Supporting information for:

Sterically Controlled Iodination of Arenes via Iridium-Catalyzed C-H Borylation

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1. General Experimental Details

All air and moisture sensitive manipulations were performed under an inert atmosphere using either an argon-filled glovebox (MBraun) or standard Schlenk techniques. All anhydrous solvents were degassed by purging with argon for 45 min and then dried with a solvent purification system using a 1 m column containing activated alumina. All reagents and solvents were used as purchased if not otherwise stated. $[Ir(COD)OMe]_2$ was obtained from Johnson Matthey and stored at -35 °C in the glovebox. B_2pin_2 was obtained from BASF and used as purchased. 4-Methoxyphenyl boronic acid pinacol ester[1] and *N*-TIPS-pyrrole[2] were prepared according to the literature. KI was dried over P_2O_5 at 110 °C under vacuum (~100 mtorr) overnight.

All borylation reactions were conducted under an atmosphere of argon in 20 mL oven-dried vials sealed with Teflon-lined caps. All iodination reactions were conducted in a 250 mL pressured vessel (Ace Glass Inc.) under air and sealed using a Teflon stopper.

NMR spectra were acquired on either a Bruker AVQ-400 or AVB-400 NMR spectrometer. ^1H and ^{13}C NMR spectra were referenced to external tetramethylsilane *via* the residual *protio* solvent (^1H) or the solvent itself (^{13}C). All chemical shifts are reported in ppm. Infrared spectra were recorded using a Thermo Scientific Nicolet iS5 machine irradiating between 4000 cm^{-1} and 600 cm^{-1}. Samples were prepared by forming a thin film of material on a KBr disk. Mass spectrometry was conducted by the University of California, Berkeley Chemistry Mass Spectrometry Facility. Elemental analysis was conducted by the University of California, Berkeley Microanalysis service. All GC-MS analyses were conducted with an Agilent 6890N GC equipped with an HP-5 column (25 m × 0.20 mm ID × 0.33 μm film) and an Agilent 5973 Mass Selective Detector. The temperature for each run was held at 50 °C for 2 min, ramped from 50 °C to 300 °C at 40 °C/min, and held at 300 °C for 5 min. GC analysis was performed on an Agilent 7890 GC equipped with an HP-5 column (25 m × 0.20 mm × 0.33 μm film) and an FID detector. Quantitative GC analysis was performed by adding 1,3,5-trimethoxybenzene as an internal standard to the reaction mixture. A response factor for the product relative to the internal standard was measured for reaction development studies. Analytical thin-layer chromatography (TLC) was performed on glass-backed plates pre-coated (0.25 mm) with silica gel (EMD Chemicals Inc., Silica Gel 60 F254). Compounds were visualised by exposure to UV light or by dipping the plates in solutions of phosphomolybdic acid or potassium permanganate followed by heating. Column chromatography was done on Silicycle Siala-P silica gel.

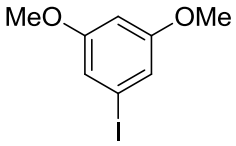
[1] Fukuda, T.; Sudo, E.-i.; Shimokawa, K.; Iwao, M. *Tetrahedron* **2008**, *64*, 328.
[2] John, E. A.; Pollet, P.; Gelbaum, L.; Kubanek, J. *J. Nat. Prod.* **2004**, *67*, 1929.

2. General Procedure for the Sequential C-H Borylation and Iodination Process.

In a glovebox,[3] the arene (1.25 mmol, 1.00 equiv) was added to a solution of $[Ir(cod)OMe)]_2$ (0.8 mg, 0.001 mmol, 0.1 mol%), dtbpy (0.7 mg, 0.003 mmol, 0.2 mol%) and B_2pin_2 (0.239 g, 0.941 mmol, 0.750 equiv) in tetrahydrofuran (2.5 mL). The vial was sealed under argon with a Teflon-lined cap. The mixture was heated at 80 °C for 24-48 h, over which time the reaction was monitored by GCMS. The mixture was cooled to room temperature and concentrated *in vacuo*. The residue was dissolved in MeOH (10 mL), and the methanol solution was transferred to a 250 mL pressure vessel containing CuI (23.8 mg, 0.125 mmol, 10.0 mol%), phen (45.0 mg, 0.250 mmol, 20.0 mol%) and KI (0.311 g, 1.88 mmol, 1.50 equiv). The mixture was stirred at room temperature, and water (2.5 mL) was added. The flask was sealed under air, and the mixture was heated at 80 °C for 1 h, over which time the reaction was monitored by GCMS. The reaction was cooled to room temperature, water (25 mL) was added, and the mixture was extracted with Et_2O (3 × 25 mL). The combined organic phases were washed with brine (25 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Silica gel chromatography was conducted with aluminium foil wrapped around the column to minimise decomposition of the aryl iodide.

3. Substrates

1-Iodo-3,5-bismethoxybenzene (3a)



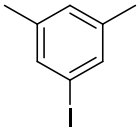
According to the general procedure, reaction of 1,3-dimethoxybenzene (0.16 mL, 1.2 mmol) followed by silica gel chromatography (3% Et_2O, 97% hexane) gave iodide **3a** (0.167 g, 52%) as a white solid. The NMR data match the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 2.2 Hz, 2H, ArH), 6.40 (t, *J* = 2.2 Hz, 1H, ArH), 3.76 (s, 6H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 115.9, 100.8, 94.2, 55.6.

[3] For a procedure for the iridium-catalyzed borylation of arenes under an inert atmosphere, outside of a glovebox, see: Murphy, J. M.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc*. **2007**, *129*, 15434.
[4] Mariampillai, B.; Alberico, D.; Bidau, V.; Lautens, M. *J. Am. Chem. Soc.* **2006**, *128*, 14436.

1-Iodo-3,5-bismethylbenzene (3b)



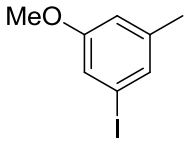
According to the general procedure, reaction of *m*-xylene (0.15 mL, 1.2 mmol) followed by silica gel chromatography (100% pentane) gave iodide **3b** (0.142 g, 50%) as a colorless oil. The NMR data match the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 2 H, ArH), 6.95 (s, 1 H, ArH), 2.26 (s, 6 H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 135.2, 129.5, 94.4, 21.0.

MS (EI) 232 (100, MI), 105 (32, MI – I), 79 (19).

1-Iodo-3-methoxy-5-methylbenzene (3c)



According to the general procedure, reaction of 3-methylanisole (0.16 mL, 1.3 mmol) followed by silica gel chromatography (5% CH_2Cl_2, 95% pentane) gave iodide **3c** (0.185 g, 59%) as a pale yellow oil. No literature data available.

^{1}H NMR (400 MHz, $CDCl_3$): 7.14 (s, 1H, ArH), 7.06 (s, 1H, ArH), 6.68 (s, 1H, ArH), 3.76 (s, 3H, OCH_3), 2.28 (s, 3H, $ArCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): 160.1, 141.3, 130.8, 120.1, 114.9, 94.3, 55.5, 21.2.

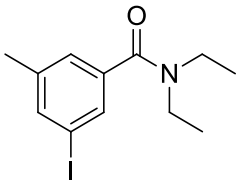
HRMS (EI) calculated for $C_8H_9{}^{127}IO$: 247.9698, found 247.9702.

MS (EI): 248 (100, MI), 121 (24 – I).

IR ν_{max} (neat) / cm^{-1}: 2922, 1593, 1307, 1153, 1052, 829, 678.

[5] Sundberg, R. J.; Heintzelman, R. W. *J. Org. Chem.* **1974**, *39*, 2546.

***N*,*N*-Diethyl-3-iodo-5-methylbenzamide (3d)**



According to the general procedure, the reaction of *N*,*N*-diethyl-3-methylbenzamide (0.24 mL, 1.3 mmol) followed by silica gel chromatography (5% Et_2O, 95% CH_2Cl_2) gave *iodide* **3d** (0.232 g, 58%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H, ArH), 7.47 (s, 1H, ArH), 7.11 (s, 1H, ArH), 3.58 – 3.42 (m, 2H, CH_2), 3.28 – 3.16 (m, 2H, CH_2), 2.30 (s, 3H, $ArCH_3$), 1.22 (br. s, 3H, NCH_3), 1.09 (br. s, 3H, NCH_3).

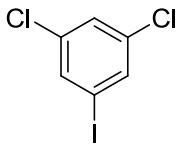
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 140.6, 139.1, 138.7, 132.1, 126.3, 94.2, 43.4, 39.3, 21.1, 14.3, 12.9.

HRMS (ESI) calculated for $C_{12}H_{17}{}^{127}INO$: 318.0349, found 318.0348.

MS (ESI) 381 (100), 340 (29, MI + Na), 318 (24, MI + H).

IR ν_{max} (neat) / cm^{-1}: 2970, 1632, 1434, 1287, 642.

1,3,-Dichloro-5-iodobenzene (3e)



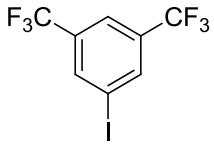
According to the general procedure, reaction of 1,3-dichlorobenzene (0.14 mL, 1.2 mmol) followed by silica gel chromatography (100% pentane) gave iodide **3e** (0.266 g, 79%) as a white solid. The NMR data match the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$): 7.61 (d, J = 1.8 Hz, 2H, ArH), 7.34 (t, J = 1.8 Hz, 1H, ArH).

^{13}C NMR (101 MHz, $CDCl_3$): 135.6, 135.6, 128.4, 93.8.

[6] Melzig, L.; Diène, C. R.; Rohbogner, C. J.; Knochel, P. *Org. Lett.* **2011**, *13*, 3174.

1-Iodo-3,5-bis(trifluoromethyl)benzene (3f)

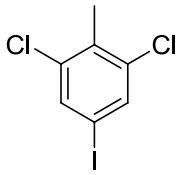


1,3-Bis(trifluoromethyl)benzene (0.19 mL, 1.2 mmol) was allowed to react according to the general procedure, with the iodination step being heated at 80 °C for 3 hours. The crude material was passed through a silica plug (100% pentane), and concentrated *in vacuo* (100 torr) to give iodide **3f** (0.266 g, 71%) as a colorless oil. The NMR data match the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): 8.14 (s, 2H, ArH), 7.84 (s, 1H, ArH).

^{13}C NMR (101 MHz, $CDCl_3$): 137.9 (q, J_F = 3.7 Hz), 133.2 (q, J_F = 33.7 Hz), 122.3 (q, J_F = 273.1 Hz), 121.9 (q, J_F = 3.8 Hz), 94.1.

1,3-Dichloro-5-iodo-2-methylbenzene (3g)



According to the general procedure, reaction of 2,5-dichlorotoluene (0.16 mL, 1.3 mmol) followed by passing the crude mixture through a plug of silica gel (100% pentane), and concentrating under reduced pressure (~100 mtorr) gave iodide **3g** (0.285 g, 80%) as a white solid. The data matches the literature values for ^{1}H NMR but not the ^{13}C NMR.[8]

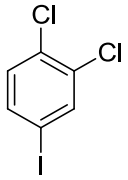
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 2H, ArH), 2.40 (s, 3H, CH_3).

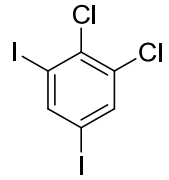
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2 (2 C), 136.1 (2 C), 134.5, 89.3, 17.4. Literature: ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9 (2 C), 134.2, 129.1 (2 C), 89.2, 17.2.

MS (EI): 286 (100, MI), 251 (58, MI – Cl), 159 (26, MI – I), 123 (38).

[7] Chambers, R. D.; Skinner, C. J.; Atherton, M. J.; Moilliet, J. S. *J Chem. Soc. Perk. T. 1*, **1996**, 1659.
[8] Schlosser, M.; Heiss, C.; Marzi, E.; Scopelliti, R. *Eur. J. Org, Chem.* **2006**, *2006*, 4398.

1,2-Dichloro-4-iodobenzene (3h)





3h-2

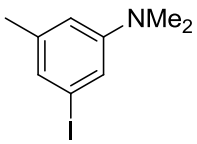
According to the general procedure, 1,2-dicholobenzene (0.14 mL, 1.3 mmol, 2 equiv) was allowed to react with B_2pin_2 (0.159 g, 0.624 mmol, 1 equiv). After work-up, the crude mixture was passed through a plug of silica gel (100% pentane), and concentrated under reduced pressure (~100 mtorr) to give iodide **3h** (0.221 g, 65%) as a colorless oil containing ~3% diiodide **3h-2**. The data matches the literature values for ^{1}H NMR but not the ^{13}C NMR.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H, ArH), 7.54 – 7.47 (m, 1H, ArH), 7.16 (d, *J* = 8.4 Hz, 1H, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.9, 133.8, 132.8, 131.9, 91.1; Literature: ^{13}C NMR (6 MHz, $CDCl_3$) δ 139.2, 137.3, 134.2, 133.3, 132.2, 91.7.[9]

MS (EI): 271 (100, MI), 145 (69, MI – I), 109 (33, MI – I – Cl).

3-Iodo-*N*,*N*-5-trimethylaniline (3i)



According to the general procedure, reaction of 3-*N*,*N*-trimethylaniline (0.18 mL, 1.2 mmol) followed by silica gel chromatography (20% CH_2Cl_2, 80% pentane) gave *iodide* **3i** (0.160 g, 50%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 6.90 (s, 1H, ArH), 6.85 (s, 1H, ArH), 6.47 (s, 1H, ArH), 2.91 (s, 6H, 2 × NCH_3), 2.26 (s, 3H, $ArCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): 151.6, 140.6, 126.3, 118.6, 112.6, 95.6, 40.5, 21.6.

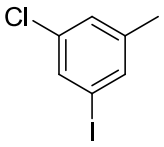
HRMS (ESI) calculated for $C_9H_{13}{}^{127}IN$: 262.0087, found 262.0084.

MS (ESI) 262 (MI + H).

IR ν_{max} (neat) / cm^{-1}: 2918, 1594, 1345, 987, 815.

[9] Nevalainen, T.; Kolehmainen, E. *Magn. Reson. Chem*, **1996**, *34*, 965.

1-Chloro-3-iodo-5-methyl-benzene (3j)

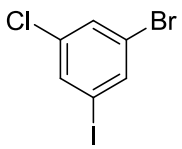


According to the general procedure, the reaction of 3-chlorotoluene (0.14 mL, 1.2 mmol) followed by silica gel chromatography (10% CH_2Cl_2, 90% pentane) gave iodide **3j** (0.225 g, 73%) as a colorless oil. The NMR data match the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$): 7.51 (s, 1H, ArH), 7.42 (s, 1H, ArH), 7.13 (s, 1H, ArH), 2.29 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): 141.7, 136.5, 134.7, 134.2, 128.9, 94.0, 20.9.

1-Bromo-3-chloro-5-iodobenzene (3k)



According to the general procedure, reaction of 1-bromo-3-chlorobenzene (0.15 mL, 1.3 mmol) was conducted. After work up, the crude mixture was passed through a plug of silica gel (100% pentane), and concentrated under reduced pressure (~100 mtorr) to give iodide **3k** (0.332 g, 82%) as a white solid. No literature data available.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 1H, ArH), 7.65 – 7.62 (m, 1H, ArH), 7.50 – 7.45 (m, 1H, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 136.0, 135.8, 131.1, 123.2, 94.2.

HRMS (EI) calculated for $C_6H_3{}^{79}Br^{35}Cl^{127}I$: 315.8151, found 315.8155.

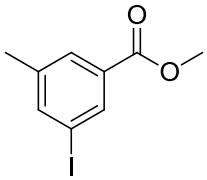
MS (EI) 318 (100, $[C_6H_3{}^{79}Br^{37}Cl^{127}I]^+$), 316 (80, $[C_6H_3{}^{79}Br^{35}Cl^{127}I]^+$), 191 (50, $[C_6H_3{}^{79}Br^{37}Cl]^+$).

IR ν_{max} (neat) / cm^{-1}: 3067, 1557, 1402, 847, 658.

Elemental Analysis: Calculated for C_6H_3BrClI: C 22.71, H 0.95, N 0.00 Found: C 22.77, H 0.84, N <0.02.

[10] Sintim, H. O.; Kool, E. T. *Angew. Chem., Int. Ed*. **2006**, *45*, 1974.

Methyl 3-iodo-5-methylbenzoate (3l)



According to the general procedure, reaction of 1,3-dimethoxybenzene (0.18 mL, 1.3 mmol) followed by silica gel chromatography (40% hexane, 60% CH_2Cl_2) gave *iodide* **3l** (0.229 g, 65%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H, ArH), 7.80 (s, 1H, ArH), 7.71 (s, 1H, ArH), 3.90 (s, 3H, OCH_3), 2.35 (s, 3H, $ArCH_3$).

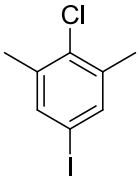
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 142.4, 140.4, 135.7, 131.8, 129.7, 93.9, 52.5, 22.0.

HRMS (EI) calculated for $C_9H_9{}^{127}IO_2$: 275.9647, found 275.9649.

MS (EI): 276 (100, MI), 245(90 – OMe), 217 (18 – CO_2Me).

IR ν_{max} (neat) / cm^{-1}: 2949, 1724, 1283, 1205, 764.

2-Chloro-5-iodo-1,3-dimethylbenzene (3m)



According to the general procedure, reaction of 2-chloro-1,3-dimethylbenzene (0.17 mL, 1.3 mmol) followed by passing the crude mixture through a plug of silica gel (100% pentane), and concentrating under reduced pressure (~100 mtorr) gave iodide **3m** (0.188 g, 55%) as a colorless oil. No literature data available.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H, ArH), 2.32 (s, 6H, ArH).

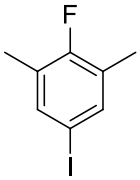
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.1, 134.9, 91.0, 20.5.

HRMS (EI) calculated for $C_8H_8{}^{35}Cl^{127}I$: 265.9359, found 265.9362.

MS (EI) 266 (100, MI), 231 (13, MI – Cl), 139 (33, MI – I).

IR ν_{max} (neat) / cm^{-1}: 2922, 1459, 1041, 854.

2-Fluoro-5-iodo-1,3-dimethylbenzene (3n)



According to the general procedure, reaction of 2-fluoro-1,3-dimethylbenzene (0.16 mL, 1.3 mmol) was conducted. After work up, the crude mixture was passed through a plug of silica gel (100% pentane), and concentrated under reduced pressure (~100 mtorr) to give *iodide* **3n** (0.172 g, 54%) as a colorless oil.

^{1}H NMR (400 MHz, CDCl3) δ 7.32 (d, J_F = 6.6 Hz, 2H, ArH), 2.21 (d, J_F = 2.2 Hz, 6H, 2 × CH_3).

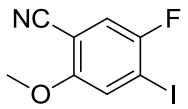
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.03 (d, J_F = 244.4 Hz), 137.56 (d, J_F = 4.7 Hz), 127.15 (d, J_F = 19.0 Hz), 86.49 (d, J_F = 3.9 Hz), 14.40 (d, J_F J = 4.1 Hz).

HRMS (EI) calculated for $C_8H_8F^{127}I$: 249.9655, found 249.9661.

MS (EI): 250 (100, MI), 123 (73, MI – I), 103 (33).

IR ν_{max} (neat) / cm^{-1}: 2923, 1475, 1190, 858, 712.

5-Fluoro-4-iodo-2-methoxybenzonitrile (3o)



According to the general procedure, 3-fluoro-5-methyoxybenzonitrile (0.189 g, 1.25 mmol) was allowed to react with $[Ir(cod)(OMe)]_2$ (4.1 mg, 6.3 μmol) and dtbpy (3.3 mg, 13 μmol). After work-up, the crude mixture was purified by silica gel chromatography (90% pentane, 10% Et_2O → 80% pentane, 20% Et_2O) to give iodide **3o** (0.196 g, 56%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J_F = 4.7 Hz, 1H, ArH), 7.23 (d, J_F = 6.7 Hz, 1H, ArH), 3.92 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6 (d, J_F = 2.3 Hz), 155.7 (d, J_F = 240.8 Hz), 122.3, 119.1 (d, J_F = 28.7 Hz), 114.9 (d, J_F = 2.0 Hz), 102.6 (d, J_F = 8.1 Hz), 88.9 (d, J_F = 27.6 Hz), 57.0.

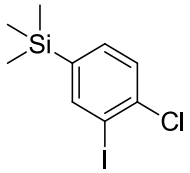
HRMS (EI) calculated for $C_8H_5F^{127}INO$: 276.9400, found 276.9402.

MS (EI): 277 (100, MI), 249 (15), 234 (18), 135 (15).

IR ν_{max} (neat) / cm^{-1}: 2981, 2231, 1481, 1221, 788.

Elemental Analysis: Calculated for C_8H_5FINO: C 34.68, H 1.82, N 5.06 Found: C 34.80, H 1.83, N 4.97.

(3-Iodo-4-methylphenyl)trimethylsilane (3p)



According to the general procedure, (4-methylphenyl)trimethylsilane (0.23 mL, 1.2 mmol, 2.0 equiv) was allowed to react with B_2pin_2 (0.159 g, 0.624 mmol, 1 equiv) at 80 °C for 48 h. After work-up, the crude mixture was passed through a plug of silica gel (100% pentane), and concentrated under reduced pressure (~100 mtorr) to give *iodide* **3p** (0.190 g, 49%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.3 Hz, 1H, ArH), 7.42 (d, *J* = 7.8 Hz, 1H, ArH, 7.38 (dd, *J* = 7.8, 1.3 Hz, 1H, ArH), 0.26 (s, 1H, 3 × CH_3).

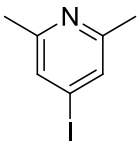
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 141.8, 139.0, 134.4, 129.1, 99.1, -1.1.

HRMS (EI) calculated for $C_9H_{12}{}^{35}Cl^{127}ISi$: 309.9442, found 309.9442.

MS (EI) 310 (27, MI), 295 (100, MI – CH_3).

IR ν_{max} (neat) / cm^{-1}: 1955, 1250, 1104, 840, 654.

4-Iodo-2,6-dimethylpyridine (3q)



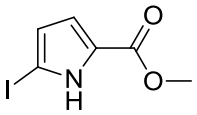
According to the general procedure, reaction of 1,3-dimethoxybenzene (0.15 mL, 1.3 mmol) followed by silica gel chromatography (10% Et_2O, 90% pentane) gave iodide **3q** (0.163 g, 54%) as a colorless oil. The NMR data matched the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H, ArH), 2.43 (s, 6H, 2 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 129.5, 106.3, 24.1.

[11] Maloney, K. M.; Nwakpuda, E.; Kuethe, J. T.; Yin, J. *J. Org. Chem.* **2009**, *74*, 5111.

Methyl 5-iodo-1H-pyrrole-2-carboxylate (3r)



According to the general procedure, the reaction of methyl-1H-pyrrole-2-carboxylate (0.156 g, 1.25 mmol) followed by silica gel chromatography (15% Et_2O, 85% pentane) gave *iodide* **3r** (0.157 g, 50%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H, NH), 6.78 (dd, *J* = 3.6, 2.8 Hz, 1H, ArH), 6.39 (dd, *J* = 3.6, 2.8 Hz, 1H, ArH), 3.91 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 126.9, 120.1, 117.5, 71.2, 52.1.

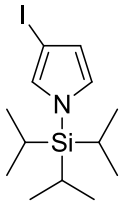
HRMS (ESI) calculated for $C_6H_6{}^{127}INO_2$: 250.9443, found 250.9446.

MS (EI): 251 (100, MI), 219 (65, MI - MeOH), 192 (10, MI – CO_2Me).

IR ν_{max} (neat) / cm^{-1}: 3260, 2944, 1682, 1441, 1199, 763.

Elemental Analysis: Calculated for $C_6H_6BINO_2$: C 28.71, H 2.41, N 5.58 Found: C 28.88, H 2.52, N 5.48.

3-Iodo-1-(triisopropylsilyl)pyrrole (3s)



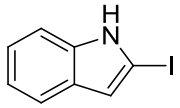
According to the general procedure, the reaction of *N*-(tri*iso*propylsilyl)pyrrole (0.290 g, 1.30 mmol) followed by silica gel chromatography (100% pentane) gave iodide **3s** (0.227 g, 48%) as a colorless oil. The NMR data matched the literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.78 (m, 1H, ArH), 6.66 (t, *J* = 2.4 Hz, 1H, ArH), 6.38 – 6.34 (m, 1H, ArH), 1.42 (h, *J* = 7.5 Hz, 3H, 3 × CH), 1.08 (d, *J* = 7.5 Hz, 18H, 6 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 128.8, 125.8, 117.6, 62.3, 17.8, 11.7.

[12] Bray, B. L.; Mathies, P. H.; Naef, R.; Solas, D. R.; Tidwell, T. T.; Artis, D. R.; Muchowski, J. M. *J. Org. Chem.* **1990**, *55*, 6317.

2-Iodoindole (3t)

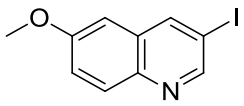


According to the general procedure, indole (0.292 g, 2.49 mmol, 4.00 equiv) was allowed to react with B_2pin_2 (0.159 g, 0.624 mmol, 1.00 equiv), $[Ir(cod)(OMe)]_2$ (0.8 mg, 1 μmol, 0.2 mol%) and dtbpy (0.7 mg, 3 μmol, 0.4 mol%). The crude was purified by silica gel chromatography (10% Et_2O, 90% pentane) to give iodide **3t** (0.103 g, 34%) as a white solid. The NMR data match the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H, NH), 7.56 (d, *J* = 7.8 Hz, 1H, ArH), 7.32 (d, *J* = 7.9 Hz, 1H, ArH), 7.20 – 7.10 (m, 2H, ArH), 6.74 (s, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 129.7, 122.4, 120.4, 119.4, 112.9, 110.3, 74.9.

3-Iodo-6-methoxyquinoline (3u)



According to the general procedure, 6-methoyxyquinoline (0.17 mL, 1.3 mmol, 2.0 equiv) was allowed to react with B_2pin_2 (0.159 g, 0.624 mmol, 1.00 equiv) followed by silica gel chromatography (30% Et_2O, 70% pentane) to give *iodide* **3u** (0.152 g, 43%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 2.0 Hz, 1H, ArH), 8.40 (d, *J* = 2.0 Hz, 1H, ArH), 7.92 (d, *J* = 9.2 Hz, 1H, ArH), 7.35 (dd, *J* = 9.2, 2.7 Hz, 1H, ArH), 6.91 (d, *J* = 2.7 Hz, 1H, ArH), 3.90 (s, 3H, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 153.1, 142.5, 142.4, 131.1, 130.9, 123.0, 104.1, 90.7, 55.7.

HRMS (ESI) calculated for $C_{10}H_9{}^{127}INO$: 285.9723, found 285.9720.

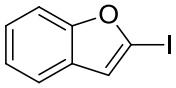
MS (ESI): 286 (100, MI + H).

IR ν_{max} (neat) / cm^{-1}: 3016, 1593, 1216, 1024, 827.

Elemental Analysis: Calculated for $C_{10}H_8INO$: C 42.13, H 2.83, N 4.91 Found: C 42.19, H 2.76, N 4.83.

[13] Miyamoto, H.; Okawa, Y.; Nakazaki, A.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2274.

2-Iodobenzofuran (3v)

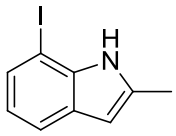


According to the general procedure, benzofuran (0.28 mL, 2.5 mmol, 4.0 equiv) was allowed to react with B_2pin_2 (0.159 g, 0.624 mmol, 1.00 equiv), $[Ir(cod)(OMe)]_2$ (4.1 mg, 6.3 μmol, 2.0 mol%) and dtbpy (3.3 mg, 13 μmol, 4.0 mol%). After work-up, the crude mixture was passed through a plug of silica gel (100% pentane), and concentrated under reduced pressure (~100 mtorr) to give iodide **3v** (0.134 g, 44%) as a yellow oil. The NMR data match the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 2H, ArH), 7.26 – 7.17 (m, 2H, ArH), 6.96 (s, 1H, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 129.3, 124.4, 123.3, 119.8, 117.4, 111.0, 96.0.

7-Iodo-2-methyl-1H-indole (3w)



According to the general procedure, 2-methylindole (0.328 g, 2.50 mmol, 4.00 equiv) was allowed to react with B_2pin_2 (0.159 g, 0.624 mmol, 1.00 equiv). After work-up, the crude mixture was purified by silica gel chromatography (20% Et_2O, 80% pentane) to give iodide **3w** (0.106 g, 33%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H, NH), 7.46 (d, J = 7.7 Hz, 1H, ArH), 7.45 (d, J = 7.6 Hz, 1H, ArH), 6.83 (dd, J = 7.7, 7.6, Hz, 1H, ArH), 6.36 (d, J = 1.0 Hz, 1H, ArH), 2.48 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 135.6, 129.6, 129.1, 121.5, 119.8, 102.1, 75.7, 13.8.

HRMS (EI) calculated for $C_9H_8{}^{127}IN$: 256.9702, found 256.9705.

MS (EI): 257 (100, MI), 130 (40, MI – I).

IR ν_{max} (neat) / cm^{-1}: 3378, 1436, 799.

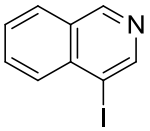
[14] L'Helgoual'ch, J.-M.; Seggio, A.; Chevallier, F.; Yonehara, M.; Jeanneau, E.; Uchiyama, M.; Mongin, F. *J. Org. Chem.* **2007**, *73*, 177.

4. General Procedure for the Iodination of Aryl Pinacol Boronic Esters

MeOH (10 mL) was added to a 250 mL pressure vessel containing the boronic ester (1.5 mmol, 1.2 equiv), Cu_2O (8.9 mg, 0.063 mmol, 5.0 mol%), phen (45.0 mg, 0.250 mmol, 20.0 mol%) and KI (0.208 g, 1.25 mmol, 1.00 equiv). The mixture was stirred at room temperature, and water (2.5 mL) was added. The flask was sealed under air, and the mixture was heated at 80 °C for 1 h, over which time the reaction was monitored by GCMS. The reaction was cooled to room temperature, water (25 mL) was added, and the mixture was extracted with Et_2O (3 × 25 mL). The combined organic phases were washed with brine (25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Silica gel chromatography was conducted with aluminium foil wrapped around the column to minimise decomposition of the aryl iodide.

5. Substrates

4-Iodoisoquinoline (4b)



According to the general procedure, reaction of 4-isoquinolineboronic acid pinacol ester (0.383 g, 1.50 mmol) followed by silica gel chromatography (30% Et_2O, 70% hexane) gave *iodide* **4b** (0.227 g, 71%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H, ArH), 8.94 (s, 1H, ArH), 8.00 (d, *J* = 8.5 Hz, 1H, ArH), 7.90 (d, *J* = 8.2 Hz, 1H, ArH), 7.83 – 7.76 (m, 1H, ArH), 7.67 (t, *J* = 7.5 Hz, 1H, ArH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 151.0, 137.1, 132.0, 130.7, 129.7, 128.4, 128.2, 96.9.

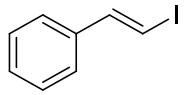
HRMS (ESI) calculated for $C_9H_7{}^{127}IN$: 255.9618, found 255.9615.

MS (ESI): 256 (100, MI + H).

IR ν_{max} (neat) / cm^{-1}: 3021, 1373, 954, 771.

Elemental Analysis: Calculated for C_9H_6IN: C 42.38, H 2.37, N 5.49 Found: C 42.37, H 2.29, N 5.36.

_E_-(2-Iodovinyl)benzene (4c)

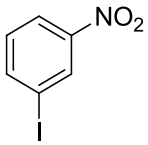


According to the general procedure, reaction of *E*-2-phenylvinylboronic acid pinacol ester (0.352 g, 1.53 mmol) followed by passing the crude material through a plug of silica gel (100% pentane), and concentrating under reduced pressure (~200 mtorr) gave iodide **4c** (0.129 g, 45%) as a yellow oil. The NMR data match the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 14.9 Hz, 1H), 7.39 – 7.28 (m, 5H), 6.84 (d, *J* = 14.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 137.8, 128.8, 128.5, 126.1, 76.8.

1-Iodo-3-nitrobenzene (4d)

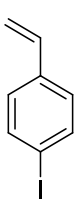


According to the general procedure, reaction of 3-nitrophenylboronic acid pinacol ester (0.374 g, 1.50 mmol) followed by passing the crude material through a plug of silica gel (0→10% Et_2O in pentane), and concentrating under reduced pressure (~100 mtorr) gave iodide **4d** (0.272 g, 87%) as a colorless oil. The NMR data match the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H, ArH), 8.24 – 8.14 (m, 1H, ArH), 8.03 (d, *J* = 7.9 Hz, 1H, ArH), 7.30 (t, *J* = 8.1 Hz, 1H, ArH);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.5, 132.4, 130.8, 122.8, 93.6.

4-Iodostyrene (4e)



According to the general procedure, reaction of 4-vinylphenylboronic acid pinacol ester (0.345 g, 1.50 mmol) followed by passing the crude material through a plug of silica gel

[15] Yang, H.; Li, Y.; Jiang, M.; Wang, J.; Fu, H. *Chem. Eur, J.* **2011**, *17*, 5652.

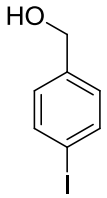
(100% pentane), and concentrating under reduced pressure (~100 mtorr) gave iodide **4e** (0.189 g, 66%) as a white solid. The NMR data match the literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H, ArH), 7.15 (d, *J* = 8.2 Hz, 1H, ArH), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H, C*H*=CH_2), 5.75 (d, *J* = 17.6 Hz, 1H, CH=C*H*H), 5.27 (d, *J* = 10.9 Hz, 1H, CH=CH*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 137.1, 135.9, 128.1, 114.8, 93.3.

MS (EI) 230 (100, MI), 103 (50, MI – I), 77 (67).

(4-Iodophenyl)methanol (4f)

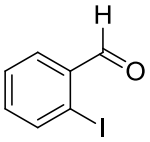


According to the general procedure, reaction of 4-(hydroxymethyl)phenylboronic acid pinacol ester (0.351 g, 1.50 mmol) followed by silica gel chromatography (20% Et_2O, 80% CH_2Cl_2) gave iodide **4f** (0.177 g, 61%) as a white solid. The NMR data match the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H, ArH), 7.08 (d, *J* = 8.0 Hz, 2H, ArH), 4.60 (s, 2H, CH_2), 2.11 (s, 1H, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 137.6, 128.9, 93.1, 64.6.

2-Iodobenzaldehyde (4g)



According to the general procedure, reaction of 2-formylphenylboronic acid pinacol ester (0.361 g, 1.56 mmol) followed by silica gel chromatography (5% Et_2O, 95% pentane) gave iodide **4g** (0.203 g, 70%) as a white solid. The NMR data match the literature.[18]

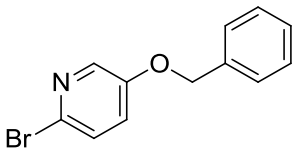
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (d, *J* = 0.7 Hz, 1H, CHO), 7.96 (dd, *J* = 7.8, 0.7 Hz, 1H, ArH), 7.89 (dd, *J* = 7.7, 1.8 Hz, 1H, ArH), 7.47 (dd, *J* = 7.7, 7.5 Hz, 1H, ArH), 7.29 (ddd, *J* = 7.8, 7.5, 1.8 Hz, 1H, ArH).

[16] Kang, S.-K.; Lee, H.-W.; Kim, J.-S.; Choi, S.-C. *Tetrahedron Lett.* **1996**, *37*, 3723.
[17] Everson, D. A.; Shrestha, R.; Weix, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 920.
[18] Tummatorn, J.; Dudley, G. B. *Org. Lett.* **2011**, *13*, 1572.

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 140.6, 135.5, 135.1, 130.3, 128.7, 100.8.

6. Synthesis of SPECT Imaging Agent 11

5-(Benzyloxy)-2-bromopyridine (6)

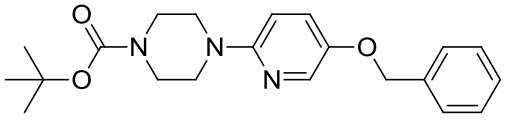


Benzyl bromide (2.6 mL, 21.6 mmol) was added to a mixture of 2-bromo-5-hydroxypyridine (2.50 g, 14.4 mmol) and K_2CO_3 (5.95 g, 43.1 mmol) in DMF (96 mL). The mixture was stirred at 60 °C for 12 hours. The reaction was cooled to room temperature, saturated aqueous $NaHCO_3$ (100 mL) and water (100 mL) were added, and the mixture was extracted with Et_2O (3 × 100 mL). The combined organic phases were washed with brine (150 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The product was purified by silica gel chromatography (50% CH_2Cl_2, 50% hexane) to give bromide **6** (3.59 g, 94%) as a pale yellow solid. The NMR data match the literature.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.9Hz, 1H, ArH), 7.44 – 7.31 (m, 6H, ArH), 7.15 (dd, *J* = 8.6, 2.9 Hz, 1H, ArH), 5.09 (s, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 138.0, 135.7, 132.5, 128.9, 128.6, 128.3, 127.6, 125.4, 70.8.

***Tert*-Butyl 4-(5-(benzyloxy)pyridin-2-yl)piperazine-1-carboxylate (7)**



Bromide **6** (0.528 g, 2.00 mmol), *N*-Boc-piperazine (0.410 g, 2.20 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.0200 mmol), (±)-BINAP (19.9 mg, 0.0320 mmol) and NaO*t*Bu (0.290 g, 3.00 mmol) were added to a oven-dried Schlenk flask under nitrogen. Anhydrous toluene (17 mL) was added, and the mixture was heated at 100 °C for 4.5 hours. The reaction was cooled to room temperature, water (50 mL) was added, and the mixture was extracted with Et_2O (3 × 30 mL). The combined organic phases were washed with brine (50 mL), dried with

[19] Schmitt-Willich, H.; Heinrich, T.; Brockschnieder, D. SPECT Imagine of Amyloid Plaques. **2011**, WO2011110511.

$MgSO_4$, and concentrated *in vacuo*. The product was purified by silica gel chromatography (20% ethyl acetate, 80% hexane) to give *piperazine* **7** (0.667 g, 90%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.9 Hz, 1H, ArH), 7.44 – 7.28 (m, 5H, ArH), 7.21 (dd, *J* = 9.1, 2.9 Hz, 1H, ArH), 6.63 (d, *J* = 9.1 Hz, 1H, ArH), 5.03 (s, 2H, OCH_2), 3.64 – 3.45 (m, 4H, piperazine), 3.45 – 3.30 (m, 4H, piperazine), 1.48 (s, 9H, 3 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 154.8, 136.8, 135.0, 128.6, 128.1, 127.5, 126.0, 108.3, 79.8, 71.3, 46.3, 43.4, 28.5.

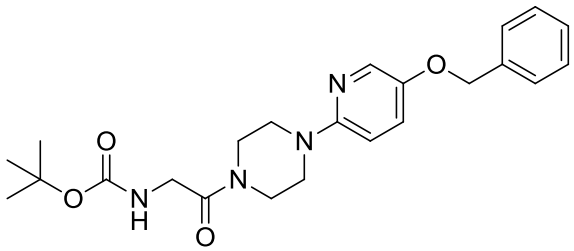
HRMS (ESI) calculated for $C_{21}H_{28}N_3O_3$: 370.2125, found 370.2120.

MS (ESI): 392 (100, MI + Na), 370 (63, MI + H).

IR ν_{max} (neat) / cm^{-1}: 2979, 1692, 1498, 1243, 1123, 734.

Elemental Analysis: Calculated for $C_{21}H_{27}N_3O_3$: C 68.27, H 7.37, N 11.37 Found: C 68.49, H 7.43, N 11.30.

<u>*Tert*-Butyl (2-(4-(5-(benzyloxy)pyridin-2-yl)piperazin-1-yl)-2-oxoethyl)carbamate (8)</u>



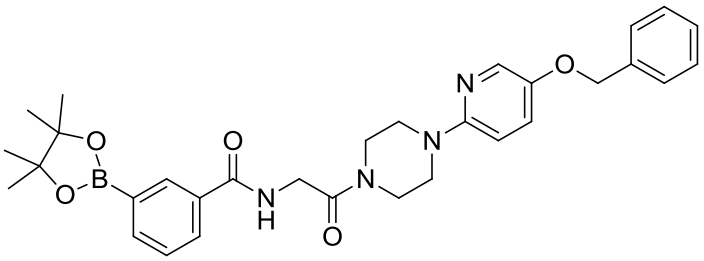
Trifluoroacetic acid (5.1 mL, 67 mmol) was added to a solution of piperazine **7** (2.46 g, 6.66 mmol) in CH_2Cl_2 (60 mL). The mixture was stirred at room temperature overnight. The mixture was made basic (pH 10) by the addition of saturated aqueous Na_2CO_3 (20 mL). Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were dried with Na_2SO_4 and concentrated *in vacuo*. In a separate flask, isobutyl chloroformate (0.95 mL, 7.3 mmol) was added to a solution of *N*-Boc-glycine (1.28 g, 7.32 mmol) and triethylamine (1.3 mL, 9.3 mmol) in tetrahydrofuran (130 mL) cooled to -20 °C. The mixture was stirred between -30 and -15 °C for 15 minutes. A solution of the deprotected amine in CH_2Cl_2 (27 mL) was added slowly. The reaction was kept below -15 °C for 30 minutes before being stirred at room temperature for 4 hours. The mixture was concentrated *in vacuo*, saturated aqueous Na_2CO_3 (20 mL) and water (100 mL) were added, and the mixture was extracted with EtOAc (3 × 100 mL). The combined organic phases were washed with brine (100 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The product was purified by silica gel chromatography (30% hexane, 70% ethyl acetate) to give piperazine **8** (2.63 g, 93%) as a white solid. The NMR data match the literature.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 3.0 Hz, 1H, ArH), 7.44 – 7.29 (m, 5H, ArH), 7.22 (dd, *J* = 9.1, 3.0 Hz, 1H, ArH), 6.63 (d, *J* = 9.1 Hz, 1H, ArH), 5.53 (s, 1H, NH), 5.03 (s, 2H,

OCH_2), 4.00 (d, J = 4.2 Hz, 2H, $HNCH_2$), 3.78 – 3.71 (m, 2H, piperazine), 3.53 – 3.44 (m, 4H, piperazine), 3.43 – 3.37 (m, 2H, piperazine), 1.45 (s, 9H, 3 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 155.8, 154.4, 148.8, 136.7, 135.0, 128.7, 128.1, 127.6, 126.0, 108.4, 79.7, 71.2, 46.3, 46.2, 44.1, 42.3, 41.6, 28.4.

***N*-(2-(4-(5-(Benzyloxy)pyridin-2-yl)piperazin-1-yl)-2-oxoethyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (10)**



Trifluoroacetic acid (1.8 mL, 23 mmol) was added to a solution of piperazine **8** (0.500 g, 1.17 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature overnight. The mixture was made basic (pH 10) using saturated aqueous Na_2CO_3 (50 mL). Water (40 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phases were dried with Na_2SO_4, and concentrated *in vacuo*. In a separate flask, triethylamine (0.33 mL, 2.4 mmol) was added to a solution of 3-carboxyphenylboronic acid pinacol ester (0.305 g, 1.23 mmol) and HBTU (0.467 g, 1.23 mmol) in CH_2Cl_2 (10 mL). The deprotected amine was added as a solution in CH_2Cl_2 (25 mL), and the mixture was stirred at room temperature for 5 hours. Saturated aqueous Na_2CO_3 (5 mL) and water (50 mL) were added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried with $MgSO_4$, and concentrated *in vacuo*. The product was purified by silica gel chromatography (20% hexane, 80% ethyl acetate) to give *boronic ester* **10** (0.493 g, 76%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H, ArH), 8.02 – 7.96 (m, 2H, ArH), 7.94 (d, J = 7.3 Hz, 1H, ArH), 7.45 (t, J = 7.6 Hz, 1H, ArH), 7.43 – 7.29 (m, 6H, ArH + NH), 7.23 (dd, J = 9.1, 3.0 Hz, 1H, ArH), 6.65 (d, J = 9.1 Hz, 1H, ArH), 5.04 (s, 2H, OCH_2), 4.31 (d, J = 3.9 Hz, 2H, $HNCH_2$), 3.84 – 3.77 (m, 2H, piperazine), 3.63 – 3.56 (m, 2H, piperazine), 3.54 – 3.48 (m, 2H, piperazine), 3.47 – 3.41 (m, 2H, piperazine), 1.35 (s, 12H, 4 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.7, 154.3, 148.8, 137.9, 136.7, 134.9, 133.2, 132.8, 130.3, 128.6, 128.1, 128.1, 127.5, 126.0, 108.5, 84.1, 71.1, 46.2, 44.2, 41.8, 41.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0.

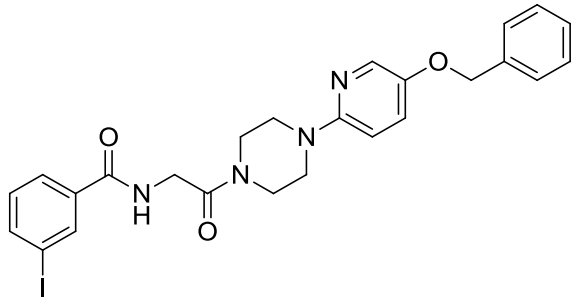
HRMS (ESI) calculated for $C_{31}H_{38}{}^{11}BN_4O_5$: 557.2930, found 557.2921.

MI (ESI): 579 (29, MI + Na), 557 (21, MI + H), 511 (37), 346 (100).

IR ν_{max} (neat) / cm^{-1}: 3400, 2978, 1644, 1486, 1233, 703.

Elemental Analysis: Calculated for $C_{31}H_{37}BN_4O_5$: C 66.91, H 6.70, N 10.07 Found: C 66.62, H 6.68, N 9.95.

***N*-(2-(4-(5-(Benzyloxy)pyridin-2-yl)piperazin-1-yl)-2-oxoethyl)-3-iodobenzamide (11)**

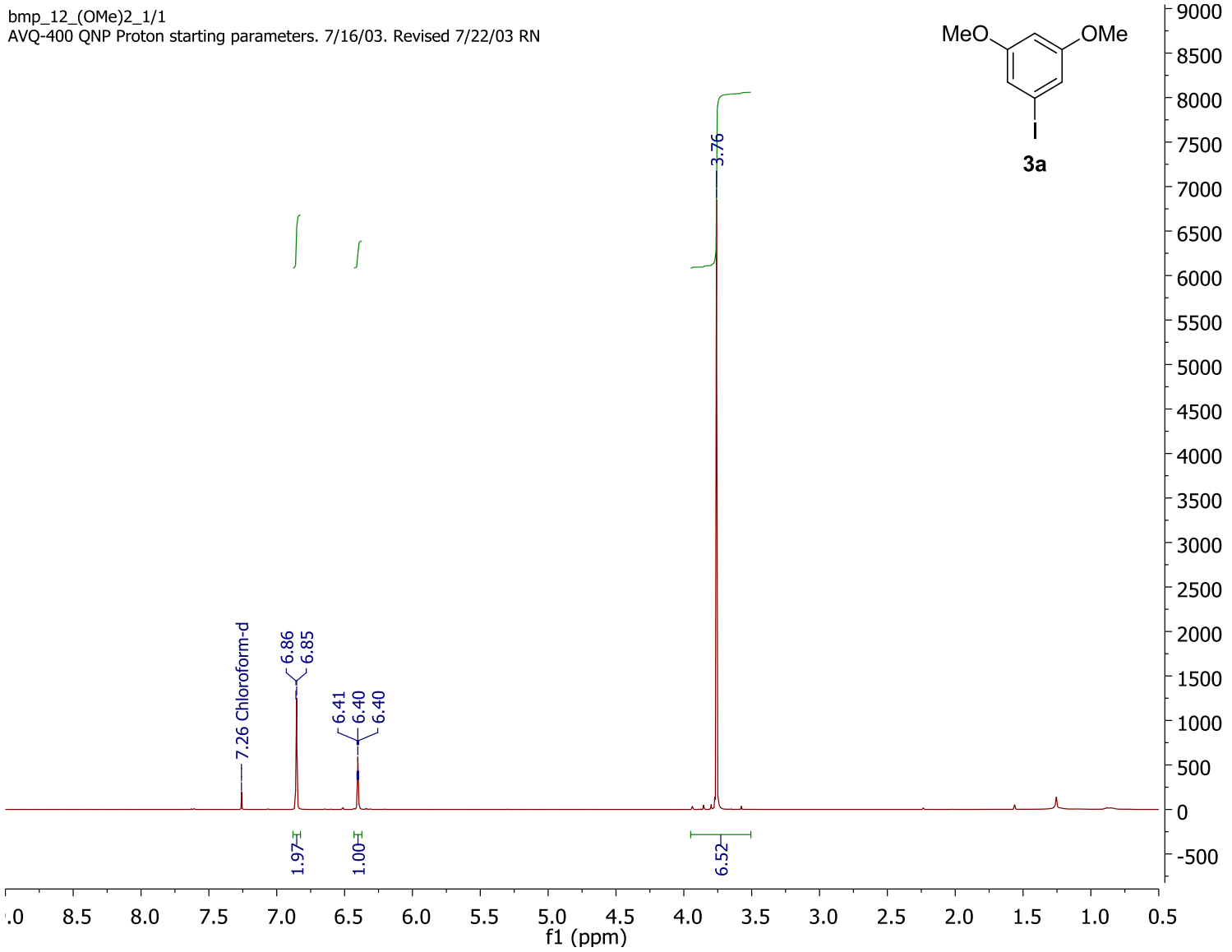


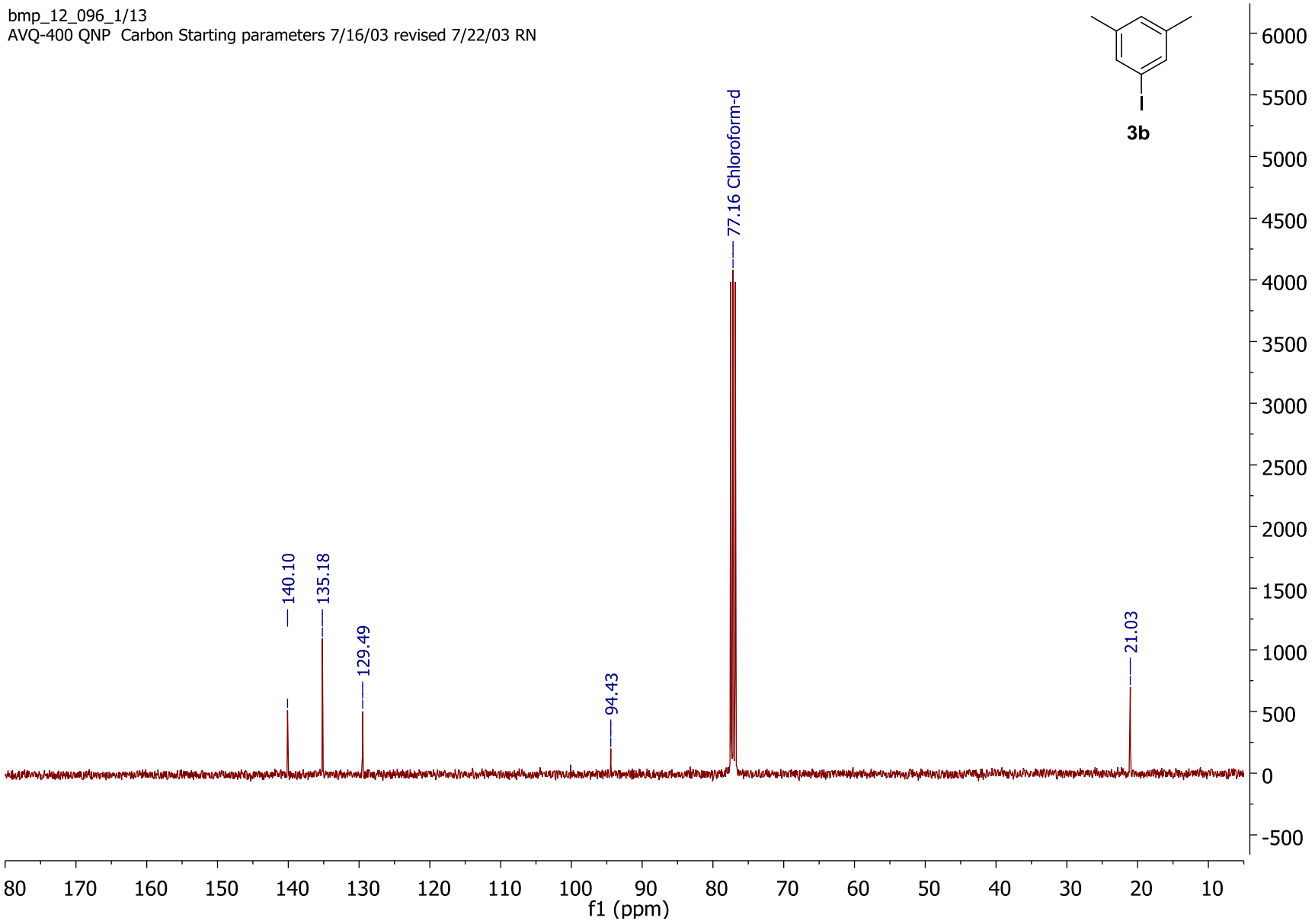
Methanol (1.44 mL) and water (0.36 mL) were added to a 20 mL vial containing boronic ester **10** (0.120 g, 0.216 mmol), Cu_2O (1.3 mg, 0.0091 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol) and KI (29.8 mg, 0.180 mmol). The vial was sealed under air, and the mixture was heated at 80 °C for 1 hour. The mixture was cooled to room temperature, water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The product was purified by silica gel chromatography (20% pentane, 80% ethyl acetate) to give iodide **11** (66.6 mg, 66%) as a white solid. The NMR data match the literature.[19]

^{1}H NMR (400 MHz, DMSO) δ 8.76 (t, *J* = 5.7 Hz, 1H, ArH), 8.24 (s, 1H, ArH), 7.95 (d, *J* = 3.0 Hz, 1H, ArH), 7.90 (t, *J* = 7.1 Hz, 2H, ArH), 7.46 – 7.35 (m, 5H, ArH), 7.35 – 7.25 (m, 2H, ArH), 6.88 (d, *J* = 9.2 Hz, 1H, ArH), 5.08 (s, 2H, OCH_2), 4.18 (d, *J* = 5.7 Hz, 2H, HNCH_2), 3.59 (s, 4H, piperazine), 3.44 (s, 2H, piperazine), 3.39 – 3.34 (m, 2H, piperazine).

^{13}C NMR (101 MHz, DMSO) δ 167.0, 165.0, 154.0, 147.8, 139.9, 137.0, 136.2, 135.8, 133.8, 130.6, 128.5, 127.9, 127.8, 126.8, 126.3, 108.8, 94.7, 70.2, 45.9, 45.6, 43.7, 41.1, 41.0.

7. NMR Spectra

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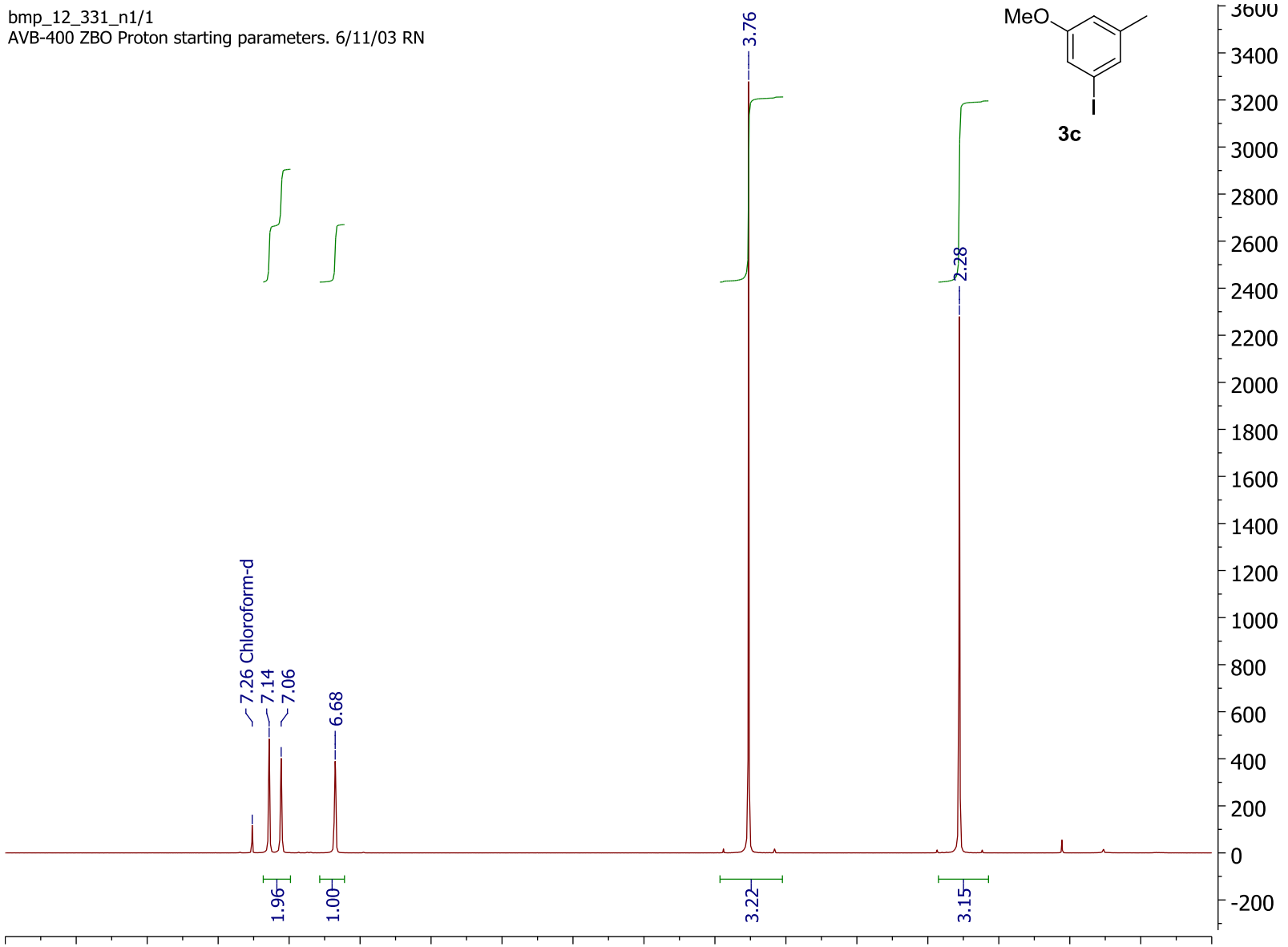
135.18
129.49
94.43
21.03
f1 (ppm)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I
3c
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7.06
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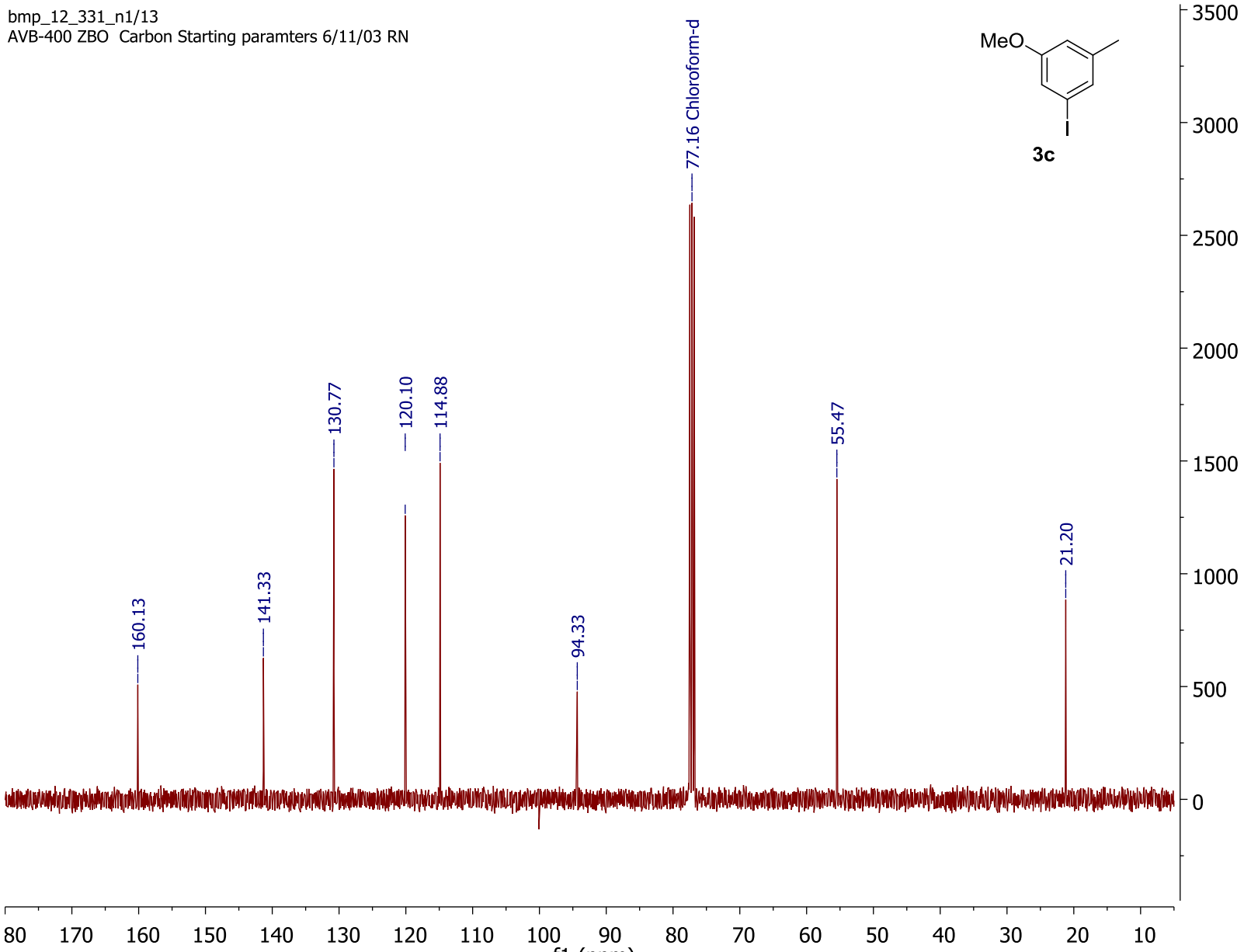
1.00
3.22
3.15
f1 (ppm)

8.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MeO
I
3c
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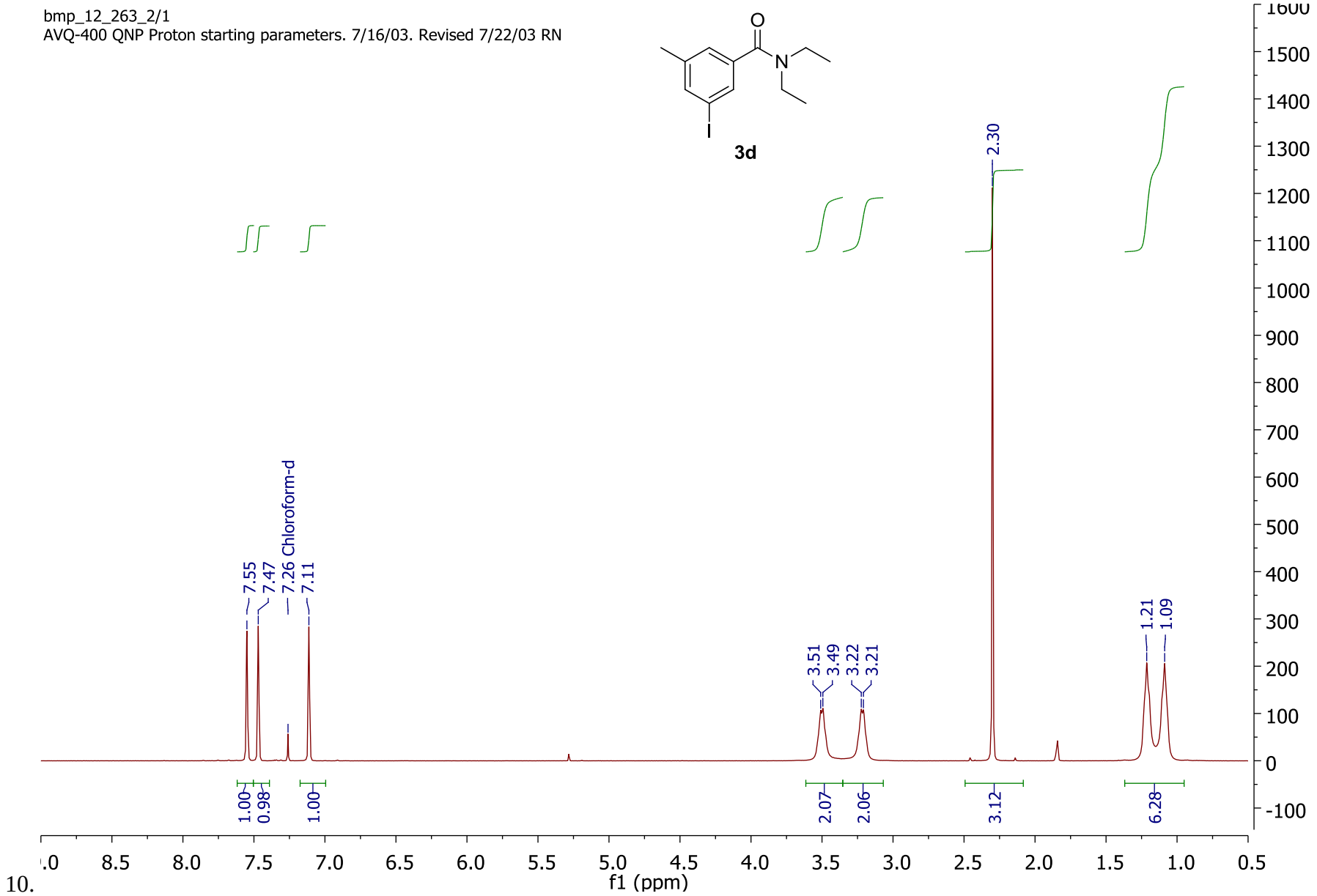
141.33
130.77
120.10
114.88
94.33
77.16 Chloroform-d
55.47
21.20
3500
3000
2500
2000
1500
1000
500
0
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

9.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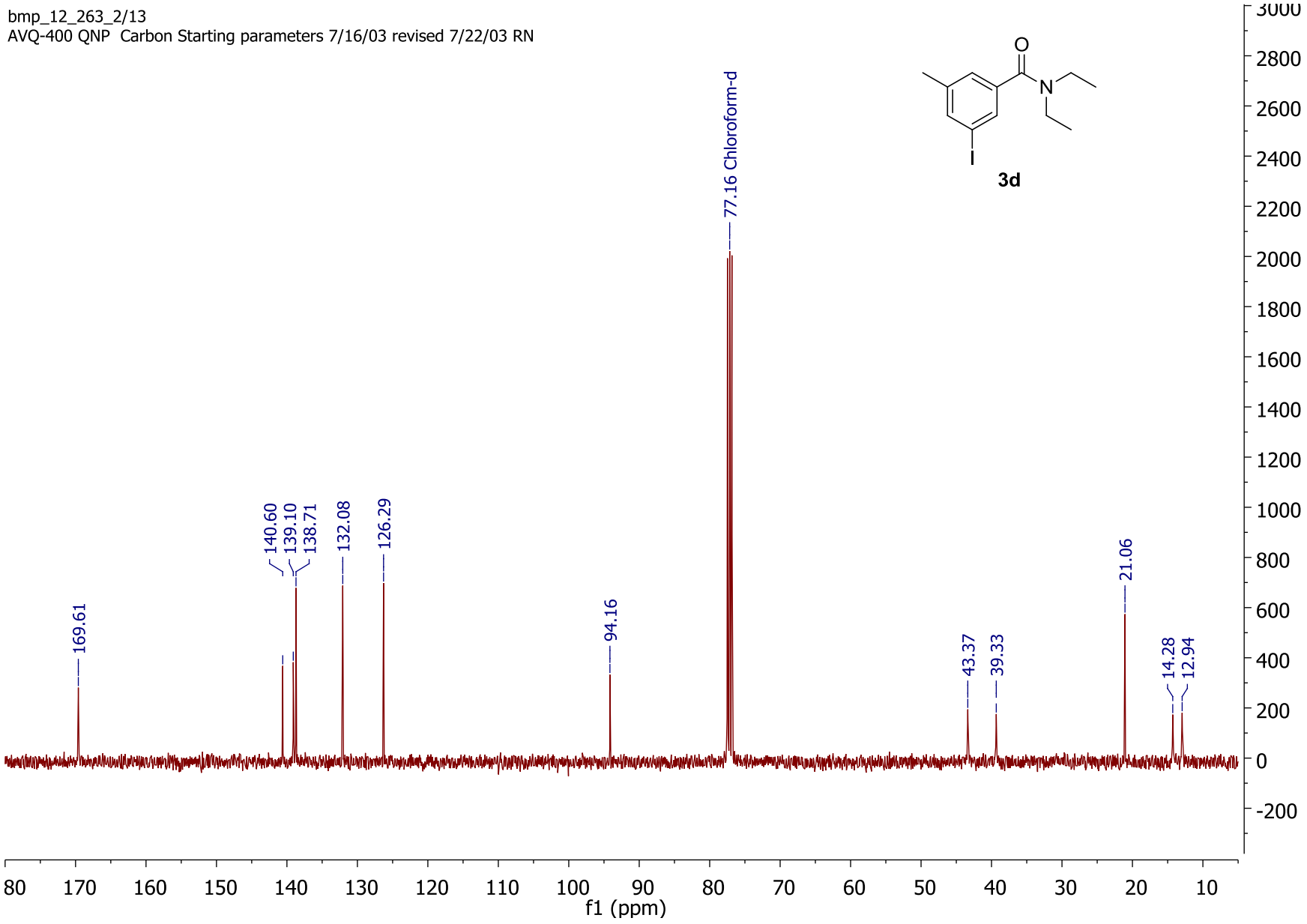
O
N
I
3d
7.55
7.47
7.26 Chloroform-d
7.11
3.51
3.49
3.22
3.21
2.30
1.21
1.09
1.00
0.98
1.00
2.07
2.06
3.12
6.28
f1 (ppm)

10.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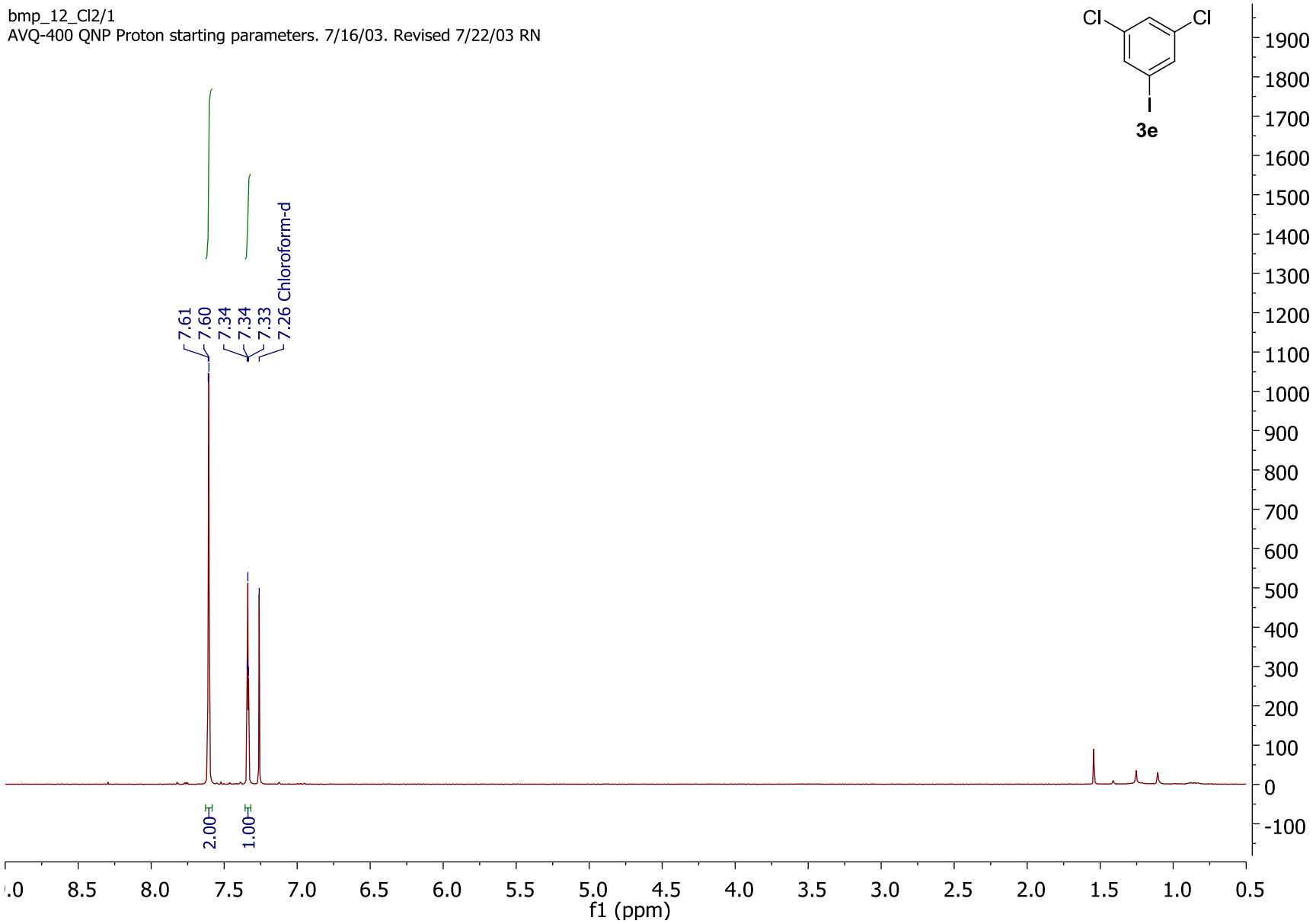
O
N
I
3d
77.16 Chloroform-d
169.61
140.60
139.10
138.71
132.08
126.29
94.16
43.37
39.33
21.06
14.28
12.94
f1 (ppm)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Cl
Cl
I
3e
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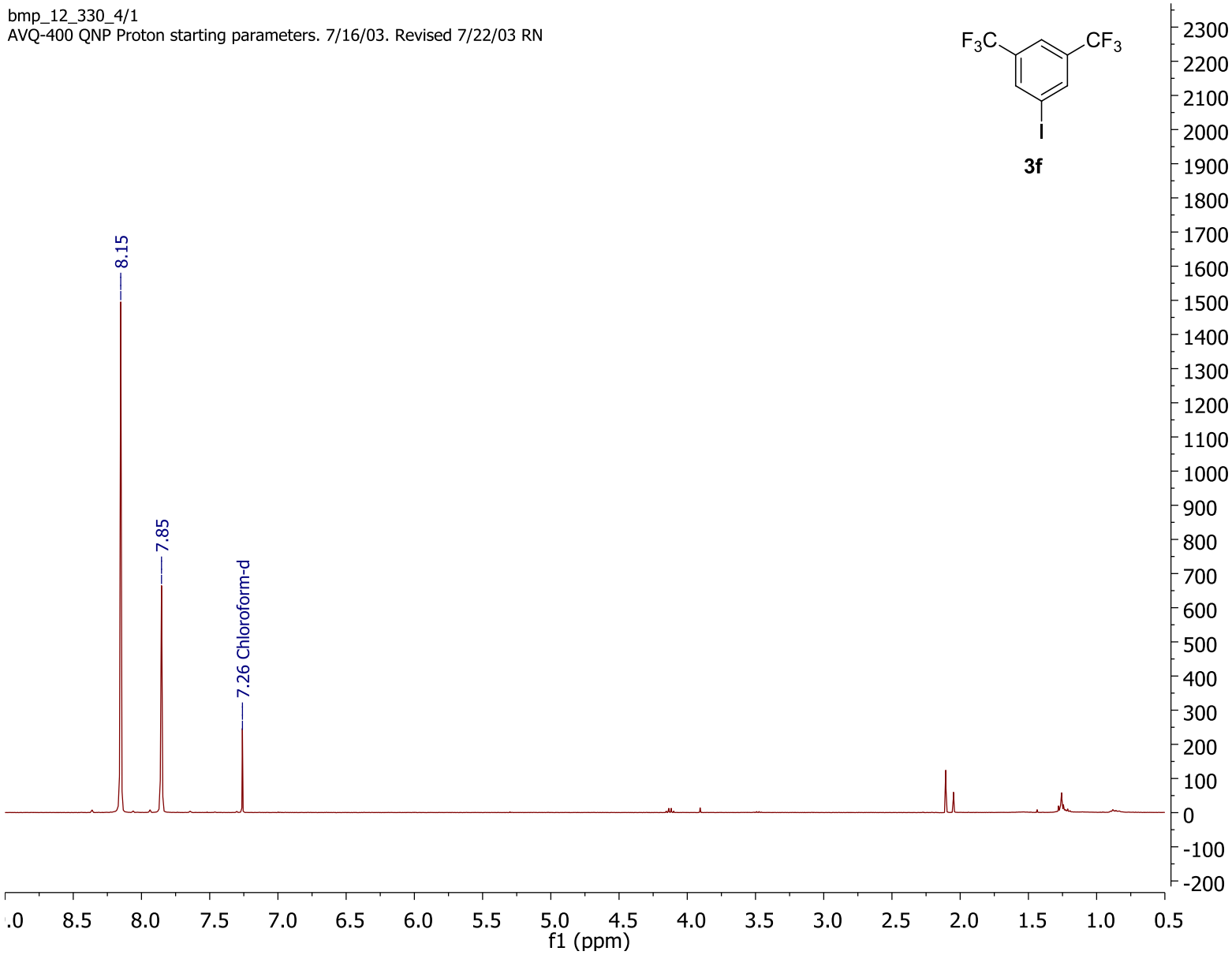
7.60
7.34
7.34
7.33
7.26 Chloroform-d
2.00
1.00
f1 (ppm)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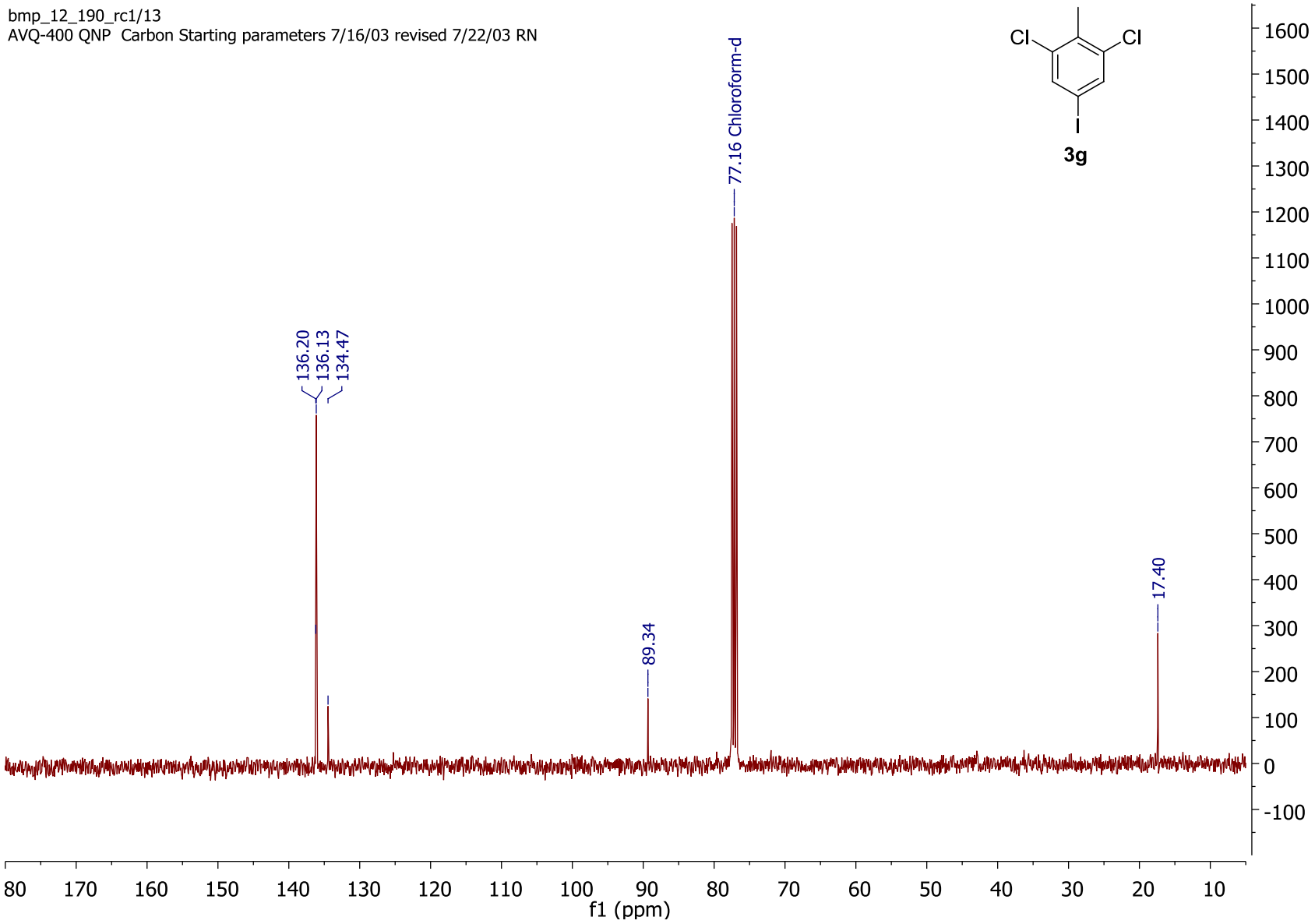
CF3
I
3f
8.15
7.85
7.26 Chloroform-d
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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Cl
Cl
I
3g
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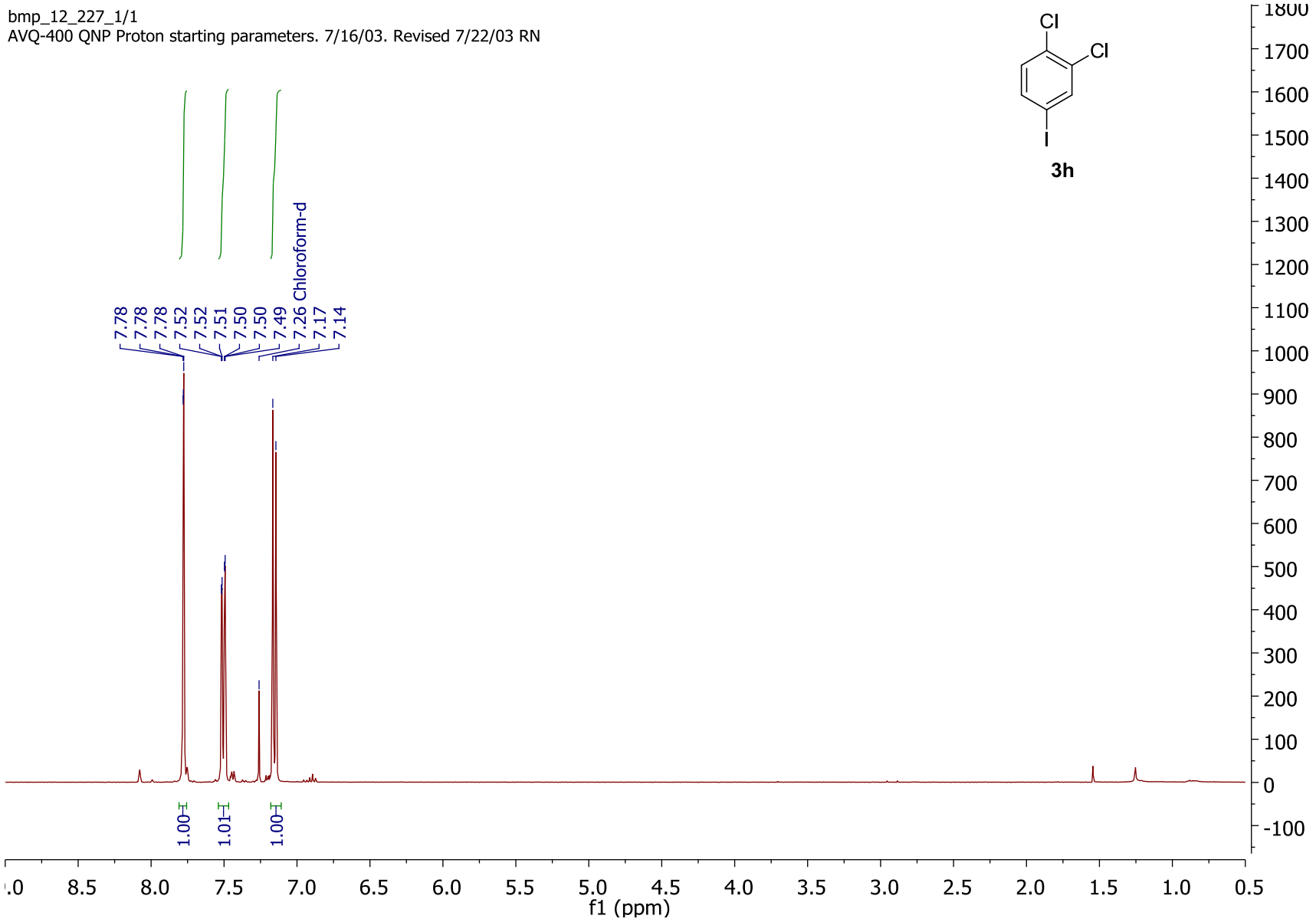
136.13
134.47
89.34
77.16 Chloroform-d
17.40
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

11.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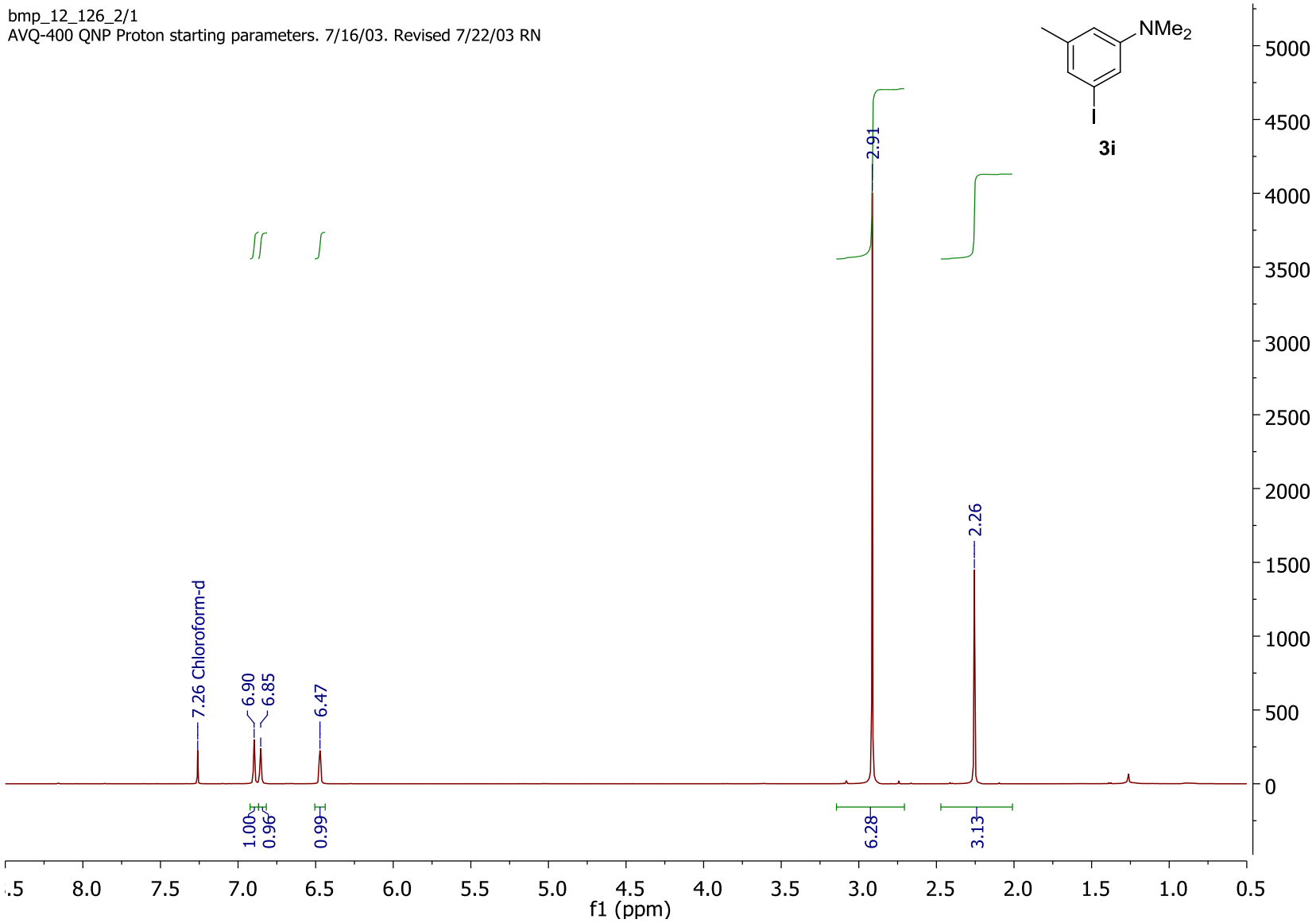
Cl
I
3h
7.78
7.78
7.78
7.52
7.52
7.51
7.50
7.50
7.49
7.26 Chloroform-d
7.17
7.14
1.00
1.01
1.00
f1 (ppm)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NMe2
3i
7.26 Chloroform-d
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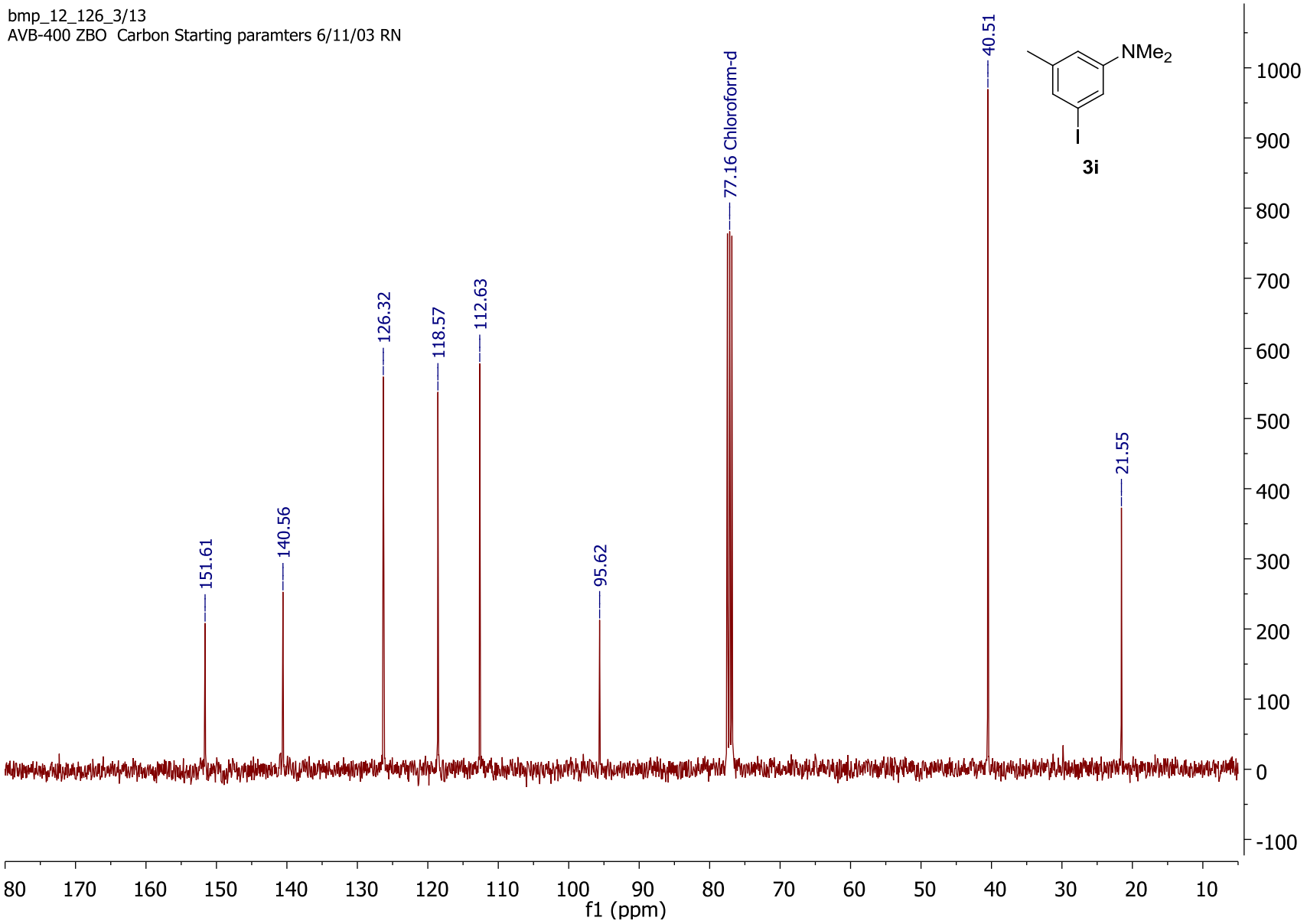
6.85
6.47
2.91
2.26
1.00
0.96
0.99
6.28
3.13
f1 (ppm)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112.63
95.62
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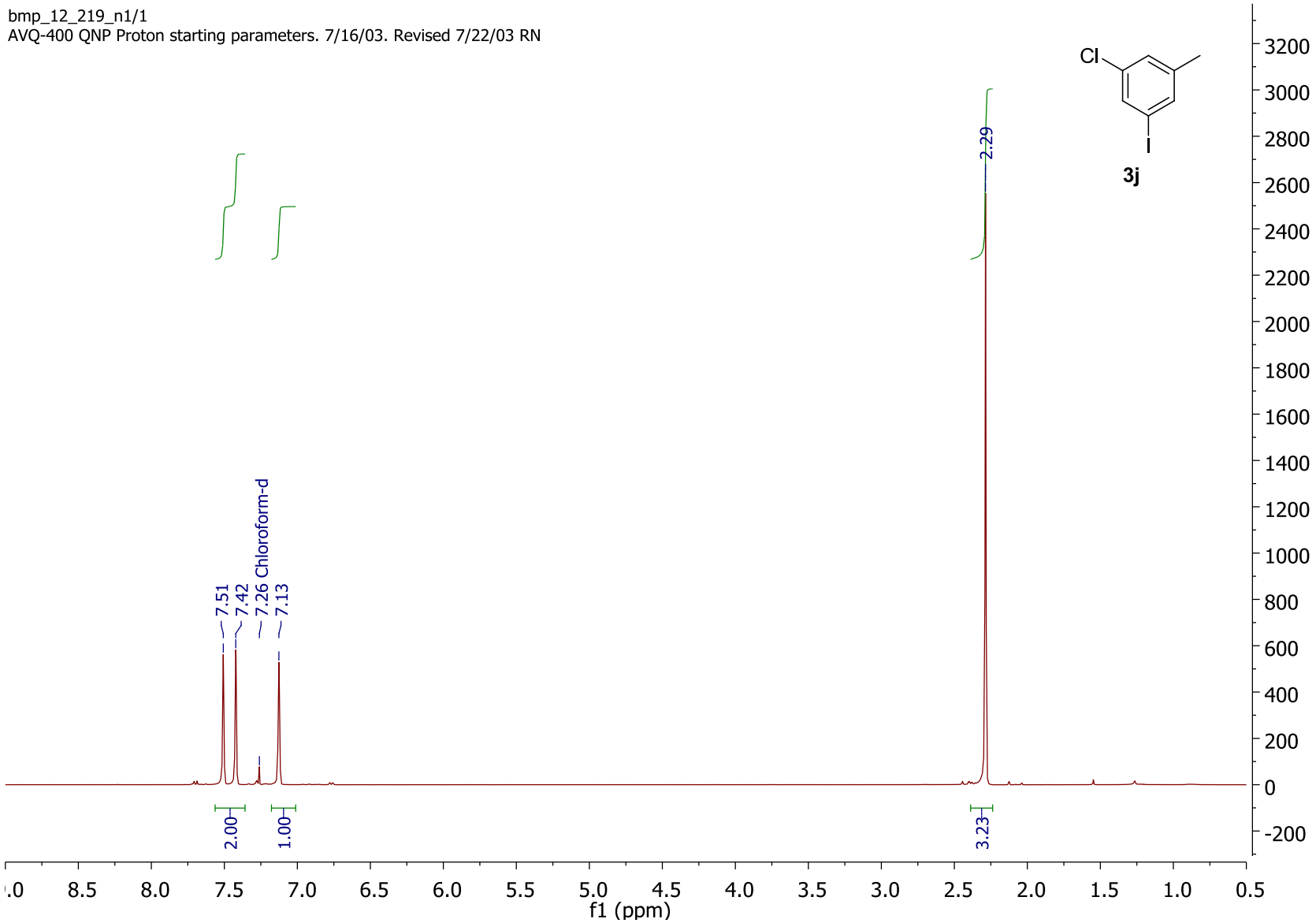
40.51
21.55
NMe2
I
3i
f1 (ppm)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Cl
I
3j
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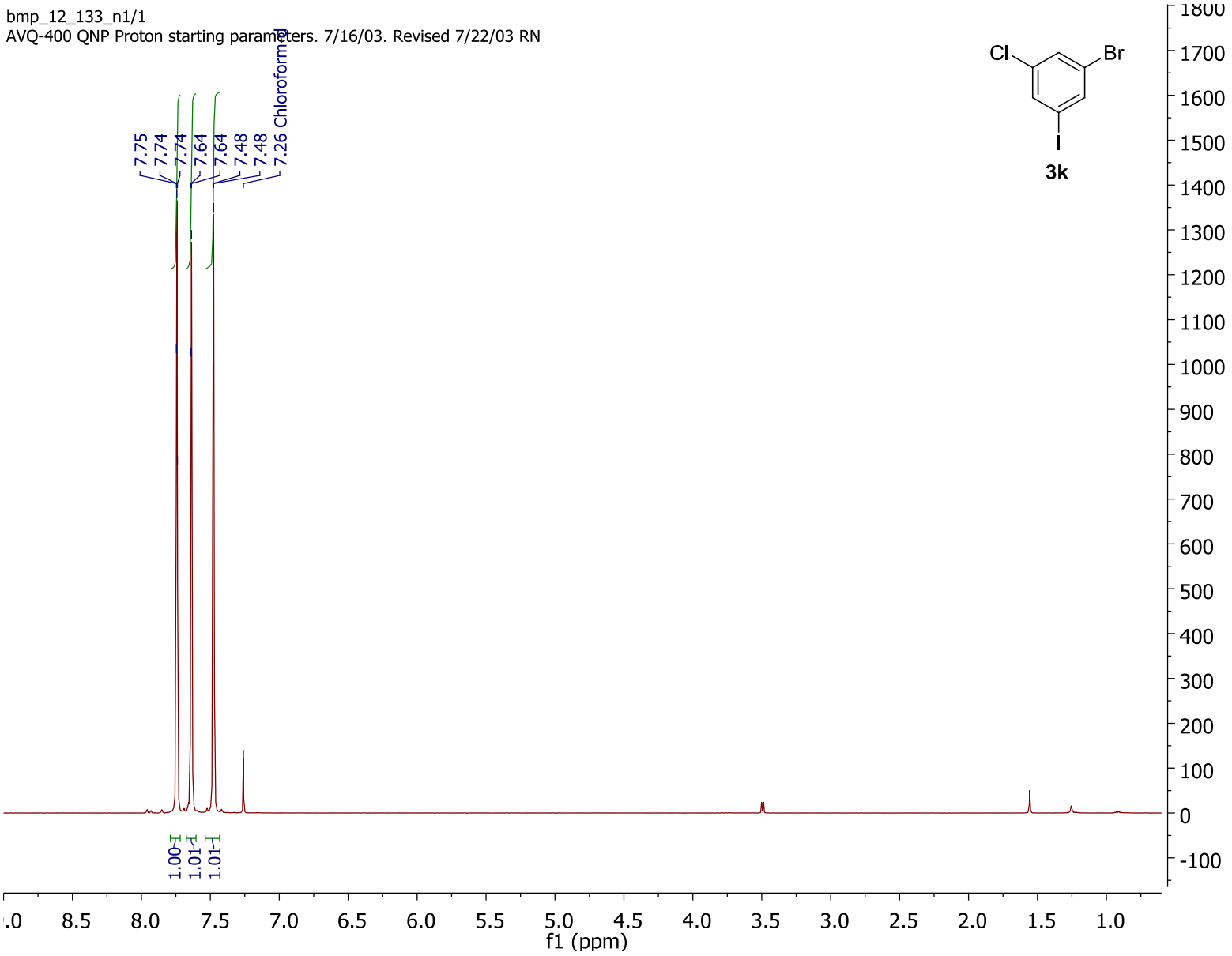
2.29
2.00
1.00
3.23
f1 (ppm)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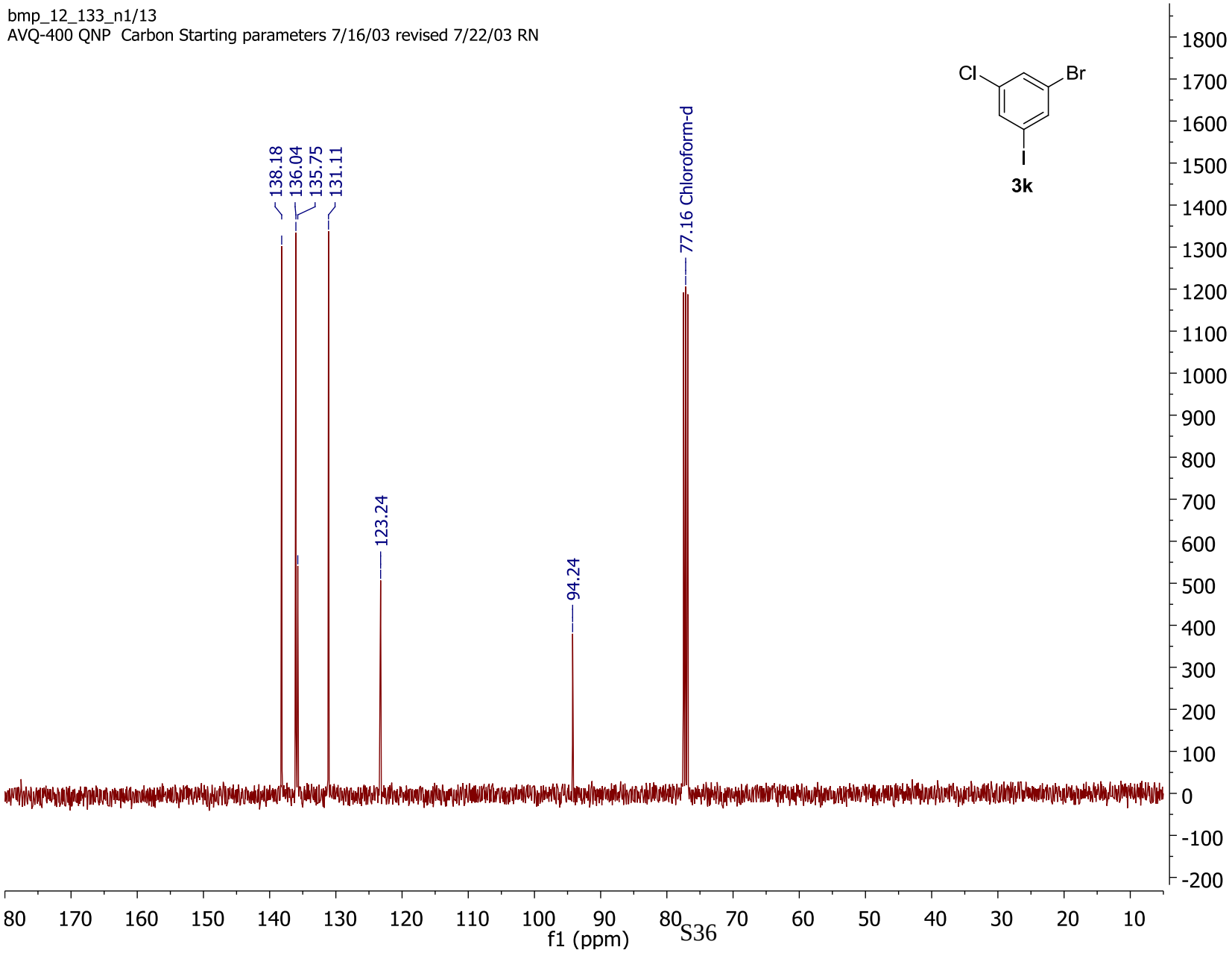
7.75
7.74
7.74
7.64
7.64
7.48
7.48
7.26 Chloroform
1.00
1.01
1.01
Cl
Br
I
3k
f1 (ppm)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AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
Cl
Br
I
3k
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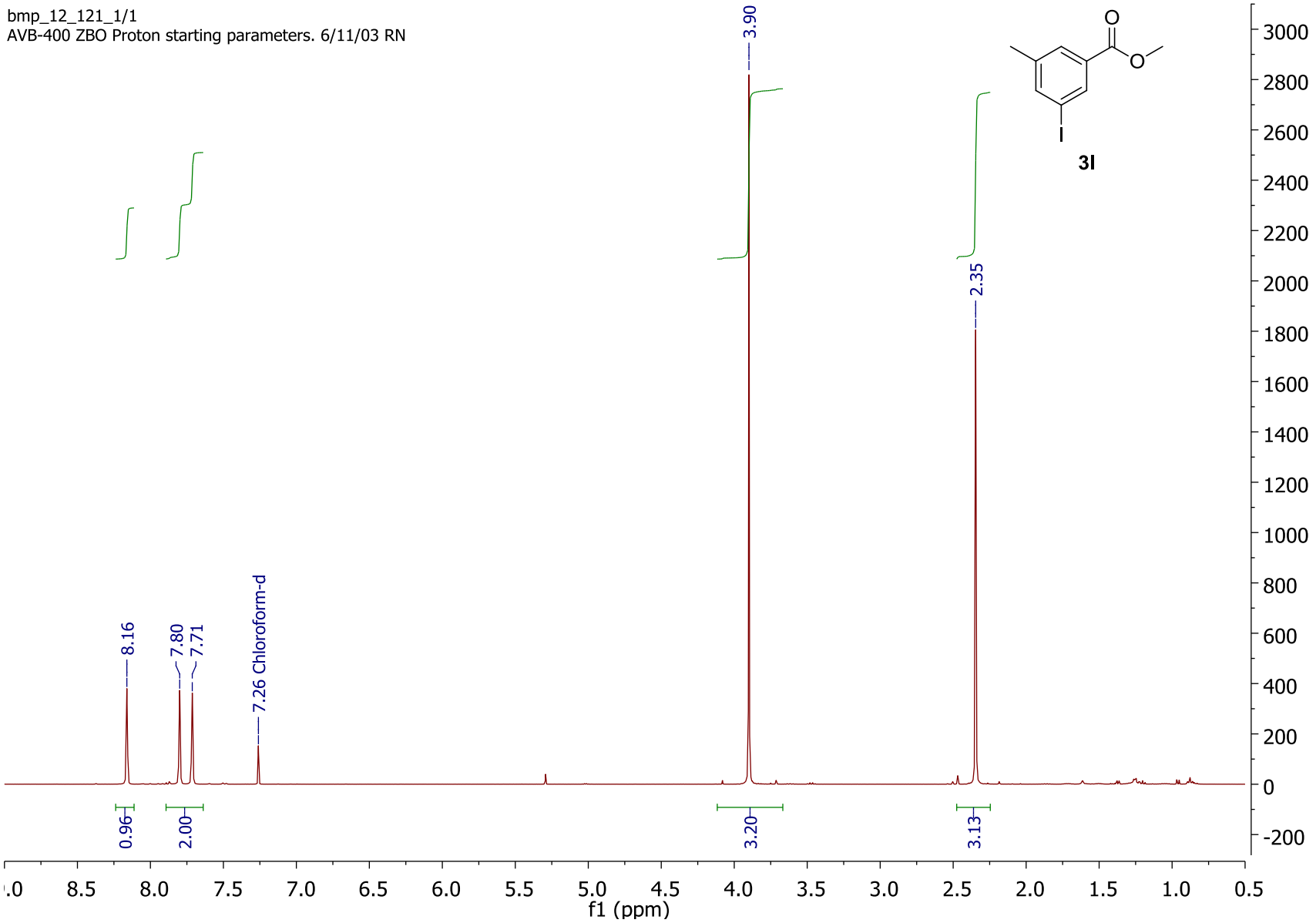
123.24
94.24
77.16 Chloroform-d
f1 (ppm)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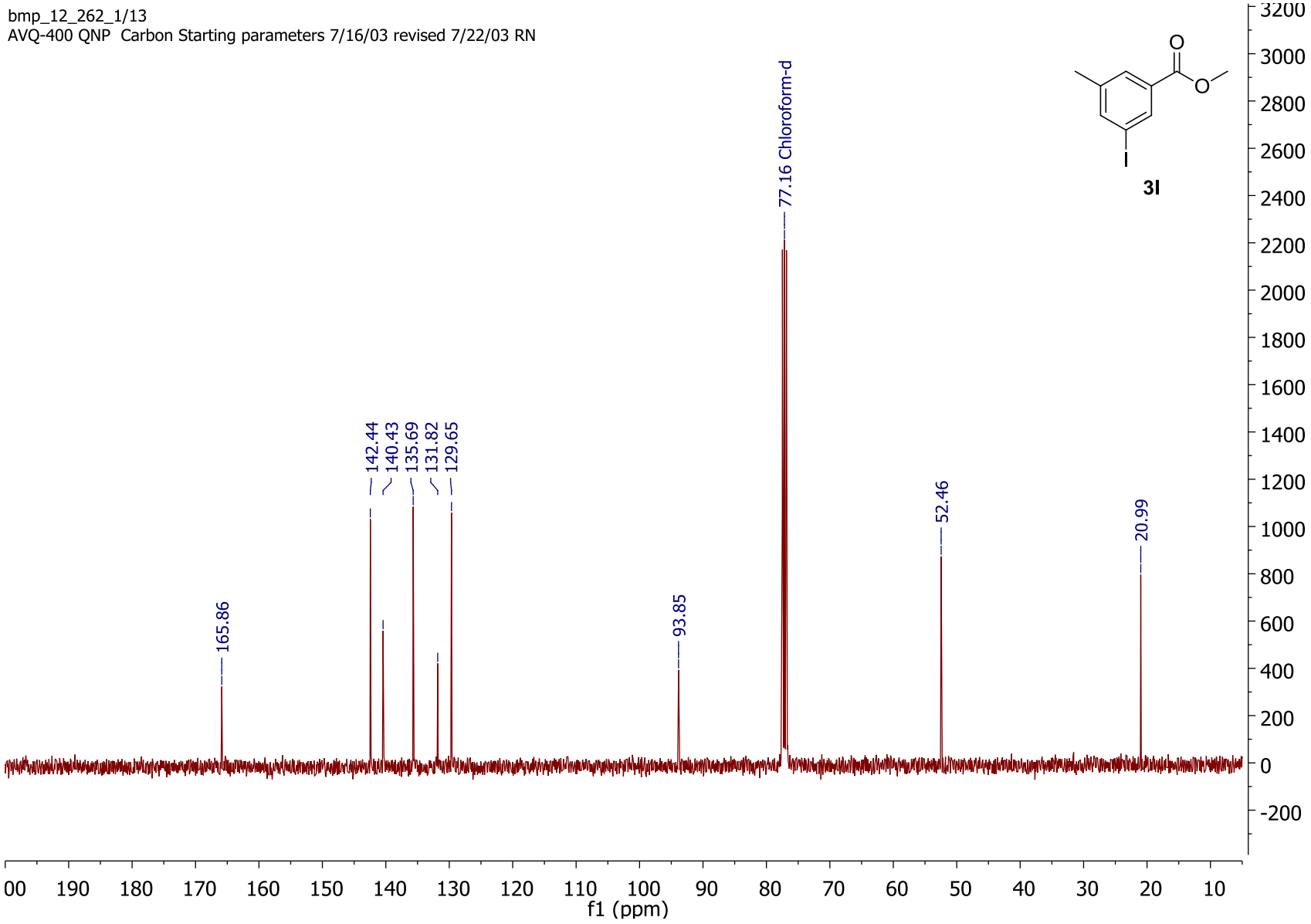
2.00
3.20
3.13
f1 (ppm)
3I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O
O
I
3l
77.16 Chloroform-d
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129.65
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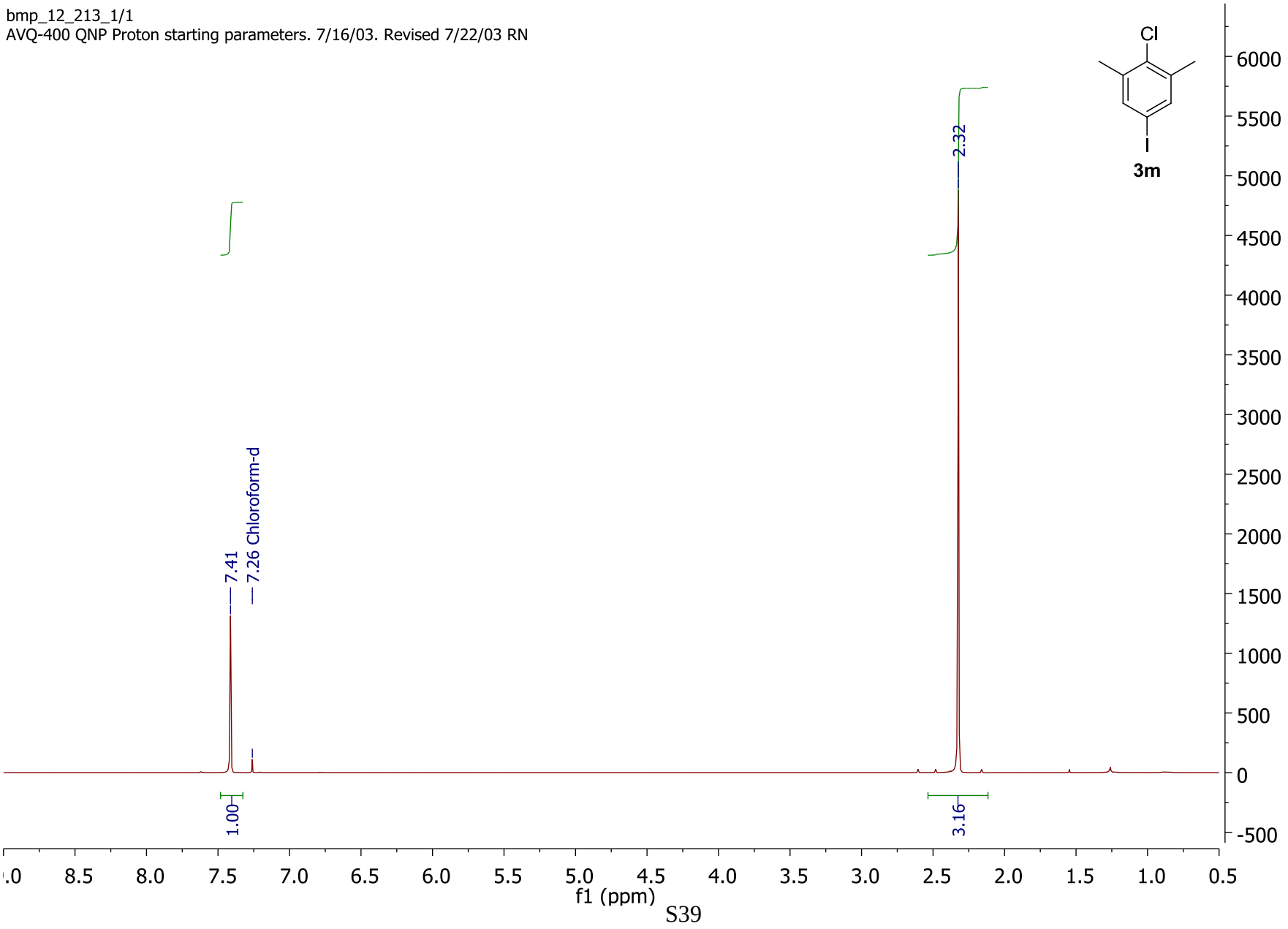
93.85
52.46
20.99
f1 (ppm)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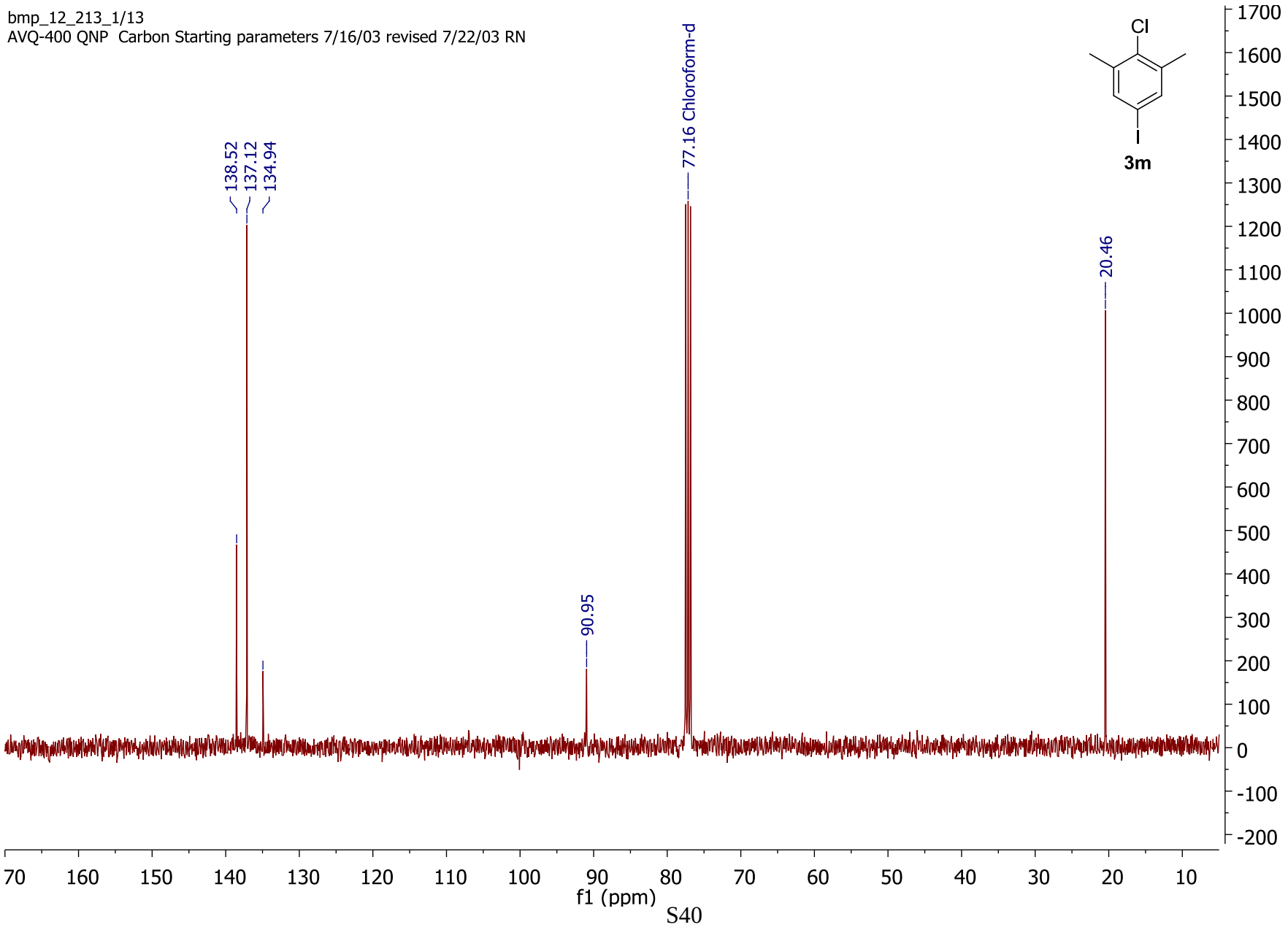
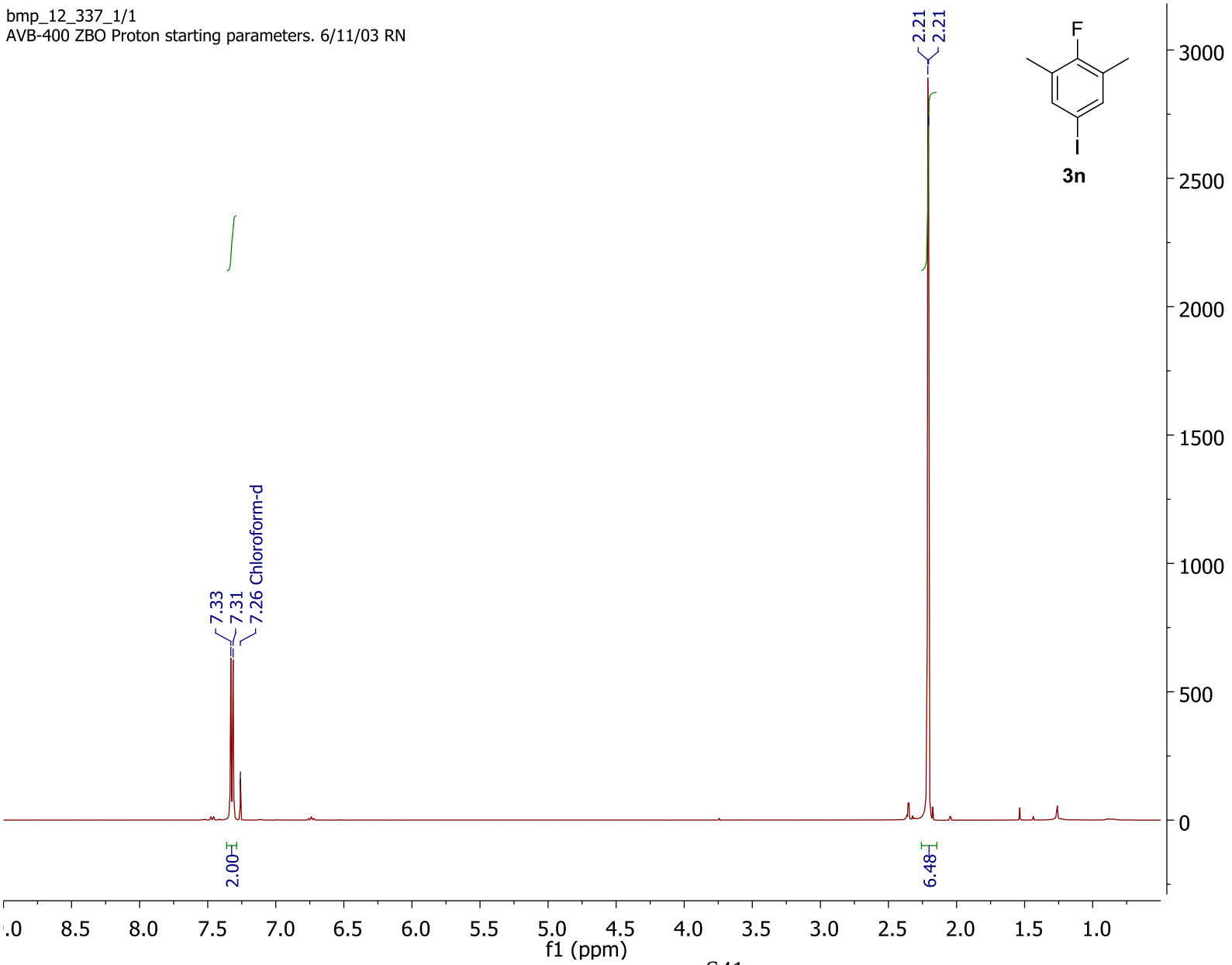
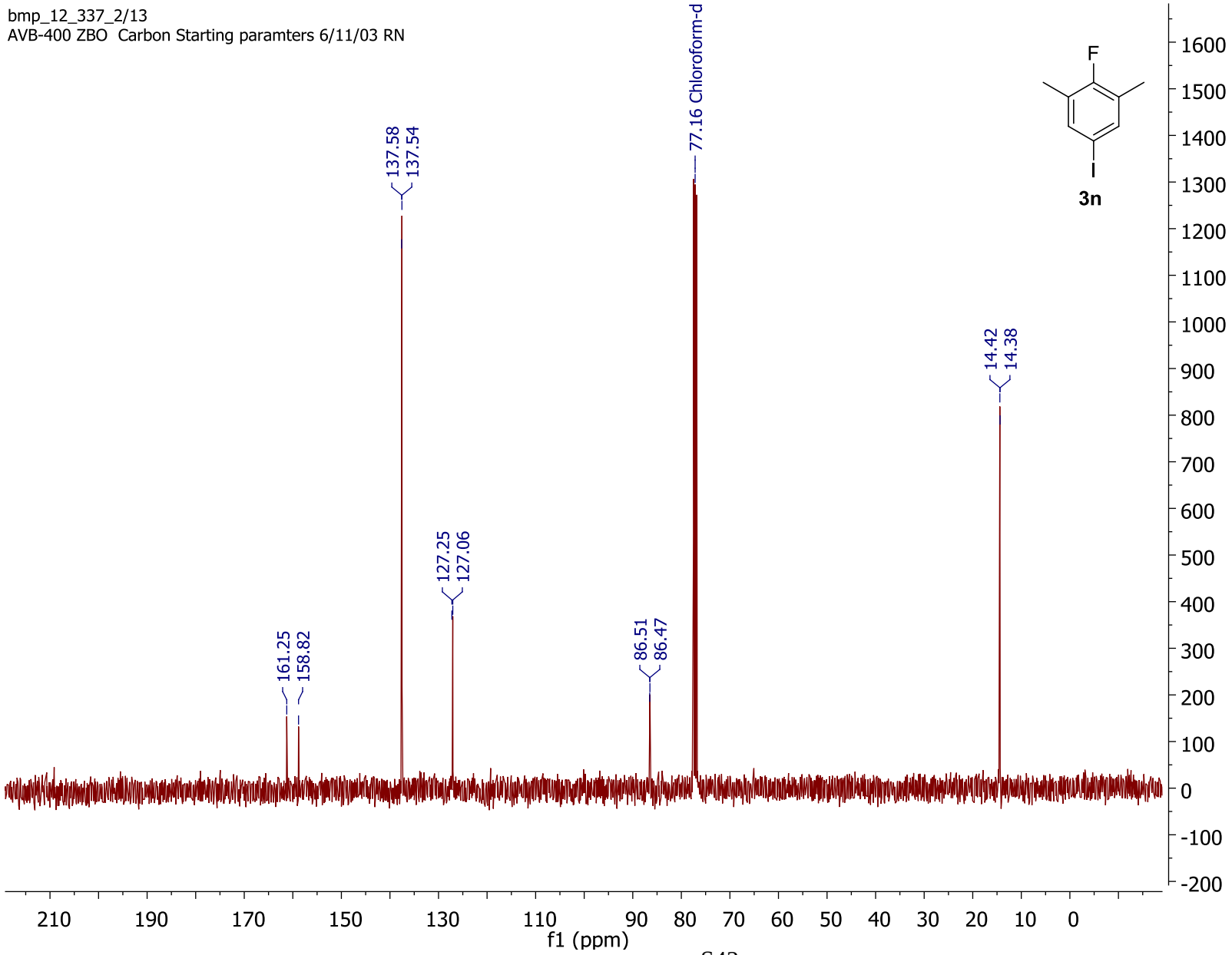
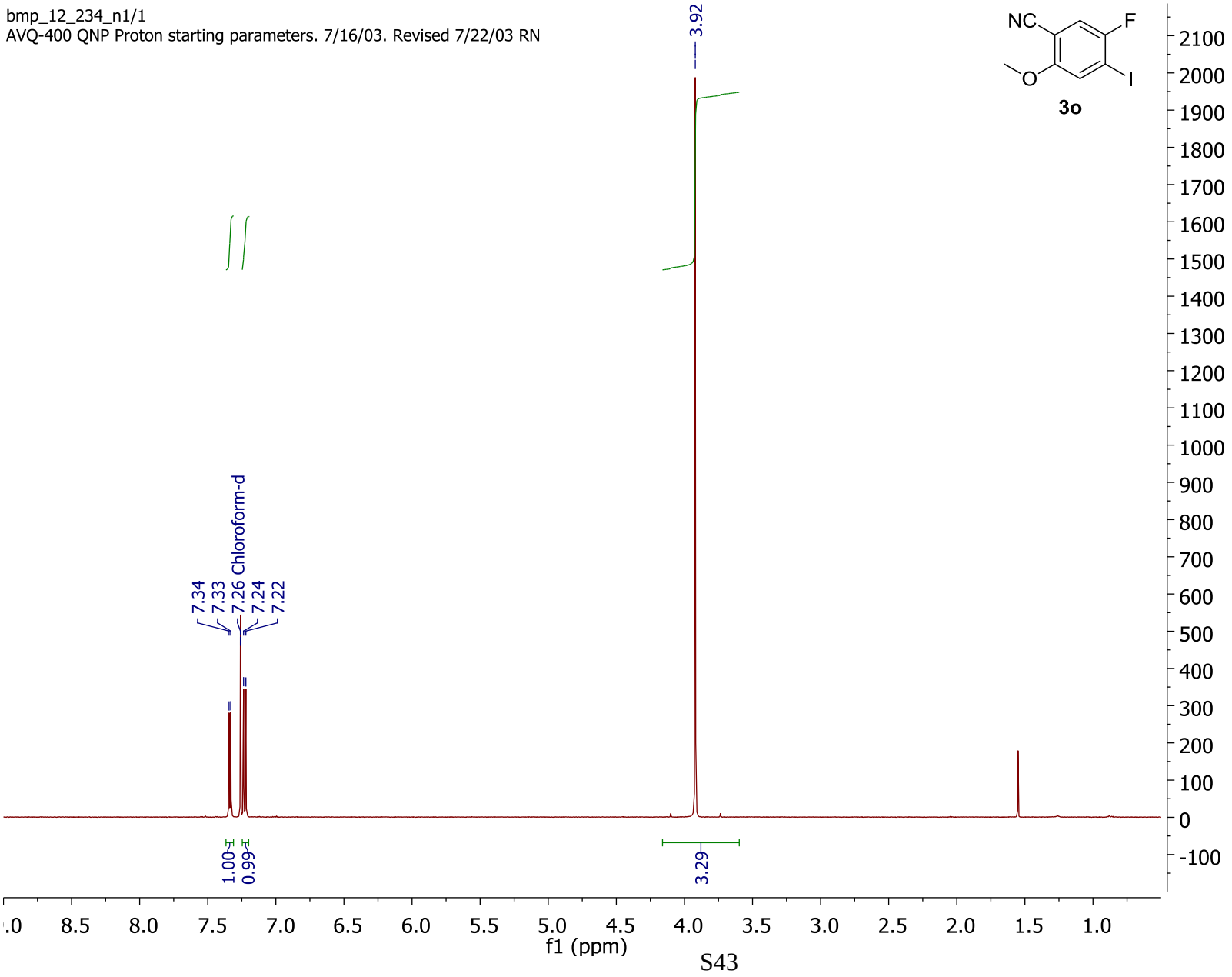
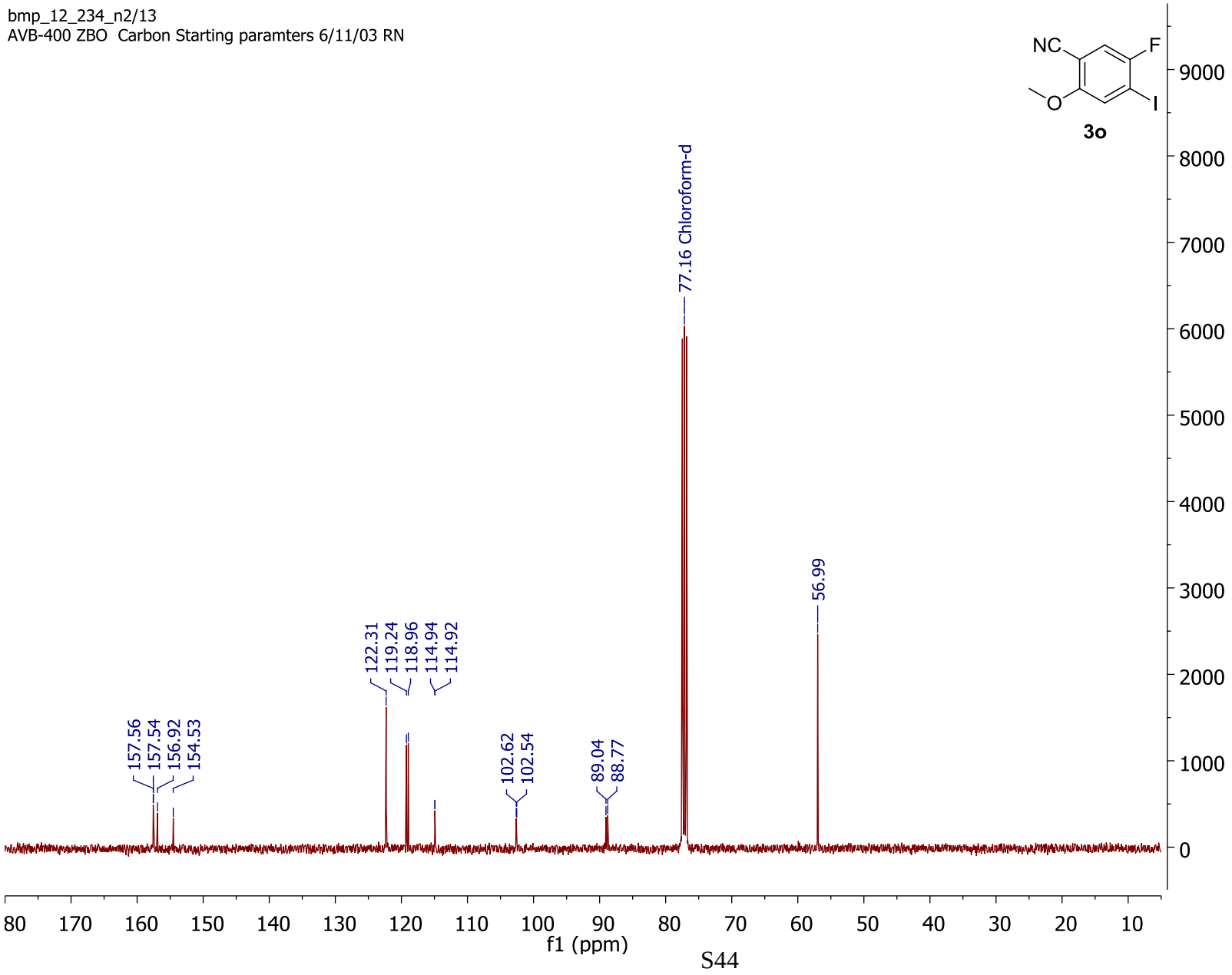
Cl
I
3m
7.41
7.26 Chloroform-d
2.32
1.00
3.16
f1 (ppm)

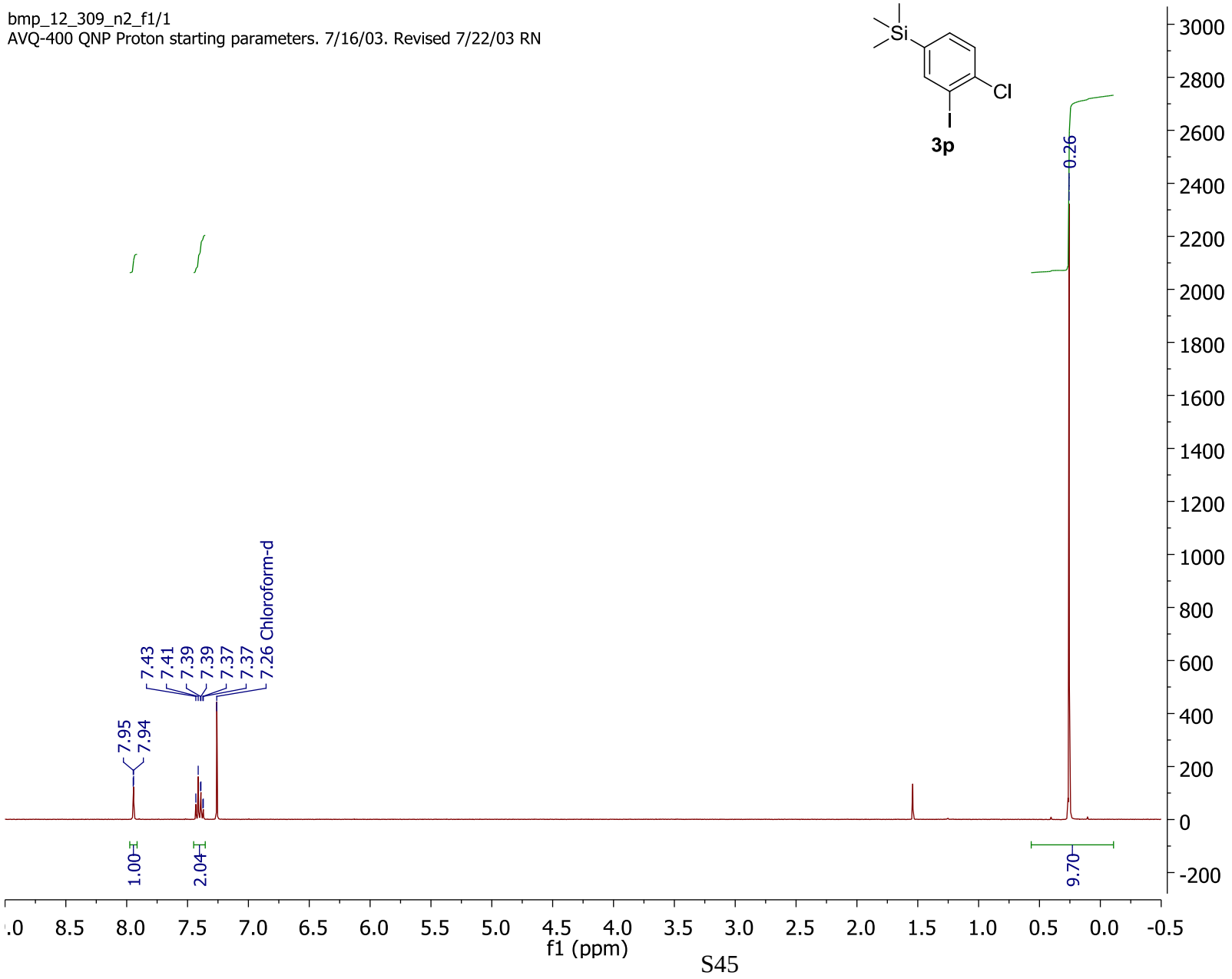

bmp_12_213_1/13
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
138.52
137.12
134.94
90.95
77.16 Chloroform-d
20.46
Cl
I
3m
f1 (ppm)

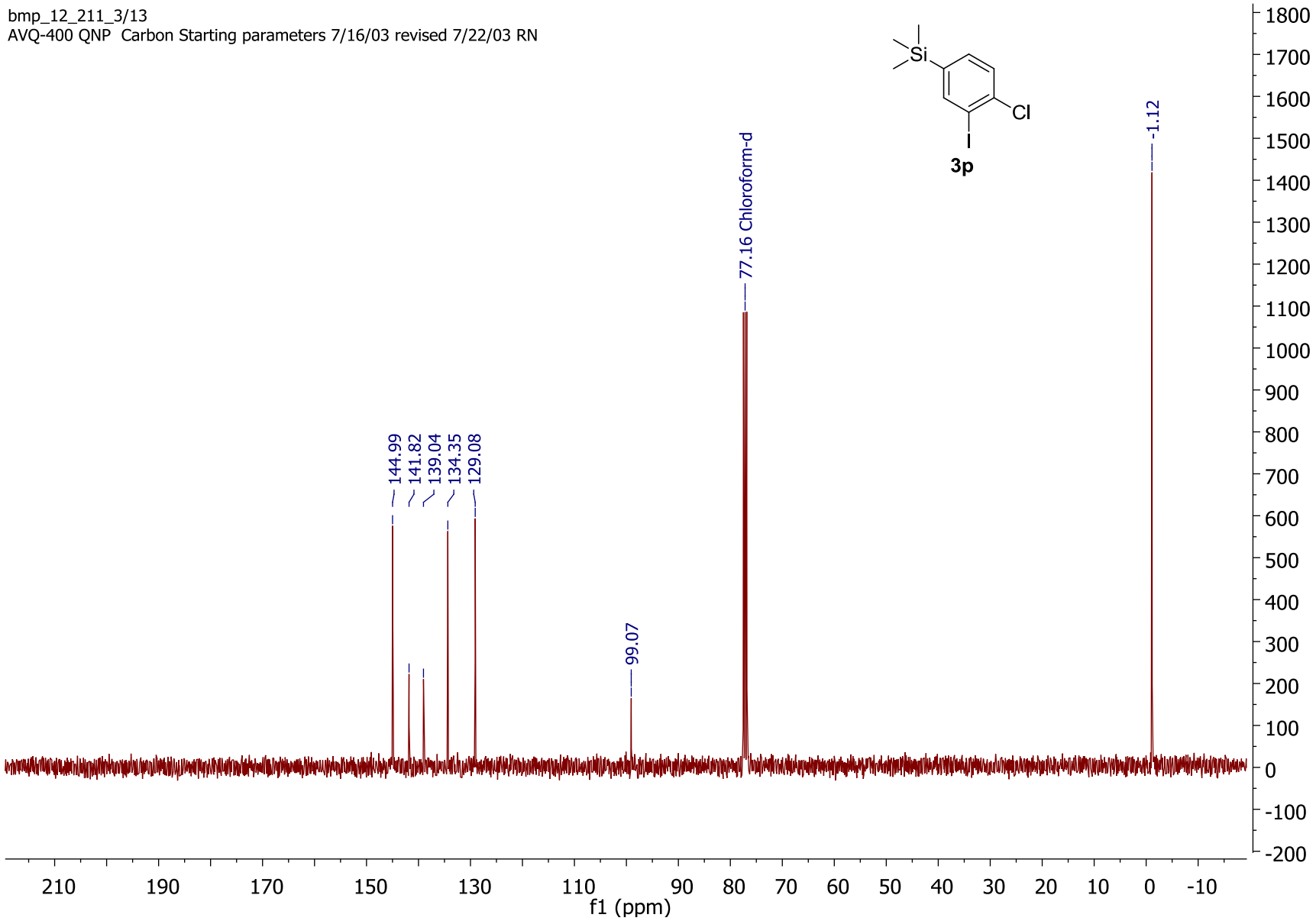

bmp_12_337_1/1
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
2.21
2.21
F
I
3n
7.33
7.31
7.26 Chloroform-d
2.00
6.48
3000
2500
2000
1500
1000
500
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

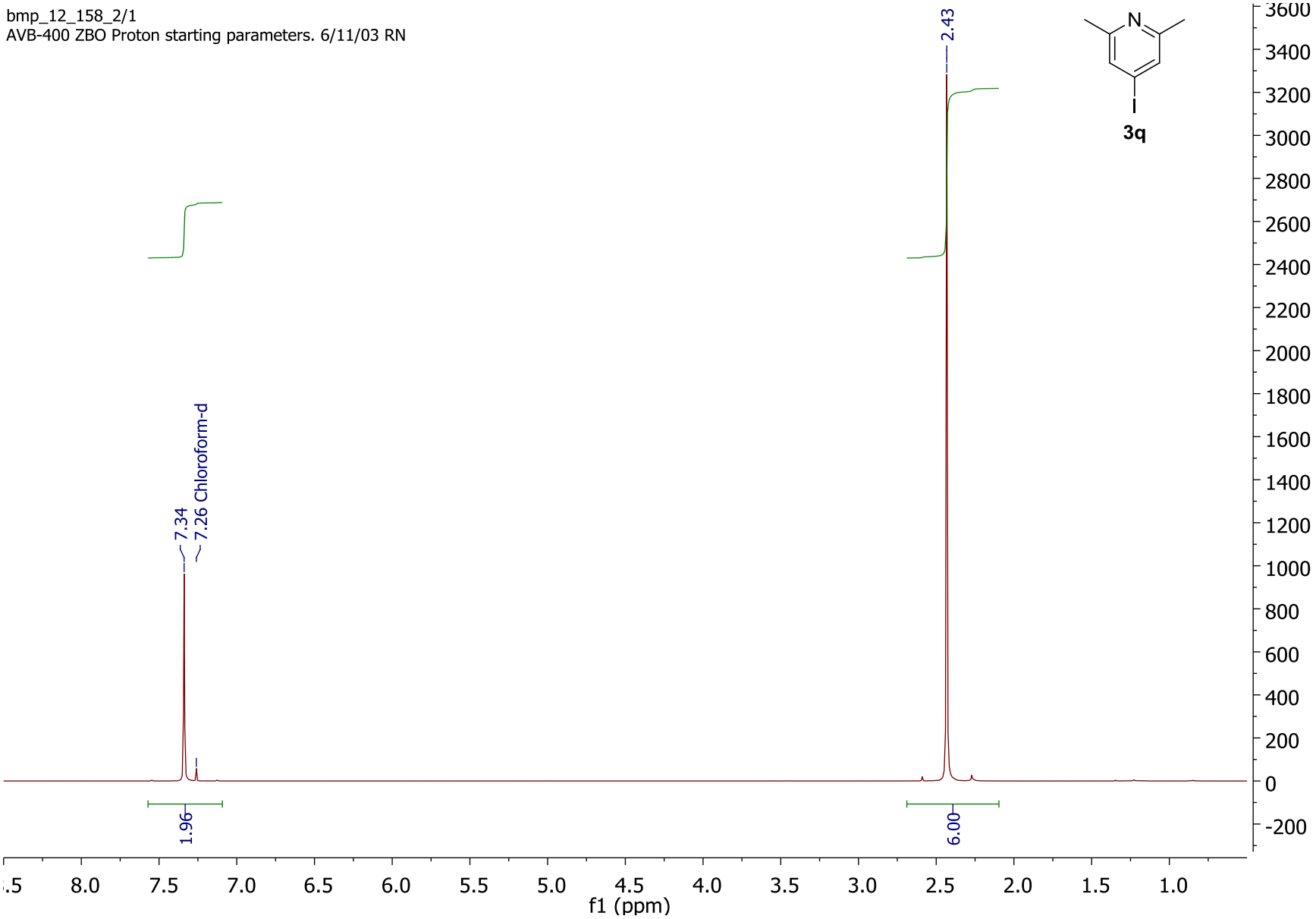

bmp_12_337_2/13
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN
161.25
158.82
137.58
137.54
127.25
127.06
86.51
86.47
77.16 Chloroform-d
14.42
14.38
F
I
3n
f1 (ppm)

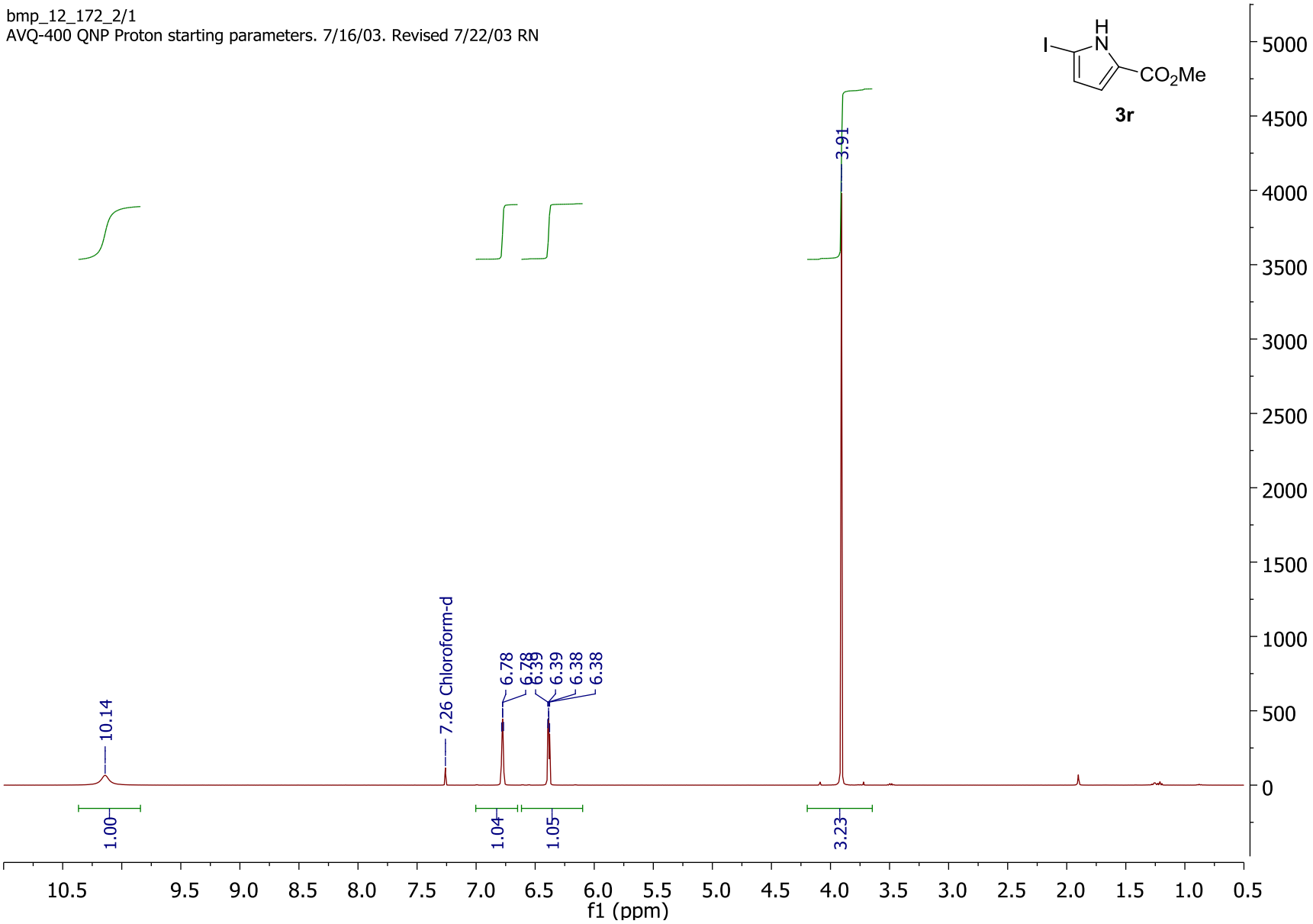

bmp_12_234_n1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
3.92
NC
F
O
I
3o
7.34
7.33
7.26 Chloroform-d
7.24
7.22
1.00
0.99
3.29
f1 (ppm)

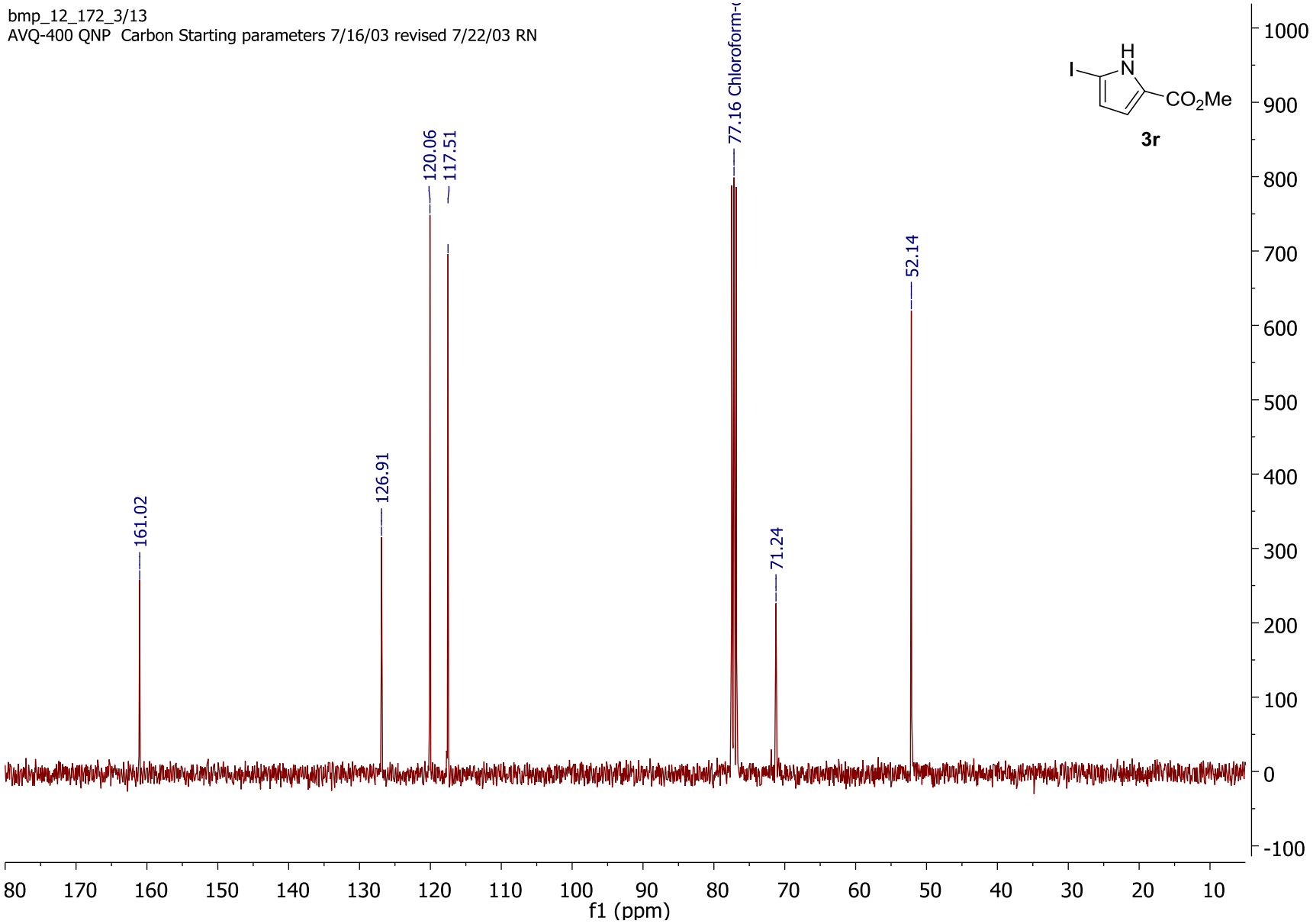

bmp_12_234_n2/13
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN
NC
F
O
I
3o
77.16 Chloroform-d
56.99
157.56
157.54
156.92
154.53
122.31
119.24
118.96
114.94
114.92
102.62
102.54
89.04
88.77
f1 (ppm)

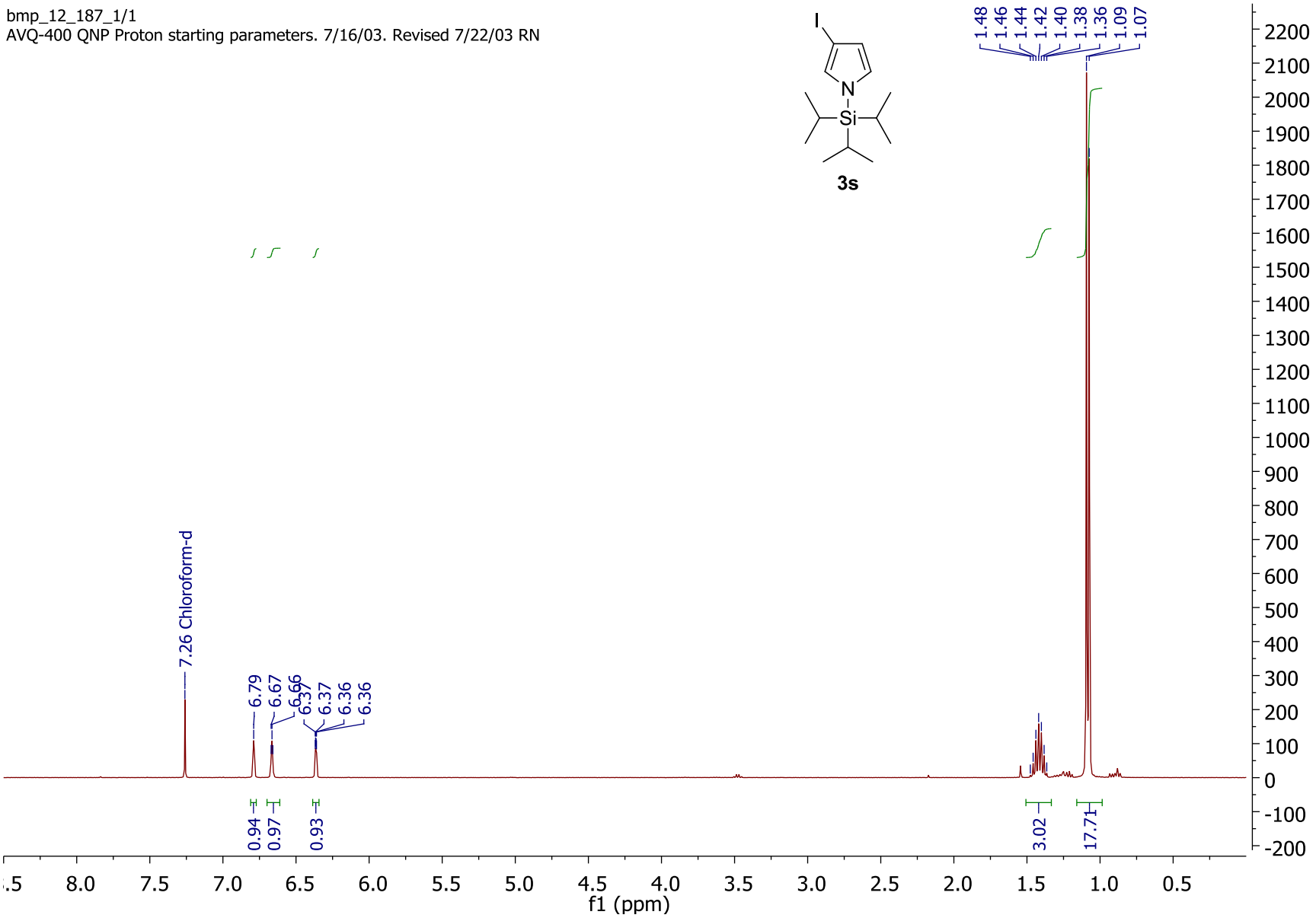

bmp_12_309_n2_f1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
Si
Cl
I
3p
0.26
7.95
7.94
7.43
7.41
7.39
7.39
7.37
7.37
7.26 Chloroform-d
1.00
2.04
9.70
f1 (ppm)

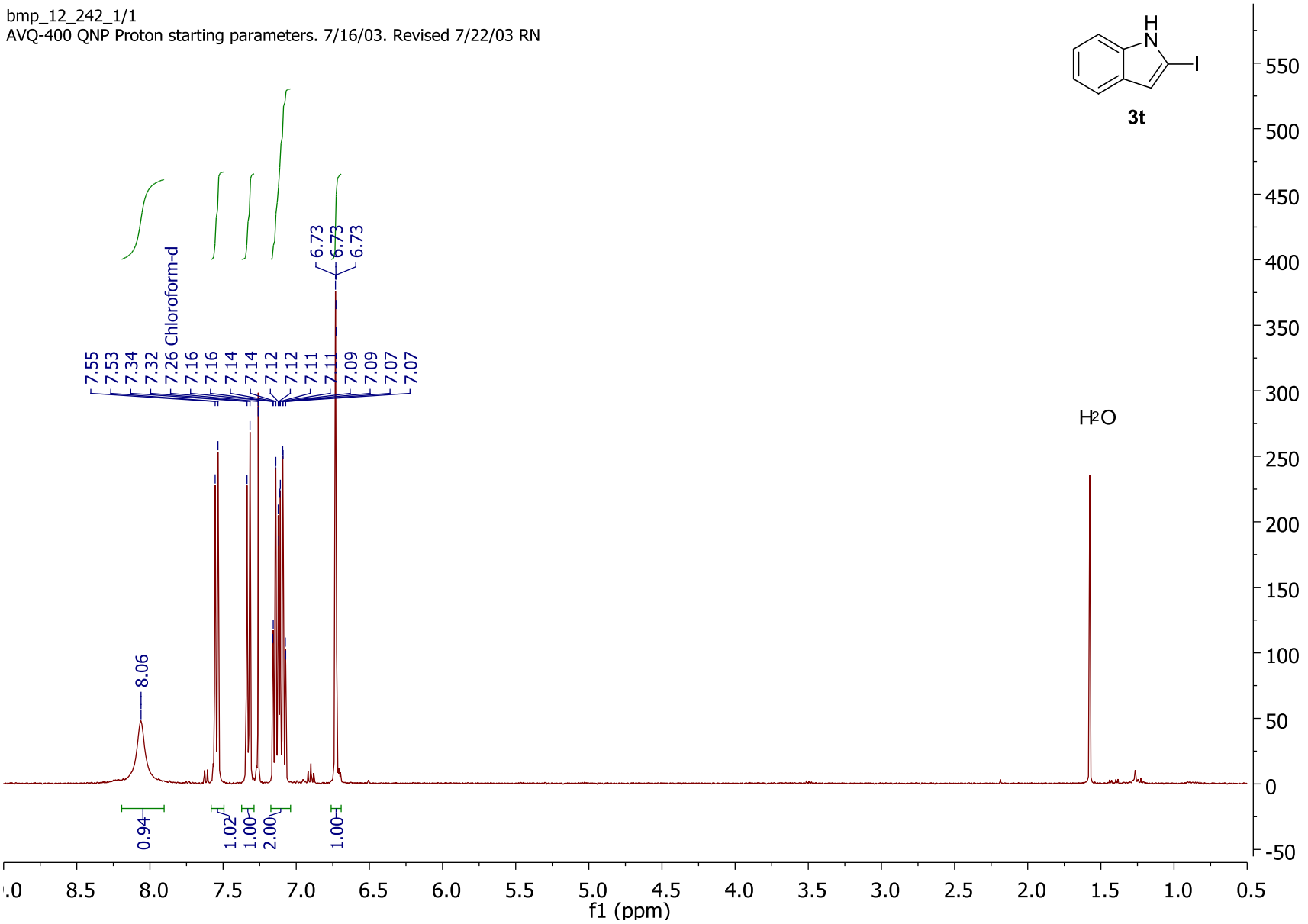

bmp_12_211_3/13
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
Si
Cl
I
3p
144.99
141.82
139.04
134.35
129.08
99.07
77.16 Chloroform-d
-1.12
f1 (ppm)

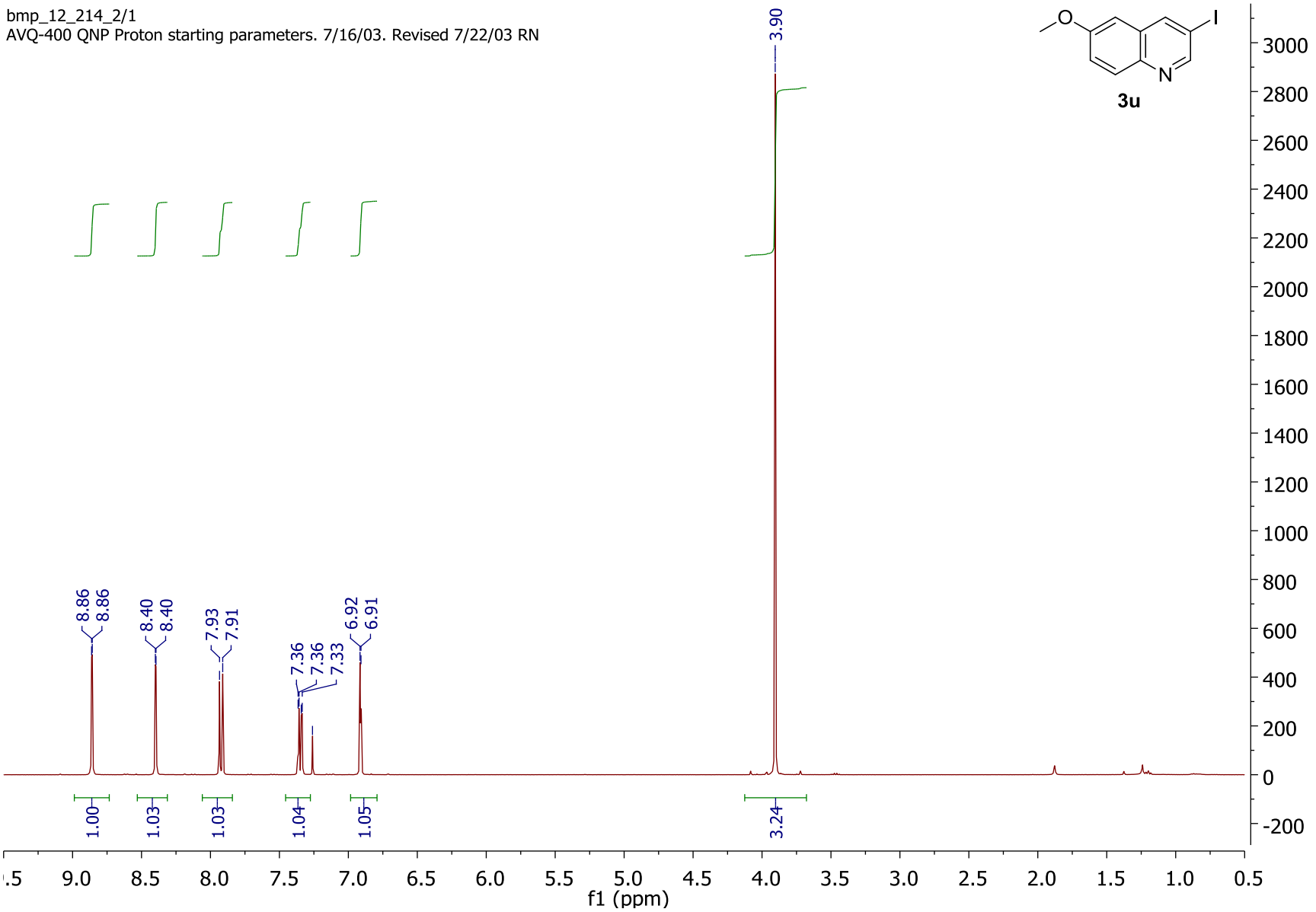

bmp_12_158_2/1
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
2.43
7.34
7.26 Chloroform-d
1.96
6.00
N
I
3q
f1 (ppm)

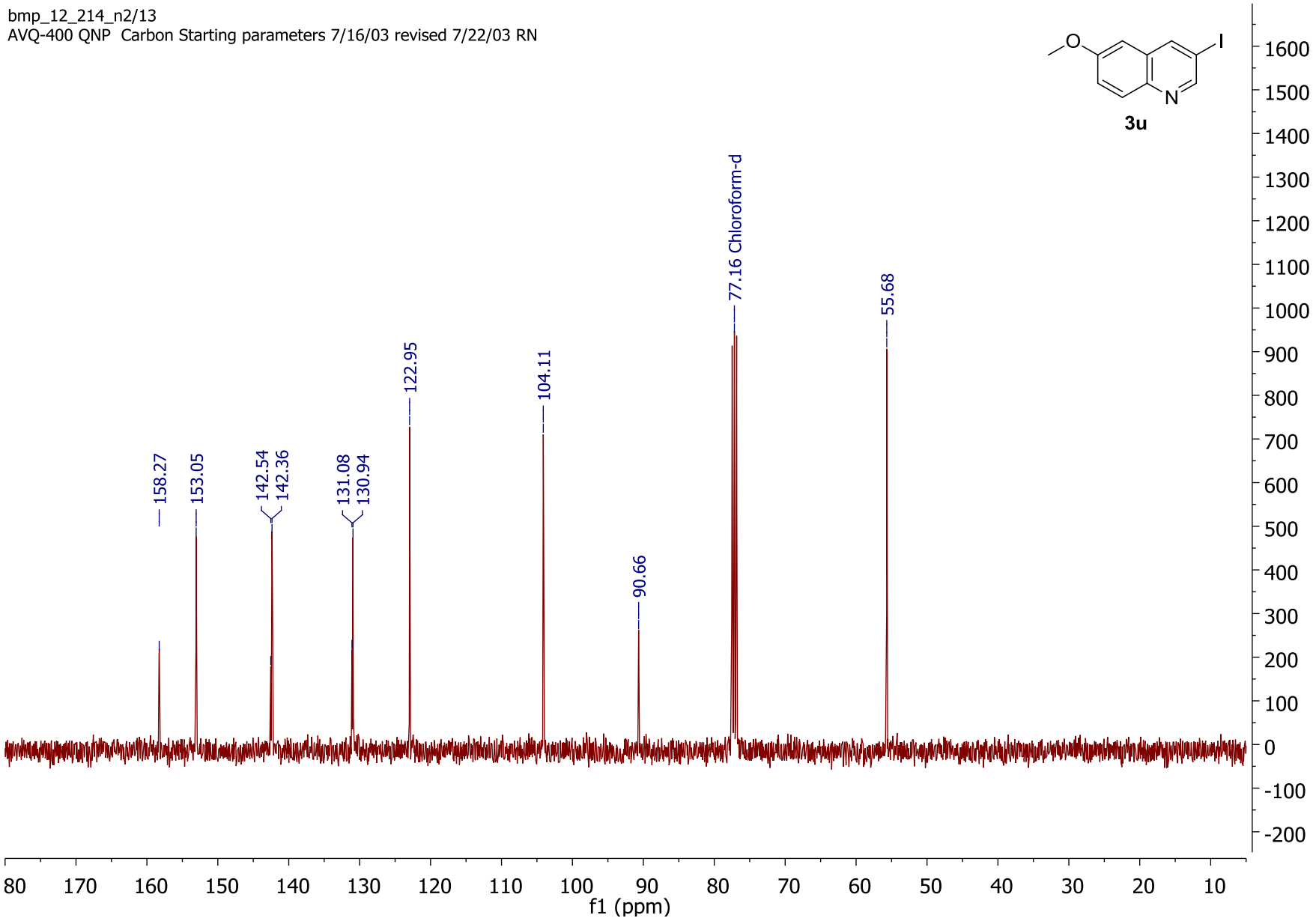

bmp_12_172_2/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
I
H
N
CO2Me
3r
10.14
7.26 Chloroform-d
6.78
6.78
6.39
6.39
6.38
6.38
3.91
1.00
1.04
1.05
3.23
f1 (ppm)

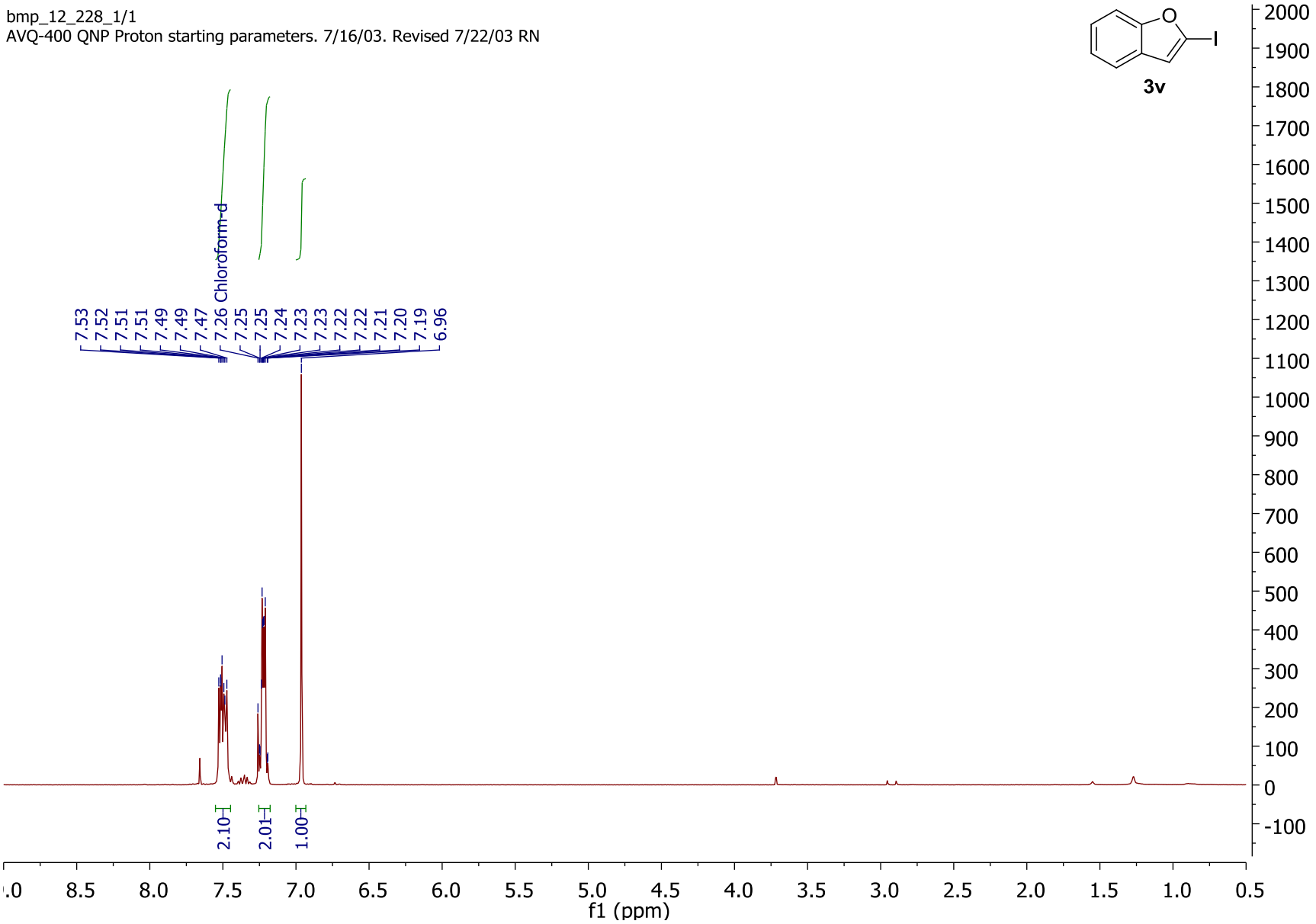

bmp_12_172_3/13
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
161.02
126.91
120.06
117.51
77.16 Chloroform-
71.24
52.14
I
H
N
CO2Me
3r
f1 (ppm)

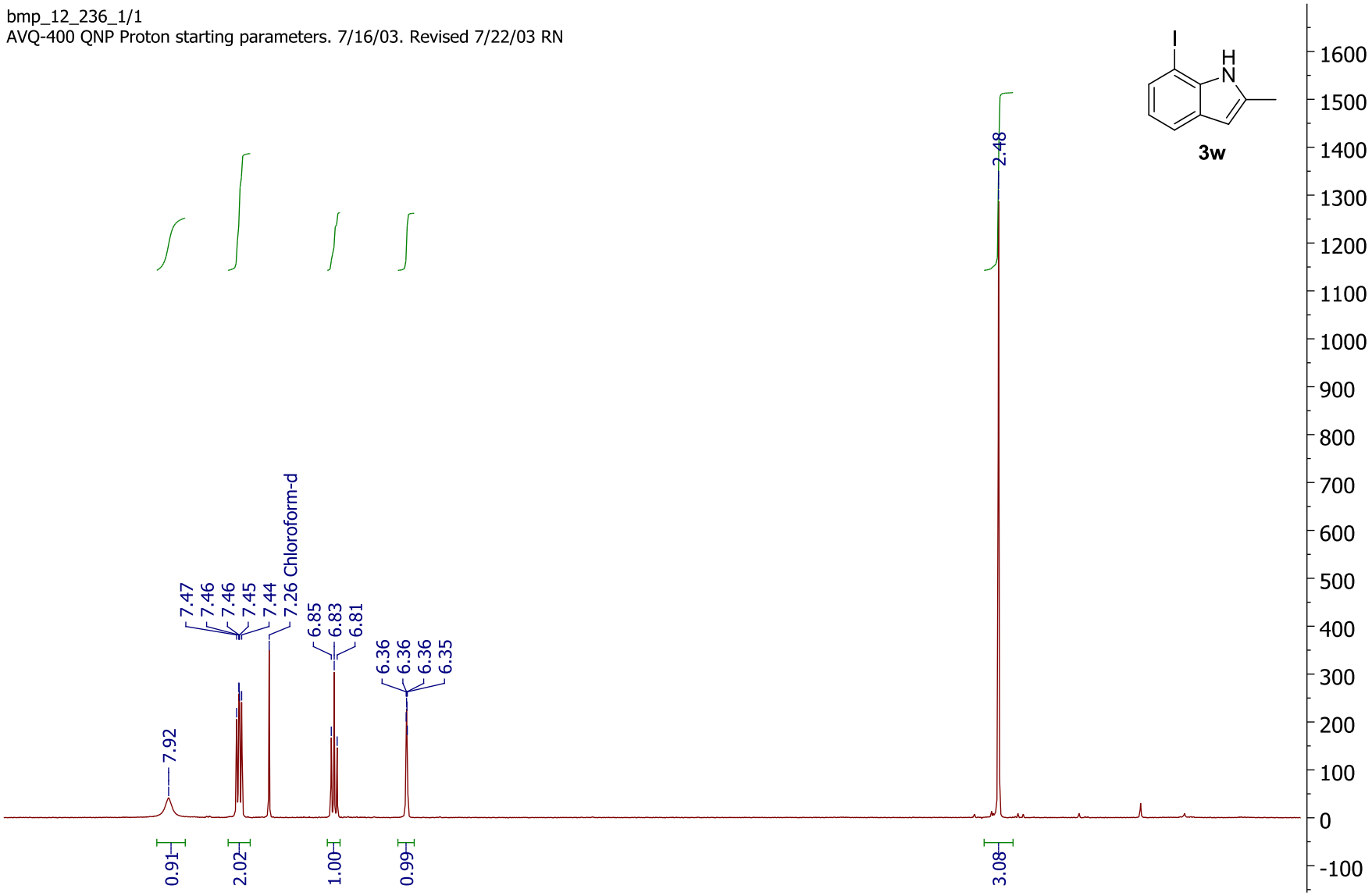

bmp_12_187_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
I
N
Si
3s
1.48
1.46
1.44
1.42
1.40
1.38
1.36
1.09
1.07
7.26 Chloroform-d
6.79
6.67
6.66
6.37
6.37
6.36
6.36
0.94
0.97
0.93
3.02
17.71
f1 (ppm)

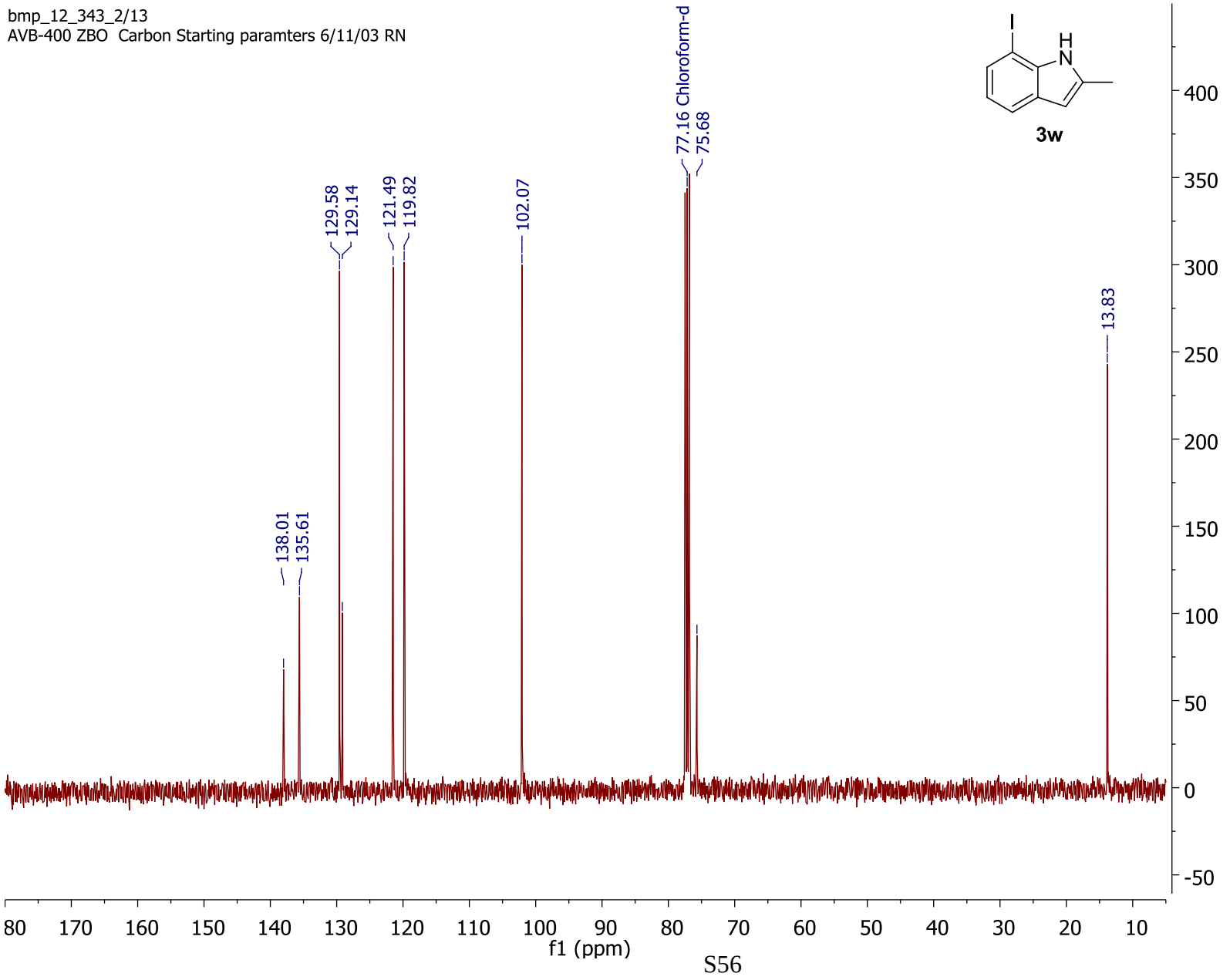

bmp_12_242_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
H
N
I
3t
6.73
6.73
6.73
Chloroform-d
7.55
7.53
7.34
7.32
7.26
7.16
7.16
7.14
7.14
7.12
7.12
7.11
7.11
7.09
7.09
7.07
7.07
H2O
8.06
0.94
1.02
1.00
2.00
1.00
f1 (ppm)

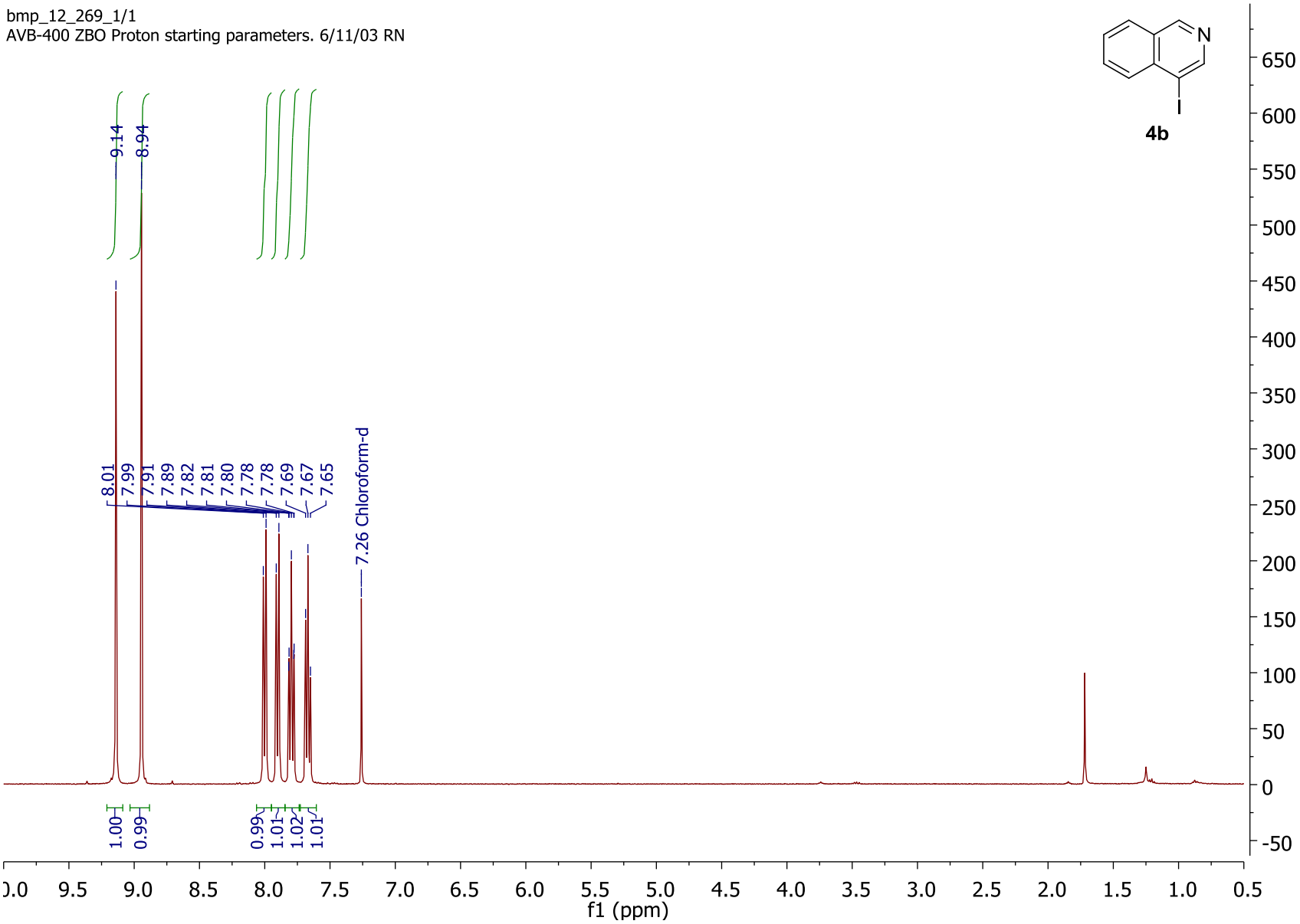

bmp_12_214_2/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
3u
8.86
8.86
8.40
8.40
7.93
7.91
7.36
7.36
7.33
6.92
6.91
3.90
1.00
1.03
1.03
1.04
1.05
3.24
f1 (ppm)

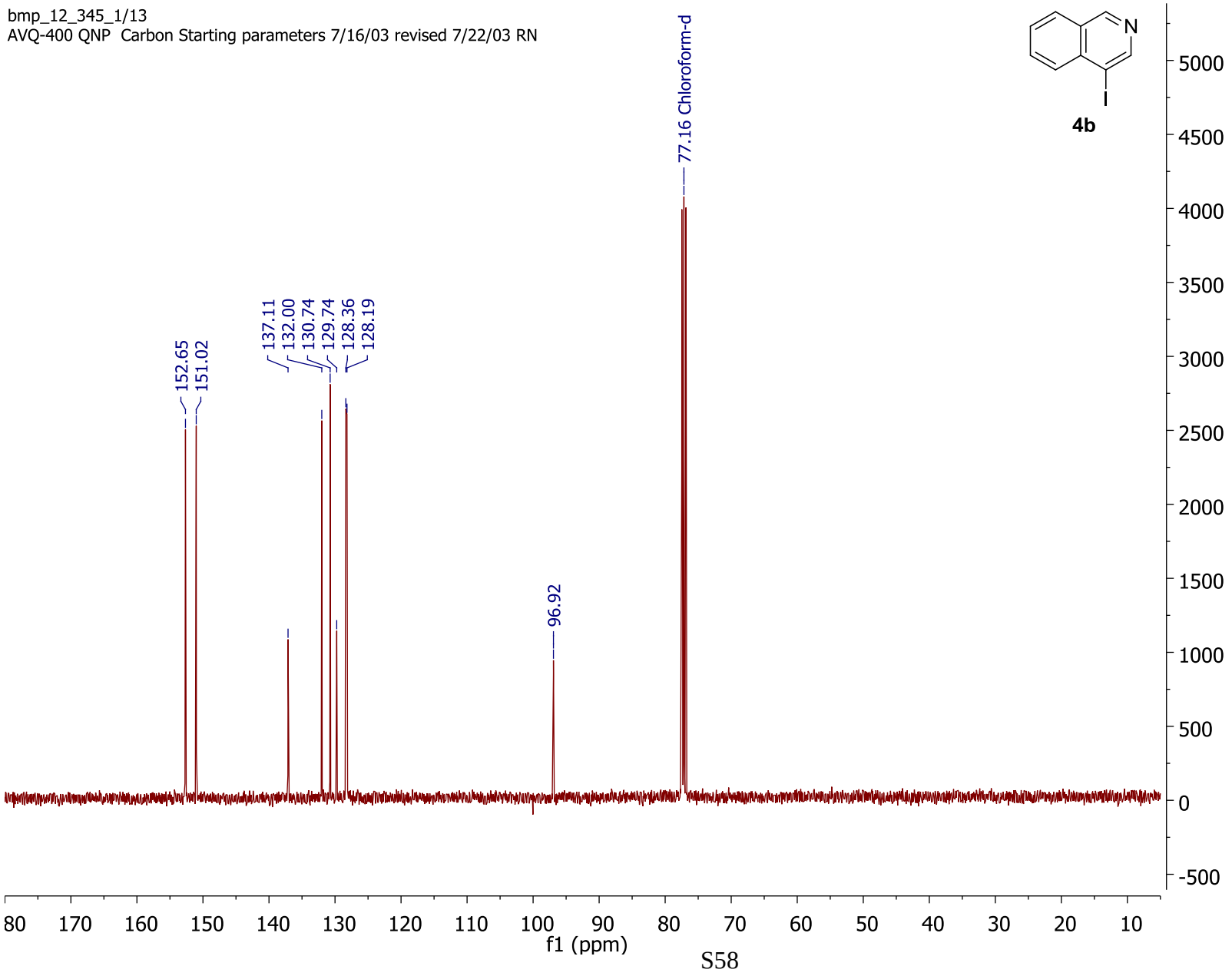

bmp_12_214_n2/13
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
O
I
N
3u
158.27
153.05
142.54
142.36
131.08
130.94
122.95
104.11
90.66
77.16 Chloroform-d
55.68
f1 (ppm)

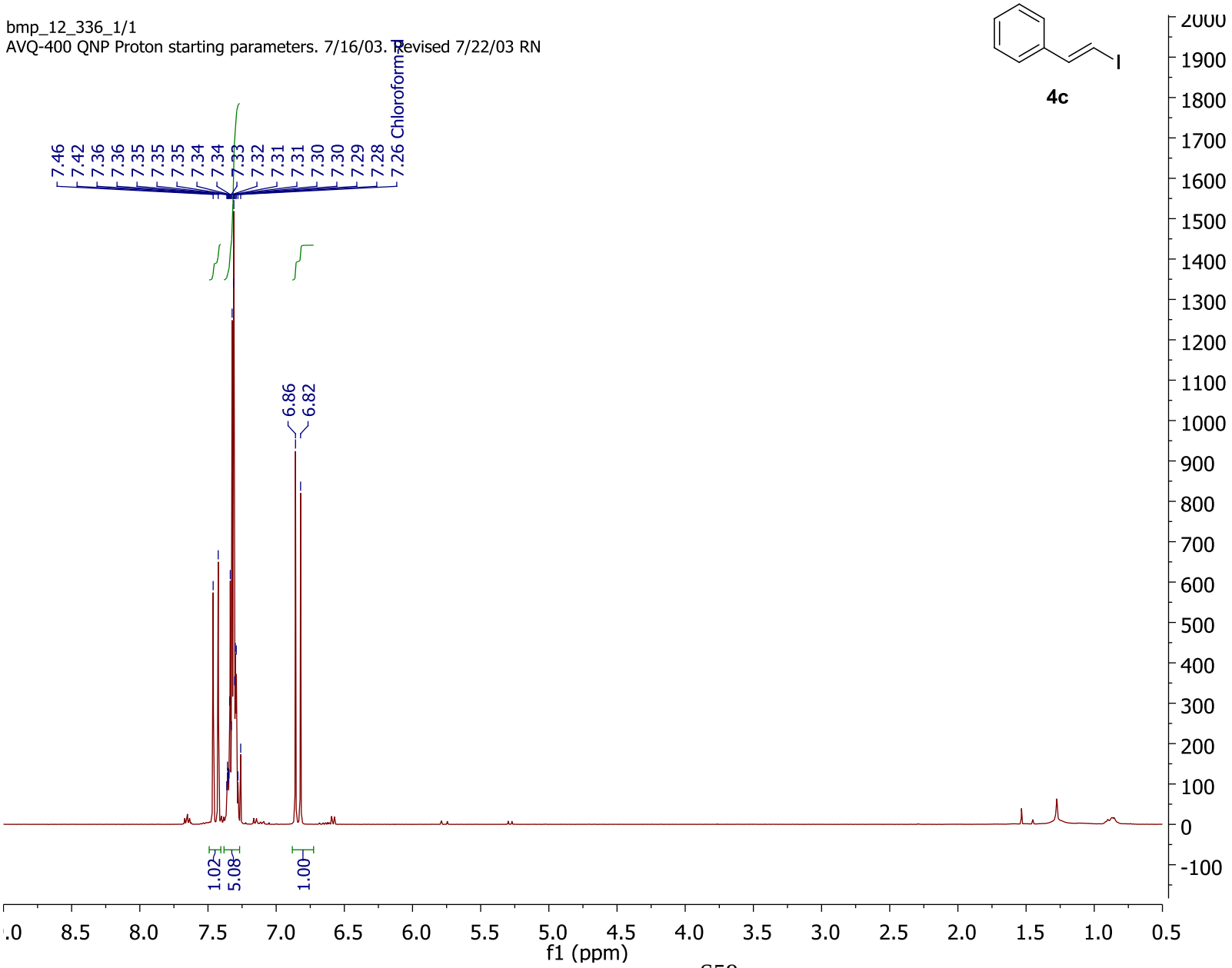

bmp_12_228_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
3v
Chloroform-d
7.53
7.52
7.51
7.51
7.49
7.49
7.47
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.19
6.96
2.10
2.01
1.00
f1 (ppm)

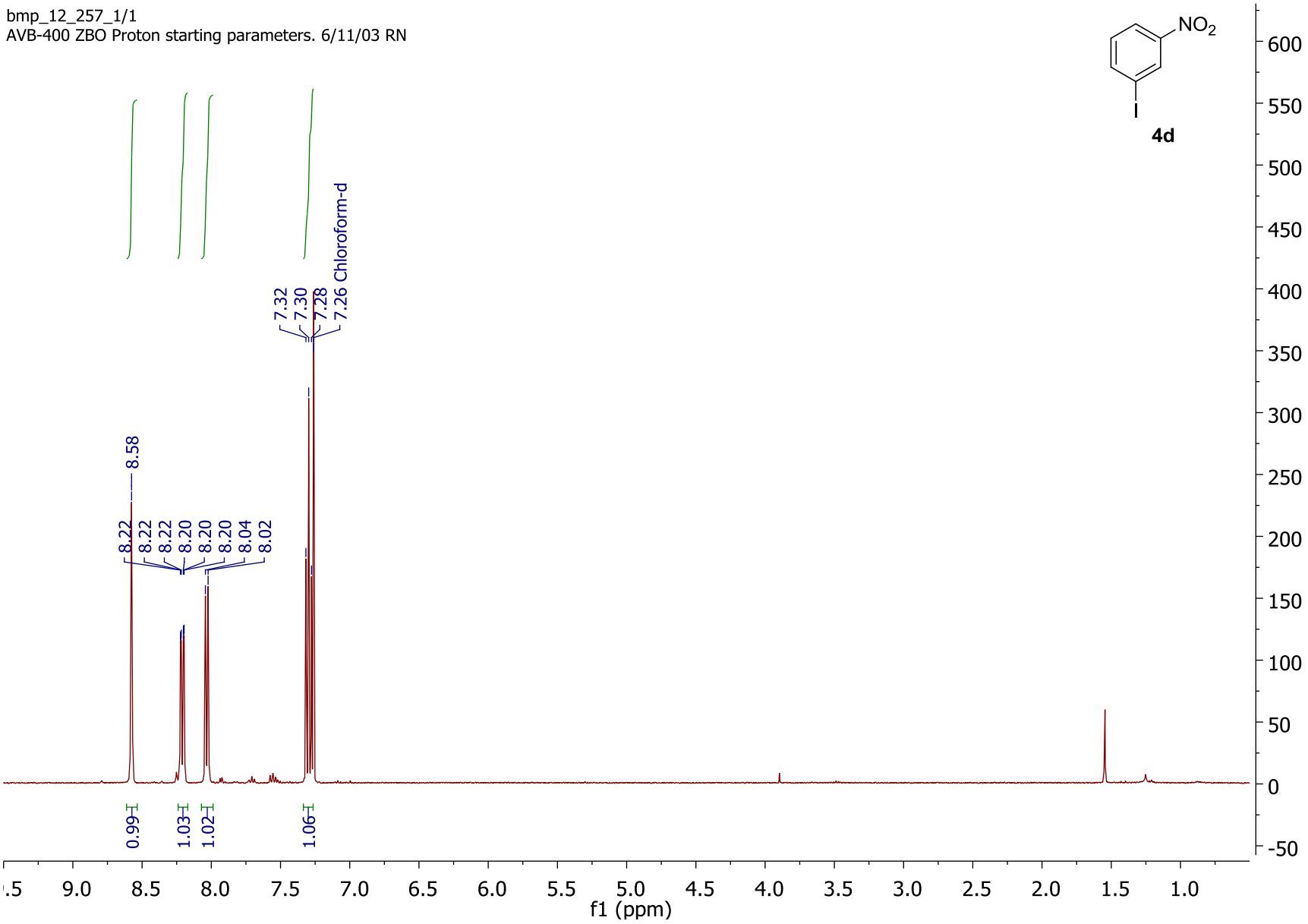

bmp_12_236_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
I
H
N
3w
2.48
7.47
7.46
7.46
7.45
7.44
7.26 Chloroform-d
6.85
6.83
6.81
6.36
6.36
6.36
6.35
7.92
0.91
2.02
1.00
0.99
3.08
f1 (ppm)

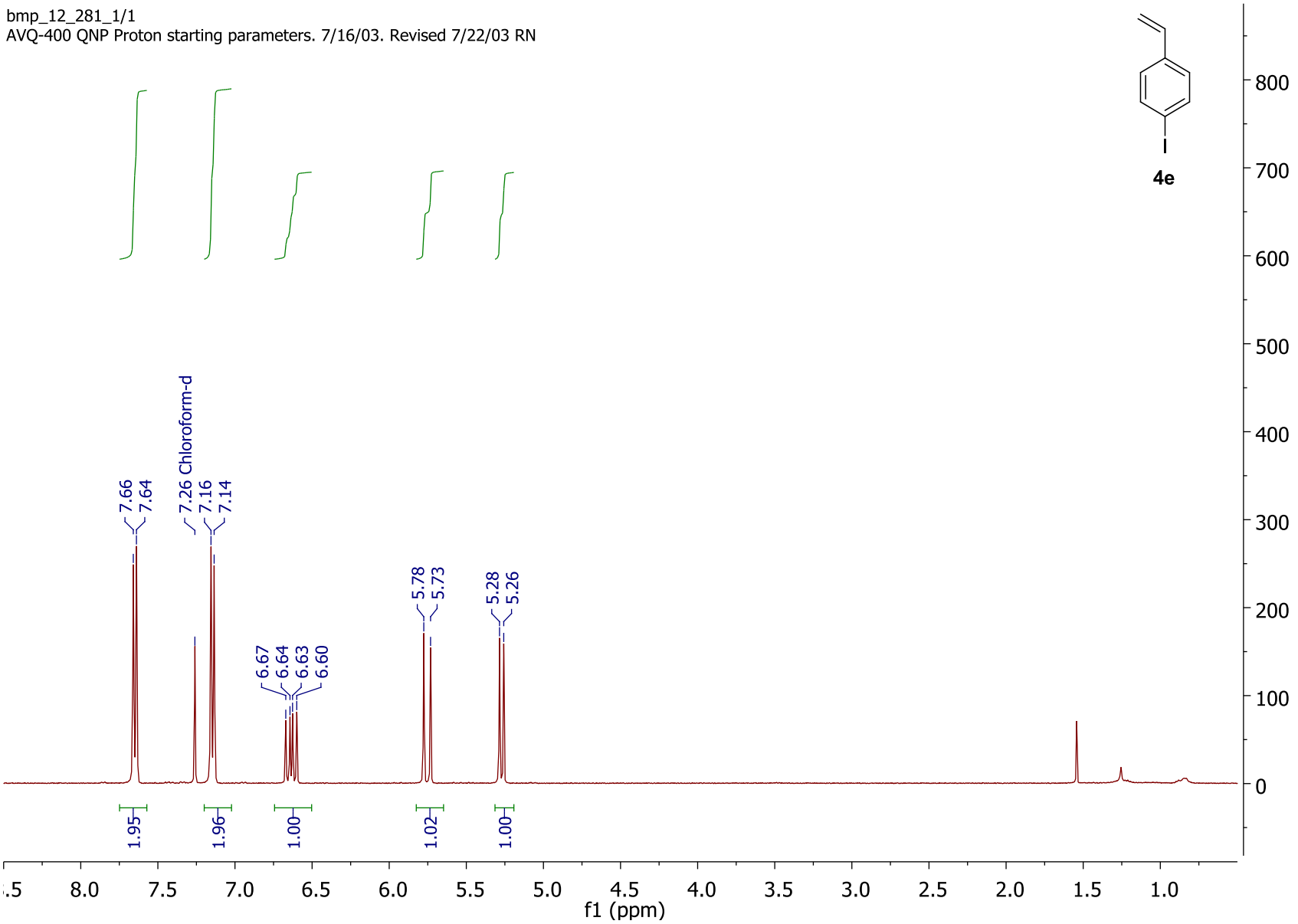

bmp_12_343_2/13
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN
I
H
N
3w
77.16 Chloroform-d
75.68
129.58
129.14
121.49
119.82
102.07
13.83
138.01
135.61
400
350
300
250
200
150
100
50
0
-50
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

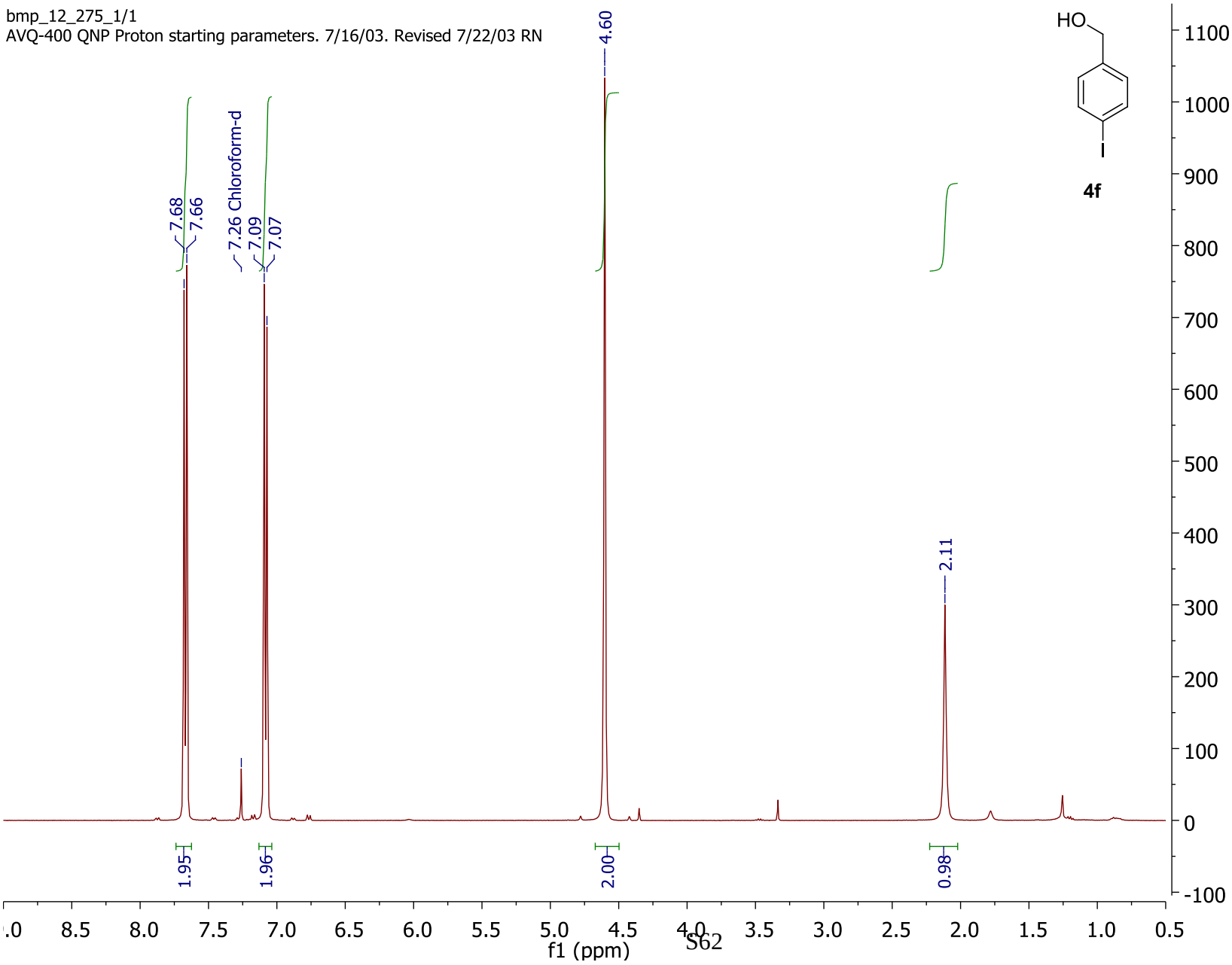

bmp_12_269_1/1
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
N
I
4b
9.14
8.94
8.01
7.99
7.91
7.89
7.82
7.81
7.80
7.78
7.78
7.69
7.67
7.65
7.26 Chloroform-d
1.00
0.99
0.99
1.01
1.02
1.01
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

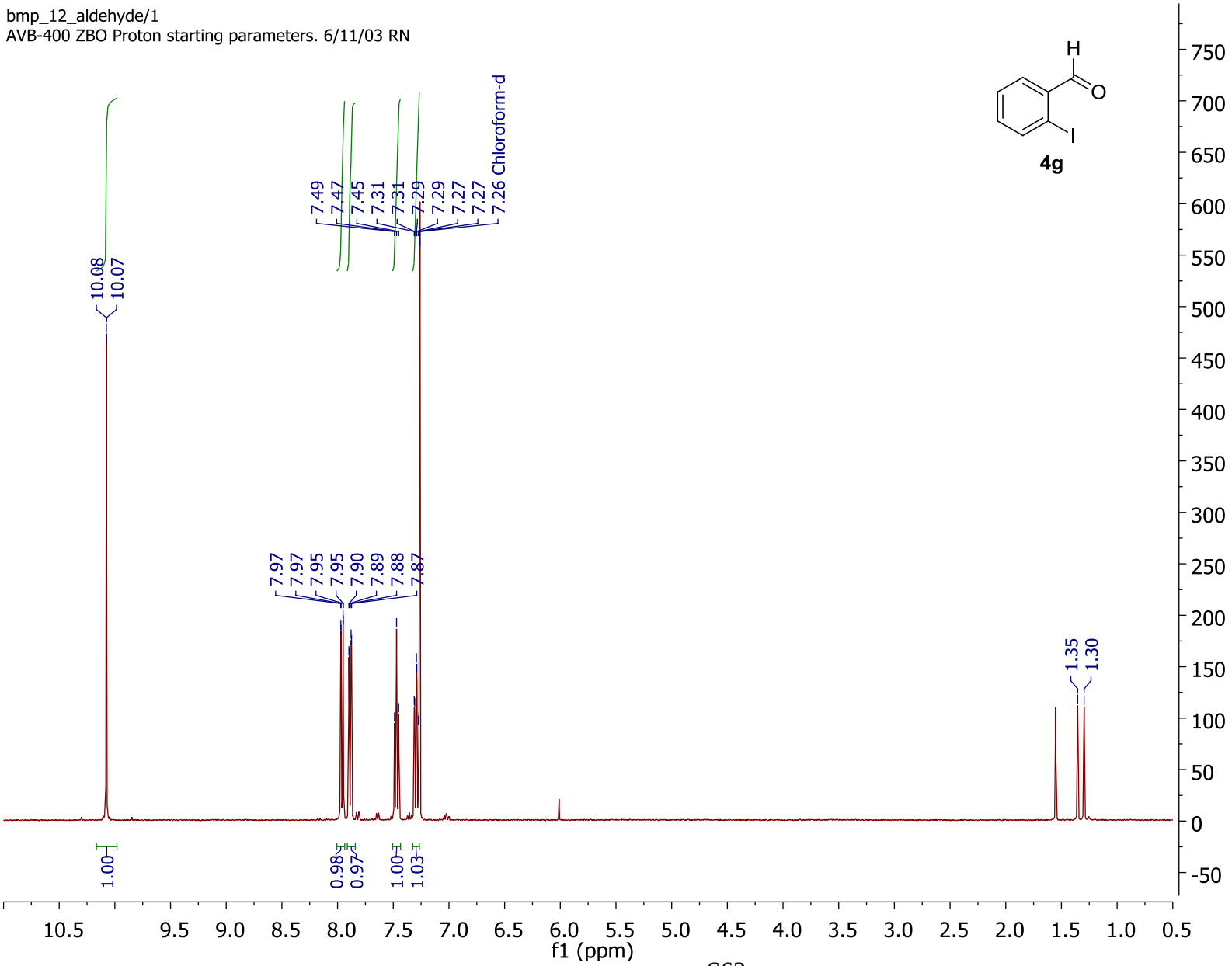

bmp_12_345_1/13
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
N
I
4b
77.16 Chloroform-d
152.65
151.02
137.11
132.00
130.74
129.74
128.36
128.19
96.92
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

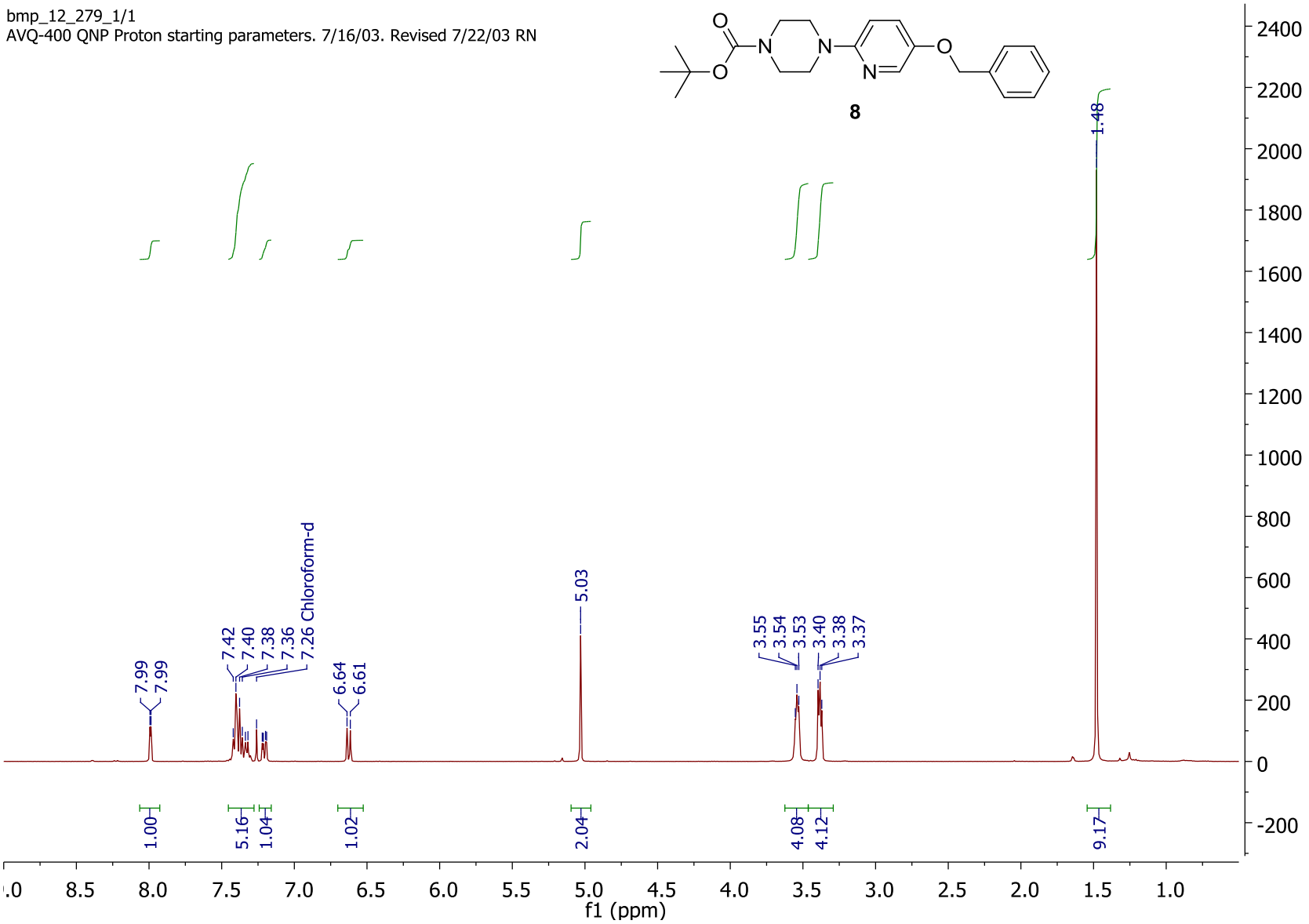

bmp_12_336_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
7.46
7.42
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.26 Chloroform
6.86
6.82
1.02
5.08
1.00
4c
f1 (ppm)

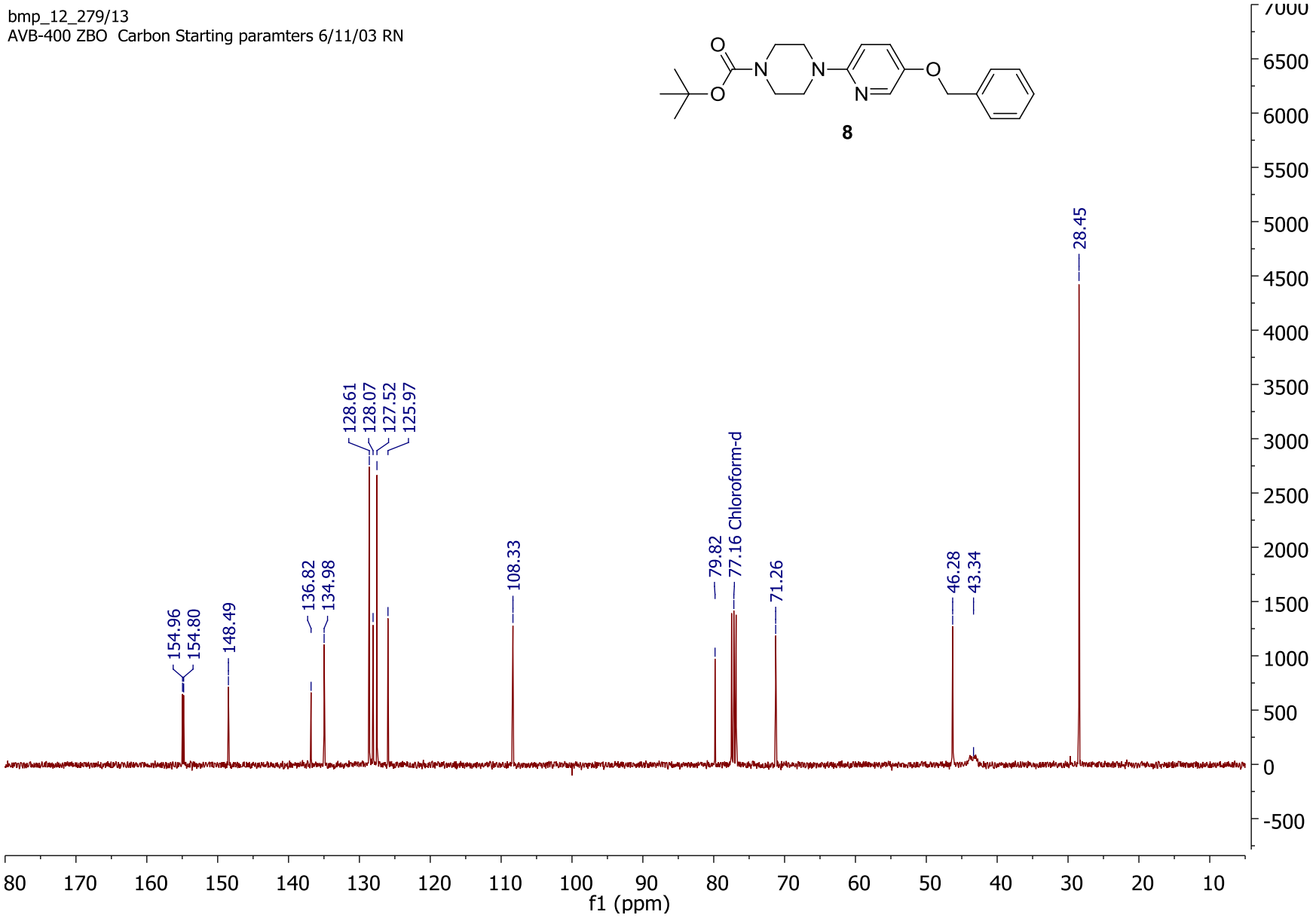

bmp_12_257_1/1
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
NO2
I
4d
7.32
7.30
7.28
7.26 Chloroform-d
8.58
8.22
8.22
8.22
8.20
8.20
8.20
8.04
8.02
0.99
1.03
1.02
1.06
f1 (ppm)

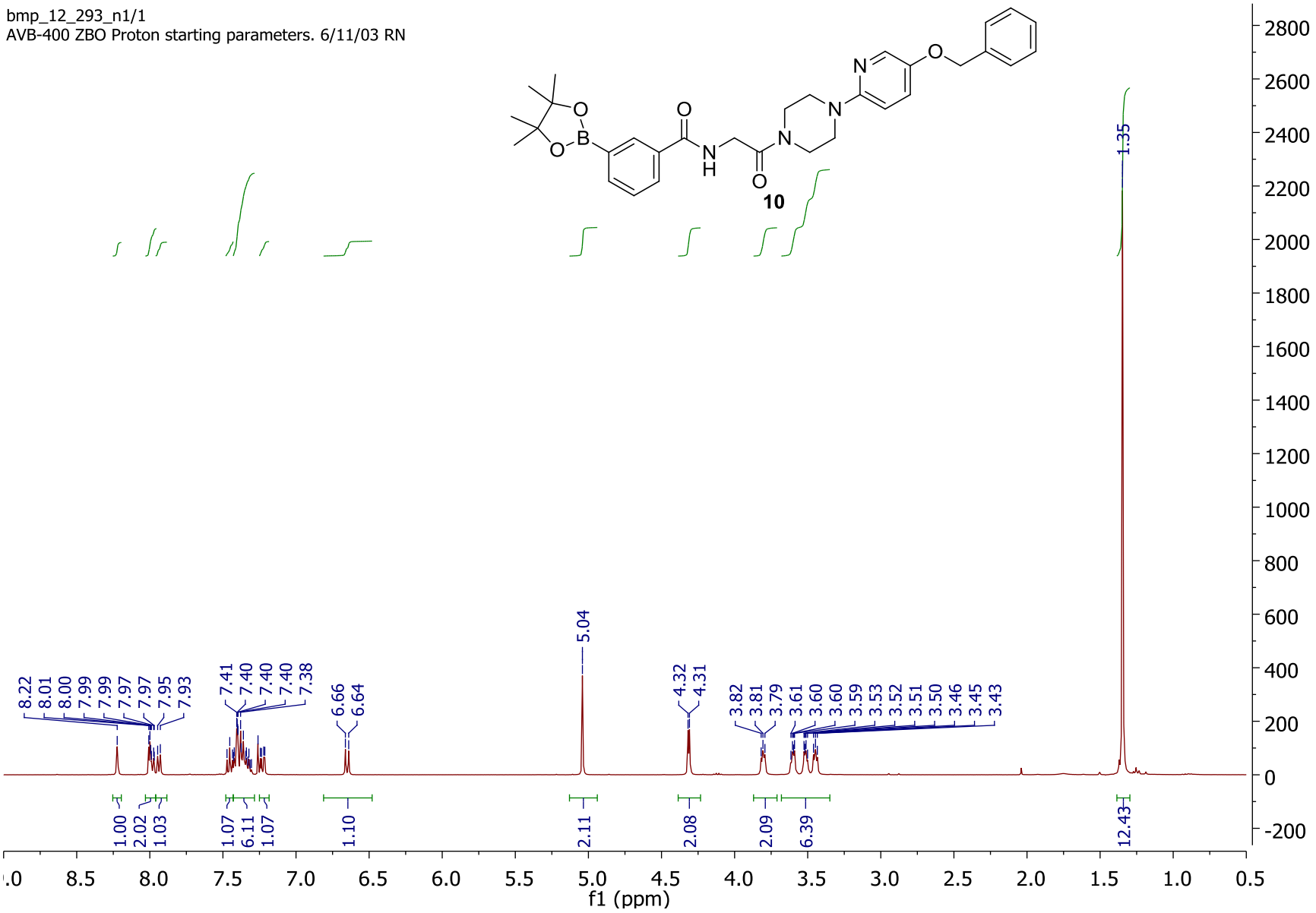

bmp_12_281_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
4e
7.66
7.64
7.26 Chloroform-d
7.16
7.14
6.67
6.64
6.63
6.60
5.78
5.73
5.28
5.26
1.95
1.96
1.00
1.02
1.00
f1 (ppm)

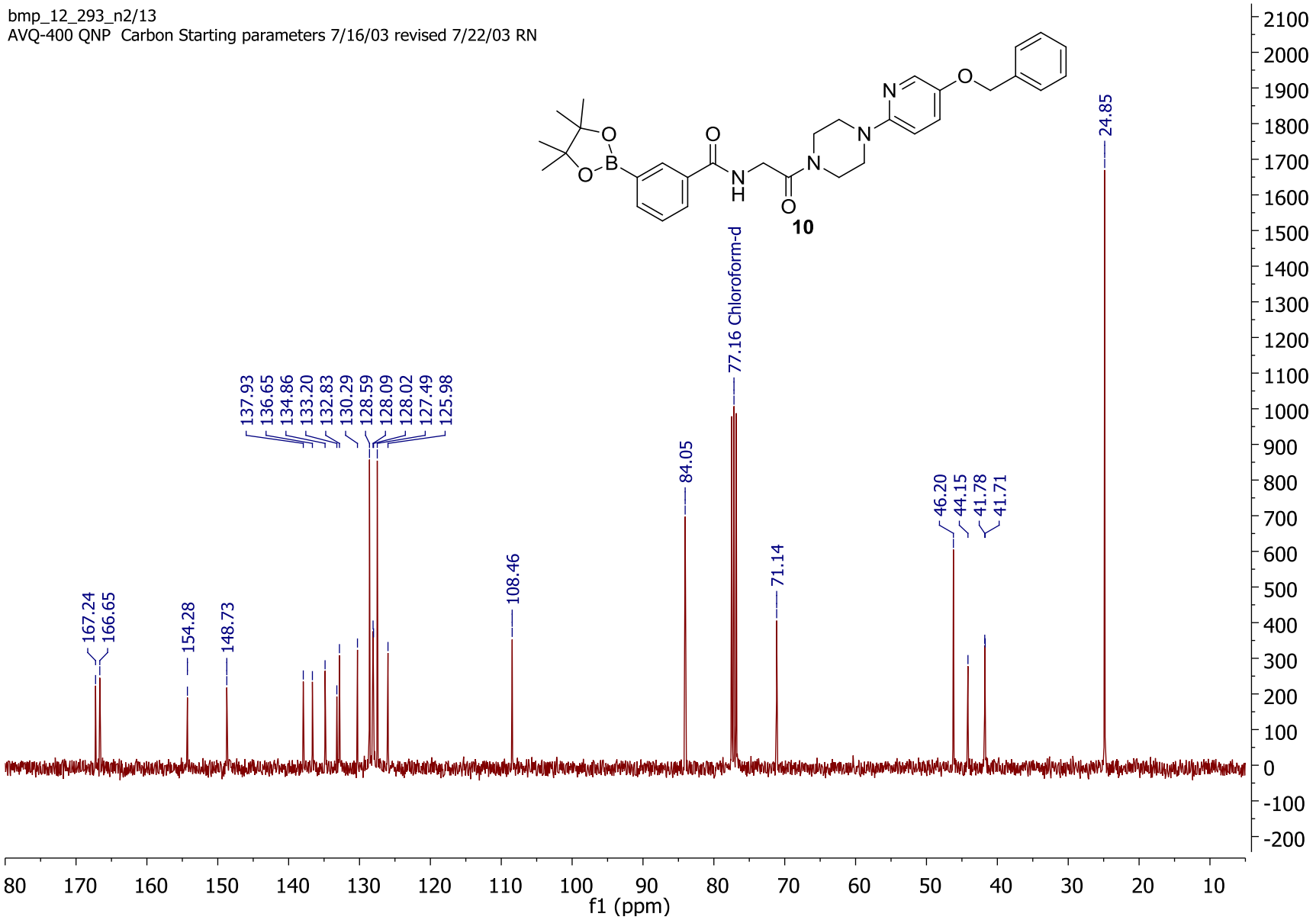

bmp_12_275_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
7.68
7.66
7.26 Chloroform-d
7.09
7.07
4.60
2.11
1.95
1.96
2.00
0.98
HO
I
4f
f1 (ppm)

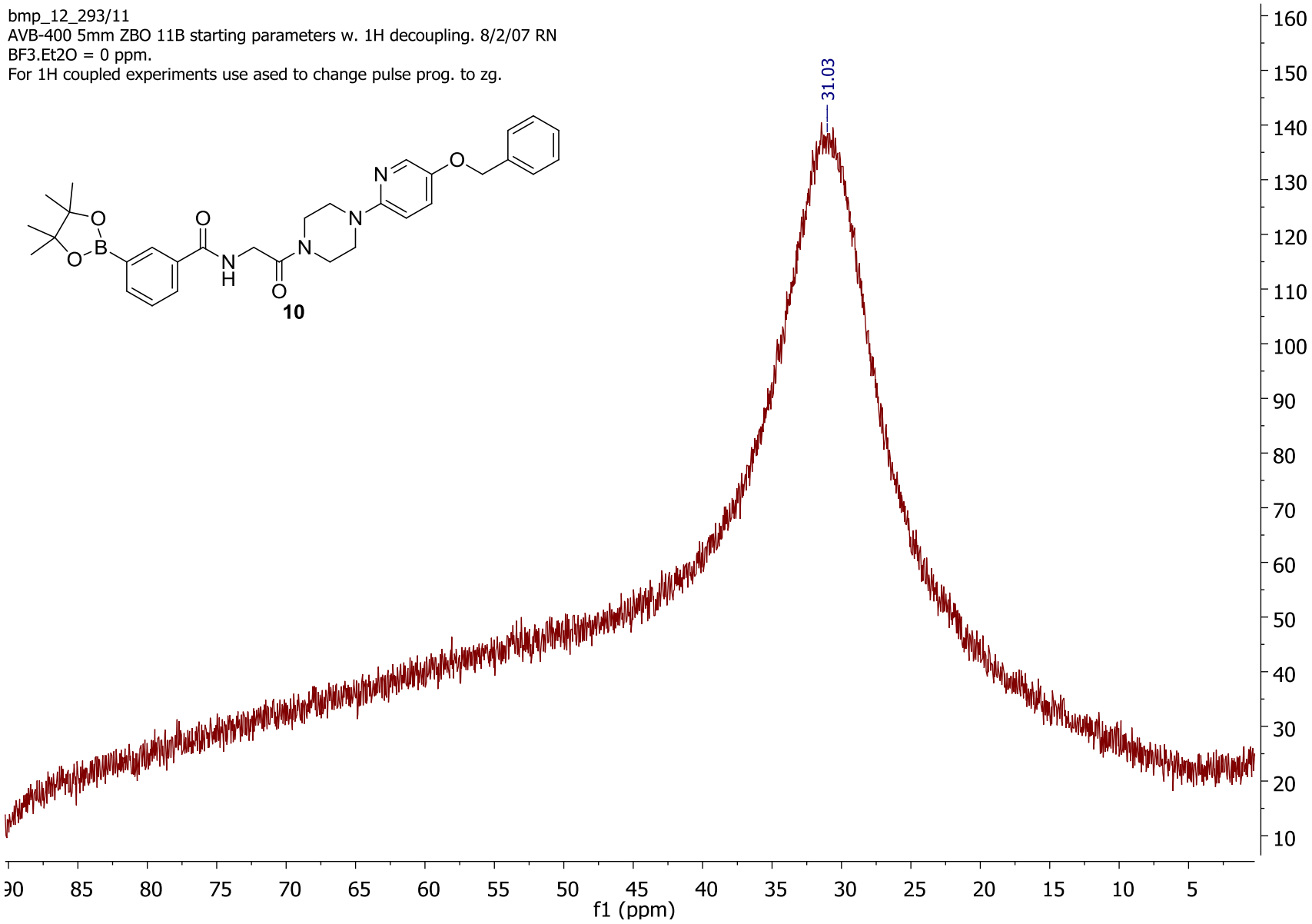

bmp_12_aldehyde/1
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
10.08
10.07
7.49
7.47
7.45
7.31
7.31
7.29
7.29
7.27
7.27
7.26 Chloroform-d
7.97
7.97
7.95
7.95
7.90
7.89
7.88
7.87
1.35
1.30
1.00
0.98
0.97
1.00
1.03
f1 (ppm)
4g

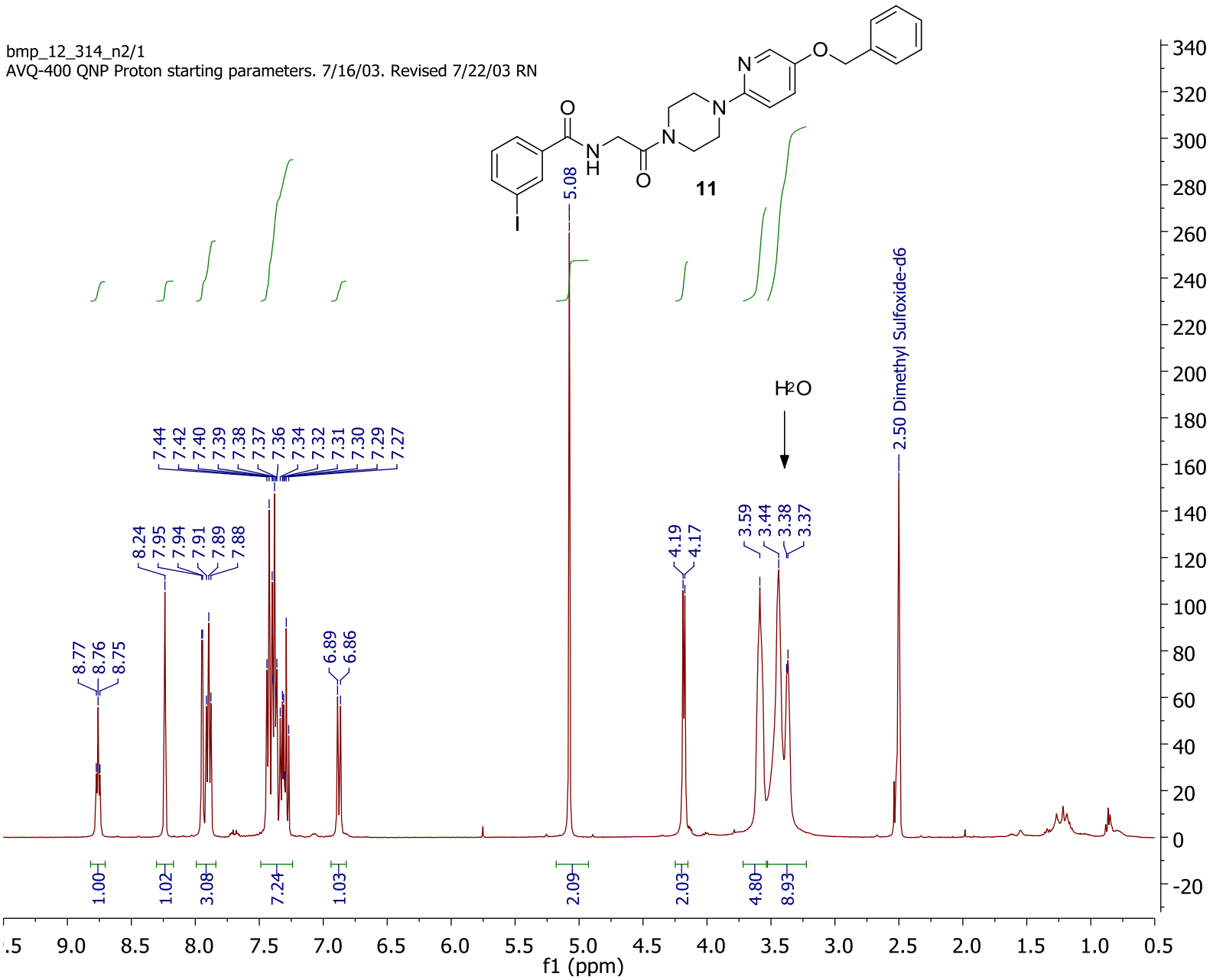

bmp_12_279_1/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
8
7.99
7.99
7.42
7.40
7.38
7.36
7.26 Chloroform-d
6.64
6.61
5.03
3.55
3.54
3.53
3.40
3.38
3.37
1.48
1.00
5.16
1.04
1.02
2.04
4.08
4.12
9.17
f1 (ppm)

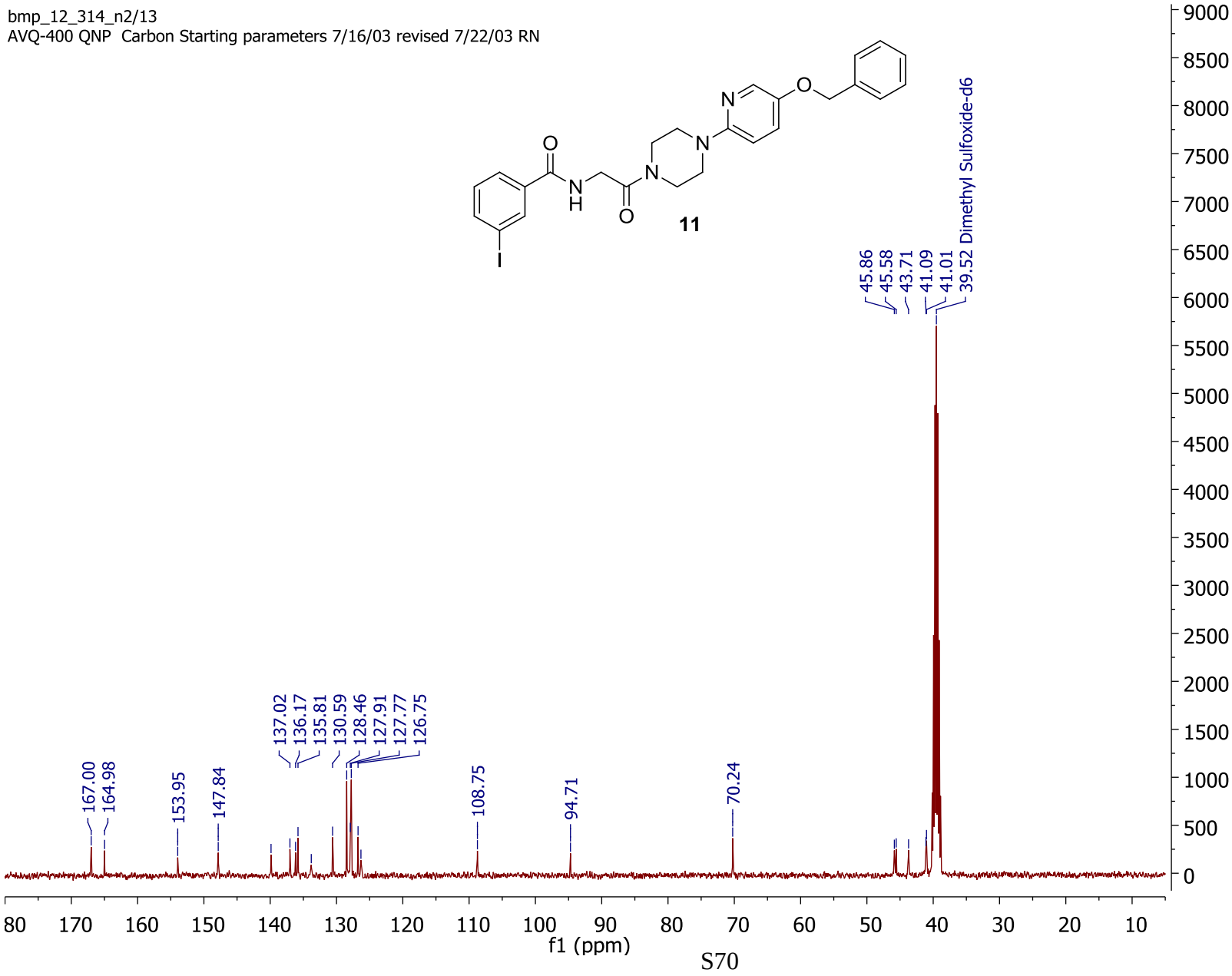

bmp_12_279/13
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN
8
154.96
154.80
148.49
136.82
134.98
128.61
128.07
127.52
125.97
108.33
79.82
77.16 Chloroform-d
71.26
46.28
43.34
28.45
f1 (ppm)


bmp_12_293_n1/1
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
10
8.22
8.01
8.00
7.99
7.99
7.97
7.97
7.95
7.93
7.41
7.40
7.40
7.40
7.38
6.66
6.64
5.04
4.32
4.31
3.82
3.81
3.79
3.61
3.60
3.60
3.59
3.53
3.52
3.51
3.50
3.46
3.45
3.43
1.35
1.00
2.02
1.03
1.07
6.11
1.07
1.10
2.11
2.08
2.09
6.39
12.43
f1 (ppm)


bmp_12_293_n2/13
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
10
167.24
166.65
154.28
148.73
137.93
136.65
134.86
133.20
132.83
130.29
128.59
128.09
128.02
127.49
125.98
108.46
84.05
77.16 Chloroform-d
71.14
46.20
44.15
41.78
41.71
24.85
f1 (ppm)


bmp_12_293/11
AVB-400 5mm ZBO 11B starting parameters w. 1H decoupling. 8/2/07 RN
BF3.Et2O = 0 ppm.
For 1H coupled experiments use ased to change pulse prog. to zg.
10
31.03
f1 (ppm)


bmp_12_314_n2/1
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
11
5.08
H2O
2.50 Dimethyl Sulfoxide-d6
8.77
8.76
8.75
8.24
7.95
7.94
7.91
7.89
7.88
7.44
7.42
7.40
7.39
7.38
7.37
7.36
7.34
7.32
7.31
7.30
7.29
7.27
6.89
6.86
4.19
4.17
3.59
3.44
3.38
3.37
1.00
1.02
3.08
7.24
1.03
2.09
2.03
4.80
8.93
f1 (ppm)


bmp_12_314_n2/13
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
11
167.00
164.98
153.95
147.84
137.02
136.17
135.81
130.59
128.46
127.91
127.77
126.75
108.75
94.71
70.24
45.86
45.58
43.71
41.09
41.01
39.52 Dimethyl Sulfoxide-d6
f1 (ppm)