SUPPORTING INFORMATION

Anti-Markovnikov addition on *N*-allylic derivatives

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A. GENERAL METHOD

The authors draw the reader's attention to the dangerous features of superacidic chemistry. Handling of hydrogen fluoride and antimony pentafluoride must be done by experienced chemists with all the necessary safety arrangements in place.

Reactions performed in superacid were carried out in a sealed Teflon® flask with a magnetic stirrer. No further precautions have to be taken to prevent mixture from moisture (test reaction worked out in anhydrous conditions leads to the same results as expected).

Yields refer to isolated pure products.

^{1}H, ^{13}C and ^{19}F NMR were recorded on a 400 MHz Bruker Advance DPX spectrometer using $CDCl_3$, CD_3COCD_3, or CD_3OD as solvent. COSY ^{1}H-^{1}H and ^{1}H-^{13}C experiments were used to confirm the NMR peaks assignments.

Melting points were determined in a capillary tube with a device Büchi melting point B-545 and were uncorrected.

Mass Spectra (MS) were performed with coupled gas chromatography (electronic impact).

All separations were done under flash-chromatography conditions on silica gel (15-40 µm).

High Resolution Mass Spectrometry (HRMS) spectra were performed at the Centre régional de mesures physiques de l'Ouest of the University of Rennes 1, France.

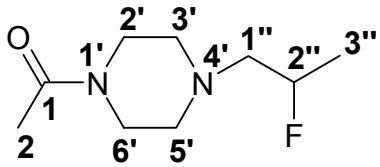
Preparation of HF/SbF_5 mixture: After liquid condensation of the desired quantity of hydrogen fluoride in a Teflon® reactor at -30 °C, antimony pentafluoride was slowly added to the reactor at the same temperature and the reactor was then sealed and maintained at reaction temperature. In these conditions, the SbF_5 molar percentage was determined accordingly: For example, 1 mL of SbF_5 ($13.8\ 10^{-3}$ mol) was added to 7 mL of anhydrous liquid HF (0.35 mol) to give a HF/SbF_5 solution with a SbF_5 molar percentage of 3.8 mol %.

B. HYDROFLUORINATION REACTION

Optimized procedure in superacidic media

To a mixture of HF/SbF_5 (4 mL, SbF_5 mol % = 3.8) maintained at -50 °C, was added nitrogen derivative. The mixture was magnetically stirred at the same temperature during 10 minutes. The reaction mixture was then neutralized with water-ice-Na_2CO_3, extracted with dichloromethane (× 3). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Products were isolated by column chromatography over silica gel.

Formation of compounds 2a and 3a:



Compound 2a: 1-(4-(2-fluoropropyl)piperazin-1-yl)ethanone

^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 1.34 (3H, dd, J=23.7 Hz, J=6.4 Hz, $\mathbf{H_{3''}}$), 2.09 (3H, s, $\mathbf{H_2}$), 2.53 (6H, m, $\mathbf{H_{3'}}$, $\mathbf{H_5}$, and $\mathbf{H_{1''}}$), 3.48 (2H, t, J=5.1 Hz, $\mathbf{H_{2',a}}$ and $\mathbf{H_{6',a}}$), 3.64 (2H, m, $\mathbf{H_{2',b}}$ and $\mathbf{H_{6',b}}$), 4.87 (1H, dm, J=49.6 Hz, $\mathbf{H_{2''}}$).

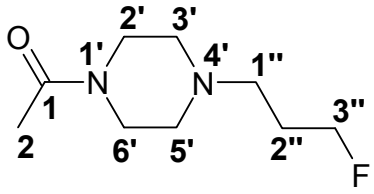
^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 19.3 (CH_3, d, J=22 Hz, $\mathbf{C_{3''}}$), 21.3 (CH_3, $\mathbf{C_2}$), 41.4 (CH_2, $\mathbf{C_{2'}}$ or $\mathbf{C_{6'}}$), 46.2 (CH_2, $\mathbf{C_{2'}}$ or $\mathbf{C_{6'}}$), 53.3 (CH_2, $\mathbf{C_{3'}}$ or $\mathbf{C_{5'}}$), 53.7 (CH_2, $\mathbf{C_{3'}}$ or $\mathbf{C_{5'}}$), 63.5 (CH_2, d, J=20 Hz, $\mathbf{C_{1''}}$), 88.9 (CH, d, J=167 Hz, $\mathbf{C_{2''}}$), 168.9 (CO, $\mathbf{C_1}$).

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, ppm) δ: -174.3.

MS (ESI, ACN): m/z 189 $[M+H]^+$.

HRMS (ESI, MeOH): Calc for $C_9H_{16}N_2OF$ $[M+H]^+$: 168.12626, found 168.1263.

Already described in: S. Thibaudeau, A. Martin-Mingot, M.-P. Jouannetaud, O. Karam and F. Zunino, *Chem. Commun.*, 2007, **30**, 3198.



Compound 3a: 1-(4-(3-fluoropropyl)piperazin-1-yl)ethanone

These compounds were obtained from the 1-(4-allylpiperazin-1-yl)ethanone **1a** (165 mg, 1 mmol) following the general procedure. The reaction crude was purified with the eluent CH_2Cl_2/(7.5% NH_3 in MeOH, weight percentage): 98/2. Compound 2a (8 mg) was first eluted and then, a mixture of starting material and compound 3a was eluted. A further purification on prepartive TLC plate allowed the separtion of pure compound 3a.

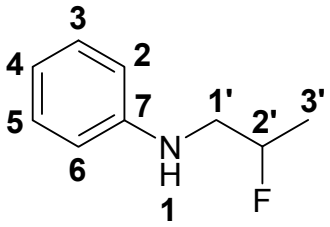
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.82 (dm, CH_2, J=25.5 Hz, $\mathbf{H_{2''}}$), 2.02 (s, CH_3, $\mathbf{H_2}$), 2.34 (t, 2H, J=5.2 Hz, $\mathbf{H_{3'}}$, $\mathbf{H_{5'}}$), 2.38 (t, 2H, J=5.2 Hz, $\mathbf{H_{3'}}$, $\mathbf{H_{5'}}$), 2.43 (t, CH_2, J=7.4 Hz, $\mathbf{H_{1''}}$), 3.40 (t, 2H, J=5.1 Hz, $\mathbf{H_{2'}}$, $\mathbf{H_{6'}}$), 3.55 (t, 2H, J=5.2 Hz, $\mathbf{H_{2'}}$, $\mathbf{H_{6'}}$), 4.45 (dt, CH_2, J=47.2 Hz, J=5.9 Hz, $\mathbf{H_{3''}}$).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.3 (s, CH_3, **C_2**), 27. 8 (d, CH_2, J=20 Hz, **$C_{2'}$**), 41.4 (CH_2, **C_2**, or **C_3**, or **C_5**, or **$C_{6'}$**), 46.2 (CH_2, **C_2**, or **C_3**, or **C_5**, or **$C_{6'}$**), 52.7 (CH_2, **C_2**, or **C_3**, or **C_5**, or **$C_{6'}$**), 53.3 (CH_2, **C_2**, or **C_3**, or **C_5**, or **$C_{6'}$**), 54.1 (d, CH_2, J=5 Hz, **$C_{1'}$**), 82.2 (d, CH_2, J=164 Hz, **$C_{3'}$**), 168.9 (CO, **C_1**).

^{19}F{1H} NMR ($CDCl_3$, 376 MHz, ppm) δ: -220.31.

MS (IES+, ACN): m/z 189 $[M+H]^+$, 211 $[M+Na]^+$.

HRMS (ESI, MeOH): Calc for $C_9H_{17}N_2OF$ $[M+H]^+$: 189.14032, found 189.1404.



Compound 2b: *N*-(2-fluoropropyl)aniline

This compound was obtained from substrate **1b** (133 mg, 1 mmol) following the general procedure. The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 99/1, thereby obtaining compound **2b** (76 mg, 50 %).

Aspect: brown oil

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.42 (dd, CH_3, J=23.8 Hz, J=6.3 Hz, **$H_{3'}$**), 3.28 (m, CH_2, **$H_{1'}$**), 3.98 (broad s, NH, **H_1**).4.89 (dm, CH, J=49.4 Hz, **$H_{2'}$**), 6.64 (dd, 2CH, J=8.5 Hz, J=0.9 Hz, **H_2**, **H_6**), 6.74 (t, CH, J=7.3 Hz, **H_4**), 7.19 (dd, 2CH, J=8.4 Hz, J=7.4 Hz, **H_3**, **H_5**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 18.8 (d, CH_3, J=22 Hz, **$C_{3'}$**), 49.6 (d, CH_2, J=21 Hz, **$C_{1'}$**), 89.6 (d, CH, J=167 Hz, **$C_{2'}$**), 113.1 (2CH, **C_2**, **C_6**), 118.1 (1CH, **C_4**), 129.4 (2CH, **C_5**, **C_3**), 147.9 (**C_7**).

^{19}F{1H} NMR ($CDCl_3$, 376 MHz, ppm) δ: -180.0.

MS (IES+, ACN): m/z 154 $[M+H]^+$.

HRMS (ESI, CH_3OH): Calc for $C_9H_{12}NF$ $[M+Na]^+$: 176.08515, found 176.0852.

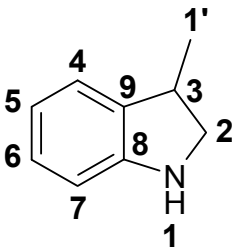
C. CYCLISATION REACTION

Optimized procedure in superacidic media

To a mixture of HF/SbF_5 (4 mL, SbF_5 mol % = 21.6) maintained at 0 °C, was added nitrogen derivative. The mixture was magnetically stirred at the same temperature for reaction time. The reaction mixture was then neutralized with water-ice-Na_2CO_3, extracted with ethyl acetate (× 3). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Products were isolated by column chromatography over silica gel.

Formation of compounds 4b and 5b:

These compounds were obtained from substrate **1b** (126 mg, 0.95 mmol) following the general procedure (reaction time: 10 minutes). The reaction crude was purified with the eluent pentane/ethyl acetate: 99/1, compound **4b** (49 mg, 39 %) first eluted followed by compound **5b** (28 mg, 22 %).



Compound 4b: 3-methylindoline

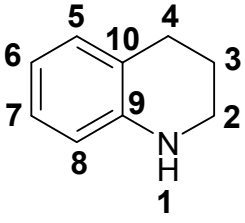
Aspect: brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.34 (d, CH_3, J=6.8 Hz, **$H_{1'}$**), 3.12 (t, 1H, J=8.6 Hz, **H_2**), 3.38 (m, CH, **H_3**), 3.51 (broad s, NH, **H_1**), 3.71 (t, 1H, J=8.6 Hz, **H_2**), 6.66 (d, CH, J=7.8 Hz, **H_7**), 6.75 (td, CH, J=7.4 Hz, J=1.0 Hz, **H_5**), 7.04 (tm, CH, J=7.7 Hz, **H_6**), 7.10 (d, CH, J=7.3 Hz, **H_4**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 18.7 (CH_3, **$C_{1'}$**), 36.8 (CH, **C_3**), 55.6 (CH_2, **C_2**), 109.6 (CH, **C_7**), 118.8 (CH, **C_5**), 123.5 (CH, **C_4**), 128.2 (CH, **C_6**), 134.5 (**C_9**), 151.3 (**C_8**).

MS (IES+, ACN): m/z 134 $[M+Na]^+$.

Already describe in: V. Gotor-Fernández, P. Fernández-Torres and V. Gotor, *Tetrahedron Asymmetry*, 2006, **17**, 2558.



Compound 5b: 1.2.3.4-tetrahydroquinoline

Aspect: brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.96 (m, CH_2, **H_3**), 2.78 (t, CH_2, J=6.4 Hz, **H_4**), 3.31 (t, CH_2, J=5.4 Hz, **H_2**), 3.56 (broad s, NH, **H_1**), 6.49 (d, CH, J=7.9 Hz, **H_8**), 6.63, (dt, CH, J=7.4 Hz, J=1.1 Hz, **H_6**), 6.98 (m, 2CH, **H_5**, **H_7**).

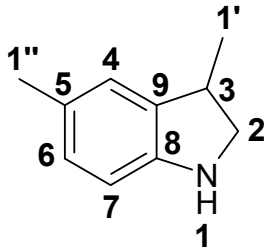
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 22.3 (CH_2, **C_3**), 27.1 (CH_2, **C_4**), 42.1 (CH_2, **C_2**), 114.35 (CH, **C_8**), 117.1 (CH, **C_6**), 121.6 (**C_{10}**), 126.8 (CH, **C_7**), 129.6 (CH, **C_5**), 144.8 (**C_9**).

MS (IES+, ACN): m/z 134 $[M+H]^+$.

Already describe in: F. Nador, Y. Moglie, C. Vitale, M. Yus, F. Alonso and G. Radivoy, *Tetrahedron*, 2010, **66**, 4318.

Formation of compounds 4c and 5c:

These compounds were obtained from substrate **1c** (137 mg, 0.93 mmol) following the general procedure (reaction time: 10 minutes). The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 98/2, compound **4c** (63 mg, 46 %) first eluted followed by compound **5c** (19 mg, 14 %).



Compound 4c: 3.5-dimethylindoline

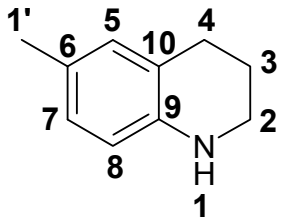
Aspect: brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.36 (d, CH_3, J=6.8 Hz, **$H_{1'}$**), 2.33 (s, CH_3, **$H_{1''}$**), 3.13 (t, CH, J=8.6 Hz, **H_3**), 3.38 (m, 1H, **H_2**), 3.55 (s, NH, **H_1**), 3.72 (t, 1H, J=8.6 Hz, **H_2**), 6.61 (d, CH, J=7.8 Hz, **H_7**), 6.89 (d, CH, J=7.8 Hz, **H_6**), 6.97 (s, CH, **H_4**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 18.6 (CH_3, **$C_{1'}$**), 20.9 (CH_3, **$C_{1''}$**), 36.8 (CH, **C_3**), 55.8 (CH_2, **C_2**), 109.6 (CH, **C_7**), 124.2 (CH, **C_6**), 127.7 (CH, **C_4**), 128.2 (**C_5**), 134.8 (**C_9**), 148.9 (**C_8**).

MS (IES+, ACN): m/z 148 $[M+H]^+$, m/z 189 $[M+Na]^+$.

HRMS (ESI, CH_3OH): Calc for $C_{10}H_{13}N$ $[M+H]^+$: 148.11262, found 148.1126.



Compound 5c: 6-methyl-1.2.3.4-tetrahydroquinoline

Aspect: brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.97 (m, CH_2, **H_3**), 2.25 (s, CH_3, **$H_{1'}$**), 2.78 (t, CH_2, J=6.3 Hz, **H_4**), 3.31 (m, CH_2, **H_2**), 3.59 (m, NH, **H_1**), 6.45 (d, CH, J=8.6 Hz, **H_8**), 6.83 (m, 2CH, **H_5**, **H_7**).

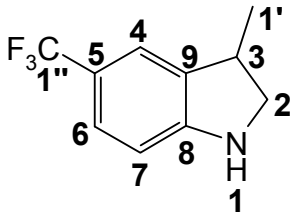
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 20.5 (CH_3, **$C_{1'}$**), 22.5 (CH_2, **C_3**), 27.0 (CH_2, **C_4**), 42.3 (CH_2, **C_2**), 114.6 (CH, **C_8**), 121.7 (**C_{10}**), 126.3 (**C_6**), 127.3 (CH, **C_7**), 130.2 (CH, **C_5**), 142.5 (**C_9**).

MS (IES+, ACN): m/z 148 $[M+H]^+$, m/z 189 $[M+Na]^+$.

Already describe in: G. Lunn and E. B. Sansone, *J. Org. Chem.*, 1986, **51**, 513.

Formation of compounds 4d and 5d:

These compounds were obtained from substrate **1d** (212 mg, 1.05 mmol) following the general procedure (reaction time: 30 minutes). The reaction crude was purified with the eluent pentane/dichloromethane: 92/8, compound **4d** (11 mg, 5 %) first eluted followed by compound **5d** (82 mg, 39 %).



Compound 4d: 3-methyl-5-(trifluoromethyl)indoline

Aspect: brown oil.

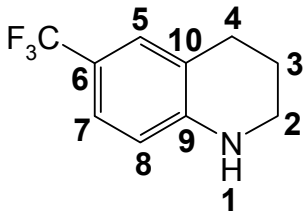
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.34 (d, CH_3, J=6.8 Hz, $\mathbf{H_{1'}}$), 3.20 (t, 1H, J=8.5 Hz, $\mathbf{H_2}$), 3.39 (m, CH, $\mathbf{H_3}$), 3.78 (t, 1H, J=8.8 Hz, $\mathbf{H_2}$), 3.95 (s, NH, $\mathbf{H_1}$), 6.60 (d, CH, J=8.7 Hz, $\mathbf{H_7}$), 7.27 (m, 2CH, J=6.1 Hz, $\mathbf{H_4}$, $\mathbf{H_6}$).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 18.9 (CH_3, $\mathbf{C_{1'}}$), 36.3 (CH, $\mathbf{C_3}$), 55.54 (CH_2, $\mathbf{C_2}$), 108.1 (CH, $\mathbf{C_7}$), 120.3 (q, J=32 Hz, $\mathbf{C_5}$), 120.6 (q, 2CH, J=4 Hz, $\mathbf{C_4}$ or $\mathbf{C_6}$), 125.26 (q, J=271 Hz, $\mathbf{C_{1''}}$), 125.4 (q, 2CH, J=4 Hz, $\mathbf{C_4}$ or $\mathbf{C_6}$), 134.5 ($\mathbf{C_9}$), 154.2 ($\mathbf{C_8}$).

^{19}F{1H} NMR ($CDCl_3$, 376 MHz, ppm) δ: -60.67 (CF_3).

MS (IES+, ACN): m/z 202 $[M+H]^+$.

HRMS (ESI, CH_3OH): Calc for $C_{10}H_{10}NF_3$ $[M+H]^+$: 202.08436, found 202.0846.



Compound 5d: 6-(trifluoromethyl)-1.2.3.4-tetrahydroquinoline

Aspect: brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.94 (m, CH_2, $\mathbf{H_3}$), 2.78 (t, CH_2, J=6.3 Hz, $\mathbf{H_4}$), 3.34 (t, CH_2, J=5.4 Hz, $\mathbf{H_2}$), 4.15 (broad s, NH, $\mathbf{H_1}$), 6.44 (d, CH, J=9.0 Hz, $\mathbf{H_8}$), 7.19 (m, 2CH, $\mathbf{H_7}$, $\mathbf{H_5}$).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.5 (CH_2, $\mathbf{C_3}$), 27.1 (CH_2, $\mathbf{C_4}$), 41.8 (CH_2, $\mathbf{C_2}$), 113.1 (CH, $\mathbf{C_8}$), 118.1 (q, J=32 Hz, $\mathbf{C_6}$), 120.7 ($\mathbf{C_{10}}$), 124.1 (q, CH, J=4 Hz, $\mathbf{C_7}$), 125.3 (q, J=270 Hz, $\mathbf{CF_3}$), 126.6 (q, CH, J=4 Hz, $\mathbf{C_5}$), 147.5 ($\mathbf{C_9}$).

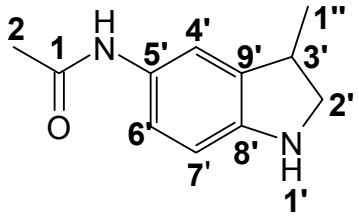
^{19}F{1H} NMR ($CDCl_3$, 376 MHz, ppm) δ: -60.80 (CF_3).

MS (IES+, ACN): m/z 202 $[M+H]^+$.

HRMS (ESI, CH_3OH): Calc for $C_{10}H_{10}NF_3$ $[M+H]^+$: 202.08436, found 202.0846.

Formation of compounds 4e and 5e:

These compounds were obtained from substrate **1e** (189 mg, 1 mmol) following the general procedure (reaction time: 10 minutes). The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 50/50, compound **4e** (33 mg, 17 %) first eluted followed by compound **5e** (135 mg, 72 %).



Compound 4e: *N*-(3-methylindolin-5-yl)acetamide

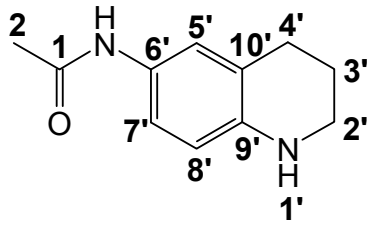
Aspect: red viscous oil

^{1}H NMR (CD_3OD, 400 MHz, ppm) δ: 1.29 (d, CH_3, J=6.8 Hz, $\mathbf{H_{1''}}$), 2.08 (s, CH_3, $\mathbf{H_2}$), 3.02 (t, 1H, J=8.7 Hz, $\mathbf{H_{2'}}$), 3.30 (m, CH, $\mathbf{H_{3'}}$), 3.61 (t, 1H, J=8.7 Hz, $\mathbf{H_{2'}}$), 6.62 (d, CH, J=8.3 Hz, $\mathbf{H_{7'}}$), 7.08 (ddd, CH, J=8.3 Hz, J=2.1 Hz, J=0.7 Hz, $\mathbf{H_{6'}}$), 7.27 (dd, CH, J=1.7 Hz, J=1.1 Hz, $\mathbf{H_{4'}}$).

^{13}C NMR (CD_3OD, 100 MHz, ppm) δ: 18.9 (CH_3, $\mathbf{C_{1''}}$), 23.5 (CH_3, $\mathbf{C_2}$), 38.2 (CH, $\mathbf{C_{3'}}$), 56.4 (CH_2, $\mathbf{C_{2'}}$), 111.3 (CH, $\mathbf{C_{7'}}$), 118.0 (CH, $\mathbf{C_{4'}}$), 121.4 (CH, $\mathbf{C_{6'}}$), 131.9 ($\mathbf{C_{5'}}$), 136.8 ($\mathbf{C_{9'}}$), 149.4 ($\mathbf{C_{8'}}$), 171.3 ($\mathbf{C_1}$).

MS (IES+, ACN): m/z 191 $[M+H]^+$, 213 $[M+Na]^+$.

HRMS (ESI, CH_3OH): Calc for $C_{11}H_{14}N_2O$ $[M+H]^+$: 191.11844, found 191.1183.



Compound 5e: *N*-(1.2.3.4-tetrahydroquinolin-6-yl)acetamide

Aspect: beige solid

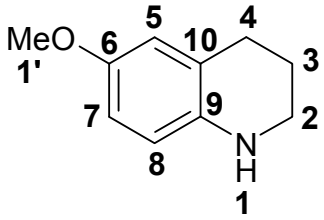
^{1}H NMR (CD_3OD, 400 MHz, ppm) δ: 1.84 (m, CH_2, $\mathbf{H_{3'}}$), 2.04 (s, CH_3, $\mathbf{H_2}$), 2.66 (t, CH_2, J=6.4 Hz, $\mathbf{H_{4'}}$), 3.16 (m, CH_2, $\mathbf{H_{2'}}$), 6.43 (d, CH, J=8.4 Hz, $\mathbf{H_{8'}}$), 7.01 (dd, CH, J=8.5 Hz, J=2.2 Hz, $\mathbf{H_{7'}}$), 7.03 (m, CH, $\mathbf{H_{5'}}$).

^{13}C NMR (CD_3OD, 100 MHz, ppm) δ: 23.2 (CH_2, $\mathbf{C_3}$), 23.5 (CH_3, $\mathbf{C_{3'}}$), 28.0 (CH_2, $\mathbf{C_4}$), 42.8 (CH_2, $\mathbf{C_2}$), 115.7 (CH, $\mathbf{C_8}$), 121.0 (CH, $\mathbf{C_7}$), 122.9 ($\mathbf{C_{10}}$), 123.3 (CH, $\mathbf{C_5}$), 129.4 ($\mathbf{C_6}$), 143.5 ($\mathbf{C_9}$), 171.1 ($\mathbf{C_{2'}}$).

MS (IES+, ACN): m/z 191 $[M+H]^+$, 213 $[M+Na]^+$.

Already describe in: K. A. Skupinska, E. J. McEachern, R. T. Skerlj, and G. J. Bridger, *J. Org. Chem.*, 2002, **67**, 7890.

Formation of compound 5f



Compound 5f: 6-methoxy-1.2.3.4-tetrahydroquinoline

This compound was obtained from substrate **1f** (165 mg, 1 mmol) following the general procedure (reaction time: 30 minutes). The reaction crude was purified with the eluent pentane/ethyl acetate: 98/1, thereby obtaining compound **5f** (52 mg, 32 %).

Aspect: brown solid.

Mp: 35-38 °C

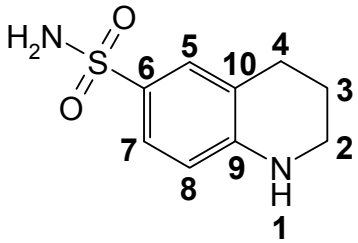
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.94 (m, CH_2, **H_3**), 2.77 (t, CH_2, J=6.5 Hz, **H_4**), 3.26 (t, CH_2, J=5.4 Hz, **H_2**), 3.56 (broad s,NH, **H_1**), 3.74 (s, CH_3, **$H_{1'}$**), 6.46 (d, CH, J=8.5 Hz, **H_8**), 6.58 (d, CH, J=2.7 Hz, **H_5**), 6.62 (dd, CH, J=8.5 Hz, J=2.9 Hz, **H_7**),

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 22.5 (CH_2, **C_3**), 27.2 (CH_2, **C_4**), 42.4 (CH_2, **C_2**), 55.9 (CH_3, **$C_{1'}$**), 112.9 (CH, **C_7**), 114.9 (CH, **C_5**), 115.6 (CH, **C_8**), 122.9 (**C_{10}**), 138.9 (**C_9**), 151.9 (**C_6**),

MS (IES+, ACN): m/z 164 $[M+H]^+$.

Already describe in: M. Ortiz-Marciales, L. D. Rivera, M. De Jesús, S. Espinosa, J. A. Benjamin, O. E. Casanova, I. G. Figueroa, S. Rodríguez and W. Correa, *J. Org. Chem.*, 2005, **70**, 10132.

Formation of compound 5g



Compound 5g: 1.2.3.4-tetrahydroquinoline-6-sulfonamide

This compound was obtained from substrate **1g** (107 mg, 0.5 mmol) following the general procedure (2 mL of HF/SbF_5 mixture, reaction time: 60 minutes). The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 25/75, thereby obtaining compound **5g** (98 mg, 92 %).

Aspect: white solid

Mp: 141-143 °C

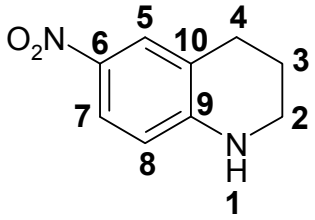
^{1}H NMR (CD_3OD, 400 MHz, ppm) δ: 1.88 (m, CH_2, **H_3**), 2.74 (t, CH_2, J=6.3 Hz, **H_4**), 3.30 (m, CH_2, **H_2**), 6.47 (d, CH, J=9.1 Hz, **H_8**), 7.39 (m, 2CH, **H_5**, **H_7**).

^{13}C NMR (CD_3OD, 100 MHz, ppm) δ: 22.3 (CH_2, **C_3**), 28.2 (CH_2, **C_4**), 42.2 (CH_2, **C_2**), 113.4 (CH, **C_8**), 121.0 (**C_{10}**), 126.5 (CH, **C_7**), 128.5 (CH, **C_5**), 129.5 (**C_6**), 150.2 (**C_9**).

MS (IES-, ACN): m/z 211 $[M-H]^+$, 235 $[M+Na]^+$.

HRMS (ESI, CH_3OH): Calc for $C_9H_{12}N_2SO_2$ $[M+Na]^+$: 235.05172, found 235.0516.

Formation of compound 5h



Compound 5h: 6-nitro-1.2.3.4-tetrahydroquinoline

This compound was obtained from substrate **1h** (155 mg, 0.87 mmol) following the general procedure (reaction time: 24 hours). The reaction crude was purified with the eluent pentane/ethyl acetate: 85/15, thereby obtaining compound **5h** (108 mg, 70 %).

Aspect: yellow solid.

Mp: 160-162 °C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.95 (m, CH_2, **H_3**), 2.79 (t, CH_2, J=6.3 Hz, **H_4**), 3.41 (m, CH_2, **H_2**), 4.72 (broad s, NH, **H_1**), 6.36 (d, CH, J=9.5 Hz, **H_8**), 7.88 (m, 2CH, **H_7**, **H_5**),

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 20.9 (CH_2, **C_3**), 27.0 (CH_2, **C_4**), 41.9 (CH_2, **C_2**), 112.3 (CH, **C_8**), 120.0 (**C_{10}**), 124.4 (CH, **C_7**), 126.1 (CH, **C_5**), 137.4 (**C_6**), 150.5 (**C_9**),

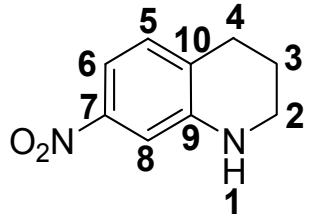
MS (IES+, ACN): m/z 179 $[M+H]^+$, 201 $[M+Na]^+$.

Already descrebed in: A. Cordeiro, J. Shaw, J. O'Brien, F. Blanco and I. Rozas, *Eur. J. Org. Chem.*, 2011, **8**, 1504.

Formation of compounds 5i and 5i':

These compounds were obtained from substrate **1i** (178 mg, 1 mmol) following the general procedure (reaction time: 24 hours). The reaction crude was purified with the eluent pentane/ CH_2Cl_2: 70/30 up to 60/40, thereby obtaining compound **5i** (116 mg, 66 %) followed by **5i'** (20 mg, 10 %).

Compound 5i: 7-nitro-1.2.3.4-tetrahydroquinoline



Aspect: Orange solid

Mp: 62-64°C

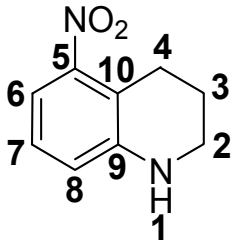
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1,93 (td, CH_2, J=6.4 Hz, J=11.6 Hz, **H_3**), 2,79 (t, CH_2, J=6.4 Hz, **H_4**), 3.33 (t, CH_2, J=5.6 Hz, **H_2**), 4.21 (broad s, NH, **1**), 7.00 (d, CH, J=8.2 Hz, **H_5**), 7.25 (d, CH, J=2.3 Hz, **H_8**), 7.37 (dd, CH, J=2.3 Hz, J=8.2 Hz, **H_6**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.1 (CH_2, **C_3**), 27.3 (CH_2, **C_4**), 41.6 (CH_2, **C_2**), 107,8 (CH, **C_8**), 111.3 (CH, **C_6**), 128.4 (**C_{10}**), 129,8 (CH, **C_5**), 145.3 (**C_9**), 147.3 (**C_7**).

MS (IES+, ACN) : m/z 179.08 $[M+H]^+$.

Already descrebed in: A. Cordeiro, J. Shaw, J. O'Brien, F. Blanco and I. Rozas, *Eur. J. Org. Chem.*, 2011, **8**, 1504.

Compound 5i': 5-nitro-1.2.3.4-tetrahydroquinoline



Aspect: Orange solid

Mp: 80-82°C

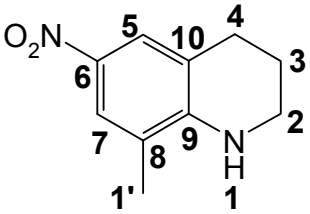
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1,92 (m, CH_2, **H_3**), 2,93 (t, CH_2, J=6.5 Hz, **H_4**), 3.32 (t, CH_2, J=5.6 Hz, **H_2**), 6.66 (dd, CH, J=1.1 Hz, J=8.0 Hz, **H_8**), 7.03 (t, CH, J=8.0 Hz, **H_7**), 7.13 (dd, CH, J=1.2 Hz, J=8.0 Hz, **H_6**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.2 (CH_2, **C_3**), 24.1 (CH_2, **C_4**), 41.2 (CH_2, **C_2**), 112,7 (CH, **C_6**), 115.5 (**C_6**), 118.3 (CH, **C_8**), 126,8 (CH, **C_7**), 146.0 (**C_9**), 150,7 (**C_5**).

MS (IES+, ACN) : m/z 179.24 $[M+H]^+$.

Already descrebed in: A. Cordeiro, J. Shaw, J. O'Brien, F. Blanco and I. Rozas, *Eur. J. Org. Chem.*, 2011, **8**, 1504.

Formation of cmopound 5j



Compound 5j: 8-methyl-6-nitro-1.2.3.4-tetrahydroquinoline

This compound was obtained from substrate **1j** (96 mg, 0.5 mmol) following the general procedure (2 mL of HF/SbF_5 mixture, reaction time: 8 hours). The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 83/17, thereby obtaining compound **5j** (81 mg, 84 %).

Aspect: orange solid.

Mp: 143-145 °C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.95 (m, CH_2, **H_3**), 2.11 (s, CH_3, **$H_{1'}$**), 2.81 (t, CH_2, J=6.3 Hz, **H_4**), 3.48 (m, CH_2, **H_2**), 4.53 (broad s, NH, **H_1**), 7.78 (d, CH, J=2.1 Hz, **H_5**), 7.81 (d, CH, J=2.1 Hz, **H_7**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 17.1 (CH_3, **$C_{1'}$**), 21.0 (CH_2, **C_3**), 27.3 (CH_2, **C_4**), 42.2 (CH_2, **C_2**), 119.4 (**C_{10}** or **C_8**), 119.6 (**C_{10}** or **C_8**), 124.1 (CH, **C_5**), 124.6 (CH, **C_7**), 136.6 (**C_6**), 148.7 (**C_9**).

MS (IES+, ACN): m/z 193 $[M+H]^+$, 215 $[M+Na]^+$.

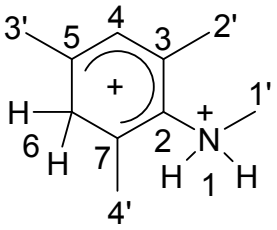
HRMS (ESI, CH_3OH): Calc for $C_{10}H_{12}N_2O_2$ $[M+Na]^+$: 215.07965, found 215.0799.

D. *in situ* NMR DATA FOR CATIONIC INTERMEDIATES

Procedure in superacidic media

To a magnetically stirred mixture of HF/SbF_5 (SbF_5 mol % = 21.6) maintained at -20 °C, was added nitrogen derivative. Using Teflon NMR tubes, ^1H, ^{13}C NMR and DEPT 135 data were acquired by using acetone D6 as external standard.

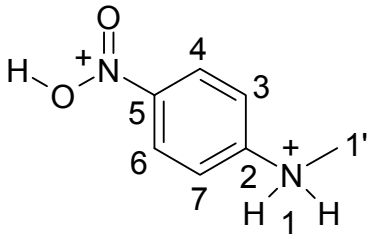
Substrates **7** and **8** led respectively to cationic intermediates **9** and **10**.



Dicationic intermediate 9:

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.29 (s, CH_3, **H_2**, or **H_3**, or **H_4**), 1.36 (s, CH_3, **H_2**, or **H_3**, or **H_4**), 1.46 (s, CH_3, **H_2**, or **H_3**, or **H_4**), 1.85 (broad s, CH_3, **H_1**), 3.48 (s, CH_2, **H_6**), 6.18 (broad s, 2H, **H_1**), 6.38 (s, CH, **H_4**).

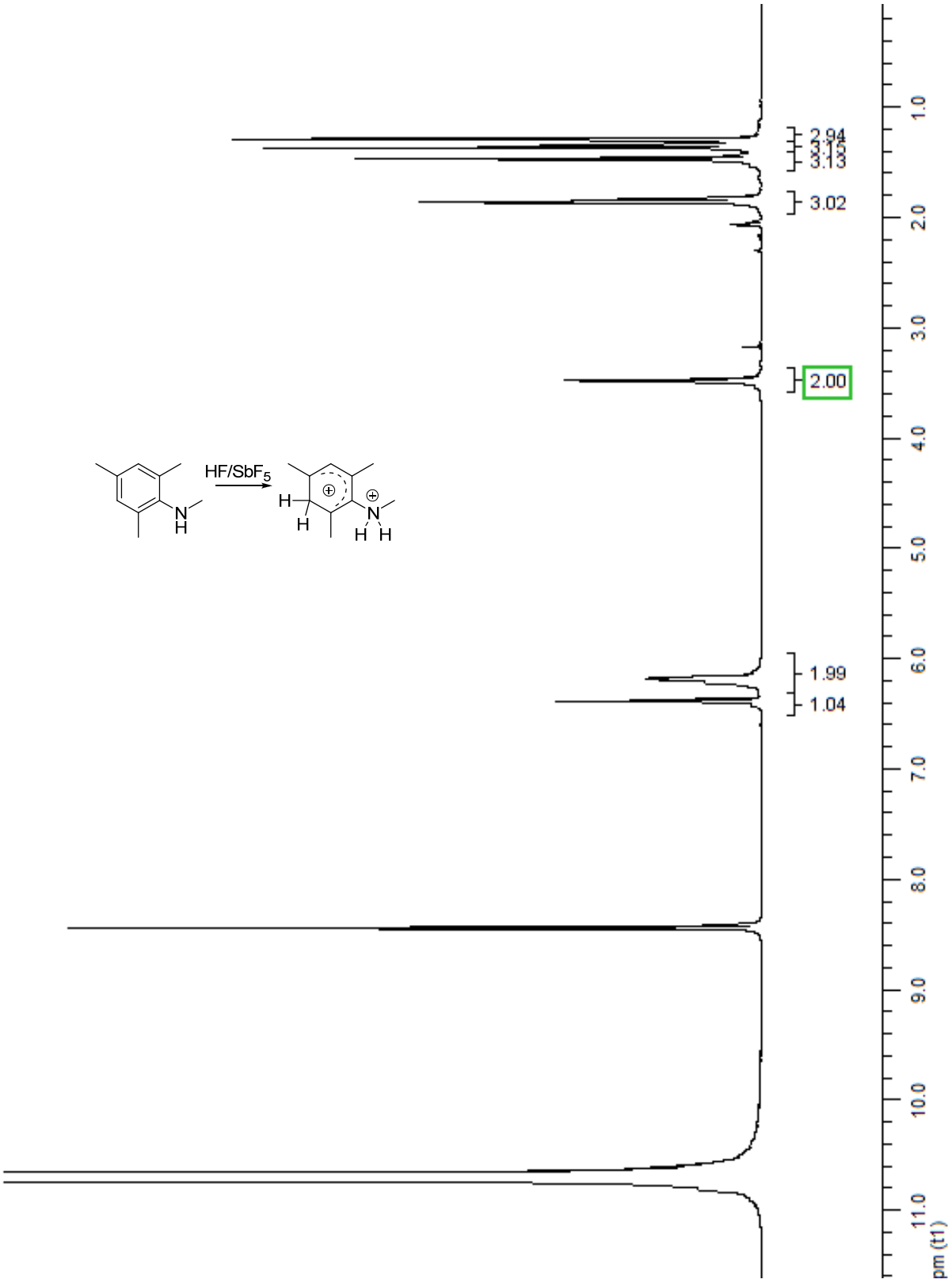
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 18.6 (CH_3), 21.3 (CH_3), 25.0 (CH_3), 37.0 (CH_3), 55.3 (CH_2, **C_6**), 134.7 (C^{IV}), 137.1 (CH), 182.9 (C^{IV}), 183.7 (C^{IV}), 206.8 (**C_5**).



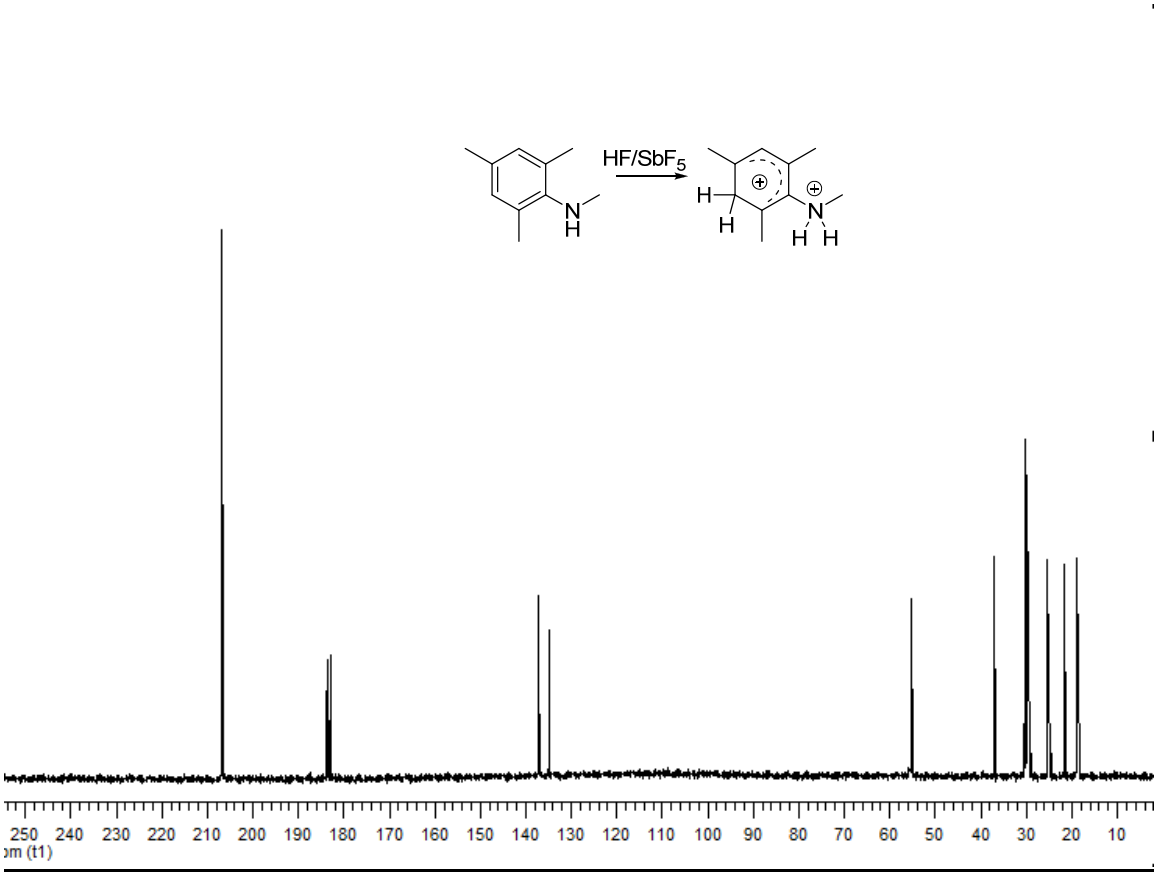
Dicationic intermediate 10:

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.94 (t, CH_3, J=5.5 Hz, **H_1**), 6.33 (m, 2H, **H_1**), 6.48 (d, 2CH, J=9.1 Hz, **H_3**, **H_7**), 7.36 (d, 2CH, J=9.1 Hz, **H_4**, **H_6**), 14.80 (broad s, 1H, **OH**).

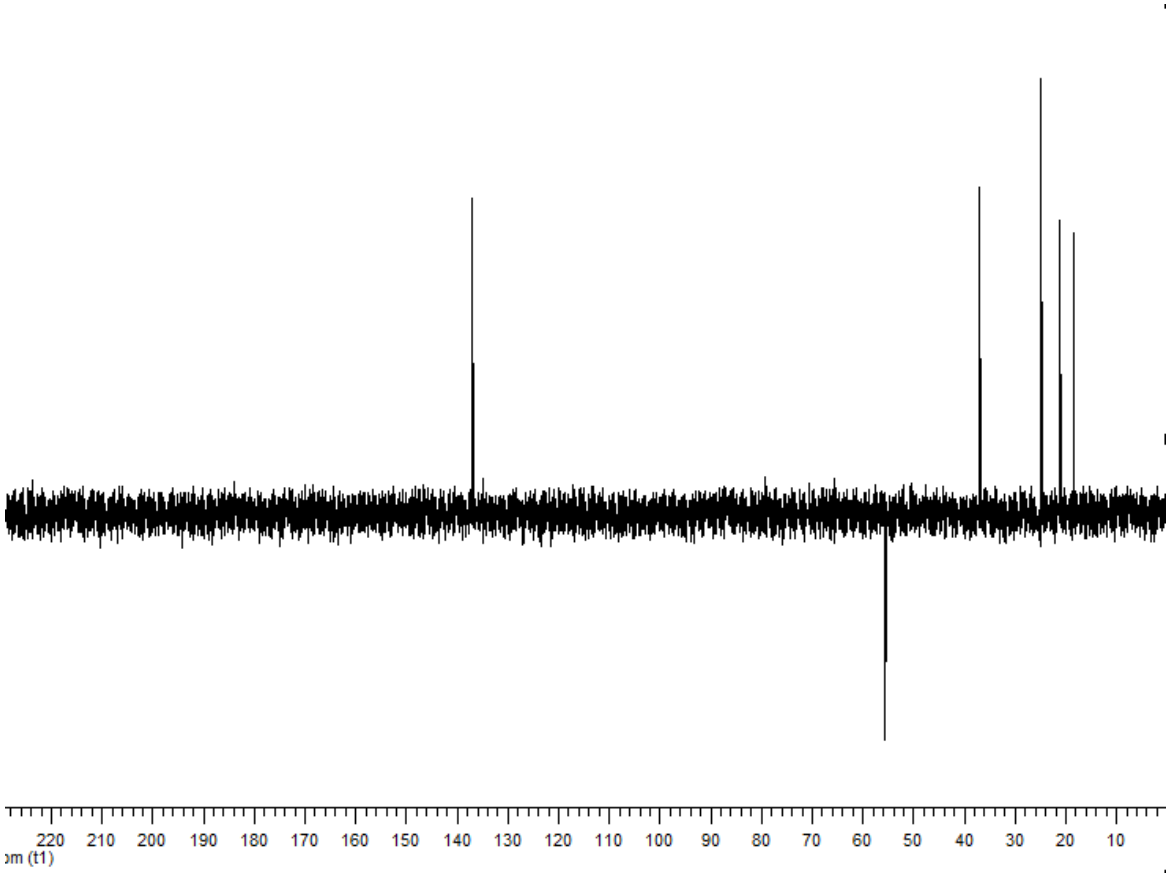
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 39.3 (CH_3, **C_1**), 125.2 (2CH, **C_3**, **C_7**), 130.1 (2CH, **C_4**, **C_6**), 142.8 (**C_5**), 146.1 (**C_2**).



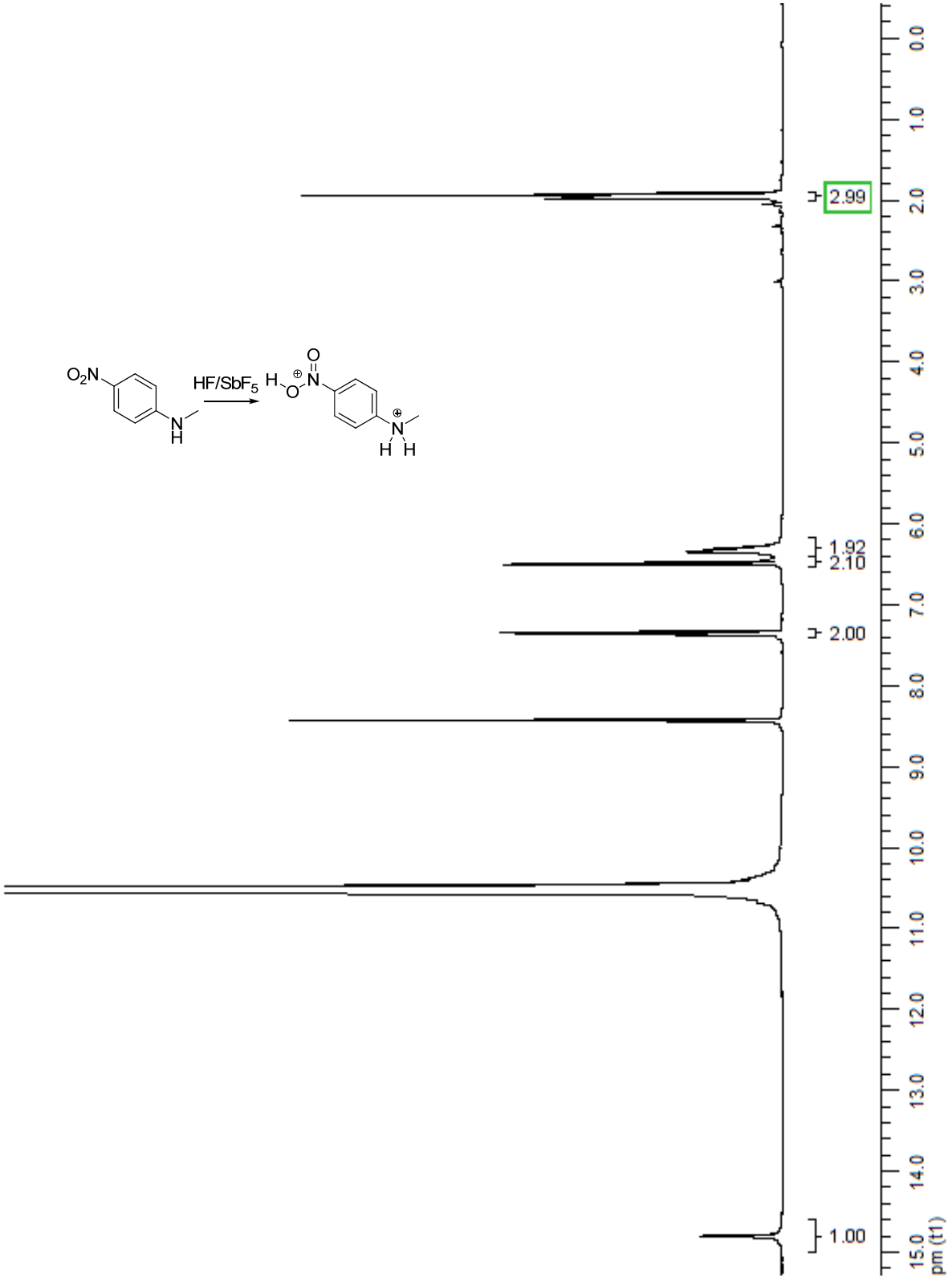
^{1}H NMR of intermediate **10**



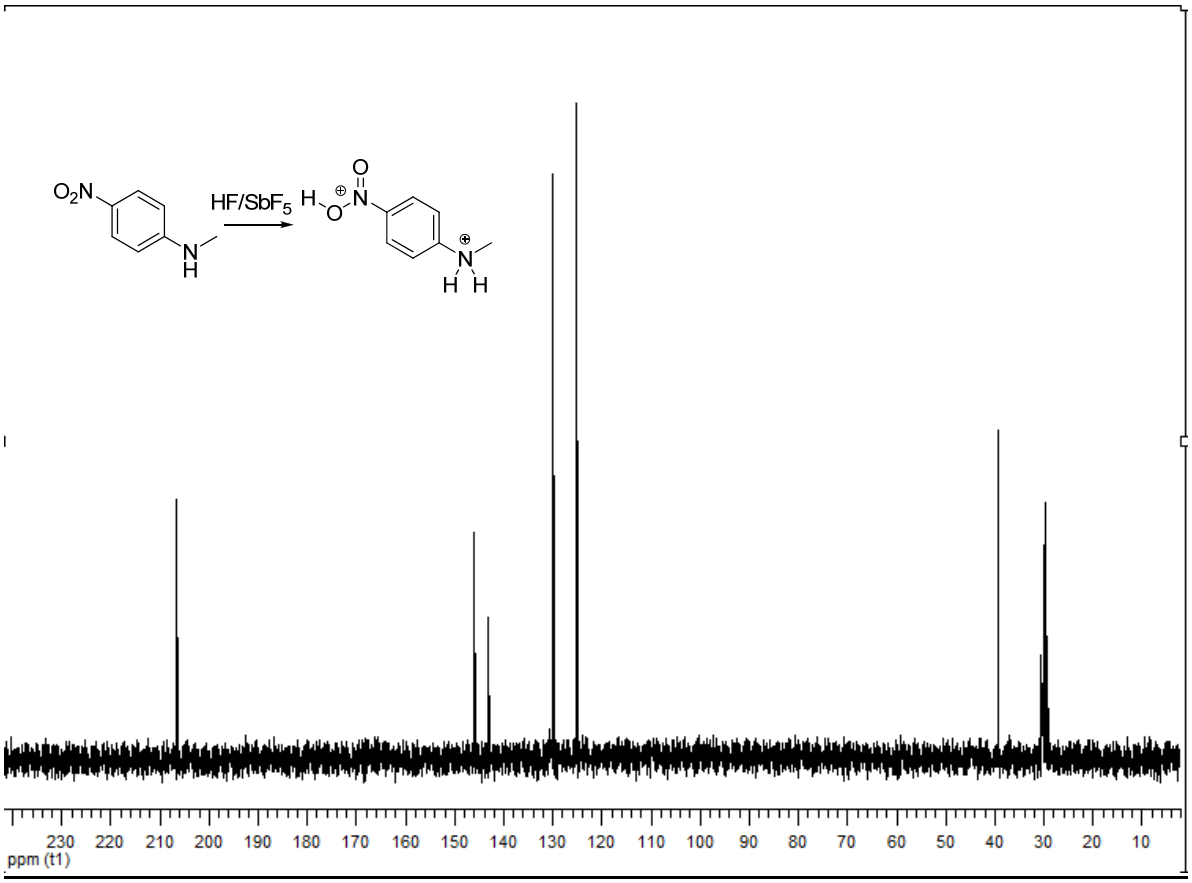
^{13}C NMR of intermediate **10**



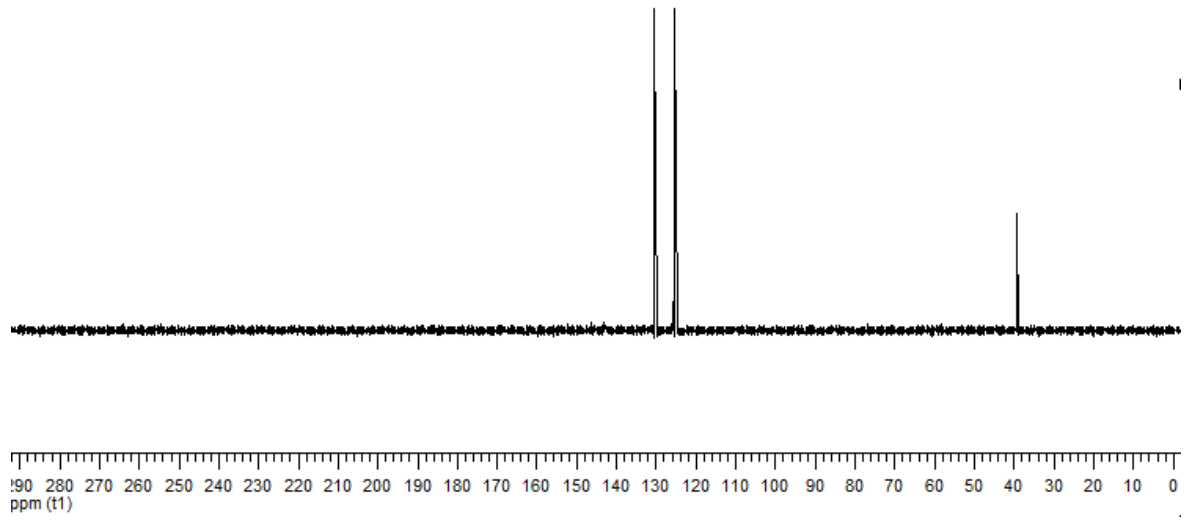
DEPT 135 of intermediate **10**



^{1}H NMR of intermediate **10**



^{13}C NMR of intermediate **10**



DEPT 135 of intermediate **10**

E. NMR CHEMICAL SHIFTS CALCULATIONS

a) Methods of calculations

All structures are studied using the B3LYP method[1] of the density functional theory. The structures are fully optimized using the correlation-consistent double zêta+polarization basis sets of Dunning[2] (B3LYP/cc-pVDZ). Chemical shifts are calculated using the GIAO method[3] (Gauge Including Atomic Orbital) with the correlation-consistent triple zêta+polarization basis sets of Dunning[2] (B3LYP/cc-pVTZ).

All calculations were performed with the Gaussian 03 package[4].

The chemical shifts were referred to TMS. Chemical shifts of carbon atoms were scaled according to:

$$\delta_{corr} = 0.9706\ \delta_{calc} - 0.89 \qquad (1)$$

This equation was deduced from a comparative study between theoretical values obtained with the method described above and known experimental values for carbocationic structures[5].

1. (a) Becke's three parameters hybrid method using the LYP correlation functional of Lee and al. (b) A. D. Becke, *J. Phys. Chem*. 1993, **98**, 5648. (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

2. T. H. Dunning, *J. Chem. Phys.*, 1989**, 90**, 1007.

3. (a) R. Ditchfield, *Mol. Phys.*, 1974**, 27**, 789. (b) K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990**, 112**, 8251.

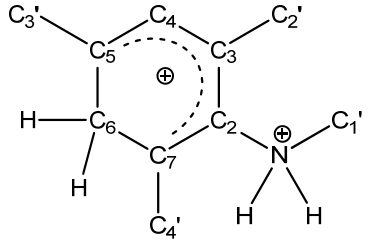
4. Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

5. V. Vrcek, O. Kronja and H. U. Siehl, *J. Chem. Soc. Perkin Trans.*, 1999, **90**, 1317.

b) Predicted Chemical Shifts for postulated intermediates 9 and 10:

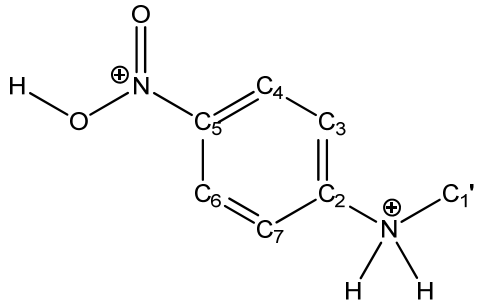
Chemical shifts in ppm were referred to TMS.

Dicationic intermediate 9:



	Chemical schifts (δ ppm)	
	Calculated	Observed
$C_{1'}$	41.6	37.0
C_2	134.3	134.7
C_3	181.3	182.9
C_4	137.4	137.1
C_5	220.5	206.8
C_6	54.5	55.3
C_7	185.9	183.7
$C_{2'}$	23.0	21.3
$C_{3'}$	31.9	25.0
$C_{4'}$	21.0	18.6

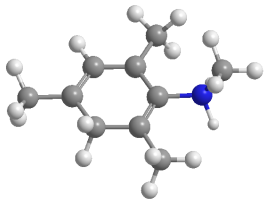
Dicationic intermediate 10:



	Chemical schifts (δ ppm)	
	Calculated	Observed
$C_{1'}$	46.3	39.3
C_2	149.8	146.1
C_3	127.1	125.2
C_4	136.2	130.1
C_5	144.1	142.8
C_6	137.1	130.1
C_7	127.6	125.2

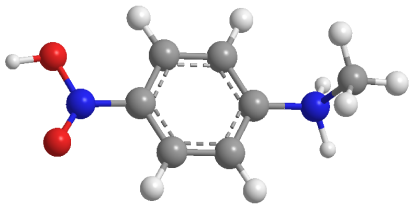
c) Cartesian coordinates (B3LYP/cc-pVDZ) for postulated intermediates 9 and 10:

Dicationic intermediate 9:



N	-2.20509500	-0.06476100	-0.39417600
C	-0.72862400	0.00103700	-0.22052000
C	-0.01242600	-1.24711900	-0.13230900
C	1.37994900	-1.23830300	0.04479700
C	2.10256800	-0.05403700	0.12044100
C	1.37187200	1.23416200	0.04083700
C	-0.10657100	1.22281100	-0.15801800
C	-3.02899500	-0.00842600	0.88544900
C	3.58001100	-0.03934000	0.25057900
C	-0.72625300	-2.55794500	-0.25822100
C	-0.77827200	2.55590000	-0.26591100
H	-2.50594500	0.70145300	-1.01371200
H	-2.44924400	-0.92540700	-0.90530800
H	1.90107200	-2.19515000	0.11077100
H	1.84692000	1.87672700	-0.73003900
H	1.59274700	1.80837500	0.96802100
H	-4.08839300	-0.09651000	0.60995400
H	-2.83513800	0.95100300	1.37880800
H	-2.72638400	-0.83963600	1.53288800
H	3.95256600	0.86041900	0.76171200
H	3.95992200	-0.94516800	0.74401700
H	4.01689900	-0.02619600	-0.77021300
H	-1.55299300	-2.65623300	0.46611400
H	-0.04494600	-3.40323800	-0.10237900
H	-1.15340800	-2.67288300	-1.27400100
H	-1.85940000	2.52221100	-0.45477100
H	-0.31250600	3.15029800	-1.07024300
H	-0.62564900	3.13082100	0.66485600

Dicationic intermediate 10:



N	-3.06961800	-0.02331600	-0.45350500
C	-1.59481400	-0.00298600	-0.31473800
C	-0.90930700	-1.22043600	-0.24751000
C	0.47699700	-1.21201300	-0.10692600
C	1.12423500	0.03351700	-0.03611100
C	0.43998800	1.25972300	-0.09921900
C	-0.94453900	1.23380900	-0.23999100
C	-3.84137000	-0.03116800	0.86515900

N	2.55641200	0.09977900	0.10184300
O	3.18047600	1.10546400	0.16851400
O	3.15032600	-1.08990100	0.15083800
H	-3.37252300	0.79040900	-1.01135400
H	-3.35069600	-0.84656000	-1.00867800
H	-1.43223200	-2.17770600	-0.30920900
H	1.03098500	-2.14928000	-0.05905600
H	0.97755700	2.20765800	-0.04453300
H	-1.49364000	2.17670500	-0.29595300
H	-4.91223600	-0.04554400	0.62308300
H	-3.57794400	0.87701200	1.42066900
H	-3.55419800	-0.93018600	1.42376800
H	4.12381400	-0.92493600	0.24409800

F. COMPUTATIONAL DATA: STRUCTURES AND ENERGIES

a) Computational details

All molecular species were optimized by DFT at the M06-2X level.[1] Correlation-consistent double zêta+polarization basis sets of Dunning[2] (M062X/cc-pVDZ) were employed. For each structure, the analytic Hessian was calculated to obtain the vibrational frequencies and to characterize the nature of stationary point (local minimum). Unscaled frequencies were used to determine the zero-point energy (ZPE) and thermodynamic corrections at 298.15 K. Unless otherwise noted, energies in the text refer to gas phase free energies. Calculations were performed using the Gaussian 09 computational program.[3]

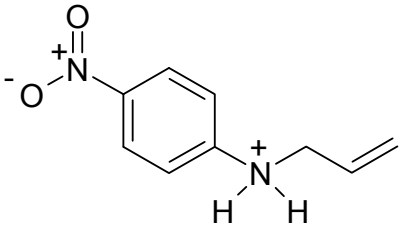
1. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120,** 215.

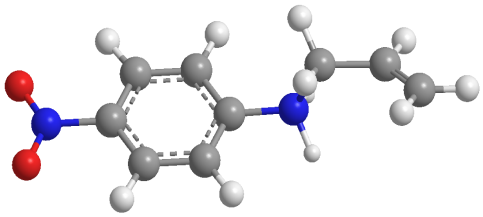
2. T. H. Dunning, *J. Chem. Phys.,* 1989, **90***,* 1007.

3. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

b) *N*-allyl-4-nitroaniline

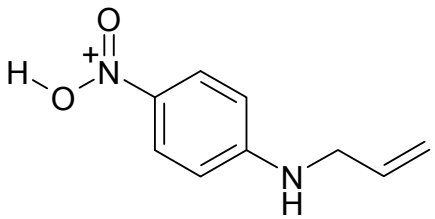
1) Calculation to evaluate the site of the first protonation:

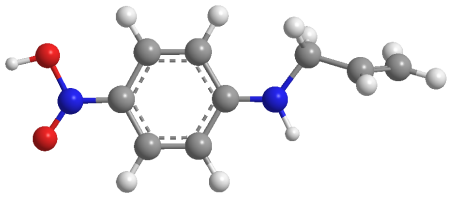




C	-2.01577400	0.02353800	0.02391200
C	-1.29774600	1.19126100	0.24285600
C	0.07036400	1.09260600	0.47908700
C	0.65308200	-0.16960400	0.48865100
C	-0.06830700	-1.33743600	0.26683500
C	-1.43678600	-1.23807000	0.03173000
N	-3.47836900	0.12920200	-0.22496300
N	2.10777100	-0.26777300	0.69693100
C	2.93118800	-0.22965900	-0.58780300
C	4.38932600	-0.30759200	-0.26637600
C	5.21146700	0.72723400	-0.44093600
O	-4.07182400	-0.90789900	-0.39656000
O	-3.94345500	1.24325900	-0.23399000
H	-1.81383900	2.15025200	0.22877000
H	0.66101400	1.99308300	0.66002600
H	0.41531300	-2.31643500	0.28177900
H	-2.05787100	-2.11592400	-0.14186800
H	2.43112400	0.49745300	1.30563300
H	2.32856100	-1.13301400	1.20955900
H	2.56875300	-1.07390300	-1.19037300
H	2.65891900	0.70936100	-1.08707200
H	4.77291500	-1.26591700	0.09766300
H	6.27610300	0.64504600	-0.21733600
H	4.85453500	1.68344700	-0.83389700

electronic energy = -608.9577039 a.u.
thermal free energies = -608.800925 a.u.



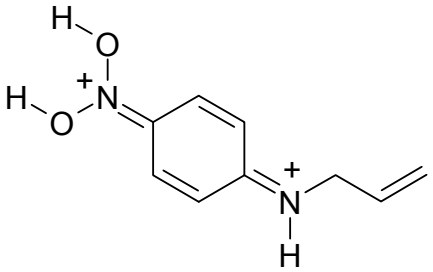


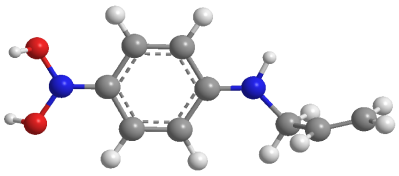
C	-2.00057000	0.04712500	0.01032700
C	-1.18971600	-1.12101700	-0.01691000
C	0.16779000	-0.99333700	-0.03544800
C	0.77465000	0.30823300	-0.02982000
C	-0.06836800	1.47307600	0.00776000
C	-1.42142200	1.34894300	0.02484300
N	-3.36153300	-0.04009500	0.02883700
N	2.09115300	0.45705500	-0.05559700
C	3.08720400	-0.62150500	-0.09330100
C	4.43924300	-0.05424300	-0.41394700
C	5.45792200	-0.08174600	0.44237000
O	-4.13786600	0.87284300	0.05466700
O	-3.85193000	-1.29504700	0.01541300

H	-1.65354400	-2.10622400	-0.01794500
H	0.79035000	-1.88539500	-0.04257700
H	0.39268000	2.46149900	0.01748800
H	-2.07151300	2.22302900	0.04834200
H	2.46263100	1.40235300	0.00193400
H	3.10337100	-1.13903500	0.87932100
H	2.78062300	-1.34217100	-0.86706800
H	4.56110100	0.38290500	-1.40991900
H	5.35610700	-0.52592900	1.43616600
H	6.43280600	0.32675200	0.17255200
H	-4.82399100	-1.17203500	0.03314500

electronic energy = -608.9664109 a.u.
thermal free energies = -608.810039 a.u.

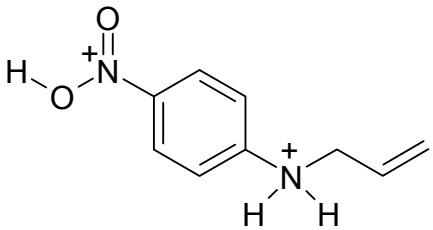
2) Calculation to evaluate the site of the second protonation:

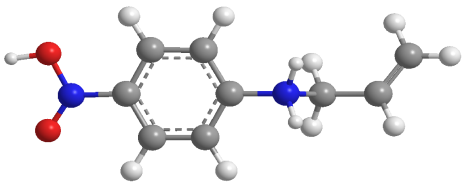




C	-1.91994900	0.01734700	0.00190800
C	-1.33249300	1.35276800	0.00091800
C	-0.00182200	1.47295200	-0.13779000
C	0.85511300	0.29113300	-0.29675700
C	0.24301600	-1.04044300	-0.28043000
C	-1.08776400	-1.17441700	-0.13994000
N	-3.21107100	-0.11651400	0.13772300
N	2.13060100	0.47063500	-0.45626400
C	3.23788800	-0.50838500	-0.56803700
C	4.11771500	-0.36814000	0.64549300
C	5.36294000	0.10320300	0.56755500
O	-3.78219400	-1.31494200	0.28681700
O	-4.03042500	0.93840900	0.13469200
H	-1.97965400	2.22300500	0.10933900
H	0.46307600	2.46205600	-0.13948400
H	0.86247100	-1.93043300	-0.38151000
H	-1.56129600	-2.15608500	-0.12362500
H	2.46408400	1.44156600	-0.42677400
H	3.78193900	-0.24496500	-1.48702500
H	2.81552300	-1.51180500	-0.68418400
H	3.69346000	-0.69808200	1.59788100
H	5.99312800	0.16046000	1.45687600
H	5.80496900	0.42267200	-0.38064100
H	-4.51395900	-1.37354000	-0.37074900
H	-4.60736100	0.86245000	0.93008000

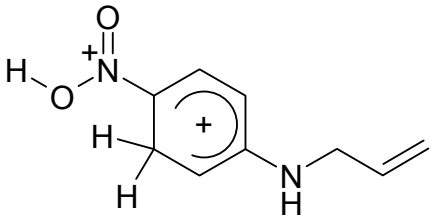
electronic energy = -609.150412 a.u.
thermal free energies = -608.983310 a.u.

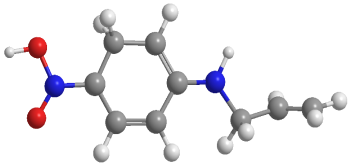




C	1.96613900	0.01276600	0.02927900
C	1.36004000	1.27244600	0.04964300
C	-0.00710800	1.32897300	0.28426400
C	-0.70646700	0.13903500	0.49135100
C	-0.09035500	-1.11139000	0.46337800
C	1.27808900	-1.18713300	0.23077700
N	3.38985100	-0.01028200	-0.21156900
N	-2.15495800	0.20471500	0.70538900
O	4.04273900	0.94464500	-0.40226900
O	3.91645500	-1.21137600	-0.20275700
C	-2.99804700	0.25423600	-0.59559800
C	-4.44750400	0.30676500	-0.24438900
C	-5.26382400	-0.72539800	-0.46667000
H	1.94021000	2.18295600	-0.10857600
H	-0.50841700	2.29863900	0.31294700
H	-0.65645900	-2.03013800	0.62926000
H	1.78603400	-2.15116900	0.21085300
H	-2.39506300	1.03012100	1.27611500
H	-2.48194500	-0.60513800	1.25467600
H	4.88606100	-1.11453600	-0.37632500
H	-2.72565800	-0.65083600	-1.15427700
H	-2.63873300	1.14359600	-1.13219700
H	-4.83335100	1.24644400	0.16280600
H	-6.32766600	-0.65964500	-0.23153100
H	-4.90859000	-1.65928000	-0.91248600

electronic energy = -609.1679007 a.u.
thermal free energies = -608.999354 a.u.

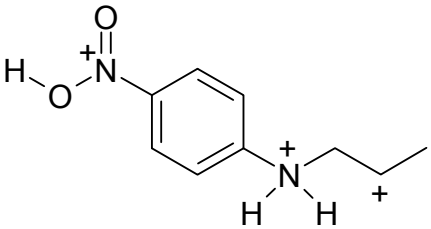


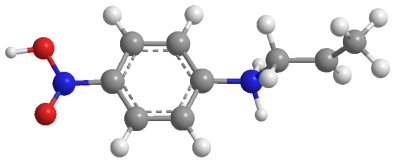


C	2.01477100	-0.06039900	-0.01272000
C	1.17719600	-1.16391700	-0.02673800
C	-0.20843600	-1.00079500	-0.05592000
C	-0.83555300	0.28762900	-0.03622200
C	0.04031100	1.41457400	-0.05948600
C	1.47993800	1.30165300	-0.04066700
N	3.40019100	-0.27152800	0.01422300
N	-2.14790500	0.46230500	-0.01611400
C	-3.15773200	-0.61222500	0.05339900
C	-4.48013100	-0.04672900	0.47720700
C	-5.54829000	-0.04817100	-0.31968900
O	4.10084600	0.85548200	0.01427000
O	3.93307200	-1.32551700	0.03701500
H	1.59798300	-2.17285500	-0.02749800
H	-0.82858500	-1.89700500	-0.10499200
H	-0.38002900	2.42696900	-0.08905700
H	1.83783300	1.92731200	0.81670100
H	1.88337100	1.91426900	-0.88464600
H	-2.52092400	1.41215600	-0.05321100
H	-3.22547900	-1.09441900	-0.93734000
H	-2.79176500	-1.35760200	0.78068500
H	-4.54110400	0.34293800	1.49770000
H	-5.51300800	-0.45808500	-1.33291000
H	-6.50415800	0.34832100	0.02621600
H	5.05606200	0.60311400	0.03632400

electronic energy = -609.084685 a.u.
thermal free energies = -608.922041 a.u.

3) Calculation to evaluate the site of the third protonation:





C	2.04989000	0.03002500	0.00672700
C	1.39286200	1.25350700	-0.12630300
C	0.03038100	1.23290400	-0.41758100
C	-0.59707900	-0.00309200	-0.55953600
C	0.06279700	-1.22152900	-0.41978600
C	1.42747200	-1.21074500	-0.12875700
N	3.48731400	0.09430800	0.28494100
N	-2.05490800	-0.02013300	-0.92145600
C	-2.98844200	-0.01002600	0.26643200
C	-4.44028800	-0.01485000	-0.02788500
C	-5.42079900	-0.00650400	0.99143500
O	4.05500500	-1.07438200	0.38707500
O	4.07606800	1.09650100	0.40274700
H	1.92473000	2.20209700	-0.02186100
H	-0.49623600	2.18153500	-0.55001000
H	-0.43944500	-2.18297600	-0.55369200
H	1.97594600	-2.14870000	-0.02844800
H	-2.24031800	0.79257500	-1.53591600
H	-2.22860900	-0.85221600	-1.51283200
H	-2.75608400	-0.88326100	0.90950000
H	-2.75958000	0.87704900	0.89168000
H	-4.79277600	-0.02446700	-1.07409600
H	-6.14718300	-0.83514500	0.75617100
H	-5.09497700	0.00244500	2.03673800
H	-6.14522400	0.82000400	0.74198000
H	5.02356400	-0.94325000	0.56933000

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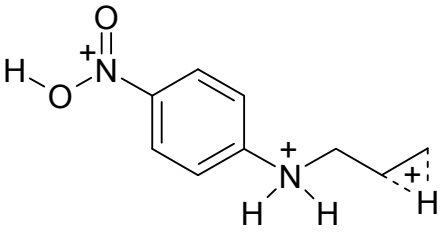
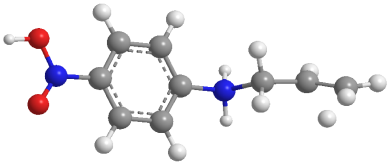
thermal free energies = -609.033146 a.u.

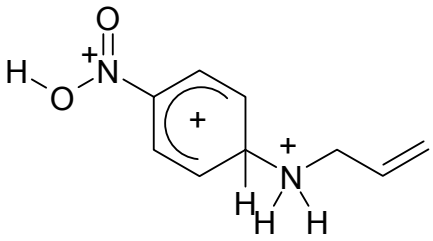


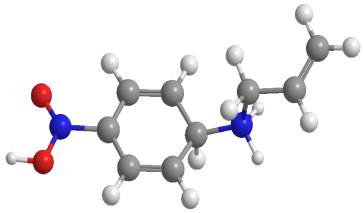


C	2.04695000	0.03581200	0.00035800
C	1.38699200	1.25191200	-0.17751600
C	0.02068800	1.21749700	-0.44835700
C	-0.60839700	-0.02296200	-0.52651500
C	0.05560600	-1.23354200	-0.34189600
C	1.42368600	-1.20996900	-0.07106400
N	3.48677300	0.11199400	0.25686600
N	-2.07002600	-0.05773000	-0.86159000
C	-2.97773600	-0.05212700	0.35129000
C	-4.45013100	-0.23300900	0.03972100
C	-5.45897800	0.16085400	0.91363200
O	4.05719800	-1.05161300	0.39796300

O	4.07717300	1.11783900	0.32764800
H	1.91992100	2.20389900	-0.12110200
H	-0.50971000	2.15858700	-0.61369000
H	-0.44881100	-2.19959000	-0.42498400
H	1.97410600	-2.14229700	0.06402200
H	-2.27578000	0.74574700	-1.47989200
H	-2.24412900	-0.89696700	-1.44207100
H	-2.68356200	-0.91601000	0.97251300
H	-2.76968000	0.86174700	0.92614700
H	-5.11393000	0.90066500	-0.13561800
H	-4.75376700	-0.83317400	-0.83209800
H	-5.24539500	0.74883200	1.81716400
H	-6.50110600	-0.11591300	0.69795200
H	5.02756900	-0.91197500	0.56191000

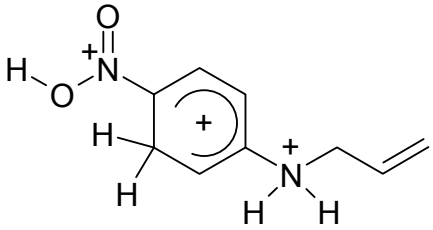
electronic energy = -609.2086191 a.u.
thermal free energies = -609.031475 a.u.

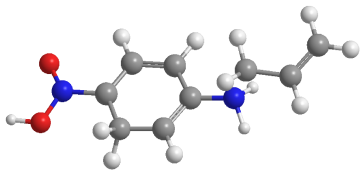




C	1.88831200	0.03744600	0.06141100
C	1.22137500	1.22657300	0.39026800
C	-0.10462000	1.12774200	0.76863800
C	-0.72770200	-0.19556400	0.94252400
C	0.01276300	-1.36933500	0.45056500
C	1.34078600	-1.25207100	0.07427900
N	3.32398100	0.20594000	-0.35359200
N	-2.21128000	-0.25721000	0.83351400
C	-2.77918000	-0.10963600	-0.63190100
C	-4.24419200	-0.33308000	-0.60357100
C	-5.12022900	0.67322800	-0.78709100
O	3.90653300	-0.91470500	-0.63488800
O	3.83471300	1.25091900	-0.41073200
H	1.71687500	2.20127800	0.33014000
H	-0.65959200	2.03330600	1.04448900
H	-0.47268000	-0.32458800	2.05479000
H	-0.45298500	-2.36281100	0.48595600
H	1.91633800	-2.13439300	-0.21869900
H	-2.66062400	0.46841700	1.42156500
H	-2.56412200	-1.15164100	1.21977900
H	-2.49893300	0.90545700	-0.94876800
H	-2.22570800	-0.86928700	-1.20833800
H	-4.59976300	-1.36371000	-0.50199200
H	-4.80135100	1.70805300	-0.94945600
H	-6.19561100	0.47678400	-0.80840200
H	4.85540400	-0.74950900	-0.90628700

electronic energy = -609.1236311 a.u.
thermal free energies = -608.947936 a.u.

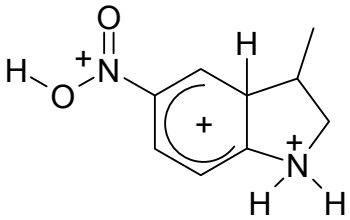


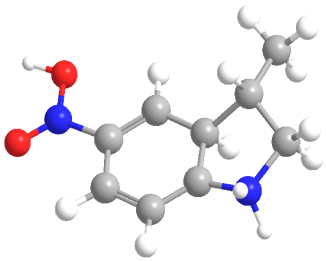


C	-2.00502000	-0.08643600	0.02990000
C	-1.27086800	-1.21337800	0.22153300
C	0.13874300	-1.06083800	0.44166000
C	0.76825500	0.19042100	0.46215000
C	0.00290400	1.33276700	0.24736400
C	-1.43884500	1.26623900	0.02715400
N	-3.46230500	-0.26315600	-0.17894500
N	2.20910900	0.27957200	0.65411900
C	3.11261000	0.11884600	-0.67360700
C	4.53285000	0.31549600	-0.29945800
C	5.39992200	-0.70584900	-0.28185600
O	-4.08649800	0.87063900	-0.29541700
O	-3.97510900	-1.30752700	-0.23111700
H	-1.71281600	-2.21635500	0.22386300
H	0.71920600	-1.97776600	0.60992900
H	0.45445700	2.33442100	0.24643500
H	-1.68311800	1.83378200	-0.90884500
H	-1.93740100	1.93868900	0.77494300
H	2.54908600	-0.43173800	1.32532400
H	2.47305700	1.18353300	1.08315600
H	2.88420000	-0.89334600	-1.03661200
H	2.70667800	0.88287400	-1.35205700
H	4.87258000	1.34039700	-0.11927900
H	5.10354600	-1.73343600	-0.51553100
H	6.45673300	-0.53427500	-0.06217700
H	-5.06428600	0.70979000	-0.43213000

electronic energy = -609.1418241 a.u.
thermal free energies = -608.967351 a.u.

4) Wheland intermediates E and E'

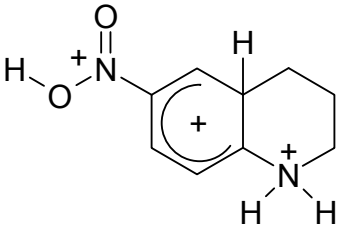
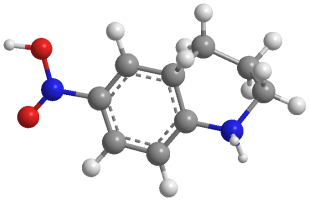




C	1.48634000	-0.15065200	0.04354200
C	0.47504300	0.77135600	0.21402100
C	-0.88948900	0.27303400	0.33819300
C	-1.07089600	-1.16323400	0.15316000
C	-0.05693500	-2.06676300	-0.02034100
C	1.25613000	-1.54124900	-0.05190300
N	2.89908400	0.28484600	-0.03894600
N	-2.50250200	-1.45784500	0.01625200
O	3.78148200	-0.46414200	-0.17285400
C	-2.15407500	0.91066800	-0.43687900
C	-3.22755900	-0.09720000	-0.00605600
C	-2.47252300	2.34666000	-0.06540000
O	3.04165700	1.57114400	0.05326400
H	0.66845900	1.84540500	0.32556700

H	-1.15620700	0.54339100	1.40040800
H	-0.21169600	-3.14043300	-0.16776800
H	2.10297800	-2.22880800	-0.18395400
H	-2.67390300	-1.98678000	-0.86218100
H	-2.85416800	-2.07898800	0.77414500
H	-1.94346300	0.81718200	-1.51388500
H	-4.08158700	-0.16439300	-0.69231300
H	-3.58679600	0.09026000	1.01603300
H	-1.67494100	3.03160300	-0.38374000
H	-3.37848900	2.65546300	-0.61056600
H	-2.65850700	2.46752500	1.01195300
H	4.01092500	1.80783300	-0.00814800

electronic energy = -609.1751448 a.u.
thermal free energies = -608.994135 a.u.

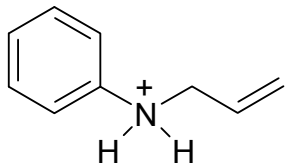
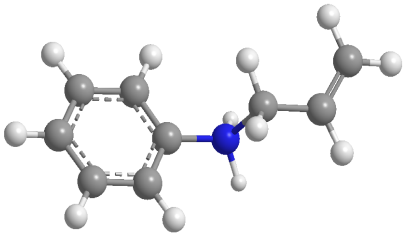



C	-1.51529200	0.14534000	-0.05915300
C	-0.66304600	-0.83497500	-0.52035800
C	0.75999700	-0.55364500	-0.58241500
C	1.16229900	0.81312800	-0.28430600
C	0.29618900	1.76857800	0.19318100
C	-1.06907500	1.43219300	0.30022400
N	-2.96756000	-0.10512000	0.05008400
N	2.59040100	1.09670900	-0.43955400
O	-3.72010100	0.70299700	0.42276200
C	1.53614000	-1.55845100	0.54972400
C	3.49920600	-0.14467200	-0.24798300
C	2.91359000	-0.97915400	0.87257300
O	-3.30694300	-1.30453700	-0.31184200
H	-1.02079400	-1.82844400	-0.81735400
H	1.20443900	-0.95405600	-1.51300400
H	0.61610200	2.77750400	0.47207300
H	-1.78137500	2.18458200	0.66365200
H	2.76394600	1.49704700	-1.38575400
H	2.87770000	1.84439000	0.21928500
H	0.89213700	-1.61424600	1.43546500
H	1.56661200	-2.52964100	0.03847500
H	3.53681500	-0.66150800	-1.21711200
H	4.49936700	0.24922600	-0.02296900
H	2.87680500	-0.38939500	1.80156600
H	3.60106100	-1.82100300	1.06296100
H	-4.29639000	-1.41330700	-0.22727600

electronic energy = -609.1845476 a.u.
thermal free energies = -609.001149 a.u.

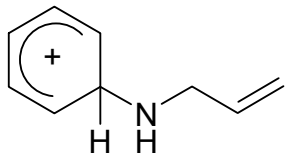
c) *N*-allylaniline

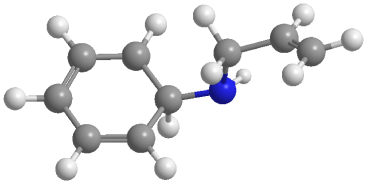
1) Calculation to evaluate the site of the first protonation:

C	3.19934400	0.19463400	-0.31796900
C	2.63784400	-1.07870800	-0.22560300
C	1.29497700	-1.22797600	0.11492300
C	0.54773500	-0.08266100	0.35979900
C	1.08183900	1.19681300	0.27202400
C	2.42633700	1.32837100	-0.06984100
N	-0.88357500	-0.22860900	0.68261600
C	-1.80182200	-0.26854600	-0.53096700
C	-3.22675000	-0.40567200	-0.09753800
C	-4.11088100	0.58287300	-0.22983200
H	4.25113900	0.30397300	-0.58222800
H	3.24542500	-1.96300900	-0.41634700
H	0.84975800	-2.22234600	0.19392900
H	0.47125900	2.08003600	0.47306900
H	2.86856900	2.32186800	-0.13909200
H	-1.18863700	0.54477100	1.28972300
H	-1.02737000	-1.08267500	1.23902400
H	-1.44591600	-1.11231800	-1.13783600
H	-1.61430100	0.66568000	-1.07578500
H	-3.53369300	-1.37055600	0.31906100
H	-5.14921300	0.45576600	0.07990800
H	-3.83372400	1.54430500	-0.67171500

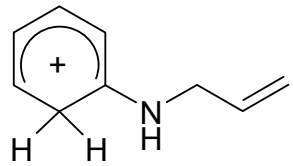
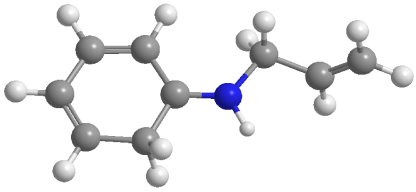
electronic energy = -404.5197061 a.u.
thermal free energies = -404.361948 a.u.





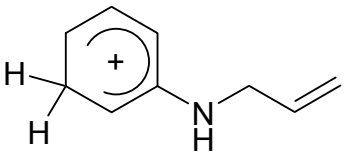
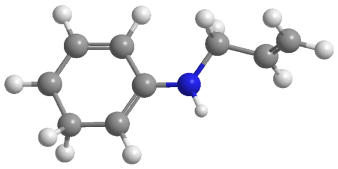
N	0.91689000	-0.18638800	0.89593000
C	-0.50540400	-0.14920200	0.73398200
C	-1.23861900	-1.27506700	0.12125600
C	1.62774000	-0.14558800	-0.39981100
C	3.09443400	-0.37970500	-0.20442500
C	4.02785300	0.53411100	-0.45916200
C	-2.46495300	-1.08697800	-0.46452700
C	-2.97070600	0.22348100	-0.59069200
C	-2.28114100	1.35553000	-0.12164700
C	-1.05679600	1.18827400	0.48063600
H	1.20079100	-1.00931900	1.42817200
H	-0.97574600	-0.23688300	1.77271500
H	-0.80826000	-2.27573900	0.22256100
H	1.46613400	0.84854700	-0.84584600
H	1.21681100	-0.89975300	-1.10341500
H	3.38744900	-1.37201200	0.15662600
H	5.08703100	0.31680000	-0.31592700
H	3.76508800	1.52869300	-0.82903900
H	-3.03352000	-1.92921100	-0.85889400
H	-3.93975200	0.36439300	-1.07638000
H	-2.70719300	2.34932700	-0.25558600
H	-0.47151400	2.03073700	0.85982700

electronic energy = -404.4341927 a.u.
thermal free energies = -404.281130 a.u.

N	0.85759900	-0.40894200	-0.06144000
C	-0.43142000	-0.17509400	-0.01747800
C	-0.95837100	1.15308500	-0.00552400
C	1.93248300	0.60279500	-0.10220600
C	3.23720400	-0.05810900	-0.43784200
C	4.24714600	-0.13907200	0.42589000
C	-2.31067400	1.33398000	0.02474600
C	-3.26439400	0.24733800	0.04762800
C	-2.82144000	-1.02181200	0.05120600
C	-1.36629000	-1.34701800	0.02629900
H	1.17265900	-1.37841200	-0.03227800
H	-0.28899900	2.01074500	-0.01058000
H	1.98502200	1.10198200	0.87741400
H	1.66247100	1.34798400	-0.86495800
H	3.33431700	-0.46687300	-1.44834600
H	5.18933200	-0.61373300	0.14833700
H	4.17266600	0.27952400	1.43322000
H	-2.69481800	2.35637500	0.03537900
H	-4.32881300	0.47597700	0.06681400
H	-3.51355300	-1.86497000	0.07576000
H	-1.12186400	-1.96135200	0.91233500
H	-1.15708000	-2.00121800	-0.83933500

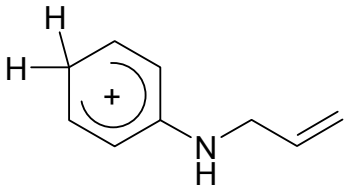
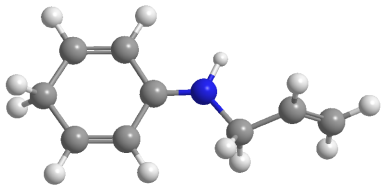
electronic energy = -404.5011433 a.u.
thermal free energies = -404.345664 a.u.

C	-3.24102500	0.36593500	0.07278400
C	-2.30959800	1.37070000	0.01340900
C	-0.94004900	1.05997100	-0.03213900
C	-0.41801100	-0.26917000	-0.04800900
C	-1.36160700	-1.29101000	0.03334200
C	-2.79394300	-1.02117700	0.08994500
N	0.91165600	-0.50722800	-0.14159700
C	1.93594100	0.53479300	-0.12574300
C	3.28044700	-0.07157000	-0.40411600
C	4.28686300	-0.04128400	0.46620200
H	-4.31049600	0.57833000	0.11239400
H	-2.61144800	2.41769700	0.01097100
H	-0.23420800	1.89304800	-0.05366500
H	-1.03761500	-2.33485800	0.04907600
H	-3.29844800	-1.57242100	-0.73738600
H	-3.24297000	-1.54440700	0.96422300
H	1.23300500	-1.45325500	0.03192200
H	1.94999600	1.06175200	0.84513100
H	1.69607600	1.27096900	-0.91179600
H	3.40424000	-0.54356200	-1.38378700
H	5.25624000	-0.47953900	0.22492900

H	4.17993700	0.43371200	1.44511900

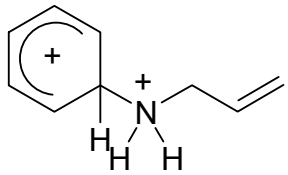
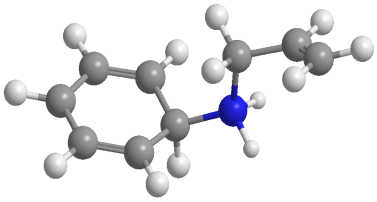
electronic energy = -404.4587295 a.u.
thermal free energies = -404.306069 a.u.

N	-0.87632500	0.41107800	-0.04204300
C	0.41762300	0.20246100	-0.01214300
C	0.96515600	-1.13904800	-0.00677100
C	-1.94532200	-0.60568200	-0.07829200
C	-3.24684600	0.04598300	-0.44467000
C	-4.26806100	0.14318700	0.40391300
C	2.30160900	-1.31265300	0.01949100
C	3.26443900	-0.18634400	0.04240900
C	2.64442500	1.16090900	0.04516100
C	1.31221600	1.34405700	0.02166600
H	-1.19847900	1.37809200	-0.00657900
H	0.29444700	-1.99627000	-0.01079500
H	-2.01188600	-1.08524300	0.91024000
H	-1.66496500	-1.36471900	-0.82286500
H	-3.32942000	0.43613600	-1.46374700
H	-5.20641300	0.61222700	0.10456400
H	-4.20681500	-0.25498200	1.42035400
H	2.70894700	-2.32617300	0.02798400
H	3.95714000	-0.27610700	-0.81629000
H	3.93356300	-0.29096000	0.91778700
H	3.30821300	2.02755000	0.06605900
H	0.87850800	2.34568500	0.02300700

electronic energy = -404.5079387 a.u.
thermal free energies = -404.352371 a.u.

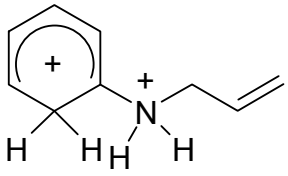
2) Calculation to evaluate the site of the second protonation:

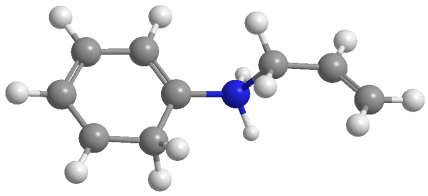



C	-2.94170800	0.24846000	-0.64431500
C	-2.24687300	1.38382700	-0.15436700
C	-1.05828300	1.21125100	0.49509700
C	-0.58180800	-0.15518500	0.82001600
C	-1.27929900	-1.28649800	0.16204700
C	-2.46414700	-1.07686500	-0.48406400
N	0.90359900	-0.29565100	0.86506300
C	1.61205300	-0.17551400	-0.50147900
C	3.07509200	-0.40318900	-0.32016600
C	3.96477200	0.58707900	-0.43039300
H	-3.88242100	0.40393500	-1.18357100
H	-2.65071000	2.38357000	-0.32273100
H	-0.49765600	2.07268600	0.87565800
H	-0.95827700	-0.26217900	1.87684100
H	-0.88382100	-2.30034700	0.29116200
H	-3.02806200	-1.91332800	-0.90075500

H	1.31929100	0.40645000	1.49973400
H	1.16055300	-1.20506800	1.28392900
H	1.38382400	0.83488000	-0.86904300
H	1.12851600	-0.92793800	-1.14314500
H	3.40404800	-1.43144300	-0.13899200
H	3.66730200	1.61473700	-0.66003500
H	5.03342500	0.39340800	-0.31875100

electronic energy = -404.6480132 a.u.
thermal free energies = -404.480076 a.u.





C	-3.25077100	0.13989600	-0.33907800
C	-2.51023900	1.27695000	-0.10793700
C	-1.09148100	1.21614700	0.27309700
C	-0.50858200	-0.13459200	0.36618100
C	-1.24327100	-1.25324900	0.13585400
C	-2.62124600	-1.10575400	-0.21294300
N	0.91222500	-0.24578900	0.67935300
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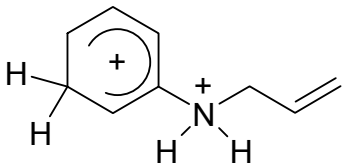

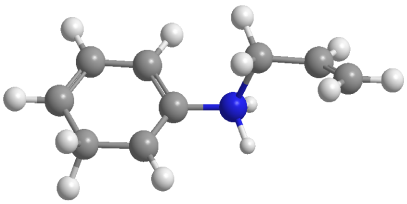

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C	4.18899600	0.53099400	-0.32416800
H	-4.28393300	-0.03490200	-0.59355700
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H	-2.72338000	1.90043200	-1.00499900
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H	-0.64662200	-2.14303200	0.26523400
H	-3.03048600	-2.19367700	-0.34197000
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H	1.71628900	0.45057500	-1.22786500
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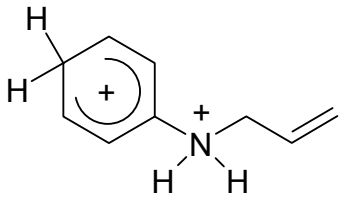

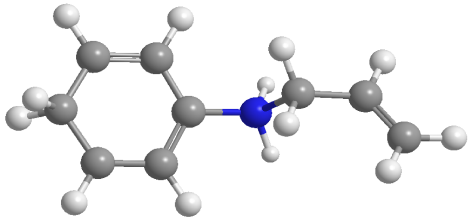

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N	0.91326700	-0.20536000	0.70609300
C	1.85749600	-0.28788100	-0.55797400
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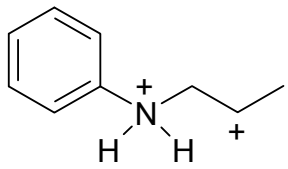

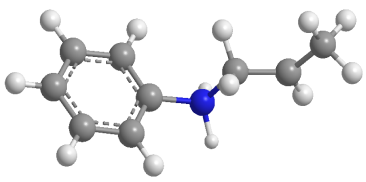

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N	0.73973700	-0.00026300	0.97795000
C	1.73014100	0.00007700	-0.14034000
C	3.15609200	-0.00057700	0.19652100
C	4.17921600	0.00033100	-0.79454600
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H	-3.08448100	-2.15746900	-0.47605000
H	-0.77852000	-2.17643100	0.44125300
H	-0.77837800	2.17620700	0.44214900
H	-3.08433000	2.15777400	-0.47519300
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H	0.86200600	-0.82600400	1.58641900
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H	3.86430200	0.00083200	-1.84299000
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electronic energy = -404.6502857 a.u.
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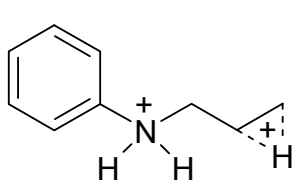

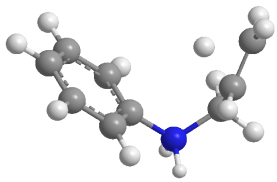

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C	2.06915900	0.16796000	1.27891200
N	-0.89570300	-1.50396500	-0.28672300
C	-2.10306500	-0.77339500	0.22337600
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C	-2.66129300	1.70488700	0.34019800
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H	0.44416100	-1.04952500	2.02264300
H	2.52006700	0.28817800	2.26429100
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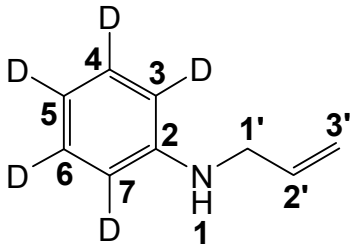
H	-1.99831500	0.74093400	-1.44224900
H	-1.38908700	1.49875400	0.23999900
H	-2.90115200	1.63102100	1.40819900
H	-2.83052500	2.65674300	-0.17738000

electronic energy = -404.6537165 a.u.
thermal free energies = -404.486737 a.u.

G. REACTIONS WITH LABELED SUBSTRATES



Compound 1'b: *N*-allyl-3.4.5.6,7-pentadeuteriolaniline

To a mixture of 982 mg of 2.3.4.5.6-pentadeuterioaniline and 1.727 g of potassium carbonate (4.22 mmol) dissolved in 20 mL of DMF, were added dropwise 0.87 mL of allyl bromide (10 mmol). The reaction mixture was magnetically stirred at room temperature during 6 hours, then hydrolyzed with 20 mL of water and extracted with a mixture ethyl acetate/toluene: 2/1 (3 × 40 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. The reaction crude mixture was purified by column chromatography over silica using the eluent petroleum ether/ethyl acetate: 98/2, and gave **1'b** (555 mg, 41%).

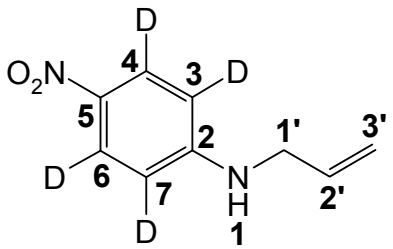
Aspect: orange oil

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 3.79 (d, CH_2, J=5.4 Hz, **$H_{1'}$**), 3.79 (broad s, NH, **H_1**), 5.18 (dd, 1H, J=10.3 Hz, J=1.4 Hz, **$H_{3'}$**), 5.30 (dd, 1H, J=17.2 Hz, J=1.5 Hz, **$H_{3'}$**), 5.98 (ddd, CH, J=17.5 Hz, J=10.3 Hz, J=5.4 Hz, **$H_{2'}$**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 46.6 (CH_2, **$C_{1'}$**), 112.7 (t, 2CD, J= 24 Hz, **C_3**, **C_7**), 116.2 (CH_2, **$C_{3'}$**), 117.1 (t, CD, J=25 Hz, **C_5**), 128.8 (t, 2CD, J=24 Hz, **C_4**, **C_6**), 135.6 (CH, **$C_{2'}$**), 148.1 (**C_2**).

MS (IES+, ACN): m/z 139.15 $[M+H]^+$.

HRMS (ESI, CH_3OH): Calc for $C_9H_6ND_5$ $[M+H]^+$: 139.12836, found 139.1284 .



Compound 1'h: *N*-allyl-2.3.5.6-tetradeuterio-4-nitroaniline

To a mixture of 583 mg of potassium carbonate (4.22 mmol) and 300 mg of 4-nitro-2.3.5.6-tetradeuterio-aniline (2.11 mmol) disolved in 10 mL of DMF, were added dropwise 184 µL of allyl bromide (2.13 mmol). The reaction mixture was magnetically stirred and heat at 80°C during 4 days, then hydrolyzed with 20 mL of water and finally extracted with a mixture ethyl acetate/toluene: 2/1 (3 × 25 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. The reaction crude mixture was purified by column chromatography over silica using the eluent petroleum ether/ethyl acetate: 94/4, to give compound **1'h** (51 mg, 13%).

Aspect: yellow solid.

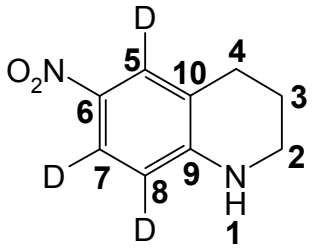
Mp: 66-68°C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 3.87 (dt, CH_2, J=5.2 Hz, J=1.6 Hz, **$H_{1'}$**), 4.80 (broad s, NH, **H_1**), 5.22 (ddd, 1H, J=10.3 Hz, J=2.8 Hz, J=1.4 Hz, **$H_{3'}$**), 5.28 (ddd, 2H, J=17.2 Hz, J=3.0 Hz, J=1.7 Hz, **$H_{3'}$**), 5.90 (ddt, CH, J=17.1 Hz, J=10.4 Hz, J=5.2 Hz, **$H_{2'}$**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 45.9 (CH_2, **$C_{1'}$**), 111.0 (t, 2CD, J=25 Hz, **C_3**, **C_7**), 117.4 (CH_2, **$C_{3'}$**), 126.1 (t, 2CD, J=25 Hz, **C_4**, **C_6**), 133.5 (CH, **$C_{2'}$**), 138.0 (**C_5**), 153.2 (**C_2**).

MS (IES+, ACN): m/z 183 $[M+H]^+$, 205 $[M+Na]^+$.

HRMS (ESI, CH_3OH): Calc for $C_9H_6N_2O_2D_4$ $[M+Na]^+$: 205.08910, found 205.0890.



Compound 5'h: 5,7,8-trideuterio-6-nitro-1.2.3.4-tetrahydroquinoline

1 mL of a mixture of HF/SbF_5 (1 mL, SbF_5 mol % = 21.6) was added into a reactor containing 43 mg of **1'h** at 0°C. The mixture was magnetically stirred at the same temperature during 24 hours, then neutralized with water-ice-Na_2CO_3 and extracted with ethyl acetate (× 3). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. The reaction crude was purified on preparative TLC plates using the eluent petroleum ether/dichloromethane: 85/15, thereby obtaining compound **5'h** (11 mg).

Aspect: yellow solid.

Mp: 153-155°C

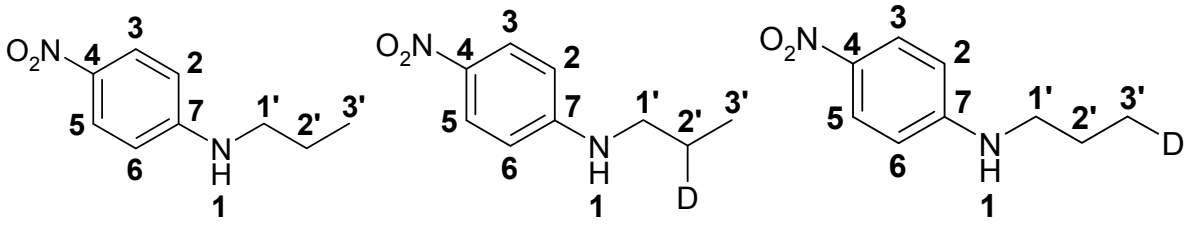
^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 1.91 (m, CH_2, **H_3**), 2.80 (t, CH_2, J=6.3 Hz, **H_4**), 3.41 (m, CH_2, **H_2**), 6.53 (broad s, NH, **H_1**).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 21.4 (CH_2, **C_3**), 27.5 (CH_2, **C_4**), 42.0 (CH_2, **C_2**), 112.5 (t, CD, J=25 Hz, **C_8**), 120.3 (**C_{10}**), 124.4 (t, CD, J=25 Hz, **C_7**), 125.9 (t, CD, J=24 Hz, **C_5**), 137.0 (**C6**), 152.3 (**C_9**).

MS (IES+, ACN): m/z 182 $[M+H]^+$, 204 $[M+Na]^+$.

HRMS (ESI, CH_3OH): Calc for $C_9H_7N_2O_2D_3$ $[M+Na]^+$: 204.08283, found 204.0826.

Reaction with substrate 1h in the presence of C_6D_{12}:



Compound 11: **4-nitro-*N*-propylaniline**

Compound 12: ***N*-(2-deuteropropyl)-4-nitroaniline**

Compound 13: ***N*-(3-deuteropropyl)-4-nitroaniline**

To a mixture of HF/SbF_5 (8 mL, SbF_5 mol % = 21.6) maintained at 0 °C, was added 4 mL (37 mmol) of perdeuterated cyclohexane following by 356 mg (2 mmol) of *N*-allyl-4-nitroaniline **1h**. The mixture was magnetically stirred at the same temperature during 10 minutes, then neutralized with water-ice-Na_2CO_3 and extracted with ethyl acetate (× 3). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. 23 mg of the mixture of **11**, **12** and **13** was isolated by column chromatography over silica gel with the eluant petroleum ether/ethyl acetate: 93/7.

Aspect: yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 1.01 (t, J=7.4 Hz, **$H_{3'}$**), 1.68 (m, **$H_{2'}$**), 3.18 (t, J=7.1 Hz, **$H_{1'}$**), 6.53 (d, 2CH, J=9.2 Hz, **H_2**, **H_6**), 8.07 (d, 2CH, J=9.2 Hz, **H_3**, **H_5**).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 11.2 (t, CH_2D, J=19 Hz, **$C_{3'}$(13)**), 11.5 (CH_3, **$C_{3'}$(11 or 12)**), 11.6 (CH_3, **$C_{3'}$(11 or 12)**), 22.1 (t, CHD, J=19 Hz, **$C_{2'}$(12)**), 22.4 (CH_2, **$C_{2'}$(13)**), 22.4 (CH_2, **$C_{2'}$(11)**), 45.3 (CH_2), 45.4 (CH_2), 111.2 (2CH, **C_2**, **C_6**), 126.6 (2CH, **C_3**, **C_5**), 138.0 (**C_4**), 153.4 (**C_7**).

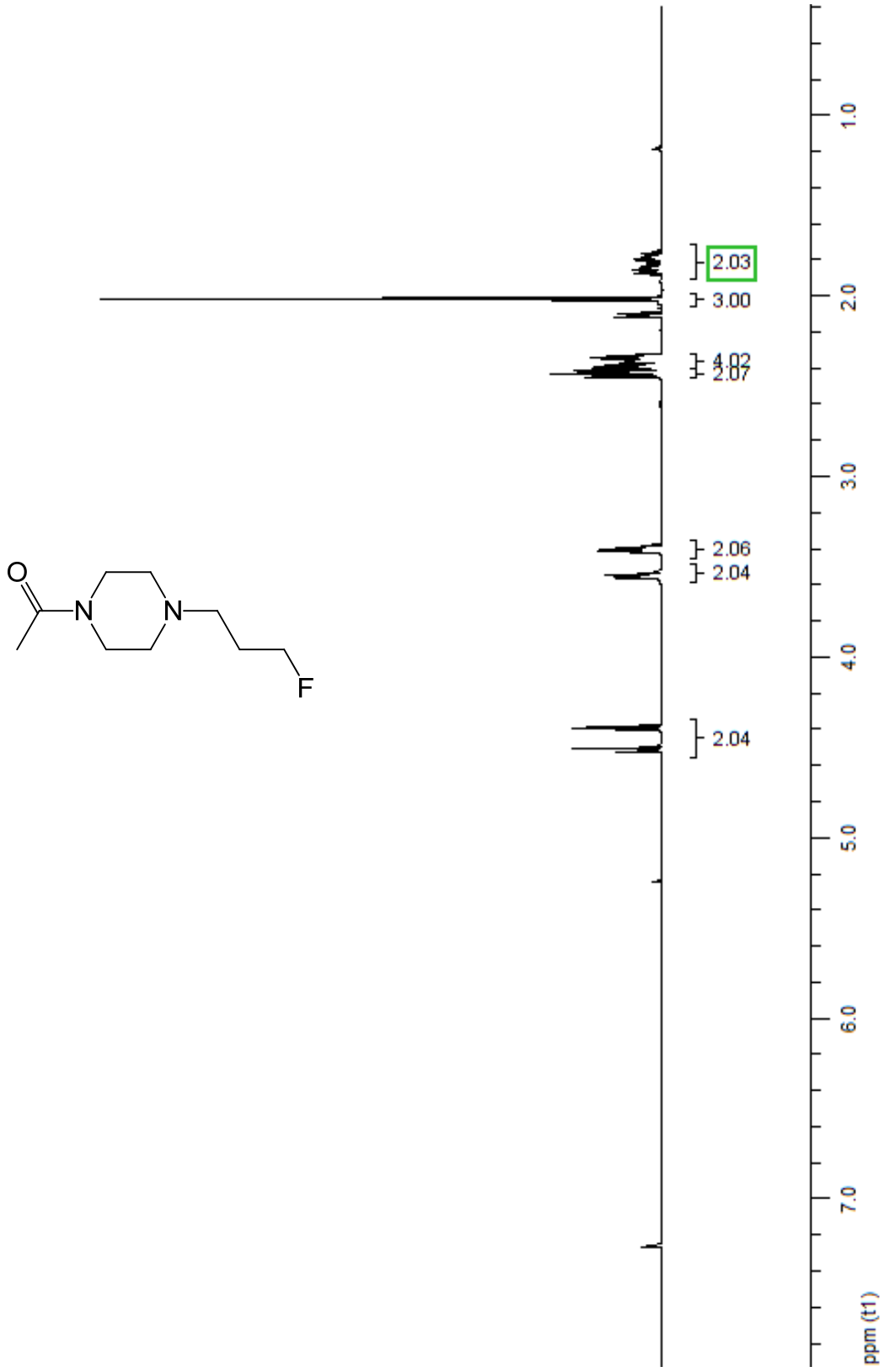
MS (IES+, ACN): m/z 182 $[M+H]^+$, 204 $[M+Na]^+$.

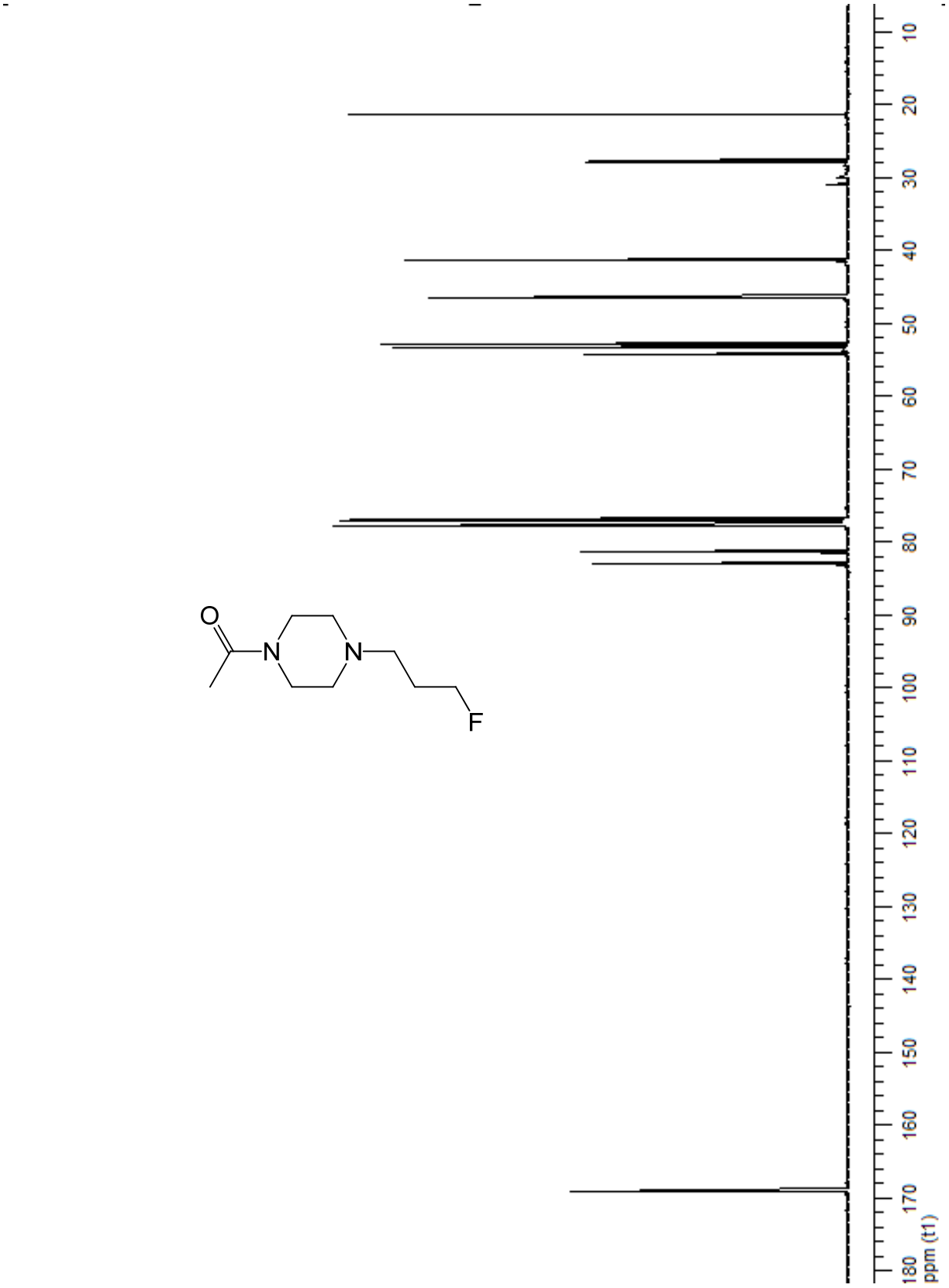
HRMS (ESI, CH_3OH): Calc for $C_9H_{12}N_2O_2$ $[M+H]^+$: 181.09770, found 181.0978.

Calc for $C_9H_{11}N_2O_2D$ $[M+H]^+$: 182.10398, found 182.1039.

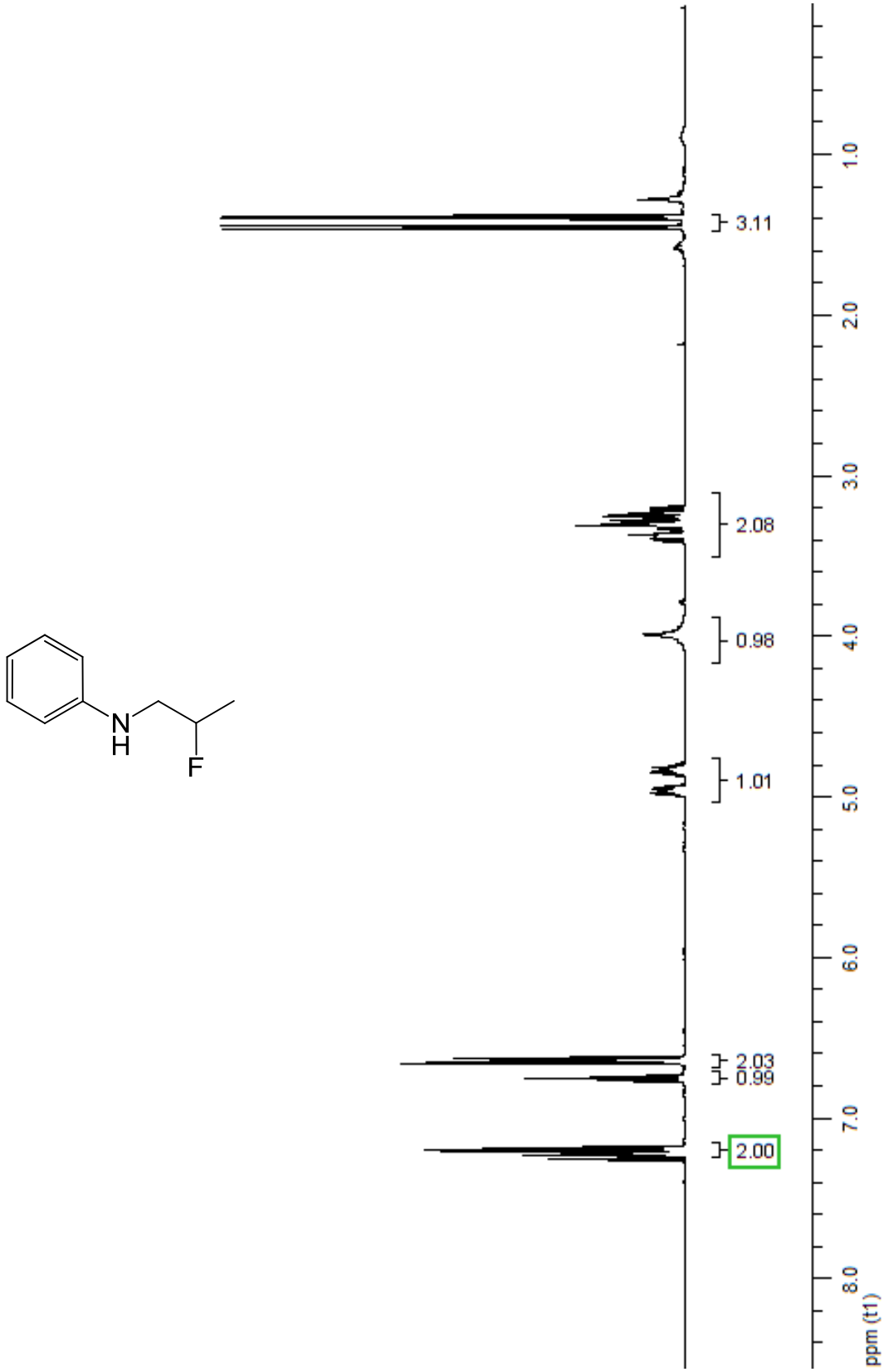
H. NMR SPECTRA

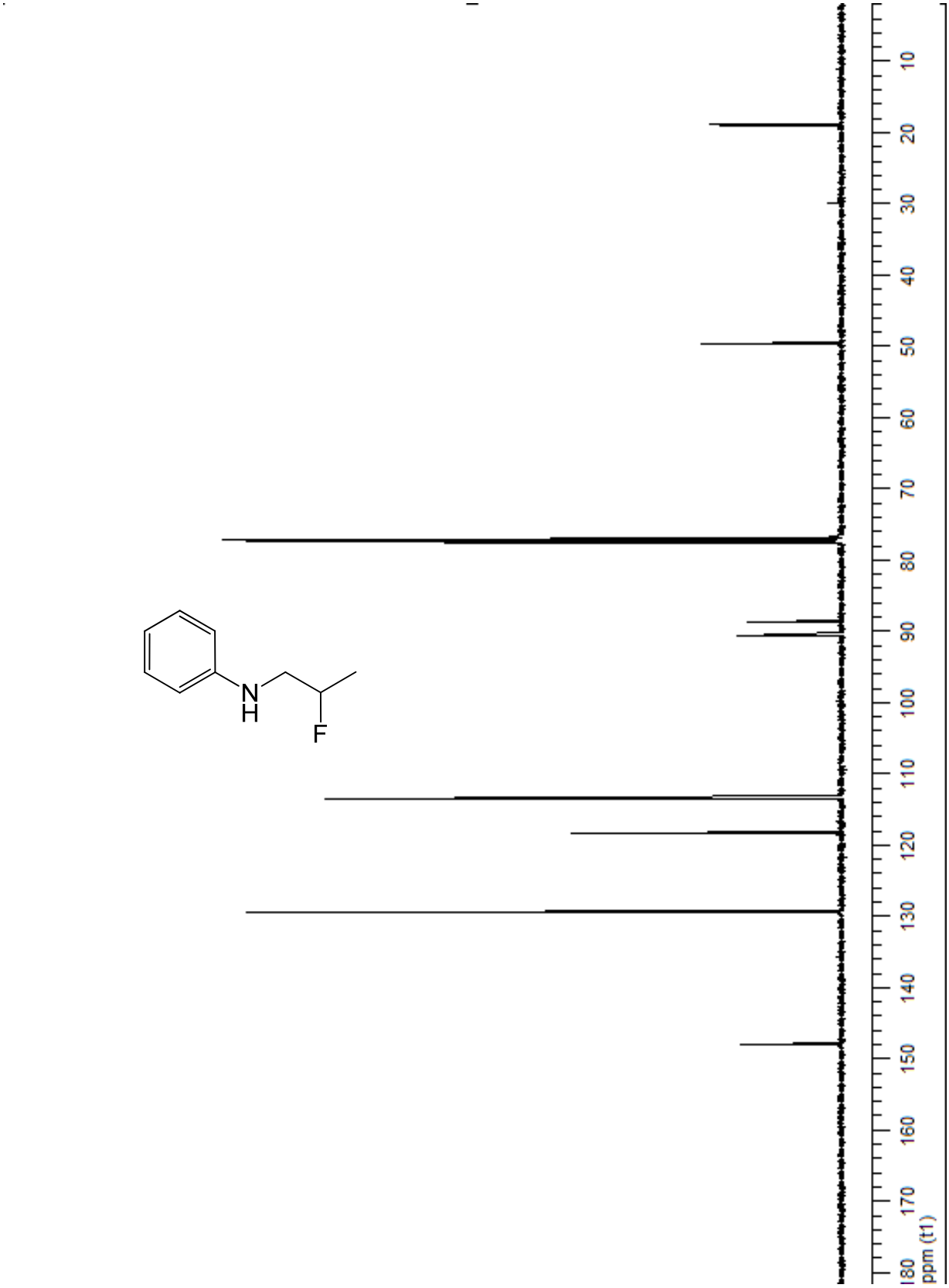
Compound 3a:



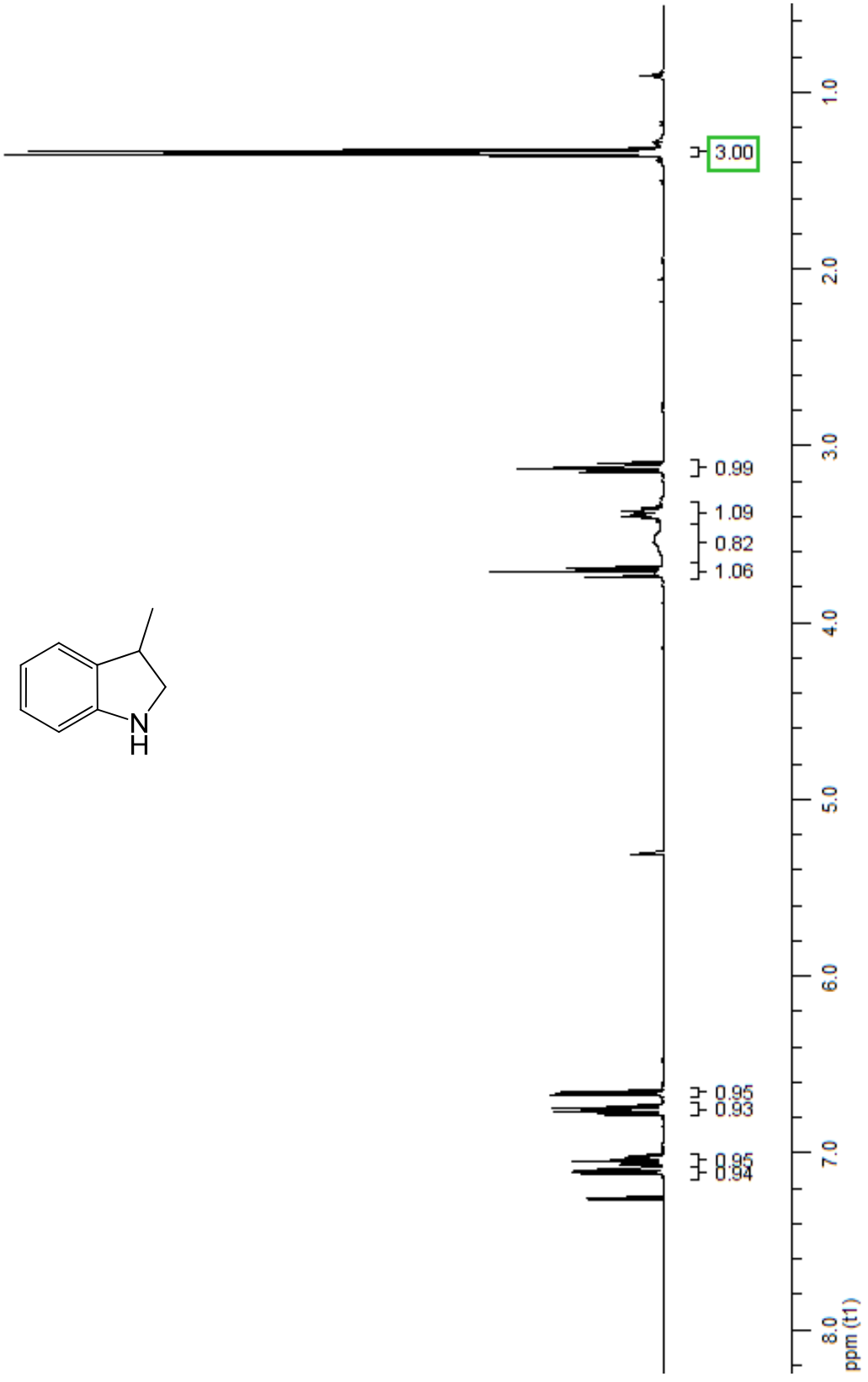

O
N
N
F
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
ppm (t1)

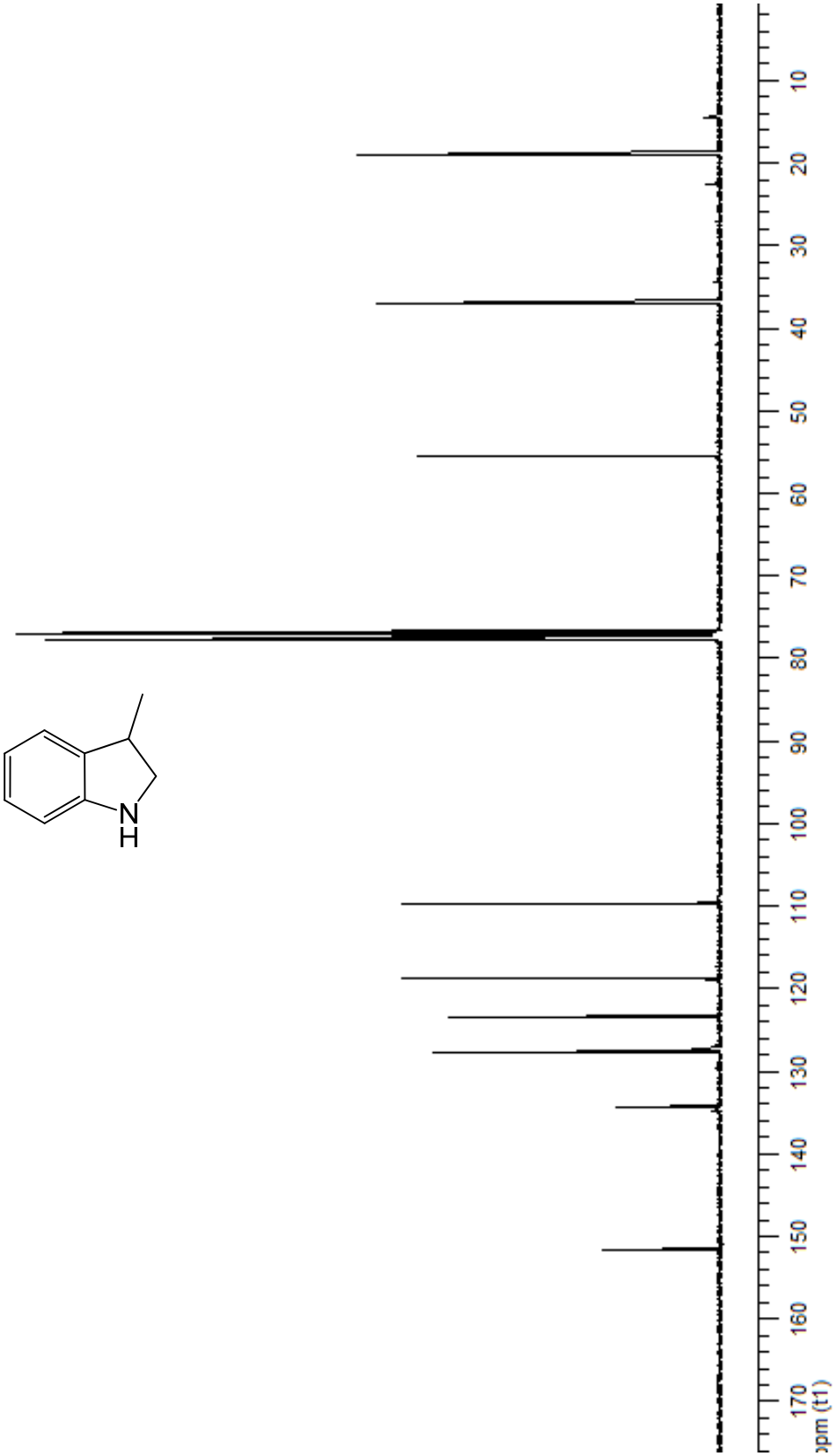
Compound 2b:



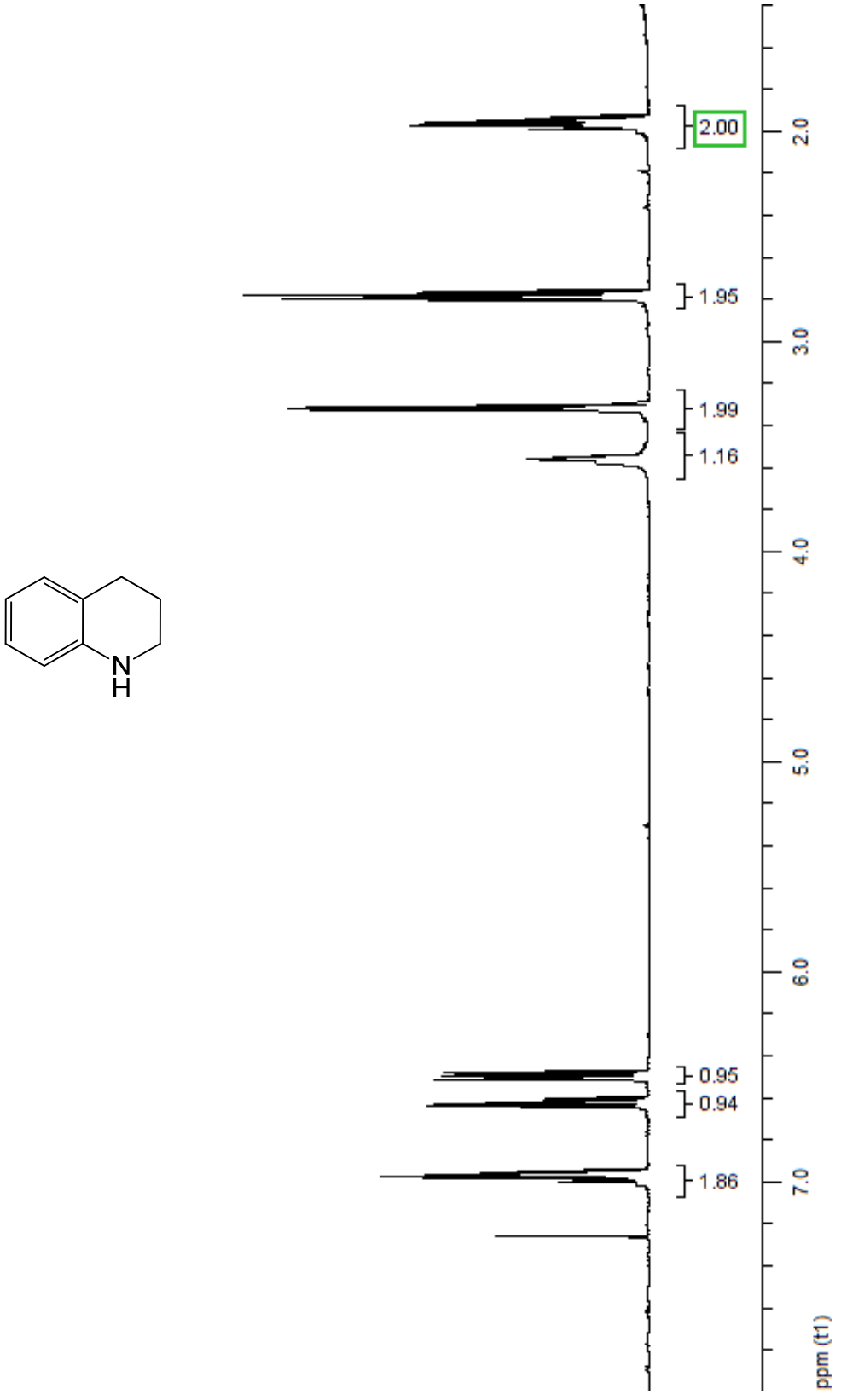


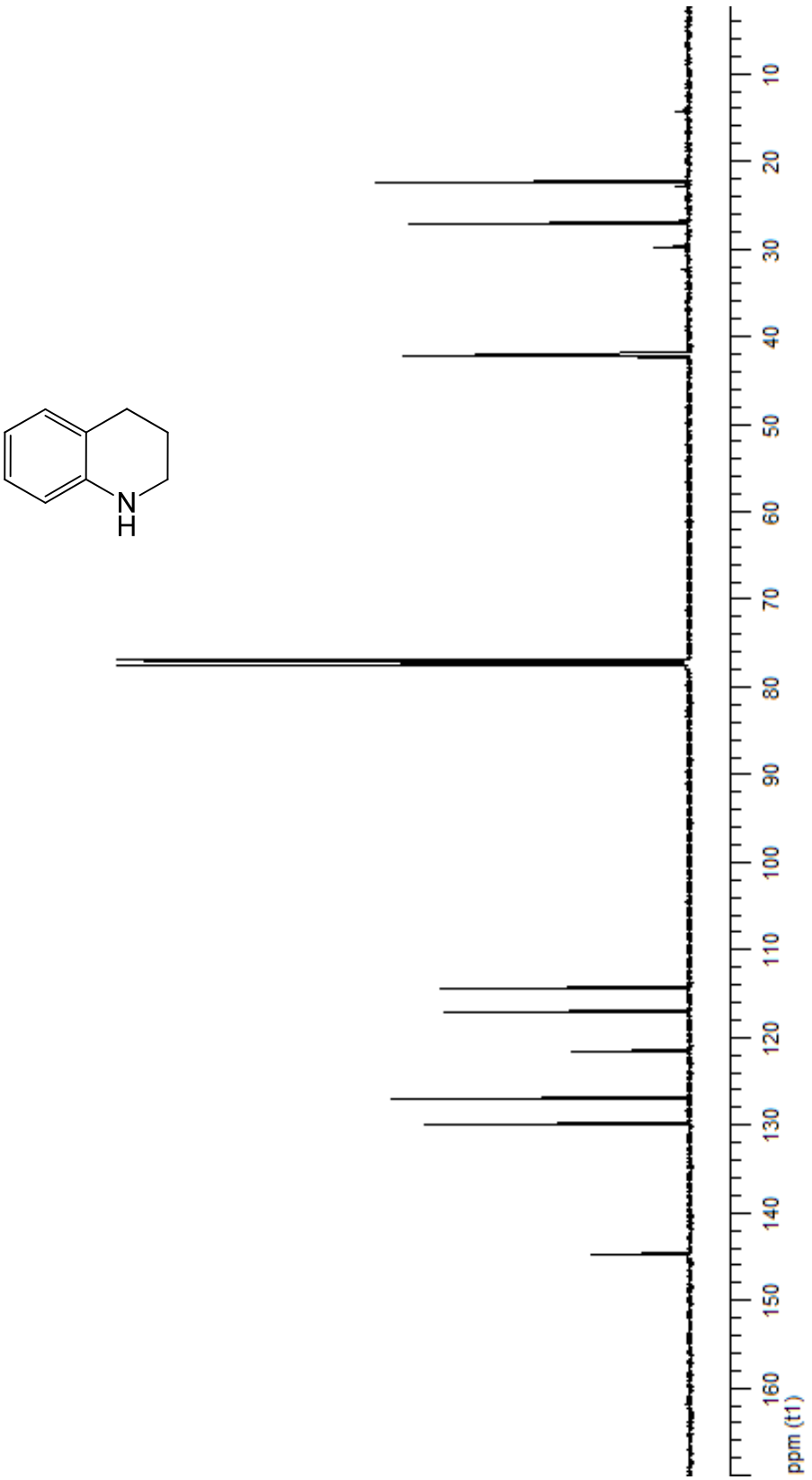
Compound 4b:


3.00
0.99
1.09
0.82
1.06
0.95
0.93
0.95
0.94
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)
N
H

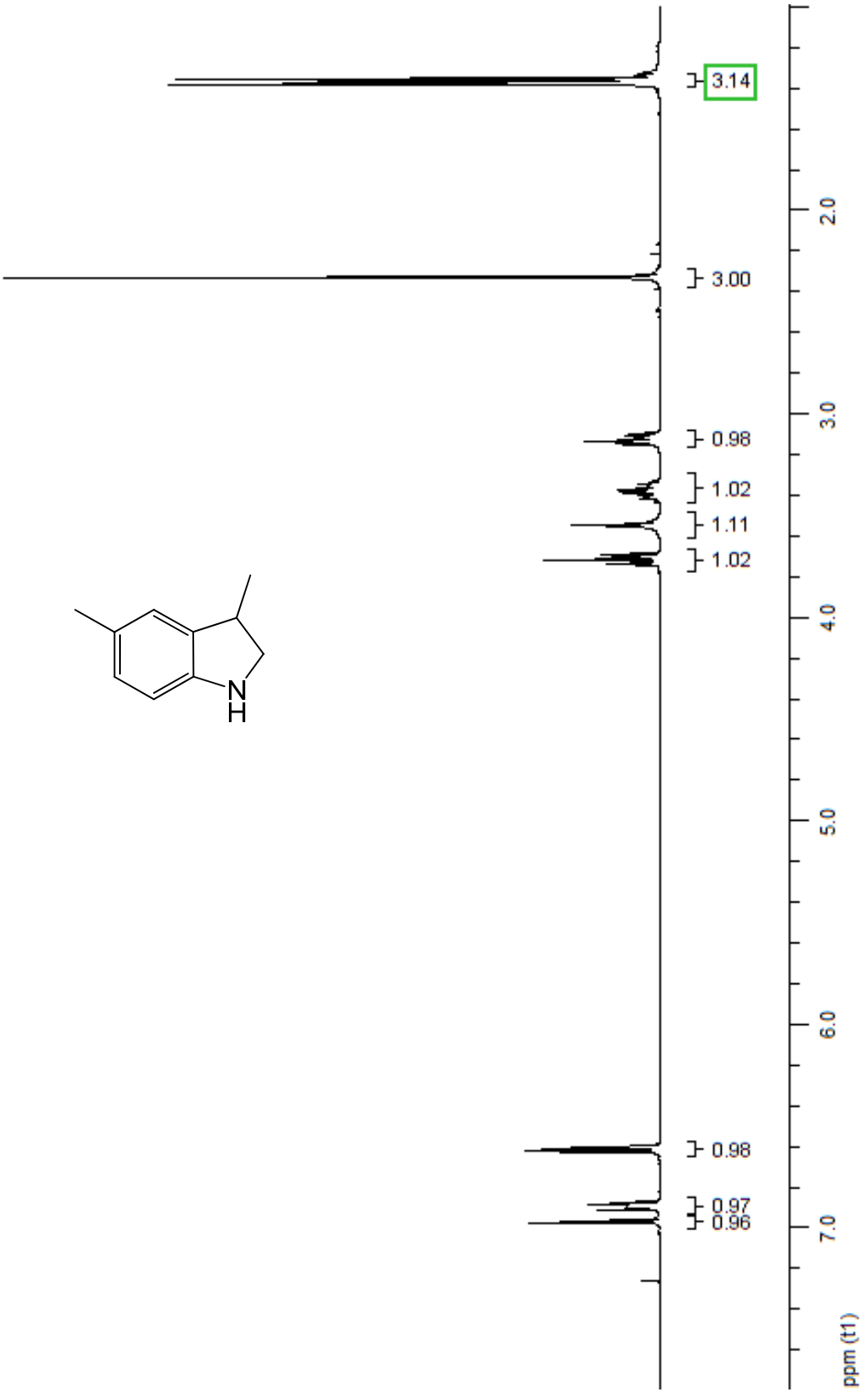

N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm (t1)

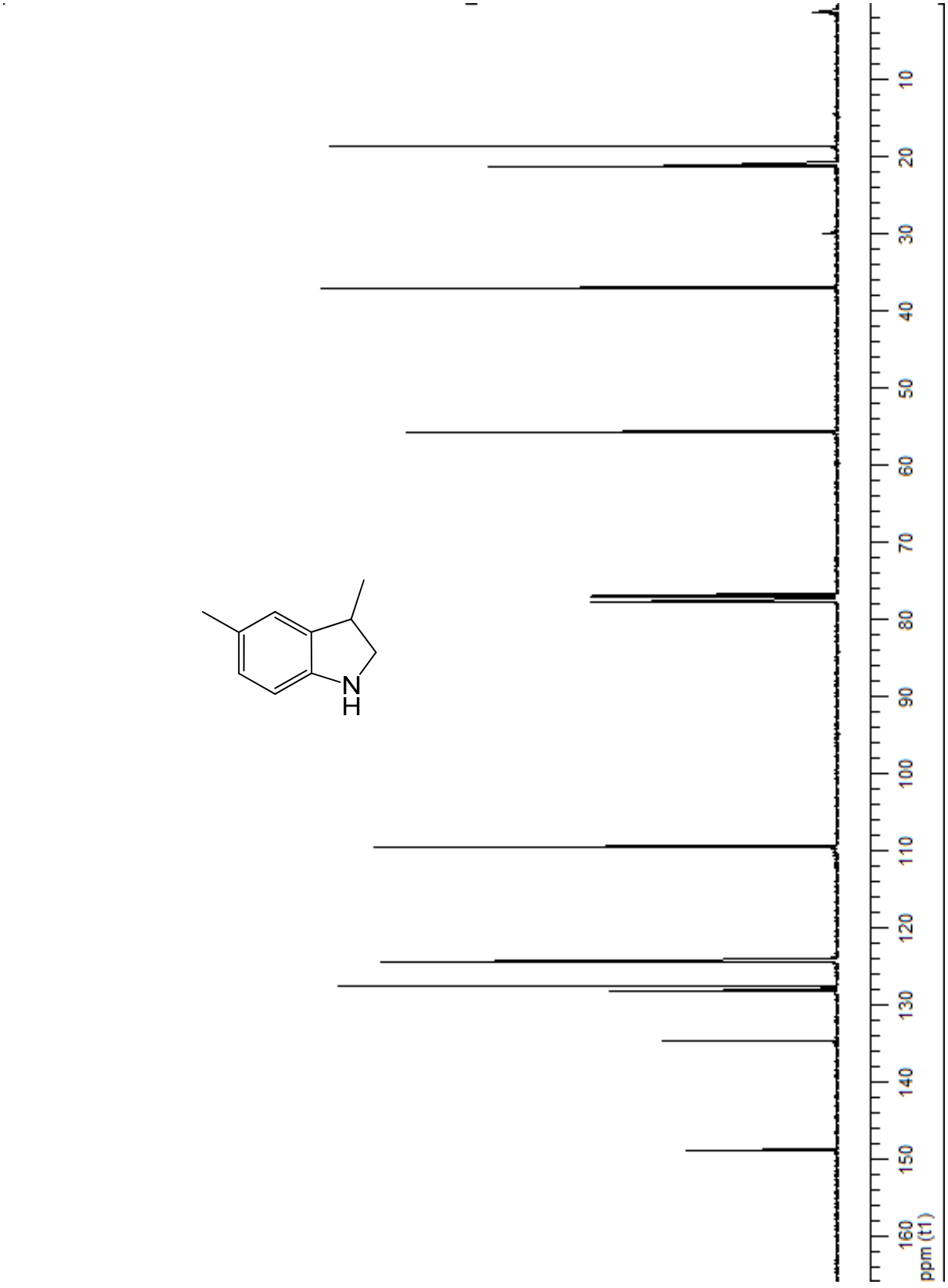
Compound 5b:



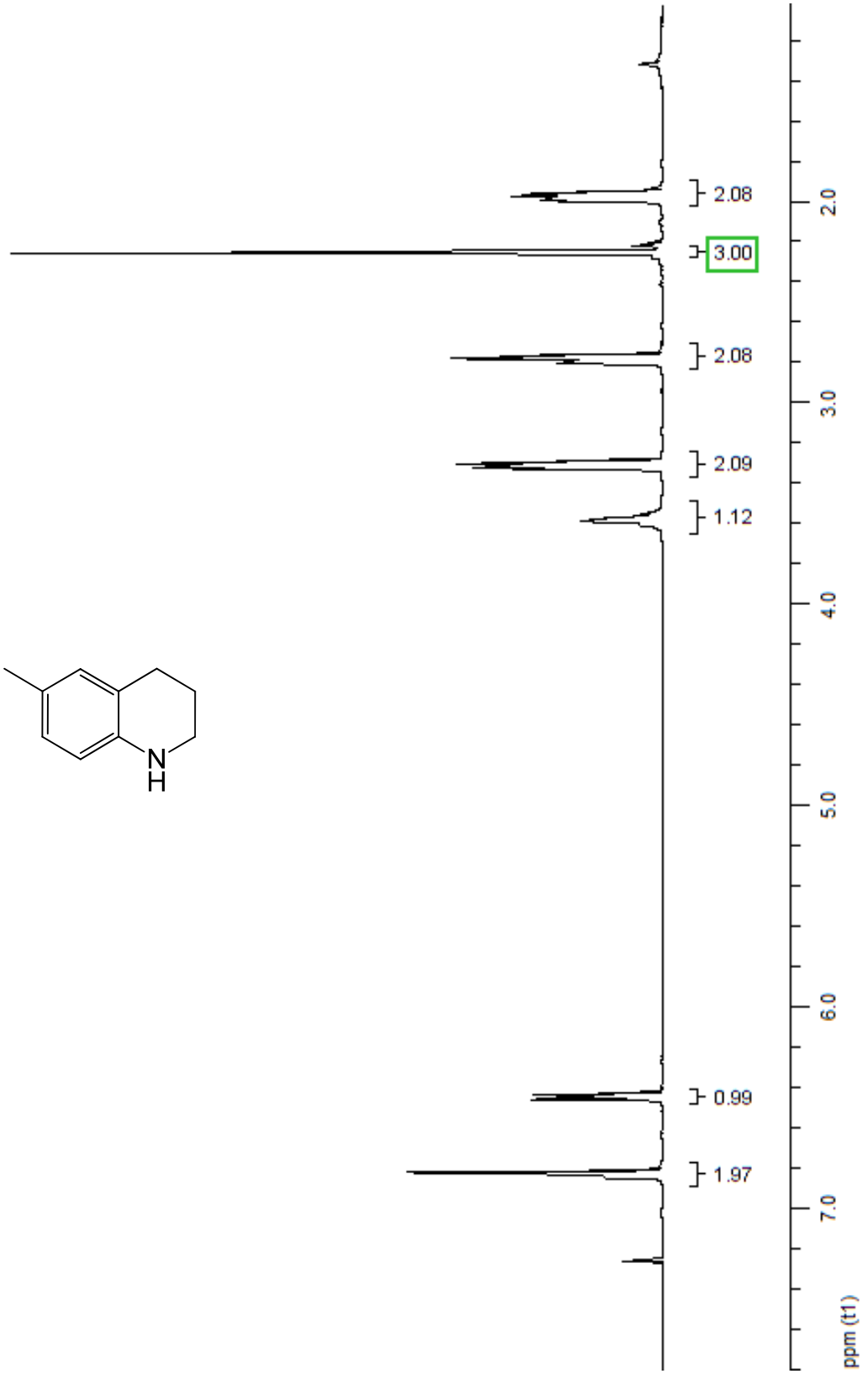

N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

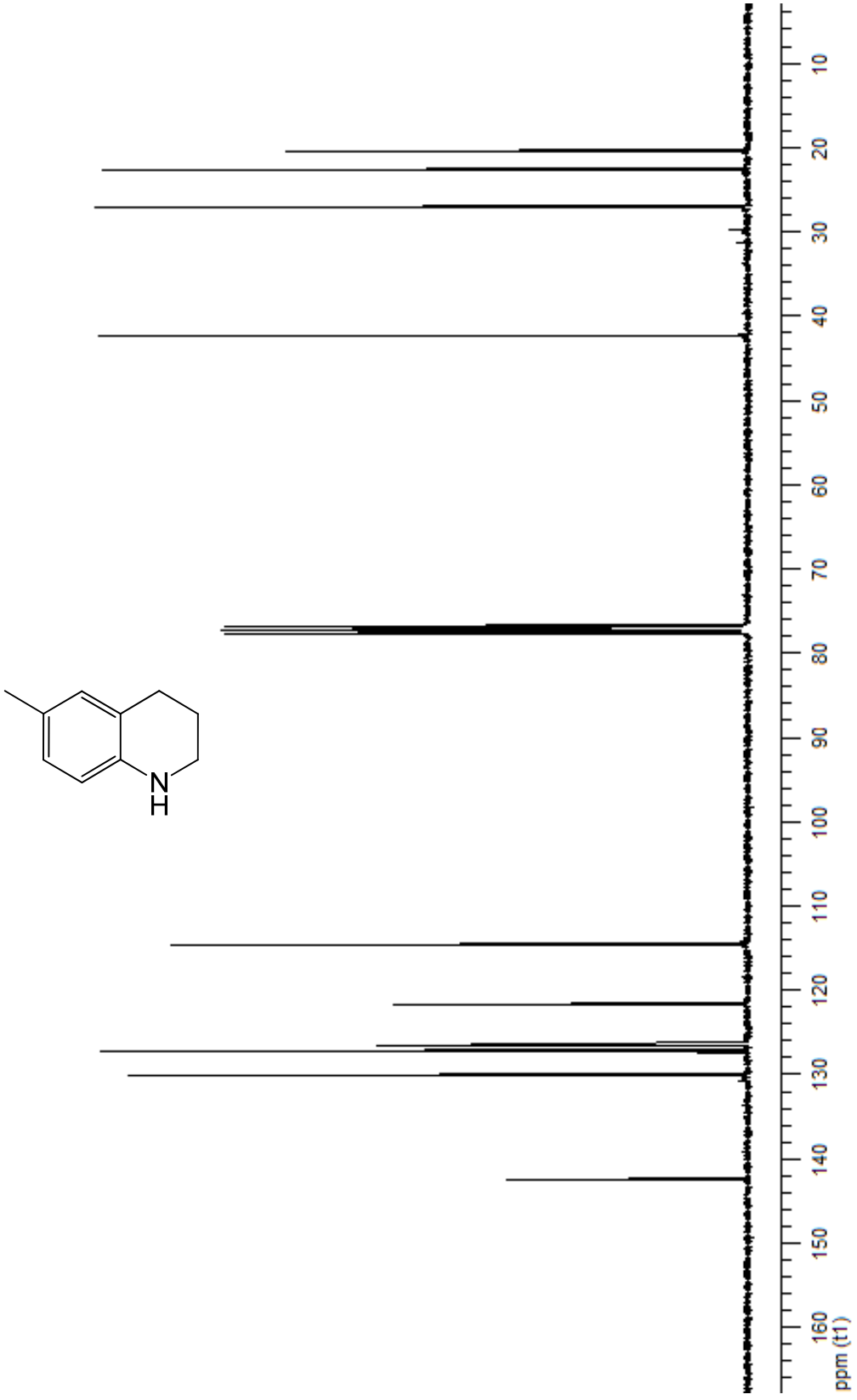
Compound 4c:



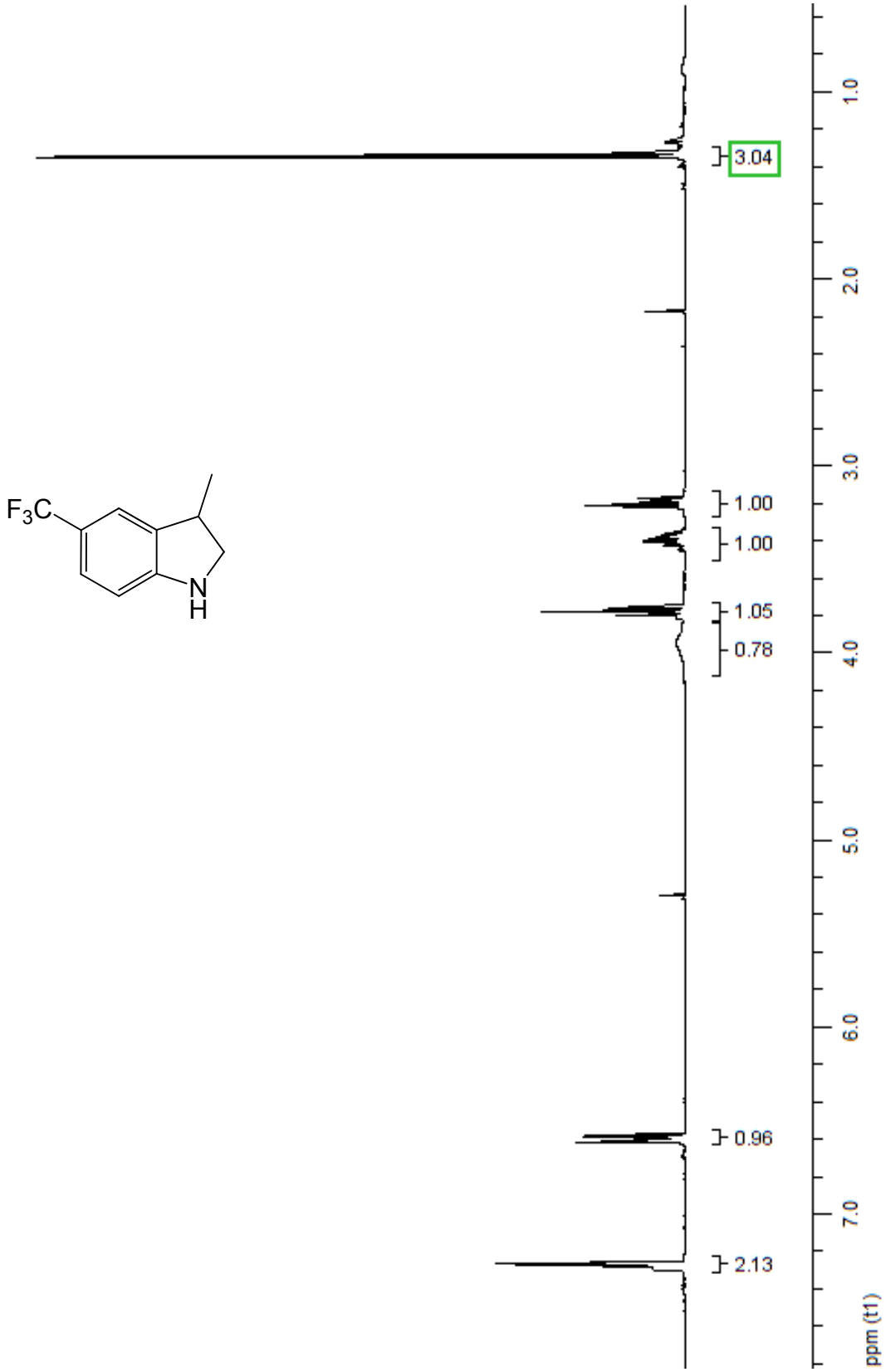

N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

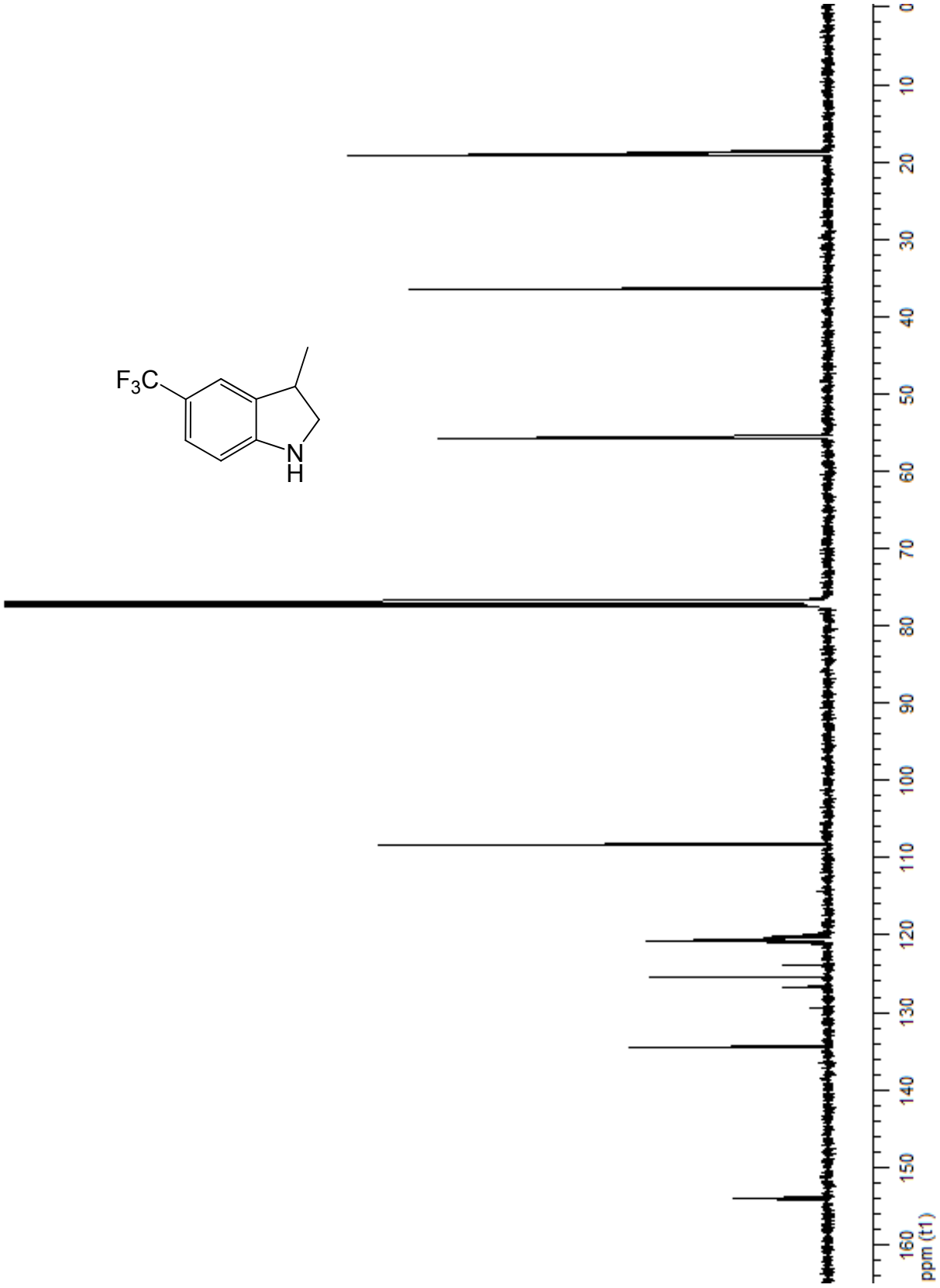
Compound 5c:



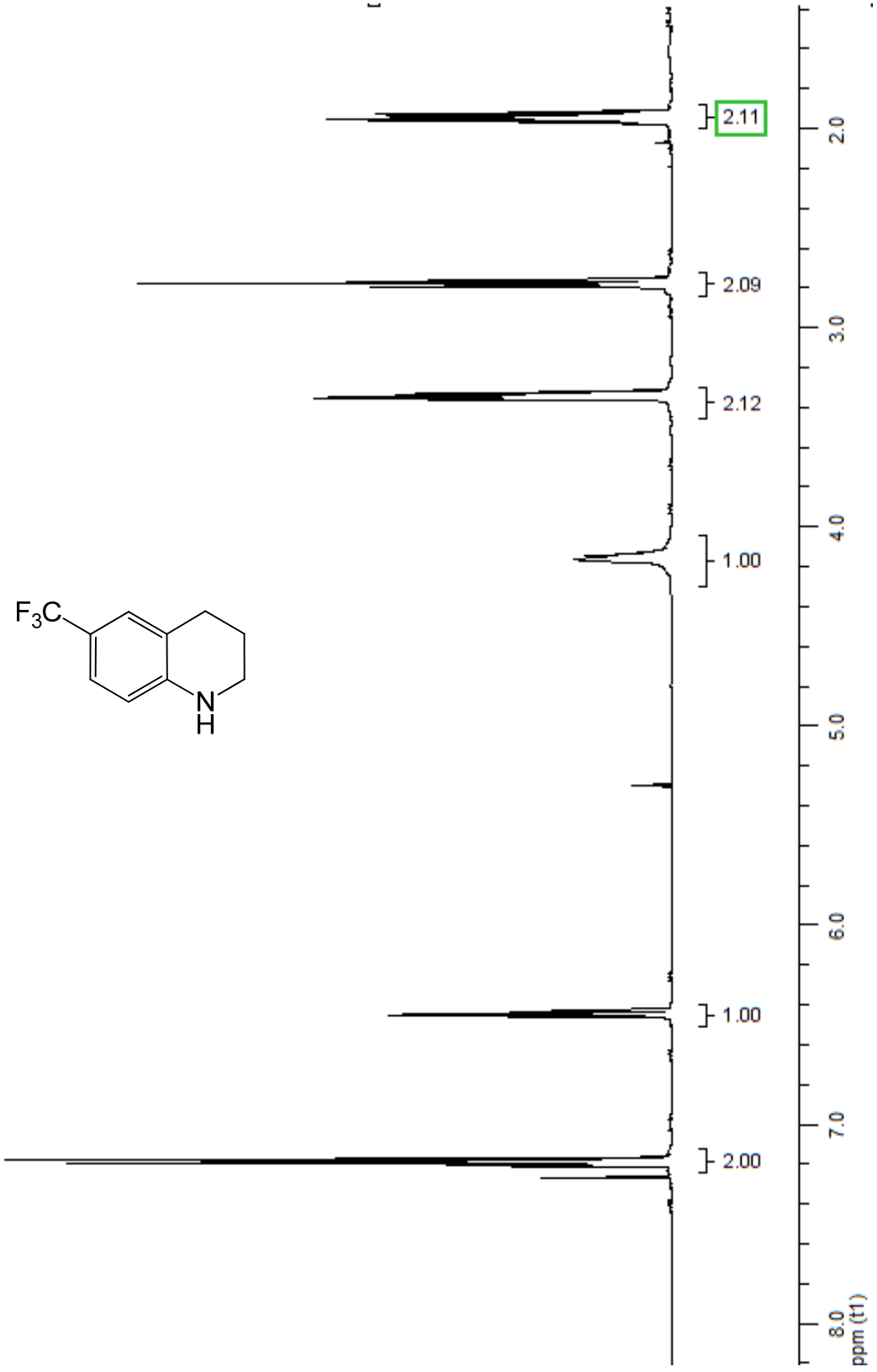

N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

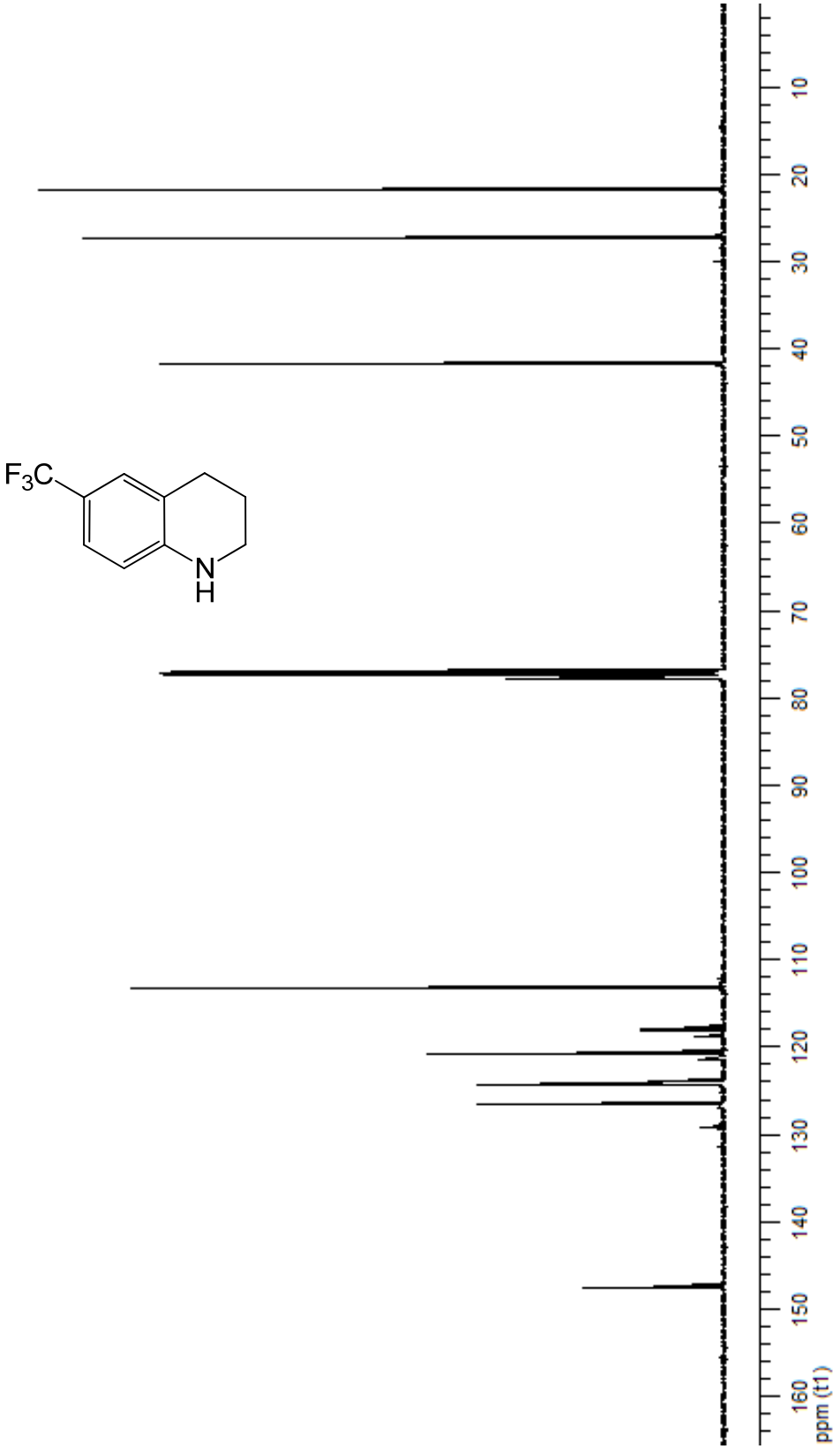
Compound 4d:



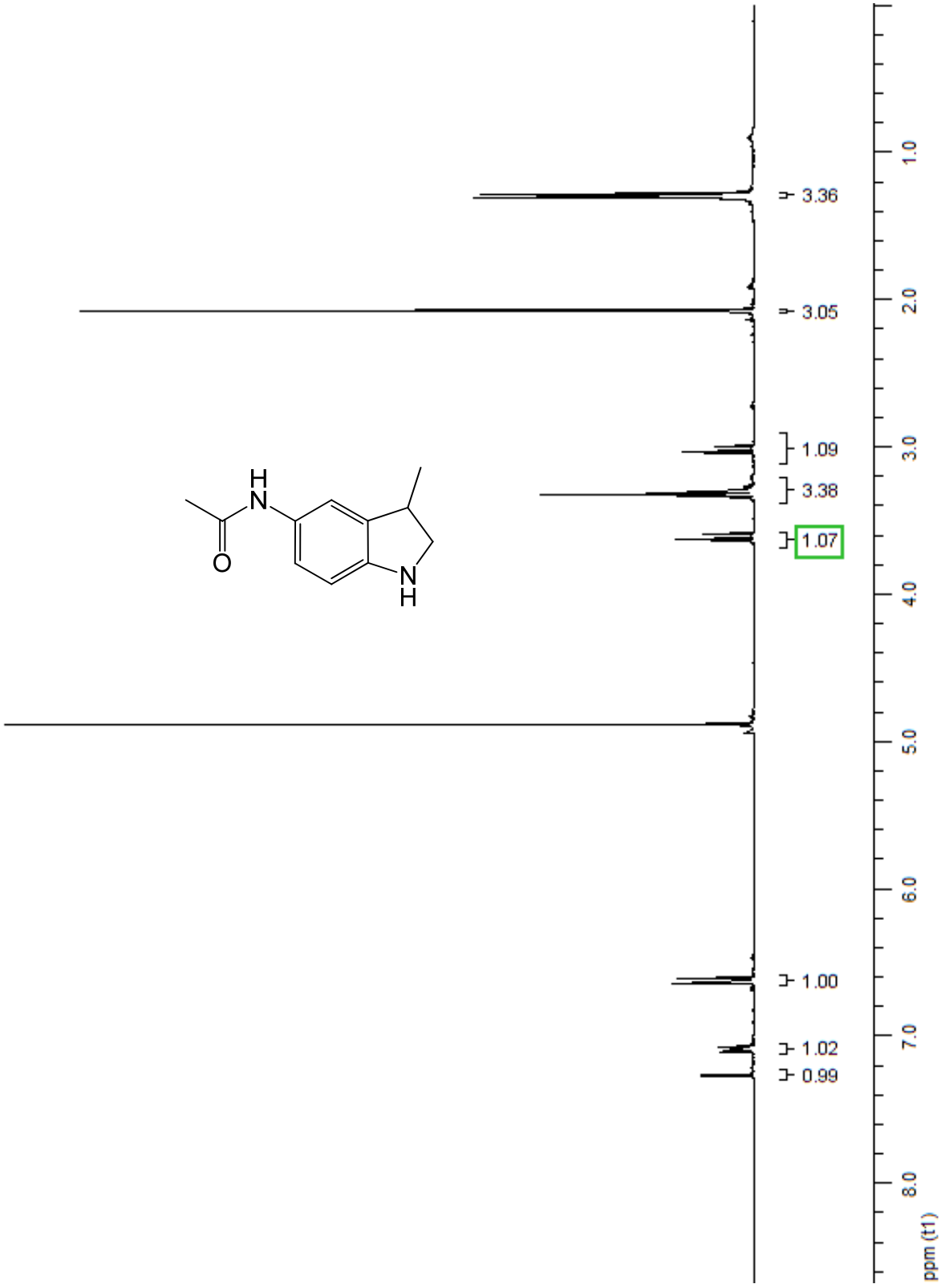


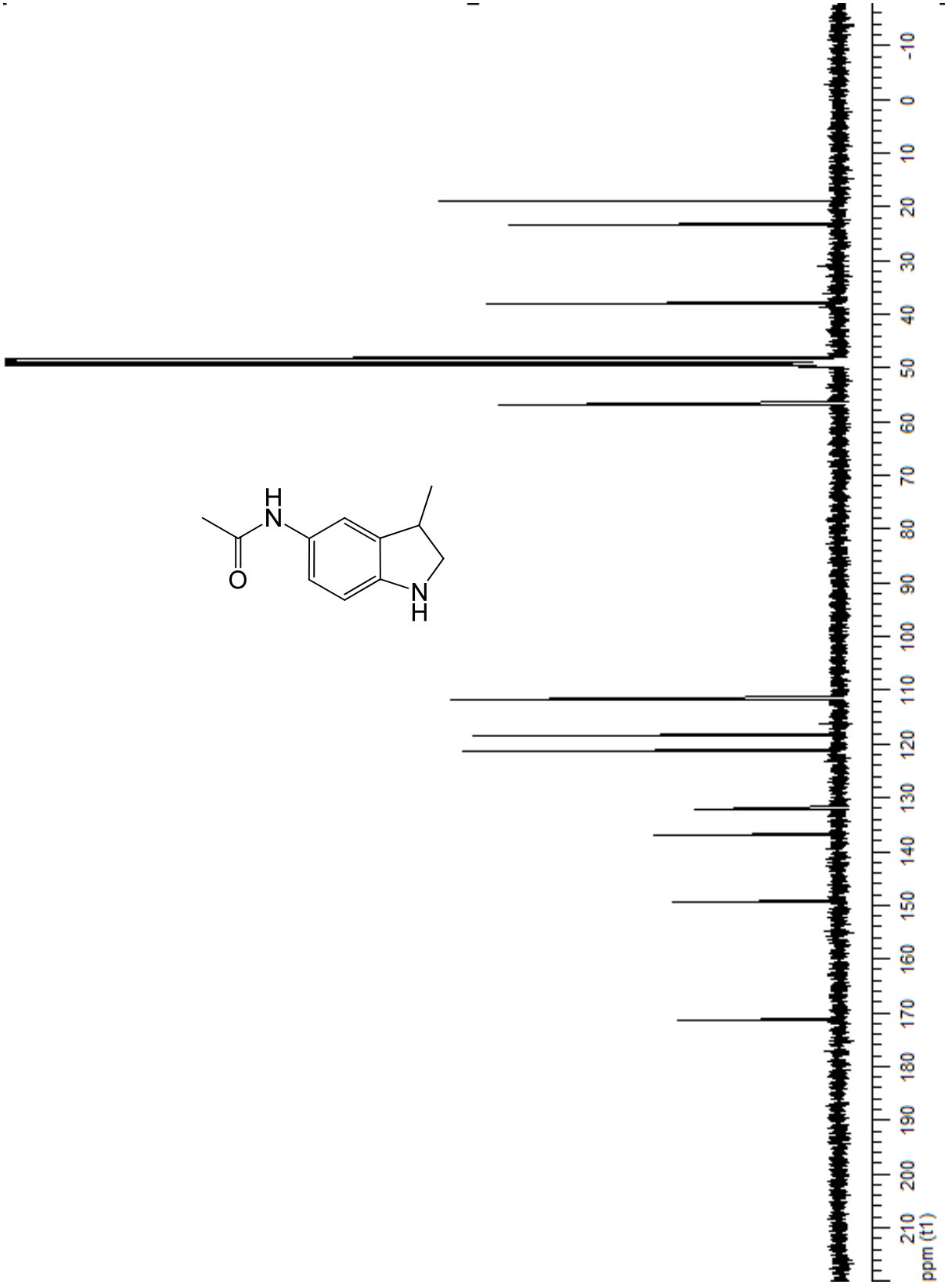
Compound 5d:



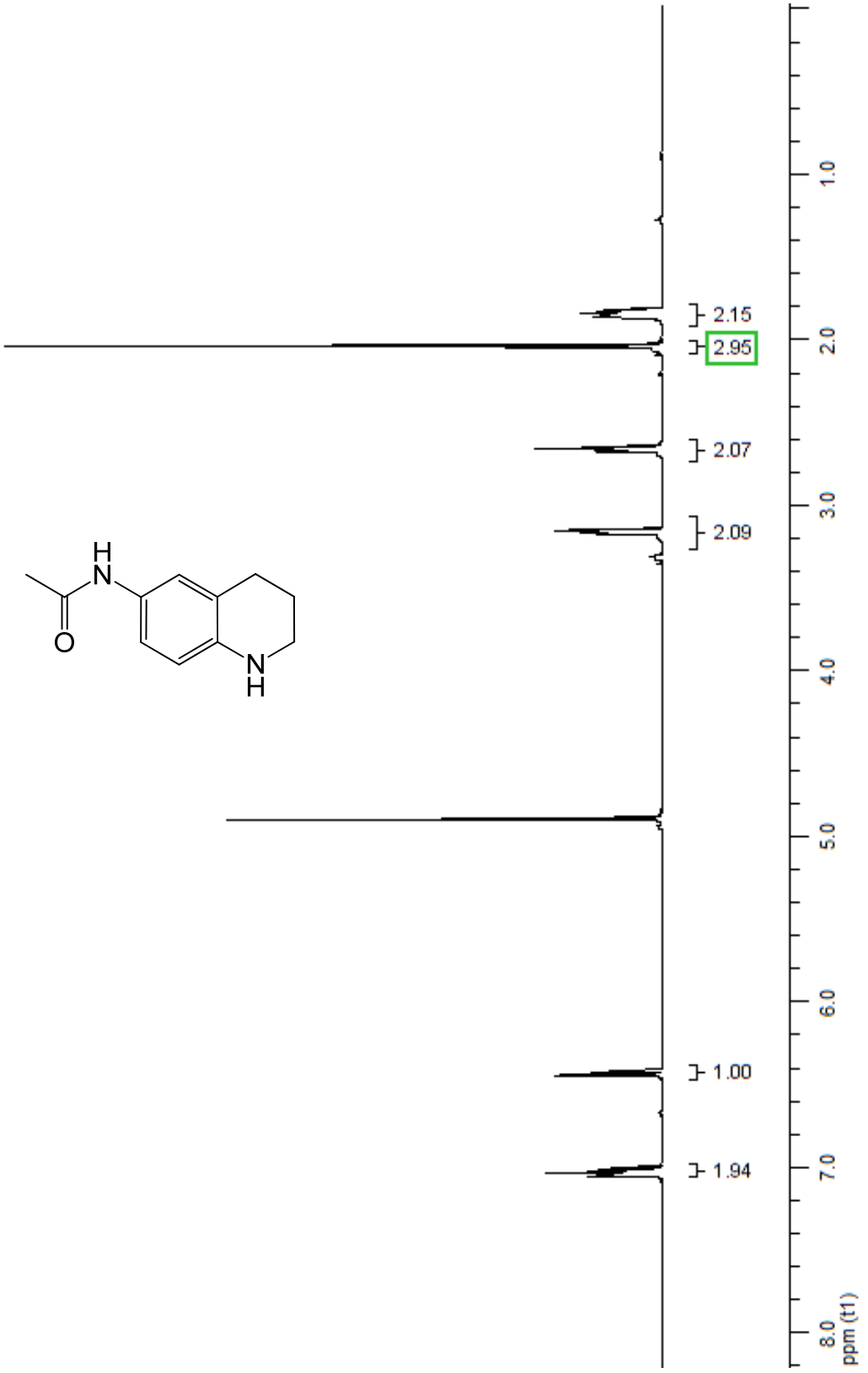

F3C
N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

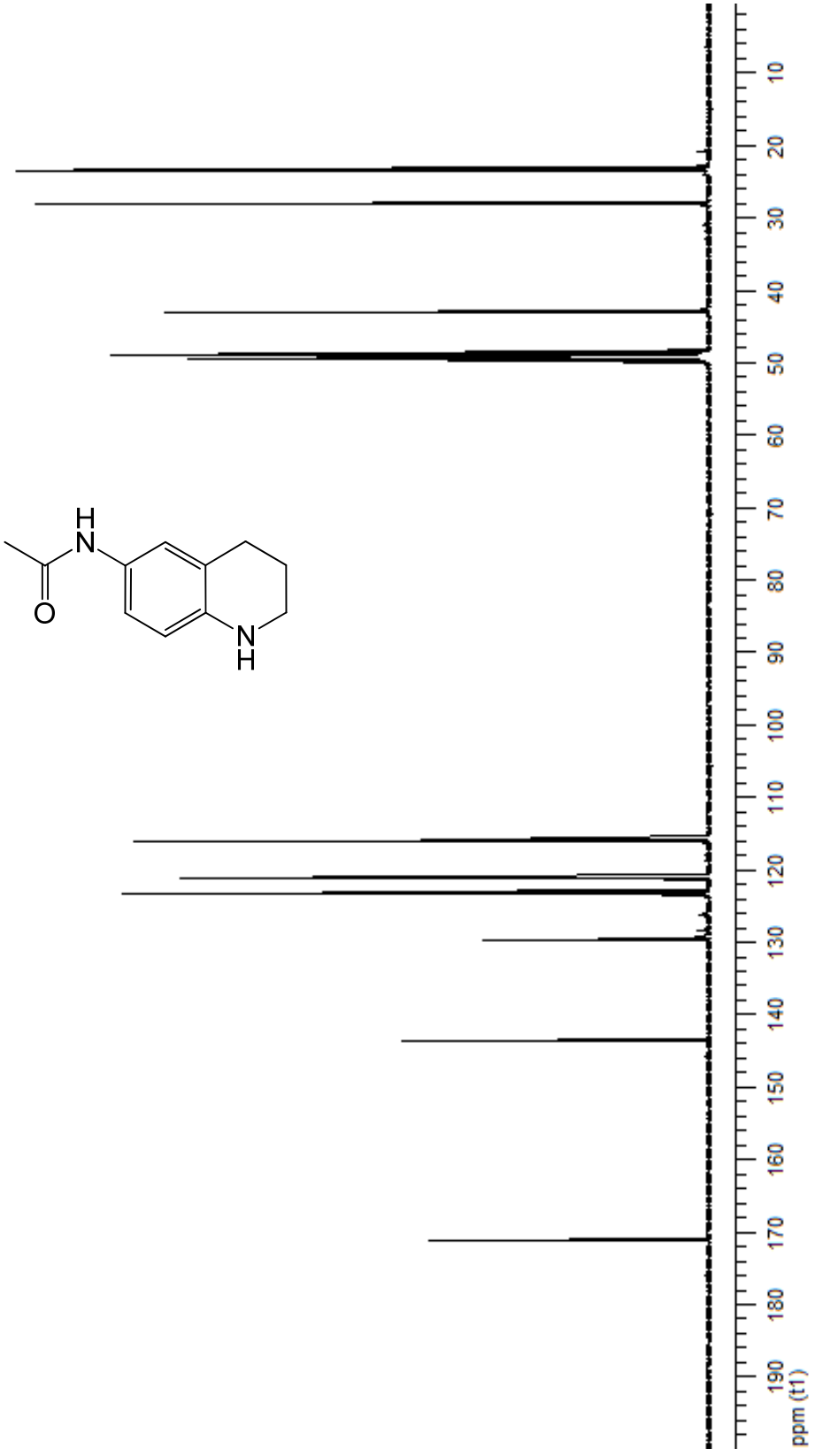
Compound 4e:


3.36
3.05
1.09
3.38
1.07
1.00
1.02
0.99
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)
H
N
O
N
H

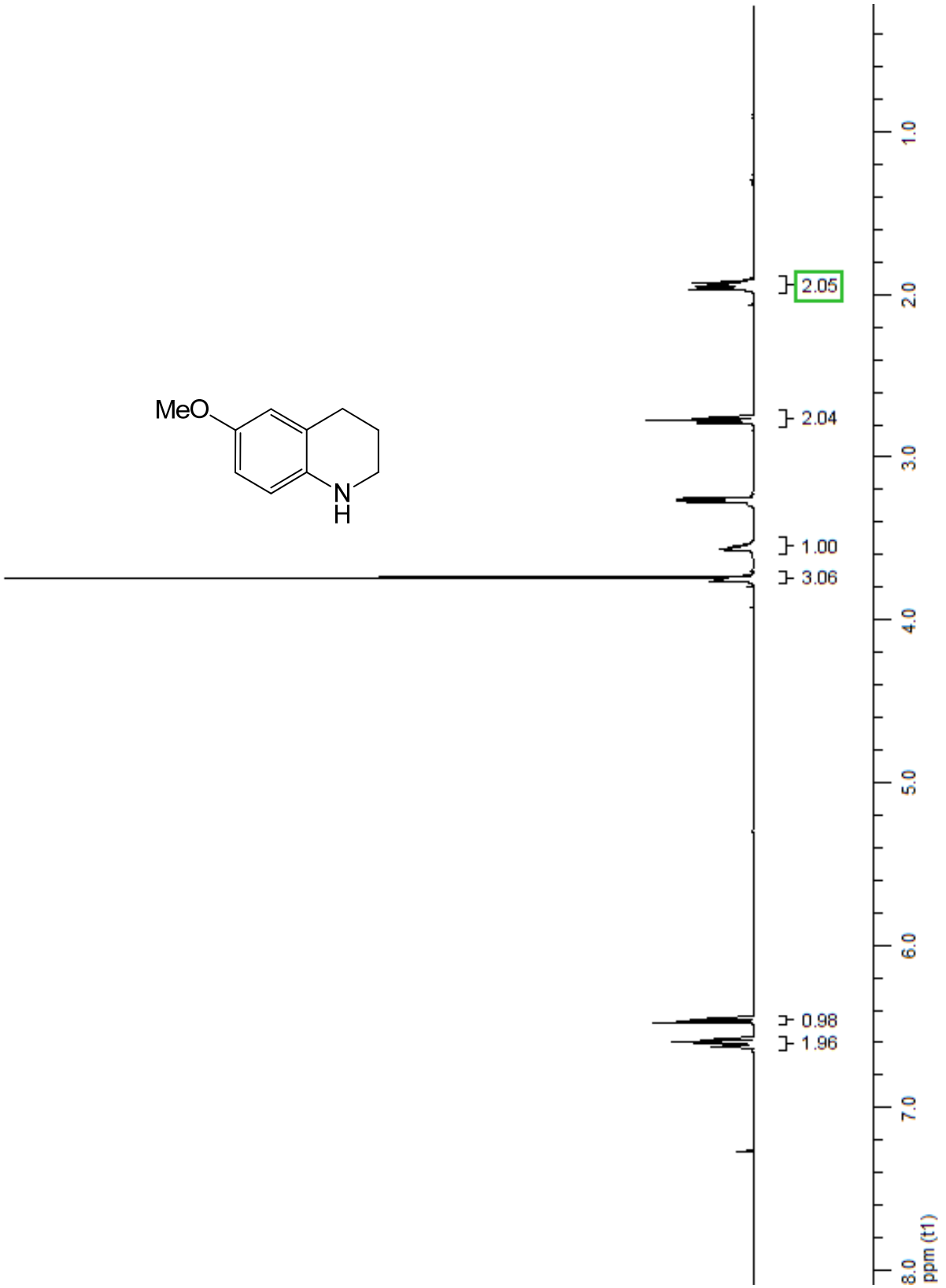

H
N
O
N
H
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm (t1)

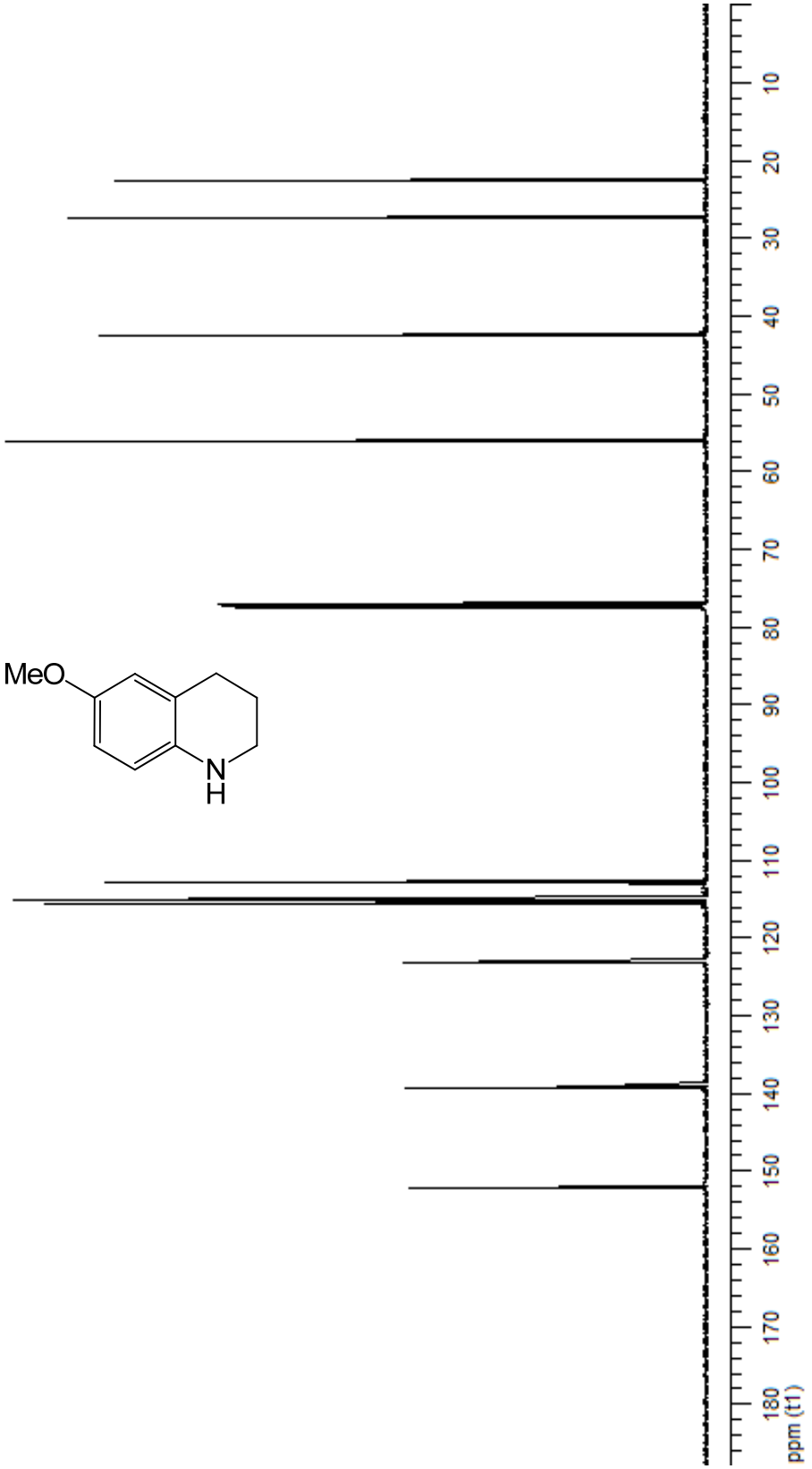
Compound 5e:



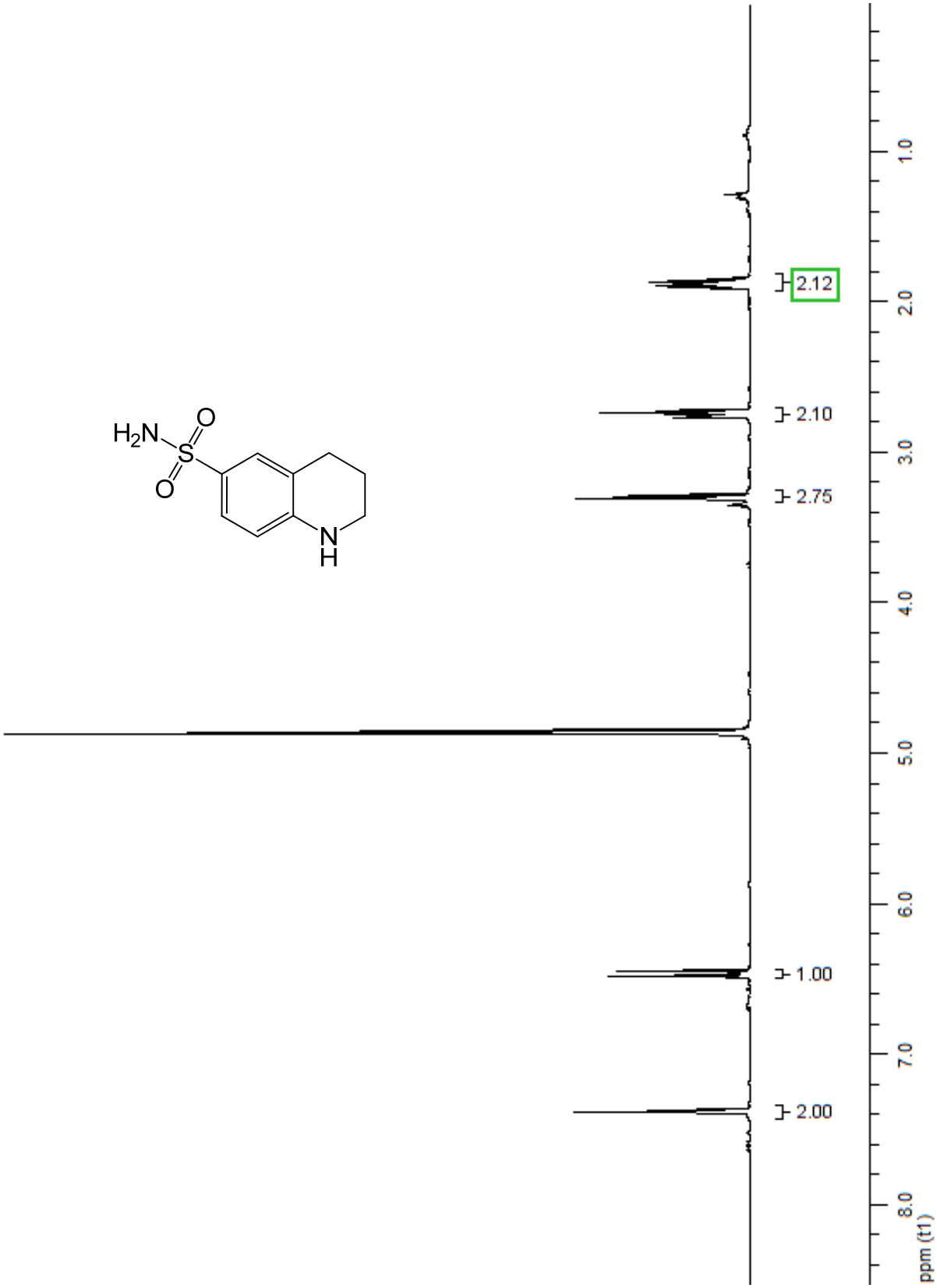

H
N
O
N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
ppm (t1)

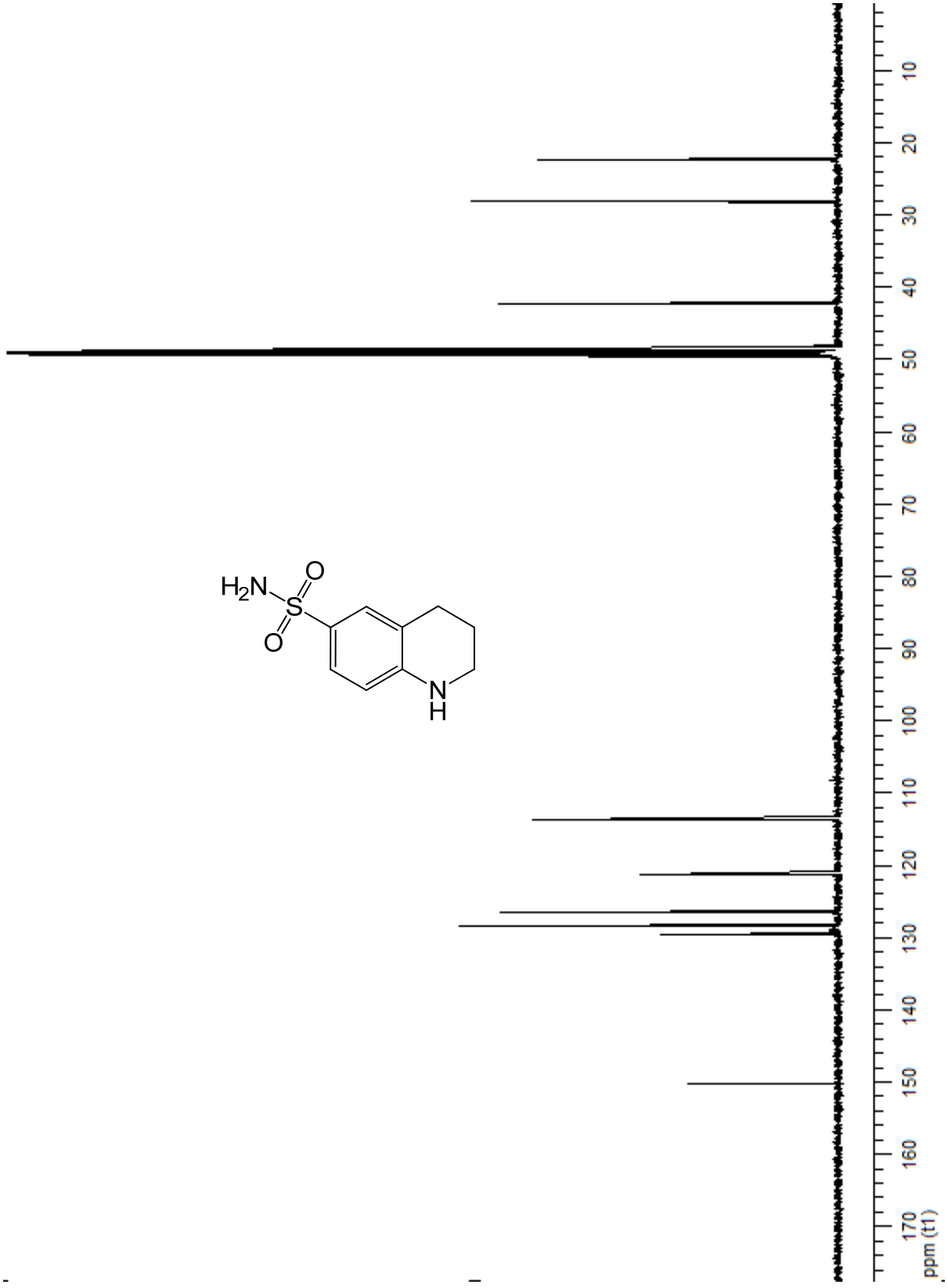
Compound 5f:



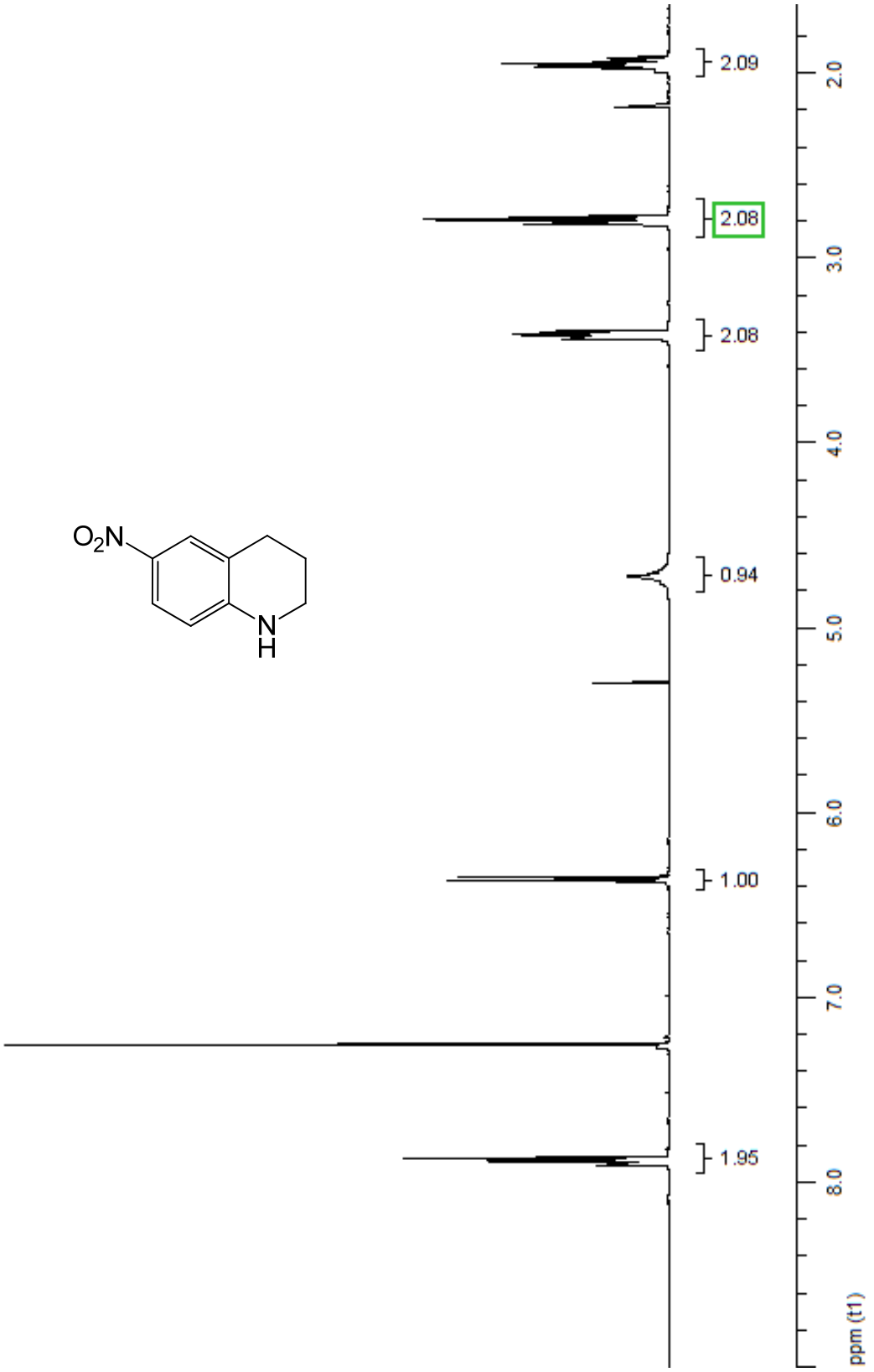

MeO
N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
ppm (t1)

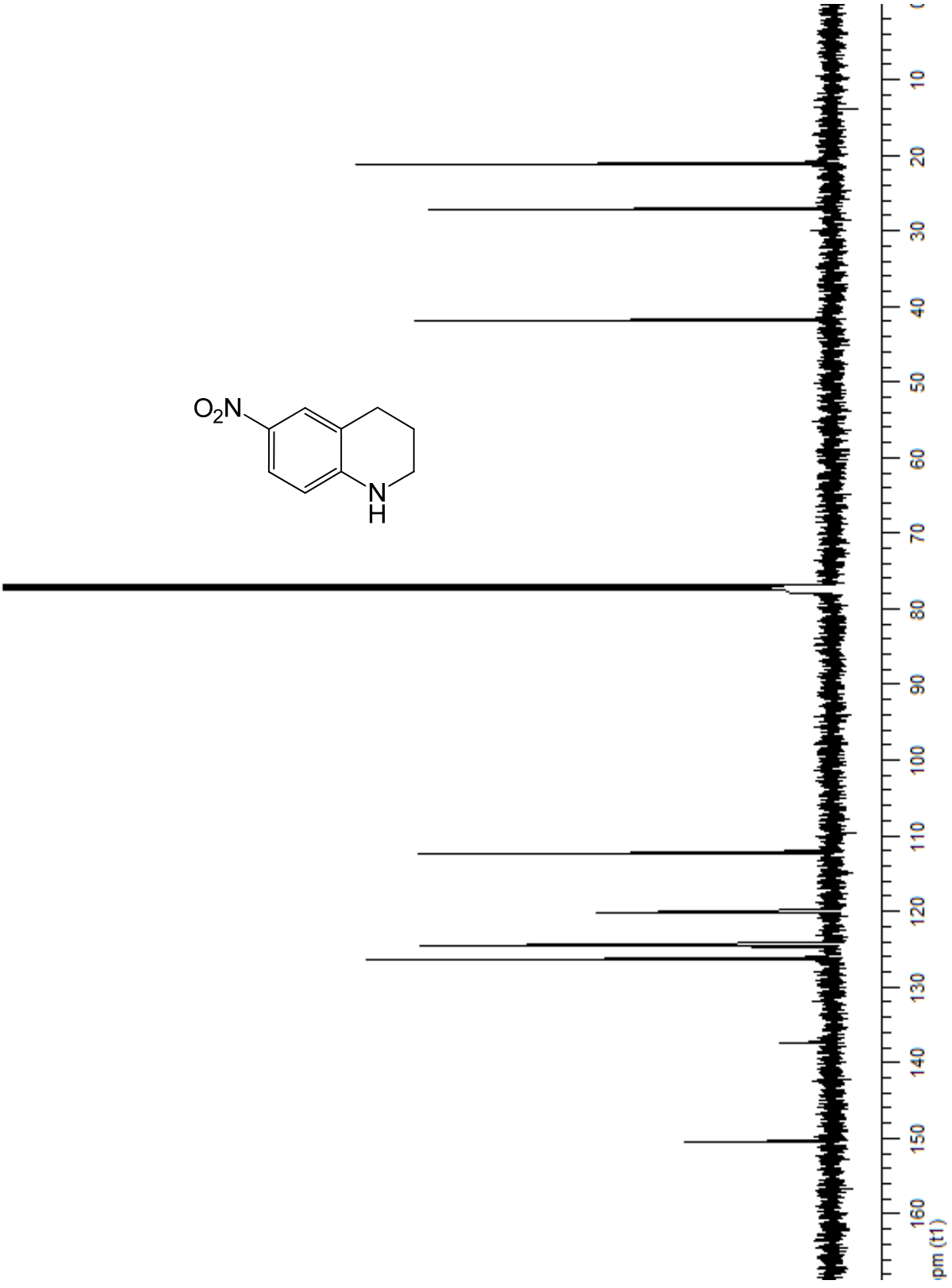
Compound 5g:



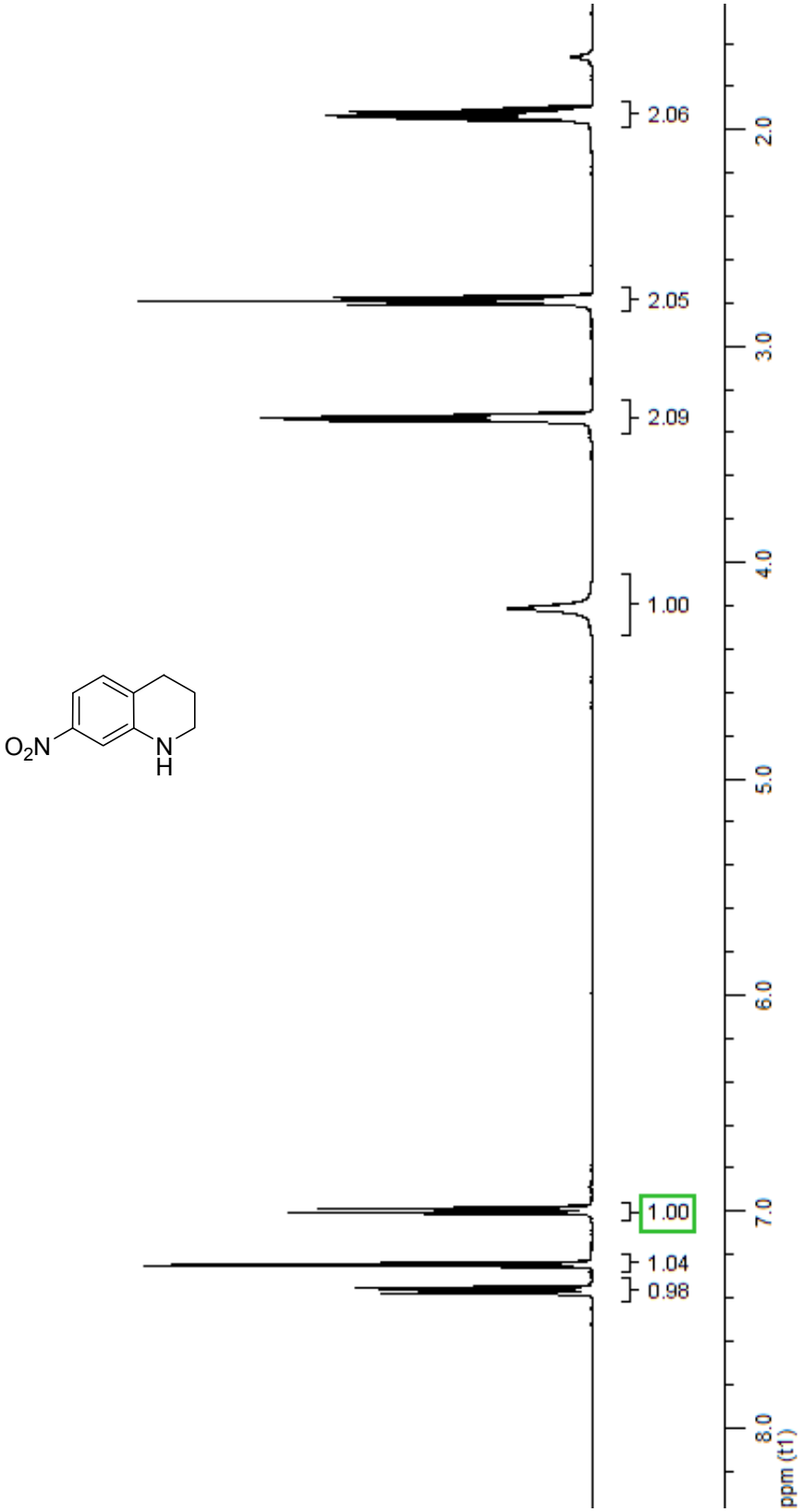

H2N
S
O
O
N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm (t1)

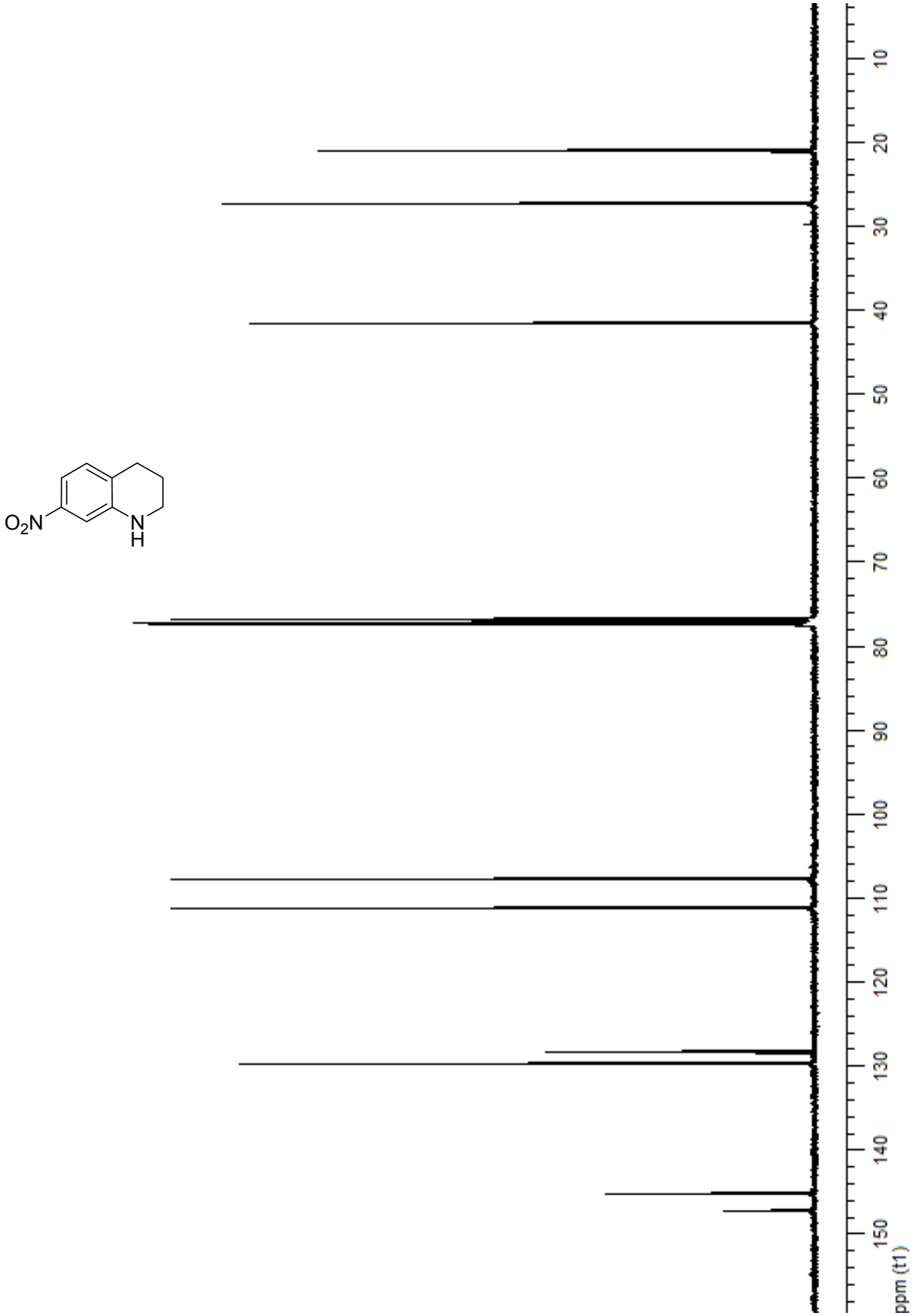
Compound 5h:



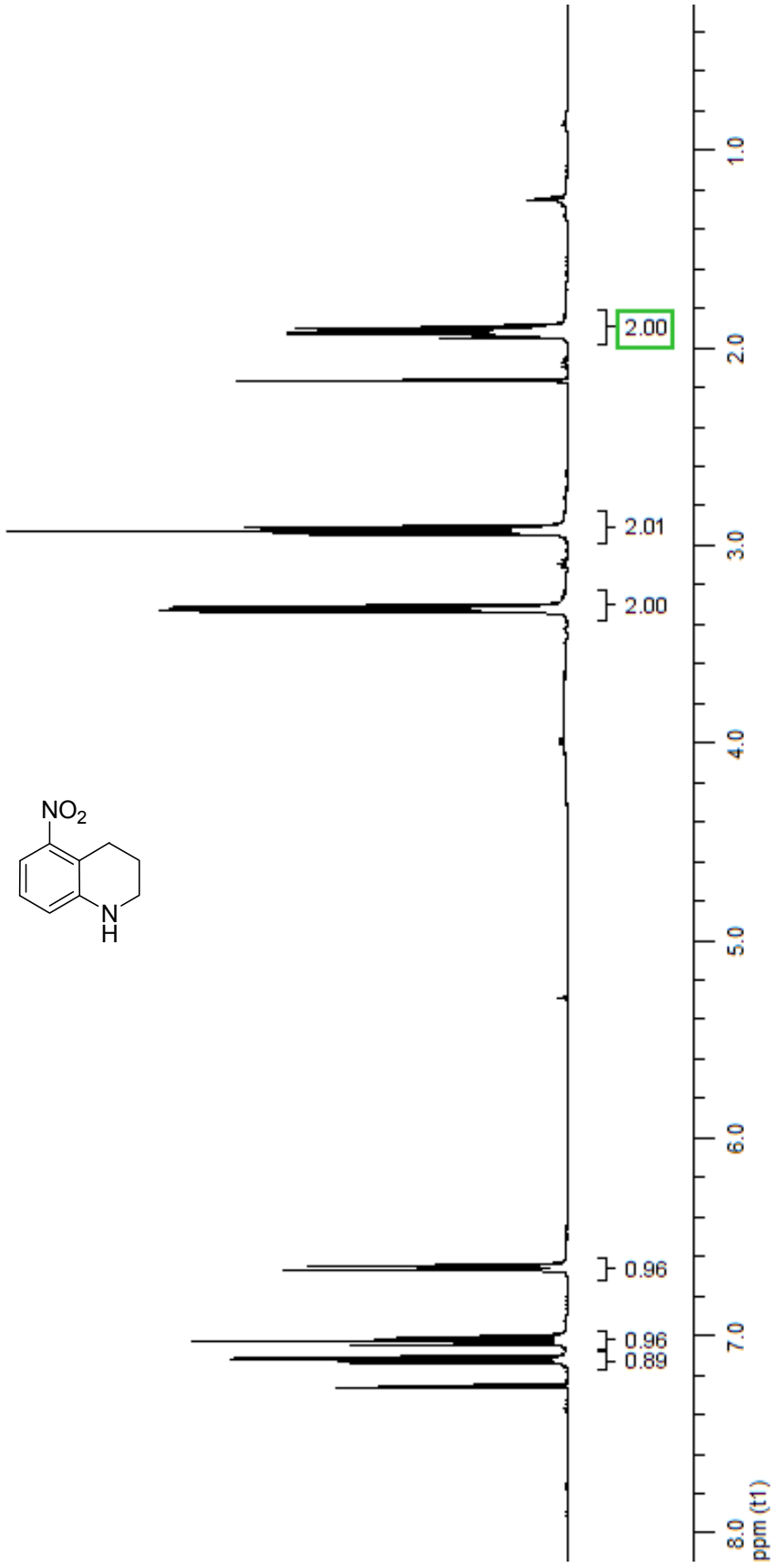

O2N
N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

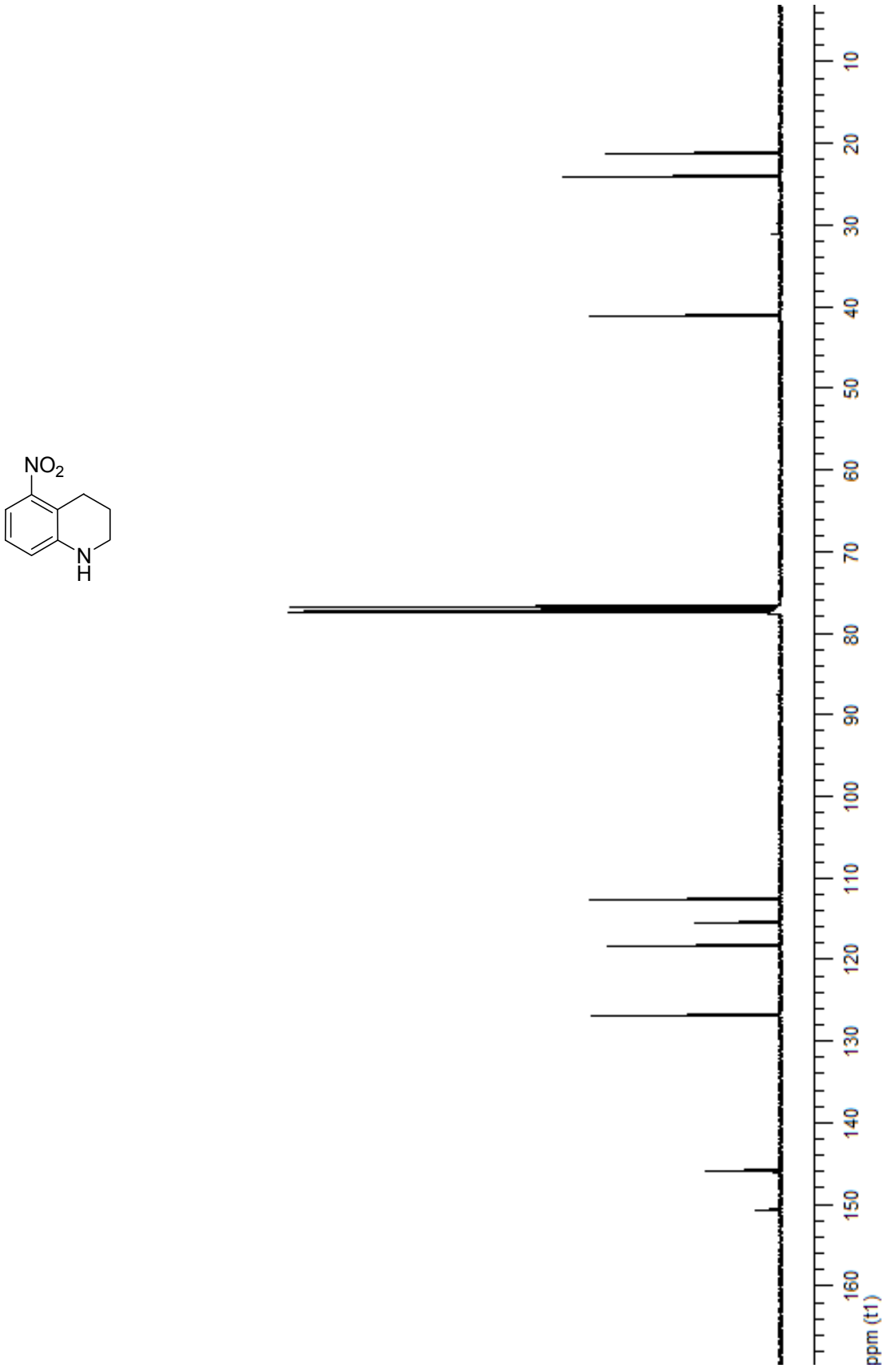
compound 5i:



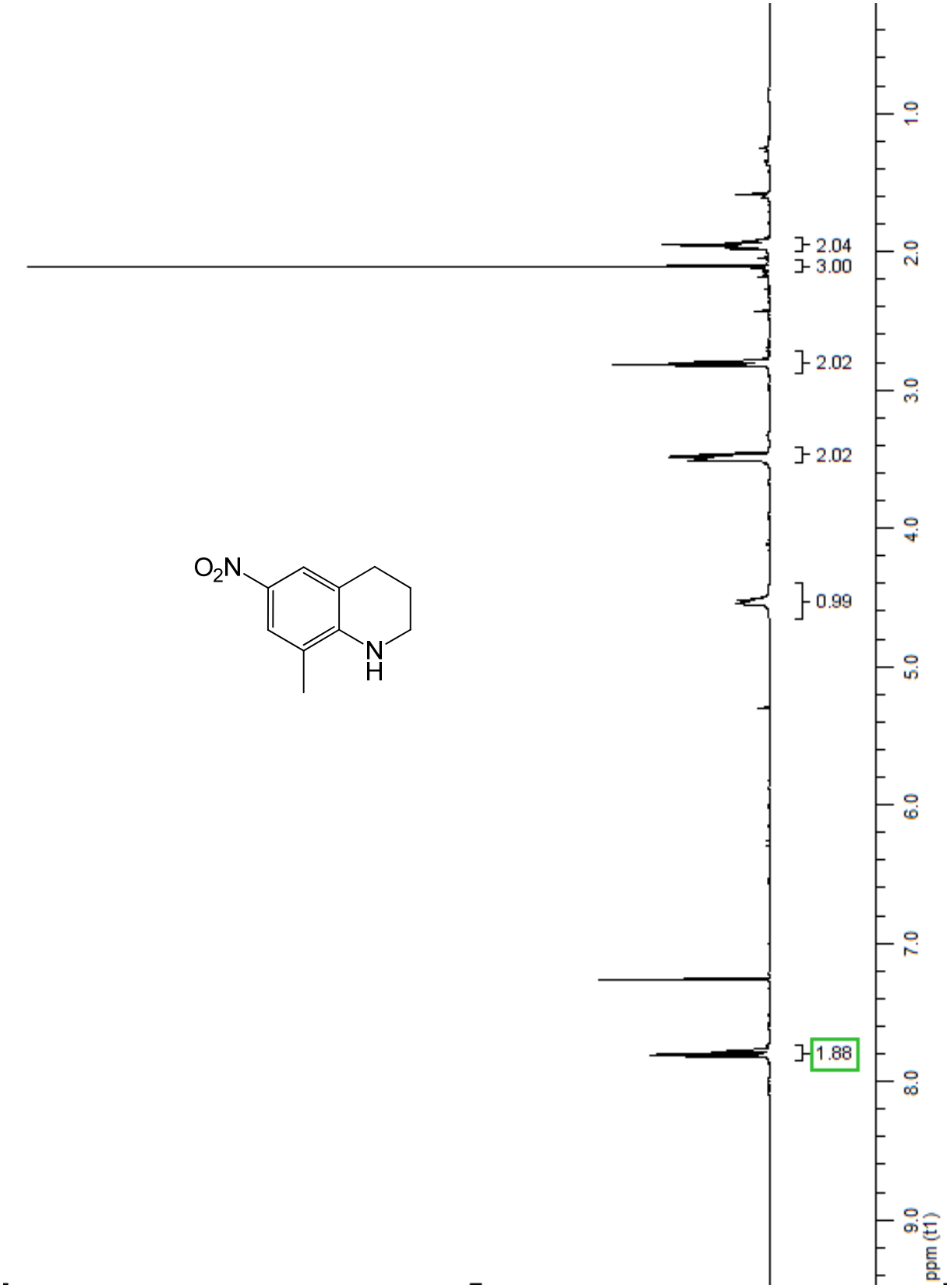

O2N
N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
ppm (t1)

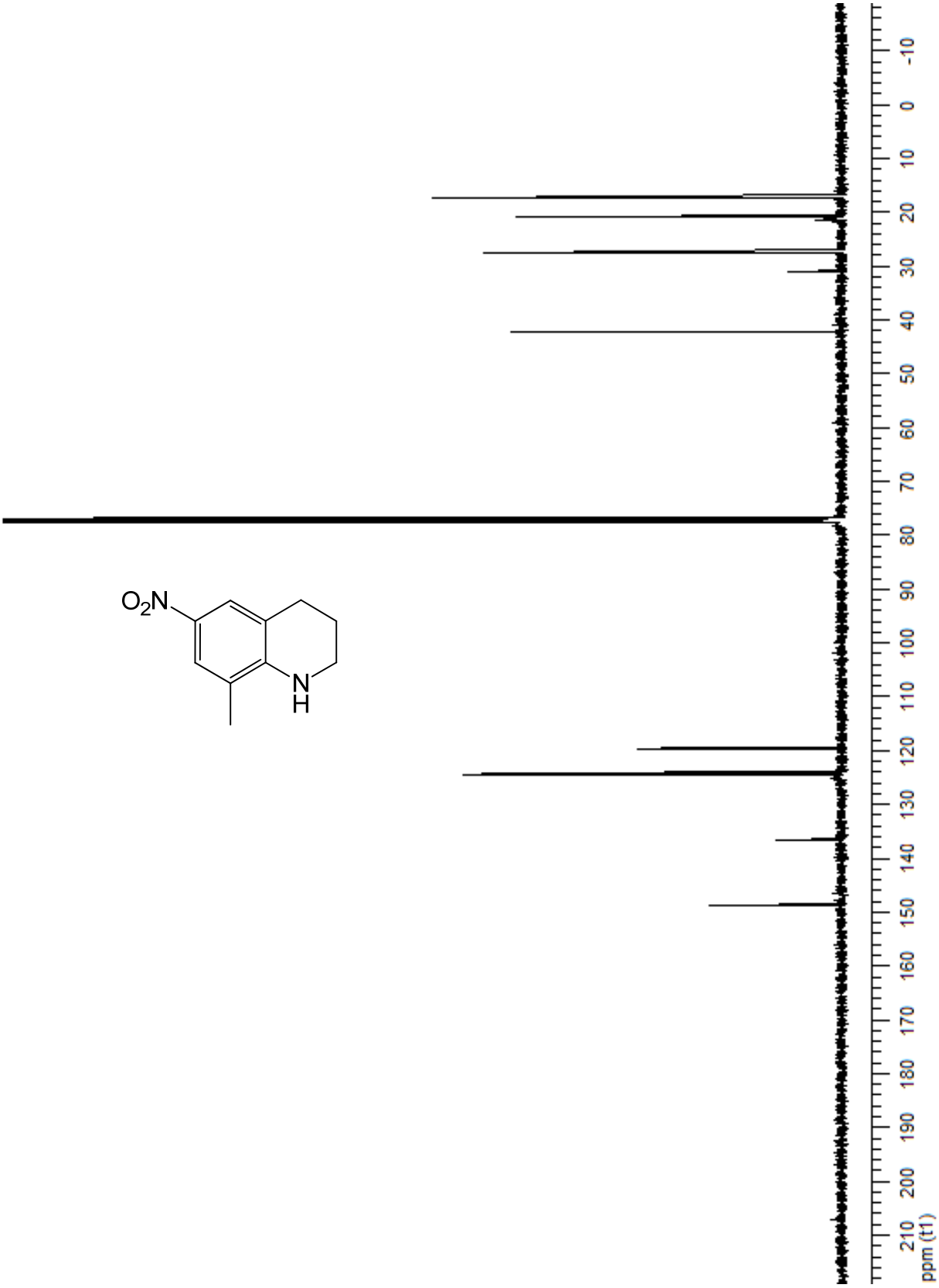
Compound 5i':



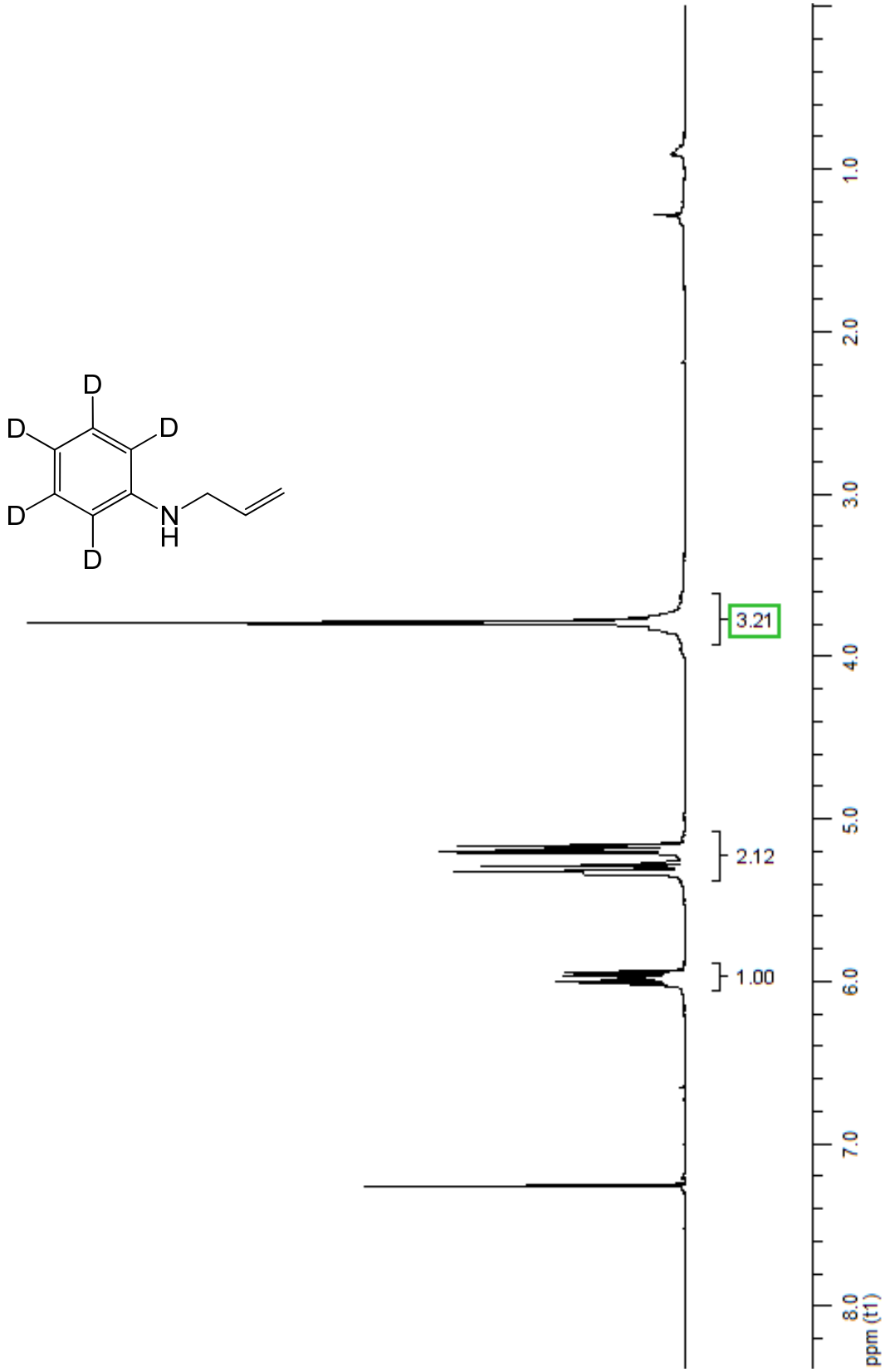


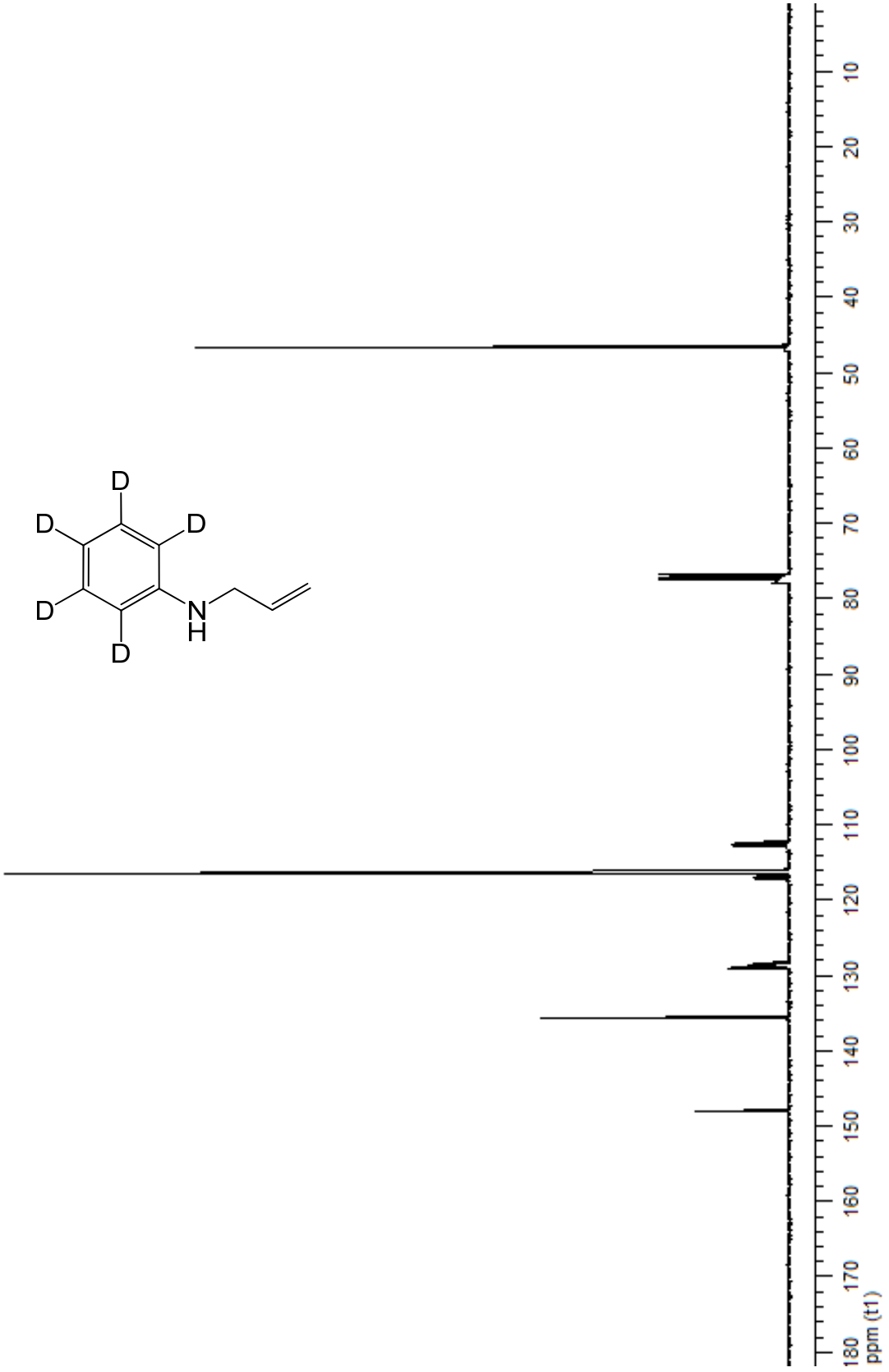
Compound 5j:



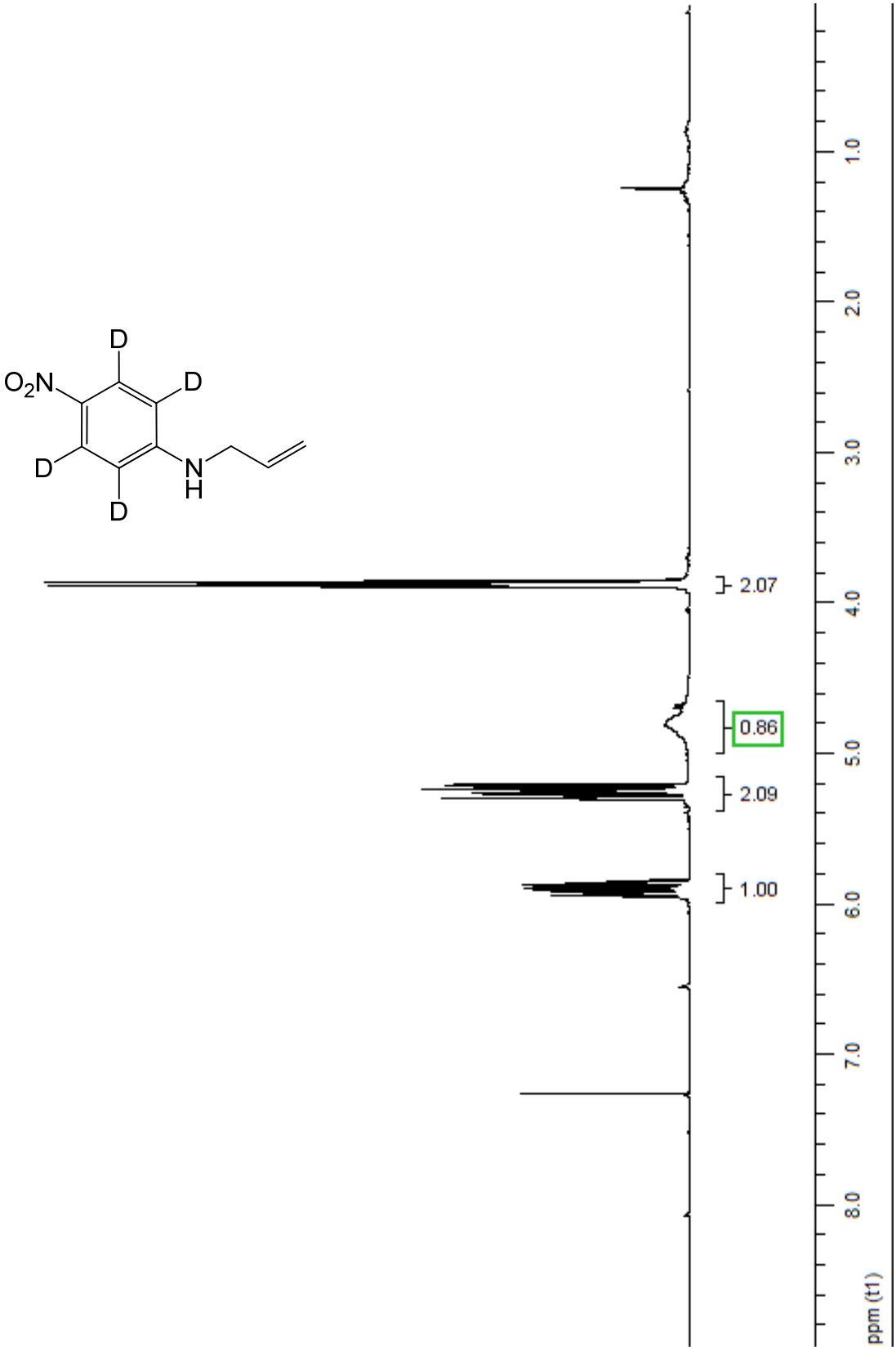

O2N
N
H
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm (t1)

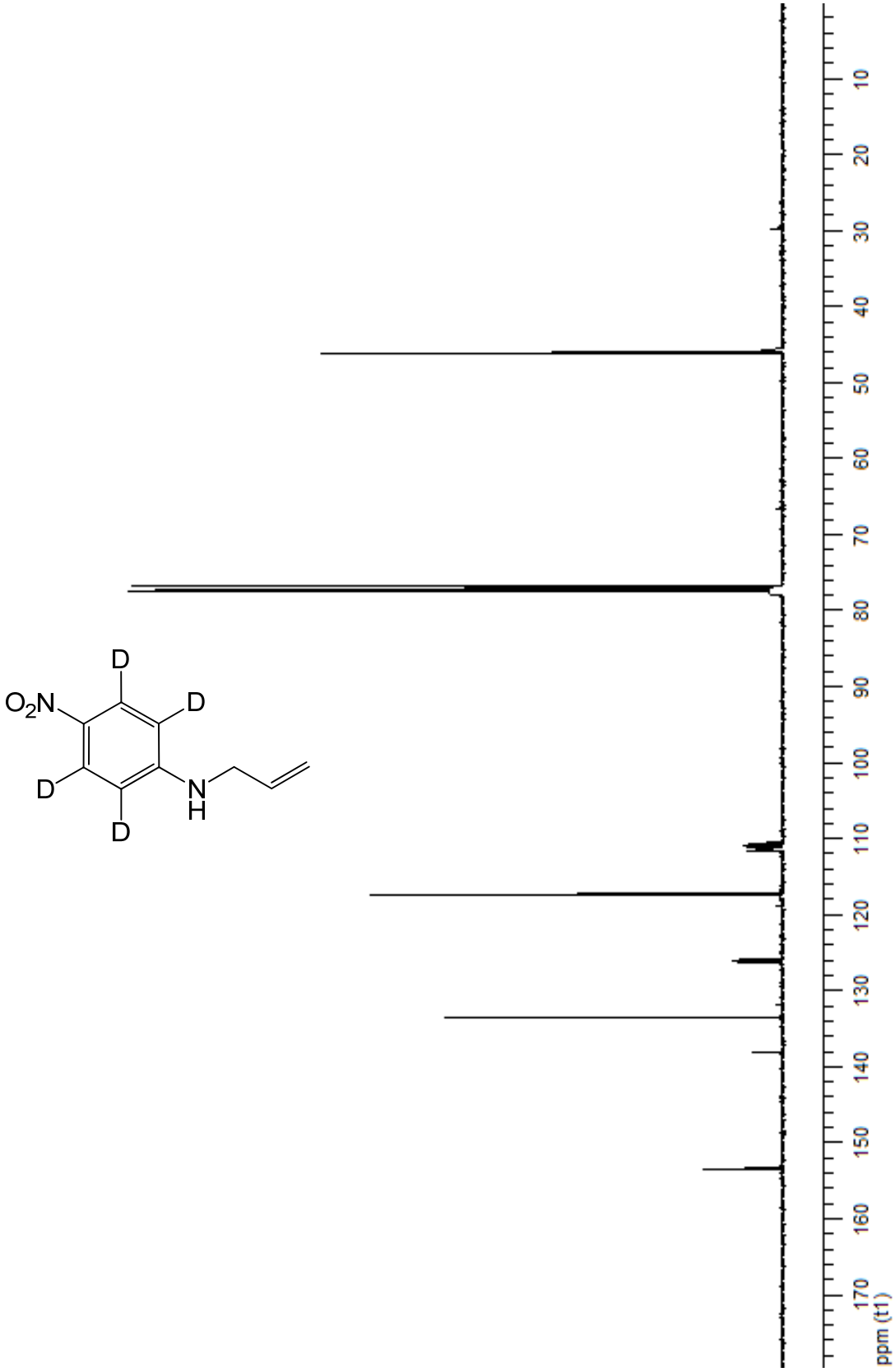
Compound 1'b:



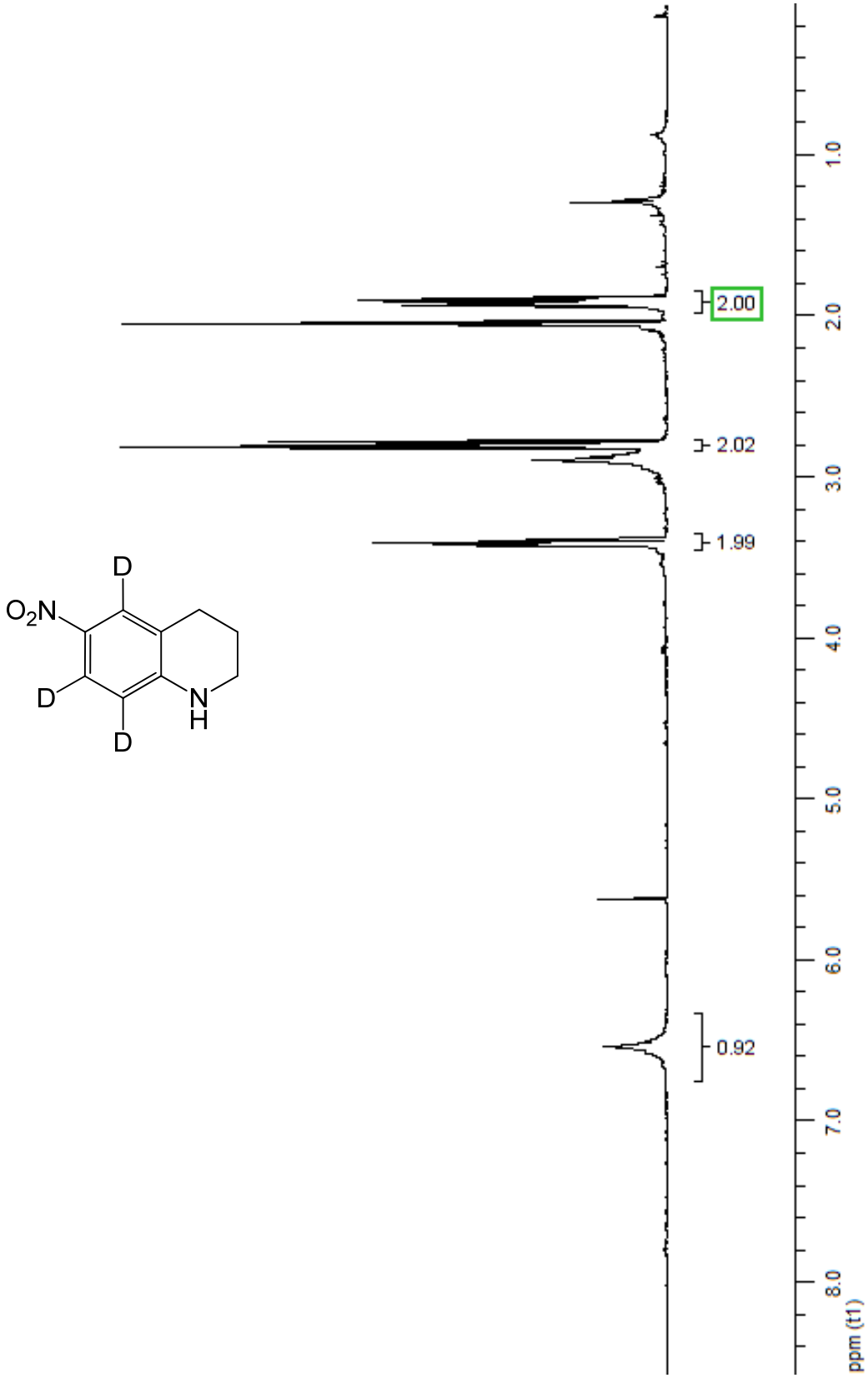

D
D
D
D
D
N
H
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
ppm (t1)

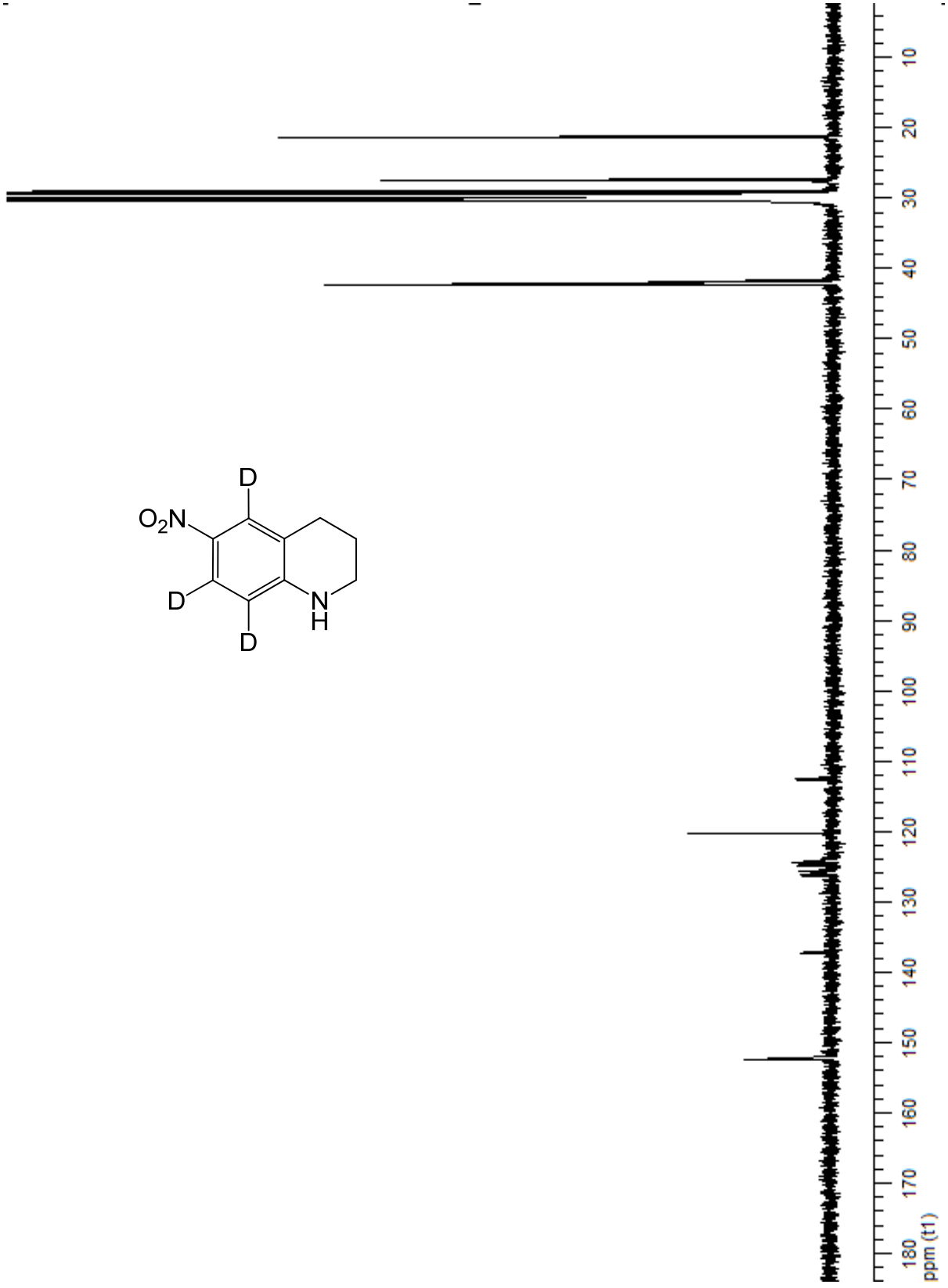
Compound 1'h:



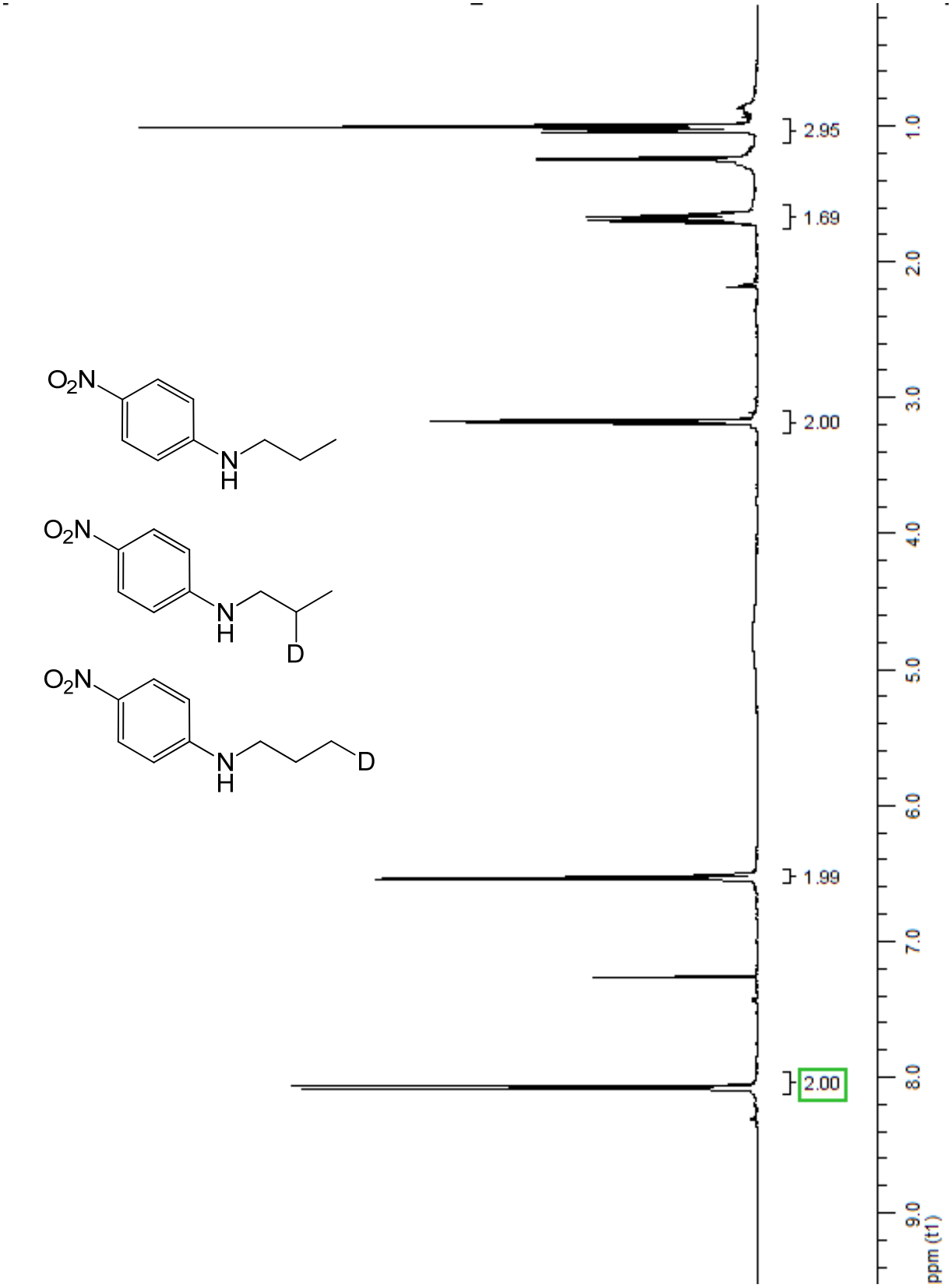

D
O2N
D
D
N
H
D
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm (t1)

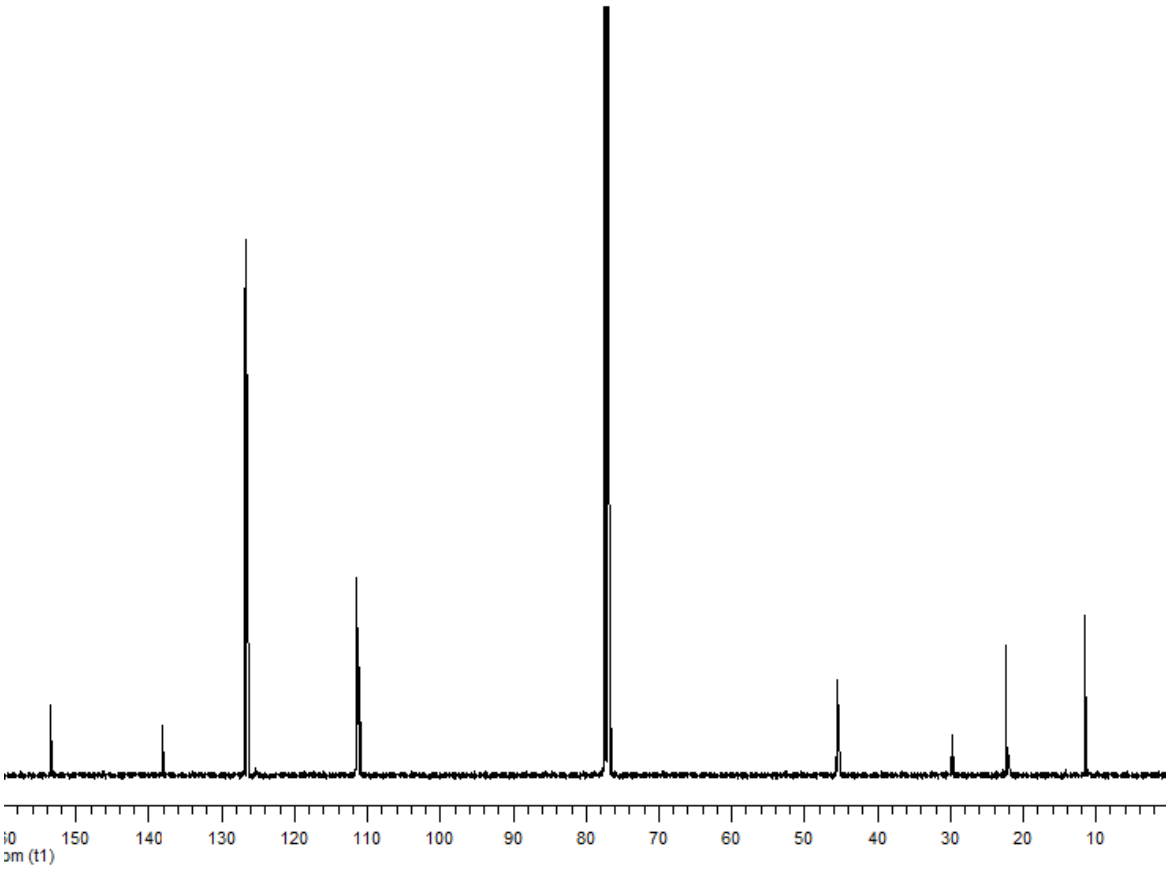
Compound 5'h:

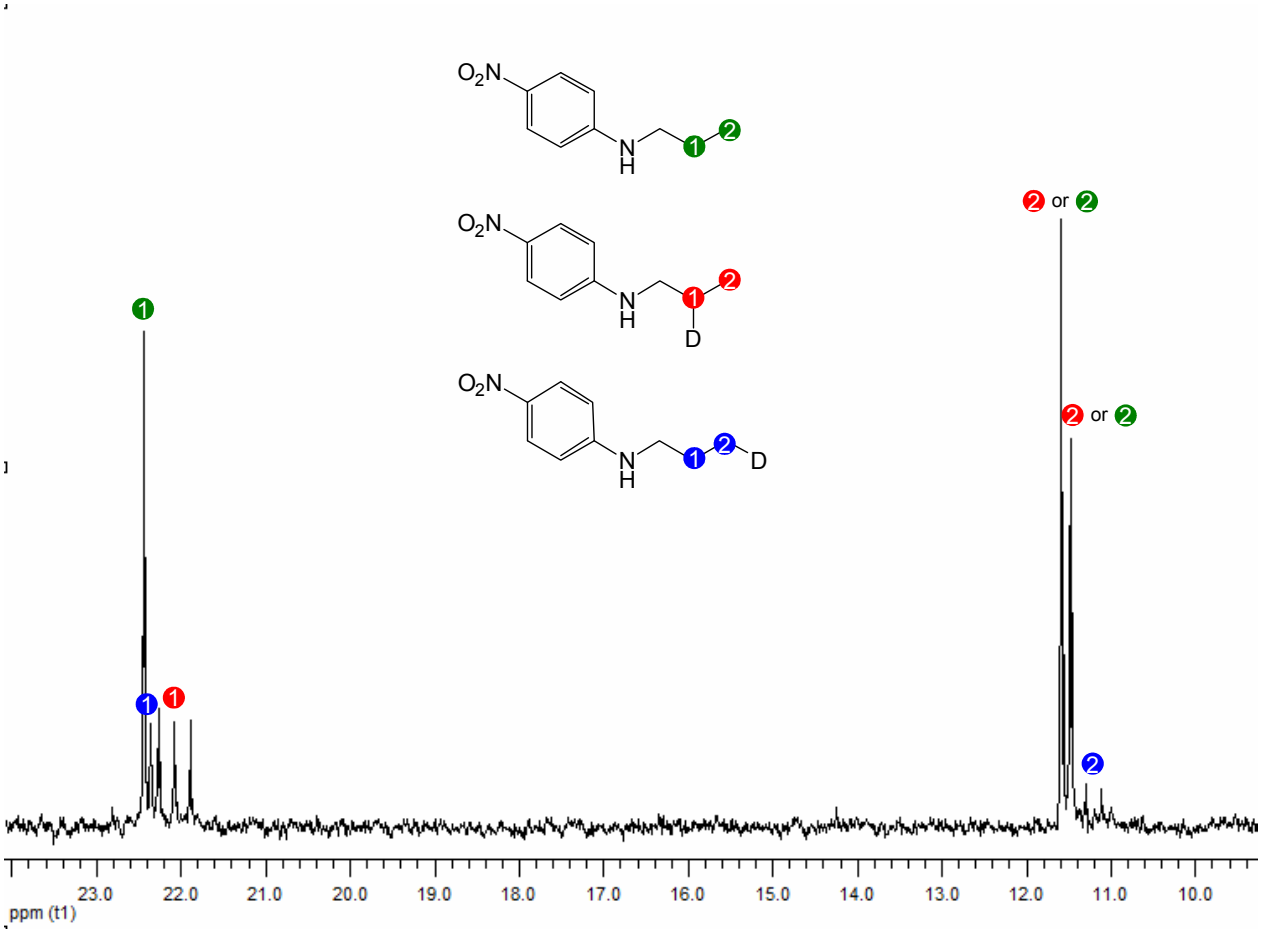


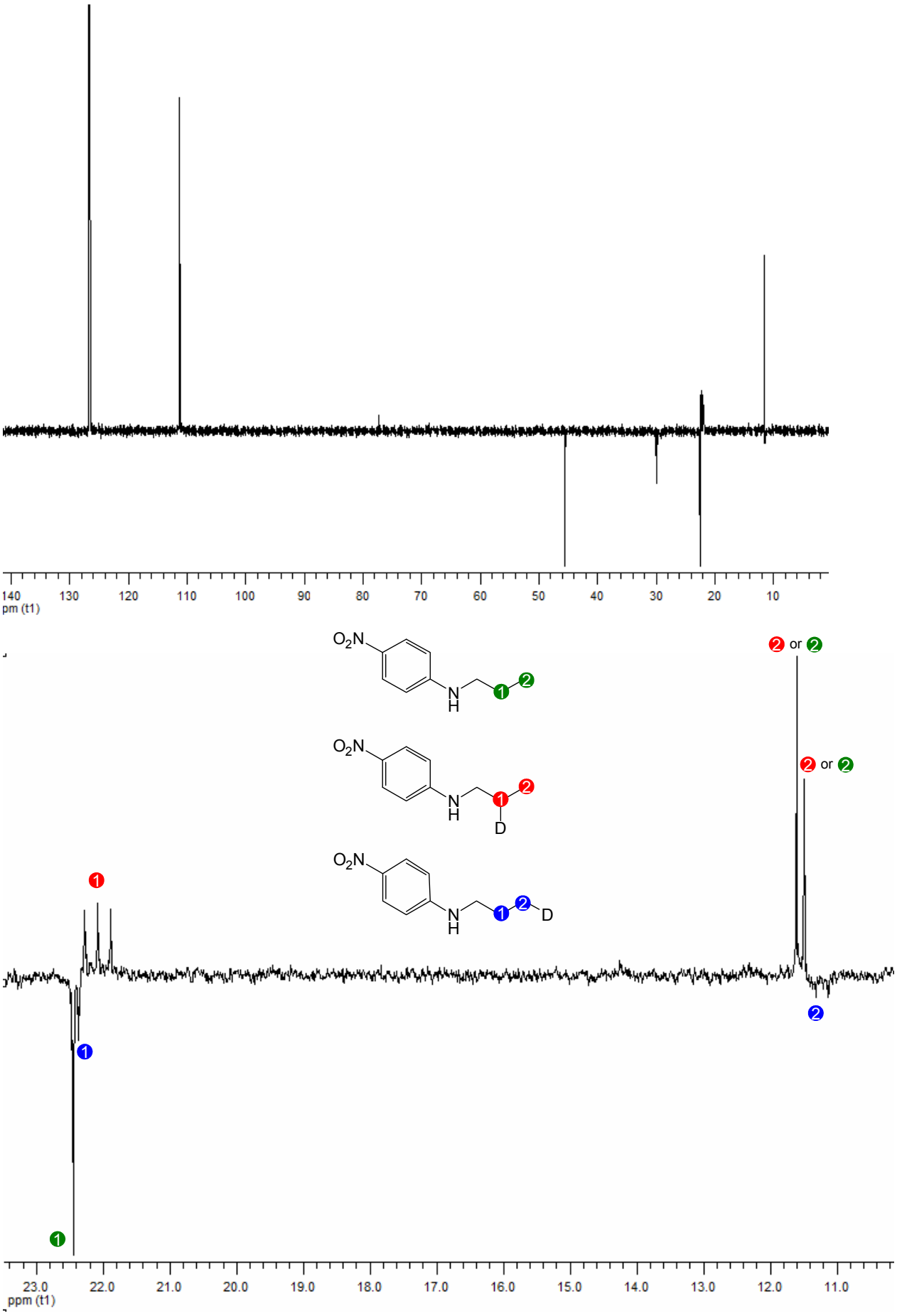

D
O2N
D
N
H
D
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
ppm (t1)

Compounds 11, 12 and 13:




150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


O2N
N
H
D
1
2
2 or 2
23.0
22.0
21.0
20.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
ppm (t1)


140
130
120
110
100
90
80
70
60
50
40
30
20
10
pm (t1)
O2N
N
H
D
2 or 2
2 or 2
23.0
22.0
21.0
20.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
ppm (t1)