Chemistry–A European Journal

Supporting Information

Selective and Scalable Electrosynthesis of *2H*-2-(Aryl)-benzo[*d*]-1,2,3-triazoles and Their N-Oxides by Using Leaded Bronze Cathodes

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General Information:

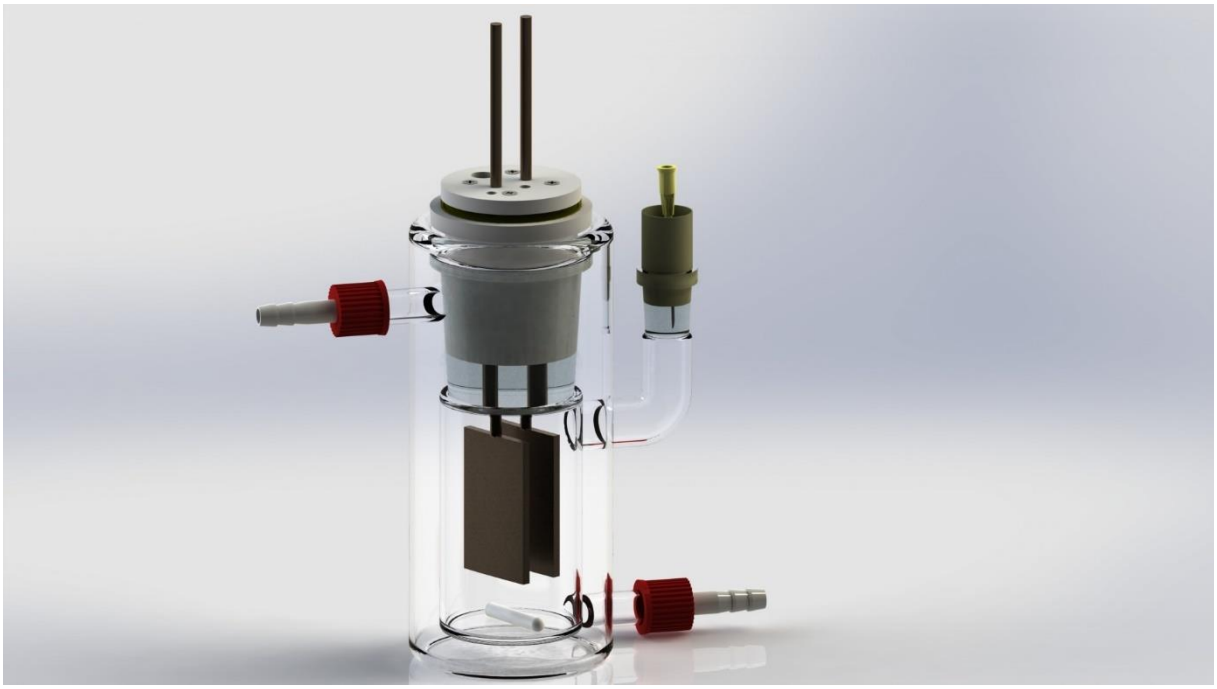
All solvents and reagents used were obtained as analytical grade from commercial suppliers or purified with standard methods. ^{1}H (300.13 MHz), ^{19}F (282.38 MHz) and $^{13}C\{^{1}H\}$ (75.48 MHz) NMR spectra were recorded at 23 °C by Bruker Avance III HD spectrometer. Chemical shifts (δ) are reported in parts per million relative to $CHCl_3$ (7.26 ppm in ^{1}H, 77.16 ppm in $^{13}C\{^{1}H\}$) and C_6F_6 (-164.90 ppm in ^{19}F) in $CDCl_3$. High-resolution mass spectra were obtained with QTof Ultima 3 (Waters, Milford, Massachusetts) using ESI, APCI and APPI ionization modes. Column chromatography was performed on silica gel 60 M (0.040 - 0.063 mm, Macherey-Nagel GmbH & Co, Düren, Germany) using distilled ethyl acetate and cyclohexane as eluents.

Electrochemical Setup:

Screening scale electrochemical reactions were carried out in a screening cell array using undivided cells which were made according to a detailed description published earlier (Scheme S1).[1] Multi-channel galvanostat was used as a power source for the constant current electrolysis. This screening set-up can also be obtained commercially (IKA Screening System Package (8 cell), Ident. No.: 0040003642) from IKA-Werke GmbH & Co. KG, Staufen, Germany. The glassy carbon electrodes were obtained from SIGRADUR® G, HTW, Thierhaupten, Germany and the leaded bronzes were purchased from Metallwerke Langenau GmbH, Riedheimer Str. 11, 89129 Langenau, Germany. The distance between electrodes was 0.5 cm and the dimensions of the electrodes were 7.0 x 1.0 x 0.3 cm. An active surface area of 1.7 cm^2 was used in the electrolysis at screening scale.

Scheme S1: Schematic pictures of the screening array (left) and the undivided cell (right) that were used in screening scale electrosyntheses

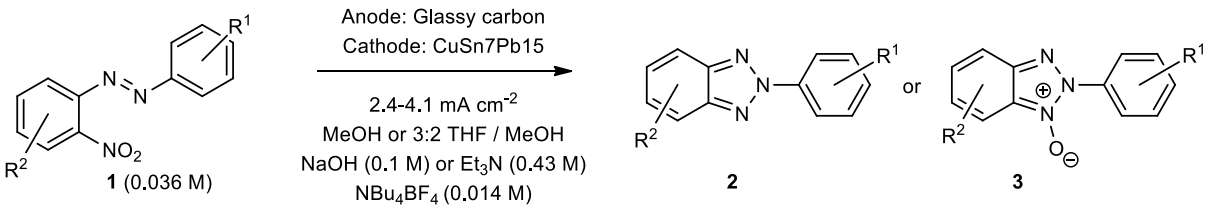
In the scale-up reaction of **2d**, a 100 mL jacketed beaker-type cell was used with an active anode and cathode surface area of 9 cm^2 and a distance between electrodes being 0.5 cm (Scheme S2).



Scheme S2: Schematic picture of the beaker-type cell used in the scale-up reaction

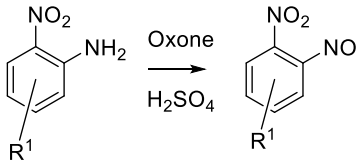
General Protocols

General protocol for the synthesis of 2*H*-2-(aryl)benzo[d]-1,2,3-triazoles and 2*H*-2-(aryl)benzo[d]-1,2,3-triazole *N*-oxide derivatives (GP I):



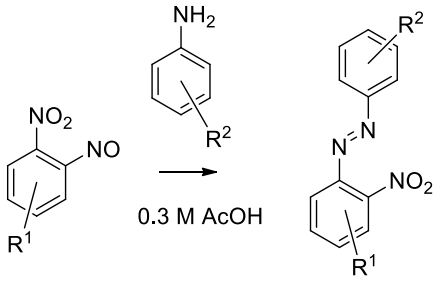
Starting material (0.18 mmol), NBu_4BF_4 (0.07 mmol), and NaOH (0.5 mmol) or Et_3N (2.16 mmol) were dissolved to either MeOH or 3:2 THF:MeOH (5 mL). The reaction mixture was then stirred for ~30 min at 33-37 °C (RT) and during that time the CuSn7Pb15 cathode was gently polished and glassy carbon anode was cleaned with H_2O and acetone before constant current electrolysis (either 2.4 or 4.1 mA cm^{-2}) was started. The reaction was controlled by analyzing the crude reaction mixture periodically by ^1H or ^{19}F NMR. After the reaction was complete, the reaction mixture was evaporated. Purification of the crude material by flash column chromatography (SiO_2) using mixtures of cyclohexane:ethyl acetate as eluents afforded the title compounds.

General protocol for the synthesis of 1-nitro-2-nitrosobenzene derivates (GP II):



Nitrosobenzene derivates were prepared by a known literature procedure.[2] To Oxone™ (20.0 g, 32.6 mmol, 1.5 equiv.) was added 24 mL (1.1 mL per $mmol^{-1}$ of nitroaniline) concentrated sulfuric acid, followed by addition of 130 g ice (6 g per $mmol^{-1}$ of nitroaniline). When ice was melted, nitroaniline (21.7 mmol, 1.0 equiv.) was added. After stirring overnight, the reaction mixture was extracted with 2x 150 mL of EtOAc and the combined organic fractions were washed with 100 mL of saturated $NaHCO_3$, 100 mL of brine and dried over Na_2SO_4. The crude materials were used in the next steps without further purification.

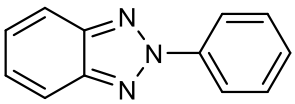
General protocol for synthesis of substituted 2-nitroazobenzene derivatives (GP III):



2-Nitroazobenzene derivatives were prepared by a known literature procedure.[3] 1-Nitro-2-nitrosobenzene or 5-bromo-1-nitro-2-nitrosobenzene (1.1 equiv.) in AcOH (0.3 M) was purged by Ar and then aniline (1.0 equiv.) was added to the reaction mixture. The reaction mixture was stirred overnight and then diluted with H_2O and extracted with 3x 100 mL of EtOAc. The organic fractions were washed with saturated $NaHCO_3$, brine, and dried over Na_2SO_4. Purification of the crude material by flash column chromatography (SiO_2) using mixtures of cyclohexane:ethyl acetate as eluents afforded the title compounds.

Synthesis of Compounds

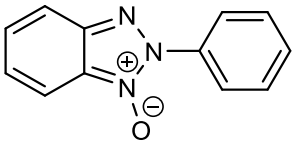
2*H*-2-(Phenyl)benzo[d]-1,2,3-triazole – 2b[4]



Following **GP I** with 40.9 mg of **1b**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL MeOH. After passing 11.2 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 50:1 cyclohexane:ethyl acetate as eluents afforded 31.2 mg (89%, 0.160 mmol) of **2b** as a colorless solid. Spectroscopic data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.39 – 8.33 (m, 2H), 7.99 – 7.90 (m, 2H), 7.62 – 7.52 (m, 2H), 7.51 – 7.39 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.2, 140.5, 129.6, 129.1, 127.3, 120.8, 118.5. **HRMS-APCI** calculated for $[C_{12}H_9N_3]^+$ 195.0796 found: 195.0793

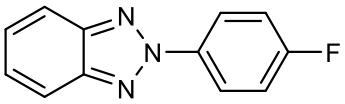
2*H*-2-(Phenyl)-benzo[d]1,2,3-triazole 1-oxide – 3b[5]



Following **GP I** with 40.9 mg of **1b**, 23.4 mg NBu_4BF_4 and 20 mg NaOH in 5mL MeOH. After passing 9.9 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 40:1 -> 3:1 -> 2:1 -> 1:1 cyclohexane:ethyl acetate as eluents afforded 31.6 mg (83%, 0.150 mmol) of **3b** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.22 – 8.09 (m, 2H), 7.84 – 7.70 (m, 2H), 7.62 – 7.48 (m, 3H), 7.48 – 7.41 (m, 1H), 7.39 – 7.29 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.2, 135.4, 130.0, 129.3, 129.3, 126.7, 126.5, 123.7, 119.2, 114.1. **HRMS-APPI** calculated for $[C_{12}H_9N_3O]^+$ 211.0746 found: 211.0753

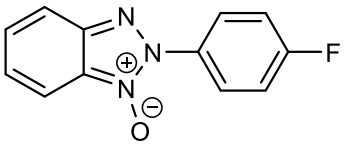
2*H*-2-(4-Fluorophenyl)benzo[d]-1,2,3-triazole – 2a[6]



Following **GP I** with 44.1 mg of **1a**, 23.0 mg NBu_4BF_4 and 20 mg of NaOH in 5 mL MeOH. After passing 12.9 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 50:1 cyclohexane:ethyl acetate as eluents afforded 32.9 mg (86%, 0.154 mmol) of **2a** as a colorless solid. Spectroscopic data are in agreement with the literature.[6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.41 – 8.24 (m, 2H), 8.00 – 7.82 (m, 2H), 7.48 – 7.38 (m, 2H), 7.30 – 7.19 (m, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 162.9 (d, J = 249.2 Hz), 145.2, 136.7 (d, J = 3.0 Hz), 127.4, 122.5 (d, J = 8.7 Hz), 118.4, 116.5 (d, J = 23.4 Hz). **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -115.44 (tt, $J_{H,F}$ = 8.1, 4.9 Hz). **HRMS-APCI** calculated for $[C_{12}H_8N_3F]^+$ 213.0702 found: 213.0708

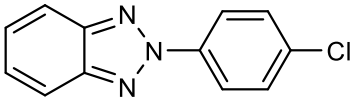
2*H*-2-(4-Fluorophenyl)benzo[d]-1,2,3-triazole 1-oxide – 3a[7]



Following **GP I** with 44.1 mg of **1a**, 23.0 mg NBu_4BF_4 and 20 mg of NaOH in 5 mL MeOH. After passing 8.4 F with a current density of 2.4 cm^{-2}, the purification of the crude material by flash chromatography using 3:1 cyclohexane:ethyl acetate as eluents afforded 41 mg (97%, 0.175 mmol) of **3a** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.26 – 8.16 (m, 2H), 7.86 – 7.73 (m, 2H), 7.52 – 7.44 (m, 1H), 7.42 – 7.25 (m, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 163.1 (d, J = 251.9 Hz), 141.3, 131.5 (d, J = 3.3 Hz), 129.5, 126.7, 126.6, 125.9 (d, J = 9.1 Hz), 119.2, 116.5 (d, J = 23.2 Hz), 114.1. ^{19}F NMR (282 MHz, Chloroform-*d*) δ -112.58 (tt, $J_{H,F}$ = 8.1, 4.8 Hz). **HRMS-APCI** calculated for $[C_{12}H_8N_3FO]^+$ 229.0651 found: 229.0657

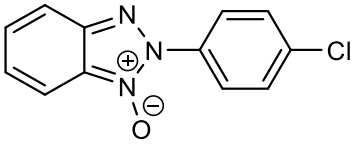
2*H*-2-(4-Chlorophenyl)benzo[d]-1,2,3-triazole – 2c[6,8]



Following **GP I** with 47.1 mg of **1c**, 23.0 mg NBu_4BF_4 and 20.5 mg of NaOH in 5 mL 3:2 THF:MeOH. After passing 8.1 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 50:1 cyclohexane:ethyl acetate afforded as eluents afforded 34.2 mg (83%, 0.149 mmol) of **2c** as a colorless solid. Spectroscopic data are in agreement with the literature.[6,8]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.33 – 8.27 (m, 2H), 7.95 – 7.87 (m, 2H), 7.54 – 7.48 (m, 2H), 7.46 – 7.38 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.2, 138.9, 134.9, 129.7, 127.6, 121.9, 118.5. **HRMS-APCI** calculated for $[C_{12}H_8N_3{}^{35}Cl]^+$ 229.0407 found: 229.0406

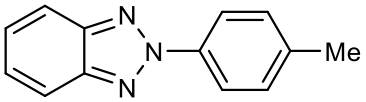
2*H*-2-(4-Chlorophenyl)benzo[d]-1,2,3-triazole 1-oxide – 3c[5]



Following **GP I** with 47.1 mg of **1c**, 23.0 mg NBu_4BF_4 and 20.2 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 5.0 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 3:1 -> cyclohexane:ethyl acetate as eluents afforded 36.0 mg (81%, 0.147 mmol) of **3c** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.22 – 8.14 (m, 2H), 7.80 – 7.70 (m, 2H), 7.58 – 7.51 (m, 2H), 7.49 – 7.40 (m, 1H), 7.38 – 7.30 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.3, 135.9, 133.9, 129.5, 126.7, 124.6, 119.2, 114.1. **HRMS-APCI** calculated for $[C_{12}H_8N_3{}^{35}ClO]^+$ 245.0356 found: 245.0347

2*H*-2-(4-Methylphenyl)benzo[d]-1,2,3-triazole – 2d[8]

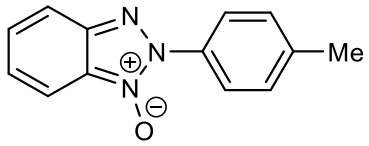


Screening scale: Following **GP I** with 43.4 mg of **1d**, 23.1 mg NBu_4BF_4 and 20 mg NaOH in 5 mL of MeOH. After passing 11.0 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 50:1 cyclohexane:ethyl acetate as eluents afforded 32.4 mg (92%, 0.165 mmol) of **2d** as a colorless solid. Spectroscopic data are in agreement with the literature.[8]

Scale up: Following **GP I** with 814.4 mg of **1d** and 376 mg NaOH in 94 mL of MeOH. After passing 11.7 F with a current density of 4.1 mA cm^{-2}, the reaction mixture was diluted to 100 mL MeOH and 5 mL fraction was separated, evaporated, and then the yield (91%) was measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The remaining organic fraction (95 mL) was evaporated and 50 mL of H_2O and EtOAc were added to the residue. The organic fraction was separated and then the water fraction was further extracted with 2x 50 mL of EtOAc. The combined organic fractions were washed with H_2O, brine, dried over Na_2SO_4 and evaporated. Purification of the crude material by flash chromatography using 50:1 cyclohexane:ethyl acetate as eluents afforded 555.6 mg (83%, 2.655 mmol) of **2d** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.26 – 8.19 (m, 2H), 7.96 – 7.89 (m, 2H), 7.45 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.0, 139.3, 138.3, 130.1, 127.1, 120.6, 118.4, 21.3. **HRMS-APCI** calculated for $[C_{13}H_{11}N_3]^+$ 209.0953 found: 209.0950

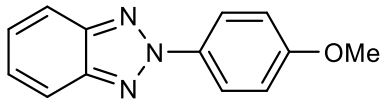
2*H*-2-(4-Methylphenyl)benzo[d]-1,2,3-triazole 1-oxide – 3d[5]



Following **GP I** with 43.4 mg of **1d**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL MeOH. After passing 10.3 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 9:1 -> 3:1 cyclohexane:ethyl acetate as eluents afforded 37.0 mg (91%, 0.164 mmol) of **3d** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.83 – 7.68 (m, 2H), 7.47 – 7.28 (m, 4H), 2.44 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.1, 140.5, 132.9, 129.9, 129.1, 126.6, 126.4, 123.6, 119.2, 114.1, 21.5. **HRMS-APCI** calculated for $[C_{13}H_{12}N_3O]^+$ 225.0902 found: 225.0905

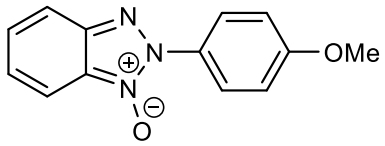
2*H*-2-(4-Methoxyphenyl)benzo[d]-1,2,3-triazole – 2e[6]



Following **GP I** with 46.4 mg of **1e**, 23.1 mg NBu_4BF_4 and 20 mg NaOH in 5 mL MeOH. After passing 9.2 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 9:1 cyclohexane:ethyl acetate as eluents afforded 35.8 mg (88%, 0.159 mmol) of **2e** as a colorless solid. Spectroscopic data are in agreement with the literature.[6]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.32 – 8.20 (m, 2H), 7.97 – 7.83 (m, 2H), 7.46 – 7.31 (m, 2H), 7.11 – 6.94 (m, 2H), 3.87 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.2, 145.0, 134.1, 126.9, 122.1, 118.3, 114.6, 55.7. **HRMS-APCI** calculated for $[C_{13}H_{11}N_3O]^+$ 225.0902 found: 225.0895

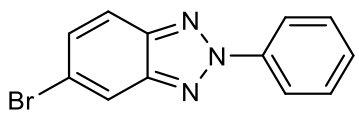
2*H*-2-(4-Methoxyphenyl)benzo[d]-1,2,3-triazole 1-oxide – 3e[5]



Following **GP I** with 46.4 mg of **1e**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL MeOH. After passing 11.9 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 9:1 -> 3:1 -> 1:1 cyclohexane:ethyl acetate as eluents afforded 35.8 mg (82%, 0.148 mmol) of **3e** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.09 – 8.02 (m, 2H), 7.76 (ddt, *J* = 12.7, 8.7, 1.0 Hz, 2H), 7.46 – 7.38 (m, 1H), 7.39 – 7.29 (m, 1H), 7.10 – 7.02 (m, 2H), 3.88 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.7, 141.0, 129.0, 128.3, 126.5, 126.3, 125.5, 119.1, 114.5, 114.0, 55.6. **HRMS-APCI** calculated for $[C_{13}H_{12}N_3O_2]^+$ 241.0851 found: 241.0851

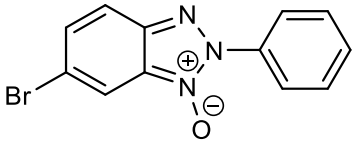
2*H*-5-Bromo-2-phenyl--benzo[d]-1,2,3-triazole – 2f[9]



Following **GP I** with 55.1 mg of **1f**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 7.1 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 0:1 -> 50:1 cyclohexane:ethyl acetate as eluents afforded 28.3 mg (57%, 0.103 mmol) of **2f** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.37 – 8.29 (m, 2H), 8.12 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.82 (dd, *J* = 9.0, 0.8 Hz, 1H), 7.61 – 7.43 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 146.0, 143.8, 140.2, 131.2, 129.7, 129.5, 121.0, 120.9, 120.8, 119.9. **HRMS-APCI** calculated for $[C_{12}H_8N_3{}^{79}Br]^+$ 272.9902 found: 272.9903

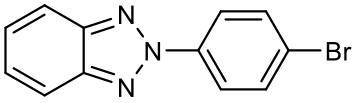
2*H*-5-Bromo-2-phenyl-benzo[d]-1,2,3-triazole 3-oxide – 3f[9]



Following **GP I** with 55.1 mg of **1f**, 23.0 mg of NBu_4BF_4 and 20 mg NaOH in 5 mL of 3:2 THF:MeOH. After passing 4.9 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 3:1 cyclohexane:ethyl acetate as eluents afforded 44.7 mg (86%, 0.154 mmol) of **3f** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.19 – 8.07 (m, 2H), 8.00 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.65 (dd, *J* = 9.2, 0.8 Hz, 1H), 7.63 – 7.48 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.7, 135.2, 133.4, 130.3, 129.4, 127.2, 123.6, 120.6, 120.3, 116.6. **HRMS-ESI** calculated for $[C_{12}H_8N_3{}^{79}BrO]^+$ 288.9851 found: 288.9848

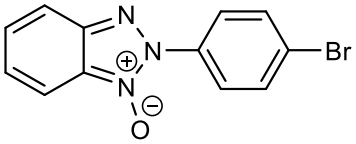
2*H*-2-(4-Bromophenyl)benzo[d]-1,2,3-triazole – 2g[10]



Following **GP I** with 55.1 mg of **1g**, 23.2 mg NBu_4BF_4 and 20.2 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 11.4 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using cyclohexane as eluent afforded 32.6 mg of a mixture containing the desired **2g** (62%, 0.112 mmol) and the dehalogenated **2b** (6%, 0.011 mmol). **2g** and **2b** were obtained as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.27 – 8.20 (m, 2H), 7.94 – 7.87 (m, 2H), 7.71 – 7.63 (m, 2H), 7.46 – 7.38 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.2, 139.4, 132.7, 127.6, 122.9, 122.1, 118.5. **HRMS-APCI** calculated for $[C_{12}H_8N_3{}^{79}Br]^+$ 272.9902 found: 272.9893

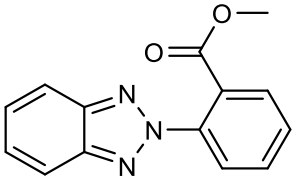
2*H*-2-(4-Bromophenyl)benzo[d]-1,2,3-triazole 1-oxide – 3g[11]



Following **GP I** with 55.1 mg of **1g**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 4.0 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 5:1 cyclohexane:ethyl acetate as eluents afforded 43.1 mg (83%, 0.149 mmol) of **3g** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.17 – 8.10 (m, 1H), 7.83 – 7.69 (m, 2H), 7.50 – 7.43 (m, 1H), 7.40 – 7.33 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.4, 134.4, 132.6, 129.6, 126.8, 124.9, 124.1, 119.3, 114.2. **HRMS-APCI** calculated for $[C_{12}H_8N_3{}^{79}BrO]^+$ 288.9851 found: 288.9854

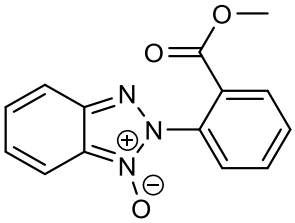
2*H*-2-(2-(Methoxycarbonyl)phenyl)benzo[d]-1,2,3-triazole – 2h



Following **GP I** with 51.3 mg of **1h**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 10.3 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 3:1 cyclohexane:ethyl acetate as eluents afforded 5.3 mg (12%, 0.0209 mmol) of **2h** as a brownish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.85 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.69 (td, *J* = 7.8, 1.6 Hz, 1H), 7.58 (td, *J* = 7.6, 1.3 Hz, 1H), 7.51 – 7.38 (m, 2H), 3.69 (s, 3H)**. ^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.4, 145.3, 139.0, 132.0, 130.2, 129.6, 128.1, 127.4, 125.4, 118.6, 52.7. **HRMS-ESI** calculated for $[C_{14}H_{11}N_3O_2]^+$ 253.0851 found: 253.0851

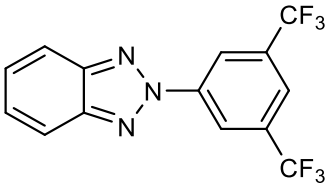
2*H*-2-(2-(Methoxycarbonyl)phenyl)benzo[d]-1,2,3-triazole 1-oxide – 3h



Following **GP I** with 51.3 mg of **1h**, 23.1 mg NBu_4BF_4 and 20 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 9.4 F with a current density of 2.4 mA cm^{-2}, the crude was evaporated and dissolved to 27:1 MeOH / H_2SO_4 and stirred overnight. Next day, the reaction was quenched with K_2CO_3, diluted with H_2O, extracted 3x30 mL of EtOAc and evaporated. The purification of the crude material by flash chromatography using 1:1 cyclohexane:ethyl acetate as eluents afforded 15.0 mg (31%, 0.056 mmol) of **3h** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.82 – 7.65 (m, 5H), 7.51 – 7.44 (m, 1H), 7.41 – 7.33 (m, 1H), 3.71 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.8, 142.0, 133.3, 133.2, 131.4, 131.2, 129.3, 128.6, 128.6, 126.6, 125.7, 119.5, 114.2, 52.9. **HRMS-ESI** calculated for $[C_{14}H_{11}N_3O_3]^+$ 269.0800 found: 269.0802

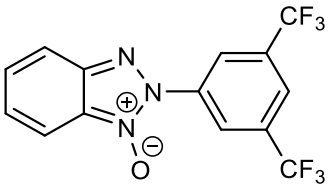
2*H*-2-(3,5-Bis(trifluoromethyl)phenyl)benzo[d]-1,2,3-triazole – 2i



Following **GP I** with 65.4 mg of **1i**, 23.0 mg NBu_4BF_4 and 20 mg of NaOH in 5 mL of MeOH. After passing 8.6 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 50:1 cyclohexane:ethyl acetate as eluents afforded 53.1 mg (89%, 0.16 mmol) of **2i** as a colorless solid. Spectroscopic data are in agreement with the literature.[12]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.88 – 8.81 (m, 2H), 7.96 – 7.86 (m, 3H), 7.50 – 7.41 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.6, 141.3, 133.3 (q, *J* = 34.3 Hz), 128.5, 122.9 (q, *J* = 273.0 Hz), 122.2 (hept, *J* = 3.8 Hz), δ 120.7 (q, *J* = 4.1 Hz), 118.7. **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -66.17 (s). **HRMS-APCI** calculated for $[C_{14}H_7N_3F_6]^+$ 331.0544 found: 331.0544

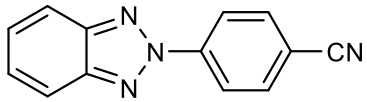
2*H*-2-(3,5-Bis(trifluoromethyl)phenyl)benzo[d]-1,2,3-triazole 1-oxide – 3i



Following **GP I** with 65.4 mg of **1i**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL MeOH. After passing 4.8 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 50:1 -> 18:1 -> 9:1 cyclohexane:ethyl acetate as eluents afforded 55.3 mg (88%, 0.159 mmol) of **3i** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.90 (s, 2H), 8.01 (s, 1H), 7.84 – 7.74 (m, 2H), 7.56 – 7.47 (m, 1H), 7.45 – 7.37 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.9, 136.6, 133.1 (q, *J* = 34.3 Hz), 130.5, 127.5, 123.4 – 122.4 (m), 122.8 (q, *J* = 273.2 Hz), 119.4, 114.2. **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -66.11 (s). **HRMS-APCI** calculated for $[C_{14}H_7N_3F_6]^+$ 347.0493 found: 347.0497

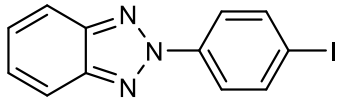
2*H*-2-(4-Cyanophenyl)benzo[d]-1,2,3-triazole – 2j[13]



Following **GP I** with 45.4 mg of **1j**, 23.1 mg NBu_4BF_4 and 300 µl of Et_3N (12 equiv.) in 5 mL 3:2 THF:MeOH. After passing 6.6 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 18:1 -> 9:1 cyclohexane:ethyl acetate as eluents afforded 17.9 mg (45%, 0.081 mmol) of **2j** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.58 – 8.46s (m, 2H), 8.00 – 7.84 (m, 3H), 7.91 – 7.81 (m, 2H), 7.51 – 7.42 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.6, 143.1, 133.7, 128.3, 121.1, 118.7, 118.2, 112.5. **HRMS-ESI** calculated for $[C_{13}H_8N_4]^+$ 220.0749 found: 220.0749

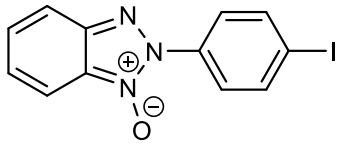
2*H*-2-(4-Iodophenyl)benzo[d]-1,2,3-triazole – 2k



Following **GP I** with 61.3 mg of **1k**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 8.6 F with a current density of 4.1 mA cm^{-2}, the purification of the crude material by flash chromatography using 0:1 -> 100:1 -> 75:1 cyclohexane:ethyl acetate as eluents afforded 20.6 mg of a mixture containing the desired **2k** (12%, 0.0214 mmol) and the dehalogenated **2b** (39%, 0.07 mmol). **2k** and **2b** were obtained as a colorless solid. We were unable to separate **2k** from **2b**. Characterization of **2k** is based on HRMS-MS, crude material ^{1}H NMR, and spectral data and isolation of **3k**.

HRMS-APCI calculated for $[C_{12}H_8N_3I]^+$ 320.9763 found: 320.9757

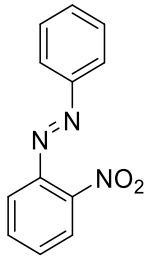
2*H*-2-(4-Iodophenyl)benzo[d]-1,2,3-triazole 1-oxide – 3k



Following **GP I** with 63.6 mg of **1k**, 23.0 mg NBu_4BF_4 and 20 mg NaOH in 5 mL 3:2 THF:MeOH. After passing 5.2 F with a current density of 2.4 mA cm^{-2}, the purification of the crude material by flash chromatography using 9:1 cyclohexane:ethyl acetate as eluents afforded 44.7 mg (74%, 0.133 mmol) of **3k** as a colorless solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.05 – 7.98 (m, 2H), 7.97 – 7.91 (m, 2H), 7.83 – 7.74 (m, 2H), 7.51 – 7.43 (m, 2H), 7.41 – 7.34 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.4, 138.5, 135.1, 129.6, 2x 126.8$^{\#}$, 124.8, 119.2, 114.1, 95.8. **HRMS-ESI** calculated for $[C_{12}H_8N_3IO]^+$ 336.9712 found: 336.9712
= Identified by ^{1}H-^{13}C HMBC

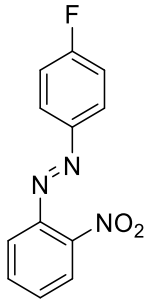
2-Nitroazobenzene – 1b[2]



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1g), aniline (6 mmol, 559 mg), and 20 mL AcOH. The reaction mixture was quenched with saturated solution of $NaHCO_3$, extracted with 3x100 mL EtOAc, washed with brine and dried over Na_2SO_4. After purification of the crude material by flash column chromatography (SiO_2) using 50:1 cyclohexane:ethyl acetate as eluents, **1b** was obtained in 81% yield (1.11 g) as a bright orange solid. Spectroscopic data are in agreement with the literature[2]

^{1}H NMR (300 MHz, Chloroform-d) δ 7.98 – 7.90 (m, 3H), 7.74 – 7.65 (m, 2H), 7.61 – 7.51 (m, 4H).

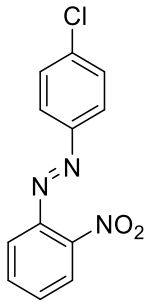
4'-Fluoro-2-nitroazobenzene – 1a



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1g), 4-fluoroaniline (6 mmol, 666 mg), and 20 mL AcOH. The reaction mixture was quenched with saturated solution of $NaHCO_3$, extracted with 3x100 mL EtOAc, washed with brine and dried over Na_2SO_4. After purification of the crude material by flash column chromatography (SiO_2) using 50:1 cyclohexane:ethyl acetate as eluents, **1a** was obtained in 83% yield (1.22 g) as a bright orange solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 – 7.90 (m, 3H), 7.73 – 7.64 (m, 2H), 7.61 – 7.54 (m, 1H), 7.25 – 7.17 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.3 (d, *J* = 254.3 Hz), 149.2 (d, *J* = 3.0 Hz), 147.4, 145.4, 133.2, 130.6, 126.0 (d, *J* = 9.2 Hz), 124.3, 118.5, 116.5 (d, *J* = 23.1 Hz). **^{19}F NMR** (282 MHz, Chloroform-d) δ -110.01 (tt, $J_{H,F}$ = 8.2, 5.2 Hz) **HRMS-APPI** calculated for $[C_{12}H_8FN_3O_2]^+$ 245.0601 found: 245.0597

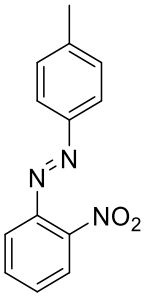
4'-Chloro-2-nitroazobenzene – 1c[11]



Following **GP III** with 1-nitro-2-nitrosobenzene (5.14 mmol, 782 mg), 4-chloroaniline (4.67 mmol, 595 mg), and 15 mL AcOH. After workup and purification of the crude material by flash column chromatography (SiO_2) using 50:1 -> 20:1 -> 10:1 cyclohexane:ethyl acetate as eluents, **1c** was obtained in 86% yield (1.04 g) as an orange solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 1H), 7.91 – 7.85 (m, 2H), 7.73 – 7.64 (m, 2H), 7.63 – 7.56 (m, 1H), 7.54 – 7.48 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.9, 147.7, 145.3, 138.6, 133.2, 130.9, 129.7, 125.0, 124.3, 118.5. **HRMS-APPI** calculated for $[C_{12}H_8{}^{35}ClN_3O_2]^+$ 261.0305 found: 261.0307

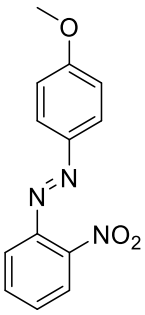
4'-Methyl-2-nitroazobenzene – 1d[11]



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1g), 4-methylaniline (6 mmol, 643 mg), and 20 mL AcOH. After workup and purification of the crude material by flash column chromatography (SiO_2) using 50:1 cyclohexane:ethyl acetate as eluents, **1d** was obtained in 71% yield (1.03 g) as a bright orange solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.90 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.61 (m, 2H), 7.61 – 7.47 (m, 1H), 7.37 – 7.26 (m, 2H), 2.44 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.7, 147.5, 145.6, 143.3, 133.1, 130.2, 130.0, 123.0, 124.1, 123.8, 118.6, 21.7. **HRMS-APCI** calculated for $[C_{13}H_{11}N_3O_2]^+$ 241.0851 found: 241.0848

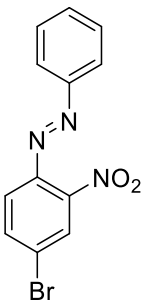
4'-Methoxy-2-nitroazobenzene – 1e[3]



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1g), 4-methoxylaniline (6 mmol, 739 mg), and 20 mL AcOH. After workup and purification of the crude material by flash column chromatography (SiO_2) using 50:1 -> 20:1 -> 10:1 cyclohexane:ethyl acetate as eluents, **1e** was obtained in 82% yield (1.27 g) as a brown solid. Spectroscopic data are in agreement with the literature[3]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.98 – 7.86 (m, 3H), 7.70 – 7.62 (m, 2H), 7.57 – 7.48 (m, 1H), 7.07 – 6.96 (m, 2H), 3.91 (s, 3H). **HRMS-ESI:** calculated for $[C_{13}H_{12}N_3O_3]^+$ 258.0800 found: 257.0806

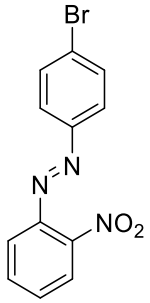
4-Bromo-2-nitroazobenzene – 1f



Following **GP III** with 5-bromo-1-nitro-2-nitrosobenzene (5.2 mmol, 1.2 g), aniline (4.74 mmol, 441 mg), and 17 mL AcOH. After workup and purification of the crude material by flash column chromatography (SiO_2) using 50:1 cyclohexane:ethyl acetate as eluents, **1f** was obtained in 69% yield (1.04 g) as a brick-red colored solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 2.0 Hz, 1H), 7.99 – 7.87 (m, 2H), 7.82 (d, *J* = 2.1 Hz, 0H), 7.79 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.48 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.5, 148.2, 144.1, 136.2, 132.8, 129.5, 127.1, 124.1, 123.9, 119.9. **HRMS-APPI** calculated for $[C_{12}H_8{}^{79}BrN_3O_2]^+$ 304.9800 found: 304.9794

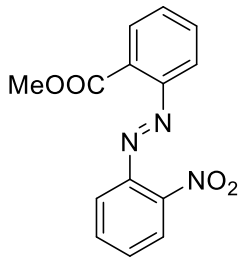
4'-Bromo-2-nitroazobenzene – 1g[11]



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1g), 4-bromoaniline (6 mmol, 1.032 g), and 20 mL AcOH. After workup and purification of the crude material by flash column chromatography (SiO_2) using 10:1 cyclohexane:ethyl acetate as eluents, **1g** was obtained in 84% yield (1.54 g) as a red-brown solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.97 – 7.90 (m, 1H), 7.84 – 7.77 (m, 2H), 7.71 – 7.66 (m, 3H), 7.67 – 7.64 (m, 1H), 7.63 – 7.55 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.3, 147.7, 145.4, 133.2, 132.7, 130.9, 127.2, 125.2, 124.3, 118.5. **HRMS-ESI** calculated for $[C_{12}H_8N_3O_2{}^{79}Br]^+$ 304.9800 found: 304.9801

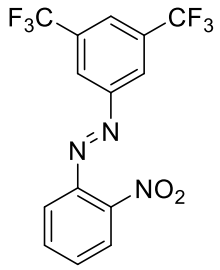
2'-(methoxycarbonyl)-2-nitroazobenzene – 1h



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1 g), anthranilic acid (6 mmol, 822 mg), and 20 mL AcOH. After workup, the reaction mixture was evaporated and dissolved to 70 mL of 6:1 MeOH:H_2SO_4 and refluxed for 3h. The mixture was quenched with K_2CO_3, diluted with H_2O, extracted 3x100 mL of EtOAc and washed with H_2O and brine. After evaporation, the crude was purified with flash column chromatography (SiO_2) using 3:1 cyclohexane:ethyl acetate as eluents, **1h** was obtained in 76% yield (1.31 g) as a red-brown solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 1H), 7.93 – 7.87 (m, 1H), 7.74 – 7.68 (m, 2H), 7.65 – 7.50 (m, 4H), 3.96 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.1, 152.1, 147.2, 146.2, 133.7, 132.7, 131.0, 130.8, 130.2, 129.3, 124.3, 119.3, 118.4, 52.8. **HRMS-APCI** calculated for $[C_{14}H_{11}N_3O_4]^+$ 285.0750 found: 285.0752

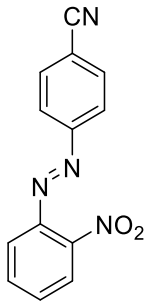
3',5'-Di(trifluoromethyl)-2-nitroazobenzene – 1i



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1g), 3,5-bis(trifluoromethyl)aniline (6 mmol, 1.674 g), and 20 mL AcOH. After workup and purification of the crude material by flash column chromatography (SiO_2) using 50:1 cyclohexane:ethyl acetate as eluents, **1i** was obtained in 67% yield (1.46 g) as a bright orange solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.35 (s, 2H), 8.04 (s, 1H), 8.02 – 7.96 (m, 1H), 7.79 – 7.59 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.6, 147.6, 145.0, 133.5, 133.1 (q, *J* = 34.1 Hz), 132.0, 125.2 (hept, *J* = 3.5 Hz), 124.6, 123.7 (q, *J* = 3.8 Hz), 123.0 (q, *J* = 273.1 Hz), 118.6. **^{19}F NMR** (282 MHz, Chloroform-*d*) δ -66.10 (s). **HRMS-APCI** calculated for $[C_{14}H_7N_3O_2F_6]^+$ 363.0442 found: 363.0441

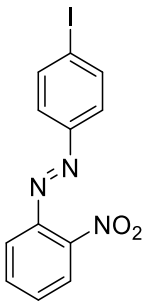
4'-Cyano-2-nitroazobenzene – 1j



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1 g), 4-cyanoaniline (6 mmol, 709 mg), and 20 mL AcOH. After stirring over weekend, the reaction mixture was quenched with saturated solution of $NaHCO_3$, diluted with 100 mL H_2O, extracted with 3x100 mL EtOAc, washed with 100 mL H_2O, 100 mL brine and dried over Na_2SO_4. After purification of the crude material by flash column chromatography (SiO_2) using 50:1 -> 20:1 -> 9:1 -> 3:1 -> 1:1 cyclohexane:ethyl acetate as eluents, **1j** was obtained in 68% yield (1.04 g) as a red-brown solid. Spectroscopic data are in agreement with the literature[4]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 – 7.96 (m, 3H), 7.87 – 7.81 (m, 2H), 7.76 – 7.62 (m, 3H).

4'-Iodo-2-nitroazobenzene – 1k



Following **GP III** with 1-nitro-2-nitrosobenzene (6.6 mmol, 1 g), 4-iodoaniline (6 mmol, 1.314 g), and 20 mL AcOH. After workup and purification of the crude material by flash column chromatography (SiO_2) using 9:1 cyclohexane:ethyl acetate as eluents, **1k** was obtained in 84% yield (1.78 g) as a brick-red colored solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 1H), 7.91 – 7.86 (m, 2H), 7.72 – 7.56 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.8, 147.7, 145.3, 138.7, 133.2, 130.9, 125.2, 125.2, 124.2, 118.4, 99.8. **HRMS-APCI** calculated for $[C_{12}H_8IN_3O_2]^+$ 352.9661 found: 352.9664

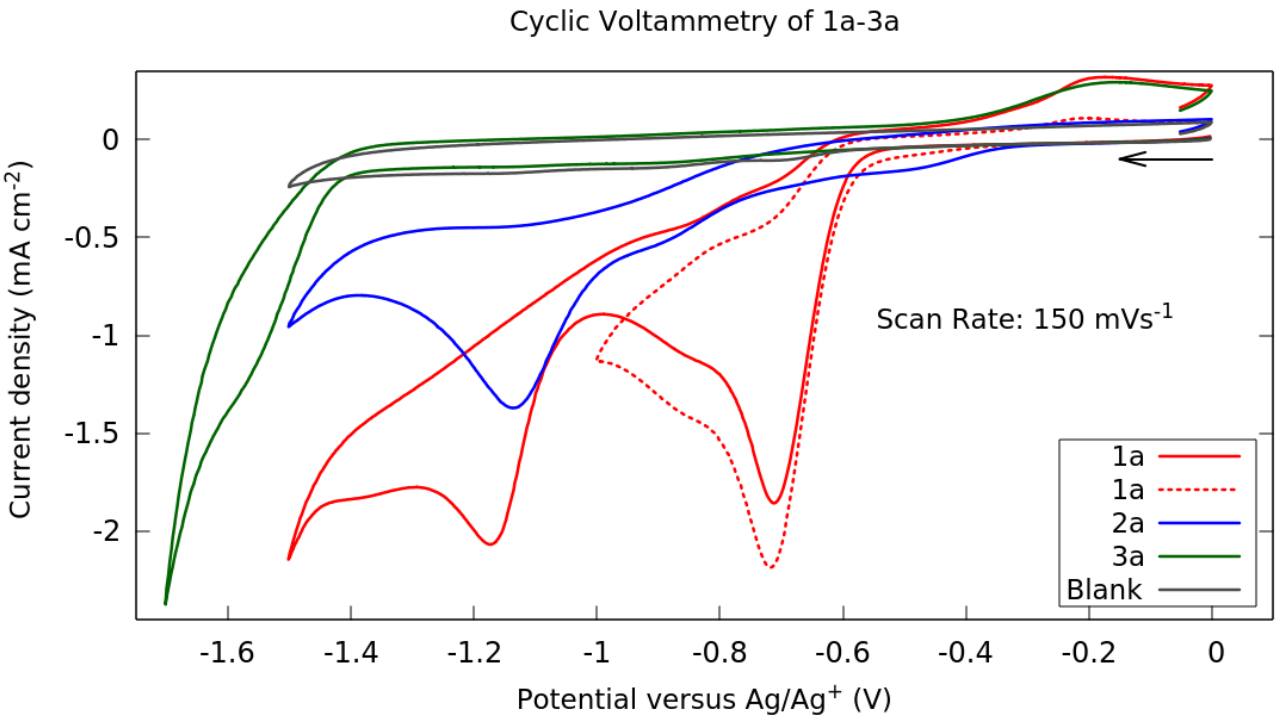
Cyclic Voltammetry:

Cyclic voltammetry was performed with an Autolab PGSTAT101 potentiostat (Metrohm AG, Herisau, Switzerland) in a 10 mL vial using 0.1 M NaOH in methanol as solvent supporting electrolyte system. 1-3a were used as 0.002 M solutions.

Working electrode: Glassy carbon disk (diameter 2 mm)

Counter electrode: Glassy carbon rod

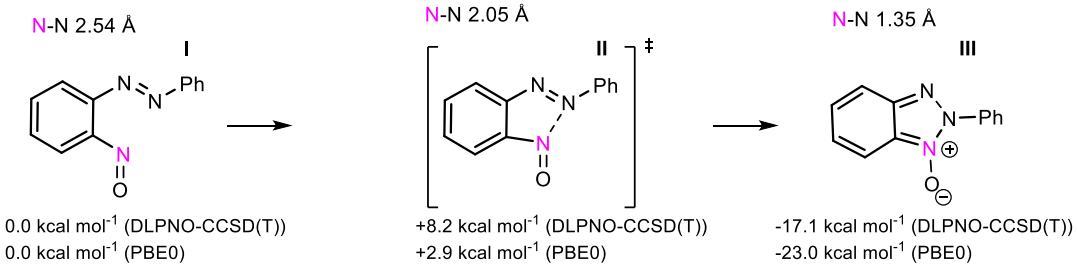
Reference electrode: Ag/AgCl in saturated LiCl/EtOH.



Scheme S3: Cyclic voltammetry of compounds 1a-3a

Computational Studies and xyz-coordinates:

All computations were performed with ORCA 4.1 program package.[14] Geometry optimizations were performed PBE0[15] hybrid functional with def2-TZVP basis sets[16] augmented with atom-pairwise dispersion correction with the Becke-Johnson damping scheme.[17] COSMO[18] solvation model was used with dielectric constants of methanol (32.7). Single point energies were calculated with DLPNO-CCSD(T)[19] level of theory with "TightPNO"[20] thresholds using def2-QZVPP basis sets[16a,21] and SMD[22] solvation model for methanol.



Scheme S4: Gibbs energies for the 5-centered 6π-cyclization with PBE0-D3/def2-TZVP/COSMO(MeOH) and DLPNO-CCSD(T)/def2-QZVPP/SMD(MeOH) // PBE0-D3/def2-TZVP/COSMO(MeOH)

I-xyz

25
i-freq: 0

C	1.02377862809780	2.35707204228287	-0.54156325993944
C	-0.34114995366720	2.15938354365102	-0.46290786362572
C	-0.82988908300085	0.98827317796544	0.12068270134371
C	0.04806575604440	0.02038967316338	0.60282813561065
C	1.41543189071513	0.22950284251285	0.52565548999740
C	1.90332506417737	1.39718665256811	-0.04518301200085
N	-2.19615171073396	0.68718244666871	0.25363158172999
N	-2.99011963432873	1.61998723287700	0.02843535130479
C	-4.32620269558015	1.24251159984096	0.02398129653088
C	-4.72932178250897	-0.05429581207455	-0.34490219216787
C	-6.07731065516234	-0.40356712011709	-0.30205718158771
C	-7.01417837516741	0.52554091358419	0.10587186153617
C	-6.61654064225307	1.81565944493285	0.45736797001511
C	-5.28390731787968	2.17919265875476	0.40131448247043
N	-3.77640754717571	-0.91487659076516	-0.93494974074429
O	-3.99069312680974	-2.10113104121910	-0.82348121618097
H	-6.36867819009247	-1.39321705102712	-0.63294913296044
H	-4.95973868400679	3.17579954735763	0.67547166197946
H	-8.06347260961565	0.25760466147267	0.13271572937520
H	-7.35777825043450	2.54138147328790	0.76953516535765
H	-1.03540518166585	2.89477535795946	-0.84906993441541
H	-0.36009314041511	-0.88375901257196	1.03929355623924
H	2.10016323580145	-0.51862358728602	0.90675688902120
H	2.97262293410518	1.56143014596704	-0.11163162060843
H	1.41190107155687	3.26169680021414	-0.99486671828076

II-xyz

25

i-freq: -129.60 cm^{-1}

C	0.97272327291108	2.26720706143456	-0.54722086163626
C	-0.38990406046298	2.18411832299125	-0.33097164301878
C	-0.92284151255150	1.01304728073225	0.20946290516404
C	-0.09983968800819	-0.06836491556581	0.51626456154719
C	1.26277353294519	0.02283112573685	0.28805098966138
C	1.79943473818014	1.18940747589109	-0.24148436847853
N	-2.29032781072240	0.83328899367814	0.45263738903663
N	-3.05607435107355	1.83073528664957	0.39564257779296
C	-4.35691406352426	1.44137051550762	0.26187002699242
C	-4.55304733885289	0.10783608662043	-0.15151376627257
C	-5.84293958033996	-0.39882849870534	-0.32458950584561
C	-6.91111953038821	0.43948616623569	-0.09443258845485
C	-6.71727158724099	1.77700675478881	0.29234481217935
C	-5.45071592736111	2.28805889942966	0.46095988206432
N	-3.40843034669200	-0.55348655358198	-0.56436138433611
O	-3.29548732319544	-1.76013317943791	-0.45881257934821
H	-5.97689149473195	-1.41965824434959	-0.66169316805825
H	-5.28475695535715	3.31454117086957	0.76458308391610
H	-7.92024983071915	0.06576039409416	-0.22168070148539
H	-7.57952676496829	2.41046768190631	0.46108779050533
H	-1.04816015214391	3.00794493088394	-0.57586868254052
H	-0.54227219752717	-0.96647461890816	0.93052275411540
H	1.90736822252013	-0.81520792262305	0.52432457480658
H	2.86591859646292	1.26118283140526	-0.42070709041232
H	1.39680215284166	3.17296295431669	-0.96443500789430

III-xyz

25

i-freq: 0

C	0.99258034433042	2.14152491468404	-0.57223261967947
C	-0.39044939513026	2.09628179026647	-0.51918208689784
C	-1.00760619031543	0.95534422396346	-0.02358375133214
C	-0.27218087006677	-0.13595713849783	0.41875743834252
C	1.11076096513929	-0.07683429734203	0.35076284952031
C	1.74441146520316	1.05573737501919	-0.14294733792341
N	-2.41921118642143	0.95210828447862	0.05755812853852
N	-3.11826988549249	2.02079982532654	0.40329262416755
C	-4.39673308438002	1.63220155653502	0.30870543439014
C	-4.46676919239851	0.28928963920626	-0.10766788961057
C	-5.67078339554315	-0.39870762208741	-0.29628071989548
C	-6.80961601698114	0.31856394050530	-0.04457128674248
C	-6.76317018430848	1.67525630050481	0.37947772517156
C	-5.58484875544337	2.34633408239446	0.56218916198476
N	-3.18354720016927	-0.11458218157697	-0.26971427349978
O	-2.72782372651376	-1.21685958718544	-0.66414736761733
H	-5.68714052148167	-1.43102338381714	-0.62061017949594
H	-5.55417427113439	3.37967187360774	0.88447082014322
H	-7.77647099455290	-0.15356564856659	-0.16965112138587
H	-7.69978214761371	2.18890465928228	0.56171746890265
H	-0.99267060255866	2.93018708085622	-0.85522120272380
H	-0.77256174446604	-1.00916300012568	0.81151090528122
H	1.69516890061140	-0.92147275106534	0.69537399832668
H	2.82626288507175	1.09351617698012	-0.19094112794180
H	1.48287480461546	3.02754388665392	-0.95708559002324

References

[1] C. Gütz, M. Bänziger, C. Bucher, T. R. Galvão, S. R. Waldvogel, *Org. Process Res. Dev.* **2015**, *19*, 1428–1433.

[2] S. Bellotto, R. Reuter, C. Heinis, H. A. Wegner, *J. Org. Chem.* **2011**, *76*, 9826–9834.

[3] T. V. Nykaza, T. S. Harrison, A. Ghosh, R. A. Putnik, A. T. Radosevich, *J. Am. Chem. Soc.* **2017**, *139*, 6839–6842.

[4] J. Dong, B. Jin, P. Sun, *Org. Lett* **2014**, *16*, 4540–4542.

[5] H.-J. Niclas, B. Góhrmann, *Synthetic Commun.* **1989**, *19*, 2141–2149.

[6] E. Nagaradja, F. Chevallier, T. Roisnel, V. Dorcet, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis, F. Mongin, *Org. Biomol. Chem.* **2014**, *12*, 1475–1487.

[7] R. Pretot, R. Kolly, T. Schafer, Van Der Schaaf, Paul Adriaan. Electroluminescent Metal Complexes With Triazoles(US 2009/0062560 A1).

[8] S. Riedmüller, B. Nachtsheim, *Synlett* **2015**, *26*, 651–655.

[9] J. Tanabe, C. Lennartz, Fluorescent Organic Light Emitting Elements Having High Efficiency (US 9,853,224 B2).

[10] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, R. J. G. Searle, *J. Chem. Soc.* **1965**, 4831–4837.

[11] E. Bamberger, R. Hübner, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3822–3827.

[12] T. Ryu, J. Min, W. Choi, W. H. Jeon, P. H. Lee, *Org. Lett.* **2014**, *16*, 2810–2813.

[13] J. H. Hall, F. W. Dolan, *J. Org. Chem.* **1978**, *43*, 4608–4612.

[14] F. Neese, *WIREs. Comput. Mol. Sci.* **2017**, *8*, e1327.

[15] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.

[16] a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297– 3305; b) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065

[17] a) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465; S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[18] A. Schäfer, A. Klamt, D. Sattel, J. C. W. Lohrenz, F. Eckert, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2187-2193.

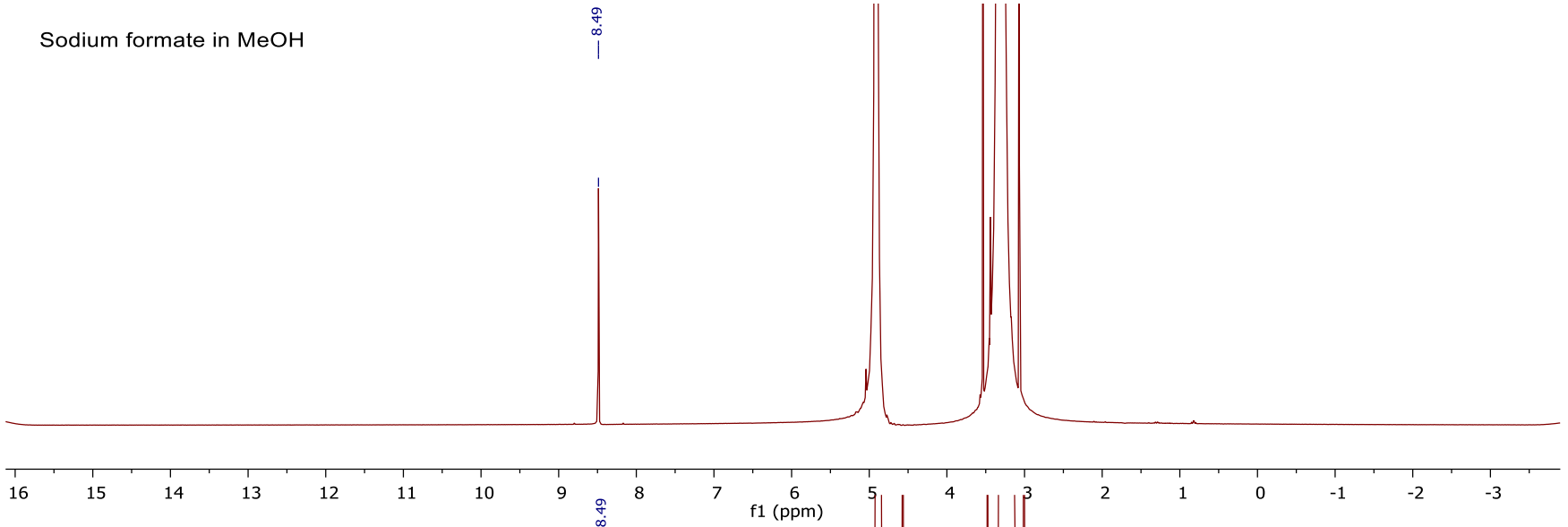
[19] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese *J. Chem. Phys.* **2016**, *144*, 024109.

[20] D. G. Liakos, M. Sparta, M. K Kesharwani, J. M. L. Martin, F. Neese *J. Chem. Theory Comput.* **2015**, 11, 4, 1525-1539

[21] A. Hellweg, C. Hattig, S. Hofener and W. Klopper, *Theor. Chem. Acc.* **2007**, *117*, 587-597

[22] A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

NMR-spectra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8.49
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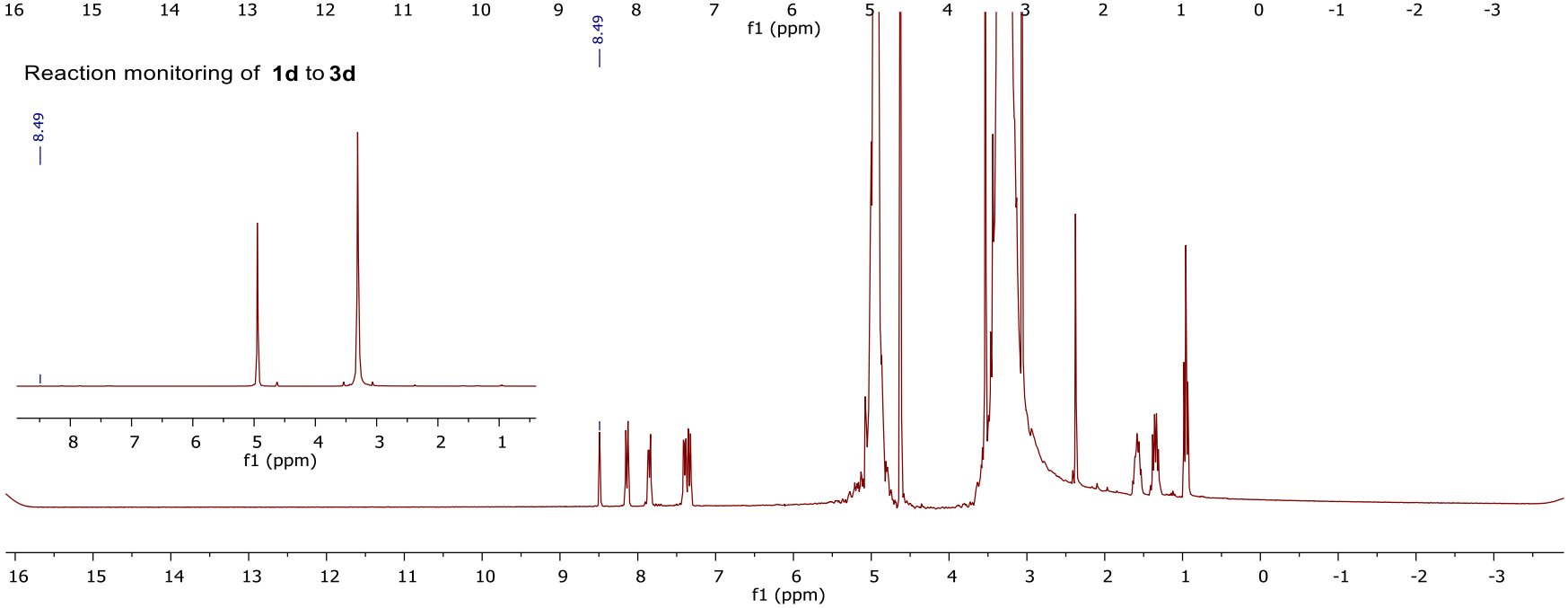
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f1 (ppm)
8.49
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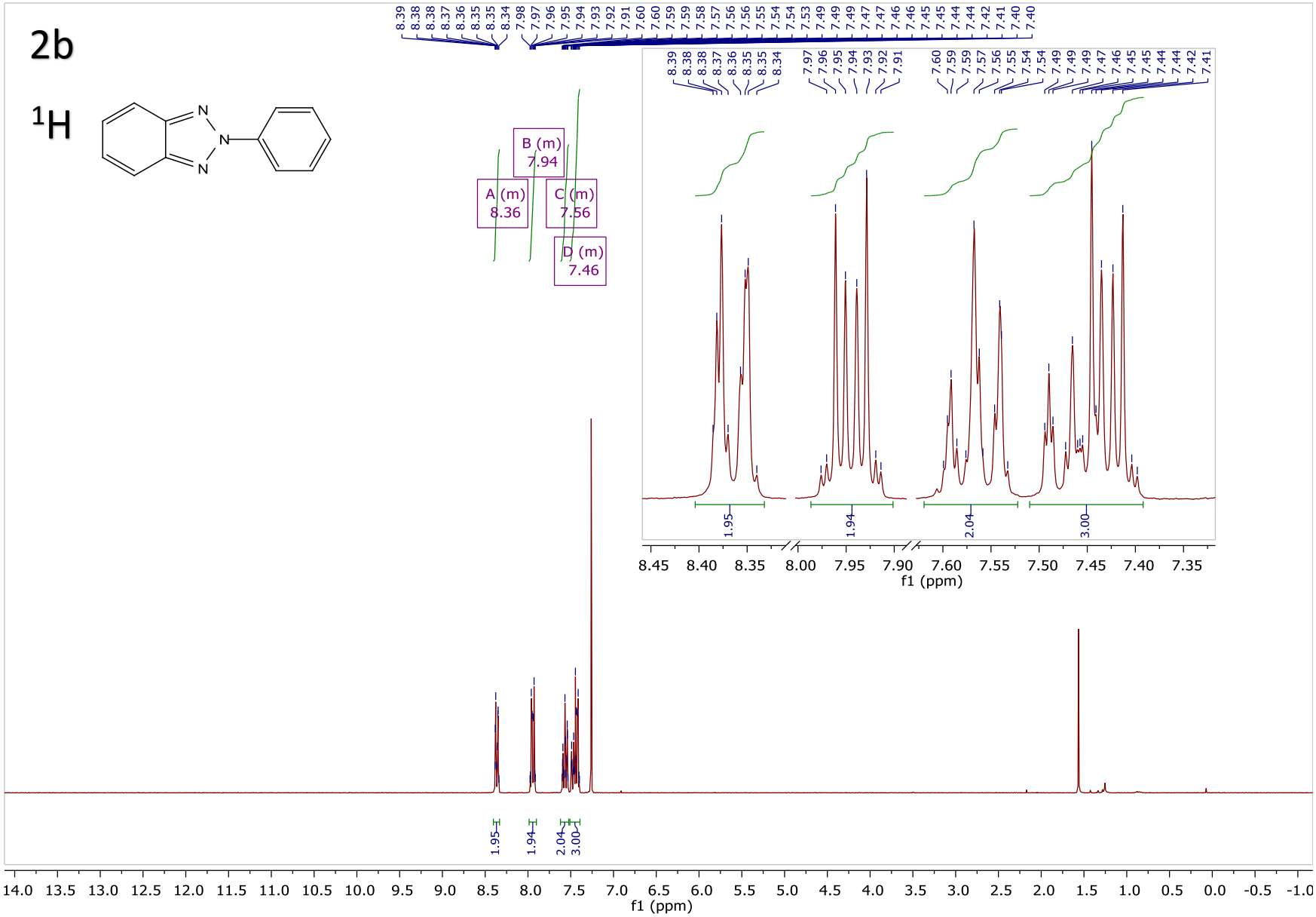
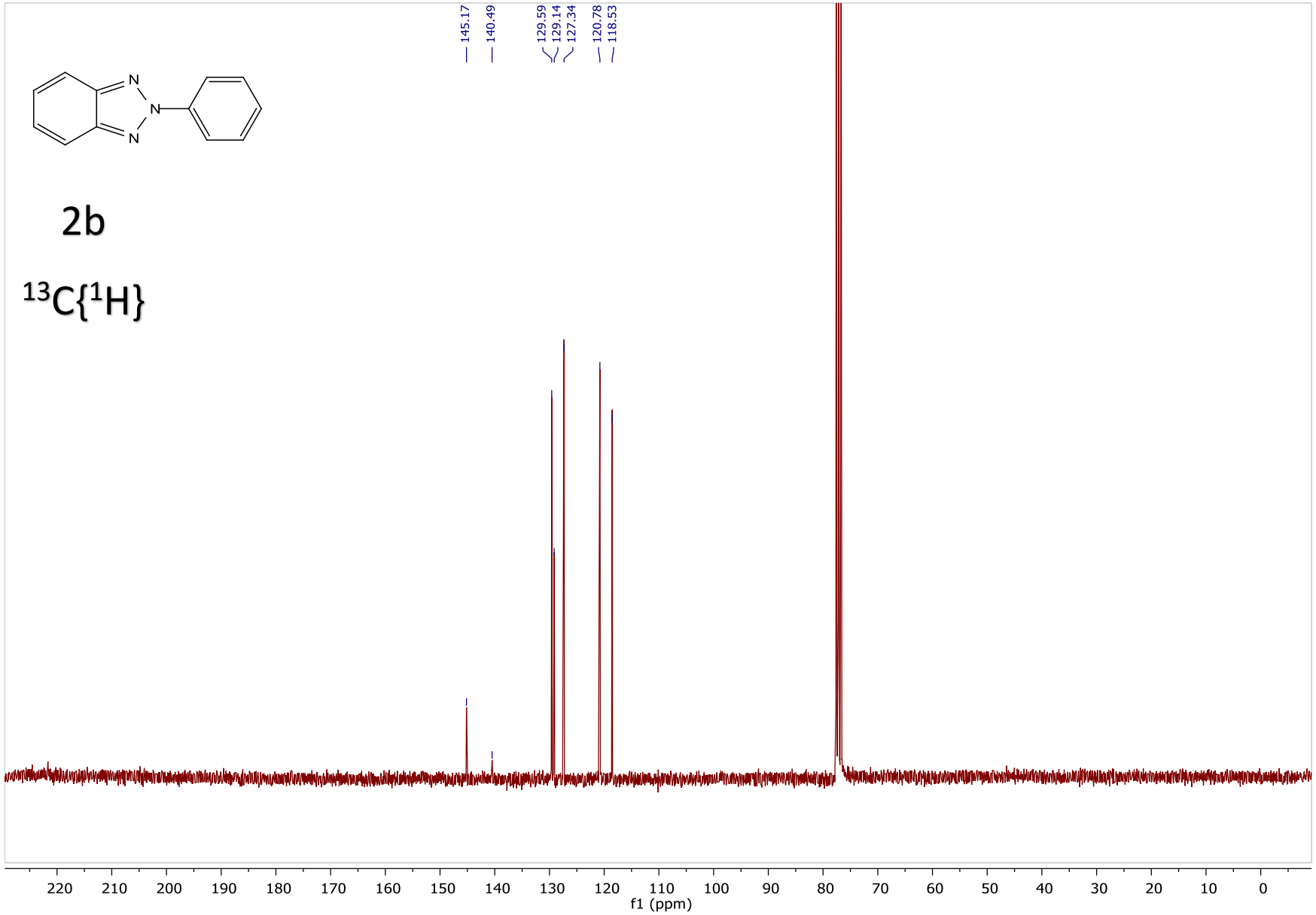
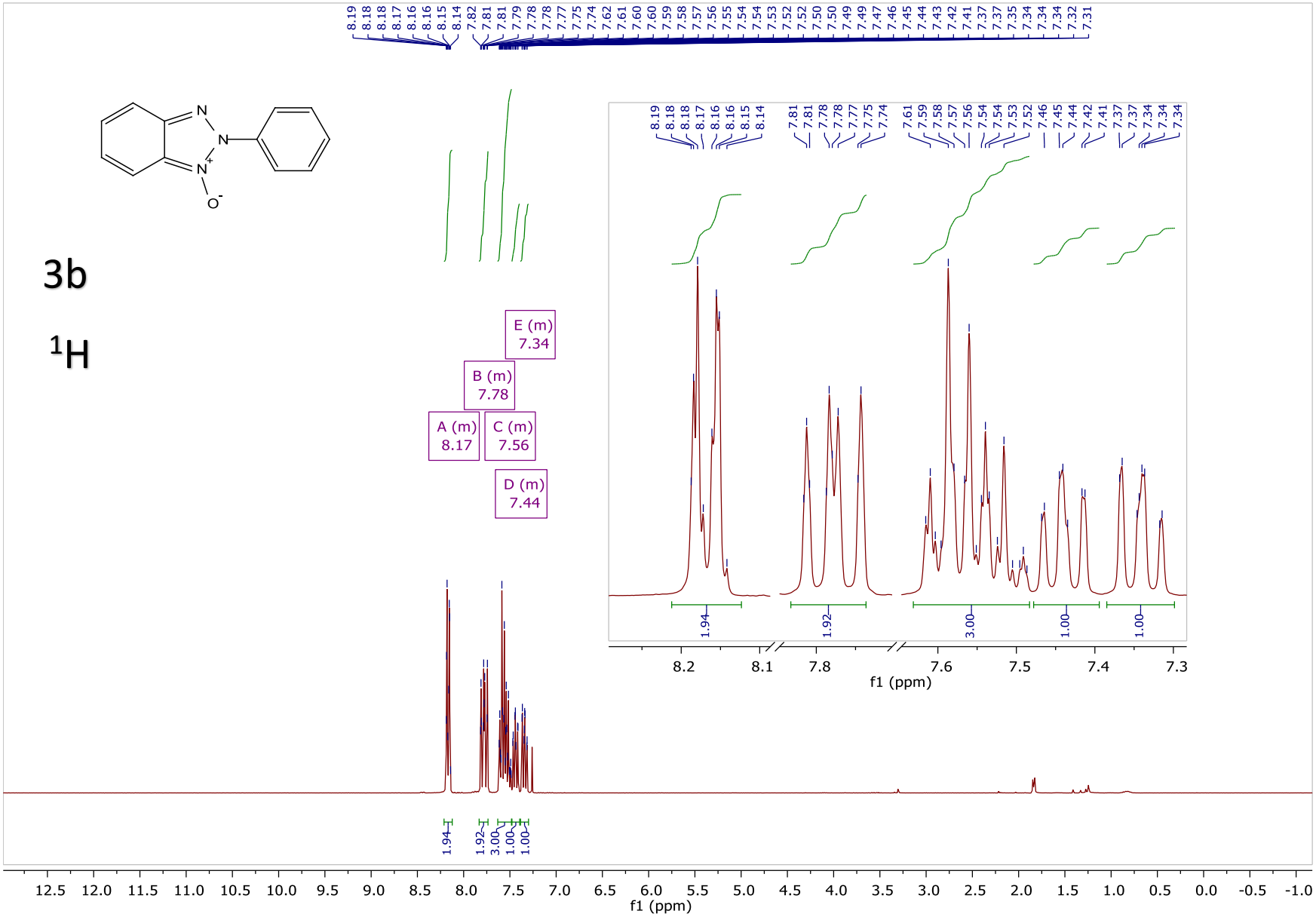
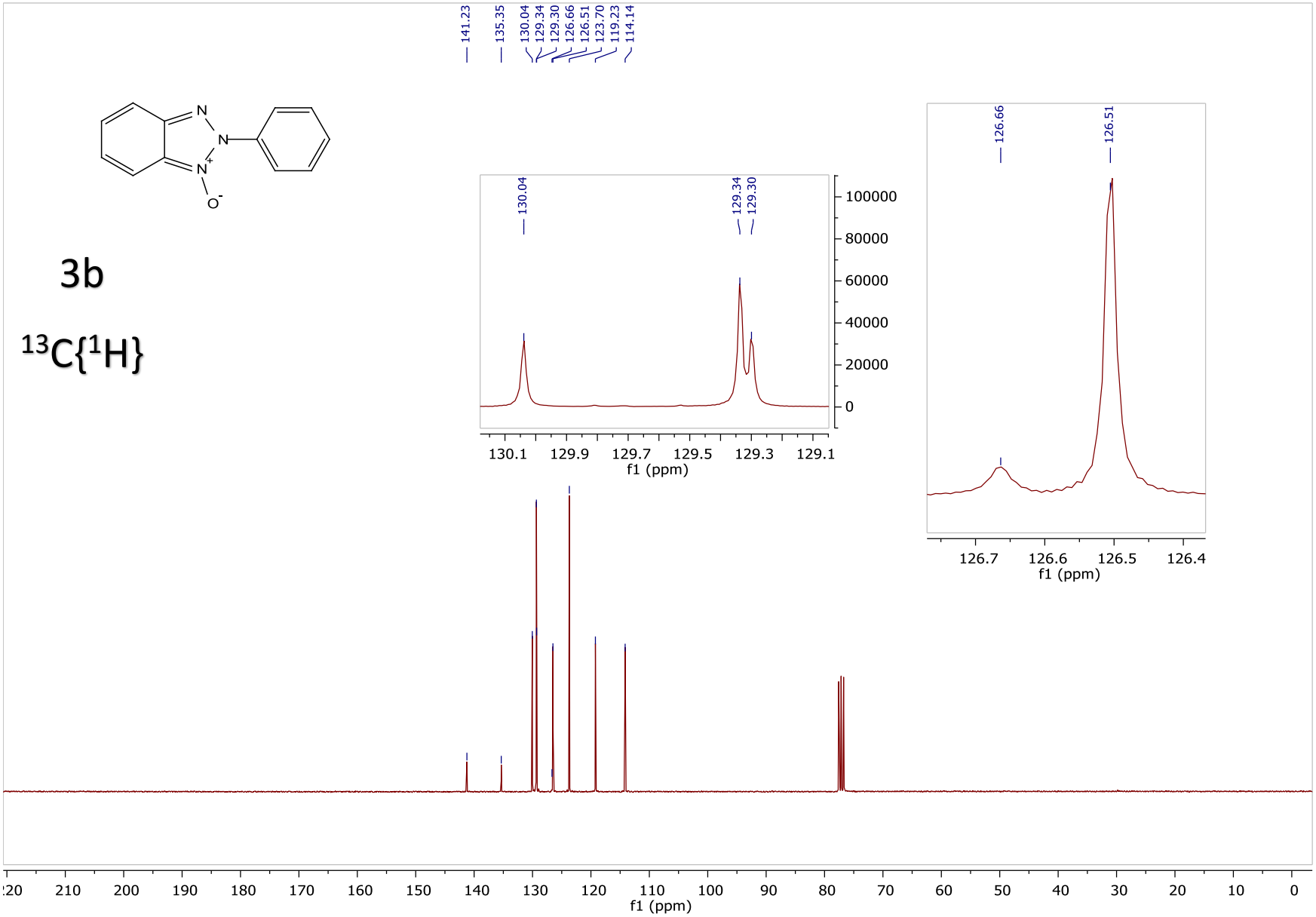
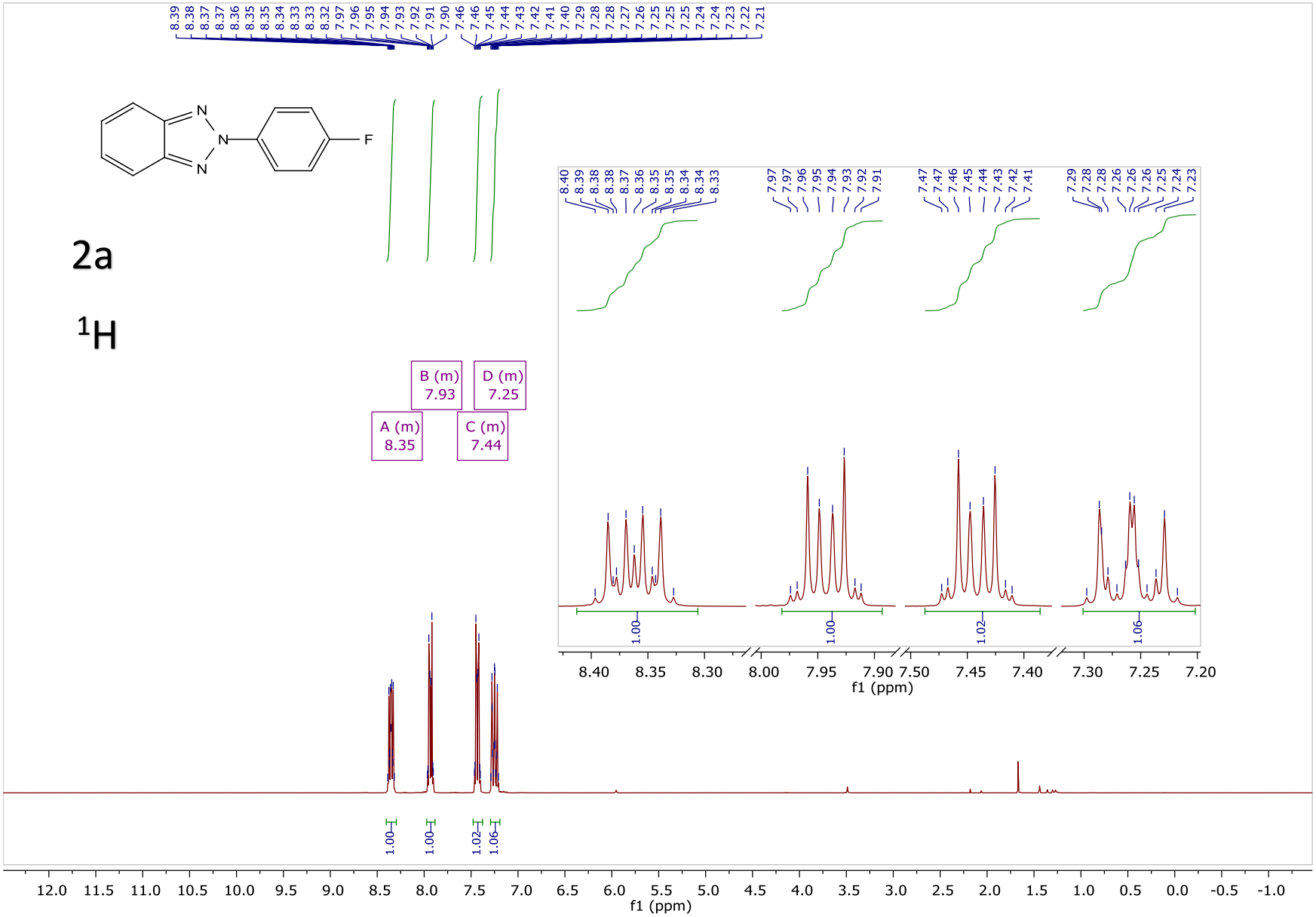
f1 (ppm)


2b
^{1}H
B (m)
7.94
A (m)
8.36
C (m)
7.56
D (m)
7.46
f1 (ppm)


145.17
140.49
129.59
129.14
127.34
120.78
118.53
N
N
N
2b
13C{1H}
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3b
^{1}H
E (m)
7.34
B (m)
7.78
A (m)
8.17
C (m)
7.56
D (m)
7.44
1.94
1.92
3.00
1.00
1.00
f1 (ppm)


141.23
135.35
130.04
129.34
129.30
126.66
126.51
123.70
119.23
114.14
N
N
N+
O-
3b
13C{1H}
130.04
129.34
129.30
100000
80000
60000
40000
20000
0
130.1
129.9
129.7
129.5
129.3
129.1
f1 (ppm)
126.66
126.51
126.7
126.6
126.5
126.4
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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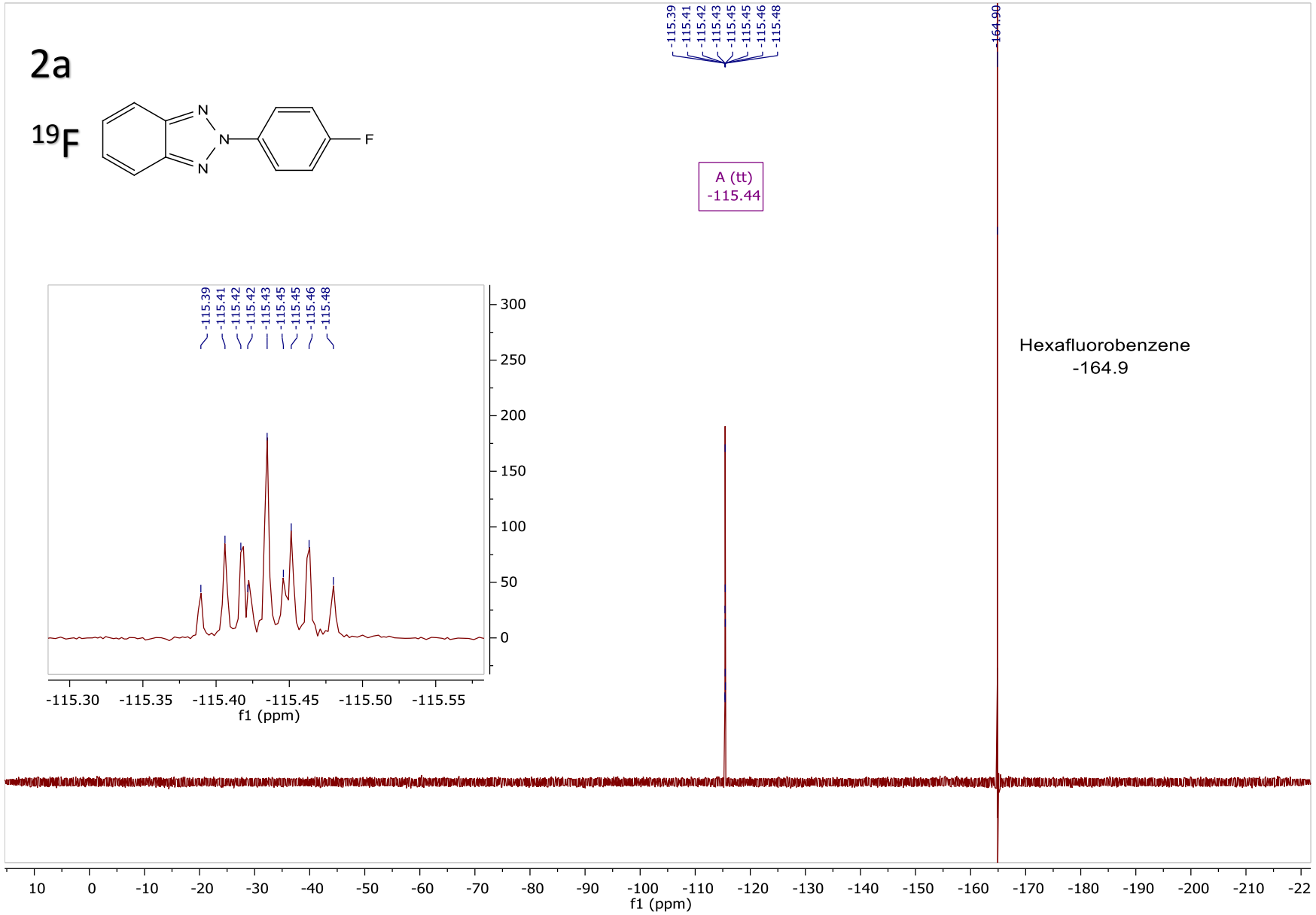
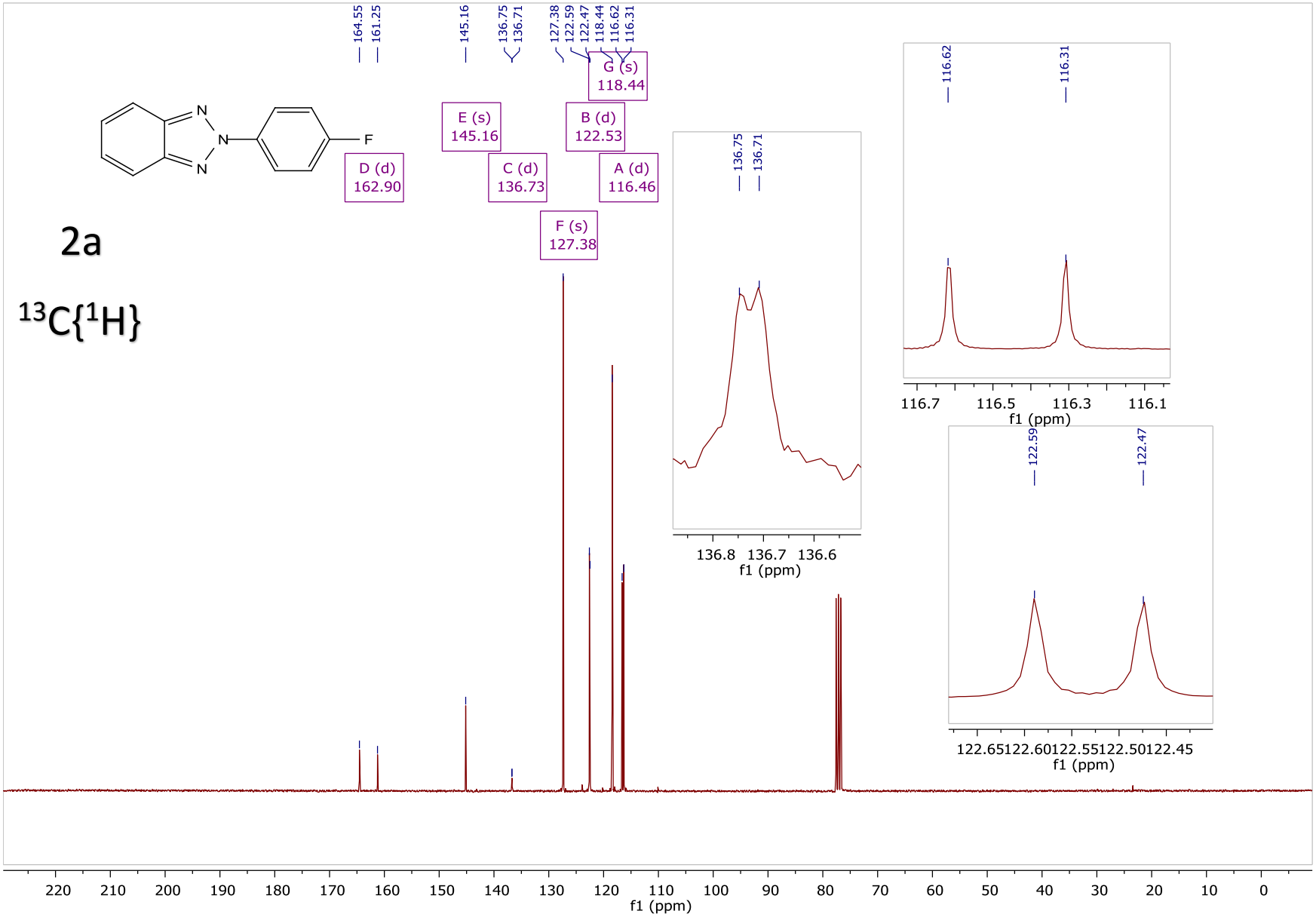
N
N
N
F
2a
1H
B (m) 7.93
D (m) 7.25
A (m) 8.35
C (m) 7.44
8.40 8.39 8.38 8.38 8.37 8.36 8.35 8.35 8.34 8.34 8.33
7.97 7.97 7.96 7.95 7.94 7.93 7.92 7.91
7.47 7.47 7.46 7.45 7.44 7.43 7.42 7.41
7.29 7.28 7.28 7.26 7.26 7.26 7.25 7.24 7.23
1.00
1.00
1.02
1.06
8.40 8.35 8.30 8.00 7.95 7.90 7.50 7.45 7.40 7.30 7.25 7.20
f1 (ppm)
1.00
1.00
1.02
1.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


2a
19F
N
N
N
F
-115.39
-115.41
-115.42
-115.43
-115.45
-115.45
-115.46
-115.48
-164.90
A (tt)
-115.44
Hexafluorobenzene
-164.9
300
250
200
150
100
50
0
-115.30
-115.35
-115.40
-115.45
-115.50
-115.55
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)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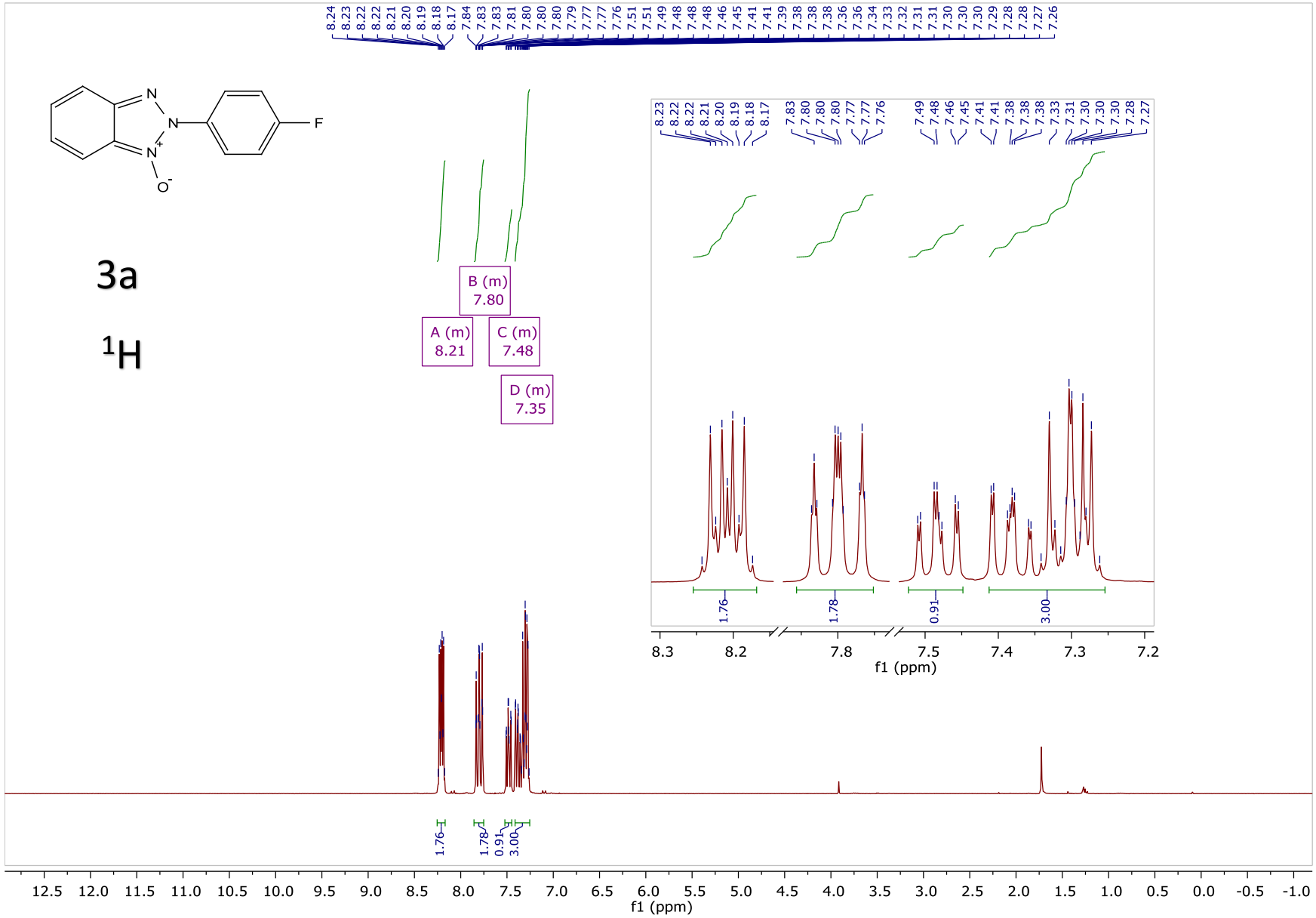
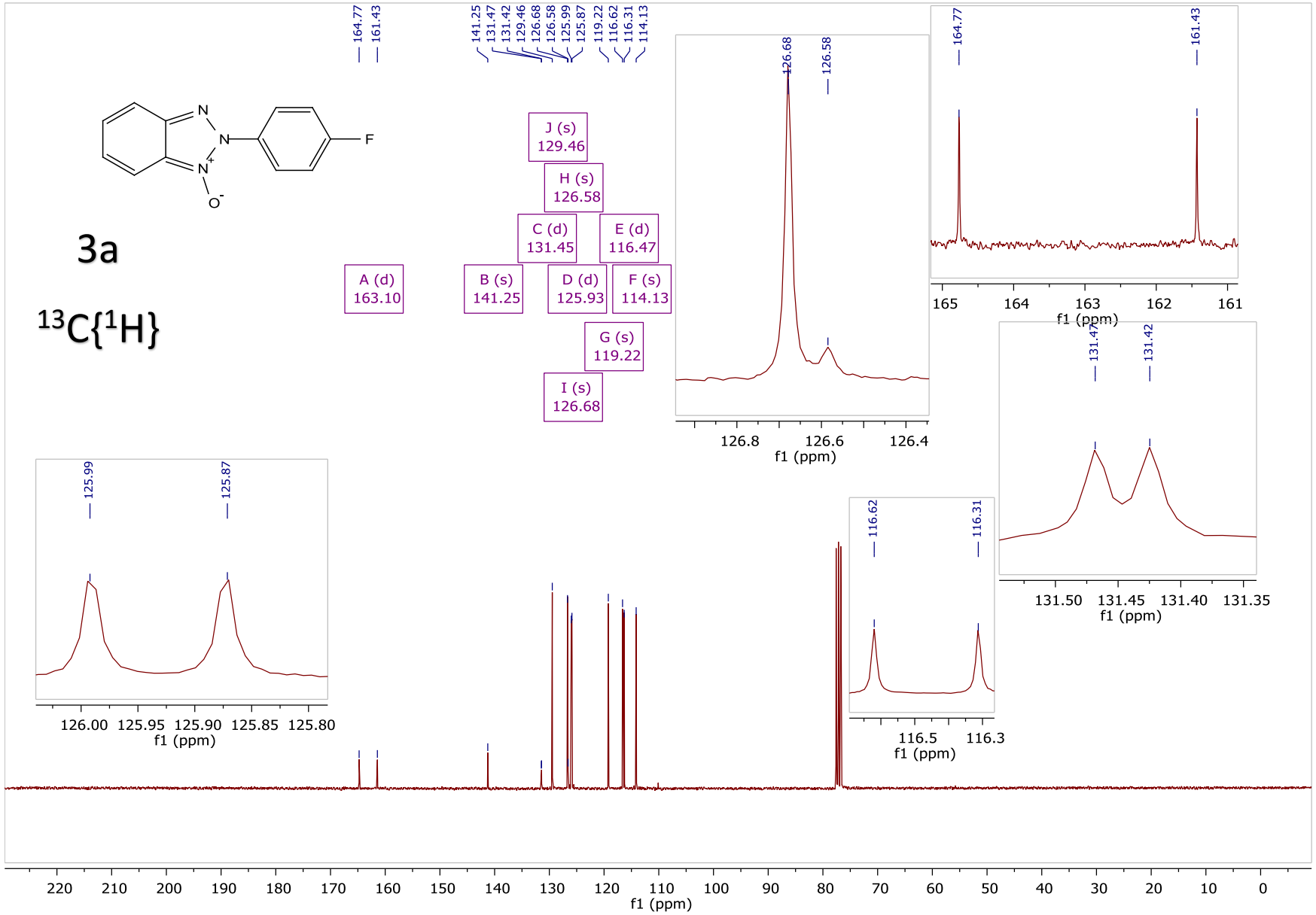
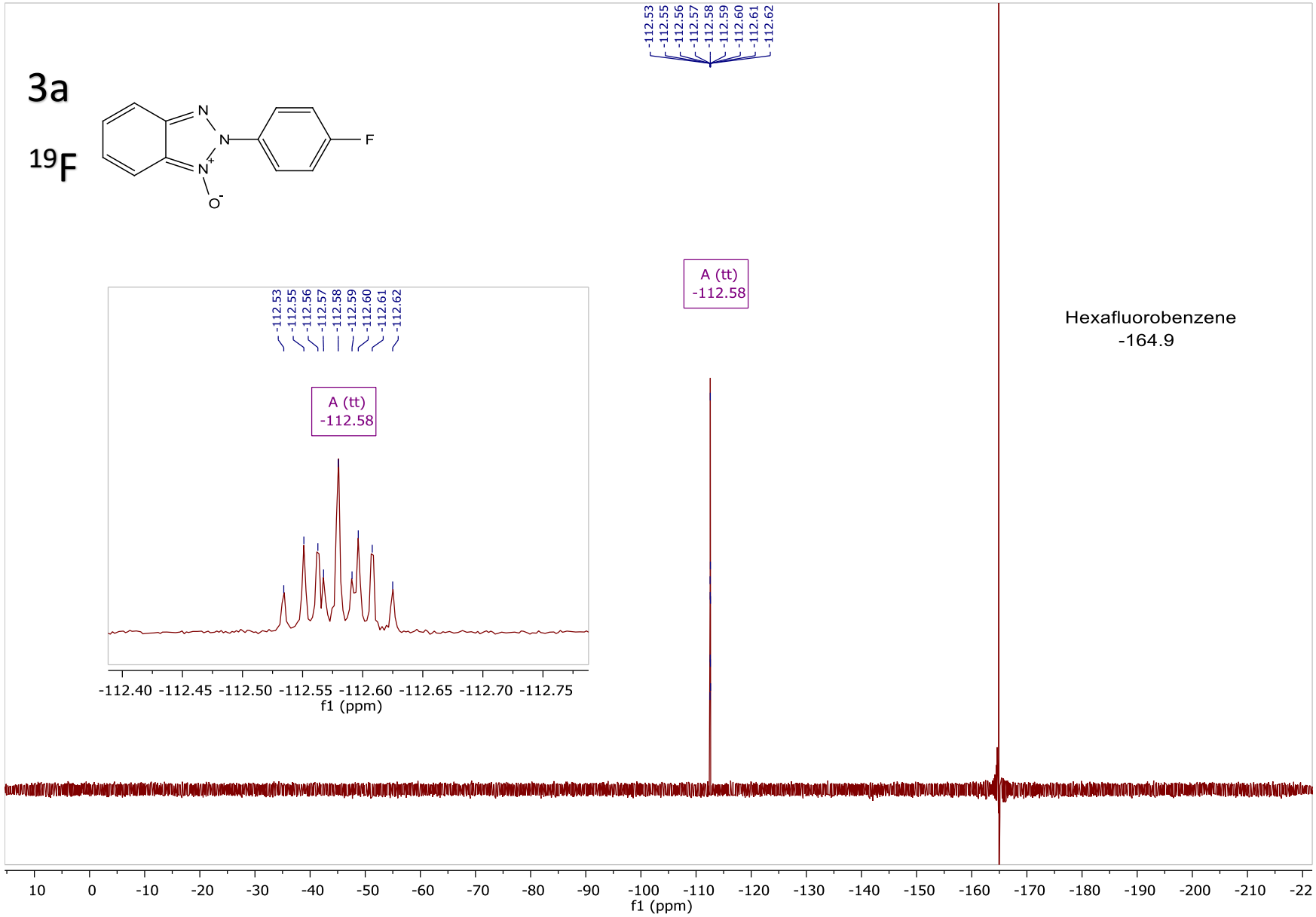
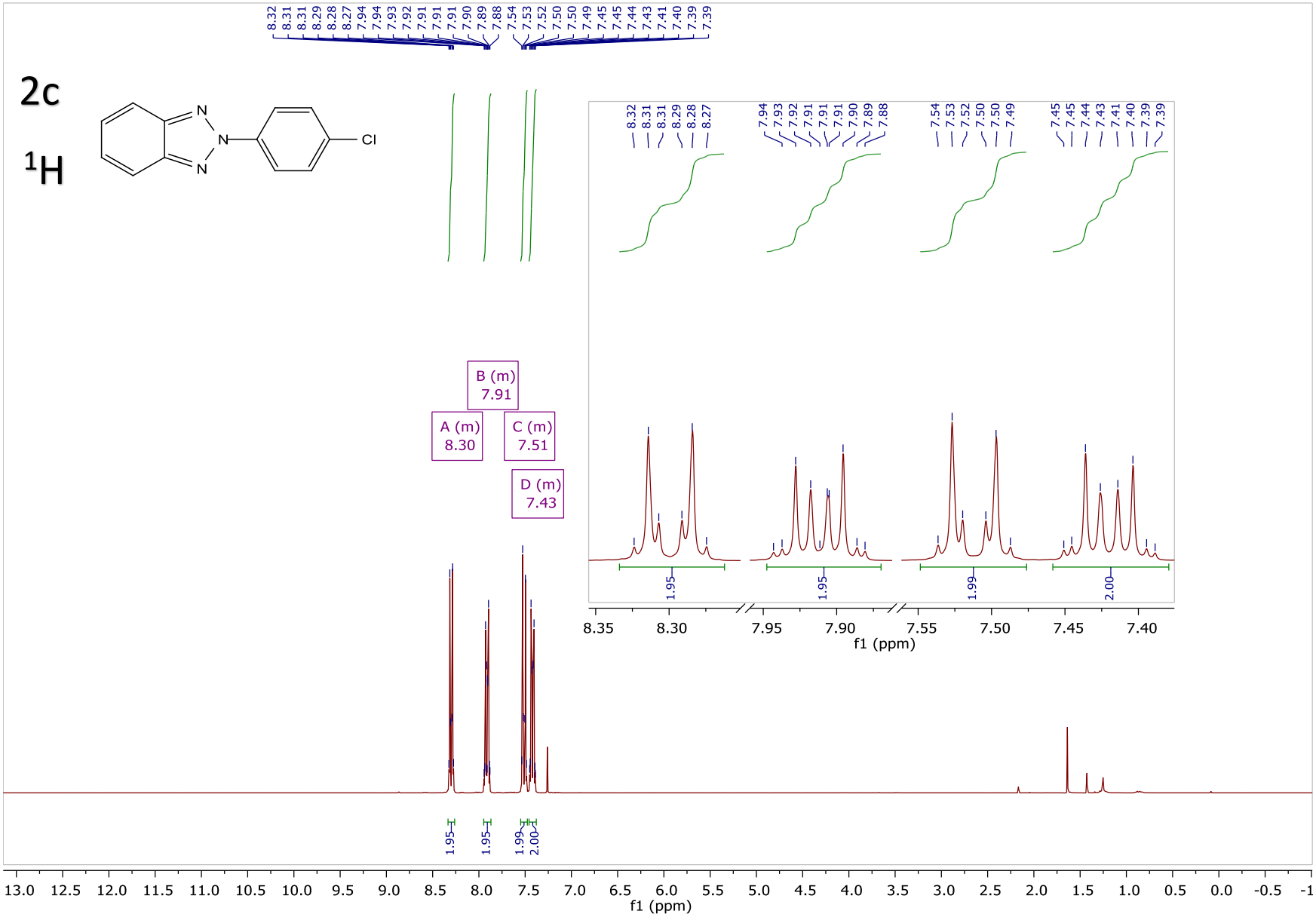
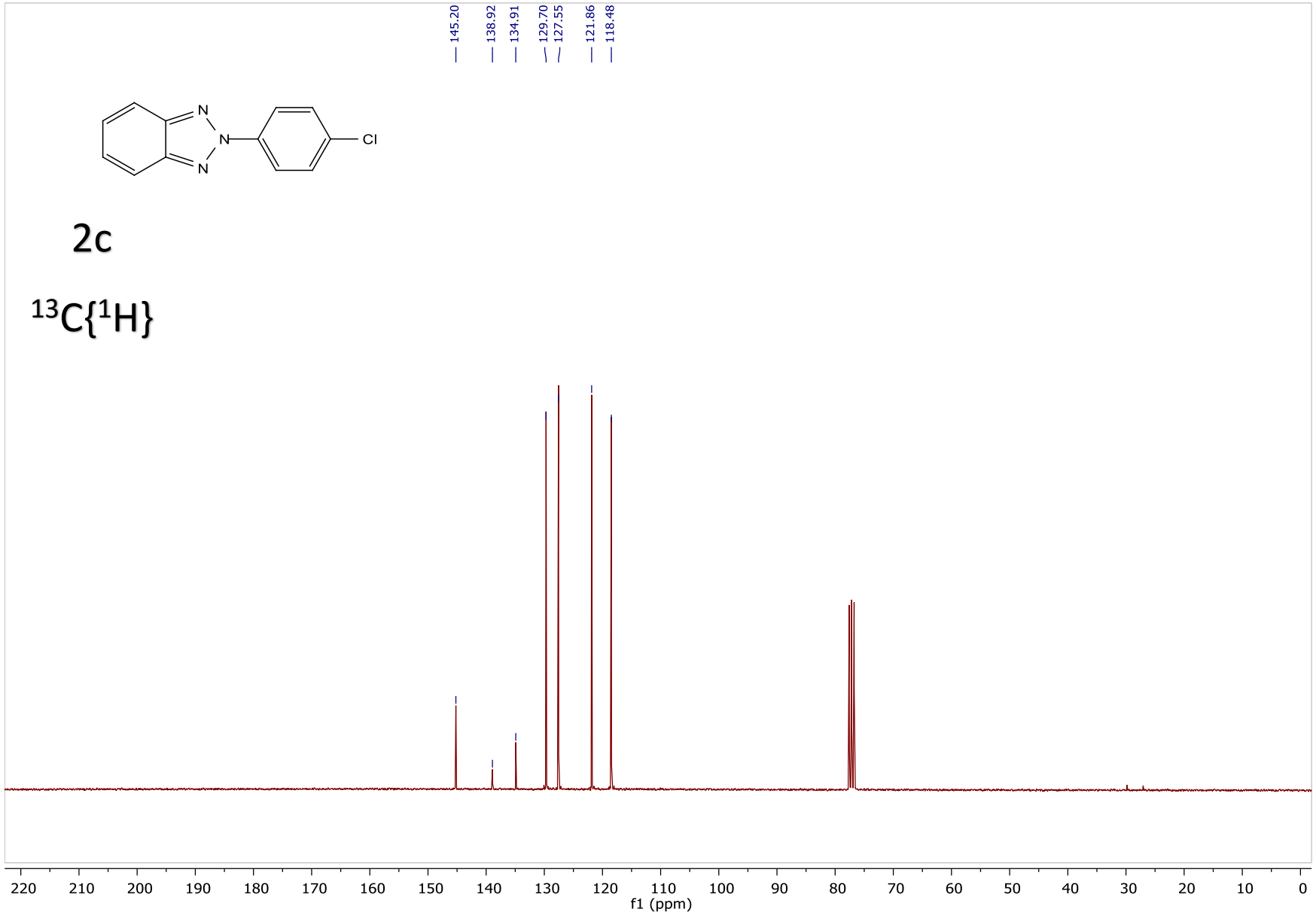
161.25
145.16
136.75
136.71
127.38
122.59
122.47
118.44
116.62
116.31
G (s)
118.44
E (s)
145.16
B (d)
122.53
D (d)
162.90
C (d)
136.73
A (d)
116.46
F (s)
127.38
F
N
N
N
2a
$^{13}C\{^{1}H\}$
136.8 136.7 136.6
f1 (ppm)
116.7 116.5 116.3 116.1
f1 (ppm)
122.65122.60122.55122.50122.45
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

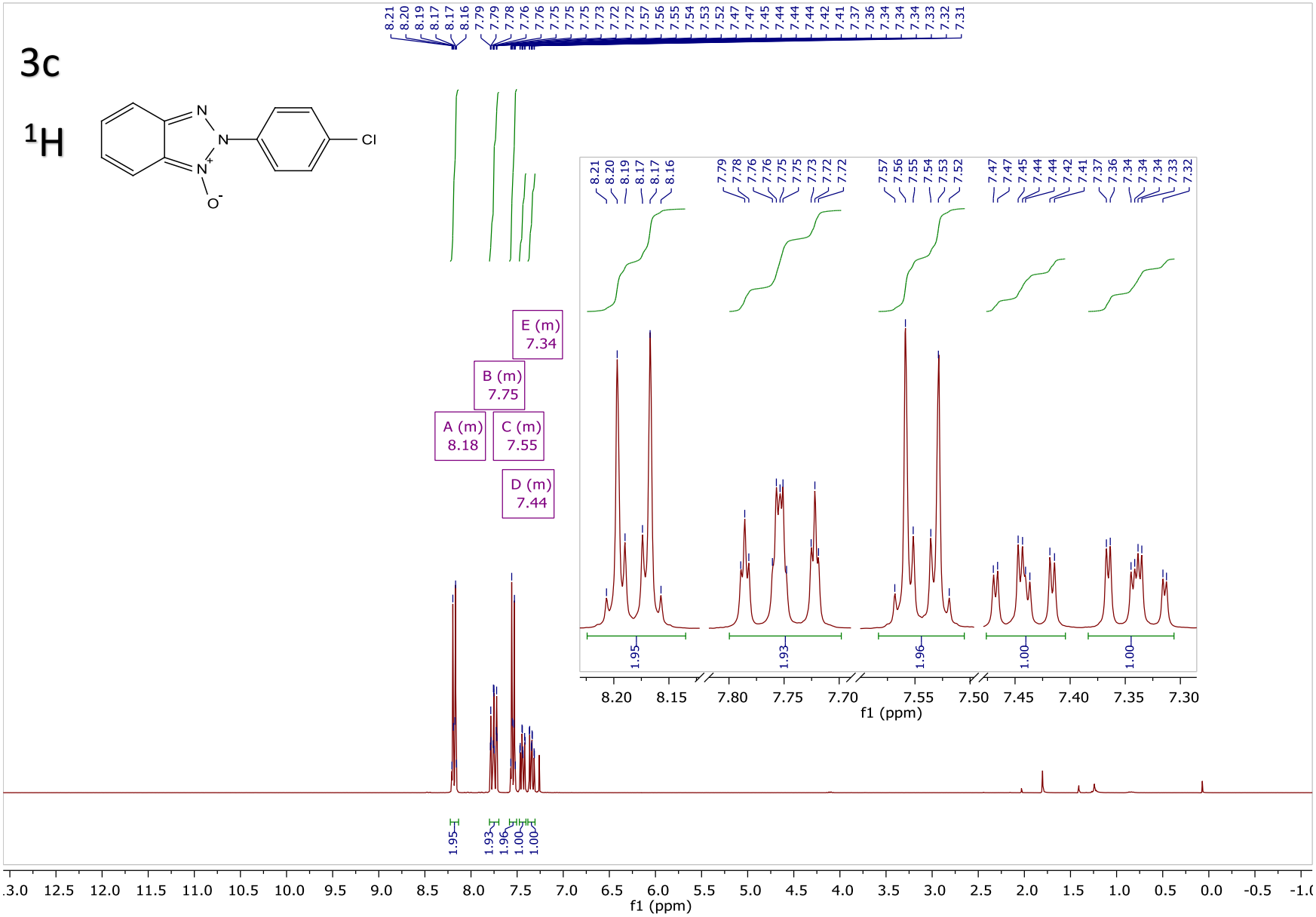

3a
1H
B (m)
7.80
A (m)
8.21
C (m)
7.48
D (m)
7.35
f1 (ppm)

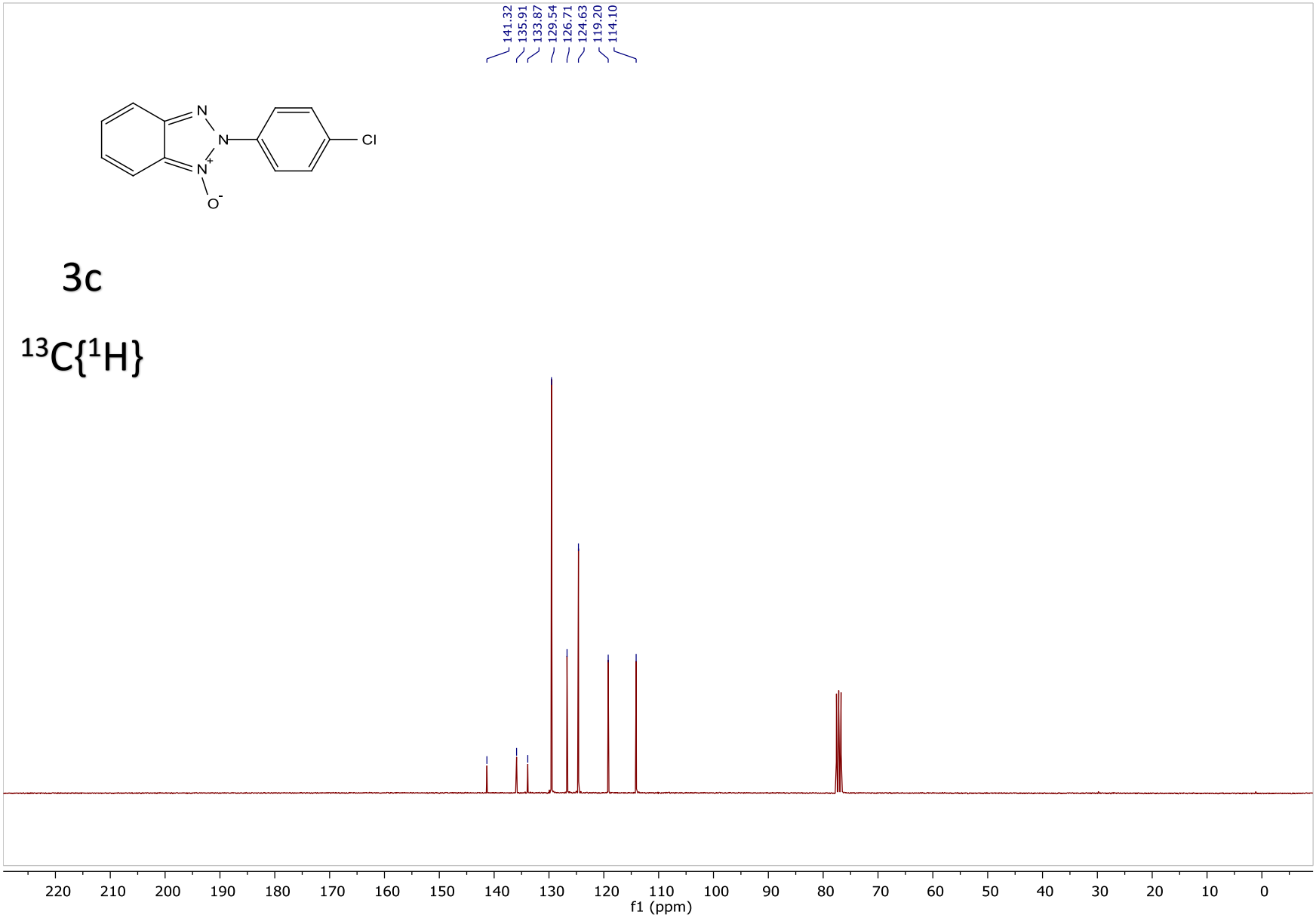

3a
$^{13}C\{^{1}H\}$
A (d) 163.10
B (s) 141.25
C (d) 131.45
D (d) 125.93
E (d) 116.47
F (s) 114.13
G (s) 119.22
H (s) 126.58
I (s) 126.68
J (s) 129.46
164.77
161.43
141.25
131.47
131.42
129.46
126.68
126.58
125.99
125.87
119.22
116.62
116.31
114.13
f1 (ppm)

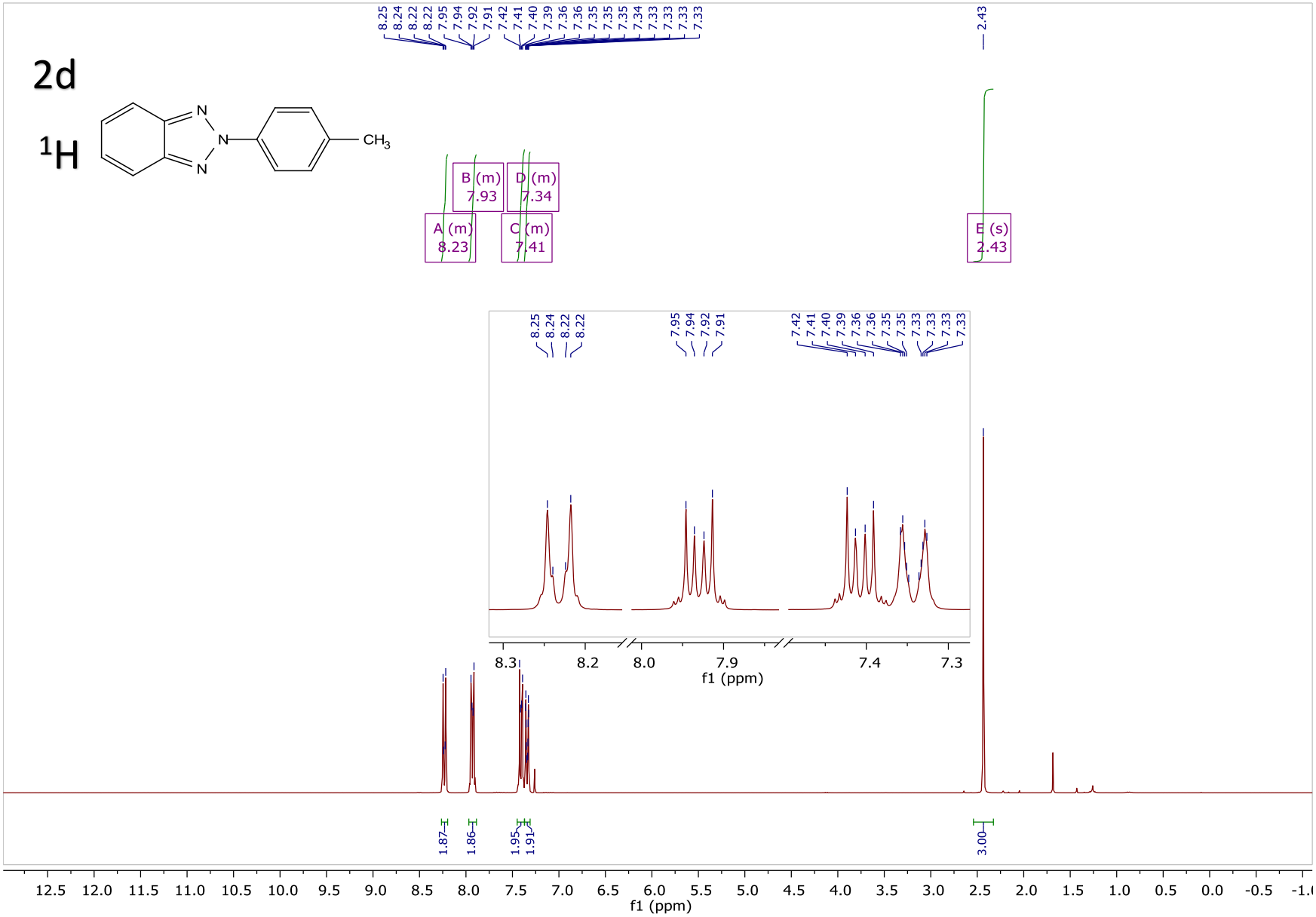

3a
19F
N
N
N+
O-
F
-112.53
-112.55
-112.56
-112.57
-112.58
-112.59
-112.60
-112.61
-112.62
A (tt)
-112.58
Hexafluorobenzene
-164.9
-112.40 -112.45 -112.50 -112.55 -112.60 -112.65 -112.70 -112.75
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

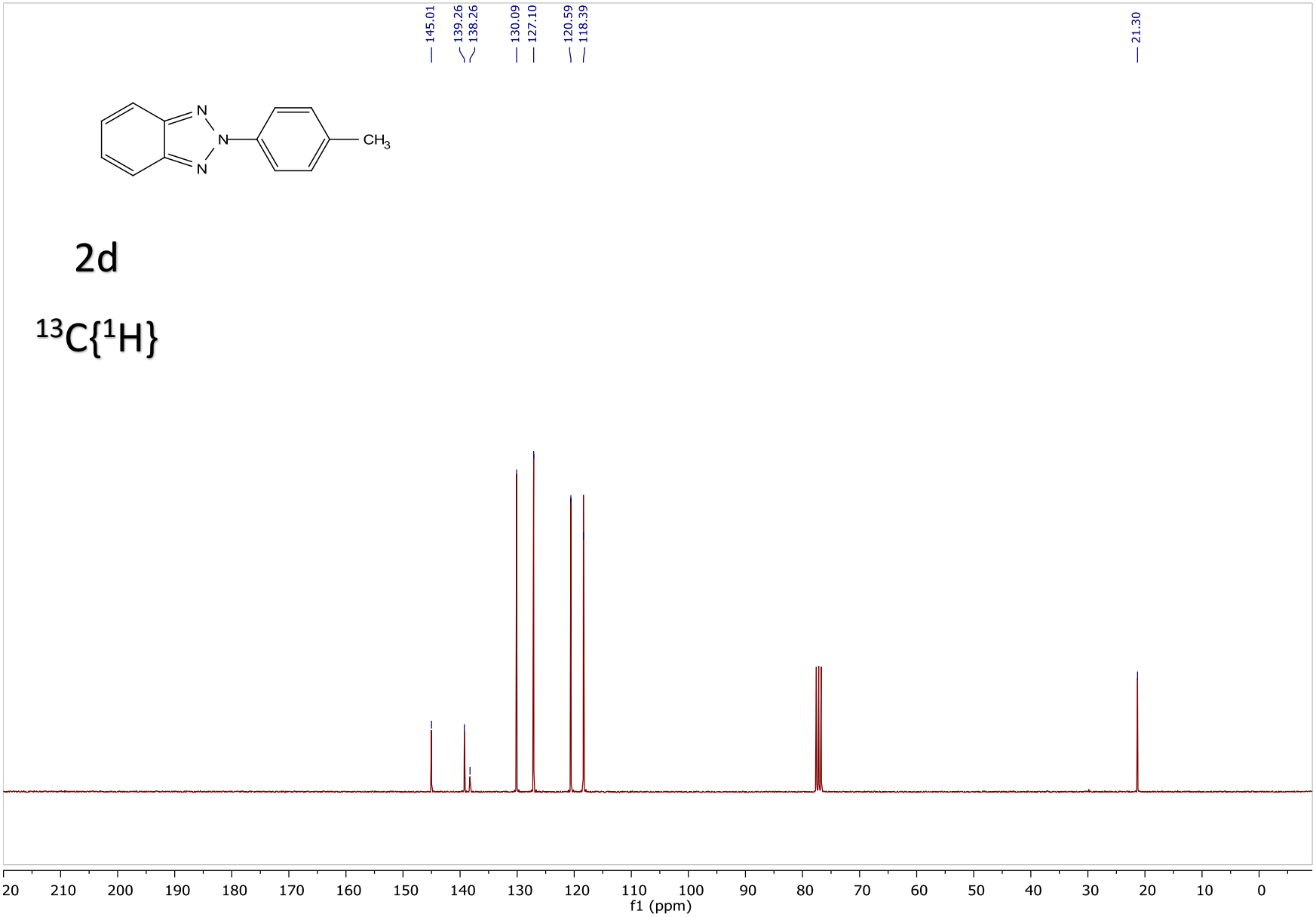

2c
1H
N
N
N
Cl
8.32 8.31 8.31 8.29 8.28 8.27 7.94 7.94 7.93 7.92 7.91 7.91 7.91 7.90 7.89 7.88 7.54 7.53 7.52 7.50 7.50 7.49 7.45 7.45 7.44 7.43 7.41 7.40 7.39 7.39
B (m) 7.91
A (m) 8.30
C (m) 7.51
D (m) 7.43
1.95 1.95 1.99 2.00
8.35 8.30 7.95 7.90 7.55 7.50 7.45 7.40
f1 (ppm)
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

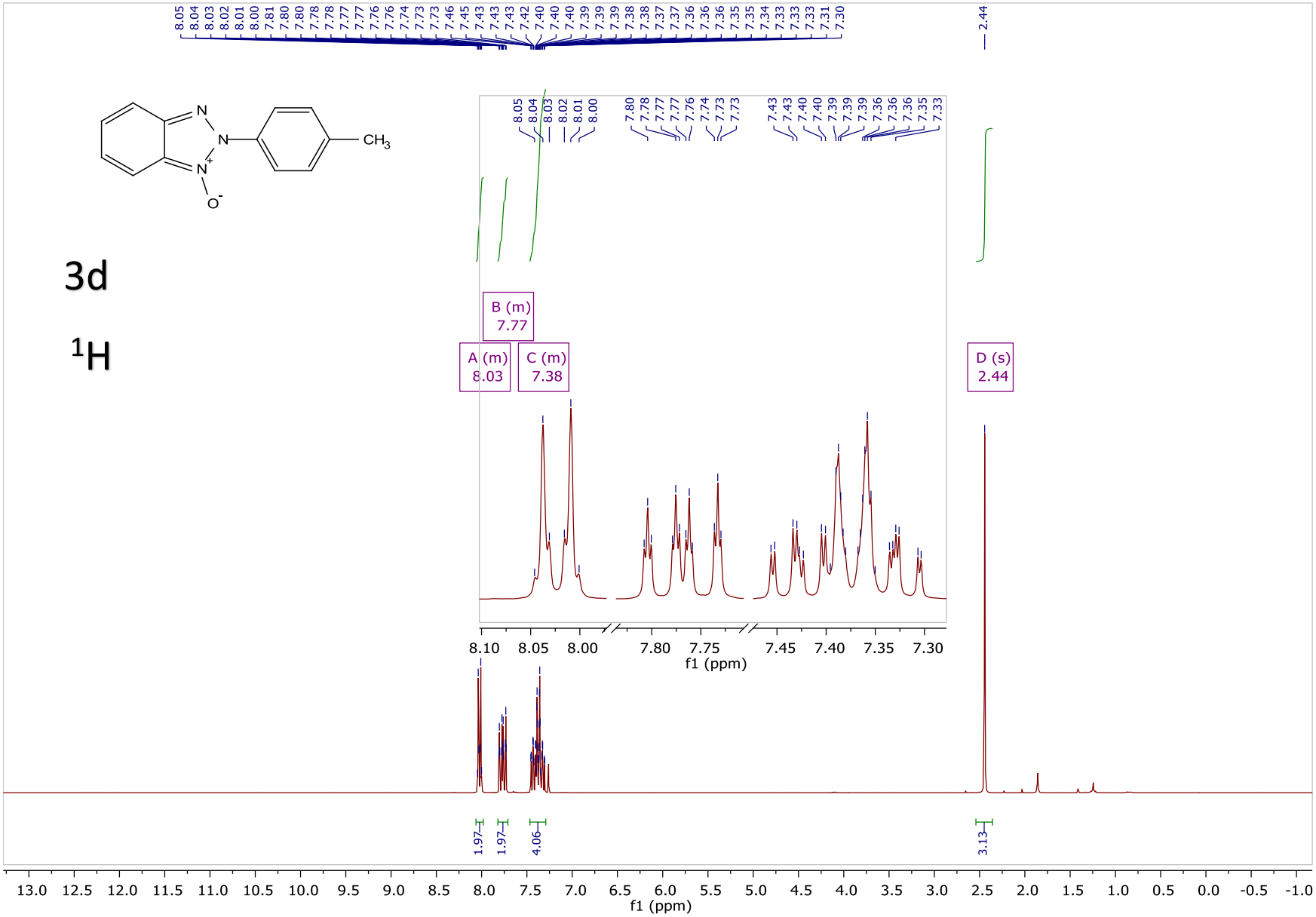

145.20
138.92
134.91
129.70
127.55
121.86
118.48
N
N
N
Cl
2c
13C{1H}
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

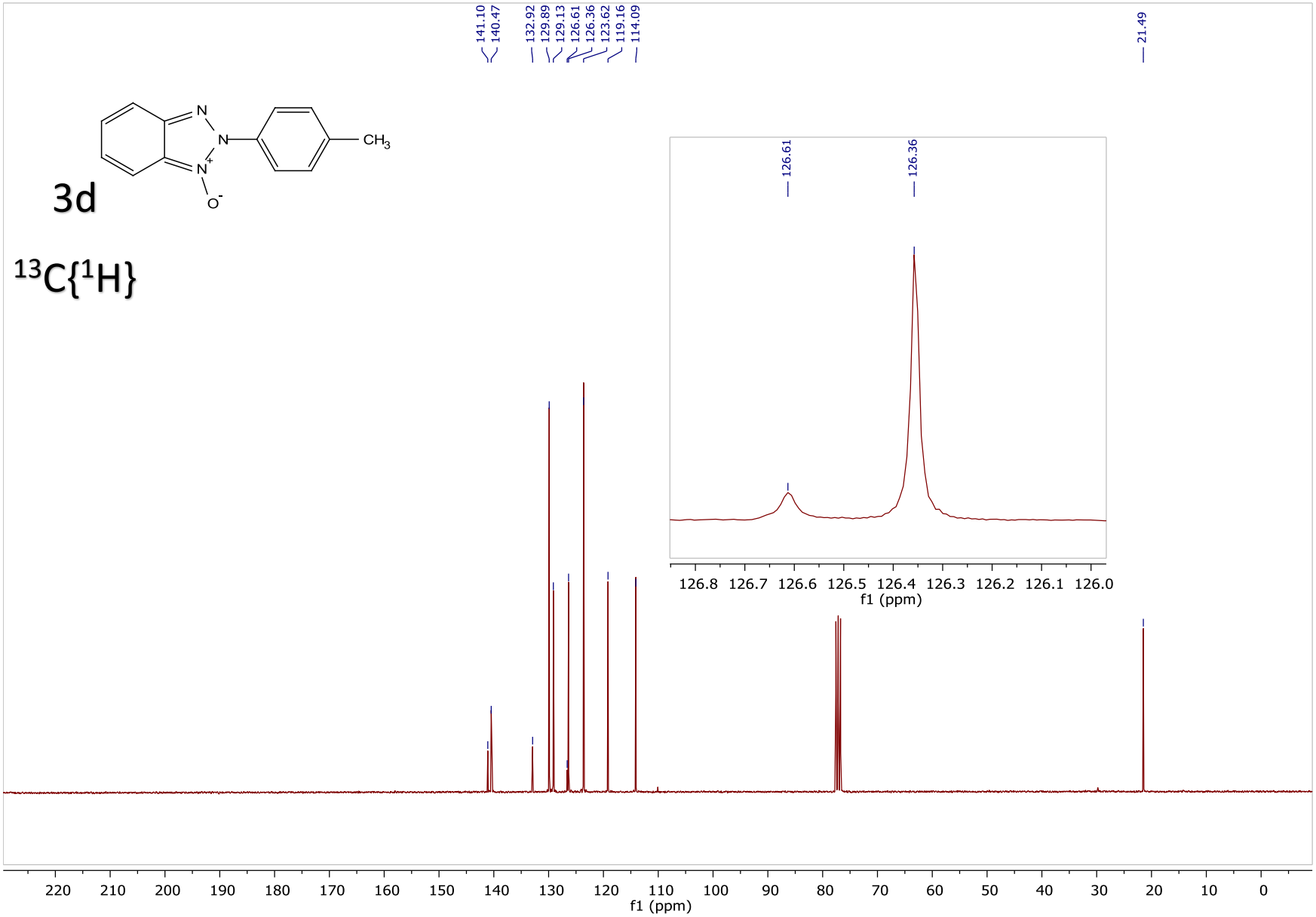

3c
^{1}H
Cl
E (m)
7.34
B (m)
7.75
A (m)
8.18
C (m)
7.55
D (m)
7.44
f1 (ppm)

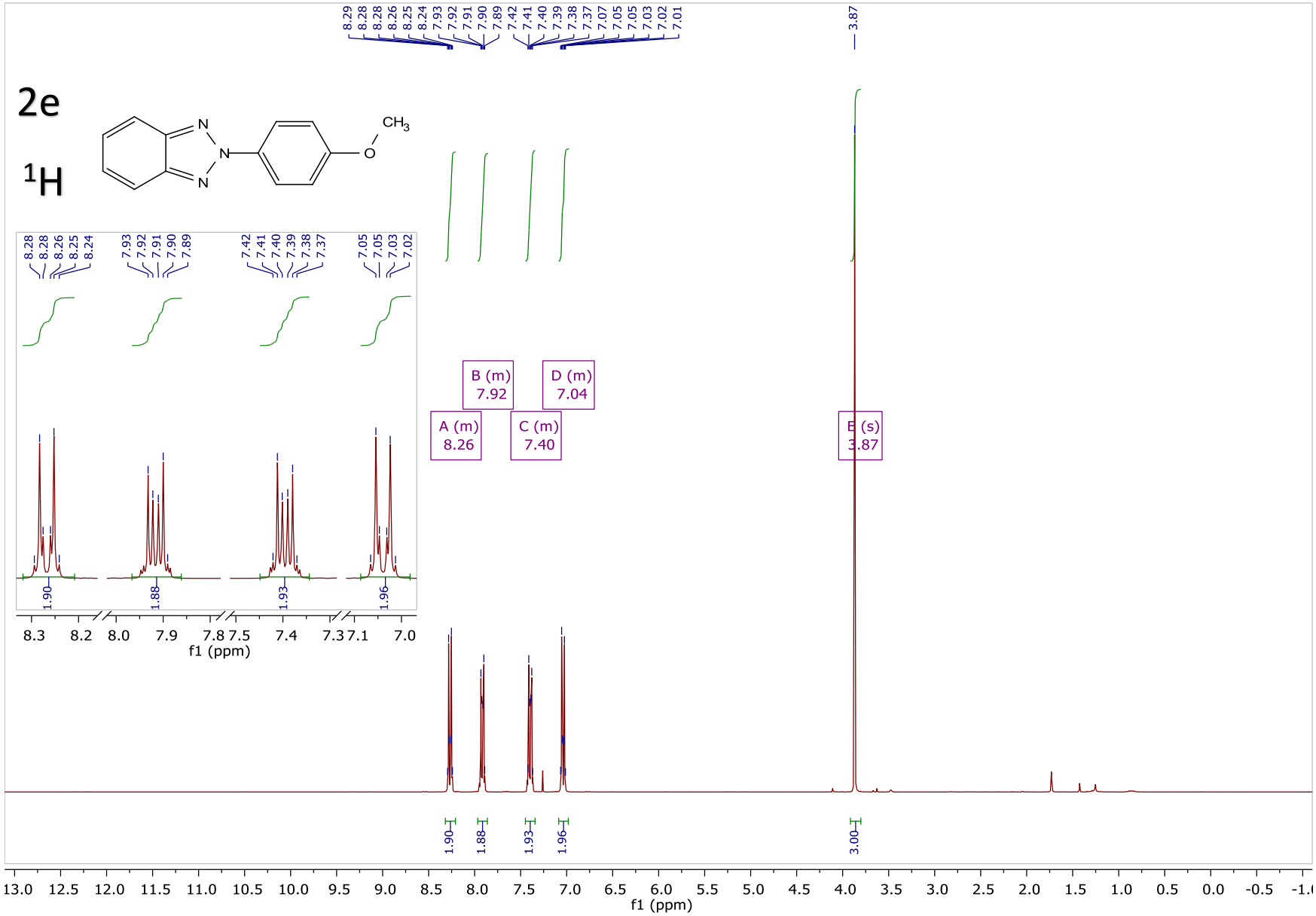

141.32
135.91
133.87
129.54
126.71
124.63
119.20
114.10
N
N
N+
O-
Cl
3c
13C{1H}
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

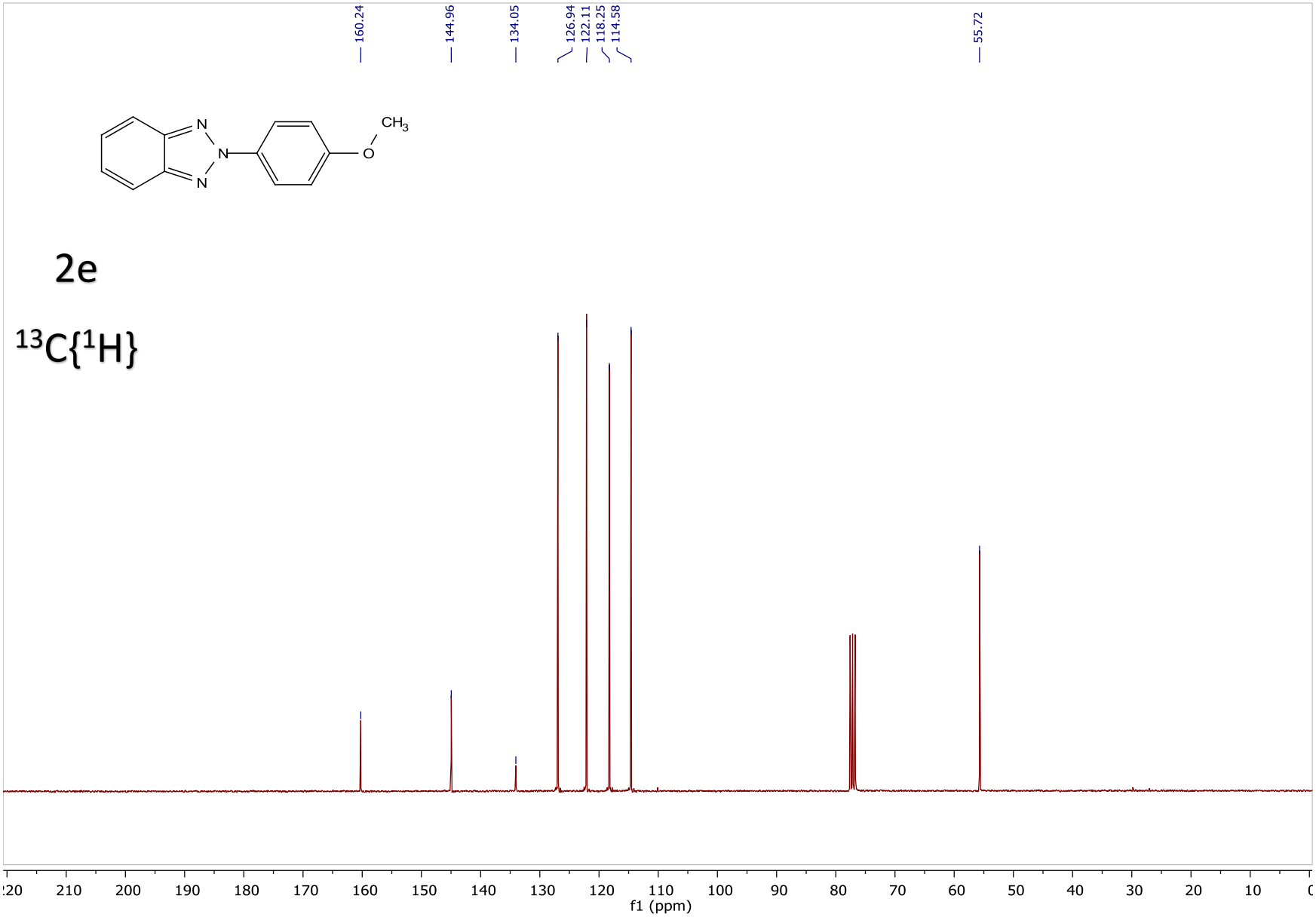

2d
^{1}H
N
N
N
CH$_3$
8.25
8.24
8.22
8.22
7.95
7.94
7.92
7.91
7.42
7.41
7.40
7.39
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.33
2.43
B (m)
7.93
D (m)
7.34
A (m)
8.23
C (m)
7.41
E (s)
2.43
8.3
8.2
8.0
7.9
7.4
7.3
f1 (ppm)
1.87
1.86
1.95
1.91
3.00
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

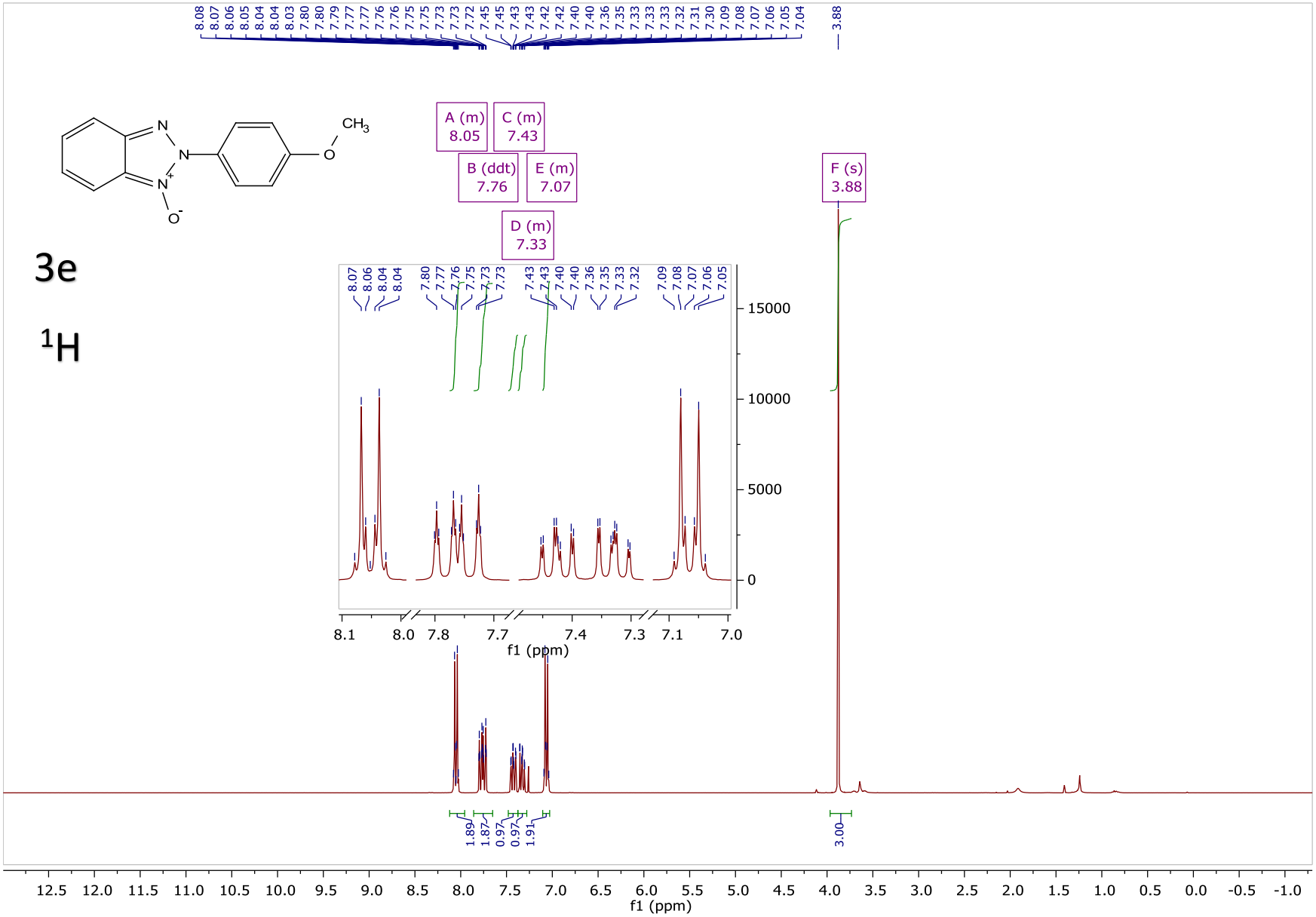

145.01
139.26
138.26
130.09
127.10
120.59
118.39
21.30
N
N
N
CH3
2d
13C{1H}
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

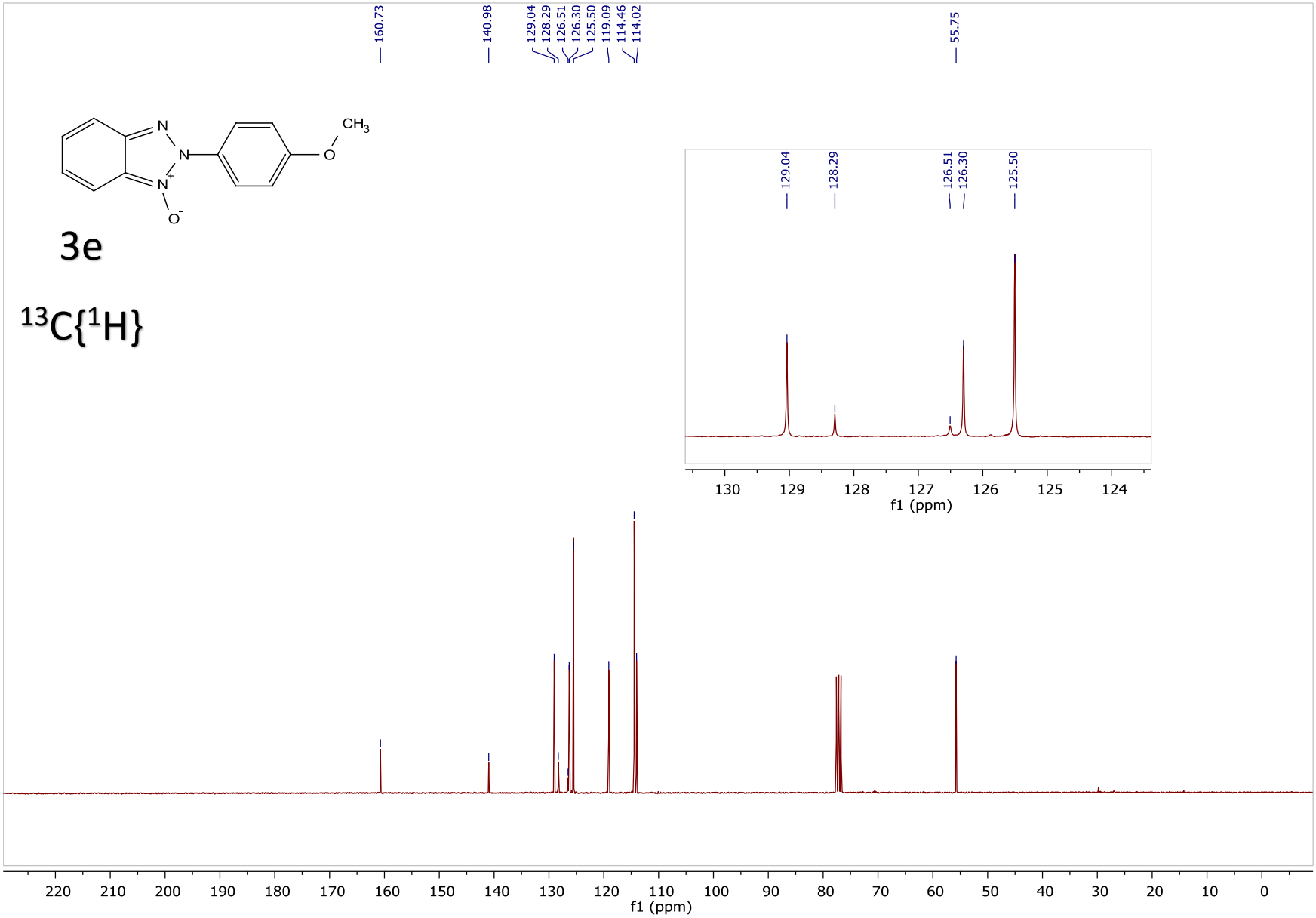

3d
^{1}H
B (m) 7.77
A (m) 8.03
C (m) 7.38
D (s) 2.44
f1 (ppm)

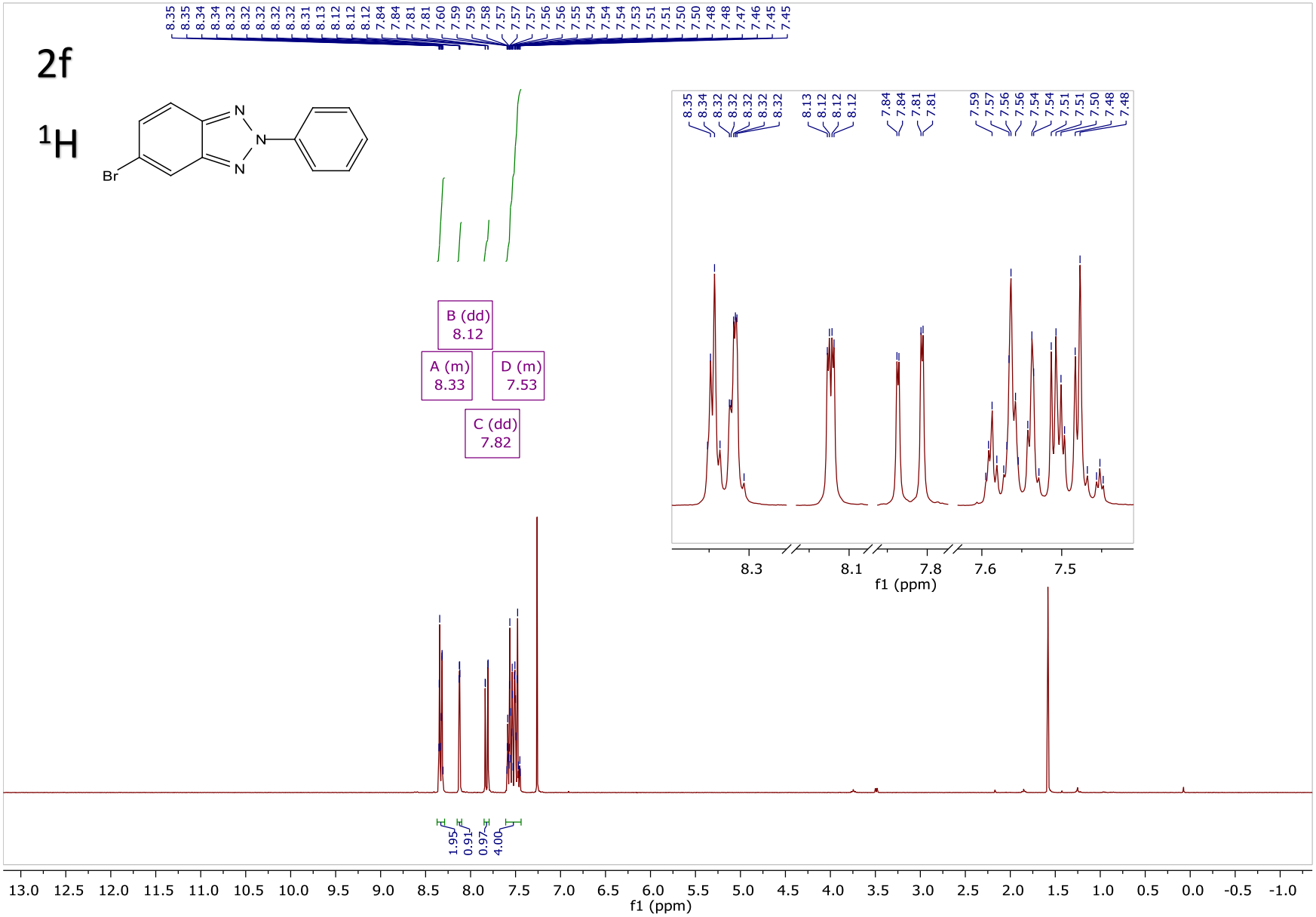

141.10
140.47
132.92
129.89
129.13
126.61
126.36
123.62
119.16
114.09
21.49
3d
$^{13}C\{^{1}H\}$
CH3
N
N
N+
O-
126.61
126.36
126.8 126.7 126.6 126.5 126.4 126.3 126.2 126.1 126.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

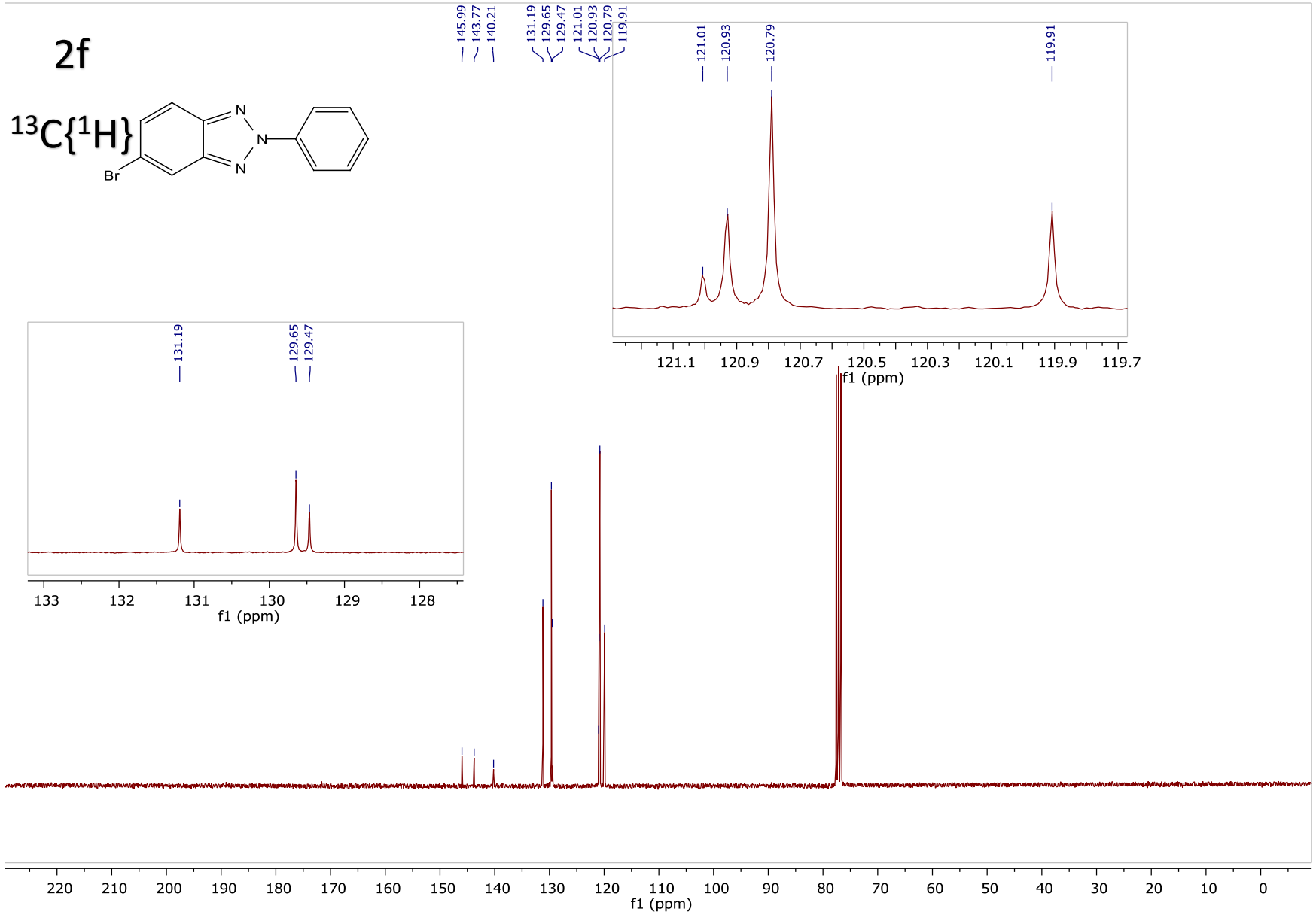

2e
^{1}H
8.29 8.28 8.28 8.26 8.25 8.24 7.93 7.92 7.91 7.90 7.89 7.42 7.41 7.40 7.39 7.38 7.37 7.07 7.05 7.05 7.03 7.02 7.01
3.87
B (m) 7.92
D (m) 7.04
A (m) 8.26
C (m) 7.40
E (s) 3.87
1.90 1.88 1.93 1.96 3.00
f1 (ppm)

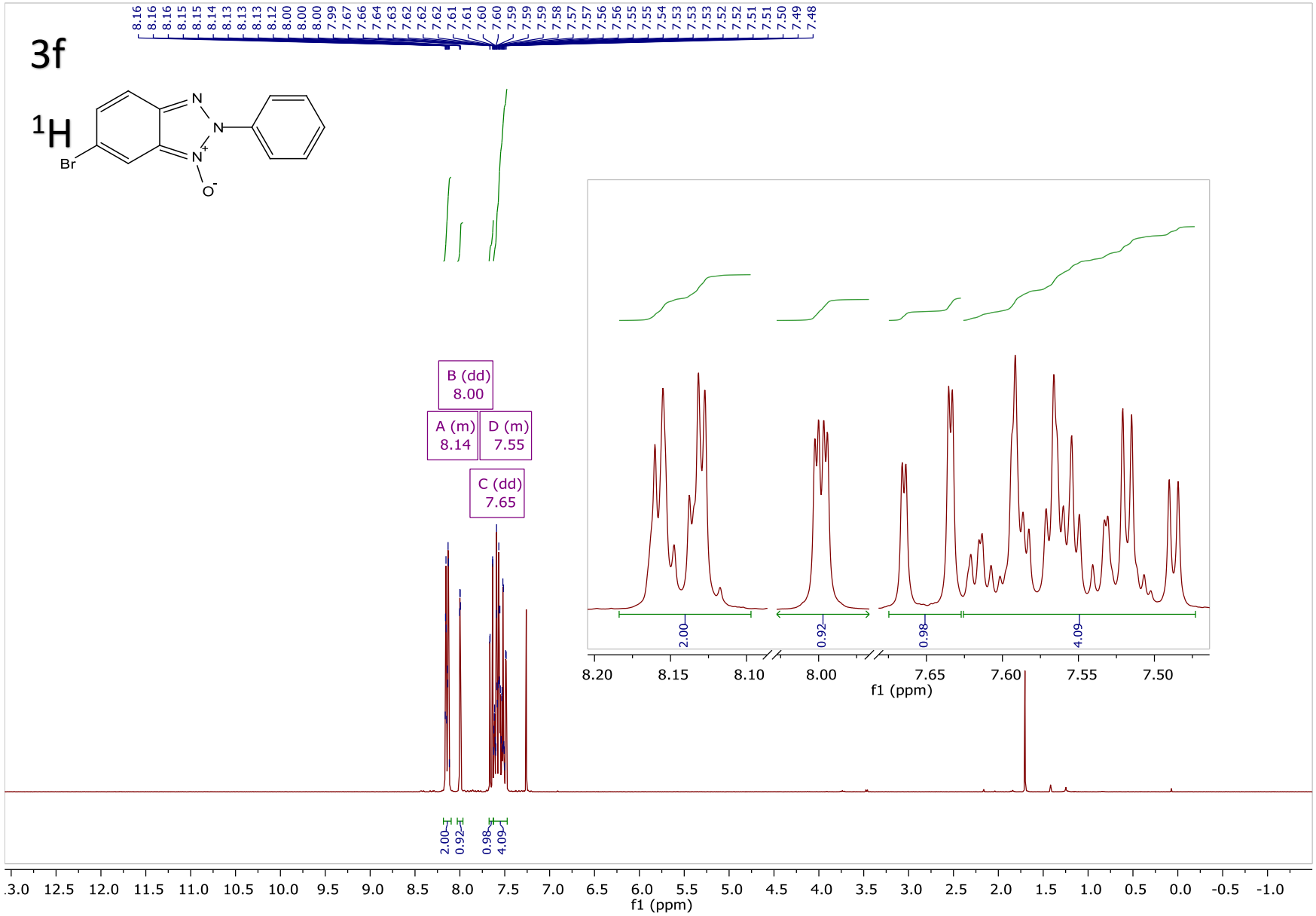

160.24
144.96
134.05
126.94
122.11
118.25
114.58
55.72
N
N
N
O
CH3
2e
13C{1H}
f1 (ppm)

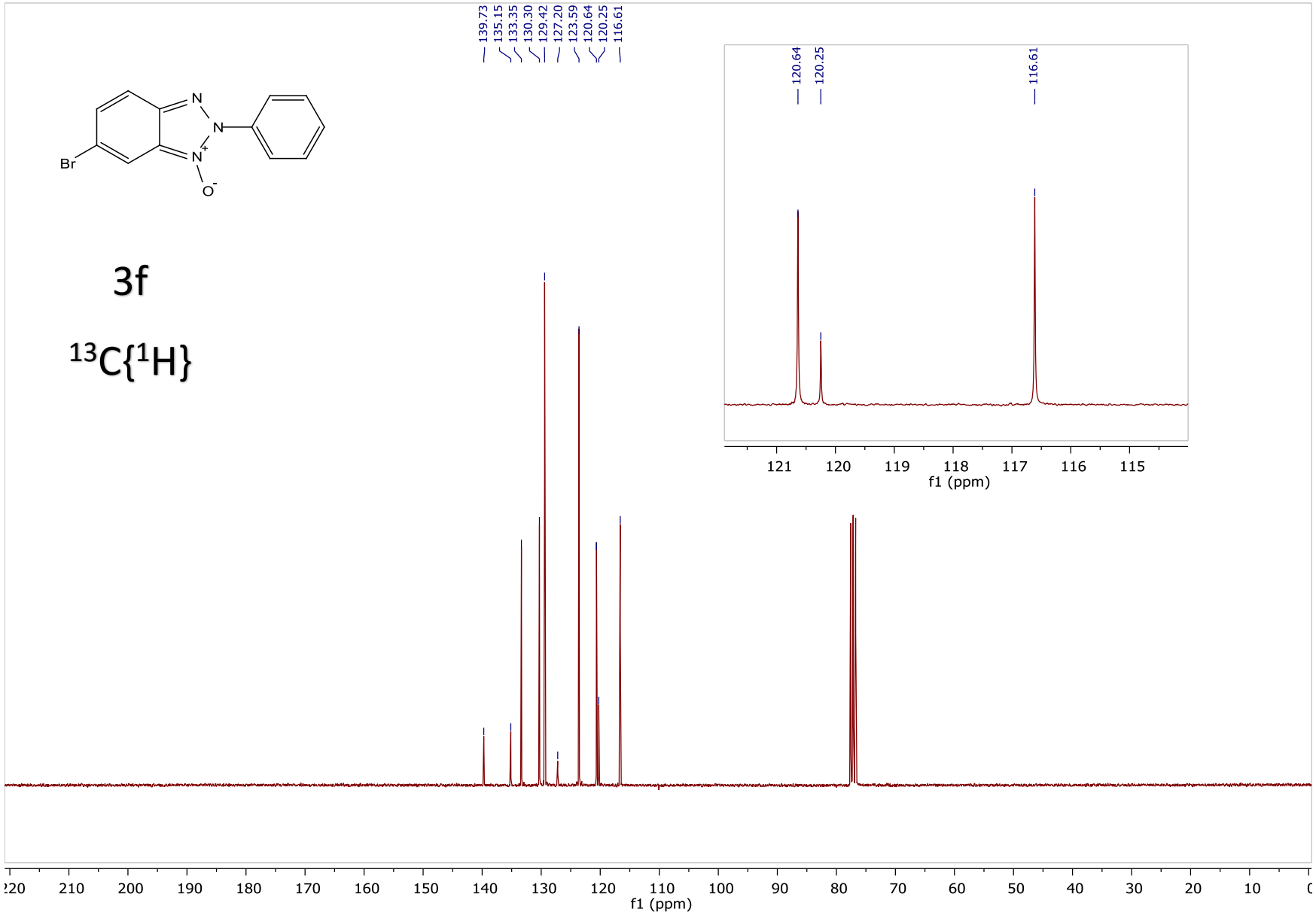

3e
^{1}H
A (m) 8.05
C (m) 7.43
B (ddt) 7.76
E (m) 7.07
D (m) 7.33
F (s) 3.88
f1 (ppm)
1.89
1.87
0.97
0.97
1.91
3.00

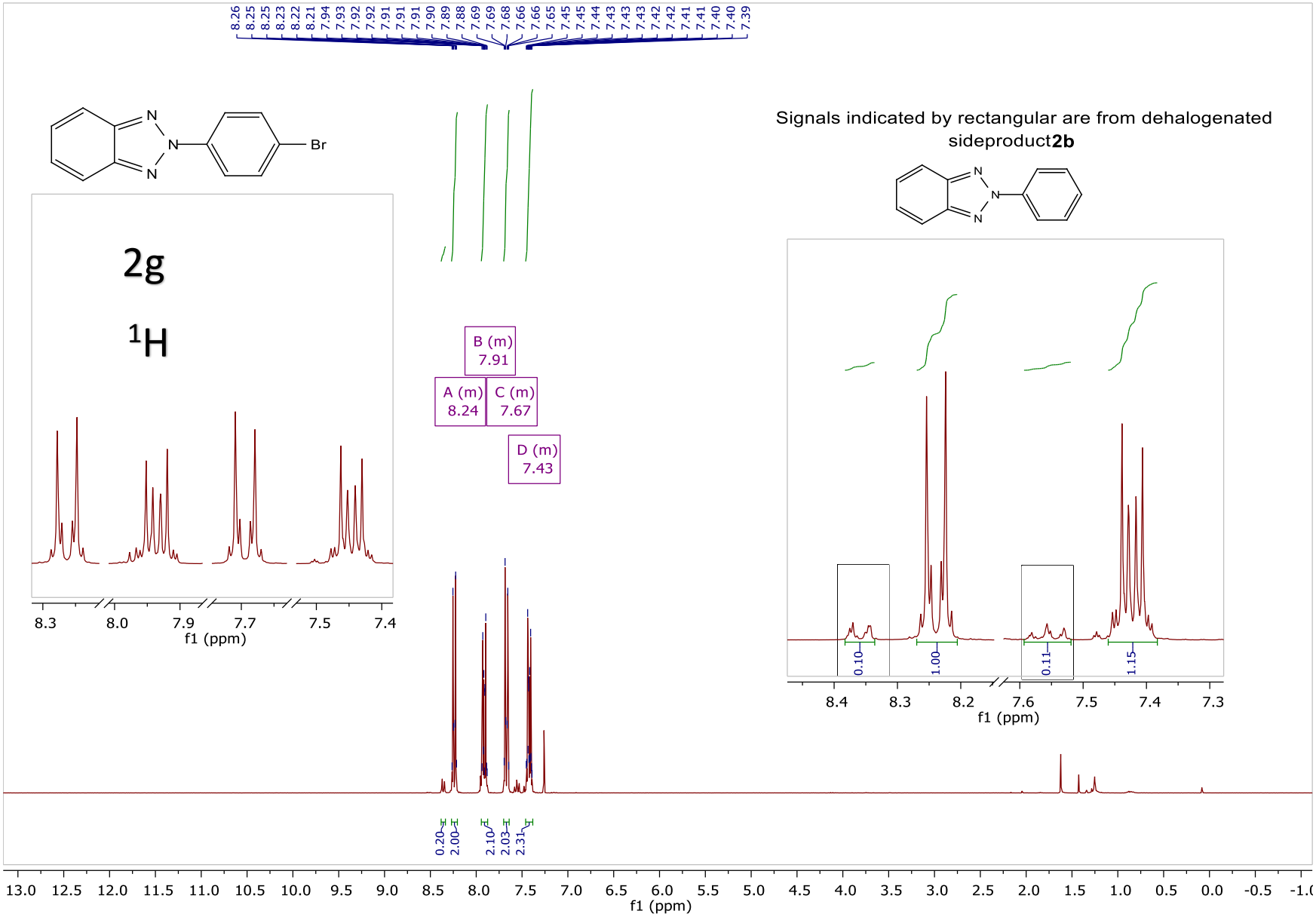

160.73
140.98
129.04
128.29
126.51
126.30
125.50
119.09
114.46
114.02
55.75
CH3
N
N
N+
O-
O
3e
13C{1H}
129.04
128.29
126.51
126.30
125.50
130
129
128
127
126
125
124
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

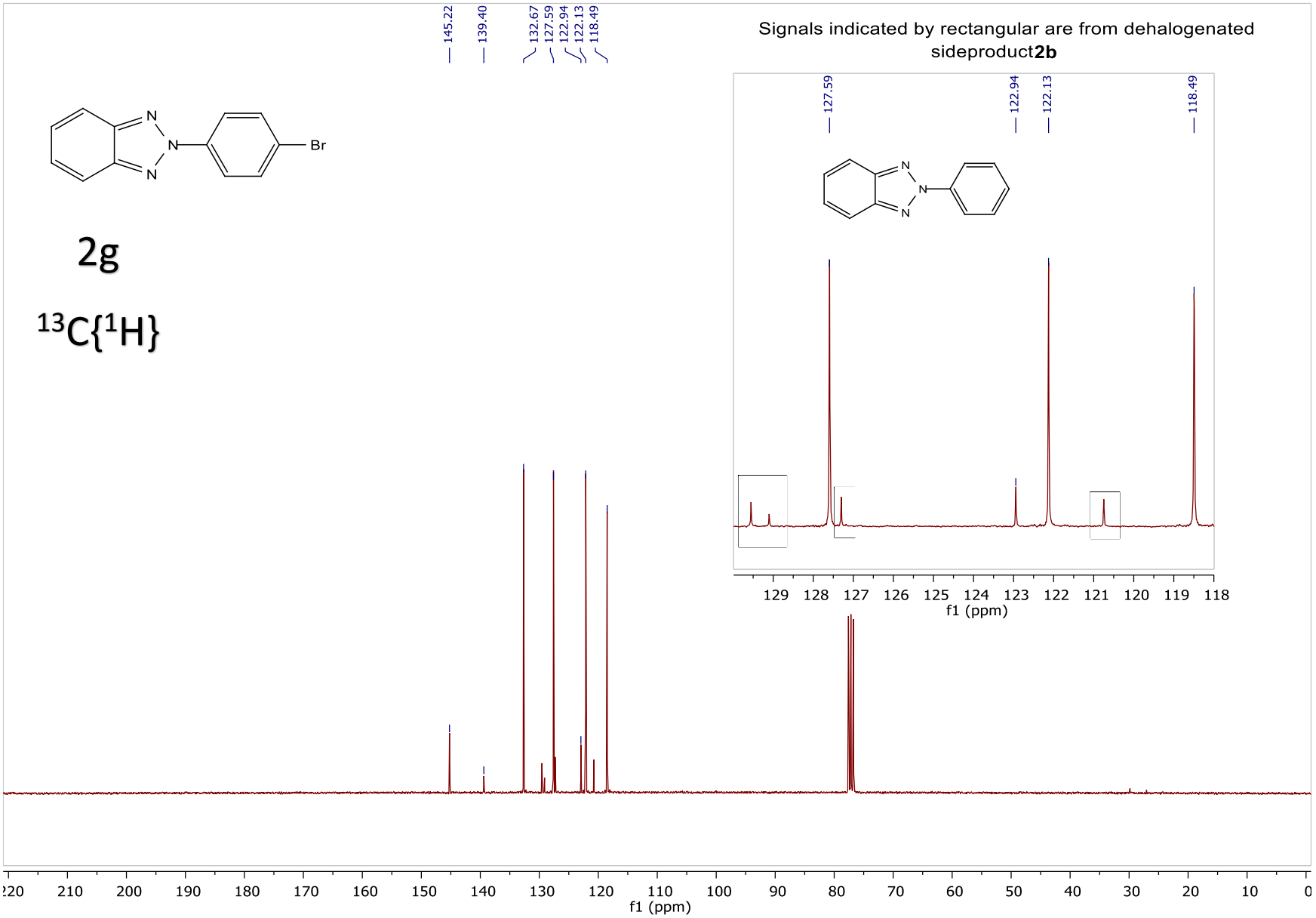

2f
^{1}H
Br
N
N
N
B (dd)
8.12
A (m)
8.33
D (m)
7.53
C (dd)
7.82
1.95
0.91
0.97
4.00
f1 (ppm)
f1 (ppm)

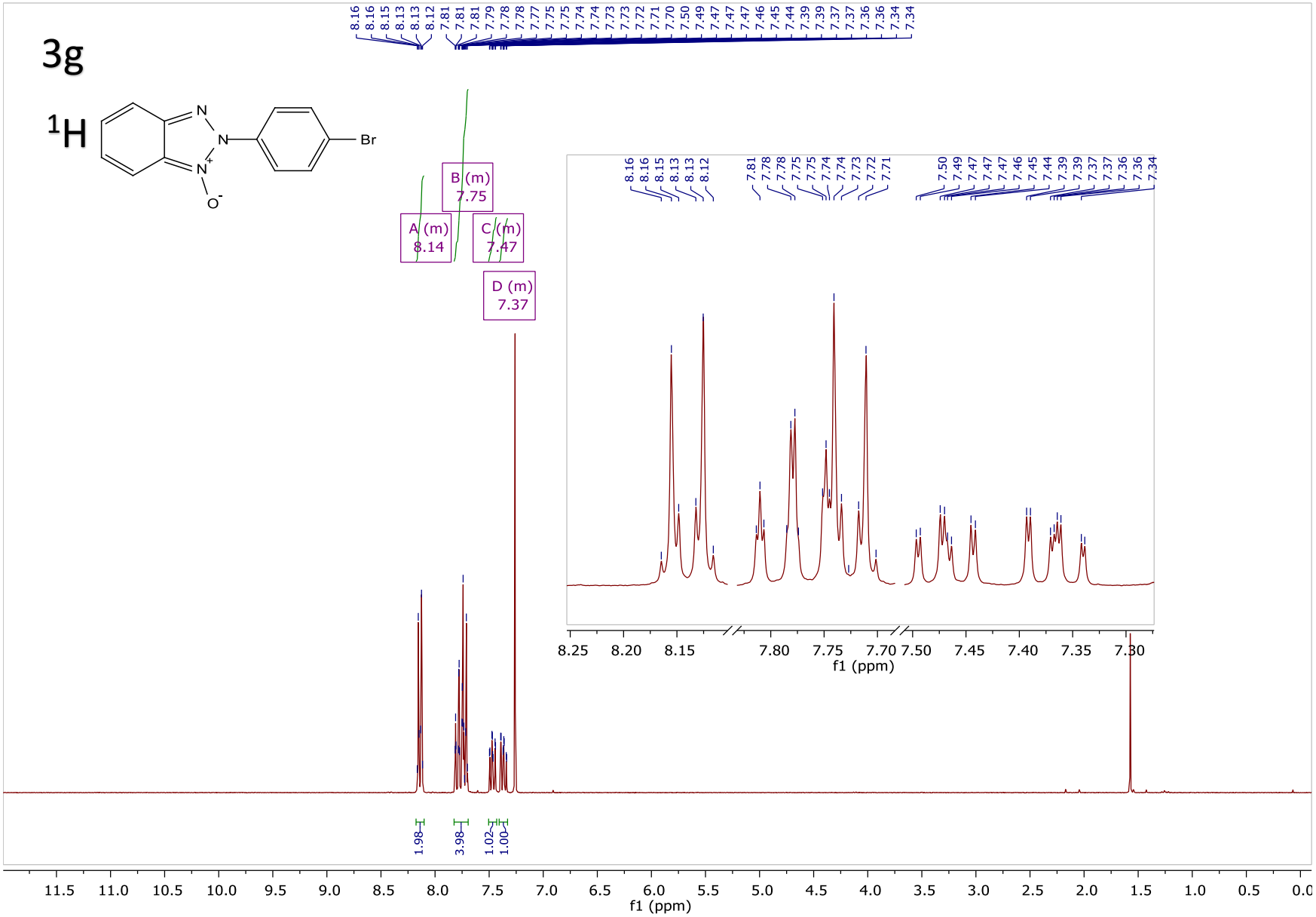

2f
$^{13}C\{^{1}H\}$
Br
N
N
N
145.99
143.77
140.21
131.19
129.65
129.47
121.01
120.93
120.79
119.91
121.1
120.9
120.7
120.5
120.3
120.1
119.9
119.7
f1 (ppm)
133
132
131
130
129
128
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

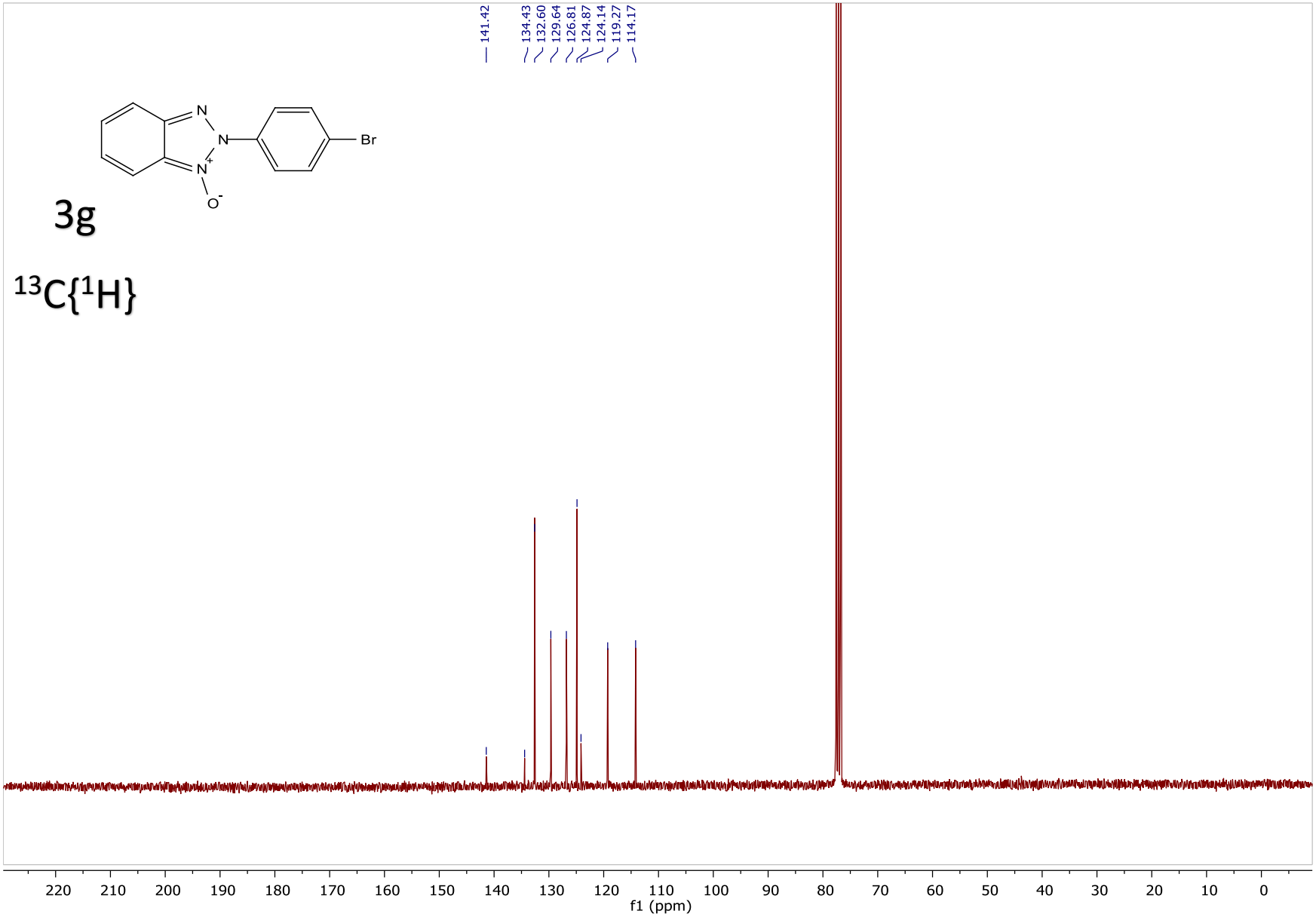

3f
1H
Br
N
N
N+
O-
B (dd)
8.00
A (m)
8.14
D (m)
7.55
C (dd)
7.65
2.00
0.92
0.98
4.09
f1 (ppm)

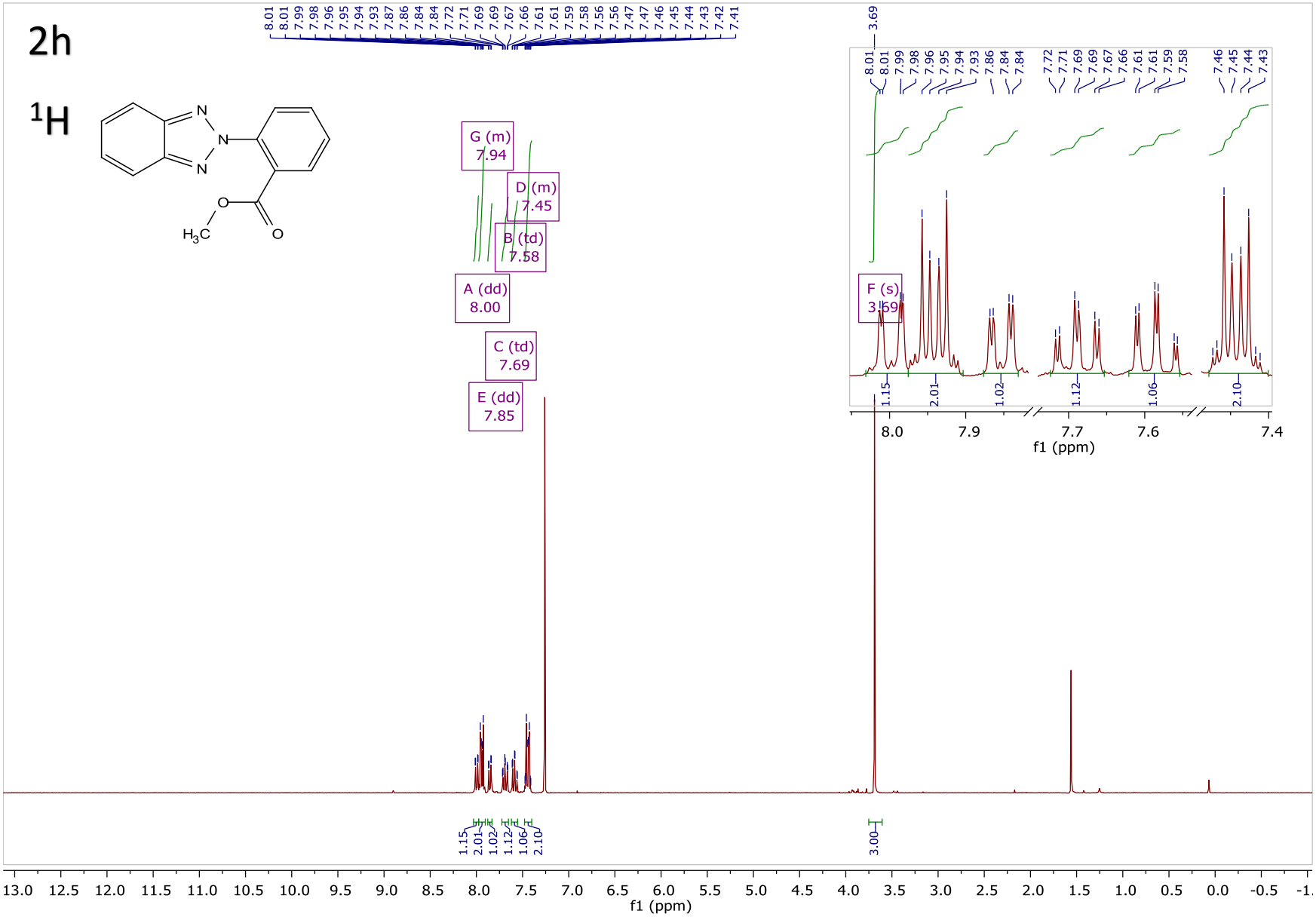

139.73
135.15
133.35
130.30
129.42
127.20
123.59
120.64
120.25
116.61
Br
N
N
N+
O-
3f
13C{1H}
120.64
120.25
116.61
121
120
119
118
117
116
115
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

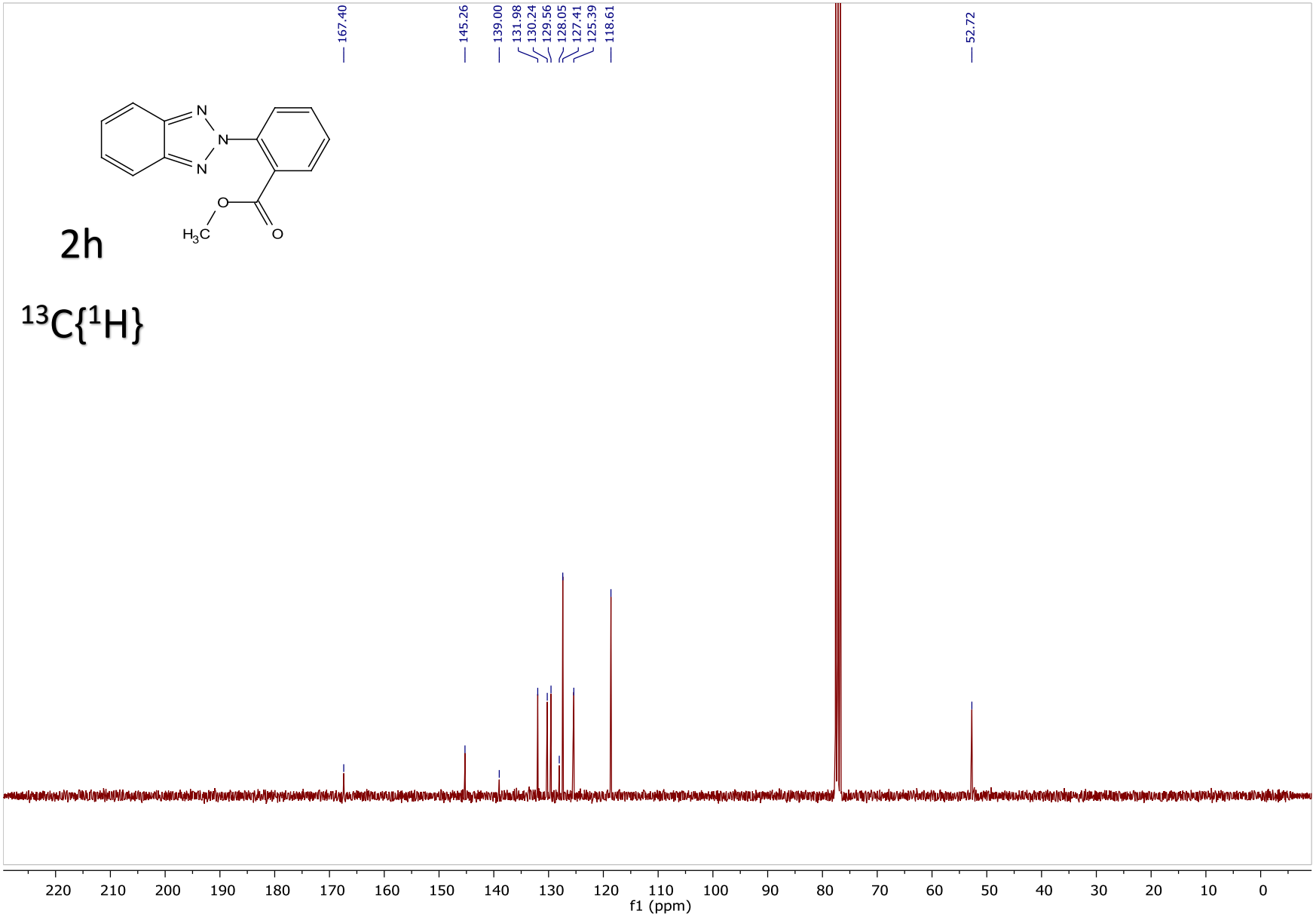

8.26 8.25 8.25 8.23 8.22 8.21 7.94 7.93 7.92 7.92 7.91 7.91 7.91 7.90 7.89 7.88 7.69 7.69 7.68 7.66 7.66 7.65 7.45 7.45 7.44 7.43 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39
Br
2g
^{1}H
B (m) 7.91
A (m) 8.24
C (m) 7.67
D (m) 7.43
8.3 8.0 7.9 7.7 7.5 7.4
f1 (ppm)
Signals indicated by rectangular are from dehalogenated sideproduct2b
0.10 1.00 0.11 1.15
8.4 8.3 8.2 7.6 7.5 7.4 7.3
f1 (ppm)
0.20 2.00 2.10 2.03 2.31
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

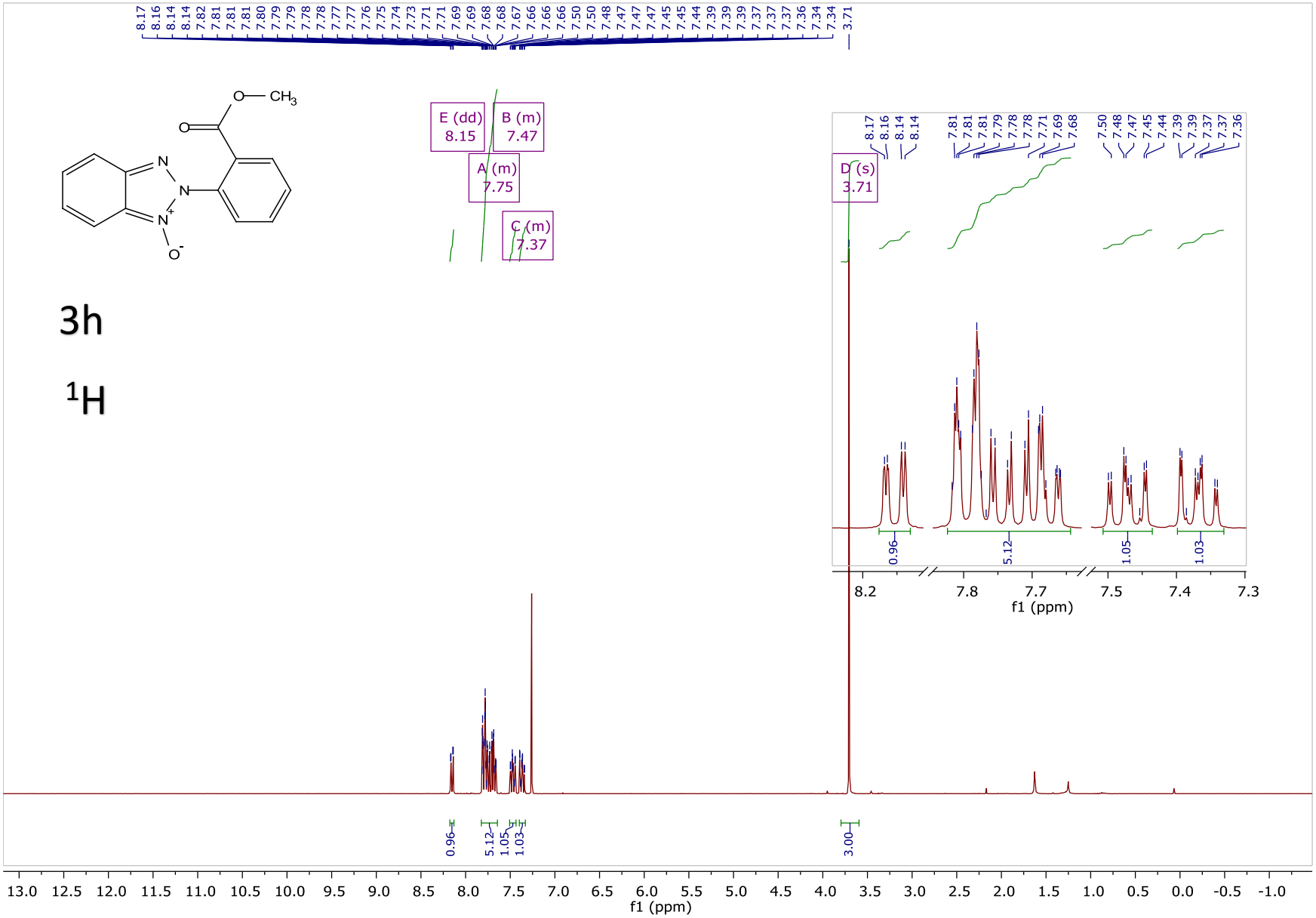

145.22
139.40
132.67
127.59
122.94
122.13
118.49
Signals indicated by rectangular are from dehalogenated sideproduct2b
127.59
122.94
122.13
118.49
Br
2g
13C{1H}
129 128 127 126 125 124 123 122 121 120 119 118
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

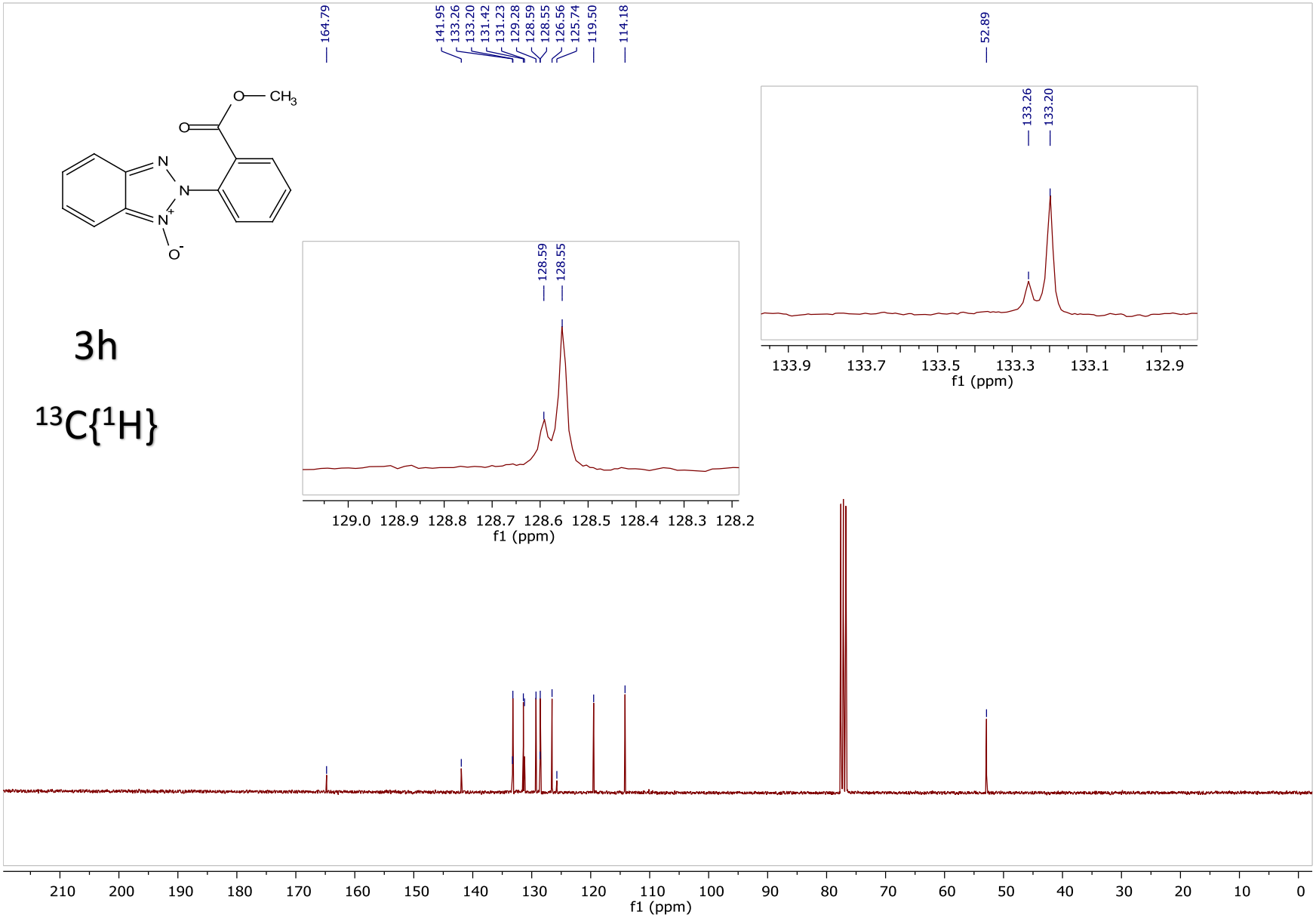

3g
^{1}H
Br
A (m)
8.14
B (m)
7.75
C (m)
7.47
D (m)
7.37
1.98
3.98
1.02
1.00
f1 (ppm)

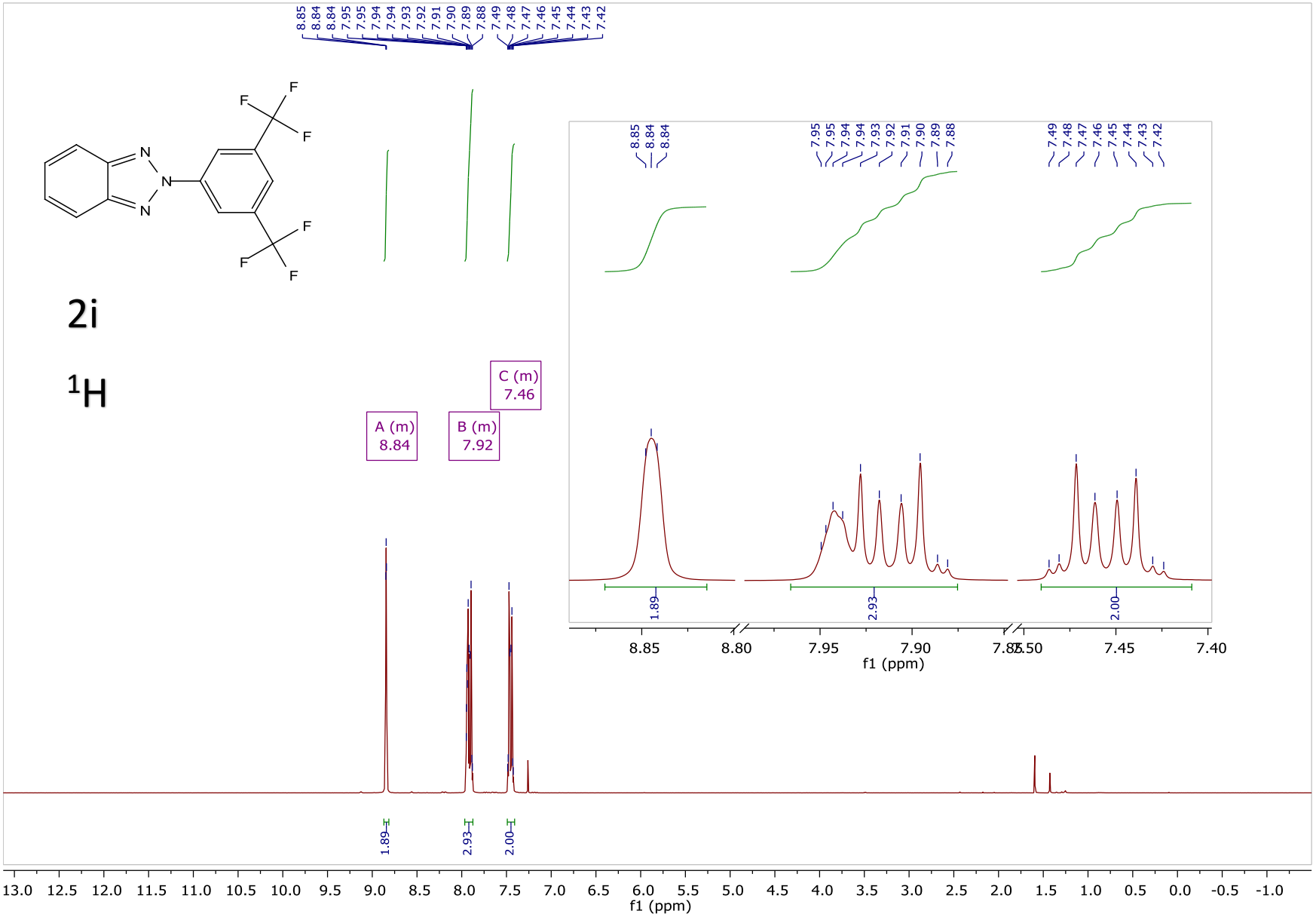

141.42
134.43
132.60
129.64
126.81
124.87
124.14
119.27
114.17
N
N
N+
O-
Br
3g
13C{1H}
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

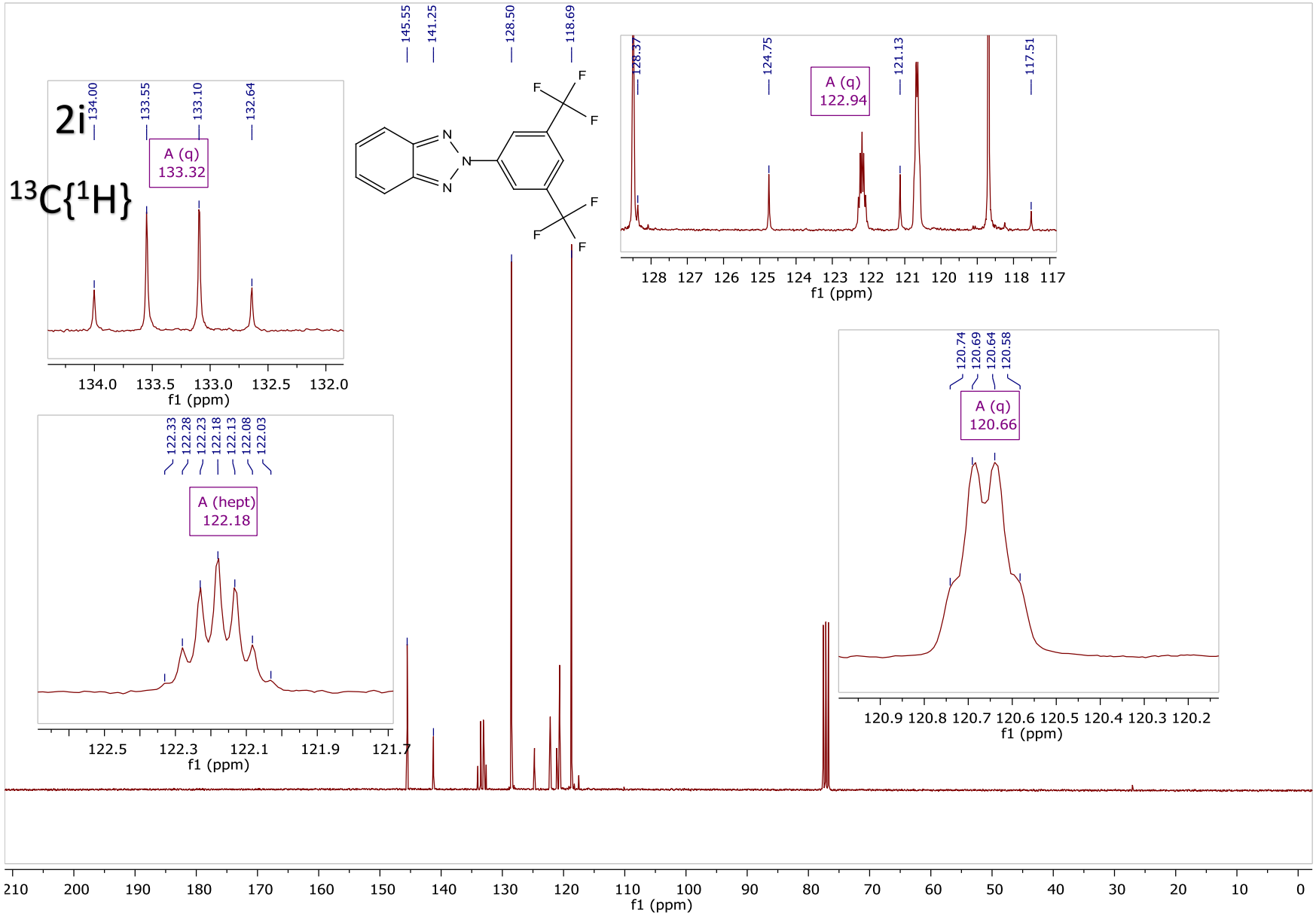

2h
1H
G (m)
7.94
D (m)
7.45
B (td)
7.58
A (dd)
8.00
C (td)
7.69
E (dd)
7.85
F (s)
3.69
f1 (ppm)

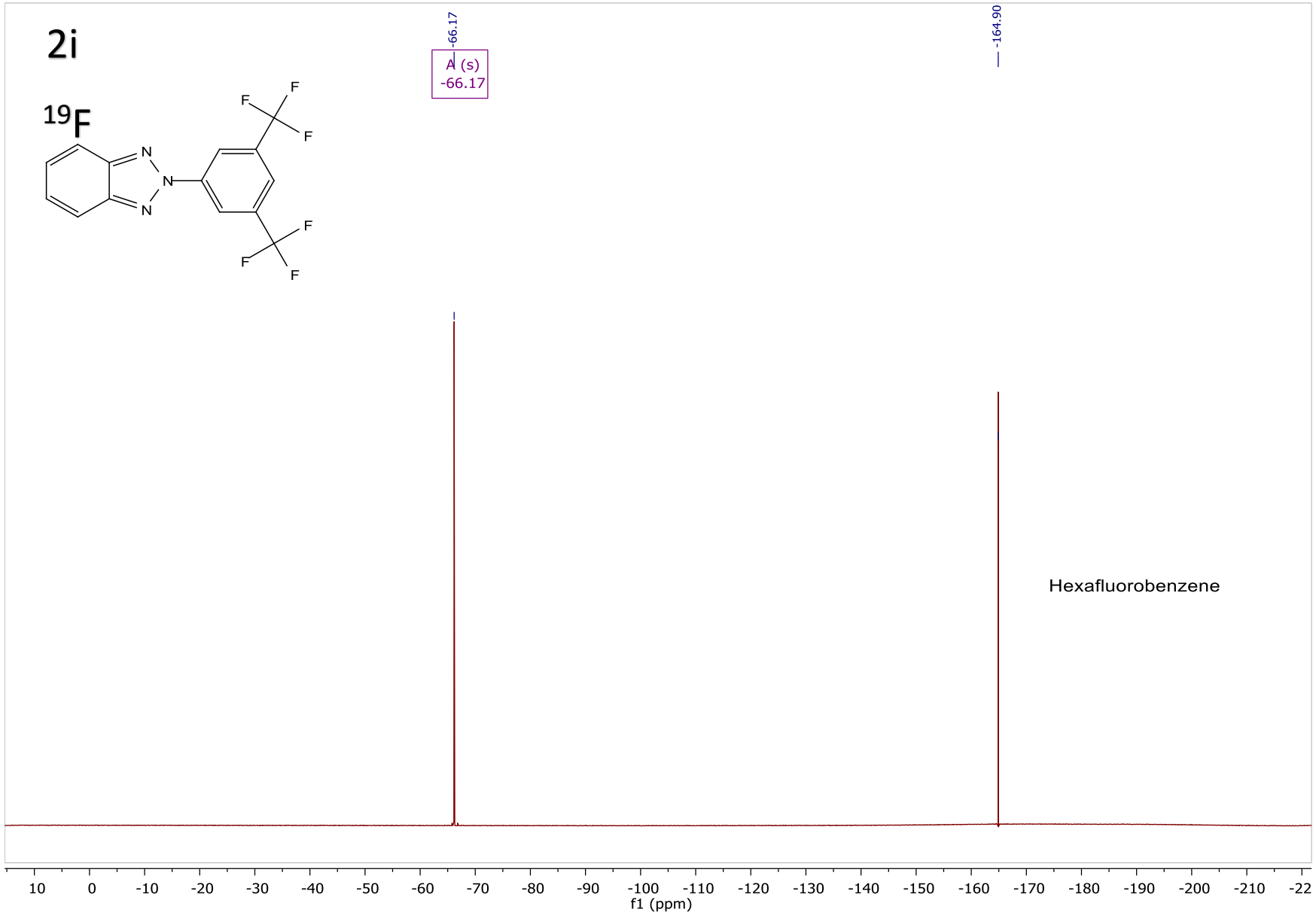

167.40
145.26
139.00
131.98
130.24
129.56
128.05
127.41
125.39
118.61
52.72
N
N
N
O
O
H3C
2h
13C{1H}
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

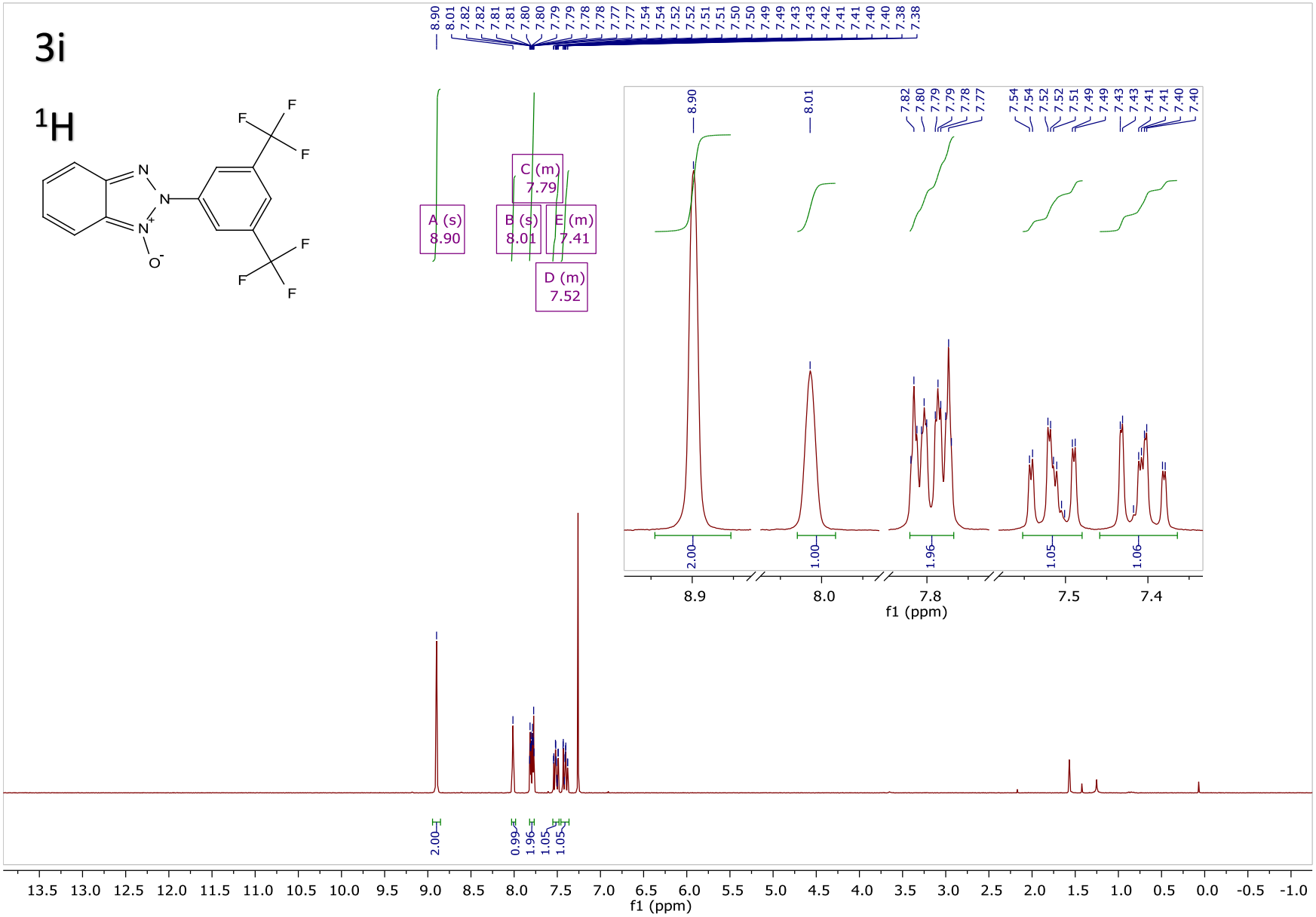

8.17 8.16 8.14 8.14 8.82 7.81 7.81 7.81 7.80 7.79 7.79 7.78 7.78 7.77 7.77 7.76 7.75 7.74 7.73 7.71 7.71 7.69 7.69 7.68 7.68 7.67 7.66 7.66 7.66 7.50 7.50 7.48 7.47 7.47 7.47 7.45 7.45 7.44 7.39 7.39 7.39 7.37 7.37 7.37 7.36 7.34 7.34 3.71
O—CH3
O
N
N
N+
O-
E (dd) 8.15
B (m) 7.47
A (m) 7.75
C (m) 7.37
D (s) 3.71
3h
1H
0.96
5.12
1.05
1.03
3.00
f1 (ppm)

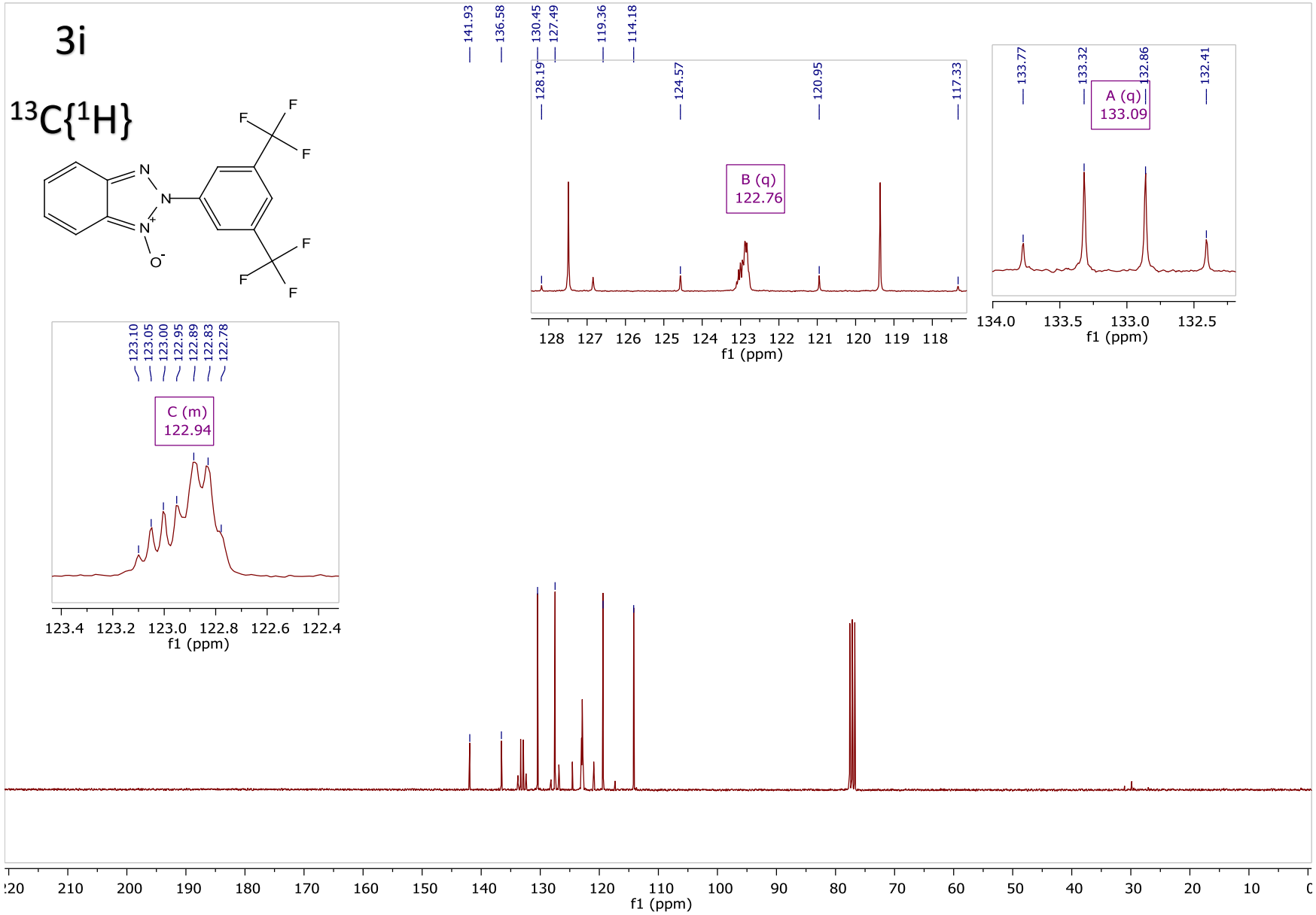

164.79
141.95
133.26
133.20
131.42
131.23
129.28
128.59
128.55
126.56
125.74
119.50
114.18
52.89
O
CH3
O
N
N
N+
O-
3h
13C{1H}
128.59
128.55
129.0 128.9 128.8 128.7 128.6 128.5 128.4 128.3 128.2
f1 (ppm)
133.26
133.20
133.9 133.7 133.5 133.3 133.1 132.9
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

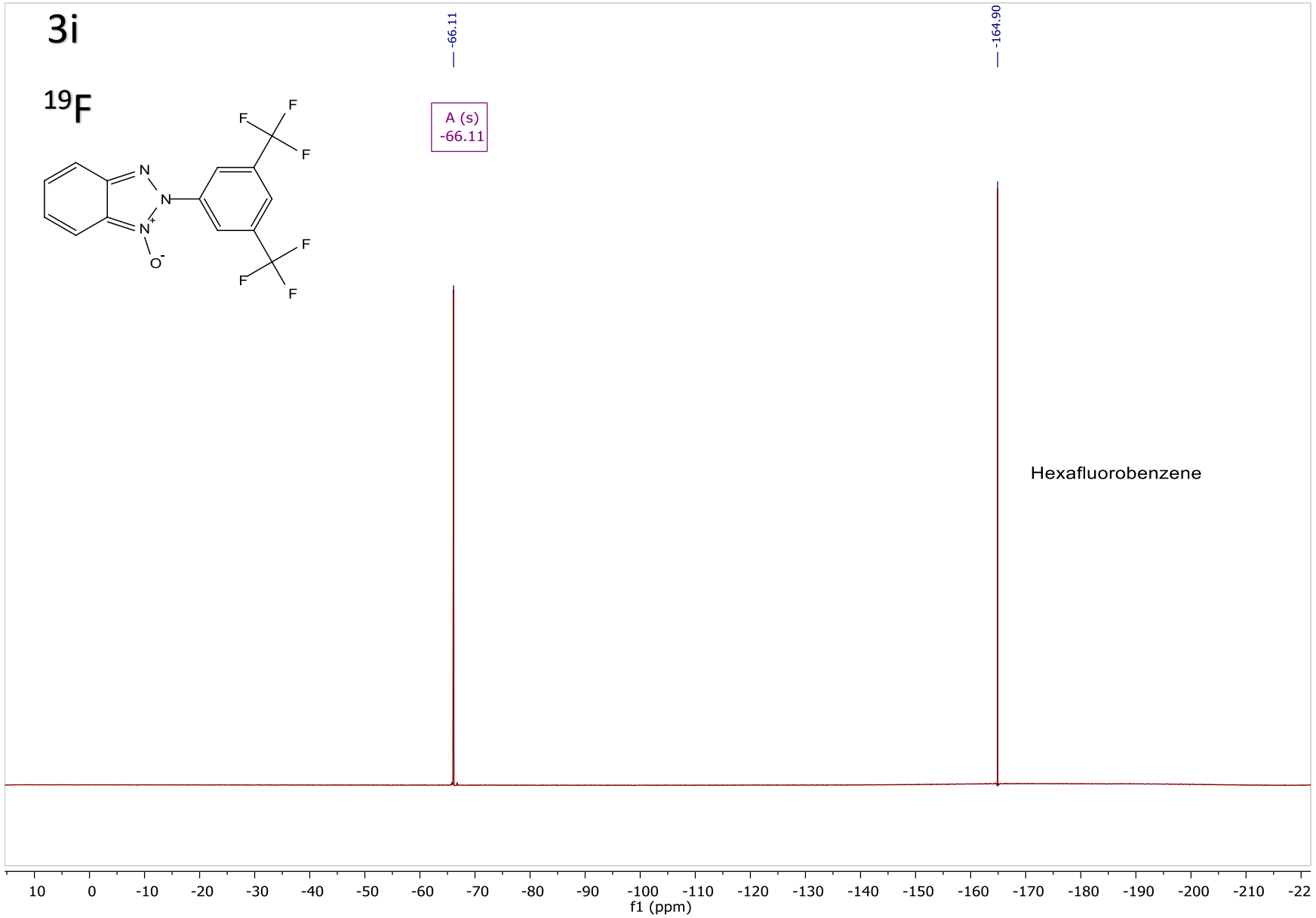

8.85 8.84 8.84 7.95 7.95 7.94 7.94 7.93 7.92 7.91 7.90 7.89 7.88 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42
F F F F F F
N N N
2i
1H
A (m) 8.84
B (m) 7.92
C (m) 7.46
1.89 2.93 2.00
f1 (ppm)
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

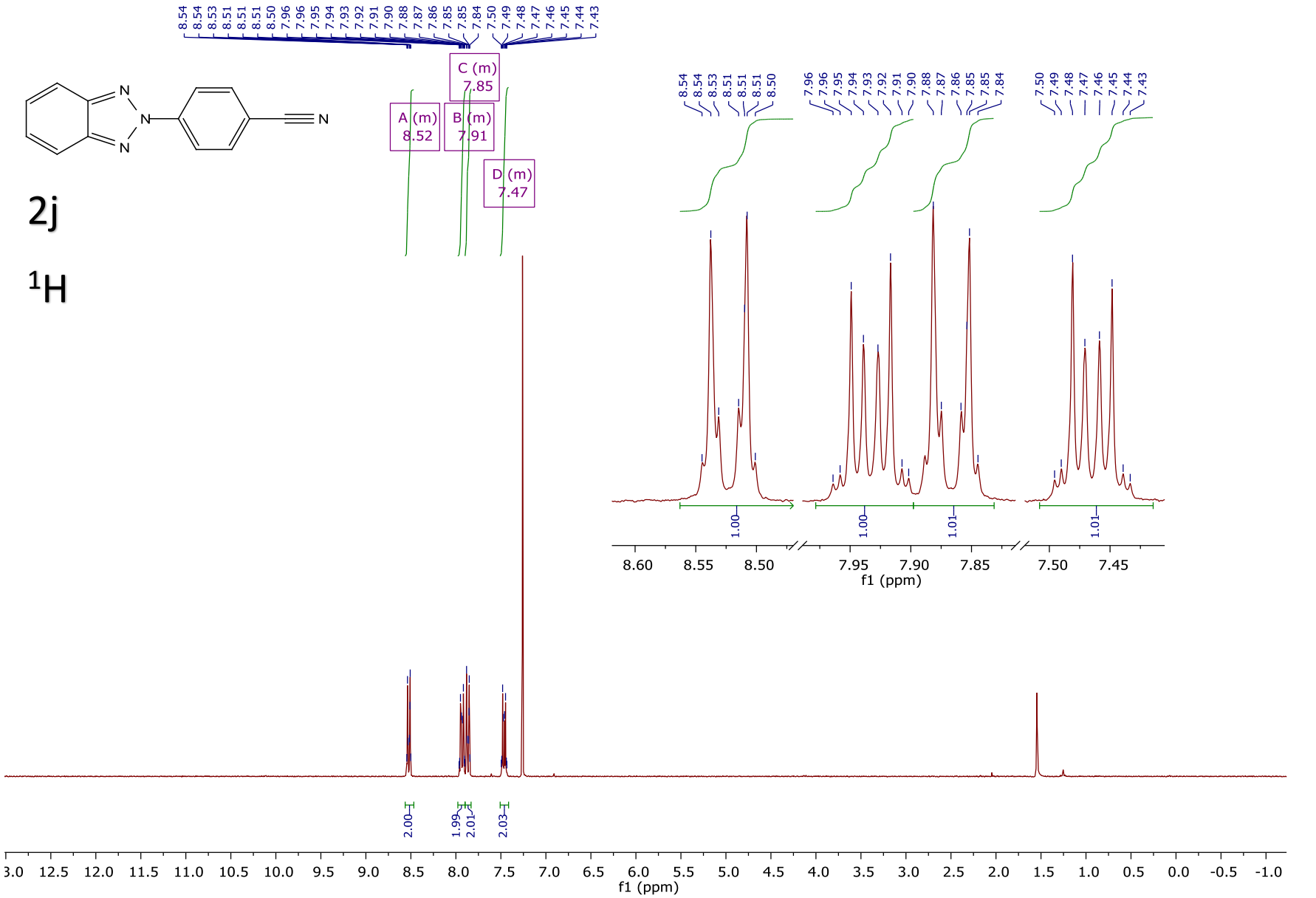

2i
$^{13}C\{^{1}H\}$
145.55
141.25
128.50
118.69
134.00
133.55
133.10
132.64
A (q)
133.32
134.0 133.5 133.0 132.5 132.0
f1 (ppm)
128.37
124.75
A (q)
122.94
121.13
117.51
128 127 126 125 124 123 122 121 120 119 118 117
f1 (ppm)
122.33
122.28
122.23
122.18
122.13
122.08
122.03
A (hept)
122.18
122.5 122.3 122.1 121.9 121.7
f1 (ppm)
120.74
120.69
120.64
120.58
A (q)
120.66
120.9 120.8 120.7 120.6 120.5 120.4 120.3 120.2
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

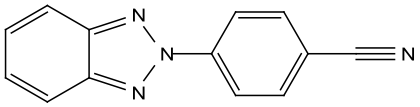

2i
19F
F
F
F
F
F
F
N
N
N
-66.17
A (s)
-66.17
-164.90
Hexafluorobenzene
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)


3i
1H
8.90
8.01
7.82
7.81
7.80
7.79
7.78
7.77
7.54
7.52
7.51
7.50
7.49
7.43
7.42
7.41
7.40
7.38
A (s) 8.90
B (s) 8.01
C (m) 7.79
D (m) 7.52
E (m) 7.41
2.00
1.00
1.96
1.05
1.06
f1 (ppm)
0.99
f1 (ppm)


3i
$^{13}C\{^{1}H\}$
141.93
136.58
130.45
127.49
119.36
114.18
128.19
124.57
120.95
117.33
B (q)
122.76
133.77
133.32
132.86
132.41
A (q)
133.09
123.10
123.05
123.00
122.95
122.89
122.83
122.78
C (m)
122.94
f1 (ppm)


3i
19F
-66.11
-164.90
A (s)
-66.11
Hexafluorobenzene
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

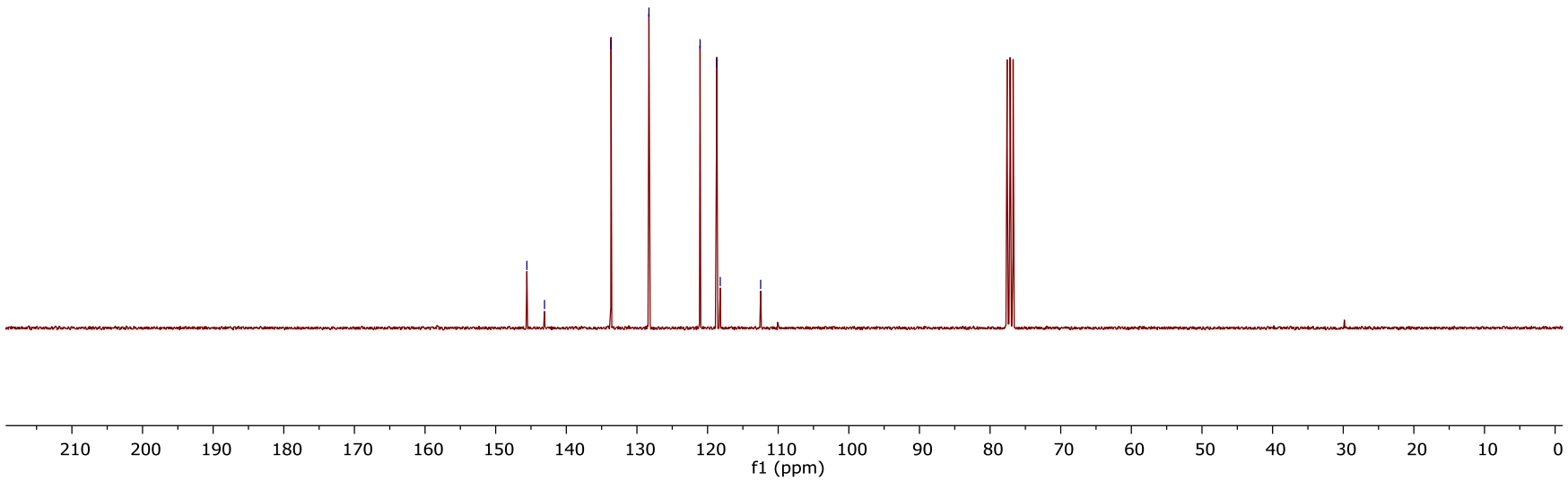

2j
1H
A (m) 8.52
B (m) 7.91
C (m) 7.85
D (m) 7.47
f1 (ppm)

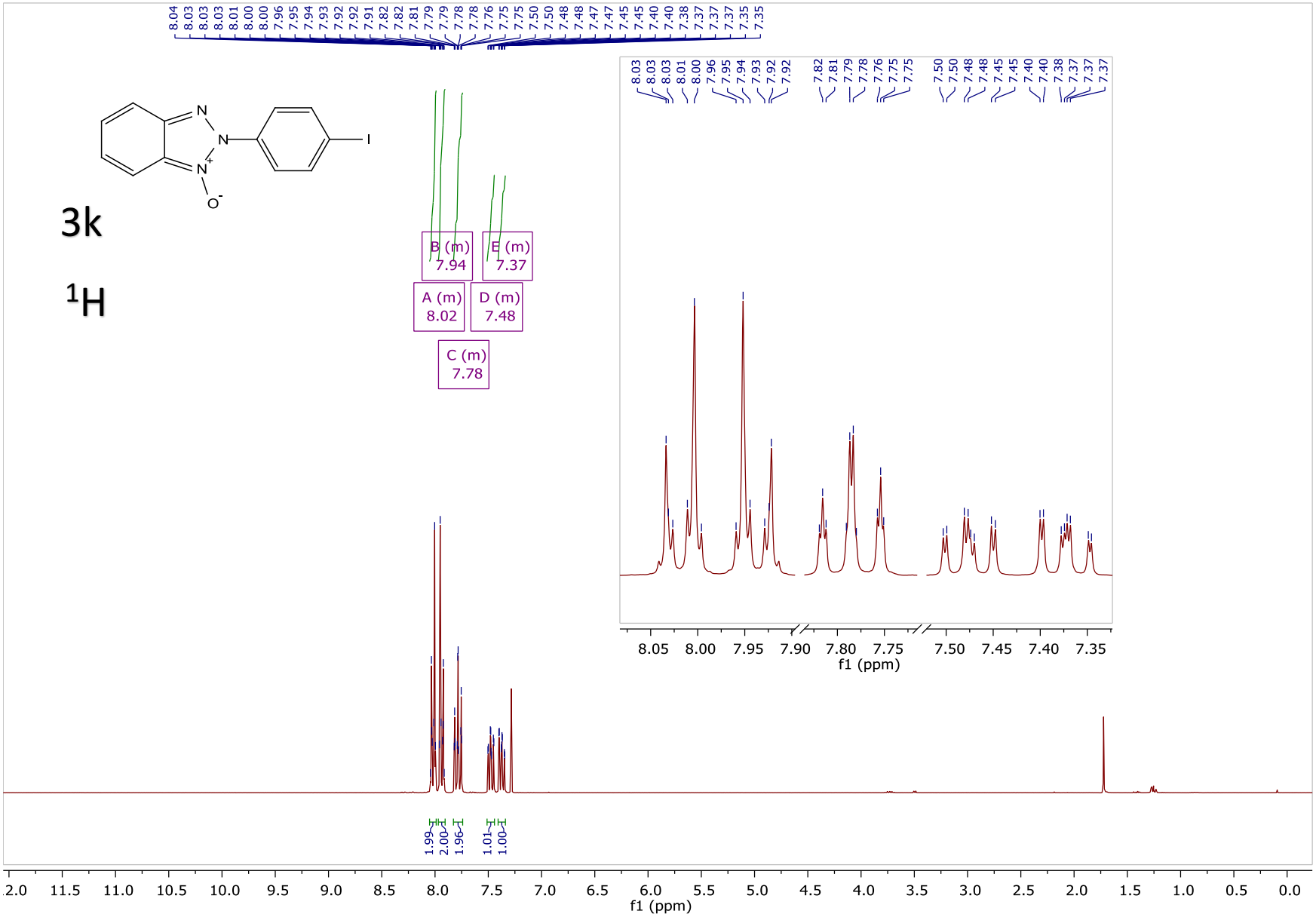


145.59
143.08
133.67
128.30
121.06
118.70
118.20
112.48

2j

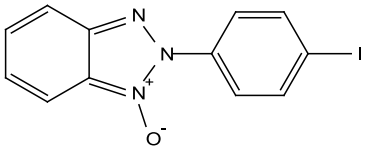
$^{13}C\{^{1}H\}$



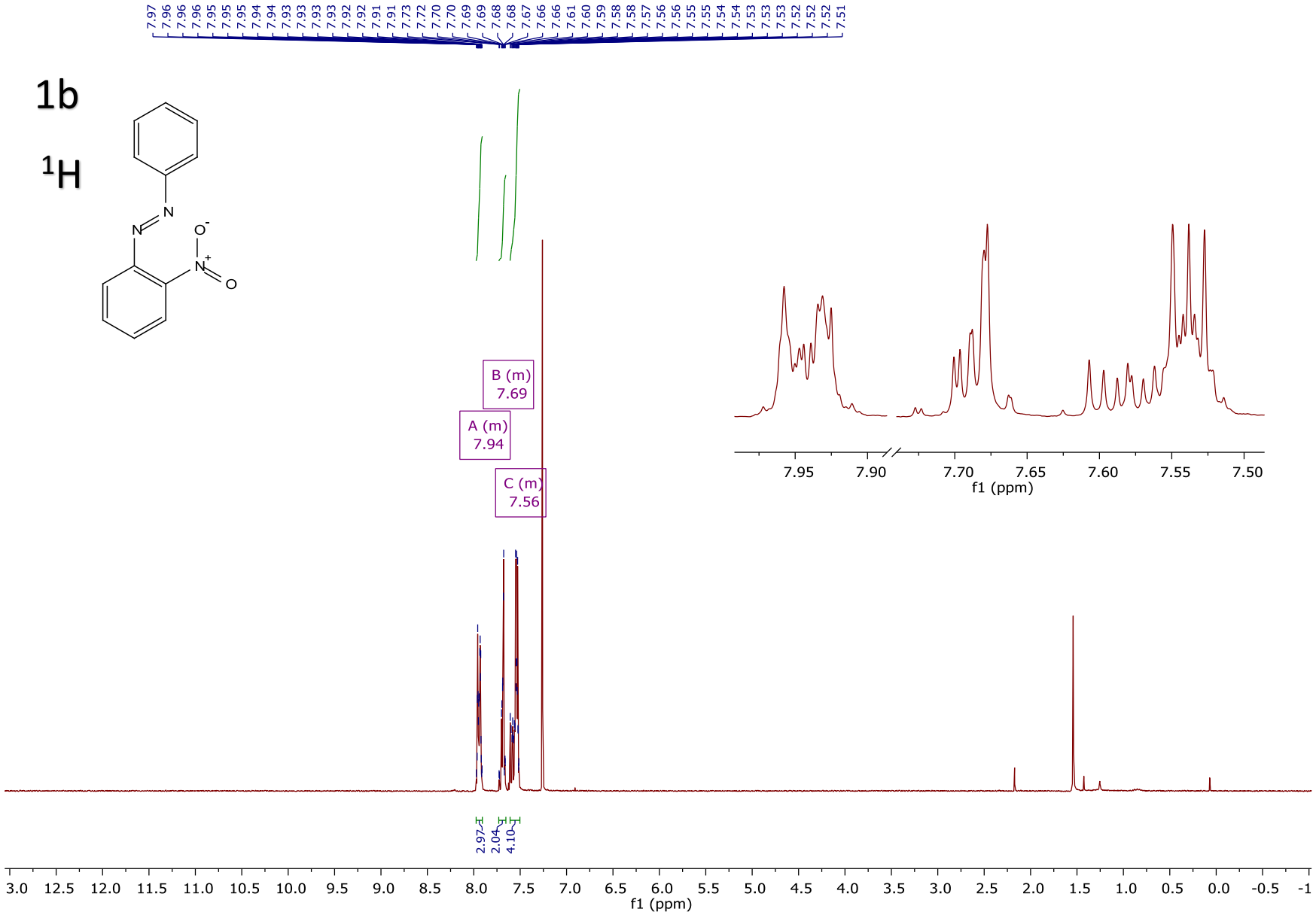

3k
1H
B (m) 7.94
E (m) 7.37
A (m) 8.02
D (m) 7.48
C (m) 7.78
f1 (ppm)

3k

$^{13}C\{^{1}H\}$

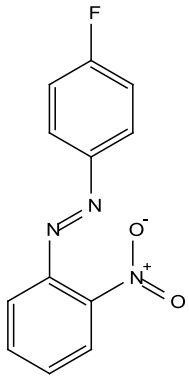

N
N
N+
O-
I

141.38
138.51
135.11
129.60
126.75
124.80
119.22
114.13
95.82
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1b
^{1}H
7.97 7.96 7.96 7.96 7.95 7.95 7.95 7.94 7.94 7.93 7.93 7.93 7.93 7.92 7.92 7.91 7.91 7.73 7.72 7.70 7.70 7.69 7.69 7.68 7.68 7.67 7.66 7.66 7.61 7.60 7.59 7.58 7.58 7.57 7.56 7.56 7.55 7.55 7.54 7.54 7.53 7.53 7.53 7.52 7.52 7.52 7.51
B (m) 7.69
A (m) 7.94
C (m) 7.56
2.97
2.04
4.10
7.95 7.90 7.70 7.65 7.60 7.55 7.50
f1 (ppm)
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

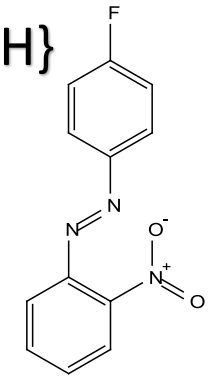
1a

^{1}H

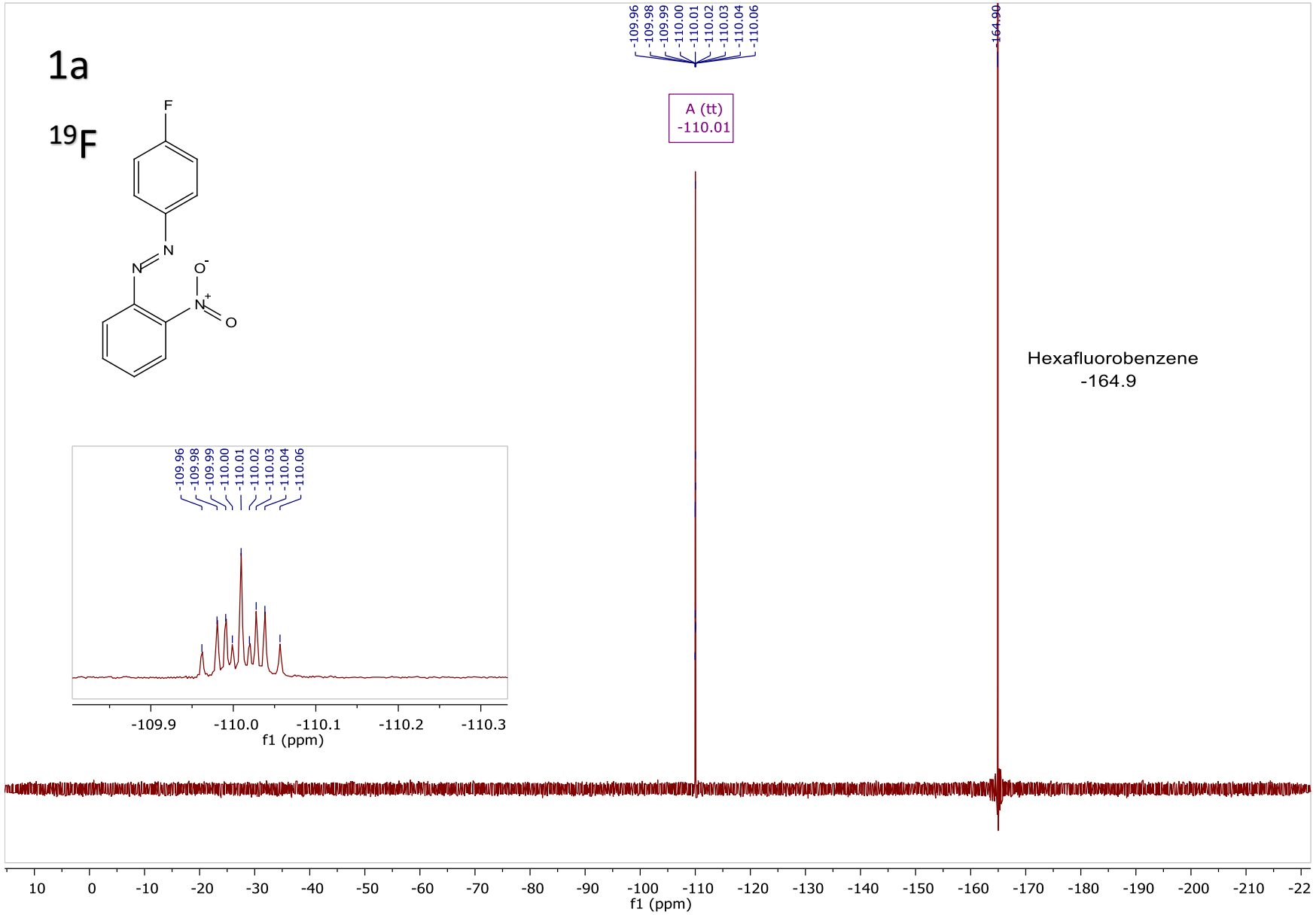


1a

$^{13}C\{^{1}H\}$

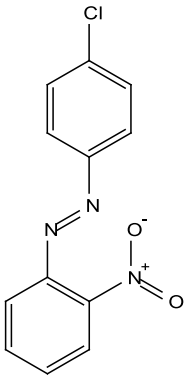

F
N
N
O
N
O

166.99
163.62
149.18
149.14
147.67
145.39
133.21
130.64
126.04
125.92
124.25
118.52
116.63
116.33
D (d)
165.31
C (d)
149.16
B (d)
125.98
A (d)
116.48
116.63
116.33
A (d)
116.48
116.8 116.7 116.6 116.5 116.4 116.3 116.2 116.1
f1 (ppm)
126.04
125.92
B (d)
125.98
126.05 126.00 125.95 125.90 125.85
f1 (ppm)
149.18
149.14
C (d)
149.16
149.30 149.20 149.10 149.00 148.90
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


1a
19F
F
N
N
O-
N+
O
-109.96
-109.98
-109.99
-110.00
-110.01
-110.02
-110.03
-110.04
-110.06
A (tt)
-110.01
-164.90
Hexafluorobenzene
-164.9
-109.9
-110.0
-110.1
-110.2
-110.3
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)

1c

^{1}H

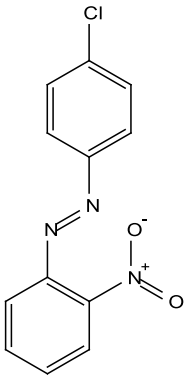

Cl
N
N
O
O
N
O

7.96 7.95 7.95 7.95 7.93 7.93 7.92 7.91 7.90 7.89 7.88 7.87 7.86 7.72 7.72 7.70 7.70 7.69 7.68 7.68 7.67 7.67 7.66 7.66 7.62 7.61 7.60 7.59 7.59 7.58 7.57 7.56 7.53 7.52 7.51 7.51 7.50 7.49 7.48
D (m) 7.59
B (m) 7.88
A (m) 7.94
C (m) 7.68
E (m) 7.50
0.95 2.00 2.03 1.00 2.01
f1 (ppm)

7.96 7.95 7.95 7.95 7.93 7.93 7.92 7.90 7.89 7.88 7.87 7.72 7.70 7.69 7.68 7.68 7.67 7.67 7.66 7.66 7.62 7.61 7.60 7.59 7.59 7.58 7.57 7.56 7.53 7.52 7.51 7.50 7.49 7.48
A (m) 7.94
B (m) 7.88
C (m) 7.68
D (m) 7.59
E (m) 7.50
0.95 2.00 2.03 1.00 2.01
f1 (ppm)

1c

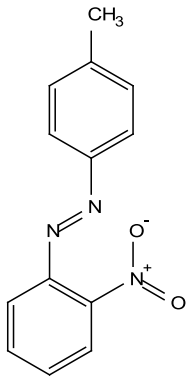
$^{3}C\{^{1}H\}$


Cl
N
N
O
N
O

150.89
147.73
145.34
138.61
133.22
130.86
129.71
125.01
124.27
118.47
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1d

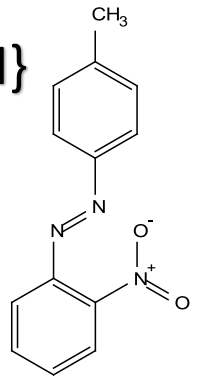
^{1}H


CH3
N
N
O
N
O

7.92 7.92 7.91 7.89 7.89 7.89 7.85 7.82 7.66 7.66 7.65 7.65 7.64 7.57 7.56 7.55 7.53 7.53 7.52 7.52 7.50 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.29
2.44
D (m) 7.53
B (d) 7.84
A (dt) 7.90
E (m) 7.32
C (m) 7.66
F (s) 2.44
1.00 1.99 2.01 1.03 2.03
f1 (ppm)

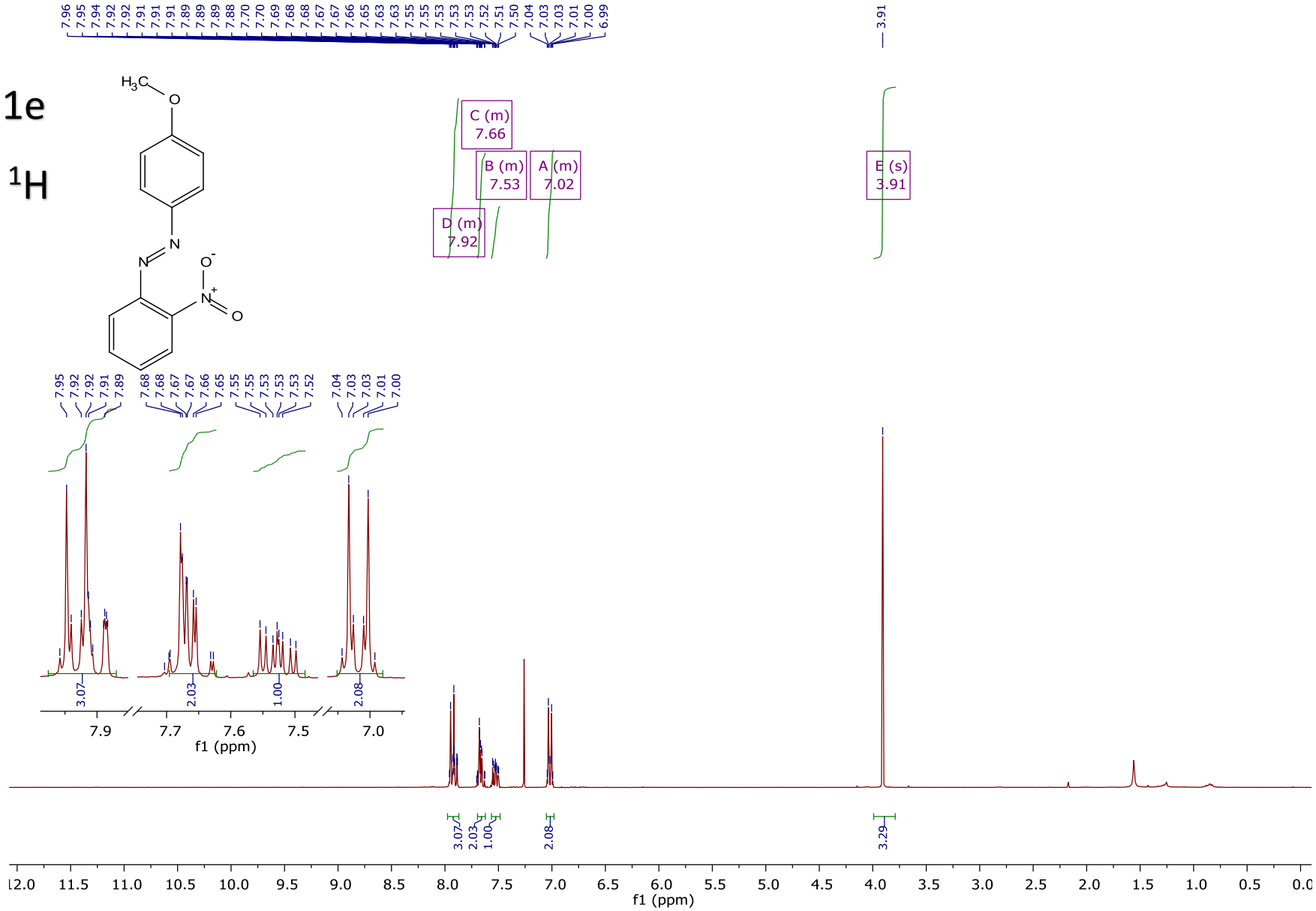
1d

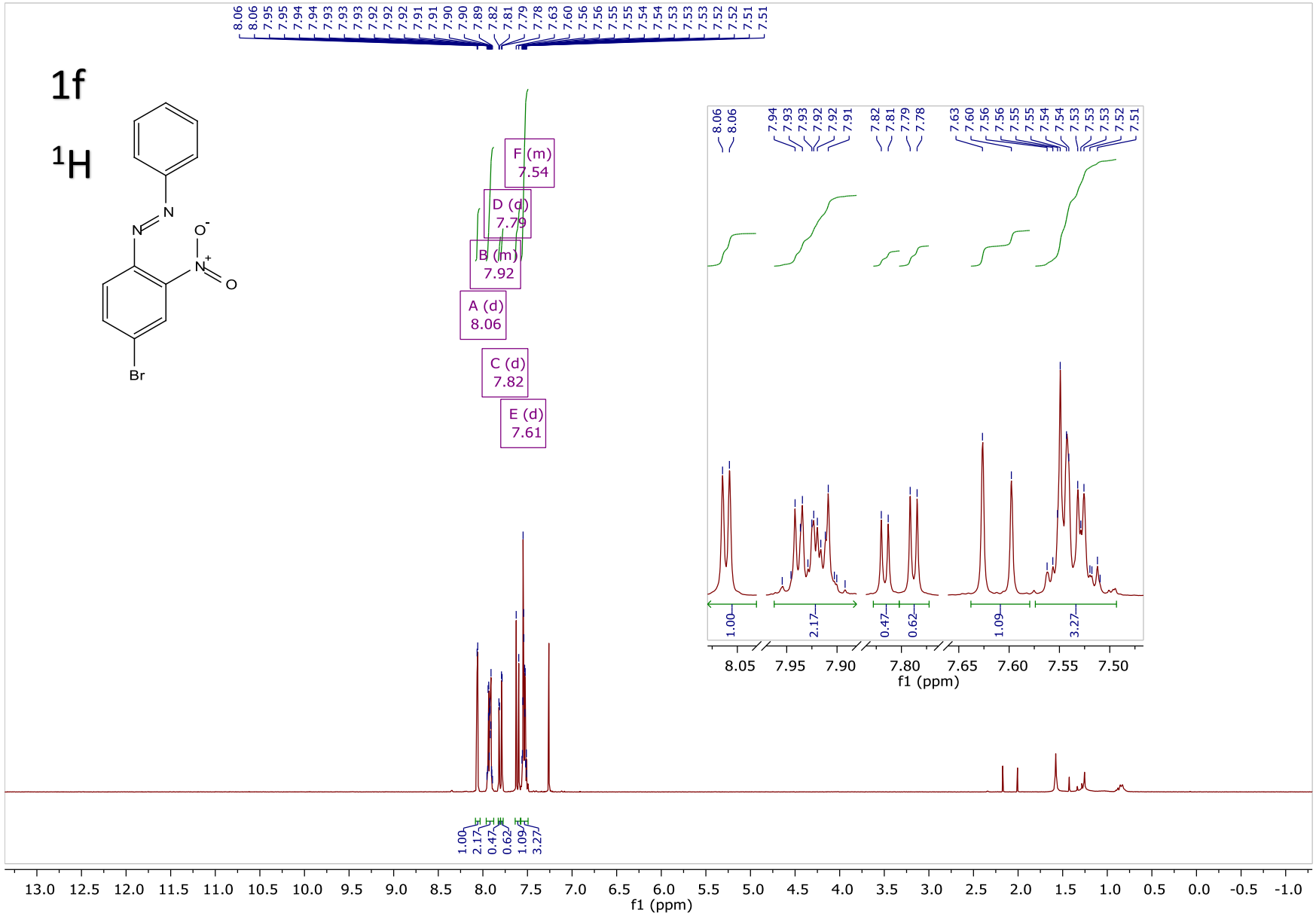
$^{13}C\{^{1}H\}$

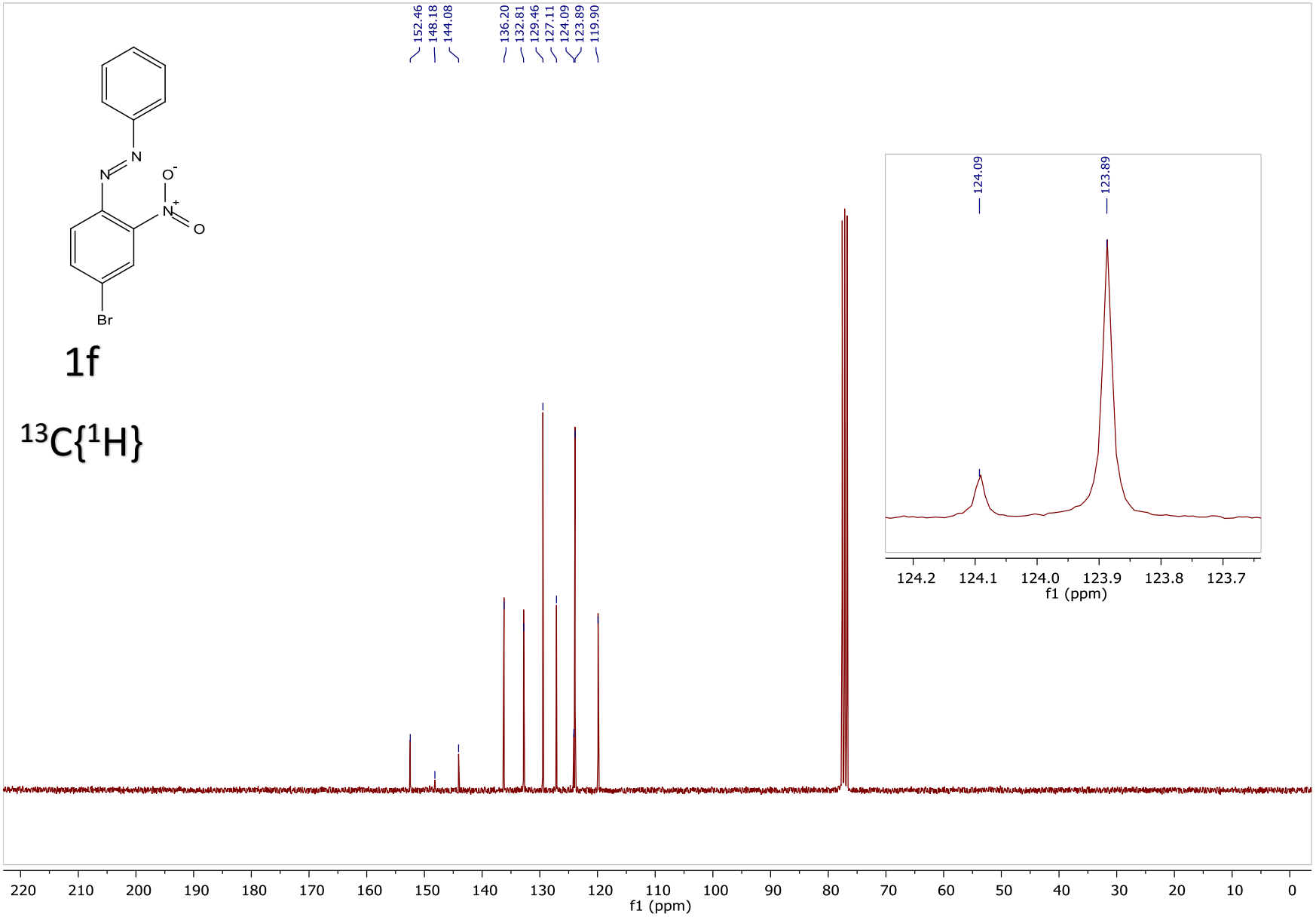

CH3
N
N
O-
N+
O

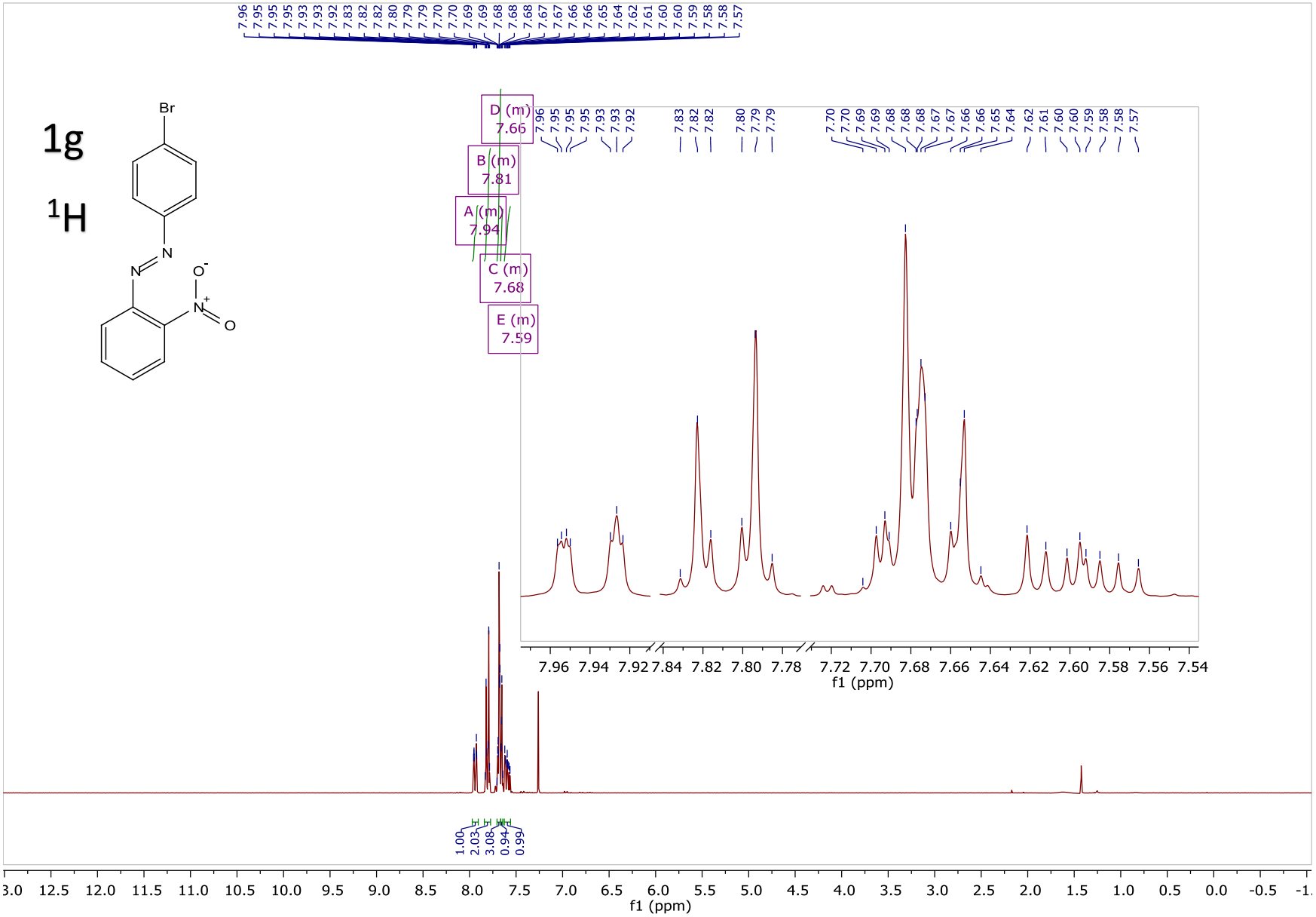
150.72
147.52
145.60
143.31
133.10
130.24
130.00
129.97
124.06
123.75
118.55
21.72
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

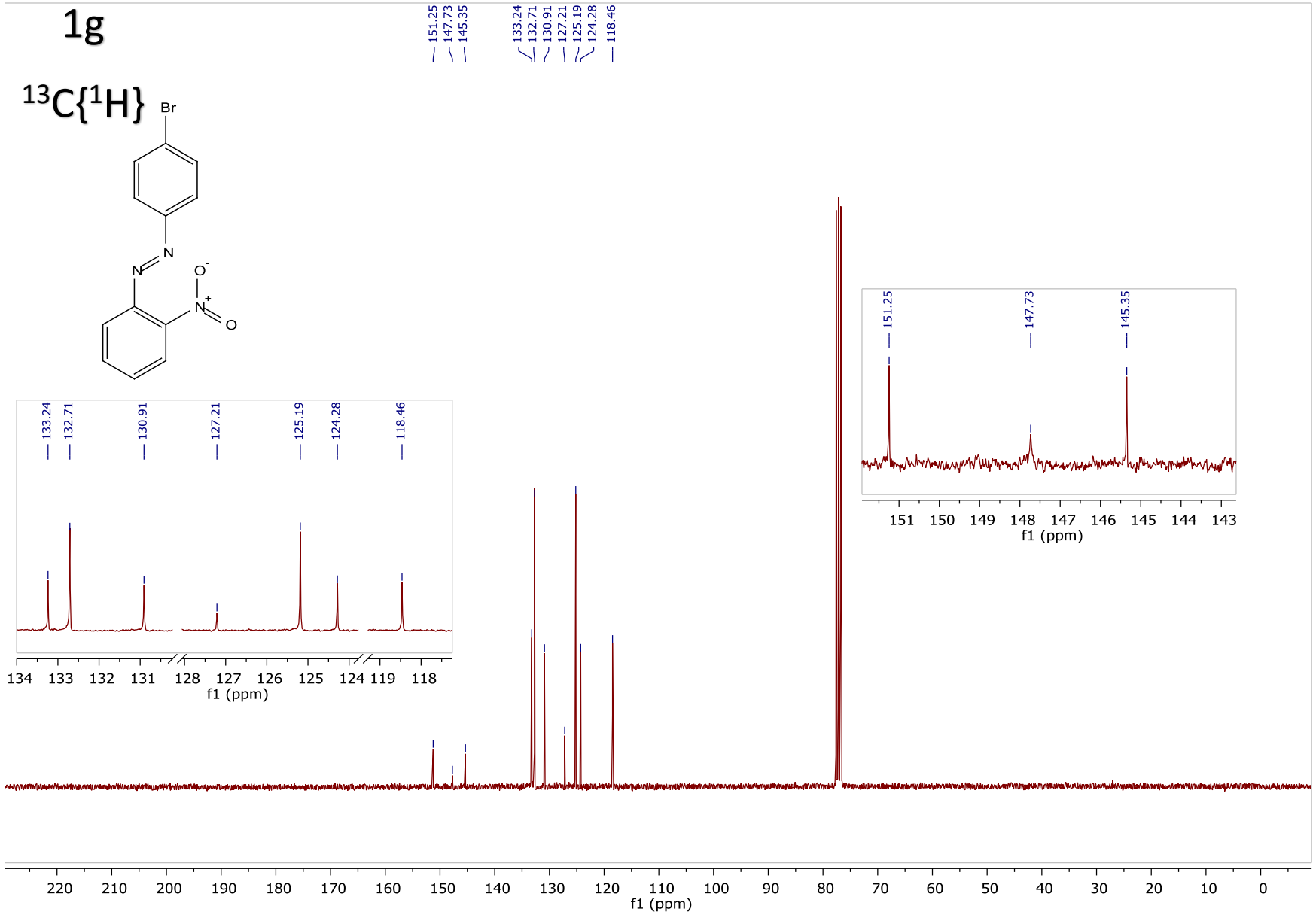
130.24
130.00
129.97
124.06
123.75
132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)


1e
^{1}H
C (m) 7.66
B (m) 7.53
A (m) 7.02
D (m) 7.92
E (s) 3.91
f1 (ppm)

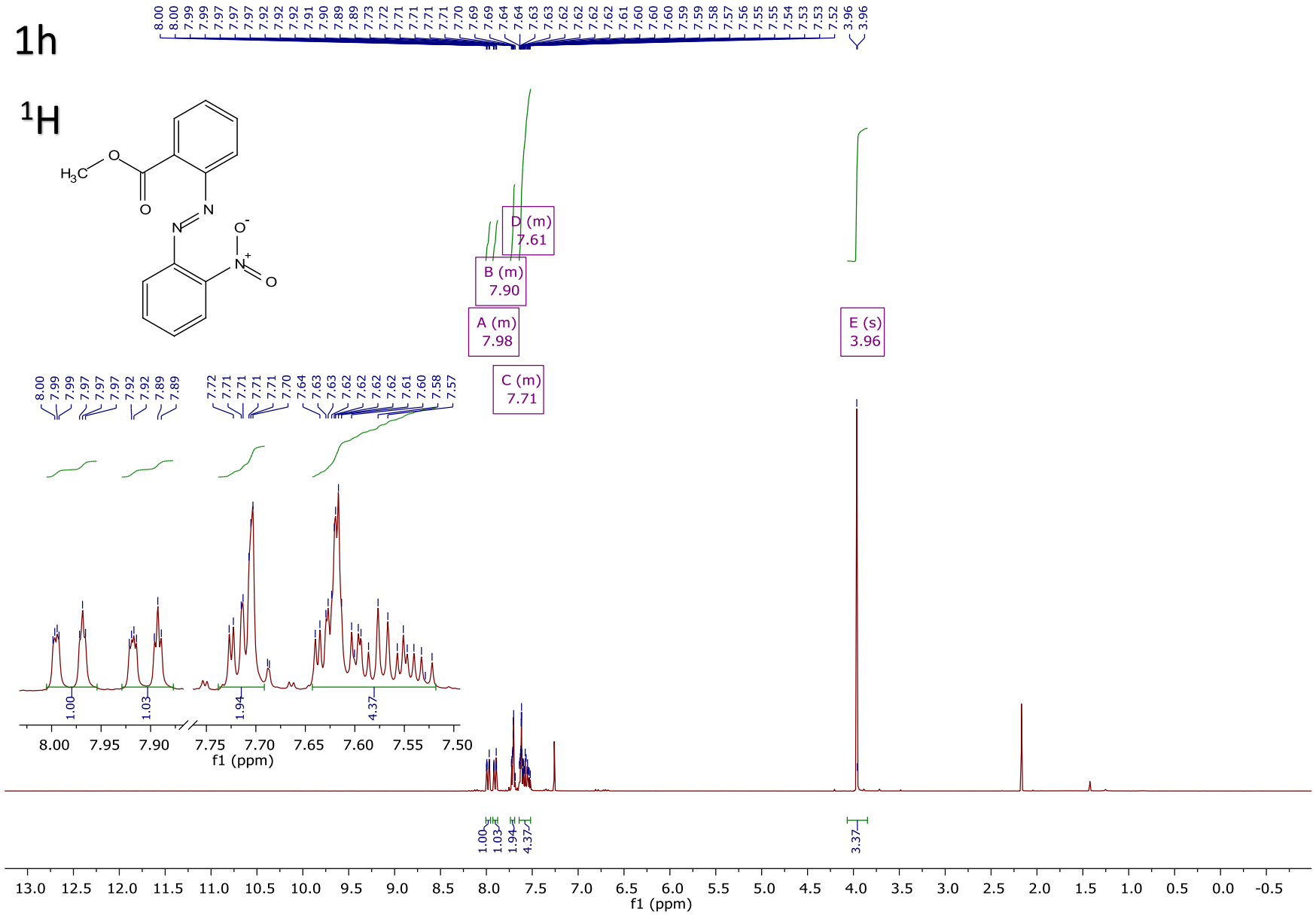

1f
1H
F (m)
7.54
D (d)
7.79
B (m)
7.92
A (d)
8.06
C (d)
7.82
E (d)
7.61
Br
f1 (ppm)


152.46
148.18
144.08
136.20
132.81
129.46
127.11
124.09
123.89
119.90
N
N
O
N
O
Br
1f
$^{13}C\{^{1}H\}$
124.09
123.89
124.2
124.1
124.0
123.9
123.8
123.7
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1g
^{1}H
Br
N
N
O
O
N
O
D (m)
7.66
B (m)
7.81
A (m)
7.94
C (m)
7.68
E (m)
7.59
7.96 7.95 7.95 7.95 7.93 7.93 7.92 7.83 7.82 7.82 7.80 7.79 7.79 7.70 7.70 7.69 7.69 7.68 7.68 7.68 7.67 7.67 7.66 7.66 7.65 7.64 7.62 7.61 7.60 7.60 7.59 7.58 7.58 7.57
7.96 7.94 7.92 7.84 7.82 7.80 7.78 7.72 7.70 7.68 7.66 7.64 7.62 7.60 7.58 7.56 7.54
f1 (ppm)
1.00 2.03 3.08 0.94 0.99
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

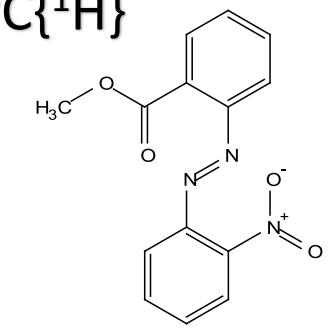

1g
$^{13}C\{^{1}H\}$
Br
N
N
O
O
N
O
151.25
147.73
145.35
133.24
132.71
130.91
127.21
125.19
124.28
118.46
f1 (ppm)

1h

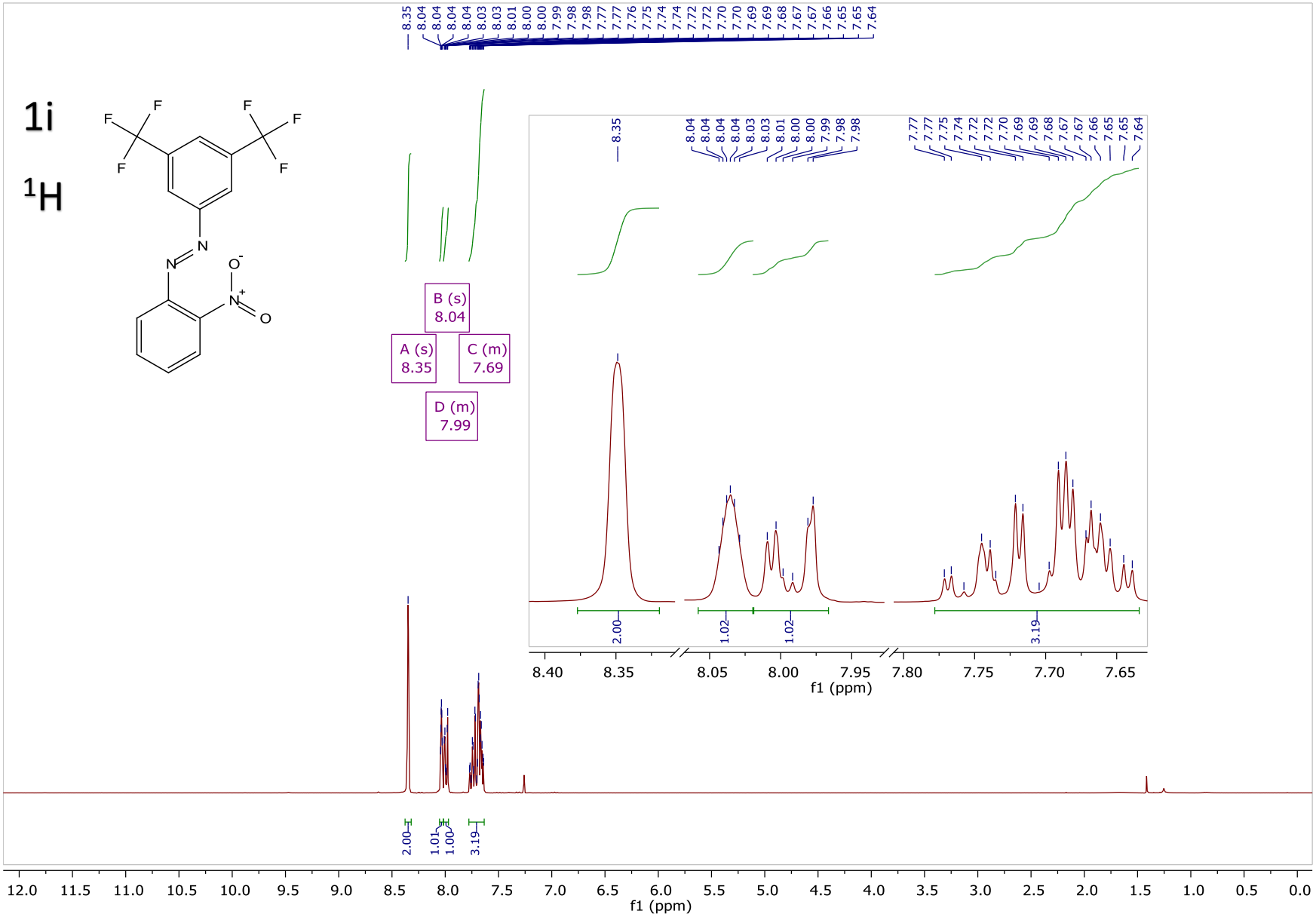


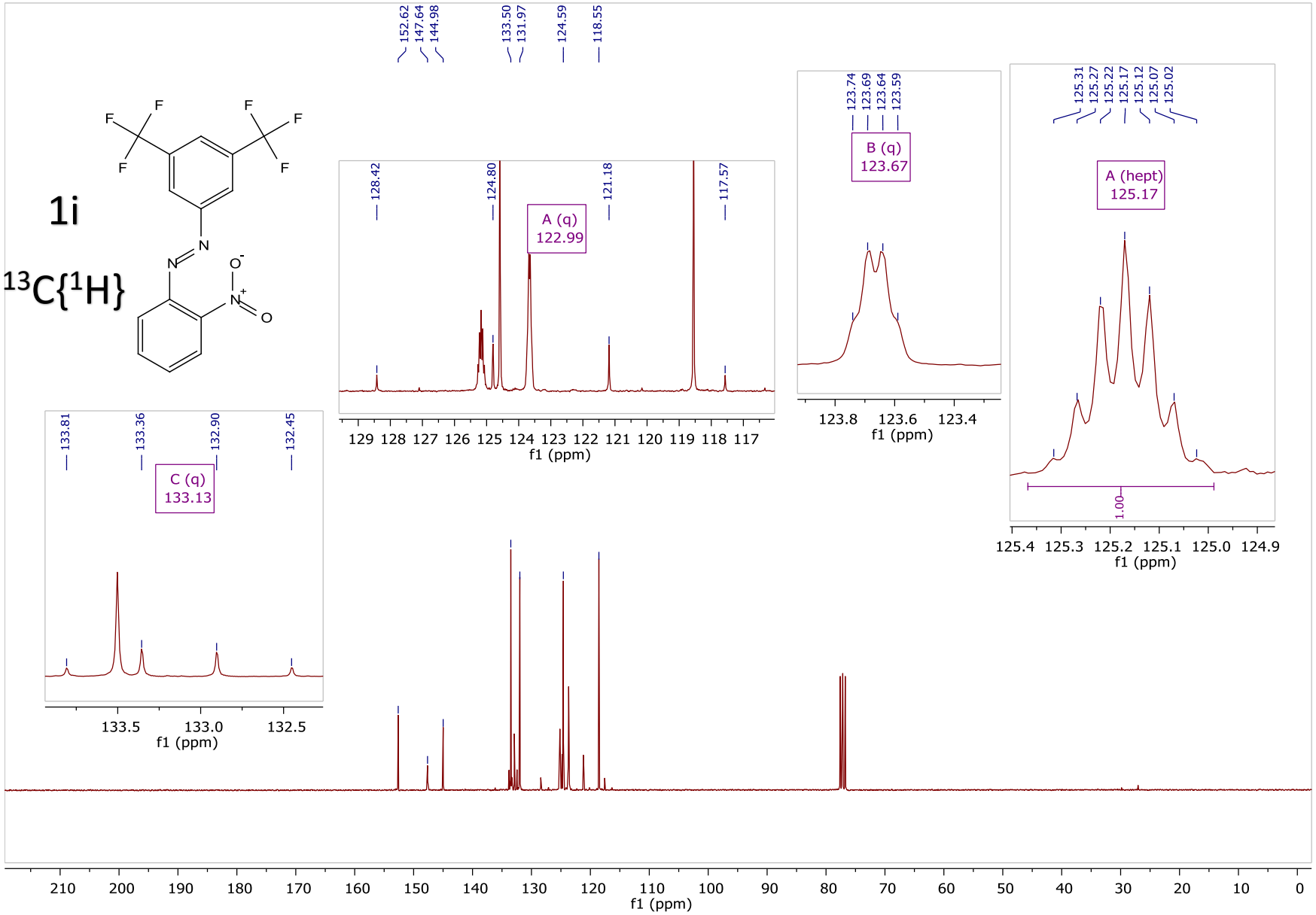
1h

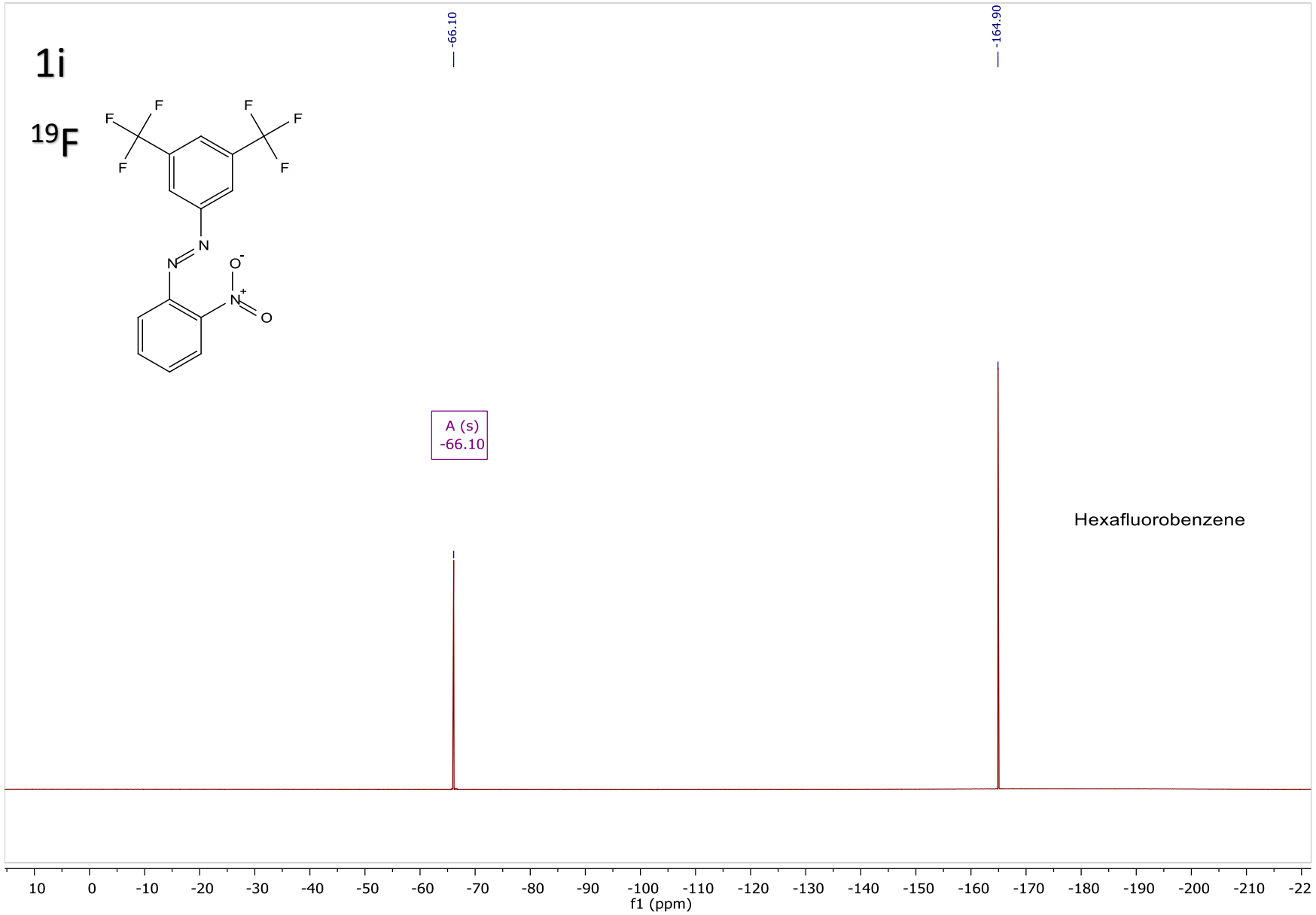
$^{13}C\{^{1}H\}$

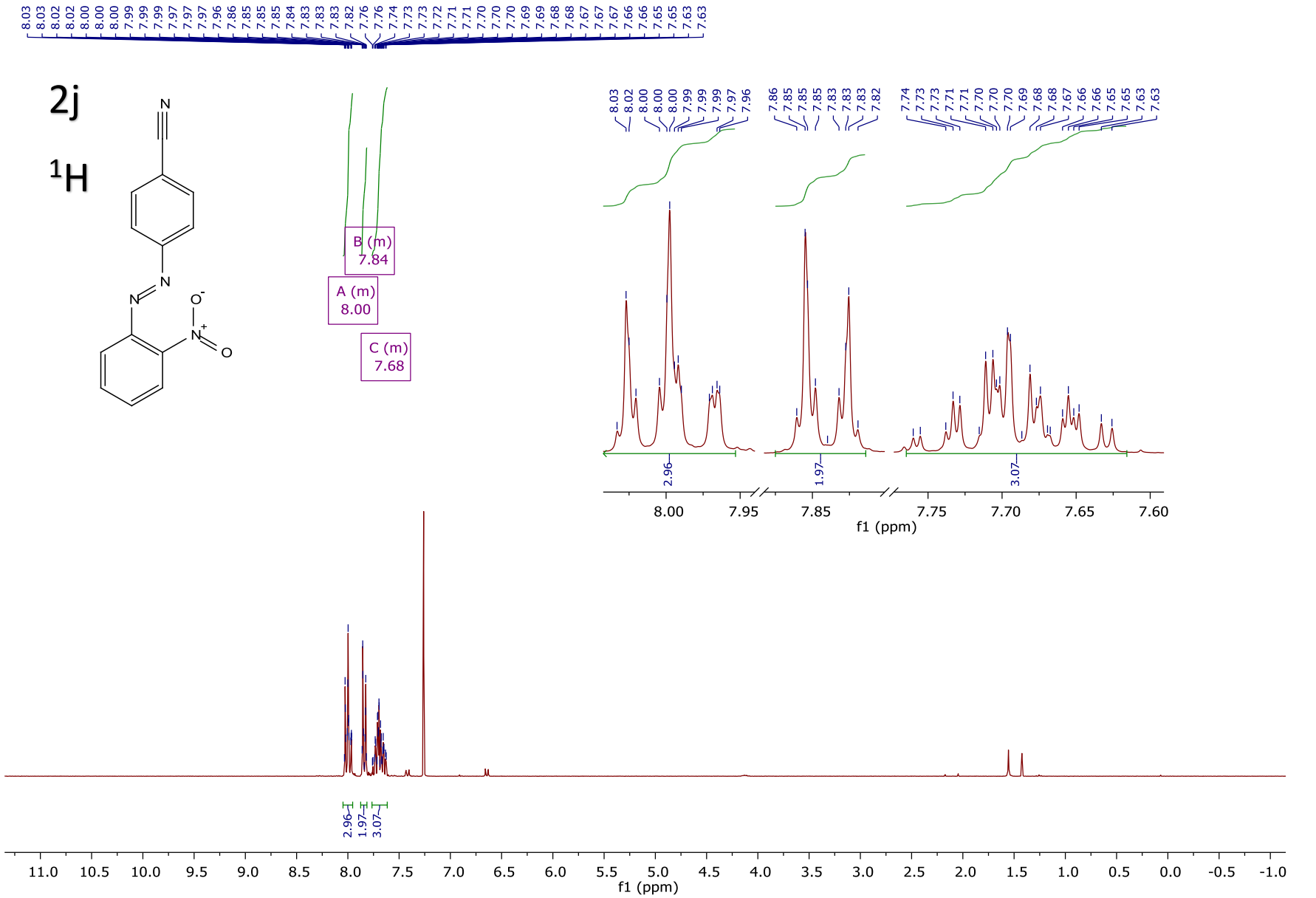

O
H3C
O
N
N
O-
N+
O

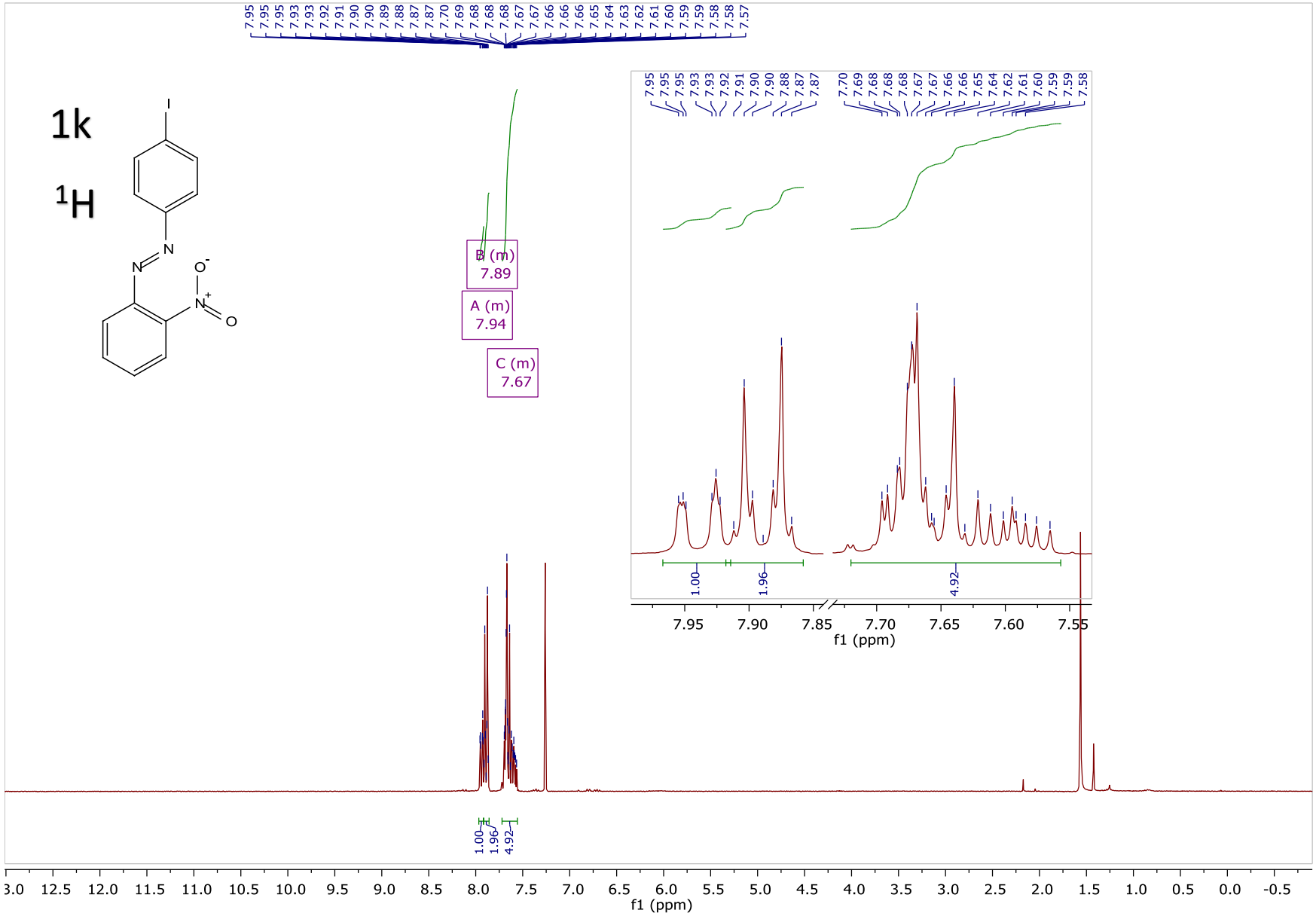
167.06
152.11
147.17
146.15
133.71
132.74
130.97
130.80
130.17
129.28
124.32
119.33
118.37
52.75
130.97
130.80
131.1
130.9
130.7
130.5
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1i
1H
B (s)
8.04
A (s)
8.35
C (m)
7.69
D (m)
7.99
f1 (ppm)


1i
$^{13}C\{^{1}H\}$
152.62
147.64
144.98
133.50
131.97
124.59
118.55
128.42
124.80
A (q)
122.99
121.18
117.57
129 128 127 126 125 124 123 122 121 120 119 118 117
f1 (ppm)
123.74
123.69
123.64
123.59
B (q)
123.67
123.8 123.6 123.4
f1 (ppm)
125.31
125.27
125.22
125.17
125.12
125.07
125.02
A (hept)
125.17
1.00
125.4 125.3 125.2 125.1 125.0 124.9
f1 (ppm)
133.81
133.36
132.90
132.45
C (q)
133.13
133.5 133.0 132.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

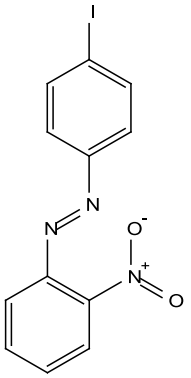

1i
19F
F
F
F
F
F
F
N
N
O
O
N
O
-66.10
-164.90
A (s)
-66.10
Hexafluorobenzene
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)


2j
1H
B (m)
7.84
A (m)
8.00
C (m)
7.68
2.96
1.97
3.07
f1 (ppm)


1k
1H
B (m)
7.89
A (m)
7.94
C (m)
7.67
1.00
1.96
4.92
f1 (ppm)

1k

$^{13}C\{^{1}H\}$


I
N
N
O
N
O

151.77
147.68
145.28
138.70
133.21
130.90
125.17
125.16
124.24
118.43
99.76
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)