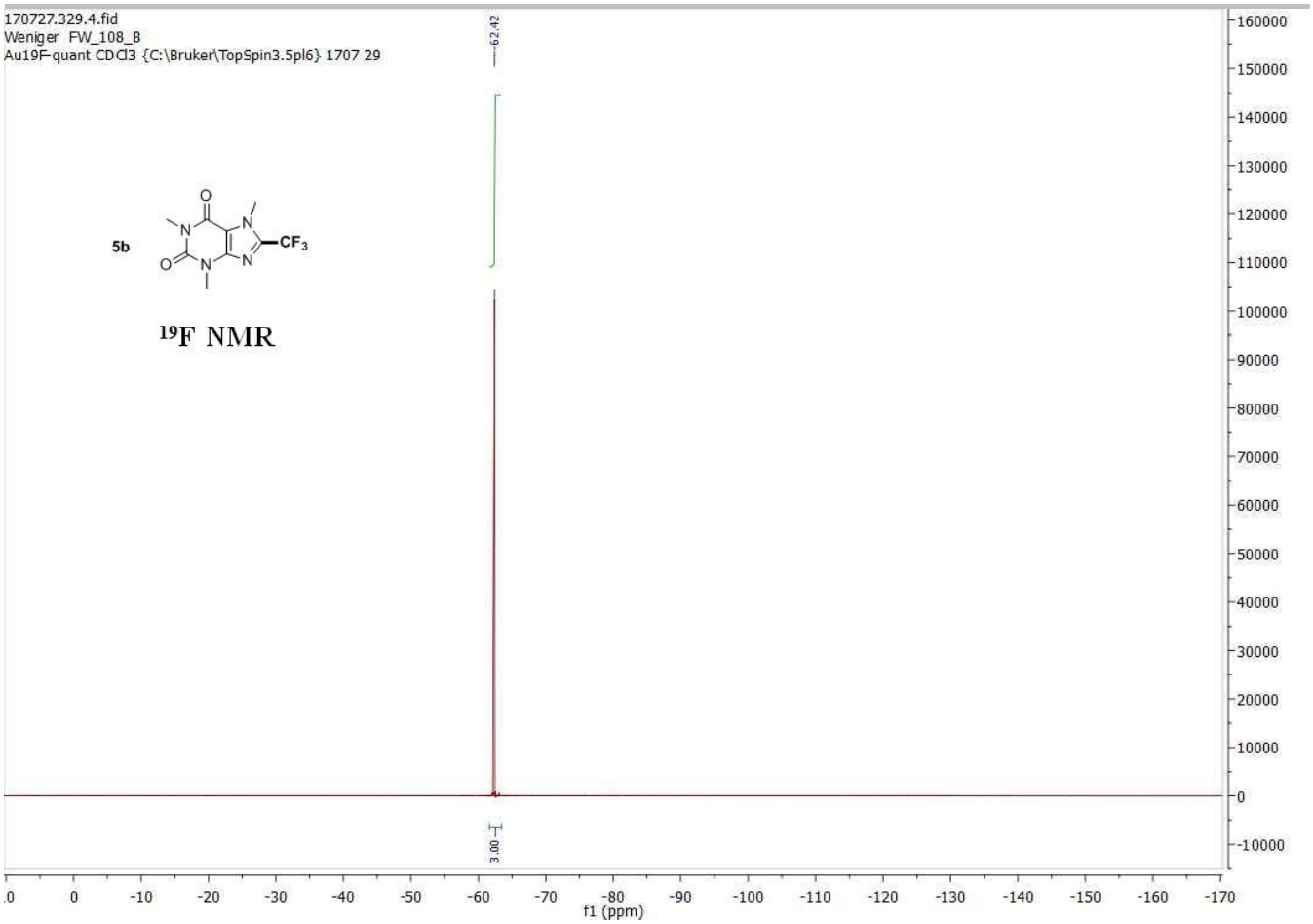



**8.2 Trifluoromethylated heteroarenes**

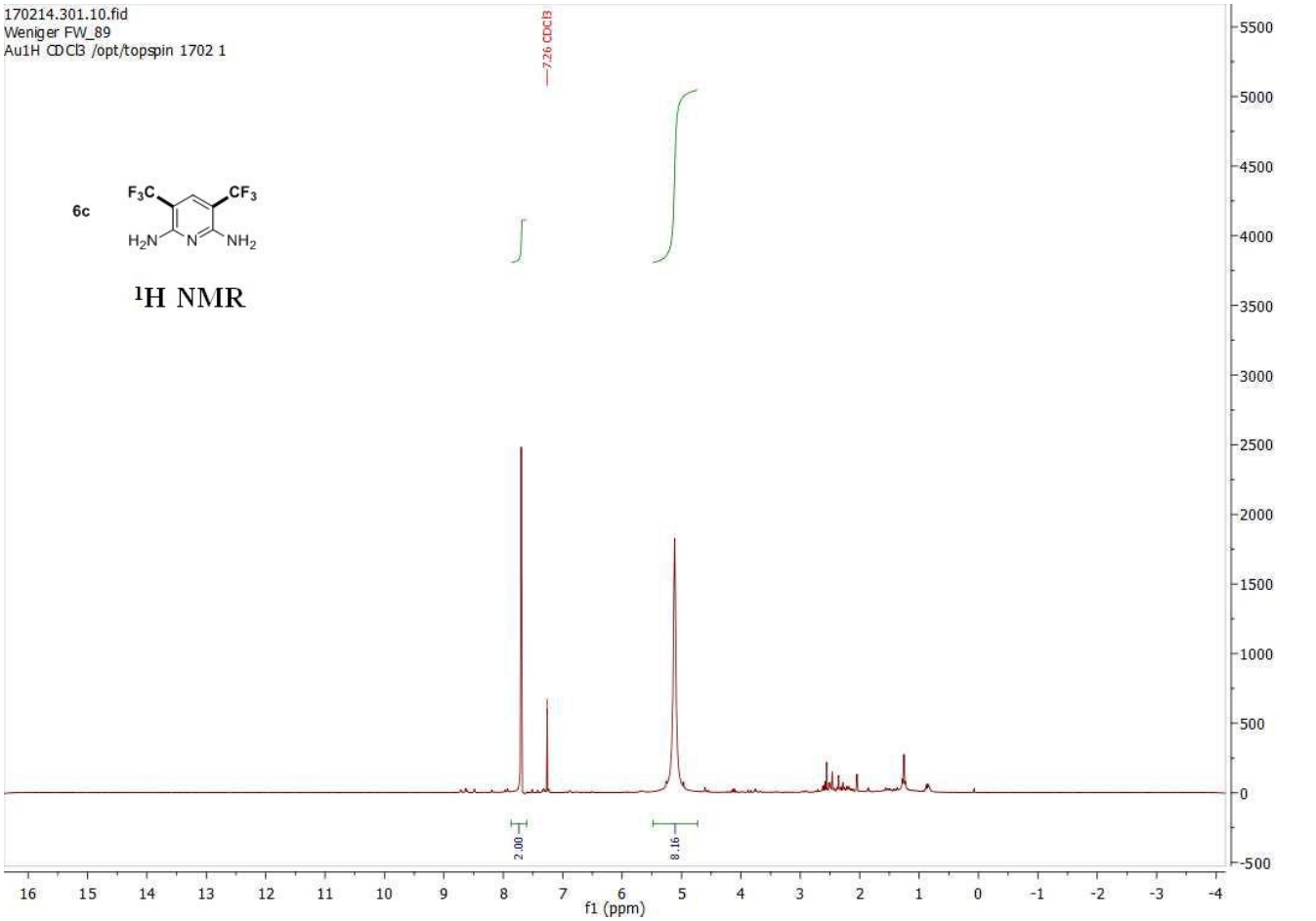



170727.329.2.fid
Weniger FW_108_B
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 29
155.40
151.27
146.46
119.94
116.34
77.00 CDCl3
33.16
33.13
29.85
28.15
5b
13C NMR
f1 (ppm)

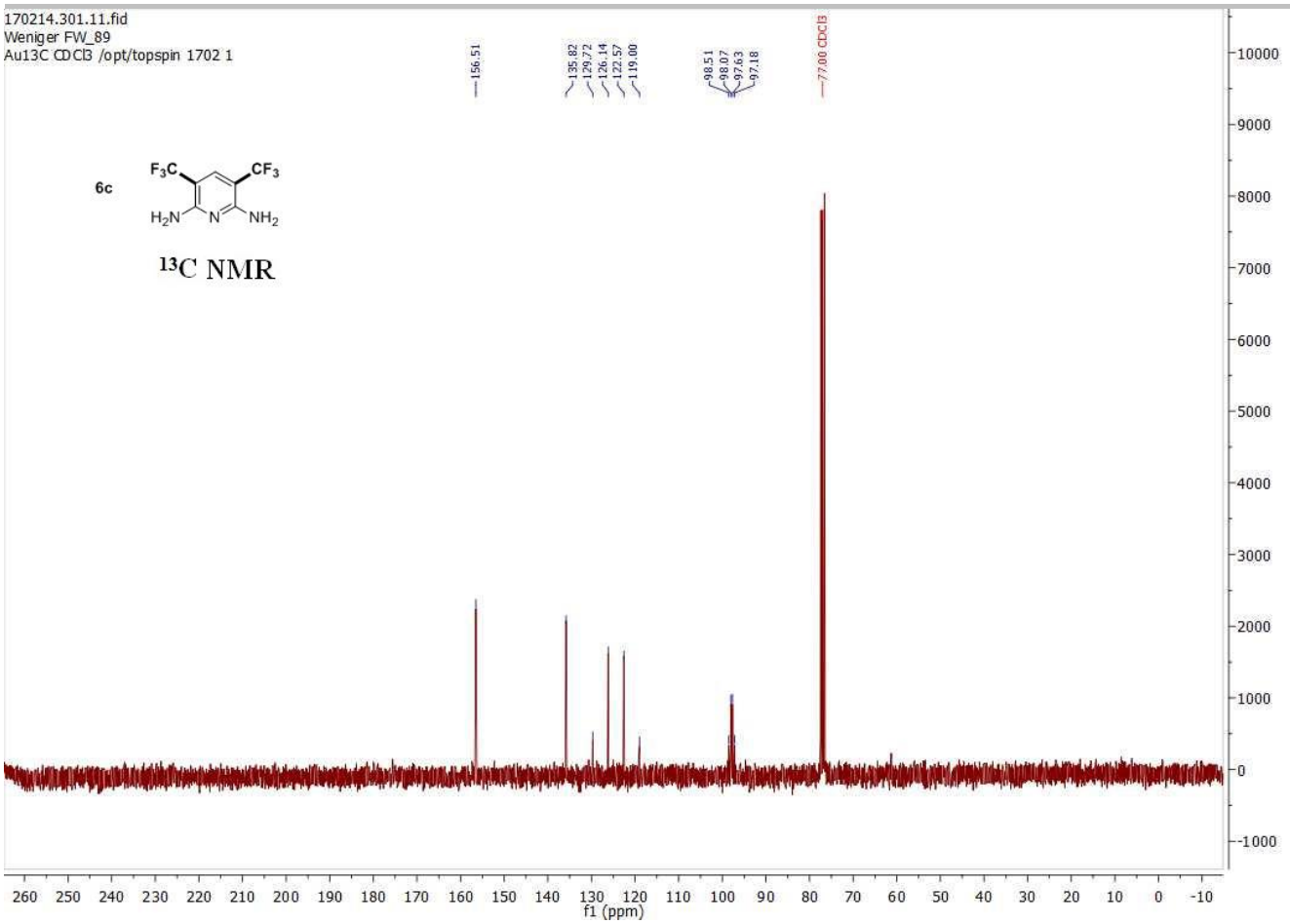

170727.329.3.fid
Weniger FW_108_B
Au13C-dept CDCl3 {C:\Bruker\TopSpin3.5pl6} 1707 29
33.19
33.17
29.89
28.19
5b
13C NMR Dept135
f1 (ppm)

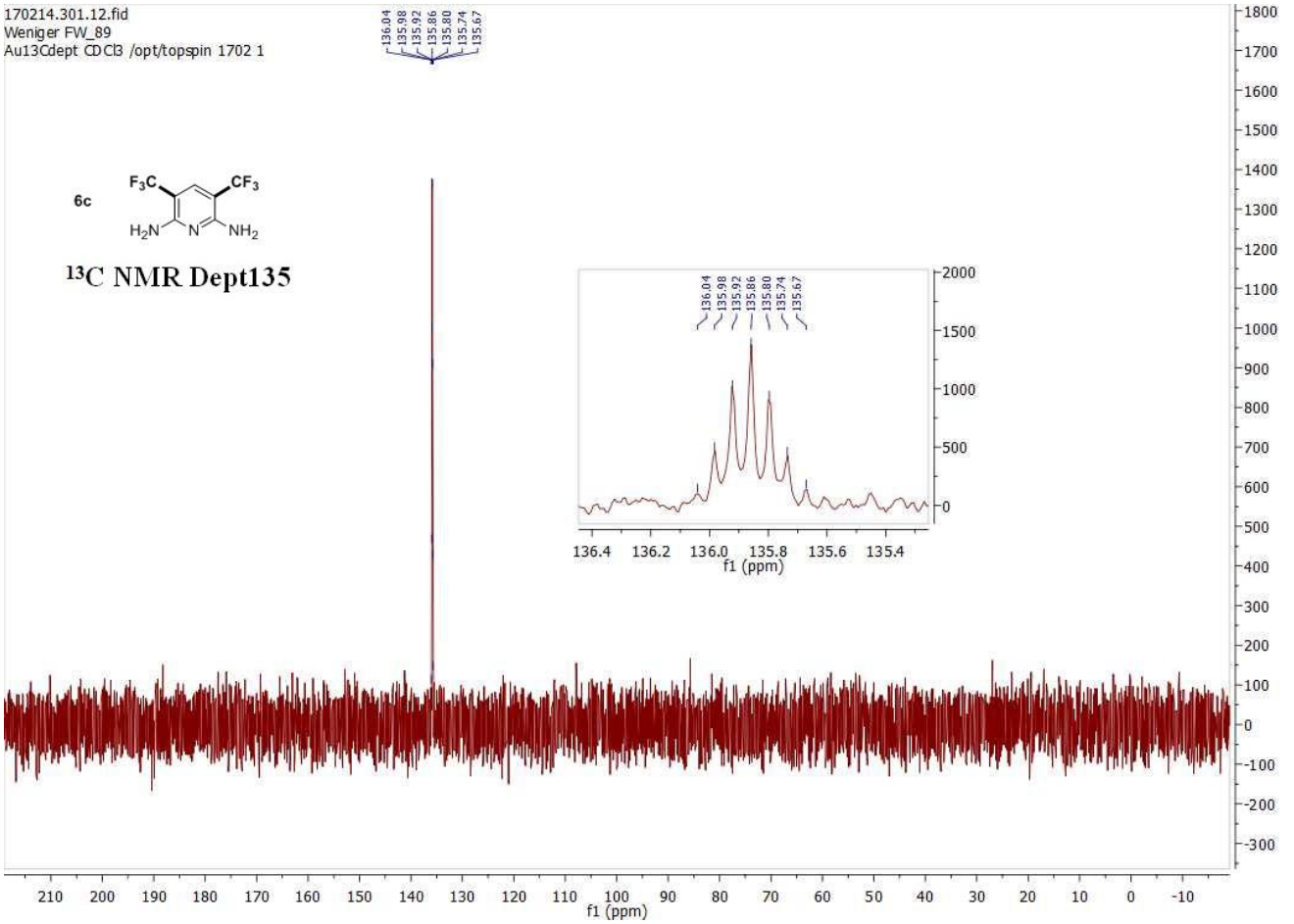


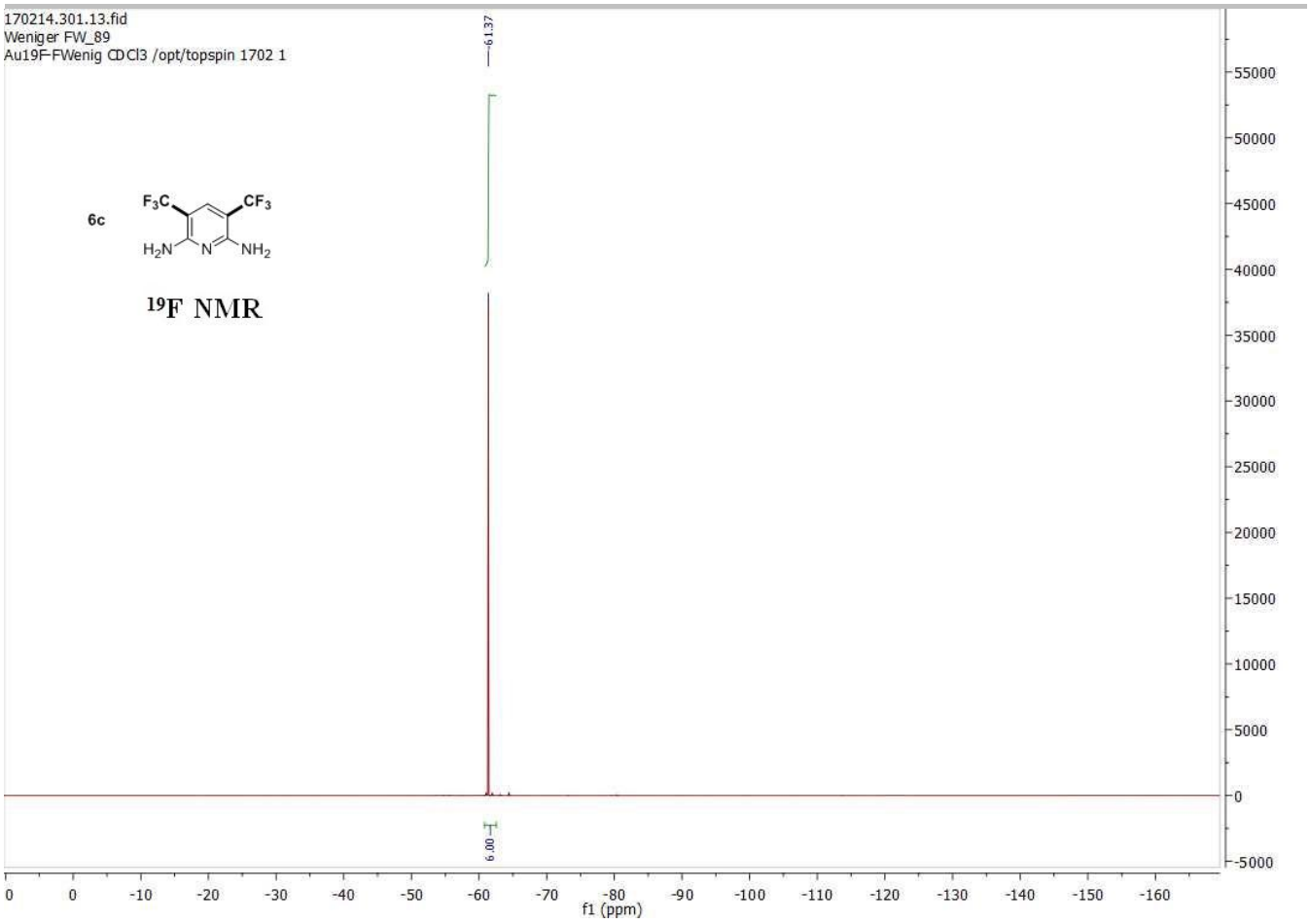

$^{19}$F NMR




$^{1}$H NMR


170214.301.11.fid
Weniger FW_89
Au13C CDCl3 /opt/topspin 1702 1
156.51
135.82
129.72
126.14
122.57
119.00
98.51
98.07
97.63
97.18
77.00 CDCl3
6c
$^{13}$C NMR
f1 (ppm)


170214.301.12.fid
Weniger FW_89
Au13Cdept CDCl3 /opt/topspin 1702 1
136.04
135.98
135.92
135.86
135.80
135.74
135.67
6c
$^{13}$C NMR Dept135
f1 (ppm)


170214.301.13.fid
Weniger FW_89
Au19F-FWenig CDCl3 /opt/topspin 1702 1
61.37
6.00
6c
$F_3C$
$CF_3$
$H_2N$
N
$NH_2$
$^{19}F$ NMR
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)