Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Sodium dithionite mediated one-pot, tandem chemoselective reduction/cyclization to the synthesis of pyrrole fused *N*-heterocycles

Joydev K. Laha,[a]* Surabhi Panday,[a] Pankaj Gupta[a] and Shiv Raj Seth[a]

[a]*Department of Pharmaceutical Technology (Process Chemistry),*
National Institute of Pharmaceutical Education and Research,
S. A. S. Nagar, Punjab 160062,
India
E-mail: jlaha@niper.ac.in

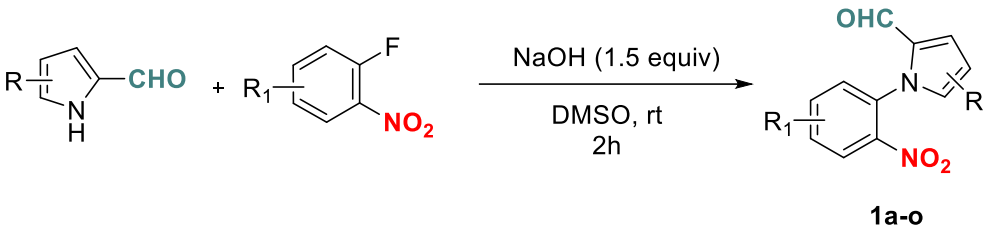
Table of Contents

1. GENERAL CONSIDERATION

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All palladium-catalyzed reactions were performed in a screw-cap sealed tube. The ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ as solvent using a 400 MHz spectrometer with Me_4Si as an internal standard. Coupling constants (*J* values) are reported in Hz. Column chromatography was performed using silica gel (60-120, 100-200, or 230-400 mesh). High Resolution Mass Spectra (HRMS) were obtained using Electron spay ionization (ESI) technique and as TOF mass analyzer. New compounds were characterized by 1H NMR, ^{13}C NMR, IR, and HRMS data. The glassware's to be used in reaction were thoroughly washed and dried in an oven and the experiments were carried out with required precautions. All the reagents are obtained from the commercial sources and were used as received. Reactions were monitored by TLC, which was performed with 0.2 mm Merck pre-coated silica gel 60 F254 Aluminium sheets. TLC plates were visualized with UV light, ^{1}H and ^{13}C spectra were recorded on Bruker Advance 400 MHz and 100 MHz NMR spectrometer in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$: 7.26/7.00) using Me_3SiCl as an internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz, pattern was designated as s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublet; dt, triplet of doublet; t, triplet; m, multiplet.

2. EXPERIMENTAL SECTION

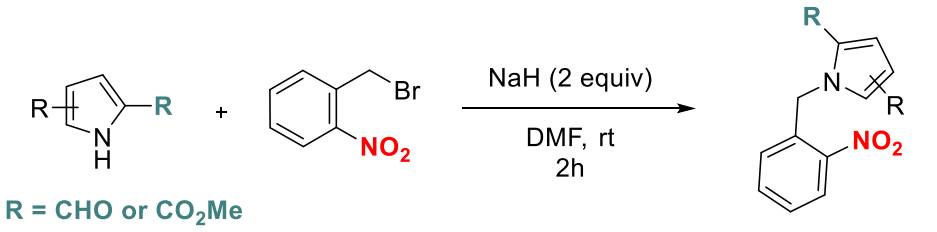
Representative procedure for *N*-arylation of substituted pyrrole-2-carboxaldehyde (1a-o)[1]



1a-o

To a stirred solution of substituted pyrrole-2-carboxaldehyde (1 mmol) in DMSO (1 mL), NaOH (1.5 mmol) and 1-fluoro-2-nitrobenzene derivatives (1.1 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure to obtain the desired product **1a-o**. The crude products were triturated with pentane and DCM to get the analytically pure **1a-o** in 96-99 % yield.

Representative procedure for *N*-benzylation of substituted pyrrole-2-carboxaldehyde and carboxylate ester (3a-3e, 5d)[2]



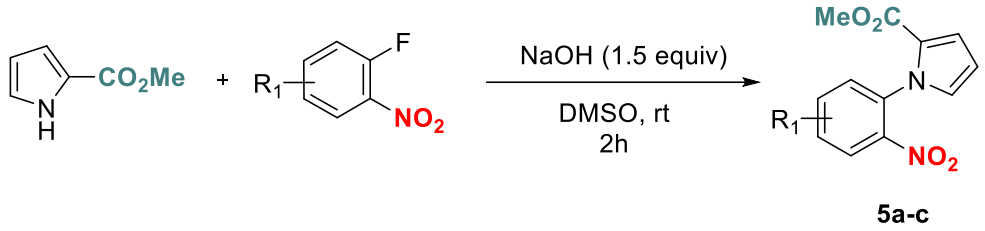
R = CHO or CO_2Me

R = CHO (**3a-e**)
R = CO_2Me (**5d**)

Following a literature protocol[2], in a dried round bottom flask equipped with a magnetic stirrer bar was charged with substituted pyrrole-2-carboxaldehyde or carboxylate ester (1 mmol) and anhydrous DMF (3 mL) under inert condition. The reaction mixture was cooled down to 0 ºC and NaH (2 mmol) was added slowly. The 2-nitrobenzyl bromide (1.1 mmol) was then added dropwise to the above reaction mixture and continued the stirring for 2 h. After completion of the reaction, the reaction mixture was quenched by cold water (10 mL) and extracted with EtOAc (20 mL x 3). The combined organic layer was dried over Na_2SO_4 and the solvent was

removed under reduced pressure. The crude product was triturated with pentane to obtain the corresponding *N*-alkylated heterocycle **3a-e** in 94-96% and **5d** in 92% yield.

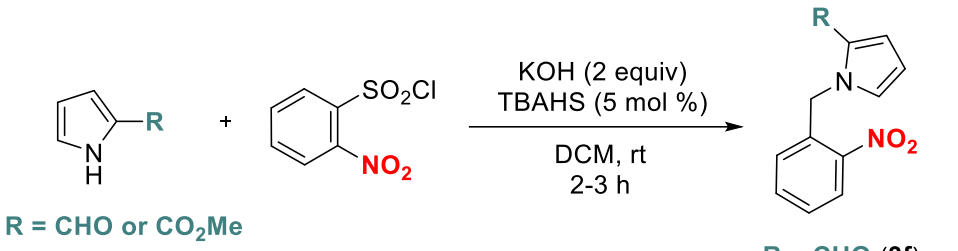
Representative procedure for *N*-arylation of substituted pyrrole-2-carboxylate (5a-c)[1]



5a-c

To a stirred solution of substituted pyrrole-2-carboxylate (1 mmol) in DMSO (1 mL), NaOH (1.5 mmol) and 1-fluoro-2-nitrobenzene derivatives (1.1 mmol) were added slowly. The reaction mixture was then stirred vigorously for 2 h at room temperature. After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with saturated brine solution and extracted with EtOAc (20 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate (Na_2SO_4). Finally, the solvent was evaporated under reduced pressure to obtain the desired product **5a-c**. The crude products were triturated with pentane to get the analytically pure **5a-c** in 96-98 % yield.

Typical procedure for *N*-sulfonylation of pyrroles (3f, 5e)[3]



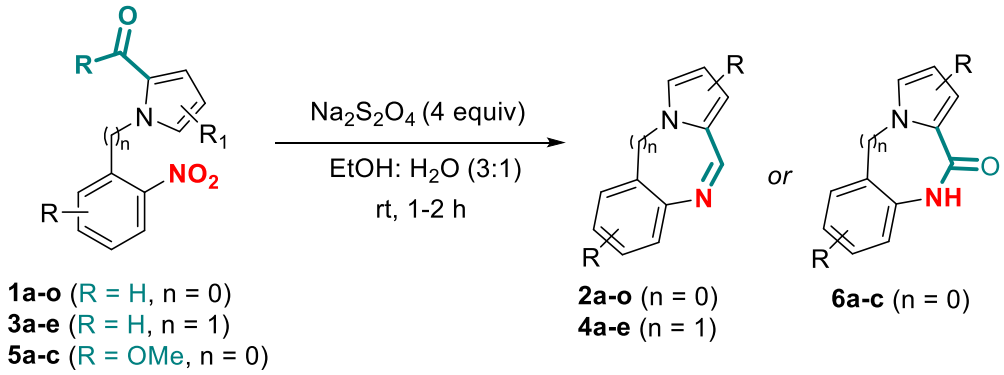
R = CHO or CO_2Me

R = CHO (**3f**)
R = CO_2Me (**5e**)

Following a literature procedure[3], to a stirred solution of substituted pyrrole-2-carboxaldehyde (0.5 mmol) in dichloromethane (2.5 mL) was added KOH (1 mmol) followed by addition of tetrabutylammonium hydrogensulfate (TBAHS) (0.025 mmol) and the resulting reaction mixture was allowed to stir at room temperature for 10 min. Further, a solution of 2-nitrobenzenesulfonyl chloride (0.6 mmol) in dichloromethane (1.0 mL) was added dropwise in the reaction mixture and stirred at room temperature until all the starting material was consumed. Water (10 mL) was then added and the aqueous layer was extracted with DCM (20 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by column chromatography [silica,

EtOAc/hexanes = 1/9] which gave the desired *N*-sulfonylated pyrroles **3f** and **5e** in good yields of about 92% and 90% respectively.

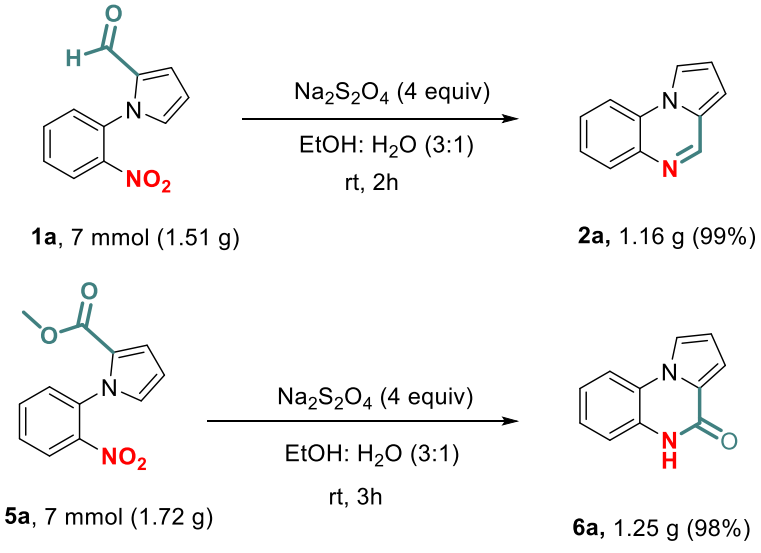
Procedure for the synthesis of pyrrolo[1,2-*a*] quinoxalines and pyrrolo[1,2-*a*] quinoxalin-4(5*H*)-ones (2a-2o, 4a-4e, 6a-6c)



To a stirred solution of substituted pyrrole-2-carboxaldehydes (**1a-o**, **3a-e**) or pyrrole-2-carboxylates (**5a-c**) (0.2 mmol) in ethanol (0.7 mL) was added $Na_2S_2O_4$ (0.8 mmol) followed by addition of 0.3 mL of water and the reaction mixture was allowed to stir at room temperature for about 0.5-2 h. After completion of the reaction, the ethanol was removed under reduced pressure, and the resulting residue was washed with cold water. The water was removed by vacuum filtration. The crude product was diluted by a very small quantity of DCM and then triturated with pentane to get analytically pure **2a-2o, 4a-4e**, and **6a-6c** with approximately 90-99% yields.

GREEN CHEMISTRY METRICS

The PMI, E-Factor and atom economy is calculated by considering the reaction below.



a) Process Mass Intensity (PMI)

$$PMI = \frac{\text{Total mass used in the process step (Kg/g)}}{\text{Mass of product (Kg/g)}}$$

$$\mathbf{PMI_1} = \frac{1.51g \text{ (wt. of } \mathbf{1}\text{)} + 4.87g \text{ (wt. of } Na_2S_2O_4\text{)} + 8.28g \text{ (wt. of EtOH)} + 3.5 \text{ g (wt. of } H_2O\text{)}}{1.16g \text{ (wt. of product formed)}}$$

$$= \mathbf{15.65\ g/g}$$

$$\mathbf{PMI_2} = \frac{1.72g \text{ (wt. of } \mathbf{4}\text{)} + 4.87g \text{ (wt. of } Na_2S_2O_4\text{)} + 8.28g \text{ (wt. of EtOH)} + 3.5 \text{ g (wt. of } H_2O\text{)}}{1.25g \text{ (wt. of product formed)}}$$

$$= \mathbf{14.696\ g/g}$$

b) E Factor = PMI-1

E Factor (E_1) = 15.65-1= **14.65 g/g**

E Factor (E_2) = 14.696-1 = **13.696 g/g**

c) Atom Economy (AE)

$$\text{Atom Economy (AE)} = \frac{\text{Molecular mass of desired product x 100}}{\text{Molecular mass of all products}}$$

Atom Economy (AE_1) = 168.1990/216.1960 x 100

= **77.79 %**

Atom Economy (AE_2) = 184.0637/246.220 x 100

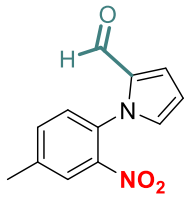
= **74.75 %**

3. CHARACTERIZATION DATA

1-(2-Nitrophenyl)-1*H*-Pyrrole-2-Carbaldehyde (1a)[4]

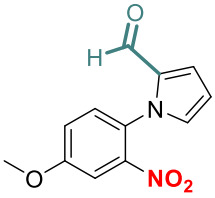
Light brown solid (210 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (d, J = 0.7 Hz, 1H), 8.11 (dd, J = 8.2, 1.4 Hz, 1H), 7.69 (td, J = 7.7, 1.5 Hz, 1H), 7.60 (td, J = 8.0, 1.3 Hz, 1H), 7.41 (dd, J = 7.8, 1.2 Hz, 1H), 7.12 (dd, J = 4.0, 1.6 Hz, 1H), 7.01 (s, 1H), 6.47 (dd, J = 3.9, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 133.7, 133.6, 132.6, 131.2, 129.8, 129.5, 125.3, 124.8, 111.7.

1-(4-Methyl-2-Nitrophenyl)-1*H*-Pyrrole-2-Carbaldehyde (1b)[5]



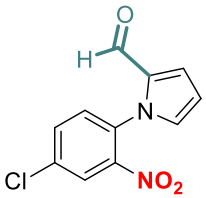
Yellow solid (228 mg, 97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (d, J = 1.0 Hz, 1H), 7.92 (d, J = 1.4 Hz, 1H), 7.48 (ddd, J = 8.0, 1.9, 0.7 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.10 (dd, J = 4.0, 1.7 Hz, 1H), 6.99 – 6.98 (m, 1H), 6.45 (dd, J = 4.0, 2.6 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 145.5, 140.4, 134.3, 132.7, 131.3, 131.0, 129.5, 125.6, 124.7, 111.5, 21.1.

1-(4-Methoxy-2-Nitrophenyl)-1*H*-Pyrrole-2-Carbaldehyde (1c)[5]



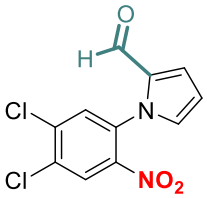
Orange solid (242 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (d, J = 0.9 Hz, 1H), 8.19 (d, J = 9.2 Hz, 1H), 7.12 (dd, J = 4.0, 1.7 Hz, 1H), 7.03 (dd, J = 9.2, 2.7 Hz, 1H), 7.00 – 6.99 (m, 1H), 6.84 (d, J = 2.7 Hz, 1H), 6.47 (dd, J = 4.0, 2.6 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 163.5, 138.9, 135.8, 132.7, 130.9, 127.7, 124.7, 115.4, 113.9, 111.6, 56.3.

1-(4-Chloro-2-Nitrophenyl)-1*H*-Pyrrole-2-Carbaldehyde (1d)[6]



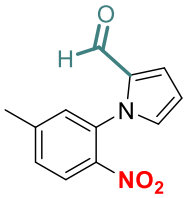
Brown solid (246 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (d, J = 0.9 Hz, 1H), 8.11 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 8.4, 2.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.12 (dd, J = 4.0, 1.6 Hz, 1H), 6.99 – 6.96 (m, 1H), 6.49 (dd, J = 4.0, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 135.4, 133.7, 132.5, 132.2, 131.1, 130.8, 125.5, 125.2, 112.0.

1-(4,5-Dichloro-2-Nitrophenyl)-1*H*-Pyrrole-2-Carbaldehyde (1e)



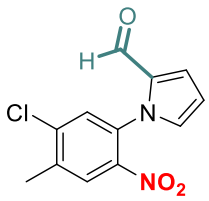
Brown solid (278 mg, 95%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (d, J = 0.7 Hz, 1H), 8.25 (s, 1H), 7.52 (s, 1H), 7.13 (dd, J = 4.0, 1.6 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.50 (dd, J = 3.9, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 144.0, 138.3, 133.9, 132.8, 132.5, 131.1, 130.8, 127.0, 125.5, 112.3. HRMS (ESI) *m/z* calcd for $C_{11}H_6Cl_2N_2O_3$ $[M+Na]^+$ 306.9653, found 306.9638.

1-(5-Methyl-2-Nitrophenyl)-1*H*-Pyrrole-2-Carbaldehyde (1f)



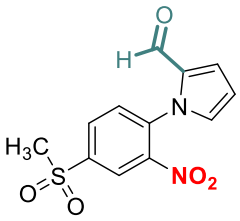
Light yellow solid (227 mg, 95%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 9.6 Hz, 1H), 7.19 (s, 1H), 7.11 (dd, J = 4.0, 1.6 Hz, 1H), 6.98 (s, 1H), 6.46 (dd, J = 3.9, 2.7 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 145.4, 143.6, 133.6, 132.8, 131.1, 130.3, 130.0, 125.4, 124.7, 111.5, 21.4. HRMS (ESI) *m/z* calcd for $C_{12}H_{10}N_2O_3$ $[M+H]^+$ 231.0769, found 231.0762.

1-(5-Chloro-4-Methyl-2-Nitrophenyl)-1*H*-Pyrrole-2-Carbaldehyde (1g)



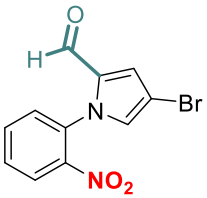
Brown solid (261 mg, 97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (d, J = 0.7 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.38 (dd, J = 8.4, 1.1 Hz, 1H), 7.19 (d, J = 1.1 Hz, 1H), 7.11 (dd, J = 4.0, 1.6 Hz, 1H), 7.02 – 6.94 (m, 1H), 6.46 (dd, J = 4.0, 2.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 145.4, 143.5, 133.5, 132.7, 131.2, 130.3, 130.0, 125.3, 124.8, 111.5, 21.4. HRMS (ESI) *m/z* calcd for $C_{12}H_9ClN_2O_3$ $[M+Na]^+$ 287.0199, found 287.0162.

1-(4-(methylsulfonyl)-2-nitrophenyl)-1*H*-pyrrole-2-carbaldehyde (1h)



Orange solid (290 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (d, J = 1.0 Hz, 1H), 8.63 (d, J = 2.0 Hz, 1H), 8.23 (dd, J = 8.2, 2.1 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.17 (dd, J = 4.0, 1.6 Hz, 1H), 7.03 – 7.02 (m, 1H), 6.54 (dd, J = 3.9, 2.8 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 146.0, 141.7, 138.0, 132.4, 132.2, 131.1, 131.0, 126.0, 124.8, 112.7, 44.5. HRMS (ESI) *m/z* calcd for $C_{12}H_{10}N_2O_5S$ $[M+H]^+$ 295.0388, found 295.0367.

4-bromo-1-(2-nitrophenyl)-1H-pyrrole-2-carbaldehyde (1i)

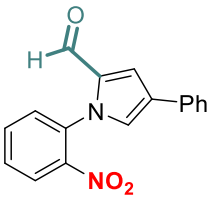


Brown solid (291 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (d, J = 0.7 Hz, 1H), 8.14 (dd, J = 8.1, 1.4 Hz, 1H), 7.71 (td, J = 7.7, 1.5 Hz, 1H), 7.64 (td, J = 7.7, 1.5 Hz, 1H), 7.39 (dd, J = 7.8, 1.4 Hz, 1H), 7.09 (d, J = 1.8 Hz, 1H), 7.00 (dd, J = 1.7, 1.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 145.7, 134.0, 132.6, 130.2, 130.1, 129.8, 125.5, 125.4, 99.4. HRMS (ESI) *m/z* calcd for $C_{11}H_7BrN_2O_3$ $[M+H]^+$ 293.9640, $[M+2]^+$ 295.9620, found $[M+H]^+$ 293.9230, $[M+2]^+$ 295.9610.

3,5-dimethyl-1-2-nitrophenyl)-1*H*-pyrrole-2-carbaldehyde (1j)

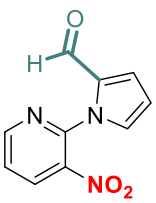
White solid (230 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.08 (dd, J = 8.1, 1.4 Hz, 1H), 7.70 (td, J = 7.7, 1.4 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.33 (dd, J = 7.8, 1.0 Hz, 1H), 6.04 (s, 1H), 2.37 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 146.9, 139.6, 135.8, 133.7, 132.7, 130.8, 129.6, 129.1, 125.2, 112.8, 12.3, 11.1 HRMS (ESI) *m/z* calcd for $C_{14}H_{14}N_2O_3$ $[M+H]^+$ 259.1082, found $[M+H]^+$ 259.1442.

1-(2-nitrophenyl)-3-phenyl-1*H*-pyrrole-2-carbaldehyde (1k)



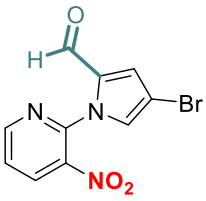
White solid (280 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (d, J = 1.0 Hz, 1H), 8.15 (dd, J = 8.2, 1.5 Hz, 1H), 7.72 (td, J = 7.7, 1.5 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.55 (dd, J = 8.3, 1.1 Hz, 2H), 7.47 (dd, J = 7.8, 1.4 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.29 – 7.28 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 145.9, 133.8, 133.4, 133.3, 133.1, 129.9, 129.7, 129.0, 127.8, 127.6, 127.2, 125.5, 125.4, 121.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}N_2O_3$ $[M+H]^+$ 293.0926, found $[M+H]^+$ 293.0906.

1-(3-nitropyridin-2-yl)-1*H*-pyrrole-2-carbaldehyde (1l)[7a]



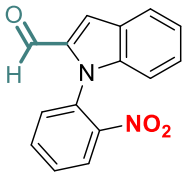
Light brown solid (210 mg, 92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.46 (d, J = 1.0 Hz, 1H), 8.73 (dd, J = 4.7, 1.6 Hz, 1H), 8.49 (dd, J = 8.2, 1.7 Hz, 1H), 7.58 (dd, J = 8.2, 4.8 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.17 (dd, J = 3.9, 1.7 Hz, 1H), 6.52 (dd, J = 3.9, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 152.1, 144.6, 141.8, 134.1, 131.9, 130.8, 126.5, 124.3, 112.1.

4-bromo-1-(3-nitropyridin-2-yl)-1*H*-pyrrole-2-carbaldehyde (1m)[7b]



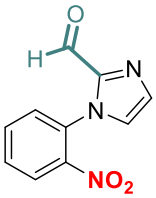
Brown solid (278 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.40 (d, J = 0.7 Hz, 1H), 8.73 – 8.71 (m, 1H), 8.51 (dt, J = 6.9, 1.6 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.31 (d, J = 0.8 Hz, 1H), 7.12 (t, J = 1.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 152.3, 143.6, 141.6, 134.3, 131.9, 129.9, 126.9, 124.8, 100.0.

1-(2-nitrophenyl)-1*H*-indole-2-carbaldehyde (1n)[8]



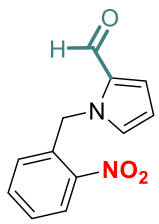
White solid (253 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.21 (dd, J = 8.2, 1.5 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.78 (td, J = 7.7, 1.5 Hz, 1H), 7.67 (td, J = 7.7, 1.5 Hz, 1H), 7.51 (dd, J = 7.8, 1.3 Hz, 1H), 7.47 (d, J = 0.7 Hz, 1H), 7.36 (ddd, J = 8.2, 7.0, 1.0 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.00 (dd, J = 8.5, 0.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.5, 146.6, 140.9, 136.1, 134.0, 132.0, 131.2, 129.6, 128.0, 126.9, 125.8, 123.7, 122.2, 118.9, 110.7.

1-(2-nitrophenyl)-1*H*-imidazole-2-carbaldehyde (1o)[6]



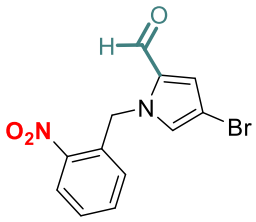
White solid (209 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.74 (d, J = 0.8 Hz, 1H), 8.21 (dd, J = 8.2, 1.4 Hz, 1H), 7.75 (td, J = 7.7, 1.5 Hz, 1H), 7.69 (td, J = 7.9, 1.4 Hz, 1H), 7.47 (d, J = 0.9 Hz, 1H), 7.40 (dd, J = 7.8, 1.4 Hz, 1H), 7.23 (t, J = 0.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.0, 145.0, 143.6, 134.2, 132.4, 131.1, 130.6, 129.4, 126.4, 125.8.

1-(2-nitrobenzyl)-1*H*-pyrrole-2-carbaldehyde (3a)[9]



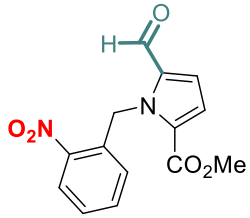
White solid (215 mg, 92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.03 (dd, J = 6.5, 5.3 Hz, 2H), 6.53 (d, J = 7.8 Hz, 1H), 6.38 – 6.35 (m, 1H), 5.92 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.3, 147.2, 134.5, 134.1, 132.1, 132.0, 131.6, 128.3, 127.7, 125.1, 110.7, 49.9.

4-bromo-1-(2-nitrobenzyl)-1*H*-pyrrole-2-carbaldehyde (3b)



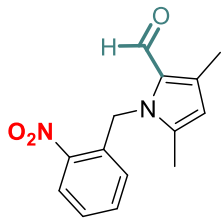
Brown solid (298 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.01 (d, J = 1.9 Hz, 2H), 6.64 (d, J = 7.8 Hz, 1H), 5.88 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 147.3, 134.2, 133.5, 131.8, 131.1, 128.6, 127.8, 125.6, 125.2, 97.9, 50.0. HRMS (ESI) *m/z* calcd for $C_{12}H_9BrN_2O_3$ $[M+H]^+$ 308.9875, $[M+2]^+$ 309.9776 found $[M+H]^+$ 308.9655 and $[M+2]^+$ 309.9676.

Methyl 5-formyl-1-(2-nitrobenzyl)-1H-pyrrole-2-carboxylate (3c)



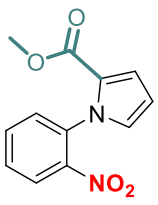
White solid (269 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.13 (dd, J = 8.1, 1.2 Hz, 1H), 7.42 (td, J = 7.6, 1.2 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 4.3 Hz, 1H), 7.03 (d, J = 4.2 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 6.40 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.9, 160.7, 147.4, 135.3, 135.0, 133.9, 129.7, 127.8, 126.6, 125.1, 122.8, 117.7, 52.1, 48.1. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}N_2O_5$ $[M+H]^+$ 289.0824 found 289.0814.

3,5-Dimethyl-1-(2-Nitrobenzyl)-1H-Pyrrole-2-Carboxylate (3e)



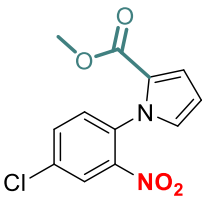
White solid (249 mg, 92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.11 (dd, J = 8.2, 1.3 Hz, 1H), 7.45 (td, J = 7.7, 1.3 Hz, 1H), 7.38 – 7.34 (m, 1H), 6.39 (dd, J = 7.9, 1.0 Hz, 1H), 5.96 (s, 1H), 5.89 (s, 2H), 2.35 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 147.1, 139.4, 135.7, 134.8, 134.2, 127.8, 127.6, 126.9, 125.1, 112.2, 46.3, 11.7, 11.0. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}N_2O_5$ $[M+H]^+$ 259.2848 found 259.2850.

Methyl 1-(2-Nitrophenyl)-1H-Pyrrole-2-Carboxylate (5a)[10]



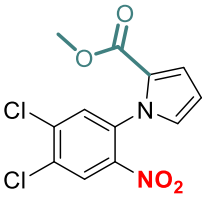
White solid (240 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.2, 1.5 Hz, 1H), 7.68 (td, J = 7.7, 1.5 Hz, 1H), 7.58 (td, J = 7.9, 1.4 Hz, 1H), 7.40 (dd, J = 7.8, 1.4 Hz, 1H), 7.10 (dd, J = 3.9, 1.8 Hz, 1H), 6.90 (dd, J = 2.5, 1.9 Hz, 1H), 6.37 (dd, J = 3.9, 2.7 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 146.2, 134.4, 133.4, 130.0, 129.3, 129.0, 124.9, 123.9, 118.9, 110.4, 51.3.

Methyl 1-(4-Chloro-2-Nitrophenyl)-1H-Pyrrole-2-Carboxylate (5b)



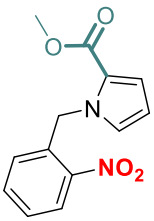
White solid (272 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 2.4 Hz, 1H), 7.65 (dd, J = 8.4, 2.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.10 (dd, J = 3.9, 1.7 Hz, 1H), 6.88 (dd, J = 2.5, 1.9 Hz, 1H), 6.38 (dd, J = 3.8, 2.8 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 146.4, 135.1, 133.5, 132.9, 131.1, 128.9, 125.2, 123.8, 119.0, 110.8, 51.4. HRMS (ESI) *m/z* calcd for $C_{12}H_9ClN_2O_4$ $[M+H]^+$ 281.0329 found 281.0322.

Methyl 1-(4,5-Dichloro-2-Nitrophenyl)-1H-Pyrrole-2Carboxylate (5c)



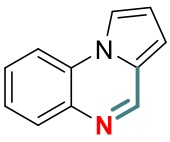
White solid (308 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.52 (s, 1H), 7.10 (dd, J = 3.9, 1.7 Hz, 1H), 6.89 (dd, J = 2.7, 1.8 Hz, 1H), 6.39 (dd, J = 3.9, 2.8 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 144.4, 138.1, 133.7, 133.5, 131.4, 128.7, 126.7, 123.9, 119.3, 111.1, 51.5. HRMS (ESI) *m/z* calcd for $C_{12}H_8Cl_2N_2O_4$ $[M+H]^+$ 314.9939 found 314.9931.

Methyl 1-(2-nitrobenzyl)-1H-pyrrole-2-carboxylate (5d)[11]



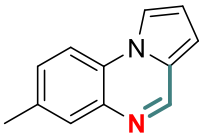
White solid (258 mg, 95%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.2, 1.1 Hz, 1H), 7.47 (td, J = 7.7, 1.1 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.06 (dd, J = 4.0, 1.8 Hz, 1H), 6.92 – 6.91 (m, 1H), 6.47 (d, J = 7.4 Hz, 1H), 6.27 (dd, J = 4.0, 2.6 Hz, 1H), 5.92 (s, 2H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 147.0, 147.0, 135.4, 134.1, 133.6, 129.6, 128.0, 127.5, 125.0, 122.3, 118.8, 109.3, 51.2, 50.2, 29.8.

Pyrrolo[1,2-a]quinoxaline (2a)[12]



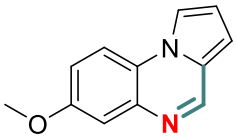
Yellow solid (33 mg, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.42 – 7.40 (m, 1H), 6.86 (dd, J = 11.9, 2.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 135.8, 130.1, 128.0, 127.8, 126.4, 125.2, 114.2, 114.0, 113.8. IR (KBr, cm^{-1}): 1670, 1614, 1589, 1547, 1450, 1336.

7-Methyl Pyrrolo[1,2-a]quinoxaline (2b)[12]



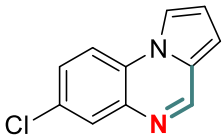
Yellow solid (35 mg, 97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.87 (s, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 8.5 Hz, 1H), 6.86 (dd, J = 3.9, 1.2 Hz, 1H), 6.84 (dd, J = 3.9, 2.6 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 135.8, 135.0, 129.9, 128.9, 126.4, 125.9, 114.0, 113.8, 113.5, 107.1, 21.1.

7-Methoxy Pyrrolo[1,2-a]quinoxaline (2c)[12]



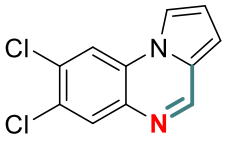
Orange solid (35.5 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.80 (s, 1H), 7.23 (d, J = 1.4 Hz, 1H), 7.02 (ddd, J = 8.9, 2.7, 0.6 Hz, 1H), 6.87 – 6.84 (m, 2H), 3.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 143.3, 131.3, 130.2, 128.8, 126.4, 114.1, 113.7, 112.8, 106.7, 97.6, 55.8.

7-Chloro Pyrrolo[1,2-a]quinoxaline (2d)[12]



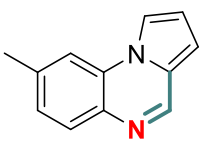
Light brown solid (39 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.91 (d, J = 2.3 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.45 (dd, J = 8.8, 2.3 Hz, 1H), 6.91 (dd, J = 4.0, 1.1 Hz, 1H), 6.88 (dd, J = 4.0, 2.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 136.8, 130.3, 129.5, 127.8, 126.7, 126.3, 115.0, 114.6, 114.5, 108.0.

7,8-Dichloro Pyrrolo[1,2-a]quinoxaline (2e)[12]



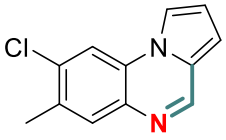
Light brown solid (46 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.02 (s, 1H), 7.93 (s, 1H), 7.84 – 7.82 (m, 1H), 6.93 (dd, J = 3.9, 0.8 Hz, 1H), 6.90 (dd, J = 3.9, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.9, 135.3, 131.5, 131.1, 131.0, 128.9, 127.2, 126.3, 115.5, 115.0, 108.6.

8-Methyl Pyrrolo[1,2-a]quinoxaline (2f)[12]



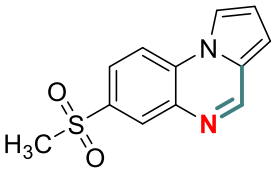
Yellow solid (35.2 mg, 97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.85 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.62 (s, 1H), 7.23 (d, J = 8.2 Hz, 1H), 6.87 – 6.79 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8, 138.3, 133.8, 129.8, 127.8, 126.6, 126.5, 126.4, 113.8, 106.9, 21.8.

8-Chloro-7-methyl Pyrrolo[1,2-a]quinoxaline (2g)



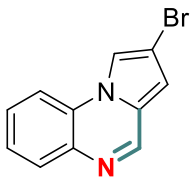
Brown solid (42 mg, 95%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.80 (s, 1H), 7.79 (d, J = 1.1 Hz, 1H), 7.76 (s, 1H), 6.85 (dt, J = 3.8, 3.4 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 134.5, 133.6, 133.2, 131.5, 126.7, 126.2, 114.3, 114.2, 107.7, 19.9. HRMS (ESI) *m/z* calcd for $C_{12}H_9ClN_2$ $[M+H]^+$ 217.0532 found 217.0543.

7-(Methyl sulfonyl) Pyrrolo[1,2-a]quinoxaline (2h)



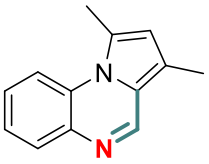
Orange solid (46 mg, 95%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.56 (d, J = 2.4 Hz, 1H), 8.51 (d, J = 8.7 Hz, 1H), 8.31 (d, J = 2.0 Hz, 1H), 8.05 (dd, J = 8.6, 2.1 Hz, 1H), 7.08 (dd, J = 3.9, 0.8 Hz, 1H), 7.00 (dd, J = 3.8, 2.8 Hz, 1H), 3.30 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 137.6, 135.4, 131.3, 128.9, 126.4, 126.2, 117.7, 116.7, 115.7, 109.4, 44.1. HRMS (ESI) *m/z* calcd for $C_{11}H_9N_2O_2S$ $[M+H]^+$ 234.0463 found 234.0456.

2-Bromo-Pyrrolo[1,2-a]quinoxaline (2i)



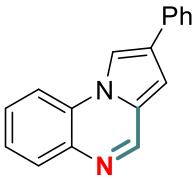
Brown solid (46 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.96 (dd, J = 8.0, 1.1 Hz, 1H), 7.90 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.55 (t, J = 8.4 Hz, 1H), 7.48 (t, J = 8.2 Hz, 1H), 6.90 (d, J = 1.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 135.5, 130.5, 128.4, 125.8, 114.1, 113.7, 109.1, 103.6. HRMS (ESI) *m/z* calcd for $C_{17}H_7BrN_2$ $[M+H]^+$ 246.9871 found 246.9631.

1,3-Dimethyl Pyrrolo[1,2-a]quinoxaline (2j)[13]



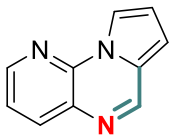
White solid (36 mg, 92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.13 (dd, J = 8.0, 1.3 Hz, 1H), 7.88 (dd, J = 7.5, 1.9 Hz, 1H), 7.39 – 7.33 (m, 2H), 6.39 (s, 1H), 2.85 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 135.5, 130.5, 128.4, 125.8, 114.1, 113.7, 109.1, 103.6.

2-Phenyl-Pyrrolo[1,2-a]quinoxaline (2k)



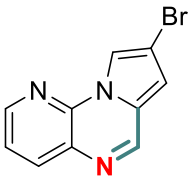
White solid (44 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.18 (s, 1H), 7.97 (dd, J = 8.0, 1.1 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 7.1 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.31 (t, J = 7.4 Hz, 1H), 7.16 (d, J = 1.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 135.7, 134.2, 130.2, 130.1, 129.1, 128.1, 127.8, 127.3, 127.2, 126.3, 125.4, 113.8, 111.1, 104.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}N_2$· $[M+H]^+$ 245.1078 found 245.1070.

Pyrido[3,2-e]Pyrrolo[1,2-a]Pyrazine (2l)[12]



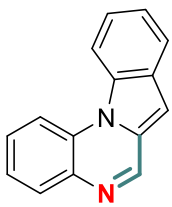
Yellow solid (30 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.52 (dd, J = 4.6, 1.4 Hz, 1H), 8.37 – 8.36 (m, 1H), 8.22 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 (dd, J = 8.0, 4.7 Hz, 1H), 6.96 (dd, J = 3.9, 1.2 Hz, 1H), 6.90 (dd, J = 3.8, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 146.6, 140.0, 137.5, 130.8, 128.0, 121.5, 115.6, 114.6, 108.9.

8-Bromo-Pyrido[3,2-e]Pyrrolo[1,2-a]Pyrazine (2m)



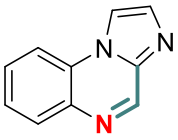
Yellow solid (46 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.52 (dd, J = 4.5, 1.4 Hz, 1H), 8.33 (s, 1H), 8.22 (dd, J = 7.9, 1.4 Hz, 1H), 7.44 (dd, J = 8.0, 4.6 Hz, 1H), 6.94 (d, J = 1.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 145.2, 138.6, 137.9, 130.4, 127.8, 122.0, 115.6, 110.6, 104.3. HRMS (ESI) *m/z* calcd for $C_{10}H_6BrN_3$ $[M+H]^+$ 246.9745, $[M+2]^+$ 248.9725 found $[M+H]^+$ 246.9734 and $[M+2]^+$ 248.9765.

Indolo[1,2-a]quinoxaline (2n)[12]



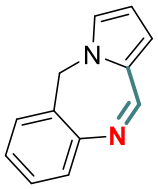
White solid (42 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.45 (ddd, J = 15.9, 8.5, 0.9 Hz, 2H), 8.00 – 7.96 (m, 2H), 7.62 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.55 (ddd, J = 8.6, 7.0, 1.3 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.15 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 136.0, 132.7, 131.1, 130.5, 129.8, 129.2, 128.8, 124.5, 124.2, 122.9, 122.8, 114.9, 114.7, 100.9.

Immidazo[1,2-a]quinoxaline (2o)[12]



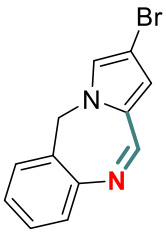
White solid (31 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.12 (dd, J = 7.1, 0.9 Hz, 2H), 7.90 (dd, J = 8.2, 1.1 Hz, 1H), 7.80 (d, J = 1.1 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.59 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 138.9, 135.9, 134.5, 130.8, 129.1, 127.4, 126.6, 114.9, 112.3.

5-*H*-Benzo[e]Pyrrolo[1,2-a][1,4]diazepine (4a)[14]



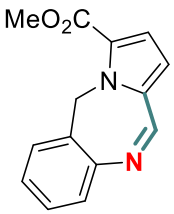
White solid (35 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.22 (d, J = 0.8 Hz, 1H), 7.21 – 7.21 (m, 1H), 6.83 – 6.81 (m, 1H), 6.58 (dd, J = 3.8, 1.6 Hz, 1H), 6.23 (dd, J = 3.8, 2.6 Hz, 1H), 4.96 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7, 147.8, 130.4, 129.1, 129.0, 128.5, 128.4, 126.8, 125.1, 115.5, 110.1, 52.0.

3-Bromo-5-*H*-Benzo[e]Pyrrolo[1,2-a][1,4]diazepine (4b)[14]



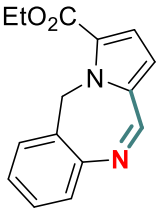
White solid (50 mg, 98%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s), 7.45 (dd, J = 7.9, 0.9 Hz), 7.39 (td, J = 7.7, 1.6 Hz), 7.23 (dd, J = 7.3, 1.2 Hz), 7.20 (dd, J = 7.5, 1.4 Hz), 6.82 (d, J = 1.6 Hz), 6.57 (d, J = 1.6 Hz), 4.91 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.7, 147.0, 130.4, 129.4, 128.9, 128.3, 128.1, 127.4, 124.6, 116.9, 97.4, 52.1, 29.8. HRMS (ESI) *m/z* calcd for $C_{12}H_9BrN_2^{\cdot}$ $[M+H]^+$ 259.9949, $[M+2]^+$ 261.9929 found $[M+H]^+$ 259.9929 and $[M+2]^+$ 261.9928.

Methyl 5H-Benzo[e]Pyrrolo[1,2-a][1,4]diazepine-3-carboxylate (4c)



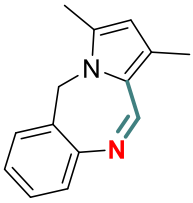
White solid (45 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.46 – 7.42 (m, 2H), 7.39 (td, J = 7.7, 1.4 Hz, 1H), 7.27 (td, J = 7.5, 1.3 Hz, 1H), 6.93 (d, J = 4.1 Hz, 1H), 6.48 (d, J = 4.1 Hz, 1H), 5.55 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7, 150.6, 147.9, 135.1, 129.2, 129.0, 128.1, 127.6, 123.9, 117.9, 112.7, 51.7, 47.6. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}N_2O_2$ $[M+H]^+$ 241.9068 found 241.9051.

Ethyl 5H-Benzo[e]Pyrrolo[1,2-a][1,4]diazepine-3-carboxylate (4d)



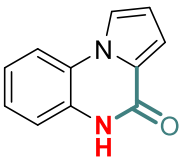
White solid (47 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.44 (dd, J = 7.9, 0.9 Hz, 1H), 7.42 (dd, J = 7.6, 0.9 Hz, 1H), 7.37 (td, J = 7.7, 1.5 Hz, 1H), 7.26 (td, J = 7.4, 1.1 Hz, 1H), 6.92 (d, J = 2.4 Hz, 1H), 6.47 (d, J = 4.1 Hz, 1H), 5.54 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 3.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.4, 161.3, 160.4, 150.6, 147.8, 135.0, 134.4, 129.1, 128.1, 127.5, 124.3, 119.8, 117.8, 115.7, 112.7, 60.6, 47.6, 14.3. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}N_2O_2$ $[M+H]^+$ 239.0821 found 239.0811.

1,3-Dimethyl-5H-Benzo[e]Pyrrolo[1,2-a][1,4]diazepine-3-carboxylate (4e)



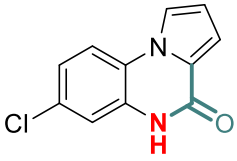
White solid (39.5mg, 97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.40 (dd, J = 7.8, 0.6 Hz, 1H), 7.34 (td, J = 7.7, 1.5 Hz, 1H), 7.21 (dd, J = 7.4, 1.3 Hz, 1H), 7.16 (td, J = 7.4, 1.2 Hz, 1H), 5.84 (s, 1H), 4.78 (s, 2H), 2.30 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 149.1, 148.7, 132.5, 129.0, 128.4, 128.2, 127.5, 126.0, 125.6, 111.3, 48.0, 12.0, 11.0. HRMS (ESI) *m/z* calcd for $C_{14}H_{14}N_2[M+H]^+$ 211.2878 found 211.2870.

Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6a)[15]



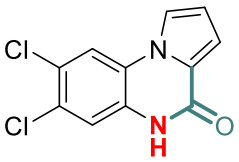
White solid (36 mg, 98%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.20 (s, 1H), 8.14 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 6.99 (dd, J = 3.8, 1.4 Hz, 1H), 6.65 – 6.64 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.4, 128.9, 126.0, 123.7, 123.0, 123.0, 118.4, 116.9, 115.4, 113.1, 111.8. IR (KBr, cm^{-1}): 1718, 1466, 1378, 1266.

7-Chloro-Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6b)[15]



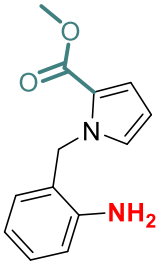
White solid (40 mg, 95%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.29 (s, 1H), 8.15 (dd, J = 2.8, 1.5 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 7.26 (d, J = 2.3 Hz, 1H), 7.22 (dd, J = 8.7, 2.3 Hz, 1H), 7.01 (dd, J = 3.8, 1.4 Hz, 1H), 6.66 (dd, J = 3.8, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.2, 130.3, 129.7, 123.3, 122.5, 122.1, 118.9, 117.1, 116.1, 113.4, 112.2.

7,8-Dichloro-Pyrrolo[1,2-a]quinoxaline-4(5H)-one (6c)[15]



White solid (43 mg, 92%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 11.34 (s, 1H), 8.39 (s, 1H), 8.21 (dd, J = 2.8, 1.4 Hz, 1H), 7.02 (dd, J = 3.8, 1.4 Hz, 1H), 6.67 (dd, J = 3.8, 2.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 155.0, 129.1, 127.6, 124.6, 123.4, 123.0, 119.5, 117.6, 117.3, 113.8, 112.7.

Methyl 1-(2-aminobenzyl)-1H-pyrrole-2-carboxylate[16]



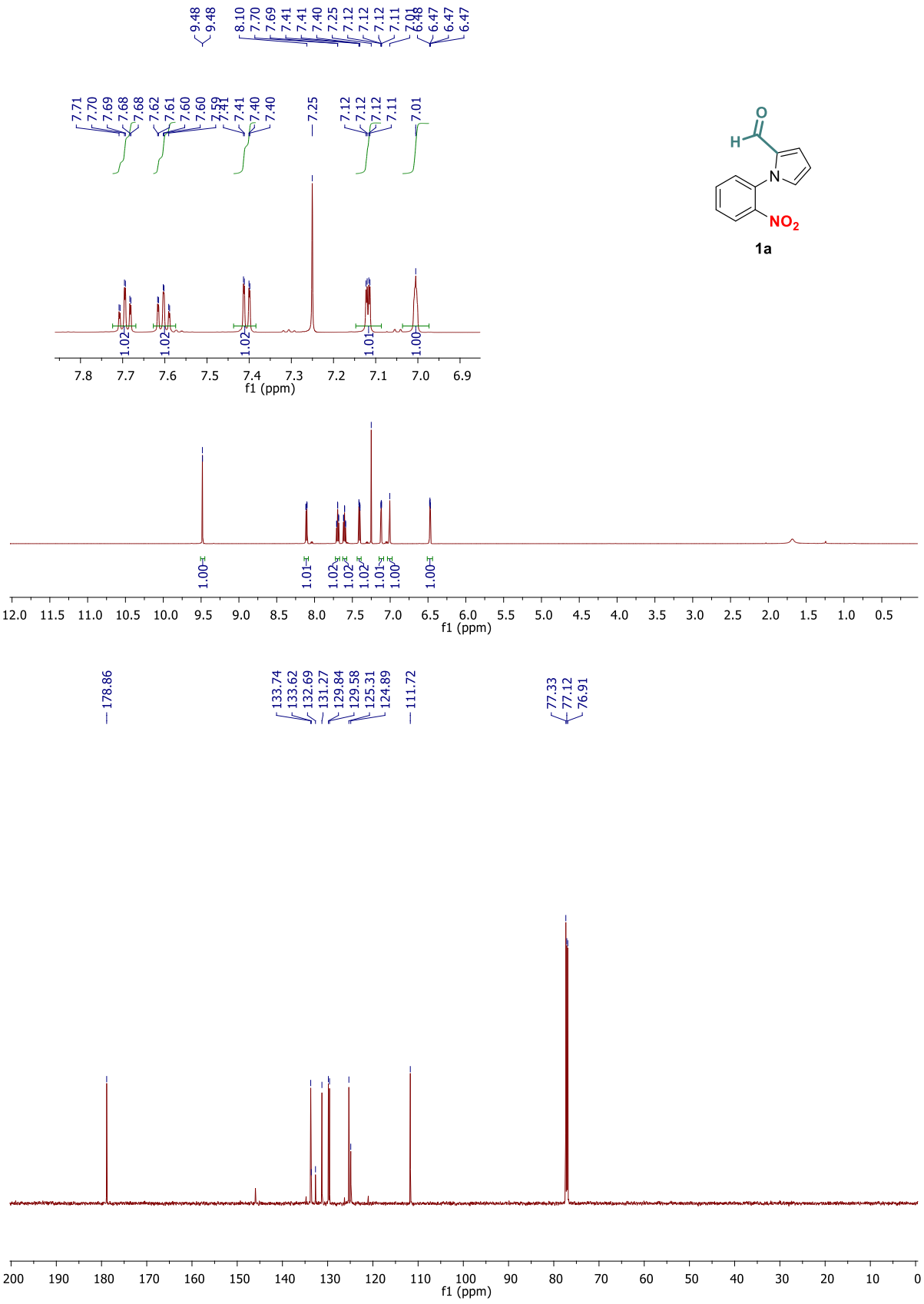
White solid (36 mg, 92%); ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 7.10 – 7.07 (m, 1H), 6.94 – 6.88 (m, 2H), 6.61 (dd, J = 7.9, 0.9 Hz, 1H), 6.40 (t, J = 7.4 Hz, 1H), 6.21 (d, J = 7.4 Hz, 1H), 6.14 (dd, J = 3.9, 2.6 Hz, 1H), 5.33 (s, 2H), 5.05 (s, 2H), 3.65 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 161.2, 145.7, 130.4, 128.2, 126.7, 122.4, 121.8, 118.2, 116.6, 115.1, 108.7, 51.3, 48.3.

4. REFERENCES

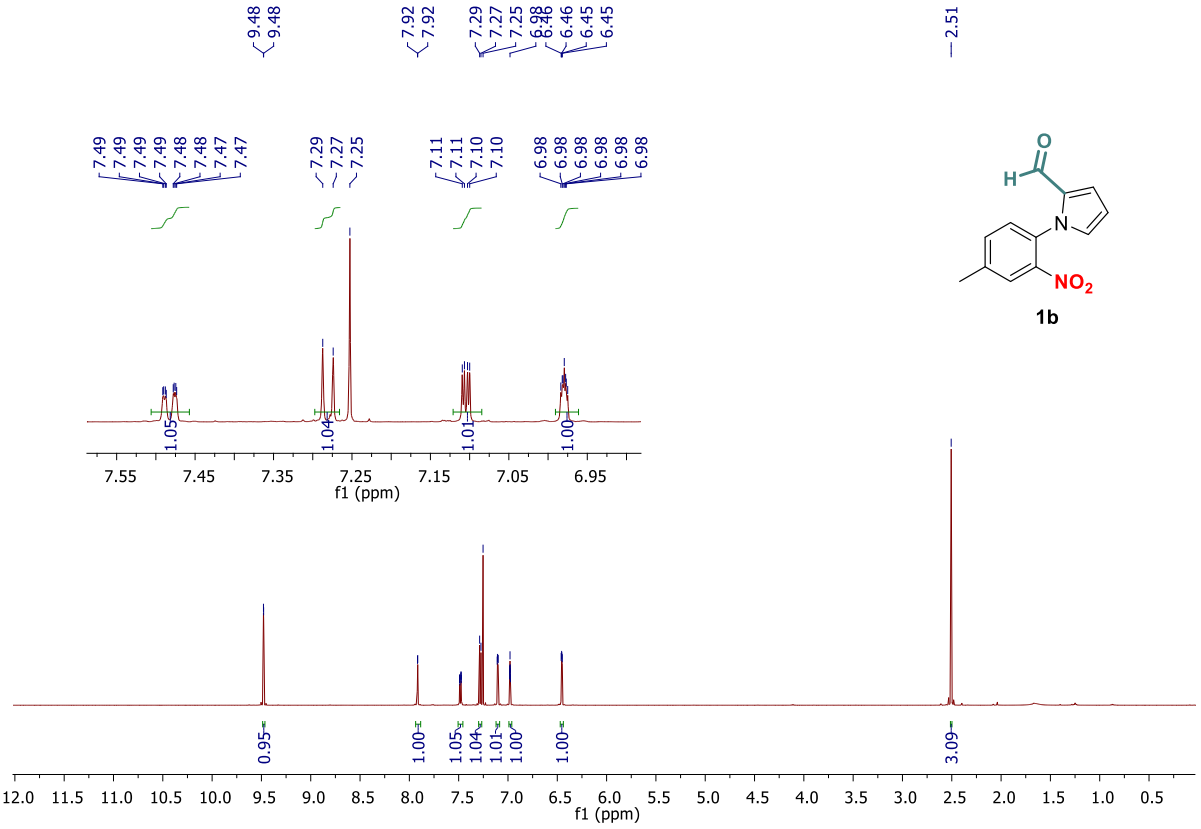
1. J. Ni, Y. Jiang, Z. Qi, R. Yan, *Chem. Asian J.* 2019, **14**, 2898−2902.
2. C. H. Escalante, E. I. Martínez-Mora, C. Espinoza-Hicks, A. A. Camacho-Davila, F. R. Ramos-Morales, F. Delgado, J. Tamariz, Beilstein *J. Org. Chem.* 2020, **16**, 1320–1334.
3. K. Wang and Z. Liu, *Synth. Commun.* 2010, **40**, 144.
4. F. W. Sum, J. Dusra, E. F. Delos Santos, G. Grosu, M. Reich, X. Du, D. Albright, P. Chan, J. Coupet, X. Ru, H. Mazandarani, T. Saunders, *Bioorg. Med. Chem. Lett., 2003, **13**, 2195-2198.*
5. N. Ono, E. Muratani, T. Ogawa, *J. Heterocycl. Chem.*, 1991, **28**, 2053 - 2055.
6. A. Mishra, S. Batra, *Eur. J. Org. Chem.*, 2010, **25**, 4832-4840.
7. (a) H. Ikegami, M. Jachmann, Y. Nokura, I. Chiemi, 2006, WO2007043677A1. (b) Y. Nokura, H. Ikegami, C. Iwata, M. Jachmann, 2013, CN101287721B.
8. S. Biswas, V. Singh, S. Batra, *Tetrahedron*, 2010, **66**, 7781-7786.
9. M. C. Frantz , L. P. Pellissier, E. Pflimlin, S. Loison , J. Gandía, M. T. Durroux, B. Mouillac, J. A. J. Becker, J. L. Merrer, C. Valencia, P. Villa, D. Bonnet, M. Hibert, *J. Med. Chem*., 2018, 8670-8692.
10. J. S. Kiely, S. Huang, *J. Hetrocycl. Chem.*, 1987, **24**, 1137-1139.
11. A. J. Molinari, E. J. Trybulski, J. Bagli, S. Croce, J. Considine, Ji. Qi, K. Ali, W. Demaio, L. Lihotz, D. Cochran, *Biorg. Med. Chem. Lett.*, 2007, **17**, 5796-5800.
12. C. Xie, Z. Zhang, D. Li, J. Gong, X. Han, X. Liu, C. Ma, *J. Org. Chem.* 2017, **82**, 7, 3491–3499.
13. J. T. Reeves, D. R. Fandrick, Z. Tan, J. J. Song, H. Lee, N. K. Lee, H. Cris, *J. Org. Chem.* 2010, **75**, 3, 992–994.
14. M. Artico, J. D. Martino, R. Giuliano, S. Massa, G.C. Porretta, *J. Chem., Soc.* D., 1969, **12**, 671a.
15. J. Nan, P. Chen, X. Gong, Y. Hu, Q. Ma. B. Wang, Y. Ma, *Org. Lett.* 2021, **23**, 9, 3761–3766.
16. A. J. Molinari, E. J. Trybulski, J. Bagli, S. Croce, J. Considine, J. Qi, K. Ali, W. DeMaio, L. Lihotz, D. Cochran, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 5796-5800.

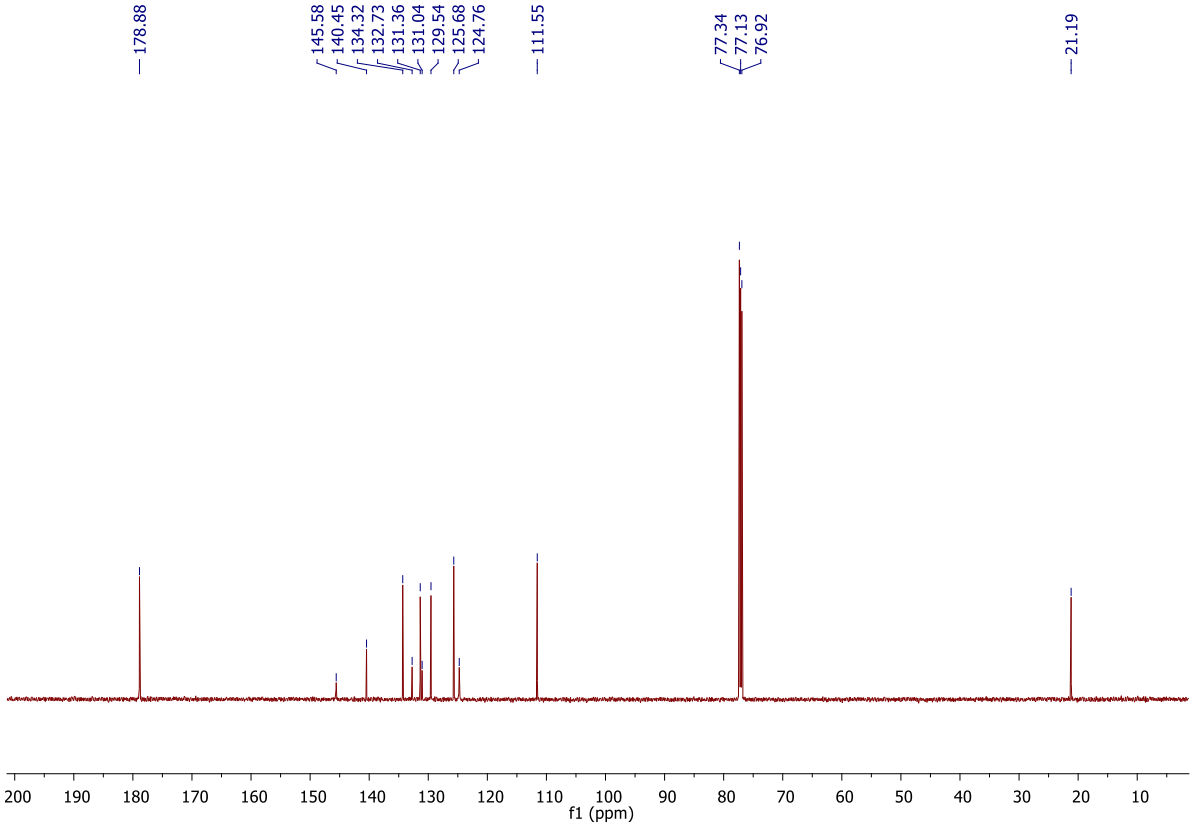
5. ^{1}H AND ^{13}C SPECTRA

1a

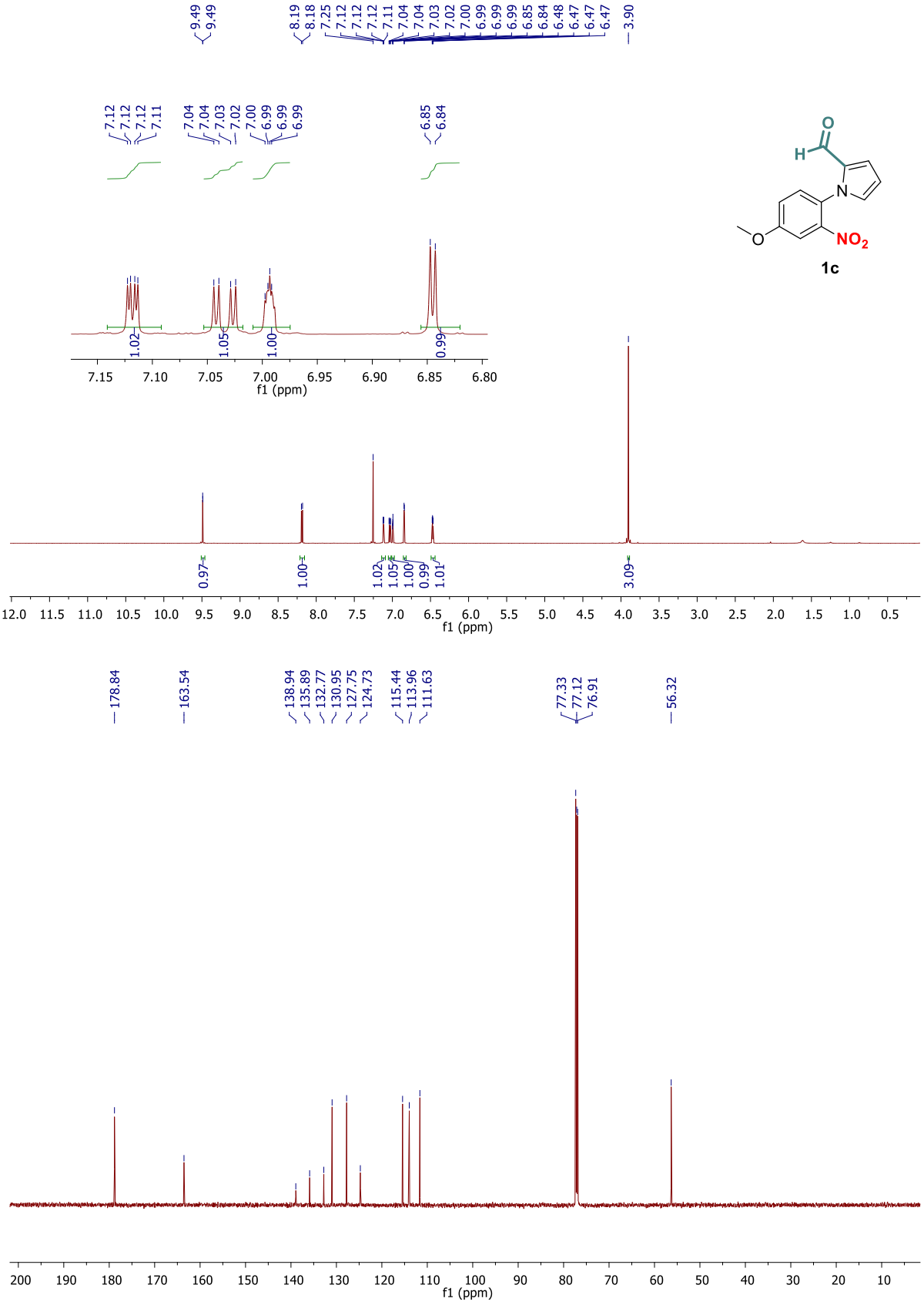


1b

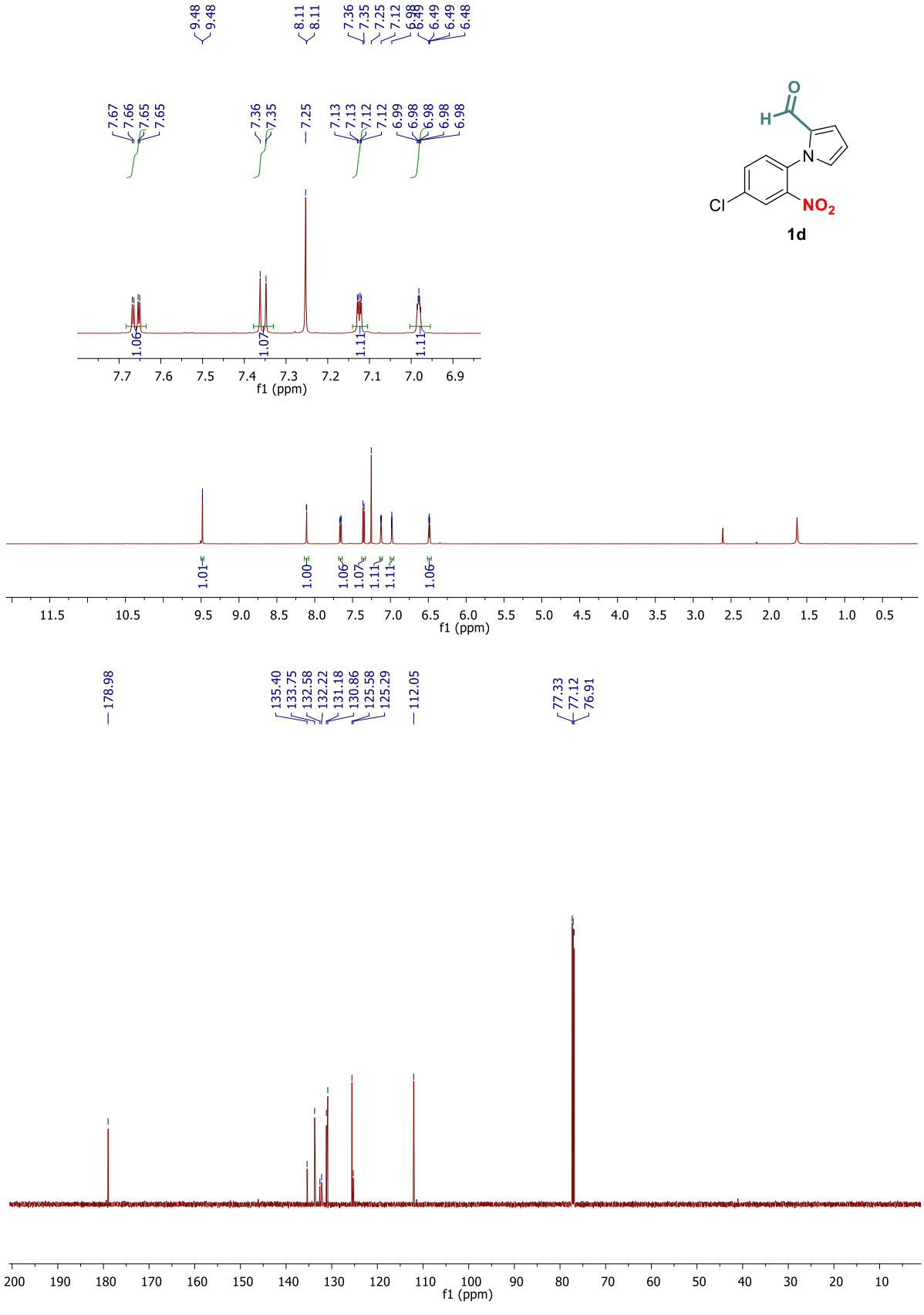

9.48
9.48
7.92
7.92
7.49
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.29
7.27
7.25
7.11
7.11
7.10
7.10
6.98
6.98
6.98
6.98
6.98
6.46
6.45
6.45
2.51
1.05
1.04
1.01
1.00
7.55
7.45
7.35
7.25
7.15
7.05
6.95
f1 (ppm)
O
H
N
NO2
1b
0.95
1.00
1.05
1.04
1.01
1.00
1.00
3.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


178.88
145.58
140.45
134.32
132.73
131.36
131.04
129.54
125.68
124.76
111.55
77.34
77.13
76.92
21.19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

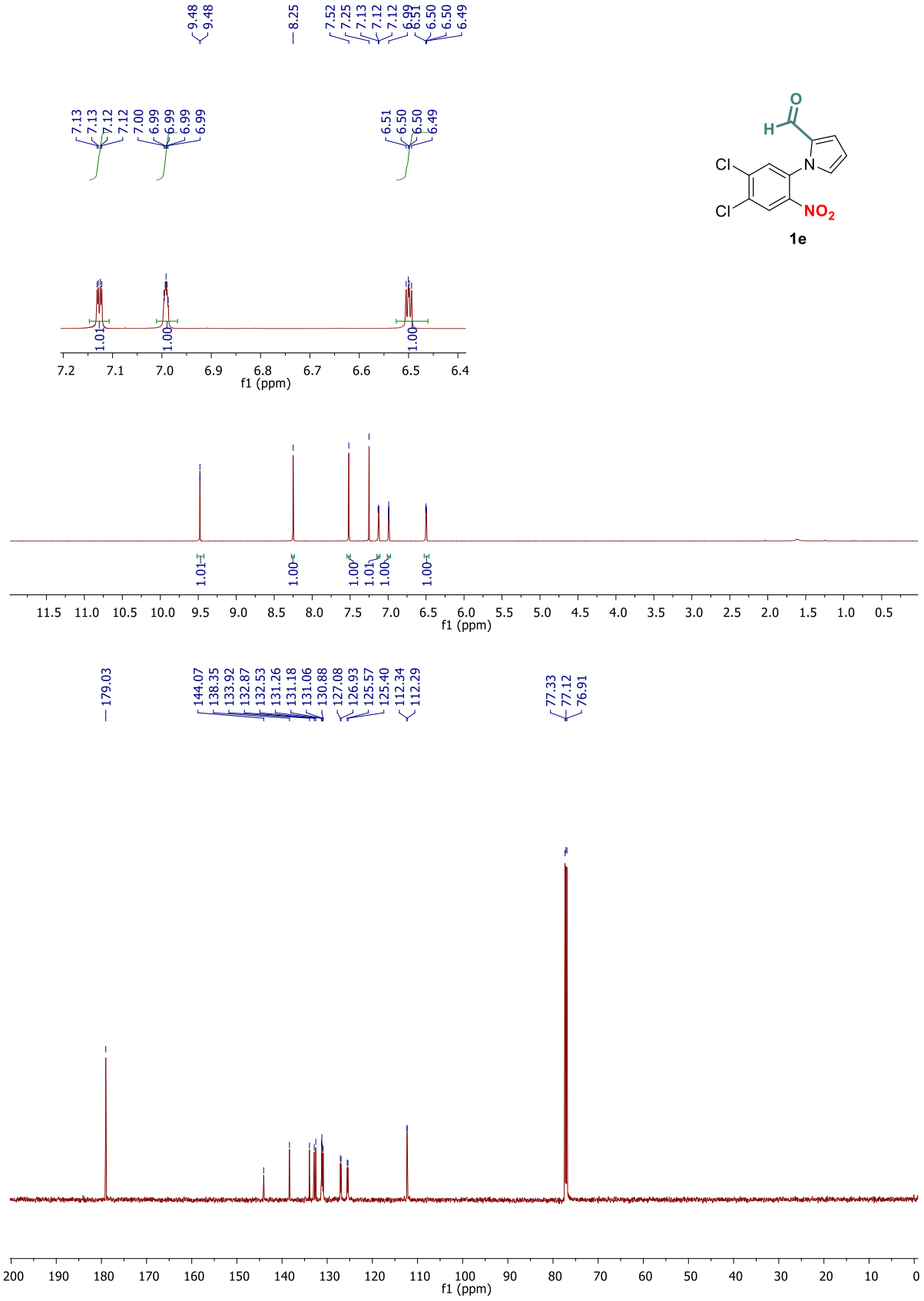
1c


9.49
9.49
8.19
8.18
7.25
7.12
7.12
7.12
7.11
7.04
7.04
7.03
7.02
7.00
6.99
6.99
6.85
6.84
6.48
6.47
6.47
3.90
O
H
N
O
NO2
1c
1.02
1.05
1.00
0.99
f1 (ppm)
0.97
1.00
1.02
1.05
1.00
0.99
1.01
3.09
f1 (ppm)
178.84
163.54
138.94
135.89
132.77
130.95
127.75
124.73
115.44
113.96
111.63
77.33
77.12
76.91
56.32
f1 (ppm)

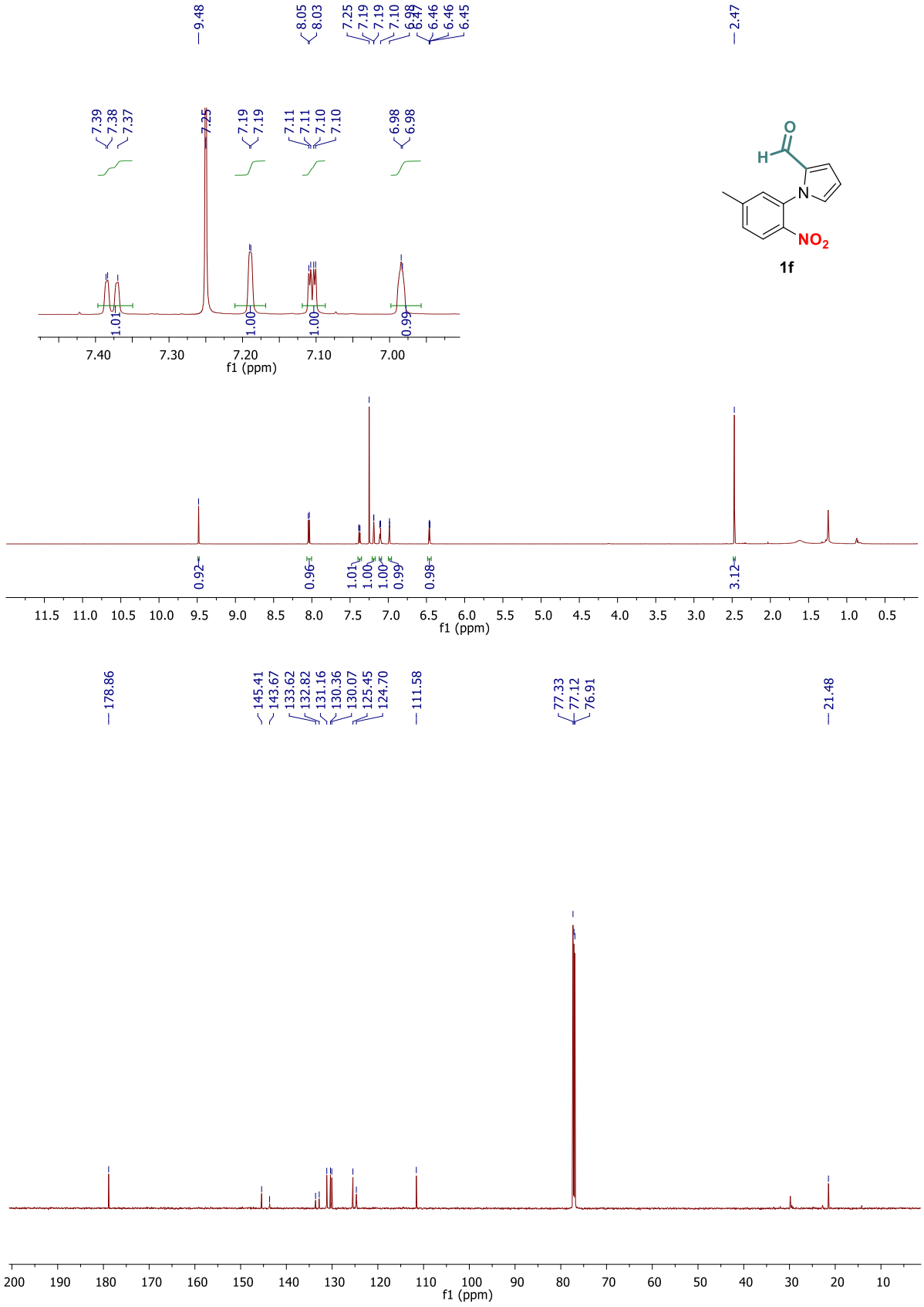
1d


9.48
9.48
8.11
8.11
7.36
7.35
7.25
7.12
6.49
6.48
7.67
7.66
7.65
7.65
7.36
7.35
7.25
7.13
7.13
7.12
7.12
6.99
6.98
6.98
6.98
6.98
1.06
1.07
1.11
1.11
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
O
H
N
Cl
NO2
1d
1.01
1.00
1.06
1.07
1.11
1.11
1.06
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
178.98
135.40
133.75
132.58
132.22
131.18
130.86
125.58
125.29
112.05
77.33
77.12
76.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

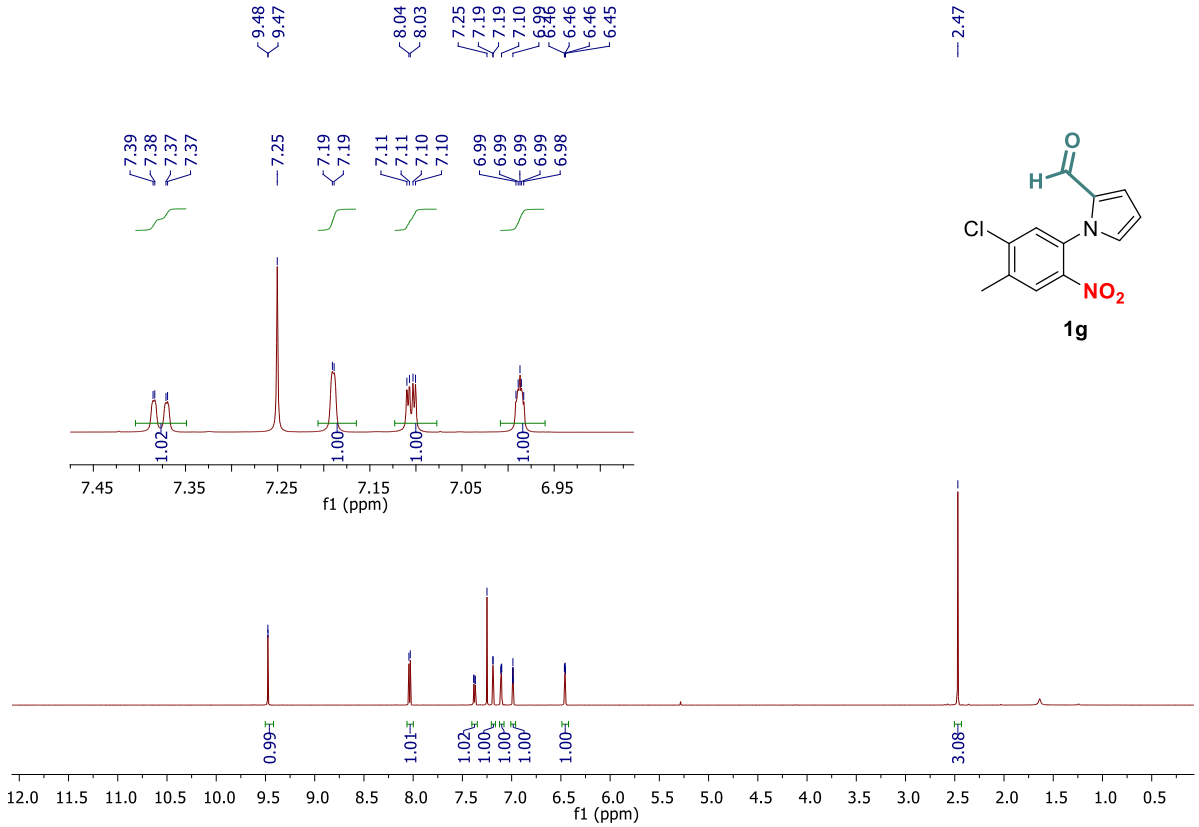
1e

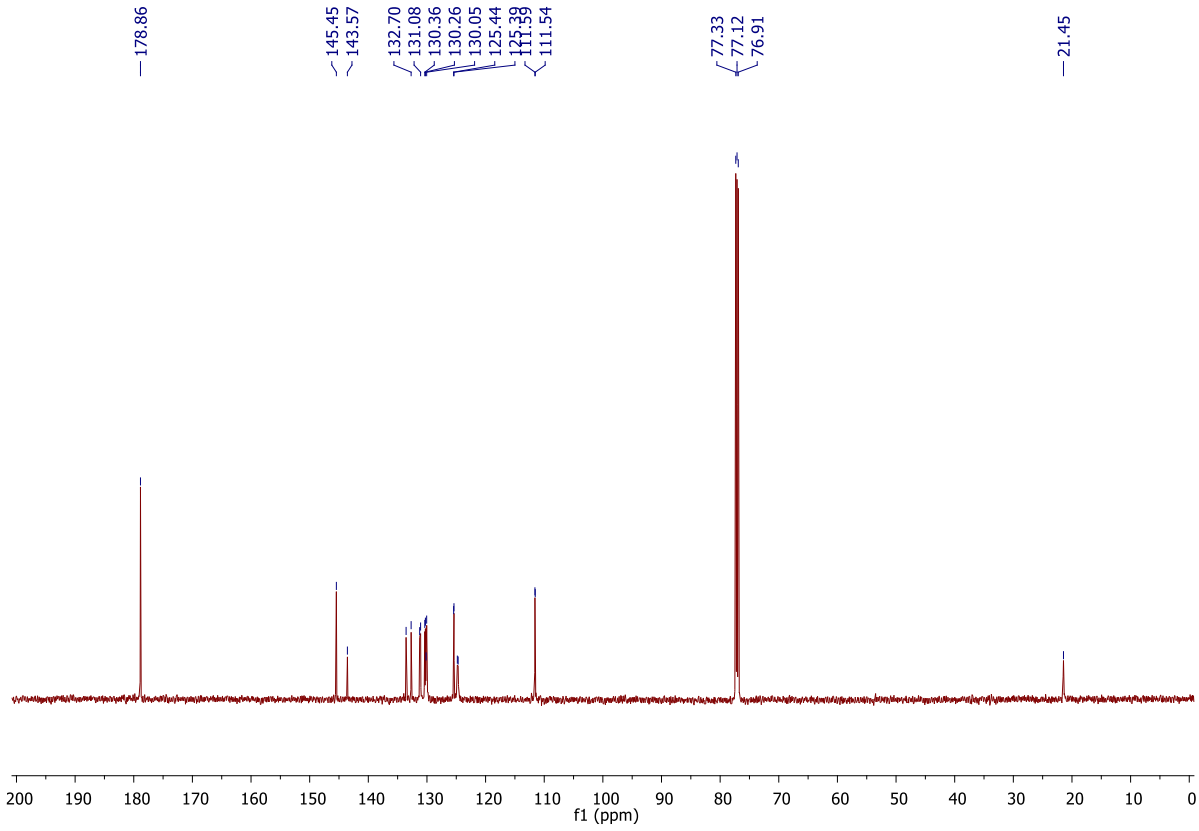

9.48
9.48
8.25
7.52
7.25
7.13
7.12
7.12
6.99
6.51
6.50
6.50
6.49
7.13
7.13
7.12
7.12
7.00
6.99
6.99
6.99
6.99
6.51
6.50
6.50
6.49
O
H
N
Cl
Cl
NO2
1e
1.01
1.00
1.00
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
f1 (ppm)
1.01
1.00
1.00
1.01
1.00
1.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
179.03
144.07
138.35
133.92
132.87
132.53
131.26
131.18
131.06
130.88
127.08
126.93
125.57
125.40
112.34
112.29
77.33
77.12
76.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1f

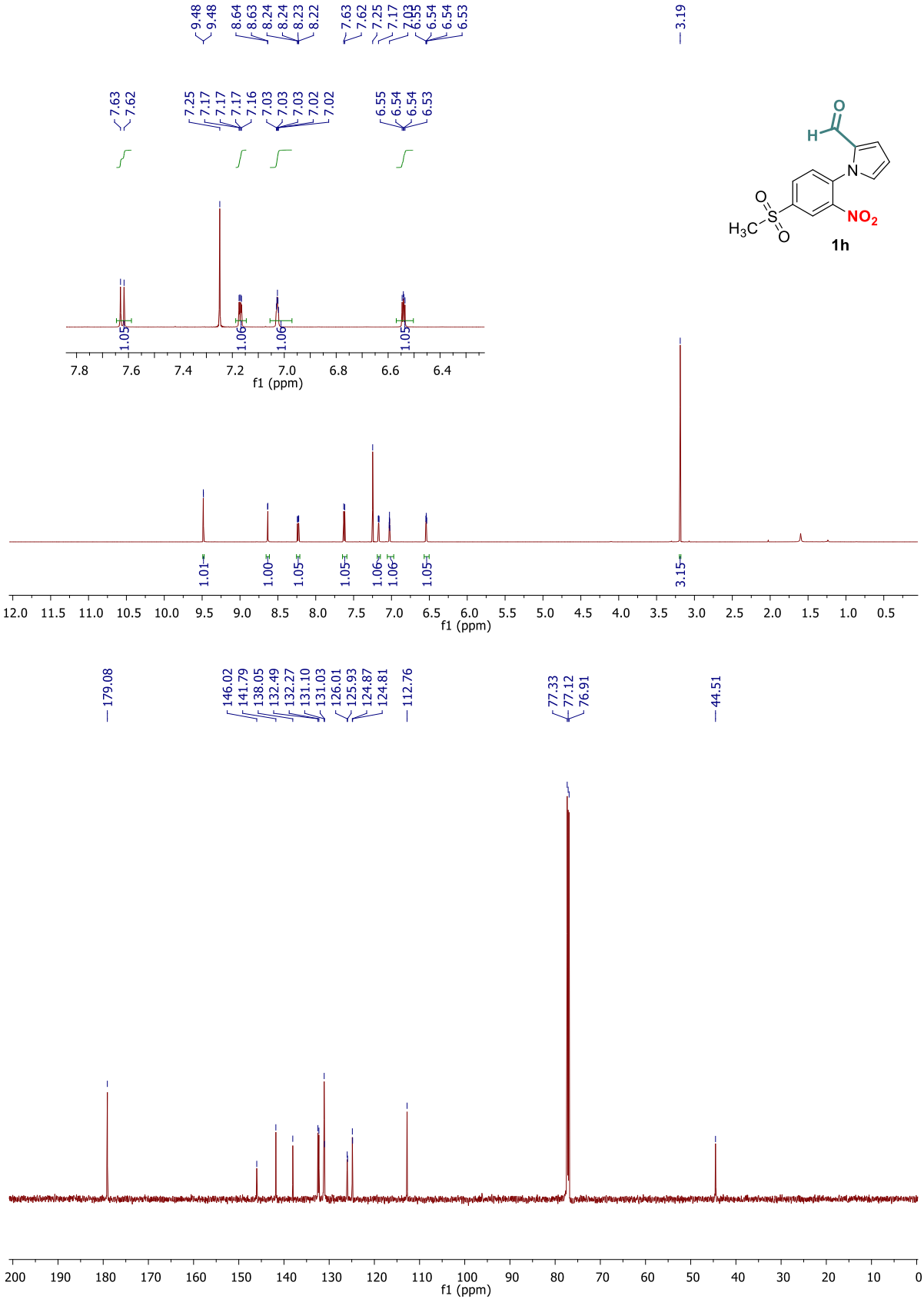

9.48
8.05
8.03
7.25
7.19
7.19
7.10
6.98
6.47
6.46
6.46
6.45
2.47
7.39
7.38
7.37
7.25
7.19
7.19
7.11
7.11
7.10
7.10
6.98
6.98
1.01
1.00
1.00
0.99
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
O
H
N
NO2
1f
0.92
0.96
1.01
1.00
1.00
0.99
0.98
3.12
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
178.86
145.41
143.67
133.62
132.82
131.16
130.36
130.07
125.45
124.70
111.58
77.33
77.12
76.91
21.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1g

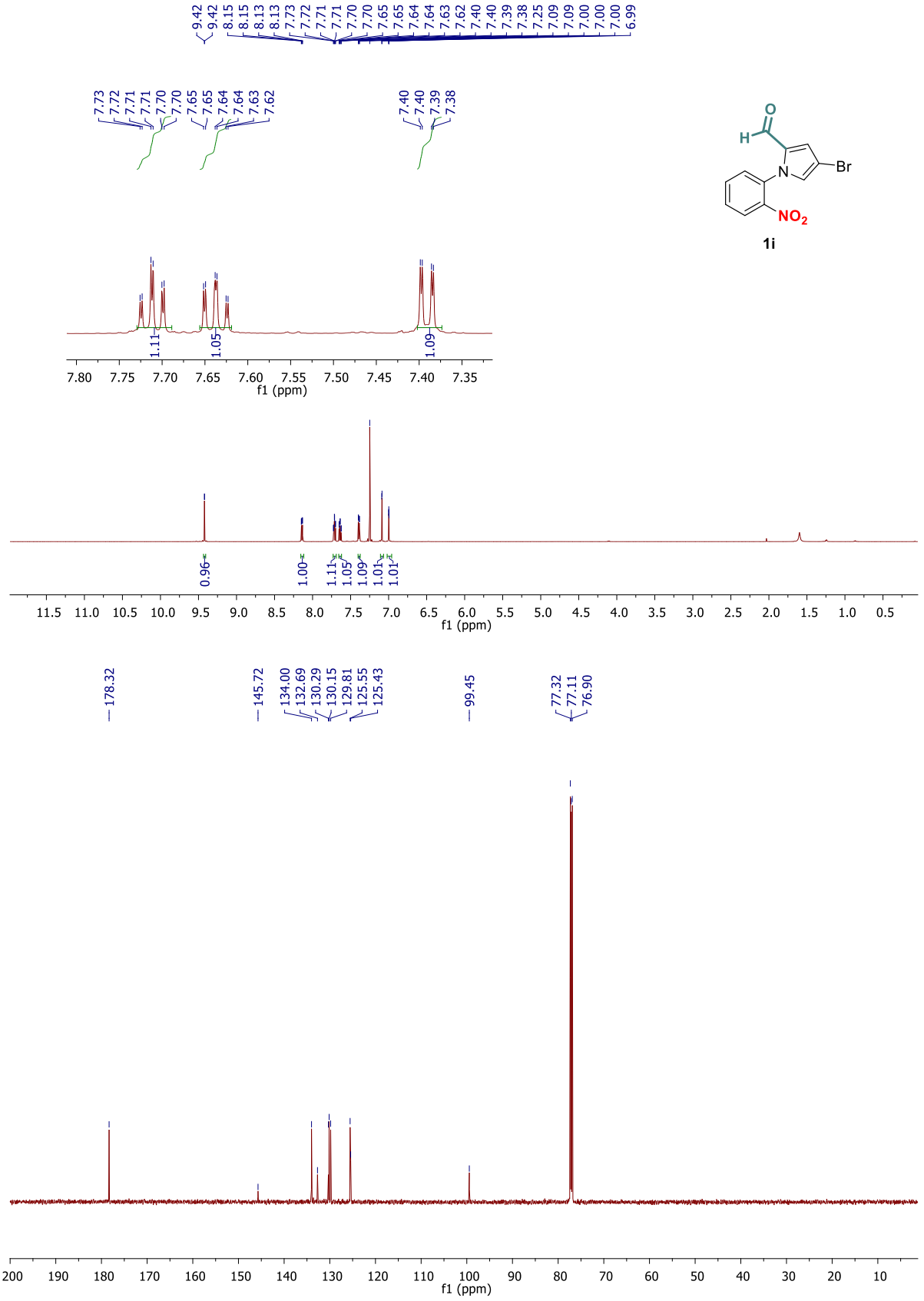

9.48
9.47
8.04
8.03
7.25
7.19
7.19
7.10
6.46
6.46
6.45
2.47
7.39
7.38
7.37
7.37
7.25
7.19
7.19
7.11
7.11
7.10
7.10
6.99
6.99
6.99
6.99
6.98
O
H
Cl
N
NO2
1g
1.02
1.00
1.00
1.00
7.45
7.35
7.25
7.15
7.05
6.95
f1 (ppm)
0.99
1.01
1.02
1.00
1.00
1.00
3.08
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


178.86
145.45
143.57
132.70
131.08
130.36
130.26
130.05
125.44
111.54
77.33
77.12
76.91
21.45
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

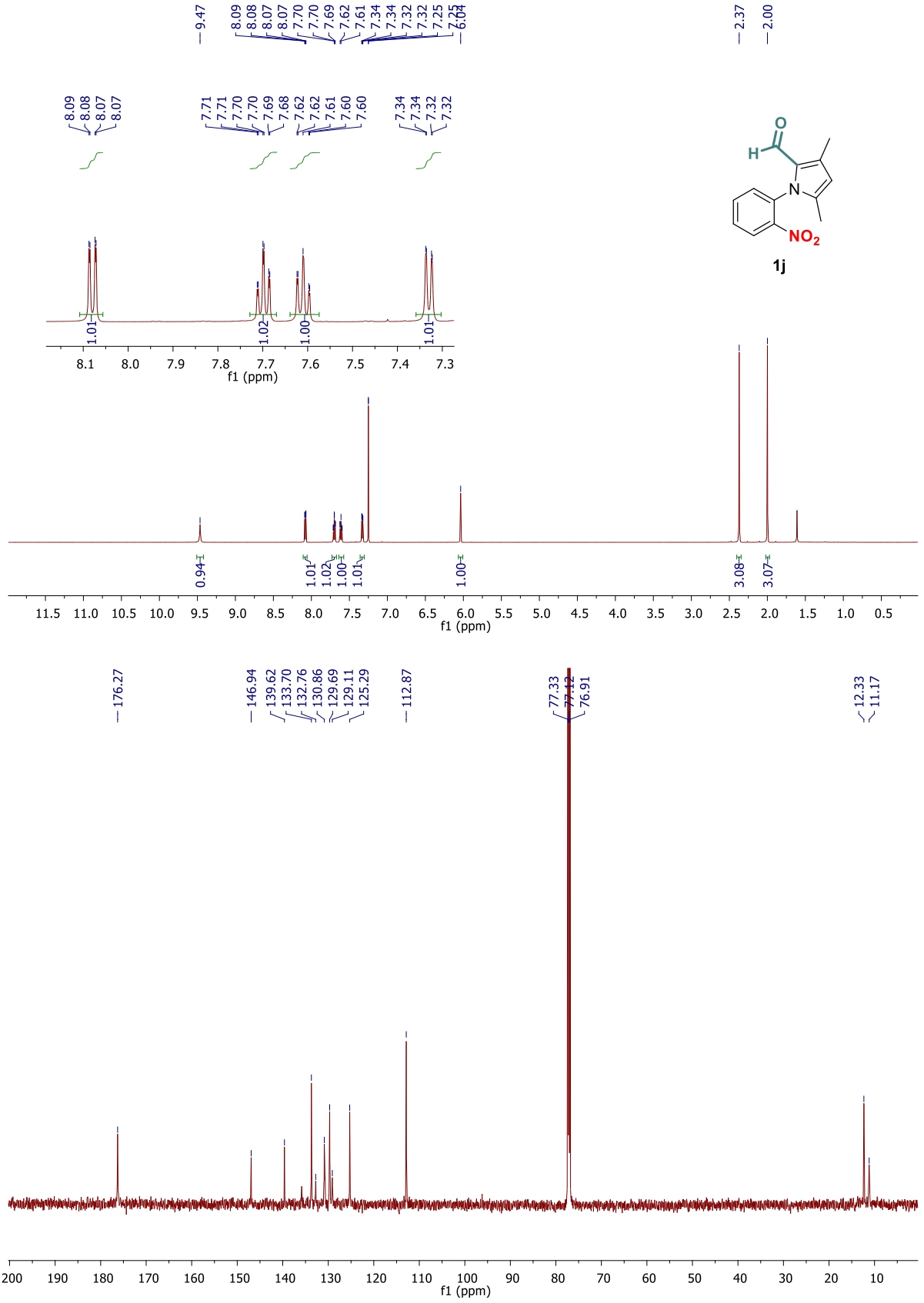
1h


9.48
9.48
8.64
8.63
8.24
8.24
8.23
8.22
7.63
7.62
7.25
7.17
7.03
6.55
6.54
6.54
6.53
3.19
7.63
7.62
7.25
7.17
7.17
7.16
7.03
7.03
7.03
7.02
7.02
6.55
6.54
6.54
6.53
O
H
N
O
S
O
H3C
NO2
1h
1.05
1.06
1.06
1.05
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
1.01
1.00
1.05
1.05
1.06
1.06
1.05
3.15
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
179.08
146.02
141.79
138.05
132.49
132.27
131.10
131.03
126.01
125.93
124.87
124.81
112.76
77.33
77.12
76.91
44.51
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

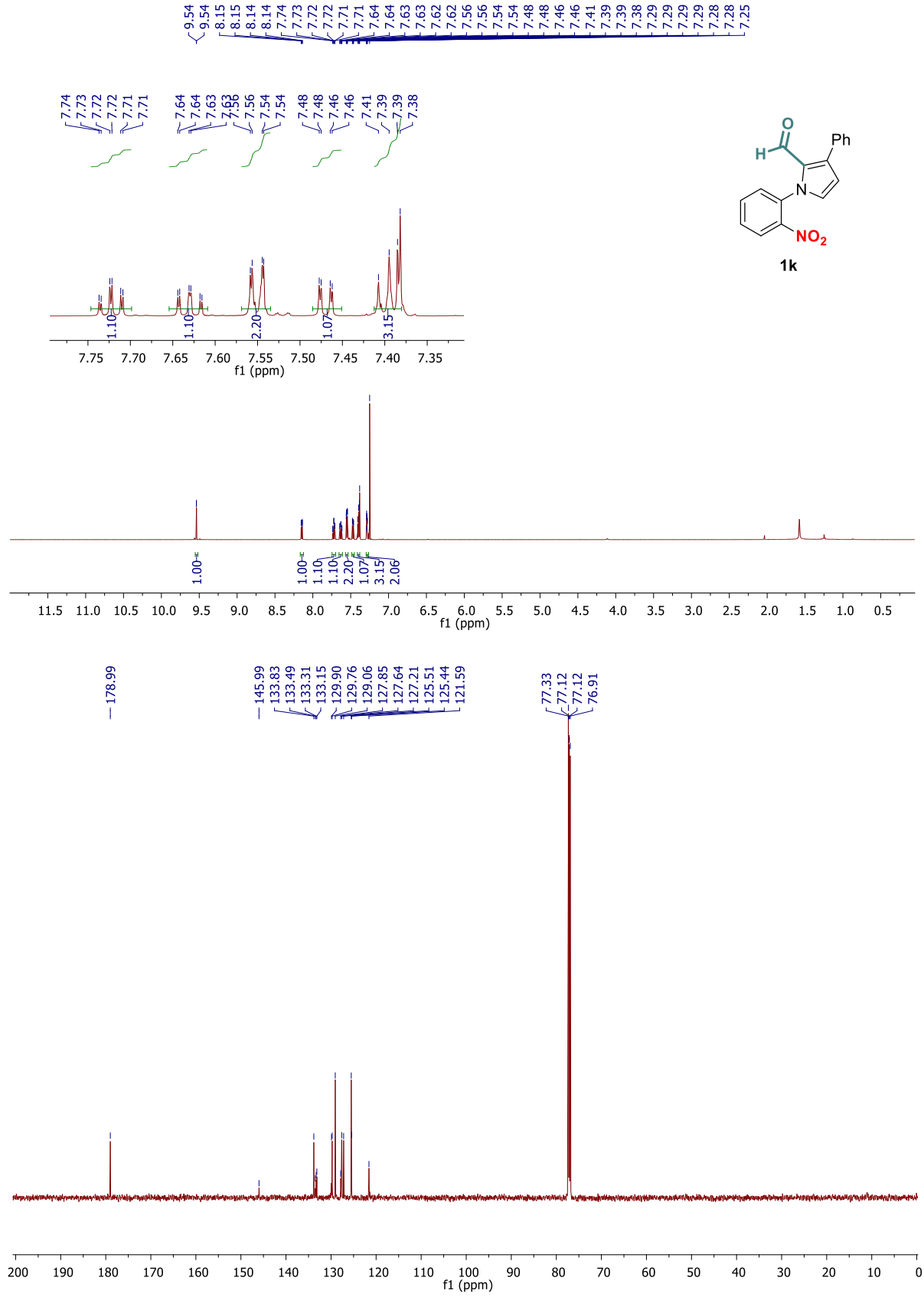
1i


9.42 9.42 8.15 8.15 8.13 8.13 7.73 7.72 7.71 7.71 7.70 7.70 7.65 7.65 7.64 7.64 7.63 7.62 7.40 7.40 7.39 7.38 7.25 7.09 7.09 7.00 7.00 7.00 6.99
O
H
N
Br
NO2
1i
1.11 1.05 1.09
7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
0.96 1.00 1.11 1.05 1.09 1.01 1.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
178.32 145.72 134.00 132.69 130.29 130.15 129.81 125.55 125.43 99.45 77.32 77.11 76.90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

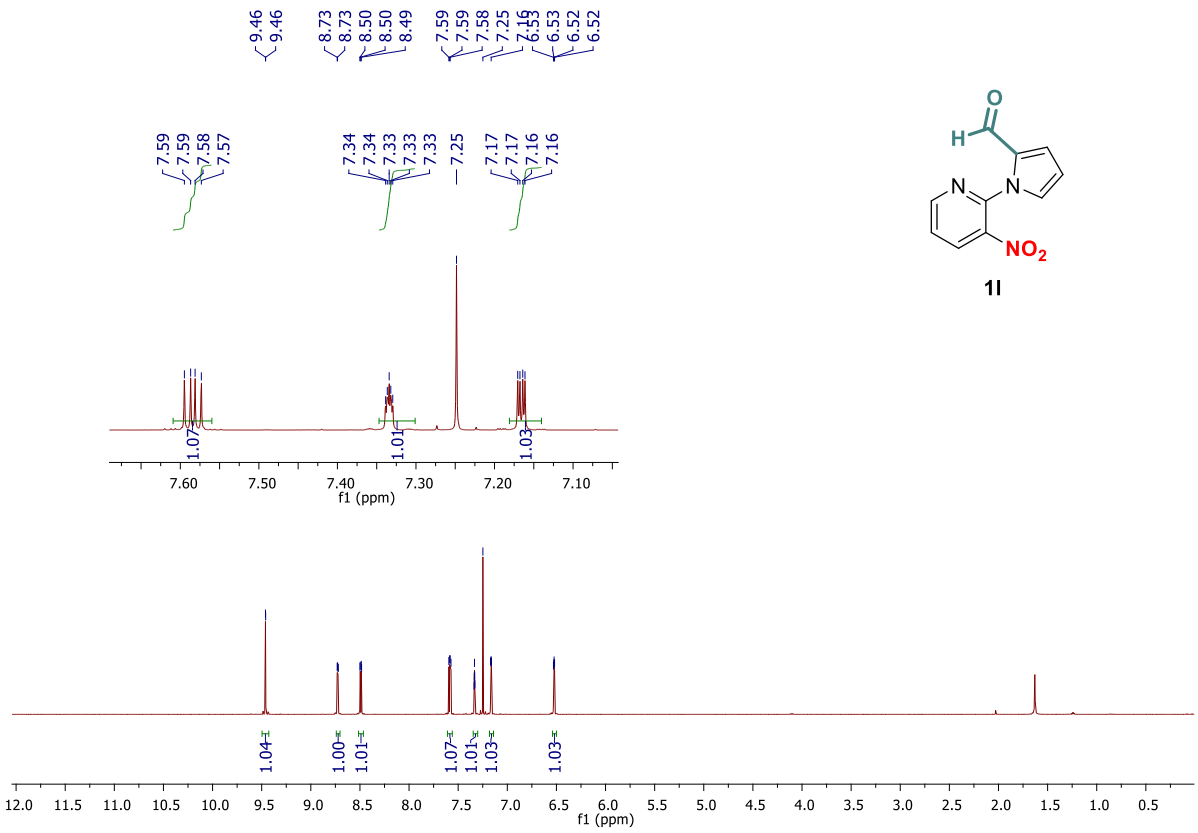
1j

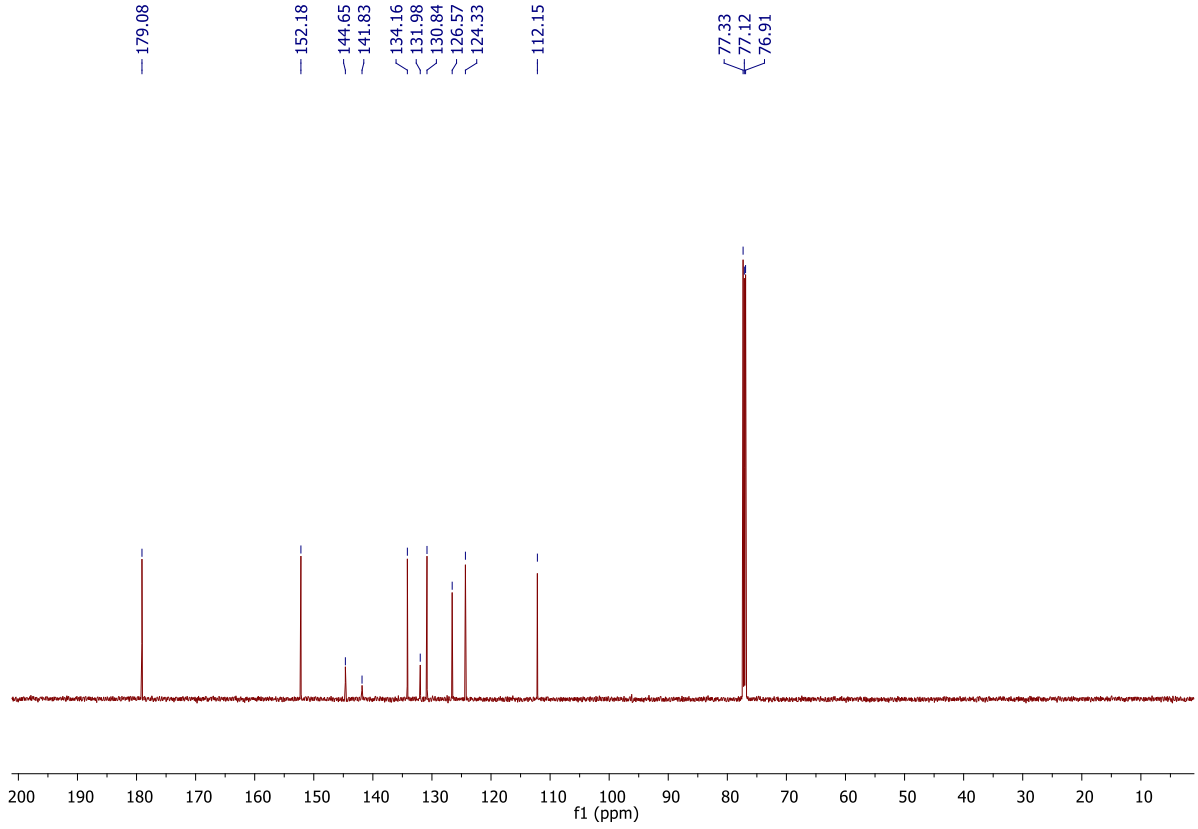

9.47
8.09
8.08
8.07
8.07
7.70
7.70
7.69
7.62
7.61
7.34
7.34
7.32
7.32
7.25
6.04
2.37
2.00
O
H
N
NO2
1j
1.01
1.02
1.00
1.01
f1 (ppm)
0.94
1.01
1.02
1.00
1.01
1.00
3.08
3.07
f1 (ppm)
176.27
146.94
139.62
133.70
132.76
130.86
129.69
129.11
125.29
112.87
77.33
77.12
76.91
12.33
11.17
f1 (ppm)

1k

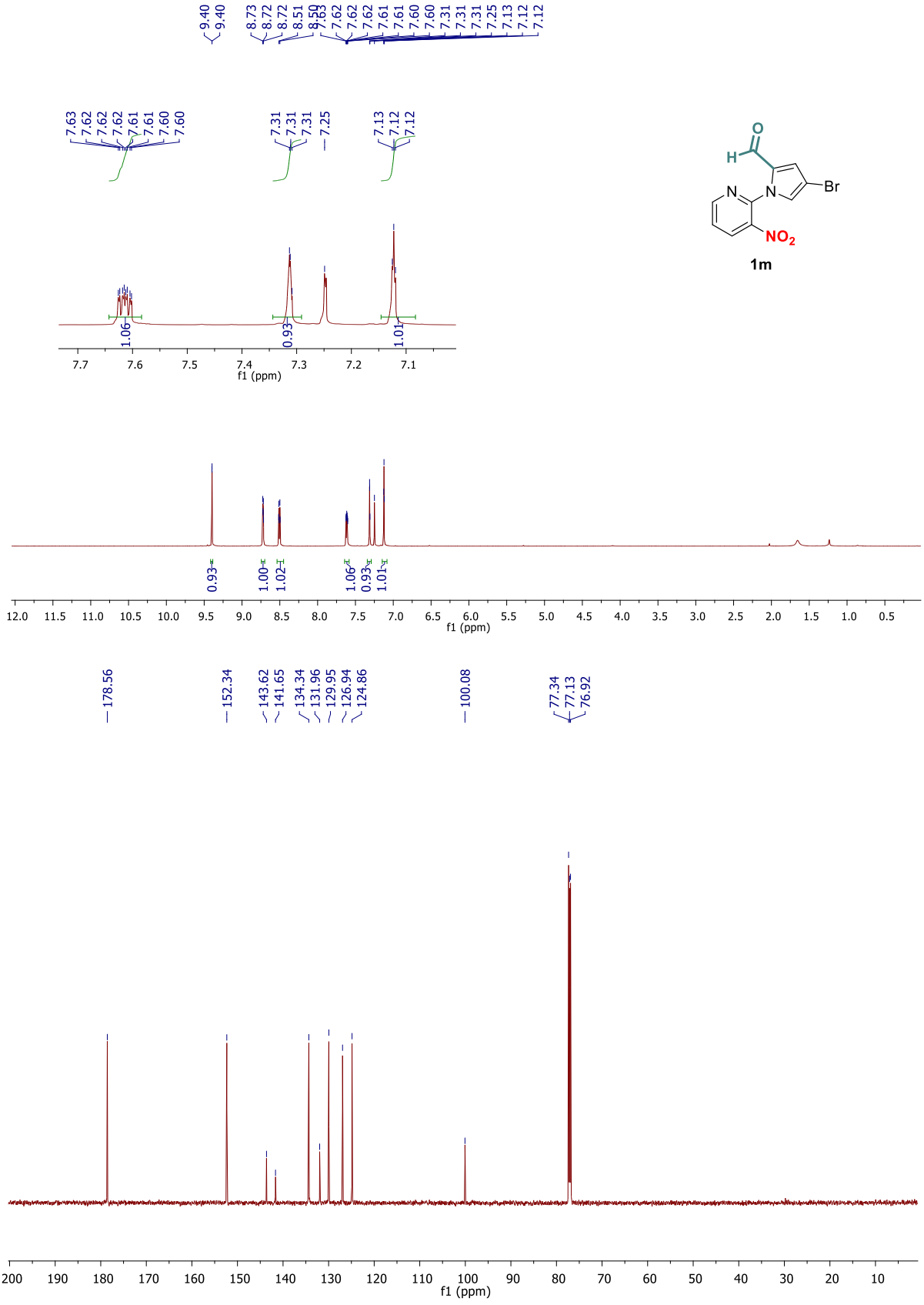

9.54 9.54 8.15 8.15 8.14 8.14 7.74 7.73 7.72 7.72 7.71 7.71 7.64 7.63 7.63 7.62 7.62 7.56 7.56 7.54 7.54 7.48 7.46 7.46 7.41 7.39 7.39 7.38 7.29 7.29 7.29 7.28 7.25
7.74 7.73 7.72 7.72 7.71 7.71 7.64 7.64 7.63 7.56 7.56 7.54 7.54 7.48 7.48 7.46 7.46 7.41 7.39 7.39 7.38
1.10 1.10 2.20 1.07 3.15
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
O
H
Ph
N
NO2
1k
1.00 1.00 1.10 1.10 2.20 1.07 3.15 2.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
178.99
145.99 133.83 133.49 133.31 133.15 129.90 129.76 129.06 127.85 127.64 127.21 125.51 125.44 121.59
77.33 77.12 77.12 76.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1l

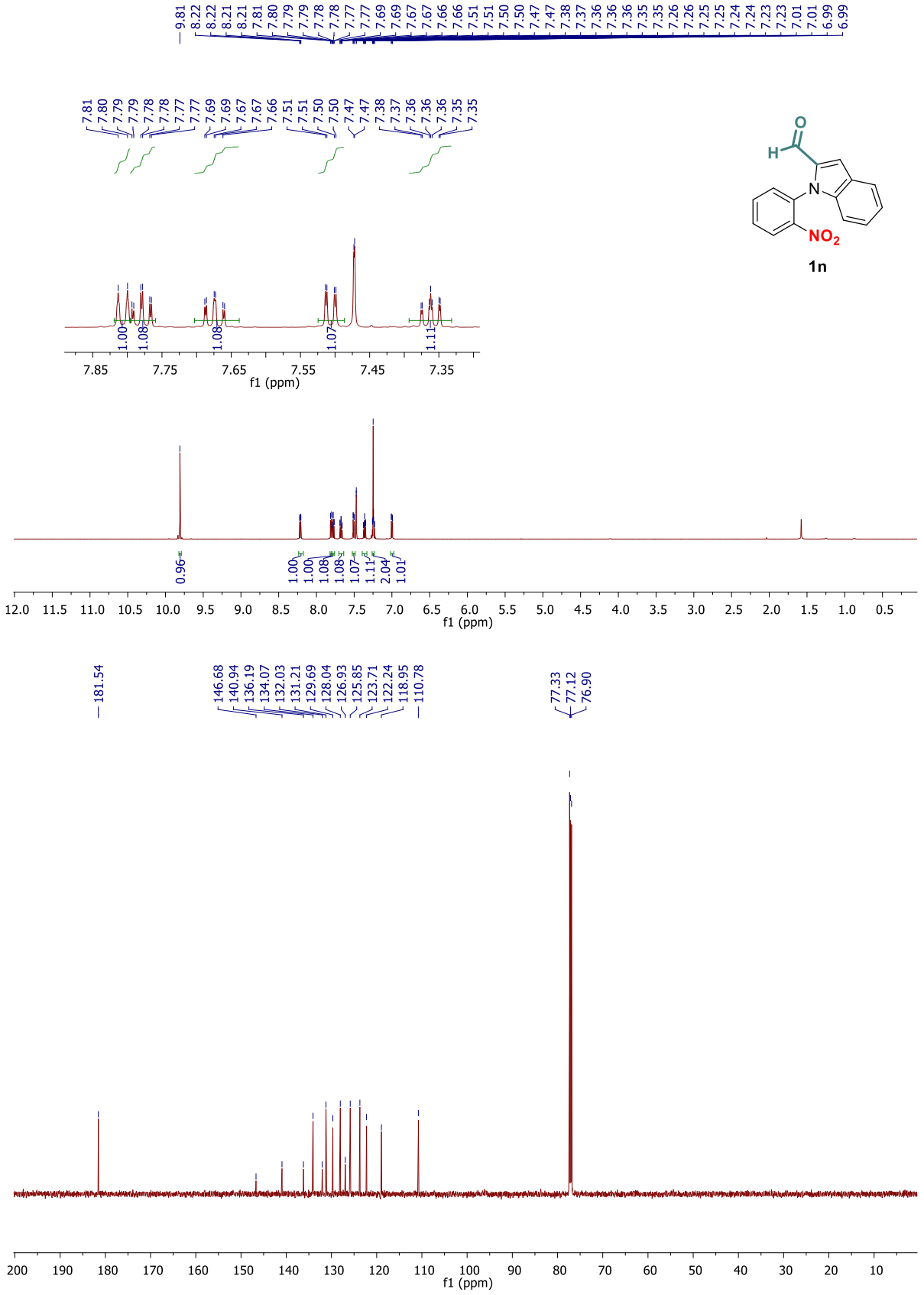

9.46
9.46
8.73
8.73
8.50
8.50
8.49
7.59
7.59
7.58
7.25
6.53
6.52
6.52
7.59
7.59
7.58
7.57
7.34
7.34
7.33
7.33
7.33
7.25
7.17
7.17
7.16
7.16
1.07
1.01
1.03
7.60
7.50
7.40
7.30
7.20
7.10
f1 (ppm)
O
H
N
N
NO2
1l
1.04
1.00
1.01
1.07
1.01
1.03
1.03
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


179.08
152.18
144.65
141.83
134.16
131.98
130.84
126.57
124.33
112.15
77.33
77.12
76.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

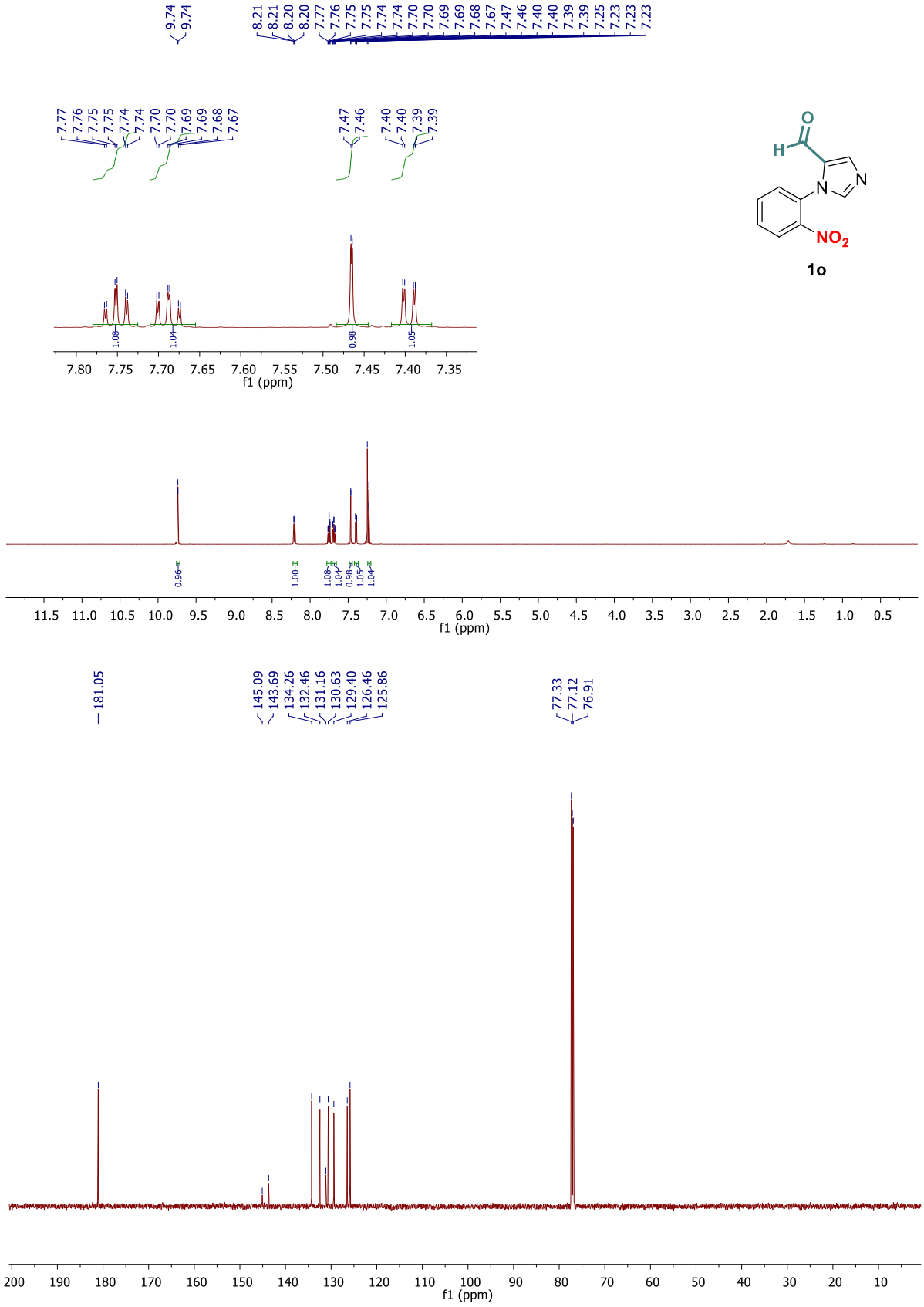
1m


9.40
9.40
8.73
8.72
8.72
8.51
8.50
7.63
7.62
7.62
7.62
7.61
7.61
7.60
7.60
7.31
7.31
7.31
7.25
7.13
7.12
7.12
1.06
0.93
1.01
f1 (ppm)
O
H
N
N
Br
NO2
1m
0.93
1.00
1.02
1.06
0.93
1.01
f1 (ppm)
178.56
152.34
143.62
141.65
134.34
131.96
129.95
126.94
124.86
100.08
77.34
77.13
76.92
f1 (ppm)

1n


9.81
8.22
8.22
8.21
8.21
7.81
7.80
7.79
7.79
7.78
7.77
7.77
7.69
7.67
7.67
7.66
7.66
7.51
7.51
7.50
7.50
7.47
7.47
7.38
7.37
7.36
7.36
7.35
7.35
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.01
7.01
6.99
6.99
7.81
7.80
7.79
7.79
7.78
7.78
7.77
7.77
7.69
7.69
7.67
7.67
7.66
7.51
7.51
7.50
7.50
7.47
7.47
7.38
7.37
7.36
7.36
7.35
7.35
1.00
1.08
1.08
1.07
1.11
7.85
7.75
7.65
7.55
7.45
7.35
f1 (ppm)
O
H
N
NO2
1n
0.96
1.00
1.00
1.08
1.08
1.07
1.11
2.04
1.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
181.54
146.68
140.94
136.19
134.07
132.03
131.21
129.69
128.04
126.93
125.85
123.71
122.24
118.95
110.78
77.33
77.12
76.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

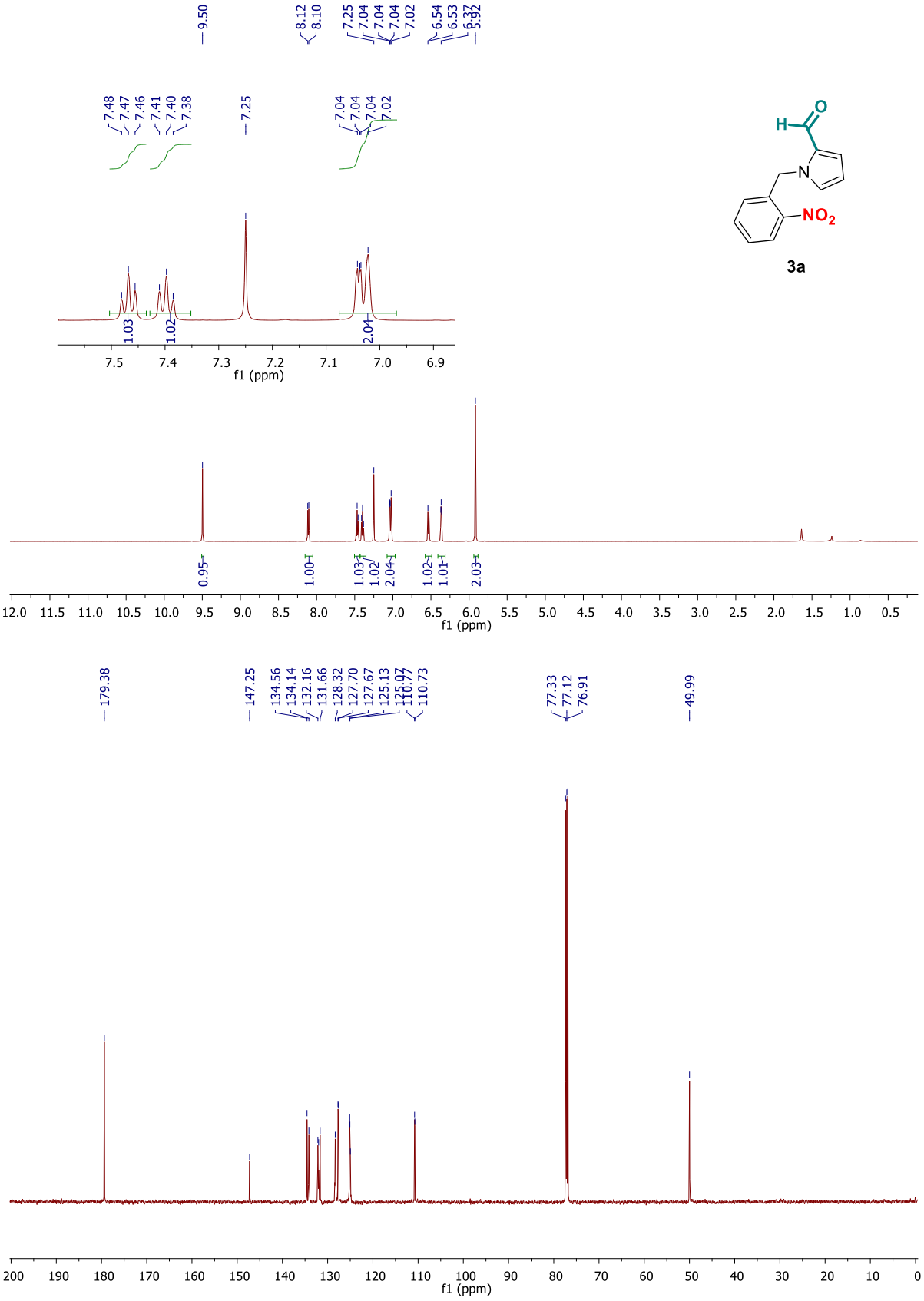
1o


9.74
9.74
8.21
8.21
8.20
8.20
7.77
7.76
7.76
7.75
7.75
7.74
7.74
7.70
7.70
7.69
7.69
7.68
7.67
7.47
7.46
7.40
7.40
7.39
7.39
7.25
7.23
7.23
1.08
1.04
0.98
1.05
7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
0.96
1.00
1.08
1.04
0.98
1.05
1.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
181.05
145.09
143.69
134.26
132.46
131.16
130.63
129.40
126.46
125.86
77.33
77.12
76.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

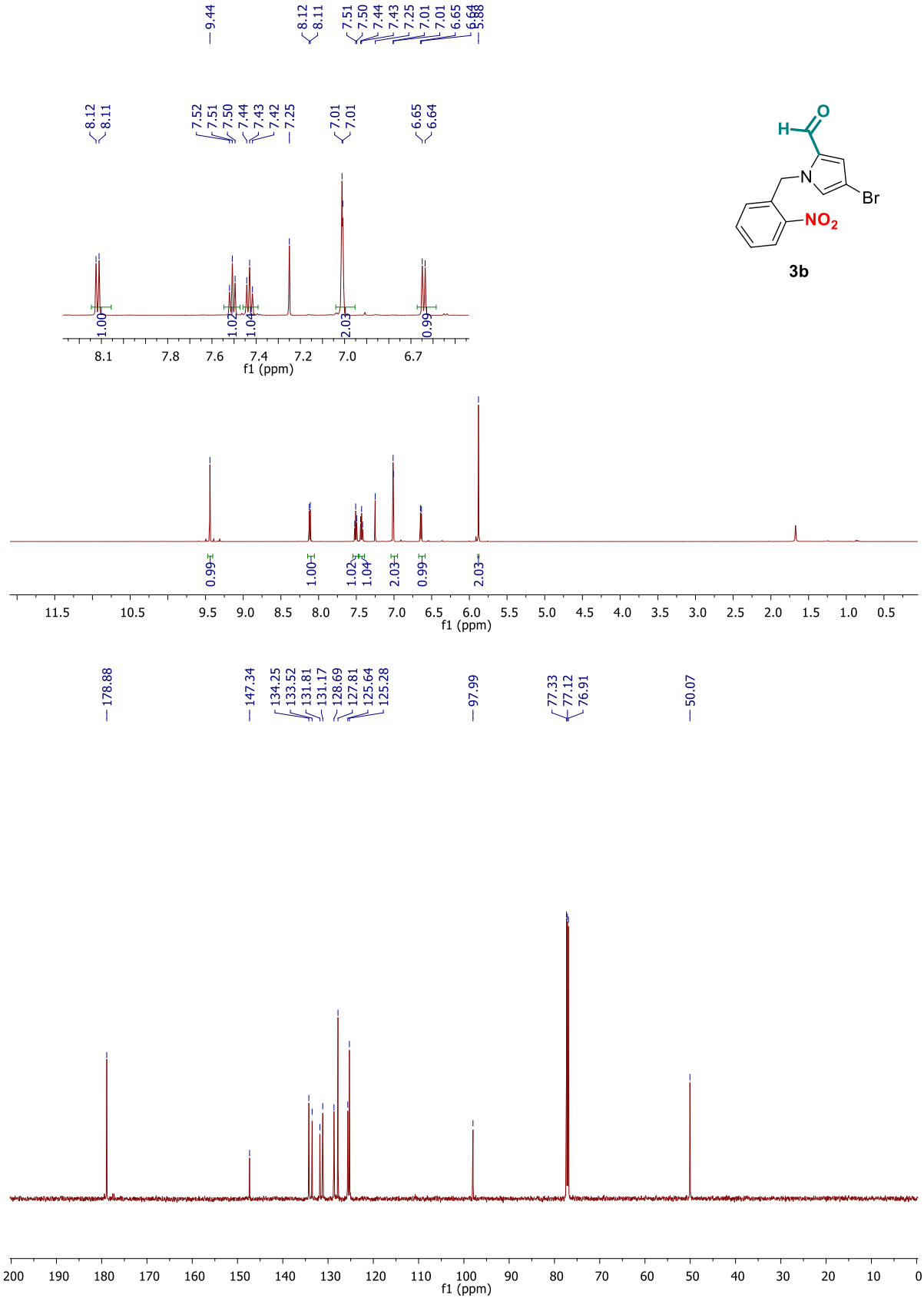
O
H
N
N
NO2

1o

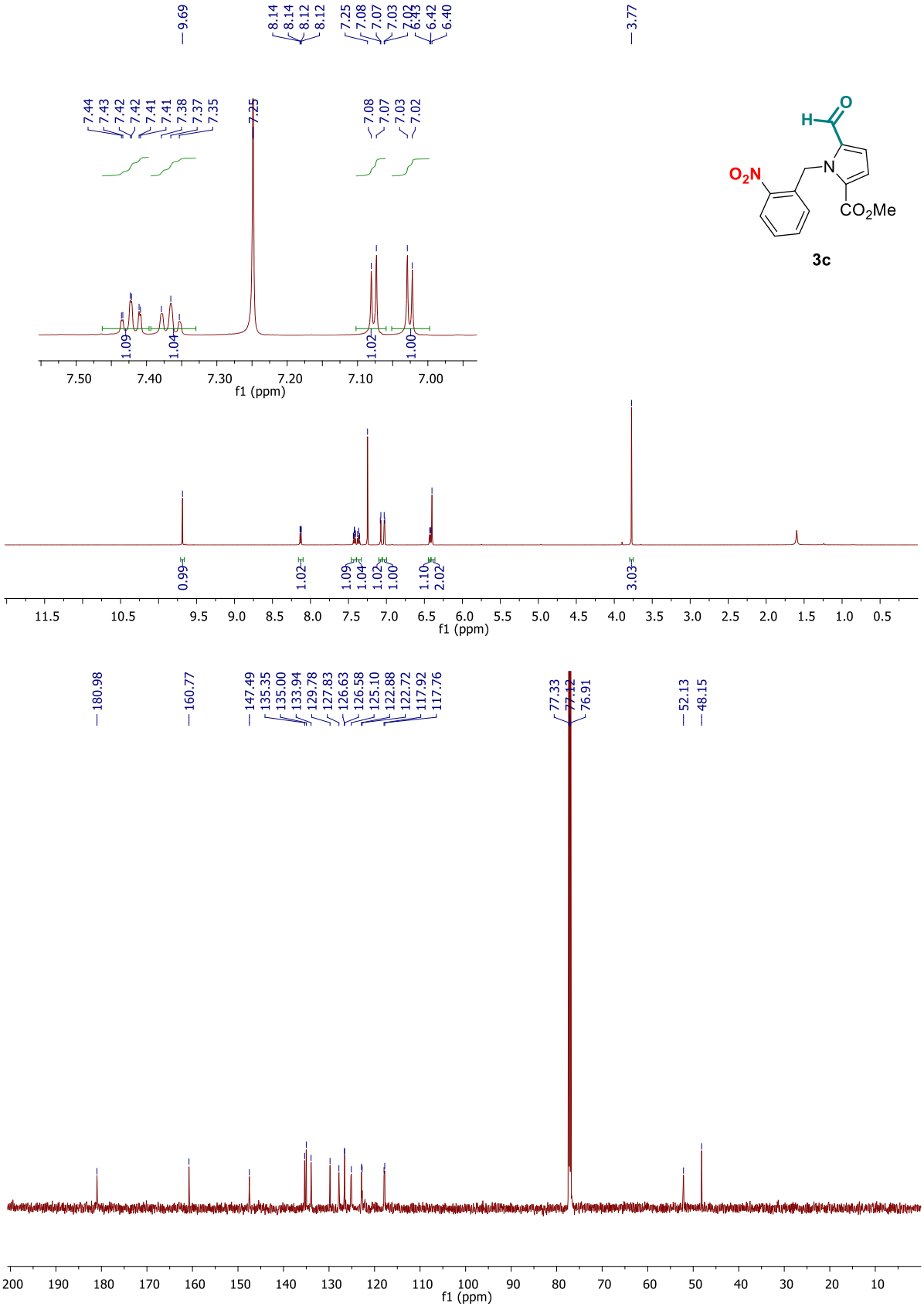
3a


9.50
8.12
8.10
7.25
7.04
7.04
7.04
7.02
6.54
6.53
6.37
5.32
7.48
7.47
7.46
7.41
7.40
7.38
7.25
7.04
7.04
7.04
7.02
1.03
1.02
2.04
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
O
H
N
NO2
3a
0.95
1.00
1.03
1.02
2.04
1.02
1.01
2.03
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
179.38
147.25
134.56
134.14
132.16
131.66
128.32
127.70
127.67
125.13
125.07
110.77
110.73
77.33
77.12
76.91
49.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

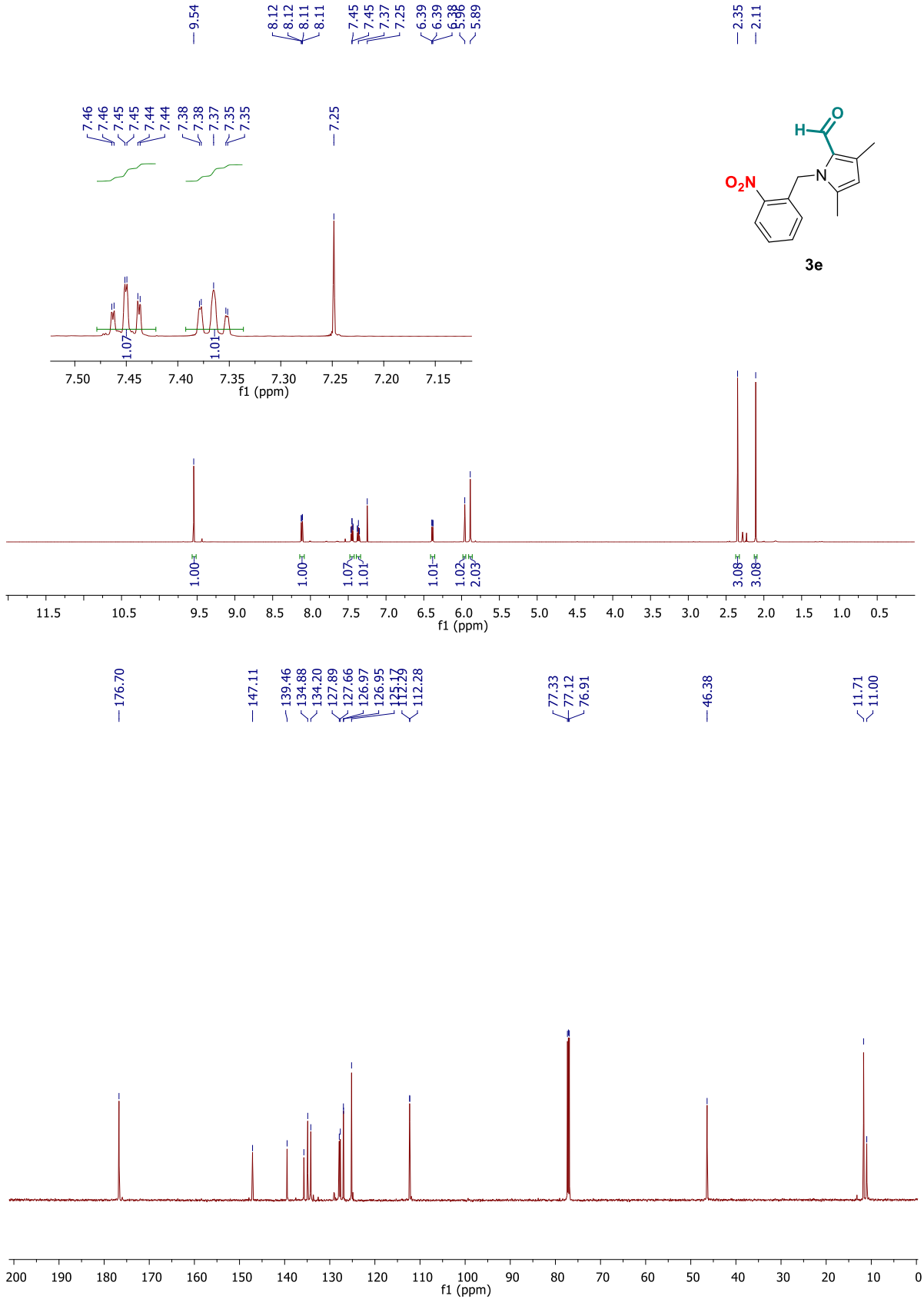
3b


9.44
8.12
8.11
7.51
7.50
7.44
7.43
7.25
7.01
7.01
6.65
6.64
5.88
7.52
7.51
7.50
7.44
7.43
7.42
7.25
7.01
7.01
6.65
6.64
1.00
1.02
1.04
2.03
0.99
f1 (ppm)
O
H
N
Br
NO2
3b
0.99
1.00
1.02
1.04
2.03
0.99
2.03
f1 (ppm)
178.88
147.34
134.25
133.52
131.81
131.17
128.69
127.81
125.64
125.28
97.99
77.33
77.12
76.91
50.07
f1 (ppm)

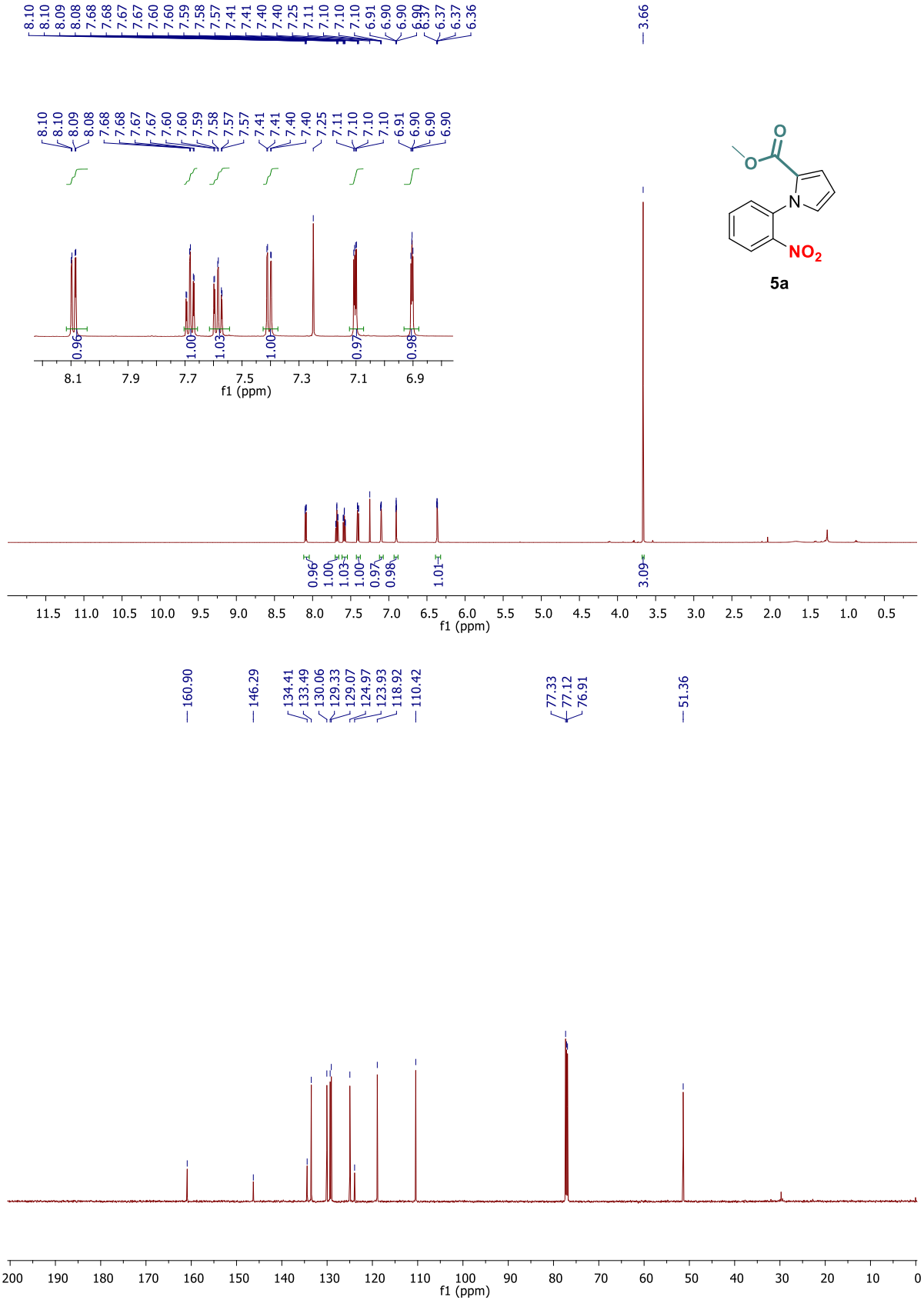
3c


9.69
8.14
8.14
8.12
8.12
7.25
7.08
7.07
7.03
7.02
6.43
6.42
6.40
3.77
7.44
7.43
7.42
7.42
7.41
7.41
7.38
7.37
7.35
7.25
7.08
7.07
7.03
7.02
1.09
1.04
1.02
1.00
7.50
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
O
H
N
O2N
CO2Me
3c
0.99
1.02
1.09
1.04
1.02
1.00
1.10
2.02
3.03
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
180.98
160.77
147.49
135.35
135.00
133.94
129.78
127.83
126.63
126.58
125.10
122.88
122.72
117.92
117.76
77.33
77.12
76.91
52.13
48.15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

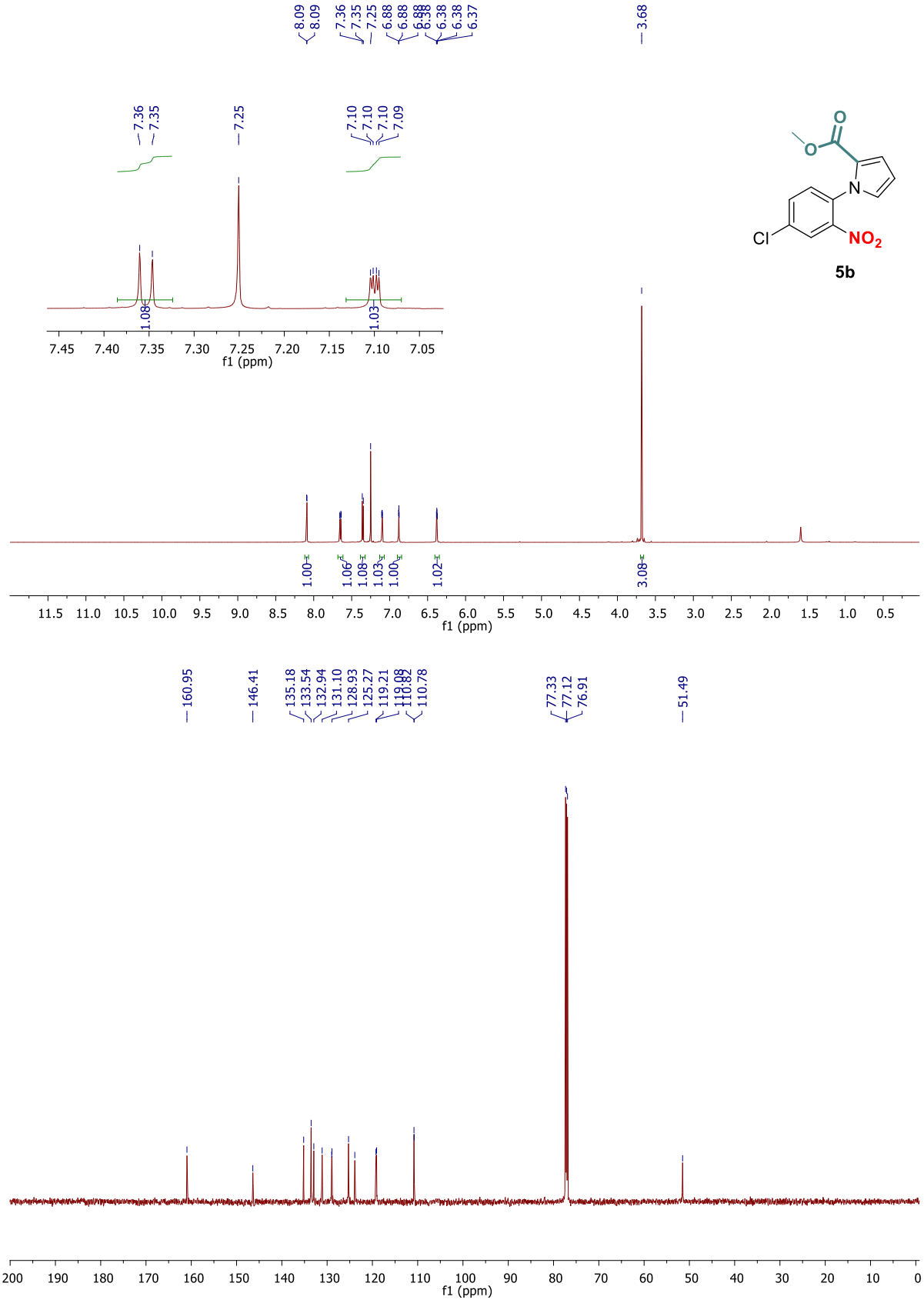
3e


9.54
8.12
8.12
8.11
8.11
7.46
7.46
7.45
7.45
7.44
7.44
7.38
7.38
7.37
7.35
7.35
7.25
6.39
6.39
5.89
2.35
2.11
1.07
1.01
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
f1 (ppm)
O
H
O2N
N
3e
1.00
1.00
1.07
1.01
1.01
1.02
2.03
3.08
3.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
176.70
147.11
139.46
134.88
134.20
127.89
127.66
126.97
126.95
125.17
125.12
112.28
77.33
77.12
76.91
46.38
11.71
11.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

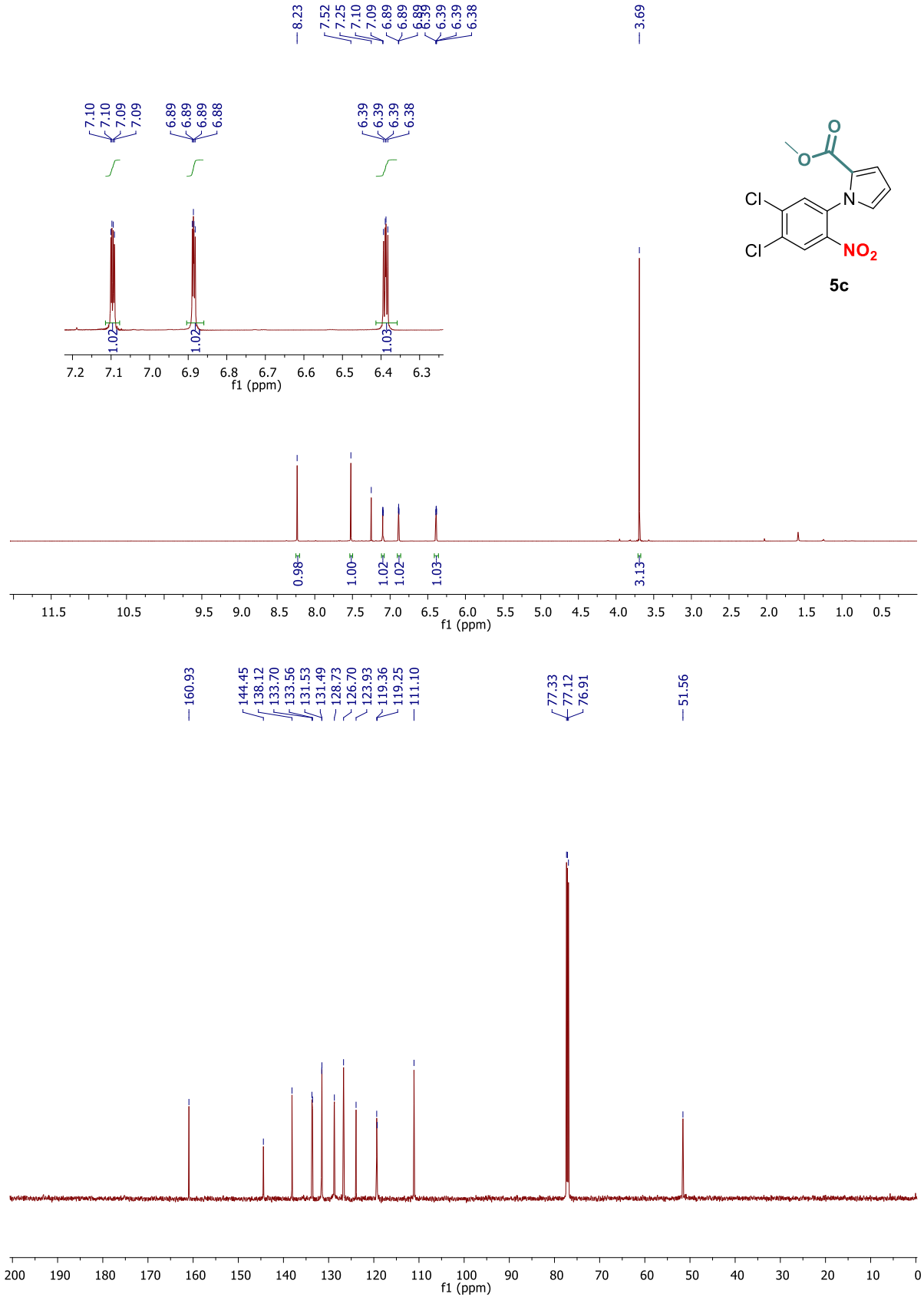
5a


8.10
8.10
8.09
8.08
8.08
7.68
7.68
7.67
7.67
7.60
7.60
7.59
7.58
7.57
7.41
7.41
7.40
7.40
7.25
7.11
7.10
7.10
7.10
6.91
6.90
6.90
6.90
6.37
6.37
6.36
3.66
0.96
1.00
1.03
1.00
0.97
0.98
f1 (ppm)
0.96
1.00
1.03
1.00
0.97
0.98
1.01
3.09
f1 (ppm)
O
O
N
NO2
5a
160.90
146.29
134.41
133.49
130.06
129.33
129.07
124.97
123.93
118.92
110.42
77.33
77.12
76.91
51.36
f1 (ppm)

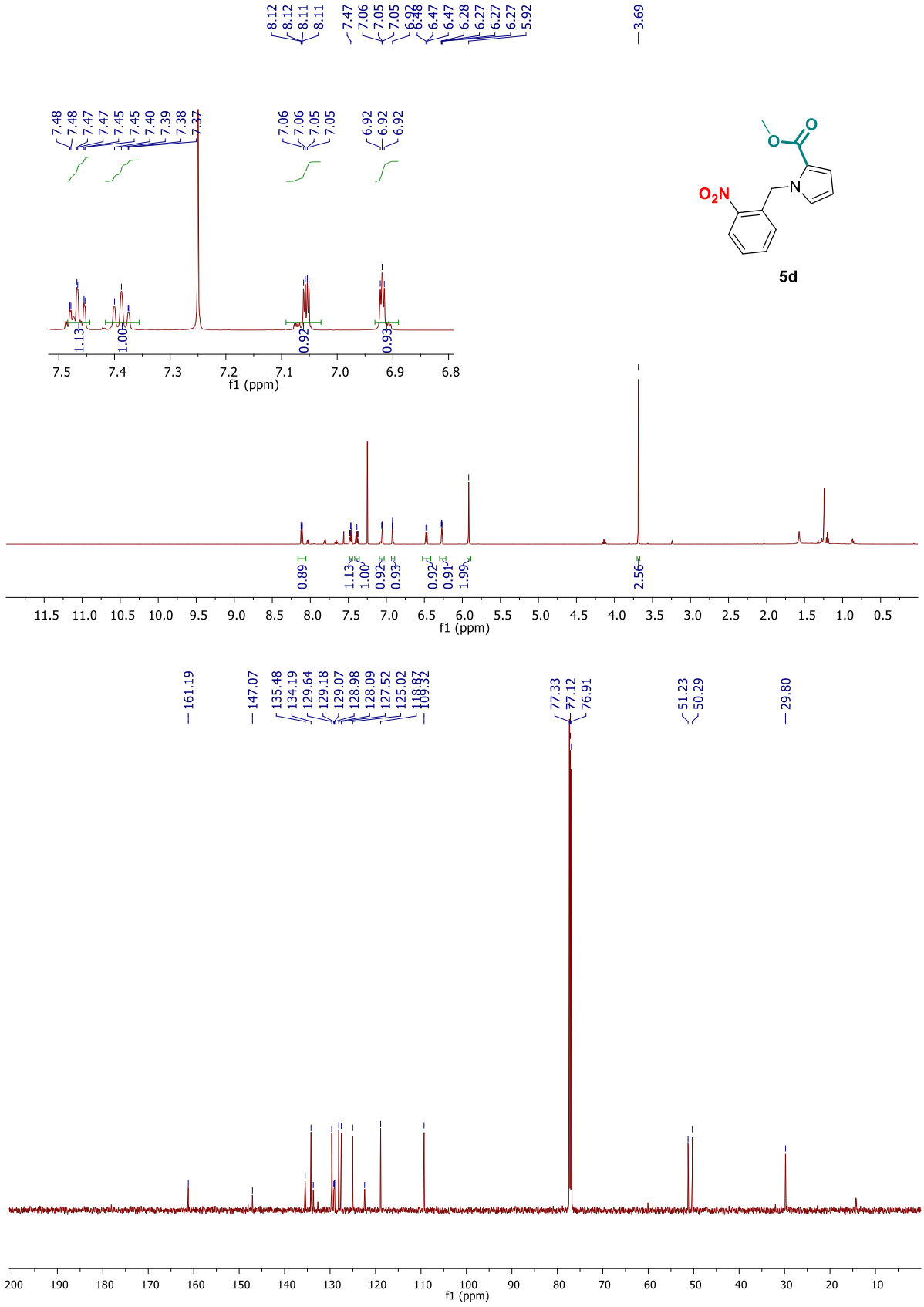
5b


8.09
8.09
7.36
7.35
7.25
6.88
6.88
6.38
6.38
6.37
3.68
7.36
7.35
7.25
7.10
7.10
7.10
7.09
1.08
1.03
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)
O
O
N
Cl
NO2
5b
1.00
1.06
1.08
1.03
1.00
1.02
3.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
160.95
146.41
135.18
133.54
132.94
131.10
128.93
125.27
119.21
110.78
77.33
77.12
76.91
51.49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

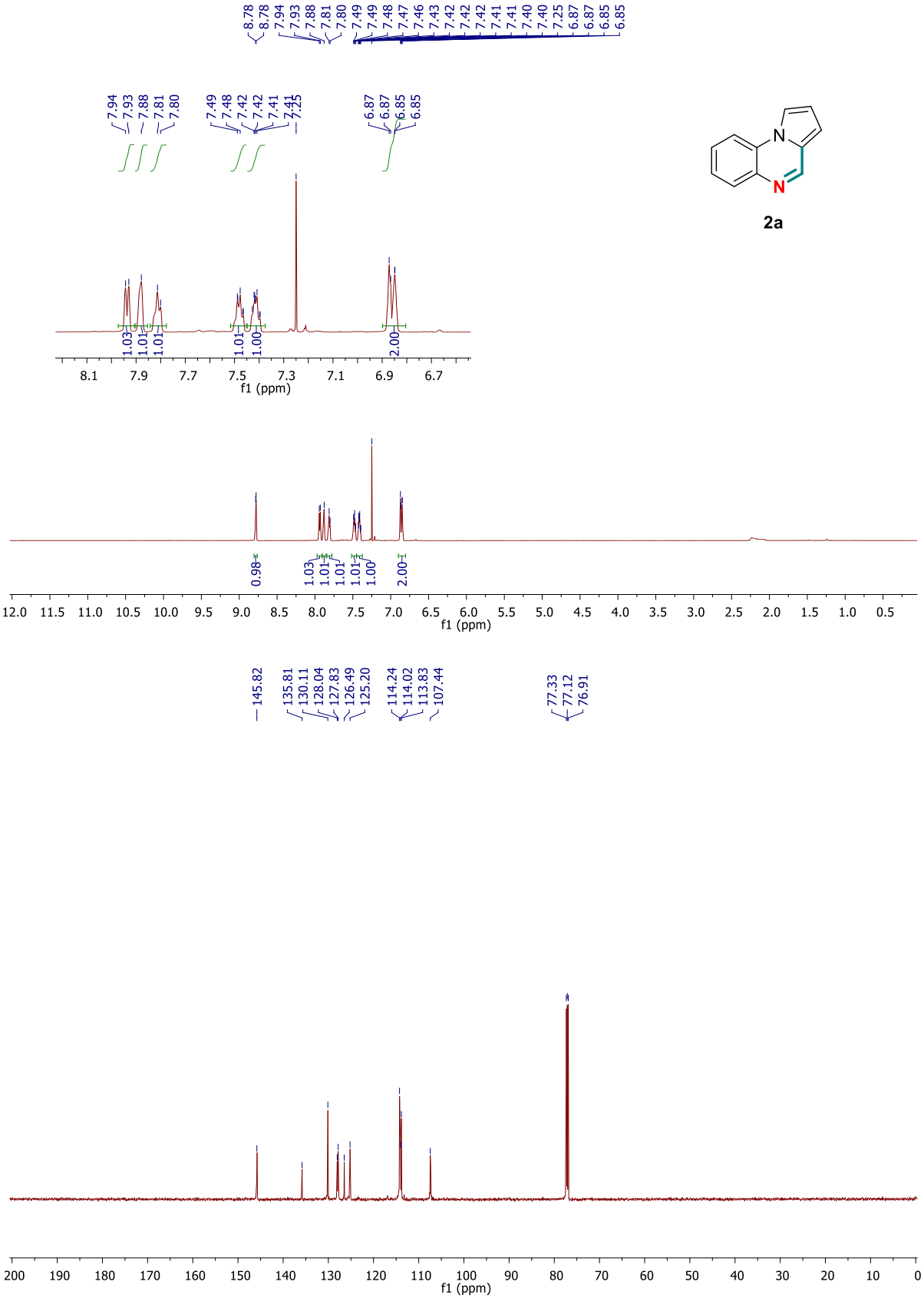
5c


8.23
7.52
7.25
7.10
7.09
6.89
6.89
6.39
6.39
6.38
3.69
7.10
7.10
7.09
7.09
6.89
6.89
6.89
6.88
6.39
6.39
6.39
6.38
1.02
1.02
1.03
7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f1 (ppm)
Cl
Cl
N
O
O
NO2
5c
0.98
1.00
1.02
1.02
1.03
3.13
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
160.93
144.45
138.12
133.70
133.56
131.53
131.49
128.73
126.70
123.93
119.36
119.25
111.10
77.33
77.12
76.91
51.56
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5d


8.12
8.12
8.11
8.11
7.47
7.06
7.05
7.05
6.92
6.92
6.47
6.47
6.28
6.27
6.27
6.27
5.92
3.69
7.48
7.48
7.47
7.47
7.45
7.45
7.40
7.39
7.38
7.37
7.06
7.06
7.05
7.05
6.92
6.92
6.92
1.13
1.00
0.92
0.93
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
O
O
N
O2N
5d
0.89
1.13
1.00
0.92
0.93
0.92
0.91
1.99
2.56
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
161.19
147.07
135.48
134.19
129.64
129.18
129.07
128.98
128.09
127.52
125.02
118.87
109.32
77.33
77.12
76.91
51.23
50.29
29.80
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

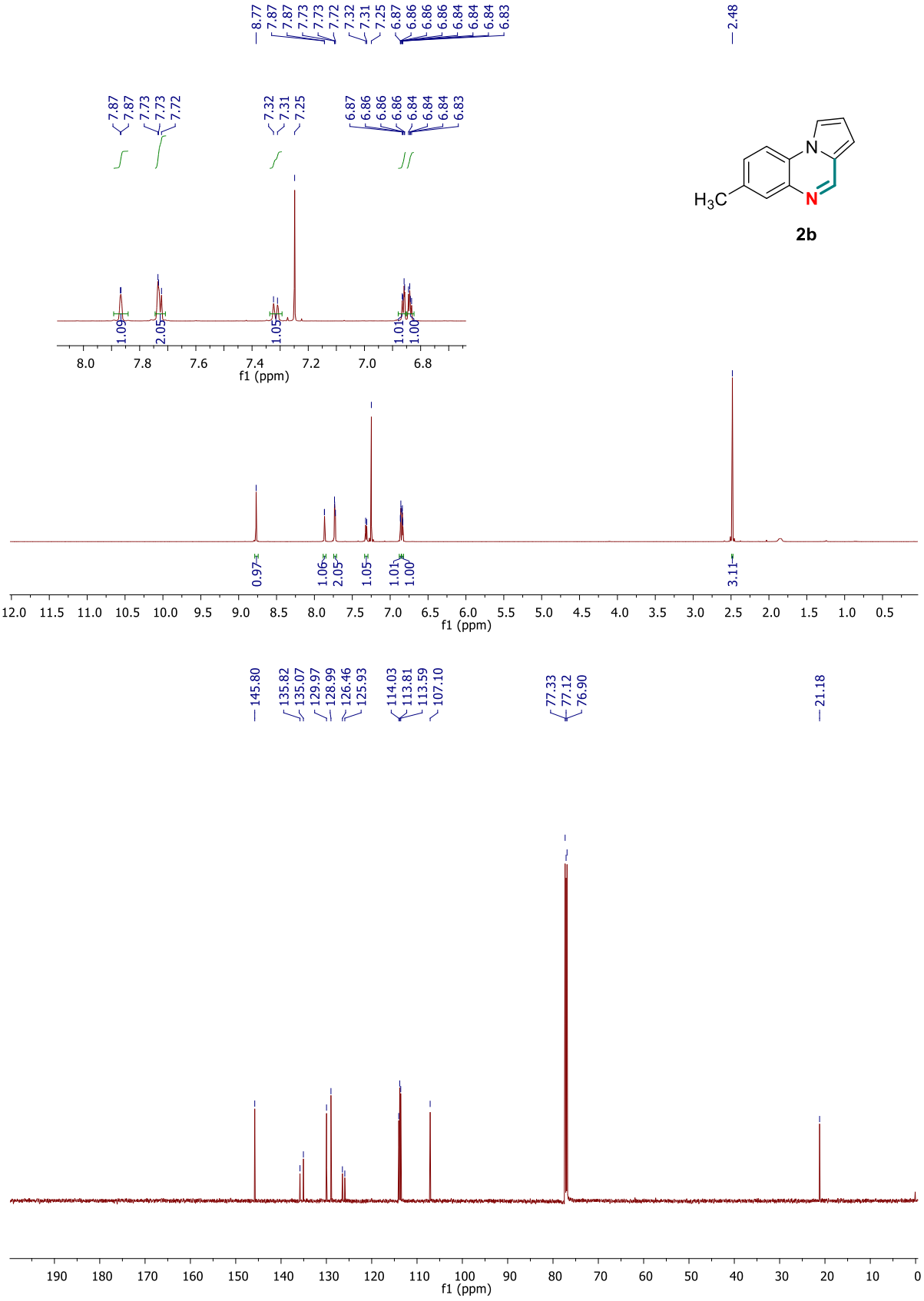
2a


8.78
8.78
7.94
7.93
7.88
7.81
7.80
7.49
7.48
7.47
7.46
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.25
6.87
6.85
6.85
1.03
1.01
1.01
1.01
1.00
2.00
f1 (ppm)
0.98
1.03
1.01
1.01
1.01
1.00
2.00
f1 (ppm)
145.82
135.81
130.11
128.04
127.83
126.49
125.20
114.24
114.02
113.83
107.44
77.33
77.12
76.91
f1 (ppm)

N
N

2a

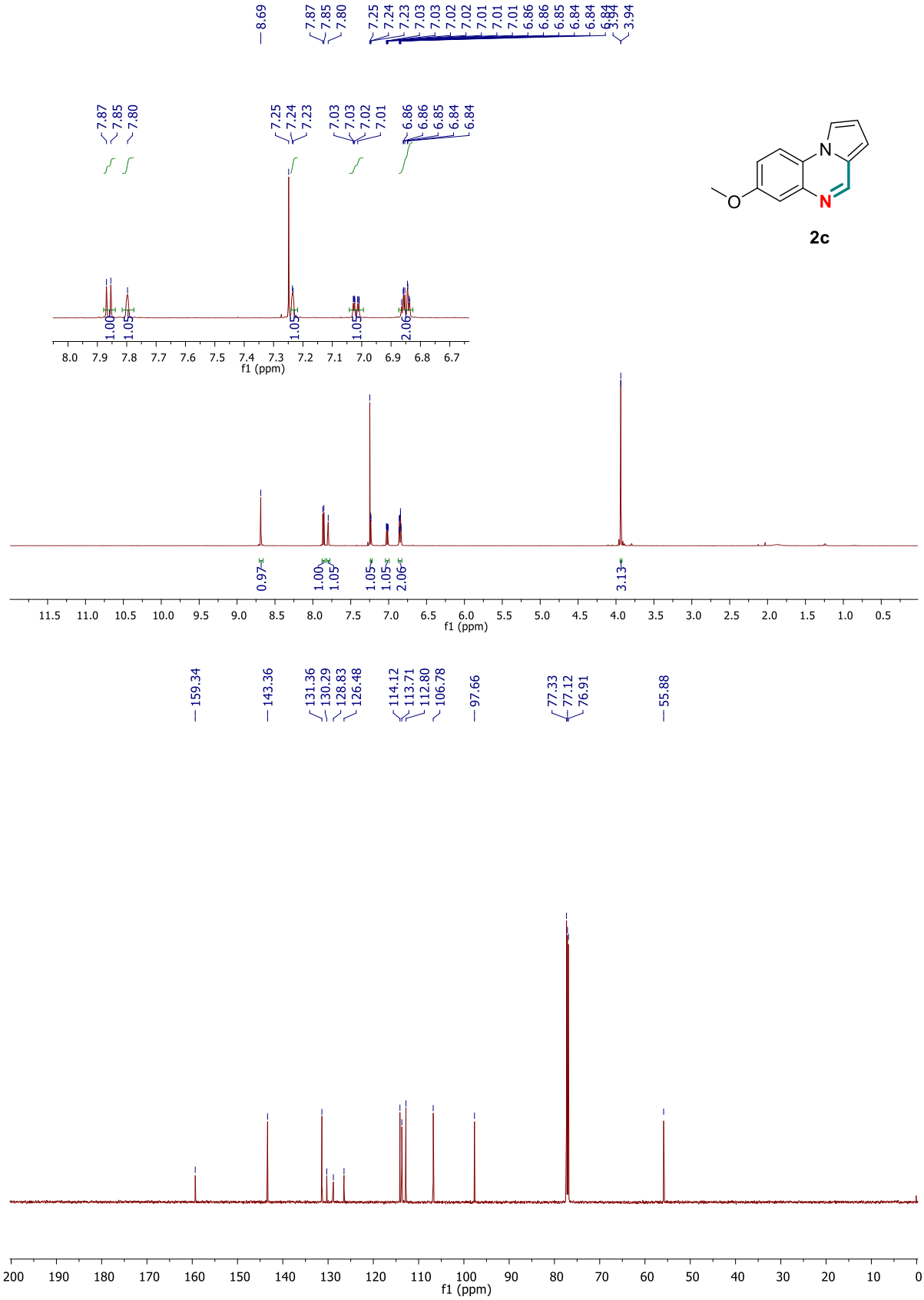
2b


8.77
7.87
7.87
7.73
7.73
7.72
7.32
7.31
7.25
6.87
6.86
6.86
6.84
6.84
6.84
6.83
2.48
1.09
2.05
1.05
1.01
1.00
f1 (ppm)
0.97
1.06
2.05
1.05
1.01
1.00
3.11
f1 (ppm)
145.80
135.82
135.07
129.97
128.99
126.46
125.93
114.03
113.81
113.59
107.10
77.33
77.12
76.90
21.18
f1 (ppm)

N
H3C
N

2b

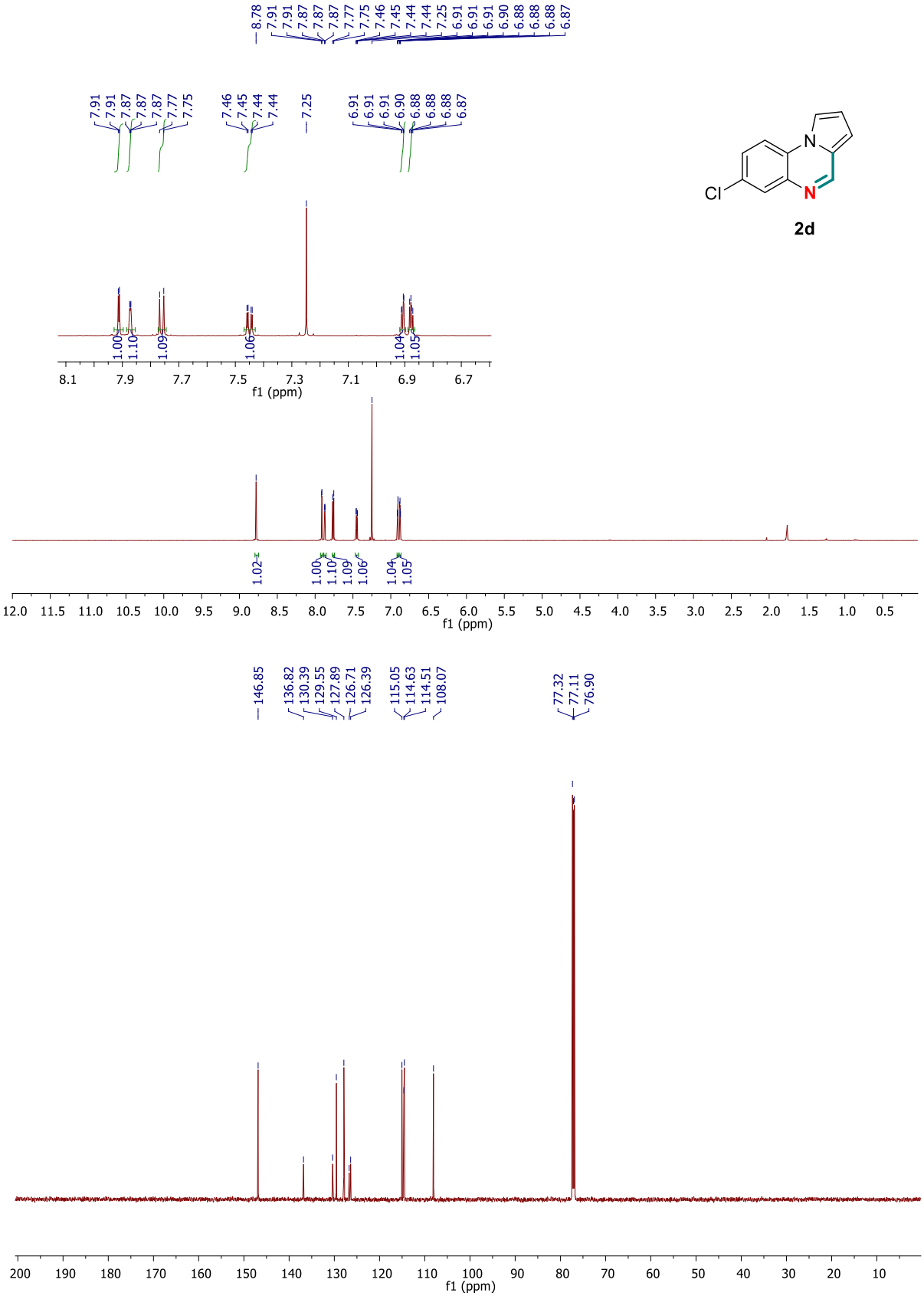
2c


8.69
7.87
7.85
7.80
7.25
7.24
7.23
7.03
7.03
7.02
7.02
7.01
7.01
7.01
6.86
6.86
6.85
6.84
6.84
3.94
1.00
1.05
1.05
1.05
2.06
f1 (ppm)
0.97
1.00
1.05
1.05
1.05
2.06
3.13
f1 (ppm)
159.34
143.36
131.36
130.29
128.83
126.48
114.12
113.71
112.80
106.78
97.66
77.33
77.12
76.91
55.88
f1 (ppm)

N
O
N

2c

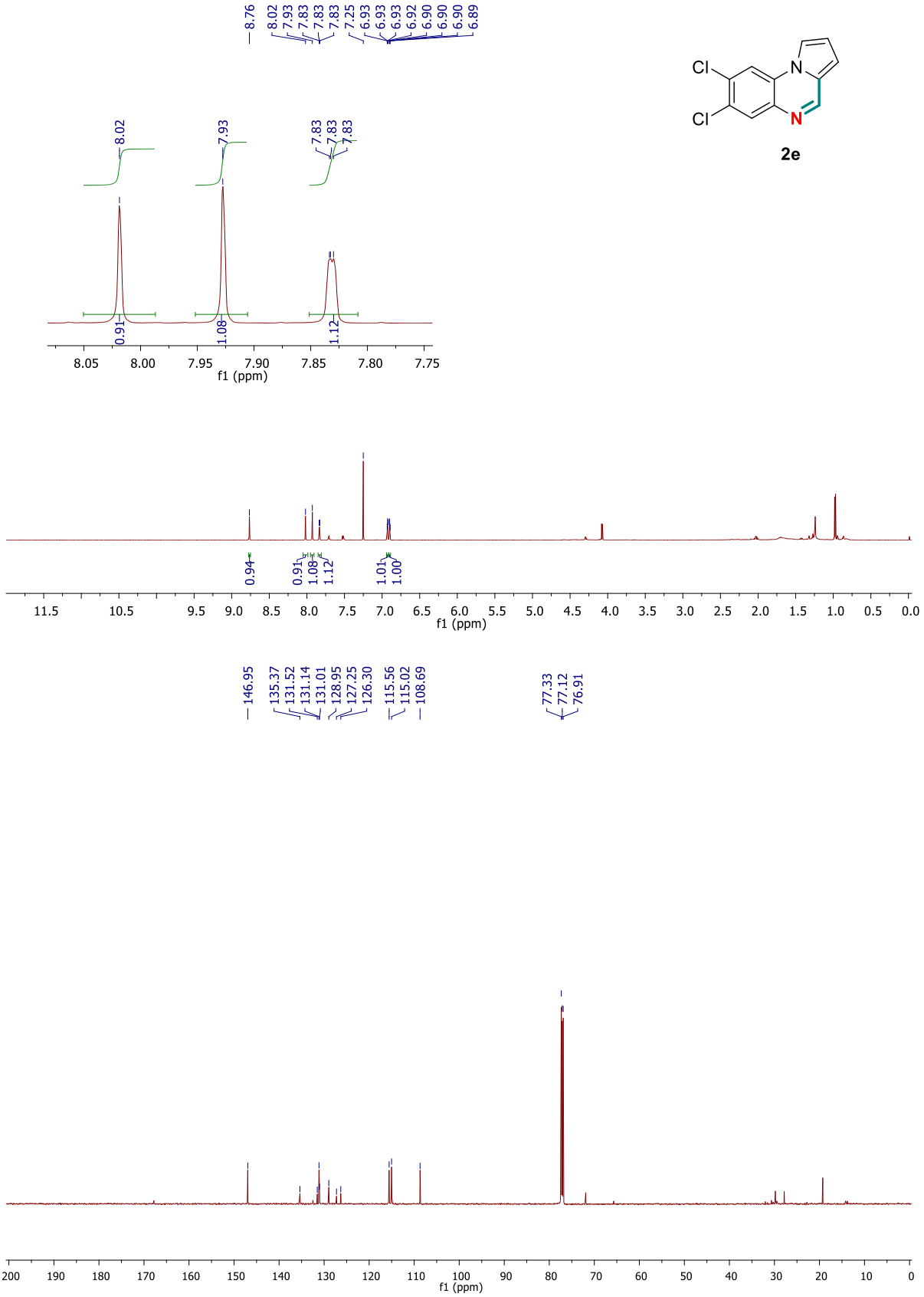
2d


8.78
7.91
7.91
7.87
7.87
7.87
7.77
7.75
7.46
7.45
7.44
7.44
7.25
6.91
6.91
6.91
6.90
6.88
6.88
6.88
6.87
1.00
1.10
1.09
1.06
1.04
1.05
f1 (ppm)
1.02
1.00
1.10
1.09
1.06
1.04
1.05
f1 (ppm)
146.85
136.82
130.39
129.55
127.89
126.71
126.39
115.05
114.63
114.51
108.07
77.32
77.11
76.90
f1 (ppm)

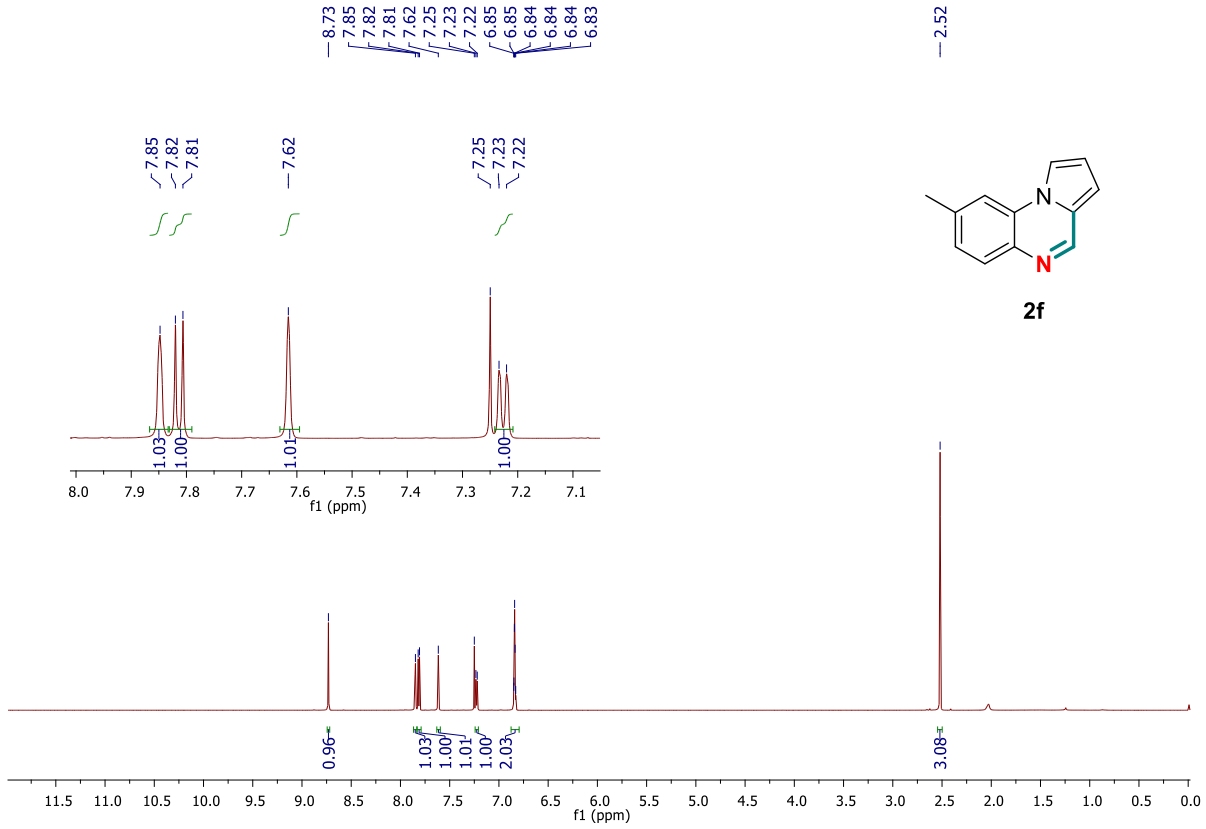
N
Cl
N

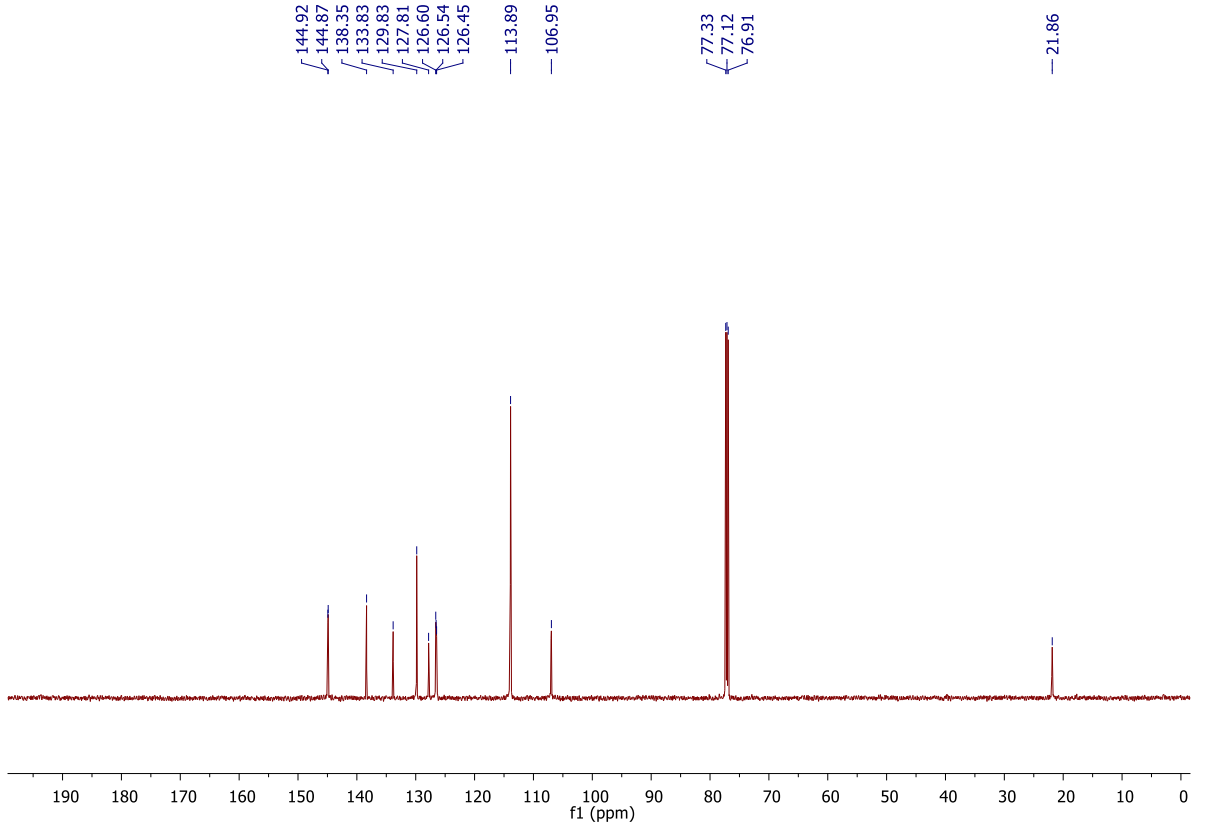
2d

2e

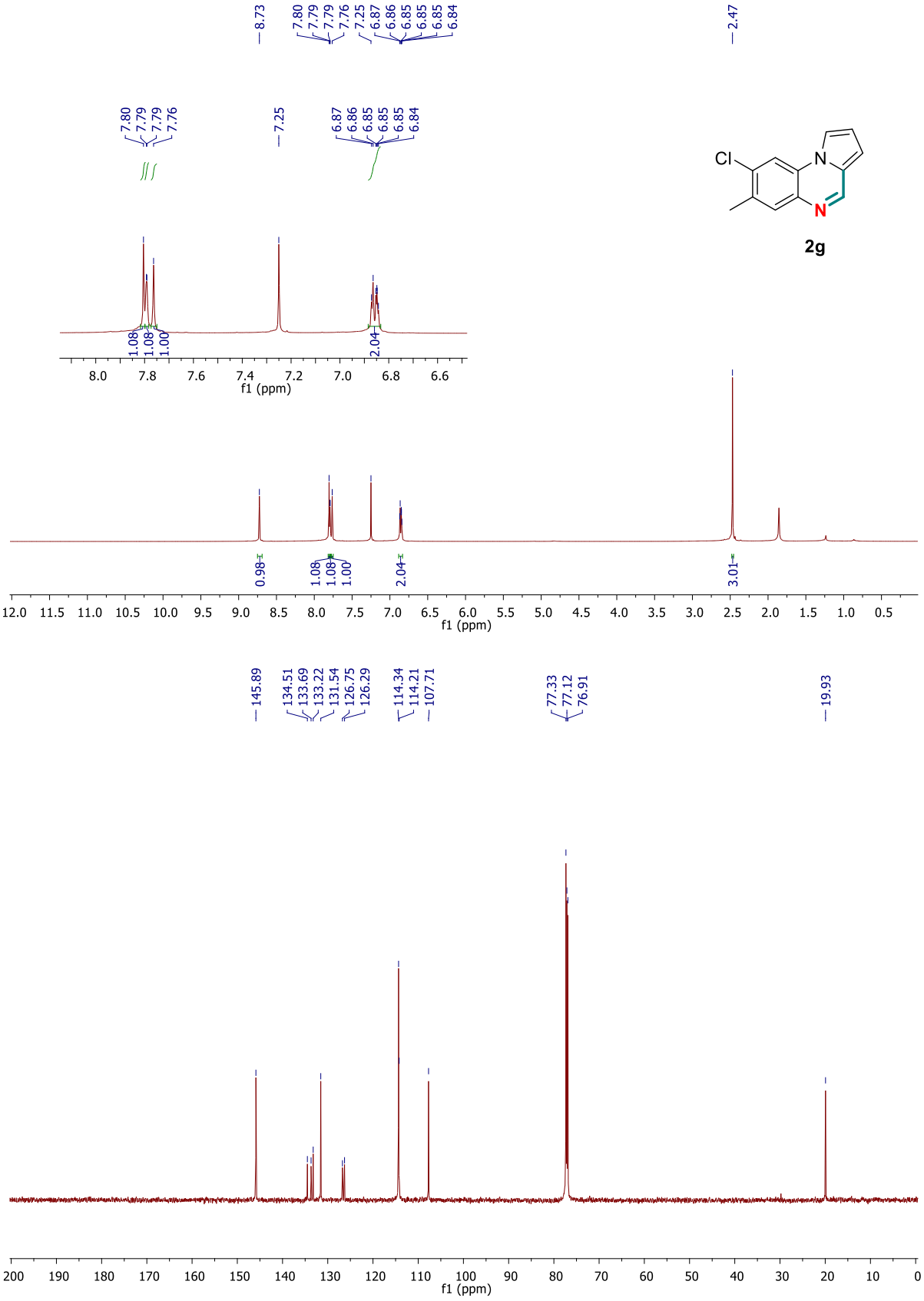

8.76
8.02
7.93
7.83
7.83
7.83
7.25
6.93
6.93
6.93
6.92
6.90
6.90
6.90
6.89
Cl
Cl
N
N
2e
8.02
7.93
7.83
7.83
7.83
0.91
1.08
1.12
8.05
8.00
7.95
7.90
7.85
7.80
7.75
f1 (ppm)
0.94
0.91
1.08
1.12
1.01
1.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
146.95
135.37
131.52
131.14
131.01
128.95
127.25
126.30
115.56
115.02
108.69
77.33
77.12
76.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2f

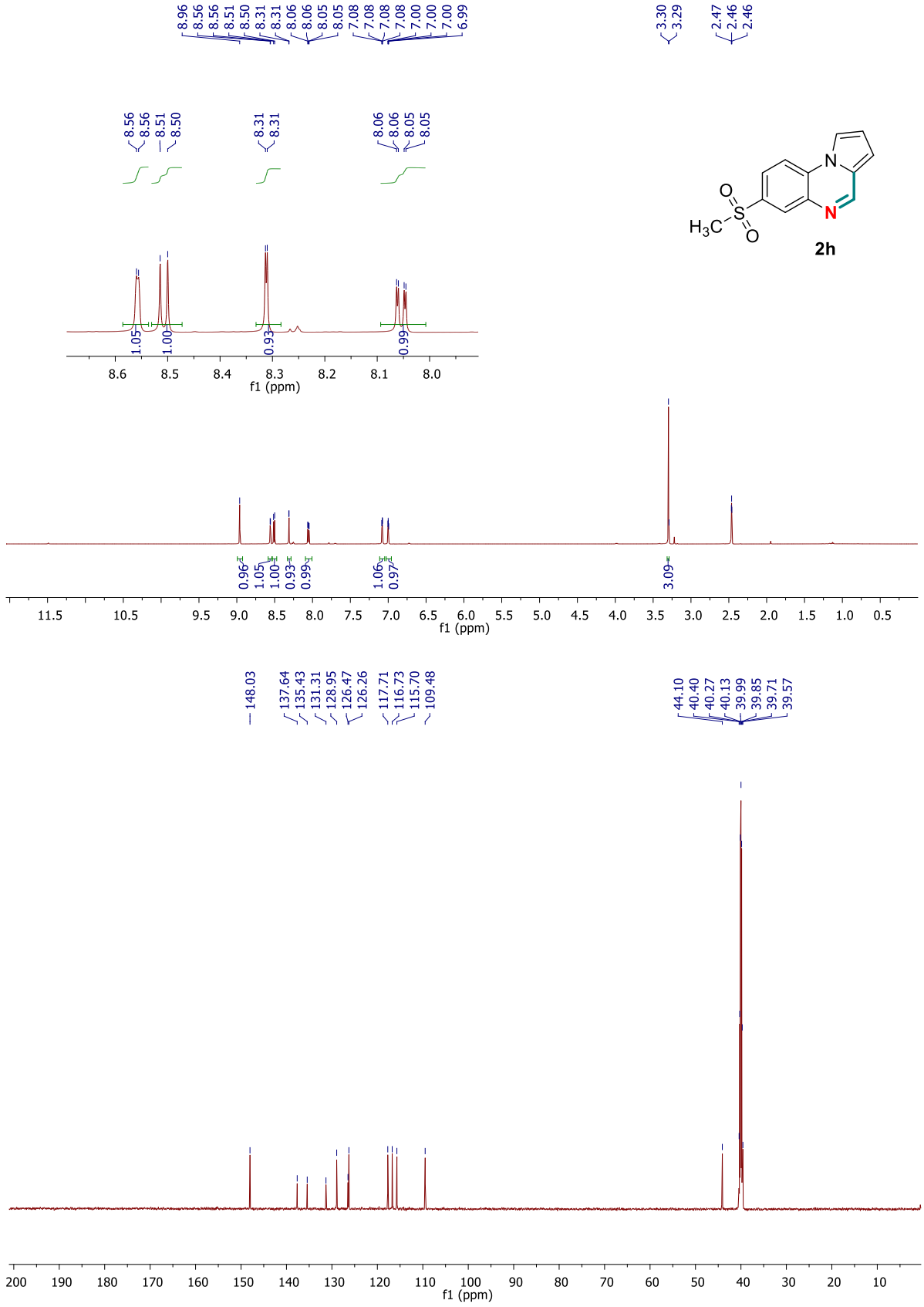

8.73
7.85
7.82
7.81
7.62
7.25
7.23
7.22
6.85
6.85
6.84
6.84
6.84
6.83
2.52
7.85
7.82
7.81
7.62
7.25
7.23
7.22
1.03
1.00
1.01
1.00
f1 (ppm)
2f
0.96
1.03
1.00
1.01
1.00
2.03
3.08
f1 (ppm)


144.92
144.87
138.35
133.83
129.83
127.81
126.60
126.54
126.45
113.89
106.95
77.33
77.12
76.91
21.86
f1 (ppm)

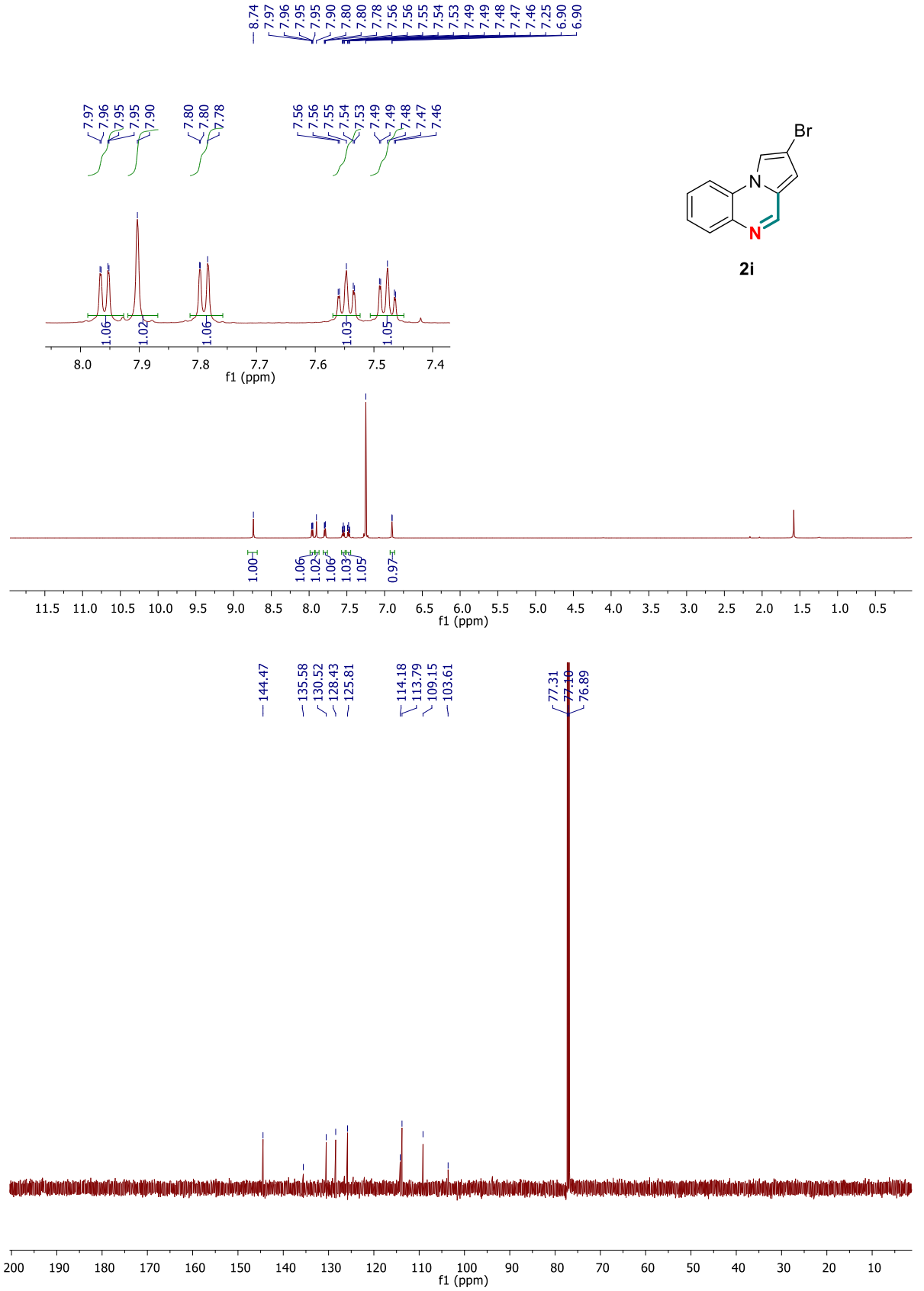
2g


8.73
7.80
7.79
7.79
7.76
7.25
6.87
6.86
6.85
6.85
6.85
6.84
2.47
Cl
N
N
2g
1.08
1.08
1.00
2.04
f1 (ppm)
0.98
1.08
1.08
1.00
2.04
3.01
f1 (ppm)
145.89
134.51
133.69
133.22
131.54
126.75
126.29
114.34
114.21
107.71
77.33
77.12
76.91
19.93
f1 (ppm)

2h


8.96
8.56
8.56
8.51
8.50
8.31
8.31
8.06
8.06
8.05
8.05
7.08
7.08
7.08
7.00
7.00
7.00
6.99
3.30
3.29
2.47
2.46
2.46
1.05
1.00
0.93
0.99
f1 (ppm)
2h
0.96
1.05
1.00
0.93
0.99
1.06
0.97
3.09
f1 (ppm)
148.03
137.64
135.43
131.31
128.95
126.47
126.26
117.71
116.73
115.70
109.48
44.10
40.40
40.27
40.13
39.99
39.85
39.71
39.57
f1 (ppm)

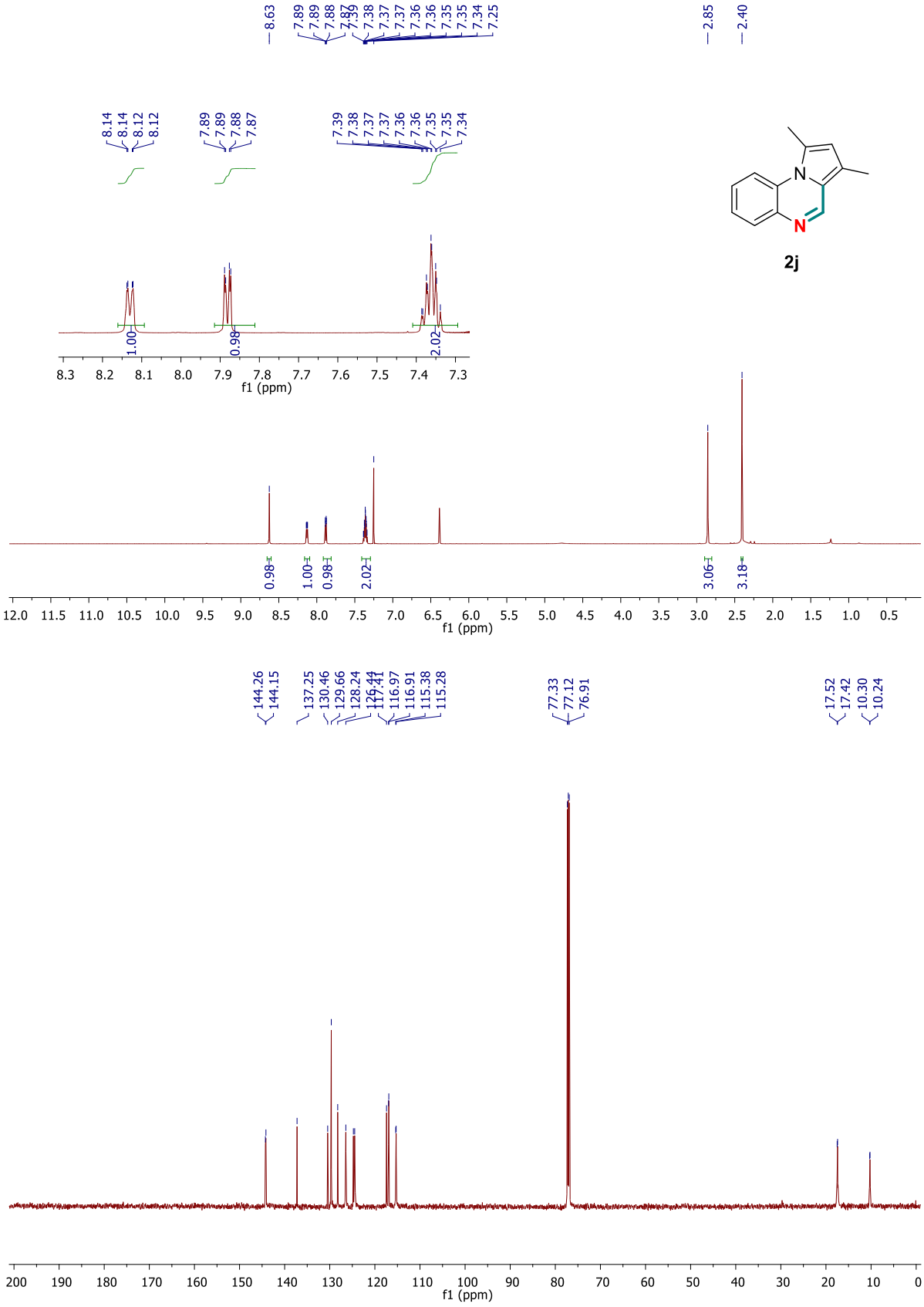
2i


8.74
7.97
7.96
7.95
7.95
7.90
7.80
7.80
7.78
7.56
7.56
7.55
7.54
7.53
7.49
7.49
7.48
7.47
7.46
7.25
6.90
6.90
1.06
1.02
1.06
1.03
1.05
f1 (ppm)
1.00
1.06
1.02
1.06
1.03
1.05
0.97
f1 (ppm)
144.47
135.58
130.52
128.43
125.81
114.18
113.79
109.15
103.61
77.31
77.10
76.89
f1 (ppm)

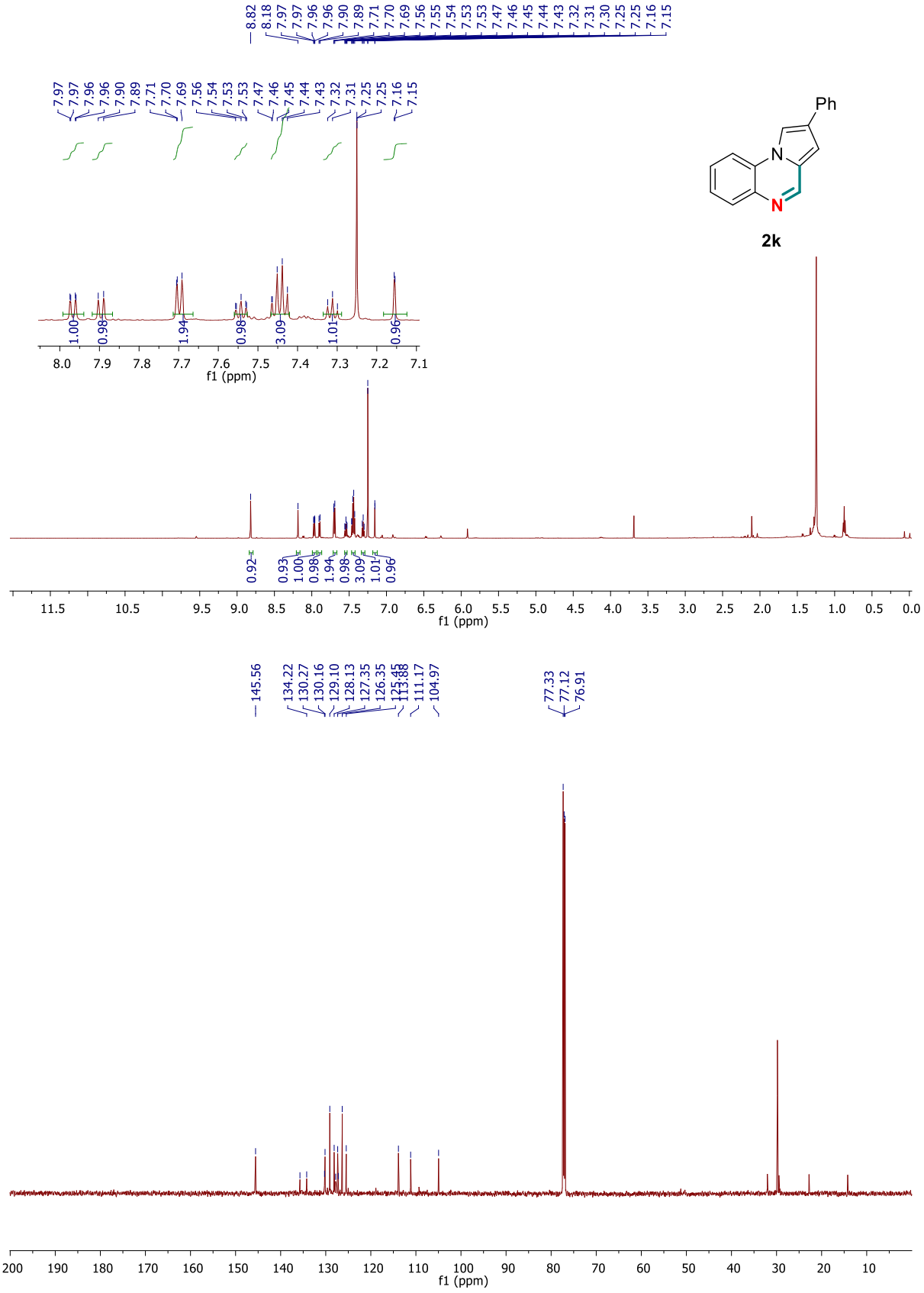
Br
N
N

2i

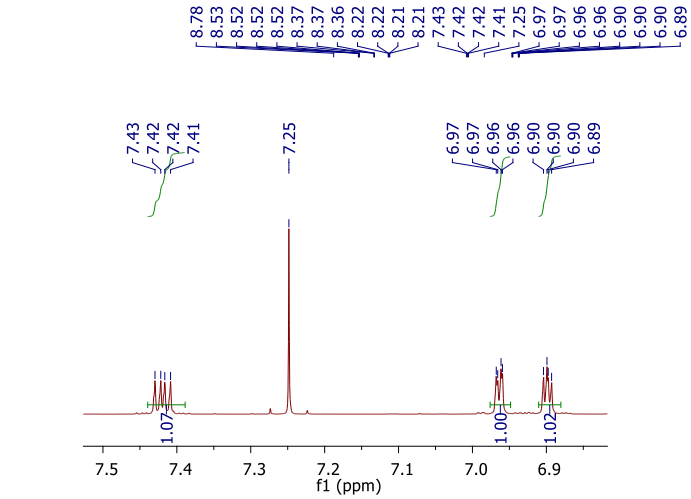
2j

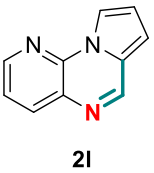

8.63
7.89
7.89
7.88
7.87
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.25
2.85
2.40
8.14
8.14
8.12
8.12
7.89
7.89
7.88
7.87
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
1.00
0.98
2.02
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
N
N
2j
0.98
1.00
0.98
2.02
3.06
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
144.26
144.15
137.25
130.46
129.66
128.24
116.97
116.91
115.38
115.28
77.33
77.12
76.91
17.52
17.42
10.30
10.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2k

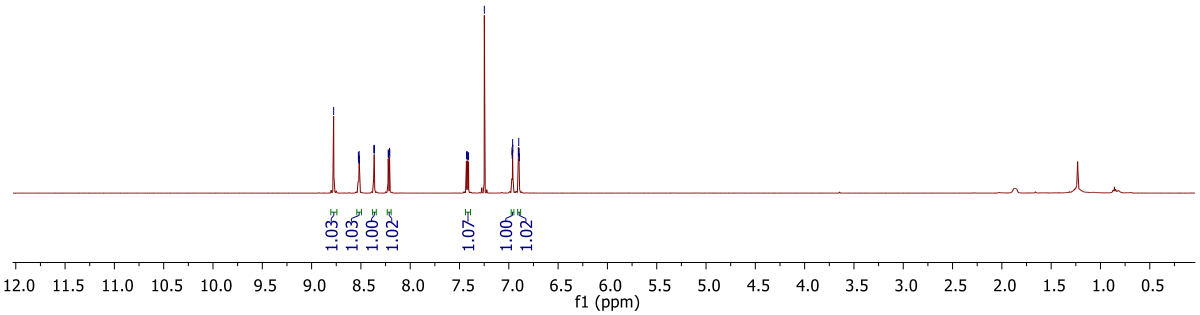

8.82
8.18
7.97
7.97
7.96
7.96
7.90
7.89
7.71
7.70
7.69
7.56
7.55
7.54
7.53
7.53
7.47
7.46
7.45
7.44
7.43
7.32
7.31
7.30
7.25
7.25
7.16
7.15
Ph
N
N
2k
1.00
0.98
1.94
0.98
3.09
1.01
0.96
f1 (ppm)
0.92
0.93
1.00
0.98
1.94
0.98
3.09
1.01
0.96
f1 (ppm)
145.56
134.22
130.27
130.16
129.10
128.13
127.35
126.35
125.45
113.88
111.17
104.97
77.33
77.12
76.91
f1 (ppm)

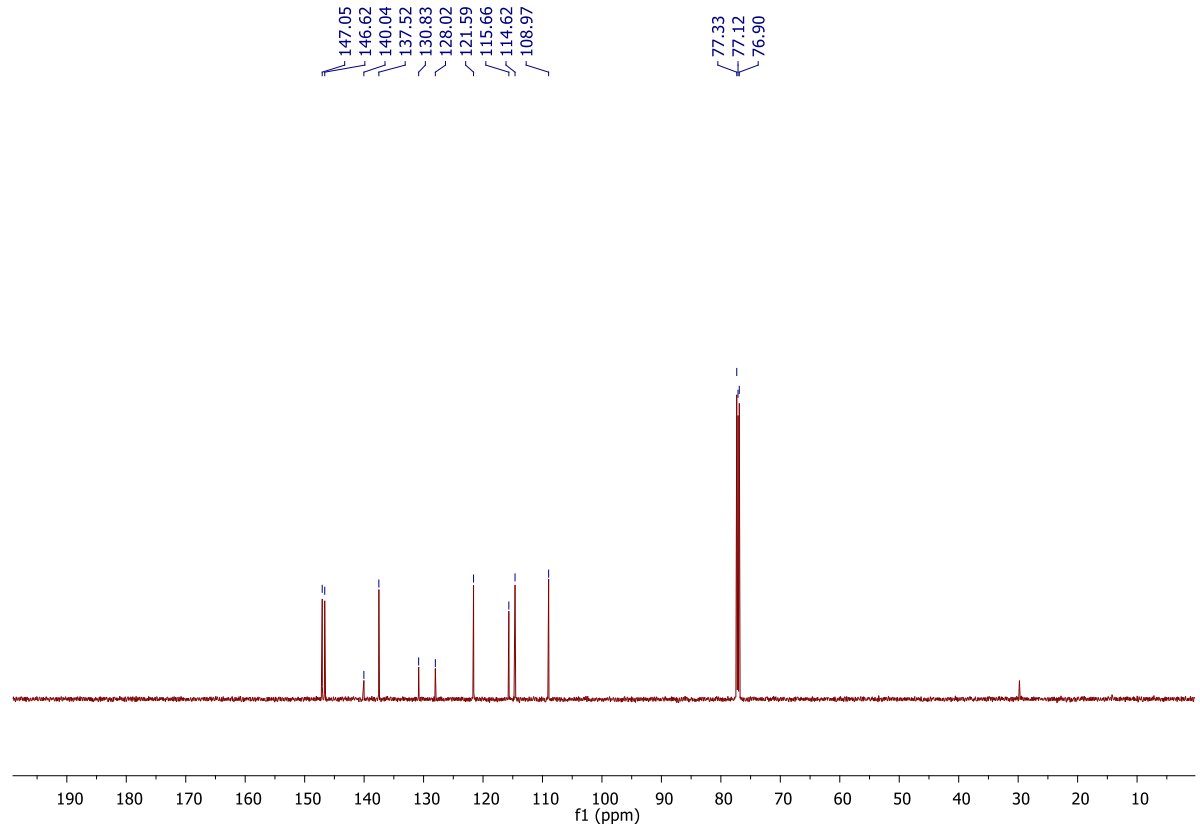
2l


8.78
8.53
8.52
8.52
8.52
8.37
8.37
8.36
8.22
8.22
8.21
8.21
7.43
7.42
7.42
7.41
7.25
6.97
6.97
6.96
6.96
6.90
6.90
6.90
6.89
7.43
7.42
7.42
7.41
7.25
6.97
6.97
6.96
6.96
6.90
6.90
6.90
6.89
1.07
1.00
1.02
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)

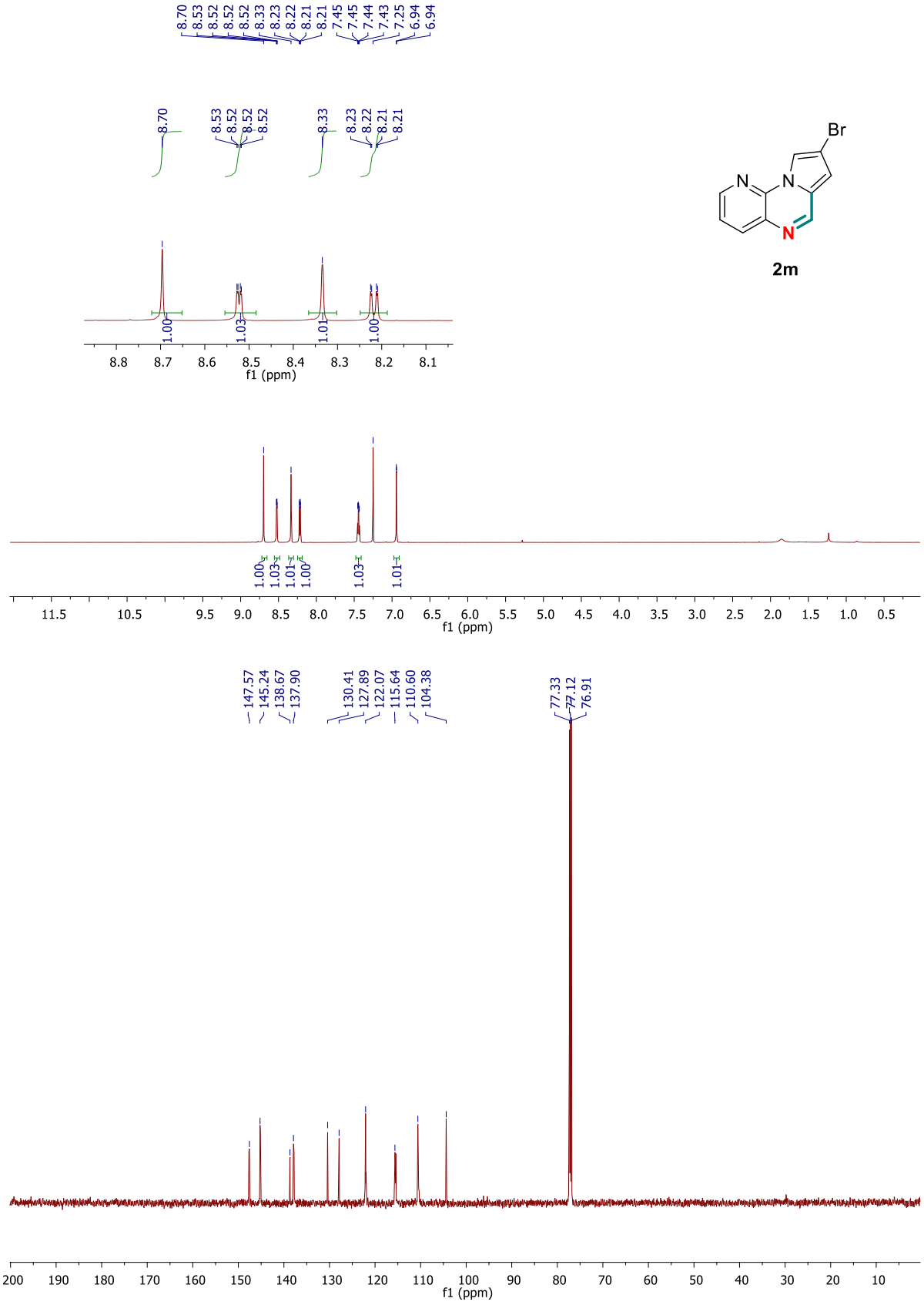


2l

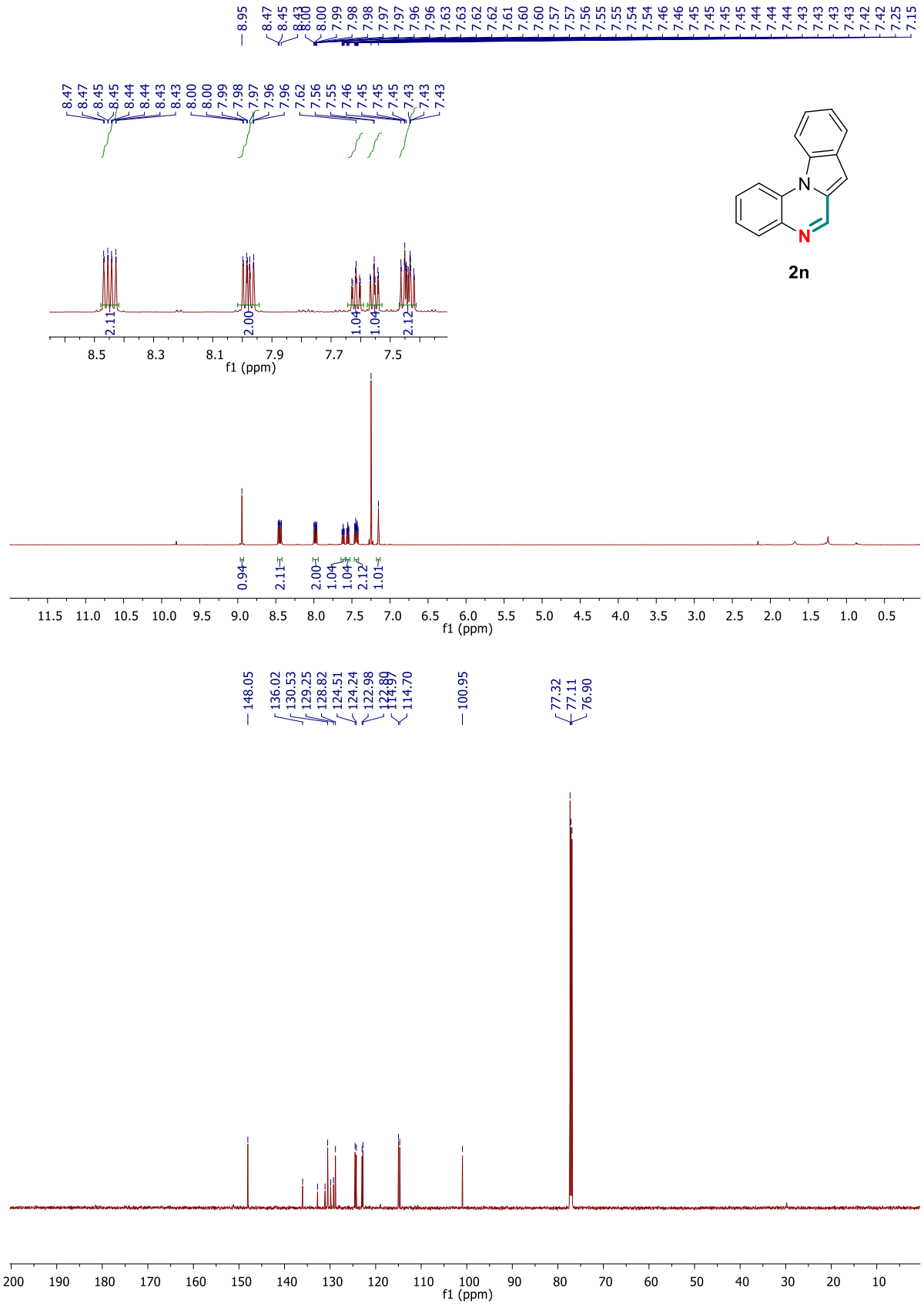

1.03
1.03
1.00
1.02
1.07
1.00
1.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


147.05
146.62
140.04
137.52
130.83
128.02
121.59
115.66
114.62
108.97
77.33
77.12
76.90
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

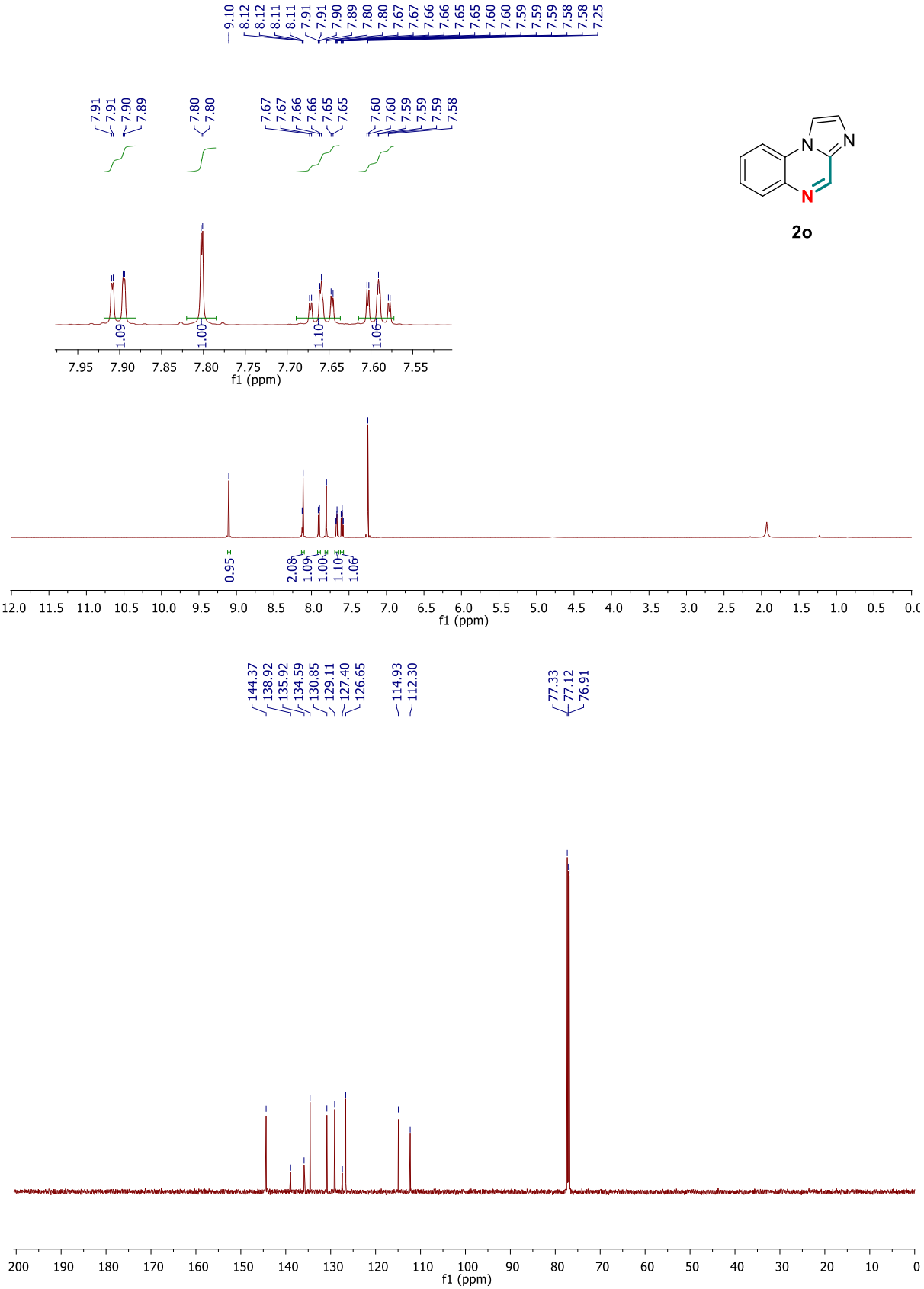
2m


8.70
8.53
8.52
8.52
8.52
8.33
8.23
8.22
8.21
8.21
7.45
7.44
7.43
7.25
6.94
6.94
1.00
1.03
1.01
1.00
f1 (ppm)
Br
N
N
N
2m
1.00
1.03
1.01
1.00
1.03
1.01
f1 (ppm)
147.57
145.24
138.67
137.90
130.41
127.89
122.07
115.64
110.60
104.38
77.33
77.12
76.91
f1 (ppm)

2n

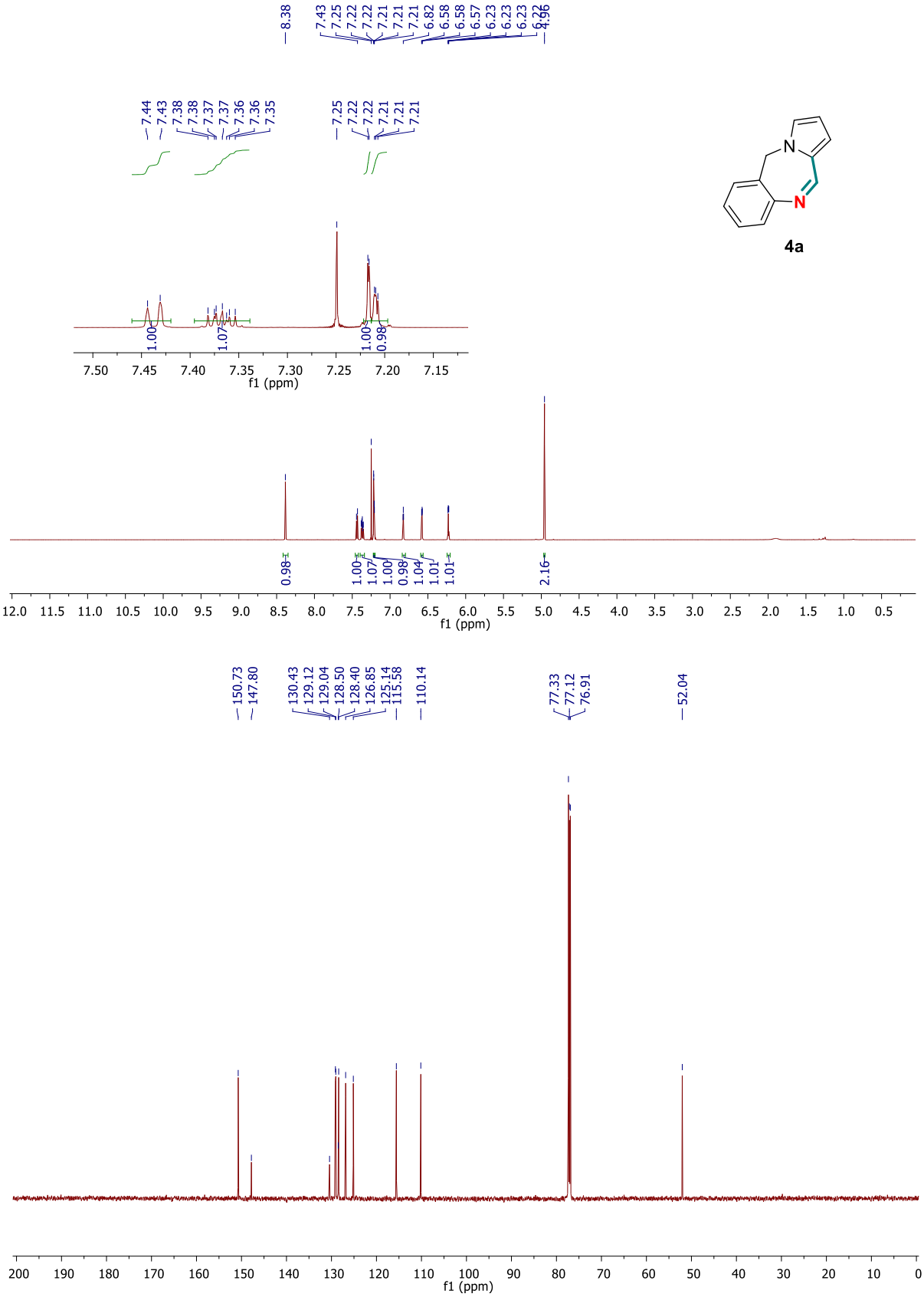

8.95 8.47 8.45 8.00 7.99 7.98 7.97 7.96 7.63 7.62 7.61 7.60 7.57 7.56 7.55 7.54 7.46 7.45 7.44 7.43 7.42 7.25 7.15
8.47 8.45 8.44 8.43 8.00 7.99 7.98 7.97 7.96 7.62 7.56 7.55 7.46 7.45 7.43
2.11 2.00 1.04 1.04 2.12
8.5 8.3 8.1 7.9 7.7 7.5
f1 (ppm)
N
N
2n
0.94 2.11 2.00 1.04 1.04 2.12 1.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
148.05 136.02 130.53 129.25 128.82 124.51 124.24 122.98 114.70 100.95 77.32 77.11 76.90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2o

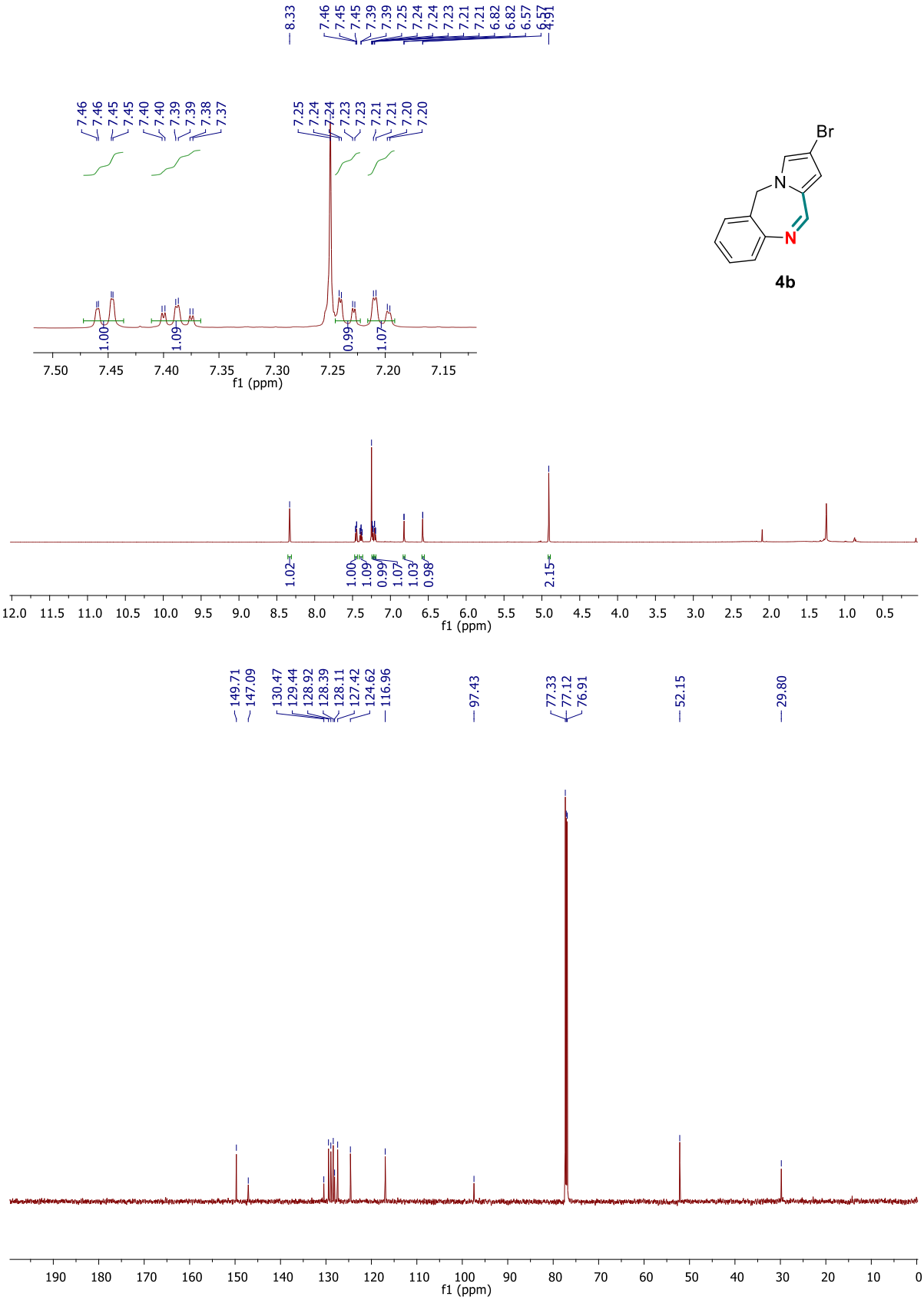

9.10
8.12
8.12
8.11
8.11
7.91
7.91
7.90
7.89
7.80
7.80
7.67
7.67
7.66
7.66
7.65
7.65
7.60
7.60
7.59
7.59
7.59
7.58
7.58
7.25
1.09
1.00
1.10
1.06
f1 (ppm)
0.95
2.08
1.09
1.00
1.10
1.06
f1 (ppm)
144.37
138.92
135.92
134.59
130.85
129.11
127.40
126.65
114.93
112.30
77.33
77.12
76.91
f1 (ppm)

2o

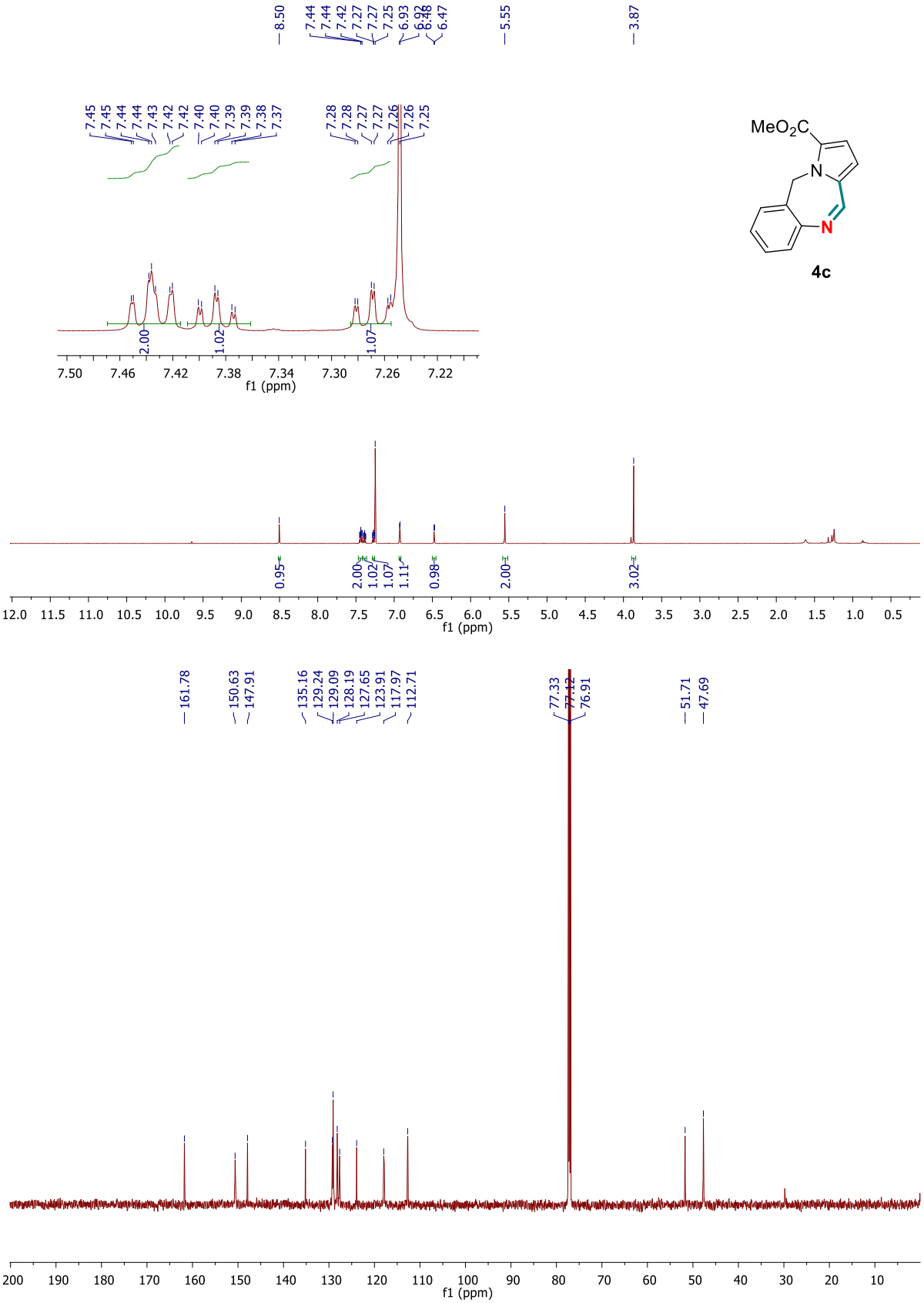
4a


8.38
7.43
7.25
7.22
7.22
7.21
7.21
7.21
6.82
6.58
6.58
6.57
6.23
6.23
6.23
6.22
4.96
7.44
7.43
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.25
7.22
7.22
7.21
7.21
7.21
1.00
1.07
1.00
0.98
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
N
N
4a
0.98
1.00
1.07
1.00
0.98
1.04
1.01
1.01
2.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
150.73
147.80
130.43
129.12
129.04
128.50
128.40
126.85
125.14
115.58
110.14
77.33
77.12
76.91
52.04
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

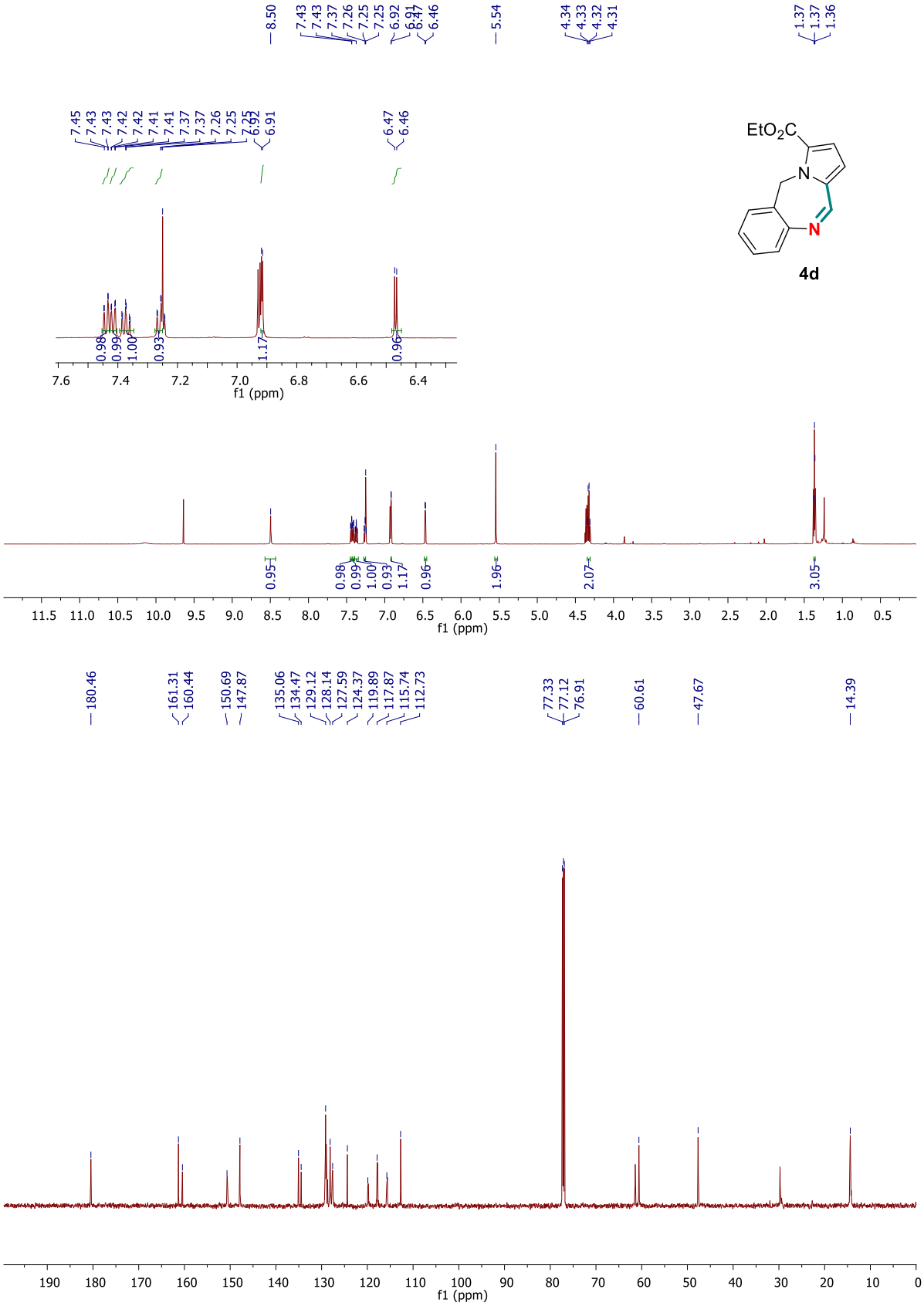
4b


8.33
7.46
7.45
7.45
7.39
7.39
7.25
7.24
7.24
7.23
7.21
7.21
6.82
6.82
6.57
6.57
4.91
7.46
7.46
7.45
7.45
7.40
7.40
7.39
7.39
7.38
7.37
7.25
7.24
7.24
7.23
7.23
7.21
7.21
7.20
7.20
1.00
1.09
0.99
1.07
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
Br
N
N
4b
1.02
1.00
1.09
0.99
1.07
1.03
0.98
2.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
149.71
147.09
130.47
129.44
128.92
128.39
128.11
127.42
124.62
116.96
97.43
77.33
77.12
76.91
52.15
29.80
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

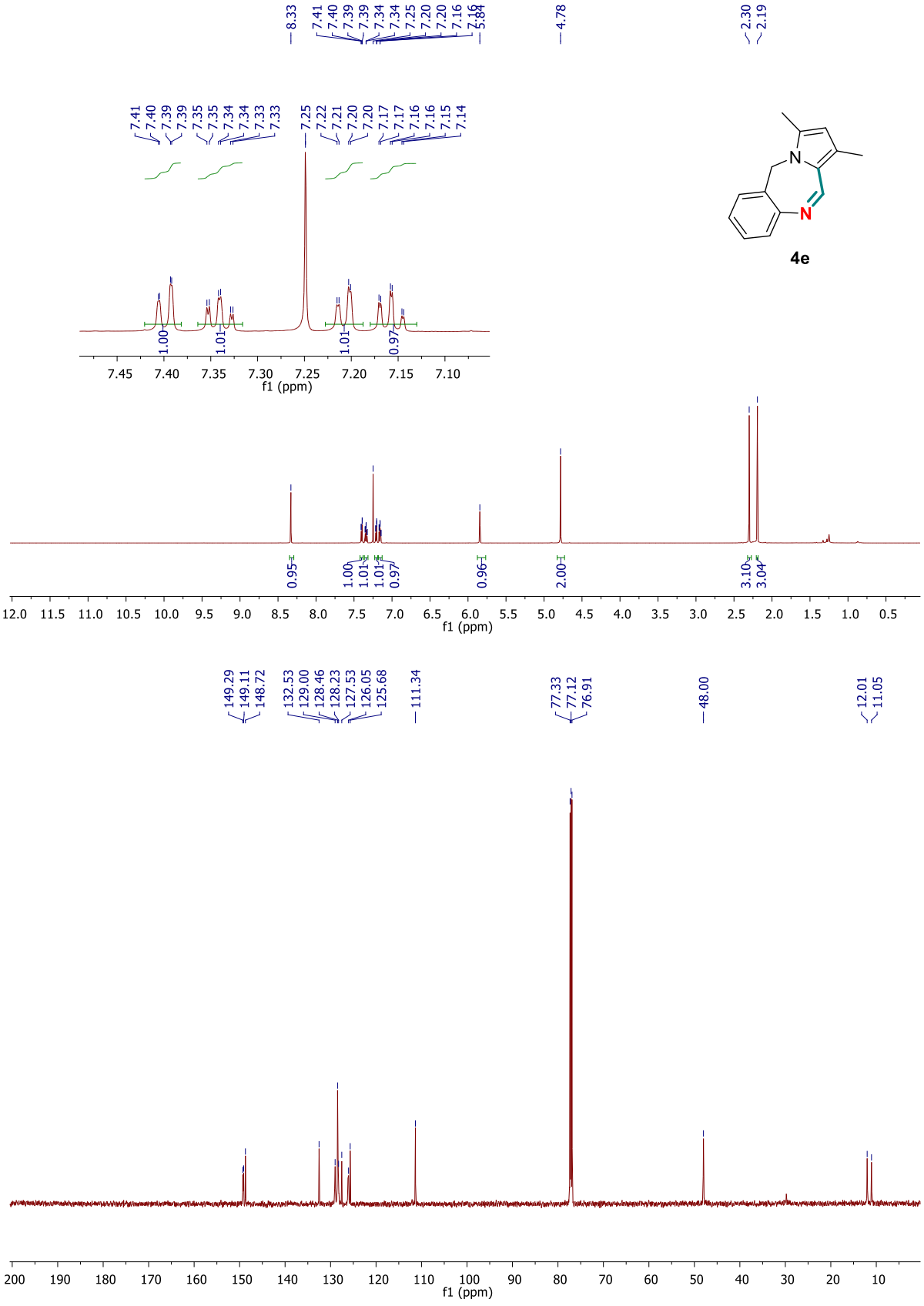
4c


8.50
7.44
7.44
7.42
7.27
7.27
7.25
6.93
6.92
6.48
6.47
5.55
3.87
MeO2C
N
N
4c
f1 (ppm)
f1 (ppm)
f1 (ppm)

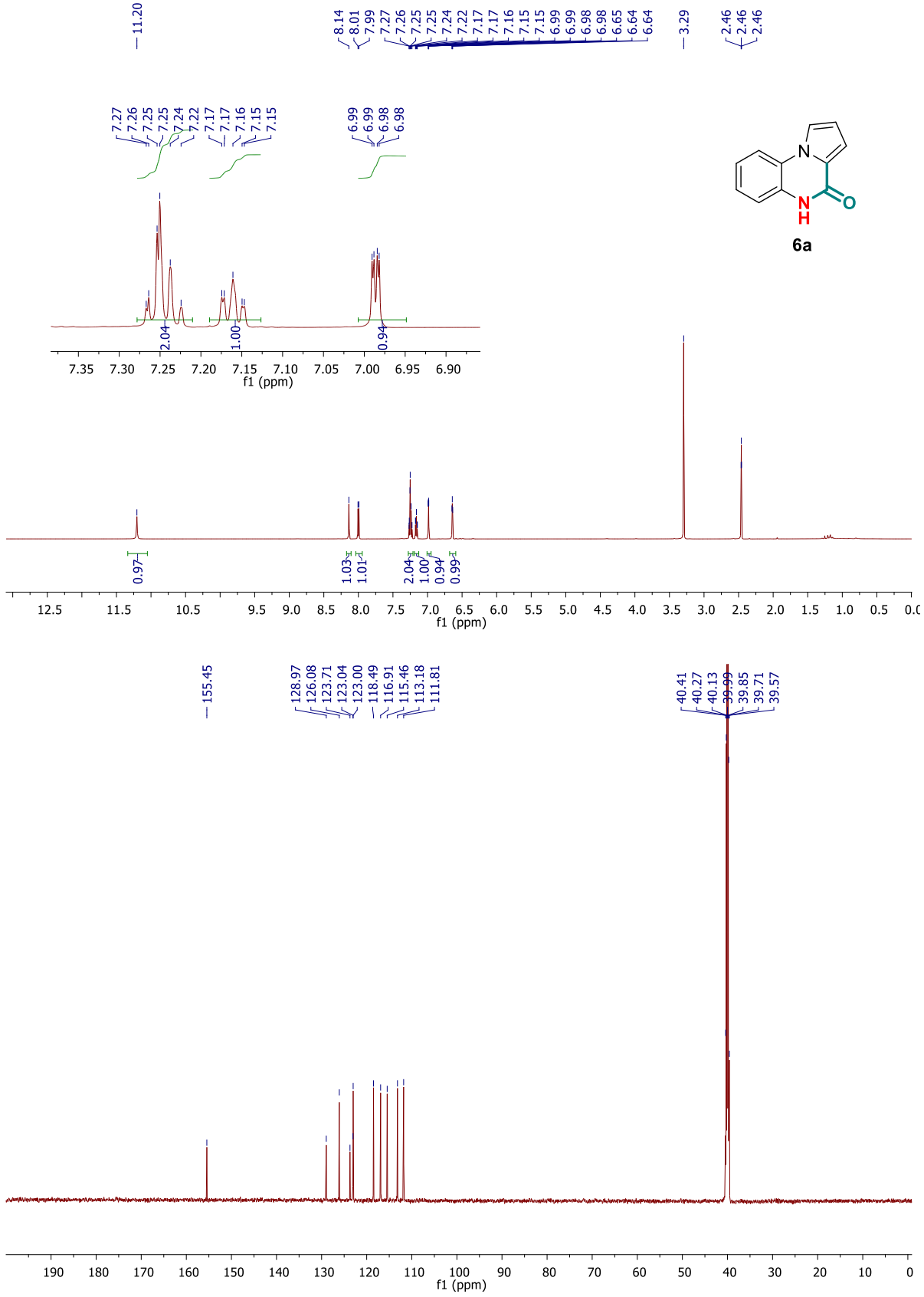
4d


8.50
7.43
7.43
7.37
7.26
7.25
7.25
6.92
6.91
6.47
6.46
5.54
4.34
4.33
4.32
4.31
1.37
1.37
1.36
EtO2C
N
N
4d
f1 (ppm)
180.46
161.31
160.44
150.69
147.87
135.06
134.47
129.12
128.14
127.59
124.37
119.89
117.87
115.74
112.73
77.33
77.12
76.91
60.61
47.67
14.39
f1 (ppm)

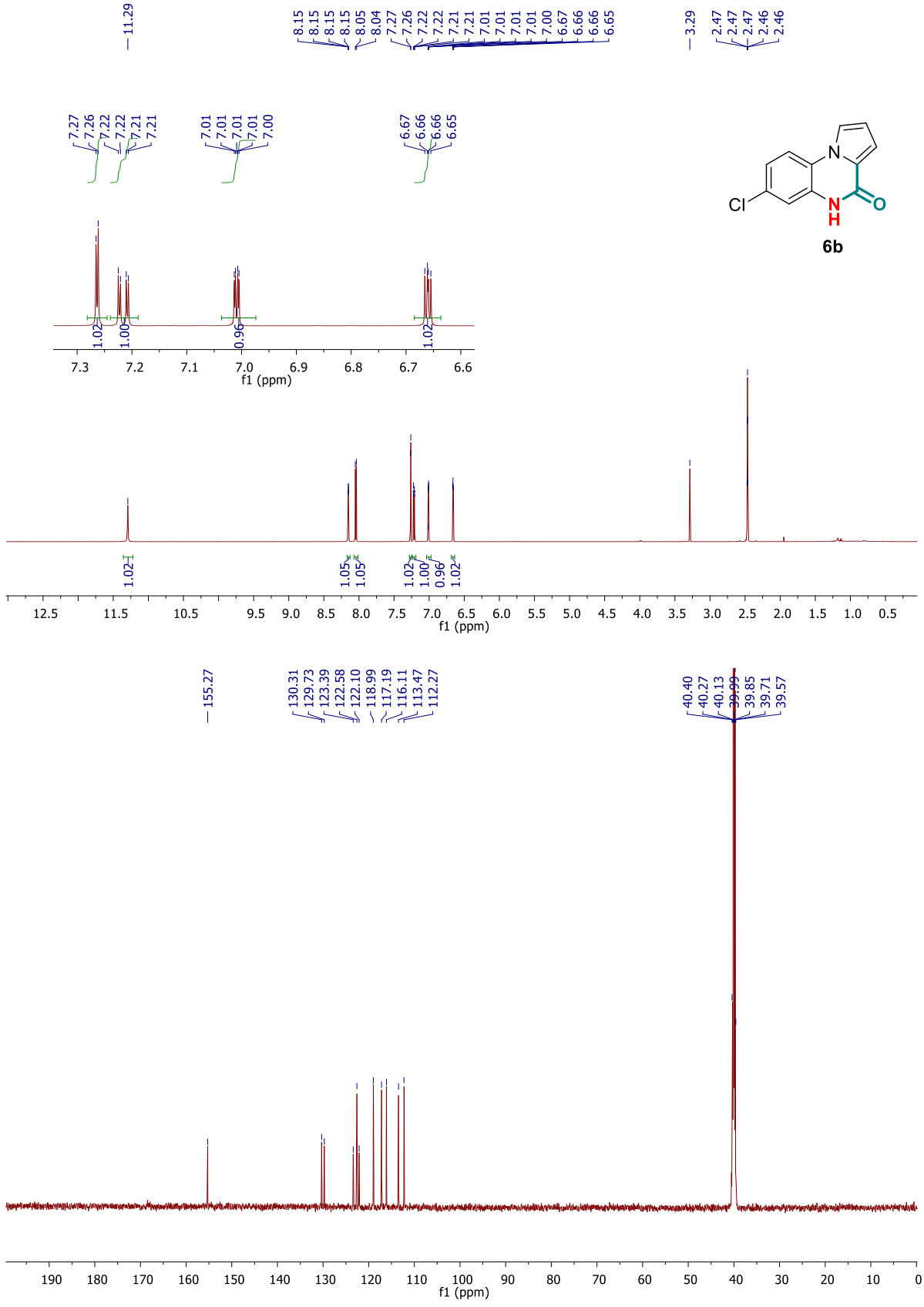
4e


8.33
7.41
7.40
7.39
7.39
7.34
7.34
7.25
7.20
7.20
7.16
7.16
5.84
4.78
2.30
2.19
7.41
7.40
7.39
7.39
7.35
7.35
7.34
7.34
7.33
7.33
7.25
7.22
7.21
7.20
7.20
7.17
7.17
7.16
7.16
7.15
7.14
1.00
1.01
1.01
0.97
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
N
N
4e
0.95
1.00
1.01
1.01
0.97
0.96
2.00
3.10
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
149.29
149.11
148.72
132.53
129.00
128.46
128.23
127.53
126.05
125.68
111.34
77.33
77.12
76.91
48.00
12.01
11.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

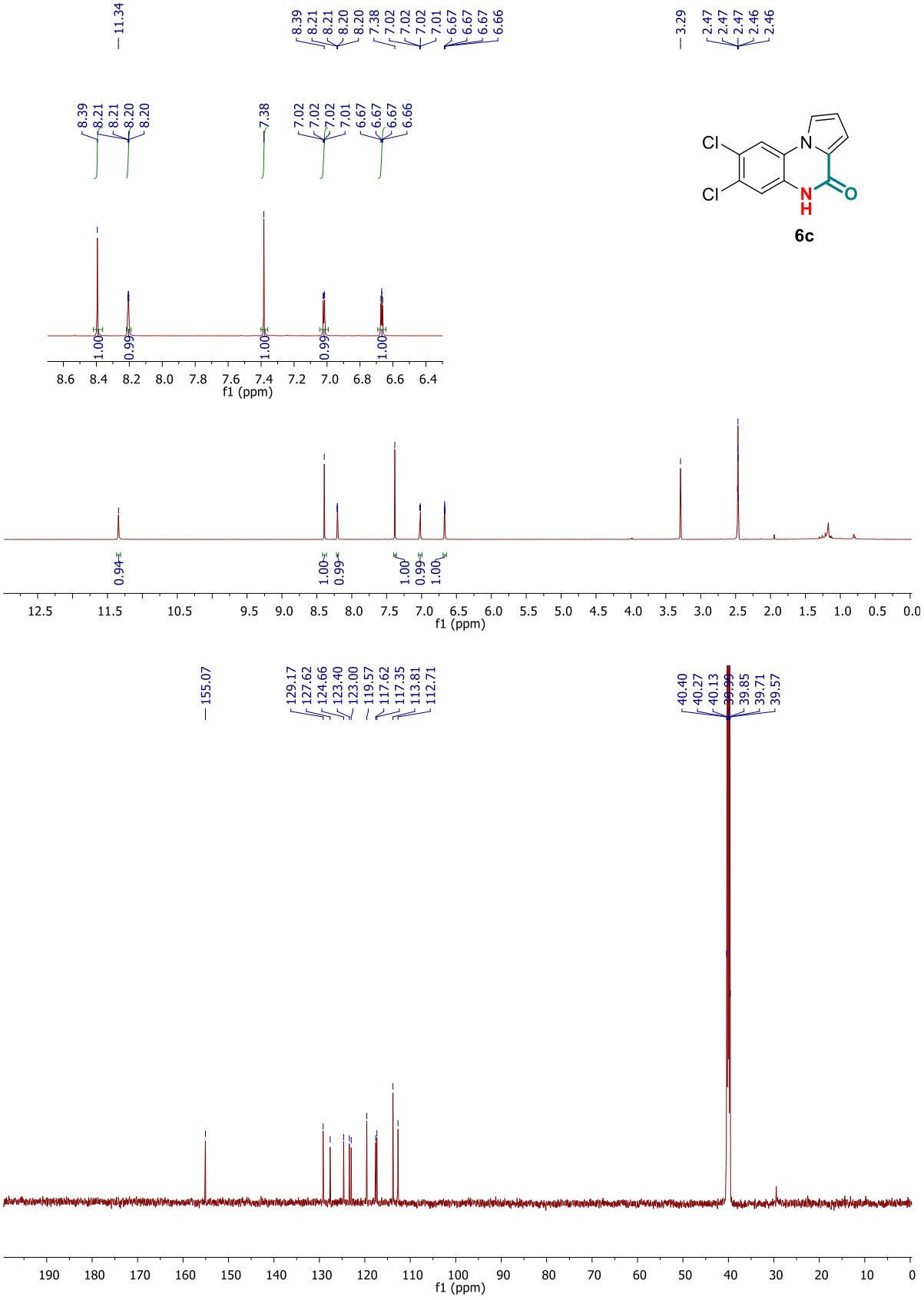
6a

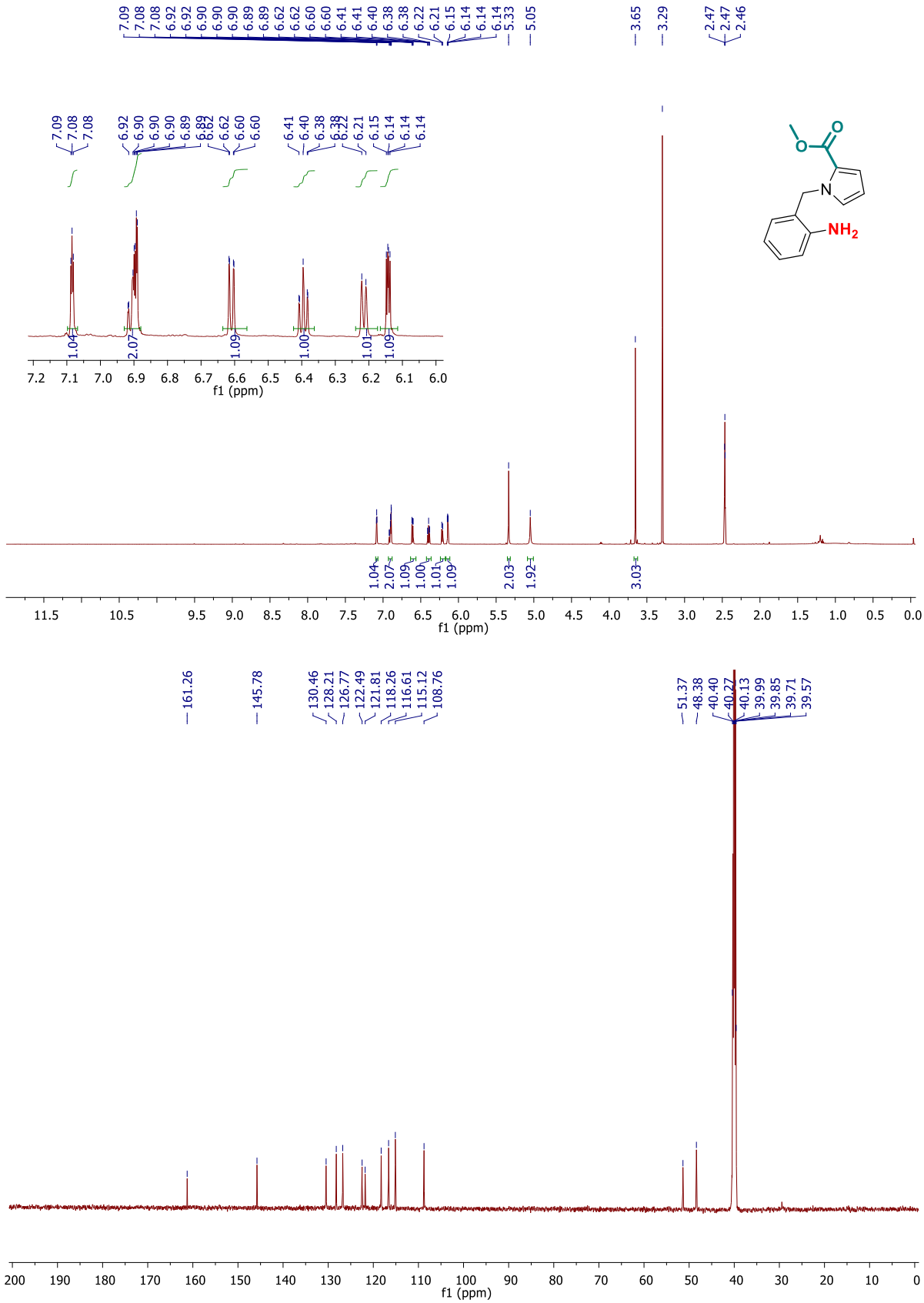

11.20
8.14
8.01
7.99
7.27
7.26
7.25
7.25
7.24
7.22
7.17
7.17
7.16
7.15
7.15
6.99
6.99
6.98
6.98
6.65
6.64
6.64
3.29
2.46
2.46
2.46
2.04
1.00
0.94
f1 (ppm)
6a
0.97
1.03
1.01
2.04
1.00
0.94
0.99
f1 (ppm)
155.45
128.97
126.08
123.71
123.04
123.00
118.49
116.91
115.46
113.18
111.81
40.41
40.27
40.13
39.99
39.85
39.71
39.57
f1 (ppm)

6b


11.29
8.15
8.15
8.15
8.05
8.04
7.27
7.26
7.22
7.22
7.21
7.21
7.01
7.01
7.01
7.01
7.00
6.67
6.66
6.66
6.65
3.29
2.47
2.47
2.47
2.46
2.46
Cl
N
N
H
O
6b
1.02
1.00
0.96
1.02
f1 (ppm)
1.02
1.05
1.05
1.02
1.00
0.96
1.02
f1 (ppm)
155.27
130.31
129.73
123.39
122.58
122.10
118.99
117.19
116.11
113.47
112.27
40.40
40.27
40.13
39.99
39.85
39.71
39.57
f1 (ppm)

6c


11.34
8.39
8.21
8.21
8.20
8.20
7.38
7.02
7.02
7.02
7.01
6.67
6.67
6.67
6.66
3.29
2.47
2.47
2.47
2.46
2.46
Cl
Cl
N
N
H
O
6c
f1 (ppm)
155.07
129.17
127.62
124.66
123.40
123.00
119.57
117.62
117.35
113.81
112.71
40.40
40.27
40.13
39.99
39.85
39.71
39.57
f1 (ppm)


7.09 7.08 7.08 6.92 6.92 6.90 6.90 6.90 6.89 6.89 6.62 6.62 6.60 6.60 6.41 6.41 6.40 6.38 6.38 6.22 6.21 6.15 6.14 6.14 6.14 5.33 5.05
3.65 3.29
2.47 2.47 2.46
1.04 2.07 1.09 1.00 1.01 1.09 2.03 1.92 3.03
f1 (ppm)
NH2

161.26 145.78 130.46 128.21 126.77 122.49 121.81 118.26 116.61 115.12 108.76
51.37 48.38 40.40 40.27 40.13 39.99 39.85 39.71 39.57
f1 (ppm)