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# *N*-alkylation of aromatic amines with alcohols by using a commercially available Ru complex under mild conditions

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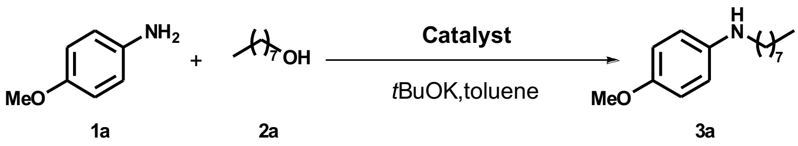
# General methods and materials

Commercially available reagents were purchased from Acros, Aldrich, Strem Chemicals, Alfa-Aesar, and TCI Europe and were used as received. (dppf) $RuCl_2$ AMPY was purchased from Johnson Matthey and was used as received. All reactions were monitored by thin-layer chromatography (TLC) performed on glass-backed silica gel 60 F254, 0.2 mm plates (Merck), and compounds were visualized under UV light (254 nm) or using iodine vapor. The eluents were technical grade. $^1H$ and $^{13}C$ liquid NMR spectra were recorded on a Bruker Avance III HD 600 MHz NMR spectrometer and a Varian 400 and 500 MHz NMR spectrometer at 298 K. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referred to the residual hydrogen of the solvent ($CDCl_3$, 7.27 ppm or DMSO 2.54 ppm) or internal tetramethylsilane (TMS). Data are represented as follows: chemical shift δ is expressed in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad singlet, and combination of thereof), coupling constant (*J*) in hertz (Hz) and integration. Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and referenced to the NMR solvent's carbon resonances ($CDCl_3$, δ 77.0 ppm or DMSO-d6 δ 39.5 ppm). Deuterated NMR solvents were obtained from Aldrich. Samples were analyzed using an Agilent 5977B MS interfaced to the GC 7890B equipped with a DB-5ms column (J & W), injector temperature at 230 °C, detector temperature at 280 °C, helium carrier gas flow rate of 1 mL/min. The GC oven temperature program was 100 °C initial temperature with a 4 min hold time and ramping at 15 °C/min to a final temperature of 270 °C with 7 min hold time. One µL of each sample was injected in split (1:20) mode. After a solvent delay of 3 minutes, mass spectra were acquired in full scan mode using 2.28 scans/s with a 50–500 amu mass range. Retention times of different compounds were determined by injecting pure compounds under identical conditions. HRMS were recorded on LTQ Orbitrap Elite (Thermofischer) instrument (ESI). All the experiments were carried out in duplicate to ensure the reproducibility of the experimental data. Yields refer to pure, isolated materials.

## Optimization experiments

### Table S1. Screening of reaction conditions for the *N*-alkylation of aromatic amines[a]




| Entry | Catalyst | Time (h) | Temperature | Yield of 3[b] |
|---|---|---|---|---|
| **1** | [Os]-1 | 36 | 25 °C | - |
| **2** | [Os]-1 | 36 | 50 °C | - |
| **3** | [Os]2 | 36 | 25 °C | 5% |
| **4** | [Os]-3 | 36 | 25 °C | - |
| **5** | [Os]-3 | 36 | 50 °C | - |
| **6** | [Os]-4 | 36 | 25 °C | - |
| **7** | [Os]-4 | 36 | 50 °C | - |
| **8** | [Ru]-1 | 36 | 25 °C | - |
| **9** | [Ru]-1 | 36 | 50 °C | - |
| **10** | [Ru]-2 | 36 | 25 °C | 2% |
| **11** | [Ru]-2 | 36 | 50 °C | 36% |
| **12** | [Ru]-7 | 36 | 25 °C | - |
| **13** | [Ru]-7 | 36 | 50 °C | - |
| **14**[c] | [Ru]-3 | 48 | 25 °C | 93% |

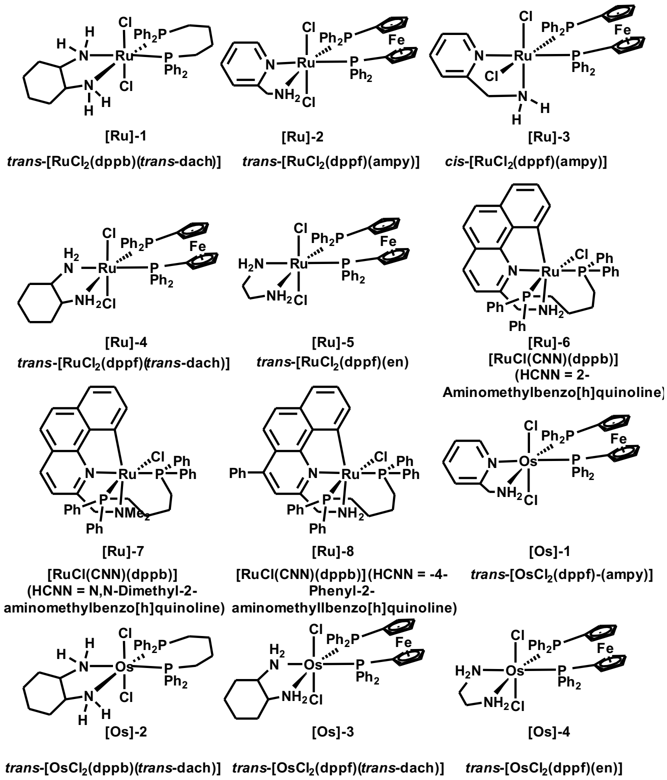
a. Reaction conditions: anisidine (1 mmol), octanol (1 mmol), potassium *tert*-butoxide (1 mmol), catalyst (2.5 mol%), in toluene (1 mL) for the given time and given temperature. b. Determined by GC-MS analysis. c. Catalyst loading 1.5 mol%.

## Table S2. Screening of reaction conditions for the methylation of aromatic amines[a]

| Entry | Solvent (mL) | Catalyst (Loading) | Time (h) | Temperature | Yield of 3[b] |
|---|---|---|---|---|---|
| **1** | Toluene/MeOH (2/1) | [Ru]-3 (2 mol%) | 48 | 75 °C | 18% |
| **2** | Toluene/MeOH (2/1) | [Ru]-3 (2 mol%) | 48 | 100 °C | 20% |
| **3[c]** | Toluene/MeOH (2/1) | [Ru]-3 (2 mol%) | 48 | 75 °C | 10 % |
| **4** | Toluene/MeOH (2/1) | [Ru]-3 (4 mol%) | 48 | 75 °C | 15% |
| **5[d]** | MeOH (2) | [Ru]-3 (2 mol%) | 48 | 65 °C | 75 % |

a. Reaction conditions: anisidine (1 mmol), potassium *tert*-butoxide (1 mmol), catalyst in the given solvent for 48h at given temperature. b. Determined by GC-MS analysis. c. Potassium *tert*-butoxide (2 mmol). d. isolated yield.

## Structure of the Tested Catalysts



## Table S3: Screening of Substrates with different catalysts

| Entry | Catalyst | Time (h) | Product | Yield[b] |
| --- | --- | --- | --- | --- |
| **1** | [Ru]-6 | 12 | 3a | 84 % |
| **2** | [Ru]-6 | 3 | 3b | 94 % |
| **3** | [Ru]-6 | 24 | 3c | 74 % |
| **4** | [Ru]-6 | 8 | 3f | 86% |
| **5**[c] | [Ru]-6 | 3 | 3j | 86% |
| **6**[d] | [Ru]-6 | 24 | 3n | 90% |
| **7**[e] | [Ru]-8 | 2.5 | 9 | 99% |

a. Reaction conditions: amine (1 mmol), alcohol (1 mmol), potassium *tert*-butoxide (1 mmol), catalyst (2 mol%), in toluene (1 mL) for the given time at r.t. b. Isolated yield c. Determined by $^{1}$H-NMR analysis

# Experiments for $H_2$ detection

## General procedure for hydrogen detection at room temperature

To a 15 mL Schlenck tube under $N_2$ atmosphere, was added aniline (0.5 mmol), alcohol (0.5 mmol), KO$^t$Bu (0.5 mmol), **[Ru]-3** (2 mol%), and toluene (0.5 mL). Then, the tube was closed with a rubber stopper, and the reaction mixture was stirred for 8 h at room temperature, the head-gas was collected using a gas-tight syringe and analyzed using a gas chromatograph 6890N (Agilent) (GC), equipped with an HP PLOT Q capillary column and a TCD detector. Analysis conditions: inlet temperature, 180 °C; column temperature, 30 °C; TCD temperature, 250 °C; gas carrier, $N_2$. Hydrogen was detected in traces.

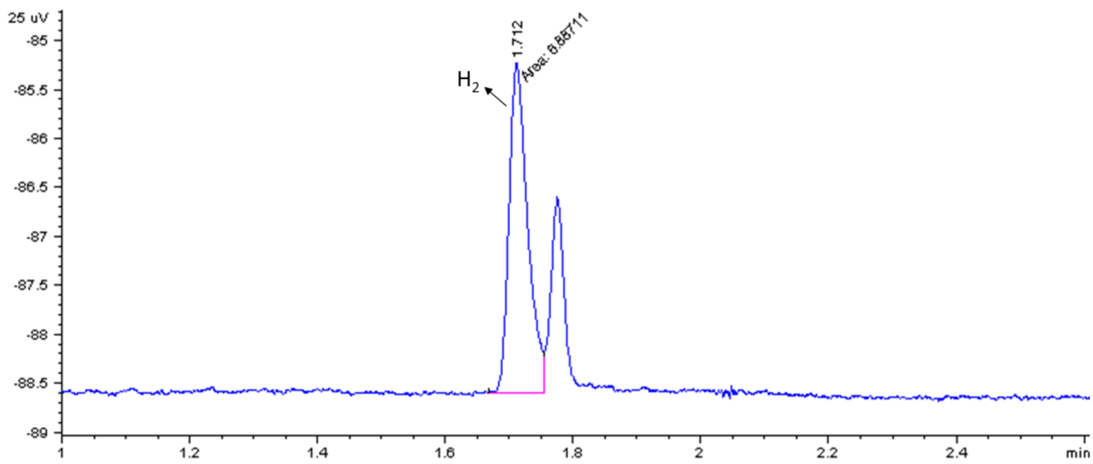



**Figura S1. Evolution of Hydrogen in the reaction of anisidine and benzyl alcohol at rt.**

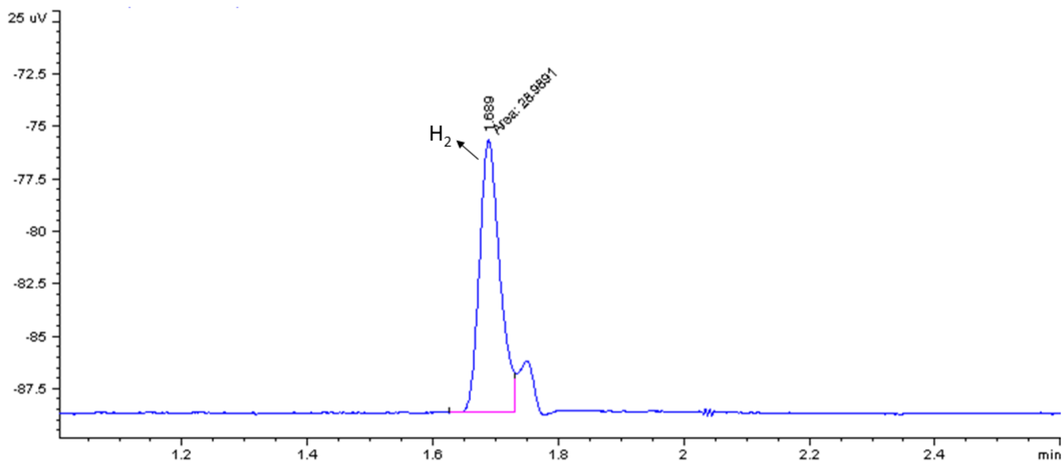



**Figura S2. Evolution of Hydrogen in the reaction of anisidine and 1-octanol at rt.**

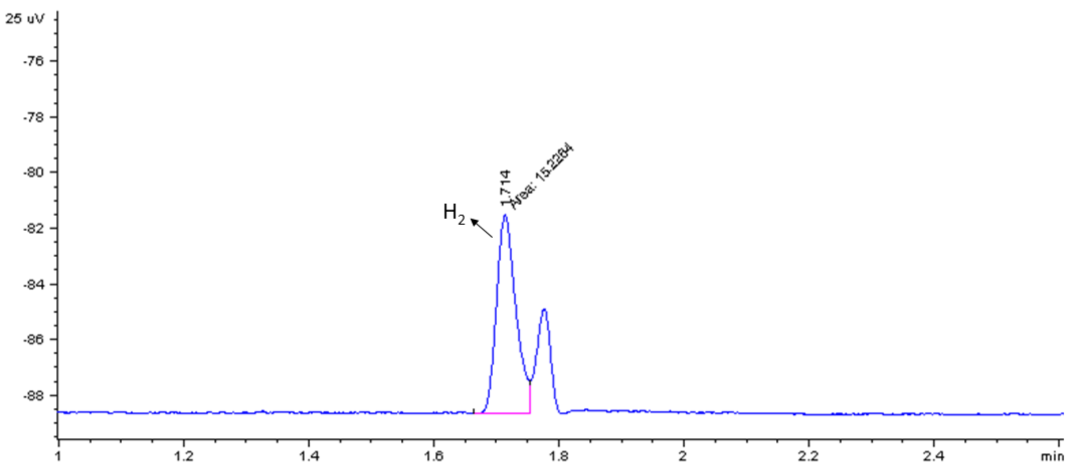



**Figura S3. Evolution of Hydrogen in the reaction of formation of indole from aminophenethylalcohl at rt.**

## General procedure for $H_2$ detection at 70 °C

To a 15 mL Schlenck tube under $N_2$ atmosphere, was added aniline (0.5 mmol), alcohol (0.5 mmol), KO*t*Bu (0.5 mmol), [Ru]-3 (2 mol%), and toluene (0.5 mL). Then the tube was closed with a rubber stopper, and the reaction mixture was stirred for 8 h at 70 °C, the head-gas was collected using a gas-tight syringe and analyzed using a gas chromatograph 6890N (Agilent) (GC), equipped with an HP PLOT Q capillary column and a TCD detector. Analysis conditions: inlet temperature, 180 °C; column temperature, 30 °C; TCD temperature, 250 °C; gas carrier, $N_2$. Hydrogen was detected in a significant amount. (6-7-fold compared to the experiments at room temperature).

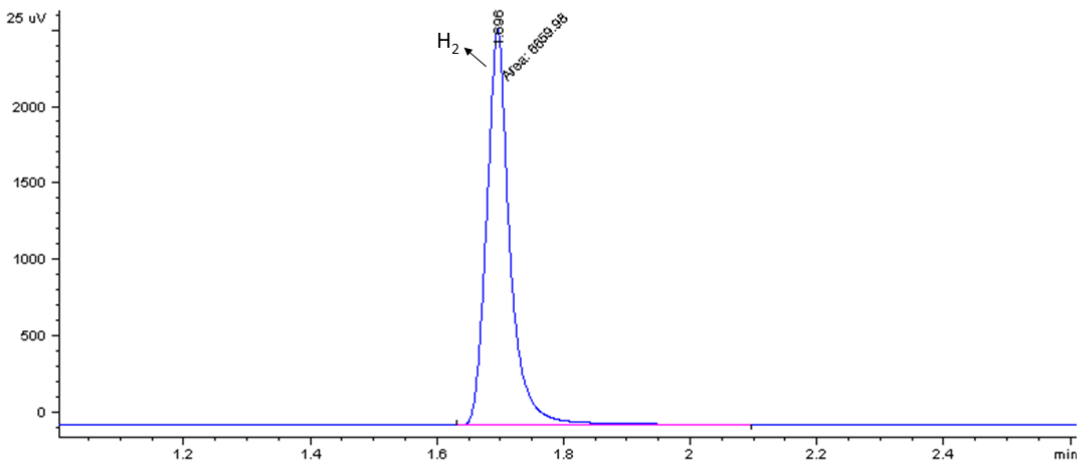



**Figura S4. Evolution of Hydrogen in the reaction of formation of indole from aminophenethylalcohl at 70 °C**

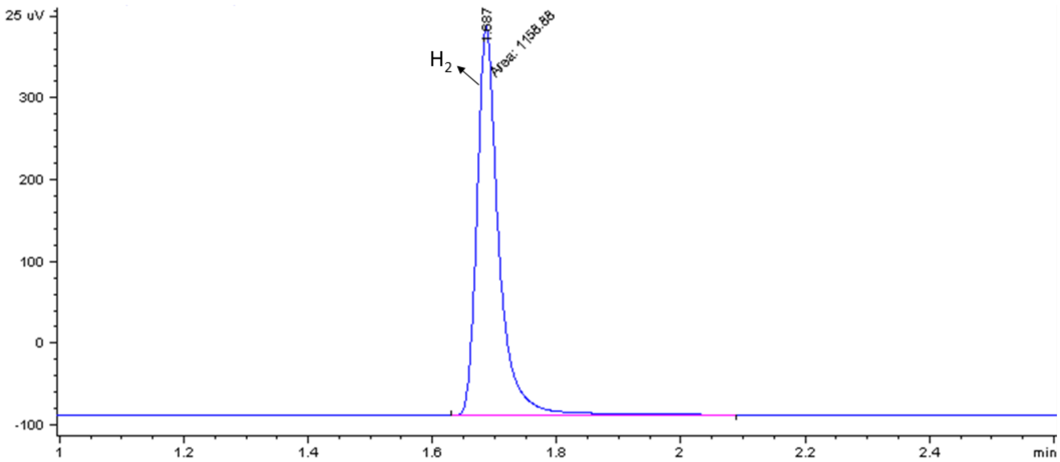



**Fig. S5. Evolution of Hydrogen in the reaction of anisidine and benzyl alcohol at 70 °C.**

# General experimental procedures for the synthesis of Products **3a-3t**, **5a**, **7a-9a**.

## General experimental procedure for the synthesis of amine **3a-3p.**

In a 15 mL Schlenck tube under an $N_2$ atmosphere, amine (1 mmol) and alcohol (1.1 mmol) were dissolved in anhydrous toluene (1.0 mL), then *t*-BuOK (1.1 mmol) and **[Ru]-3** (0.02 mmol) were added, and then the tube was closed with a rubber stopper. The reaction mixture was stirred for 24 h at rt. After that, the crude reaction mixture was extracted with ethyl acetate. The solvent was evaporated to dryness, and the corresponding amine was purified by column chromatography with silica gel (ethyl acetate/ hexane: 9/1). The yields were calculated based on isolated products.

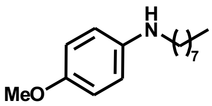
## General experimental procedure for the synthesis of methylamines **3q-3t**

In a 15 mL Schlenck tube under an $N_2$ atmosphere, amine (1 mmol) was dissolved in methanol (2 mL), then *t*-BuOK (1.1 mmol) and **[Ru]-3** (0.02 mmol) were added, and then the vial was closed with the cap. The reaction mixture was heated at reflux and stirred for 48 h. After that, the solvent was evaporated to dryness, and the corresponding amine was purified by column chromatography with silica gel (ethyl acetate/ hexane. 9/1). The yields were calculated based on isolated products.

## Experimental procedure for the synthesis of benzimidazole **7a**

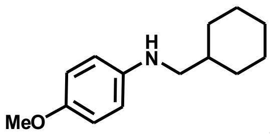
In a 15 mL Schlenck tube under an $N_2$ atmosphere, *o*-phenylenediamine (1 mmol) and benzylic alcohol (2 mmol) were dissolved in anhydrous toluene (2 mL), then *t*-BuOK (2 mmol) and **[Ru]-3** (0.02 mmol) were added, and then the vial was closed with the cap. The reaction mixture was heated at reflux and stirred for 48 h. After that, the solvent was evaporated to dryness, and the corresponding amine was purified by column chromatography with silica gel (ethyl acetate/hexane: 8/2). The yields were calculated based on isolated products.

## Spectral data for products 3a-3t, 5a, 7a, 9a

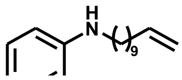



**4-methoxy-*N*-octylaniline (3a)** Yellow oil, 197 mg, 84% yield. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.06 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.44 – 1.36 (m, 2H), 1.38 – 1.25 (m, 9H), 0.94 – 0.84 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.2, 143.0, 115.1, 114.2, 56.0, 45.3, 32.0, 29.8, 29.6, 29.4, 27.3, 22.8, 14.2. Spectroscopic data are in agreement with those reported earlier.[1]

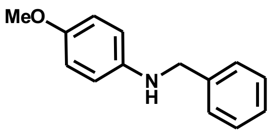
**4-methoxy-N-(3-phenylpropyl)aniline (3b)** Yellow oil, 217 mg, 90% yield **$^1$H NMR**.(600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 3H), 6.82 (dd, *J* = 8.6, 1.5 Hz, 2H), 6.60 (dd, *J* = 8.6, 1.5 Hz, 2H), 3.78 (s, 3H), 3.35 (bs, 1H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 2H), 1.97 (p, *J* = 7.3 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 152.2, 142.6, 141.8, 128.5, 128.5, 126.0, 115.0, 114.3, 55.9, 44.7, 33.5, 31.2. Spectroscopic data are in agreement with those reported earlier.[2,3]



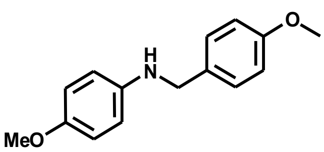

***N*-(cyclohexylmethyl)-4-methoxyaniline (3c)** Colorless oil, 174 mg, 74 % yield. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.81 – 6.75 (m, 2H), 6.64 – 6.55 (m, 2H), 3.75 (s, 3H), 2.92 (d, *J* = 6.4 Hz, 2H), 1.85 – 1.79 (m, 2H), 1.79 – 1.72 (m, 2H), 1.72 – 1.65 (m, 1H), 1.57 (ddt, *J* = 11.1, 7.5, 3.8 Hz, 1H), 1.30-1.16 (m, 3H), 0.98 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 151.9, 142.7, 115.1, 114.4, 56.0, 52.0, 37.7, 31.5, 26.7, 26.1. Spectroscopic data are in agreement with those reported earlier[4]




**4-methoxy-*N*-(undec-10-en-1-yl)aniline (3d)** Yellow oil**,** 176 mg**, 95% purity** 61% yield. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 6.80 – 6.77 (m, 2H), 6.64 – 6.60 (m, 2H), 5.82 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.00 (dq, *J* = 17.1, 1.8 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 3.75 (s, 3H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.08 – 2.02 (m, 2H), 1.63 – 1.56 (m, 2H), 1.38 (p, *J* = 7.2 Hz, 4H), 1.33 – 1.25 (m, 8H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 152.5, 142.3, 139.3, 115.1, 114.7, 114.3, 56.0, 45.6, 33.9, 29.7, 29.6, 29. 6, 29.2, 29.1, 27.3. **HRMS (ESI):** 276.2322 m/z calcd for: $C_{18}H_{30}NO$ $[M+H]^+$. Found 276.2319.

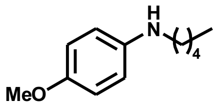



***N*-benzyl-4-methoxyaniline (3e)** Colorless oil, 183 mg, 86% yield. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 6.85 – 6.81 (m, 2H), 6.66 – 6.61 (m, 2H), 4.32 (s, 2H), 3.77 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 152.3, 142.6, 139.8, 128. 7, 127.6, 127.2, 115.01, 114.2, 55.9, 49.3. Spectroscopic data are in agreement with those reported earlier.[5]




**4-methoxy-*N*-(4-methoxybenzyl)aniline (3f)** White solid, m.p. 90-92 °C (lit.:[6] 94 °C) 119 mg 49% yield**. $^1$H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.21 (s, 2H), 3.80 (s, 3H), 3.75 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.1, 152.8, 141.7, 131.2, 129.2, 115.1, 115.0, 114.2, 56.0, 55.4, 49.4. Spectroscopic data are in agreement with those reported earlier.[7]

***N*-(4-chlorobenzyl)-4-methoxyaniline (3g)** Colorless oil, 150 mg, 61% yield. **$^1$H NMR** (600 MHz, DMSO) δ 7.36 (s, 4H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.50 (d, *J* = 6.8 Hz, 2H), 5.84 (s, 1H), 4.19 (s, 2H), 3.60 (s, 3H). **$^{13}$C NMR** (151 MHz, DMSO) δ 150.8, 142.6, 139.7, 130.9, 129.0, 128.1, 114.5, 113.3, 55.2, 46.5. Spectroscopic data are in agreement with those reported earlier.[8]




**4-methoxy-N-pentylaniline (3h)** Yellow oil, Yield: 67.5 mg, 85 % yield. **$^1$H NMR** (500 MHz**,** $CDCl_3$) δ = 6.85 – 6.74 (m, 2H), 6.59 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.76 (s, 3H), 3.31 (s, 1H), 3.07 (t, *J* = 7.2 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.39 (dd, *J* = 8.9, 5.4 Hz, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ = 151.4, 142.4, 114.4, 113.5, 55.3, 44.5, 28.9, 28.9, 22.0, 13.5. Spectroscopic data are in agreement with those reported earlier.[9–11]

***N*-pentylaniline (3i)** Yellow oil, 116 mg, 95% purity, 67 % yield **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 2H), 6.71 (dd, *J* = 7.8, 6.7 Hz, 1H), 6.65 – 6.59 (m, 2H), 3.60 (bs, 1H), 3.13 (t, *J* = 7.2 Hz, 2H), 1.65 (dd, *J* = 8.5, 5.8 Hz, 2H), 1.40 (dq, *J* = 6.5, 3.3, 2.9 Hz, 4H), 0.98 – 0.92 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 148.7, 129.3, 117.2, 112.8, 44.1, 29.5, 29.4, 22.6, 14.1. Spectroscopic data are in agreement with those reported earlier.[12]

**4-methyl-*N*-pentylaniline (3j)** Yellow oil, Yield: 110 mg, 62 % **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.00 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 3.44 (s, 1H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.69 – 1.57 (m, 2H), 1.38 (dd, *J* = 7.1, 3.5 Hz, 4H), 0.93 (t, *J* = 7.0 Hz, 3H).**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 146.5, 129.8, 126.4, 113.0, 44.5, 29.5, 29.5, 22.7, 20.5, 14.2. Spectroscopic data are in agreement with those reported earlier.[9]

**4-fluoro-N-pentylaniline (3k)** Yellow oil, 63 mg, 70% Yield **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 6.92 – 6.81 (m, 2H), 6.56 – 6.46 (m, 2H), 3.45 (s, 1H), 3.05 (t, *J* = 7.1 Hz, 2H), 1.75 – 1.45 (m, 2H), 1.37 (dd, *J* = 6.6, 3.2 Hz, 4H), 0.92 (dd, *J* = 9.5, 4.5 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.8 (d, *J* = 234.2 Hz), 145.1 (d, *J* = 1.6 Hz), 115.7 (d, *J* = 22.4 Hz), 113.6 (d, *J* = 7.4 Hz), 45.0, 29.5, 29.4, 22.6, 14.1. Spectroscopic data are in agreement with those reported earlier.[13]

**3-chloro-*N*-pentylaniline (3l)** Yellow oil, 154 mg, 78% yield **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.57 (s, 1H), 6.46 (dd, *J* = 8.3, 2.3 Hz, 1H), 3.69 (s, 1H), 3.08 (t, *J* = 7.2 Hz, 2H), 1.68 – 1.55 (m, 2H), 1.39 (p, *J* = 3.7 Hz, 4H), 1.00 – 0.88 (m, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 149.8, 135.1, 130.2, 116.91, 112.3, 111.1, 43.9, 29.4, 29.2, 22.6, 14.1. **HRMS (ESI):** 198,1044 m/z calcd for $C_{11}H_{17}ClN$ $[M+H]^+$. Found 198.1036.

**4-(methylthio)-*N*-pentylaniline (3m)** Brown oil, 113 mg, 54% yield**.** **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 3.64 (bs, 1H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.61 (p, *J* = 7.3 Hz, 2H), 1.37 (tt, *J* = 6.1, 3.5 Hz, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 147. 6, 131.8, 126.2, 123.9, 123.4, 113.4, 44.1, 29.4, 29.3, 22.6, 19.5, 14.1. **HRMS (ESI):** 210,1311 m/z calcd for: $C_{12}H_{20}NS$ $[M+H]^+$. Found 210.1317.

**4-(pentylamino)benzonitrile (3n)** Yellow oil, 158 mg, 84% yield **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 8.6 Hz, 2H), 4.19 (bs, 1H), 3.13 (td, *J* = 7.2, 5.5 Hz, 2H), 1.64 – 1.60 (m, 2H), 1.42 – 1.33 (m, 4H), 0.99 – 0.86 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 151.6, 133.8, 120.7, 112.2, 98.5, 43.3, 29.3, 29.0, 22.5, 14.1. Spectroscopic data are in agreement with those reported earlier.[14]

**2-methoxy-N-pentylaniline (3o)** Yellow oil, 67 mg, 95% purity, 33% yield. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 6.87 (td, *J* = 7.6, 1.4 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.65 (td, *J* = 7.7, 1.6 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.19 (bs, 1H), 3.85 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 1.66 (q, *J* = 7.4 Hz, 2H), 1.45 – 1.37 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3iH). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 146.9, 138., 121., 116.2, 109.9, 109.5, 55.5, 43., 29.57, 29.40, 22.7, 14.2. Spectroscopic data are in agreement with those reported earlier.[13]

***N*-pentylnaphthalen-1-amine (3p)** Yellow oil, 124 mg, 58% **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.70 (t, *J* = 9.0 Hz, 2H), 7.34 (qd, *J* = 6.9, 3.3 Hz, 2H), 7.26 (td, *J* = 7.9, 1.5 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 1H), 3.18 (t, *J* = 7.2 Hz, 2H), 1.69 (q, *J* = 7.7 Hz, 2H), 1.41 – 1.31 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 143.7, 134.5, 128.8, 126.8, 125.8, 124.7, 123.5, 119.9, 117.3, 104.5, 44.4, 29.7, 29.3, 22.7, 14.2. Spectroscopic data are in agreement with those reported earlier.

**4-methoxy-*N*-methylaniline (3q)** Colourless oil, 103 mg, 95% purity71% yield, **$^1$H NMR** (600 MHz, $CDCl_3$) δ 6.83 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 3.77 (s, 3H), 3.33 (s, 1H), 2.82 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 152.1, 143.8, 114.9, 113.7, 55.9, 31.6. Spectroscopic data are in agreement with those reported earlier.[15]

***N*-methylaniline (3r)** Colorless oil, 68 mg, 64% yield, **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 6.84 (q, *J* = 7.4 Hz, 1H), 6.71 (ddq, *J* = 7.1, 3.8, 1.2 Hz, 2H), 3.73 (s, 1H), 2.91 (s, 2H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 149.4, 129.2, 117.2, 112.4, 30.7. Spectroscopic data are in agreement with those reported earlier.[16]

**4-fluoro-*N*-methylaniline (3s)** Colorless oil. 106 mg, 85% yield, **$^1$H NMR** (600 MHz, $CDCl_3$) δ 6.91 (t, *J* = 8.8 Hz, 2H), 6.57 – 6.52 (m, 2H), 2.81 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 155.9 (d, *J* = 234.4 Hz), 145.8 (d, *J* = 2.0 Hz), 115.7 (d, *J* = 22.4 Hz), 113.2 (d, *J* = 7.6 Hz), 31.4. Spectroscopic data are in agreement with those reported earlier.[16]

**4-bromo-*N*-methylaniline (3t)** Colorless oil, 141 mg, 76% yield **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 3.70 (bs, 1H), 2.79 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 148.4, 131.9, 114.0, 108.8, 30.7. Spectroscopic data are in agreement with those reported earlier.[15]

**1H-indole (5a)** The synthesis was performed according to the general procedure at the temperature of 70 °C. Pale yellow solid**,** m.p. 52-54 °C (Lit.[17]: 51 °C) 71 mg**,** 61% yield **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.14 (bs, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 1H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 135.9, 128.0, 124.2, 122.1, 120.9, 119.5, 111.1, 102.8. Spectroscopic data are in agreement with those reported earlier. [18]

**1-benzyl-2-phenyl-1H-benzo[d]imidazole (7a)** The synthesis was performed according to the general procedure at the temperature of 75 °C. Yellow oil, 176 mg, 95% purity 59% **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.50 – 7.43 (m, 3H), 7.37 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 7.11 (dq, *J* = 7.0, 1.0 Hz, 2H), 5.46 (s, 2H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 154.3, 143.3, 136.5, 136.2, 130.2, 130.1, 129.4, 129.2, 128.9, 127.9, 126.1, 123.2, 122.8, 120.1, 110. 7, 48.5. Spectroscopic data are in agreement with those reported earlier. [19]

***N*$^1$-pentylbenzene-1,2-diamine (7a)** The synthesis was performed according to the general procedure at the temperature of 75 °C. Yellow oil, 107 mg /76% purity , 43% **$^1$H NMR** δ 6.83 (dd, *J* = 8.4, 6.8 Hz, 1H), 6.73 – 6.70 (m, 1H), 6.66 (t, *J* = 7.3 Hz, 2H), 3.31 (bs, 3H), 3.10 (t, *J* = 7.2 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.41 (dq, *J* = 14.1, 7.7, 7.2 Hz, 4H), 0.93 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 138.3, 134.1, 120.9, 118.4, 116.6, 111.7, 44.4, 29.6, 29.6, 22.7, 14.3.

**Quinoxaline (9a)** The synthesis was performed according to the general procedure at the temperature of 90 °C. Yellow oil, 34 mg, 49% **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.86 (s, 2H), 8.13 (dt, *J* = 6.5, 3.4 Hz, 2H), 7.80 (dt, *J* = 6.5, 3.4 Hz, 2H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 145.1, 143.2, 130.2, 129.7. Spectroscopic data are in agreement with those reported earlier.[20]

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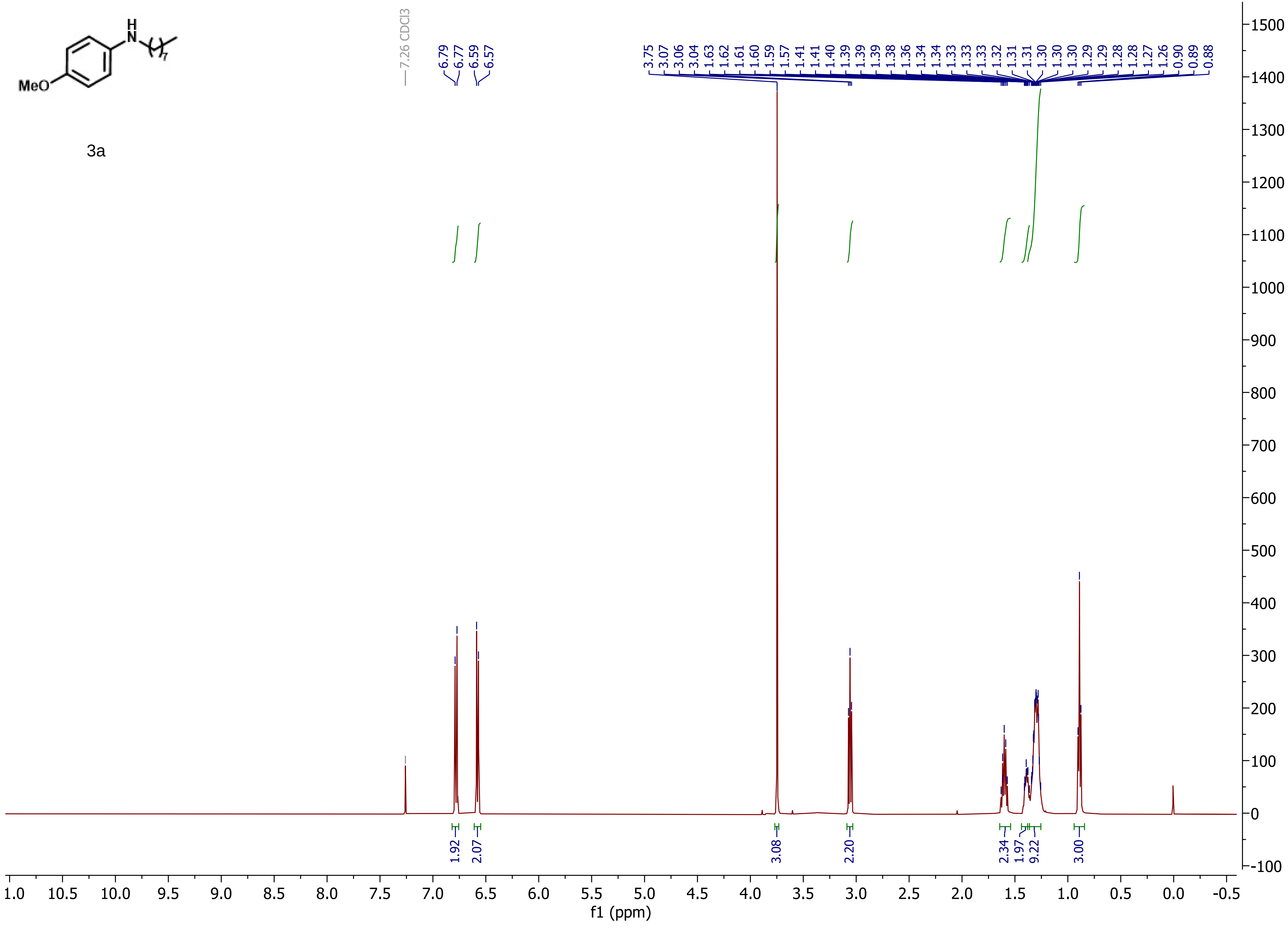
$^{1}H$ and $^{13}C$ NMR spectra for compounds **3a–3t** and **5a**, **7a**-**9a**



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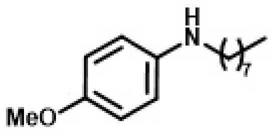

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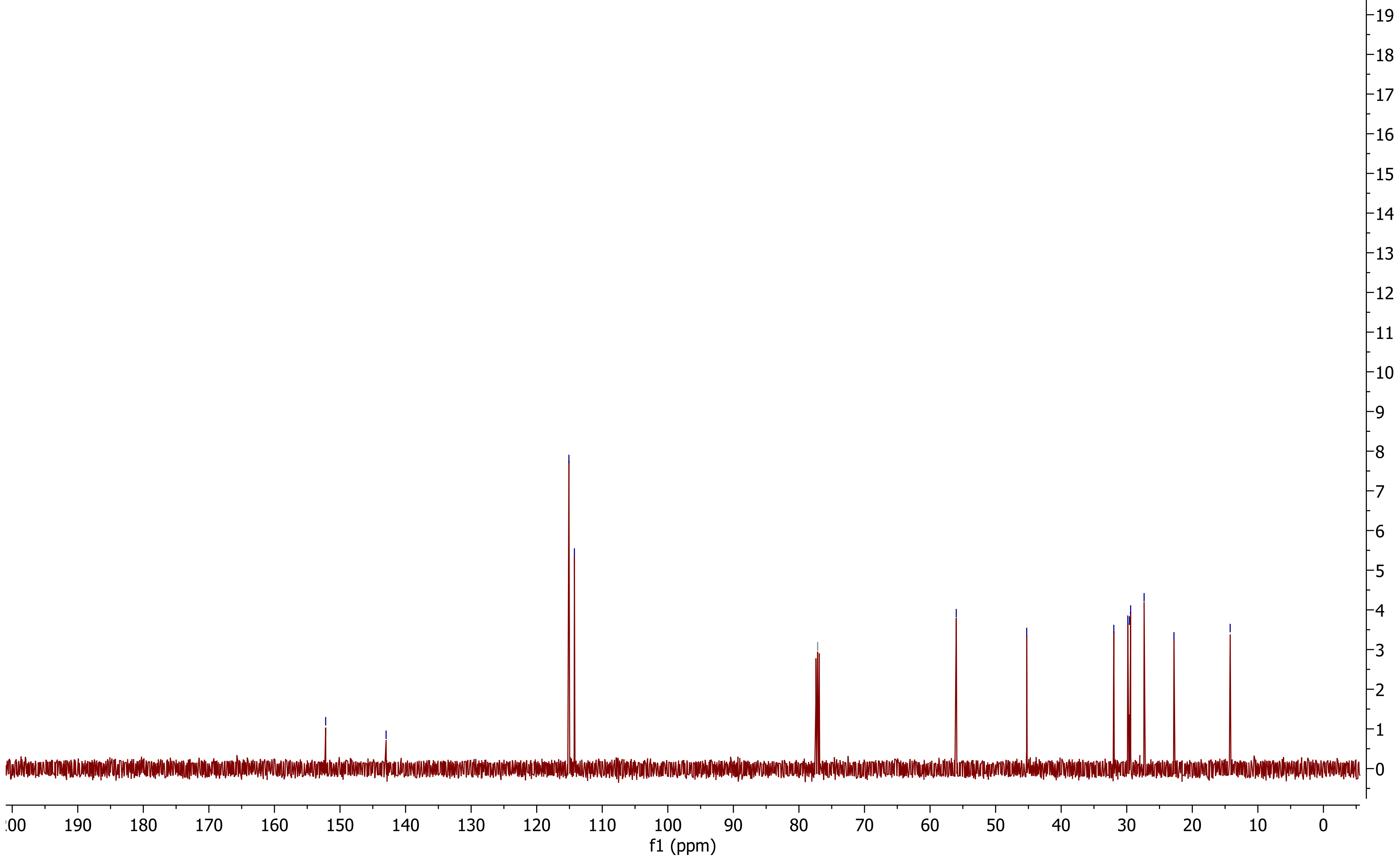

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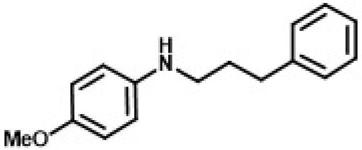

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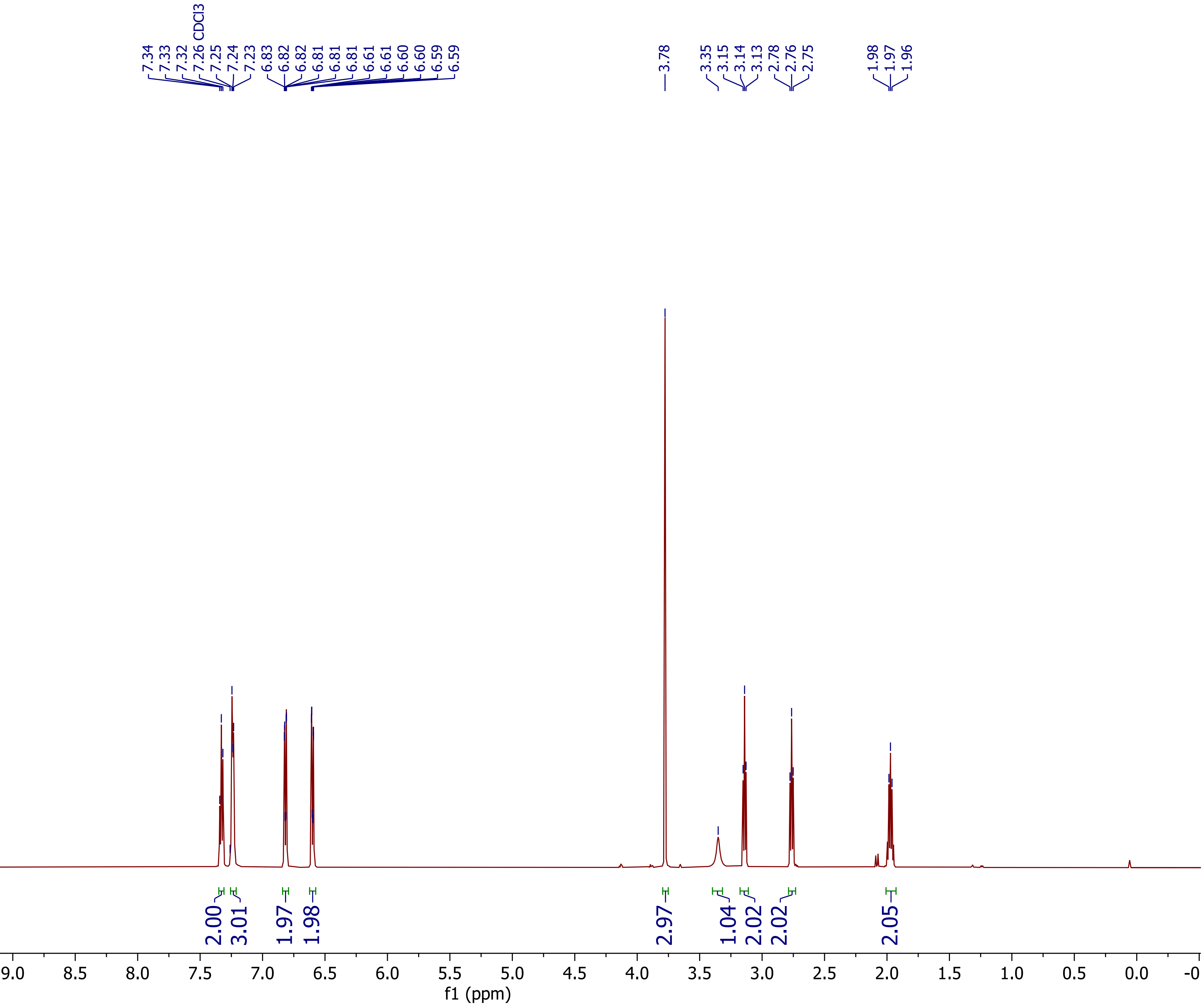

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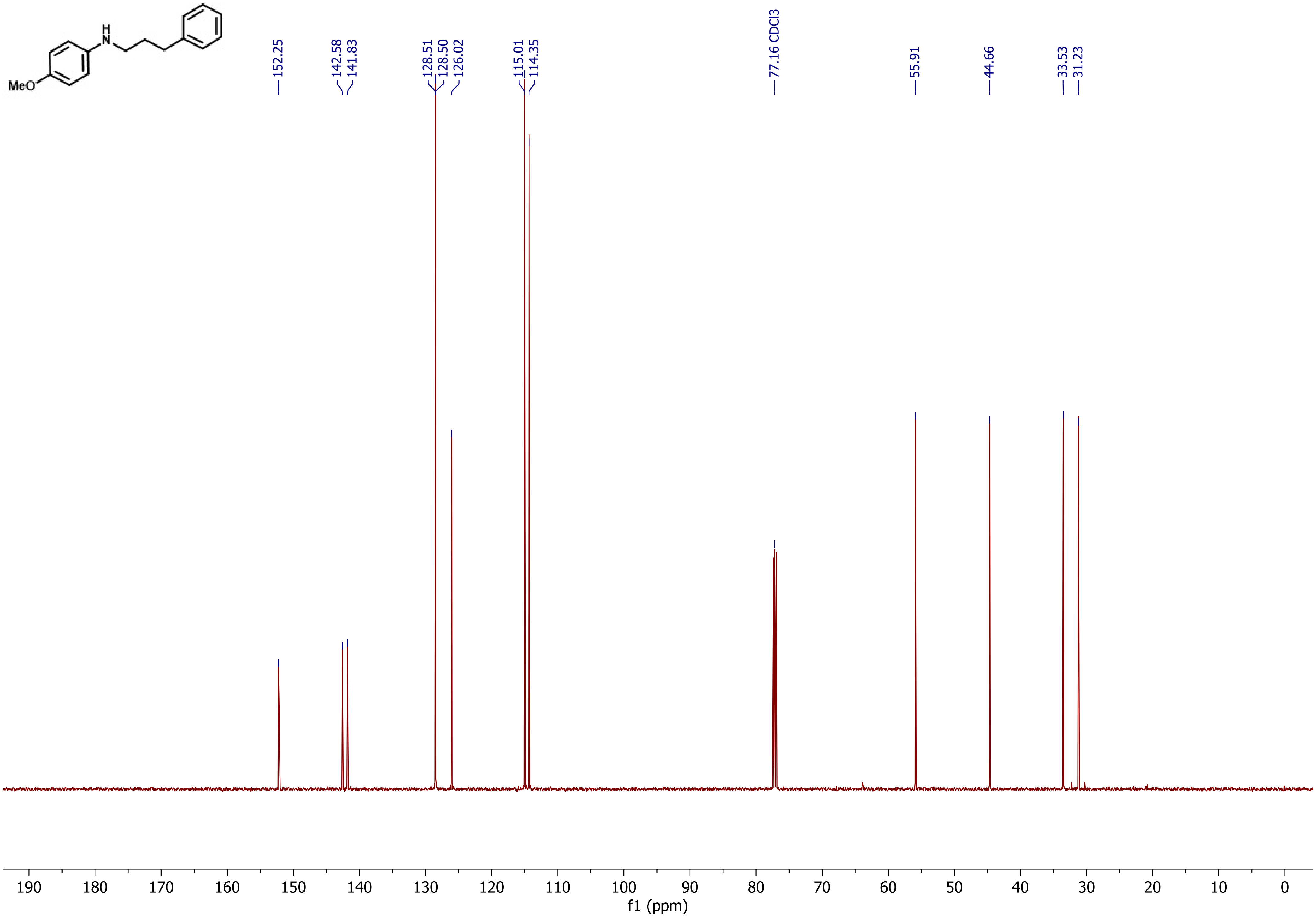

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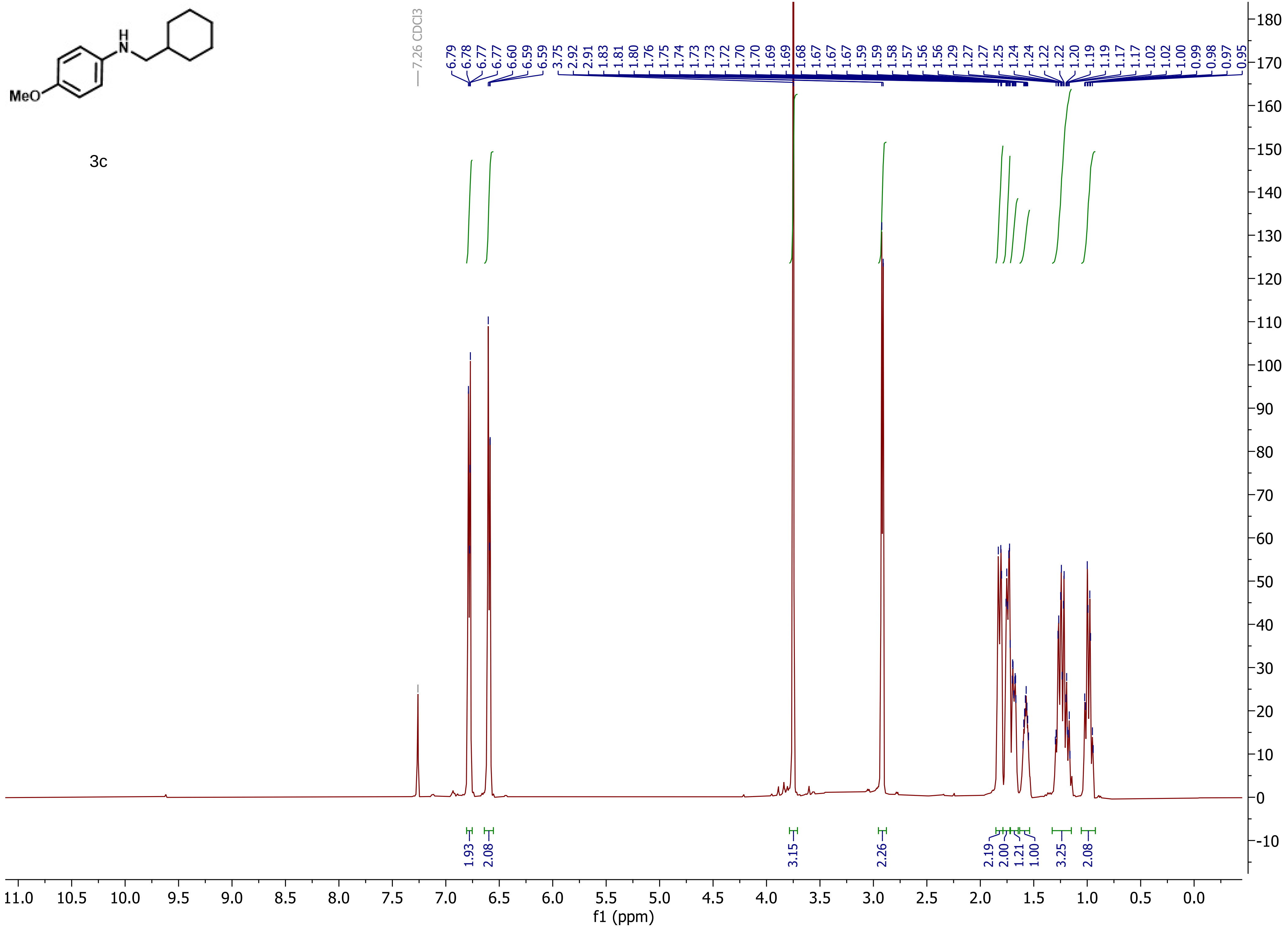
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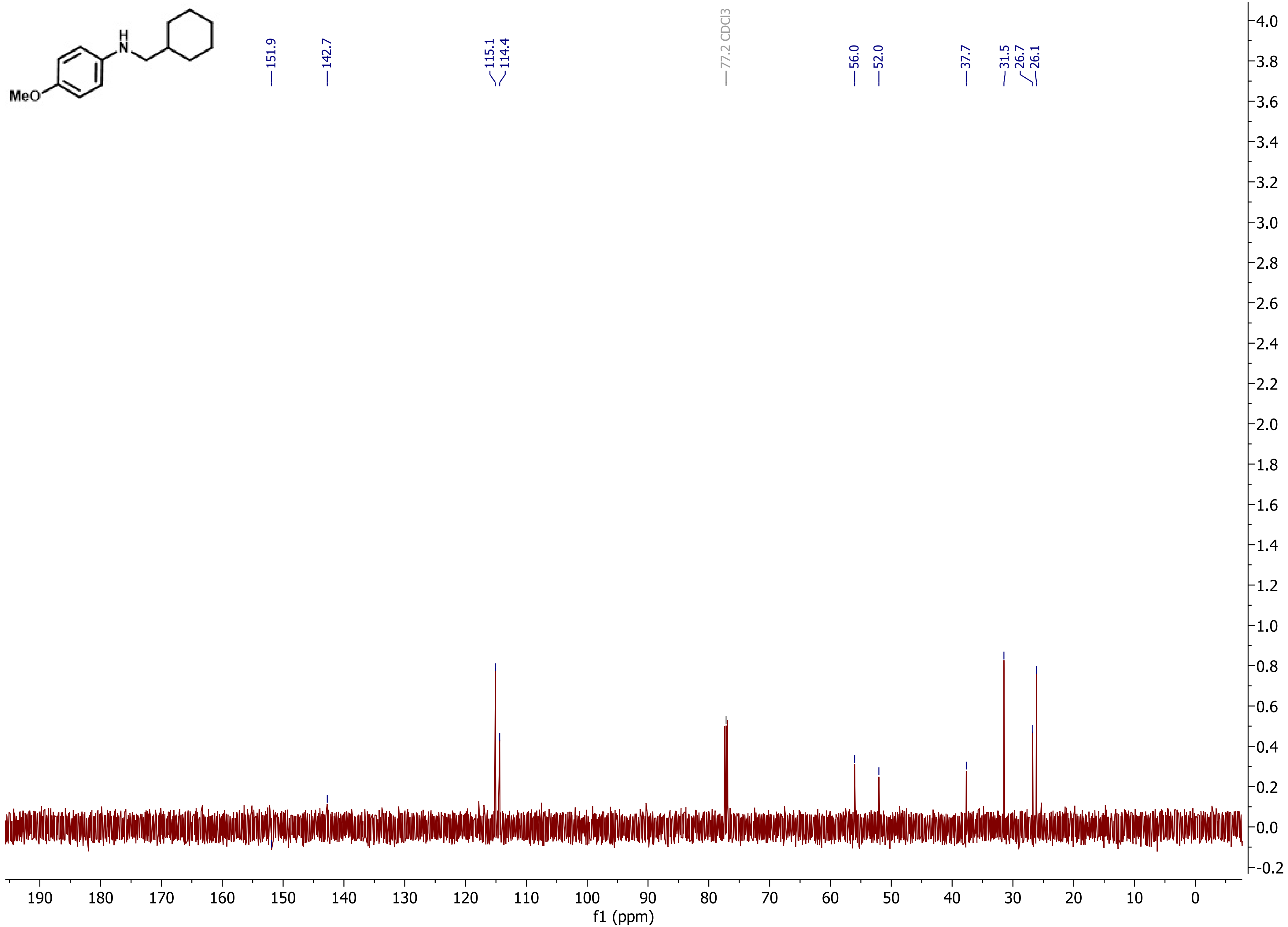

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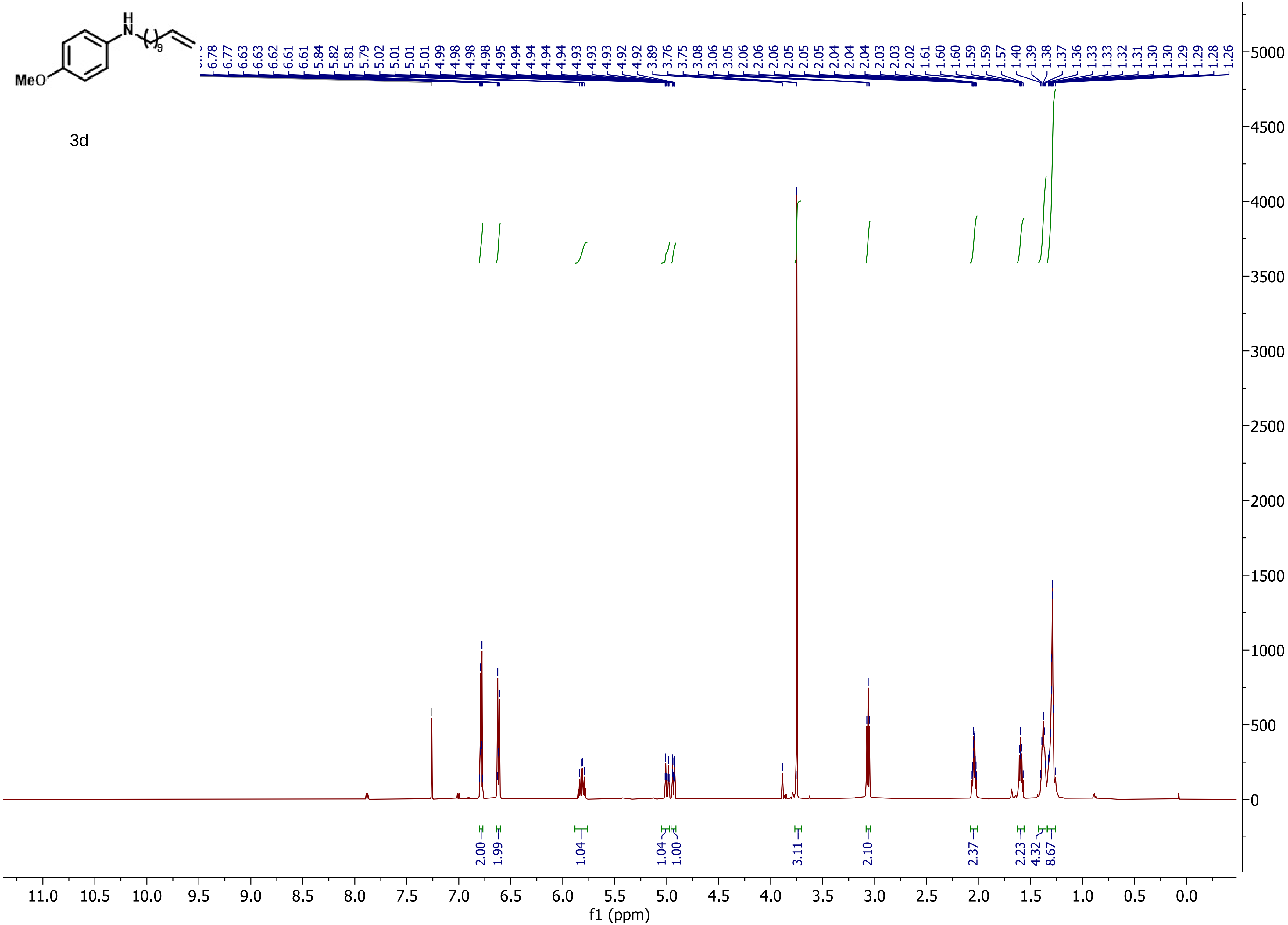

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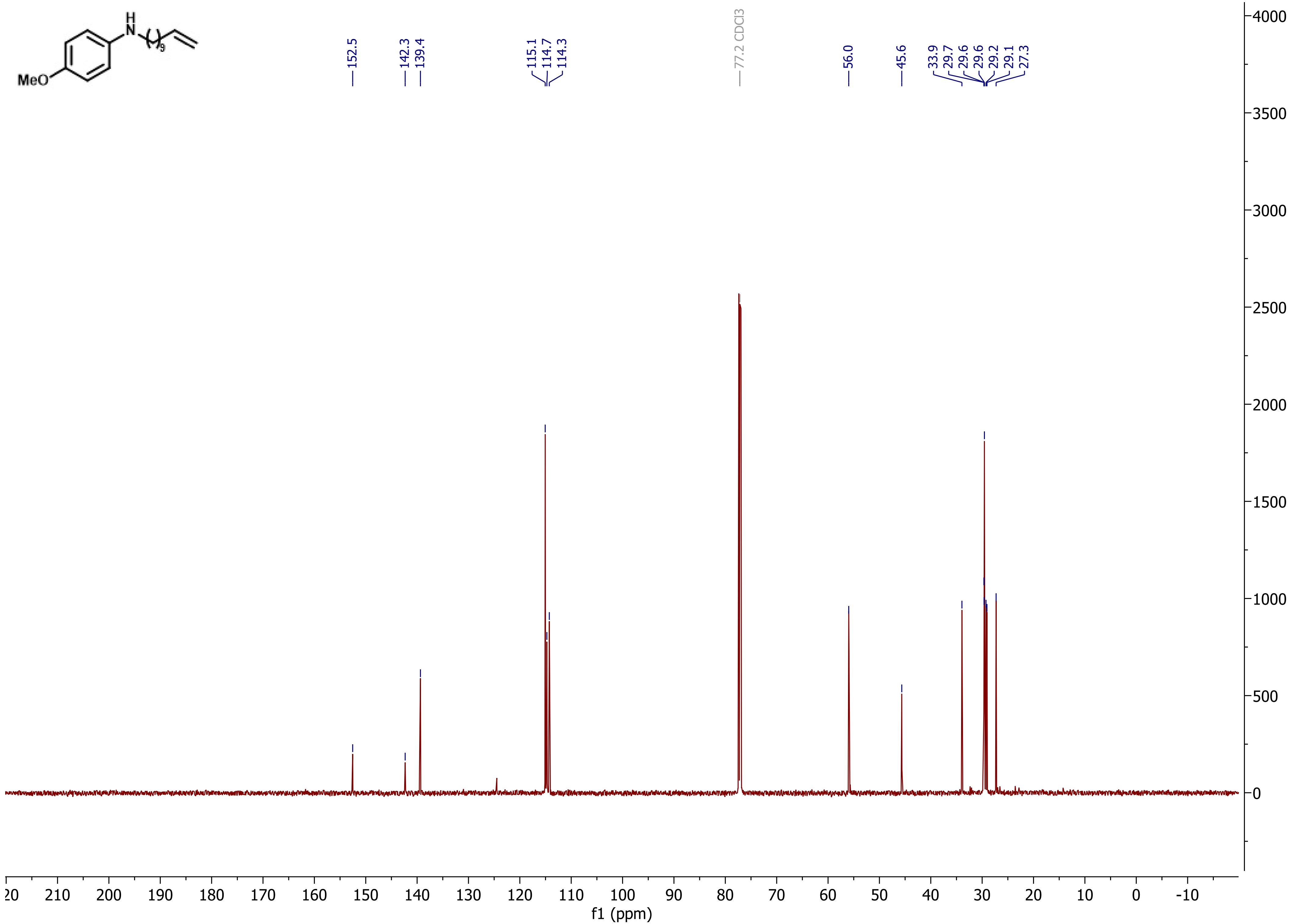
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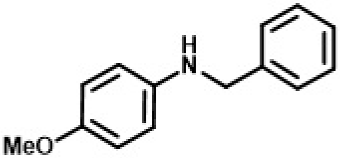
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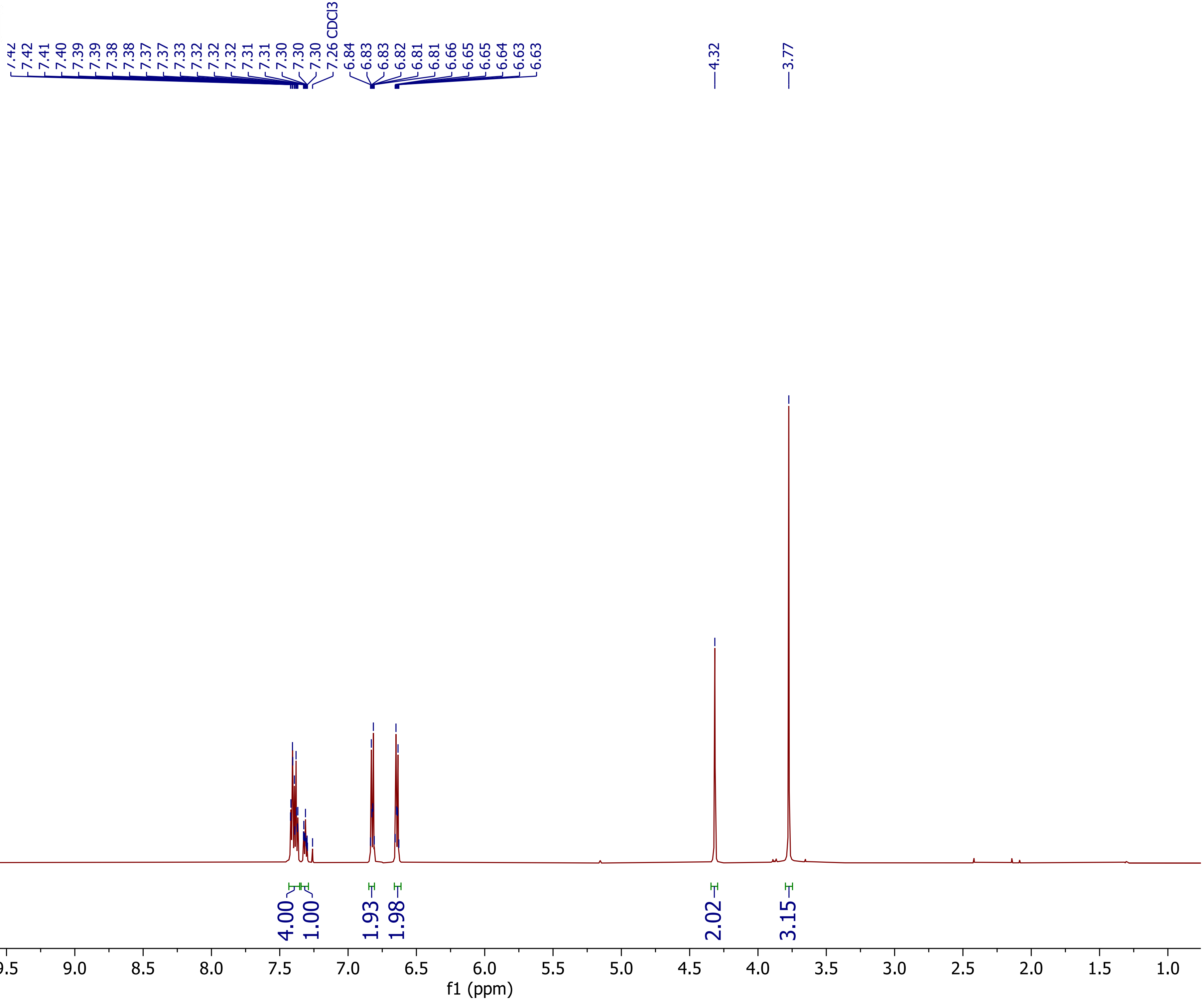
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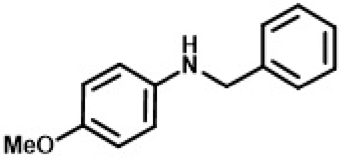
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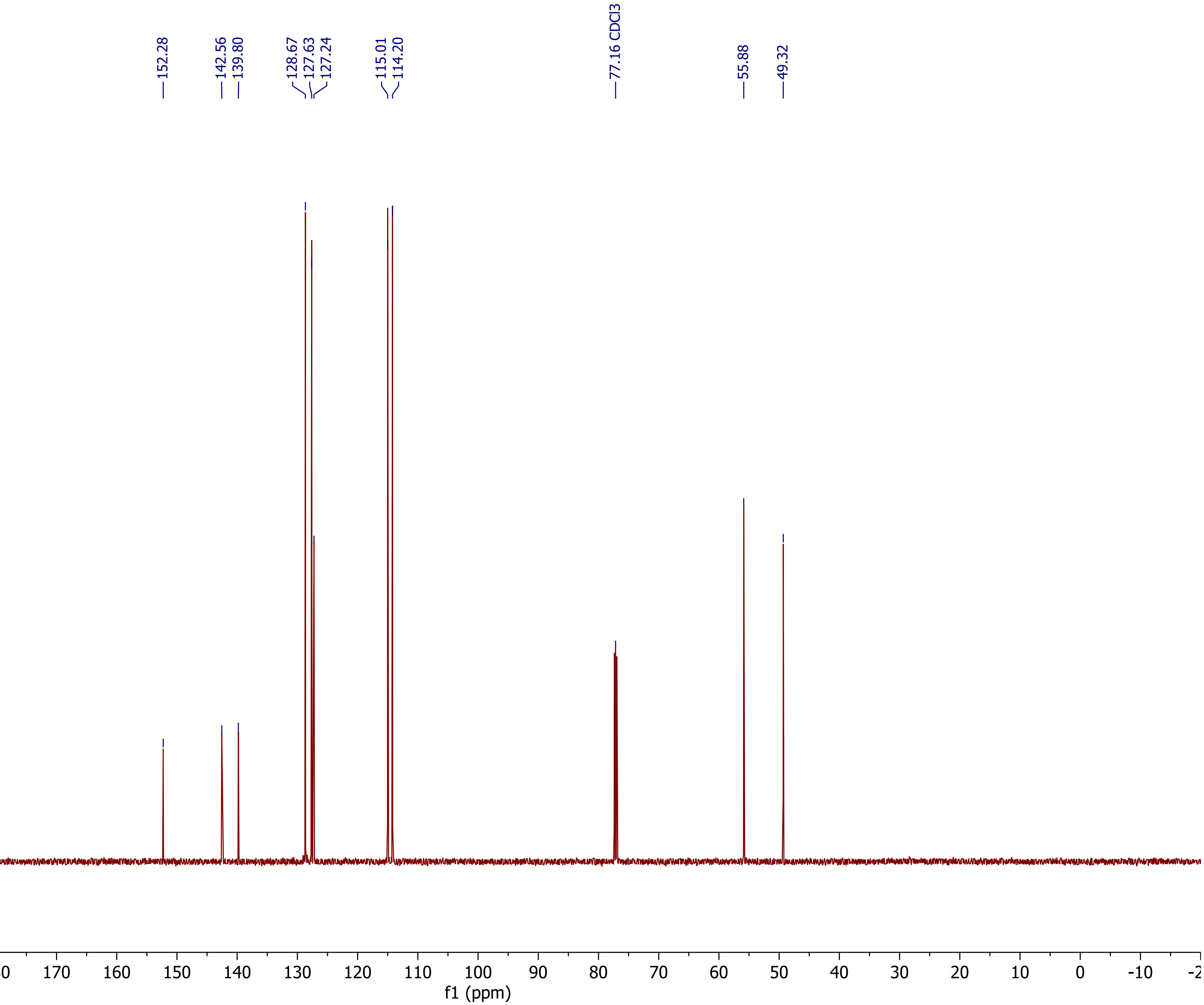
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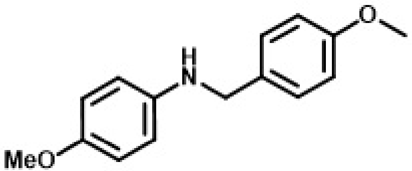
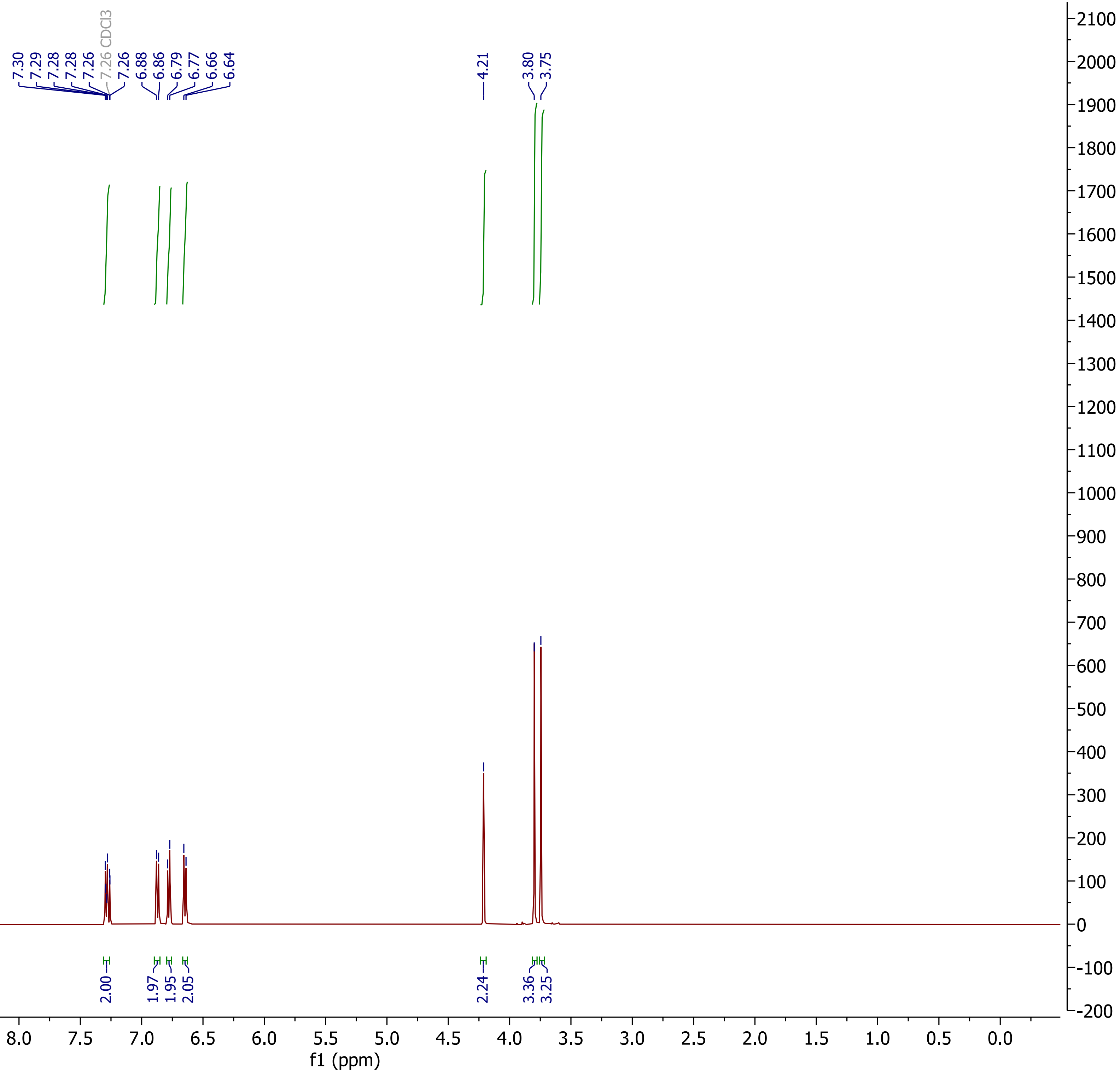
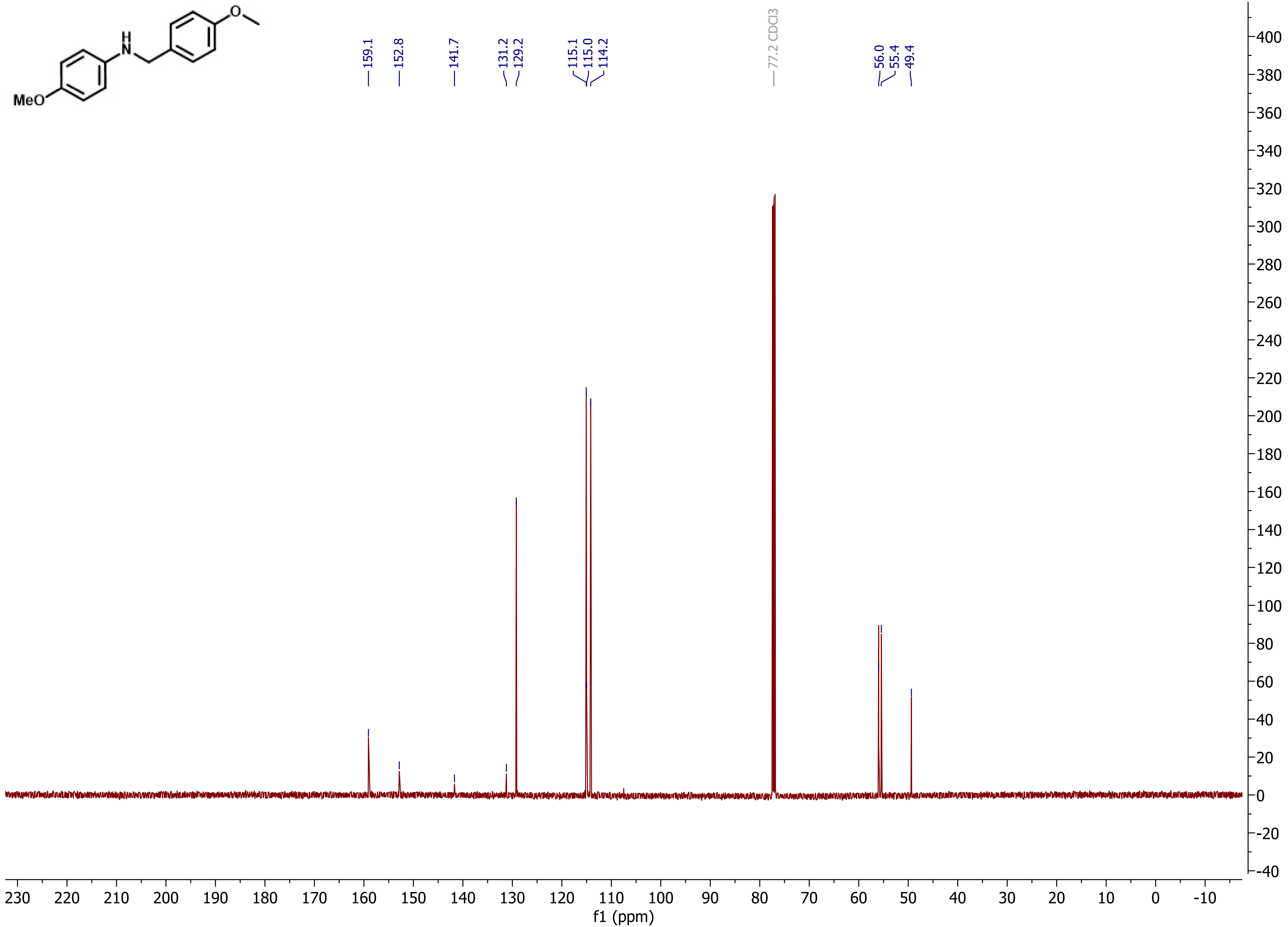
50
40
30
20
10
0
-10
-2
f1 (ppm)

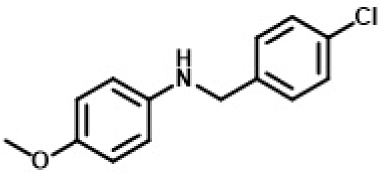

MeO
H
N
O

3f


7.30
7.29
7.28
7.28
7.26
7.26 CDCl3
7.26
6.88
6.86
6.79
6.77
6.66
6.64
4.21
3.80
3.75
2.00
1.97
1.95
2.05
2.24
3.36
3.25
f1 (ppm)

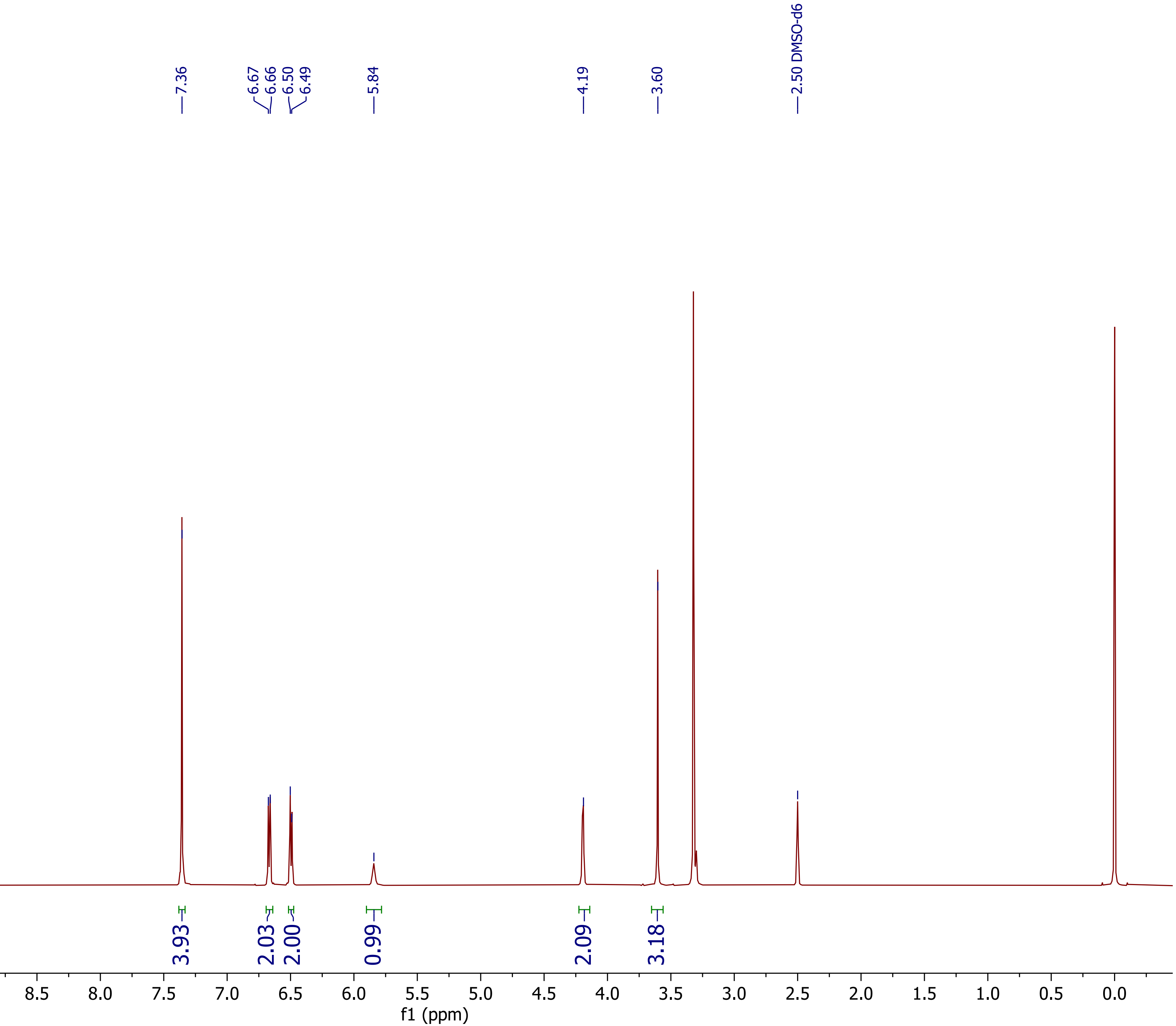


MeO
H
N
O
159.1
152.8
141.7
131.2
129.2
115.1
115.0
114.2
77.2 CDCl3
56.0
55.4
49.4
f1 (ppm)

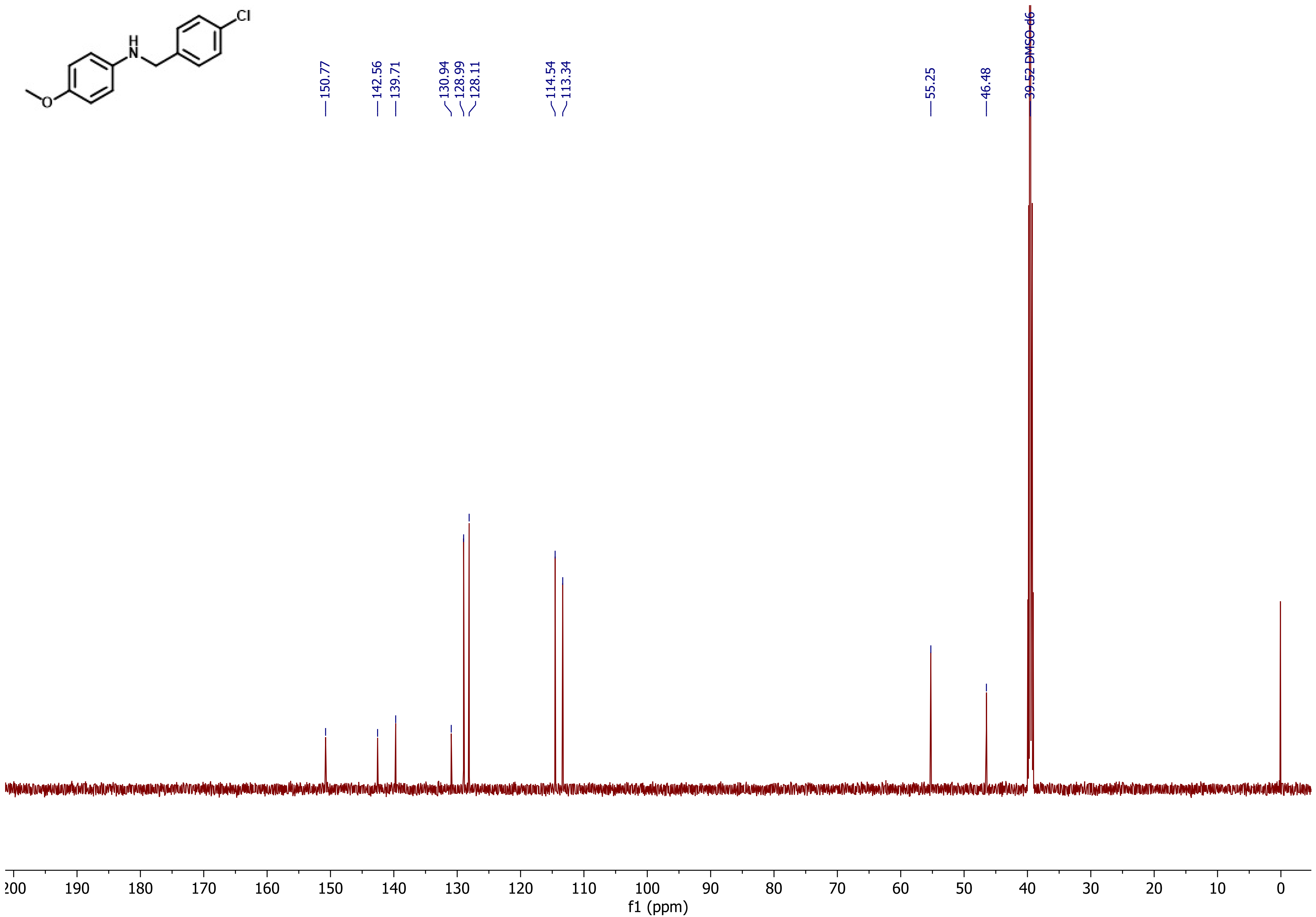


H
N
Cl
O

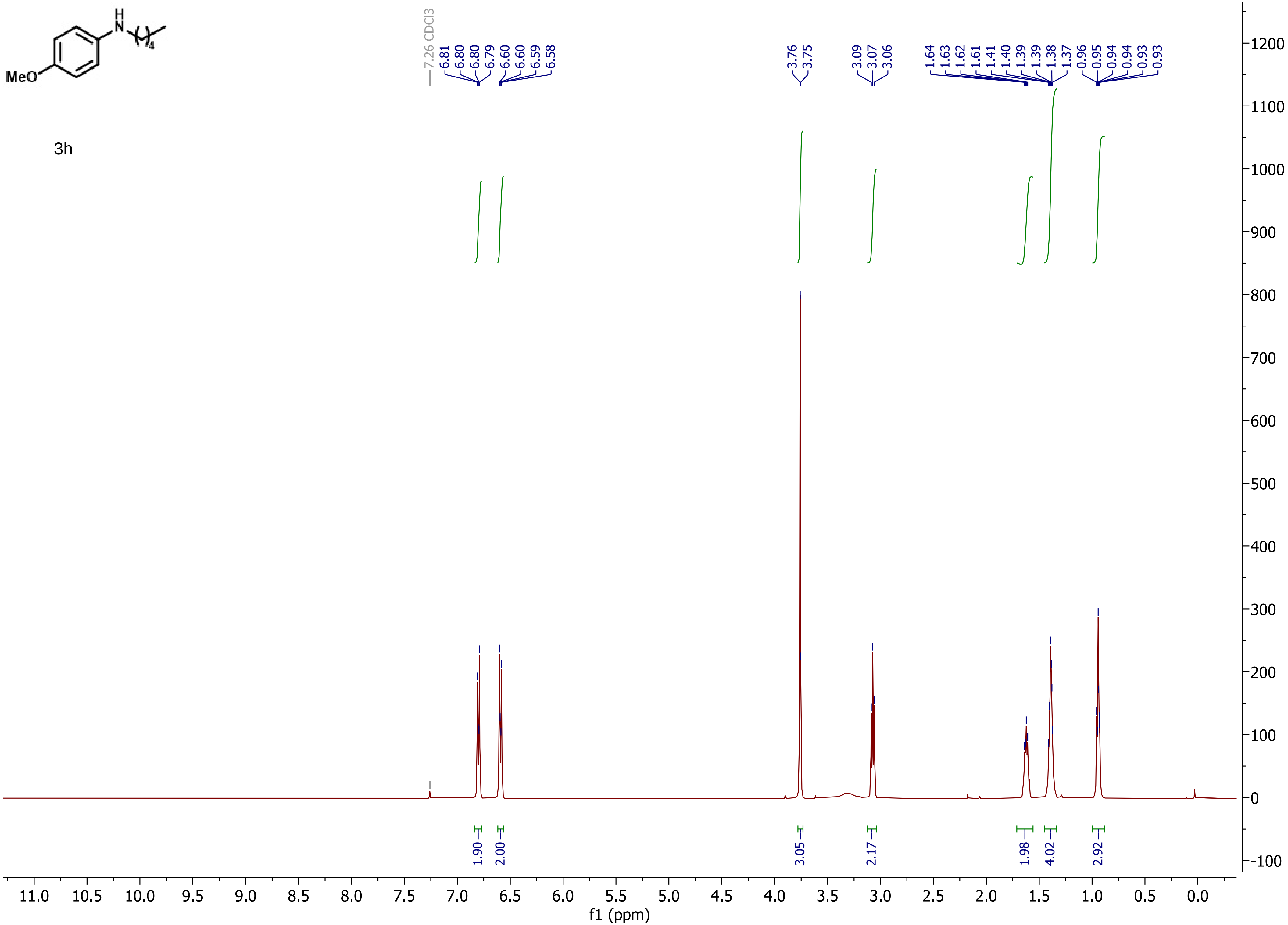

3g



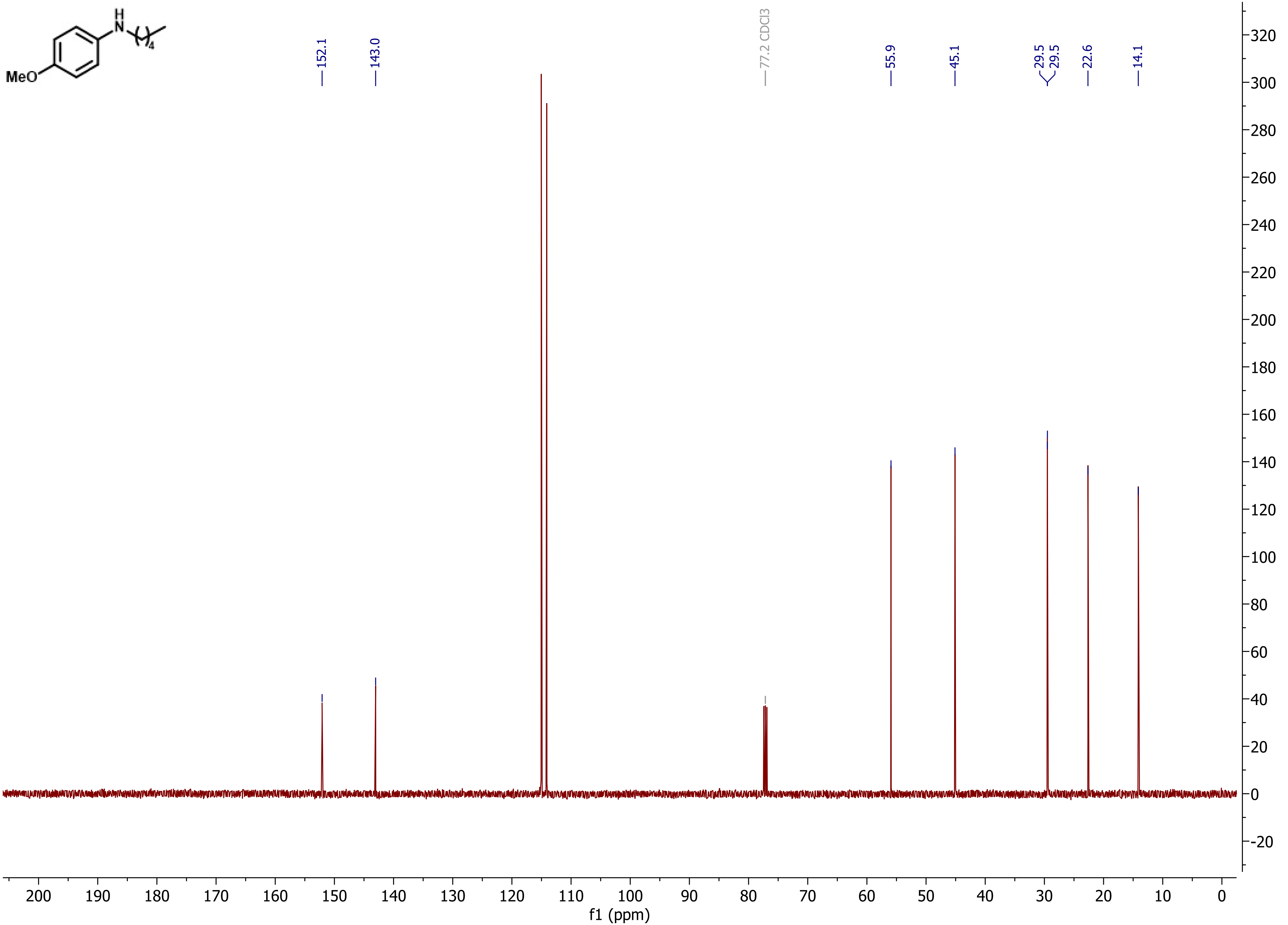
7.36
6.67
6.66
6.50
6.49
5.84
4.19
3.60
2.50 DMSO-d6
3.93
2.03
2.00
0.99
2.09
3.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



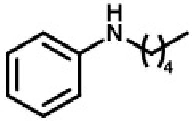
Cl
H
N
O
150.77
142.56
139.71
130.94
128.99
128.11
114.54
113.34
55.25
46.48
39.52 DMSO d6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



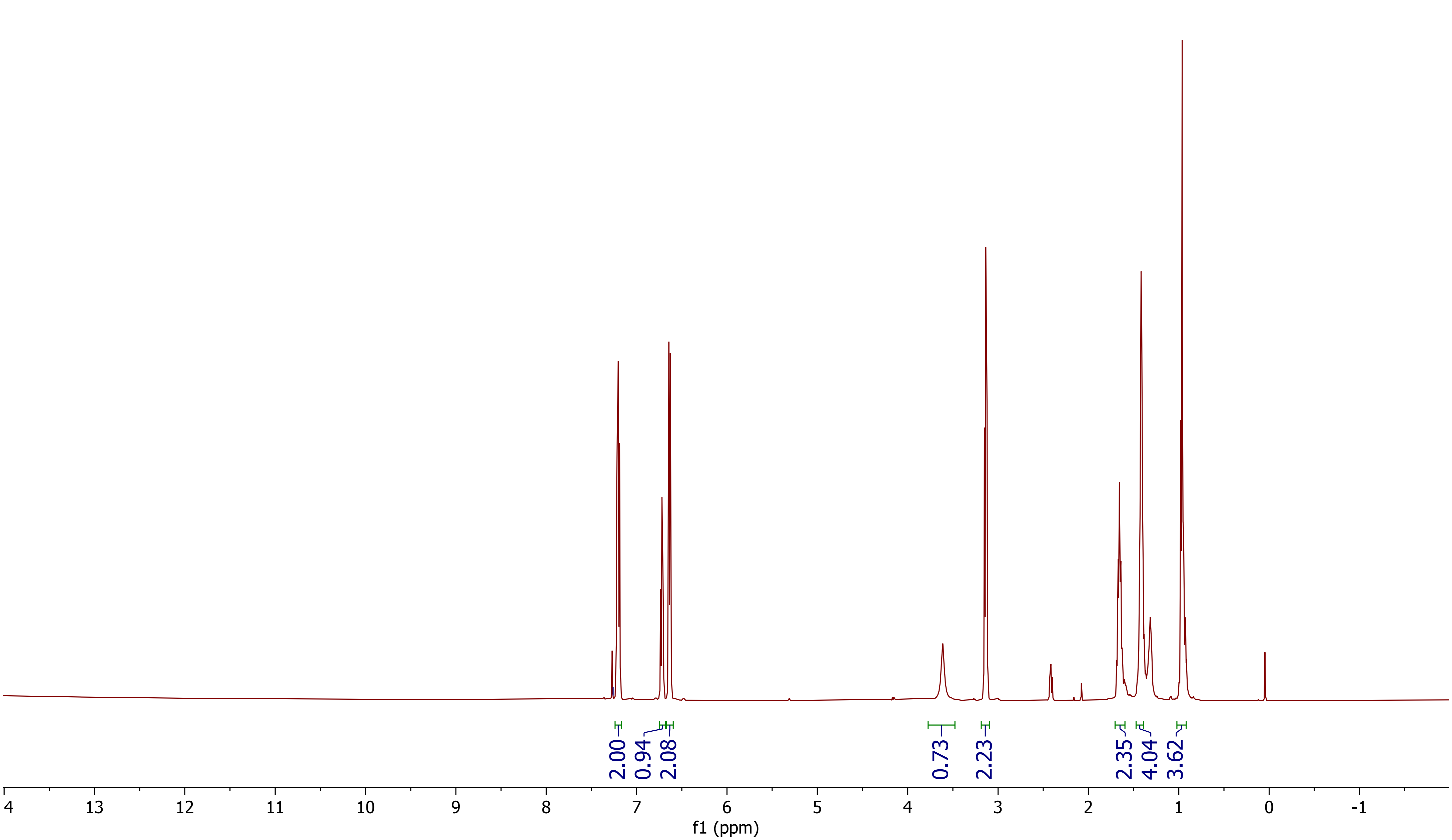
MeO
N
H
4
3h
7.26 CDCl3
6.81
6.80
6.80
6.79
6.60
6.60
6.59
6.58
3.76
3.75
3.09
3.07
3.06
1.64
1.63
1.62
1.61
1.41
1.40
1.39
1.39
1.38
1.37
0.96
0.95
0.94
0.93
0.93
1.90
2.00
3.05
2.17
1.98
4.02
2.92
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100



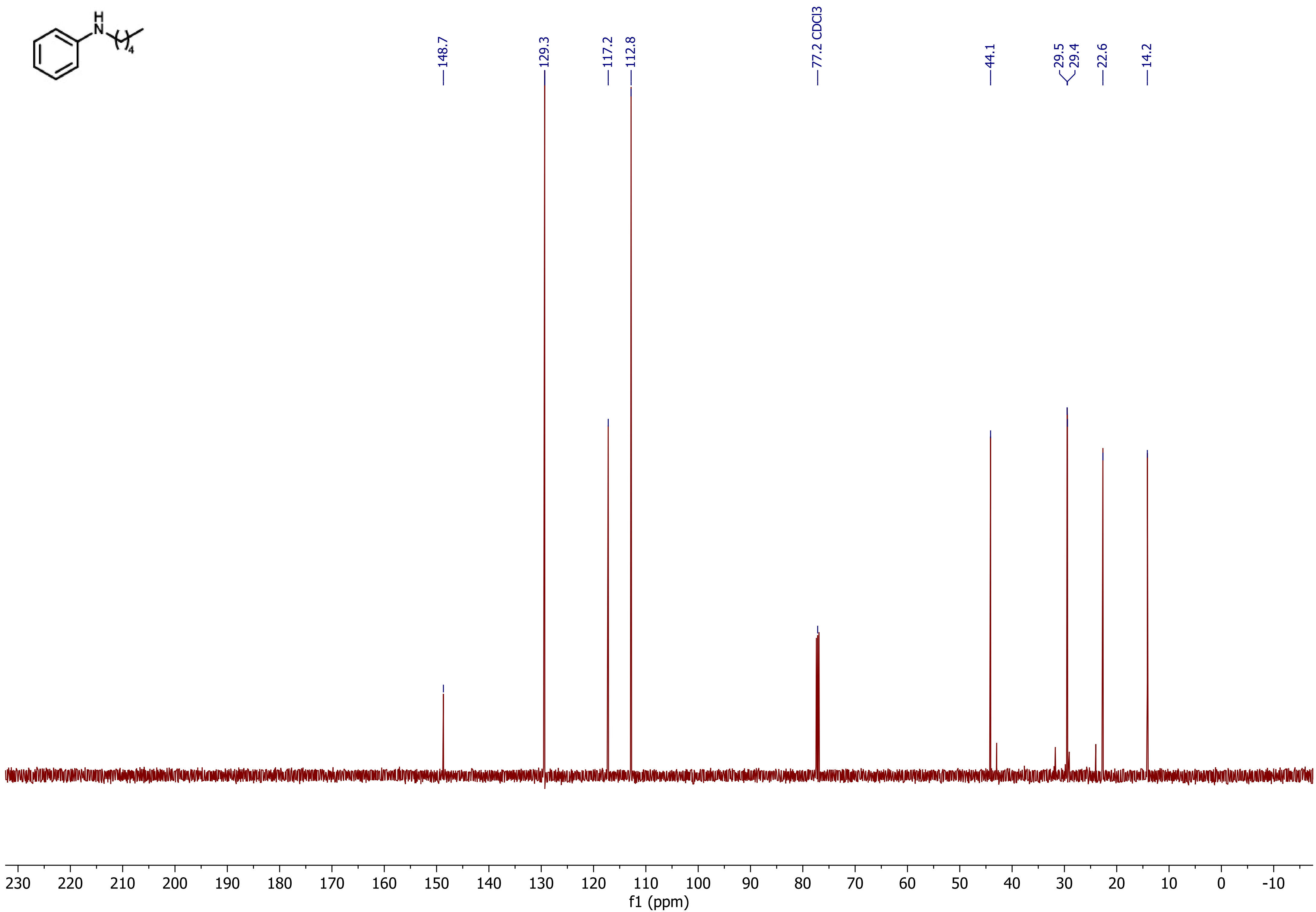
MeO
H
N
4
152.1
143.0
77.2 CDCl3
55.9
45.1
29.5
29.5
22.6
14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20



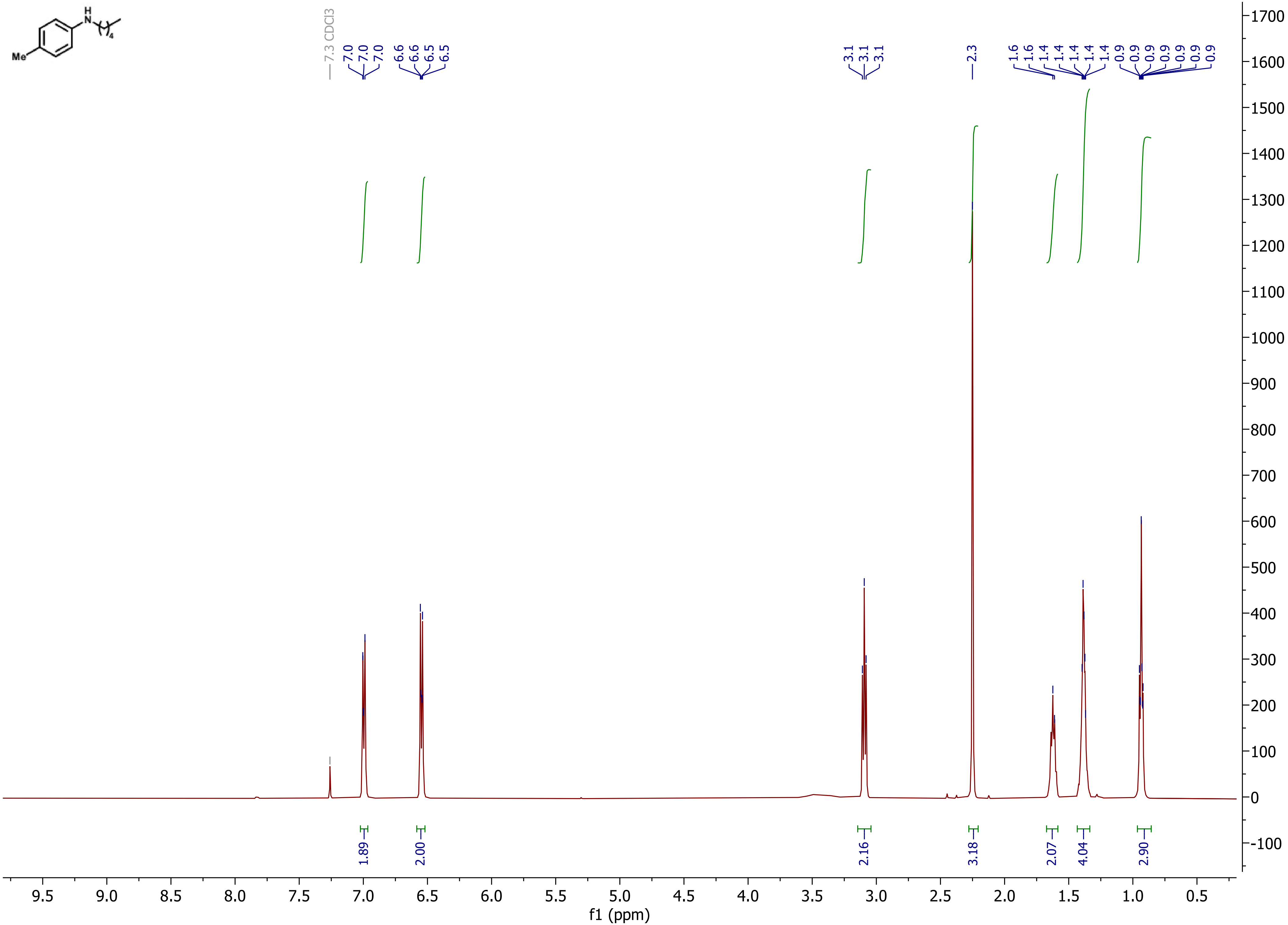
3i



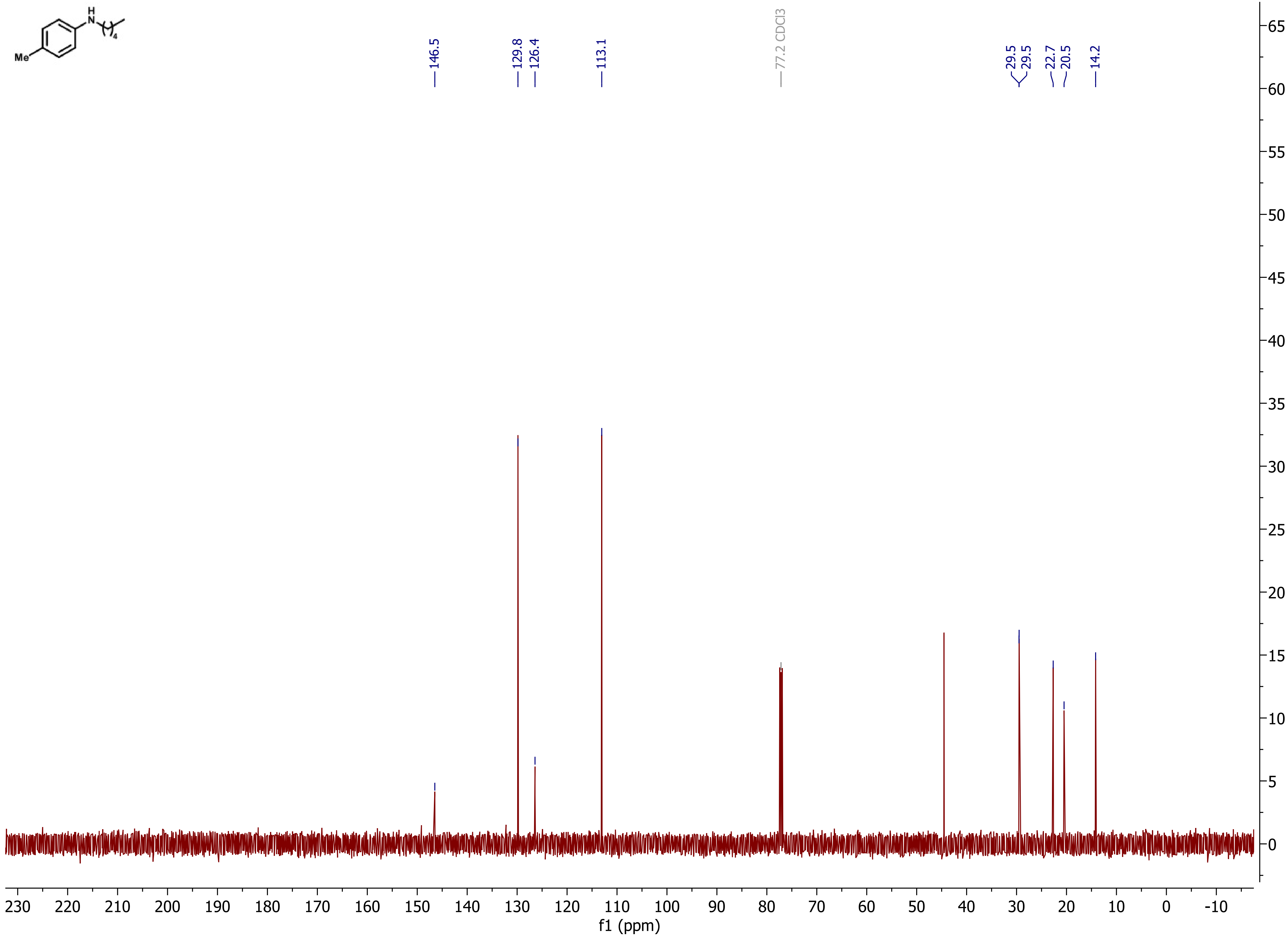
7.3 CDCl3
2.00
0.94
2.08
0.73
2.23
2.35
4.04
3.62
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



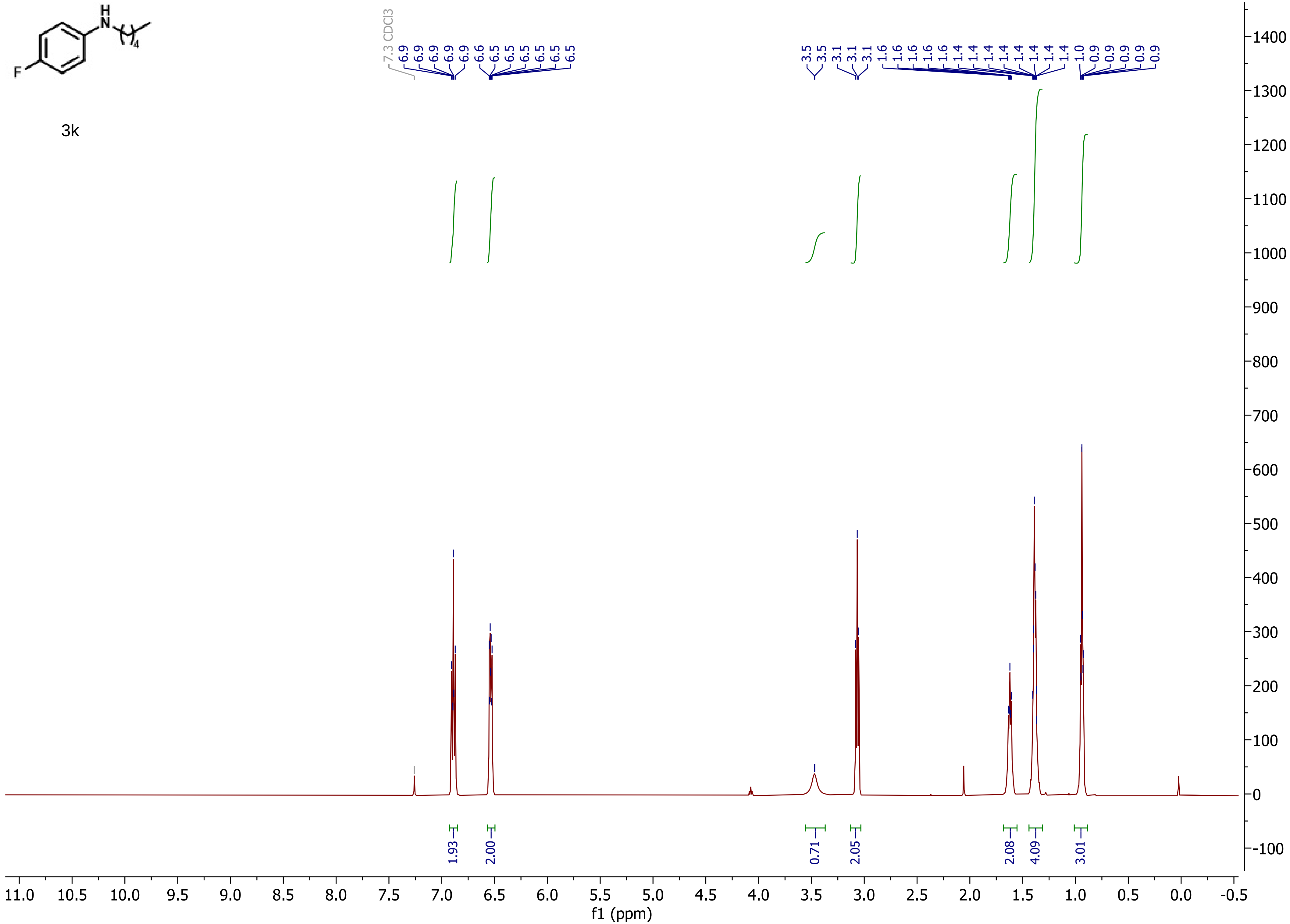
148.7
129.3
117.2
112.8
77.2 CDCl3
44.1
29.5
29.4
22.6
14.2
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



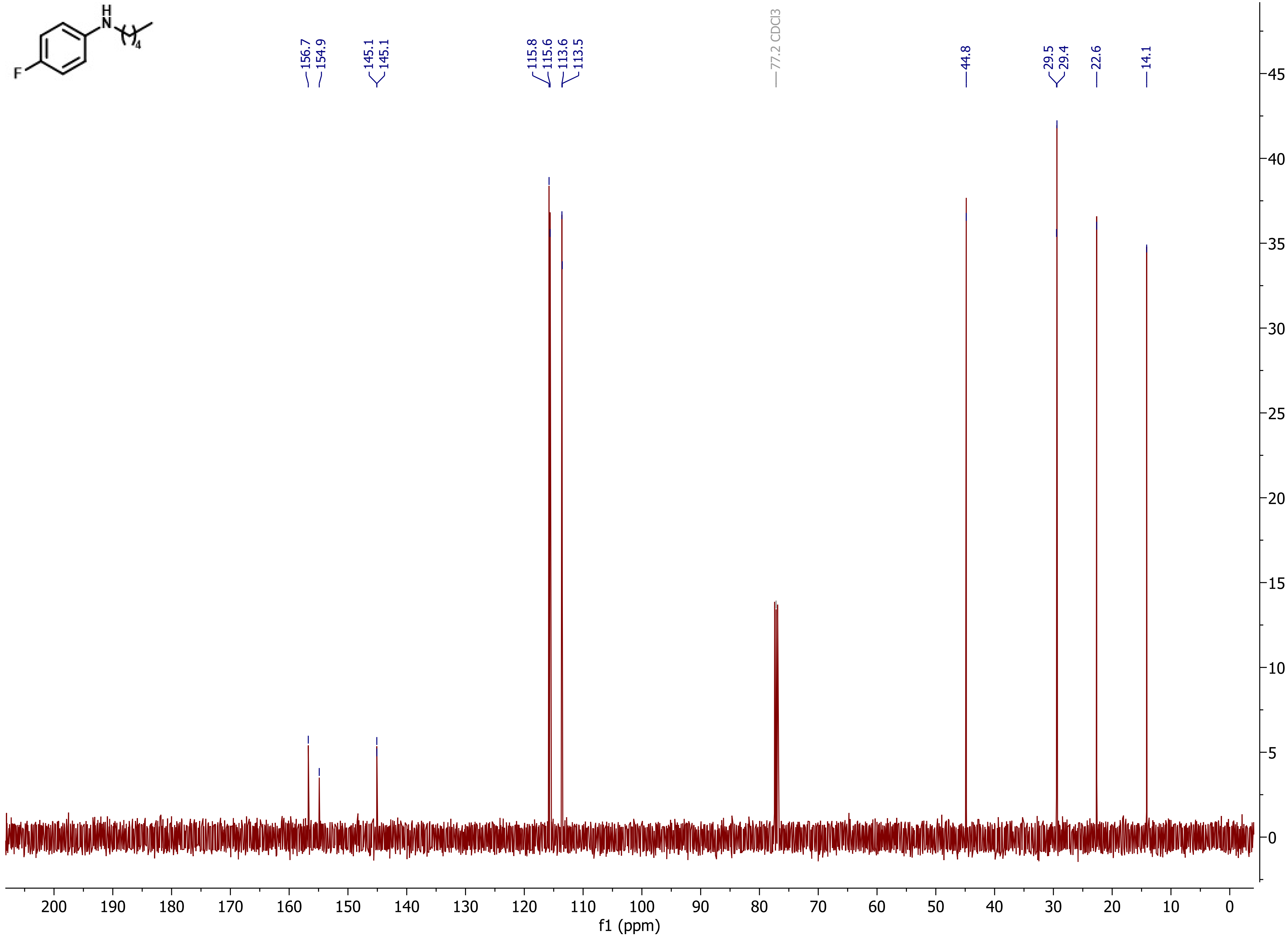
Me
H
N
4
7.3 CDCl3
7.0
7.0
7.0
6.6
6.6
6.5
6.5
3.1
3.1
3.1
2.3
1.6
1.6
1.4
1.4
1.4
1.4
1.4
0.9
0.9
0.9
0.9
0.9
0.9
0.9
1.89
2.00
2.16
3.18
2.07
4.04
2.90
f1 (ppm)

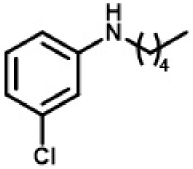


Me
H
N
4
146.5
129.8
126.4
113.1
77.2 CDCl3
29.5
29.5
22.7
20.5
14.2
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
65 60 55 50 45 40 35 30 25 20 15 10 5 0

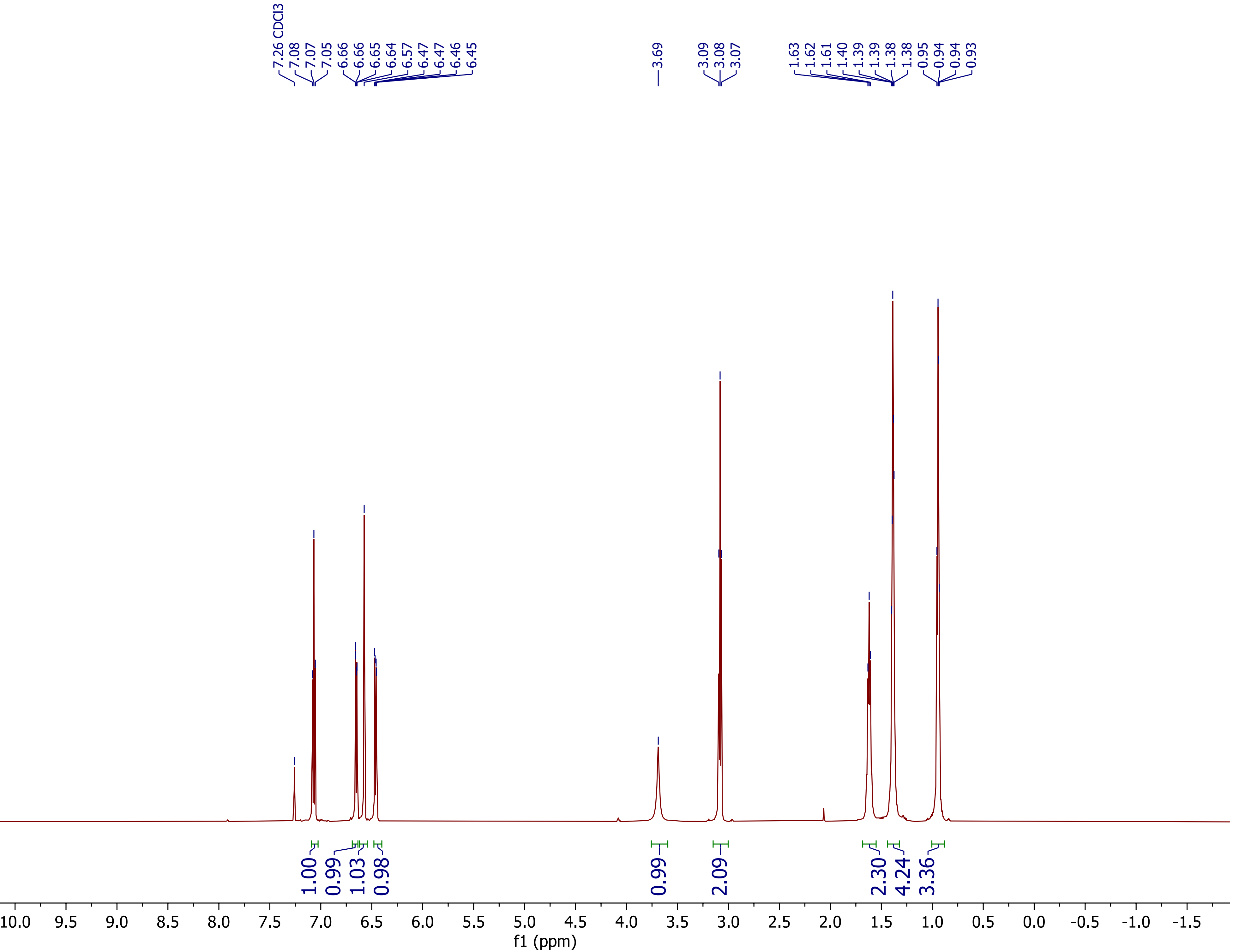


3k
7.3 CDCl3
6.9
6.9
6.9
6.9
6.9
6.6
6.5
6.5
6.5
6.5
6.5
6.5
3.5
3.5
3.1
3.1
3.1
1.6
1.6
1.6
1.6
1.6
1.4
1.4
1.4
1.4
1.4
1.4
1.4
1.4
1.0
0.9
0.9
0.9
0.9
0.9
1.93
2.00
0.71
2.05
2.08
4.09
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

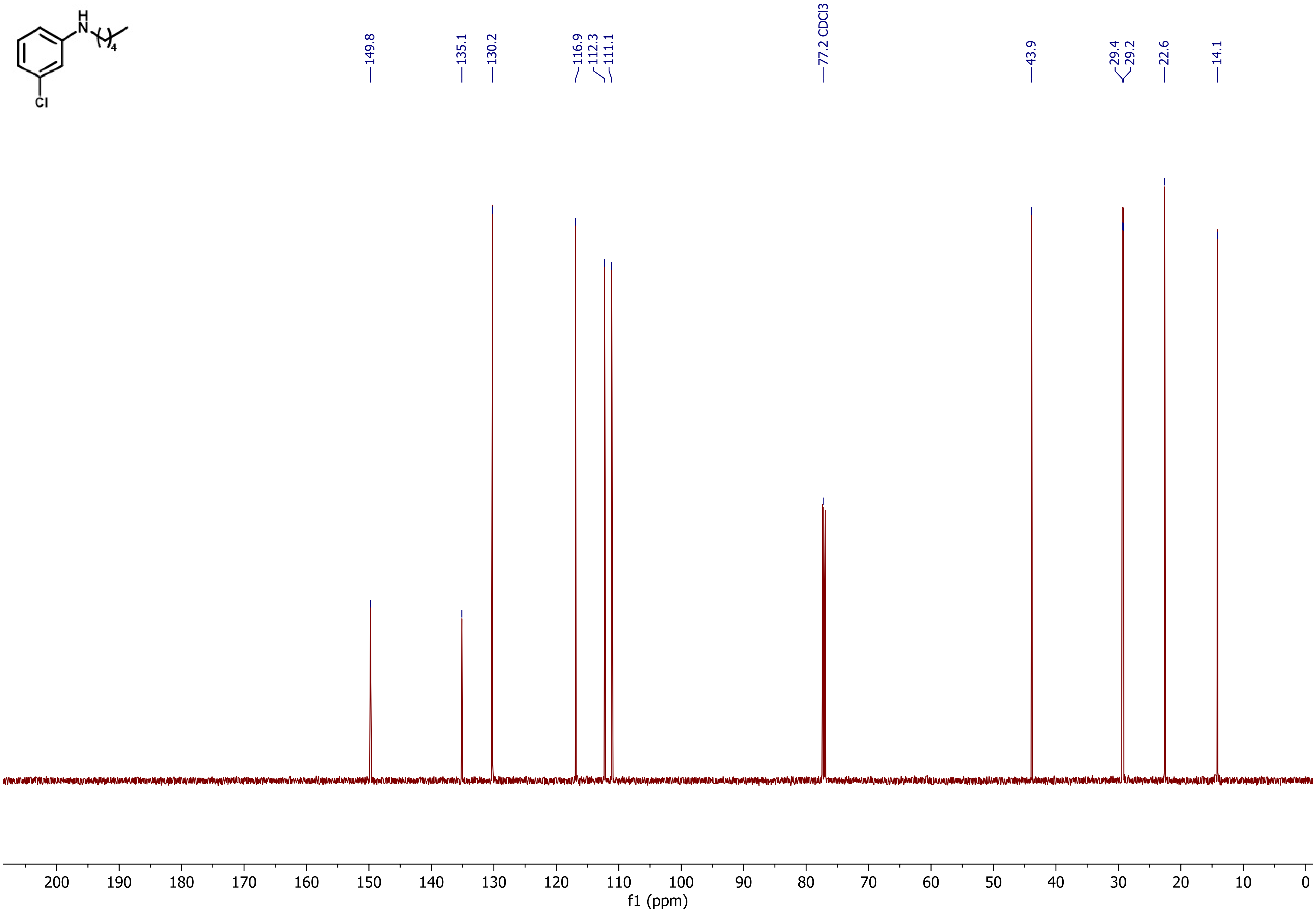

156.7
154.9
145.1
145.1
115.8
115.6
113.6
113.5
77.2 CDCl3
44.8
29.5
29.4
22.6
14.1
f1 (ppm)

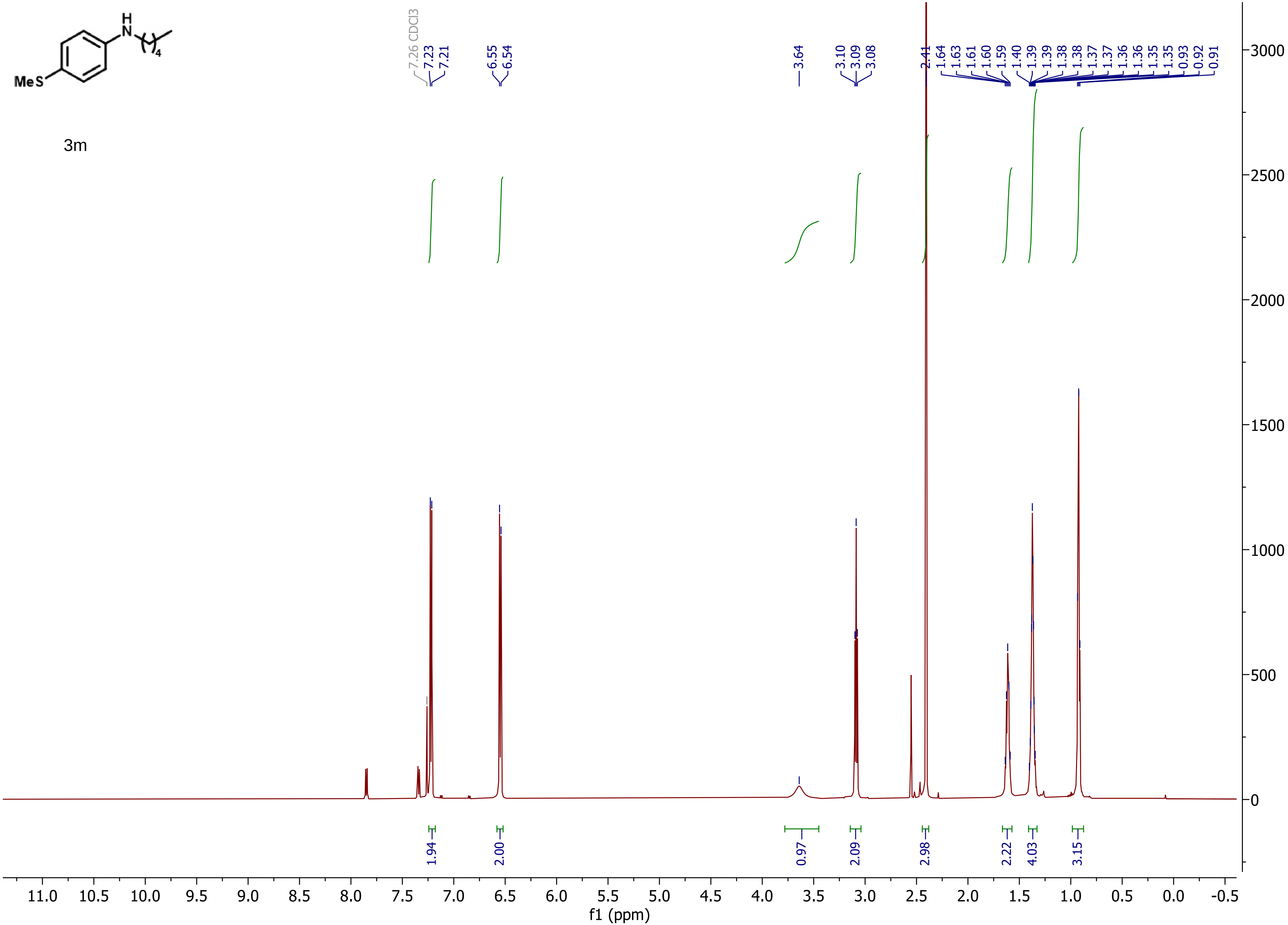


3l

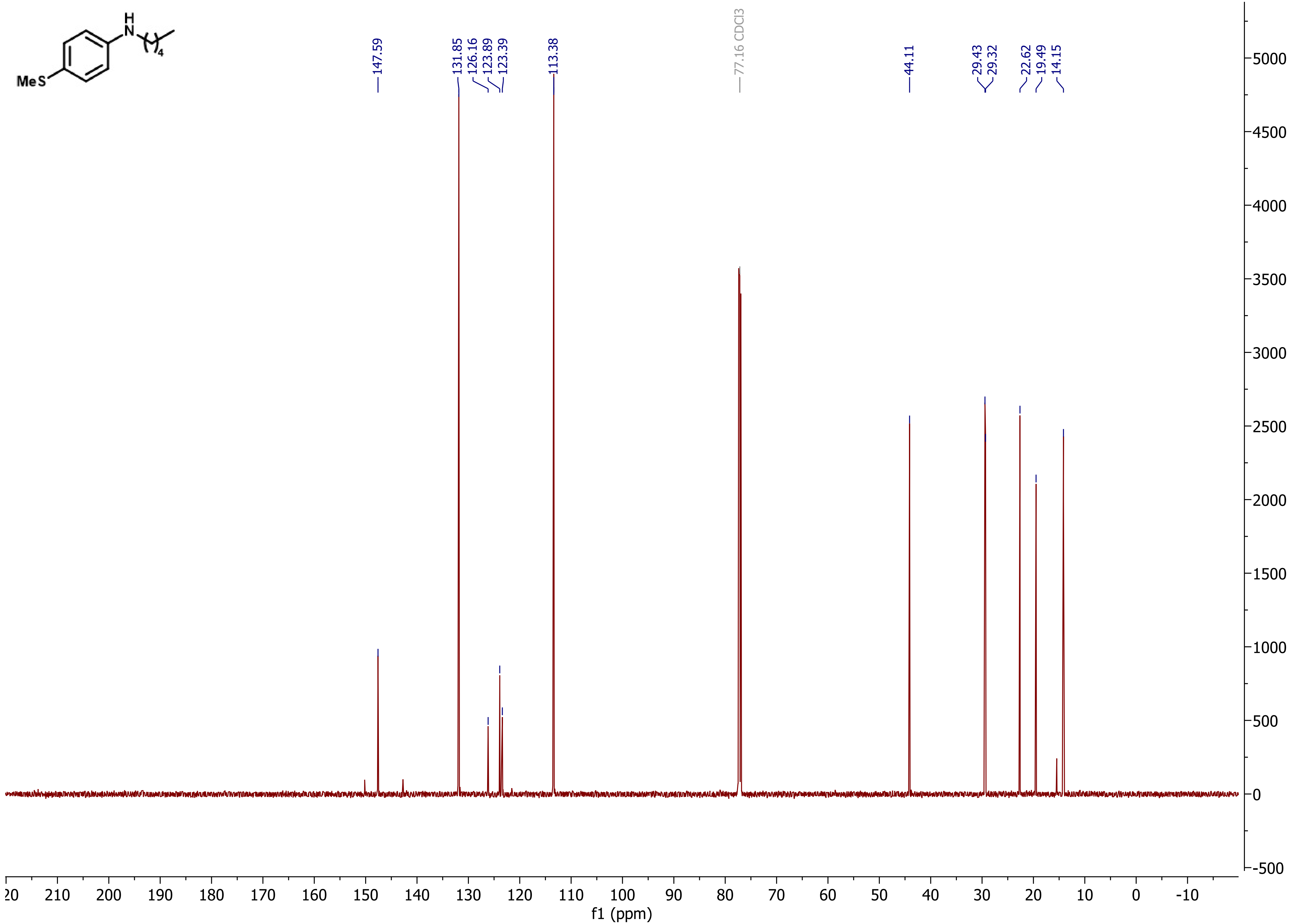


7.26 CDCl3
7.08
7.07
7.05
6.66
6.66
6.65
6.64
6.57
6.47
6.47
6.46
6.45
3.69
3.09
3.08
3.07
1.63
1.62
1.61
1.40
1.39
1.39
1.38
1.38
0.95
0.94
0.94
0.93
1.00
0.99
1.03
0.98
0.99
2.09
2.30
4.24
3.36
f1 (ppm)

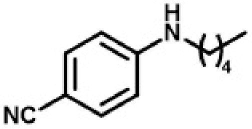

H
N
4
Cl
149.8
135.1
130.2
116.9
112.3
111.1
77.2 CDCl3
43.9
29.4
29.2
22.6
14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



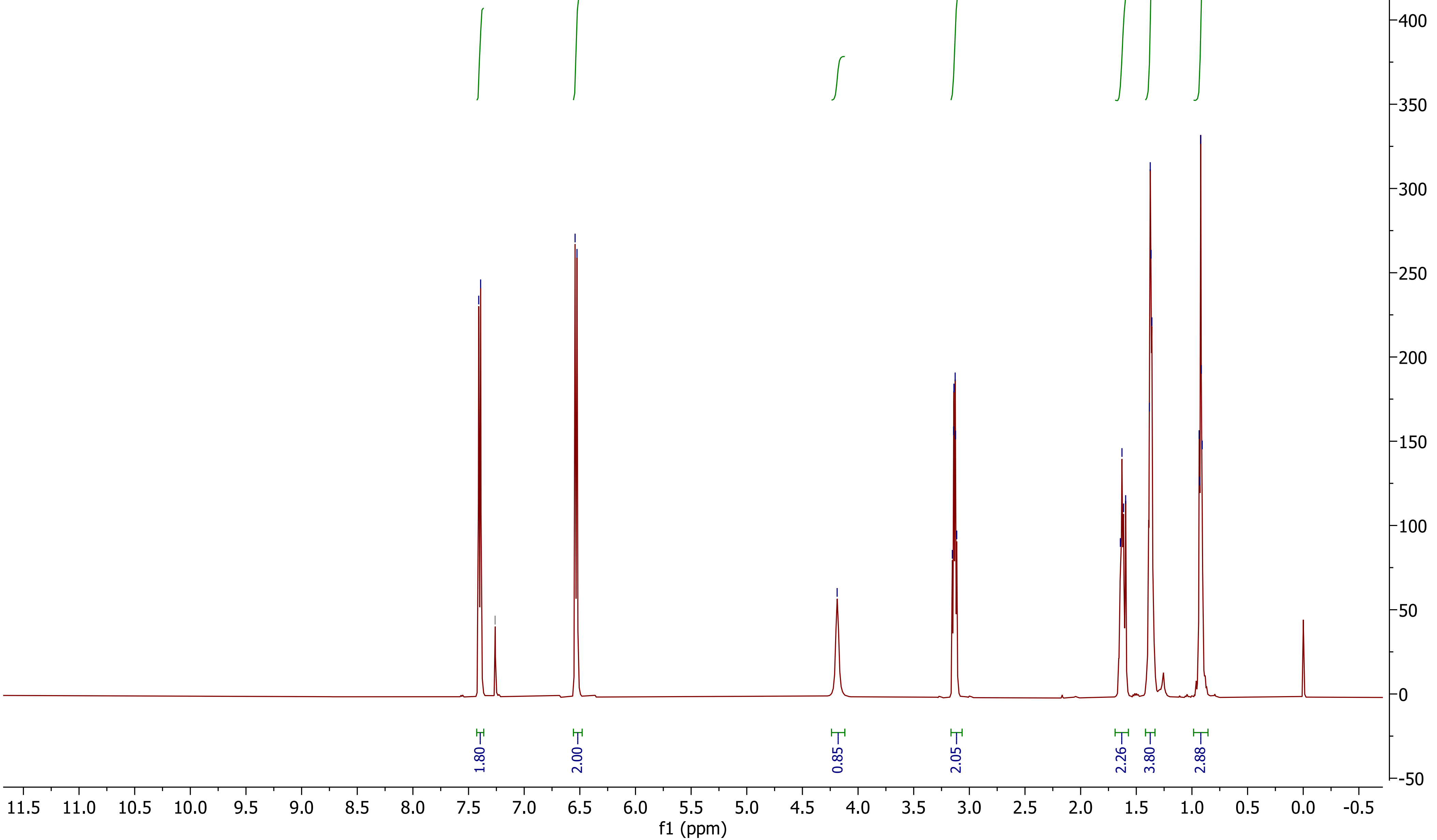
MeS
H
N
4
3m
7.26 CDCl3
7.23
7.21
6.55
6.54
3.64
3.10
3.09
3.08
2.41
1.64
1.63
1.61
1.60
1.59
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.36
1.36
1.35
1.35
0.93
0.92
0.91
1.94
2.00
0.97
2.09
2.98
2.22
4.03
3.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
3000
2500
2000
1500
1000
500
0

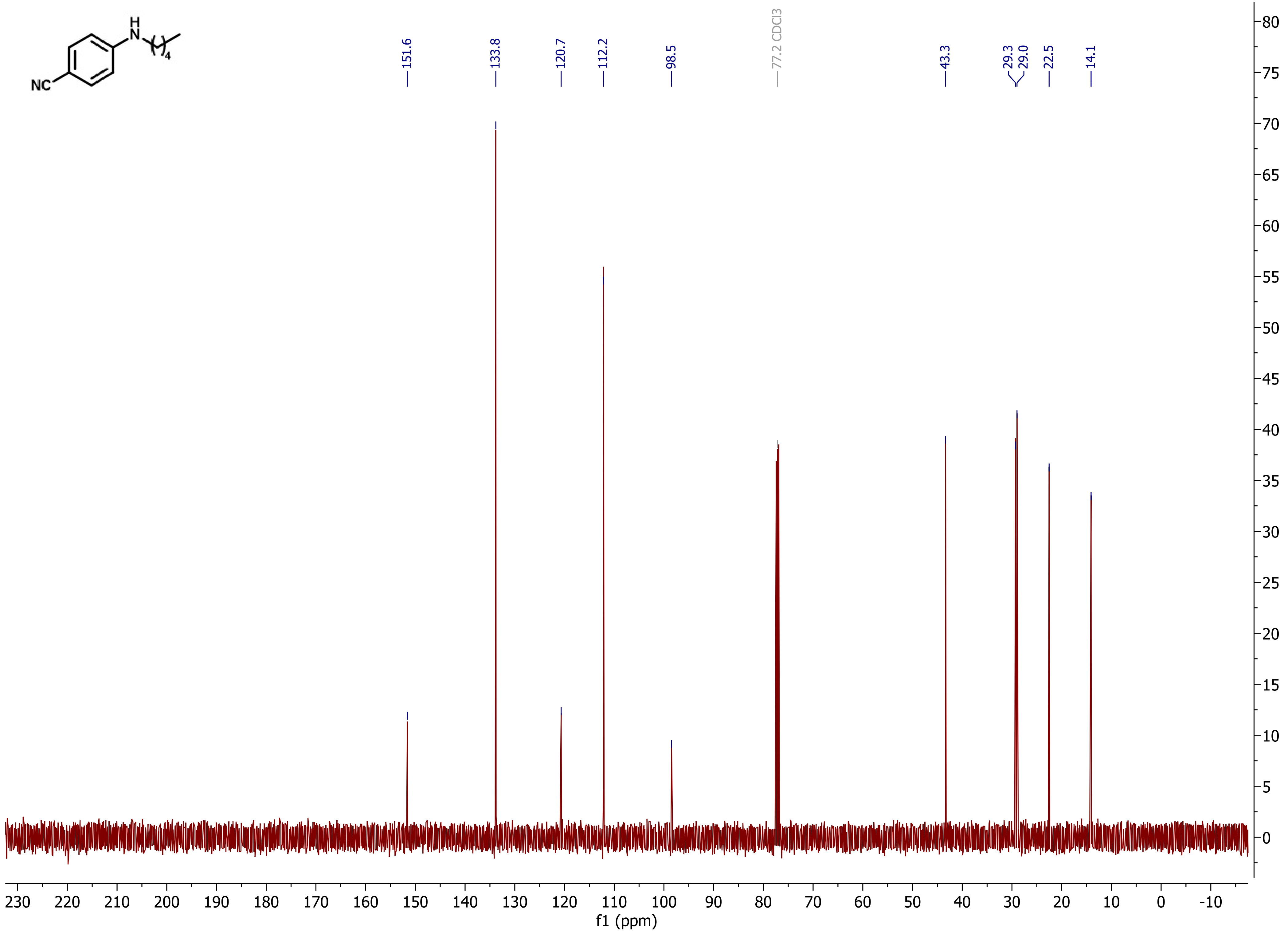


MeS
H
N
4
147.59
131.85
126.16
123.89
123.39
113.38
77.16 CDCl3
44.11
29.43
29.32
22.62
19.49
14.15
f1 (ppm)

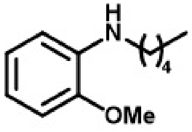

NC
H
N
4

3n

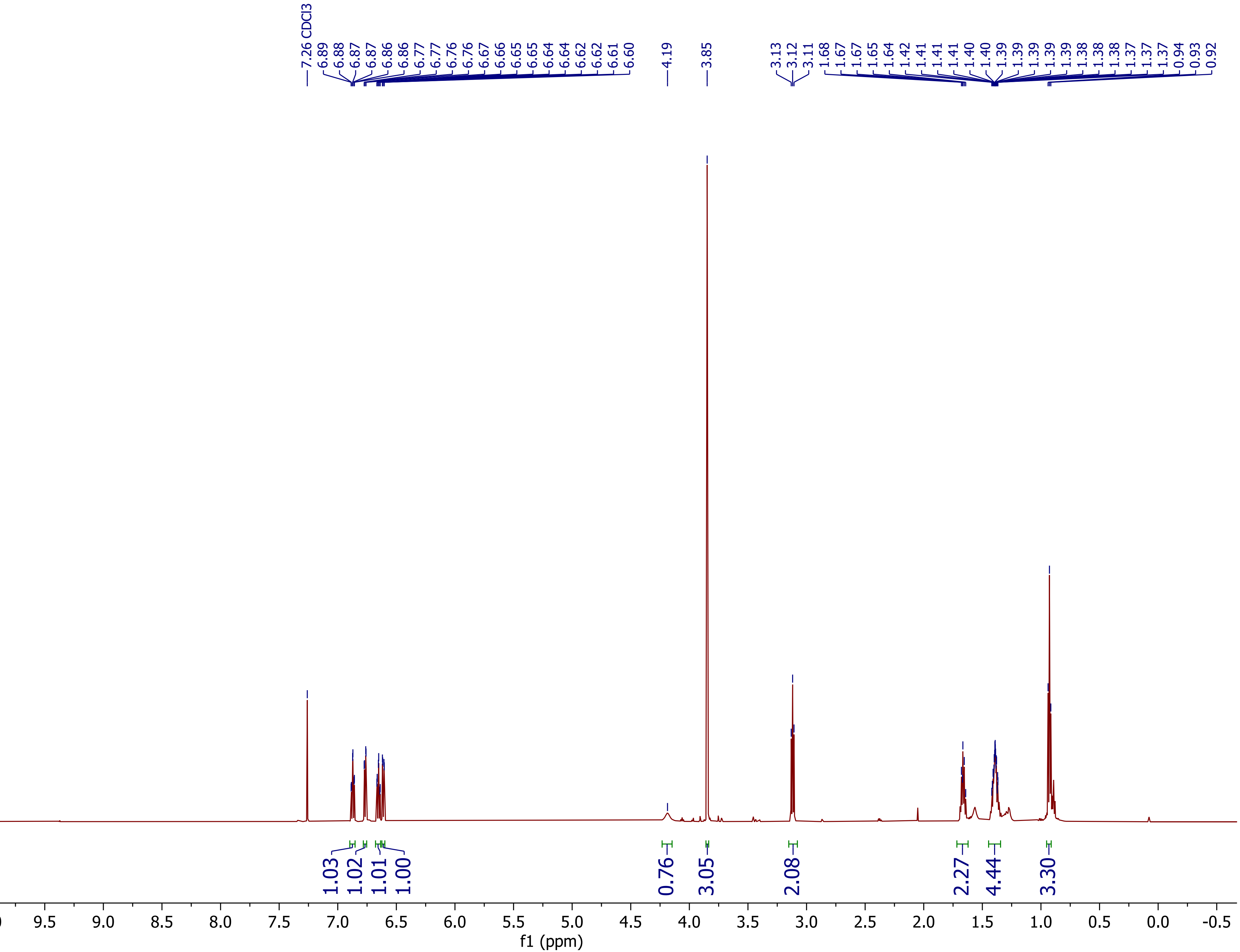

7.41
7.39
7.26 CDCl3
6.54
6.53
4.19
3.15
3.14
3.14
3.13
3.12
3.11
1.64
1.63
1.61
1.60
1.38
1.37
1.37
1.36
0.94
0.93
0.92
0.92
0.91
1.80
2.00
0.85
2.05
2.26
3.80
2.88
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0
-50

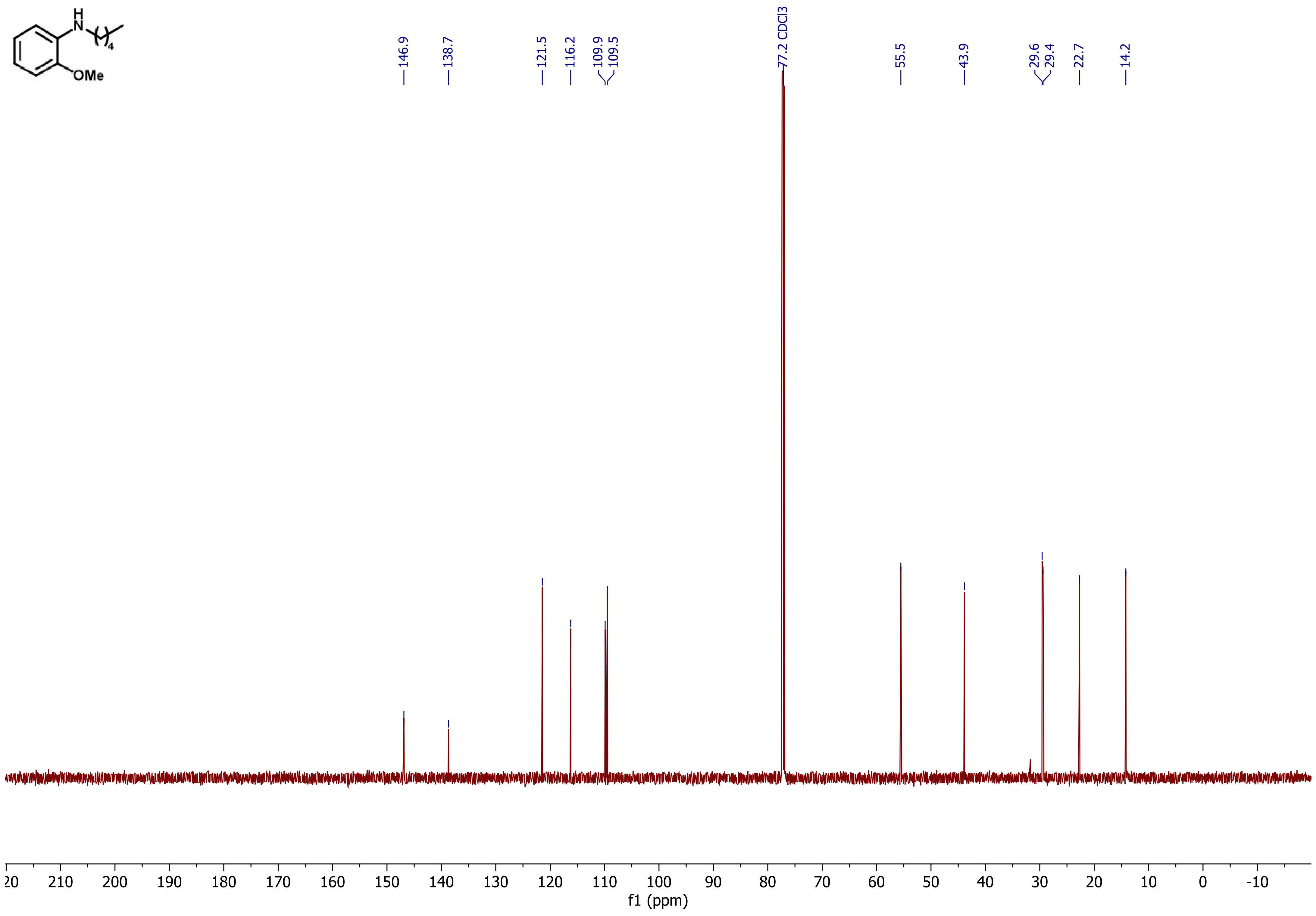


NC
H
N
4
151.6
133.8
120.7
112.2
98.5
77.2 CDCl3
43.3
29.3
29.0
22.5
14.1
f1 (ppm)

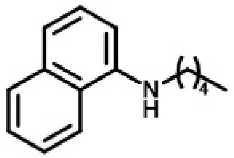

H
N
4
OMe

3o

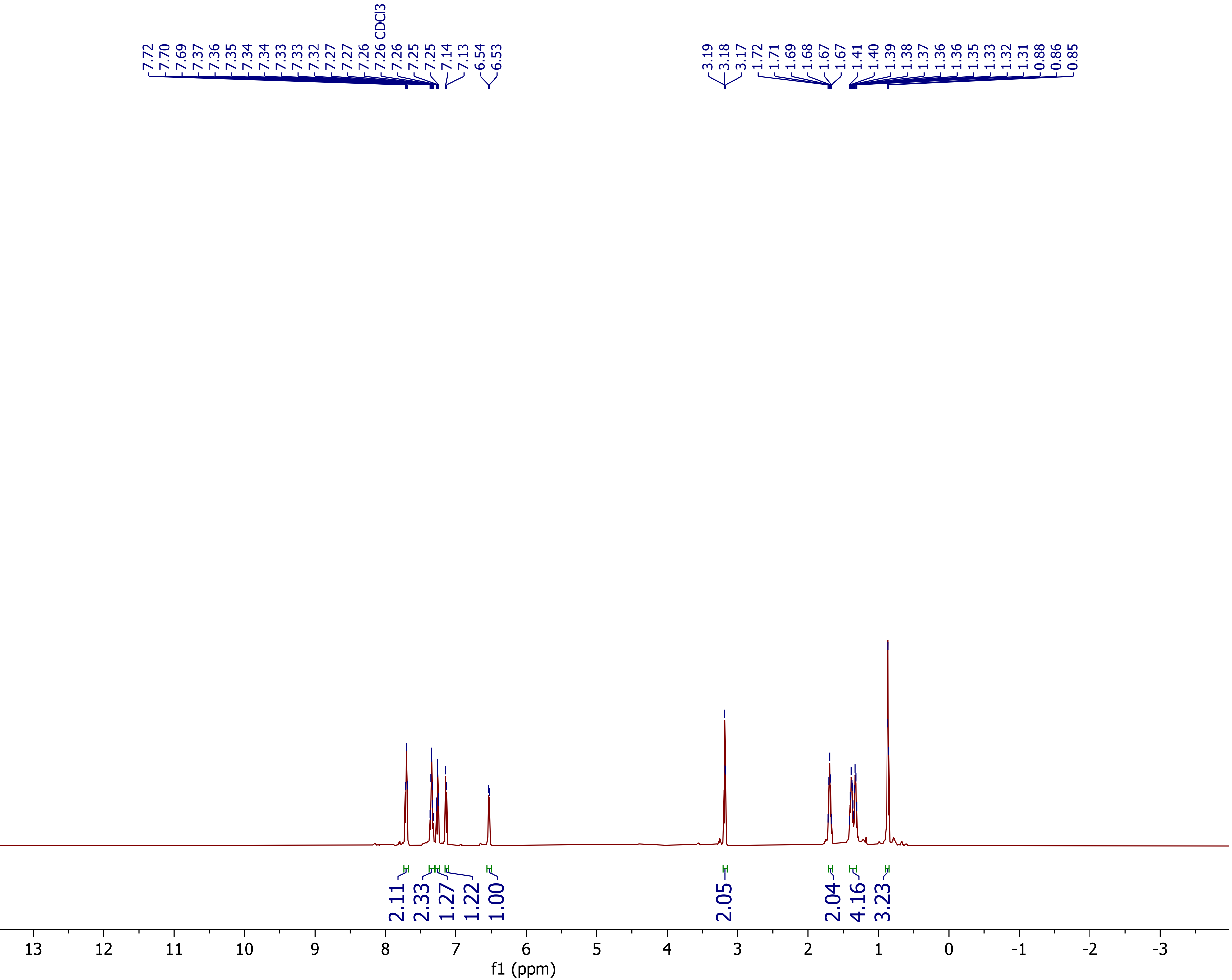

7.26 CDCl3
6.89
6.88
6.87
6.87
6.86
6.86
6.77
6.77
6.76
6.76
6.67
6.66
6.65
6.65
6.64
6.64
6.62
6.62
6.61
6.60
4.19
3.85
3.13
3.12
3.11
1.68
1.67
1.67
1.65
1.64
1.42
1.41
1.41
1.41
1.40
1.40
1.39
1.39
1.39
1.39
1.38
1.38
1.38
1.37
1.37
1.37
0.94
0.93
0.92
1.03
1.02
1.01
1.00
0.76
3.05
2.08
2.27
4.44
3.30
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



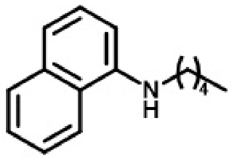
H
N
4
OMe
146.9
138.7
121.5
116.2
109.9
109.5
77.2 CDCl3
55.5
43.9
29.6
29.4
22.7
14.2
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

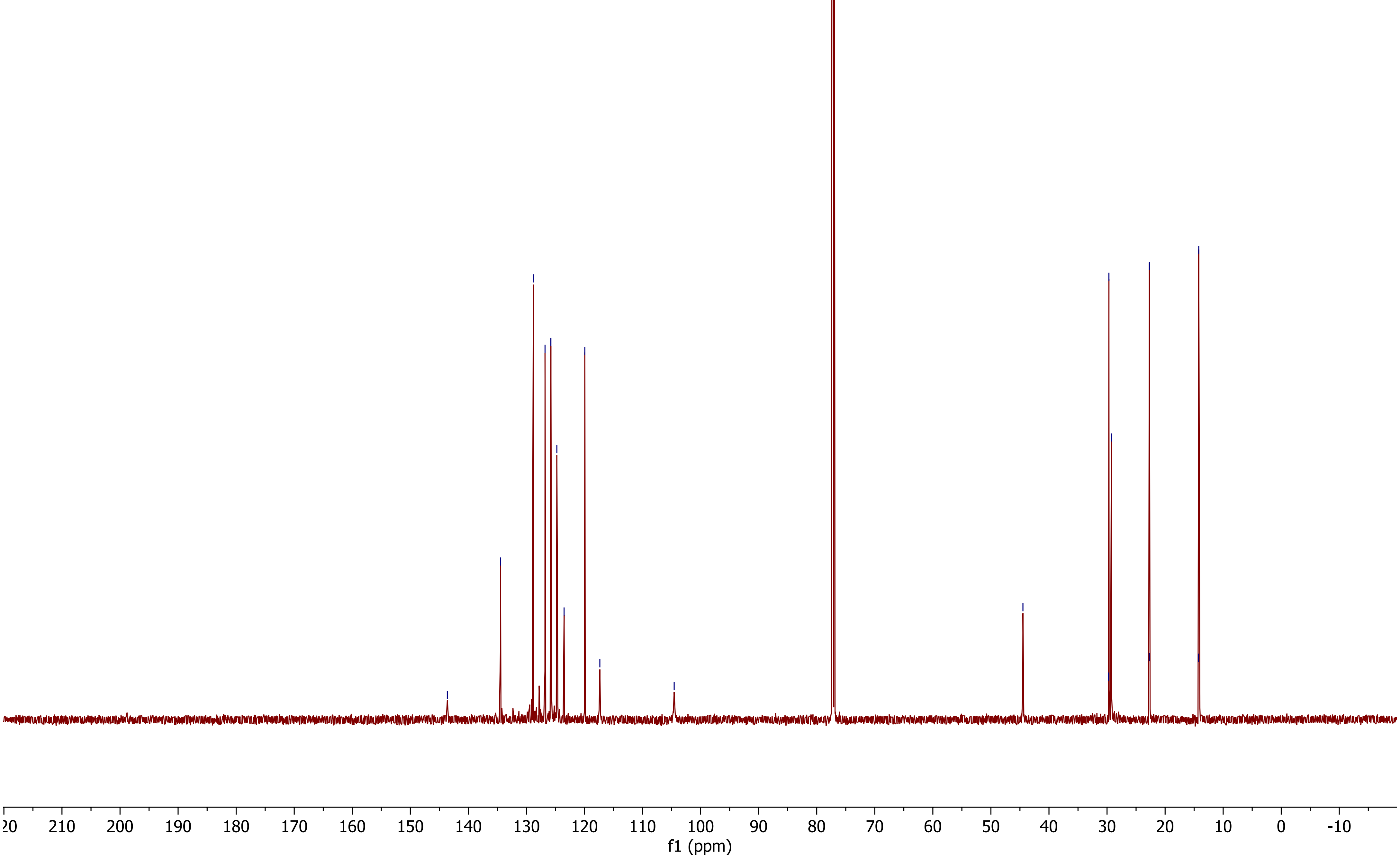


3p

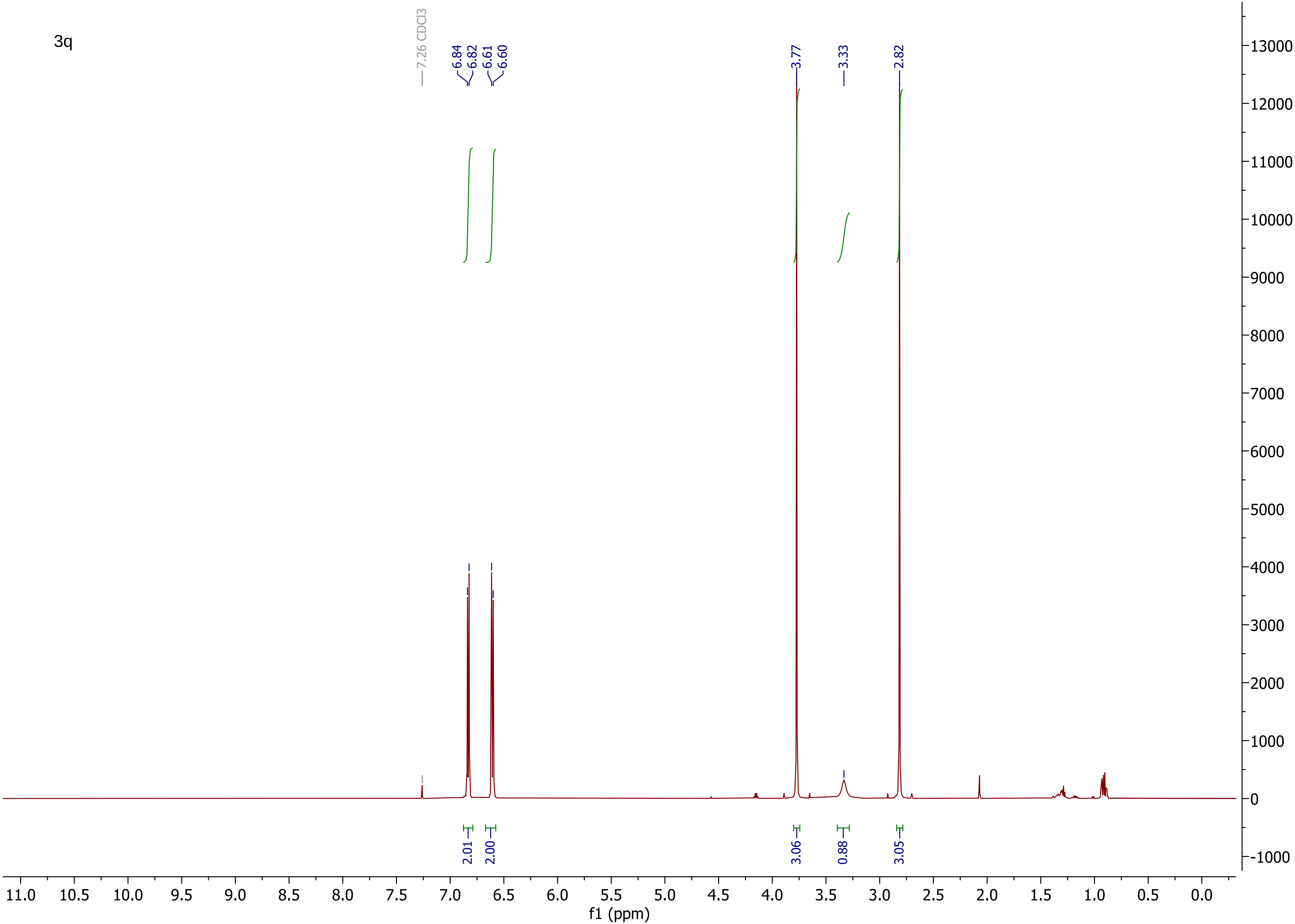


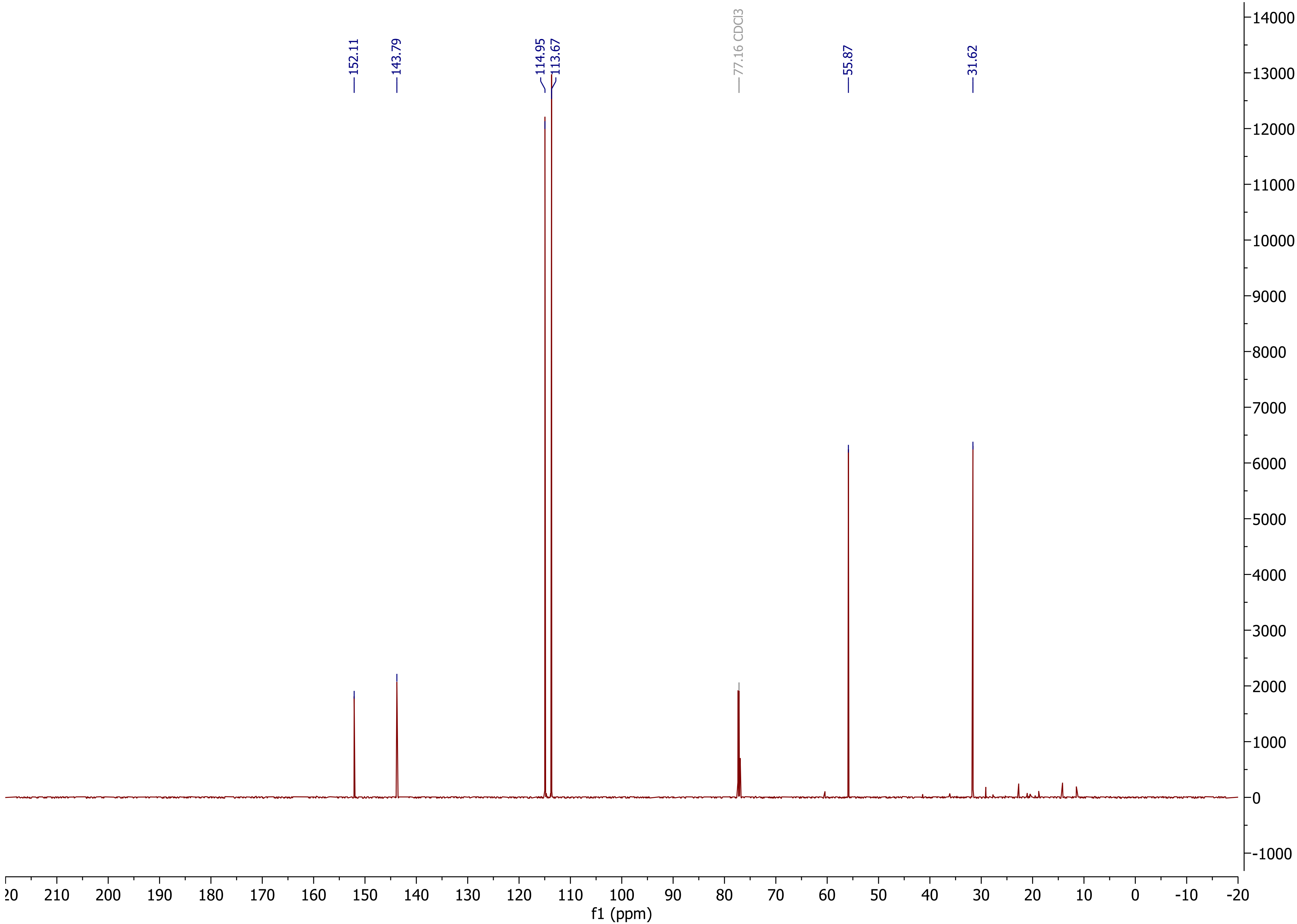
7.72
7.70
7.69
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.27
7.27
7.26
7.26 CDCl3
7.26
7.25
7.25
7.14
7.13
6.54
6.53
3.19
3.18
3.17
1.72
1.71
1.69
1.68
1.67
1.67
1.41
1.40
1.39
1.38
1.37
1.36
1.36
1.35
1.33
1.32
1.31
0.88
0.86
0.85
2.11
2.33
1.27
1.22
1.00
2.05
2.04
4.16
3.23
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)



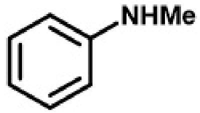

143.63
134.47
128.81
126.80
125.79
124.76
123.52
119.94
117.35
104.56
77.16 CDCl3
44.48
29.72
29.67
29.25
22.74
22.71
14.23
14.20
f1 (ppm)

3q

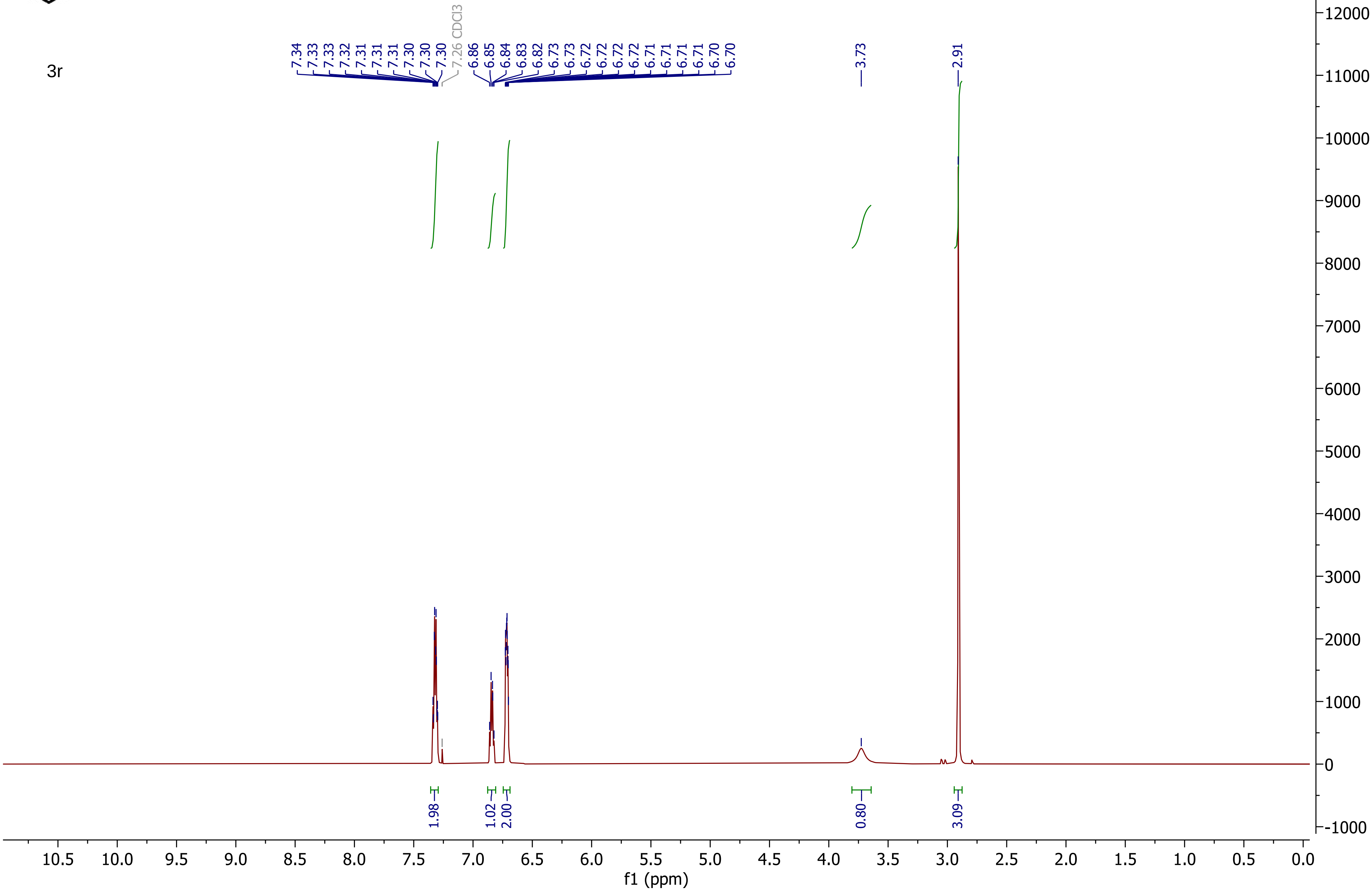


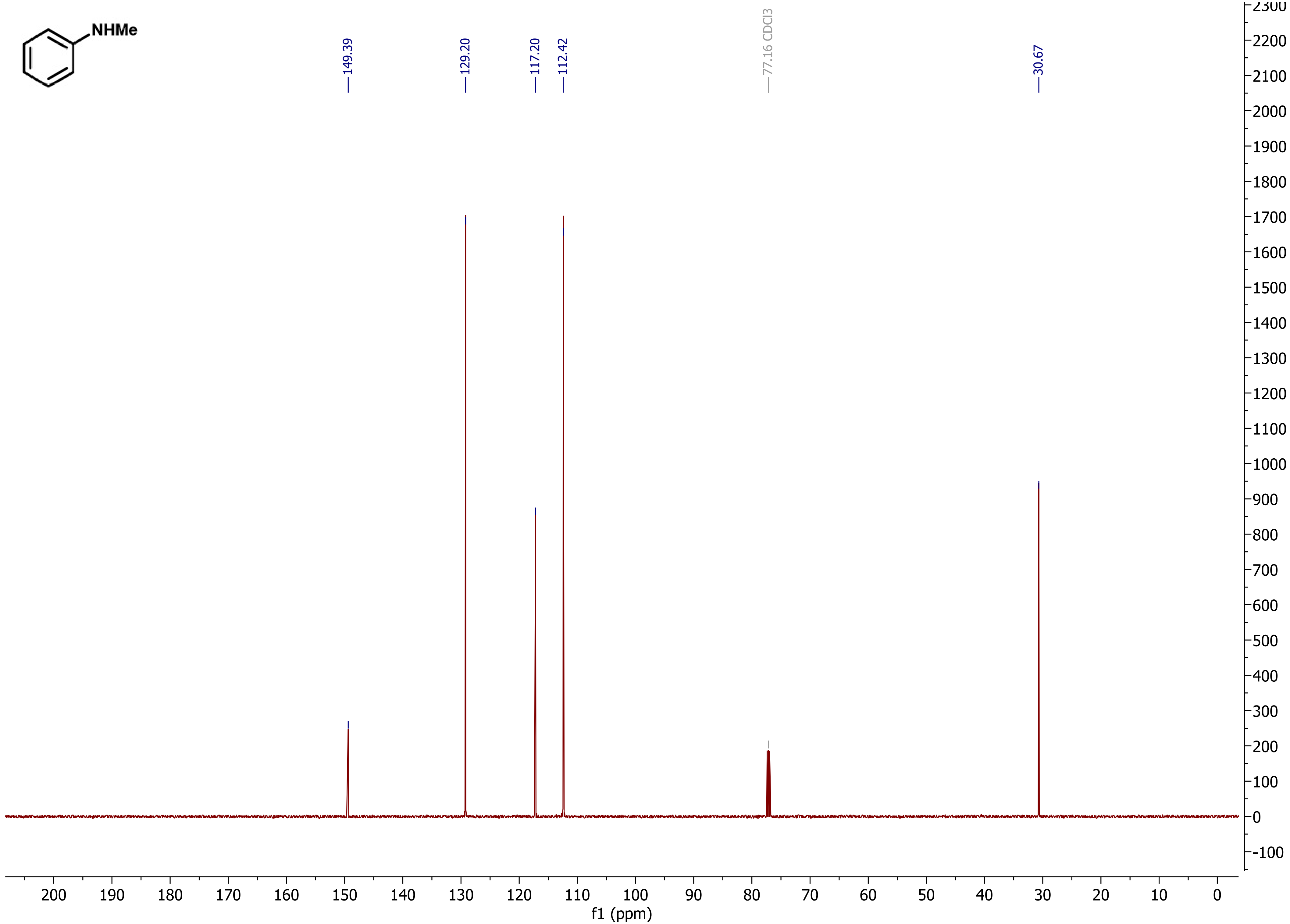


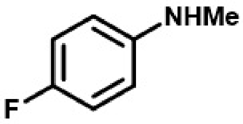
152.11
143.79
114.95
113.67
77.16 CDCl3
55.87
31.62
f1 (ppm)



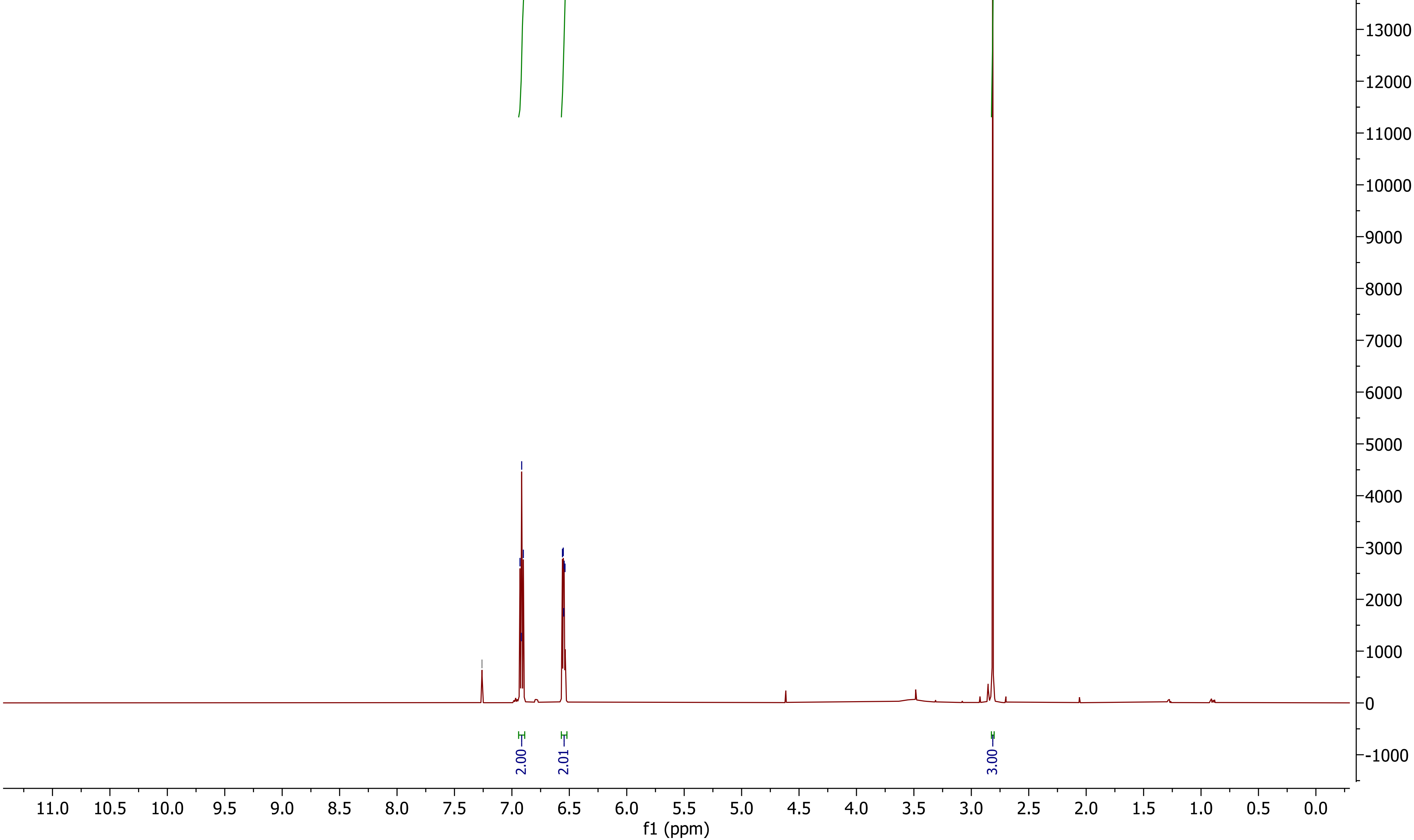
3r

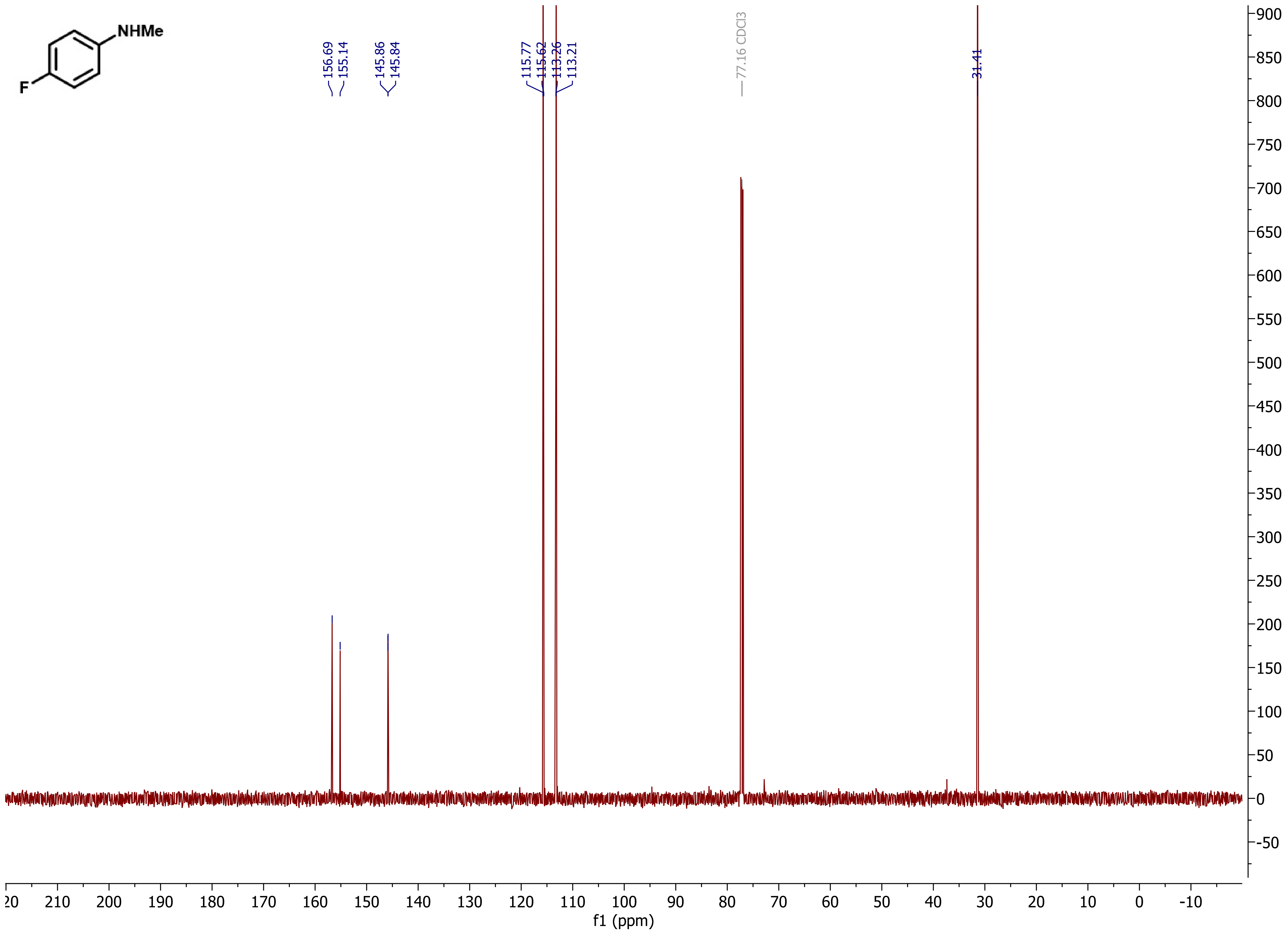

7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.26 CDCl3
6.86
6.85
6.84
6.83
6.82
6.73
6.73
6.72
6.72
6.72
6.72
6.71
6.71
6.71
6.70
6.70
3.73
2.91
1.98
1.02
2.00
0.80
3.09
f1 (ppm)


NHMe
149.39
129.20
117.20
112.42
77.16 CDCl3
30.67
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

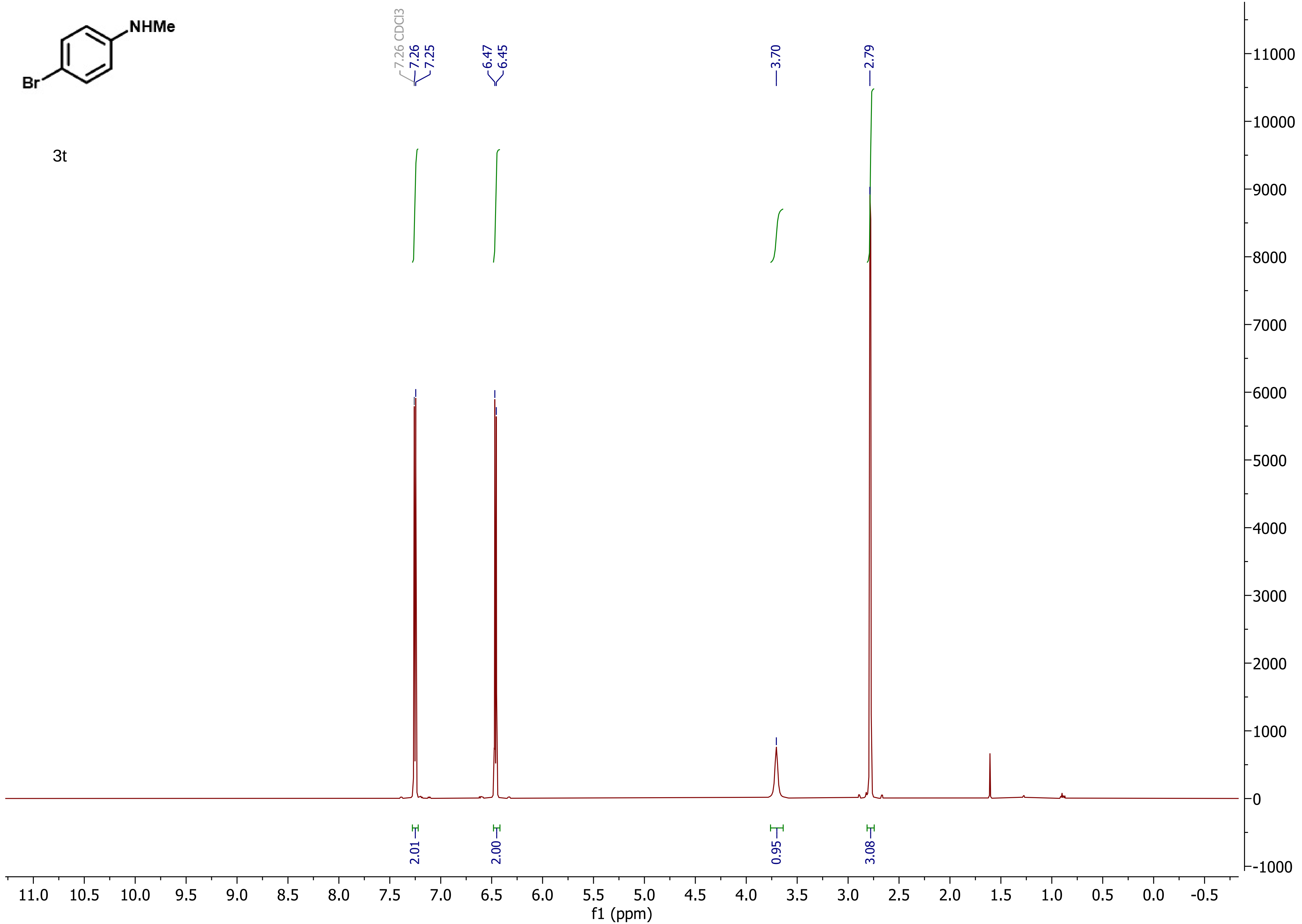

NHMe
F

3s

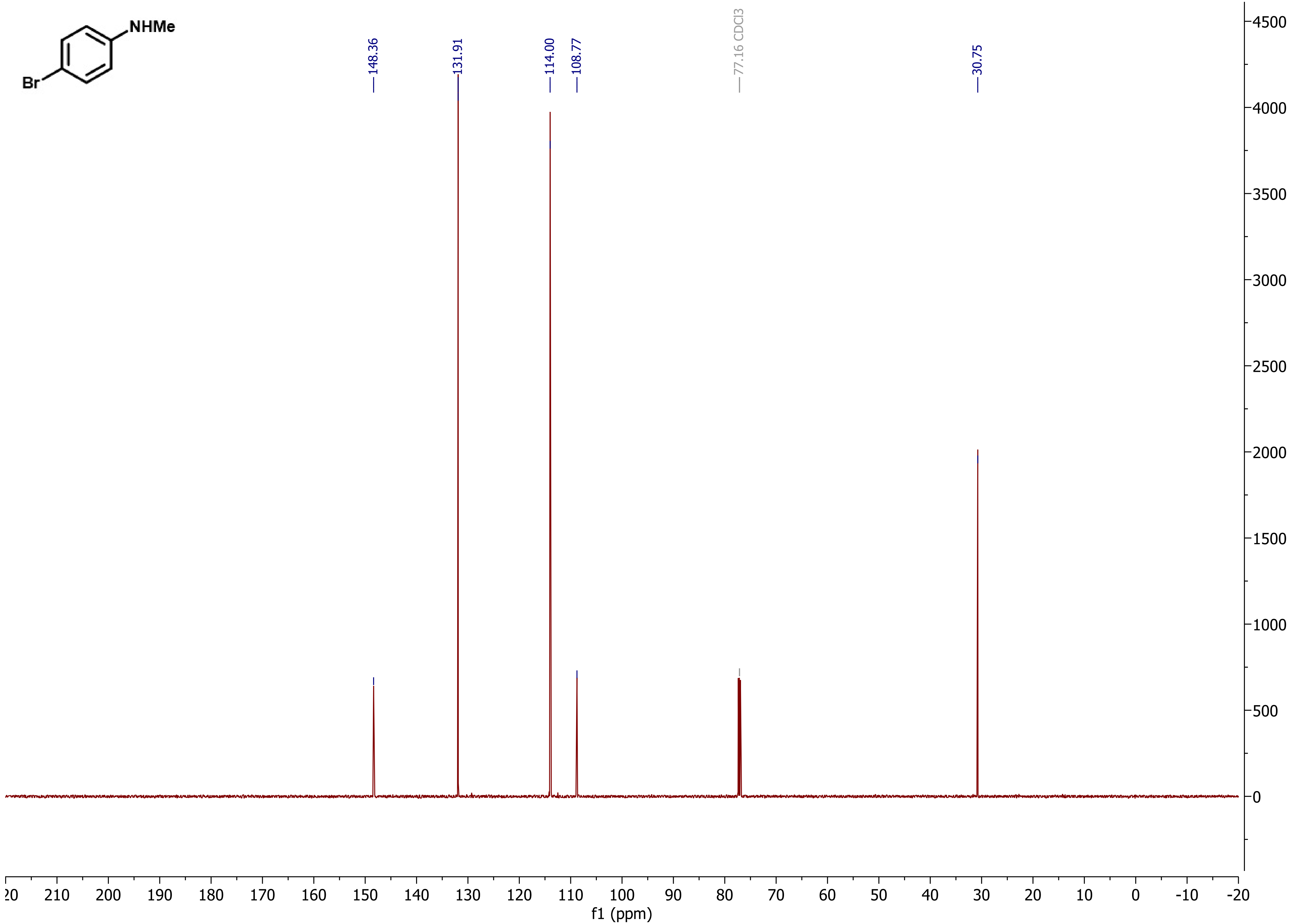

7.26 CDCl3
6.93
6.92
6.91
6.90
6.56
6.55
6.55
6.54
6.54
2.81
2.00
2.01
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

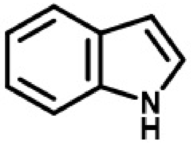


NHMe
F
156.69
155.14
145.86
145.84
115.77
115.62
113.26
113.21
77.16 CDCl3
31.41
f1 (ppm)

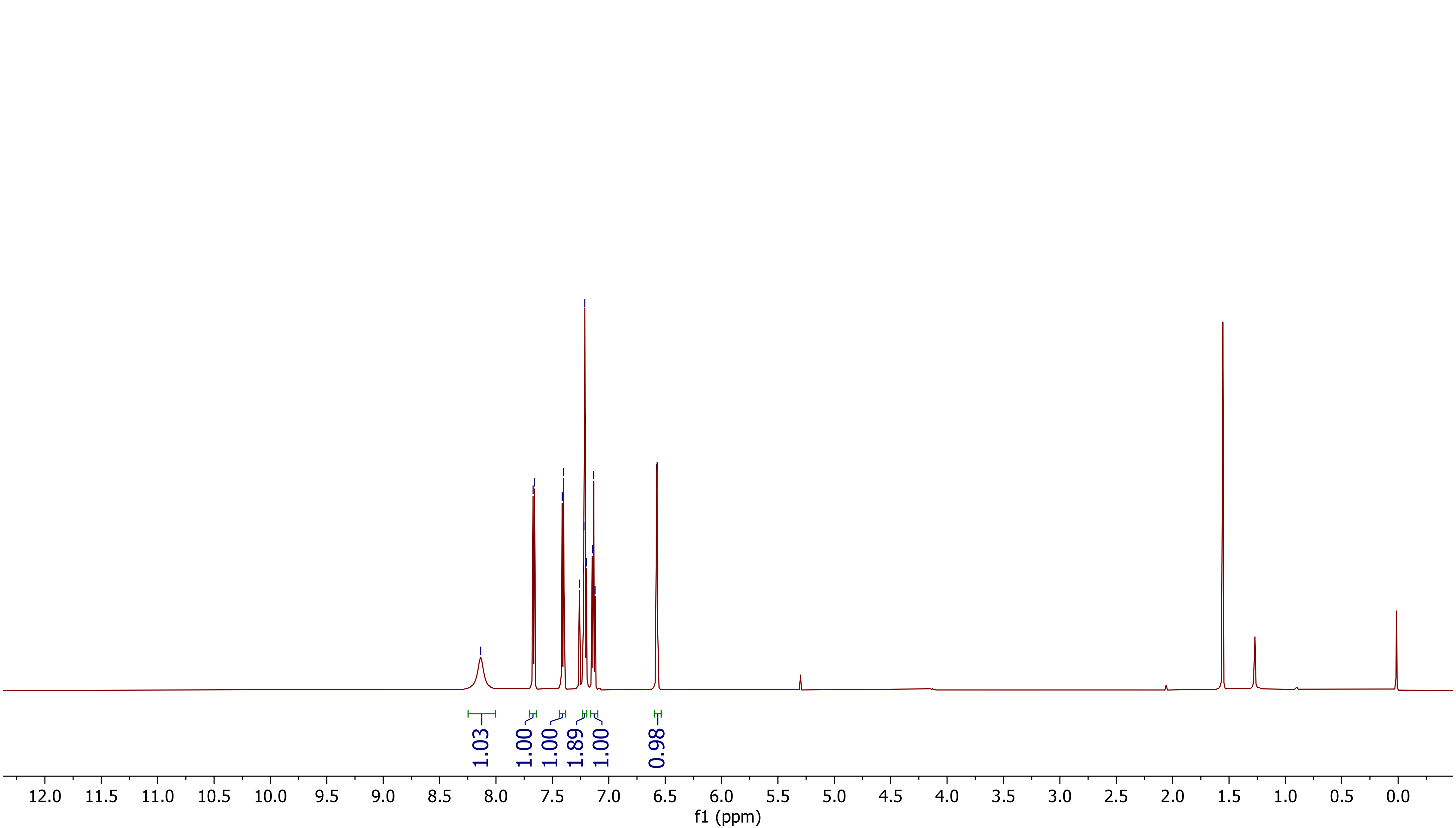


NHMe
Br
3t
7.26 CDCl3
7.26
7.25
6.47
6.45
3.70
2.79
2.01
2.00
0.95
3.08
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

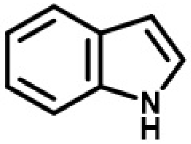

NHMe
Br
148.36
131.91
114.00
108.77
77.16 CDCl3
30.75
f1 (ppm)

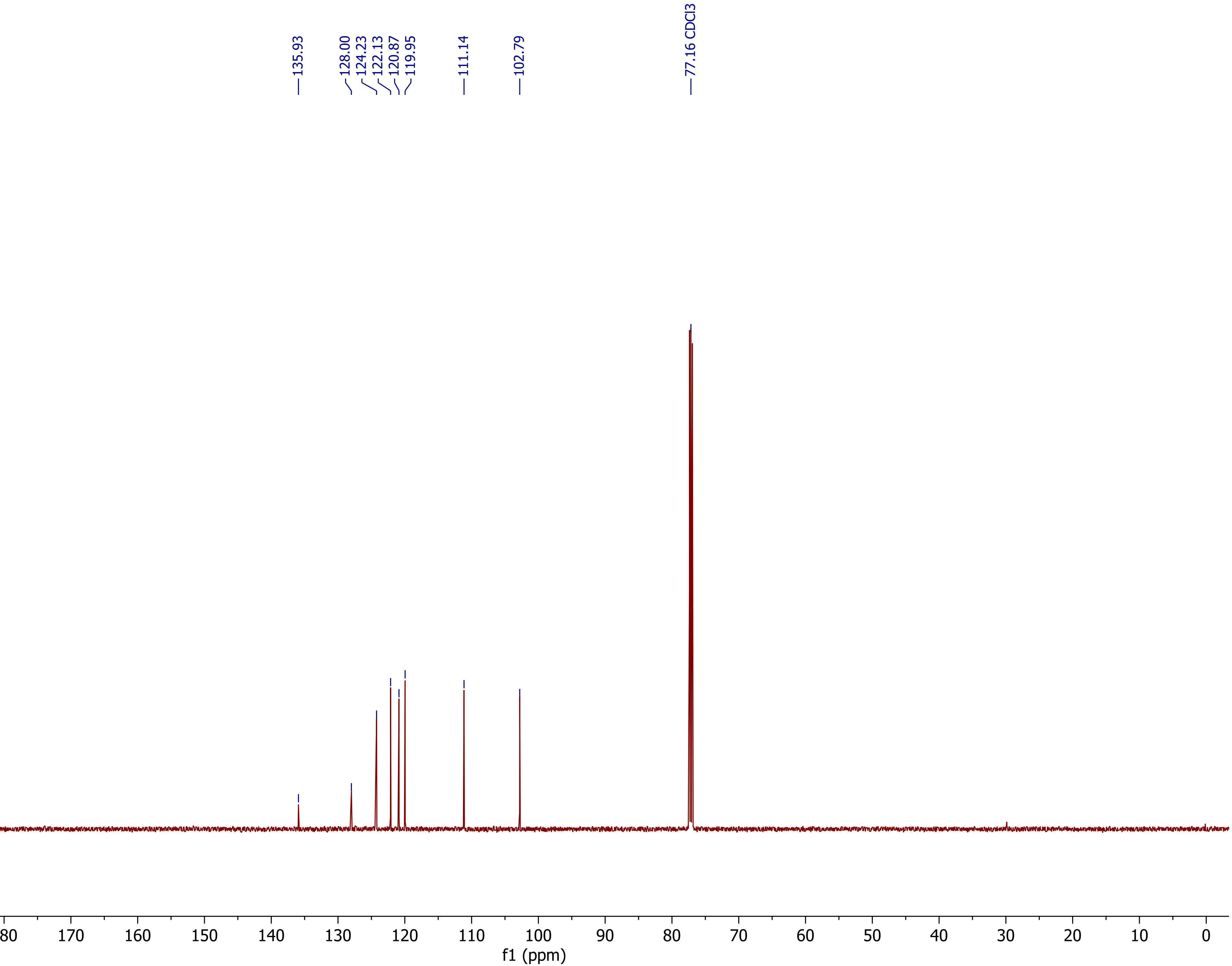


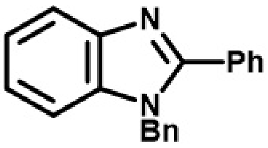
5a



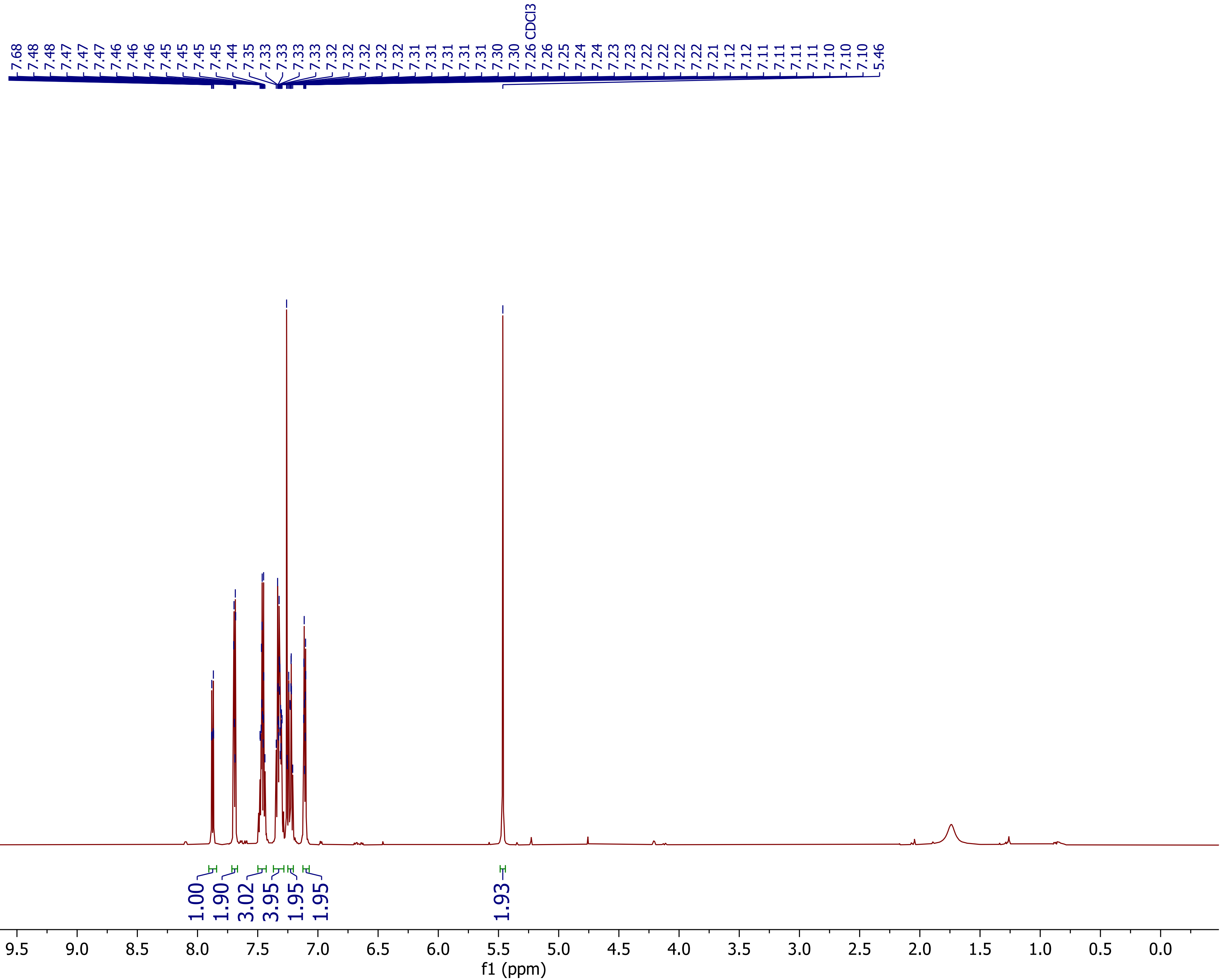
8.14
7.67
7.66
7.41
7.40
7.26 CDCl3
7.22
7.22
7.21
7.21
7.20
7.15
7.13
7.12
6.57
1.03
1.00
1.00
1.89
1.00
0.98
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

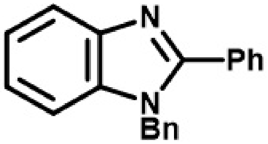

N
H

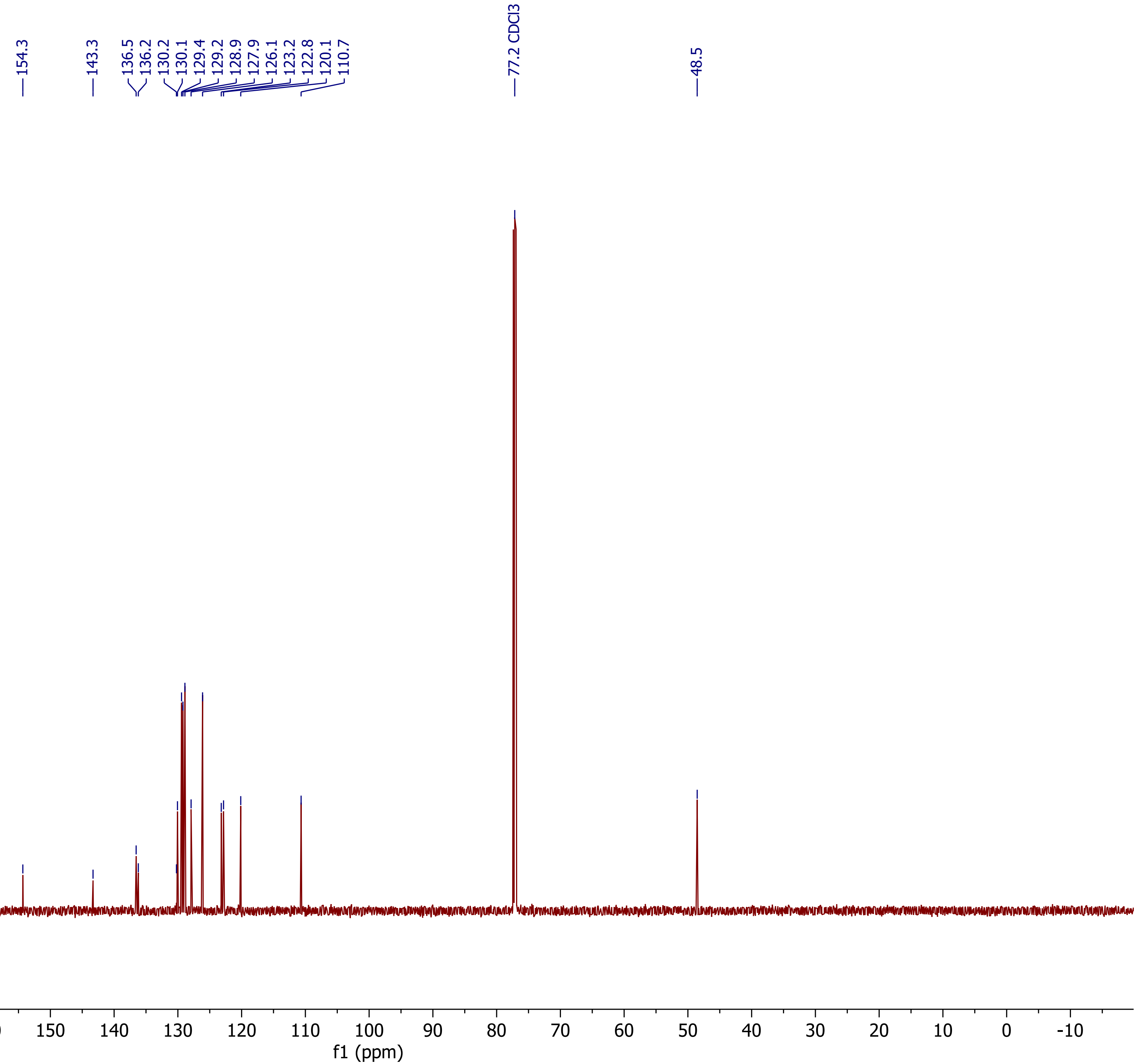

135.93
128.00
124.23
122.13
120.87
119.95
111.14
102.79
77.16 CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

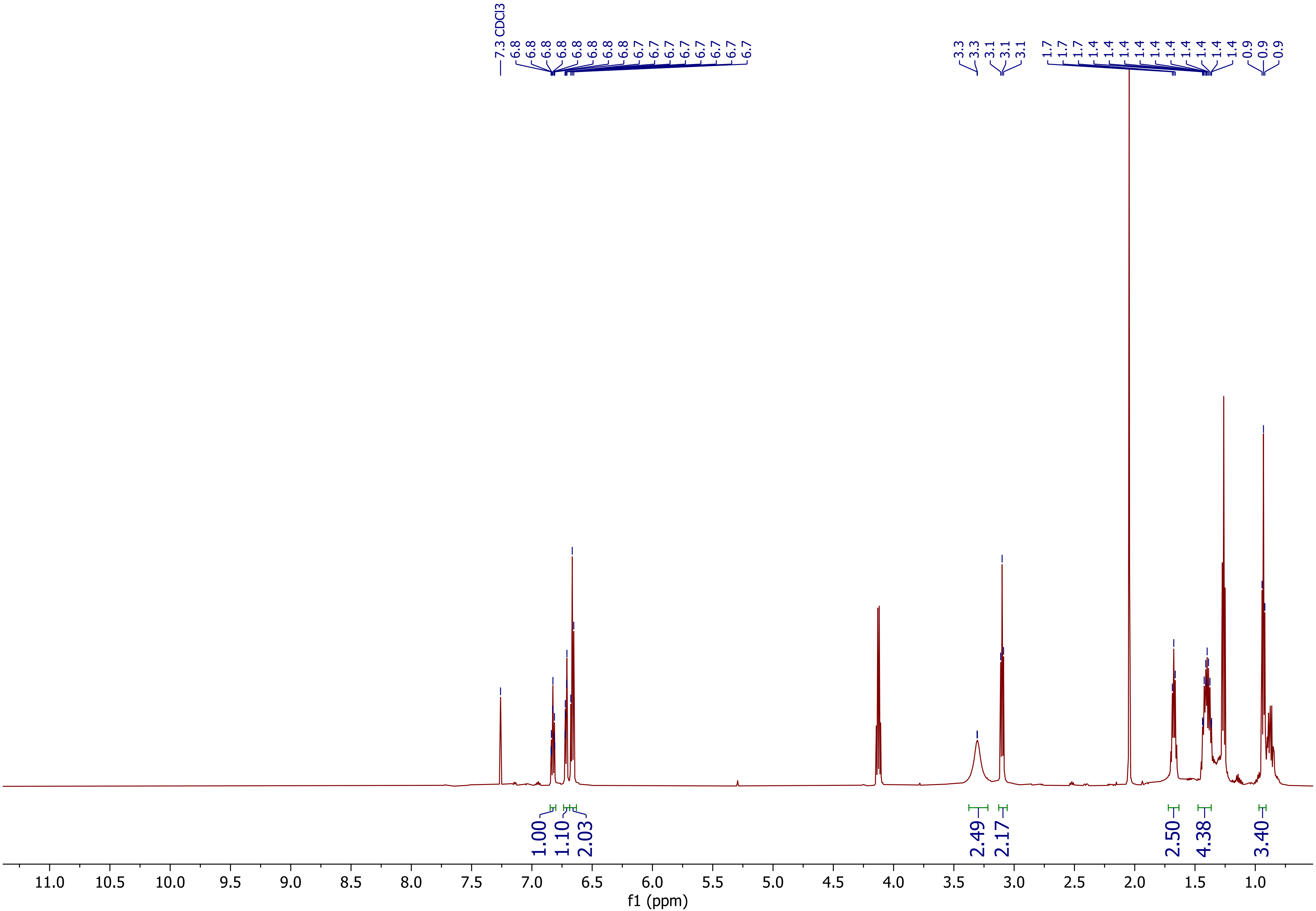

N
Ph
N
Bn

7a

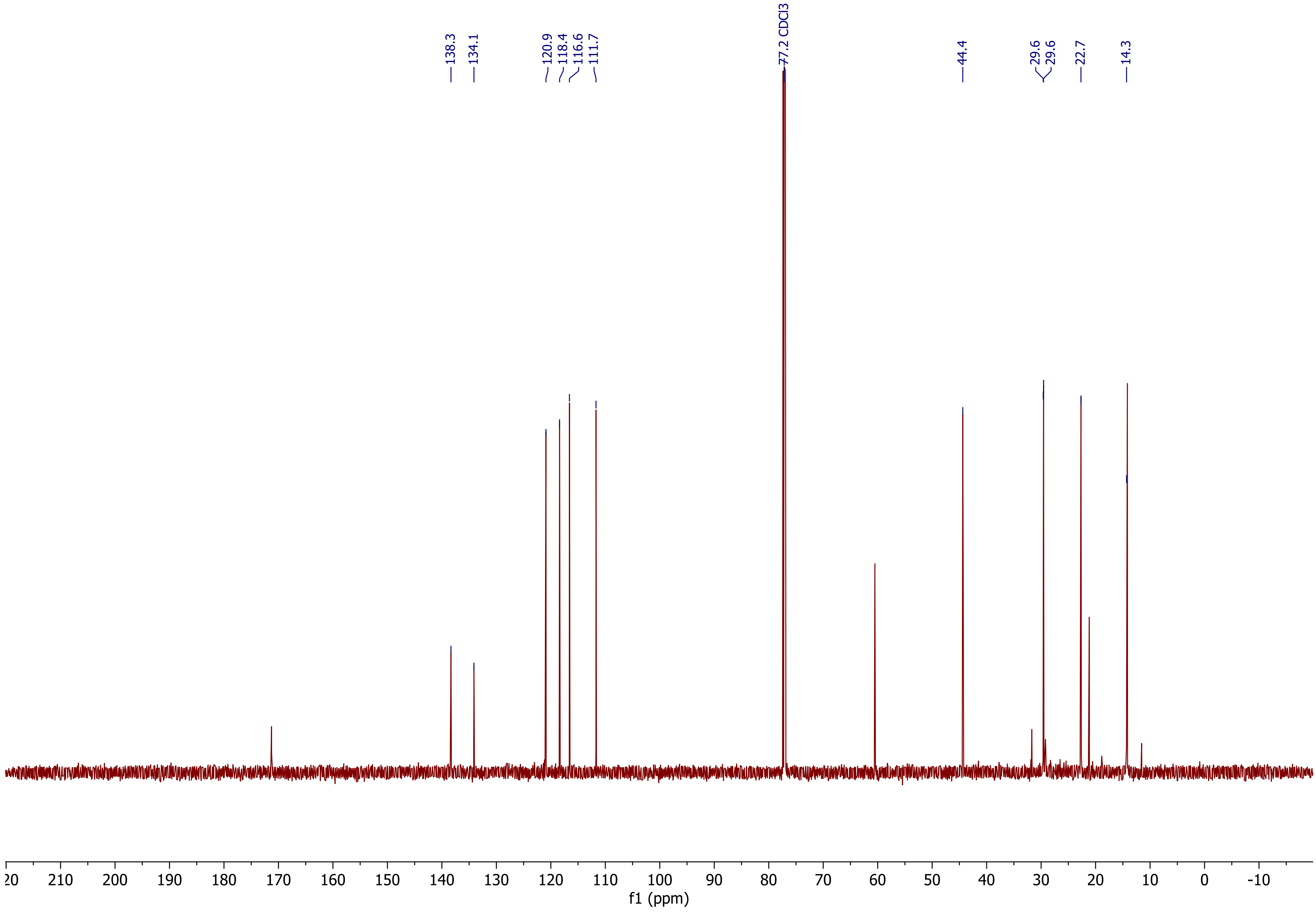

7.68
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.45
7.45
7.44
7.35
7.33
7.33
7.33
7.33
7.32
7.32
7.32
7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.26 CDCl3
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.22
7.21
7.12
7.12
7.11
7.11
7.11
7.11
7.10
7.10
7.10
5.46
1.00
1.90
3.02
3.95
1.95
1.95
1.93
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
Ph
N
Bn

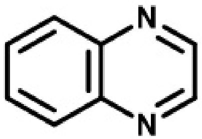

154.3
143.3
136.5
136.2
130.2
130.1
129.4
129.2
128.9
127.9
126.1
123.2
122.8
120.1
110.7
77.2 CDCl3
48.5
f1 (ppm)



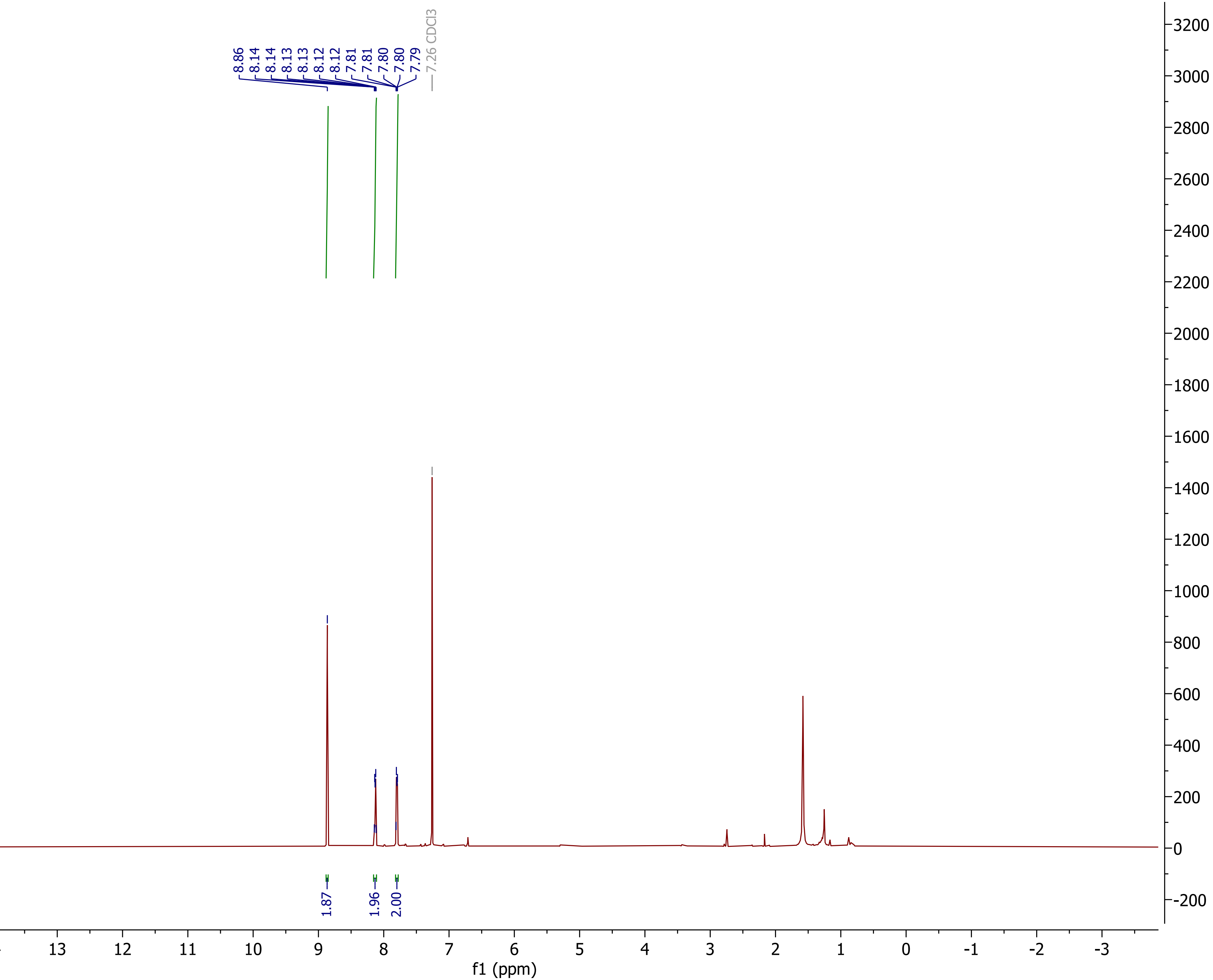
7.3 CDCl3
6.8
6.8
6.8
6.8
6.8
6.8
6.8
6.8
6.7
6.7
6.7
6.7
6.7
6.7
6.7
6.7
3.3
3.3
3.1
3.1
3.1
1.7
1.7
1.7
1.4
1.4
1.4
1.4
1.4
1.4
1.4
1.4
1.4
1.4
0.9
0.9
0.9
1.00
1.10
2.03
2.49
2.17
2.50
4.38
3.40
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

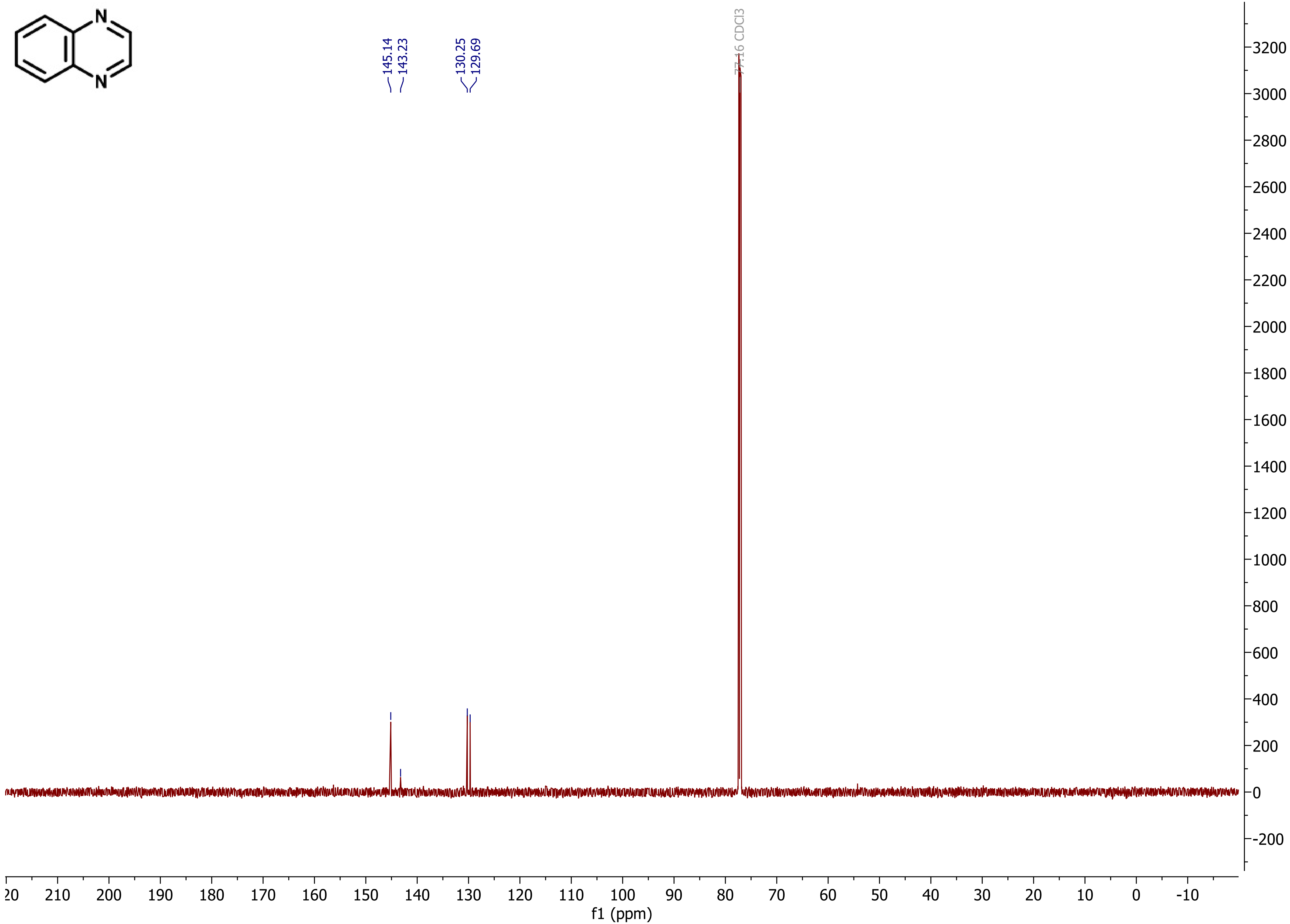


138.3
134.1
120.9
118.4
116.6
111.7
77.2 CDCl3
44.4
29.6
29.6
22.7
14.3
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
N

9a


8.86
8.14
8.14
8.13
8.13
8.12
8.12
7.81
7.81
7.80
7.80
7.79
7.26 CDCl3
1.87
1.96
2.00
f1 (ppm)



145.14
143.23
130.25
129.69
77.16 CDCl3
f1 (ppm)