Supporting Information for:

P(III)/P(V)-Catalyzed Methylamination of Arylboronic Acids and Esters: Reductive C–N Coupling with Nitromethane as a Methylamine Surrogate

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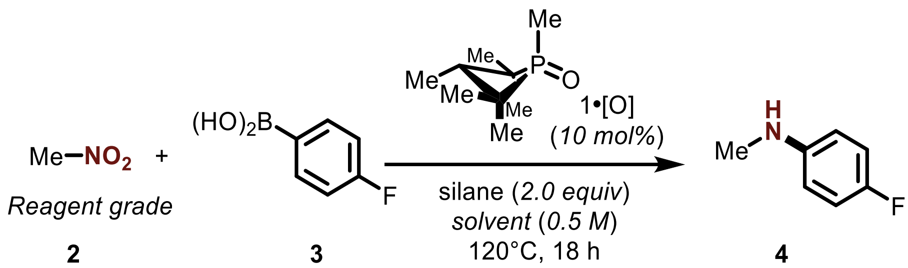
I. General Materials and Methods

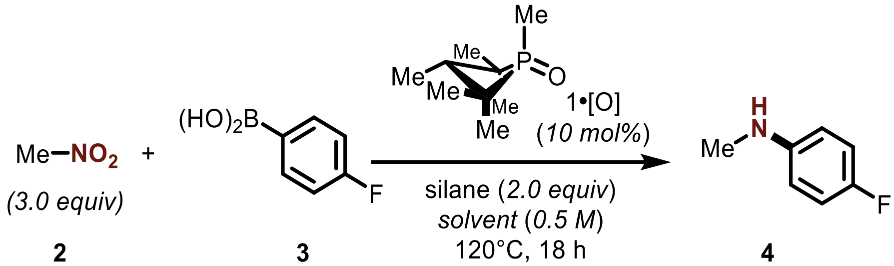
All reagents (including commercial phosphorus reagents used in optimization studies) were purchased from commercial vendors (Sigma-Aldrich, Alfa Aesar, Acros, TCI, Oakwood Chemical or Combi-Blocks) and used without further purification unless otherwise indicated. Dichloromethane, diethyl ether, dimethylformamide, and tetrahydrofuran were purified and collected under argon using a Glass Contour Solvent Purification System. Anhydrous *m*-xylene and cyclopentyl methyl ether were obtained from a Sigma-Aldrich (sure-seal® bottle) and used as received. All other solvents were ACS grade or better and were used without further purification unless otherwise noted. Manipulations were conducted under an atmosphere of dry N_2 gas unless otherwise noted. The catalytic methylamination reactions were carried out in glass culture tubes with threaded end (20 x 125 mm; Fisher Scientific part # 14-959-35A), outfitted with a phenolic screw-thread open top cap (Kimble-Chase part #73804-15425), and PTFE-lined silicone septum (Thermo Fisher part # B7995-15). Column chromatography was carried out on silica gel (SiliFlash® Irregular Silica Gel, P60 40-63μm) or aluminum oxide (activated, neutral, Brockmann I) as noted. ^{1}H, ^{2}H, ^{13}C, ^{19}F, and ^{31}P NMR were collected with either Bruker AVANCE-400, DPX 400, VARIAN Inova-500, or JEOL 500 MHz spectrometers and processed using either MestReNova or Bruker software. ^{1}H NMR chemical shifts are given in ppm with respect to solvent residual peak ($CDCl_3$, δ 7.26 ppm; DMSO-d_6, δ 2.50 ppm; TMS, δ 0.00 ppm). ^{2}H NMR chemical shifts are given in ppm with respect to solvent residual peak ($CDCl_3$, δ 7.26 ppm; CD_2Cl_2-d_6, δ 5.30 ppm). $^{13}C\{^{1}H\}$ NMR shifts are given in ppm with respect to ($CDCl_3$ δ 77.16 ppm, DMSO-d_6, δ 39.52 ppm). ^{31}P NMR shifts are given in ppm with respect to 85% H_3PO_4 (δ 0.0 ppm) as an external standard. Multiplicities are described as s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. Coupling constants are reported in Hertz (Hz). High-resolution ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the MIT department of chemistry instrumentation on a JEOL AccuTOF-DART (JMS-T100LP, ionSense DART source).

II. Optimization of the Reductive C–N Coupling Reaction



To an oven-dried glass culture tube described in the General Methods section was added a small stir bar, 4-fluorophenylboronic acid **2** (36 mg, 0.25 mmol, 1.0 equiv, 97% purity), phosphine oxide precatalyst (10 mol% unless otherwise noted), and nitromethane **3** (41 μL, 0.75 mmol, 3.0 equiv unless otherwise noted). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. Following evacuation and the introduction of nitrogen on a Schlenk line, dry solvent (0.5 M) was added via syringe from a sure-seal® bottle. Lastly, silane was added and the reaction mixture was stirred at 120 °C. When complete, the reaction vessel screw cap was unscrewed (note that in some cases pressure release was observed) and dibromomethane (17.5 μL, 0.25 mmol, 1.0 equiv) was added as internal standard. The reaction mixture was diluted with 3 mL of $CDCl_3$ and analyzed by quantitative ^{1}H NMR. The yield was determined by relative integration between CH_2Br_2 (4.93 ppm, 1.0 equiv x 2H = 200%) and product **4** [(2.81 ppm, 3H) or (6.51-6.58 ppm, 2H)]. Number of scans = 16 and relaxation delay = 4 seconds.

Table S1. Discovery and Optimization of Organophosphorus-Catalyzed *N*-methyl-amine Synthesis.



Entry	Solvent	Silane	$R_3P=O$	Yield (%)
1	CPME	$PhSiH_3$	**1**•[O]	95(90)%
2	CPME	$PhSiH_3$	**1**	94%
3	CPME	$PhSiH_3$	None	0%
4	CPME	None	**1**•[O]	0%
5[b]	CPME	Ph_2SiH_2	**1**•[O]	87%
6[b]	CPME	PMHS	**1**•[O]	85%
7	*m*-xylene	$PhSiH_3$	**1**•[O]	51%
8	dioxane	$PhSiH_3$	**1**•[O]	90%
9[c]	CPME	$PhSiH_3$	**1**•[O]	73%
10[d,f]	CPME	$PhSiH_3$	**1**•[O]	84%
11[e,f]	CPME	$PhSiH_3$	**1**•[O]	89%

[a] Yields were determined through ^{1}H NMR analysis with the aid of dibromomethane as an internal standard. [b] 24 h reaction time. [c] 2 equiv of nitromethane was used. [d] Reaction run under air. [e] 2.0 equiv of H_2O added.

III. Examples of Methylamination of Boronic Acids (Esters)

A. General procedure:

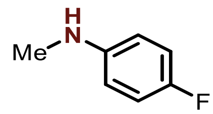
General Procedure 1A. To a glass culture tube described in the General Methods section was added a small stir bar, the appropriate boronic acid/boronic acid ester (if solid), phosphetane oxide precatalyst **1**•[O] (10 mol% unless otherwise noted). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *cyclopentyl methyl ether* (0.5 M) was added via syringe from a sure-seal® bottle. Lastly, phenylsilane (or diphenylsilane) and nitromethane were added and the reaction mixture was stirred at 120 °C. Upon completion, the reaction vessel screw cap was unscrewed (note that in some cases pressure release was observed) and 10 mL of ethyl acetate was added following by extraction with 4x15 mL 5 M aqueous HCl solution. After mixing and separating the organic layer, the aqueous layer was neutralized with 1 M NaOH aqueous solution to pH=14, then transferred to a separatory funnel. Each aqueous phase was back-extracted with 4x15 mL portions of DCM. The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with aid of a rotary evaporator. The crude residues were purified via column chromatography to yield pure coupling products. Columns were primarily slurry packed with hexanes and mobile phase polarity was increased gradually to the mixture indicated. Note: hexanes = Hex, dichloromethane = DCM, ethyl acetate = EA.

General Procedure 1B. To a glass culture tube described in the General Methods section was added a small stir bar, the appropriate boronic acid/boronic acid ester (if solid), phosphetane oxide precatalyst **1**•[O] (10 mol% unless otherwise noted). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *cyclopentyl methyl ether* (0.5 M) was added via syringe from a sure-seal® bottle. Lastly, phenylsilane (or diphenylsilane) and nitromethane were added and the reaction mixture was stirred at 120 °C. When completed, the reaction vessel screw cap was unscrewed (note that in some cases pressure release was observed) and diluted with 10 mL ethyl acetate. The mixture were transferred to a 40 mL vial and concentrated with aid of a rotary evaporator. The crude residues were purified via column chromatography to yield pure coupling products. Columns were primarily slurry packed with hexanes and mobile phase polarity was increased gradually to the mixture indicated. Note: hexanes = Hex, dichloromethane = DCM, ethyl acetate = EA.

General Procedure 1C. To a glass culture tube described in the General Methods section was added a small stir bar, the appropriate boronic acid/boronic acid ester (if solid), phosphetane oxide precatalyst **1**•[O] (15 mol% unless otherwise noted). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *cyclopentyl methyl ether* (0.5 M) was added via syringe from a sure-seal® bottle. Lastly, phenylsilane (or diphenylsilane) and nitromethane were added and the reaction mixture was stirred at 120 °C. Upon completion, the reaction vessel screw cap was unscrewed (note that in some cases pressure release was observed) and 10 mL of ethyl acetate was added following by extraction with 4x15 mL 5 M aqueous HCl solution. After mixing and separating the organic layer, the aqueous layer was neutralized with 1 M NaOH aqueous solution to pH=14, then transferred to a separatory funnel. Each aqueous phase was back-extracted with 4x15 mL portions of DCM. The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with aid of a rotary evaporator. The crude residues were purified via column chromatography to yield pure coupling products. Columns were primarily slurry packed with hexanes and mobile phase polarity was increased gradually to the mixture indicated. Note: hexanes = Hex, dichloromethane = DCM, ethyl acetate = EA.

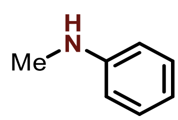
B. Analytical Data for Methylaminatiion Products

4-Fluoro-*N*-methylaniline (4):



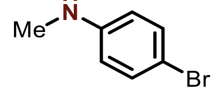
Following the **General Procedure 1A** using 4-fluorophenylboronic acid (70 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 18 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (56 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.94 – 6.88 (m, 2H), 6.59 – 6.50 (m, 2H), 3.59 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.9 (d, *J* = 234.4 Hz), 145.8 (d, *J* = 1.8 Hz), 115.7 (d, *J* = 22.3 Hz), 113.2 (d, *J* = 7.3 Hz), 31.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -128.53 (tt, J = 8.6, 4.3 Hz). HRMS (ESI) calculated for C_7H_9FN $[M+H]^+$: 126.0713; Found: 126.0714.

***N*-methylaniline (5):**



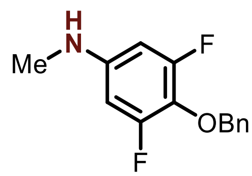
Following the **General Procedure 1A** using phenylboronic acid (1.2 g, 10 mmol, 1.0 equiv), phenylsilane (2.46 mL, 1.00 mmol, 2.0 equiv) and nitromethane (1.62 mL, 1.50 mmol, 3.0 equiv) for 18 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (0.89 g, 83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 2H), 6.72 (ddt, *J* = 8.7, 7.3, 1.4 Hz, 1H), 6.68 – 6.56 (m, 2H), 3.70 (br s, 1H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 129.3, 117.4, 112.5, 30.9. HRMS (ESI) calculated for C_7H_9N $[M+H]^+$: 108.0813, Found: 108.0814.

4-Bromo-*N*-methylaniline (6):



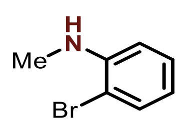
Following the **General Procedure 1A** using 4-bromophenylboronic acid (104 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (86 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 6.54 – 6.44 (m, 2H), 3.69 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4, 132.0, 114.1, 108.9, 30.8. HRMS (ESI) calculated for C_7H_9BrN $[M+H]^+$: 185.9913; Found: 185.9914.

4-(Benzyloxy)-3,5-difluoro-*N*-methylaniline (7):



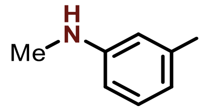
Following the **General Procedure 1A** using 4-benzyloxy-3,5-difluorophenylboronic acid (135 mg, 0.50 mmol, 1.0 equiv), diphenylsilane (372 µL, 2.00 mmol, 4.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (64 mg, 52%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.42 (m, 2H), 7.40 – 7.30 (m, 3H), 6.16 – 6.04 (m, 2H), 5.01 (s, 2H), 3.74 (s, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6 (d, *J* = 8.4 Hz), 156.1 (d, *J* = 8.3 Hz), 145.8 (t, *J* = 12.5 Hz), 137.1, 128.5 (d, *J* = 6.9 Hz), 128.4, 96.0 (d, *J* = 7.9 Hz), 95.8 (d, *J* = 7.7 Hz), 76.7 (t, *J* = 2.4 Hz), 30.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -127.71. HRMS (ESI) calculated for $C_{14}H_{14}F_2NO$ $[M+H]^+$: 250.1038; Found: 250.1035.

2-Bromo-*N*-methylaniline (8):



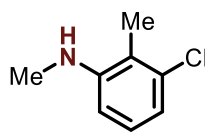
Following the **General Procedure 1A** using 2-bromophenylboronic acid (104 mg, 0.50 mmol, 1.0 equiv), diphenylsilane (279 µL, 1.50 mmol, 3.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=9:1 on silica gel (78 mg, 84%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.22 (ddd, *J* = 8.5, 7.4, 1.5 Hz, 1H), 6.69 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.61 (td, *J* = 7.6, 1.5 Hz, 1H), 4.80 (s, 1H), 2.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.7, 132.4, 128.7, 118.2, 111.4, 110.0, 31.0. HRMS (ESI) calculated for C_7H_9BrN $[M+H]^+$: 185.9913; Found: 185.9913.

3-Iodo-*N*-methylaniline (9):



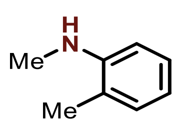
Following the **General Procedure 1B** using 3-iodophenylboronic acid (124 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 µl, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=9:1 on silica gel (95 mg, 81%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.94 (t, *J* = 2.0 Hz, 1H), 6.88 (t, *J* = 7.9 Hz, 1H), 6.55 (ddd, *J* = 8.2, 2.4, 0.9 Hz, 1H), 3.73 (s, 1H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.6, 130.7, 126.2, 120.9, 112.0, 95.4, 30.6. HRMS (ESI) calculated for C_7H_9IN $[M+H]^+$: 233.9774.9913; Found: 233.9773.

3-Chloro-*N*,2-dimethylaniline (10):



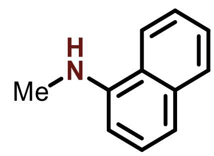
Following the **General Procedure 1A** using 3-chloro-2-methylphenylboronic acid (87 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=30:1 on silica gel (47 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (t, *J* = 8.1 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.52 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.70 (s, 1H), 2.90 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.5, 134.5, 127.4, 119.6, 117.9, 107.6, 31.1, 13.5. HRMS (ESI) calculated for $C_8H_{11}ClN$ $[M+H]^+$: 156.0575, Found: 156.0575.

***N*,2-dimethylaniline (11):**



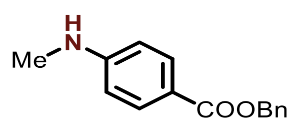
Following the **General Procedure 1A** using 2-methylphenylboronic acid (70 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=15:1 on silica gel (40 mg, 66%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (td, *J* = 7.7, 1.6 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.68 (td, J = 7.4, 1.2 Hz, 1H), 6.62 (dd, J = 8.0, 1.1 Hz, 1H), 3.58 (s, 1H), 2.90 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 130.0, 127.3, 122.0, 117.0, 109.3, 30.9, 17.5. HRMS (ESI) calculated for $C_8H_{12}N$ [M+H]$^+$: 122.0964; Found: 122.0967.

***N*-methylnaphthalen-1-amine (12):**



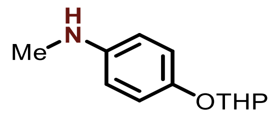
Following the **General Procedure 1A** using naphthalene-1-boronic acid (89 mg, 0.50 mmol, 1.0 equiv), diphenylsilane (372 µL, 2.00 mmol, 4.0 equiv) and nitromethane (108 µL, 2.00 mmol, 4.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=20:1 on silica (56 mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.76 (m, 2H), 7.49 (dd, J = 7.5, 1.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 6.64 (d, J = 7.5 Hz, 1H), 4.44 (s, 1H), 3.04 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 134.3, 128.7, 126.8, 125.8, 124.8, 123.6, 119.9, 117.4, 103.9, 31.1. HRMS (ESI) calculated for $C_{11}H_{12}N$ [M+H]$^+$: 158.0964, Found: 158.0961.

Benzyl 4-(methylamino)benzoate (13):



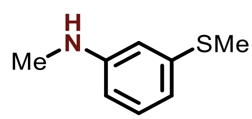
Following the **General Procedure 1B** using 4-benzylcarbonylphenylboronic acid (132 mg, 0.50 mmol, 1.0 equiv), diphenylsilane (279 µL, 1.50 mmol, 3.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=15:1 on silica gel (96 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.88 (m, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 6.59 – 6.51 (m, 2H), 5.32 (s, 2H), 4.19 (s, 1H), 2.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 153.1, 136.9, 131.8, 128.6, 128.1(128.13), 128.1(128.09), 118.3, 111.2, 66.1, 30.3. HRMS (ESI) calculated for $C_{15}H_{16}NO_2$ [M+H]$^+$: 242.1176, Found: 242.1179.

***N*-methyl-4-((tetrahydro-*2H*-pyran-2-yl)oxy)aniline (14):**



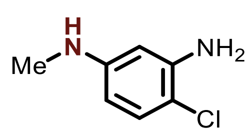
Following the **General Procedure 1B** using 4-(tetrahydro-2*H*-pyran-2-yloxy)phenylboronic acid (117 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 µl, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (81 mg, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.01 – 6.88 (m, 2H), 6.61 – 6.52 (m, 2H), 5.25 (t, *J* = 3.4 Hz, 1H), 3.97 (ddd, *J* = 11.9, 9.0, 3.2 Hz, 1H), 3.58 (dtd, *J* = 11.3, 4.3, 1.5 Hz, 1H), 3.23 (s, 1H), 2.80 (s, 3H), 2.07 – 1.91 (m, 1H), 1.91 – 1.79 (m, 2H), 1.75 – 1.55 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 144.7, 118.3, 113.5, 97.9, 62.3, 31.6, 30.7, 25.5, 19.2. HRMS (ESI) calculated for $C_{12}H_{18}NO_2$ $[M+H]^+$: 208.1332; Found: 208.1343.

***N*-methyl-4-(methylthio)aniline (15):**



Following the **General Procedure 1A** using 4-(methylthio)phenylboronic acid (88 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 µl, 1.5 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (59 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (t, *J* = 7.9 Hz, 1H), 6.61 (ddd, *J* = 7.7, 1.8, 0.9 Hz, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 6.40 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 1H), 3.79 (s, 1H), 2.83 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 139.4, 129.7, 115.6, 110.4, 109.9, 30.8, 16.0. HRMS (ESI) calculated for $C_8H_{12}NS$ $[M+H]^+$: 154.0685; Found: 154.0687.

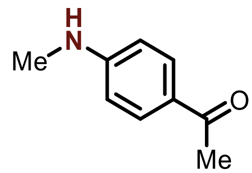
4-Chloro-*N*^{1}-phenylbenzene-1,3-diamine (16):



Following the **General Procedure 1A** using 3-amino-4-chlorophenylboronic acid (86 mg, 0.50 mmol, 1.0 equiv), diphenylsilane (372 µL, 2.00 mmol, 4.0 equiv) and nitromethane (108 µL, 2.00 mmol, 4.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=15:1 on silica gel (44 mg, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 9.3 Hz, 1H), 6.02 – 5.99 (m, 2H), 3.80

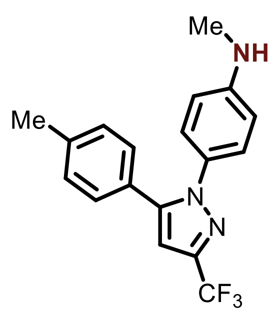
(s, 3H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 143.5, 129.8, 108.2, 104.7, 99.3, 31.0. HRMS (ESI) calculated for $C_7H_{10}ClN_2$ [M+H]$^+$: 157.0524, Found: 157.0527.

1-(4-(Methylamino)phenyl)ethan-1-one (17):



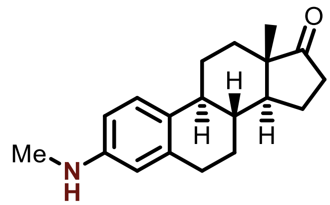
Following the **General Procedure 1A** using (4-acetylphenyl)boronic acid (82 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (81 µl, 1.5 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=20:1 on silica gel (45 mg, 61%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.75 (m, 2H), 6.63 – 6.44 (m, 2H), 4.42 (s, 1H), 2.88 (d, *J* = 5.1 Hz, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 153.3, 130.8, 126.5, 111.1, 30.1, 26.1. HRMS (ESI) calculated for $C_9H_{12}N_2O$ [M+H]$^+$: 150.0913, Found: 150.0913.

4-(6-Methoxybenzo*[d]*thiazol-2-yl)-*N*-methylaniline (18):



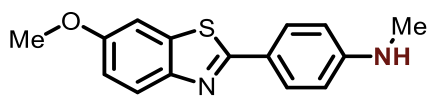
Following the **General Procedure 1A** using (4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)boronic acid (87 mg, 0.25 mmol, 1.0 equiv), diphenylsilane (186 µL, 1.00 mmol, 4.0 equiv) and nitromethane (41.0 µL, 1.50 mmol, 3.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=15:1 on silica gel (53 mg, 63%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.06 (m, 6H), 6.68 (s, 1H), 6.57 – 6.49 (m, 2H), 3.89 (s, 1H), 2.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 144.6, 142.4 (q, *J* = 38.2 Hz), 138.6, 129.4, 129.3, 128.6, 126.8, 126.6, 121.7 (q, *J* = 268.9 Hz) 112.1, 104.5 (q, *J* = 1.9 Hz), 30.6, 21.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.02. HRMS (ESI) calculated for $C_{18}H_{17}F_3N_3$ [M+H]$^+$:332.1369, Found: 332.1373.

(8R,9S,13S,14S)-13-Methyl-3-(methylamino)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta*[a]*phenanthren-17-one (19):



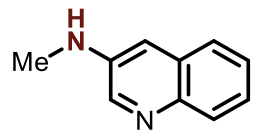
Following the **General Procedure 1A** using ((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta*[a]*phenanthren-3-yl)boronic acid (75 mg, 0.25 mmol, 1.0 equiv), phenylsilane (61 μL, 0.50 mmol, 2.0 equiv) and nitromethane (41 μL, 0.75 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=20:1 on silica (40 mg, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.4 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.38 (s, 1H), 3.58 (s, 1H), 2.87 (dd, *J* = 10.4, 6.6 Hz, 2H), 2.82 (s, 3H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.44 – 2.30 (m, 1H), 2.29 – 1.87 (m, 5H), 1.72 – 1.35 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.6, 137.4, 128.9, 126.3, 112.6, 110.9, 50.6, 48.2, 44.1, 38.7, 36.0, 31.8, 31.10, 29.9, 26.8, 26.1, 21.7, 14.0. HRMS (ESI) calculated for $C_{19}H_{26}NO$ [M+H]$^+$: 284.2009, Found: 284.1997.

4-(6-Methoxybenzo*[d]*thiazol-2-yl)-*N*-methylaniline (20):



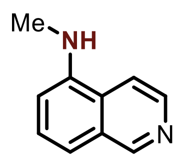
Following the **General Procedure 1A** using (4-(6-methoxybenzo[d]thiazol-2-yl)phenyl)boronic acid (71 mg, 0.25 mmol, 1.0 equiv), phosphetane oxide precatalyst **1**•[O] (8.7 mg, 0.05 mmol, 20 mol%), diphenylsilane (186 μL, 1.00 mmol, 4.0 equiv) and nitromethane (41 μL, 0.75 mmol, 3.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=9:1 on silica (52 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 3H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.68 – 6.60 (m, 2H), 4.09 (s, 1H), 3.88 (s, 3H), 2.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 157.3, 151.4, 149.0, 136.0, 128.9, 123.0, 122.9, 115.1, 112.2, 104.5, 56.0, 30.5. HRMS (ESI) calculated for $C_{15}H_{15}N_2OS$ [M+H]$^+$: 271.0900, Found: 271.0901.

***N*-methylquinolin-3-amine (21):**



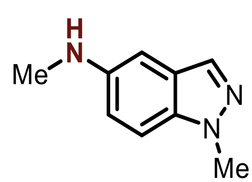
Following the **General Procedure 1C** using quinoline-3-ylboronic acid 1,3-propanediol ester (109 mg, 0.50 mmol, 1.0 equiv), diphenylsilane (372 µL, 2.00 mmol, 4.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=15:1 on silica gel (74 mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 2.8 Hz, 1H), 7.98 – 7.90 (m, 1H), 7.67 – 7.60 (m, 1H), 7.42 (tt, *J* = 7.0, 5.1 Hz, 2H), 7.00 (d, *J* = 2.8 Hz, 1H), 4.06 (s, 1H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 142.7, 142.2, 129.7, 129.2, 127.1, 126.1, 125.0, 109.6, 30.5. HRMS (ESI) calculated for $C_{10}H_{11}N_2$ [M+H]$^+$: 159.0917, Found: 159.0914.

***N*-methylisoquinolin-5-amine (22):**



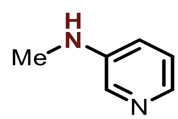
Following the **General Procedure 1C** using Isoquinoline-5-ylboronic acid 1,3-propanediol ester (109 mg, 0.50 mmol, 1.0 equiv), diphenylsilane (372 µL, 2.00 mmol, 4.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=9:1 on silica gel (73 mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (s, 1H), 8.46 (d, *J* = 6.0 Hz, 1H), 7.54 (d, *J* = 6.0 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 4.48 (s, 1H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.0, 143.7, 142.0, 129.4, 128.3, 126.2, 116.1, 113.5, 107.2, 30.9. HRMS (ESI) calculated for $C_{10}H_{11}N_2$ [M+H]$^+$: 159.0917, Found: 159.0923.

***N*,1-dimethyl-1*H*-indazol-5-amine (23):**



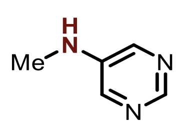
Following the **General Procedure 1C** using (1-methyl-1H-indazol-5-yl)boronic acid 1,3-propanediol ester (90 mg, 0.50 mmol, 1.0 equiv), phenylsilane (185 μL, 1.50 mmol, 3.0 equiv) and nitromethane (108 μL, 2.00 mmol, 4.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=15:1 on silica gel (57 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.62 (t, *J* = 1.4 Hz, 1H), 7.34 (d, *J* = 1.9 Hz, 2H), 4.04 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.0, 134.7, 132.7, 124.2, 119.8, 110.6, 110.3, 36.5, 35.9. HRMS calculated for $C_9H_{12}N_3$ $[M+H]^+$: 162.1026, Found: 162.1026.

***N*-methylpyridin-3-amine (24):**



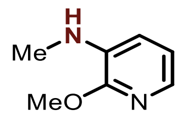
Following the **General Procedure 1C** using 3-pyridineboronic acid 1,3-propanediol ester (83 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 μL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 μL, 1.50 mmol, 3.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=4:1 on silica gel (48 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 3.0 Hz, 1H), 7.95 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.08 (dd, *J* = 8.3, 4.7 Hz, 1H), 6.85 (ddd, *J* = 8.3, 3.0, 1.4 Hz, 1H), 3.82 (s, 1H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.3, 138.7, 135.9, 123.8, 118.1, 30.4. HRMS (ESI) calculated for $C_6H_9N_2$ $[M+H]^+$: 109.0760, Found: 109.0761.

***N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (26):**



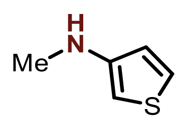
Following the **General Procedure 1C** using 3-pyrimidineboronic acid 1,3-propanediol ester (82 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 μL, 1.00 mmol, 2.0 equiv) and nitromethane (81.0 μL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=9:1 on silica gel (31 mg, 57%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.11 (d, *J* = 1.1 Hz, 2H), 3.78 (s, 1H), 2.90 (d, *J* = 4.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 142.7, 140.6, 30.1. HRMS (ESI) calculated for $C_5H_8N_3$ $[M+H]^+$: 110.0714, Found: 110.0713.

2-Methoxy-*N*-methylpyridin-3-amine (27):



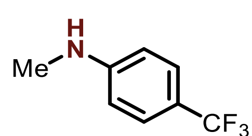
Following the **General Procedure 1C** using (2-methoxypyridin-3-yl)boronic acid 1,3-propanediol ester (97 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (108 µL, 2.00 mmol, 4.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (42 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 5.1, 1.6 Hz, 1H), 6.79 (dd, *J* = 7.6, 5.0 Hz, 1H), 6.68 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.19 (s, 1H), 3.97 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.6, 134.3, 132.6, 117.5, 114.0, 53.3, 30.0. HRMS (ESI) calculated for $C_7H_{11}N_2O$ [M+H]$^+$: 139.0864, Found: 139.0866.

***N*-methylthiophen-3-amine (28):**



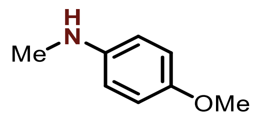
Following the **General Procedure 1C** using thiophen-3-ylboronic acid 1,3-propanediol ester (84 mg, 0.50 mmol, 1.0 equiv), phenylsilane (185 µL, 1.50 mmol, 3.0 equiv) and nitromethane (108 µL, 2.00 mmol, 4.0 equiv) for 48 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (29 mg, 51%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (dd, *J* = 5.1, 3.1 Hz, 1H), 6.62 (dd, *J* = 5.1, 1.5 Hz, 1H), 5.96 (dd, *J* = 3.1, 1.5 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 125.4, 119.9, 95.3, 33.0. HRMS (ESI) calculated for C_5H_8NS [M+H]$^+$: 114.0372, Found: 114.0350.

***N*-methyl-4-(trifluoromethyl)aniline (28):**



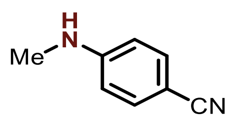
Following the **General Procedure 1C** using 4-trifluoromethylphenylboronic acid 1,3-propanediol ester (87 mg, 0.50 mmol, 1.0 equiv), phenylsilane (185 µL, 1.50 mmol, 3.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 30 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=30:1 on silica gel (72 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 6.60 (d, J = 8.5 Hz, 2H), 4.10 (s, 1H), 2.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.7, 126.7 (q, J = 3.8 Hz), 122.6 (q, J = 270.2 Hz), 118.7 (q, J = 32.1 Hz), 111.6, 30.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.95. HRMS (ESI) calculated for $C_8H_9F_3N$ $[M+H]^+$: 176.0682, Found: 176.0682.

4-Methoxy-*N*-methylaniline (29):



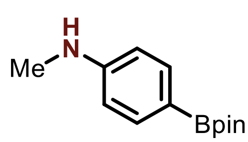
Following the **General Procedure 1C** using 4-methoxylphenylboronic acid 1,3-propanediol ester (96 mg, 0.50 mmol, 1.0 equiv), phenylsilane (185 µL, 1.50 mmol, 3.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=30:1 on silica gel (43 mg, 62%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.84 – 6.77 (m, 2H), 6.64 – 6.55 (m, 2H), 3.76 (s, 3H), 3.44 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.2, 143.8, 115.0, 113.8, 56.0, 31.8. HRMS (ESI) calculated for $C_8H_{12}NO$ $[M+H]^+$: 138.0913, Found: 138.0913.

4-(Methylamino)benzonitrile (30):



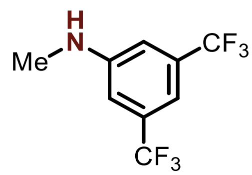
Following the **General Procedure 1C** using (4-cyanophenyl)boronic acid neopentyl ester (94 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane (135 µL, 2.50 mmol, 5.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (54 mg, 81%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.37 (m, 2H), 6.60 – 6.51 (m, 2H), 4.29 (s, 1H), 2.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.3, 133.8, 120.7, 112.0, 98.7, 30.1. HRMS (ESI) calculated for $C_8H_9N_2$ $[M+H]^+$: 133.0760, Found: 133.0761.

***N*-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (31):**



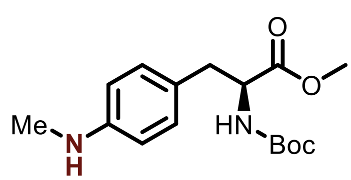
Following the **General Procedure 1B** using 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (83 mg, 0.25 mmol, 1.0 equiv), phenylsilane (61 µL, 0.50 mmol, 2.0 equiv) and nitromethane (68.0 µL, 1.25 mmol, 5.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=15:1 on silica gel (53 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 2H), 6.62 – 6.54 (m, 2H), 3.92 (s, 1H), 2.85 (s, 4H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9, 136.5, 111.6, 83.3, 30.4, 25.0. [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus][1] HRMS (ESI) calculated for $C_{13}H_{21}BNO_2$ [M+H]$^+$: 234.1662, Found: 234.1666.

***N*-methyl-3,5-bis(trifluoromethyl)aniline (32):**



Following the **General Procedure 1C** using 3,5-ditrifluoromethylphenylboronic acid pinacol ester (87 mg, 0.25 mmol, 1.0 equiv), phenylsilane (62 µL, 0,50 mmol, 2.0 equiv) and nitromethane (41 µL, 0.75 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (56 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (s, 1H), 6.92 (s, 2H), 4.16 (s, 1H), 2.91 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 132.5 (q, *J* = 32.9 Hz), 123.8 (q, *J* = 272.5 Hz), 111.6 (d, *J* = 3.8 Hz), 110.23 – 110.0 (m, 1C), 30.50. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.21. HRMS calculated for $C_9H_8F_6N$ [M+H]$^+$: 244.0555, Found: 244.0559.

Methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(methylamino)phenyl)propanoate (33):



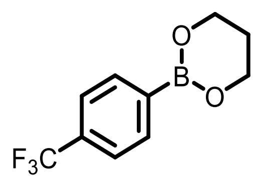
Following the **General Procedure 1B** using methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (101 mg, 0.25 mmol, 1.0 equiv), **1**•[O] (8.70 mg, 0.0375 mmol, 0.15 equiv), phenylsilane (61 µL, 0.50 mmol, 2.0 equiv) and nitromethane (68.0 µL, 1.25 mmol, 5.0 equiv) for 36 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=9:1 on silica gel (61.8 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.00 – 6.92 (m, 2H), 6.61 – 6.53 (m, 2H), 4.96 (d, *J* = 8.3 Hz, 1H), 4.53 (q, *J* = 6.5 Hz, 1H), 3,77 (brs, 1H), 3.73 (s, 3H), 3.00 (dd, *J*

= 4.8, 2.4 Hz, 2H), 2.84 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 155.3, 148.4, 130.2, 124.5, 112.8, 54.8, 52.3, 37.6, 31.0, 30.9, 28.5. HRMS (ESI) calculated for $C_{16}H_{24}N_2O_4Na$ $[M+Na]^+$: 331.1628, Found: 331.1620.

C. Preparation of Boronic Acid (Esters).

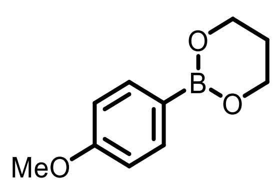
General procedure 1D for preparation of Boronic Acid 1,3-Propanediol Esters: To a glass culture tube described in the General Methods section was added an appropriate stir bar and the appropriate boronic acid (if solid). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *toluene* (0.5 M) (unless otherwise noted) was added via syringe from solvent system. Lastly, 1,3-propanediol was added and the reaction mixture was stirred at 80 °C overnight. Upon completion, the mixture was dried over anhydrous calcium chloride, filtered and concentrated with aid of a rotary evaporator to yield the product in sufficient purity for subsequent use without further purification.

4-Trifluoromethylphenylboronic acid 1,3-propanediol ester:



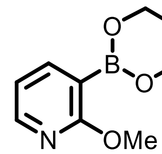
Following the **General Procedure 1D** using 4-Trifluoromethylphenylboronic acid (3.8 g, 20 mmol, 1.0 equiv), 1,3-propanediol (1.6 mL, 22 mmol, 1.1 equiv) at 80 °C for overnight. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 4.18 (t, J = 5.5 Hz, 4H), 2.08 (p, J = 5.5 Hz, 2H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.88.

4-Methoxylphenylboronic acid 1,3-propanediol ester:



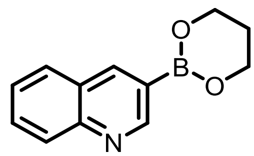
Following the **General Procedure 1D** using 4-Methoxylphenylboronic acid (3.0 g, 20 mmol, 1.0 equiv), 1,3-propanediol (1.6 mL, 22 mmol, 1.1 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dt, J = 9.2, 2.2 Hz, 2H), 6.92 – 6.84 (m, 2H), 4.15 (t, J = 5.5 Hz, 4H), 3.82 (s, 3H), 2.04 (p, J = 5.5 Hz, 2H).

(2-Methoxypyridin-3-yl)boronic acid 1,3-propanediol ester:



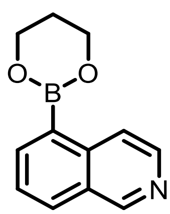
Following the **General Procedure 1D** using (2-methoxypyridin-3-yl)boronic acid (0.61 g, 4.0 mmol, 1.0 equiv), 1,3-propanediol (0.6 mL, 8.2 mmol, 2.0 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 5.0, 2.2 Hz, 1H), 7.96 (dd, *J* = 7.1, 2.2 Hz, 1H), 6.85 (dd, *J* = 7.1, 5.0 Hz, 1H), 4.19 (t, *J* = 5.5 Hz, 4H), 3.97 (s, 3H), 2.08 (p, *J* = 5.5, 2H).

Quinolin-3-ylboronic acid 1,3-propanediol ester:



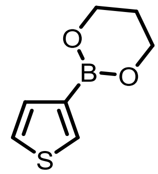
Following the **General Procedure 1D** using Quinolin-3-ylboronic acid (0.86 g, 4.0 mmol, 1.0 equiv), 1,3-propanediol (0.60 mL, 8.2 mmol, 2.0 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (d, *J* = 1.8 Hz, 1H), 8.56 (d, *J* = 1.3 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.73 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 4.24 (t, *J* = 5.5 Hz, 4H), 2.13 (p, *J* = 5.6 Hz, 2H).

Isoquinolin-5-ylboronic acid 1,3-propanediol ester:



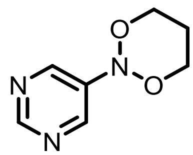
Following the **General Procedure 1D** using Isoquinolin-5-ylboronic acid (0.43 g, 2.0 mmol, 1.0 equiv), 1,3-propanediol (0.30 mL, 4.1 mmol, 2.0 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 8.58 (d, *J* = 6.1 Hz, 1H), 8.51 (d, *J* = 6.0 Hz, 1H), 8.23 (dd, *J* = 7.0, 1.4 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 8.2, 7.0 Hz, 1H), 4.29 (t, *J* = 5.5 Hz, 4H), 2.16 (p, *J* = 5.5 Hz, 2H).

Thiophen-3-ylboronic acid 1,3-propanediol ester:



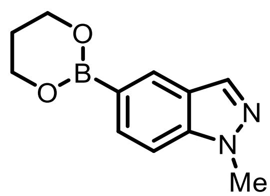
Following the **General Procedure 1D** using Thiophen-3-ylboronic acid (2.6 g, 20 mmol, 1.0 equiv), 1,3-propanediol (1.6 mL, 22 mmol, 1.1 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 2.7 Hz, 1H), 7.35 (d, *J* = 4.8 Hz, 1H), 7.30 (dd, *J* = 5.0, 2.7 Hz, 1H), 4.14 (t, *J* = 5.5 Hz, 4H), 2.05 (p, *J* = 5.5 Hz, 2H).

Pyrimidin-3-ylboronic acid 1,3-propanediol ester:



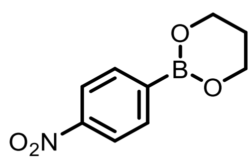
Following the **General Procedure 1D** using Pyrimidin-3-ylboronic acid (0.62 g, 5.0 mmol, 1.0 equiv), 1,3-propanediol (0.70 mL, 10 mmol, 2.0 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 8.96 (s, 2H), 4.19 (t, *J* = 5.5 Hz, 4H), 2.10 (p, *J* = 5.5 Hz, 2H).

1-Methyl-1*H*-indazol-5-ylboronic acid 1,3-propanediol ester:



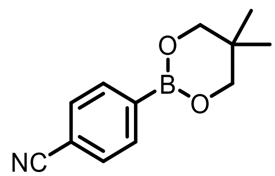
Following the **General Procedure 1D** using 1-Methyl-1*H*-indazol-5-ylboronic acid (0.52 g, 3.0 mmol, 1.0 equiv), 1,3-propanediol (0.4 mL, 6.0 mmol, 2.0 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.98 (s, 1H), 7.78 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.35 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.20 (t, *J* = 5.5 Hz, 4H), 4.07 (s, 3H), 2.09 (p, *J* = 5.5 Hz, 2H).

2-(4-Nitrophenyl)-1,3,2-dioxaborinane:



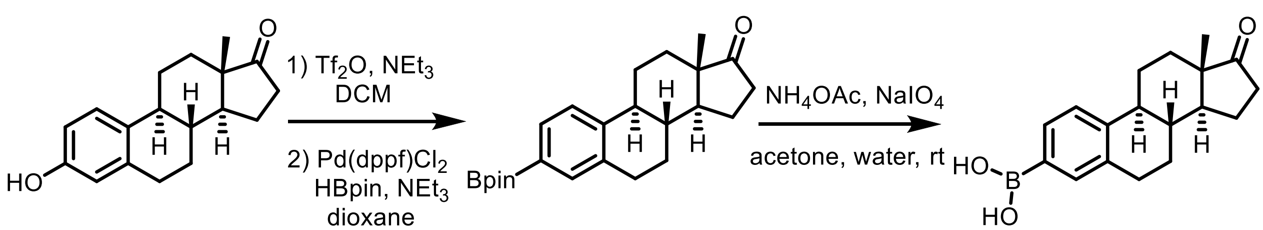
Following the **General Procedure 1D** using (4-nitrophenyl)boronic acid (1.0 g, 6.0 mmol, 1.0 equiv), 1,3-propanediol (0.48 mL, 7.2 mmol, 1.2 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 4.14 (t, J = 5.4 Hz, 4H), 2.03 (p, J = 5.4 Hz, 2H).

4-Cyanophenylboronic acid 2,2-dimethyl-1,3-propandiol ester:



Following the **General Procedure 1D** using 4-Cyanophenylboronic acid (0.73 g, 5.0 mmol, 1.0 equiv), 2,2-dimethyl-1,3-propanediol (0.7 mL, 10.0 mmol, 2.0 equiv) at 80 °C for overnight. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.7 Hz, 2H), 3.78 (s, 4H), 1.03 (s, 6H).

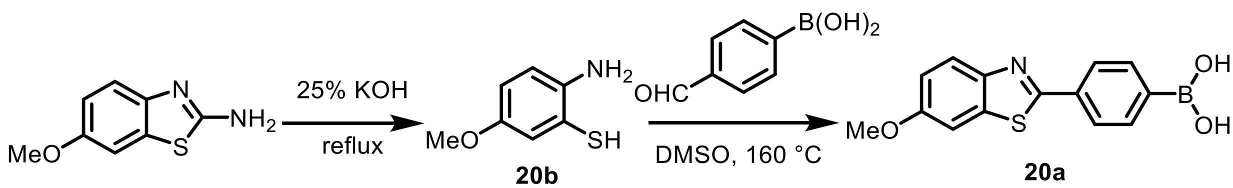
Synthesis of ((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-*6H*-cyclopenta*[a]*phenanthren-3-yl)boronic acid (19a):



To a solution of estrone (1.0 g, 3.7 mmol) and triethylamine (1.0 mL, 7.4 mmol) in DCM (20 mL) was added Tf_2O (0.7 mL, 4.1 mmol,) at 0°C. The reaction mixture was stirred at same temperature for 1h, then warmed to room temperature and stirred overnight. After completion, the reaction was washed with $NaHCO_3$ (20 mL). The aqueous phase was extracted with DCM (2 x 20 mL), and the combined organic phase was washed brine (40 mL), dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (Hex: EA =10:1) on silica to give 3-(trifluoromethanesulfonyl)estrone as a white solid (1.3 g, 90%). A portion of this product (1.0 g, 2.5 mmol) was added to a sealed tube containing Pd(dppf)Cl_2 (122 mg, 0.15 mmol), triethylamine (2.1 mL, 6.0 equiv), dioxane (10 mL), followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 mL, 7.2 mmol). The reaction mixture was then heated to 100°C and stirred for 24 h. The reaction mixture was cooled to room temperature and filtered through a pad of cellite. The filtrate was concentrated and purified by flash column chromatography (Hex: EA =10:1) on silica to give 3-deoxyestrone-3-boronic acid pinacol ester (0.70 g, 74%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.53 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 2.93 (dt, *J* = 6.8, 4.3 Hz, 2H), 2.57 – 2.40 (m, 2H), 2.33 (td, *J* = 10.8, 4.2 Hz, 1H), 2.19 – 1.89 (m, 4H), 1.73 – 1.39 (m, 6H), 1.34 (s, 12H), 0.90 (s, 3H).

To a solution of 3-deoxyestrone-3-boronic acid pinacol ester (0.70 g, 1.8 mmol) in acetone (15 mL) and water (10 mL), NH_4OAc (0.82 g, 11 mmol) and $NaIO_4$ (2.4 g, 11 mmol) were added. The resulting reaction mixture was stirred at room temperature for 48 h. When completed, the reaction was diluted with Et_2O and filtered through a pad of celite. The filtrate was concentrated and purified by flash column chromatography (Hex: EA = 10:1) to afford aryl boronic acid **19a** (307 mg, 56%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 2.93 – 2.81 (m, 2H), 2.51 – 2.33 (m, 2H), 2.28 – 2.19 (m, 1H), 2.19 – 1.90 (m, 4H), 1.67 – 1.36 (m, 6H), 0.91 (s, 3H).

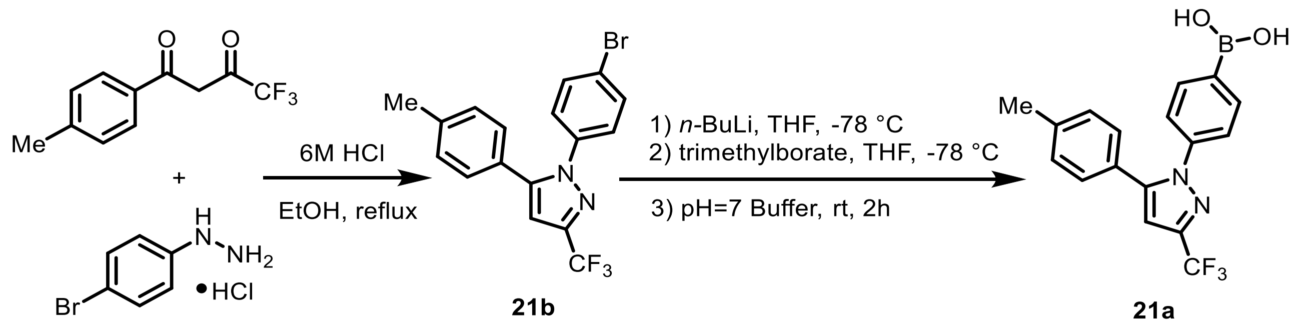
Synthesis of (4-(6-methoxybenzo[d]thiazol-2-yl)phenyl)boronic acid (20a):



To a solution of 25% potassium hydroxide (7.50 g KOH in 22.5 mL pure water) in 100 mL round-bottomed flask, 2-amino-methoxybenzothiazole (6.0 g, 33 mmol) was added. The suspension was heated to reflux for 24 h. After cooling down to room temperature, the pale yellow solution was acidified to pH=6 with aqueous 6N HCl then acetic acid. The precipitated solid was filtered and purified by flash column chromatography (Hex: EA=15:1) on silica to afford the desired product **20b** as a yellow solid (4.6 g, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.80 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.73 – 6.63 (m, 2H), 4.12 – 3.98 (m, 2H), 3.61 (s, 3H).

To a sealed tube charged with nitrogen were added **20b** (0.78 mg, 5.0 mmol) and 4-Formylphenylboronic acid (0.75 mg, 5.0 mmol) followed by DMSO (30 mL). The suspension was heated to 160 °C and stirred for 2 h. After completion of the reaction, the mixture was poured into ice water to precipitate the product, which was collected by suction filtration and washed with a sparing amount of dichloromethane to afford desired product (4-(6-methoxybenzo*[d]*thiazol-2-yl)phenyl)boronic acid **20a** (1.4 g, 99%) as a solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (s, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.97 – 7.89 (m, 3H), 7.73 (d, *J* = 2.6 Hz, 1H), 7.14 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.86 (s, 3H).

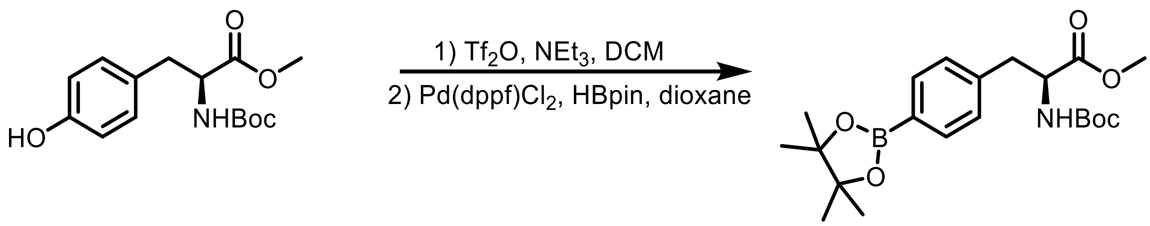
Synthesis of (4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)boronic acid (21a):



To a 100 mL round-bottomed flask charged with nitrogen and equipped with a magnetic stir bar were added 4,4,4-trifluoro-1-(*p*-tolyl)butane-1,3-dione (2.37 g, 10.3 mmol), (4- bromophenyl)hydrazine hydrochloride (2.24 g, 10.0 mmol), ethanol (20 mL) and 6N HCl (3.4 mL, 20 mmol). The reaction vessel was heated to reflux and stirred for 12 h. After cooling to room temperature, the reaction mixture was diluted with EA (40 mL) and washed with 30 mL saturated K_2CO_3, followed by 30 mL saturated brine. Then the combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hex: EA =10:1) to afford **21b** as a white solid (3.5 g, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 2H), 7.25 – 7.09 (m, 6H), 6.74 (s, 1H), 2.38 (s, 3H).

To a 25 mL round-bottomed flask equipped with a magnetic stir bar were added 1-(4-bromophenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (0.76 g, 2.0 mmol), THF (5.6 mL) under an atmosphere of nitrogen and cooled to -78℃. A solution of *n*-BuLi (0.88 mL, 2.2 mmol) in hexane (2.5 M) was added dropwise. At this temperature, the suspension was stirred for 15 min. Neat triisopropylborate (0.8 mL, 3.0 mmol) was added dropwise. The resulting solution was stirred at -78℃ for further 5 min then warmed to room temperature and stirred for another 1 h. Next, aqueous buffer (pH=7, 1.0 vol) was added and the biphasic mixture was stirred vigorously for 2 h. The reaction mixture was partitioned between water and ethyl acetate, the phases were separated, and the aqueous phase was extracted with EA (3 x 20 mL). The combined organic phases were washed with brine (20 mL) and then dried over Na_2SO_4, Removal of all volatiles *in vacuo* gave the crude product a white solid, which could be purified by flash column chromatography on silica gel (Hex:EA = 4:1) to afford pure product ***21a*** as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (s, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.11 (m, 5H), 2.30 (s, 3H).

Synthesis of (S)-(4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)boronic acid (22a):



22a

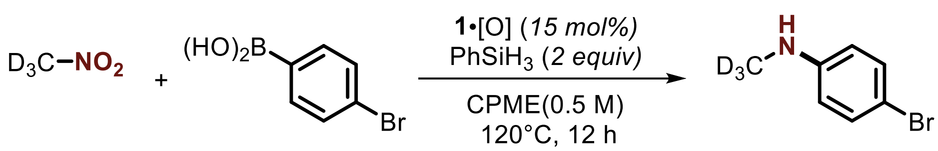
To a solution of Boc-Tyr-OMe (5.0 g, 17 mmol) and NEt_3 (4.7 mL, 34 mmol,) in DCM (50 mL) was added Tf_2O (3.3 mL, 19 mmol) at 0ºC. The reaction mixture was stirred at same temperature for 1 h, then warmed to room temperature and stirred overnight. After completion, the reaction was washed with $NaHCO_3$ (50 mL). The aqueous phase was extracted with DCM (2 x 50 mL), and the combined organic phase was washed brine (50 mL), dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (Hex: EA =10:1) on silica to give trifluoromethanesulfonic ester (5.1 g, 70%) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.17 (m, 4H), 5.01 (d, *J* = 8.2 Hz, 1H), 4.60 (q, *J* = 6.9 Hz, 1H), 3.71 (s, 3H), 3.10 (ddd, *J* = 53.2, 13.9, 6.1 Hz, 2H), 1.41 (s, 9H).

To a sealed tube were added trifluoromethanesulfonic ester (2.5 g, 5.8 mmol), Pd(dppf)Cl_2 (0.22 g, 0.3 mmol), 4-methylmorpholine (1.8 mL, 1.5 equiv), dioxane (20 mL), followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.6 mL, 18 mmol). The reaction mixture was then heated to 80ºC and stirred for 24 h. The reaction mixture was cooled to room temperature and filtered through a pad of cellite. The filtrate was concentrated and purified by flash column chromatography (Hex: EA =10:1) on silica to give ***22b*** (1.51 g, 63%) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 4.94 (d, *J* = 8.2 Hz, 1H), 4.58 (q, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 3.11 (tt, *J* = 13.8, 6.9 Hz, 2H), 1.42 (s, 9H), 1.34 (s, 12H).

IV. Mechanistic Experiments

A. *In Situ* Spectroscopic Investigations

In situ NMR observation of the catalytic reaction: To a glass culture tube described in the General Methods section was added a small stir bar, 4-bromophenylboronic acid (208 mg, 1.00 mmol, 1.0 equiv), phosphetane oxide precatalyst **1**•[O] (26 mg, 15 mol%). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *cyclopentyl methyl ether* (0.5 M) was added via syringe from a sure-seal® bottle. Lastly, phenylsilane (246 µL, 2.00 mmol, 2.0 equiv) and d_3-nitromethane (162 µL, 3.0 mmol, 3.0 equiv) were added and the reaction mixture was stirred at 120 °C for 12 h. For every time point, a 50 µL aliquot of the diluted reaction mixture was then added to a screwed NMR tube containing 0.4 mL of DCM. The ^{2}H (ppm calibrated relative to *d*-DCM(*l*) internal standard) and ^{31}P NMR spectra (ppm are relative to 85% H_3PO_4 external standard) were collected at 0 h, 4 h, 9 h and 12 h.



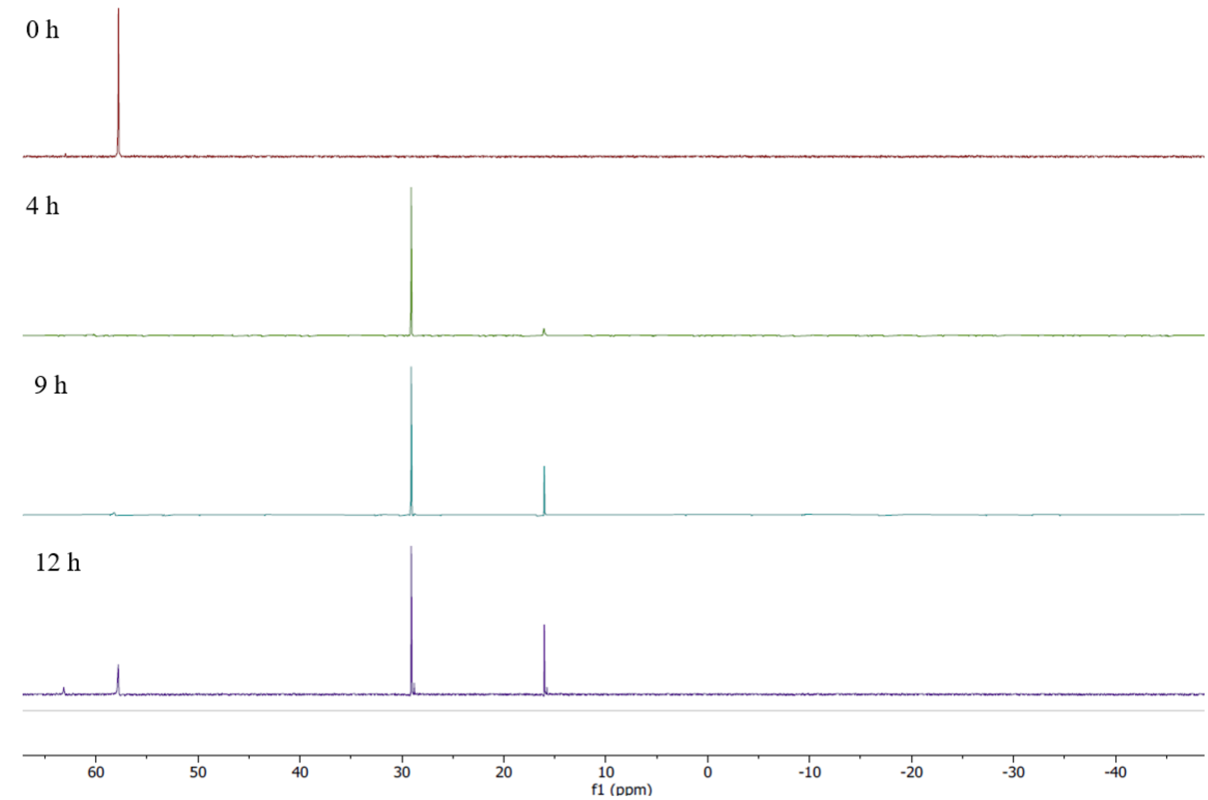


Figure S1. Time-stacked in situ ^{31}P NMR spectra (T = 25 ℃, CH_2Cl_2) at t = 0 h, 4 h, 9 h and 12 h. Chemical shifts: **1**•[O], δ 57.8 (*anti*) and 62.3 (*syn*) ppm; **1**, δ 29.1 (*anti*) and 16.0 (*syn*) ppm. Units of chemical shift (δ) are ppm relative to 85% H_3PO_4 as an external standard.

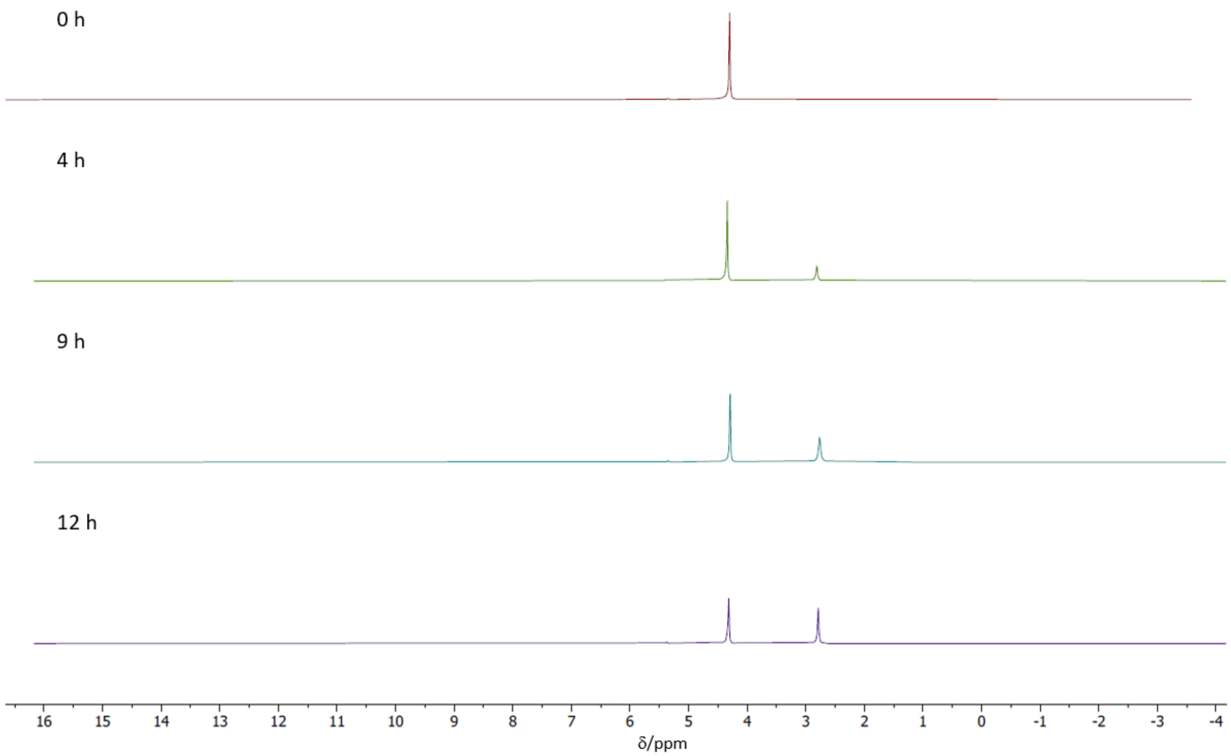


Figure S2. Time-stacked in situ ^{2}H NMR spectra (T = 25 ℃, dichloromethane) at t = 0 h, 4 h, 9 h and 12 h. Chemical shifts: d_3-nitromethane, δ 4.32 ppm; 4-bromo-*N*-(methyl-d_3)aniline, δ 2.79 ppm. Units of chemical shift (δ) are ppm relative to d_2-dichloromethane as an internal standard.

B. ***Control reactions with formaldoxime trimer***

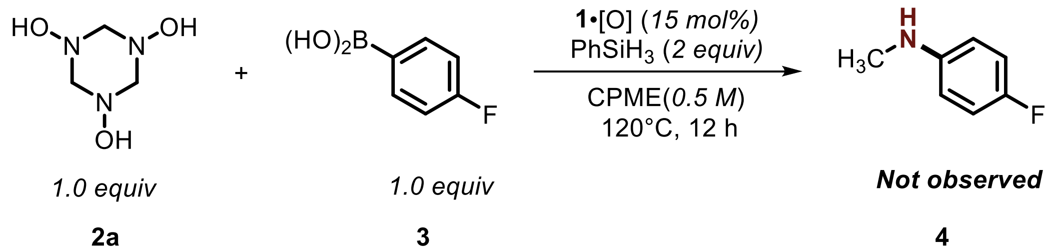
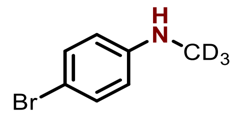


Figure S3. Control reactions with formaldoxime trimer instead of nitromethane as the starting material under the standard conditions.

V. Specialized Applications and Examples

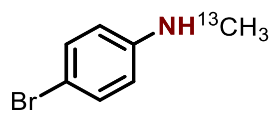
A. Isotopic labelling from $H_3C–NO_2$ isotopologues

a. 4-Bromo-*N*-(methyl-d_3)aniline synthesis (***5b***):



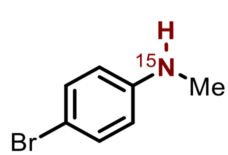
Following the **General Procedure 1C** using 4-bromophenylboronic acid (104 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane-d_3 (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (84 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 6.53 – 6.42 (m, 2H), 3.70 (s, 1H), 2.77 (s, 0.06H, 98% D). ^{2}H NMR (61 MHz, Chloroform-*d*) δ 2.79 (s, 3D). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4, 132.0, 114.1, 108.9.[2] HRMS (ESI) calculated for C_7H_9BrN $[M+H]^+$: 189.0101; Found: 189.0102.

b. 4-bromo-*N*-(methyl-^{13}C)aniline synthesis (***5c***):



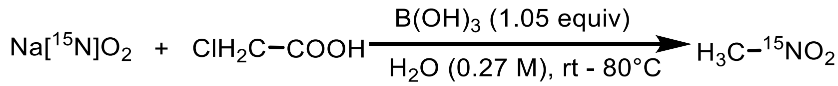
Following the **General Procedure 1C** using 4-bromophenylboronic acid (104 mg, 0.50 mmol, 1.0 equiv), phenylsilane (123 µL, 1.00 mmol, 2.0 equiv) and nitromethane-^{13}C (81.0 µL, 1.50 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (86 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.18 (m, 2H), 6.58 – 6.35 (m, 2H), 3.82 (s, 1H), 2.79 (d, J = 135.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.1, 131.8, 114.0 (d, J = 3.4 Hz), 108.9, 30.7. HRMS (DART) calculated for $C_6[^{13}C]H_9BrN$ $[M+H]^+$: 186.9946; Found: 186.9949, 98% [^{13}C]

c. 4-Bromo-*N*-methylaniline-^{15}N synthesis (***5d***):

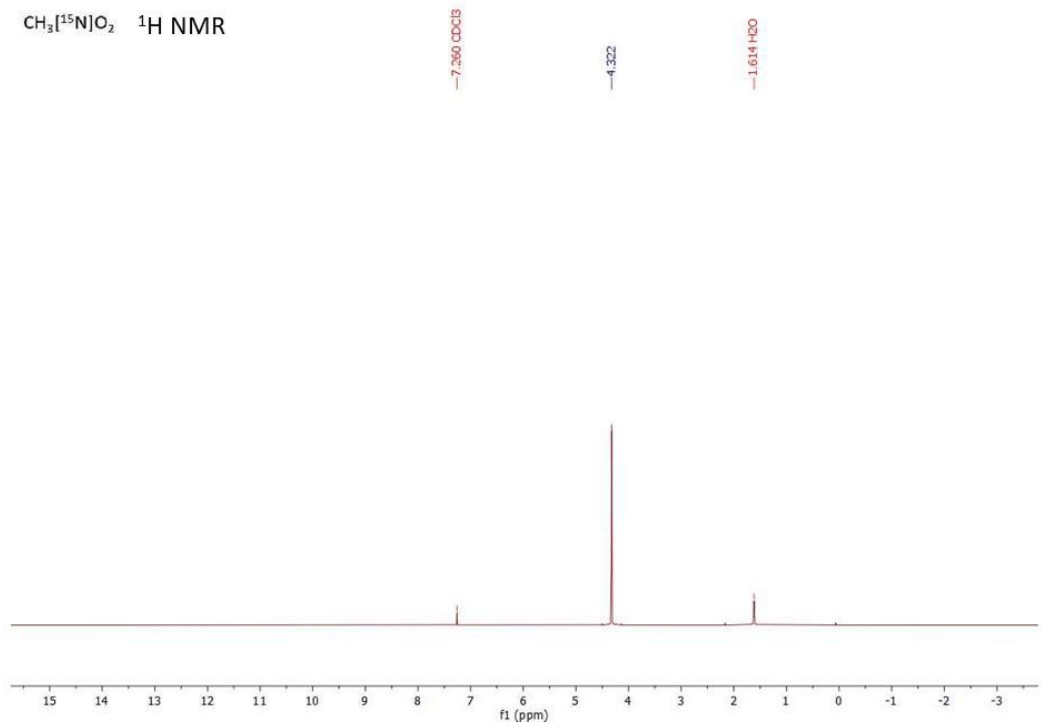


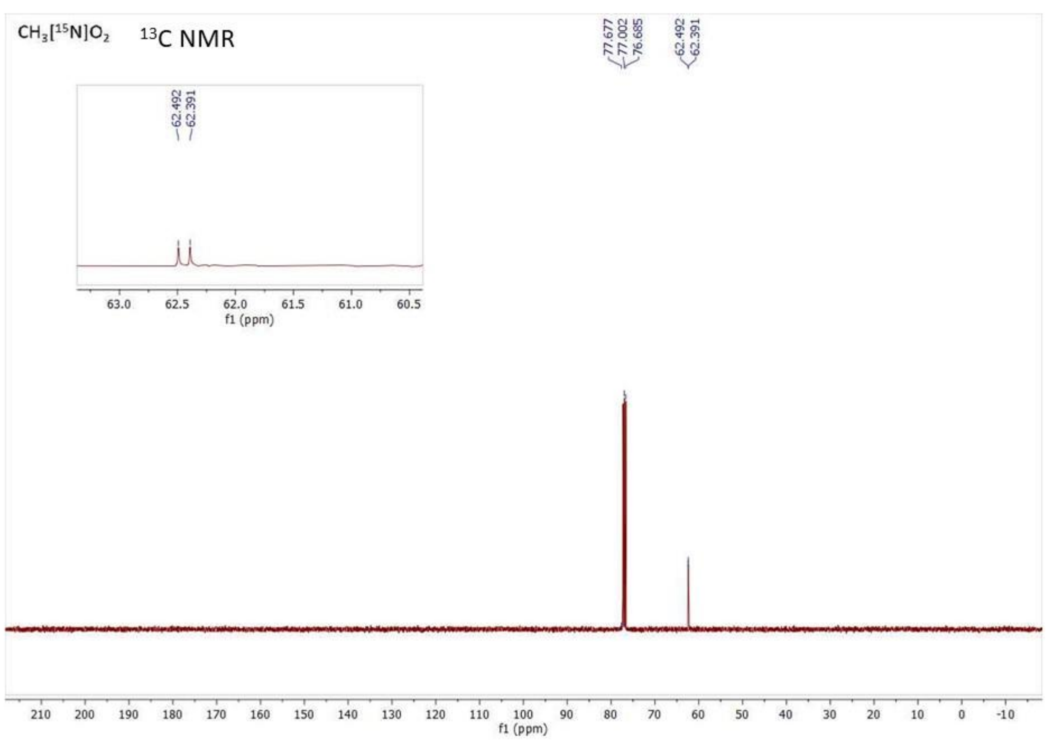
Following the **General Procedure 1C** using 4-Bromophenylboronic acid (41 mg, 0.20 mmol, 1.0 equiv), phenylsilane (50 µL, 0.40 mmol, 2.0 equiv) and (nitro-^{15}N)methane (32 µL, 0.60 mmol, 3.0 equiv) for 24 h at 120 °C. The product was purified by flash column chromatography with Hex:EA=19:1 on silica gel (34 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.19 (m, 2H), 6.59 – 6.41 (m, 2H), 3.93 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.9 (d, J = 21.6 Hz), 131.9 (d, J = 1.6 Hz), 114.2 (d, J = 2.8 Hz), 109.2, 30.9 (d, J = 9.8 Hz). ^{15}N NMR (41 MHz, Chloroform-*d*) δ 52.4. HRMS (DAR) calculated for $C_7H_9Br[^{15}N]$ $[M+H]^+$: 186.9883; Found: 186.9873. 99%$[^{15}N]$

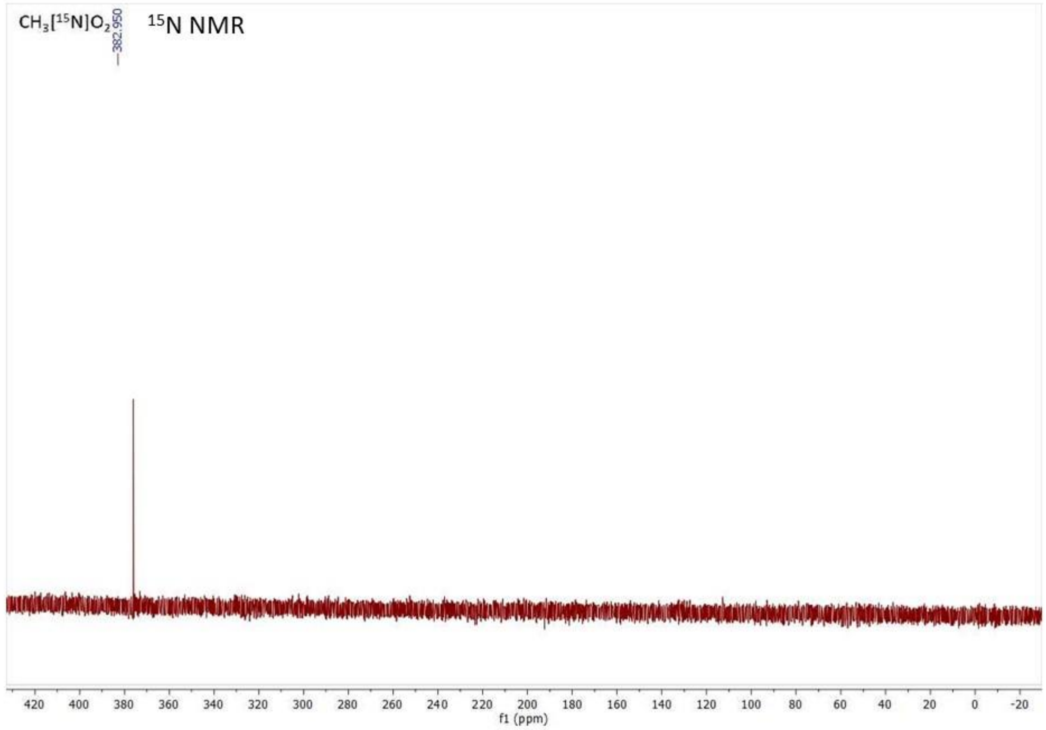
B. (nitro-^{15}*N*)methane Preparation



Preparation followed a modification of a reported procedure:[3] To a stirred mixture of chloroacetic acid (1.6 g, 14 mmol, 1.4 equiv) and cracked ice (25 g) was added cold 1 M NaOH just enough to make the solution alkaline to phenolphthalein. The solution was mixed with $^{15}NO_2Na$ (0.70 g, 10 mmol) in H_2O (10 mL) and with boric acid (0.65 g, 1.05 equiv). The reaction mixture was heated until bubbles of carbon dioxide appeared (around 60 °C) and held at this temperature for 4 h. The reaction temperature was then increased to 80 °C and held for an additional 2 h. Nitromethane and H_2O were then distilled and nitromethane was extracted with diethyl ether (2 x 10 mL) and dried with Na_2SO_4. Careful distillation of the crude mixture gave the pure product (nitro-^{15}*N*)methane (0.20 g, 32%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 62.4 (d, J = 10.1 Hz). ^{15}N NMR (41 MHz, Chloroform-*d*) δ 383.0.

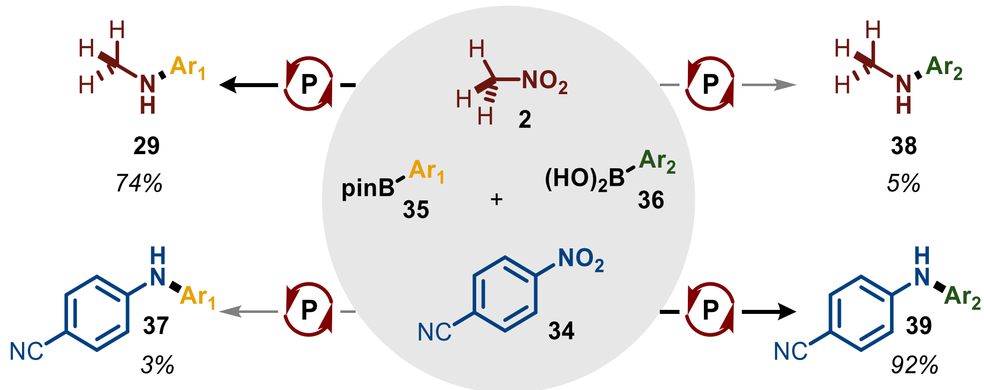

$CH_3[^{15}N]O_2$ ^1H NMR
7.260 CDCl3
4.322
1.614 H2O
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


$CH_3[^{15}N]O_2$ ^{13}C NMR
77.677
77.002
76.685
62.492
62.391
63.0 62.5 62.0 61.5 61.0 60.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



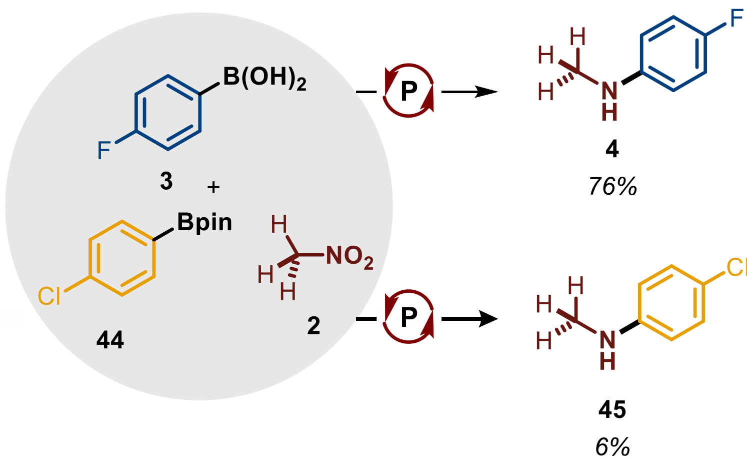
CH3[15N]O2
382.950
15N NMR
420 400 380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
f1 (ppm)

C. Reactivity comparison for ($MeNO_2$ vs $ArNO_2$) and ($ArB(OH)_2$ vs ArBpin).



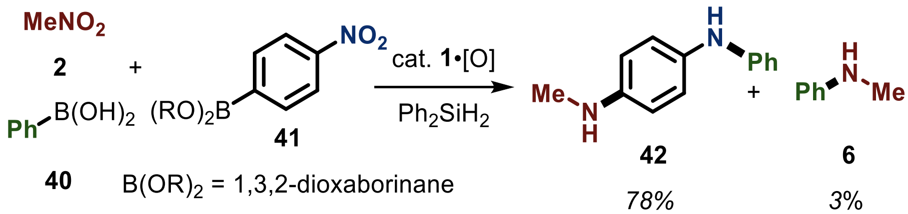
To a glass culture tube described in the General Methods section was added a small stir bar, 3,5-ditrifluoromethylphenylboronic acid pinacol ester (87 mg, 0.25 mmol, 1.0 equiv), 4-methoxyphenylboronic acid (38 mg, 0.25 mmol, 1.0 equiv), 4-nitrobenzonitrile (37 mg, 0.25 mmol, 1.0 equiv) and phosphetane oxide precatalyst **1**•[O] (13 mg, 0.075 mmol%, 30 mol%). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *cyclopentyl methyl ether* (1.0 mL, 0.25 M) was added via syringe from a sure-seal® bottle. Lastly, phenylsilane (123 µL, 1.00 mmol, 4.0 equiv) and nitromethane (41.0 µL, 0.75 mmol, 3.0 equiv) were added and the reaction mixture was stirred at 120 °C for 12 h. Upon completion, the yield of 4-((3,5-bis(trifluoromethyl)phenyl)amino)benzonitrile **37** was determined by ^{19}F NMR with trifluorotoluene as the internal standard, and the yield of 4-methoxy-*N*-methylaniline **38** was determined by ^{1}H NMR with dibromomethane as the internal standard. The crude mixture was purified directly by flash column chromatography with Hex:EA=10:1 on silica gel to obtain *N*-methyl-3,5-bis(trifluoromethyl)aniline **29** (45 mg, 74%) and 4-((4-methoxyphenyl)amino)benzonitrile **39** (52 mg, 92%), ^{1}H NMR (400 MHz, Chloroform-d) δ 7.41 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.01 (br s, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 157.0, 149.8, 133.7, 132.6, 125.0, 120.3, 114.9, 113.8, 100.0, 55.6. HRMS (ESI) calculated for $C_{14}H_{13}N_2O$ $[M+H]^+$: 225.1028; Found: 225.1031.

.



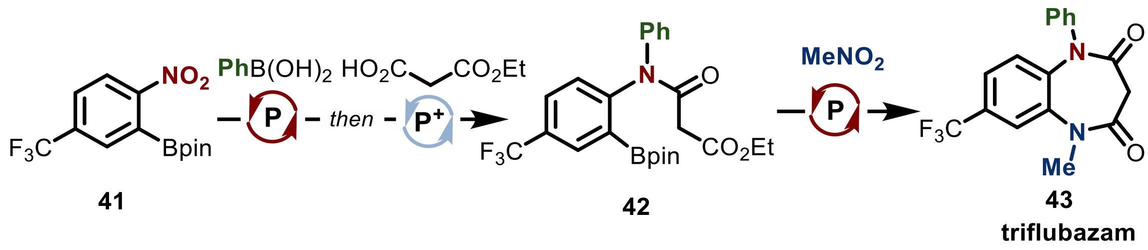
To a glass culture tube described in the General Methods section was added a small stir bar, 4-chlorophenylboronic acid pinacol ester (60 mg, 0.25 mmol, 1.0 equiv), 4-fluorophenylboronic acid (35 mg, 0.25 mmol, 1.0 equiv) and phosphetane oxide precatalyst **1**•[O] (6.5 mg, 0.0375 mmol%, 15 mol%). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry cyclopentyl methyl ether (0.5 mL, 0.5 M) was added via syringe from a sure-seal® bottle. Lastly, phenylsilane (62 µL, 0.50 mmol, 2.0 equiv) and nitromethane (41.0 µL, 0.75 mmol, 3.0 equiv) were added and the reaction mixture was stirred at 120 °C for 8 h. NMR yield of 4-fluoro-*N*-methylaniline **4** (76%) was obtained by ^{19}F NMR with 4-fluorotoluene as the internal standard, and the NMR yield of 4-chloro-*N*-methylaniline **45** was determined by ^{1}H NMR with dibromomethane as the internal standard.

D. Benzene-1,4-diamine synthesis from a three-component reaction.



To a glass culture tube described in the General Methods section was added a small stir bar, 2-(4-nitrophenyl)-1,3,2-dioxaborinane (103 mg, 0.50 mmol, 1.0 equiv), phenylboronic acid (61 mg, 0.50 mmol, 1.0 equiv) and phosphetane oxide precatalyst **1**•[O] (18 mg, 0.10 mmol, 20 mol%). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *cyclopentyl methyl ether* (0.5 M) was added via syringe from a sure-seal® bottle. Lastly, diphenylsilane (557 µL, 3.00 mmol, 6.0 equiv) and nitromethane (81.0 µL, 1.50 mmol, 3.0 equiv) were added and the reaction mixture was stirred at 120 °C for 12 h. Upon completion, the yield of *N*-methylaniline **6** was determined by ^{1}H NMR with dibromomethane as the internal standard. The crude mixture was purified directly by flash column chromatography with Hex:EA=10:1 on silica gel to obtain product **42** (77 mg, 78%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 (s, 1H), 7.08 (dd, J = 8.4, 7.1 Hz, 2H), 6.94 – 6.86 (m, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.54 – 6.46 (m, 2H), 5.34 (s, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.7, 145.6, 131.4, 128.9, 122.6, 117.0, 113.6, 112.4, 30.2. HRMS (ESI) calculated for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230; Found: 199.1230.

E. Target molecule synthesis: Triflubazam (anxiolytic, anti-obsessive efficacy).



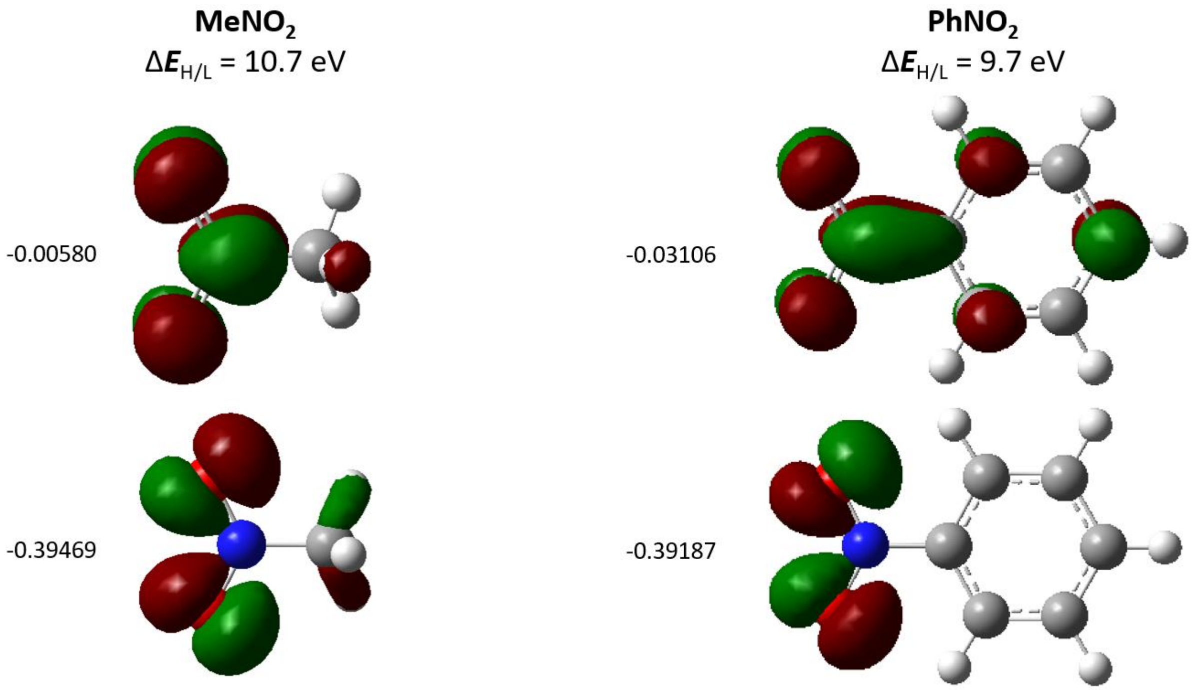
To a glass culture tube described in the General Methods section was added a small stir bar, compound **41** (79 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (34 mg, 0.28 mmol, 1.1 equiv) and phosphetane oxide precatalyst **1**•[O] (13 mg, 0.08 mmol, 30 mol%). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, dry *cyclopentyl methyl ether* (0.5 mL, 0.5 M) was added via syringe from a sure-seal® bottle. Lastly, diphenylsilane (186 µL, 1.0 mmol, 4.0 equiv) was added and the reaction mixture was stirred at 120 °C. After 2 h, the reaction mixture was cooled to 80 °C and diethyl (methyl)bromomalonate (72 µL, 0.375 mmol, 1.5 equiv) and hydrogen ethyl malonate (34 µL, 0.30 mmol, 1.2 equiv) were added. After 10 min, the reaction mixture was moved to another oil bath at 40 °C and the reaction mixture was stirred for 24 h. Upon completion, the reaction vessel screw cap was unscrewed (note that in some cases pressure release was observed) and 10 mL of distilled water was added. With the aid of DCM, the reaction mixture was transferred to a separatory funnel. After mixing and separating the aqueous layer, the organic layer was washed with 10 mL of a 1 M NaOH aqueous solution, and 10 mL of brine. Each aqueous phase was back-extracted with 10 mL portions of DCM. The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with aid of a rotary evaporator to obtain the crude product, which was advanced without further purification to the next step.

To a glass culture tube described in the General Methods section was added a small stir bar, phosphetane oxide precatalyst **1**•[O] (6.5 mg, 0.04 mmol, 15 mol%). The tube thread was wrapped once with Teflon tape and a phenolic screw-thread open-top cap fitted with a PTFE-lined silicone septum (Thermo Scientific) was screwed on. No special drying of the reaction vessel components was conducted prior. Following evacuation and the introduction of nitrogen on a Schlenk line, a solution of crude mixture from the first step in dry *cyclopentyl methyl ether* (1.0 mL, 0.25 M) from a sure-seal® bottle was added via syringe. Lastly, nitromethane (41.0 µL, 0.75 mmol, 3.0 equiv) and diphenylsilane (139 µL, 0.75 mmol, 3.0 equiv) were added and the reaction mixture was stirred at 120 °C. Upon completion, the mixture was purified directly by flash column chromatography with Hex:EA=1:1 on silica gel (42 mg, 51%). ^{1}H NMR

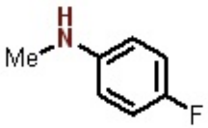
(400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.47 (m, 2H), 7.44 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.40 – 7.32 (m, 1H), 7.19 (dt, *J* = 5.8, 1.4 Hz, 3H), 3.61 (d, *J* = 12.3 Hz, 1H), 3.55 (s, 3H), 3.69 – 3.40 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 164.3, 140.2, 139.7, 136.3, 129.8, 128.70 (q, *J* = 33.9 Hz), 128.0, 124.5, 123.1 (q, *J* = 270.9 Hz), 123.7 – 123.4 (m, 3C), 44.4, 35.8. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.64. HRMS (ESI) calculated for $C_{17}H_{17}N_3F_3O_2$ $[M+NH_4]^+$: 352.1267; Found: 352.1277.

VI. DFT Computation

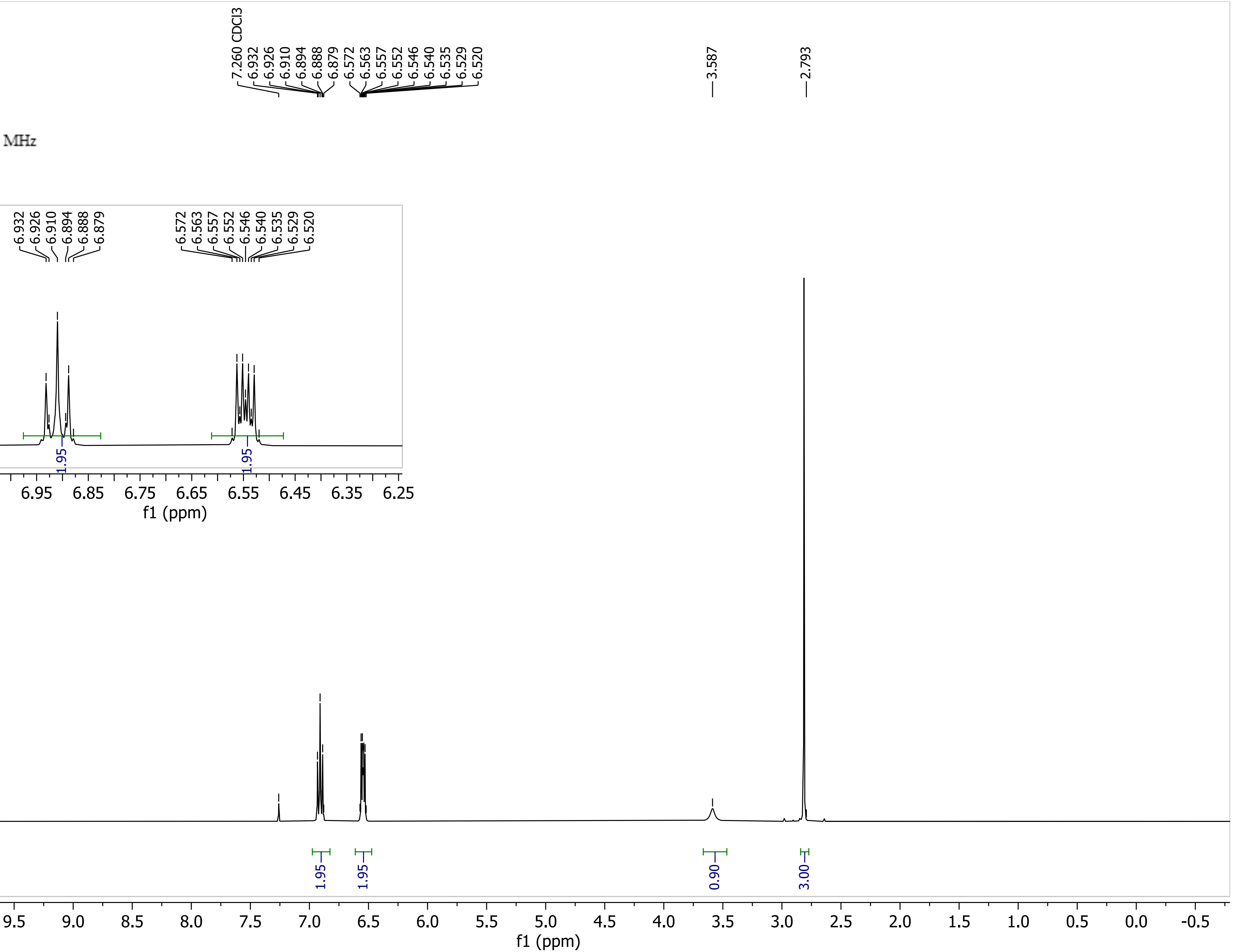
Kohn-Sham frontier orbital eigenvalues (in hartrees) for $H_3C\text{-}NO_2$ and $H_5C_6\text{-}NO_2$ at the ωB97XD/6-311++G(2d,2p) level of theory are as follows:

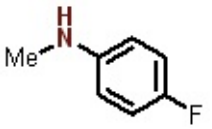


VI. Spectra Data



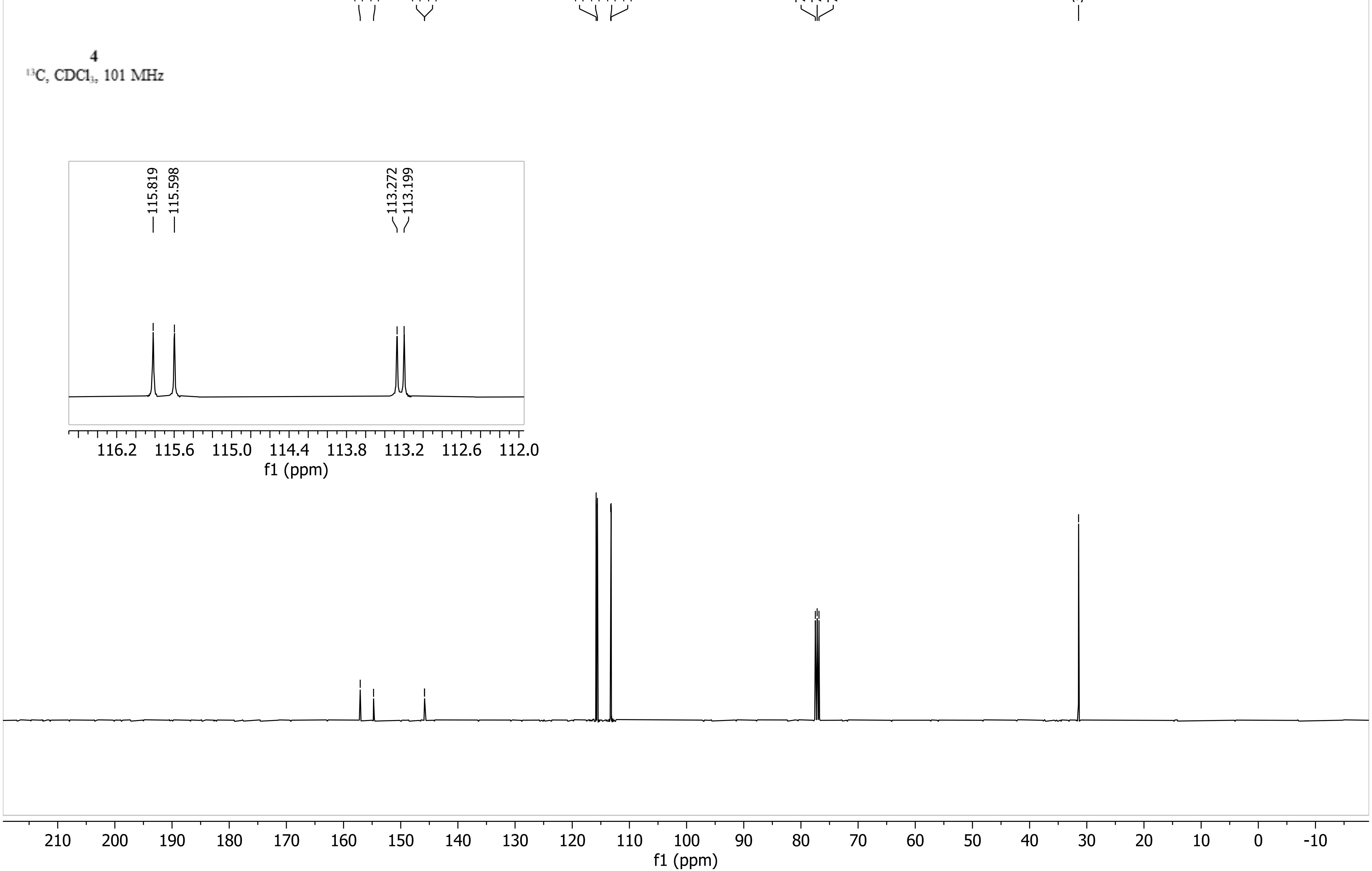
4,
^1H, $CDCl_3$, 400 MHz

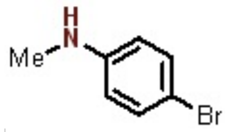




4

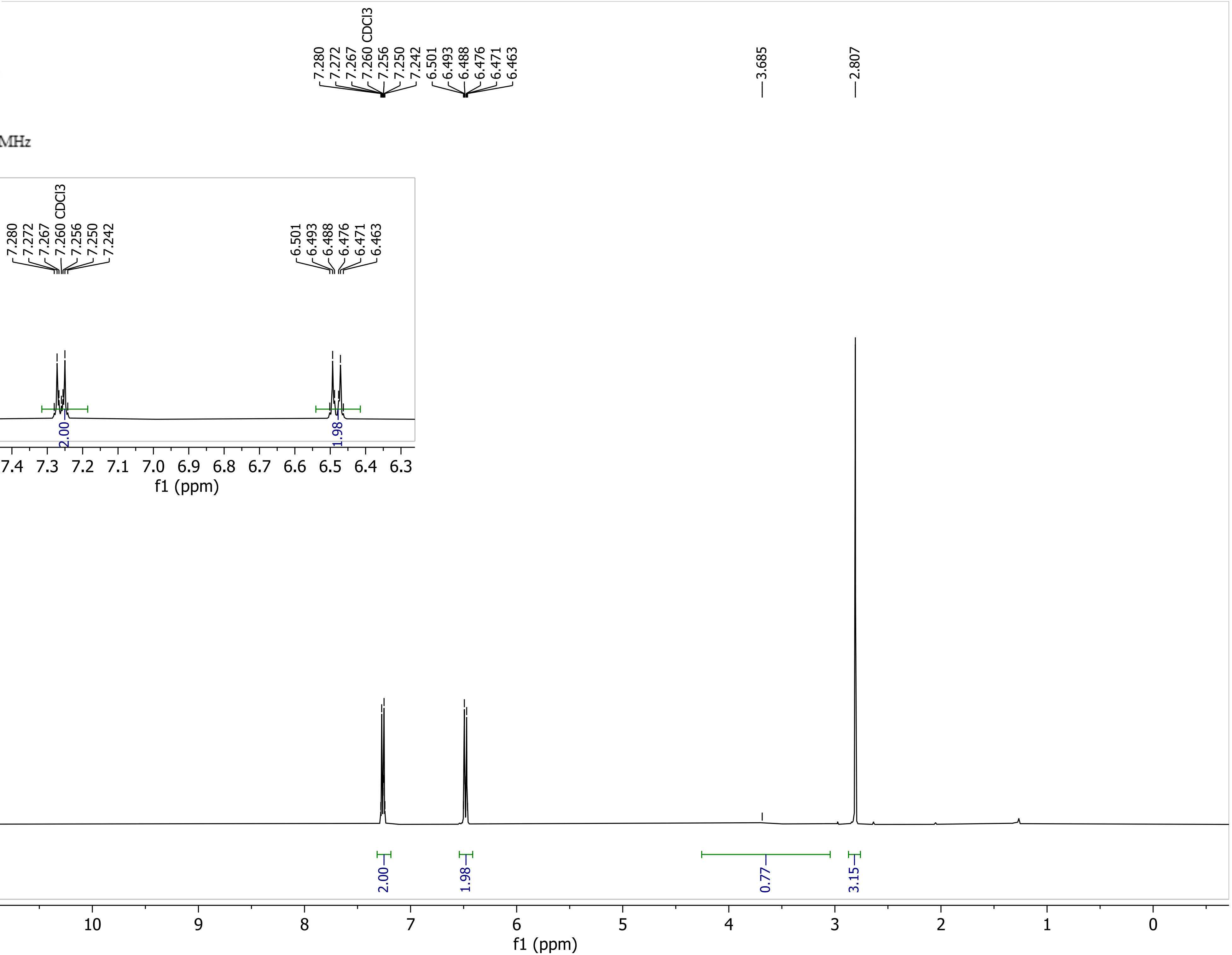
^{13}C, $CDCl_3$, 101 MHz

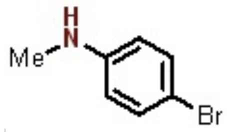




5

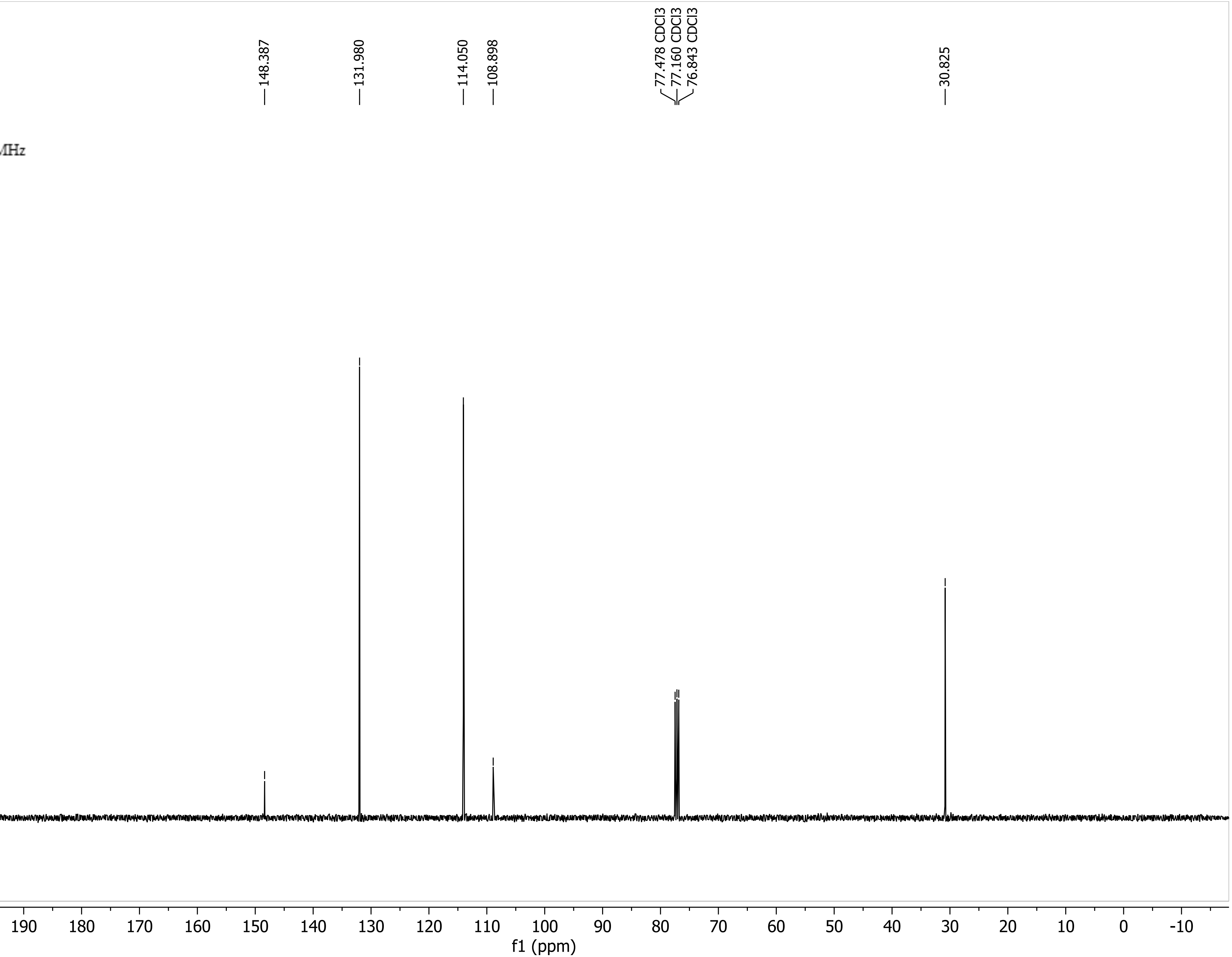
^1H, $CDCl_3$, 400 MHz

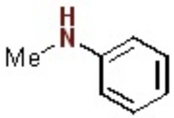




5

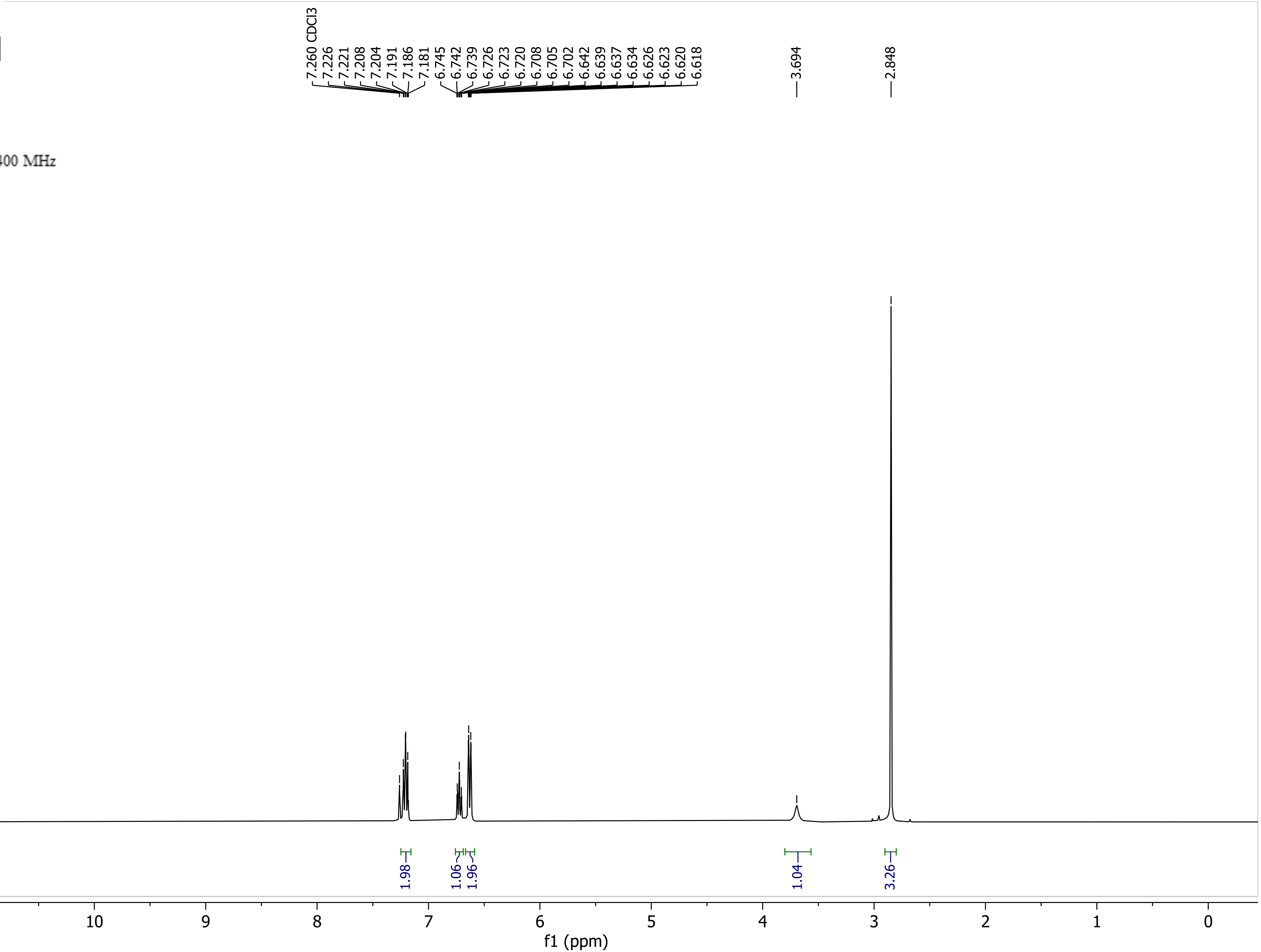
^{13}C, $CDCl_3$, 101 MHz

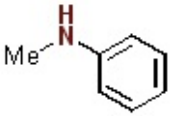




6

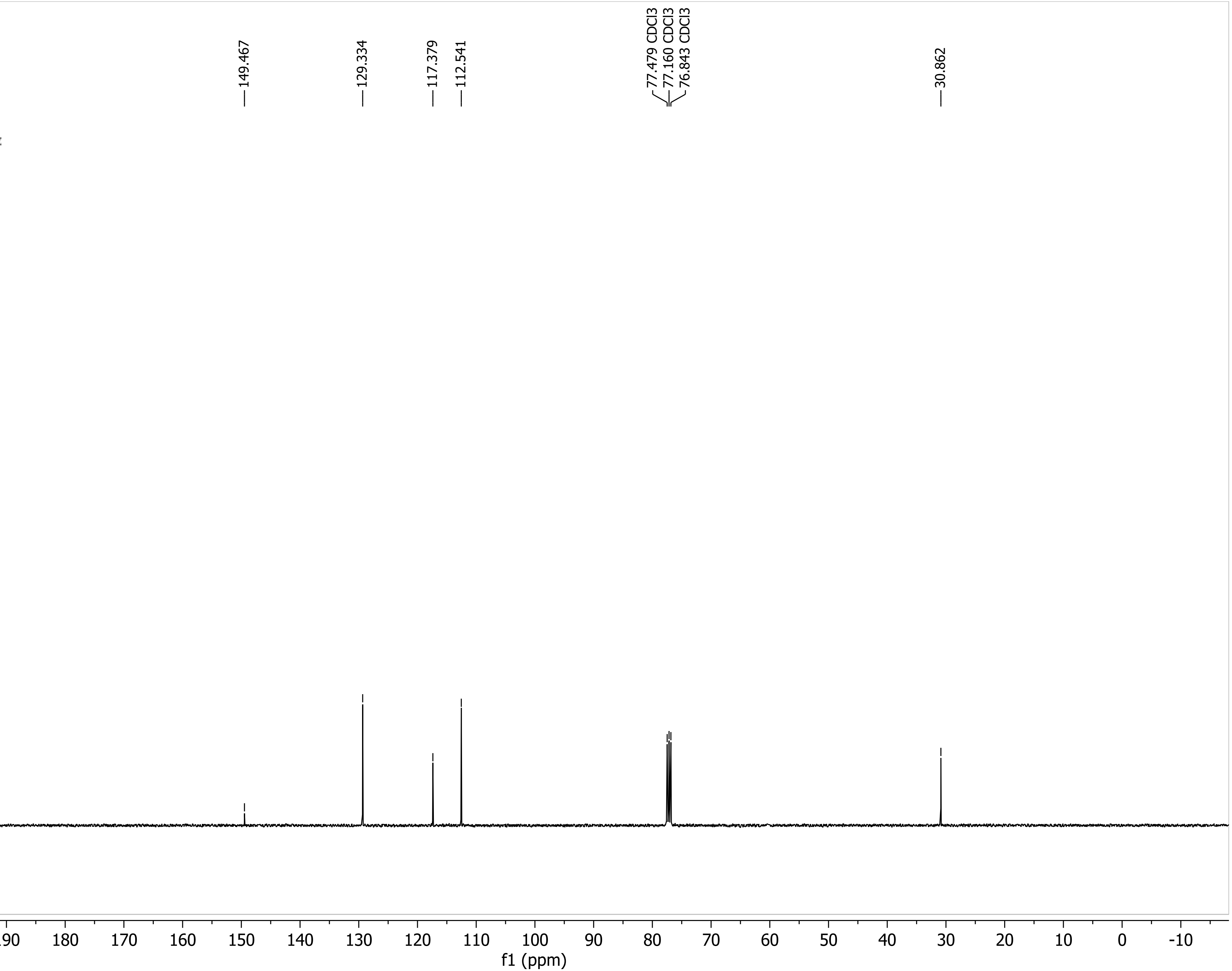
^{1}H, $CDCl_3$, 400 MHz

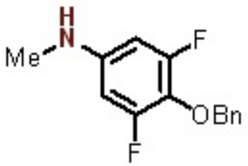




6

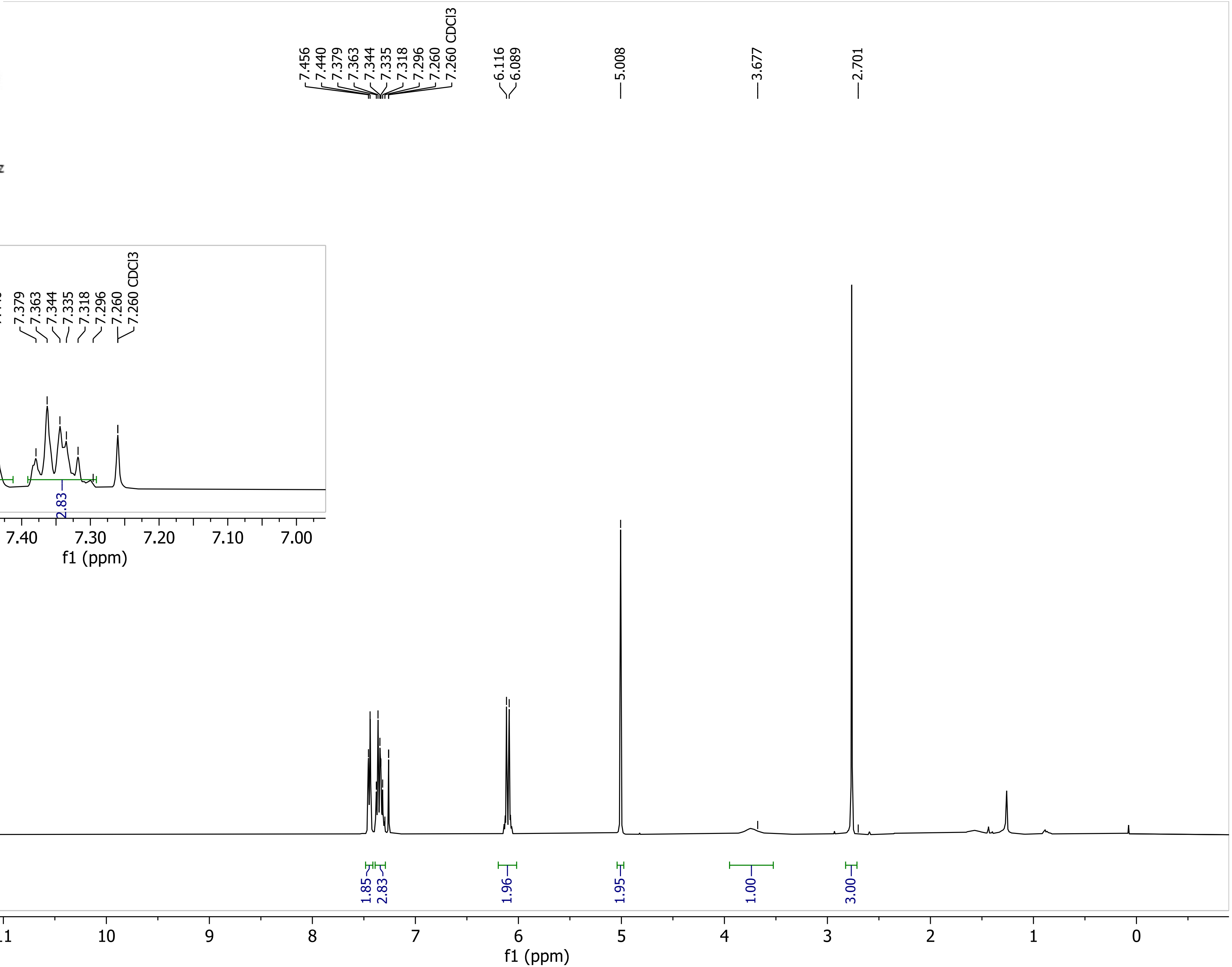
^{13}C, $CDCl_3$, 101 MHz

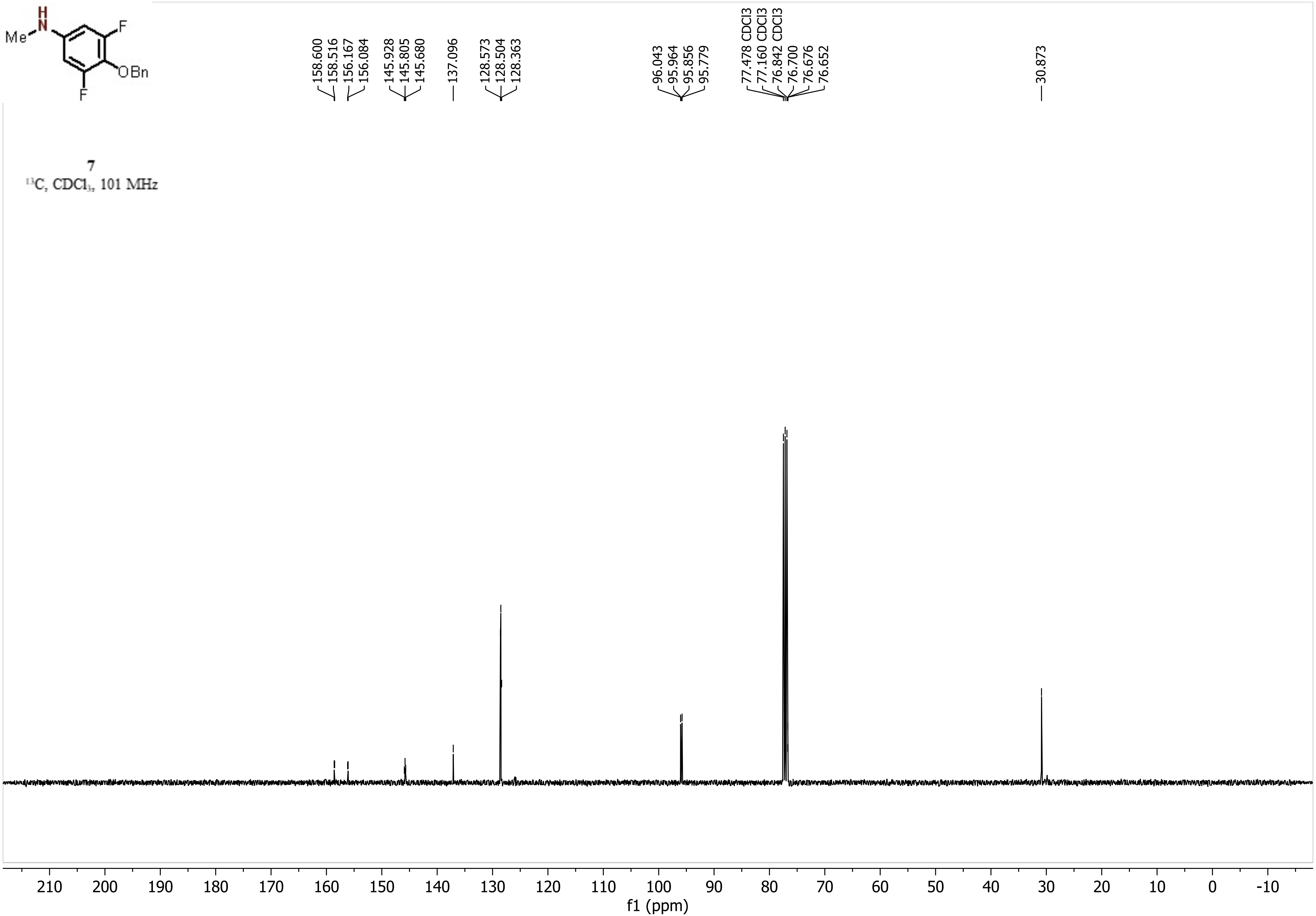




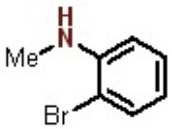
7

^{1}H, CDCl$_3$, 400 MHz



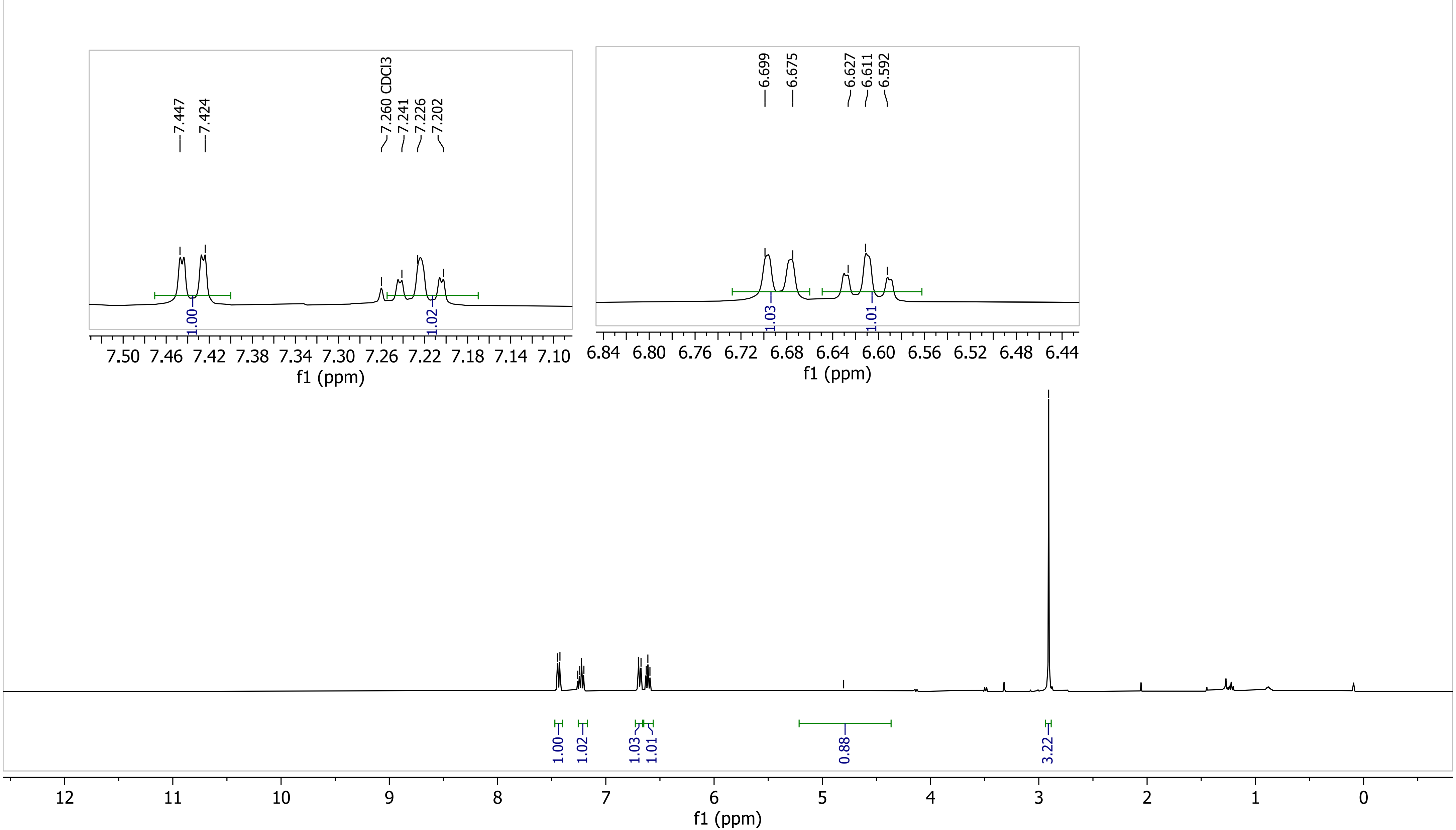


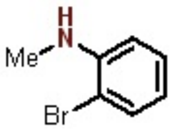
Me
N
H
F
OBn
F
7
13C, CDCl3, 101 MHz
158.600
158.516
156.167
156.084
145.928
145.805
145.680
137.096
128.573
128.504
128.363
96.043
95.964
95.856
95.779
77.478 CDCl3
77.160 CDCl3
76.842 CDCl3
76.700
76.676
76.652
30.873
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



8

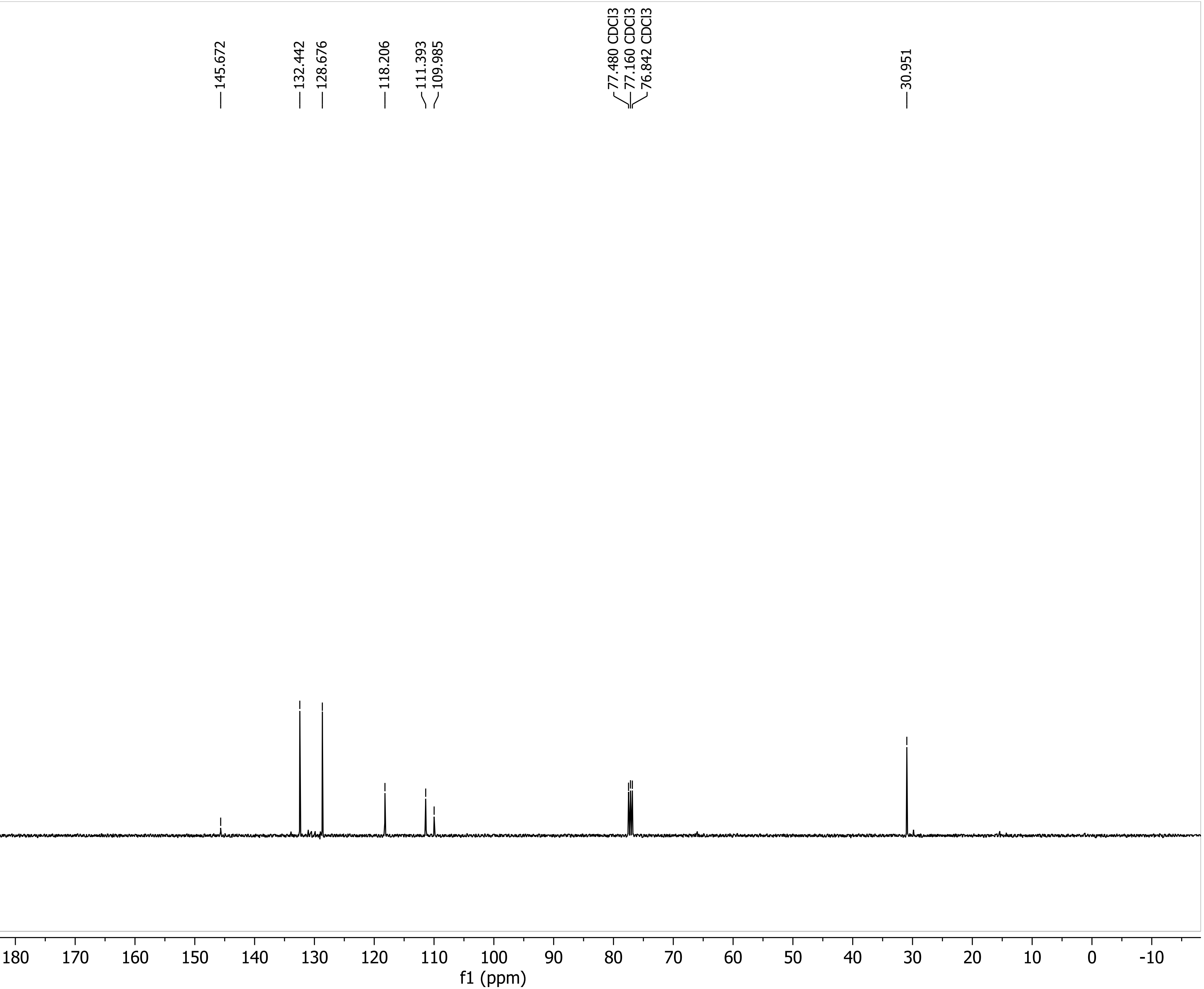
^{1}H, $CDCl_3$, 400 MHz

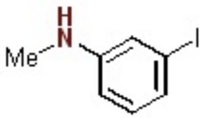




8

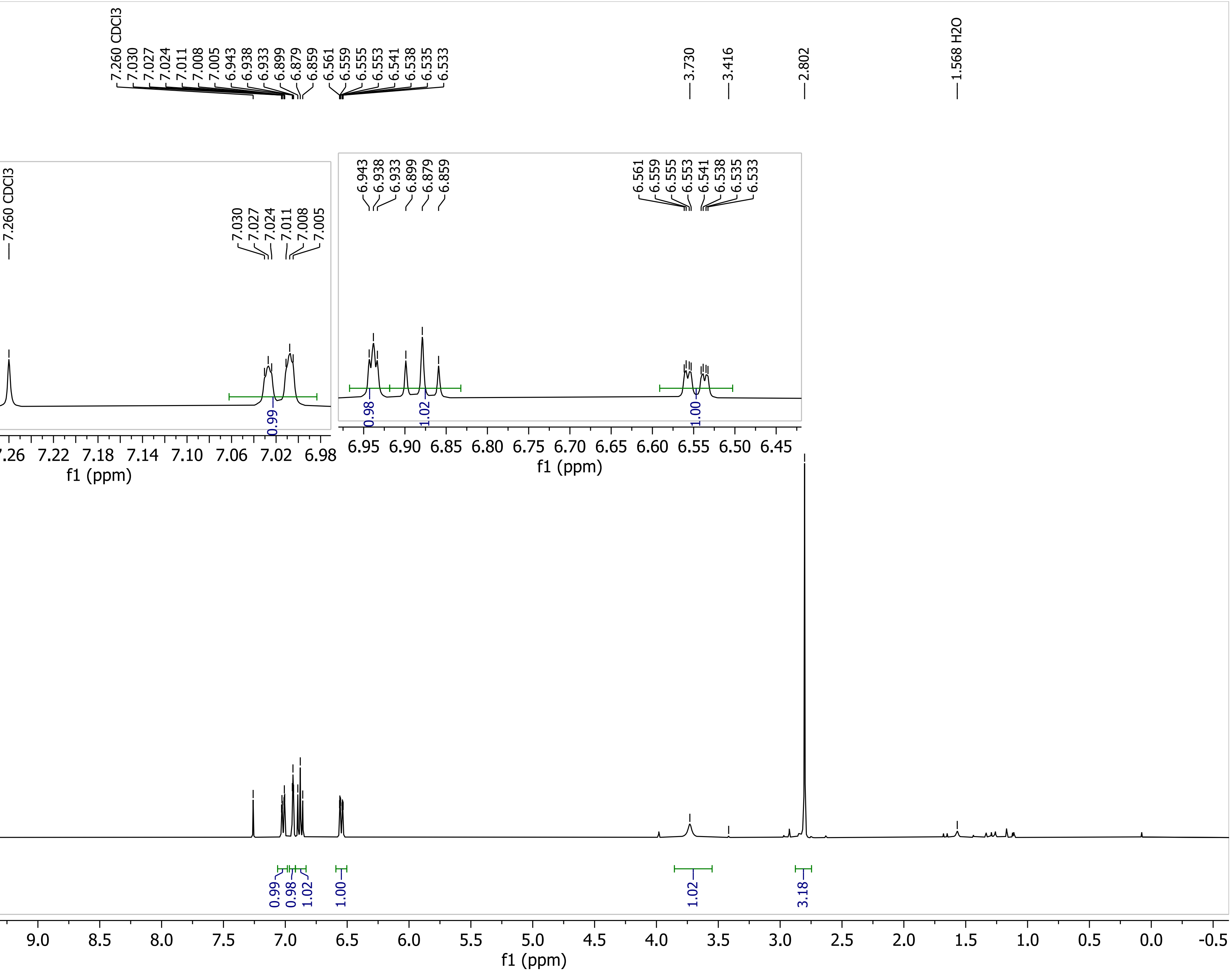
^{13}C, $CDCl_3$, 101 MHz

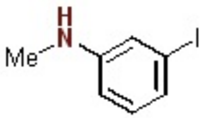




9

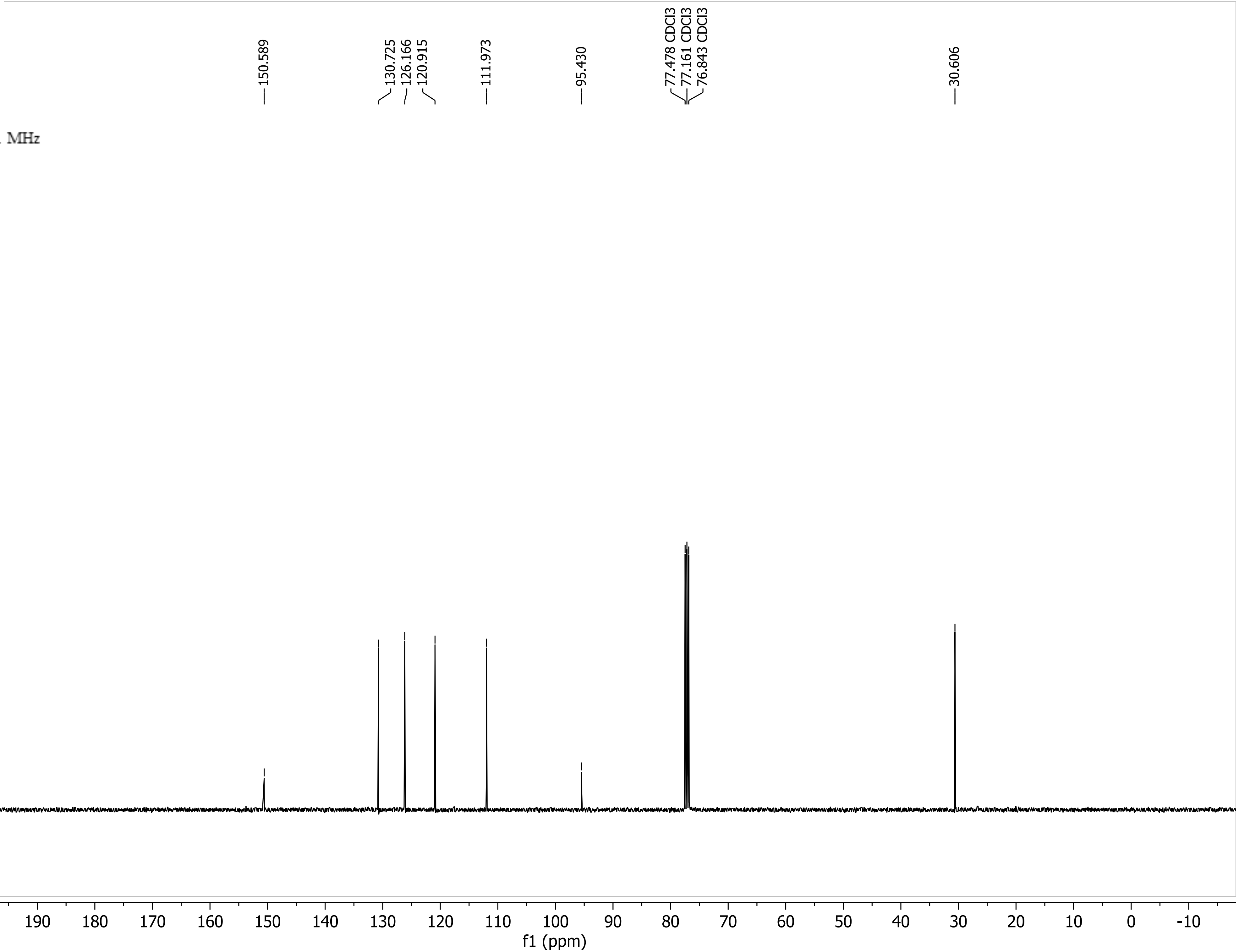
^{1}H, $CDCl_3$, 400 MHz

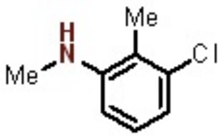




9

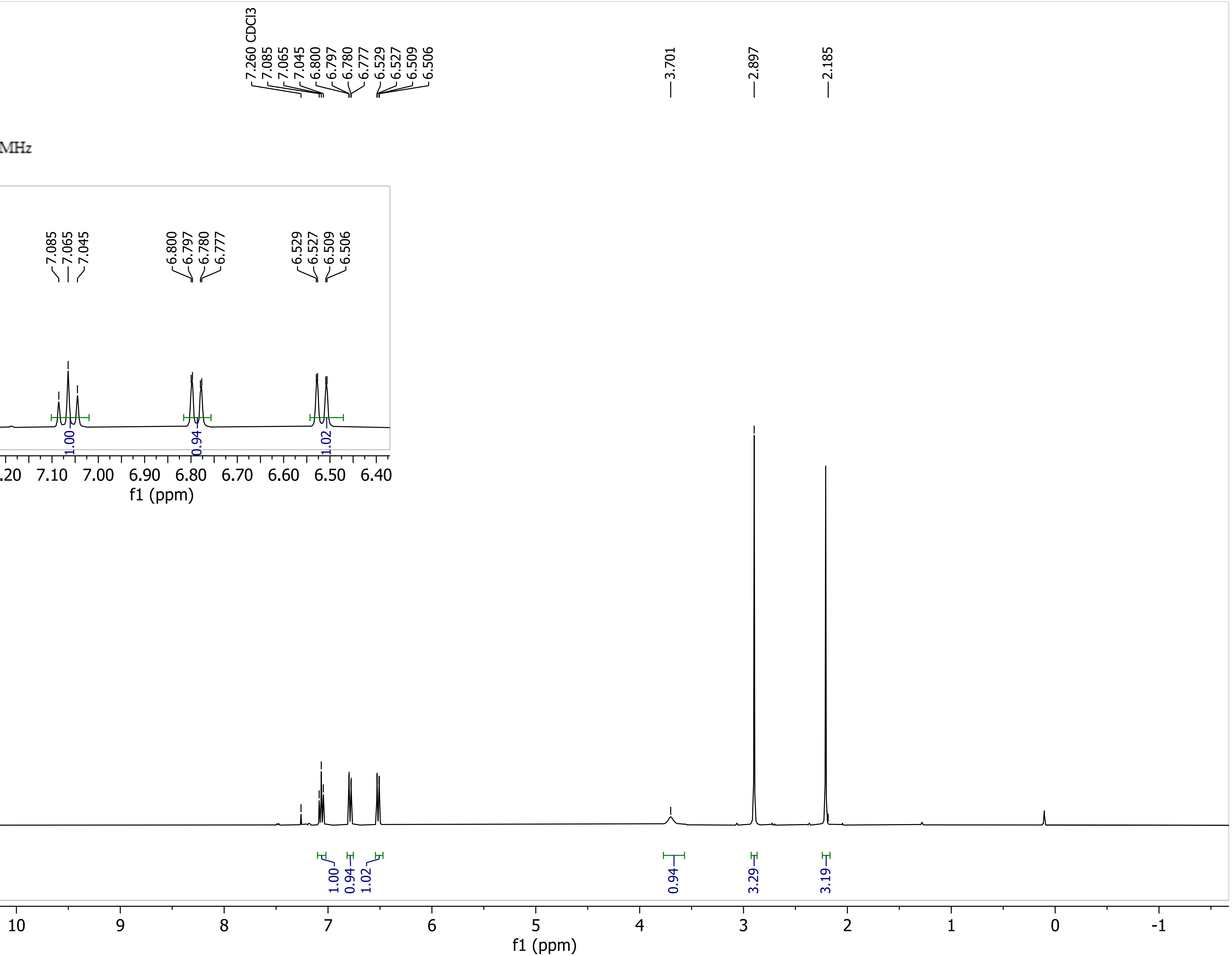
^{13}C, $CDCl_3$, 101 MHz

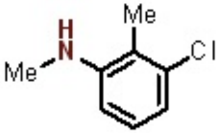




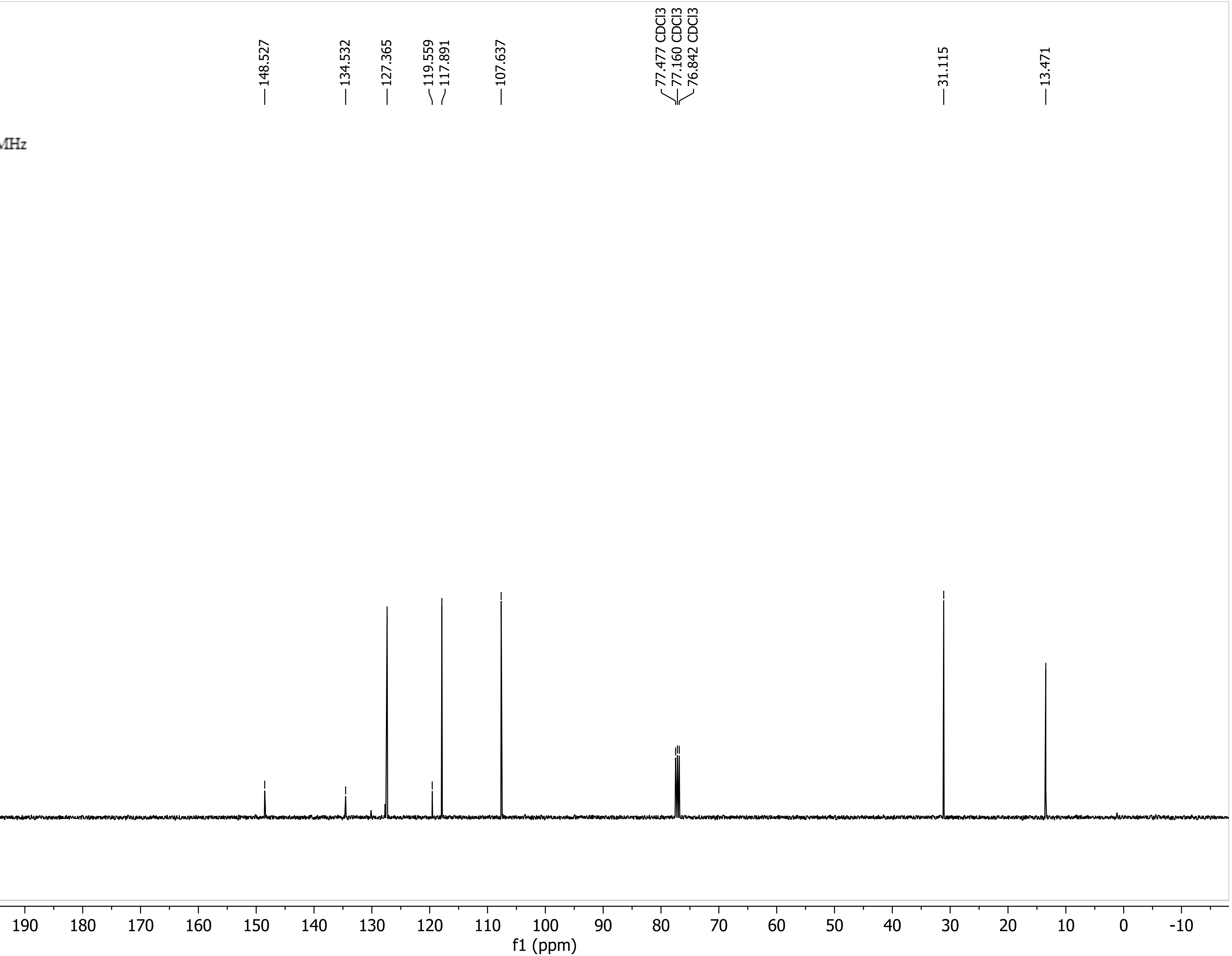
10

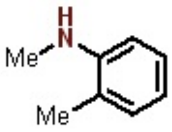
^1H, $CDCl_3$, 400 MHz





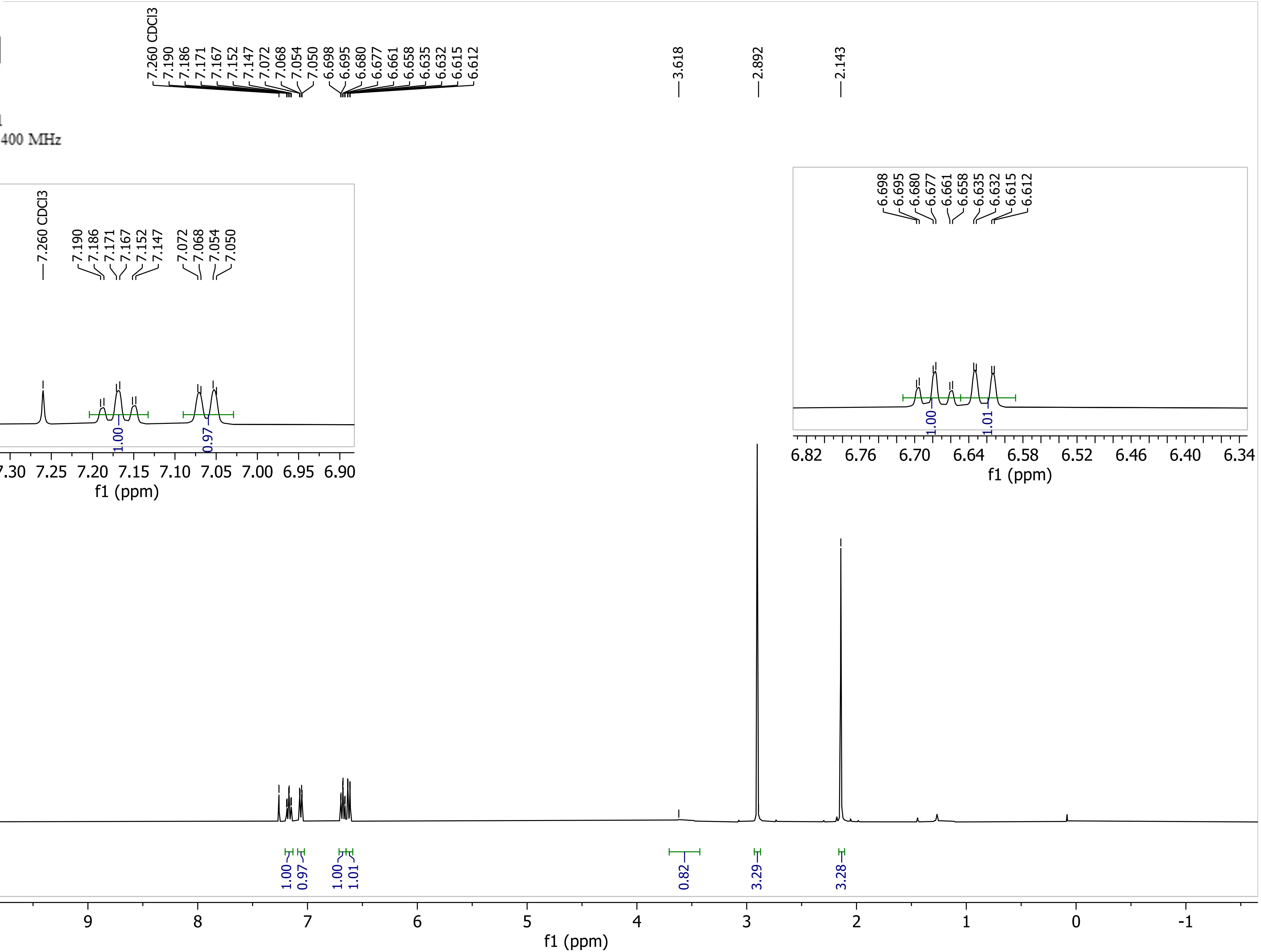
10
^{13}C, $CDCl_3$, 101 MHz

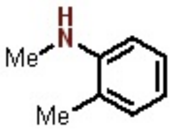




11

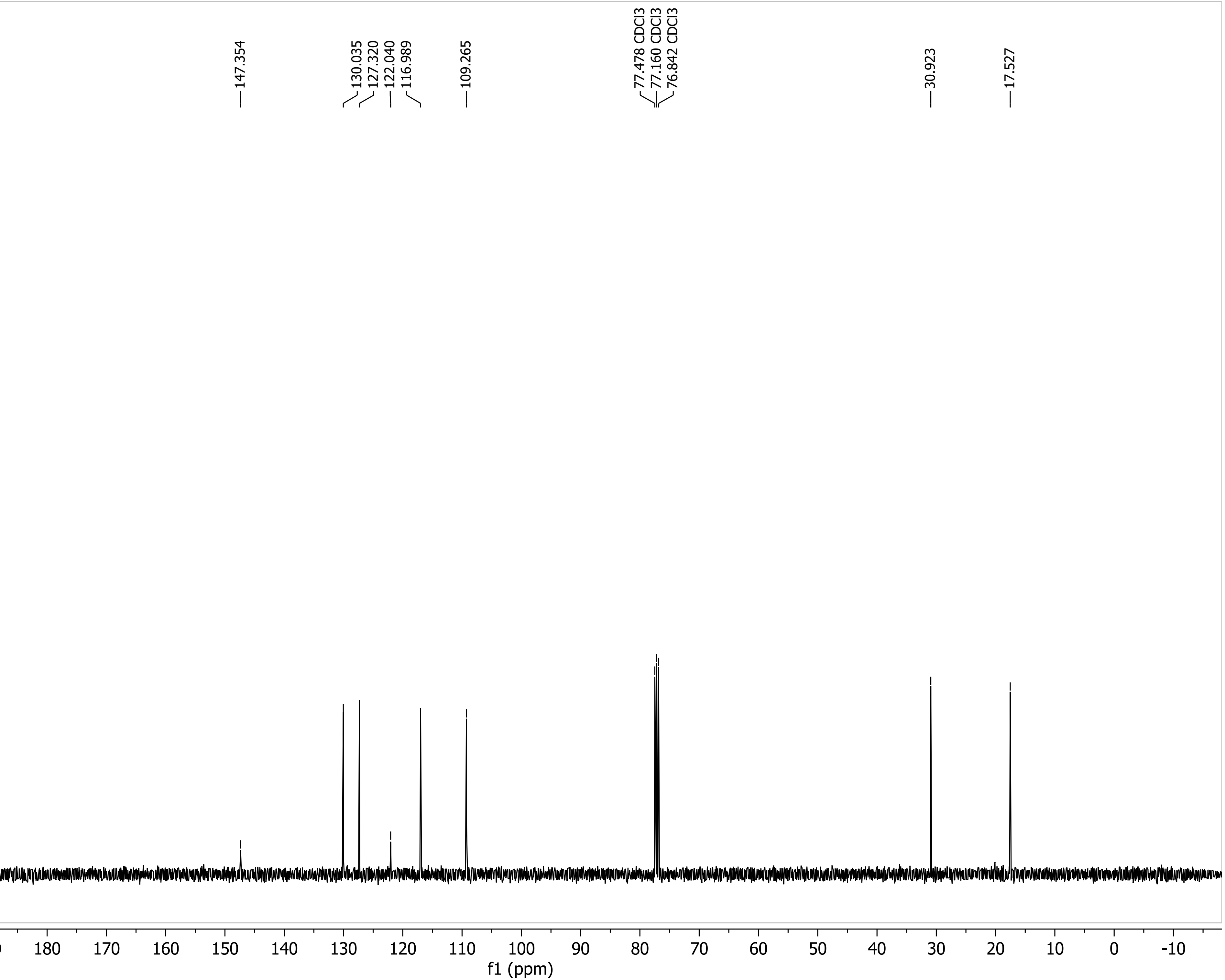
^1H, $CDCl_3$, 400 MHz

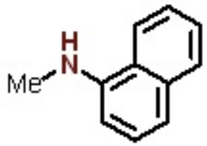




11

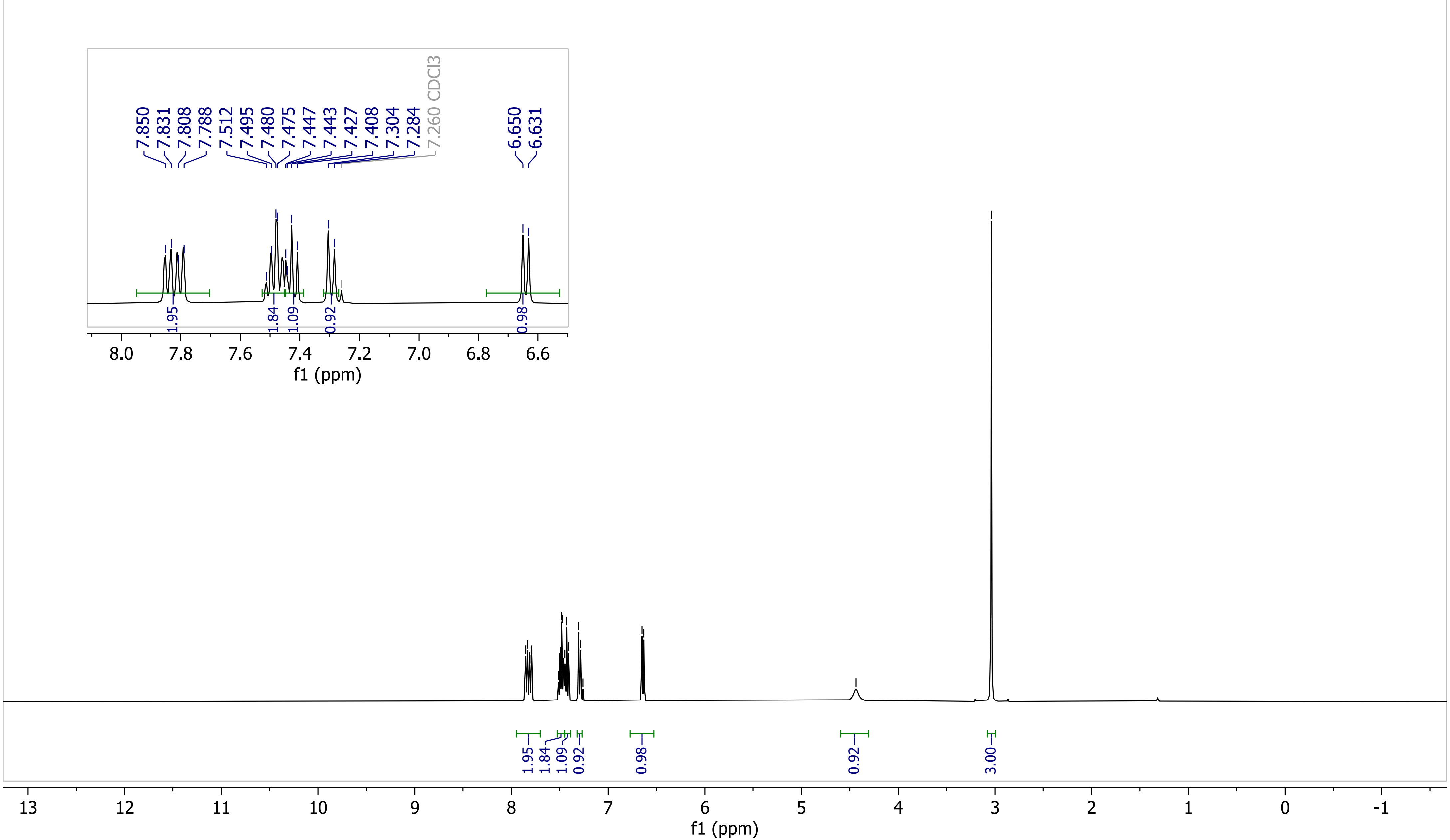
^{13}C, $CDCl_3$, 101 MHz

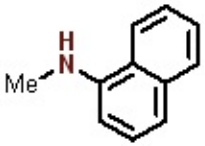




12

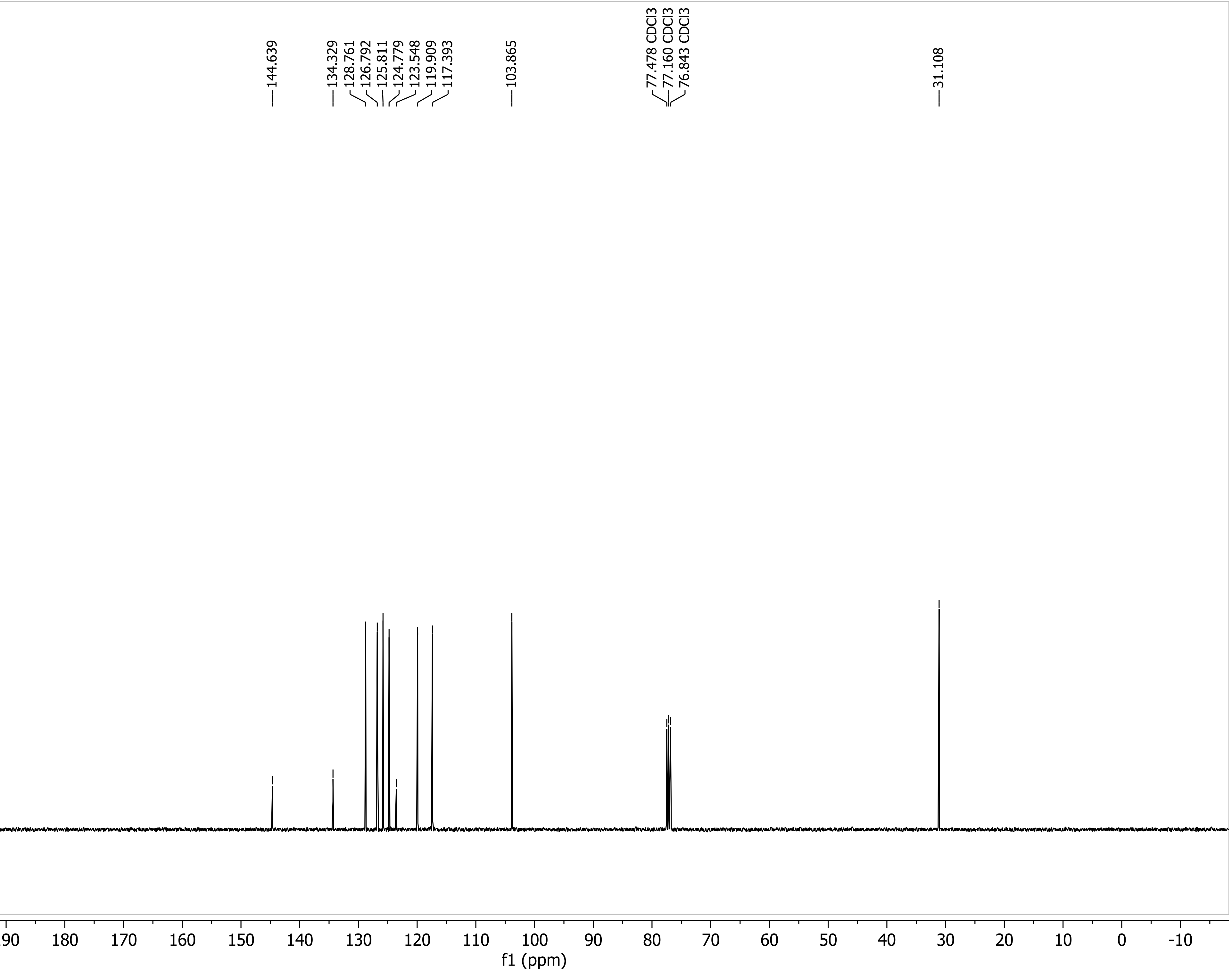
^{1}H, $CDCl_3$, 400 MHz

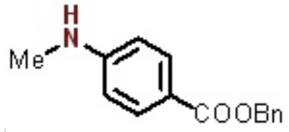




12

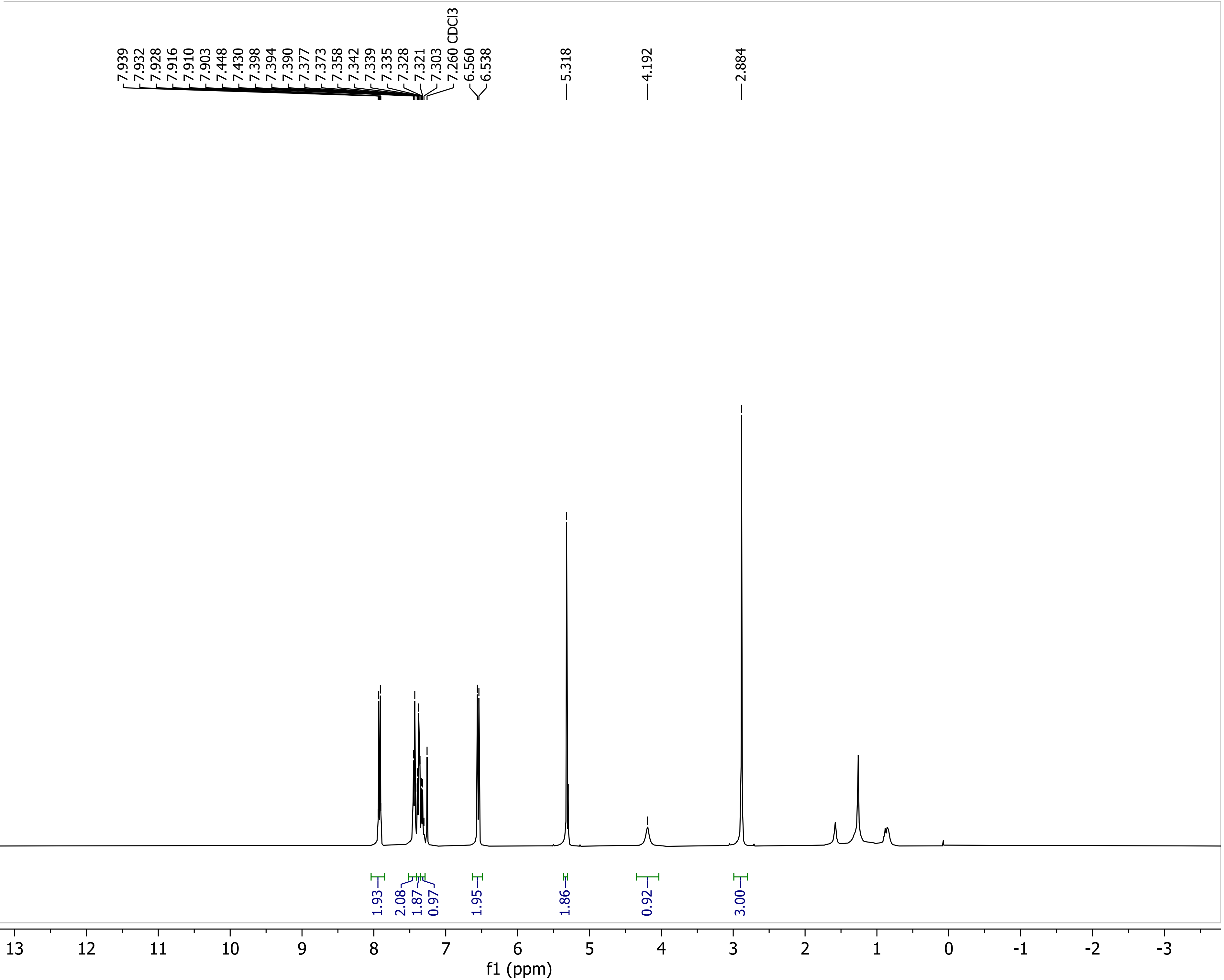
^{13}C, $CDCl_3$, 101 MHz

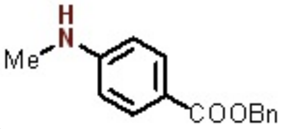




13

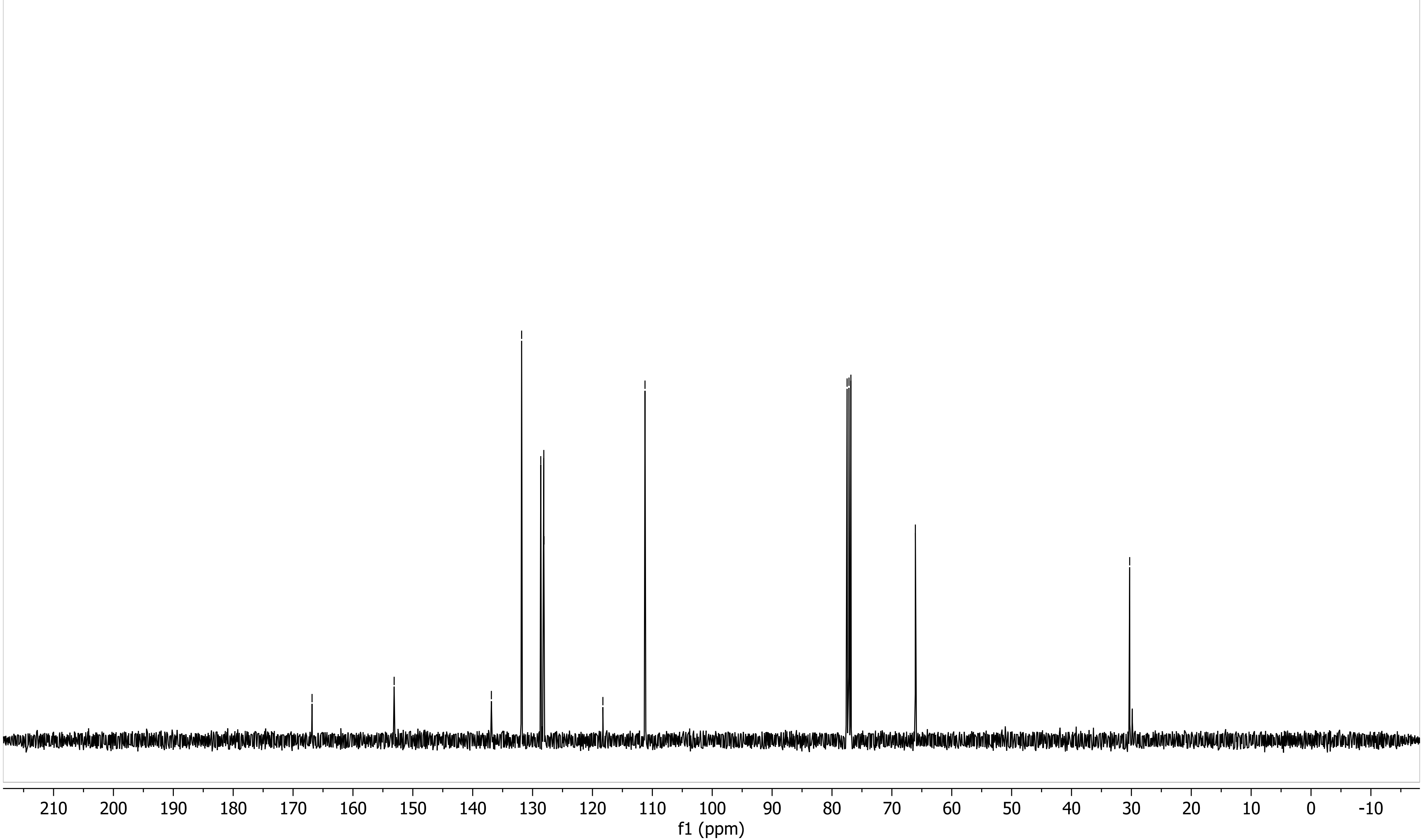
^{1}H, $CDCl_3$, 400 MHz

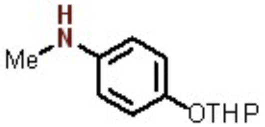




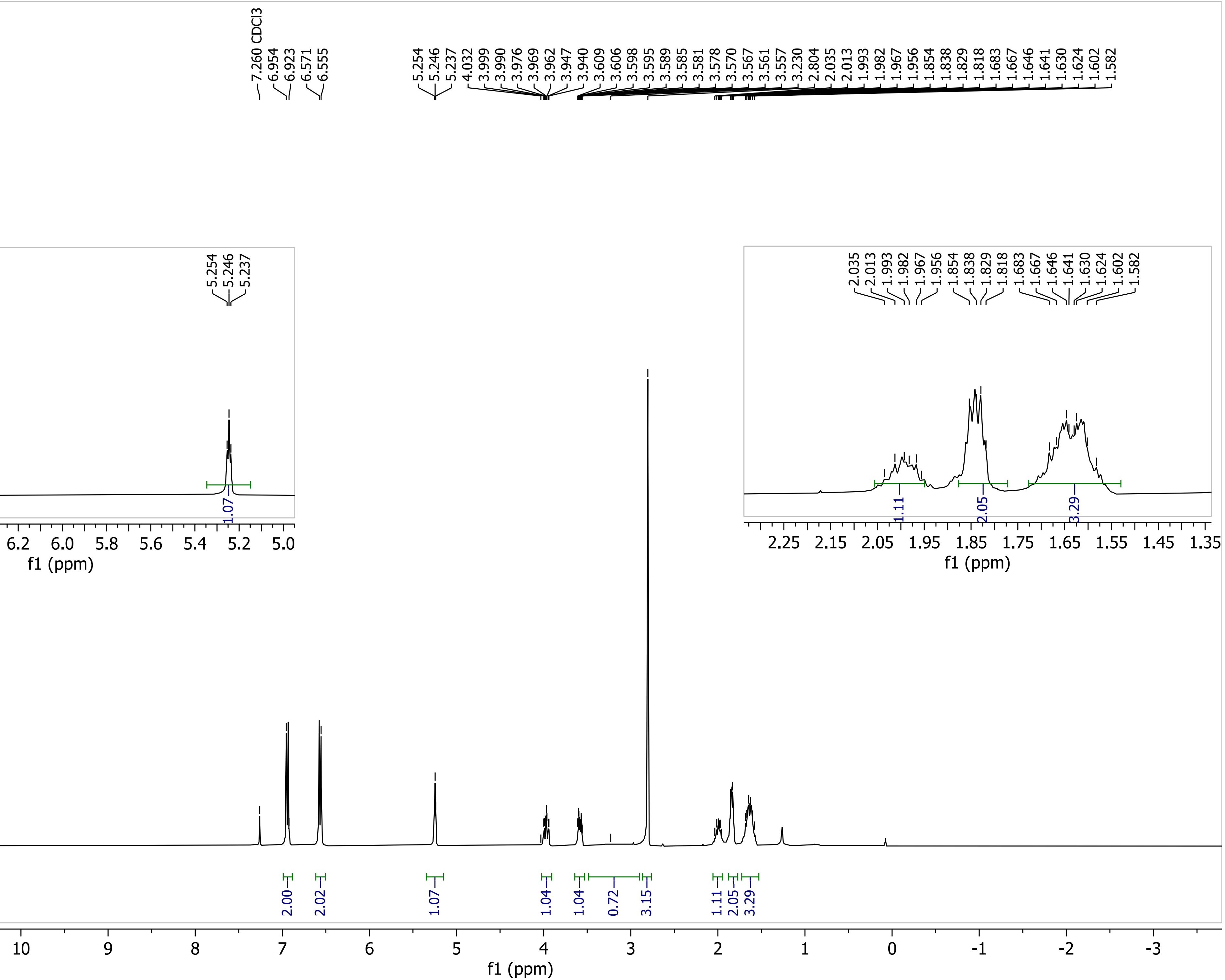
13

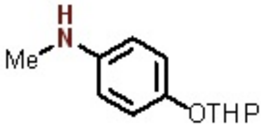
^{13}C, $CDCl_3$, 101 MHz





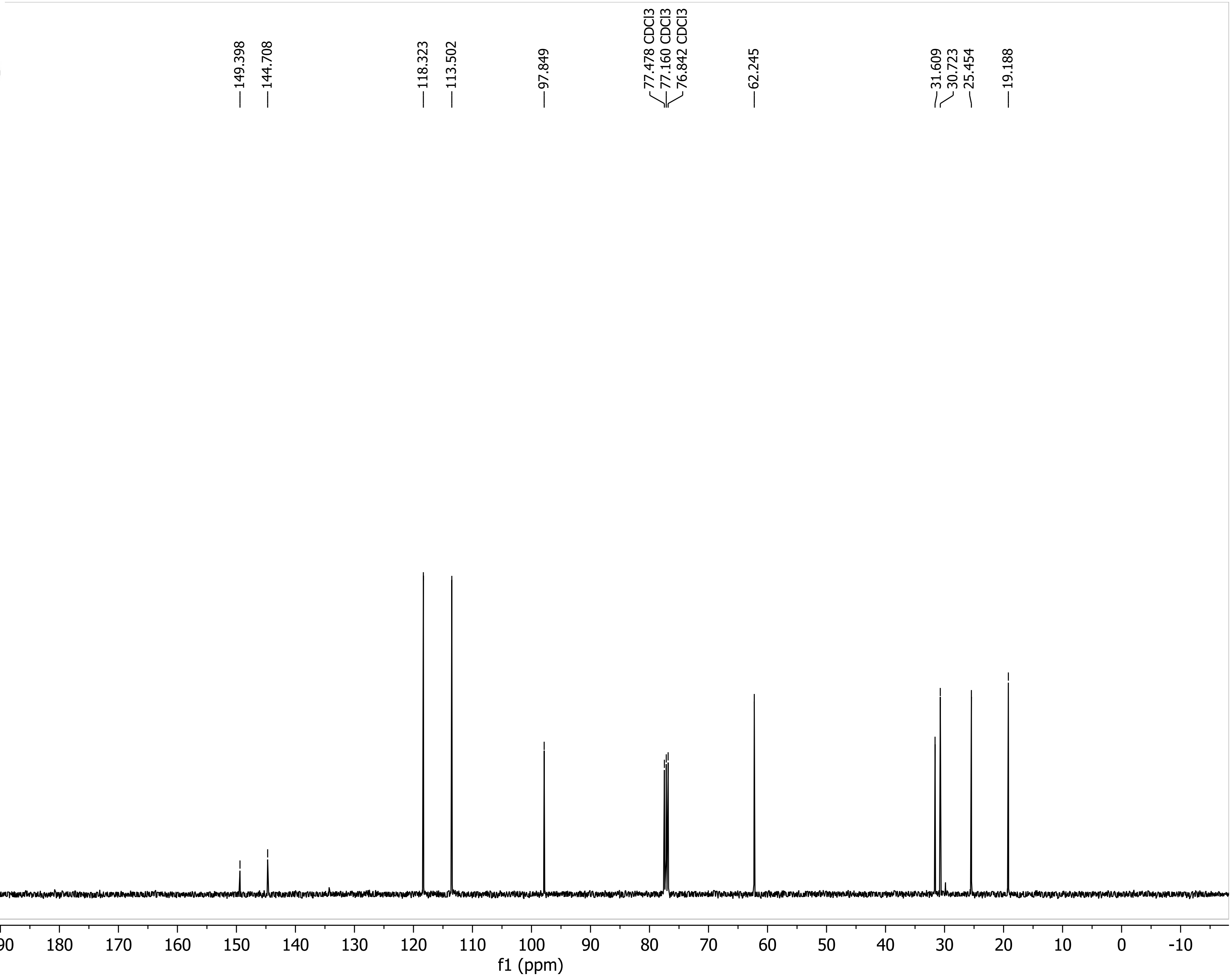
14
^1H, $CDCl_3$, 400 MHz

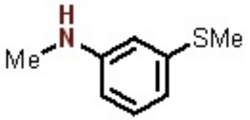




14

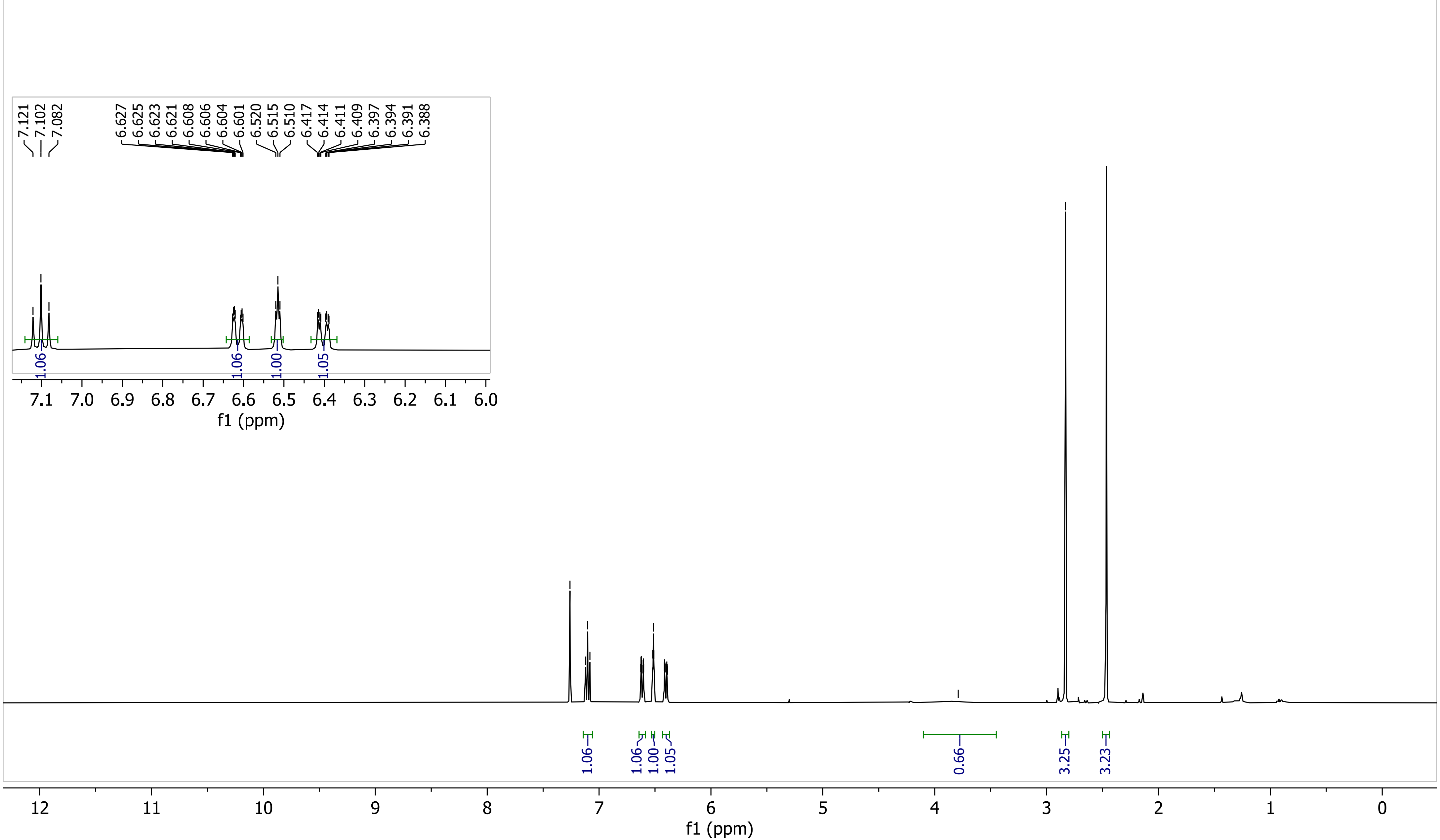
^{13}C, $CDCl_3$, 101 MHz

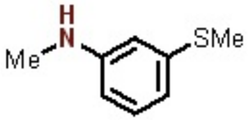




15

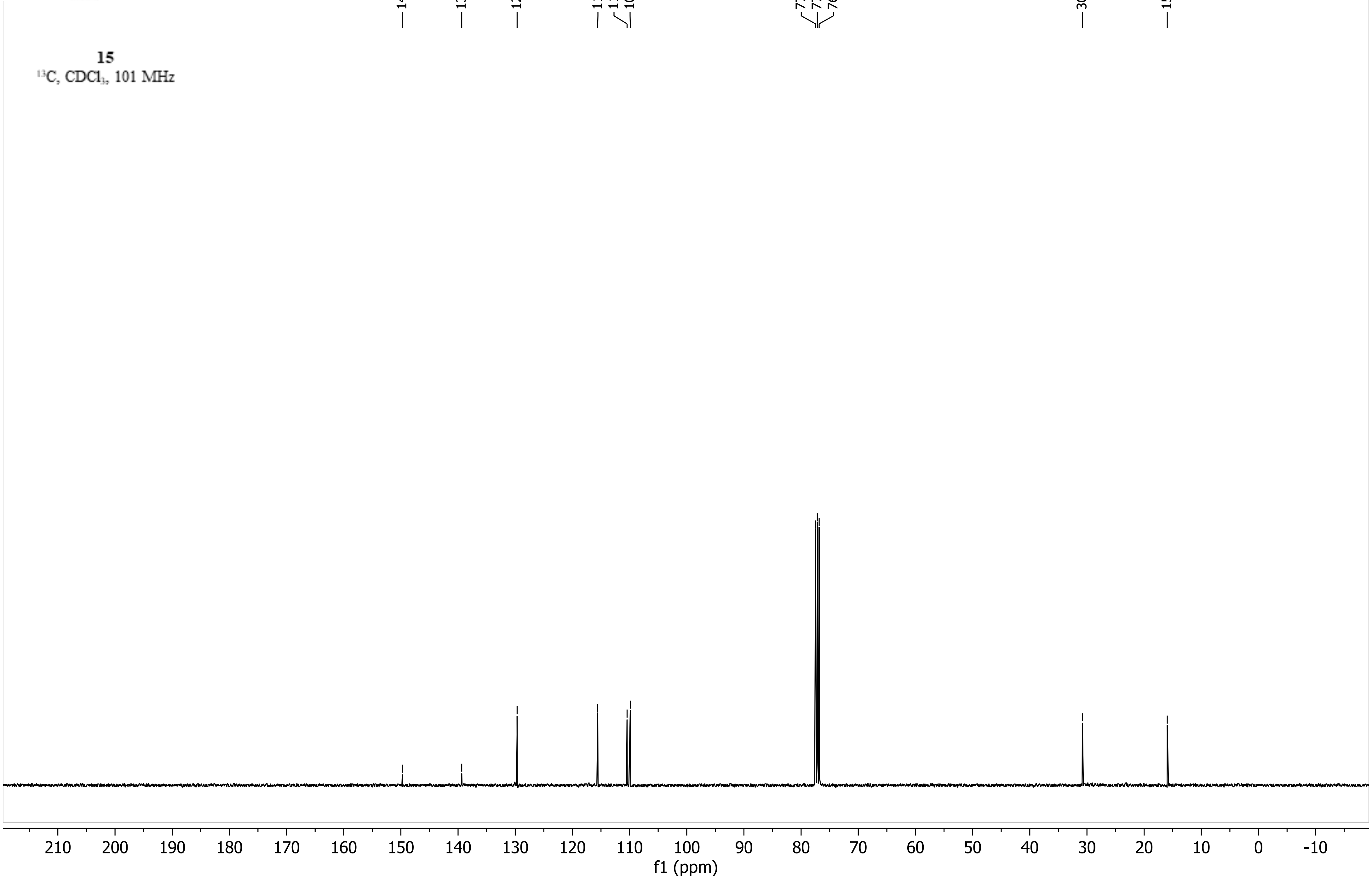
^{1}H, $CDCl_3$, 400 MHz

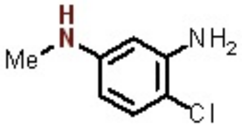




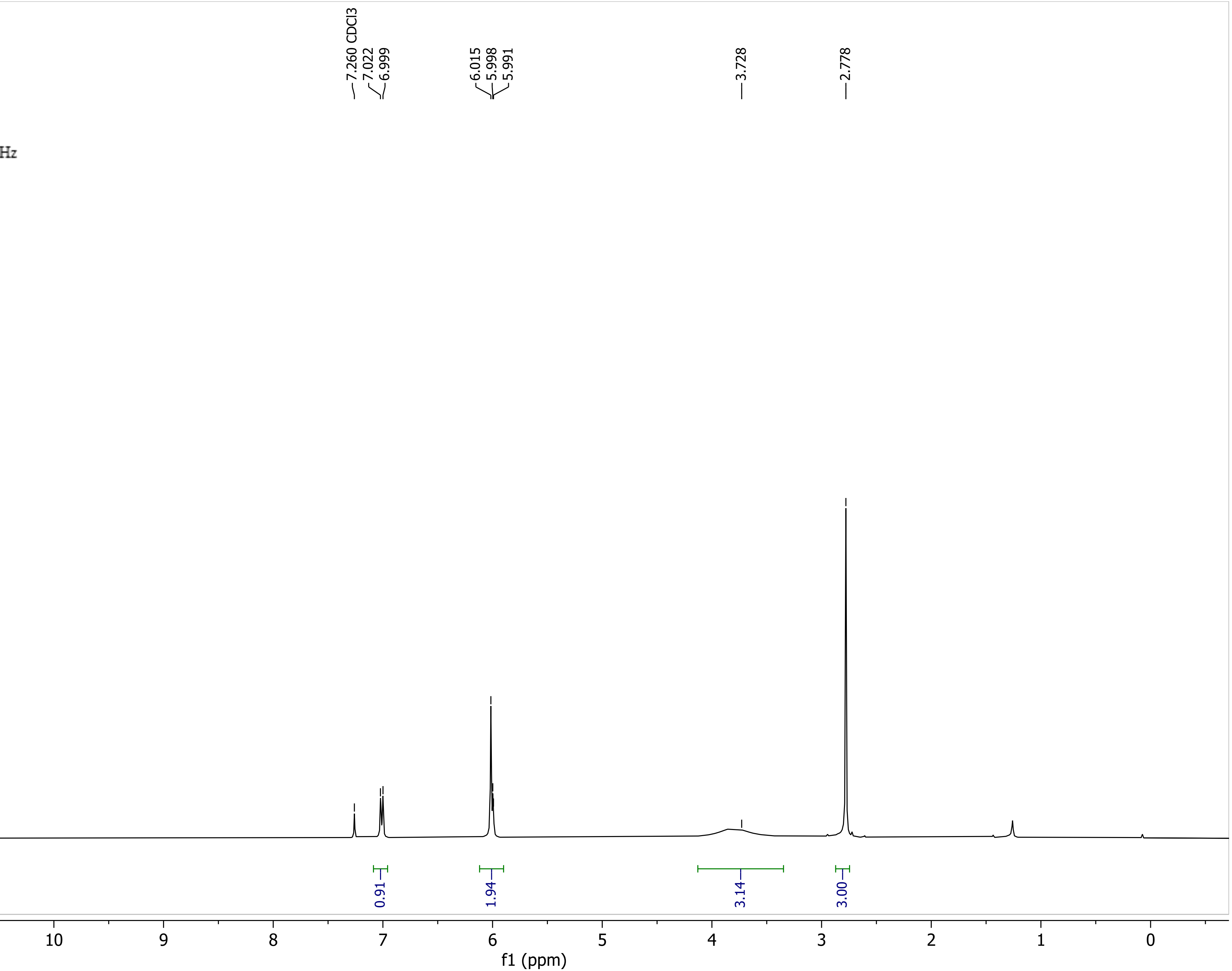
15

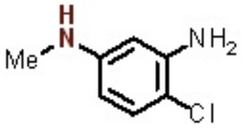
^{13}C, $CDCl_3$, 101 MHz





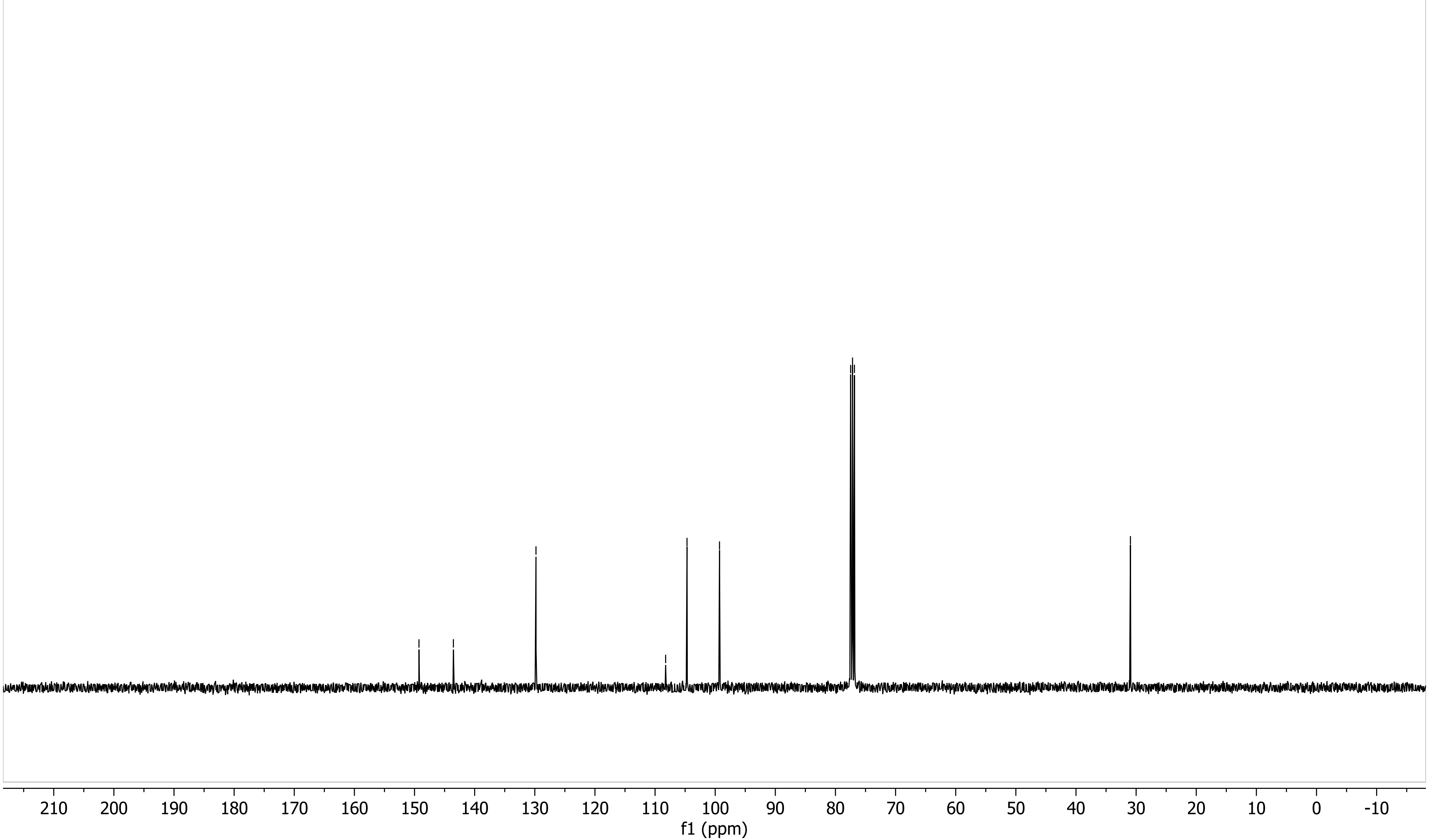
16
^{1}H, $CDCl_3$, 400 MHz

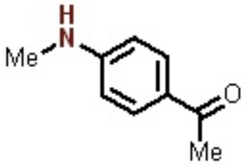




16

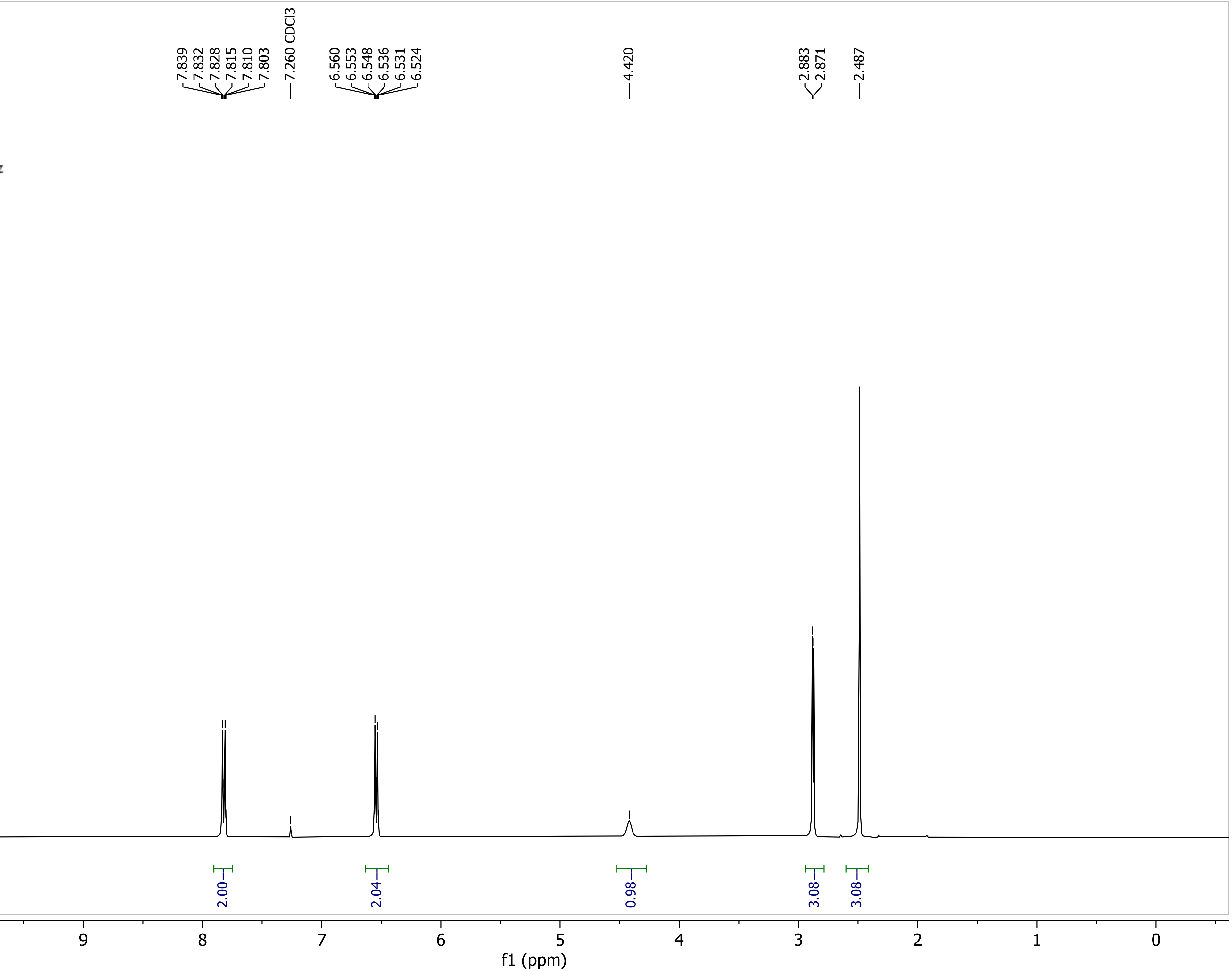
^{13}C, $CDCl_3$, 101 MHz

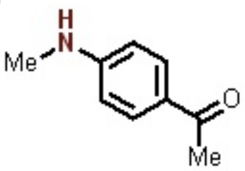




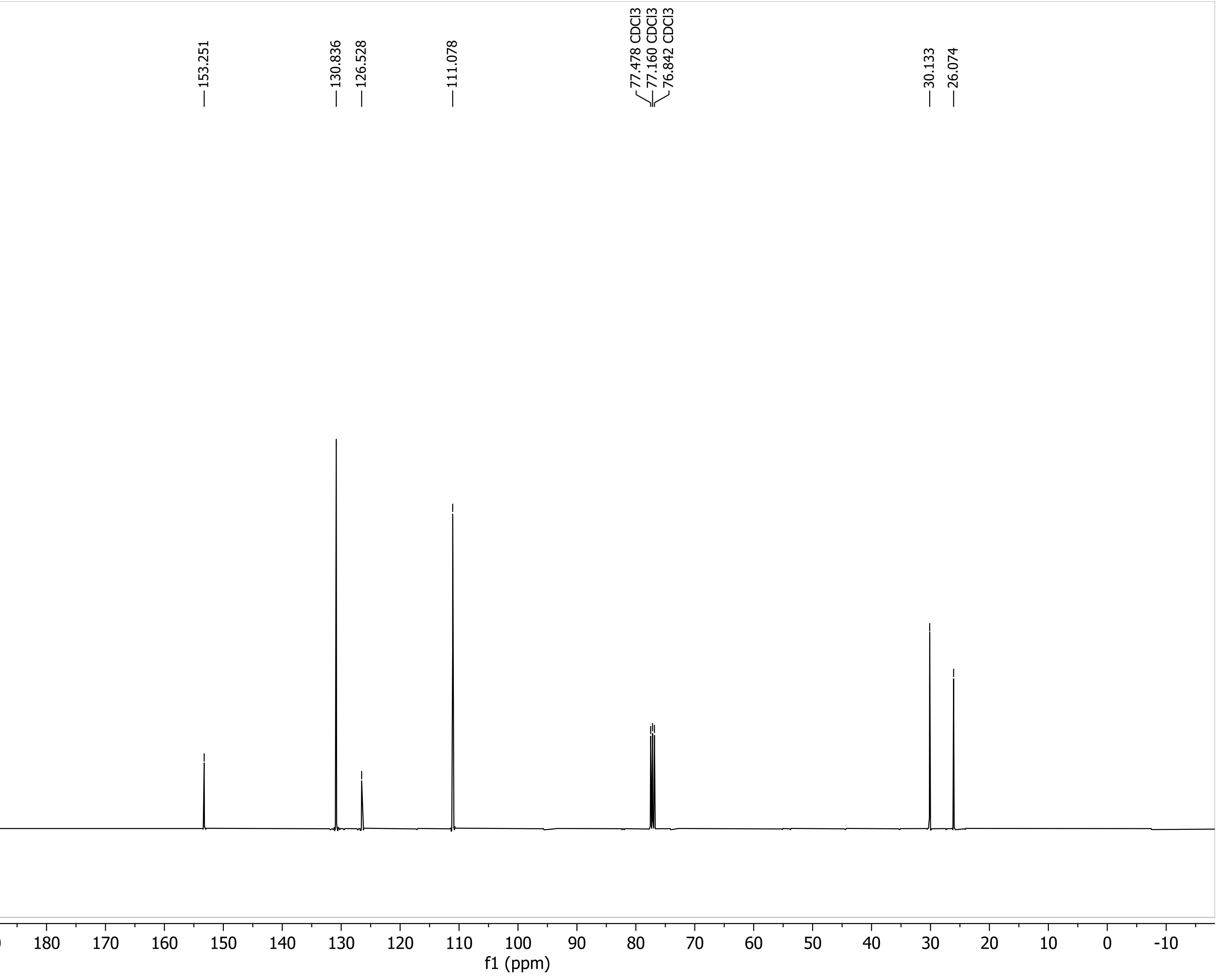
17

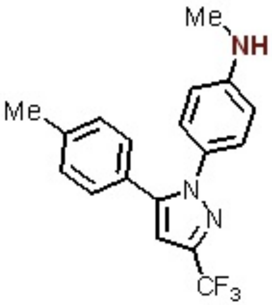
^1H, $CDCl_3$, 400 MHz



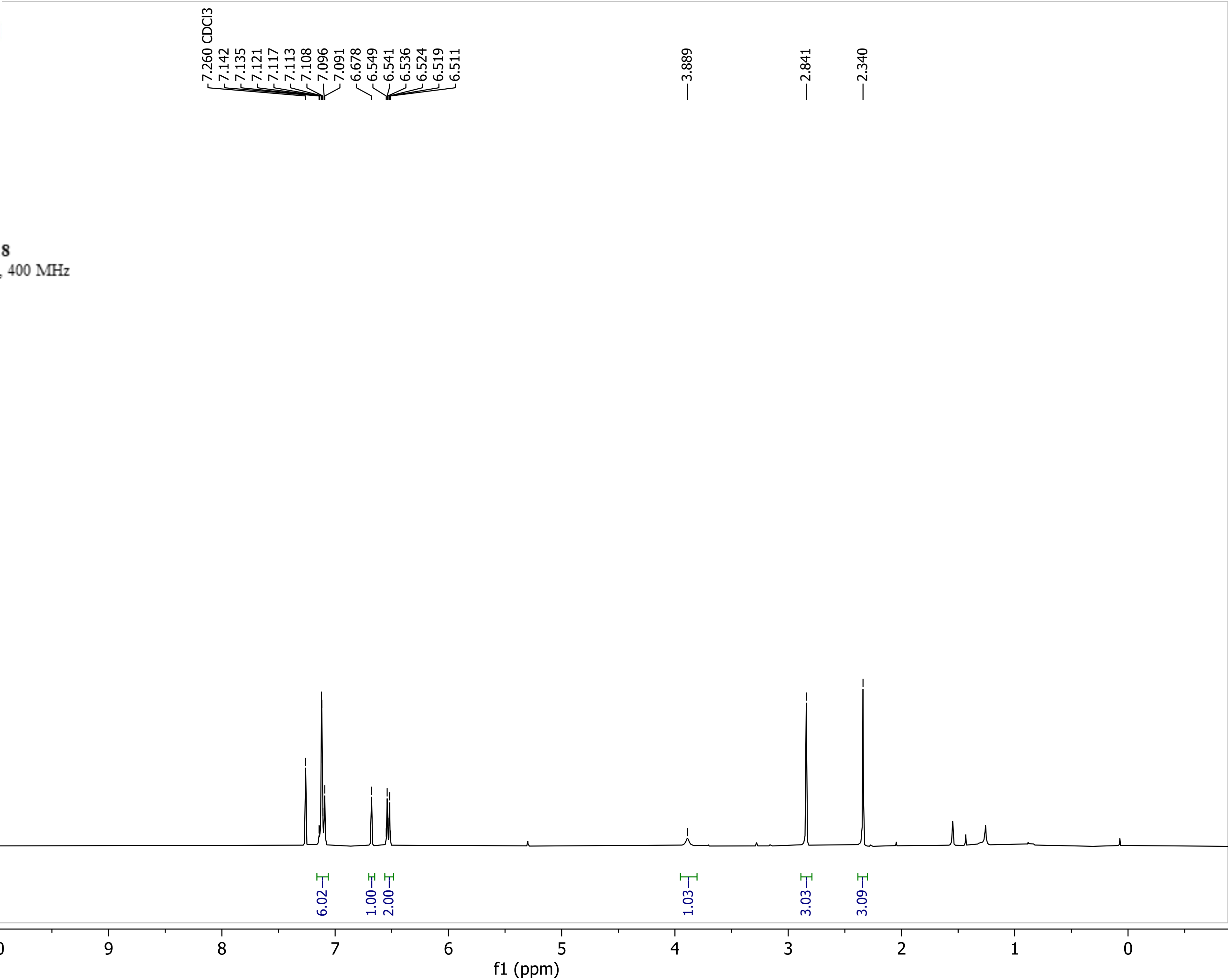


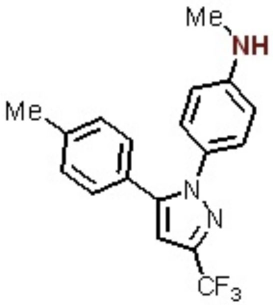
17
^{13}C, $CDCl_3$, 101 MHz



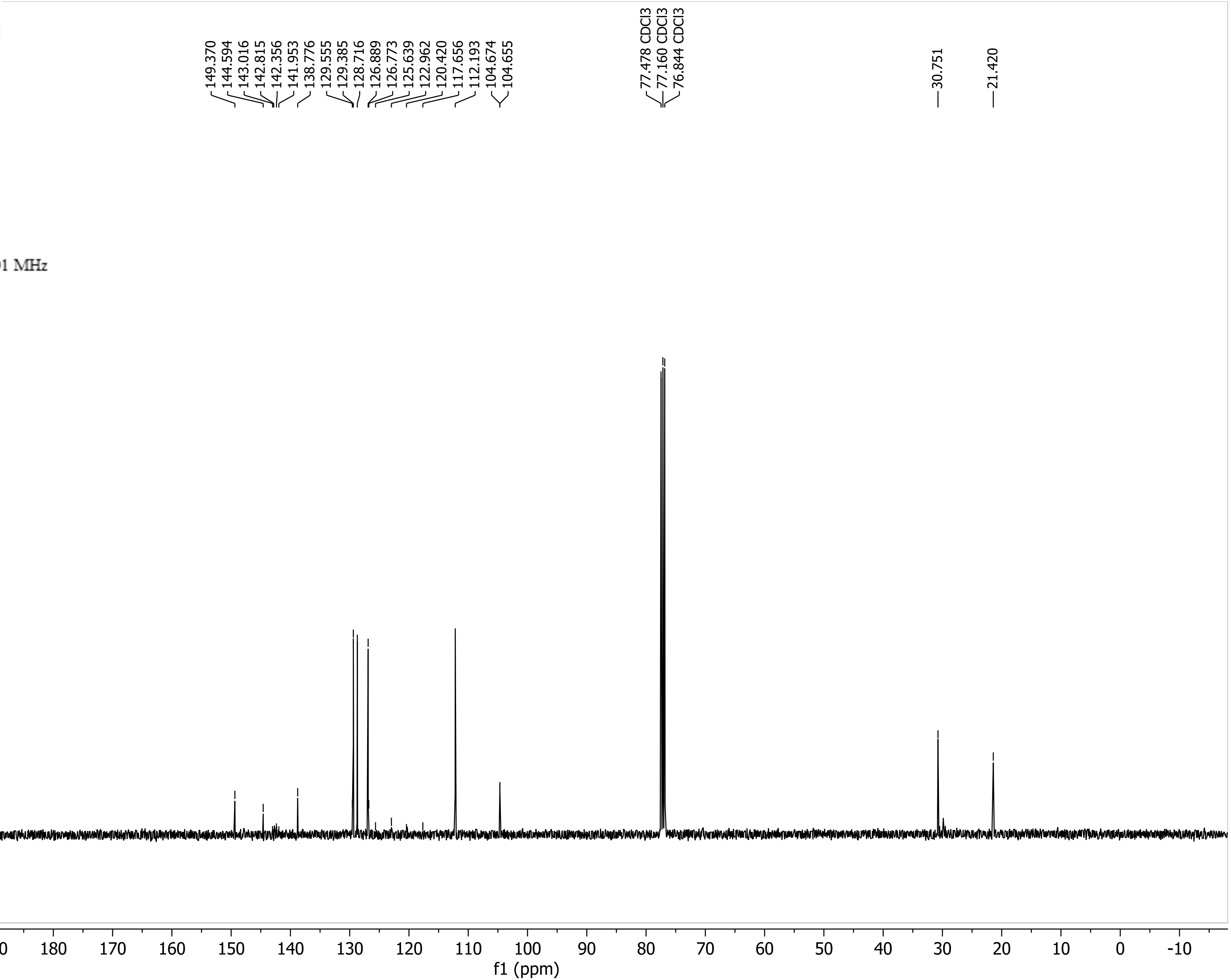


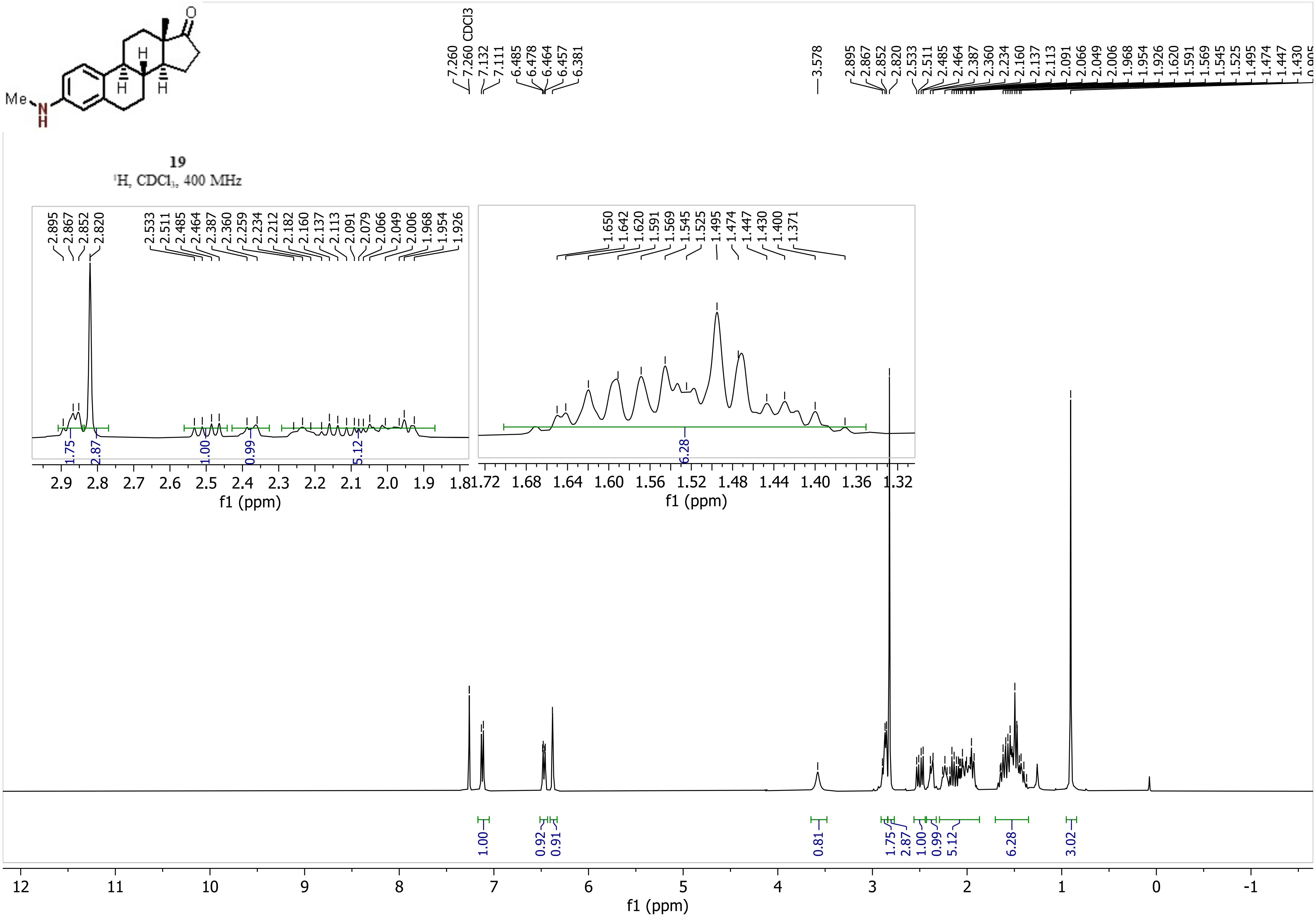
18
^{1}H, CDCl$_3$, 400 MHz





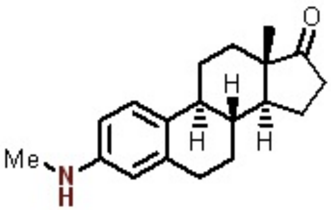
18
^{13}C, $CDCl_3$, 101 MHz



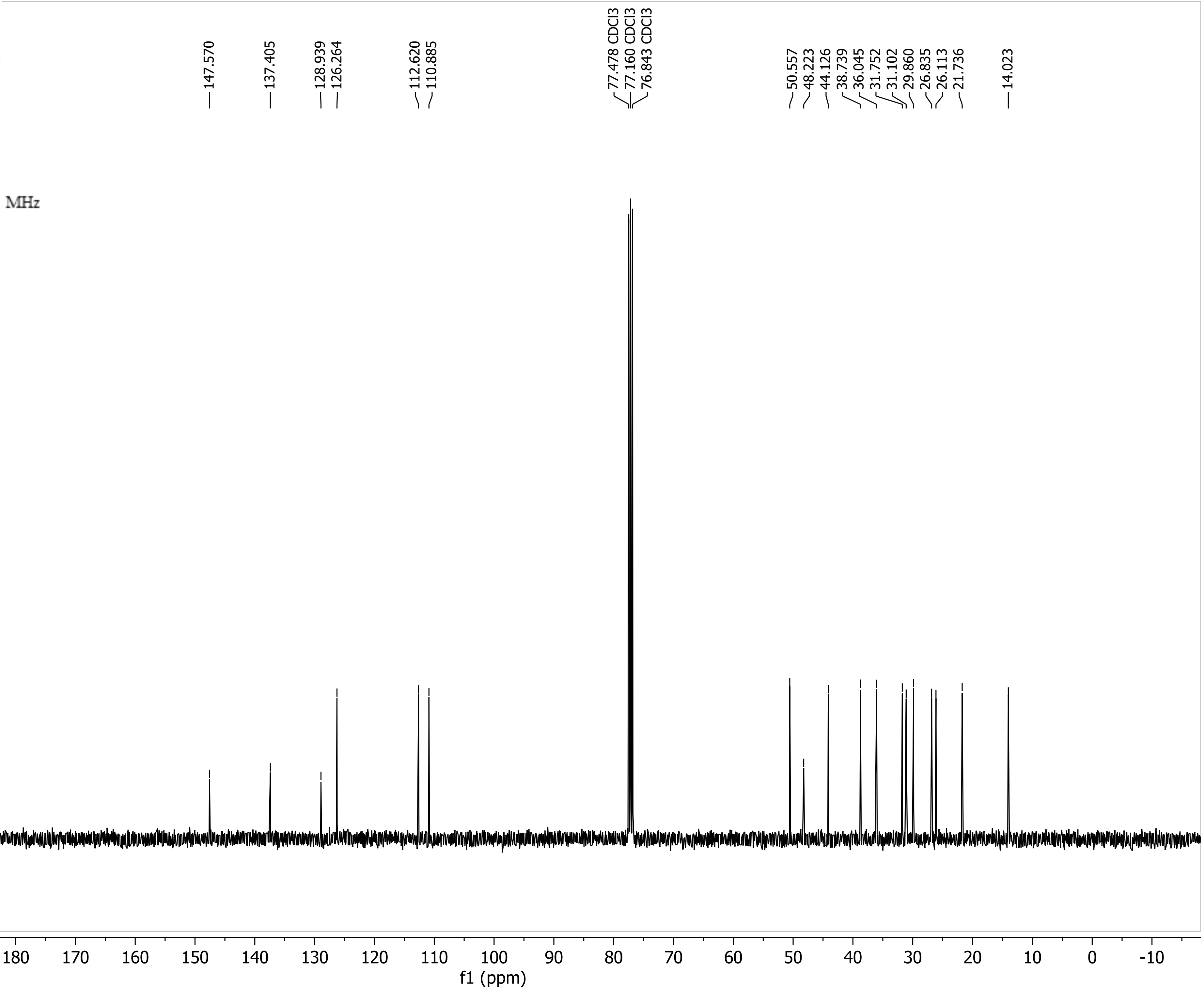


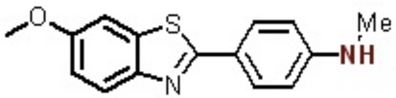
19

^1H, $CDCl_3$, 400 MHz

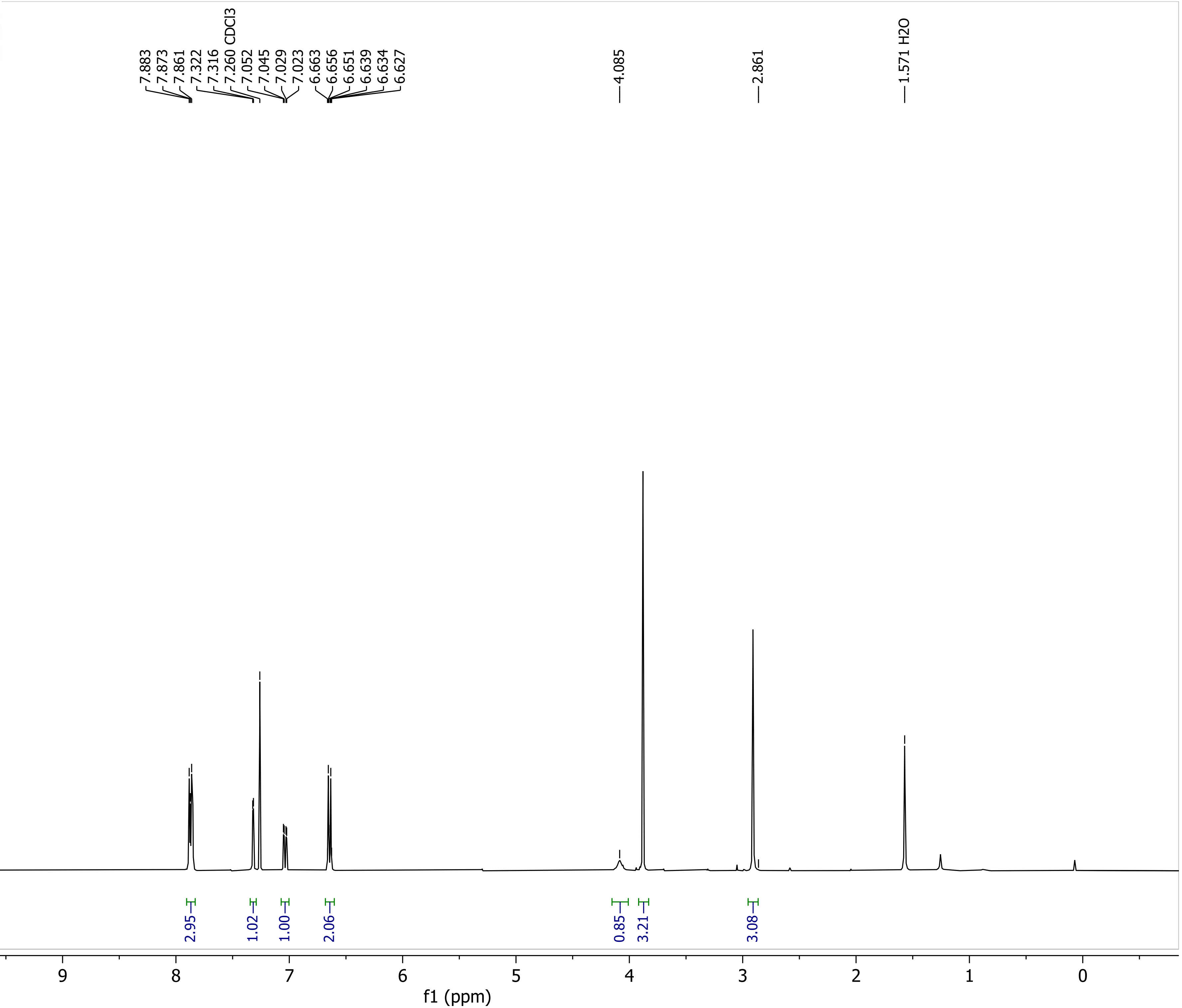


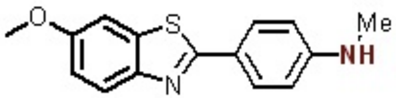
19
^{13}C, $CDCl_3$, 101 MHz





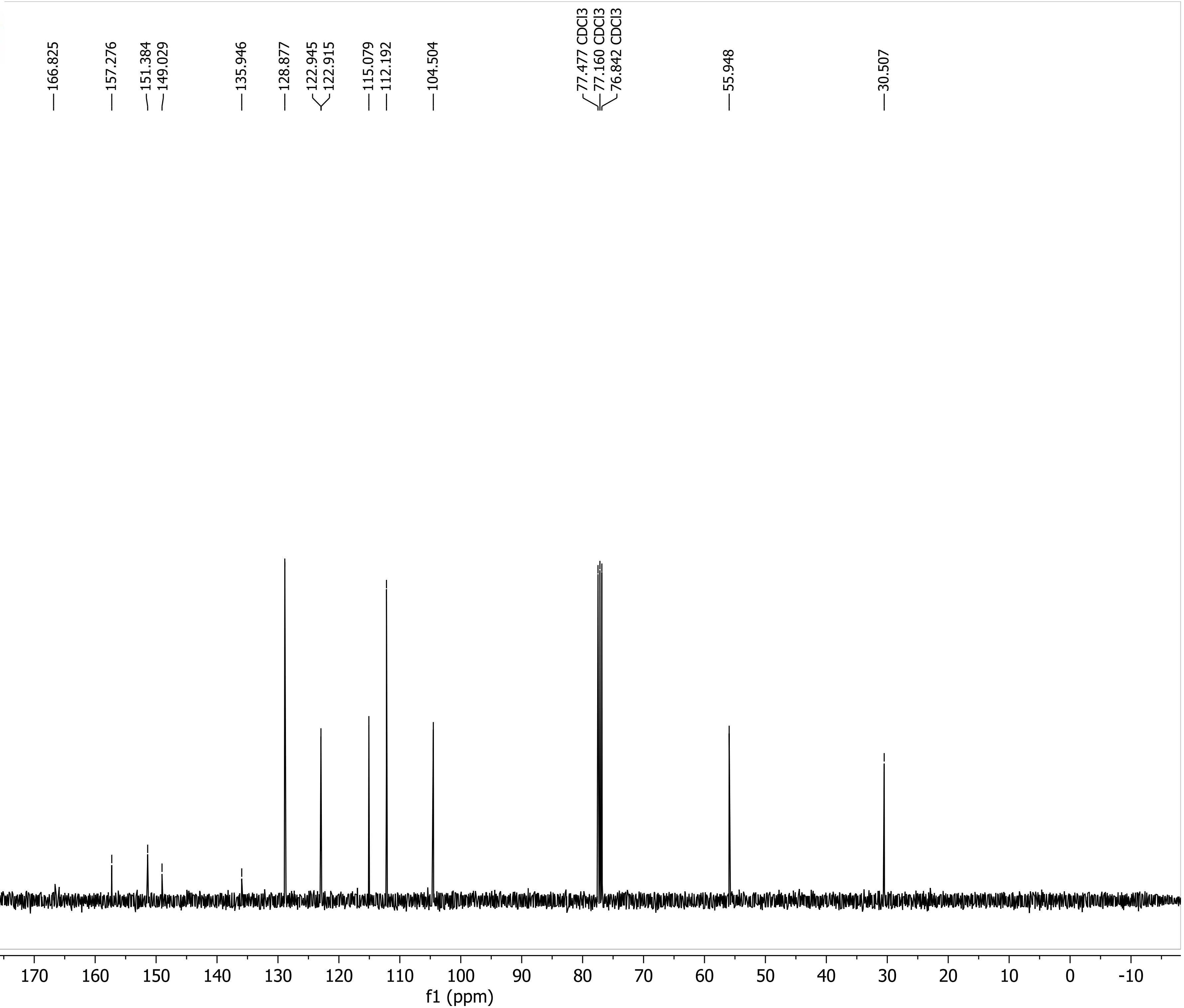
20
^{1}H, $CDCl_3$, 400 MHz

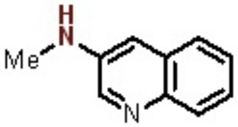




20

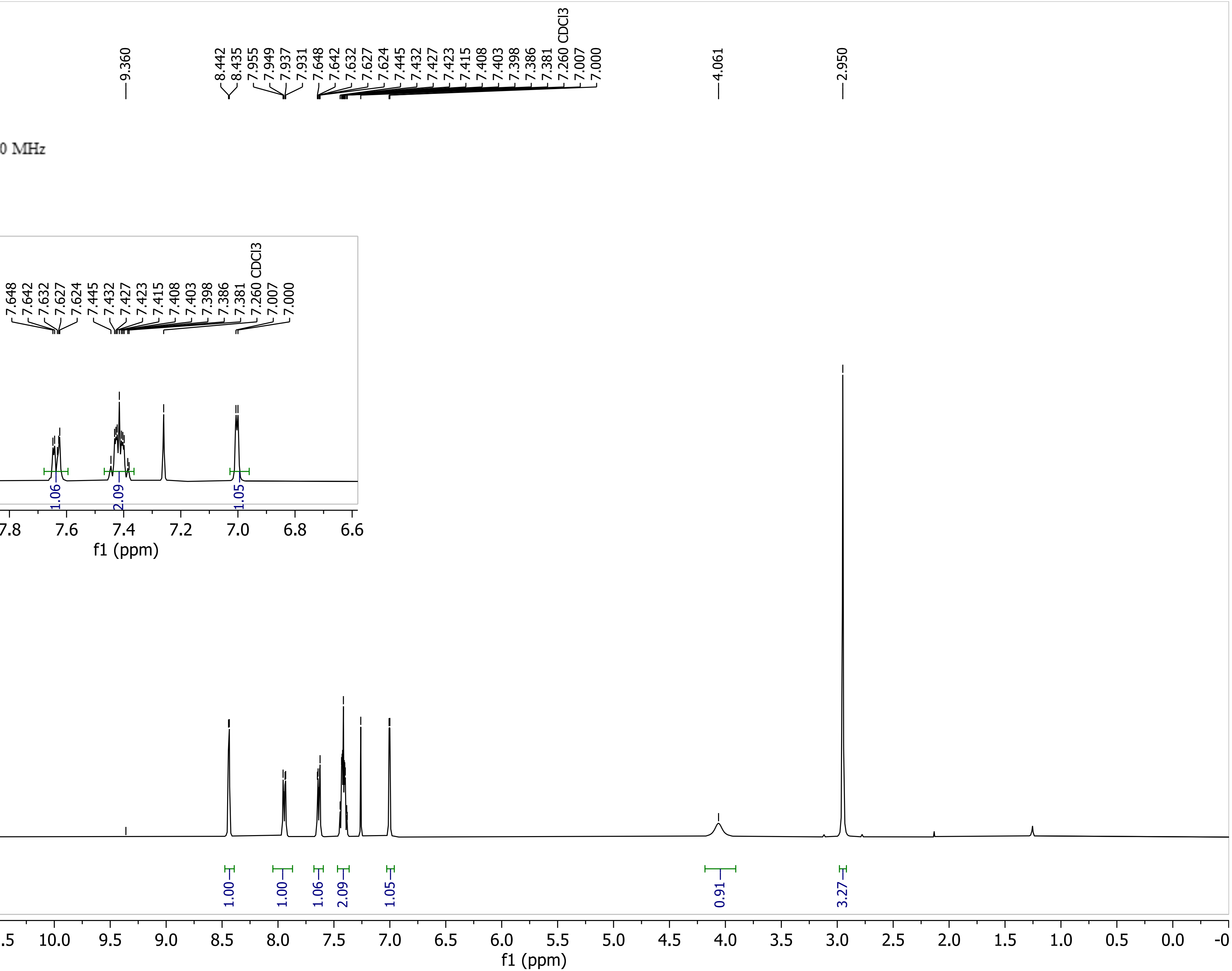
^{13}C, $CDCl_3$, 101 MHz

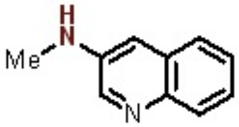




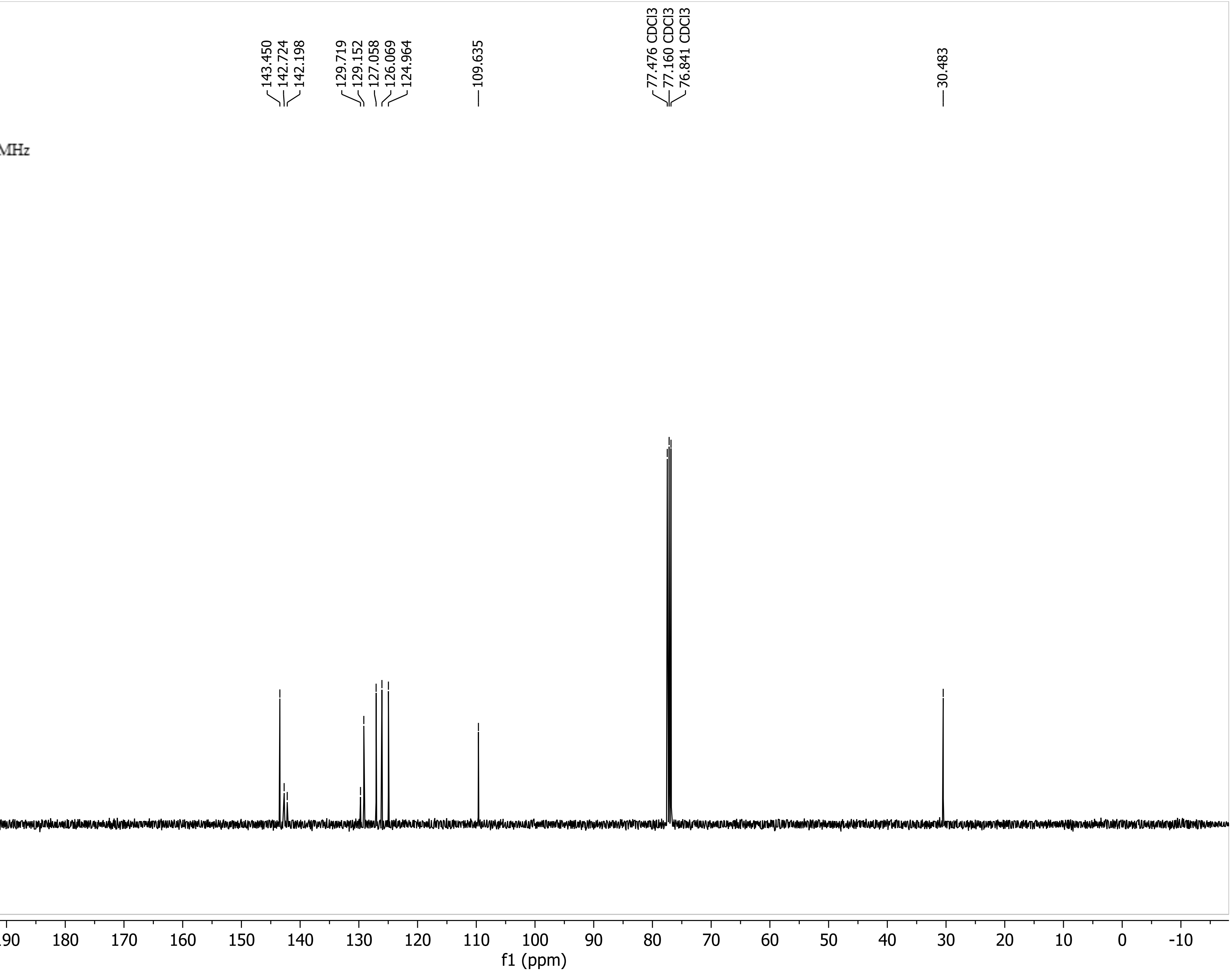
21

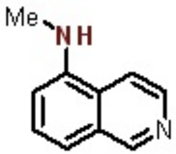
^1H, $CDCl_3$, 400 MHz



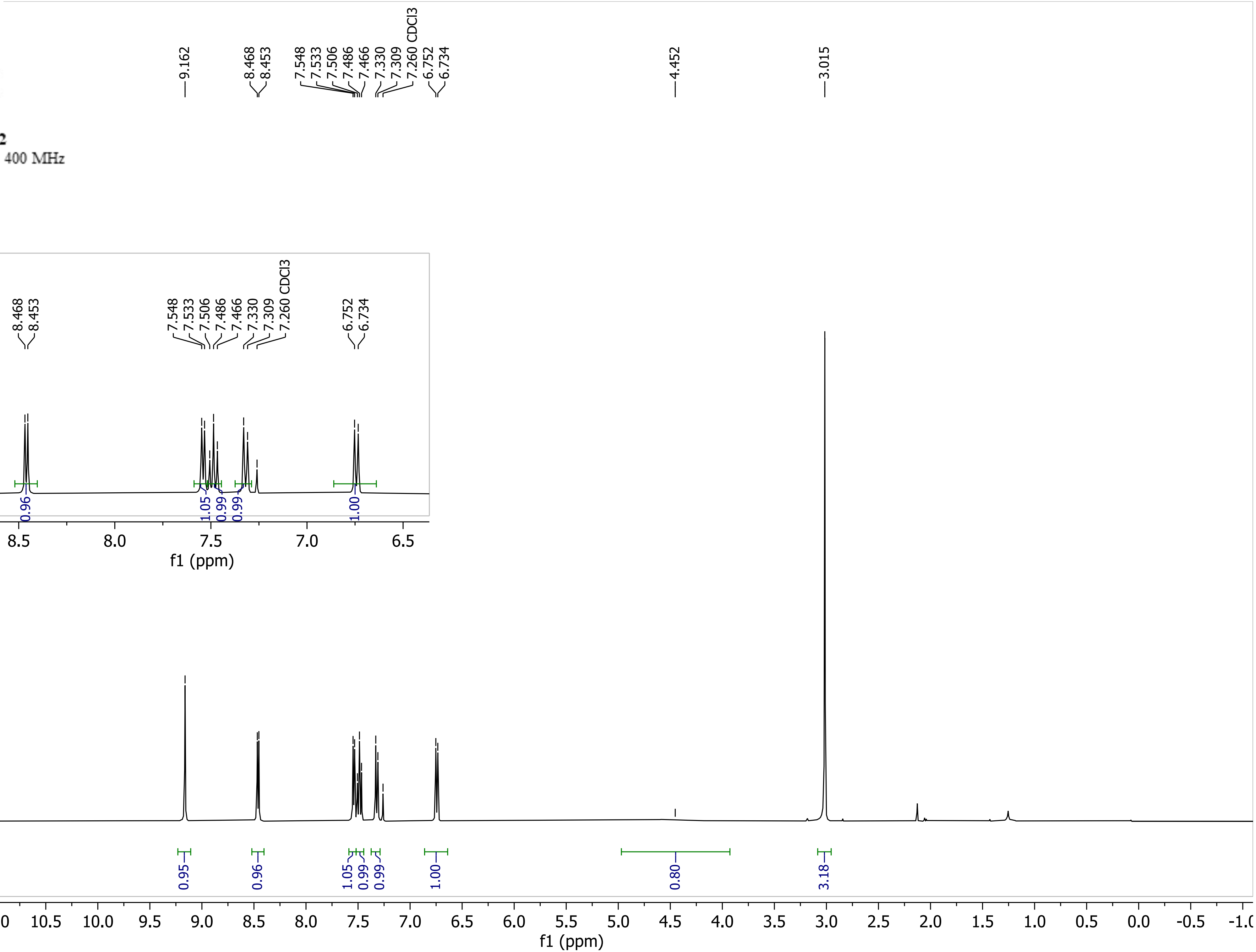


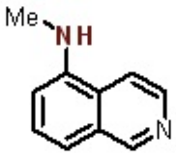
21
^{13}C, $CDCl_3$, 101 MHz





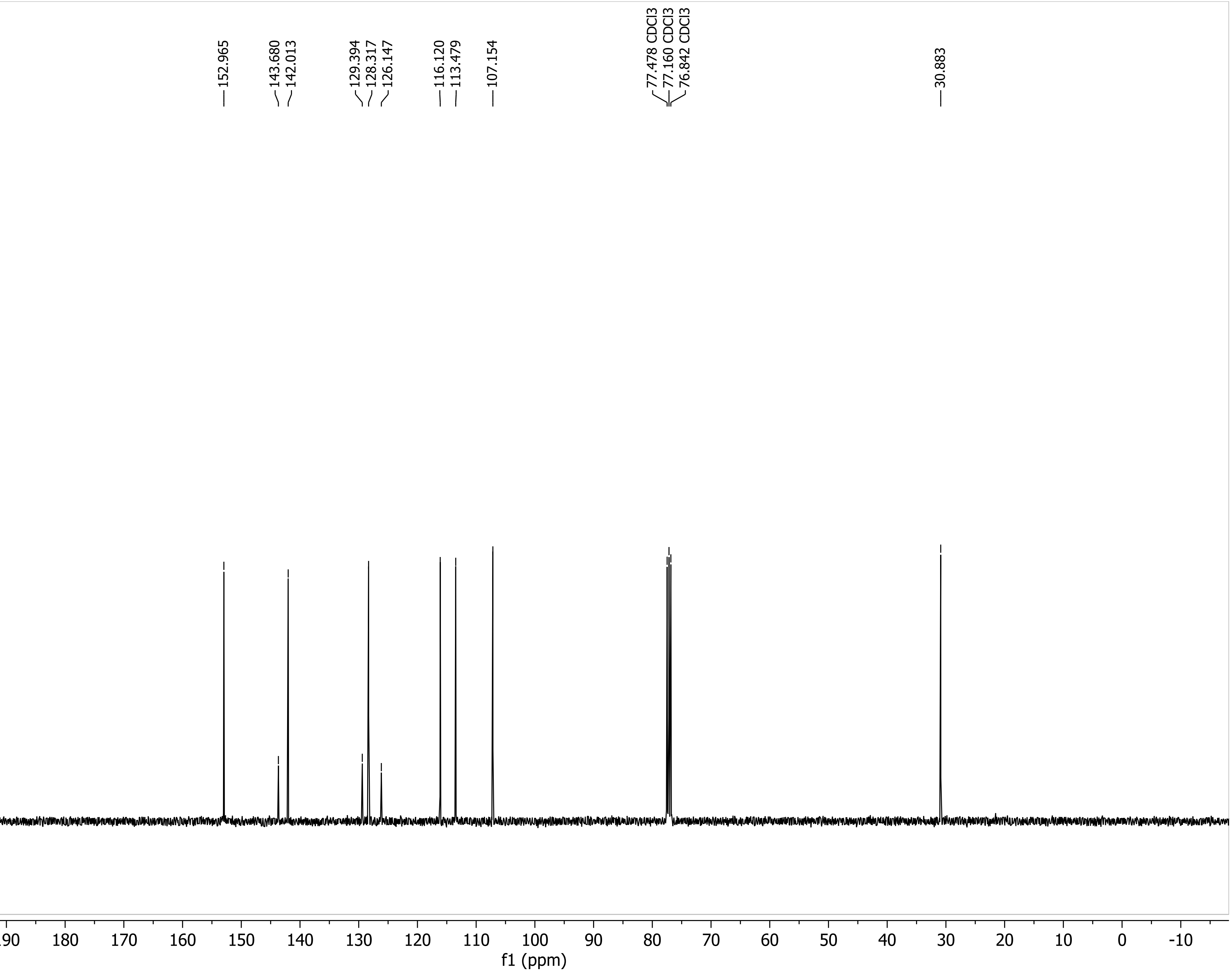
22
^1H, $CDCl_3$, 400 MHz

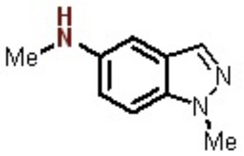




22

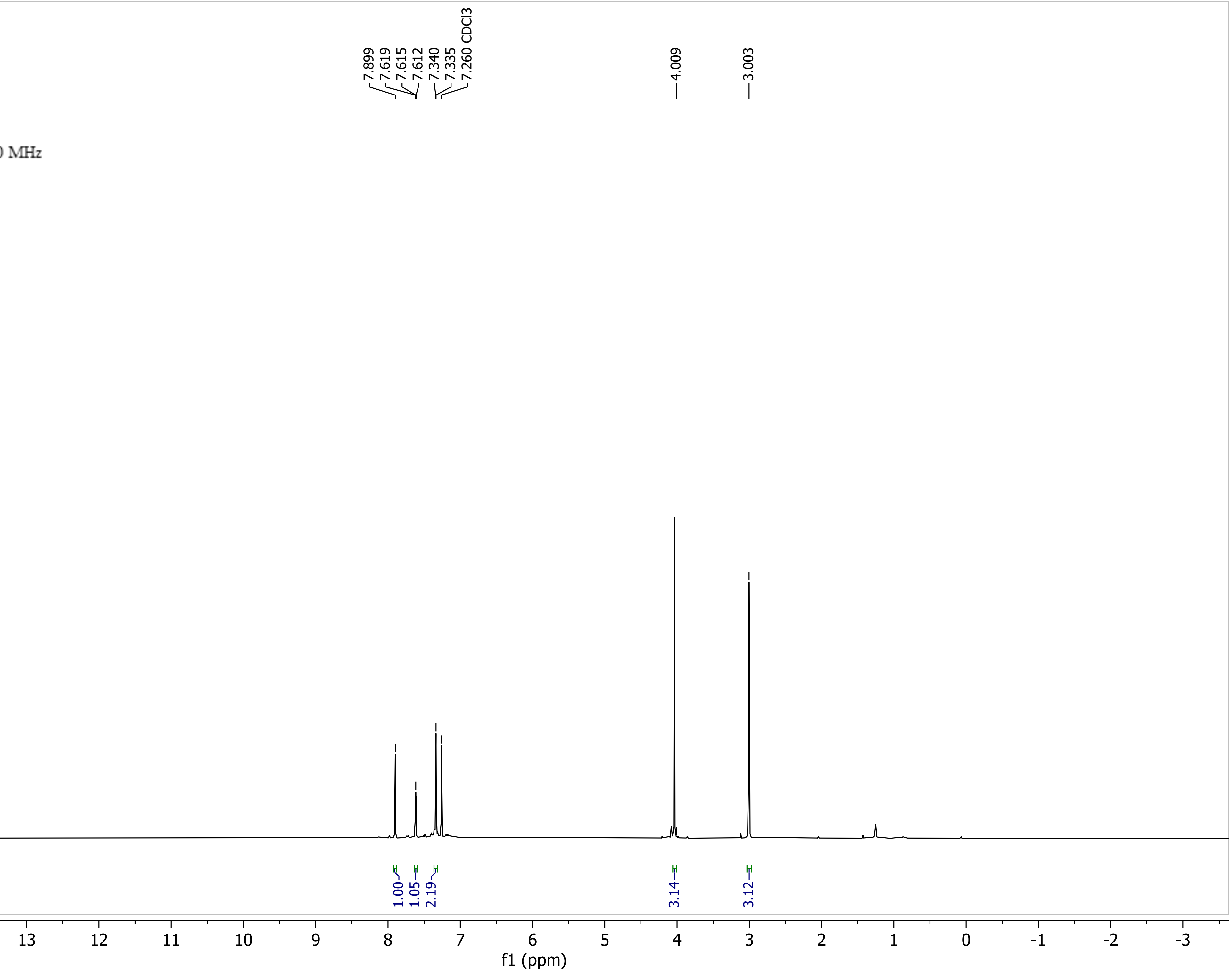
^{13}C, $CDCl_3$, 101 MHz

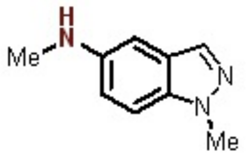




23

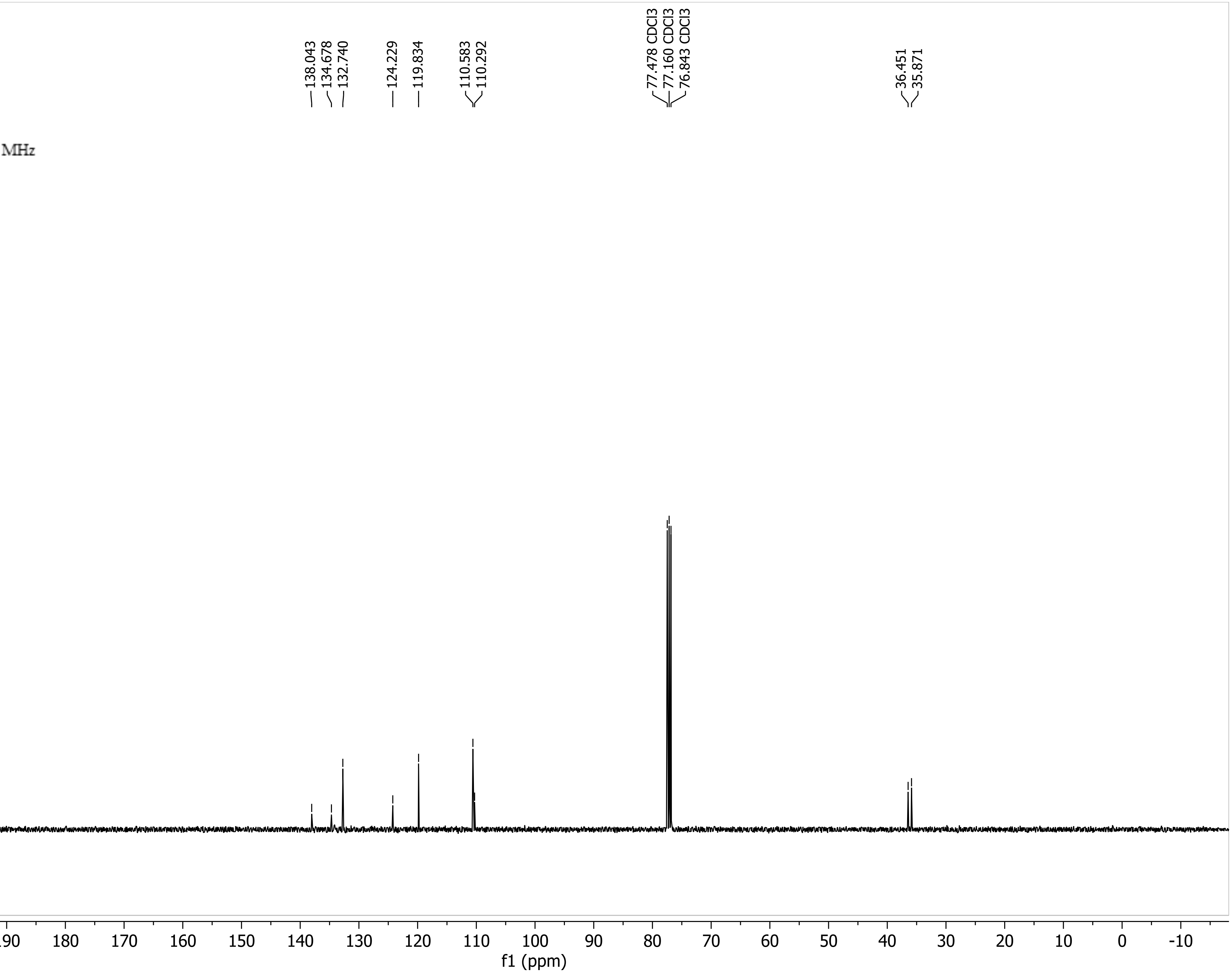
^{1}H, CDCl$_3$, 400 MHz

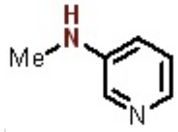




23

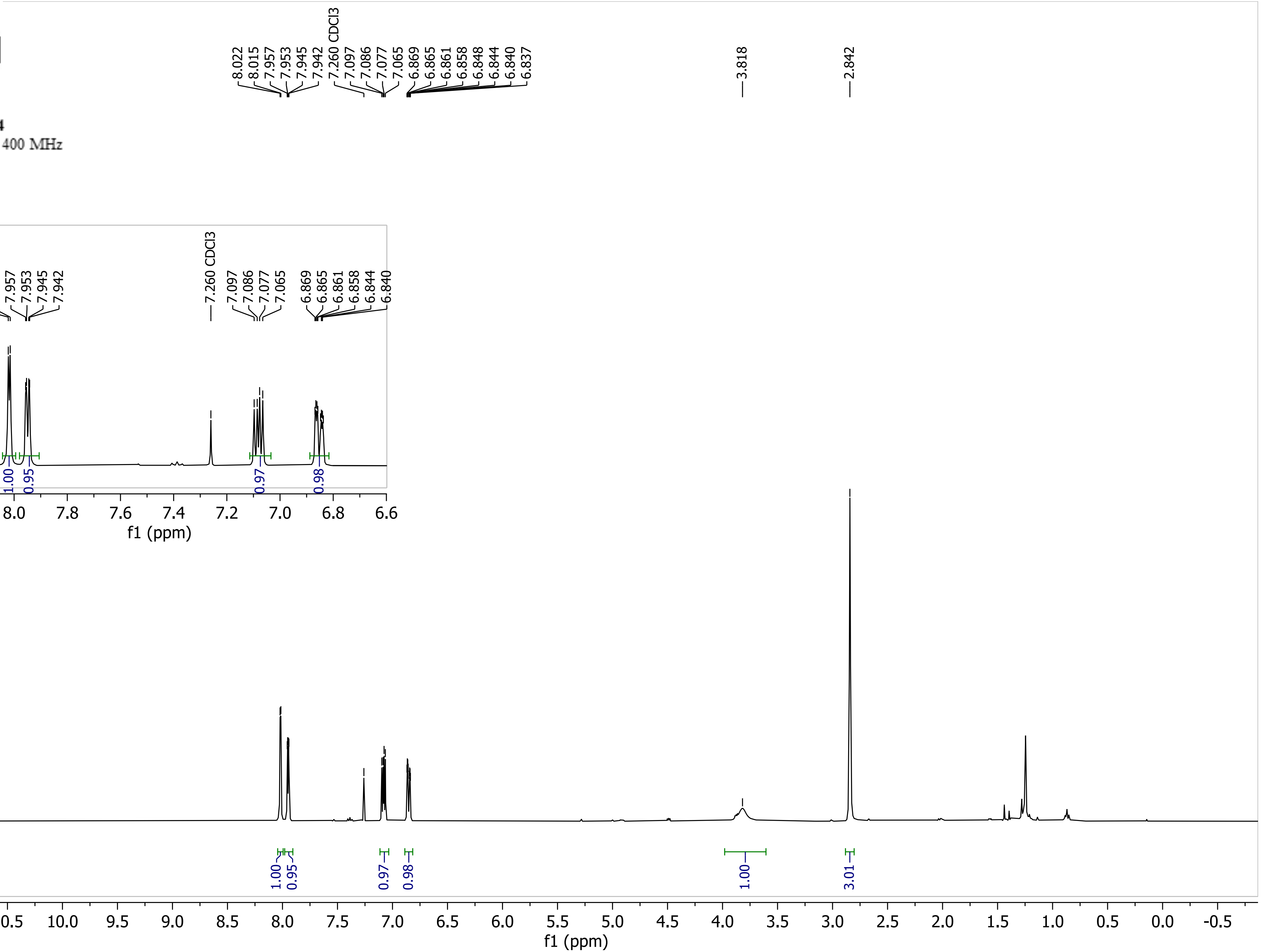
^{13}C, $CDCl_3$, 101 MHz

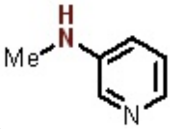




24

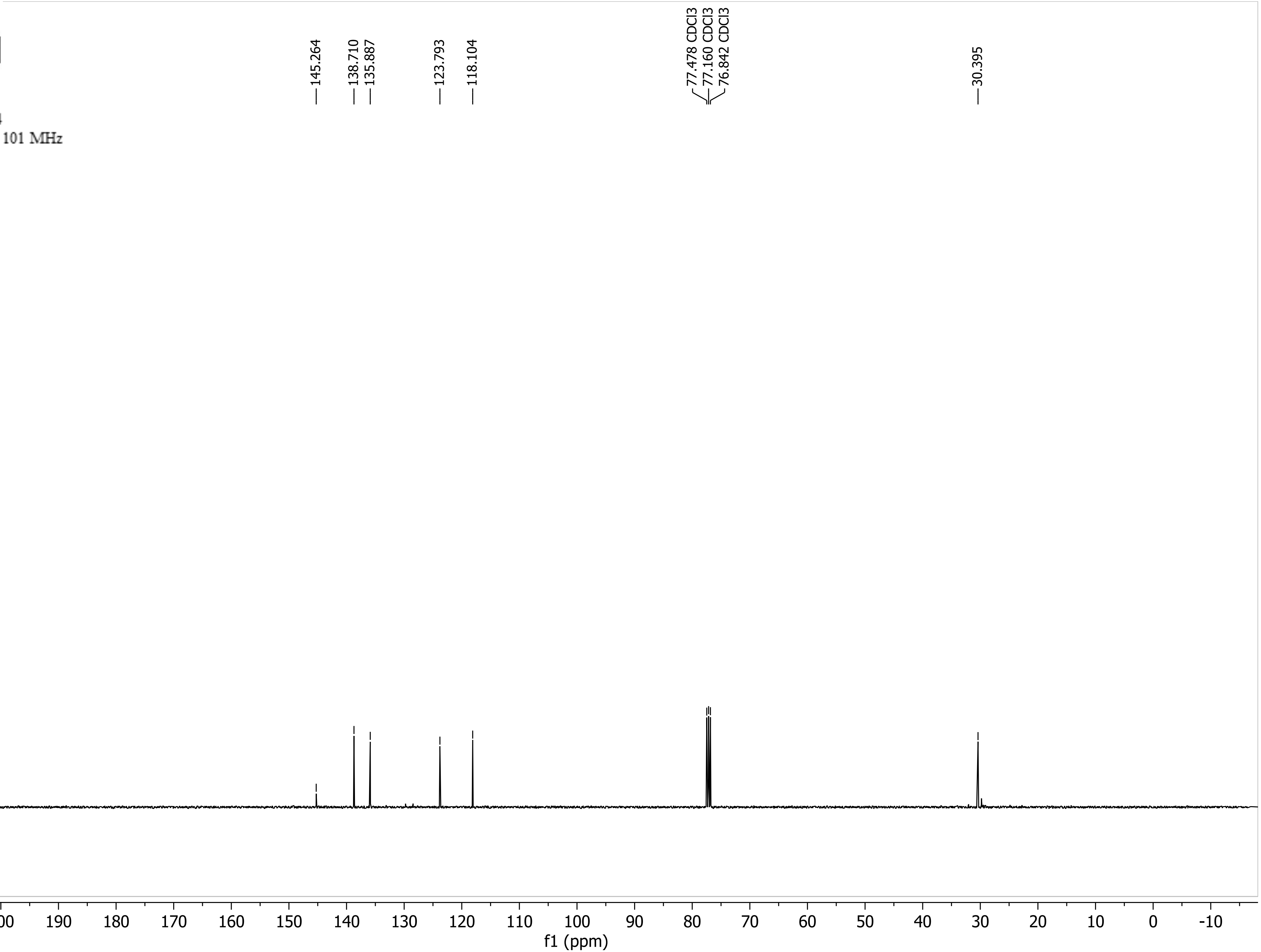
^{1}H, $CDCl_3$, 400 MHz

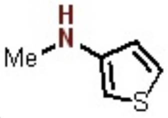




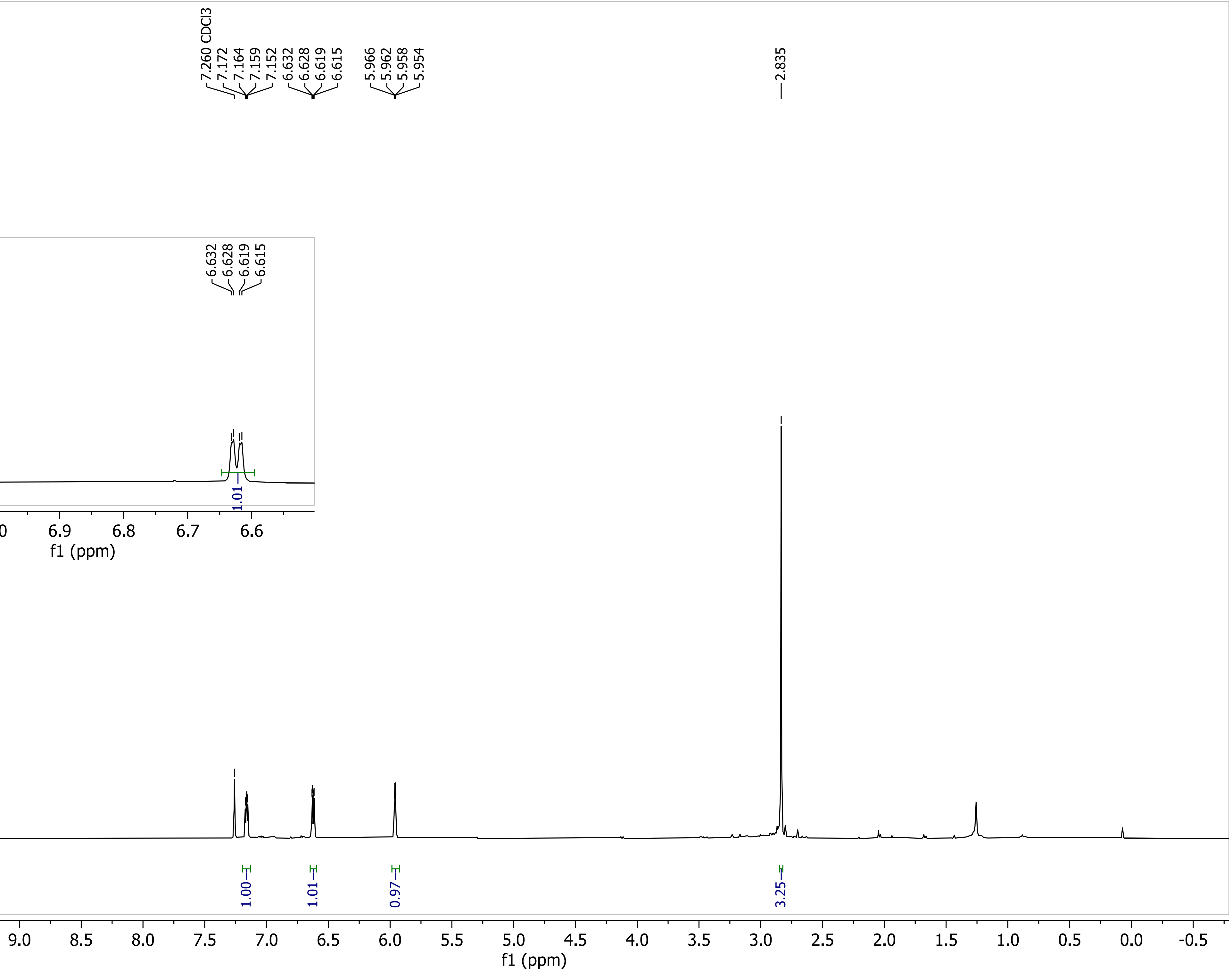
24

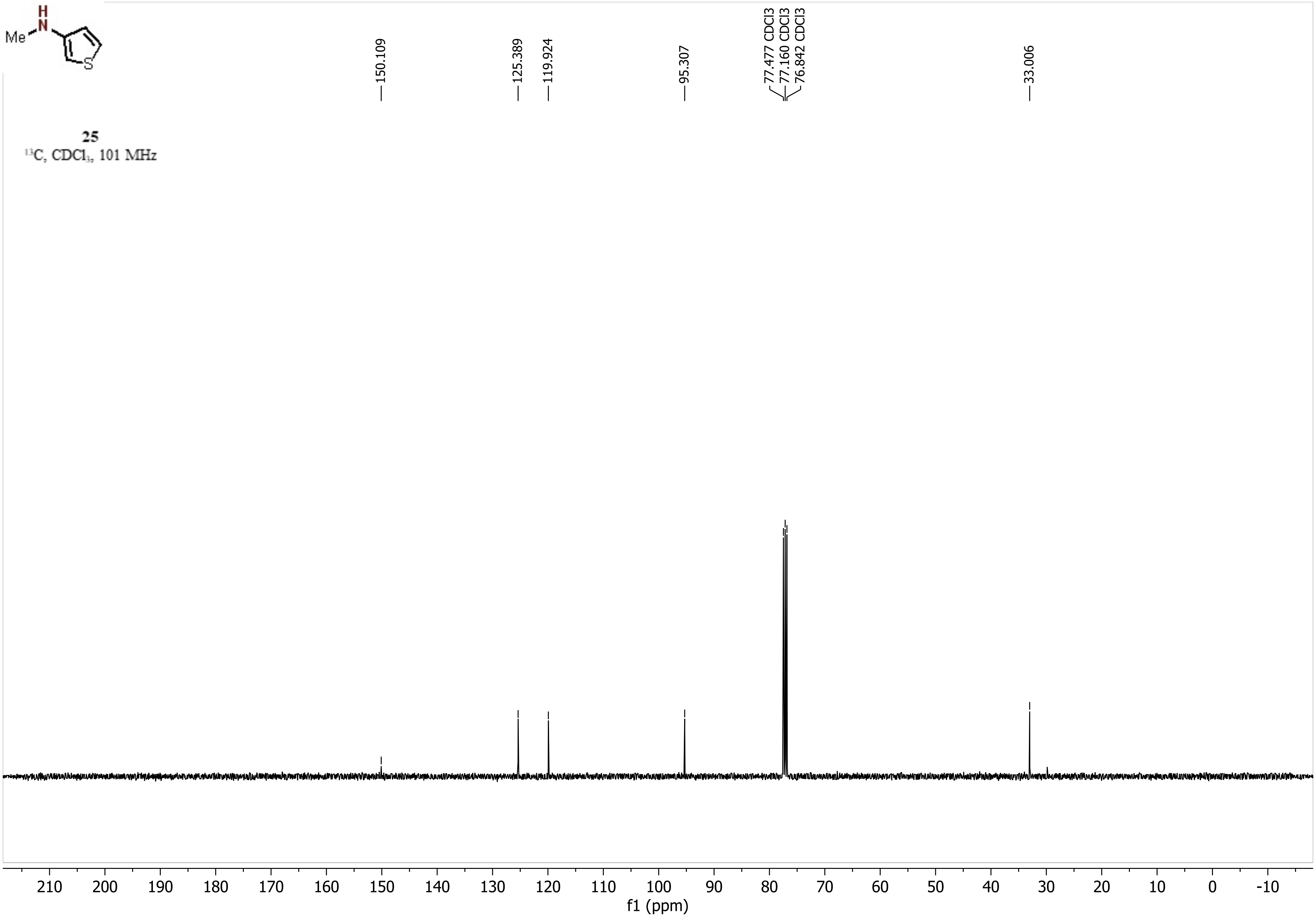
^{13}C, $CDCl_3$, 101 MHz





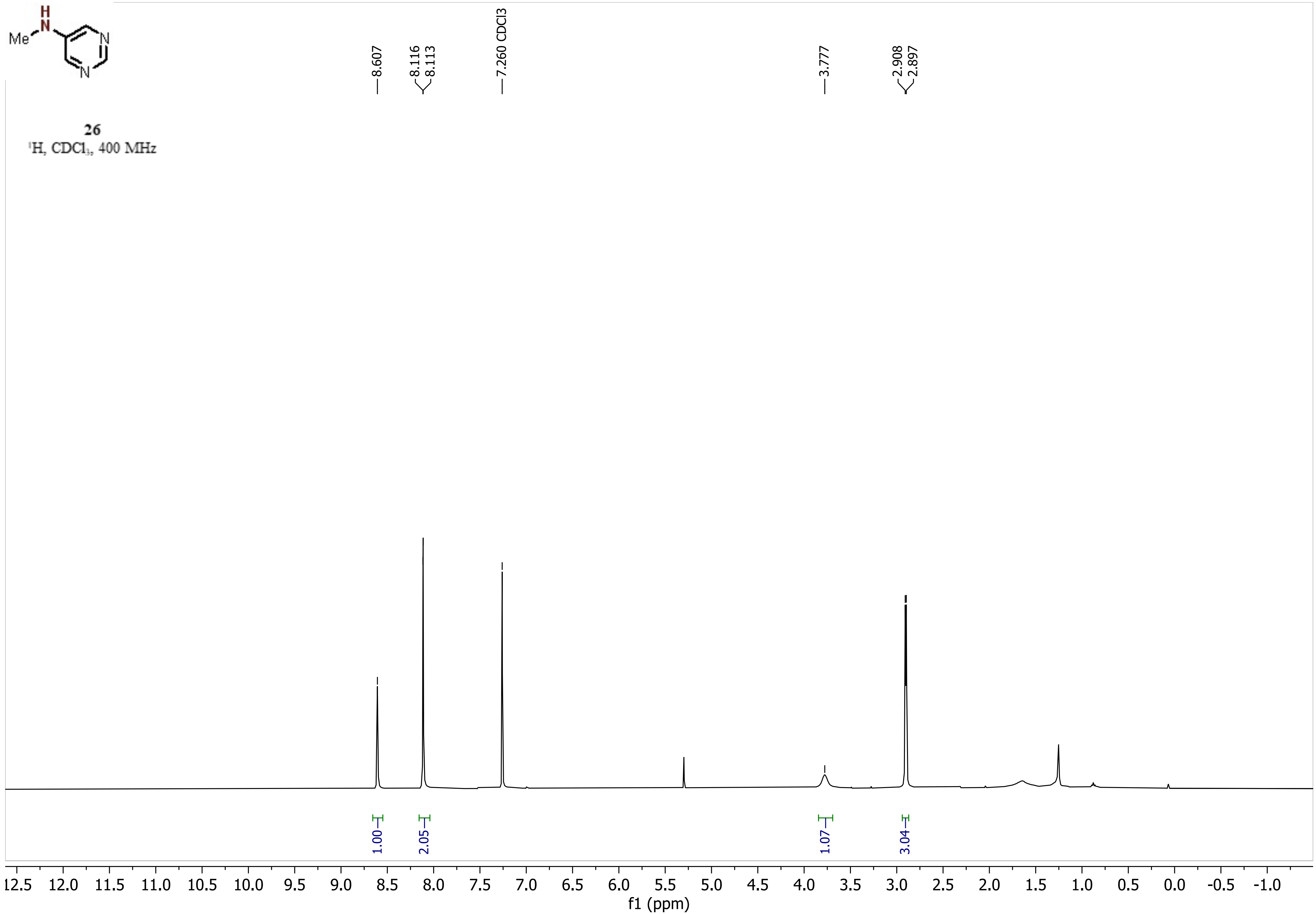
25
^1H, $CDCl_3$, 400 MHz



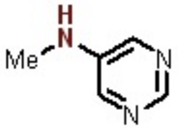


25

^{13}C, $CDCl_3$, 101 MHz

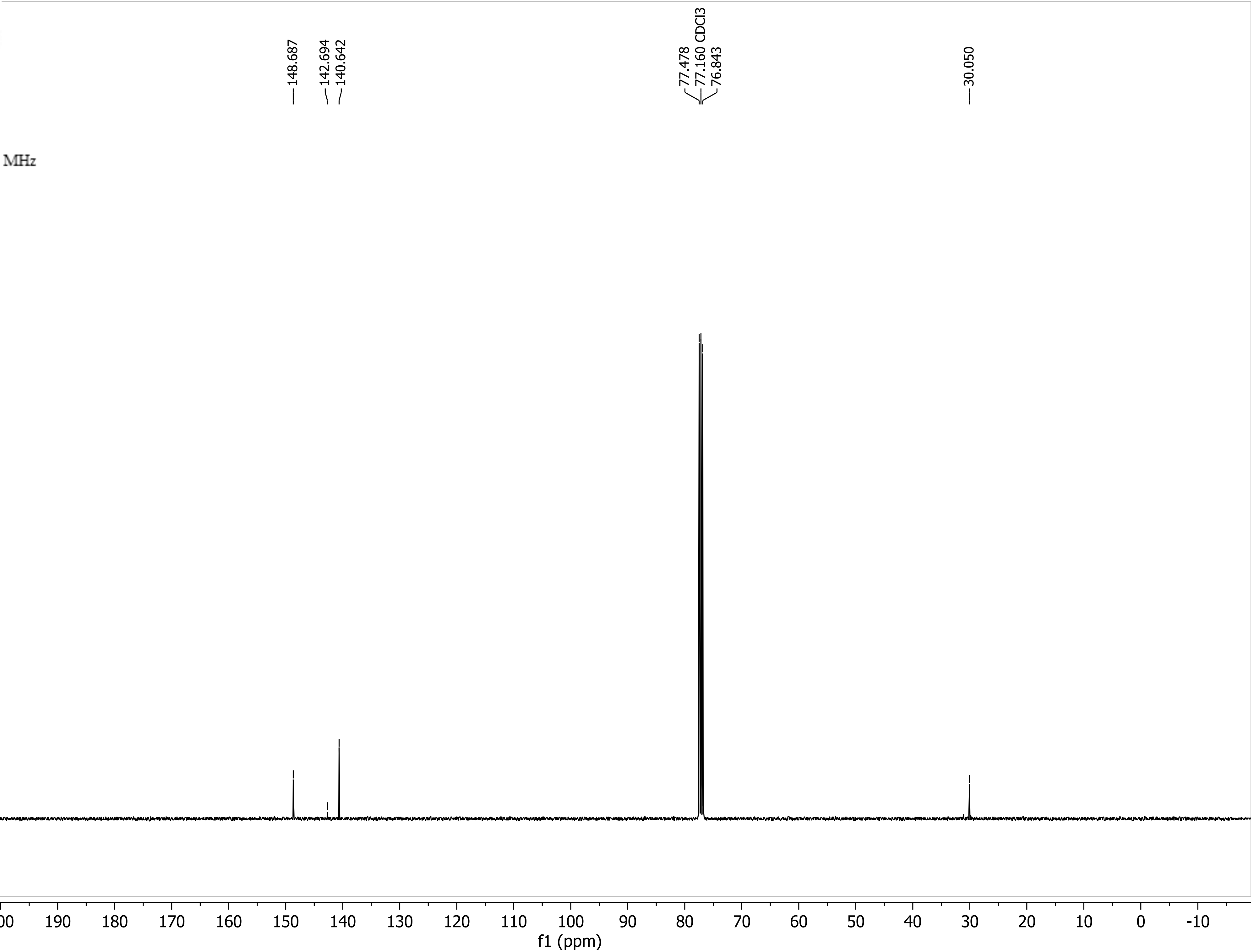


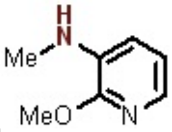
Me
N
H
N
N
26
¹H, CDCl₃, 400 MHz
8.607
8.116
8.113
7.260 CDCl3
3.777
2.908
2.897
1.00
2.05
1.07
3.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



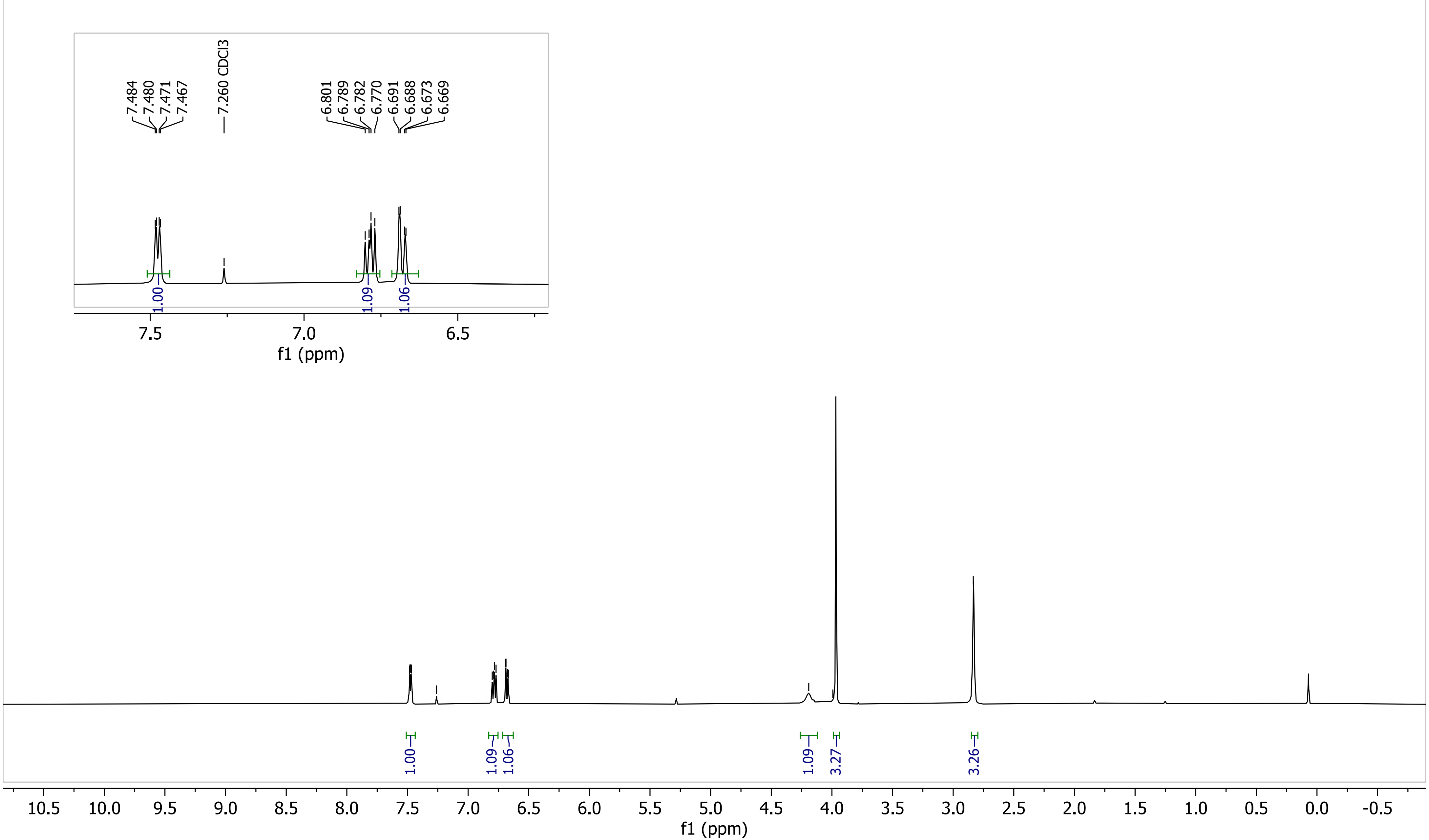
26

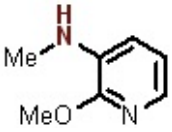
^{13}C, $CDCl_3$, 101 MHz





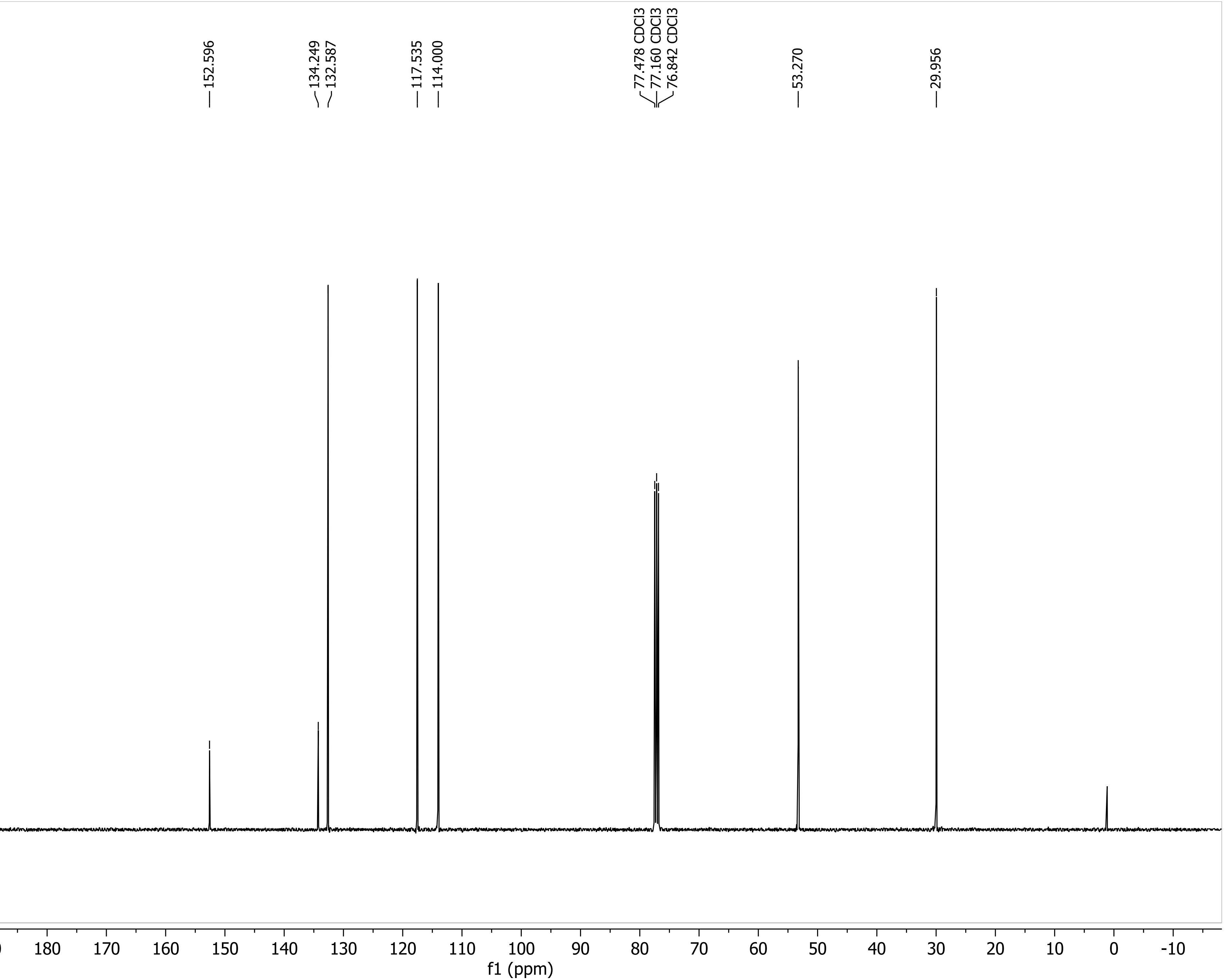
27
^{1}H, CDCl$_3$, 400 MHz

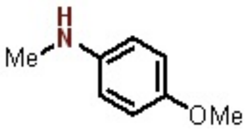




27

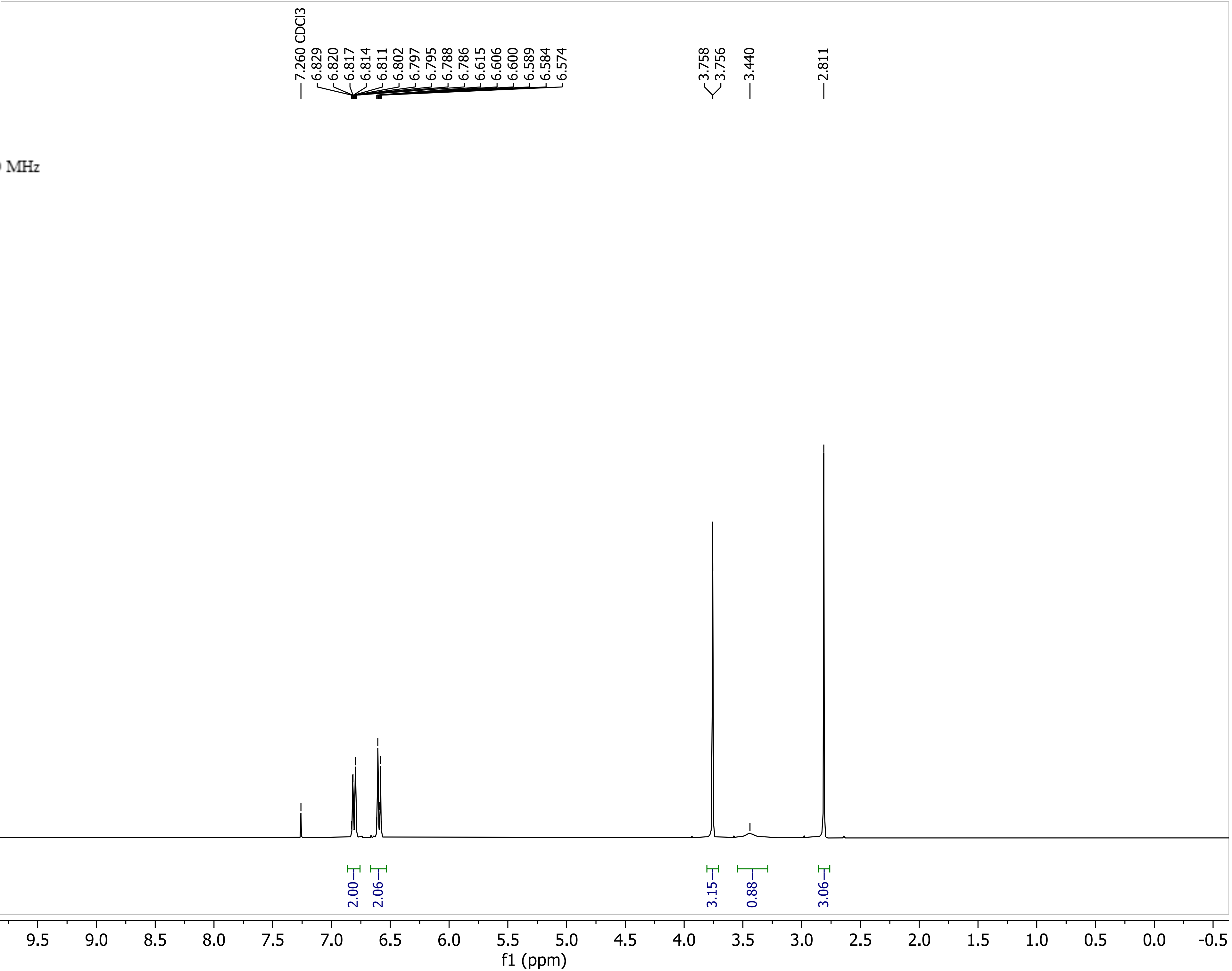
^{13}C, $CDCl_3$, 101 MHz

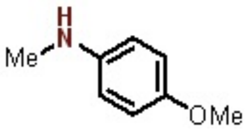




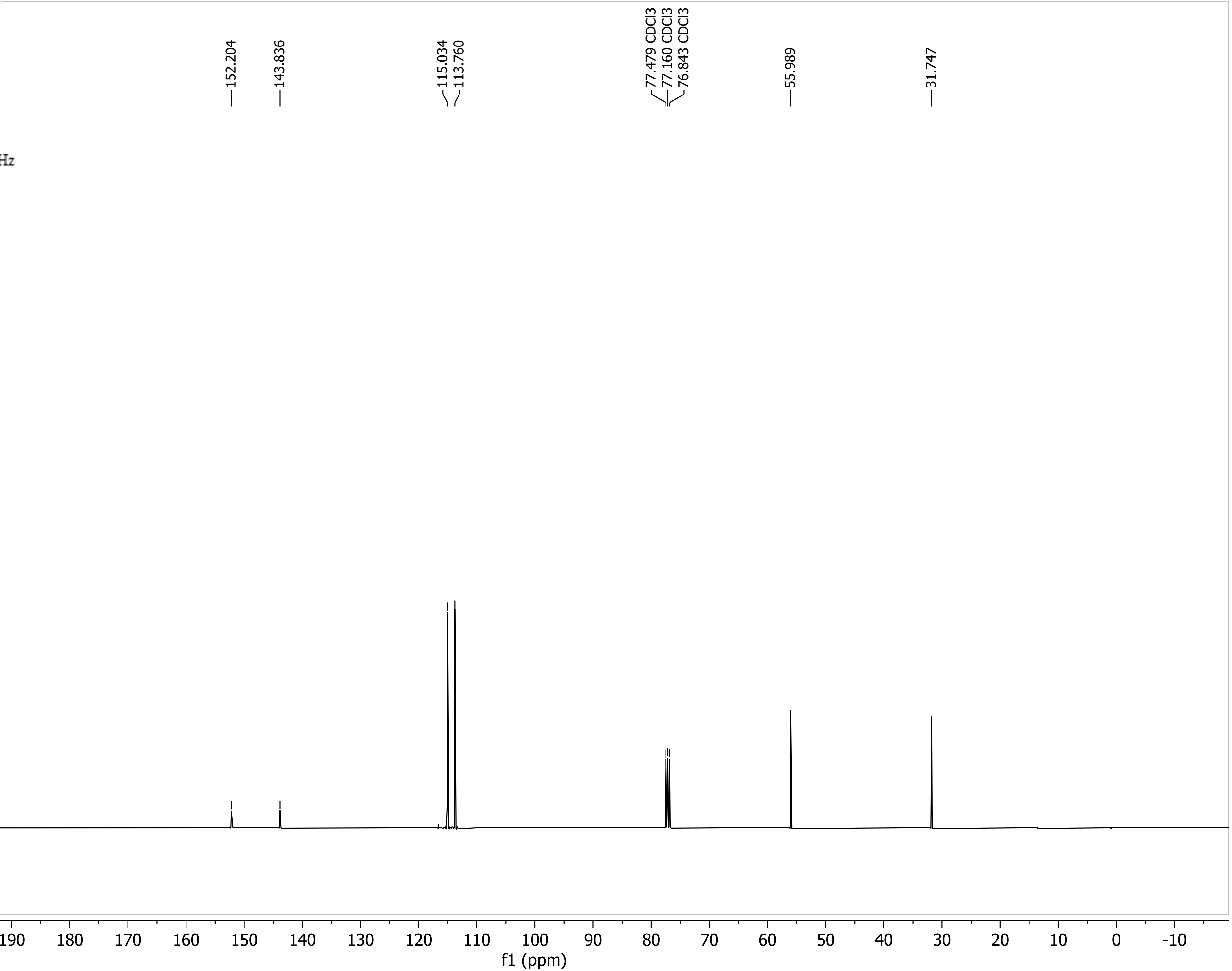
28

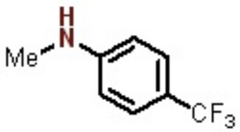
^1H, $CDCl_3$, 400 MHz





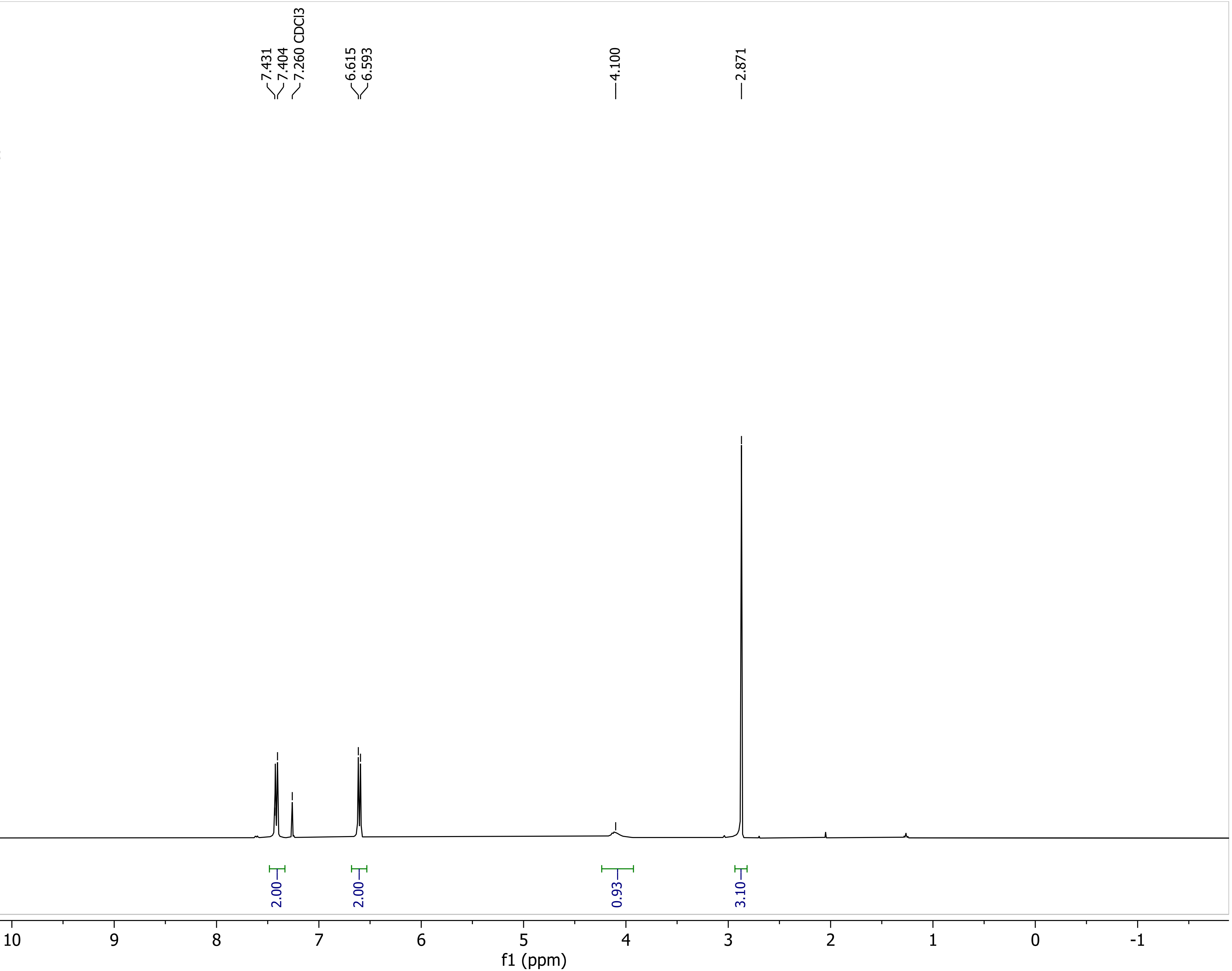
28
^{13}C, $CDCl_3$, 101 MHz

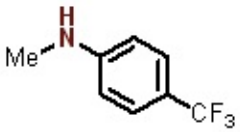




29

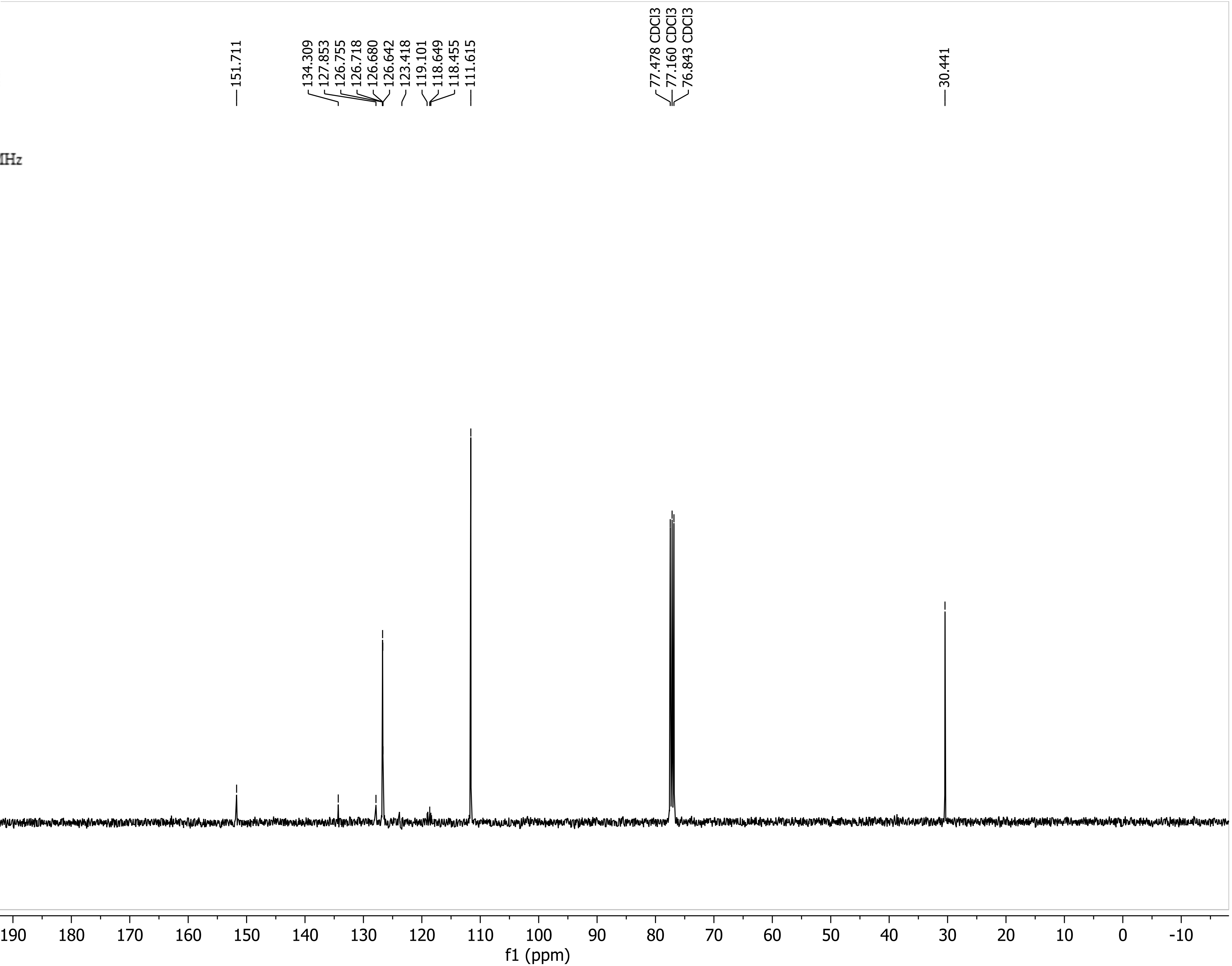
^{1}H, $CDCl_3$, 400 MHz

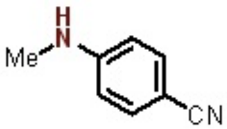




29

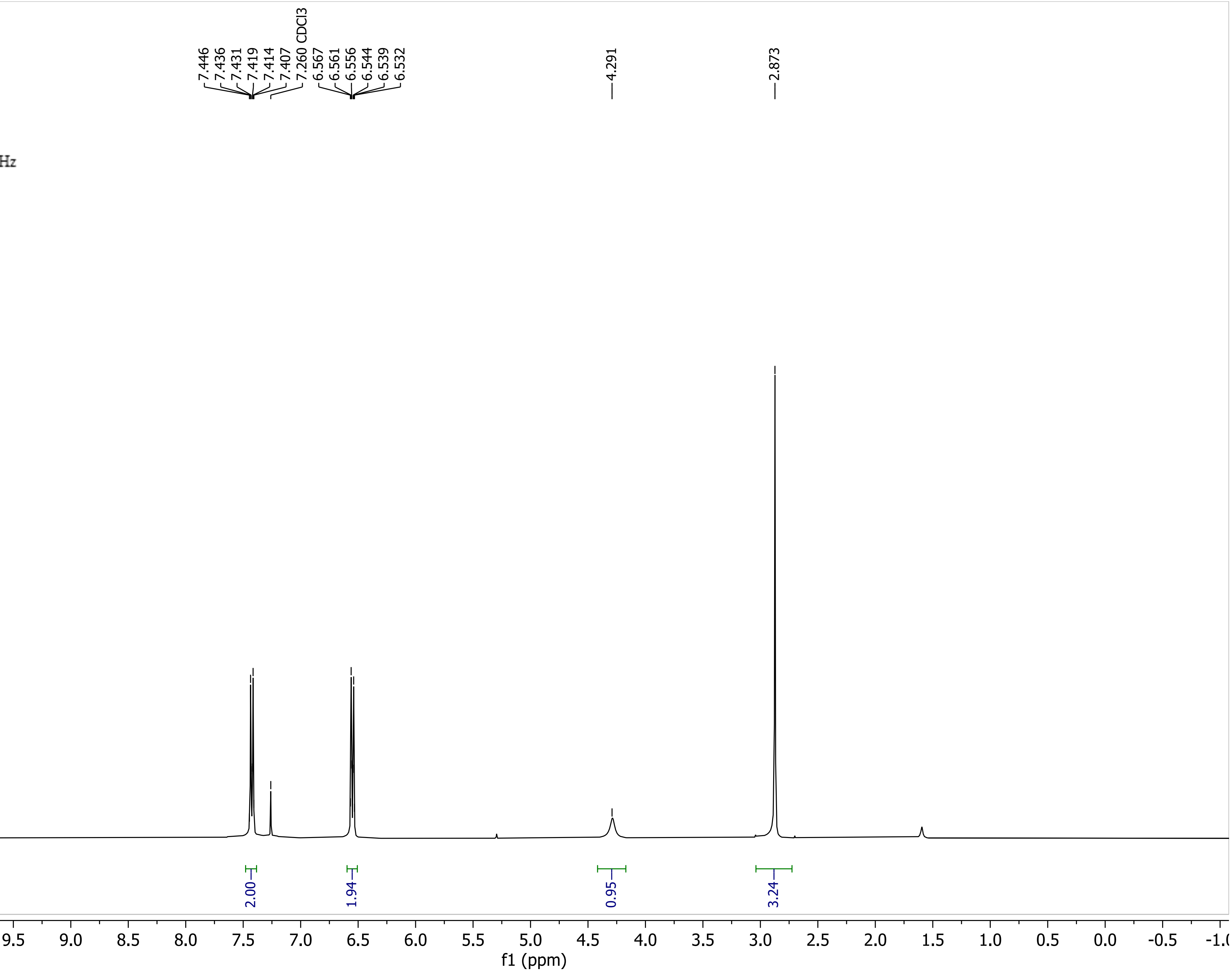
^{13}C, $CDCl_3$, 101 MHz

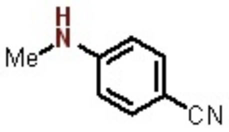




30

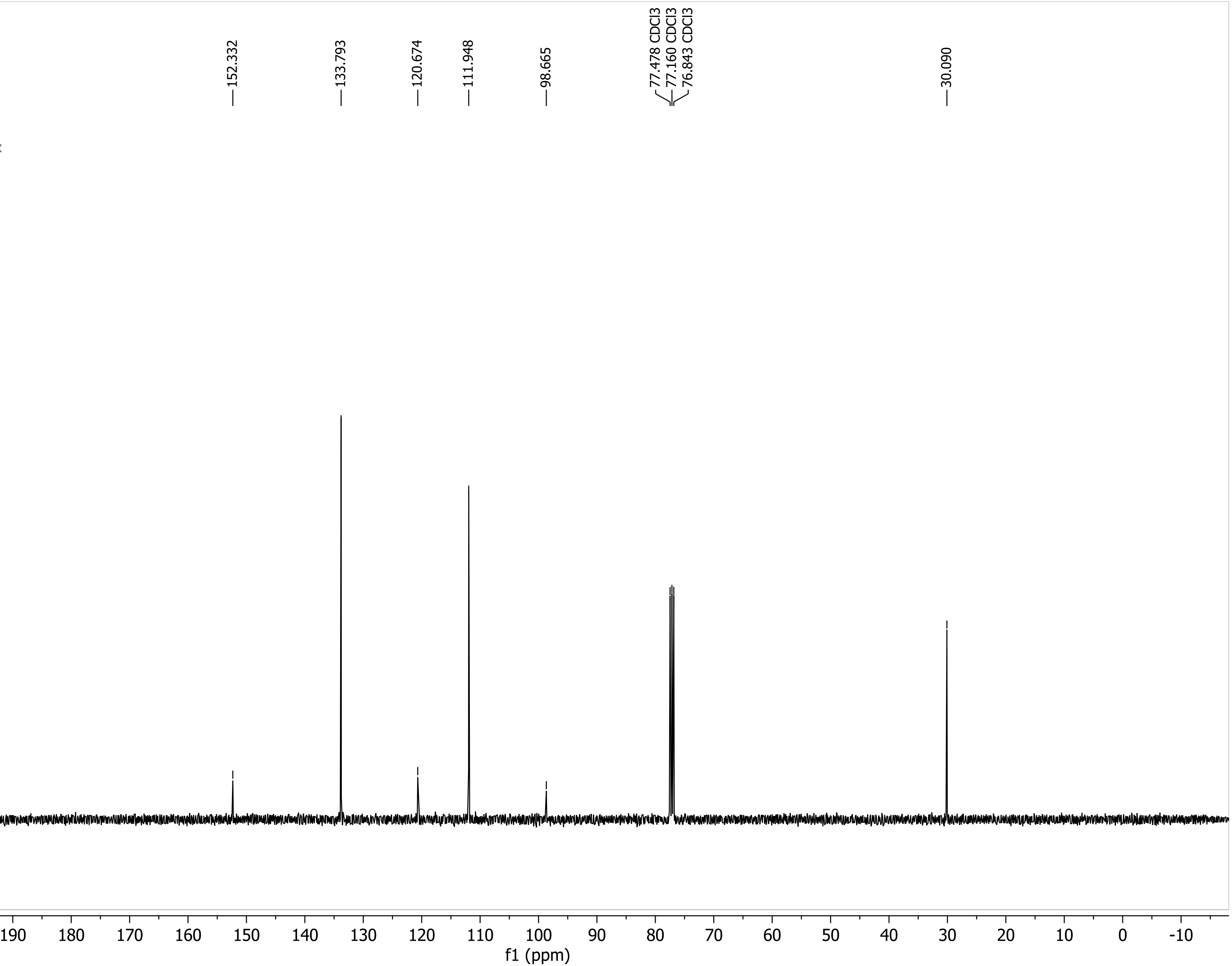
^1H, $CDCl_3$, 400 MHz

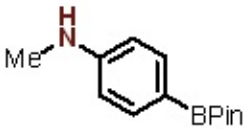




30

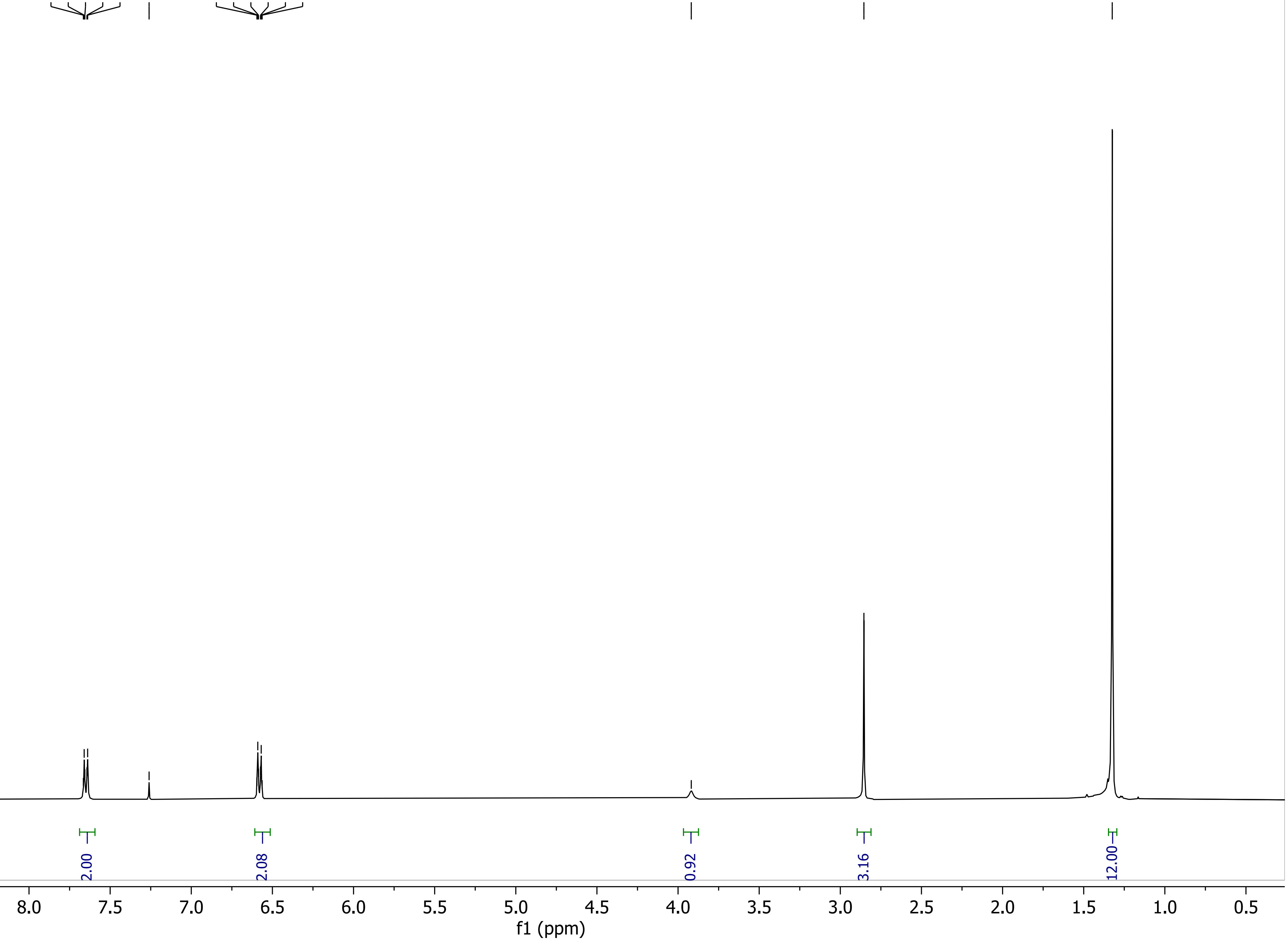
^{13}C, $CDCl_3$, 101 MHz

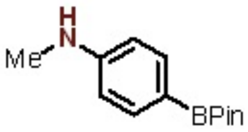




31

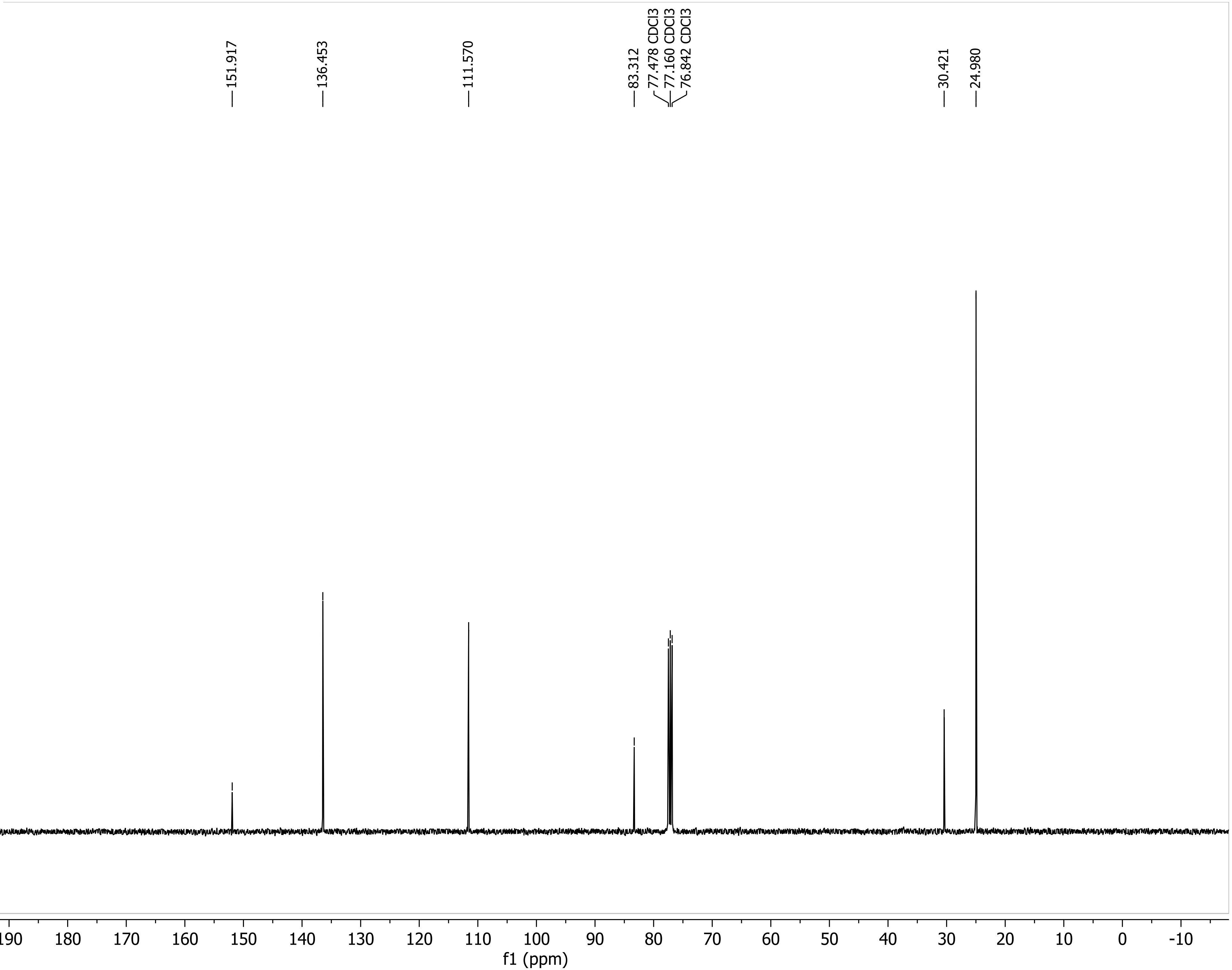
^{1}H, $CDCl_3$, 400 MHz

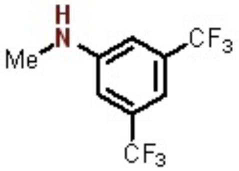




31

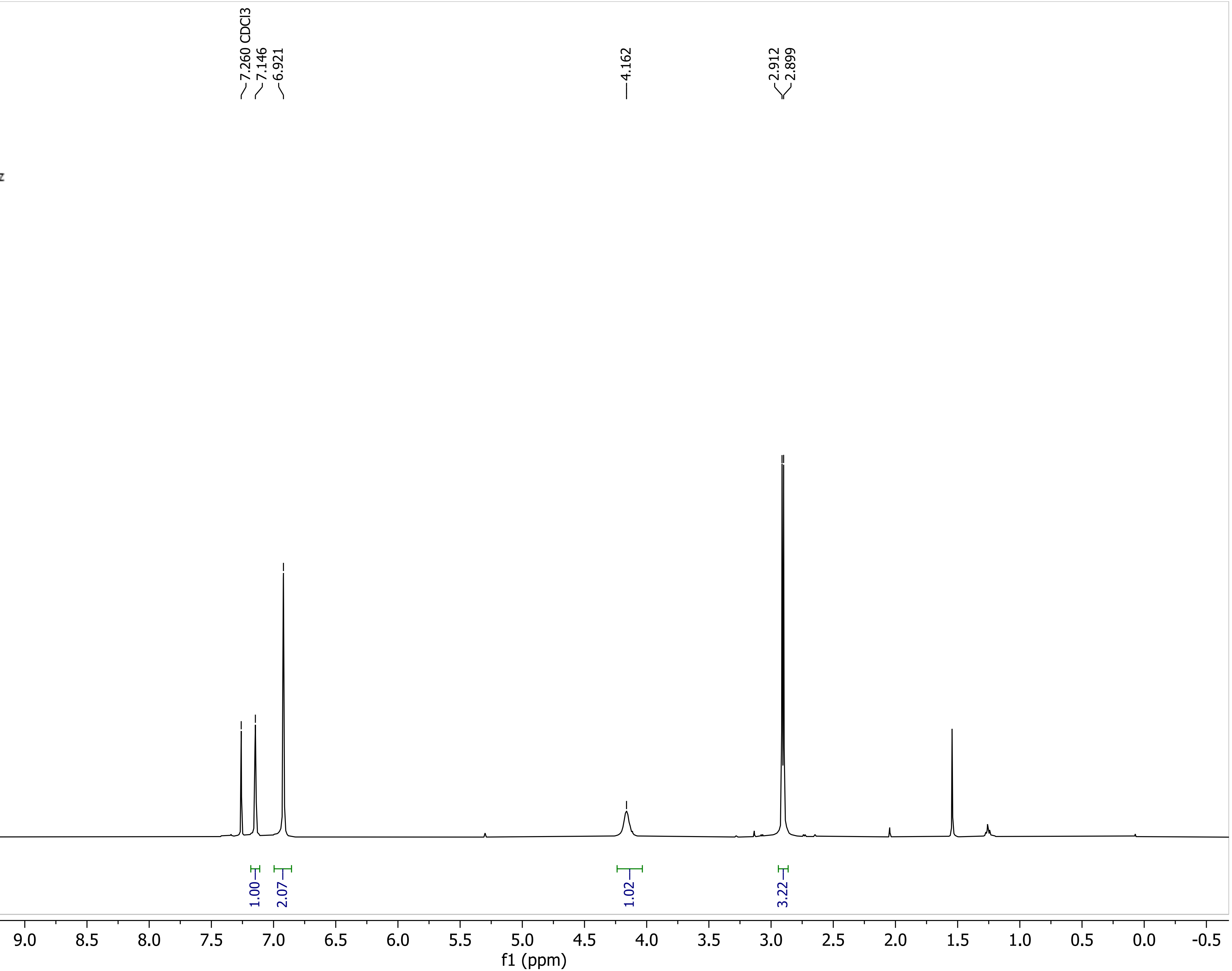
^{13}C, $CDCl_3$, 101 MHz

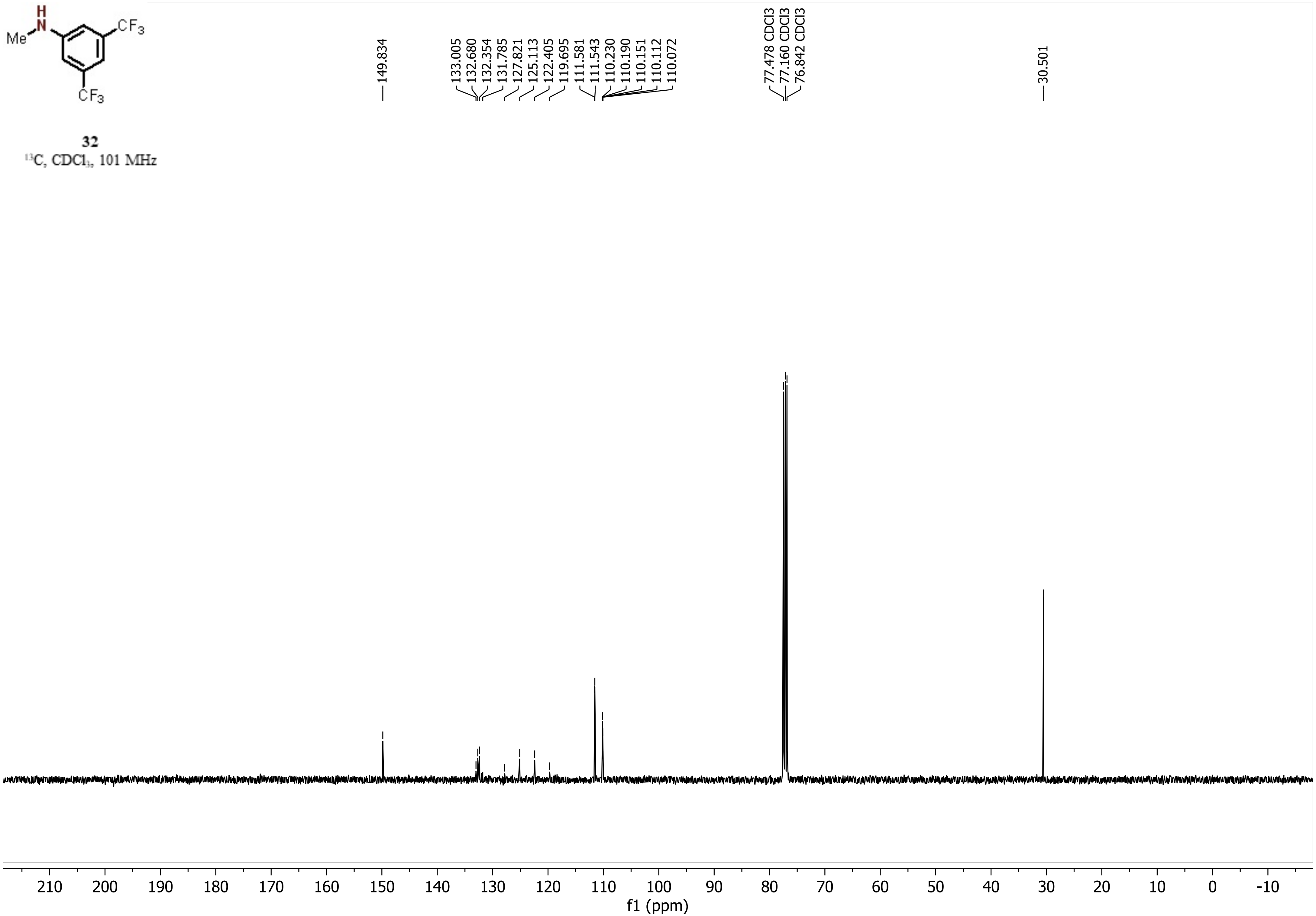




32

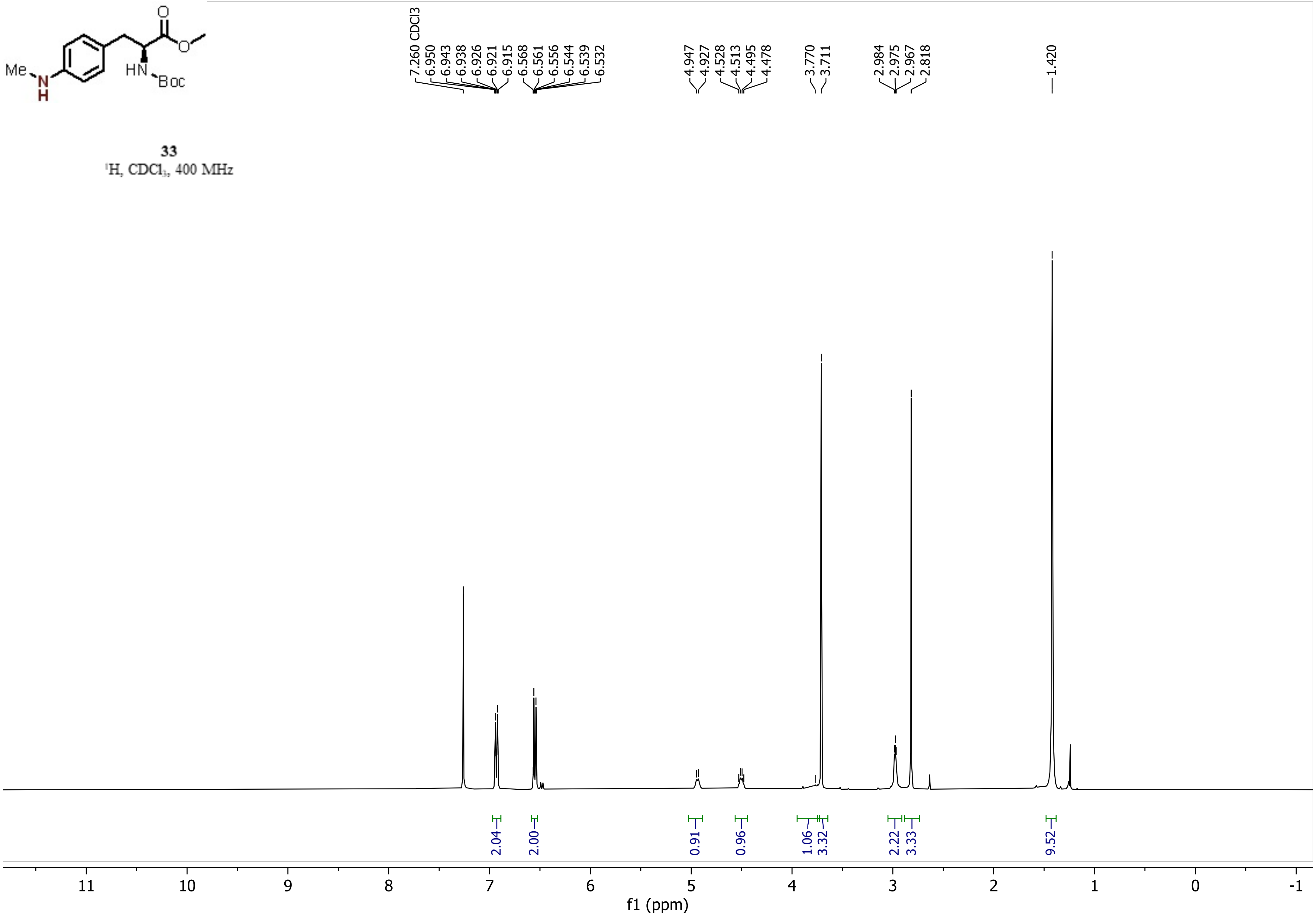
^{1}H, $CDCl_3$, 400 MHz

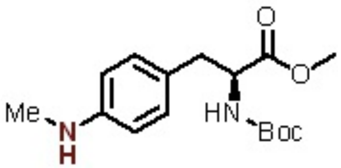




32

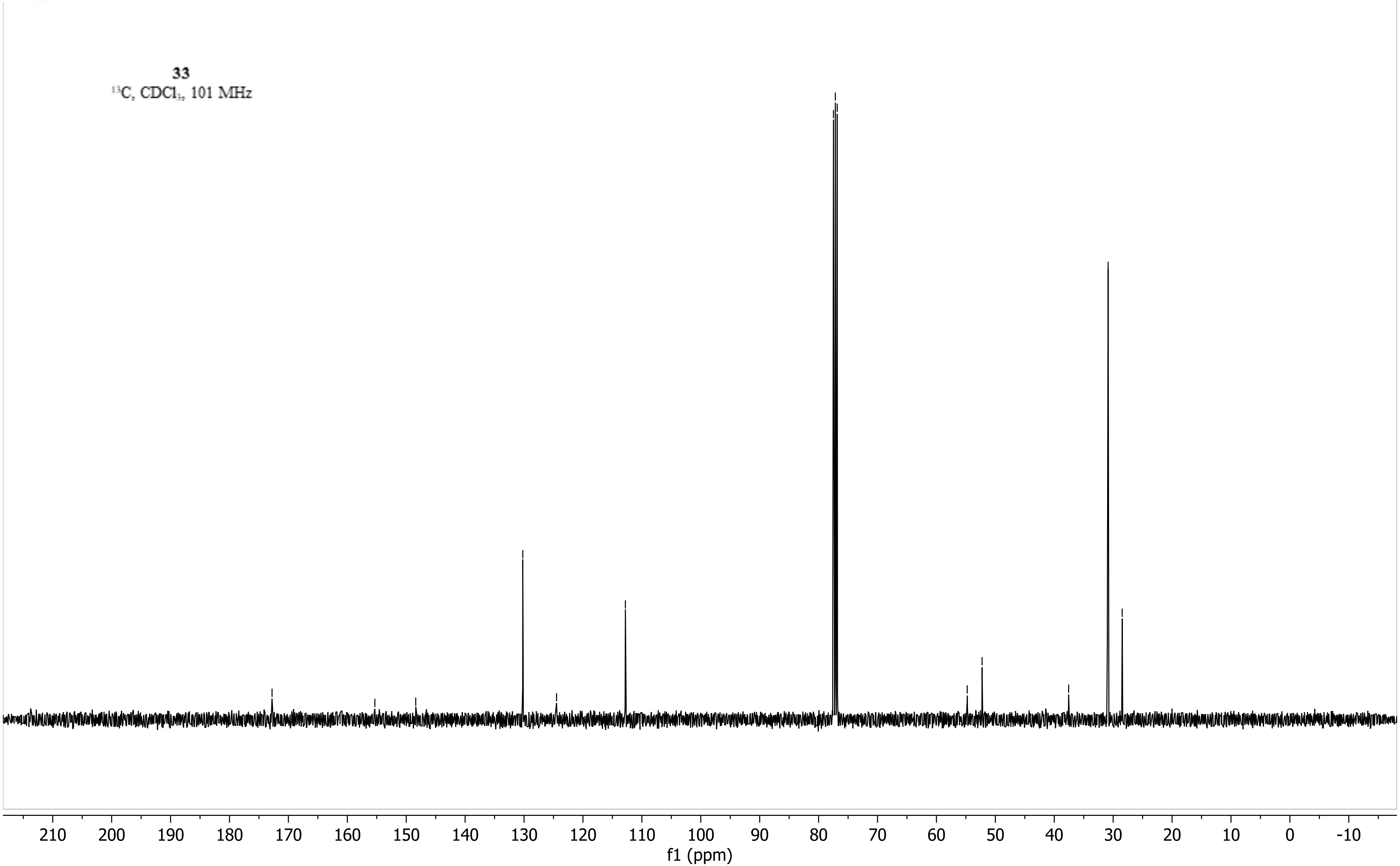
^{13}C, $CDCl_3$, 101 MHz

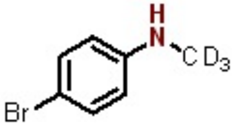

Me
N
H
HN
Boc
O
O
33
1H, CDCl3, 400 MHz
7.260 CDCl3
6.950
6.943
6.938
6.926
6.921
6.915
6.568
6.561
6.556
6.544
6.539
6.532
4.947
4.927
4.528
4.513
4.495
4.478
3.770
3.711
2.984
2.975
2.967
2.818
1.420
2.04
2.00
0.91
0.96
1.06
3.32
2.22
3.33
9.52
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



33

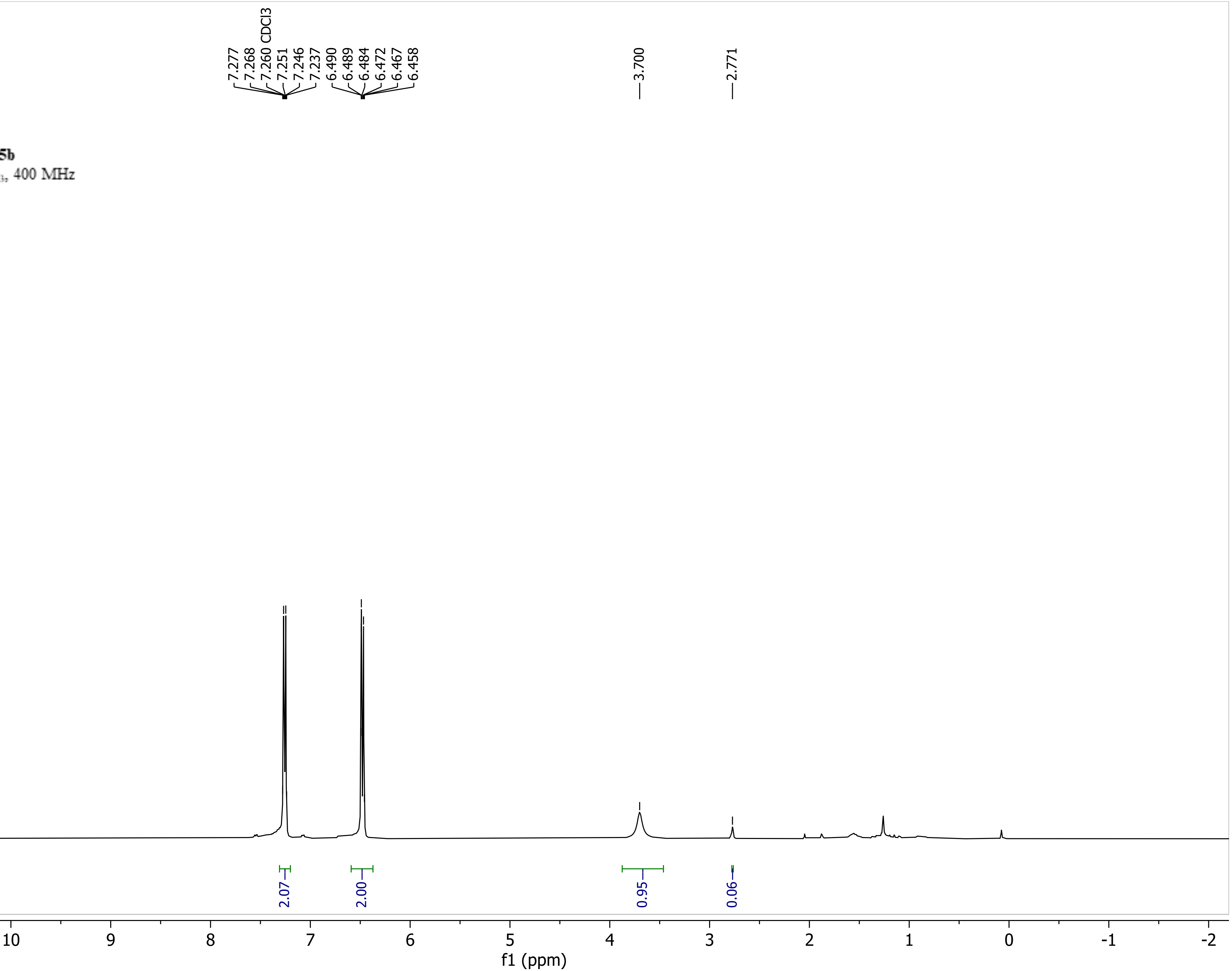
^{13}C, $CDCl_3$, 101 MHz

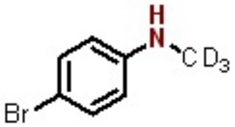




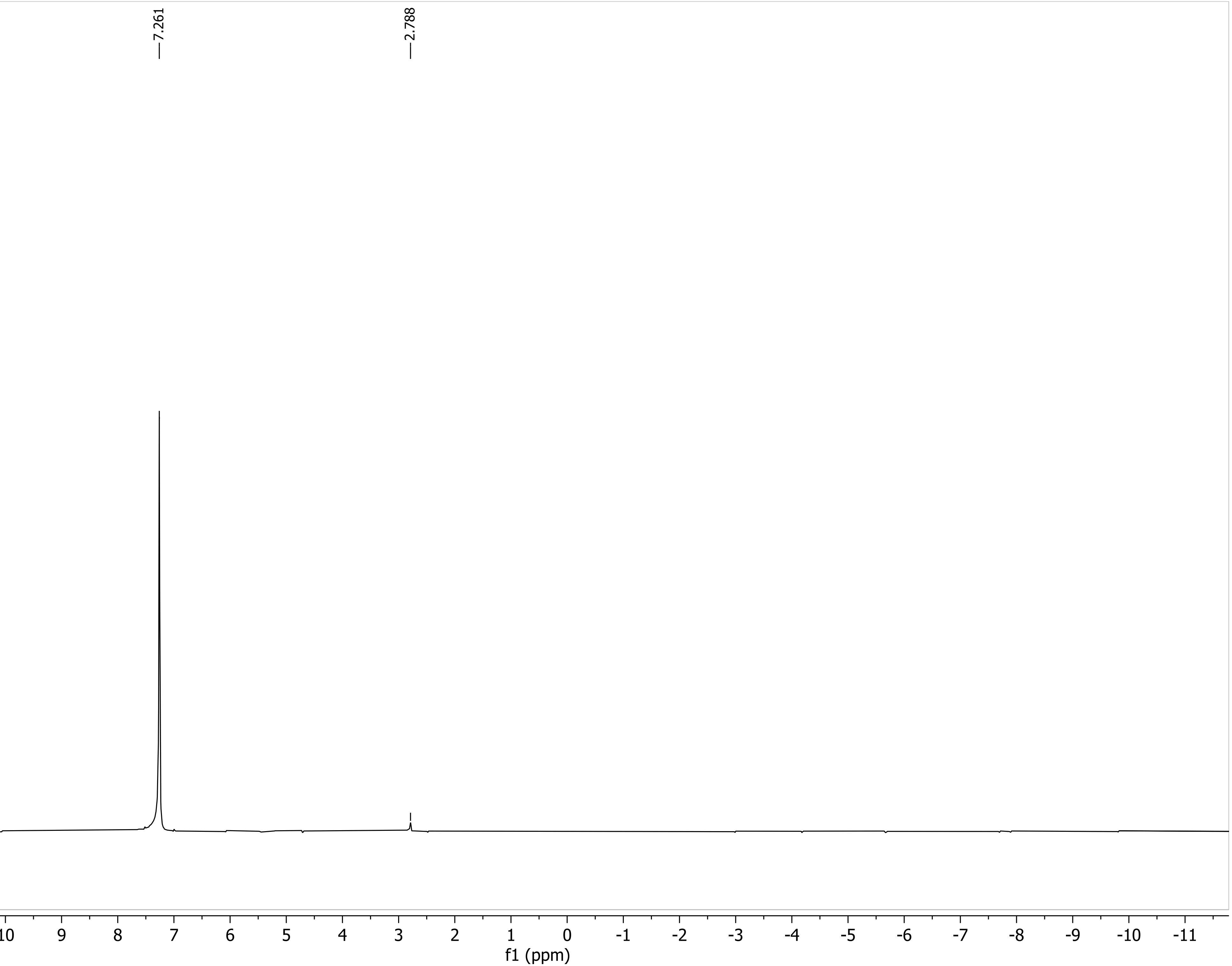
5b

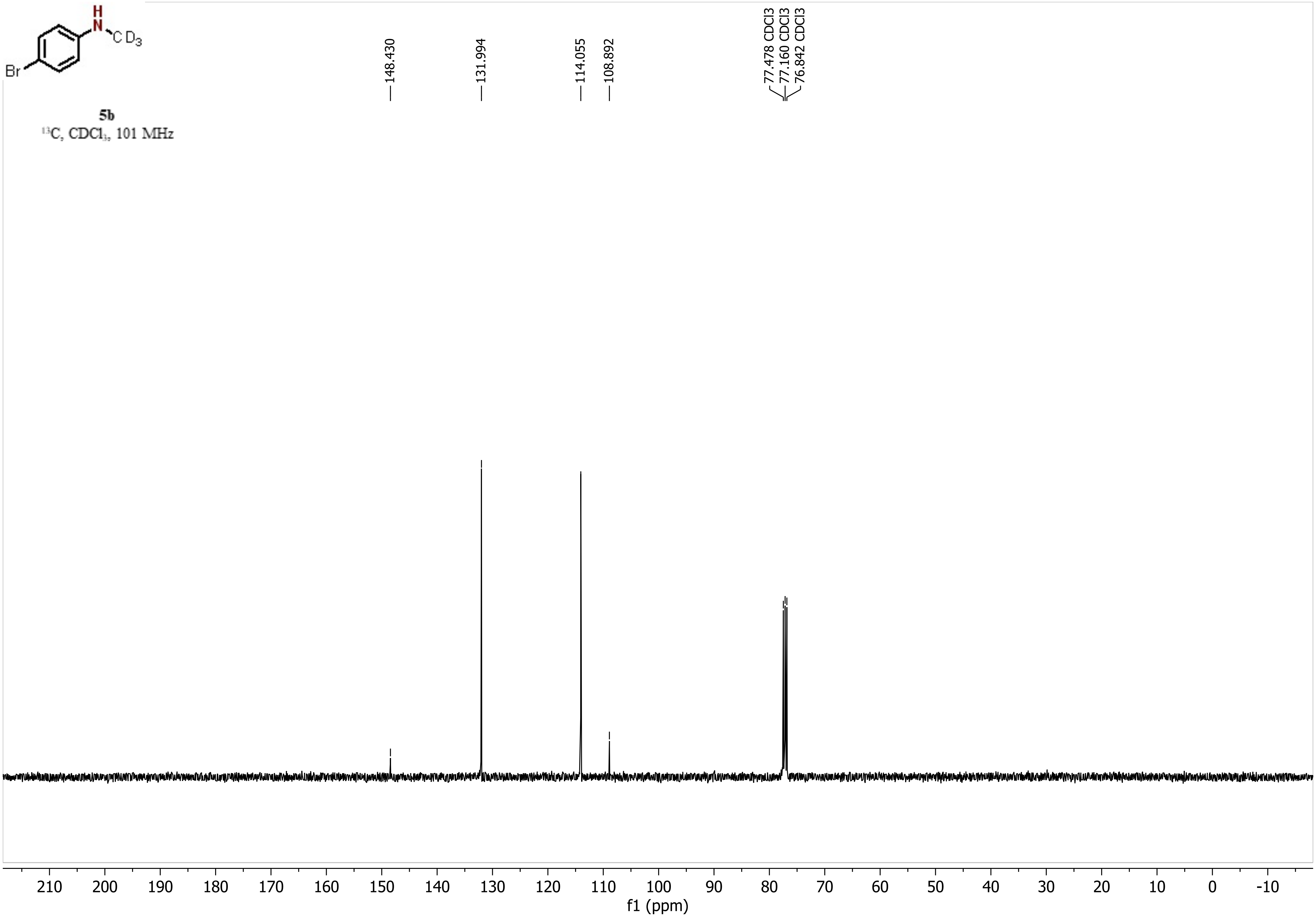
^1H, $CDCl_3$, 400 MHz





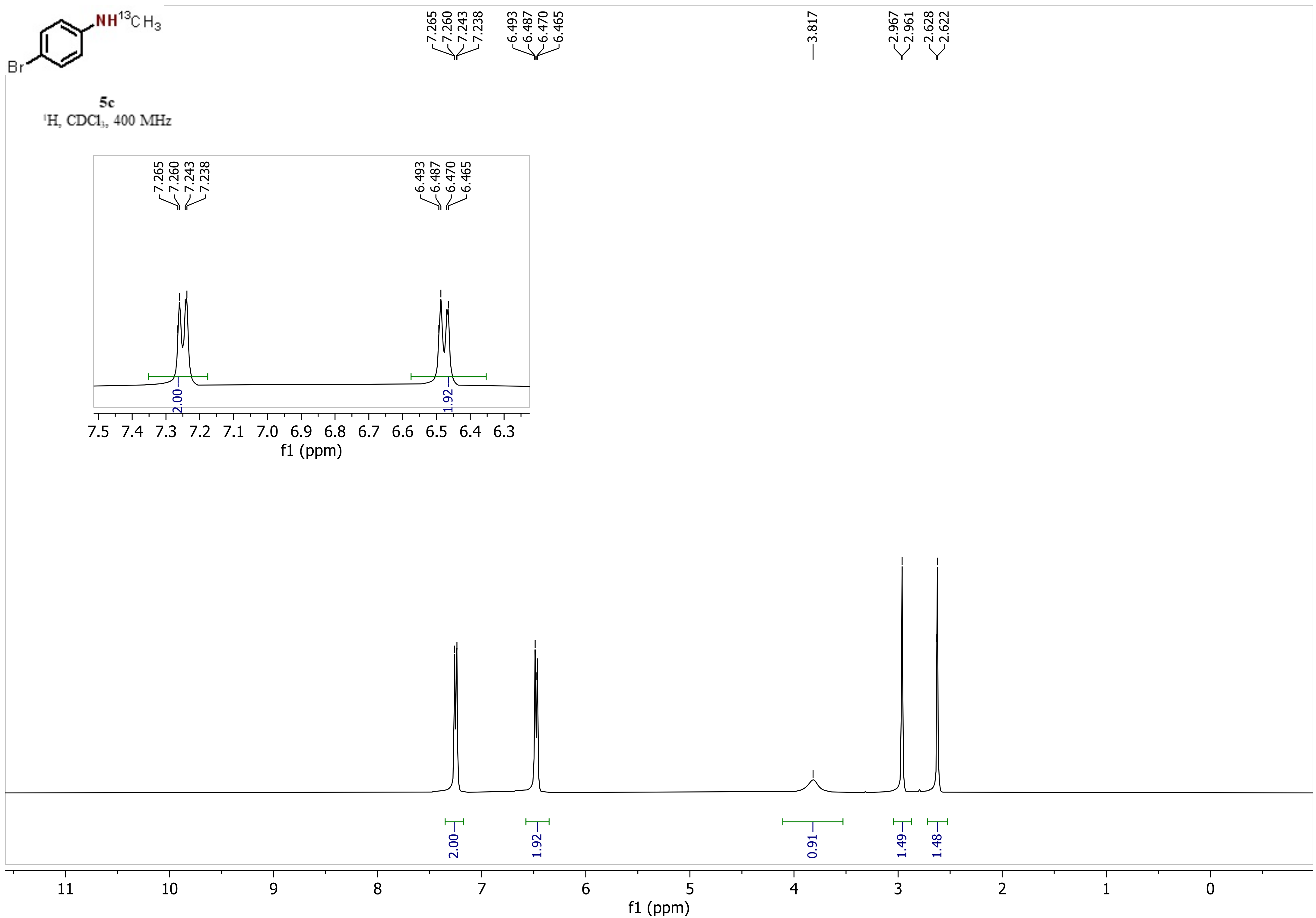
5b
^{2}H, $CDCl_3$, 61 MHz



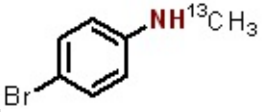


5b

^{13}C, $CDCl_3$, 101 MHz

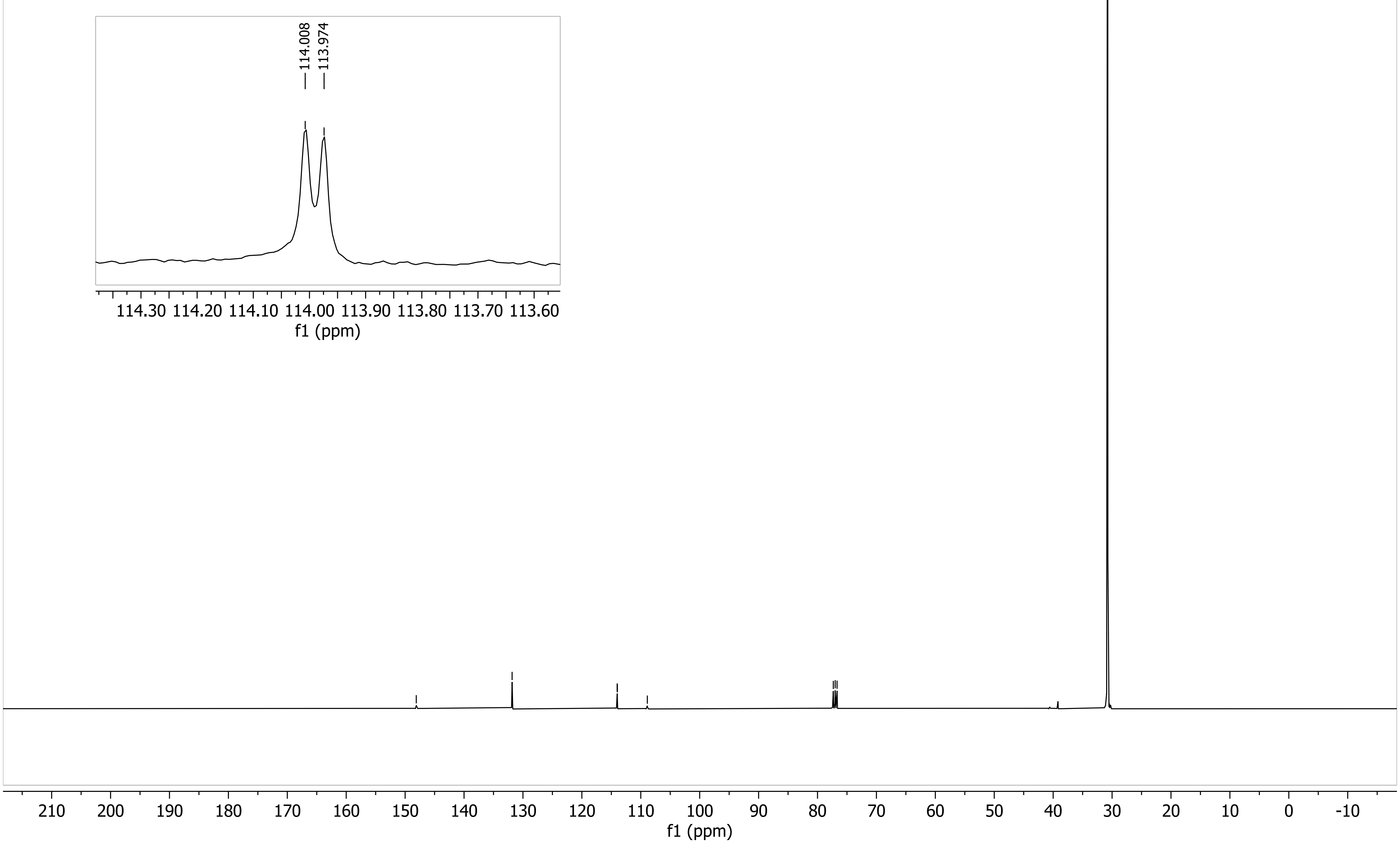


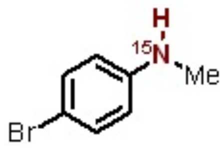
NH^{13}CH$_3$
Br
5c
^{1}H, CDCl$_3$, 400 MHz
7.265
7.260
7.243
7.238
6.493
6.487
6.470
6.465
3.817
2.967
2.961
2.628
2.622
2.00
1.92
0.91
1.49
1.48
f1 (ppm)



5c

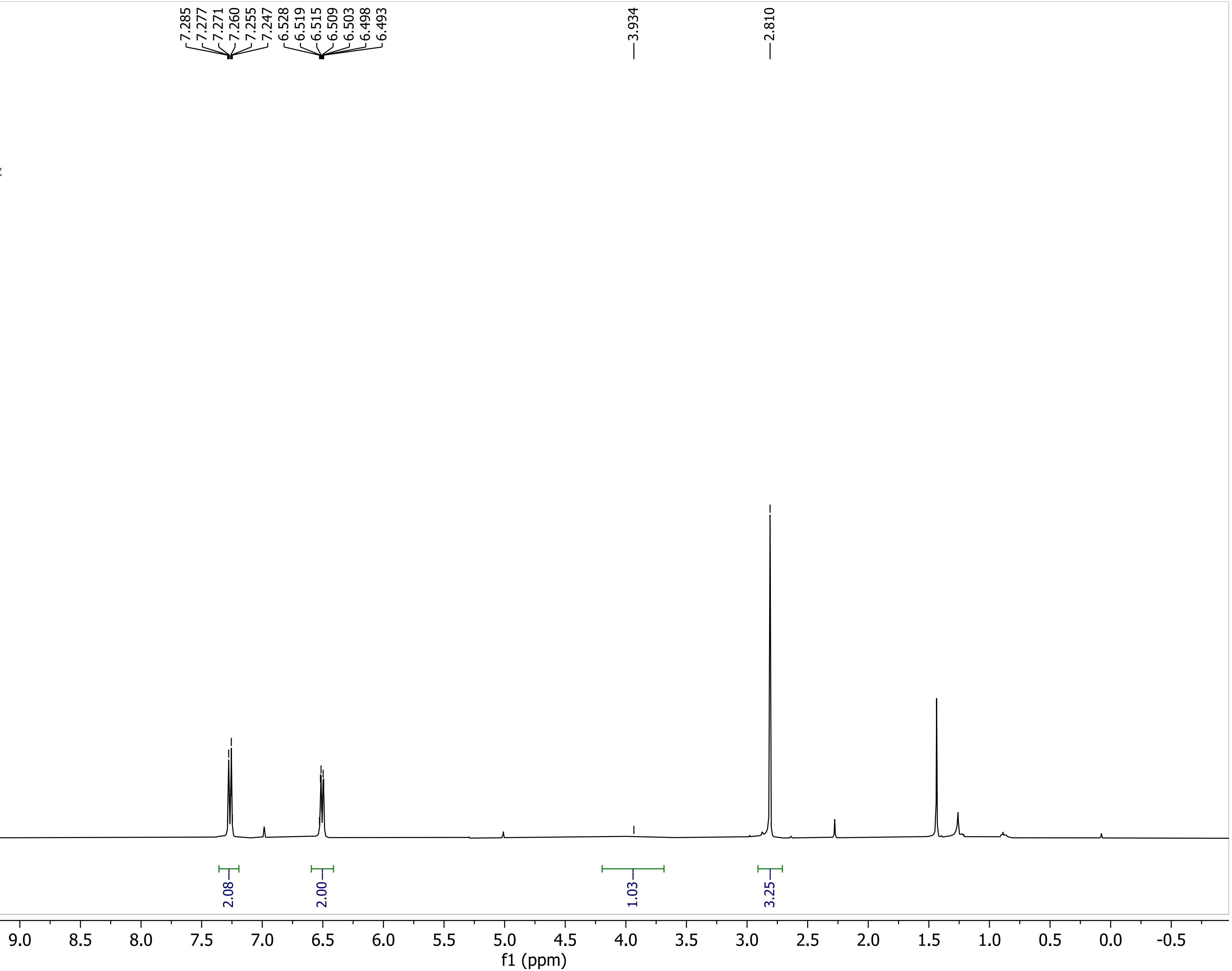
^{13}C, $CDCl_3$, 101 MHz

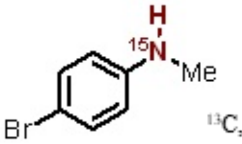




5d

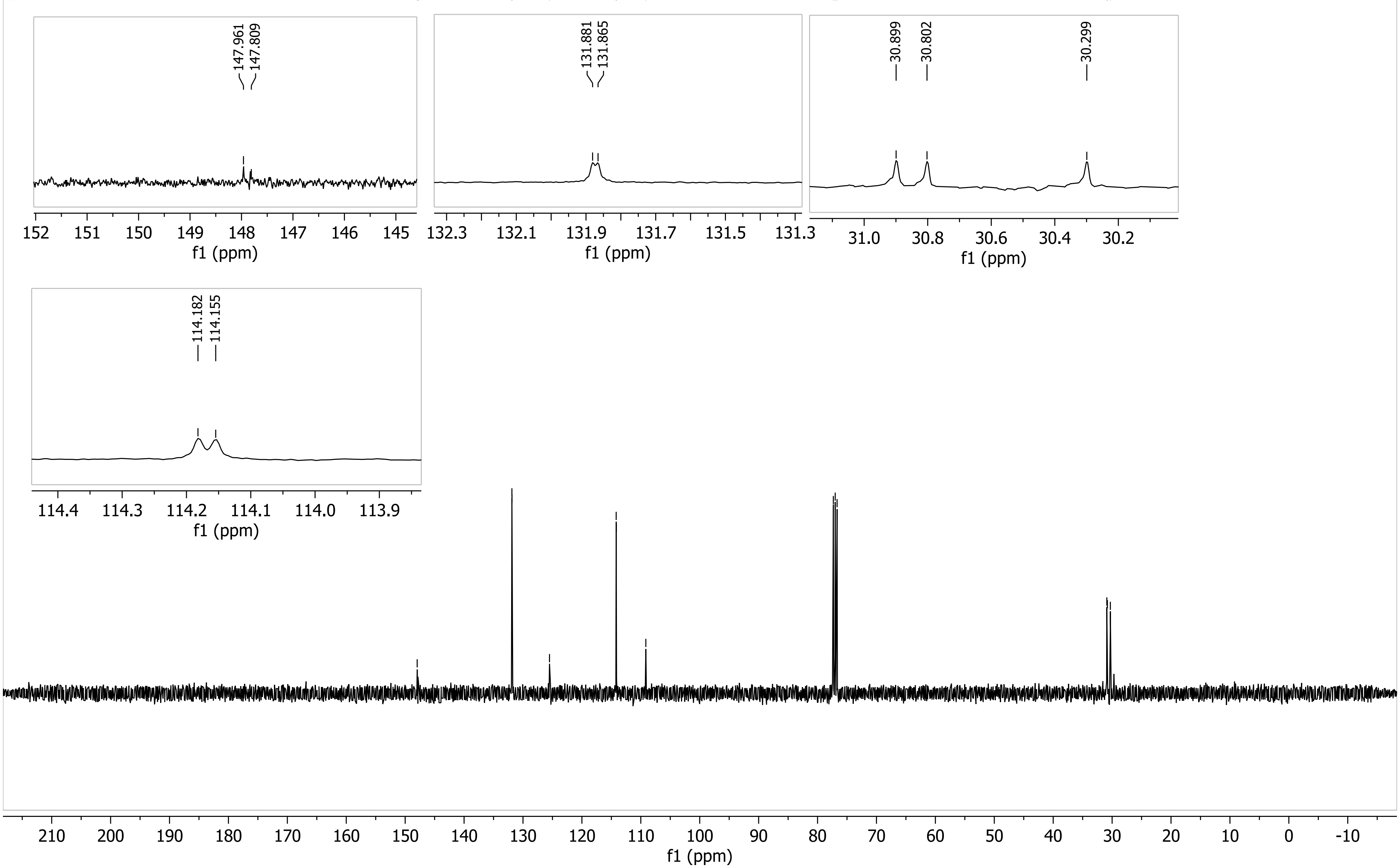
^{1}H, $CDCl_3$, 400 MHz

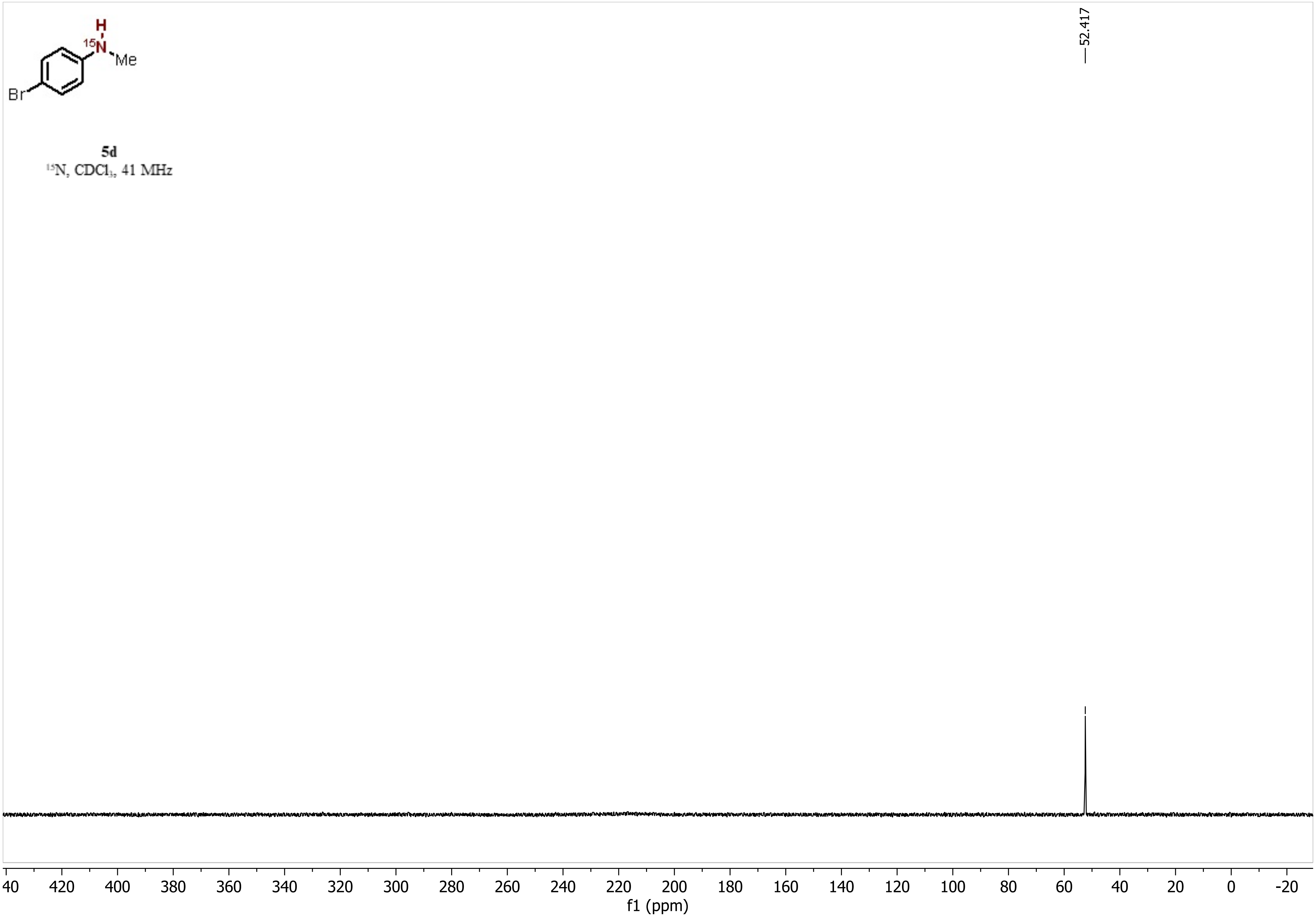




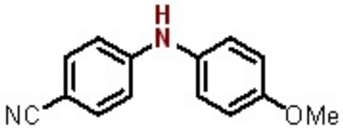
5d

^{13}C, $CDCl_3$, 101 MHz



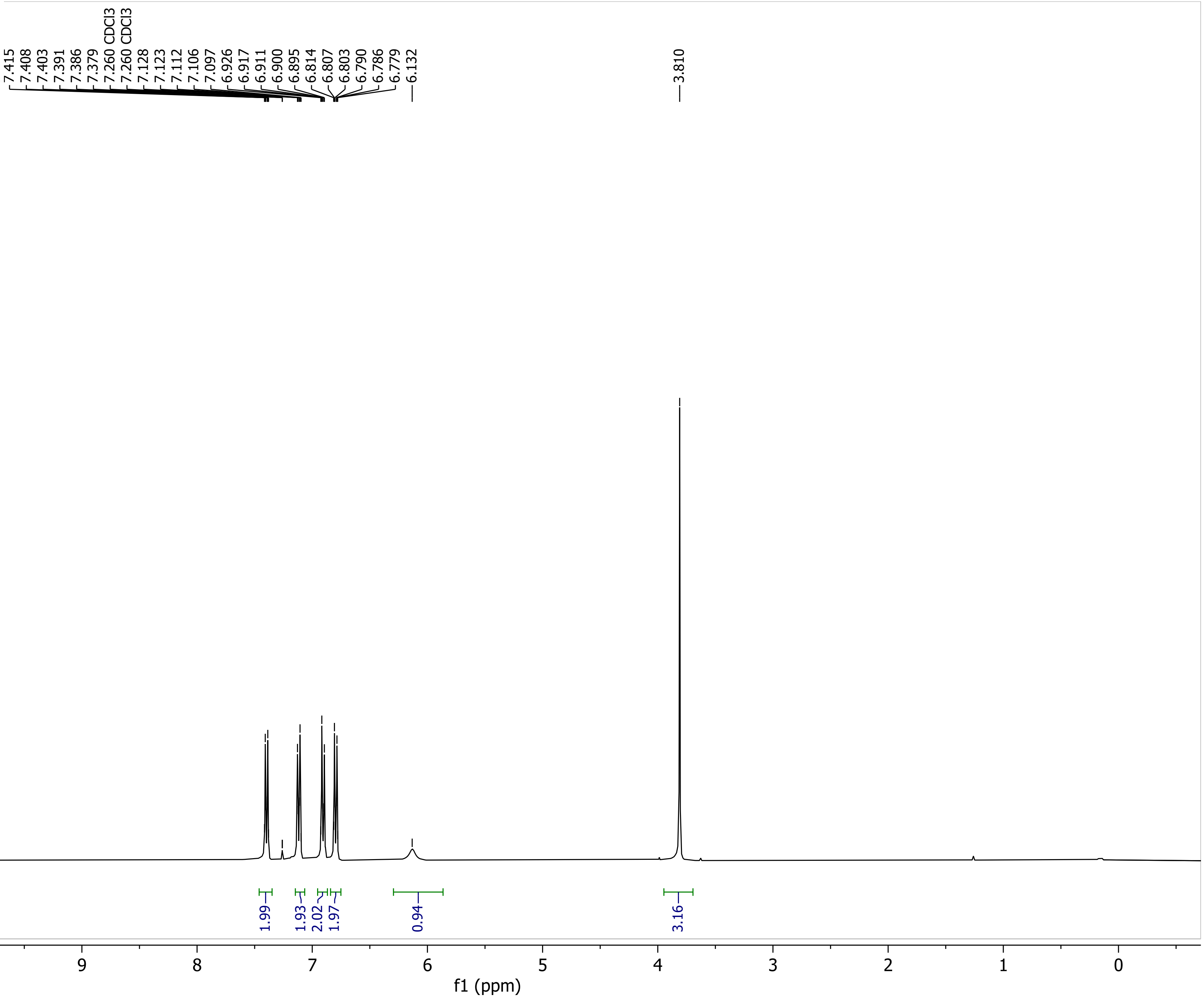


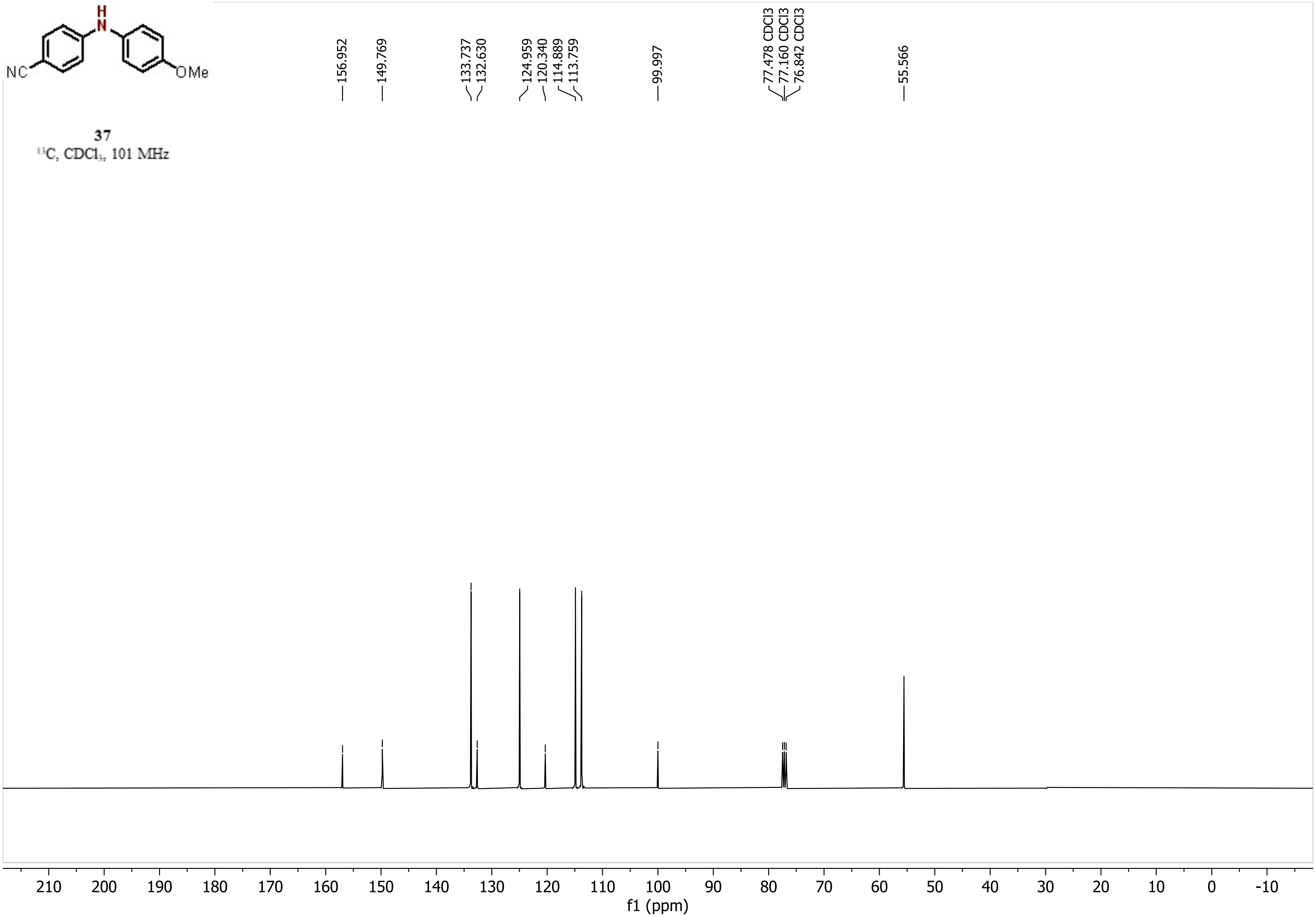
52.417
15N
Me
Br
5d
15N, CDCl3, 41 MHz
40 420 400 380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
f1 (ppm)



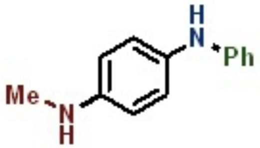
37

^1H, $CDCl_3$, 400 MHz



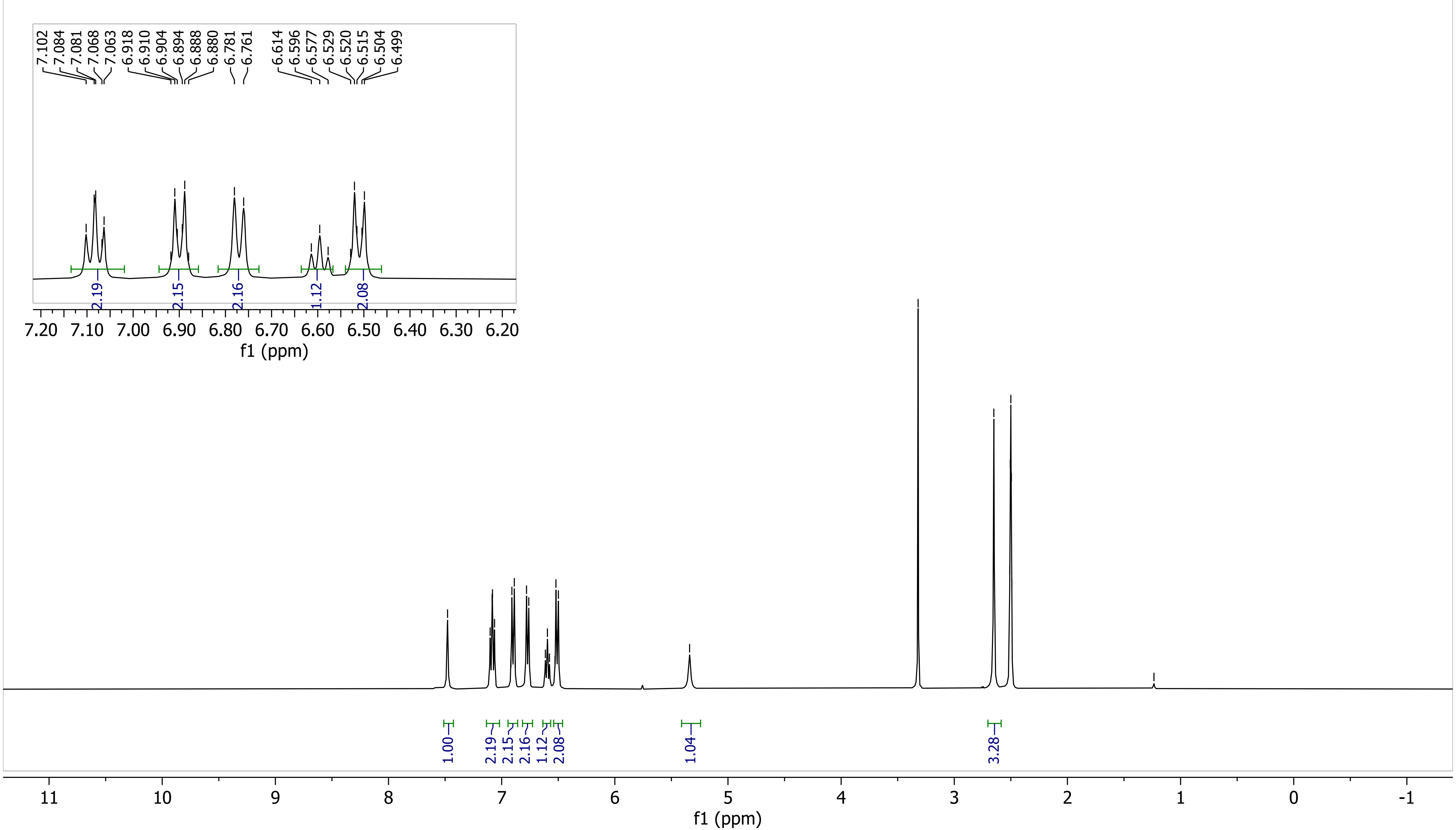


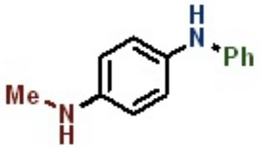
NC
OMe
H
N
37
^{13}C, CDCl$_3$, 101 MHz
156.952
149.769
133.737
132.630
124.959
120.340
114.889
113.759
99.997
77.478 CDCl3
77.160 CDCl3
76.842 CDCl3
55.566
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



40

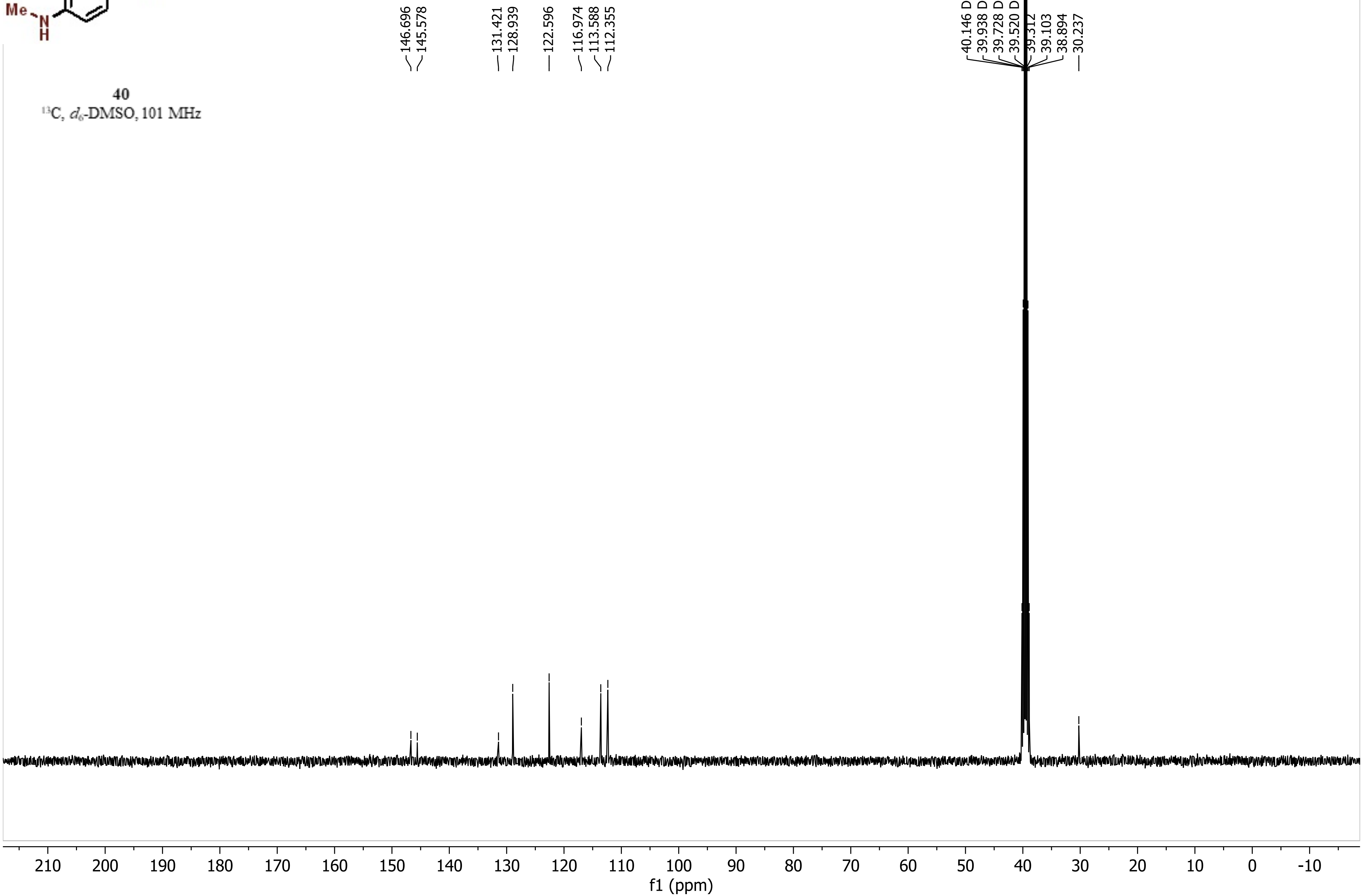
^1H, d_6-DMSO, 400 MHz

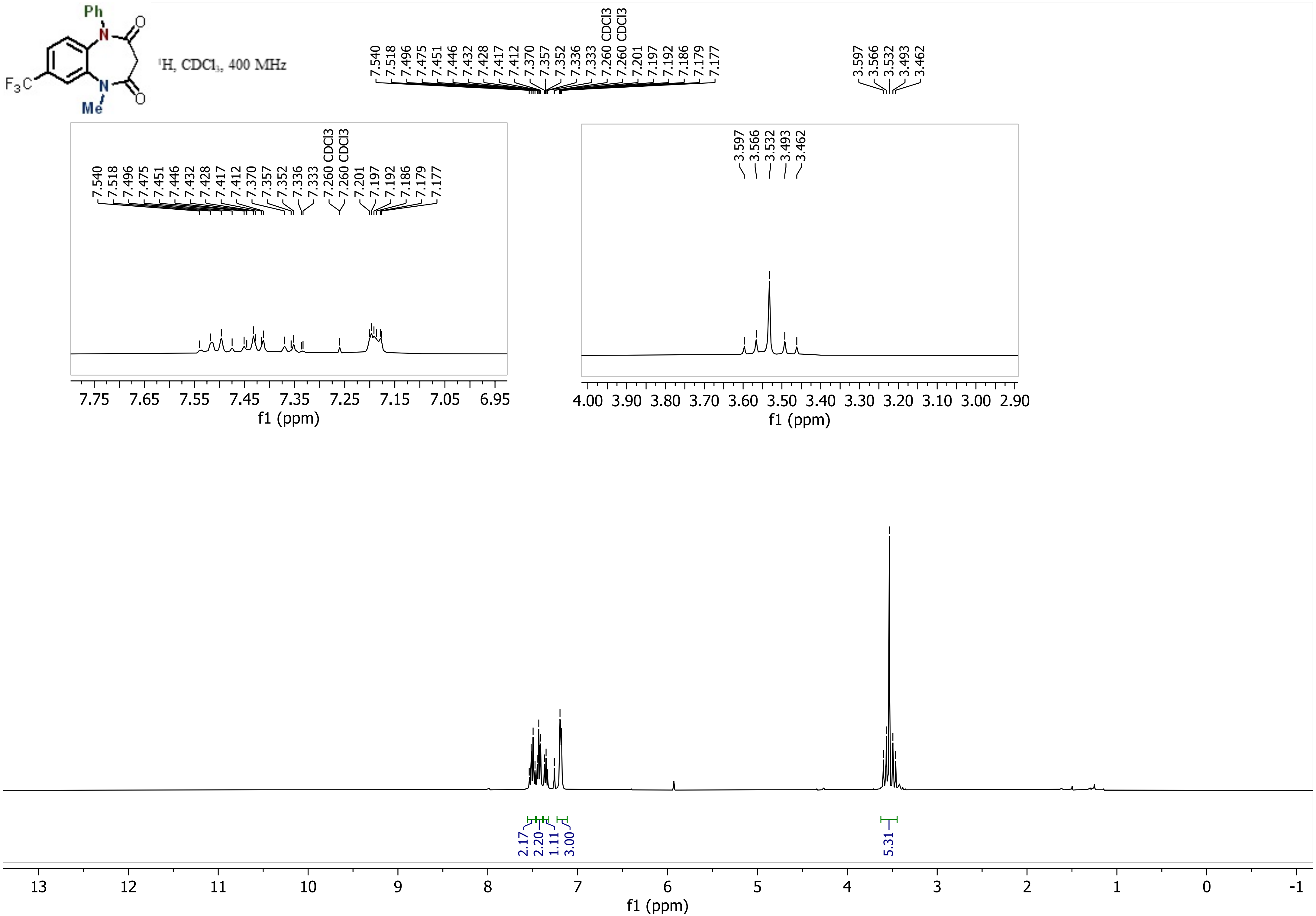




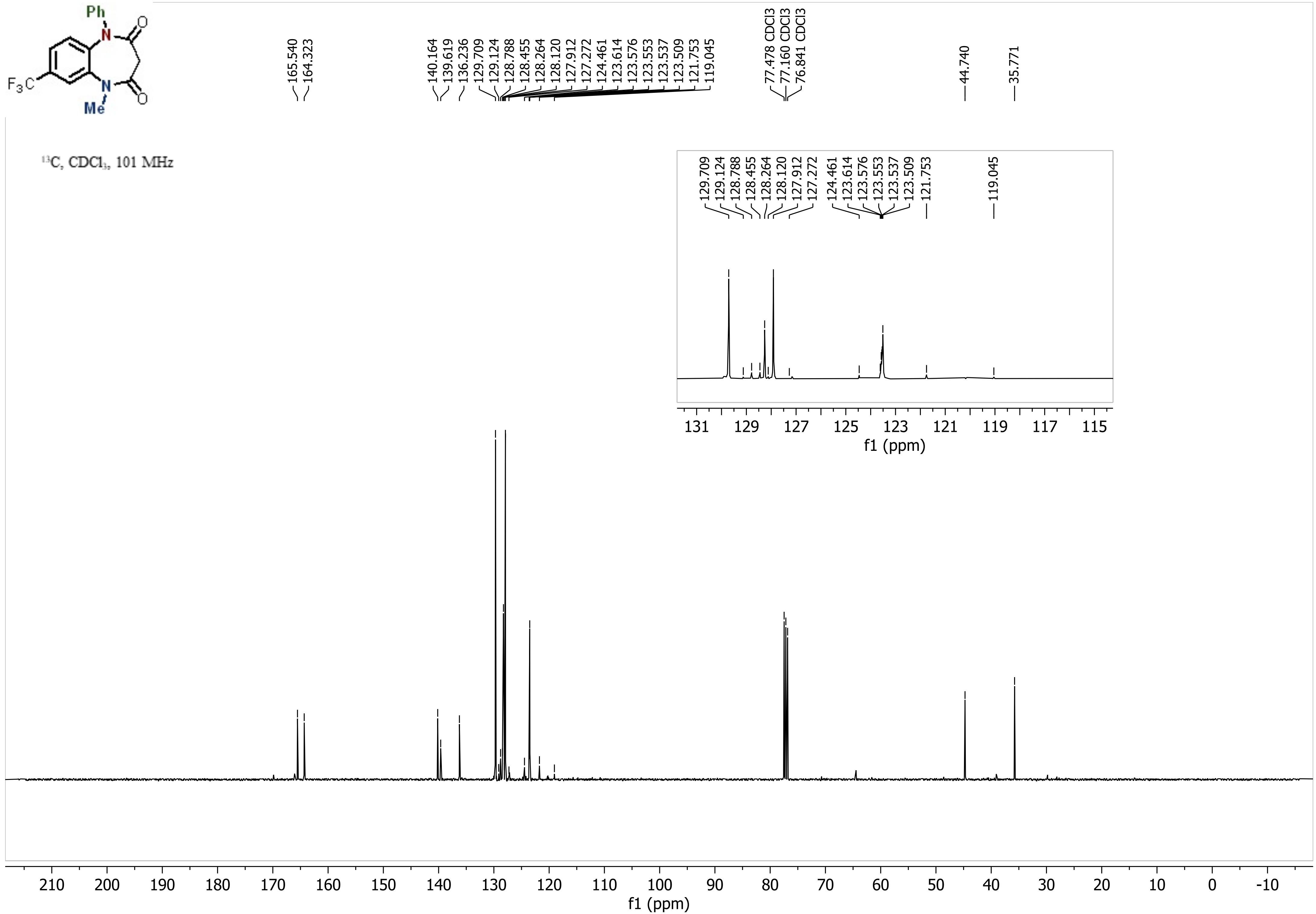
40

^{13}C, d_6-DMSO, 101 MHz





Ph
N
O
F3C
N
O
Me
1H, CDCl3, 400 MHz
7.540
7.518
7.496
7.475
7.451
7.446
7.432
7.428
7.417
7.412
7.370
7.357
7.352
7.336
7.333
7.260 CDCl3
7.260 CDCl3
7.201
7.197
7.192
7.186
7.179
7.177
3.597
3.566
3.532
3.493
3.462
7.75 7.65 7.55 7.45 7.35 7.25 7.15 7.05 6.95
f1 (ppm)
4.00 3.90 3.80 3.70 3.60 3.50 3.40 3.30 3.20 3.10 3.00 2.90
f1 (ppm)
2.17
2.20
1.11
3.00
5.31
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



^{13}C, $CDCl_3$, 101 MHz

Reference:

[1] Murata, M.; Sambommatsu, T.; Watanabe, S.; Masuda, Y. An efficient catalyst system for palladium-catalyzed borylation of aryl halides with pinacolborane. *Synlett*, **2006**, *12*, 1867.
[2] ^{13}C NMR peak for CD_3 was not resolved. Similar report see: Reznichenko, A. L.; Hultzsch, K. C. The Mechanism of Hydroaminoalkylation Catalyzed by Group 5 Metal Binaphtholate Complexes. *J. Am. Chem. Soc.* **2012**, *134*, 3300.
[3] Mansuy, D.; Battioni, P.; Chottard, J. C.; Riche, C.; Chiaroni, A. Nitrosoalkane Complexes of Iron-Porphyrins: Analogy between the Bonding Properties of Nitrosoalkanes and Dioxygen. *J. Am. Chem. Soc.* **1983**, *105*, 455.