Selective *N*-monomethylation of Primary Anilines with the Controllable Installation of *N*-CH_2D, *N*-CHD_2, and *N*-CD_3 Units

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1. General

^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{1}H, $\delta = 7.26$) as the internal standard]. ^{13}C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.0$) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet oftriplet, m = multiplet, s br = single broad. High-resolution mass spectra were obtained with a Thermo LTQ-Orbitrap (Thermo Fisher) using ESI, APCI or Thermo Q Exactive GC (Thermo Fisher) using EI or Waters Micromass GCT Premier (Milford, MA, USA) using CI. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus.Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Commercially available reagentswere purchased from Energy Chemical, J & K Scientific, Adamas-beta and Sigma-Aldrich Co., Inc. $Me_3N–BD_3$ was prepared according to the literature procedure.[1]

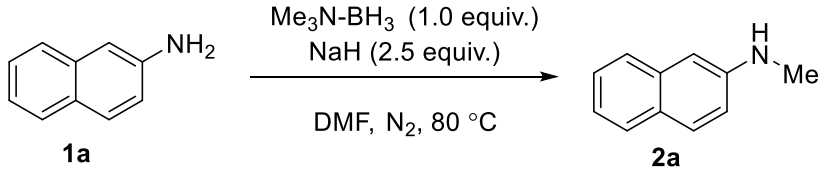
The percentage of D content was based on a decrease in the integral of the ^{1}H NMR signals of CDH_2 or CD_2H or CD_3 groups, as compared to the integral of the corresponding CH_3 signals in the methylated products. The ^{1}H NMR signals of interest were integrated relative to the resonance for aryl or alkyl hydrogen atoms that are not involved in the D-incorporation.

2. Synthesis of primary anilines 1

Aniline **1u**[2] was known compounds and prepared according to the literature procedures. Other anilines were commercially available and used without further purification.

3. *N*-monomethylation of primary anilines

General procedure A:



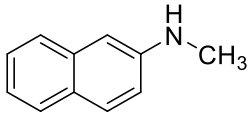
1a **2a**

To an N_2 flushed, oven-dried glass tube with a magnetic stir bar, 2-aminonaphthalene **1a** (58.5 mg, 0.409 mmol), $Me_3N–BH_3$ (31.8 mg, 0.436 mmol), NaH (43.3 mg, 1.80 mmol), and DMF (5 mL) were added. The reaction mixture was stirred at 80 ℃ for 1.5 h. The reaction was then quenched with saturated NH_4Cl (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford **2a** (52.4 mg, 0.333 mmol) in 82%yield.

Large scale reaction:

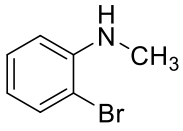
To an N_2 flushed, oven-dried glass vessel with a magnetic stir bar, 2-aminonaphthalene **1a** (2.000 g, 14.15 mmol), $Me_3N–BH_3$ (1.039 g, 14.24 mmol), NaH (1.435 g, 59.80 mmol), and DMF (50 mL) were added. The reaction mixture was stirred at 80 ℃ for 2 h. The reaction was then quenched with saturated NH_4Cl (50 mL) and extracted with ethyl acetate (50 mL x 3). The combined organic layers were washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford **2a** (1.918 g, 12.20 mmol) in 86%yield.

***N*-Methylnaphthalen-2-amine (2a)**



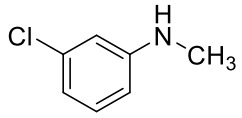
Brown oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (3H, s),3.57 (1H, s br), 6.77 (1H, d, *J*= 1.6 Hz), 6.83 (1H, dd, *J* = 8.8, 2.4 Hz),7.18 (1H, dd, *J* = 8.0,6.8 Hz), 7.35 (1H, dd, *J* = 8.0,7.2 Hz), 7.56-7.69 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 103.6, 117.8, 121.8, 125.9, 126.2, 127.4, 127.6, 128.7, 135.2, 146.9.The spectral data for this compound match that reported in the literature.[3]

2-Bromo-*N*-methylaniline (2b)



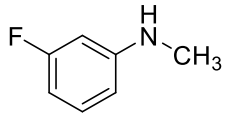
According to the general procedure A, the reaction of **1b** (71.3 mg, 0.415 mmol), $Me_3N–BH_3$ (30.0 mg, 0.411 mmol), NaH (41.4 mg, 1.73 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 3.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1) afford 42.5 mg (55%) **2b** as brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (3H, s), 4.36 (1H, s br), 6.55-6.66 (2H, m), 7.22 (1H, ddd, *J* = 8.0, 7.6, 0.8 Hz), 7.43 (1H, dd, *J* = 8.0, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 109.5, 110.7, 117.5, 128.5, 132.2, 145.9. The spectral data for this compound match that reported in the literature. [4]

3-Chloro-*N*-methylaniline (2c)



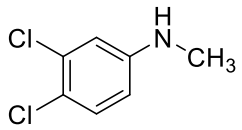
According to the general procedure A, the reaction of **1c** (53.6 mg, 0.420 mmol), $Me_3N–BH_3$ (29.3 mg, 0.402 mmol), NaH (43.9 mg, 1.83 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 2 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) afford 42.7 mg (72%) **2c** as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (3H, s), 3.79 (1H, s br), 6.47 (1H, ddd, *J* = 8.0, 2.0, 0.8 Hz), 6.58 (1H, dd, *J* = 2.0, 2.0 Hz), 6.68 (1H, ddd, *J* = 8.0, 2.0, 0.8 Hz), 7.09 (1H, dd, *J* = 8.0, 8.0 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 30.5, 110.8, 111.8, 116.9, 130.1, 135.0, 150.4. The spectral data for this compound match that reported in the literature.[5]

3-Fluoro-*N*-methylaniline (2d)



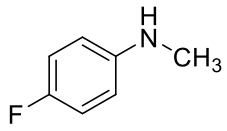
According to the general procedure A, the reaction of **1d** (45.7 mg, 0.411 mmol), $Me_3N–BH_3$ (30.0 mg, 0.411 mmol), NaH (40.4 mg, 1.68 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1) afford 30.9 mg (60%) **2d** as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ2.81(3H, s), 6.28(1H, ddd, *J* = 11.6, 2.4, 2.4 Hz), 6.34-6.41 (2H, m), 7.09 (1H, ddd, *J* = 8.0, 8.0, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 98.8 (d, *J* = 25.4 Hz), 103.5 (d, *J* = 21.3 Hz), 108.3 (d, *J* = 2.2 Hz), 130.2 (d, *J* = 10.2 Hz), 151.1 (d, *J* = 10.8 Hz), 164.2 (d, *J* = 240.9 Hz). The spectral data for this compound match that reported in the literature.[6]

3,4-Dichloro-*N*-methylaniline (2e)



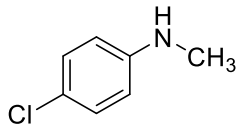
According to the general procedure A, the reaction of **1e** (65.6 mg, 0.405 mmol), $Me_3N–BH_3$ (29.9 mg, 0.410 mmol), NaH (41.6 mg, 1.73 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 49.9 mg (70%) **2e** as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (3H, s), 3.79 (1H, s br), 6.42 (1H, dd, *J* = 8.8, 2.8 Hz), 6.65 (1H, d, *J* = 2.8 Hz), 7.18 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 112.2, 113.1, 119.5, 130.4, 132.7, 148.7. The spectral data for this compound match that reported in the literature. [7]

4-Fluoro-*N*-methylaniline (2f)



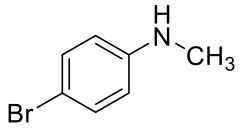
According to the general procedure A, the reaction of **1f** (46.4 mg, 0.418 mmol), $Me_3N–BH_3$ (30.4 mg, 0.417 mmol), NaH (42.5 mg, 1.77 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 32.5 mg (62%) **2f** as pale yellow oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 2.81 (3H, s), 3.50 (1H, s br), 6.52-6.57 (2H, m), 6.88-6.94 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 113.1 (d, *J* = 7.3 Hz), 115.6 (d, *J* = 22.4 Hz), 145.7, 155.8 (d, *J* = 233.2 Hz).The spectral data for this compound match that reported in the literature. [5]

4-Chloro-*N*-methylaniline (2g)



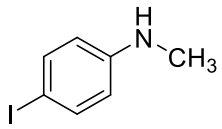
According to the general procedure A, the reaction of **1g** (51.3 mg, 0.402 mmol), $Me_3N–BH_3$ (29.7 mg, 1.0 equiv), NaH (41.5 mg, 2.5 equiv), and DMF (5 mL) under nitrogen at 80 ℃ for 1.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 51.9 mg (91%) **2g** as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (3H, s), 3.72 (1H, s br), 6.53 (1H, d, *J* = 8.8 Hz), 7.14 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 113.4, 121.7, 128.9, 147.8. The spectral data for this compound match that reported in the literature. [3]

4-Bromo-*N*-methylaniline (2h)



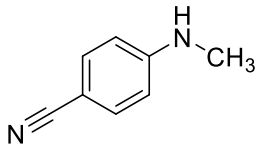
According to the general procedure A, the reaction of **1h** (68.8 mg, 0.400 mmol), $Me_3N–BH_3$ (30.1 mg, 0.413 mmol), NaH (40.9 mg, 1.70 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded 61.8 mg (83%) **2h** as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (3H, s), 3.71 (1H, s br), 6.47 (2H, d, *J* = 8.8 Hz), 7.25 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 108.7, 113.9, 131.8, 148.2. The spectral data for this compound match that reported in the literature. [3]

4-Iodo-*N*-methylaniline (2i)



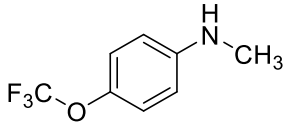
According to the general procedure A, the reaction of **1i** (88.6 mg, 0.405 mmol), $Me_3N–BH_3$ (30.5 mg, 0.418 mmol), NaH (40.5 mg, 1.69 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) afforded 66.1 mg (70%) **2i** as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (3H, s), 3.71 (1H, s br), 6.36 (2H, d, *J* = 8.8 Hz), 7.40 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 77.6, 114.5, 137.6, 148.7.The spectral data for this compound match that reported in the literature. [8]

4-(Methylamino)benzonitrile (2j)



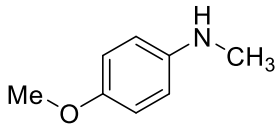
According to the general procedure A, the reaction of **1j** (47.9 mg, 0.406 mmol), $Me_3N–BH_3$ (31.1 mg, 0.426 mmol), NaH (41.0 mg, 1.71 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) afforded 39.0 mg (73%) **2j** as pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (3H, d, *J* = 4.8 Hz), 4.42 (1H, s br), 6.54 (2H, d, *J* = 8.8 Hz), 7.40 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.8, 97.9, 111.7, 120.6, 133.5, 152.2. The spectral data for this compound match that reported in the literature. [9]

_N_-Methyl-4-(trifluoromethoxy)aniline (2k)



According to the general procedure A, the reaction of **1k** (77.1 mg, 0.435 mmol), $Me_3N–BH_3$ (29.5 mg, 0.404 mmol), NaH (42.4 mg, 1.77 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 56.0 mg (67%) **2k** as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (3H, s), 3.78 (1H, s br), 6.56 (2H, d, *J* = 8.4 Hz), 7.06 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 112.5, 120.7 (q, *J* = 253.4 Hz), 122.3, 140.3, 148.1. The spectral data for this compound match that reported in the literature. [5]

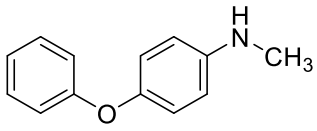
4-Methoxy-_N_-methylaniline (2l)



According to the general procedure A, the reaction of **1l** (50.1 mg, 0.407 mmol), $Me_3N–BH_3$ (30.3 mg, 0.415 mmol), NaH (41.8 mg, 1.74 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded 49.1 mg (88%) **2l** as pale yellow solid; ^{1}H

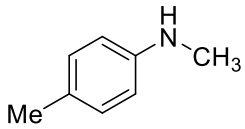
NMR(400 MHz, $CDCl_3$) δ 2.81 (3H, s), 3.26 (1H, s br), 3.76 (3H, s), 6.60 (2H, ddd, *J* = 8.8, 3.6, 2.4 Hz), 6.81 (2H, ddd, *J* = 8.8, 3.6, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 55.8, 113.6, 114.8, 143.6, 152.0. The spectral data for this compound match that reported in the literature.[10]

***N*-Methyl-4-phenoxyaniline (2m)**



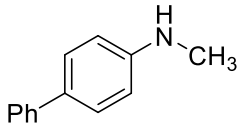
According to the general procedure A, the reaction of **1m** (76.2 mg, 0.411 mmol), $Me_3N–BH_3$ (30.6 mg, 0.419 mmol), NaH (42.6 mg, 1.78 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 4 h 40 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 70.7 mg (86%) **2m** as yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.78 (3H, s), 3.44 (1H, s br), 6.56 (2H, ddd, *J* = 9.2, 3.2, 2.4 Hz), 6.88-6.95 (4H, m), 6.98 (1H, t, *J* = 7.2 Hz), 7.22-7.28 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 113.2, 116.9, 121.2, 121.8, 129.4, 145.9, 147.4, 159.1. The spectral data for this compound match that reported in the literature.[11]

***N*,4-Dimethylaniline (2n)**



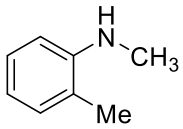
According to the general procedure A, the reaction of **1n** (44.0 mg, 0.411 mmol), $Me_3N–BH_3$ (30.4 mg, 0.417 mmol), NaH (39.7 mg, 1.65 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 3 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afford 35.9 mg (72%) **2n** as yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (3H, s), 2.86 (3H, s), 3.52 (1H, s br), 6.60 (2H, d, *J* = 8.4 Hz), 7.07 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 31.0, 112.5, 126.3, 129.6, 147.1. The spectral data for this compound match that reported in the literature. [12]

***N*-Methyl-[1,1'-biphenyl]-4-amine (2o)**



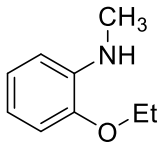
According to the general procedure A, the reaction of **1o** (67.7 mg, 0.400 mmol), $Me_3N–BH_3$ (30.3 mg, 0.415 mmol), NaH (40.5 mg, 1.69 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 8 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) afforded 36.3 mg (50%) **2o** as yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (3H, s), 3.75 (1H, s br), 6.66 (2H, d, *J* = 8.8 Hz), 7.24 (1H, t, *J* = 7.2 Hz), 7.38 (2H, dd, *J* = 7.6,7.2 Hz), 7.45 (2H, d, *J* = 8.8 Hz), 7.54 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 112.6, 126.0, 126.2, 127.9, 128.6, 130.1, 141.3, 148.7. The spectral data for this compound match that reported in the literature. [10]

_N_,2-Dimethylaniline (2p)



According to the general procedure A, the reaction of **1p** (44.6 mg, 0.416 mmol), $Me_3N–BH_3$ (31.0 mg, 0.425mmol), NaH (40.2 mg, 1.68 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1h 40 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) afford 33.1 mg (66%) **2p** as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (3H, s), 2.94 (3H, s), 3.60 (1H, s br), 6.66 (1H, d, *J* = 8.0 Hz), 6.72 (1H, dd, *J* = 7.6, 7.2Hz), 7.10 (1H, d, *J* = 7.2 Hz), 7.21 (1H, dd, *J* = 8.0, 7.6Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 30.7, 109.1, 116.8, 121.8, 127.1, 129.8, 147.2. The spectral data for this compound match that reported in the literature. [9]

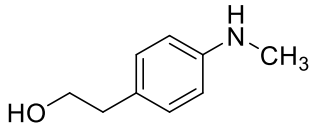
2-Ethoxy-_N_-methylaniline (2q)



According to the general procedure A, the reaction of **1q** (55.4 mg, 0.404 mmol), $Me_3N–BH_3$ (30.2 mg, 0.414 mmol), NaH (42.8 mg, 1.78 mmol), and DMF (5 mL) under

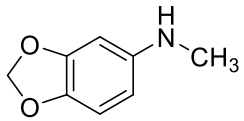
nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 27.1 mg (44%) **2q** as orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (3H, t, *J* = 7.2 Hz), 2.90 (3H, s), 4.08 (2H, q, *J* = 7.2Hz), 6.61-6.71 (2H, m), 6.78 (1H, dd, *J* = 8.0, 1.6 Hz), 6.92 (1H, ddd, *J* = 7.6, 7.6, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 30.3, 63.6, 109.3, 110.1, 116.2, 121.2, 139.4, 146.1.The spectral data for this compound match that reported in the literature.[11]

2-(4-(Methylamino)phenyl)ethan-1-ol (2s)



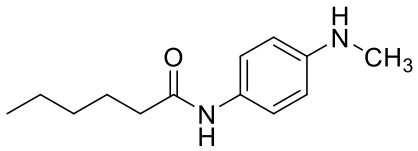
According to the general procedure A, the reaction of **1s** (57.6 mg, 0.420 mmol), $Me_3N–BH_3$ (30.3 mg, 0.415 mmol), NaH (44.1 mg, 1.84 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 3 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2 : 1) afforded 39.4 mg (62%) **2s**as white solid, mp 84-85 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (2H, t, *J* = 6.4 Hz), 2.82 (3H, s), 3.79 (2H, t, *J* = 6.4 Hz), 6.59 (2H, d, *J* = 8.4 Hz), 7.06 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 38.2, 63.9, 112.7, 126.7, 129.7, 147.9. The spectral data for this compound match that reported in the literature.[13]

***N*-Methylbenzo[d][1,3]dioxol-5-amine (2t)**



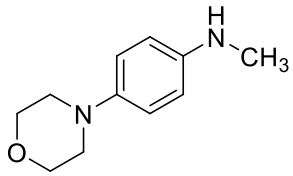
According to the general procedure A, the reaction of **1t** (58.4 mg, 0.426 mmol), $Me_3N–BH_3$ (31.3 mg, 0.429 mmol), NaH (42.8 mg, 1.78 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2 : 1) afforded 56.7 mg (88%) **2t** as pale yellow solid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 2.78 (3H, s), 3.47 (1H, sbr), 5.86 (2H, s), 6.05 (1H, dd, *J* = 8.0, 2.4 Hz), 6.25 (1H, d, *J* = 2.4 Hz), 6.69 (1H, d, *J* = 8.0Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 95.4, 100.4, 103.6, 108.5, 139.4, 145.1, 148.2. The spectral data for this compound match that reported in the literature. [3]

***N*-(4-(Methylamino)phenyl)hexanamide (2u)**



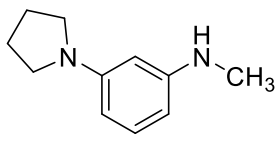
According to the general procedure A, the reaction of **1u** (83.1 mg, 0.403 mmol), $Me_3H–BH_3$ (30.7 mg, 0.421 mmol), NaH (41.4 mg, 1.73 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 3 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 1 : 1) afforded 50.2 mg (57%) **2u** as pale yellow solid, mp 67-68 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26-1.34 (4H, m), 1.63-1.71(2H, m), 2.26 (2H, t, *J* = 7.6 Hz), 2.77 (3H, s), 3.60 (1H, s br), 6.50 (2H, ddd, *J* = 8.8, 3.2, 2.0 Hz), 7.23-7.31 (2H, ddd, *J* = 8.8, 3.2, 2.0 Hz), 7.79 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.3, 25.4, 30.8, 31.3, 37.2, 112.3, 122.1, 128.3, 146.2, 171.6. EIHRMS: Found: *m/z*221.1651. Calcd for $C_{13}H_{21}N_2O$: $(M+H)^+$221.1654.

***N*-Methyl-4-morpholinoaniline (2v)**



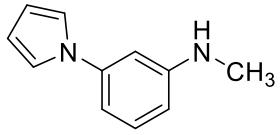
According to the general procedure A, the reaction of **1v** (73.5 mg, 0.412 mmol), $Me_3N–BH_3$ (29.6 mg, 0.406 mmol), NaH (39.7 mg, 1.65 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 1 : 1) afford 61.8 mg (78%) **2v** as pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (3H, s), 3.02 (4H, t, *J* = 4.8 Hz), 3.35 (1H, s br), 3.86 (4H, t, *J* = 4.8 Hz), 6.61 (2H, d, *J* = 8.8 Hz), 6.86 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 51.3, 67.0, 113.4, 118.3, 143.4, 144.0. The spectral data for this compound match that reported in the literature. [11]

***N*-Methyl-3-(pyrrolidin-1-yl)aniline (2w)**



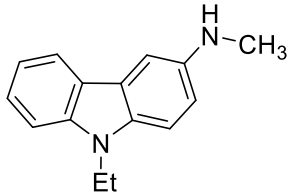
According to the general procedure A, the reaction of **1w** (64.5 mg, 0.398 mmol), $Me_3N–BH_3$ (30.7 mg, 0.421 mmol), NaH (42.2 mg, 1.76 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1) afforded 28.7 mg (41%) **2w** as a pale yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97-2.04 (4H, m), 2.86 (3H, s), 3.27-3.34 (4H, m), 5.86 (1H, dd, *J* = 2.4,2.0 Hz), 6.01-6.04 (2H, m), 7.07 (1H, dd, *J* = 8.0, 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 30.9, 47.5, 95.8, 100.8, 101.9, 129.7, 149.0, 150.4. The spectral data for this compound match that reported in the literature. [11]

_N_-Methyl-3-(1H-pyrrol-1-yl)aniline (2x)



According to the general procedure A, the reaction of **1x** (66.2 mg, 0.418 mmol), $Me_3N–BH_3$ (30.0 mg, 0.411 mmol), NaH (42.6 mg, 1.78 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 4.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 61.0 mg (85%) **2x** as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (3H, s), 3.78 (1H, s br), 6.31 (2H, dd, *J* = 2.4, 2.0 Hz), 6.44 (1H, ddd, *J* = 8.0, 2.4, 0.8 Hz), 6.55 (1H, dd, *J* = 2.4,2.0 Hz), 6.70 (1H, ddd, *J* = 8.0, 2.0, 0.8 Hz), 7.05 (2H, dd, *J* =2.4,2.0Hz), 7.17 (1H, dd, *J* = 8.0, 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 104.3, 109.4, 109.8, 119.4, 130.0, 141.8, 150.3. The spectral data for this compound match that reported in the literature.[11]

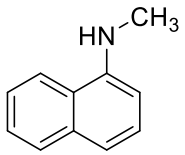
9-Ethyl-_N_-methyl-9H-carbazol-3-amine (2y)



According to the general procedure A, the reaction of **1y** (86.8 mg, 0.413 mmol), $Me_3N–BH_3$ (30.5 mg, 0.418 mmol), NaH (42.0 mg, 1.75 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 3 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3 : 1) afforded 72.4 mg (78%) **2y** as brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, t, *J* = 7.2 Hz), 2.89 (3H, s), 3.51 (1H, s br), 4.22 (2H, q, *J* =

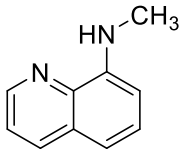
7.2 Hz), 6.82 (1H, dd, *J* = 8.8, 1.6 Hz), 7.12-7.19 (2H, m), 7.29-7.30(2H, m), 7.39 (1H, t, *J* = 7.6 Hz), 8.01 (1H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 32.1, 37.4, 102.6, 108.3, 109.0, 114.2, 117.8, 120.3, 122.6, 123.5, 125.2, 133.9, 140.2, 142.8. EIHRMS: Found: *m/z*224.1317. Calcd for $C_{15}H_{16}N_2$: M^+ 224.1308.

_N_-Methylnaphthalen-1-amine (2z)



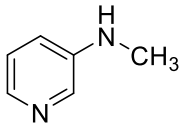
According to the general procedure A, the reaction of **1z** (59.3 mg, 0.414 mmol), Me_3N–BH_3 (30.3 mg, 0.415 mmol), NaH (41.1 mg, 1.71 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 1.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) afforded 51.3 mg (79%) **2z** as brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (3H, s), 4.26 (1H, s br), 6.57 (1H, d, *J* = 7.2 Hz), 7.23 (1H, d, *J* = 8.0 Hz), 7.31-7.43 (3H, m), 7.72 (1H, d, *J* = 8.0 Hz), 7.77 (1H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 103.7, 117.2, 119.8, 123.4, 124.6, 125.6, 126.6, 128.6, 134.1, 144.4. The spectral data for this compound match that reported in the literature. [3]

_N_-Methylquinolin-8-amine (2aa)



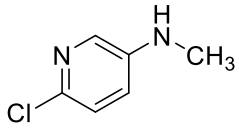
According to the general procedure A, the reaction of **1aa** (57.8 mg, 0.401 mmol), Me_3N–BH_3 (29.5 mg, 0.404 mmol), NaH (40.5 mg, 1.69 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afford 23.9 mg (38%) **2aa** as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (3H, s), 6.15 (1H, s br), 6.66 (1H, d, *J* = 7.6 Hz), 7.06 (1H, d, *J* = 8.0 Hz), 7.36 (1H, dd, *J* = 4.0, 8.0 Hz), 7.42 (1H, dd, *J* = 7.6, 8.0 Hz), 8.06 (1H, dd, *J* = 8.0, 1.6 Hz), 8.72 (1H, dd, *J* = 4.0, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.0, 104.1, 113.6, 121.3, 127.8, 128.5, 136.0, 138.2, 145.8, 146.8. The spectral data for this compound match that reported in the literature. [14]

_N_-Methylpyridin-3-amine (2ab)



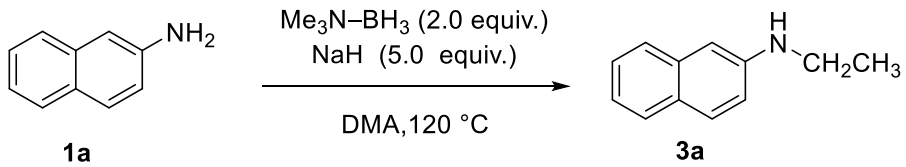
According to the general procedure A, the reaction of **1ab** (37.4 mg, 0.397 mmol), $Me_3N–BH_3$ (29.8 mg, 0.408 mmol), NaH (40.3 mg, 1.68 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 2 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) afford 16.6 mg (39%) **2ab** as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (3H, s), 3.91 (1H, s br), 6.84 (1H, ddd, *J* = 8.4, 2.8, 1.6 Hz), 7.07 (1H, dd, *J* = 8.4, 4.4Hz), 7.93 (1H, dd, *J* = 4.4, 1.2 Hz), 8.00 (1H, d, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2, 117.9, 123.62, 135.6, 138.4, 145.1. The spectral data for this compound match that reported in the literature. [3]

6-Chloro-*N*-methylpyridin-3-amine (2ac)



According to the general procedure A, the reaction of **1ac** (52.2 mg, 0.406 mmol), $Me_3N–BH_3$ (30.1 mg, 0.413 mmol), NaH (40.1 mg, 1.67 mmol), and DMF (5 mL) under nitrogen at 80 ℃ for 3 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) afforded 39.0 mg (67%) **2ac** as pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (3H, s), 3.99 (1H, s br), 6.83 (1H, dd, *J* = 8.4, 2.8 Hz), 7.06 (1H, d, *J* = 8.4 Hz), 7.72 (1H, d, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 121.6, 123.9, 133.9, 138.4, 144.3. The spectral data for this compound match that reported in the literature. [15]

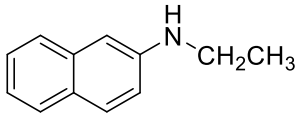
4. Synthesis of ethylated aniline3a



1a **3a**

To an N_2 flushed, oven-dried glass tube with a magnetic stir bar,**1a** (59.4 mg, 0.415 mmol), $Me_3N–BH_3$ (61.1 mg, 0.838 mmol), NaH (82.4 mg, 3.43 mmol), and DMA (5 ml) were added. The reaction mixture was stirred at 120 ℃ for 24 h. The reaction was then quenched with saturated NH_4Cl (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1 then 5 : 1) to afford **3a** (23.9 mg, 0.140 mmol) in 34% yield and **1a** was recovered in 51% yield.

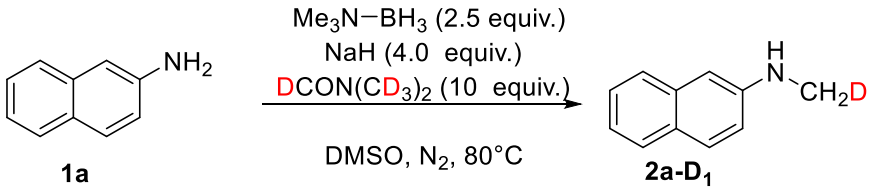
***N*-Ethylnaphthalen-2-amine (3a)**



Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, t, *J* = 7.2 Hz), 3.28 (2H, q, *J* = 7.2 Hz), 3.73 (1H, s br), 6.82 (1H, d, *J* = 2.4 Hz), 6.88 (1H, dd, *J* = 8.4, 2.4 Hz), 7.20 (1H, ddd, *J* = 7.6, 7.2, 1.2 Hz), 7.37 (1H, ddd, *J* = 8.4, 7.2, 1.2 Hz), 7.63 (2H, d, *J* = 8.4 Hz), 7.68 (1H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 38.5, 104.2, 118.0, 121.8, 125.9, 126.2, 127.4, 127.6, 128.8, 135.3, 146.0.The spectral data for this compound match that reported in the literature. [16]

5. Synthesis of N-CH_2D anilines

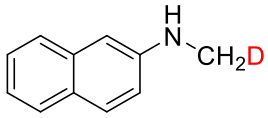
General procedure B:



To an N_2flushed, oven-dried glass tube with a magnetic stir bar, 2-aminonaphthalene **1a** (30.0 mg, 0.210 mmol), $Me_3N–BH_3$ (36.5 mg, 0.500 mmol), NaH (34.0 mg, 1.42 mmol), *d*$_7$-DMF (156μl, 2.00 mmol), and DMSO (3 mL) were added. The reaction mixture was stirred at 80 ℃ for 24 h. The reaction was then quenched with saturated NH_4Cl (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layers were washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. The crude residue was purified by flash column chromatography on silica

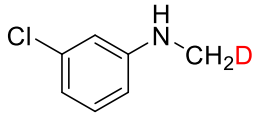
gel (petroleum ether : ethyl acetate =10 : 1) to afford **2a-D$_1$** (21.8, 0.138 mmol) in 66% yield (>98% D$_1$incorporation). Deuterium incorporation was determined by ^{1}H NMR analysis.

_N_-(Methyl-_d_)naphthalen-2-amine (2a-D$_1$)



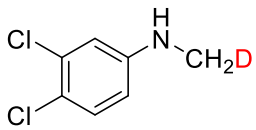
Brown oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 2.93 (2H, t, *J* = 1.6 Hz), 3.88 (1H, s br), 6.82 (1H, d, *J* = 2.0 Hz), 6.89 (1H, dd, *J* =8.8, 2.4 Hz), 7.22 (1H,ddd, *J* = 8.0, 6.8, 1.2 Hz), 7.39 (1H,ddd, *J* = 8.0, 7.2, 1.2 Hz), 7.61-7.73 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5 (t, *J* = 20.2 Hz), 103.8, 117.9, 121.9, 125.9, 126.3, 127.5, 127.6, 128.8, 135.2, 146.9; EIHRMS: Found: *m/z*159.1031. Calcd for $C_{11}H_{11}DN$: $(M+H)^+$ 159.1033.

3-Chloro-_N_-(methyl-_d_)aniline (2c-D$_1$)



According to the general procedure B, the reaction of **1c** (27.6 mg, 0.216 mmol), Me_3N–BH_3 (37.2 mg, 0.510 mmol), NaH (34.4 mg, 1.43 mmol) in d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 16.5 mg (53%) **2c-D$_1$** as yellow oil; >96% D$_1$ incorporation.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (2H, t, *J* = 2.0 Hz), 3.79 (1H, s br), 6.47 (1H, ddd, *J* = 8.0, 2.0, 0.8 Hz), 6.57 (1H, dd, *J* = 2.0, 2.0 Hz), 6.66 (1H, ddd, *J* = 8.0, 2.0, 0.8 Hz), 7.08 (1H, dd, *J* = 8.0, 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (t, *J* = 20.6 Hz), 110.8, 111.8, 117.0, 130.1, 135.0, 150.4; EIHRMS: Found: *m/z* 143.0486. Calcd for C_7H_8DClN: $(M+H)^+$ 143.0486.

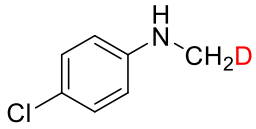
3,4-Dichloro-_N_-(methyl-_d_)aniline (2e-D$_1$)



According to the general procedure B, the reaction of **1e** (33.3 mg, 0.206 mmol), Me_3N–BH_3 (38.1 mg, 0.522 mmol), NaH (33.4 mg, 1.39 mmol) in d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column

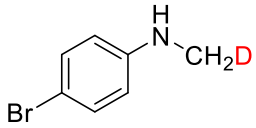
chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 21.2 mg (58%) **2e-D$_1$** as yellow oil; >95% D_1 incorporation.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (2H, t, *J* = 2.0 Hz), 3.77 (1H, s br), 6.42 (1H, dd, *J* = 8.4, 2.8 Hz), 6.65 (1H, d, *J* = 2.8 Hz), 7.18 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3 (t, *J*=20.8 Hz), 112.2, 113.1, 119.5, 130.5, 132.7, 148.7; EIHRMS: Found: *m/z* 177.0096. Calcd for $C_7H_7DCl_2N$: $(M+H)^+$ 177.0097.

4-Chloro-*N*-(methyl-*d*)aniline(2g-D$_1$)



According to the general procedure B, the reaction of **1g** (29.5 mg, 0.231 mmol), Me_3N–BH_3 (38.5 mg, 0.528 mmol), NaH (35.5 mg, 1.48 mmol), d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 24.2 mg (73%) **2g-D$_1$** as light yellow oil; >98% D_1 incorporation.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (2H, t, *J* = 1.6 Hz), 3.73 (1H, s br), 6.52 (2H, ddd, *J* = 8.8, 3.2, 2.4 Hz), 7.13 (2H, ddd, *J* = 8.8, 3.2, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5 (t, *J* = 20.8 Hz), 113.4, 121.8, 129.0, 147.8; EIHRMS: Found: *m/z* 143.0486. Calcd for C_7H_8DClN: $(M+H)^+$ 143.0486.

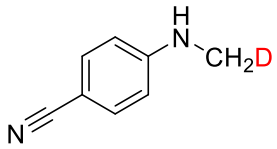
4-Bromo-*N*-(methyl-*d*)aniline (2h-D$_1$)



According to the general procedure B, the reaction of **1h** (34.4 mg, 0.200 mmol), Me_3N–BH_3 (37.7 mg, 0.517 mmol), NaH (33.0 mg, 1.38 mmol), d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 15 : 1) afforded 18.0 mg (48%) **2h-D$_1$** as pale yellow oil; >97% D_1 incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (2H, t, *J* = 1.6 Hz), 3.76 (1H, s br), 6.48 (2H, ddd, *J* = 8.8, 2.8, 1.6 Hz), 7.26 (2H, ddd, *J* = 8.8, 2.8, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4 (t, *J* = 20.8

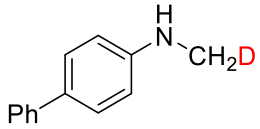
Hz), 108.7, 113.9, 131.8, 148.2; EIHRMS: Found: *m/z*186.9980.Calcd for C_7H_8DBrN: $(M+H)^+$ 186.9981.

4-((Methyl-*d*)amino)benzonitrile (2j-D$_1$)



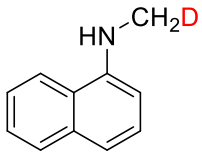
According to the general procedure B, the reaction of **1j** (25.5 mg, 0.216 mmol), $Me_3N–BH_3$ (37.0 mg, 0.507 mmol), NaH (34.0 mg, 1.42 mmol), d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) afforded 20.1 mg (70%) **2j-D$_1$** as pale yellow solid, mp 77-78 ℃; >98% D_1 incorporation.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (2H, dt, *J* = 5.2, 1.6 Hz), 4.33 (1H, s br), 6.55 (2H, ddd, *J* = 8.8, 2.4, 2.0 Hz), 7.42 (2H, ddd, *J* = 8.8, 2.4, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.6 (t, *J* = 20.9 Hz), 98.3, 111.7, 120.6, 133.6, 152.2; ESIHRMS: Found: *m/z* 134.0827. Calcd for $C_8H_8DN_2$: $(M+H)^+$ 134.0829.

***N*-(Methyl-*d*)-[1,1'-biphenyl]-4-amine (2o-D$_1$)**



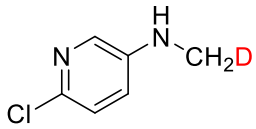
According to the general procedure B, the reaction of **1o** (35.3 mg, 0.209 mmol), $Me_3N–BH_3$ (37.0 mg, 0.507 mmol), NaH (33.7 mg, 1.40 mmol), d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 17.4 mg (45%) **2o-D$_1$** as yellow solid, mp 24-25 ℃; >98% D_1 incorporation.^{1}H NMR(400 MHz, $CDCl_3$) δ 2.86 (2H, t, *J* = 2.0 Hz), 3.75 (1H, s br), 6.68 (2H, ddd, *J* = 8.4, 2.8, 2.0 Hz), 7.25 (1H, tt, *J* = 7.6, 1.2 Hz), 7.39 (2H, dd, *J* = 8.0, 7.6 Hz), 7.46 (2H, ddd, *J* = 8.4, 2.8, 2.4 Hz), 7.52-7.55 (2H,m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5 (t, *J* = 20.9 Hz), 112.6, 126.0, 126.3, 127.9, 128.6, 130.1, 141.3, 148.7; EIHRMS: Found: *m/z* 184.1114. Calcd for $C_{13}H_{12}DN$: M^+ 184.1105.

***N*-(Methyl-*d*)naphthalen-1-amine (2z-D$_1$)**



According to the general procedure B, the reaction of **1z** (28.7 mg, 0.200 mmol), $Me_3N–BH_3$ (37.4 mg, 0.513 mmol), NaH (34.3mg, 1.43 mmol), d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 27.3 mg (86%) **2z-D₁** as brown oil; >98% D_1 incorporation.^{1}H NMR(400 MHz, $CDCl_3$) δ 3.02 (2H, t, *J* = 1.6 Hz), 4.42 (1H, sbr), 6.63 (1H, d, *J* = 7.6 Hz), 7.28 (1H, d, *J* = 8.4 Hz), 7.38-7.52 (3H, m), 7.77-7.86 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7 (t, *J* = 20.5 Hz), 103.7, 117.2, 119.8, 123.4, 124.6, 125.7, 126.6, 128.6, 134.2, 144.5; EIHRMS: Found: *m/z* 158.0960. Calcd for $C_{11}H_{10}DN$: M^+ 158.0949.

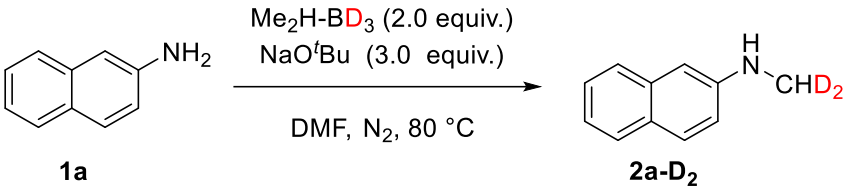
6-Chloro-*N*-(methyl-d)pyridin-3-amine (2ac-D₁)



According to the general procedure B, the reaction of **1ac** (26.3 mg, 0.205 mmol), $Me_3N–BH_3$ (36.6 mg, 0.502 mmol), NaH (33.7 mg, 1.40 mmol) in d_7-DMF (156 μl, 2.00 mmol) in DMSO (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3 : 1) afforded 20.9 mg (71%) **2ac-D₂** as pale yellow solid, mp 62-63 ℃; >98% D_1 incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (2H, t, *J* =2.0 Hz), 3.81 (1H, s br), 6.85 (1H, dd, *J* = 8.8, 2.8 Hz), 7.09 (1H, d, *J* = 8.8 Hz), 7.75 (1H, d, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (t, *J* = 20.6 Hz), 121.7, 124.0, 134.1, 138.8, 144.2; EIHRMS: Found: *m/z* 144.0437. Calcd for $C_6H_7DClN_2$: $(M+H)^+$ 144.0433.

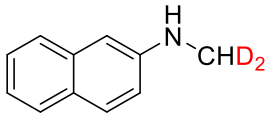
6. Synthesis of N-CHD₂anilines

General procedure C:



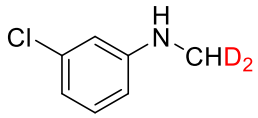
To an N_2flushed, oven-dried glass tube with a magnetic stir bar, 2-aminonaphthalene **1a** (29.9 mg, 0.209 mmol), Me_3N–BD_3 (32.4 mg, 0.427 mmol), NaO^{t}Bu (59.3 mg, 0.617 mmol), and DMF (3mL)were added. The reaction mixture was stirred at 80 ℃ for 0.5 h. The reaction was then quenched with H_2O (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford **2a-D$_2$** (25.0 mg, 0.157 mmol) in 75% yield and >98% D_2 incorporation. Deuterium incorporation was determined by ^{1}H NMR analysis.

***N*-(Methyl-*d*$_2$)naphthalen-2-amine (2a-D$_2$)**



Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (1H, qui, *J* = 2.0 Hz), 3.84 (1H, s br), 6.82 (1H, d, *J* = 2.4 Hz), 6.89 (1H, dd, *J* =8.8, 2.4 Hz),7.22 (1H, ddd, *J* =8.4, 7.2, 1.2 Hz), 7.39 (1H, ddd, *J* =8.4, 7.2, 1.6 Hz), 7.62-7.72 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (qui, *J* = 20.5 Hz), 103.7, 117.8, 121.8, 125.9, 126.3, 127.4, 127.6, 128.8, 135.3, 147.0;EIHRMS: Found: *m/z* 160.1095. Calcd for $C_{11}H_{10}D_2N$: $(M+H)^+$ 160.1095.

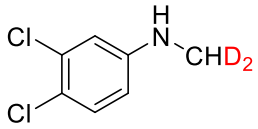
3-Chloro-*N*-(methyl-*d*$_2$)aniline (2c-D$_2$)



According to the general procedure C, the reaction of **1c** (26.6 mg, 0.209 mmol), Me_3N–BD_3 (46.2 mg, 0.608 mmol), *t*-BuONa (57.2 mg, 0.595 mmol) in DMF (3 mL) under nitrogen at 80 ℃ for 10 min after flashcolumn chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 18.1 mg (60%) **2c-D$_2$** as light yellow oil; >97% D_2 incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (1H, s), 3.71 (1H, s br), 6.47 (1H, dd, *J* = 8.0, 2.0 Hz), 6.58 (1H, dd, *J* = 2.0, 2.0 Hz), 6.67 (1H, dd, *J* = 8.0, 2.0 Hz), 7.08 (1H, dd, *J* = 8.0, 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.0 (qui, *J* =

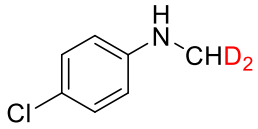
20.5 Hz), 110.8, 111.8, 116.9, 130.1, 135.0, 150.4; EIHRMS: Found: *m/z* 144.0546. Calcd for $C_7H_7D_2ClN$: $(M+H)^+$ 144.0549.

3,4-Dichloro-*N*-(methyl-*d*$_2$)aniline (2e-D$_2$)



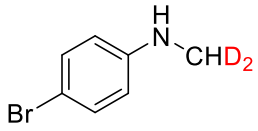
According to the general procedure C, the reaction of **1e** (32.8 mg, 0.202 mmol), Me_3N–BD_3 (30.9 mg, 0.407 mmol), *t*-BuONa (58.1 mg, 0.605 mmol) in DMF (3 mL) under nitrogen at 80 ℃ for 1 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 22.2 mg (62%) **2e-D$_2$** as yellow oil; >98% D_2 incorporation.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (1H, qui, *J* = 1.6 Hz), 3.78 (1H, s br), 6.42 (1H, dd, *J* = 8.8, 2.8 Hz), 6.64 (1H, d, *J* = 2.8 Hz), 7.18 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1 (qui, *J* = 20.6 Hz), 112.2, 113.2, 119.5, 130.5, 132.8, 148.7; EIHRMS: Found: *m/z* 178.0161. Calcd for $C_7H_6D_2Cl_2N$: $(M+H)^+$ 178.0159.

4-Chloro-*N*-(methyl-*d*$_2$)aniline(2g-D$_2$)



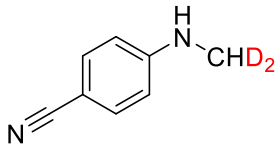
According to the general procedure C, the reaction of **1g** (26.6 mg, 0.209 mmol), Me_3N–BD_3 (46.2mg, 0.608 mmol), *t*-BuONa (57.2mg, 0.595 mmol) in DMF (3 mL) under nitrogen at 80 ℃ for 10minafter flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded18.1 mg (60%) **2g-D$_2$** as yellow oil; >98% D_2 incorporation.^{1}H NMR(400 MHz, $CDCl_3$) δ 2.78 (1H, qui, *J* = *2*.0 Hz), 3.63 (1H, sbr), 6.52 (2H, ddd, *J* = 8.8, 3.2, 2.0 Hz), 7.13 (2H, ddd, *J* = 8.8, 3.2, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (qui, *J* = 20.5 Hz), 113.4, 121.8, 129.0, 147.9; EIHRMS: Found:*m/z* 144.0546. Calcd for $C_7H_7D_2ClN$: $(M+H)^+$ 144.0549.

4-Bromo-*N*-(methyl-*d*$_2$)aniline (2h-D$_2$)



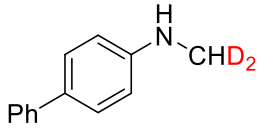
According to the general procedure C, the reaction of **1h** (36.9 mg, 0.215 mmol), $Me_3N–BD_3$ (30.7 mg, 0.404 mmol), *t*-BuONa (55.8 mg, 0.581 mmol) in DMF (3 mL) under nitrogen at 80 ℃ for 25 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 26.5 mg (66%) **2h-D₂** aspale yellow oil; >98% D_1 incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (1H, qui, *J* = 1.6 Hz), 3.70 (1H, s br), 6.47 (2H, ddd, *J* = 8.8, 3.2, 2.4 Hz), 7.25 (2H, ddd, *J* = 8.8, 3.2, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1 (qui, *J* = 20.6 Hz), 108.7, 113.9, 131.8, 148.3; EIHRMS: Found: *m/z*188.0041. Calcd for $C_7H_7D_2BrN$: $(M+H)^+$ 188.0044.

4-((Methyl-*d*₂)amino)benzonitrile (2j-D₂)



According to the general procedure C, the reaction of **1j** (25.4 mg, 0.215 mmol), $Me_3N–BD_3$ (30.7mg, 0.404 mmol), *t*-BuONa (58.1mg, 0.605 mmol) in DMF (3 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate =5 : 1) afforded 10.8mg (37%) **2j-D₂** as pale yellow solid, mp 59 -60 ℃; >98% D_1 incorporation. ^{1}H NMR(400 MHz, $CDCl_3$) δ 2.84 (1H, s), 4.27 (1H, s br), 6.55 (2H, ddd, *J* = 8.8, 2.4, 2.0 Hz), 7.42 (2H, ddd, *J* = 8.8, 2.4, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.4 (qui, *J* = 20.8 Hz), 98.4, 111.8, 120.5, 133.6, 152.2; ESIHRMS: Found: *m/z* 135.0883. Calcd for $C_8H_7D_2N_2$: $(M+H)^+$ 135.0891.

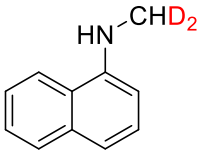
***N*-(Methyl-*d*₂)-[1,1'-biphenyl]-4-amine (2o-D₂)**



According to the general procedure C, the reaction of **1o** (68.9 mg, 0.407mmol), $Me_3N–BD_3$ (92.1 mg, 1.21 mmol), *t*-BuONa (153.5 mg, 1.60 mmol) in DMF (5 mL) under nitrogen at 80 ℃ for 24 h after flash column chromatography on silica gel

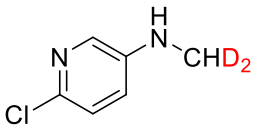
(petroleum ether : ethyl acetate = 5 : 1) afforded 34.2 mg (45%) **2o-D$_2$** as yellow solid, mp 19-20 ℃; >98% D_1 incorporation.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (1H, s), 3.53 (1H, s br), 6.68 (2H, d, *J* = 8.4 Hz), 7.24 (1H, t, *J* = 7.6 Hz), 7.38 (2H, dd, *J* = 7.6, 7.6 Hz), 7.45 (2H, d, *J* = 8.4 Hz), 7.34 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (qui, *J* = 20.6 Hz), 112.7, 126.0, 126.3, 127.9, 128.6, 130.1, 141.3, 148.7; EIHRMS: Found: *m/z*186.1250. Calcd for $C_{13}H_{12}D_2N$: $(M+H)^+$186.1252.

_N_-(Methyl-_d_$_2$)naphthalen-1-amine (2z-D$_2$)



According to the general procedure C, the reaction of **1z** (28.9mg, 0.202 mmol), Me_3N–BD_3 (30.3 mg, 0.399 mmol), *t*-BuONa (59.9mg, 0.623 mmol) in DMF (3 mL) under nitrogen at 80 ℃ for 0.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 24.5 mg (76%) **2z-D$_2$** as pale brown oil; >98% D_1 incorporation.^{1}H NMR(400 MHz, $CDCl_3$) δ 3.00 (1H, qui, *J* = 2.0 Hz),4.38 (1H, s br), 6.63 (1H, dd, *J* = 7.6, 0.8 Hz), 7.28 (1H, d, *J* = 8.4 Hz), 7.41(1H, dd, *J* = 8.0, 8.0 Hz), 7.45-7.50(2H, m), 7.79-7.84(2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5 (qui, *J* = 20.7 Hz), 103.7, 117.3, 119.8, 123.4, 124.6, 125.7, 126.6, 128.6, 134.2, 144.5;EIHRMS: Found: *m/z*160.1095. Calcd for $C_{11}H_{10}D_2N$: $(M+H)^+$ 160.1095.

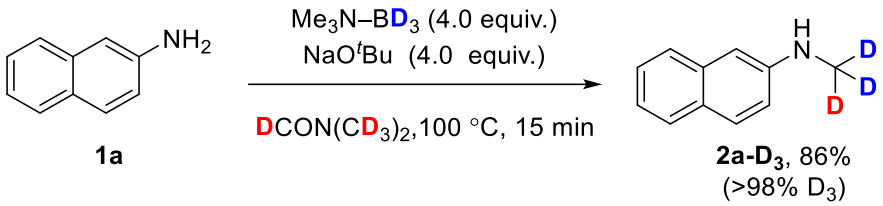
6-Chloro-_N_-(methyl-d$_2$)pyridin-3-amine (2ac-D$_2$)



According to the general procedure C, the reaction of **1ac** (54.8 mg, 0.426 mmol), Me_3N–BD_3 (62.2 mg, 0.819 mmol), *t*-BuONa(111.1 mg, 1.16 mmol) in DMF (5 mL) under nitrogen at 80 ℃ for 5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2 : 1) afforded 31.9 mg (52%) **2ac-D$_2$** as yellow solid, mp 59-60 ℃; >98% D_2 incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (1H, qui, *J* = 2.0 Hz), 3.55 (1H, s br), 6.84 (dd, 1H, *J* =8.8, 3.2 Hz), 7.07 (d, 1H, *J* =8.4 Hz), 7.73 (d, 1H, *J* = 3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.8 (qui, *J* = 20.6 Hz), 121.6,

123.9, 134.0, 138.5, 144.3; EIHRMS: Found: *m/z*145.0498. Calcd for $C_6H_6D_2ClN_2$: $(M+H)^+$ 145.0502.

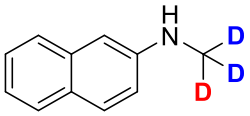
7. Synthesis of N-CD_3 aniline



1a **2a-D_3**, 86% (>98% D_3)

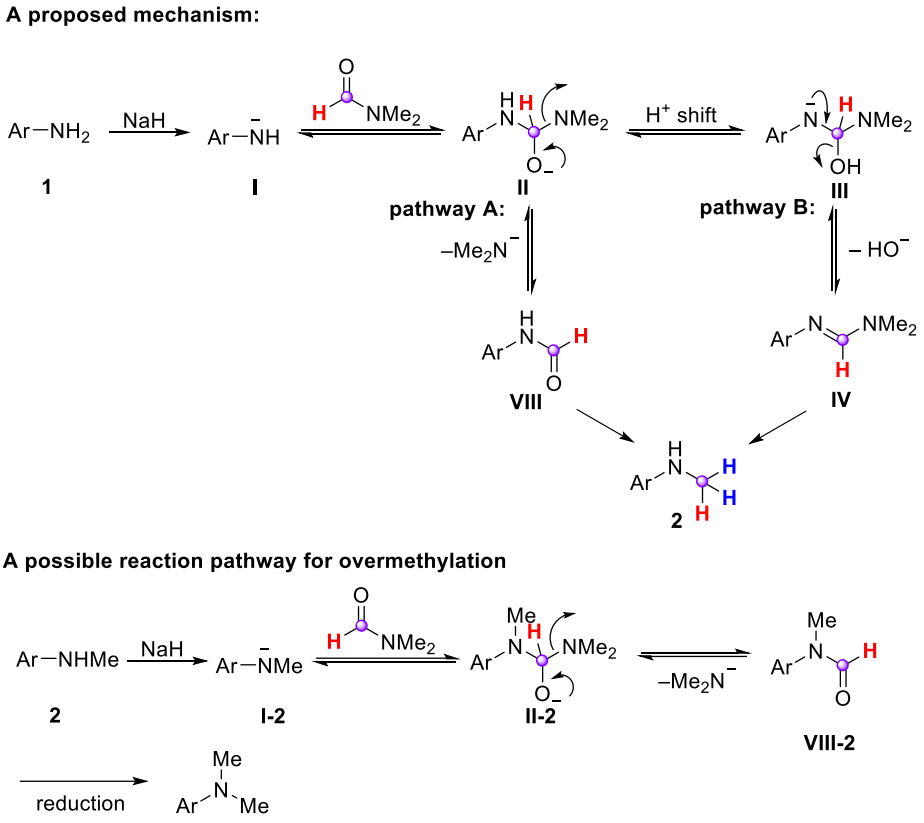
To an N_2flushed, oven-dried glass tube with a magnetic stir bar, 2-aminonaphthalene**1a** (14.2 mg, 0.0992 mmol), $Me_3N–BD_3$ (31.4 mg, 0.413 mmol), NaO^tBu (37.6 mg, 0.391 mmol), and d_7-DMF (1.2 mL) were added. The reaction mixture was stirred at 100 ℃ for 15 min. The reaction was then quenched with H_2O (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1) to afford **2a-D_3** (13.6mg, 0.0849 mmol) in 86% yield and >98% D_3 incorporation. Deuterium incorporation was determined by ^{1}H NMR analysis.

***N*-(methyl-d_3)naphthalen-2-amine (2a-D_3)**



Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (1H, s br), 6.81 (1H, d, *J* = 2.0 Hz), 6.89 (1H, dd, *J* = 9.0, 2.5 Hz), 7.21 (1H, ddd, *J* = 14.5, 7.5, 7.0 Hz), 7.38 (1H, ddd, *J* = 15.0, 8.0, 7.0 Hz), 7.60-7.71 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.7, 103.7, 117.9, 121.8, 125.9, 126.3, 127.4, 127.6, 128.8, 135.3, 147.0. EIHRMS: Found: *m/z*161.1156. Calcd for $C_{11}H_9D_3N$: $(M+H)^+$ 161.1158.

8. A proposed reaction mechanism



Scheme S1. A proposed reaction mechanism

For the methylation of primary anilines **1**, there are two possible pathways. Deprotonation of primary aniline **1** by NaH generates nitrogen anion **I**, which attacks the formyl group of DMF to give intermediate **II**. There is an equilibrium between **II** and **III** through the intramolecular proton shift. For pathway A, elimination of Me_2N- from **II** affords **VIII**, which could be converted to the methylated product **2** through further hydride reduction. For pathway B, elimination of hydroxide from **III** generates amidine **IV**, which could be converted to the methylated product **2** through further hydride reduction. Both pathways are considered to be possible. However, if the pathway A works, the over-methylation of product **2** should proceed. In this case, deprotonation of aniline **2** by NaH generates nitrogen anion **I-2**, which attacks the formyl group of DMF to give intermediate **II-2**. Elimination of Me_2N- from **II-2** affords **VIII-2**, which could be converted to the dimethylated product through further hydride reduction.

However, based on the reaction results, no dimethylated product was detected in any of the substrates. Moreover, when ArNHMe **2a** was re-subjected to the standard reaction conditions, no reaction occurred. This suggests that pathway B involving the elimination of hydroxide to generate amidine is more likely. Since in this case, the

intramolecular hydrogen transfer is not possible and the elimination of hydroxide becomes somehow more difficult.

Besides, the reduction of amidine intermediate to form the *N*-monomethylated anilines has been reported.[17] Therefore, at this moment, we think that the pathway B is a preferential route, while the elimination of Me_2N-group (pathway A) still cannot be fully excluded.

9. References

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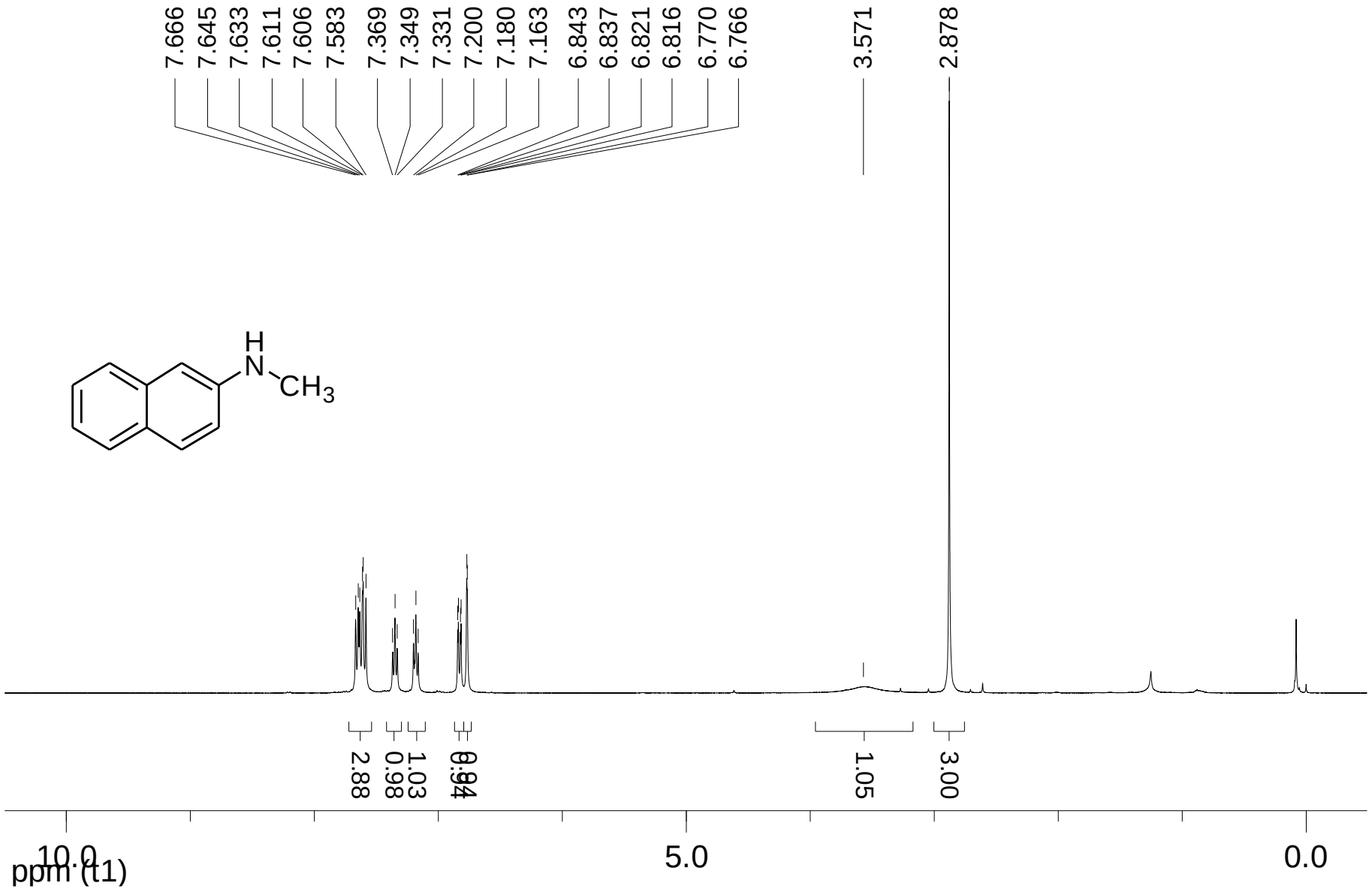
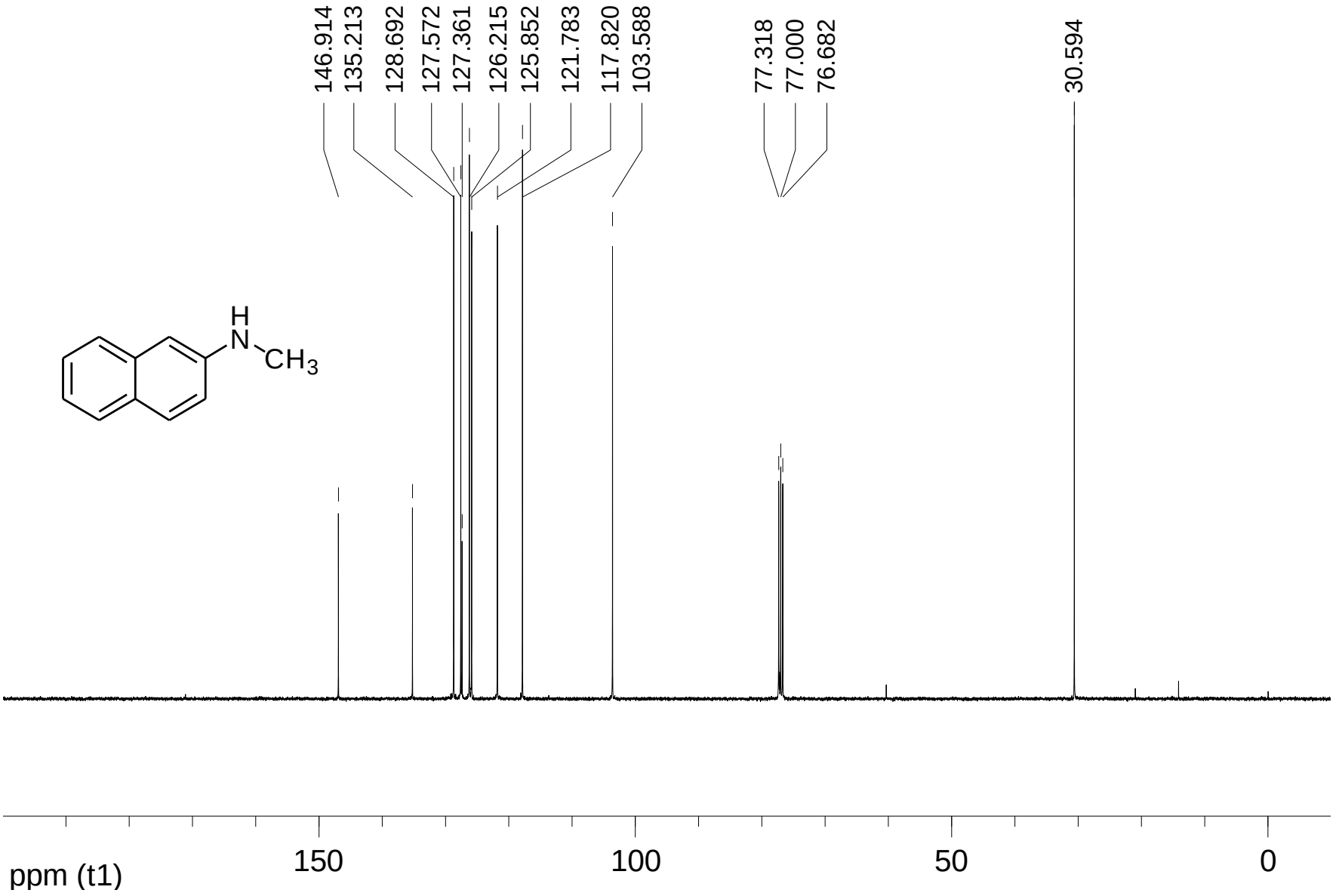
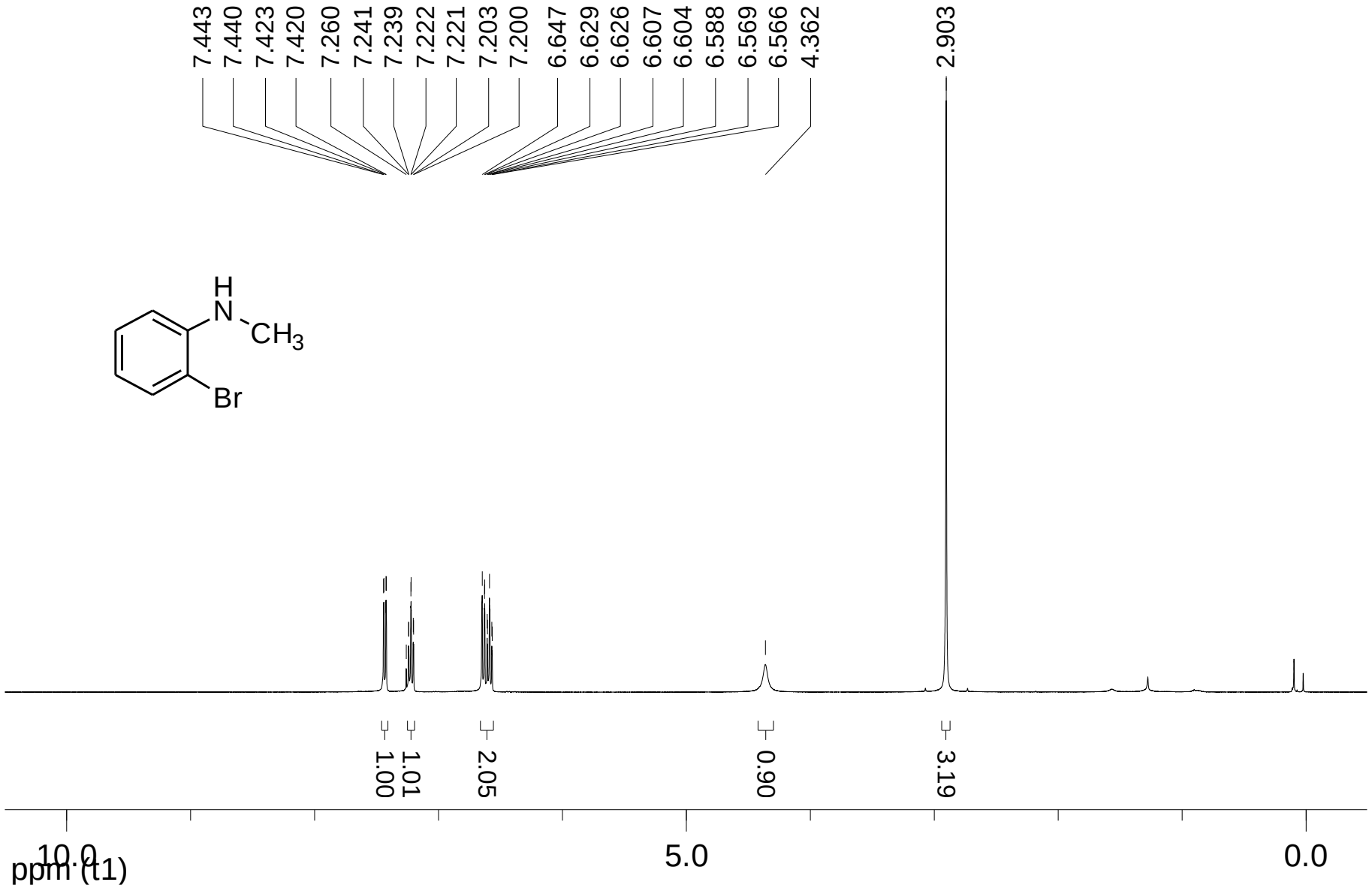
^{1}H NMR spectrum of **2a** (400M Hz, $CDCl_3$)



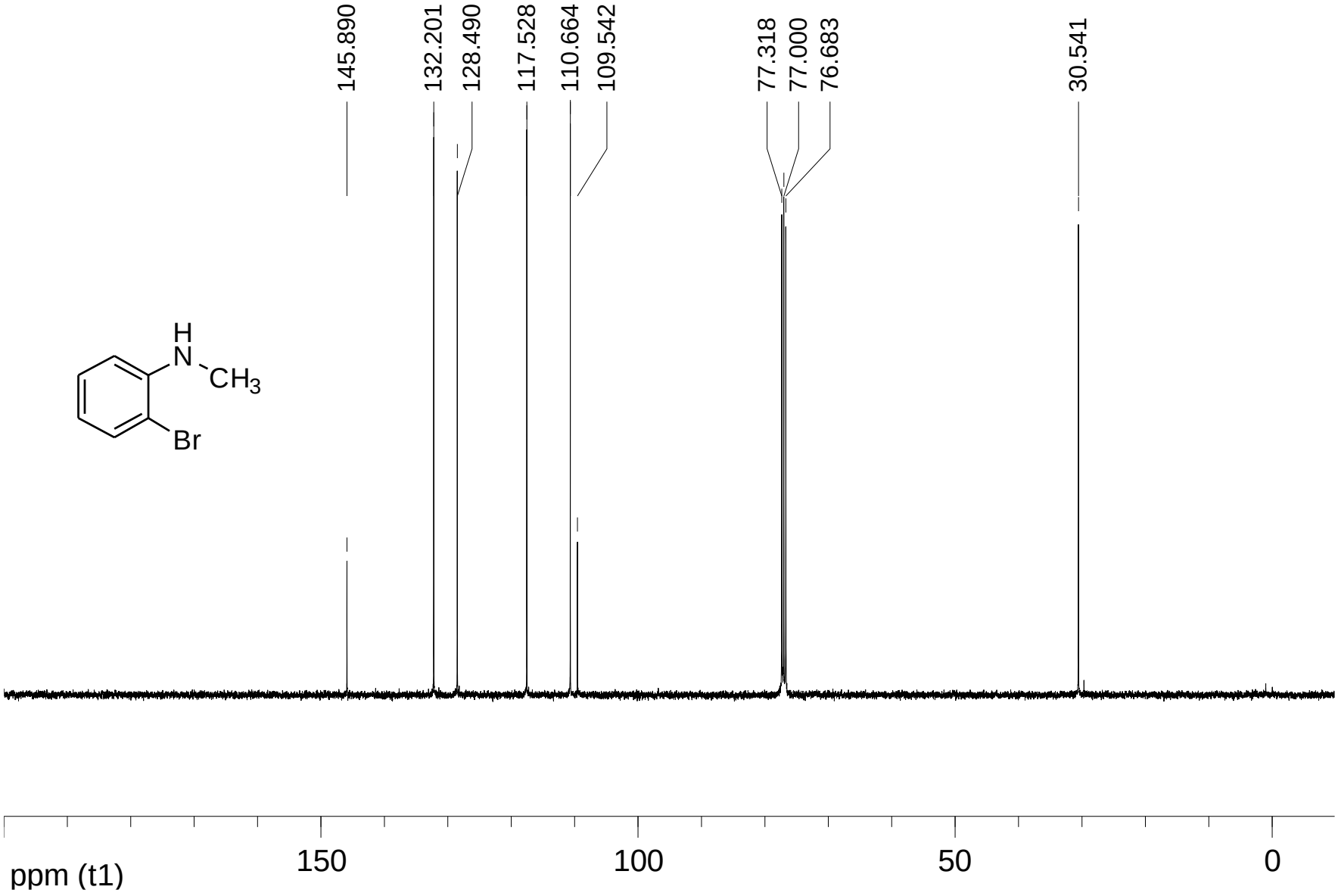
^{13}C NMR spectrum of **2a** (100M Hz, $CDCl_3$)



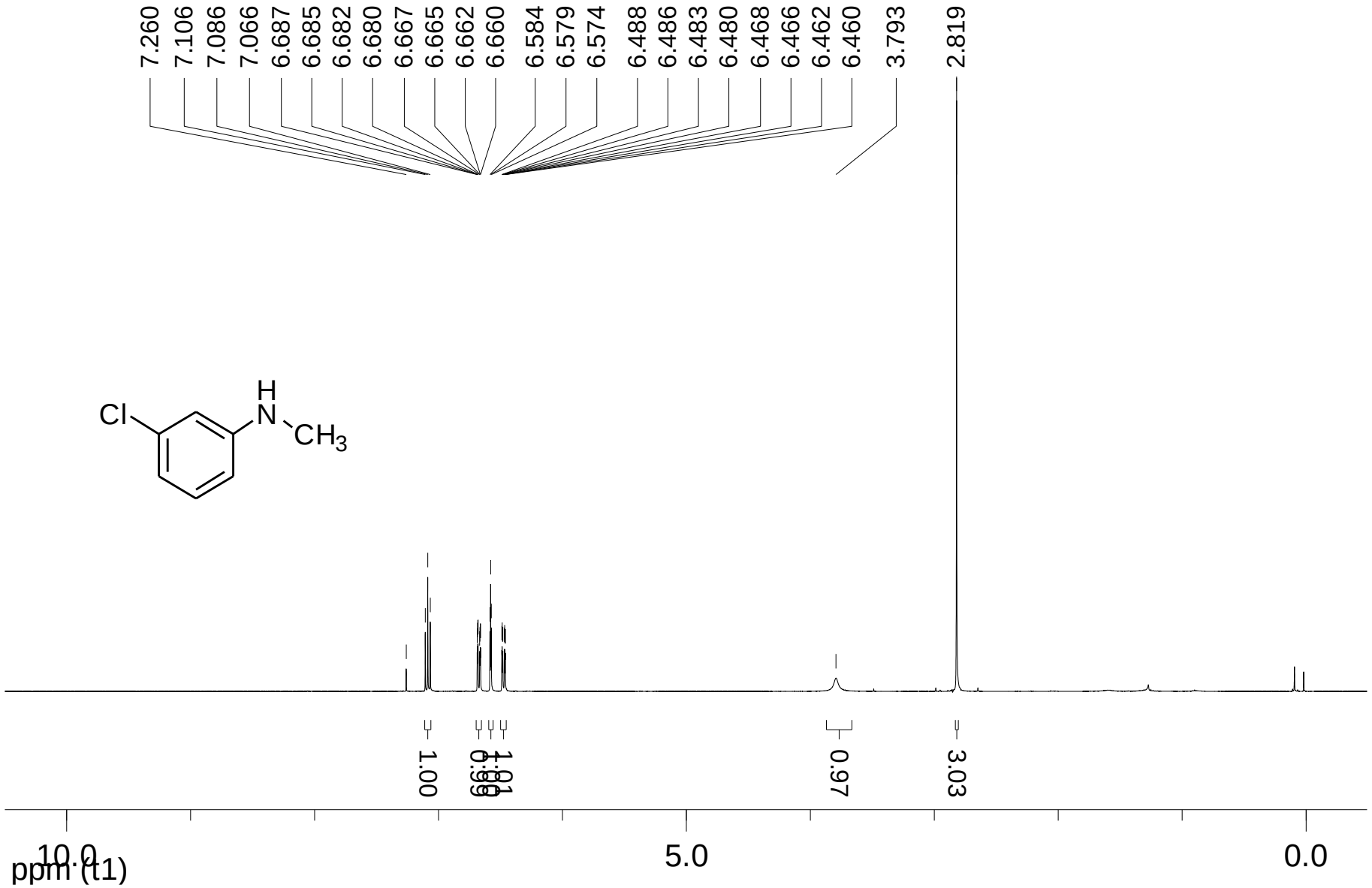
^{1}H NMR spectrum of **2b** (400M Hz, $CDCl_3$)



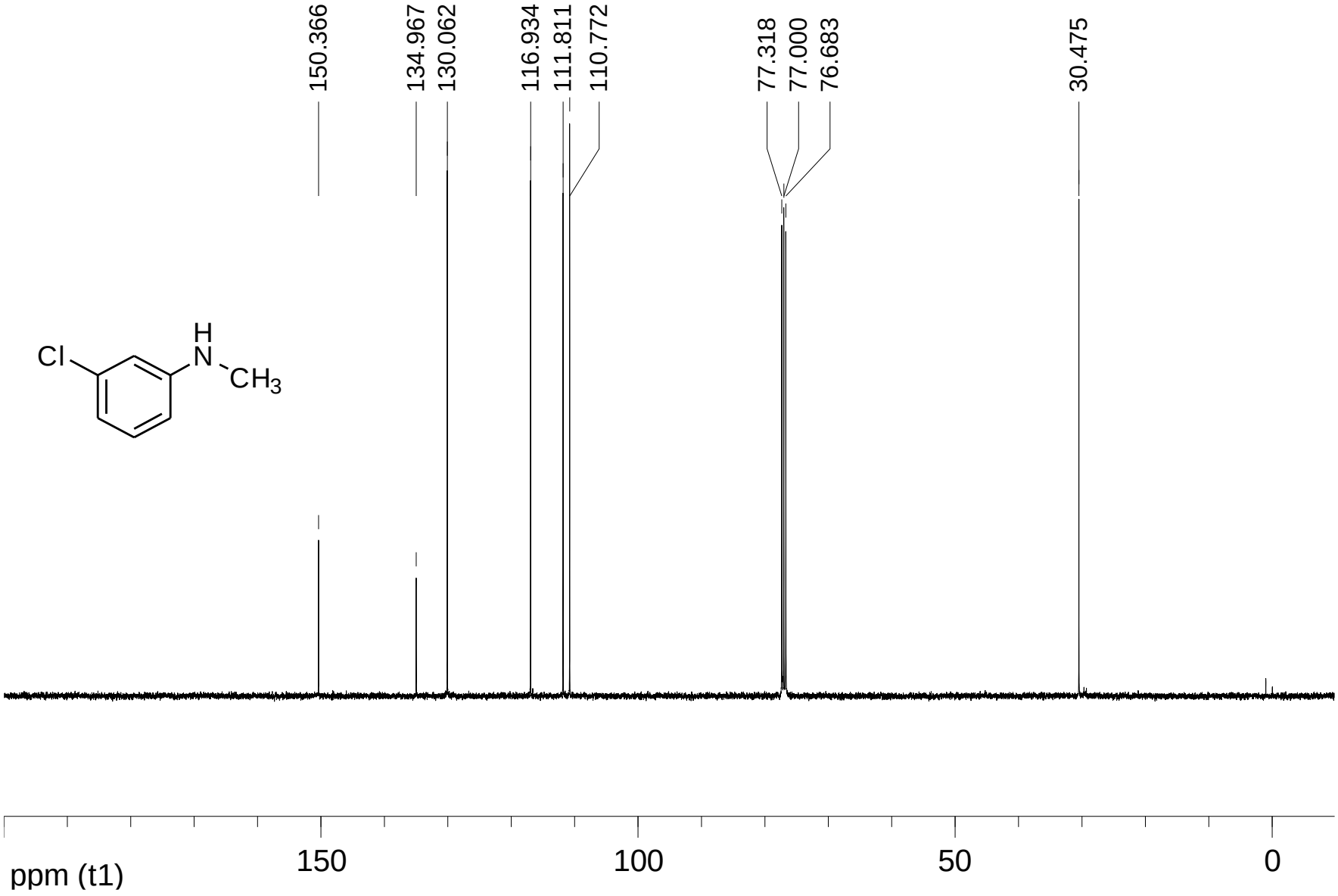
^{13}C NMR spectrum of **2b** (100M Hz, $CDCl_3$)



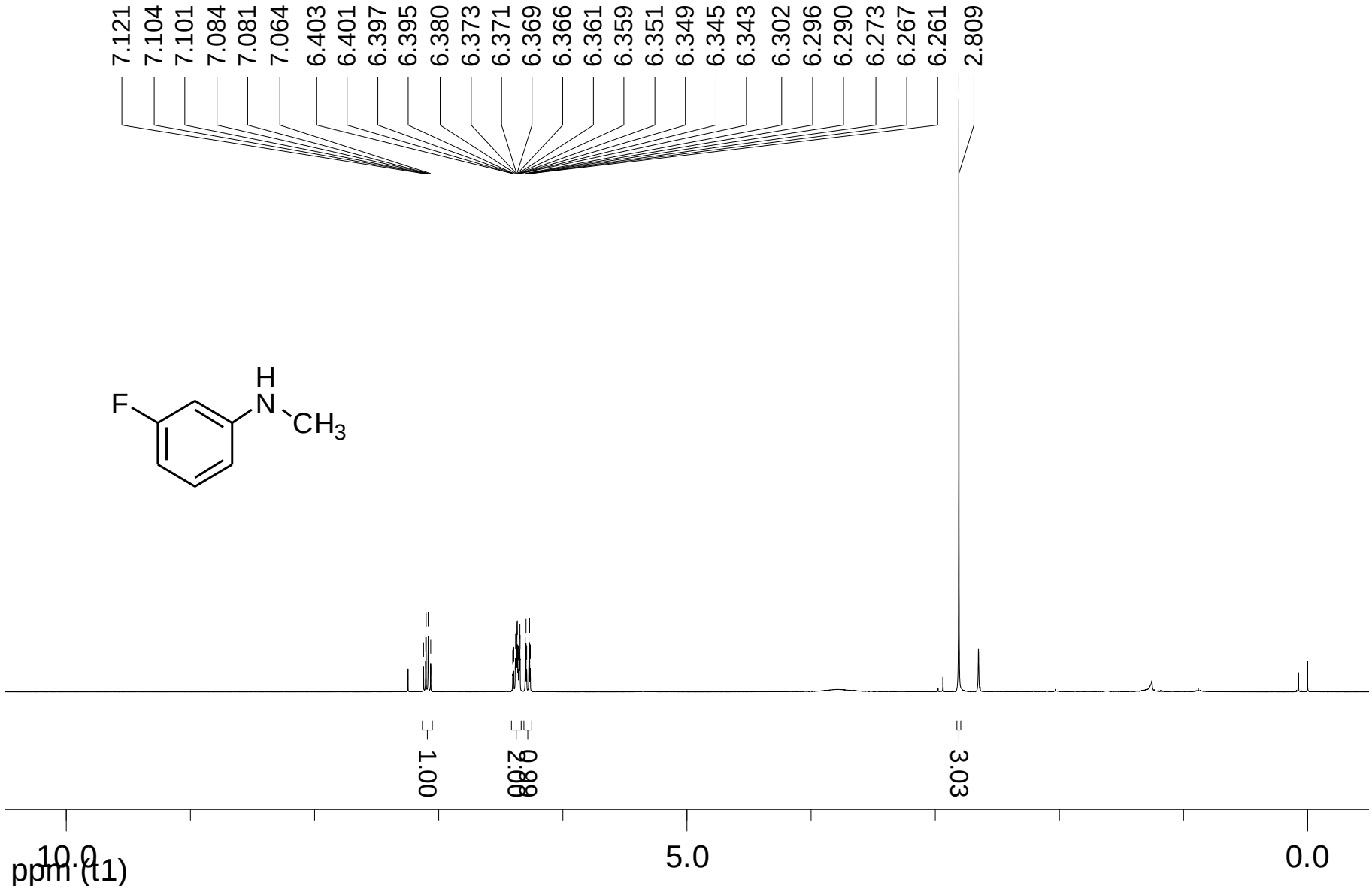
^{1}H NMR spectrum of **2c** (400M Hz, $CDCl_3$)



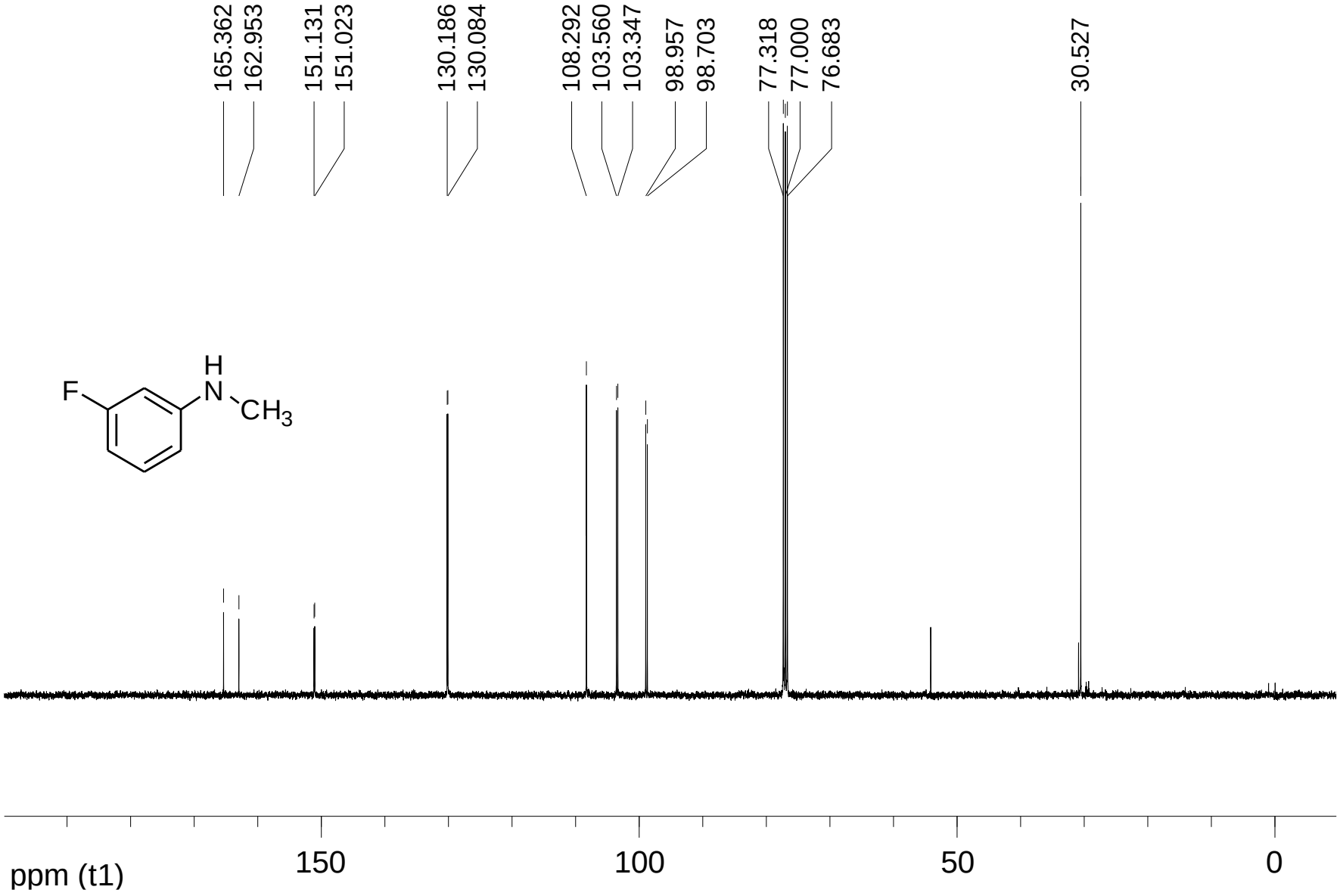
^{13}C NMR spectrum of **2c** (100M Hz, $CDCl_3$)



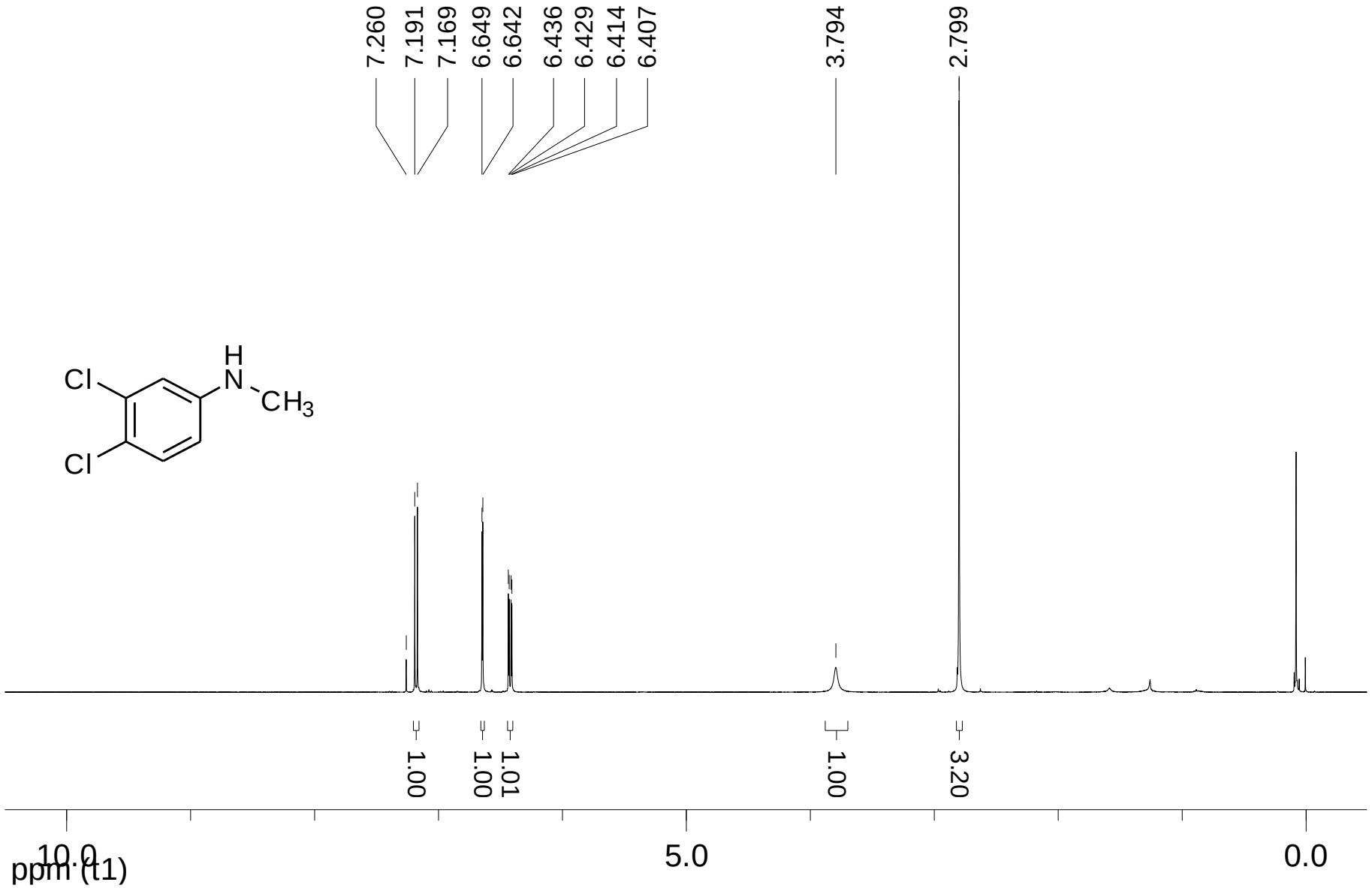
^{1}H NMR spectrum of **2d** (400M Hz, $CDCl_3$)



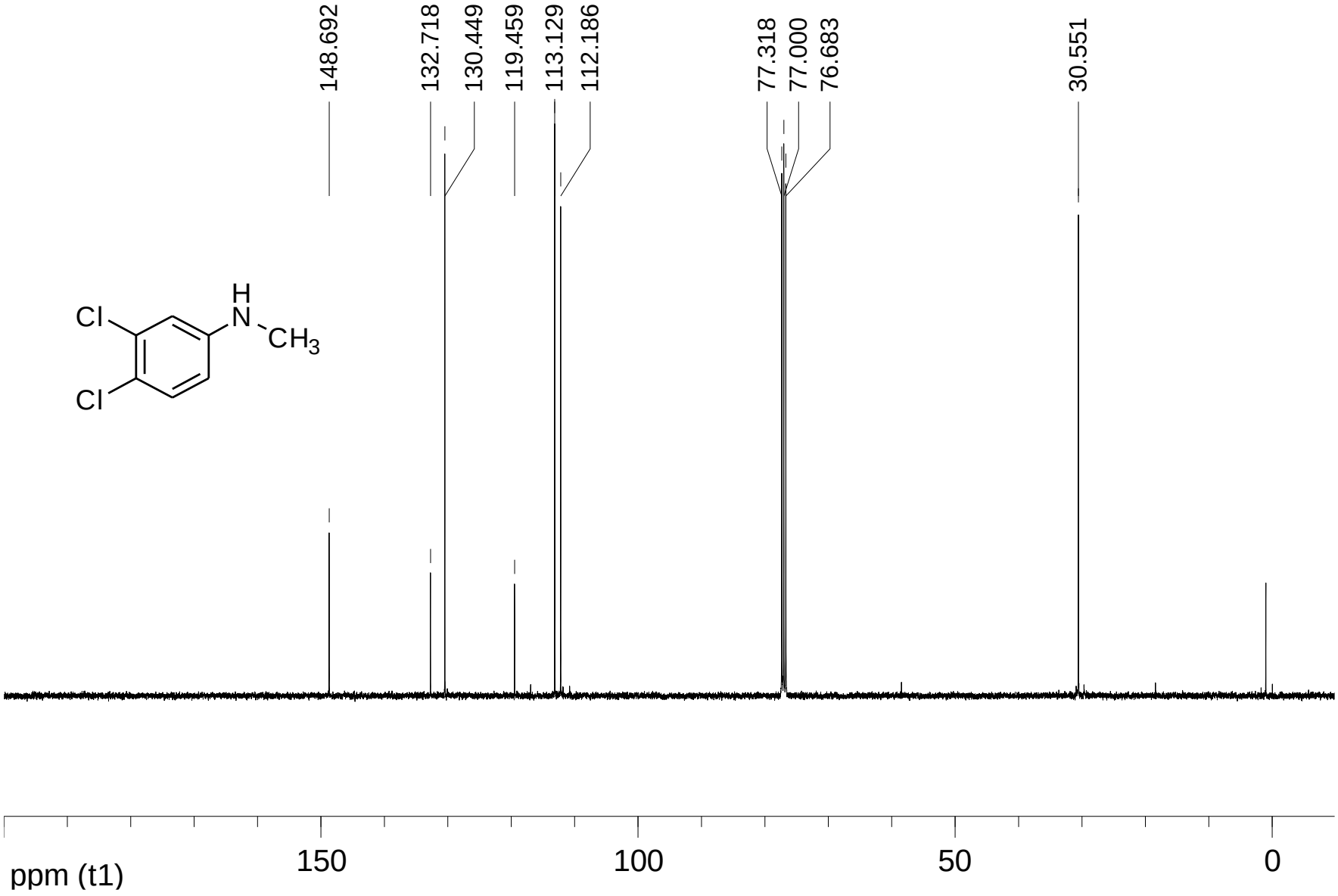
^{13}C NMR spectrum of **2d** (100M Hz, $CDCl_3$)



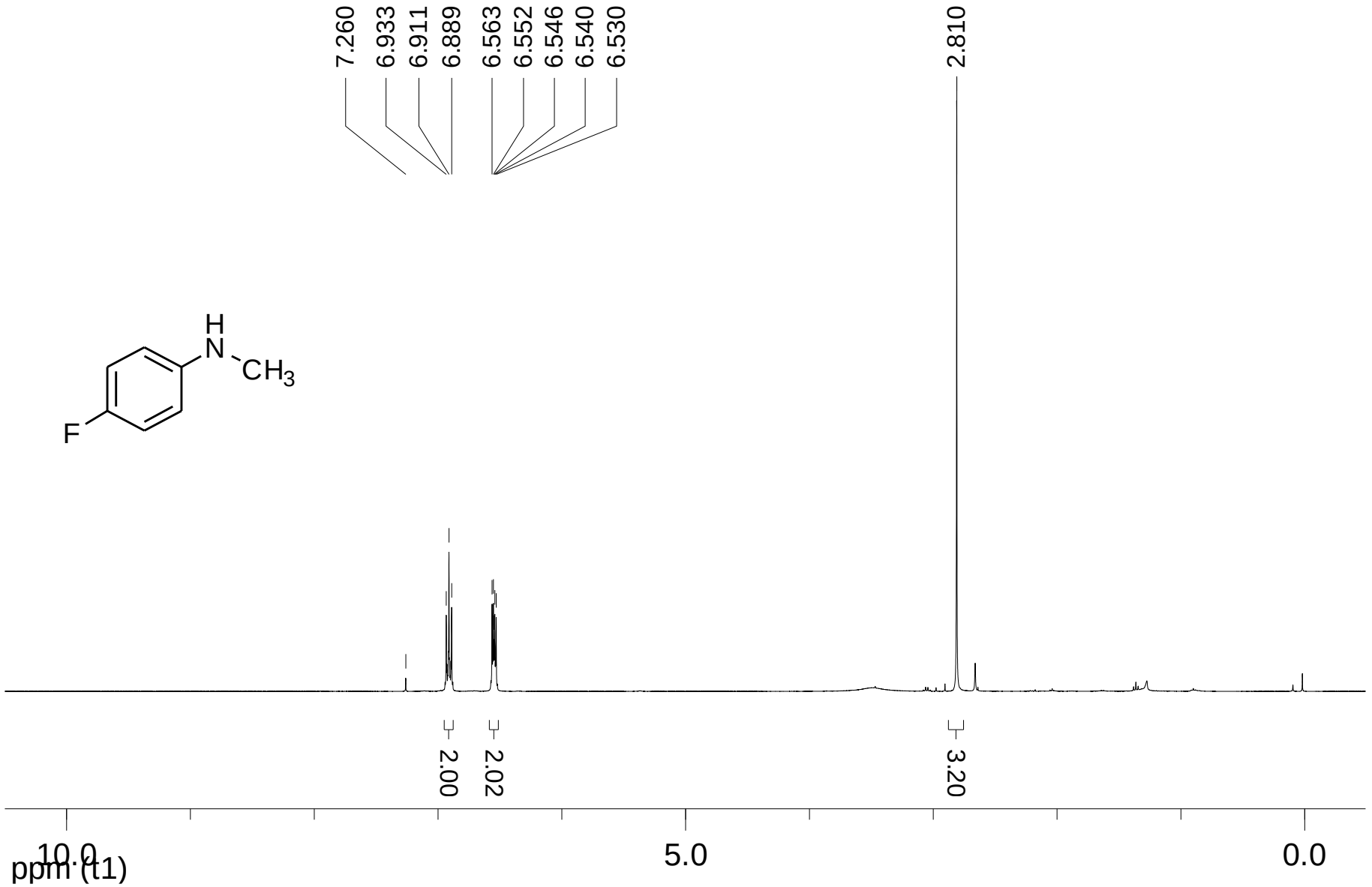
^{1}H NMR spectrum of **2e** (400M Hz, $CDCl_3$)



^{13}C NMR spectrum of **2e** (100M Hz, $CDCl_3$)



^{1}H NMR spectrum of **2f** (400M Hz, $CDCl_3$)



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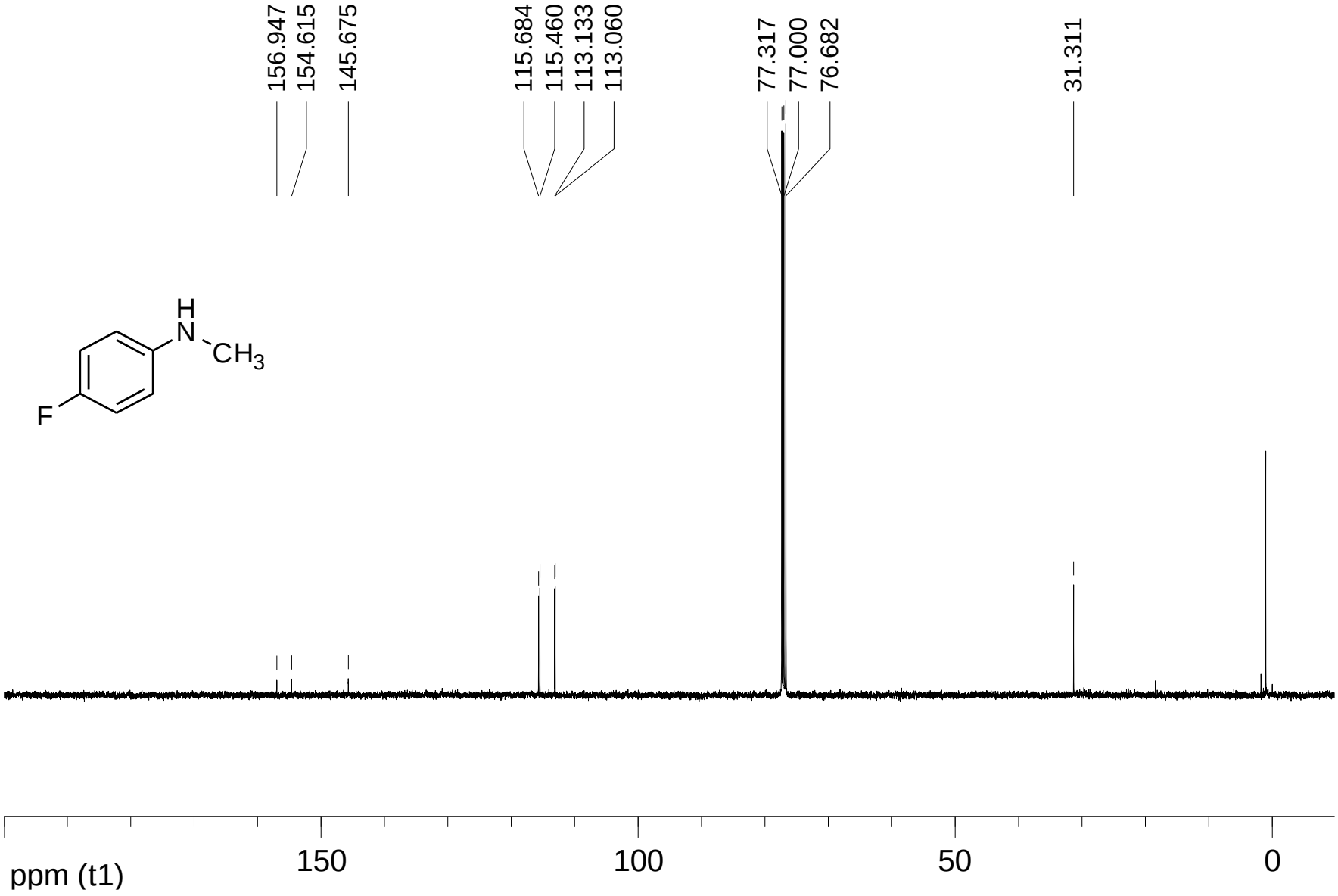
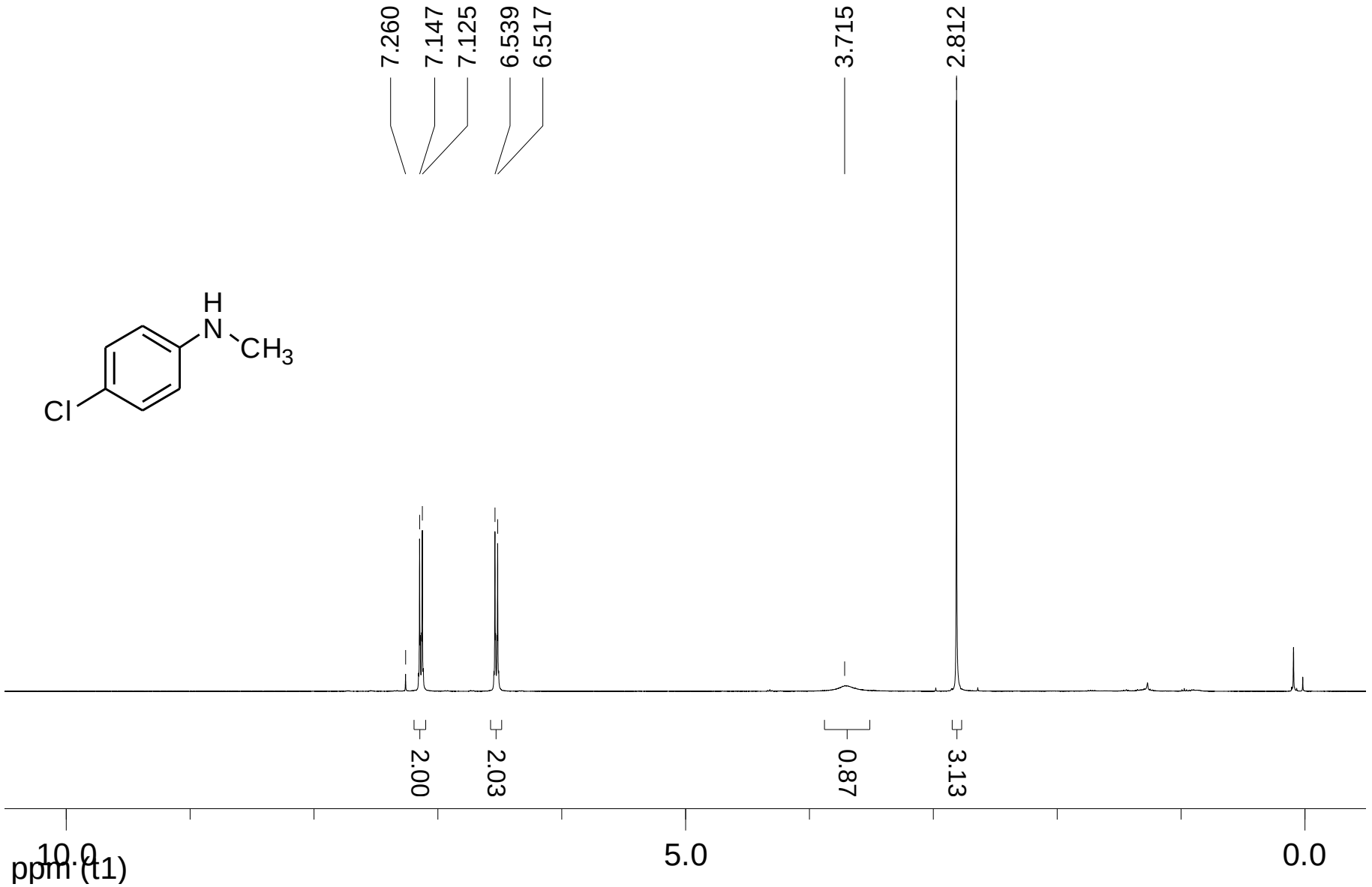
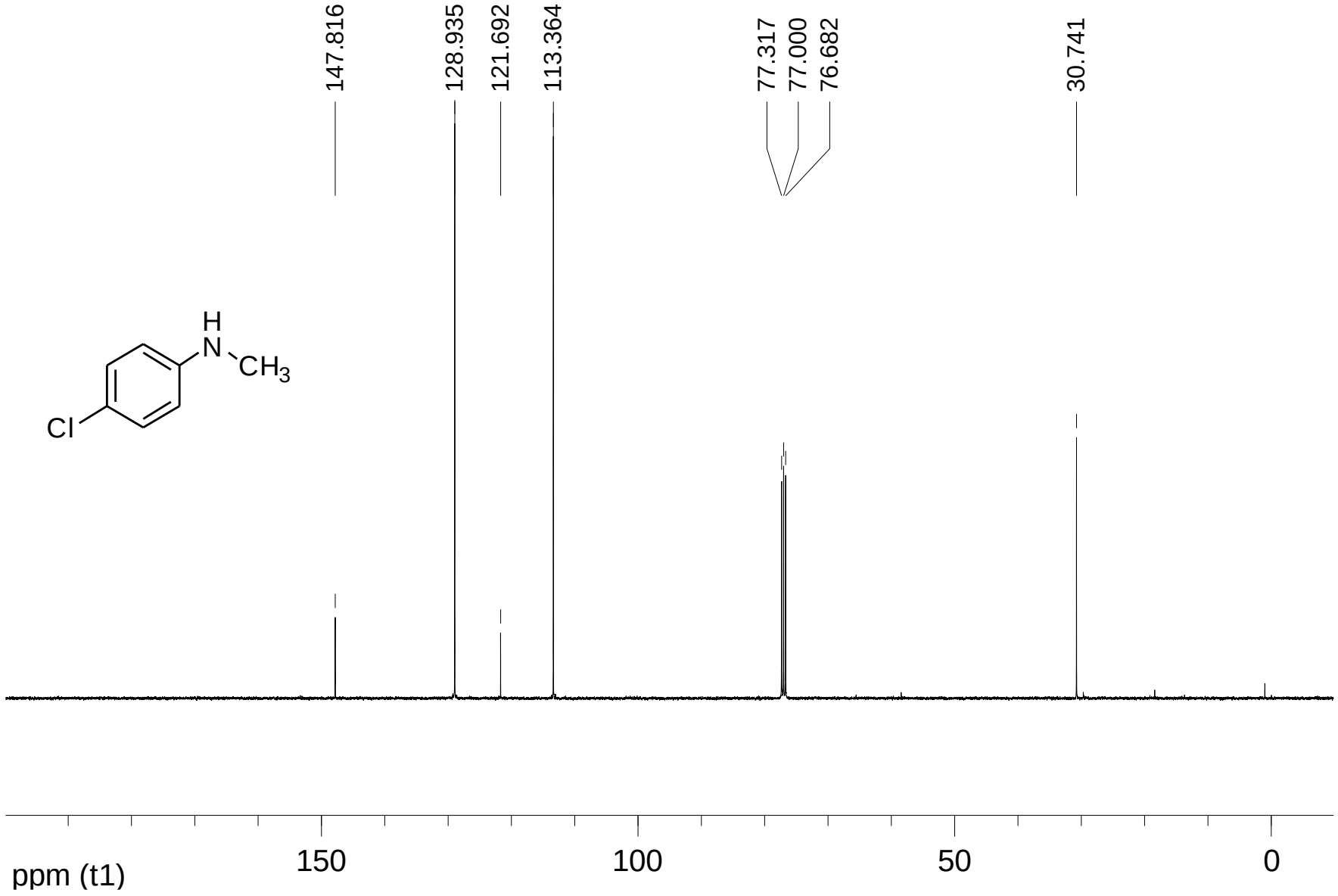


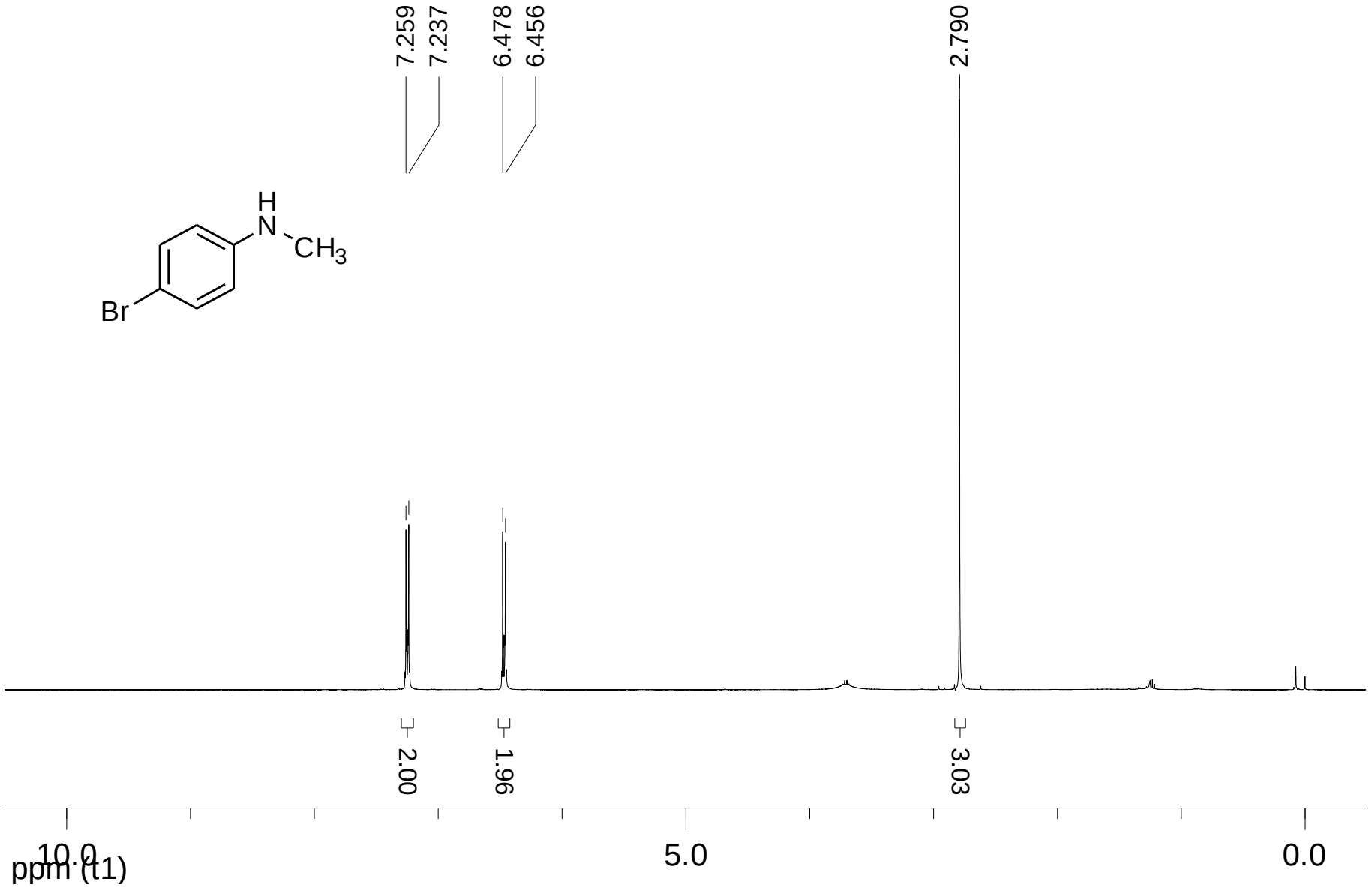
^{1}H NMR spectrum of **2g** (400M Hz, $CDCl_3$)



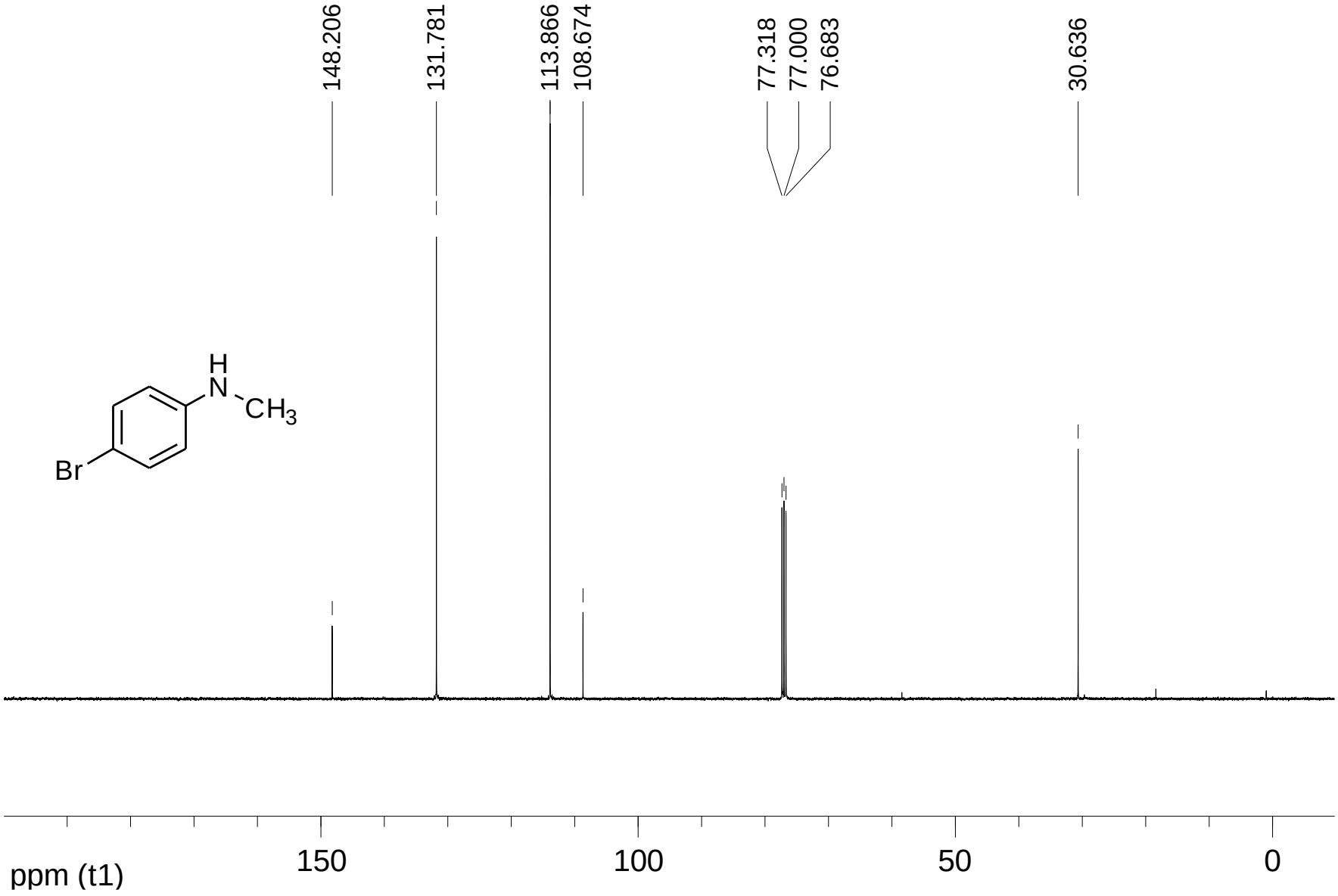
^{13}C NMR spectrum of **2g** (100M Hz, $CDCl_3$)



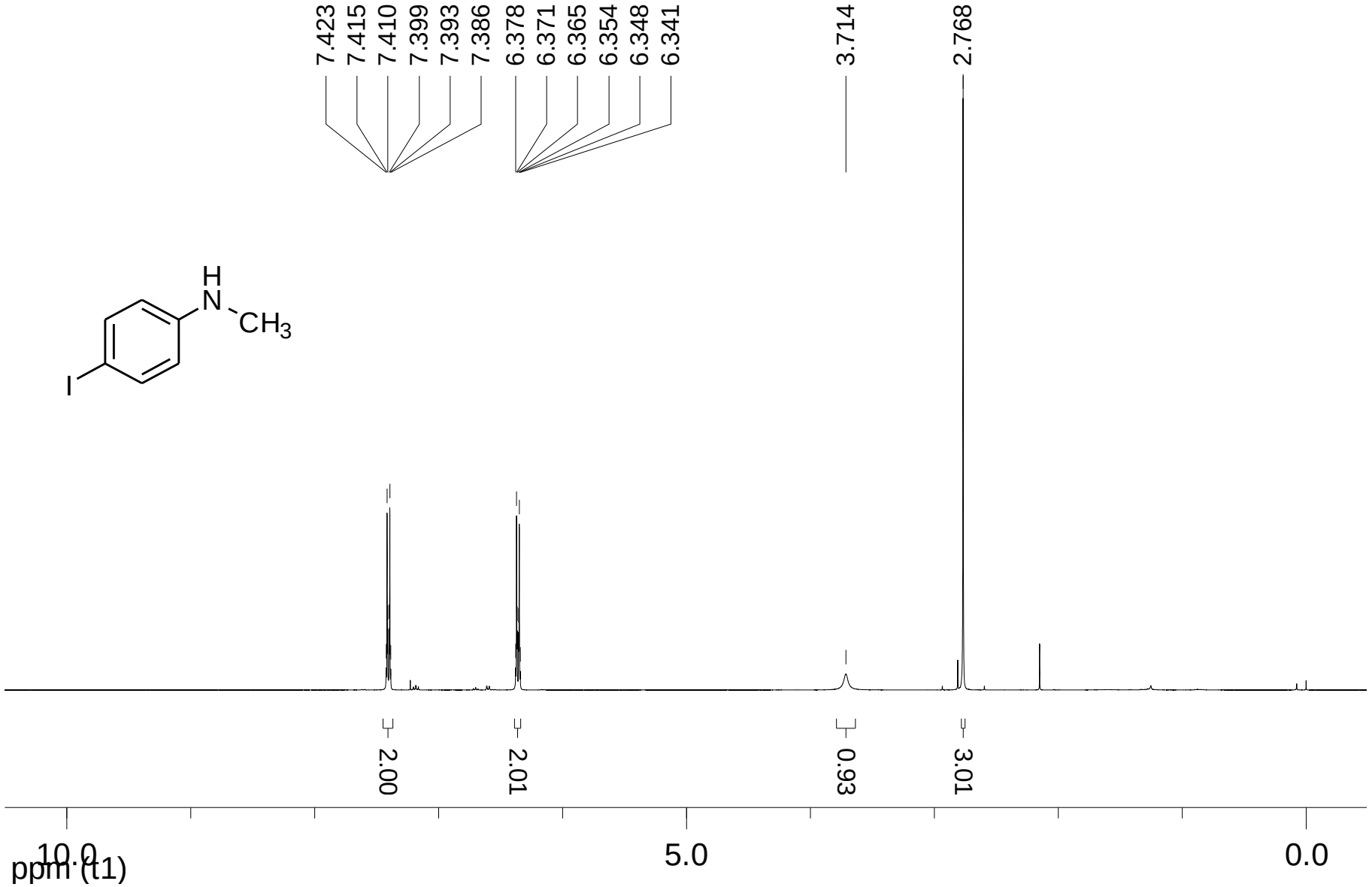
^{1}H NMR spectrum of **2h** (400M Hz, $CDCl_3$)



^{13}C NMR spectrum of **2h** (100M Hz, $CDCl_3$)



^{1}H NMR spectrum of **2i** (400M Hz, $CDCl_3$)



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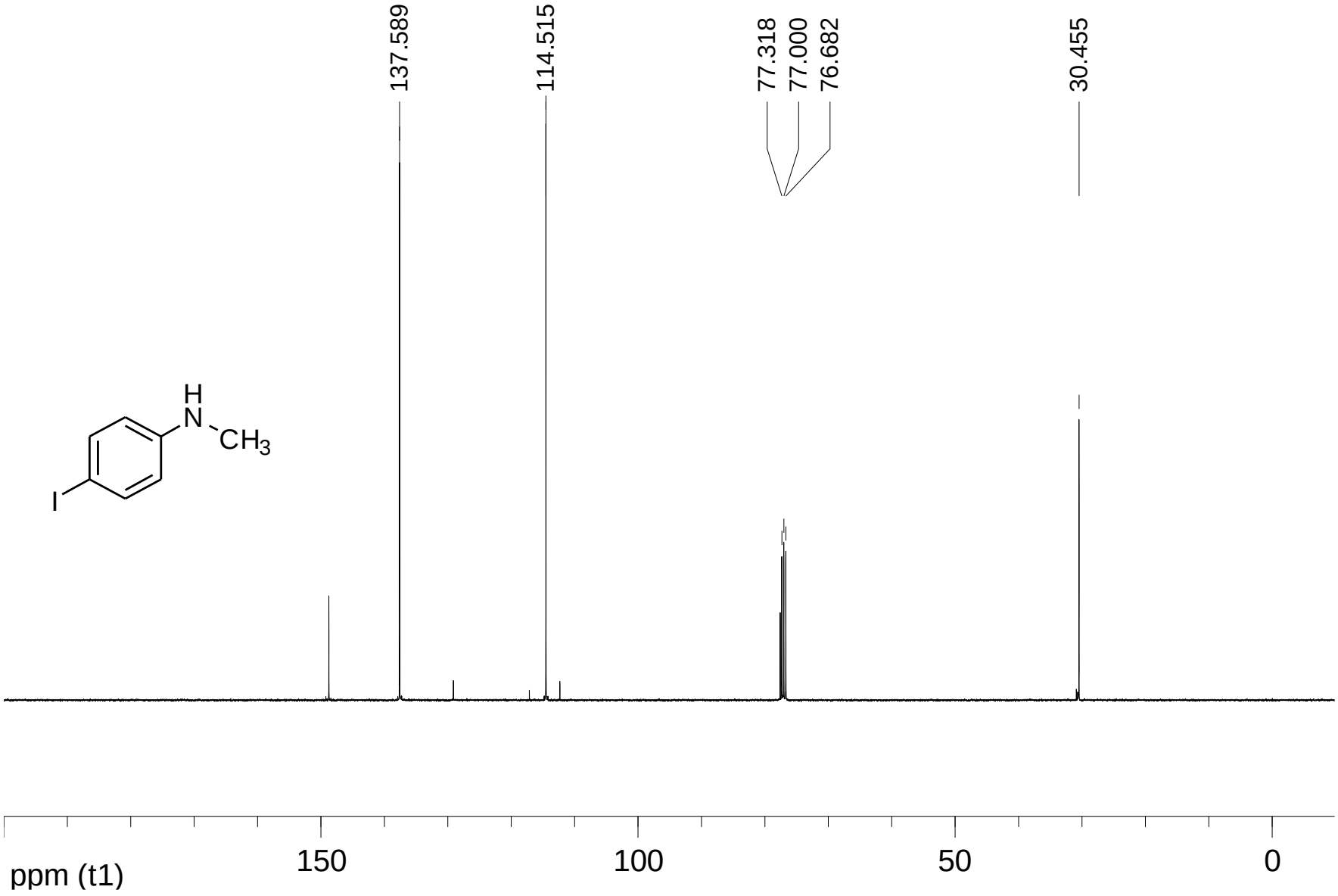

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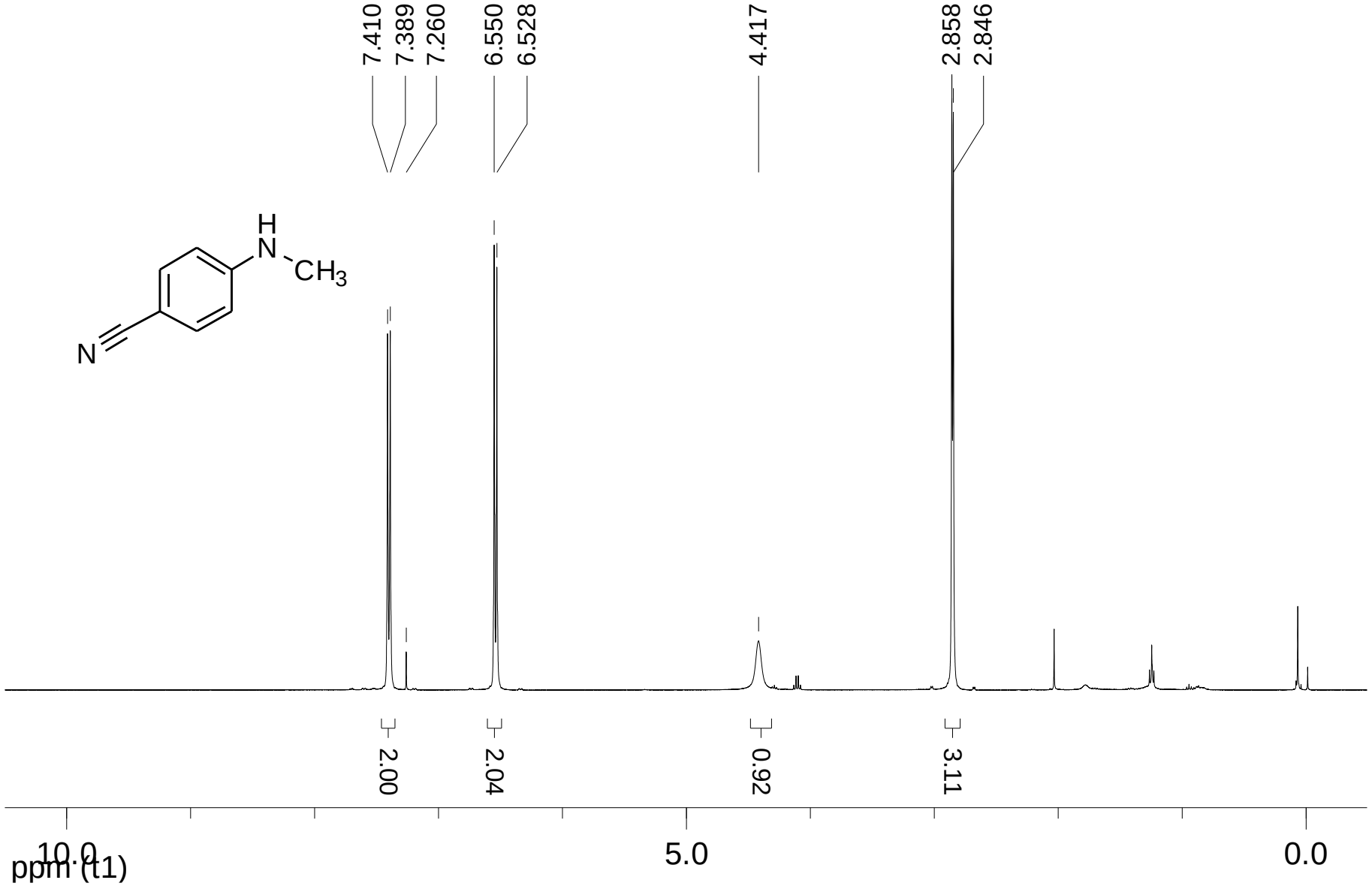

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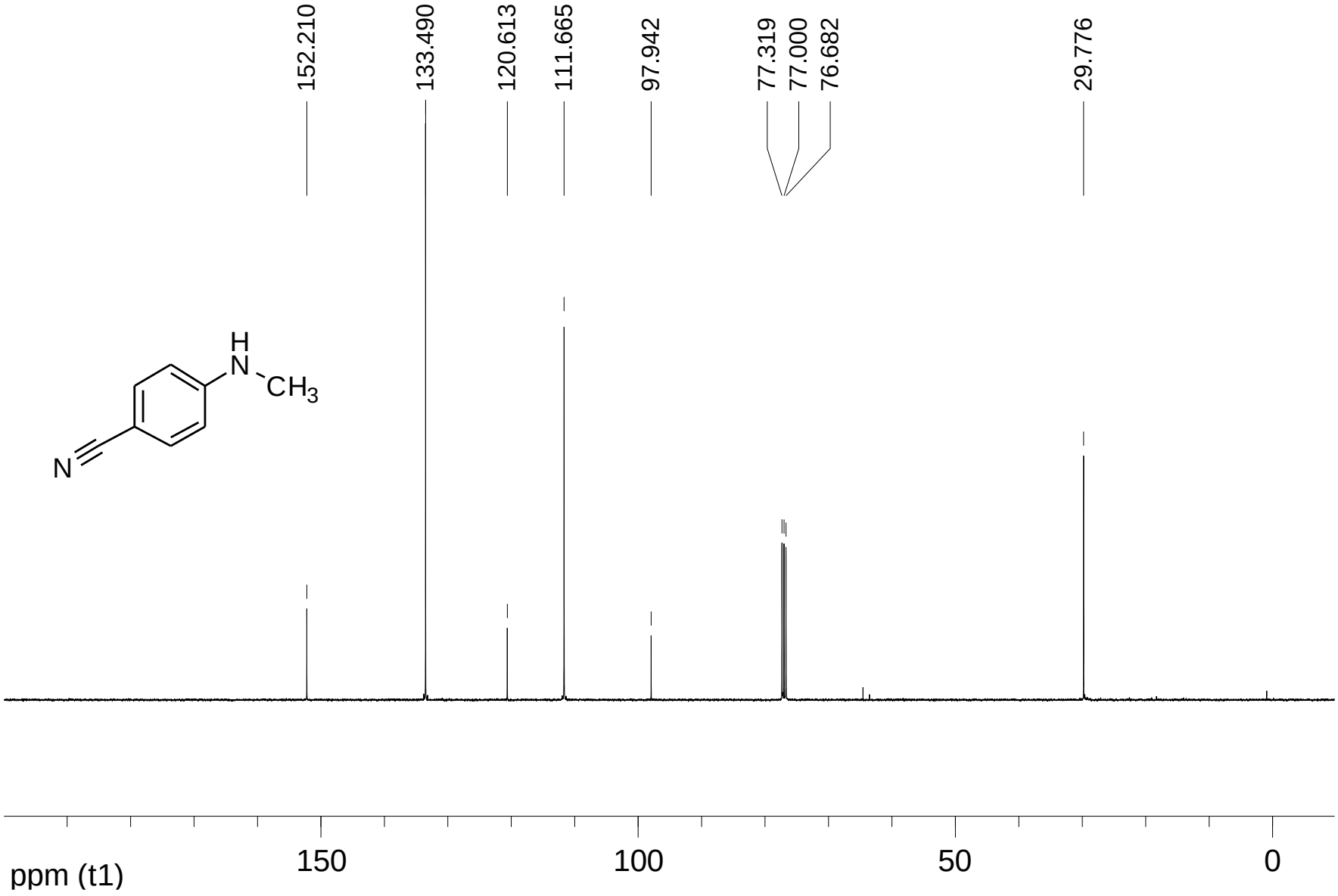
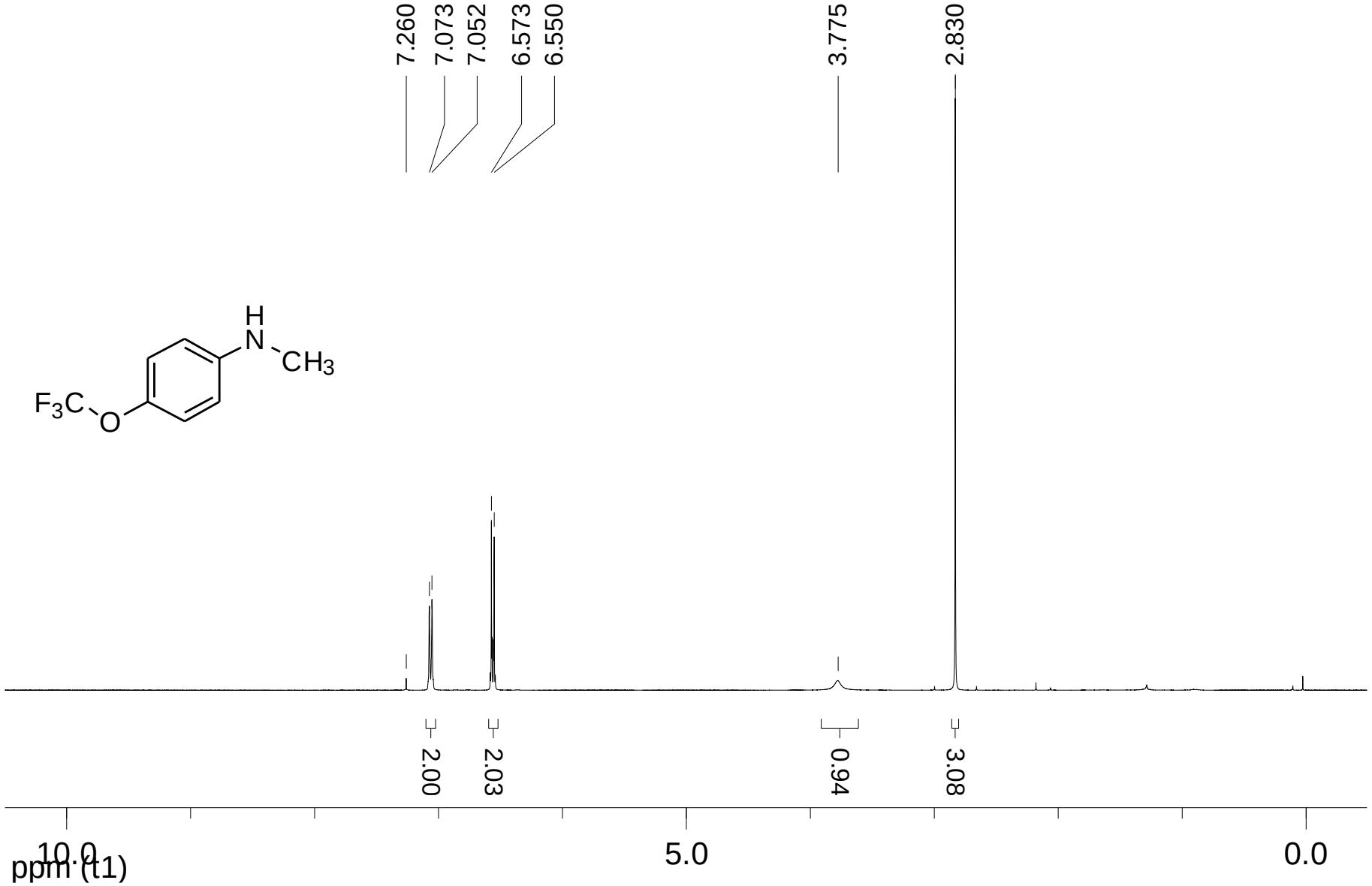


^{1}H NMR spectrum of **2k** (400M Hz, $CDCl_3$)



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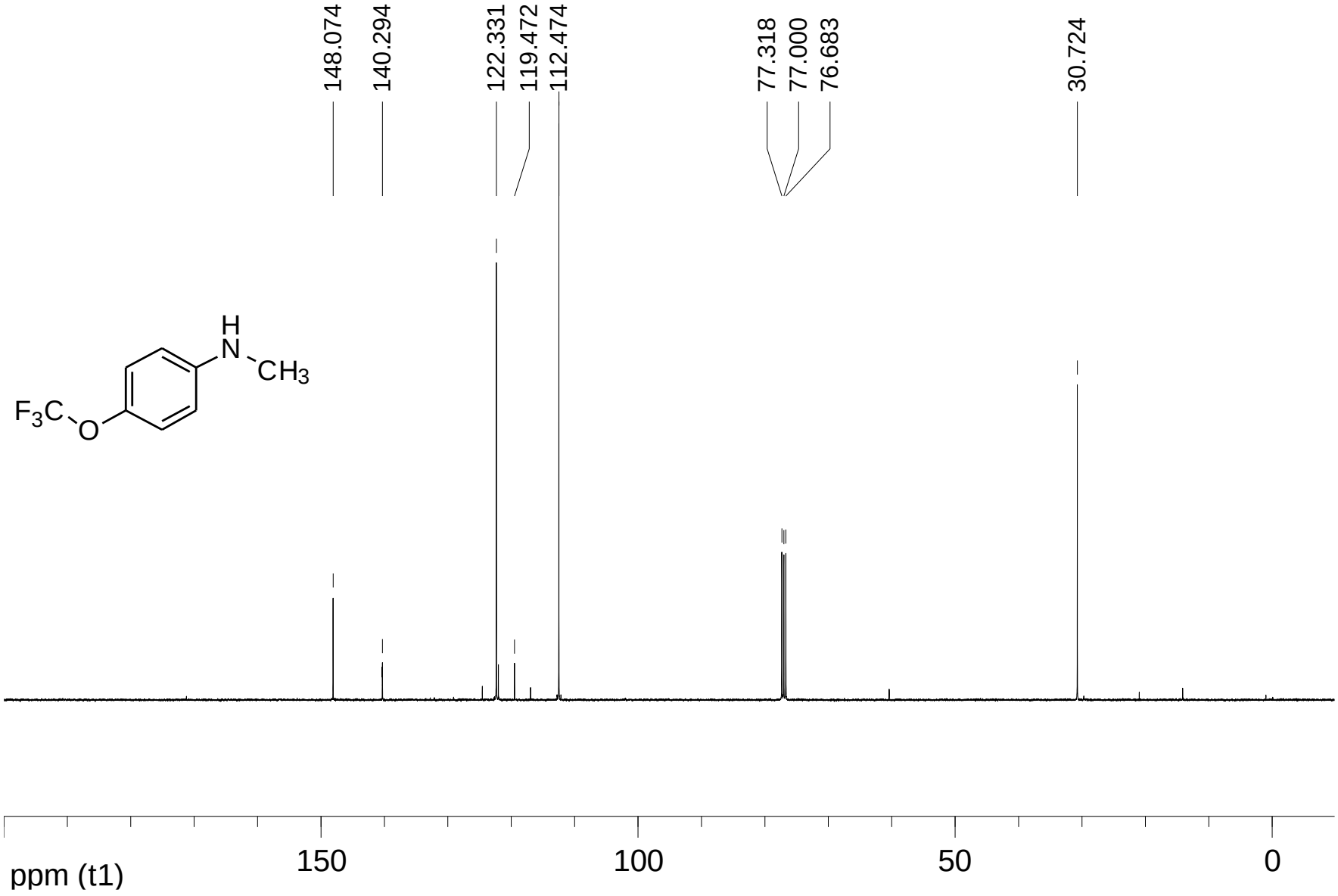
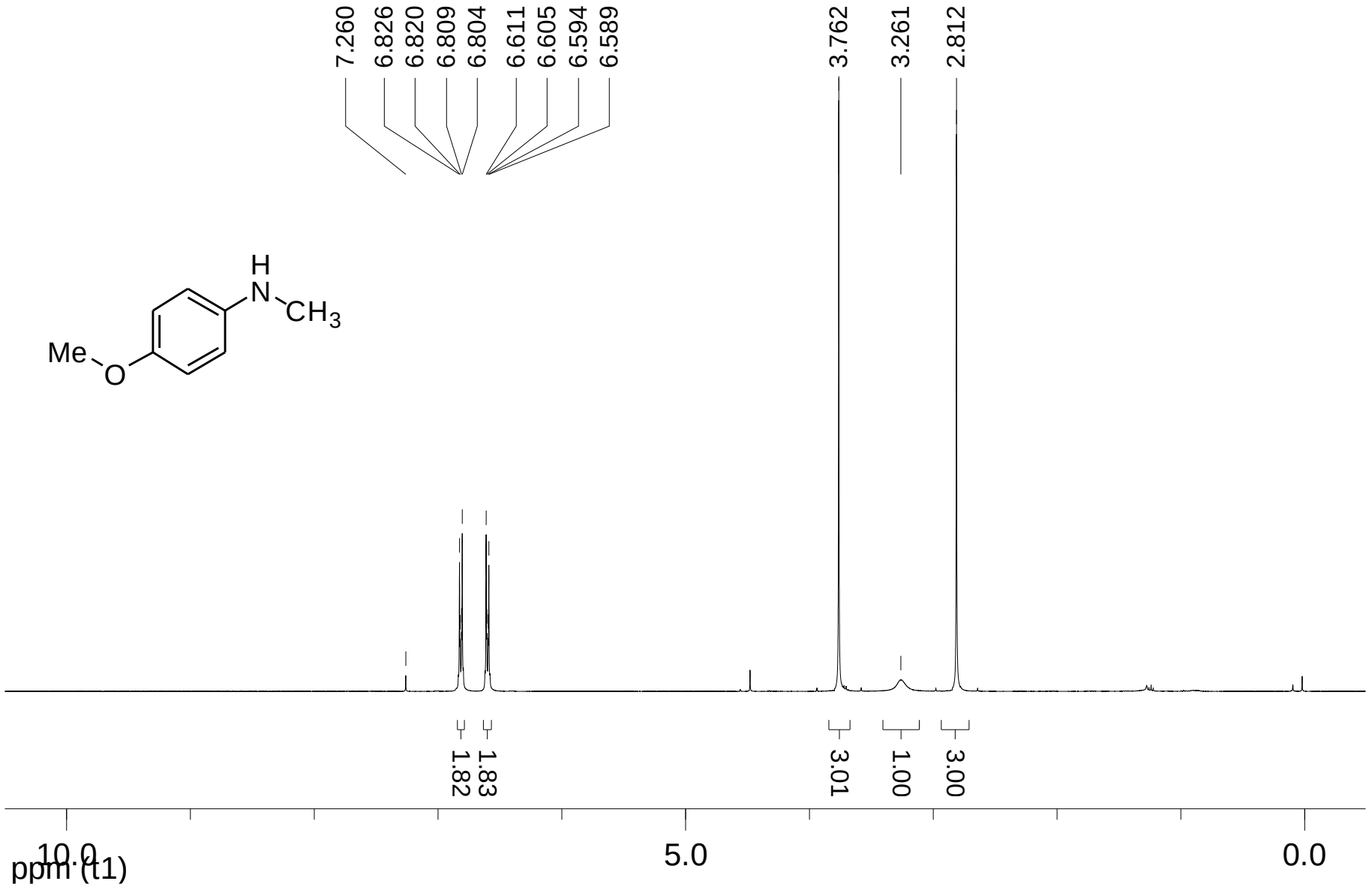
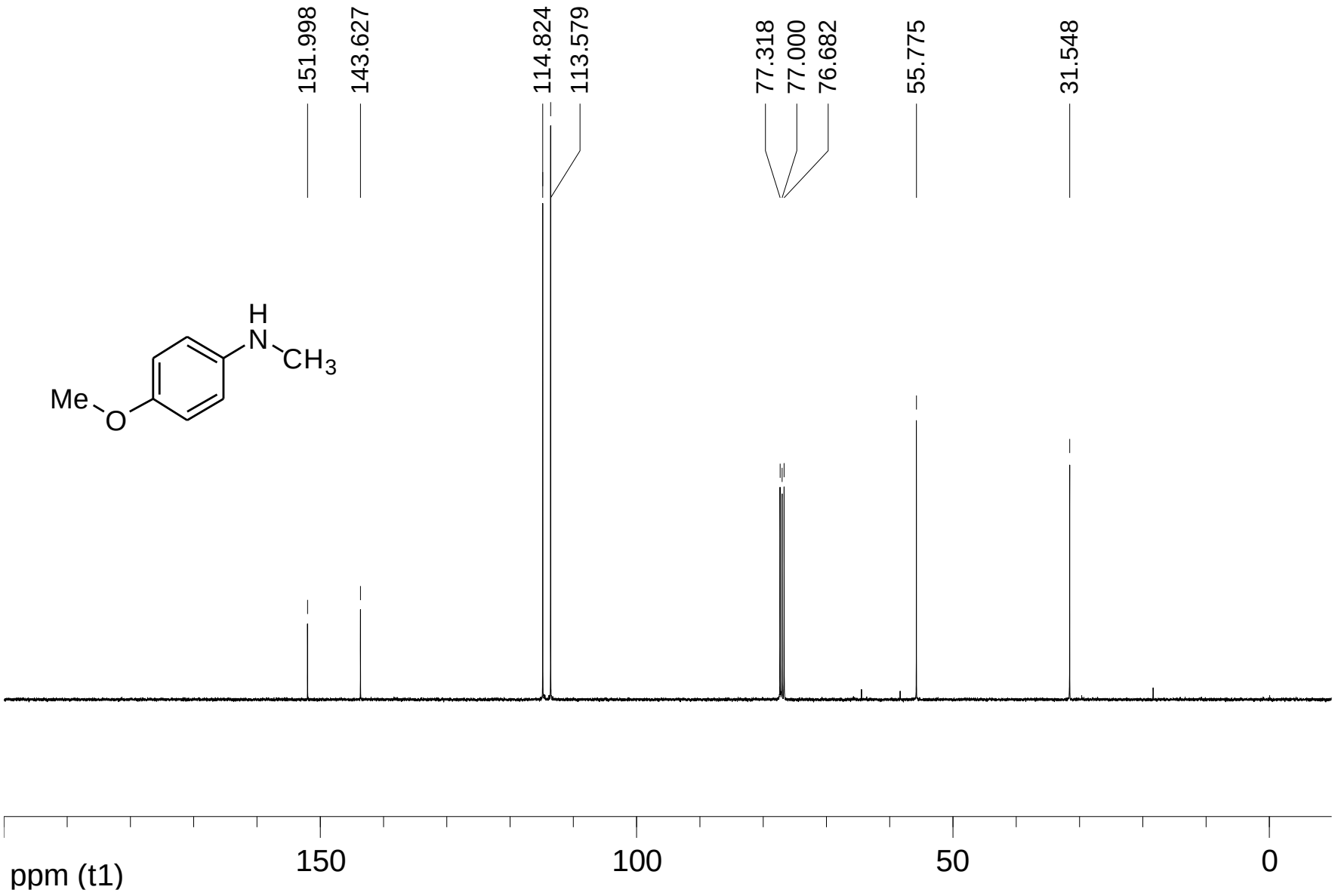


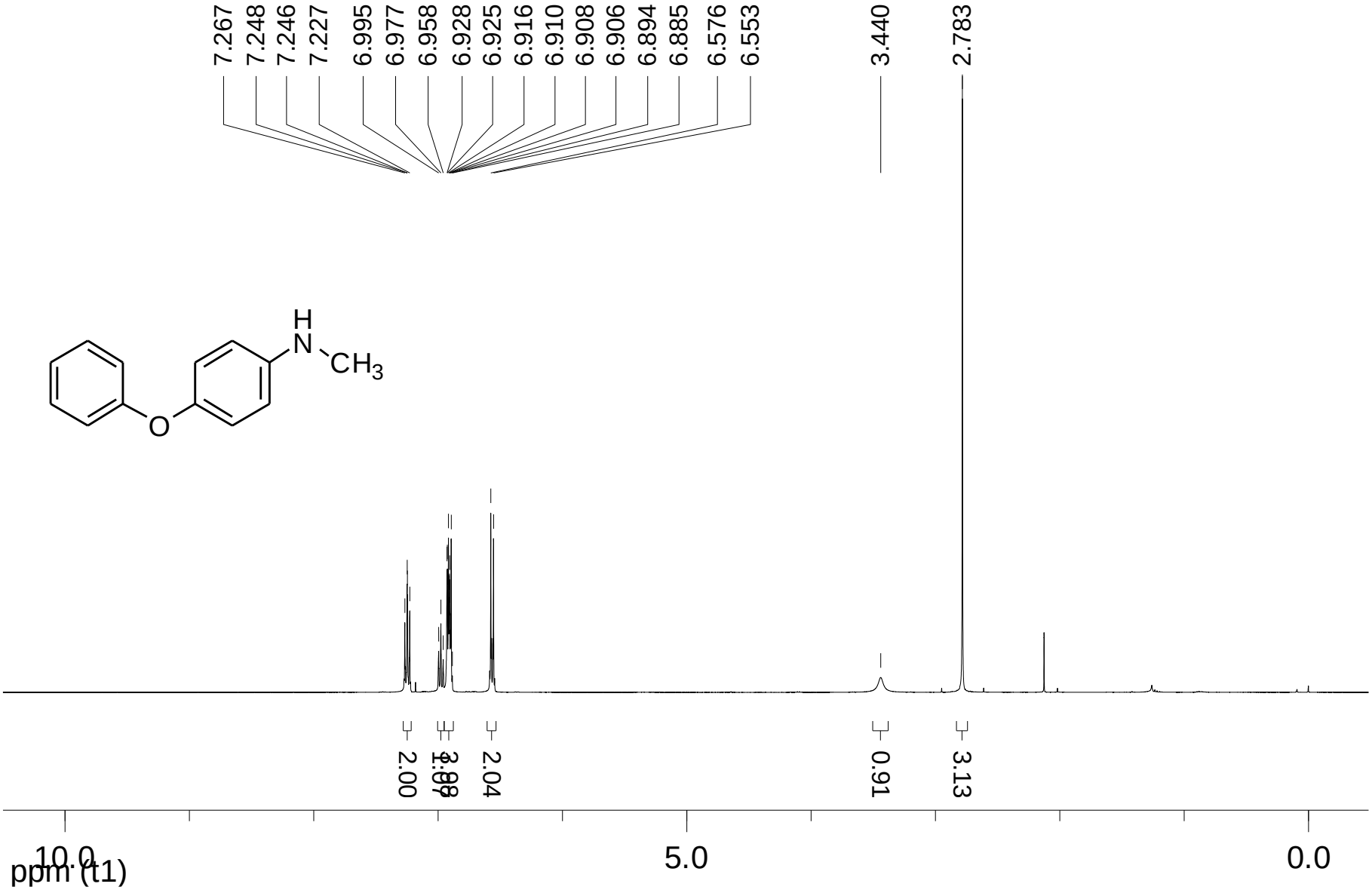
^{1}H NMR spectrum of **2l** (400M Hz, $CDCl_3$)



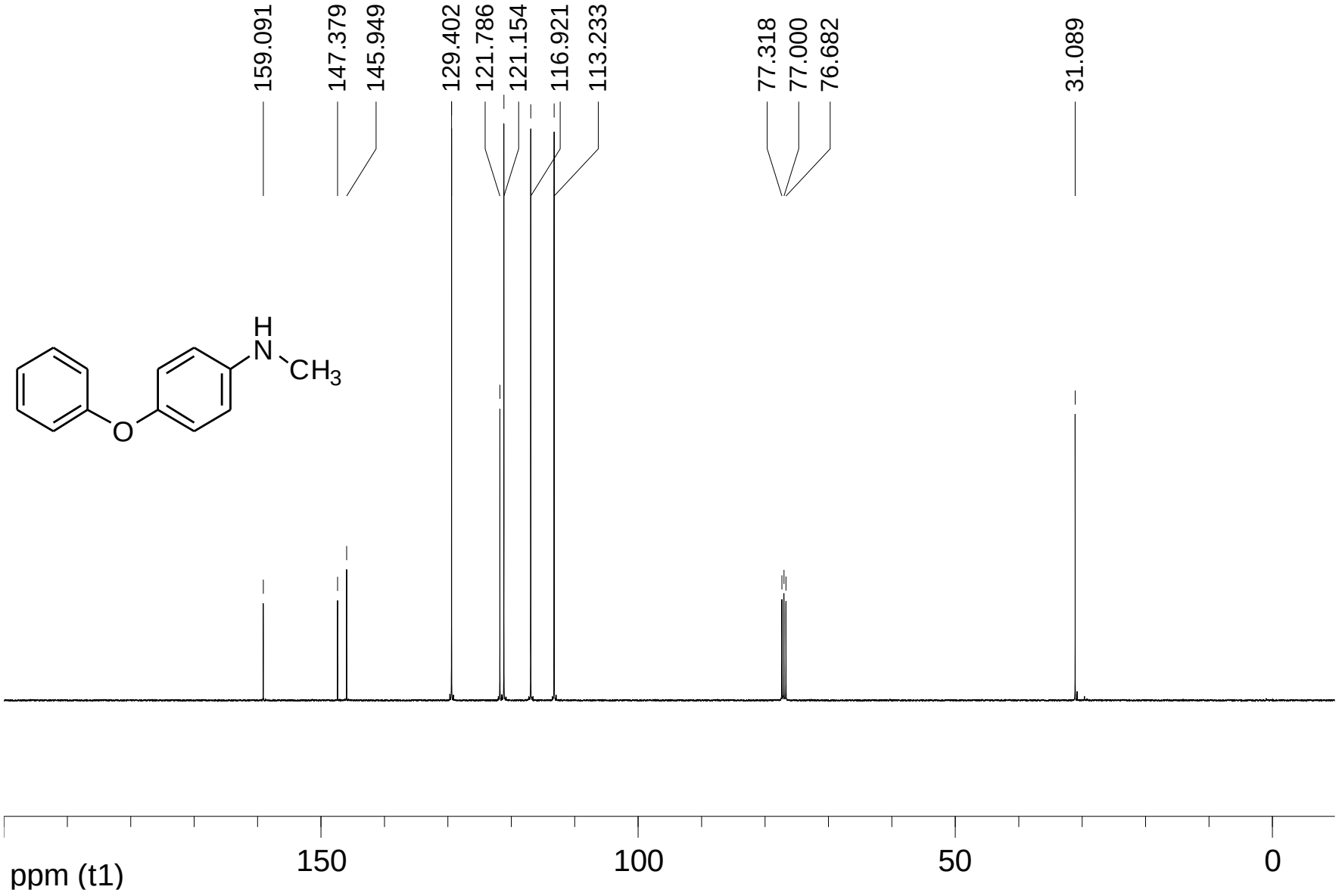
^{13}C NMR spectrum of **2l** (100M Hz, $CDCl_3$)



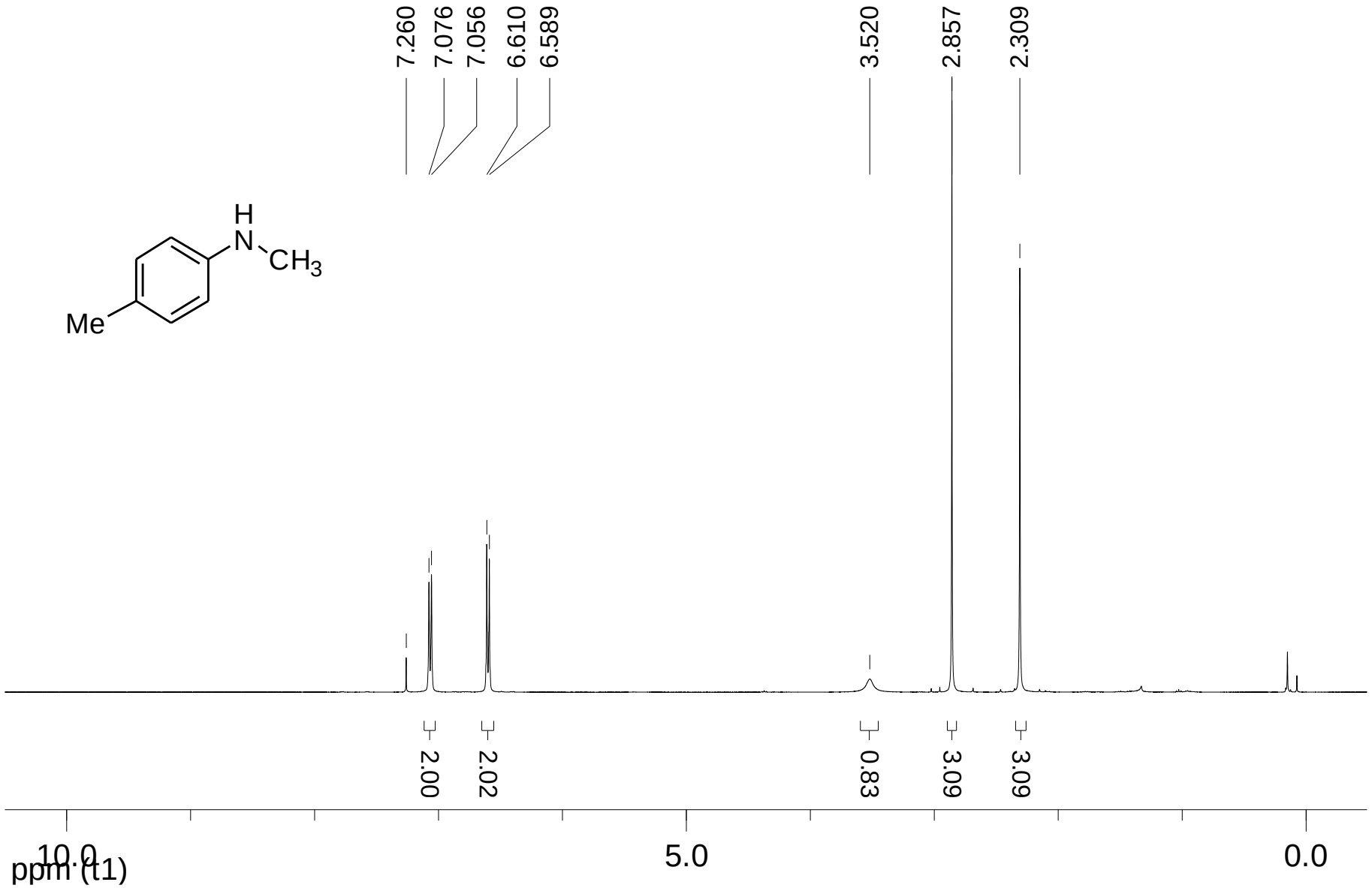
^{1}H NMR spectrum of **2m** (400M Hz, $CDCl_3$)



^{13}C NMR spectrum of **2m** (100M Hz, $CDCl_3$)



^{1}H NMR spectrum of **2n** (400M Hz, $CDCl_3$)



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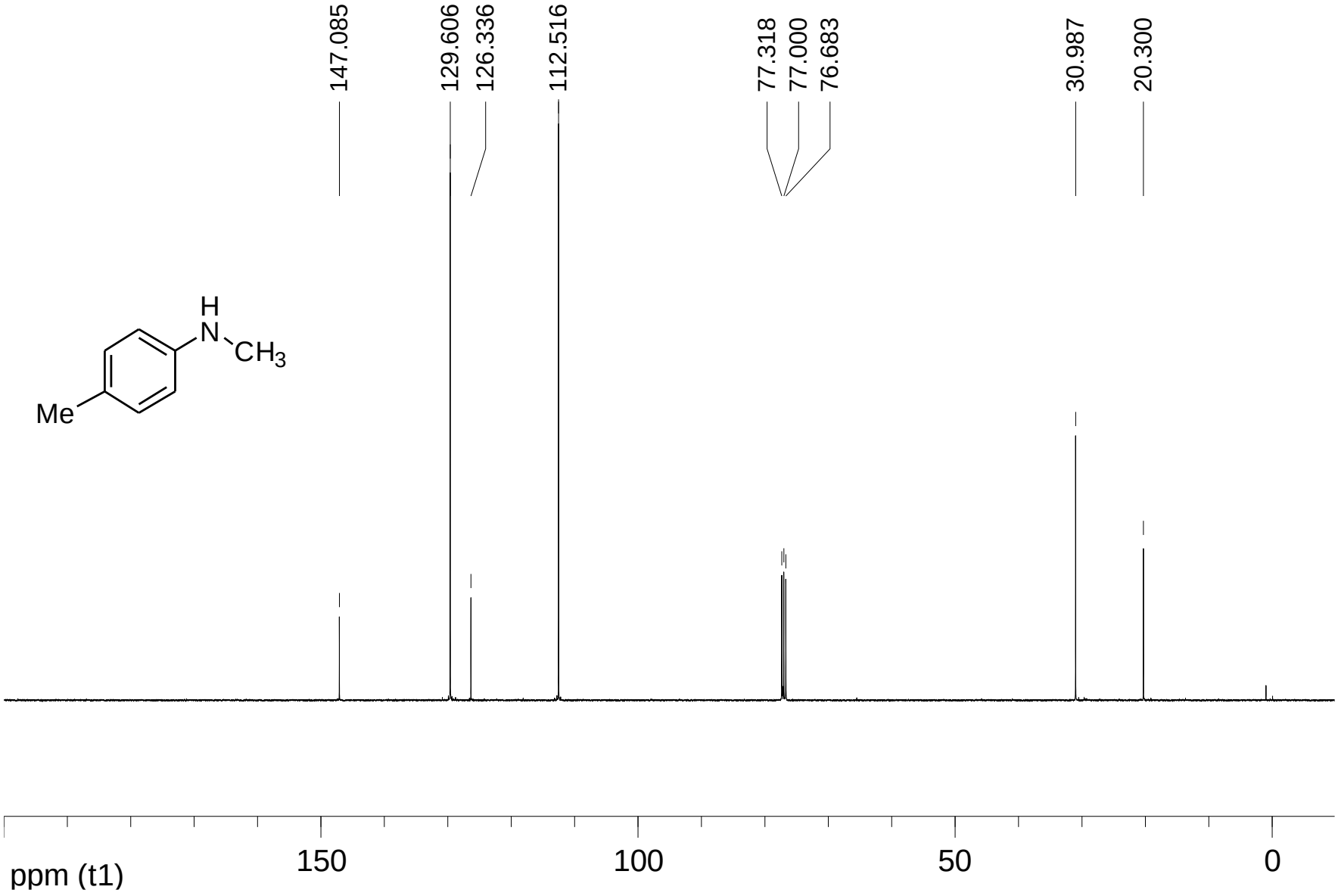
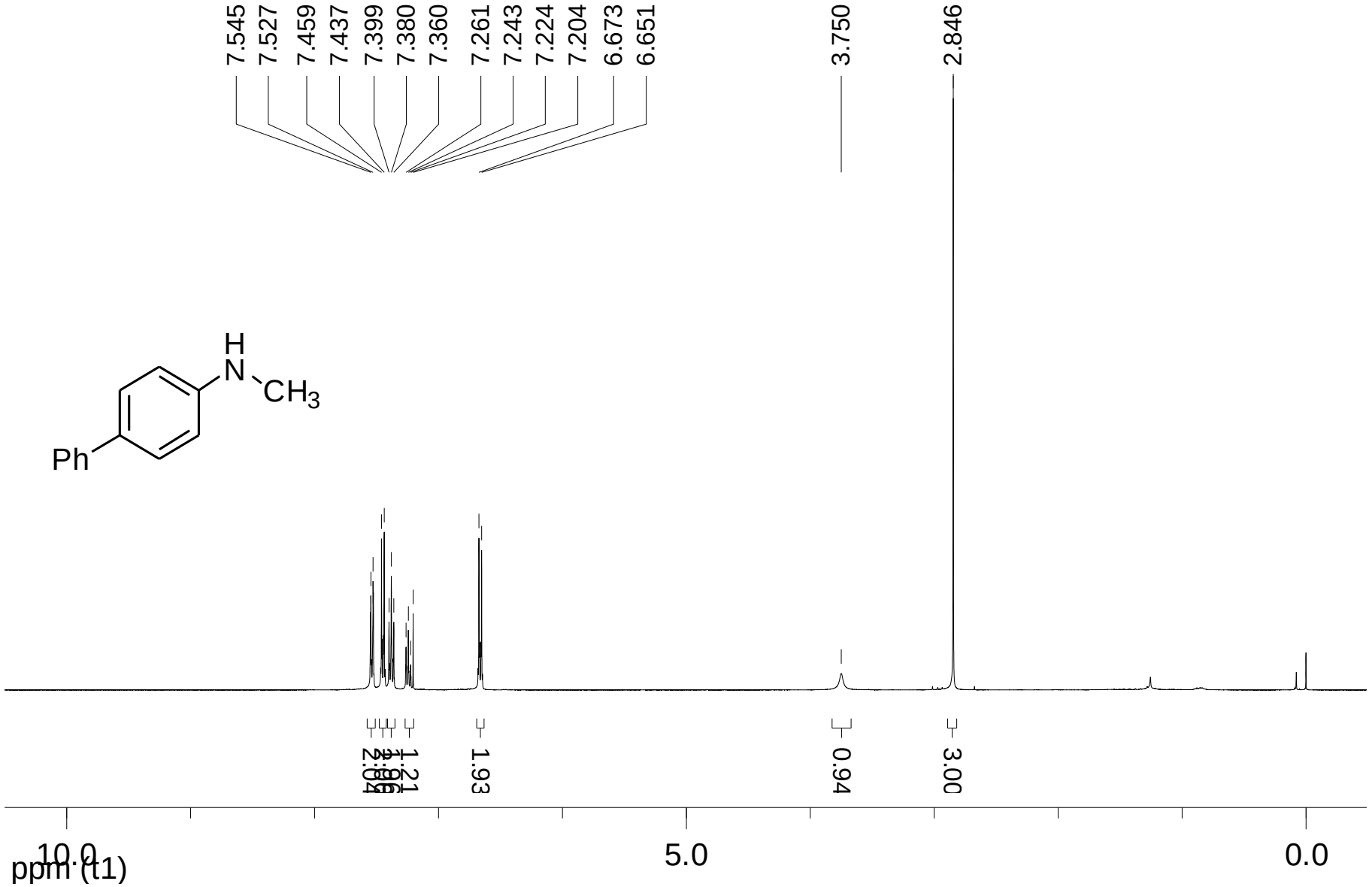
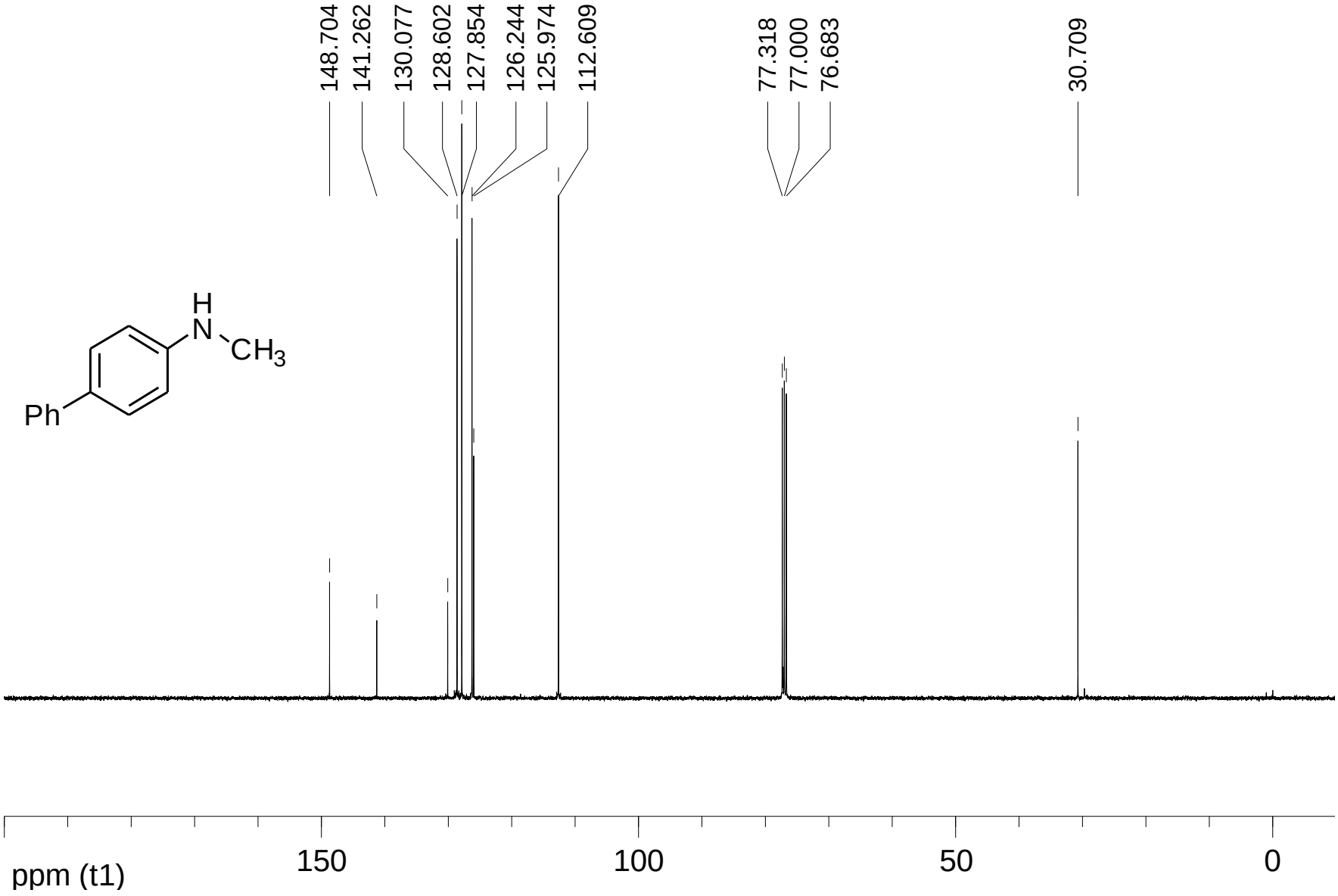


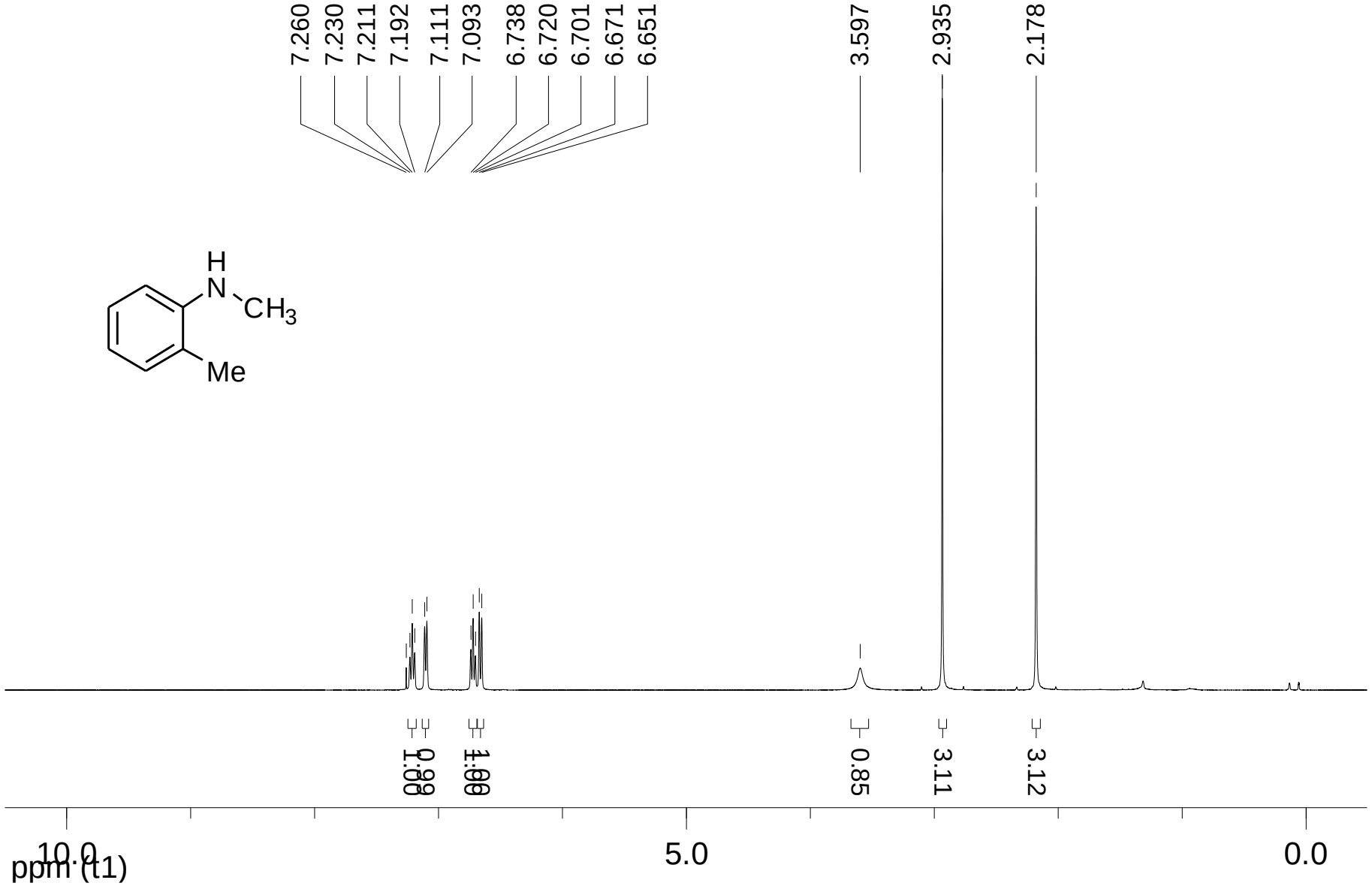
^{1}H NMR spectrum of **2o** (400M Hz, $CDCl_3$)



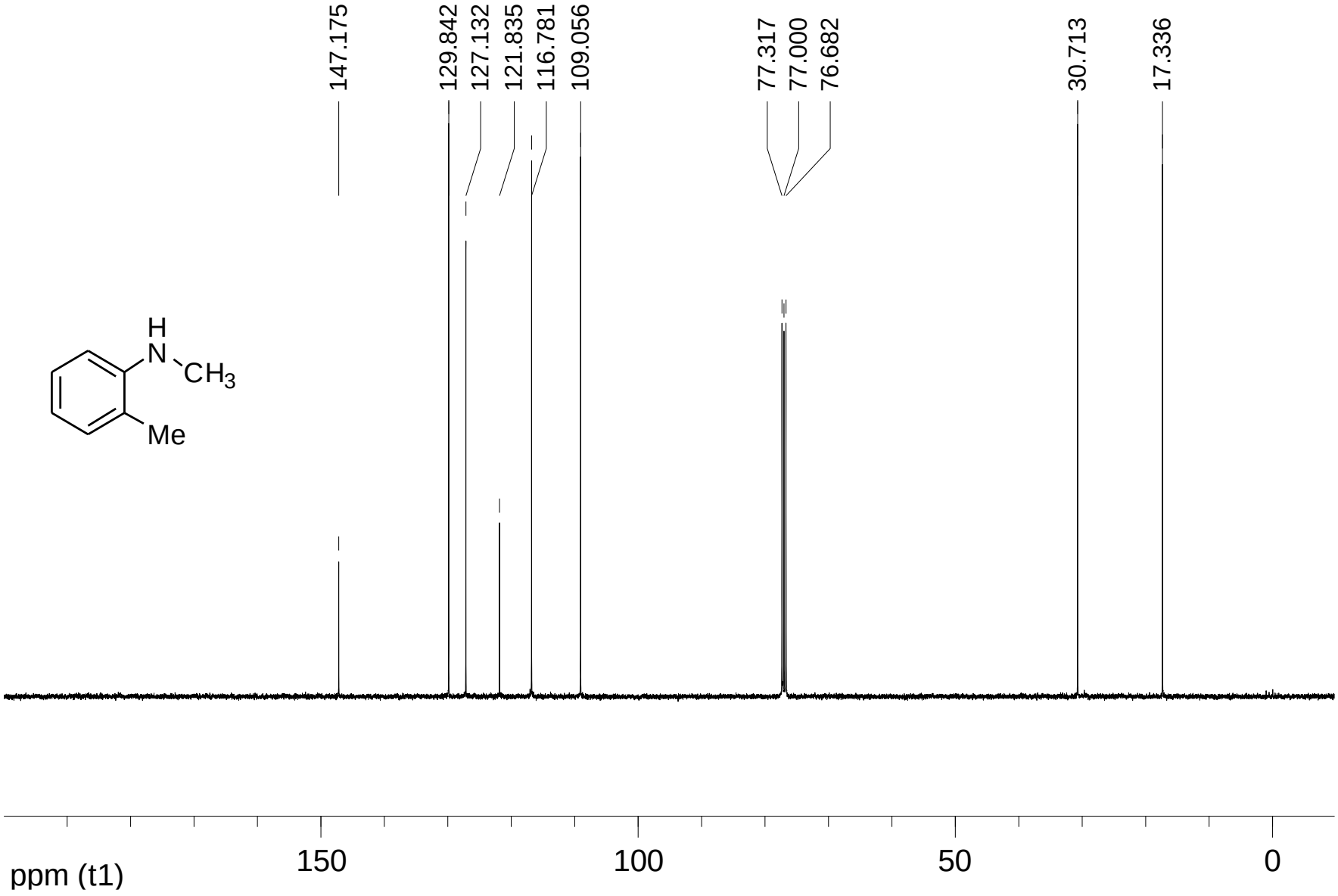
^{13}C NMR spectrum of **2o** (100M Hz, $CDCl_3$)



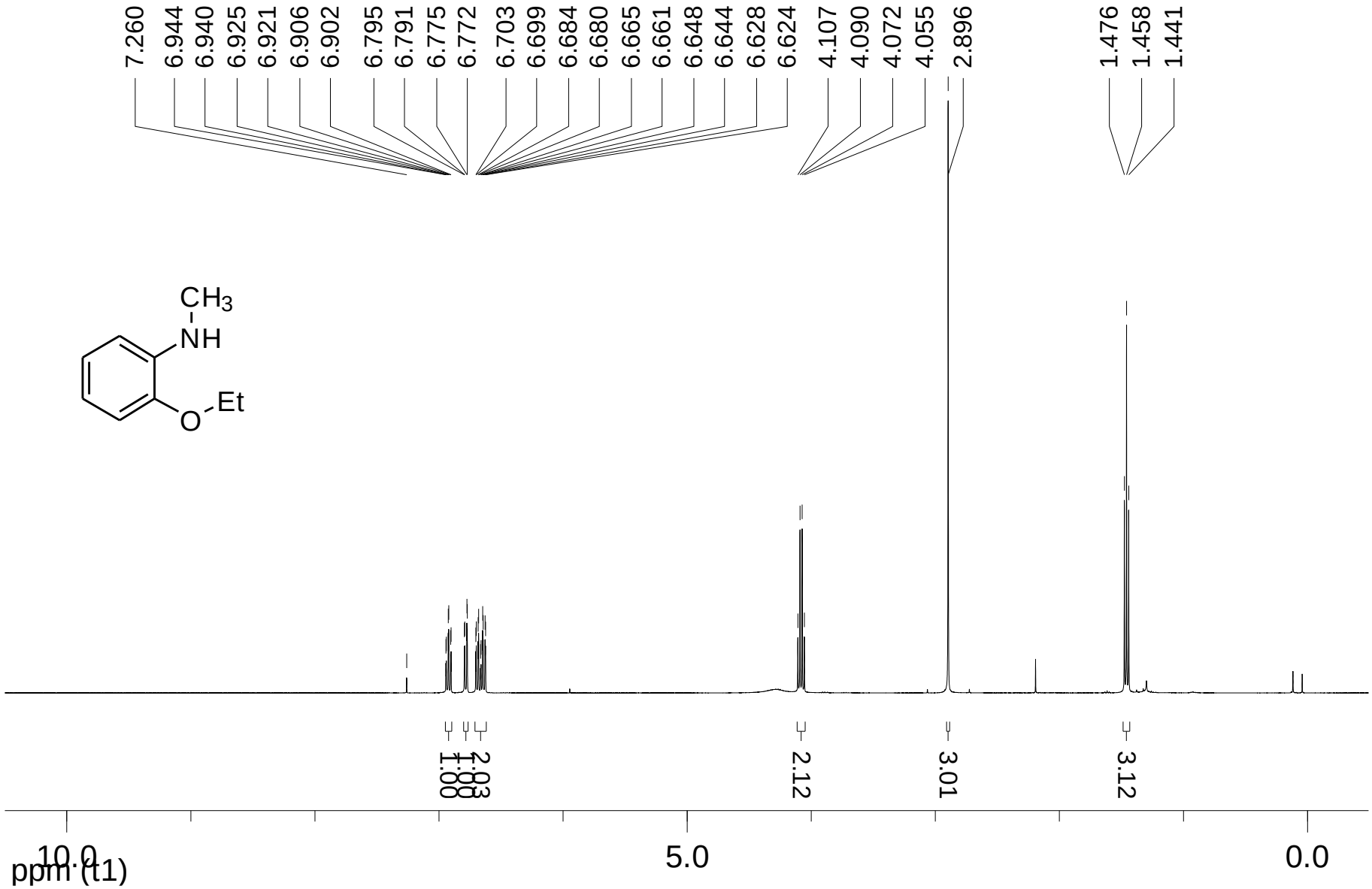
^{1}H NMR spectrum of **2p** (400M Hz, $CDCl_3$)



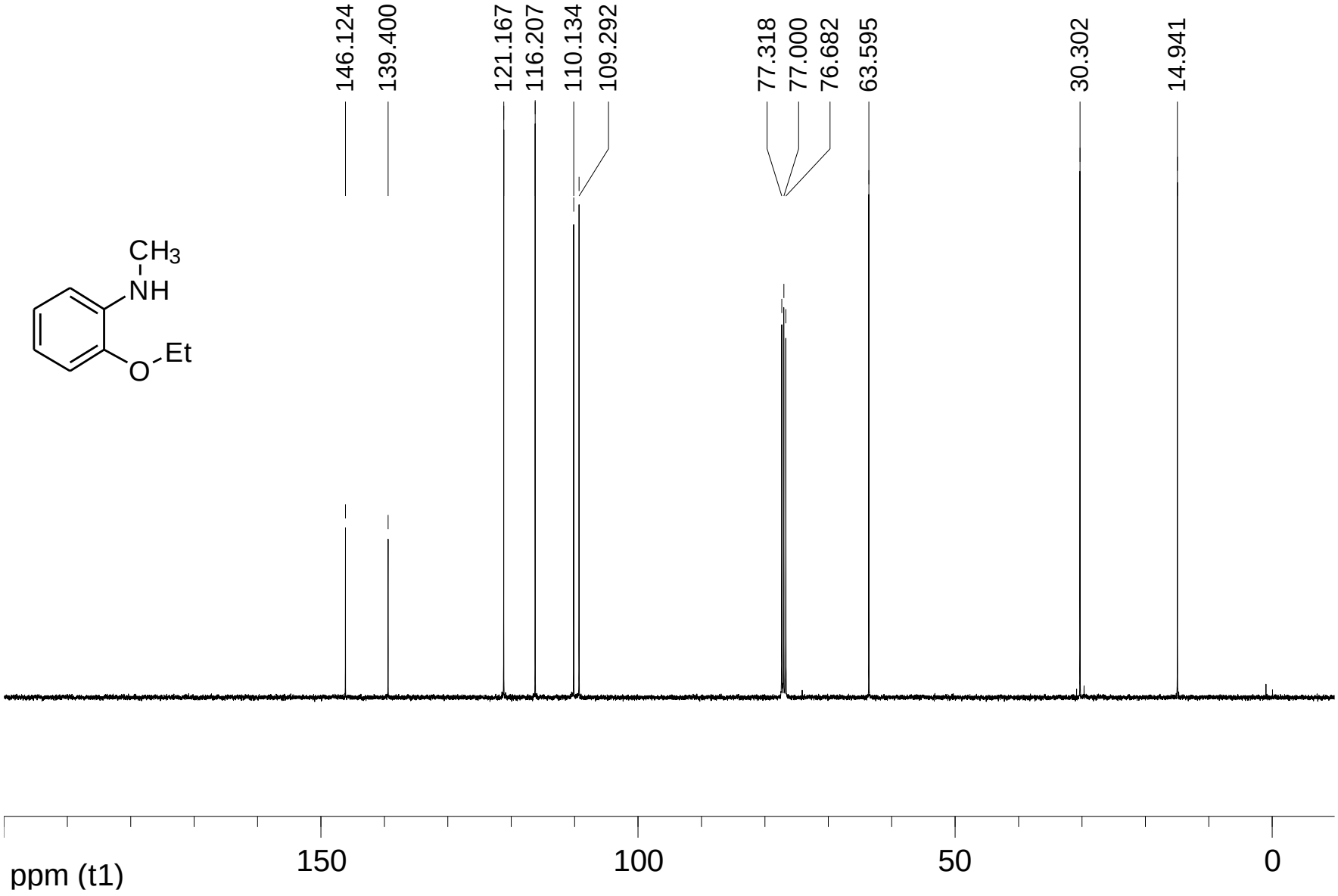
^{13}C NMR spectrum of **2p** (100M Hz, $CDCl_3$)



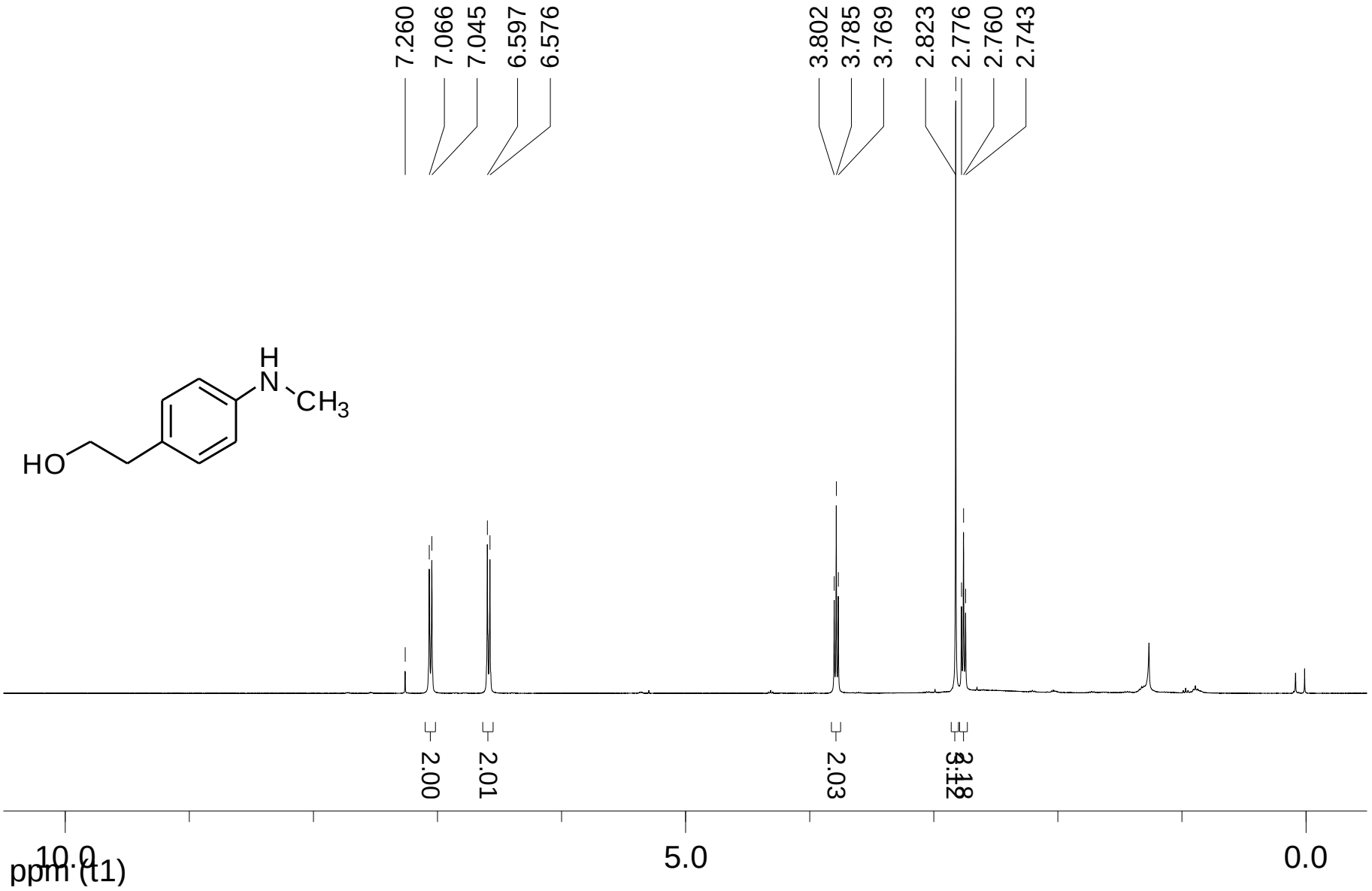
^{1}H NMR spectrum of **2q** (400M Hz, $CDCl_3$)



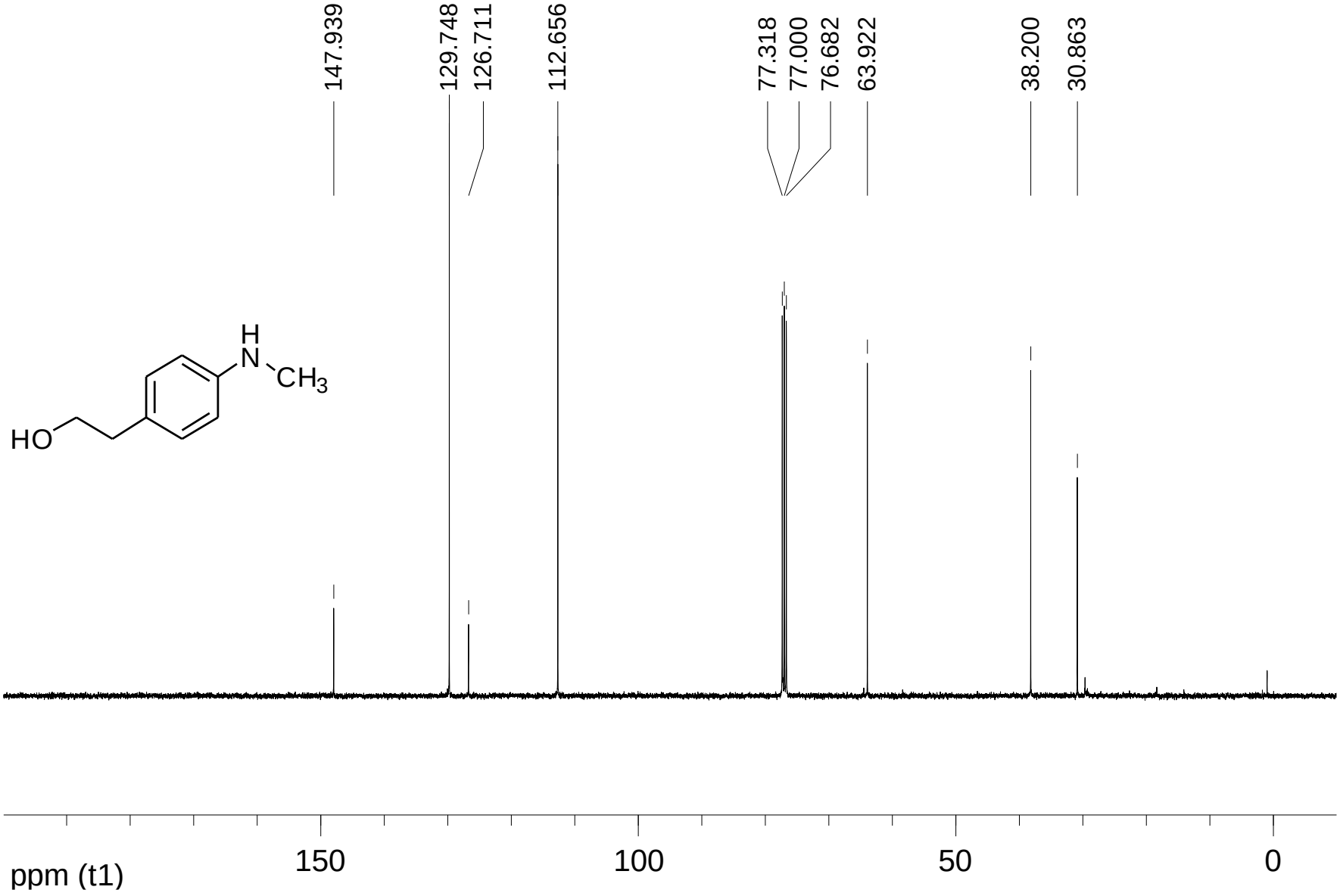
^{13}C NMR spectrum of **2q** (100M Hz, $CDCl_3$)



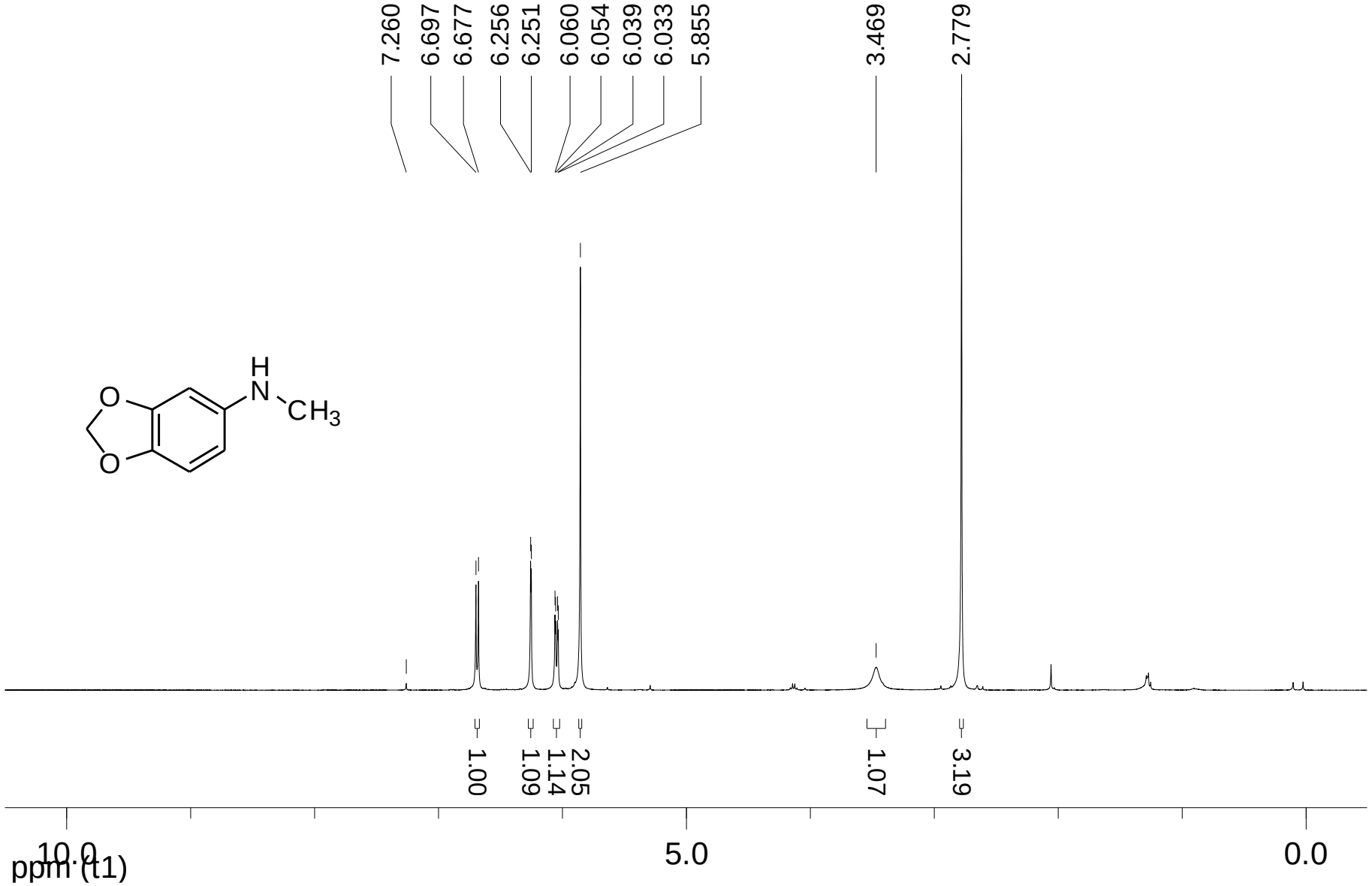
^{1}H NMR spectrum of **2s** (400M Hz, $CDCl_3$)



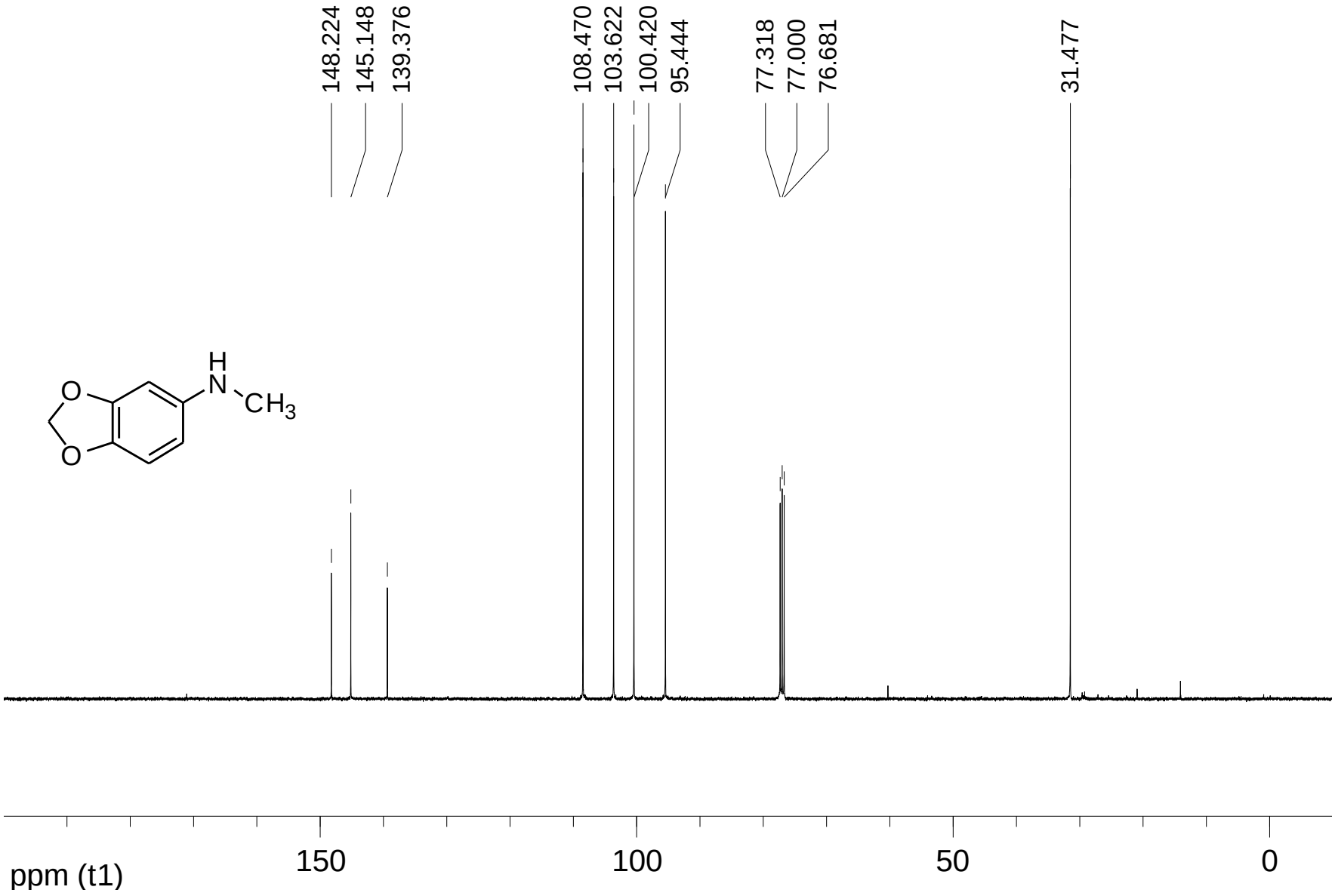
^{13}C NMR spectrum of **2s** (100M Hz, $CDCl_3$)



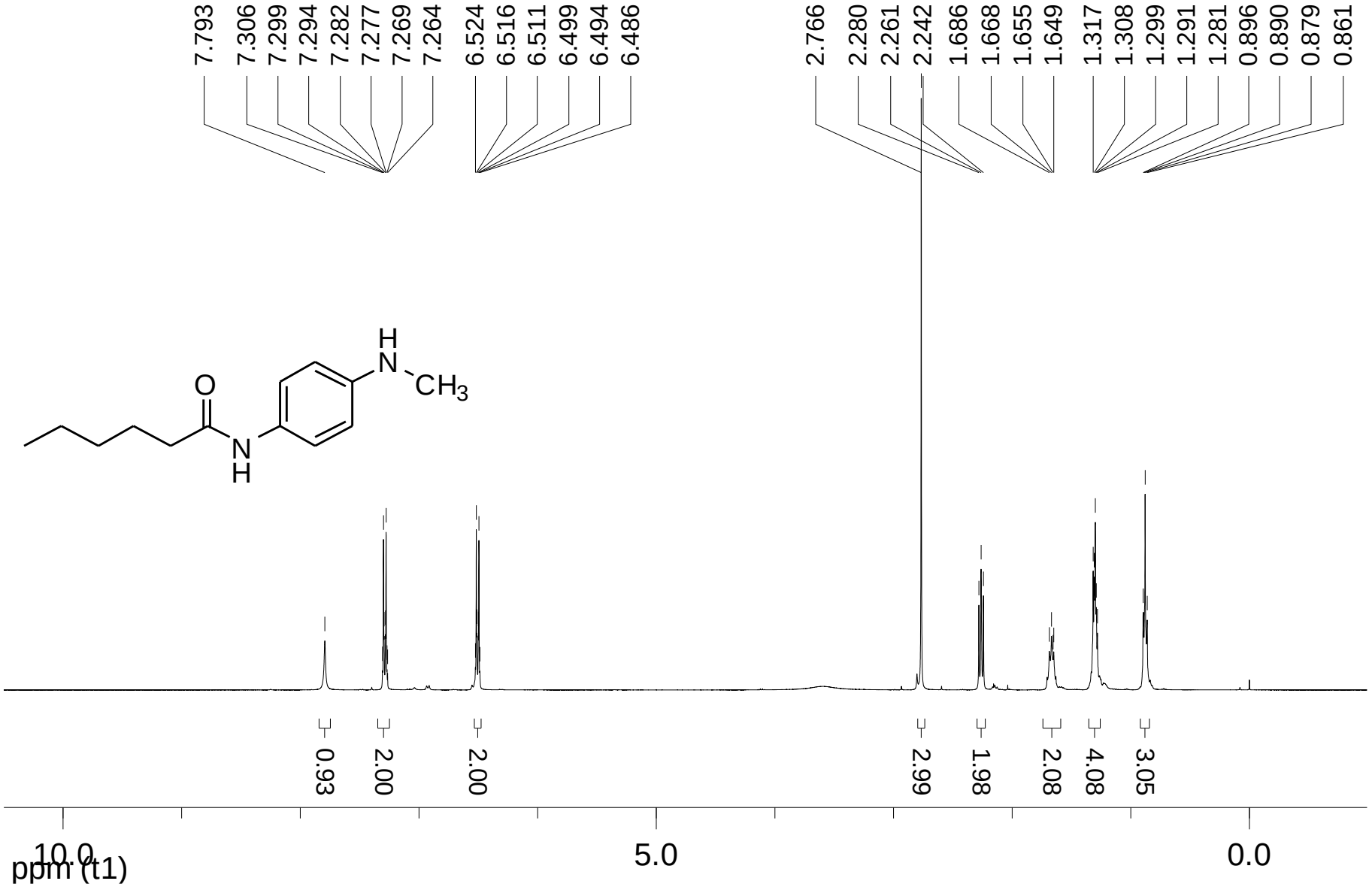
^{1}H NMR spectrum of **2t** (400M Hz, $CDCl_3$)



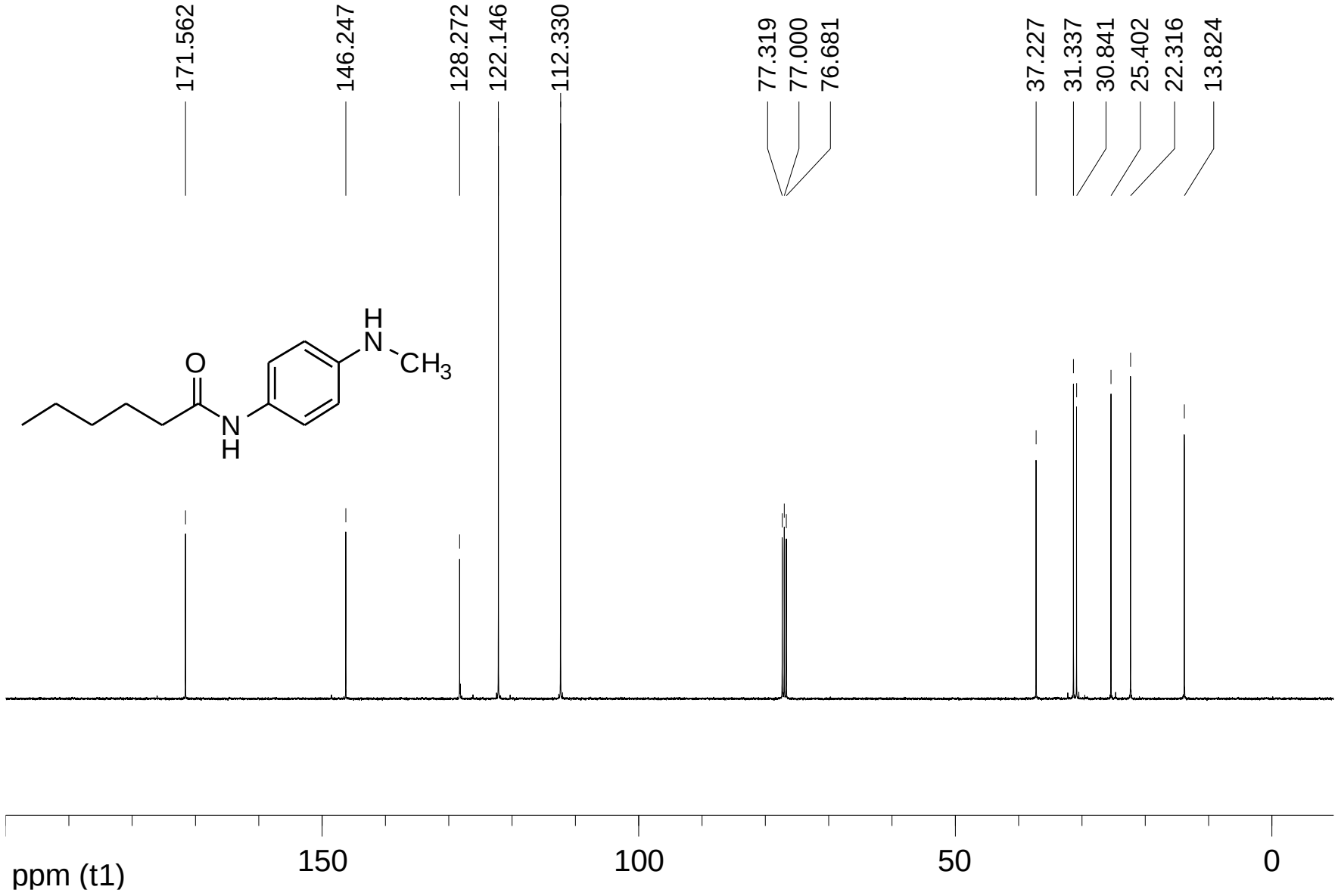
^{13}C NMR spectrum of **2t** (100M Hz, $CDCl_3$)



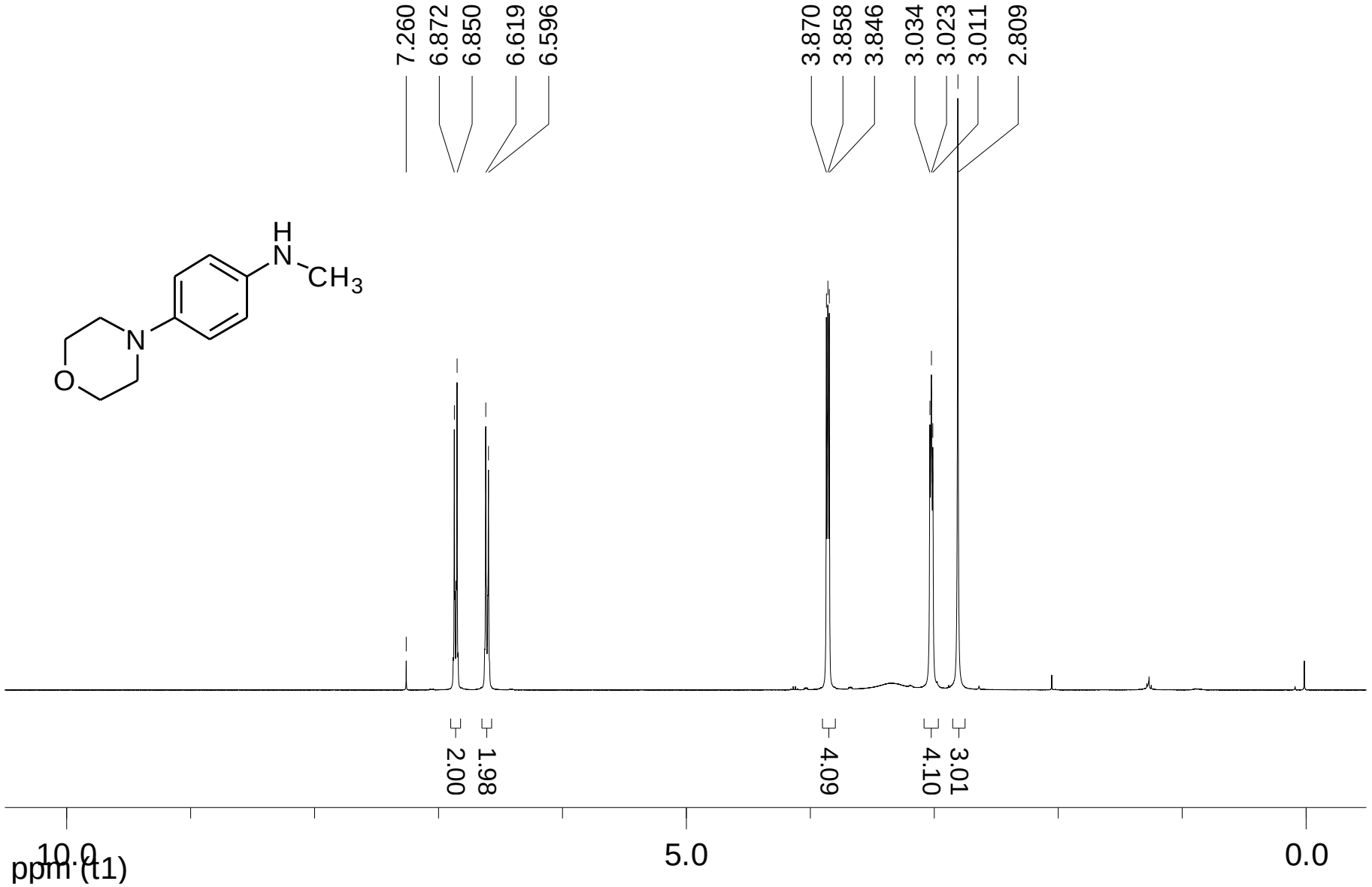
^{1}H NMR spectrum of **2u** (400M Hz, $CDCl_3$)



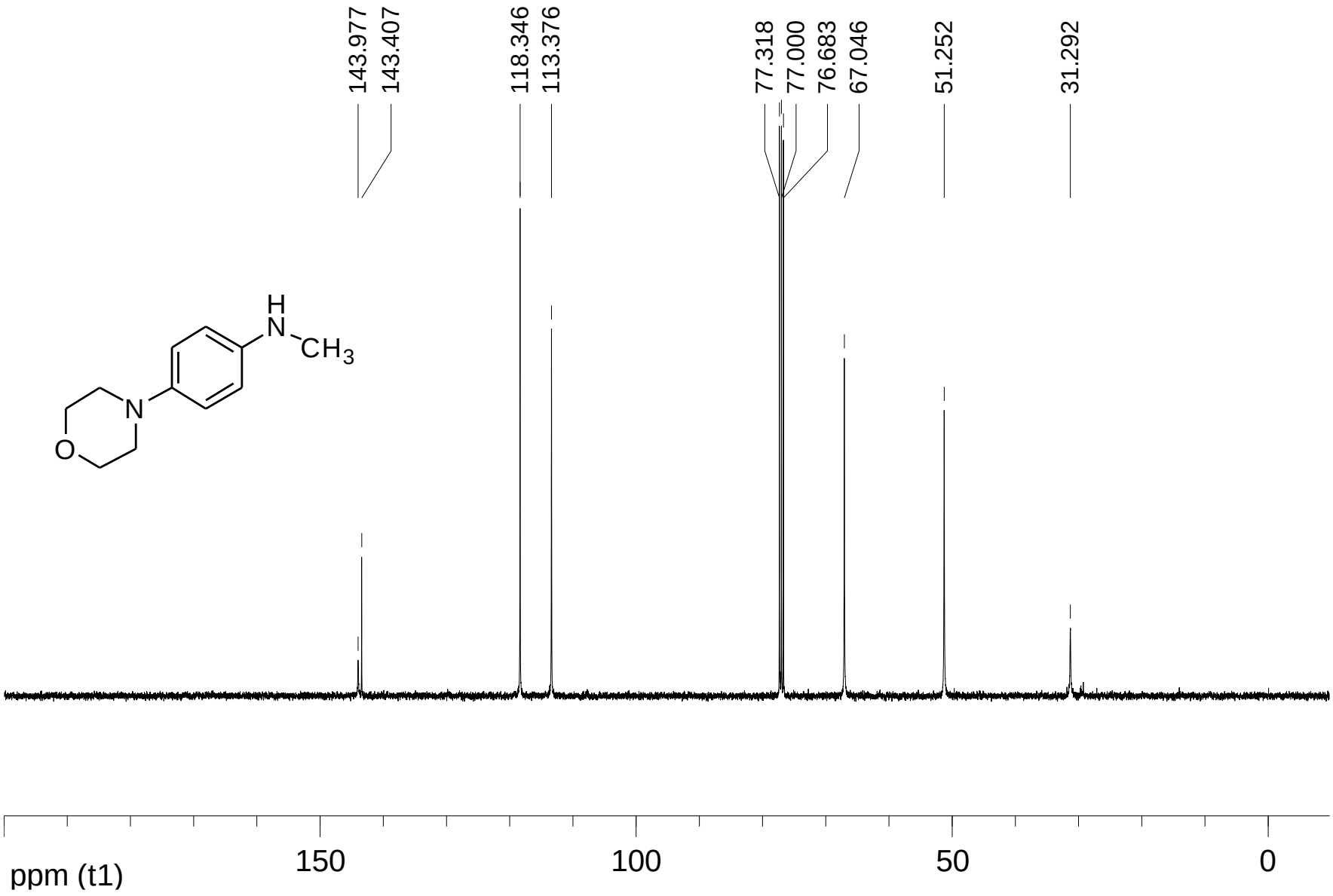
^{13}C NMR spectrum of **2u** (100M Hz, $CDCl_3$)



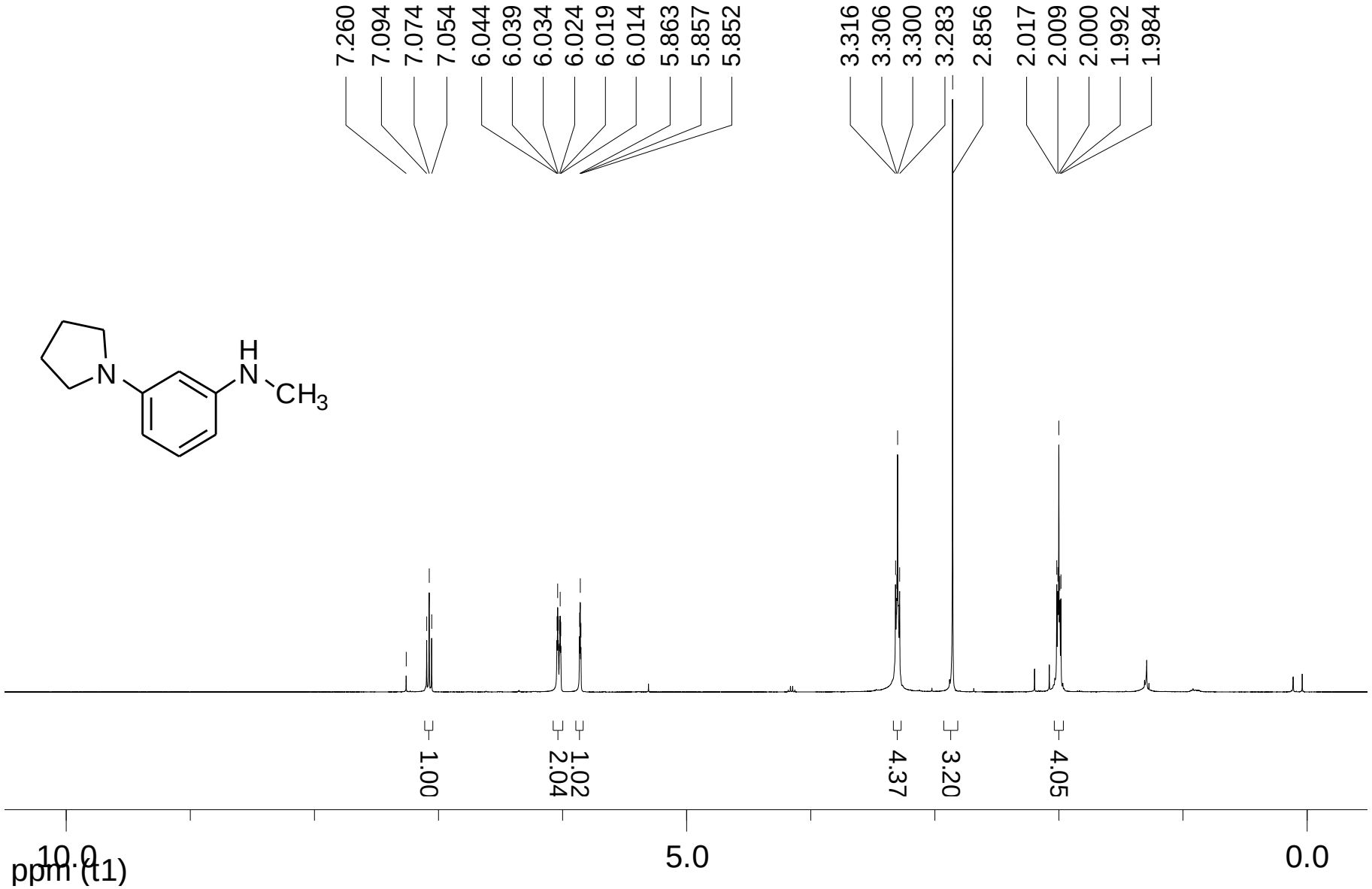
^{1}H NMR spectrum of **2v** (400M Hz, $CDCl_3$)



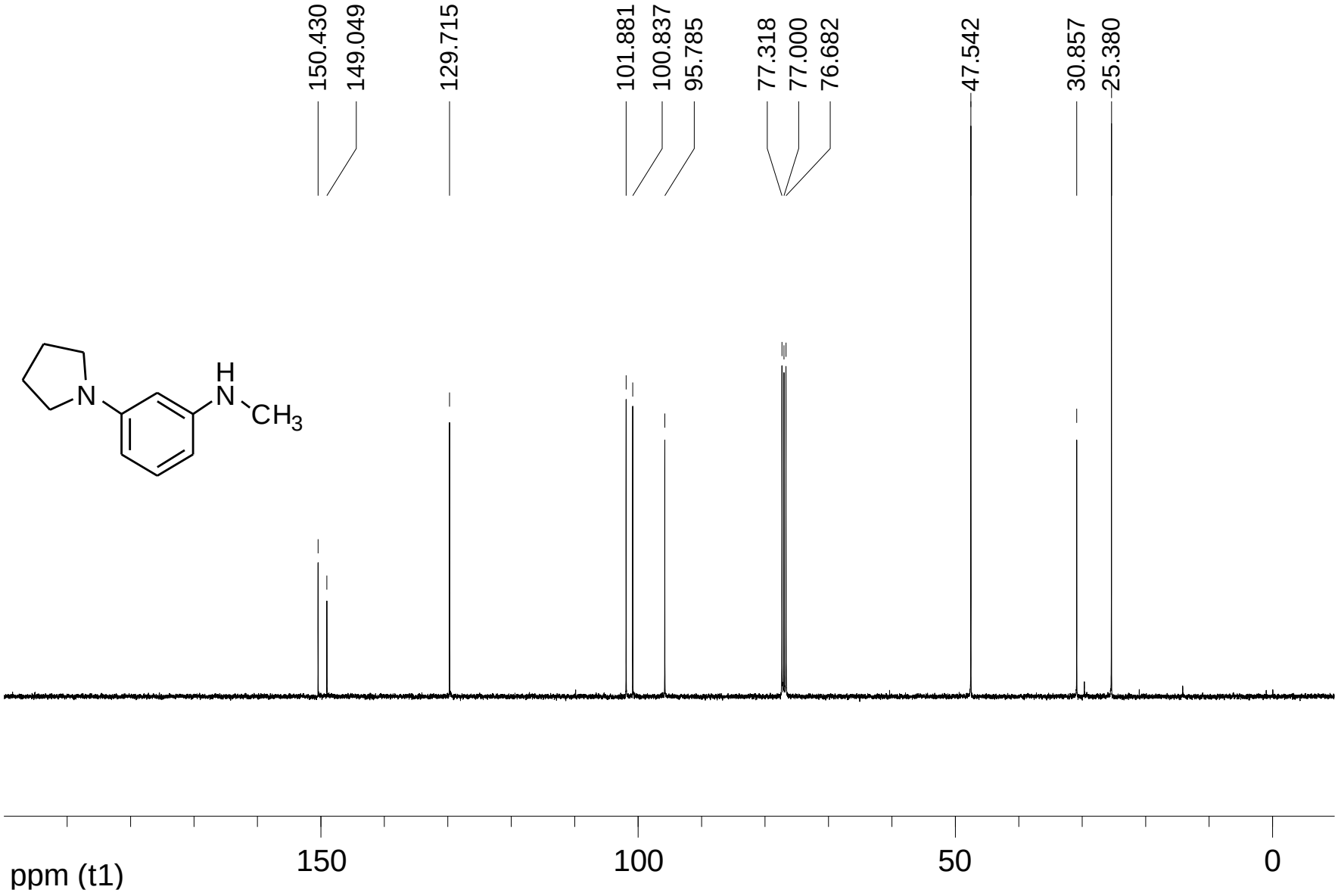
^{13}C NMR spectrum of **2v** (100M Hz, $CDCl_3$)



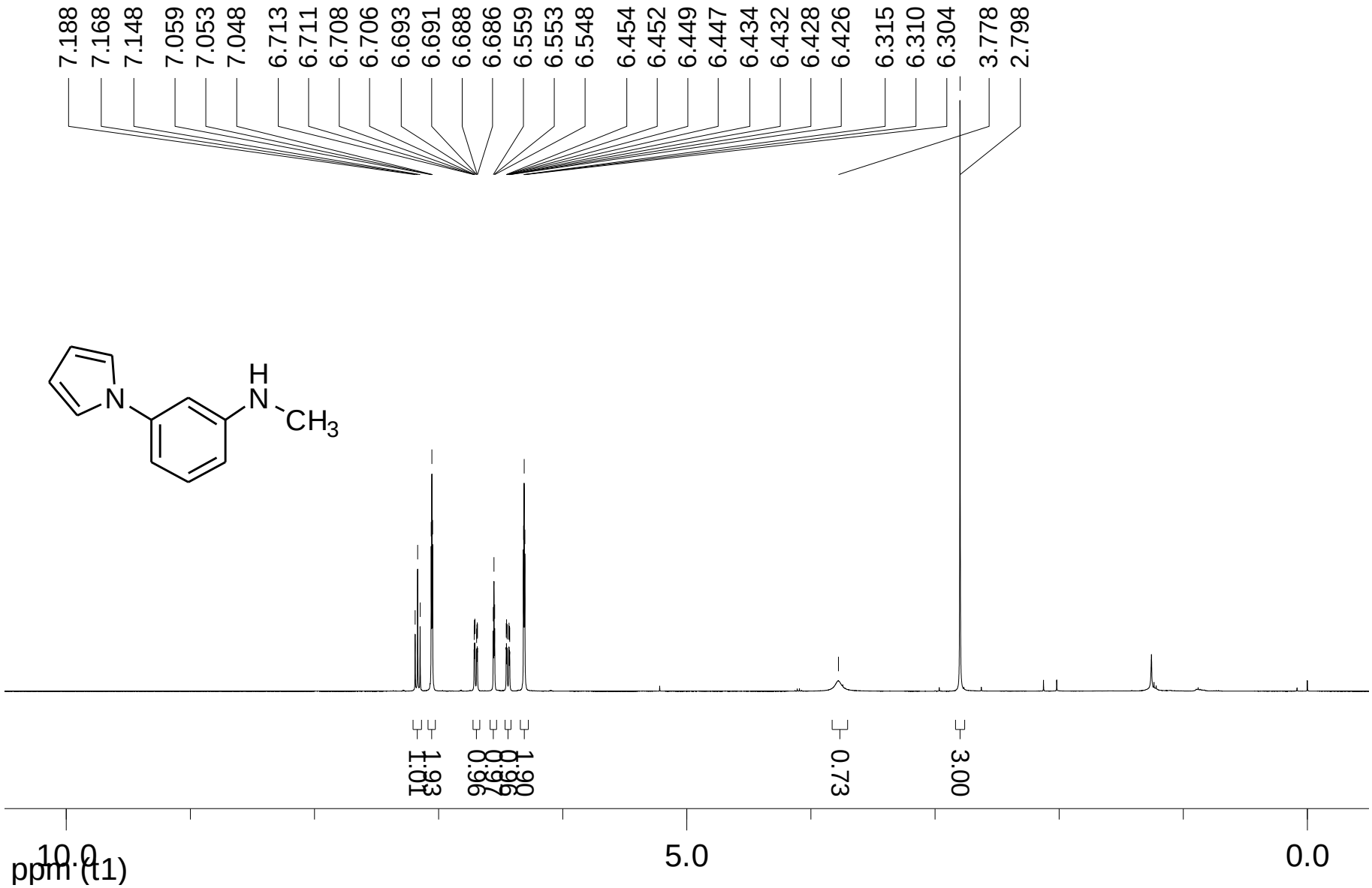
^{1}H NMR spectrum of **2w** (400M Hz, $CDCl_3$)



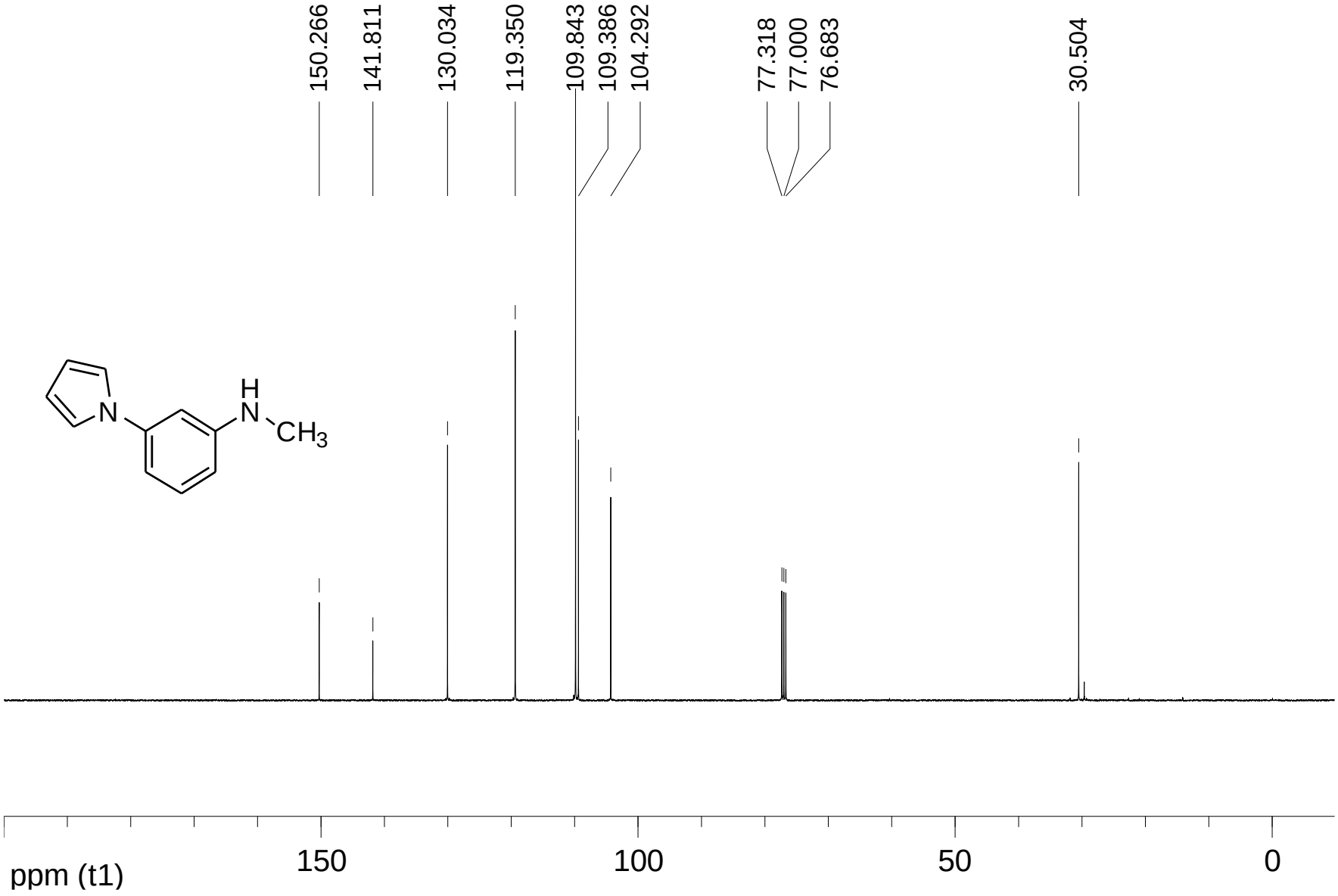
^{13}C NMR spectrum of **2w** (100M Hz, $CDCl_3$)



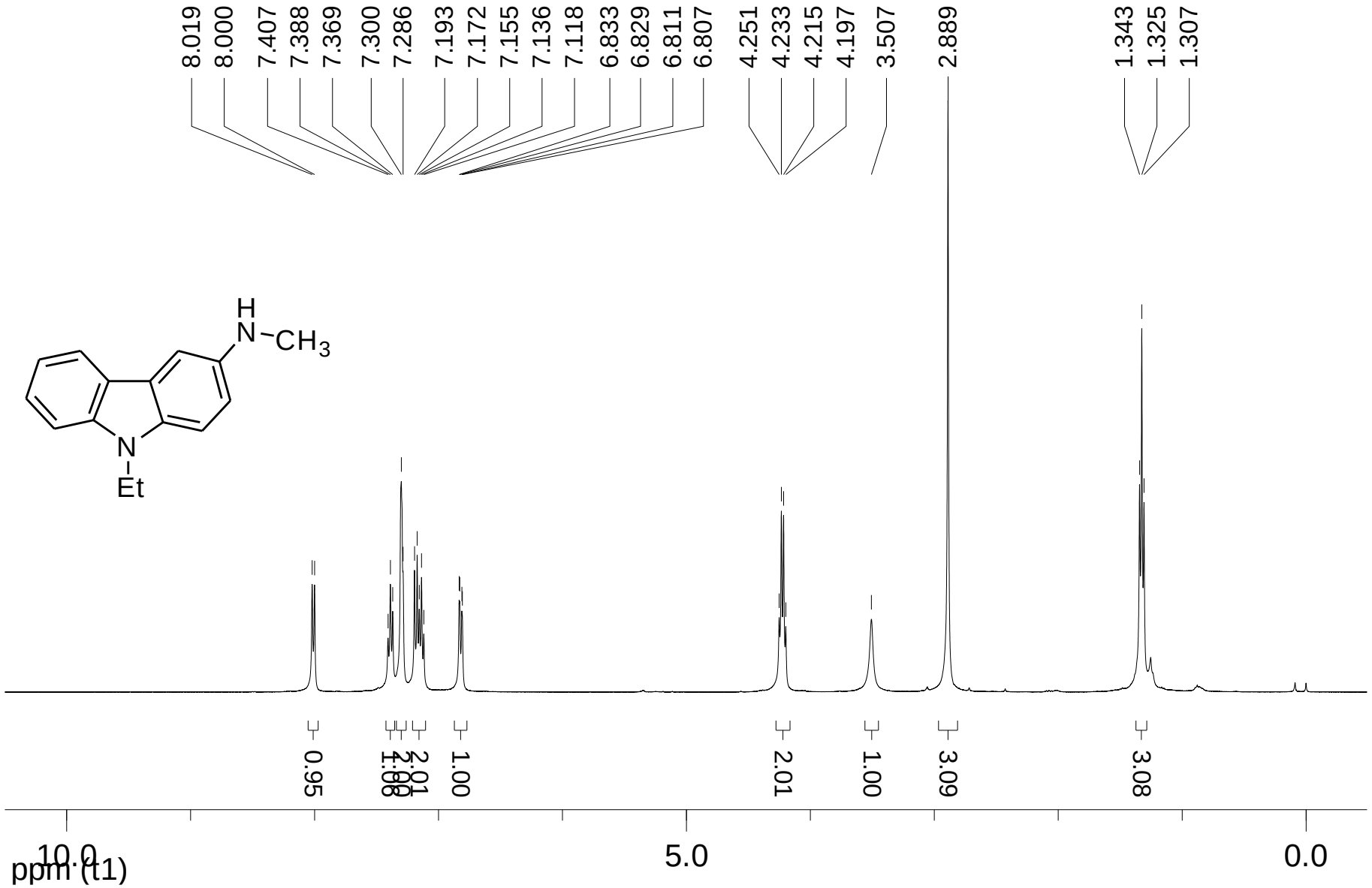
^{1}H NMR spectrum of **2x**(400M Hz, $CDCl_3$)



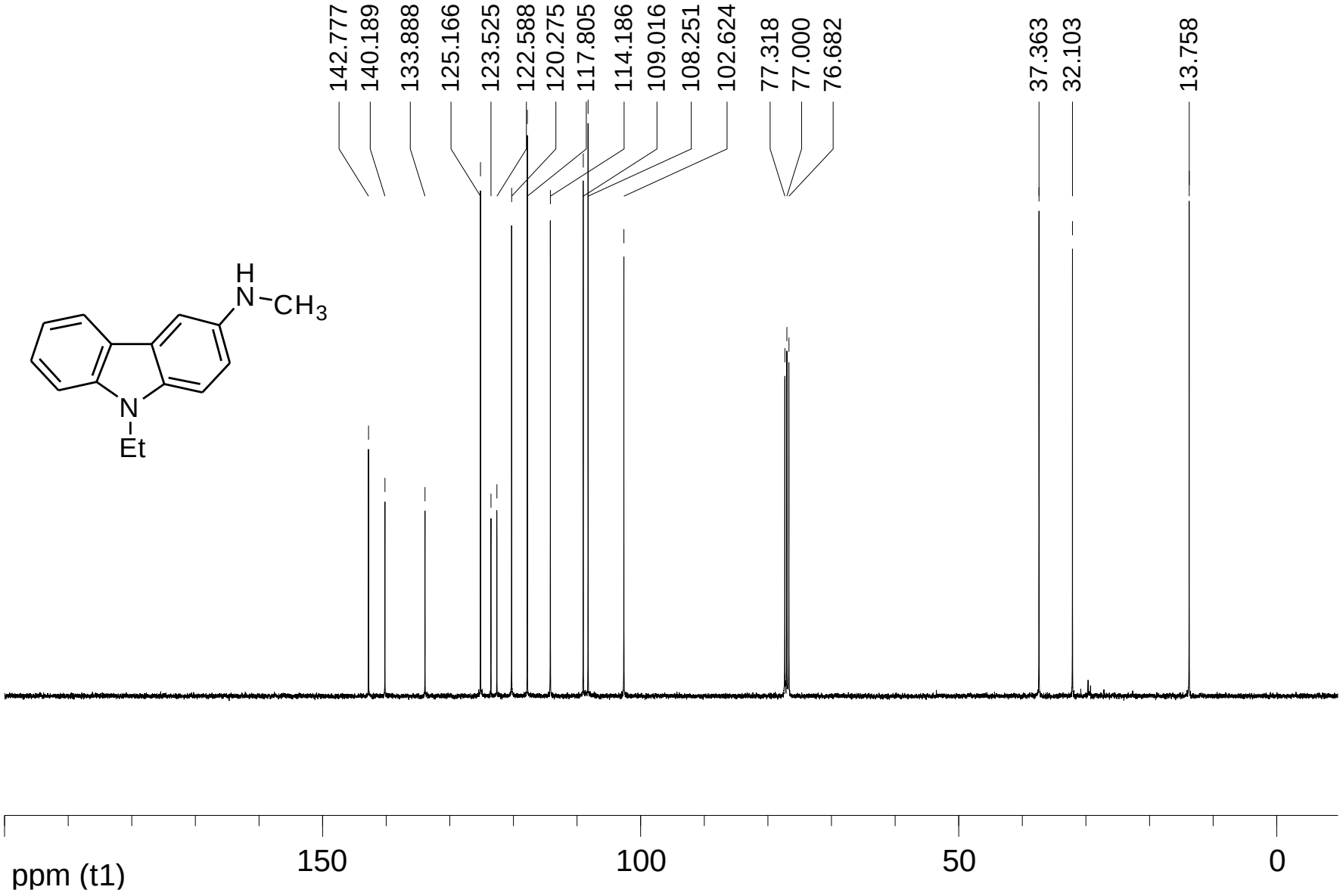
^{13}C NMR spectrum of **2x** (100M Hz, $CDCl_3$)



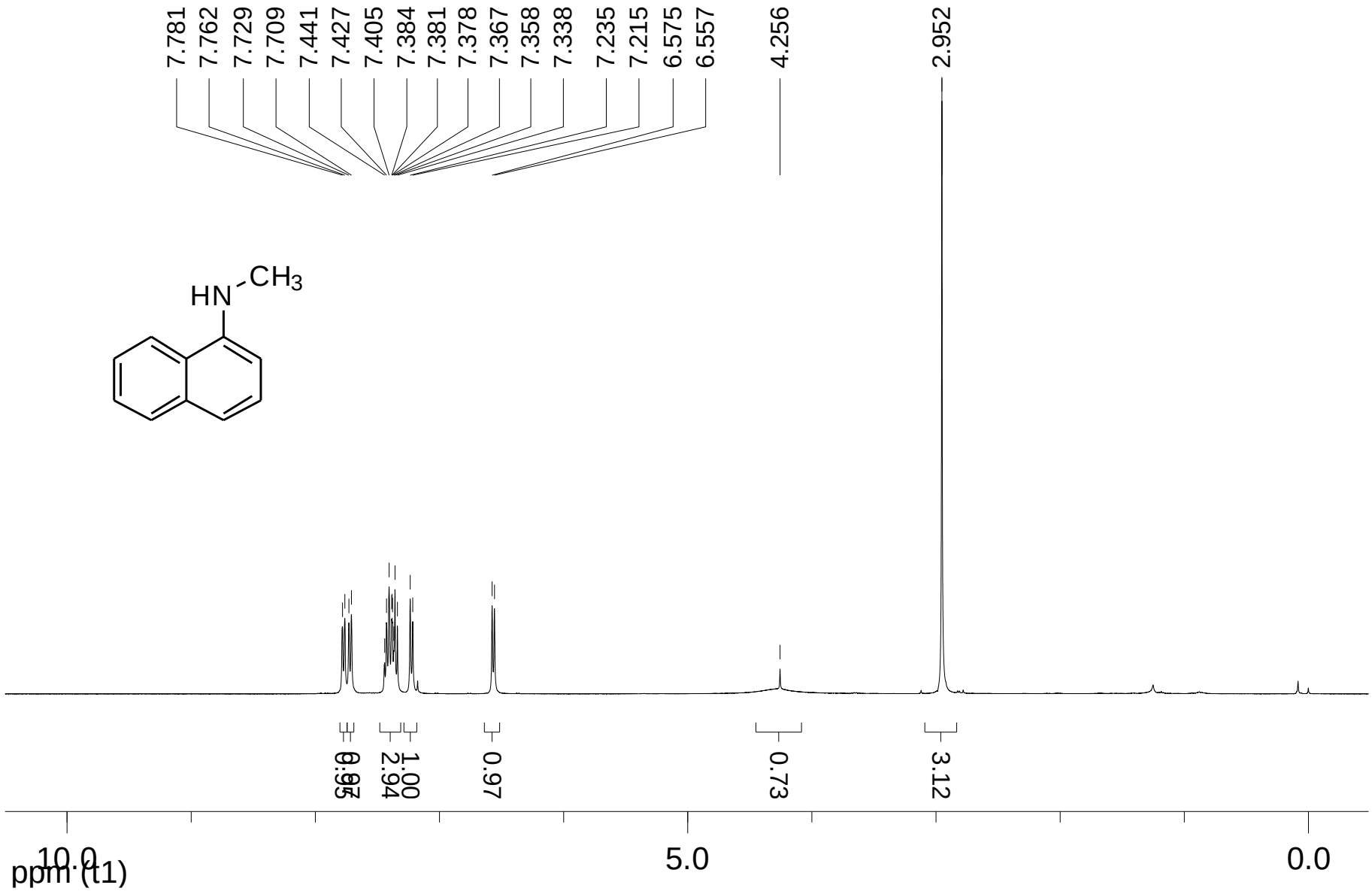
^{1}H NMR spectrum of **2y** (400M Hz, $CDCl_3$)



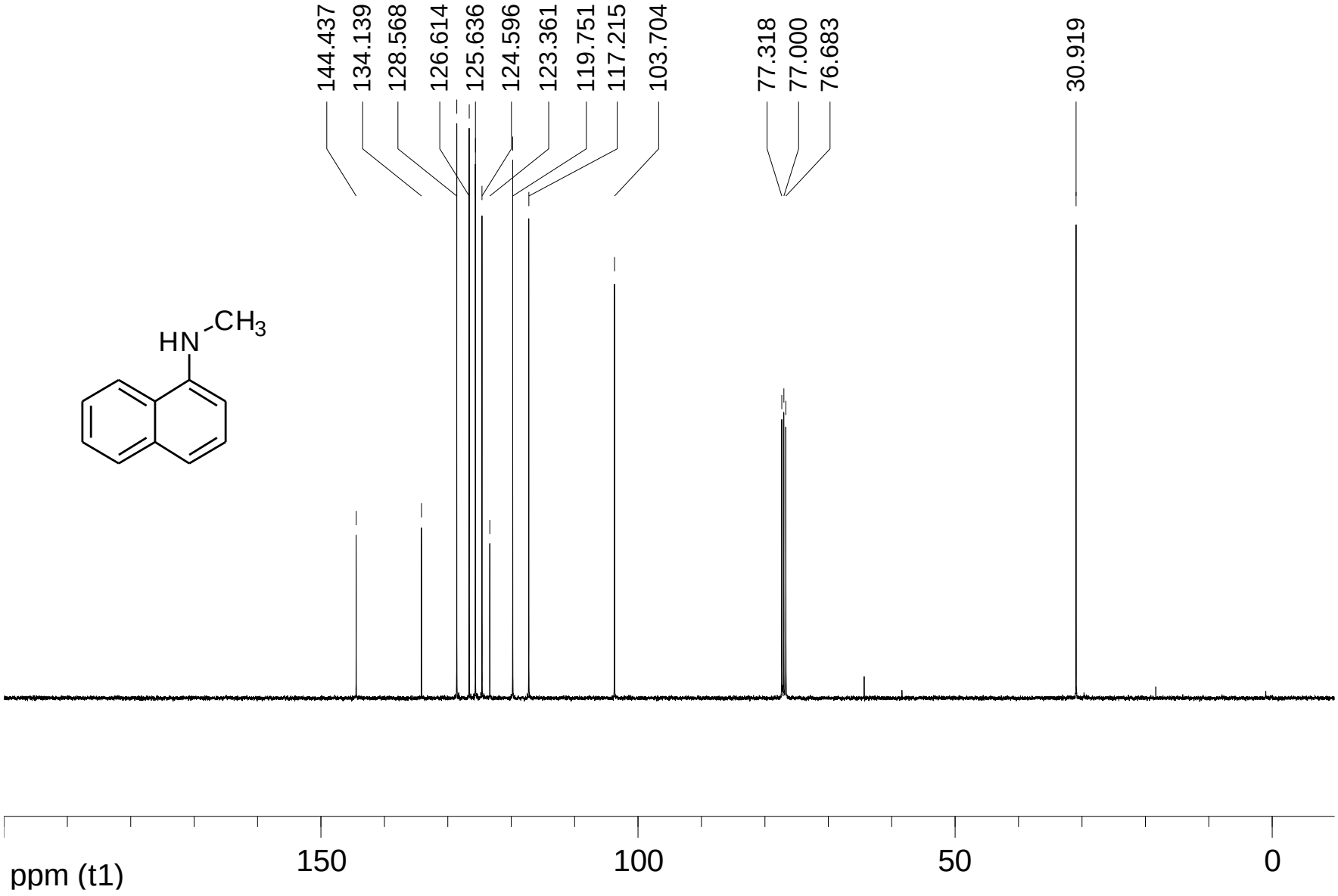
^{13}C NMR spectrum of **2y** (100M Hz, $CDCl_3$)



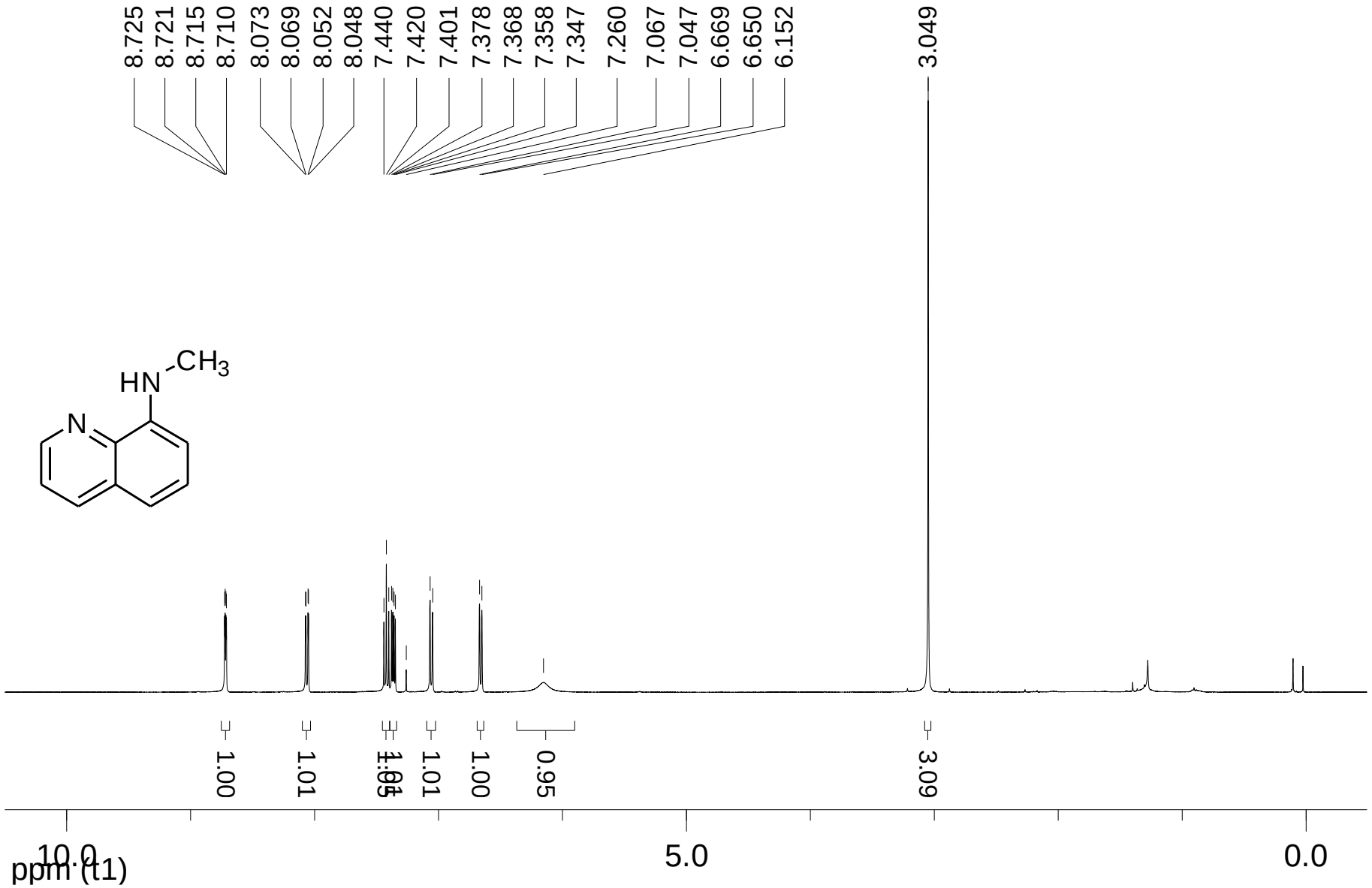
^{1}H NMR spectrum of **2z** (400M Hz, $CDCl_3$)



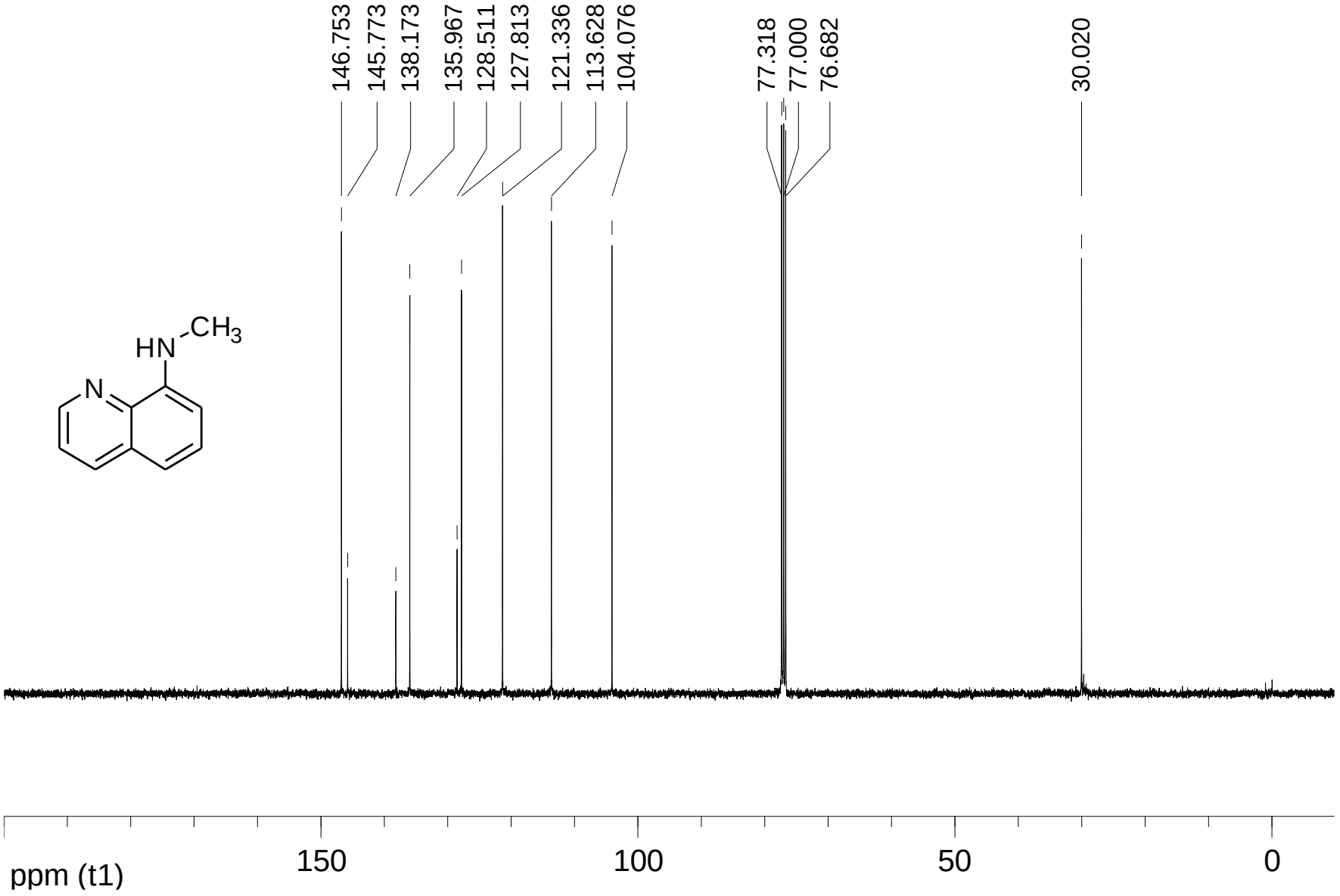
^{13}C NMR spectrum of **2z** (100M Hz, $CDCl_3$)



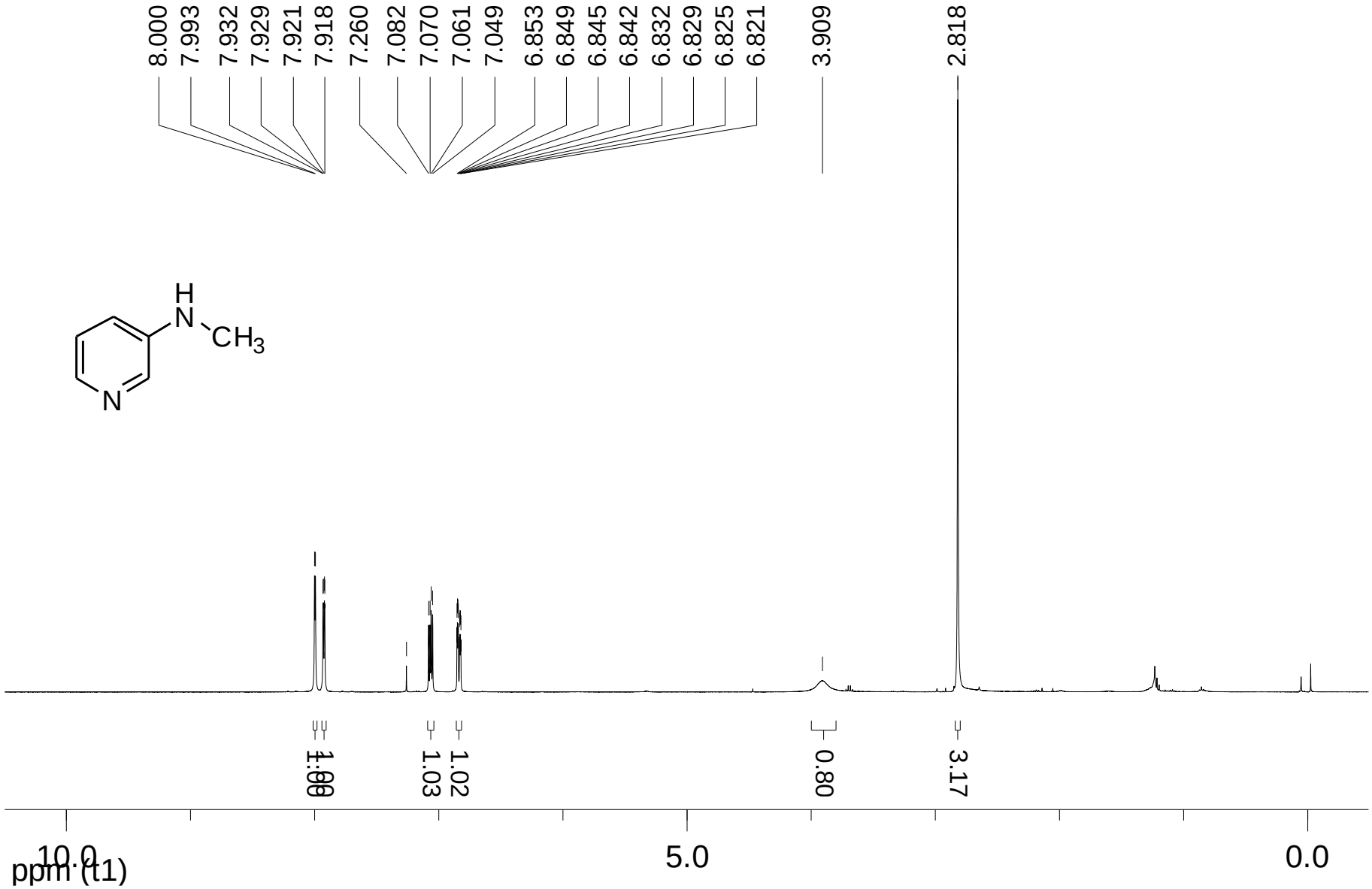
^{1}H NMR spectrum of **2aa** (400M Hz, $CDCl_3$)



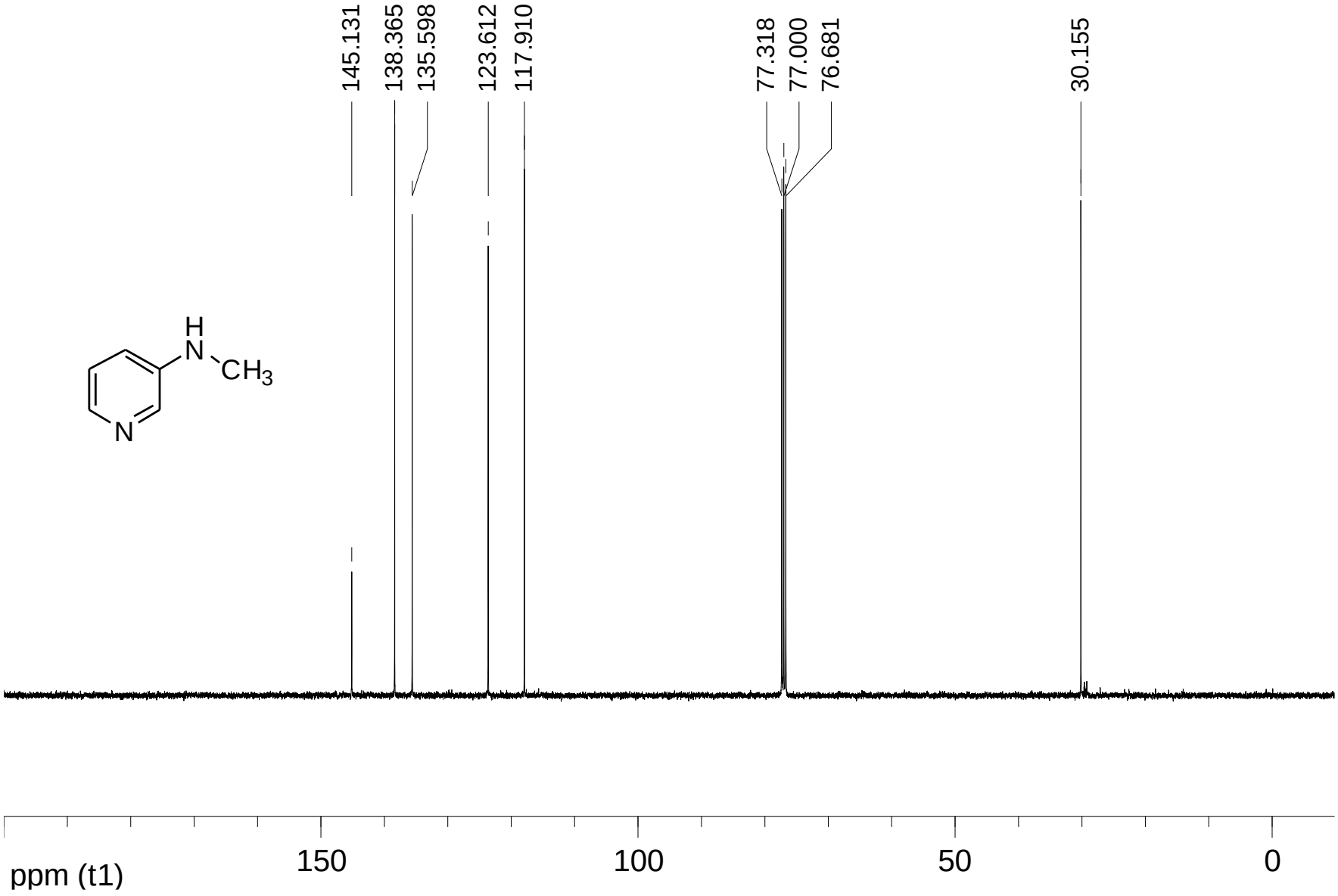
^{13}C NMR spectrum of **2aa** (100M Hz, $CDCl_3$)



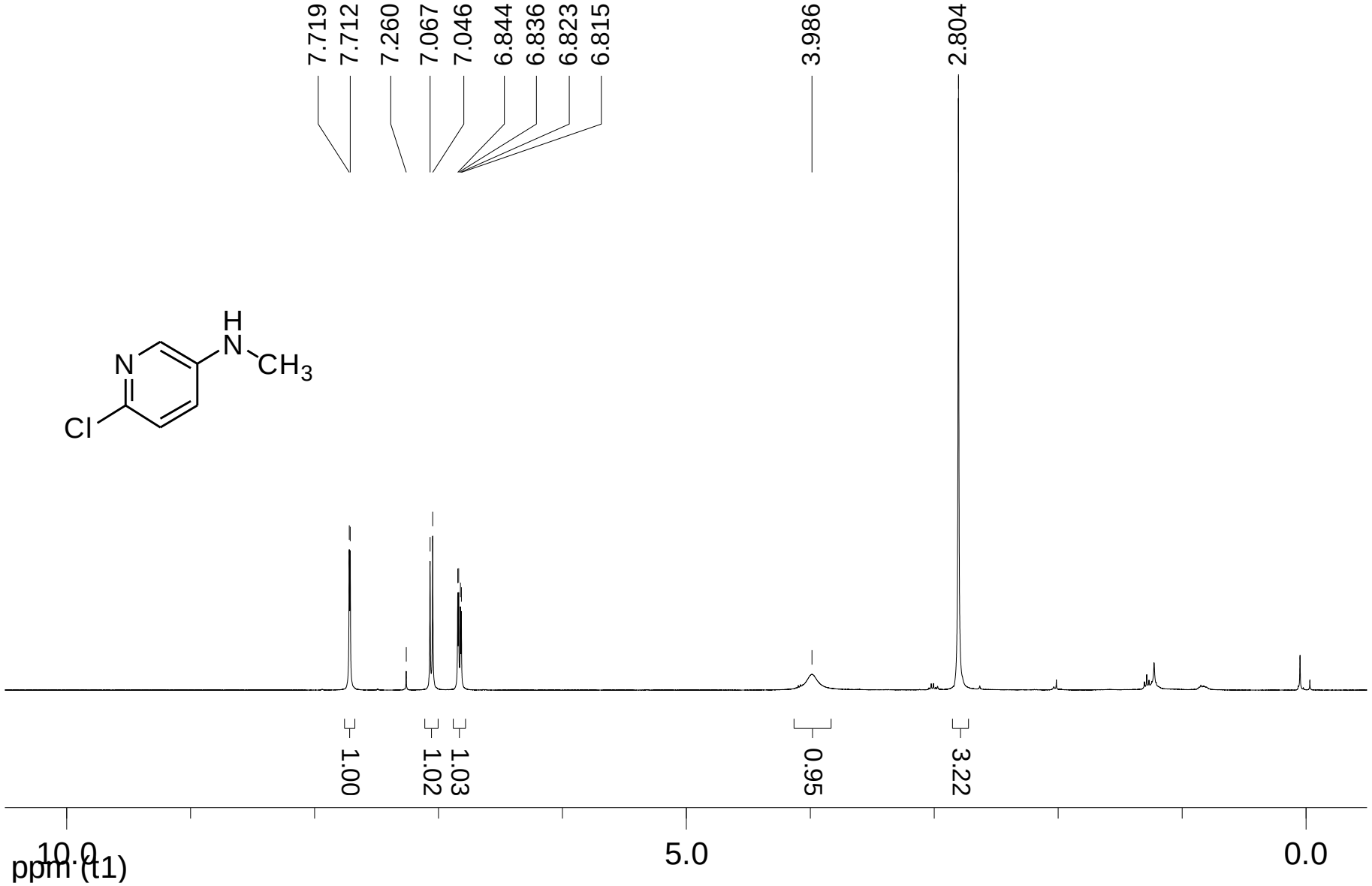
^{1}H NMR spectrum of **2ab** (400M Hz, $CDCl_3$)



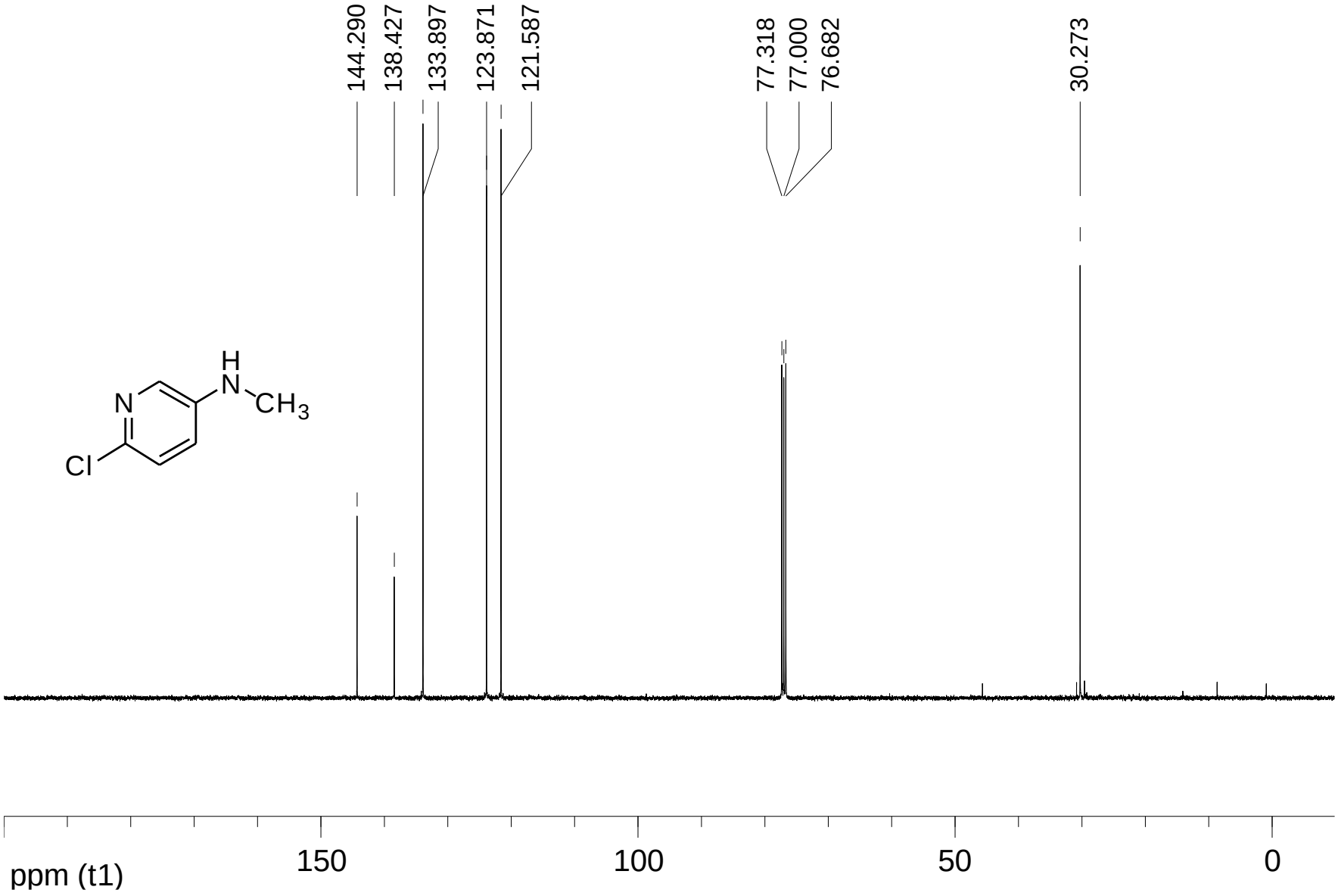
^{13}C NMR spectrum of **2ab** (100M Hz, $CDCl_3$)



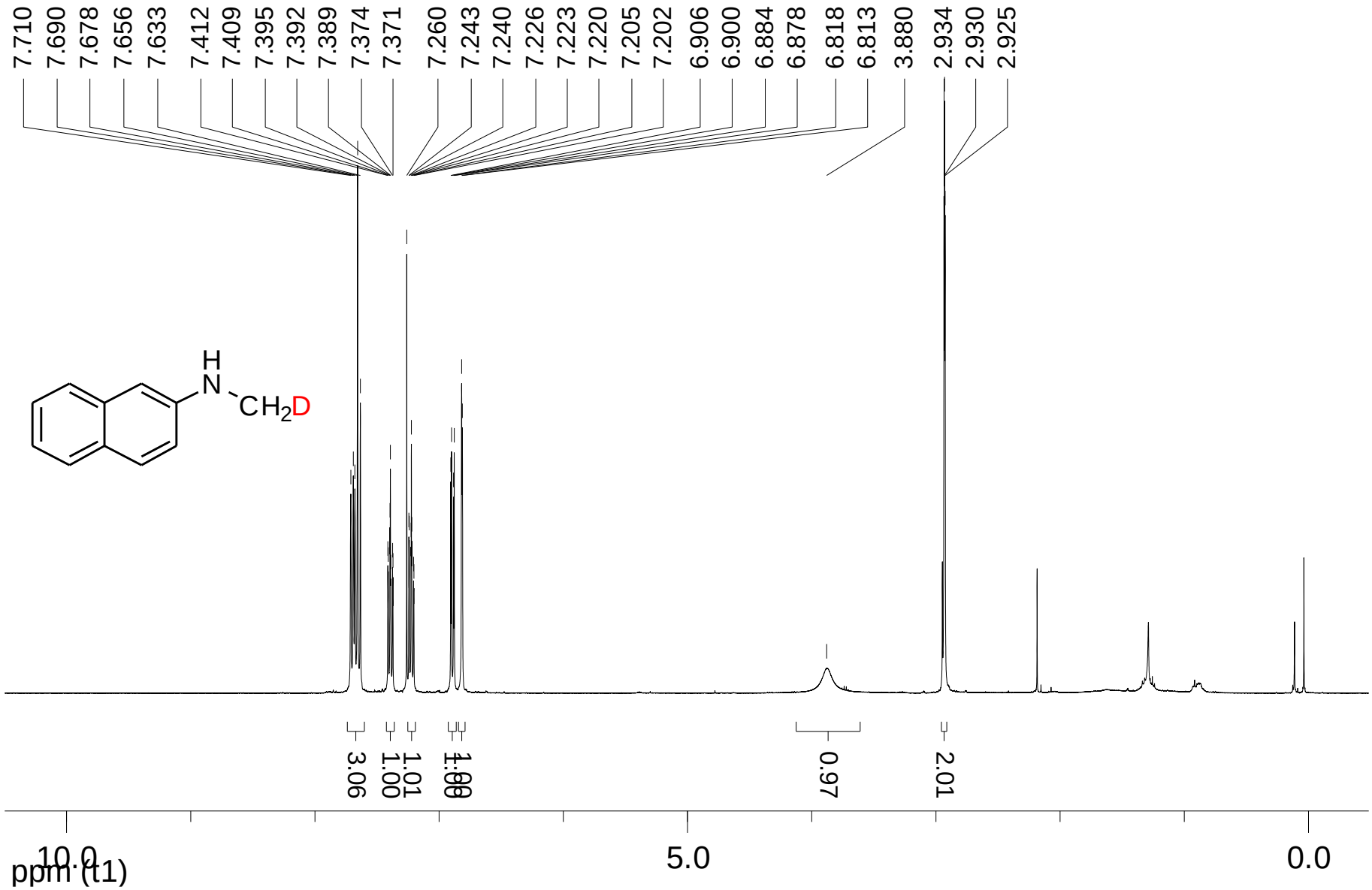
^{1}H NMR spectrum of **2ac** (400M Hz, $CDCl_3$)



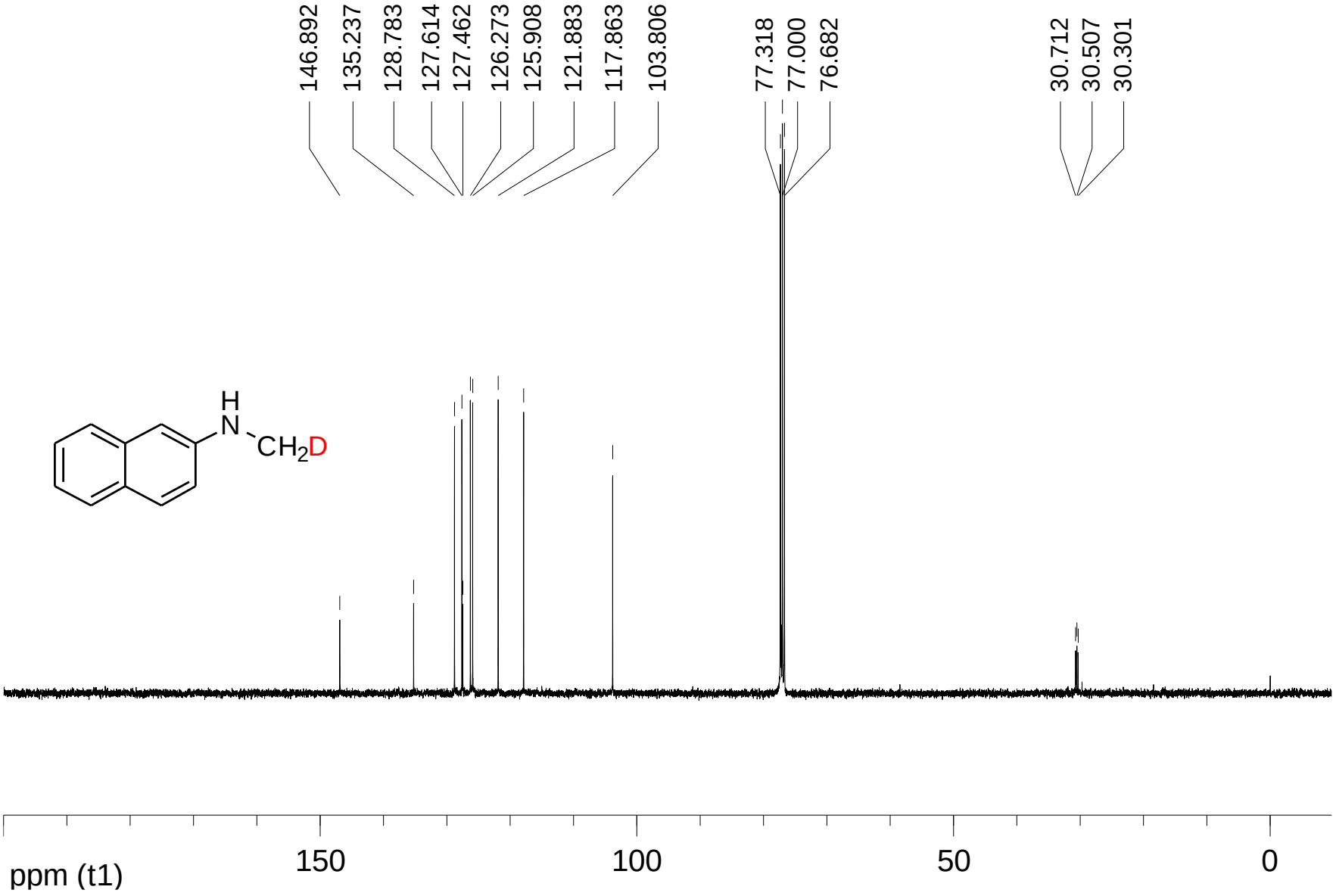
^{13}C NMR spectrum of **2ac** (100M Hz, $CDCl_3$)



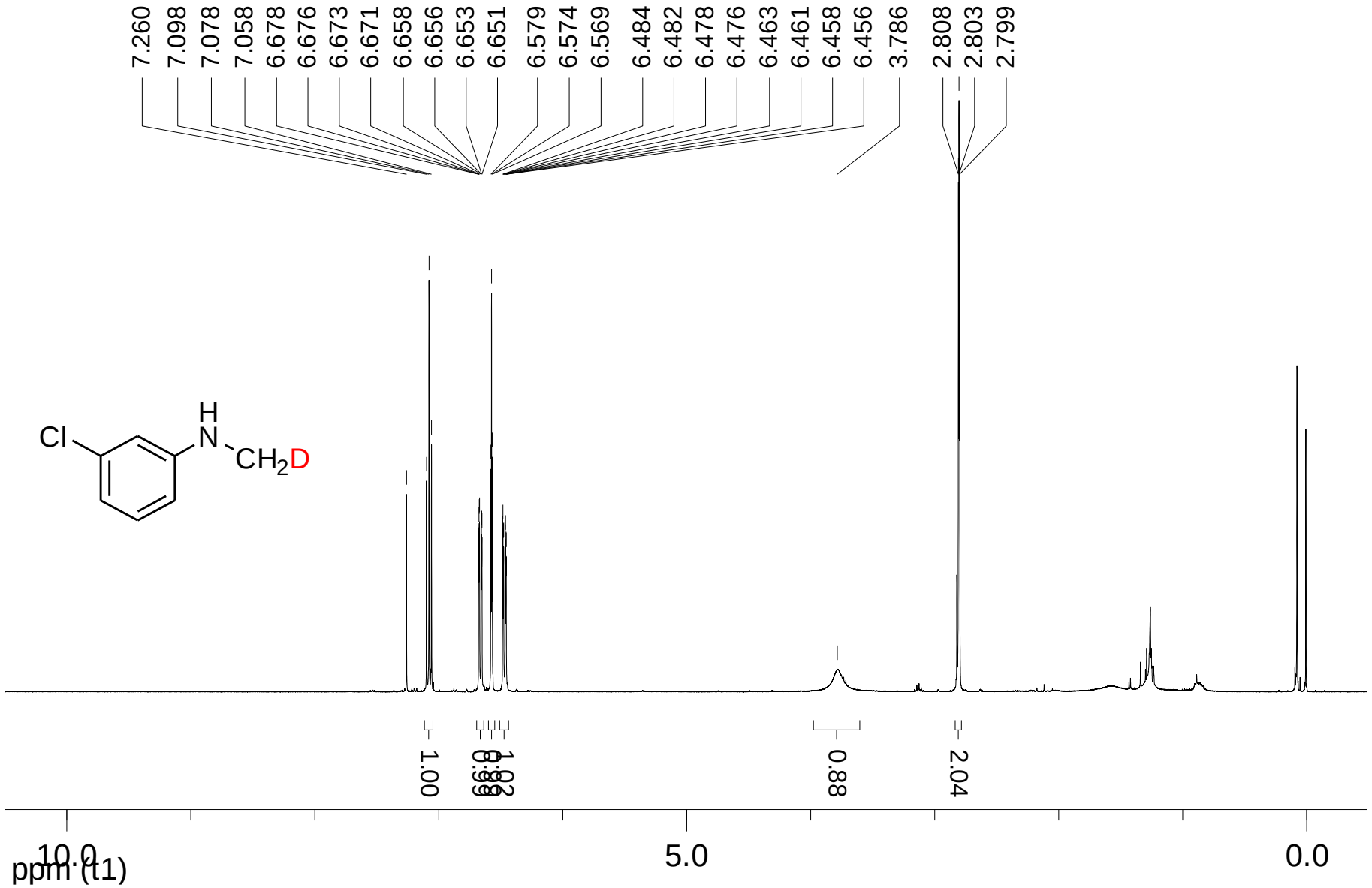
^{1}H NMR spectrum of **2a-D$_1$** (400M Hz,$CDCl_3$)



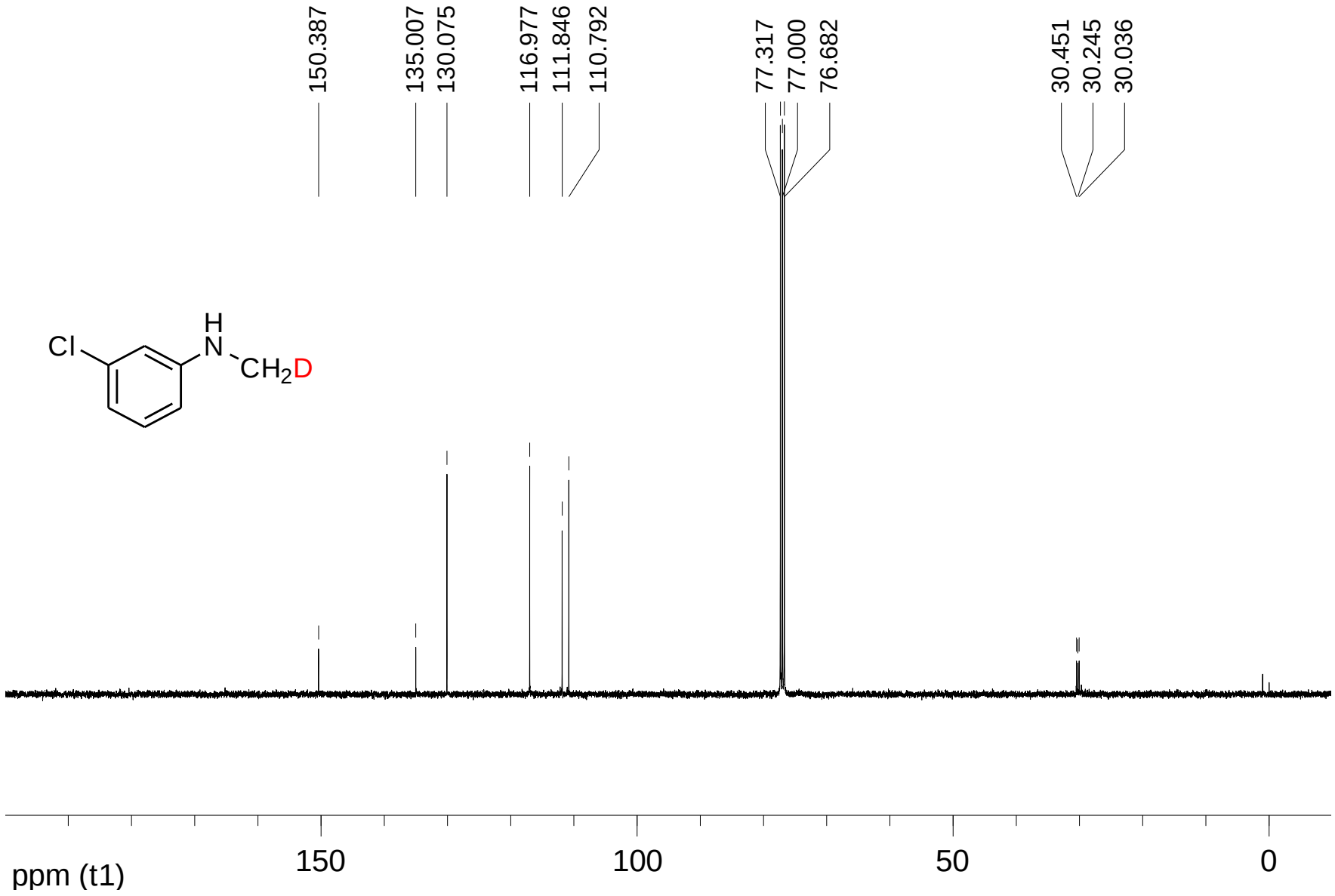
^{13}C NMR spectrum of **2a-D$_1$** (100M Hz, $CDCl_3$)



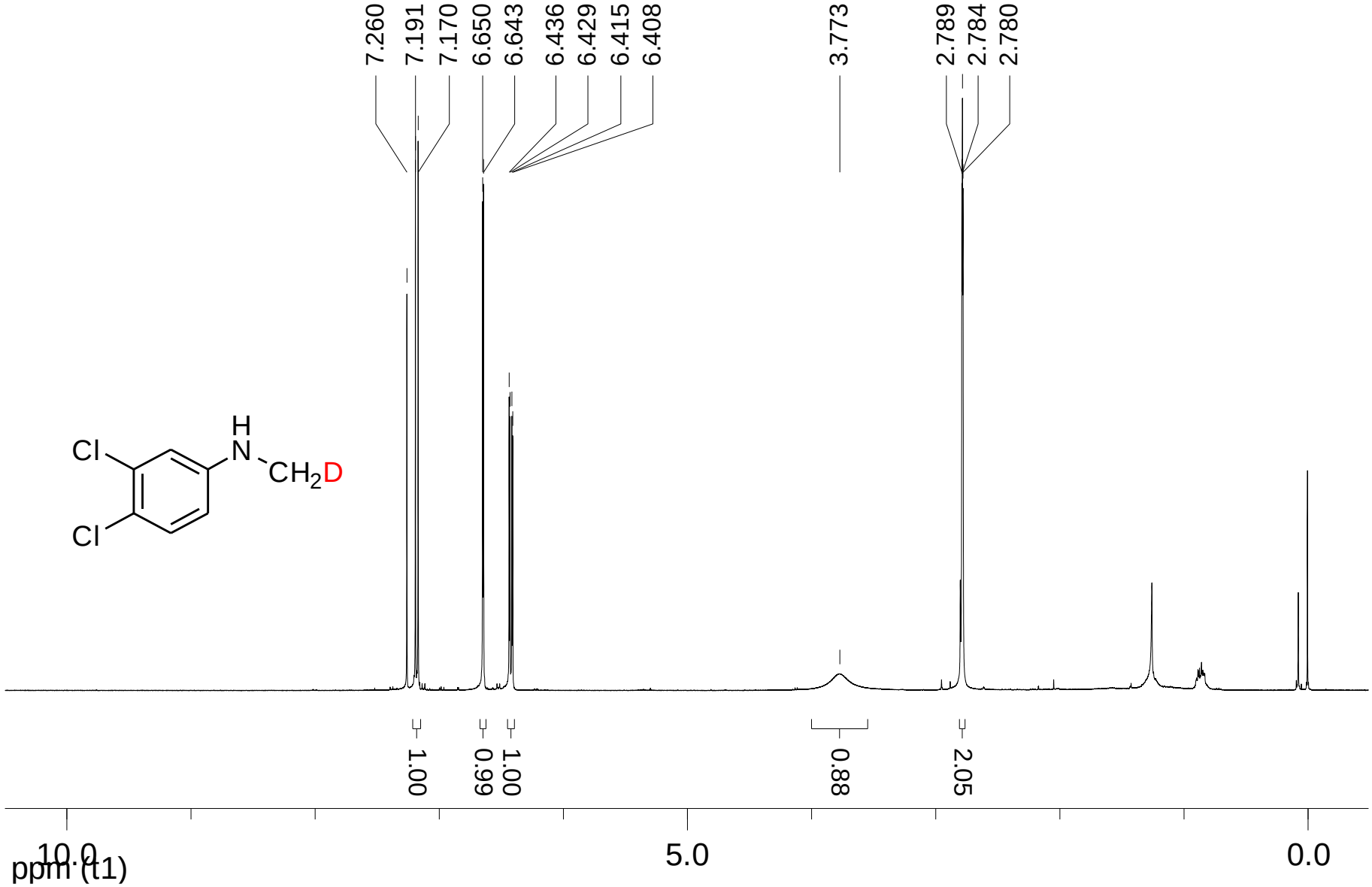
^{1}H NMR spectrum of **2c-D$_1$** (400M Hz, $CDCl_3$)



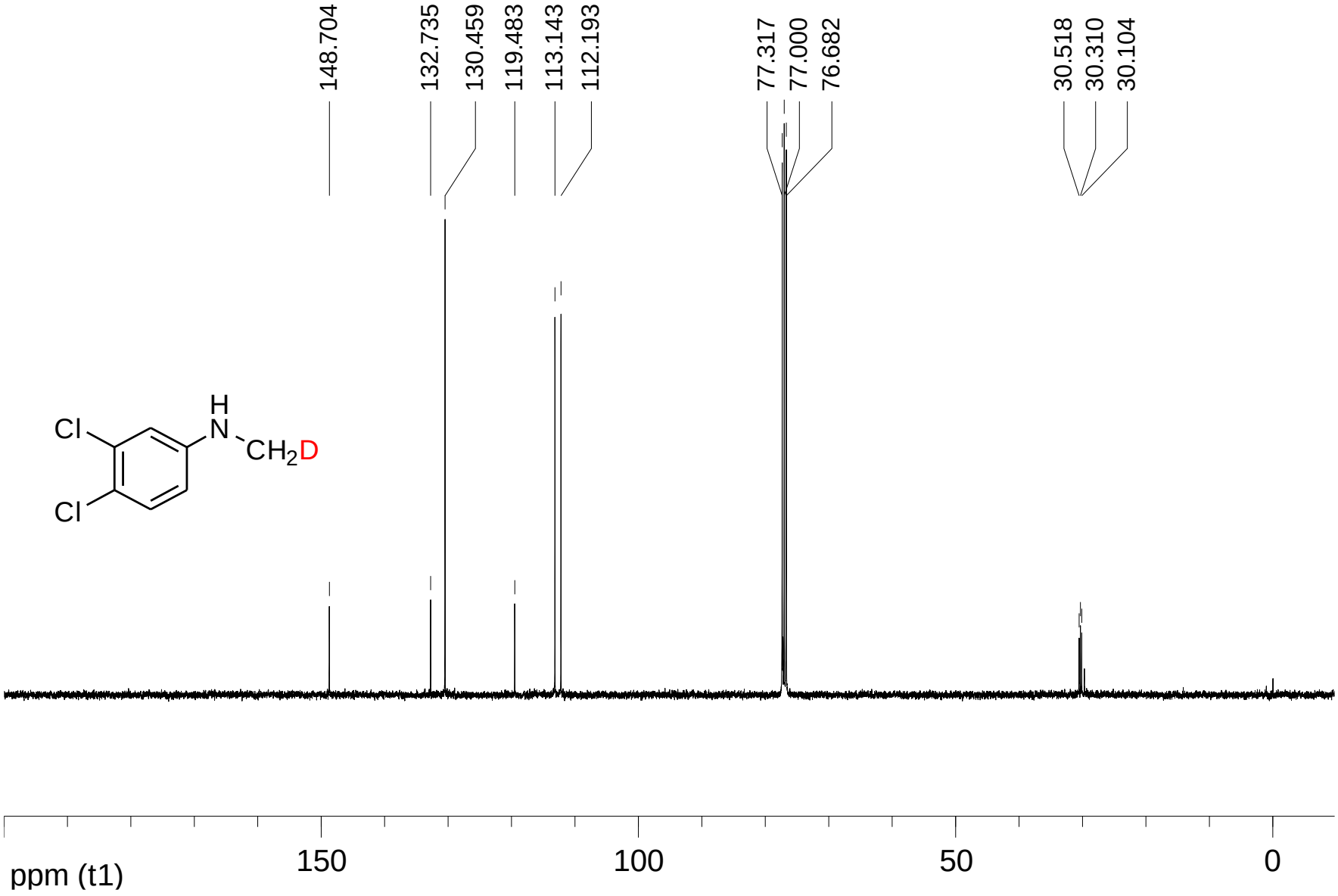
^{13}C NMR spectrum of **2c-D$_1$** (100M Hz, $CDCl_3$)



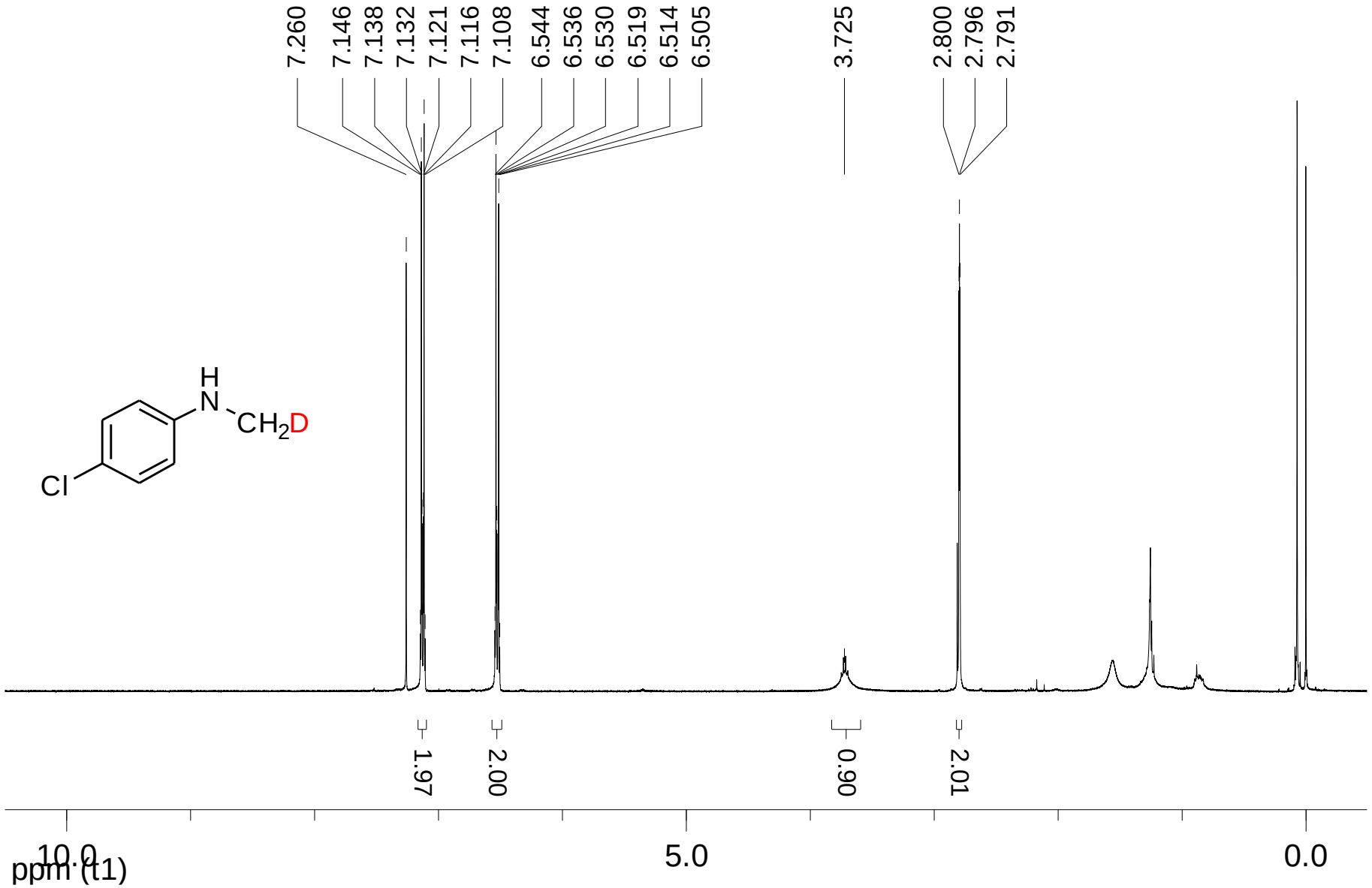
^{1}H NMR spectrum of **2e-D$_1$** (400M Hz, $CDCl_3$)



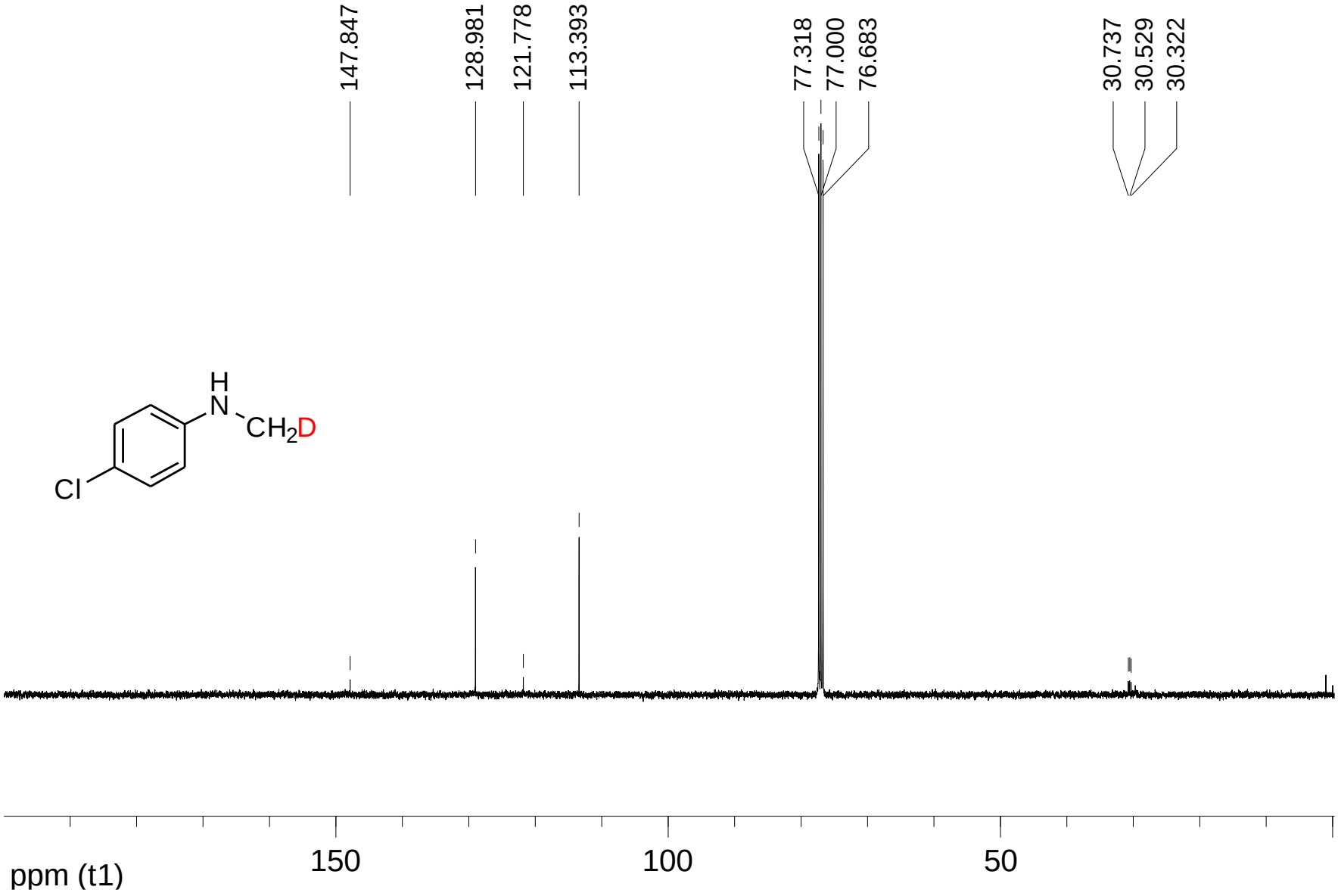
^{13}C NMR spectrum of **2e-D$_1$**(100M Hz, $CDCl_3$)



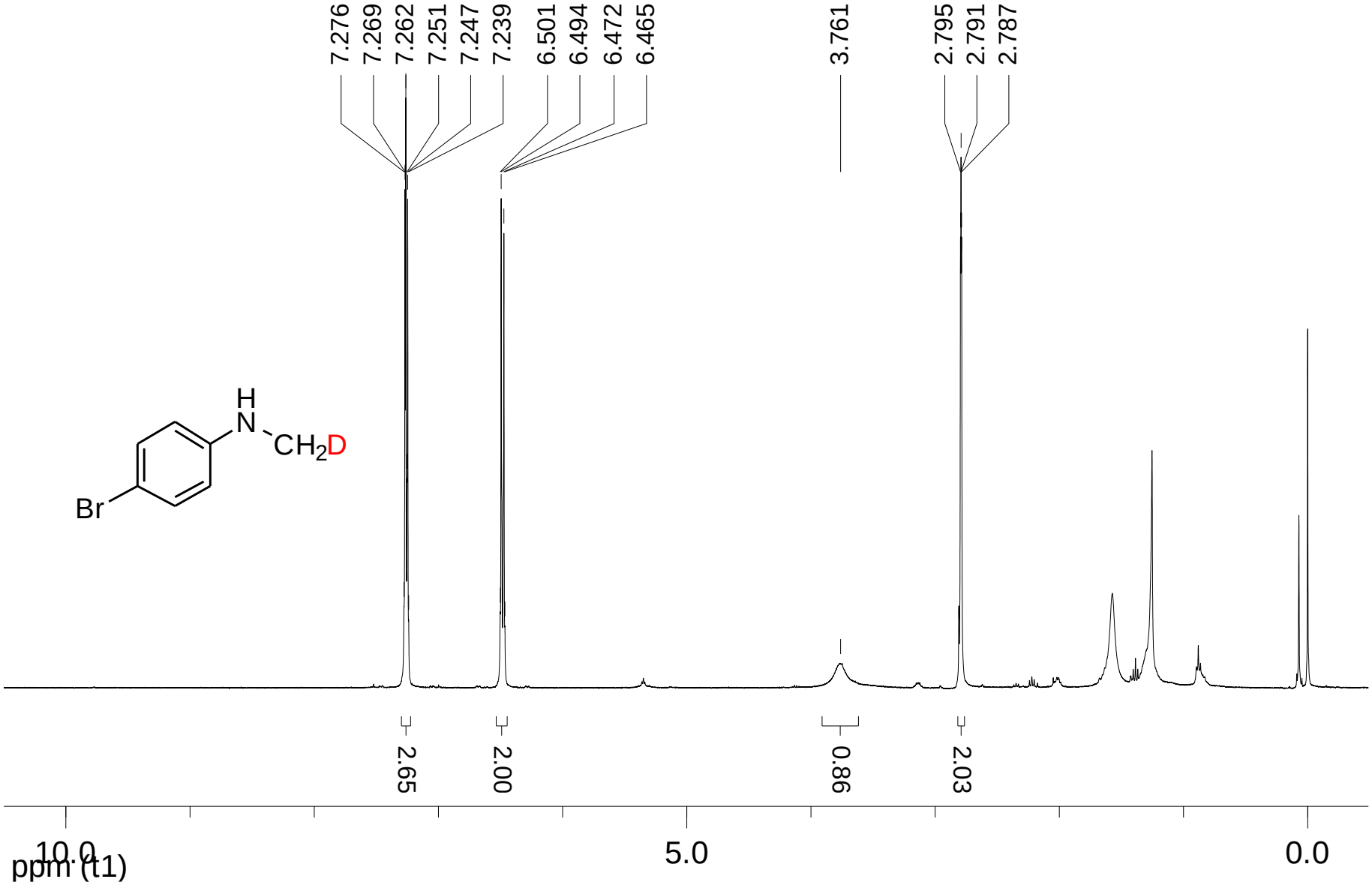
^{1}H NMR spectrum of **2g-D$_1$** (400M Hz, $CDCl_3$)



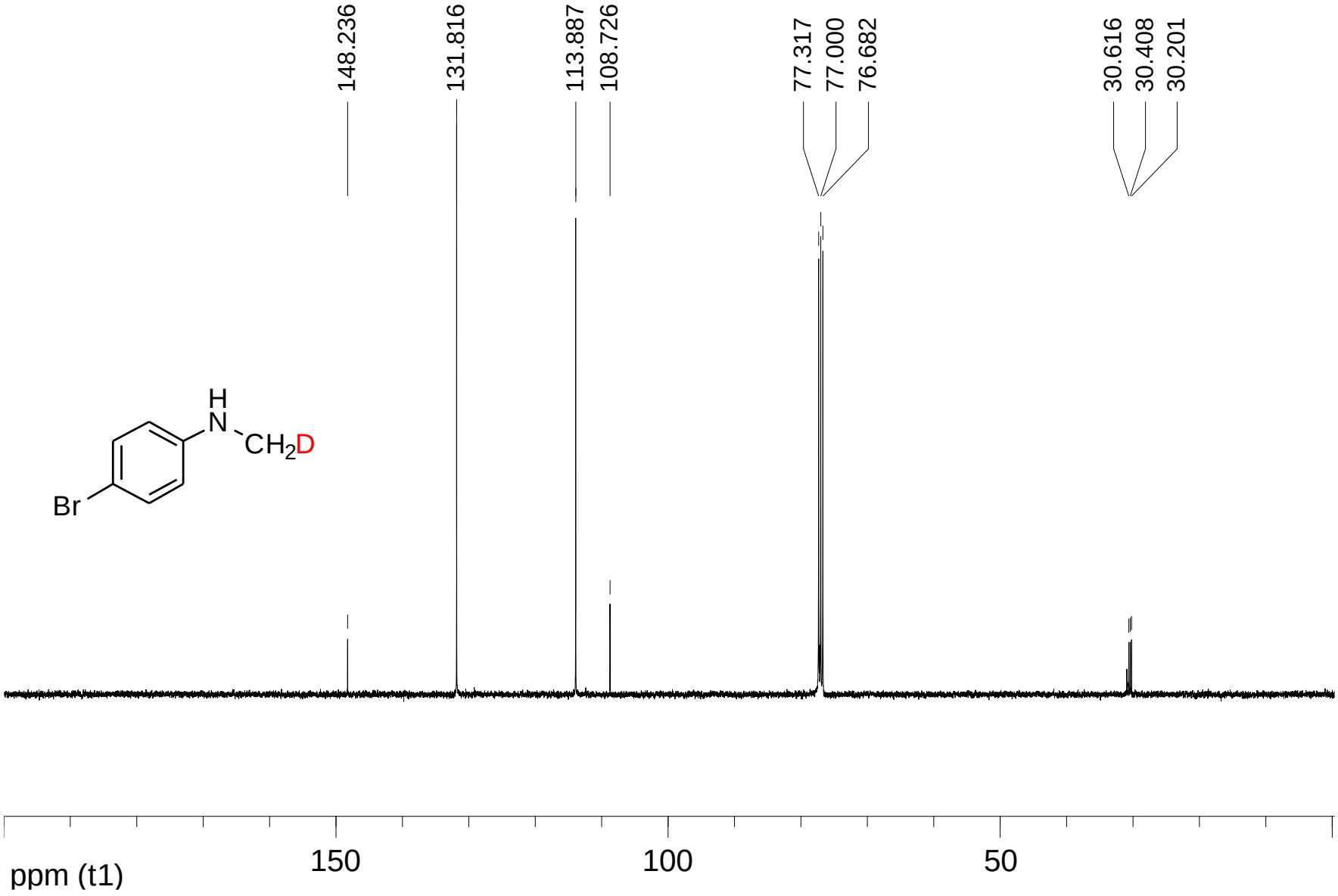
^{13}C NMR spectrum of **2g-D$_1$**(100M Hz, $CDCl_3$)



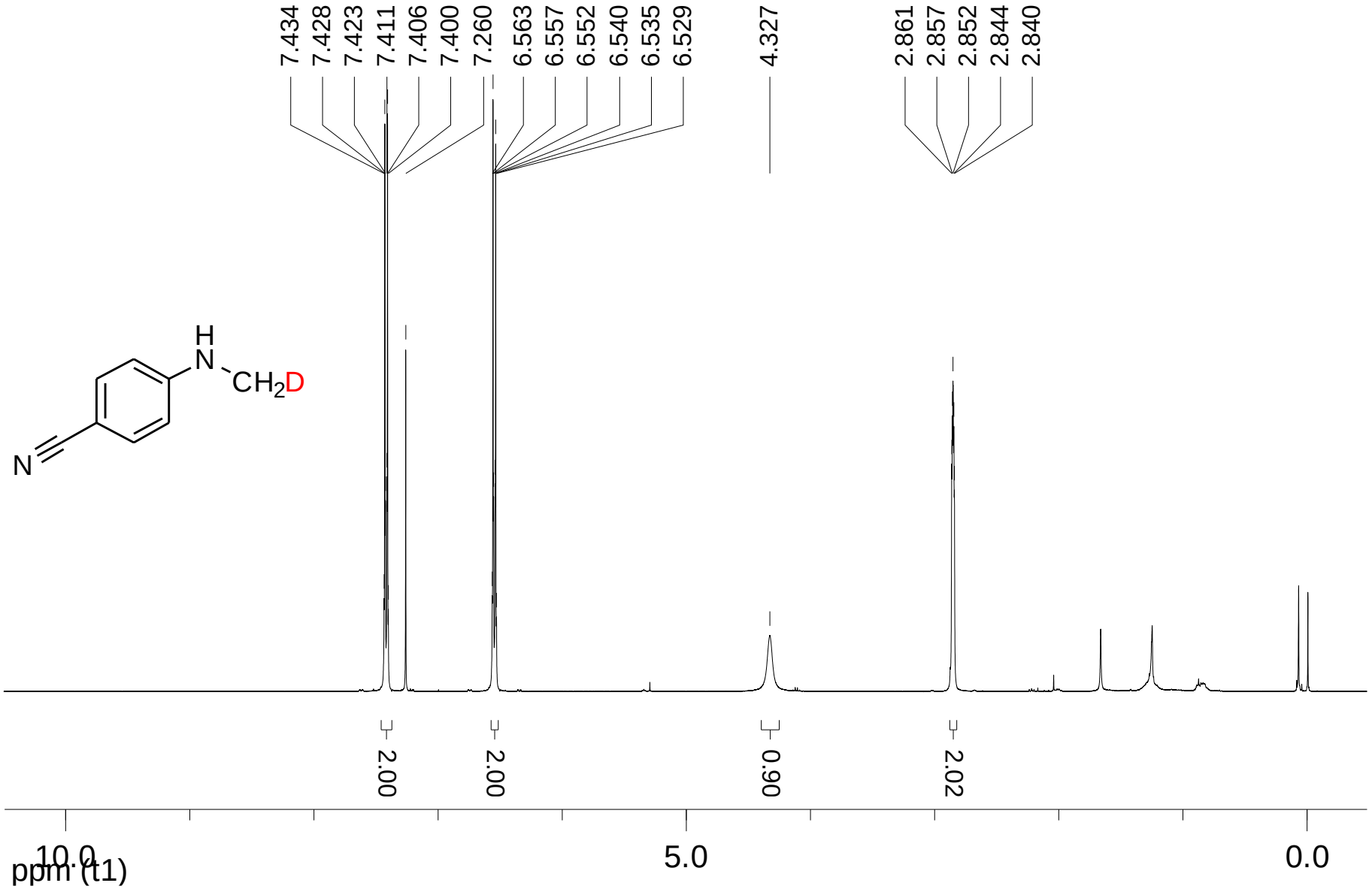
^{1}H NMR spectrum of **2h-D$_1$** (400M Hz, $CDCl_3$)



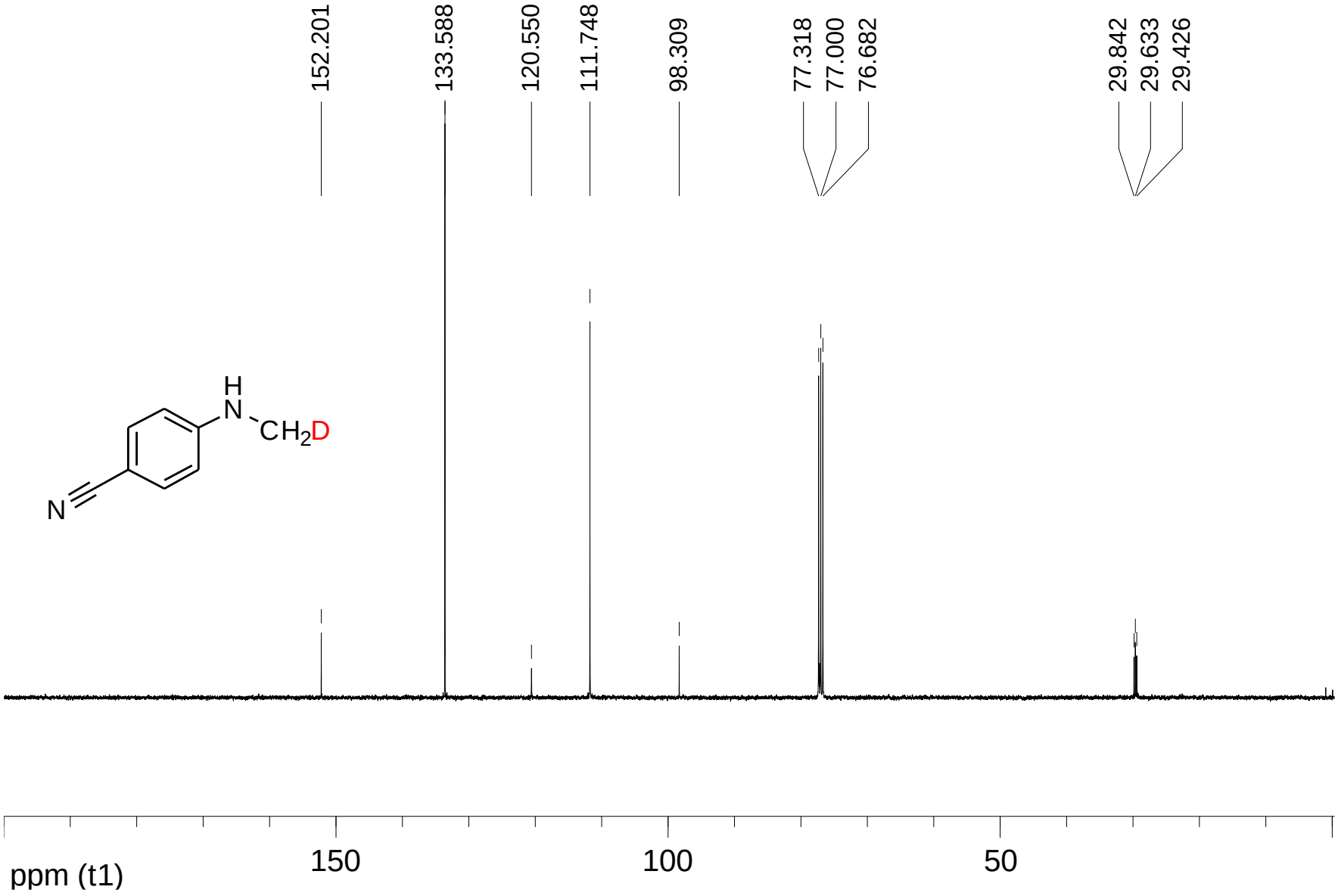
^{13}C NMR spectrum of **2h-D$_1$**(100M Hz, $CDCl_3$)



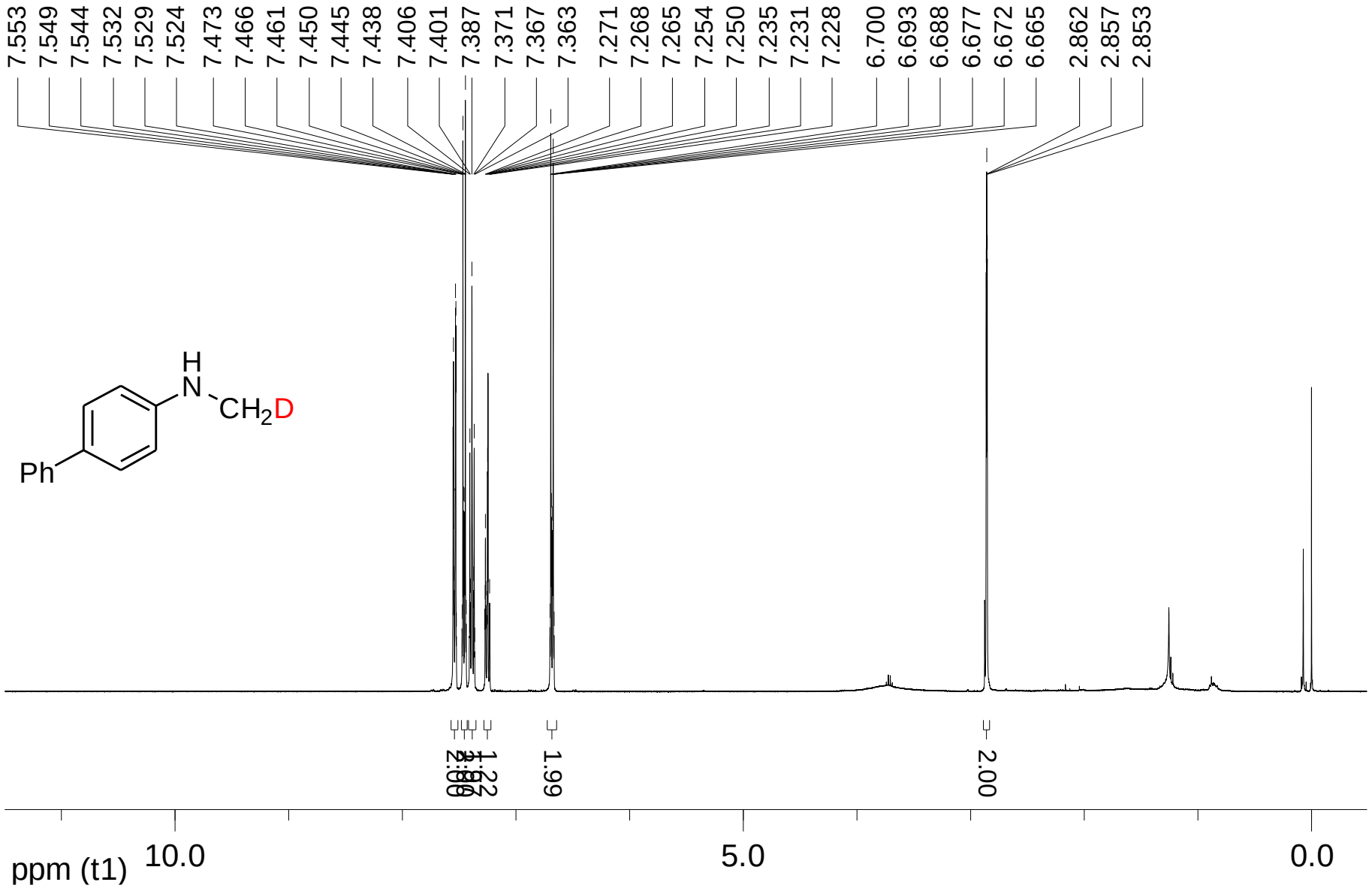
^{1}H NMR spectrum of **2j-D$_1$** (400M Hz, $CDCl_3$)



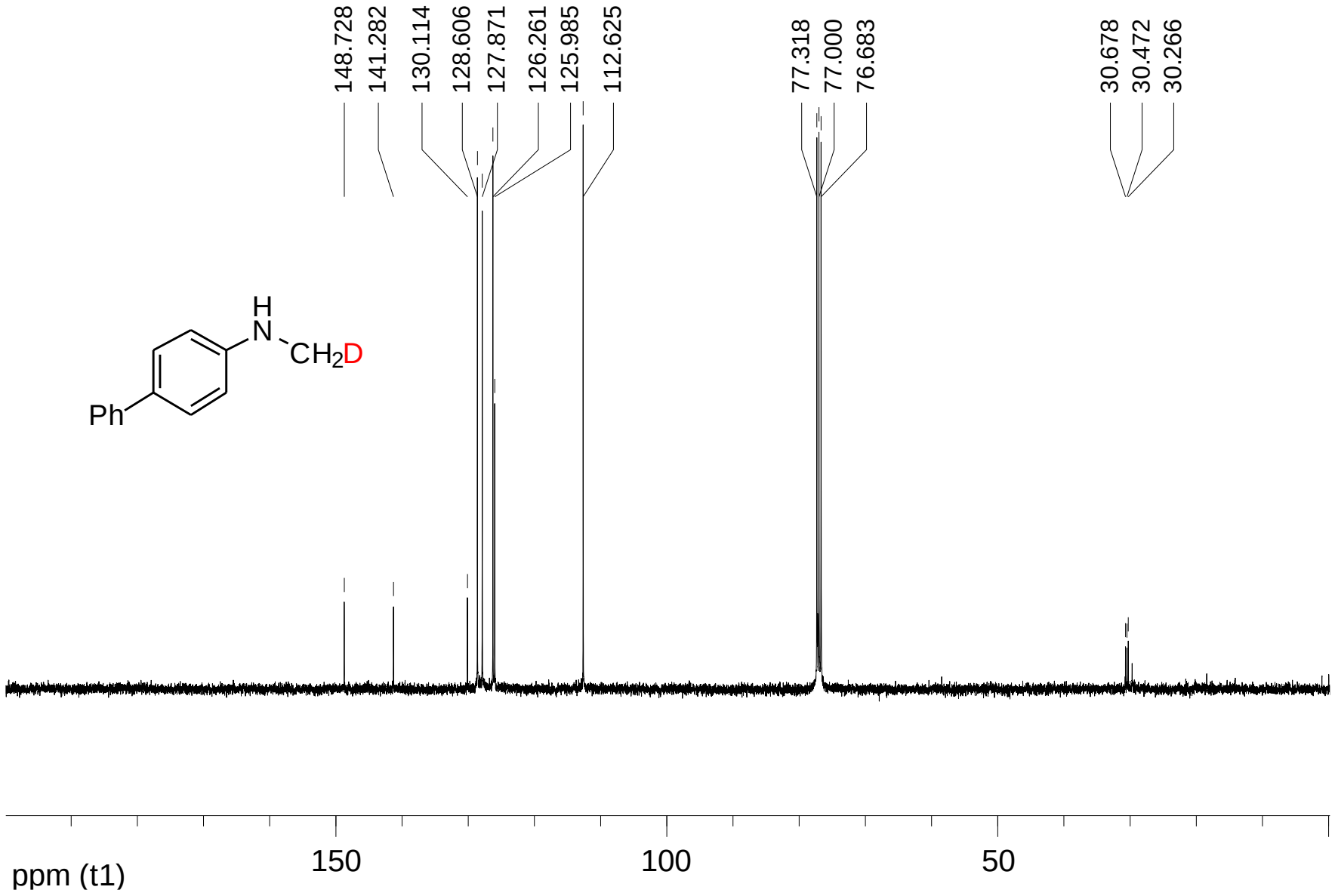
^{13}C NMR spectrum of **2j-D$_1$** (100M Hz, $CDCl_3$)



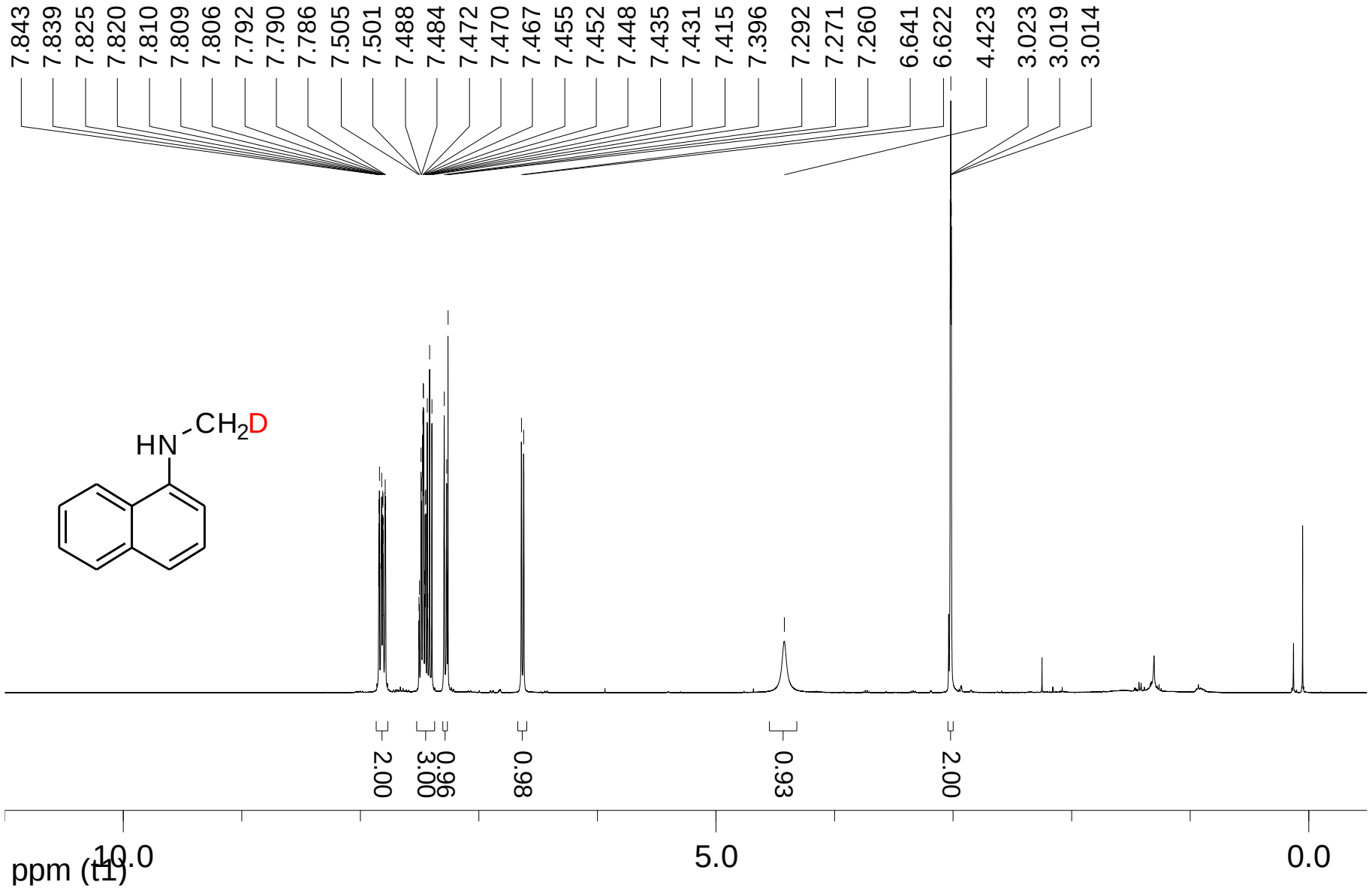
^{1}H NMR spectrum of **2o-D$_1$** (400M Hz, $CDCl_3$)



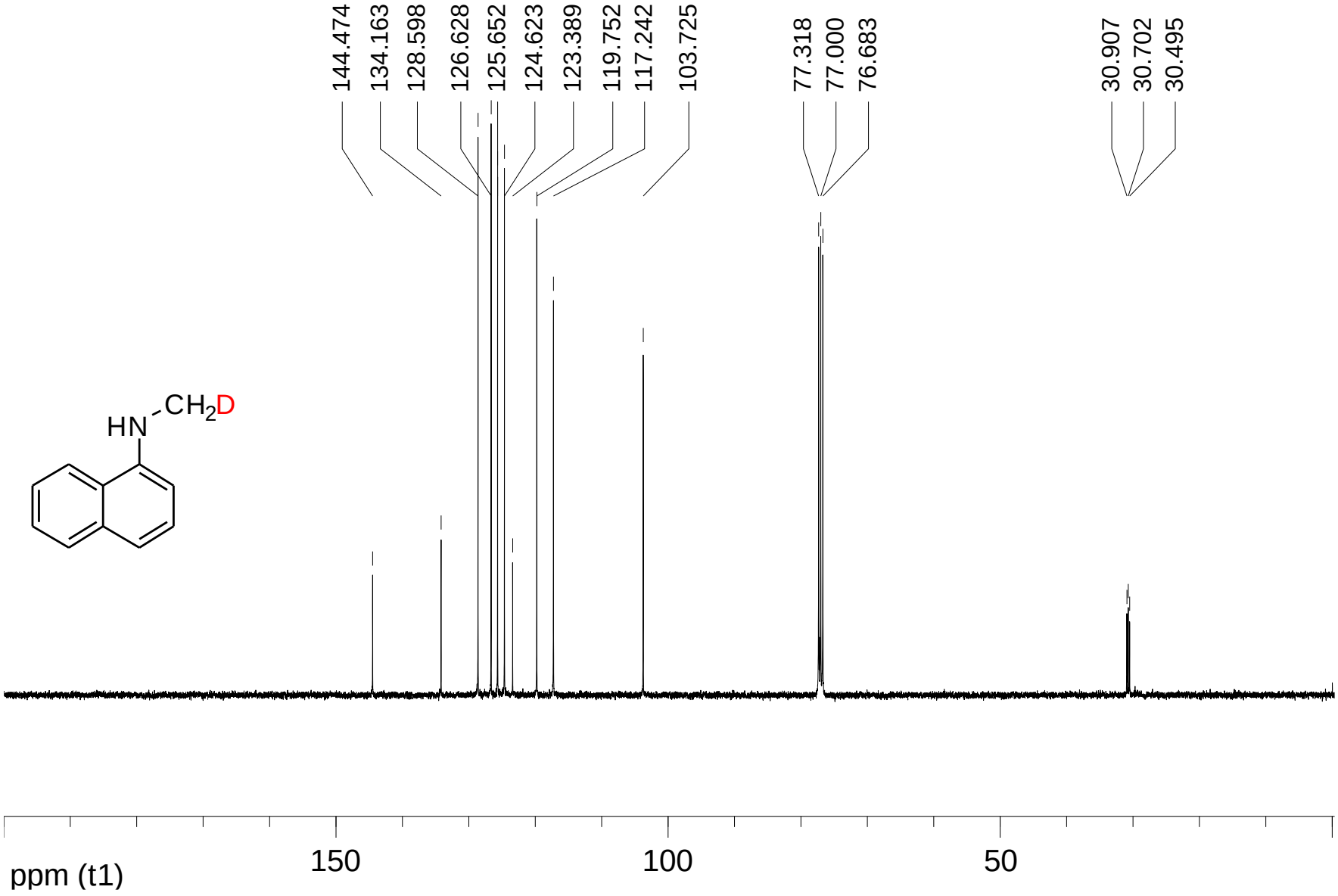
^{13}C NMR spectrum of **2o-D$_1$** (100M Hz, $CDCl_3$)



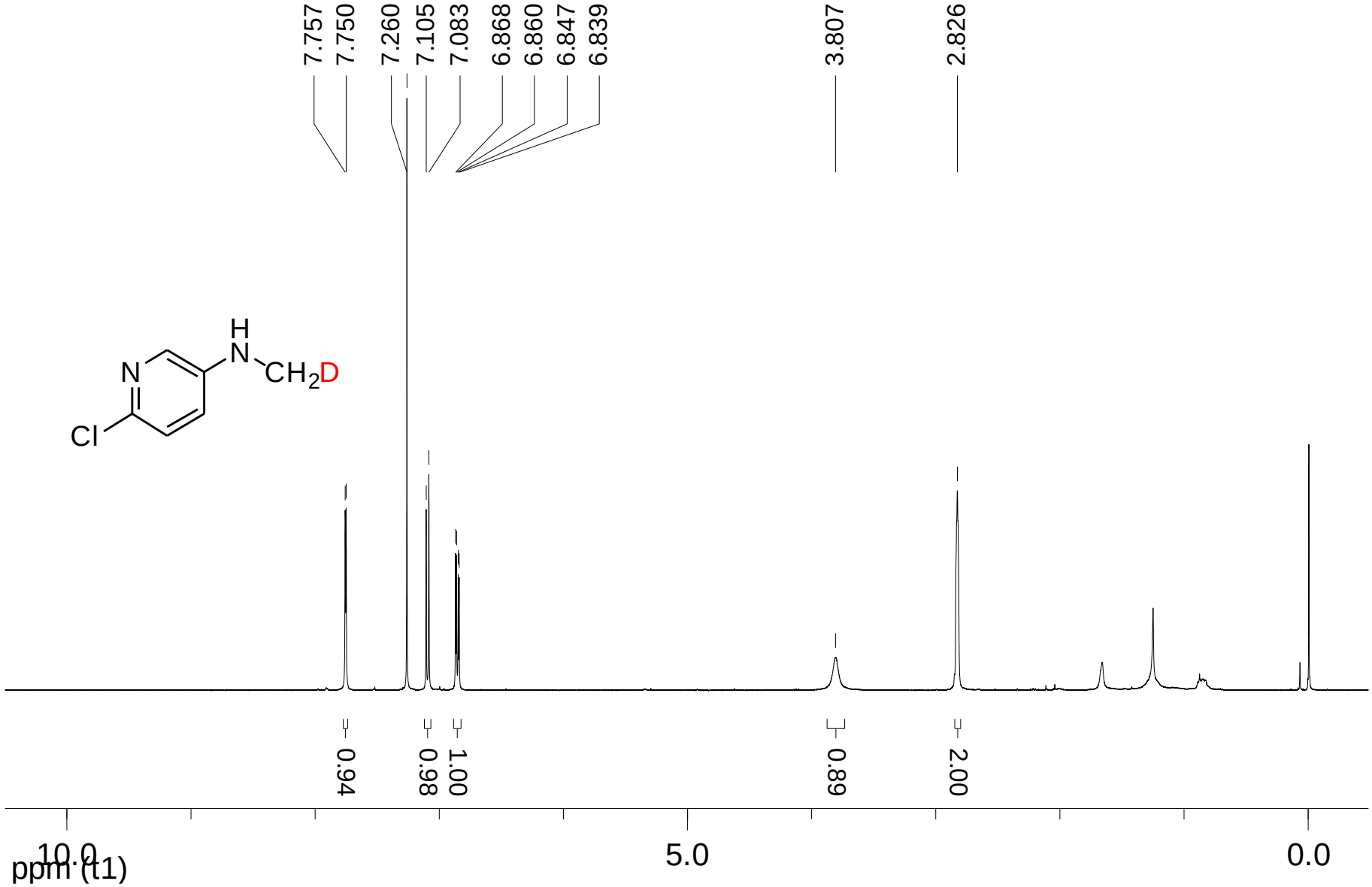
^{1}H NMR spectrum of **2z-D$_1$** (400M Hz, $CDCl_3$)



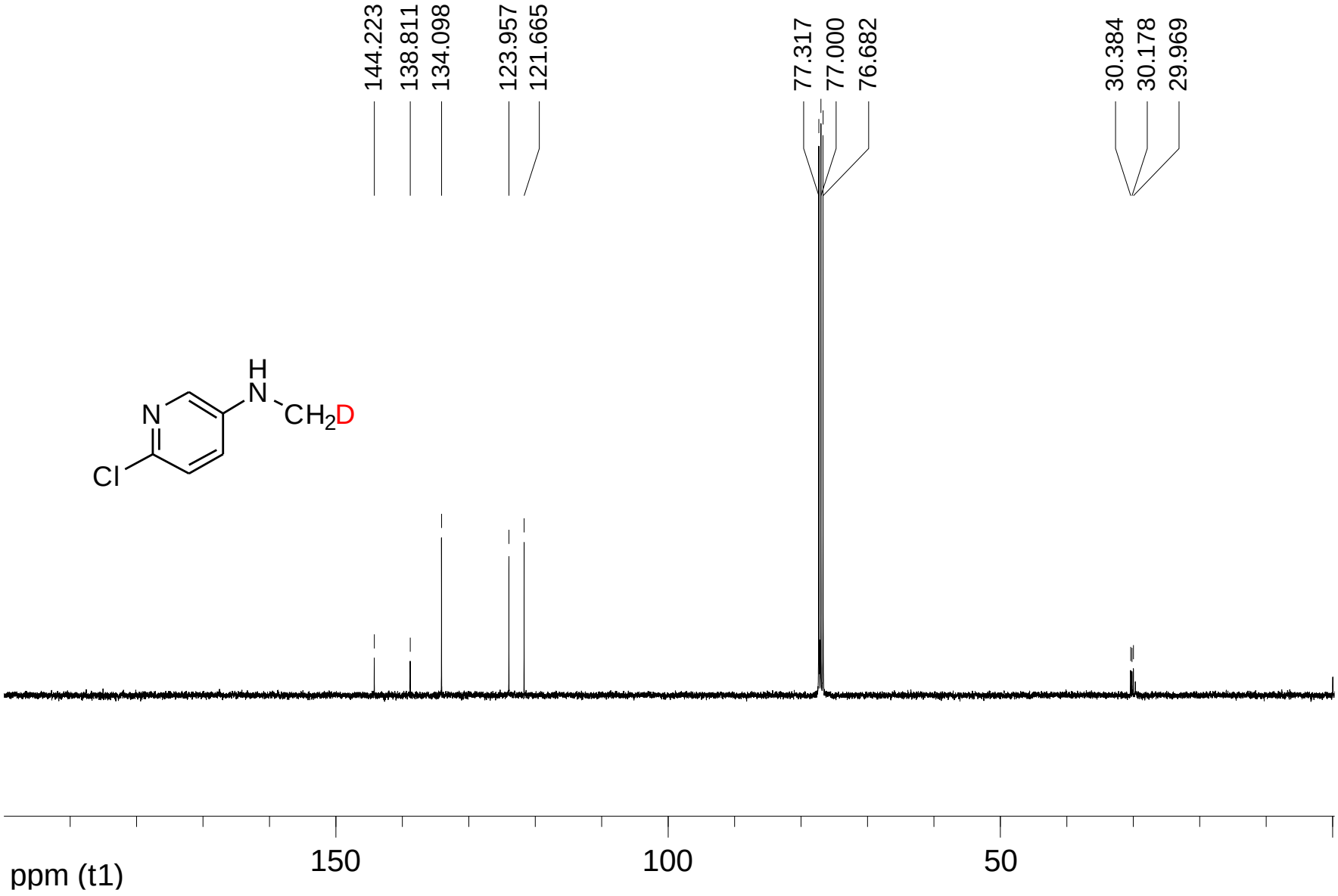
^{13}C NMR spectrum of **2z-D$_1$**(100M Hz, $CDCl_3$)



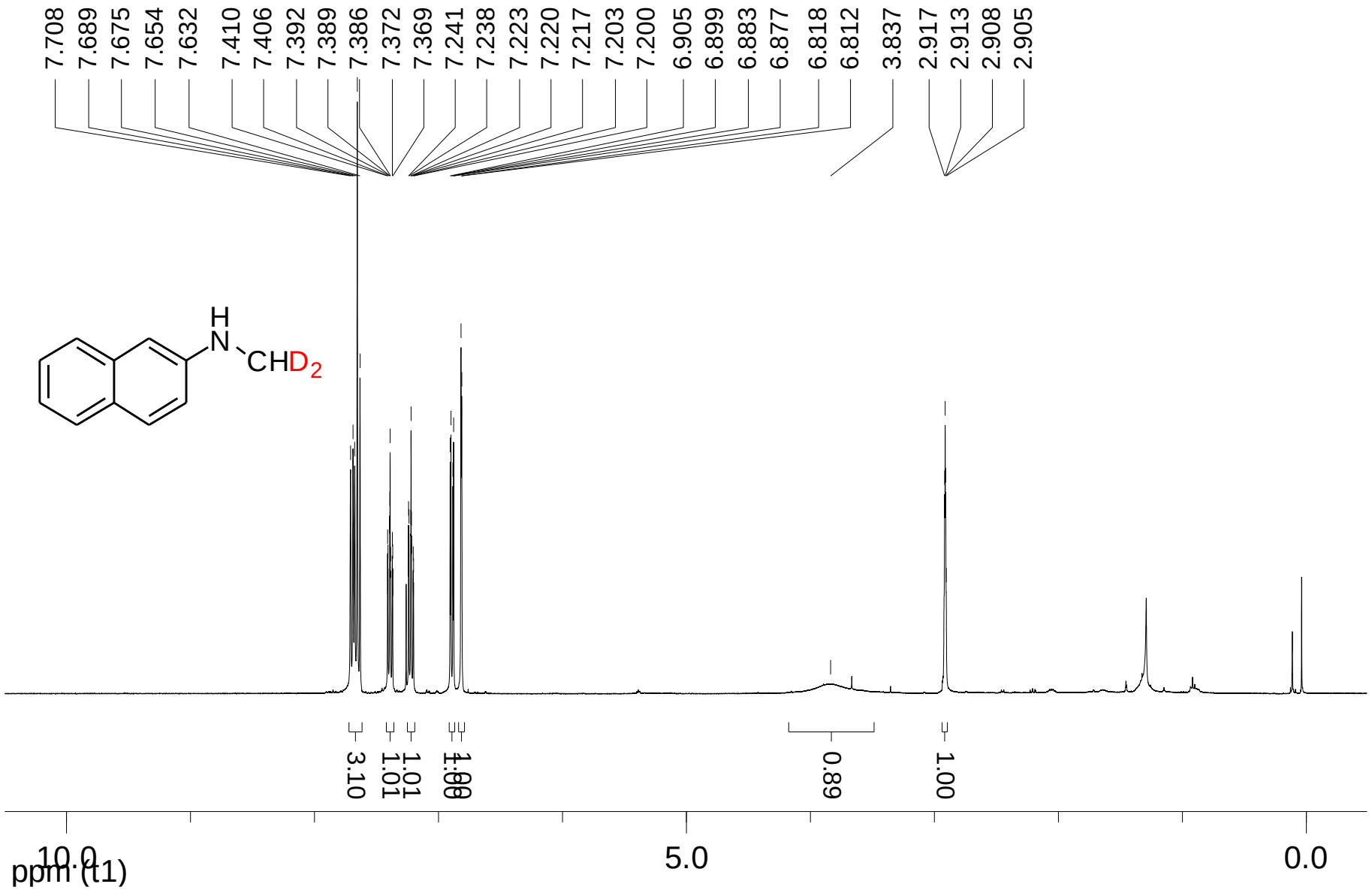
^{1}H NMR spectrum of **2ac-D$_1$** (400M Hz, $CDCl_3$)



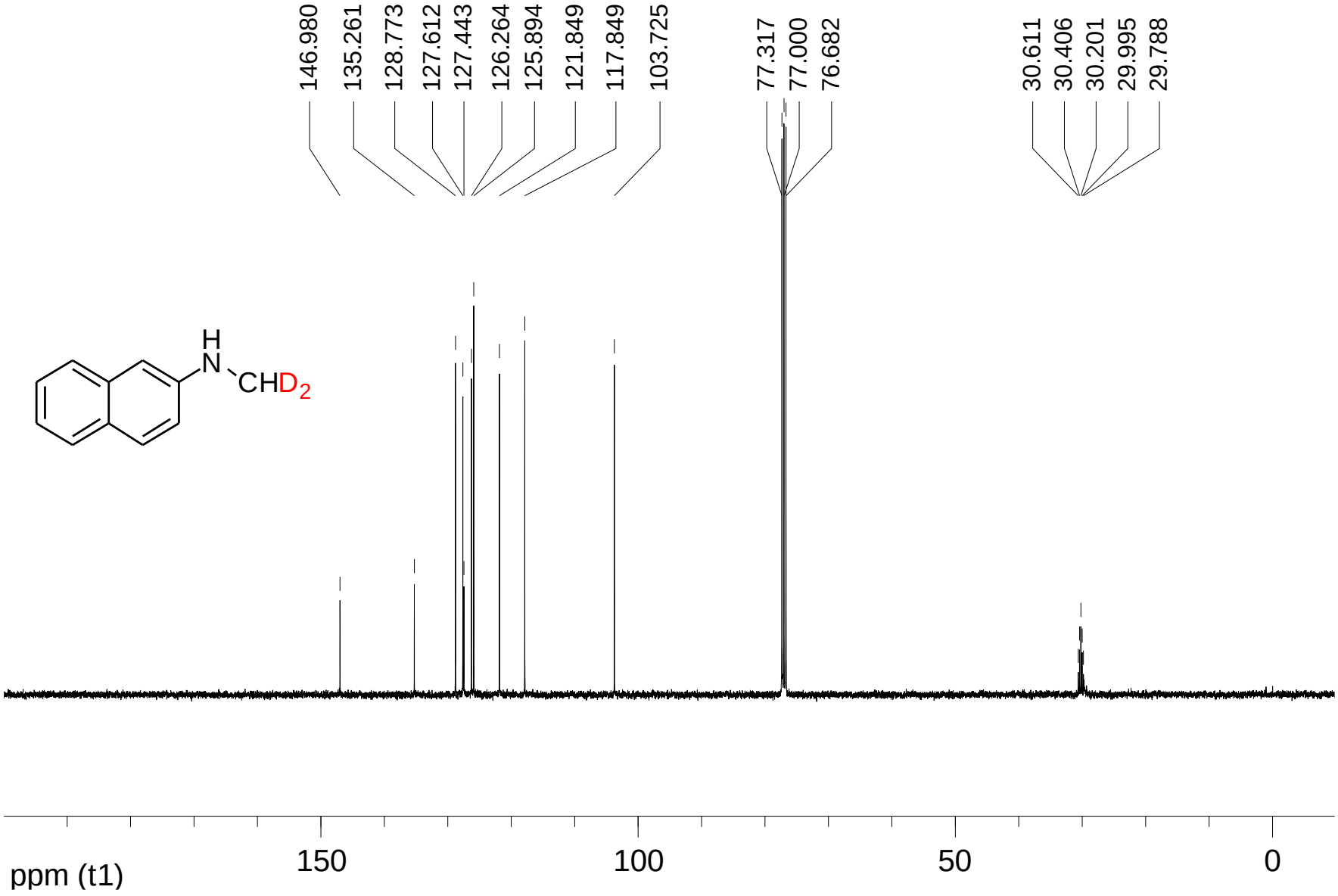
^{13}C NMR spectrum of **2ac-D$_1$** (100M Hz, $CDCl_3$)



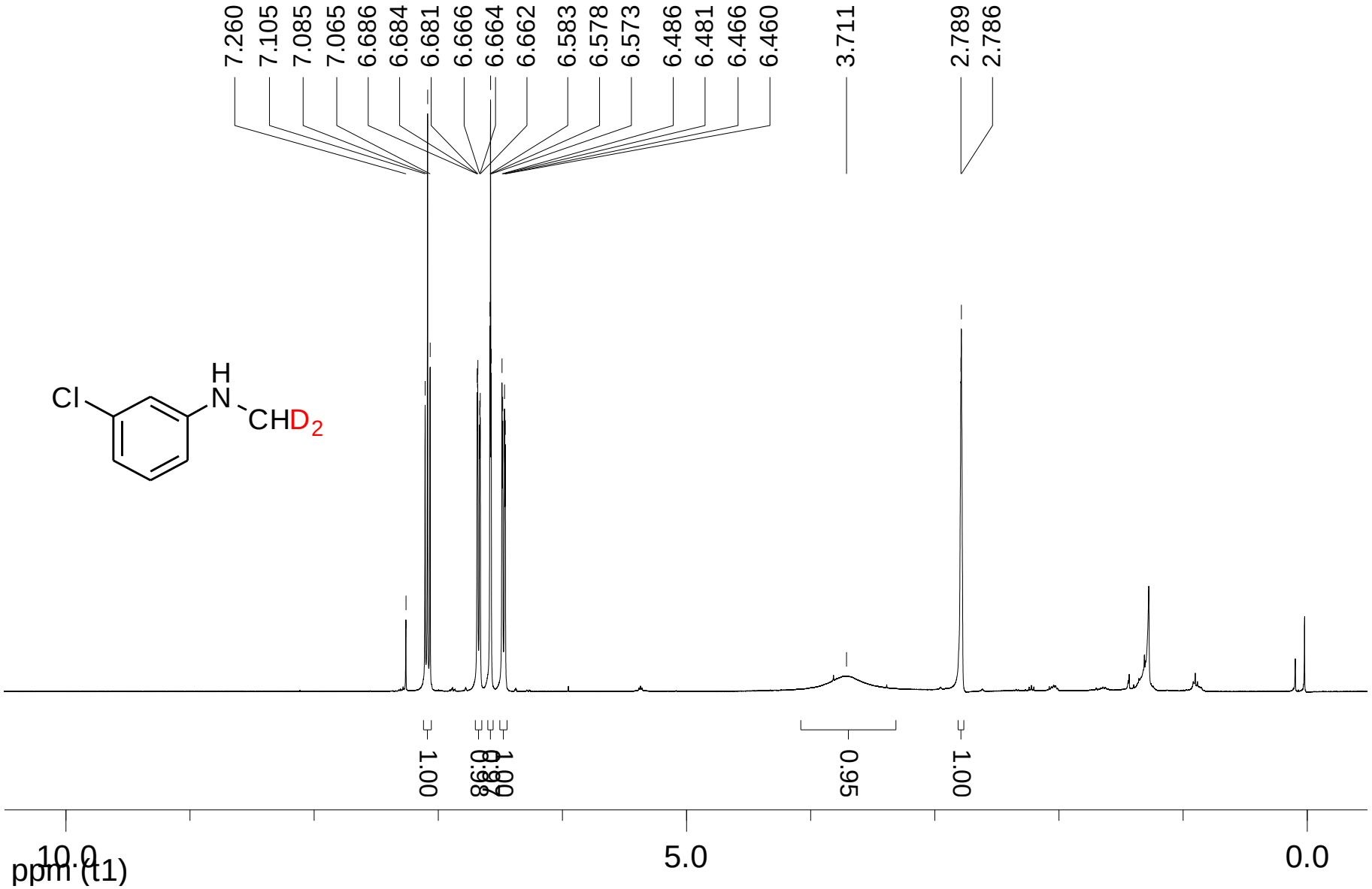
^{1}H NMR spectrum of **2a-D$_2$**(400M Hz, $CDCl_3$)



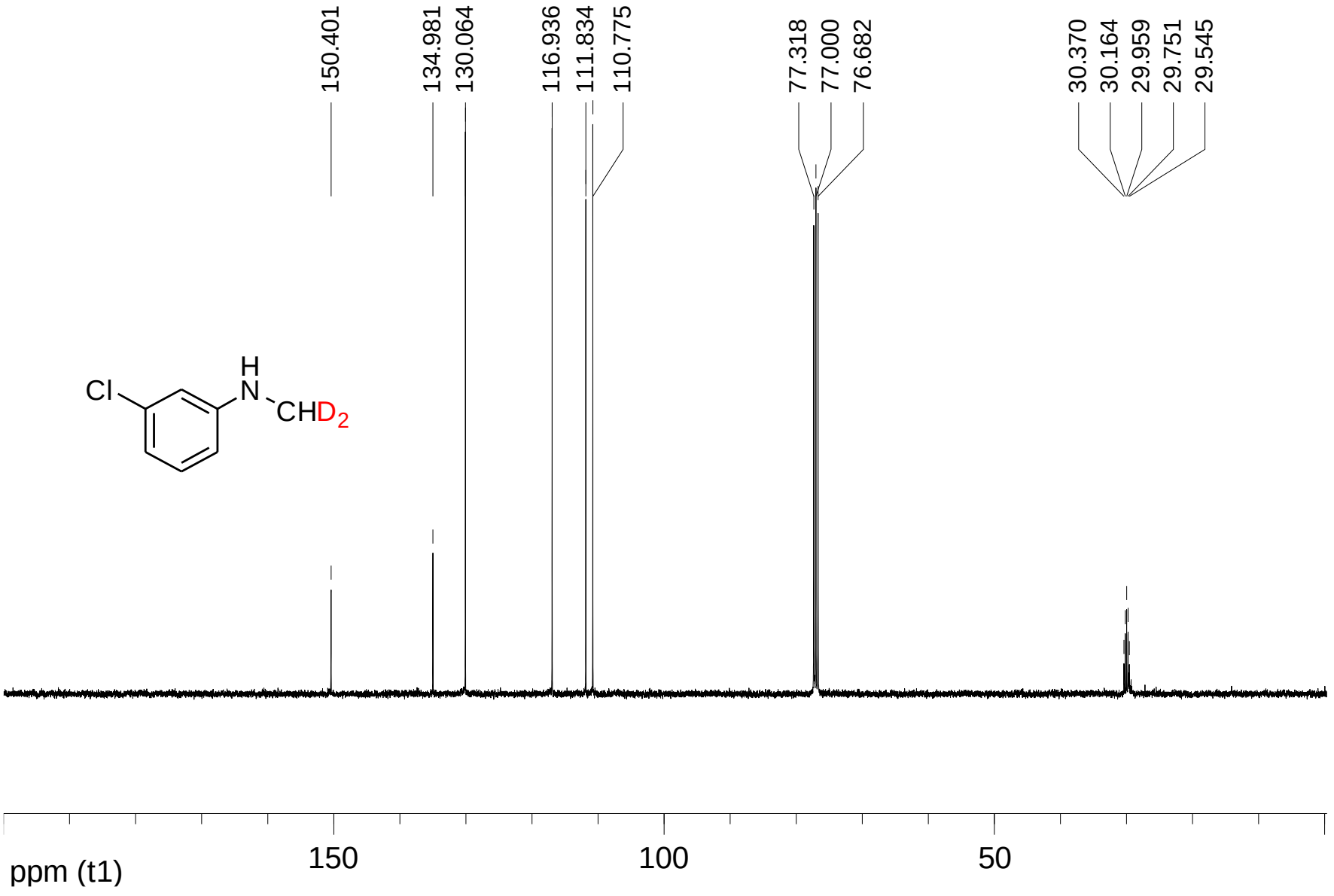
^{13}C NMR spectrum of **2a-D_2**(100M Hz, $CDCl_3$)



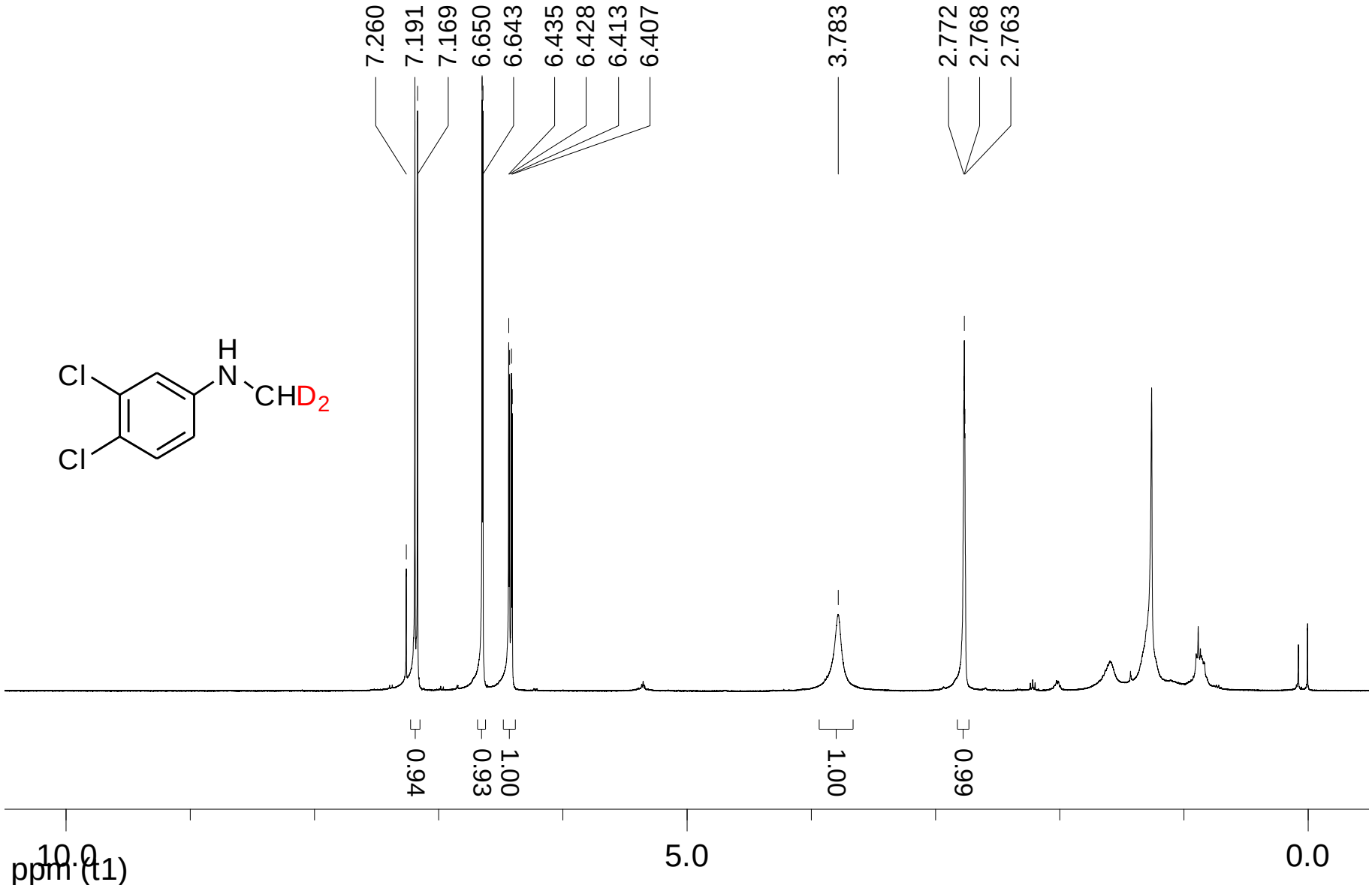
^{1}H NMR spectrum of **2c-D_2**(400M Hz, $CDCl_3$)



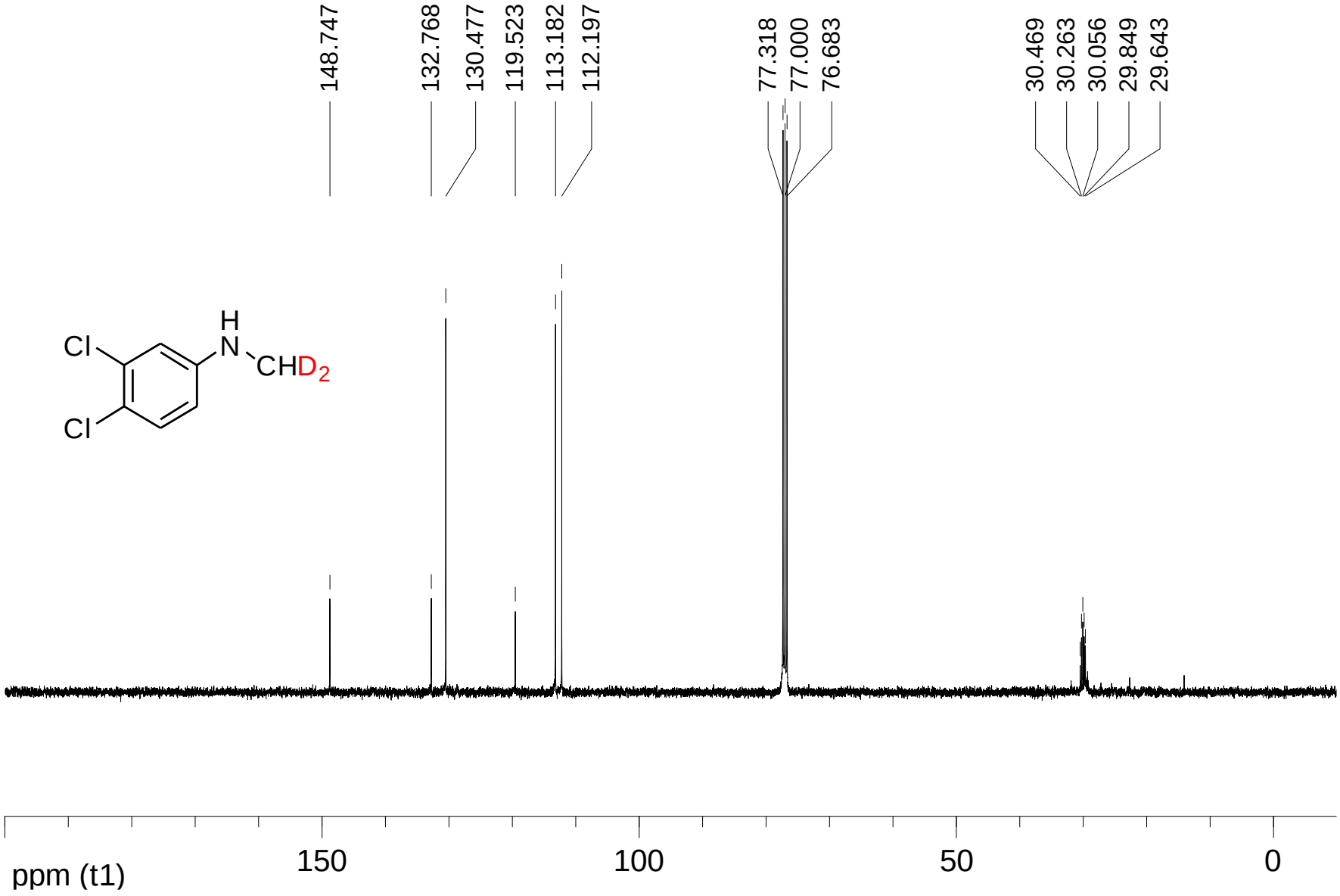
^{13}C NMR spectrum of **2c-D_2**(100M Hz, $CDCl_3$)



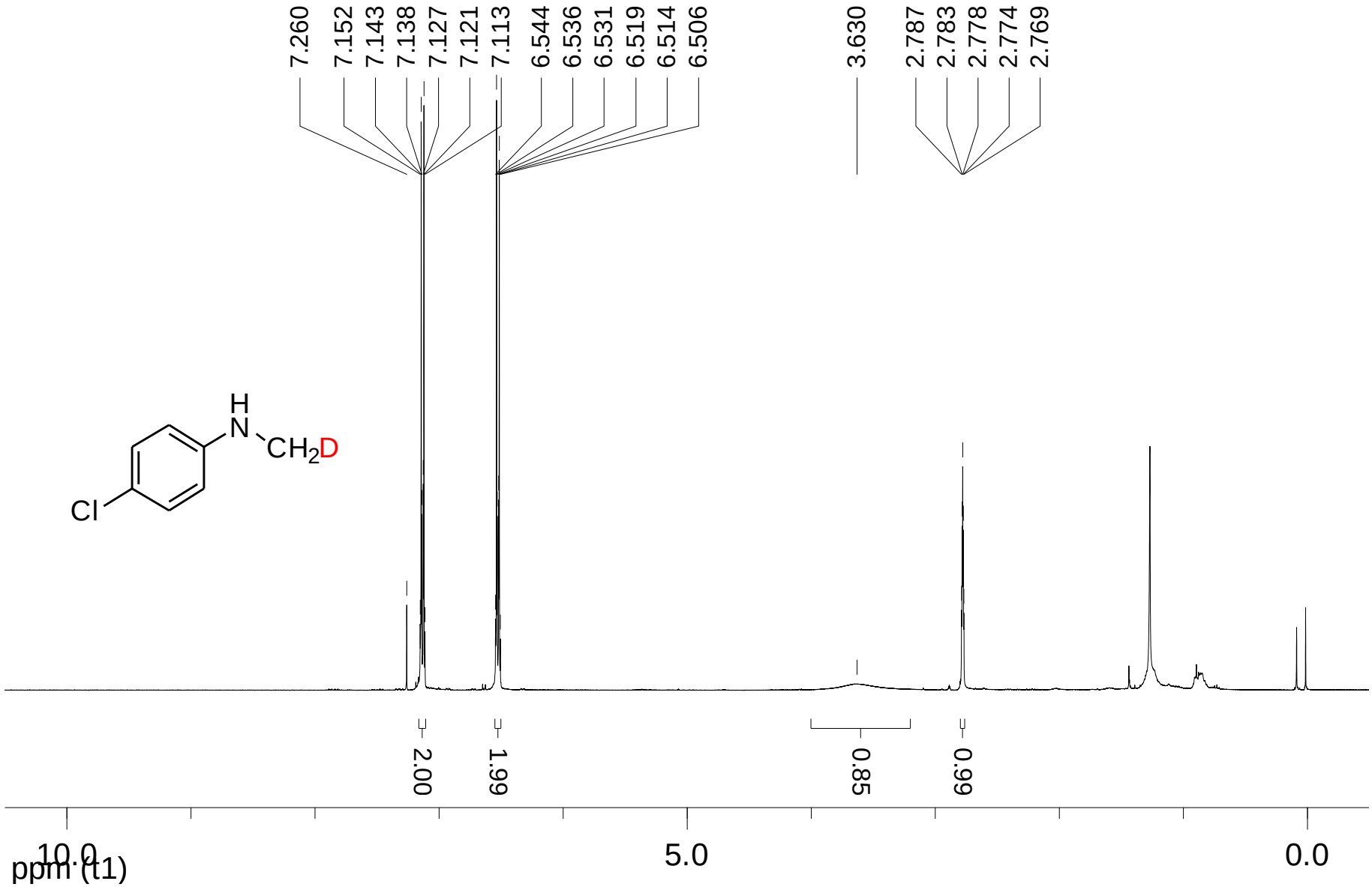
^{1}H NMR spectrum of **2e-D$_2$** (400M Hz, $CDCl_3$)



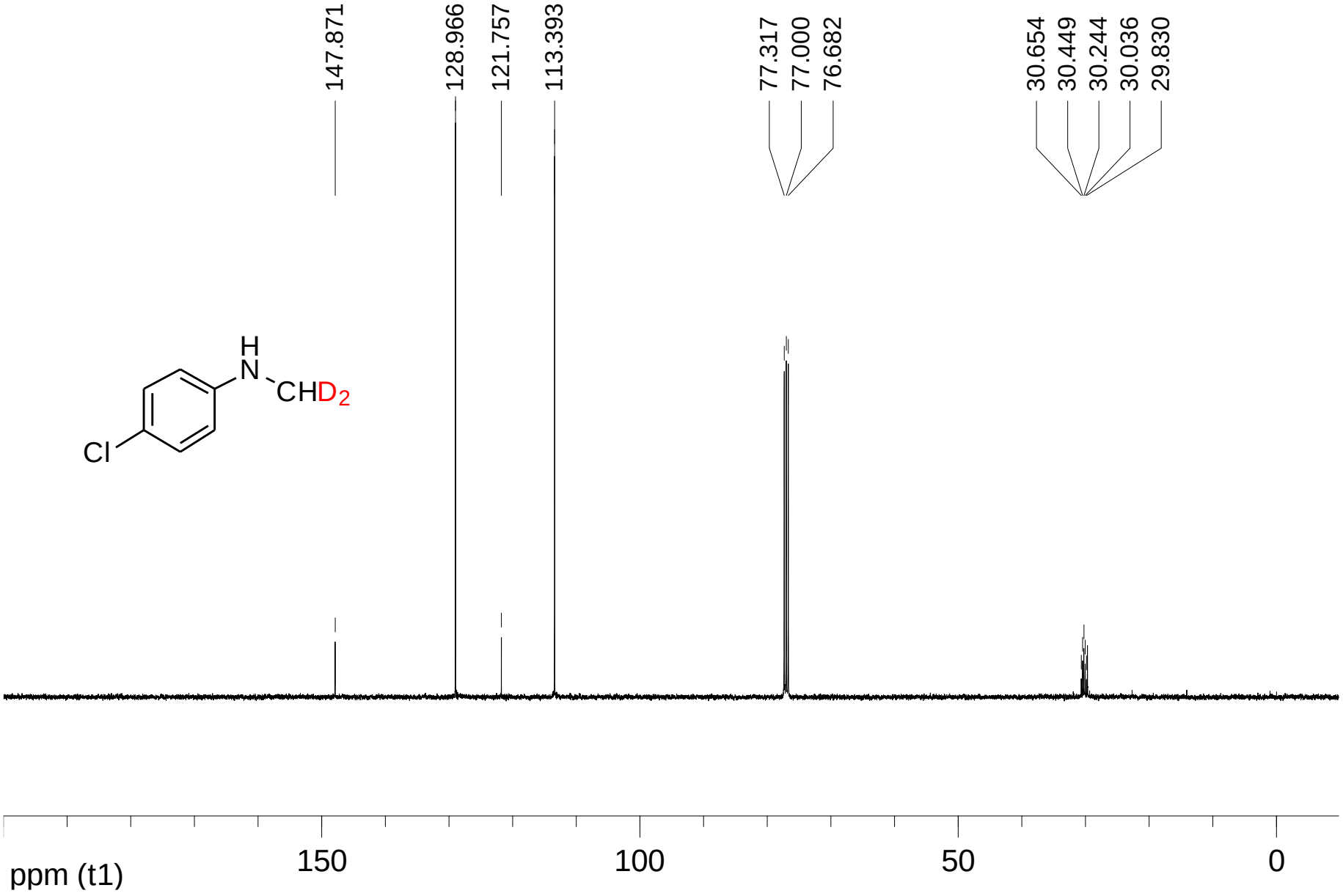
^{13}C NMR spectrum of **2e-D$_2$**(100M Hz, $CDCl_3$)



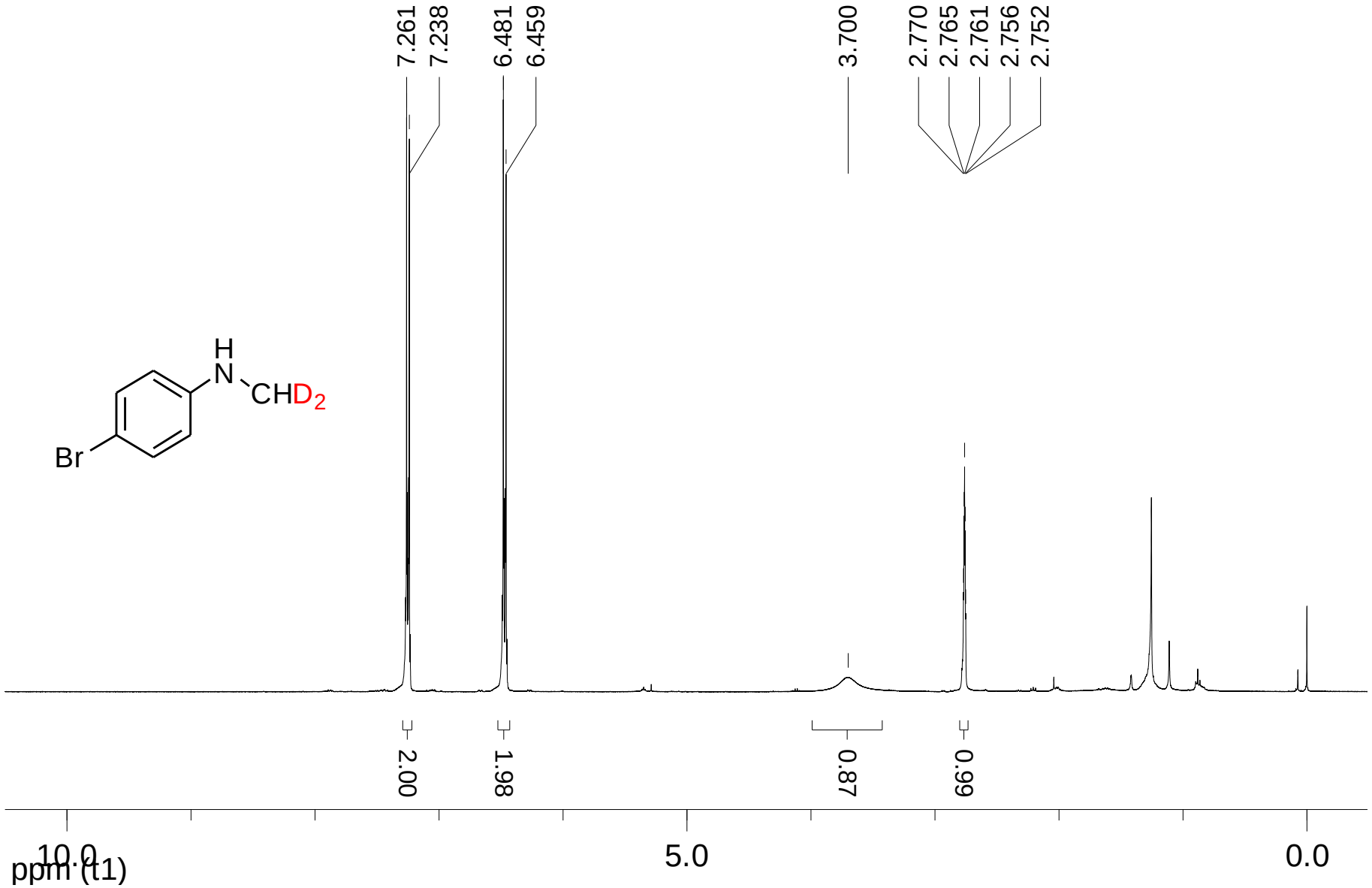
^{1}H NMR spectrum of **2g-D$_2$** (400M Hz, $CDCl_3$)



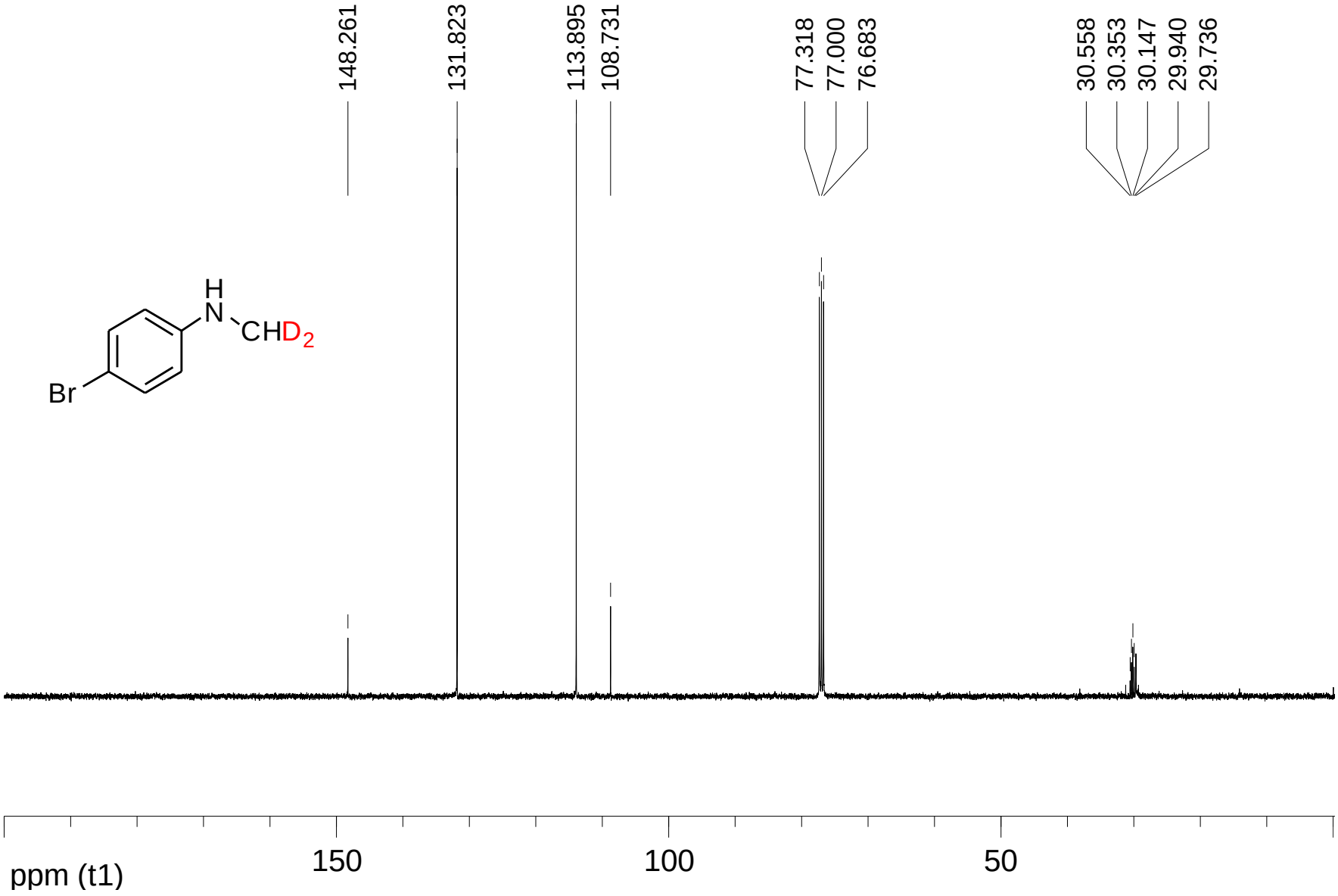
^{13}C NMR spectrum of **2g-D_2**(100M Hz, $CDCl_3$)



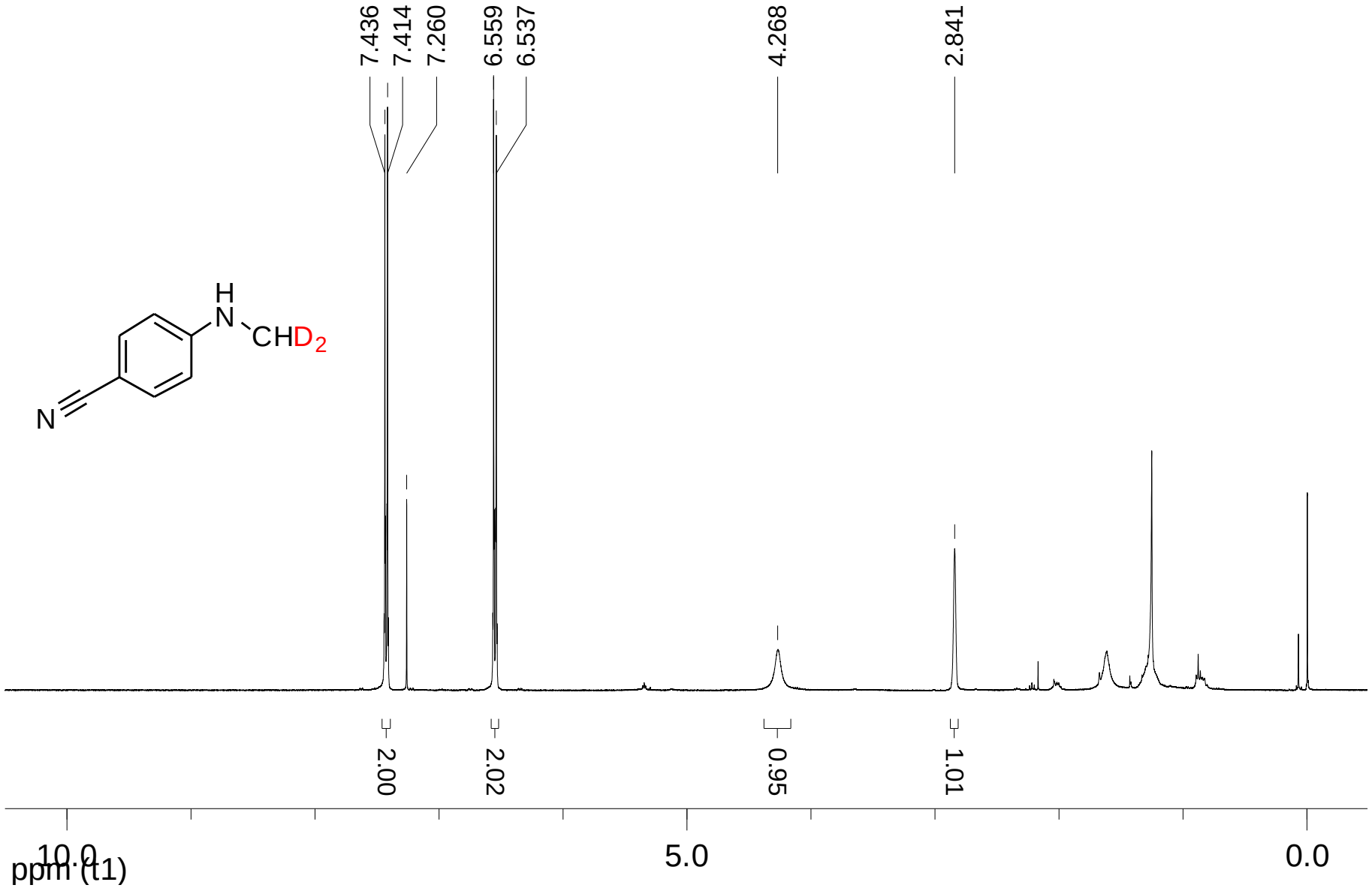
^{1}H NMR spectrum of **2h-D$_2$** (400M Hz, $CDCl_3$)



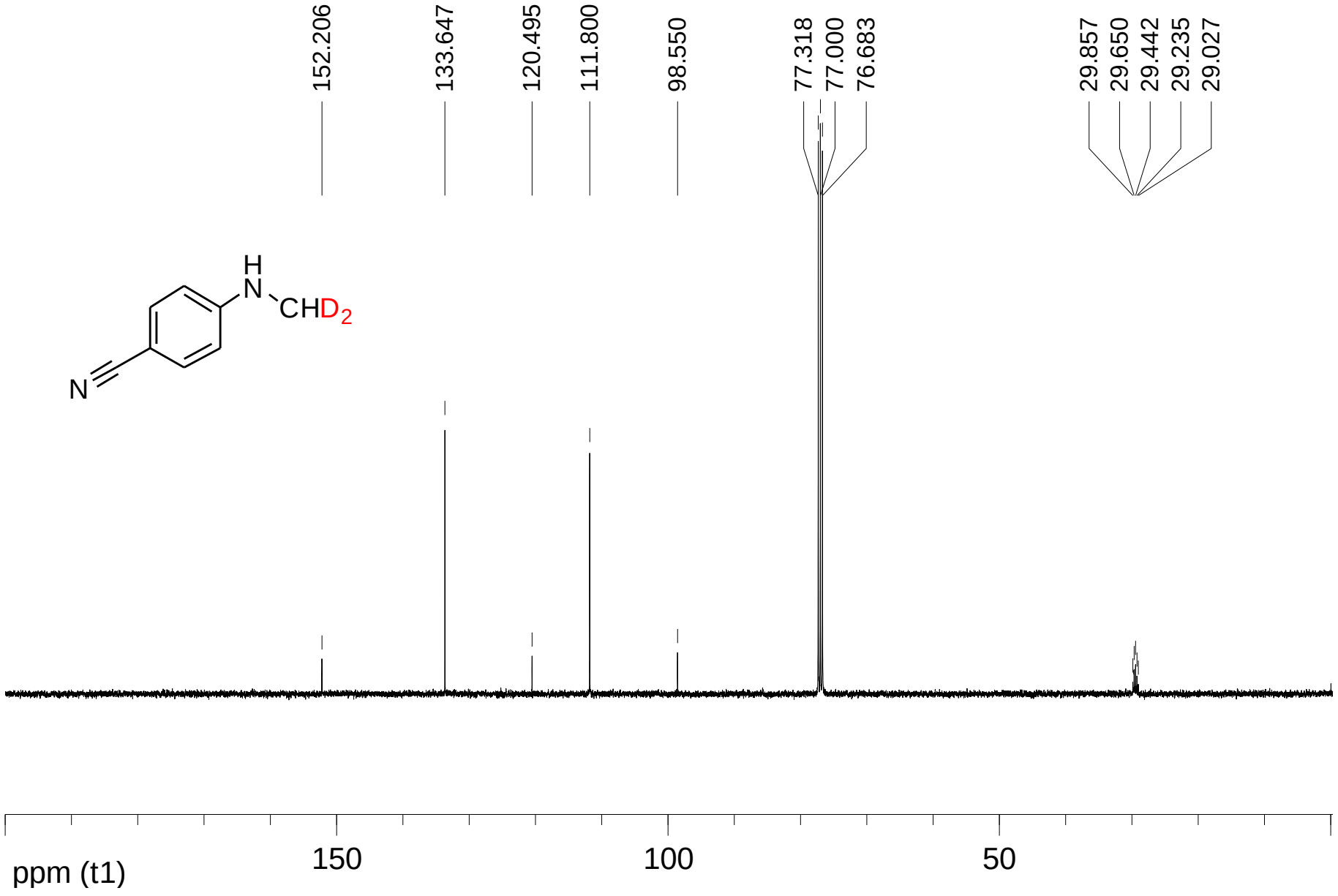
^{13}C NMR spectrum of **2h-D$_2$** (100M Hz, $CDCl_3$)



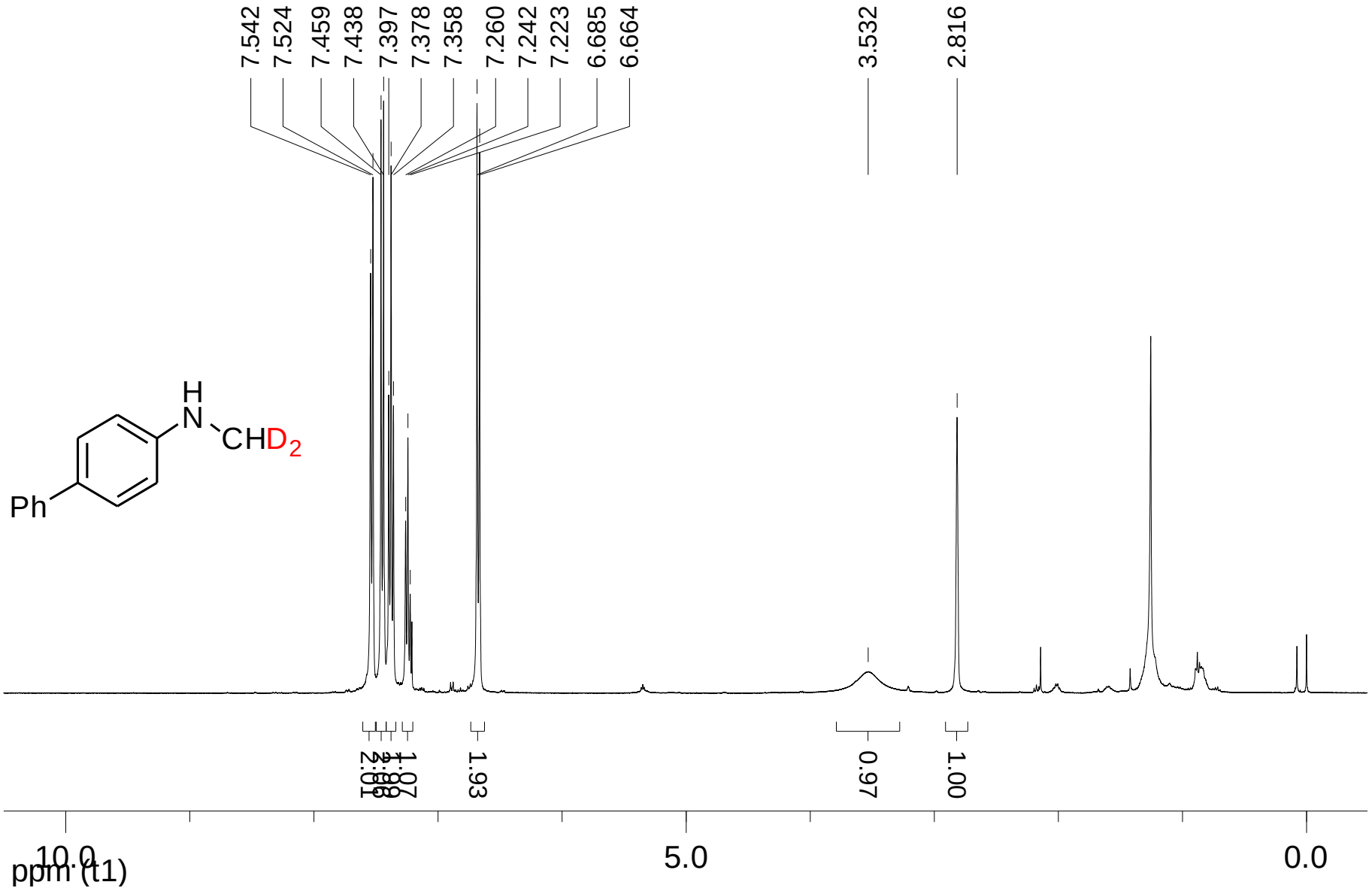
^{1}H NMR spectrum of **2j-D_2**(400M Hz, $CDCl_3$)



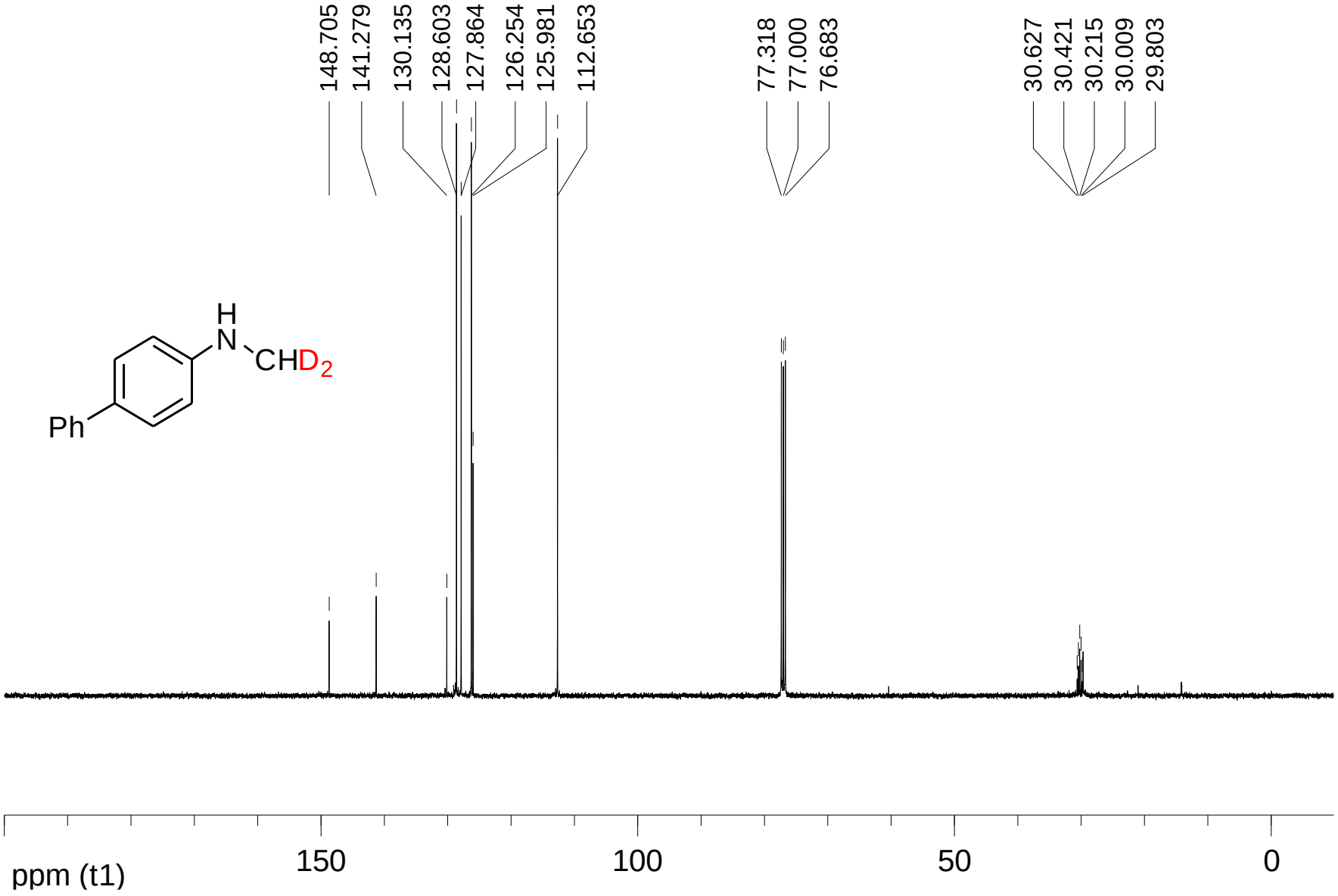
^{13}C NMR spectrum of **2j-D$_2$**(100M Hz, $CDCl_3$)



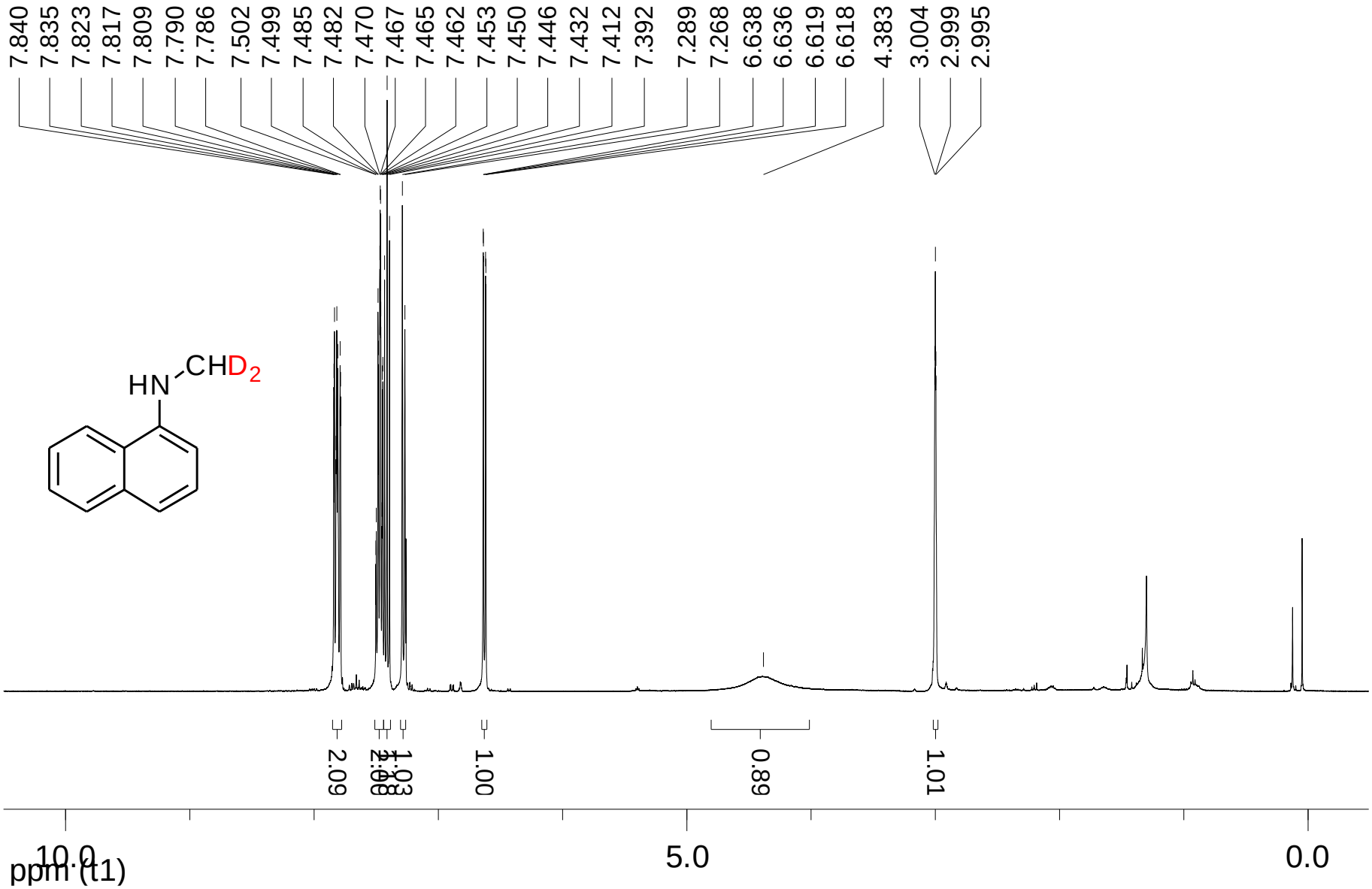
^{1}H NMR spectrum of **2o-D$_2$**(400M Hz, $CDCl_3$)



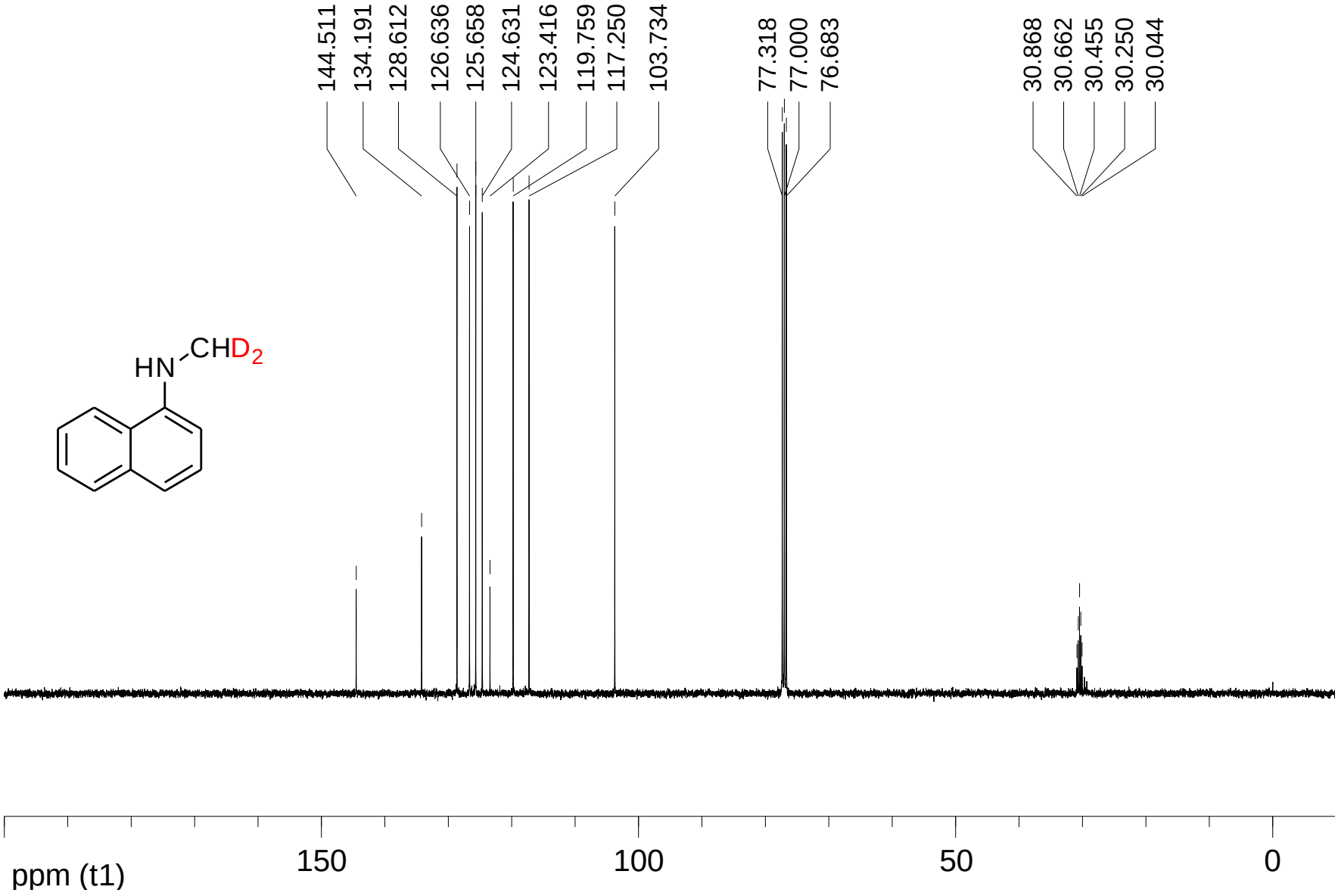
^{13}C NMR spectrum of **2o-D$_2$** (100M Hz, $CDCl_3$)



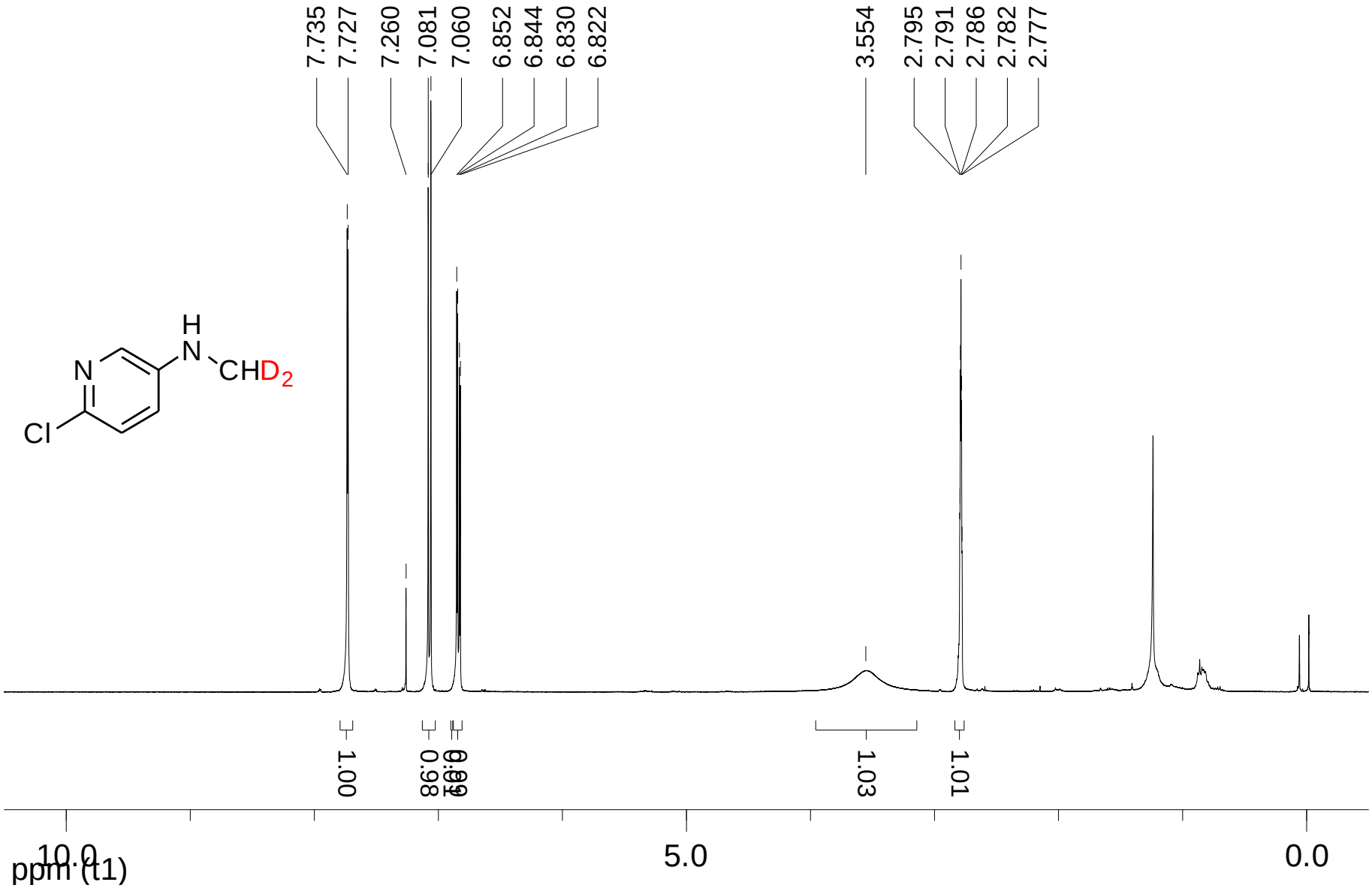
^{1}H NMR spectrum of **2z-D$_2$** (400M Hz, $CDCl_3$)



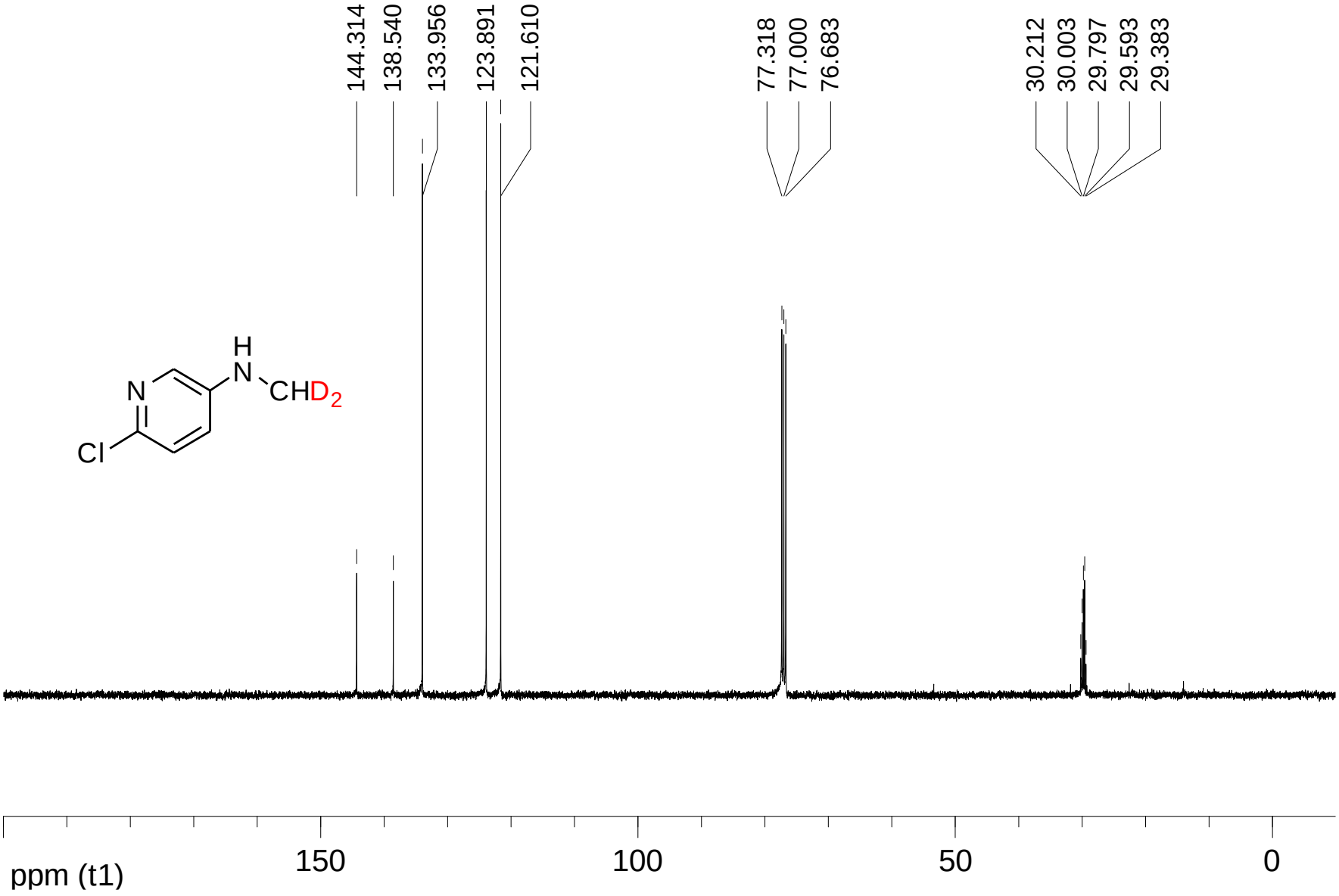
^{13}C NMR spectrum of **2z-D$_2$** (100M Hz, $CDCl_3$)



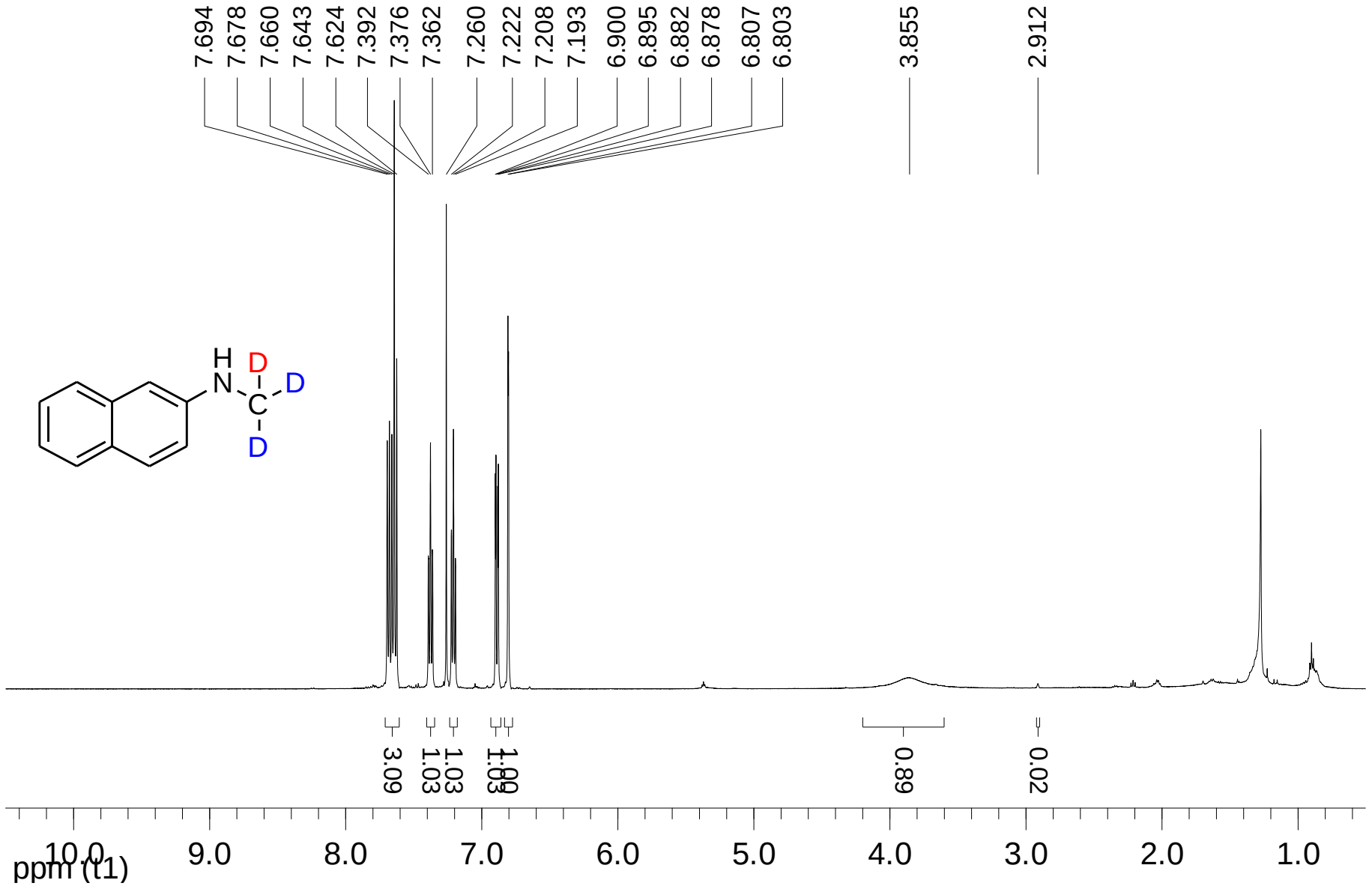
^{1}H NMR spectrum of **2ac-D$_2$** (400M Hz, $CDCl_3$)



^{13}C NMR spectrum of **2ac-D$_2$** (100M Hz, $CDCl_3$)



^{1}H NMR spectrum of **2a-D$_3$** (500M Hz, $CDCl_3$)



^{13}C NMR spectrum of **2a-D$_2$** (125M Hz, $CDCl_3$)