Supporting Information

Formic Acid as a Sustainable and Complementary Reductant: Approach to Fused Benzimidazoles by Molecular Iodine-Catalyzed Reductive Redox Cyclization of *o*-Nitro-*t*-Anilines

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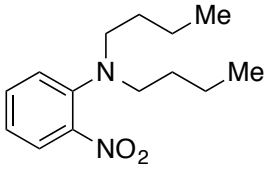
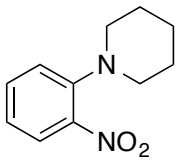
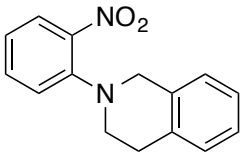
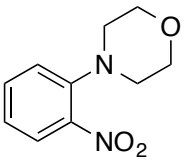
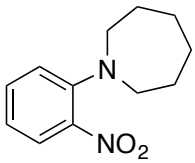
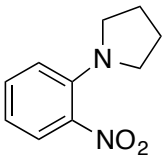
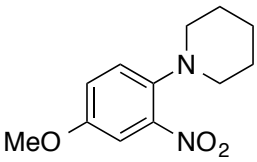
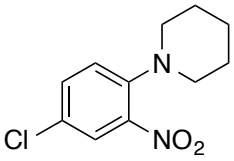
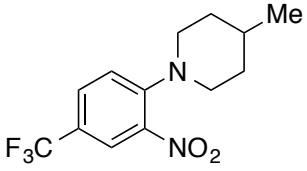
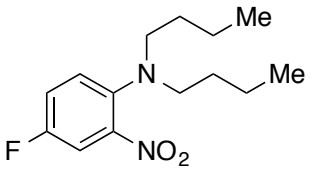
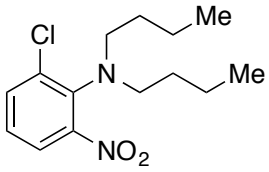
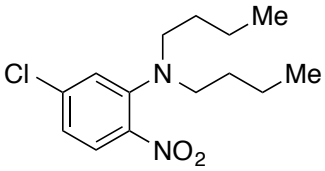
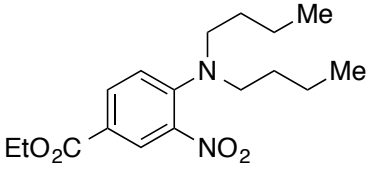
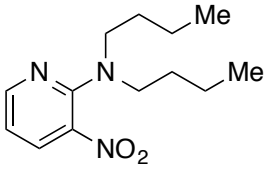
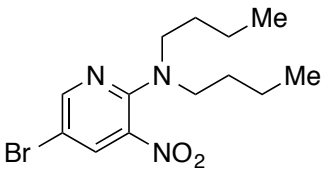
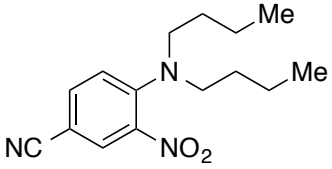
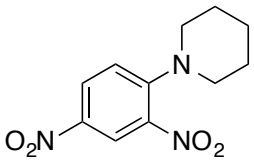
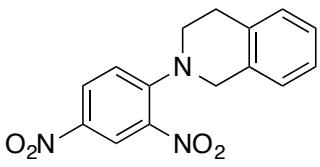
General information

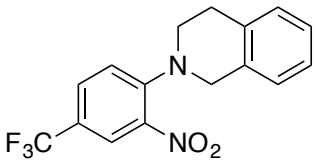
Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^{1}H and δ 77.0 ppm for ^{13}C; CD_3OD, *δ* 3.31 ppm for ^{1}H and δ 49.0 ppm for ^{13}C; DMSO-d6, δ 2.50 ppm for ^{1}H and δ 39.5 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

General procedure for the synthesis of *o*-nitroanilines 1

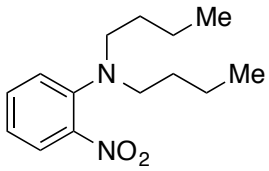
Amine (15 mmol) was added dropwise to *o*-halonitrobenzene (5 mmol) at rt (dilution of *o*-halonitrobenzene with CH_2Cl_2 was necessary when the reaction was too exothermic). The resulting mixture was stirred according to the conditions indicated in the following table. The reaction mixture cooled to rt was diluted with minimum amount CH_2Cl_2, filtered through a short path of silical gel. The orange fractions were collected and evaporated to afford the corresponding *o*-nitroanilines **1** in practically quantitative yields.

Entry	**1**		conditions
1	**1a**		120 °C, 24 h
2	**1b**		100 °C, 1 h
3	**1c**		100 °C, 1 h
4	**1d**		110 °C, 1 h
5	**1e**		120 °C, 16 h
6	**1f**		80 °C, 1 h
7	**1g**		110 °C, 16 h
8	**1h**		60 °C, 16 h
8	**1i**		rt, 20 min

9	**1j**		80 °C, 16 h from 1,4-difluoro-2-nitrobenzene
10	**1k**		120 °C, 20 h
11	**1l**		60 °C, 20 h
12	**1m**		rt, 20 h
13	**1n**		CH_2Cl_2 (1 mL for 2 mmol nitro compound) rt, 16 h
14	**1o**		CH_2Cl_2 (1 mL for 2 mmol nitro compound) rt, 16 h
15	**1p**		rt, 2 h then 70 °C, 16 h
16	**1q**		PhMe (1 mL for 1 mmol 2,4-dinitrofluorobenzene), rt, 15 min
17	**1r**		CH_2Cl_2 (1 mL for 1 mmol 2,4-dinitrofluorobenzene), rt, 15 min

18	**1s**		70 °C, 1h

_N,N_-Dibutyl-2-nitroaniline (1a)



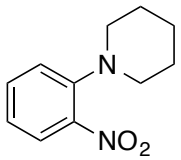
Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.1, 1.5 Hz, 1H), 7.39 (td, J = 8.1, 1.5 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.10 (t, J = 8.1 Hz, 1H), 6.87 (t, J = 7.4 Hz, 4H), 3.06 (triplet, J = 7.4 Hz, 4H), 1.46 (quintuplet, J = 7.4 Hz, 4H), 1.24 (sextuplet, J = 7.4 Hz, 4H), 0.85 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 143.4, 132.7, 126.0, 122.4, 119.9, 52.5, 29.7, 20.3, 14.1.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{14}H_{23}N_2O_2$: 251.1760. Found: 251.1773.

1-(2-Nitrophenyl)piperidine (1b)

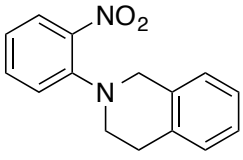


Orange solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.1, 1.5 Hz, 1H), 7.42 (td, J = 8.1, 1.5 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.94 (t, J = 8.1 Hz, 1H), 3.03-2.95 (m, 4H), 1.74-1.52 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 142.8, 133.5, 126.2, 121.0, 120.8, 53.1, 26.1, 24.2.

2-(2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (1c)[1]



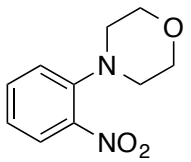
Orange solid. mp. 100 °C (lit. 100-102 °C).[1]

[1] Hedley, K. A.; Stanforth, S. P. *Tetrahedron* **1992**, *48*, 743.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.80 (m, 1H), 7.50-7.44 (m, 1H), 7.23-7.08 (m, 5H), 7.00-6.95 (m, 1H), 4.33 (s, 2H), 3.40 (t, J = 5.8 Hz, 2H), 3.02 (t, J = 5.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 141.8, 134.7, 133.9, 133.6, 128.9, 126.8, 126.6, 126.5, 126.3, 120.4, 120.0, 52.7, 50.3, 29.0.

4-(2-Nitrophenyl)morpholine (1d)

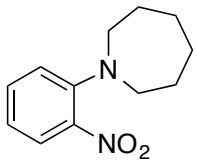


Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.1, 1.5 Hz, 1H), 7.47 (td, J = 8.1, 1.5 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 7.05 (t, J = 8.1 Hz, 1H), 3.80 (m, 4H), 3.03 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 143.9, 133.7, 126.1, 122.5, 121.1, 67.0, 52.3.

1-(2-Nitrophenyl)azepane (1e)

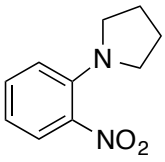


Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.1, 1.5 Hz, 1H), 7.32 (td, J = 8.1, 1.5 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.69 (t, J = 8.1 Hz, 1H), 3.27-3.23 (m, 4H), 1.81-1.73 (m, 4H), 1.60-1.53 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 138.9, 132.8 ,126.9, 118.5, 116.8, 52.1, 28.4, 28.3.

1-(2-Nitrophenyl)pyrrolidine (1f)

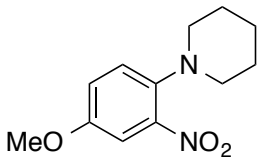


Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.1, 1.5 Hz, 1H), 7.33 (td, J = 8.1, 1.5 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.68 (t, J = 8.1 Hz, 1H), 3.20-3.16 (m, 4H), 1.97-1.93 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 137.2, 133.1, 126.8, 116.1, 115.6, 50.5, 25.9

1-(4-Methoxy-2-nitrophenyl)piperidine (1g)



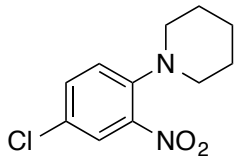
Orange red solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 3.0 Hz, 1H), 7.14 (d, J = 9.0 Hz, 1H), 7.05 (dd, J = 9.0, 3.0 Hz, 1H), 3.81 (s, 3H), 2.93-2.89 (m, 4H), 1.74-1.66 (m, 4H), 1.60-1.51 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 144.8, 141.3, 123.3, 120.2, 109.6, 56.0, 54.2, 26.4, 24.2.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{12}H_{17}N_2O_3$: 237.1239. Found: 237.1230.

1-(4-Chloro-2-nitrophenyl)piperidine (1h)



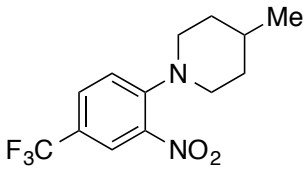
Orange solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 2.7 Hz, 1H), 7.36 (dd, J = 9.0, 2.7 Hz, 1H), 7.03 (d, J = 9.0 Hz, 1H), 2.99-2.95 (m, 4H), 1.72-1.53 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 142.5, 133.5, 126.0, 125.6, 122.4, 53.2, 26.0, 24.1

HRMS-ESI+: m/z [M + H]+ calcd for $C_{11}H_{14}ClN_2O_2$: 241.0744. Found: 241.0752.

4-Methyl-1-(2-nitro-4-(trifluoromethyl)phenyl)piperidine (1i)



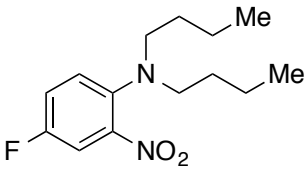
Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 2.2 Hz, 1H), 7.60 (dd, J = 8.9, 2.2 Hz, 1H), 7.14 (d, J = 8.9 Hz, 1H), 3.35-3.29 (m, 2H), 2.99-2.90 (m, 2H), 1.76-1.70 (m, 2H), 1.65-1.52 (m, 1H), 1.45-1.31 (m, 2H), 0.99 (d, J = 6.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 139.9, 130.1 (q, J = 3.5 Hz), 124.6 (q, J = 3.4 Hz), 123.7 (q, J = 271 Hz), 120.9 (q, J = 35.9 Hz), 120.7, 51.7, 34.0, 30.6, 21.9.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{13}H_{16}F_3N_2O_2$: 289.1164. Found: 289.1172.

***N*,*N*-Dibutyl-4-fluoro-2-nitroaniline (1j)**



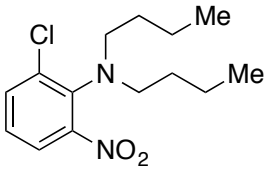
Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.35 (m,1H), 7.16-7.13 (m, 2H), 2.99 (triplet, J = 7.4 Hz, 4H), 1.41 (quintuplet, J = 7.4 Hz, 4H), 1.24 (sextuplet, J = 7.4 Hz, 4H), 0.84 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4 (d, J = 241 Hz), 144.6 (d, J = 8.5 Hz), 141.9, 125.1 (d, J = 7.5 Hz), 120.1 (d, J = 22.0 Hz), 112.3 (d, J = 26.7 Hz), 53.4, 29.7, 20.3, 14.1.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{14}H_{22}FN_2O_2$: 269.1665. Found: 269.1674.

_N_,_N_-Dibutyl-2-chloro-6-nitroaniline (1k)



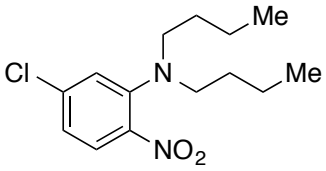
Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 8.0 Hz, 1H), 3.03 (triplet, J = 7.4 Hz, 4H), 1.41 (quintuplet, J = 7.4 Hz, 4H), 1.24 (sextuplet, J = 7.4 Hz, 4H), 0.85 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 142.1, 136.2, 134.0, 124.8, 122.7, 53.0, 30.9, 20.4, 14.1.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{14}H_{22}ClN_2O_2$: 285.1370. Found: 285.1367.

_N_,_N_-Dibutyl-5-chloro-2-nitroaniline (1l)



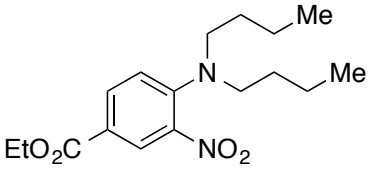
Orange oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.8 Hz, 1H), 7.08 (broad s, 1H), 6.83 (m, 1H), 3.11 (triplet, J = 7.4 Hz, 4H), 1.52 (quintuplet, J = 7.4 Hz, 4H), 1.30 (sextuplet, J = 7.4 Hz, 4H), 0.90 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 140.4, 139.1, 127.7, 121.5, 119.2, 52.1, 29.6, 20.3, 14.0.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{14}H_{22}ClN_2O_2$: 285.1370. Found: 285.1376.

Ethyl 4-(dibutylamino)-3-nitrobenzoate (1m)



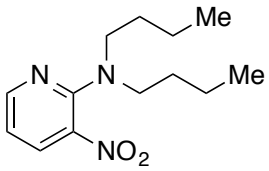
Orange oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (broad s, 1H), 8.00 (m, 1H), 7.06 (d, J = 9.1 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.22 (triplet, J = 7.4 Hz, 4H), 1.57 (quintuplet, J = 7.4 Hz, 4H), 1.39 (t, J = 7.1 Hz, 3H), 1.30 (sextuplet, J = 7.4 Hz, 4H), 0.90 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 148.0, 139.7, 133.8, 133.6, 128.9, 119.6, 61.2, 51.8, 29.6, 20.2, 14.6, 13.9.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{17}H_{27}N_2O_4$: 323.1971. Found: 323.1977.

***N*,*N*-Dibutyl-3-nitropyridin-2-amine (1n)**



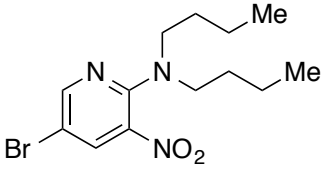
Orange oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26-8.25 (m, 1H), 8.01-7.99 (m, 1H), 6.62-6.59 (m, 1H), 3.34 (triplet, J = 7.4 Hz, 4H), 1.55 (quintuplet, J = 7.4 Hz, 4H), 1.25 (sextuplet, J = 7.4 Hz, 4H), 0.87 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 151.5, 135.4, 133.0, 112.1, 49.8, 29.8, 20.3, 14.0.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{13}H_{22}N_3O_2$: 252.1712. Found: 252.1719.

***N*,*N*-Dibutyl-3-nitropyridin-2-amine (1o)**



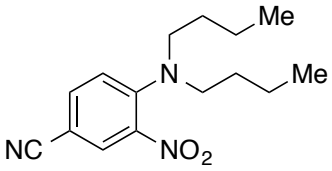
Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, J = 2.3 Hz, 1H), 8.13 (d, J = 2.3 Hz, 1H), 3.32 (triplet, J = 7.4 Hz, 4H), 1.53 (quintuplet, J = 7.4 Hz, 4H), 1.25 (sextuplet, J = 7.4 Hz, 4H), 0.87 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 151.4, 137.0, 132.5, 104.6, 50.0, 29.6, 20.2, 14.0.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{13}H_{21}BrN_3O_2$: 330.0817. Found: 330.0829.

4-(Dibutylamino)-3-nitrobenzonitrile (1p)



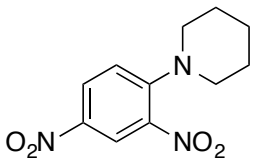
Orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 2.2 Hz, 1H), 7.50 (dd, J = 8.9, 2.2 Hz, 1H), 7.04 (d, J = 8.9 Hz, 1H), 3.17 (triplet, J = 7.4 Hz, 4H), 1.52 (quintuplet, J = 7.4 Hz, 4H), 1.24 (sextuplet, J = 7.4 Hz, 4H), 0.85 (triplet, J = 7.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 139.1, 135.3, 131.6, 120.3, 118.1, 99.5, 51.8, 29.5, 20.1, 13.8.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{15}H_{22}N_3O_2$: 276.1712. Found: 252.1725.

1-(2,4-Dinitrophenyl)piperidine (1q)

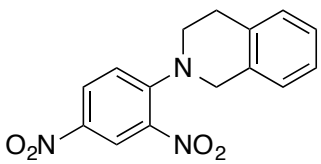


Orange solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, J = 2.8 Hz, 1H), 8.17 (dd, J = 9.5, 2.8 Hz, 1H), 7.06 (d, J = 9.5 Hz, 1H), 3.25-3.19 (m, 4H), 1.76-1.64 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 137.5, 137.5, 128.2, 119.3, 52.0, 25.6, 23.7.

2-(2,4-Dinitrophenyl)-1,2,3,4-tetrahydroisoquinoline (1r)



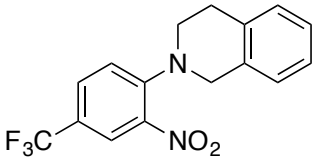
Orange solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, J = 2.8 Hz, 1H), 8.27 (dd, J = 9.5, 2.8 Hz, 1H), 7.30-7.21 (m, 4H), 7.16-7.10 (m, 1H), 4.40 (s, 2H), 3.64-3.60 (m, 2H), 3.09-3.05 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 137.4, 136.8, 134.4, 132.4, 128.5, 128.3, 127.6, 127.0, 126.5, 124.4, 117.4, 52.1, 48.9, 28.6.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{15}H_{14}N_3O_4$: 300.0984. Found: 300.0975.

2-(2-Nitro-4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (1s)



Yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 2.1 Hz, 1H), 7.67 (dd, J = 8.9, 2.1 Hz, 1H), 7.29-7.10 (m, 5H), 4.37 (s, 2H), 3.53 (t, J = 5.8 Hz, 2H), 3.05 (t, J = 5.8 Hz, 2H).

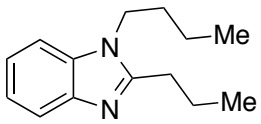
^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 138.7, 134.6, 133.1, 130.1 (q, J = 2.8 Hz), 128.7, 127.2, 126.7, 126.4, 124.9 (q, J = 3.3 Hz), 123.6 (q, J = 271 Hz), 120.5 (q, J = 34 Hz), 118.9, 52.0, 49.2, 28.7.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{16}H_{14}F_3N_2O_2$: 323.1007. Found: 323.1022.

General procedure for reductive cyclization of *o*-nitro-*t*-anilines (1) into benzimidazoles (2)

A mixture of *o*-nitro-*t*-anilines **1** (0.25 mmol) and molecular iodine (10-20 mol%) in formic acid (0.2-0.5 mL) was heated at indicated conditions of temperatures and reaction times (see the manuscript) in a closed 17-mL test tube under an argon atmosphere. The tube cooled to rt was carefully opened. After removal of excess formic acid (80 °C, 0.01 mmHg), the residue was dissolved in DCM (2-4 mL) and treated with a saturated ammonia solution in methanol (3-5 drops). After removal of excess NH_3 and volatiles, purification of the residue by chromatography afforded the desired benzimidazole **2**.

1-Butyl-2-propyl-1*H*-benzo[*d*]imidazole (2a)



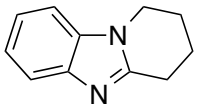
Purification of the crude mixture by silica gel column chromatography (AcOEt) afforded the product as a pale yellow powder (46 mg, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.2, 2.0 Hz, 1H), 7.44 (dd, J = 7.6, 2.0 Hz, 1H), 7.24 (m, 2H), 4.22 (t, J = 7.6 Hz, 2H), 2.89 (t, J = 7.7 Hz, 2H), 1.91 (m, 2H), 1.79 (m, 2H), 1.40 (m, 2H), 1.08 (t, J = 7.3 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 141.6, 134.8, 122.0, 121.8, 117.6, 109.7, 43.0, 31.7, 28.6, 21.0, 19.7, 12.9, 12.8.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{14}H_{21}N_2$: 217.1705. Found: 217.1700.

1,2,3,4-Tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2b)



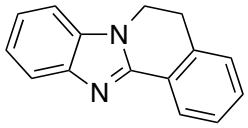
Purification of the crude mixture by silica gel column chromatography (AcOEt) afforded the product as a pale yellow powder (38.7 mg, 90%).

^{1}H NMR (300 MHz, CD_3OD) δ 7.55-7.49 (m, 1H), 7.33-7.29 (m, 1H), 7.22-7.16 (m, 2H), 4.00-3.96 (m, 2H), 2.97-2.93 (m, 2H), 2.09-1.90 (m, 4H).

^{13}C NMR (75 MHz, CD_3OD) δ 153.3, 142.9, 135.8, 123.6, 123.2, 118.8, 110.6, 43.6, 25.9, 23.6, 21.5.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{11}H_{13}N_2$: 173.1079. Found: 173.1070.

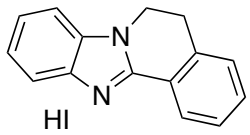
5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (2c)



Purification of the crude mixture by silica gel column chromatography (AcOEt) afforded the product as a pale yellow powder (50.6 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29-8.27 (m, 1H), 7.82-7.79 (m, 1H), 7.40-7.24 (m, 6H), 4.29 (t, J = 6.9 Hz, 2H), 3.25 (t, J = 6.9 Hz, 2H).

5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline hydroiodide (2c·HI)



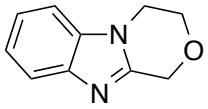
The crude mixture cooled to rt was diluted with Et_2O (5 mL). The solid was filtered, washed with Et_2O to provide the expected product as a pale yellow solid (80 mg, 92%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 14.46 (broad s, 1H), 8.16-8.14 (m, 1H), 8.05-8.00 (m, 1H), 7.92-7.86 (m, 1H), 7.74-7.58 (m, 5H), 4.66 (t, J = 7.1 Hz, 2H), 3.44 (t, J = 7.1 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 145.8, 136.8, 133.8, 131.6, 131.3, 129.2, 128.0, 126.4, 126.0, 125.8, 119.8, 114.2, 112.8, 40.9, 26.2.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{15}H_{13}N_2$: 221,1079. Found: 221,1067.

3,4-Dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2d)



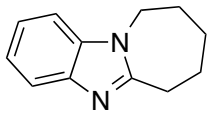
Purification of the crude mixture by silica gel column chromatography (AcOEt) afforded the product as a yellow powder (24.8 mg, 57%).

^{1}H NMR (300 MHz, CD_3OD) δ 7.60 (m, 1H), 7.48 (m, 1H), 7.28 (m, 2H), 4.98 (s, 2H), 4.20 (s, 2H).

^{13}C NMR (75 MHz, CD_3OD) δ 149.7, 142.9, 135.3, 124.0, 123.8, 119.4, 110.6, 65.7, 65.1, 43.2.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{10}H_{11}N_2O$: 175.0871. Found: 175.0862.

7,8,9,10-Tetrahydro-6*H*-benzo[4,5]imidazo[1,2-*a*]azepine (2e)



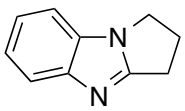
Purification of the crude mixture by silica gel column chromatography (AcOEt) afforded the product as a yellow powder (34.9 mg, 75%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.44 (m, 1H), 7.22 (m, 2H), 4.28 (m, 2H), 3.10 (m, 2H), 1.99 (m, 2H), 1.82 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 142.5, 137.0, 123.4, 123.0, 119.1, 110.4, 45.4, 31.7, 30.3, 29.8, 26.7.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{12}H_{15}N_2$: 187.1235. Found: 187.1220.

2,3-Dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole (2f)



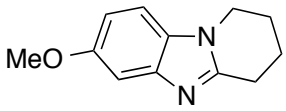
Purification of the crude mixture by silica gel column chromatography (AcOEt) afforded the product as a yellow powder (27.7 mg, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (m, 1H), 7.45 (m, 1H), 7.24 (m, 2H), 4.21 (t, J = 7.0 Hz, 2H), 3.07 (dd, J = 8.4, 7.0 Hz, 2H), 2.77 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 147.1, 132.0, 122.1, 121.9, 117.9, 110.0, 42.8, 25.5, 22.8.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{10}H_{11}N_2$: 159.0922. Found: 159.0935.

7-Methoxy-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2g)



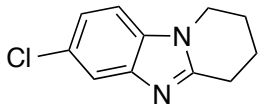
Purification of the crude mixture by silica gel column chromatography (CH_2Cl_2:CH_3OH 100:0 to 98:2) afforded the product as a yellow powder (45 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, *J* = 2.3 Hz, 1H), 7.10 (d, J= 8.9 Hz, 1H), 6.81 (dd, *J* = 2.3, 8.9 Hz, 1H), 3.97 (t, *J* = 6.1 Hz, 2H), 3.80 (s, 3H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.09-2.00 (m, 2H), 1.98-1.90 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 152.0, 143.6, 129.3, 111.3, 109.1, 101.7, 56.0, 42.5, 25.5, 22.7, 20.8.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{12}H_{15}N_2O$: 203.1184. Found: 203.1166.

7-Chloro-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2h)



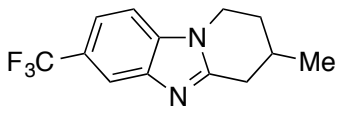
Purification of the crude mixture by silica gel column chromatography (CH_2Cl_2) afforded the product as a pale yellow powder (42.7 mg, 83%).

^{1}H NMR (300 MHz, CD_3OD) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.04 (t, *J* = 6.0 Hz, 2H), 2.99 (t, *J* = 6.4 Hz, 2H), 2.14-2.06 (m, 2H), 2.03-1.95 (m, 2H).

^{13}C NMR (75 MHz, CD_3OD) δ 155.0, 143.9, 134.5, 123.3, 118.5, 111.6, 43.8, 25.9, 23.4, 21.3.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{11}H_{12}ClN_2$: 207.0689. Found: 207.0673.

3-Methyl-7-(trifluoromethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2i)



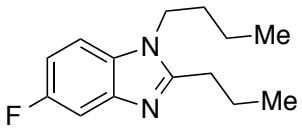
Purification of the crude mixture by silica gel column chromatography (AcOEt) afforded the product as a pale yellow powder (55.9 mg, 88%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.56 (dd, J = 9.7, 8.4 Hz, 2H), 4.32 (m, 1H), 4.02 (m, 1H), 3.16 (dd, J = 8.4, 4.3 Hz, 1H), 2.62 (dd, J = 17.5, 10.5 Hz, 1H), 2.18 (m, 2H), 1.81 (m, 1H), 1.21 (d, J = 6.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 142.8, 136.7, 125.2 (q, J = 273 Hz), 124.7 (q, J = 31 Hz), 118.8 (q, J = 4.4 Hz), 116.7 (q, J = 5.1 Hz), 109.3, 42.0, 33.6, 30.5, 27.7, 21.2.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{13}H_{14}F_3N_2$: 255.1109. Found: 255.1117.

1-Butyl-5-fluoro-2-propyl-1*H*-benzo[*d*]imidazole (2j)



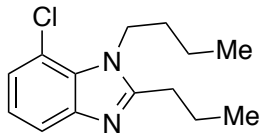
Purification of the crude mixture by TLC chromatography (AcOEt) afforded the product as a colorless oil (49.7 mg, 85%).

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.35 (dd, J = 9.6, 2.3 Hz, 1H), 7.15 (dd, J = 9.6, 4.6 Hz, 1H), 6.93 (td, J = 9.6, 2.3 Hz, 1H), 4.03 (t, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 1.88 (m, 2H), 1.72 (m, 2H), 1.35 (m, 2H), 1.03 (t, J = 7.5 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 160.7, 157.0 (J = 88 Hz), 143.1, 131.6, 109.9 (J = 26 Hz), 109.4 (J = 13 Hz), 105.0 (J = 23 Hz), 43.7, 32.0, 29.6, 21.2, 20.3, 14.2, 13.8.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{14}H_{20}FN_2$: 235.1611. Found: 235.1608.

1-Butyl-7-chloro-2-propyl-1*H*-benzo[*d*]imidazole (2k)



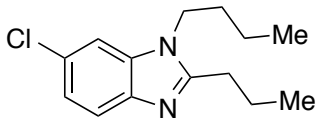
Purification of the crude mixture by TLC chromatography (AcOEt) afforded the product as a colorless oil (40.6 mg, 65%).

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.61 (dd, J = 7.4, 1.3 Hz, 1H), 7.14 (m, 2H), 4.40 (t, J = 7.5 Hz, 2H), 2.83 (t, J = 7.5 Hz, 2H), 1.96 (m, 2H), 1.45 (m, 2H), 1.35 (m, 2H), 1.10 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 156.2, 144.9, 130.8, 123.7, 122.3, 118.0,115.6, 44.5, 34.1, 29.5, 21.1, 20.0, 14.1, 13.8.

HRMS-ESI+: *m/z* [M + H]+ calcd for $C_{14}H_{20}ClN_2$: 251.1315. Found: 251.1302.

1-Butyl-6-chloro-2-propyl-1*H*-benzo[*d*]imidazole (2l)



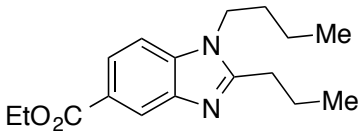
Purification of the crude mixture by TLC chromatography (AcOEt) afforded the product as a colorless oil (38.8 mg, 62%).

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.54 (d, J = 8.5 Hz, 1H), 7.20 (d, J = 2.0 Hz, 1H), 7.10 (dd, J = 8.5, 2.0 Hz, 1H), 3.97 (t, J = 7.5 Hz, 2H), 2.74 (t, J = 7.5 Hz, 2H), 1.86 (m, 2H), 1.69 (m, 2H), 1.32 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 155.8, 141.3, 135.6, 127.6, 122.3, 119.9, 109.4, 43.7, 32.0, 29.4, 21.1, 20.3, 14.1, 13.8.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{14}H_{20}ClN_2$: 251.1315. Found: 251.1302.

Ethyl 1-butyl-2-propyl-1*H*-benzo[*d*]imidazole-5-carboxylate (2m)



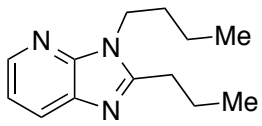
Purification of the crude mixture by TLC chromatography (AcOEt) afforded the product as a colorless oil (51 mg, 71%).

^{1}H NMR (300 MHz, $CDCl_3$), δ 8.44 (d, J = 1.3 Hz, 1H), 7.96 (dd, J = 8.4, 1.3 Hz, 1H), 7.29 (d, J = 8.4 Hz,1H), 4.39 (dd, J = 14.3, 7.3 Hz, 2H), 4.11 (t, J = 7.3 Hz, 2H), 2.84 (t, J = 7.9 Hz, 2H), 1.94 (m, 2H), 1.77 (m, 2H), 1.39 (m, 5H), 1.07 (t, J = 7.5 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 167.5, 156.7, 142.3, 138.3, 124.2, 123.6, 121.5,108.8, 60.8, 43.5, 32.2, 29.6, 21.3, 20.4, 14.4, 14.1, 13.7.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{17}H_{25}N_2O_2$: 289.1916. Found: 289.1898.

3-Butyl-2-propyl-3*H*-imidazo[4,5-*b*]pyridine (2n)



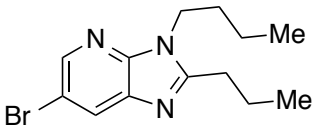
Purification of the crude mixture by TLC chromatography (AcOEt) afforded the product as a colorless oil (40.7 mg, 75%).

^{1}H NMR (300 MHz, $CDCl_3$), δ 8.24 (dd, J = 5.0, 1.5 Hz, 1H), 7.88 (dd, J = 8.0, 1.5 Hz, 1H), 7.28 (2d, J = 8.0, 5.0 Hz, 1H), 4.17 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 1.89 (m, 2H), 1.75 (m, 2H), 1.35 (m, 2H), 1.02 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 156.3, 148.2, 142.9, 134.7, 126.3, 117.9, 42.1, 32.4, 29.9, 20.8, 20.2, 14.1, 13.8.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{13}H_{20}N_3$: 218.1657. Found: 218.1640.

6-Bromo-3-butyl-2-propyl-3*H*-imidazo[4,5-*b*]pyridine (2o)



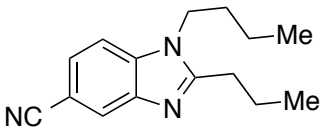
Purification of the crude mixture by TLC chromatography (AcOEt) afforded the product as a colorless oil (48.8 mg, 66%).

^{1}H NMR (300 MHz, $CDCl_3$), *δ* 8.34 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 4.21 (t, *J* = 7.5 Hz, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.95 (m, 2H), 1.80 (m, 2H), 1.39 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 157.7, 146.9, 143.5, 135.9, 128.6, 113.5, 42.4, 32.0, 29.9, 20.8, 20.1, 14.1, 13.8.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{13}H_{19}BrN_3$: 296.0762. Found: 296.0773.

1-Butyl-2-propyl-1*H*-benzo[*d*]imidazole-5-carbonitrile (2p)



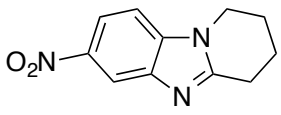
Purification of the crude mixture by TLC chromatography (AcOEt) afforded the product as a colorless oil (44.6 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.97 (d, *J* = 1.5 Hz, 1H), 7.43 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 4.09 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 1.97-1.84 (m, 2H), 1.79-1.68 (m, 2H), 1.42-1.30 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 157.9, 142.5, 138.0, 125.6, 124.2, 120.3, 110.4, 104.9, 3.9, 32.1, 29.5, 21.0, 20.3, 14.2, 13.9.

HRMS-ESI+: *m*/*z* [M + H]+ calcd for $C_{15}H_{20}N_3$: 242.1657. Found: 242.1673.

7-Nitro-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2q)



Purification of the crude mixture by column chromatography (CH_2Cl_2) afforded the product

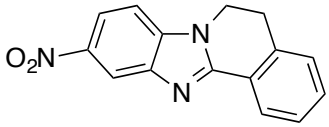
as a colorless solid (43.4 mg, 80%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, J = 2.2 Hz, 1H), 8.08 (dd, J = 8.9, 2.2 Hz, 1H), 7.28 (d, J = 8.9 Hz, 1H), 4.12 (t, J = 6.2 Hz, 2H), 3.09 (f, J = 6.2 Hz, 1H), 2.19-2.10 (m, 2H), 2.08-1.99 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 143.7, 142.2, 138.9, 117.9, 115.5, 108.7, 43.2, 25.7, 22.5, 20.5

HRMS-ESI+: m/z [M + H]+ calcd for $C_{11}H_{12}N_3O_2$: 218.0930. Found: 218.0926.

10-nitro-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (2r)



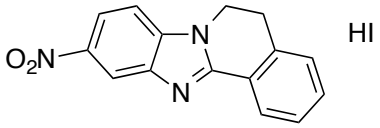
Purification of the crude mixture by column chromatography (CH_2Cl_2 to CH_2Cl_2:MeOH 95:5) afforded the product as a colorless solid (58.4 mg, 88%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, J = 2.0 Hz, 1H), 8.26-8.23 (m, 1H), 8.17 (dd, J = 8.9, 2.0 Hz, 1H), 7.48-7.33 (m, 5H), 4.39 (t, J = 7.0 Hz, 2H), 3.34 (t, J = 7.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 143.9, 143.3, 138.9, 134.6, 131.5, 128.4, 128.1, 126.3, 125.7, 118.7, 116.2, 109.0, 41.0, 28.1.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{15}H_{12}N_3O_2$: 266.0930. Found: 266.0939.

10-Nitro-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline hydroiodide (2r·HI)



After removal of volatiles (0.01 mmHg, 100 °C), the solid residue was washed with Et_2O to provide a yellow solid (93.2 mg, 95%).

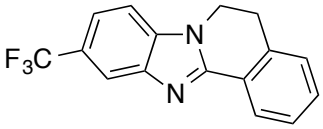
^{1}H NMR (300 MHz, DMSO-d_6) δ 9.71 (broad s, 1H), 8.55 (d, J = 2.0 Hz, 1H), 8.21 (dd, J = 8.9, 2.0 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.58-7.45 (m, 3H), 4.53 (t, J = 7.0 Hz, 2H), 3.34 (t, J = 7.0 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 152.0, 143.1, 141.2, 138.7, 135.9, 131.6, 128.7, 127.6, 125.5, 124.6, 118.3, 114.4, 111.0, 40.6, 26.9.

HRMS-ESI+: m/z [M + H]+ calcd for $C_{15}H_{12}N_3O_2$: 266.0930. Found: 266.0918.

Elemental analysis calcd for $C_{15}H_{12}IN_3O_2$: C, 45.8; H, 3.1; N, 10.7. Found: C, 46.1; H, 3.3; N, 10.7.

10-(Trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline hydroiodide (2s·HI)



The crude reaction mixture was shaken with Et_2O (3 mL) and filtered. The pale yellow solid was washed with Et_2O (3 mL × 2) and dried in vacuo to provide 83 mg of **2s·HI** (80%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 14.45 (broad s, 1H), 8.20-8.14 (m, 3H), 7.89 (d, J = 9.1 Hz, 1H), 7.72-7.67 (m, 1H), 7.62-7.58 (m, 2H), 4.66 (t, J = 7.0 Hz, 2H), 3.43 (t, J = 7.0 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 149.0, 136.9, 134.8, 134.0, 133.6, 129.1, 128.0, 126.2, 125.6 (q, J = 32 Hz), 124.2 (q, J = 272 Hz), 121.6, 121.0, 113.5, 113.0, 41.1, 26.4.

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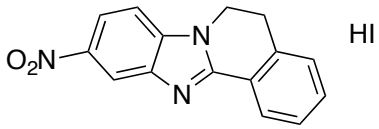
Analyse n° **18925** du **21.12.2015**
A l'attention de **Mr NGUYEN Thanh-binh**
Téléphone: 3083 Réf. Produit: **B41933 solid**

CNRS UPR 2301

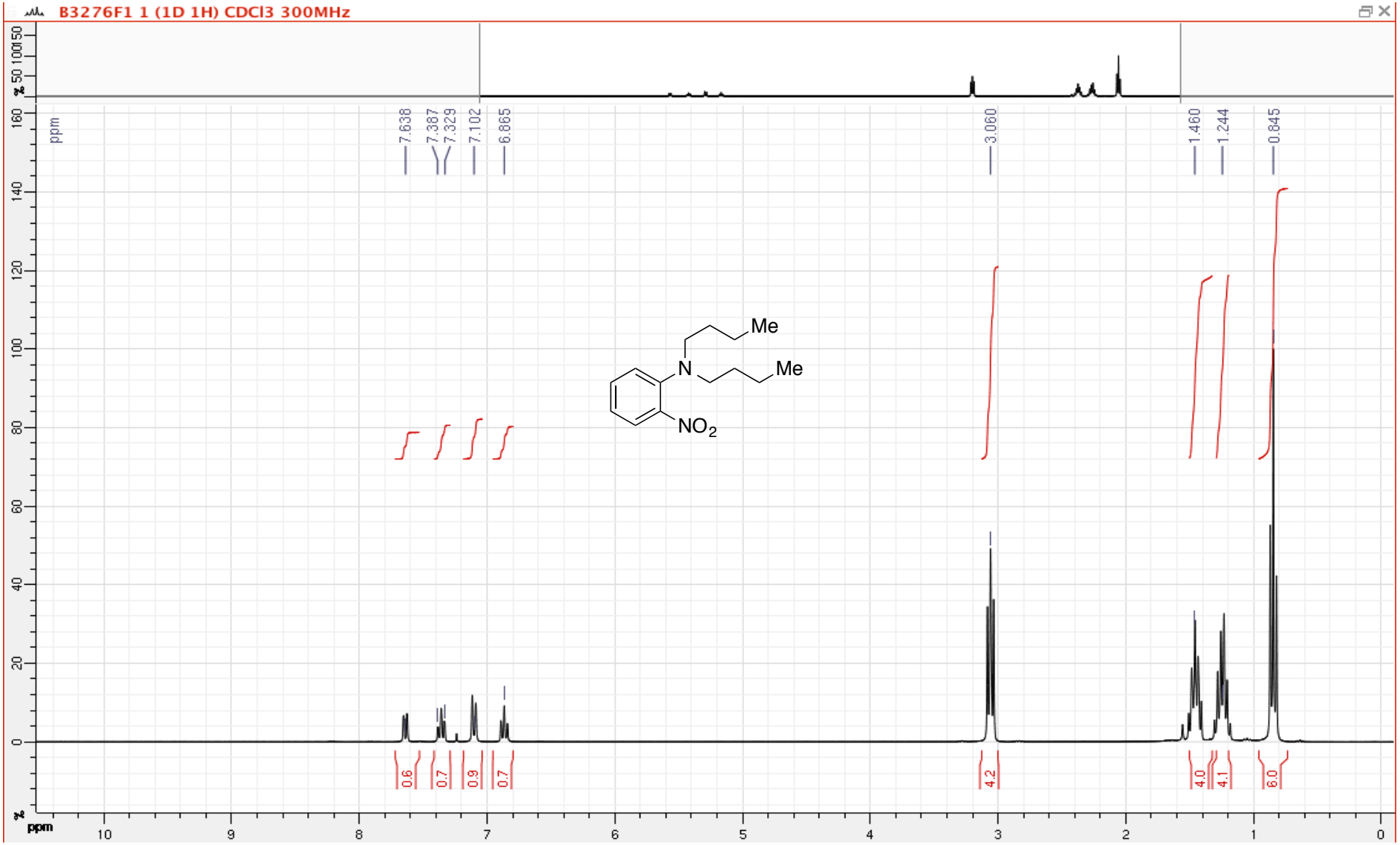
Service **Al Mourabit**
CNRS-ICSN
Avenue de la Terrasse
91198 Gif sur Yvette cedex

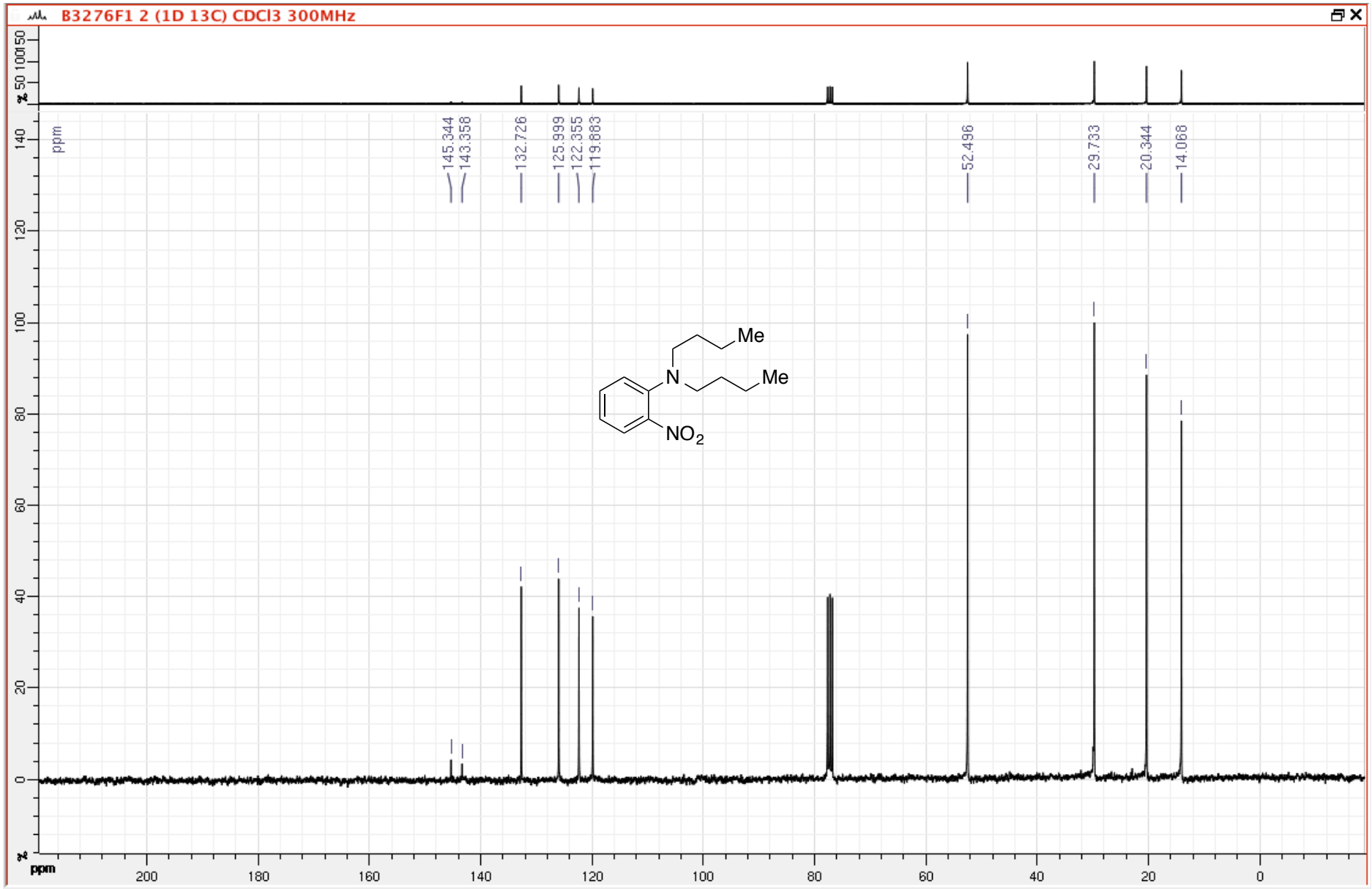
Elément	Mesure 1	Mesure 2	Mesure 3
% Carbone	46.17	45.96	
% Hydrogène	3.30	3.29	
% Azote	10.73	10.73	



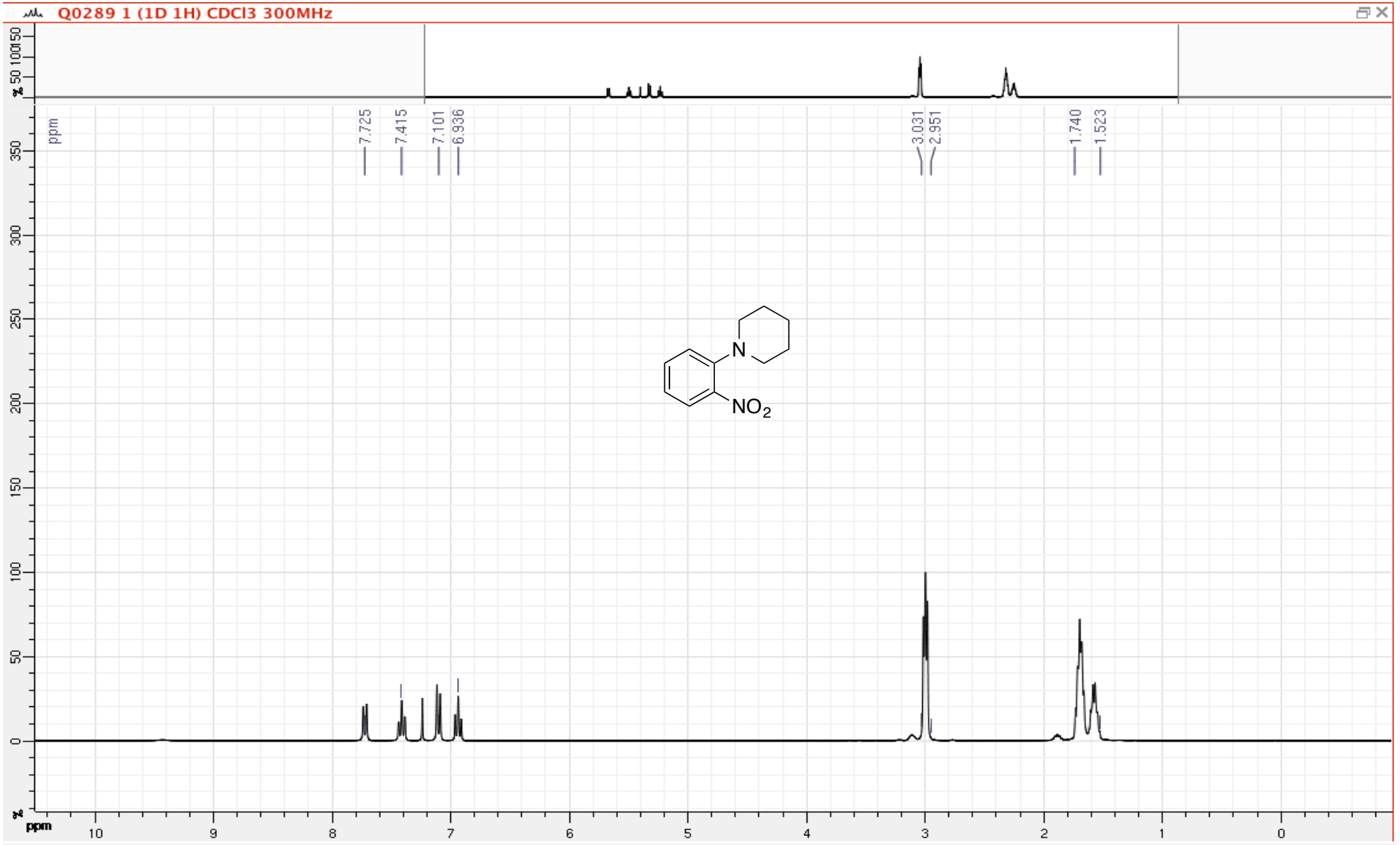
Chemical Formula: $C_{15}H_{12}IN_3O_2$
Elemental Analysis: C, 45.82; H, 3.08; I, 32.28; N, 10.69; O, 8.14

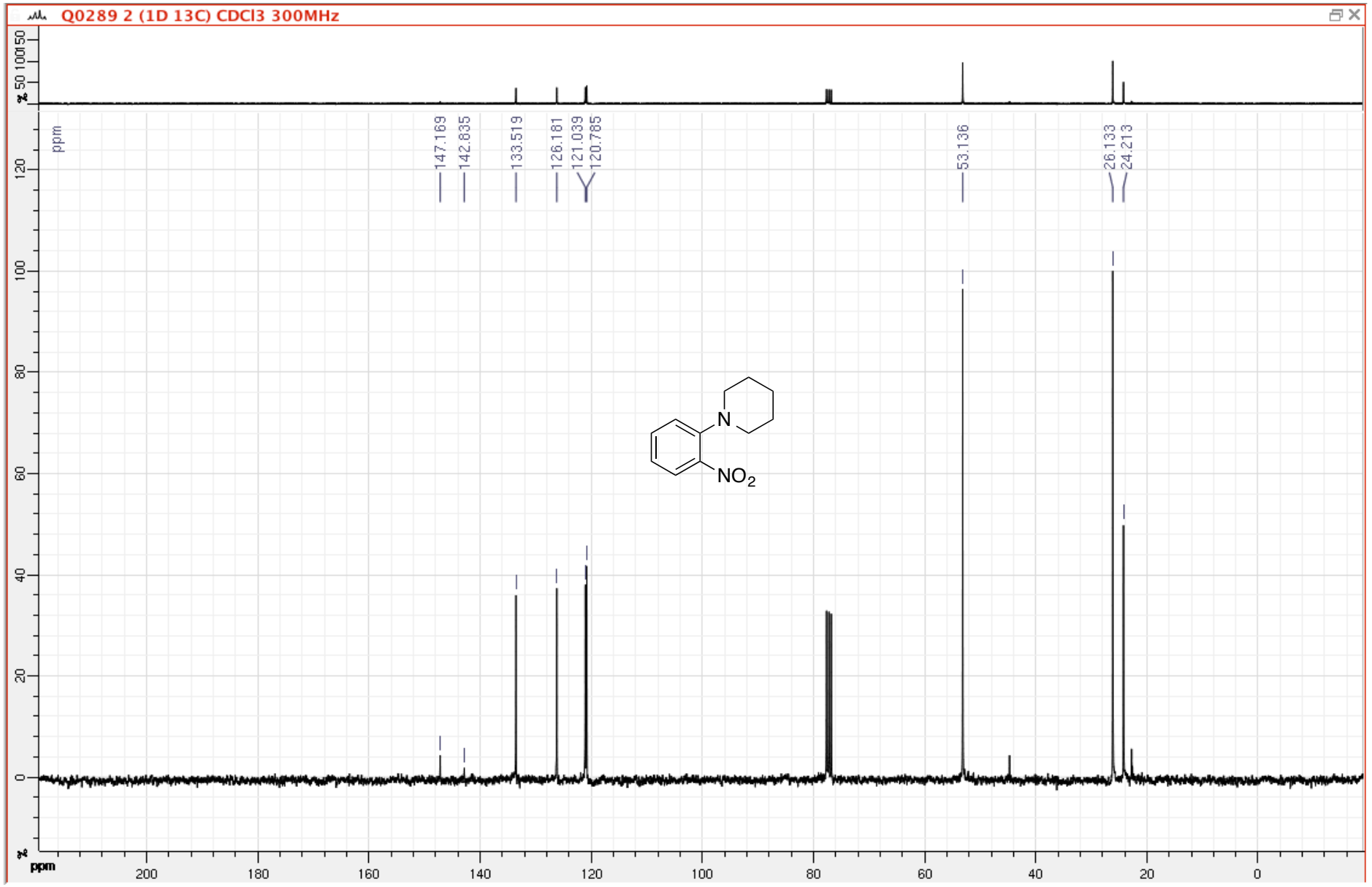
***N*,*N*-Dibutyl-2-nitroaniline (1a)**



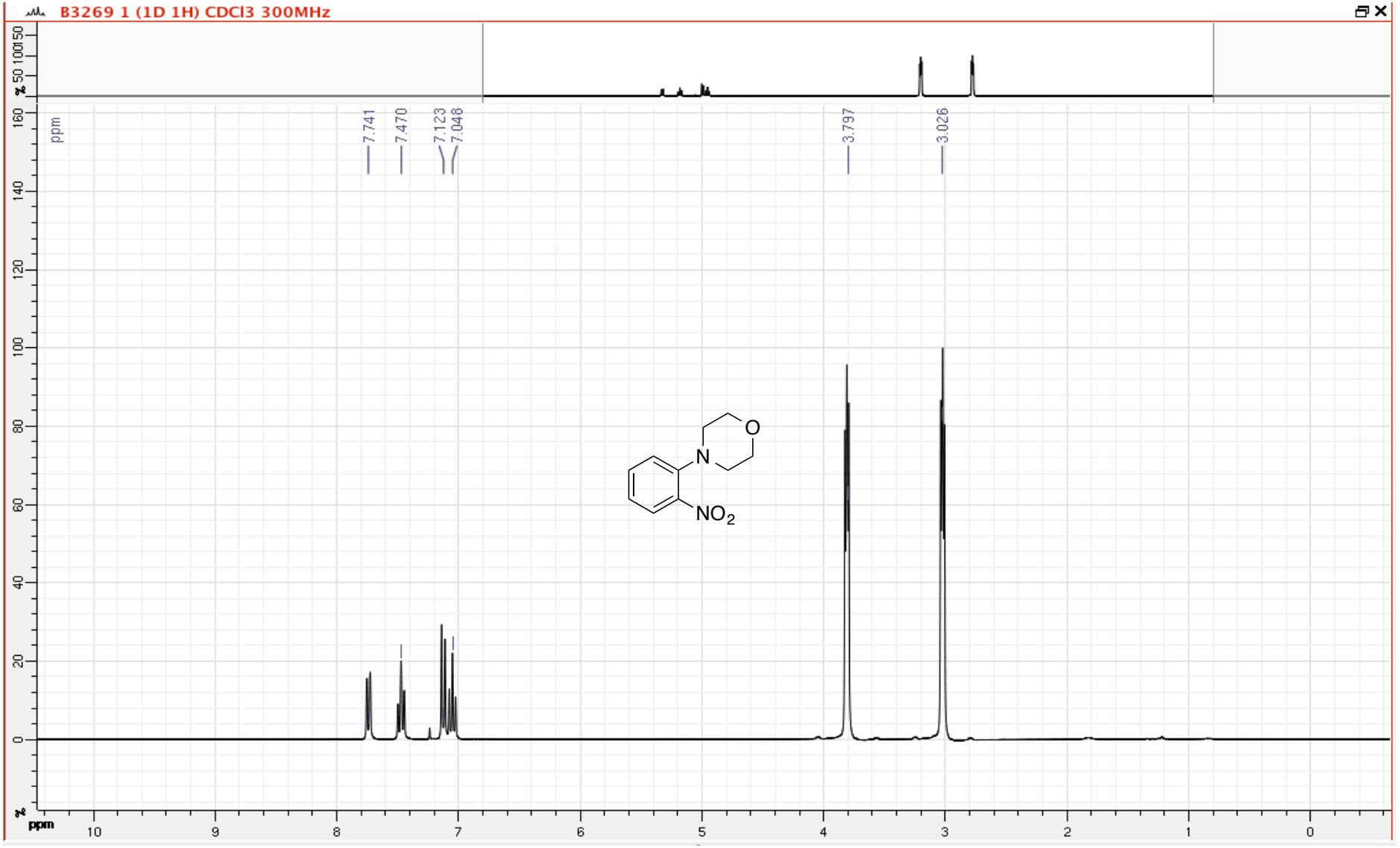

B3276F1 2 (1D 13C) CDCl3 300MHz
ppm
145.344
143.358
132.726
125.999
122.355
119.883
52.496
29.733
20.344
14.068
Me
N
Me
NO2

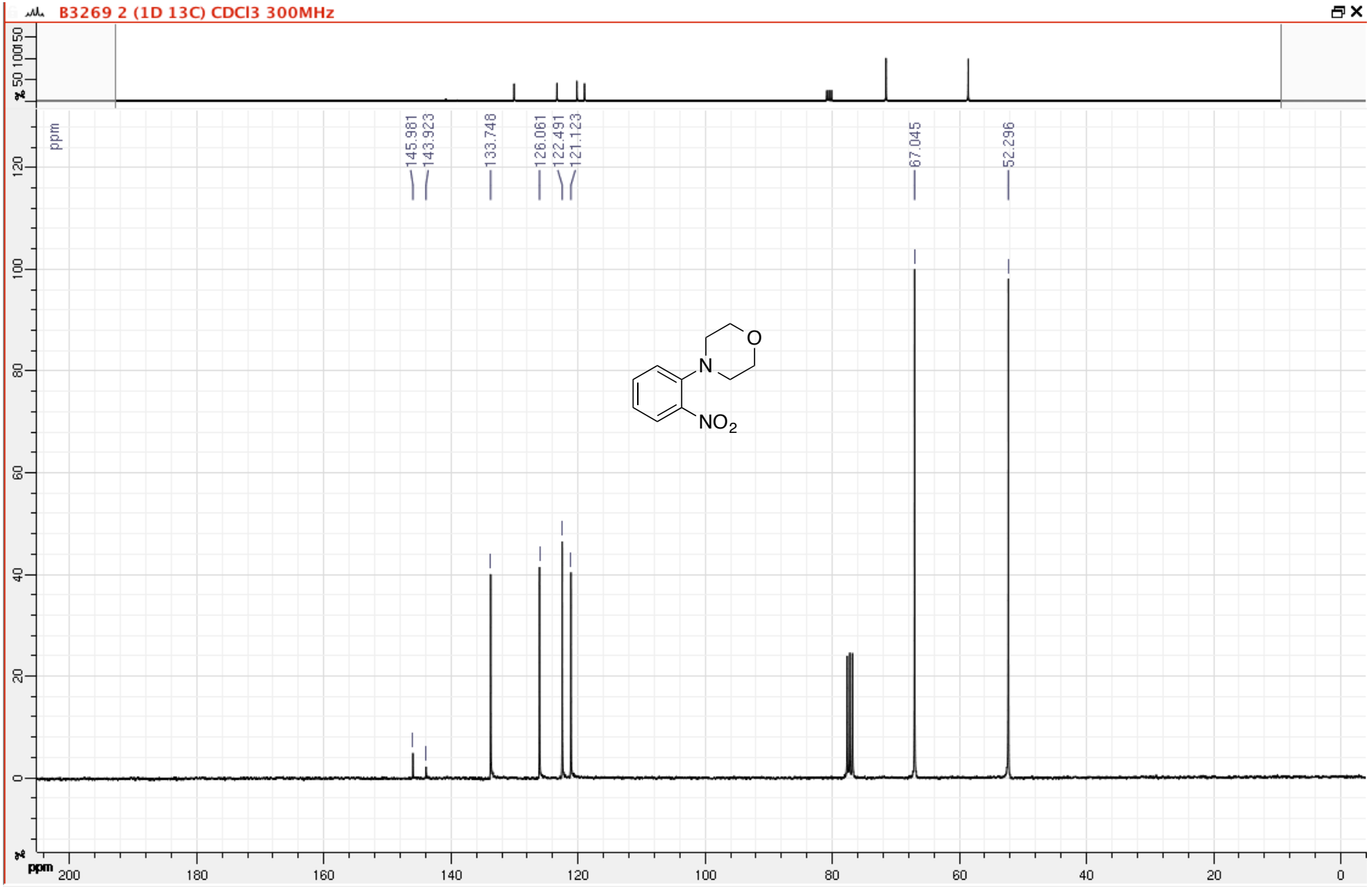
1-(2-Nitrophenyl)piperidine (1b)



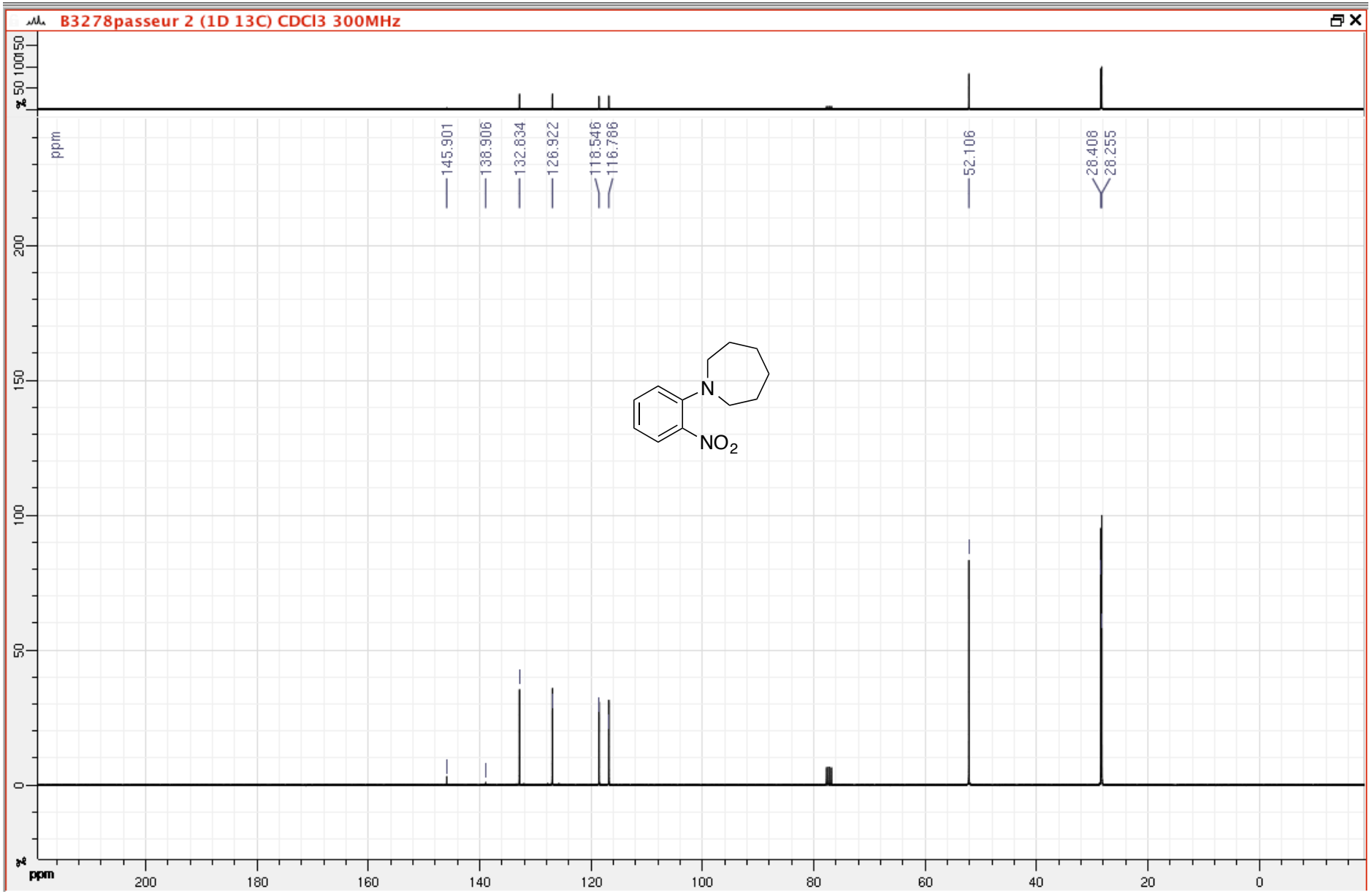

Q0289 2 (1D 13C) CDCl3 300MHz
ppm
147.169
142.835
133.519
126.181
121.039
120.785
53.136
26.133
24.213
N
NO2

4-(2-Nitrophenyl)morpholine (1d)




B3269 2 (1D 13C) CDCl3 300MHz
ppm
145.981
143.923
133.748
126.061
122.491
121.123
67.045
52.296
O
N
NO2

1-(2-Nitrophenyl)azepane (1e)


B3278passeur 2 (1D 13C) CDCl3 300MHz
ppm
145.901
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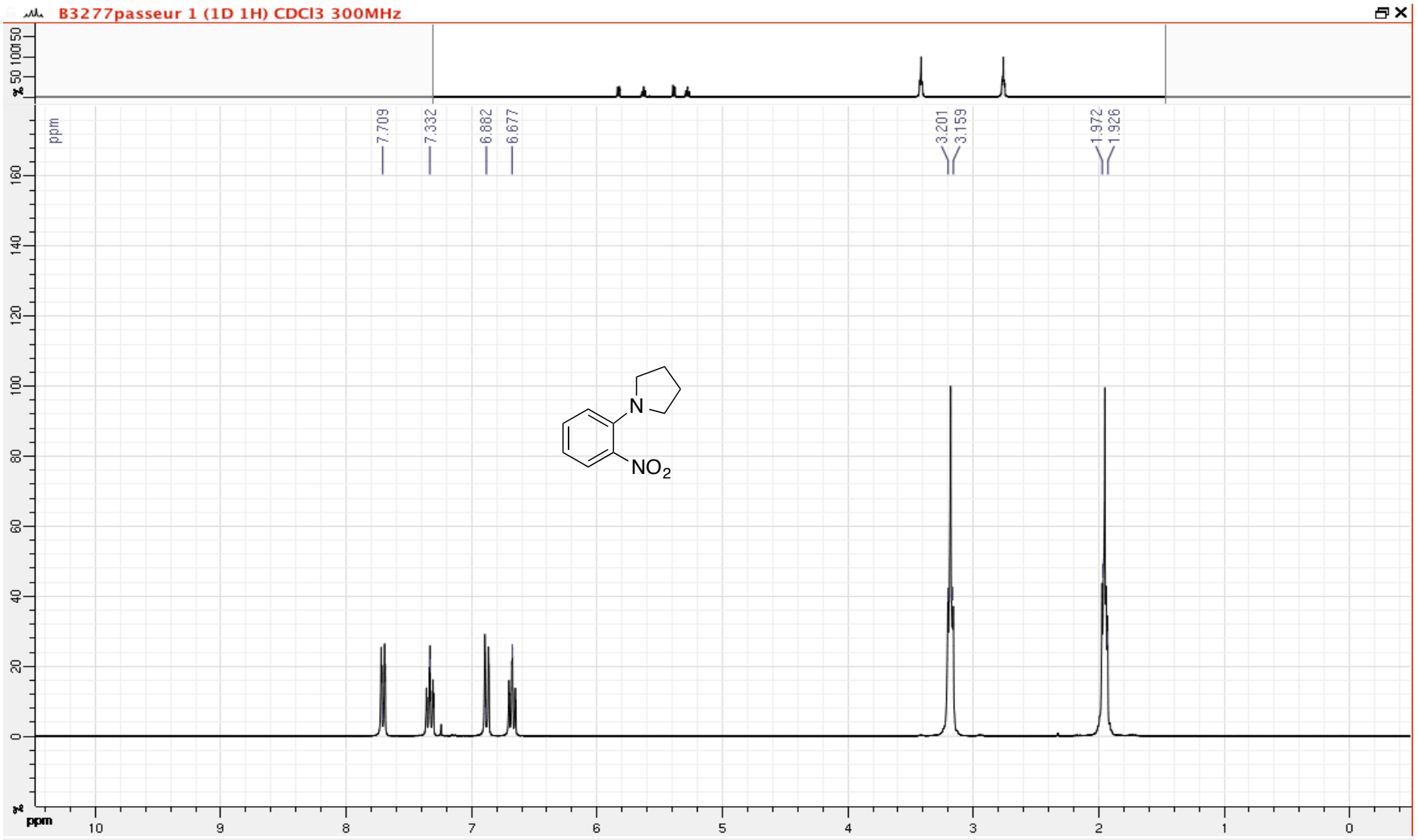
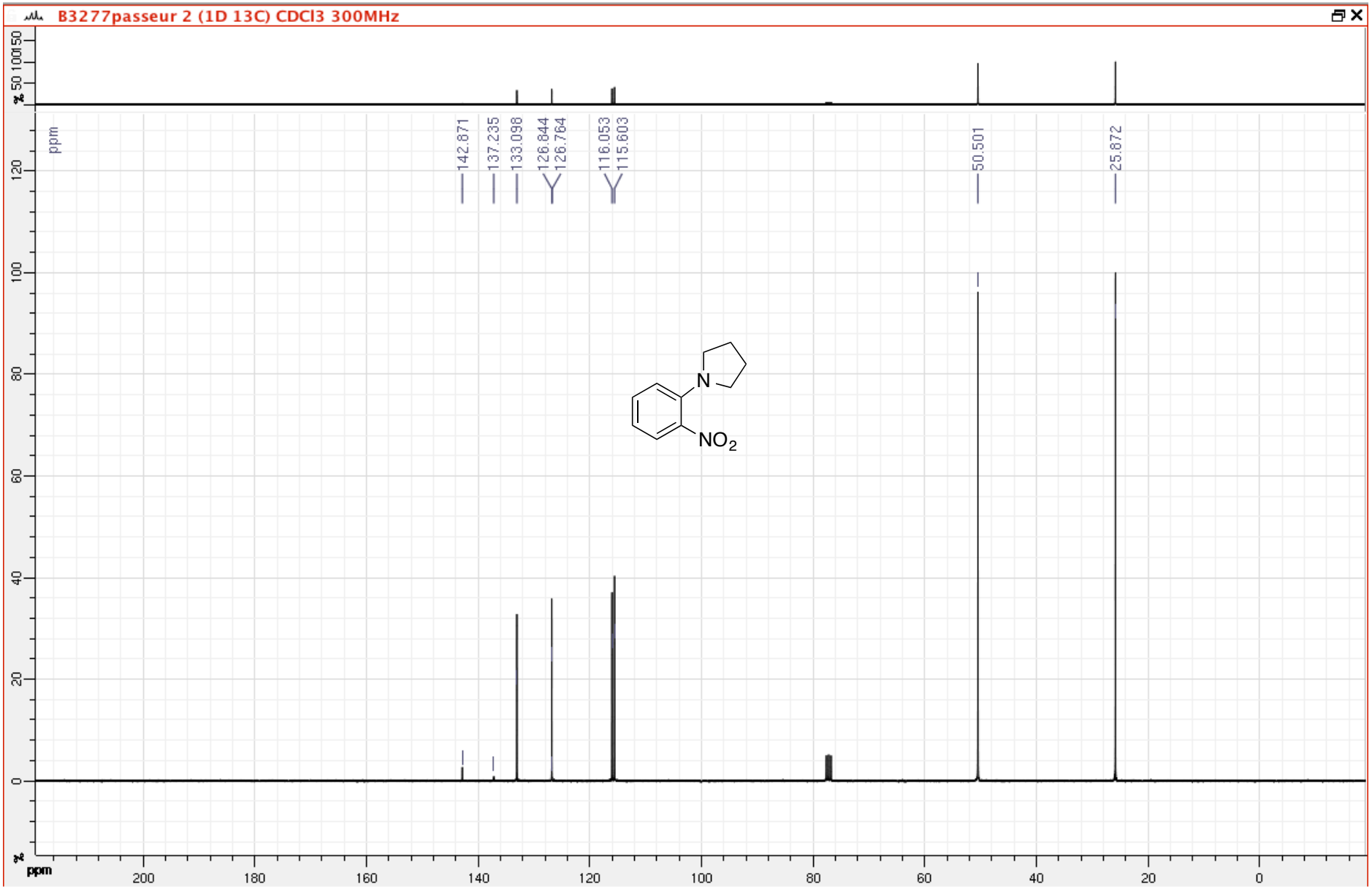
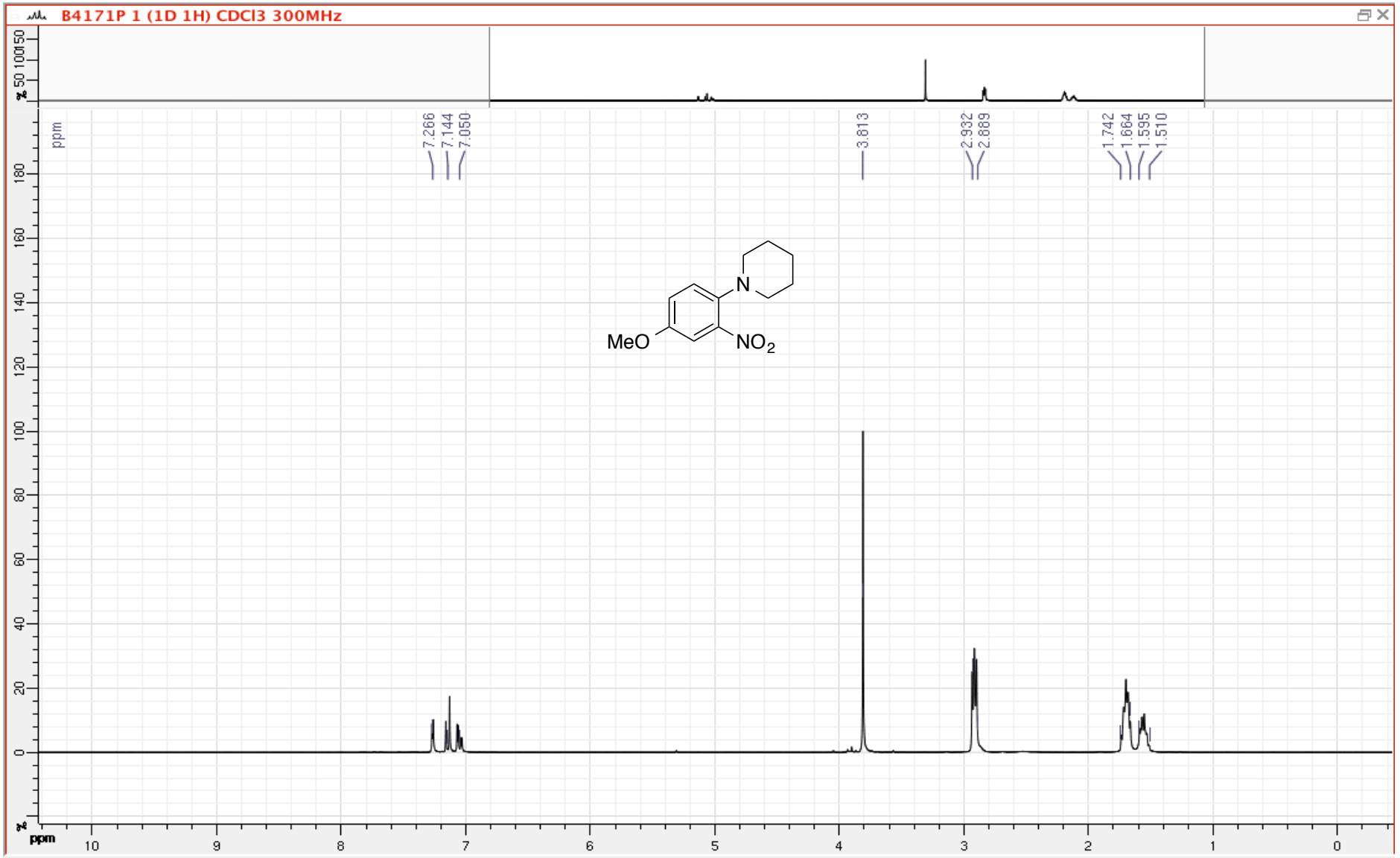
132.834
126.922
118.546
116.786
52.106
28.408
28.255
N
NO2

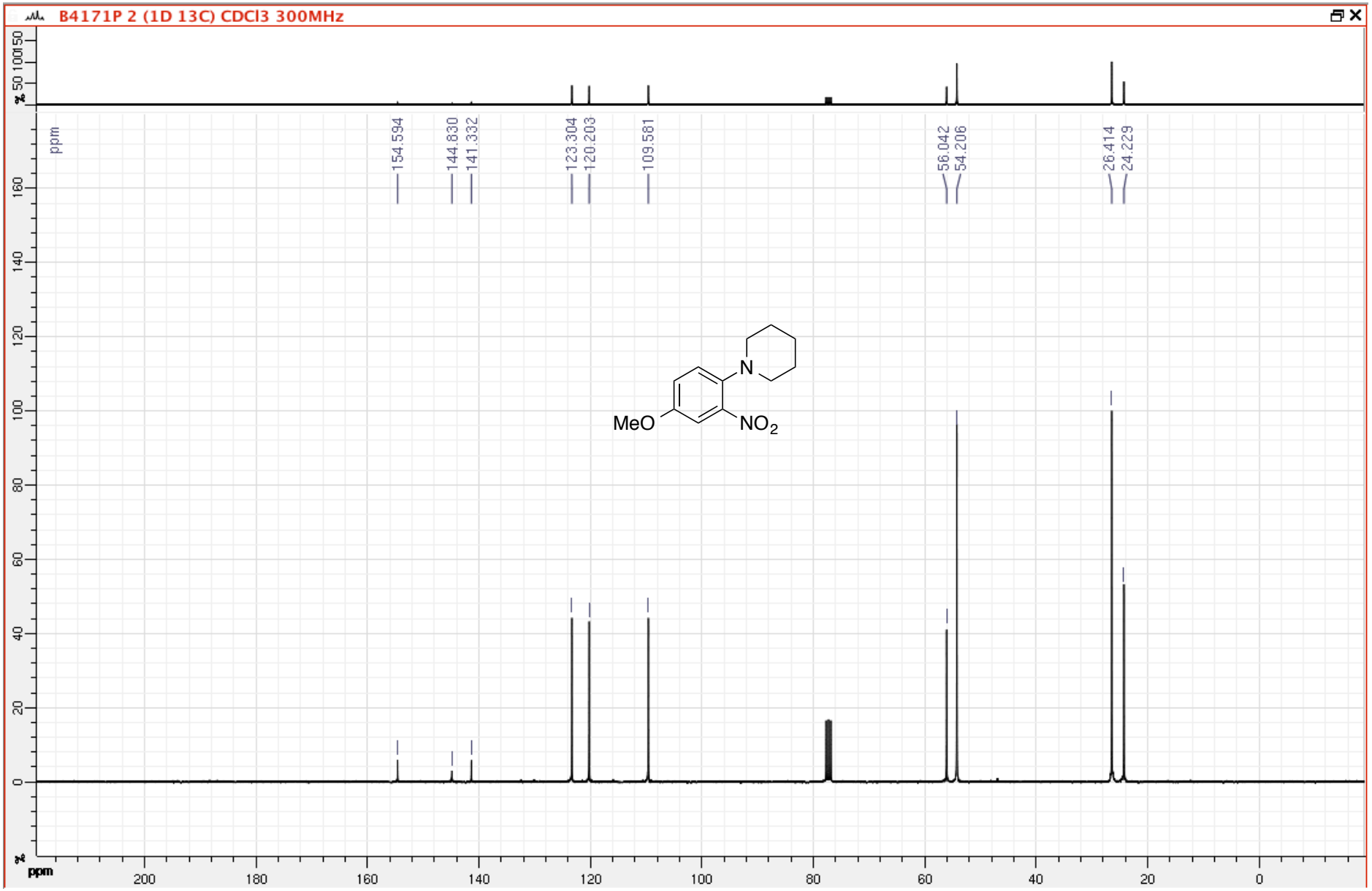
1-(2-Nitrophenyl)pyrrolidine (1f)



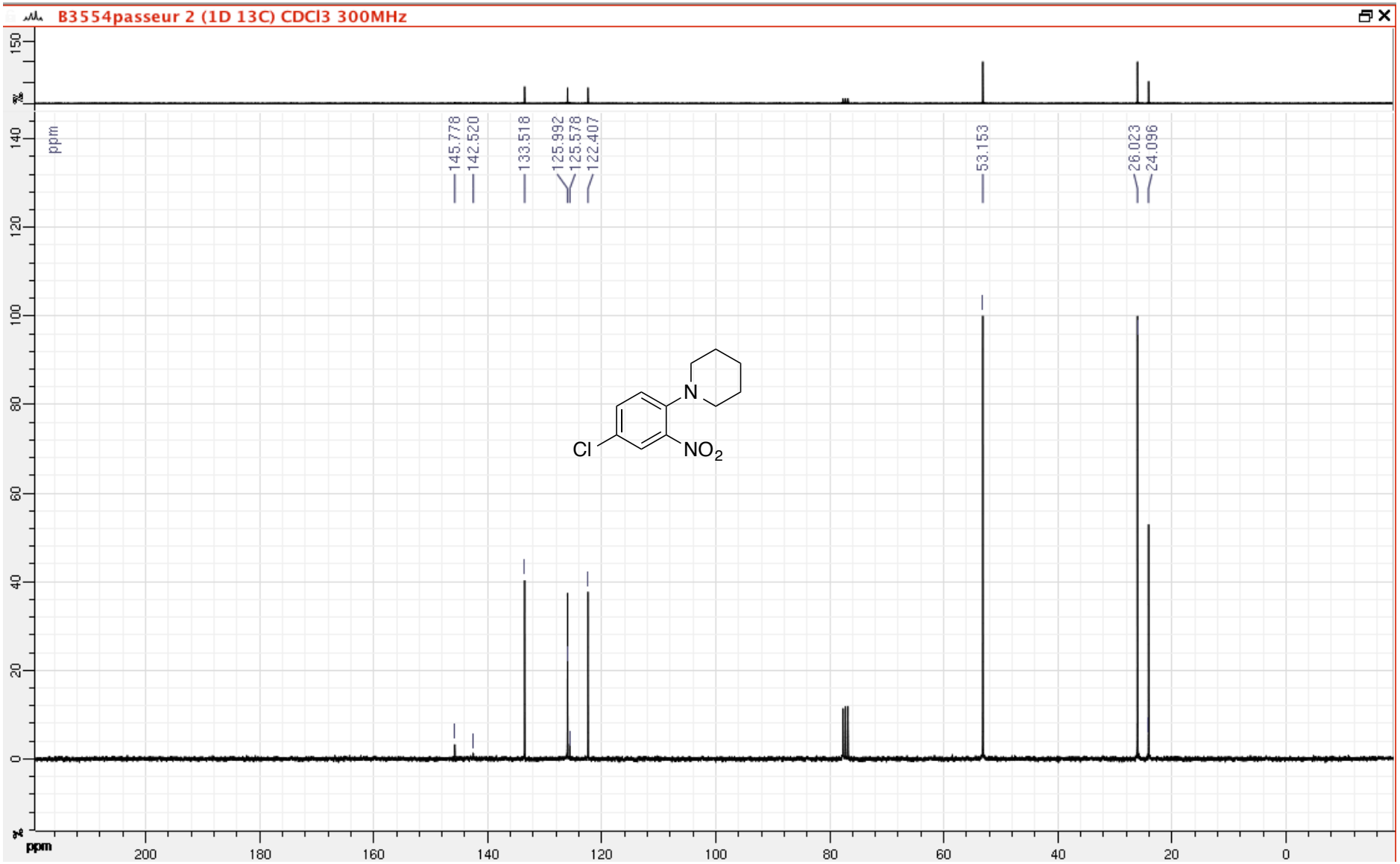

B3277passeur 2 (1D 13C) CDCl3 300MHz
ppm
142.871
137.235
133.098
126.844
126.764
116.053
115.603
50.501
25.872
N
NO2

1-(4-Methoxy-2-nitrophenyl)piperidine (1g)

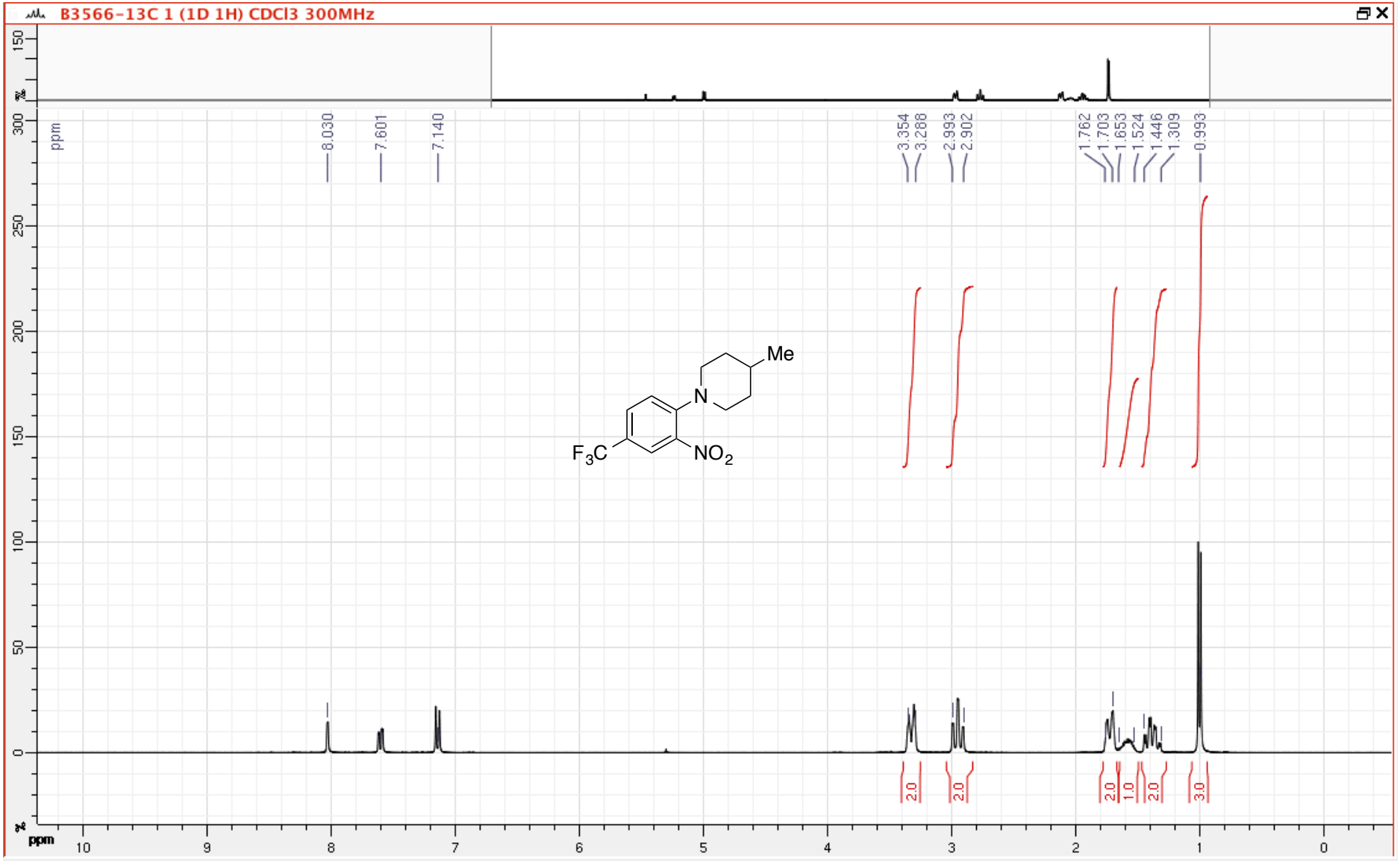


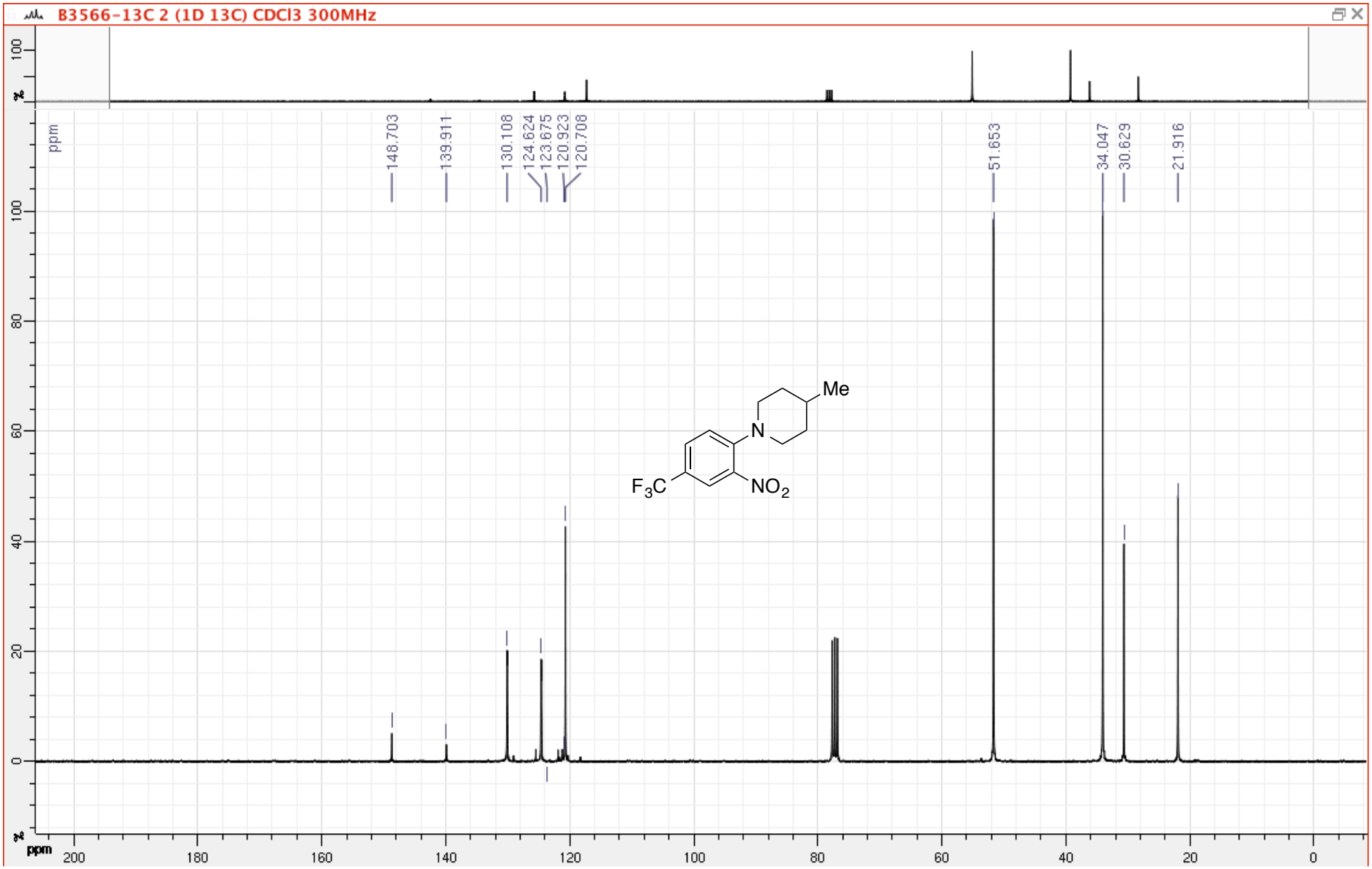

B4171P 2 (1D 13C) CDCl3 300MHz
ppm
154.594
144.830
141.332
123.304
120.203
109.581
56.042
54.206
26.414
24.229
MeO
NO2
N

1-(4-Chloro-2-nitrophenyl)piperidine (1h)

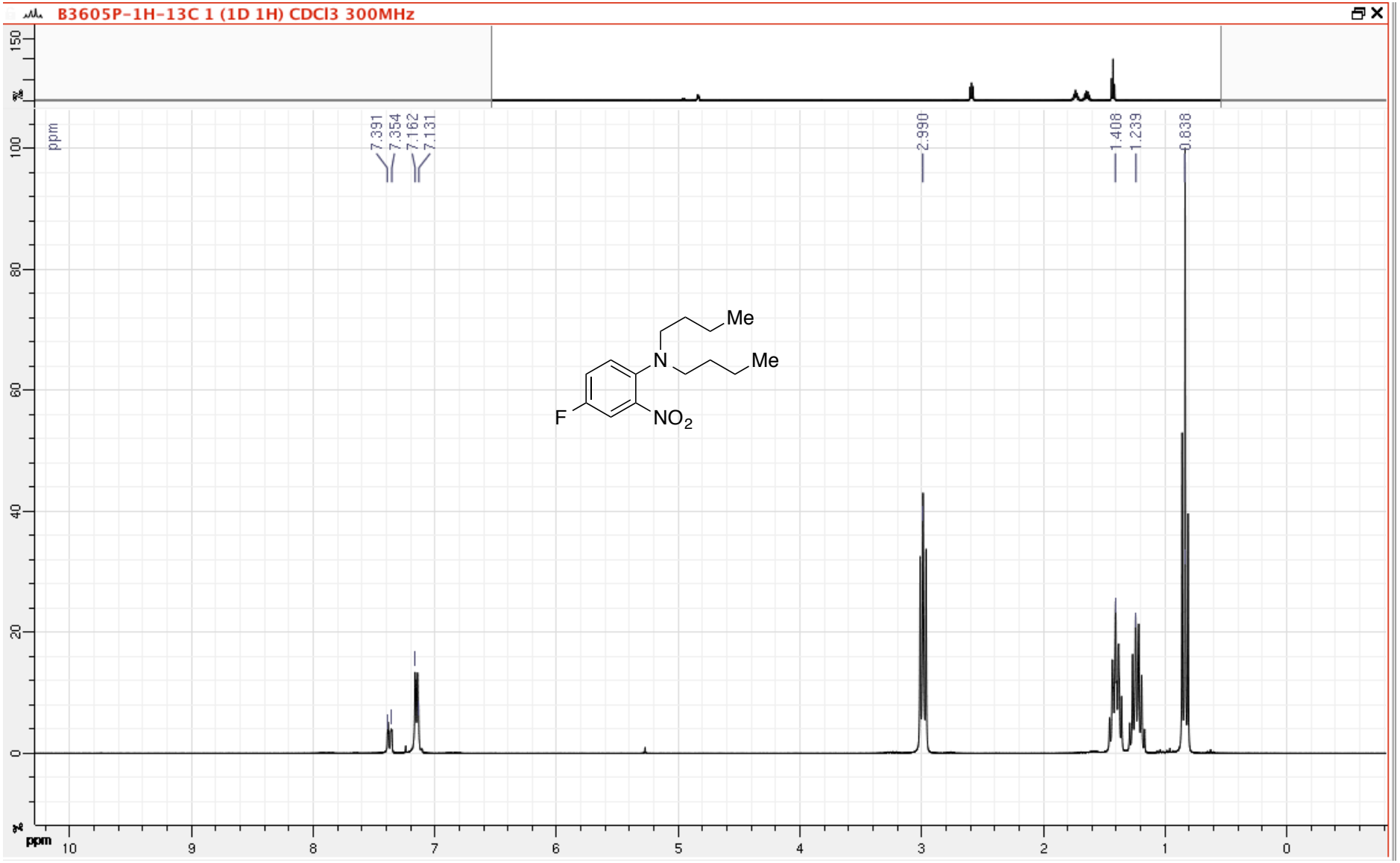

B3554passeur 2 (1D 13C) CDCl3 300MHz
ppm
145.778
142.520
133.518
125.992
125.578
122.407
53.153
26.023
24.096
N
Cl
NO2

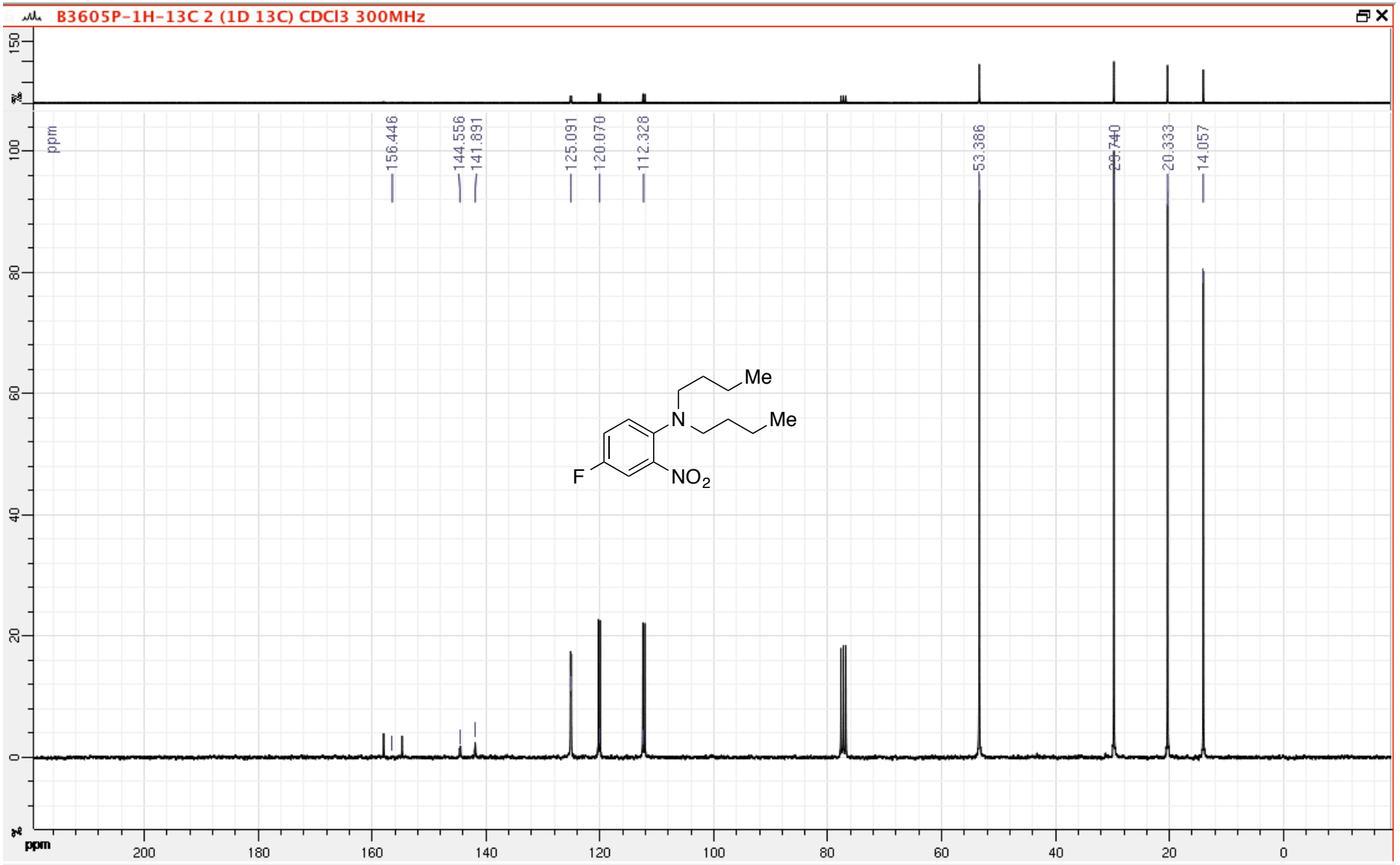
4-Methyl-1-(2-nitro-4-(trifluoromethyl)phenyl)piperidine (1i)



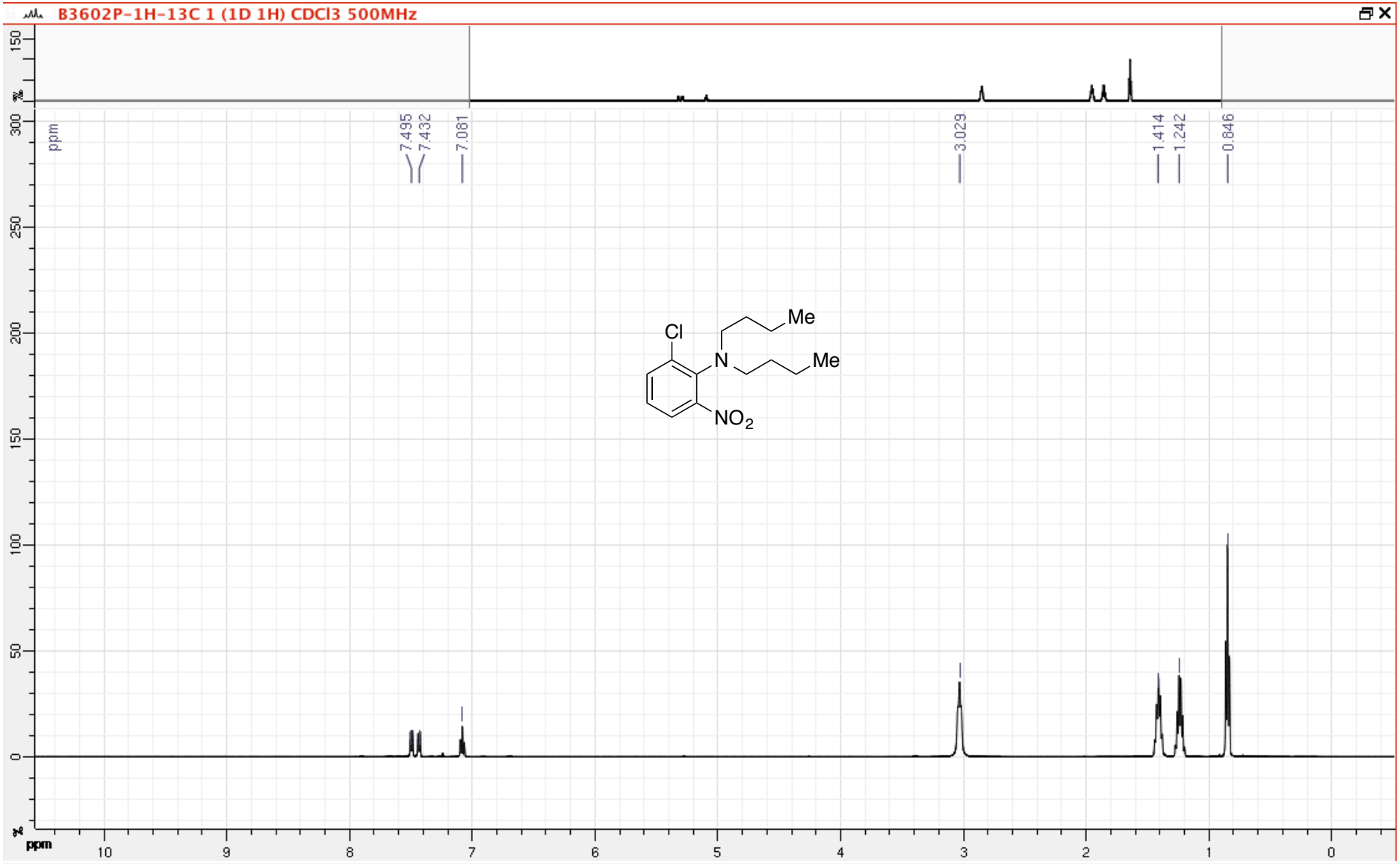

B3566-13C 2 (1D 13C) CDCl3 300MHz
ppm
148.703
139.911
130.108
124.624
123.675
120.923
120.708
51.653
34.047
30.629
21.916
Me
N
F3C
NO2

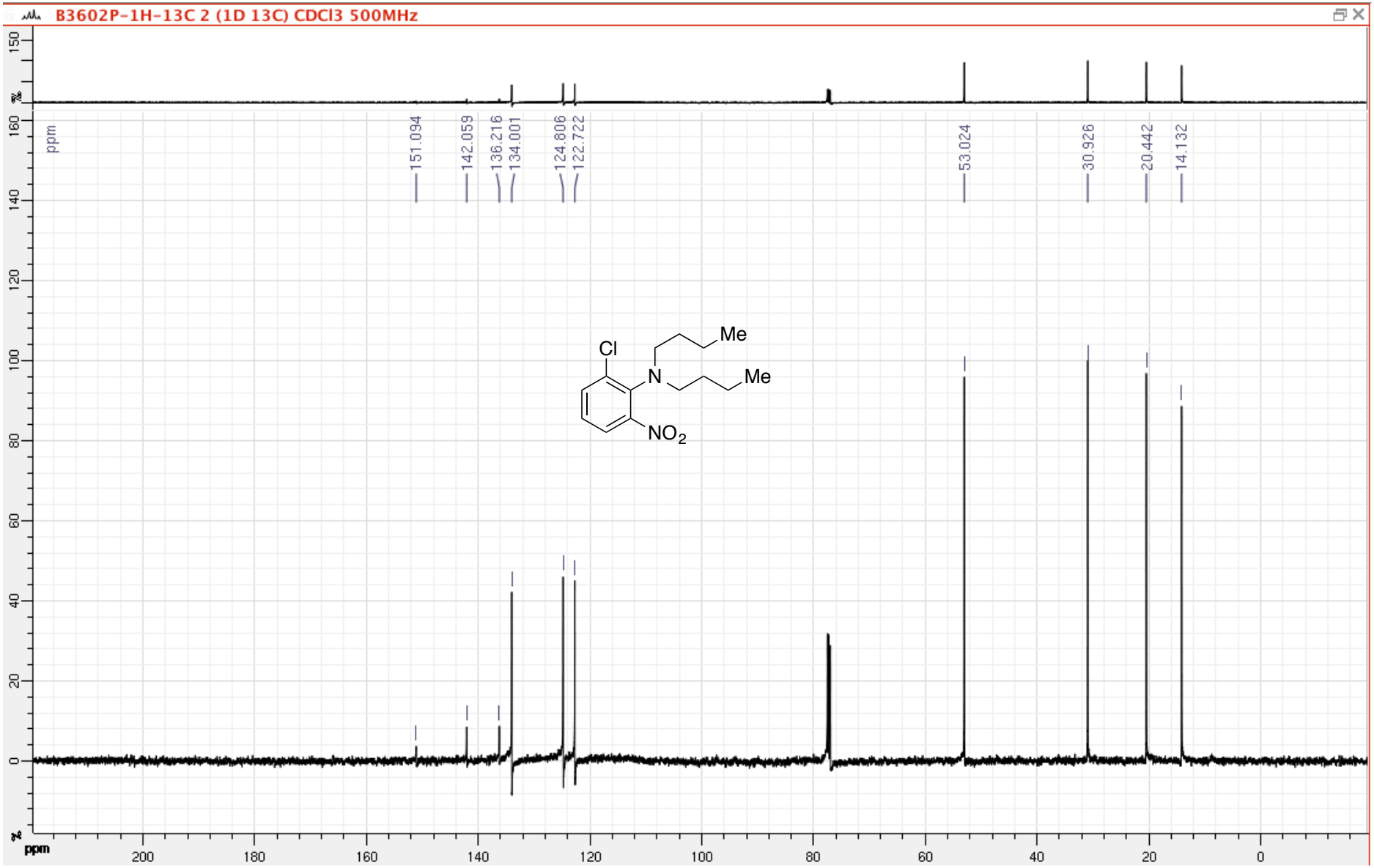
***N*,*N*-Dibutyl-4-fluoro-2-nitroaniline (1j)**



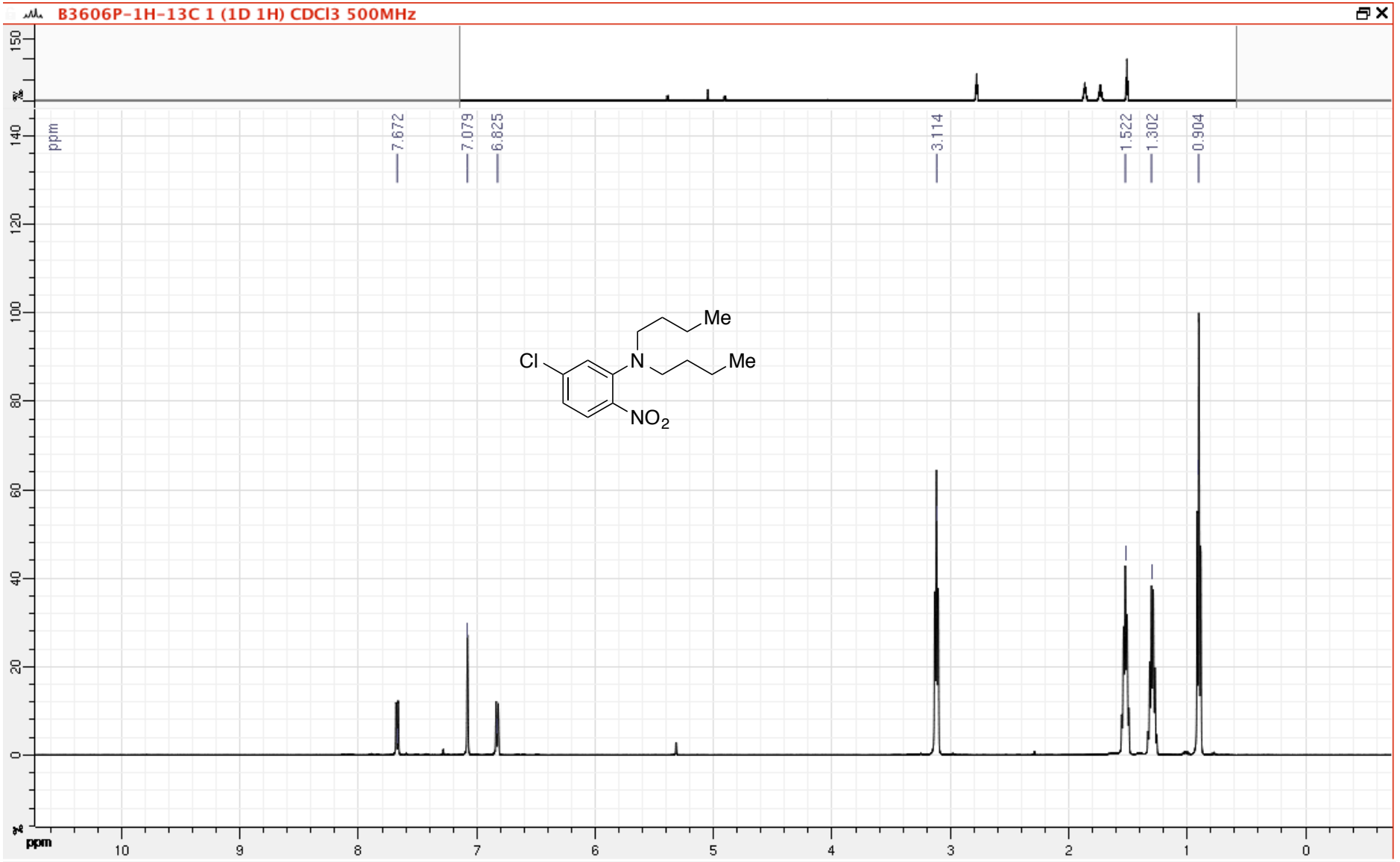

B3605P-1H-13C 2 (1D 13C) CDCl3 300MHz
ppm
156.446
144.556
141.891
125.091
120.070
112.328
53.386
29.740
20.333
14.057
Me
N
Me
F
NO2

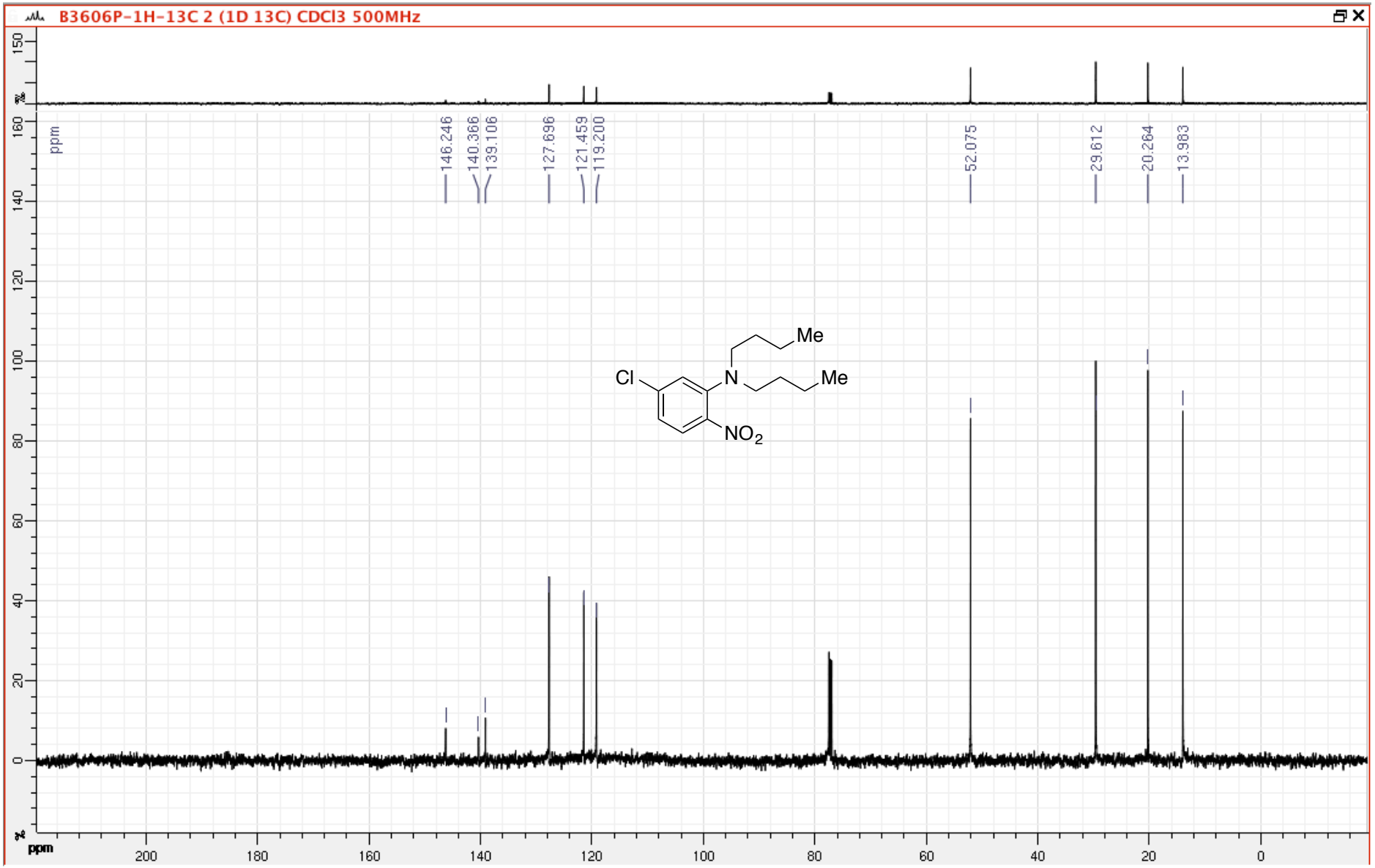
***N*,*N*-Dibutyl-2-chloro-6-nitroaniline (1k)**



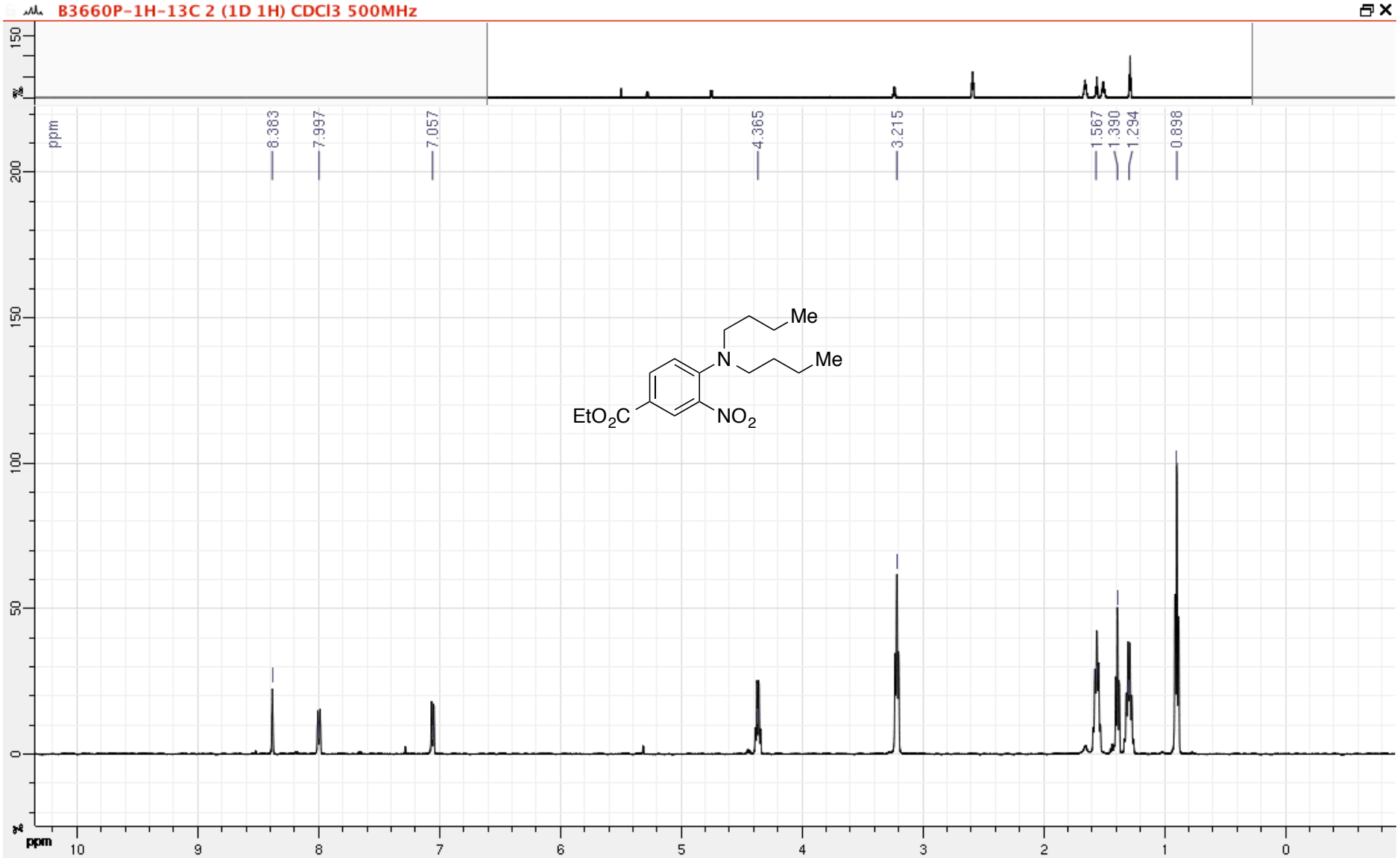

B3602P-1H-13C 2 (1D 13C) CDCl3 500MHz
ppm
151.094
142.059
136.216
134.001
124.806
122.722
53.024
30.926
20.442
14.132
Cl
N
Me
Me
NO2

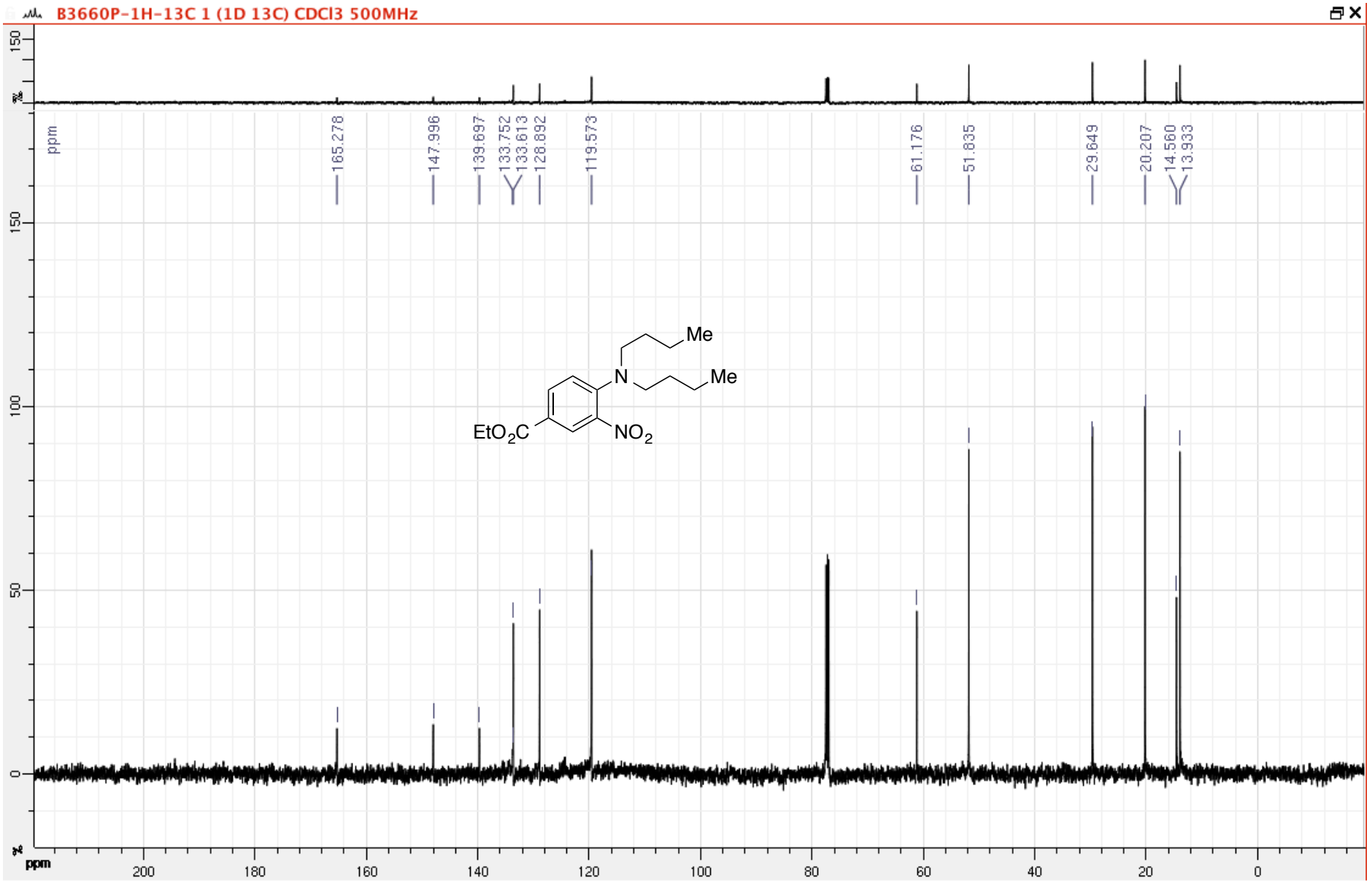
***N*,*N*-Dibutyl-5-chloro-2-nitroaniline (1l)**



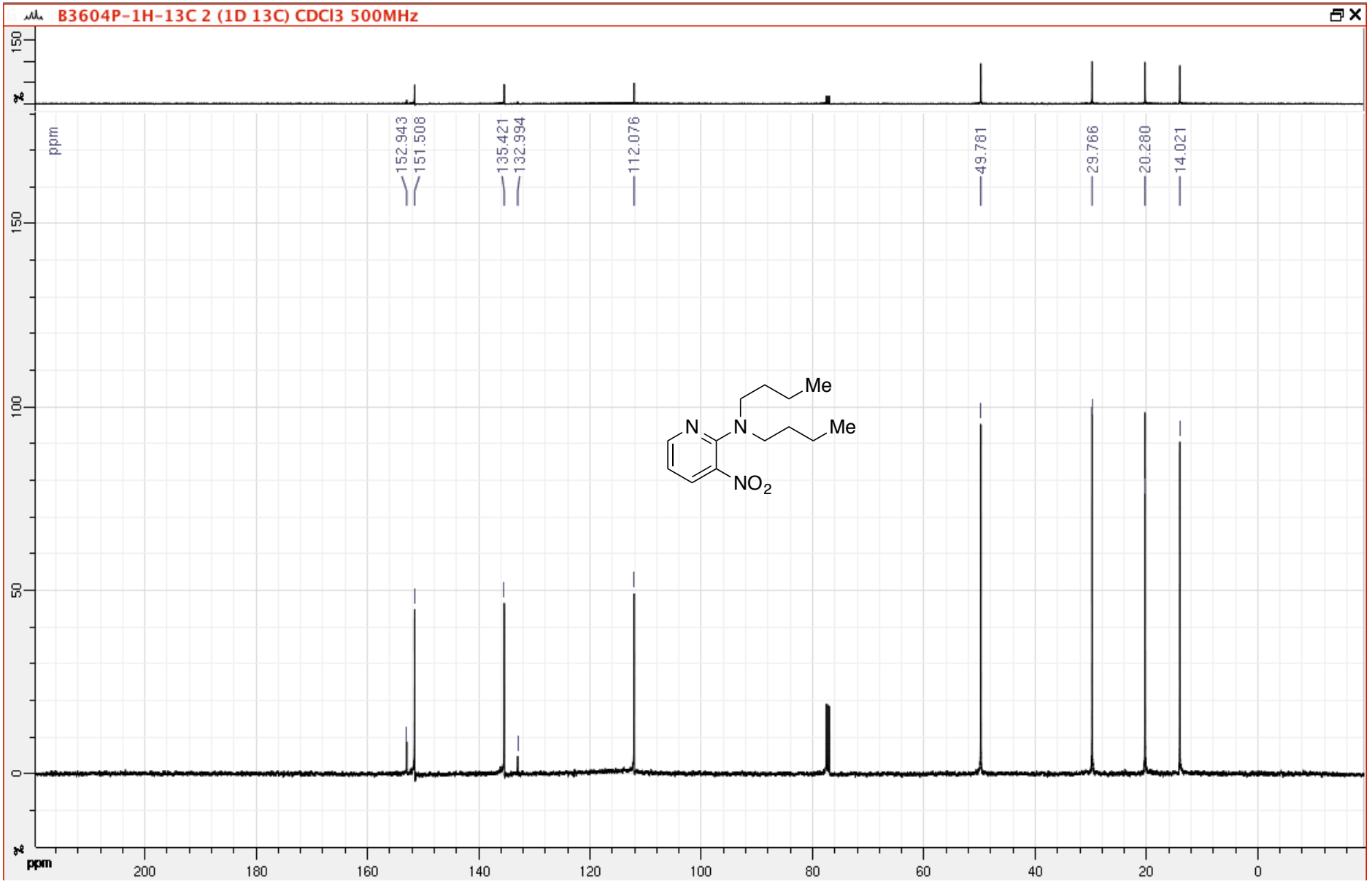

B3606P-1H-13C 2 (1D 13C) CDCl3 500MHz
ppm
146.246
140.366
139.106
127.696
121.459
119.200
52.075
29.612
20.264
13.983
Cl
N
Me
Me
NO2
200
180
160
140
120
100
80
60
40
20
0

Ethyl 4-(dibutylamino)-3-nitrobenzoate (1m)

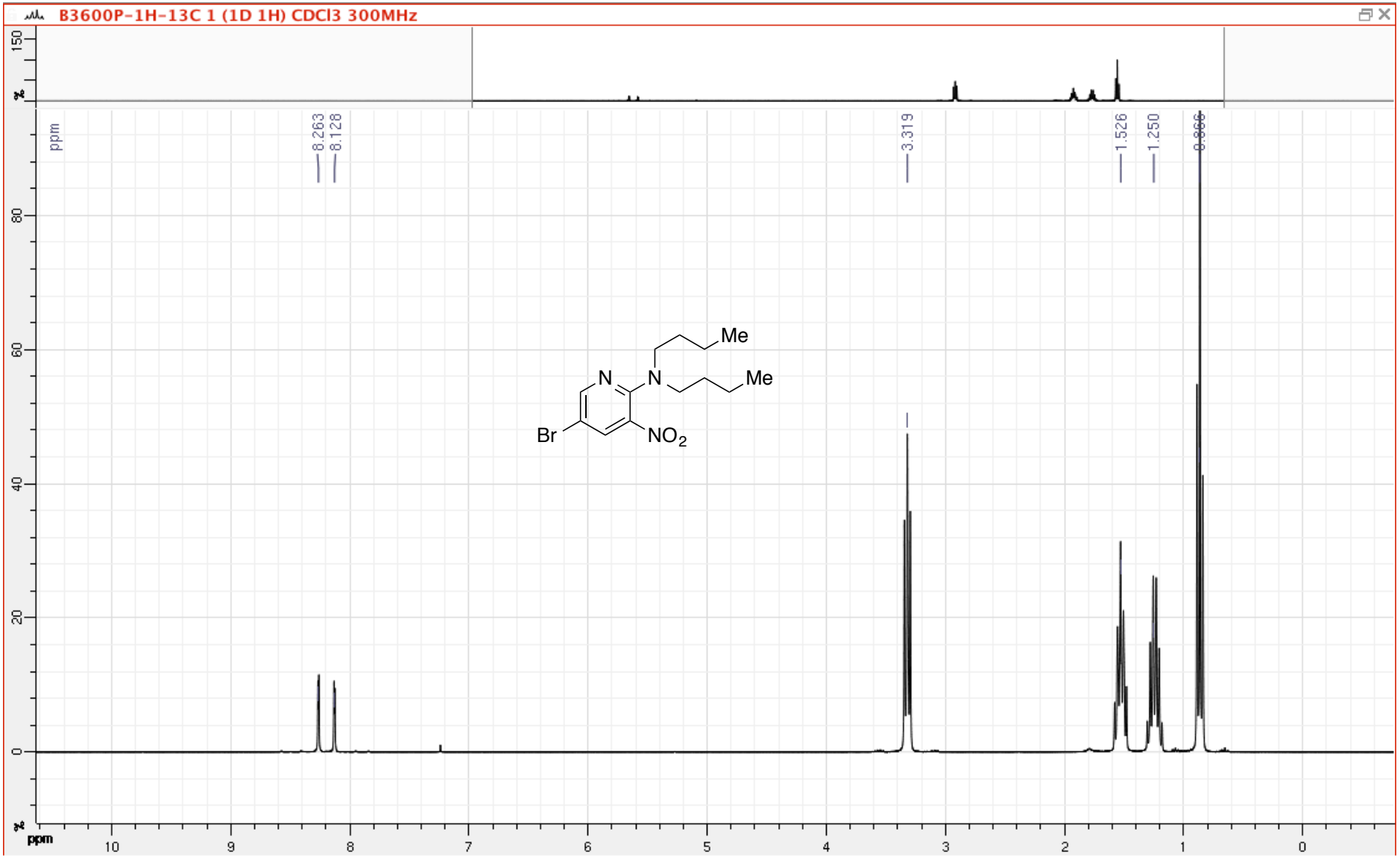


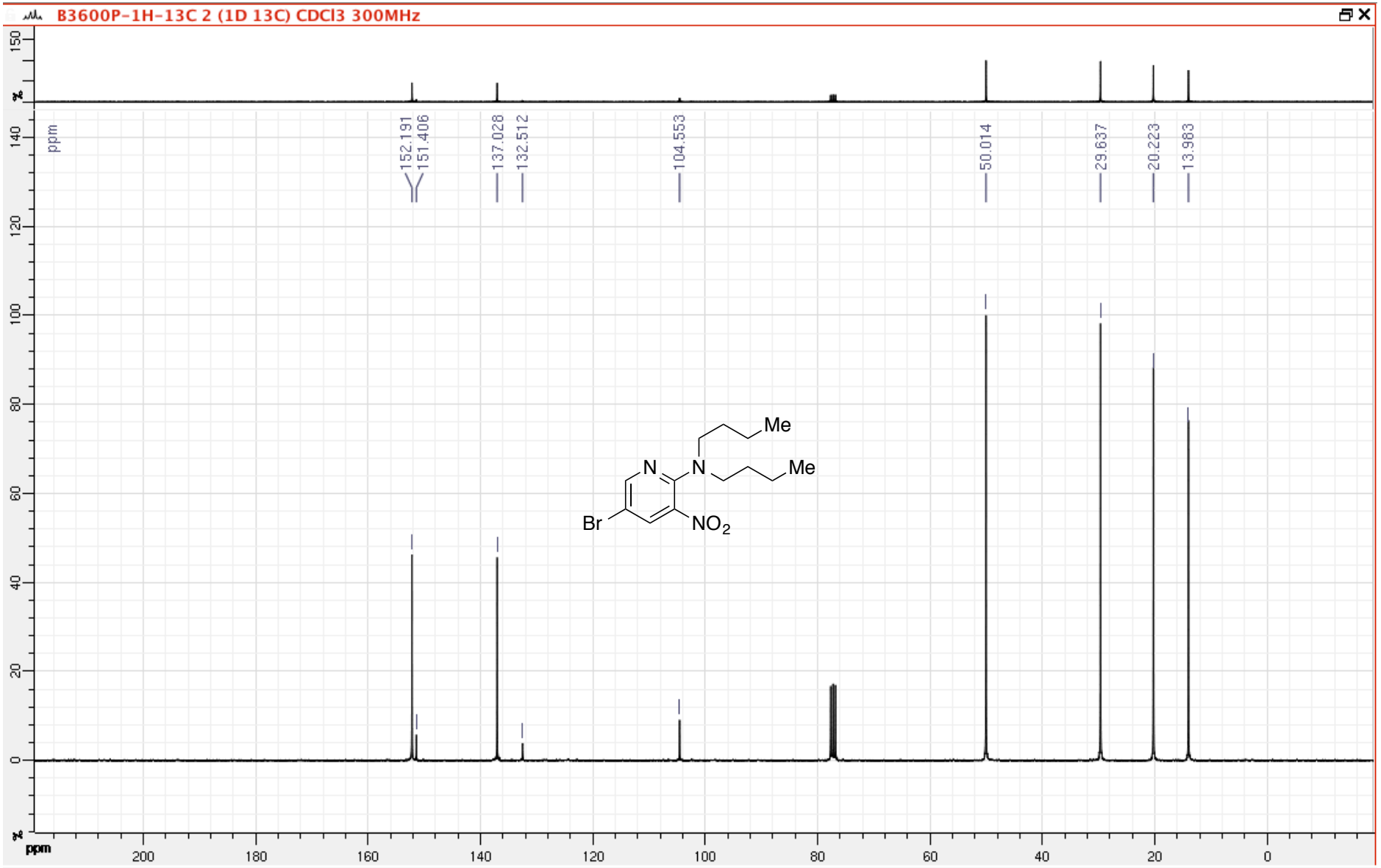

B3660P-1H-13C 1 (1D 13C) CDCl3 500MHz
ppm
165.278
147.996
139.697
133.752
133.613
128.892
119.573
61.176
51.835
29.649
20.207
14.560
13.933
Me
N
Me
EtO2C
NO2
200
180
160
140
120
100
80
60
40
20
0

***N*,*N*-Dibutyl-3-nitropyridin-2-amine (1n)**

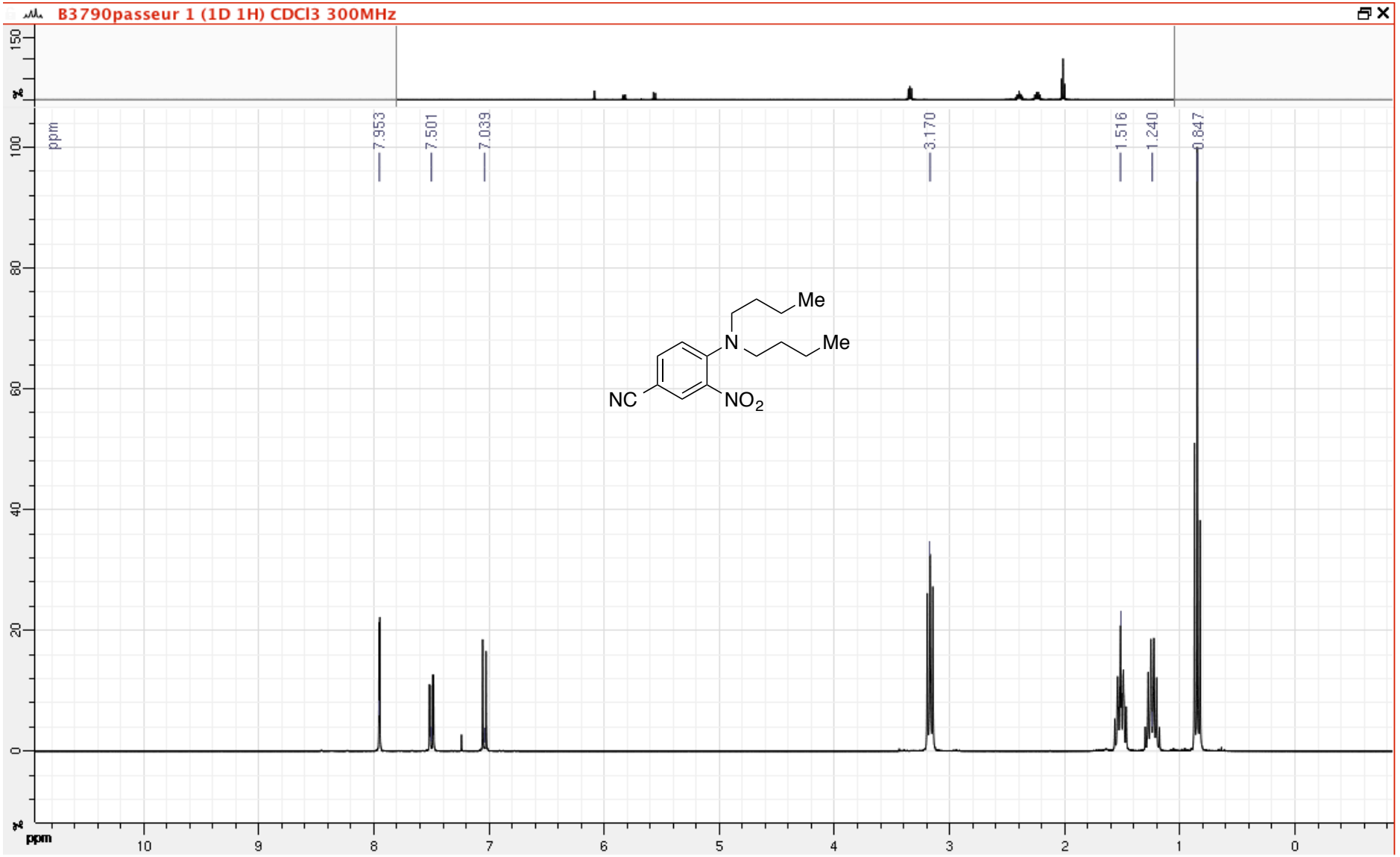

B3604P-1H-13C 2 (1D 13C) CDCl3 500MHz
ppm
152.943
151.508
135.421
132.994
112.076
49.781
29.766
20.280
14.021
Me
N
N
Me
NO2
200
180
160
140
120
100
80
60
40
20
0

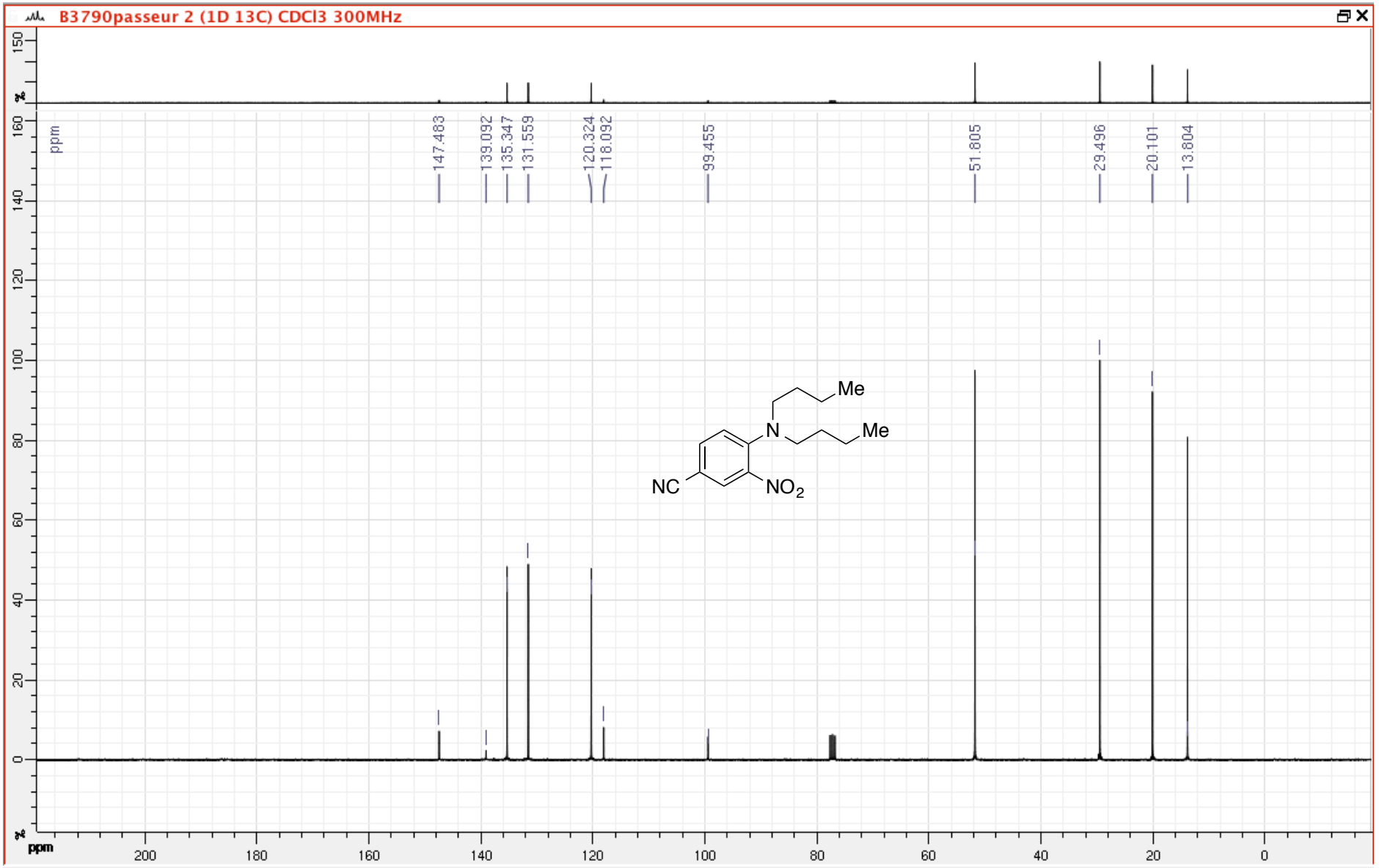
***N*,*N*-Dibutyl-3-nitropyridin-2-amine (1o)**



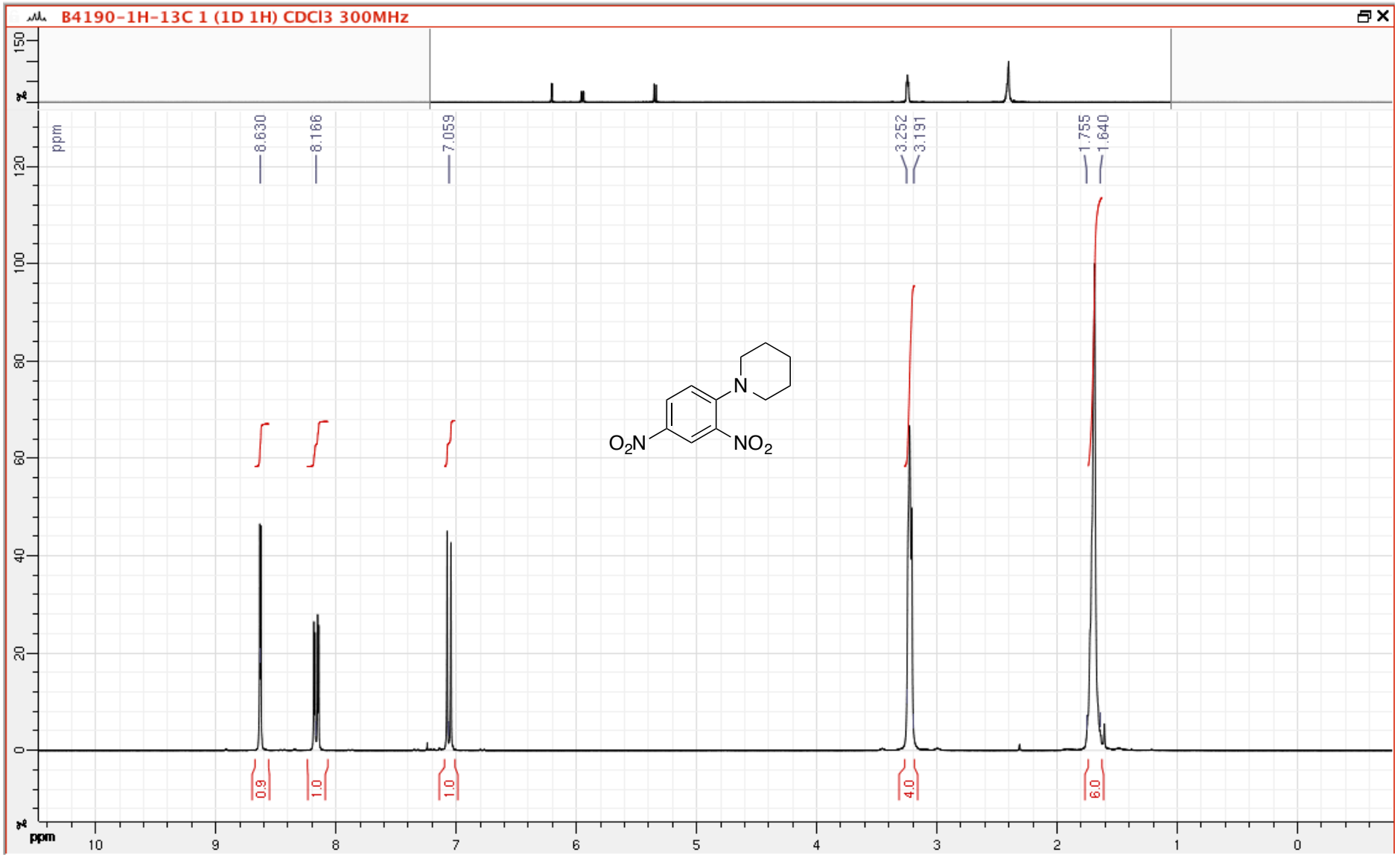

B3600P-1H-13C 2 (1D 13C) CDCl3 300MHz
ppm
152.191
151.406
137.028
132.512
104.553
50.014
29.637
20.223
13.983
Me
N
N
Me
Br
NO2

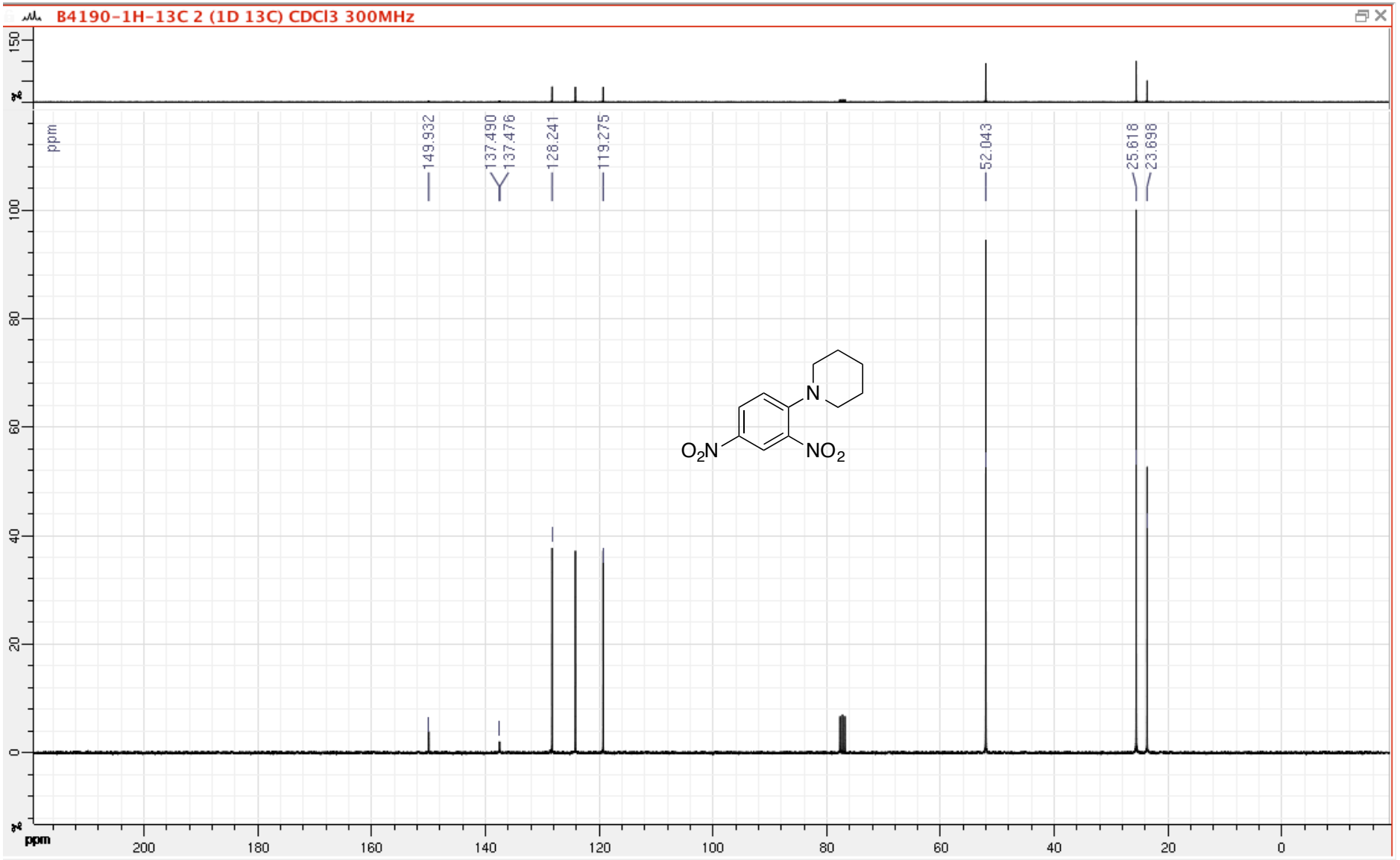
4-(Dibutylamino)-3-nitrobenzonitrile (1p)



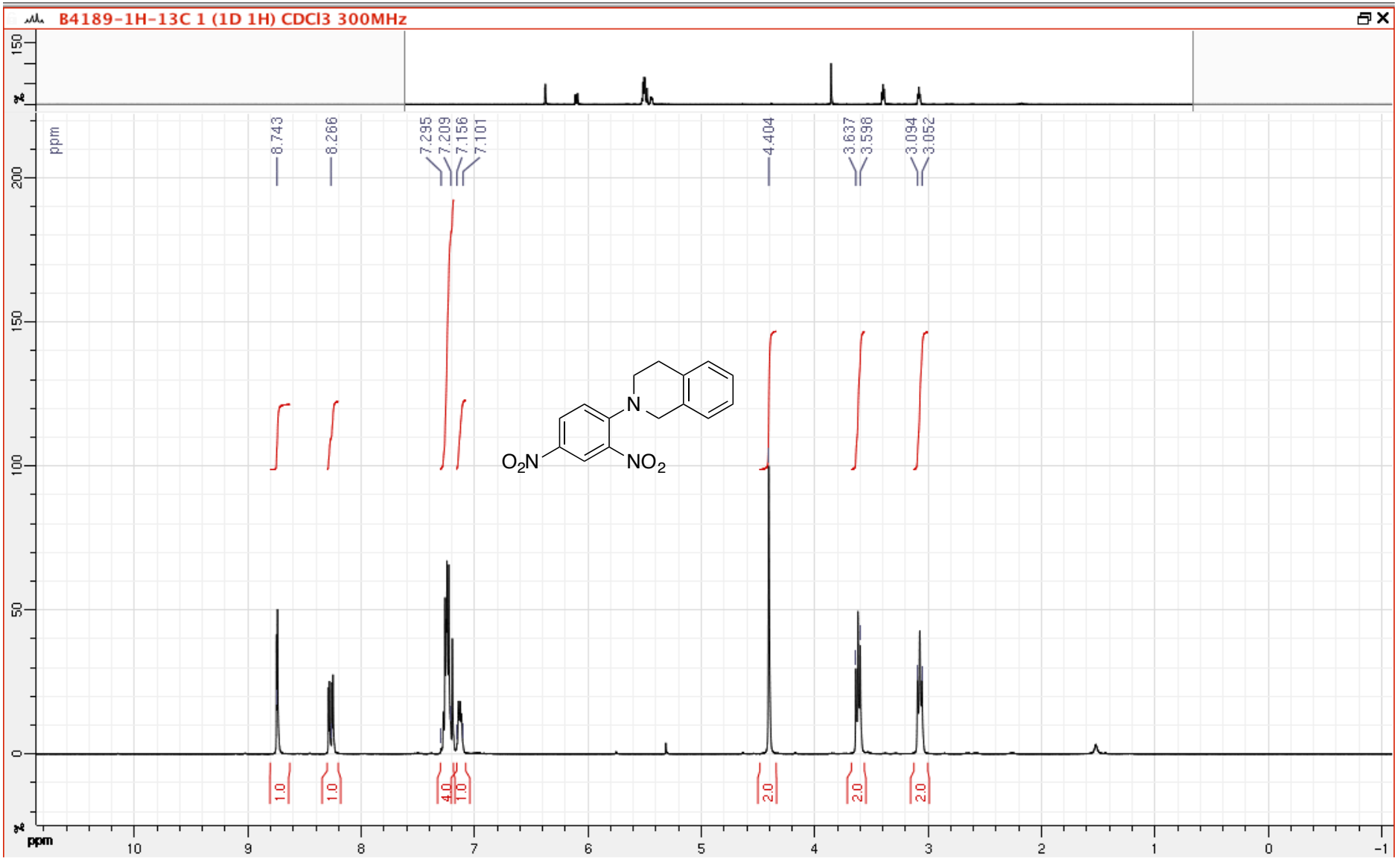

B3790passeur 2 (1D 13C) CDCl3 300MHz
ppm
147.483
139.092
135.347
131.559
120.324
118.092
99.455
51.805
29.496
20.101
13.804
Me
N
Me
NC
NO2

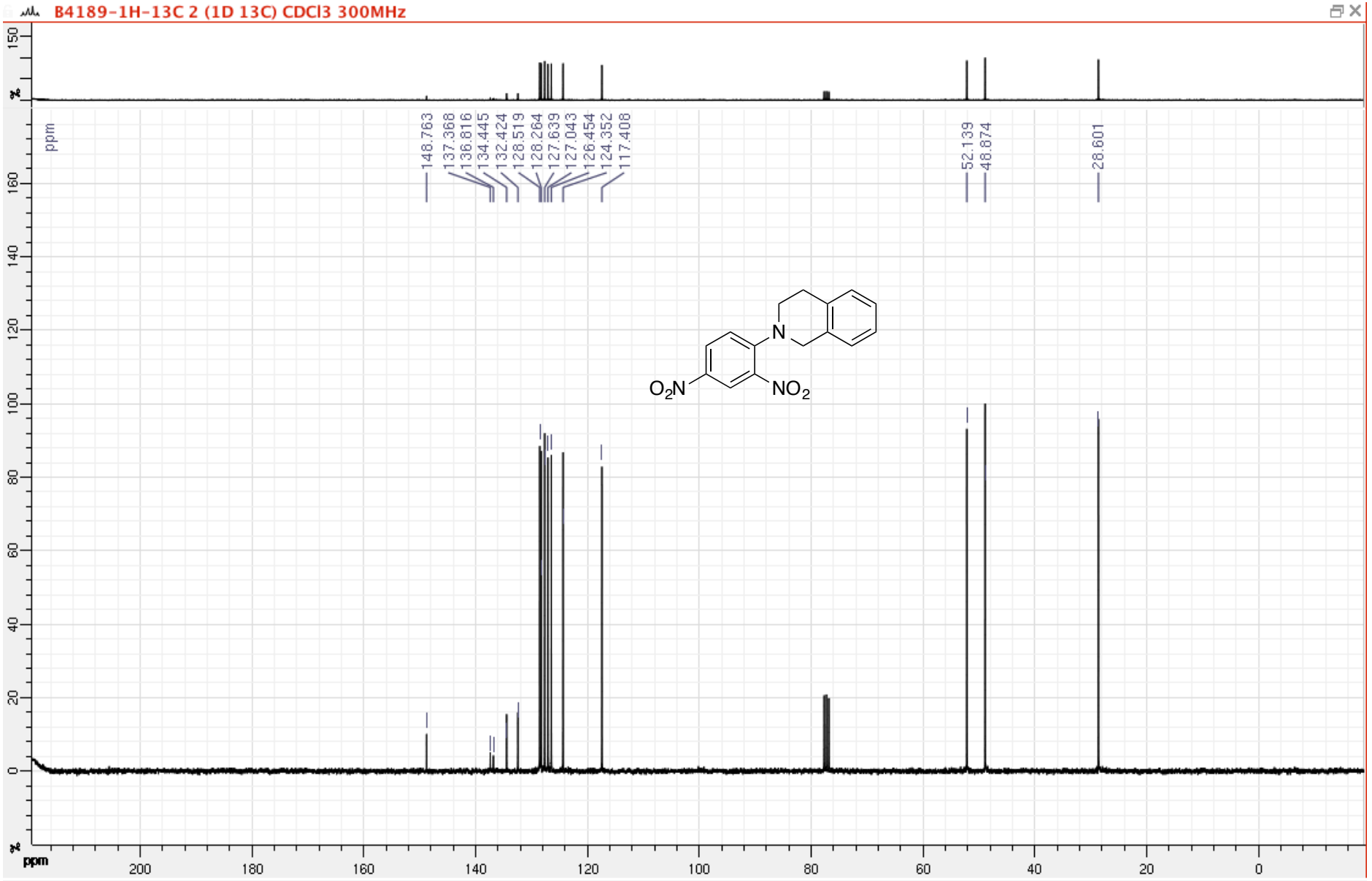
1-(2,4-Dinitrophenyl)piperidine (1q)



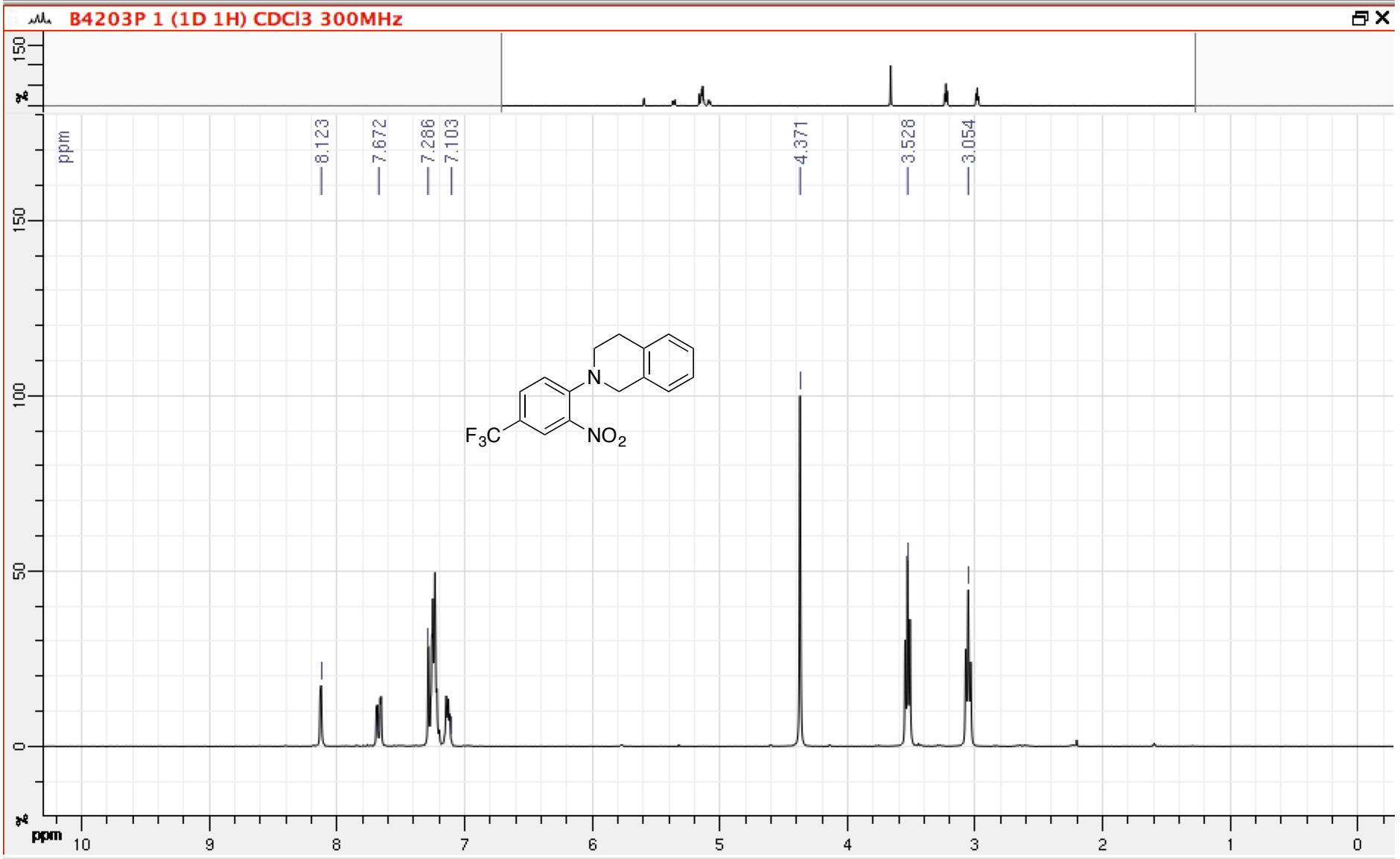

B4190-1H-13C 2 (1D 13C) CDCl3 300MHz
ppm
149.932
137.490
137.476
128.241
119.275
52.043
25.618
23.698
N
O2N
NO2
200
180
160
140
120
100
80
60
40
20
0

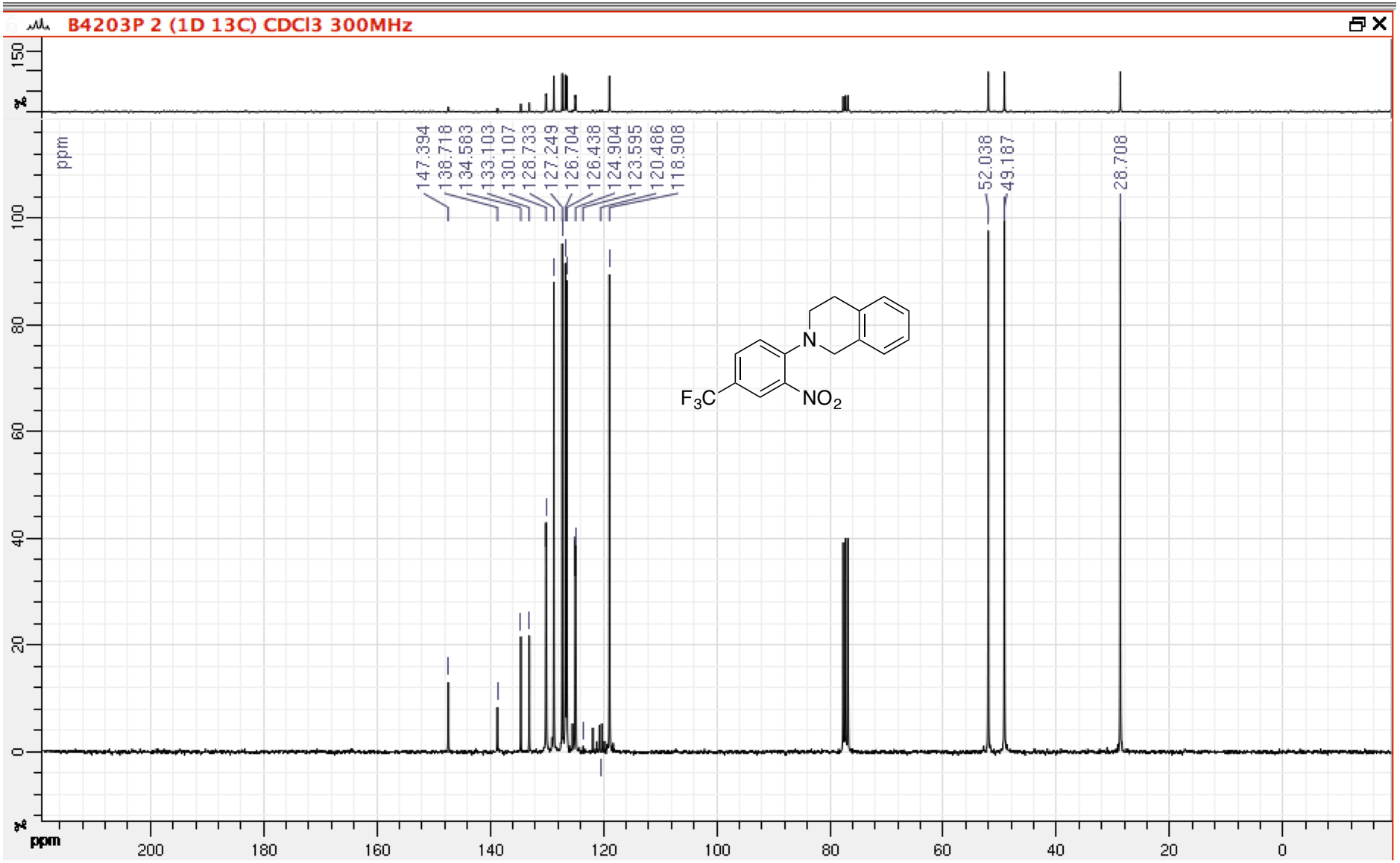
2-(2,4-Dinitrophenyl)-1,2,3,4-tetrahydroisoquinoline (1r)



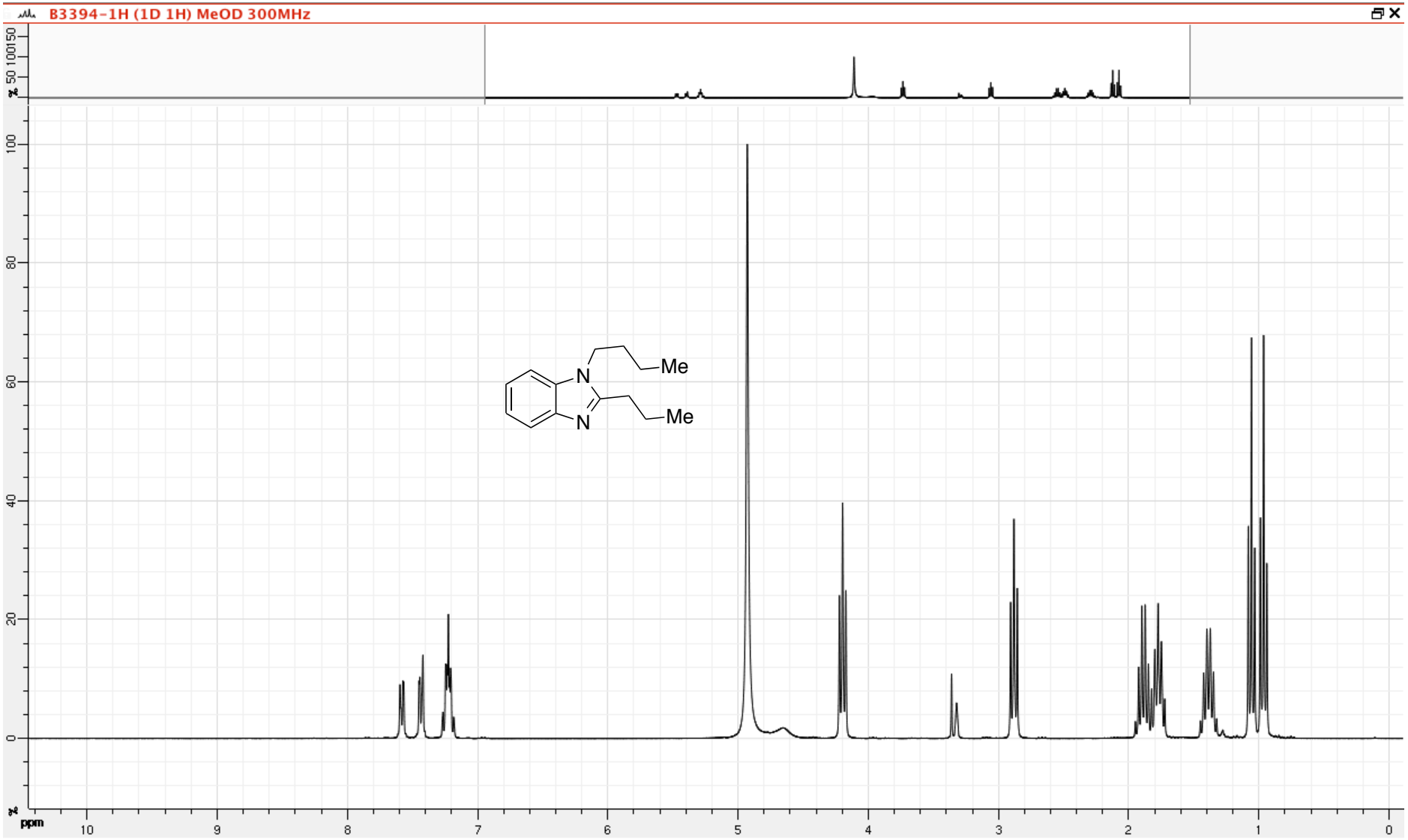

B4189-1H-13C 2 (1D 13C) CDCl3 300MHz
ppm
148.763
137.368
136.816
134.445
132.424
128.519
128.264
127.639
127.043
126.454
124.352
117.408
52.139
48.874
28.601
N
O2N
NO2
ppm
200
180
160
140
120
100
80
60
40
20
0

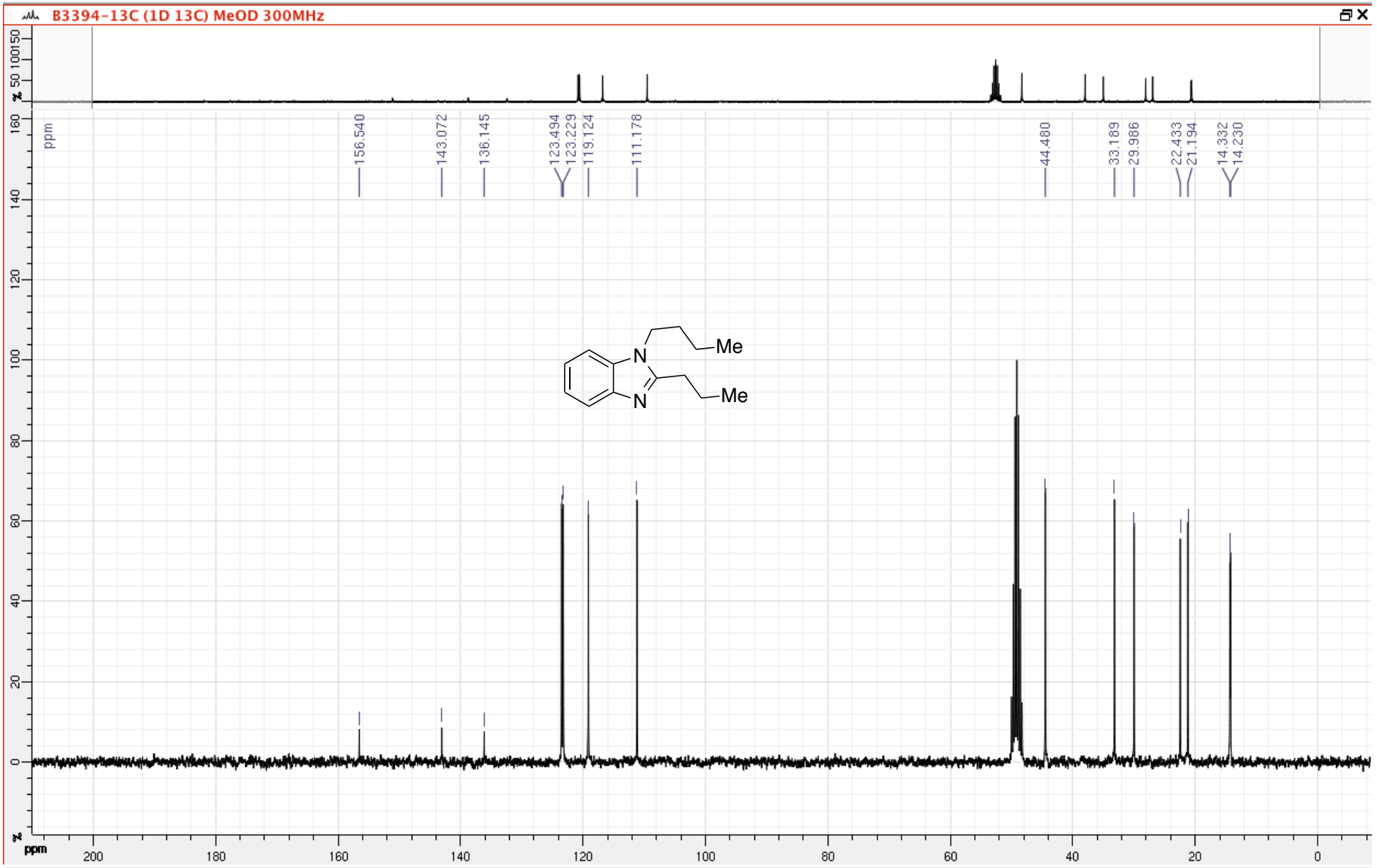
2-(2-Nitro-4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (1s)



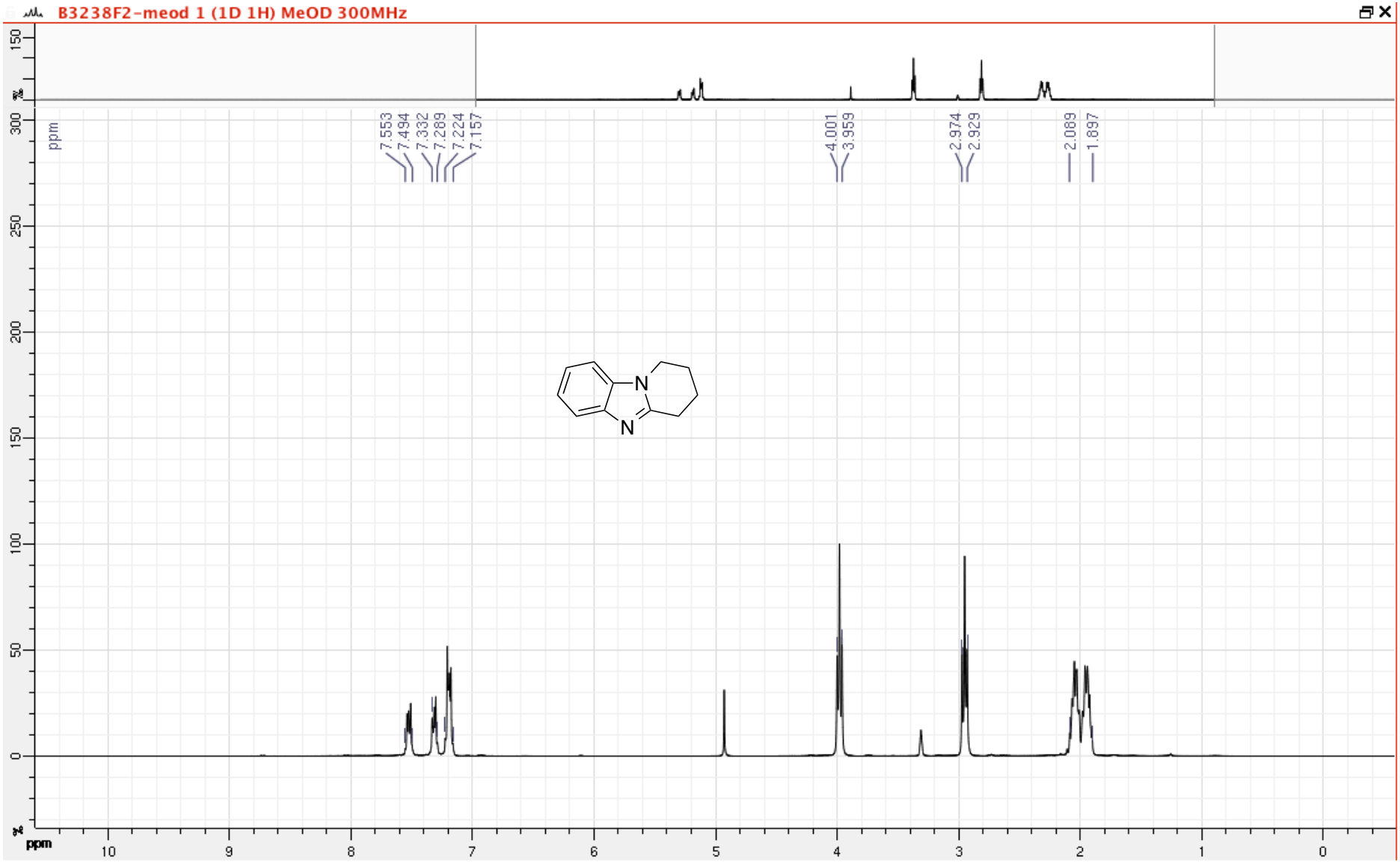

B4203P 2 (1D 13C) CDCl3 300MHz
ppm
147.394
138.718
134.583
133.103
130.107
128.733
127.249
126.704
126.438
124.904
123.595
120.486
118.908
52.038
49.187
28.708
N
F3C
NO2

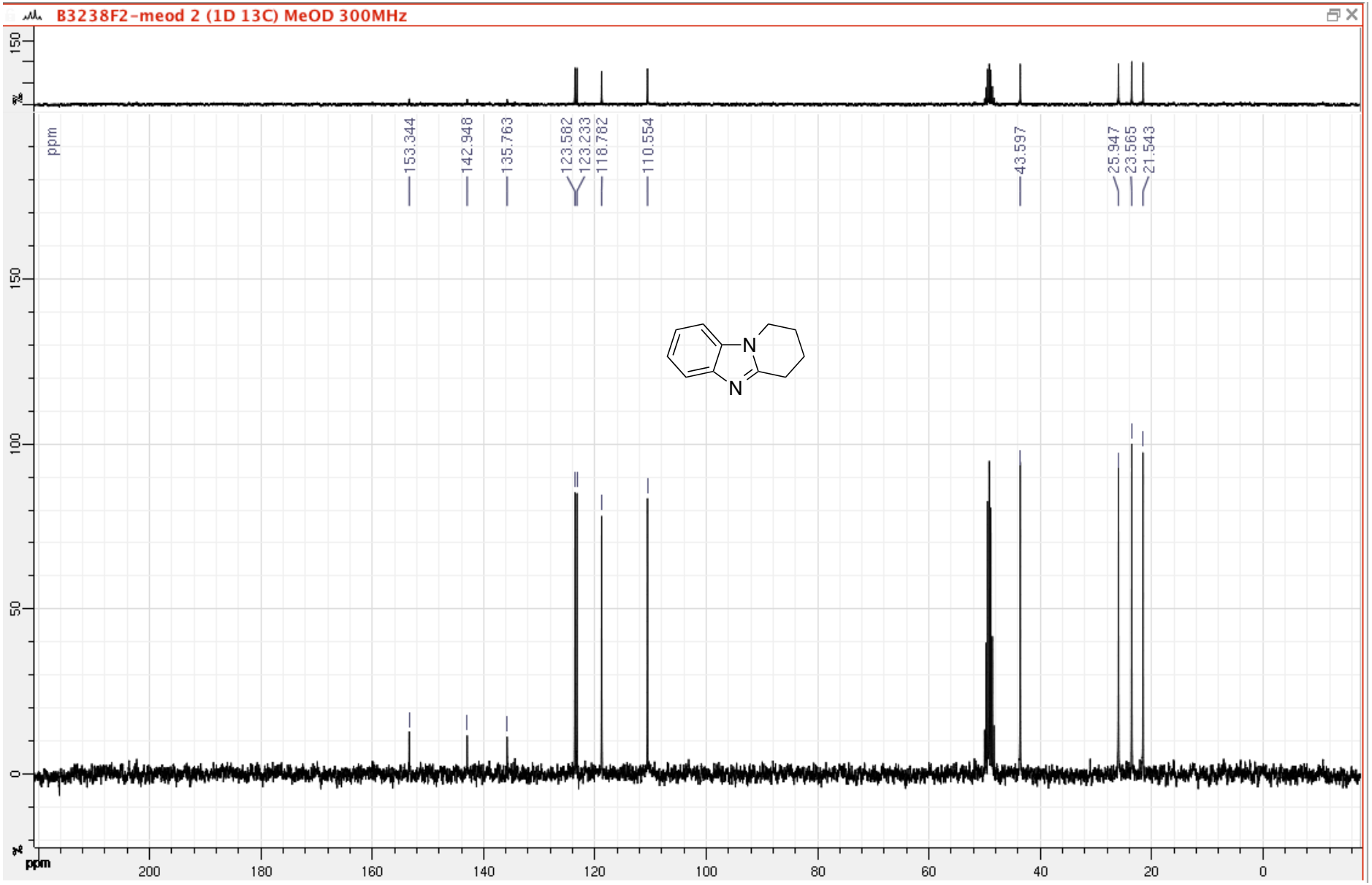
1-Butyl-2-propyl-1*H*-benzo[*d*]imidazole (2a)



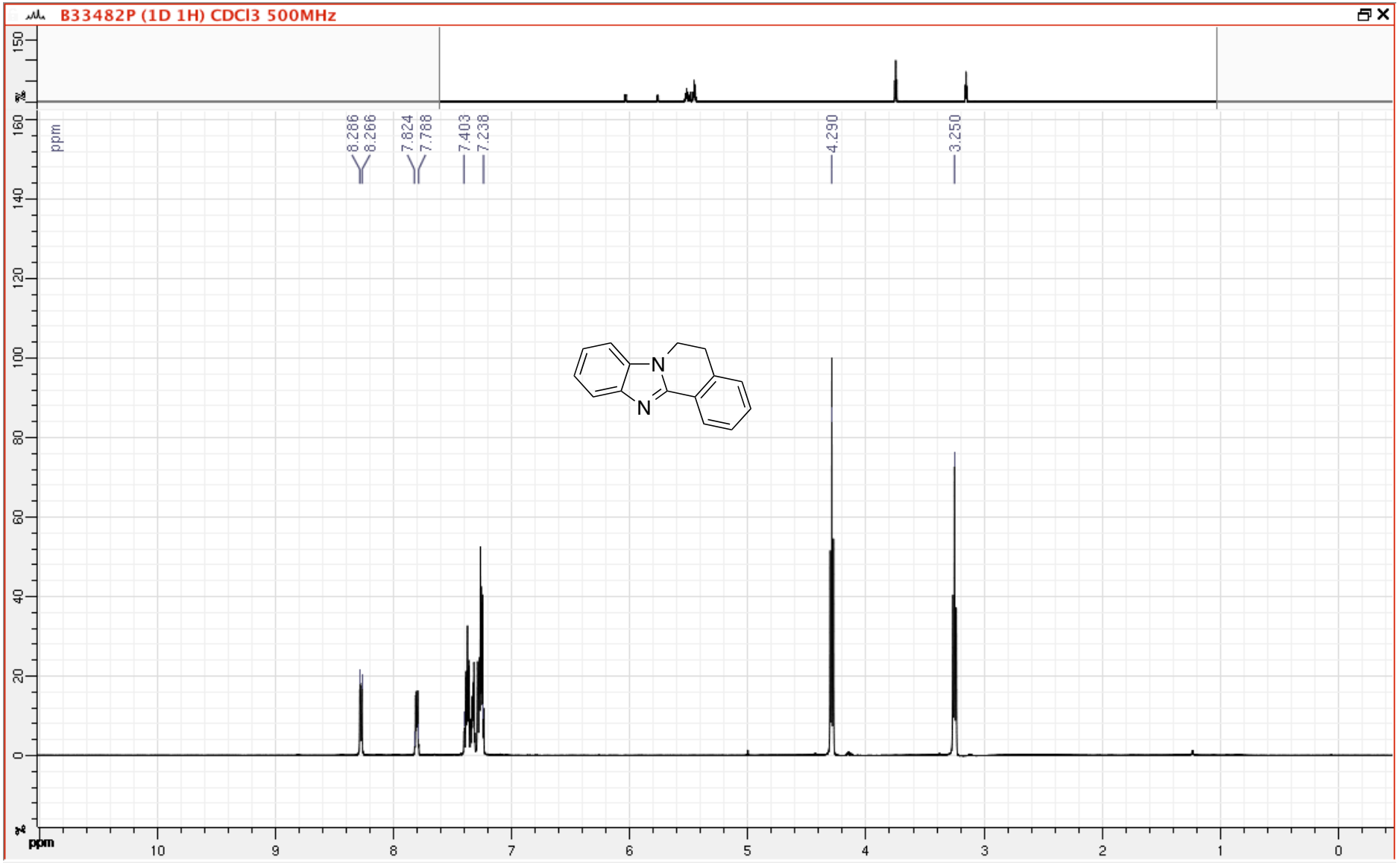

B3394-13C (1D 13C) MeOD 300MHz
ppm
156.540
143.072
136.145
123.494
123.229
119.124
111.178
44.480
33.189
29.986
22.433
21.194
14.332
14.230
N
N
Me
Me

1,2,3,4-Tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2b)

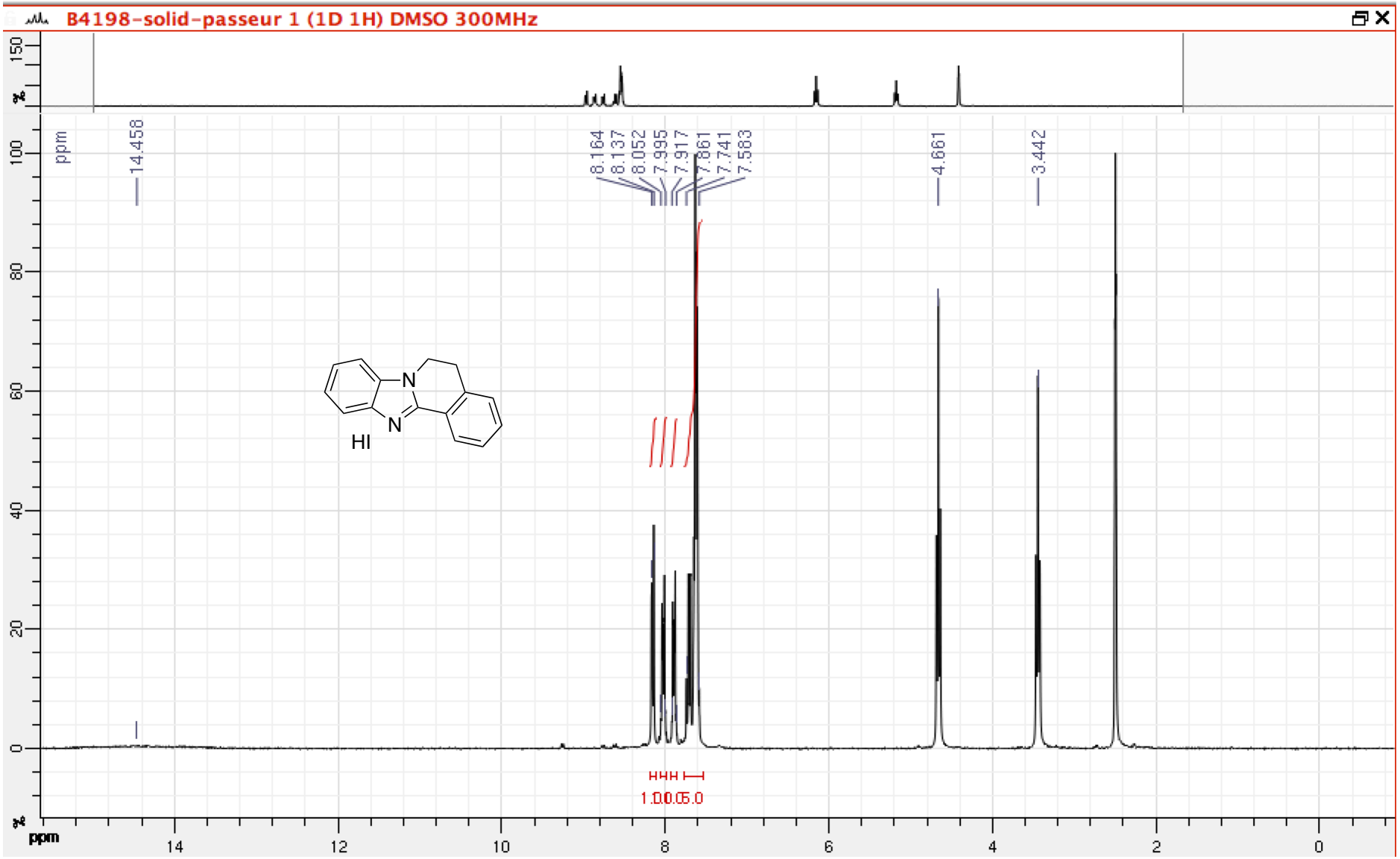


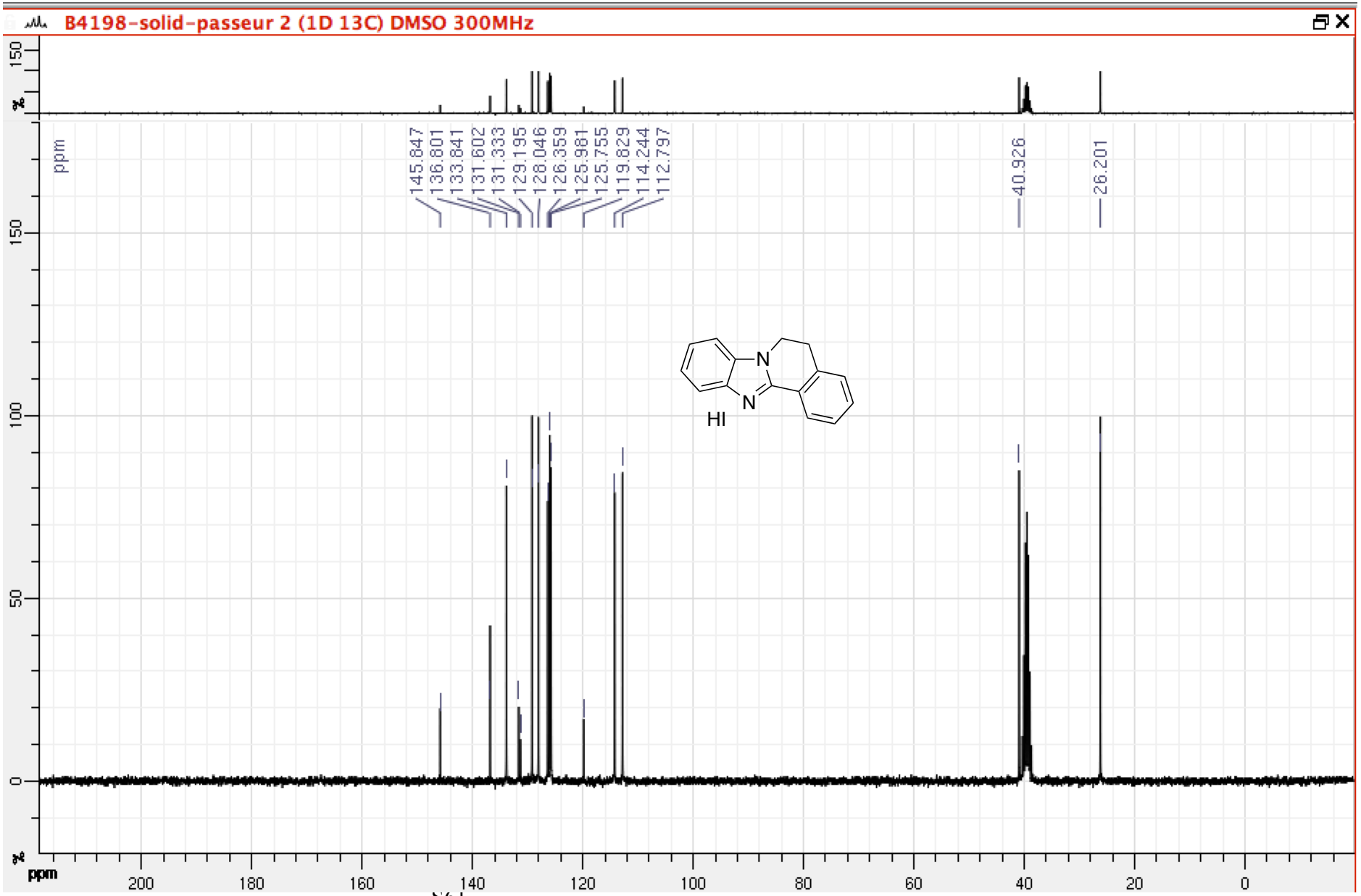

B3238F2-meod 2 (1D 13C) MeOD 300MHz
ppm
153.344
142.948
135.763
123.582
123.233
118.782
110.554
43.597
25.947
23.565
21.543
N
N
150
100
50
0
200
180
160
140
120
100
80
60
40
20
0

5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (2c)

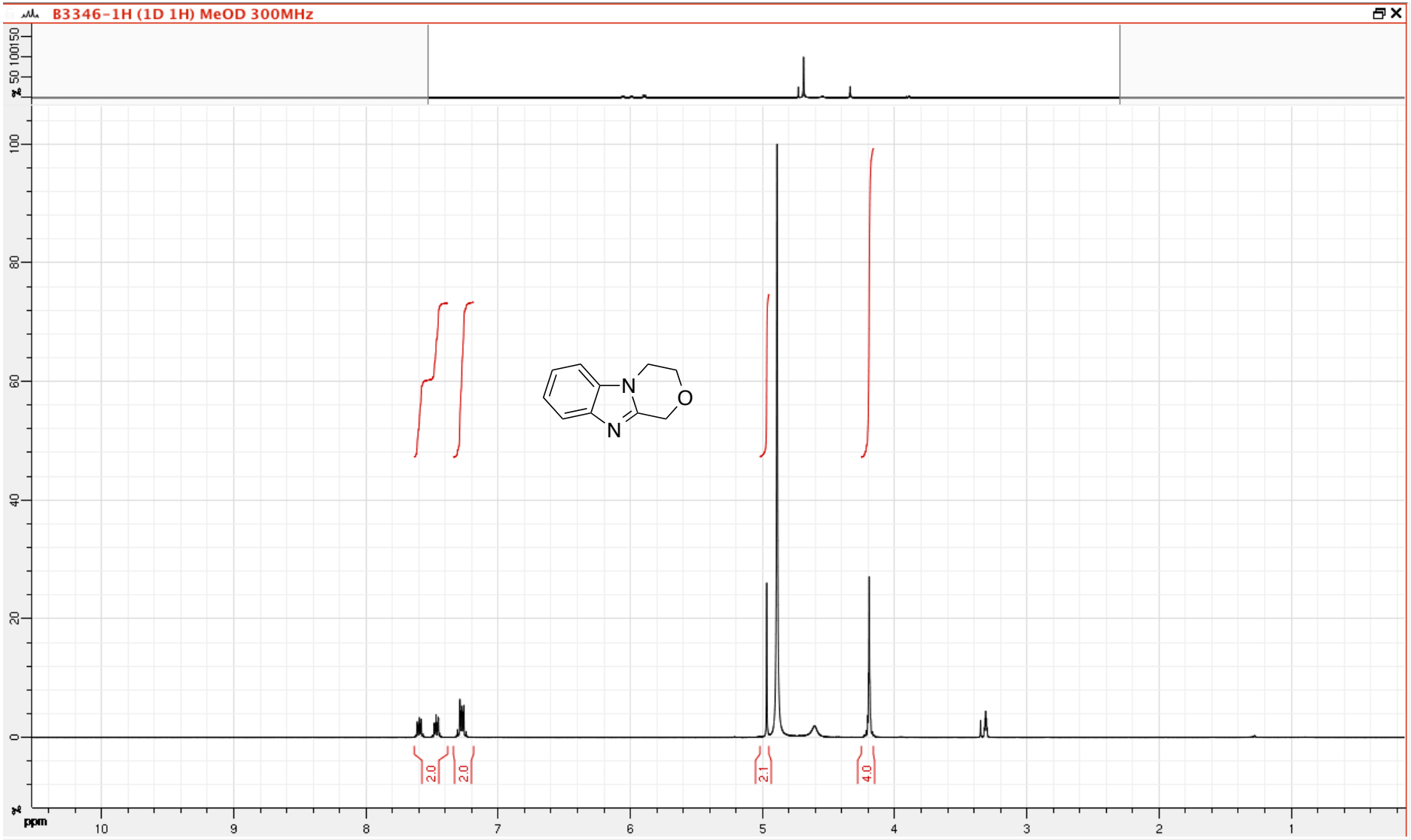


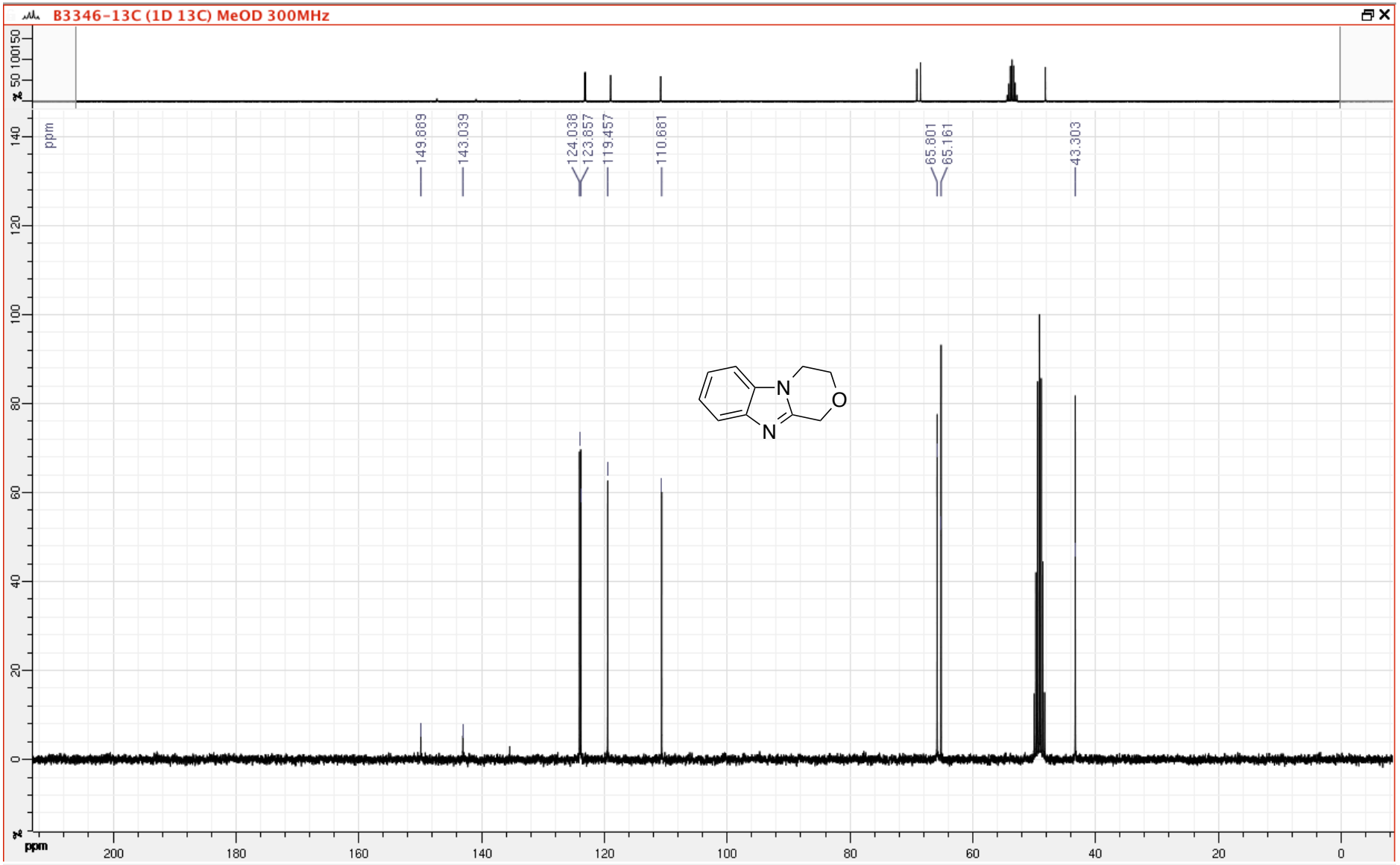
5,6-Dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline hydroiodide (2c·HI)



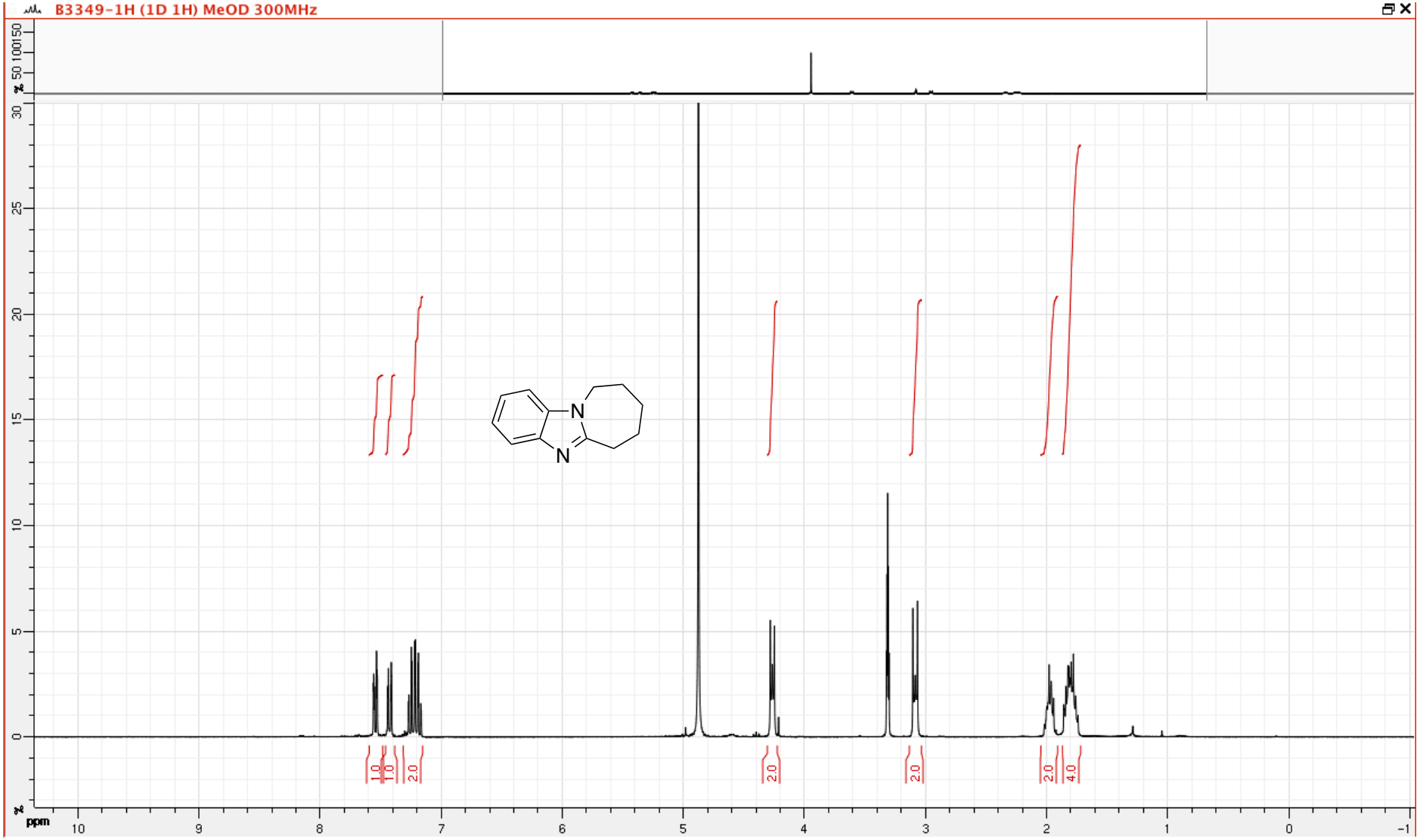

B4198-solid-passeur 2 (1D 13C) DMSO 300MHz
ppm
145.847
136.801
133.841
131.602
131.333
129.195
128.046
126.359
125.981
125.755
119.829
114.244
112.797
40.926
26.201
N
N
HI
200
180
160
140
120
100
80
60
40
20
0

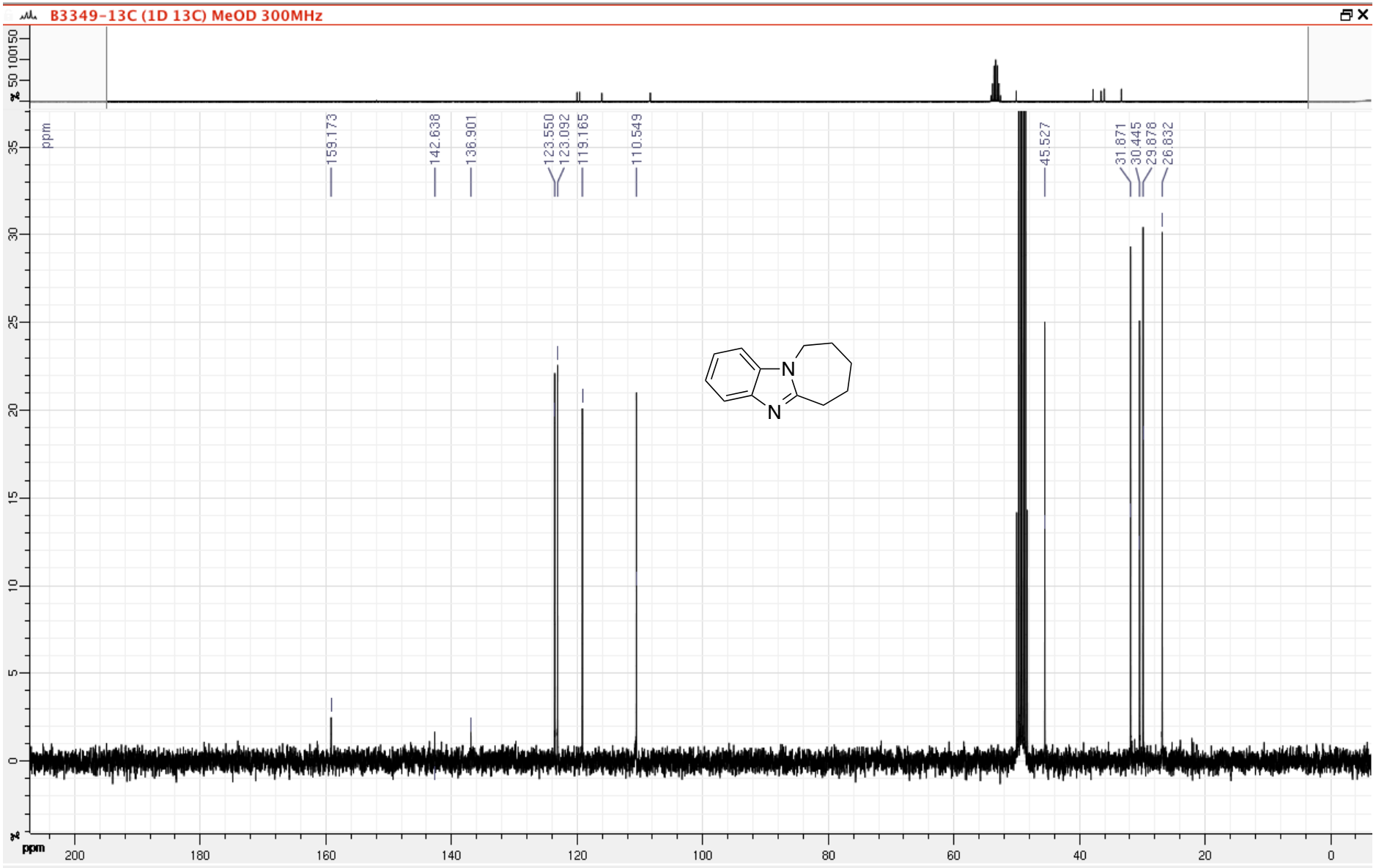
3,4-Dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2d)



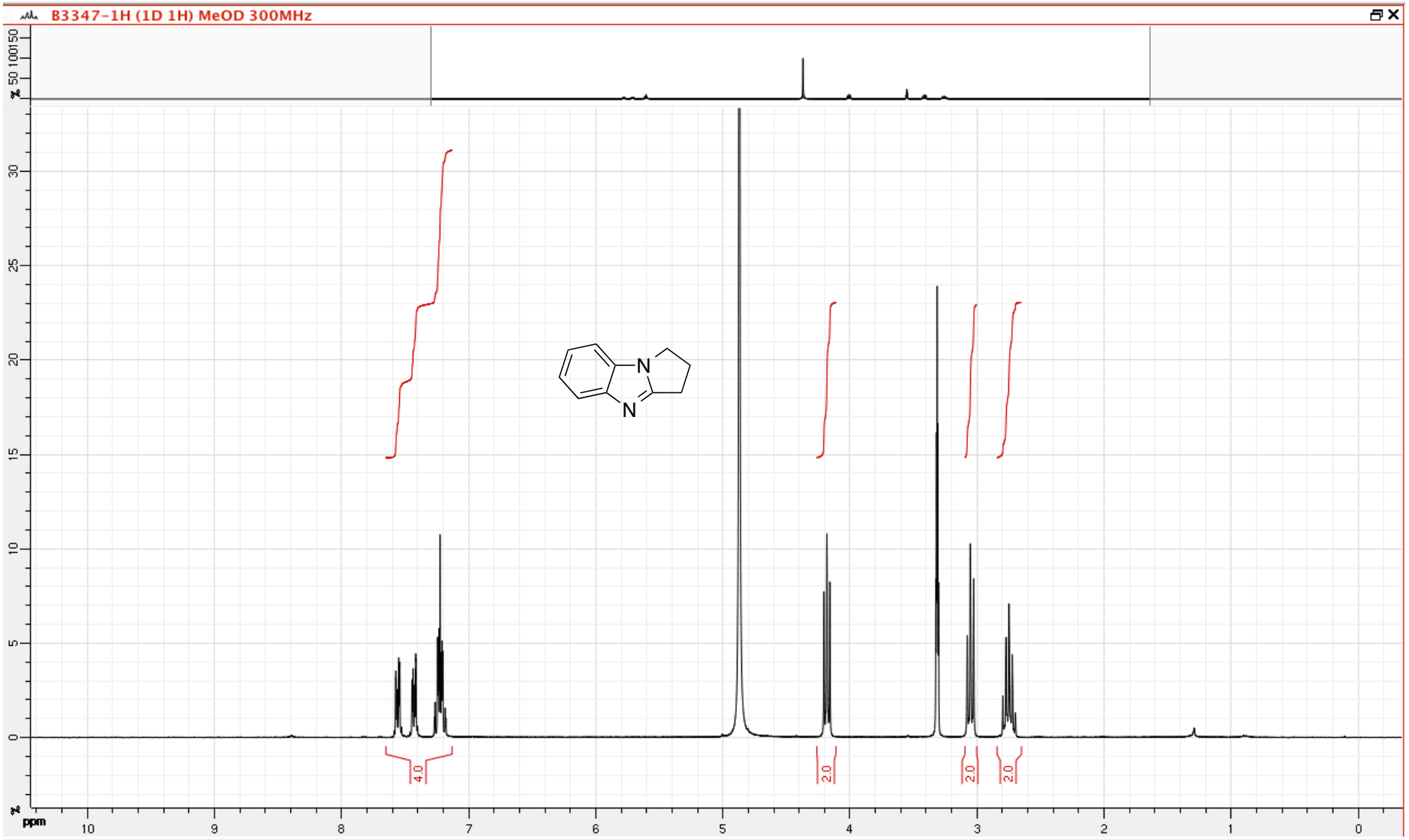

B3346-13C (1D 13C) MeOD 300MHz
ppm
149.889
143.039
124.038
123.857
119.457
110.681
65.801
65.161
43.303
N
O
N

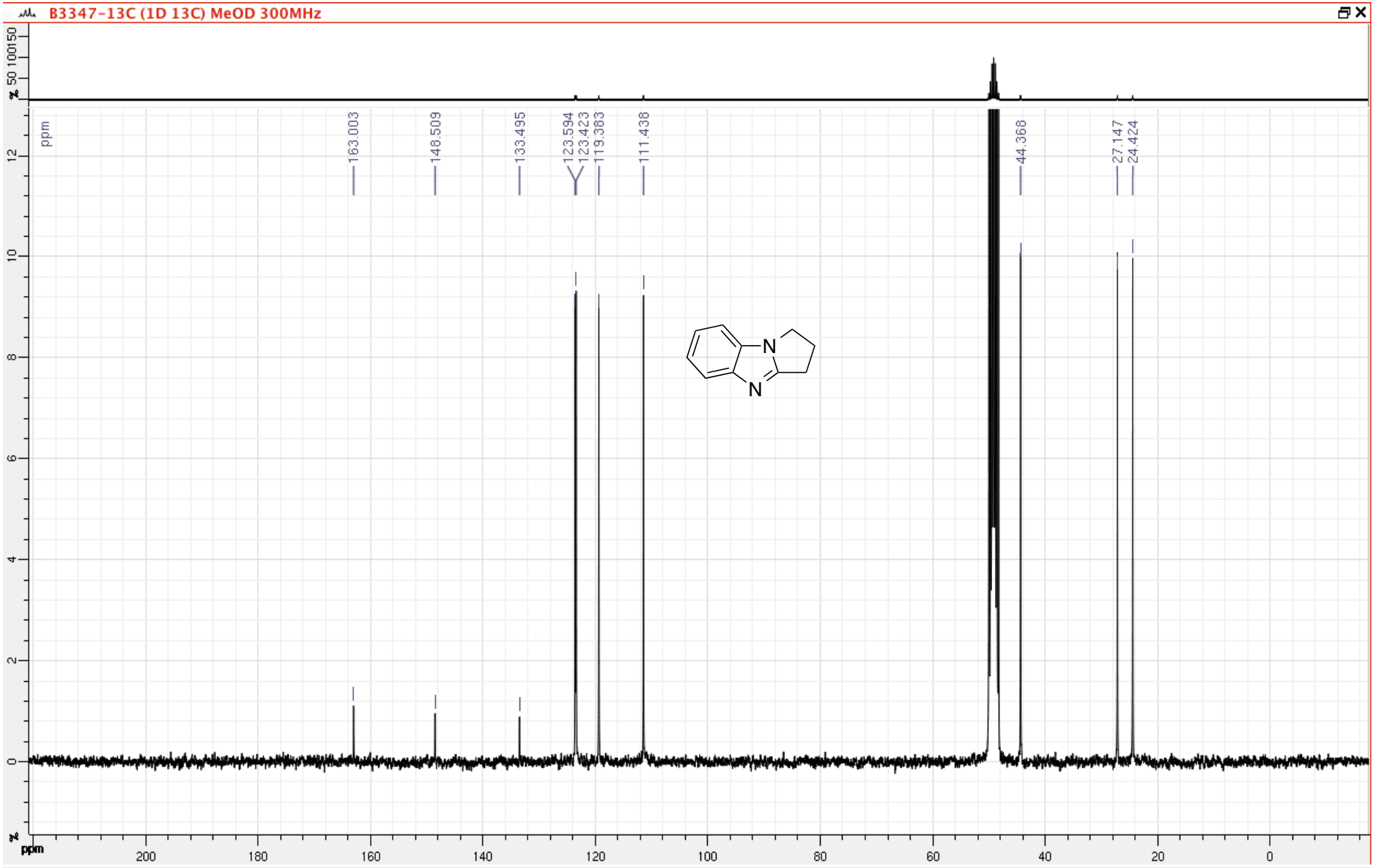
7,8,9,10-Tetrahydro-6*H*-benzo[4,5]imidazo[1,2-*a*]azepine (2e)



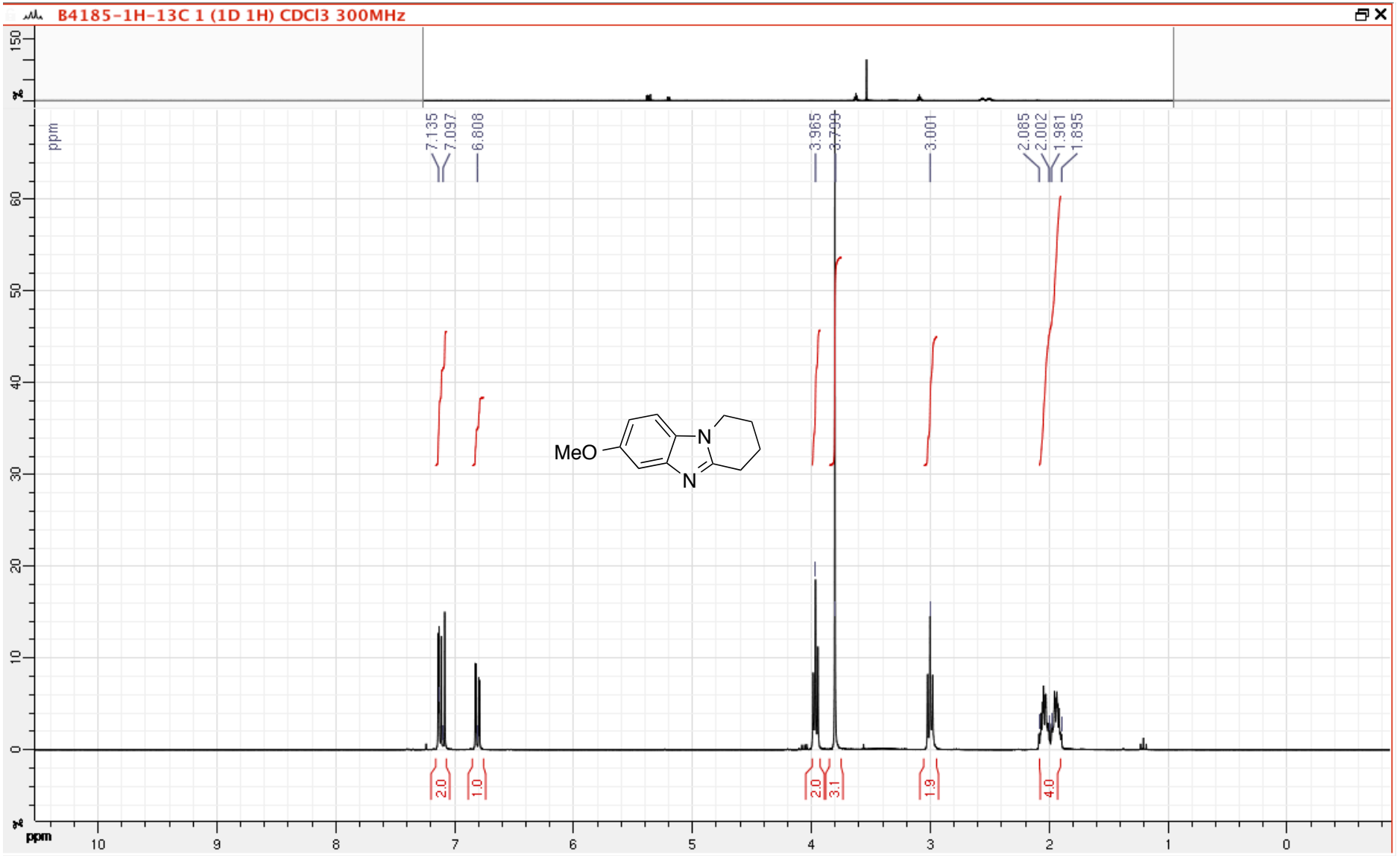

B3349-13C (1D 13C) MeOD 300MHz
ppm
159.173
142.638
136.901
123.550
123.092
119.165
110.549
45.527
31.871
30.445
29.878
26.832
N
N
200
180
160
140
120
100
80
60
40
20
0

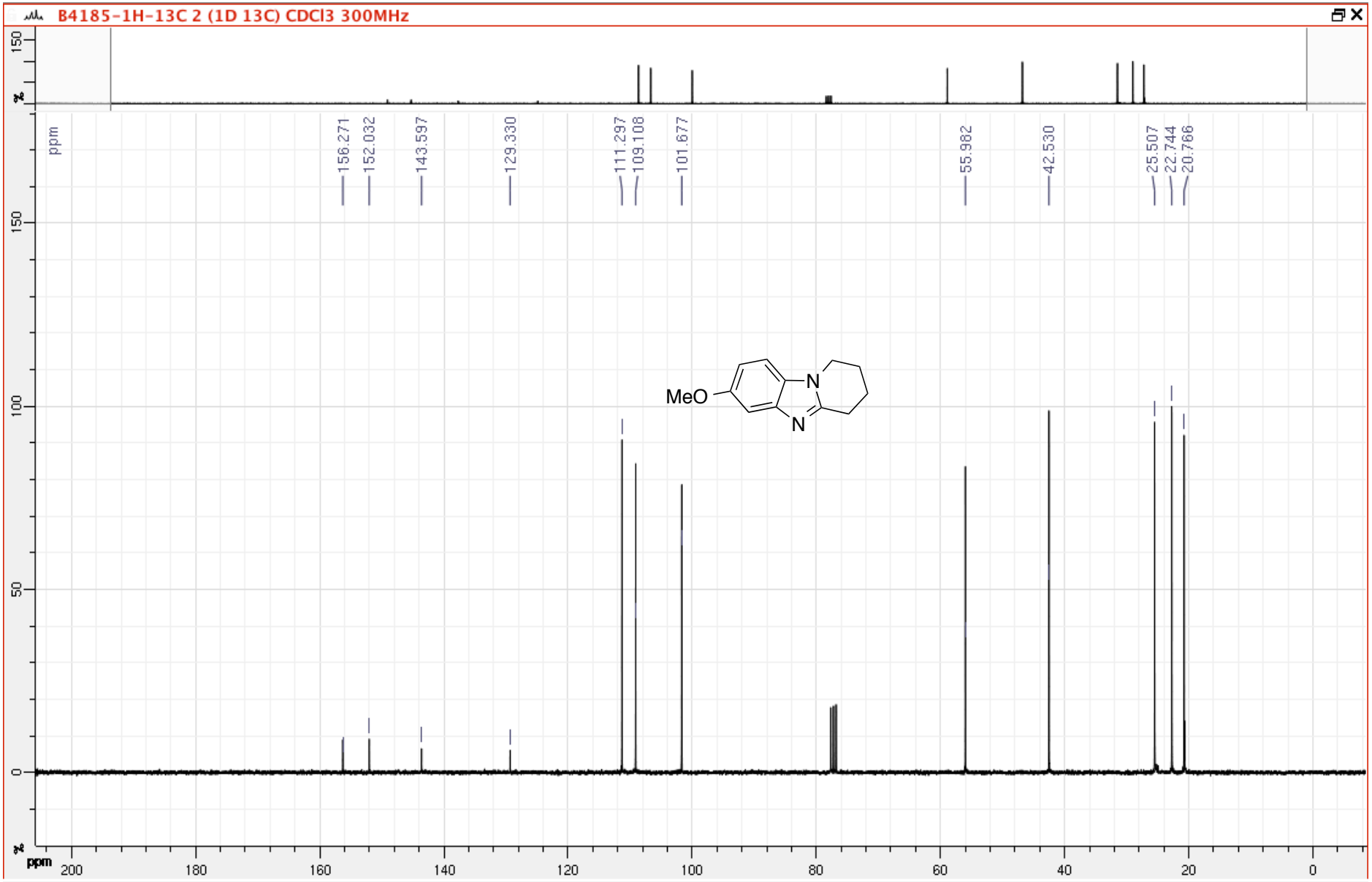
2,3-Dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole (2f)



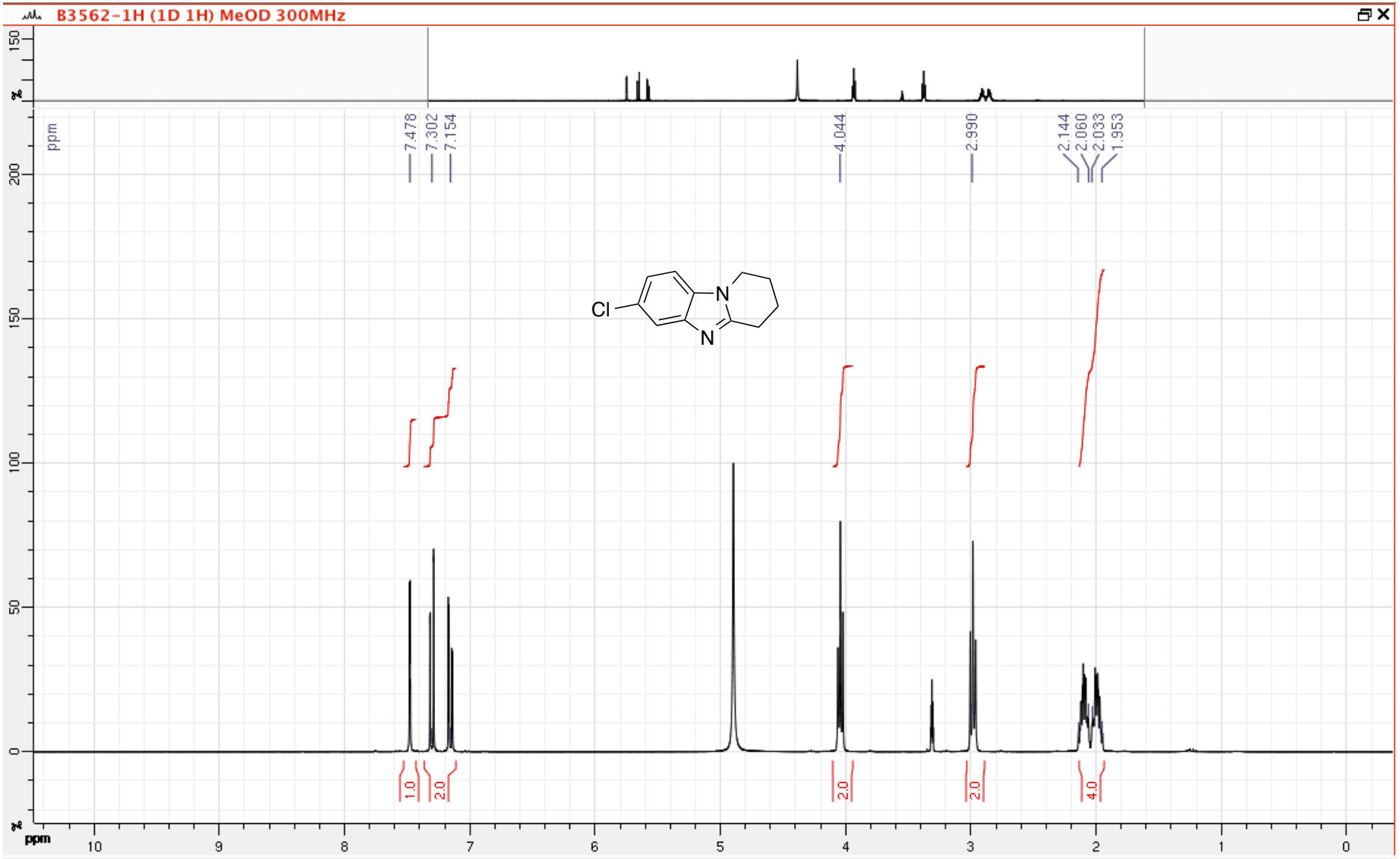

B3347-13C (1D 13C) MeOD 300MHz
ppm
163.003
148.509
133.495
123.594
123.423
119.383
111.438
44.368
27.147
24.424
N
N

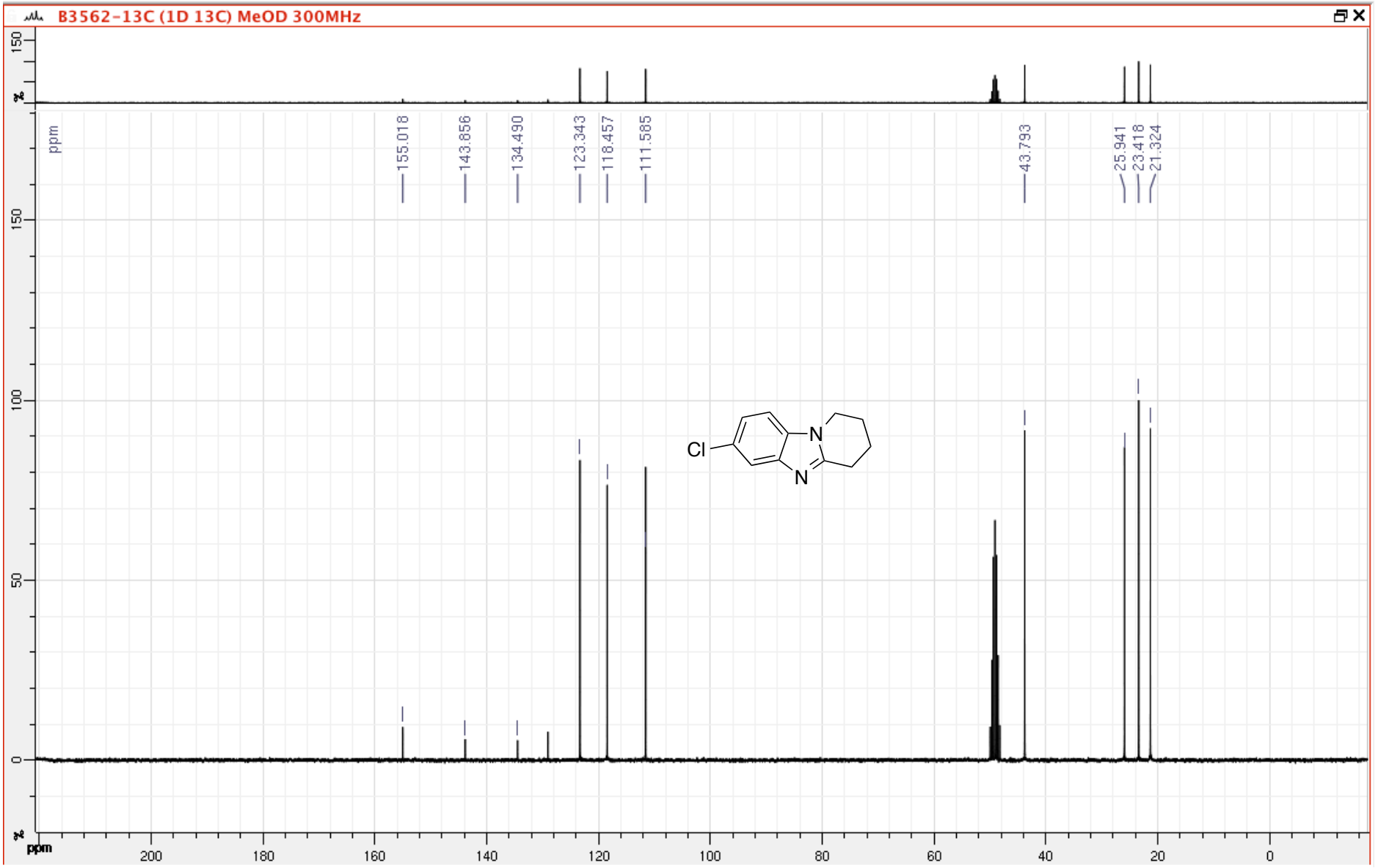
7-Methoxy-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2g)



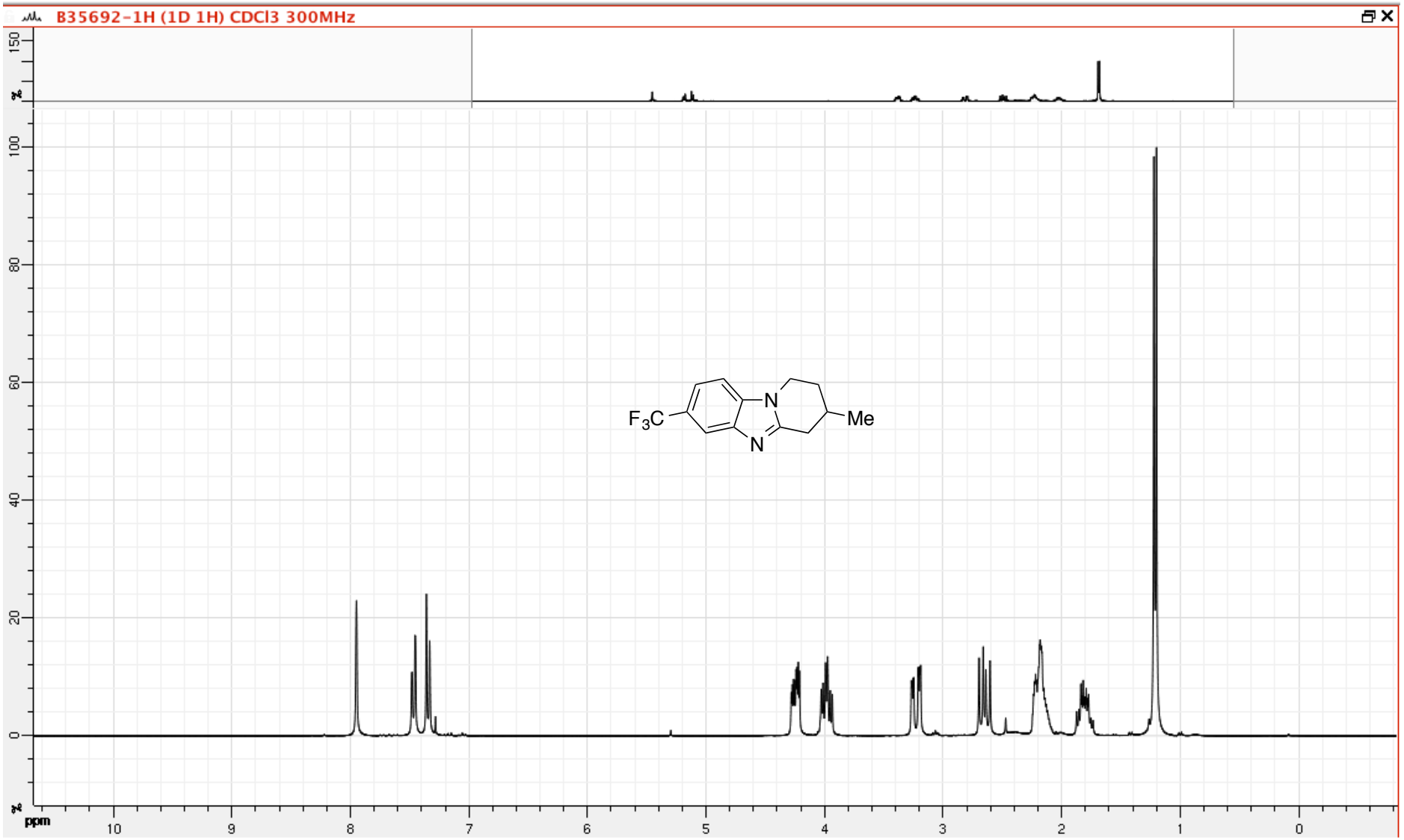

B4185-1H-13C 2 (1D 13C) CDCl3 300MHz
ppm
156.271
152.032
143.597
129.330
111.297
109.108
101.677
55.982
42.530
25.507
22.744
20.766
MeO
N
N
150
100
50
0
200
180
160
140
120
100
80
60
40
20
0

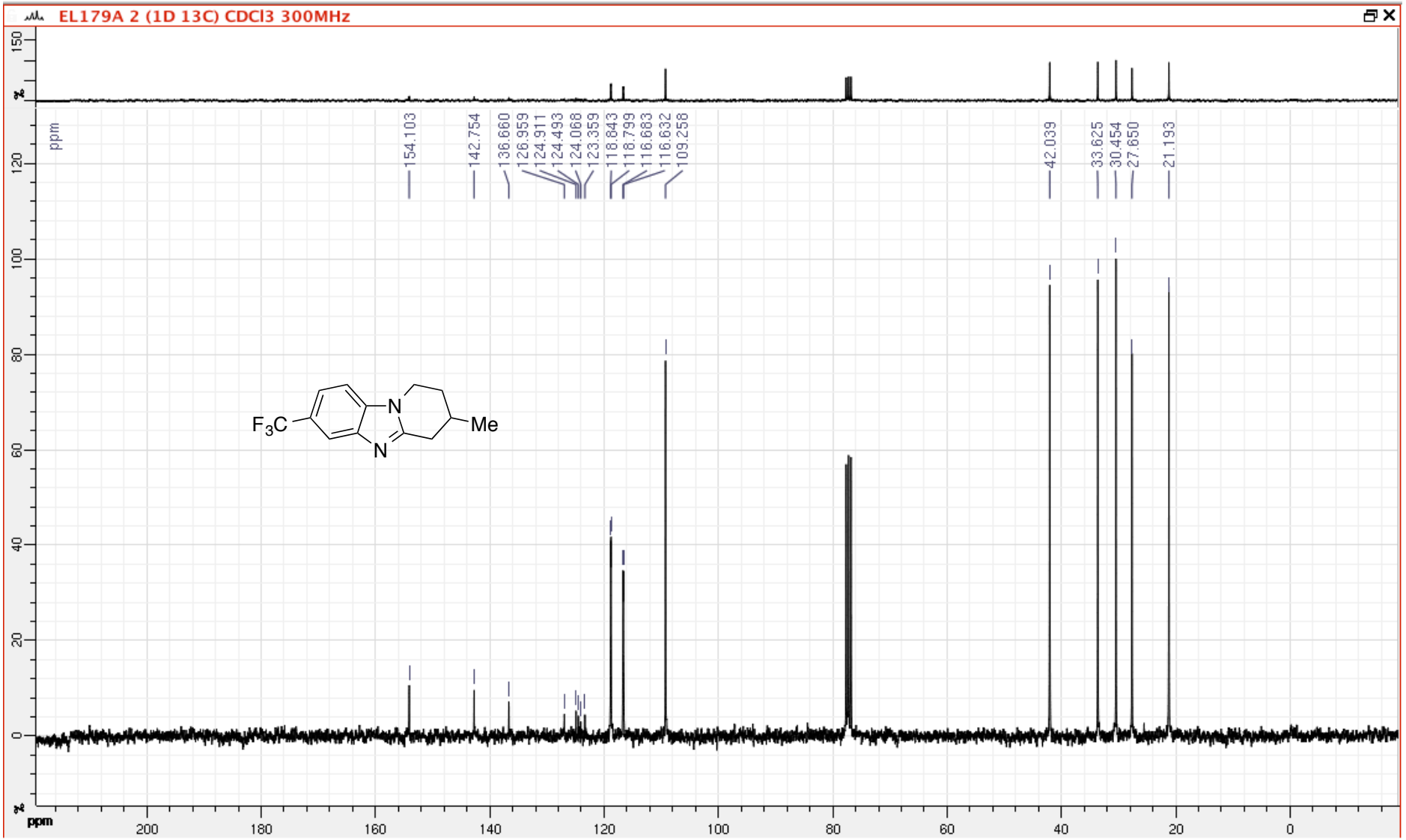
7-Chloro-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2h)



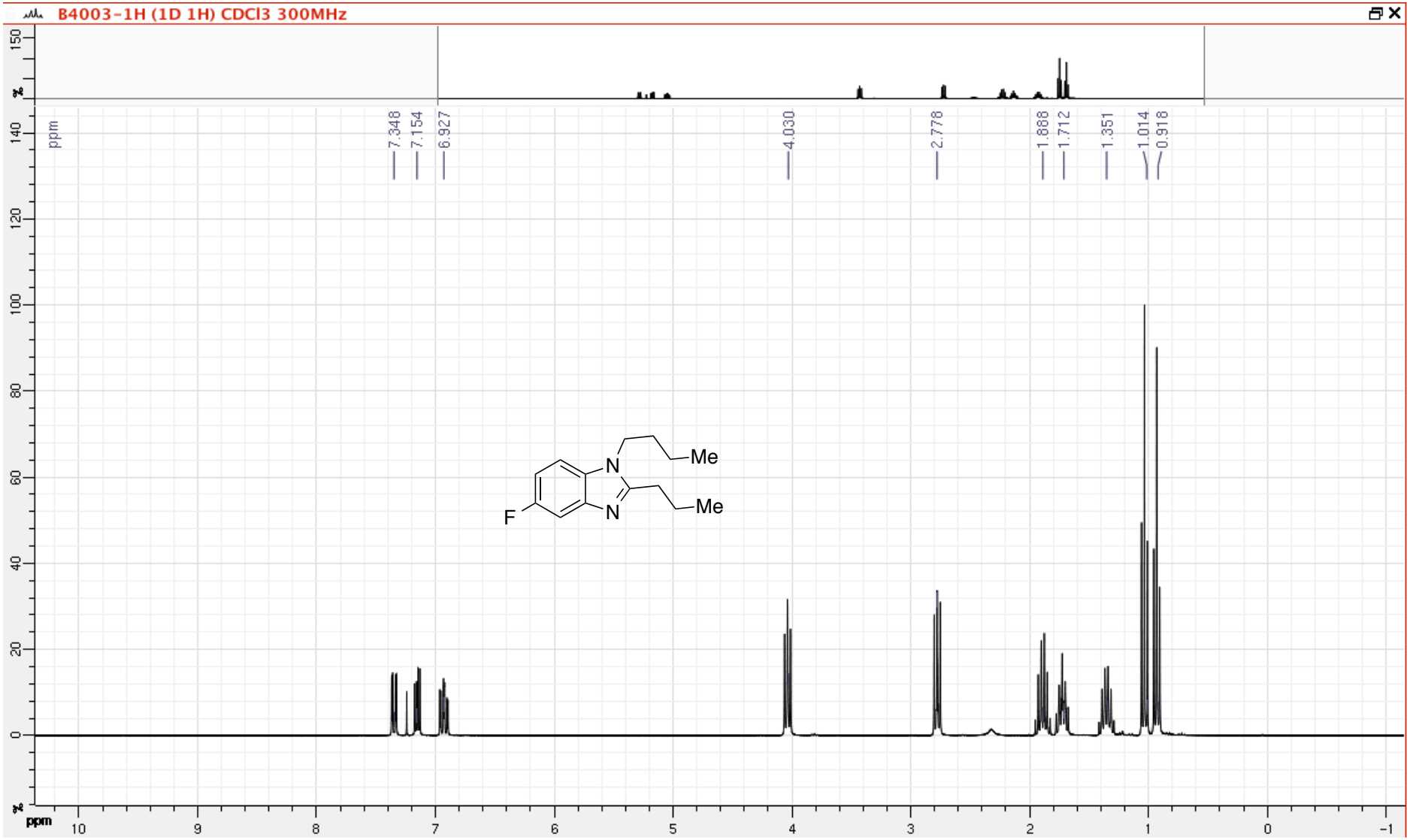

B3562-13C (1D 13C) MeOD 300MHz
ppm
155.018
143.856
134.490
123.343
118.457
111.585
43.793
25.941
23.418
21.324
Cl
N
N
200
180
160
140
120
100
80
60
40
20
0

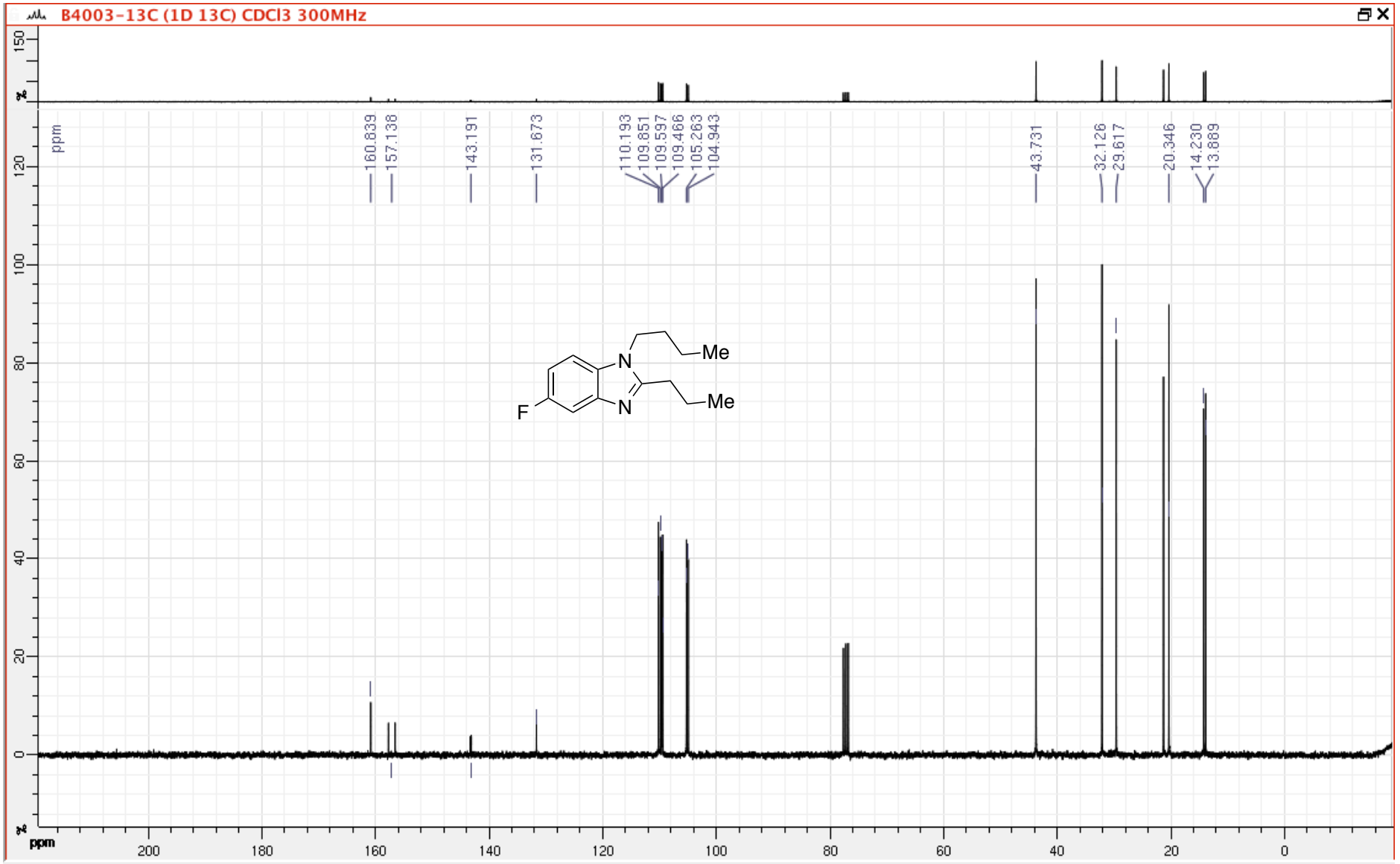
3-Methyl-7-(trifluoromethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2i)



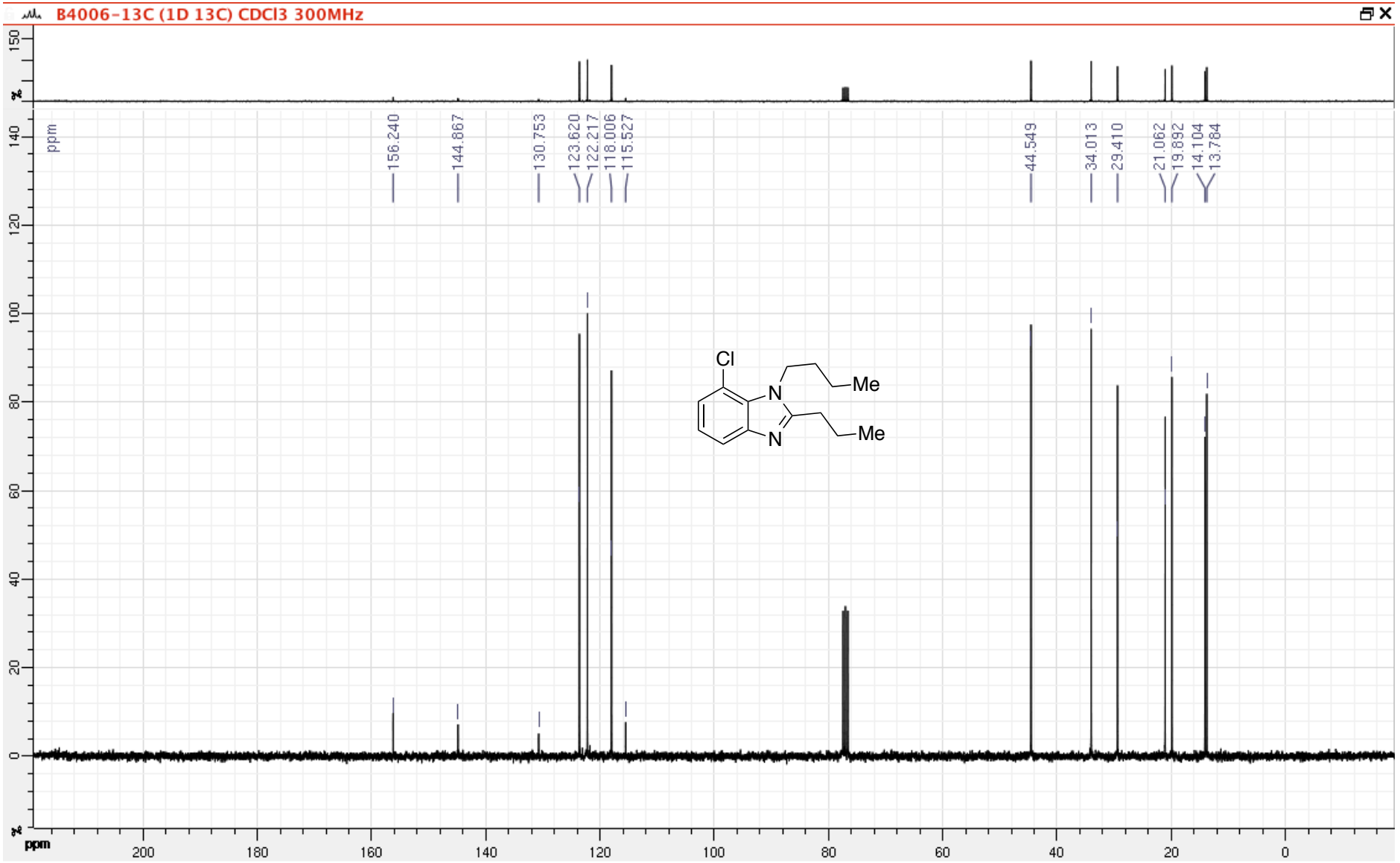

EL179A 2 (1D 13C) CDCl3 300MHz
ppm
154.103
142.754
136.660
126.959
124.911
124.493
124.068
123.359
118.843
118.799
116.683
116.632
109.258
42.039
33.625
30.454
27.650
21.193
F3C
N
N
Me
200
180
160
140
120
100
80
60
40
20
0

1-Butyl-5-fluoro-2-propyl-1*H*-benzo[*d*]imidazole (2j)

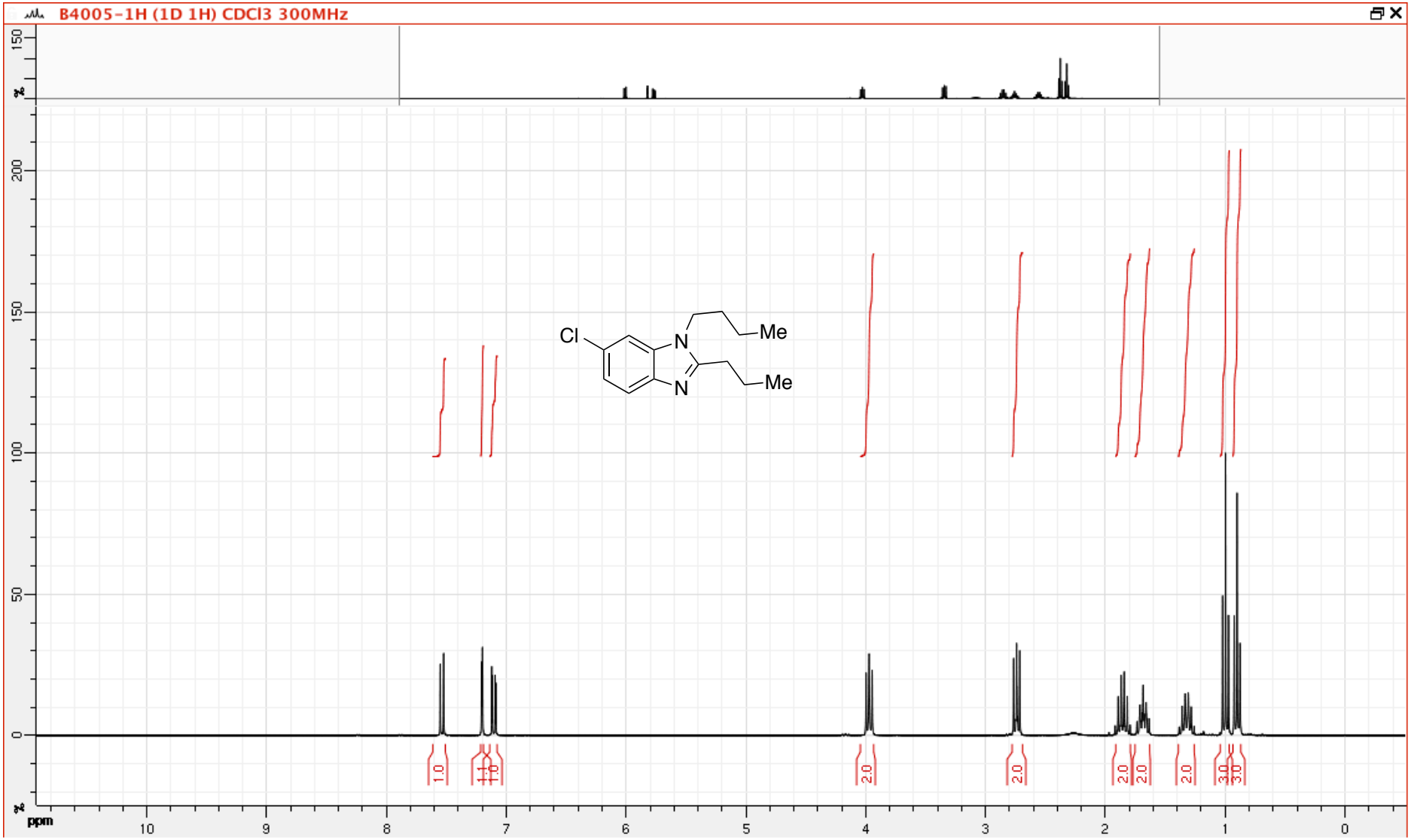


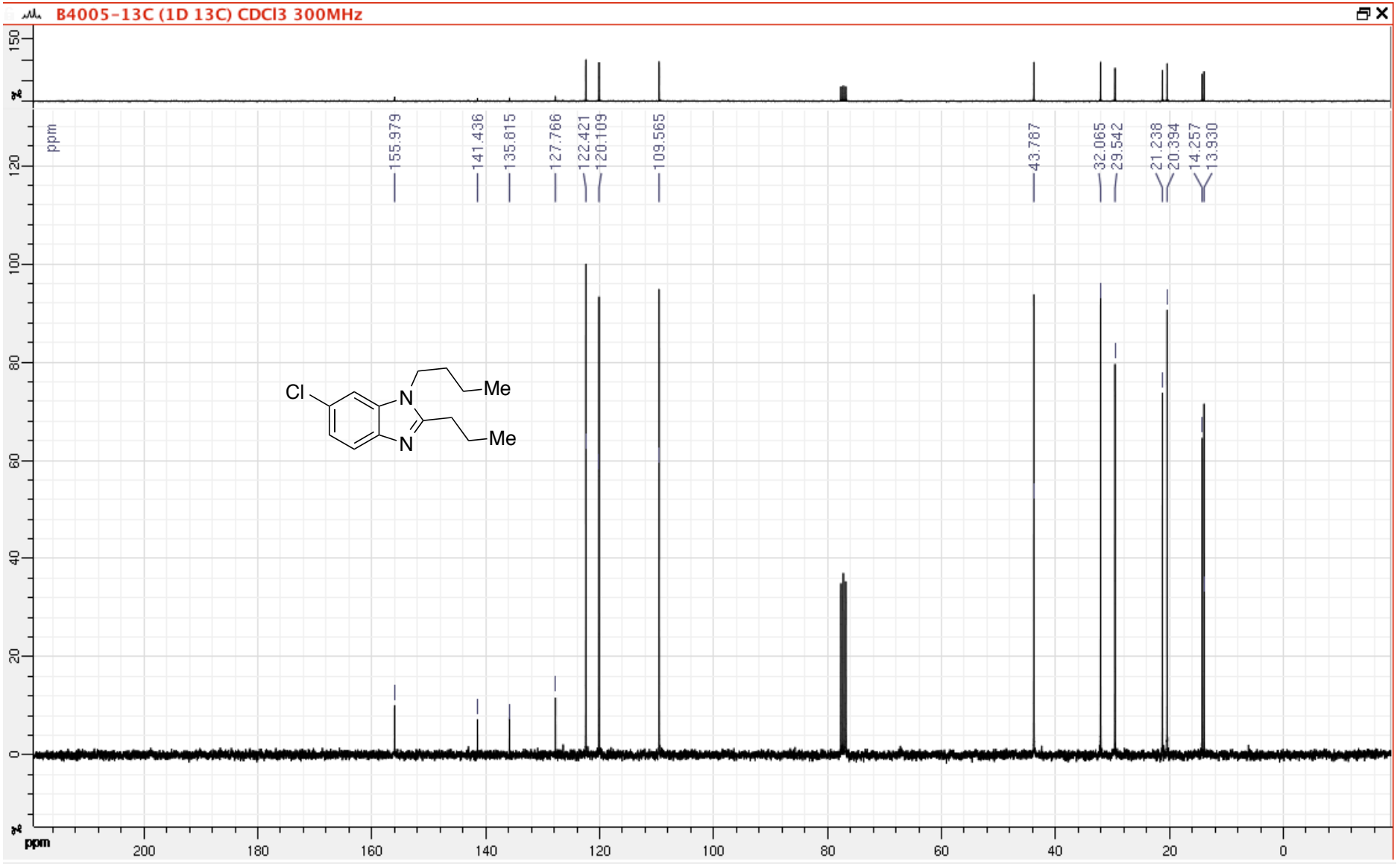

B4003-13C (1D 13C) CDCl3 300MHz
ppm
160.839
157.138
143.191
131.673
110.193
109.851
109.597
109.466
105.263
104.943
43.731
32.126
29.617
20.346
14.230
13.889
N
N
Me
Me
F
200
180
160
140
120
100
80
60
40
20
0

1-Butyl-7-chloro-2-propyl-1*H*-benzo[*d*]imidazole (2k)

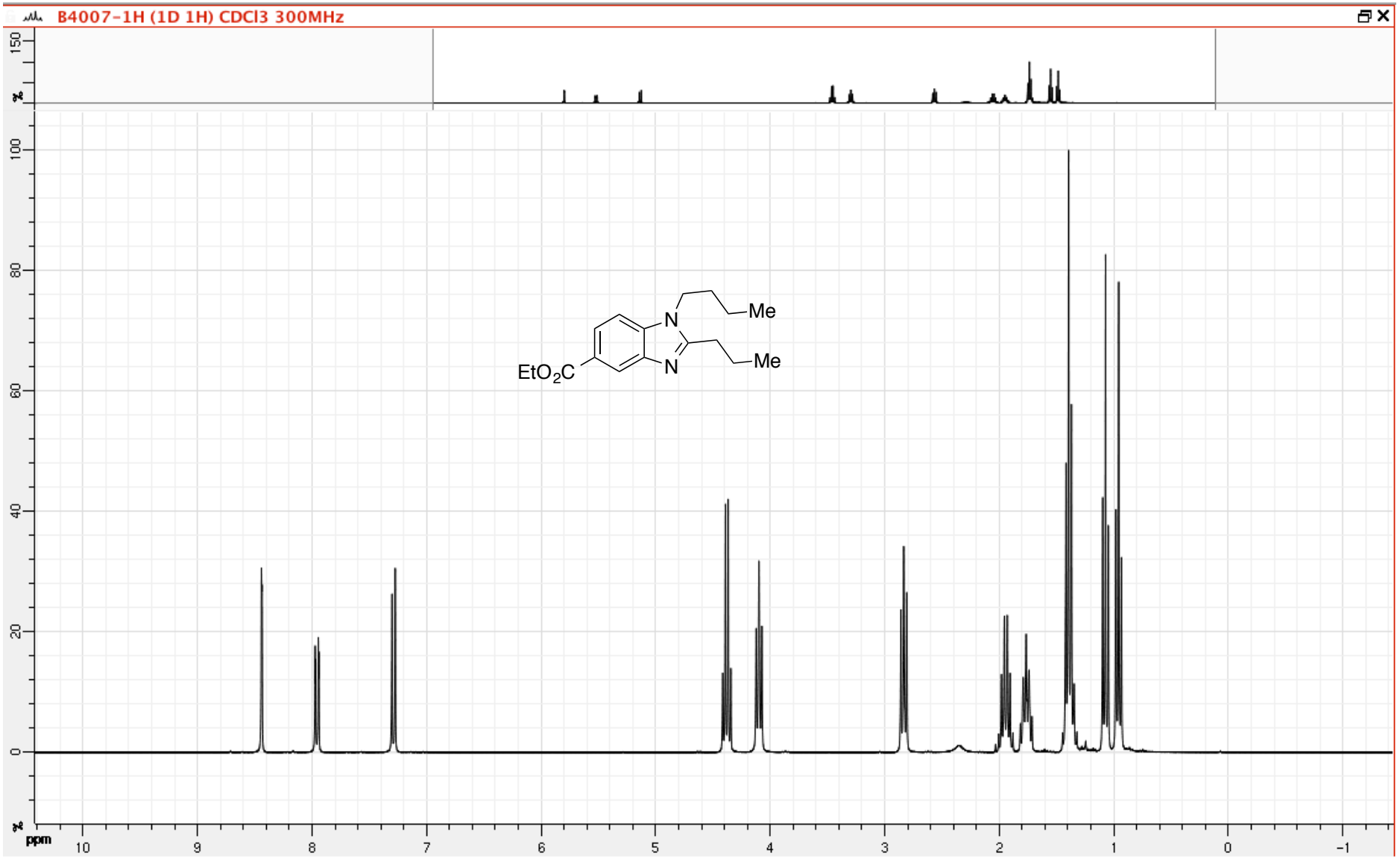

B4006-13C (1D 13C) CDCl3 300MHz
ppm
156.240
144.867
130.753
123.620
122.217
118.006
115.527
44.549
34.013
29.410
21.062
19.892
14.104
13.784
Cl
N
N
Me
Me

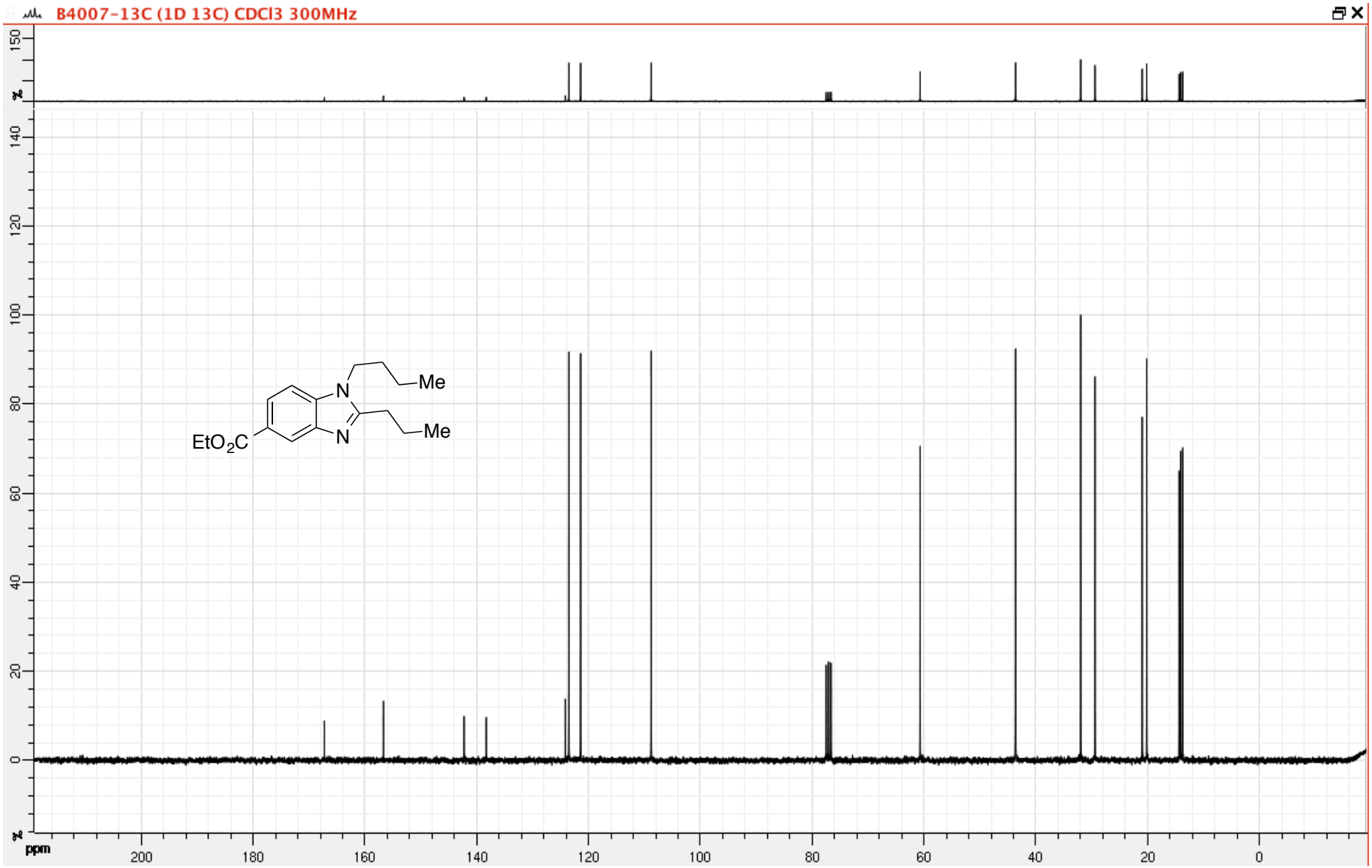
1-Butyl-6-chloro-2-propyl-1*H*-benzo[*d*]imidazole (2l)



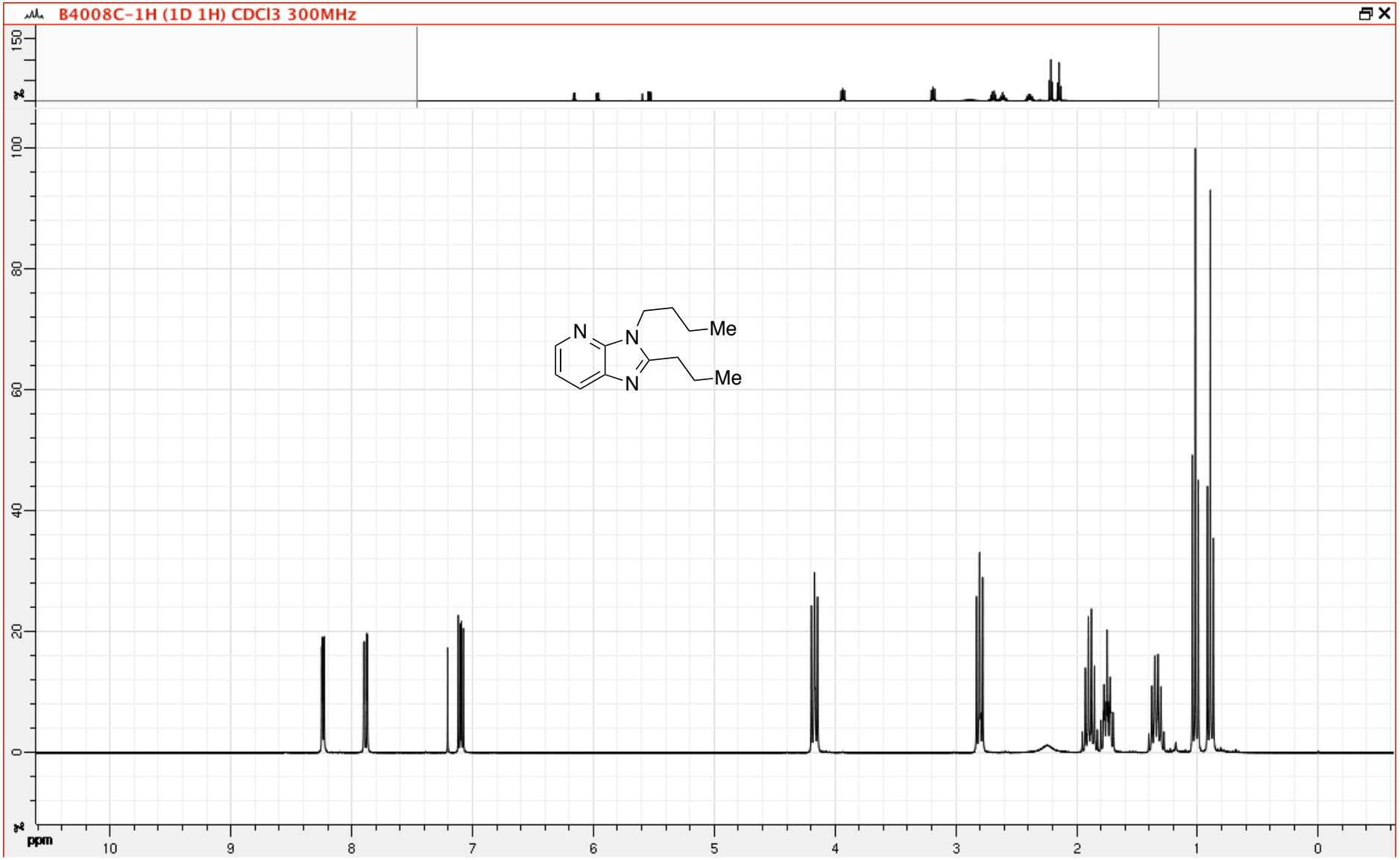

B4005-13C (1D 13C) CDCl3 300MHz
ppm
155.979
141.436
135.815
127.766
122.421
120.109
109.565
43.787
32.065
29.542
21.238
20.394
14.257
13.930
Cl
N
N
Me
Me

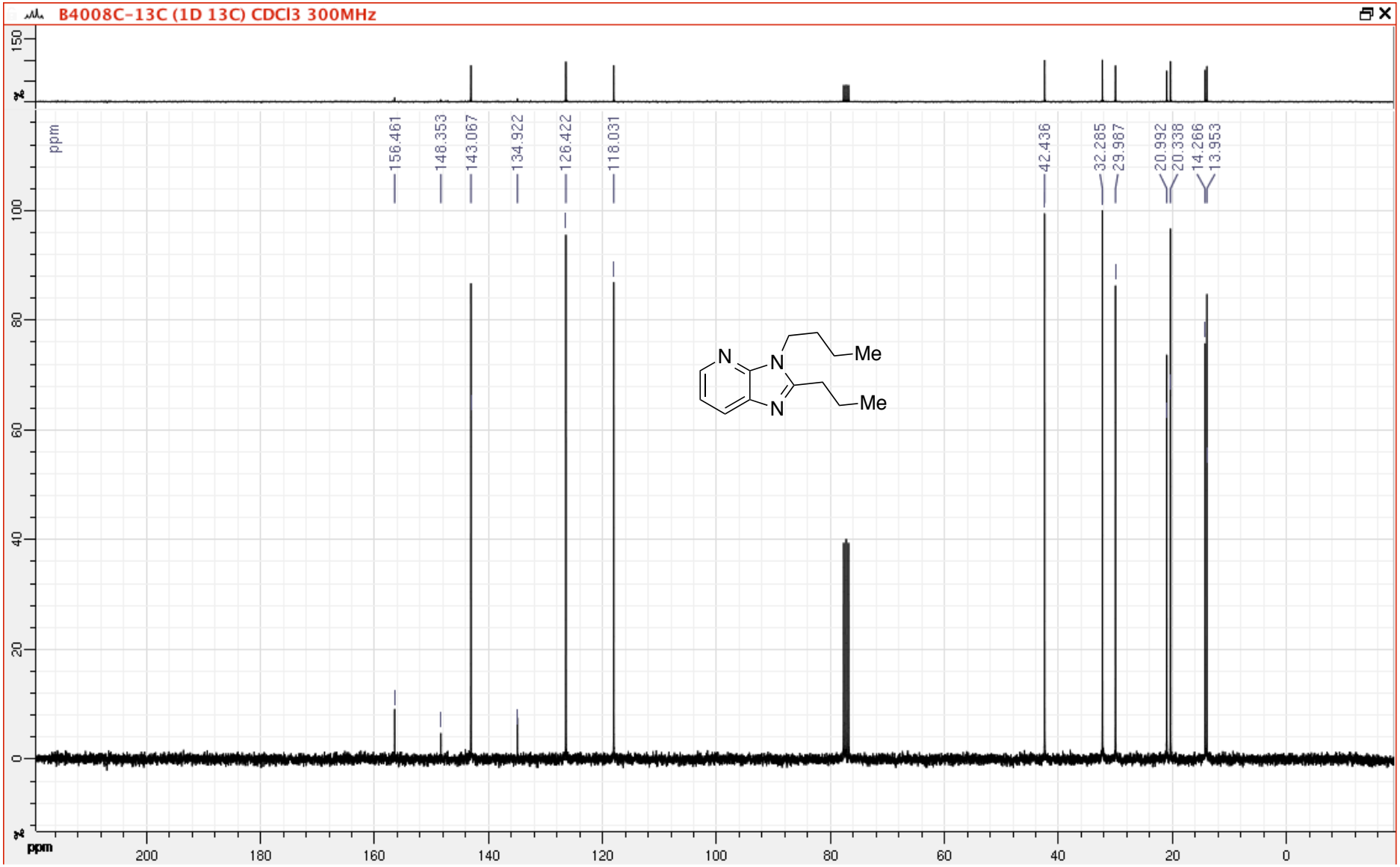
Ethyl 1-butyl-2-propyl-1*H*-benzo[*d*]imidazole-5-carboxylate (2m)



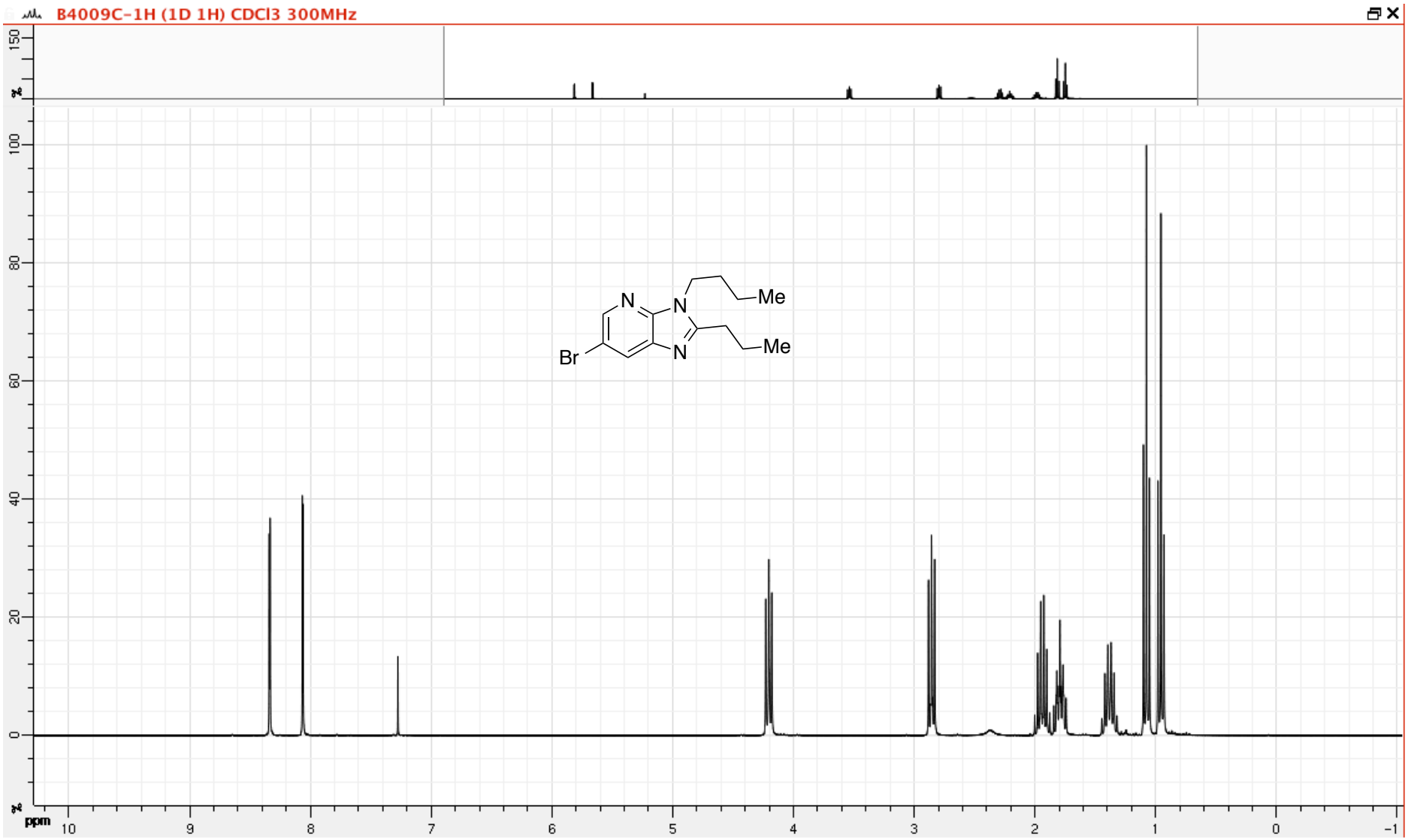

B4007-13C (1D 13C) CDCl3 300MHz
Me
N
Me
N
EtO2C
ppm
200
180
160
140
120
100
80
60
40
20
0

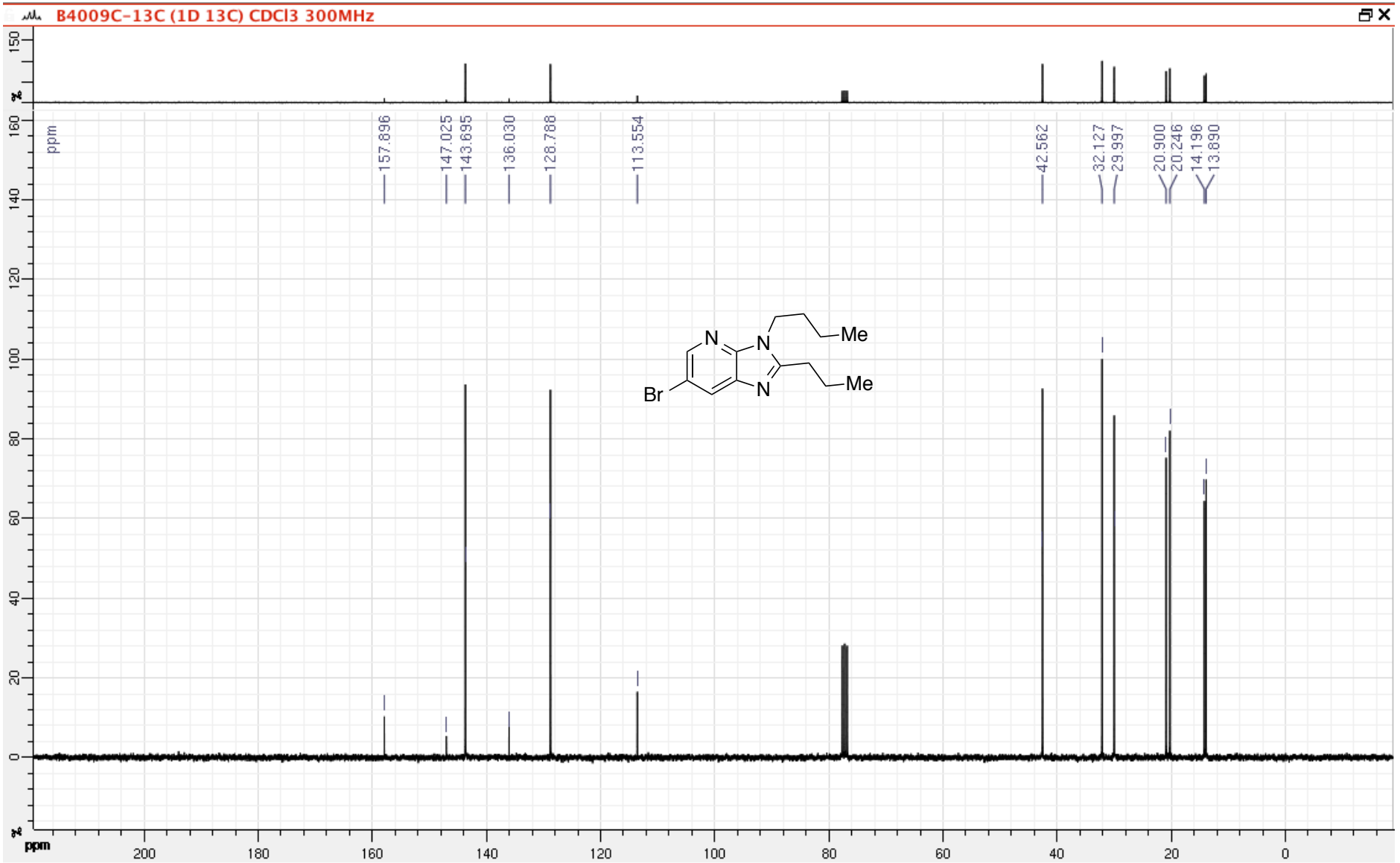
3-Butyl-2-propyl-3*H*-imidazo[4,5-*b*]pyridine (2n)



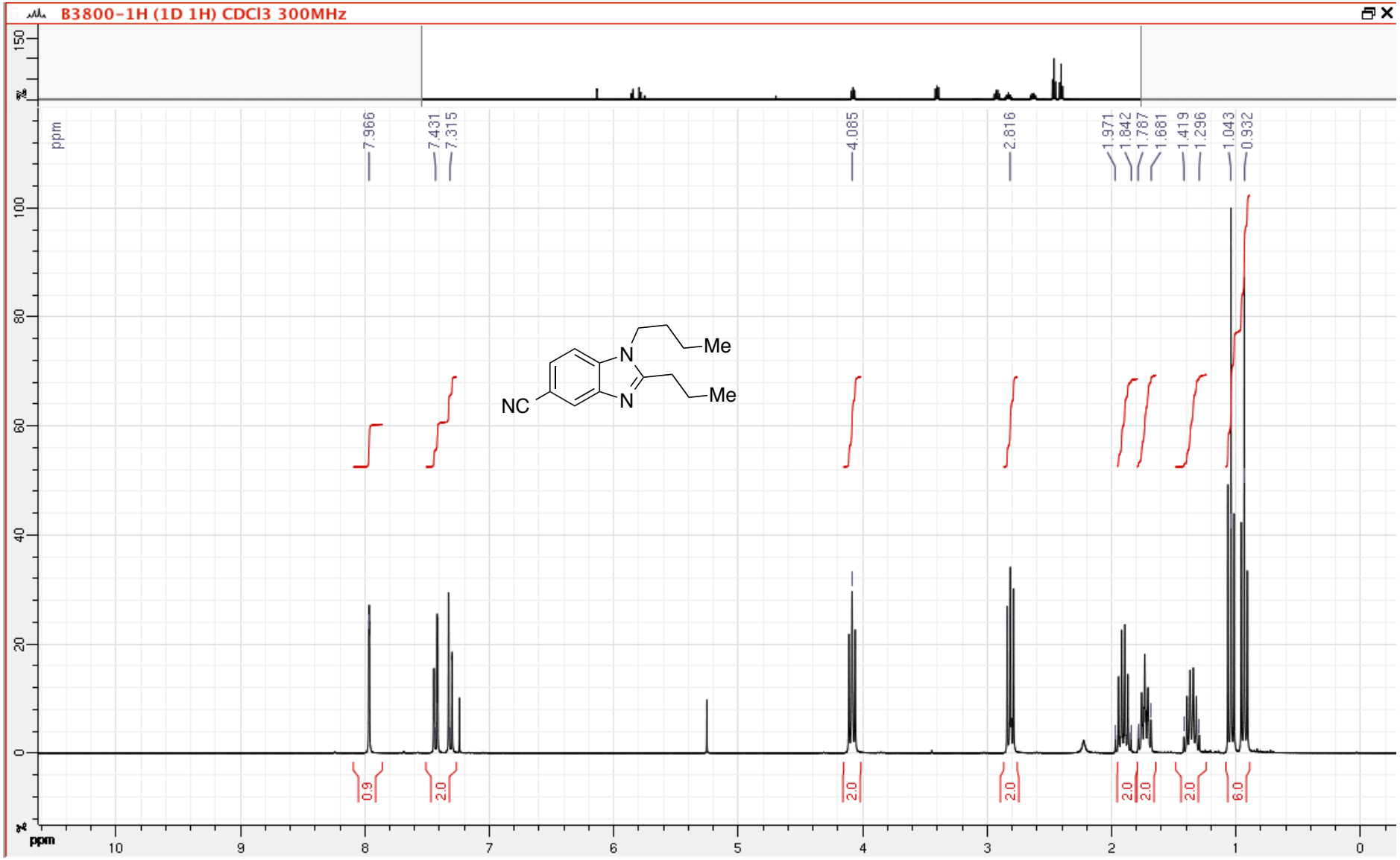

B4008C-13C (1D 13C) CDCl3 300MHz
ppm
156.461
148.353
143.067
134.922
126.422
118.031
42.436
32.285
29.987
20.992
20.338
14.266
13.953
N
N
N
Me
Me
200
180
160
140
120
100
80
60
40
20
0

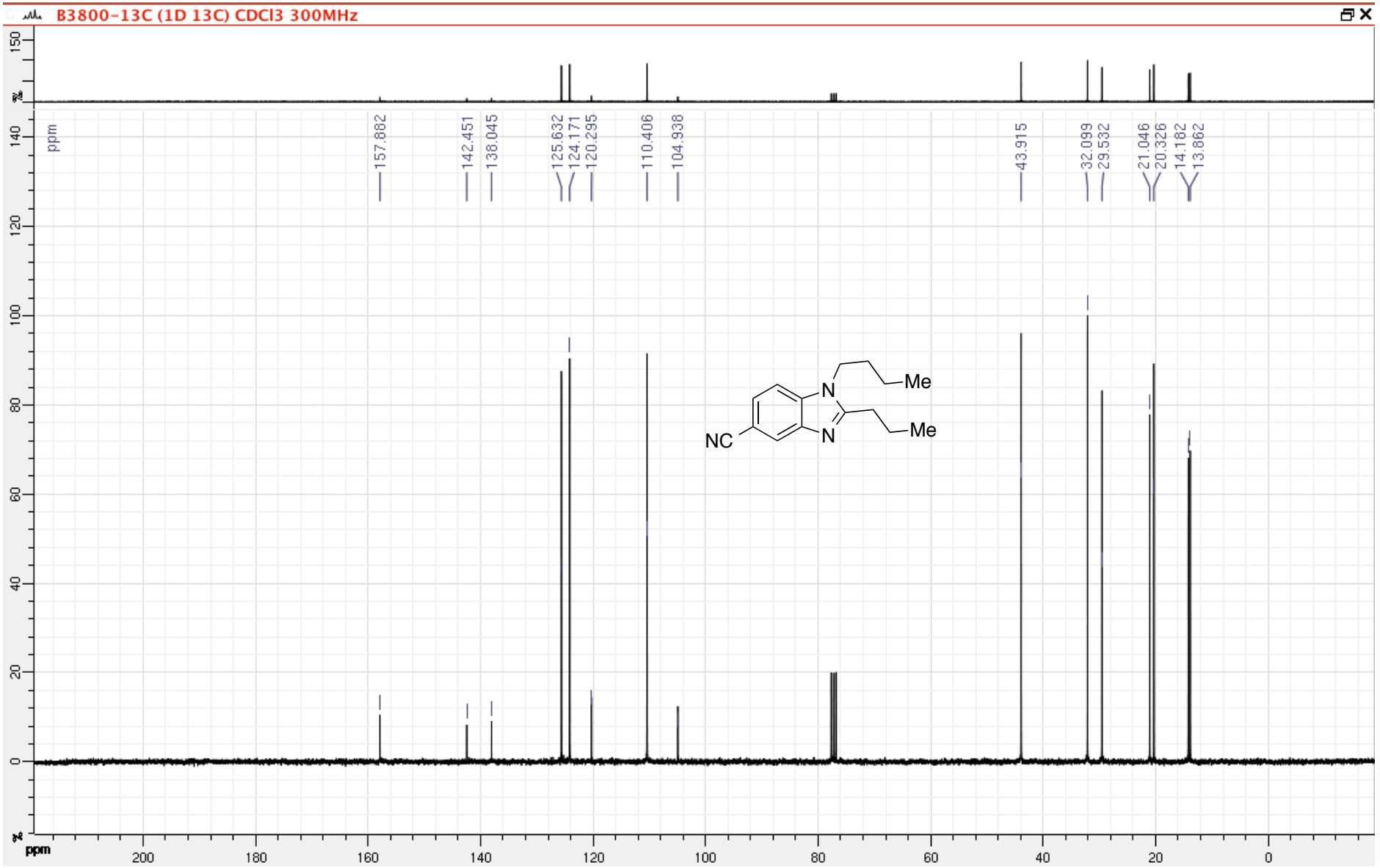
6-Bromo-3-butyl-2-propyl-3*H*-imidazo[4,5-*b*]pyridine (2o)



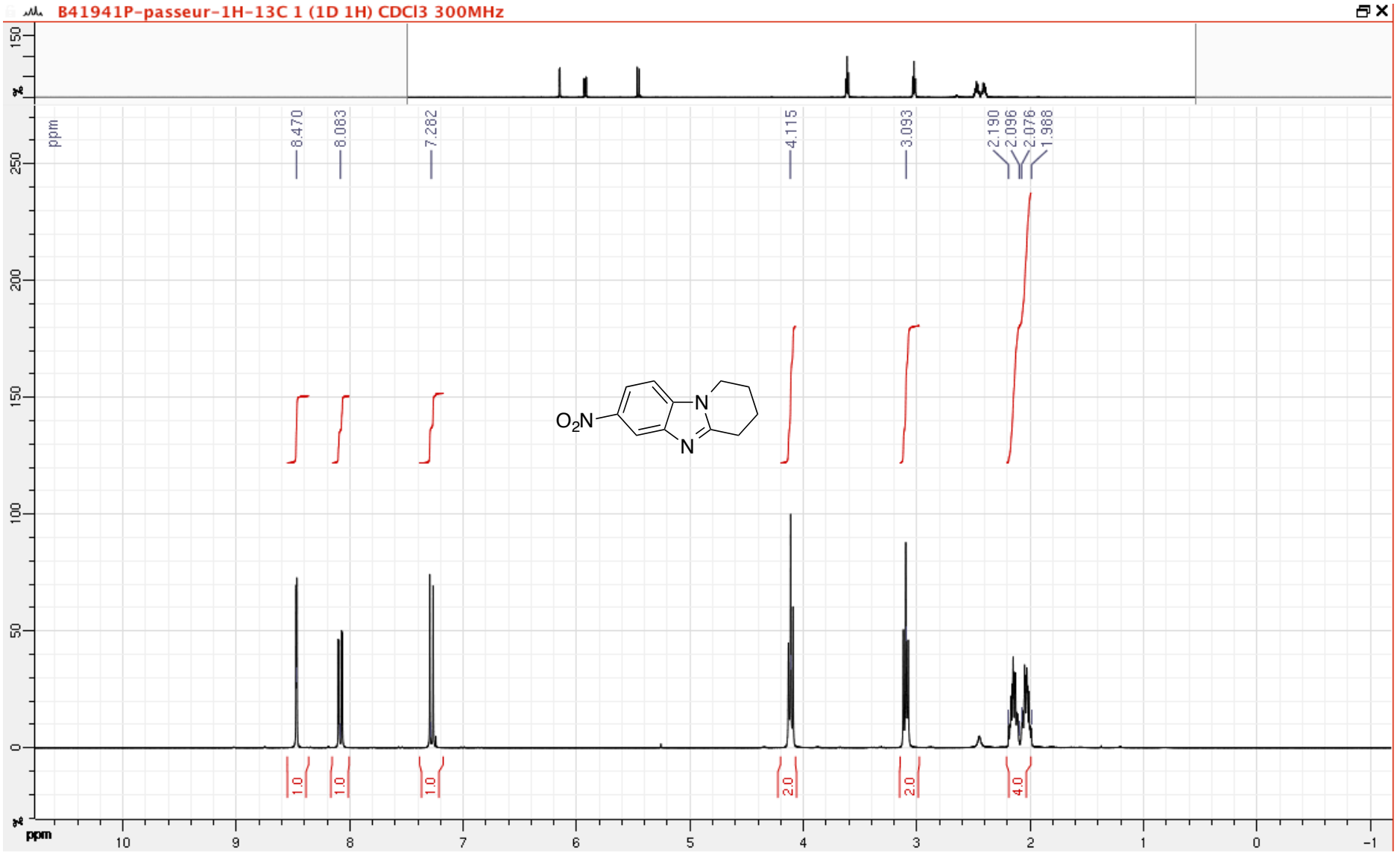

B4009C-13C (1D 13C) CDCl3 300MHz
ppm
157.896
147.025
143.695
136.030
128.788
113.554
42.562
32.127
29.997
20.900
20.246
14.196
13.890
N
N
N
Me
Me
Br

1-Butyl-2-propyl-1*H*-benzo[*d*]imidazole-5-carbonitrile (2p)



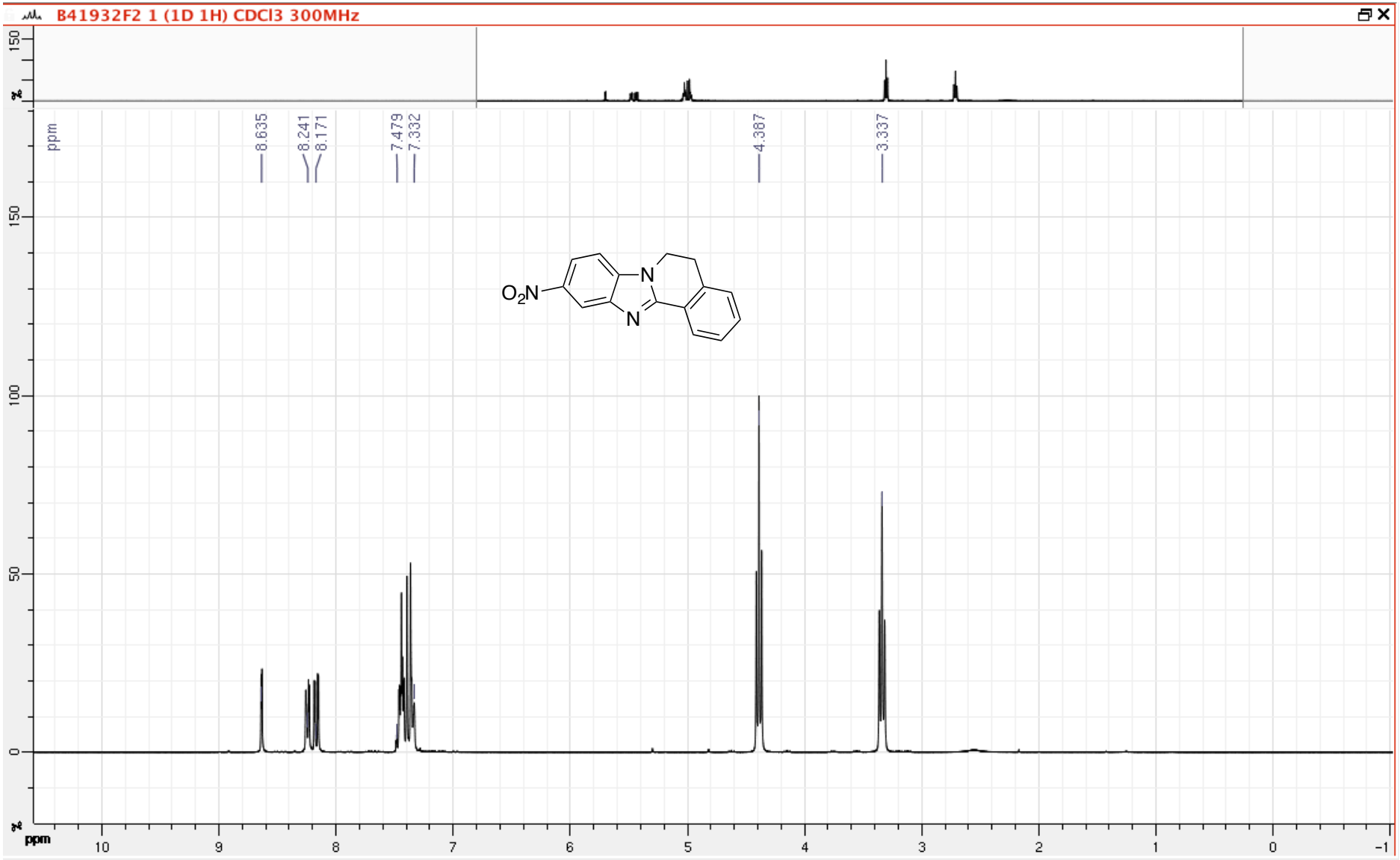

B3800-13C (1D 13C) CDCl3 300MHz
ppm
157.882
142.451
138.045
125.632
124.171
120.295
110.406
104.938
43.915
32.099
29.532
21.046
20.326
14.182
13.862
NC
N
N
Me
Me

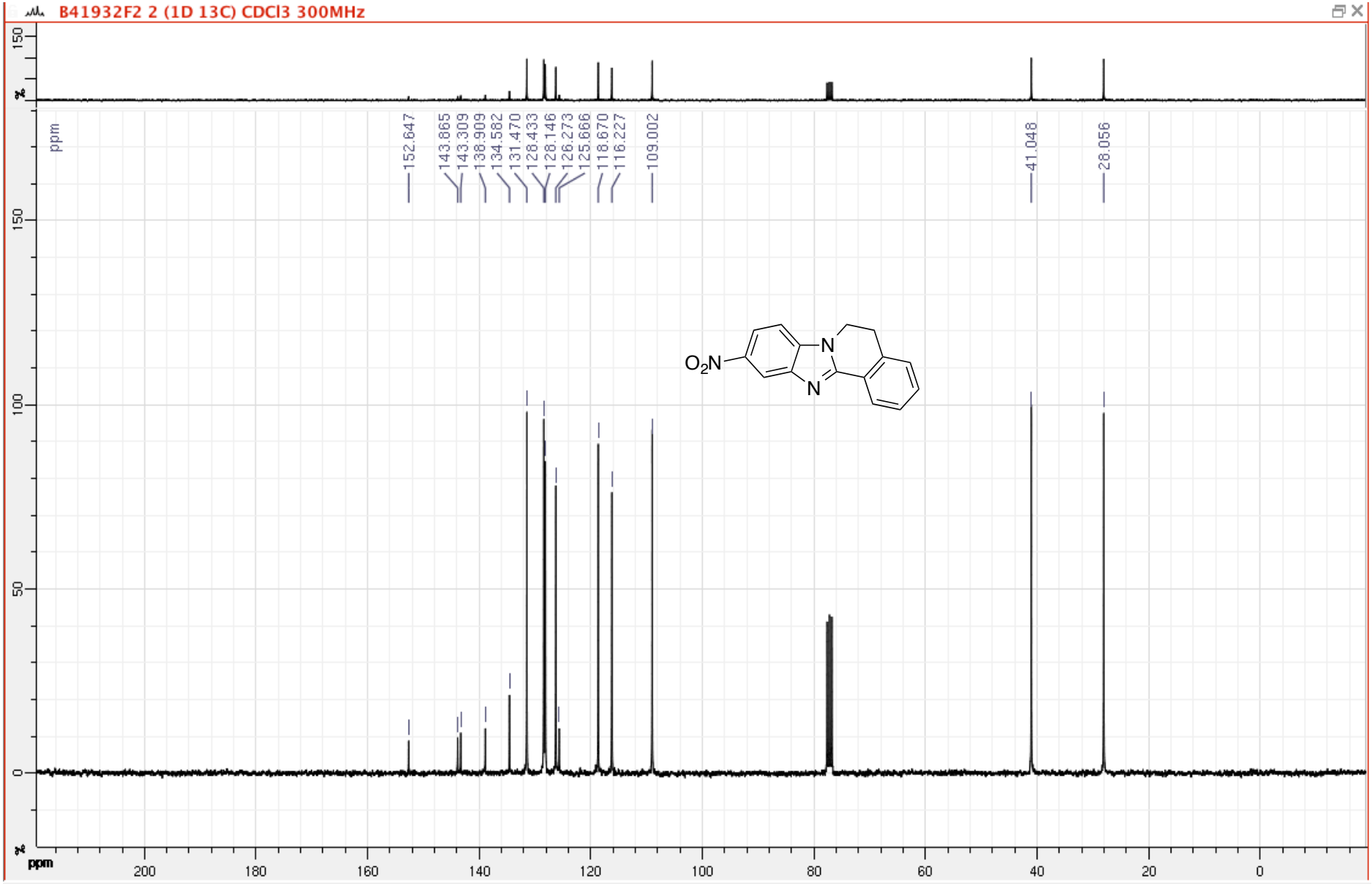
7-Nitro-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2q)



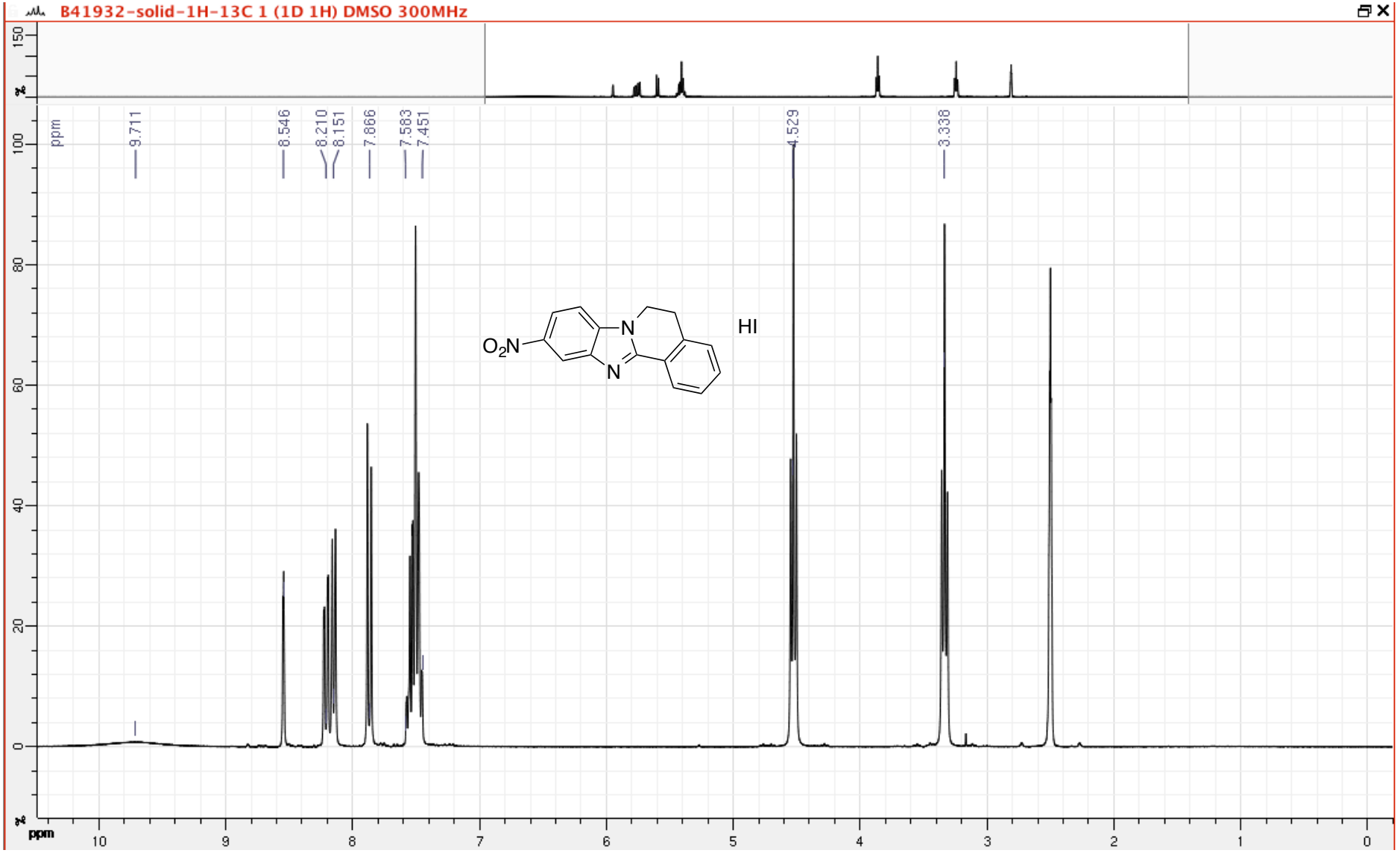

B41941P-passeur-1H-13C 2 (1D 13C) CDCl3 300MHz
ppm
155.798
143.734
142.236
138.906
117.862
115.499
108.736
43.183
25.703
22.510
20.453
O2N
N
N
ppm
200
180
160
140
120
100
80
60
40
20
0

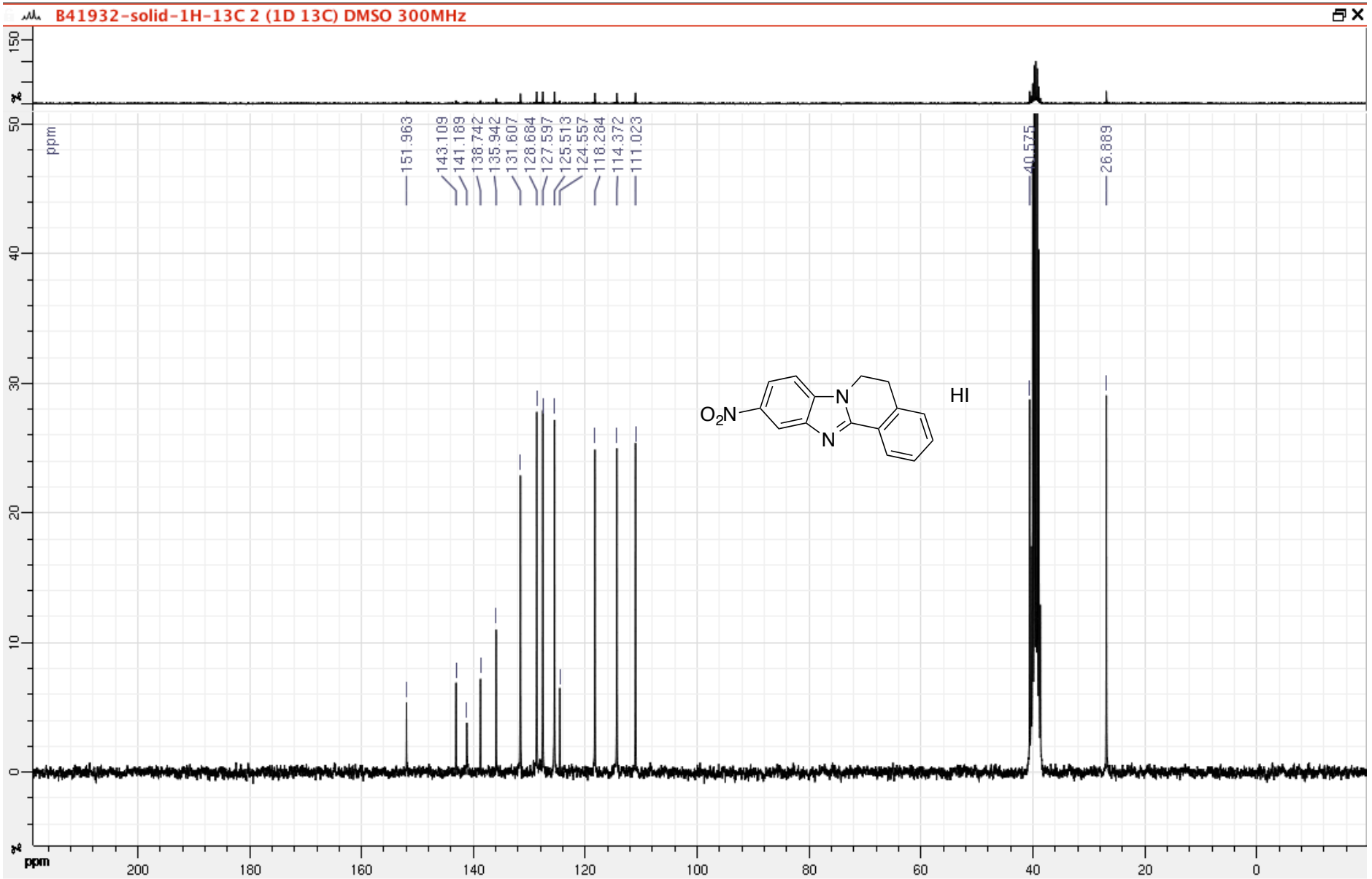
10-Nitro-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (2r)



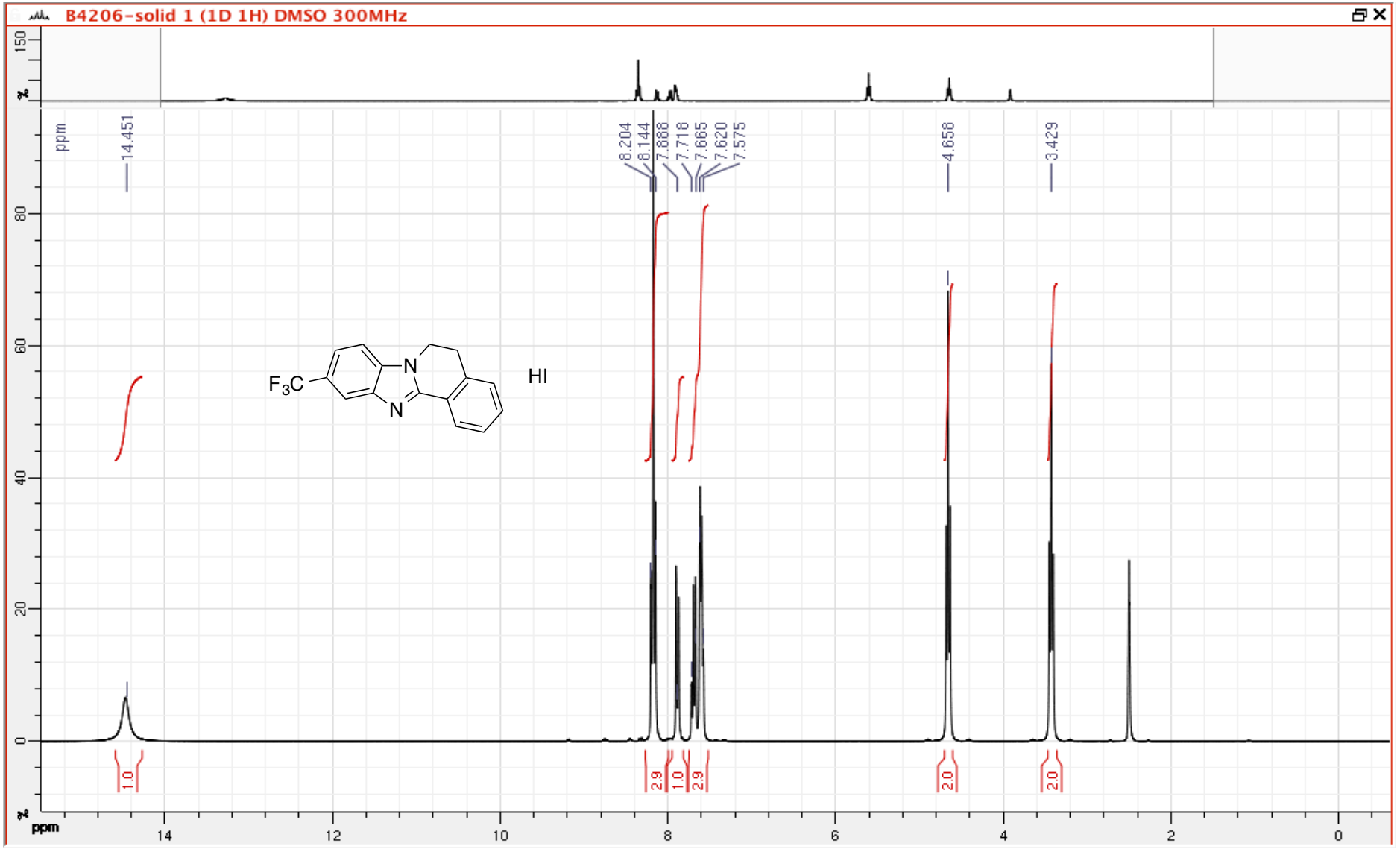

B41932F2 2 (1D 13C) CDCl3 300MHz
ppm
152.647
143.865
143.309
138.909
134.582
131.470
128.433
128.146
126.273
125.666
118.670
116.227
109.002
41.048
28.056
O2N
N
N
150
100
50
0
200
180
160
140
120
100
80
60
40
20
0

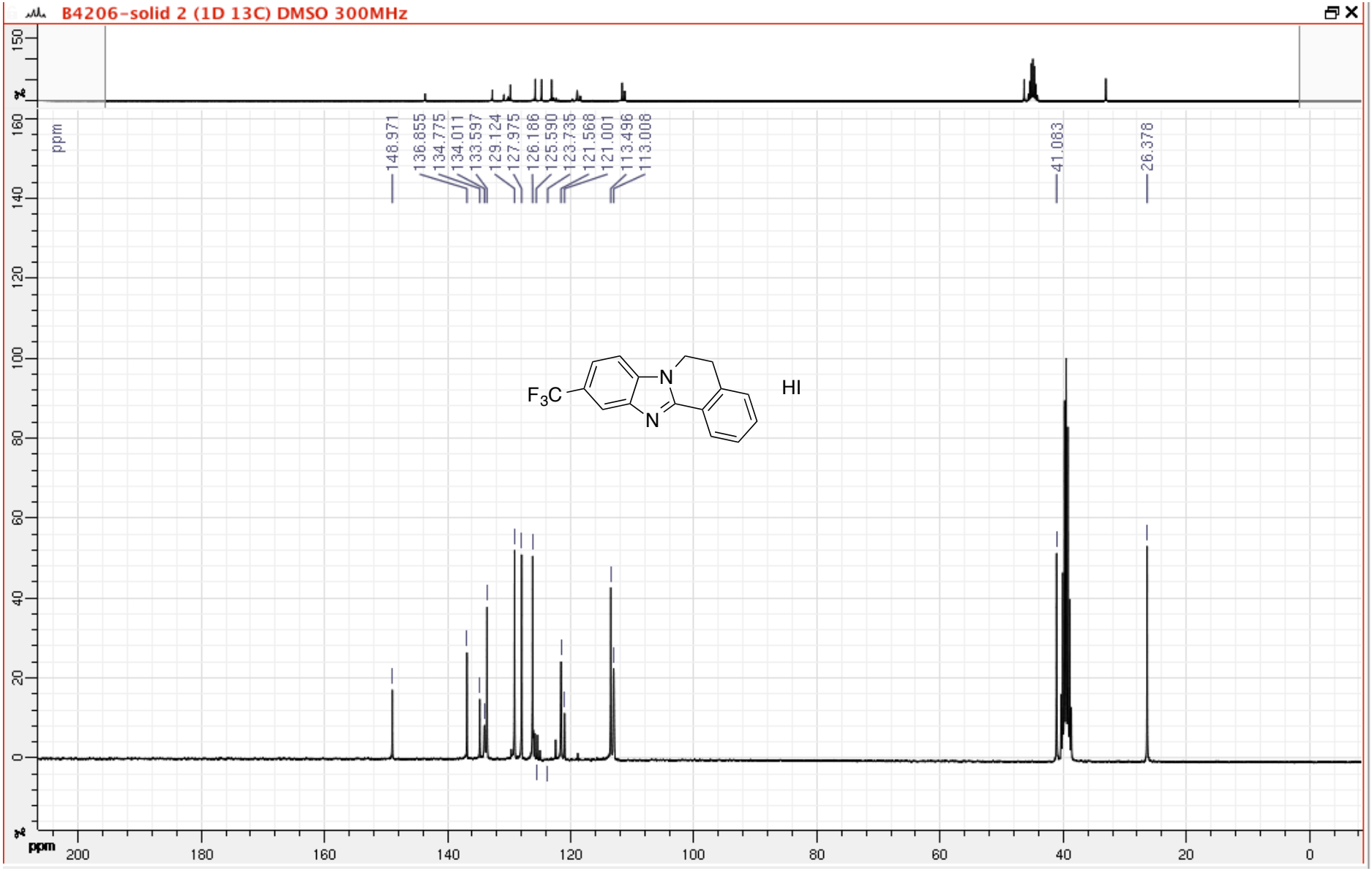
10-Nitro-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline hydroiodide (2r·HI)




B41932-solid-1H-13C 2 (1D 13C) DMSO 300MHz
ppm
151.963
143.109
141.189
138.742
135.942
131.607
128.684
127.597
125.513
124.557
118.284
114.372
111.023
40.575
26.889
O2N
N
N
HI
ppm
200
180
160
140
120
100
80
60
40
20
0

10-(Trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline hydroiodide (2s·HI)




B4206-solid 2 (1D 13C) DMSO 300MHz
ppm
148.971
136.855
134.775
134.011
133.597
129.124
127.975
126.186
125.590
123.735
121.568
121.001
113.496
113.008
41.083
26.378
F3C
N
N
HI
ppm
200
180
160
140
120
100
80
60
40
20
0