# Calcium-catalysed synthesis of amines through imines hydrosilylation: an experimental and theoretical study

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**Table of contents**

**1. General remarks** **S2**

**2. General procedures for catalytic reactions** **S2**

**3. Characterisation data of isolated amines** **S3**

**4. NMR experiments** **S14**

4.1 Study of the $Ca(NTf_2)_2$ / $KPF_6$ / $PhSiH_3$ (1:1:1) in THF $d_8$ mixture by $^1H$ NMR at different temperature. S14

4.2 Monitoring of the reaction mixture by $^1H$ NMR. S15

**5. Computational section** **S16**

5.1 Full computational details. S16

5.2 Coordinates for the optimized structures of all extrema. S16

5.3 NBO Analyses. S28

5.4 NMR Calculations. S29

**6. $^1H$ and $^{13}C$ NMR spectra of isolated amines** **S30**

## 1. General remarks

Reactants were purchased from commercial sources (Merck, Alfa Aesar, Acros) and used without purification. Imines 1a-w were prepared according to previously reported procedures.[1,2,3,4,5,6,7] $^{1}H$, $^{19}F$ and $^{13}C$ NMR spectra were carried out on a Bruker spectrometer Ascend III HD operating at 400 MHz for $^{1}H$, 376MHz for $^{19}F$ and 100 MHz for $^{13}C$. Samples were analyzed with a two channel (1H and XBB) Smartprobe. Variable Temperature from -65°C until +25°C were obtained with a Bruker temperature unit BCU II. $^{1}H$ NMR spectra were recorded with 3kHz for spectral width, 1600Hz for transmitter frequency offset, 3s for acquisition time and 4 scans. A 30° pulse (3µs) and a relaxation delay of 1s were applied. Standard Bruker pulse sequence zgig30 was used. $^{13}C$ NMR spectra were recorded with 29kHz for spectral width, 1kHz for transmitter frequency offset, 0.8s for acquisition time and 4096 scans. A 30° pulse (3.3µs) and a relaxation delay of 5s were applied. $^{1}H$ decoupling was applied during whole sequence. Standard Bruker pulse sequence zgpg was used. $^{19}F$ spectra were recorded with 56kHz for spectral width, -33kHz for transmitter frequency offset, 4.5s for acquisition time and 16 scans. A 30° pulse (4µs) and a relaxation delay of 2s were applied. $^{1}H$ decoupling was applied during acquisition (waltz16 with a pulse of 90µs). Standard Bruker pulse sequence zgig30 was used. All $^{1}H$, $^{13}C$, $^{19}F$ NMR spectra were evaluated in parts per million parties (ppm) and coupling constants (J) are reported in Hertz (Hz). The signals in the spectra are described as s (singulet), d (doublet), t (triplet), q (quadruplet), m (multiplet). Gas chromatography−mass spectroscopy (GC−MS) spectra were recorded on a Shimadzu QP2012-SE with a ZebronZB-5MS (20 m × 0.18 mm), capillary apolar column (stationary phase: 0.18 µm film). GC-MS method: initial temperature, 50°C; initial time, 2 min; ramp, 22 °C/min; final temperature, 280 °C; final time, 15 min. HRMS (Q-TOF) were performed on a JEOL JMS-DX300 spectrometer (3 keV, xenon) in a m-nitrobenzylalcohol matrix. Thin layer chromatographies (TLC) were performed on aluminum plates coated with 60 $F_{254}$ Macherey-Nagel silica gel and revealed by UV lamp (254 nm). Column chromatographies were carried out on $PF_{254}$ Macherey-Nagel 0.04-0.063 mm silica gel.

## 2. General procedures for catalytic reactions

### Procedure A : To determine NMR yields (0.25 mmol scale)

An round-bottom flask or a Schlenk tube containing a stirring bar was charged with $Ca(NTf_2)_2$ (15.1 mg, 0.025 mmol, 10 mol %), $KPF_6$ (4.6 mg, 0.025 mmol, 10 mol %), $PhSiH_3$ (62.0 µL, 0.5 mmol, 2 eq) and THF (1 mL). The mixture was stirred at 25 °C for 10 minutes before adding the imine (0.25 mmol, 1 eq) **1a-w** and THF (0.5 mL). Then, the reaction mixture was stirred at the required temperature for 16h. The reaction was next hydrolysed by adding 1.5 mL of MeOH and 1.5 mL of NaOH (2N). After 2h stirring, ethyl acetate and 1,3,5-trimethoxybenzene (standard) were added. After 2h stirring, the mixture was extracted with ethyl acetate (3 x 3 mL), the combined organic fractions washed with brine and dried over $MgSO_4$. Yield determined by NMR using 1,3,5-trimethoxybenzene as the standard.

### Procedure B : Isolation of amines (1 mmol scale)

An round-bottom flask or a Schlenk tube containing a stirring bar was charged with $Ca(NTf_2)_2$ (60,4 mg, 0.1 mmol, 10 mol %), $KPF_6$ (18,4 mg, 0.1 mmol, 10 mol %), $PhSiH_3$ (248 µL, 2 mmol, 2 eq) and THF (4 mL). The mixture was stirred at 25 °C for 10 minutes before adding the imine (1 mmol, 1 eq) **1a-w** and THF (2 mL). Then, the reaction mixture was stirred at the required temperature for 16h. The reaction was next hydrolysed by adding 6 mL of MeOH and 6 mL of

NaOH (2N). After 2h stirring, the mixture was extracted with ethyl acetate (3 x 15 mL), the combined organic fractions washed with brine and dried over $MgSO_4$. The solution was concentrated under reduced pressure and the crude residue was purified by using a silica gel chromatography column and a mixture of dichloromethane/cyclohexane/2% triethylamine as the eluent.

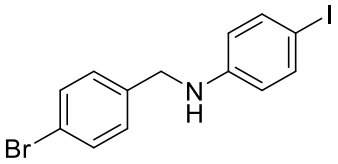
### Procedure C : Hydrosilylation of the in situ formed imine 1w (main manuscript, Scheme 3)

To a solution of 3,4-dichloroaniline (7.0 mmol, 1 equiv) in 2-methyltetrahydrofuran (25 mL) was added the furfural (7.0 mmol, 1.0 equiv). The reaction mixture was stirred for 6 h at 25 °C. Then it is added to a freshly prepared solution of $Ca(NTf_2)_2$ (0.35 mmol, 0.05 eq) and $KPF_6$ (0.35 mmol, 0.05 eq), $PhSiH_3$ (8.4 mmol, 1.2 eq) in 2-methyltetrahydrofuran (17 mL). The resulting mixture was stirred at 25 °C for 24 h. The reaction was next hydrolysed by adding 42 mL of MeOH and 42 mL of NaOH (2N). After 2h stirring, the mixture was extracted with ethyl acetate (3 x 40 mL), the combined organic fractions washed with brine and dried over $MgSO_4$. The solution was concentrated under reduced pressure and the crude residue was purified by using a silica gel chromatography column and a mixture of dichloromethane/cyclohexane/1% triethylamine as the eluent. The product was obtained as a yellow oil (1.44 g, 5.9 mmol) in 85% yield.

## 3. Characterisation data of isolated amines

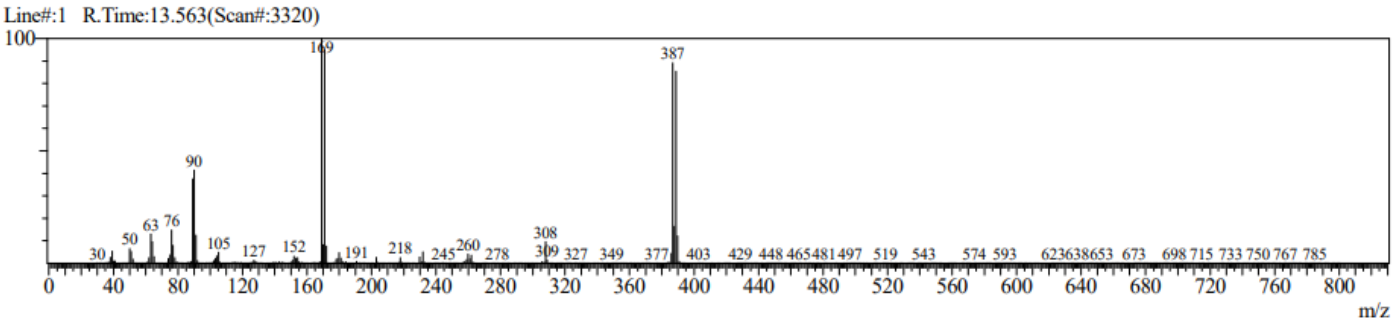
Spectroscopic data obtained are consistent with the data reported in the literature for amines **2a-n** and **2p-w**.

**Amine 2a** (N-(4-bromobenzyl)-4-iodoaniline)[8]

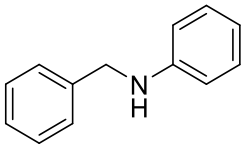



Following the general procedure **B**, imine **1n** (386.1 mg, 1.0 mmol) gave **2a** isolated as a white solid (374.5 mg, 97% yield).

**$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.47 – 7.44 (m, 2H), 7.42 – 7.39 (m, 2H), 7.23 – 7.20 (m, 2H), 6.40 – 6.36 (m, 2H), 4.26 (d, J = 4.5 Hz, 1H), 4.12 (br s, 1H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 147.40, 138.01, 137.95, 131.89, 129.04, 121.21, 115.22, 78.58, 47.51.
**GC Mass Spectrum** (retention time : 13.56 min) :

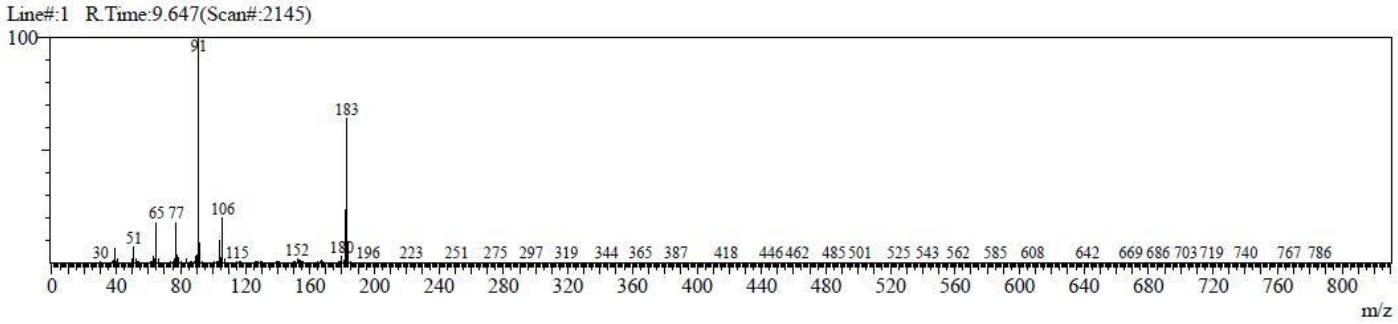


**Amine 2b** (N-benzylaniline)[8]

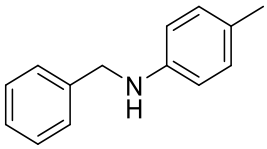


Following the general procedure **B**, imine **1b** (181.3 mg, 1.0 mmol) gave **2b** isolated as a brown solid (180.9 mg, 99% yield).

**$^1$H NMR (400 MHz, DMSO) δ (ppm)** 7.37 – 7.29 (m, 4H), 7.23 – 7.19 (m, 1H), 7.05 – 7.00 (m, 2H), 6.58 – 6.55 (m, 2H), 6.50 (tt, J = 7.3, 1.1 Hz, 1H), 6.20 (t, J = 6.0 Hz, 1H), 4.25 (d, J = 6.1 Hz, 2H).
**$^{13}$C NMR (101 MHz, DMSO) δ (ppm)** 148.67, 140.33, 128.81, 128.27, 127.17, 126.59, 115.73, 112.28, 46.46.
**GC Mass Spectrum** (retention time : 9.65 min) :

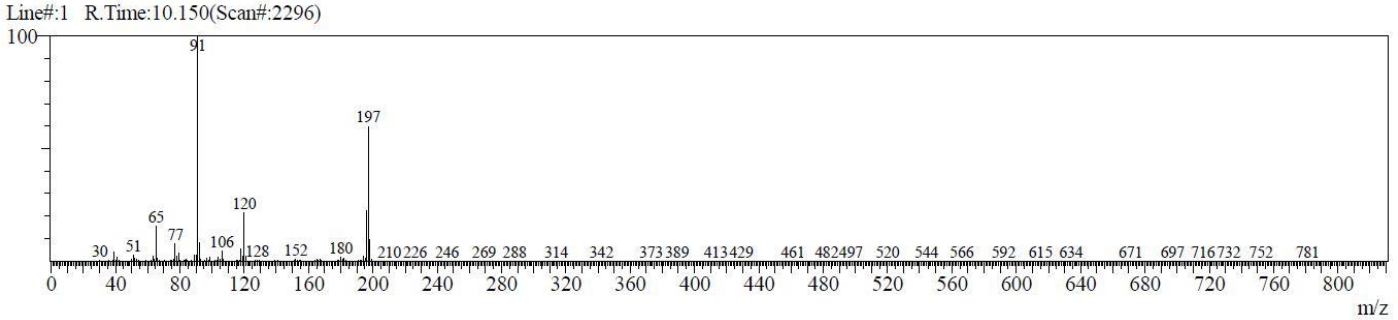



**Amine 2c** (N-benzyl-4-methylaniline) [8]

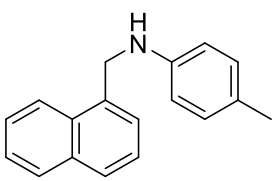


Following the general procedure **B**, imine **1c** (195.3 mg, 1.0 mmol) gave **2c** isolated as a pale yellow oil (191.4 mg, 98% yield).

**$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.40 – 7.33 (m, 4H), 7.29 (m, 1H), 7.02 – 6.99 (m, 2H), 6.60 – 6.56 (m, 2H), 4.32 (s, 2H), 3.89 (s, 1H), 2.25 (s, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 146.07, 139.81, 129.88, 128.73, 127.63, 127.28, 126.90, 113.14, 48.79, 20.52.
**GC Mass Spectrum** (retention time : 10.15 min) :




**Amine 2d** (4-methyl-N-(naphthalen-2-ylmethyl)aniline)[4]

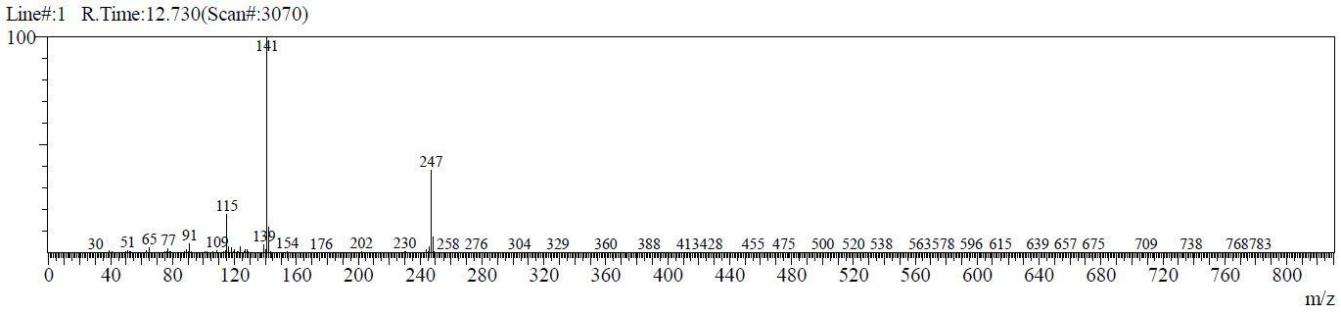


Following the general procedure **B**, imine **1d** (245.5 mg, 1.0 mmol) gave **2d** isolated as a beige solid (203.6 mg, 82% yield).

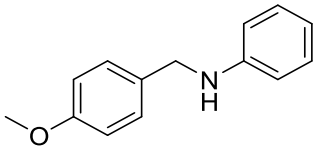
**$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 8.10 – 8.07 (m, 1H), 7.91 – 7.89 (m, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.52 (m, 3H), 7.43 (d, J = 8.2 Hz, 1H), 7.03 (d, J = 8.2 Hz, 2H), 6.64 – 6.62 (m, 2H), 4.73 (s, 2H), 3.90 (s, 1H), 2.27 (s, 3H).

**$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm)** 146.16, 134.70, 133.99, 131.68, 129.93, 128.87, 128.21, 126.88, 126.40, 126.09, 125.92, 125.67, 123.73, 112.99, 46.84, 20.55

**GC Mass Spectrum** (retention time : 12.73 min) :

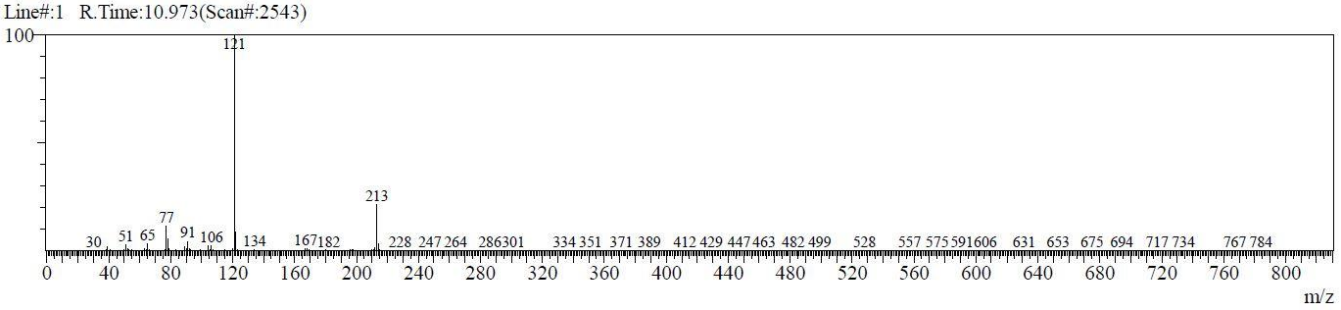



**Amine 2e** (N-(4-methoxybenzyl)aniline) [8]

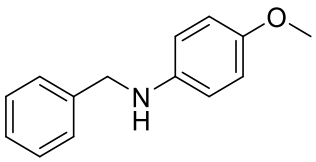



Following the general procedure **B**, imine **1f** (211.4 mg, 1.0 mmol) gave **2f** isolated as a pale yellow solid (192.8 mg, 91% yield).

**$^{1}H$ NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.32 – 7.28 (m, 2H), 7.21 – 7.16 (m, 2H), 6.91 – 6.87 (m, 2H), 6.72 (tt, J = 7.4, 1.1 Hz, 1H), 6.64 (ddd, J = 4.3, 3.2, 1.7 Hz, 2H), 4.26 (s, 2H), 3.95 (s, 1H), 3.81 (s, 3H).
**$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm)** 158.95, 148.31, 131.52, 129.34, 128.89, 117.57, 114.11, 112.93, 55.37, 47.86.
**GC Mass Spectrum** (retention time : 10.97 min) :

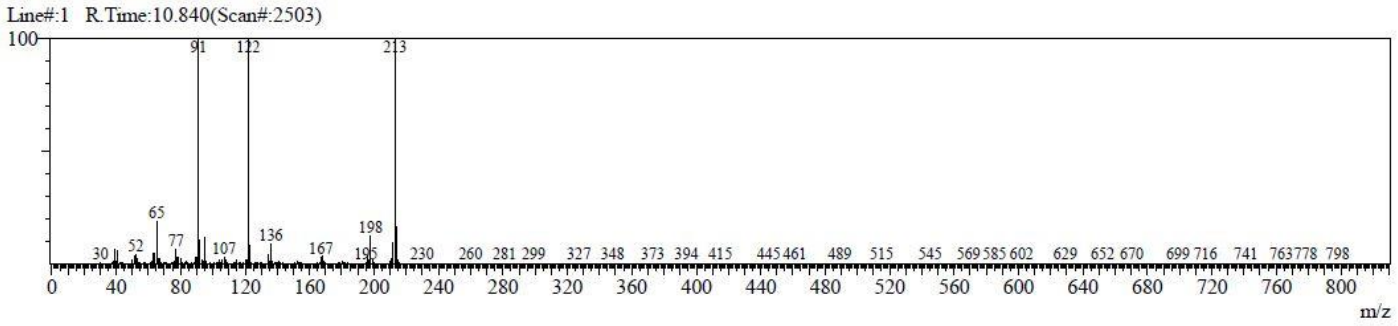



**Amine 2f** (N-benzyl-4-methoxyaniline) [8]

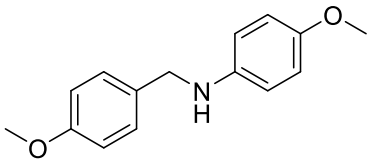



Following the general procedure **B** (65 °C), imine **1e** (211.5 mg, 1.0 mmol) gave **2e** isolated as a yellowish solid (137.5 mg, 65% yield).

**$^{1}H$ NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.39 – 7.32 (m, 4H), 7.28 (d, J = 7.1 Hz,1H), 6.80 – 6.76 (m, 2H), 6.63 – 6.59 (m, 2H), 4.29 (s, 2H), 3.78 (s, 1H), 3.75 (s, 3H).
**$^{13}C$ NMR (101 MHz, $CDCl_3$) δ (ppm)** 152.29, 142.56, 139.81, 128.69, 127.65, 127.26, 115.01, 114.21, 55.89, 49.33.
**GC Mass Spectrum** (retention time : 10.84 min) :

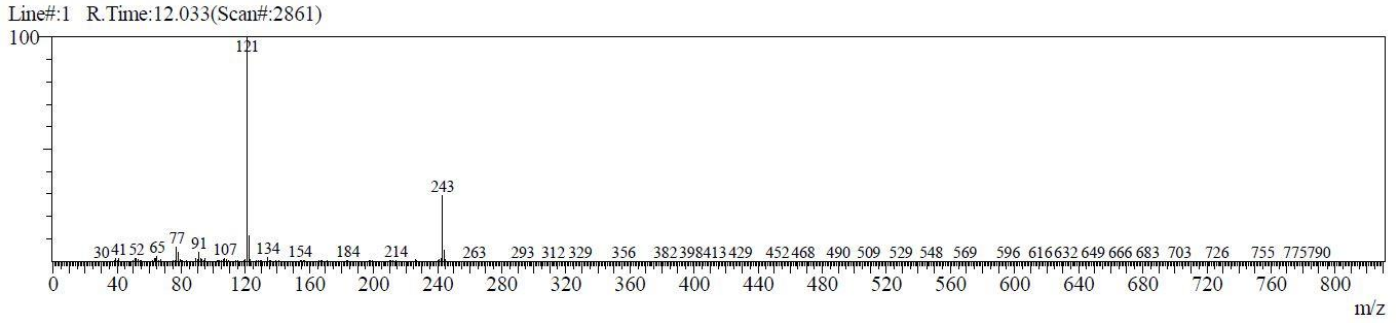



**Amine 2g** (4-methoxy-N-(4-methoxybenzyl)aniline) [1]

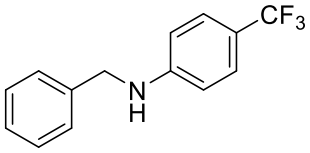



Following the general procedure **B** (65 °C), imine **1g** (241.4 mg, 1.0 mmol) gave **2g** isolated as a white solid (193.5 mg, 80% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.31 – 7.27 (m, 2H), 6.90 – 6.86 (m, 2H), 6.80 – 6.76 (m, 2H), 6.63 – 6.59 (m, 2H), 4.21 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 158.91, 152.25, 142.63, 131.78, 128.91, 114.99, 114.21, 114.08, 55.89, 55.37, 48.81.
**GC Mass Spectrum** (retention time : 12.03 min) :

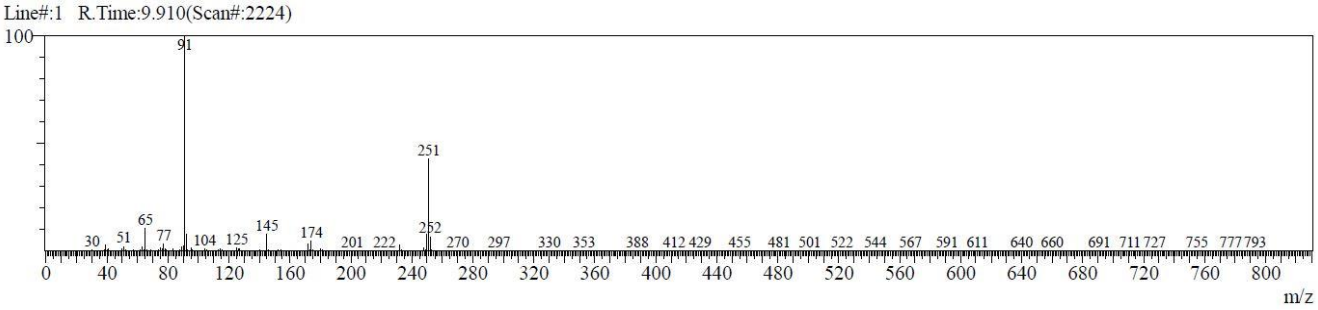



**Amine 2h** (N-benzyl-4-(trifluoromethyl)aniline)[1]

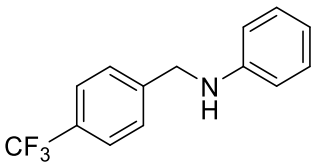



Following the general procedure **B**, imine **1h** (251.5 mg, 1.0 mmol) gave **2n** isolated as a pale yellow solid (221.2 mg, 88% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.40 (d, J = 8.4 Hz, 2H), 7.37 – 7.34 (m, 4H), 7.33 – 7.27 (m, 1H), 6.63 (d, J = 8.5 Hz, 2H), 4.38 (s, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 150.31, 138.37, 128.92, 127.70, 127.56, 126.78 (q, J = 3.8 Hz), 125.12 (q, J = 270 Hz), 119.58 (q, J = 35 Hz), 112.38, 48.09.
**$^{19}$F{$^{1}$H} $CDCl_3$ δ (ppm)** - 61.03.
**GC Mass Spectrum** (retention time : 9.91 min) :

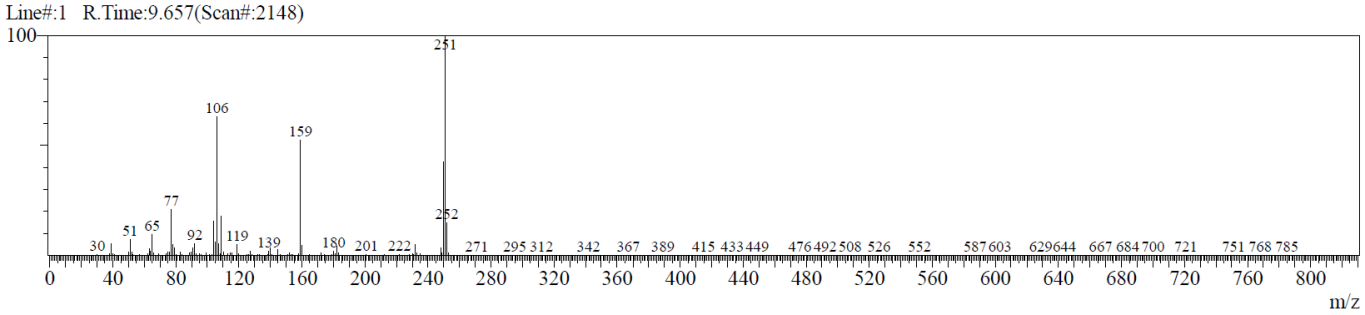



**Amine 2i** (N-(4-(trifluoromethyl)benzyl)aniline)[1]

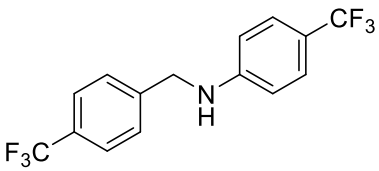


Following the general procedure **B**, imine **1i** (249.5 mg, 1.0 mmol) gave **2i** isolated as a pale yellow oil (242.5 mg, 97% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.60 (m, 2H), 7.50 – 7.48 (m, 2H), 7.21 – 7.16 (m, 2H), 6.77 – 6.73 (m, 1H), 6.63 – 6.60 (m, 2H), 4.42 (s, 2H), 4.15 (br s, 1H).
**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ (ppm)** 147.82, 143.90, 129.72 (q, J = 35 Hz), 129.49, 127.59, 125.73 (q, J = 3.8 Hz), 124.23 (q, J = 270 Hz), 118.12, 113.05, 47.94.
**$^{19}$F{$^{1}$H} $CDCl_3$ δ (ppm)** - 62.41.
**GC Mass Spectrum** (retention time : 9.66 min) :

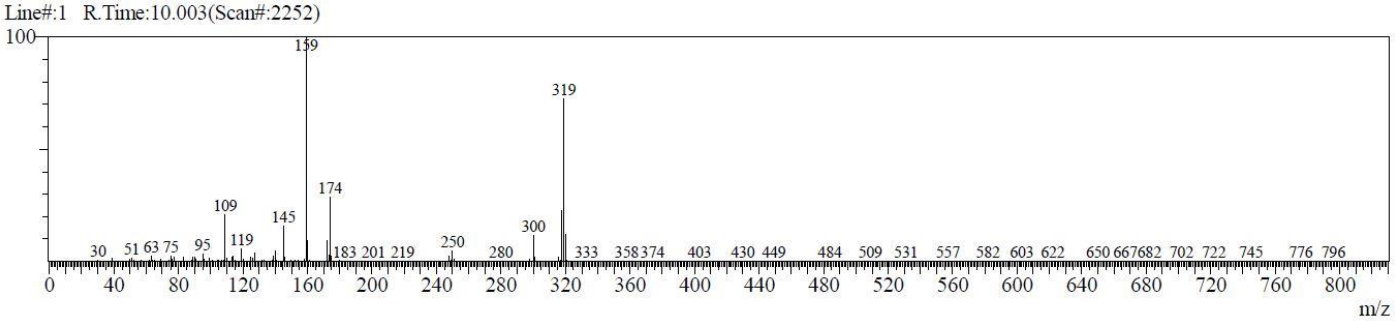



**Amine 2j (**4-(trifluoromethyl)-N-(4-(trifluoromethyl)benzyl)aniline) [9]

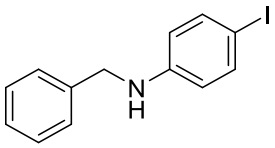


Following the general procedure **B**, imine **1j** (319.4 mg, 1 mmol) gave **2j** isolated as a pale yellow solid (287.5 mg, 90% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.61 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 6.61 (d, J = 8.5 Hz, 2H), 4.49 (s, 1H), 4.46 (d, J = 4.7 Hz, 2H).
**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ (ppm)** 150.20, 142.36, 129.79 (q, J = 32 Hz), 126.73 (q, J = 3.8 Hz), 125.76 (q, J = 3.8 Hz), 124.88 (q, J = 270 Hz), 124.13 (q, J = 270 Hz), 119.56 (q, J = 32 Hz), 112.24, 47.41.
**$^{19}$F{$^{1}$H} $CDCl_3$ δ (ppm)** - 61.22, - 62.62.
**GC Mass Spectrum** (retention time : 10.00 min) :

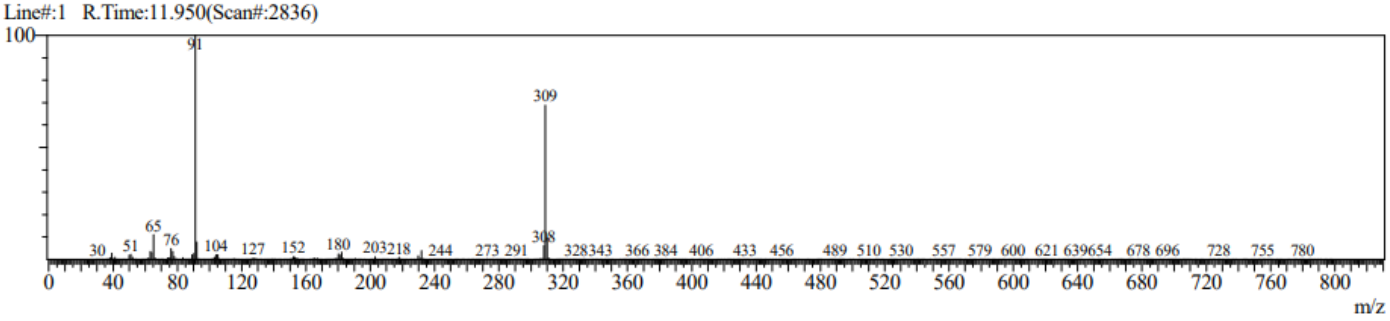



**Amine 2k** (N-benzyl-4-iodoaniline)[8]

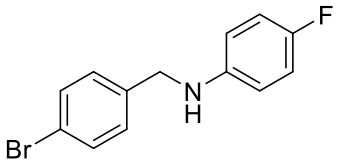


Following the general procedure **B**, imine **1k** (307.3 mg, 1.0 mmol) gave **2k** isolated as a pale yellow solid (218 mg, 71% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.44 – 7.40 (m, 2H), 7.39 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 6.44 – 6.41 (m, 2H), 4.31 (s, 2H), 4.11 (br s, 1H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 147.74, 138.94, 137.90, 128.82, 127.49, 127.48, 115.19, 78.23, 48.16.
**GC Mass Spectrum** (retention time : 11.95 min) :

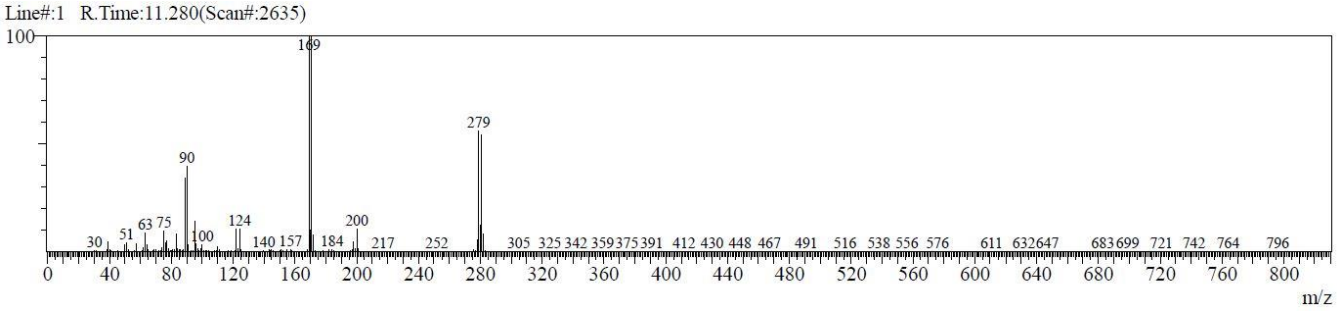



**Amine 2 l** (N-(4-bromobenzyl)-4-fluoroaniline) [10]

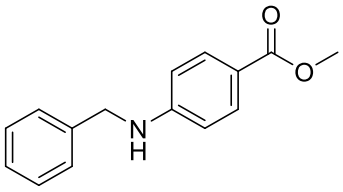


Following the general procedure **B**, imine **1l** (278.1 mg, 1,0 mmol) gave **2l** isolated as a white solid (267.5 mg, 96% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.48 – 7.45 (m, 2H), 7.25 – 7.22 (m, 2H), 6.91 – 6.84 (m, 2H), 6.55 – 6.50 (m, 2H), 4.26 (s, 2H), 3.96 (br s, 1H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 156.10 (d, J = 233 Hz), 144.25, 138.46, 131.86, 129.16, 121.13, 115.84 (d, J = 22 Hz), 113.87, 48.37.
**$^{19}$F{1H} $CDCl_3$ δ (ppm)** - 127.57.
**GC Mass Spectrum** (retention time : 11.28 min) :

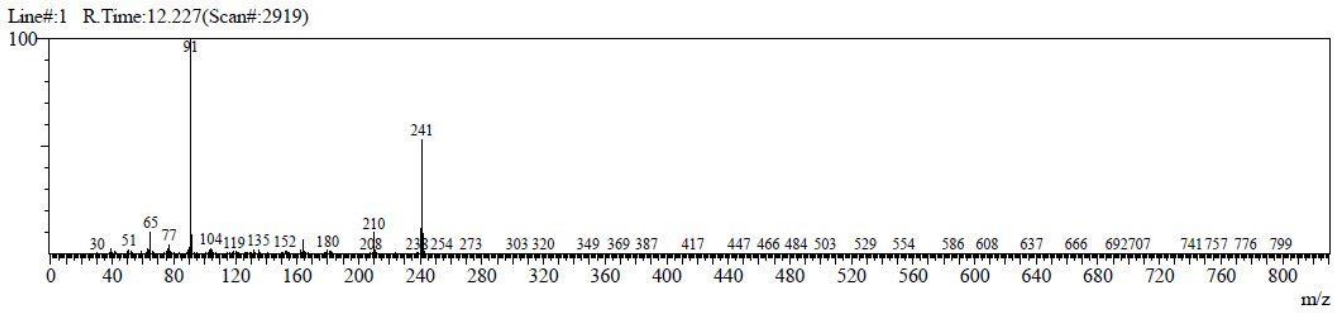


**Amine 2m** (methyl 4-(benzylamino)benzoate) [1]

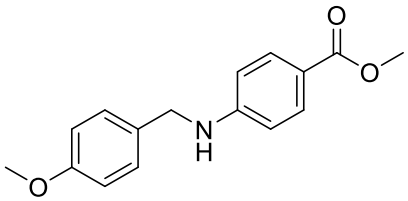


Following the general procedure **B**, imine **1m** (239.9 mg, 1.0 mmol) gave **2m** (239.9 mg, 1.0 mmol) isolated as a yellowish solid (216.7 mg, 90% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ **(ppm)** 7.89 – 7.85 (m, 2H), 7.38 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 6.61 – 6.58 (m, 2H), 4.49 (br s, 1H), 4.39 (d, J = 5.5 Hz, 2H), 3.85 (s, 3H).
**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ (ppm)** 167.36, 151.60, 138.29, 131.63, 128.86, 127.64, 127.56, 118.94, 112.00, 51.64, 47.89.
**GC Mass Spectrum** (retention time : 12.23 min) :

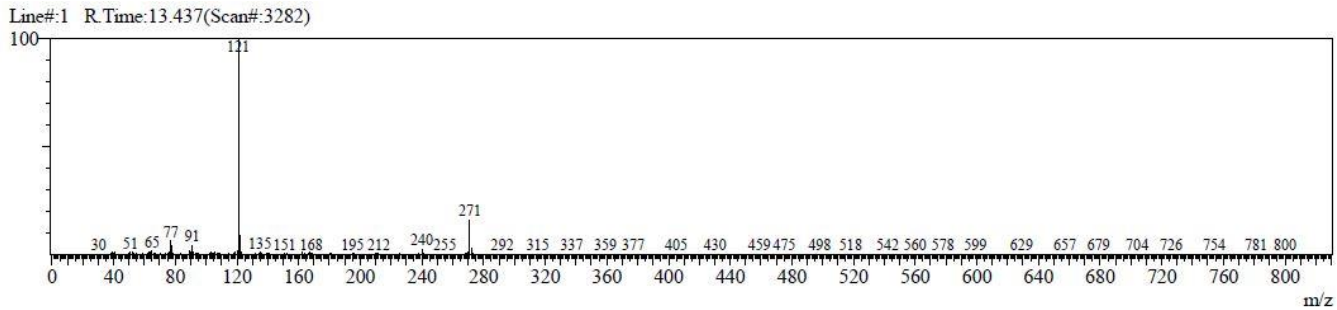



**Amine 2n** (methyl 4-((4-methoxybenzyl)amino)benzoate)[11]

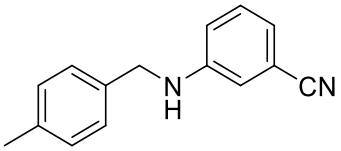


Following the general procedure **B**, imine **1n** (270.1 mg, 1.0 mmol) gave **2n** isolated as a white solid (221.5 mg, 82% yield).

**$^1$H NMR (400 MHz, CDCl3) δ (ppm)** 7.87 – 7.85 (m, 2H), 7.28 – 7.25 (m, 2H), 6.90 – 6.88 (m, 2H), 6.60 – 6.57 (m, 2H), 4.41 (s, 1H), 4.31 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H).
**$^{13}$C{$^1$H} NMR (101 MHz, CDCl3) δ (ppm)** 167.40, 159.16, 151.66, 131.63, 130.26, 128.91, 118.80, 114.25, 111.92, 55.39, 51.64, 47.37.
**GC Mass Spectrum** (retention time : 13.44 min) :

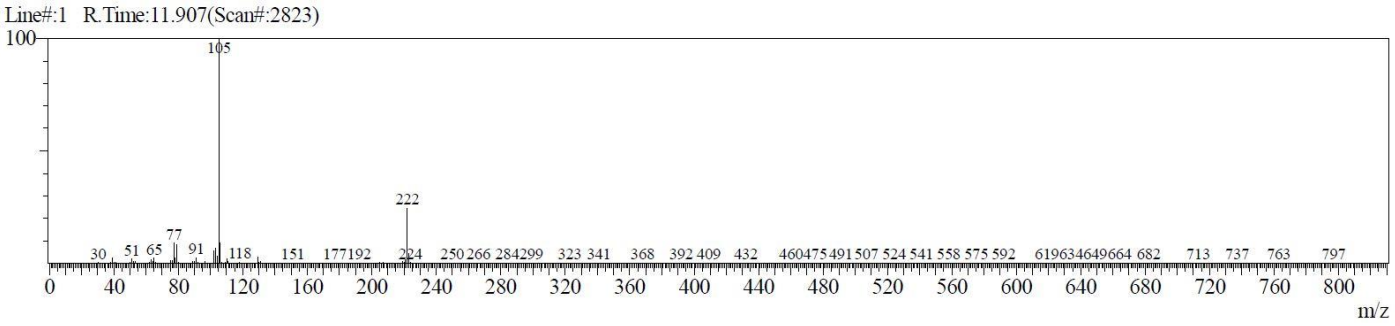


**Amine 2o** (3-((4-methylbenzyl)amino)benzonitrile)




Following the general procedure **B**, imine **1o** (220.3 mg, 1.0 mmol) gave **2o** isolated as a white solid (195.4 mg, 88% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.24 (s, 1H), 7.22 (dd, J = 5.6, 2.6 Hz, 2H), 7.18 (dd, J = 8.9, 4.3 Hz, 2H), 6.98 – 6.94 (m, 1H), 6.83 – 6.80 (m, 1H), 6.79 (dd, J = 2.5, 0.9 Hz, 1H), 4.28 (d, J = 4.7 Hz, 2H), 4.26 (s, 1H), 2.35 (s, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 148.40, 137.44, 135.18, 129.99, 129.61, 127.48, 120.97, 119.58, 117.36, 115.14, 113.04, 47.75, 21.21.
**ESI-HRMS** m/z: found: 223.1236 $[M+H]^+$ (theoretical: 223.1230 $[M+H]^+$).
**GC Mass Spectrum** (retention time : 11.91 min) :




## High Resolution Mass Result

**Analysis Info**

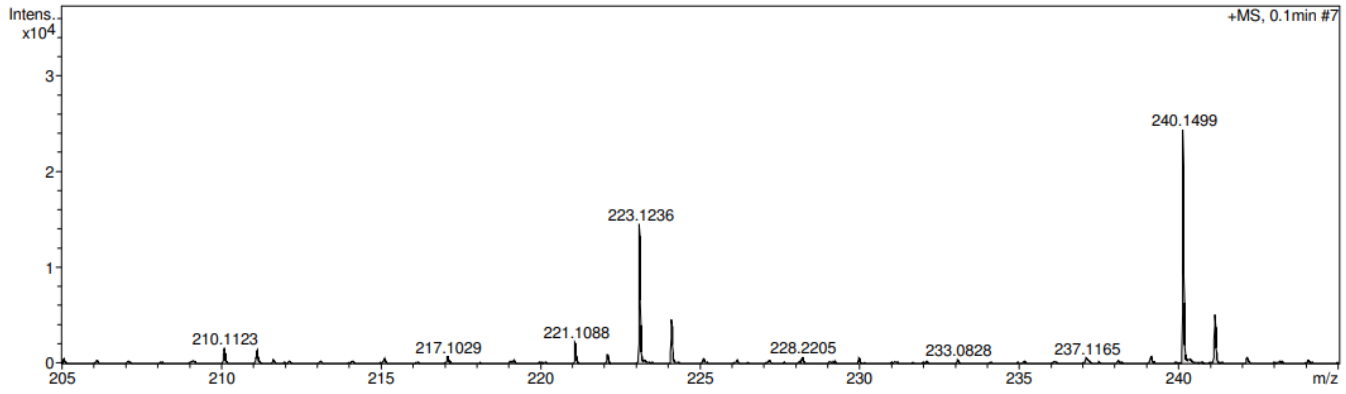
Sample Name **OUA-13**

Acquisition Date 9/22/2022 9:54:18 AM

Instrument / Ser# micrOTOF-Q 228888.10300

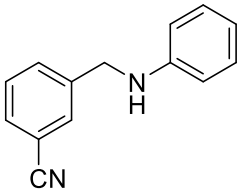
**Acquisition Parameter**

Source Type ESI | Ion Polarity Positive | Scan Begin 50 m/z | Scan End 2200 m/z



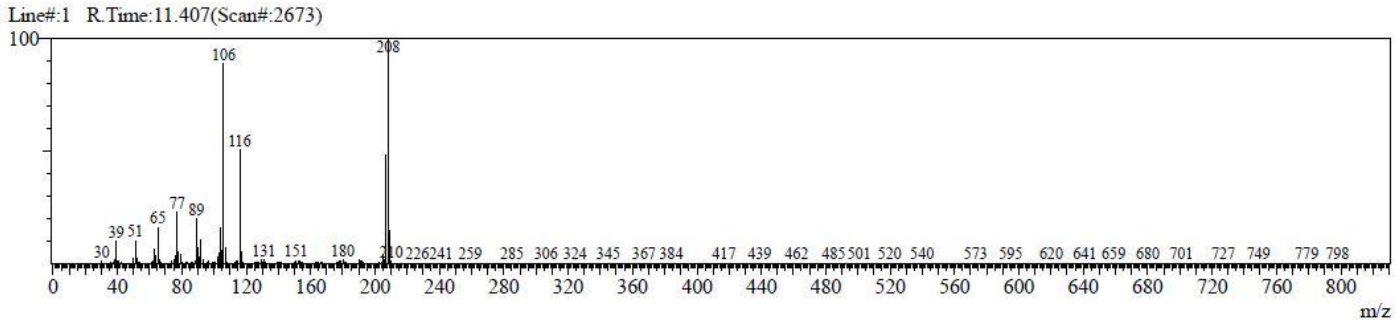

| Meas. m/z | # | Ion Formula | m/z | err [ppm] | mSigma | # Sigma | Score | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 223.1236 | 1 | C15H15N2 | 223.1230 | 2.6 | 82.5 | 1 | 100.00 | 9.5 | even | ok |
| 240.1499 | 1 | C15H18N3 | 240.1495 | 1.5 | 21.2 | 1 | 100.00 | 8.5 | even | ok |

**Amine 2p** (3-((phenylamino)methyl)benzonitrile) [12]

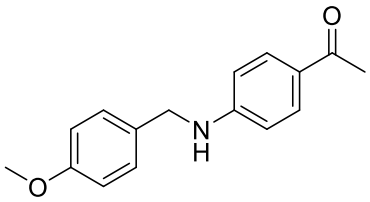



Following the general procedure **B** (65 °C), imine **1p** (206.4 mg, 1.0 mmol) gave **2p** isolated as a colorless oil (157.3 mg, 76% yield).

**$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.67 (s, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.18 (t, J = 7.8 Hz, 2H), 6.75 (m, 1H), 6.59 (m, 2H), 4.40 (s, 2H), 4.17 (s, 1H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 147.53, 141.45, 131.70, 130.98, 130.77, 129.51, 129.48, 118.97, 118.23, 113.01, 112.75, 47.54.
**GC Mass Spectrum** (retention time : 11.41 min) :

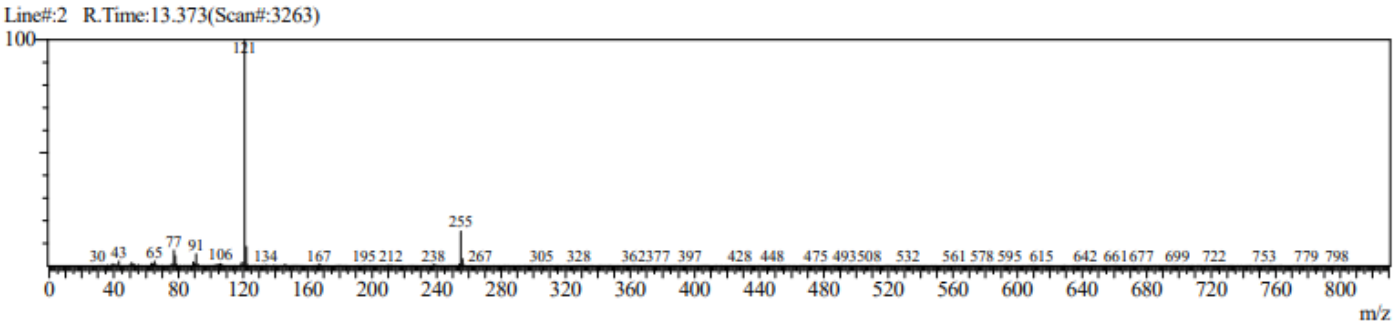



**Amine 2q** (1-(4-((4-methoxybenzyl)amino)phenyl)ethan-1-one)[6]

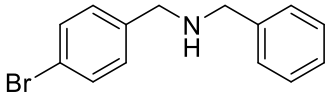



Following the general procedure **B**, imine **1q** (253.2 mg, 1 mmol) gave **2q** isolated as a white solid (239.7 mg, 94% yield).

**$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.82 (d, J = 8.7 Hz, 2H), 7.27 – 7.25 (m, 2H), 6.89 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.7 Hz, 2H), 4.54 (s, 1H), 4.32 (s, 2H), 3.80 (s, 3H), 2.49 (s, 3H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 196.48, 159.24, 152.09, 130.93, 130.31, 128.87, 127.07, 114.33, 111.70, 55.45, 47.24, 26.13.
**GC Mass Spectrum** (retention time : 13.37 min) :

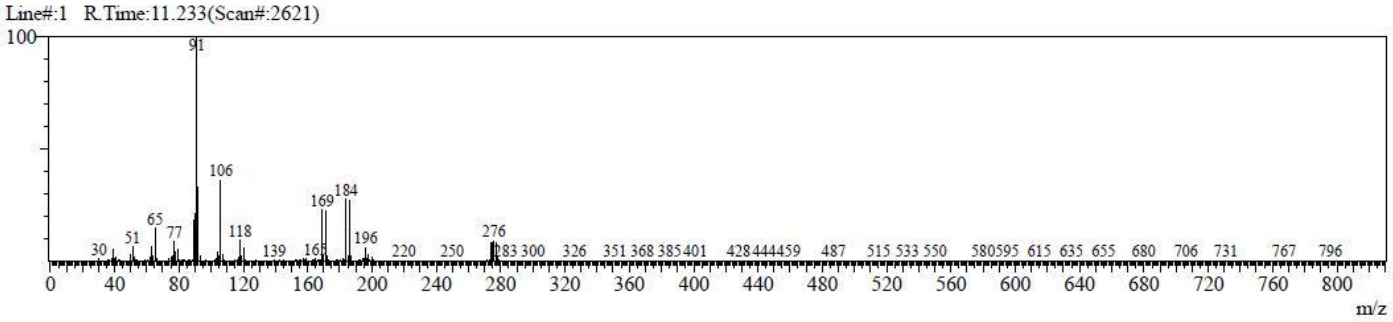


**Amine 2s** (N-benzyl-1-(4-bromophenyl)methanamine)[13]

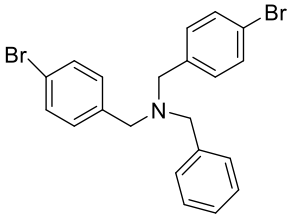


Following the general procedure **B** (65 °C), imine **1s** (274.2 mg, 1.0 mmol) gave **2s** isolated as a pale yellow oil (96.7 mg, 35% yield).

**$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.48 – 7.44 (m, 2H), 7.37 – 7.33 (m, 4H), 7.28 (m, 1H), 7.26 – 7.22 (m, 2H), 3.80 (s, 2H), 3.77 (s, 2H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 140.09, 139.33, 131.50, 129.93, 128.51, 128.20, 127.12, 120.76, 53.12, 52.43.
**GC Mass Spectrum** (retention time : 11.23 min) :

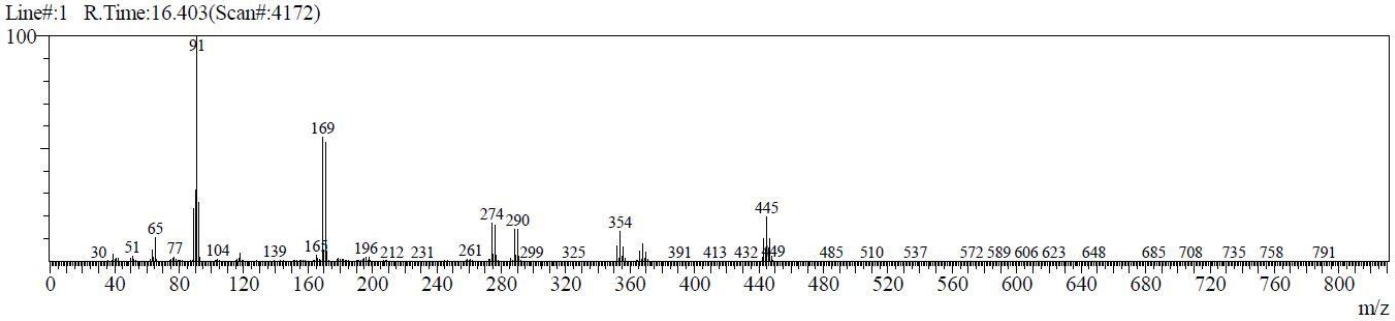



**Amine 3s** (N-benzyl-N-(4-bromobenzyl)-1-(4-bromophenyl)methanamine)[14]

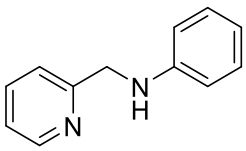


**3s** was isolated as a white solid (87 mg, 20% yield).

**$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.45 – 7.42 (m, 4H), 7.36 – 7.30 (m, 4H), 7.25– 7.22 (m, 5H), 3.52 (s, 2H), 3.47 (s, 4H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 139.15, 138.56, 131.54, 130.53, 128.85, 128.49, 127.26, 120.88, 57.97, 57.37.
**GC Mass Spectrum** (retention time : 16.40 min) :

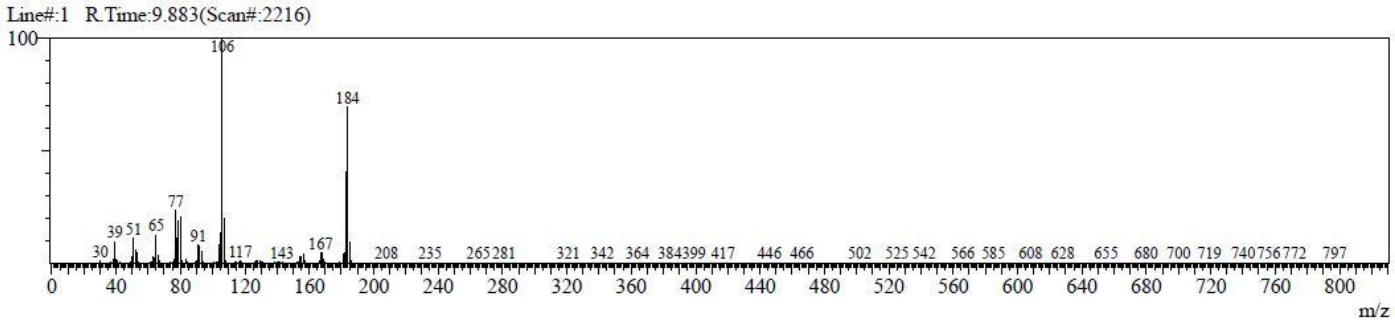



**Amine 2 v** (N-(pyridin-2-ylmethyl)aniline)[8]

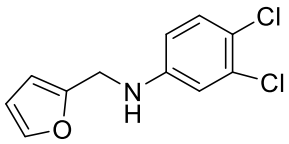


Following the general procedure **B**, imine **1v** (182,3 mg, 1.0 mmol) gave **2v** isolated as a greenish solid (132.2 mg, 72% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 8.59 (ddd, J = 4.9, 1.7, 0.9 Hz, 1H), 7.64 (td, J = 7.7, 1.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.21 – 7.17 (m, 3H), 6.72 (tt, J = 7.4, 1.1 Hz, 1H), 6.69 – 6.67 (m, 2H), 4.78 (s, 1H), 4.47 (s, 2H).
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm)** 158.65, 149.32, 148.01, 136.73, 129.36, 122.22, 121.72, 117.71, 113.17, 49.43.
**GC Mass Spectrum** (retention time : 9.88 min) :

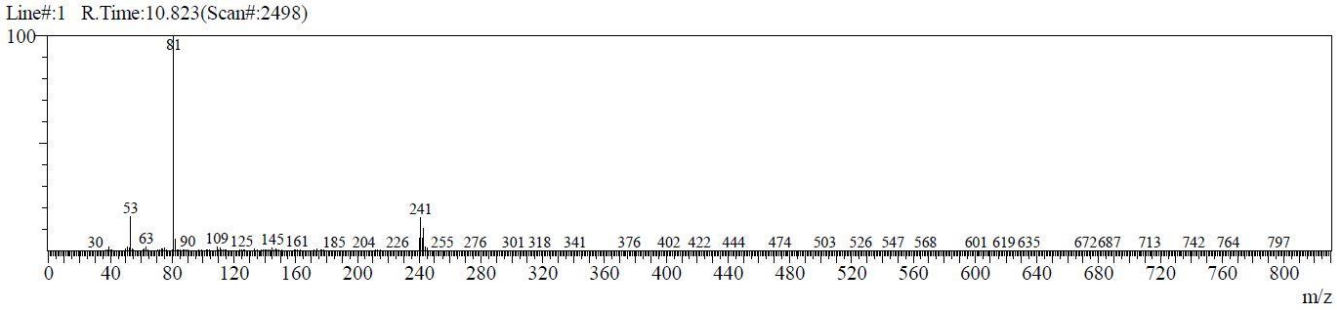



**Amine 2w** (3,4-dichloro-N-(furan-2-ylmethyl)aniline)[7]




Following the general procedure **B**, imine **1w** (240,2 mg, 1.0 mmol) gave **2w** isolated as a yellow oil (217,4 mg, 90% yield).

**$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 7.37 (dd, J = 1.8, 0.8 Hz, 1H), 7.19 (d, J = 8.7 Hz, 1H), 6.74 (d, J = 2.8 Hz, 1H), 6.49 (dd, J = 8.7, 2.8 Hz, 1H), 6.33 (dd, J = 3.2, 1.9 Hz, 1H), 6.24 (dd, J = 3.2, 0.8 Hz, 1H), 4.28 (d, J = 5.1 Hz, 2H), 4.11 (br s, 1H).
**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ (ppm)** 151.80, 147.16, 142.35, 132.95, 130.74, 120.62, 114.34, 112.95, 110.55, 107.53, 41.37.
**GC Mass Spectrum** (retention time : 10.82 min) :



## 4. NMR experiments

### 4.1 Study of the $Ca(NTf_2)_2$ / $KPF_6$ / $PhSiH_3$ (1:1:1) in THF $d_8$ mixture by $^1H$ NMR at different temperatures.

$Ca(NTf_2)_2$ (15.1 mg, 0.025 mmol) was dissoved in 1 mL of THF-$d_8$ and stirred for 5 minutes before adding $KPF_6$ (4.6 mg, 0.025 mmol). $PhSiH_3$ (3.0 µL, 0.025 mmol) was then added and the mixture stirred for 5 minutes. The first $^1H$ spectrum was then recorded at 25 ° C (**Figure S1**, bottom, Spectrum 1) and following spectra were collected at lower temperatures (25 °C → - 65 °C, **Figure S1**). Next the temperature of the spectrometer was allowed to increase back to 25 °C and the spectra recorded at the same temperatures than during the temperature decrease (- 65 °C → 25 °C, **Figure S2**).

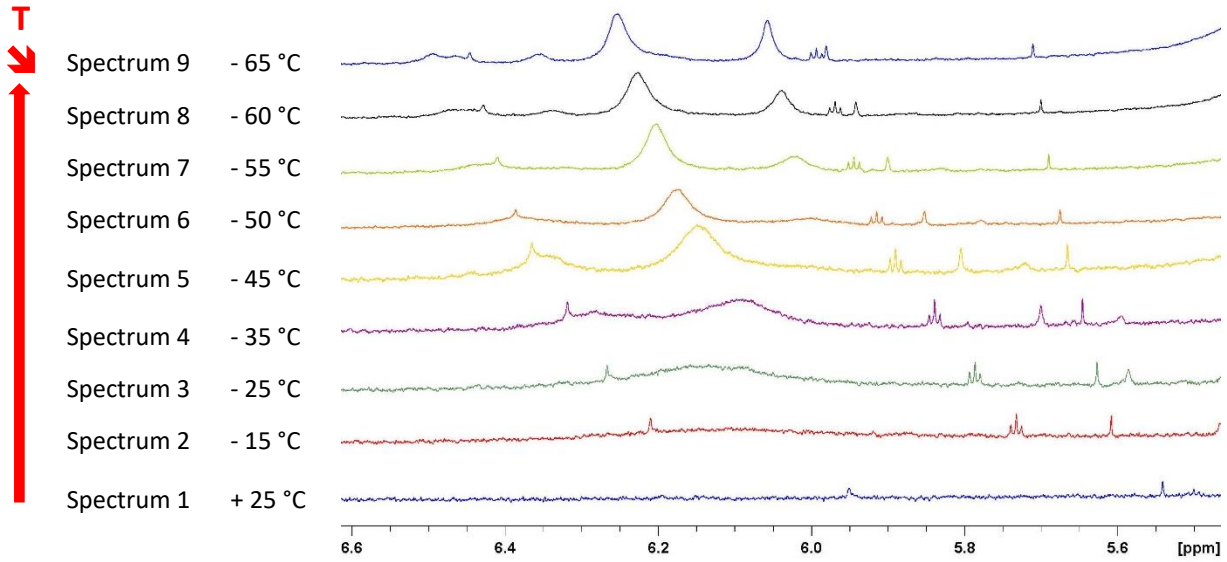



**Figure S1: $^1H$ NMR spectra of the stoichiometric mixture $Ca(NTf_2)_2$ + $KPF_6$ + $PhSiH_3$ in THF-$d_8$ when decresing the temperature from 25 °C to - 65 °C (spectra 1 to 9) : appearance of broad signals in the 6-6.4 ppm area from – 25 °C**

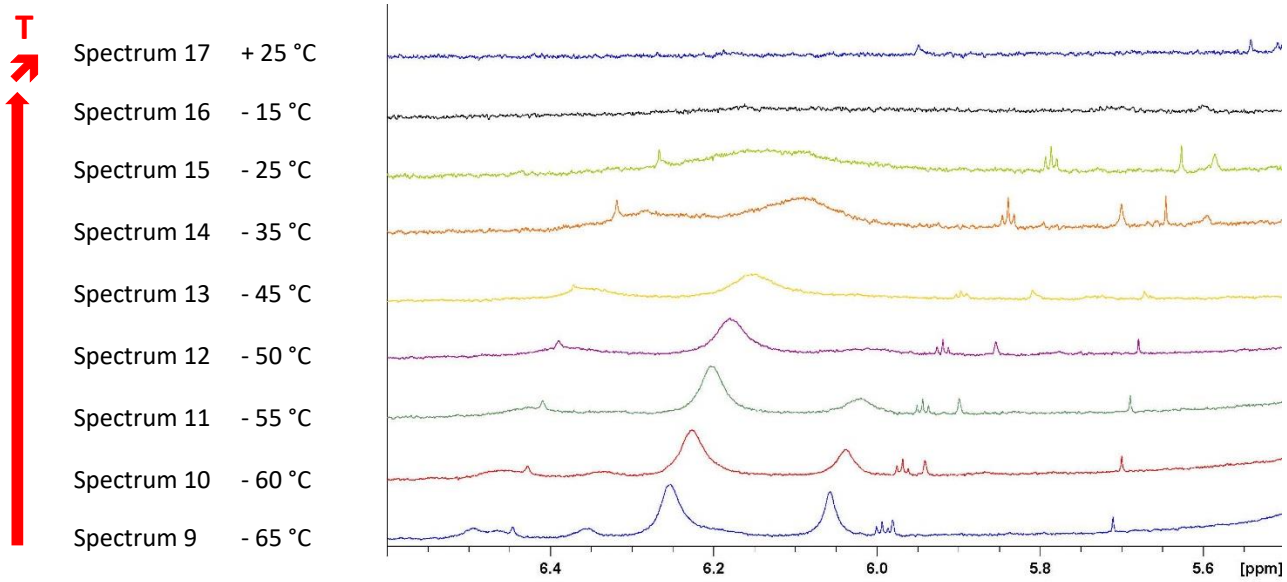



**Figure S2: $^1H$ NMR spectra of the stoichiometric mixture $Ca(NTf_2)_2$ + $KPF_6$ + $PhSiH_3$ in THF-$d_8$ when increasing back the temperature from - 65 °C to 25 °C : (spectra 9 to 18) : reversibility of the phenomenon**

**4.2 Monitoring of the reaction mixture by $^{1}$H NMR.**

The general procedure B (1 mmol scale, substrate **1h**) is followed by replacing THF by THF-$d_8$. An aliquote of the reaction mixture was collected after 0.5 h, 1h, 1h30, 2h, 2h30, 6h50 and 8h and analyzed by $^{1}$H NMR (Fig. S3).

The signal at 10 ppm is transient : its appears within the first 30 minutes of the reaction, its integration increases to reach a maximum after about 90 minutes and next, it decreases to totally disappear when the reaction is finished. The species giving rise to this signal at 10 ppm is proposed to be an iminium intermediate, the chemical shift being consistent with an iminium moiety (see calculated value §**5.4** and previous examples of $^{1}$H NMR data for iminium species[15]).

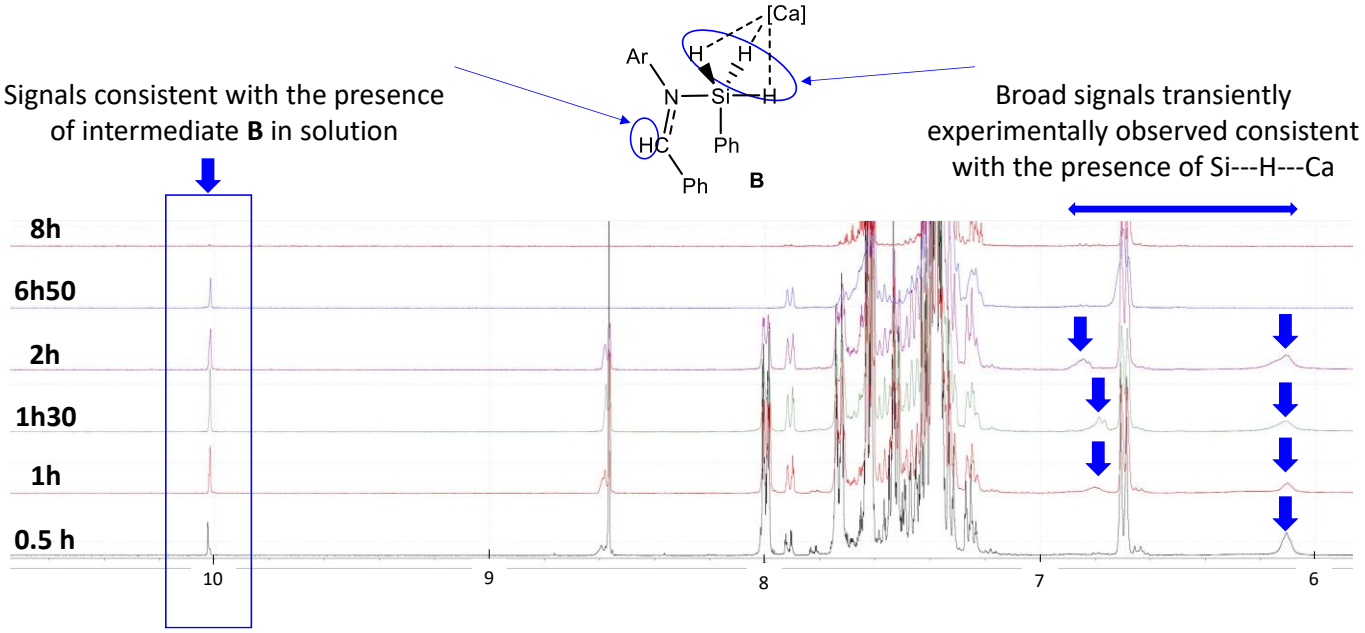



**Figure S3**

## 5. Computational Section

### 5.1 Full Computational details

All calculations have been performed with the Orca program (version 5.0.3). [16]

All geometry optimisations were performed on the full molecules considered in vacuum, with the PBE0 functional [17] including the Grimme correction for dispersion effects (D3 correction with Becke-Johnson damping) [18] and with a triple-zeta Def2-TZVP(-f) basis set [19] for all atoms (BS1 level).

Single point calculations were carried out with BS2 level, which is defined as follows. The same hybrid functional (PBE0) has been used, including the D3BJ Grimme correction for dispersion, with a triple-zeta def2-TZVPP basis set for all atoms.[19] The solvent effects (THF) were included with the SMD solvation model.[20]

The nature of the extrema as minima was confirmed by analytical frequency calculations at the BS1 level. This level was also used for the statistical mechanics calculations of the thermal and entropic effects which were carried out using the quasi rigid rotor/harmonic oscillator (qRRHO) approximation [21] at room temperature and 1 atm. The reported Gibbs energies were calculated at 298.15 K and 1 atm as follows:

$$G^{THF,PBE0-D3BJ,BS2} = E^{THF,PBE0-D3BJ,BS2} + G^{gas,PBE0-D3BJ,BS1}_{contribution}$$

NBO analysis were carried out with the NBO6 program [22] (BS2 level).

Calculations of $^{1}$H NMR shieldings, σ, and related chemical shifts, δ, were performed within the gauge-including atomic orbital (GIAO) framework at the BS2 level.

The $^{1}$H shielding of the reference compound (TMS) has been computed using the same protocol, leading to a value of 31.5 ppm.

### 5.2 Coordinates for the optimized structures of all extrema

Imine **1b**

| | | | |
|---|---|---|---|
| N | 8.43306795845624 | 7.56269383071643 | 7.70442959385039 |
| C | 8.59116676727776 | 6.48815208665793 | 7.04628731660883 |
| C | 7.15684183300434 | 8.11930873130641 | 7.81199923785720 |
| H | 7.73804884091787 | 5.95216855640887 | 6.60798072343460 |
| C | 9.89970370658500 | 5.87568072392095 | 6.83896531322545 |
| C | 6.78998587883774 | 8.68860101632053 | 9.03131958149704 |
| C | 6.26055512423691 | 8.17123189583800 | 6.74271934878794 |
| C | 11.06477720975239 | 6.46158389661226 | 7.33652653100340 |
| C | 9.98655950465034 | 4.68091916753387 | 6.12801091140815 |
| C | 5.53659430906778 | 9.25144776139039 | 9.19150741368741 |
| H | 7.50298120191291 | 8.66599193909164 | 9.84669697470636 |
| C | 5.01423749326555 | 8.75390478634781 | 6.90449570433007 |
| H | 6.56045277300808 | 7.78535177250624 | 5.77512207748153 |
| C | 12.28867427082738 | 5.85781642775874 | 7.12407213212512 |
| H | 10.98189521575464 | 7.39060996963114 | 7.88726556062234 |
| C | 11.21521242526327 | 4.07686958619178 | 5.91481267166307 |
| H | 9.08061955700916 | 4.22532800722403 | 5.74127736453254 |

| | | | |
|---|---|---|---|
| C | 4.64231838762981 | 9.28700243133028 | 8.12964667103345 |
| H | 5.25840175800167 | 9.67649134227794 | 10.14904443956353 |
| H | 4.33164995932821 | 8.79930463981517 | 6.06350061194172 |
| C | 12.36755811822689 | 4.66475425542655 | 6.41292426000680 |
| H | 13.19115648851471 | 6.31551818225147 | 7.51229825370650 |
| H | 11.27383599228869 | 3.14752923472238 | 5.36070019865988 |
| H | 3.66724017449210 | 9.74312809566194 | 8.25224023894082 |
| H | 13.33039805169047 | 4.19512066305719 | 6.24814586932575 |

Imine **1f**

| | | | |
|---|---|---|---|
| N | 8.494479 | 7.659559 | 7.485928 |
| C | 8.627843 | 6.519807 | 6.940178 |
| C | 7.243904 | 8.279326 | 7.510232 |
| H | 7.769896 | 5.970564 | 6.529083 |
| C | 9.916995 | 5.843818 | 6.836463 |
| C | 6.944032 | 9.099433 | 8.592206 |
| C | 6.292727 | 8.157698 | 6.490506 |
| C | 11.090518 | 6.434989 | 7.308107 |
| C | 9.978548 | 4.579191 | 6.254849 |
| C | 5.718975 | 9.739241 | 8.696963 |
| H | 7.689237 | 9.217264 | 9.369717 |
| C | 5.079600 | 8.805932 | 6.574952 |
| H | 6.524168 | 7.576792 | 5.605246 |
| C | 12.295271 | 5.768366 | 7.199049 |
| H | 11.028709 | 7.418820 | 7.756837 |
| C | 11.188051 | 3.912107 | 6.144945 |
| H | 9.067130 | 4.118533 | 5.887441 |
| C | 4.775641 | 9.592732 | 7.685056 |
| H | 5.517132 | 10.355833 | 9.562205 |
| H | 4.348032 | 8.728623 | 5.779654 |
| C | 12.348303 | 4.505749 | 6.617285 |
| H | 13.203461 | 6.231456 | 7.567160 |
| H | 11.225463 | 2.928810 | 5.691130 |
| H | 13.296226 | 3.987140 | 6.532715 |
| O | 3.557467 | 10.184352 | 7.678711 |
| C | 3.227691 | 11.001671 | 8.776767 |
| H | 2.223067 | 11.374722 | 8.586528 |
| H | 3.230011 | 10.434339 | 9.713542 |
| H | 3.916029 | 11.848672 | 8.866766 |

Imine **1h**

| | | | |
|---|---|---|---|
| N | 8.435606 | 7.576127 | 7.700647 |
| C | 8.591524 | 6.485656 | 7.067365 |
| C | 7.159319 | 8.123243 | 7.811955 |
| H | 7.733391 | 5.933505 | 6.660299 |
| C | 9.898644 | 5.877227 | 6.849698 |
| C | 6.778988 | 8.671771 | 9.037707 |
| C | 6.271503 | 8.185729 | 6.736388 |
| C | 11.069736 | 6.484579 | 7.305857 |
| C | 9.976698 | 4.664214 | 6.169047 |
| C | 5.524363 | 9.224301 | 9.197077 |
| H | 7.481494 | 8.640045 | 9.861127 |
| C | 5.021277 | 8.756135 | 6.893353 |
| H | 6.579123 | 7.811141 | 5.767429 |
| C | 12.292542 | 5.883229 | 7.081586 |
| H | 10.993539 | 7.427209 | 7.833855 |
| C | 11.204281 | 4.062704 | 5.944542 |
| H | 9.065531 | 4.192818 | 5.815224 |
| C | 4.640255 | 9.265995 | 8.125209 |
| H | 5.227689 | 9.628413 | 10.157074 |
| H | 4.338210 | 8.804436 | 6.054668 |
| C | 12.362917 | 4.671962 | 6.400851 |
| H | 13.200435 | 6.356581 | 7.436530 |
| H | 11.257370 | 3.119278 | 5.414524 |
| H | 13.325013 | 4.204286 | 6.227003 |
| C | 3.304891 | 9.920725 | 8.290373 |
| F | 3.376992 | 11.255685 | 8.133790 |
| F | 2.409627 | 9.476318 | 7.396264 |
| F | 2.788957 | 9.706981 | 9.510679 |

Phenylsilane **PhSiH3**

| | | | |
|---|---|---|---|
| Si | 7.19461250330853 | 7.81460987462199 | 10.34180506672471 |
| H | 5.76207887146481 | 7.98386526311262 | 10.70159431625552 |
| H | 7.93339695032940 | 9.07348750828819 | 10.62578329873244 |
| C | 7.33732722715048 | 7.38226074134624 | 8.52906691028263 |
| C | 6.27582663996462 | 6.78175248917738 | 7.85090557320035 |
| C | 8.51566174801233 | 7.63123367201208 | 7.82316368861660 |
| C | 6.38840402292252 | 6.43490690541955 | 6.51290181441810 |
| H | 5.34417252338695 | 6.58507794433013 | 8.37181735431414 |
| C | 8.63271513142362 | 7.28638056799004 | 6.48577002982856 |
| H | 9.35519784406416 | 8.10603975631380 | 8.32137582520626 |
| C | 7.56820613395581 | 6.68631604850847 | 5.82895920738808 |

| | | | |
|---|---|---|---|
| H | 5.55249314603311 | 5.97066345299384 | 6.00217418419673 |
| H | 9.55497474200448 | 7.48897257869862 | 5.95332982059463 |
| H | 7.65732381111069 | 6.41813150771505 | 4.78247878555451 |
| H | 7.76823670486842 | 6.74255468947198 | 11.20014112468670 |

**Ca(NTf2)$^{+}$**

| | | | |
|---|---|---|---|
| Ca | 10.03600303379964 | 10.77331907384627 | 10.86569142100563 |
| S | 8.80858362073075 | 11.48084734939287 | 13.74238175511564 |
| S | 8.92936330406654 | 8.69929094818158 | 13.27711437371320 |
| F | 11.32942115259079 | 9.06463053211064 | 14.20503166955215 |
| F | 10.05519025667050 | 7.85705735228770 | 15.46835271601151 |
| F | 10.87304542021244 | 7.02580456324082 | 13.64900398691789 |
| F | 6.27925696175103 | 11.57061310916956 | 12.92624767063003 |
| F | 7.76342391918837 | 11.46831011022558 | 11.33460505471609 |
| F | 7.44598366601978 | 13.31444647581449 | 12.44062887902995 |
| O | 9.96907663770170 | 11.66390827902667 | 12.82905065452704 |
| O | 9.52523103207787 | 9.01054822710354 | 11.94385302204052 |
| O | 7.93745362266916 | 7.69330098125969 | 13.28736457074566 |
| O | 8.75267505091504 | 12.31267312245230 | 14.88035928509505 |
| N | 8.47726607910653 | 9.99537850694138 | 14.04259331742946 |
| C | 10.40758031629229 | 8.10809869528485 | 14.23441669189643 |
| C | 7.44652192620735 | 12.01950367366182 | 12.59345693157342 |

Adduct **A**

| | | | |
|---|---|---|---|
| Ca | -0.591976 | -1.933758 | 1.215010 |
| S | 2.615265 | -2.794589 | 2.146960 |
| S | 0.805052 | -2.187409 | 4.215309 |
| F | -0.676950 | -3.918595 | 2.931930 |
| F | 0.293633 | -4.749612 | 4.685761 |
| F | -1.393580 | -3.428261 | 4.916870 |
| F | 4.649320 | -1.269121 | 2.746924 |
| F | 2.850652 | -0.195400 | 2.213756 |
| F | 4.019898 | -1.173758 | 0.682792 |
| O | 1.520673 | -2.597974 | 1.178242 |
| O | 0.050286 | -1.328535 | 3.284934 |
| O | 0.926805 | -1.745018 | 5.553889 |
| O | 3.474302 | -3.896610 | 1.912275 |
| N | 2.149229 | -2.732565 | 3.646198 |
| C | -0.298069 | -3.679007 | 4.236374 |
| C | 3.615759 | -1.249537 | 1.939128 |
| C | -1.565147 | 2.240112 | -0.149660 |

| | | | |
|---|---|---|---|
| C | -0.775681 | 3.071044 | -0.948182 |
| C | -2.944577 | 2.209337 | -0.365492 |
| C | -1.351294 | 3.847895 | -1.938615 |
| H | 0.298512 | 3.115646 | -0.802128 |
| C | -3.520172 | 2.984121 | -1.361182 |
| H | -3.582468 | 1.593640 | 0.261292 |
| C | -2.722299 | 3.802675 | -2.146692 |
| H | -0.727898 | 4.482507 | -2.556059 |
| H | -4.592607 | 2.960347 | -1.513964 |
| H | -3.171299 | 4.412744 | -2.921390 |
| Si | -0.791508 | 1.221197 | 1.182732 |
| H | -1.821793 | 0.278977 | 1.745965 |
| H | -0.124487 | 1.935978 | 2.288542 |
| H | 0.222021 | 0.268376 | 0.596199 |
| N | -0.558057 | -0.837955 | -2.260654 |
| C | -1.164404 | -0.092215 | -3.102742 |
| C | -1.256763 | -1.781448 | -1.539405 |
| H | -2.225270 | -0.251401 | -3.334967 |
| C | -0.514008 | 0.981978 | -3.819341 |
| C | -0.682430 | -3.052778 | -1.355856 |
| C | -2.462337 | -1.490650 | -0.875388 |
| C | 0.828728 | 1.299682 | -3.596251 |
| C | -1.258967 | 1.723911 | -4.735373 |
| C | -1.308839 | -4.004476 | -0.563527 |
| H | 0.260146 | -3.269744 | -1.843710 |
| C | -3.077113 | -2.447651 | -0.071823 |
| H | -2.896669 | -0.503493 | -0.984634 |
| C | 1.407663 | 2.350470 | -4.276903 |
| H | 1.398776 | 0.708218 | -2.890346 |
| C | -0.674270 | 2.775252 | -5.419499 |
| H | -2.300558 | 1.473618 | -4.905746 |
| C | -2.505053 | -3.706785 | 0.094346 |
| H | -0.853206 | -4.980422 | -0.443020 |
| H | -4.008129 | -2.205824 | 0.428773 |
| C | 0.656912 | 3.089003 | -5.188231 |
| H | 2.449159 | 2.597242 | -4.110251 |
| H | -1.251978 | 3.347436 | -6.134783 |
| H | -2.986357 | -4.450201 | 0.717641 |
| H | 1.118497 | 3.909320 | -5.725206 |

Transition State **TSAB**

| | | | |
|---|---|---|---|
| Ca | 0.87851851674978 | -0.66920464207850 | 2.17759577923122 |
| S | 3.18393896913977 | -3.15635407327104 | 2.60244111771207 |
| S | 2.63536433633629 | -1.50202812100567 | 4.82334238997905 |
| F | 0.16085577018451 | -2.05325846724926 | 4.19155757474062 |
| F | 0.89129459530590 | -3.20785645228326 | 5.87944774245911 |
| F | 0.39847340304639 | -1.12595414732635 | 6.13941261873987 |
| F | 5.75388508994947 | -3.53842455968948 | 2.75100104791574 |
| F | 5.17360400412287 | -1.50203654507065 | 2.31397643178132 |
| F | 5.02587965597064 | -3.02115429071780 | 0.78332315828384 |
| O | 2.38454222449743 | -2.24098327557936 | 1.76558321620461 |
| O | 2.28804976413818 | -0.40580302548720 | 3.90289877631985 |
| O | 3.35360069938879 | -1.17107639215947 | 5.99581752697318 |
| O | 2.95513446161157 | -4.54170491186758 | 2.39292980000615 |
| N | 3.17862183699486 | -2.78454561100334 | 4.12522808146178 |
| C | 0.93366750343323 | -2.02143813814422 | 5.34644829170025 |
| C | 4.91888391216471 | -2.78123523913957 | 2.07838439120331 |
| C | -1.21155011856380 | 2.32292984576811 | -0.46849862435426 |
| C | -0.60814123717242 | 3.56121406709104 | -0.24317287580312 |
| C | -2.43059348885885 | 2.27562775448126 | -1.14475735962423 |
| C | -1.19237604517037 | 4.72313835880157 | -0.71971315219511 |
| H | 0.32426126726913 | 3.62192281854627 | 0.30826775172379 |
| C | -3.02604652536708 | 3.43932310877773 | -1.59945160610360 |
| H | -2.92029377907513 | 1.32572037367149 | -1.32422198436332 |
| C | -2.40025477749381 | 4.66161588191103 | -1.39921360316515 |
| H | -0.71140872686816 | 5.67898967341471 | -0.55083470666106 |
| H | -3.97747772352311 | 3.39352619394790 | -2.11533231429624 |
| H | -2.86203281820596 | 5.57107617933226 | -1.76477466829323 |
| Si | -0.37632375720584 | 0.80285774023649 | 0.15783478348306 |
| H | -1.11565194547479 | -0.26674216891027 | 0.91961986408243 |
| H | 0.17807800918823 | 1.39848634877976 | 1.52081279953871 |
| H | 0.99812447195118 | 0.25462820641948 | -0.15290115932638 |
| N | -0.88941545599982 | -0.52056436762297 | -1.49751165596241 |
| C | -1.10086992493517 | -0.39108113449362 | -2.75767142436758 |
| C | -1.06539452728034 | -1.81544216443015 | -0.92766254907037 |
| H | -1.48435509164037 | -1.26058634695929 | -3.29722769290848 |
| C | -0.88536384728231 | 0.79678657813779 | -3.55059343950463 |
| C | 0.06215584578918 | -2.51943046544284 | -0.50996954423056 |
| C | -2.33464356359517 | -2.31612640757386 | -0.67708849505351 |
| C | 0.06626508177111 | 1.76467400043878 | -3.22168001594921 |
| C | -1.66129471705036 | 0.95568814689873 | -4.70185099427772 |
| C | -0.08873178504857 | -3.72202630258046 | 0.17084090531180 |

| | | | |
|---|---|---|---|
| H | 1.05145527086402 | -2.15025653504394 | -0.75698857733697 |
| C | -2.47553358081585 | -3.52338207335839 | -0.00824601214333 |
| H | -3.20643423811280 | -1.75291460601581 | -0.98927032884131 |
| C | 0.20056465231689 | 2.89423965845837 | -4.00209880400830 |
| H | 0.72045774028221 | 1.61190962507600 | -2.37383690888169 |
| C | -1.54133387896869 | 2.09993085972941 | -5.46809169234166 |
| H | -2.37461705003279 | 0.18715053152739 | -4.97911521884742 |
| C | -1.35803775872350 | -4.22120713289816 | 0.42752065841130 |
| H | 0.79000399500406 | -4.27356854940941 | 0.48372951388071 |
| H | -3.46742153572518 | -3.91622332899640 | 0.17954140478967 |
| C | -0.61477813641716 | 3.07071813294558 | -5.11412478868017 |
| H | 0.94283477892115 | 3.64075901057305 | -3.74911389307445 |
| H | -2.15841232351313 | 2.23083371927880 | -6.34807350603812 |
| H | -1.47400555367652 | -5.16067590637242 | 0.95338510265140 |
| H | -0.51096094459451 | 3.96253456793778 | -5.72058913288113 |

Intermediate **B**

| | | | |
|---|---|---|---|
| Ca | 11.60161375052614 | 4.89466934607689 | 10.66814849606479 |
| S | 14.00899714263045 | 2.47933098948156 | 10.16929506244808 |
| S | 14.78281143510704 | 4.80872828743649 | 11.53809887551961 |
| F | 12.62293587826227 | 4.28185077308688 | 12.93585495208358 |
| F | 14.45045949228808 | 3.56398344708961 | 13.86032630111123 |
| F | 13.99020211205173 | 5.66892211798751 | 13.88656352086201 |
| F | 15.78768317966932 | 2.44031555739270 | 8.24869722879270 |
| F | 14.35415089961634 | 4.05051335940432 | 8.10690753126784 |
| F | 13.76027482403555 | 2.02823399787511 | 7.62648535013889 |
| O | 12.62489249291075 | 2.98324879219430 | 10.17093302087804 |
| O | 13.73239185707242 | 5.56169621369891 | 10.82924534360101 |
| O | 16.00556350102405 | 5.47363876970573 | 11.78887458509849 |
| O | 14.17926918281096 | 1.09623799445111 | 10.42718897005235 |
| N | 15.00323825854700 | 3.35778340144719 | 11.00690216124131 |
| C | 13.95584288015508 | 4.56213061032928 | 13.18608077741695 |
| C | 14.52965331695520 | 2.77089461883731 | 8.41709024313552 |
| C | 8.24976708279358 | 5.55765296405582 | 7.85130467355399 |
| C | 7.67861110173389 | 6.65921166140017 | 8.49406687033783 |
| C | 7.66660169077111 | 5.10940596212717 | 6.66201107589670 |
| C | 6.55816347593704 | 7.28579664401860 | 7.97264092731814 |
| H | 8.11527290595693 | 7.03163281932776 | 9.41326581877889 |
| C | 6.55129951262496 | 5.73856954544439 | 6.13608952576184 |
| H | 8.08385997766961 | 4.26218522386277 | 6.13189526451753 |
| C | 5.99352913912775 | 6.82645643977551 | 6.79271097044534 |

| | | | |
|---|---|---|---|
| H | 6.12670540335795 | 8.13557532414011 | 8.48763492240747 |
| H | 6.11539439272357 | 5.37889827387303 | 5.21180806912291 |
| H | 5.11915753449634 | 7.31718693403204 | 6.38204183864410 |
| Si | 9.73889076550856 | 4.75246038431918 | 8.61980422937711 |
| H | 9.72363714090782 | 3.71909202648466 | 9.72553450983682 |
| H | 9.88748957591693 | 5.88880921072173 | 9.77142513325380 |
| H | 11.20950393618846 | 4.96681187907549 | 8.31777099349135 |
| N | 9.86311440685250 | 3.16050931091578 | 7.38444360862903 |
| C | 10.66650507520243 | 3.00280494586690 | 6.38844289687500 |
| C | 9.29437653033124 | 1.97728680827525 | 7.95635047800788 |
| H | 10.83101473448005 | 1.97833961934928 | 6.05304825206187 |
| C | 11.39873195081939 | 4.01124543096805 | 5.66337945348721 |
| C | 10.11651869016984 | 0.92268062524859 | 8.33362732367836 |
| C | 7.92578929302728 | 1.92411647296356 | 8.18506718655952 |
| C | 11.07890530593670 | 5.37436738833075 | 5.65176049994717 |
| C | 12.49052618933489 | 3.56005356183200 | 4.91092220765506 |
| C | 9.55881044128547 | -0.20464606221803 | 8.91448317050573 |
| H | 11.18998404719271 | 0.99956419070007 | 8.20527188085441 |
| C | 7.37782711092152 | 0.78924557190475 | 8.76107297014309 |
| H | 7.29365596259566 | 2.75565832816374 | 7.89976672709512 |
| C | 11.85804702712194 | 6.26042202214348 | 4.93518162814699 |
| H | 10.19179730526720 | 5.73738000359920 | 6.15407605312644 |
| C | 13.27847134408587 | 4.45325523412405 | 4.21179852190712 |
| H | 12.72515930549140 | 2.50160046639218 | 4.89459979180894 |
| C | 8.18966387326988 | -0.27558763965876 | 9.12425801032262 |
| H | 10.20072059503775 | -1.02407338840468 | 9.21384965750151 |
| H | 6.30825017586622 | 0.73774488290423 | 8.92370191348181 |
| C | 12.96422279049215 | 5.80511836046748 | 4.22709994012219 |
| H | 11.59695638913797 | 7.31121957344546 | 4.91573136519127 |
| H | 14.12899219239638 | 4.09708874346772 | 3.64432960065469 |
| H | 7.75586825903611 | -1.15770592565128 | 9.57863291947704 |
| H | 13.57203930526650 | 6.50672632571539 | 3.66840181030068 |

Transition State **TSBC**

| | | | |
|---|---|---|---|
| Ca | 10.45958336705128 | 1.49491114305114 | 9.72133009371155 |
| S | 11.57432408490247 | 3.17103668175704 | 12.51286814569257 |
| S | 8.81157428983919 | 3.38993937889042 | 12.08520968068244 |
| F | 8.89969747992135 | 1.63935782423765 | 14.01782864195284 |
| F | 8.06607806149401 | 3.55301779604311 | 14.57756120969647 |
| F | 6.90975928046023 | 2.18235514033305 | 13.37202886531736 |
| F | 12.57766620706109 | 5.50151180722370 | 13.14789021792494 |

| | | | |
|---|---|---|---|
| F | 12.46329740849083 | 5.13495740850035 | 11.02224105315364 |
| F | 13.95774788612098 | 4.12863103118922 | 12.21280262585799 |
| O | 11.78029154845684 | 2.32354376152910 | 11.32319597157213 |
| O | 8.89052015227822 | 2.22999683893879 | 11.18173866255484 |
| O | 7.92793259213097 | 4.44065098713947 | 11.70903875236342 |
| O | 11.91604225406329 | 2.58828734637621 | 13.76255695907703 |
| N | 10.21397283745998 | 3.96305540229044 | 12.46803058267042 |
| C | 8.12370744610923 | 2.63996128725888 | 13.63247990333132 |
| C | 12.72386784757192 | 4.59125320827550 | 12.21058169003126 |
| C | 9.42488689682170 | 6.52822319496641 | 8.73549235106650 |
| C | 9.50272319470598 | 7.02652959979396 | 10.03847082863673 |
| C | 8.76286385516894 | 7.27774671730372 | 7.75935176454647 |
| C | 8.94292313998092 | 8.25436538617928 | 10.35204258194606 |
| H | 9.98200454891409 | 6.44801304330169 | 10.82061330956276 |
| C | 8.20182400341882 | 8.50315178187172 | 8.07638285435342 |
| H | 8.65739355432508 | 6.89988044271381 | 6.74701811049493 |
| C | 8.29596773158535 | 8.99236065827817 | 9.37223910342241 |
| H | 9.00178048899498 | 8.62927571127170 | 11.36645783316128 |
| H | 7.68587543130527 | 9.07553997177099 | 7.31503698678845 |
| H | 7.85343652964687 | 9.94962080700637 | 9.62057309116117 |
| Si | 10.21357610465096 | 4.90443517949064 | 8.38196295371162 |
| H | 11.00032256901422 | 1.82141318862117 | 7.76875241911039 |
| H | 10.12144458533984 | 4.02318145561797 | 9.56831423051675 |
| H | 11.59428518077249 | 4.91437317816699 | 7.87407539425279 |
| N | 9.23980007177817 | 3.94387495315601 | 7.15523833460868 |
| C | 9.77453748225243 | 3.48796120417823 | 6.05663447067236 |
| C | 8.14564260571382 | 3.22938987002445 | 7.75222005727787 |
| H | 9.31823156371000 | 2.60026985144927 | 5.62837418310752 |
| C | 10.83866167688923 | 4.07657654651855 | 5.30186586457873 |
| C | 8.03360820795965 | 1.84249433691826 | 7.62577248831031 |
| C | 7.22522346993728 | 3.94053768059994 | 8.51085850961002 |
| C | 11.15995291650512 | 5.43970227883910 | 5.35409897868457 |
| C | 11.54687130135764 | 3.23239329419413 | 4.43631366971837 |
| C | 6.98858096512712 | 1.18506296196424 | 8.26008099841651 |
| H | 8.75697021414751 | 1.28309380732486 | 7.04601220659277 |
| C | 6.19117804354618 | 3.26849307468491 | 9.14238843845807 |
| H | 7.31338661492737 | 5.01492053566286 | 8.60882990703160 |
| C | 12.19137504688009 | 5.93405556628327 | 4.58433996703520 |
| H | 10.57270941332063 | 6.12396013844144 | 5.95496937398049 |
| C | 12.59483762950090 | 3.72824475096315 | 3.68845527557958 |
| H | 11.28734420364195 | 2.18128199523411 | 4.38719604502393 |
| C | 6.07004871058299 | 1.89388681761239 | 9.02190115867570 |

| | | | |
|---|---|---|---|
| H | 6.88898206612509 | 0.11164309225783 | 8.14742612463055 |
| H | 5.48376250902474 | 3.82994740779991 | 9.73868269750838 |
| C | 12.91771414042653 | 5.07732117458890 | 3.76406630549819 |
| H | 12.42744842860262 | 6.99027277095562 | 4.61209172947775 |
| H | 13.15650487823498 | 3.06948844654853 | 3.03851259072714 |
| H | 5.26009846858747 | 1.37368254503833 | 9.51769002736413 |
| H | 13.73060072316097 | 5.47016124937216 | 3.16509604910758 |

Adduct **C**

| | | | |
|---|---|---|---|
| Ca | 8.63411983259352 | 2.07594375329958 | 10.38735035362856 |
| S | 11.06354540890764 | 2.21906977843344 | 12.74272124635401 |
| S | 9.00071458959291 | 4.10600791491473 | 13.04852017019826 |
| F | 8.44639325772778 | 2.37494238732666 | 14.91362717240465 |
| F | 9.05673544380747 | 4.31597029613850 | 15.64259538922069 |
| F | 7.08551883065817 | 4.05013940977834 | 14.79883336690583 |
| F | 13.39420766002694 | 3.34484090432854 | 13.08506347741704 |
| F | 12.63444062604382 | 3.47384416083332 | 11.06588574957126 |
| F | 13.39223323946477 | 1.59710321190817 | 11.81568595900428 |
| O | 10.44882822228261 | 1.60305309995675 | 11.54105234375234 |
| O | 8.14551791378408 | 3.27784489118890 | 12.16742372598831 |
| O | 8.88617381079874 | 5.51271470876150 | 12.88385457242229 |
| O | 11.22129248528056 | 1.35362277568675 | 13.85712284784657 |
| N | 10.49304395243710 | 3.65183368751818 | 13.03608579592558 |
| C | 8.35186658915181 | 3.68296252864311 | 14.73261087049275 |
| C | 12.74835491379197 | 2.70271273035833 | 12.14056646351166 |
| C | 9.67517600256236 | 6.43793525172233 | 8.44496032962890 |
| C | 9.02719812573134 | 6.97146736654494 | 9.56261601849371 |
| C | 9.82971294336081 | 7.22817870674507 | 7.30182921340311 |
| C | 8.53553553554431 | 8.26740164990443 | 9.53438485928855 |
| H | 8.91579791232615 | 6.38533561181415 | 10.46962789547821 |
| C | 9.33410491061533 | 8.52044870437584 | 7.27784429902174 |
| H | 10.33740530183532 | 6.83713442341493 | 6.42685777630589 |
| C | 8.68667470343069 | 9.03883615523671 | 8.39182825213600 |
| H | 8.04091841087684 | 8.67558978935714 | 10.40744996528096 |
| H | 9.45737555567431 | 9.12842703074526 | 6.38956542728954 |
| H | 8.30358739922074 | 10.05226119719914 | 8.37047268590257 |
| Si | 10.35331480501740 | 4.73039910365072 | 8.51890051351693 |
| H | 11.42127556895595 | 2.50507978117402 | 6.68439853829596 |
| H | 9.93072545199684 | 4.15723359296134 | 9.85118113639307 |
| H | 11.81775698888470 | 4.60429253671939 | 8.38677631258832 |
| N | 9.69608215629956 | 3.52763658169748 | 7.39447782401227 |

| | | | |
|---|---|---|---|
| C | 10.54160342529886 | 3.02947168910227 | 6.29810045077660 |
| C | 8.55722959921667 | 2.86170569194637 | 7.75746393096659 |
| H | 9.95681191102209 | 2.31482019552159 | 5.71542217009975 |
| C | 10.96377559849376 | 4.16815943069466 | 5.41234327043255 |
| C | 8.41329321616960 | 1.46087499302759 | 7.63727685846148 |
| C | 7.50933985846100 | 3.57044197189419 | 8.39186497292631 |
| C | 10.02880874271957 | 4.77674986980928 | 4.57851624412331 |
| C | 12.26691797639758 | 4.64885821876365 | 5.43610002592817 |
| C | 7.30357876585831 | 0.81172073249485 | 8.16751379208197 |
| H | 9.18664999616260 | 0.88018815070041 | 7.14974260514936 |
| C | 6.40913691337833 | 2.90878803788550 | 8.91805339837396 |
| H | 7.56834950369797 | 4.65203527224574 | 8.44899776751174 |
| C | 10.39153750802680 | 5.85045087091475 | 3.78464487061183 |
| H | 9.00889781496690 | 4.40728551996224 | 4.55327089413830 |
| C | 12.63133247205973 | 5.73031741033275 | 4.64532498343734 |
| H | 13.00530675506321 | 4.17443598602137 | 6.07337174252906 |
| C | 6.30596766611822 | 1.51904954564607 | 8.83939949949993 |
| H | 7.22601196242705 | -0.26522024764605 | 8.06670081476567 |
| H | 5.62764179285163 | 3.48514878486938 | 9.39962856206827 |
| C | 11.69443206778144 | 6.33234047287314 | 3.82100218111324 |
| H | 9.65947778741953 | 6.31259004380568 | 3.13339761936070 |
| H | 13.64983595210810 | 6.09794542244338 | 4.67119303150969 |
| H | 5.44426367207090 | 1.00508758502813 | 9.24609593981066 |
| H | 11.97895749354512 | 7.17315562932427 | 3.20008882264147 |

Product: free silylamine

| | | | |
|---|---|---|---|
| C | 10.87738646964697 | 12.46169578360566 | 11.05922646715661 |
| C | 9.66898502828292 | 12.21656961390727 | 11.69126965482433 |
| C | 9.32691357148180 | 10.92582905286131 | 12.07055756215928 |
| C | 10.18835928247100 | 9.86625005668924 | 11.82422589315096 |
| C | 11.40198539866036 | 10.12112743000962 | 11.19314678442911 |
| C | 11.74591459215652 | 11.40695075252105 | 10.81203251894225 |
| C | 9.83631269153605 | 8.44363402264461 | 12.19176521926732 |
| N | 8.50275044913433 | 8.24395071085158 | 12.71693938556574 |
| C | 8.27892009319694 | 8.46437943717040 | 14.07428355146036 |
| C | 7.06938792696771 | 8.06665970002784 | 14.65874687801744 |
| C | 6.82038416505224 | 8.28356997034019 | 16.00142894303227 |
| C | 7.76924866896947 | 8.89300656919177 | 16.80912255046719 |
| C | 8.97151770163928 | 9.28468094977122 | 16.24258635502686 |
| C | 9.22866526410149 | 9.08145536005321 | 14.89659862001519 |
| Si | 7.18633870951328 | 7.84434279727575 | 11.63600481973248 |

| | | | |
|---|---|---|---|
| C | 7.80992934338462 | 7.89113827360495 | 9.88270010051911 |
| C | 8.07102343848066 | 6.70358530927880 | 9.19708395947390 |
| C | 8.55901099713500 | 6.72164235501153 | 7.89882667527326 |
| C | 8.79144713182249 | 7.93314546205834 | 7.26544728684847 |
| C | 8.53088400587471 | 9.12385910105019 | 7.92918598186304 |
| C | 8.04151882126080 | 9.10174845639122 | 9.22493495204479 |
| H | 7.89072022539411 | 5.75048721375476 | 9.68415957085149 |
| H | 7.85042794418109 | 10.04050604128414 | 9.73317902453354 |
| H | 8.75681682022143 | 5.79014667389327 | 7.38100256209271 |
| H | 8.71113858947493 | 10.07214310195352 | 7.43635779705845 |
| H | 9.17405281227906 | 7.95022499654128 | 6.25130962968969 |
| H | 9.94951304573312 | 7.82997788158624 | 11.29491121123167 |
| H | 6.66023099985130 | 6.47589470157509 | 11.90110239453449 |
| H | 6.08498339358178 | 8.82127370136697 | 11.84571002331192 |
| H | 10.56630931512514 | 8.05889262121509 | 12.91291619833294 |
| H | 6.31957353345474 | 7.55835538762411 | 14.06199449216498 |
| H | 10.16363414743009 | 9.43264827431839 | 14.48142282994845 |
| H | 8.38184444604221 | 10.73817743808303 | 12.56653228338345 |
| H | 12.08044057636144 | 9.29857526350353 | 10.98769914169397 |
| H | 5.87446838584060 | 7.96075963487551 | 16.42122711969471 |
| H | 9.72602161622697 | 9.76839865652349 | 16.85270651763190 |
| H | 8.98615190249764 | 13.03379195668967 | 11.89374955640238 |
| H | 12.69238313739322 | 11.58745263366006 | 10.31538191688060 |
| H | 7.57401593189702 | 9.05889962144826 | 17.86126103303750 |
| H | 11.14395142624508 | 13.46890203578735 | 10.76118153825463 |

Tetramethylsilane TMS

| | | | |
|---|---|---|---|
| Si | -0.00000006761295 | 0.00061752044942 | 0.00000692027439 |
| C | -0.00000012340359 | -0.00091761652326 | 1.87517110661852 |
| C | -0.00000014015280 | -1.76713021761777 | -0.62571929798270 |
| C | -1.53173022012649 | 0.88429186431124 | -0.62459910778134 |
| C | 1.53173011350356 | 0.88429198208676 | -0.62459905235184 |
| H | -0.00000187123703 | 1.01765131779107 | 2.27018864078229 |
| H | -0.88243382666438 | -0.51094326778007 | 2.26848973249471 |
| H | 0.88243536686180 | -0.51094018743633 | 2.26848974818529 |
| H | 0.00000029476567 | -1.79906385818450 | -1.71781023667550 |
| H | 0.88234297536874 | -2.30856719409228 | -0.27658879743838 |
| H | -0.88234370904866 | -2.30856692411385 | -0.27658960420785 |
| H | -1.56175885930534 | 0.89589317670653 | -1.71669051575825 |
| H | -2.44159274211078 | 0.39315757095046 | -0.27180549095818 |
| H | -1.55744122153114 | 1.92058955633118 | -0.27972350336581 |

| | | | |
|---|---|---|---|
| H | 1.56175732042634 | 0.89589458315667 | -1.71669047625867 |
| H | 1.55744210814001 | 1.92058916543091 | -0.27972193700011 |
| H | 2.44159260212703 | 0.39315652853382 | -0.27180712857657 |

**5.3 NBO analysis**

*NBO analysis for intermediate **B***

Selected output of Second order perturbation theory analysis of Fock matrix in NBO basis. NBO #90 corresponds to the lone pair of N, NBOs #(120, 121 and 122) and #(186, 187 and 188) correspond to the 3 $\sigma_{Si-H}$ / $\sigma^*_{Si-H}$ bonds/antibonds, respectively; NBO #156 corresponds to the 3s – LV - NBO centered on Ca.

| Donor (L) NBO | Acceptor (NL) NBO | E(2) kcal/mol | E(NL)-E(L) a.u. | F(L,NL) a.u. |
|---|---|---|---|---|
| 90. LP ( 1) N 32 | 186. BD*( 1)Si 28- H 29 | **12.82** | 0.59 | 0.078 |
| 90. LP ( 1) N 32 | 187. BD*( 1)Si 28- H 30 | **43.42** | 0.59 | 0.143 |
| 90. LP ( 1) N 32 | 188. BD*( 1)Si 28- H 31 | **13.70** | 0.58 | 0.080 |
| 120. BD ( 1)Si 28- H 29 | 156. LV ( 1)Ca 1 | 0.98 | 0.56 | 0.021 |
| 121. BD ( 1)Si 28- H 30 | 156. LV ( 1)Ca 1 | **8.42** | 0.51 | 0.058 |
| 122. BD ( 1)Si 28- H 31 | 156. LV ( 1)Ca 1 | 0.64 | 0.56 | 0.017 |

*NBO analysis for **TSBC***

Selected output of Natural Population Analysis. Hydrogens 29, 30 and 31 are bounded to Si. The transferred H corresponds to #29.

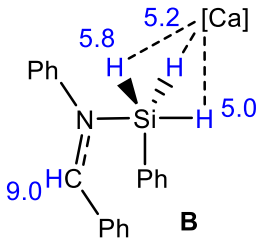
| Atom No | Natural Charge |
|---|---|
| Ca 1 | 1.798 |
| Si 28 | 1.343 |
| H 29 | -0.819 |
| H 30 | -0.237 |
| H 31 | -0.129 |
| N 32 | -0.623 |

*NBO analysis **1f** and **1h** imine*

The natural charge of the imine C atom is +0.140 e / +0.115 e for **1h** / **1f** imines, respectively.

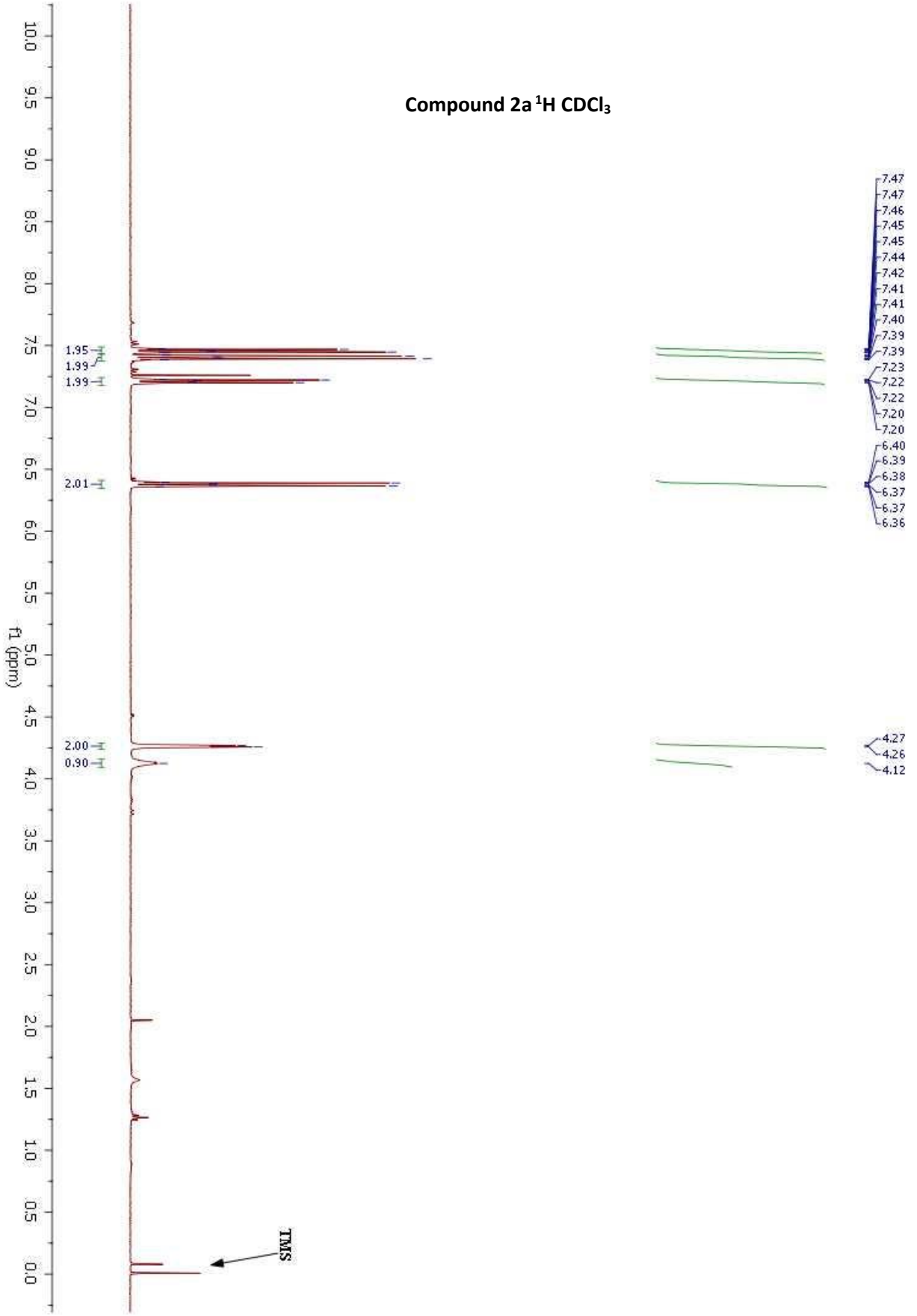
**5.4 NMR calculations**

Selected $^{1}$H chemical shifts (ppm) calculated for intermediate **B**:

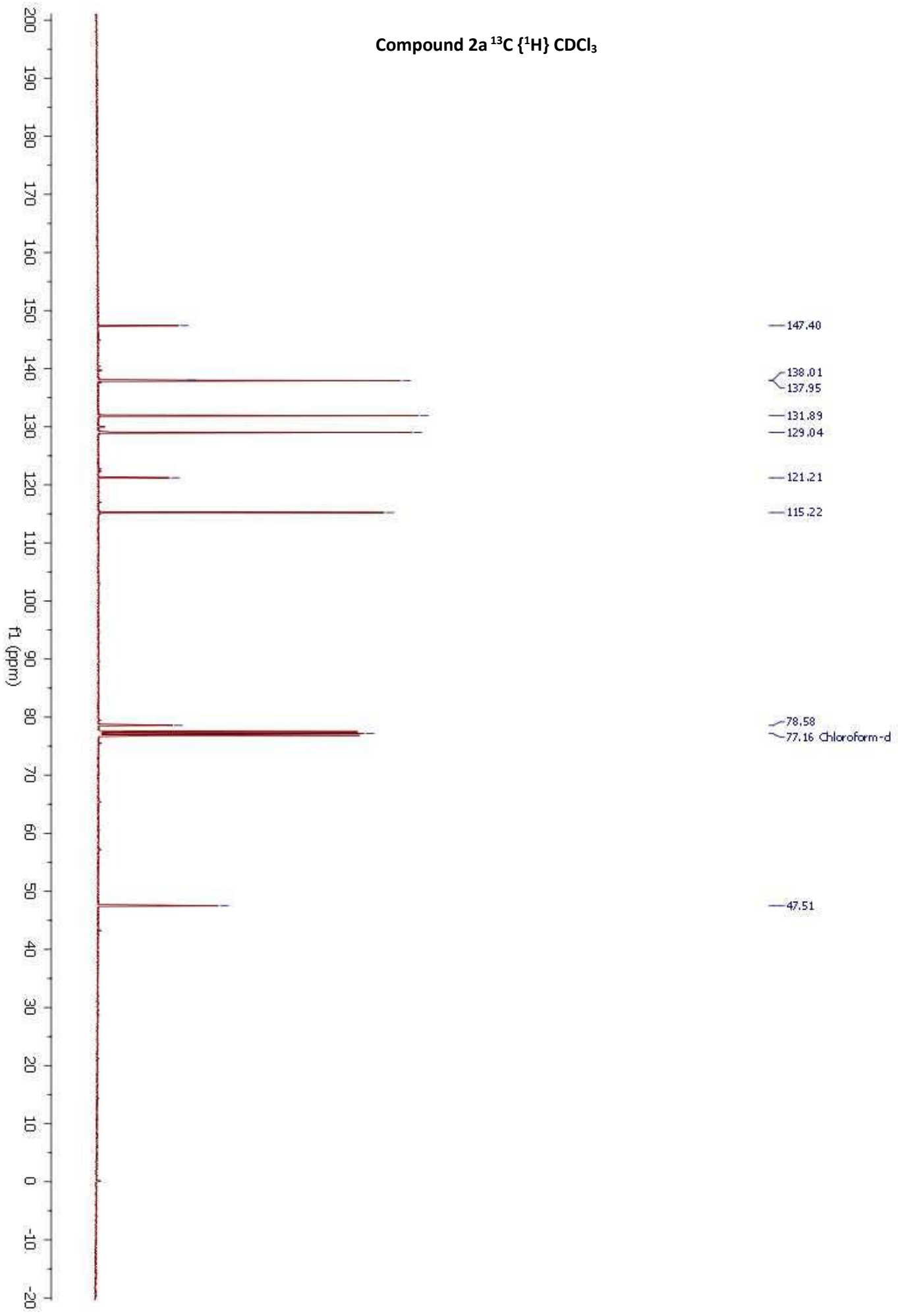



**B**

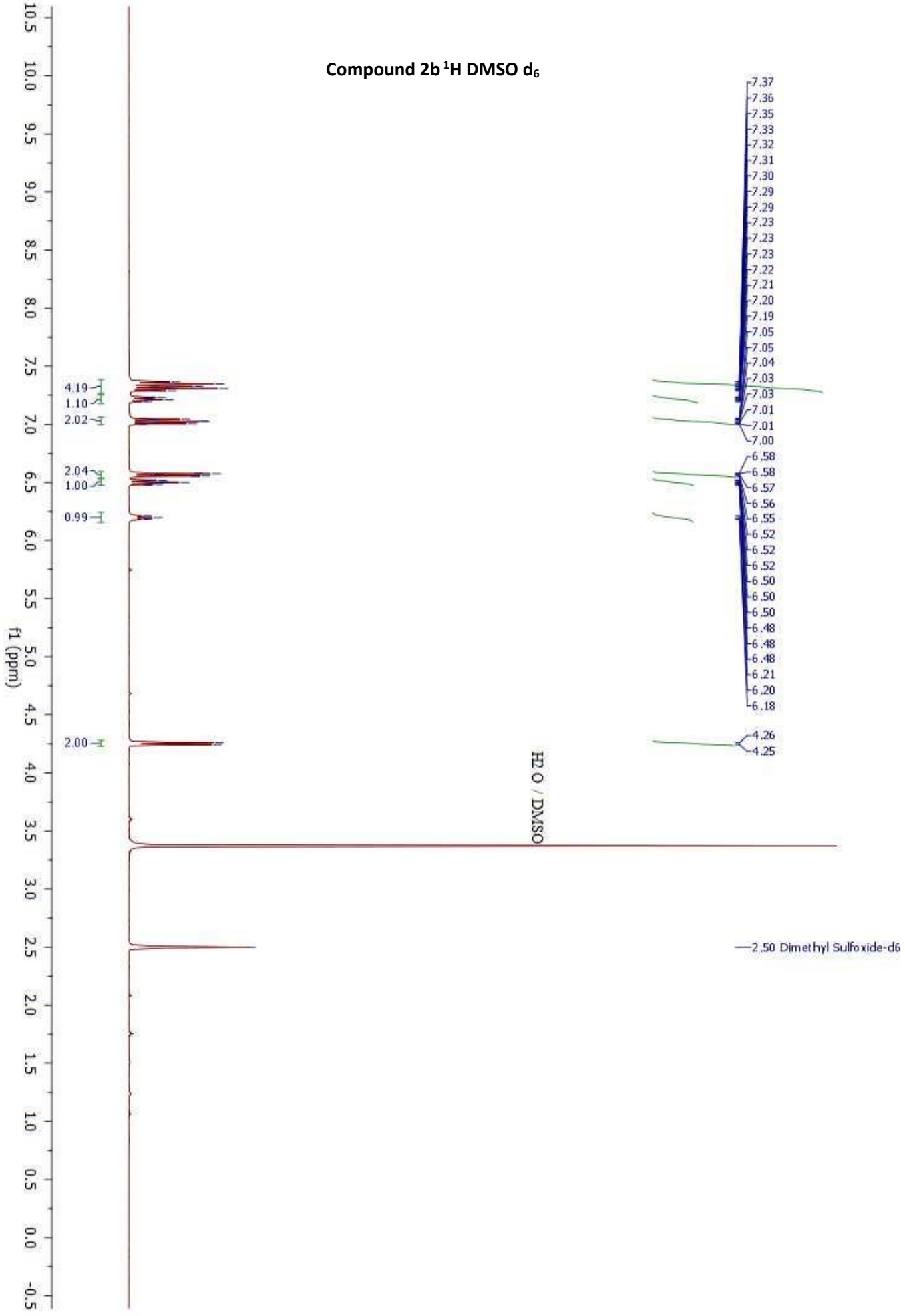
## 6. $^{1}H$ and $^{13}C$ NMR spectra of isolated amines



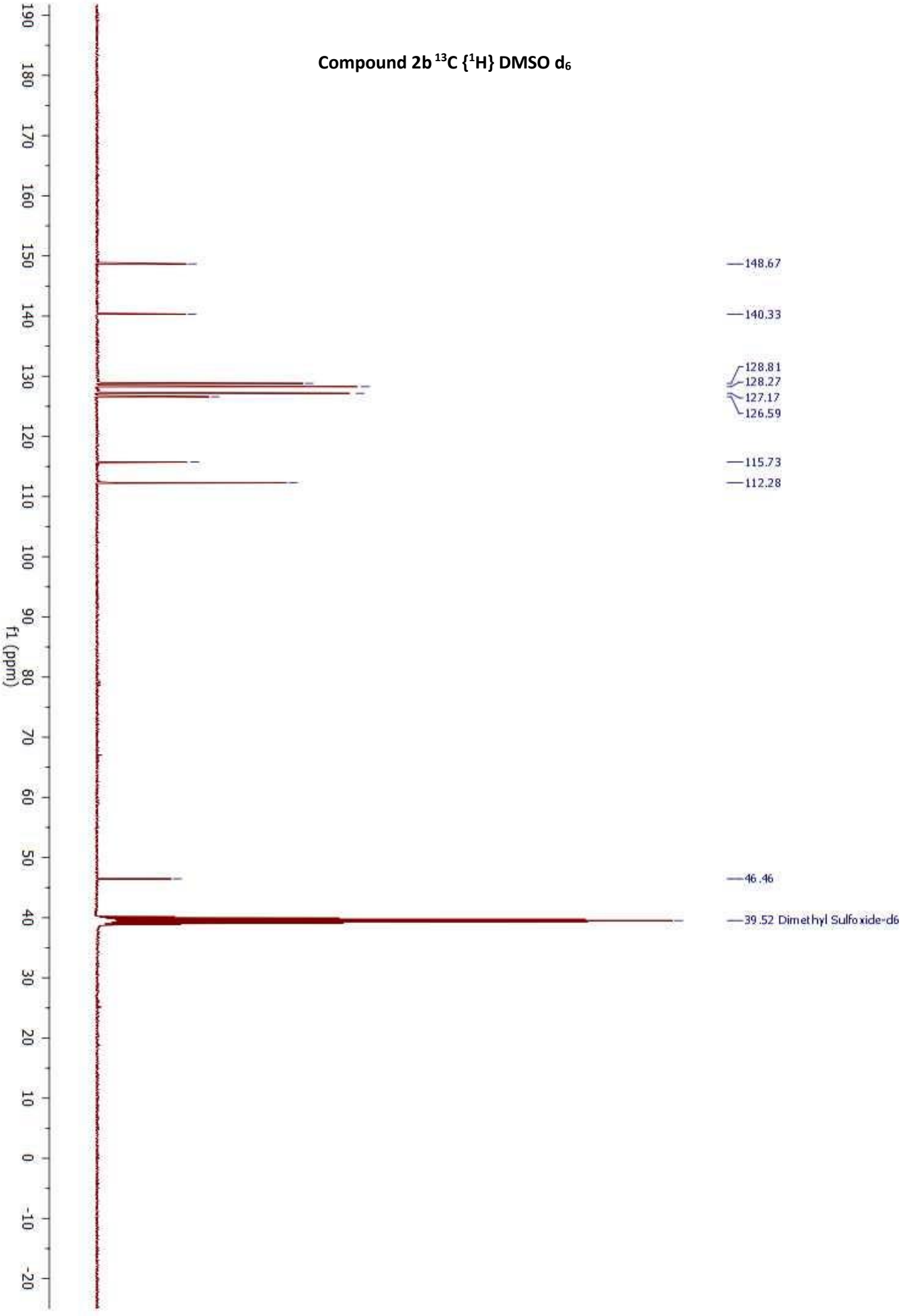
**Compound 2a $^{13}C$ {$^{1}H$} $CDCl_3$**



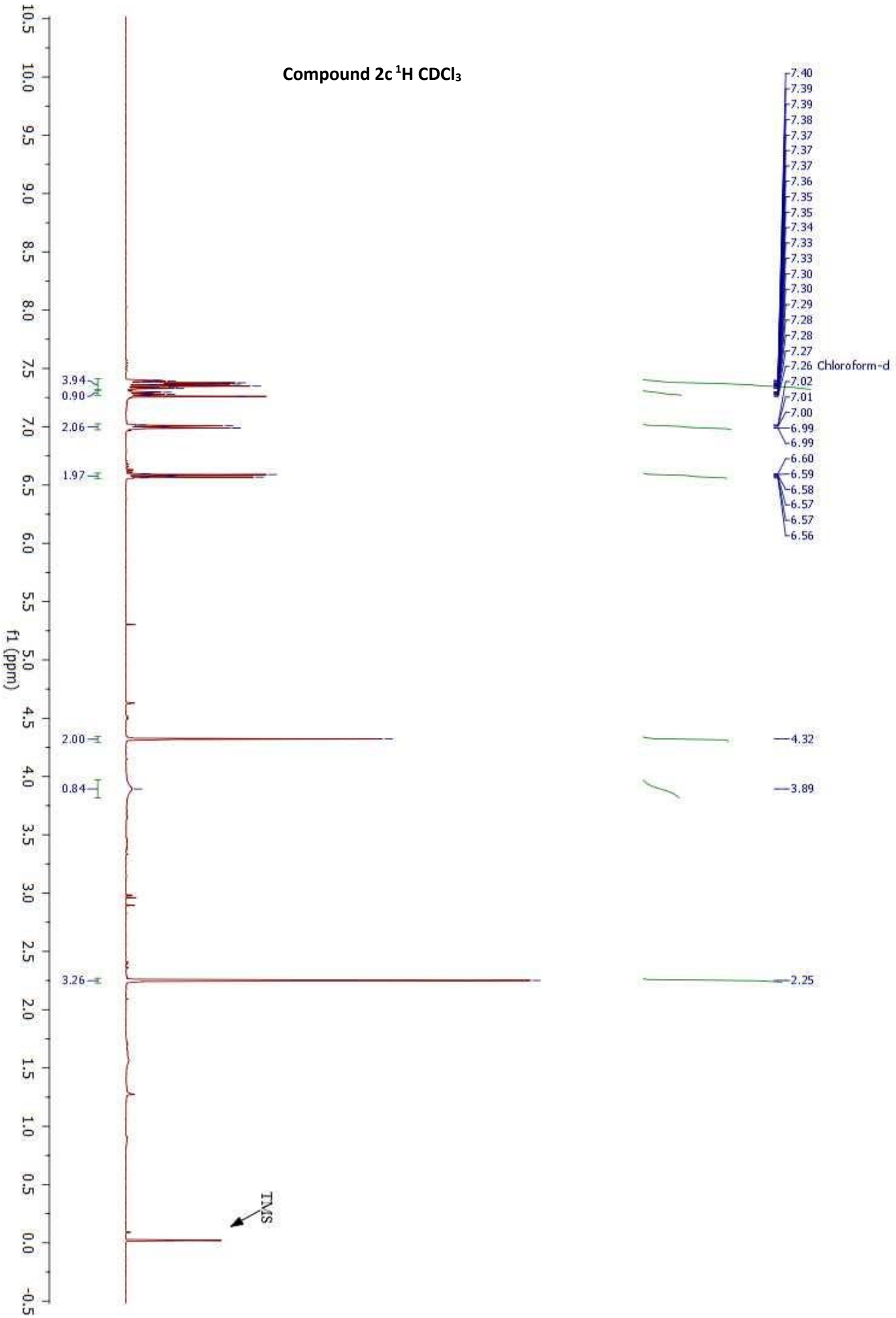
**Compound 2b $^{1}$H DMSO $d_6$**



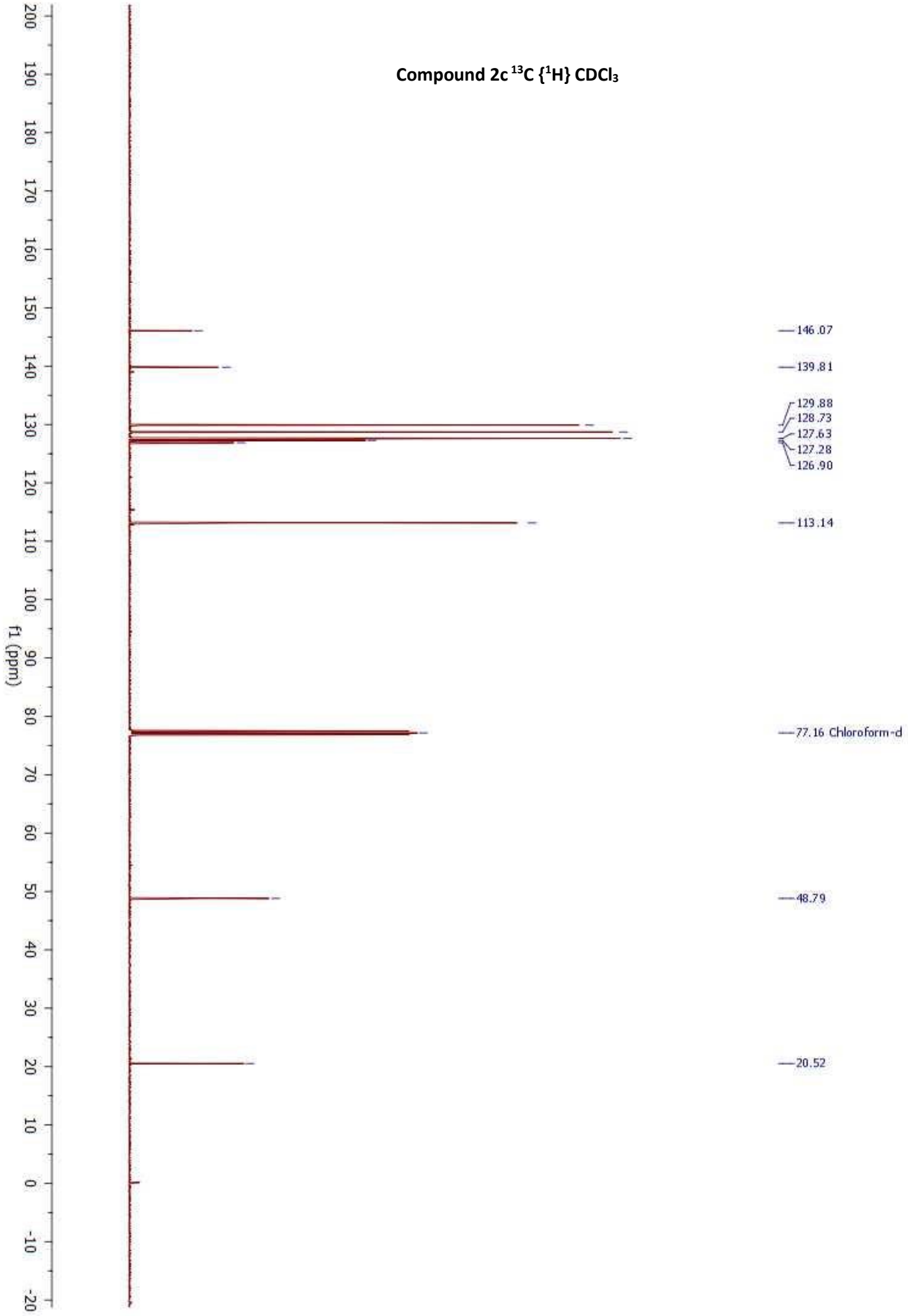
**Compound 2b $^{13}C$ {$^{1}H$} DMSO $d_6$**



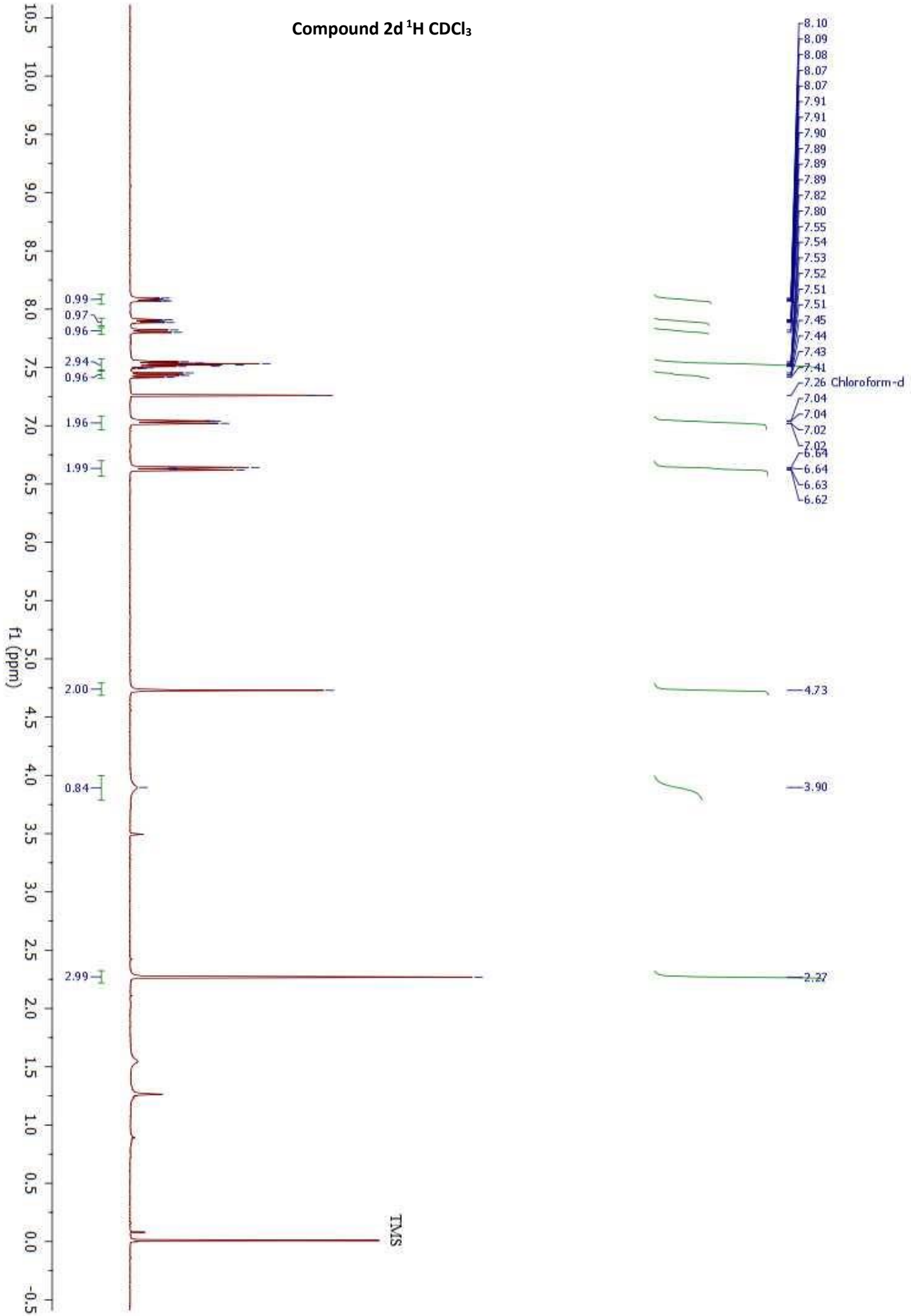
**Compound 2c $^{1}$H $CDCl_3$**



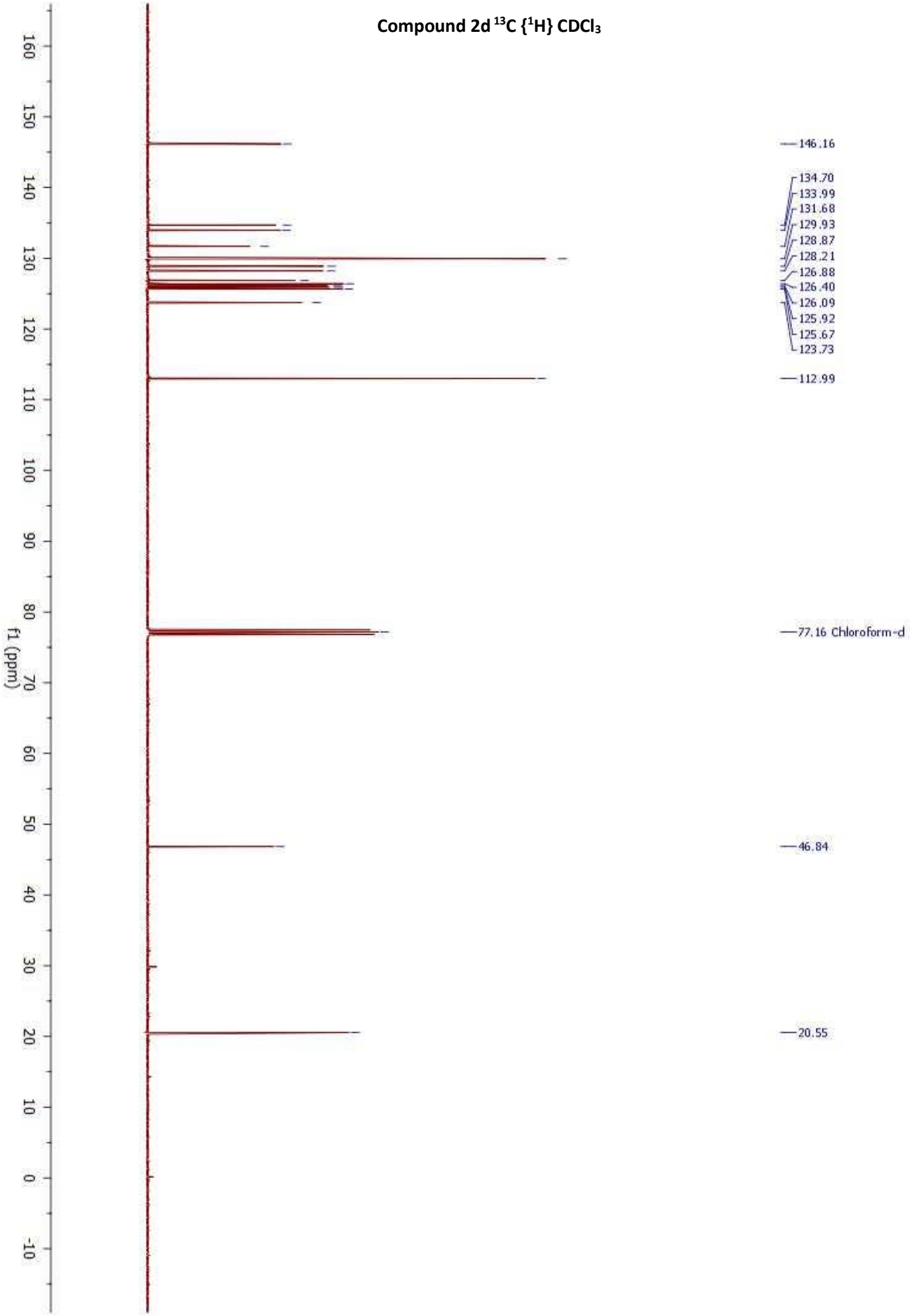
**Compound 2c $^{13}C$ {$^{1}H$} $CDCl_3$**



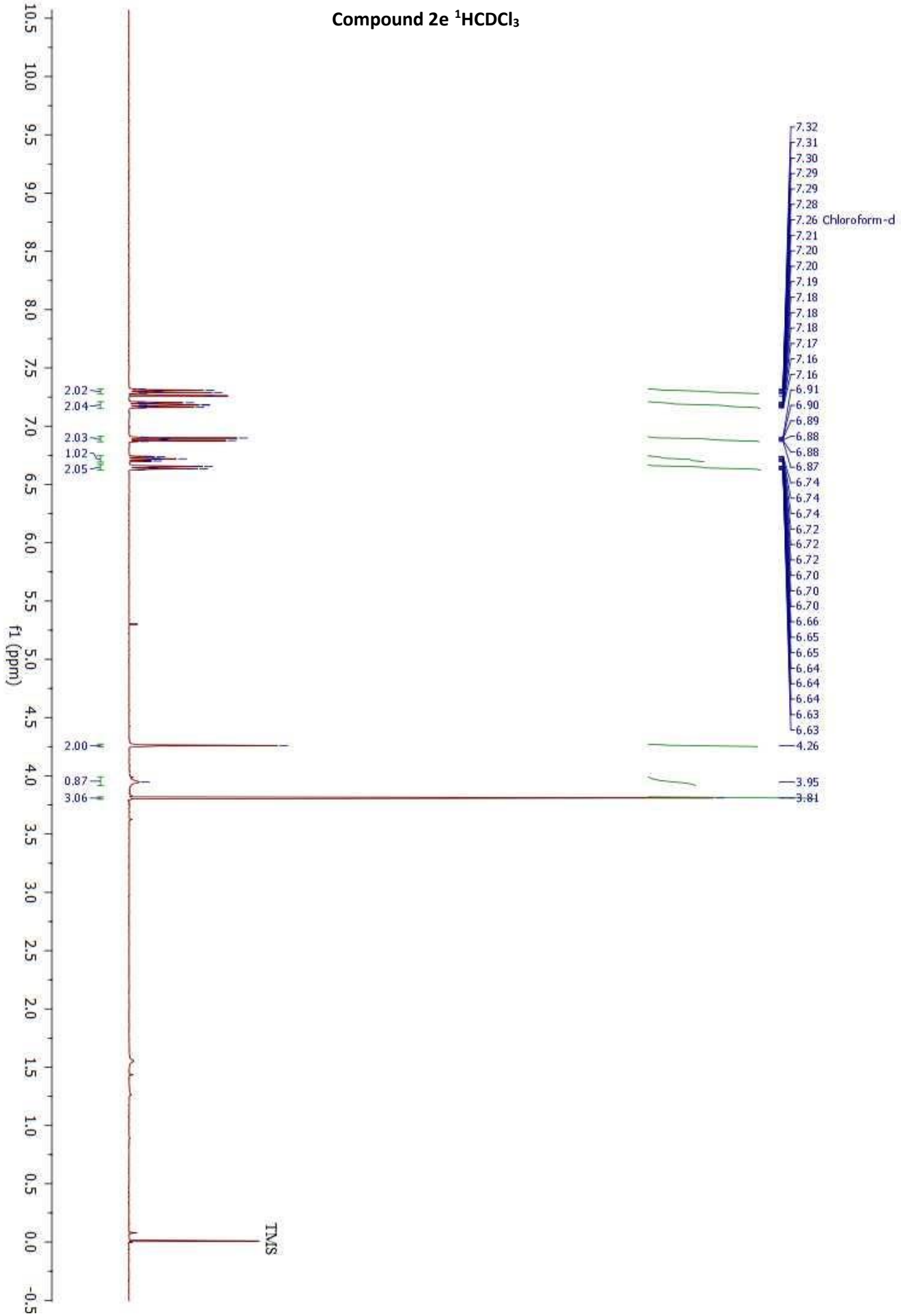
**Compound 2d $^{1}$H $CDCl_3$**



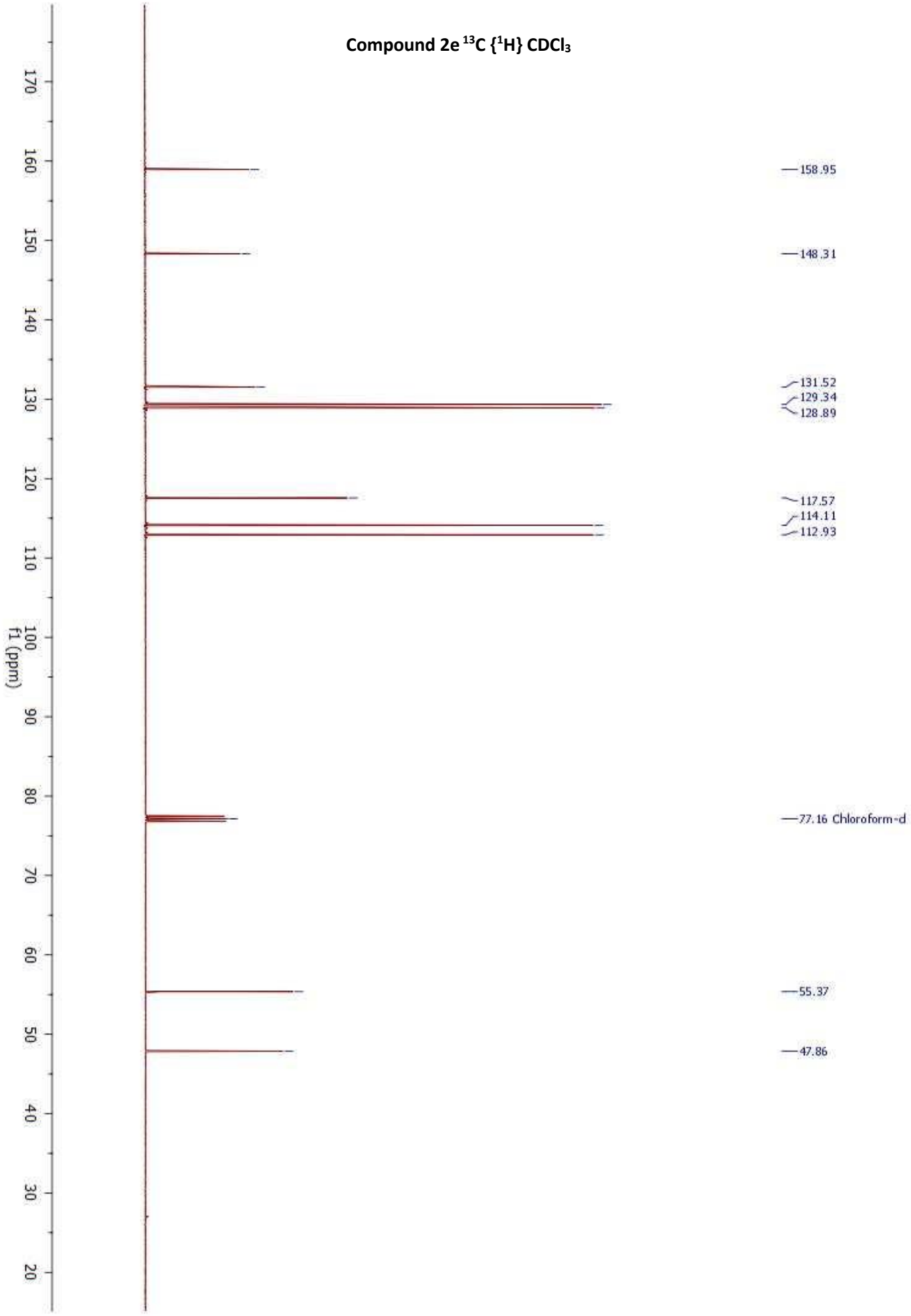
**Compound 2d $^{13}C$ {$^{1}H$} $CDCl_3$**



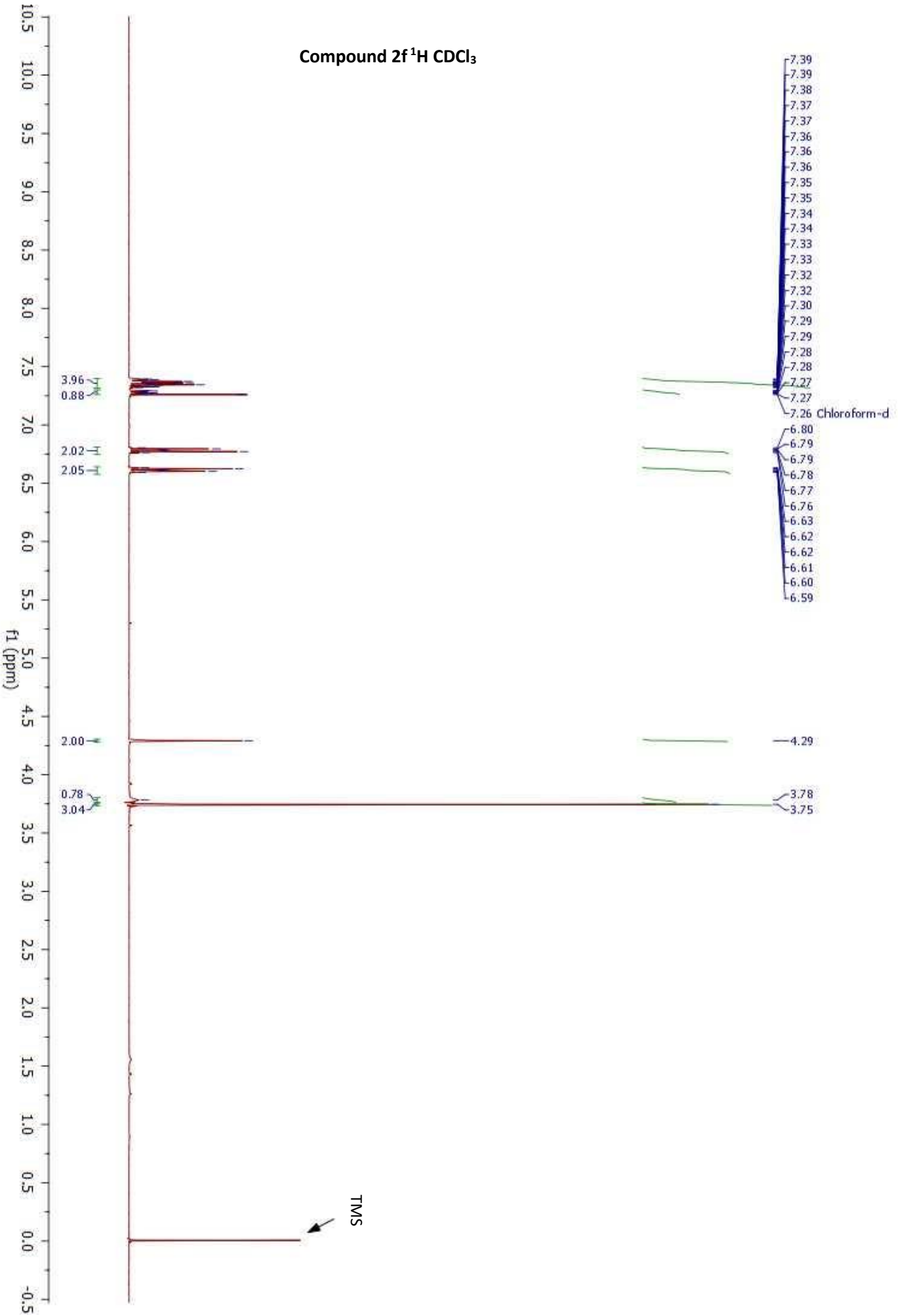
**Compound 2e $^{1}HCDCl_3$**



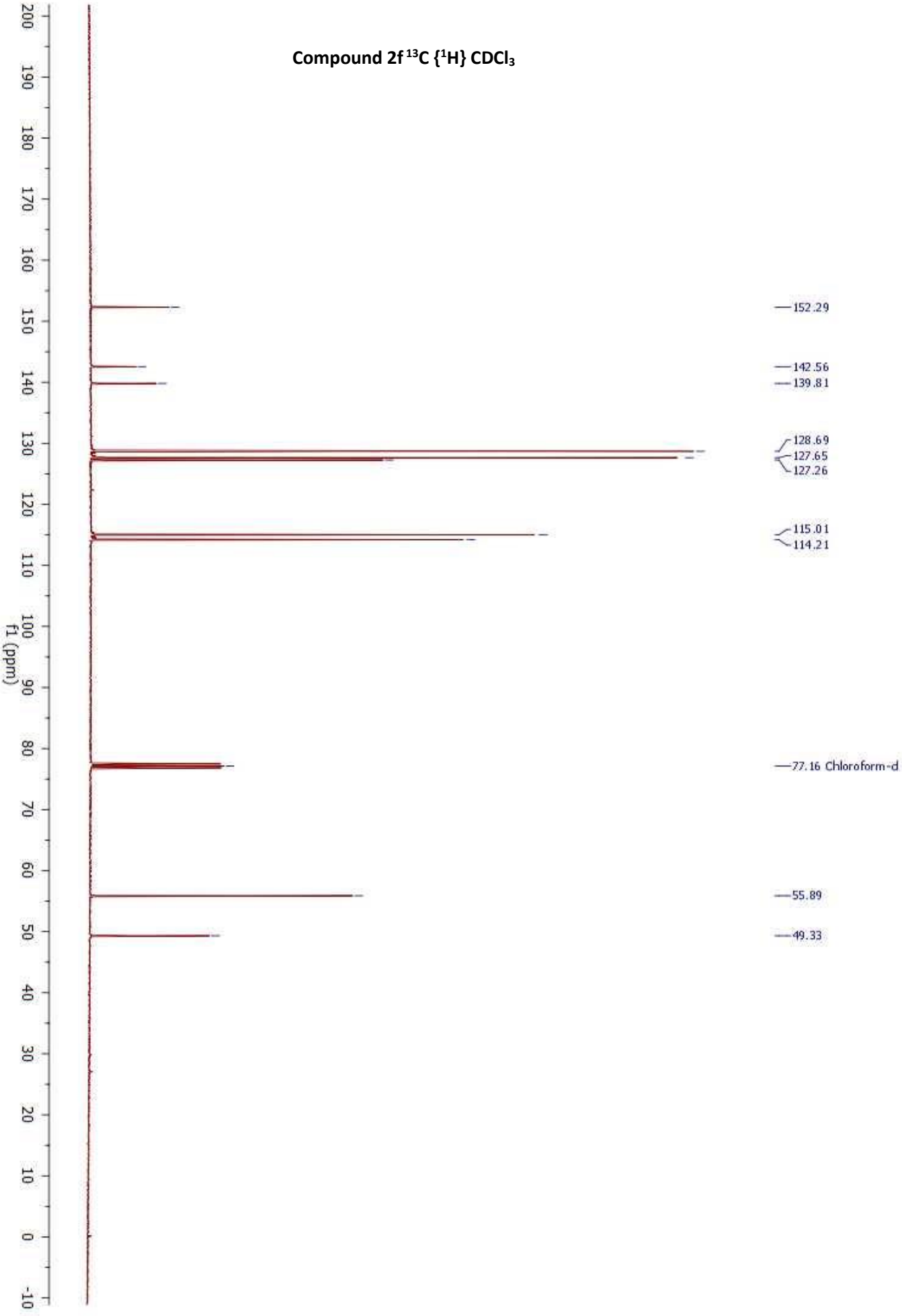
**Compound 2e $^{13}C$ {$^{1}H$} $CDCl_3$**



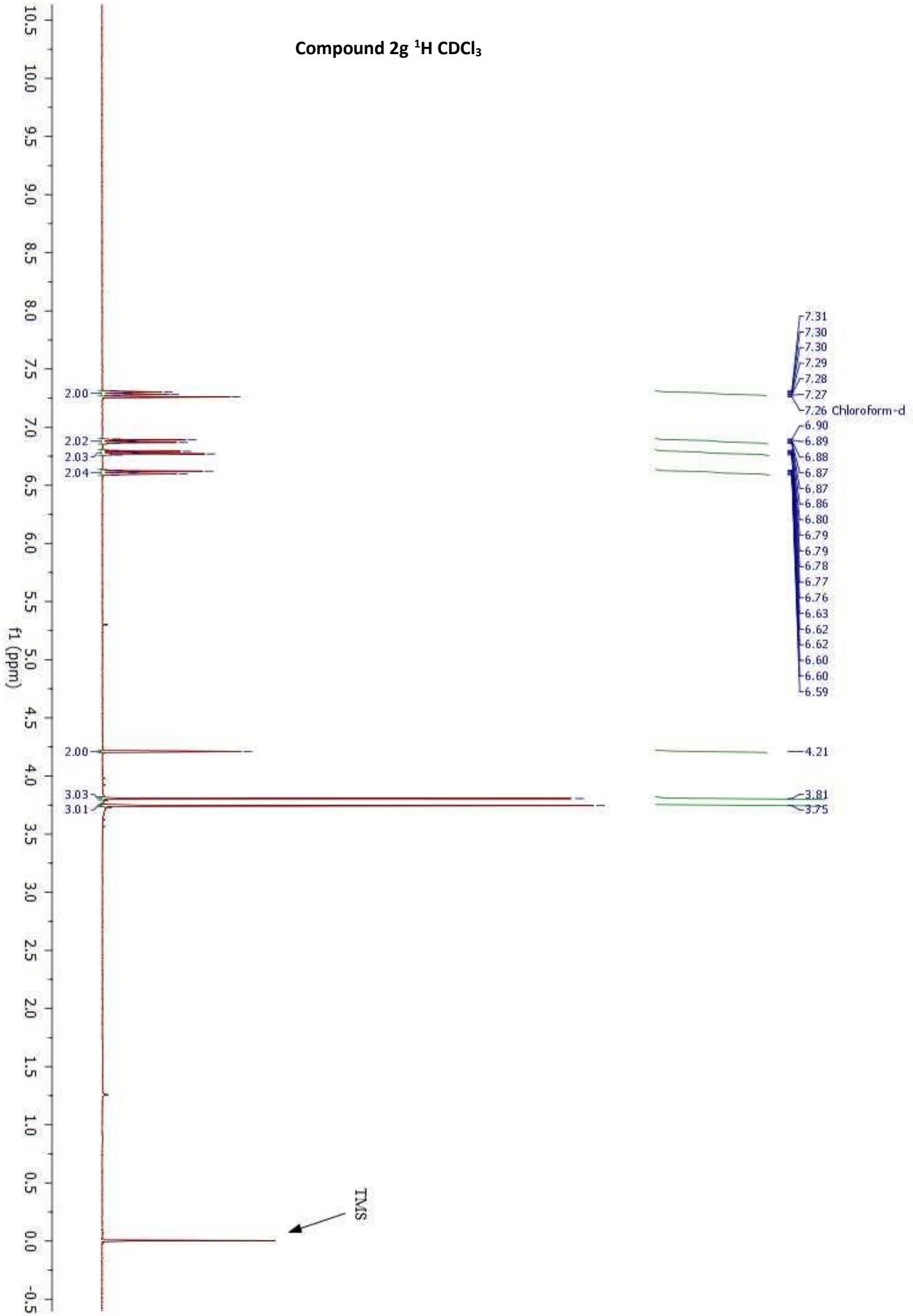
**Compound 2f $^{1}$H $CDCl_3$**



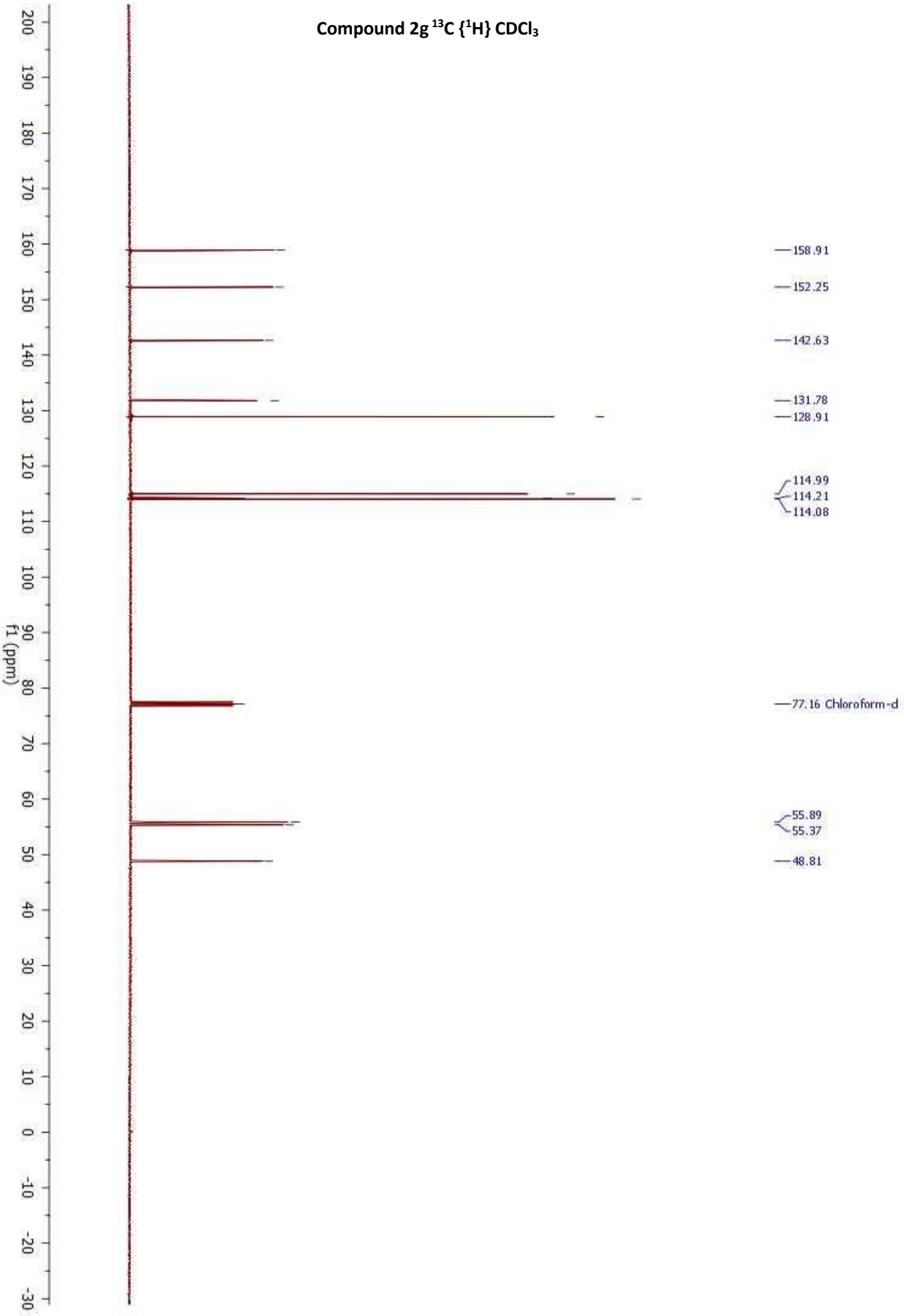
**Compound 2f $^{13}C$ {$^{1}H$} $CDCl_3$**



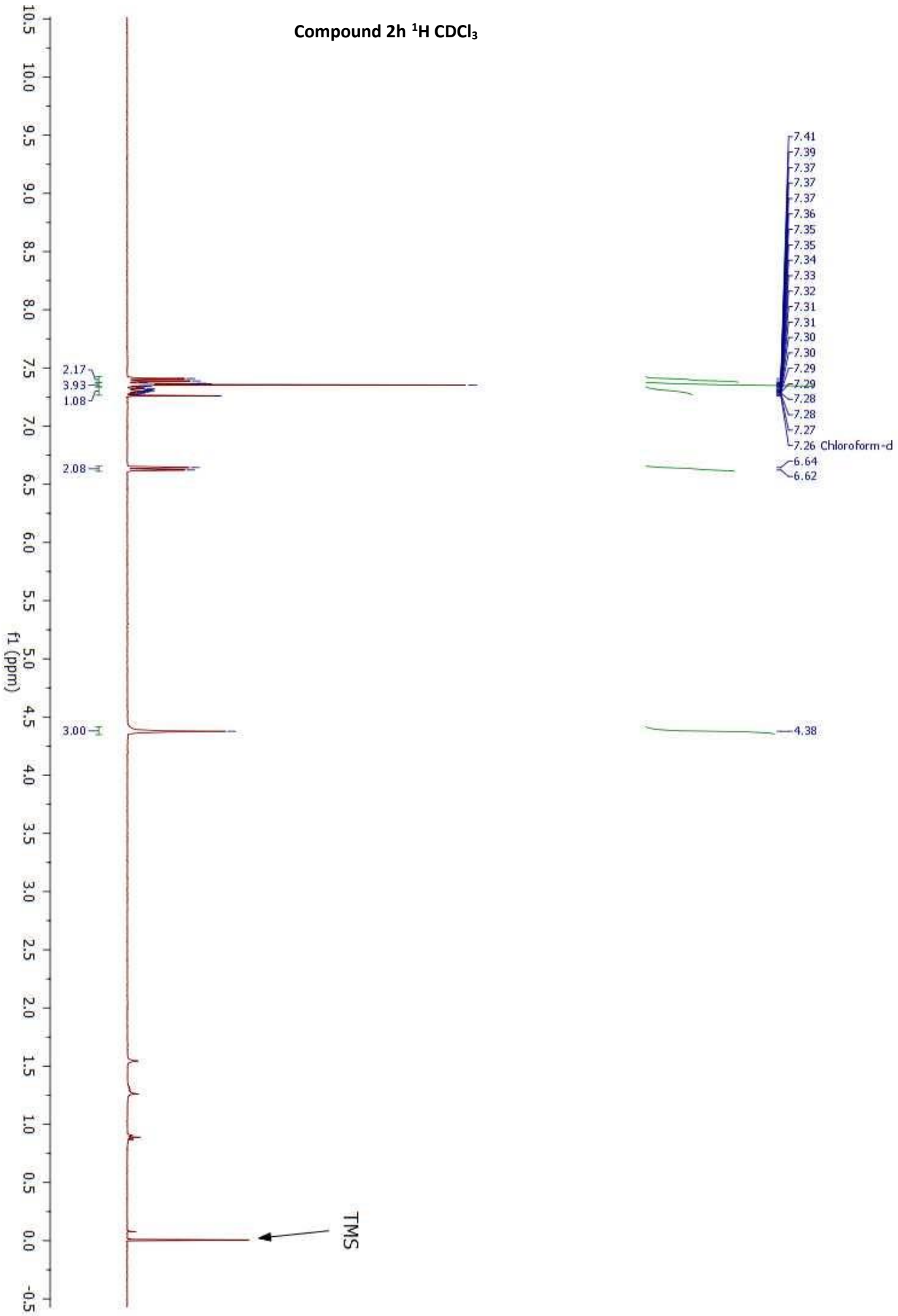
**Compound 2g $^{1}H$ $CDCl_3$**



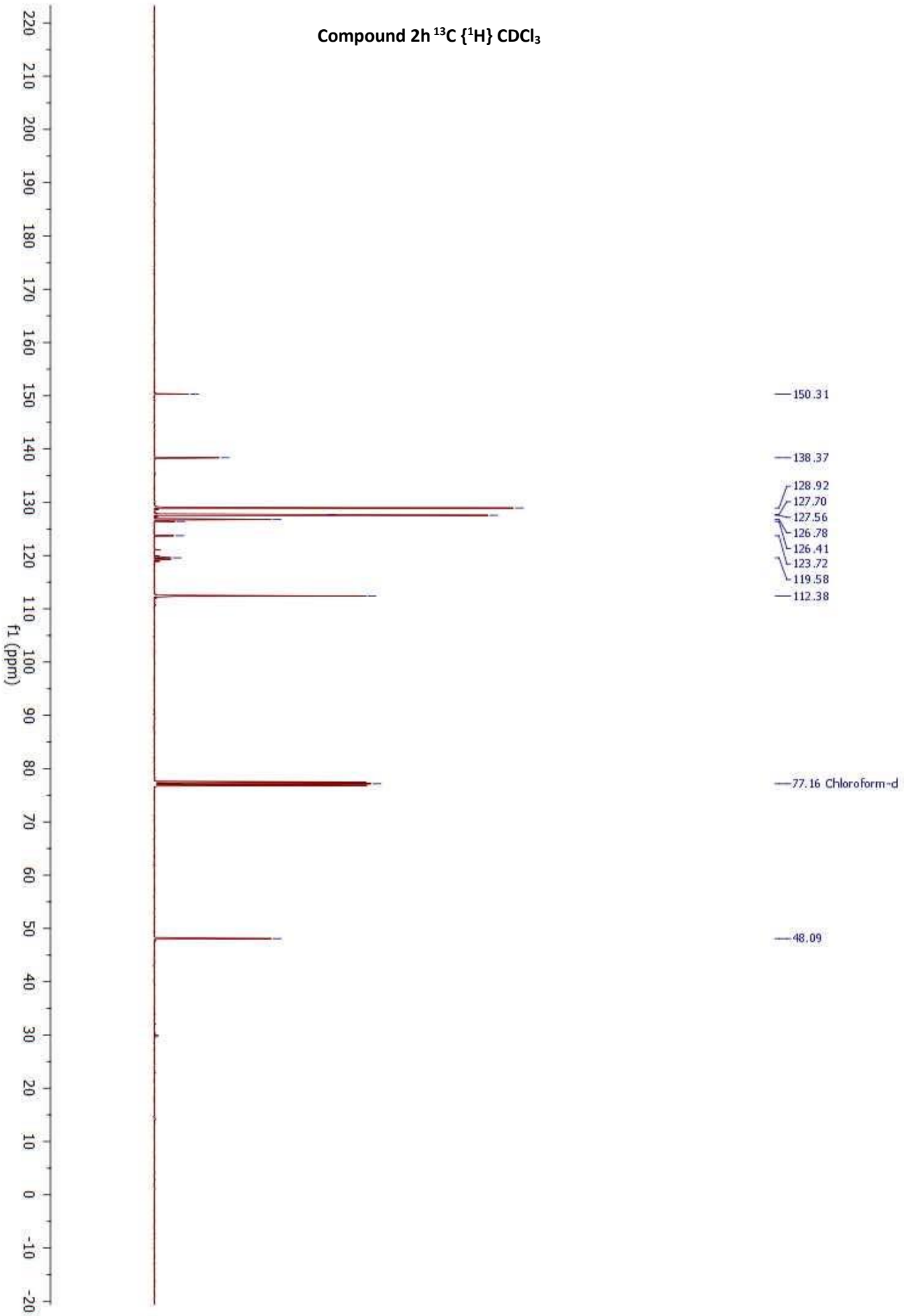
**Compound 2g $^{13}C$ {$^{1}H$} $CDCl_3$**



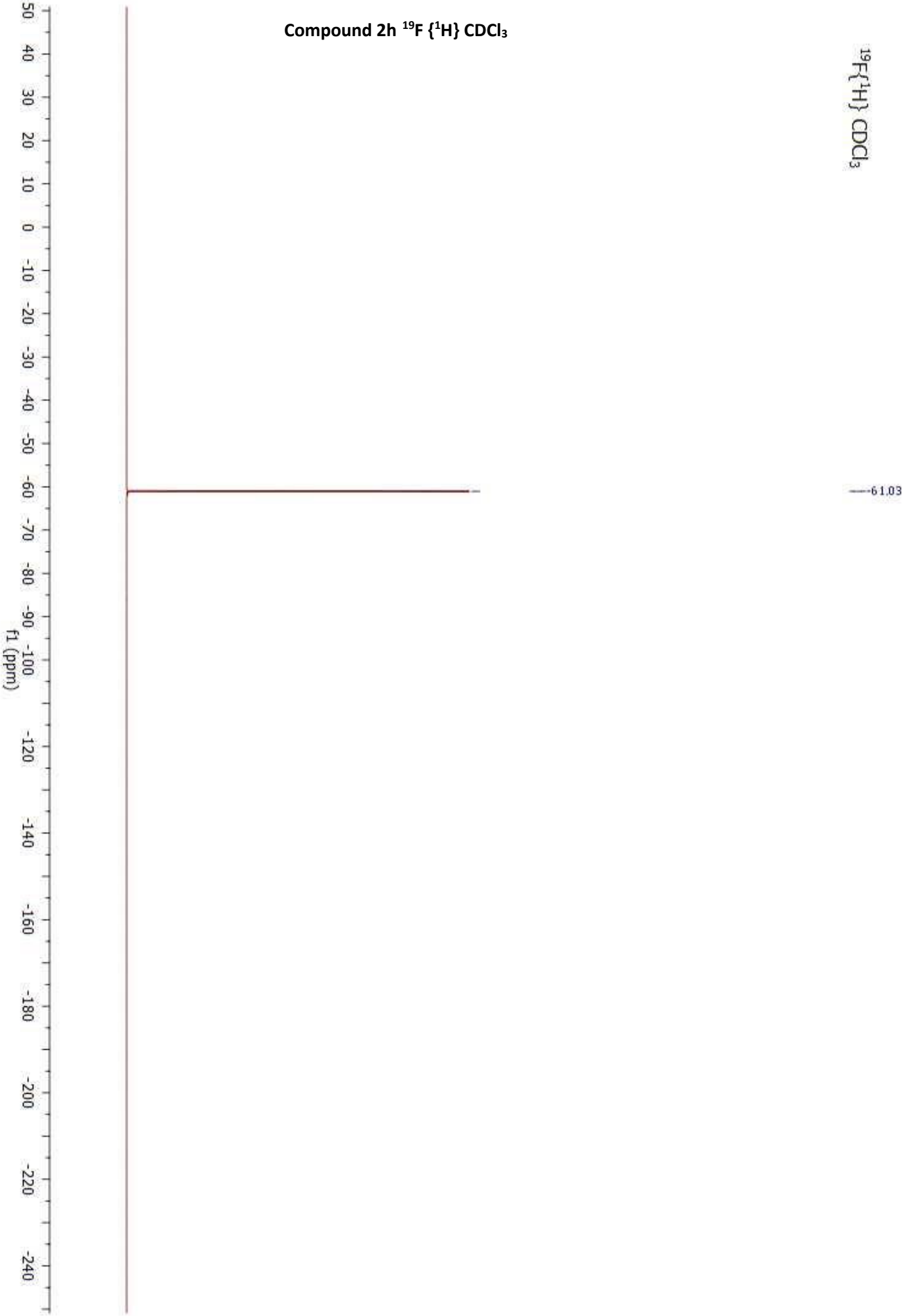
**Compound 2h $^{1}H$ $CDCl_3$**



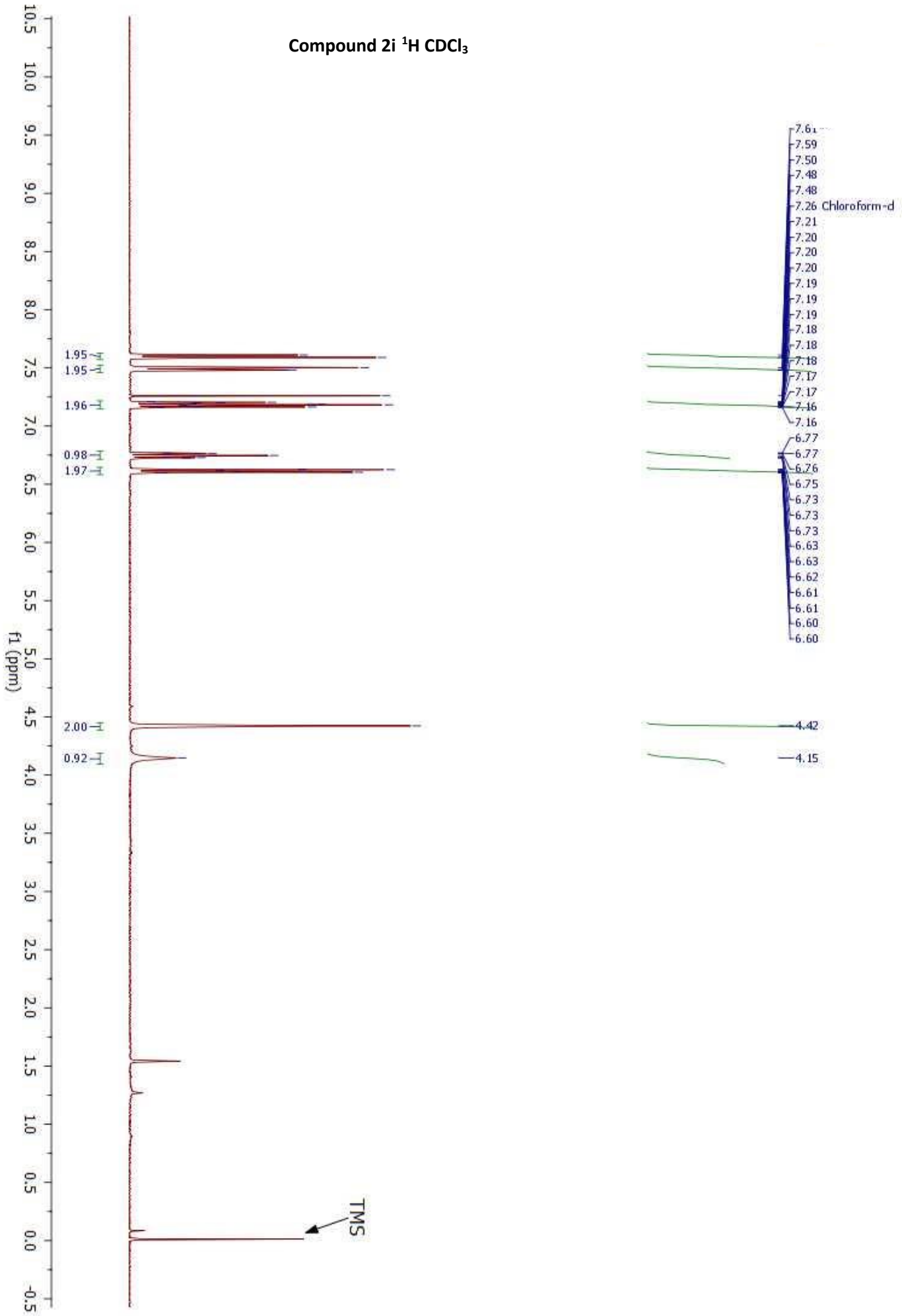
**Compound 2h $^{13}C$ {$^{1}H$} $CDCl_3$**



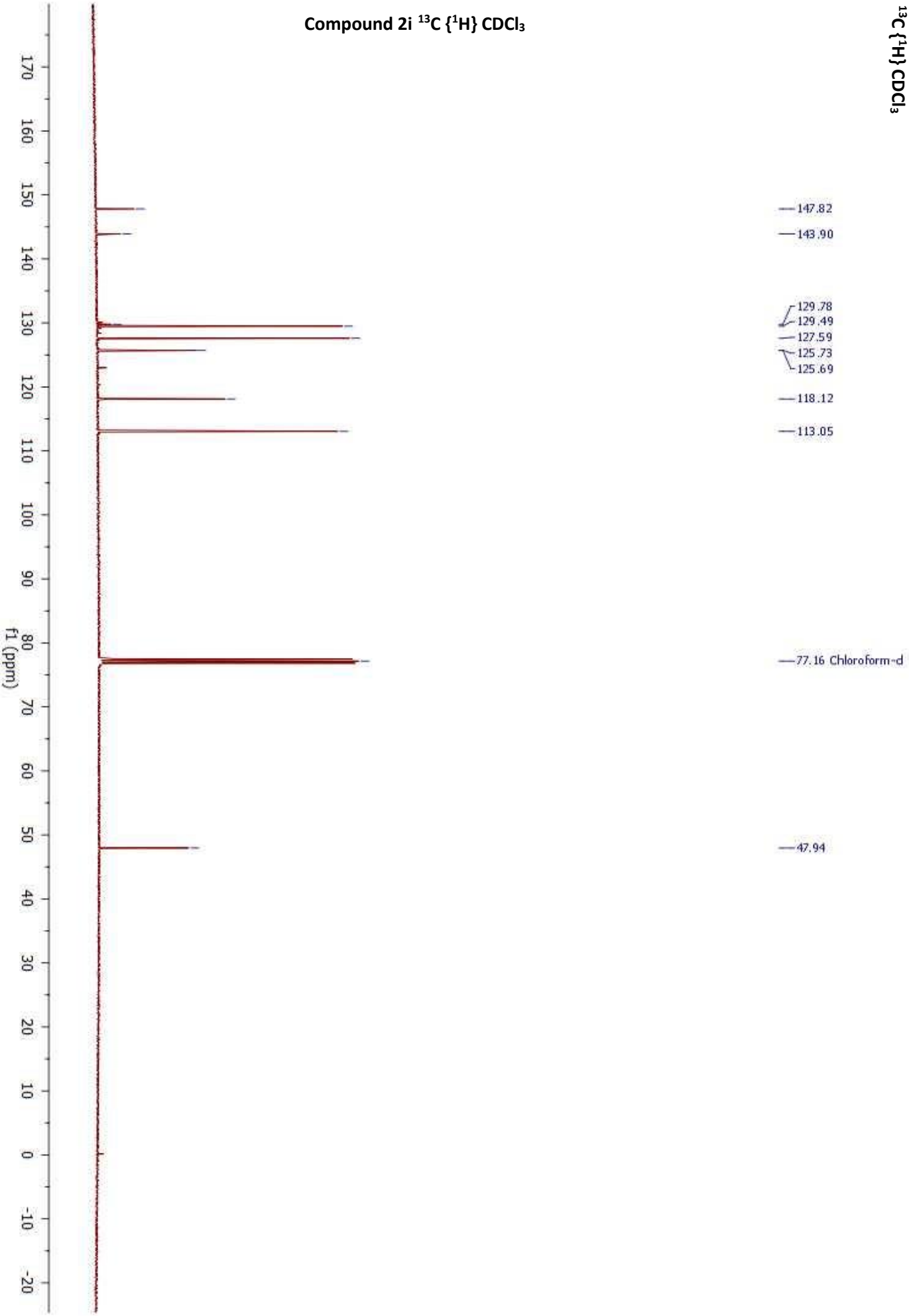
**Compound 2h $^{19}F$ {$^{1}H$} $CDCl_3$**



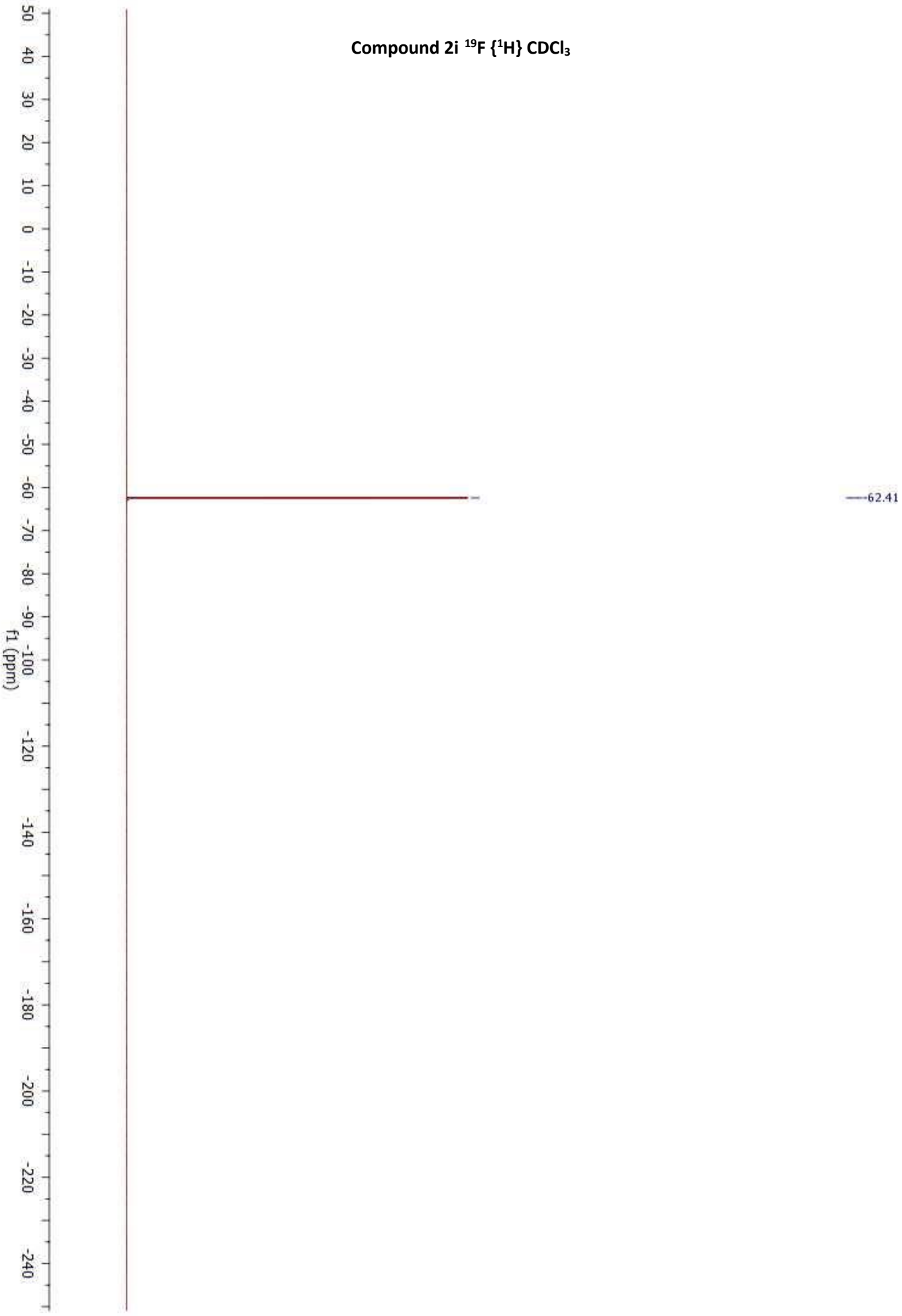
**Compound 2i $^{1}H$ $CDCl_3$**



**Compound 2i $^{13}C$ {$^{1}H$} $CDCl_3$**



**Compound 2i $^{19}F$ {$^{1}H$} $CDCl_3$**



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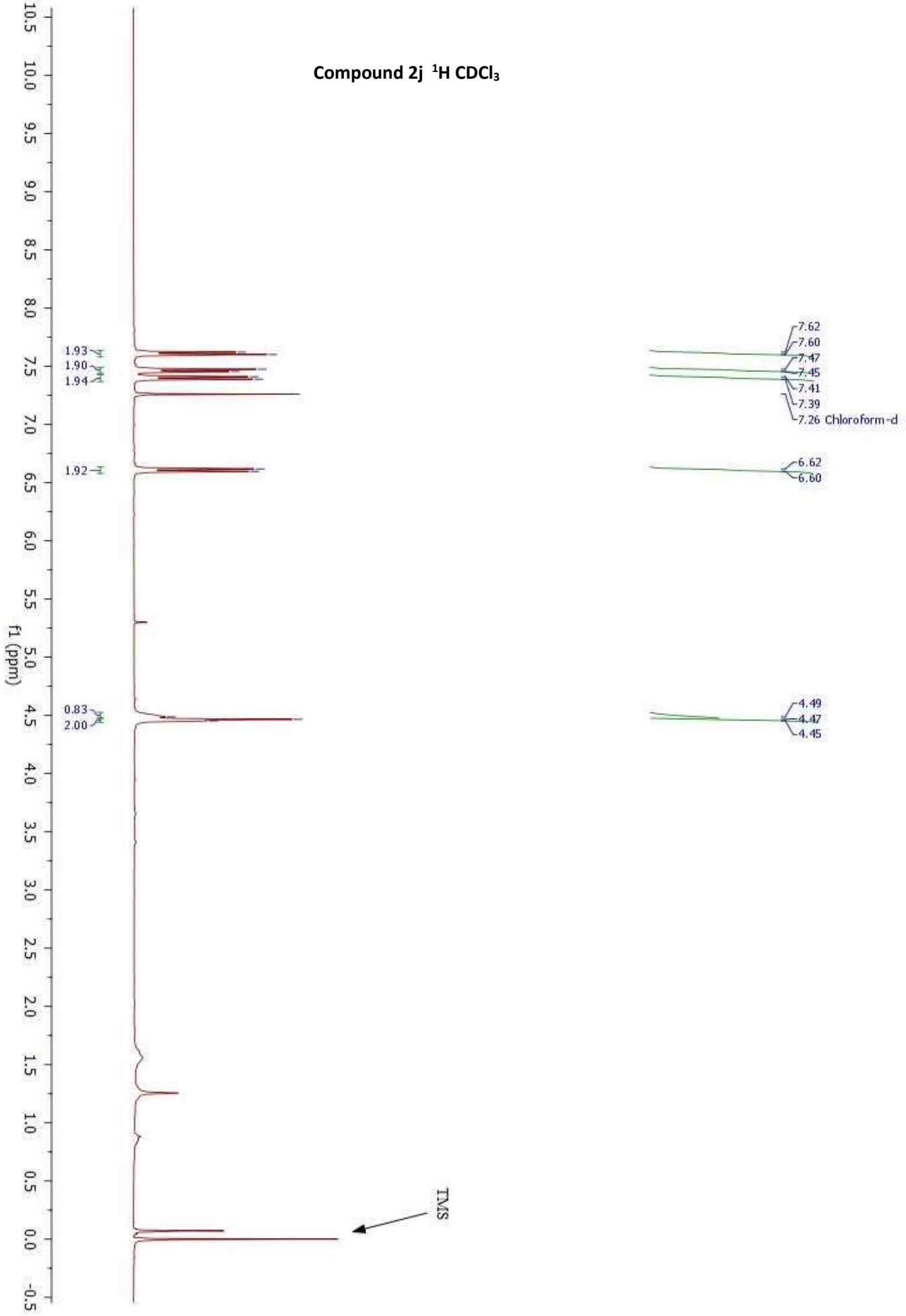

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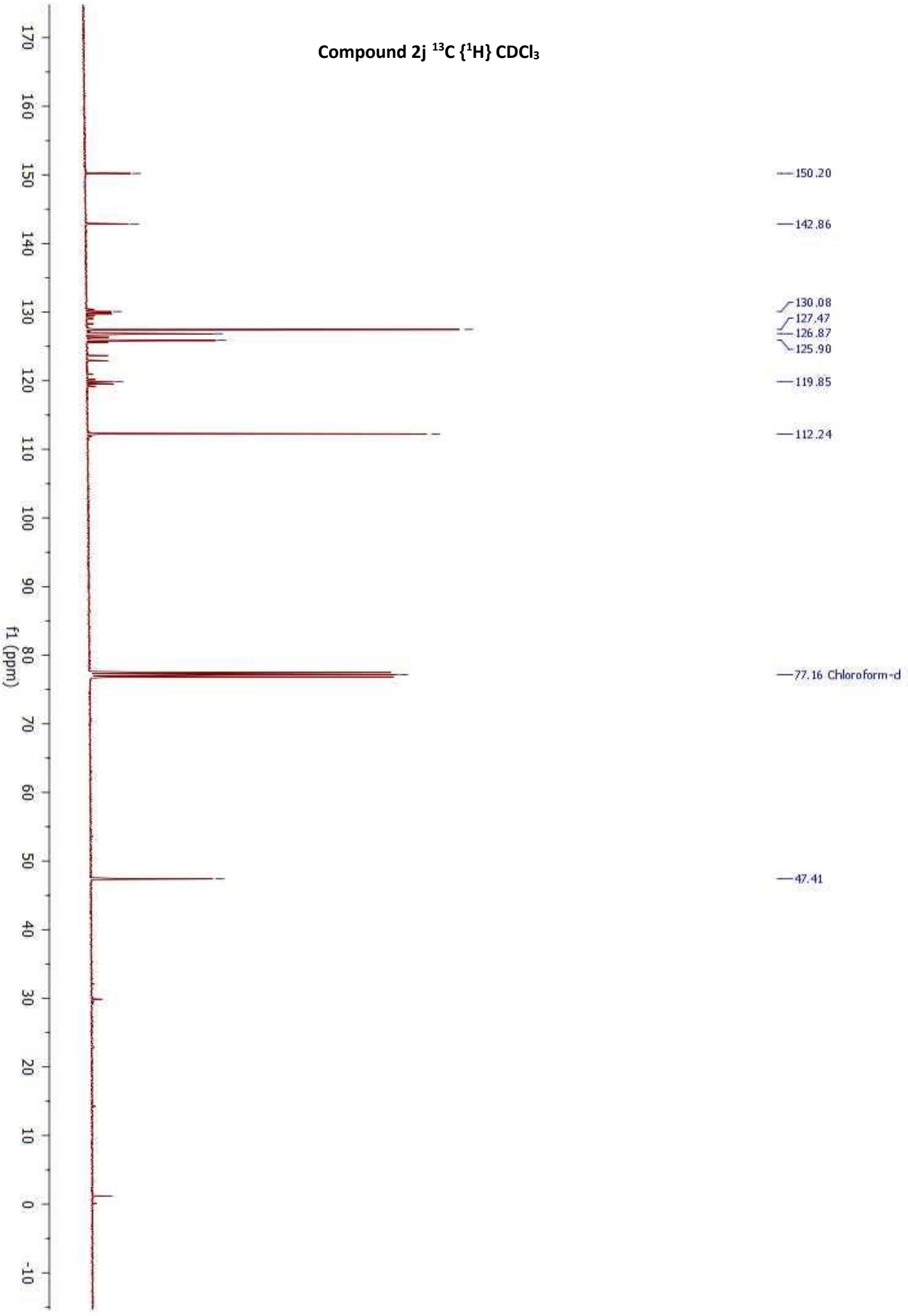
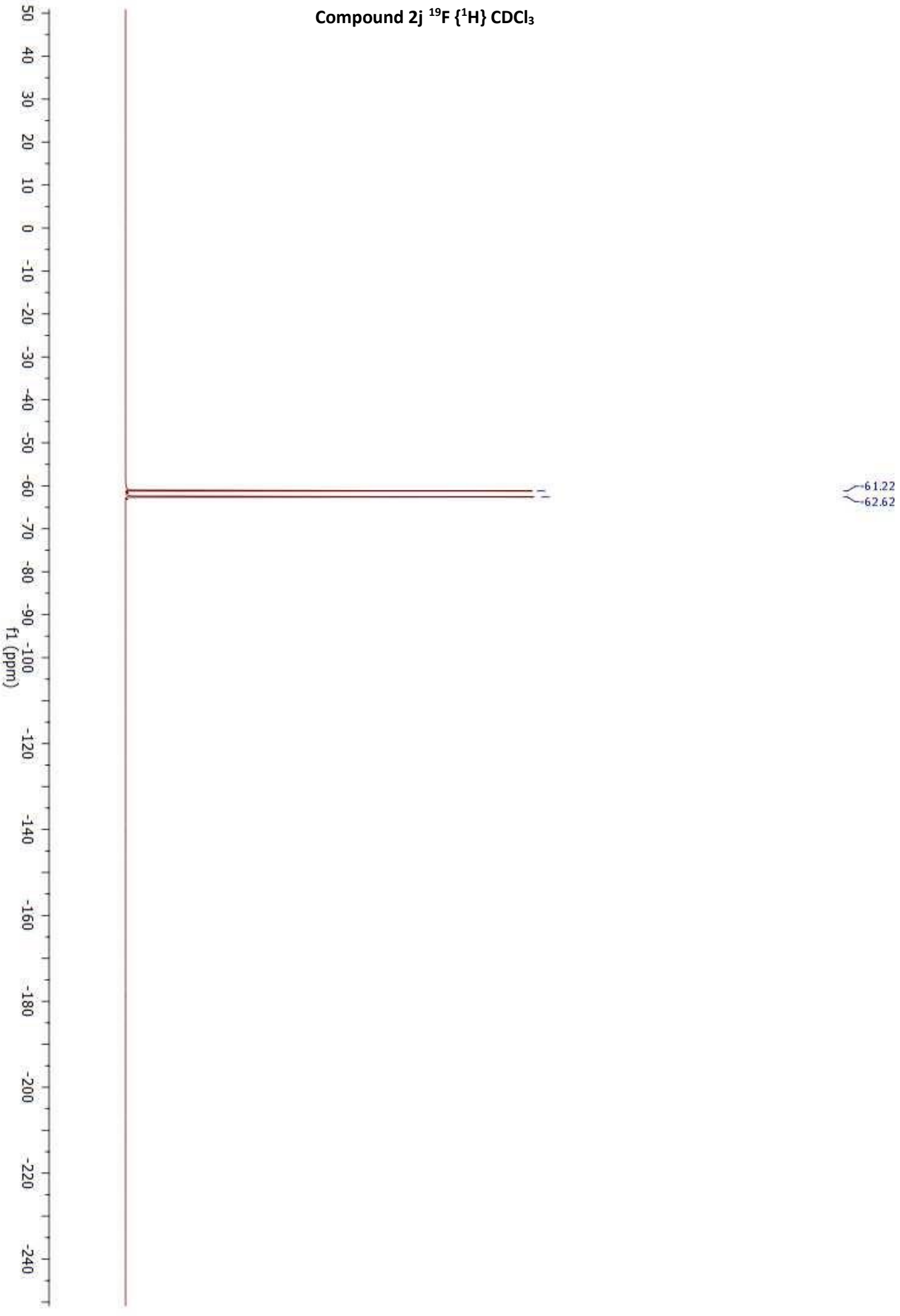


**Compound 2j $^{19}F$ {$^{1}H$} $CDCl_3$**



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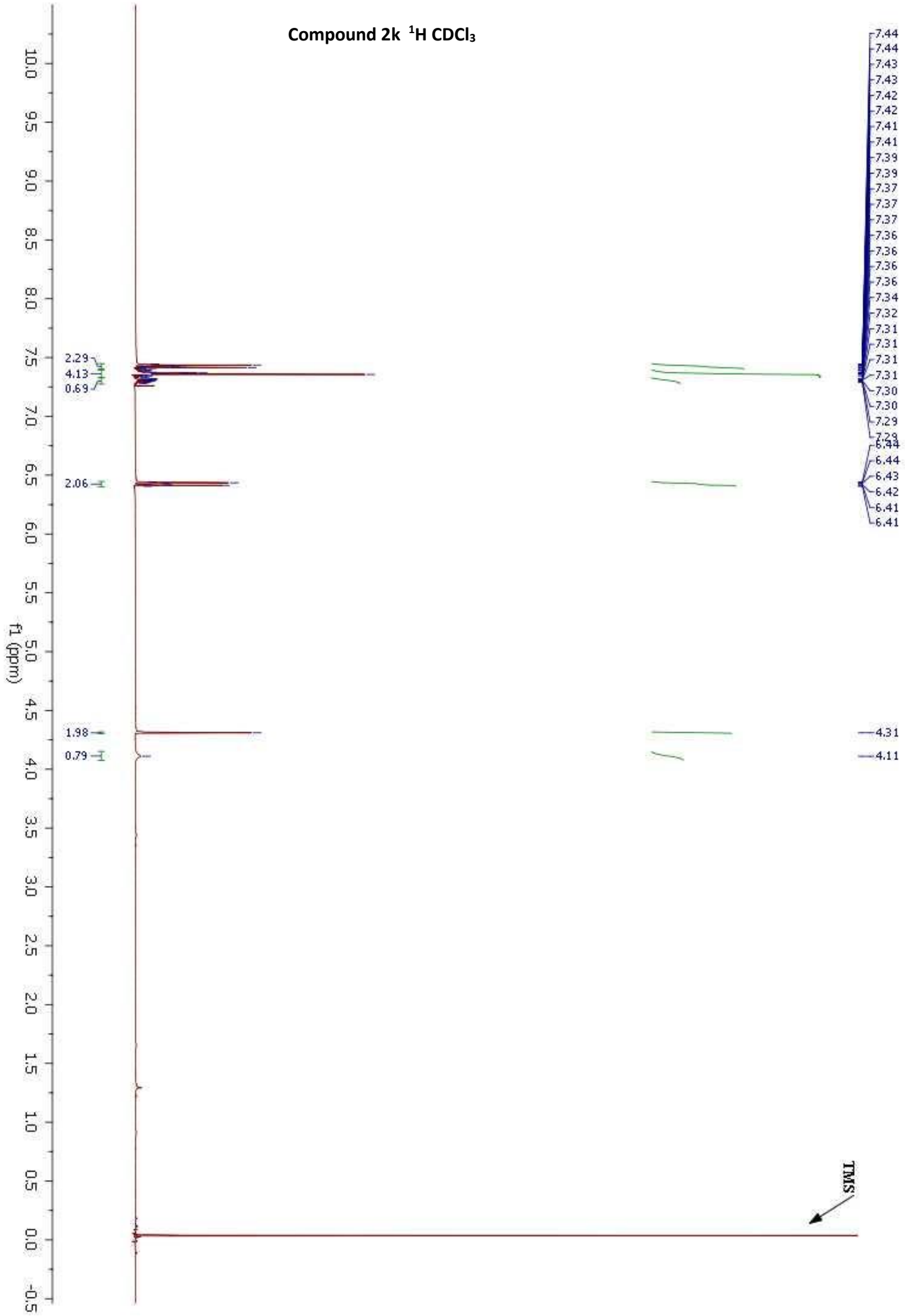
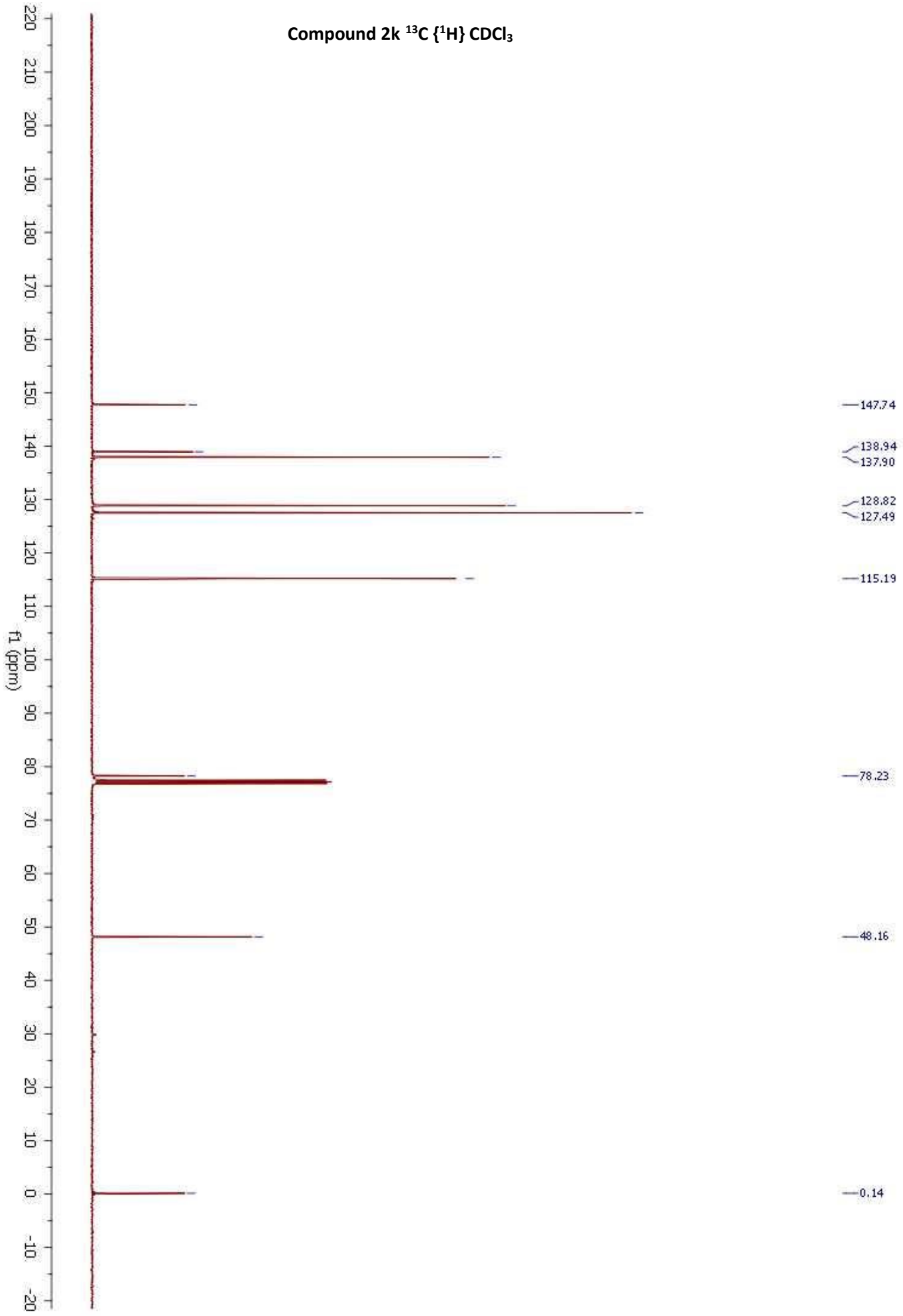


**Compound 2k $^{13}C$ {$^{1}H$} $CDCl_3$**



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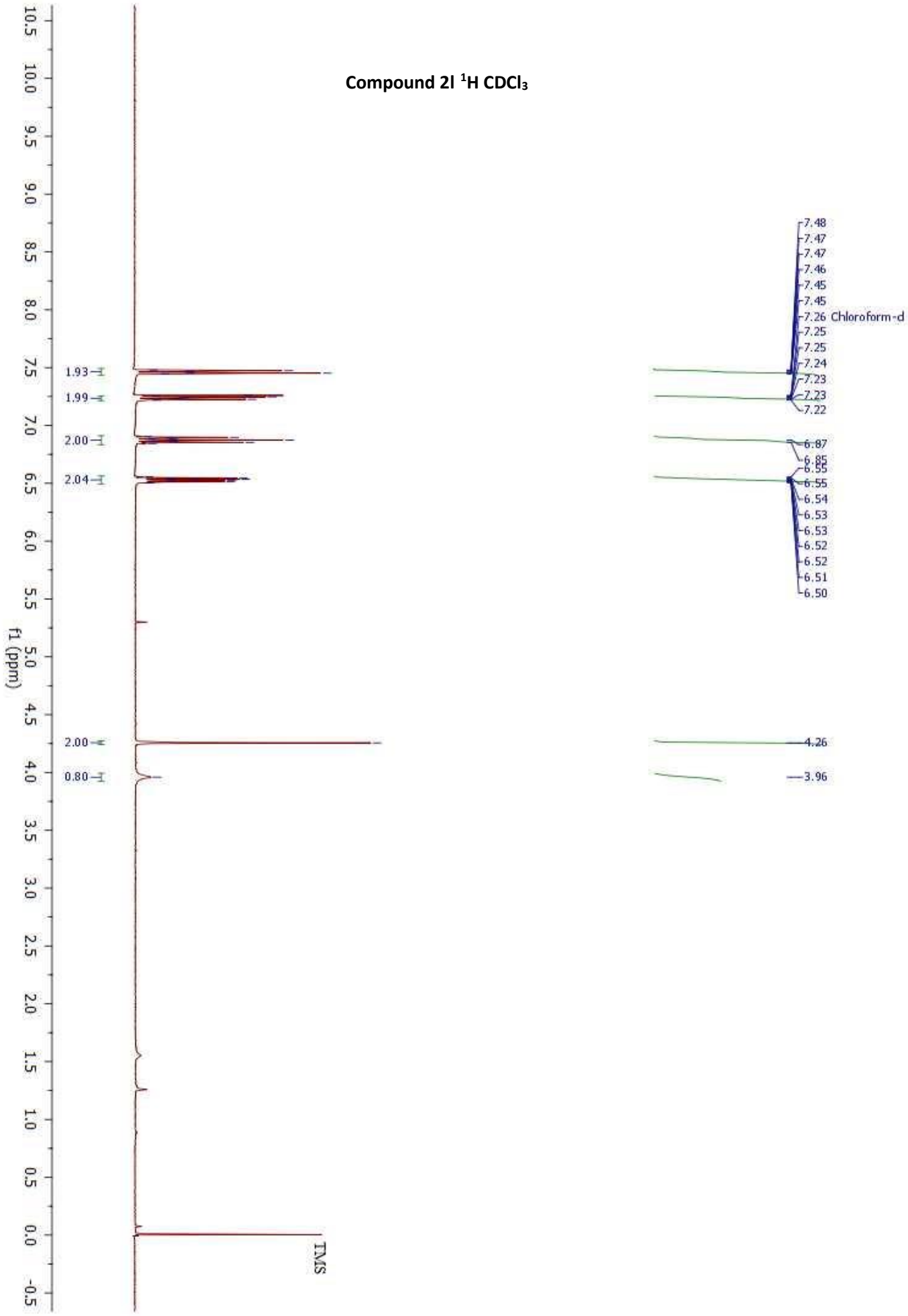

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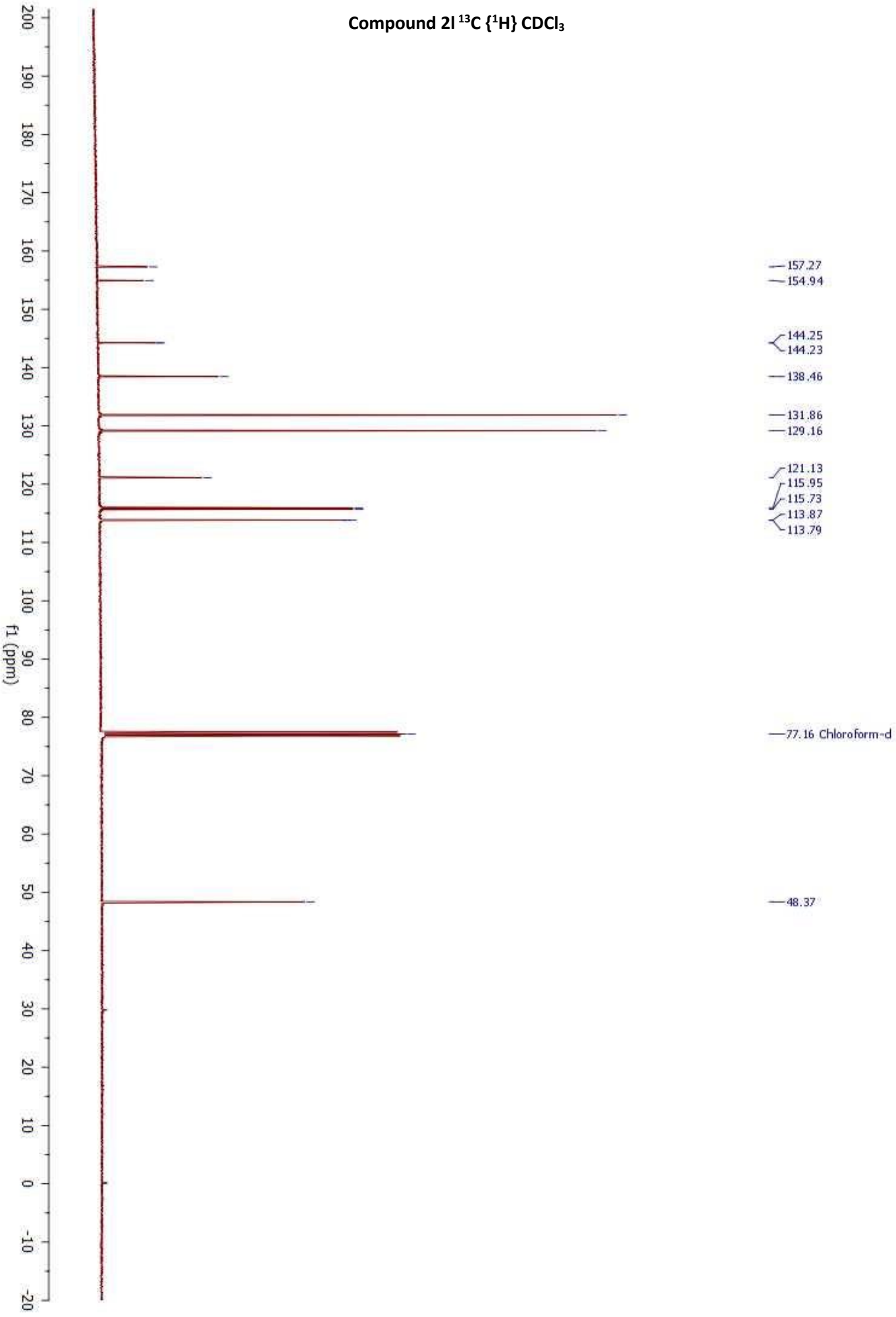

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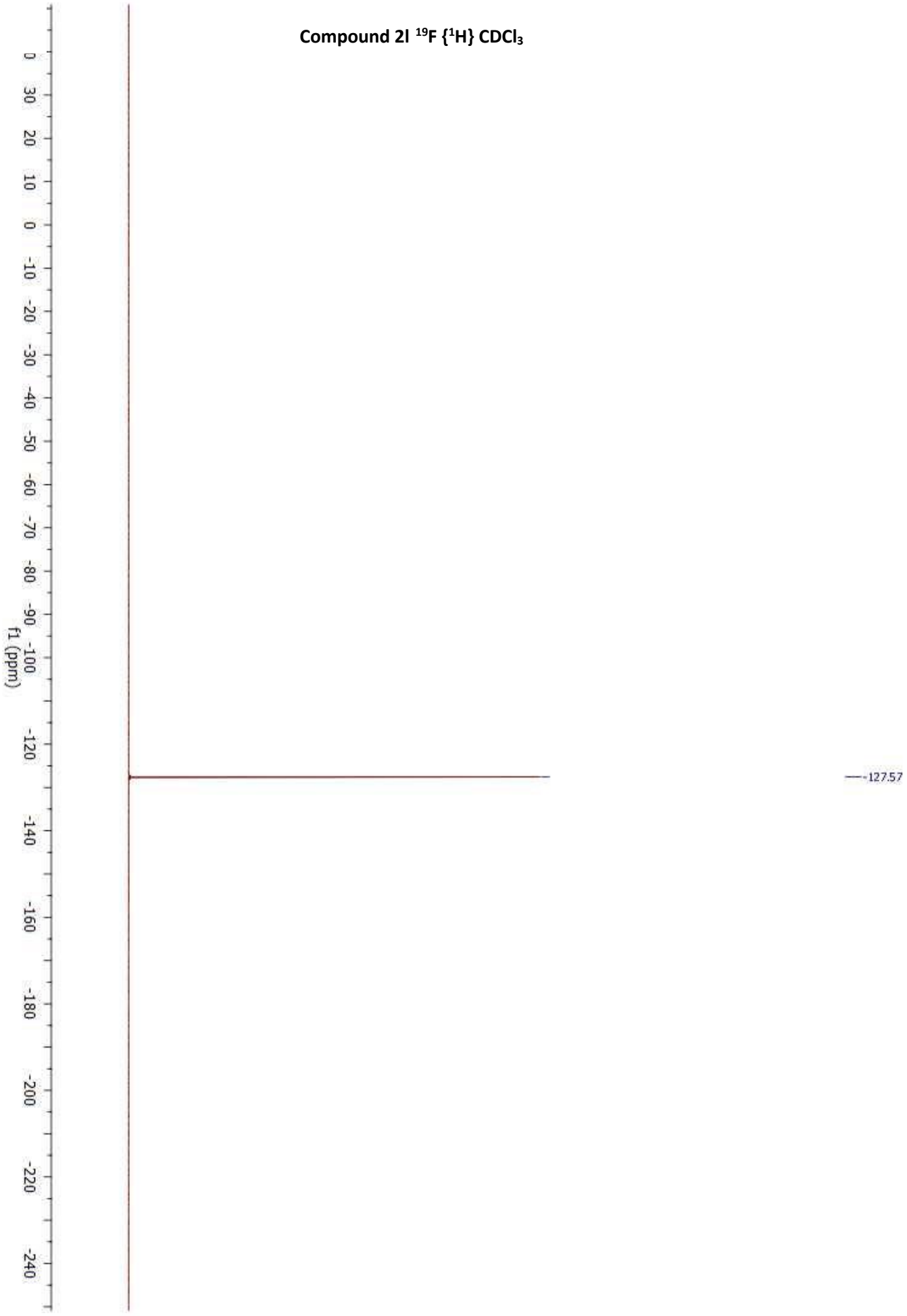
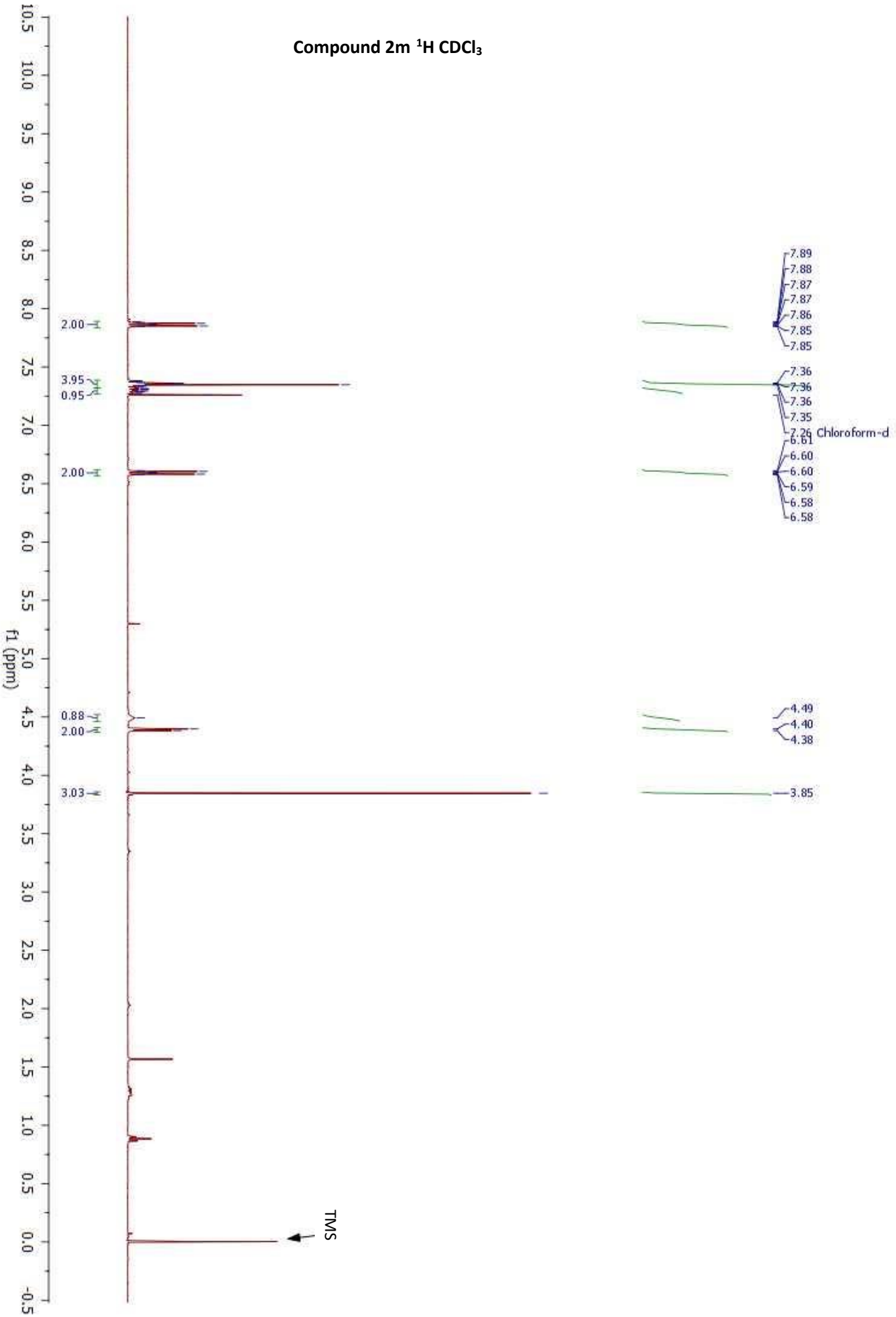
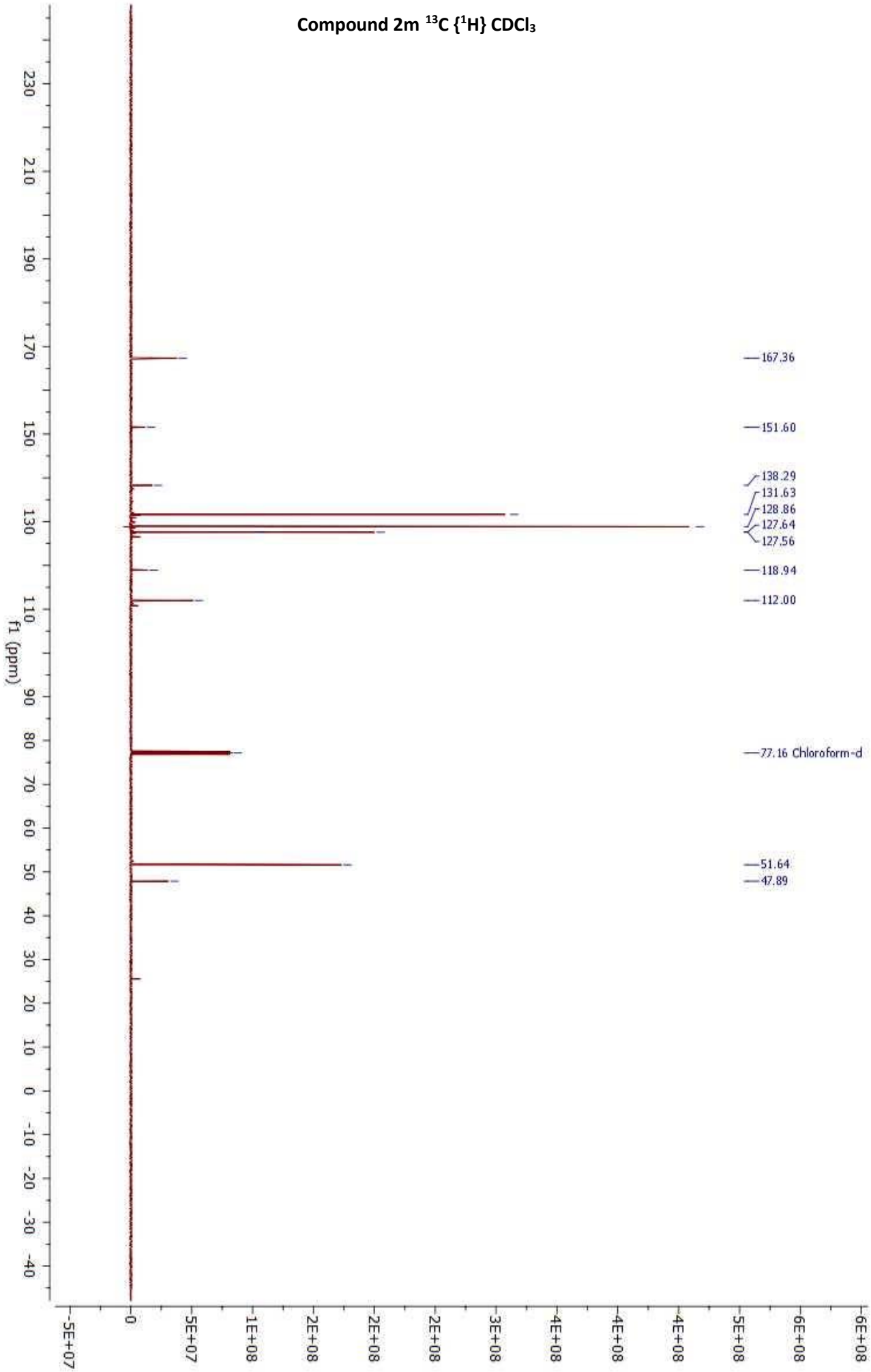


**Compound 2m $^{1}H$ $CDCl_3$**



**Compound 2m $^{13}C$ {$^{1}H$} $CDCl_3$**



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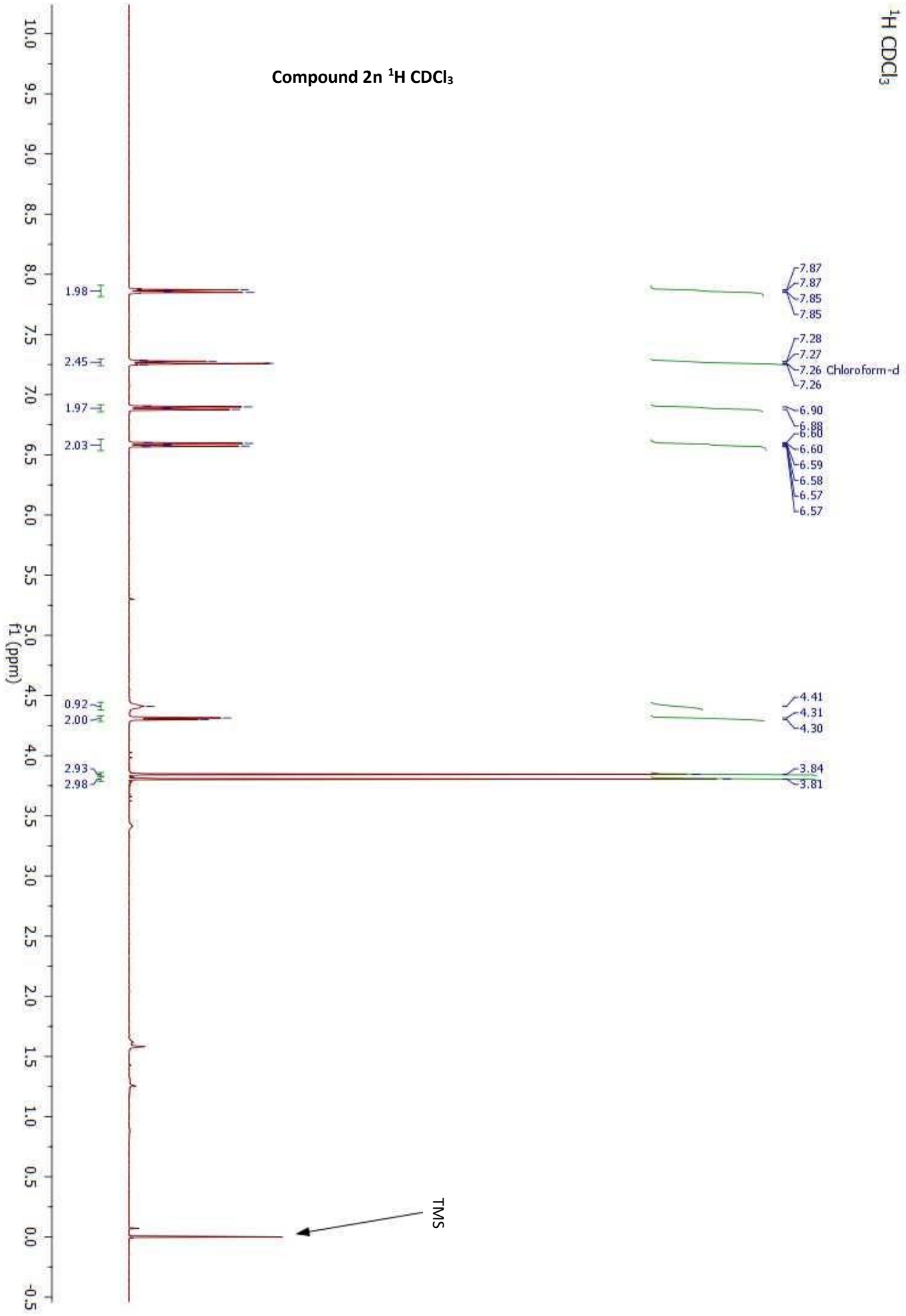
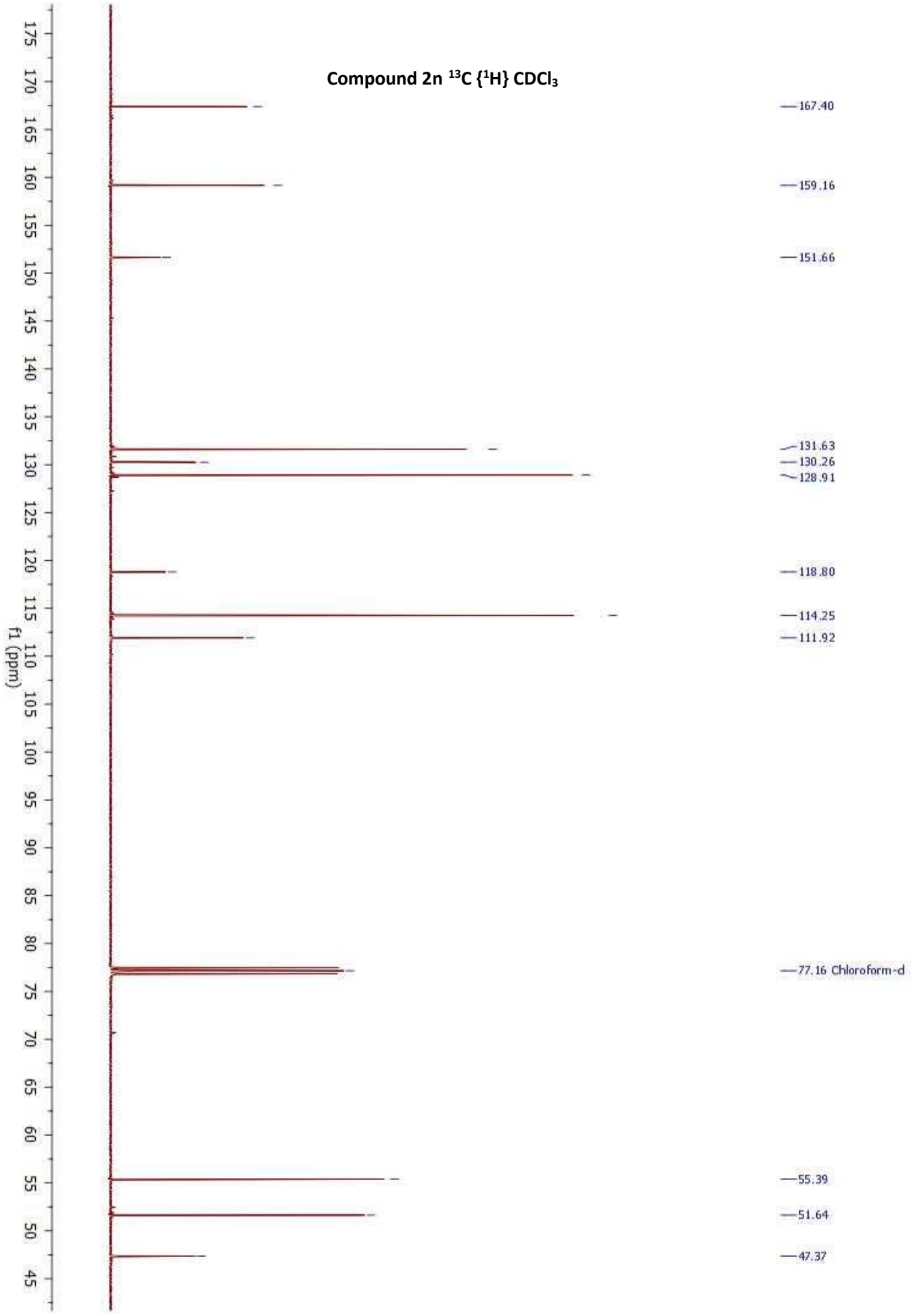


**Compound 2n $^{13}C$ {$^{1}H$} $CDCl_3$**



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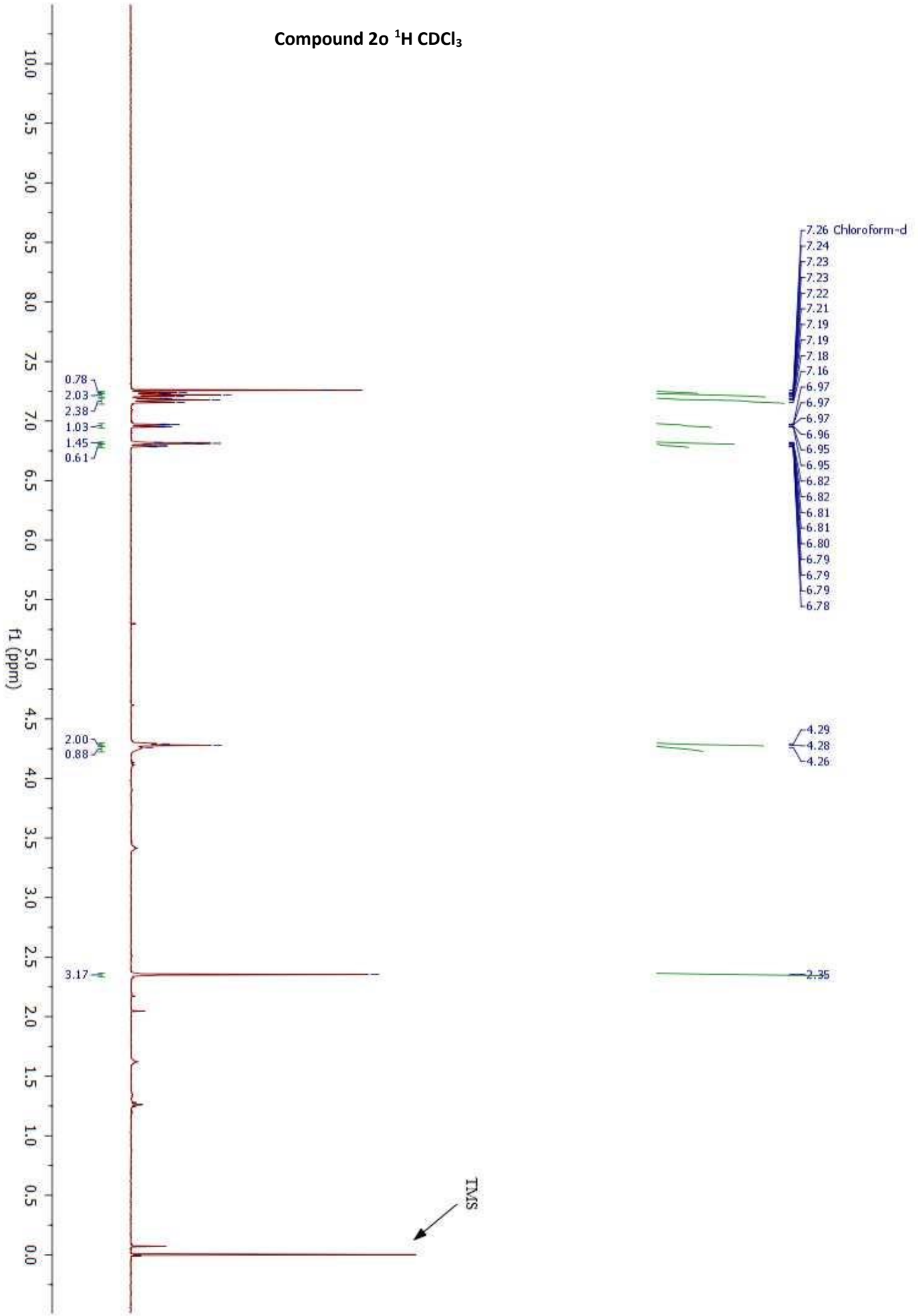

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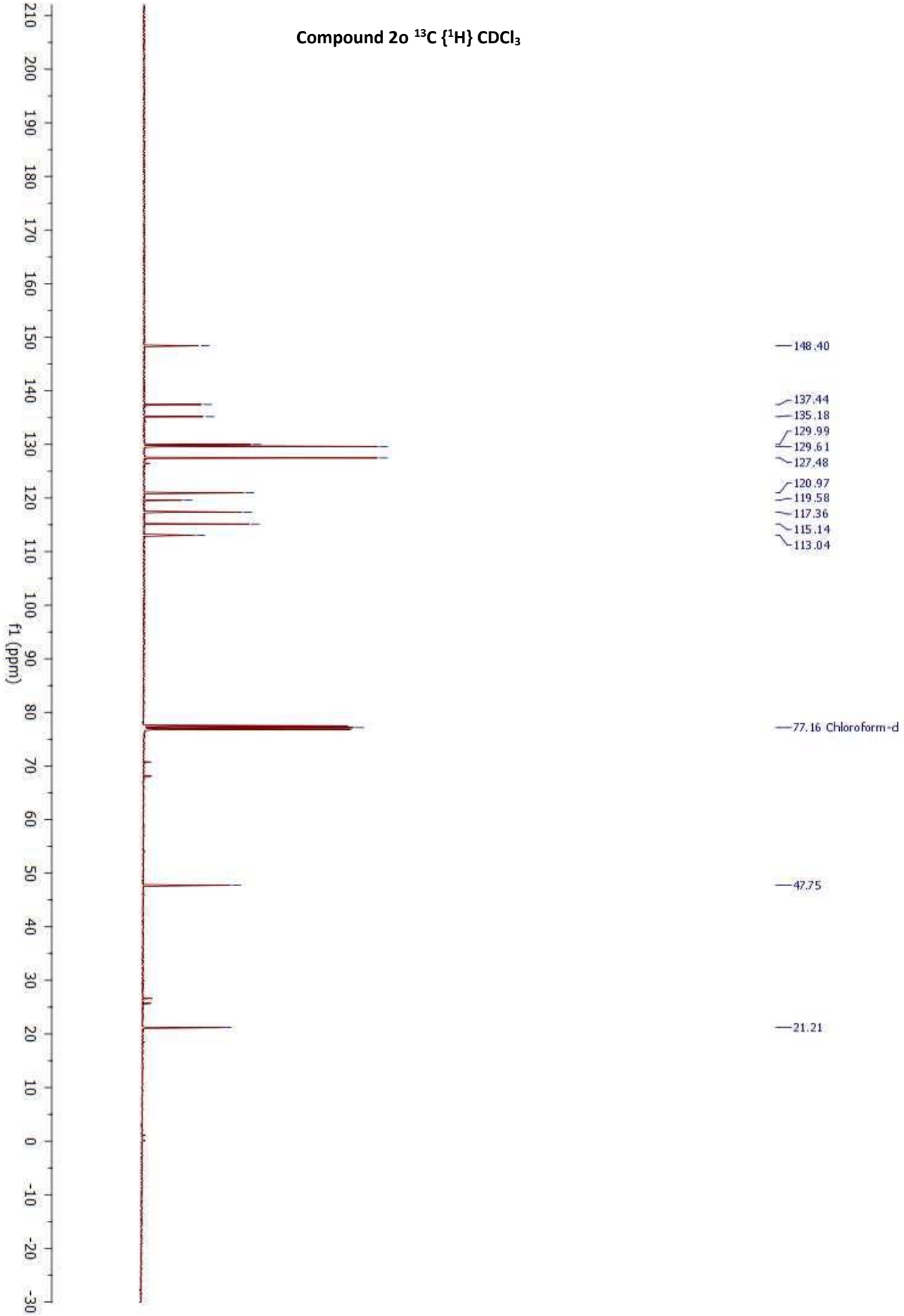

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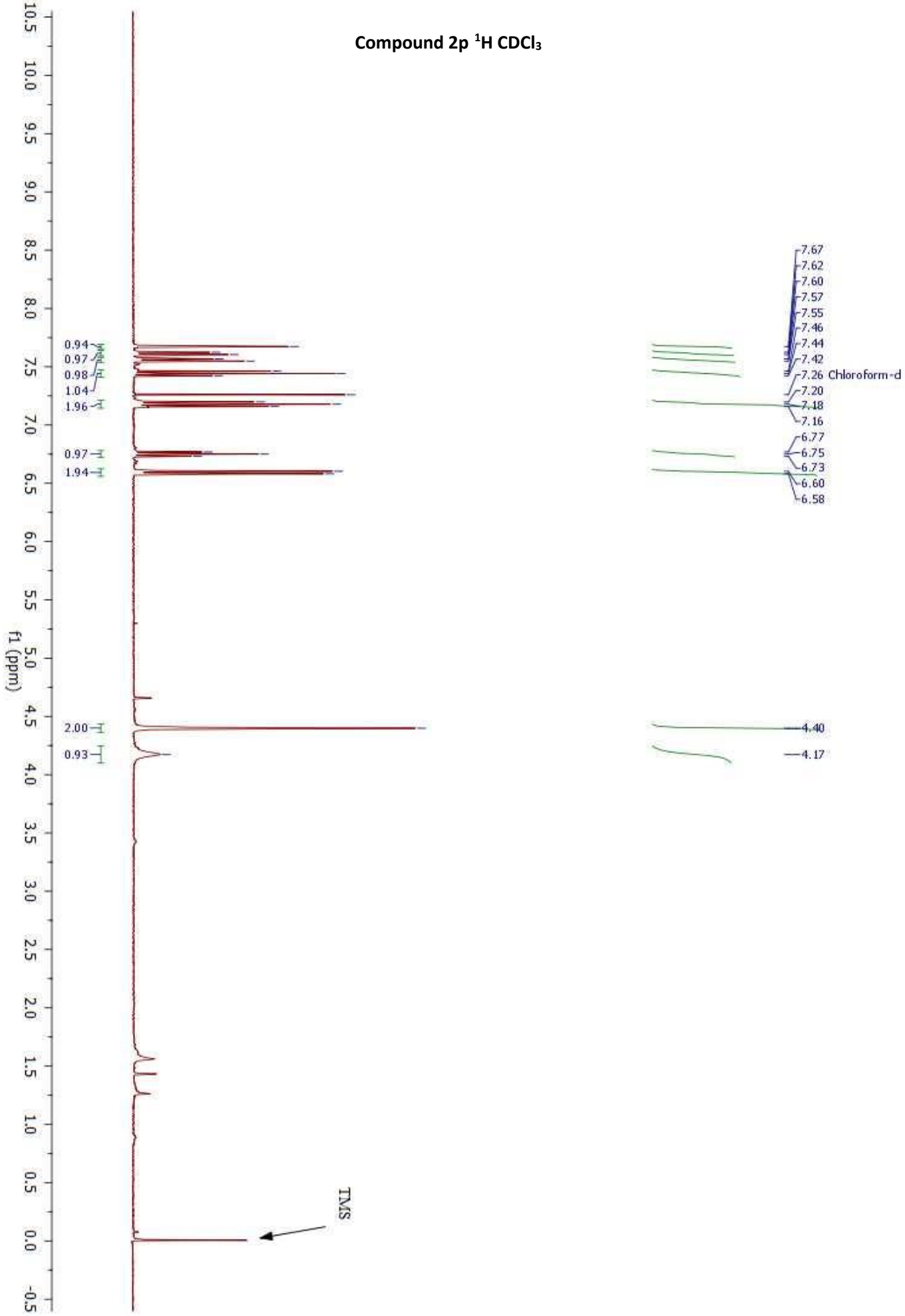
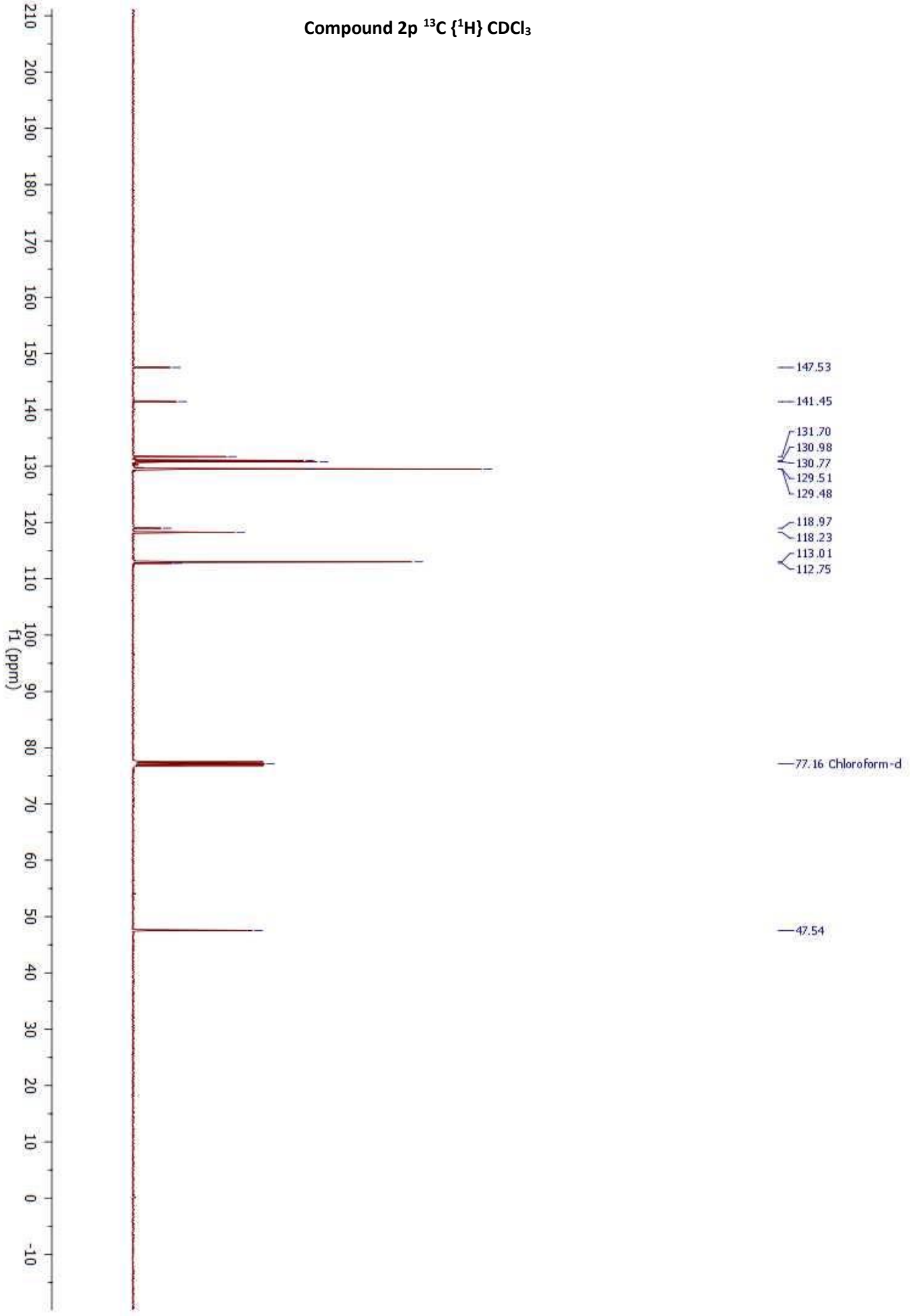


**Compound 2p $^{13}C$ {$^{1}H$} $CDCl_3$**



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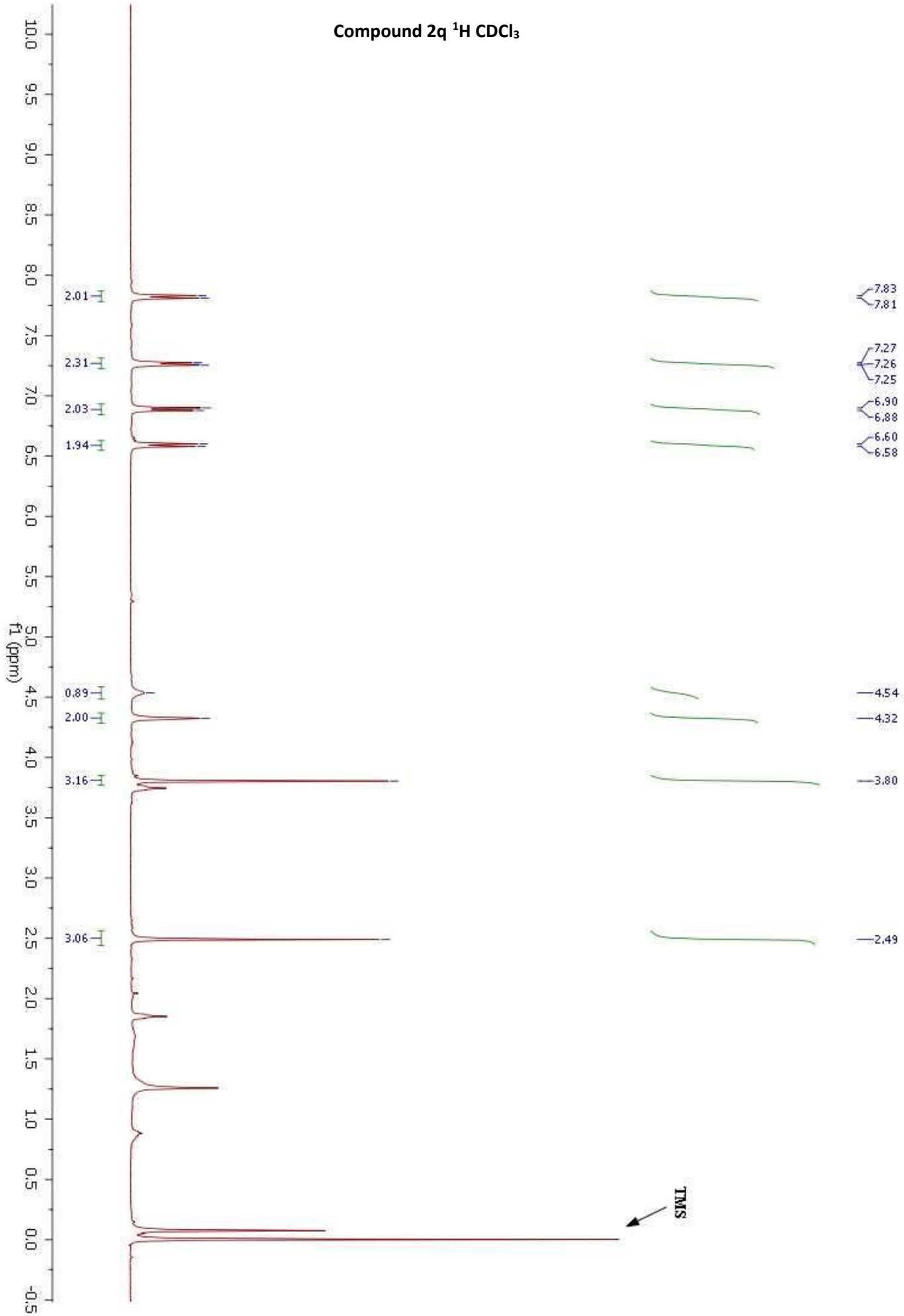
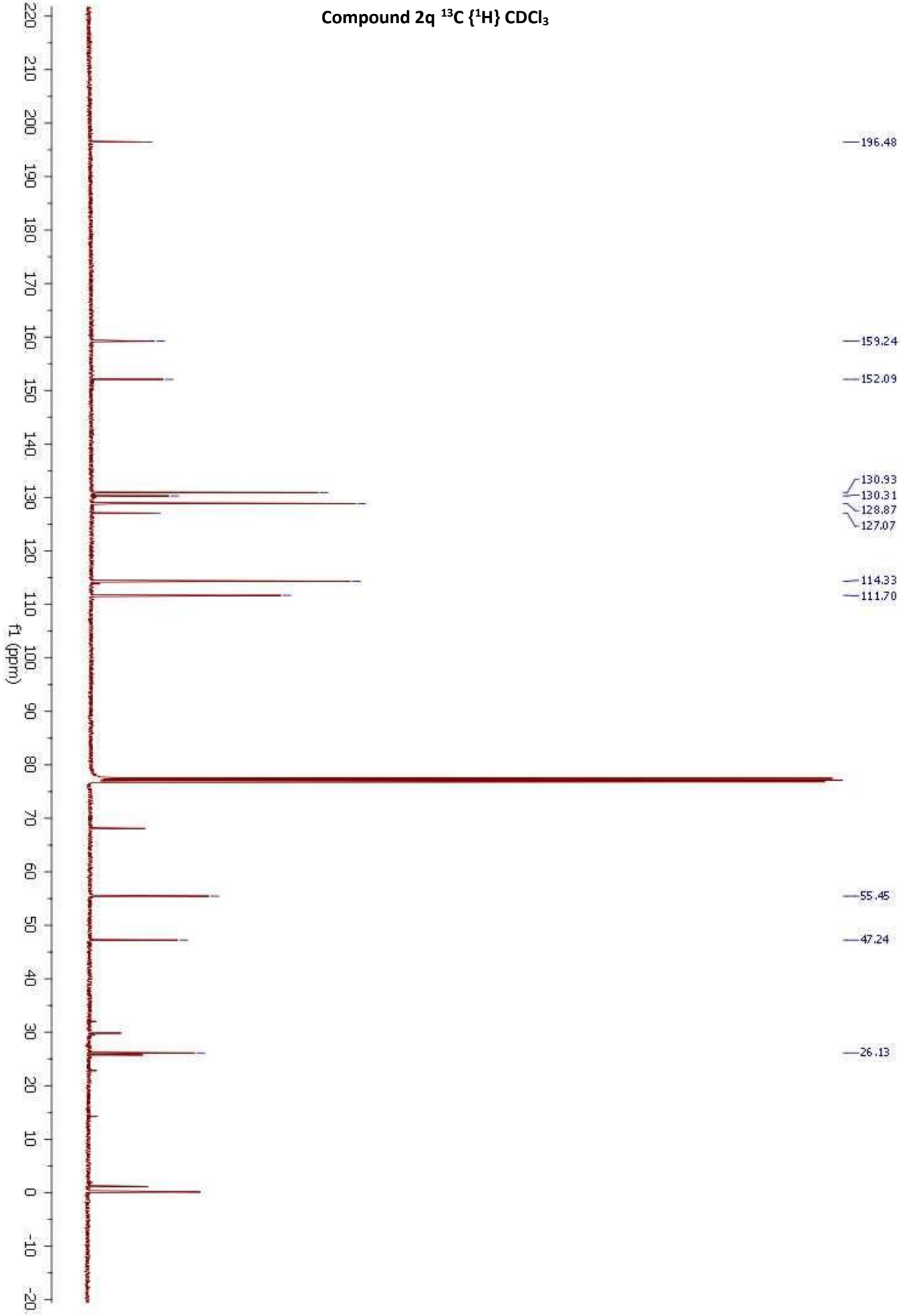
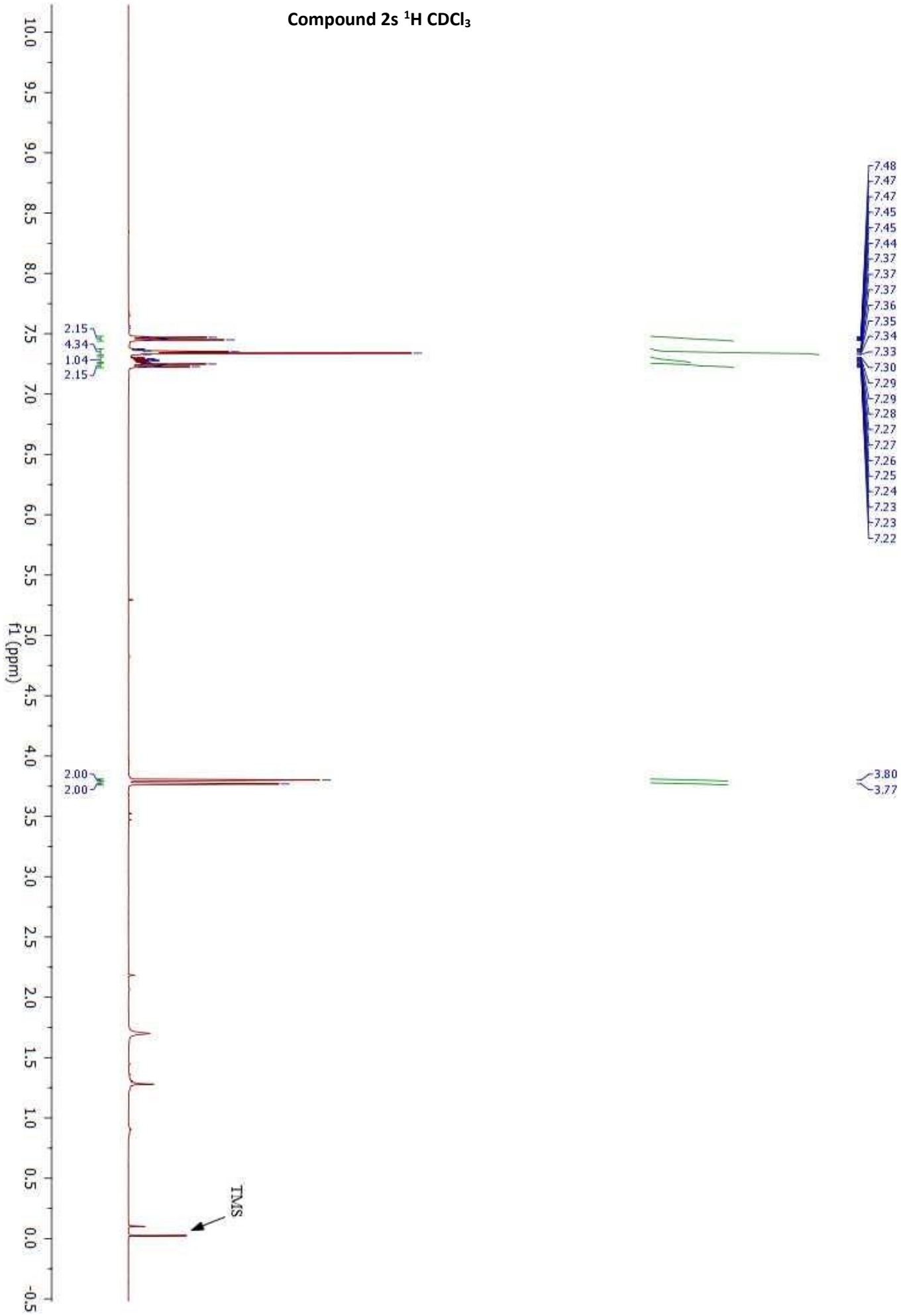


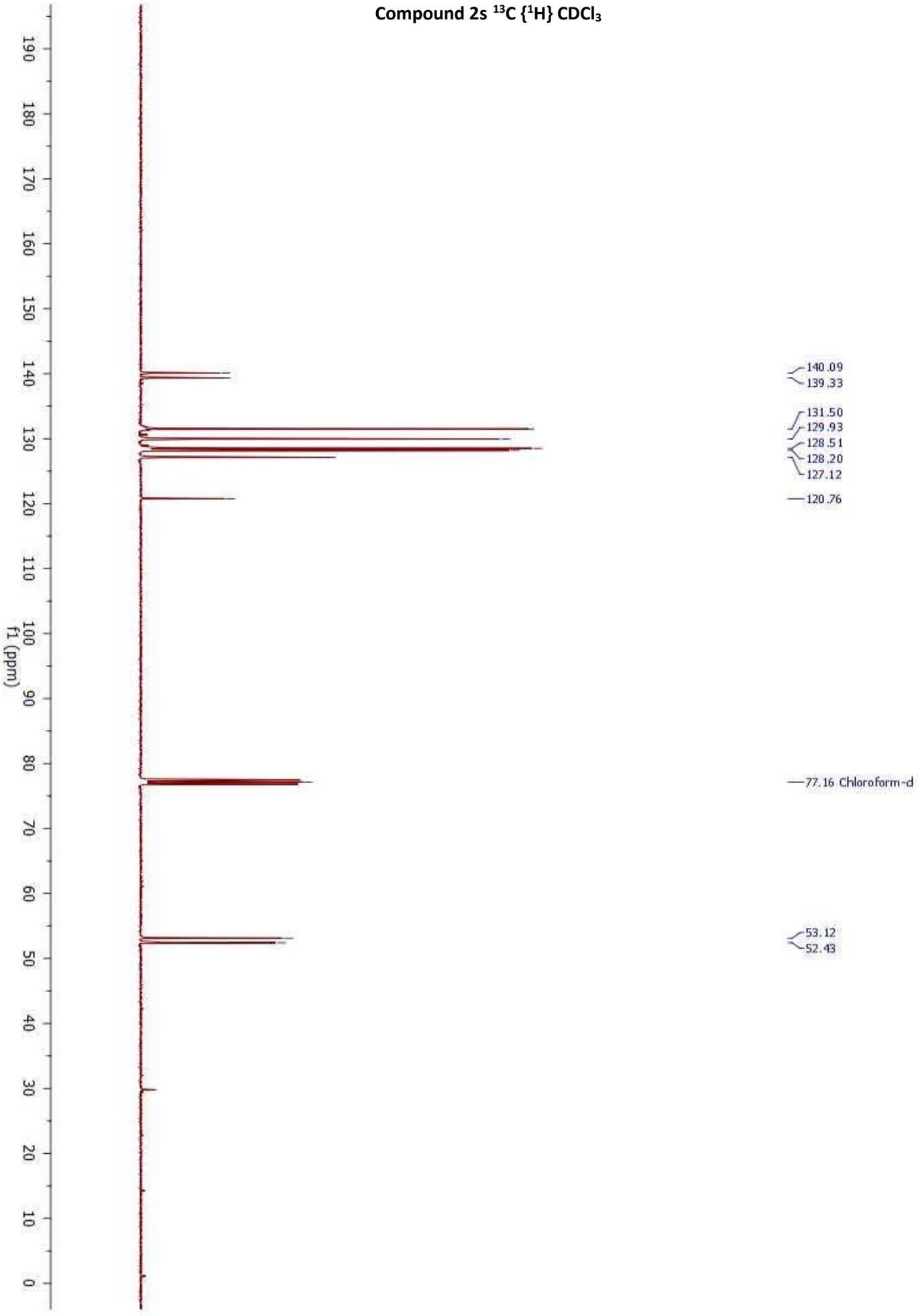
**Compound 2q $^{13}C$ {$^{1}H$} $CDCl_3$**



**Compound 2s $^{1}H$ $CDCl_3$**



**Compound 2s $^{13}C$ {$^{1}H$} $CDCl_3$**



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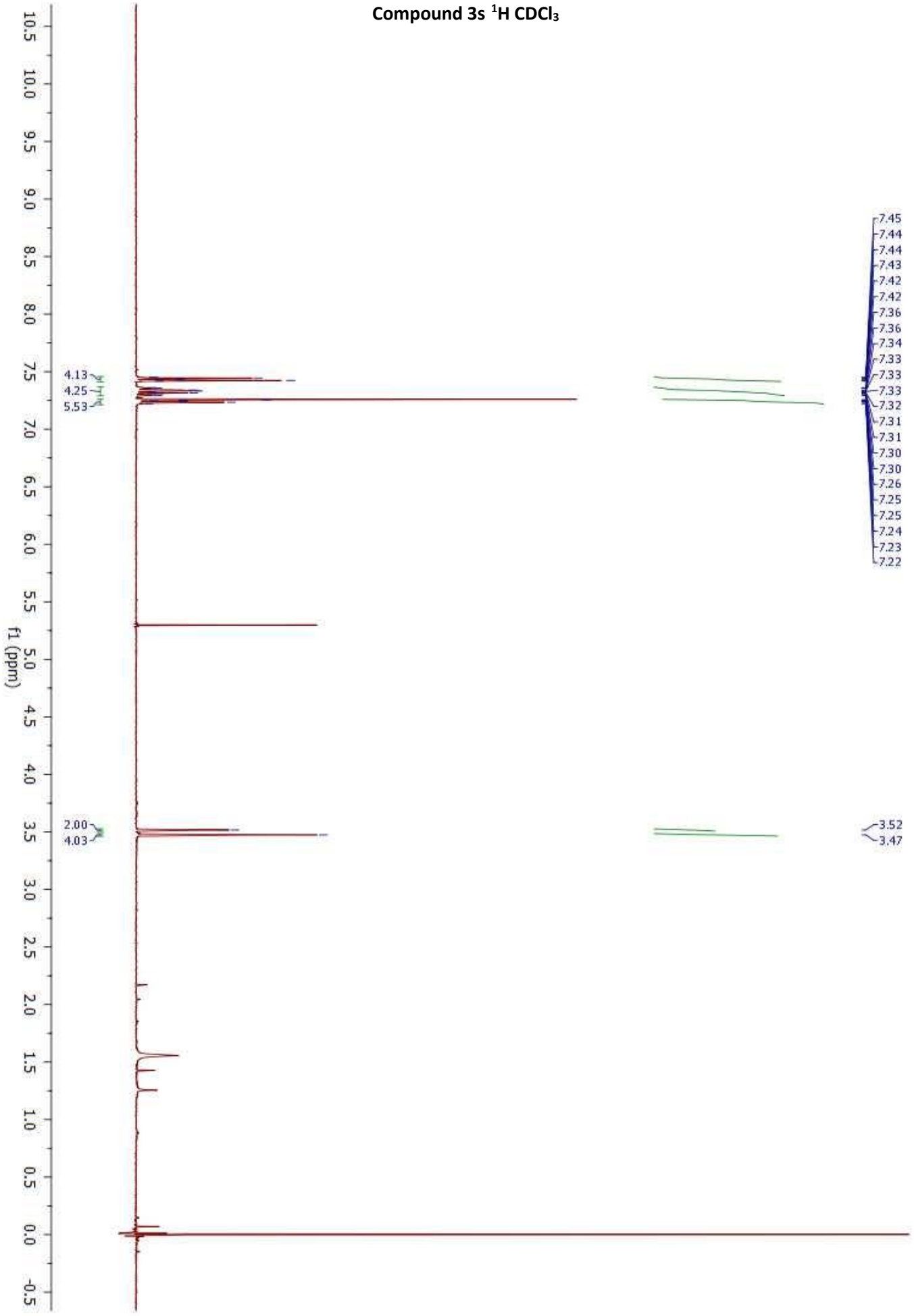
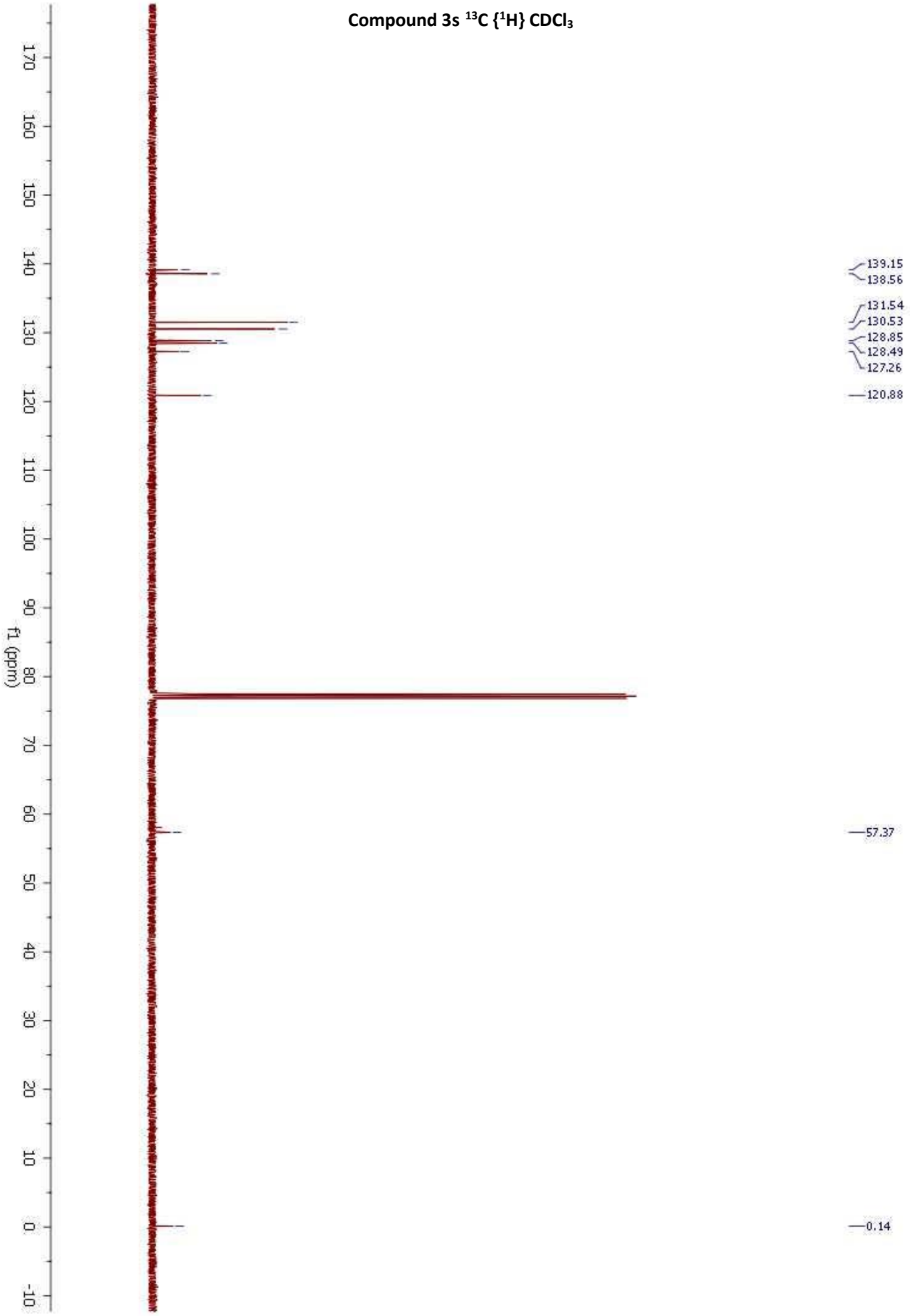


**Compound 3s $^{13}C$ {$^{1}H$} $CDCl_3$**



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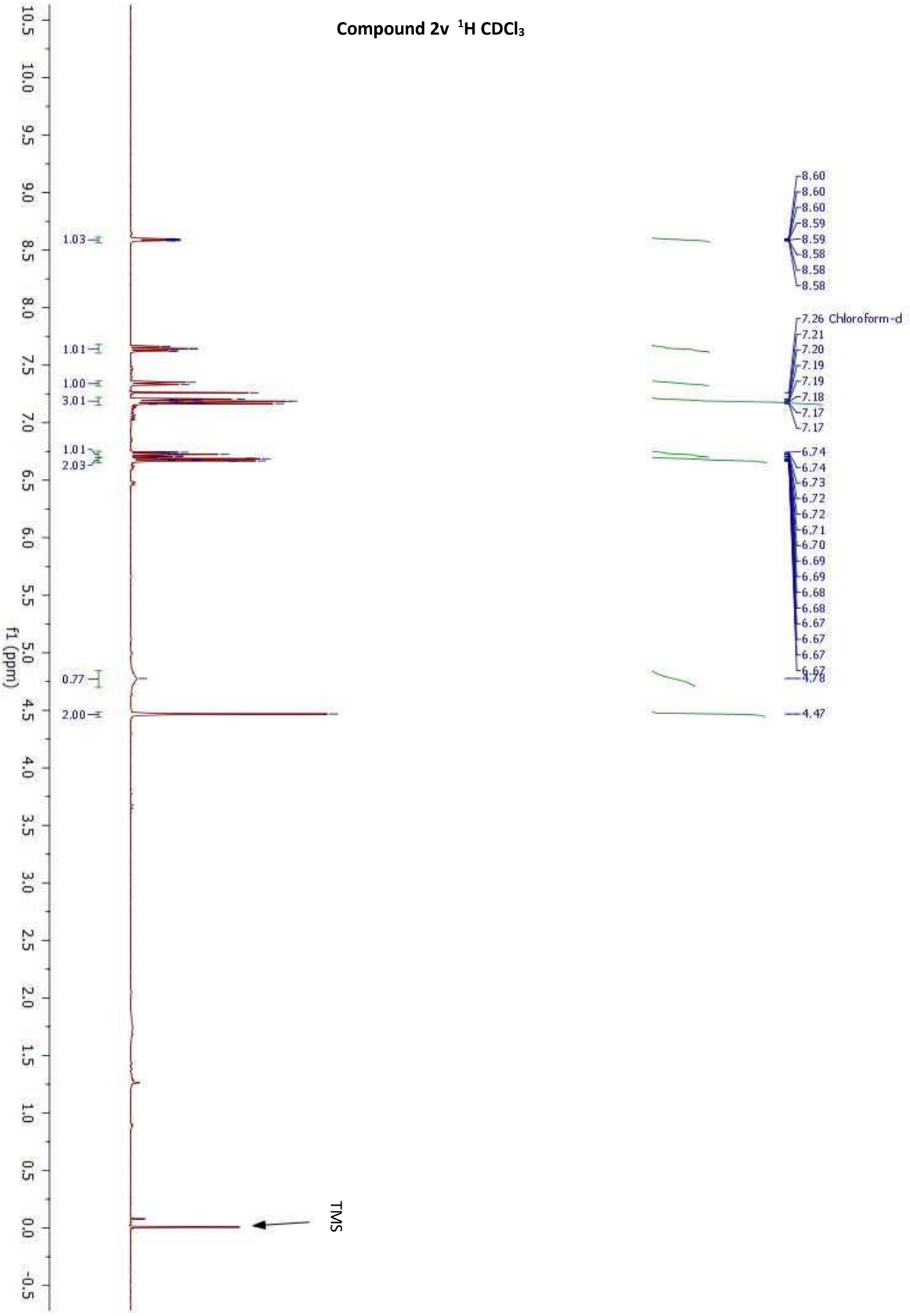
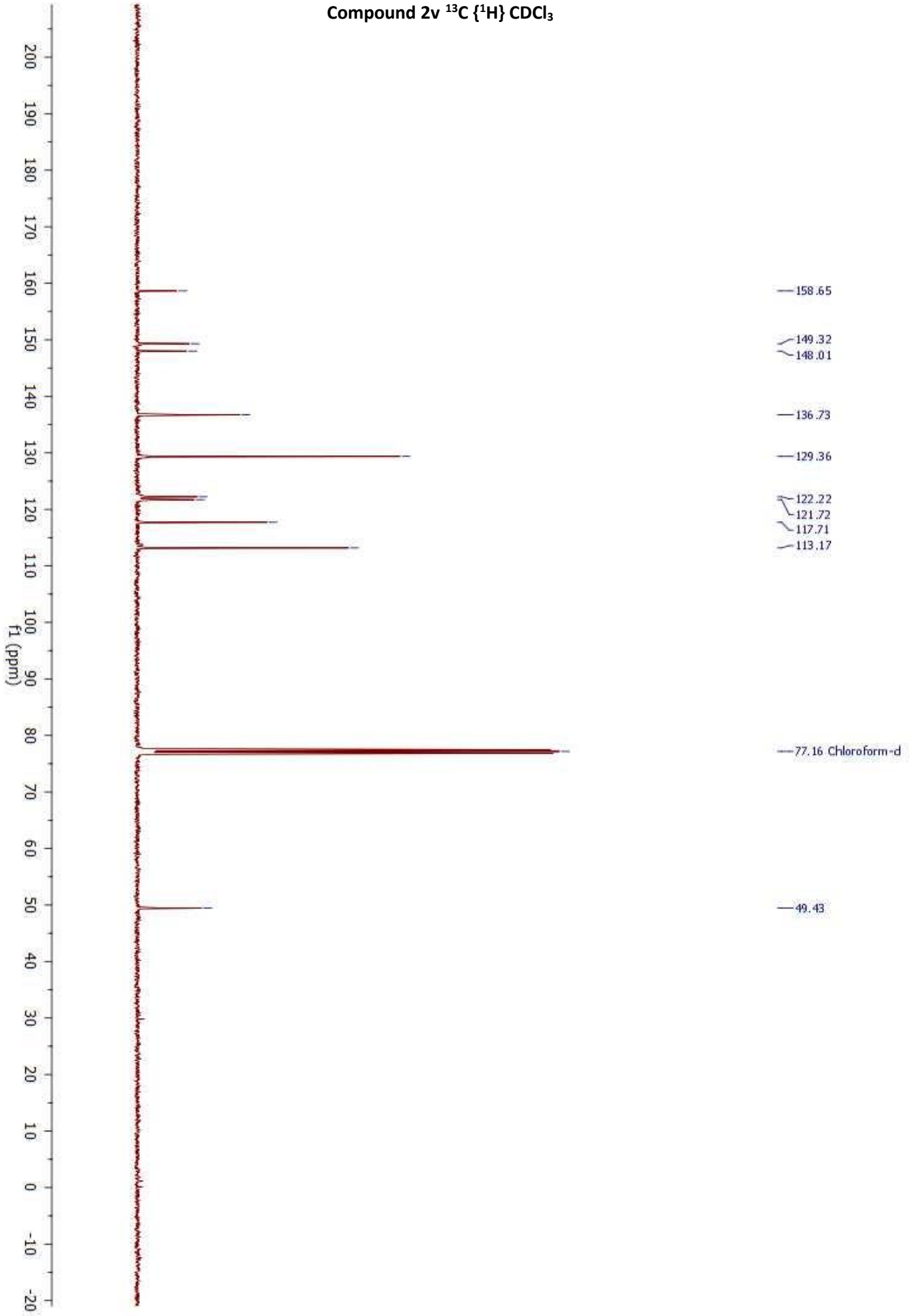


**Compound 2v $^{13}C$ {$^{1}H$} $CDCl_3$**



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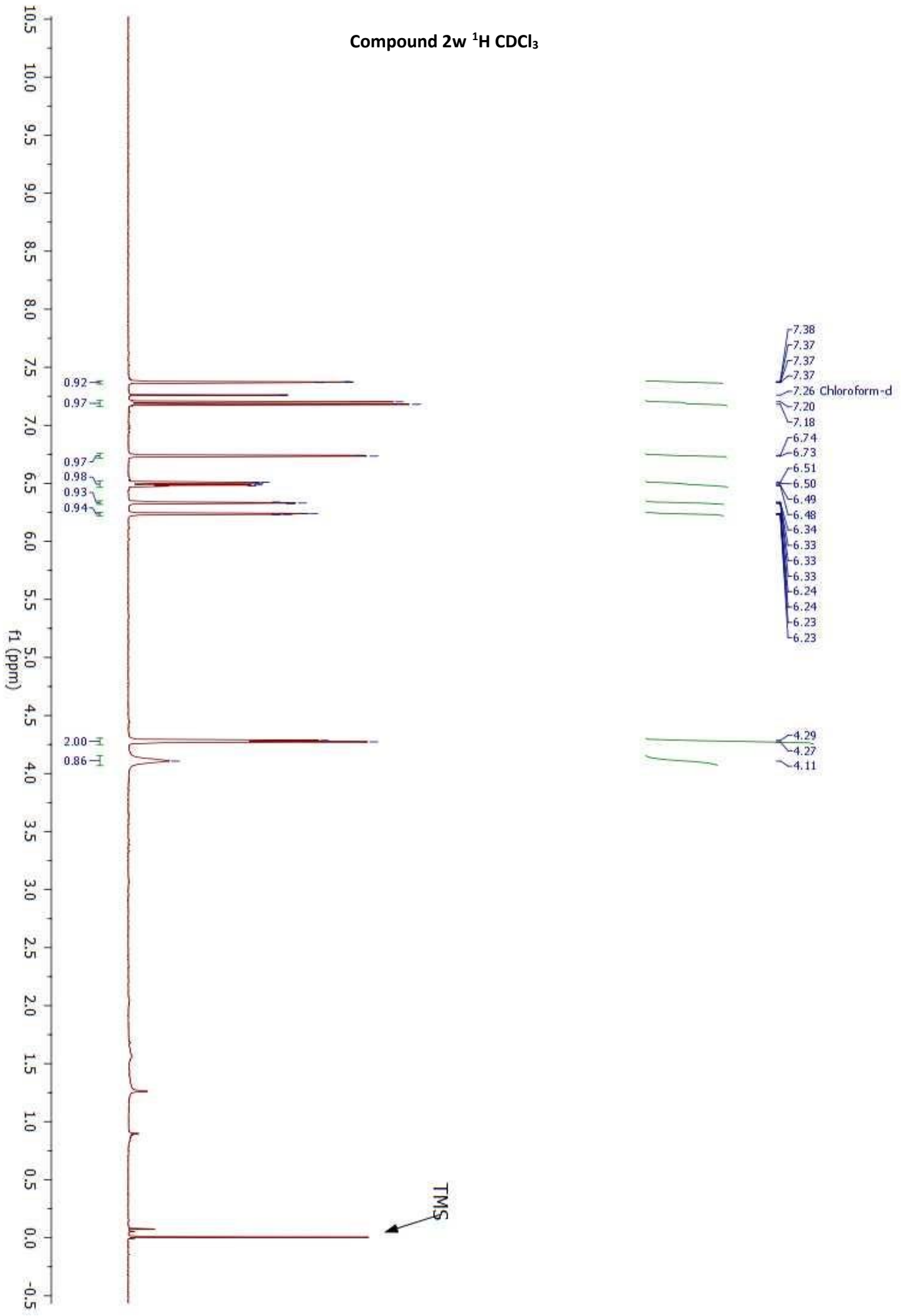
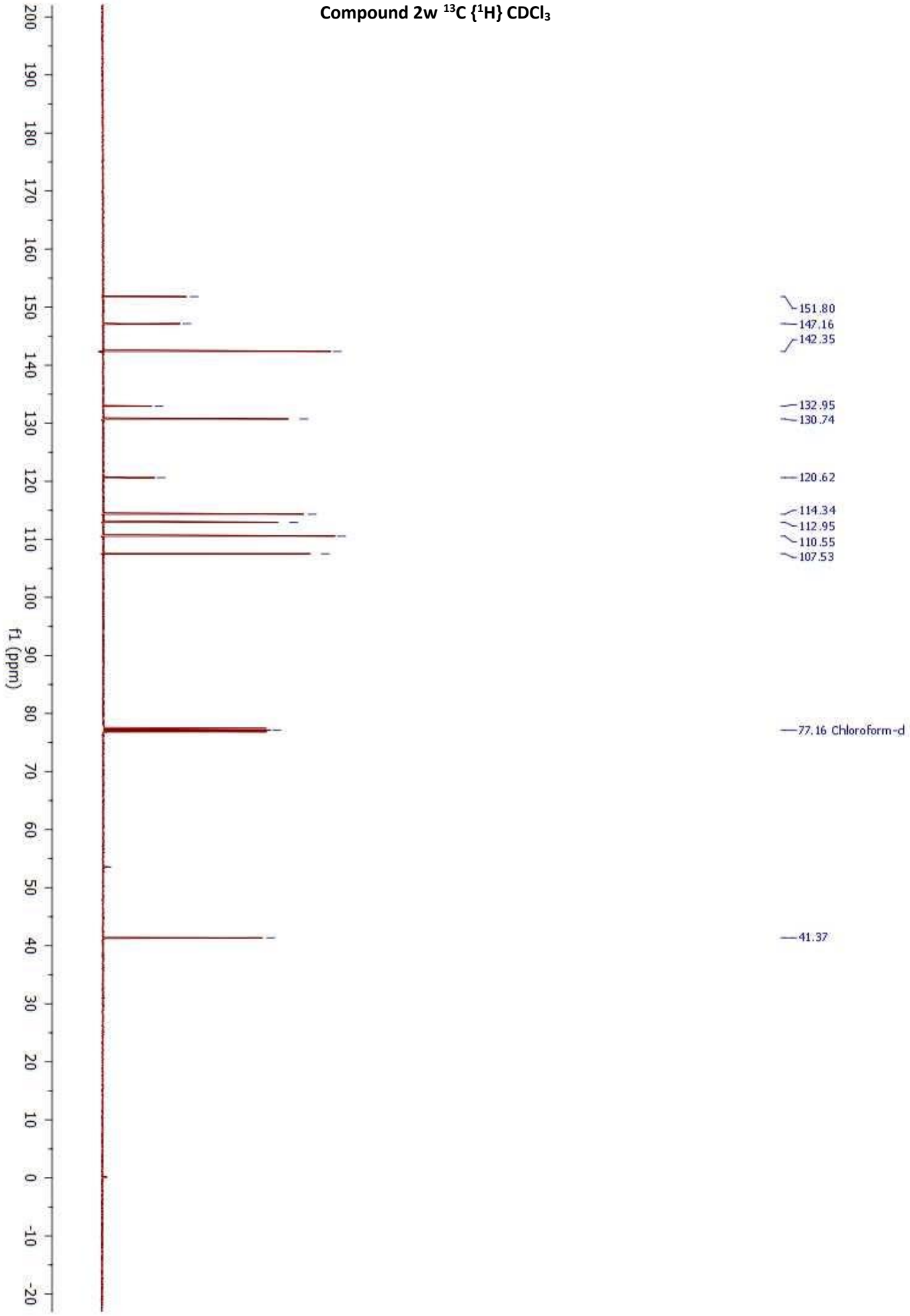


**Compound 2w $^{13}C$ {$^{1}H$} $CDCl_3$**



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