Urethanes Synthesis from oxamic acids under Electrochemical Conditions

Ikechukwu Martin Ogbu,[a] Jonathan Lusseau,[a] Gülbin Kurtay,[a] Frédéric Robert,[a] and Yannick Landais*[a]

[a.] *University of Bordeaux, Institute of Molecular sciences (ISM), UMR-CNRS 5255, 351, Cours de la Libération, 33405 Talence Cedex, France.*

Email: yannick.landais@u-bordeaux.fr

Supporting Information

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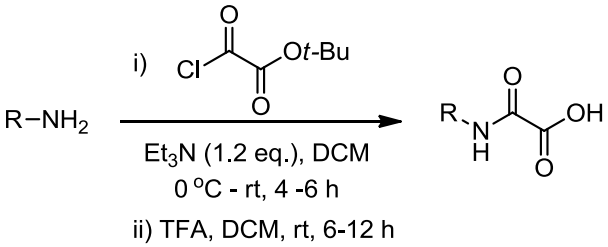
1. General Information

Solvents/reagents such as triethylamine (Et_3N), dichloroethane (DCE), acetonitrile (MeCN), ethanol (EtOH), isopropanol, isobutanol were distilled using calcium hydride. Other alcohols of higher boiling point (> 100°C) were distilled under reduced pressure. MeOH, Et_2O, CH_2Cl_2 (DCM) and THF were dried over activated alumina columns on MBraun Solvent Purification System (SPS-800). All other reagent-grade chemicals procured from commercial suppliers were used directly without further purification unless otherwise indicated. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous material unless otherwise stated.

^{1}H-NMR and ^{13}C-NMR were done using the following spectrometers: Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), using $CDCl_3$ as an internal reference. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively unless otherwise indicated. For the multiplicity: broad singlet = bs, singlet = s, doublet = d, triplet = t, quartet = q, doublet of doublets = dd and multiplets = m. FTIR analysis was performed using a Perkin-Elmer Spectrum 100 using a KBr disc or pellet. High-resolution mass spectra (HRMS) analysis was done using a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mode. High-performance liquid chromatography (HPLC) was done with a Thermo Scientific Dionex Ultimate 3000 with a column Lux 5µm Cellulose-3, 250x4.6 mm, using a mixture of water: acetonitrile: trifluoroacetic acid (22:45:0.1) as eluent. Optical rotations were recorded on a Rudolph Research Analytical Autopol III Automatic Polarimeter. Melting points (m.p.) were done using Stuart melting point apparatus. Thin layer chromatography (TLC) was done using silica gel 60 F254 pre-coated plates (Merck) and visualized with ultraviolet light, potassium permanganate or ceric ammonium molybdate. Flash chromatography was done using silica gel (0.043-0.063 mm).

2. General procedure for Preparation of Oxamic Acid

Method A[1, 2]:



Scheme S1: preparation of oxamic acid

Amine (10 mmol) and triethylamine (1.2 eq.) were added to a two-neck round-bottom flask containing dry CH_2Cl_2 (0.3 M) under argon atm. The solution was cooled to 0°C using ice bath. *t*-Butyl-2-chloro-2-oxo acetate (1.2 eq.) was added drop wise for about 10 min. The solution was then warmed to room temperature and stirred for 4 – 6 h. Note: for solid amine, the amine was added into the flask first, flushed with argon before CH_2Cl_2 and triethylamine were added. The reaction mixture was then washed successively with 1M HCl (20 mL), the aqueous layer was further extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine and dried using anhydrous Na_2SO_4 and concentrated in vacuo. The ester obtained (light brown gel) was then dissolved in DCM (0.3 M), TFA (5.0 eq.) was added and the solution was stirred at room temperature for 6 to 12 h. TLC was used to monitor the completion of the reaction. The solution was concentrated at reduced pressure using rotary evaporator to obtain oxamic acid as a white solid product.

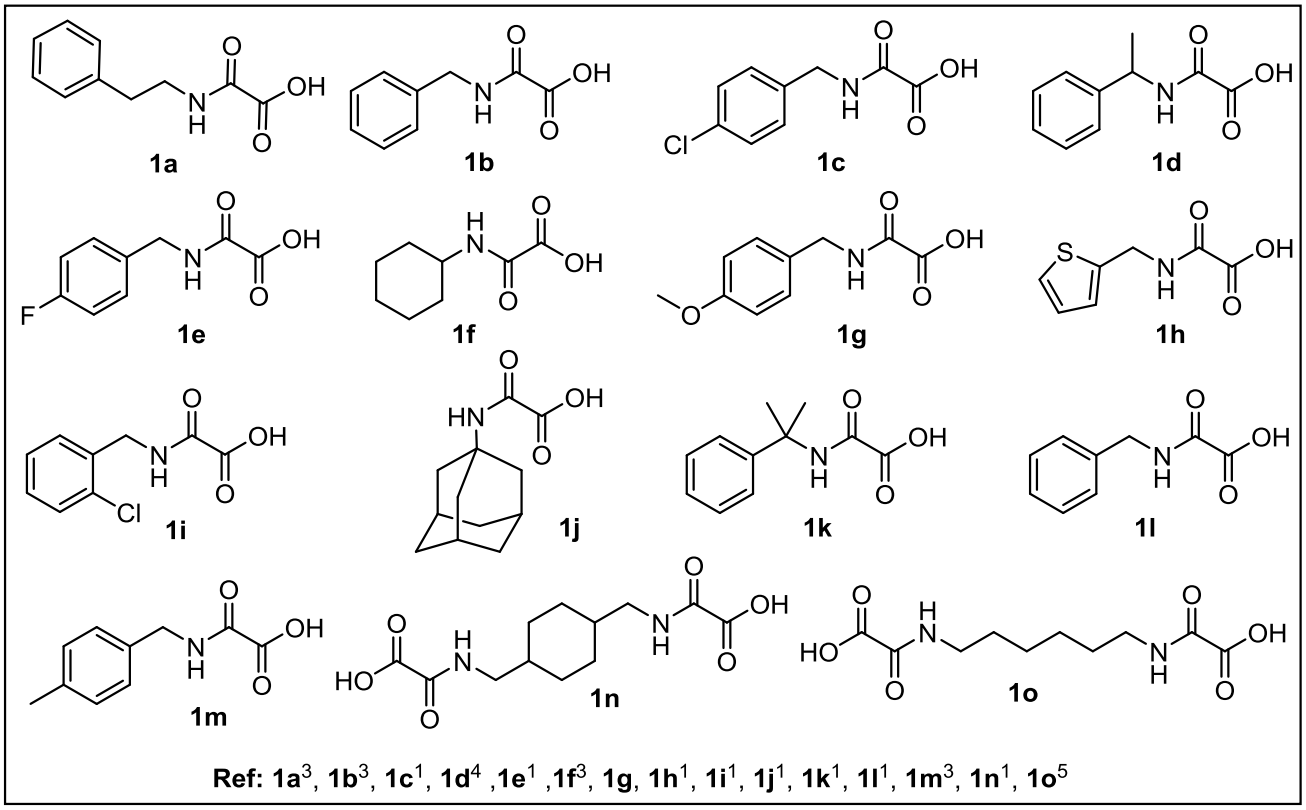
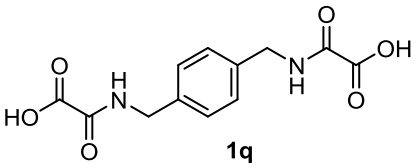


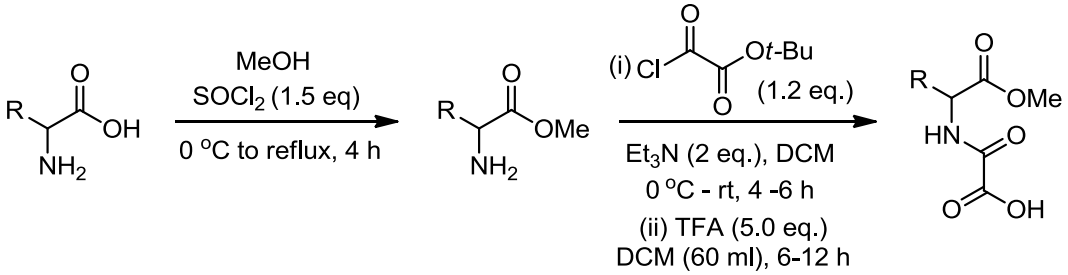
Figure S1: Oxamic acid substrates previously reported[1-5]

2,2'-((1,4-Phenylenebis(methylene))bis(azanediyl))bis(2-oxoacetic acid) (1q)



Following the general procedure 2A, using 7.3 mmol of the corresponding diamine, oxamic acid **1q** (2.29 g, 90 %) was obtained as a white solid, m.p. = 204 – 205°C. ^{1}H NMR (300 MHz, MeOD) δ 7.28 (s, 4H), 4.44 (s, J = 8.9 Hz, 4H). ^{13}C NMR (76 MHz, MeOD) δ 161.4, 158.9, 137.0, 127.5, 42.6. IR (neat) υmax (cm-^{1}) = 3347, 3168, 1757, 1677, 1554. HRMS (ESI): Calcd. For $C_{12}H_{11}O_6N_2$ $[M-H]^+$ 279.0622, found 279.0620.

Method B[2, 6]



Scheme S2: preparation of amino acid derived oxamic acid

To a dry two-neck round-bottom flask equipped with a reflux condenser, the corresponding amino acid (30.07 mmol) was added. Methanol (25 mL) was added under nitrogen. The heterogeneous mixture was cooled to 0°C using ice bath. Thionyl chloride (45.11 mmol) was added dropwise over 15 min under

constant stirring, resulting in a homogeneous solution. The mixture was warmed to room temperature and then heated to reflux for 4 h. The resulted solution was concentrated in vacuo to afford a colorless oil. Hexane was added to this crude oily product and was stirred for 10 min. The hexane was decanted, and this procedure was repeated twice to afford a solid compound. The solid product was dissolved in DCM (60 mL) at 0°C and under nitrogen, triethylamine (60.15 mmol) was added into the mixture followed by addition of t-butyl-2-chloro-2-oxo acetate (36.08 mmol) dropwise over 10 min. The solution was then allowed to stir at room temperature for 4–6 h. The reaction mixture was then washed successively with water (100 mL), and brine (100 mL), dried over sodium sulfate and concentrated under reduced pressure resulting in a crude solid product. The crude product was dissolved in DCM (60 mL), TFA (150 mmol) was added and the mixture was stirred at room temperature 6 h and then concentrated under reduced pressure to afford the desired product as a light brown oily substance.

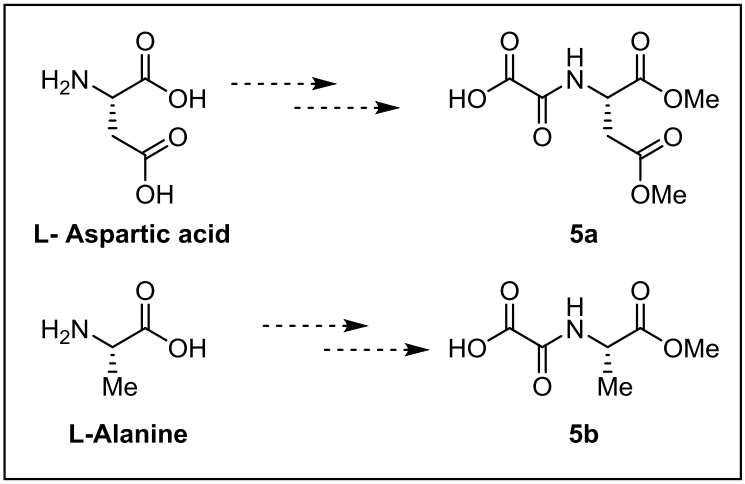
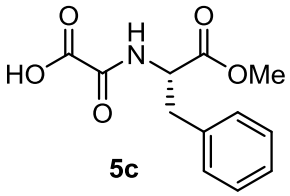


Figure S2: Amino acid derived oxamic acid substrates previously reported[2]

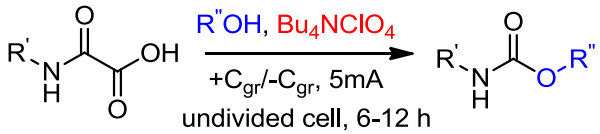
(*S*)-2-((1-Methoxy-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoacetic acid (5c)



Following the general procedure 2B, using 12 mmol of corresponding amino acid, the corresponding oxamic acid **5c** (1.22 g, 80 %) was obtained as a light brown gel which later solidified, m.p. = 101 – 102°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.44 – 7.20 (m, 3H), 7.13 (dd, J = 7.5, 1.7 Hz, 2H), 4.98 – 4.72 (m, 1H), 3.79 (s, 3H), 3.21 (m, J = 14.0, 6.1 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 170.2, 158.9, 156.9, 134.7, 129.1, 128.9, 127.6, 54.3, 52.8, 37.8. IR (neat) υmax (cm^{-1}) = 3327, 3023, 2943, 1742, 1692, 1535. HRMS (ESI): Calcd. For $C_{12}H_{13}O_5N$ [M+Na]+ 274.0685, found 274.0679. $[\alpha]_D^{25}$ +43.04 (c 0.5, $CHCl_3$).

3. General Procedure for Electrochemical Synthesis of Urethane

Method A:



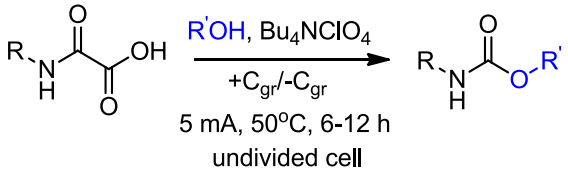
ElectraSyn vial (5 mL) equipped with a stir bar was charged with oxamic acid (0.5 mmol, 1.0 eq.) and Bu_4NClO_4 (0.01 M). The vial was covered with the cap bearing graphite electrodes as both cathode and anode. The orifice on the vial cap was sealed with a septum and the vial was flushed with argon for 10 min through the septum, Figure S3(a). Dry alcohol (3 mL) was added into the vial under argon using a plastic syringe and metal needle. The vial was fitted on the ElectraSyn machine and pre-stirred for 15 minutes. The reaction mixture was electrolyzed at a constant current of 5 mA for 6-12 h under argon. The reaction was monitored with TLC. Thereafter, the reaction mixture was transferred to a round-bottom flask, the vial and electrodes were rinsed with DCM (3 x 3 mL). The combined solution was concentrated under reduced pressure and the resulted crude reaction mixture was purified by column chromatography (AcOEt/petroleum ether).

Note 1: Using MeOH as solvent, the reaction can progress without supporting electrolyte, however not all the oxamic acid can support 5 mA at the beginning of the reaction without supporting electrolyte. Therefore, supporting electrolyte may be added also with MeOH if needed.

Note 2: with methanol as solvent, Increase in temperature neither improved the product yield nor shortened reaction time. Effect of temperature appeared to be significant when more viscous alcohols are used. This could be due to improved viscosity/mobility and current conductivity under the mild heating condition.

Note 3: From the optimization table, it was shown that though the reaction can progress more rapidly at higher current density (60 mA) and complete within 2 to 5 h, the product yield is however higher when 5 mA was used. Also, these milder reaction conditions are more favourable for the reaction with other alcohols.

Method B. General Procedure for Electrochemical Synthesis of Urethane at 50°C



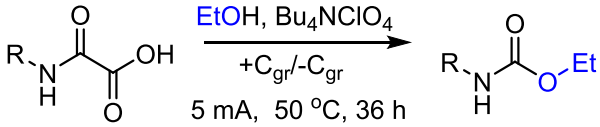
ElectraSyn vial (5 mL) equipped with a stir bar was charged with oxamic acid (0.5 mmol, 1.0 eq.) and Bu_4NClO_4 (0.03M). The vial was covered with the cap bearing graphite electrodes as both cathode and anode. The orifice on the vial cap was sealed with a septum and the vial was flushed with argon through the septum for 10 min. Dry alcohol (3 mL) was added into the vial under argon using a plastic syringe and metal needle. The vial was then clamped in an oil bath at 50°C. The cathode and anode of the vial were connected to the ElectraSyn machine using external flexible wire with alligator clips (4 mm), Figure S3(b). After pre-stirring for 15 minutes, the reaction mixture was electrolyzed at a constant current of 5 mA for 6-12 h under argon. The reaction was monitored with TLC. Thereafter, the reaction mixture was transferred to a round-bottom flask and the vial and the electrode were rinsed with DCM (3x3 mL). The combined solution was concentrated under reduced pressure and the resulted crude reaction mixture was purified by column chromatography (AcOEt/petroleum ether).

(a) Setup for reaction at room temperature

(b) Setup for reaction at 50°C

Figure S3: Set-up for Urethane Synthesis by Electrochemical Decarboxylation of Oxamic

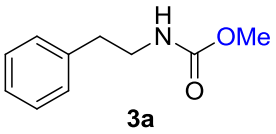
Method C. General Procedure for Electrochemical Synthesis of Urethane on gram-scale



ElectraSyn vial (10 mL) equipped with a stir bar was charged with oxamic acid (1.0 g, 5.18 mmol) and Bu_4NClO_4 (0.03M). The vial was covered with the cap bearing graphite cathode and anode. The orifice on the vial cap was sealed with a septum and the vial was flushed with argon through the septum for 15 min. Dry ethanol (10 mL) was added into the vial under argon using a plastic syringe with a metal needle. The vial was then clamped in an oil bath at 50°C. The cathode and anode of the vial were connected to the ElectraSyn machine using external flexible wire with alligator clips (4 mm), and after pre-stirring for 15 minutes, the reaction mixture was electrolyzed at a constant current of 5 mA for 36 h under argon. The reaction was monitored with TLC. Thereafter, the reaction mixture was transferred to round-bottom flask, the vial and the electrode were rinsed with DCM (3 x 10 mL). The combined solution was concentrated under reduced pressure and the resulted crude reaction mixture was purified by column chromatography (AcOEt/petroleum ether).

4. ^{1}H and ^{13}C NMR Data of Urethanes

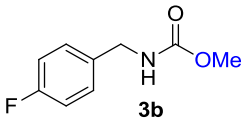
Methyl phenethyl carbamate (3a)



3a

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) was used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **3a** (65 mg, 72 %) as a colourless viscous liquid. Rf = 0.25 (EtOAc-petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.11 (m, 5H), 4.78 (s, 1H), 3.68 (s, 3H), 3.46 (dd, J = 13.1, 6.6 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.0, 138.8, 128.8, 128.6, 126.5, 52.0, 42.2, 36.2. IR (neat) υmax (cm^{-1}) = 3336, 3027, 2946, 1709, 1603, 1532. HRMS (ESI): Calcd. For $C_{10}H_{14}O_2N$ $[M+H]^+$ 180.1019, found 180.1010.

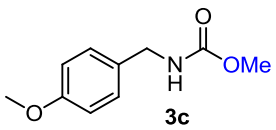
Methyl 4-fluorobenzylcarbamate (3b)



3b

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) was used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **3b** (71.4 mg, 78 %) as a white solid, m.p. = 68 – 70ºC, Rf = 0.25 (EtOAc- petroleum ether, 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.12 (m, 2H), 7.01 (t, J = 8.7 Hz, 2H), 5.04 (s, 1H), 4.32 (d, J = 6.0 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $^{1}J_{CF}$ = 245.6 Hz), 157.1, 134.4, 129.2 (d, $^{3}J_{CF}$ = 7.3 Hz), 115.5 (d, $^{2}J_{CF}$ = 21.5 Hz), 52.3, 44.4. IR (neat) υmax (cm^{-1}) = 3318, 3000, 2879, 1688, 1600, 1548. HRMS (ESI): Calcd. For $C_9H_{11}O_2NF$ $[M+H]^+$ 184.0768, found 184.0760.

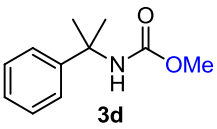
Methyl 4-methoxybenzylcarbamate (3c)



3c

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) was used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **3c** (79 mg, 76 %) as a light golden gel. Rf = 0.15 (EtOAc-petroleum ether, 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.18 (m, 1H), 6.95 – 6.75 (m, 3H), 5.09 (s, 1H), 4.36 (d, *J* = 5.9 Hz, 2H), 3.82 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 157.10, 140.2, 129.7, 112.9, 55.2, 52.2, 45.1. IR (neat) υmax (cm-^{1}) = 3340, 3008, 2943, 2831, 1705. HRMS (ESI): Calcd. For $C_{10}H_{13}O_3N$ $[M+Na]^+$ 218.0787, found 218.0788.

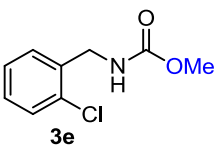
Methyl (2-phenylpropan-2-yl) carbamate (3d)



3d

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) was used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **3d** (51 mg, 53 %) as a colourless viscous liquid, Rf = 0.35 (EtOAc/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.11 (m, 5H), 5.17 (s, 1H), 3.62 (s, 3H), 1.69 (s, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.7, 141.3, 126.9, 125.7, 125.1, 52.3, 39.9. IR (neat) υmax (cm^{-1}) = 3340, 3056, 2958, 2926, 1713. HRMS (ESI): Calcd. For $C_{11}H_{15}O_2N$ $[M+Na]^+$ 216.0995, found 216.0993.

Methyl 2-chlorobenzyl carbamate (3e)

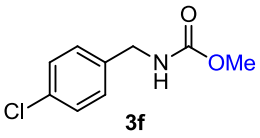


3e

Following the general procedure 3.A, the corresponding oxamic acid (0.3 mmol) was used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **3e** (42.5 mg, 71 %) as a colourless liquid that solidified into a white solid afterwards, m.p. = 61 – 63ºC. Rf = 0.29 (EtOAc- petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.15 (m, 4H), 5.06 (s, 1H), 4.35 (d, J = 6.1 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (76

MHz, $CDCl_3$) δ 157.0, 135.9, 133.5, 129.5, 128.9, 127.0, 52.3, 43.0. IR (neat) υmax (cm^{-1}) = 3329, 3080, 2951, 1707, 1529. HRMS (ESI): Calcd. For $C_9H_{10}O_2N^{35}Cl$ $[M+Na]^+$ 222.0292, found 222.0292.

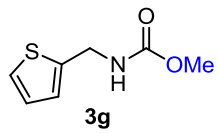
Methyl 4-chlorobenzylcarbamate (3f)



3f

Following the general procedure 3.A, the corresponding oxamic acid (0.4 mmol) was used. Purification by column chromatography (silica, cyclohexane/ethyl acetate 85/15) afforded **3f** (54 mg, 68 %) as white solid, m.p. = 83 – 86ºC. Rf = 0.36 (EtOAc-petroleum ether 20/80). ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.08 (m, 4H), 5.06 (s, 1H), 4.35 (d, J = 6.2 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.1, 137.1, 133.3, 128.8, 52.3, 44.4. IR (neat) υmax (cm^{-1}) = 3312, 2995, 1689, 1545. HRMS (ESI): Calcd. For $C_9H_9O_2N^{35}Cl$ $[M-H]^+$ 198.0327, found 198.0326.

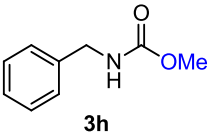
Methyl (thiophen-2-ylmethyl) carbamate (3g)



3g

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.01M) were used. Purification by column chromatography (silica, cyclohexane/ethyl acetate 85/15) afforded **3g** (45 mg, 41 %) as a light brown gel. Rf = 0.23 (AcOEt/petroleum ether, 20/80). ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 1H), 7.00 – 6.93 (m, 2H), 5.20 (s, 1H), 4.54 (d, J = 5.8 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.7, 141.3, 126.8, 125.7, 125.1, 52.3, 39.9. IR (neat) υmax (cm^{-1}) = 3327, 3064, 2952, 1703, 1529. HRMS (ESI): Calcd. For $C_7H_9O_2NS$ $[M+Na]^+$ 194.0246, found 194.0246.

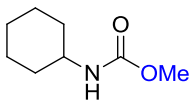
Methyl benzyl carbamate (3h)



3h

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) was used. Purification by column chromatography (silica, 100% DCM) afforded **3h** (63 mg, 76 %) as a white solid, m.p. = 50 – 52ºC. Rf = 0.34 (DCM). ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 –7.25 (m, 5H), 5.06 (s, 1H), 4.39 (d, J = 5.9 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.1, 138.5, 128.7, 127.5, 52.2, 45.1. IR (neat) υmax (cm^{-1}) = 3331, 3030, 2950, 1705, 1530. Spectroscopic data were in good agreement with literature[t]. HRMS (ESI): Calcd. For $C_9H_{11}O_2N$ $[M+Na]^+$ 188.0682, found 188.0681.

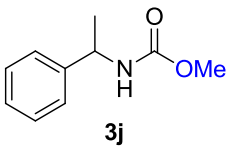
Methyl cyclohexyl carbamate (3i)



3i

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) was used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **3i** (57 mg, 73 %) as a white crystalline solid, m.p. = 75ºC. Rf = 0.41 (AcOEt/petroleum ether, 20/80). ^1H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 1H), 3.64 (s, 3H), 3.45 (s, 1H), 2.02 – 1.78 (m, 2H), 1.76 – 1.48 (m, 3H), 1.48 – 1.23 (m, 2H), 1.22 – 1.03 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 51.7, 49.8, 33.4, 25.5, 24.8. IR (neat) υmax (cm^{-1}) = 3344, 2941, 2841, 1691, 1536. HRMS (ESI): Calcd. For $C_8H_{16}O_2N$ $[M+H]^+$ 158.1175, found 158.1175.

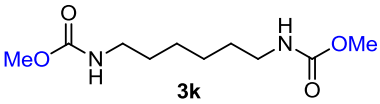
Methyl (1-phenylethyl)carbamate (3j)



3j

Following the general procedure 3.A, the corresponding oxamic acid (1.0 mmol) used. Purification by column chromatography (silica, 100% DCM) afforded **3j** (125 mg, 70 %) as a white solid, m.p. = 59°C. Rf = 0.25 (AcOEt/petroleum ether, 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5H), 5.04 (s, 1H), 4.79 (s, 1H), 3.59 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 143.7, 128.6, 127.3, 125.9, 52.1, 50.7, 22.4. IR (neat) υmax (cm-^{1}) = 3318, 3038, 2982, 1703, 1530. HRMS (ESI): Calcd. For $C_{10}H_{13}O_2N$ $[M+Na]^+$ 202.0836, found 202.0838.

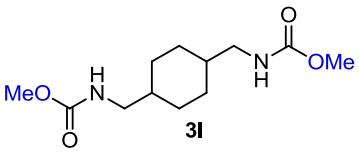
Dimethyl hexane-1,6-diyldicarbamate (3k)



3k

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.01M) were used. Purification by column chromatography (silica, DCM/MeOH 98/2) afforded **3k** (56 mg, 50 %) as a white solid, m.p. = 117 – 119°C. Rf = 0.37 (MeOH- DCM, 4/96). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (s, 2H), 3.66 (s, 6H), 3.26 – 2.93 (m, 4H), 1.63 – 1.41 (m, 4H), 1.39 – 1.22 (m, 4H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.1, 52.0, 40.8, 29.9, 26.2. IR (neat) υmax (cm^{-1}) = 3337, 2942, 2855, 1689, 1535. HRMS (ESI): Calcd. For $C_{10}H_{21}O_4N_2$ $[M+H]^+$ 233.1495, found 233.1493.

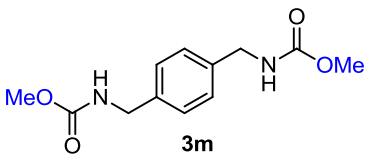
Dimethyl (cyclohexane-1,4-diylbis(methylene))dicarbamate (3l)



3l

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.01M) were used. Purification by column chromatography (silica, DCE/MeOH 98/2) afforded **3l** (70 mg, 54 %) as white solid, m.p. = 119-123°C. Rf = 0.36 (MeOH- CH_2Cl_2 4/96). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (s, 2H), 3.66 (s, 6H), 3.08 (dt, J = 27.2, 6.6 Hz, 4H), 1.87 – 1.57 (m, 3H), 1.57 – 1.28 (m, 5H), 1.02 – 0.83 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.2, 52.0, 47.1, 44.6, 38.3, 35.8, 29.9, 26.1. IR (neat) υmax (cm^{-1}) = 3330, 2923, 2854, 1704, 1539. HRMS (ESI): Calcd. For $C_{12}H_{22}O_4N_2$ $[M+Na]^+$ 281.1471, found 281.1468.

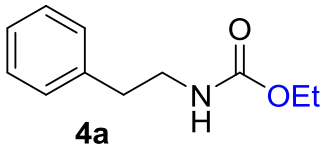
Dimethyl (1,4-phenylenebis(methylene)) dicarbamate (3m)



3m

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.01M) were used. Purification by column chromatography (silica, DCM/MeOH 98/2) afforded **3m** (80 mg, 64 %) as a white solid, m.p. = 190 – 193°C. Rf = 0.14 MeOH-DCM, 4/96) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (s, 4H), 5.03 (s, 2H), 4.36 (d, J = 6.0 Hz, 4H), 3.72 (s, 6H). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28, 7.27, 5.03, 4.37, 4.35, 3.72. ^{13}C NMR (101 MHz, DMSO) δ 157.3, 138.8, 127.5, 51.8, 44.1, 43.9. IR (neat) υmax (cm^{-1}) = 3313, 3047, 2939, 1688, 1535. HRMS (ESI): Calcd. For $C_{12}H_{16}O_4N_2$ $[M+Na]^+$ 275.1001, found 275.0997.

Ethyl phenethylcarbamate (**4a**)

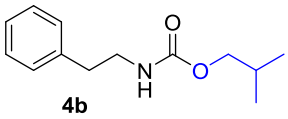


4a

Following the general procedure 3.A, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.03M) were used. Purification by column chromatography (silica, 100% DCM) afforded **4a** (59 mg, 62 %) as a colourless gel; Rf = 0.40 (EtOAc-Hexane 10/90). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* ppm 7.40 – 7.16 (m, 5H), 4.69 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.46 (q, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 156.6, 138.8, 130.0,

128.8, 128.7, 128.6, 126.5, 60.7, 42.1, 36.2, 14.6. IR (neat) υmax (cm^{-1}) = 3334, 2980, 2934, 1702, 1533. Spectroscopic data were in good agreement with literature[1].

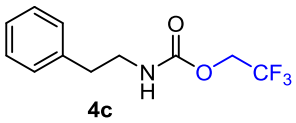
Isobutyl phenethyl carbamate (4b)



4b

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.03M) were used. Purification by column chromatography (silica, 100% DCM) afforded **4b** (71 mg, 64 %) as a light brown viscous liquid. Rf = 0.35 (AcOEt/petroleum ether, 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.17 (m, 5H), 4.70 (s, 1H), 3.86 (d, J = 6.6 Hz, 2H), 3.46 (dd, J = 13.1, 6.6 Hz, 2H), 2.84 (t, J = 7.0 Hz, 2H), 1.91 (dt, J = 13.0, 6.5 Hz, 1H), 0.94 (d, J = 6.6 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.7, 138.8, 128.8, 128.6, 126.5, 71.0, 42.1, 36.2, 28.0, 19.0. IR (neat) υmax (cm-^{1}) = 3331, 3021, 2965, 2866, 1703, 1529. HRMS (ESI): Calcd. For $C_{13}H_{19}O_2N$ $[M+Na]^+$ 244.1308, found 244.1308.

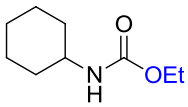
2,2,2-Trifluoroethyl phenethylcarbamate (4c)



4c

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **4c** (61 mg, 50 %) as a colourless liquid. Rf = 0.6 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.05 (m, 5H), 4.93 (s, 1H), 4.47 (q, J = 8.5 Hz, 2H), 3.51 (dd, J = 13.1, 6.8 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 138.4, 123.3 (q, $^1J_{CF}$ = 277.5 Hz), 60.9 (q, $^2J_{CF}$ = 36.4 Hz), 42.6, 36.0. IR (neat) υmax (cm^{-1}) = 3345, 3064, 3030, 2945, 1730, 1604, 1604, 1526. HRMS (ESI): Calcd. For $C_{11}H_{12}O_2NF_3$ $[M+Na]^+$ 270.0712, found 270.0708. Spectroscopic data were in good agreement with literature[1].

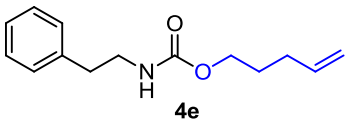
Ethyl cyclohexylcarbamate (4d)



4d

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.03M) were used. Purification by column chromatography (silica, 100% DCM) afforded **4d** (54 mg, 63 %) as a white crystalline solid, mp = 59ºC. Rf = 0.40 (AcOEt/petroleum ether, 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.52 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.49 (s, 1H), 2.04 – 1.86 (m, 2H), 1.80 – 1.55 (m, 3H), 1.46 – 1.03 (m, 8H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.8, 60.4, 49.7, 33.4, 25.5, 24.8, 14.6. IR (neat) υmax (cm-^{1}) = 3314, 2978, 2922, 2853, 1688, 1542. HRMS (ESI): Calcd. For $C_9H_{18}O_2N$ $[M+H]^+$ 172.1332, found 172.1331.

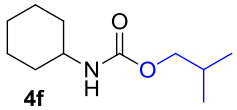
Pent-4-en-1-yl phenethylcarbamate (4e)



4e

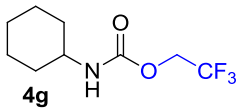
Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **4e** (24 mg, 21 %) as a colourless gel. Rf = 0.56 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 6.99 (m, 5H), 5.83 (m, J = 16.9, 10.2, 6.6 Hz, 1H), 5.01 (d, J = 10.2 Hz, 2H), 4.68 (s, 1H), 4.09 (t, J = 6.6 Hz, 2H), 3.47 (dd, J = 13.0, 6.5 Hz, 2H), 2.84 (t, J = 7.0 Hz, 2H), 2.13 (dd, J = 13.9, 6.8 Hz, 2H), 1.81 – 1.62 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.6, 138.8, 137.6, 128.8, 128.6, 126.5, 115.1, 64.3, 42.1, 36.2, 30.0, 28.3. IR (neat) υmax (cm^{-1}) = 3335, 3065, 3028, 2940, 1703, 1641, 1531. HRMS (ESI): Calcd. For $C_{14}H_{20}O_2N$ $[M+H]^+$ 234.1488, found 234.1482.

Isobutyl cyclohexylcarbamate (4f)



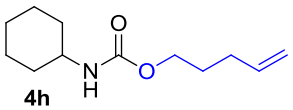
Following the general procedure 3.B, the corresponding oxamic acid (0.7 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 95/5) afforded **4f** (99 mg, 71 %) as a white solid, 51 - 52ºC. Rf = 0.71 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.56 (s, 1H), 3.80 (d, J = 6.6 Hz, 2H), 3.52 – 3.34 (m, 1H), 1.90 (dt, J = 17.3, 6.5 Hz, 3H), 1.74 – 1.52 (m, 3H), 1.40 – 1.22 (m, 2H), 1.21 – 1.03 (m, 3H), 0.90 (d, J = 6.7 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.0, 49.8, 33.5, 28.0, 25.5, 24.8, 19.1. IR (neat) υmax (cm^{-1}) = 3324, 2856, 2932, 1694. HRMS (ESI): Calcd. For $C_{11}H_{21}O_2N$ $[M+Na]^+$ 222.1464, found 222.1464.

2,2,2-Trifluoroethyl cyclohexylcarbamate (4g)



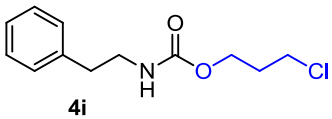
Following the general procedure 3.B, the corresponding oxamic acid (0.7 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 95/5) afforded **4g** (71 mg, 45 %) as a white solid, 82 - 85ºC. Rf = 0.76 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.82 (s, 1H), 4.43 (q, J = 8.6 Hz, 2H), 3.55 – 3.39 (m, 1H), 1.93 (dd, J = 8.4, 4.0 Hz, 2H), 1.78 – 1.51 (m, 3H), 1.42 – 1.07 (m, 5H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 153.5, 123.2 (q, $^1J_{CF}$ = 277.4 Hz), 60.7 (q, $^2J_{CF}$ = 36.2 Hz), 50.3, 33.1, 25.4, 24.7. IR (neat) υmax (cm^{-1}) = 3325, 2925, 2859, 1703. HRMS (ESI): Calcd. For $C_9H_{13}O_2NF_3$ $[M+H]^+$ 224.0903, found 224.0898.

Pent-4-en-1-yl cyclohexylcarbamate (4h)



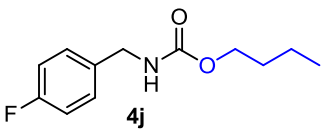
Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by column chromatography (petroleum ether/ethyl acetate 93/7) afforded **4h** (56 mg, 53 %) as a white solid, m.p. = 40 - 41ºC. Rf = 0.54 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (m, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.13 – 4.91 (m, 2H), 4.55 (s, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.47 (s, 1H), 2.22 – 2.02 (m, 2H), 2.05 – 1.83 (m, 2H), 1.77 – 1.53 (m, 5H), 1.47 – 1.00 (m, 5H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.8, 137.7, 115.0, 64.0, 49.7, 33.4, 30.0, 28.3, 25.5, 24.8. IR (neat) υmax (cm^{-1}) = 3325, 3077, 2932, 2855, 1697, 1533. HRMS (ESI): Calcd. For $C_{12}H_{21}O_2N$ $[M+Na]^+$ 234.1464, found 234.1459.

3-Chloropropyl phenethylcarbamate (4i)



Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.08M) were used. Purification: vacuum distillation to remove excess alcohol, column chromatography (silica, petroleum ether/ ethyl acetate 90/10) afforded **4i** (54%, NMR yield, 38 mg isolated, 31 %) as a colourless liquid. Rf = 0.42 (EtOAc-Hexane 20/80).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.16 (m, 5H), 4.71 (s, 1H), 4.23 (t, J = 6.0 Hz, 2H), 3.61 (t, J = 6.5 Hz, 2H), 3.47 (dd, J = 13.1, 6.6 Hz, 2H), 2.84 (t, J = 6.9 Hz, 2H), 2.09 (p, J = 6.2 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.2, 138.7, 128.8, 128.6, 126.5, 61.5, 42.1, 41.3, 36.1, 32.0. IR (neat) υmax (cm^{-1}) = 3334, 3063, 3028, 2960, 1706, 1603, 1603, 1528. HRMS (ESI): Calcd. For $C_{12}H_{16}O_2NCl^{35}$ [M+Na]+ 264.0761, found 264.0757.

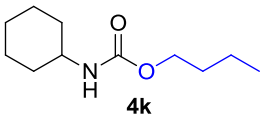
Butyl 4-fluorobenzylcarbamate (4j)



4j

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol), Bu_4NClO_4 (0.1M) and DCE (0.5 mL) and were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 95/5) afforded **4j** (50.6 mg, 45 %) as a light brown gel. Rf = 0.58 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 5.01 (s, 1H), 4.34 (d, *J* = 5.9 Hz, 2H), 4.11 (t, *J* = 6.7 Hz, 2H), 1.62 (tt, *J* = 8.2, 6.7 Hz, 2H), 1.38 (dt, *J* = 14.4, 7.4 Hz, 2H), 0.94 (dd, *J* = 9.6, 5.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 162.2 (d, $^1J_{CF}$ = 245.6 Hz), 156.7, 134.4, 129.2 (d, $^3J_{CF}$ = 6.8 Hz), 115.5 (d, $^2J_{CF}$ = 21.5 Hz), 65.0, 44.3, 31.1, 19.1, 13.7. IR (neat) υmax (cm^{-1}) = 3332, 2958, 2928, 2883 1701, 1606, 1510. HRMS (ESI): Calcd. For $C_{12}H_{16}O_2NF$ $[M+Na]^+$ 248.1057, found 248.1055.

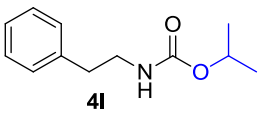
Butyl cyclohexylcarbamate (4k)



4k

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.1M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 90/10) afforded **4k** (52 mg, 52 %) as a white crystalline solid, mp. = 52 – 53ºC. Rf = 0.67 (AcOEt/petroleum ether, 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.71 – 4.29 (s, 1H), 4.05 (t, J = 6.5 Hz, 2H), 3.64 – 3.23 (s, 1H), 2.03 – 1.85 (m, 2H), 1.78 – 1.49 (m, 5H), 1.49 – 1.24 (m, 4H), 1.25 – 1.03 (m, 3H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (76MHz, $CDCl_3$) δ 156.0, 64.4, 49.7, 33.5, 31.1, 25.5, 24.8, 19.1, 13.7. IR (neat) υmax (cm-^{1}) = 3318, 2939, 2853, 1686, 1537. HRMS (ESI): Calcd. For $C_{11}H_{21}O_2N$ $[M+Na]^+$ 222.1464, found 222.1459.

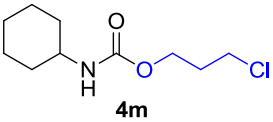
Isopropyl phenethylcarbamate (4l)



4l

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.03M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 93/7) afforded **4l** (28 mg, 30 %) as a colourless liquid, Rf = 0.0.54 (AcOEt/petroleum ether, 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.07 (m, 5H), 4.91 (dt, J = 12.5, 6.2 Hz, 1H), 4.62 (s, 1H), 3.43 (d, J = 6.1 Hz, 2H), 2.81 (t, J = 7.0 Hz, 2H), 1.22 (d, J = 6.2 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.2, 138.9, 128.8, 128.6, 126.4, 68.0, 42.0, 22.2. IR (neat) υmax (cm-^{1}) = 3340, 3034, 2978, 2935, 1694, 1532. HRMS (ESI): Calcd. For $C_{12}H_{17}O_2N$ $[M+Na]^+$ 230.1151, found 230.1146.

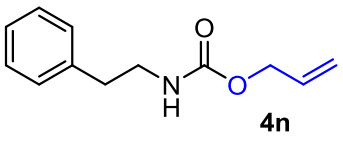
3-chloropropyl cyclohexylcarbamate (4m)



4m

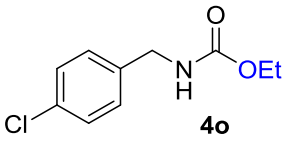
Following the general procedure 3.B, the corresponding oxamic acid (0.7 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by vacuum distillation to remove excess alcohol, then column chromatography (silica, petroleum ether/ ethyl acetate 93/7) afforded **4m** (50% NMR yield, 63 mg isolated, 41 %) as a white solid, 59 - 60ºC. Rf = 0.54 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55 (s, 1H), 4.19 (t, *J* = 5.8 Hz, 2H), 3.60 (t, *J* = 6.5 Hz, 2H), 3.46 (s, 1H), 2.12 – 2.00 (m, 2H), 1.97 – 1.85 (m, 2H), 1.75 – 1.55 (m, 3H), 1.41 – 1.04 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 61.3, 49.8, 41.4, 33.4, 32.1, 25.5, 24.8. IR (neat) υmax (cm^{-1}) = 3328, 2932, 2856, 1706. HRMS (ESI): Calcd. For $C_{10}H_{18}O_2N^{35}Cl$ $[M+Na]^+$ 242.0918, found 242.0912.

Allyl phenethylcarbamate (4n)



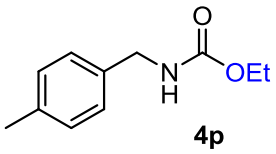
Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 92/8) afforded **4n** (51 mg, 50 %) as a colourless liquid. Rf = 0.57 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, J = 13.7, 7.8, 4.1 Hz, 5H), 5.94 (m, J = 22.7, 10.8, 5.6 Hz, 1H), 5.27 (m, J = 13.8, 11.5, 1.2 Hz, 2H), 4.81 (s, 1H), 4.58 (d, J = 5.5 Hz, 2H), 3.64 – 3.34 (dd, 2H), 2.84 (t, J = 7.0 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.2, 138.7, 132.9, 128.7, 128.6, 126.5, 117.6, 65.5, 42.2, 36.1. IR (neat) υmax (cm^{-1}) = 3335, 3085, 3064, 3028, 2938, 2878, 1708, 1603, 1530. HRMS (ESI): Calcd. For $C_{12}H_{15}O_2N$ [M+Na]+ 228.0995, found 228.0992.

Ethyl 4-chlorobenzylcarbamate (4o)



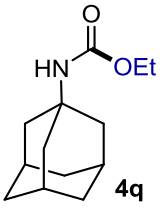
Following the general procedure 3.B, the corresponding oxamic acid (0.3 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 93/7) afforded **2j** (29 mg, 50 %) as a gel. Rf = 0.46 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 4H), 4.99 (s, 1H), 4.32 (d, *J* = 6.0 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). HRMS (ESI): ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.6, 137.2, 133.2, 128.8, 61.1, 44.3, 14.6. Calcd. For $C_{10}H_{12}O_2N^{35}Cl$ $[M+Na]^+$ 236.0448, found 236.0447.

Ethyl 4-methylbenzylcarbamate (4p)



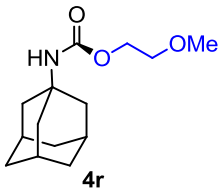
Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.03M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 93/7) afforded **4p** (54 mg, 62 %) as a colourless liquid. Rf = 0.46 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (q, *J* = 8.2 Hz, 4H), 4.92 (s, 1H), 4.35 (d, *J* = 5.7 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.6, 137.1, 135.5, 129.3, 127.5, 60.9, 44.8, 21.1, 14.7. IR (neat) υmax (cm^{-1}) = 3317, 2980, 2860, 1689. HRMS (ESI): Calcd. For $C_{11}H_{15}O_2N$ $[M+Na]^+$ 216.0995, found 216.0993.

Ethyl (3s,5s,7s)-adamantan-1-ylcarbamate (4q)



Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.03M) were used. Purification by column chromatography (silica, petroleum) afforded **4q** (79 mg, 71 %), as a white solid, m.p. = 94 -96°C. Rf = 0.76 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (s, 1H), 4.05 (q, J = 7.1 Hz, 2H), 2.17 – 2.00 (m, 3H), 1.93 (d, J = 2.7 Hz, 6H), 1.66 (t, J = 3.0 Hz, 6H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 154.6, 59.8, 50.5, 41.8, 36.5, 36.4, 36.3, 36.1, 29.6, 29.4, 29.2, 14.6. IR (neat) υmax (cm^{-1}) = 3339, 2908, 2851, 1706, 1527. HRMS (ESI): Calcd. For $C_{13}H_{22}O_2N$ $[M+H]^+$ 224.1645, found 224.1641.

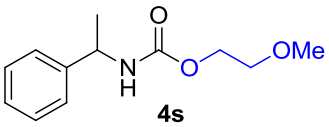
2-Methoxyethyl (3s,5s,7s)-adamantan-1-ylcarbamate (4r)



4r

Following the general procedure 3.B, the corresponding oxamic acid (0.4 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 90/10) afforded **4r** (81 mg, 80 %) as a white gel. Rf = 0.64 (EtOAc-Hexane 30/70). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.65 (s, 1H), 4.18 – 4.10 (t, 2H), 3.60 – 3.52 (m, 2H), 3.39 (s, 3H), 2.06 (s, 3H), 1.92 (d, J = 3.0 Hz, 6H), 1.66 (t, J = 3.1 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 154.2, 71.0, 63.0, 58.9, 50.7, 41.8, 36.3, 29.4. IR (neat) υmax (cm-^{1}) = 3344, 2909, 2844, 1709, 1527. HRMS (ESI): Calcd. For $C_{14}H_{24}O_3N$ $[M+H]^+$ 254.1750, found 254.1749.

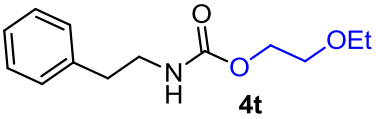
2-Methoxyethyl (1-phenylethyl)carbamate (4s)



4s

Following the general procedure 3.B, the corresponding oxamic acid (0.4 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 90/10) afforded **4s** (58 mg, 65 %) as a colourless gel. Rf = 0.32 (EtOAc-Hexane 30/70. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.15 (5, 1H), 5.10 (s, 1H), 4.83 (p, J = 7.1 Hz, 1H), 4.34 – 4.09 (m, 2H), 3.56 (t, J = 4.7 Hz, 2H), 3.37 (s, 3H), 1.47 (s, J = 6.9 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.5, 128.6, 127.3, 125.9, 63.8, 58.9, 50.7, 22.5. IR (neat) υmax (cm-^{1}) = 3323, 3030, 2975, 2893, 1706, 1531. HRMS (ESI): Calcd. For $C_{12}H_{17}O_3N$ $[M+Na]^+$ 246.1100, found 246.1095.

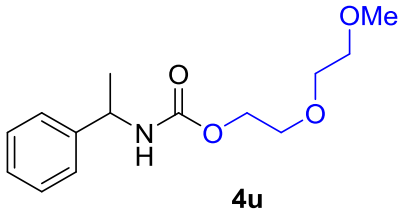
2-Ethoxyethyl phenethylcarbamate (4t)



4t

Following the general procedure 3.B, the corresponding oxamic acid (0.37 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 85/15) afforded **4t** (53 mg, 60 %) as a colourless gel. Rf = 0.40 (EtOAc-Hexane 30/70. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.12 (m, 5H), 4.77 (s, J = 5.3 Hz, 1H), 4.26 – 4.11 (t, 2H), 3.65 – 3.38 (m, 6H), 2.81 (t, J = 7.0 Hz, 2H), 1.21 (t, J = 7.0 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.3, 138.7, 128.8, 128.6, 126.5, 68.8, 66.6, 64.0, 42.1, 36.1, 15.1. IR (neat) υmax (cm-^{1}) = 3335, 3028, 2974, 2869, 1709, 1530. HRMS (ESI): Calcd. For $C_{13}H_{19}O_3N$ $[M+Na]^+$ 260.1275, found 260.1253.

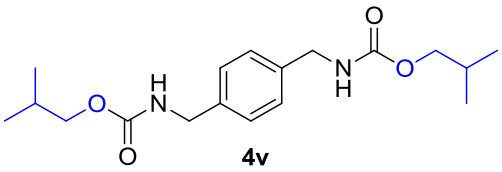
2-(2-Methoxyethoxy)ethyl (1-phenylethyl)carbamate (4u)



4u

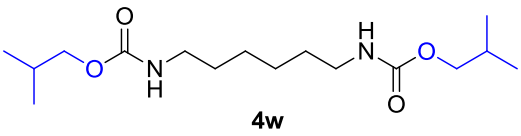
Following the general procedure 3.B, the corresponding oxamic acid (0.4 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 75/25) afforded **4u** (50 mg, 47 %) as a light brown gel. Rf = 0.42 (EtOAc-Hexane 50/50. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 5H), 5.11 (s, 1H), 4.84 (p, J = 7.2 Hz, 1H), 4.23 (q, J = 4.4 Hz, 2H), 3.76 – 3.50 (m, 6H), 3.39 (s, 3H), 1.49 (d, J = 6.9 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.5, 143.5, 128.6, 127.3, 125.9, 71.8, 70.4, 69.6, 63.9, 59.0, 50.7, 22.5. IR (neat) υmax (cm-^{1}) = HRMS (ESI): Calcd. For $C_{14}H_{20}O_4N$ $[M-H]^+$ 266.1397, found 266.1396.

Diisobutyl (1,4-phenylenebis(methylene))dicarbamate (4v)



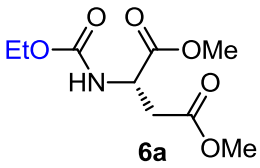
Following the general procedure 3.B, the corresponding oxamic acid (0.25 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, DCM/MeOH 99/1) afforded **4v** (42 mg, 50 %) as a white crystalline solid, m.p. = 161 - 163ºC. Rf = 0.21 (EtOAc-Hexane 20/80). Mp = 16—163ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 4H), 4.98 (s, 2H), 4.37 (d, J = 5.8 Hz, 4H), 3.90 (d, J = 6.6 Hz, 4H), 1.93 (m, J = 13.4, 6.7 Hz, 2H), 0.94 (d, J = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 137.9, 127.9, 71.2, 44.7, 28.0, 19.0. IR (neat) υmax (cm^{-1}) = 3313, 3064, 2957, 2865, 1683, 1540. HRMS (ESI): Calcd. For $C_{18}H_{29}O_4N_2$ $[M+H]^+$ 337.2121, found 337.2116.

Diisobutyl hexane-1,6-diyldicarbamate (4w)



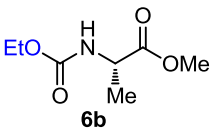
Following the general procedure 3.B, the corresponding oxamic acid (0.25 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ethyl acetate 85/15) afforded **4w** (50 mg, 63 %) as a white crystalline solid, m.p. = 116 - 118ºC. Rf = 0.43 (EtOAc-Hexane 30/70). Mp = 116 - 118ºC, ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 2H), 3.85 (d, J = 6.6 Hz, 4H), 3.18 (dd, J = 13.0, 6.5 Hz, 4H), 1.91 (m, J = 13.2, 6.6 Hz, 2H), 1.56 – 1.45 (m, 4H), 1.37 (dd, J = 4.1, 3.0 Hz, 4H), 0.94 (d, J = 6.7 Hz, 12H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.9, 70.9, 40.7, 30.0, 28.0, 26.3, 19.1. IR (neat) υmax (cm^{-1}) = 3334, 2956, 2876, 1682, 1534. HRMS (ESI): Calcd. For $C_{16}H_{33}O_4N_2$ $[M+H]^+$ 317.2434, found 317.24305.

(*S*)-Dimethyl 2-((ethoxycarbonyl)amino)succinate (6a)



Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 88/12) afforded **6a** (59 mg, 51 %) as a light brown gel. Rf = 0.31 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (d, J = 7.8 Hz, 1H), 4.62 (dt, J = 8.7, 4.5 Hz, 1H), 4.12 (dd, J = 9.5, 4.7 Hz, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 3.03 (dd, J = 17.1, 4.5 Hz, 1H), 2.85 (dd, J = 17.1, 4.7 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.3, 156.1, 77.5, 77.0, 76.6, 61.3, 52.8, 52.0, 50.2, 36.5, 14.5. IR (neat) υmax (cm-1) = 3366, 2993, 2956. 1733, 1524. HRMS (ESI): Calcd. For $C_9H_{15}O_6N$ $[M+Na]^+$ 256.0791, found 256.0787. $[\alpha]_D^{25}$ +32.47 (c 0.72, $CHCl_3$).

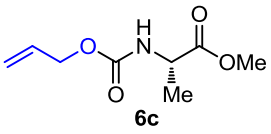
(*S*)-Methyl 2-((ethoxycarbonyl)amino)propanoate (6b)



Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 93/7) afforded **6b** (54 mg, 50 %) as a light brown liquid. Rf = 0.43 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.26 (s, 1H), 4.40 – 4.24 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H), 1.25 – 1.15 (m, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 173.6, 155.8, 61.0, 52.4, 49.4, 18.6, 14.5. IR (neat) υmax (cm^{-1}) = 3336, 2982, 1739,

1722, 1529. HRMS (ESI): Calcd. For $C_7H_{13}O_4N$ [M+Na]+ 198.0736, found 198.0733. $[\alpha]_D^{25}$ -4.65 (c 0.51, $CHCl_3$).

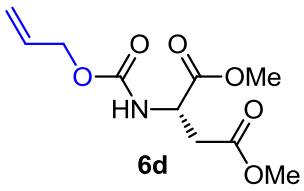
(*S*)-Methyl 2-(((allyloxy)carbonyl)amino)propanoate (6c)



6c

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 93/7) afforded **6c** (56 mg, 61 %) as a light brown liquid. Rf = 0.41 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (m, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.38 – 5.13 (m, 2H), 4.59 (d, *J* = 5.6 Hz, 2H), 4.47 – 4.28 (m, 1H), 3.77 (s, 3H), 1.43 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 173.5, 155.4, 132.6, 117.8, 65.8, 52.4, 49.5, 18.7. IR (neat) υmax (cm-^{1}) = 3344, 2991, 2952, 1722, 1528. HRMS (ESI): Calcd. For $C_8H_{13}O_4N$ [M+Na]+ 210.0736, found 210.0734. $[\alpha]_D^{25}$ -3.72 (c 0.3, $CHCl_3$).

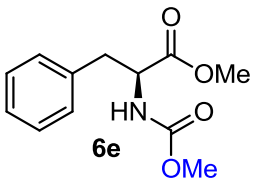
(*S*)-Dimethyl 2-(((allyloxy)carbonyl)amino)succinate (6d)



6d

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.05M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 85/15) afforded **6d** (44 mg, 41 %) as a light brown gel. Rf = 0.28 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (m, J = 17.2, 10.5, 5.6 Hz, 1H), 5.72 (d, J = 7.6 Hz, 1H), 5.38 – 5.18 (m, 2H), 4.57 (d, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.03 (dd, J = 17.1, 4.5 Hz, 1H), 2.90 – 2.78 (dd, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.3, 171.1, 155.8, 132.5, 117.9, 66.0, 52.8, 52.1, 50.3, 36.5. IR (neat) υmax (cm-^{1}) = 3340, 3025, 2956, 1729, 1650, 1520. HRMS (ESI): Calcd. For $C_{10}H_{15}O_6N$ $[M+Na]^+$ 268.0791, found 268.0783. $[\alpha]_D^{25}$ +21.32 (c 0.5, $CHCl_3$).

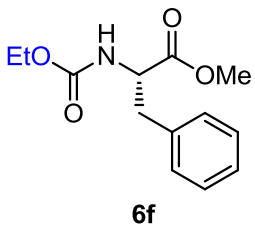
(*S*)-Methyl 2-((methoxycarbonyl)amino)-3-phenylpropanoate (6e)



6e

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 90/10) afforded **6e** (85 mg, 70 %) as a colourless gel. Rf = 0.4 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 3H), 7.19 – 7.06 (m, 2H), 5.24 (s, 1H), 4.66 (dd, J = 13.7, 6.2 Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 3.23 – 2.93 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 172.1, 156.3, 135.7, 129.2, 128.6, 127.1, 54.7, 52.3, 38.3. IR (neat) υmax (cm-^{1}) = 3340, 3025, 2956, 2844, 1729, 1526. HRMS (ESI): Calcd. For $C_{12}H_{15}O_4N$ $[M+Na]^+$ 260.0893, found 260.0892. $[\alpha]_D^{25}$ +58.92 (c 0.52, $CHCl_3$).

(*S*)-Methyl 2-((ethoxycarbonyl)amino)-3-phenylpropanoate (6f)

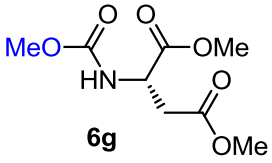


6f

Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.08M) were used. Purification column by chromatography (silica, petroleum ether/ ethyl acetate 85/15) afforded **6f** (82 mg, 65 %) as a colourless gel. Rf = 0.37 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 3H), 7.16 – 7.04 (m, 2H), 5.07 (s, 1H), 4.63 (dd, J = 13.8, 6.0 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.70 (s, 3H), 3.15 – 2.95 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (76

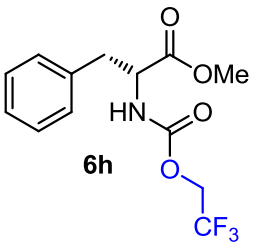
MHz, $CDCl_3$) δ 172.1, 155.9, 135.8, 129.2, 128.6, 127.1, 61.2, 52.3, 38.3, 14.5. IR (neat) υmax (cm^{-1}) = 3340, 3030, 2987, 1746, 1722, 1524. HRMS (ESI): Calcd. For $C_{13}H_{17}O_4N$ $[M+Na]^+$ 274.1094, found 274.1044. $[\alpha]_D^{25}$ +56.74 (c 0.46, $CHCl_3$).

(*S*)-Dimethyl 2-((methoxycarbonyl)amino)succinate (6g)



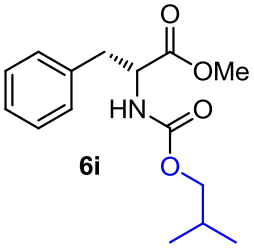
Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.01M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 85/15) afforded **6g** (85 mg, 78 %) as a gel. Rf = 0.25 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (d, J = 7.6 Hz, 1H), 4.62 (dt, J = 8.7, 4.5 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 6H), 3.03 (dd, J = 17.1, 4.5 Hz, 1H), 2.85 (dd, J = 17.1, 4.6 Hz, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.3, 171.2, 156.5, 52.8, 52.0, 50.3, 36.5. IR (neat) υmax (cm^{-1}) = 3357, 3000, 2961, 2853, 1721, 1524. HRMS (ESI): Calcd. For $C_8H_{13}O_6N$ $[M+Na]^+$ 242.0635, found 242.0631. $[\alpha]_D^{25}$ +37.93 (c 0.64, $CHCl_3$).

(*S*)-Methyl 3-phenyl-2-(((2,2,2-trifluoroethoxy)carbonyl)amino)propanoate (6h)



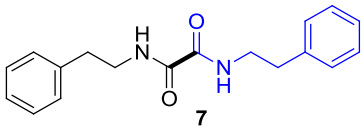
Following the general procedure 3.B, the corresponding oxamic acid (0.3 mmol) and Bu_4NClO_4 (0.05M) were used. Purification column chromatography (silica, petroleum ether/ ethyl acetate 92/8) afforded **6h** (39 mg, 40 %) as a colourless gel. Rf = 0.45 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.20 (m, 3H), 7.20 – 7.07 (m, 2H), 5.41 (d, J = 7.8 Hz, 1H), 4.74 – 4.60 (m, 1H), 4.58 – 4.33 (m, 2H), 3.76 (s, J = 7.8 Hz, 3H), 3.16 (m, J = 13.9, 5.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 153.7, 135.3, 129.2, 128.7, 127.3, 122.9 (q, $^1J_{CF}$ = 277.5 Hz), 61.1 (q, $^2J_{CF}$ = 36.6 Hz), 55.0, 52.5, 38.1. HRMS (ESI): IR (neat) υmax (cm^{-1}) = 3344, 3038, 2956, 1742, 1520. HRMS (ESI): Calcd. For $C_{13}H_{14}O_4NF_3$ $[M+Na]^+$ 328.0767, found 328.0760. $[\alpha]_D^{25}$ +49.86 (c 0.66, $CHCl_3$).

(*S*)-Methyl 2-((isobutoxycarbonyl)amino)-3-phenylpropanoate (6i)



Following the general procedure 3.B, the corresponding oxamic acid (0.4 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 92/8) afforded **6i** (69 mg, 50 %) as a colourless gel. Rf = 0.45 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 3H), 7.15 – 7.08 (m, 2H), 5.13 (d, J = 7.6 Hz, 1H), 4.64 (dd, J = 13.9, 6.0 Hz, 1H), 3.83 (dd, J = 6.7, 1.6 Hz, 2H), 3.71 (s, 3H), 3.10 (m, J = 6.1 Hz, 2H), 1.88 (m, J = 13.4, 6.7 Hz, 3H), 0.90 (d, J = 6.7 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 172.1, 156.7, 156.0, 135.8, 129.3, 128.6, 127.1, 71.3, 54.7, 52.3, 38.3, 28.0, 19.0. IR (neat) υmax (cm^{-1}) = 3349, 3021, 2961, 2875, 1724, 1730, 1518. HRMS (ESI): Calcd. For $C_{15}H_{21}O_4N$ $[M+Na]^+$ 302.1373, found 302.1357. $[\alpha]_D^{25}$ +46.32 (c 0.61, $CHCl_3$).

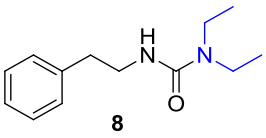
N^1, N^2-Diphenethyloxalamide (7)



7 (22 mg) was obtained in 15 % as a white solid, m.p. = 164-167°C. Rf = 0.14 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.41 – 7.16 (m, 10H), 3.59 (dd, J = 13.5, 7.1 Hz, 4H), 2.88 (t, J = 7.2 Hz, 4H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 159.7, 138.1, 128.7, 128.7, 126.7, 40.8,

35.4. IR (neat) υmax (cm^{-1}) = 3292, 3056, 2929, 2867, 1646. HRMS (ESI): Calcd. For $C_{18}H_{20}O_2N_2$ $[M+Na]^+$ 319.1417, found 319.1414.

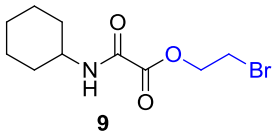
1,1-Diethyl-3-phenethylurea (8)



8

8 (20% (^{1}H-NMR), 17 mg, 15%) was obtained as a light brown gel. Rf = 0.20 (AcOEt/DCM 10/90) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.06 (m, 5H), 4.30 (s, 1H), 3.59 – 3.36 (m, 2H), 3.21 (q, *J* = 7.1 Hz, 4H), 2.91 – 2.77 (m, 2H), 1.12 – 1.01 (m, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.2, 139.5, 128.9, 128.8, 128.5, 126.3, 42.0, 41.1, 36.4, 13.8. IR (neat) υmax (cm^{-1}) = 3345, 3027, 2972, 2929, 2871, 1625. HRMS (ESI): Calcd. For $C_{13}H_{21}ON_2$ $[M+H]^+$ 221.1684, found 221.1638.

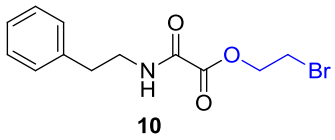
2-Bromoethyl 2-(cyclohexylamino)-2-oxoacetate (9)



9

Following the general procedure 3.B, the corresponding oxamic acid (0.7 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 90/10) afforded **9** (138 mg, 79 %) as a white solid, m.p. = 74 - 77ºC. Rf = 0.2 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 1H), 4.57 (t, *J* = 6.6 Hz, 2H), 3.92 – 3.71 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 1.96 (dd, *J* = 12.1, 2.9 Hz, 2H), 1.82 – 1.56 (m, 3H), 1.50 – 1.08 (m, 5H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 160.4, 154.8, 65.7, 49.0, 32.5, 27.2, 25.3, 24.6. IR (neat) υmax (cm^{-1}) = 3289, 2933, 2856, 1740, 1683. HRMS (ESI): Calcd. For $C_{10}H_{16}O_3N^{79}Br$ $[M+Na]^+$ 300.0192, found 300.0198.

2-Bromoethyl 2-oxo-2-(phenethylamino)acetate (10)

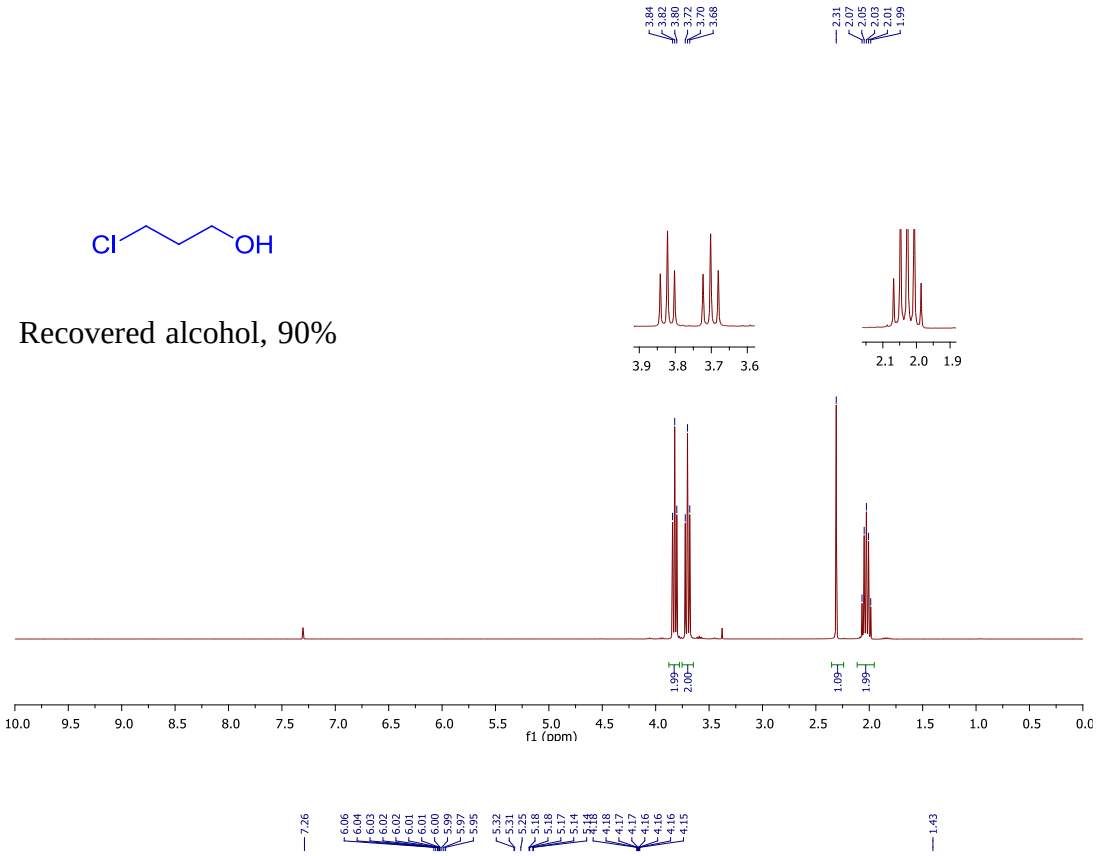


10

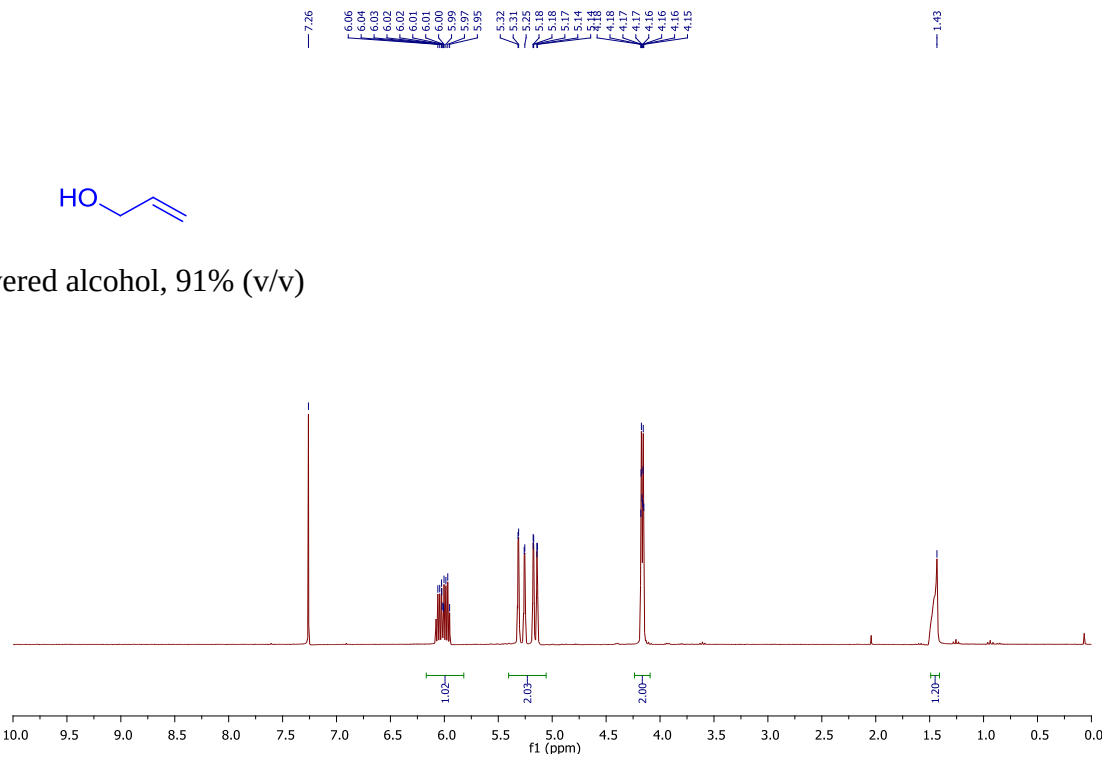
Following the general procedure 3.B, the corresponding oxamic acid (0.5 mmol) and Bu_4NClO_4 (0.08M) were used. Purification by column chromatography (silica, petroleum ether/ ethyl acetate 90/10) afforded **10** (78.6 mg, 53 %) % as a white solid, m.p. = 69 - 71ºC. Rf = 0.2 (EtOAc-Hexane 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.17 (m, 5H), 7.11 (s, 1H), 4.56 (t, *J* = 6.5 Hz, 2H), 3.69 – 3.53 (m, 4H), 2.89 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 160.0, 155.8, 138.0, 126.8, 65.7, 41.1, 35.2, 27.1. IR (neat) υmax (cm^{-1}) = 3331, 2924, 1738, 1693. HRMS (ESI): Calcd. For $C_{12}H_{14}O_3N^{79}Br$ $[M+Na]^+$ 322.0049, found 322.0049.

5. Alcohol Recovery after Electrochemical Reaction

After the electrochemical reaction, residual alcohol was recovered by vacuum distillation at low temperature (≤ 50ºC), allowed about 90% alcohol recovery with satisfying purity. Some spectra of the recovered alcohol are shown below.



Recovered alcohol, 90%



Recovered alcohol, 91% (v/v)

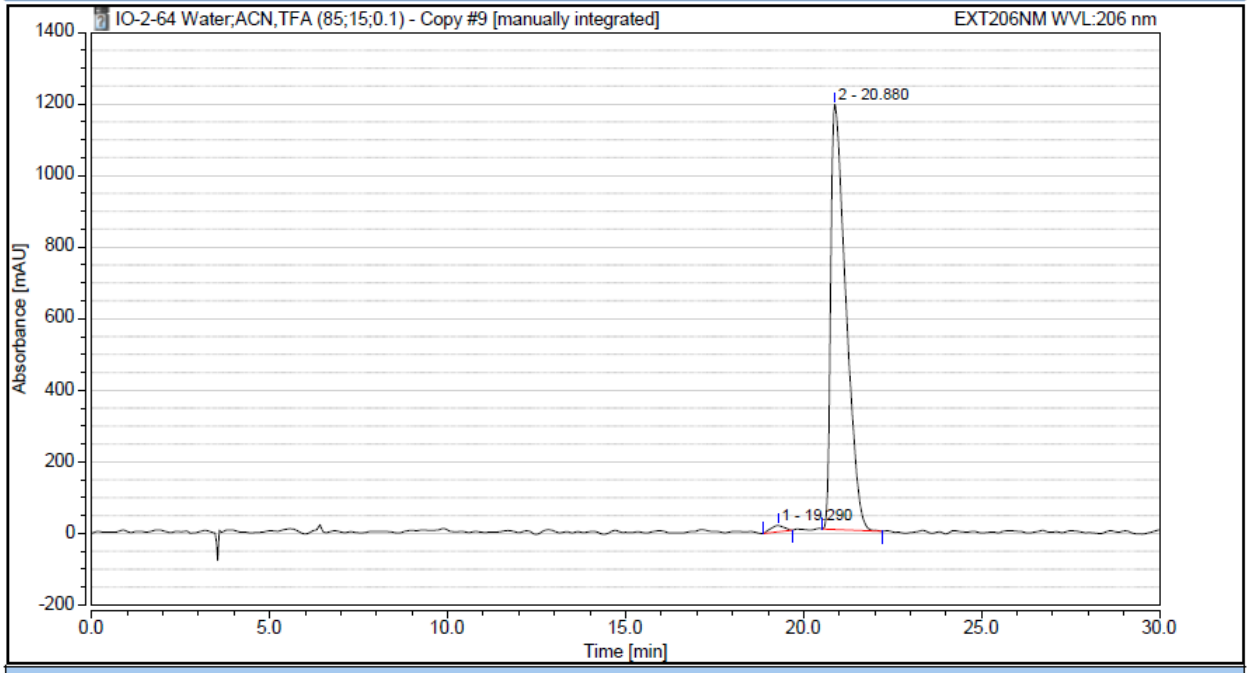
6. HPLC Data for (*S*)-Methyl 2-((ethoxycarbonyl)amino)-3-phenylpropanoate (6f)

Chromatogram and Results

Injection Details

Injection Name:	**IO-2-65-chiral3-Water;ACN.TFA (75;25;0.1) 1mL;mi**	*Run Time (min):*	**30.00**
Vial Number:	**GC4**	*Injection Volume:*	**5.00**
Injection Type:	**Unknown**	*Channel:*	**EXT206NM**
Calibration Level:		*Wavelength:*	**200.0**
Instrument Method:	**LJ method Water;ACN;DEA (75;25;0,1) 1 mL;min**	*Bandwidth:*	**1**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**06/juil./20 16:32**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.290	7.724	17.530	1.31	1.45	n.a.
2		20.880	582.472	1187.402	98.69	98.55	n.a.
Total:			**590.196**	**1204.932**	**100.00**	**100.00**	

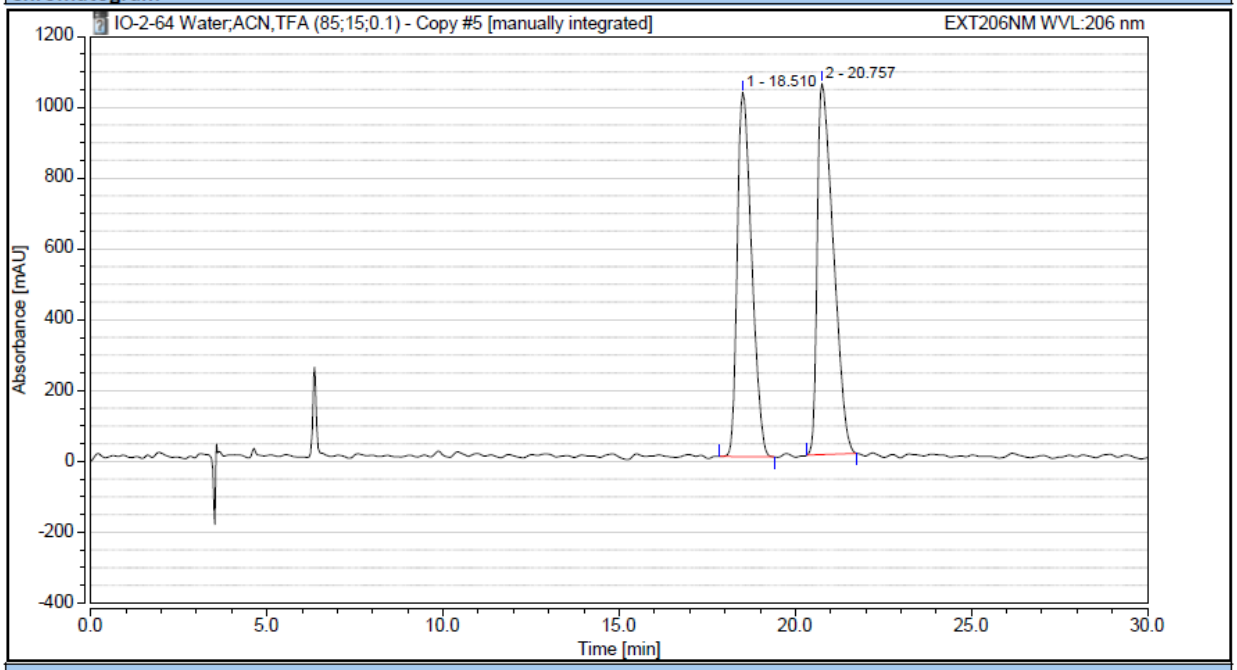
HPLC Data for (*S*)-Methyl 2-((ethoxycarbonyl)amino)-3-phenylpropanoate (rac-6f)

Chromatogram and Results

Injection Details

Injection Name:	**IO-2-64-Race2-Water;ACN.TFA (85;15;0.1) 1mL;mi**	*Run Time (min):*	**30.00**
Vial Number:	**GC3**	*Injection Volume:*	**10.00**
Injection Type:	**Unknown**	*Channel:*	**EXT206NM**
Calibration Level:		*Wavelength:*	**200.0**
Instrument Method:	**LJ method Water;ACN;DEA (75;25;0,1) 1 mL;min**	*Bandwidth:*	**1**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**06/juil./20 14:13**	*Sample Weight:*	**1.0000**

Chromatogram

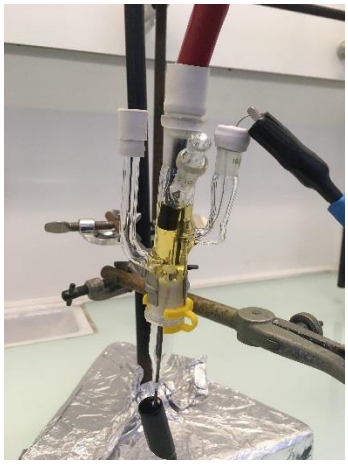


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.510	488.606	1028.990	46.90	49.53	n.a.
2		20.757	553.277	1048.400	53.10	50.47	n.a.
Total:			**1041.883**	**2077.390**	**100.00**	**100.00**	

7. Cyclic voltammetry studies

Cyclic voltammetry studies were performed using a μAUTOLAB TYPE II potentiostat/galvanostat coupled to the electrochemical Systems (GPES, v.4.9 software; Serial No: AUT72173) (Eco Chemie BV, Utrecht, The Netherlands) and equipped with a cell containing three-electrodes, *i.e.* a silver wire as the pseudo-reference electrode (pseudo-RE), a glassy carbon electrode (∅: 3 mm) as a working electrode and finally a Pt-wire counter-electrode. The glassy carbon electrode (GCE) was polished prior to each measurement.

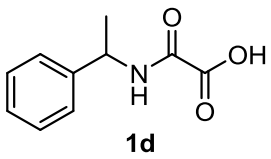


5 mM solutions of oxamic acid **1d** and 0.1 M *n*-Bu_4N PF_6 in CH_3CN were used. Reaction set-up was degassed using highly pure Argon gas bubbling for at least 5 min. This was done before each measurement, and the argon atmosphere was kept over the solution during the process.

Cyclic voltammetry were recorded at 100 mV/s scan rate, at a temperature of 25±0.5 °C.

Generally, we also used the ferrocene as an external reference in which we measured the redox potential according to the same experimental conditions.

For some specific cases, we used ferrocene as an internal standard (in 0.1 M of *n*-Bu_4N PF_6 in MeCN as supporting electrolyte solution).



1d

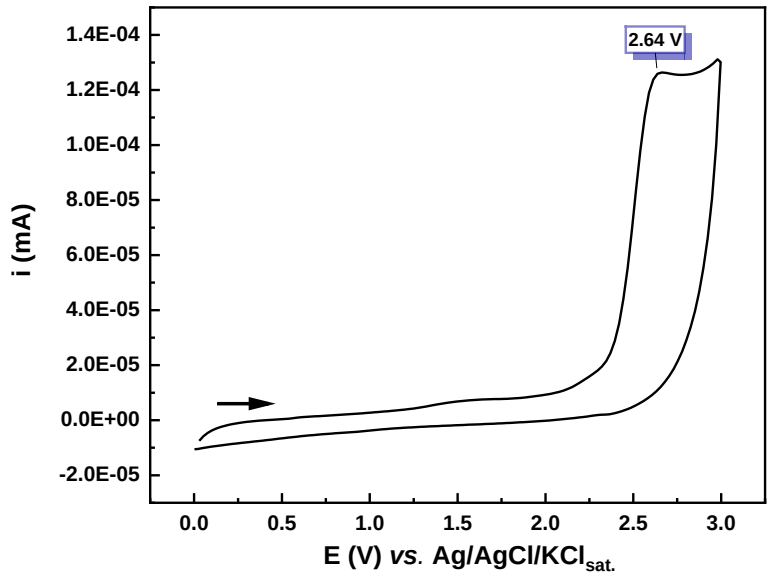


Figure S1. Cyclic voltammogram for oxamic acid **1d** (5 mM) in CH_3CN/*n*-Bu_4NPF_6 (0.1 M). Potential scan rate 100 mV s^{-1}. (E_{ox} = 2.595 V vs SCE)

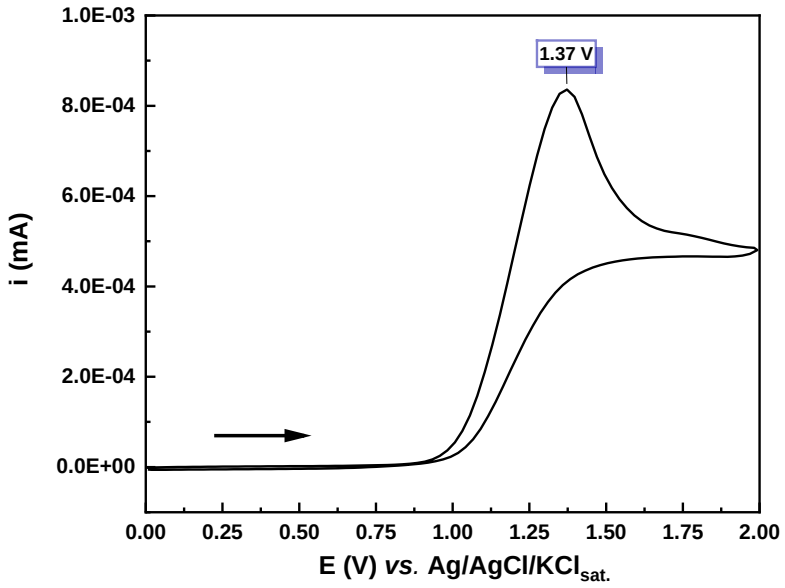


Figure S2. Cyclic voltammogram for oxamic acid **1d** (5 mM), Et_3N (5 mM), in CH_3CN/*n*-Bu_4NPF_6 (0.1 M). Potential scan rate 100 mV s^{-1}. (E_{ox} = 1.32 V vs SCE. Litt.[8] E_{ox} = 1.17 V vs SCE)

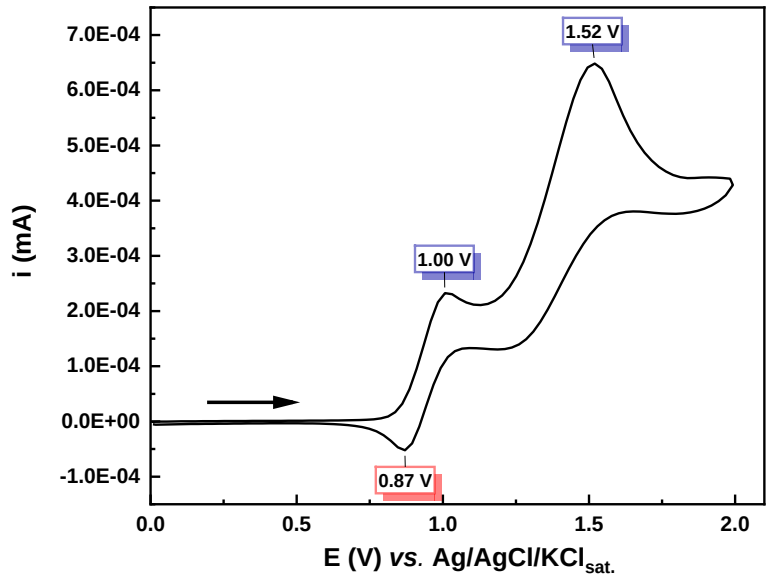


Figure S3. Cyclic voltammogram for oxamic acid **1d** (5 mM), Et_3N (5 mM) in CH_3CN/*n*-Bu_4NPF_6 (0.1 M) with ferrocene (5 mM) as internal reference. Potential scan rate 100 mV s^{-1}. (E_{ox} = 1.47 V vs SCE)

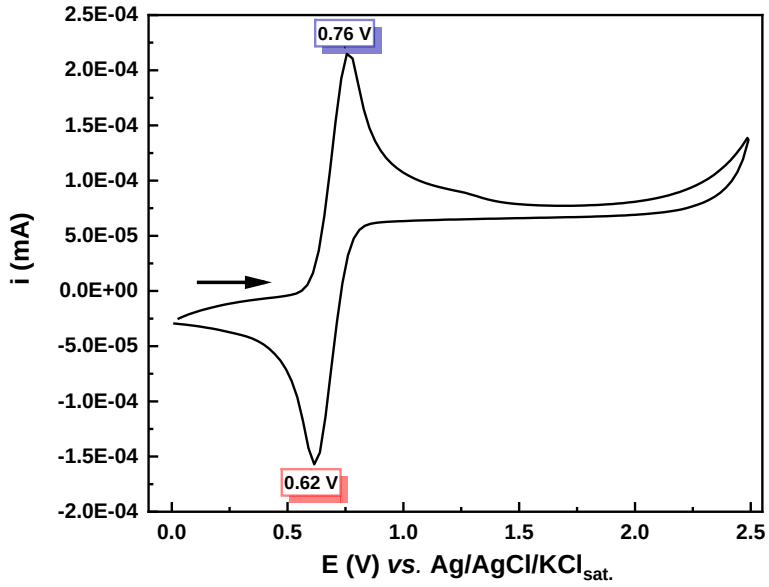
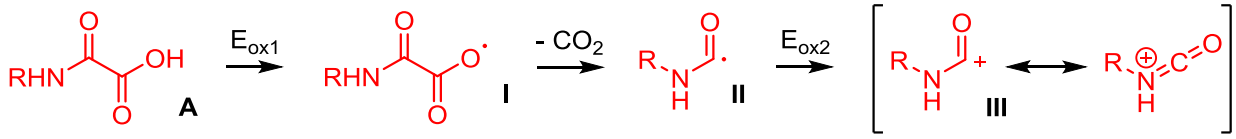


Figure S4. Cyclic voltammogram for ferrocene (5 mM) in CH_3CN/*n*-Bu_4NPF_6 (0.1 M). Potential scan rate 100 mV s^{-1}.

While we could expect two waves for our *ECE* type process, only one wave is observed as the voltage difference between E_{ox1} and E_{ox2} may be quite small as a result of the stabilization of the carbamoyl cation **III** by resonance with the nitrogen center. Similar observations have been made by Waldvogel et al during anodic oxidation of arylamides.[7]



8. References

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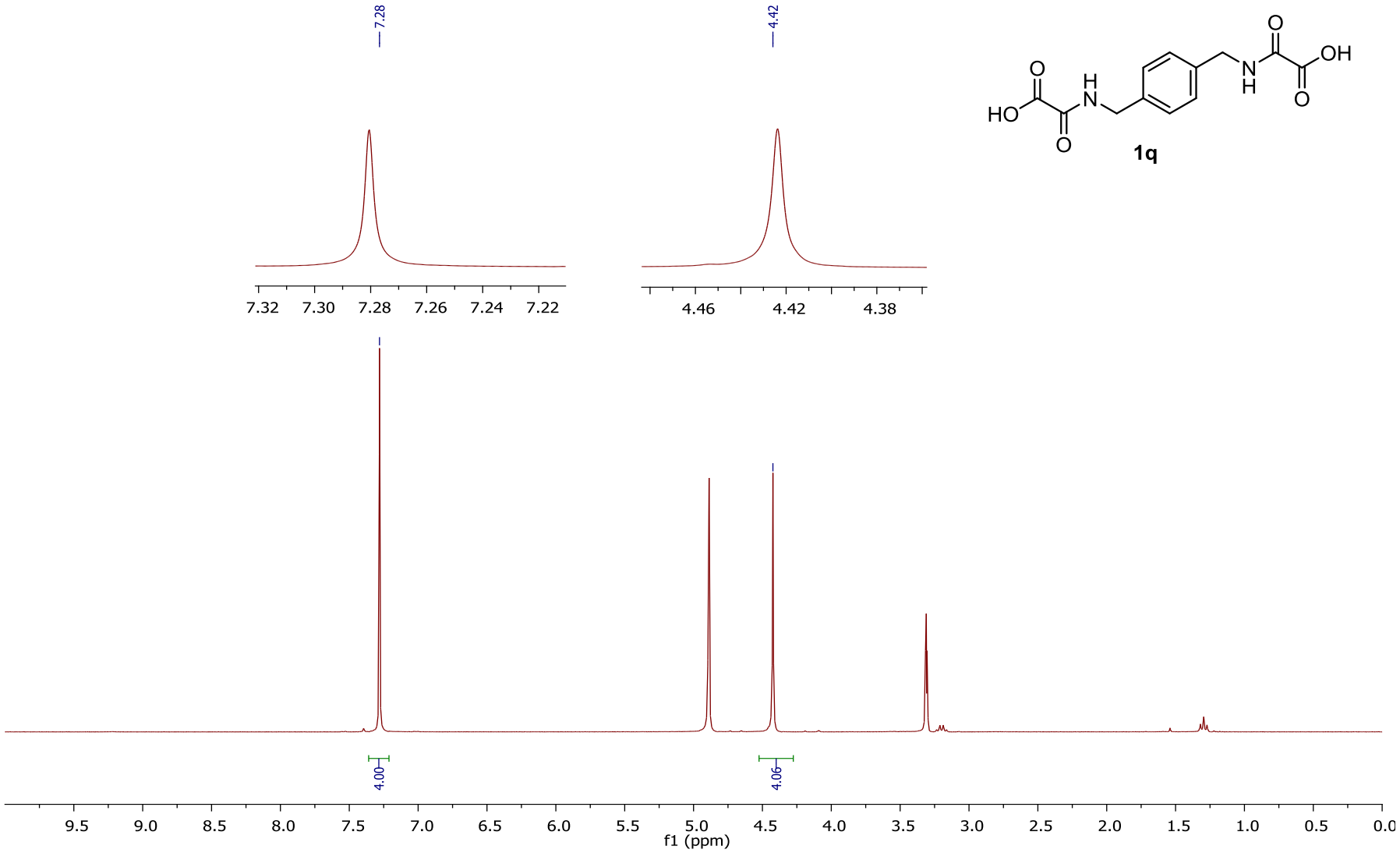
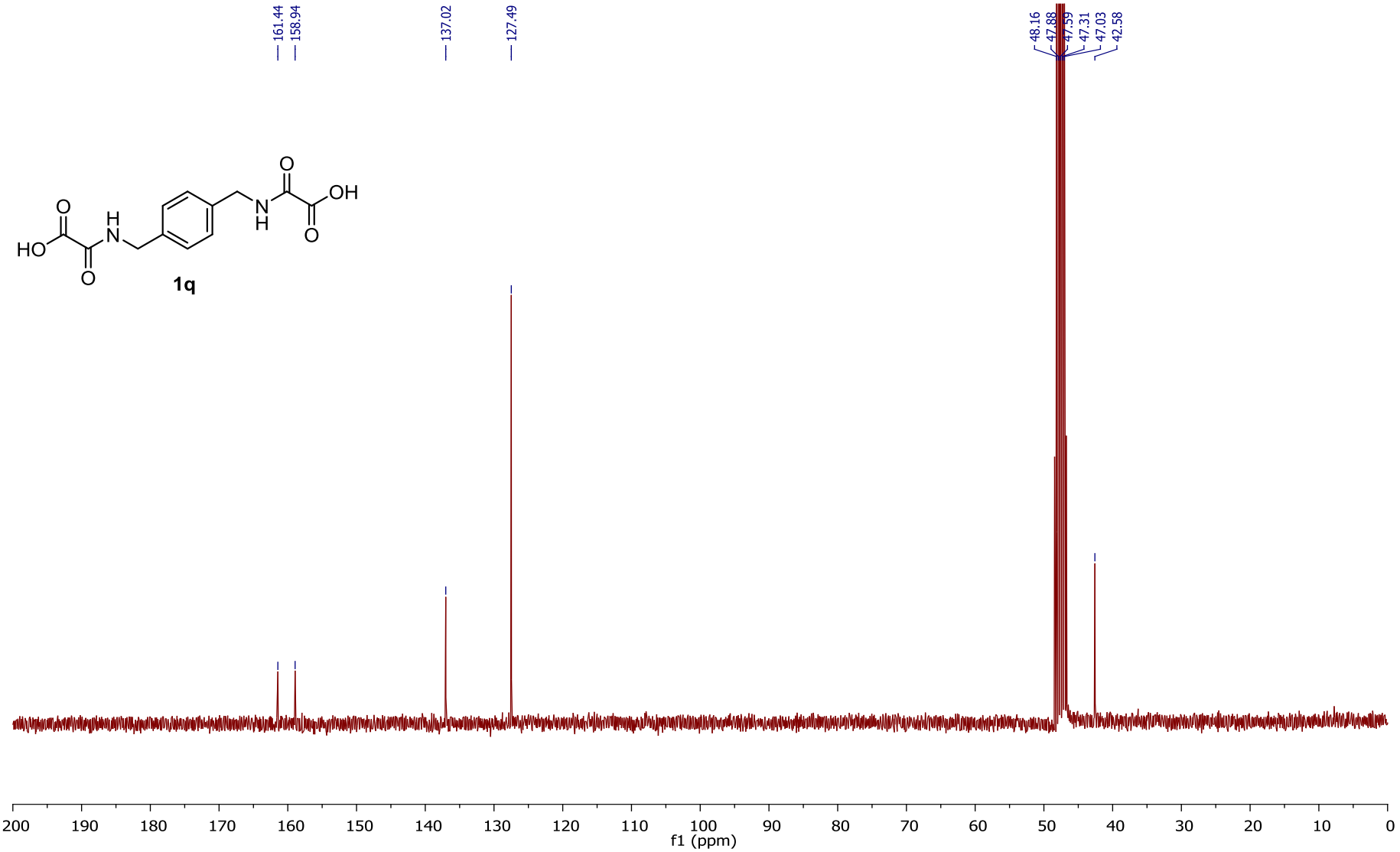
9. Copies of ^{1}H and ^{13}C NMR Spectra


7.28
4.42
7.32
7.30
7.28
7.26
7.24
7.22
4.46
4.42
4.38
4.00
4.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

O
HO
O
H
N
N
H
O
OH
O

1q


161.44
158.94
137.02
127.49
48.16
47.88
47.59
47.31
47.03
42.58
HO
O
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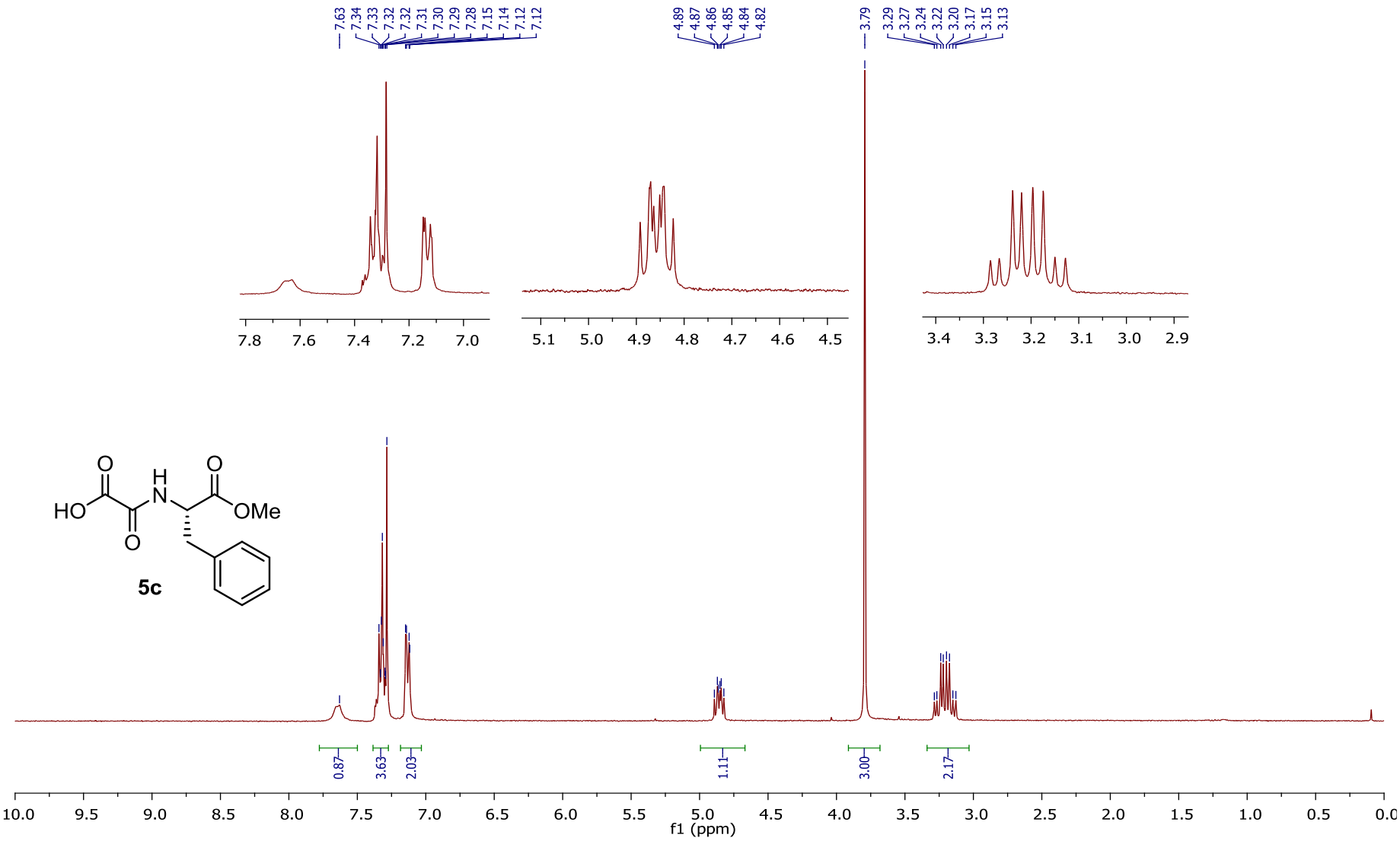
H
N
O
N
H
O
OH
1q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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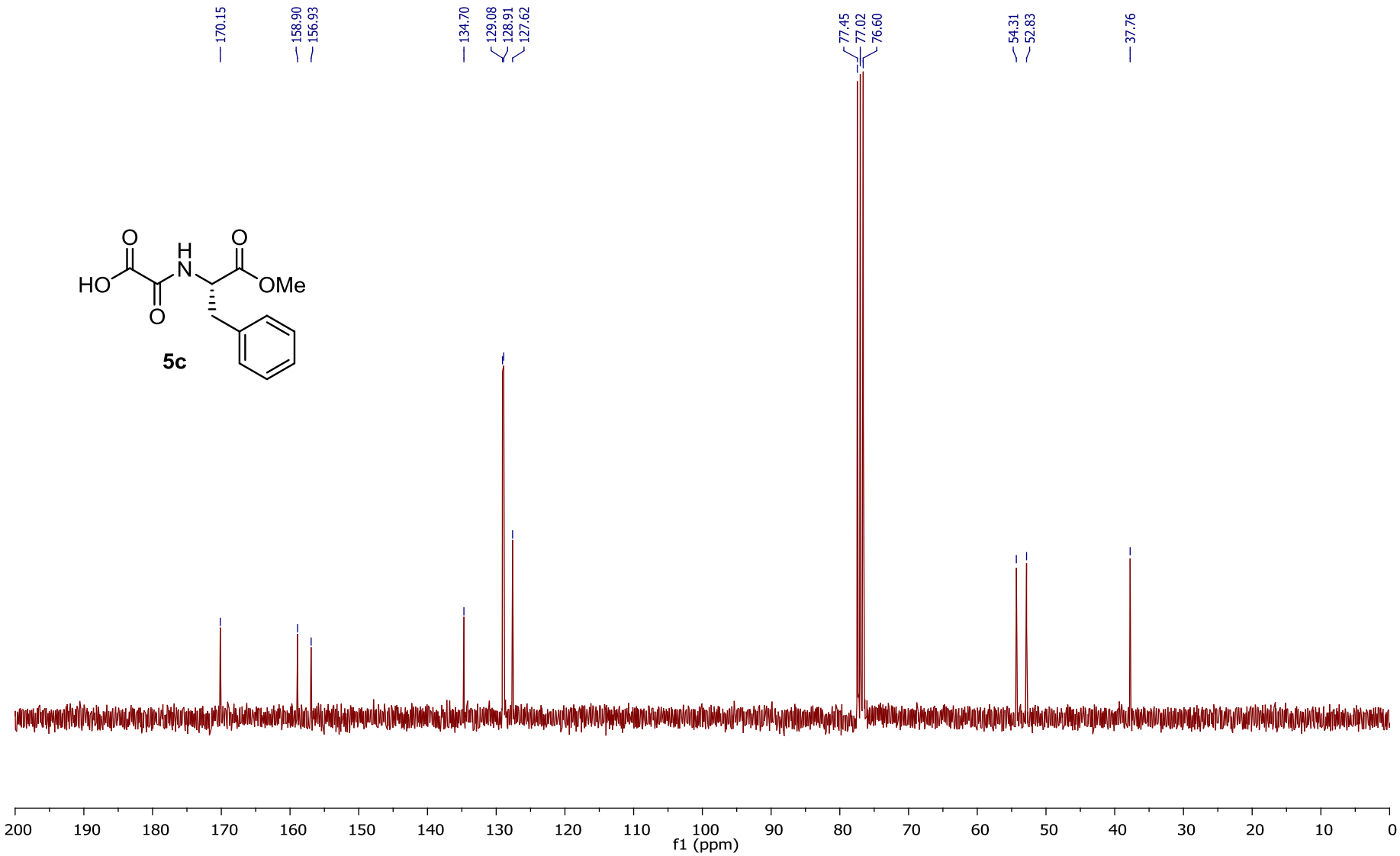
7.29
7.28
7.15
7.14
7.12
7.12
4.89
4.87
4.86
4.85
4.84
4.82
3.79
3.29
3.27
3.24
3.22
3.20
3.17
3.15
3.13
7.8 7.6 7.4 7.2 7.0
5.1 5.0 4.9 4.8 4.7 4.6 4.5
3.4 3.3 3.2 3.1 3.0 2.9
HO
O
O
H
N
O
OMe
5c
0.87
3.63
2.03
1.11
3.00
2.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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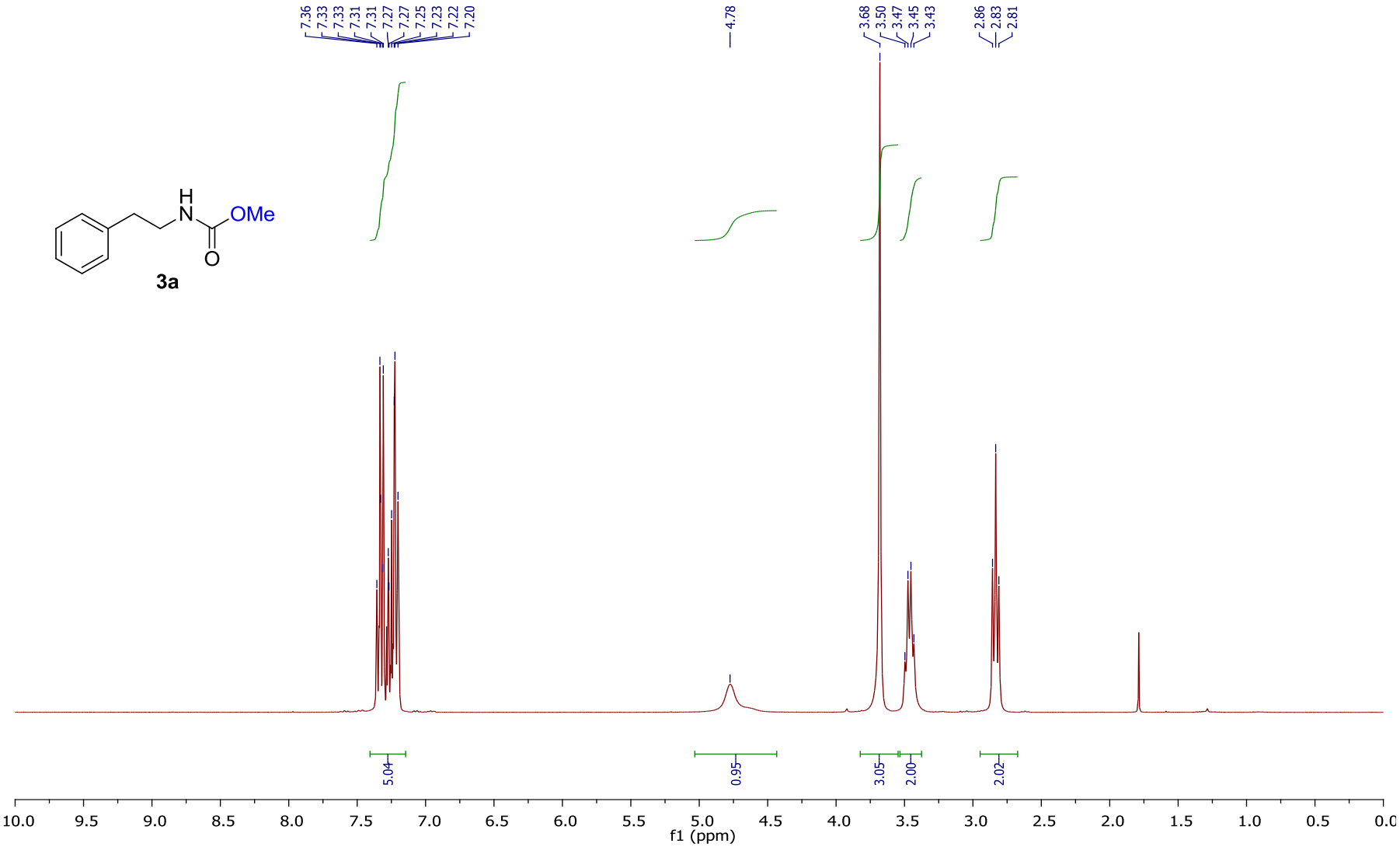
158.90
156.93
134.70
129.08
128.91
127.62
77.45
77.02
76.60
54.31
52.83
37.76
HO
O
O
H
N
O
OMe
5c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.27
7.25
7.23
7.22
7.20
4.78
3.68
3.50
3.47
3.45
3.43
2.86
2.83
2.81
H
N
OMe
O
3a
5.04
0.95
3.05
2.00
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
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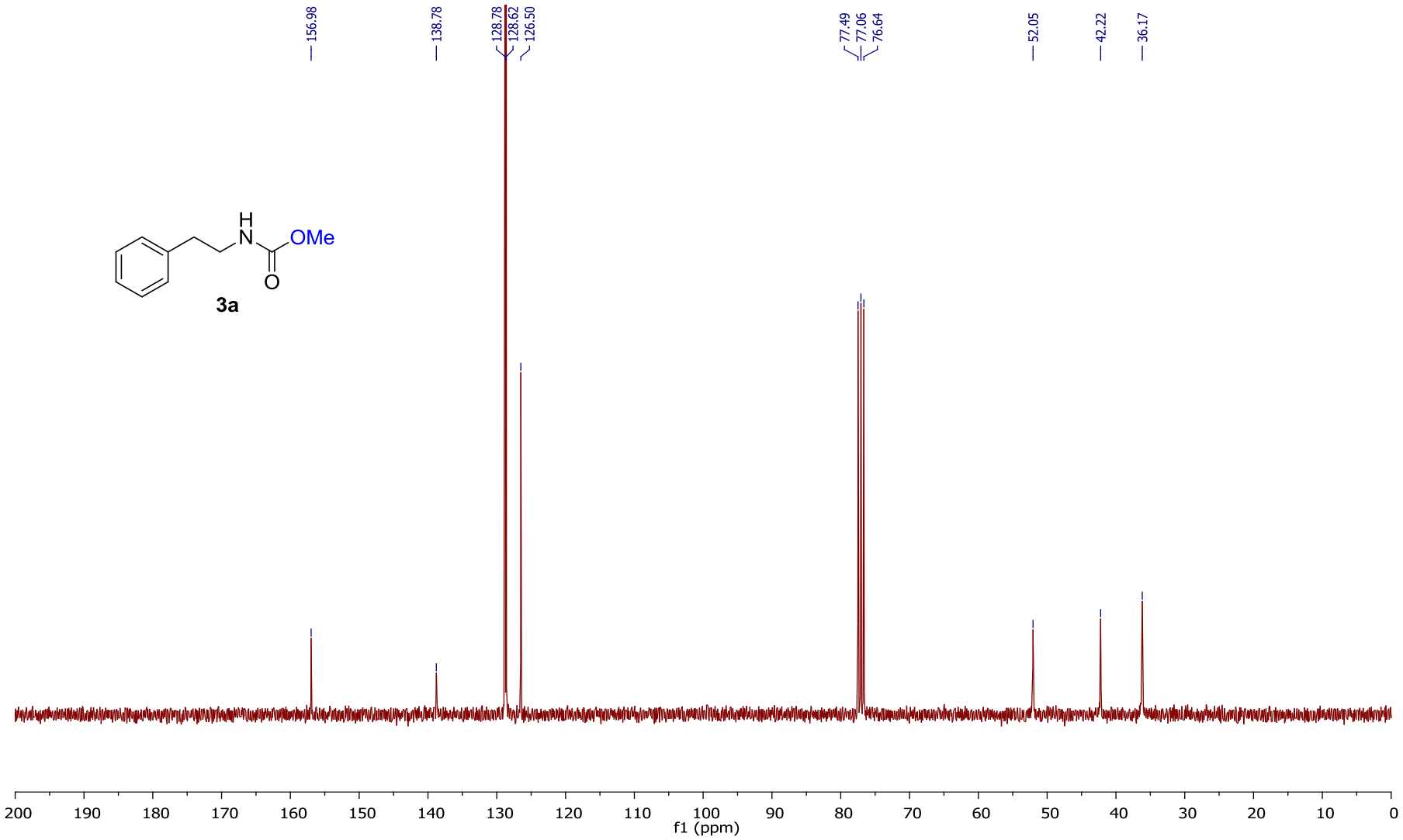
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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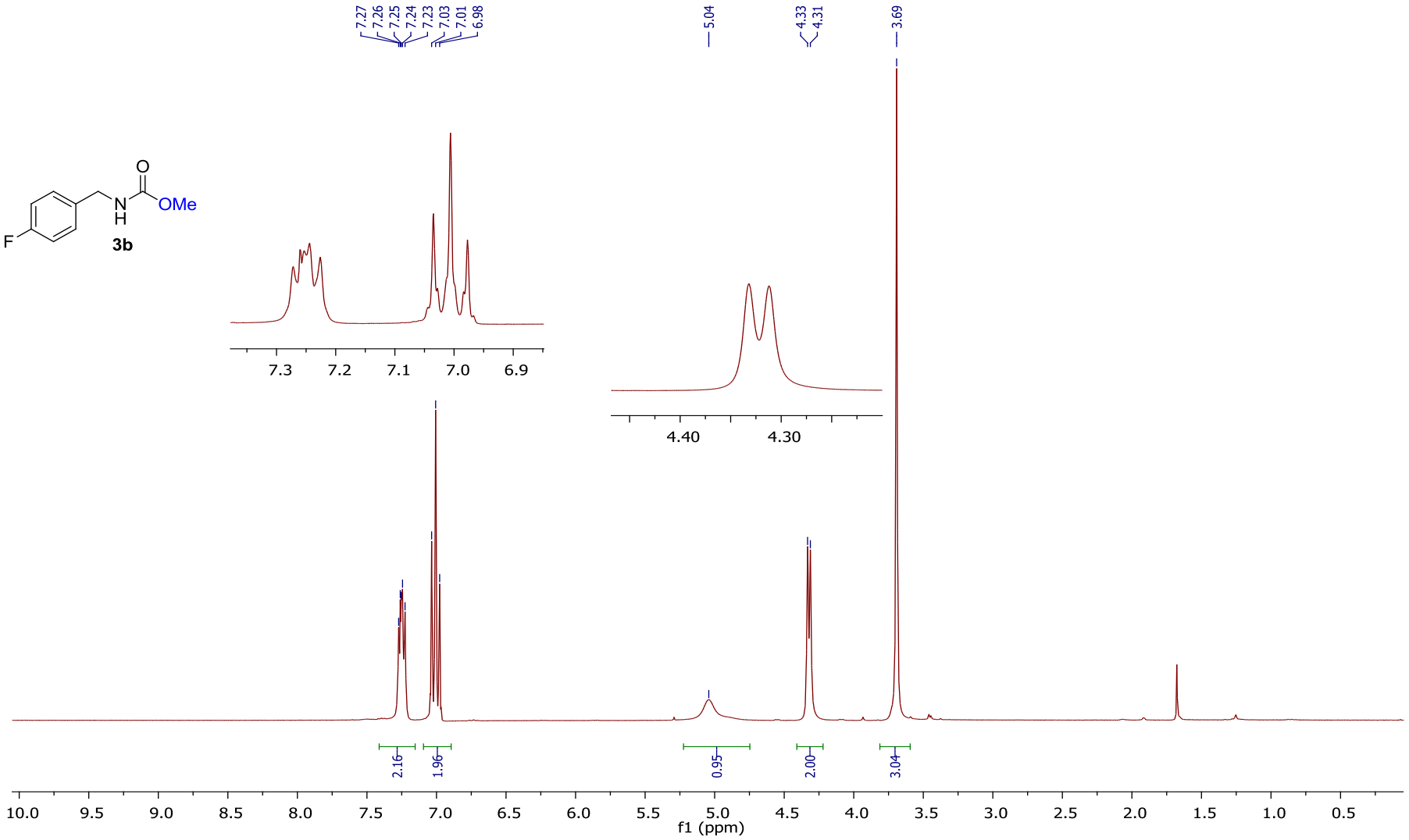
138.78
128.78
128.62
126.50
77.49
77.06
76.64
52.05
42.22
36.17
H
N
OMe
O
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
7.26
7.25
7.24
7.23
7.03
7.01
6.98
5.04
4.33
4.31
3.69
O
N
H
OMe
F
3b
7.3
7.2
7.1
7.0
6.9
4.40
4.30
2.16
1.96
0.95
2.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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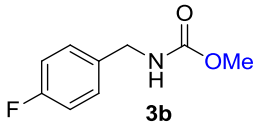
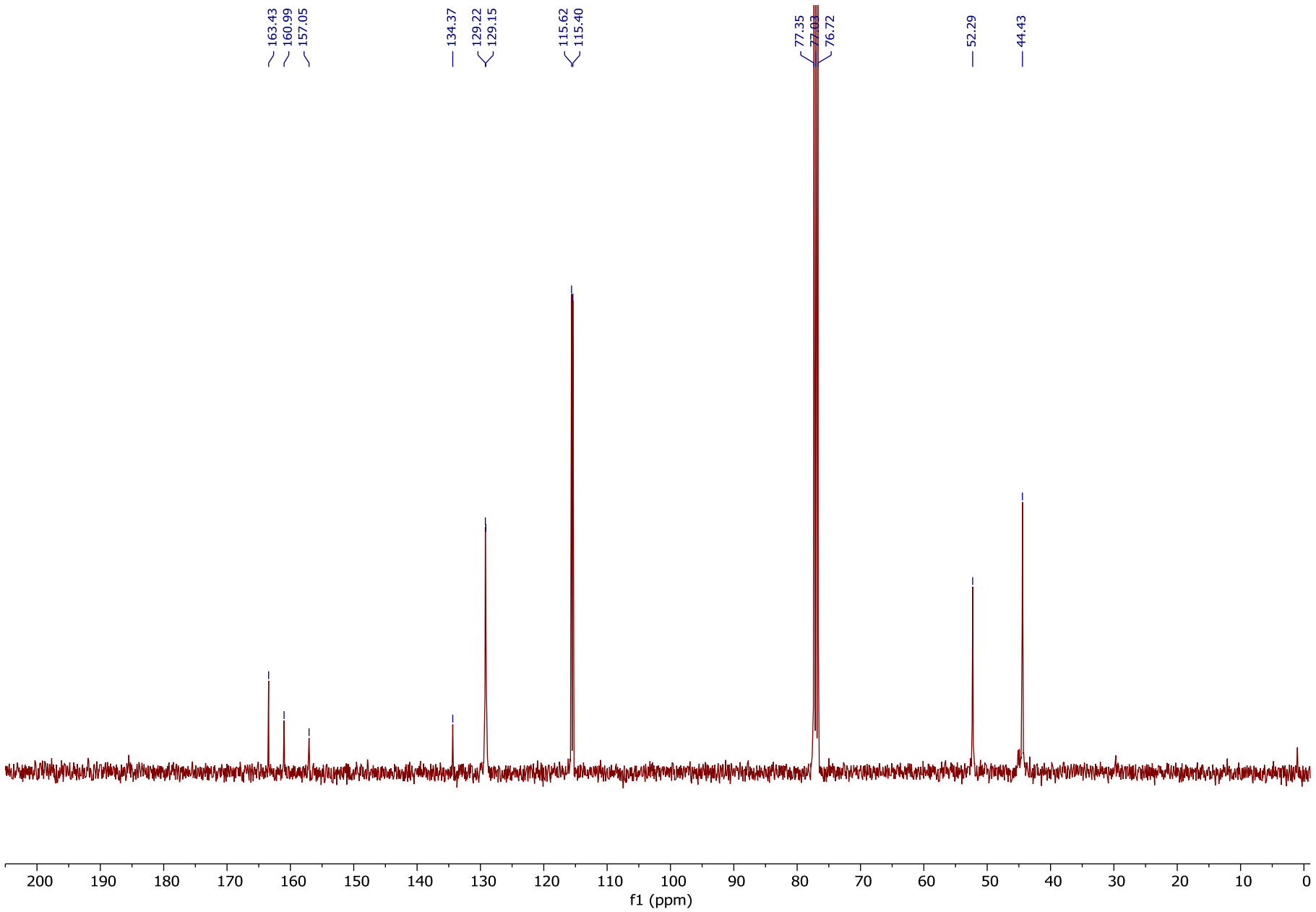
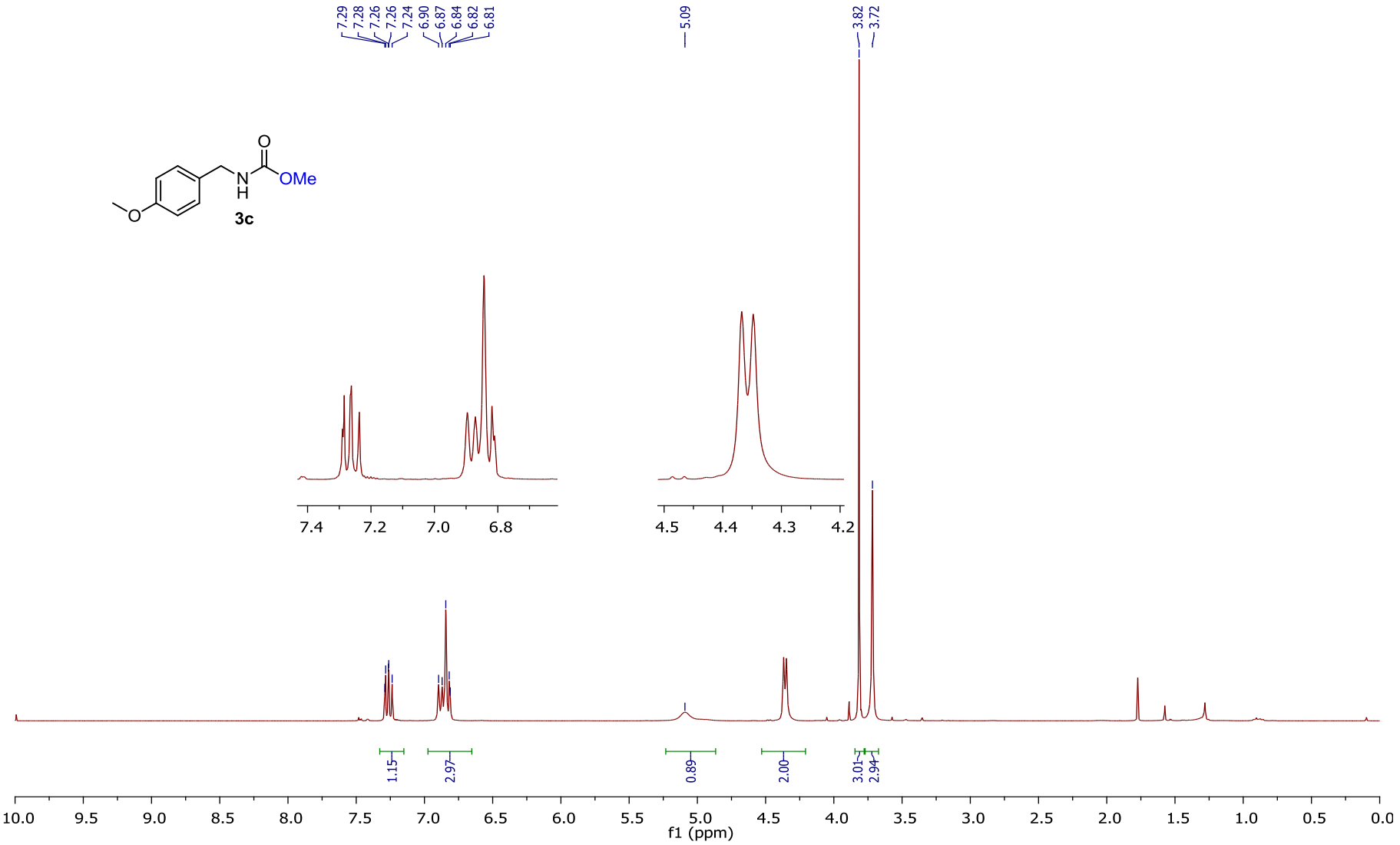
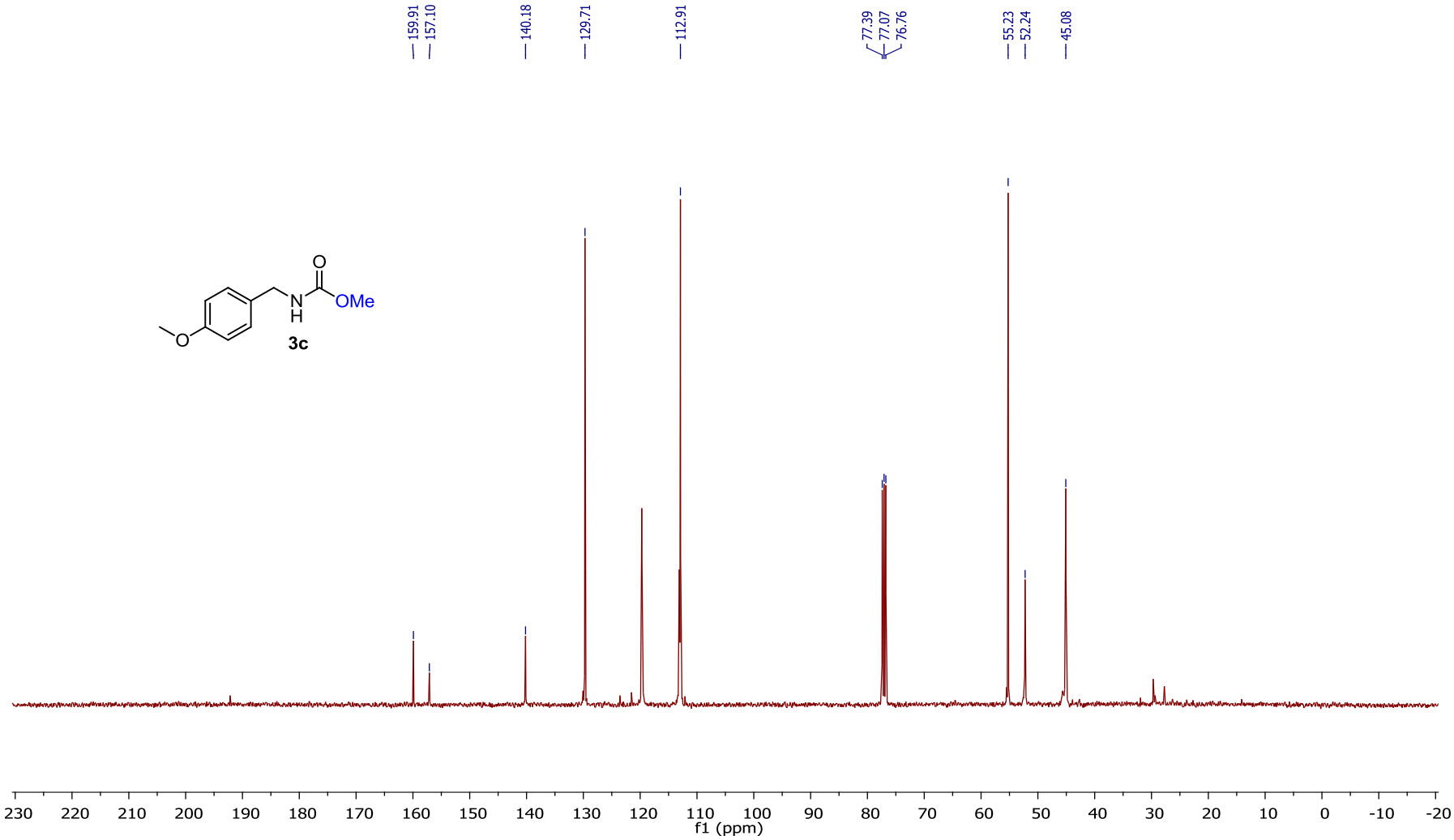
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

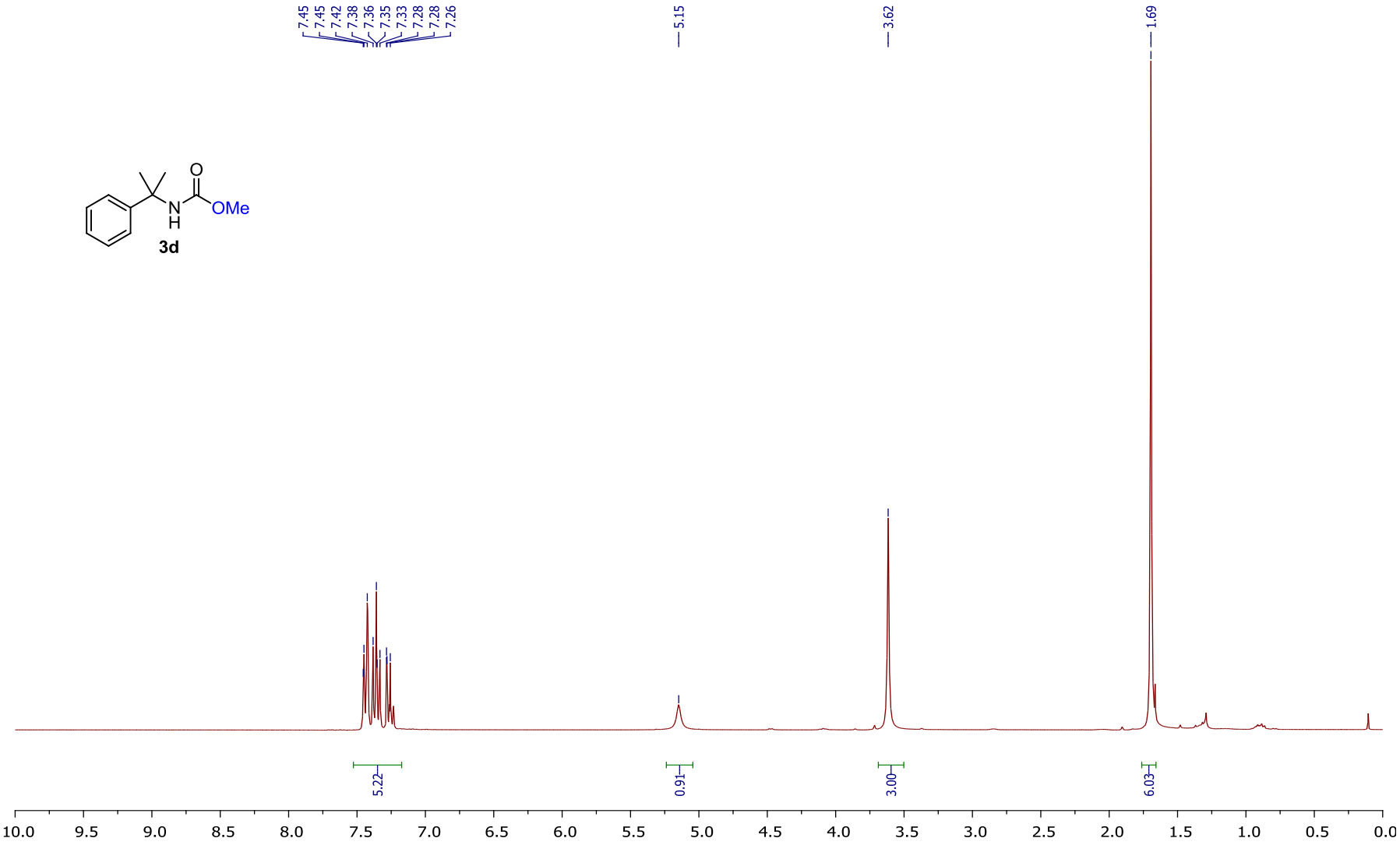


3b


163.43
160.99
157.05
134.37
129.22
129.15
115.62
115.40
77.35
77.03
76.72
52.29
44.43
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.29
7.28
7.26
7.26
7.24
6.90
6.87
6.84
6.82
6.81
5.09
3.82
3.72
O
N
H
OMe
O
3c
7.4
7.2
7.0
6.8
4.5
4.4
4.3
4.2
1.15
2.97
0.89
2.00
3.01
2.94
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
f1 (ppm)


159.91
157.10
140.18
129.71
112.91
77.39
77.07
76.76
55.23
52.24
45.08
O
N
H
OMe
O
3c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.35
7.33
7.28
7.28
7.26
5.15
3.62
1.69
O
N
H
OMe
3d
5.22
0.91
3.00
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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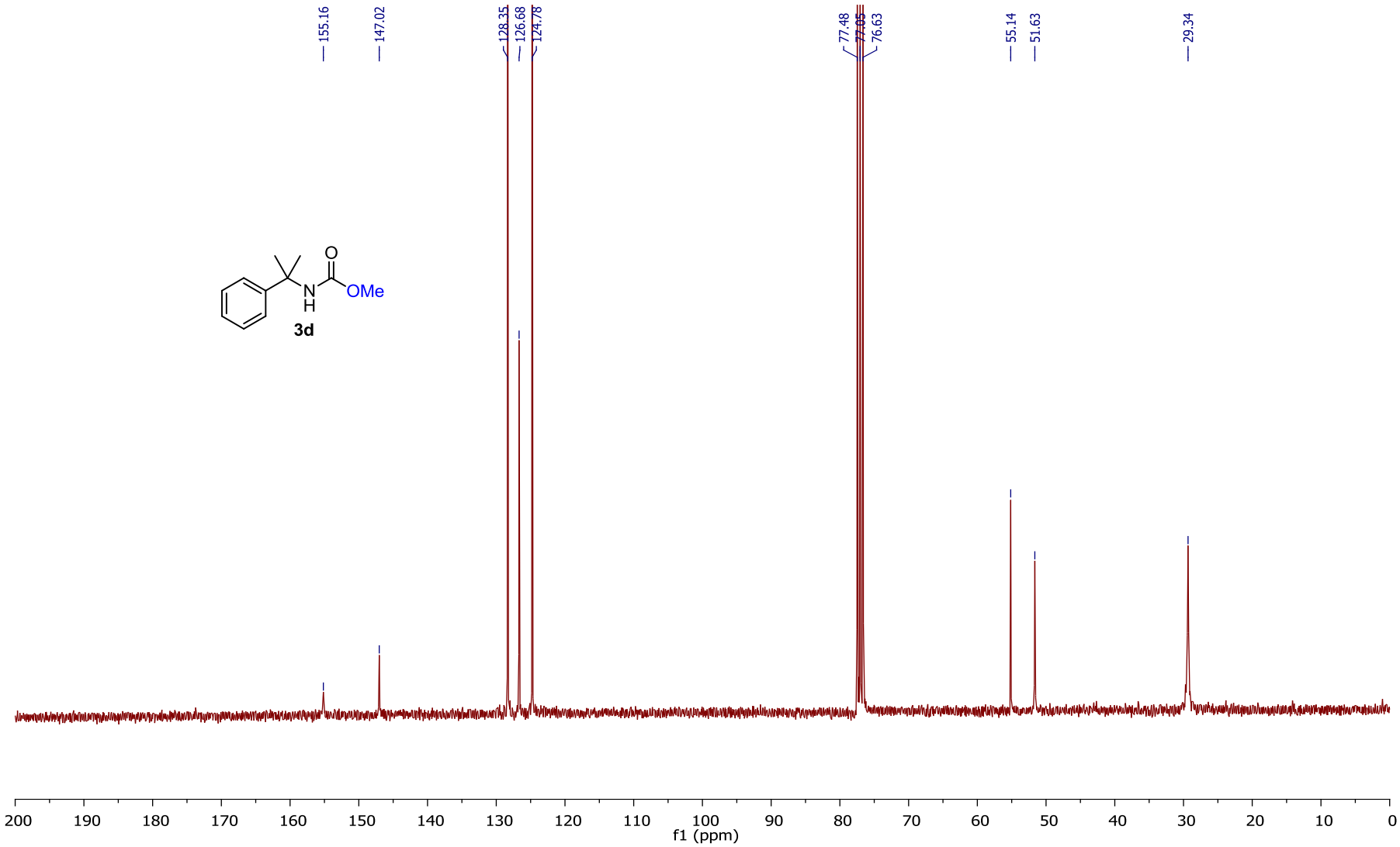
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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147.02
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124.78
77.48
77.05
76.63
55.14
51.63
29.34
O
N
H
OMe
3d
200
190
180
170
160
150
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130
120
110
100
90
80
70
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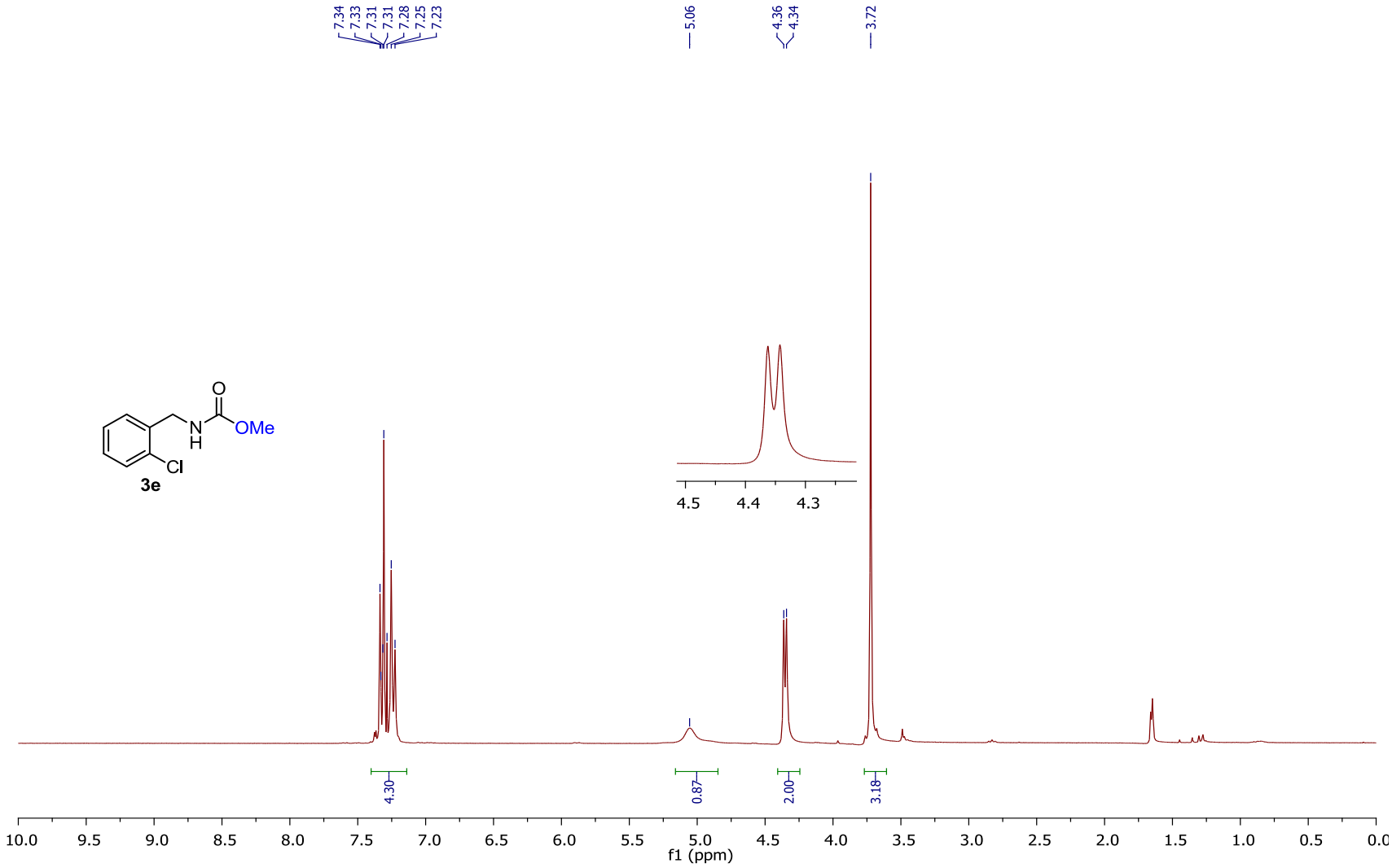
50
40
30
20
10
0
f1 (ppm)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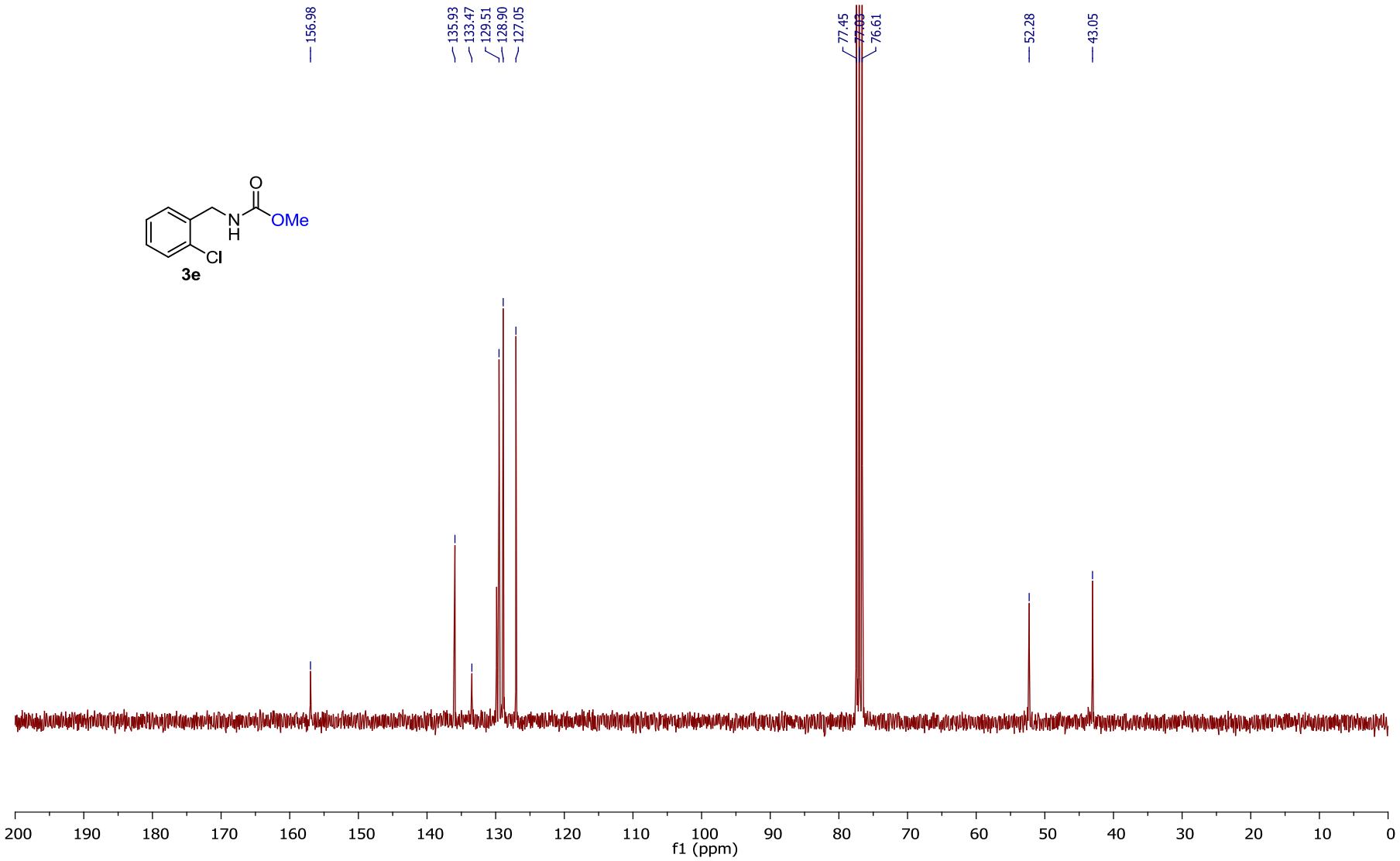
7.33
7.31
7.31
7.28
7.25
7.23
5.06
4.36
4.34
3.72
O
N
H
OMe
Cl
3e
4.5
4.4
4.3
4.30
0.87
2.00
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.47
129.51
128.90
127.05
77.45
77.03
76.61
52.28
43.05
O
N
H
OMe
Cl
3e
200
190
180
170
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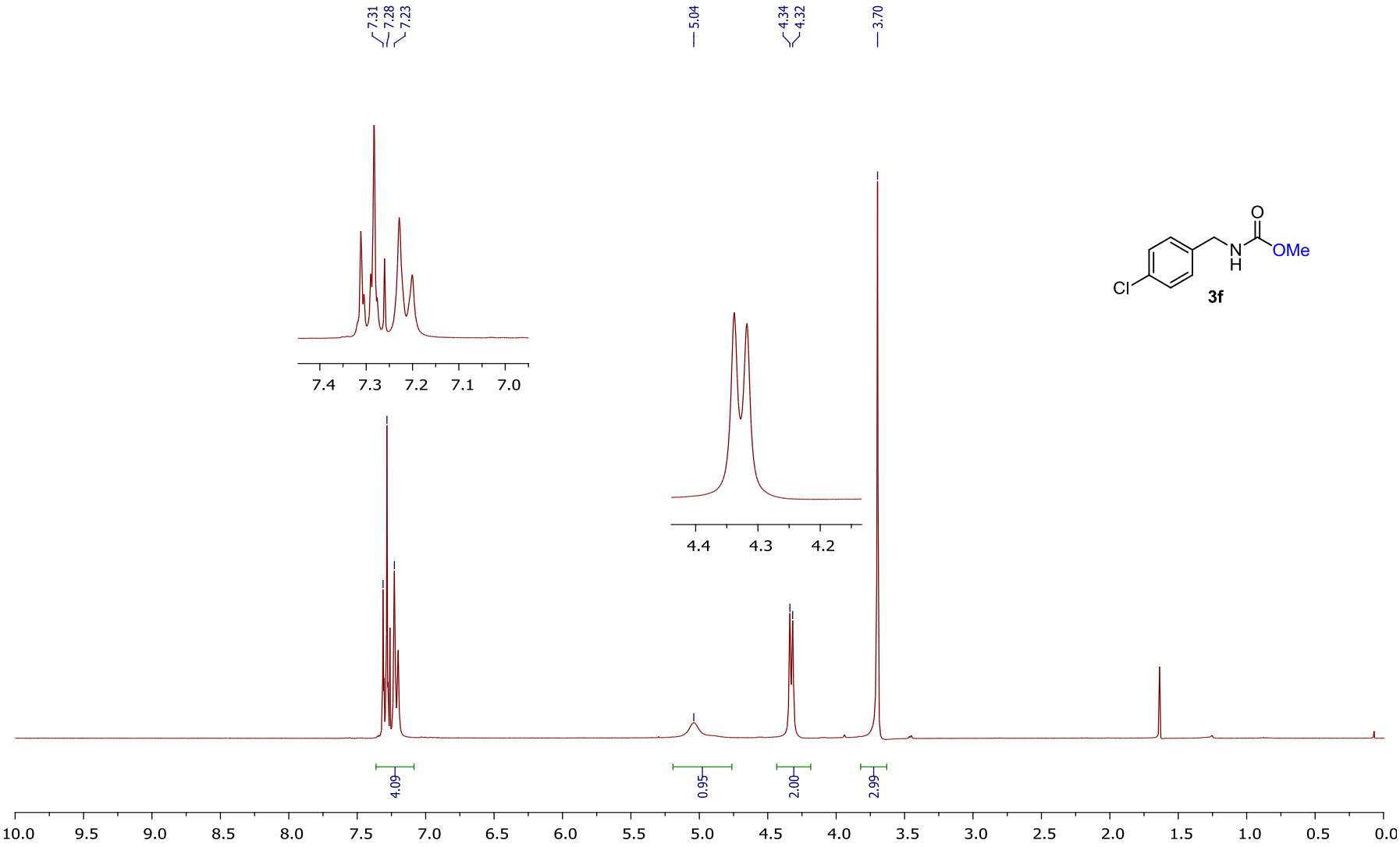
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.28
7.23
5.04
4.34
4.32
3.70
7.4
7.3
7.2
7.1
7.0
4.4
4.3
4.2
O
OMe
N
H
Cl
3f
4.09
0.95
2.00
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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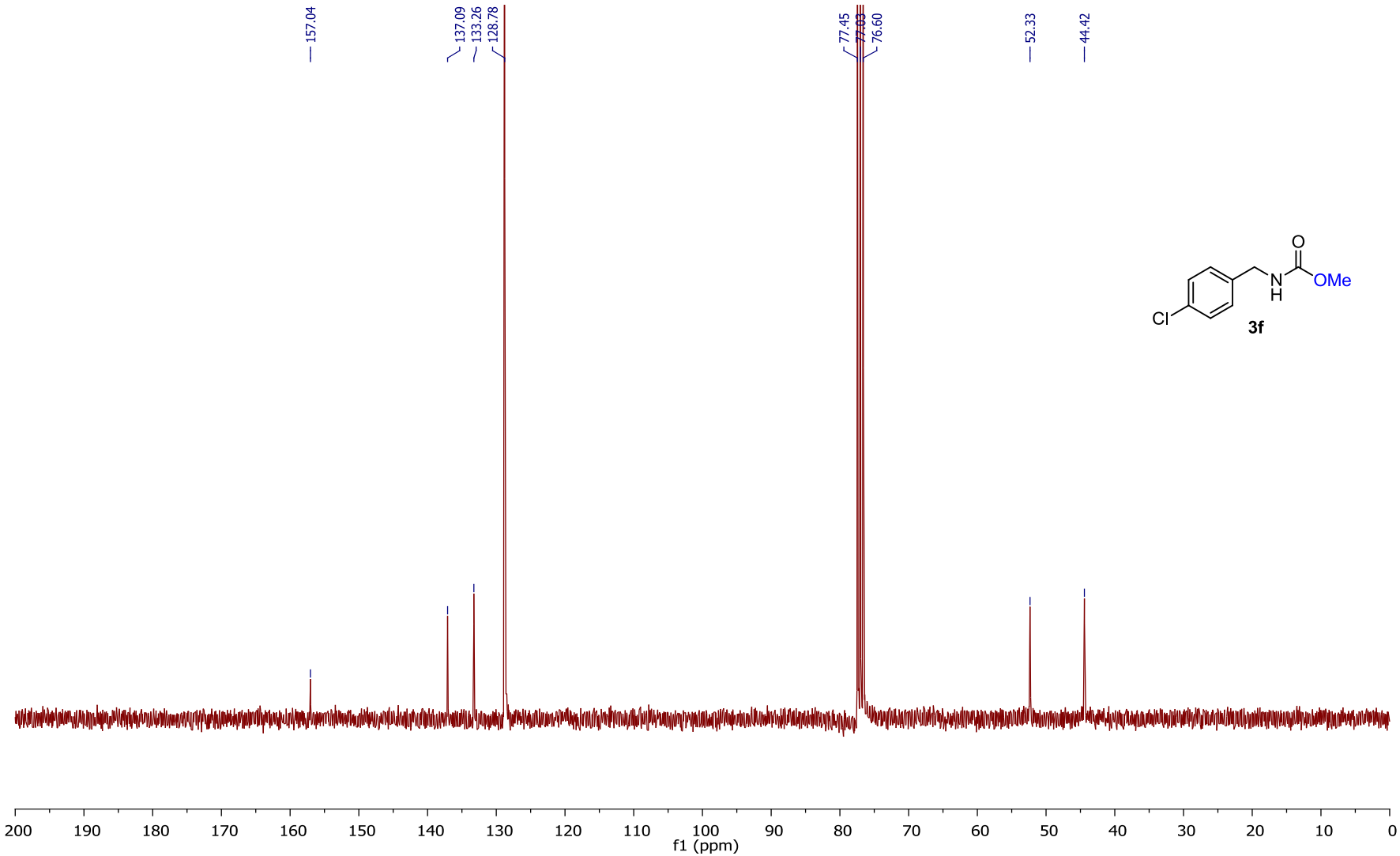
2.0
1.5
1.0
0.5
0.0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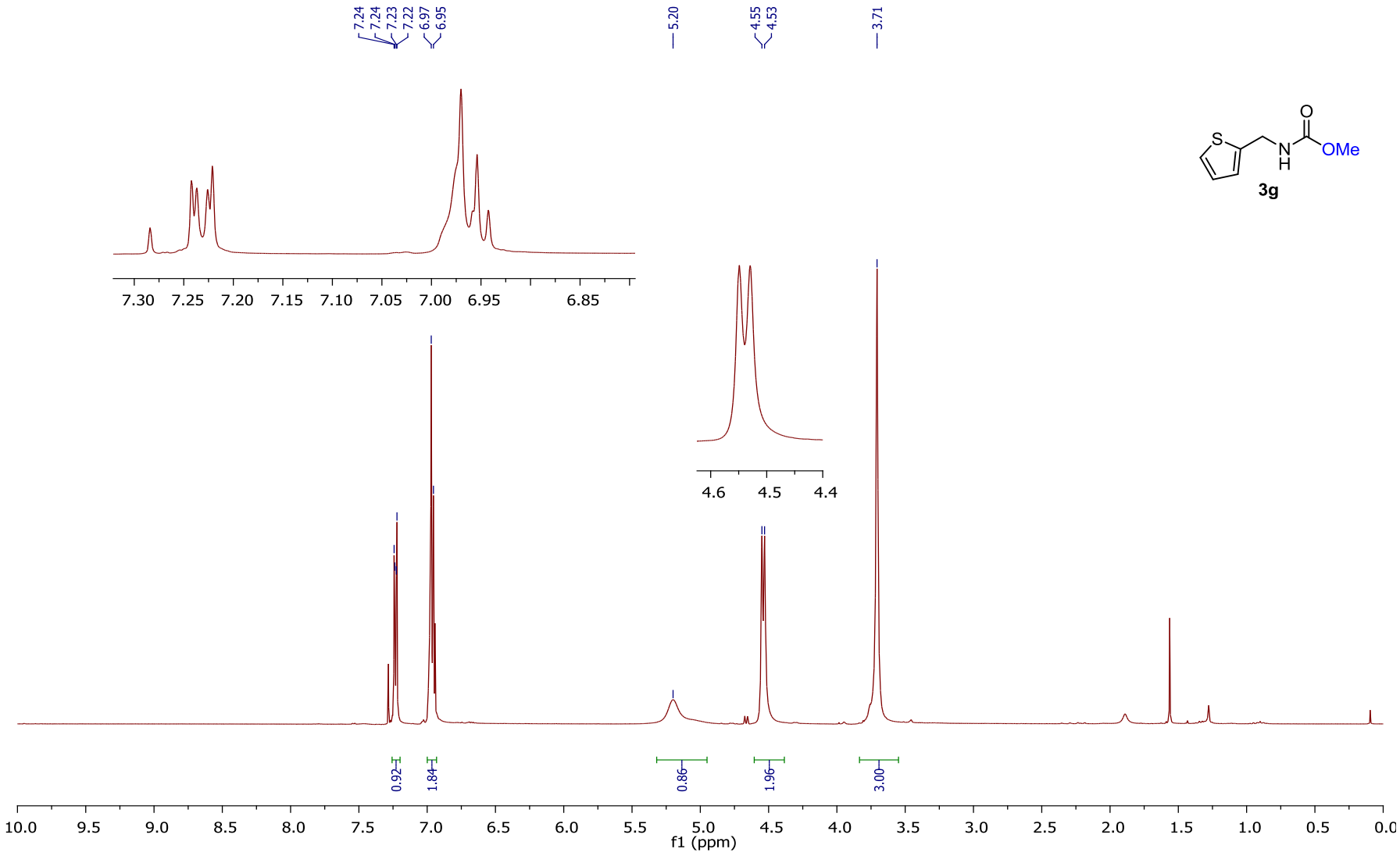
137.09
133.26
128.78
77.45
77.03
76.60
52.33
44.42
O
N
H
OMe
Cl
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.24
7.23
7.22
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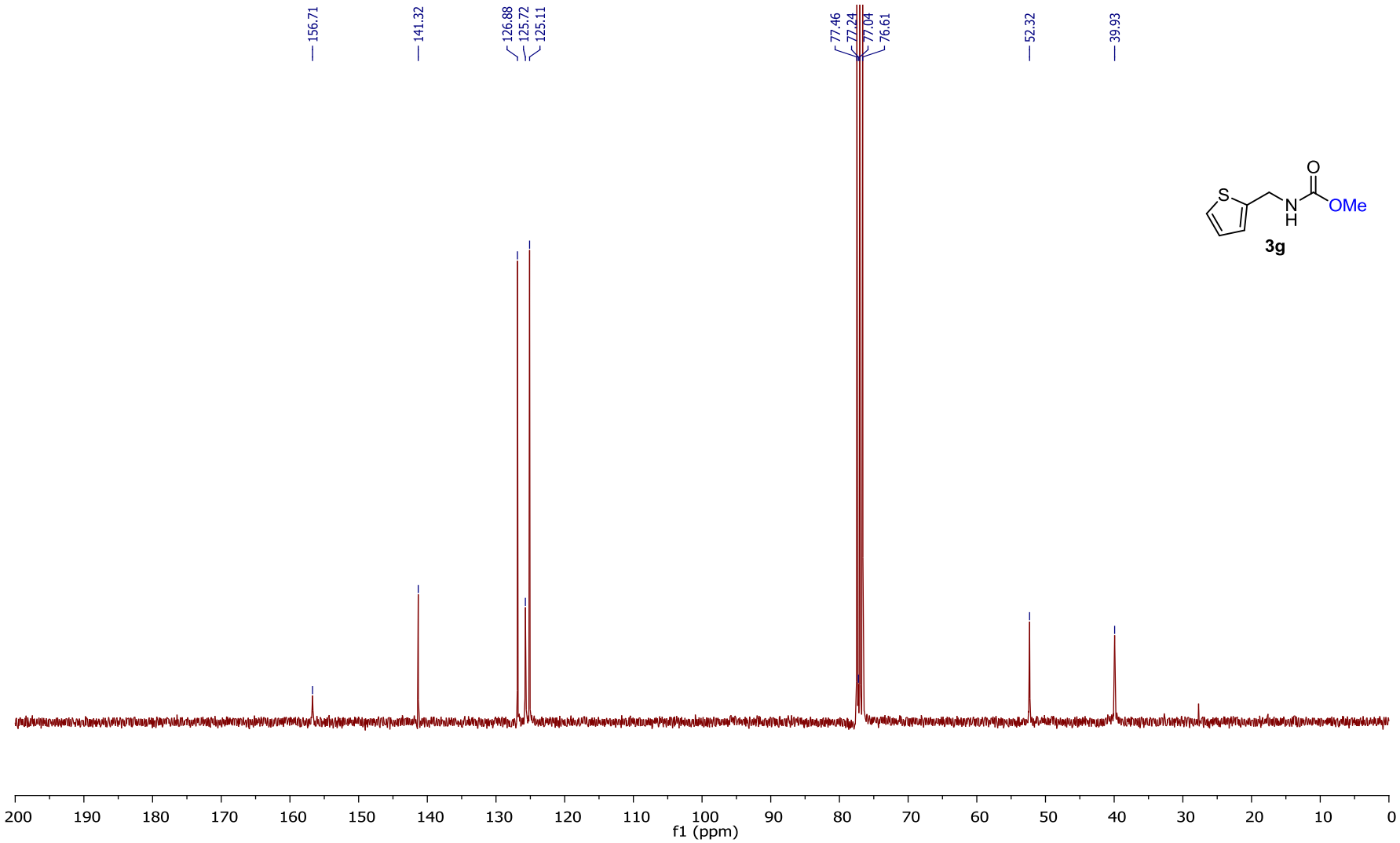
6.95
5.20
4.55
4.53
3.71
7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.85
4.6 4.5 4.4
0.92
1.84
0.86
1.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

S
N
H
O
OMe

3g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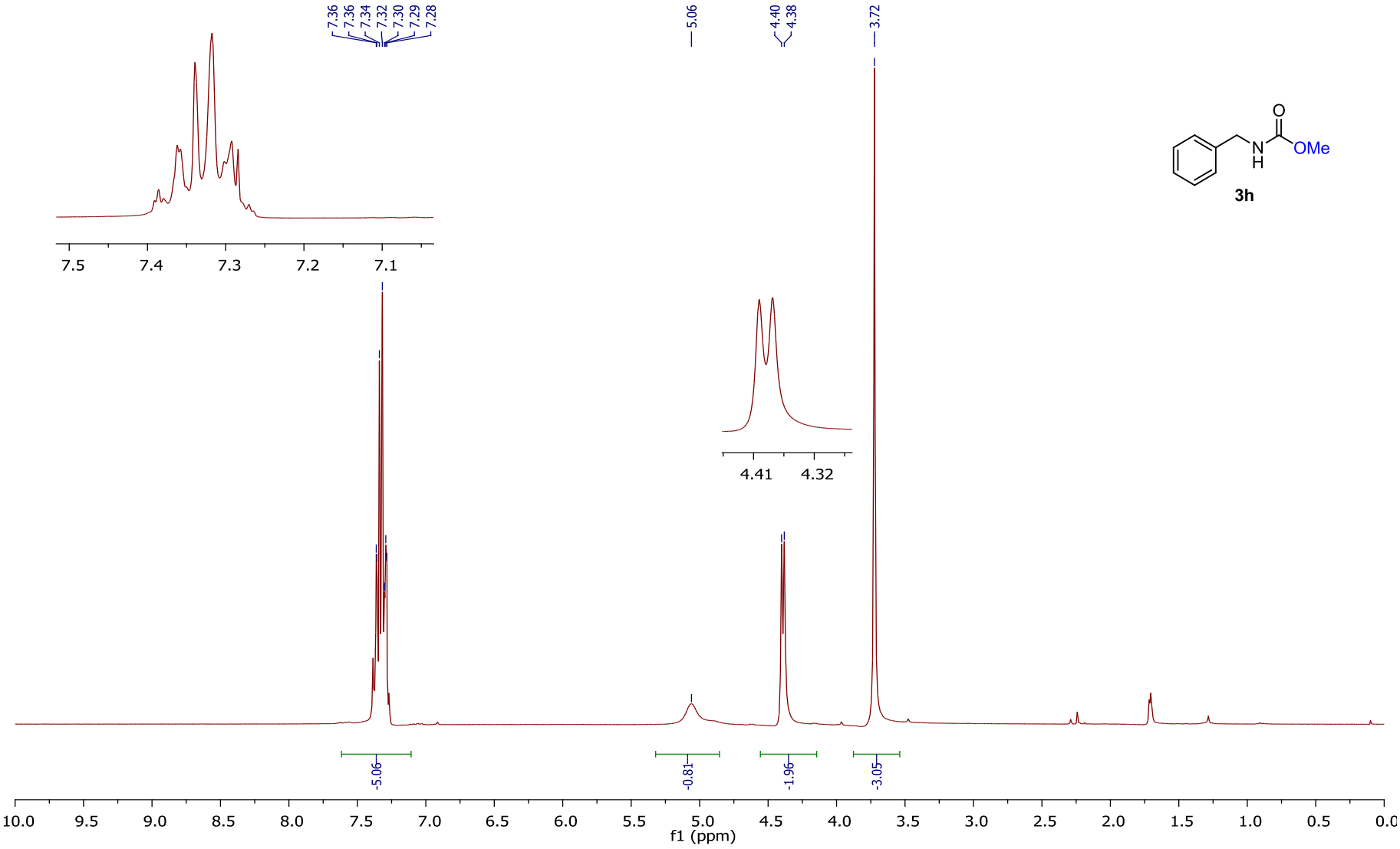
141.32
126.88
125.72
125.11
77.46
77.24
77.04
76.61
52.32
39.93
S
N
H
O
OMe
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.36
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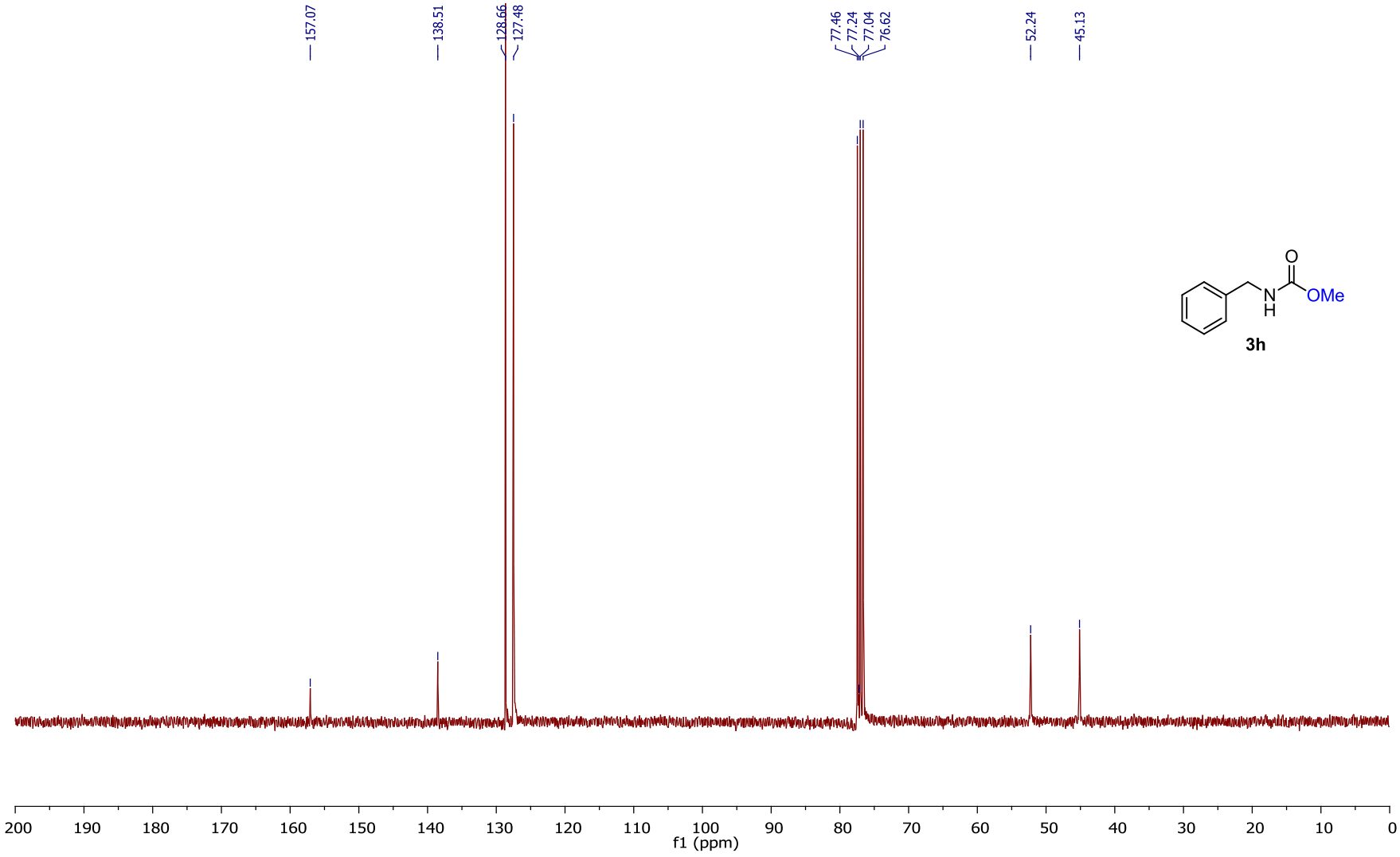
7.32
7.30
7.29
7.28
5.06
4.40
4.38
3.72
7.5
7.4
7.3
7.2
7.1
4.41
4.32
O
N
H
OMe
3h
-5.06
-0.81
-1.96
-3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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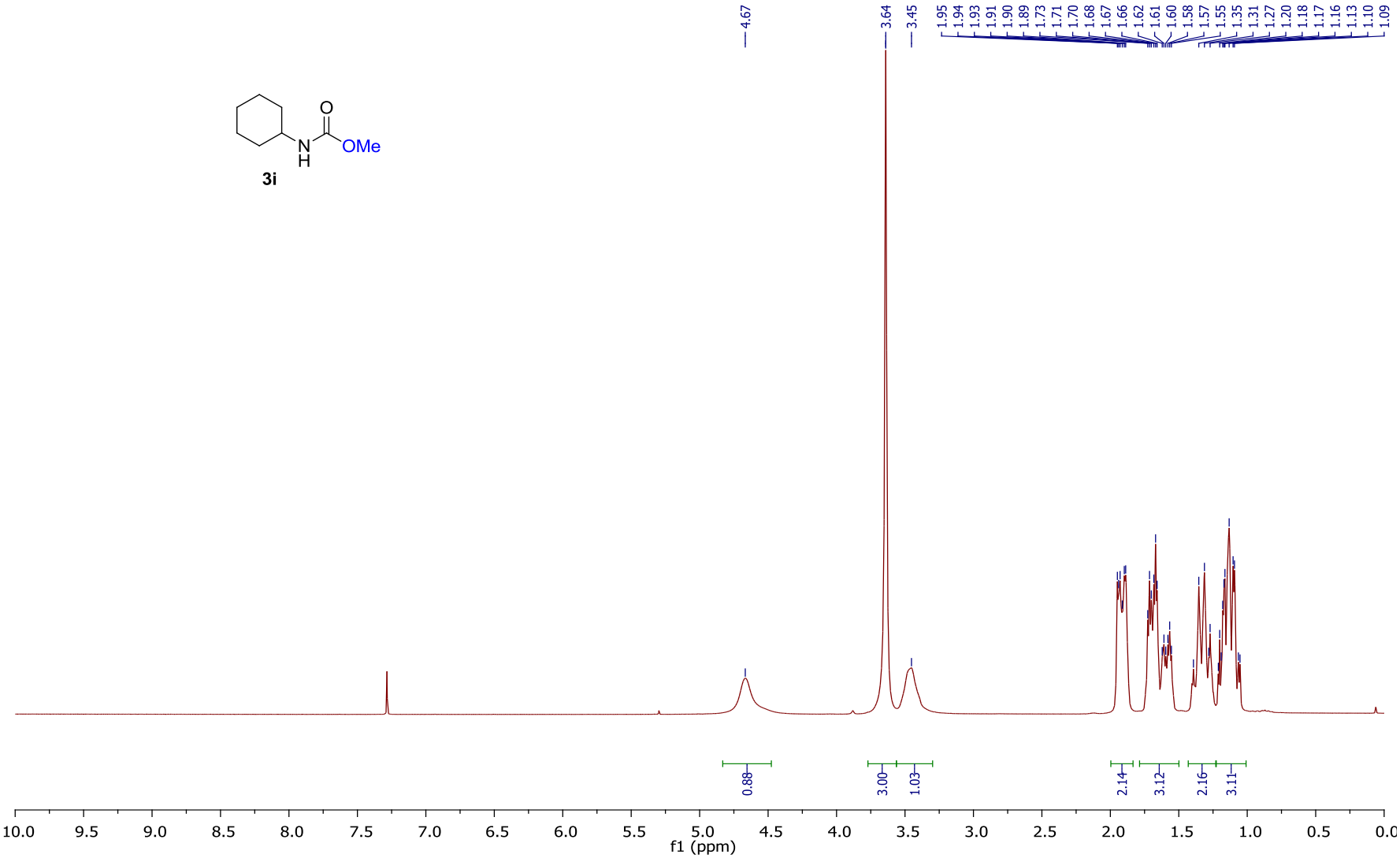
77.24
77.04
76.62
52.24
45.13
O
N
H
OMe
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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1.93
1.91
1.90
1.89
1.73
1.71
1.70
1.68
1.67
1.66
1.62
1.61
1.60
1.58
1.57
1.55
1.35
1.31
1.27
1.20
1.18
1.17
1.16
1.13
1.10
1.09
O
N
H
OMe
3i
0.88
3.00
1.03
2.14
3.12
2.16
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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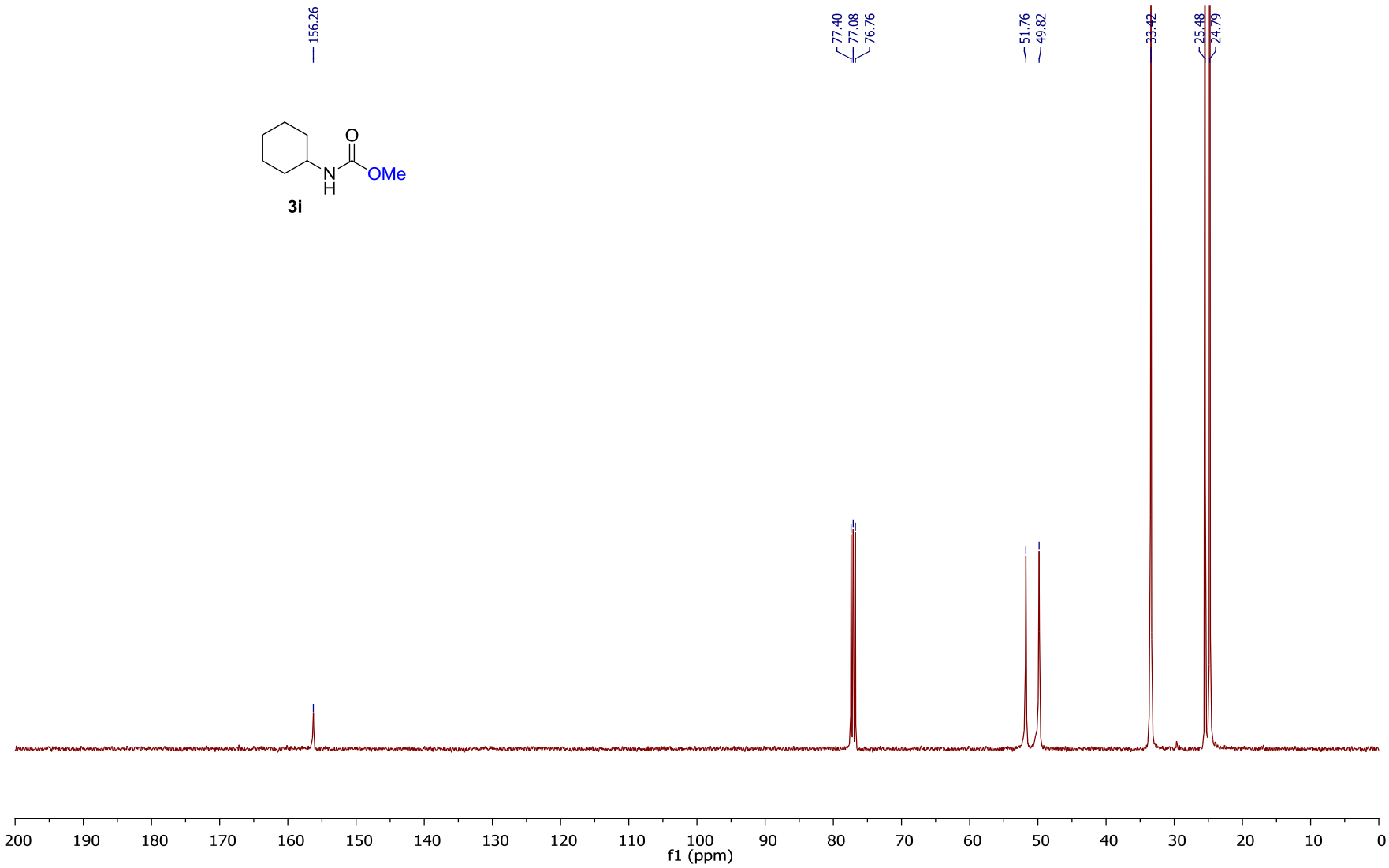
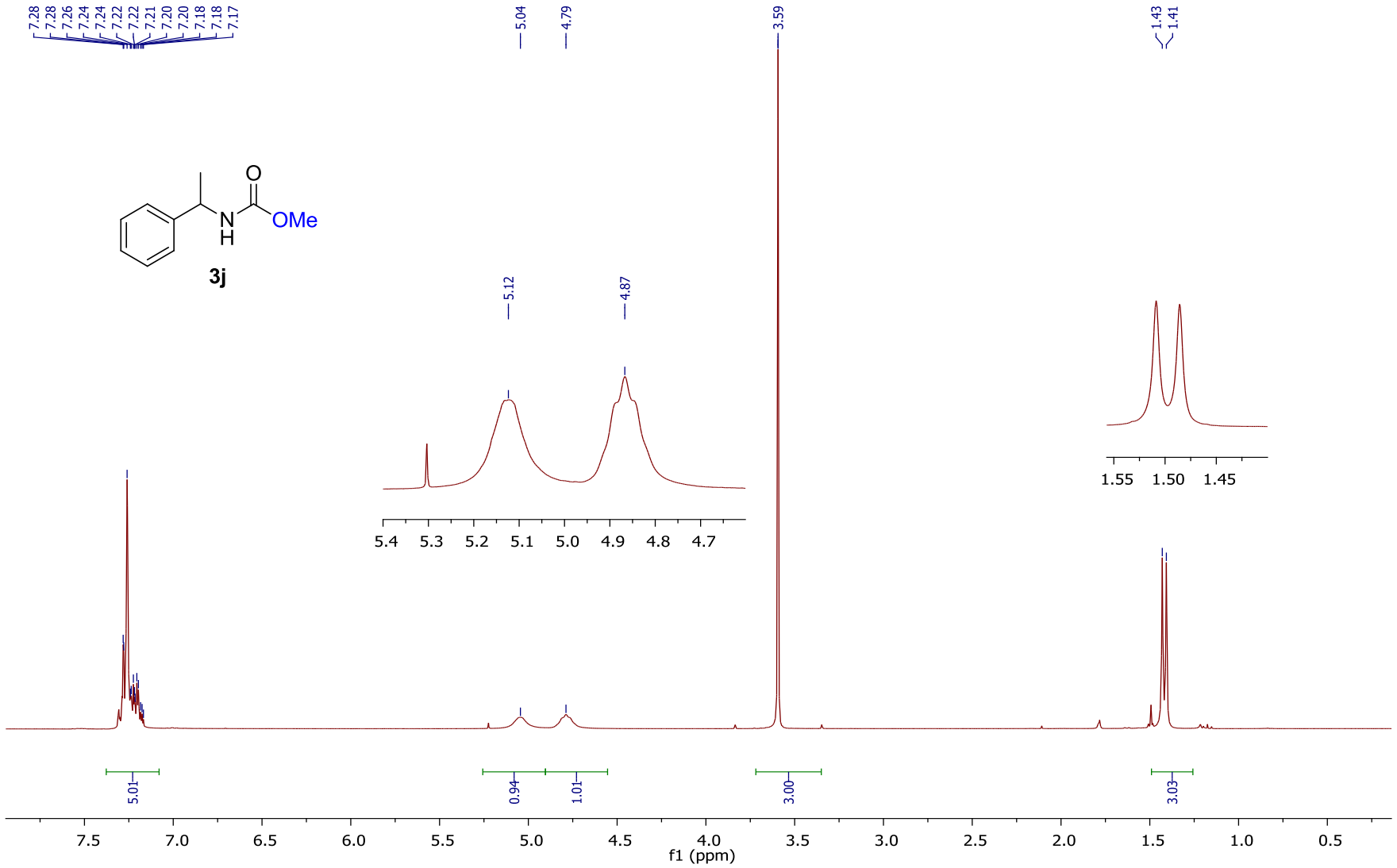
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.26
77.40
77.08
76.76
51.76
49.82
33.42
25.48
24.79
O
N
H
OMe
3i
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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7.28
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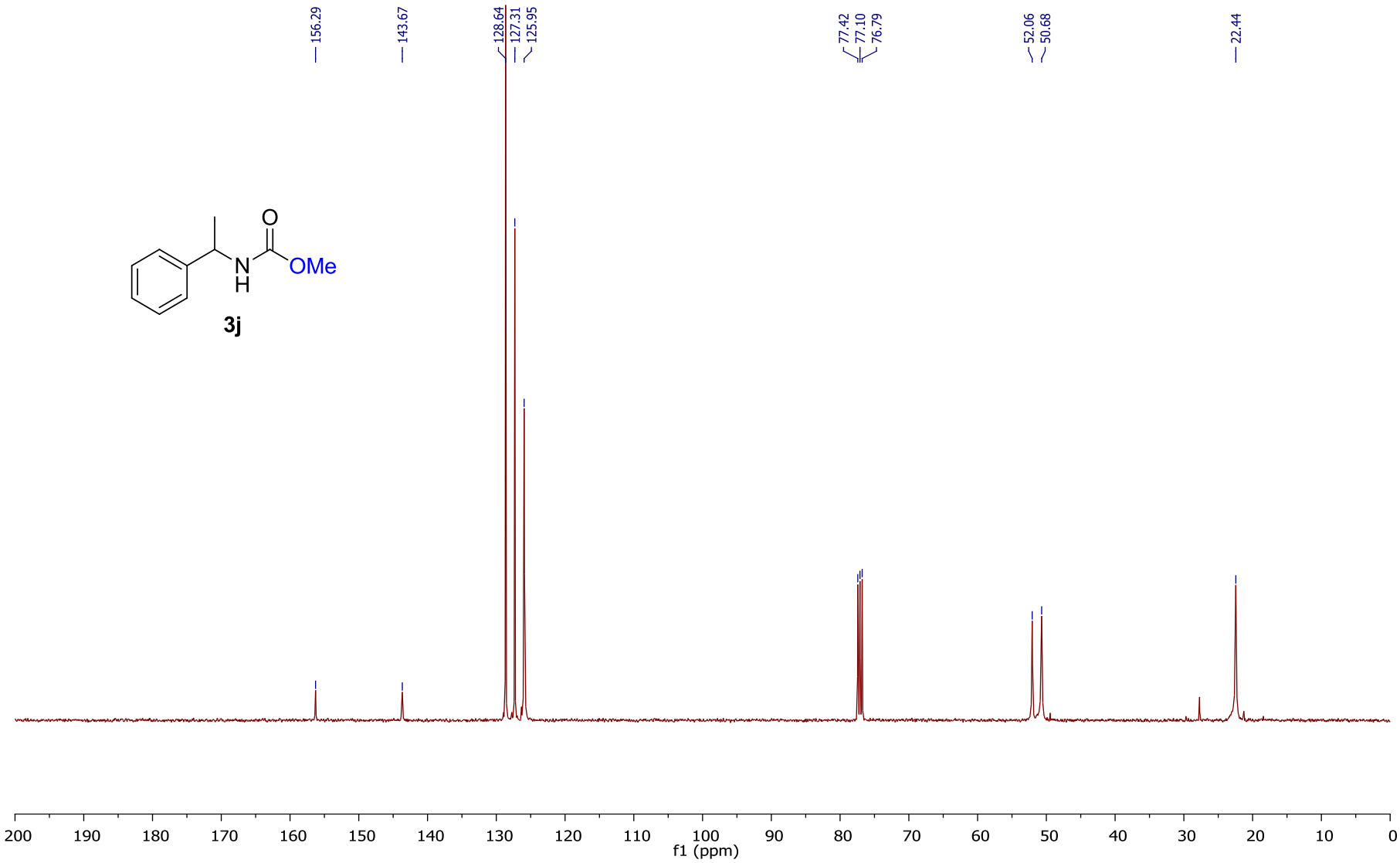
7.24
7.24
7.22
7.22
7.21
7.20
7.20
7.18
7.18
7.17
5.04
4.79
3.59
1.43
1.41
O
N
H
OMe
3j
5.12
4.87
5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7
1.55 1.50 1.45
5.01
0.94
1.01
3.00
3.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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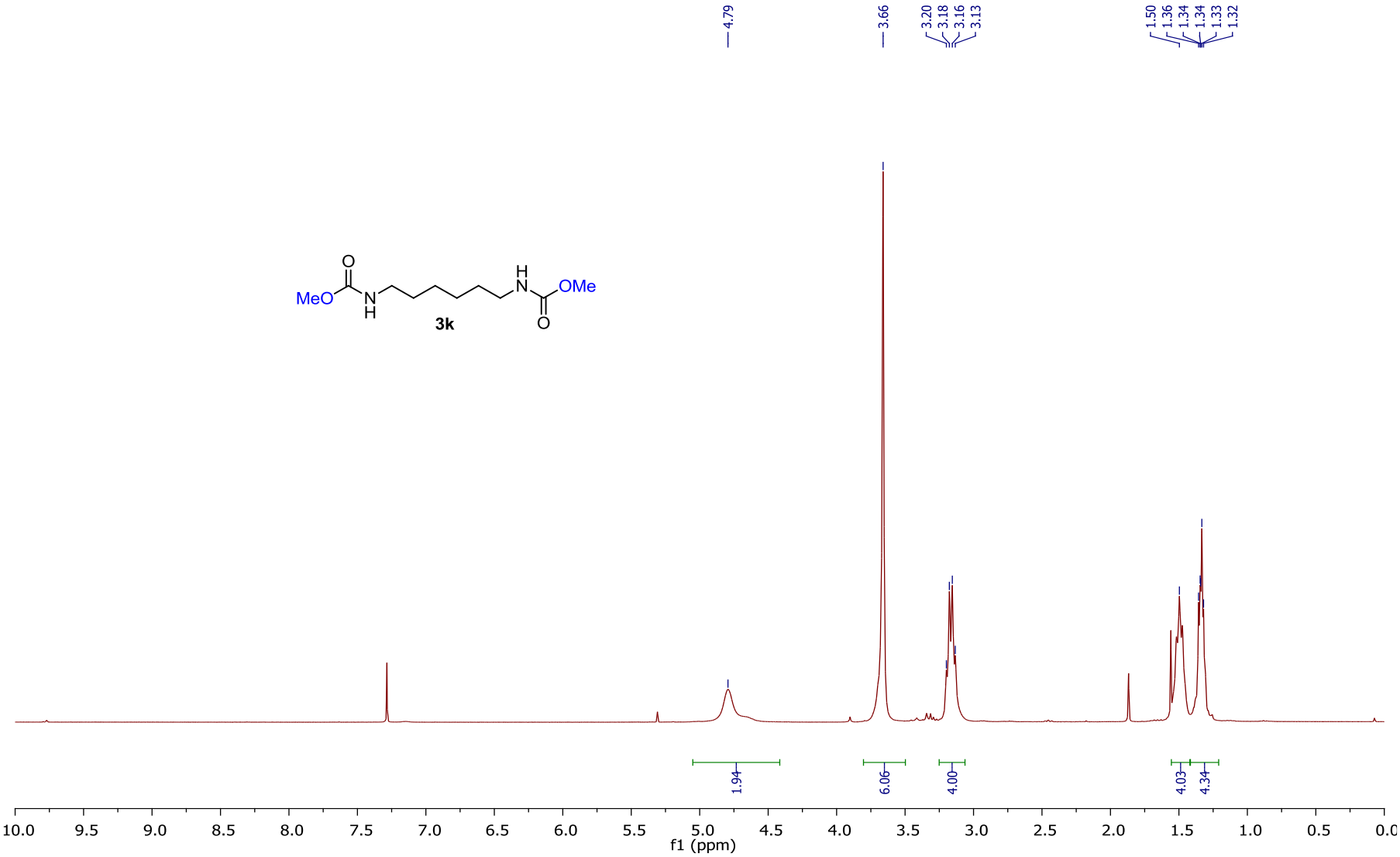
127.31
125.95
77.42
77.10
76.79
52.06
50.68
22.44
O
N
H
OMe
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.18
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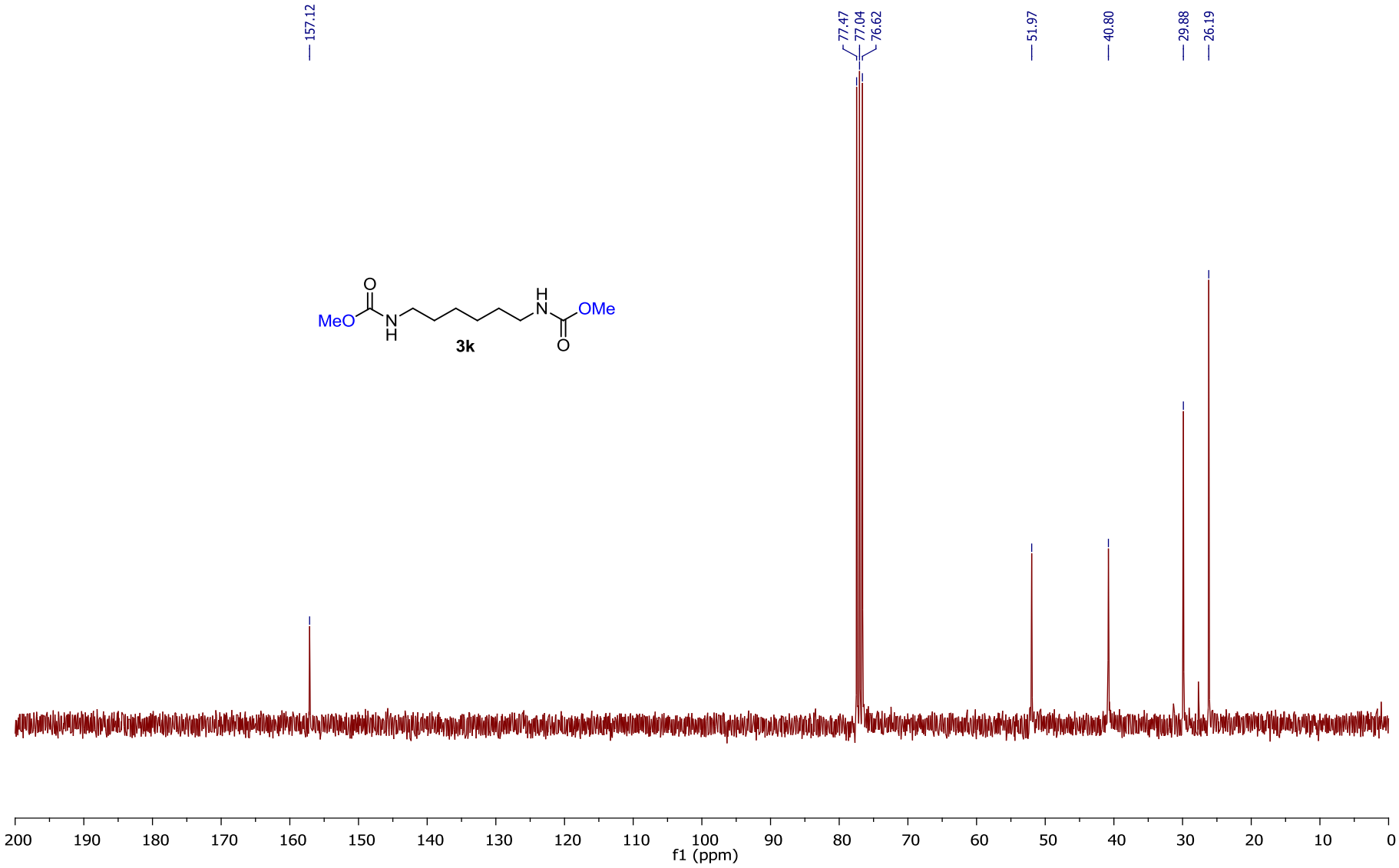
3.13
1.50
1.36
1.34
1.34
1.33
1.32
MeO
OMe
3k
1.94
6.06
4.00
4.03
4.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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76.62
51.97
40.80
29.88
26.19
MeO
OMe
3k
200
190
180
170
160
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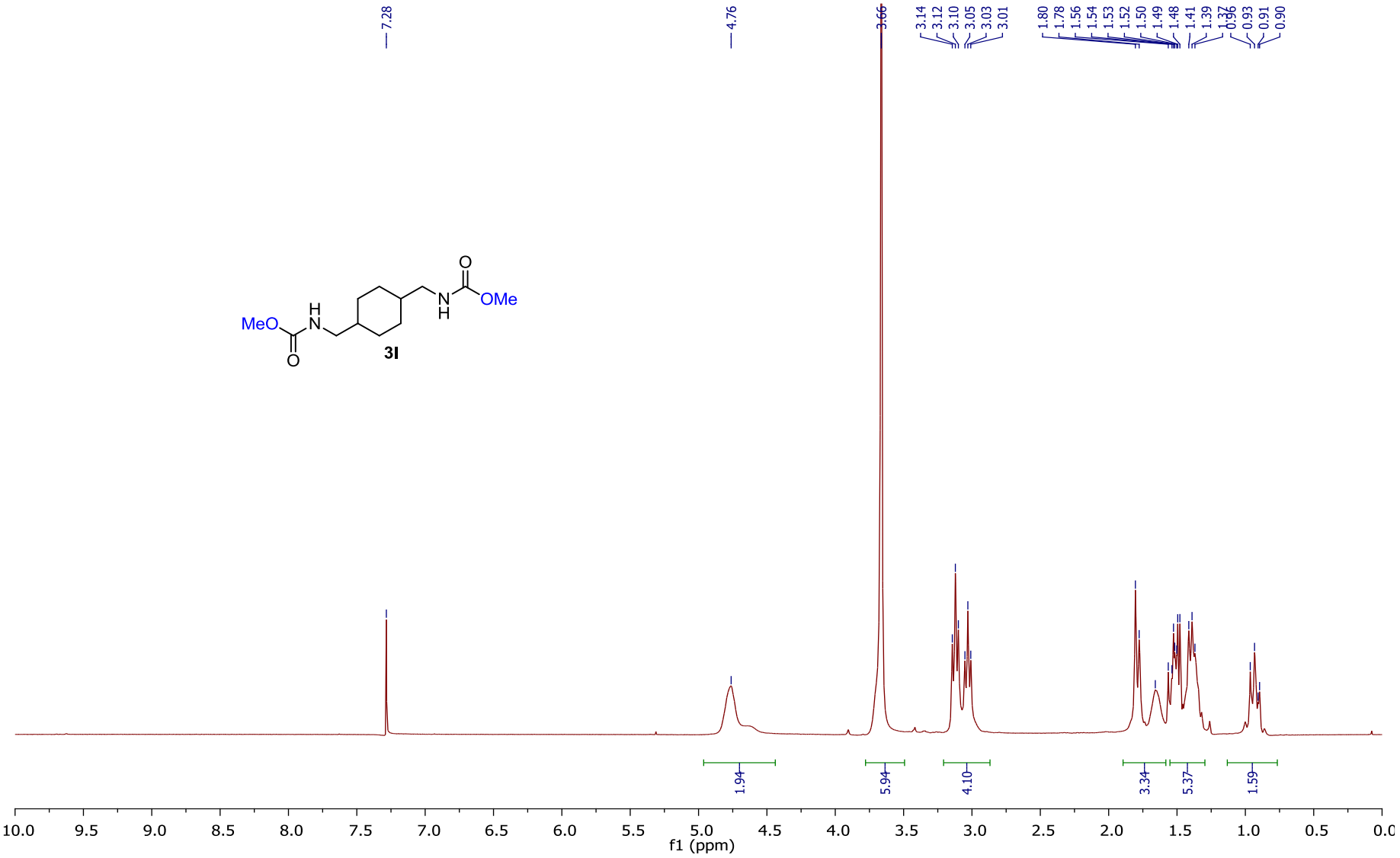
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.14
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3.10
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3.03
3.01
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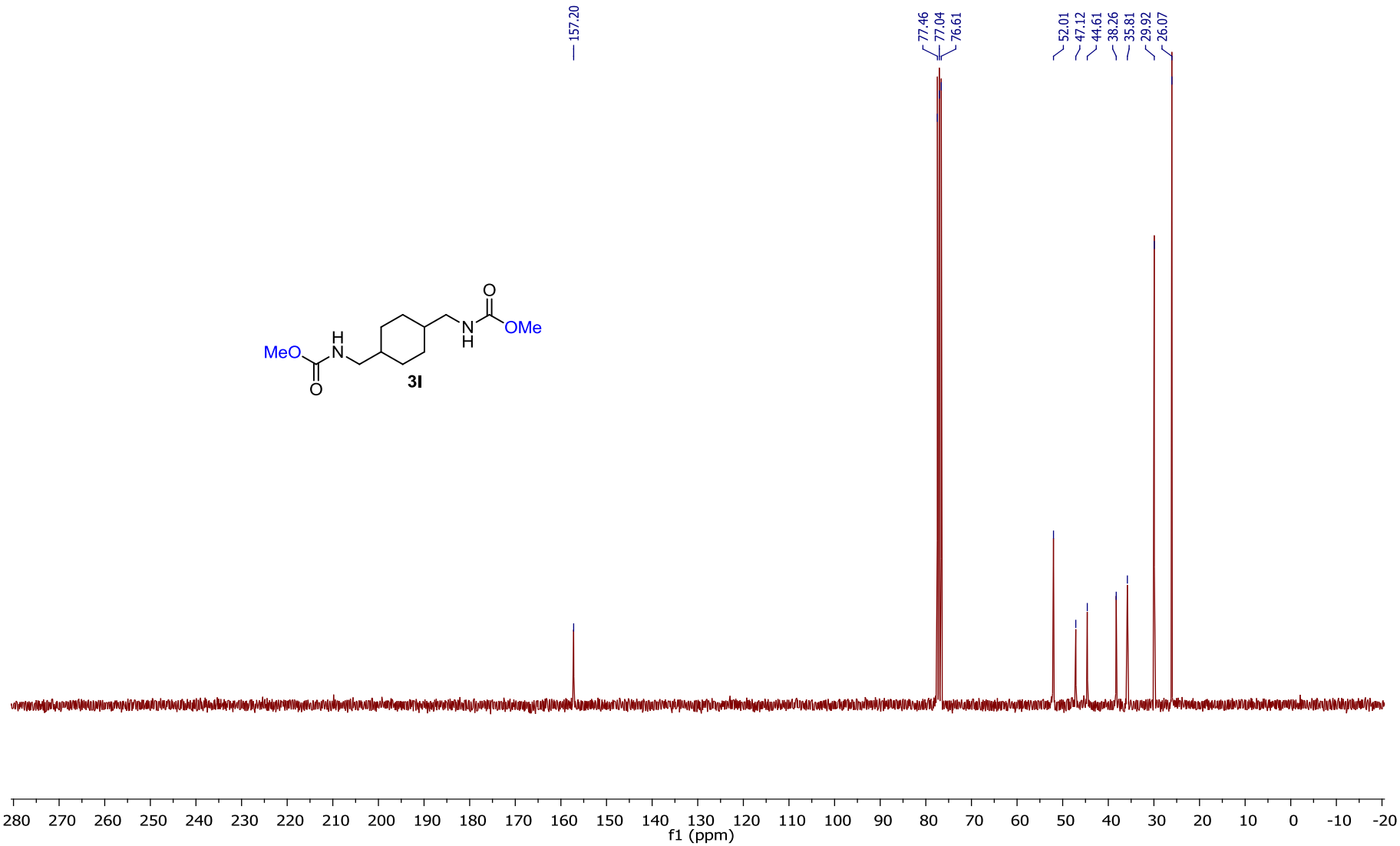
1.78
1.56
1.54
1.53
1.52
1.50
1.49
1.48
1.41
1.39
0.93
0.91
0.90
MeO
OMe
3l
1.94
5.94
4.10
3.34
5.37
1.59
f1 (ppm)


157.20
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77.04
76.61
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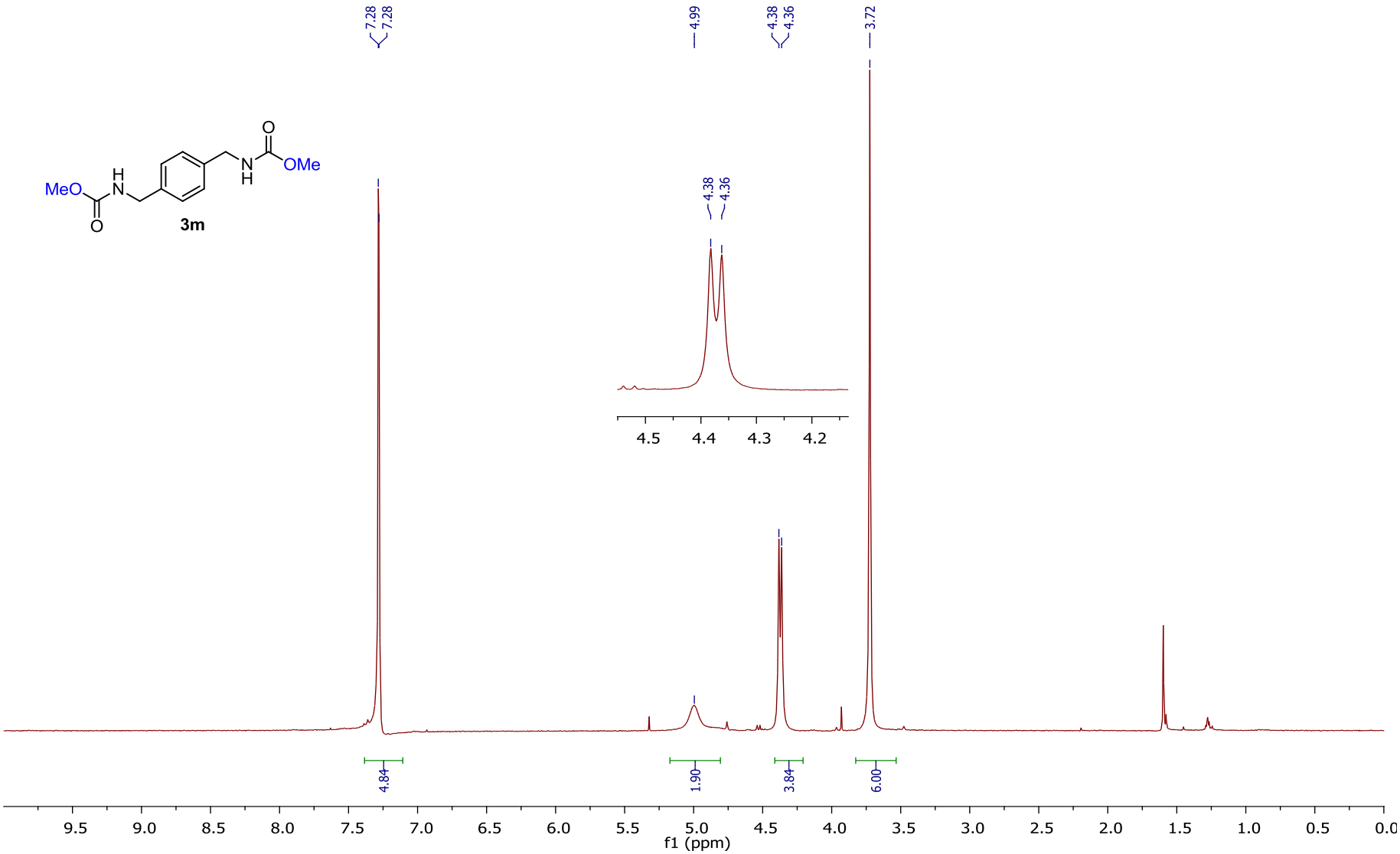
47.12
44.61
38.26
35.81
29.92
26.07
MeO
OMe
3l
f1 (ppm)


7.28
7.28
4.99
4.38
4.36
3.72
MeO
OMe
3m
4.38
4.36
4.5
4.4
4.3
4.2
4.84
1.90
3.84
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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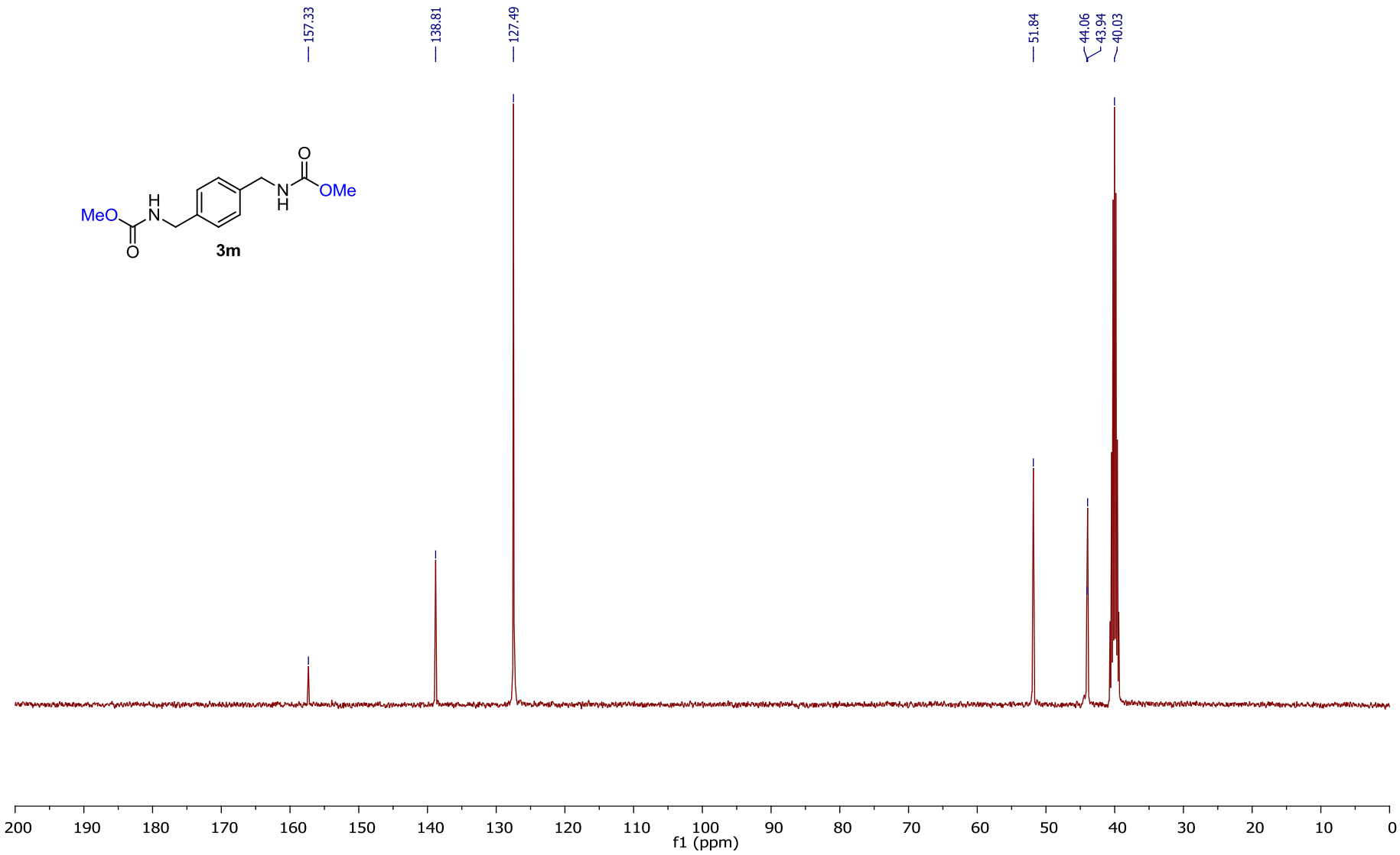
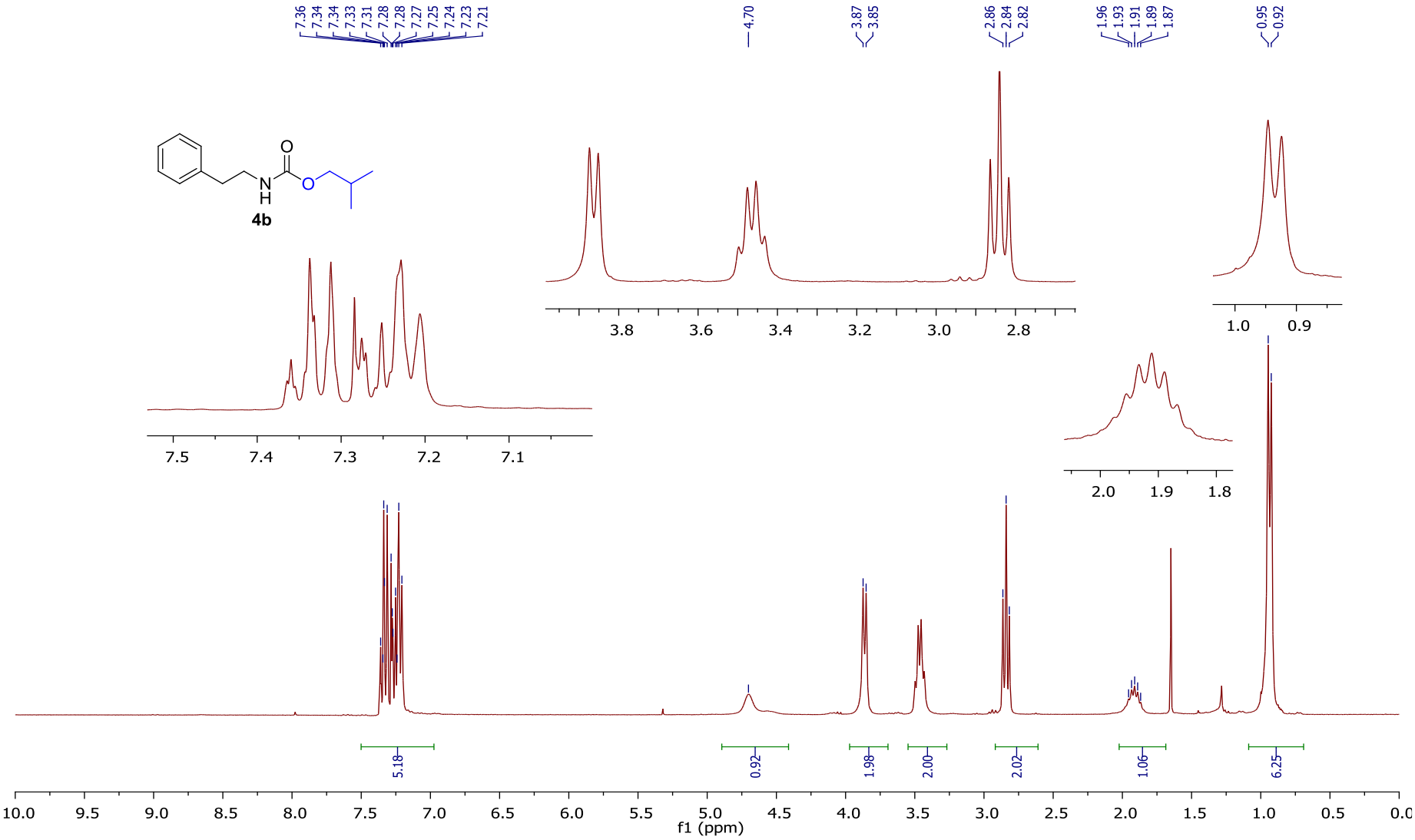
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.33
138.81
127.49
51.84
44.06
43.94
40.03
MeO
O
H
N
O
N
H
OMe
3m
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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7.34
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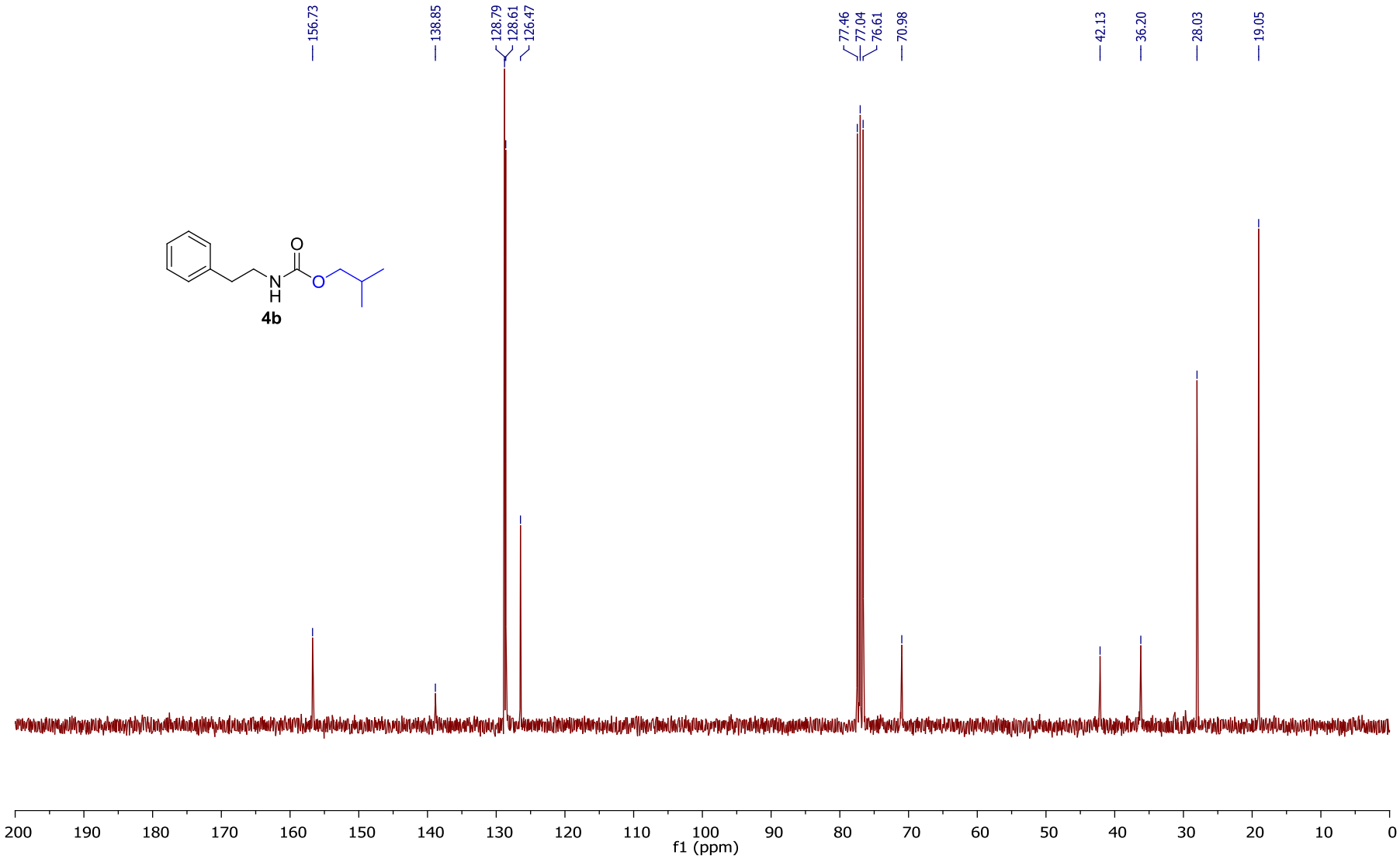
7.28
7.28
7.27
7.25
7.24
7.23
7.21
4.70
3.87
3.85
2.86
2.84
2.82
1.96
1.93
1.91
1.89
1.87
0.95
0.92
4b
7.5
7.4
7.3
7.2
7.1
3.8
3.6
3.4
3.2
3.0
2.8
1.0
0.9
2.0
1.9
1.8
5.18
0.92
1.98
2.00
2.02
1.06
6.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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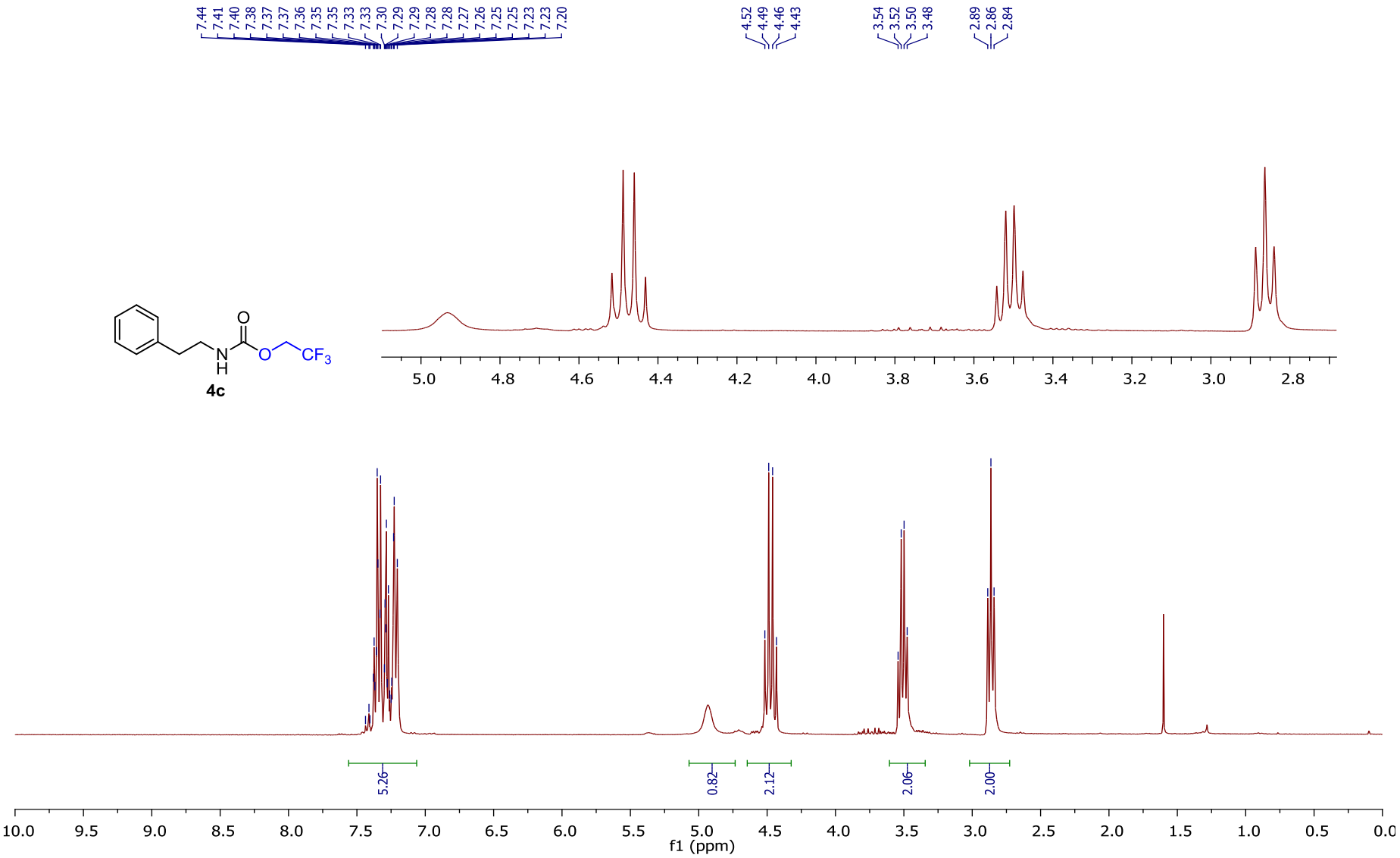
138.85
128.79
128.61
126.47
77.46
77.04
76.61
70.98
42.13
36.20
28.03
19.05
O
N
H
O
4b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.36
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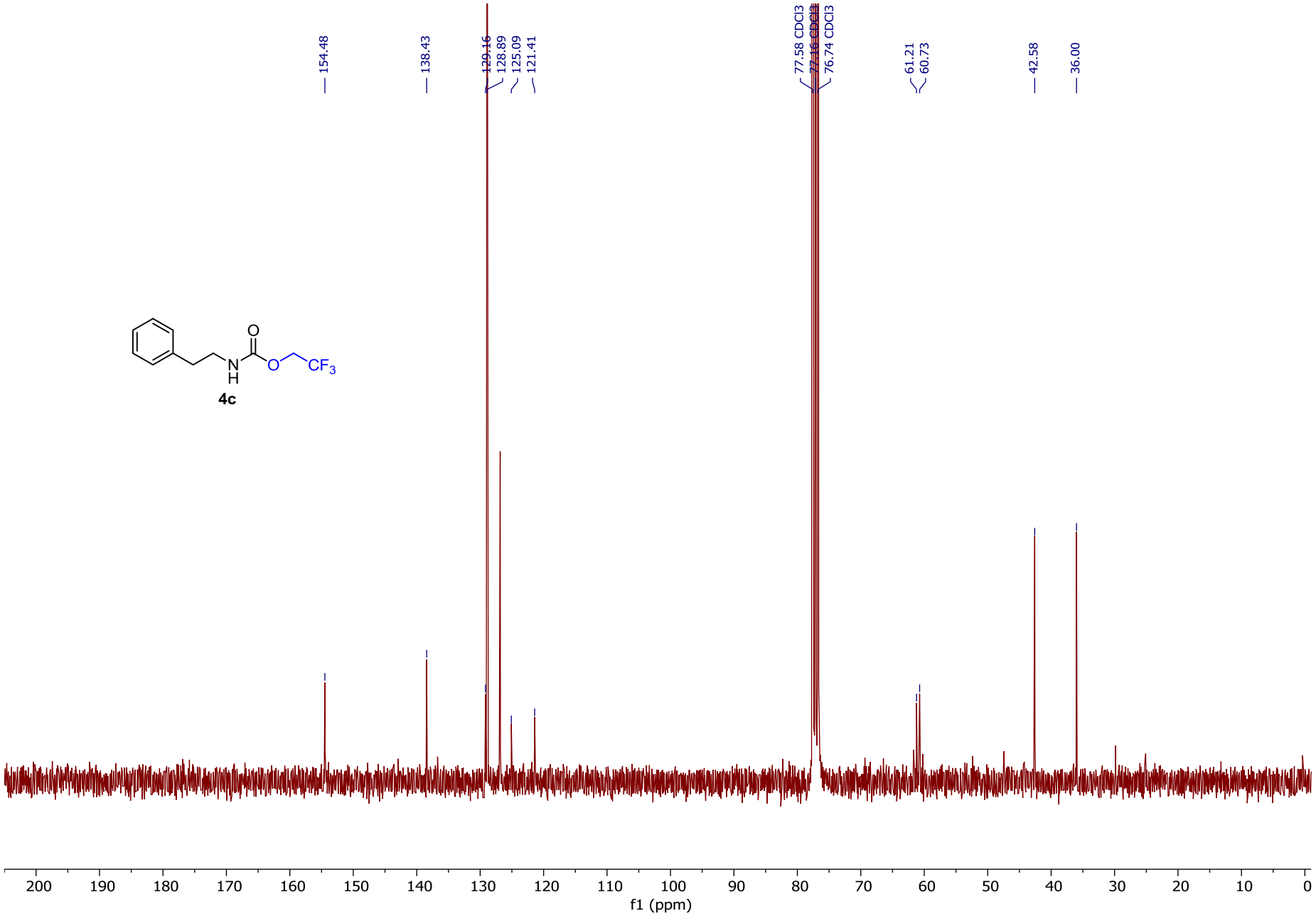
7.35
7.33
7.33
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.25
7.23
7.23
7.20
4.52
4.49
4.46
4.43
3.54
3.52
3.50
3.48
2.89
2.86
2.84
4c
5.26
0.82
2.12
2.06
2.00
f1 (ppm)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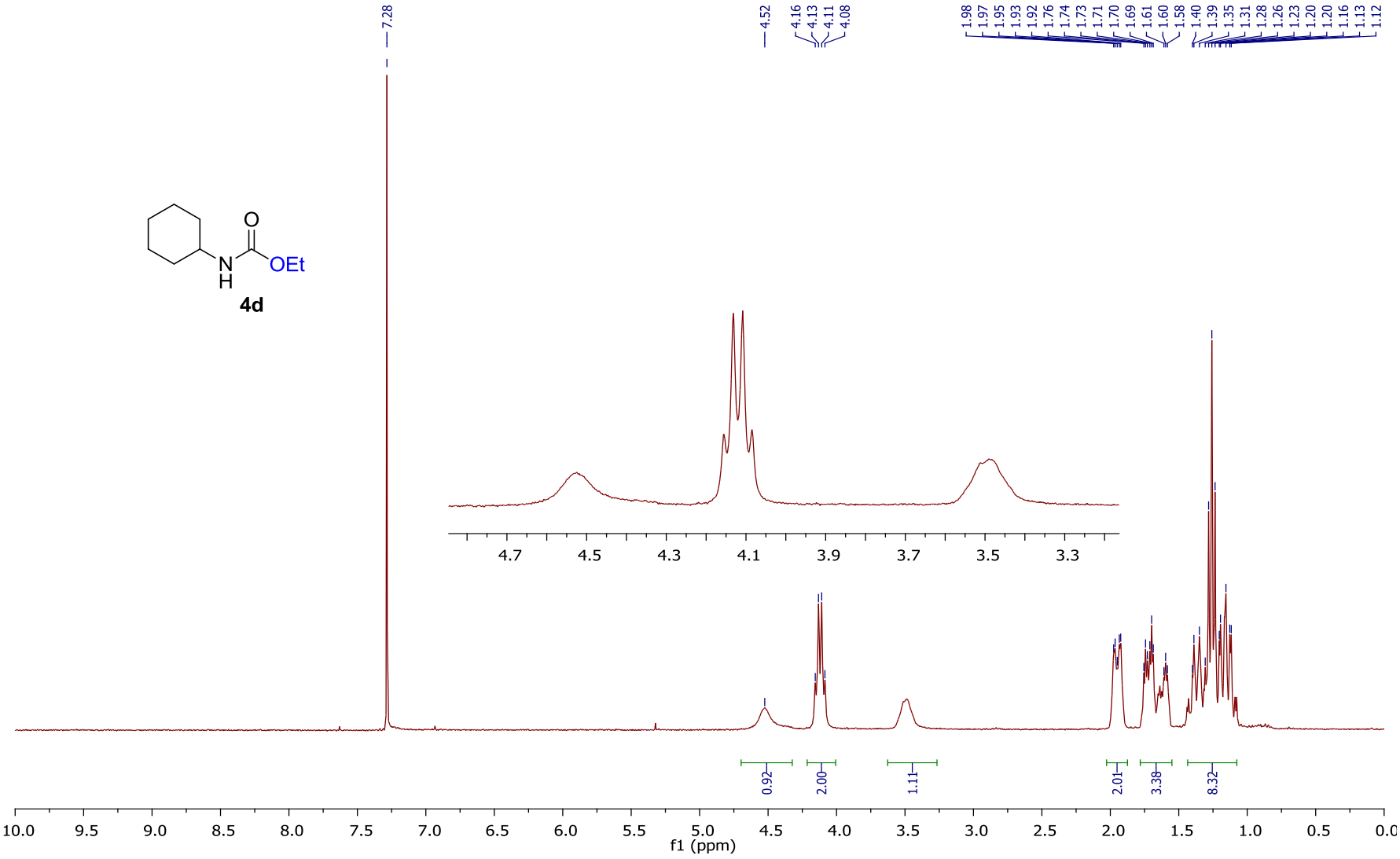
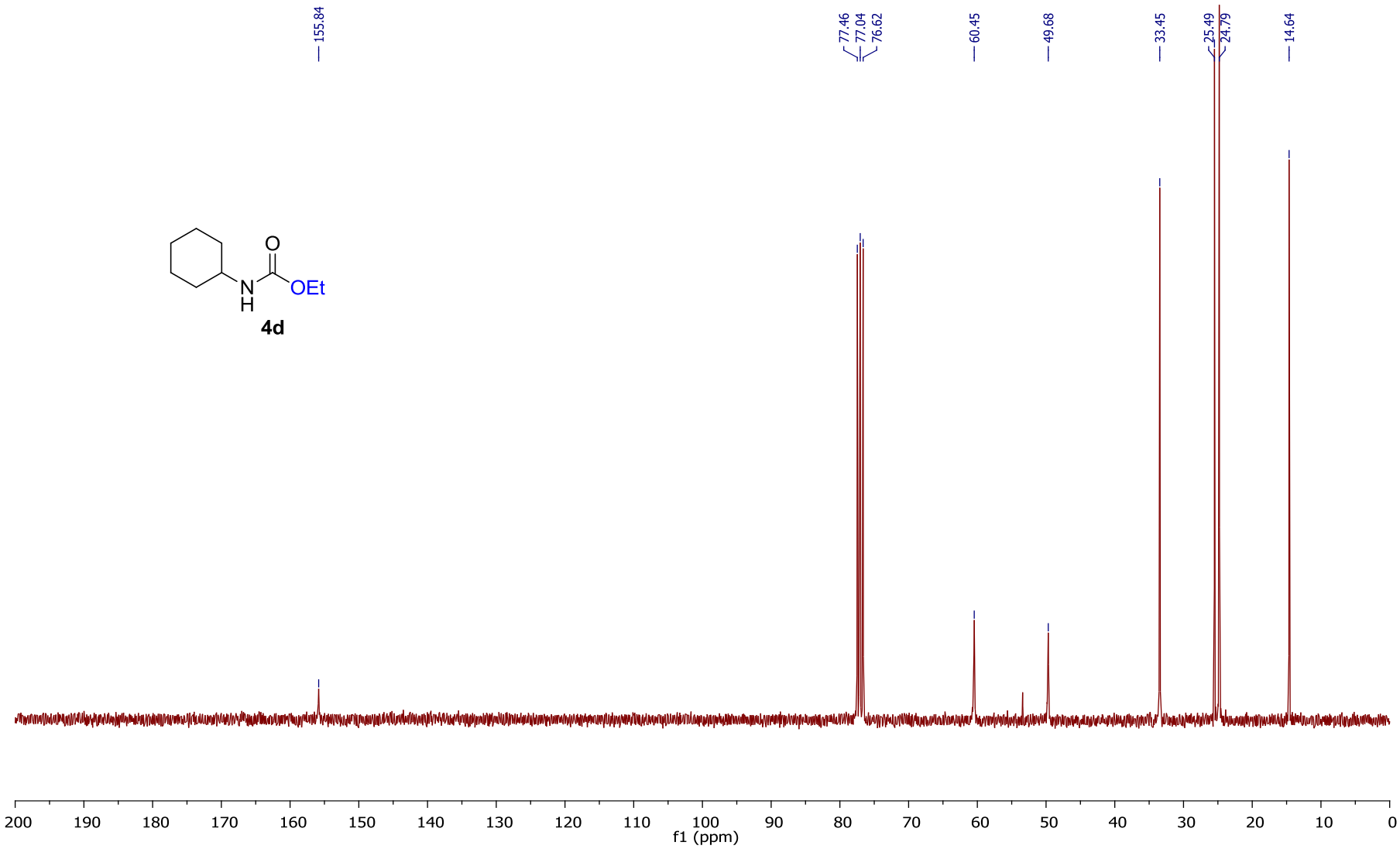
138.43
129.16
128.89
125.09
121.41
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
61.21
60.73
42.58
36.00
O
N
H
O
CF3
4c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.28
4.52
4.16
4.13
4.11
4.08
1.98
1.97
1.95
1.93
1.92
1.76
1.74
1.73
1.71
1.70
1.69
1.61
1.60
1.58
1.40
1.39
1.35
1.31
1.28
1.26
1.23
1.20
1.16
1.13
1.12
O
N
H
OEt
4d
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
0.92
2.00
1.11
2.01
3.38
8.32
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
f1 (ppm)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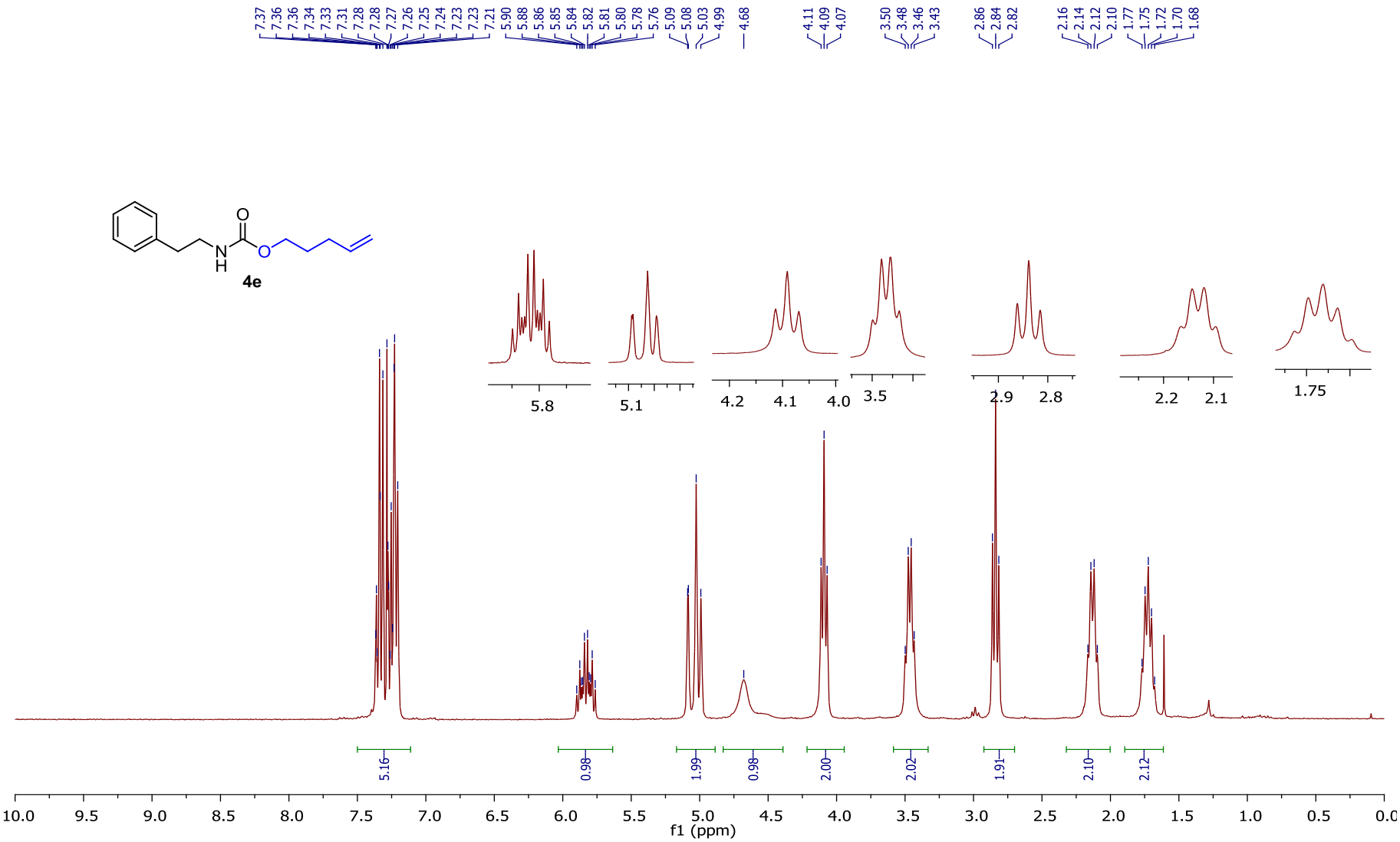
77.46
77.04
76.62
60.45
49.68
33.45
25.49
24.79
14.64
O
N
H
OEt
4d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37
7.36
7.36
7.34
7.33
7.31
7.28
7.28
7.27
7.26
7.25
7.24
7.23
7.23
7.21
5.90
5.88
5.86
5.85
5.84
5.82
5.81
5.80
5.78
5.76
5.09
5.08
5.03
4.99
4.68
4.11
4.09
4.07
3.50
3.48
3.46
3.43
2.86
2.84
2.82
2.16
2.14
2.12
2.10
1.77
1.75
1.72
1.70
1.68
4e
5.8
5.1
4.2
4.1
4.0
3.5
2.9
2.8
2.2
2.1
1.75
5.16
0.98
1.99
0.98
2.00
2.02
1.91
2.10
2.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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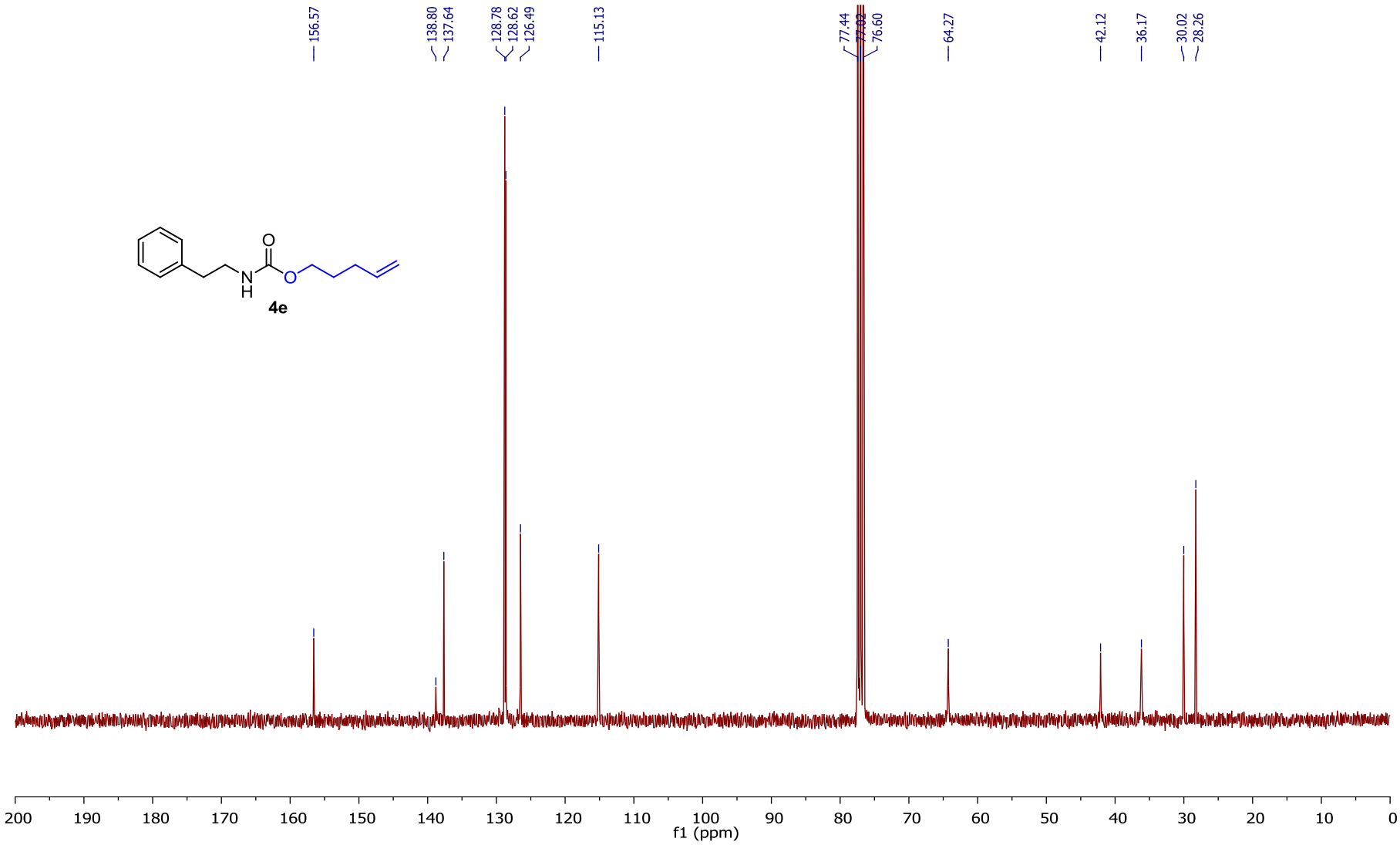
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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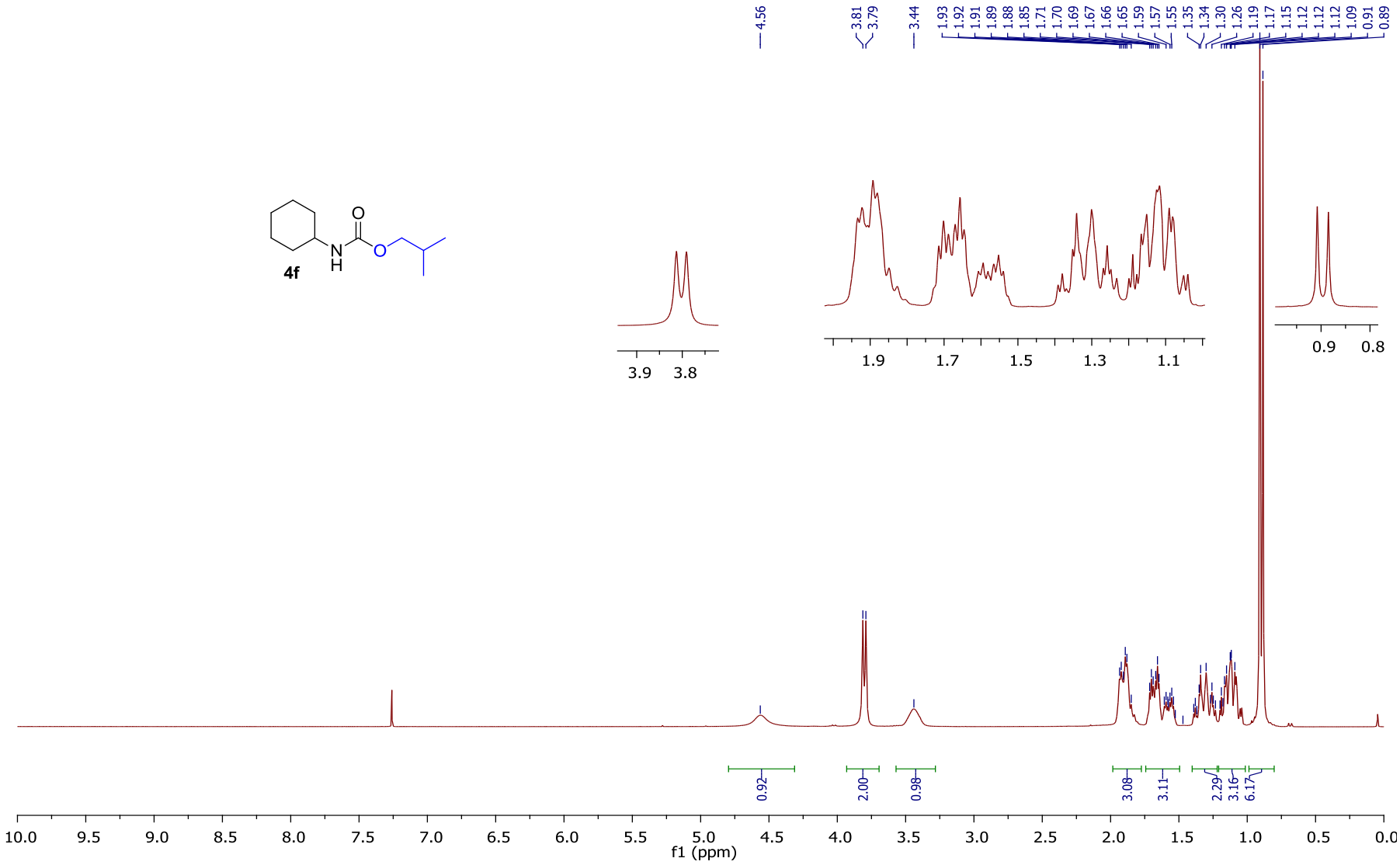
128.62
126.49
115.13
77.44
77.00
76.60
64.27
42.12
36.17
30.02
28.26
4e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4f
4.56
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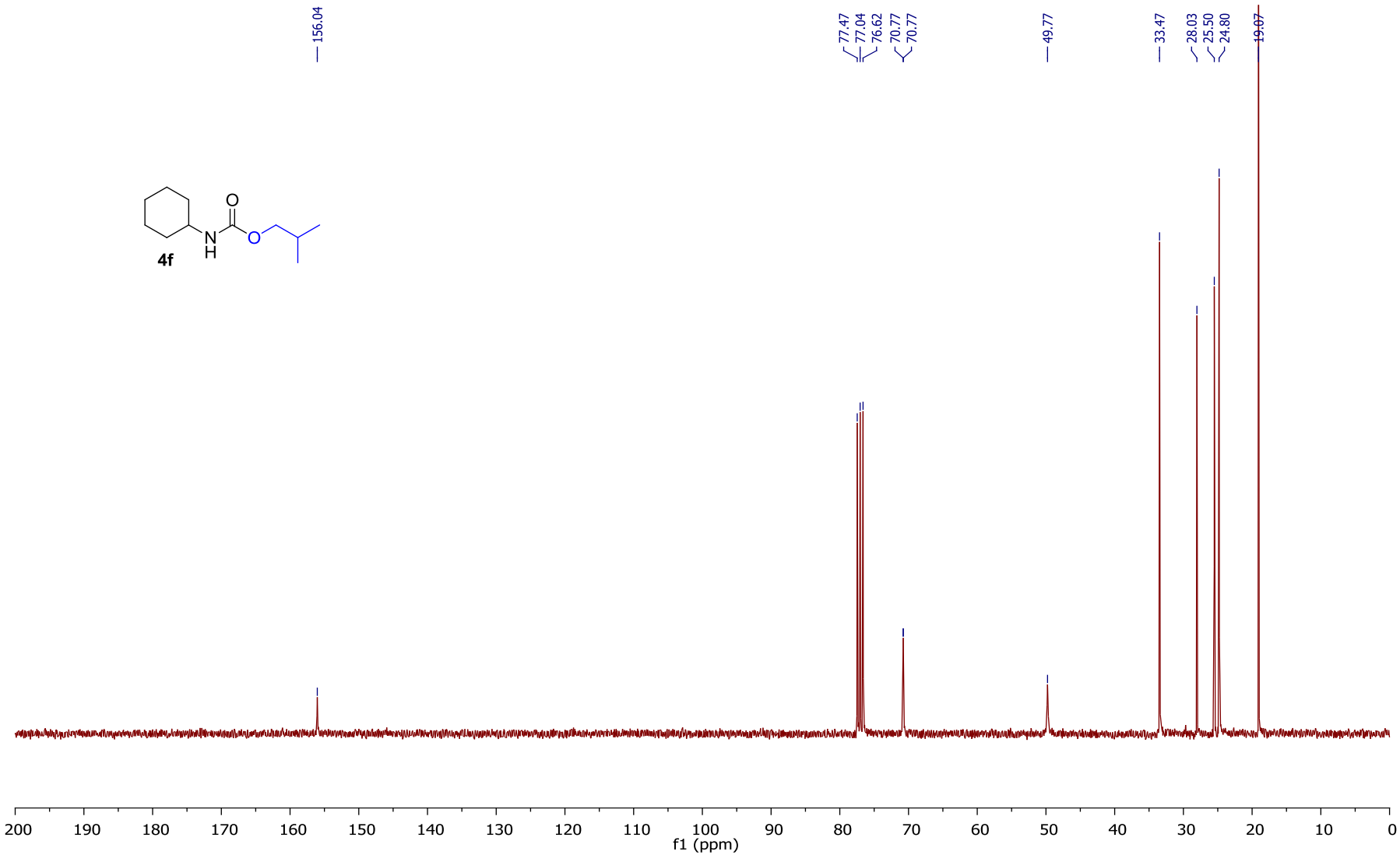
3.79
3.44
1.93
1.92
1.91
1.89
1.88
1.85
1.71
1.70
1.69
1.67
1.66
1.65
1.59
1.57
1.55
1.35
1.34
1.30
1.26
1.19
1.17
1.15
1.12
1.12
1.12
1.09
0.91
0.89
3.9
3.8
1.9
1.7
1.5
1.3
1.1
0.9
0.8
0.92
2.00
0.98
3.08
3.11
2.29
3.16
6.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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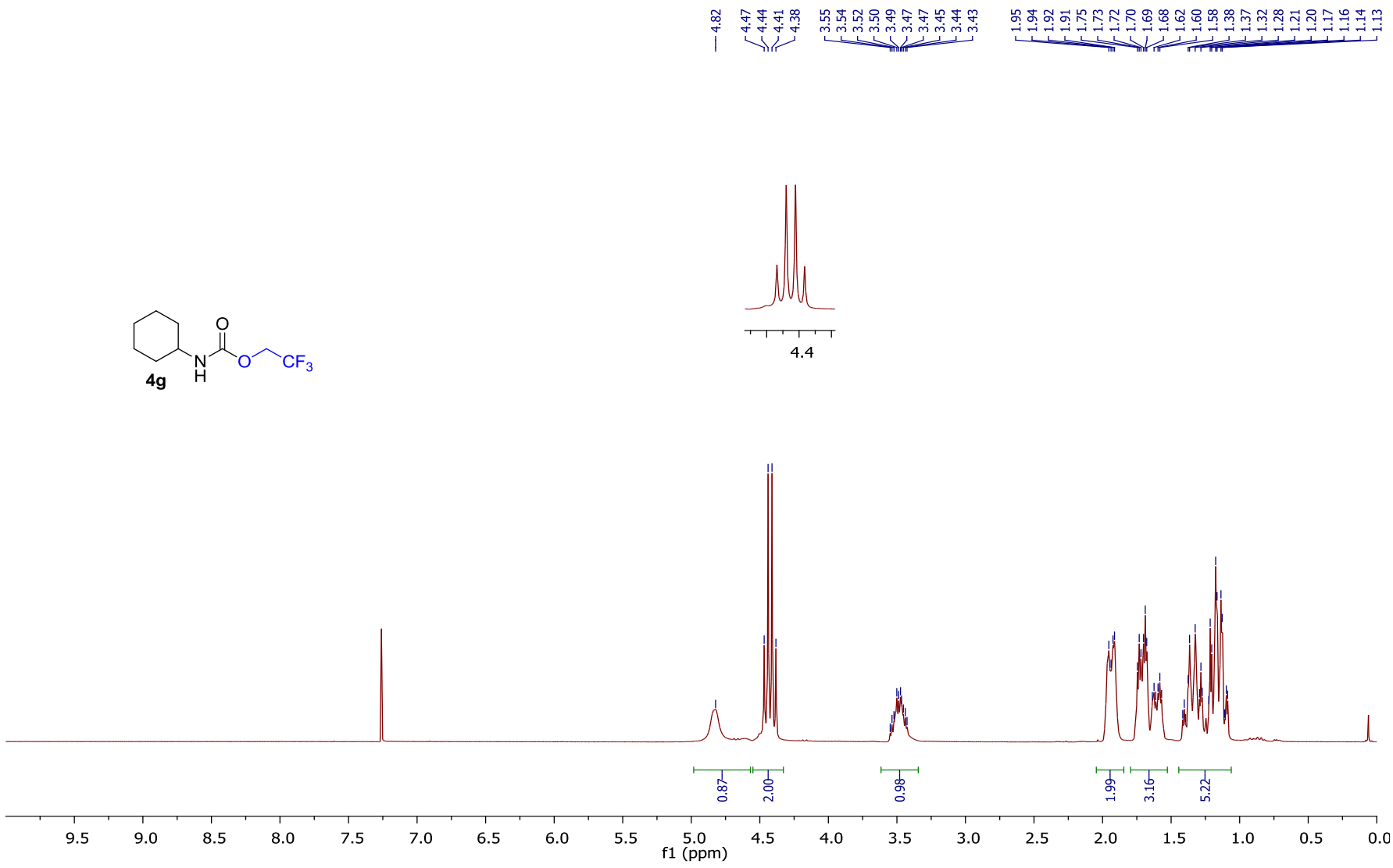
77.47
77.04
76.62
70.77
70.77
49.77
33.47
28.03
25.50
24.80
19.07
4f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4.82
4.47
4.44
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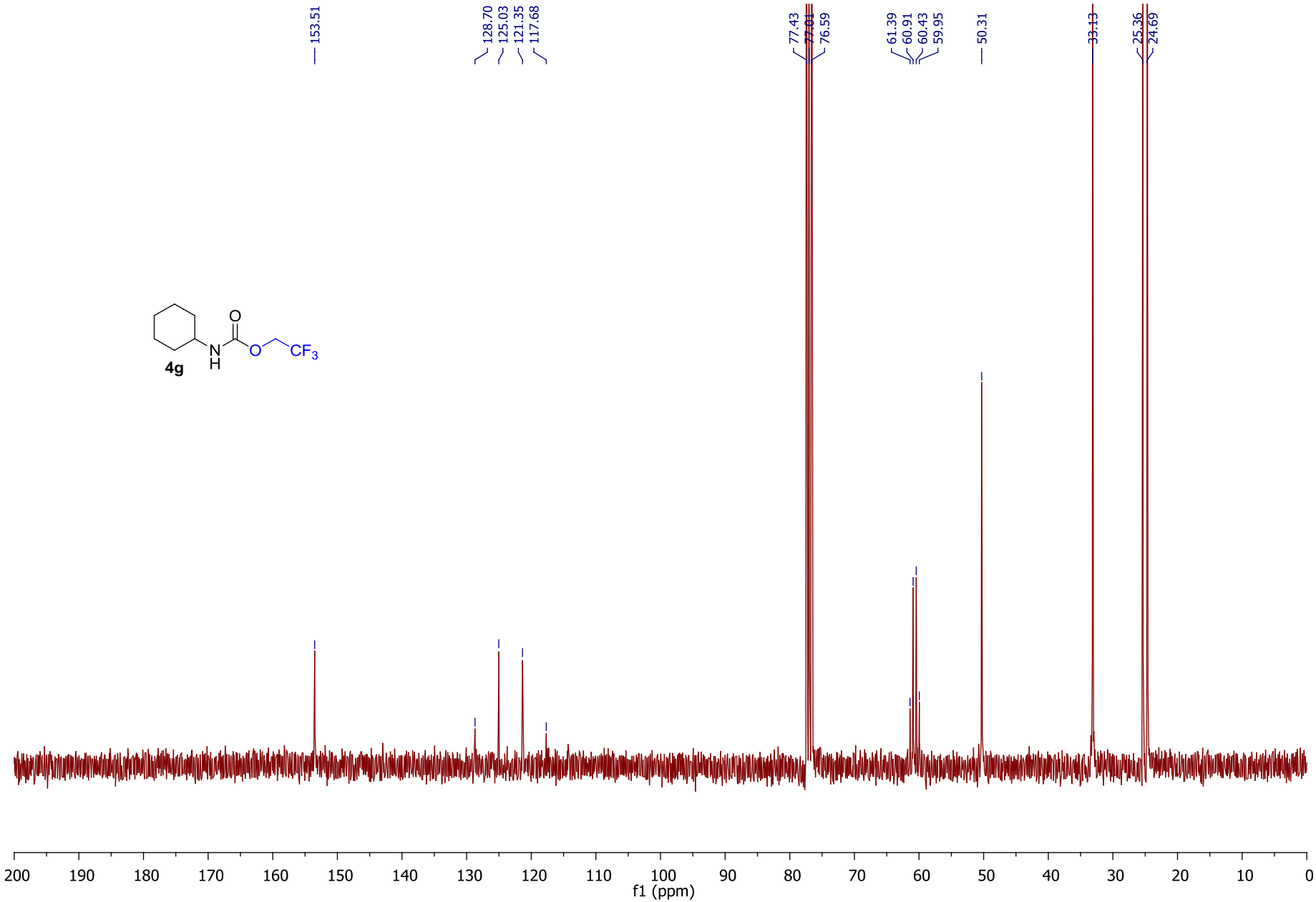
4.38
3.55
3.54
3.52
3.50
3.49
3.47
3.47
3.45
3.44
3.43
1.95
1.94
1.92
1.91
1.75
1.73
1.72
1.70
1.69
1.68
1.62
1.60
1.58
1.38
1.37
1.32
1.28
1.21
1.20
1.17
1.16
1.14
1.13
4.4
O
N
H
O
CF3
4g
0.87
2.00
0.98
1.99
3.16
5.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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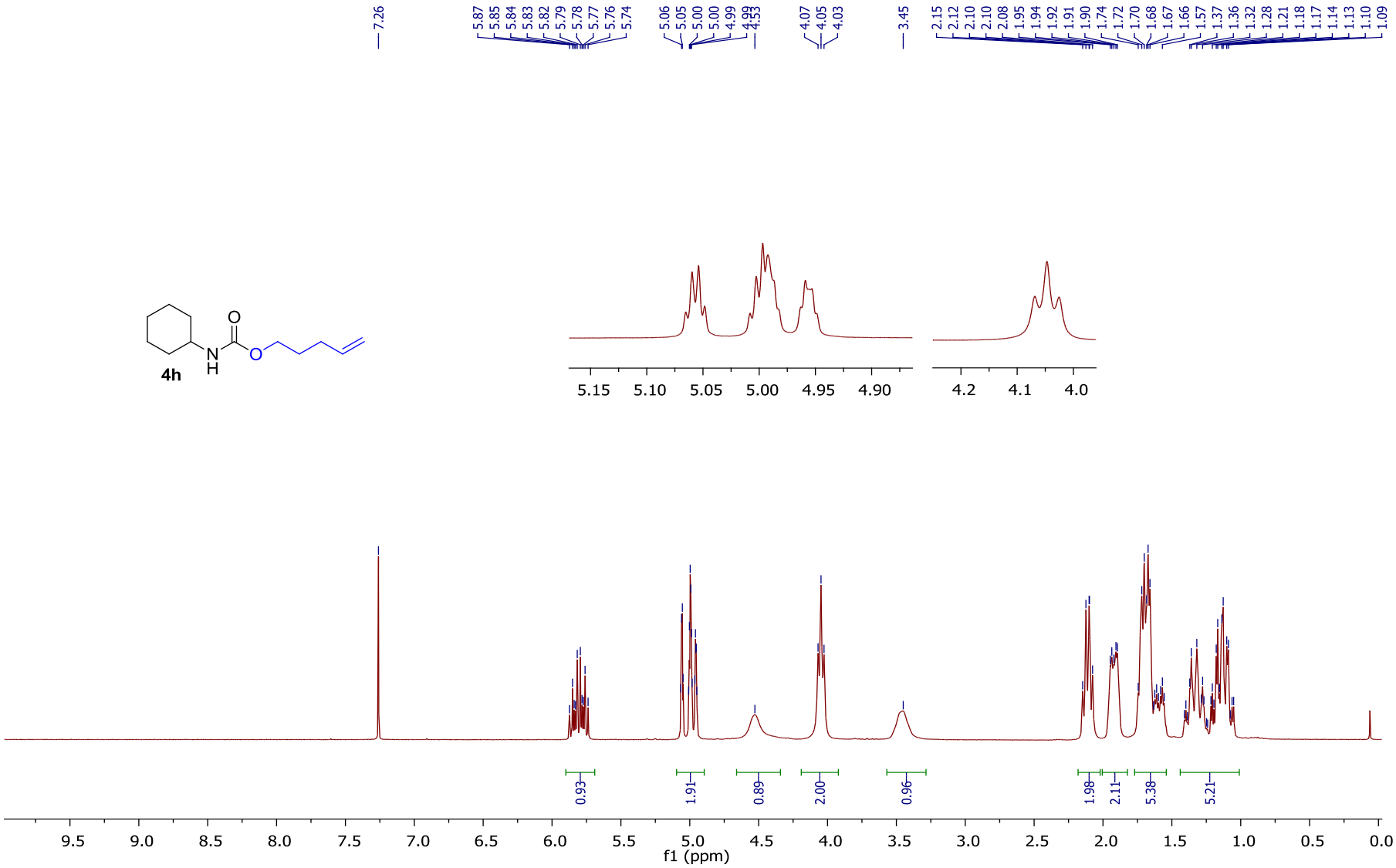
76.59
61.39
60.91
60.43
59.95
50.31
33.13
25.36
24.69
4g
f1 (ppm)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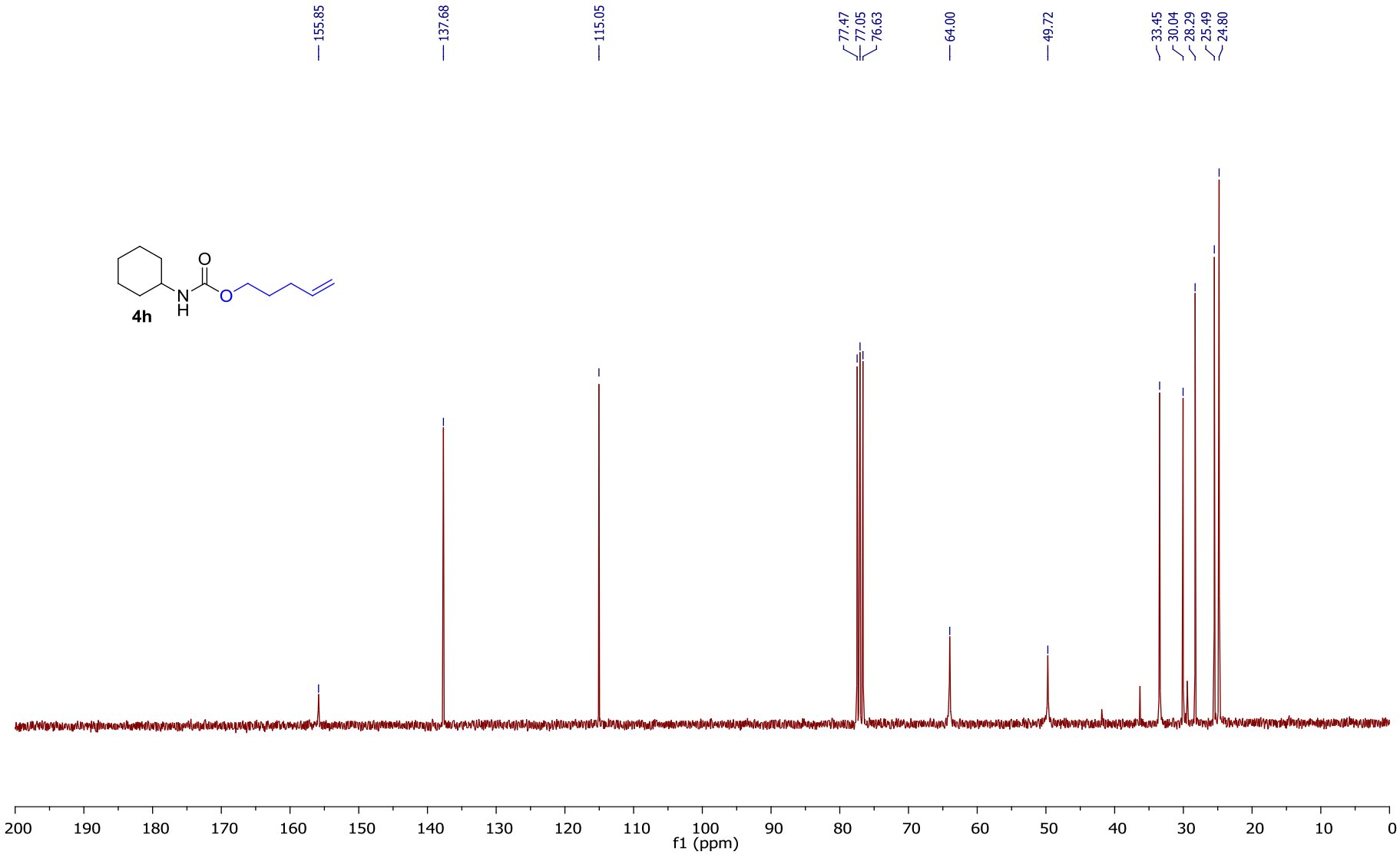
5.82
5.79
5.78
5.77
5.76
5.74
5.06
5.05
5.00
5.00
4.99
4.99
4.53
4.07
4.05
4.03
3.45
2.15
2.12
2.10
2.10
2.08
1.95
1.94
1.92
1.91
1.90
1.74
1.72
1.70
1.68
1.67
1.66
1.57
1.37
1.36
1.32
1.28
1.21
1.18
1.17
1.14
1.13
1.10
1.09
O
N
H
O
4h
5.15
5.10
5.05
5.00
4.95
4.90
4.2
4.1
4.0
0.93
1.91
0.89
2.00
0.96
1.98
2.11
5.38
5.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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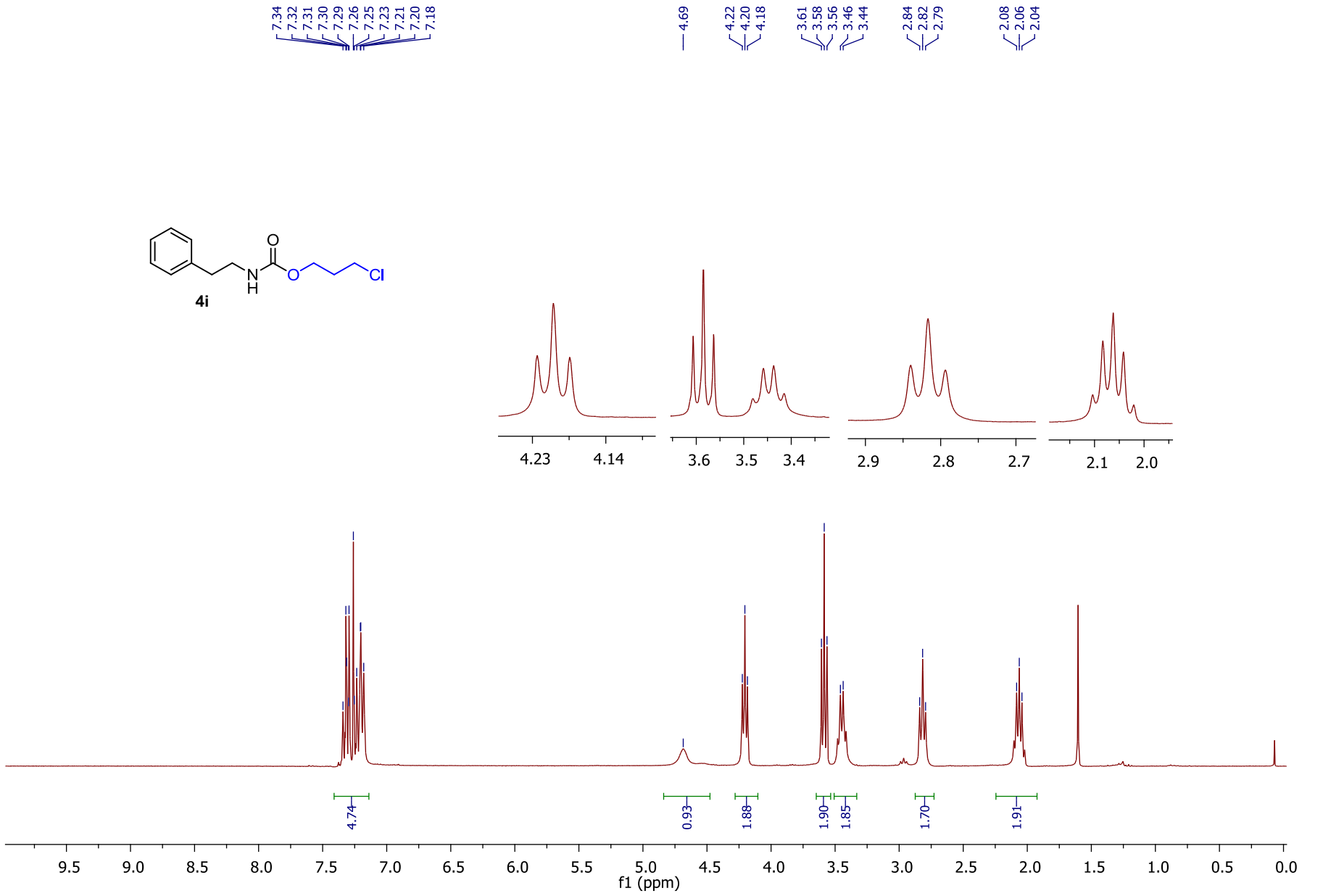
115.05
77.47
77.05
76.63
64.00
49.72
33.45
30.04
28.29
25.49
24.80
4h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26
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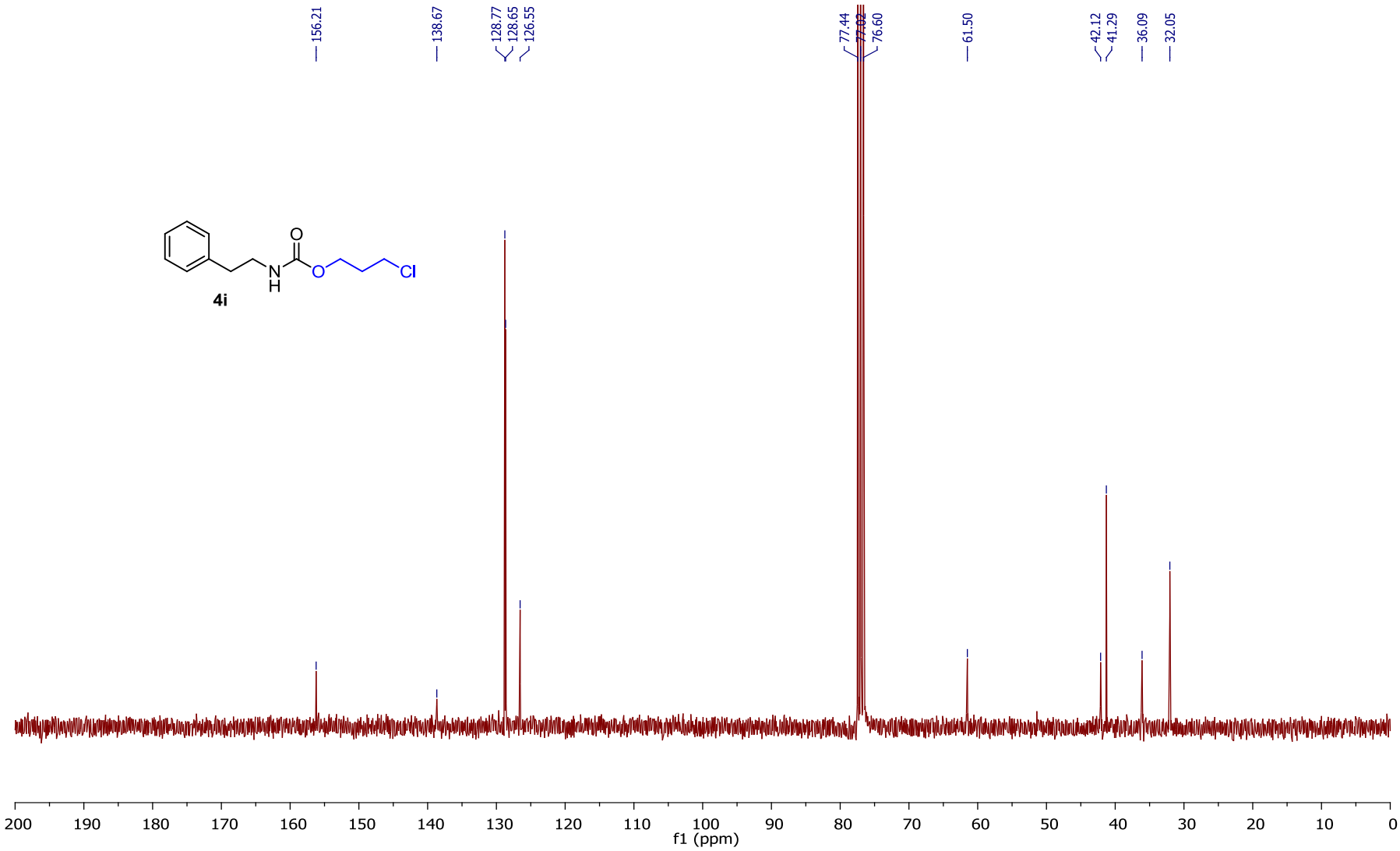
7.23
7.21
7.20
7.18
4.69
4.22
4.20
4.18
3.61
3.58
3.56
3.46
3.44
2.84
2.82
2.79
2.08
2.06
2.04
O
N
H
O
Cl
4i
4.23
4.14
3.6
3.5
3.4
2.9
2.8
2.7
2.1
2.0
4.74
0.93
1.88
1.90
1.85
1.70
1.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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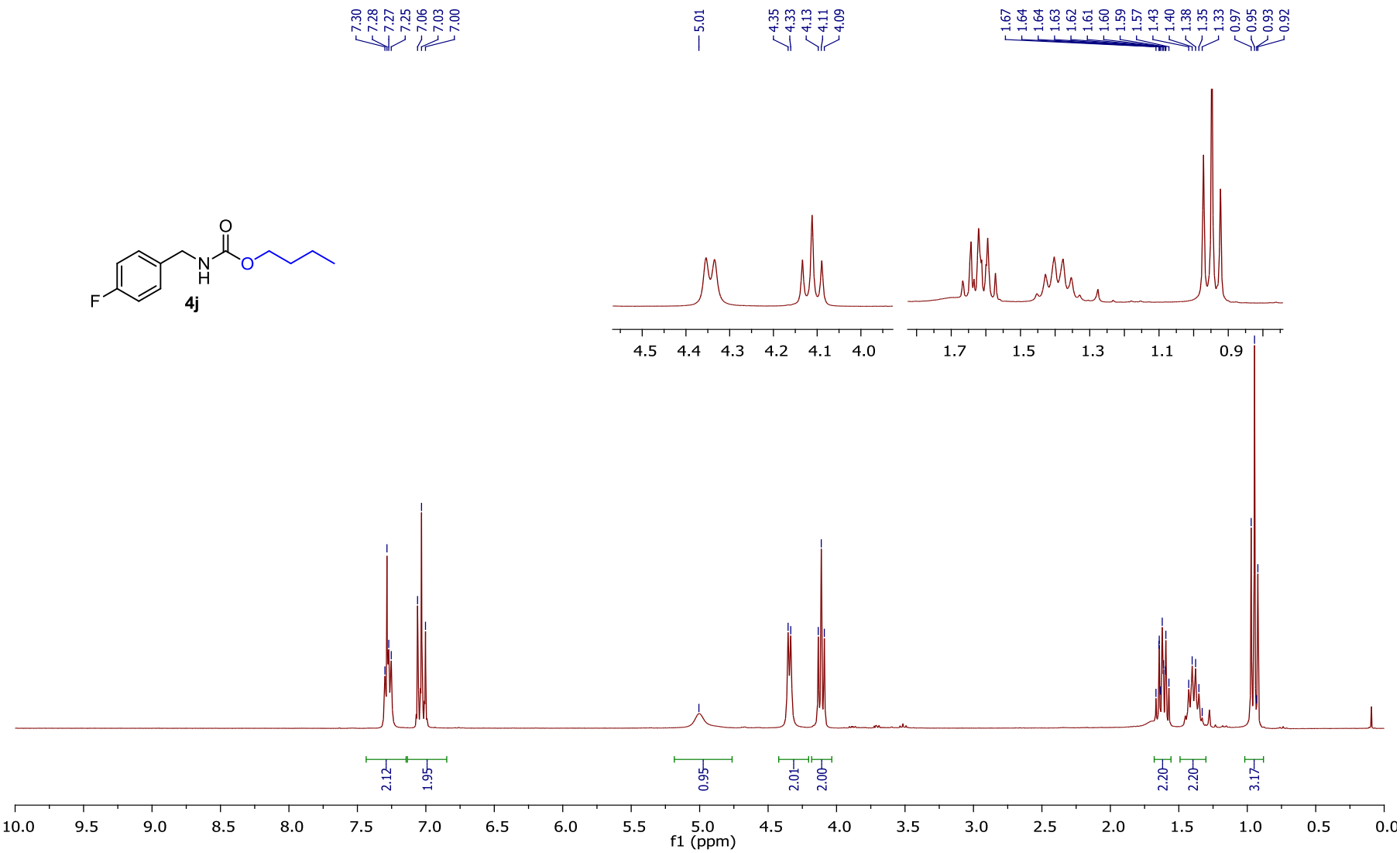
128.65
126.55
77.44
77.02
76.60
61.50
42.12
41.29
36.09
32.05
O
N
H
O
Cl
4i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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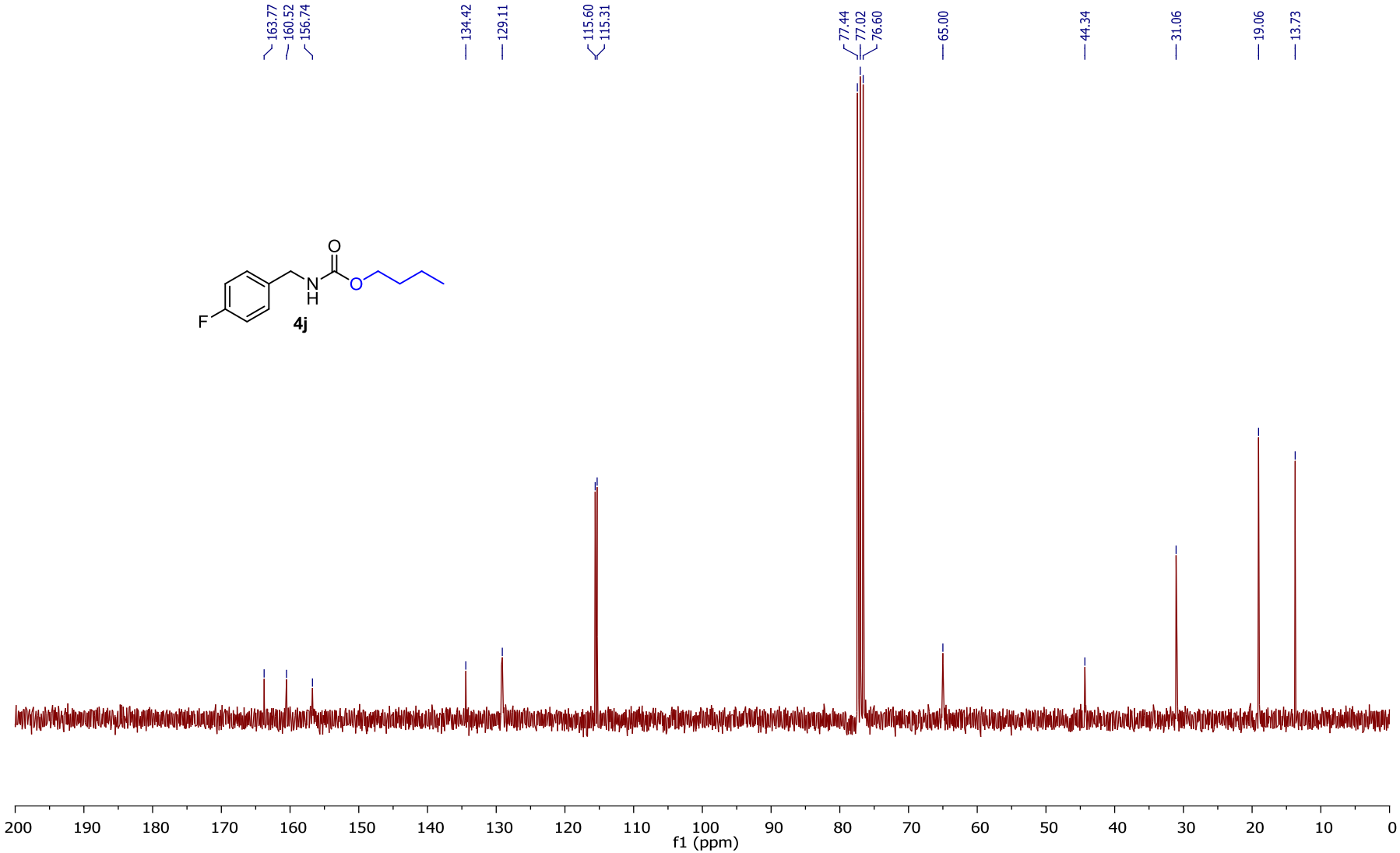
7.27
7.25
7.06
7.03
7.00
5.01
4.35
4.33
4.13
4.11
4.09
1.67
1.64
1.64
1.63
1.62
1.61
1.60
1.59
1.57
1.43
1.40
1.38
1.35
1.33
0.97
0.95
0.93
0.92
O
N
H
O
F
4j
4.5 4.4 4.3 4.2 4.1 4.0
1.7 1.5 1.3 1.1 0.9
2.12
1.95
0.95
2.01
2.00
2.20
2.20
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.42
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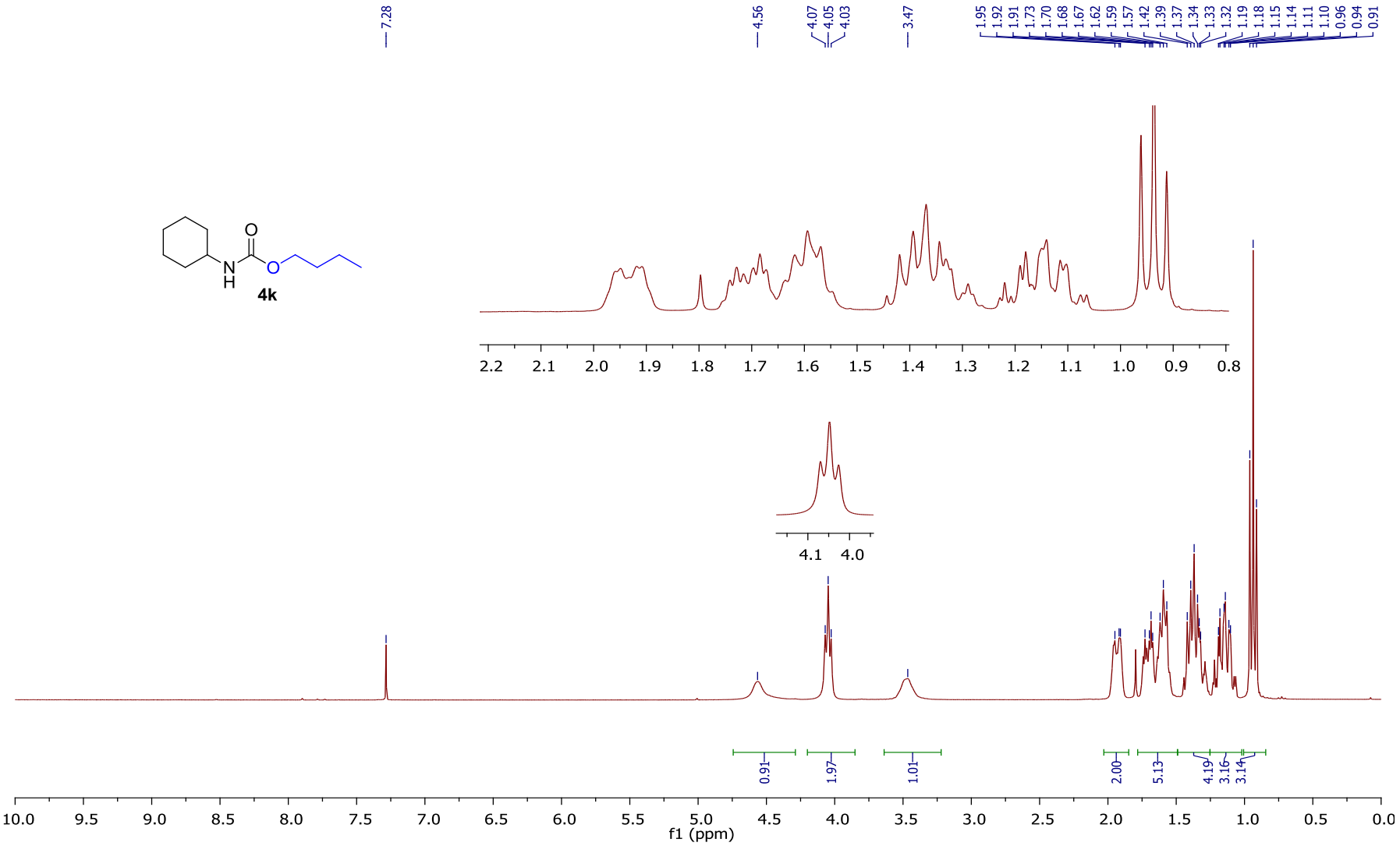
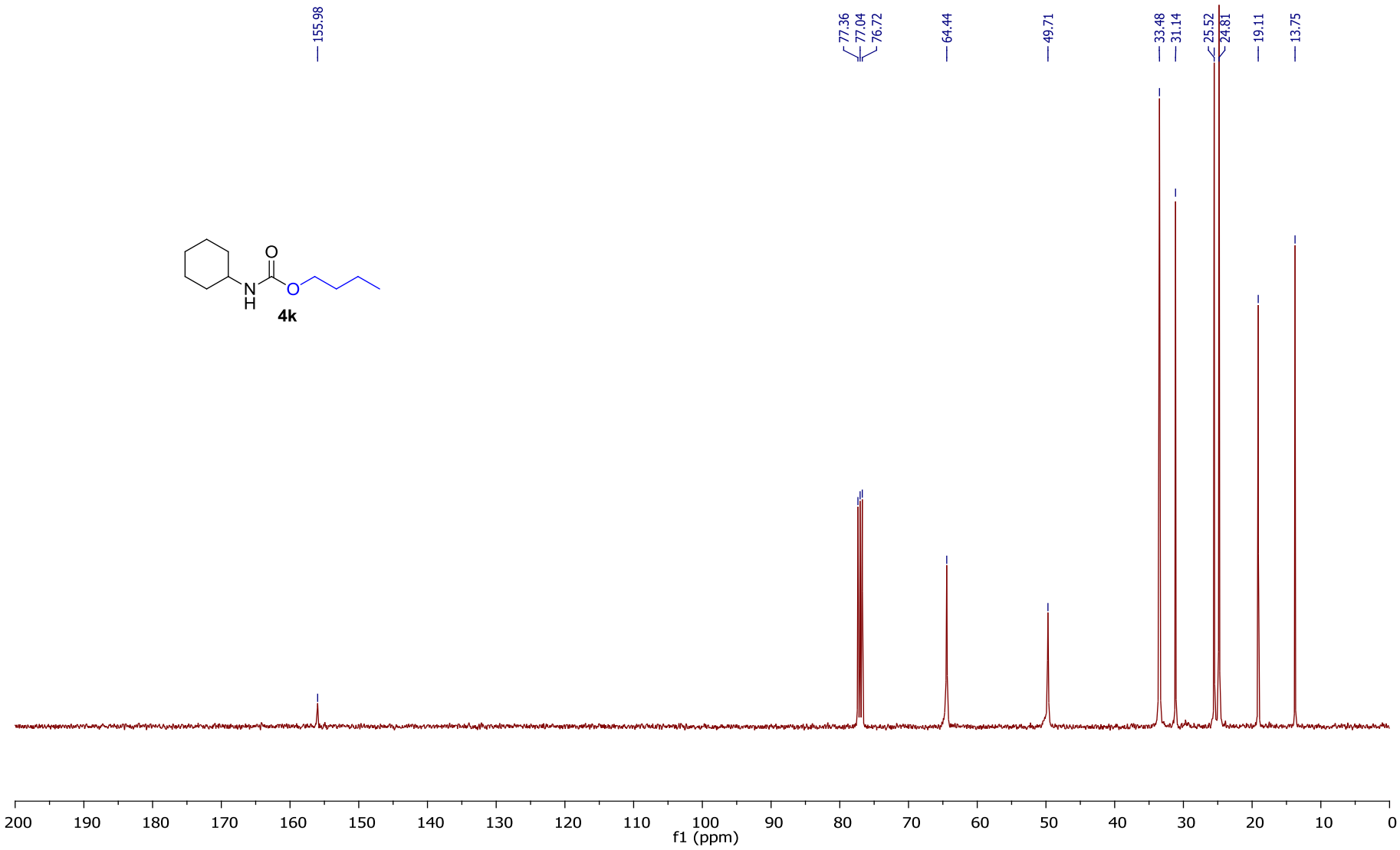
115.60
115.31
77.44
77.02
76.60
65.00
44.34
31.06
19.06
13.73
O
N
H
O
F
4j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.28
4.56
4.07
4.05
4.03
3.47
1.95
1.92
1.91
1.73
1.70
1.68
1.67
1.62
1.59
1.57
1.42
1.39
1.37
1.34
1.33
1.32
1.19
1.18
1.15
1.14
1.11
1.10
0.96
0.94
0.91
O
N
H
O
4k
2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8
4.1 4.0
0.91
1.97
1.01
2.00
5.13
4.19
3.16
3.14
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
f1 (ppm)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76.72
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49.71
33.48
31.14
25.52
24.81
19.11
13.75
O
N
H
O
4k
200
190
180
170
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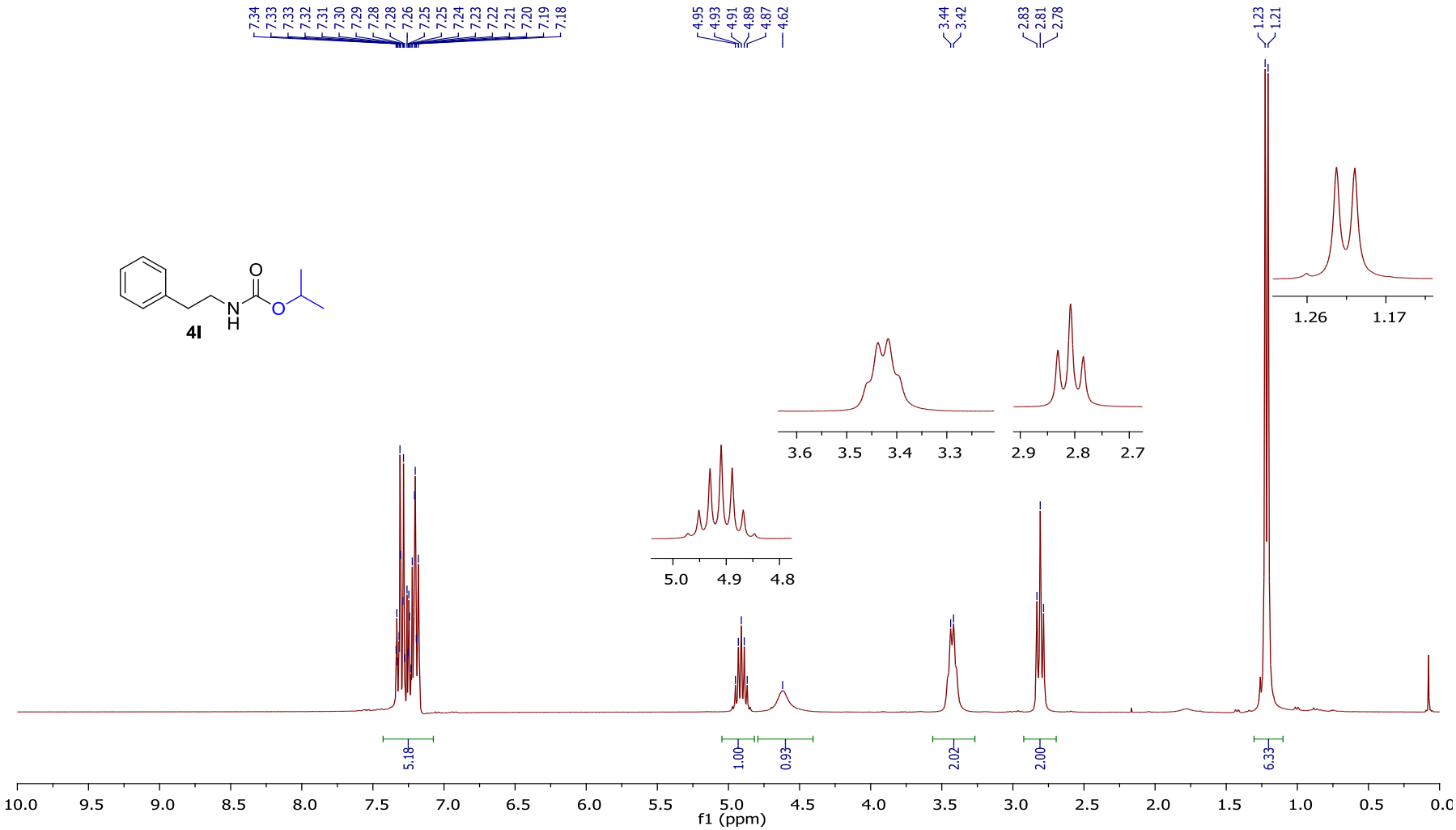
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.28
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7.26
7.25
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7.24
7.23
7.22
7.21
7.20
7.19
7.18
4.95
4.93
4.91
4.89
4.87
4.62
3.44
3.42
2.83
2.81
2.78
1.23
1.21
4l
1.26
1.17
3.6
3.5
3.4
3.3
2.9
2.8
2.7
5.0
4.9
4.8
5.18
1.00
0.93
2.02
2.00
6.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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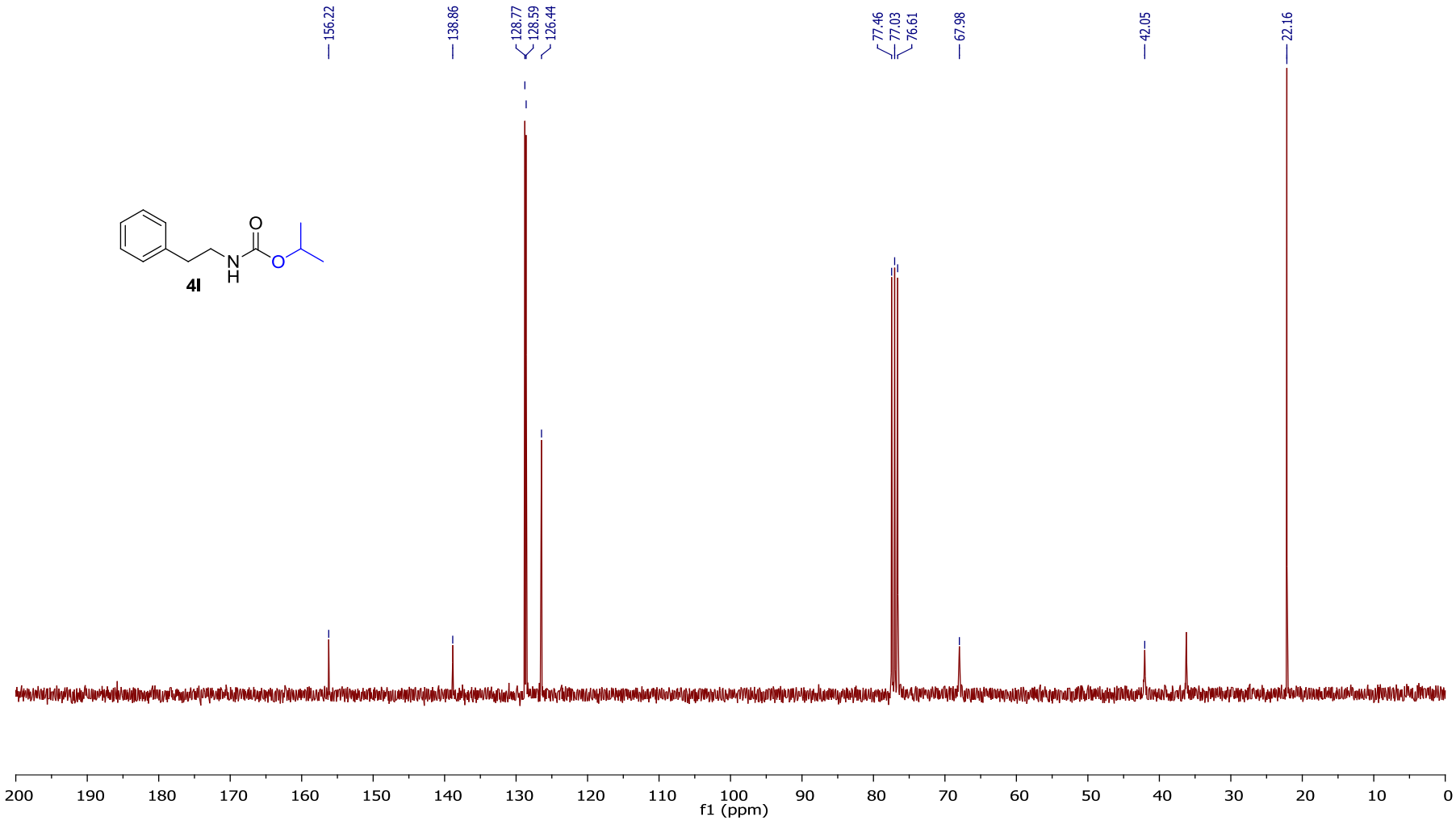
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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77.46
77.03
76.61
67.98
42.05
22.16
O
N
H
O
4l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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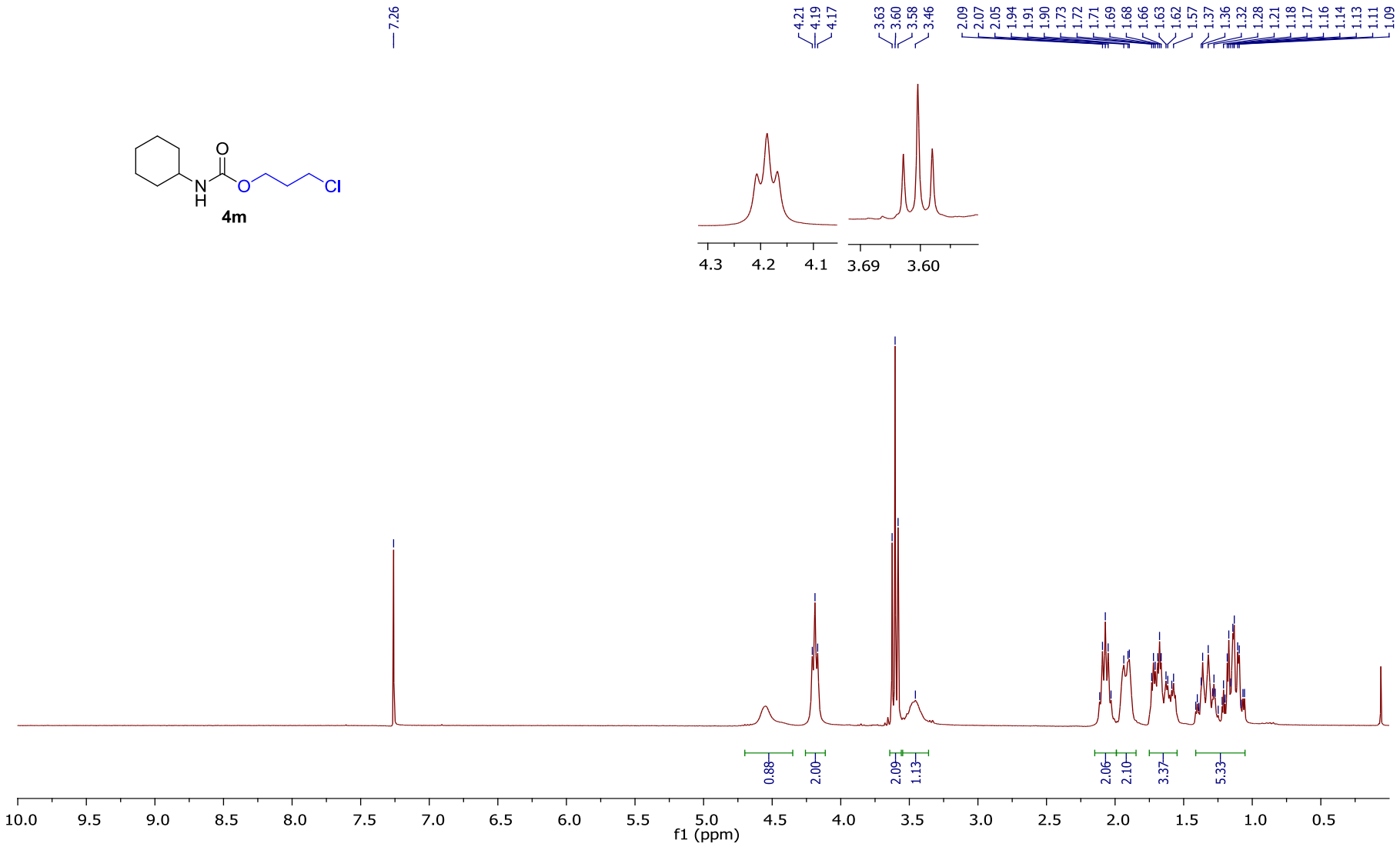
50
40
30
20
10
0
f1 (ppm)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3.58
3.46
2.09
2.07
2.05
1.94
1.91
1.90
1.73
1.72
1.71
1.69
1.68
1.66
1.63
1.62
1.57
1.37
1.36
1.32
1.28
1.21
1.18
1.17
1.16
1.14
1.13
1.11
1.09
O
N
H
O
Cl
4m
4.3
4.2
4.1
3.69
3.60
0.88
2.00
2.09
1.13
2.06
2.10
3.37
5.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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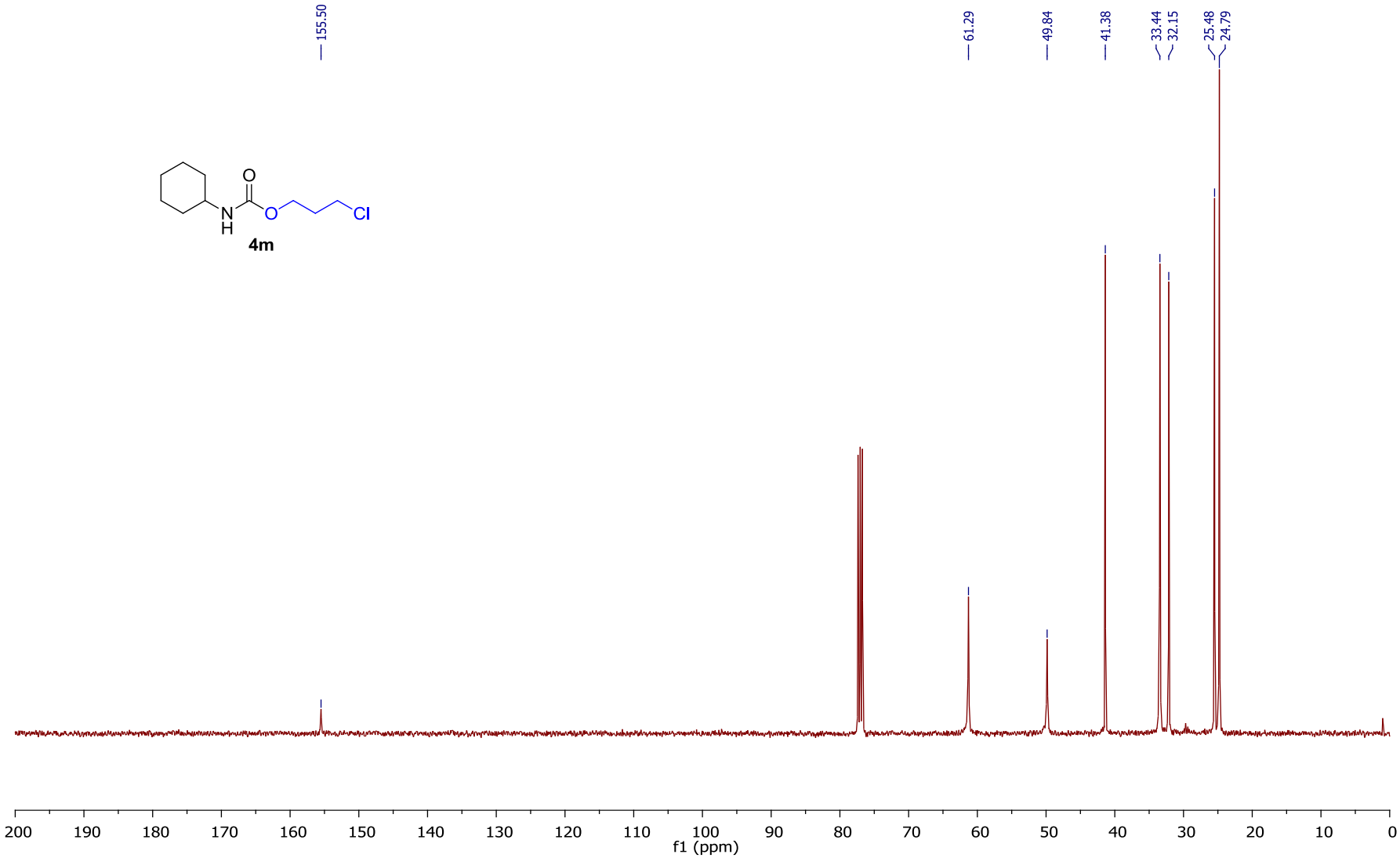
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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32.15
25.48
24.79
O
N
H
O
Cl
4m
200
190
180
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130
120
110
100
90
80
70
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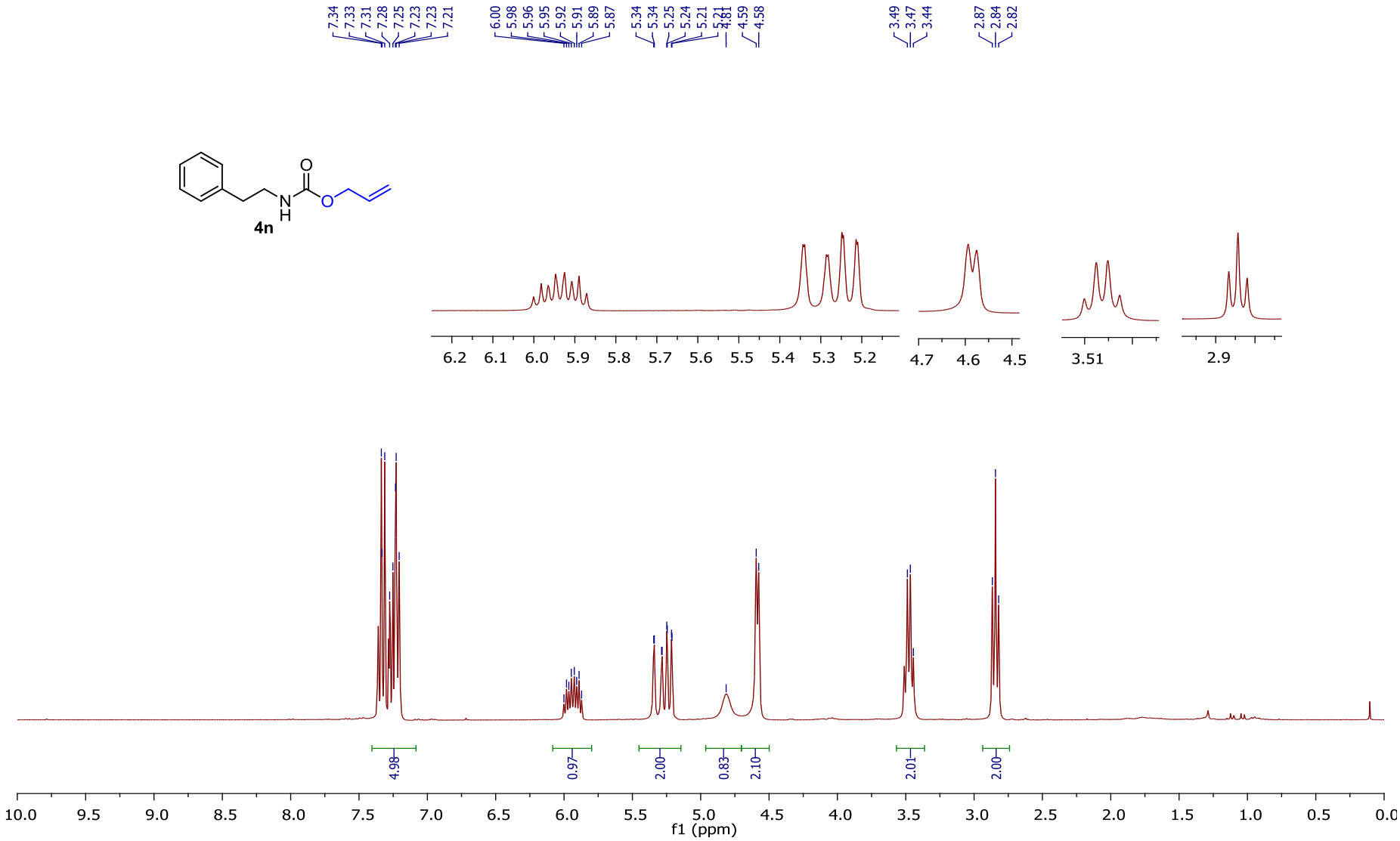
50
40
30
20
10
0
f1 (ppm)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7.23
7.23
7.21
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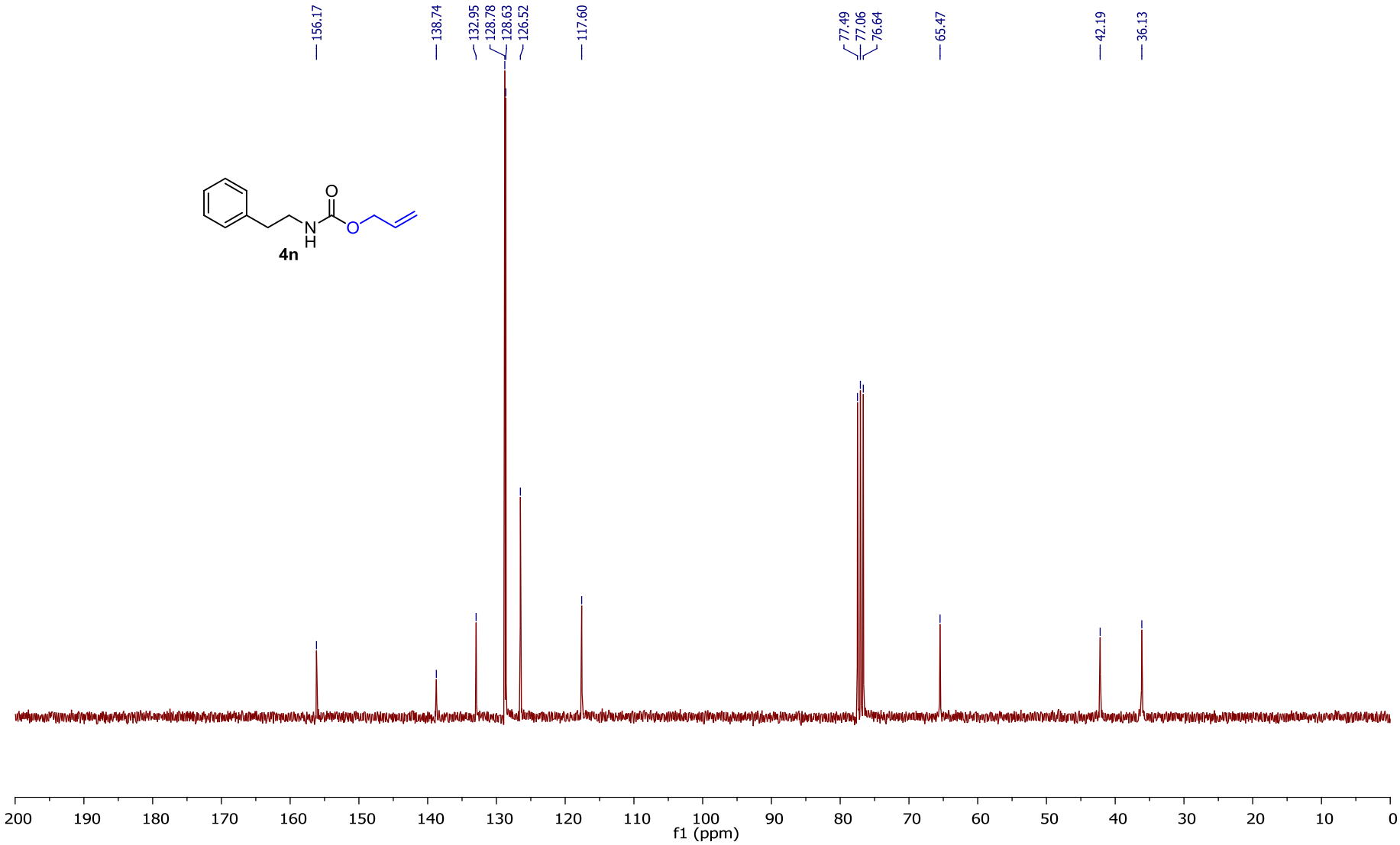
5.98
5.96
5.95
5.92
5.91
5.89
5.87
5.34
5.34
5.25
5.24
5.21
5.21
4.59
4.58
3.49
3.47
3.44
2.87
2.84
2.82
O
N
H
O
4n
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
4.7
4.6
4.5
3.51
2.9
4.98
0.97
2.00
0.83
2.10
2.01
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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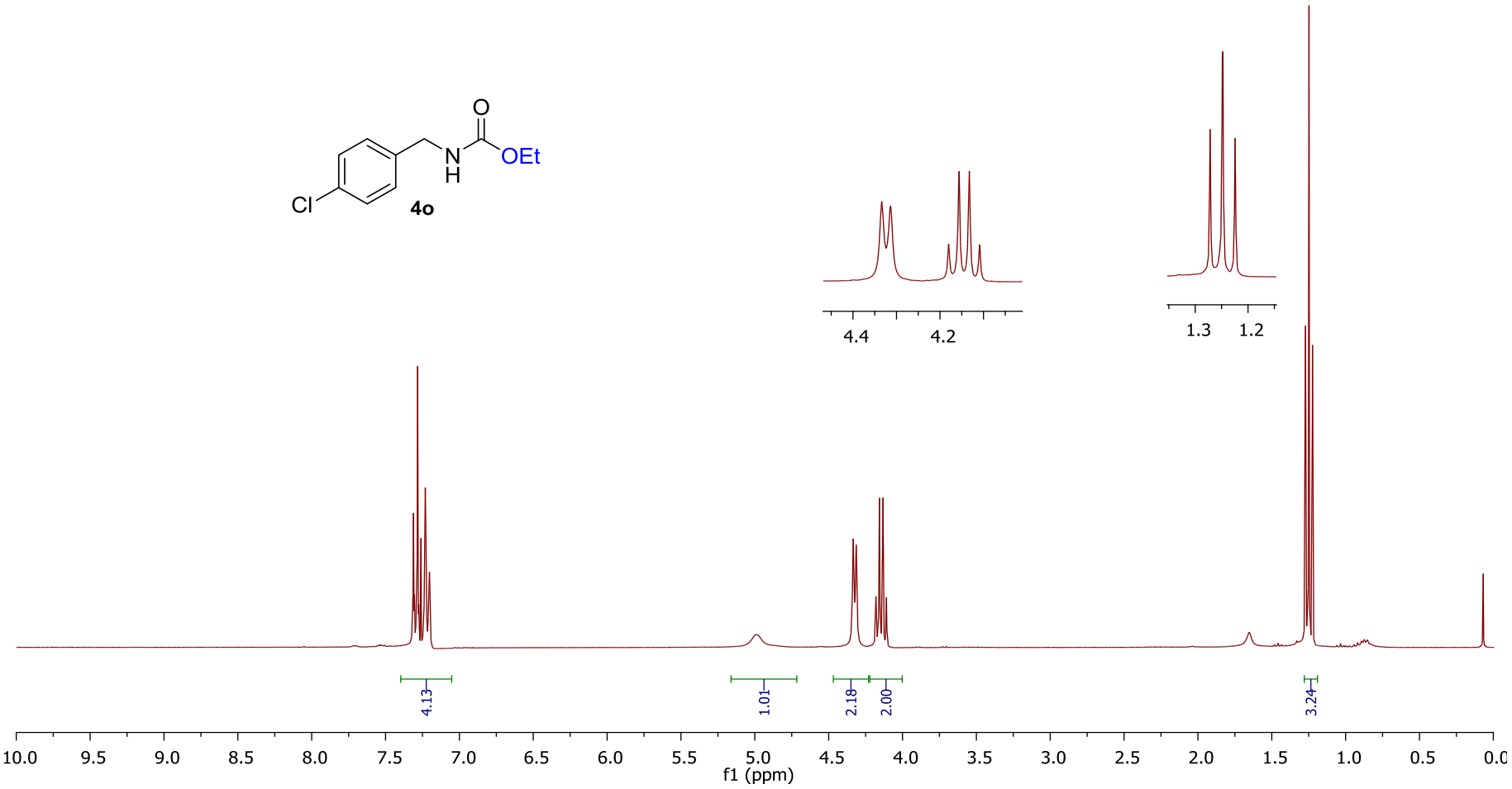
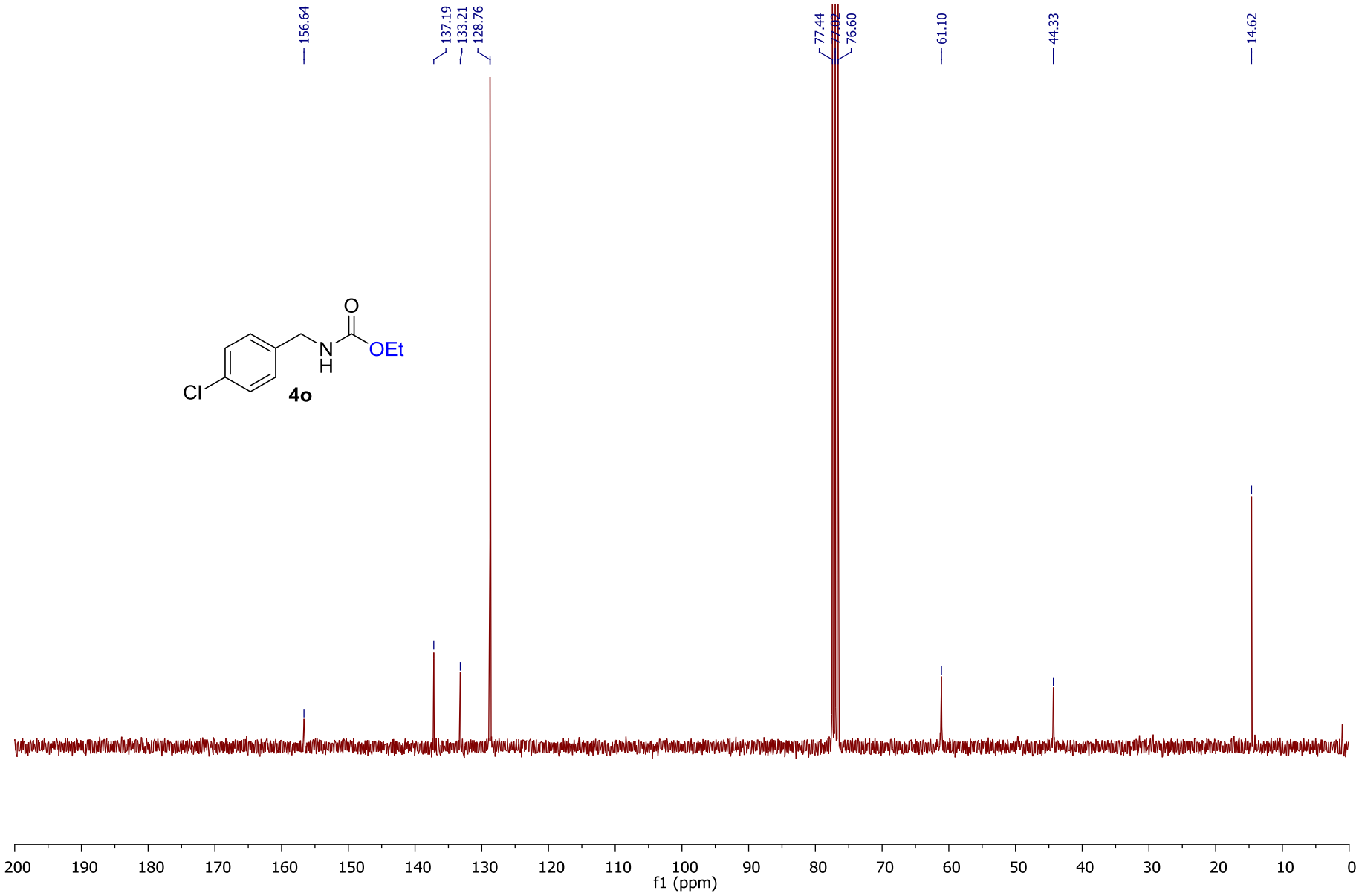
132.95
128.78
128.63
126.52
117.60
77.49
77.06
76.64
65.47
42.19
36.13
O
N
H
O
4n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
H
OEt
Cl
4o
4.4
4.2
1.3
1.2
4.13
1.01
2.18
2.00
3.24
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
f1 (ppm)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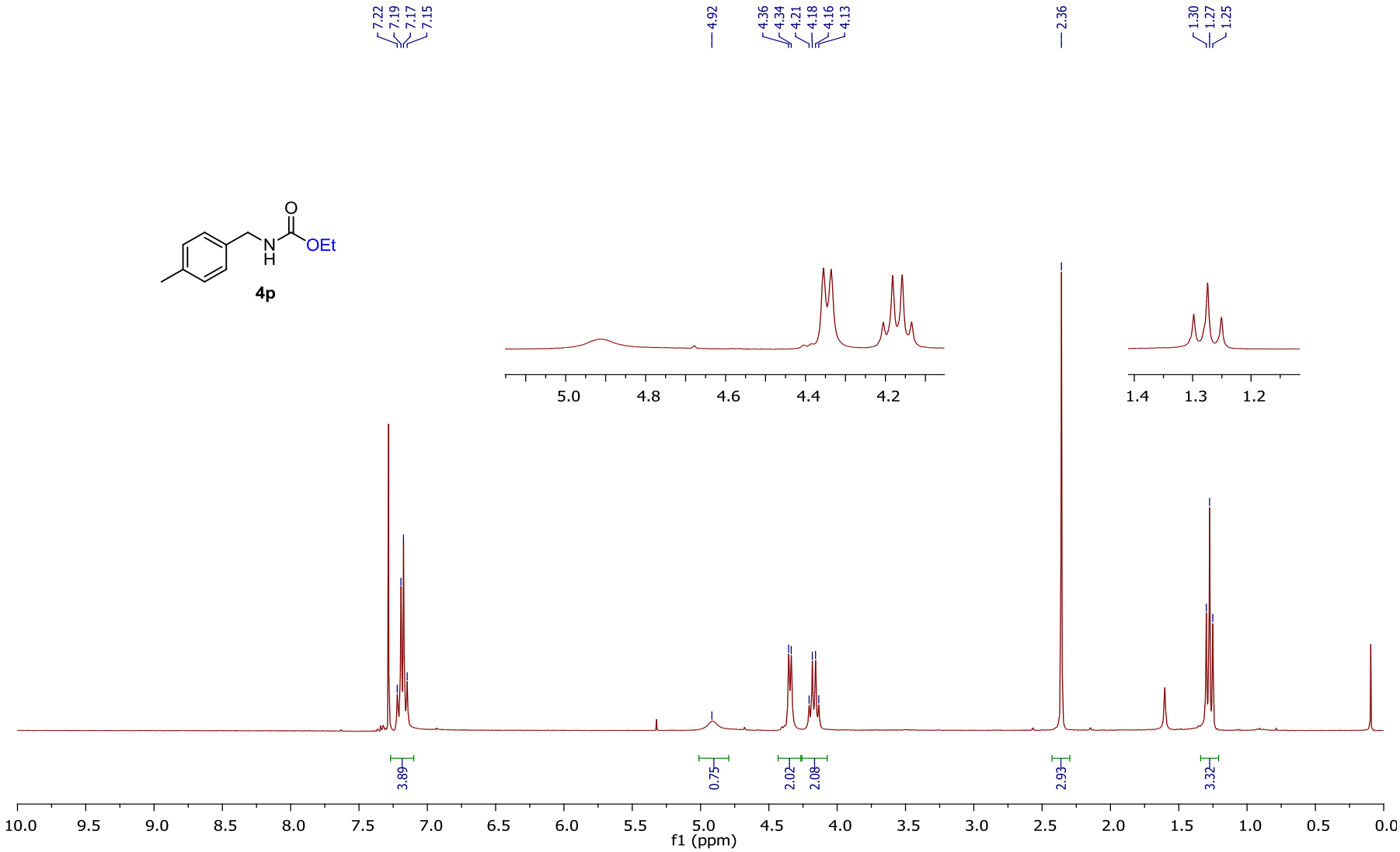
133.21
128.76
77.44
77.02
76.60
61.10
44.33
14.62
O
N
H
OEt
Cl
4o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.19
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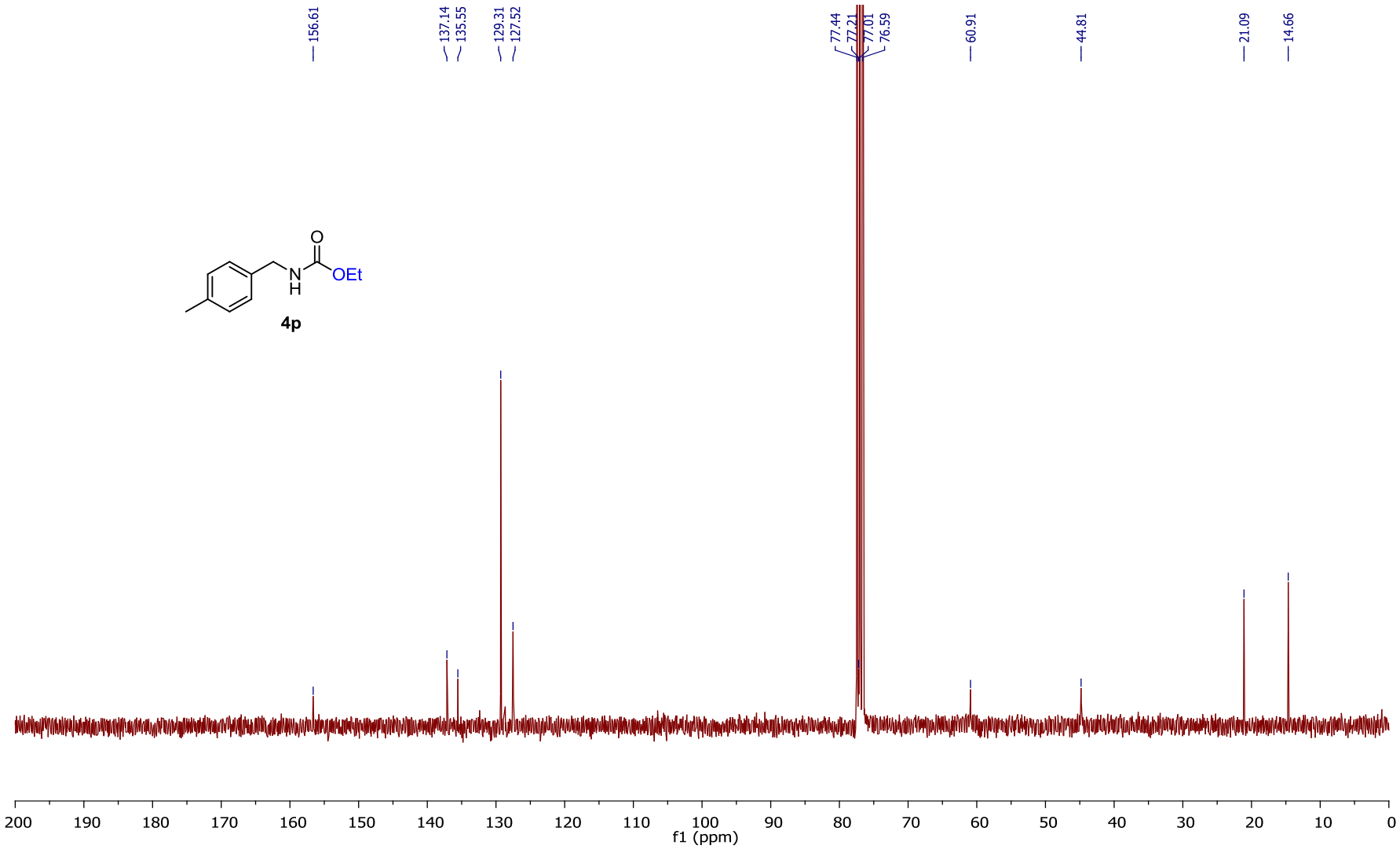
4.36
4.34
4.21
4.18
4.16
4.13
2.36
1.30
1.27
1.25
O
N
H
OEt
4p
3.89
0.75
2.02
2.08
2.93
3.32
f1 (ppm)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127.52
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77.21
77.01
76.59
60.91
44.81
21.09
14.66
O
N
H
OEt
4p
200
190
180
170
160
150
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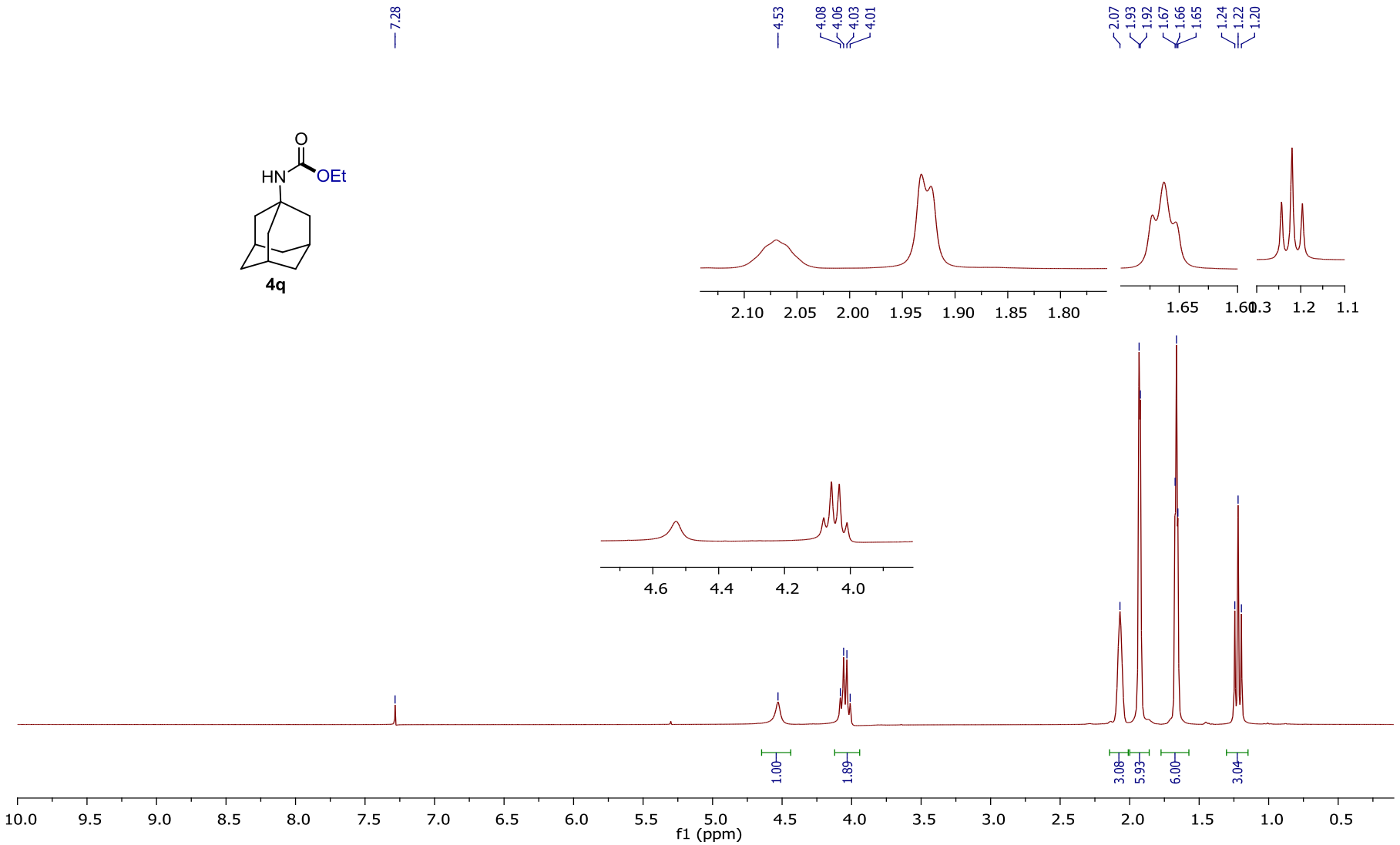
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.08
4.06
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4.01
2.07
1.93
1.92
1.67
1.66
1.65
1.24
1.22
1.20
HN
O
OEt
4q
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.65
1.60
1.3
1.2
1.1
4.6
4.4
4.2
4.0
1.00
1.89
3.08
5.93
6.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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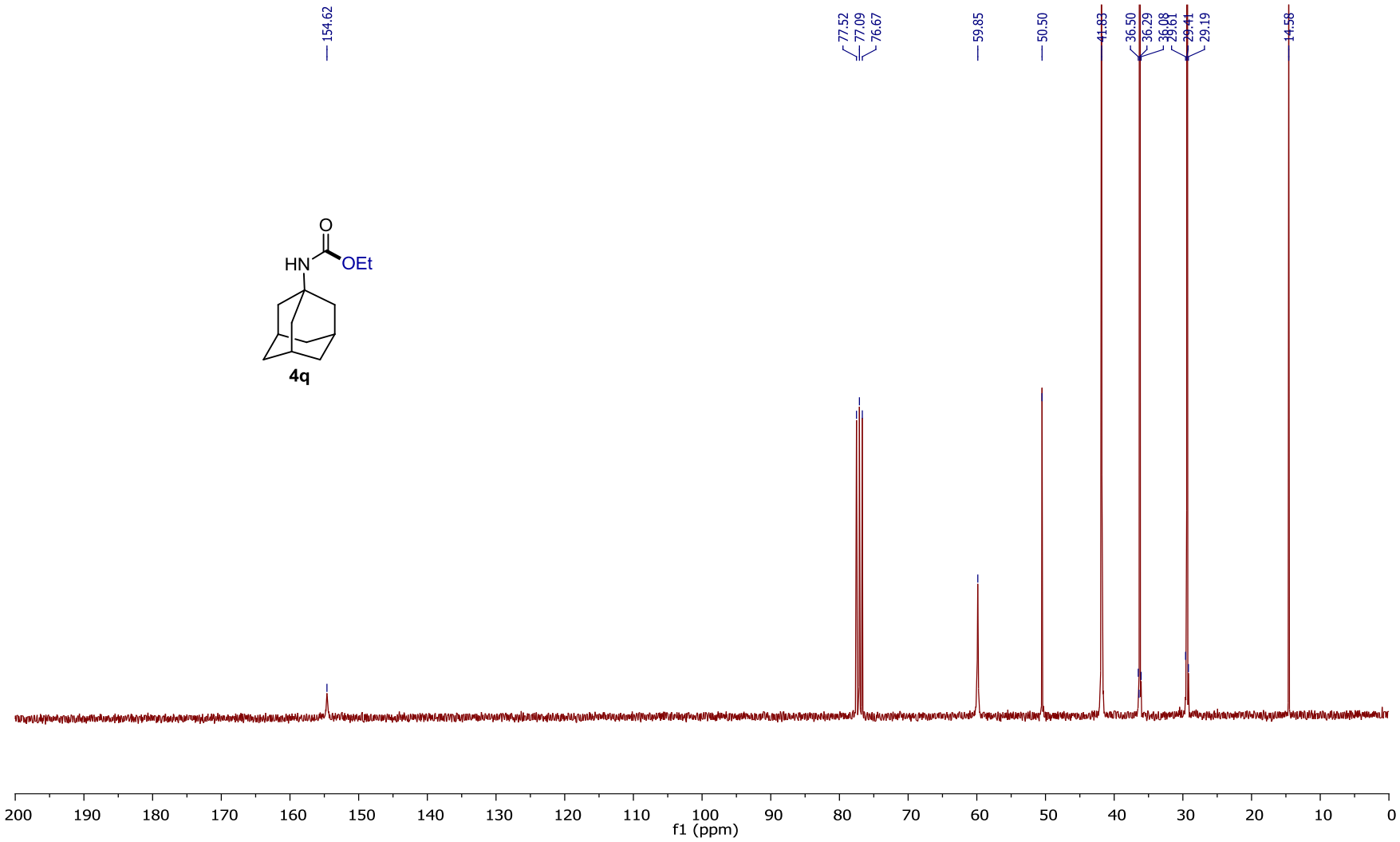
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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76.67
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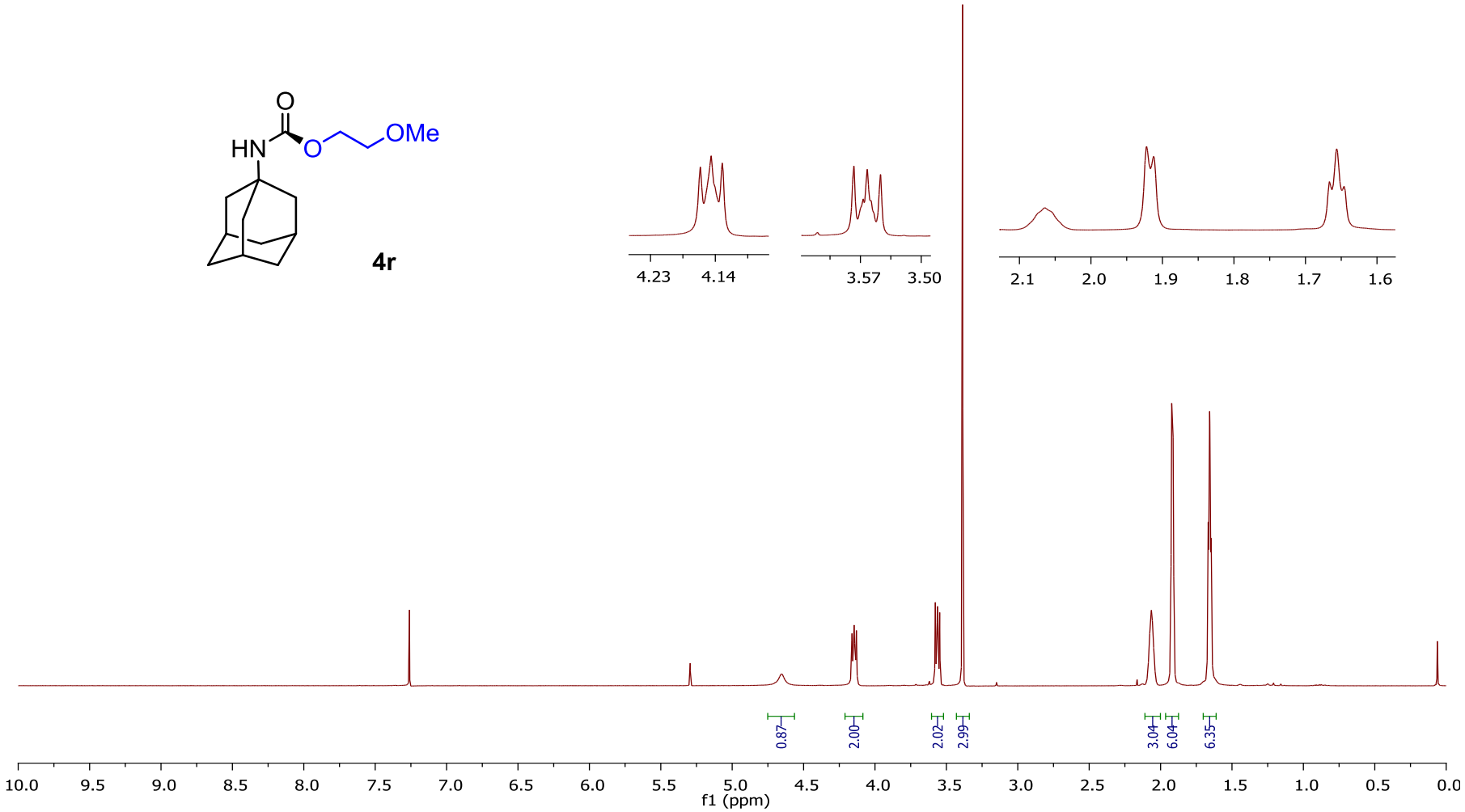
50.50
41.83
36.50
36.29
36.08
29.61
29.41
29.19
14.58
O
HN
OEt
4q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
HN
O
OMe
4r
4.23
4.14
3.57
3.50
2.1
2.0
1.9
1.8
1.7
1.6
0.87
2.00
2.02
2.99
3.04
6.04
6.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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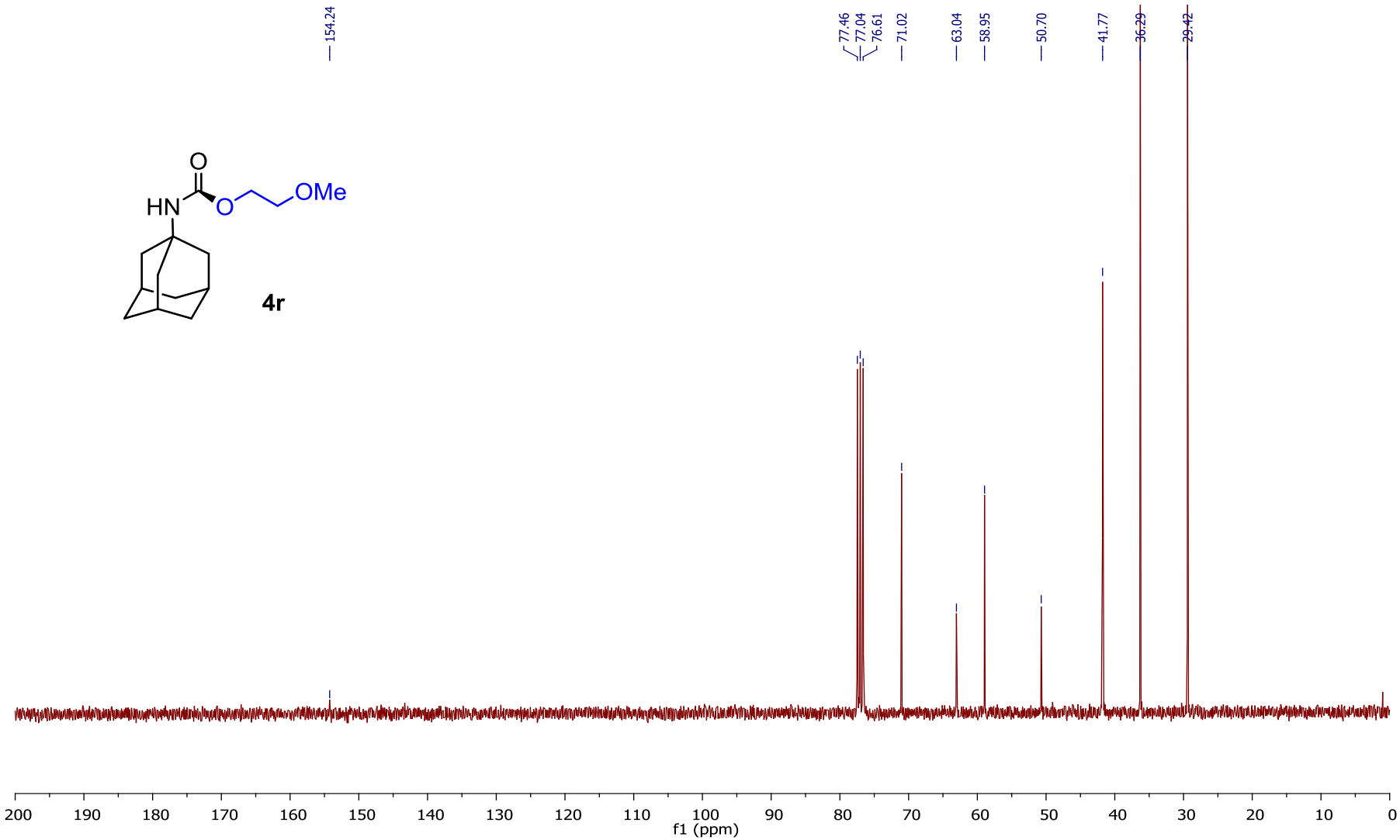
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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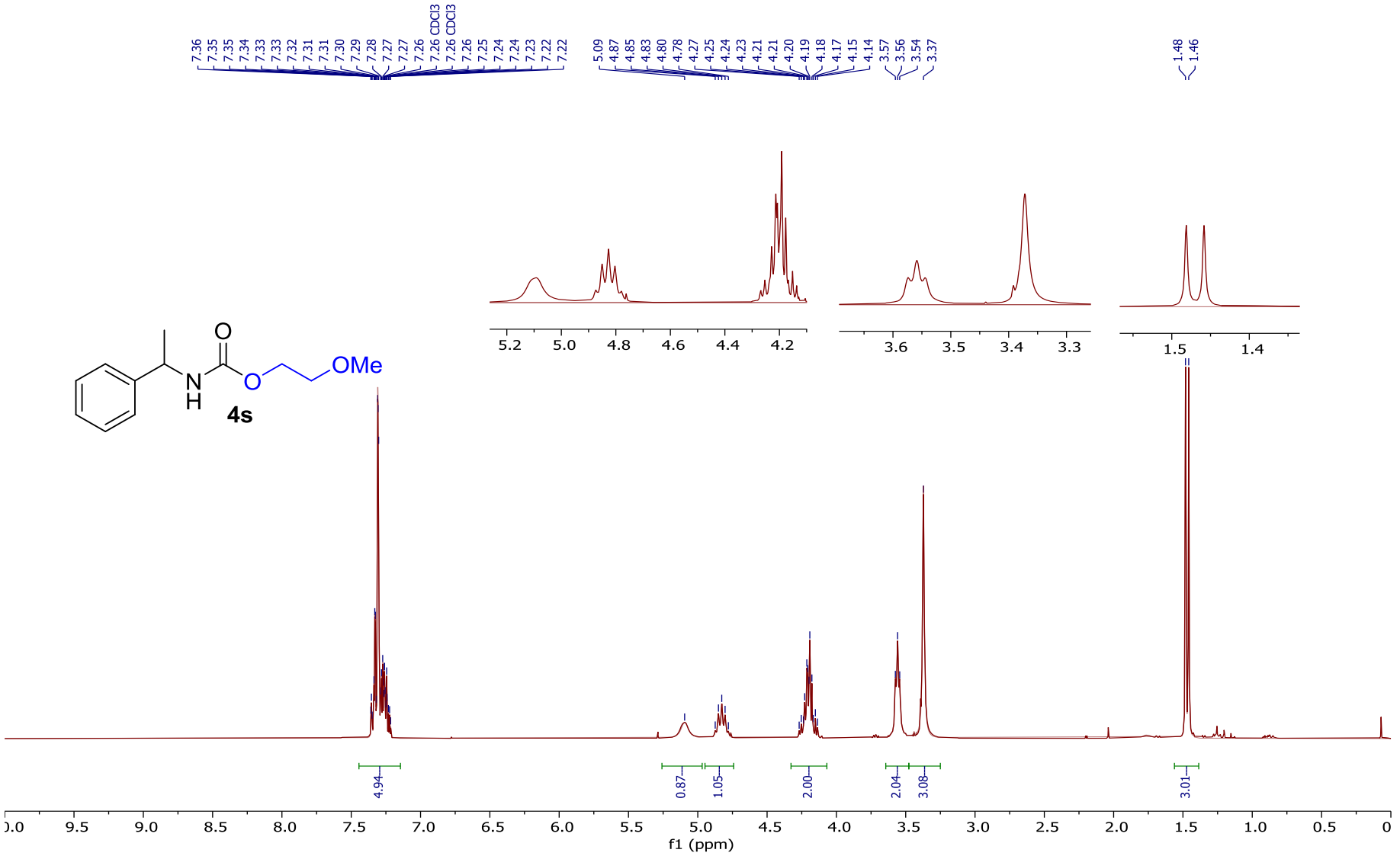
71.02
63.04
58.95
50.70
41.77
36.29
29.42
HN
O
O
OMe
4r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.34
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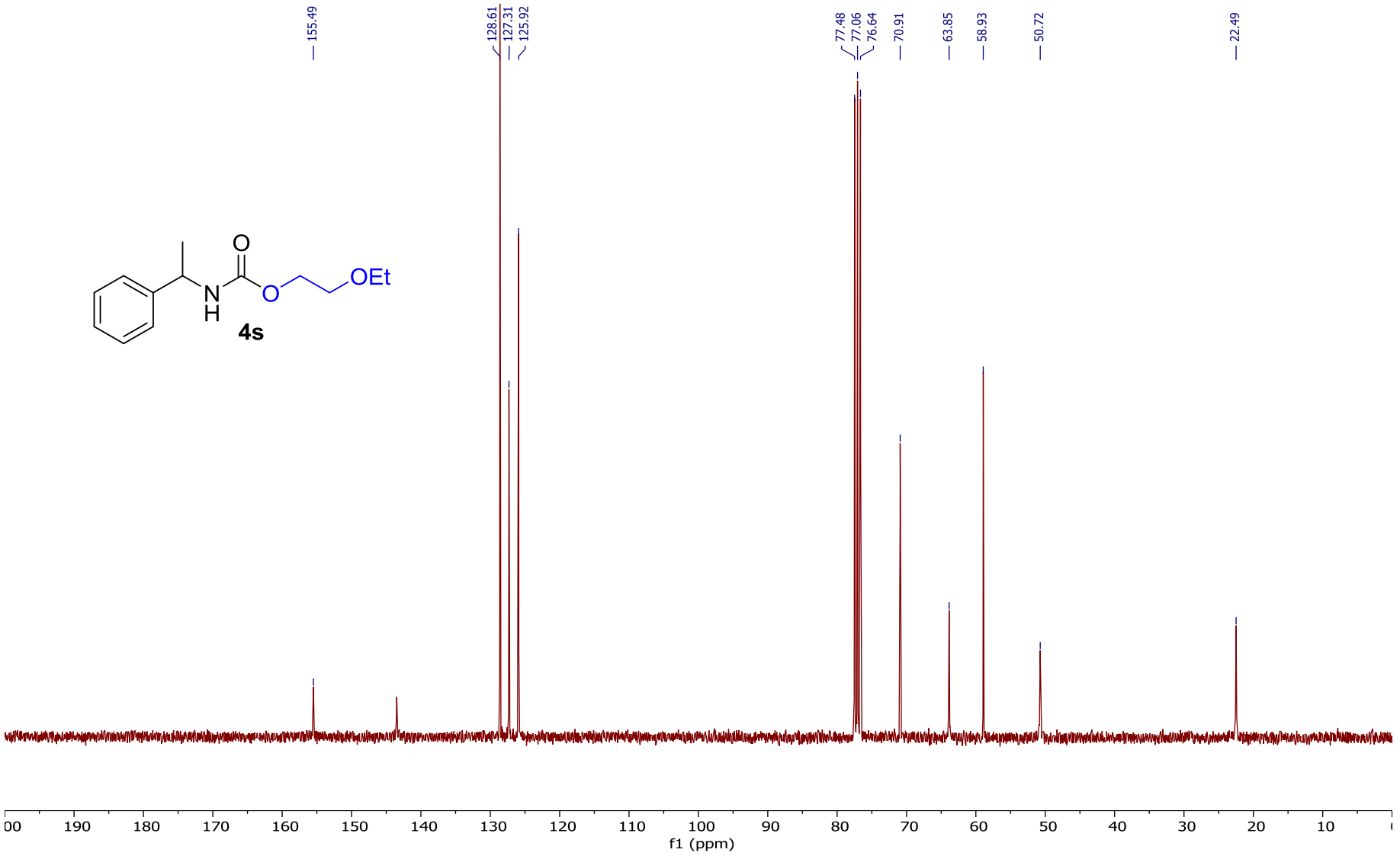
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.26 CDCl3
7.26 CDCl3
7.26
7.25
7.24
7.24
7.23
7.22
7.22
5.09
4.87
4.85
4.83
4.80
4.78
4.27
4.25
4.24
4.23
4.21
4.21
4.20
4.19
4.18
4.17
4.15
4.14
3.57
3.56
3.54
3.37
1.48
1.46
O
N
H
O
O
OMe
4s
4.94
0.87
1.05
2.00
2.04
3.08
3.01
f1 (ppm)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125.92
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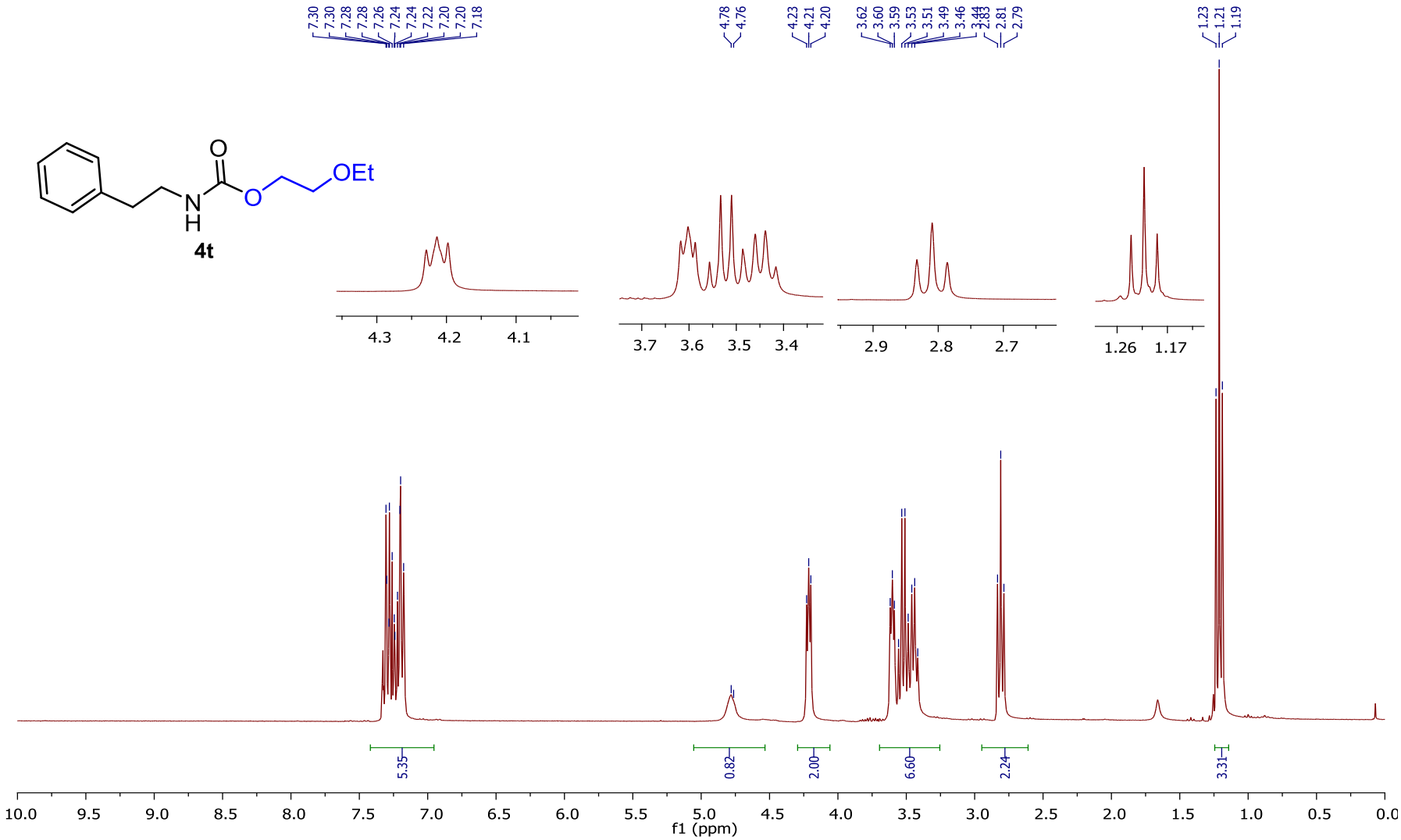
63.85
58.93
50.72
22.49
O
N
H
O
OEt
4s
f1 (ppm)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7.28
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7.24
7.24
7.22
7.20
7.20
7.18
4.78
4.76
4.23
4.21
4.20
3.62
3.60
3.59
3.53
3.51
3.49
3.46
2.83
2.81
2.79
1.23
1.21
1.19
O
OEt
N
H
O
4t
4.3
4.2
4.1
3.7
3.6
3.5
3.4
2.9
2.8
2.7
1.26
1.17
5.35
0.82
2.00
6.60
2.24
3.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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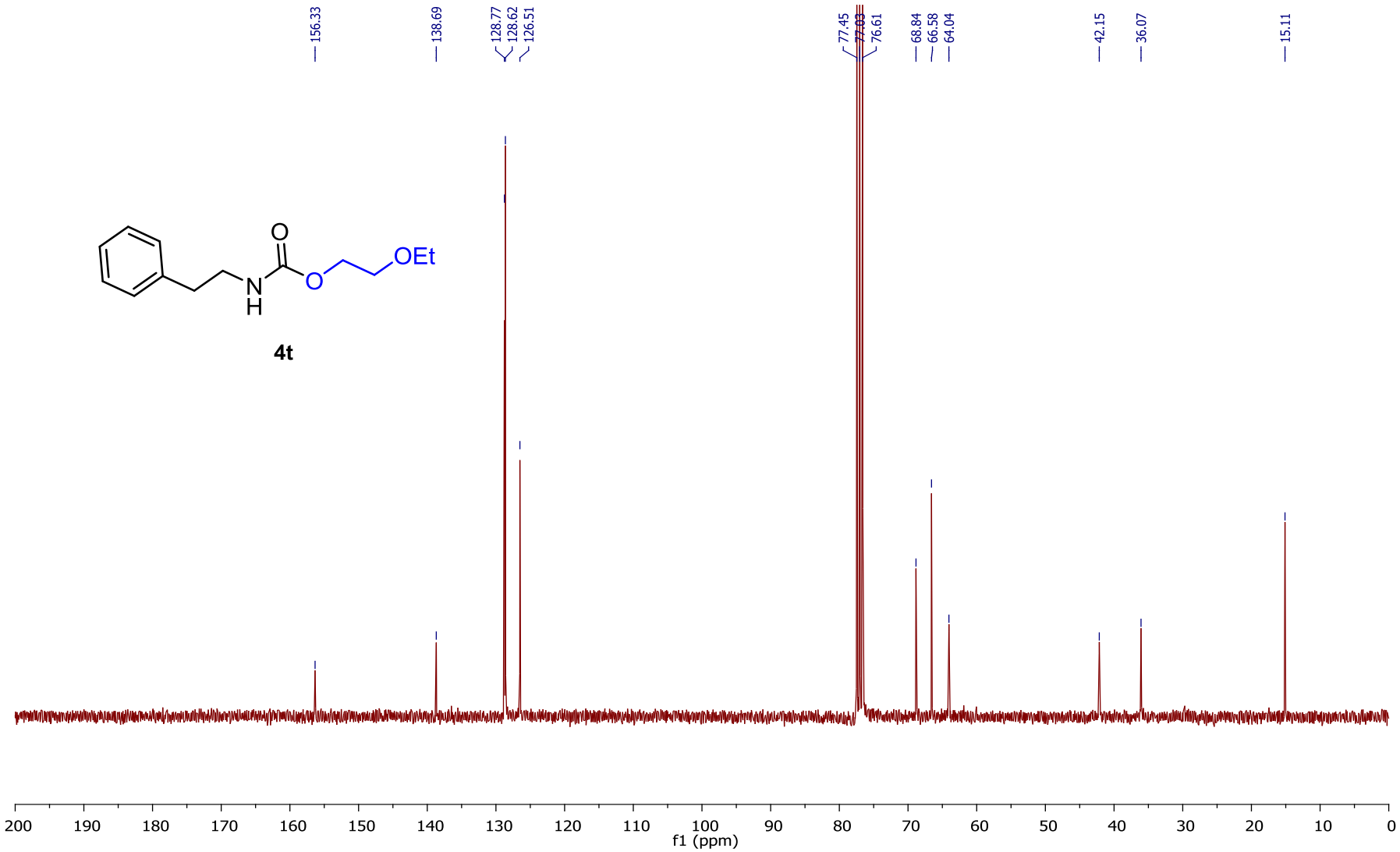
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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126.51
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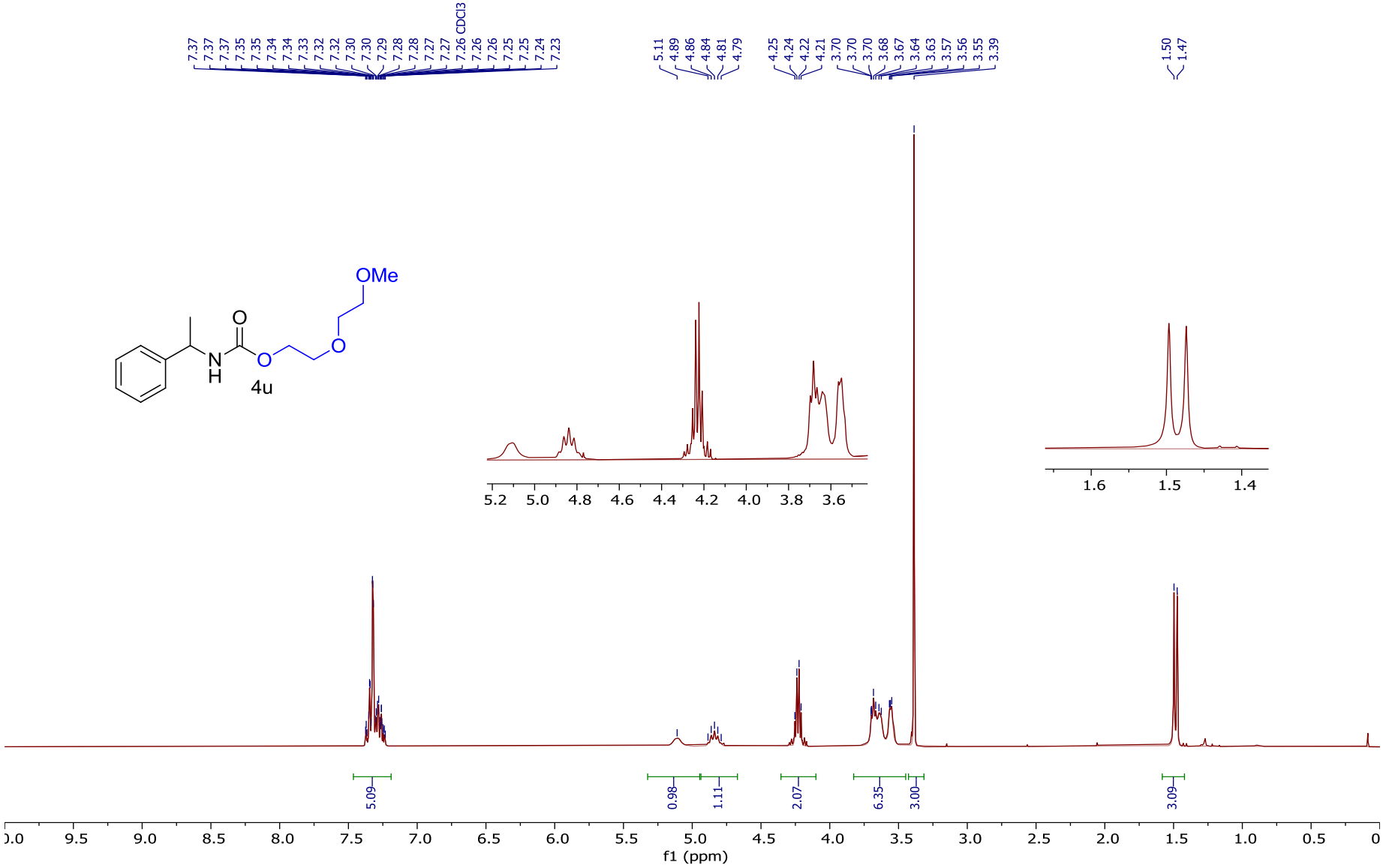
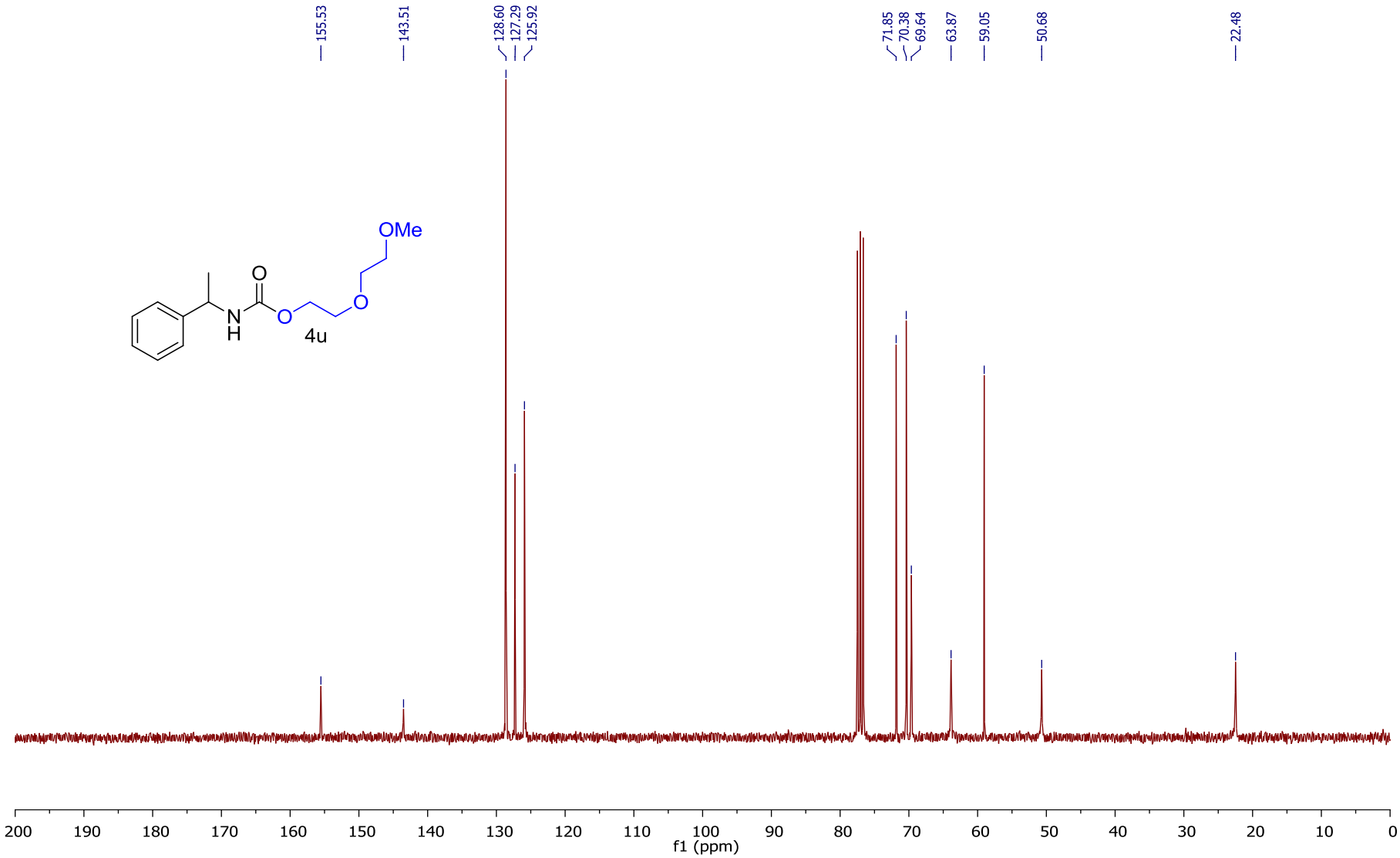
76.61
68.84
66.58
64.04
42.15
36.07
15.11
O
N
H
O
OEt
4t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37 7.37 7.37 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.26 7.26 7.25 7.25 7.24 7.23
5.11 4.89 4.86 4.84 4.81 4.79
4.25 4.24 4.22 4.21 3.70 3.70 3.70 3.68 3.67 3.64 3.63 3.57 3.56 3.55 3.39
1.50 1.47
OMe
O
N
H
O
O
4u
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
1.6 1.5 1.4
5.09
0.98
1.11
2.07
6.35
3.00
3.09
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
f1 (ppm)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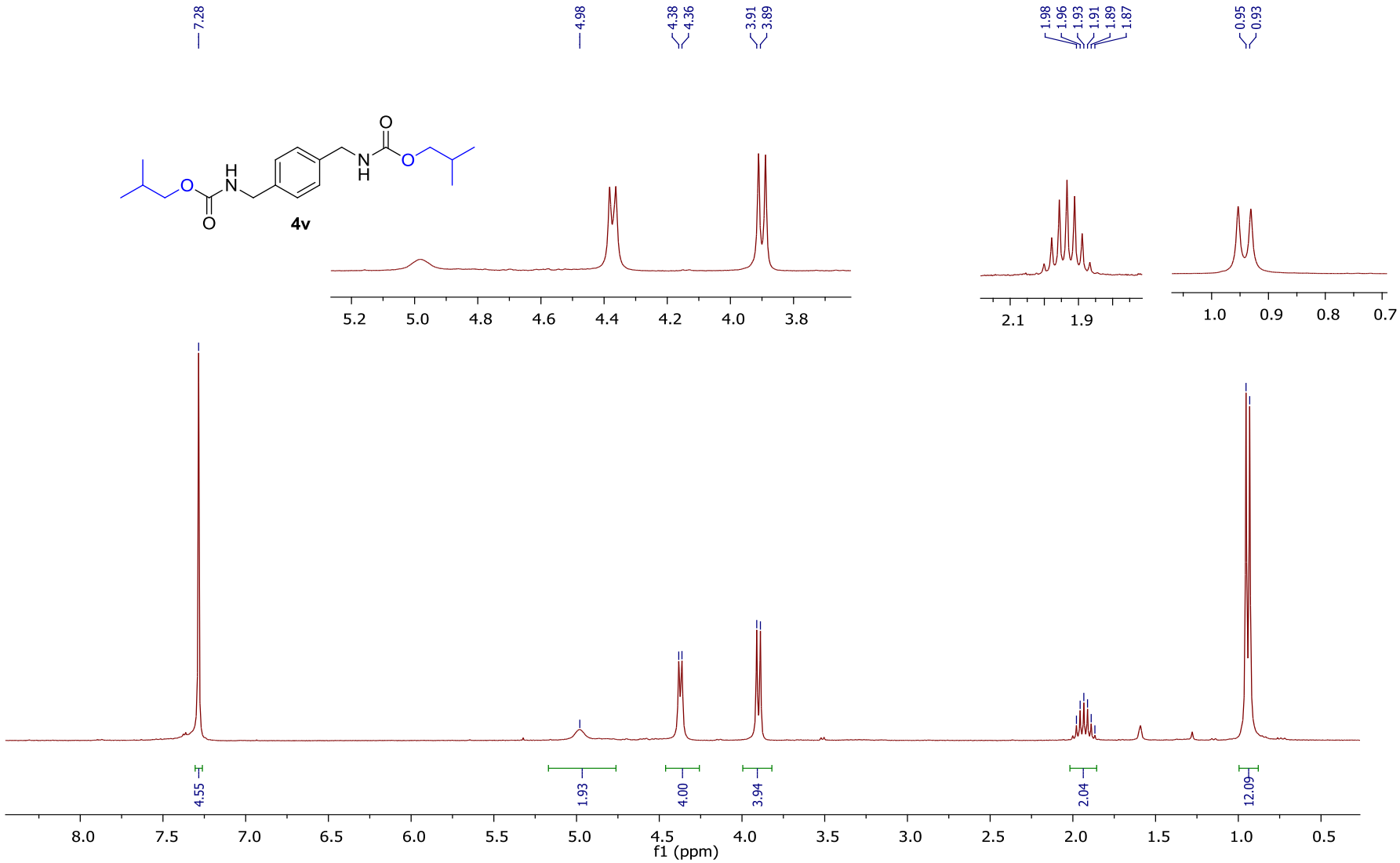
71.85
70.38
69.64
63.87
59.05
50.68
22.48
OMe
O
N
H
O
O
4u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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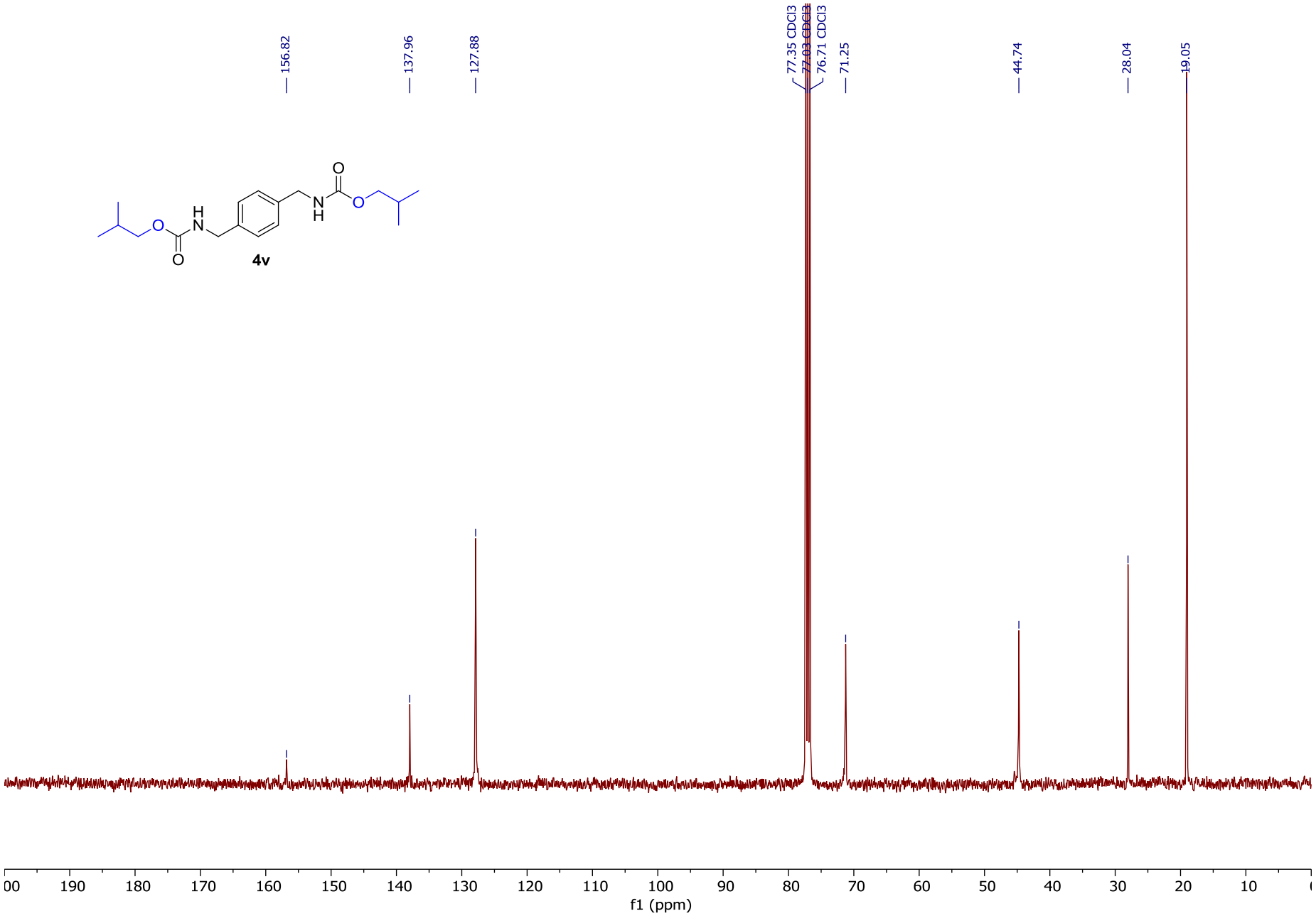
4.38
4.36
3.91
3.89
1.98
1.96
1.93
1.91
1.89
1.87
0.95
0.93
4v
4.55
1.93
4.00
3.94
2.04
12.09
f1 (ppm)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137.96
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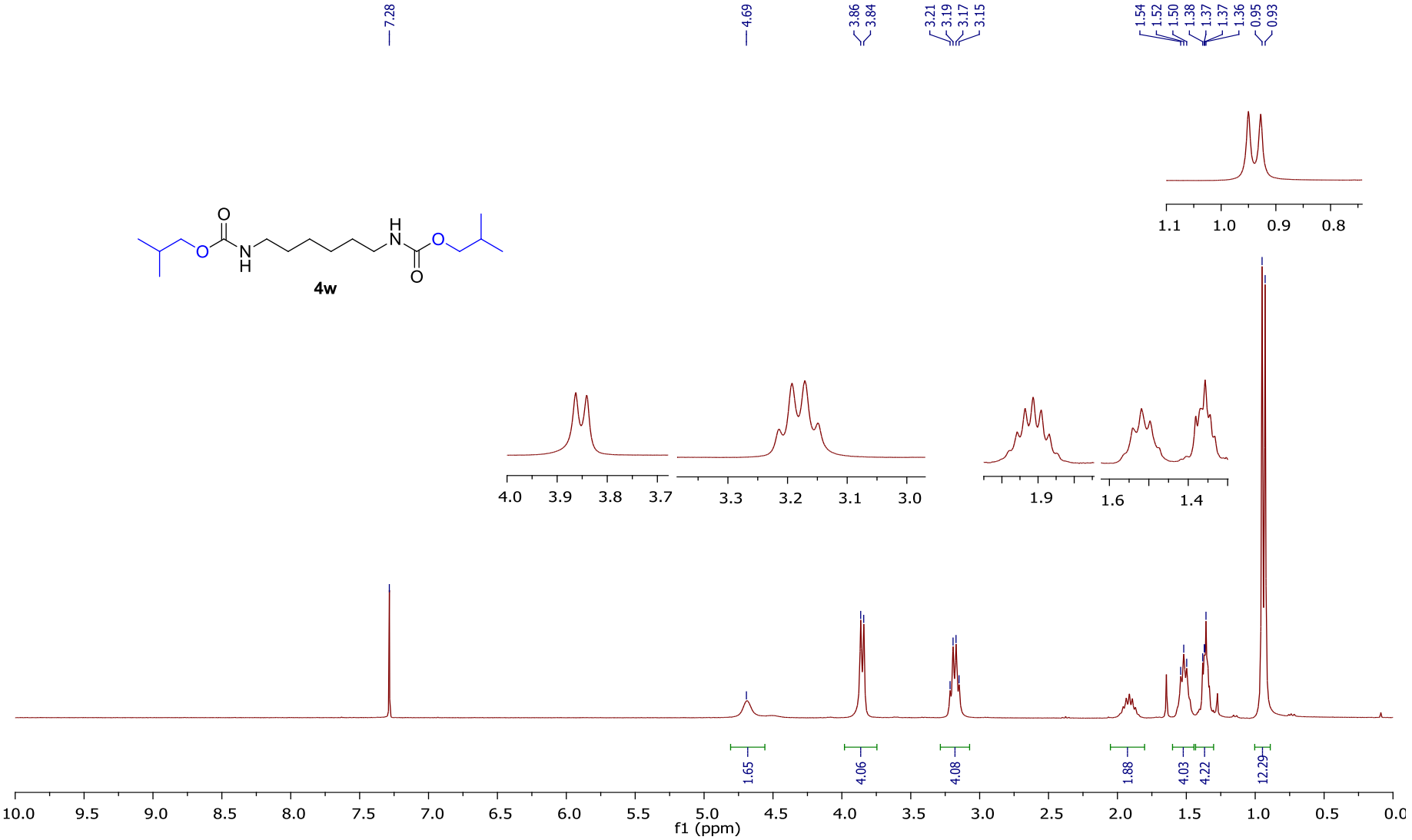
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
71.25
44.74
28.04
19.05
4v
f1 (ppm)


7.28
4.69
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3.84
3.21
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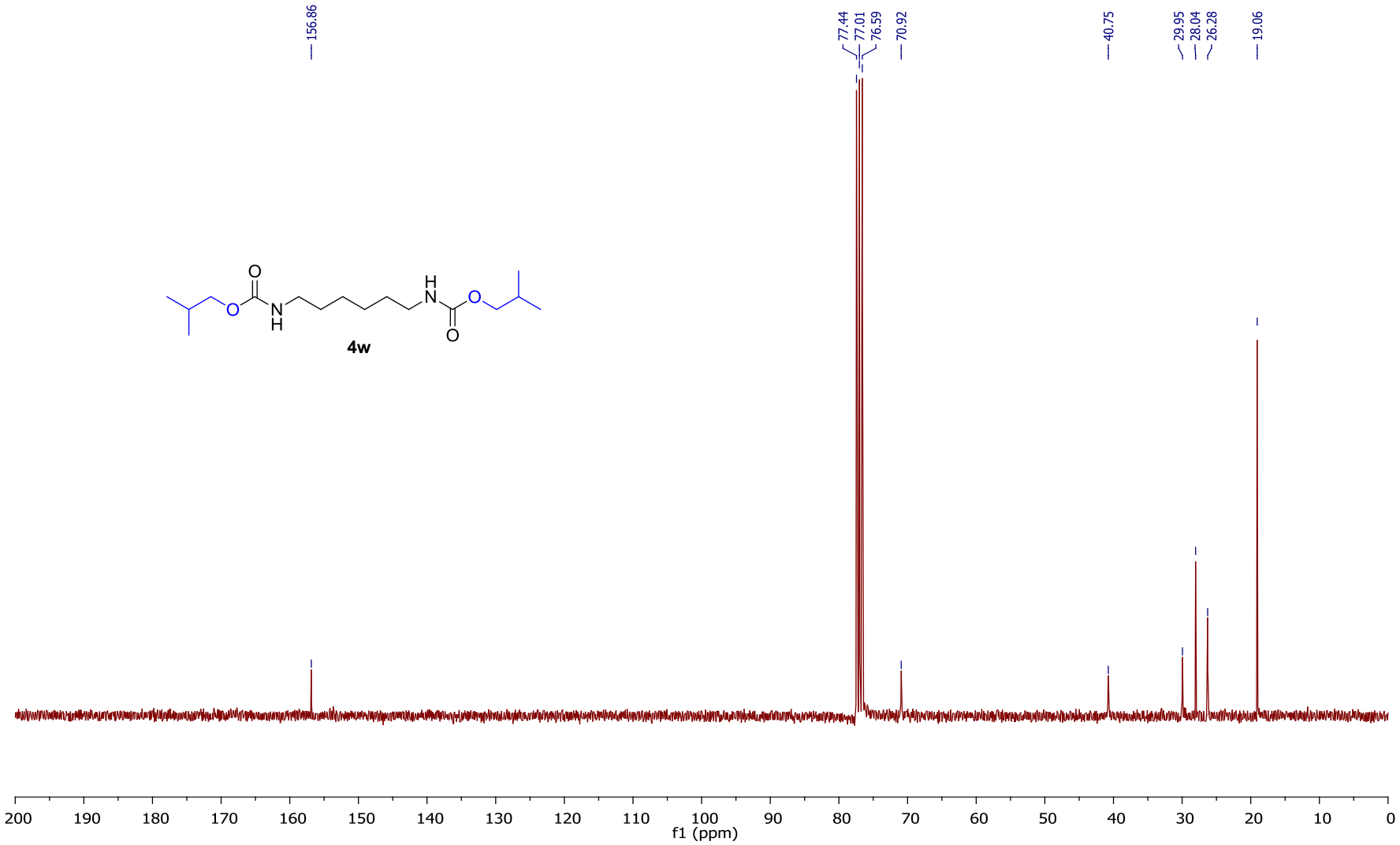
3.17
3.15
1.54
1.52
1.50
1.38
1.37
1.37
1.36
0.95
0.93
4w
1.65
4.06
4.08
1.88
4.03
4.22
12.29
f1 (ppm)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77.44
77.01
76.59
70.92
40.75
29.95
28.04
26.28
19.06
4w
200
190
180
170
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150
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130
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90
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50
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30
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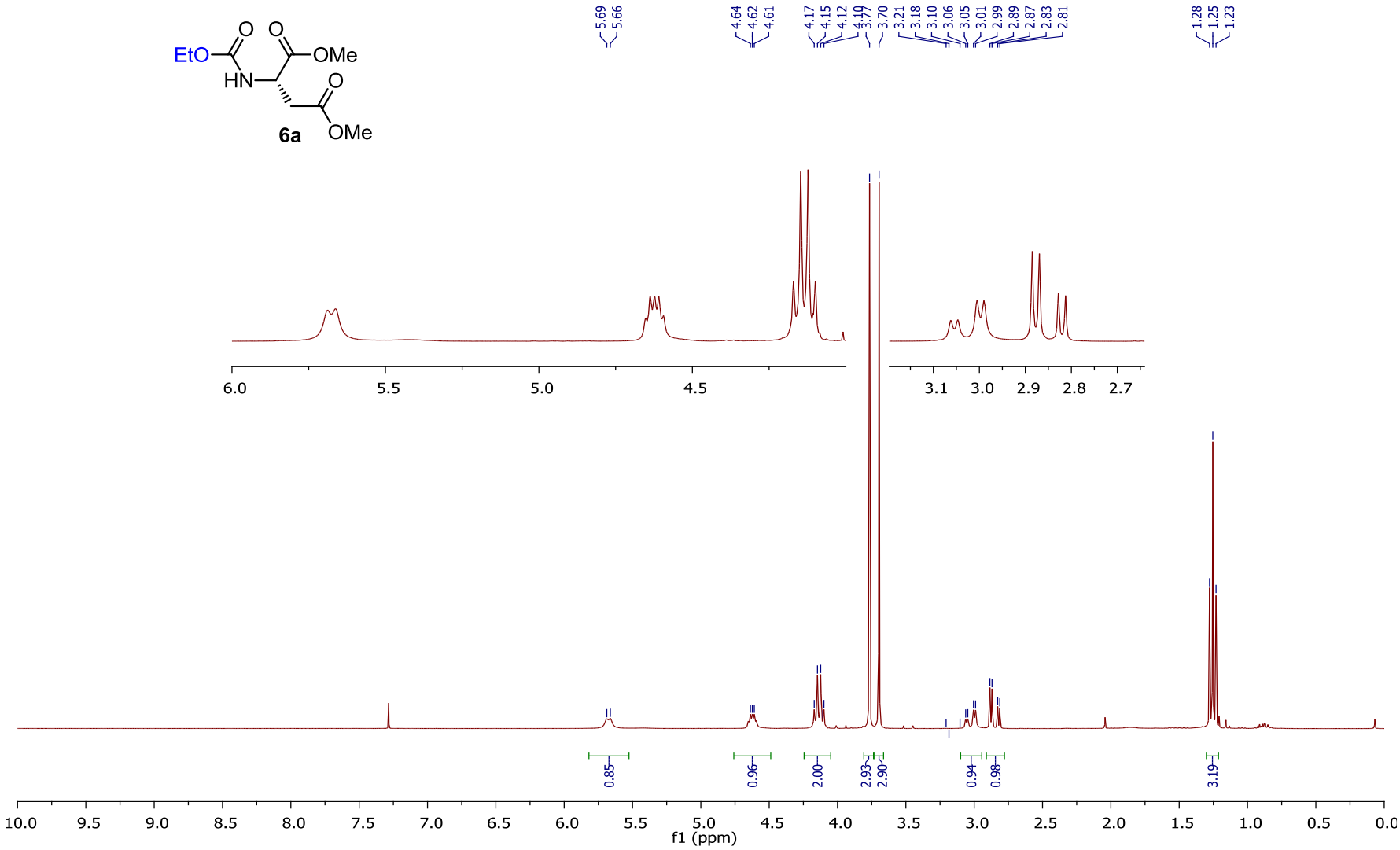
10
0
f1 (ppm)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O
OMe
HN
O
OMe
6a
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5.66
4.64
4.62
4.61
4.17
4.15
4.12
3.77
3.70
3.21
3.18
3.10
3.06
3.05
3.01
2.99
2.89
2.87
2.83
2.81
1.28
1.25
1.23
6.0
5.5
5.0
4.5
3.1
3.0
2.9
2.8
2.7
0.85
0.96
2.00
2.93
2.90
0.94
0.98
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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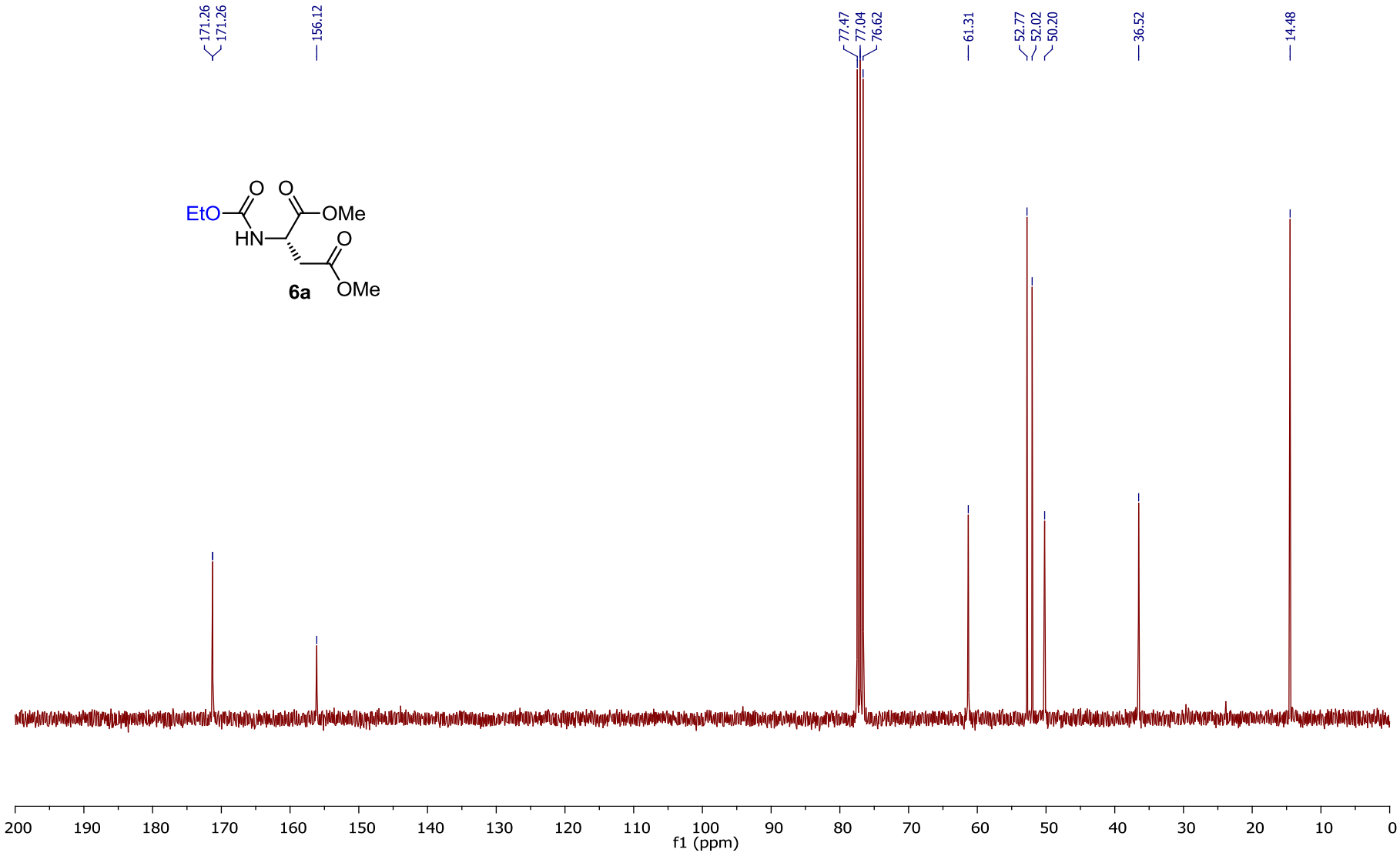
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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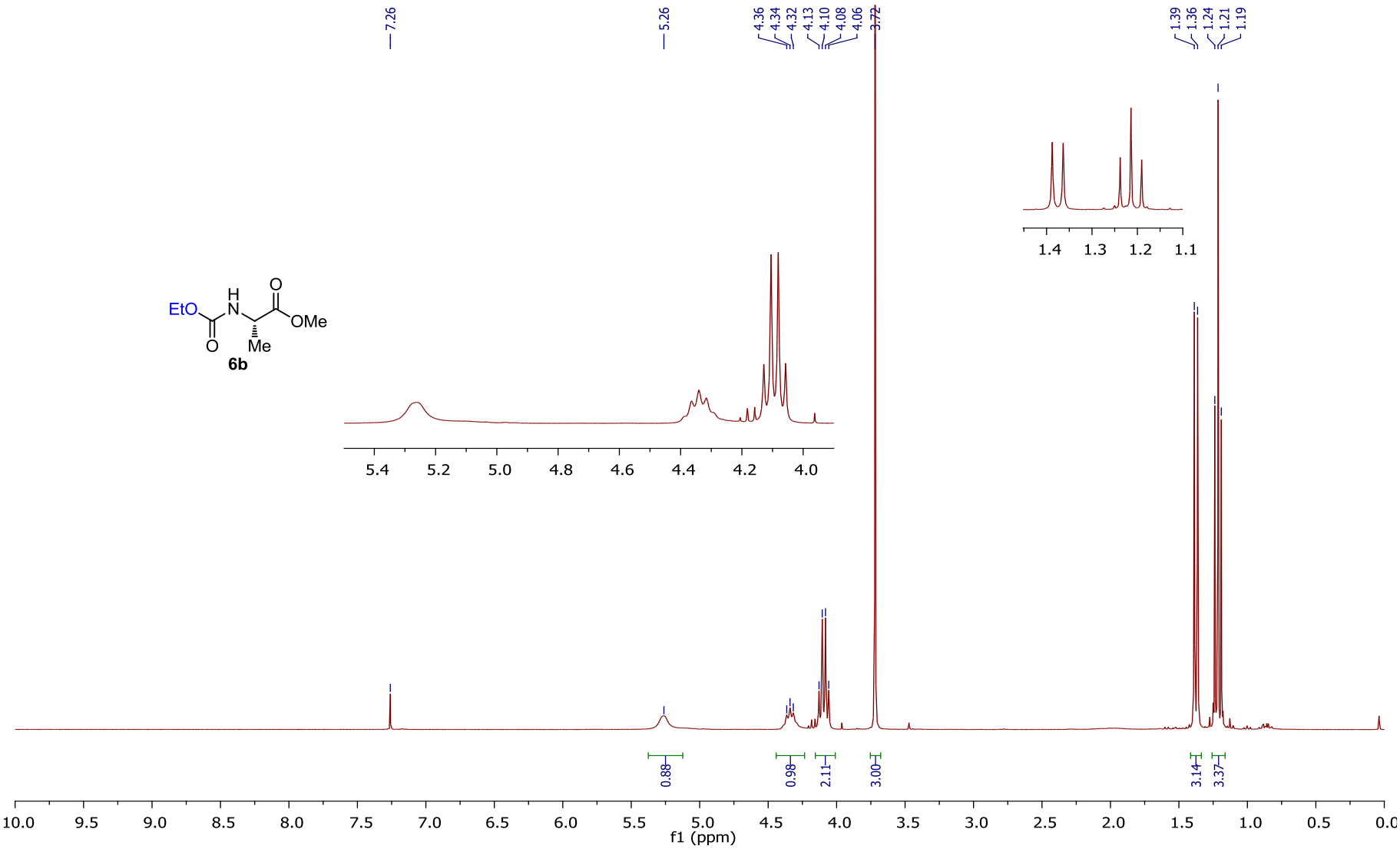
171.26
156.12
77.47
77.04
76.62
61.31
52.77
52.02
50.20
36.52
14.48
EtO
HN
OMe
OMe
6a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
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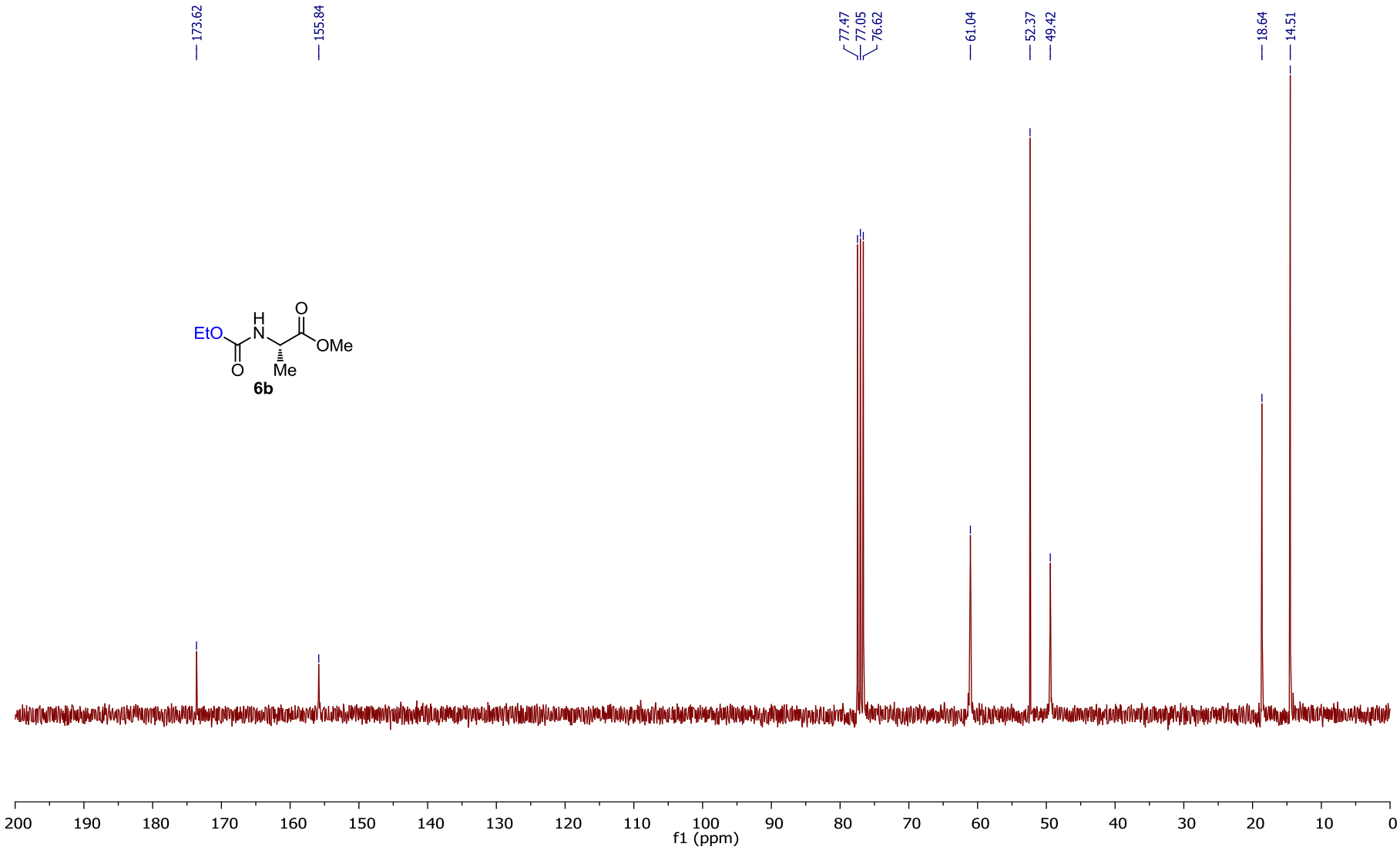
4.34
4.32
4.13
4.10
4.08
4.06
3.72
1.39
1.36
1.24
1.21
1.19
EtO
O
H
N
O
OMe
Me
O
6b
0.88
0.98
2.11
3.00
3.14
3.37
f1 (ppm)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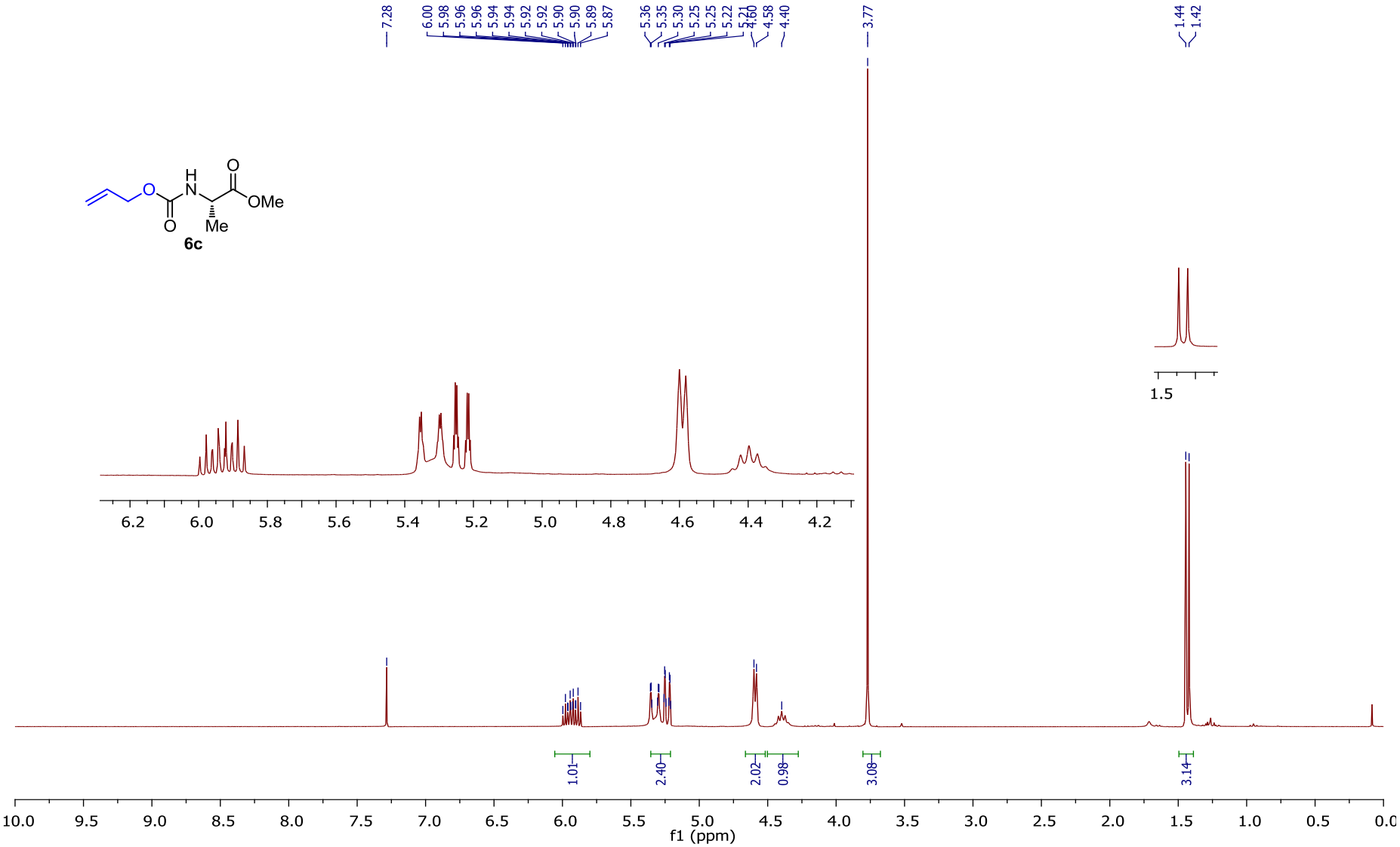
61.04
52.37
49.42
18.64
14.51
EtO
H
N
O
O
OMe
O
Me
6b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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5.98
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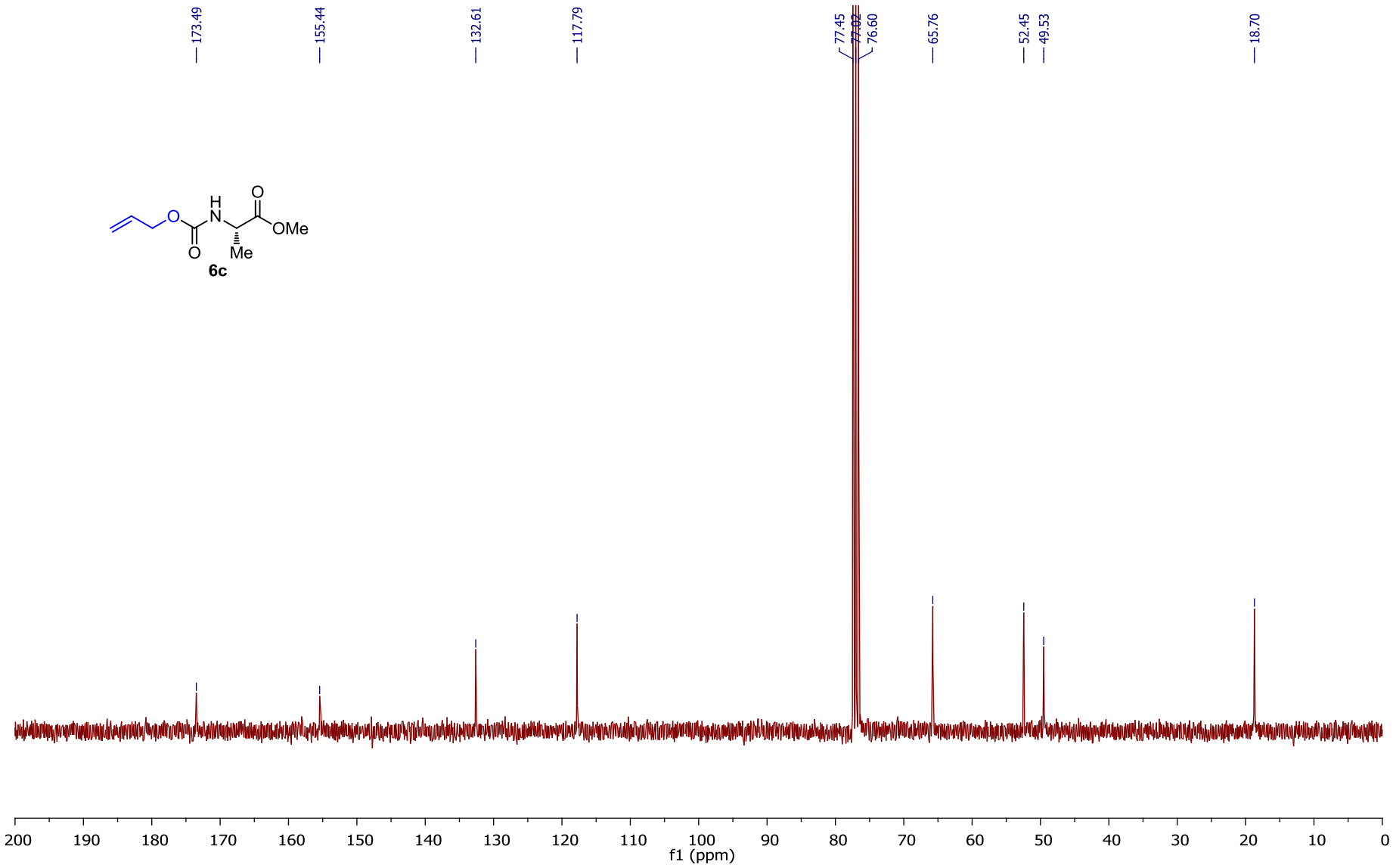
5.94
5.94
5.92
5.92
5.90
5.90
5.89
5.87
5.36
5.35
5.30
5.25
5.25
5.22
5.21
5.20
4.58
4.40
3.77
1.44
1.42
H
N
O
O
O
OMe
Me
6c
1.5
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
1.01
2.40
2.02
0.98
3.08
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.61
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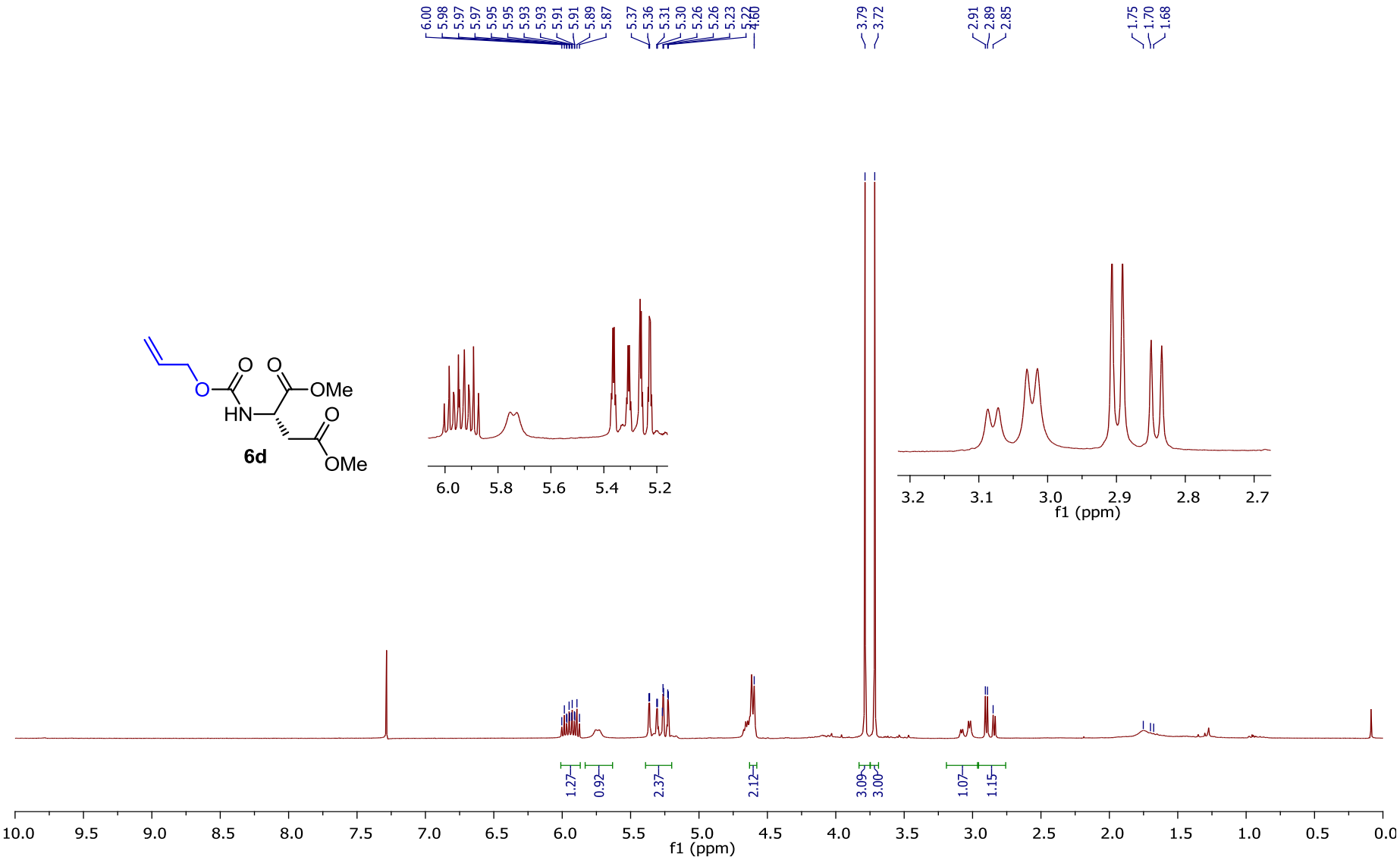
77.45
77.02
76.60
65.76
52.45
49.53
18.70
O
H
N
O
OMe
O
Me
6c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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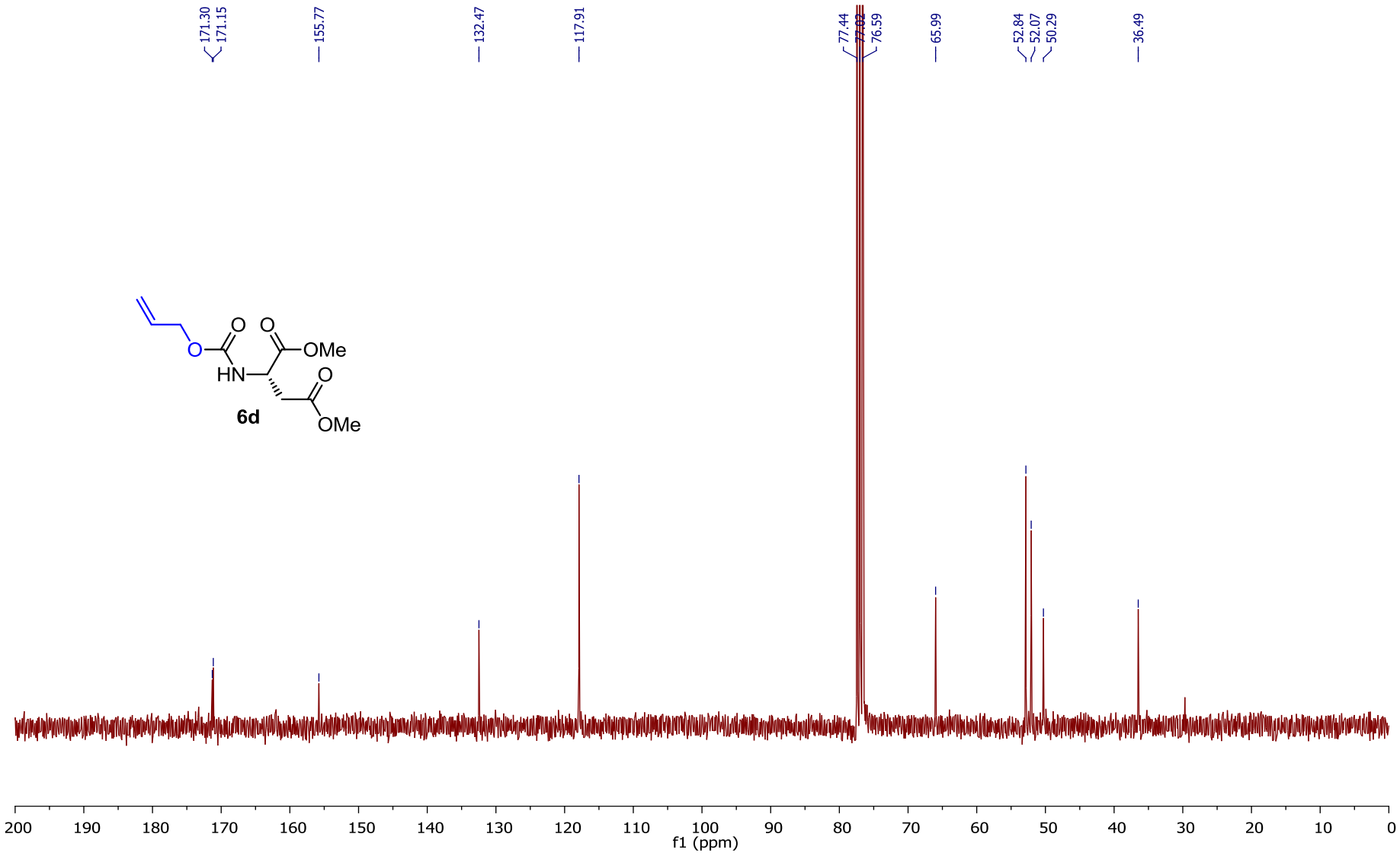
5.98
5.97
5.97
5.95
5.95
5.93
5.93
5.91
5.91
5.89
5.87
5.37
5.36
5.31
5.30
5.26
5.26
5.23
5.22
4.60
3.79
3.72
2.91
2.89
2.85
1.75
1.70
1.68
O
O
OMe
HN
O
OMe
6d
6.0
5.8
5.6
5.4
5.2
3.2
3.1
3.0
2.9
2.8
2.7
f1 (ppm)
1.27
0.92
2.37
2.12
3.09
3.00
1.07
1.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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171.15
155.77
132.47
117.91
77.44
77.02
76.59
65.99
52.84
52.07
50.29
36.49
O
O
OMe
HN
O
OMe
6d
200
190
180
170
160
150
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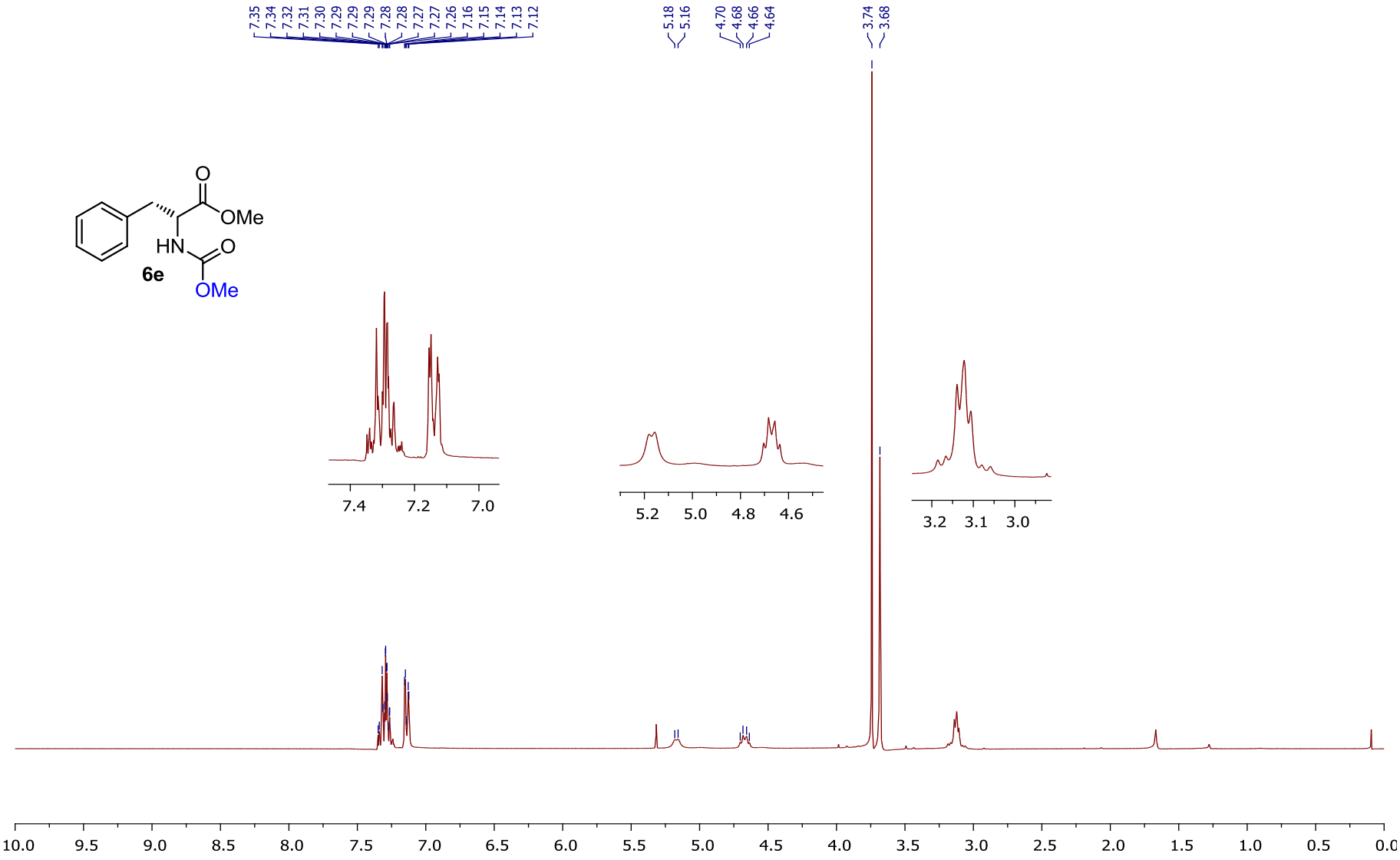
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.29
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7.29
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7.28
7.27
7.27
7.26
7.16
7.15
7.14
7.13
7.12
5.18
5.16
4.70
4.68
4.66
4.64
3.74
3.68
O
OMe
HN
O
6e
OMe
7.4
7.2
7.0
5.2
5.0
4.8
4.6
3.2
3.1
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
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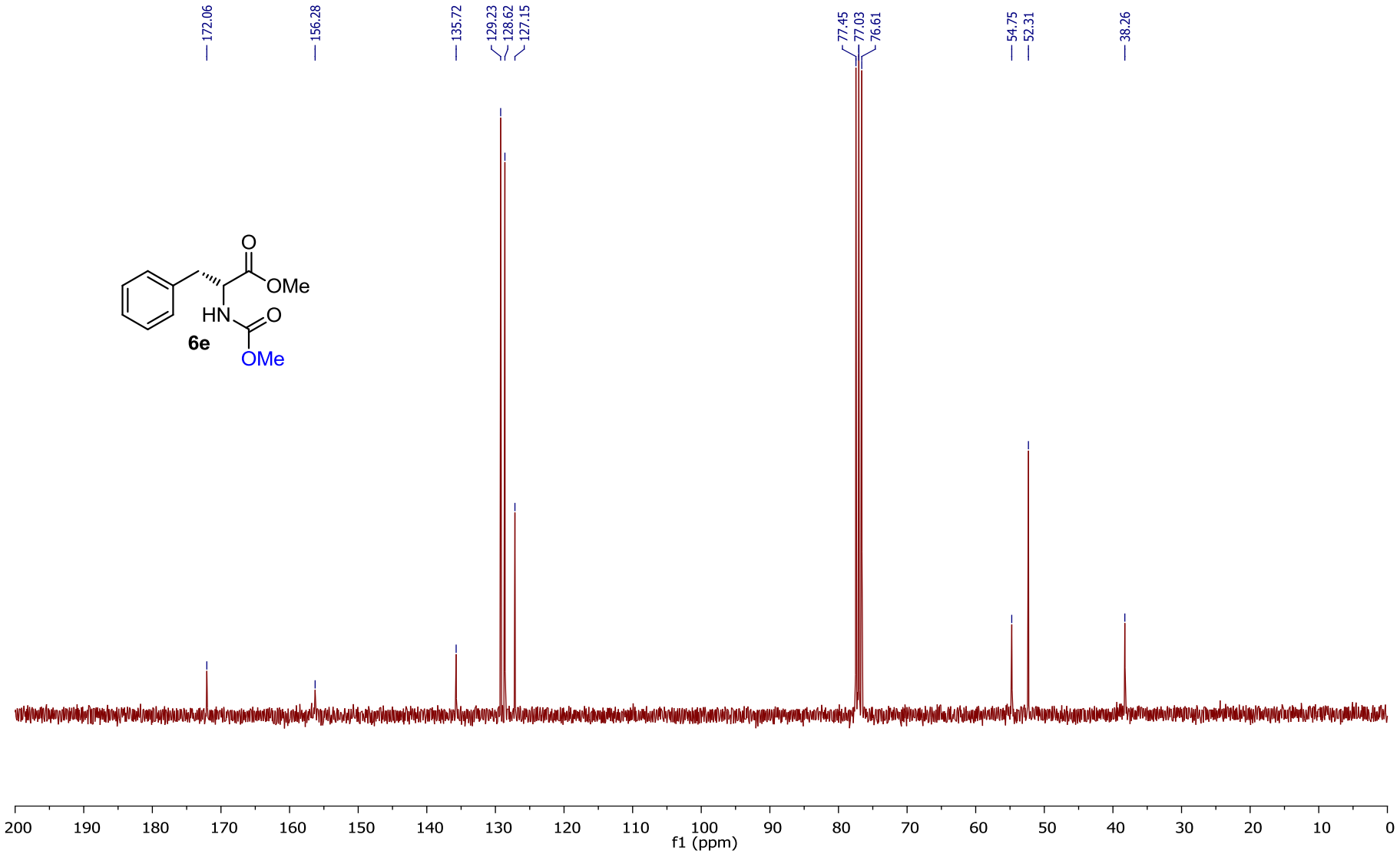
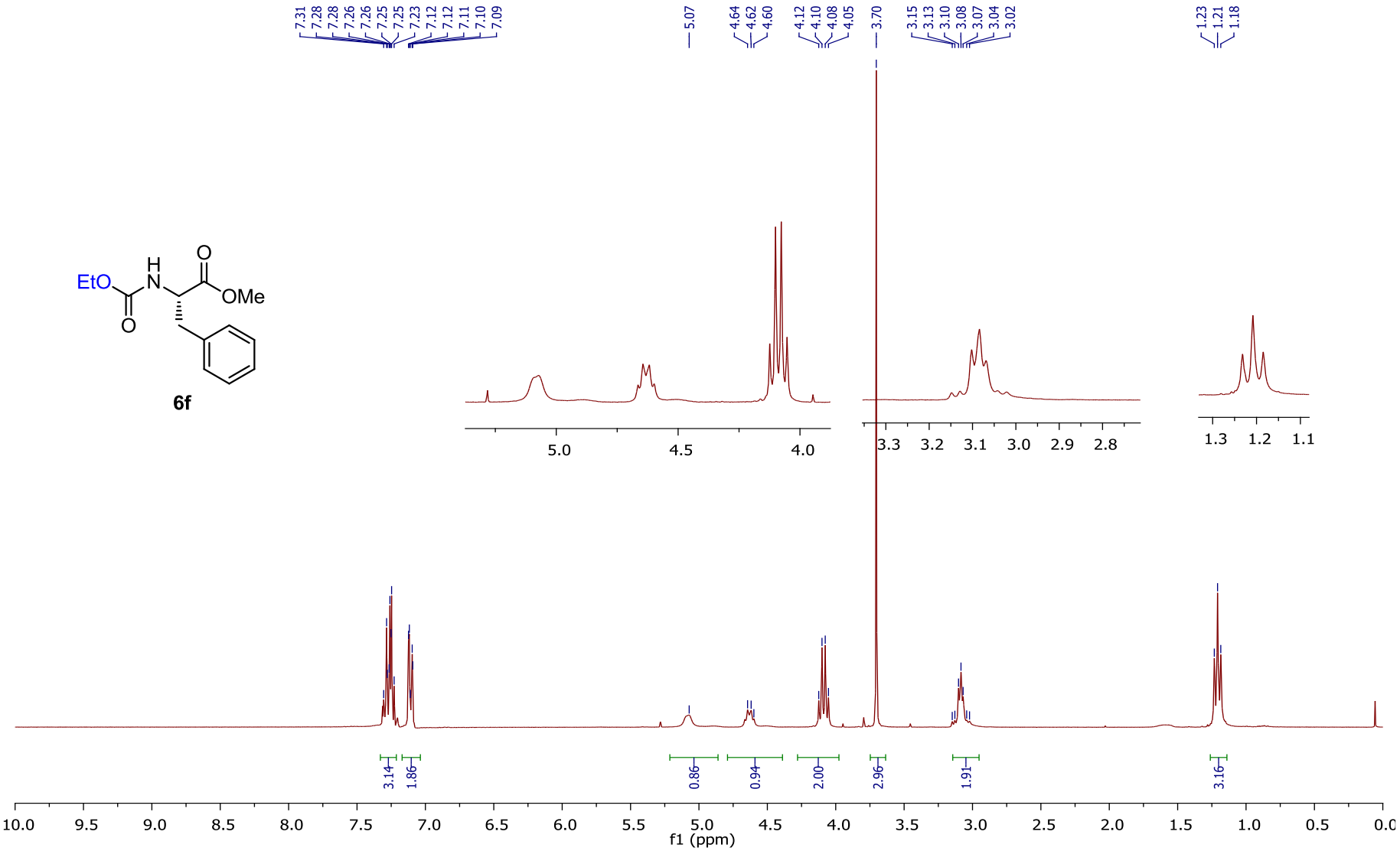
0.5
0.0


172.06
156.28
135.72
129.23
128.62
127.15
77.45
77.03
76.61
54.75
52.31
38.26
O
OMe
HN
O
6e
OMe
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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7.28
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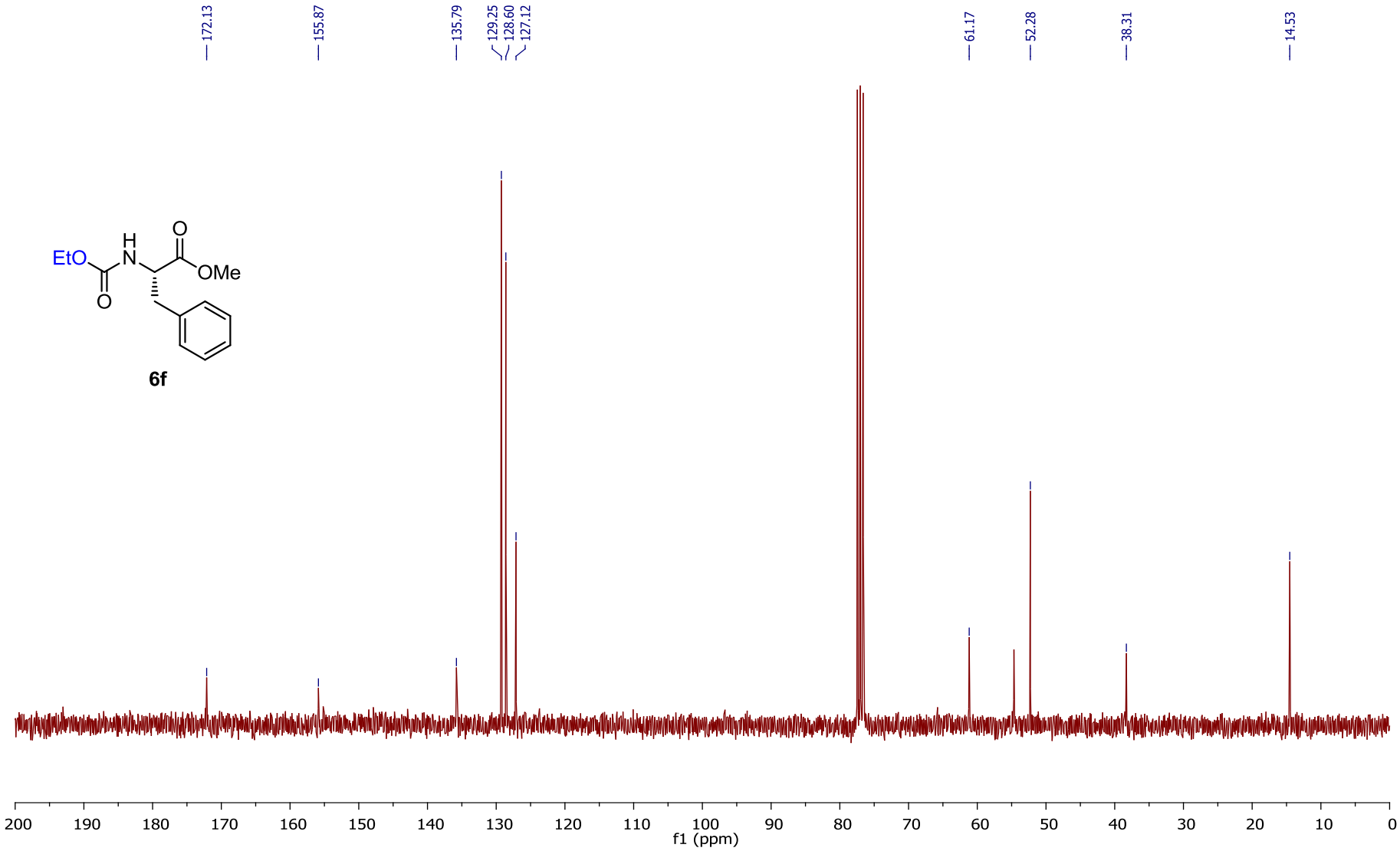
7.26
7.26
7.25
7.25
7.23
7.12
7.12
7.11
7.10
7.09
5.07
4.64
4.62
4.60
4.12
4.10
4.08
4.05
3.70
3.15
3.13
3.10
3.08
3.07
3.04
3.02
1.23
1.21
1.18
EtO
H
N
O
O
OMe
O
6f
5.0
4.5
4.0
3.3
3.2
3.1
3.0
2.9
2.8
1.3
1.2
1.1
3.14
1.86
0.86
0.94
2.00
2.96
1.91
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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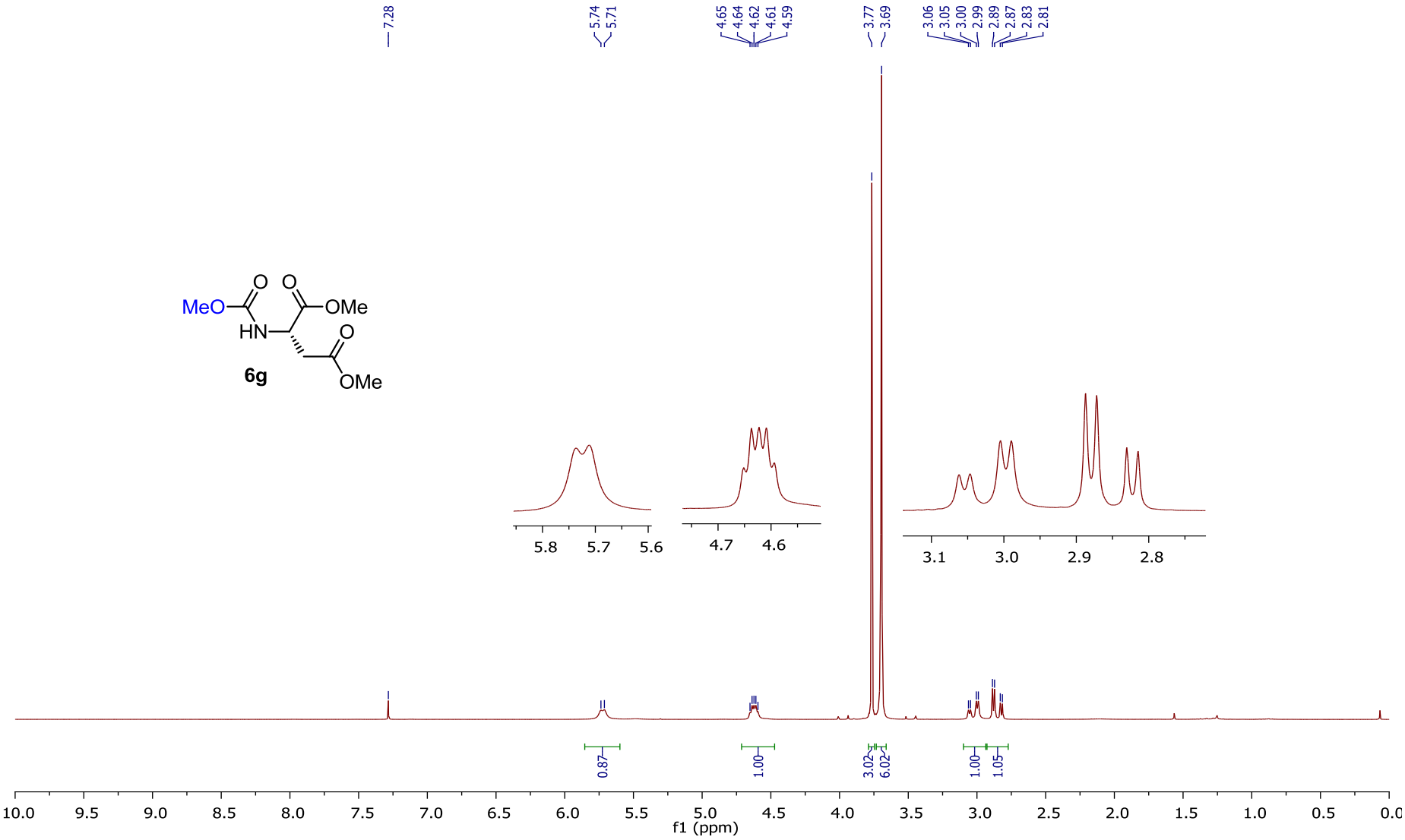
135.79
129.25
128.60
127.12
61.17
52.28
38.31
14.53
EtO
H
N
O
O
OMe
O
6f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.62
4.61
4.59
3.77
3.69
3.06
3.05
3.00
2.99
2.89
2.87
2.83
2.81
MeO
O
O
OMe
HN
O
OMe
6g
5.8
5.7
5.6
4.7
4.6
3.1
3.0
2.9
2.8
0.87
1.00
3.02
6.02
1.00
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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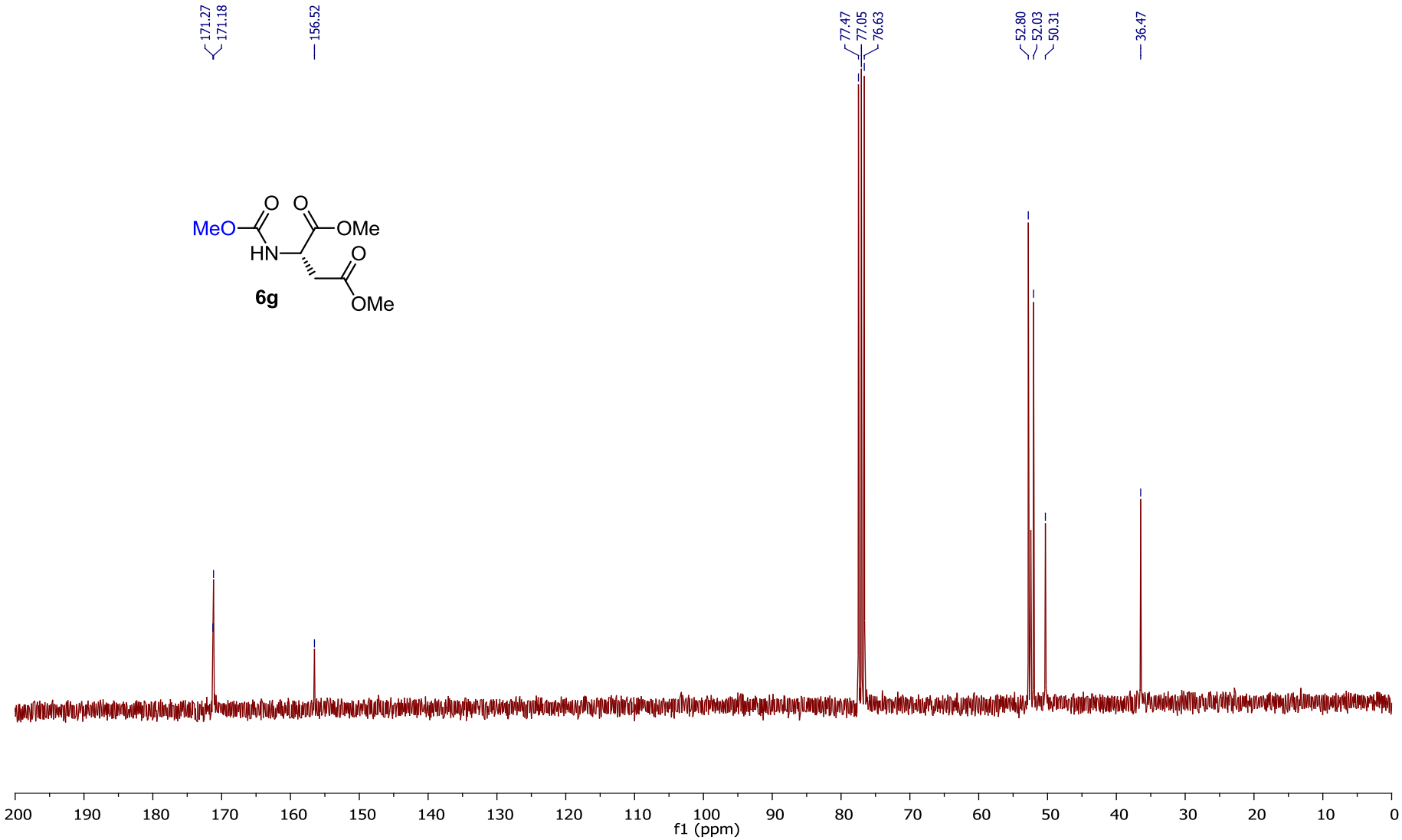
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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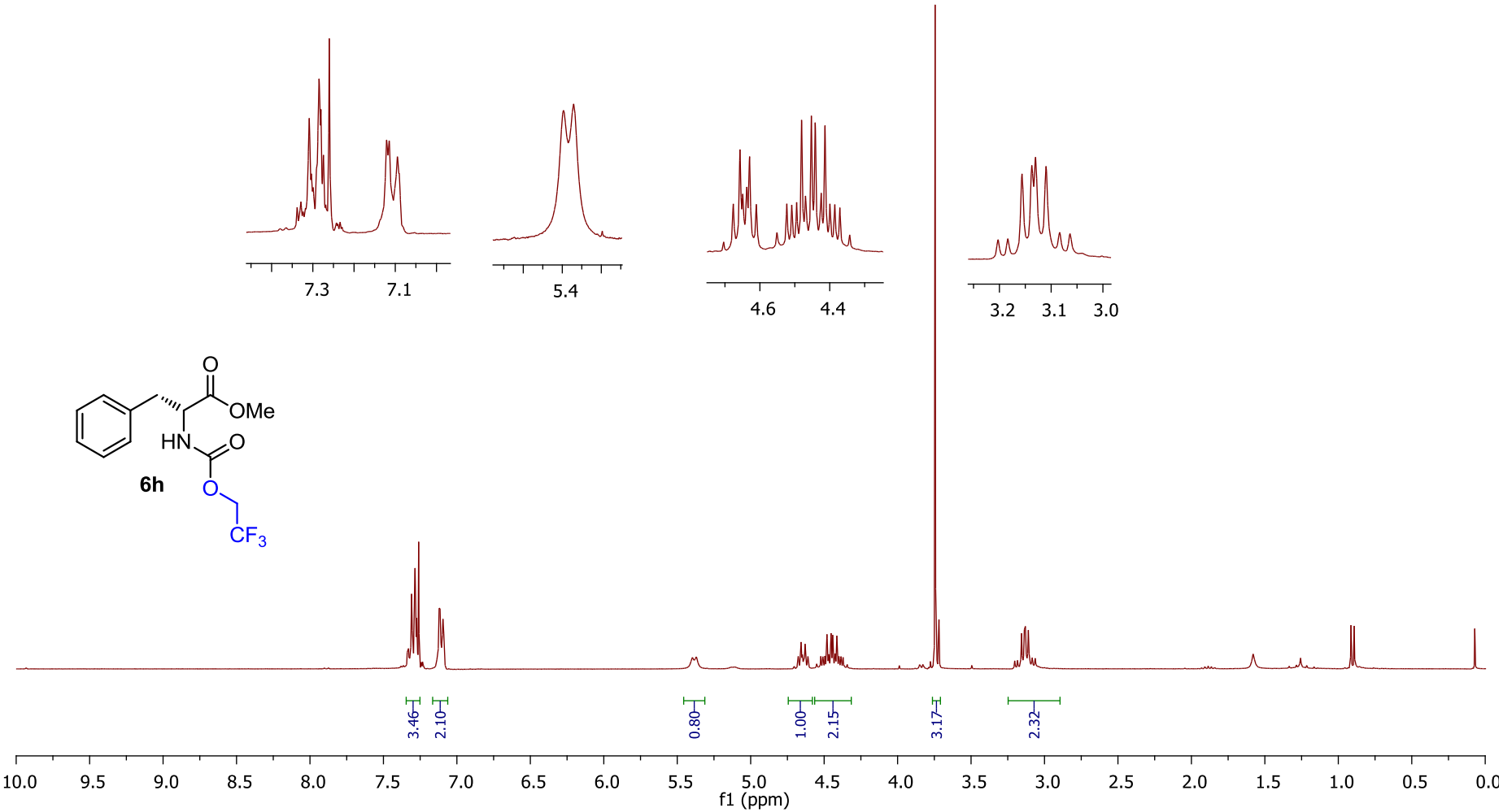
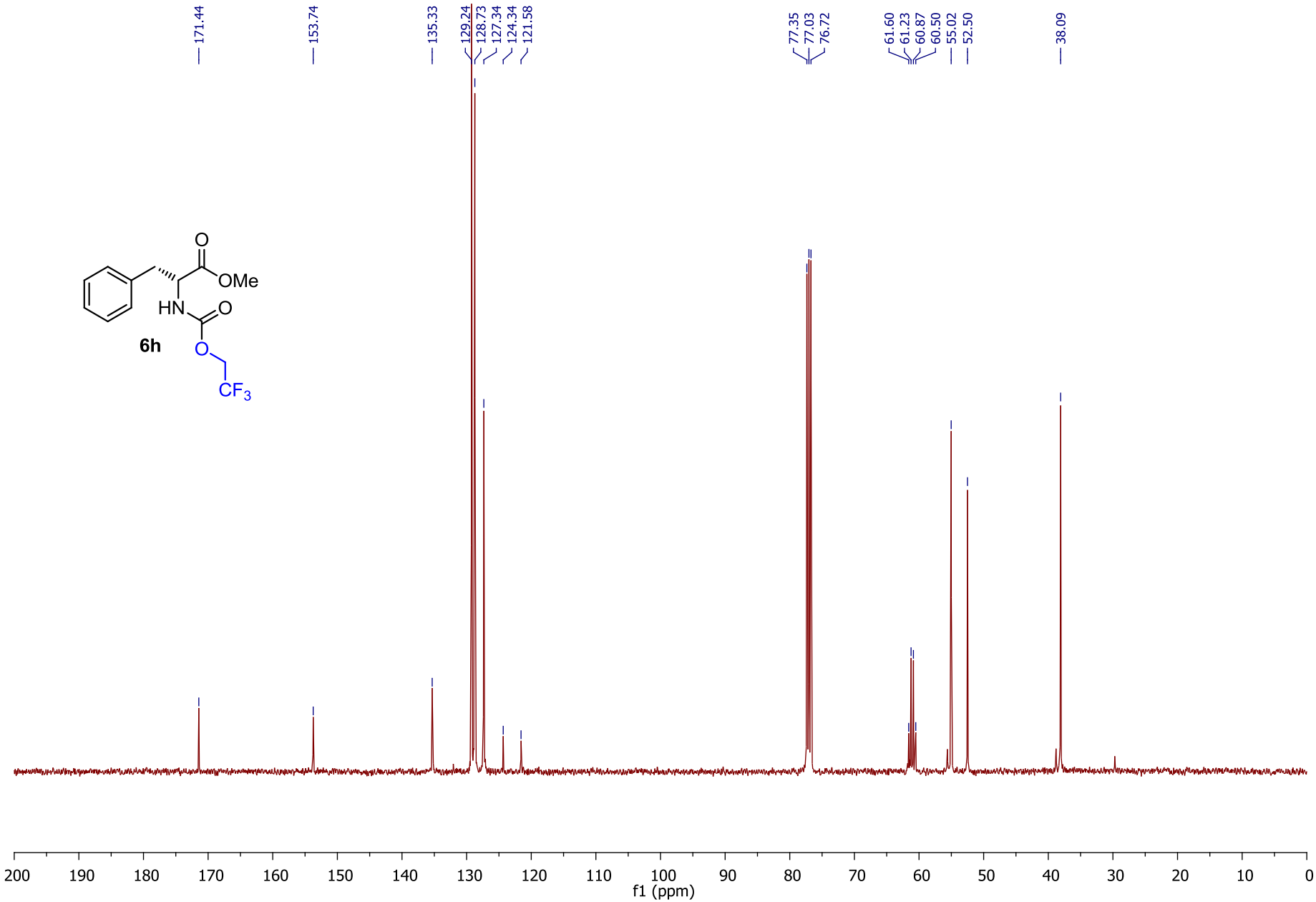
171.18
156.52
77.47
77.05
76.63
52.80
52.03
50.31
36.47
MeO
O
HN
O
O
OMe
O
OMe
6g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.3
7.1
5.4
4.6
4.4
3.2
3.1
3.0
O
OMe
HN
O
O
6h
CF3
3.46
2.10
0.80
1.00
2.15
3.17
2.32
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
f1 (ppm)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135.33
129.24
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127.34
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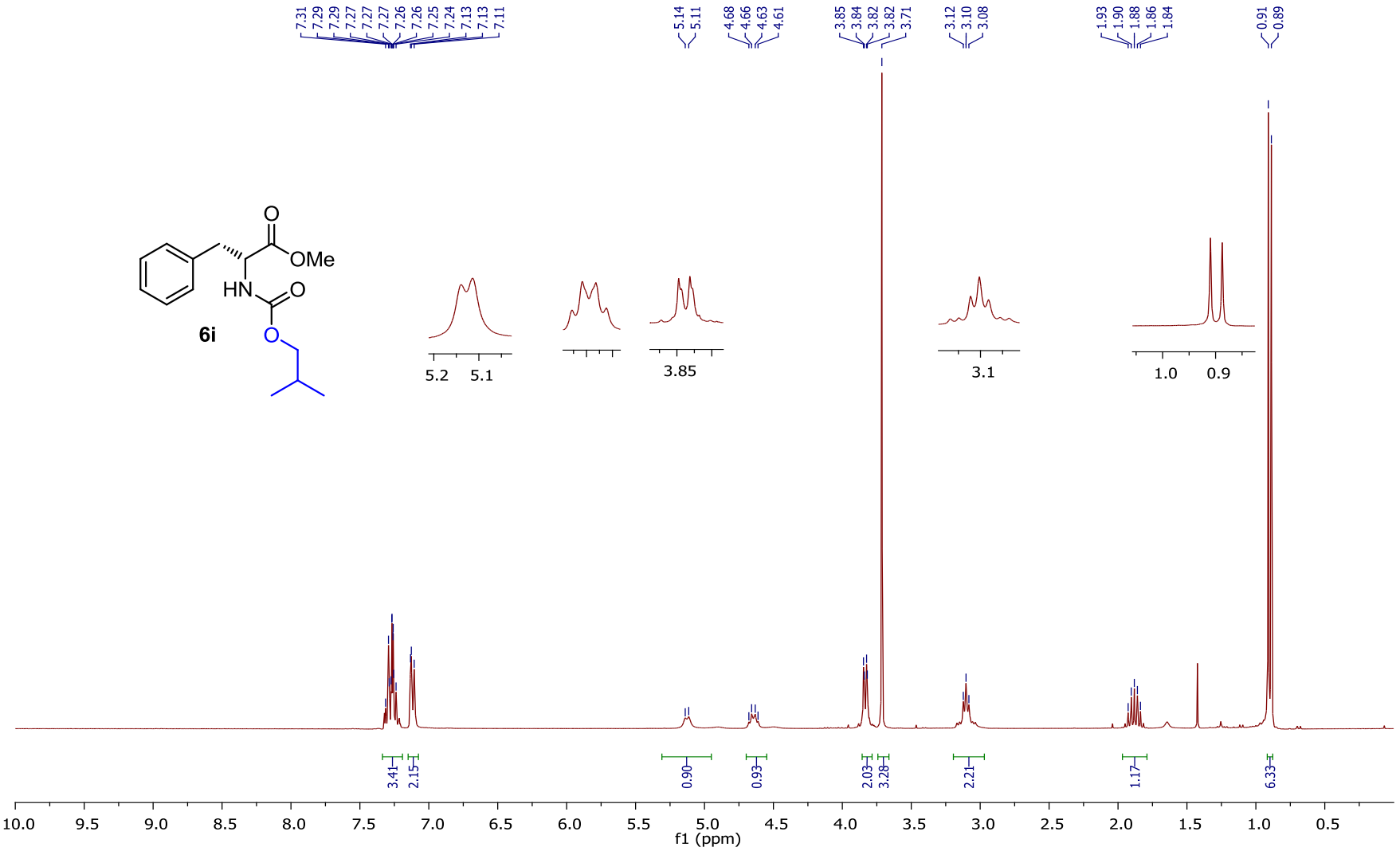
121.58
77.35
77.03
76.72
61.60
61.23
60.87
60.50
55.02
52.50
38.09
O
OMe
HN
O
O
CF3
6h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.29
7.29
7.27
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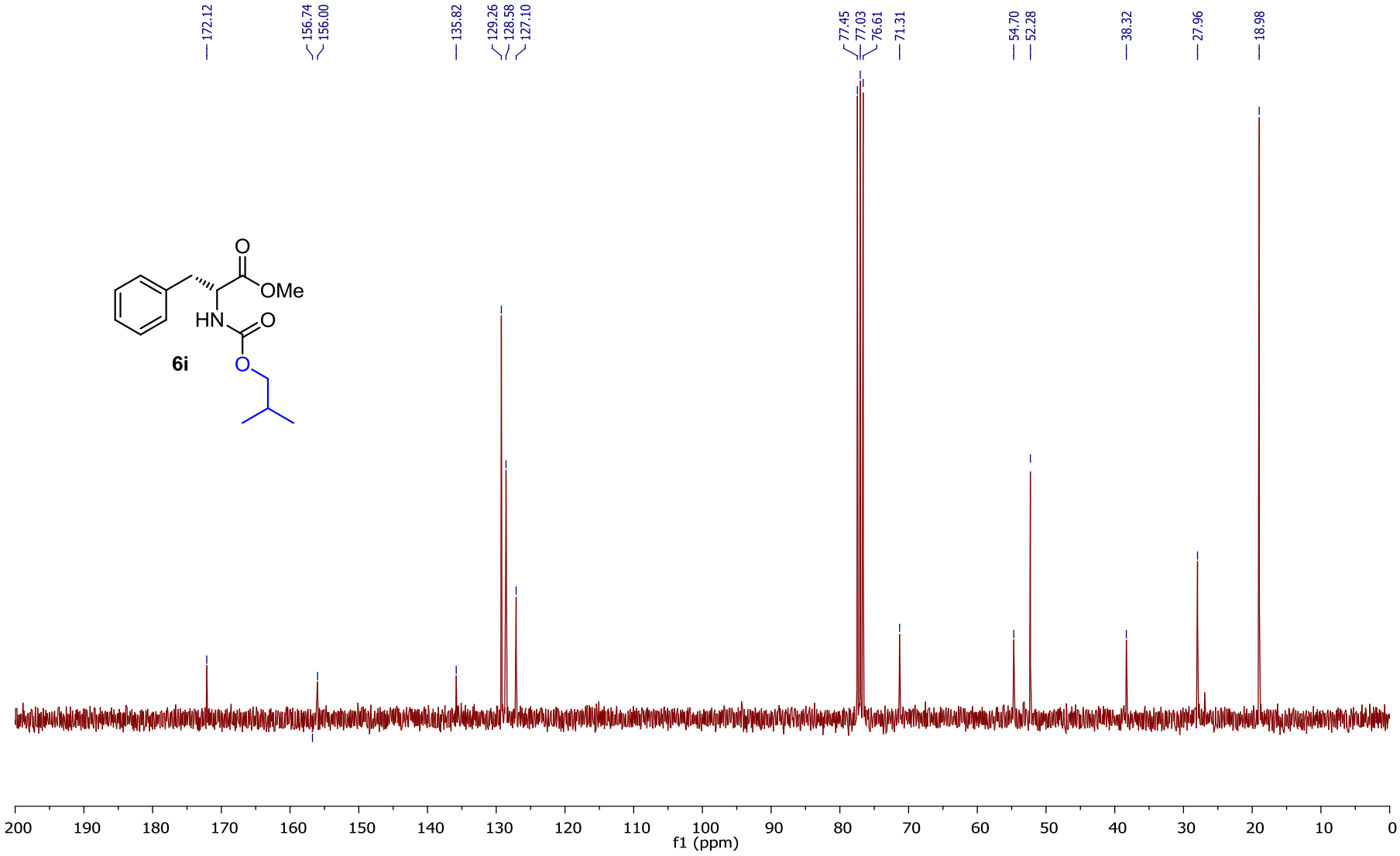
7.27
7.26
7.26
7.25
7.24
7.13
7.13
7.11
5.14
5.11
4.68
4.66
4.63
4.61
3.85
3.84
3.82
3.82
3.71
3.12
3.10
3.08
1.93
1.90
1.88
1.86
1.84
0.91
0.89
O
OMe
HN
O
O
6i
5.2
5.1
3.85
3.1
1.0
0.9
3.41
2.15
0.90
0.93
2.03
3.28
2.21
1.17
6.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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156.00
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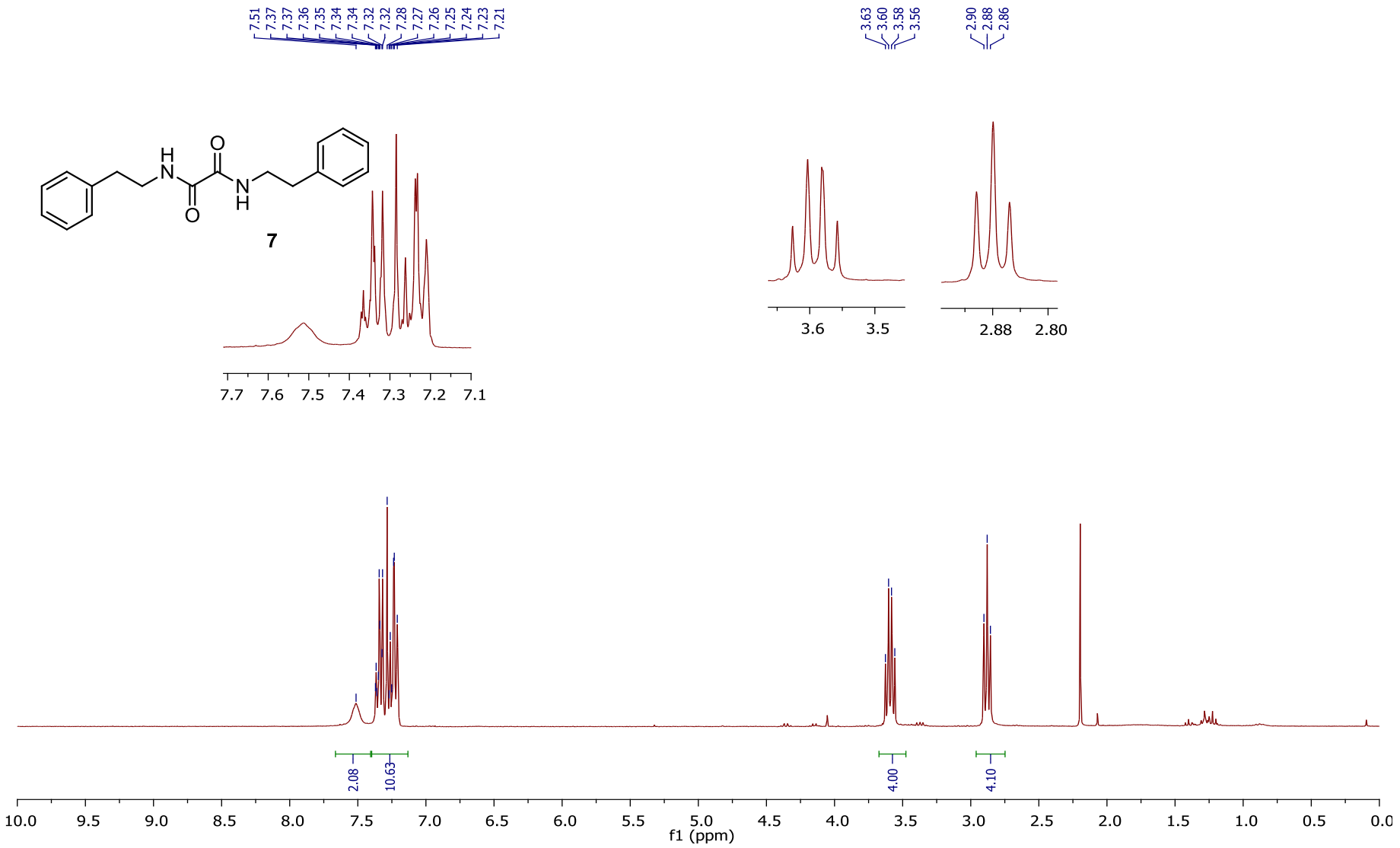
127.10
77.45
77.03
76.61
71.31
54.70
52.28
38.32
27.96
18.98
O
OMe
HN
O
O
6i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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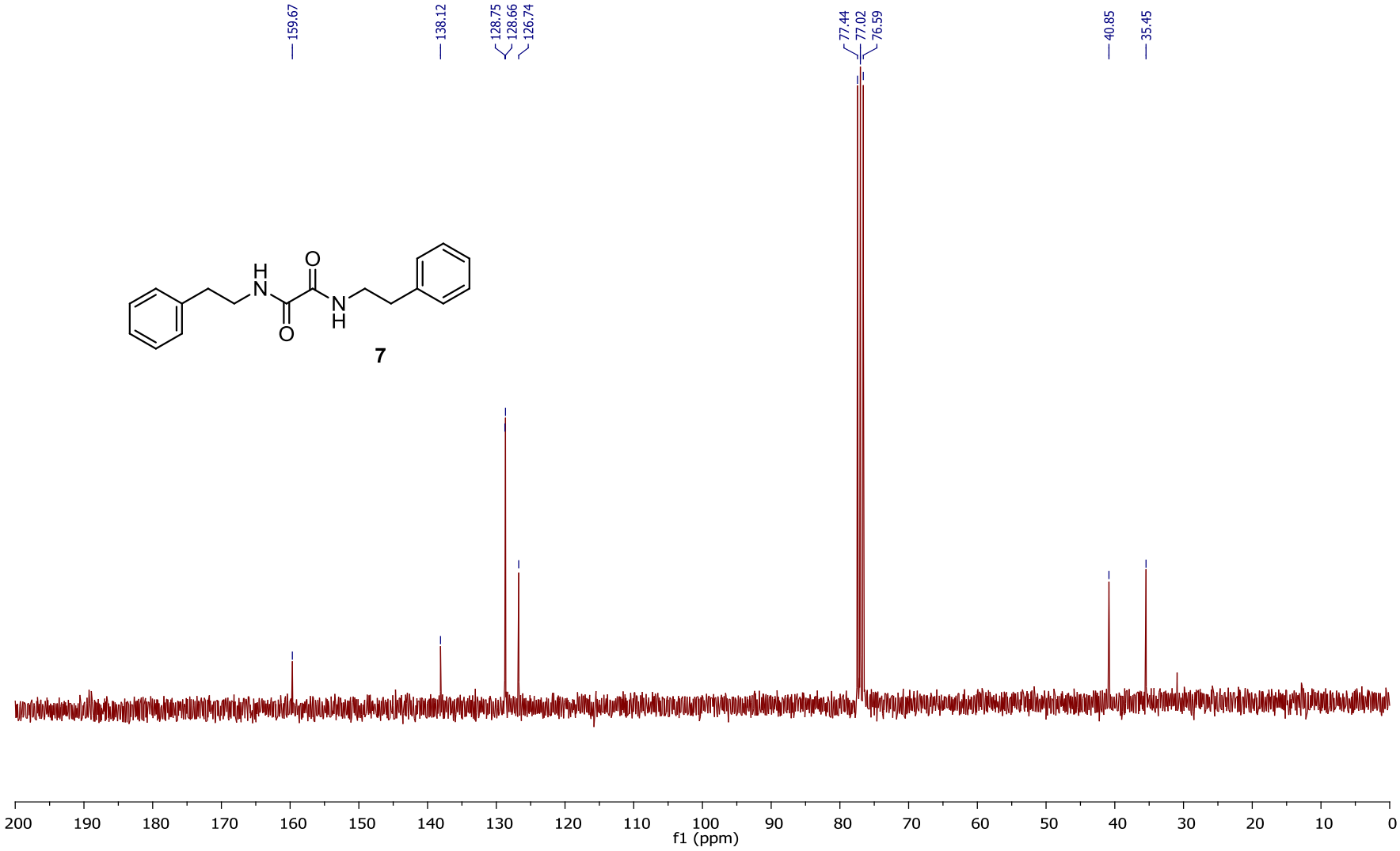
7.34
7.34
7.32
7.32
7.28
7.27
7.26
7.25
7.24
7.23
7.21
3.63
3.60
3.58
3.56
2.90
2.88
2.86
7
7.7 7.6 7.5 7.4 7.3 7.2 7.1
3.6 3.5
2.88 2.80
2.08
10.63
4.00
4.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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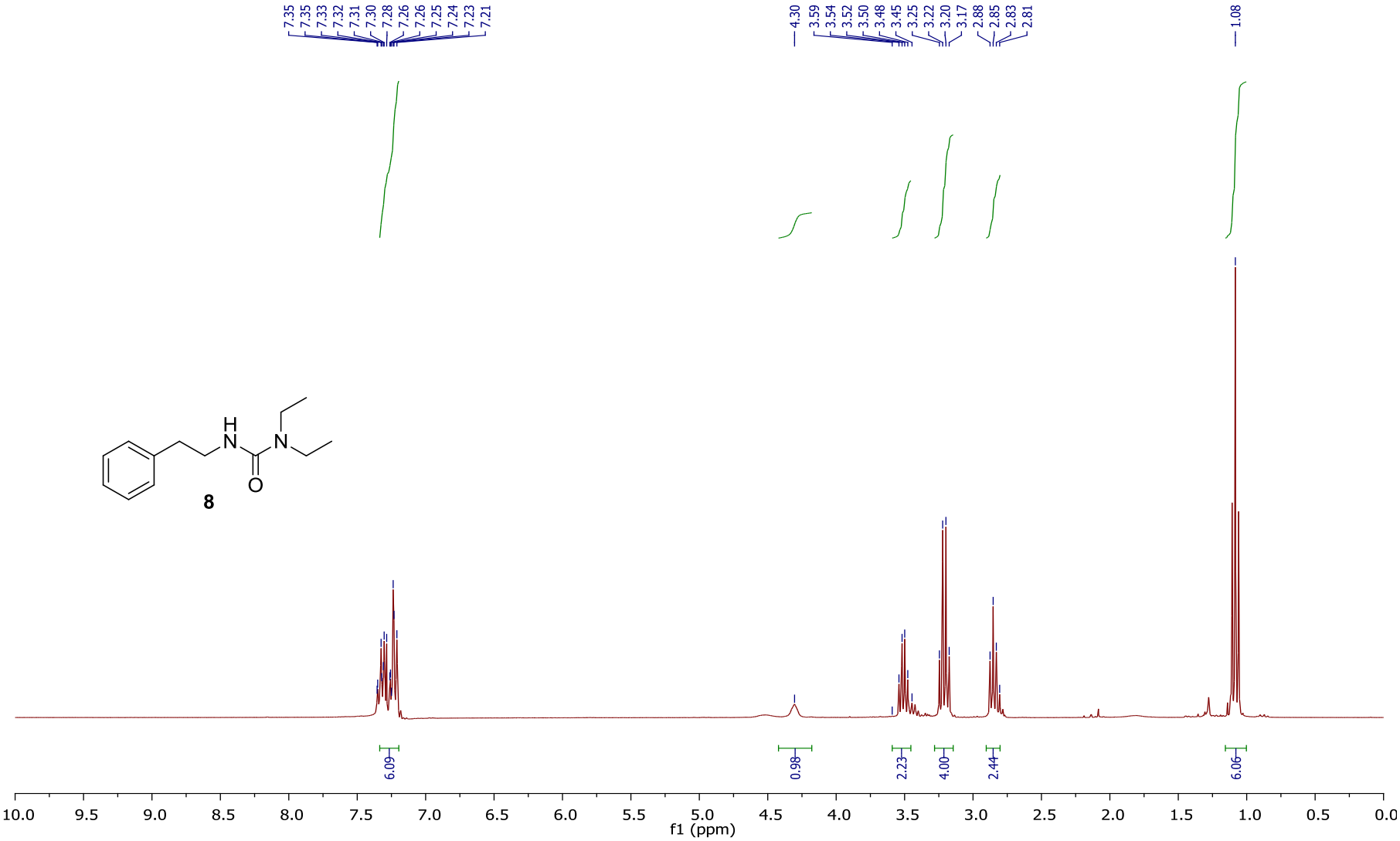
138.12
128.75
128.66
126.74
77.44
77.02
76.59
40.85
35.45
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.35
7.35
7.33
7.32
7.31
7.30
7.28
7.26
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7.25
7.24
7.23
7.21
4.30
3.59
3.54
3.52
3.50
3.48
3.45
3.25
3.22
3.20
3.17
2.88
2.85
2.83
2.81
1.08
H
N
N
O
8
6.09
0.98
2.23
4.00
2.44
6.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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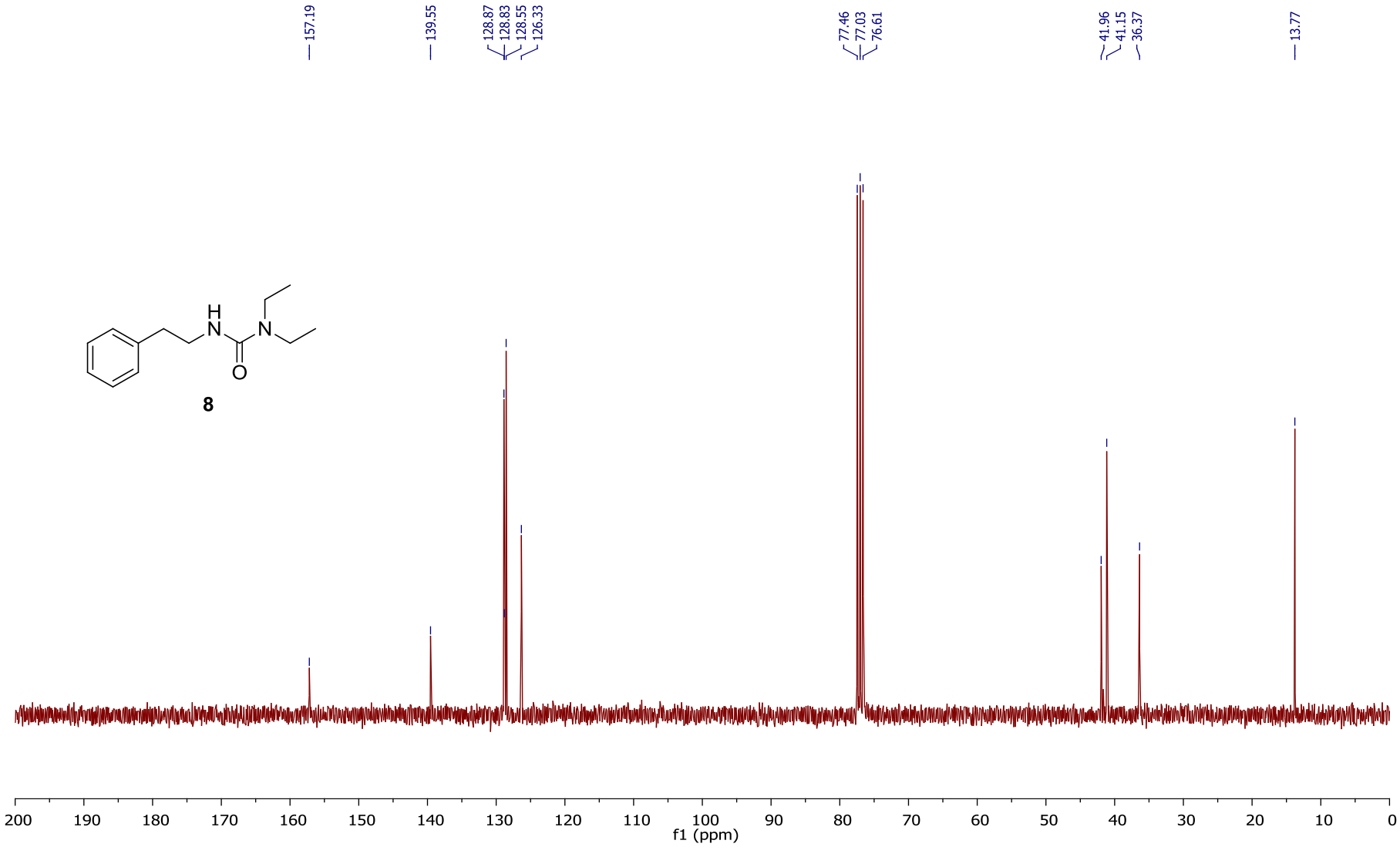
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.19
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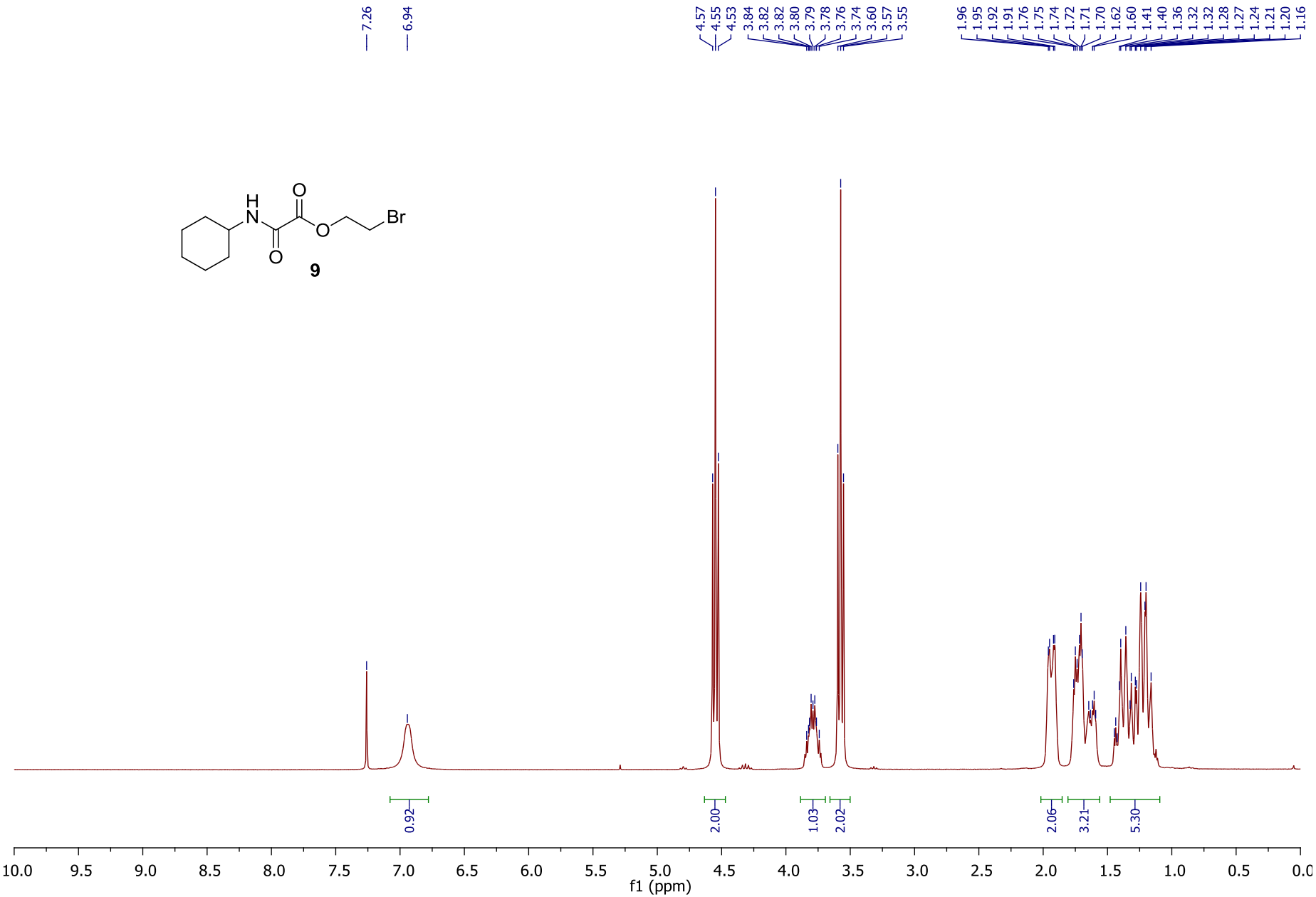
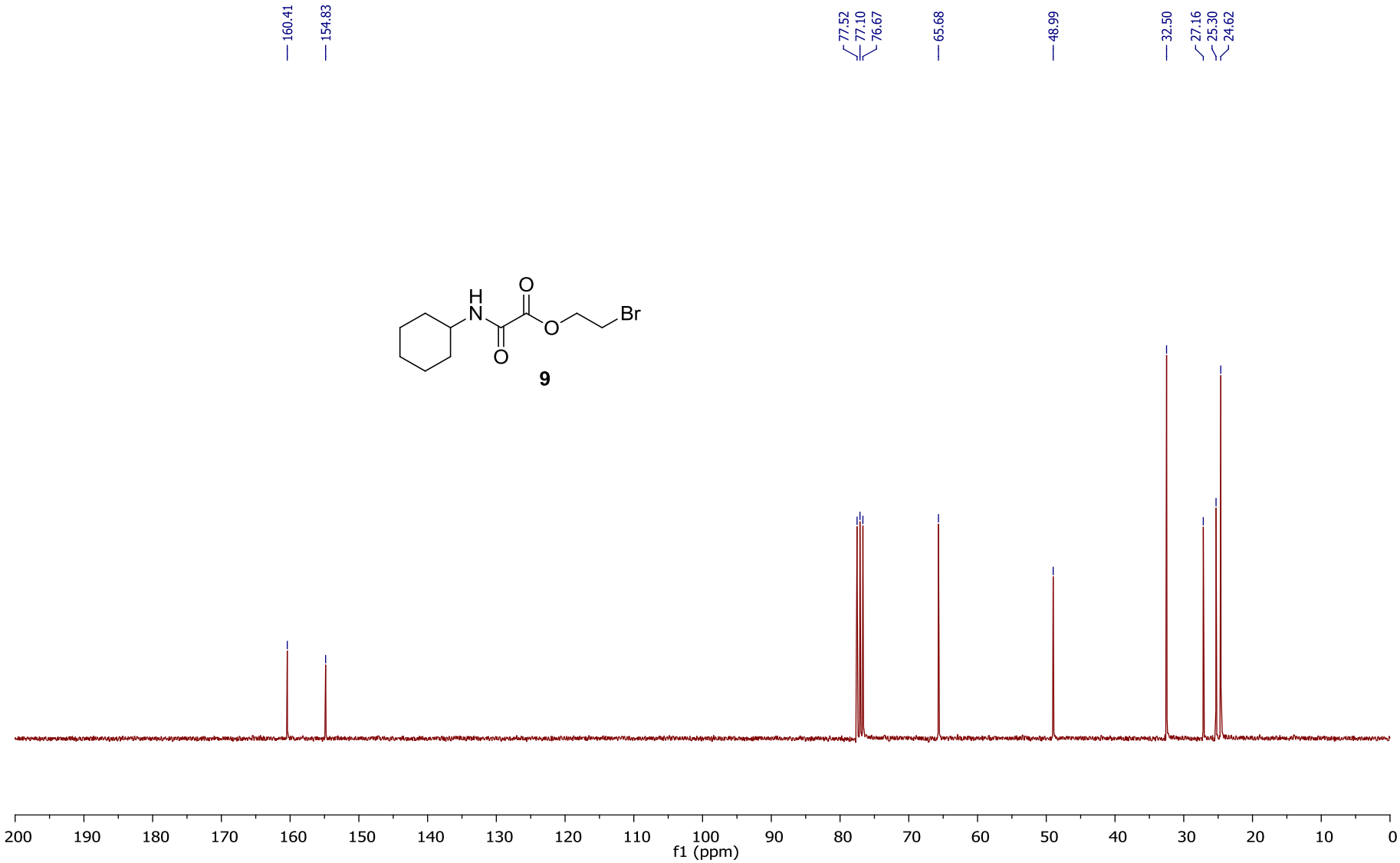
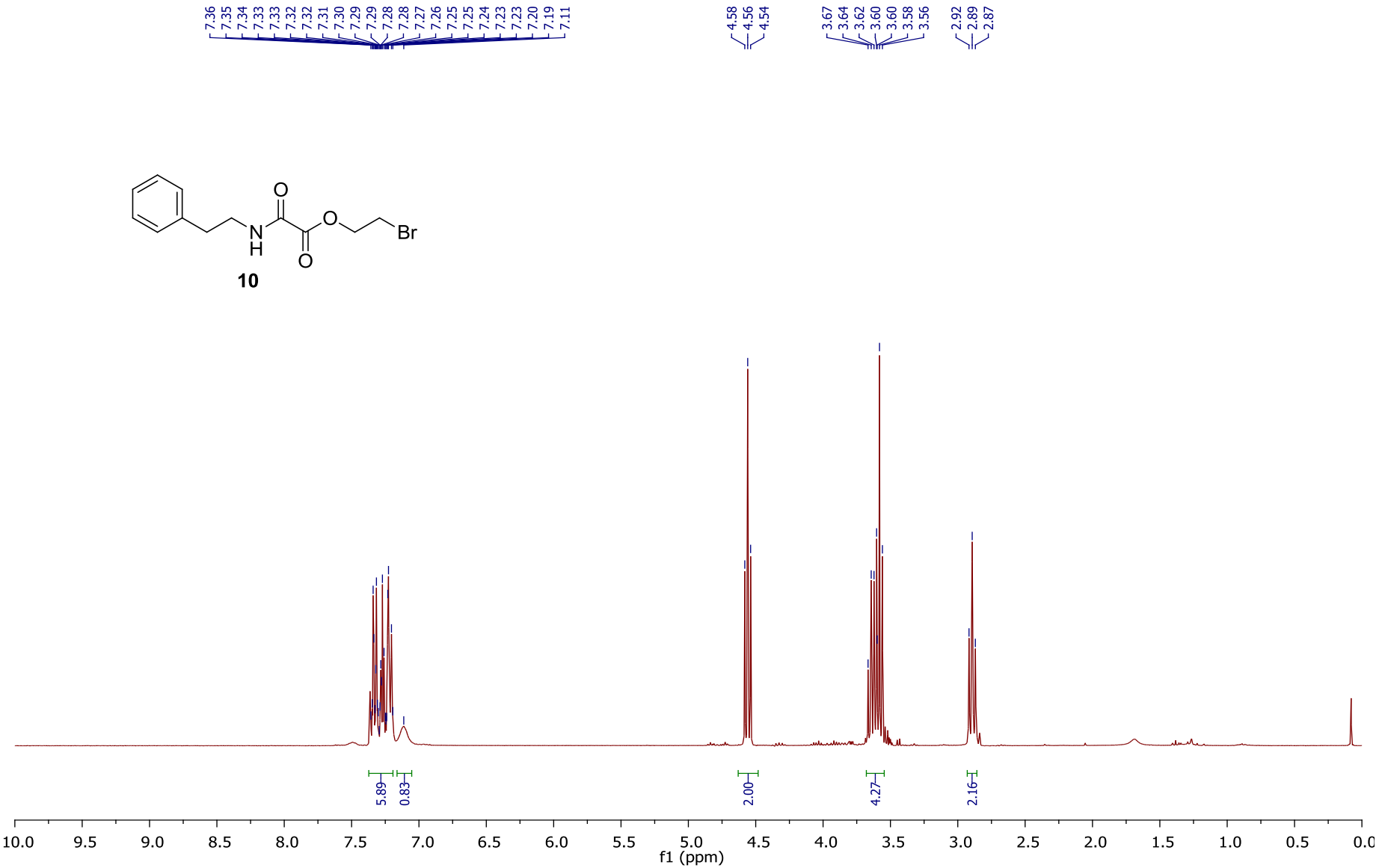
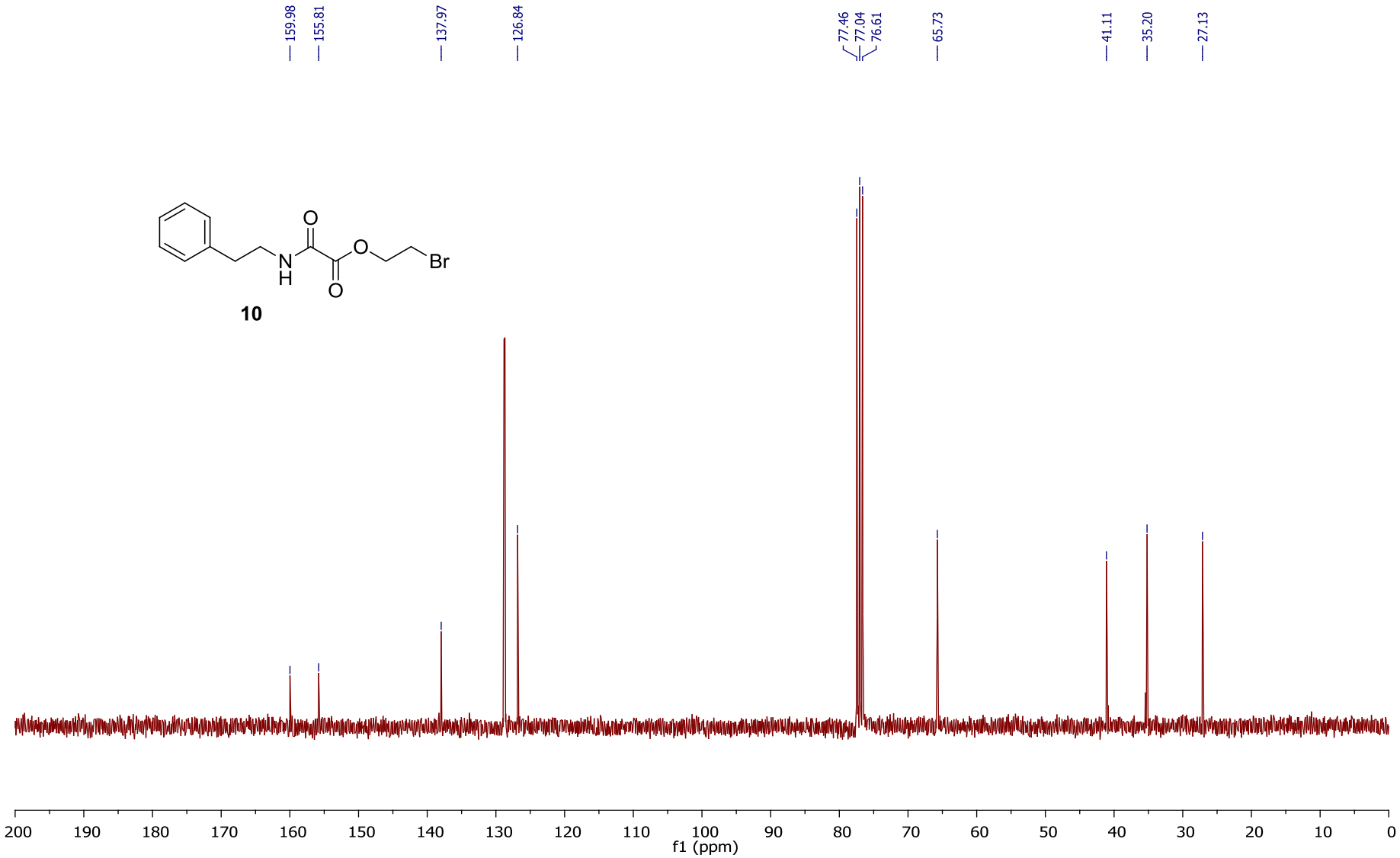
128.83
128.55
126.33
77.46
77.03
76.61
41.96
41.15
36.37
13.77
H
N
N
O
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
6.94
4.57
4.55
4.53
3.84
3.82
3.82
3.80
3.79
3.78
3.76
3.74
3.60
3.57
3.55
1.96
1.95
1.92
1.91
1.76
1.75
1.74
1.72
1.71
1.70
1.62
1.60
1.41
1.40
1.36
1.32
1.32
1.28
1.27
1.24
1.21
1.20
1.16
H
N
O
O
O
O
Br
9
0.92
2.00
1.03
2.02
2.06
3.21
5.30
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
f1 (ppm)


160.41
154.83
77.52
77.10
76.67
65.68
48.99
32.50
27.16
25.30
24.62
H
N
O
O
O
Br
9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.20
7.19
7.11
4.58
4.56
4.54
3.67
3.64
3.62
3.60
3.60
3.58
3.56
2.92
2.89
2.87
O
O
O
N
H
Br
10
5.89
0.83
2.00
4.27
2.16
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
f1 (ppm)


159.98
155.81
137.97
126.84
77.46
77.04
76.61
65.73
41.11
35.20
27.13
O
N
H
O
O
Br
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)