

Visible-Light Photocatalyzed Oxidative Decarboxylation of Oxamic Acids: A Green Route to Carbamates and Ureas

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1. General Information

Reagents:

All reagent-grade chemicals were obtained from commercial suppliers and were used as received unless otherwise noted. CH₂Cl₂ and THF were dried over activated alumina columns on MBraun Solvent Purification System (SPS-800). DCE, MeCN were distilled from CaH₂ and anhydrous dimethylformamide, dimethylsulfoxide triethylamine (reagent grade, ≥98%) and DMSO (anhydrous, ≥99.9%) were purchased from Sigma Aldrich.

Reactions: All reactions for the Visible-Light Photocatalyzed Oxidation of Oxamic Acids were set up on bench-top in the open air and carried out in re-sealable test tubes with Teflon septa under an argon atmosphere. Unless otherwise noted, the reaction test tubes were cooled to room temperature prior to other operations. Unless otherwise noted, the solvents and the solutions of reagents/reactants were transferred *via* microsyringe or plastic syringe (fitted with metal needle) into the reaction test tubes under a positive argon pressure.

Photochemical reactions were performed with 455 nm blue LEDs ($\lambda = 455 \text{ nm} (\pm 15\text{nm})$, 12 V, 500 mA).

Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light, ceric Ammonium molybdate and ninhydrin. Flash chromatography was performed on silica gel (0.043-0.063 mm). Yields refer to chromatographically and spectroscopically (¹H-NMR) homogeneous materials, unless otherwise stated.

Instruments: ¹H-NMR and ¹³C-NMR were recorded on various spectrometers: a Brüker DPX 200 (¹H: 200 MHz, ¹³C: 50.25 MHz), a Brüker Avance 300 (¹H: 300 MHz, ¹³C: 75.46 MHz), a Brüker DRX400 (¹H: 400 MHz, ¹³C: 100.6 MHz) and a Brüker Avance 600 (¹H: 600 MHz, ¹³C: 150.9 MHz) using CDCl₃ as internal

Oxamic acids **1a**,² **1b**,¹ **1d**,¹ **1k**,¹ **1s**,¹ **1p**,¹ **1aa**,¹ **1g**,³ and **4b**,⁴ were reported and synthesized using general procedure.

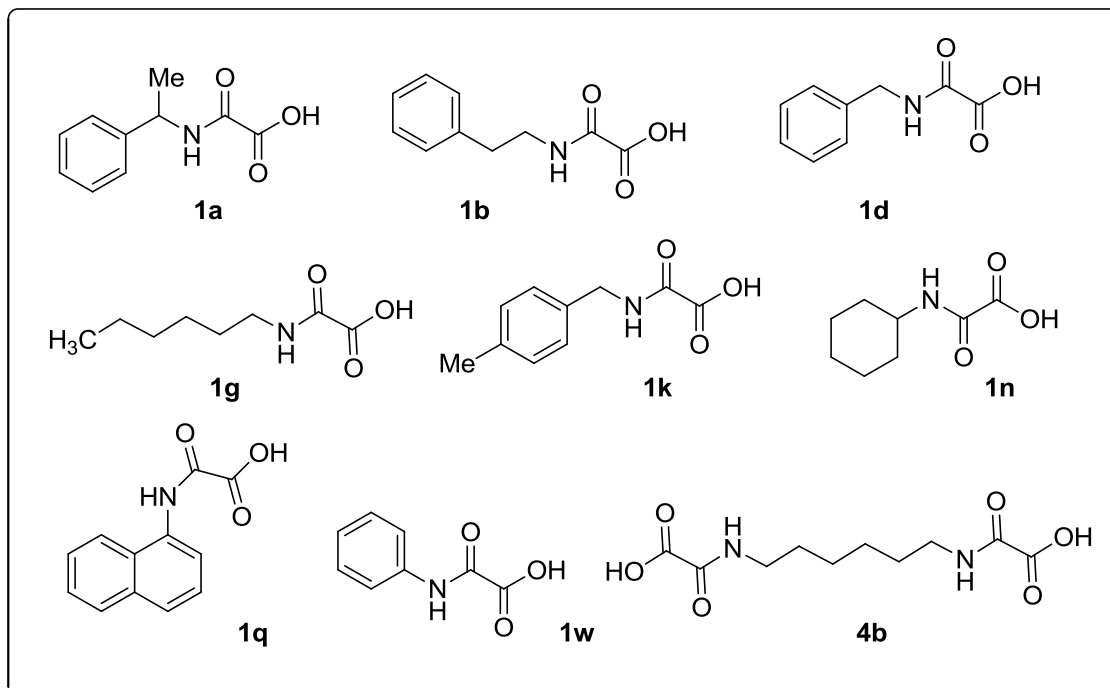
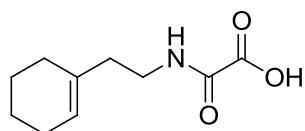
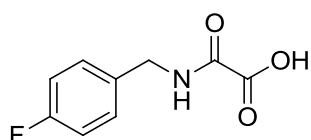


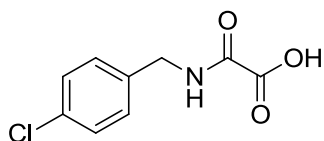
Figure 1. Previously reported oxamic acids



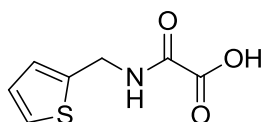
2-((2-(cyclohex-1-en-1-yl)ethyl)amino)-2-oxoacetic acid (3i): **1t** (1.1 g, 57%) was obtained through the general procedure as a white solid; mp 121-123 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.82 (s, 1H), 7.32 (s, 1H), 5.60 – 5.46 (m, 1H), 3.57 – 3.36 (m, 2H), 2.25 (t, *J* = 6.8 Hz, 2H), 2.11 – 1.90 (m, 4H), 1.74 – 1.52 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 159.69, 133.86, 124.03, 37.53, 37.25, 29.70, 27.96, 25.20, 22.79, 22.27. IR (neat) ν_{\max} (cm⁻¹) = 3293, 2922, 1769, 1666. HRMS (ESI): Calcd. For C₁₀H₁₄NO₃ [M-H]⁺ 196.0979, found 196.0976.



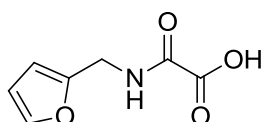
2-((4-fluorobenzyl)amino)-2-oxoacetic acid (1j): **1j** (1.5 g, 78%) was obtained through the general procedure as a white solid; mp 118-121 °C; ¹H NMR (300 MHz, MeOD): δ 7.43 – 7.28 (m, 1H), 7.13 – 6.97 (m, 1H), 4.43 (s, 1H). ¹³C NMR (75 MHz, MeOD) δ 163.77, 161.30, 160.54, 158.74, 133.85 (d, *J* = Hz), 129.25 (d, *J* = Hz), 114.78 (d, *J* = Hz), 42.19. IR (neat) ν_{\max} (cm⁻¹) = 3280, 2922, 2443, 1761, 1683. HRMS (ESI): Calcd. For C₉H₇NFO₃ [M-H]⁺ 196.0415, found 196.0422.



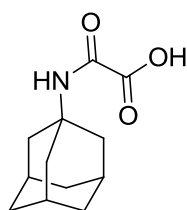
2-((4-chlorobenzyl)amino)-2-oxoacetic acid (1m): **1m** (1.6 g, 76%) was obtained through the general procedure as a white solid; mp 132-135 °C; ¹H NMR (300 MHz, MeOD) δ 7.46 – 7.17 (m, 4H), 4.44 (s, 2H). ¹³C NMR (75 MHz, MeOD) δ 161.25, 158.84, 136.68, 132.77, 128.88, 128.21, 42.19. IR (neat) ν_{\max} (cm⁻¹) = 3268, 2926, 1755, 1684. HRMS (ESI): Calcd. For C₉H₇NCIO₃ [M-H]⁺ 212.0119, found 212.0119.



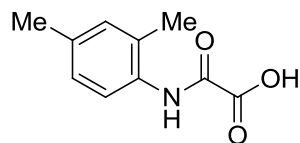
2-Oxo-2-((thiophen-2-ylmethyl)amino)acetic acid (1o): **1o** (1.45 g, 82 %) was obtained through the general procedure as a white solid; mp 124-127 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm 13.88 (s, 1H), 9.44 (t, *J* = 6.3 Hz, 1H), 7.38 (dd, *J* = 5.0, 1.4 Hz, 1H), 6.97 (ddd, *J* = 8.4, 4.8, 3.4 Hz, 2H), 4.48 (d, *J* = 6.3 Hz, 2H). ¹³C NMR (75 MHz, DMSO): δ ppm 162.42, 158.64, 141.54, 127.13, 126.41, 125.68, 37.91. IR (neat) ν_{\max} (cm⁻¹) = 3302, 2920, 1659, 1579. HRMS (ESI): Calcd. For C₇H₆NSO₃ [M-H]⁺ 184.0073, found 184.0077.



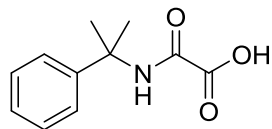
2-((Furan-2-ylmethyl)amino)-2-oxoacetic acid (1p): **1p** (950 mg, 56%) was obtained through the general procedure as a white solid; mp 118-121 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm 13.91 (s, 1H), 9.26 (t, *J* = 6.2 Hz, 1H), 7.57 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.39 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.42 – 4.20 (m, 2H). ¹³C NMR (75 MHz, DMSO) δ ppm 162.45, 158.85, 151.78, 142.61, 110.95, 107.65, 36.22. IR (neat) *v*_{max} (cm⁻¹) = 3297, 2919, 1760, 1680. HRMS (ESI): Calcd. For C₇H₆NO₄ [M-H]⁺ 168.0302, found 168.0304.



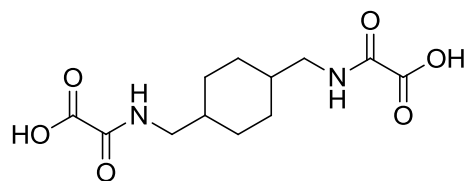
2-((3s,5s,7s)-Adamantan-1-ylamino)-2-oxoacetic acid (1r): **1r** (1.7 g, 77 %) was obtained through the general procedure as a white solid; mp 181-183 °C; ¹H NMR (300 MHz, CDCl₃) δ ppm 7.05 (s, 1H), 2.22 – 2.10 (m, 3H), 2.10 – 1.98 (m, 6H), 1.73 (t, *J* = 3.2 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 160.79, 156.08, 53.28, 40.77, 35.98, 29.39, 29.20, 28.97. IR (neat) *v*_{max} (cm⁻¹) = 3363, 3189, 1759, 1696. Spectroscopic data were in good agreement with literature.⁵



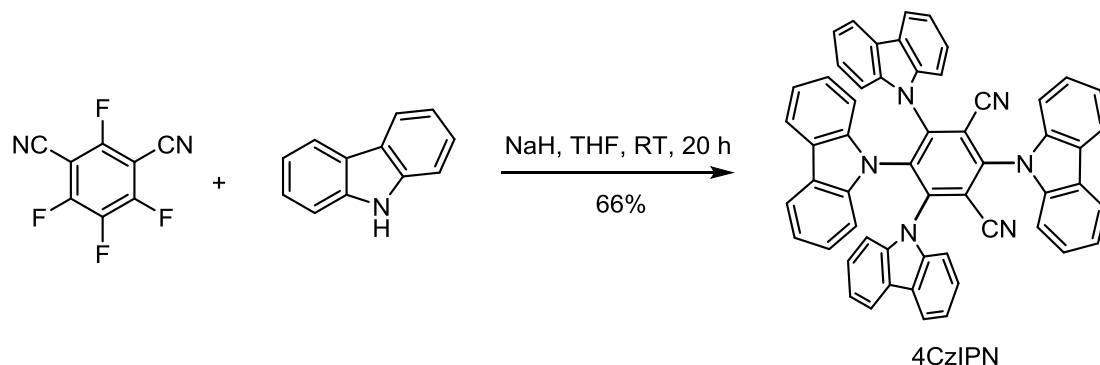
2-((2,4-Dimethylphenyl)amino)-2-oxoacetic acid (1aa): **1aa** (1.2 g, 62 %) was obtained through the general procedure as a white solid; mp 155-158 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ ppm 6.62 – 6.51 (m, 1H), 6.33 (d, *J* = 7.6 Hz, 1H), 6.19 (dd, *J* = 7.6, 1.8 Hz, 1H), 1.51 (s, 3H), 1.43 (s, 3H). ¹³C NMR (75 MHz, DMSO) δ ppm 160.82, 156.05, 135.20, 133.29, 129.31, 127.90, 126.28, 123.82, 18.80, 15.16. IR (neat) *v*_{max} (cm⁻¹) = 3374, 2921, 1760, 1680. HRMS (ESI): Calcd. For C₁₀H₁₀NO₃ [M-H]⁺ 192.0666, found 196.0669.⁶



2-Oxo-2-((2-phenylpropan-2-yl)amino)acetic acid (2ab): **2ab** (1.5 g, 70 %) was obtained through the general procedure as a white solid; mp 101-103 °C; ¹H NMR (300 MHz, CDCl₃) δ ppm 9.38 (s, 1H), 7.68 (s, 1H), 7.47 – 7.26 (m, 5H), 1.80 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 160.56, 156.35, 144.61, 128.68, 127.46, 124.77, 57.13, 28.27. IR (neat) ν_{\max} (cm⁻¹) = 3338, 2981, 1759, 1691. Spectroscopic data were in good agreement with literature.⁷



2,2'-((cyclohexane-1,4-diylbis(methylene))bis(azanediyl))bis(2-oxoacetic acid) (4a): **4a** (1.5 g, 52%) was obtained through the general procedure as a white solid; mp 203-206 °C; ¹H NMR (300 MHz, MeOD) δ 3.38 – 3.07 (m, 6H), 1.91 – 1.69 (m, 2H), 1.64 – 1.34 (m, 6H). ¹³C NMR (75 MHz, MeOD) δ 161.43, 158.82, 43.00, 35.08, 29.87, 25.89. IR (neat) ν_{\max} (cm⁻¹) = 3297, 2909, 1761, 1673.

3. Synthesis of 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)**Scheme 2.** Synthesis of 4CzIPN

4CzIPN was synthesized according to the following reported procedure.⁸ NaH (60% in oil, 1.4 g, 60 mmol) was added slowly to a stirred solution of carbazole (4.18 g, 25.0 mmol) in dry THF (100 mL) under a nitrogen atmosphere at room temperature. After 30 min, tetrafluoroisophthalonitrile (1.0 g, 5.0 mmol), was added. After stirring at room temperature for 12 h, 4-5 mL water was added to the reaction mixture to quench the excess NaH. The resulting mixture was then concentrated under reduced pressure and successively washed by water and EtOH to yield the crude yellow solid. The crude product was dissolved in the minimum quantity of CH₂Cl₂ and crystallized by addition of pentane to give pure 4CzIPN (2.21 g, 66%) as a yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 8.25 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.80 – 7.66 (m, 8H), 7.57 – 7.47 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.21 (m, 5H), 7.19 – 7.05 (m, 8H), 6.91 – 6.79 (m, 4H), 6.73 – 6.60 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 145.23, 144.63, 140.00, 138.19, 136.97, 134.77, 126.98, 125.79, 124.97, 124.76, 124.54, 123.86, 122.41, 121.95, 121.42, 121.00, 120.44, 119.67, 116.37, 111.64, 109.97, 109.49, 109.44. Spectroscopic data were in good agreement with literature.⁸

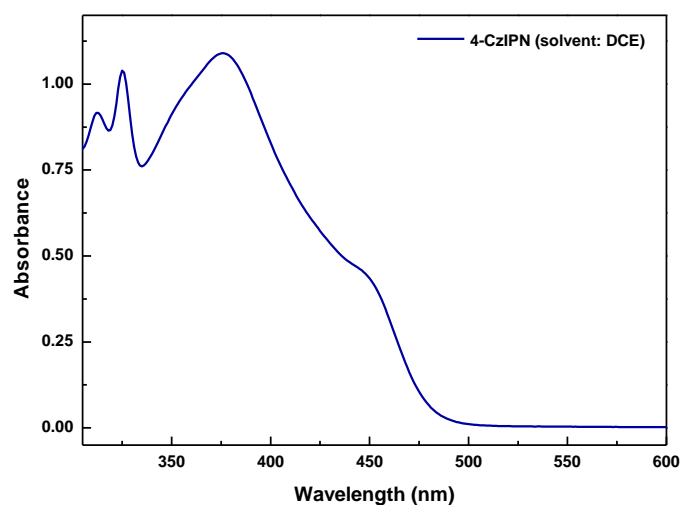
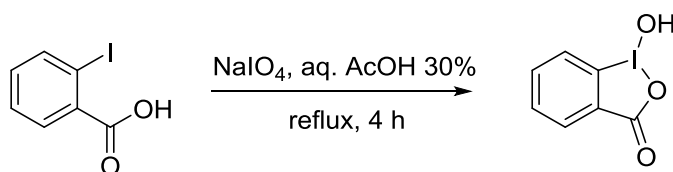


Figure 2. Absorption spectra of 4CzIPN in DCE

4. Hypervalent Iodine Reagents (HIR)

1-Hydroxy-1,2-benziodoxol-3(1H)-one (CAS: 131-62-4)

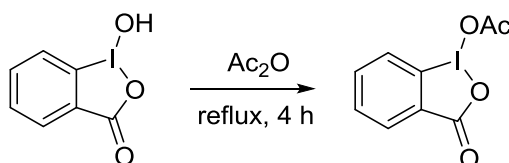


Scheme 3. Preparation of BI-OH

Following a reported procedure,⁹ NaIO_4 (6.7 g, 31.0 mmol, 1.00 equiv) and 2-iodobenzoic acid (7.4 g, 30.0 mmol, 1.00 equiv.) were suspended in 30% (v:v) aqueous AcOH (45 mL) under air. The mixture was vigorously stirred and refluxed for 4 h protected from light. Cold water (120 mL) was added and the mixture was allowed to cool to room temperature. After 1 h, the crude product was collected by filtration, washed with ice water (3 x 30 mL) and cold acetone (3 x 30 mL). After air dried in the dark overnight pure BI-OH (6.8 g, 86%) was obtained as a white solid; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.09 – 7.91 (m, 3H), 7.85 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.70 (td, $J = 7.3, 1.1$ Hz, 1H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 168.20, 134.93, 131.97,

131.57, 130.83, 126.75, 120.90. Spectroscopic data were in good agreement with literature.⁹

1-Acetoxy-1,2-benziodoxol-3-(1H)-one (CAS:1829-25-0)



Scheme 4. Preparation of BI-OAc

Following a reported procedure,¹⁰ BI-OH (6.00 g, 22.7 mmol) was heated in Ac₂O (20 mL) under reflux until the solution turned clear (without suspension). The mixture was then left to cool down and white crystals started to form. The crystallization was continued at -20 °C. The crystals were then collected and dried overnight under high vacuum to give compound BI-OAc (6.1 g, 88%) as a white solid; ¹H NMR (300 MHz, CDCl₃) δ 8.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.07 – 8.01 (m, 1H), 8.00 – 7.92 (m, 1H), 7.79 – 7.71 (m, 1H), 2.29 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 176.38, 168.17, 136.15, 133.18, 131.33, 129.32, 129.00, 118.34, 20.32. Spectroscopic data were in good agreement with literature.¹⁰

5. General procedures for the oxidation of Oxamic acids into urethanes.

Conditions A:

The Oxamic Acid (1.0 equiv., 0.5 mmol), ROH (2-3 equiv. 1.0-1.5 mmol), 4CzIPN (1.0 mol%, 0.005 mmol), and BIOAc (1.5 equiv., 0.75 mmol) were placed into a re-sealable test tube with Teflon septa (10 mL) equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and DCE (0.2 M) was added afterwards (Note: for liquid substrates, they were added after the tube was backfilled with argon). The reaction mixture was stirred at room temperature under blue LED irradiation for 24-48 h. The reaction mixture was concentrated and purified

directly by column chromatography to afford the product (eluting with ethyl acetate/hexanes or dichloromethane/methanol).

Conditions B:

The ROH (1.0 equiv., 0.25 mmol), Oxamic Acid (3.0 equiv., 0.75 mmol), 4CzIPN (1.0 mol%, 0.002), and BIOAc (2.0 equiv., 0.5 mmol) were placed into a re-sealable test tube with Teflon septa (10 mL), equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and DCE (0.1 M) was added afterwards (Note: for liquid substrates, they were added after the tube was backfilled with argon). The reaction mixture was stirred at room temperature under blue LED irradiation for 24-48 h. The reaction mixture was concentrated and purified directly by column chromatography to afford the product (eluting with ethyl acetate/hexanes or dichloromethane/methanol).

Experimental Setup

Photochemical reactions were performed with 455 nm blue LEDs ($\lambda = 455 \text{ nm} (\pm 15\text{nm})$, 12 V, 500 mA).

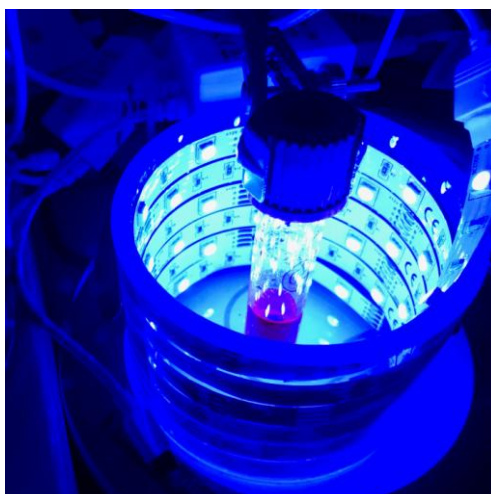
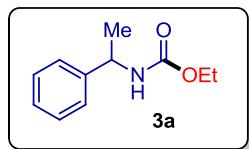
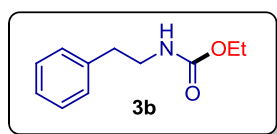


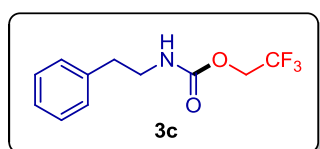
Figure 3. Experimental Setup

6. ^1H and ^{13}C NMR Data of urethanes

Ethyl (1-phenylethyl)carbamate (3a): **3a** (83 mg, 86%) was obtained through the general procedure A as a colorless gel; $R_f = 0.35$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.42 – 7.22 (m, 5H), 4.96 (bs, 1H), 4.92 – 4.77 (m, 1H), 4.12 (q, $J = 7.2, 1.8$ Hz, 2H), 1.50 (d, $J = 6.8$ Hz, 3H), 1.24 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 155.88, 143.78, 128.59, 127.23, 125.94, 60.78, 50.55, 22.51, 14.61. IR (neat) ν_{max} (cm^{-1}) = 3318, 2979, 1695, 1532. HRMS (ESI): Calcd. For $\text{C}_{11}\text{H}_{15}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 216.0995, found 216.0998.

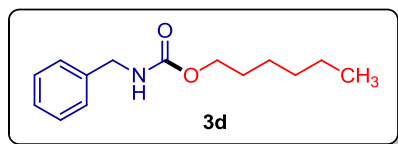


Ethyl phenethylcarbamate (3b): **3b** (78 mg, 80%) was obtained through the general procedure A as a colorless gel; $R_f = 0.40$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.40 – 7.16 (m, 5H), 4.69 (bs, 1H), 4.13 (q, $J = 7.2$ Hz, 1H), 3.46 (q, $J = 6.8$ Hz, 1H), 2.84 (t, $J = 7.0$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.59, 138.82, 129.97, 128.78, 128.68, 128.61, 126.48, 60.74, 42.10, 36.19, 14.65. IR (neat) ν_{max} (cm^{-1}) = 3334, 2980, 2934, 1702, 1533. HRMS (ESI): Calcd. For $\text{C}_{11}\text{H}_{12}\text{NO}_2\text{F}_3$ $[\text{M}+\text{Na}]^+$ 270.0712, found 270.0710.

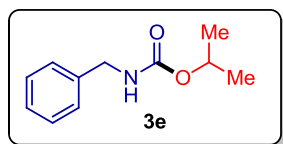


2,2,2-Trifluoroethyl phenethylcarbamate (3c): **3c** (60 mg, 48%) was obtained through the general procedure A as a colorless oil; $R_f = 0.60$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.48 – 7.04 (m, 5H), 4.94 (bs, 1H), 4.47 (q, $J =$

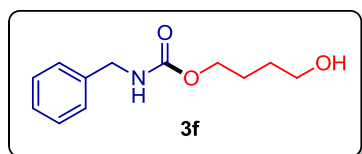
8.4 Hz, 1H), 3.51 (q, $J = 6.8$ Hz, 2H), 2.86 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 154.35, 138.30, 128.75, 126.69, 60.58, 42.44, 35.85. IR (neat) ν_{max} (cm^{-1}) = 3348, 2934, 1719, 1522. HRMS (ESI): Calcd. For $\text{C}_{11}\text{H}_{12}\text{NO}_2\text{F}_3$ $[\text{M}+\text{Na}]^+$ 270.0712, found 2070.0710.¹¹



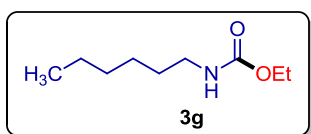
Hexyl benzylcarbamate (3d): 3d (90 mg, 77%) was obtained through the general procedure A as a white gel; $R_f = 0.56$ (EtOAc-Hexane 10/90). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.42 – 7.22 (m, 5H), 5.07 (bs, 1H), 4.38 (d, $J = 6.0$ Hz, 2H), 4.11 (t, $J = 6.7$ Hz, 2H), 1.72 -1.53 (m, 2H), 1.46 – 1.21 (m, 6H), 1.01 – 0.76 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.82, 138.67, 128.63, 127.51, 127.42, 65.22, 45.04, 31.49, 29.02, 25.54, 22.57, 14.02. IR (neat) ν_{max} (cm^{-1}) = 3316, 2957, 2928, 1686, 1553. HRMS (ESI): Calcd. For $\text{C}_{14}\text{H}_{21}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 258.1464, found 258.1460.



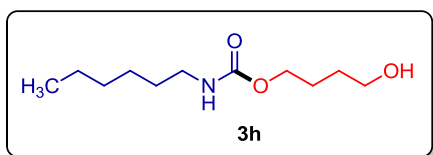
Isopropyl benzylcarbamate (3e): 3e (56 mg, 58%) was obtained through the general procedure A as a white gel; $R_f = 0.42$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.41 – 7.22 (m, 5H), 5.06 - 4.91 (m, 2H), 4.38 (d, $J = 5.8$ Hz, 2H), 1.27 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.31, 138.72, 128.63, 127.50, 127.40, 68.26, 44.97, 22.18. IR (neat) ν_{max} (cm^{-1}) = 3153, 2930, 2878, 1692, 1520. HRMS (ESI): Calcd. For $\text{C}_{11}\text{H}_{15}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 216.0995, found 216.1003.



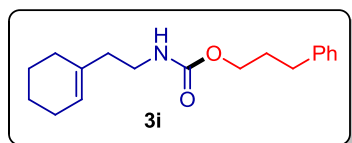
4-Hydroxybutyl benzylcarbamate (3f): **3f** (78 mg, 74%) was obtained through the general procedure A as a white gel; $R_f = 0.15$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.45 – 7.24 (m, 5H), 5.13 (s, 1H), 4.39 (d, $J = 5.4$ Hz, 2H), 4.16 (t, $J = 6.2$ Hz, 2H), 3.69 (t, $J = 6.2$ Hz, 2H), 1.93 (s, 1H), 1.83 – 1.52 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.70, 138.52, 128.67, 127.88, 127.49, 64.84, 62.41, 45.06, 29.04, 25.52. IR (neat) ν_{max} (cm^{-1}) = 3324, 2983, 2685, 1699, 1530. HRMS (ESI): Calcd. For $\text{C}_{12}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{Na}]^+$ 246.1100, found 246.1100.



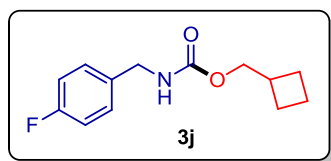
Ethyl hexylcarbamate (3g): **3g** (78 mg, 90%) was obtained through the general procedure A as a colorless gel; $R_f = 0.70$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 4.72 (bs, 1H), 4.10 (q, $J = 7.2$ Hz, 2H), 3.15 (q, $J = 6.8$ Hz, 2H), 1.59 – 1.40 (m, 2H), 1.39 – 1.15 (m, 9H), 0.97 – 0.78 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.69, 60.58, 40.96, 31.46, 29.97, 26.39, 22.54, 14.64, 13.98. IR (neat) ν_{max} (cm^{-1}) = 3336, 2930, 2859, 1701, 1536. HRMS (ESI): Calcd. For $\text{C}_9\text{H}_{19}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 196.1308, found 196.1312.



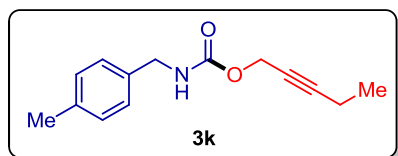
4-Hydroxybutyl hexylcarbamate (3h): **3h** (74 mg, 68%) was obtained through the general procedure A as a yellow oil; $R_f = 0.17$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 4.82 (bs, 1H), 4.07 (t, $J = 6.2$ Hz, 2H), 3.65 (t, $J = 6.2$ Hz, 2H), 3.14 (q, $J = 6.4$ Hz, 2H), 2.31 (s, 1H), 1.78 – 1.54 (m, 4H), 1.55 – 1.39 (m, 2H), 1.38 – 1.17 (m, 6H), 0.97 – 0.80 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.80, 64.51, 62.21, 40.99, 31.45, 29.92, 29.02, 26.39, 25.53, 22.53, 13.98. IR (neat) ν_{max} (cm^{-1}) = 3351, 2930, 2859, 1697. HRMS (ESI): Calcd. For $\text{C}_{11}\text{H}_{23}\text{NO}_3$ $[\text{M}+\text{Na}]^+$ 240.1570, found 240.1576.



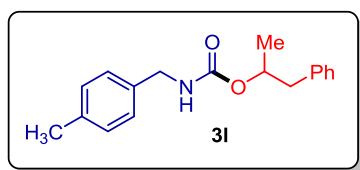
3-Phenylpropyl (2-(cyclohex-1-en-1-yl)ethyl)carbamate (3i): **3i** (43 mg, 30%) was obtained through the general procedure A as a colorless oil; $R_f = 0.54$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.36 – 7.26 (m, 2H), 7.21 (m, 3H), 5.53 – 5.47 (m, 1H), 4.64 (bs, 1H), 4.11 (t, $J = 6.4$ Hz, 2H), 3.28 (q, $J = 6.4$ Hz, 2H), 2.71 (t, $J = 7.6$ Hz, 2H), 2.15 (t, $J = 6.4, 1.2$ Hz, 2H), 2.09 – 1.82 (m, 6H), 1.78 – 1.43 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.58, 141.45, 134.48, 128.40, 125.92, 123.58, 64.15, 38.70, 38.08, 32.19, 30.71, 27.90, 25.24, 22.83, 22.36. IR (neat) ν_{max} (cm^{-1}) = 3344, 2928, 2836, 1704. HRMS (APCI): Calcd. For $\text{C}_{18}\text{H}_{25}\text{NO}_2$ $[\text{M}+\text{H}]^+ 288.1958$, found 288.1958.



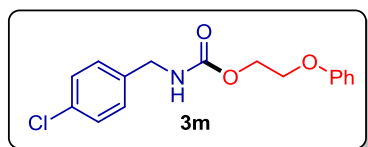
Cyclobutylmethyl 4-fluorobenzylcarbamate (3j): **3j** (85 mg, 72%) was obtained through the general procedure A as a white solid; mp 57-60°C; $R_f = 0.57$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.36 – 7.18 (m, 2H), 7.09 – 6.96 (m, 2H), 5.05 (bs, 1H), 4.34 (d, $J = 6.2$ Hz, 2H), 4.08 (d, $J = 6.8$ Hz, 2H), 2.70 – 2.52 (m, 1H), 2.15 – 1.65 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 163.76, 160.51, 156.84, 134.45, 129.23, 115.58, 115.30, 68.95, 44.33, 34.35, 24.63, 18.41. IR (neat) ν_{max} (cm^{-1}) = 3336, 2942, 2867, 1700. HRMS (ESI): Calcd. For $\text{C}_{13}\text{H}_{16}\text{NFO}_2$ $[\text{M}+\text{Na}]^+ 260.1057$, found 260.1050.



Pent-2-yn-1-yl 4-methylbenzylcarbamate (3k): **3k** (49 mg, 42%) was obtained through the general procedure A as a colorless oil; $R_f = 0.53$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.24 – 7.08 (m, 4H), 5.07 (bs, 1H), 4.72 (t, $J = 2.2$ Hz, 2H), 4.36 (d, $J = 5.8$ Hz, 2H), 2.36 (s, 3H), 2.26 (qt, $J = 7.4, 2.2$ Hz, 2H), 1.17 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 155.72, 137.24, 135.18, 129.33, 127.51, 88.75, 73.80, 53.43, 44.94, 29.71, 21.09, 13.59, 12.47. IR (neat) ν_{max} (cm^{-1}) = 3324, 2977, 2932, 1698.

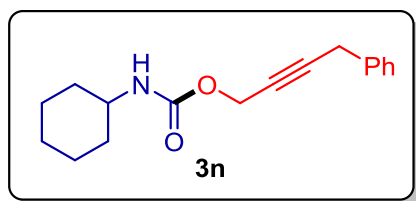


1-Phenylpropan-2-yl 4-methylbenzylcarbamate (3l): **3l** (52 mg, 74%) was obtained through the general procedure A as a white solid; mp 67-70°C; $R_f = 0.35$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.38 – 7.20 (m, 5H), 7.17 (bs, 4H), 5.12 (h, $J = 6.2$ Hz, 1H), 4.98 (bs, 1H), 4.33 (d, $J = 5.8$ Hz, 2H), 2.99 (dd, $J = 13.6, 6.4$ Hz, 1H), 2.80 (dd, $J = 13.6, 6.4$ Hz, 1H), 2.38 (s, 3H), 1.27 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.20, 137.77, 137.07, 135.64, 129.53, 129.31, 128.54, 128.32, 127.47, 126.67, 126.39, 71.93, 44.72, 42.53, 21.13, 19.75. IR (neat) ν_{max} (cm^{-1}) = 3338, 2926, 2870, 1700. HRMS (ESI): Calcd. For $\text{C}_{18}\text{H}_{21}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 306.1470, found 306.2.

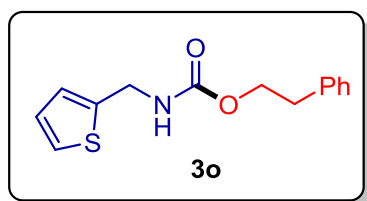


2-Phenoxyethyl 4-chlorobenzylcarbamate (3m): **3m** (58 mg, 75%) was obtained through the general procedure B as a white solid; mp 77-80°C; $R_f = 0.21$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.37 – 7.17 (m, 6H), 7.06 – 6.88 (m, 3H), 5.23 (bs, 1H), 4.53 – 4.43 (m, 2H), 4.35 (d, $J = 6.2$ Hz, 2H), 4.23 – 4.12 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 158.48, 156.32, 136.91, 133.29,

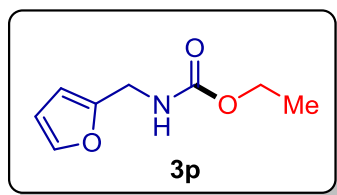
129.55, 128.84, 128.79, 121.18, 114.59, 66.30, 63.57, 44.42. IR (neat) ν_{\max} (cm^{-1}) = 3311, 2933, 1689. HRMS (ESI): Calcd. For $\text{C}_{16}\text{H}_{16}\text{NClO}_3$ $[\text{M}+\text{Na}]^+$ 328.0710, found 328.0712.



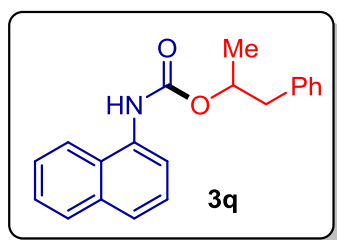
4-Phenylbut-2-yn-1-yl cyclohexylcarbamate (3n): **3n** (60 mg, 42%) was obtained through the general procedure A as a colorless oil; $R_f = 0.35$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.53 – 7.42 (m, 2H), 7.38 – 7.30 (m, 3H), 4.93 (s, 2H), 4.77 (bs, 1H), 3.67 – 3.42 (m, 1H), 2.05 – 1.90 (m, 2H), 1.81 – 1.55 (m, 4H), 1.47 – 1.07 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 154.72, 131.89, 128.64, 128.26, 122.30, 86.15, 83.66, 53.07, 50.00, 33.34, 29.70, 25.46, 24.74. IR (neat) ν_{\max} (cm^{-1}) = 3323, 2950, 2928, 1690.



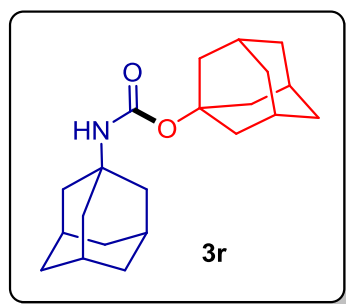
Phenethyl (thiophen-2-ylmethyl)carbamate (3o): **3o** (32 mg, 52%) was obtained through the general procedure A as a colorless oil; $R_f = 0.45$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.40 – 7.16 (m, 6H), 7.05 – 6.90 (m, 2H), 5.07 (bs, 1H), 4.55 (d, $J = 5.8$ Hz, 2H), 4.35 (t, $J = 7.0$ Hz, 2H), 2.97 (t, $J = 7.0$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.16, 141.32, 137.93, 128.93, 128.48, 126.89, 126.50, 125.75, 125.12, 65.56, 39.85, 35.51. IR (neat) ν_{\max} (cm^{-1}) = 3330, 2947, 1704. HRMS (ESI): Calcd. For $\text{C}_{14}\text{H}_{15}\text{NSO}_2$ $[\text{M}+\text{Na}]^+$ 284.0715, found 284.0717.



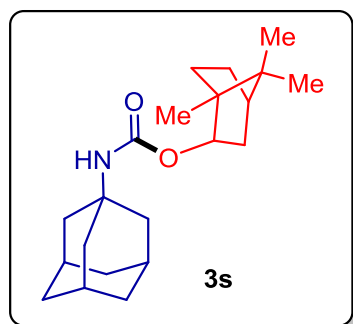
Ethyl (furan-2-ylmethyl)carbamate (3p): **3p** (35 mg, 40%) was obtained through the general procedure A as a colorless oil; $R_f = 0.67$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.36 (dd, $J = 1.8, 1.0$ Hz, 1H), 6.33 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.23 (d, $J = 3.2$ Hz, 1H), 5.03 (bs, 1H), 4.36 (d, $J = 5.8$ Hz, 2H), 4.15 (q, $J = 7.2$ Hz, 2H), 1.26 (t, $J = 7.2$ Hz, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.39, 151.72, 142.14, 110.36, 107.10, 61.06, 38.00, 14.59. IR (neat) ν_{max} (cm^{-1}) = 3333, 2982, 2933, 1704. HRMS (ESI): Calcd. For $\text{C}_8\text{H}_{11}\text{NO}_3$ $[\text{M}+\text{Na}]^+$ 192.0631, found 192.0628.



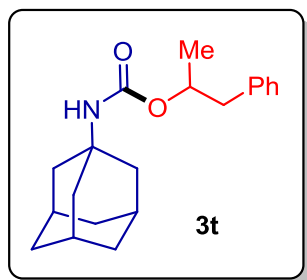
1-Phenylpropan-2-yl naphthalen-1-ylcarbamate (3q): **3q** (43 mg, 56%) was obtained through the general procedure A as a brown colored solid; mp 79–82 °C; $R_f = 0.30$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.98 – 7.75 (m, 3H), 7.71 (d, $J = 8.2$, 1H), 7.61 – 7.43 (m, 3H), 7.40 – 7.20 (m, 5H), 6.96 (bs, 1H), 5.25 (h, $J = 6.4$ Hz, 1H), 3.08 (dd, $J = 13.6, 6.4$ Hz, 1H), 2.89 (dd, $J = 13.6, 6.4$ Hz, 1H), 1.37 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 154.12, 137.57, 134.10, 132.59, 129.97, 129.55, 128.71, 128.66, 128.41, 126.93, 126.53, 126.20, 125.99, 125.81, 125.07, 120.64, 119.50, 72.76, 42.48, 19.73. IR (neat) ν_{max} (cm^{-1}) = 3387, 2921, 1707. HRMS (APCI): Calcd. For $\text{C}_{20}\text{H}_{19}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 306.1480, found 306.1488.



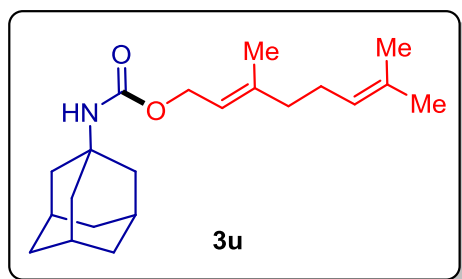
(3S,5S,7S)-Adamantan-1-yl (3S,5S,7S)-adamantan-1-ylcarbamate (3r): **3r** (114 mg, 68%) was obtained through the general procedure B as a white solid; mp 260-263 °C; $R_f = 0.45$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 4.40 (bs, 1H), 2.21 – 2.00 (m, 12H), 1.98 – 1.86 (m, 6H), 1.73 – 1.56 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 153.89, 78.63, 50.43, 41.90, 41.78, 36.39, 36.28, 30.83, 29.66, 29.47. IR (neat) ν_{max} (cm^{-1}) = 3344, 2906, 2849, 1714. HRMS (ESI): Calcd. For $\text{C}_{21}\text{H}_{31}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 352.2247, found 352.2256.



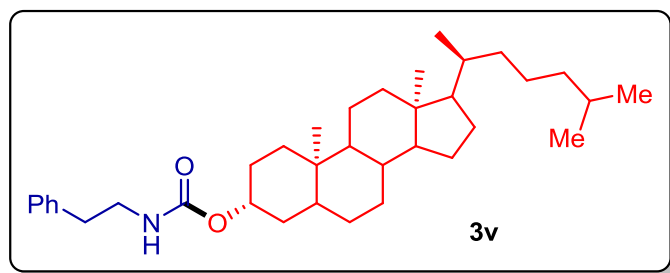
(2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl(3S,5S,7S)-adamantan-1-ylcarbamate (3s): **3s** (71 mg, 85%) was obtained through the general procedure B as a white solid; mp 238-241 °C; $R_f = 0.62$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 4.79 (d, $J = 9.2$ Hz, 1H), 4.53 (s, 1H), 2.40 – 2.23 (m, 1H), 2.12 - 2.04 (m, 3H), 1.94 (s, 3H), 1.93 (s, 3H), 1.66 (m, 8H), 1.23 (m, 2H), 1.00 (dd, $J = 13.6, 3.2$ Hz, 1H), 0.93 – 0.78 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 155.30, 79.24, 50.58, 48.66, 47.71, 44.82, 41.92, 36.81, 36.35, 29.47, 28.09, 27.21, 19.76, 18.81, 13.58. IR (neat) ν_{max} (cm^{-1}) = 3322, 2907, 2850, 1687. HRMS (APCI): Calcd. For $\text{C}_{21}\text{H}_{33}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 332.2584, found 332.2584.



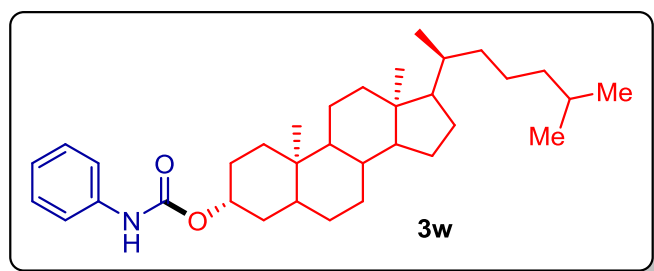
1-Phenylpropan-2-yl (3s,5s,7s)-adamantan-1-ylcarbamate (3t): **3t** (121 mg, 81%) was obtained through the general procedure B as a colorless oil; $R_f = 0.46$ (EtOAc-Hexane 10/90). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ ppm 7.39 – 7.15 (m, 5H), 5.03 (h, $J = 6.4$ Hz, 1H), 4.52 (bs, 1H), 3.00 (dd, $J = 13.4, 5.8$ Hz, 1H), 2.76 (dd, $J = 13.4, 7.2$ Hz, 1H), 2.11 (bs, 3H), 1.95 (d, $J = 3.0$ Hz, 6H), 1.70 (t, $J = 3.2$ Hz, 6H), 1.22 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ ppm 154.22, 137.86, 129.97, 129.52, 128.27, 126.31, 70.89, 50.61, 42.57, 41.90, 36.35, 29.67, 29.47, 29.25, 19.57. IR (neat) ν_{max} (cm^{-1}) = 3342, 2908, 2850, 1722. HRMS (ESI): Calcd. For $\text{C}_{20}\text{H}_{27}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 336.1934, found 336.1943.



(E)-3,7-Dimethylocta-2,6-dien-1-yl (3s,5s,7s)-adamantan-1-ylcarbamate (3u): **3u** (58 mg, 35%) was obtained through the general procedure B as a colorless oil; $R_f = 0.80$ (EtOAc-Hexane 10/90). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ ppm 5.42 – 5.27 (m, 1H), 5.17 – 5.01 (m, 1H), 4.54 (d, $J = 6.8$ Hz, 3H), 2.19 – 1.99 (m, 6H), 1.95 (d, $J = 2.8$ Hz, 6H), 1.76 – 1.64 (m, 12H), 1.62 (d, $J = 1.2$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ ppm 141.62, 131.76, 123.83, 118.98, 60.92, 50.65, 41.88, 39.56, 36.33, 29.46, 26.35, 25.69, 17.70, 16.46. IR (neat) ν_{max} (cm^{-1}) = 3351, 2909, 2851, 1713. HRMS (APCI): Calcd. For $\text{C}_{21}\text{H}_{33}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 332.2584, found 332.2580.

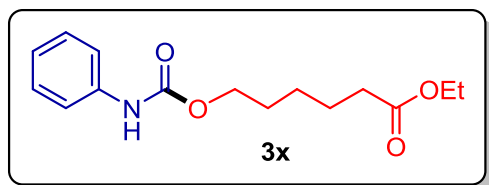


(3R,10R,13S)-10,13-Dimethyl-17-((S)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl phenethylcarbamate (3v): **3v** (212 mg, 79%) was obtained through the general procedure B as a white solid; mp 79-81 °C; $R_f = 0.47$ (EtOAc-Hexane 10/90). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ ppm 7.38 – 7.17 (m, 5H), 4.68 – 4.53 (m, 2H), 3.45 (d, $J = 6.4$ Hz, 2H), 2.83 (t, $J = 7.2$ Hz, 2H), 1.98 (dt, $J = 12.4, 3.2$ Hz, 1H), 1.91 – 1.46 (m, 8H), 1.42 – 0.97 (m, 20H), 0.95 – 0.85 (m, 10H), 0.82 (s, 3H), 0.67 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ ppm 156.25, 138.88, 128.79, 128.60, 126.45, 77.24, 76.62, 74.09, 56.43, 56.28, 54.23, 44.66, 42.60, 42.07, 40.00, 39.53, 36.80, 36.19, 35.82, 35.50, 35.44, 34.47, 32.02, 29.73, 28.65, 28.27, 28.03, 27.89, 24.23, 23.86, 22.84, 22.59, 21.23, 18.69, 12.25, 12.09. IR (neat) ν_{max} (cm^{-1}) = 3350, 2935, 2866, 1702, 1517. HRMS (ESI): Calcd. For $\text{C}_{36}\text{H}_{57}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 558.4281, found 558.4270.

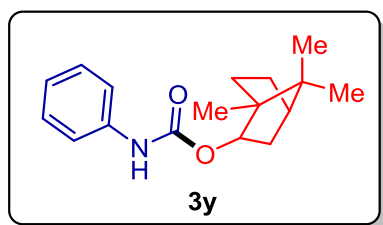


(3R,10R,13S)-10,13-Dimethyl-17-((S)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl phenylcarbamate (3w): **3w** (90 mg, 71%) was obtained through the general procedure B as a white solid; mp 140-143 °C; $R_f = 0.57$ (EtOAc-Hexane 10/90). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ ppm 7.48 – 7.22 (m, 4H), 7.14 – 6.97 (m, 1H), 6.62 (s, 1H), 4.84 – 4.59 (m, 1H), 2.12 – 0.98 (m, 28H), 0.99 – 0.80 (m, 14H), 0.68 (s, 4H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ ppm 153.23, 138.13, 129.01, 123.19, 118.56, 74.76, 56.43, 56.30, 54.22, 44.68, 42.61, 40.00, 39.54, 36.79, 36.20,

35.83, 35.50, 35.46, 34.38, 32.01, 28.66, 28.27, 28.03, 27.83, 24.23, 23.88, 22.85, 22.60, 21.25, 18.70, 12.27, 12.10. IR (neat) ν_{\max} (cm^{-1}) = 3391, 2936, 2897, 1730. HRMS (ESI): Calcd. For $\text{C}_{34}\text{H}_{53}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 530.3968, found 530.3970.

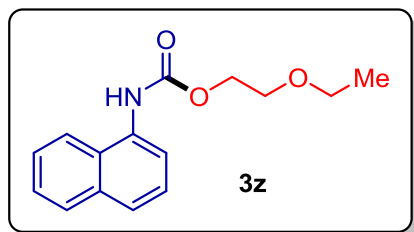


Ethyl 6-((phenylcarbamoyl)oxy)hexanoate (3x): **3x** (43 mg, 62%) was obtained through the general procedure B as a white solid; mp 58-61 °C; R_f = 0.42 (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.48 – 7.28 (m, 4H), 7.15 – 7.03 (m, 1H), 6.74 (s, 1H), 4.31 – 4.04 (m, 4H), 2.36 (t, J = 7.2 Hz, 2H), 1.72 (m, 4H), 1.57 – 1.38 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 173.63, 153.63, 137.97, 129.03, 123.34, 118.63, 65.04, 64.30, 60.30, 34.17, 28.58, 28.31, 25.50, 24.61, 14.25. IR (neat) ν_{\max} (cm^{-1}) = 3332, 2943, 1715, 1730, 1600. HRMS (ESI): Calcd. For $\text{C}_{15}\text{H}_{21}\text{NO}_4$ $[\text{M}+\text{Na}]^+$ 302.1362, found 302.1352.

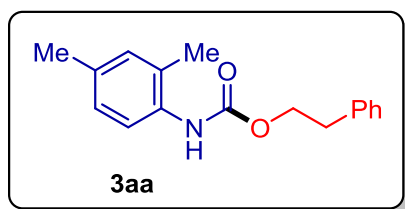


1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl phenylcarbamate (3y): **3y** (56 mg, 82%) was obtained through the general procedure B as a white solid; mp 130-133 °C; R_f = 0.80 (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.48 – 7.38 (m, 2H), 7.36 – 7.28 (m, 2H), 7.14 – 7.01 (m, 1H), 6.74 (s, 1H), 4.98 (ddd, J = 9.8, 3.4, 2.0 Hz, 1H), 2.43 (dddd, J = 13.6, 9.8, 4.6, 3.2 Hz, 1H), 2.04 – 1.89 (m, 1H), 1.83 – 1.68 (m, 2H), 1.44 – 1.20 (m, 2H), 1.12 (dd, J = 13.8, 3.4 Hz, 1H), 0.95 (s, 3H), 0.92 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 153.97, 138.08, 129.03, 123.22, 118.52, 80.88, 48.82, 47.88, 44.85, 36.80, 28.09, 27.15, 19.76, 18.87, 13.57. IR (neat) ν_{\max} (cm^{-1}) =

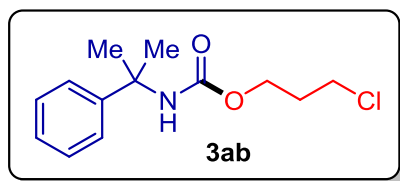
3316, 2953, 2877, 1703. HRMS (ESI): Calcd. For $C_{17}H_{23}NO_2$ $[M+Na]^+$ 296.1621, found 296.1627.



2-Ethoxyethyl naphthalen-1-ylcarbamate (3z): **3z** (41 mg, 60%) was obtained through the general procedure B as a brown colored solid; mp 62-65°C; $R_f = 0.37$ (EtOAc-Hexane 10/90). 1H NMR (300 MHz, $CDCl_3$) δ ppm 7.95 – 7.85 (m, 3H), 7.69 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.60 – 7.45 (m, 3H), 7.11 (bs, 1H), 4.51 – 4.32 (m, 2H), 3.83 – 3.68 (m, 2H), 3.61 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 154.28, 134.07, 132.44, 128.73, 126.23, 125.99, 125.81, 125.02, 120.46, 68.71, 66.70, 64.67, 15.15. IR (neat) ν_{max} (cm^{-1}) = 3346, 2970, 2874, 1719. HRMS (APCI): Calcd. For $C_{15}H_{17}NO_2$ $[M+H]^+$ 260.1281, found 260.1284.



Phenethyl (2,4-dimethylphenyl)carbamate (3aa): **3aa** (32 mg, 78% (brsm)) was obtained through the general procedure B as a colorless oil; $R_f = 0.53$ (EtOAc-Hexane 10/90). 1H NMR (300 MHz, $CDCl_3$) δ ppm 7.62 (s, 1H), 7.42 – 7.22 (m, 5H), 7.07 (d, $J = 7.7$ Hz, 1H), 6.94 – 6.83 (m, 1H), 6.38 (bs, 1H), 4.43 (t, $J = 7.0$ Hz, 1H), 3.04 (t, $J = 7.0$ Hz, 1H), 2.36 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 153.89, 137.82, 136.62, 135.52, 130.20, 129.97, 128.95, 128.56, 126.60, 125.03, 65.71, 35.48, 21.21, 17.24. IR (neat) ν_{max} (cm^{-1}) = 3287, 2962, 2820, 1693. HRMS (APCI): Calcd. For $C_{17}H_{19}NO_2$ $[M+H]^+$ 270.1488, found 270.1491.

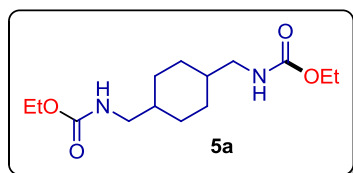


3-Chloropropyl (2-phenylpropan-2-yl)carbamate (3ab): **3ab** (42 mg, 66%) was obtained through the general procedure B as a colorless oil; $R_f = 0.60$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.51 – 7.18 (m, 5H), 5.16 (s, 1H), 4.15 (t, $J = 5.8$ Hz, 2H), 3.62 (s, 2H), 2.07 (s, 2H), 1.69 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 154.33, 146.96, 128.38, 126.71, 124.73, 61.15, 55.22, 41.32, 32.05, 29.28. IR (neat) ν_{max} (cm^{-1}) = 3339, 2972, 1710. HRMS (ESI): Calcd. For $\text{C}_{13}\text{H}_{18}\text{NClO}_2$ $[\text{M}+\text{Na}]^+$ 278.0918, found 278.0925.

Bis-oxamic acids as bis-urethane precursors

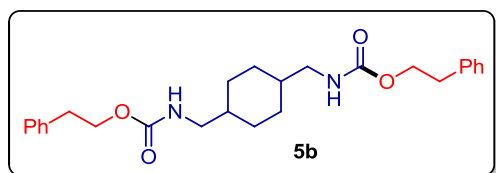
Conditions C:

The oxamic Acid (1.0 equiv., 0.5 mmol), 4CzIPN (2.0 mol%, 0.01 mmol), and BIOAc (2.0 equiv., 1.0 mmol) were placed into a re-sealable test tube with Teflon septa (10 mL), equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, ROH (3.0 equiv. 1.5 mmol), and DCE (0.2 M) was added afterwards. The reaction mixture was stirred at room temperature under blue LED irradiation for 24-48 h. The reaction mixture was concentrated and purified directly by column chromatography to afford the product. (Eluting with ethyl acetate/hexanes or dichloromethane/methanol).



Diethyl (cyclohexane-1,4-diylbis(methylene))dicarbamate (5a): **5a** (104 mg, 71%) was obtained through the general procedure C as a white solid. mp 90-93°C; $R_f = 0.20$ (EtOAc-Hexane 30/70). ^1H NMR (300 MHz, CDCl_3) δ ppm 4.89 (bs, 2H), 4.05 (q, $J = 7.2$ Hz, 4H), 3.18 – 2.82 (m, 4H), 1.79 – 1.26 (m, 10 H), 1.18 (t, $J = 7.2$ Hz, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.84, 60.62, 44.50, 35.83, 29.94, 26.10, 14.62. IR (neat) ν_{max} (cm^{-1}) = 3339, 2922, 2856, 1696. HRMS (ESI): Calcd. For $\text{C}_{14}\text{H}_{26}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 287.1965 found 287.1970.



Diphenethyl (cyclohexane-1,4-diylbis(methylene))dicarbamate (5b): (128 mg, 58%) was obtained through the general procedure C as a white solid. mp 126-129°C; R_f = 0.26 (EtOAc-Hexane 30/70). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.50 – 7.04 (m, 10H), 4.71 (bs, 2H), 4.30 (t, J = 7.2 Hz, 4H), 3.12 (t, J = 7.2 Hz, 4H), 2.95 (t, J = 7.2 Hz, 4H), 1.87 – 1.30 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.63, 138.06, 128.91, 128.44, 126.45, 65.18, 44.53, 35.81, 35.57, 26.09. IR (neat) ν_{max} (cm^{-1}) = 3352, 2921, 2823, 1700. HRMS (APCI): Calcd. For $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 439.2591, found 439.2587.



Dihexyl hexane-1,6-diyl dicarbamate (5c): **5c** (116 mg, 62%) was obtained through the general procedure C as a colorless oil; R_f = 0.30 (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 4.68 (bs, 2H), 4.05 (t, J = 6.8 Hz, 4H), 3.17 (q, J = 6.8 Hz, 4H), 1.67 – 1.56 (m, 4H), 1.55 – 1.44 (m, 4H), 1.42 – 1.28 (m, 16H), 1.11 – 0.74 (m, 6H). ^{13}C NMR (76 MHz, CDCl_3) δ ppm 156.84, 64.93, 40.75, 31.48, 29.95, 29.03, 26.28, 25.55, 22.56, 14.01. IR (neat) ν_{max} (cm^{-1}) = 3330, 2924, 2850, 1690. HRMS (ESI): Calcd. For $\text{C}_{20}\text{H}_{40}\text{N}_2\text{O}_4$ $[\text{M} + \text{Na}]^+$ 395.2880, found 395.2870.

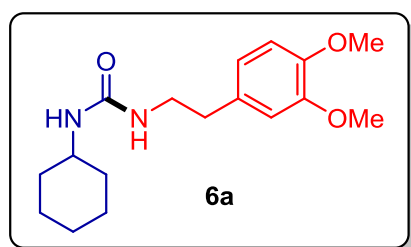


Diethyl hexane-1,6-diylidicarbamate (5d): **5d** (87 mg, 68%) was obtained through the general procedure C as a white solid. mp 71-73°C; $R_f = 0.36$ (EtOAc-Hexane 20/80). ^1H NMR (300 MHz, CDCl_3) δ ppm 4.70 (bs, 2H), 4.12 (q, $J = 7.2$ Hz, 4H), 3.17 (q, $J = 6.6$ Hz, 4H), 1.67 – 1.43 (m, 4H), 1.40 – 1.31 (m, 4H), 1.09 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 156.72, 60.64, 40.72, 29.93, 26.26, 14.66. IR (neat) ν_{max} (cm^{-1}) = 3314, 2984, 2936, 1685. HRMS (ESI): Calcd. For $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_4$ [$\text{M} + \text{Na}$] $^+$ 283.1628, found 283.1630.

7. General procedure for the Oxidation of Oxamic acids into Ureas.

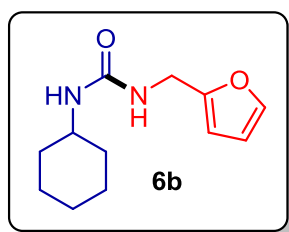
Conditions D:

The Oxamic Acid (1.0 equiv. 0.5 mmol), 4CzIPN (1.0 mol%, 0.005 mmol), and BIOAc (1.5 equiv., 0.75 mmol) were placed into a re-sealable test tube with Teflon septa (10 mL), equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and DCE (2 mL) was added afterwards. The reaction mixture was stirred at room temperature under blue LED irradiation for 24 h. Blue LED was then switched off and Et_3N (1.5 mmol) was added to the reaction mixture slowly at rt and stirred for next 3-5 mins under Ar atmosphere. The amine $\text{R}'\text{NH}_2$ (0.5 equiv.) was then added and the reaction mixture stirred for 4 - 6 h, at 30°C. The reaction mixture was concentrated and purified directly by column chromatography to afford the product. (Eluting with ethyl acetate/hexanes or dichloromethane/methanol).

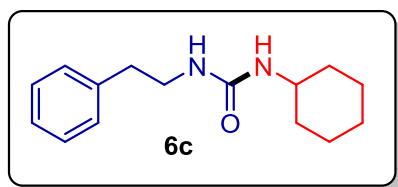


1-Cyclohexyl-3-(3,4-dimethoxyphenethyl)urea (6a): **6a** (55 mg, 70%) was obtained through the general procedure D as a brown colored solid; mp 127-131°C; $R_f = 0.36$ (EtOAc-Hexane 40/60). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.38 – 7.30 (m, 1H), 6.31

(dd, $J = 3.2, 1.8$ Hz, 1H), 6.23 – 6.15 (m, 1H), 5.08 (s, 1H), 4.75 (s, 1H), 4.34 (d, $J = 4.2$ Hz, 2H), 3.69 – 3.37 (m, 1H), 2.02 – 1.81 (m, 2H), 1.79 – 1.51 (m, 2H), 1.44 – 1.25 (m, 2H), 1.25 – 1.00 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 157.44, 152.72, 141.82, 110.35, 106.74, 49.05, 37.44, 33.85, 25.59, 24.90. IR (neat) ν_{max} (cm^{-1}) = 3332, 2929, 2854, 1628, 1584. HRMS (APCI): Calcd. For $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$ 307.2016, found 307.2011.

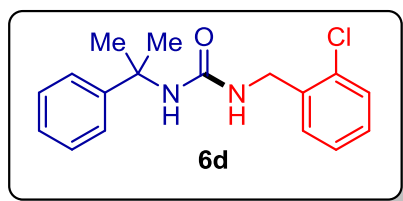


1-Cyclohexyl-3-(furan-2-ylmethyl)urea (6b): **6b** (43 mg, 78%) was obtained through the general procedure D as a yellow colored solid; mp 125-128°C; $R_f = 0.32$ (EtOAc-Hexane 40/60). ^1H NMR (300 MHz, CDCl_3) δ ppm 6.88 – 6.60 (m, 3H), 5.09 (bs, 1H), 4.93 (bs, 1H), 3.82 (s, 6H), 3.57 – 3.24 (m, 3H), 2.71 (t, $J = 7.2$ Hz, 2H), 1.90 – 1.80 (m, 2H), 1.72– 1.50 (m, 3H), 1.38 – 1.20 (m, 2H), 1.14 – 0.98 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 158.00, 148.86, 147.44, 131.96, 120.62, 112.02, 111.30, 55.85, 55.74, 48.84, 41.81, 36.19, 33.93, 25.60, 24.97. IR (neat) ν_{max} (cm^{-1}) = 3340, 2920, 2853, 1632. HRMS (APCI): Calcd. For $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 223.1441, found 223.1443.

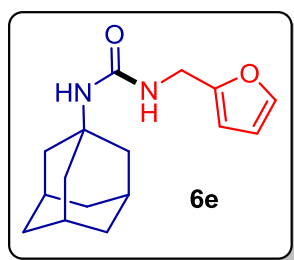


1-Cyclohexyl-3-phenethylurea (6c): **6c** (42 mg, 68%) was obtained through the general procedure D as a brown colored solid; mp 128-133°C; $R_f = 0.30$ (EtOAc-Hexane 20/80). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.37 – 7.14 (m, 5H), 4.69 (t, $J = 5.8$ Hz, 1H), 4.55 (d, $J = 8.0$ Hz, 1H), 3.49 – 3.34 (m, 3H), 2.81 (t, $J = 7.0$ Hz, 2H), 1.99 – 1.81 (m, 2H), 1.78 – 1.51 (m, 3H), 1.43 – 1.23 (m, 2H), 1.22 – 0.97 (m,

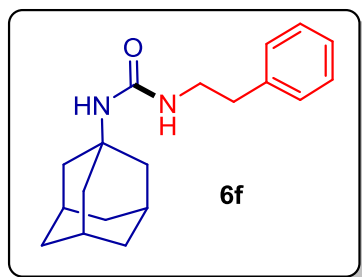
3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 157.68, 139.30, 128.82, 128.55, 126.35, 49.05, 41.69, 36.52, 33.92, 25.61, 24.96. IR (neat) ν_{max} (cm^{-1}) = 3328, 2928, 2953, 1627. HRMS (ESI): Calcd. For $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 247.1804, found 247.1817.



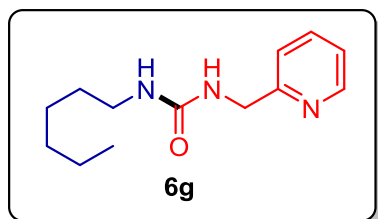
1-(2-Chlorobenzyl)-3-(2-phenylpropan-2-yl)urea (6d): **6d** (53 mg, 69%) was obtained through the general procedure D as a white solid; mp 150-153°C; R_f = 0.20 (EtOAc-Hexane 20/80). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ ppm 7.44 – 7.24 (m, 8H), 7.20 – 7.12 (m, 1H), 4.23 (d, J = 4.2 Hz, 2H), 1.55 (s, 6H). ^{13}C NMR (75 MHz, DMSO) δ ppm 157.26, 149.53, 149.39, 138.41, 132.33, 129.44, 128.99, 128.76, 128.27, 127.53, 126.15, 125.24, 54.59, 54.51, 30.49. IR (neat) ν_{max} (cm^{-1}) = 3337, 2974, 2927, 1638. HRMS (ESI): Calcd. For $\text{C}_{17}\text{H}_{19}\text{N}_2\text{OCl}$ $[\text{M}+\text{Na}]^+$ 325.1070, found 325.1078.



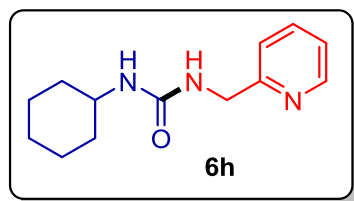
1-((3s,5s,7s)-Adamantan-1-yl)-3-(furan-2-ylmethyl)urea (6e): **6e** (56 mg, 82%) was obtained through the general procedure D as a white solid; mp 189-193°C; R_f = 0.30 (EtOAc-Hexane 30/70). ^1H NMR (300 MHz, $\text{Methanol}-d_4$) δ ppm 7.41 (dd, J = 1.8, 1.0 Hz, 1H), 6.34 (dd, J = 3.2, 1.8 Hz, 1H), 6.23 – 6.15 (m, 1H), 4.24 (d, J = 0.8 Hz, 2H), 2.13 – 2.89 (m, 9H), 1.72 (t, J = 3.2 Hz, 6H). ^{13}C NMR (75 MHz, MeOD) δ ppm 158.30, 153.15, 141.58, 109.83, 105.78, 50.13, 42.00, 36.17, 36.14, 29.64. IR (neat) ν_{max} (cm^{-1}) = 3334, 2905, 2849, 1627, 1562. HRMS (APCI): Calcd. For $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}]^+$ 275.1754, found 275.1752.



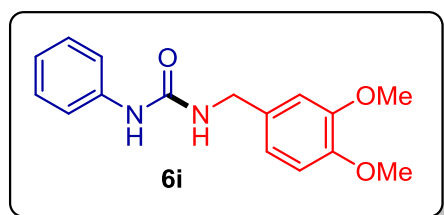
1-((3s,5s,7s)-Adamantan-1-yl)-3-phenethylurea (6f): **6f** (55 mg, 74%) was obtained through the general procedure D as a white solid; mp 131-133°C; $R_f = 0.35$ (EtOAc-Hexane 30/70). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.38 – 7.25 (m, 2H), 7.27 – 7.18 (m, 3H), 3.39 (t, $J = 7.0$ Hz, 2H), 2.80 (t, $J = 7.0$ Hz, 2H), 2.13 – 2.01 (m, 3H), 2.00 – 1.85 (m, 6H), 1.67 (t, $J = 3.2$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 157.37, 139.42, 128.85, 128.54, 126.30, 50.76, 42.52, 41.52, 36.45, 36.24, 29.57. IR (neat) ν_{max} (cm^{-1}) = 3303, 2907, 2849, 1644, 1560. HRMS (APCI): Calcd. For $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 299.2117, found 299.2120.



1-Hexyl-3-(pyridin-2-ylmethyl)urea (6g): **6g** (38 mg, 64%) was obtained through the general procedure D as a brown colored solid; mp 80-83°C; $R_f = 0.35$ (EtOAc-Hexane 20/80). ^1H NMR (300 MHz, CDCl_3) δ ppm 8.56 – 8.41 (m, 1H), 7.65 (td, $J = 7.6, 1.8$ Hz, 1H), 7.35 – 7.24 (m, 1H), 7.24 – 7.10 (m, 1H), 5.92 (s, 1H), 5.16 (s, 1H), 4.48 (d, $J = 4.8$ Hz, 2H), 3.23 – 3.08 (m, 2H), 1.55 – 1.39 (m, 2H), 1.37 – 1.18 (m, 6H), 0.95 – 0.81 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 158.69, 158.25, 148.74, 136.87, 122.20, 122.09, 45.68, 40.60, 31.53, 30.15, 26.57, 22.58, 14.02. IR (neat) ν_{max} (cm^{-1}) = 3336, 2928, 2857, 1638, 1570. HRMS (ESI): Calcd. For $\text{C}_{13}\text{H}_{21}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 236.1757, found 236.1748.



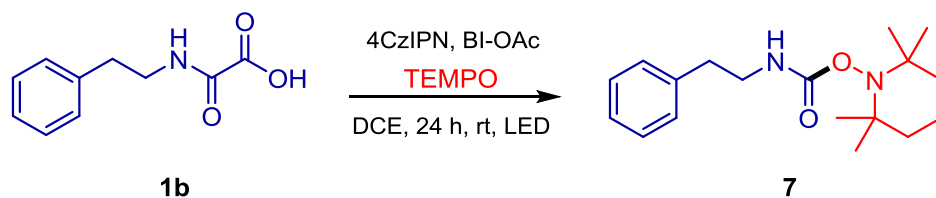
1-Cyclohexyl-3-(pyridin-2-ylmethyl)urea (6h): **6h** (46 mg, 78%) was obtained through the general procedure D as a brown colored solid; mp 139-142°C; $R_f = 0.20$ (EtOAc-Hexane 50/50). ^1H NMR (300 MHz, CDCl_3) δ ppm 8.45 (dd, $J = 4.8, 2.0$ Hz, 1H), 7.65-7.57 (m, 1H), 7.36 – 7.20 (m, 1H), 7.17-7.10 (m, 1H), 6.12 (s, 1H), 5.34 (s, 1H), 4.43 (d, $J = 5.2$ Hz, 2H), 3.60-3.44 (m., 1H), 1.96 – 1.80 (m, 3H), 1.72-1.45 (m, 3H), 1.39 – 0.96 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 158.70, 158.18, 148.68, 136.80, 122.06, 121.84, 48.90, 45.64, 33.80, 25.60, 24.87. IR (neat) ν_{max} (cm^{-1}) = 3327, 2930, 2853, 1626, 1594. HRMS (APCI): Calcd. For $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 234.1600, found 234.1598.



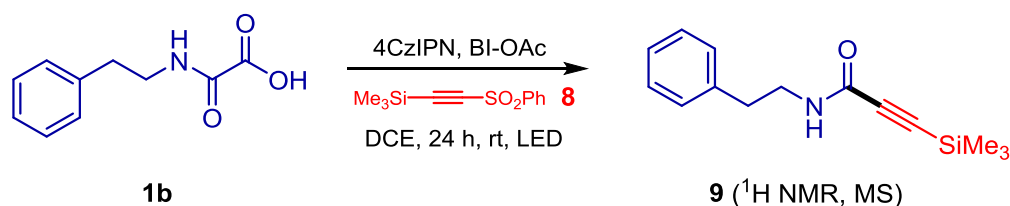
1-(3,4-Dimethoxybenzyl)-3-phenylurea (6i): **6i** (38 mg, 52%) was obtained through the general procedure D as a white solid; mp 141-143°C; $R_f = 0.35$ (EtOAc-Hexane 50/50). ^1H NMR (300 MHz, Methanol- d_4) δ ppm 7.42 – 7.33 (m, 2H), 7.31 – 7.20 (m, 2H), 7.03 – 6.86 (m, 4H), 4.33 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, MeOD) δ ppm 156.81, 149.16, 148.29, 139.51, 132.42, 128.39, 122.06, 119.47, 118.82, 111.63, 111.08, 55.11, 55.01, 42.95. IR (neat) ν_{max} (cm^{-1}) = 3336, 2933, 1657, 1596. HRMS (APCI): Calcd. For $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 287.1390, found 287.1388.

8. Control Experiments:

Radical Trapping Experiment with TEMPO

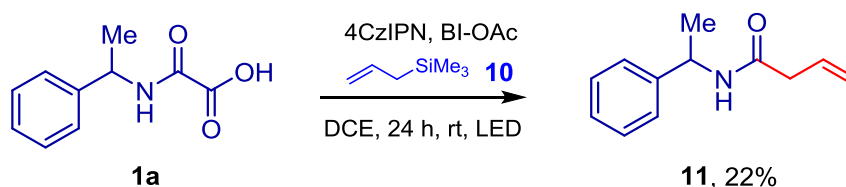


As per the general procedure condition A, **1b** (48 mg, 0.25 mmol), 4CzIPN (1.0 mol%), BIOAc (114.7 mg, 0.37 mmol, 1.0 equiv.) and 2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) (78 mg, 0.5 mmol, 2.0 equiv.) were placed into a re-sealable test tube with Teflon septa (10 mL), equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and DCE (0.2 M) was added afterwards. The reaction mixture was stirred at room temperature under blue LED irradiation for 24 h. The reaction mixture was concentrated and purified directly by column chromatography to afford the product **2,2,6,6-tetramethylpiperidin-1-yl phenethylcarbamate (7)** as a yellow oil contaminated with some impurities (16 mg); $R_f = 0.25$ (EtOAc-Hexane 10/90). ^1H NMR (300 MHz, CDCl_3) δ ppm 7.39 – 7.31 (m, 2H), 7.28 – 7.20 (m, 3H), 3.60 – 3.45 (m, 2H), 2.88 (t, $J = 7.0$ Hz, 2H), 1.71 – 1.50 (m, 2H), 1.47 – 1.24 (m, 4H), 1.19 (s, 6H), 0.97 (s, 6H). IR (neat) ν_{max} (cm^{-1}) = 3365, 2934, 1712, 1494, 1459. HRMS (ESI): Calcd. For $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 305.2223, found 305.2233.

Radical Trapping Experiment with sulfone **8**

As per the general procedure condition A, **1b** (48 mg, 0.25 mmol), 4CzIPN (1.0 mol%), BIOAc (114.7 mg, 0.37 mmol, 1.0 equiv.) and trimethyl((phenylsulfonyl)ethynyl)silane **8** (119 mg, 0.5 mmol, 2.0 equiv.) were placed into a re-sealable test tube with Teflon septa (10 mL), equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, and DCE (0.2 M) was added afterwards. The reaction mixture was stirred at room temperature under blue LED irradiation for 24 h. The reaction mixture was concentrated and purified directly by column chromatography to afford the product **N-phenethyl-3-(trimethylsilyl)propiolamide (9)** as a colorless oil contaminated with *o*-iodobenzoic acid (11 mg); $R_f = 0.45$ (EtOAc-Hexane 10/90). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ ppm 7.26 – 7.21 (m, 5H), 3.59 (q, $J = 7.0$ Hz, 2H), 2.87 (t, $J = 7.0$ Hz, 2H), 0.23 (s, 9H). IR (neat) ν_{max} (cm^{-1}) = 3366, 2927, 2254, 1650. HRMS (APCI): Calcd. For $\text{C}_{14}\text{H}_{19}\text{NSiO}$ $[\text{M}+\text{H}]^+$ 246.1308, found 246.1310.

Radical Trapping Experiment with allylsilane **10**



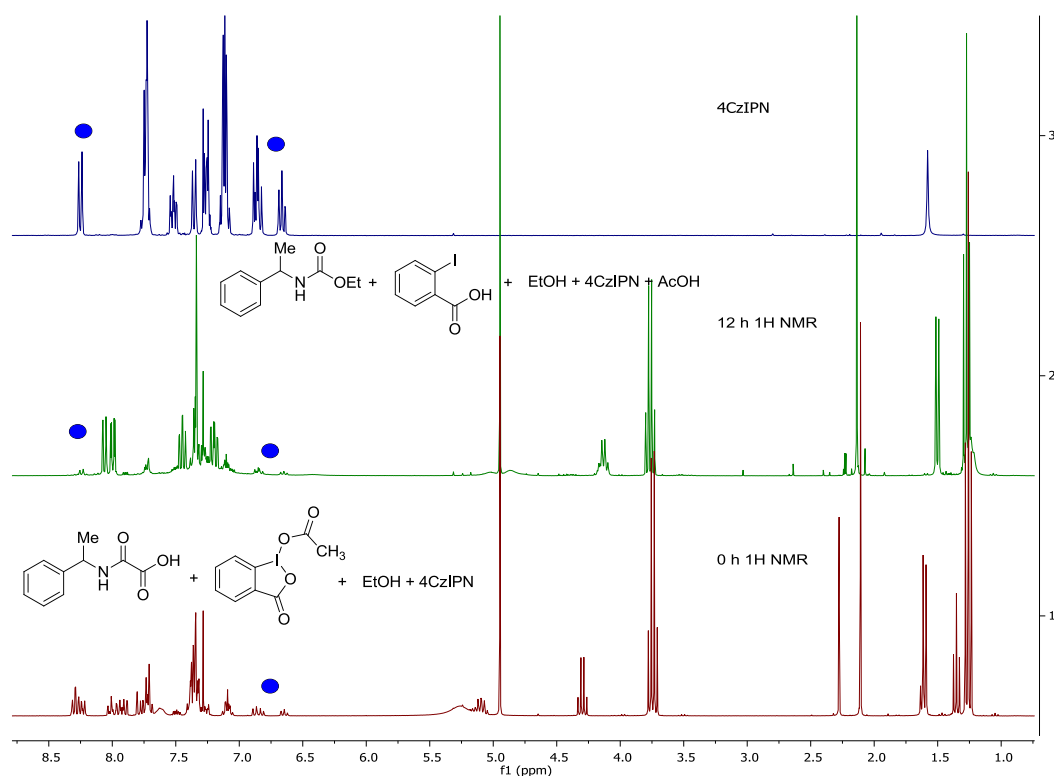
As per the general procedure condition A, **1b** (48 mg, 0.25 mmol), 4CzIPN (1.0 mol%), and BIOAc (114.7 mg, 0.37 mmol, 1.0 equiv.) were placed into a re-sealable test tube with Teflon septa (10 mL), equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, allyltrimethylsilane **10** (0.08 mL, 0.5 mmol, 2.0 equiv.) and DCE (0.2 M) was added afterwards. The reaction mixture was stirred at room temperature under blue LED irradiation for 24 h. The reaction mixture was concentrated and purified directly by column chromatography to afford the product **N-(1-phenylethyl)but-3-enamide (11)** as a white solid (11 mg, 22%); mp 118-121°C; $R_f = 0.34$ (EtOAc-Hexane 10/90). $^1\text{H NMR}$ (300 MHz, CDCl_3)

δ ppm 7.40 – 7.30 (m, 5H), 6.04 – 5.89 (m, 1H) 5.81 (bs, 1H), 5.31 – 5.09 (m, 3H), 3.04 (dt, $J = 7.2, 1.2$ Hz, 2H), 1.51 (d, $J = 6.8$ Hz, 3H). IR (neat) ν_{\max} (cm^{-1}) = 3324, 2962, 1625, 1570. Spectroscopic data were in good agreement with literature.¹²

Catalyst Stability

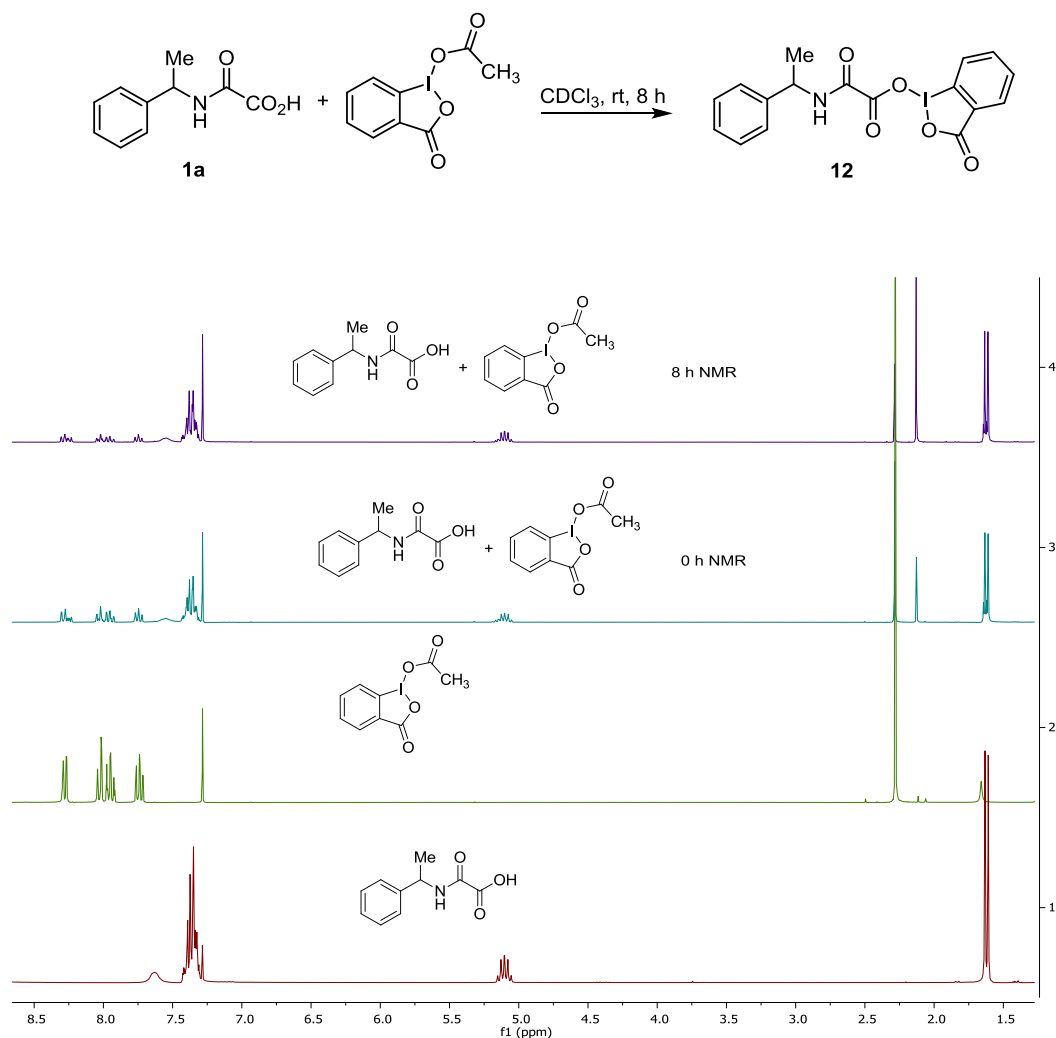


Solutions of oxamic acid **1a** (9.6 mg, 0.05 mmol), BI-OAc (23.0 mg, 0.07 mmol), 4CzIPN (10.0 mol%, 3.9 mg) and dibromomethane (0.003 mL, 0.05 mmol) as an internal standard in 0.6 mL CDCl_3 were added into an NMR tube. The reaction was monitored by ^1H NMR at 0 h and 12 h. After 12 h, the reaction was completed and ^1H NMR indicated that 4CzIPN catalyst was still present in the reaction mixture.

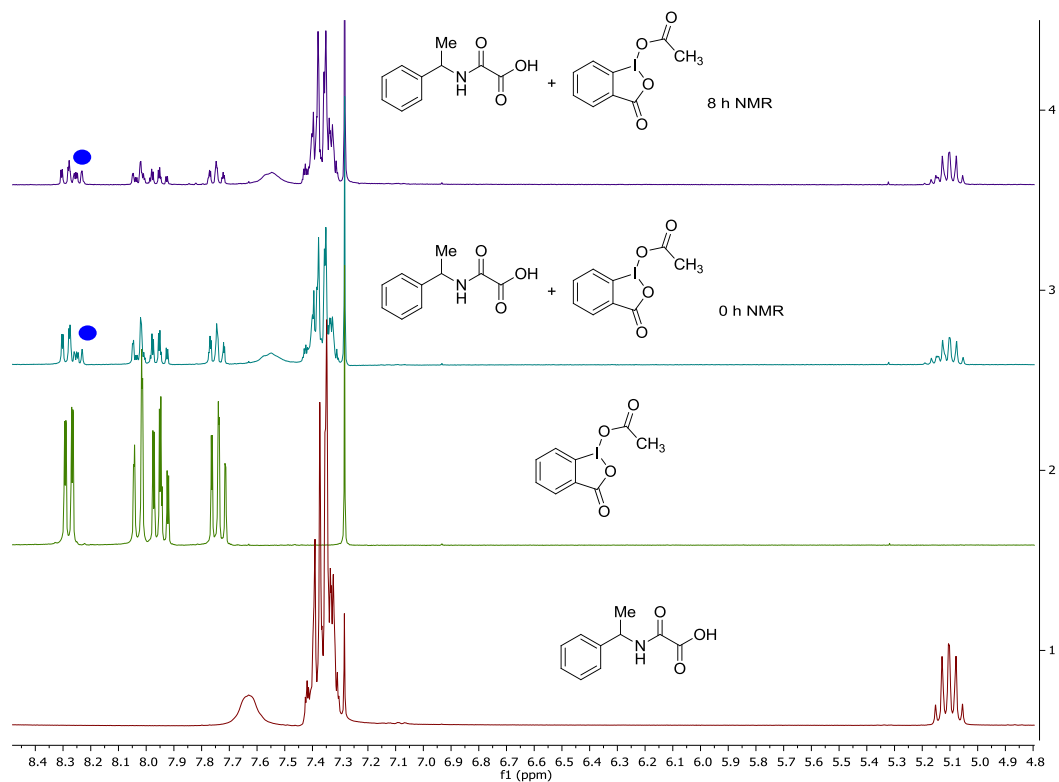
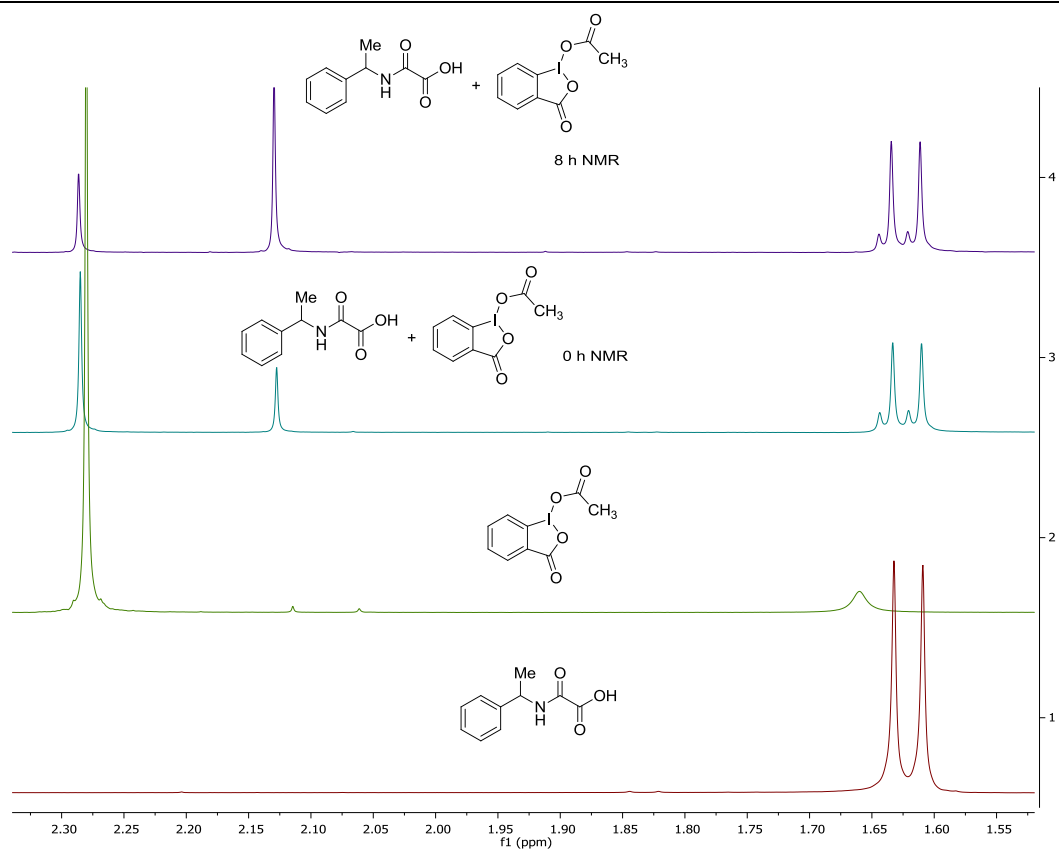


Attempt a detecting intermediate 12. The BI-OAc and Oxamic Acid ^1H NMR Experiment

Solutions of oxamic acid **1a** (4.8 mg, 0.025 mmol) and BI-OAc (11.4 mg, 0.03 mmol) in 0.6 mL CDCl_3 were added into an NMR tube. After 5 mins, ^1H NMR was recorded and showed that the oxamic acid reacted with the hypervalent iodine reagent to generate acetic acid and a new compound which could not be isolated but might be **12**.



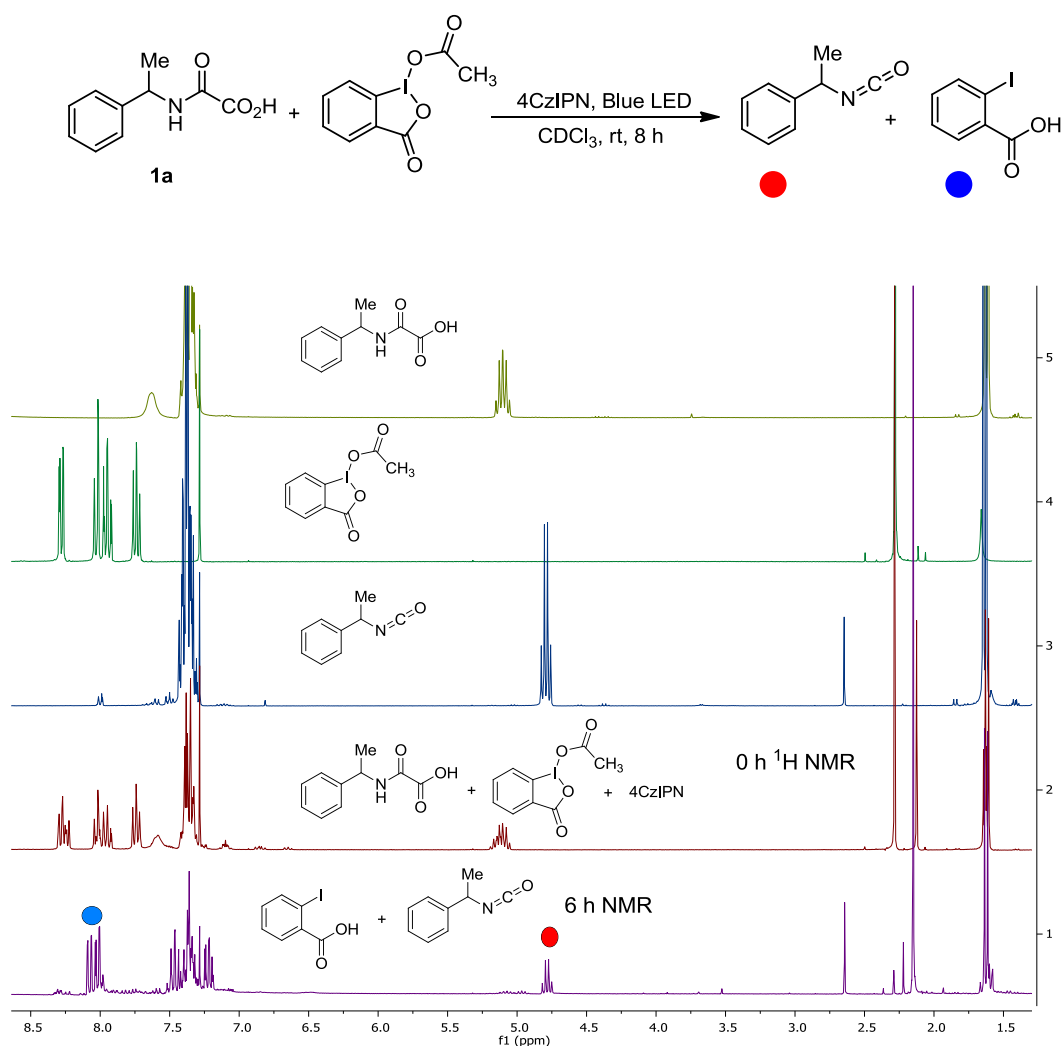
Supporting Information



* Blue dot correspond to the new formed species.

Formation of Isocyanate monitored by ^1H NMR

Solutions of oxamic acid **1a** (4.8 mg, 0.025 mmol), BI-OAc (11.4 mg, 0.03 mmol) and 4CzIPN (1.0 mol%, 0.2 mg) in 0.6 mL CDCl_3 were added into an NMR tube. The mixture was monitored by ^1H NMR at 0 h and 6 h. At 0 h, the complexation of oxamic acid and BIOAc was observed as in previous experiment above. After 6 h, the signal of the benzyl CH (around 5 ppm) shifted to upfield (4.75 ppm) the chemical shift being identical with that of an authentic isocyanate NMR spectrum. 2-Iodobenzoic acid and AcOH peaks also emerged.

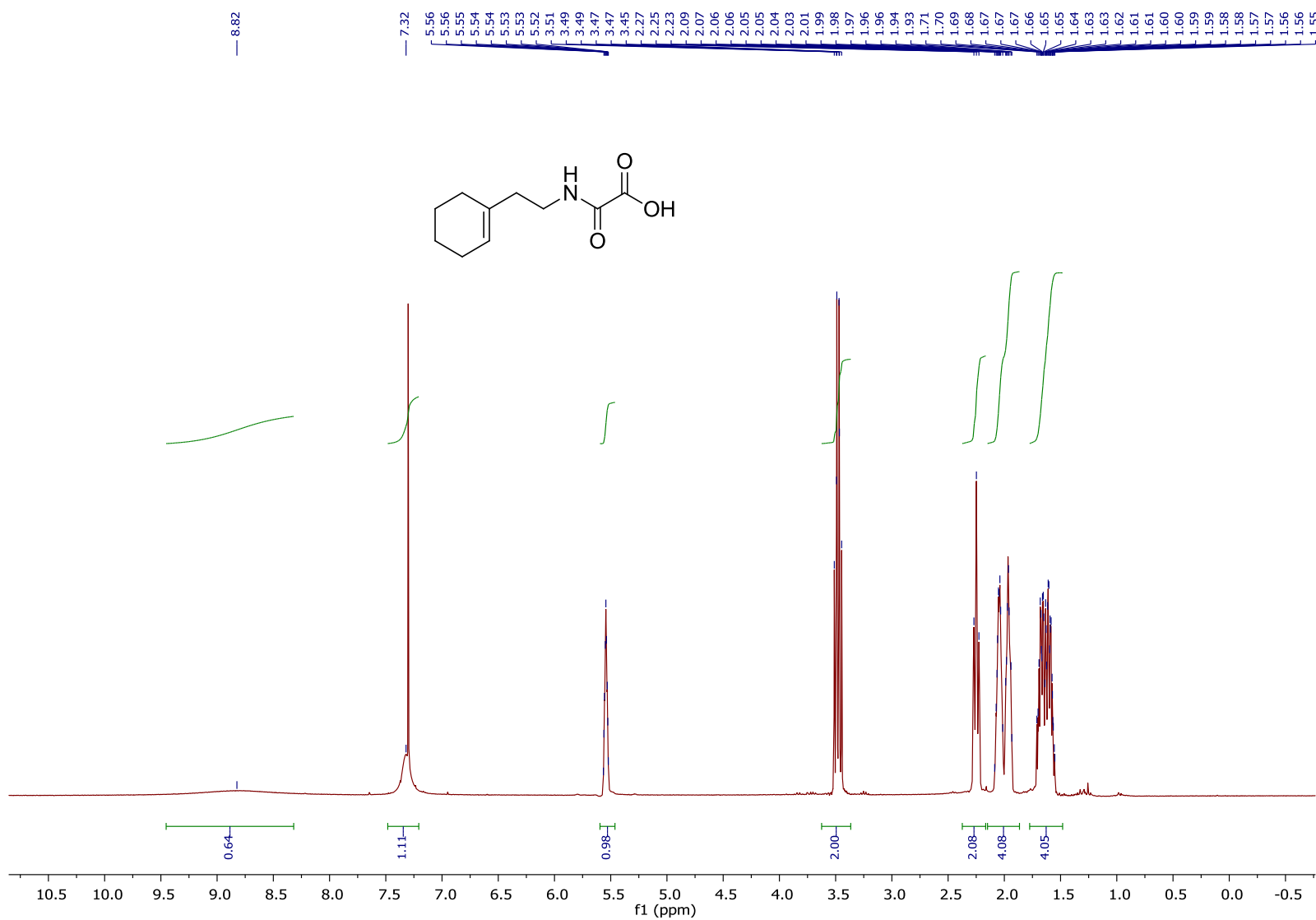


9. References

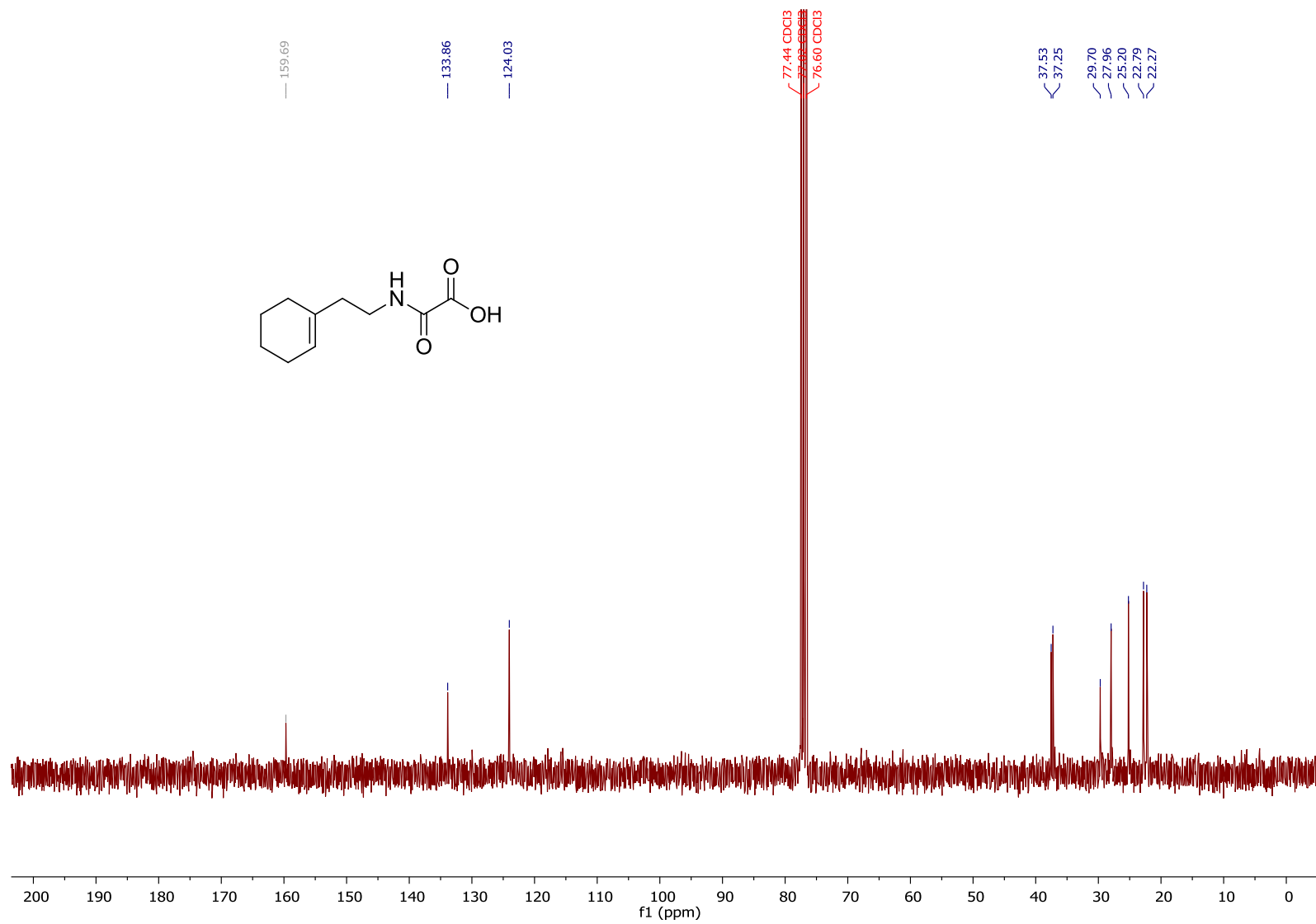
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10. Copies of ¹H and ¹³C NMR Spectra

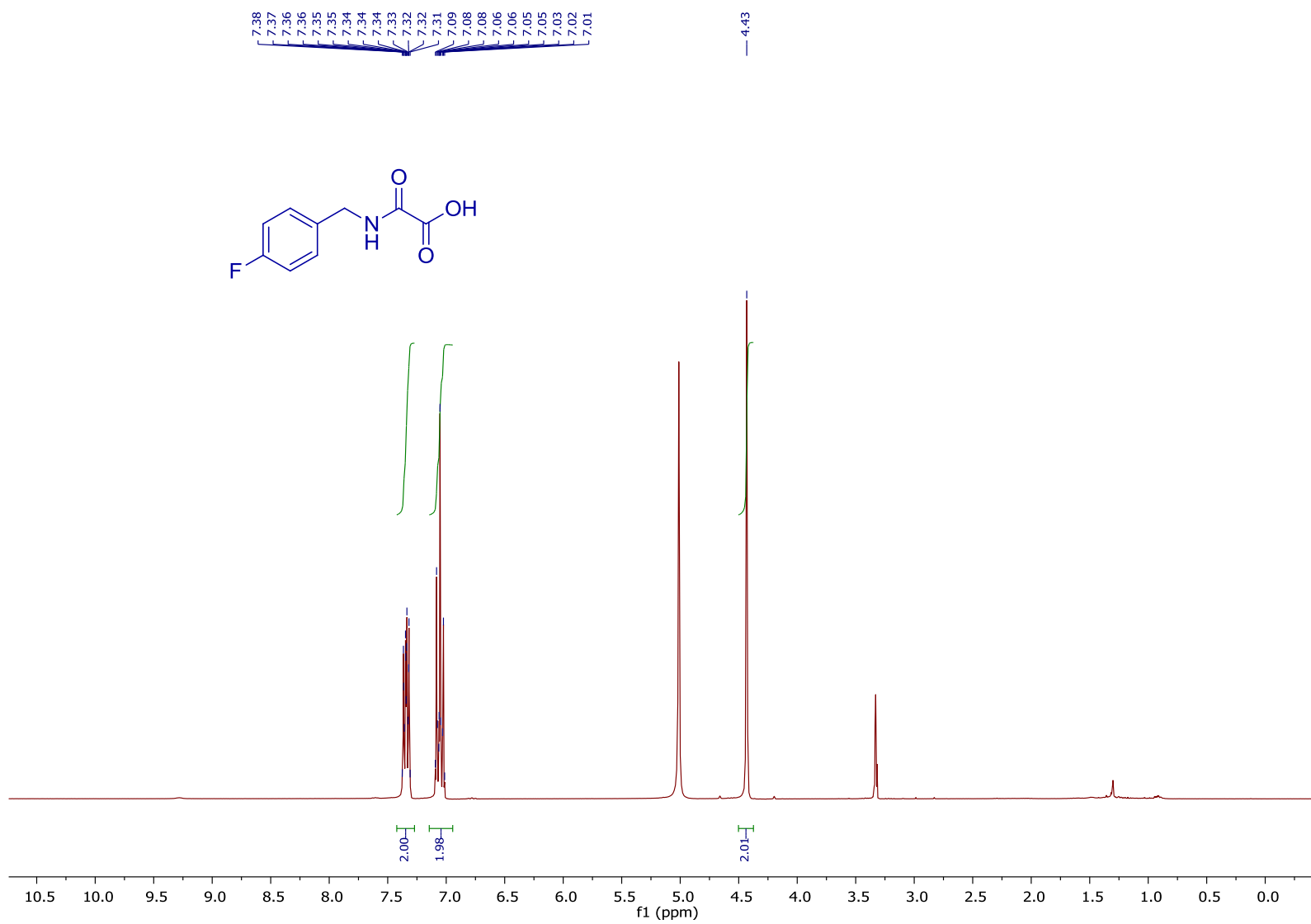
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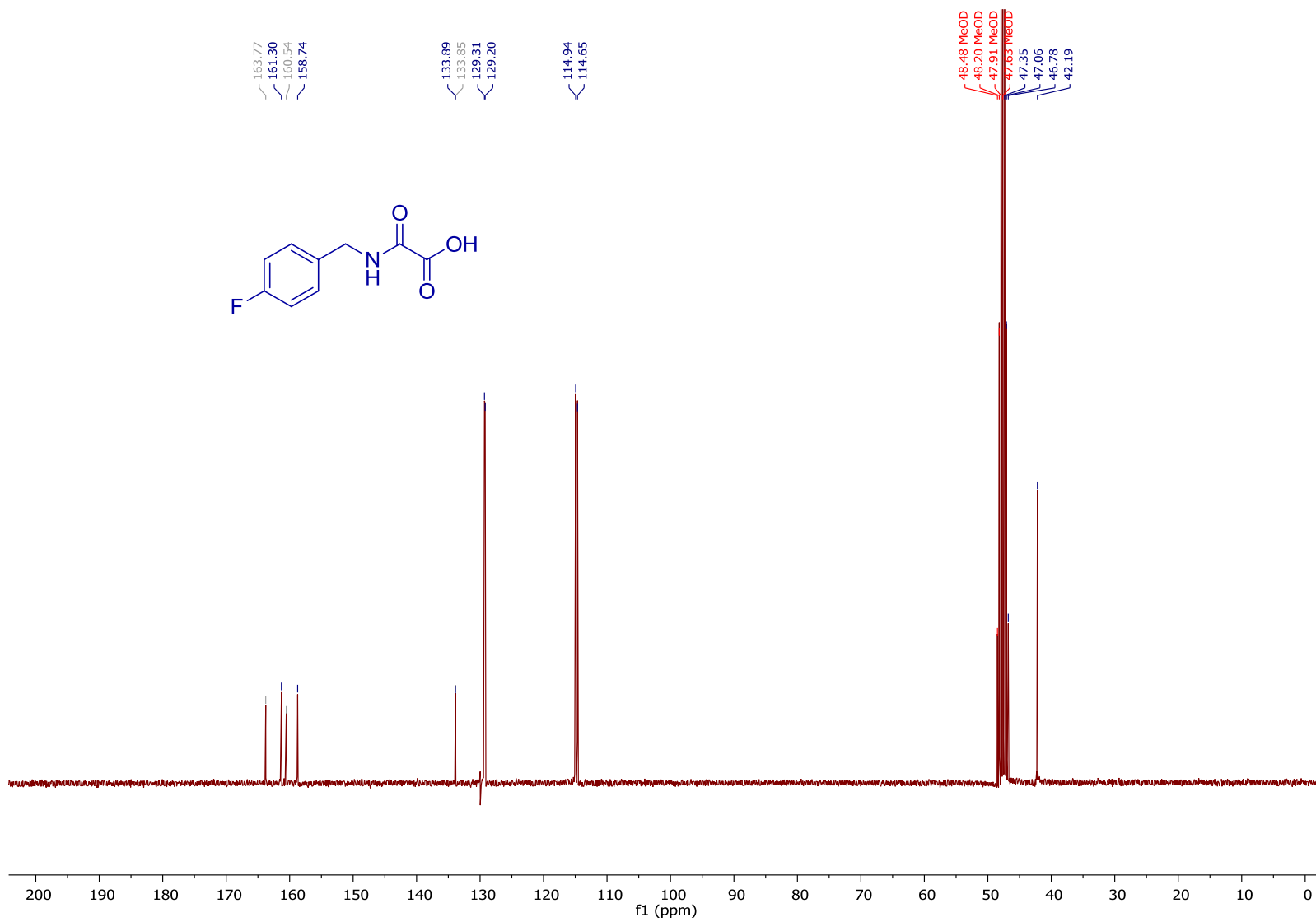
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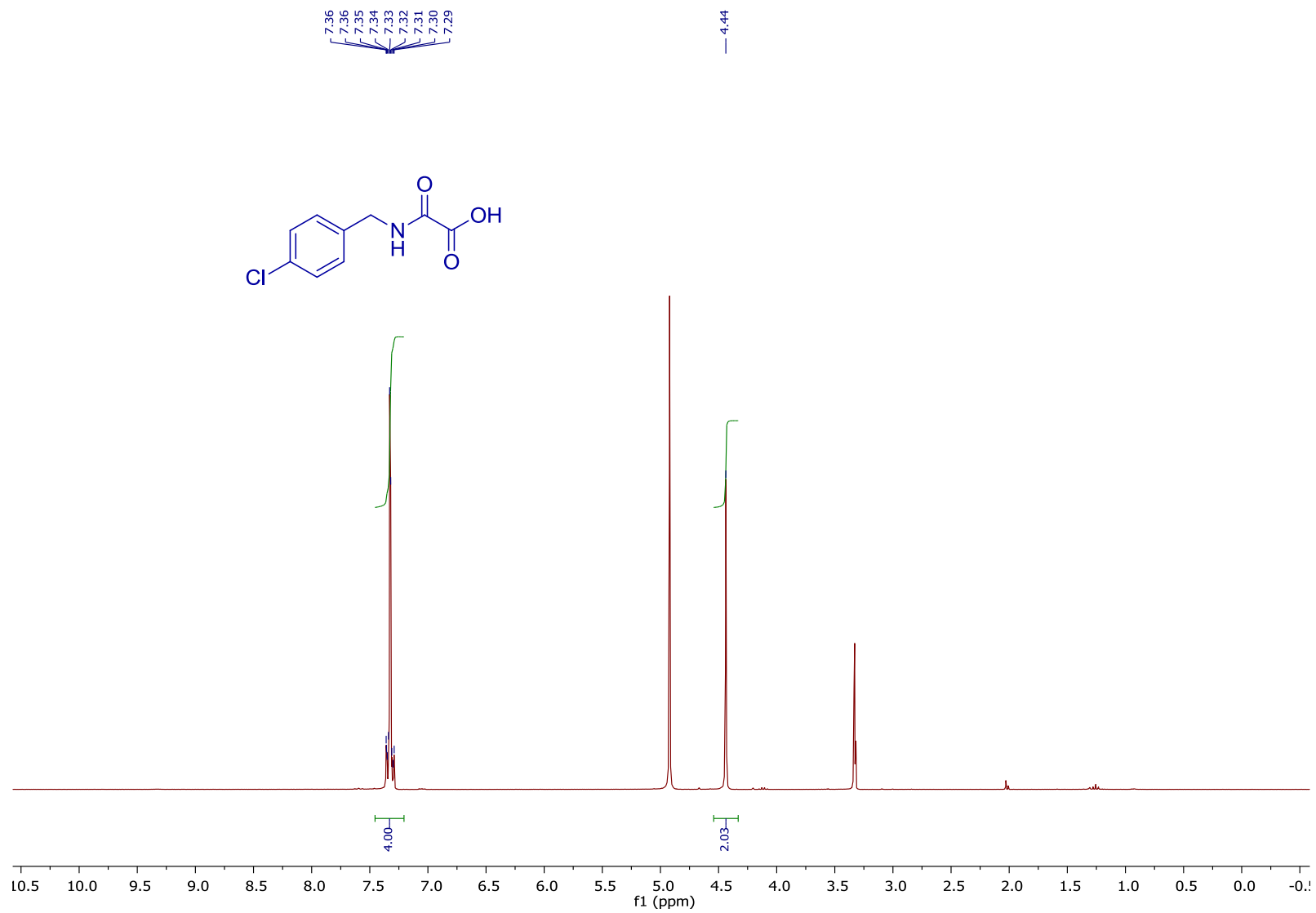
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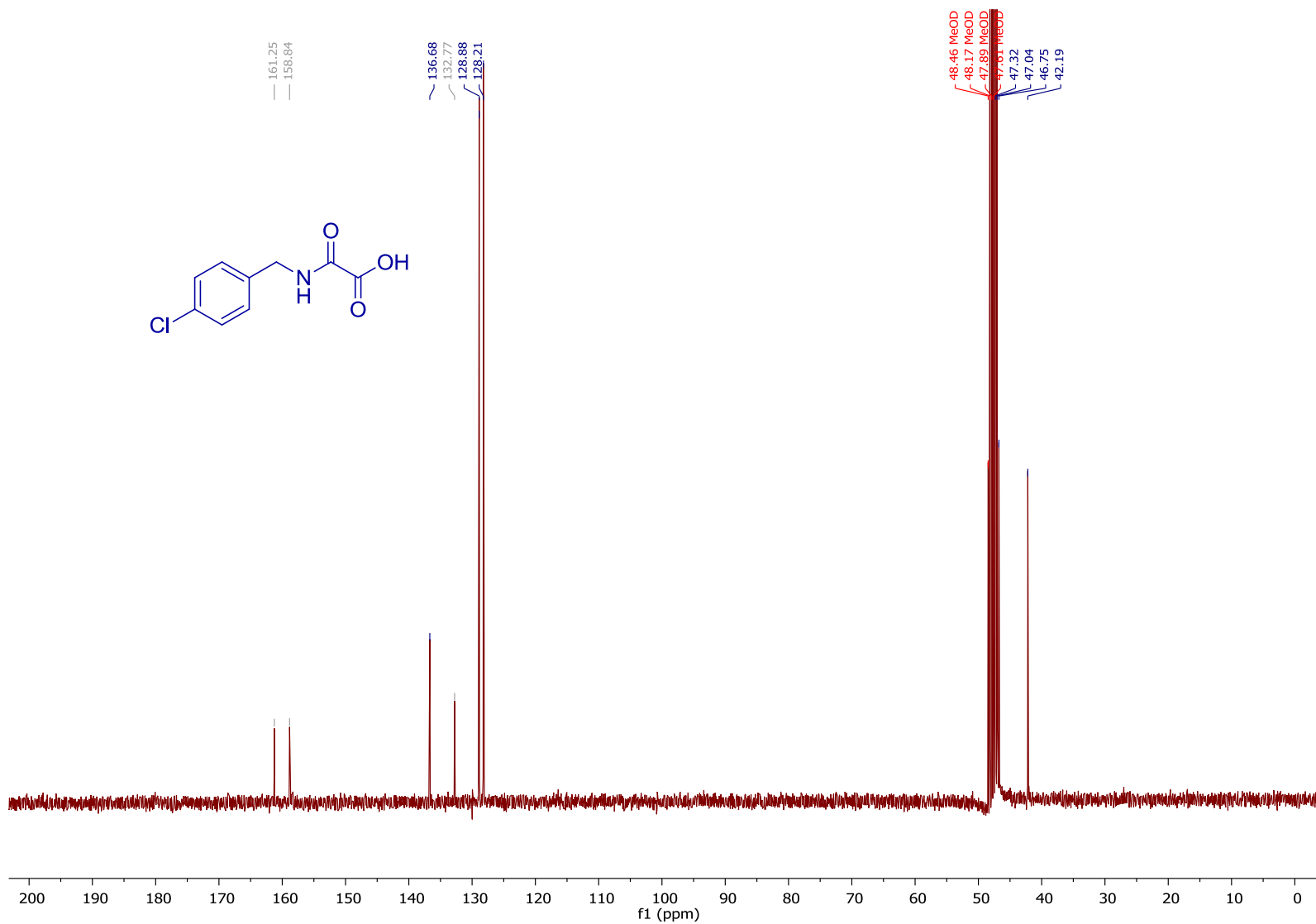
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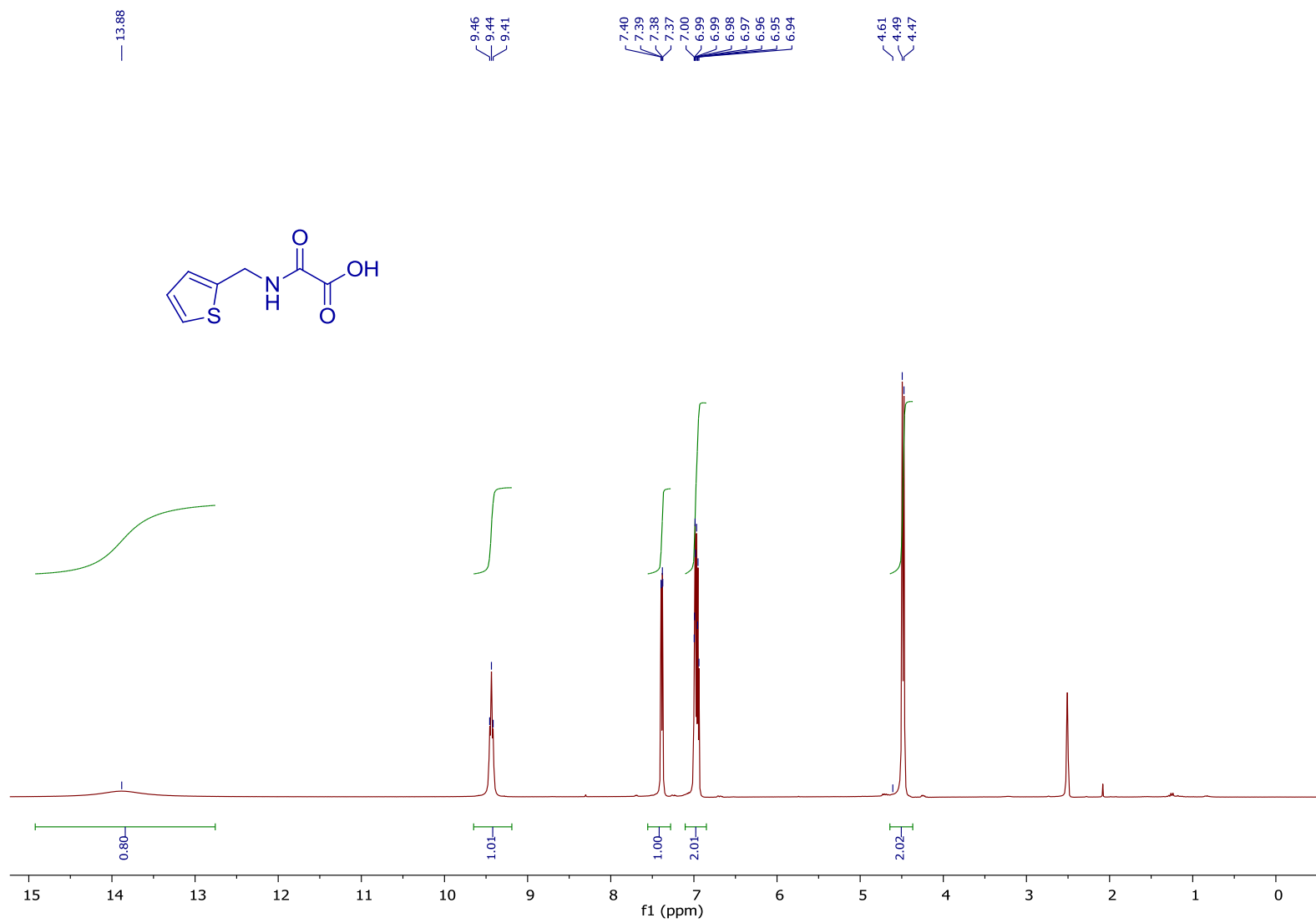
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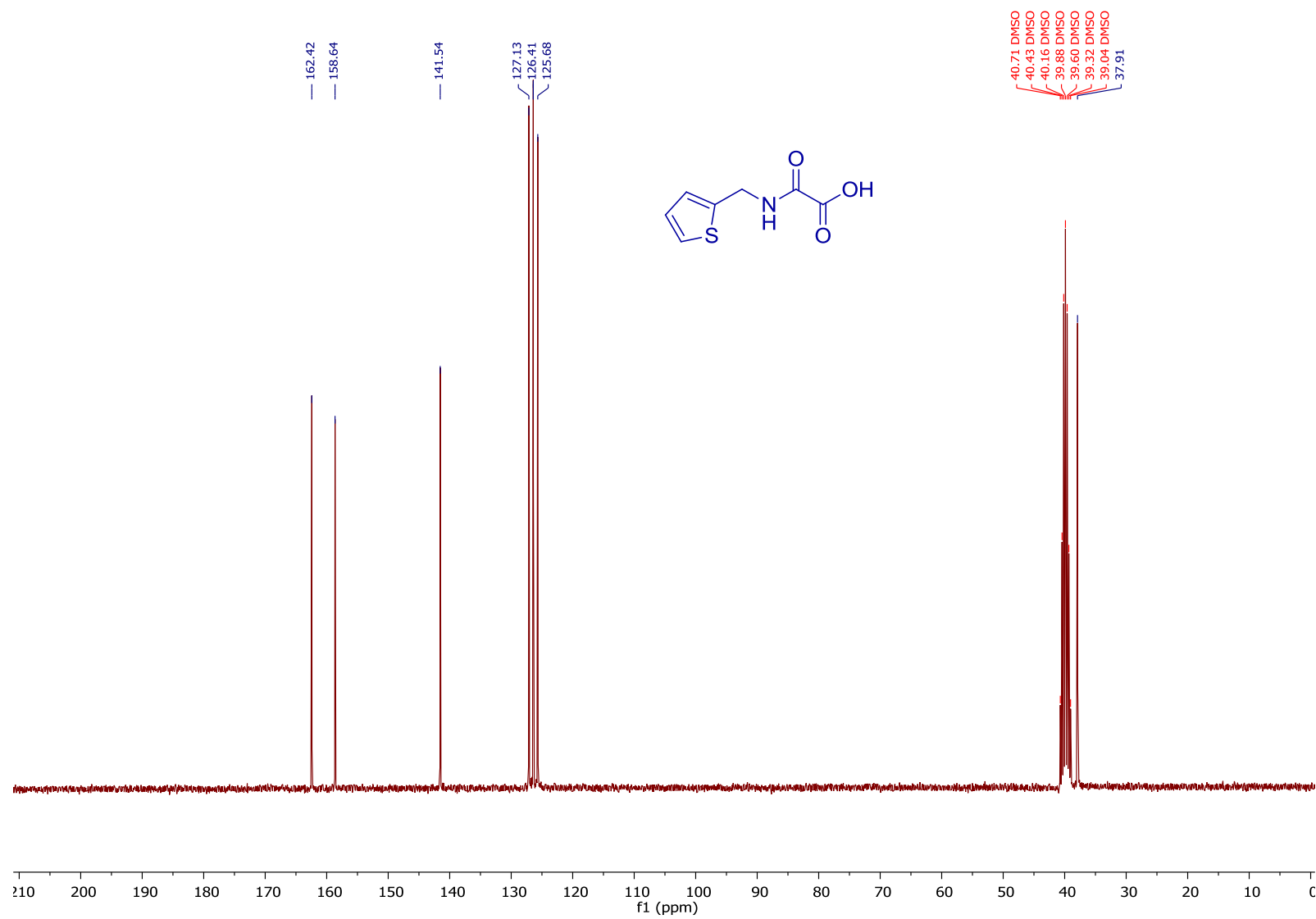
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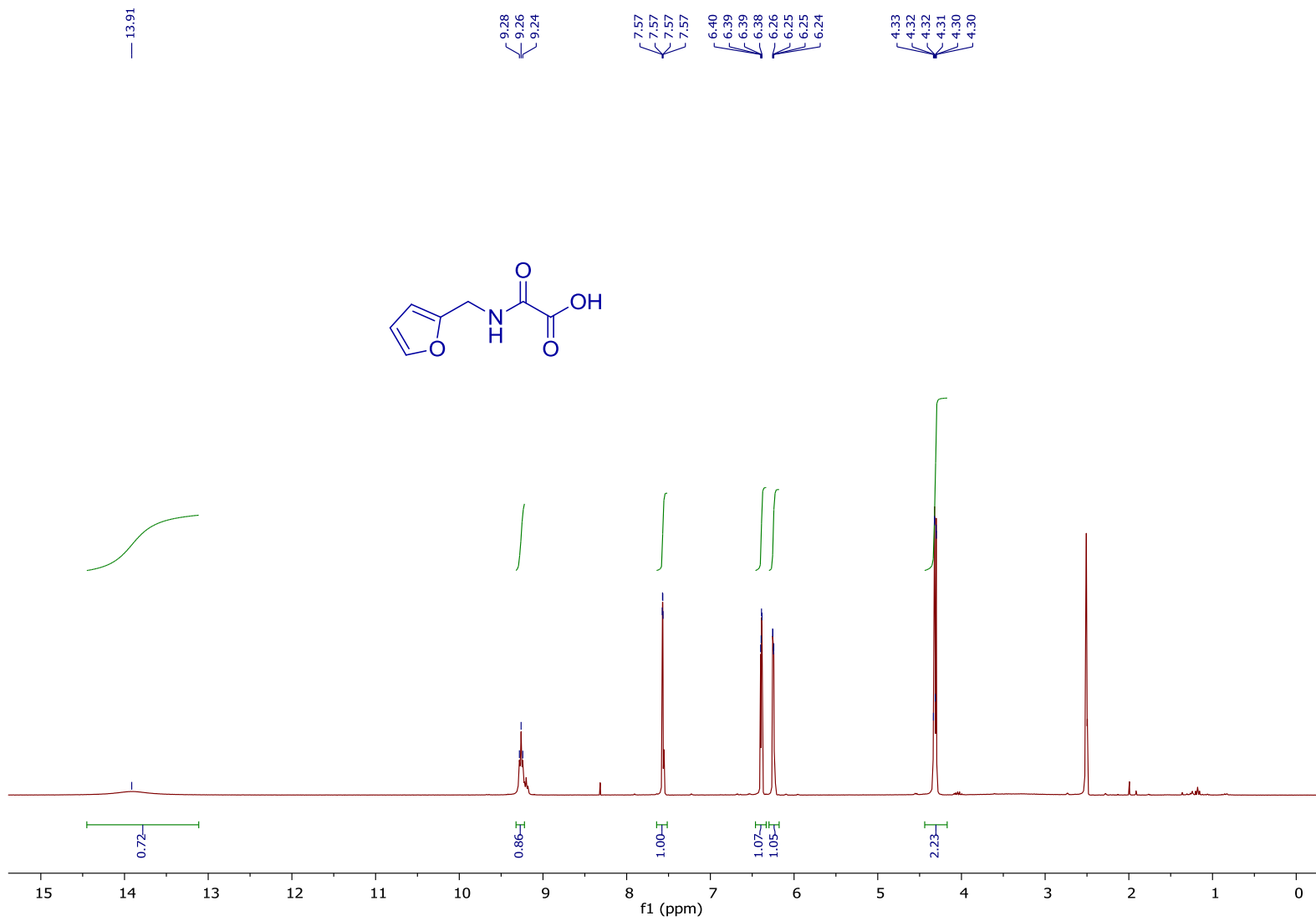
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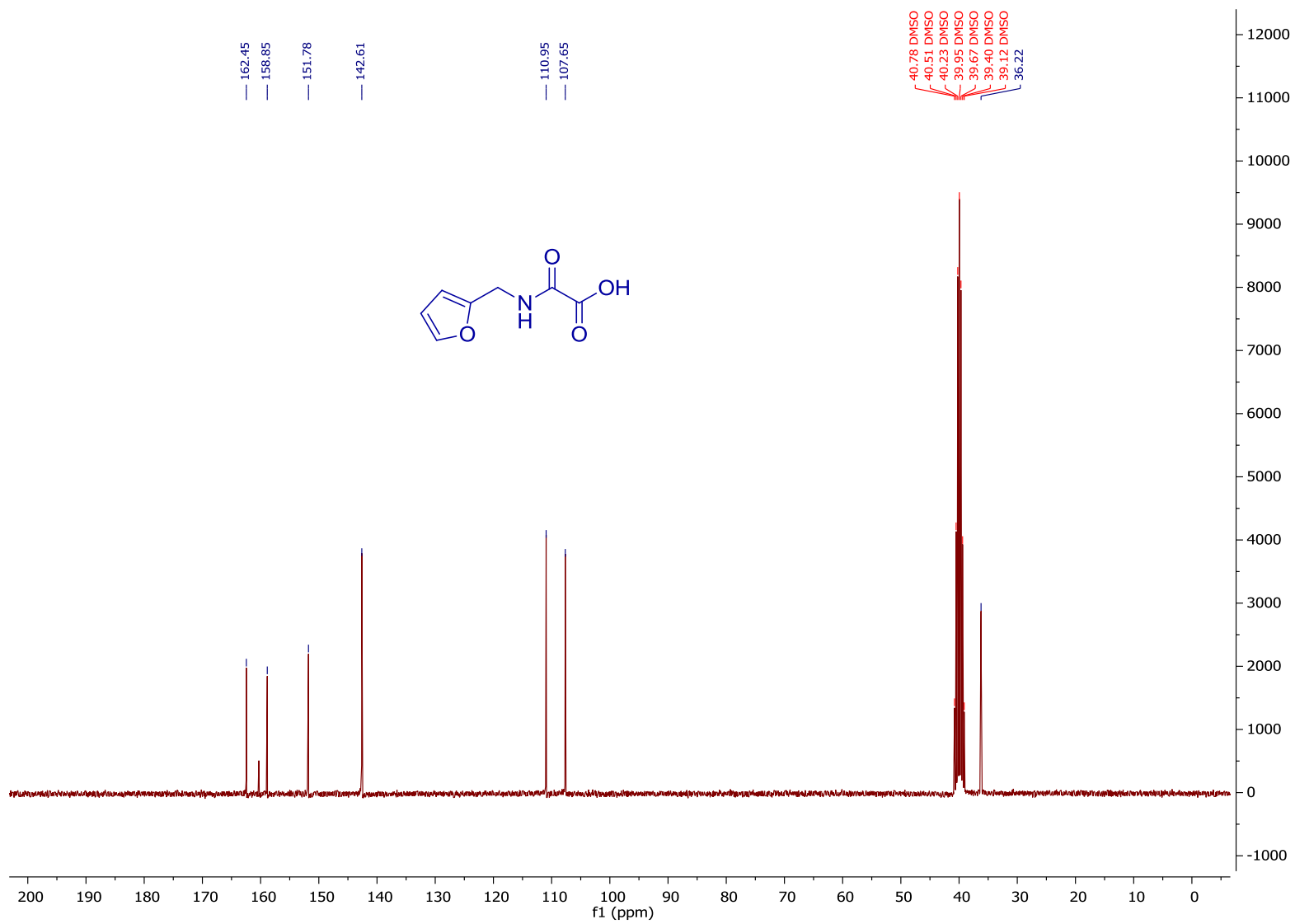
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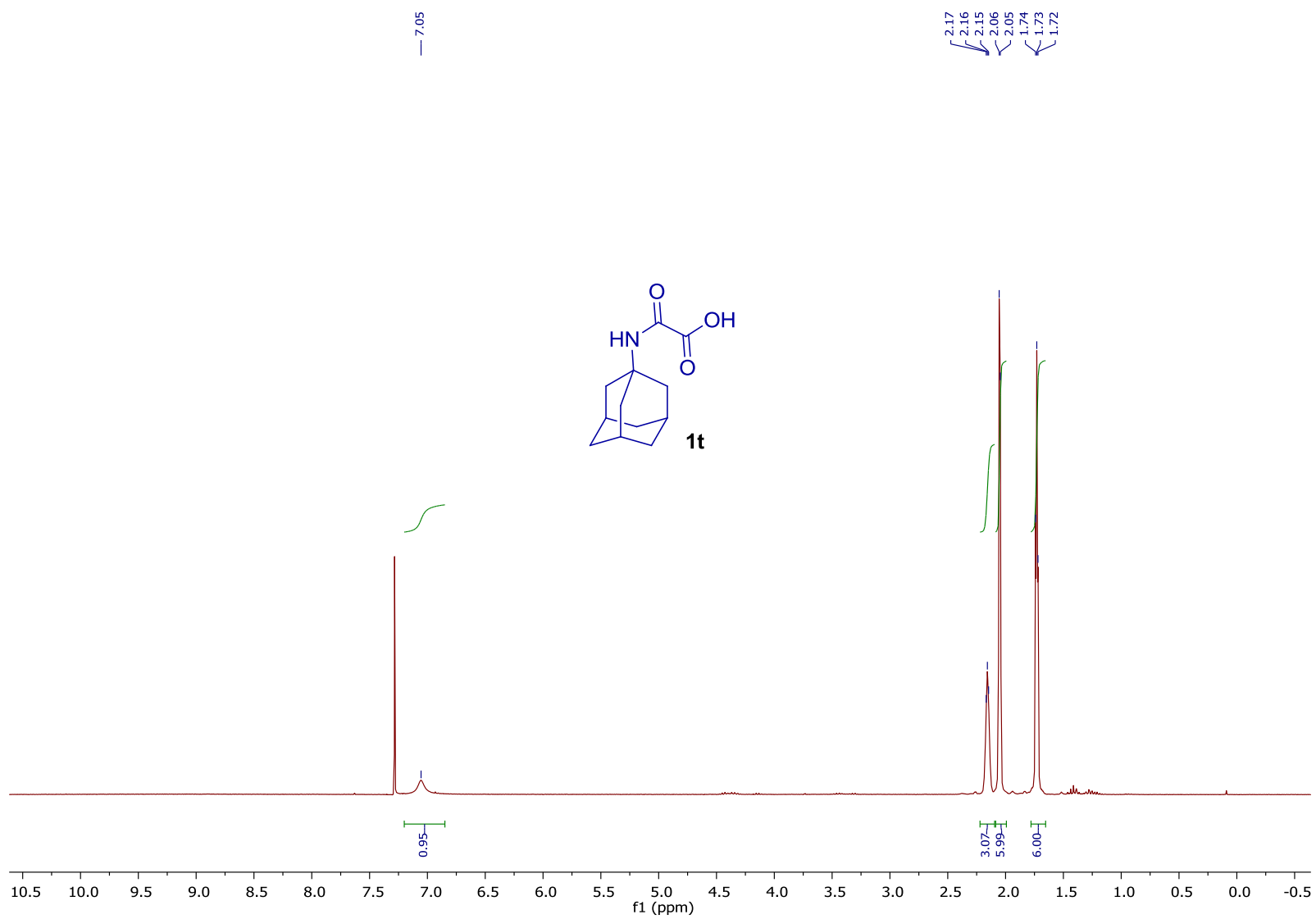
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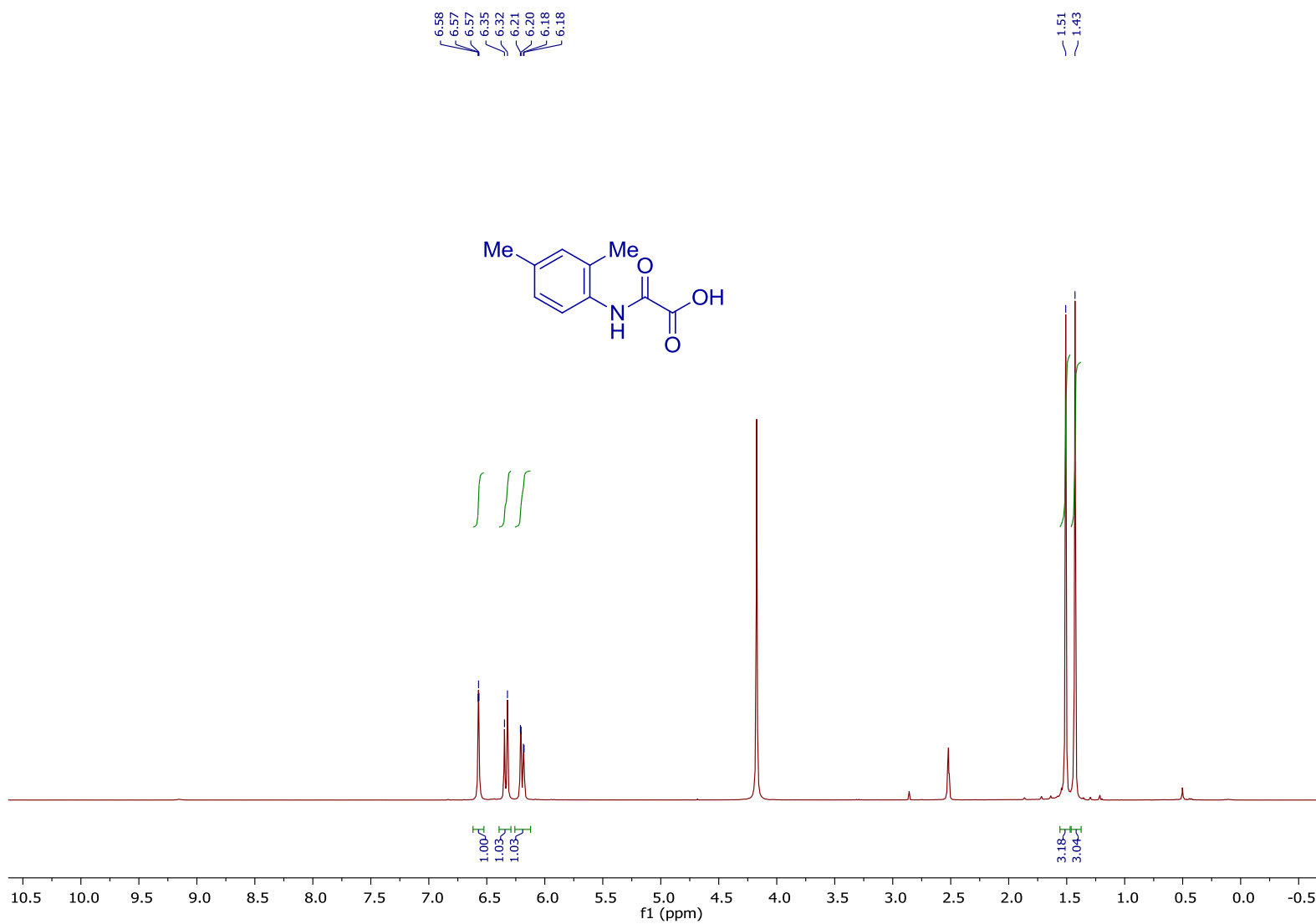
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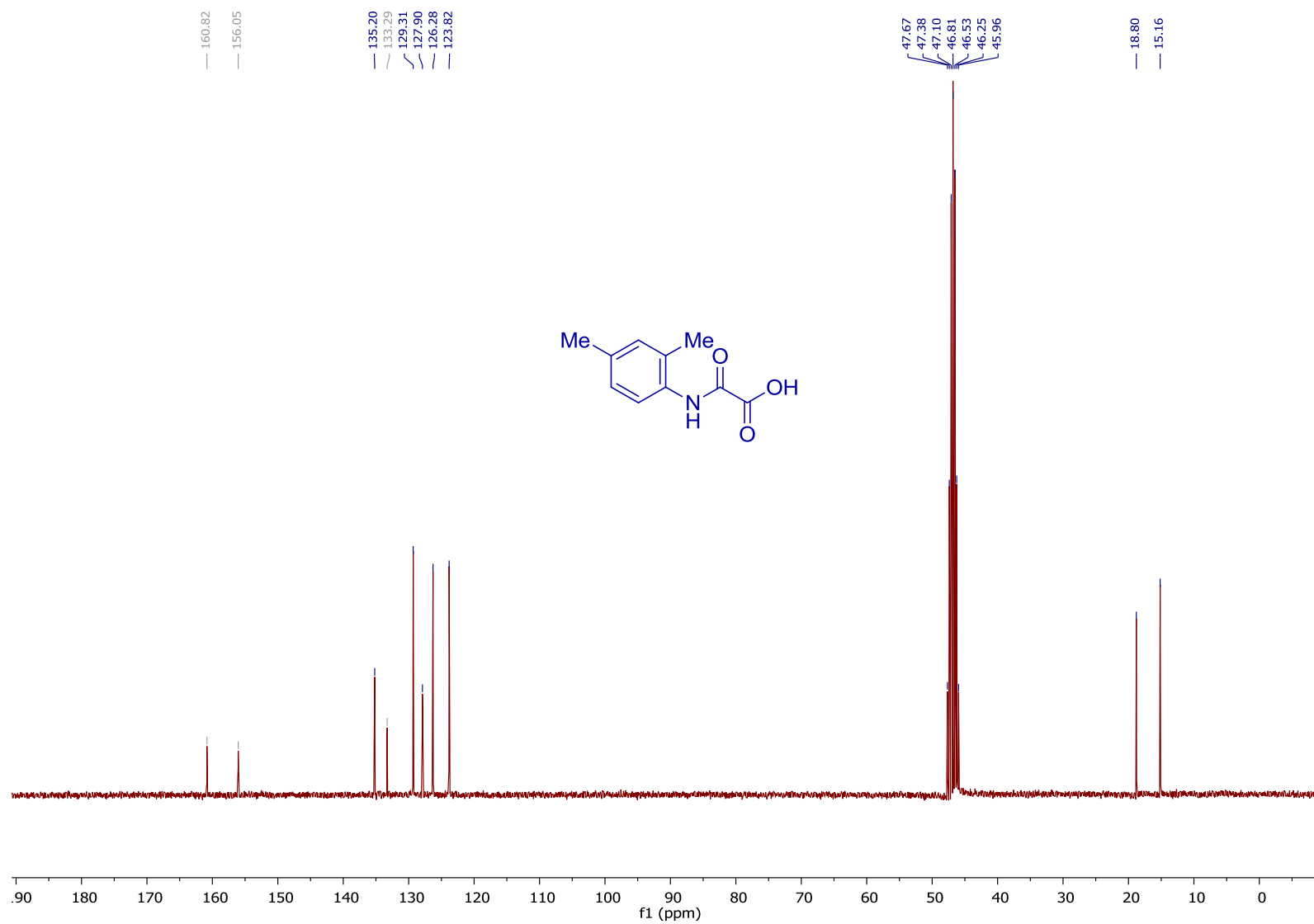
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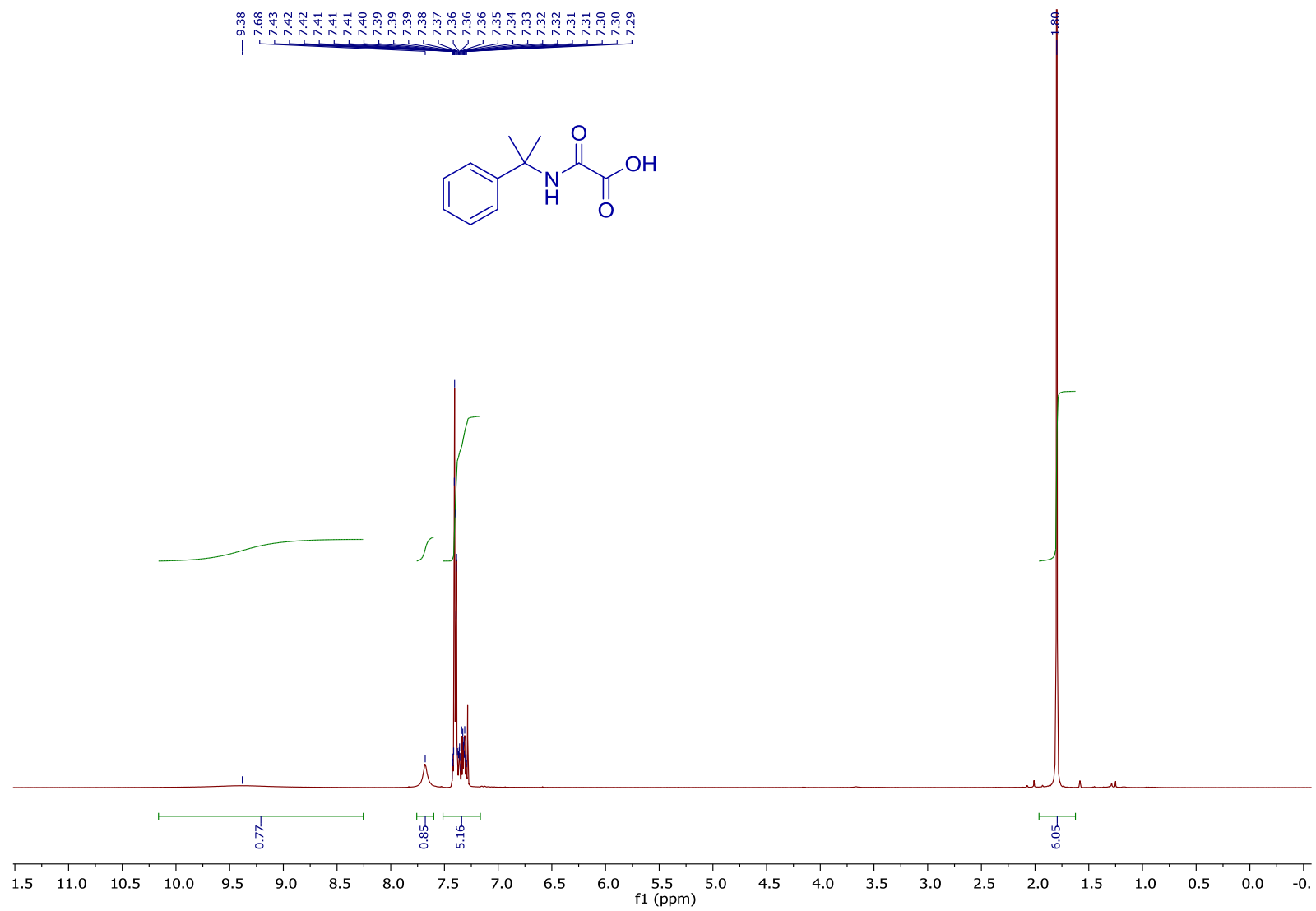


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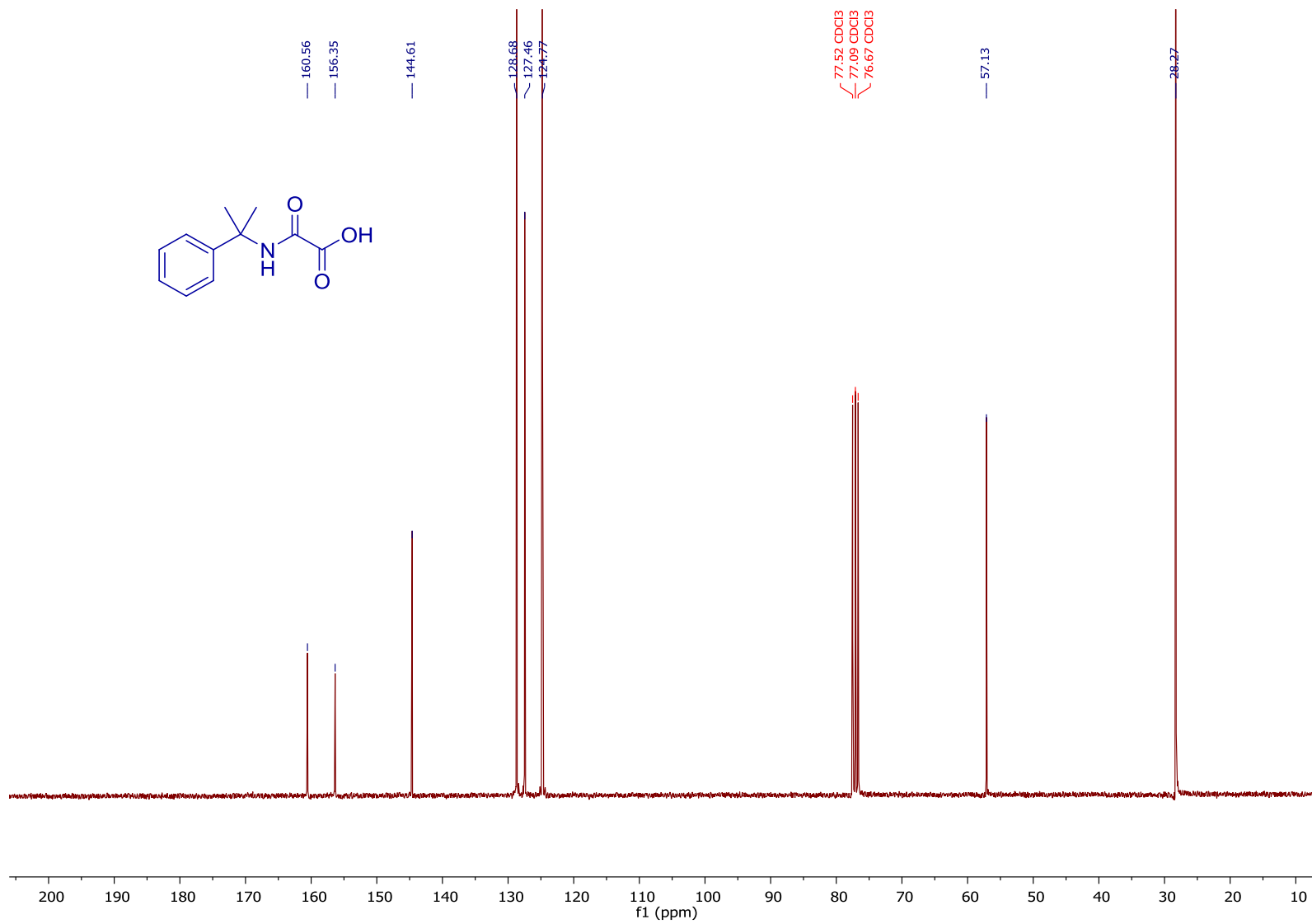


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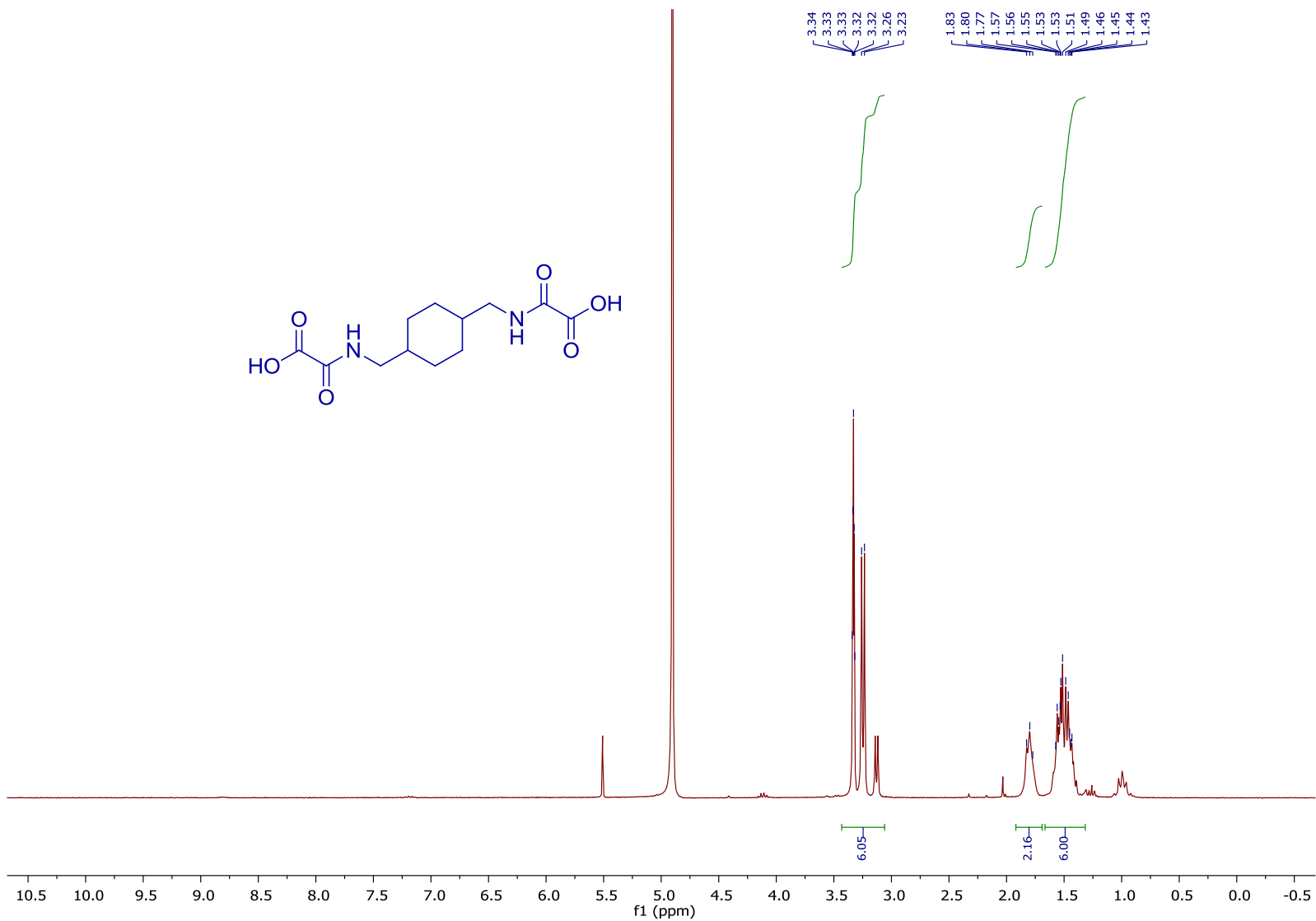
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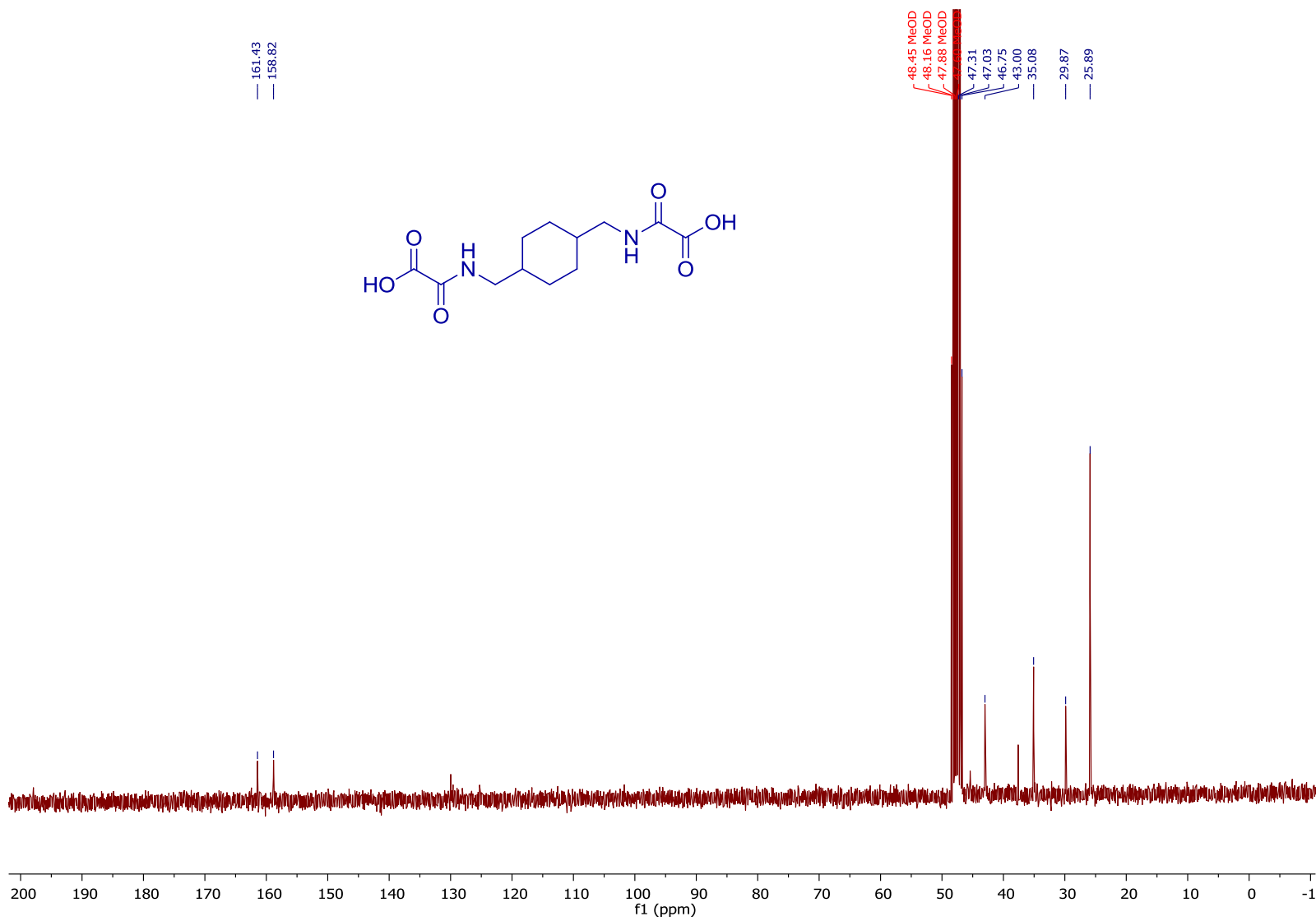


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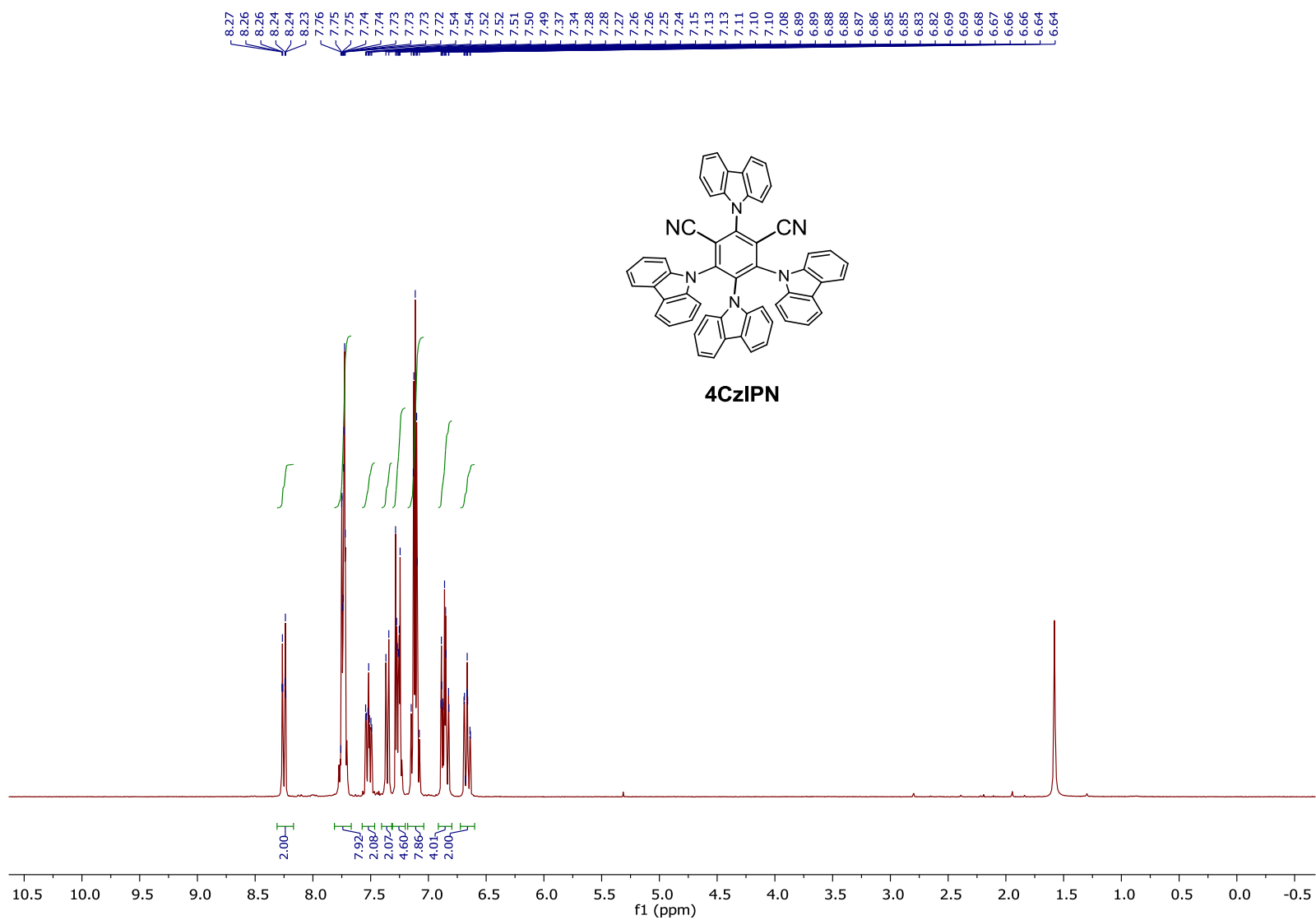


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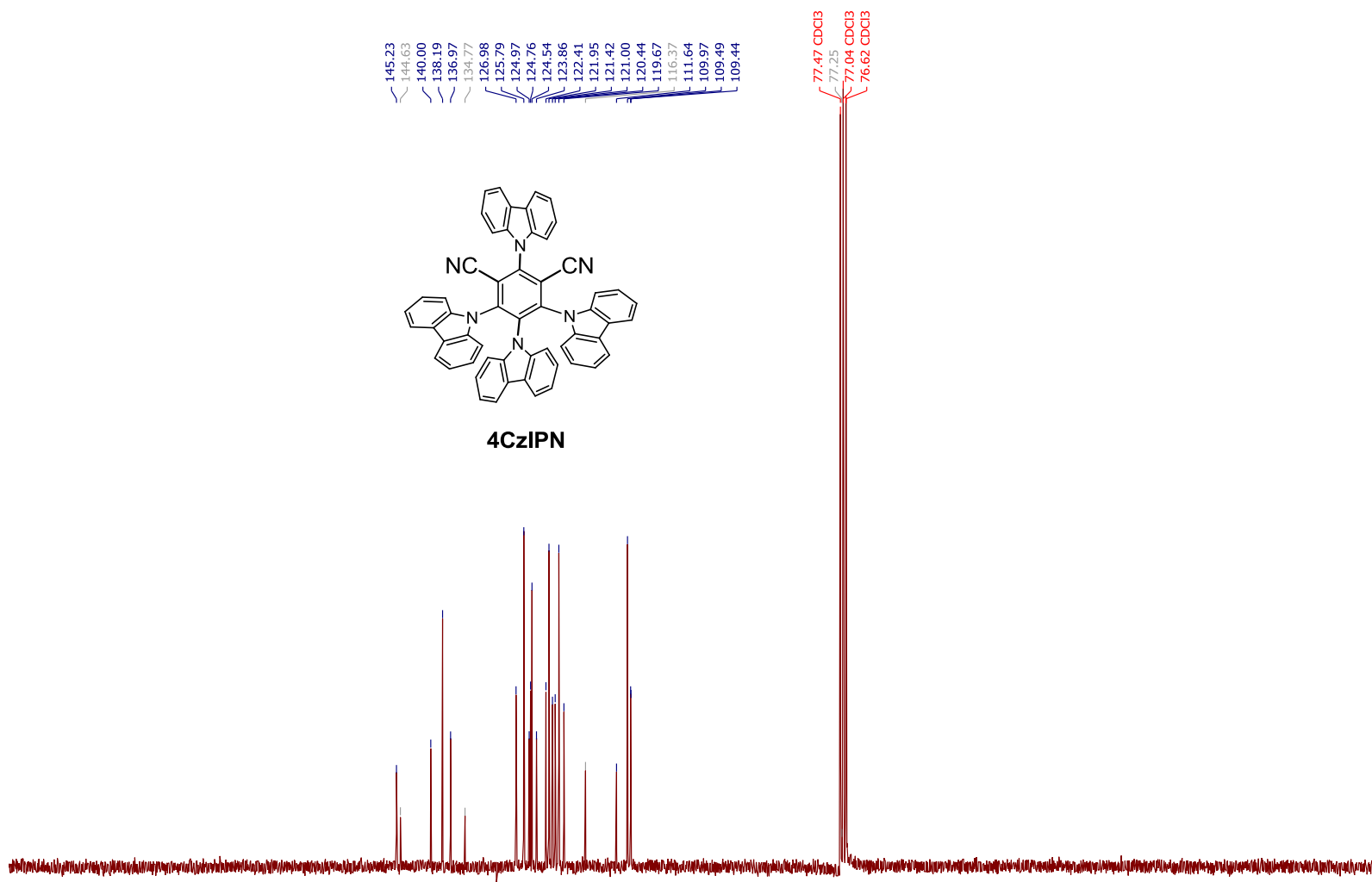
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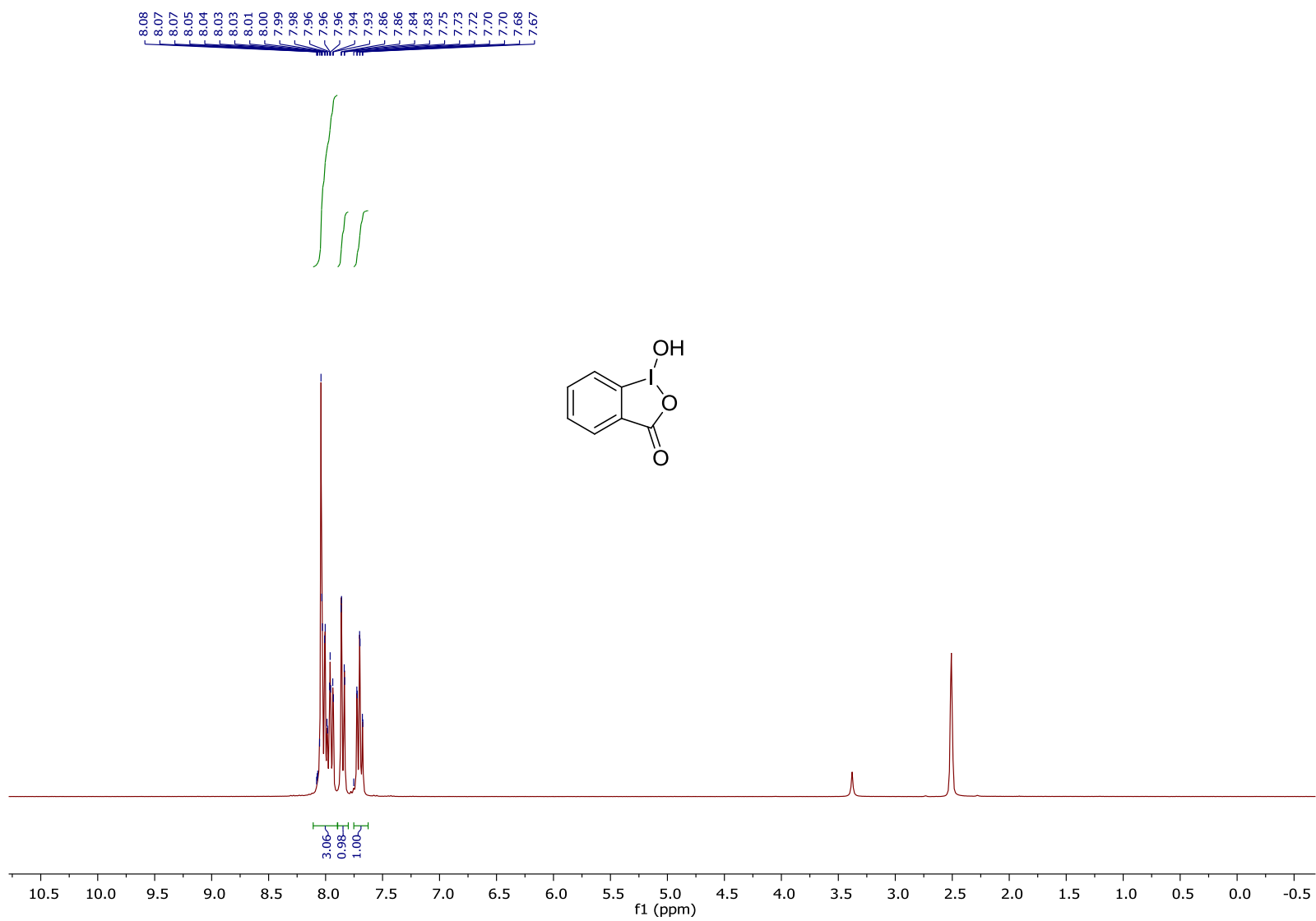
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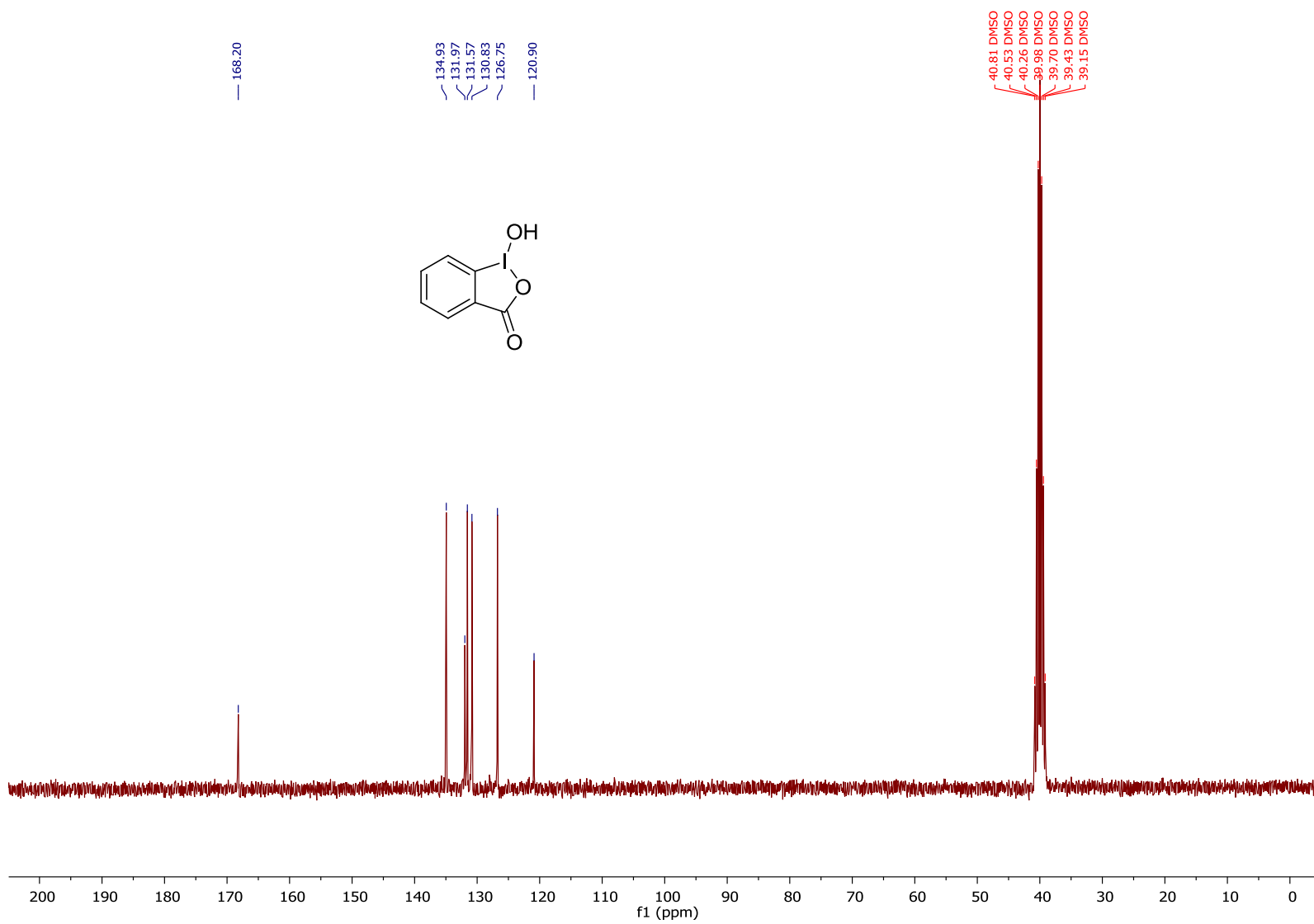
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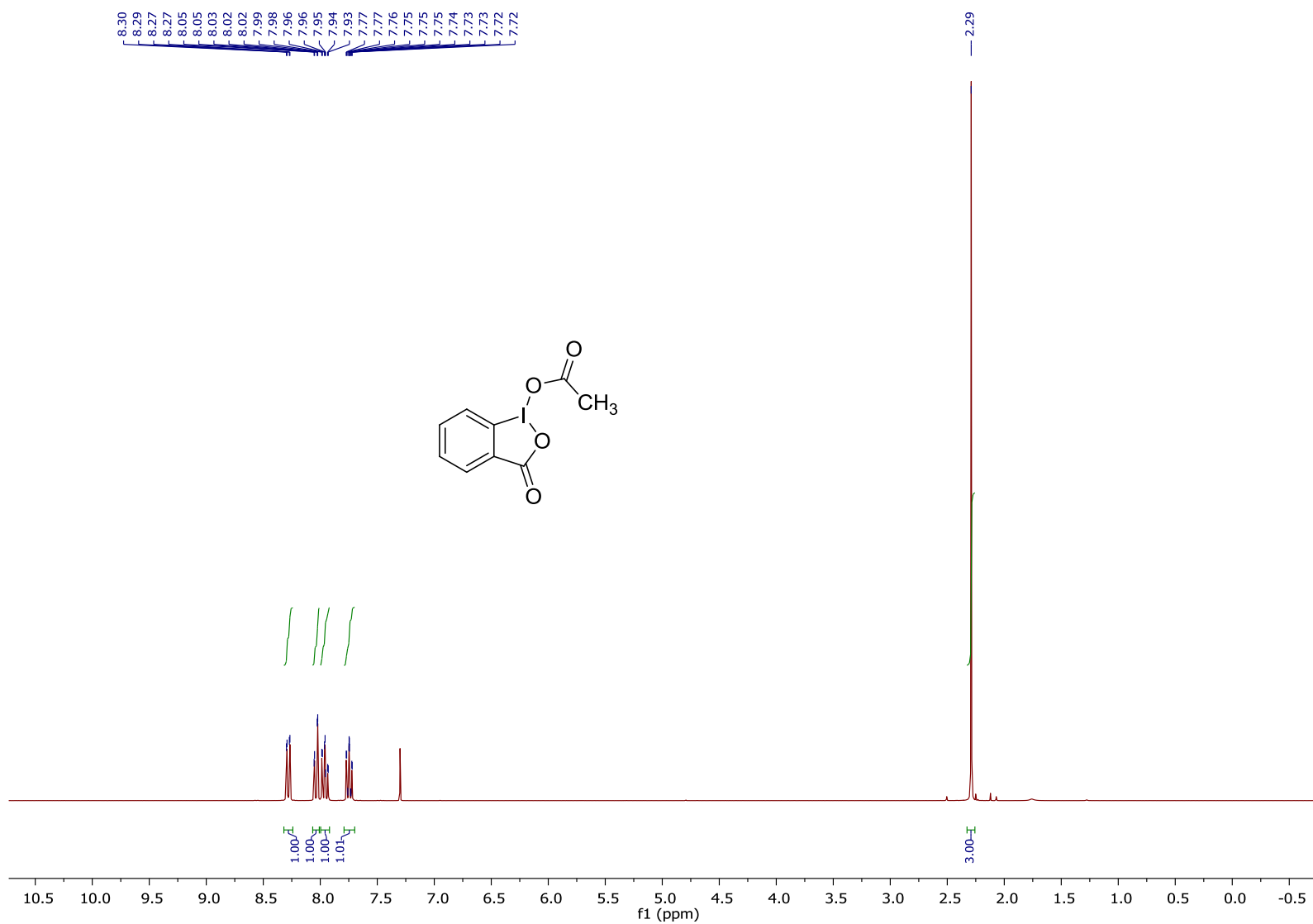
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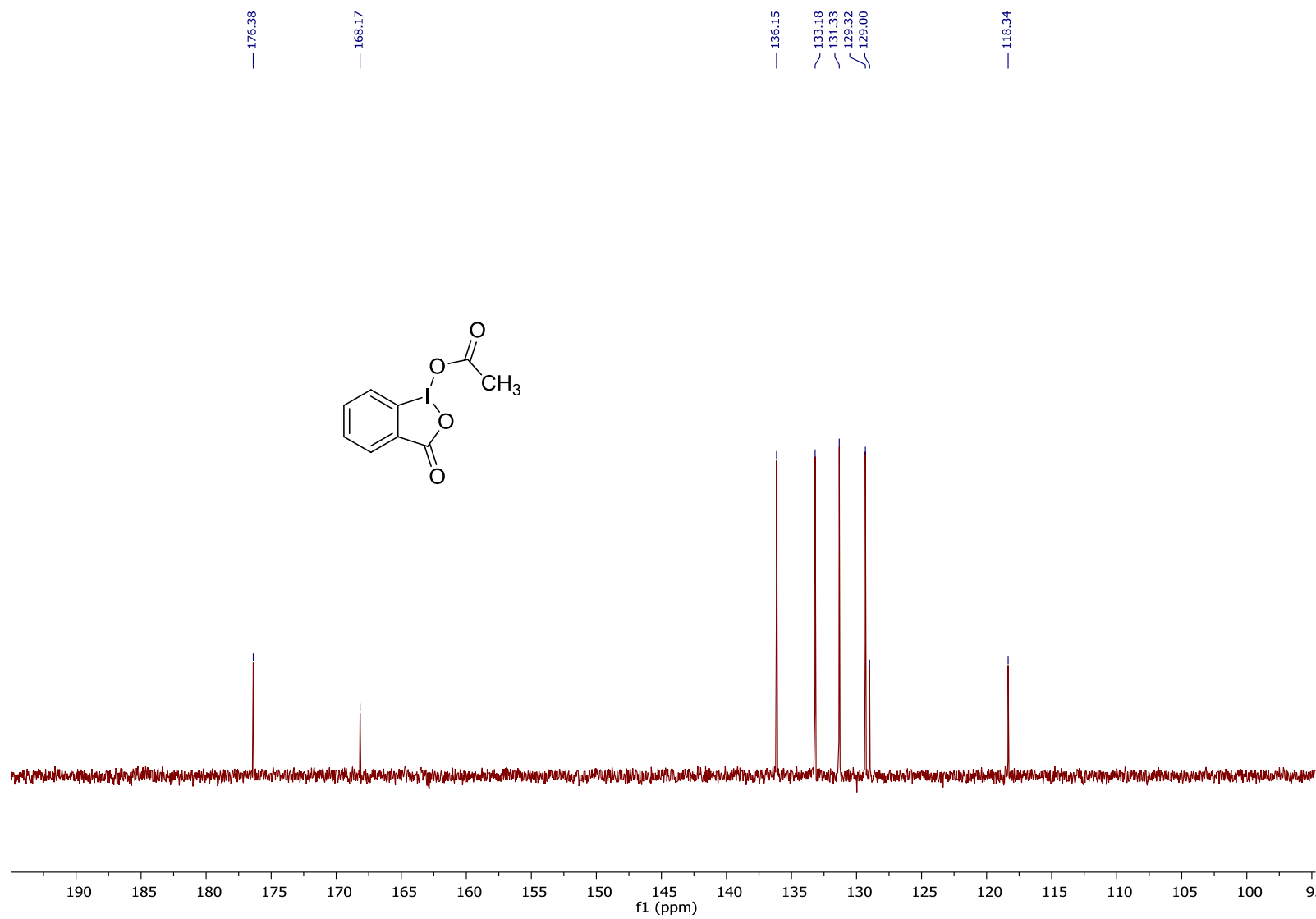
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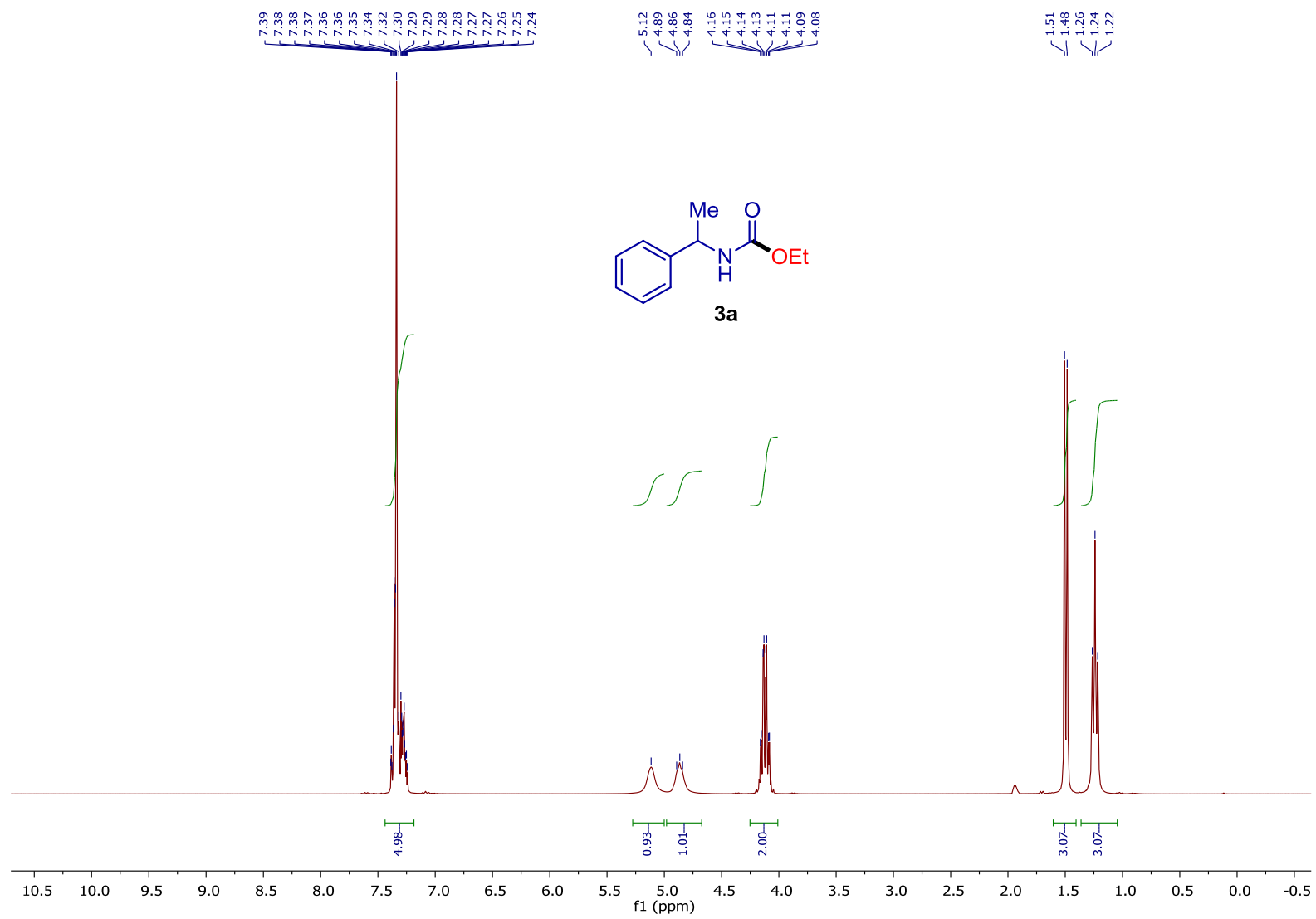


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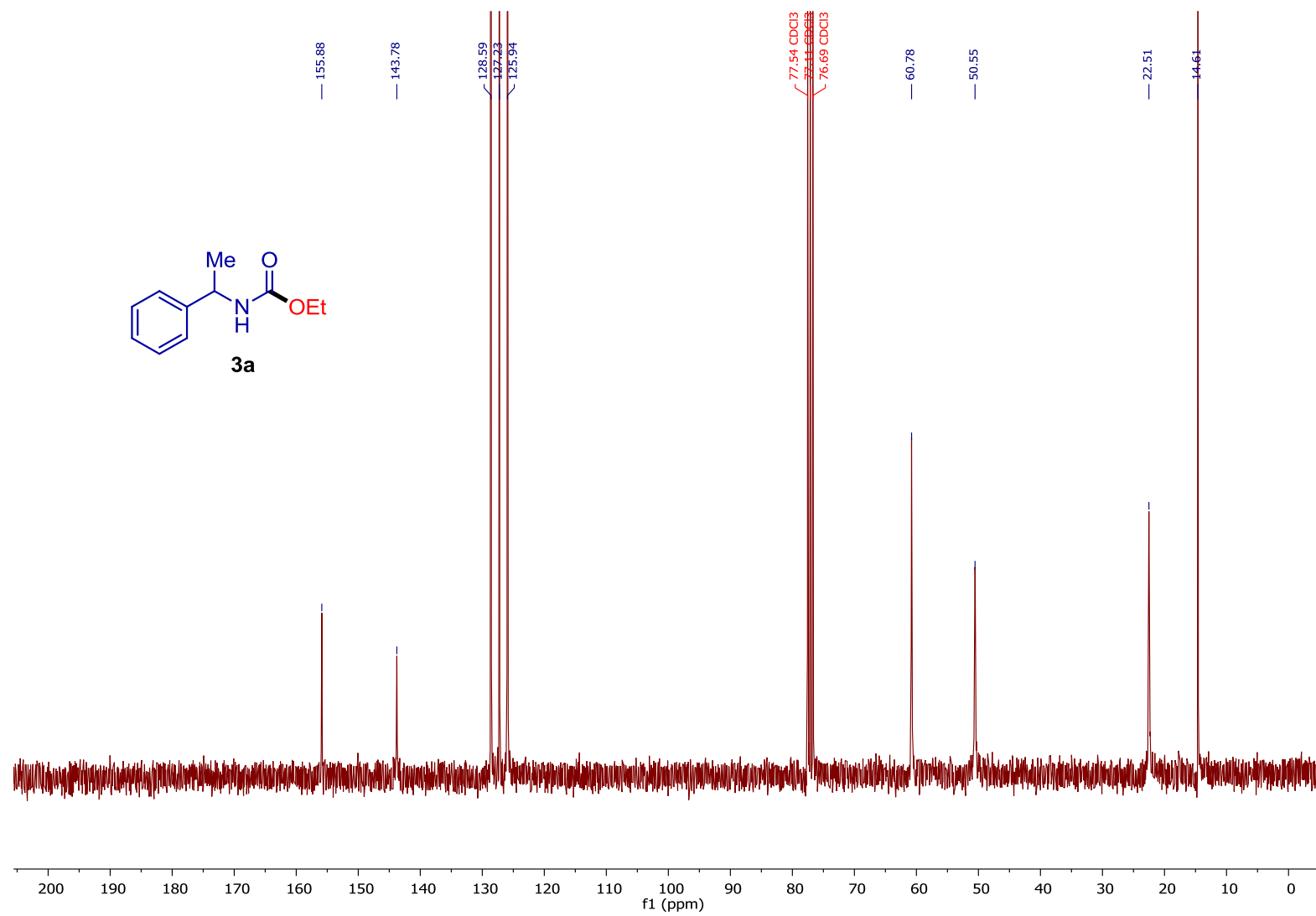


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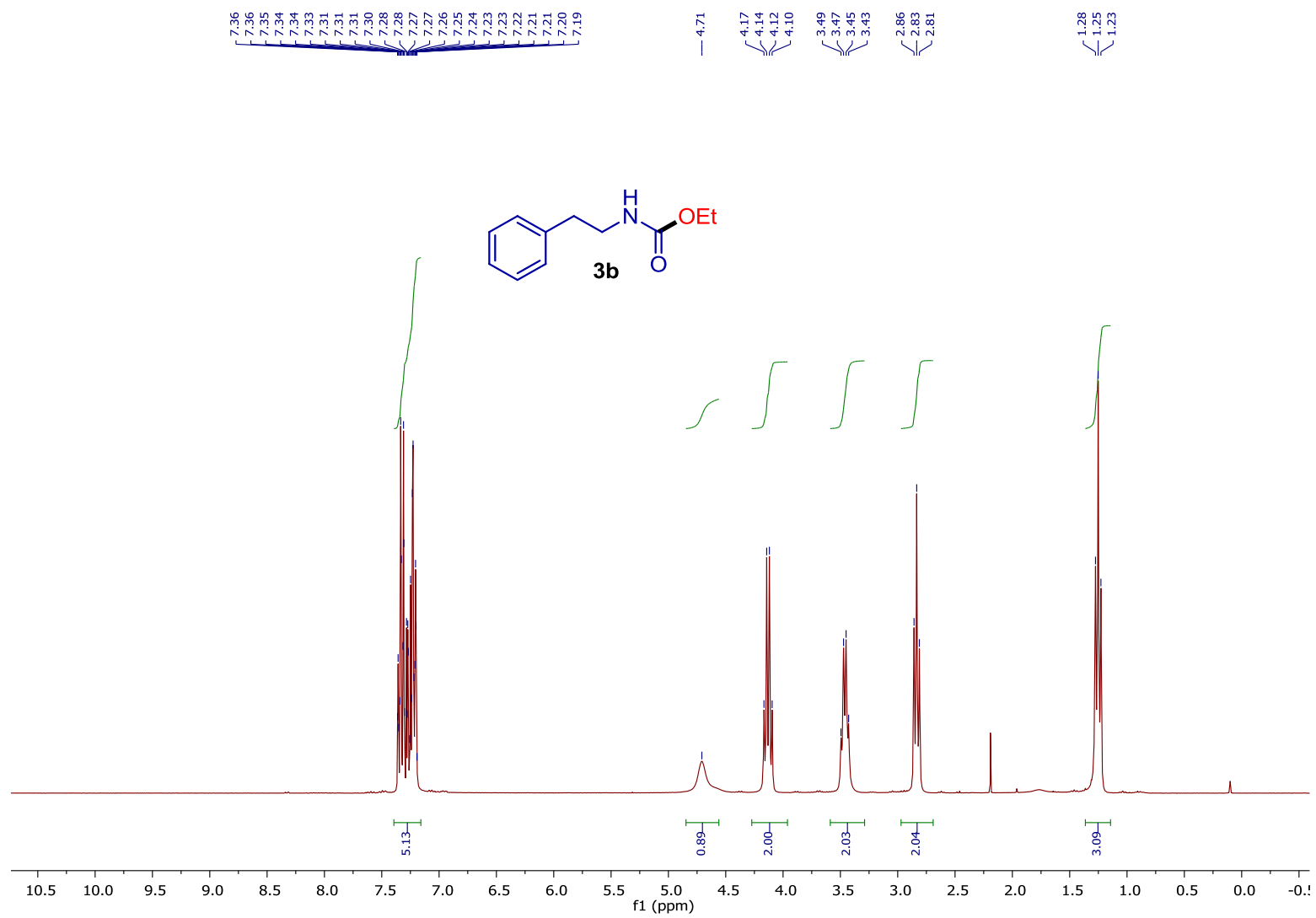
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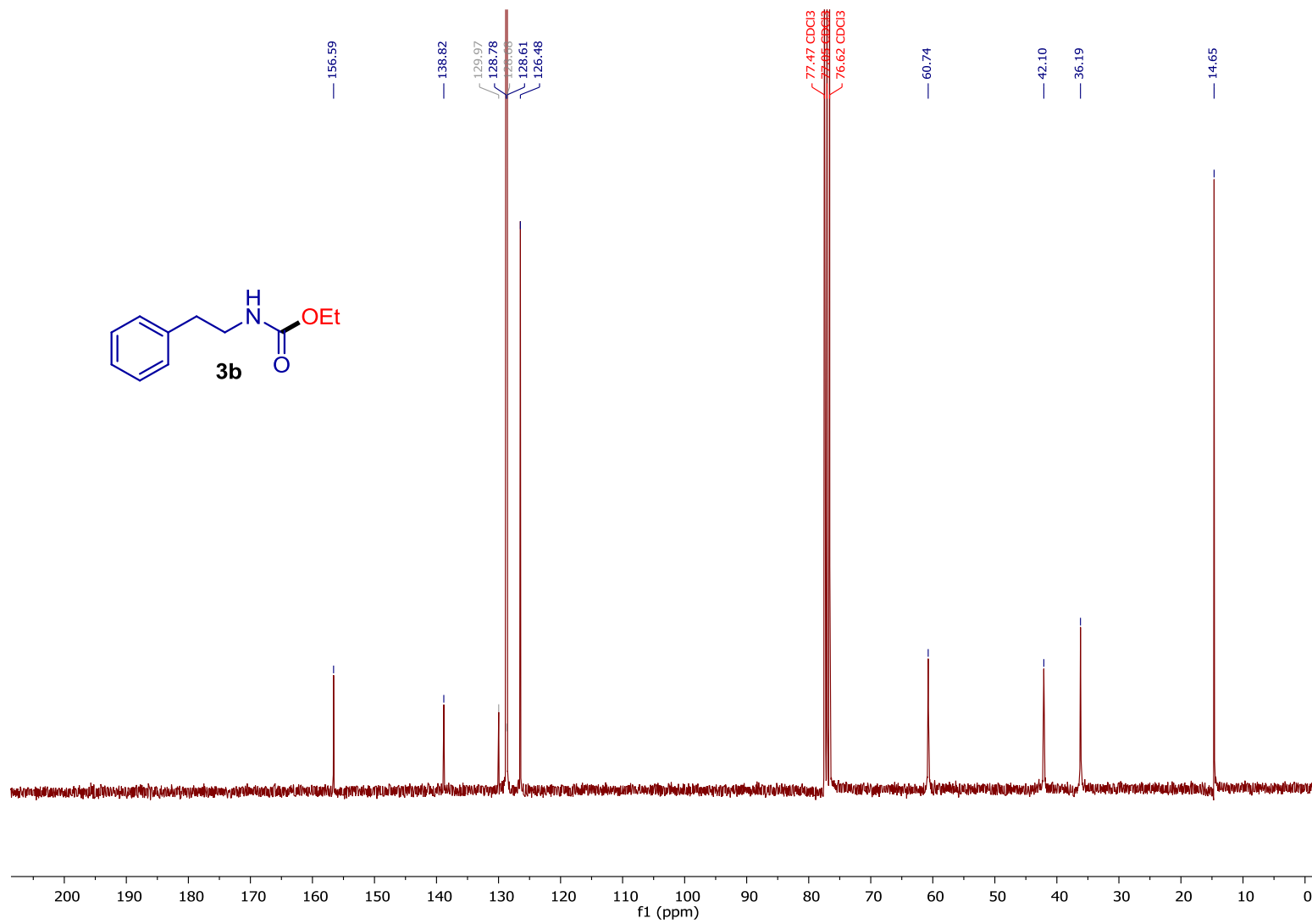
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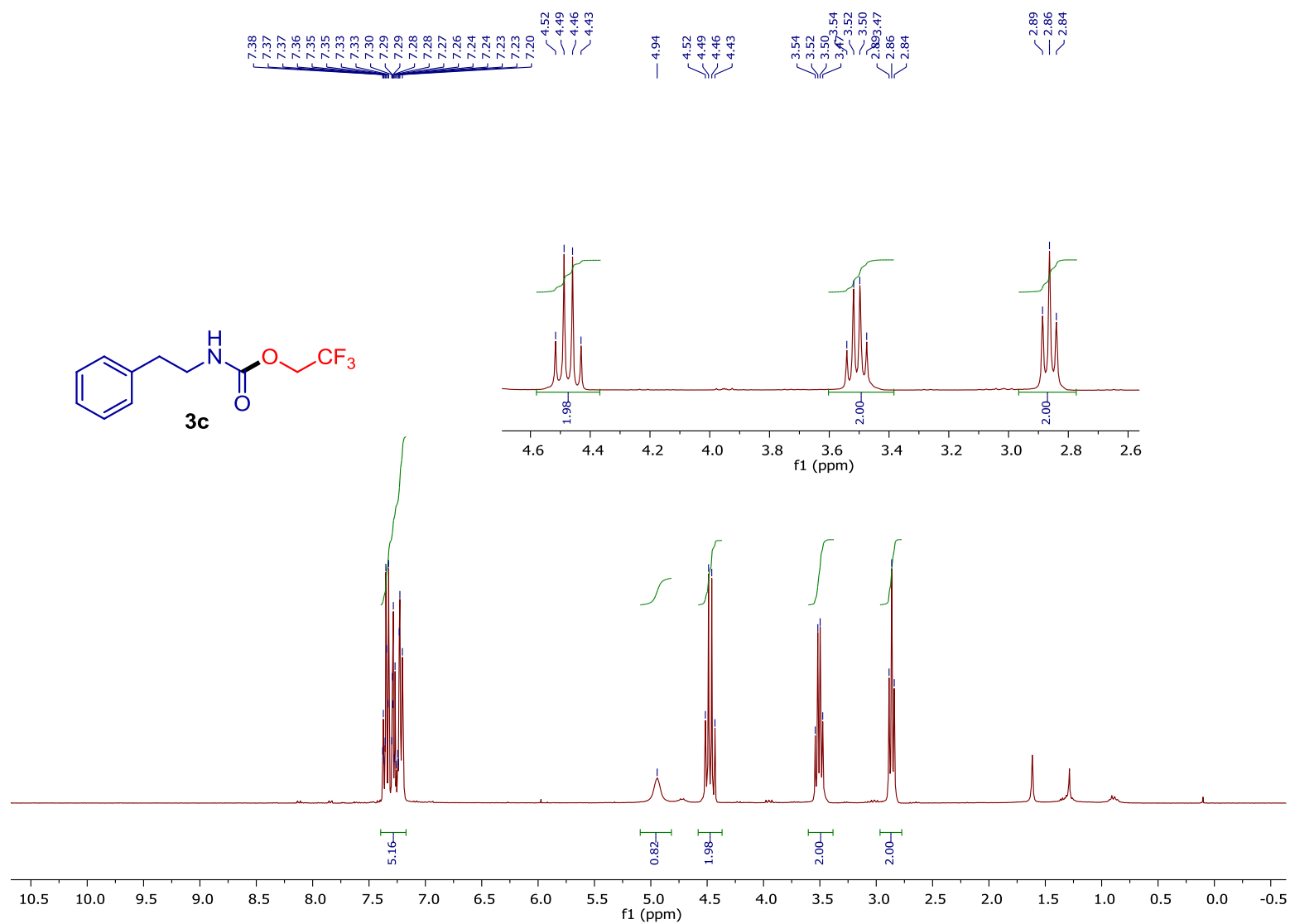
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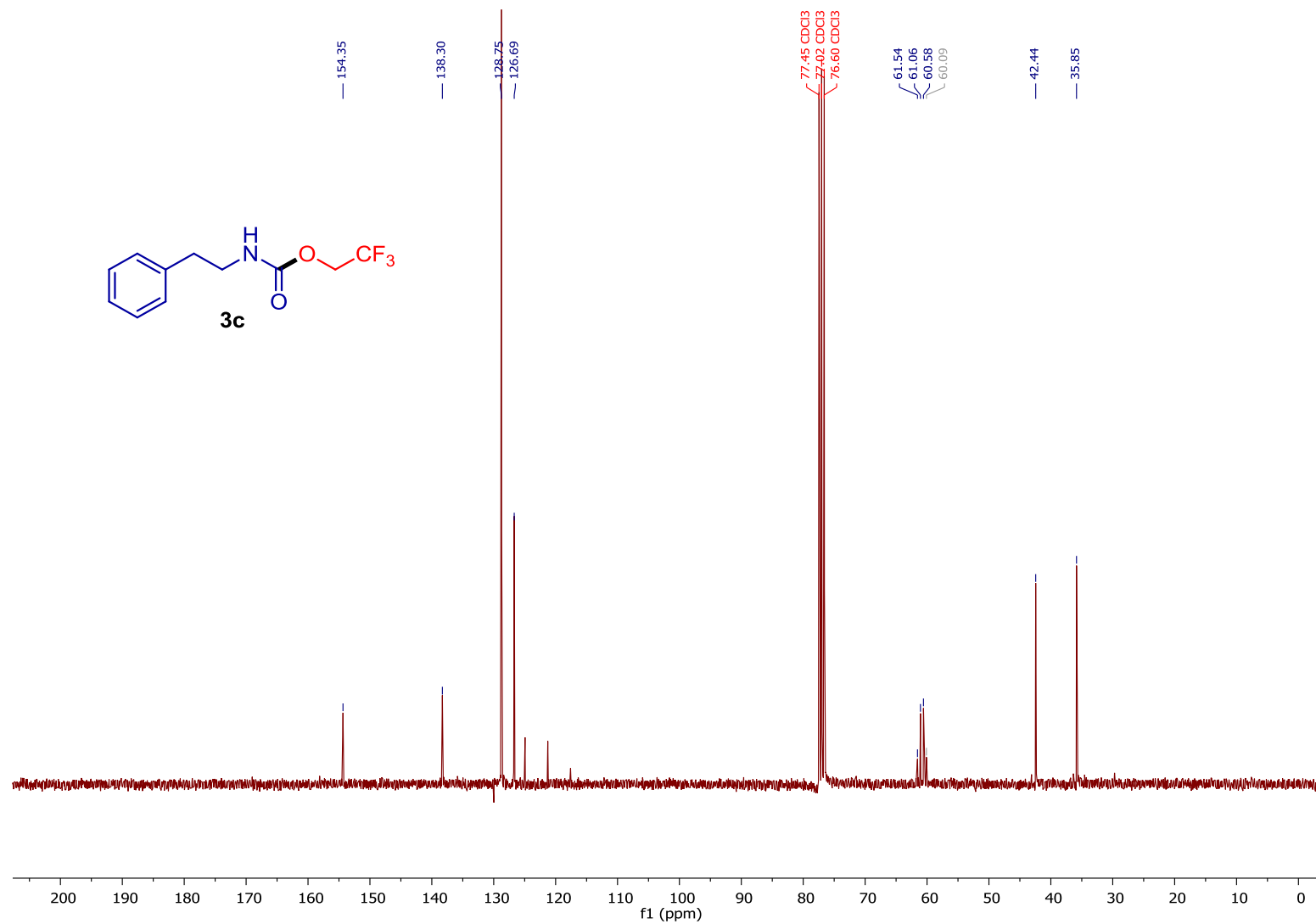
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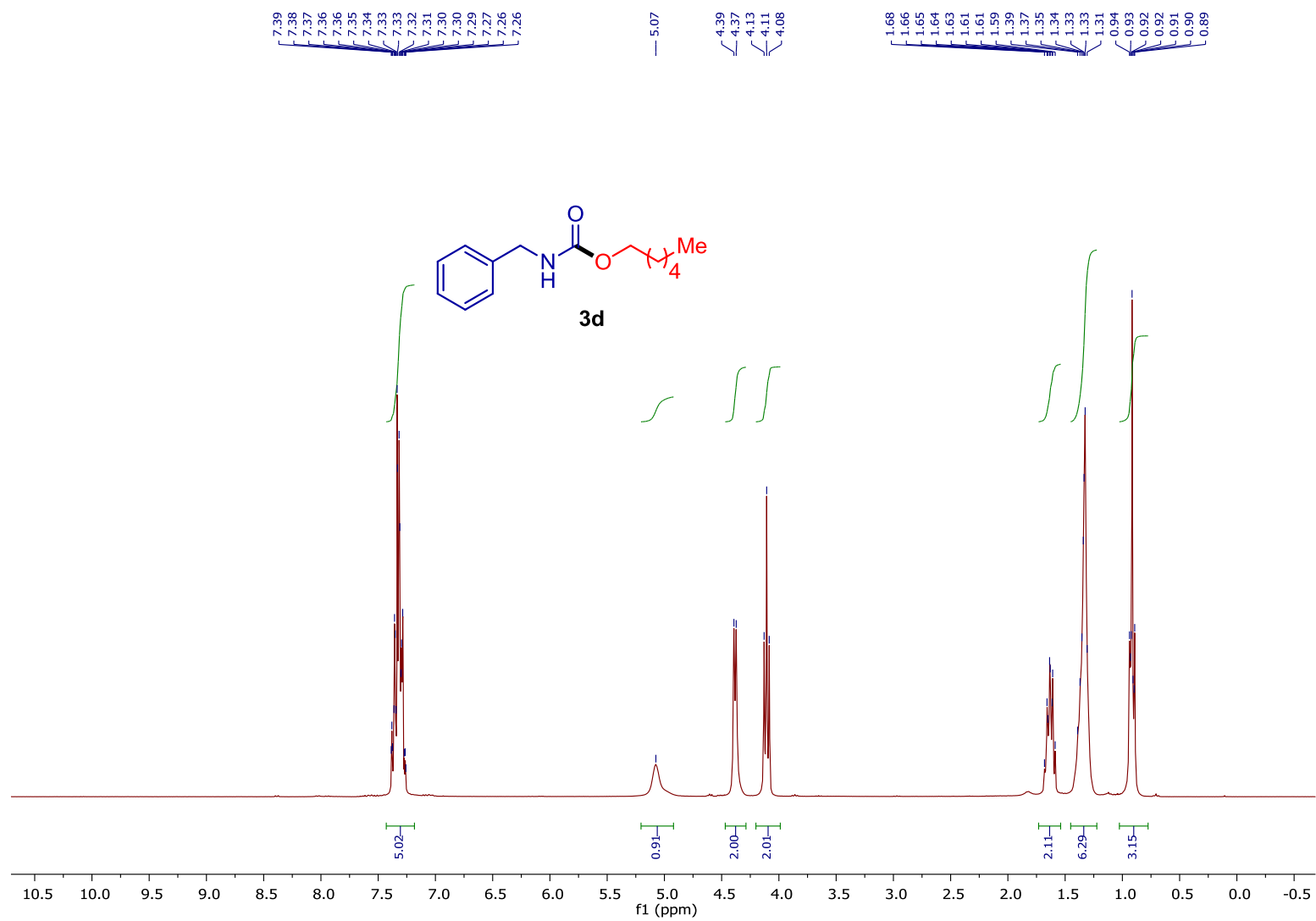
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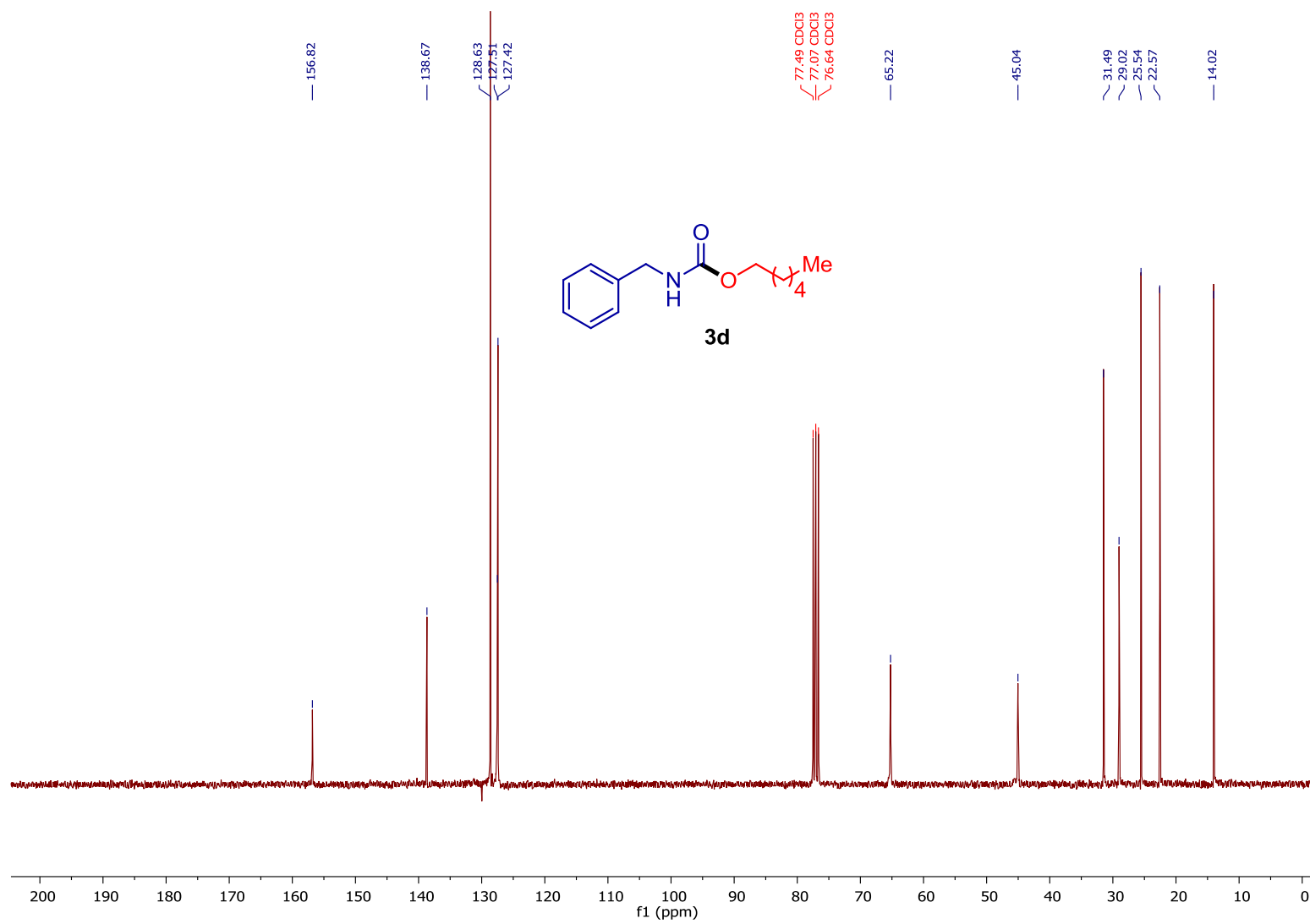
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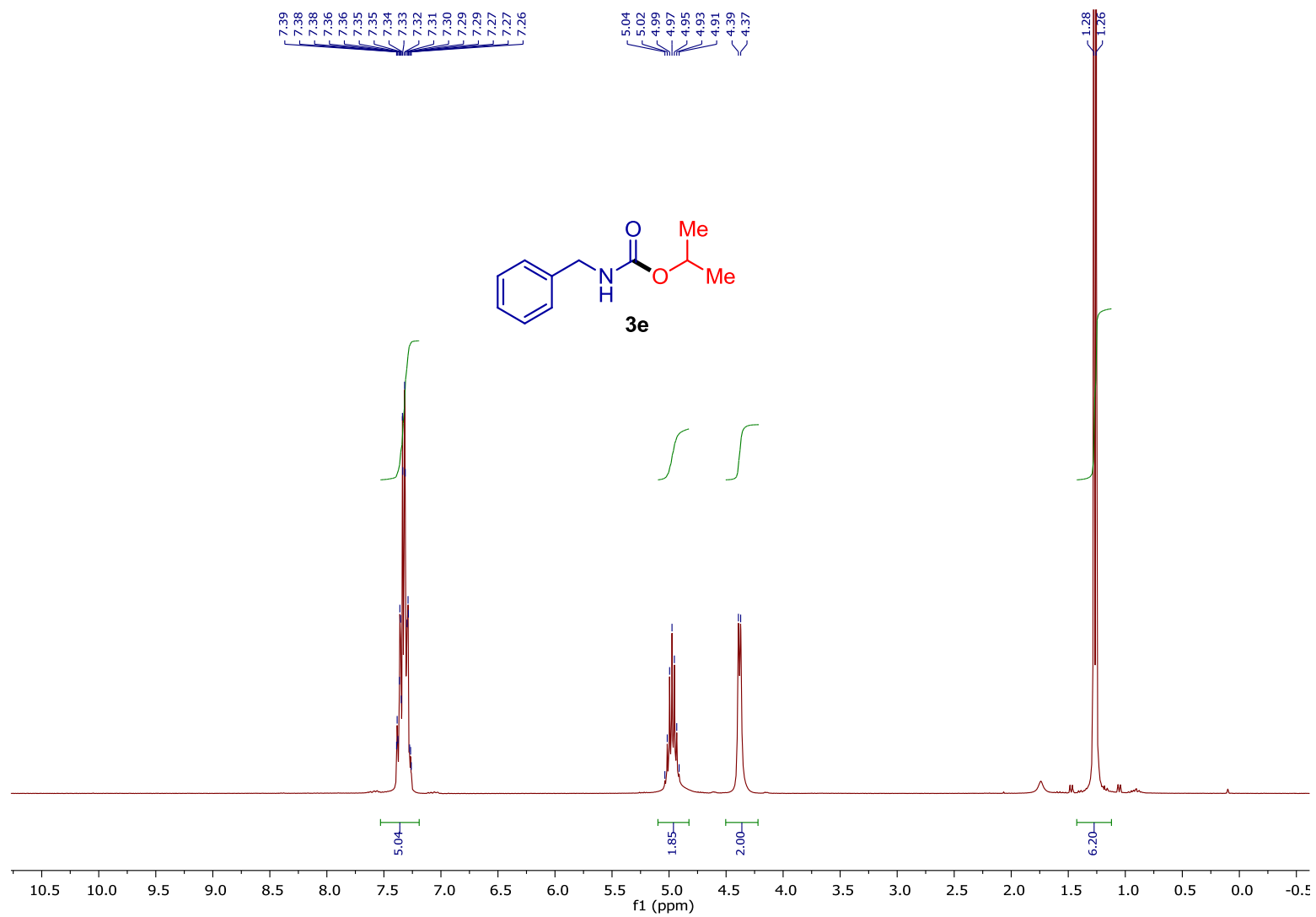
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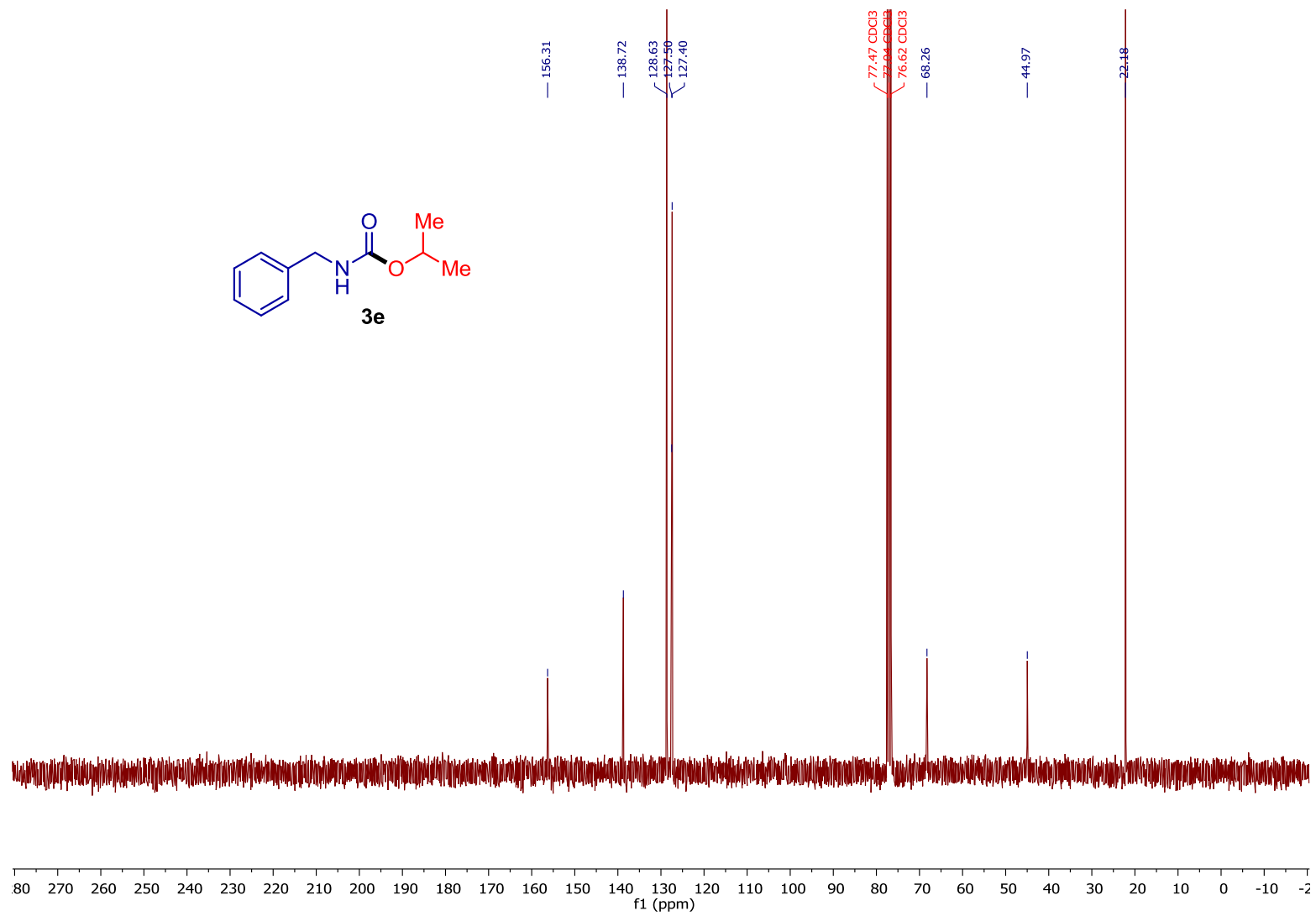
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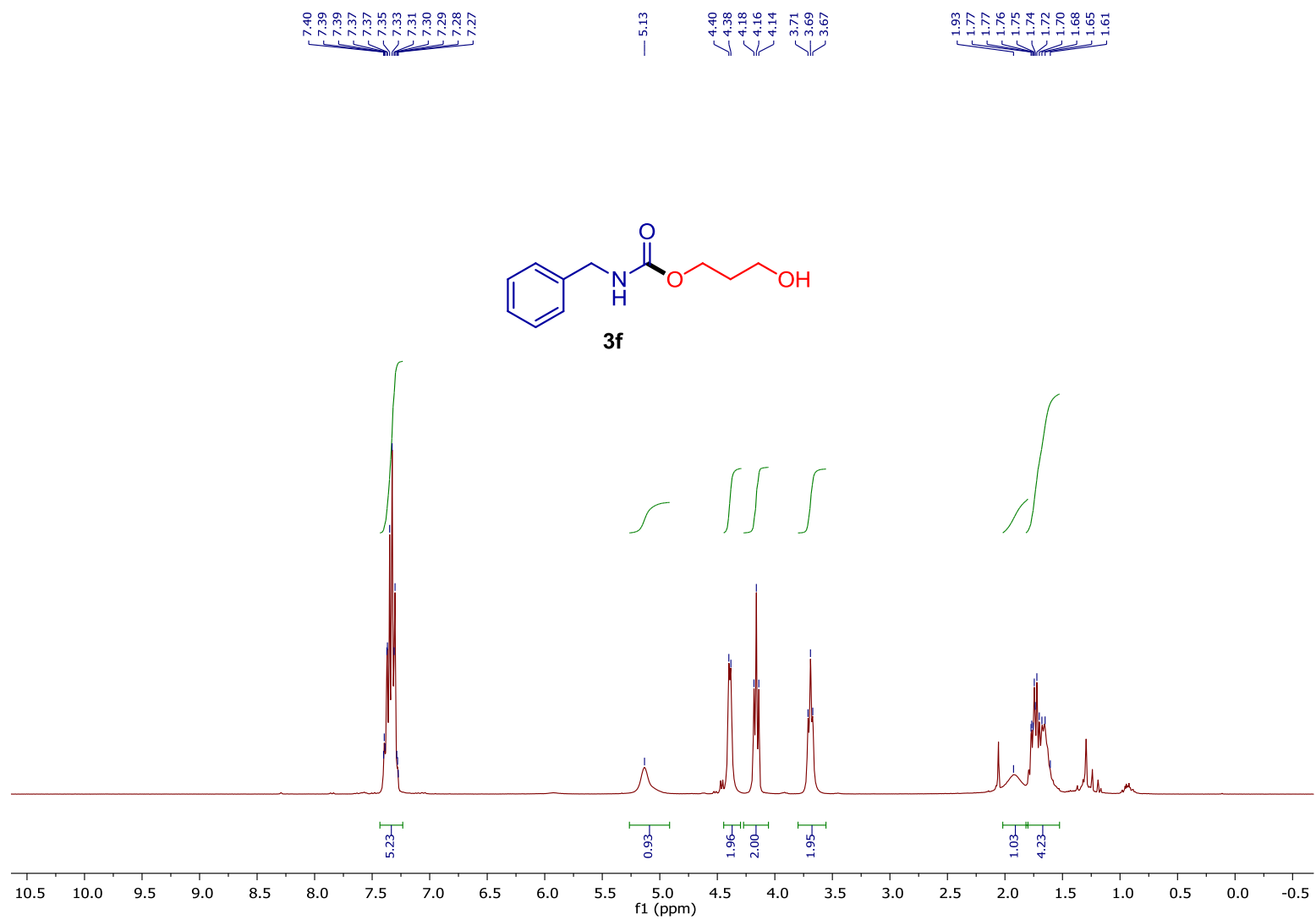
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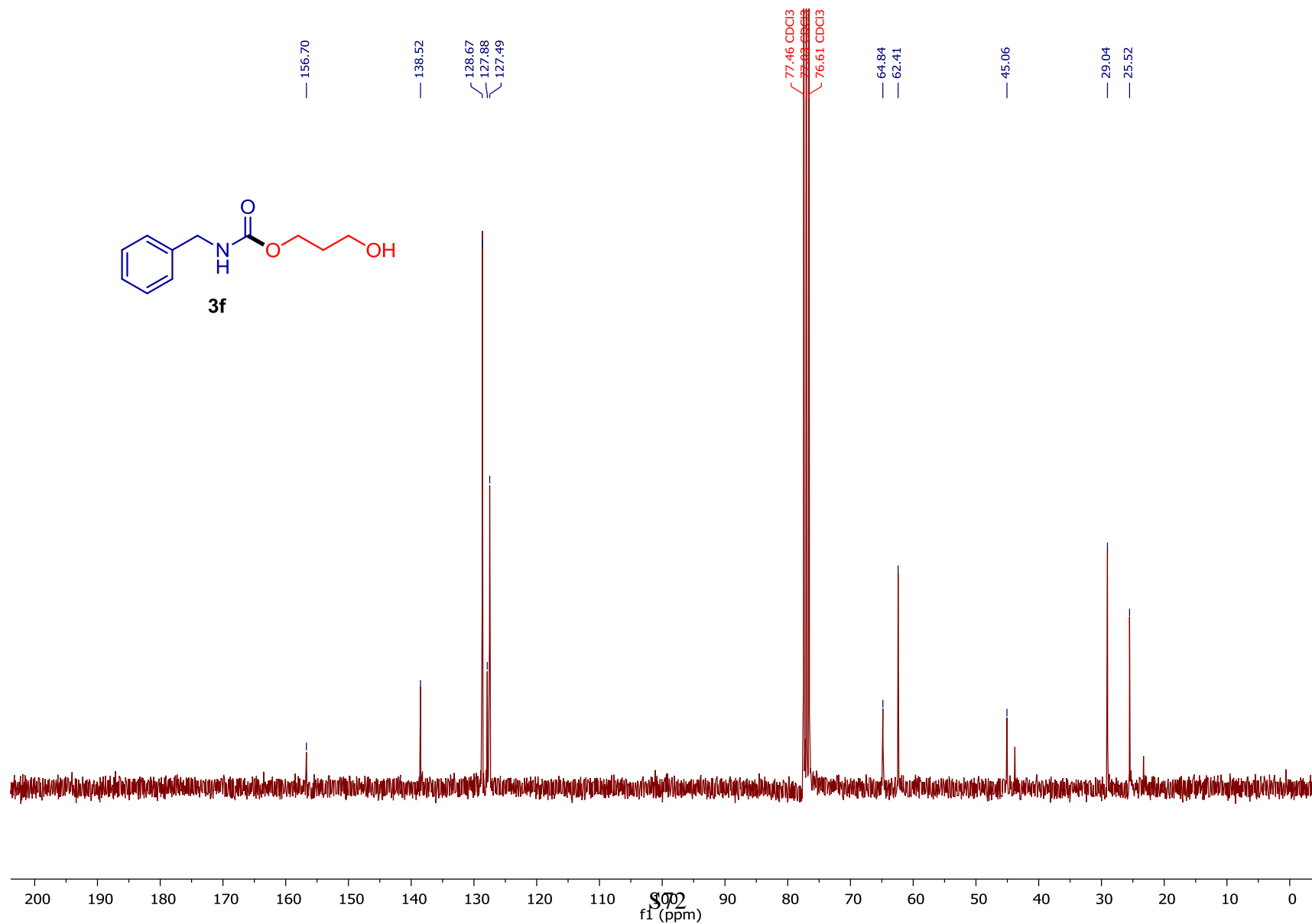
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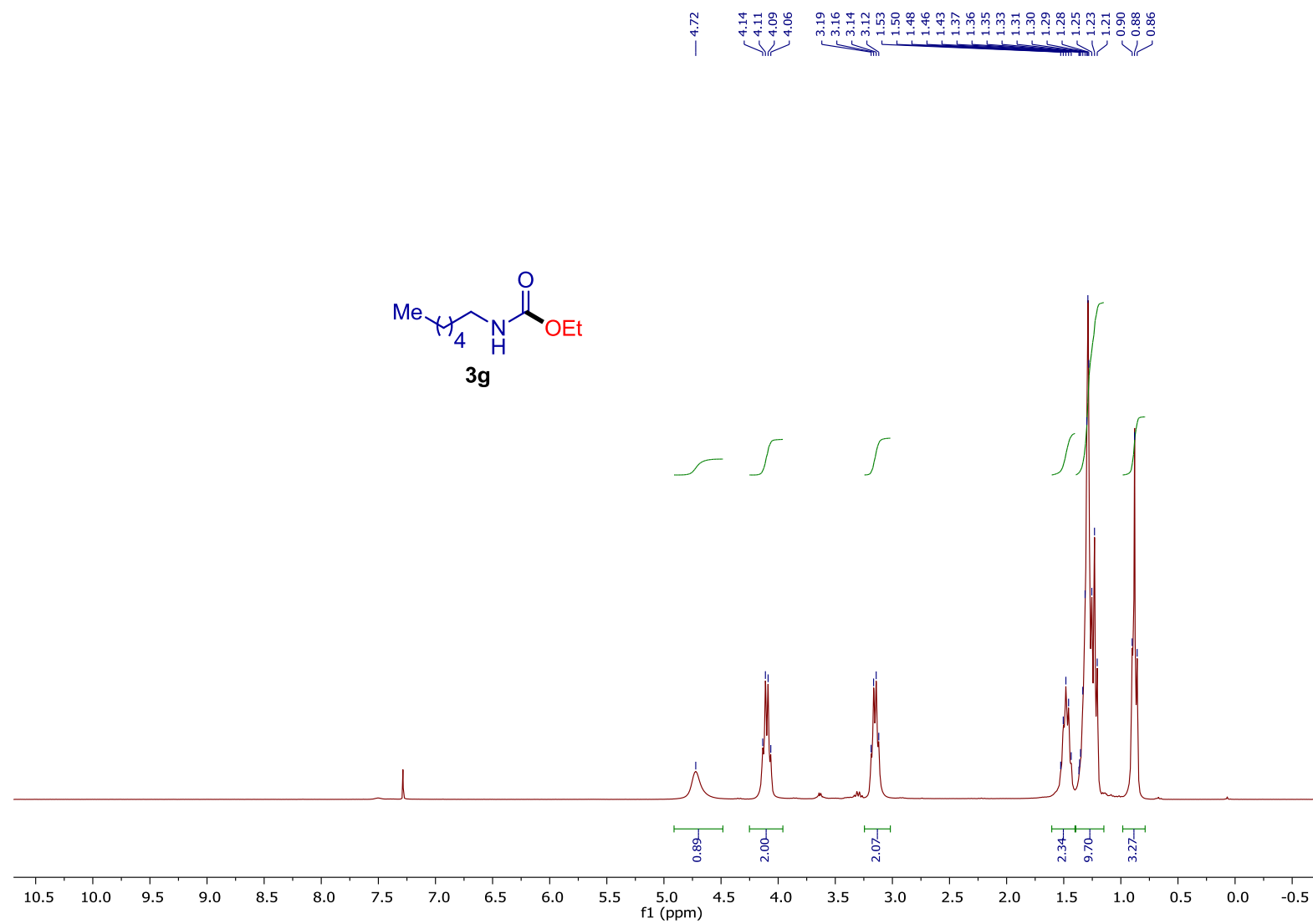
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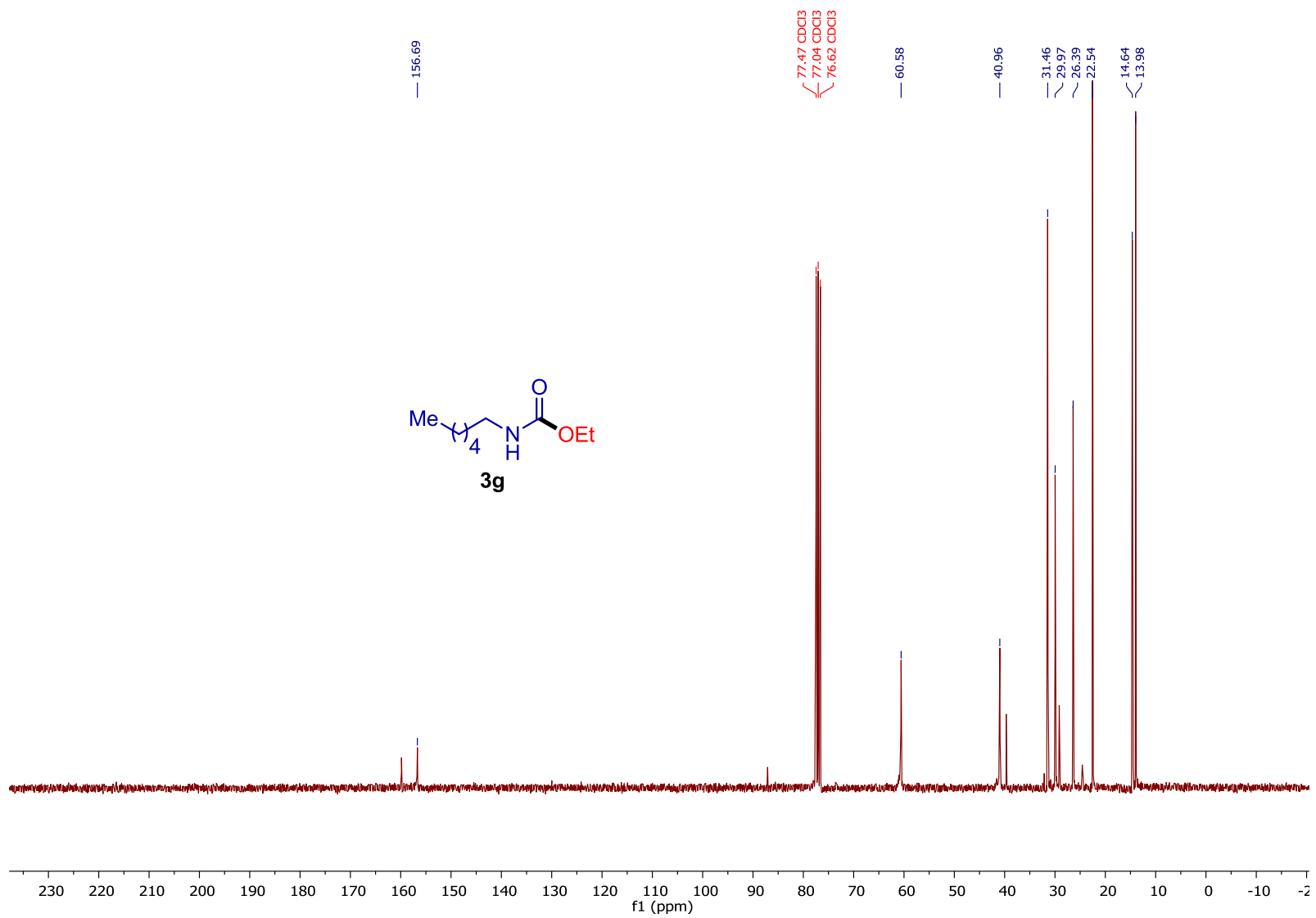
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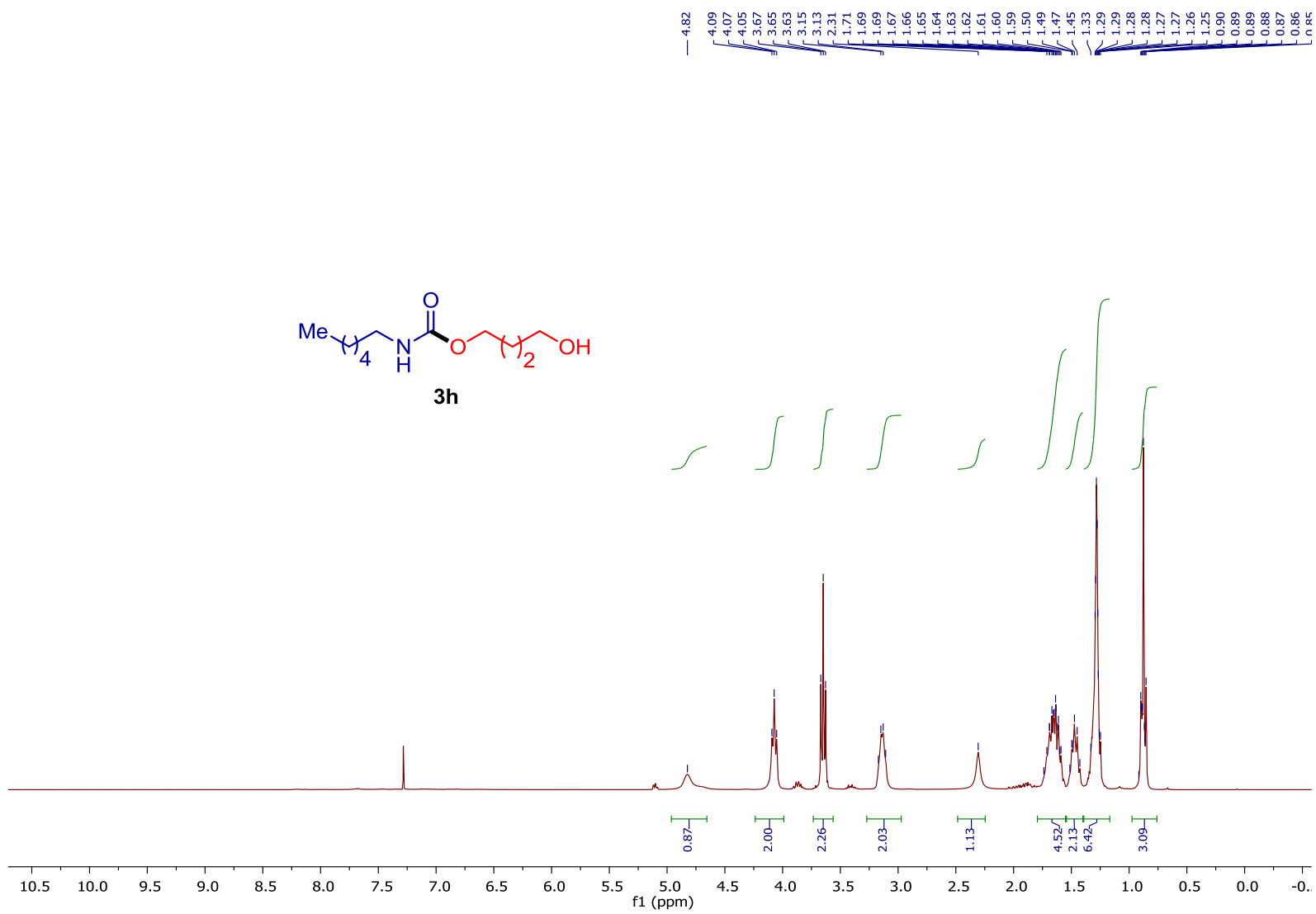
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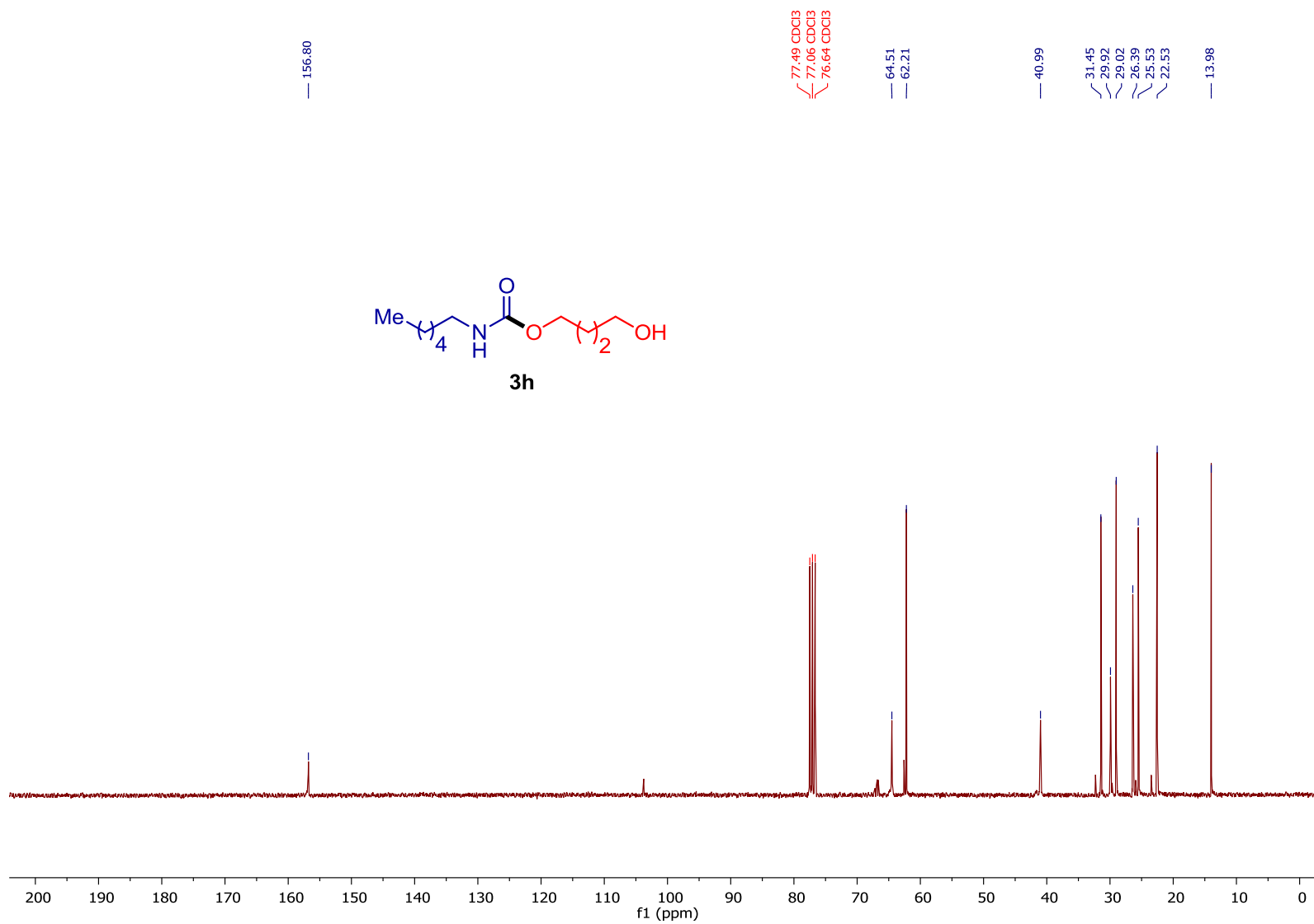
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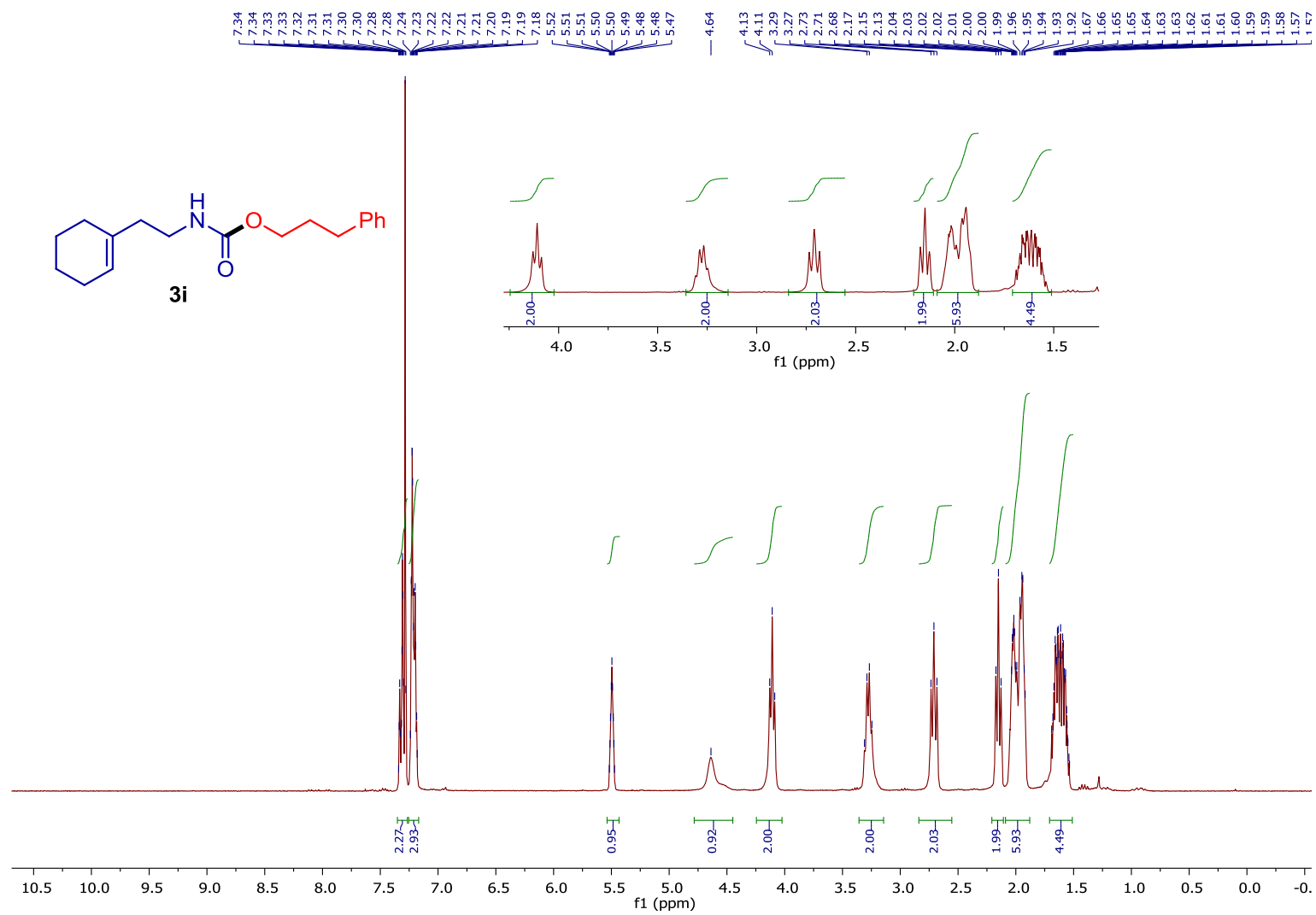
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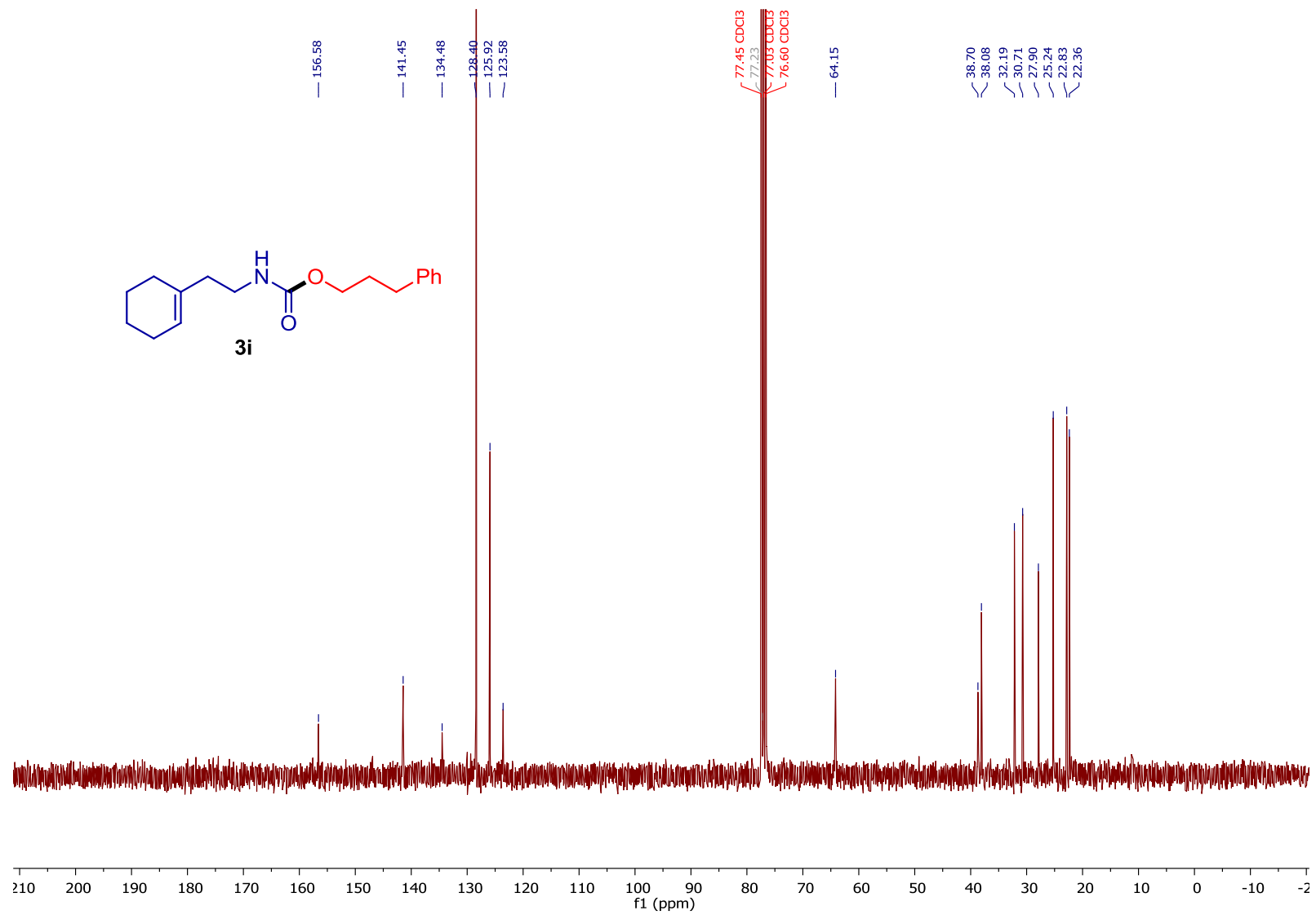
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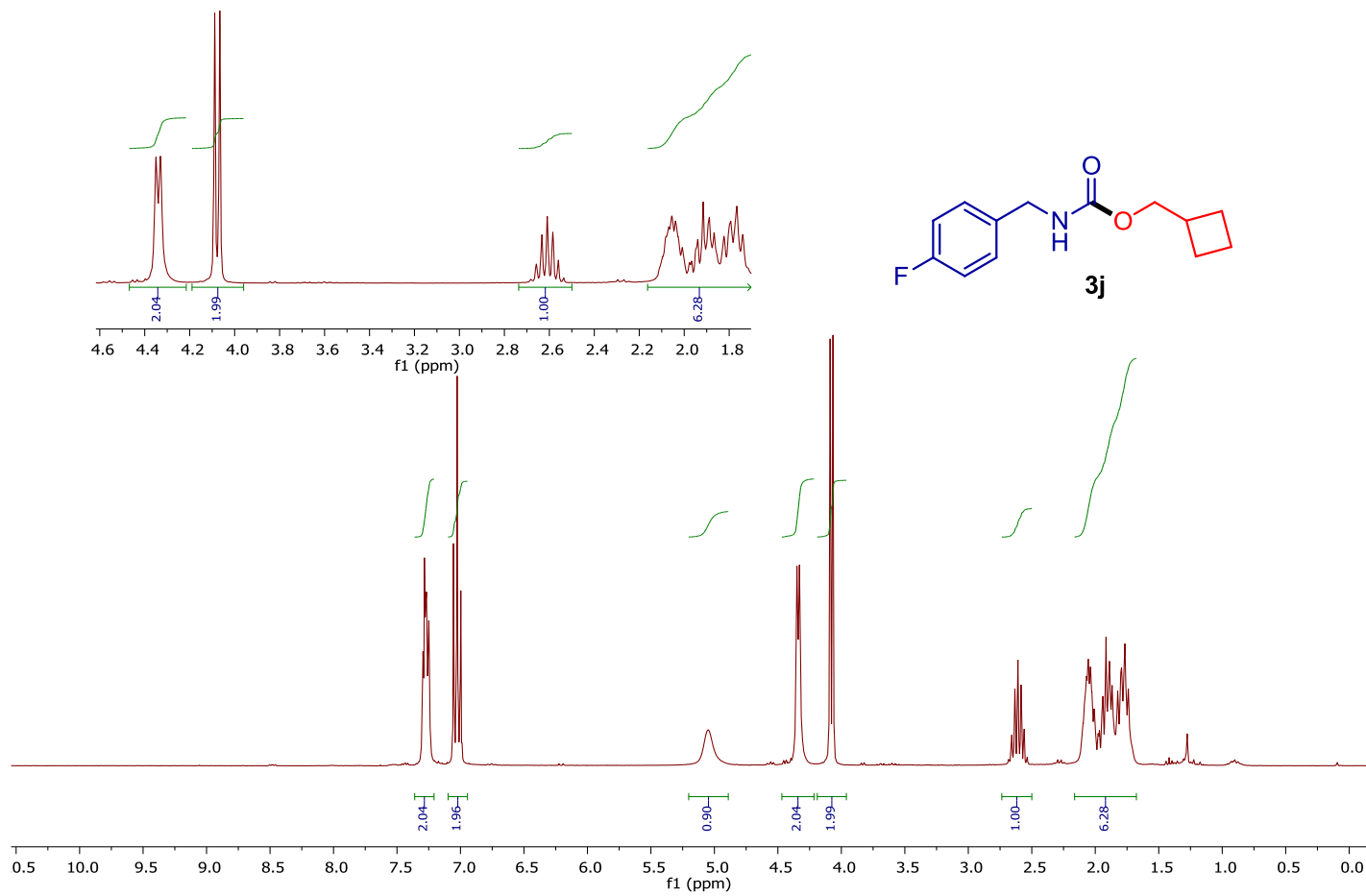
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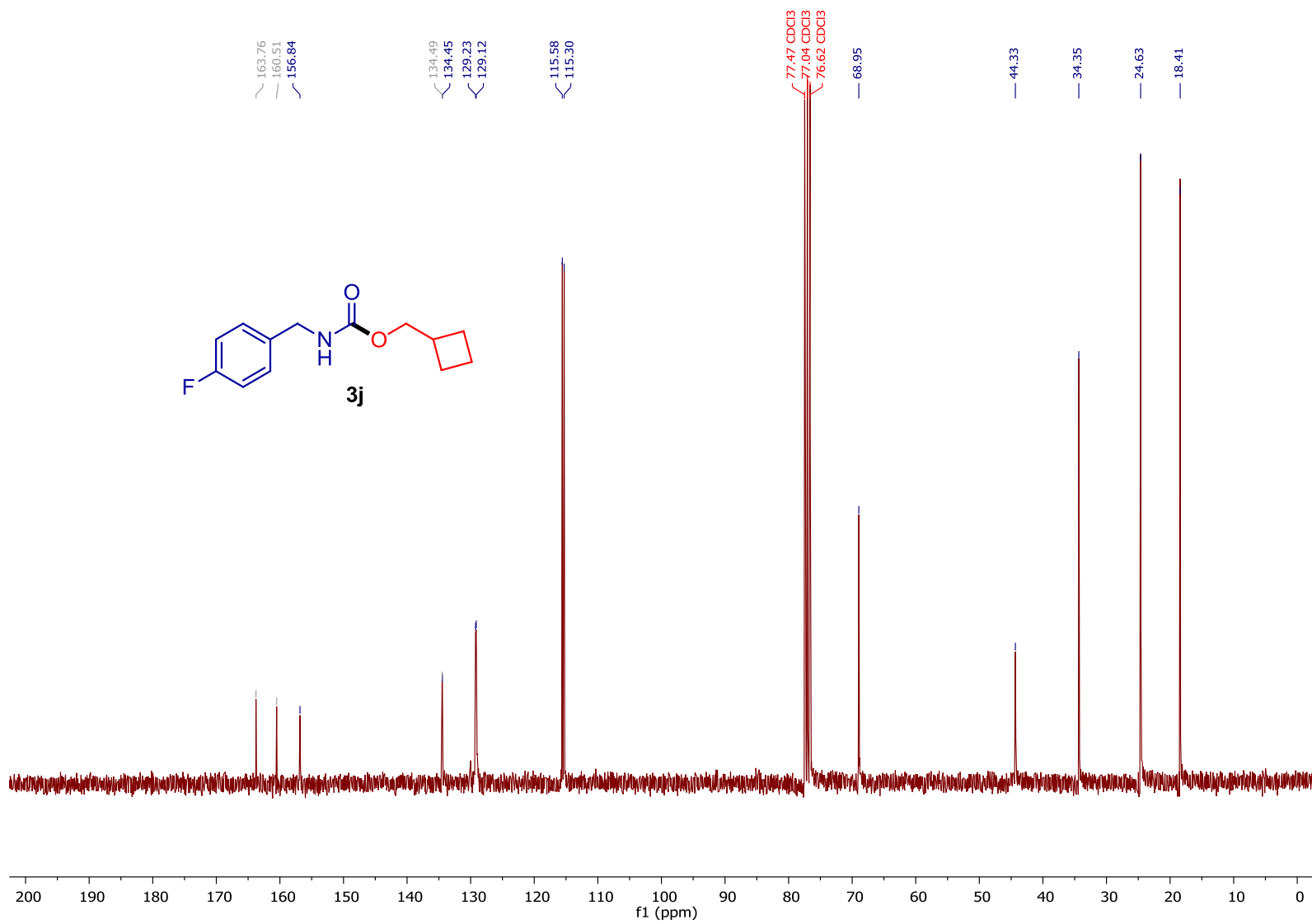
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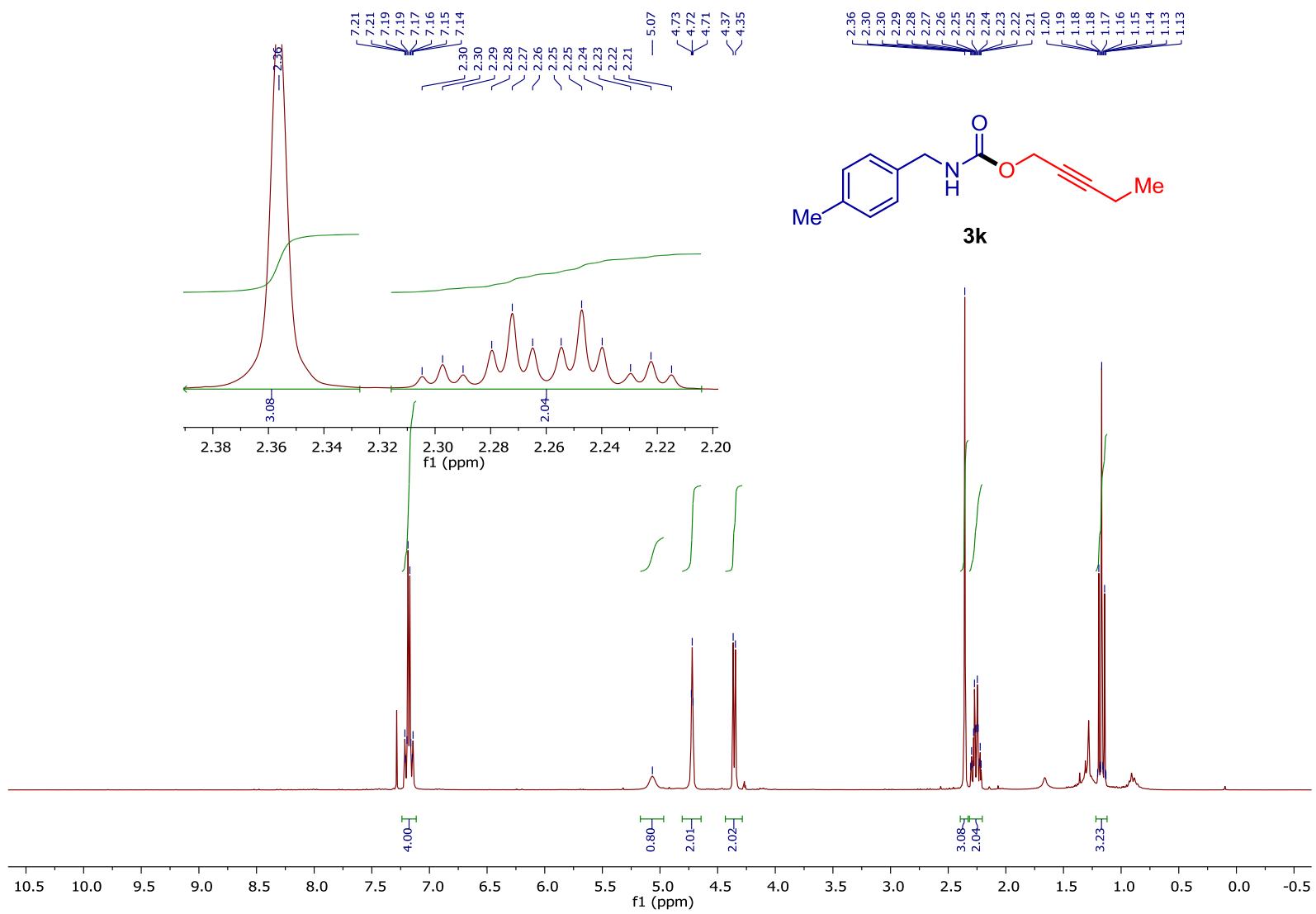
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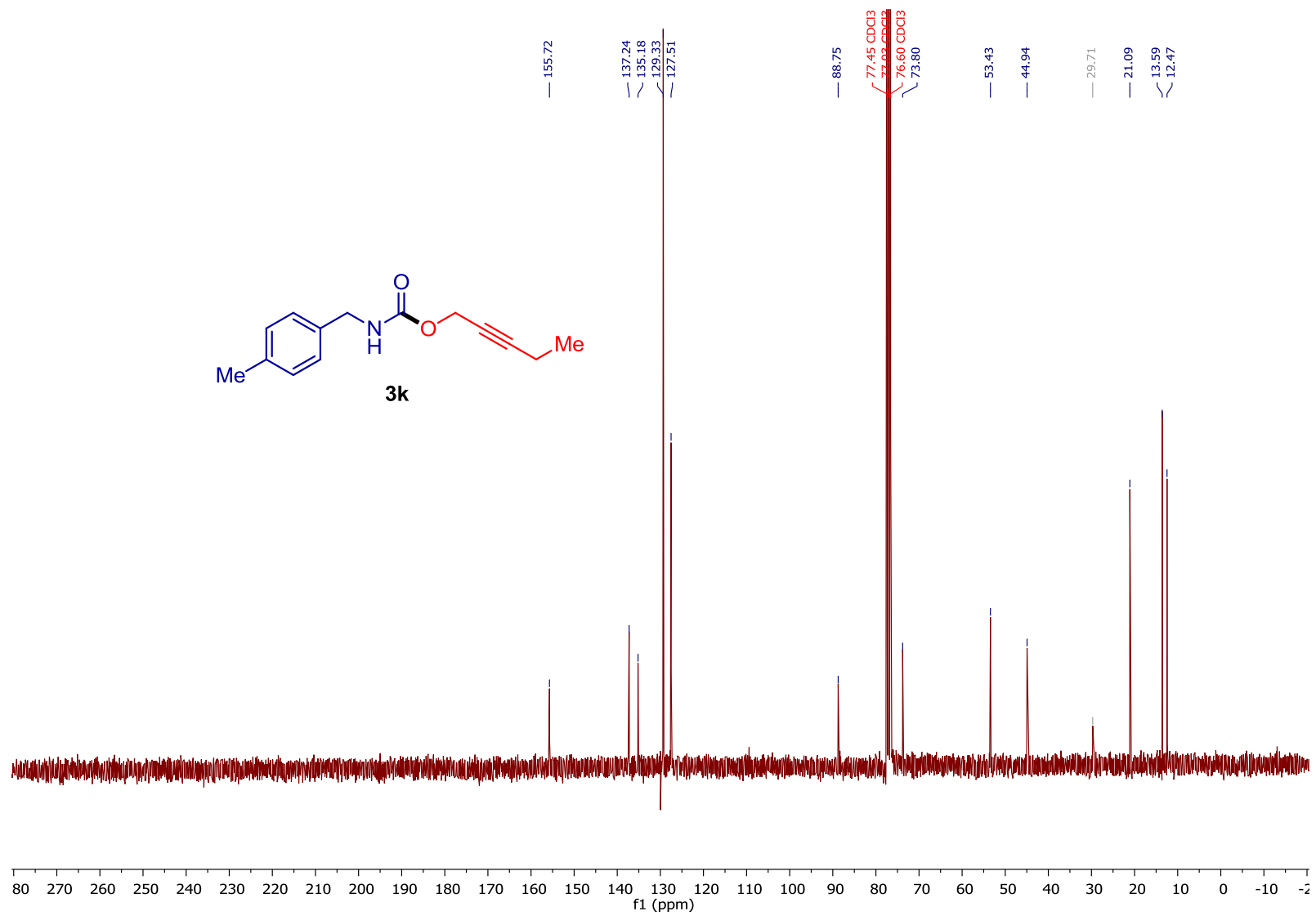
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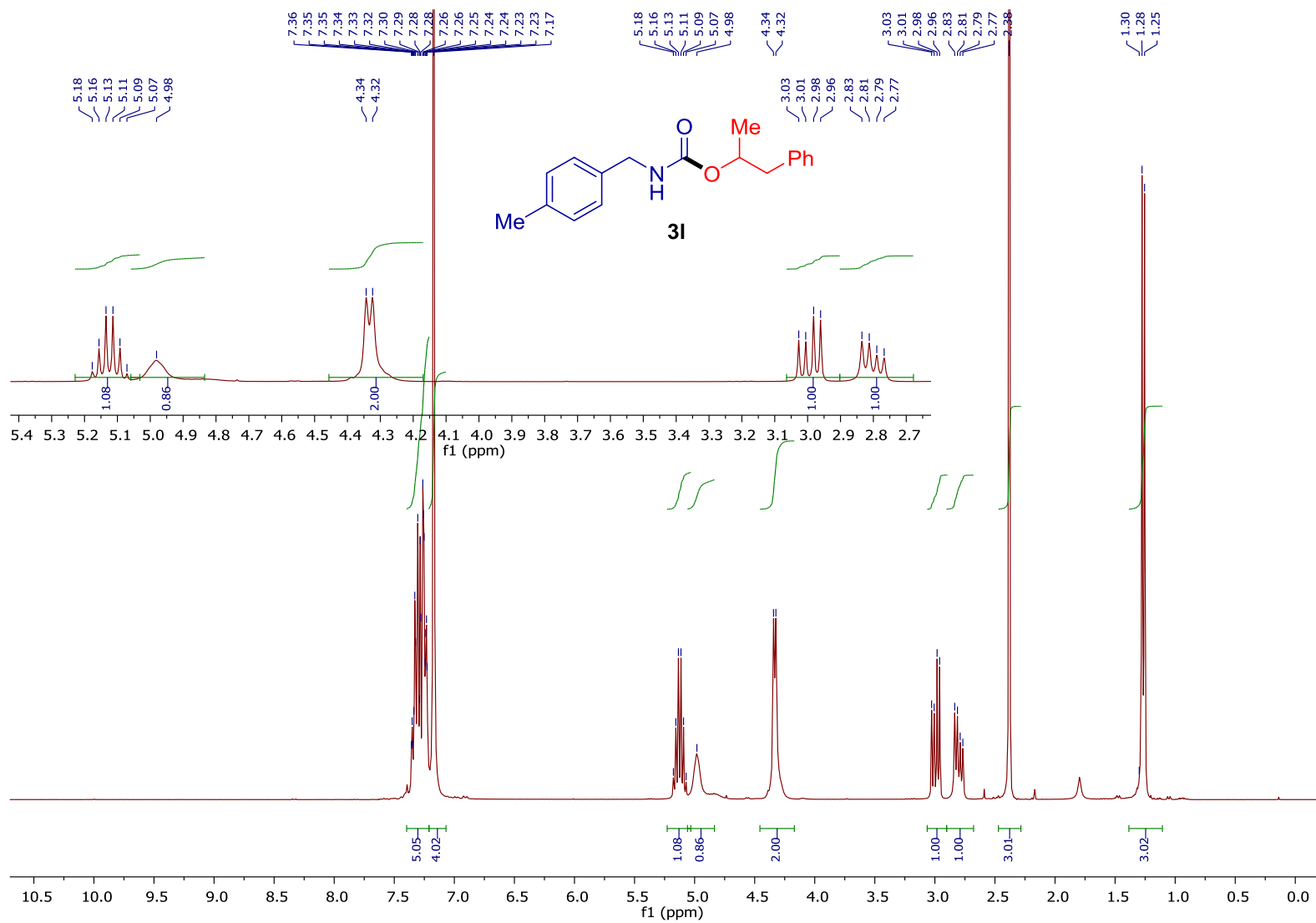
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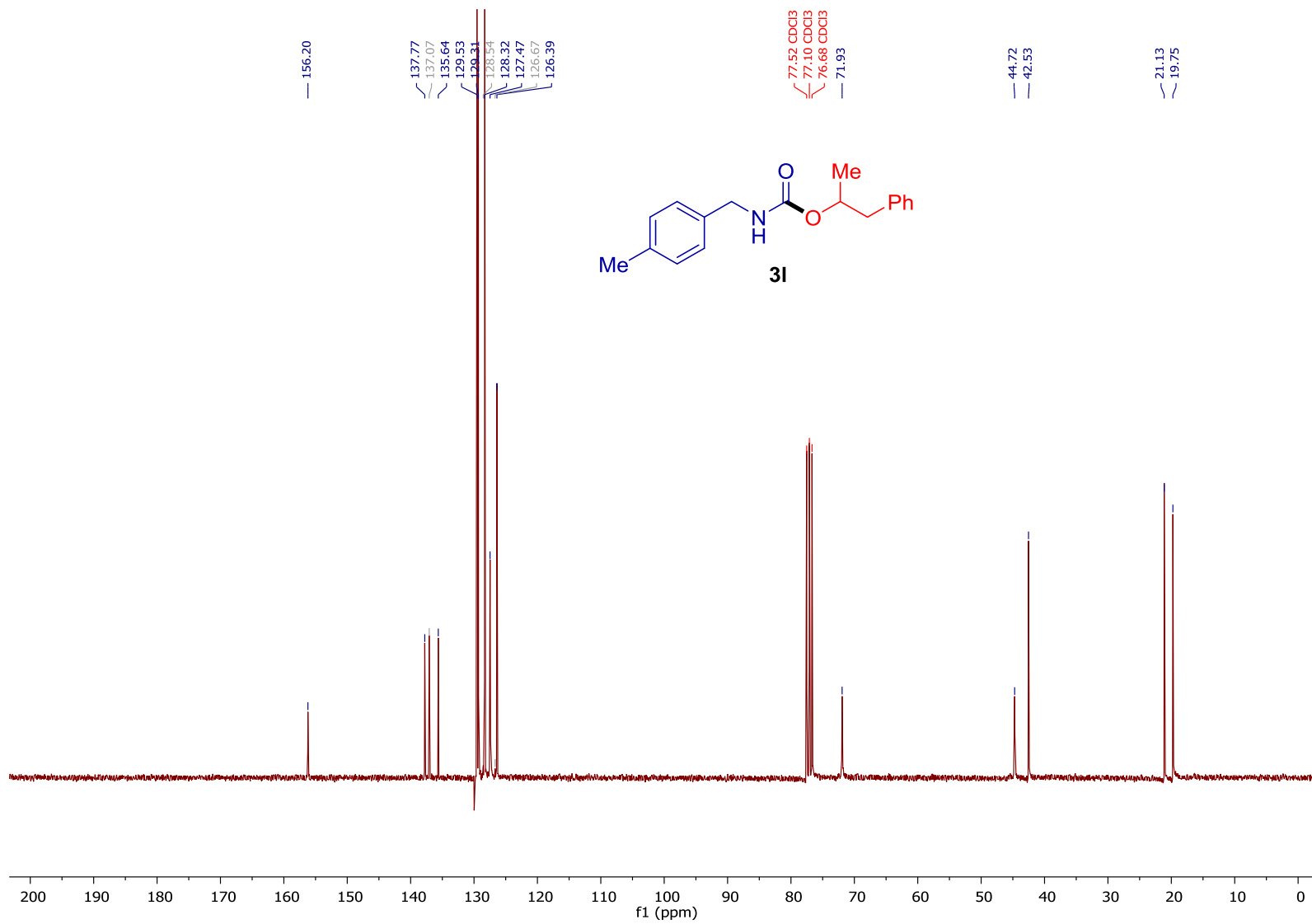
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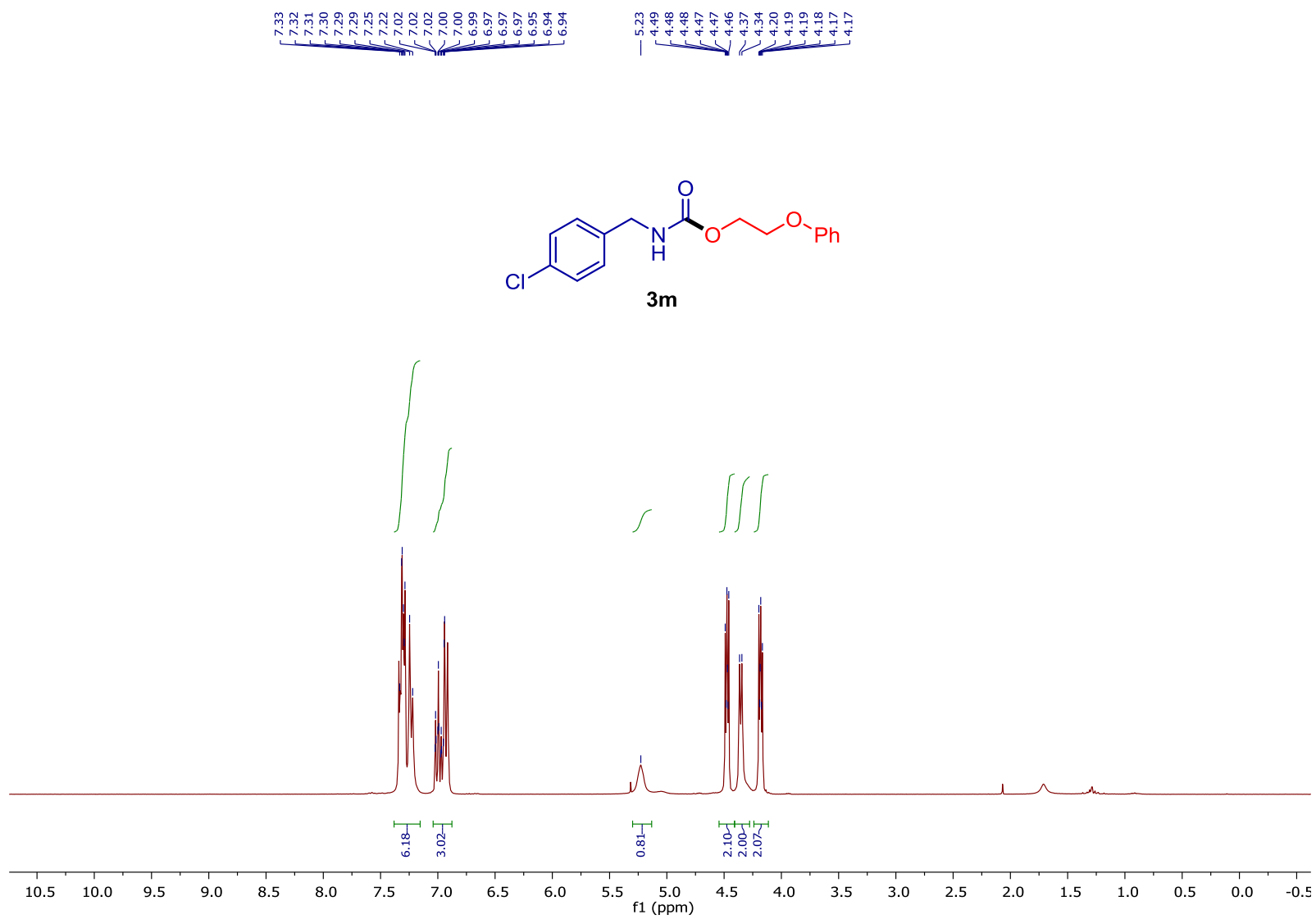
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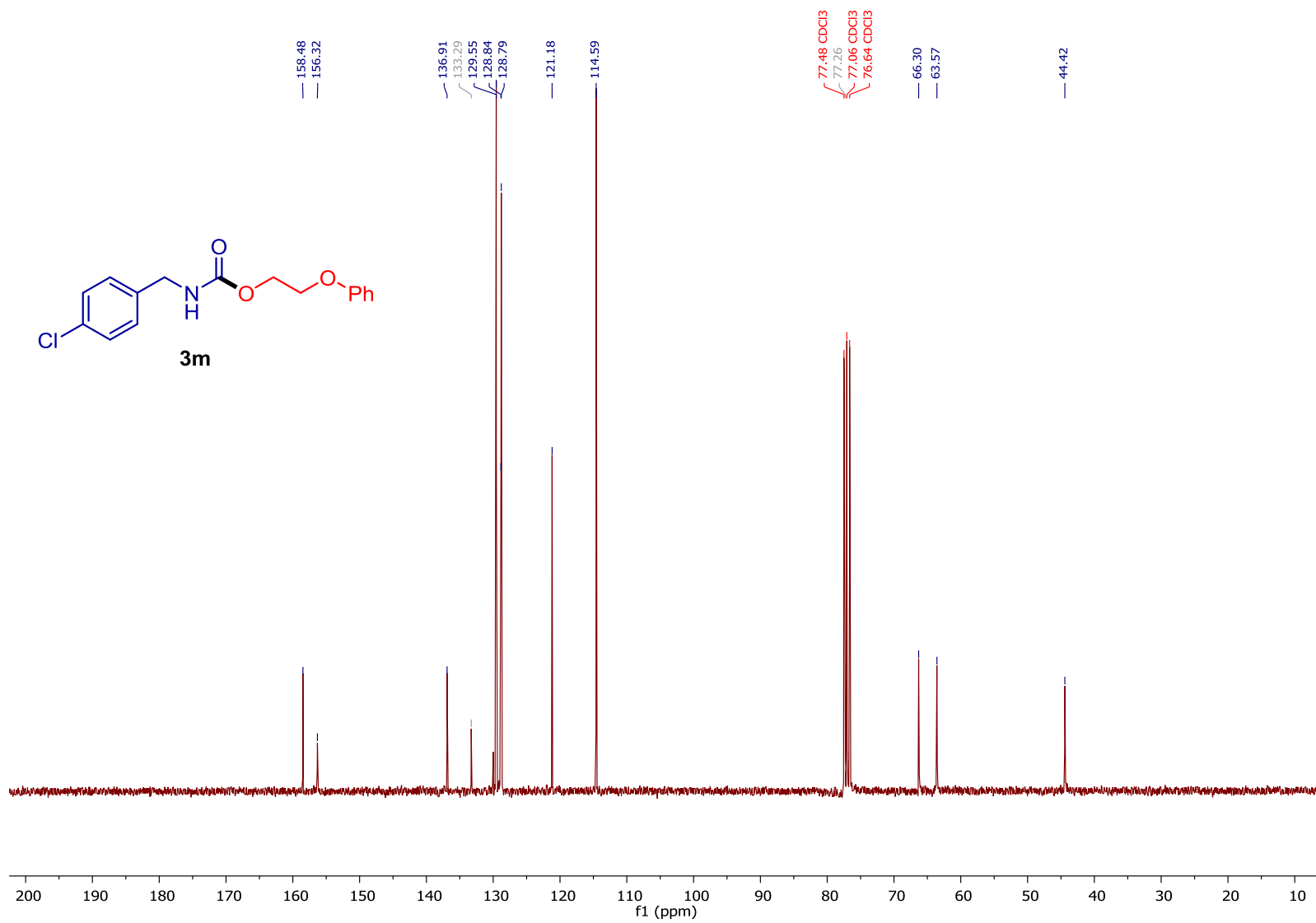


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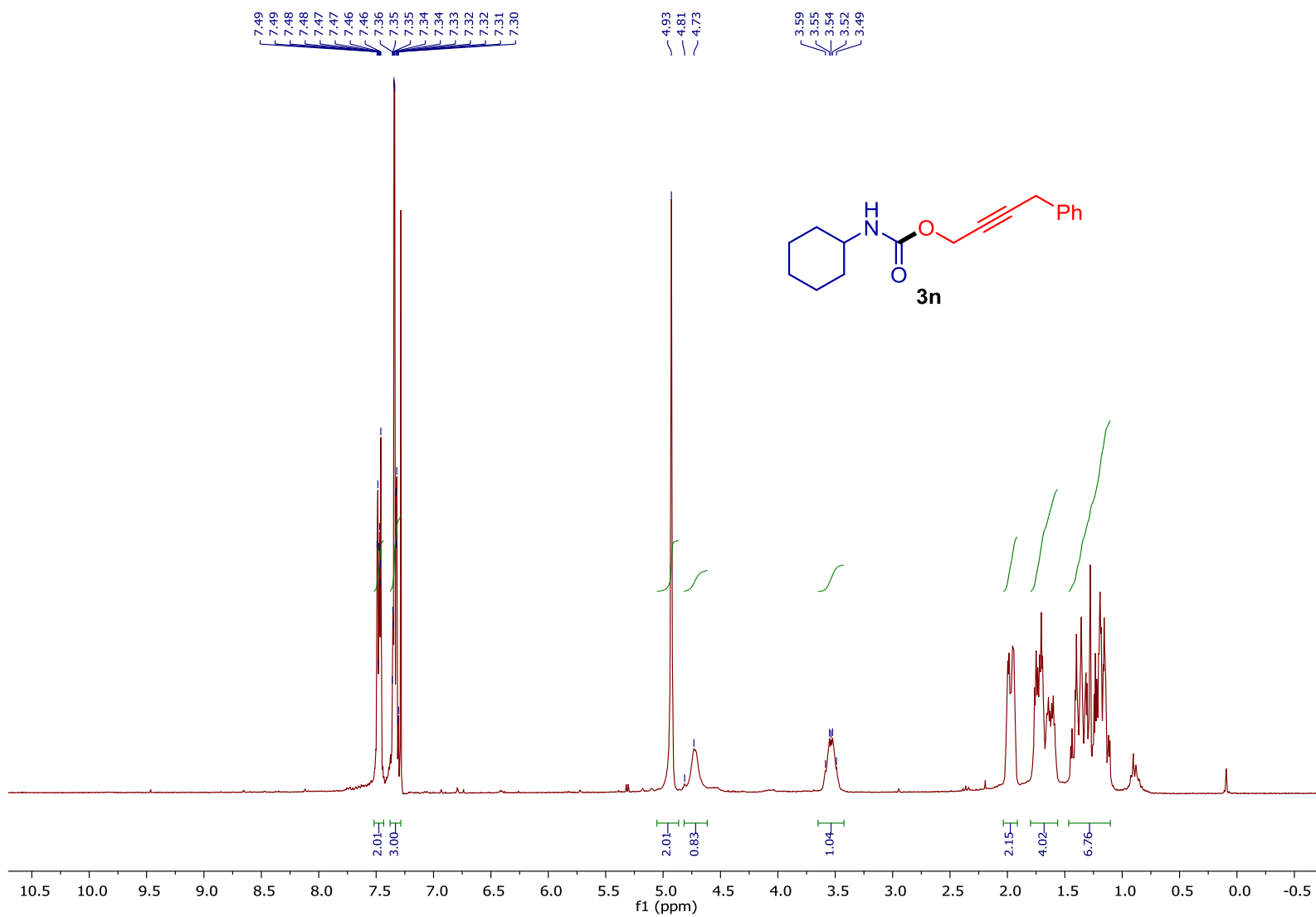


S85

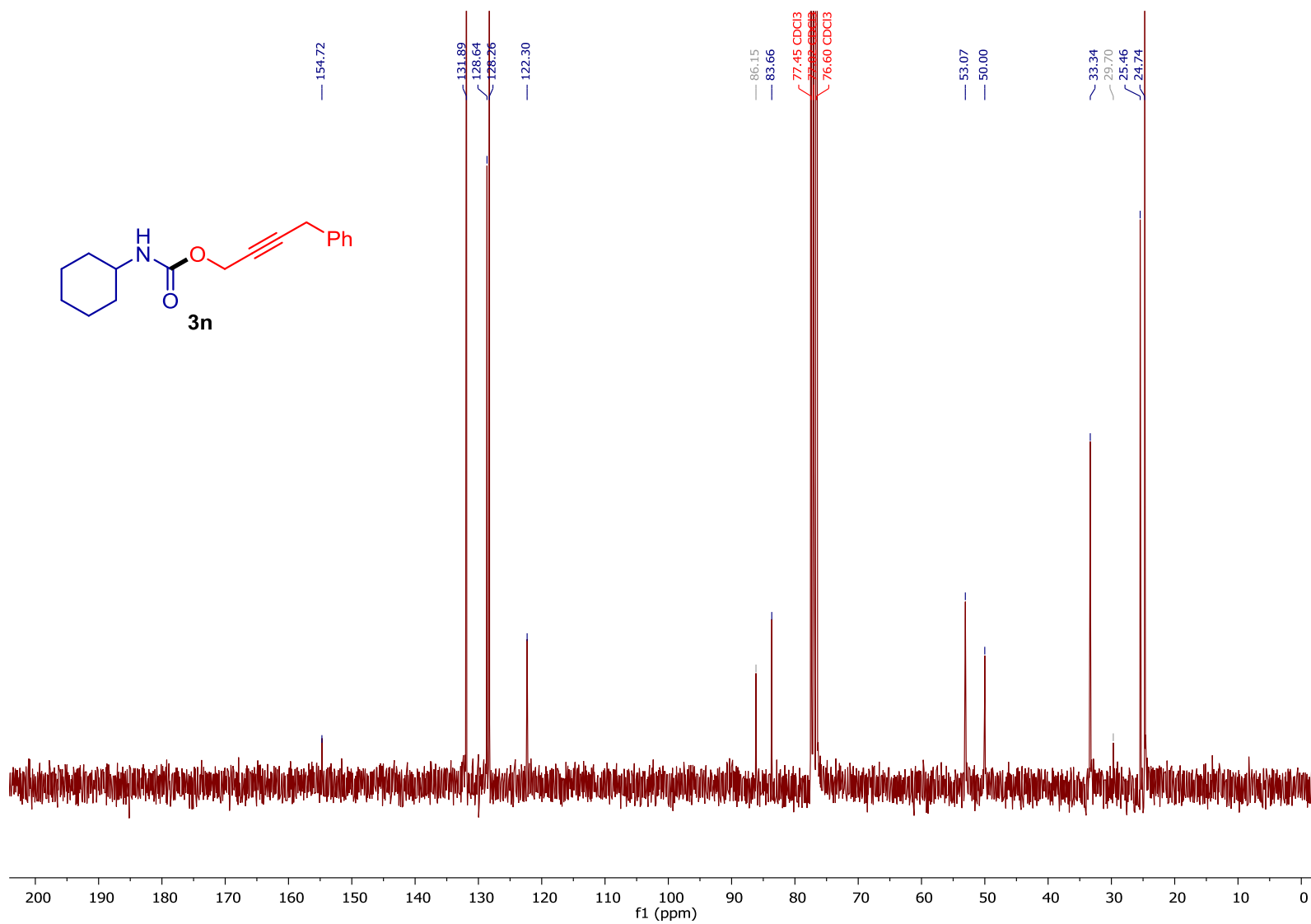
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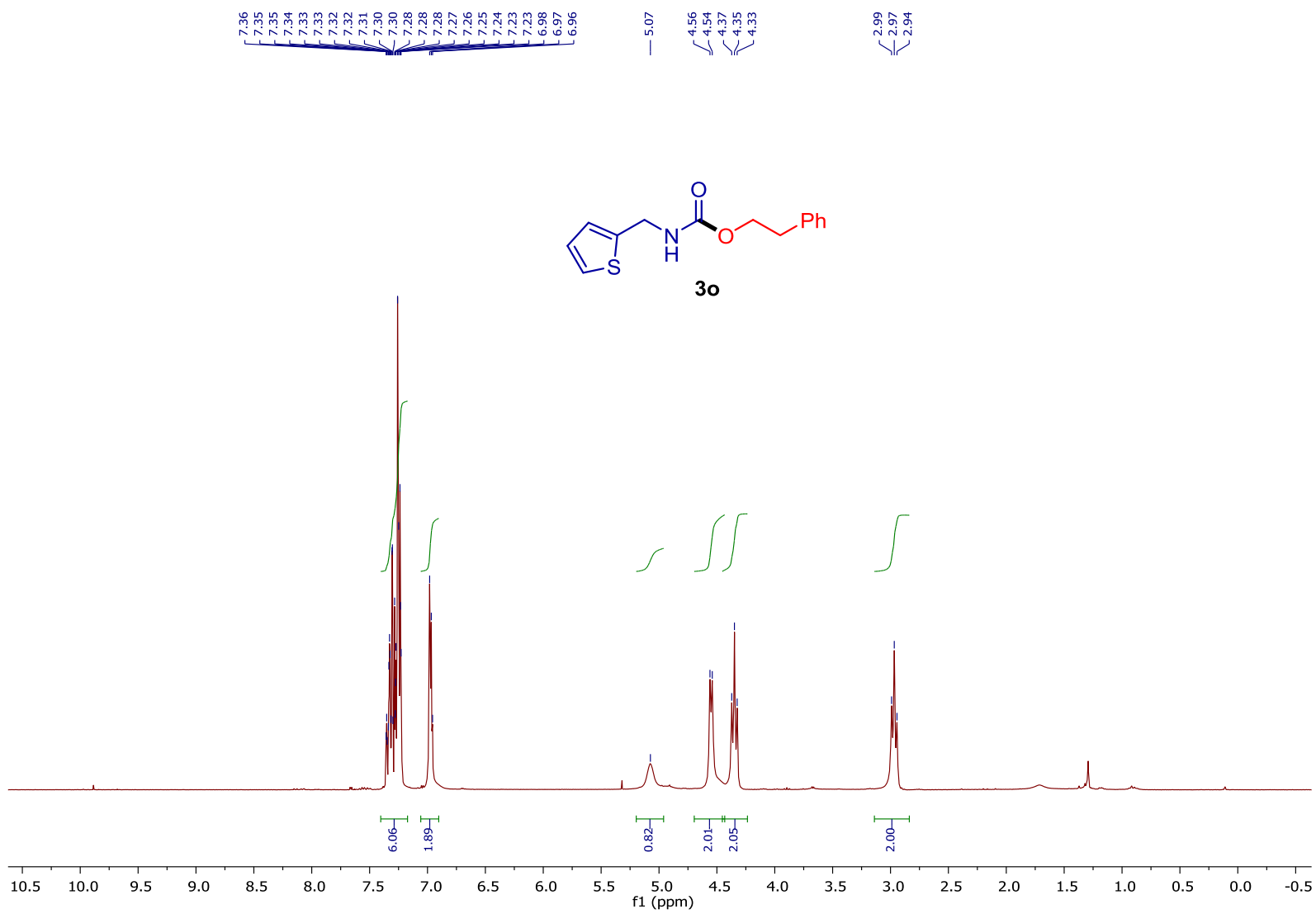
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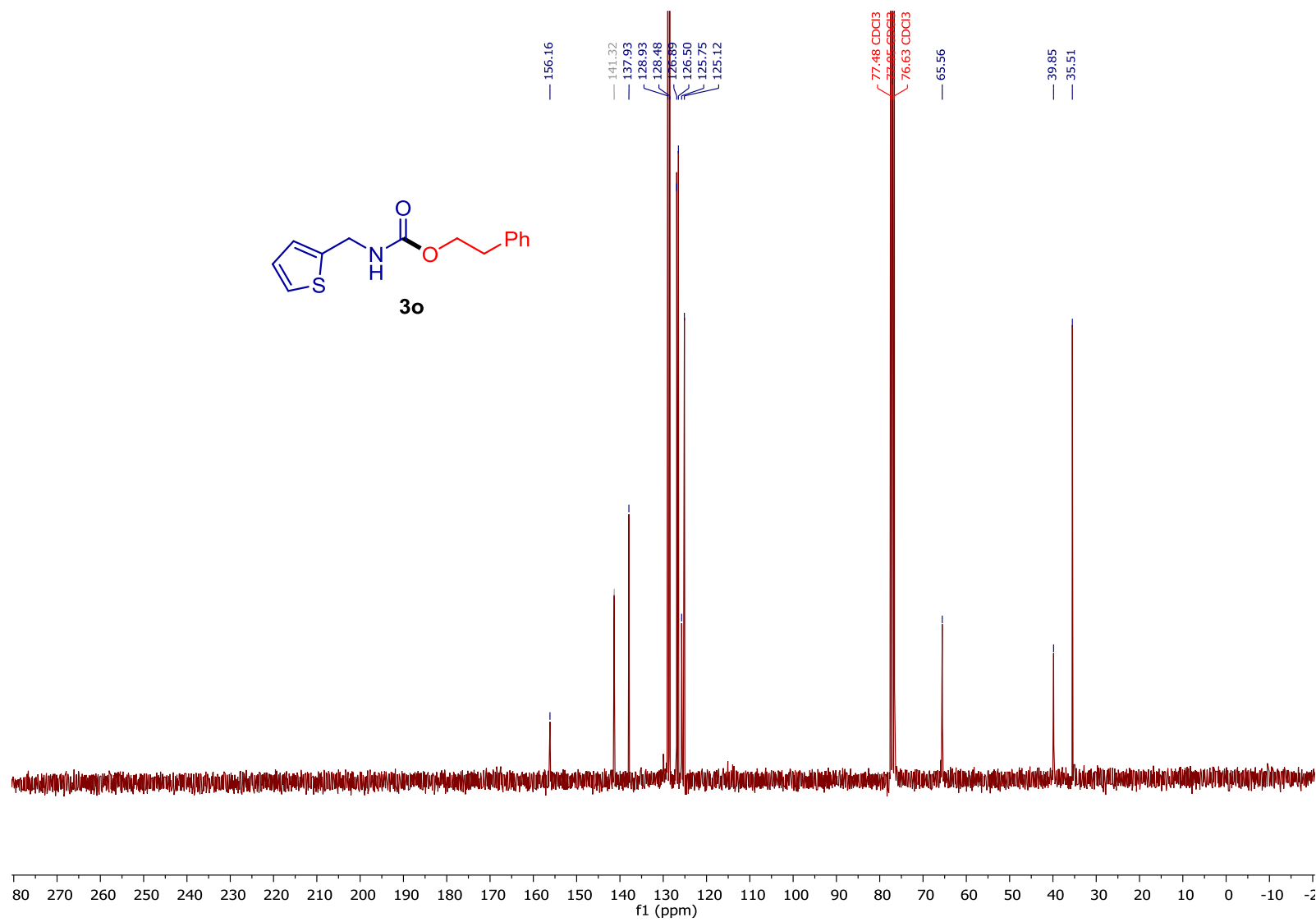
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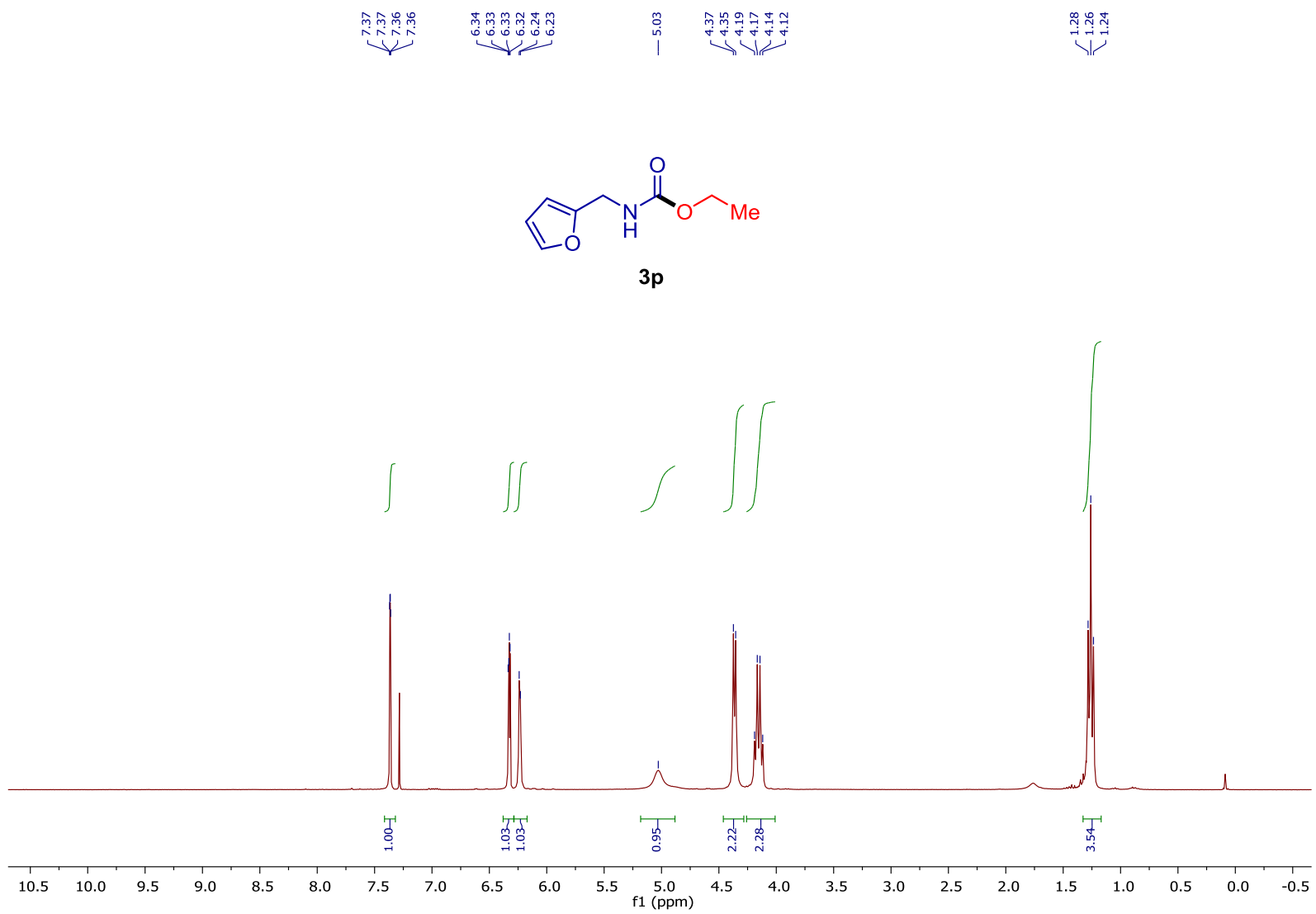
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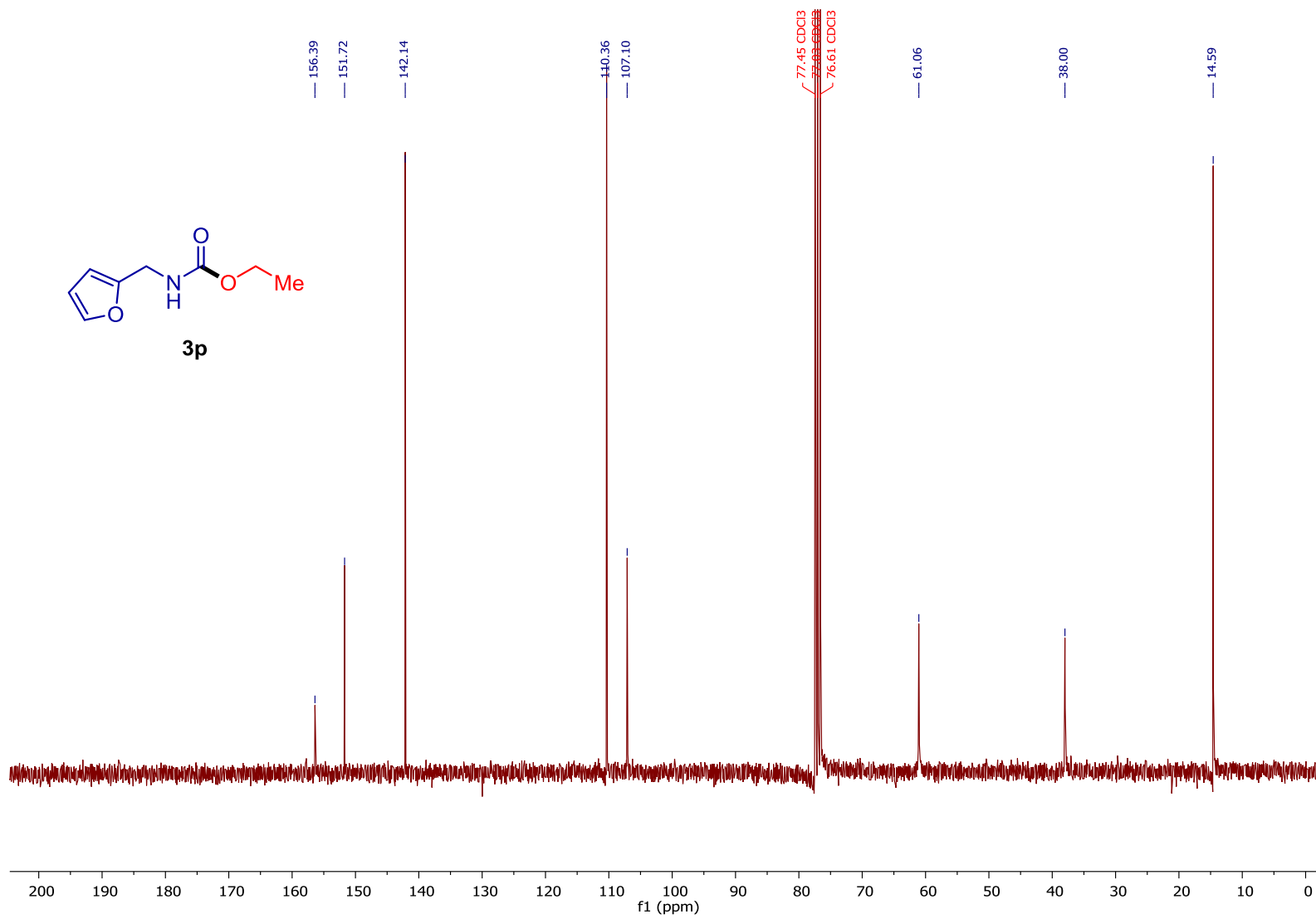
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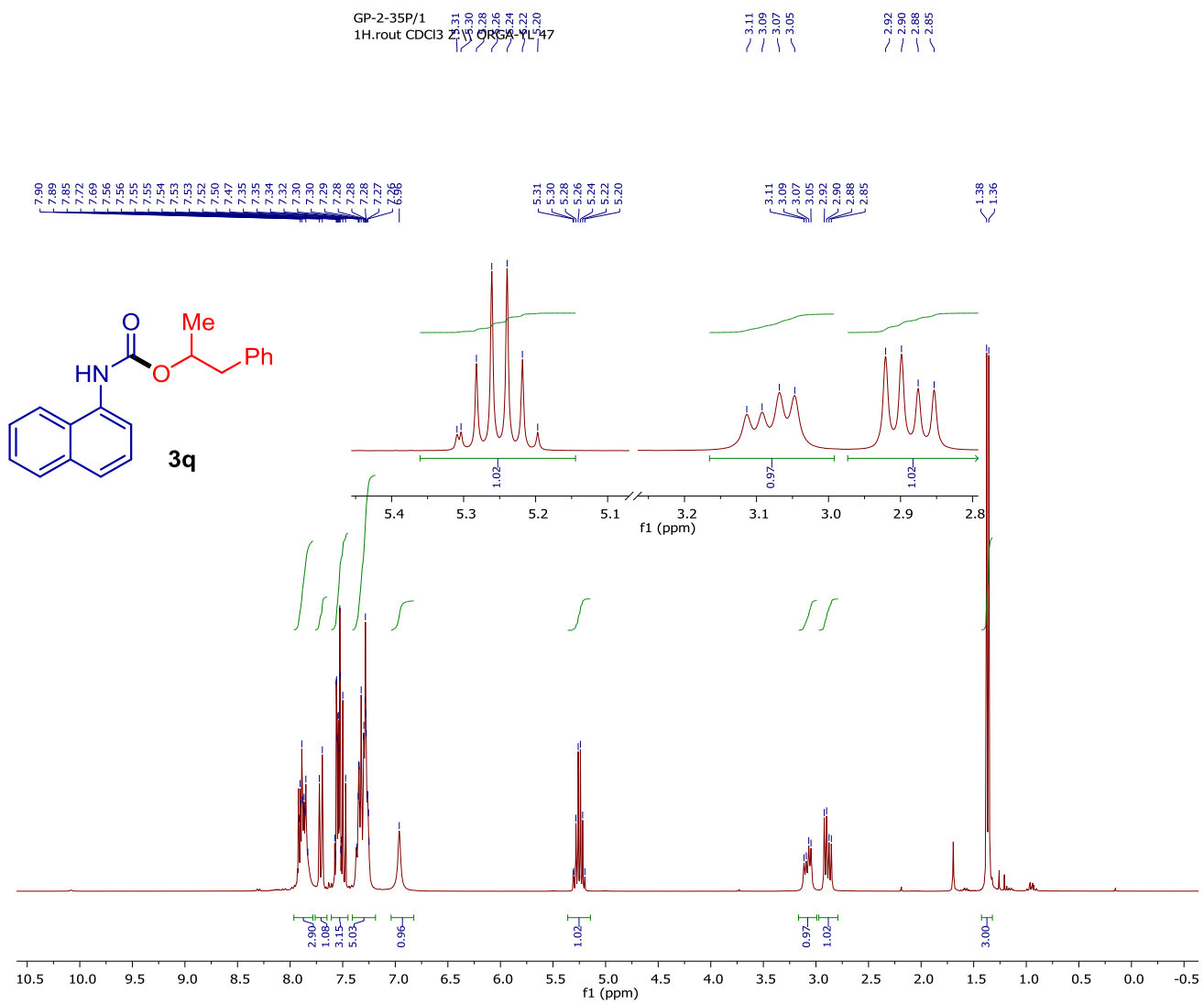
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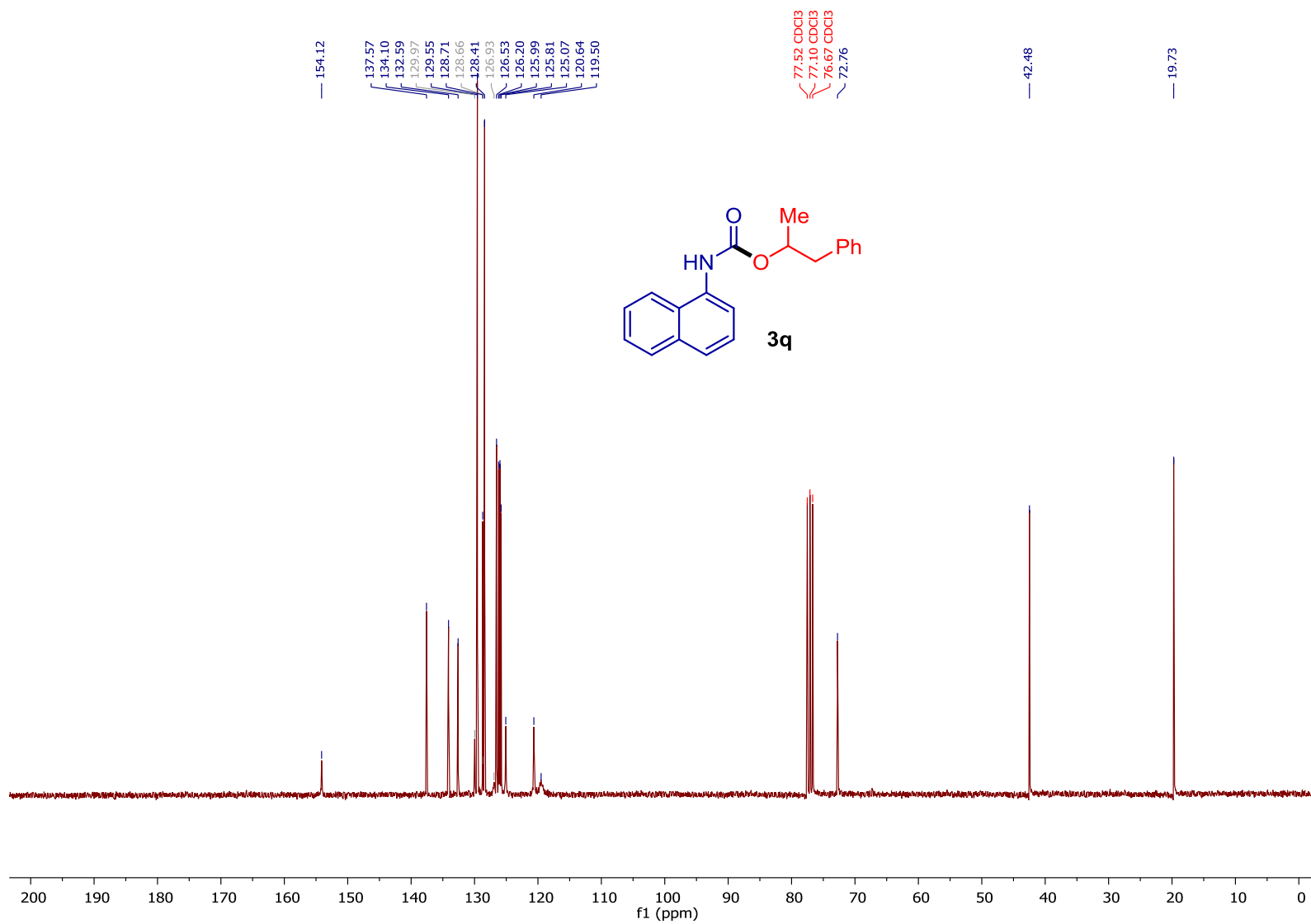
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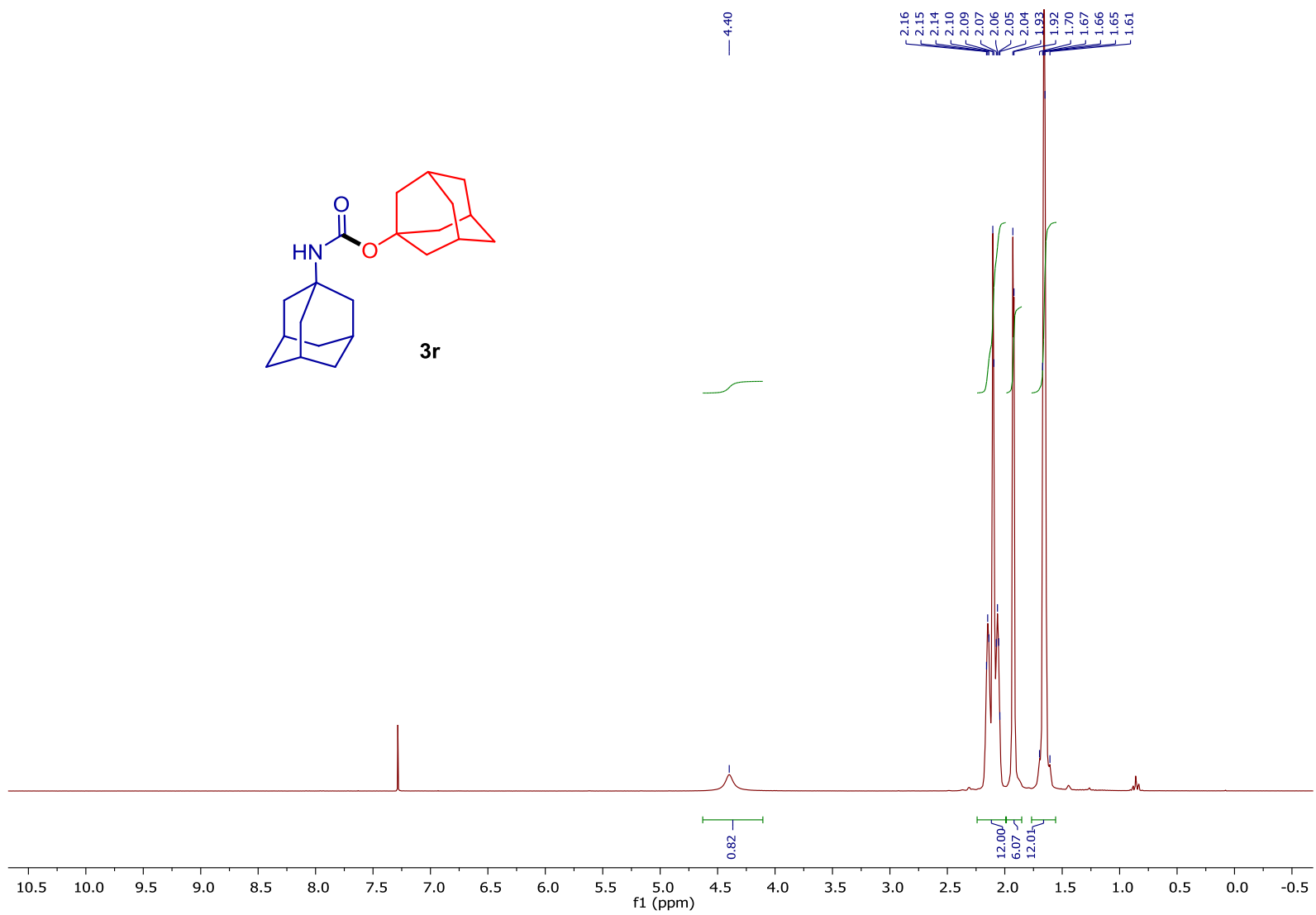
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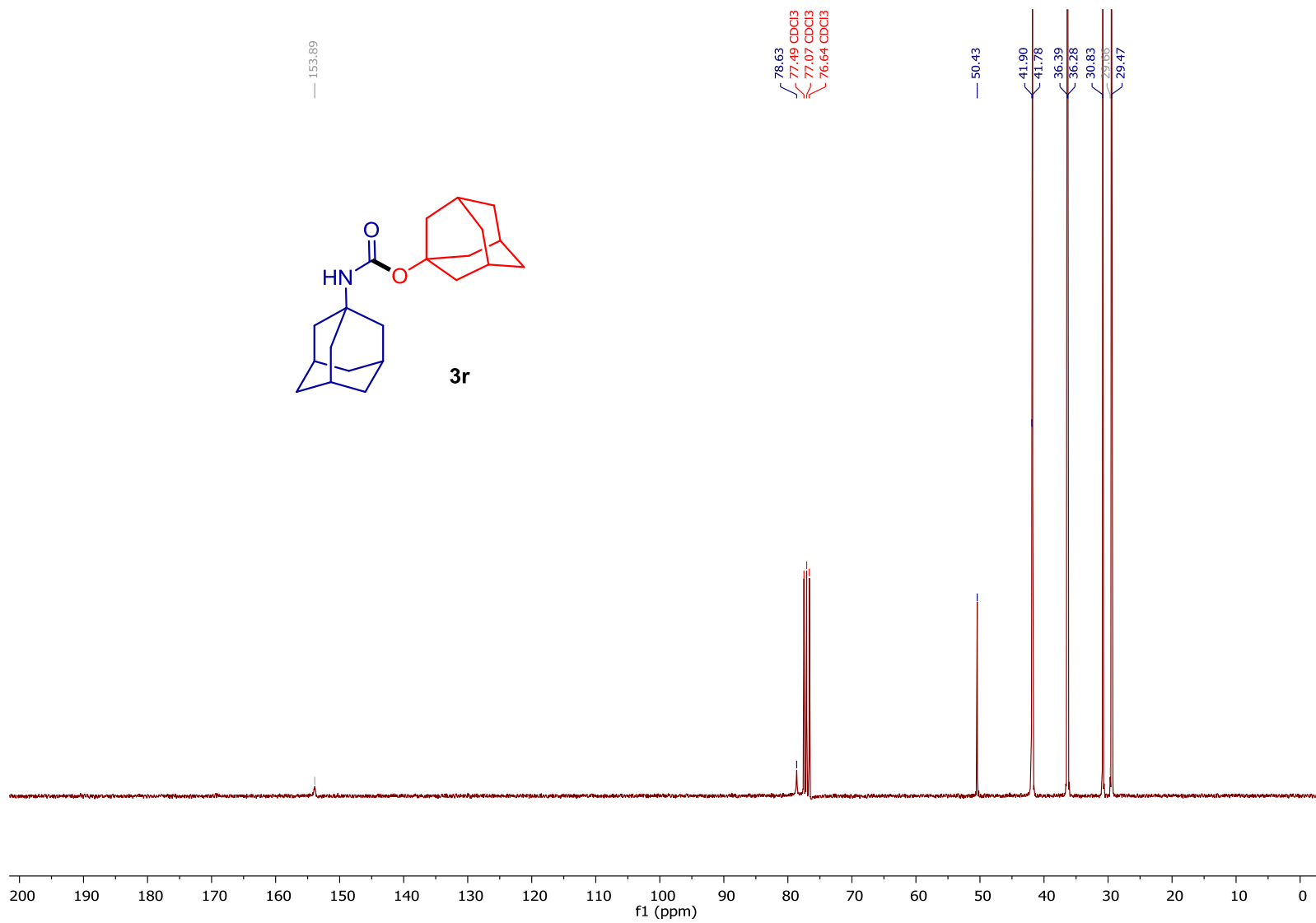
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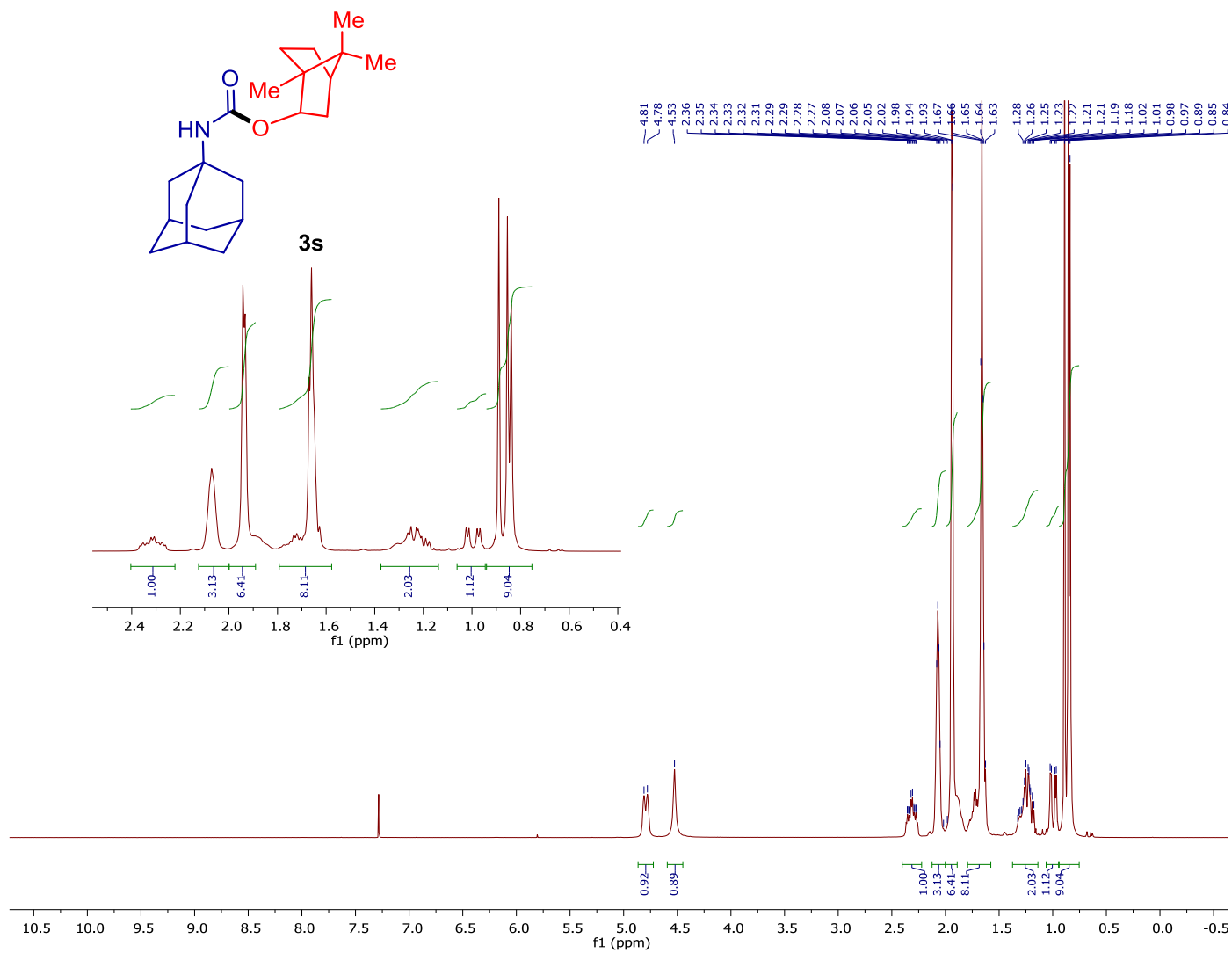
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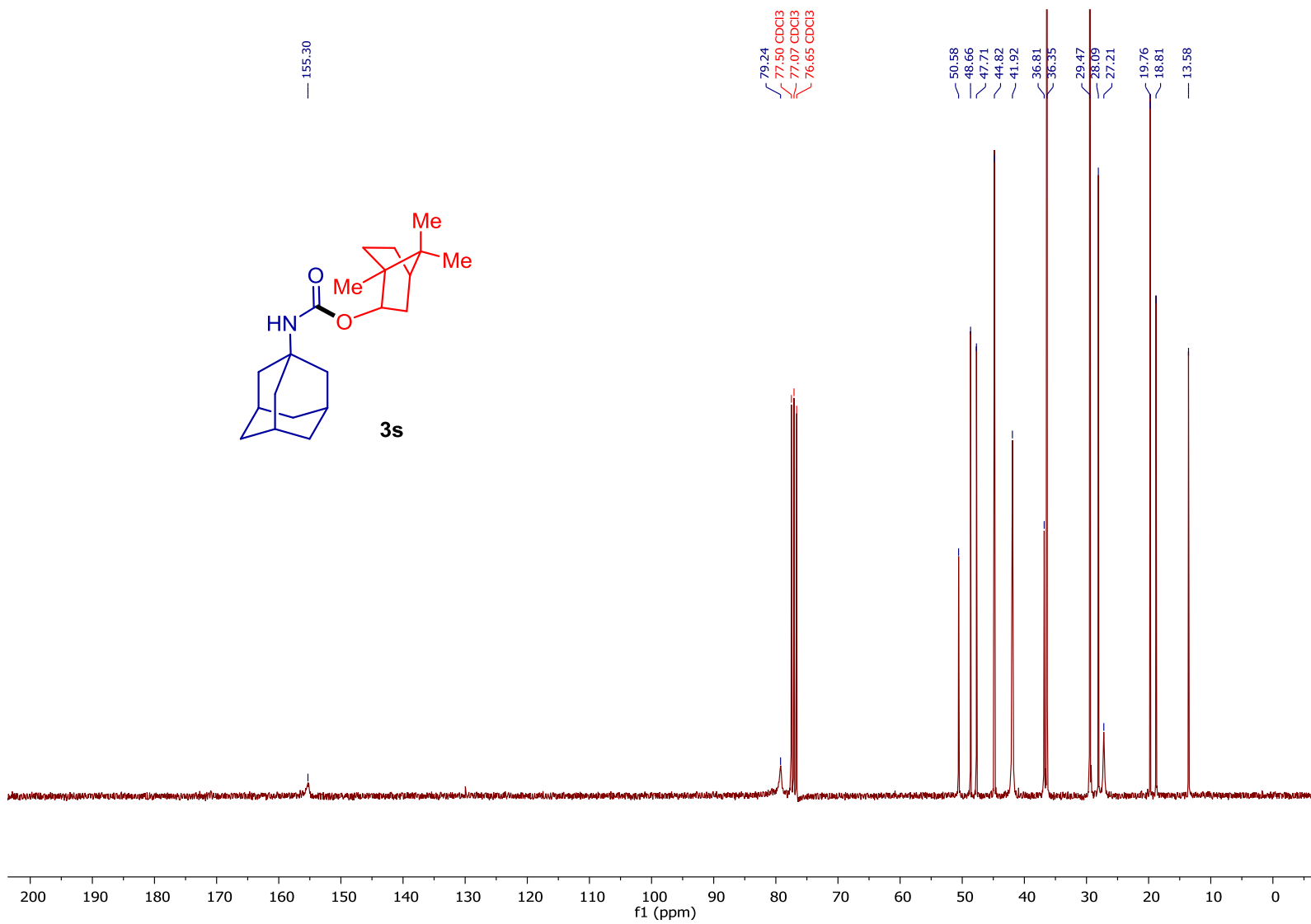
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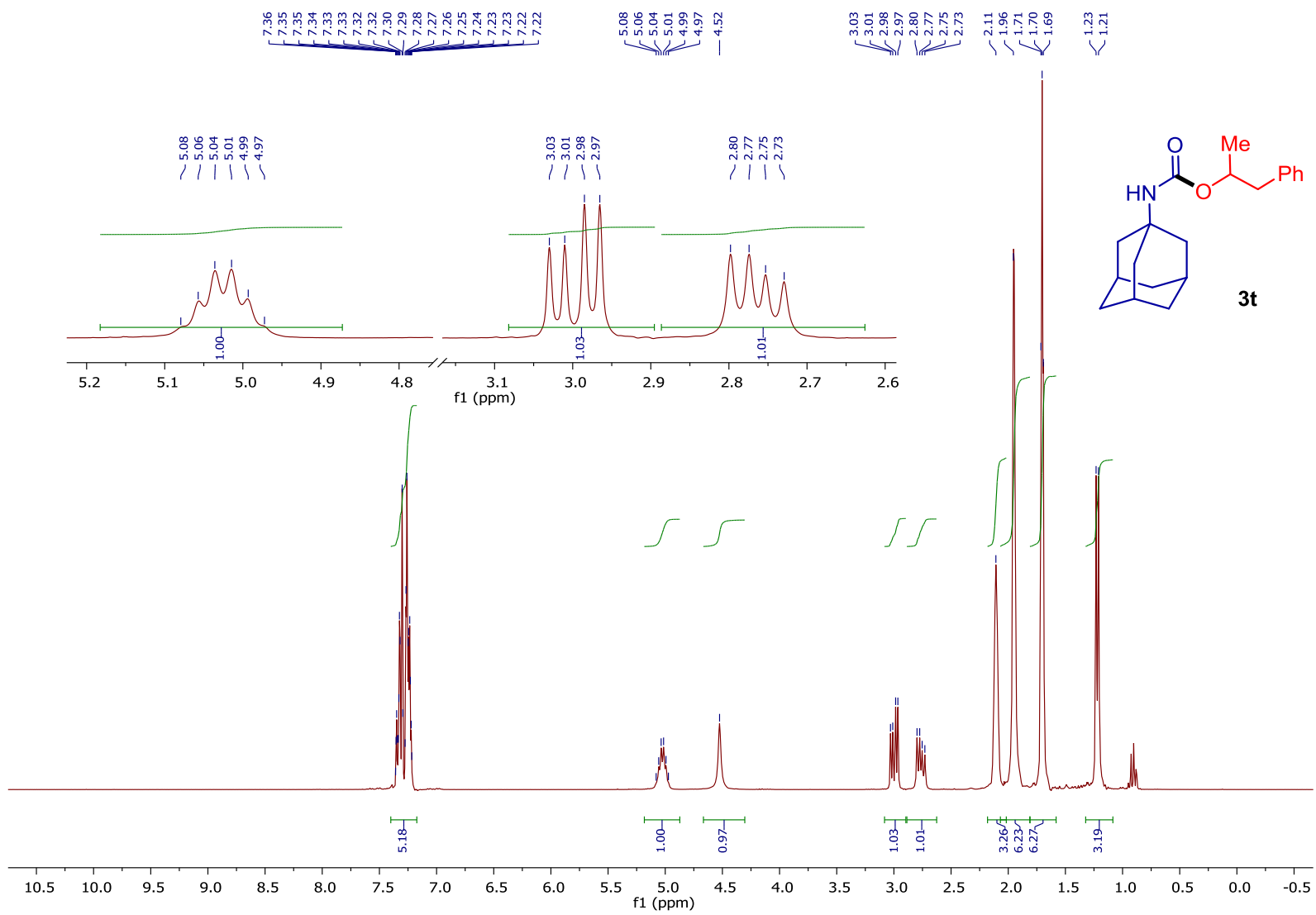
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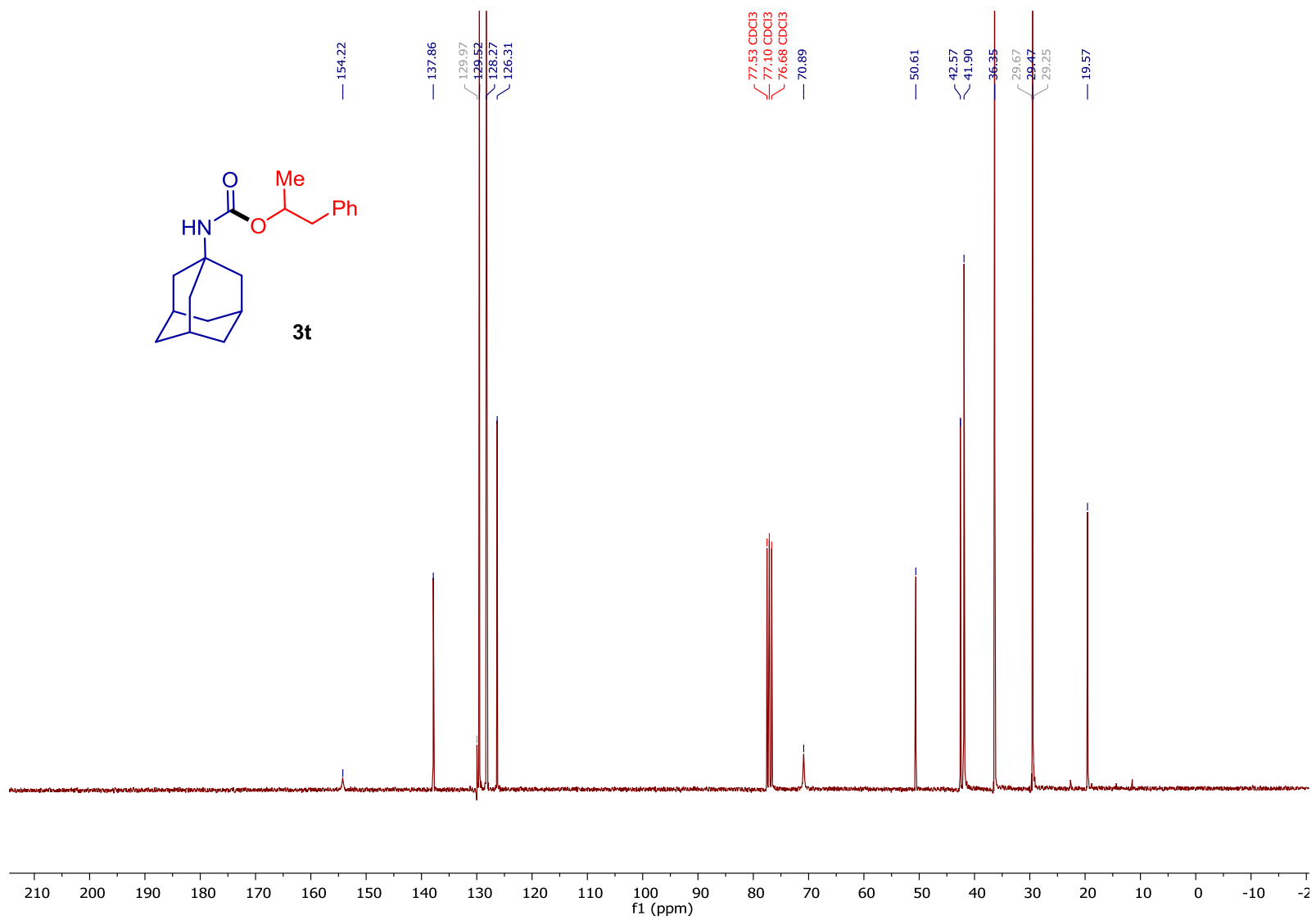
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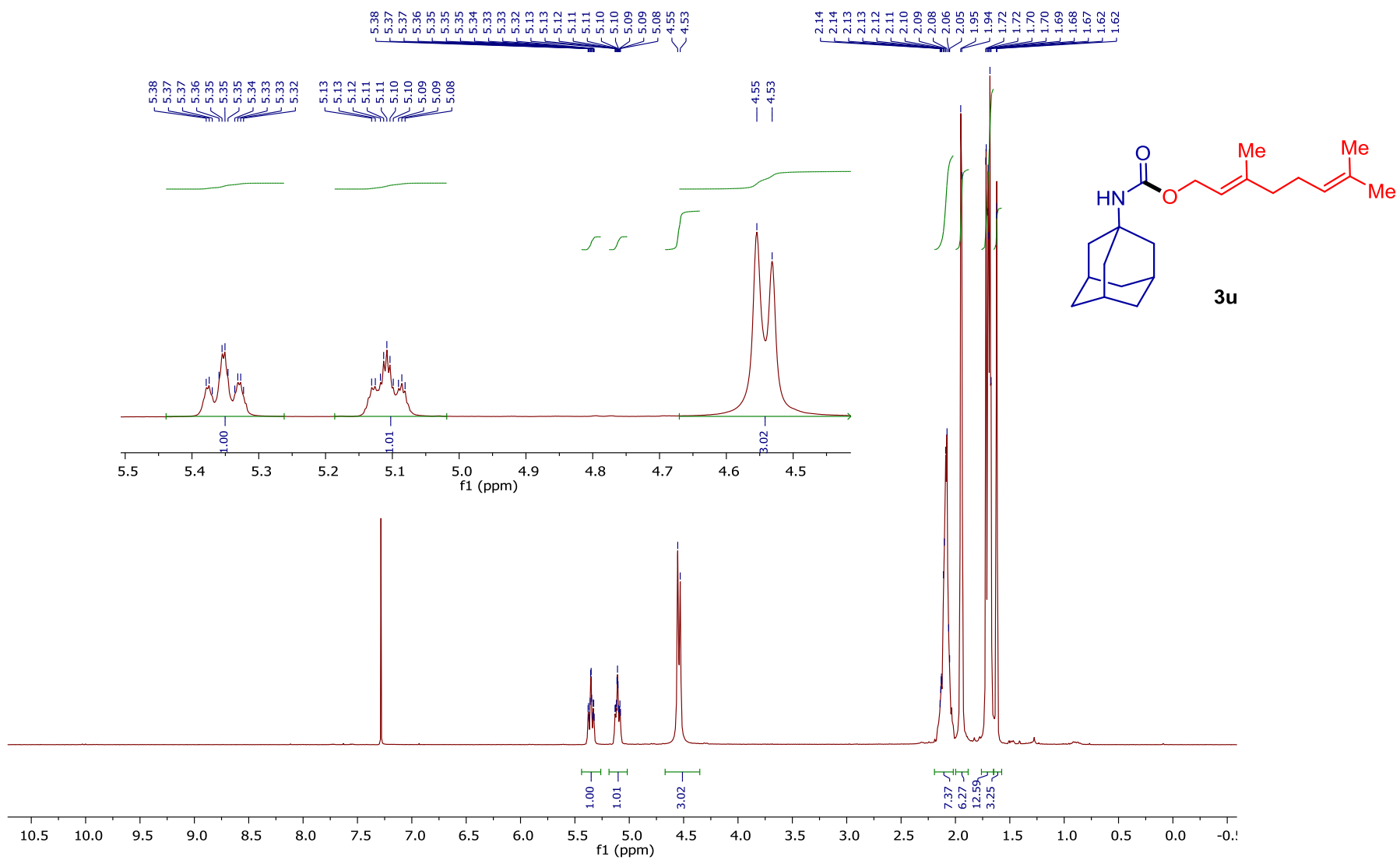
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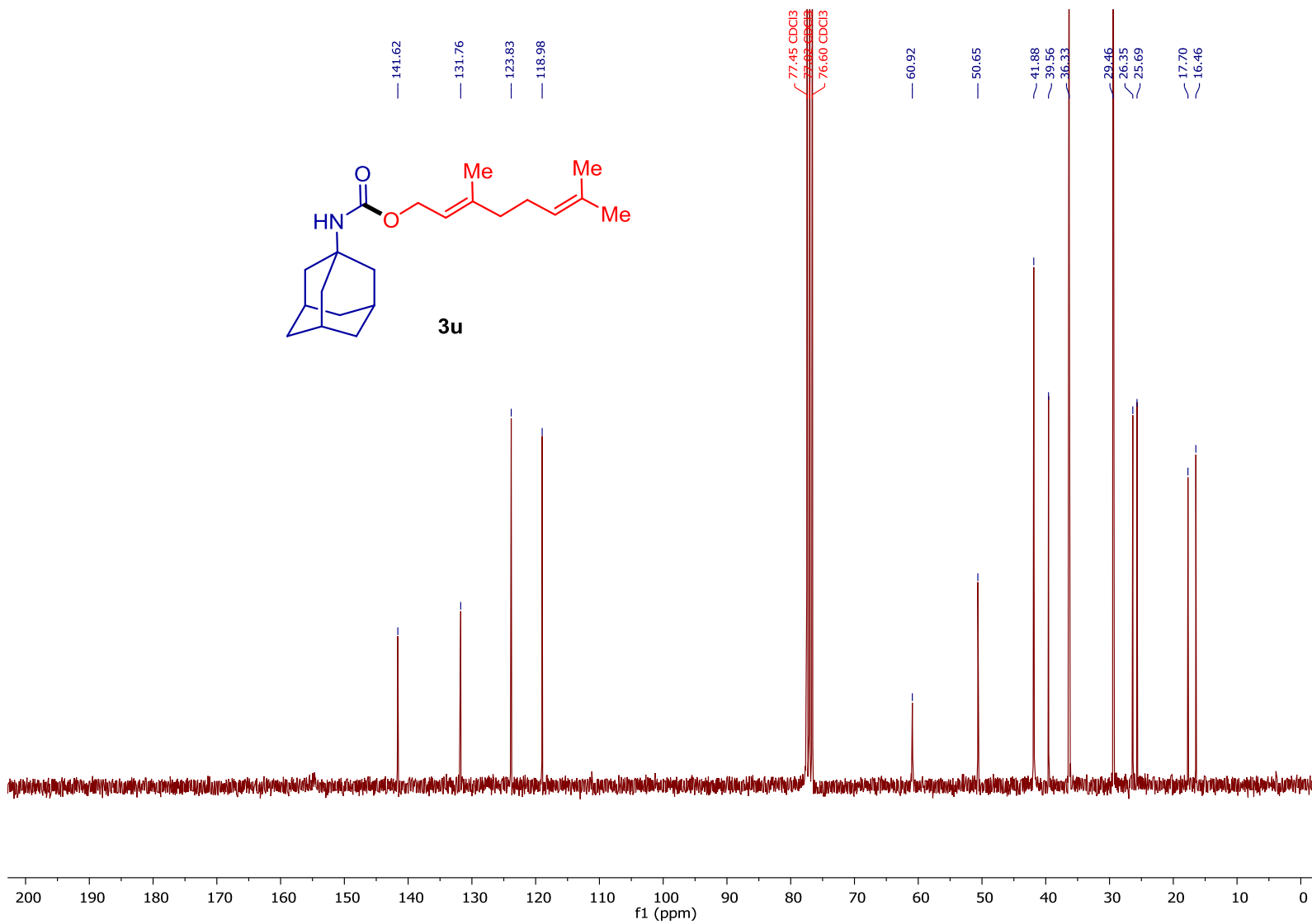
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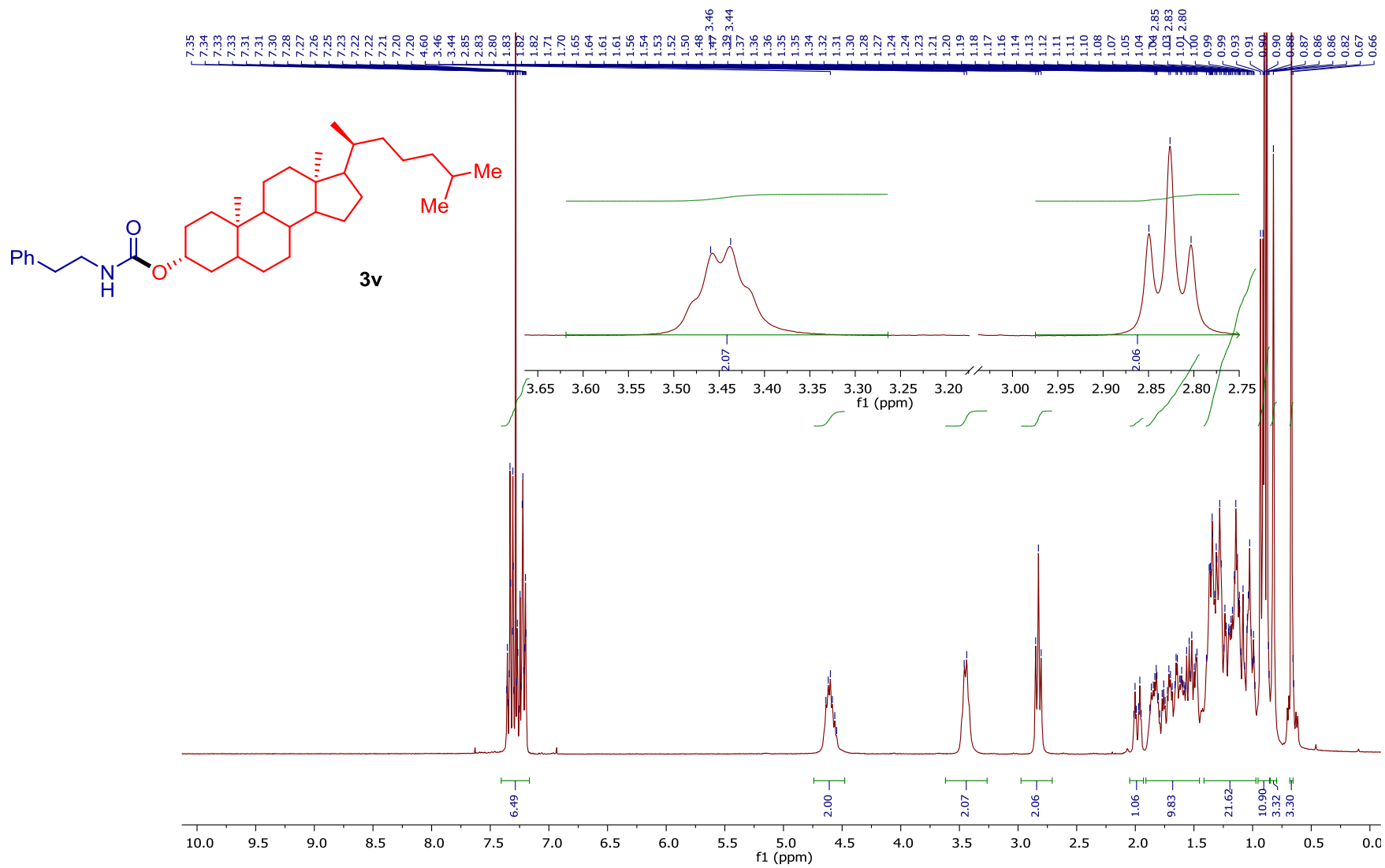
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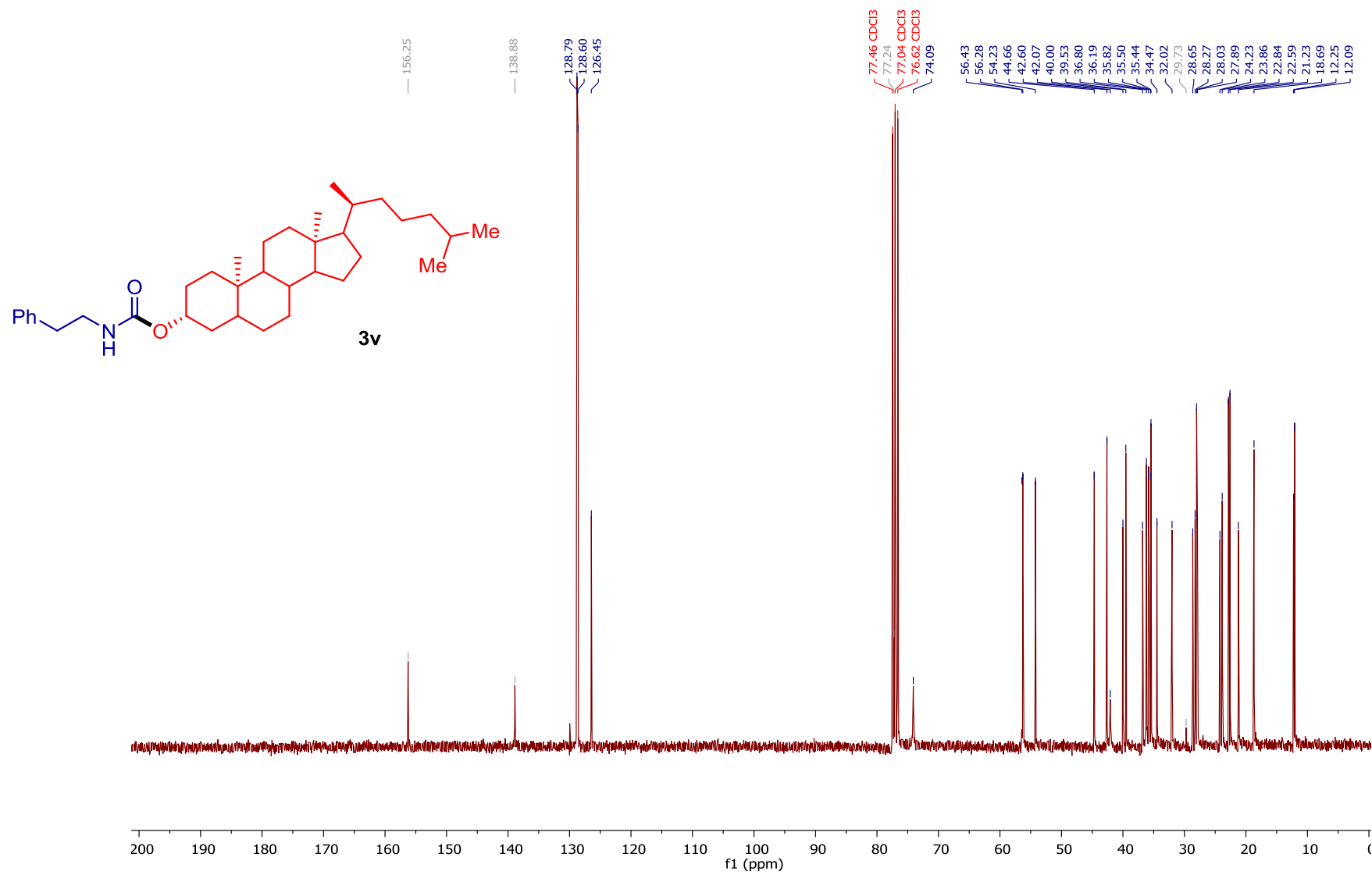
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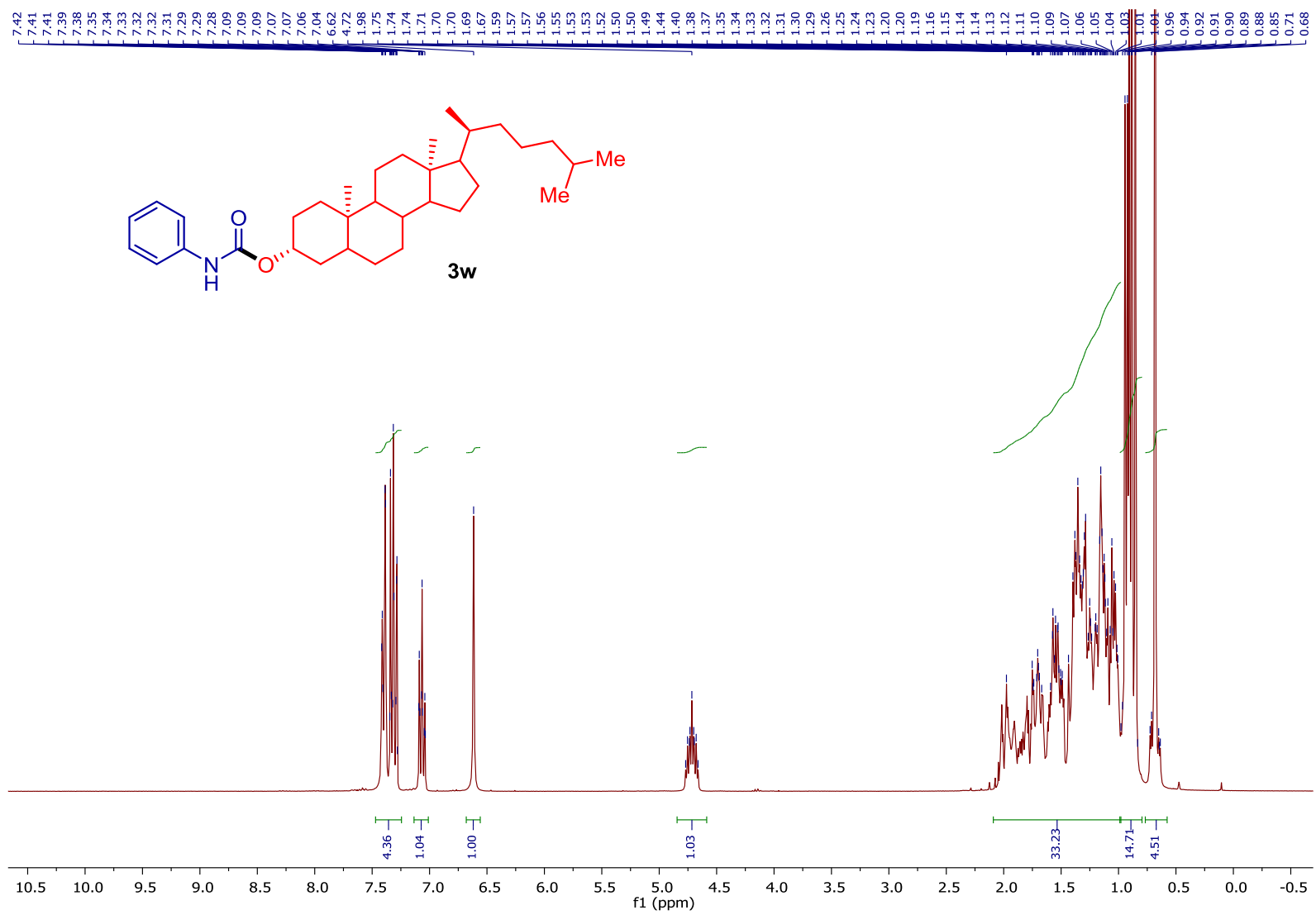
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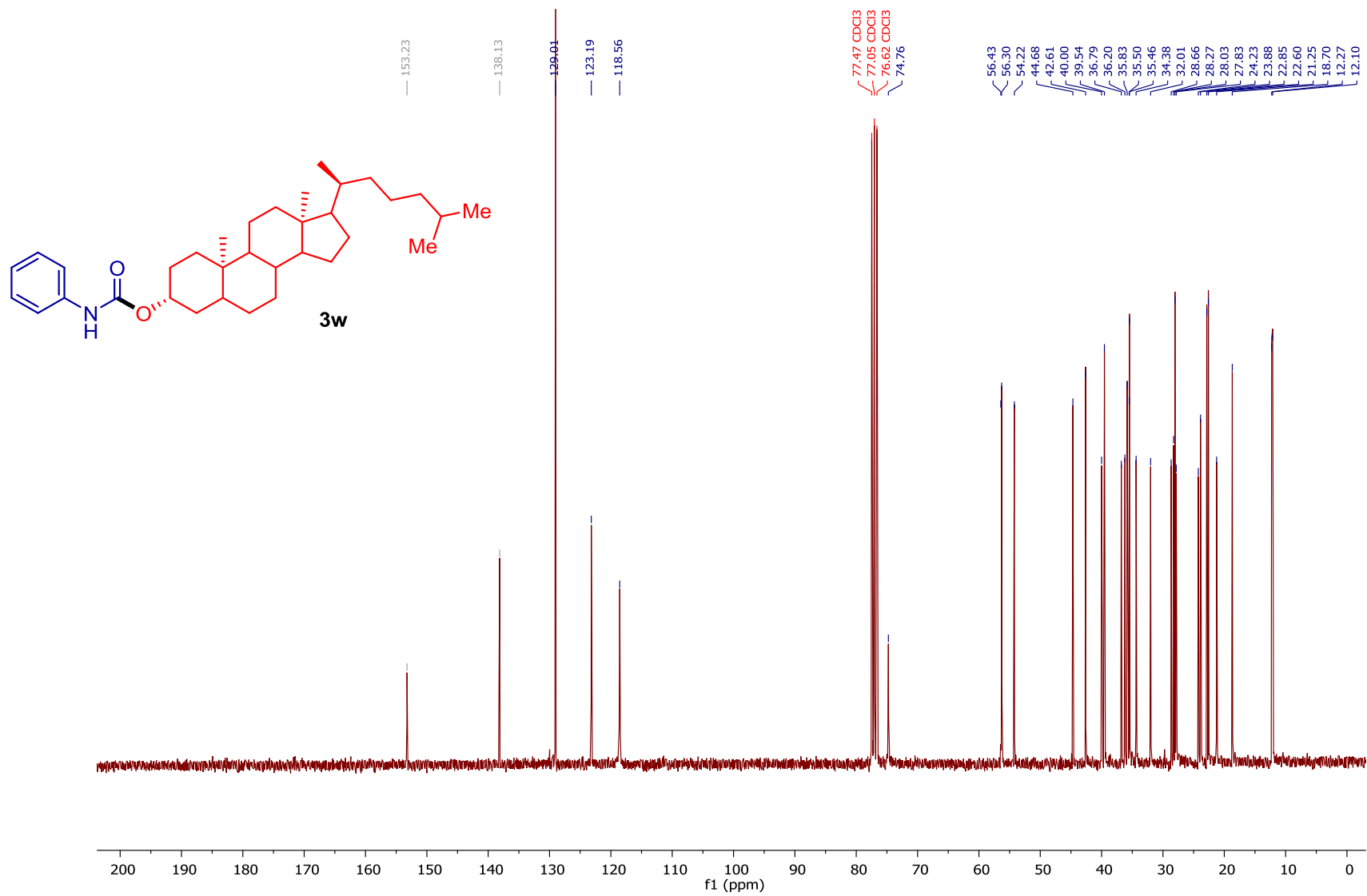


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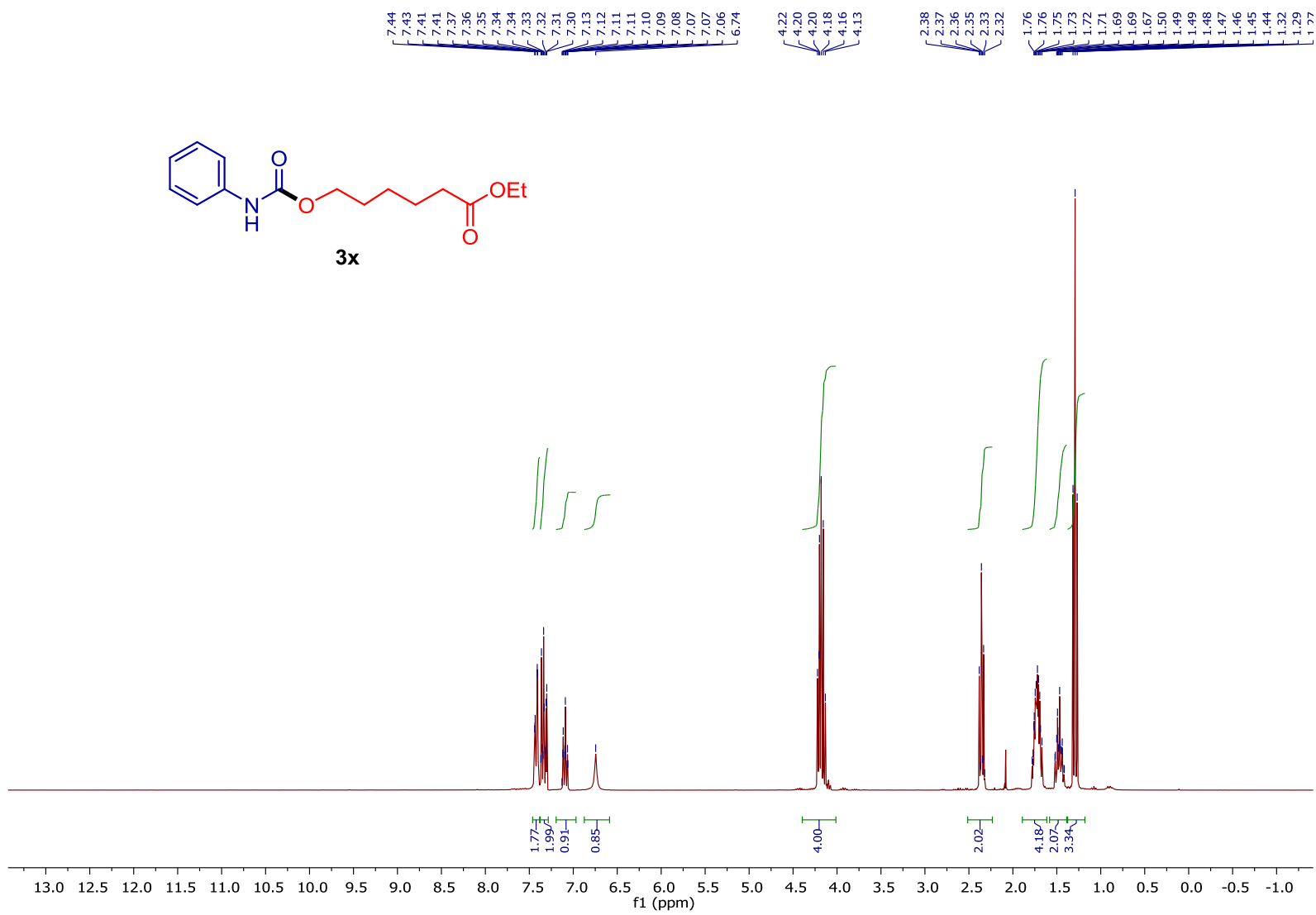


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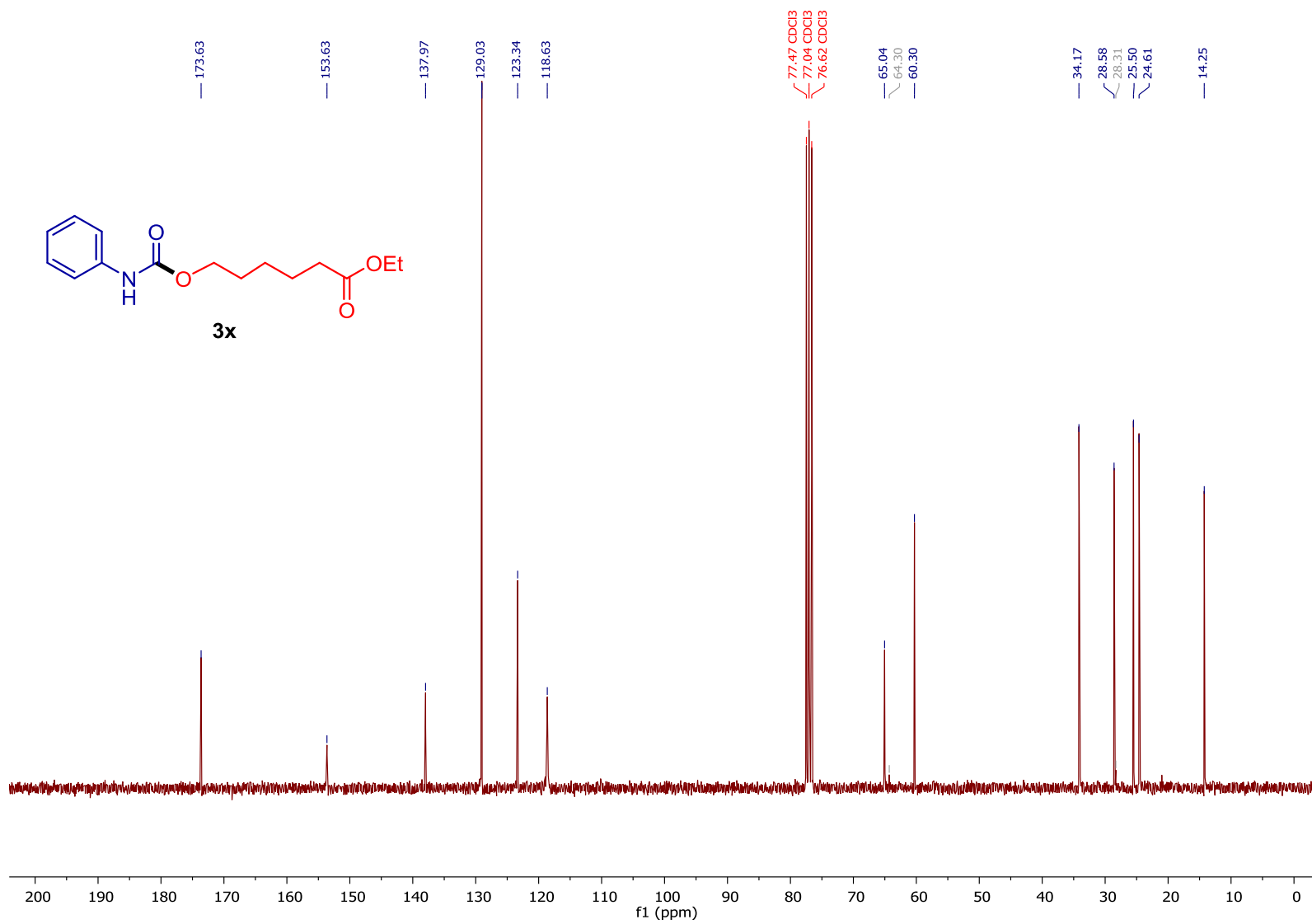
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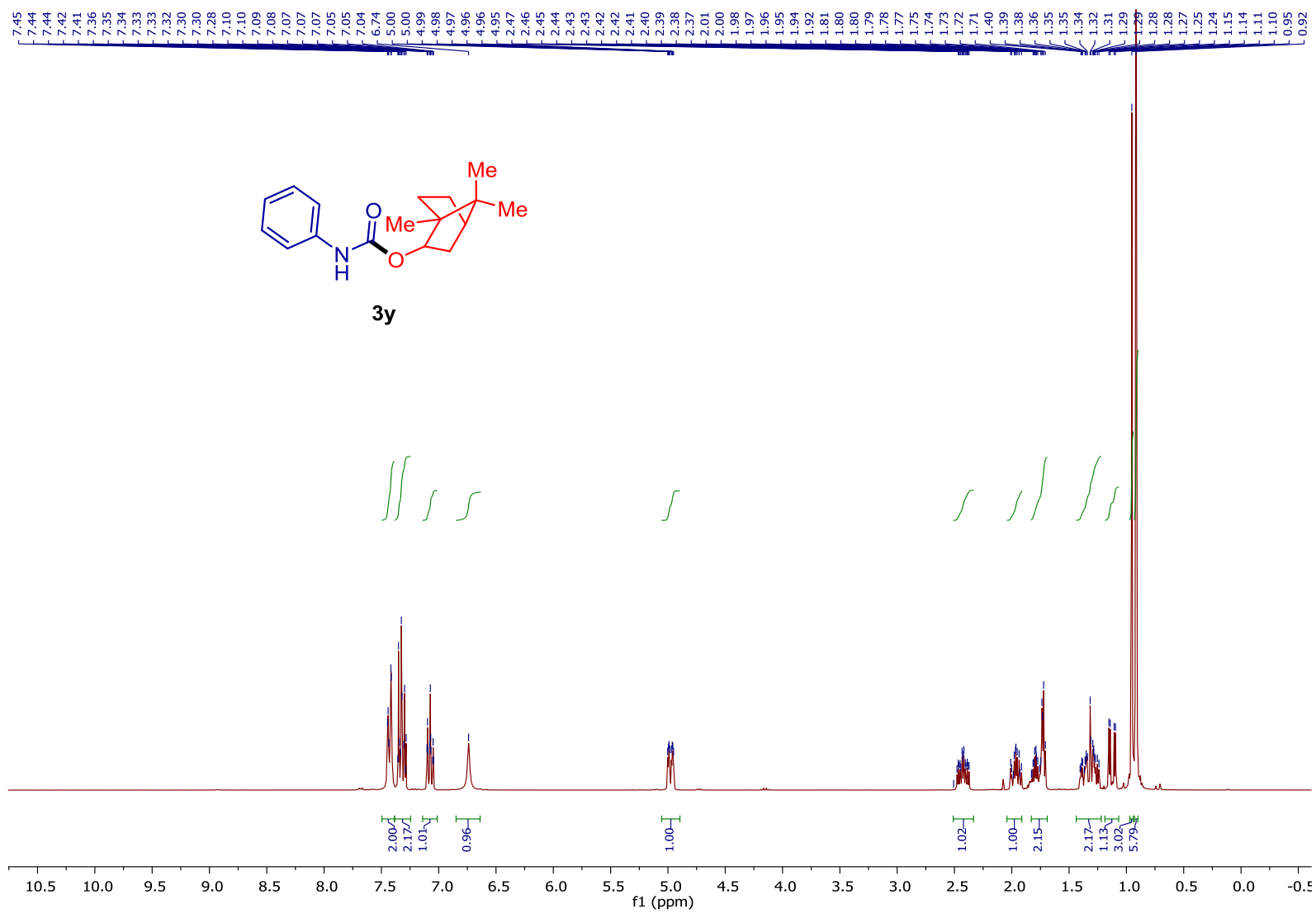
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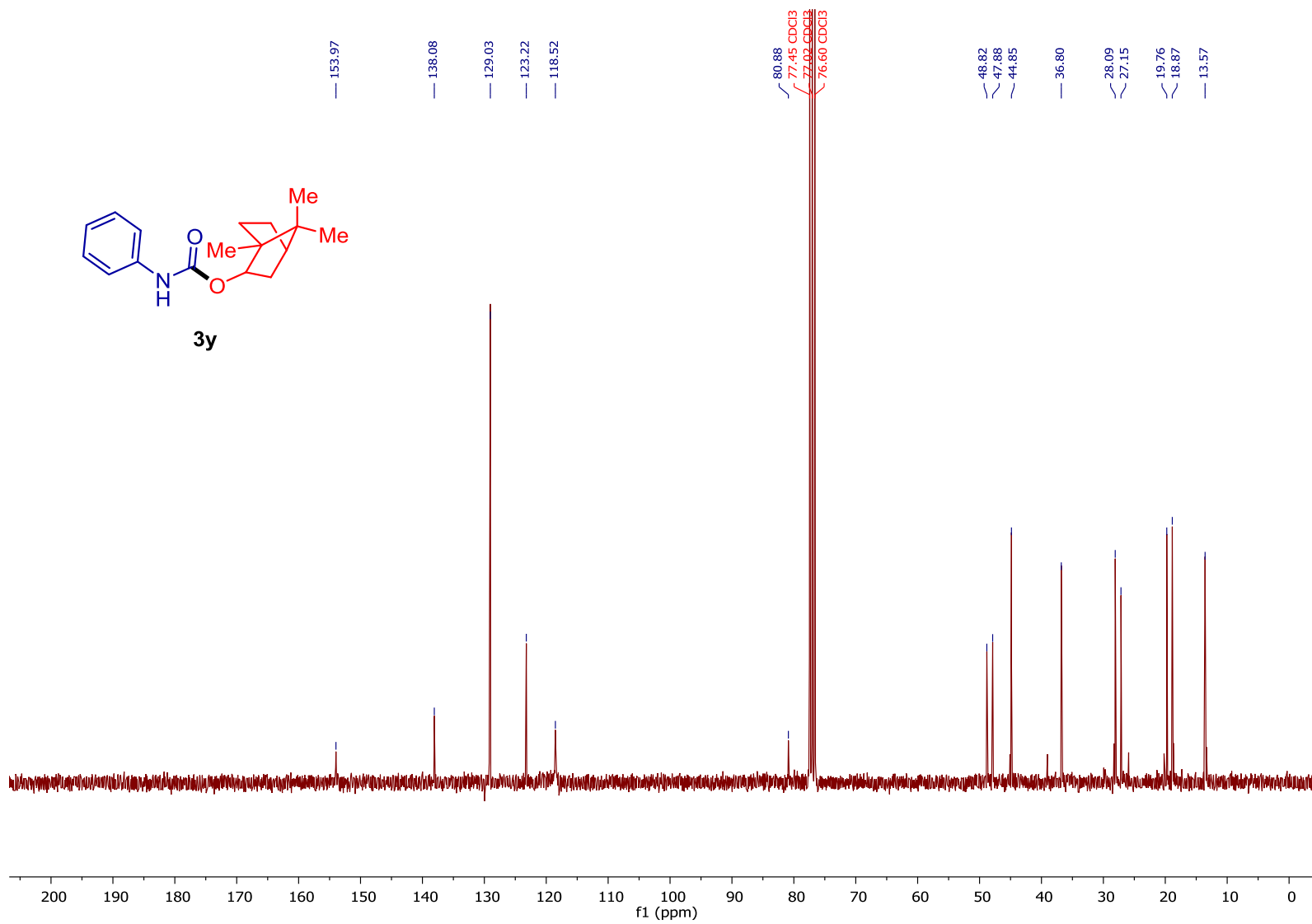
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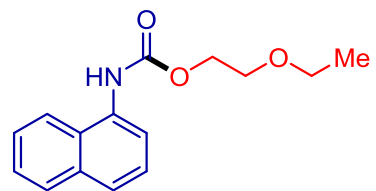


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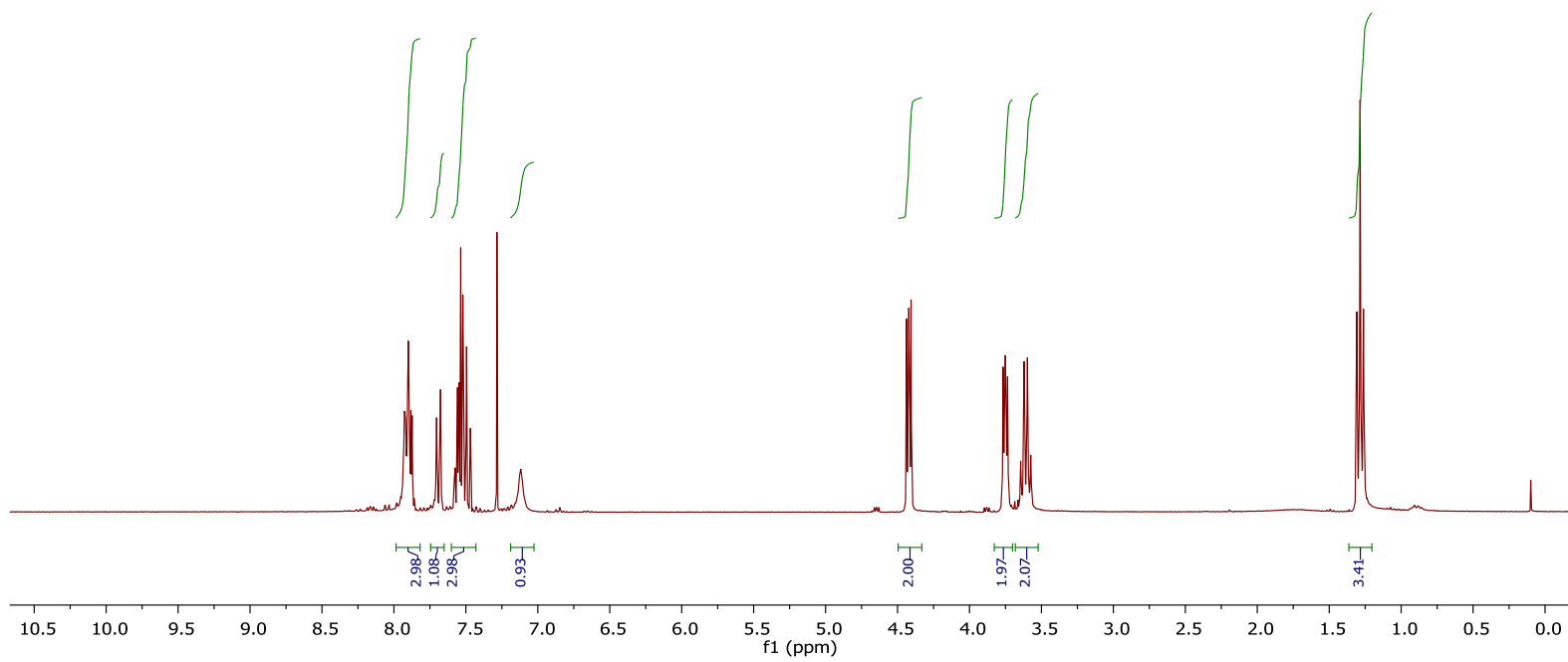


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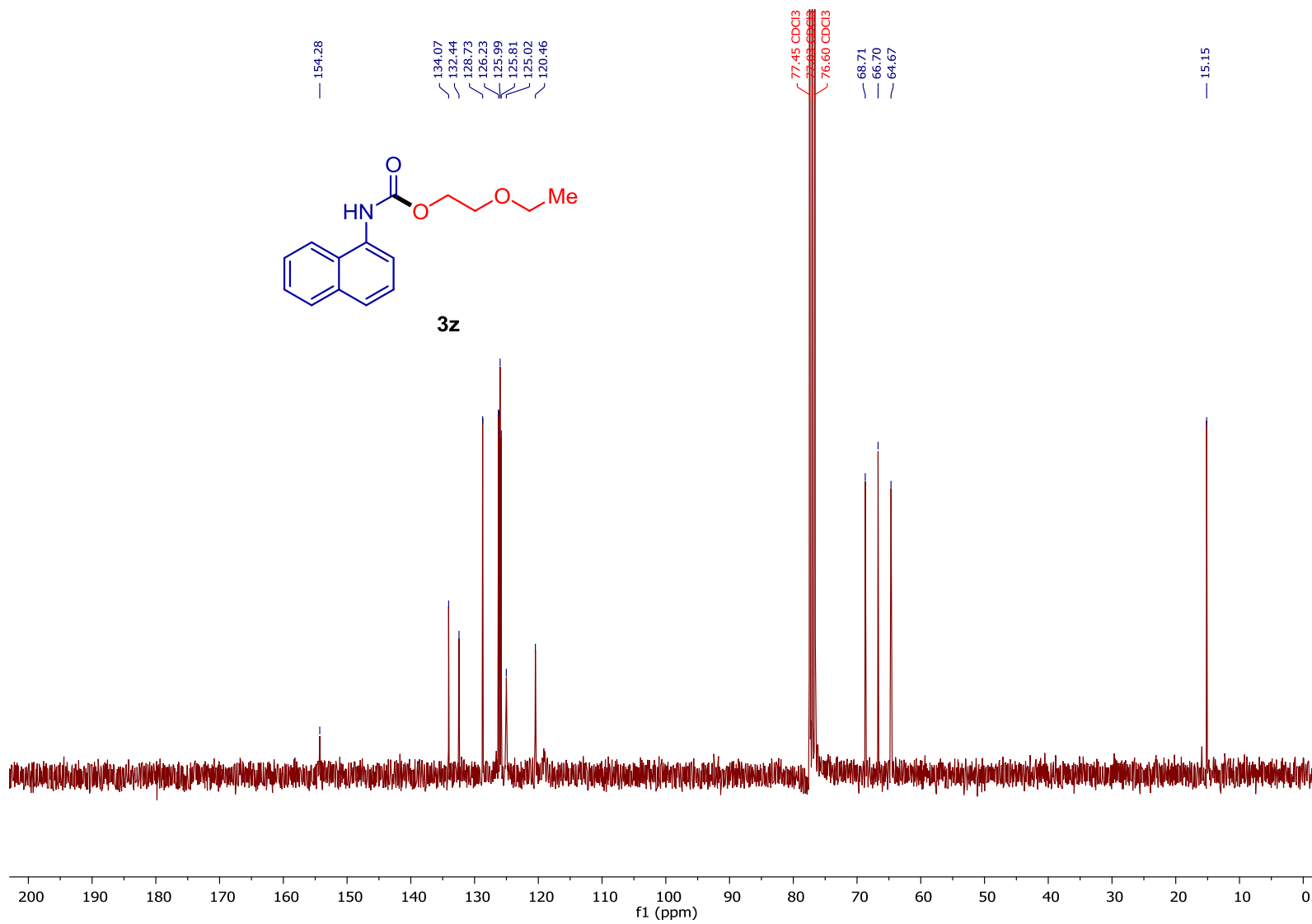




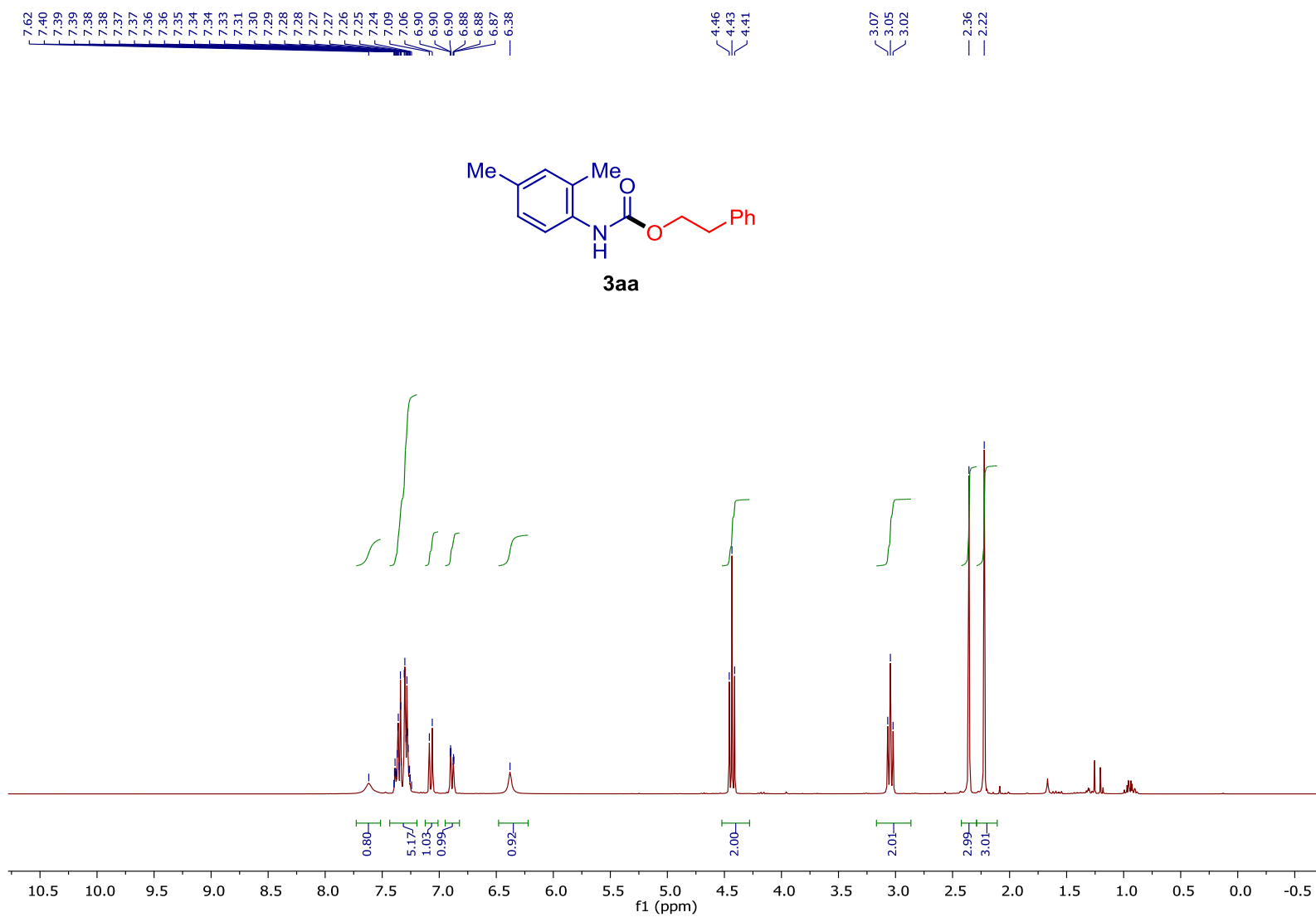
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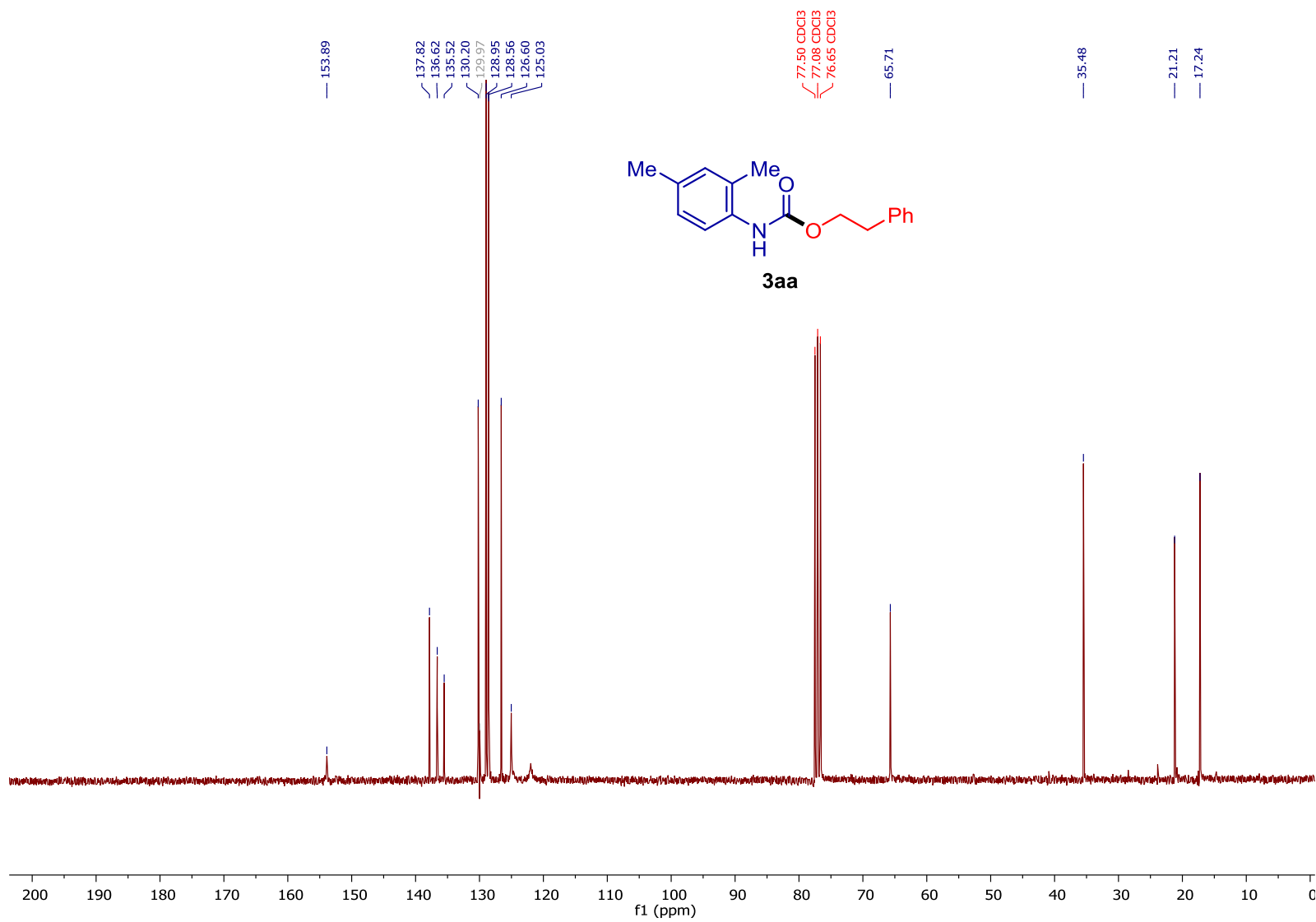
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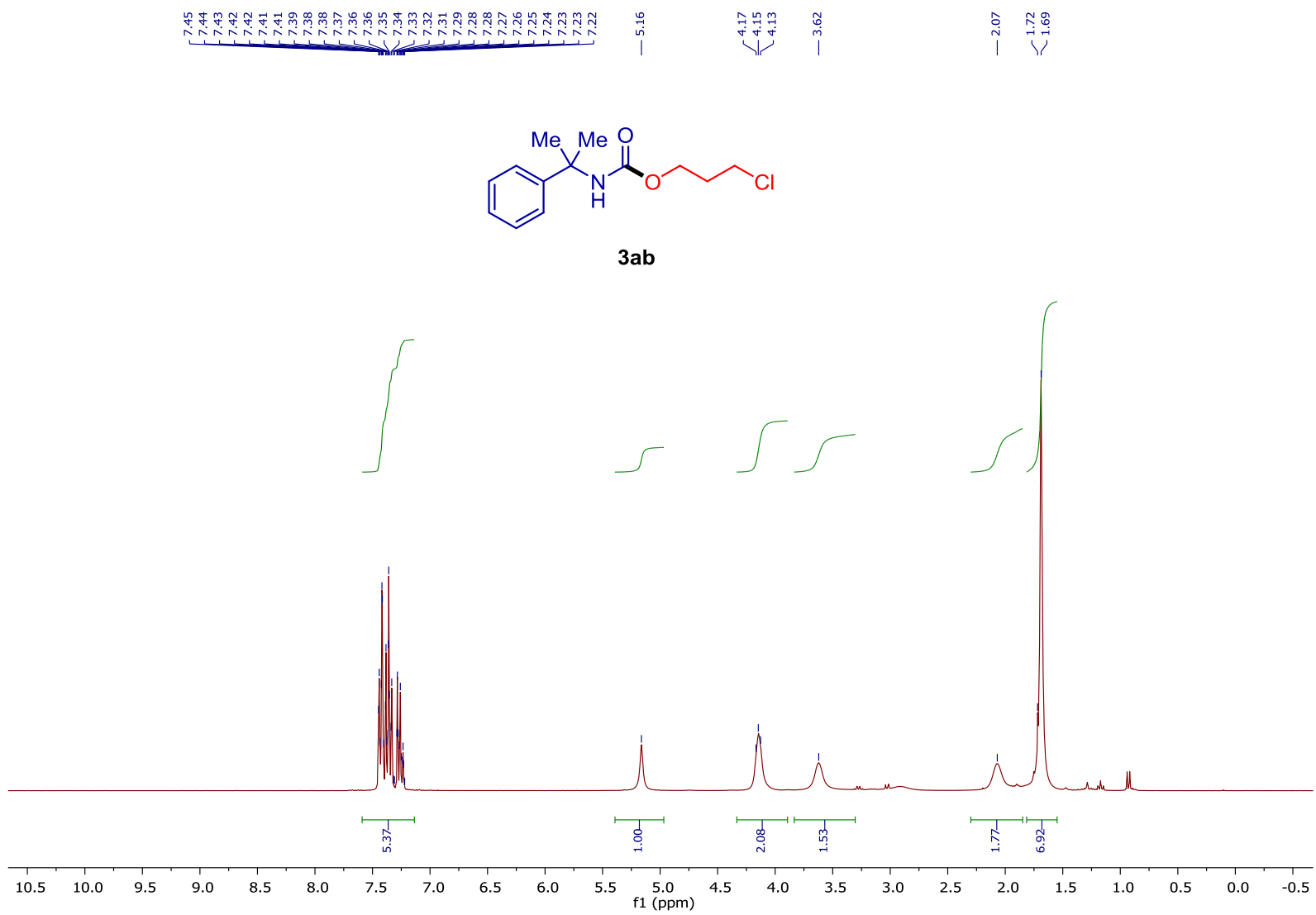
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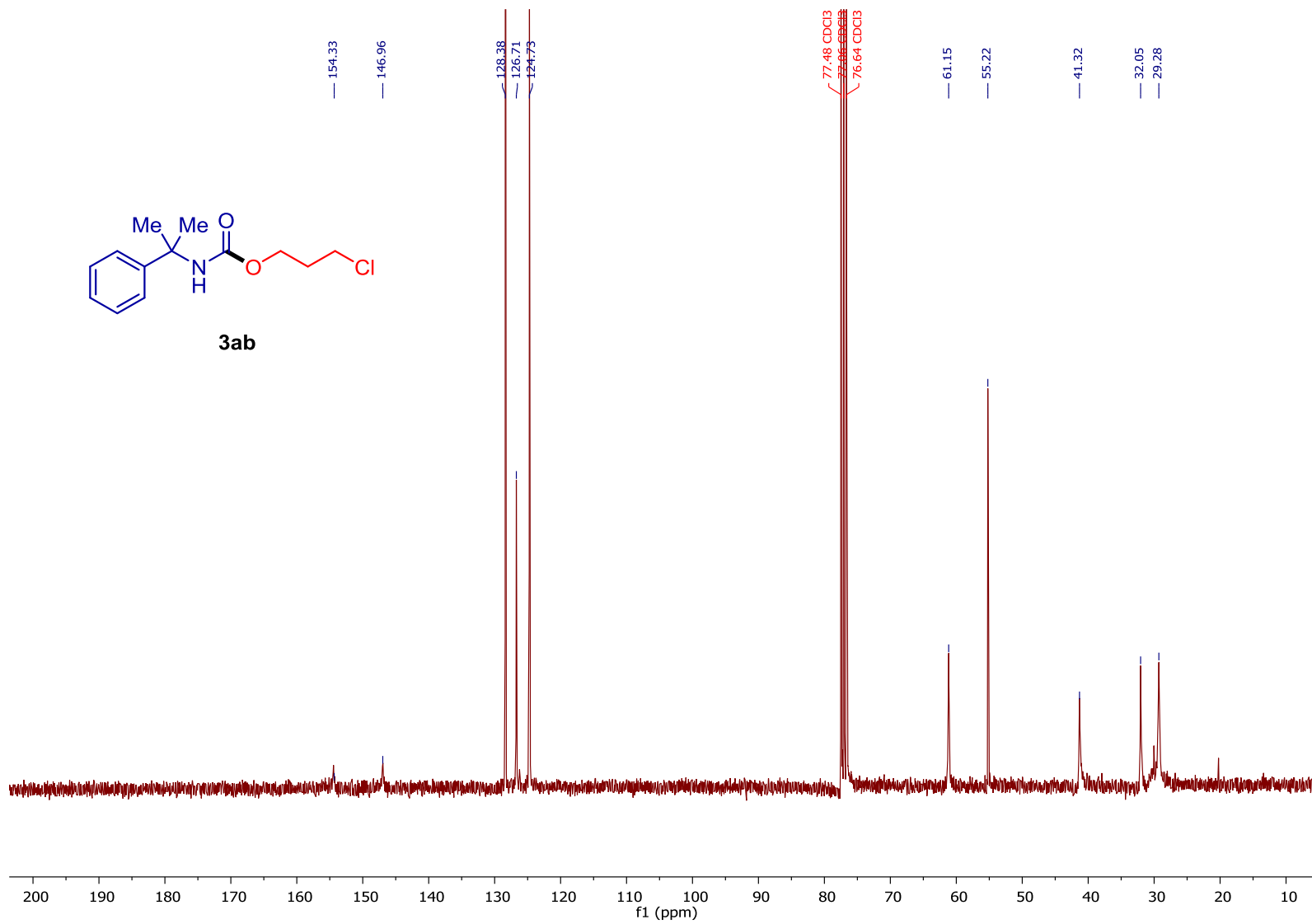
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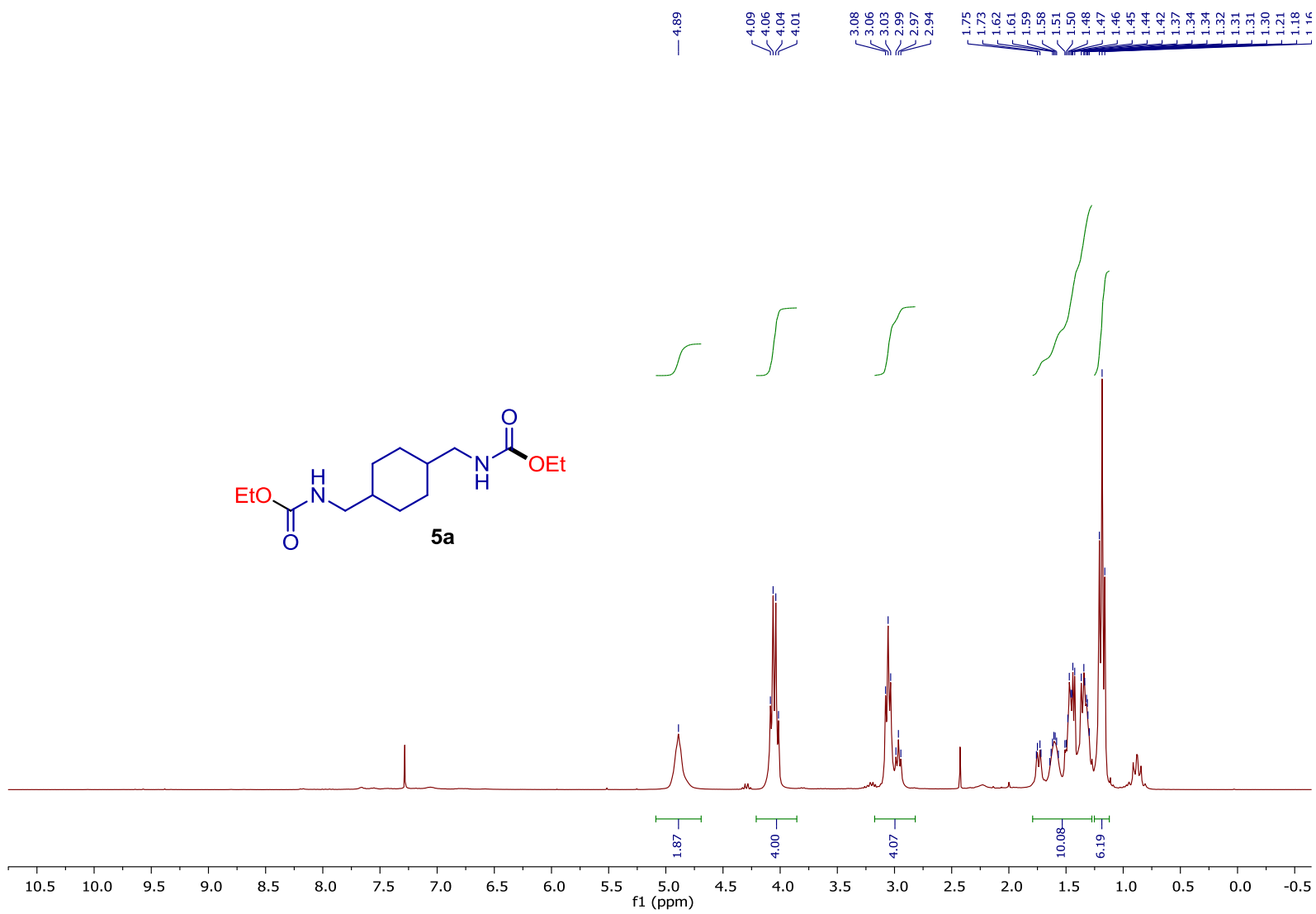
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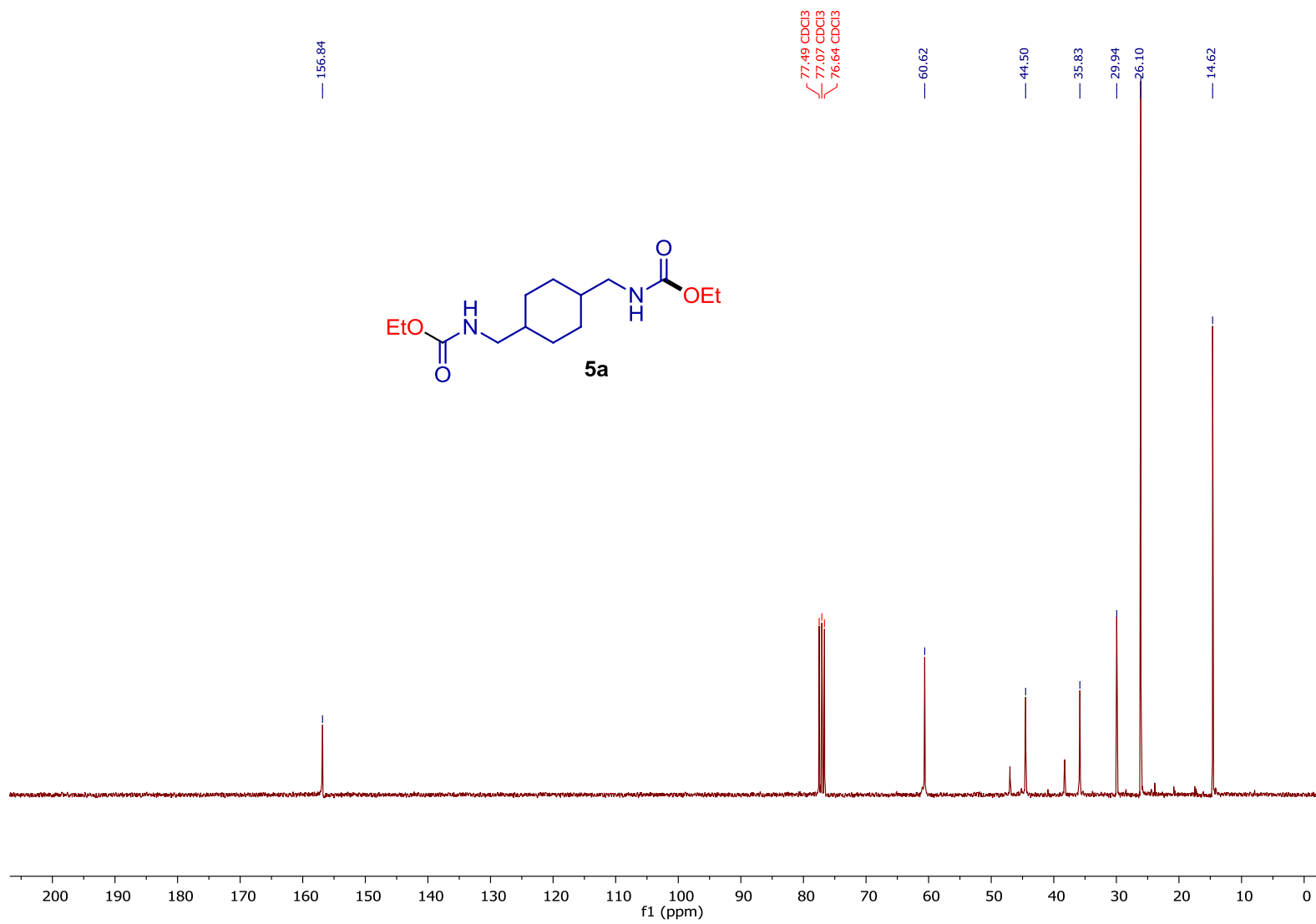
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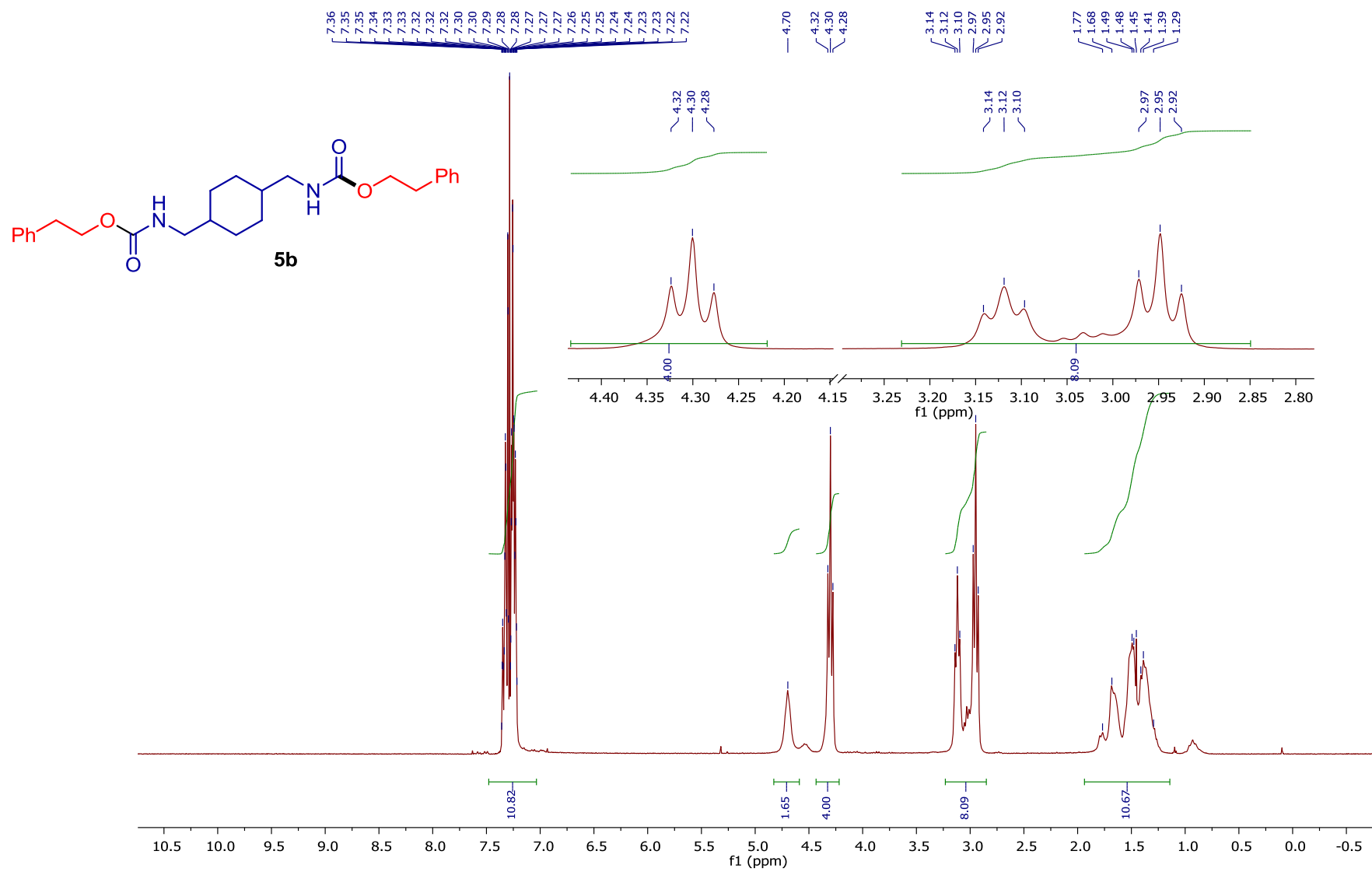
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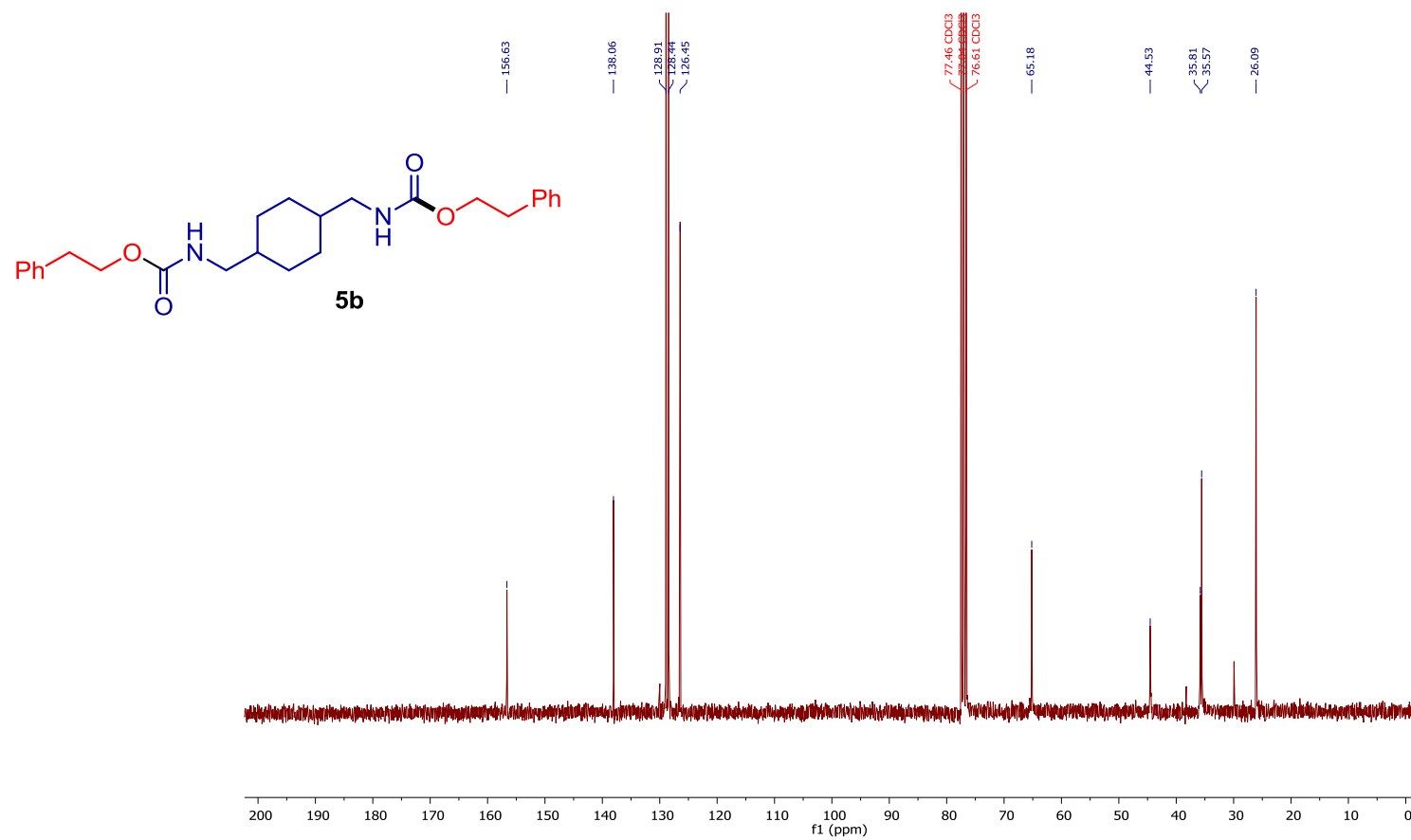
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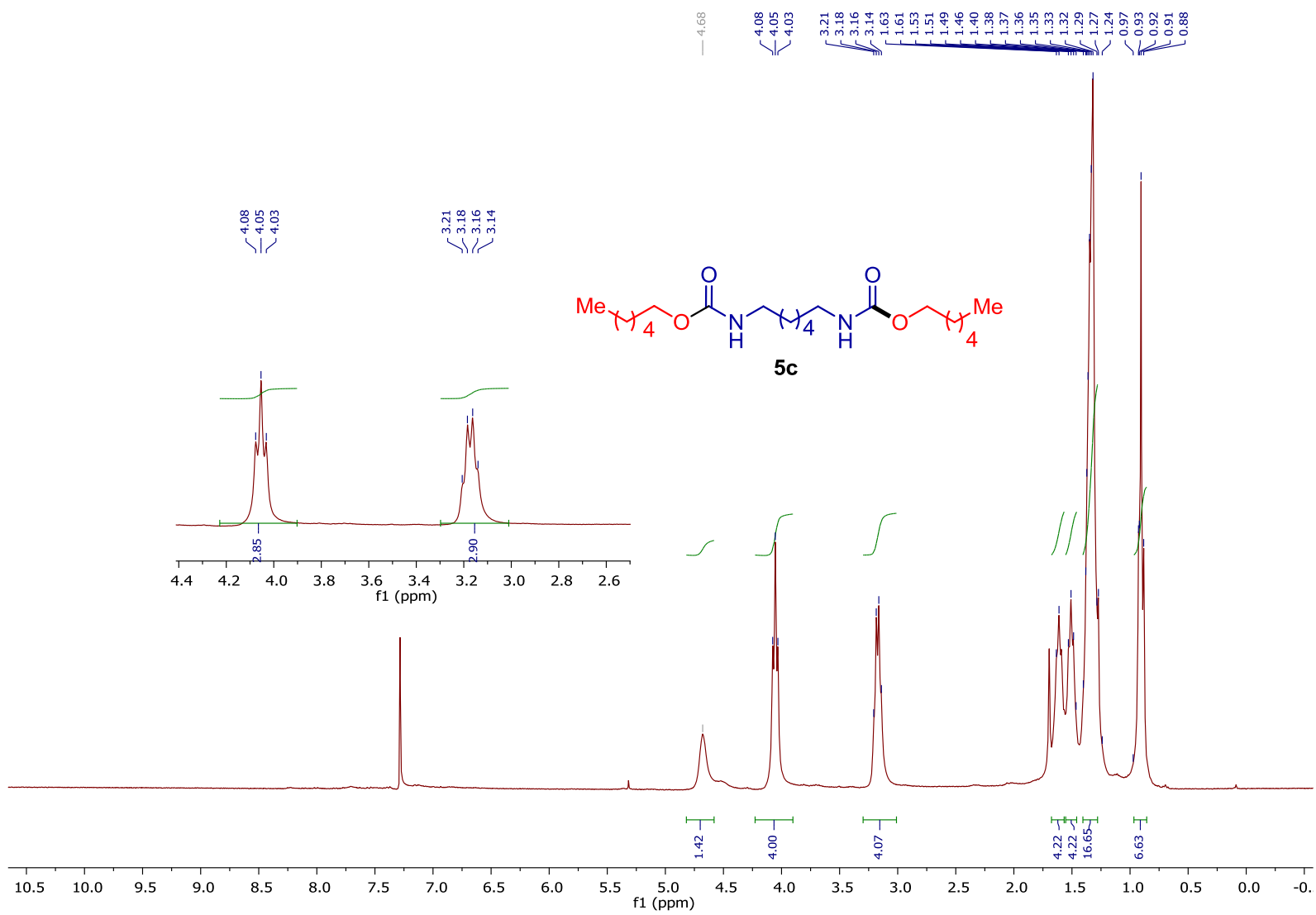
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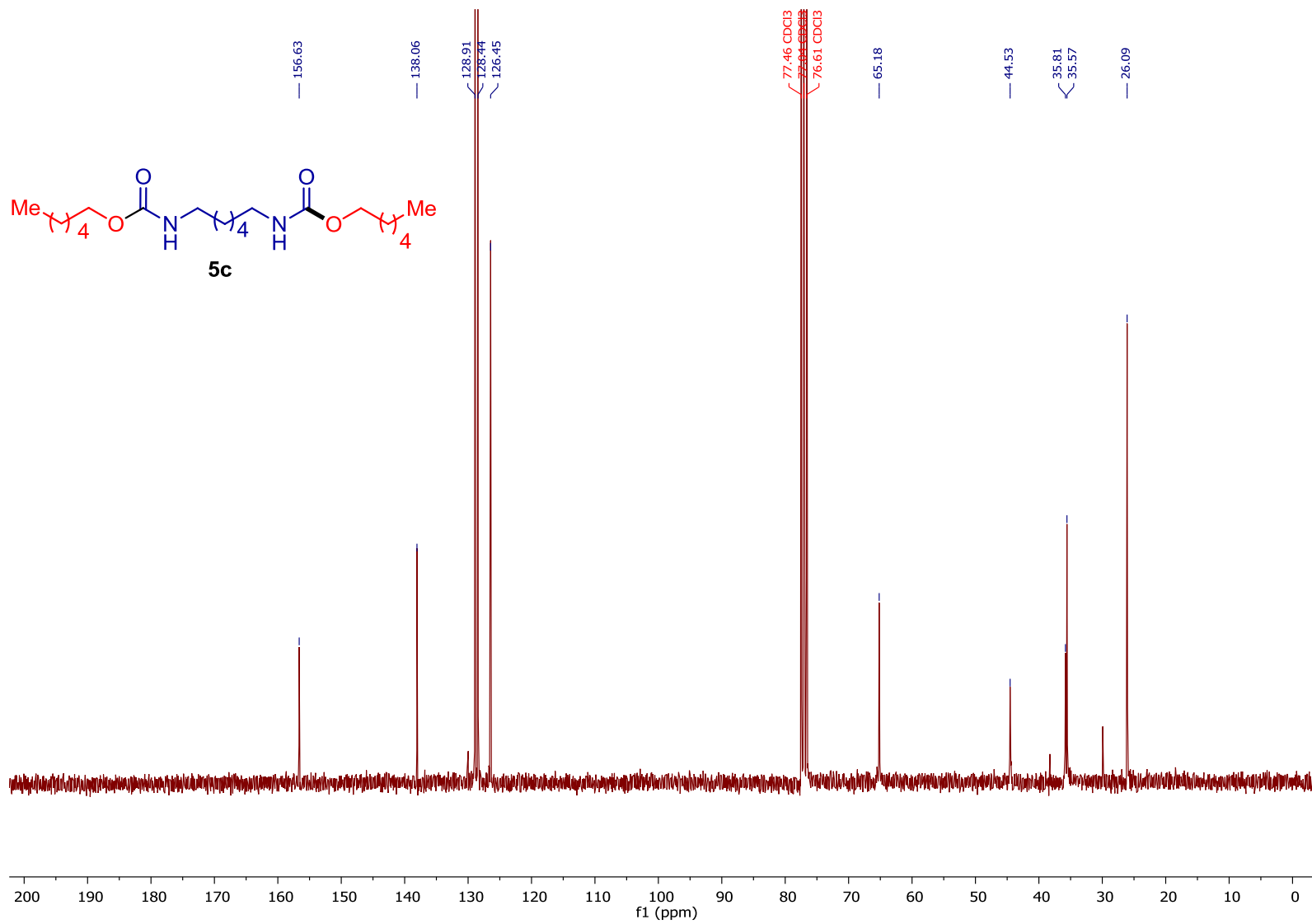
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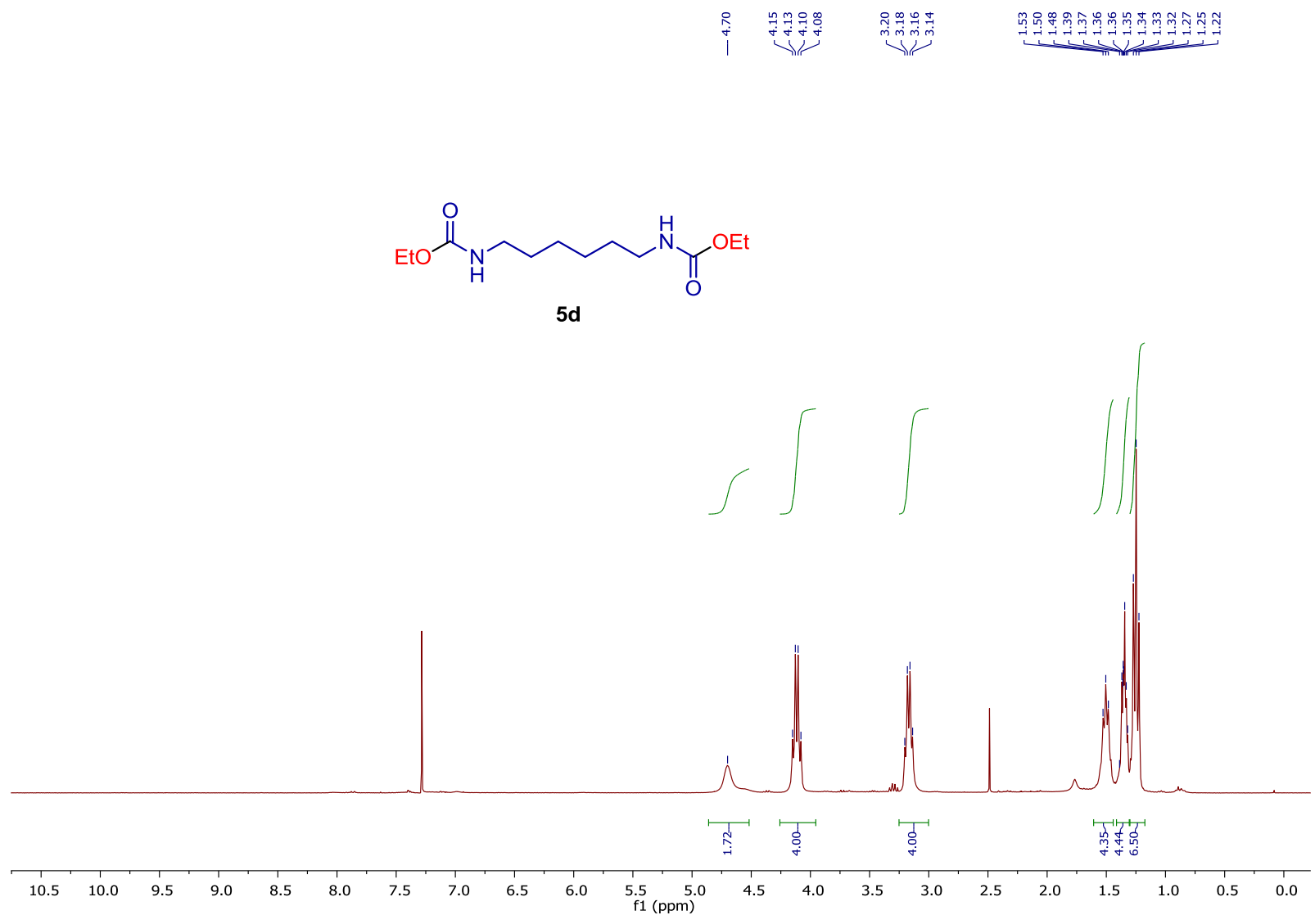
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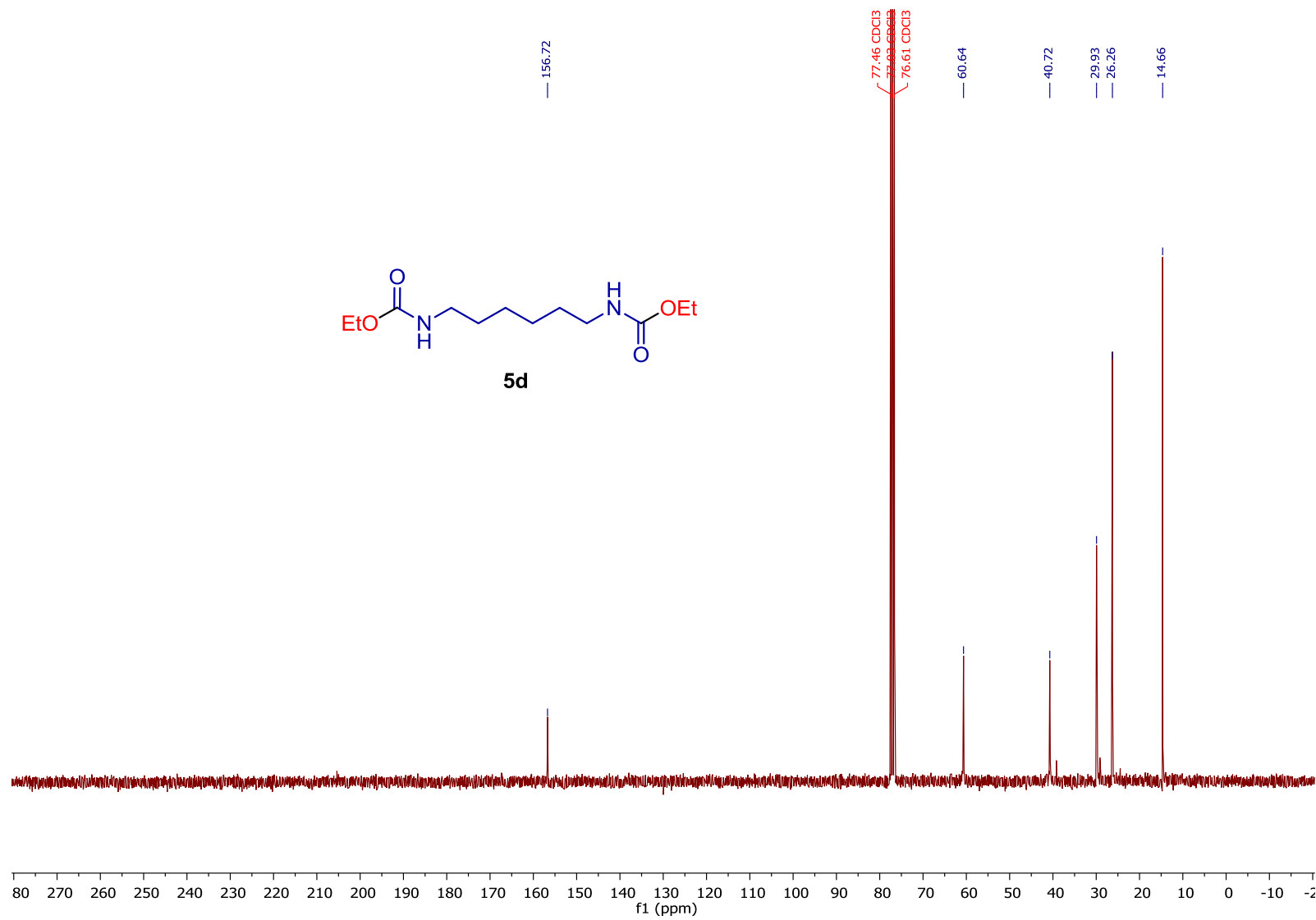
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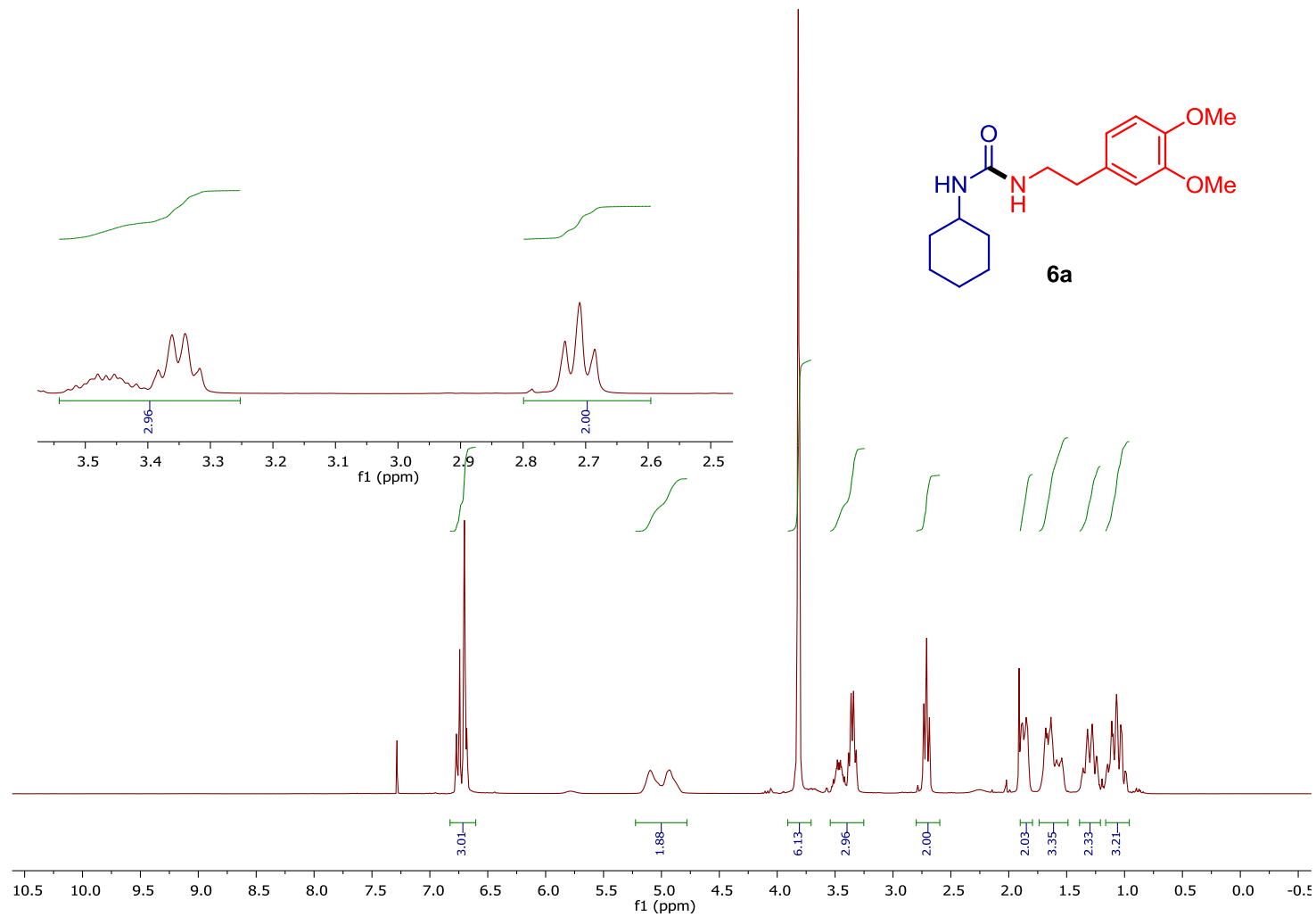
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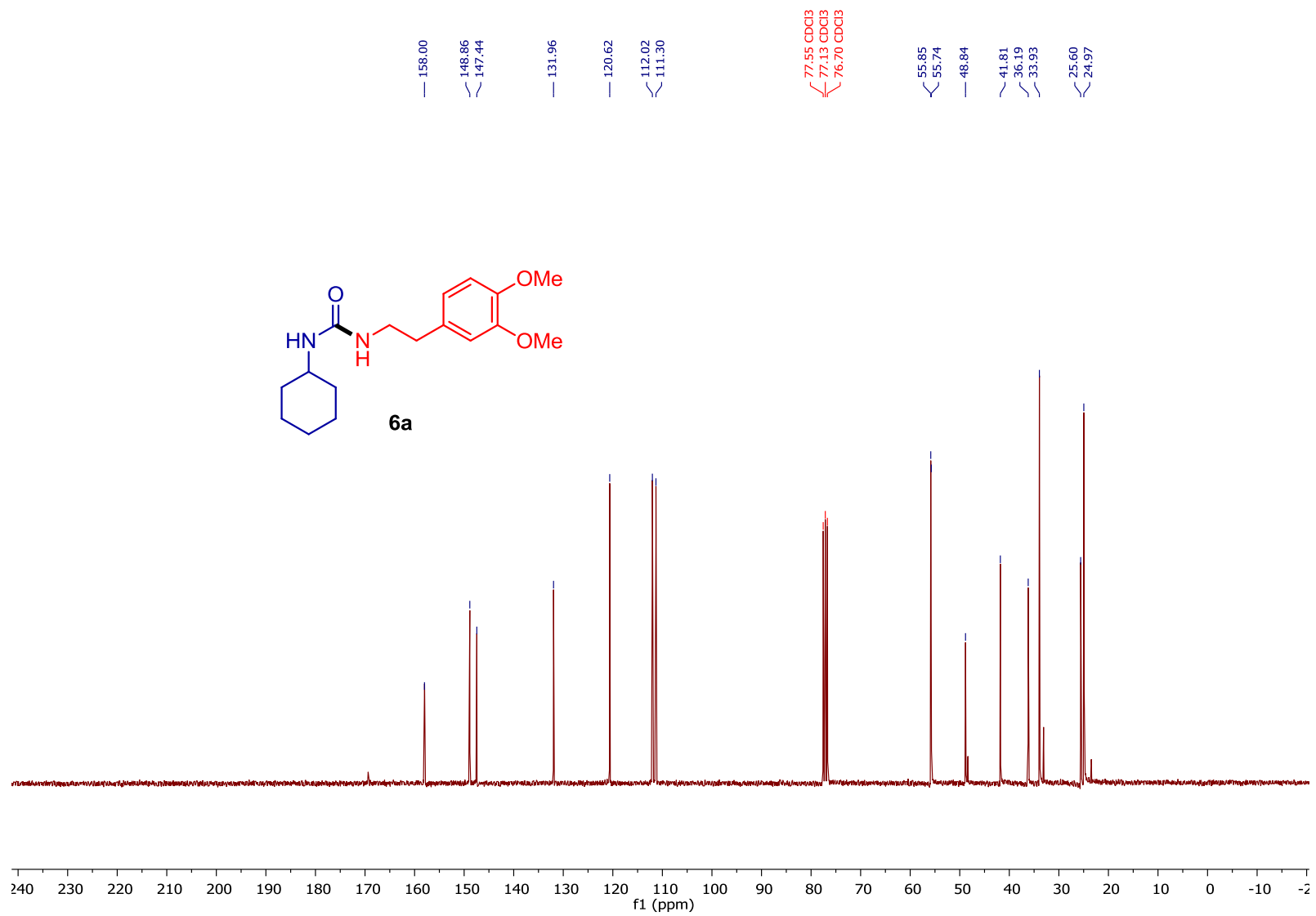
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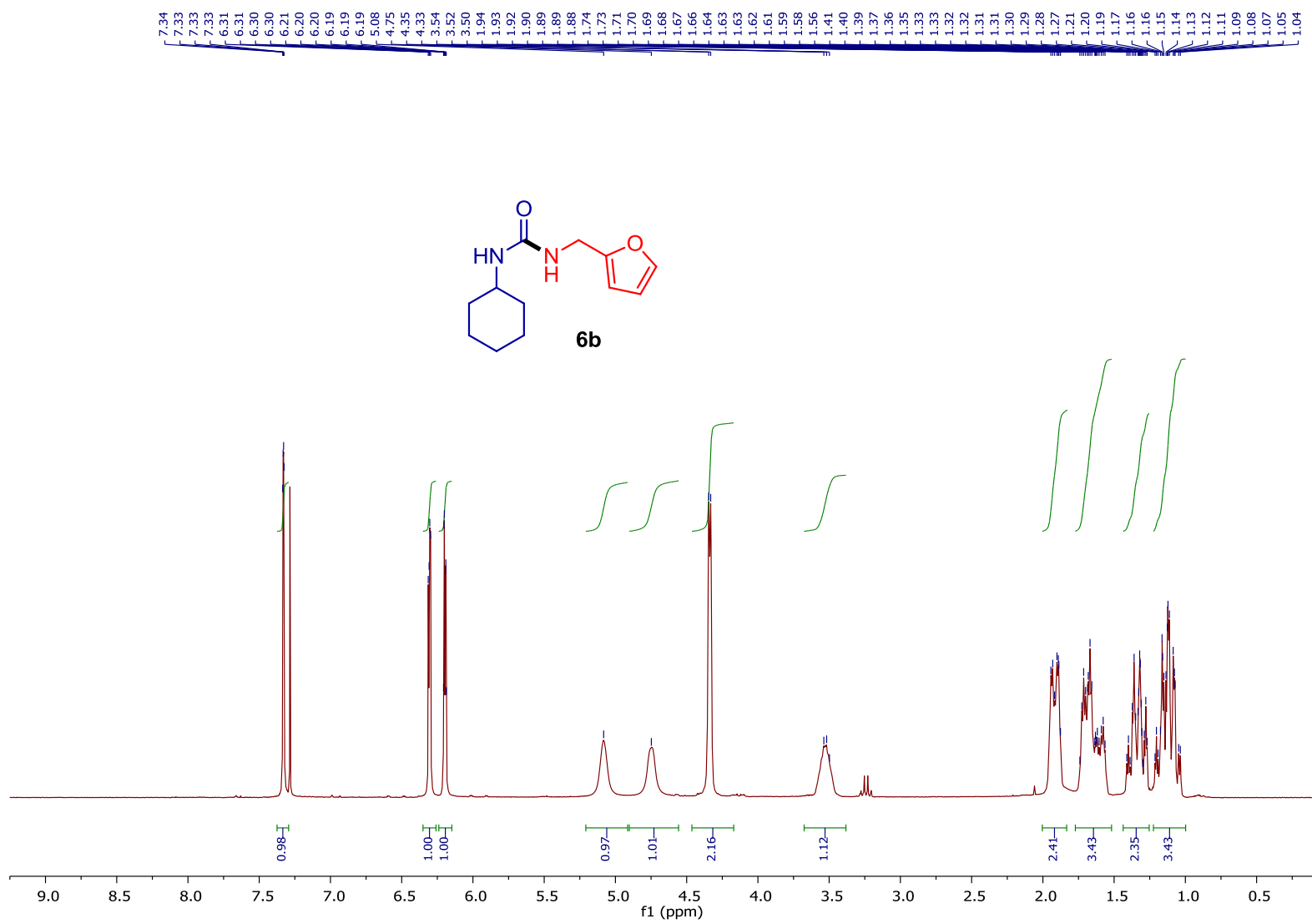
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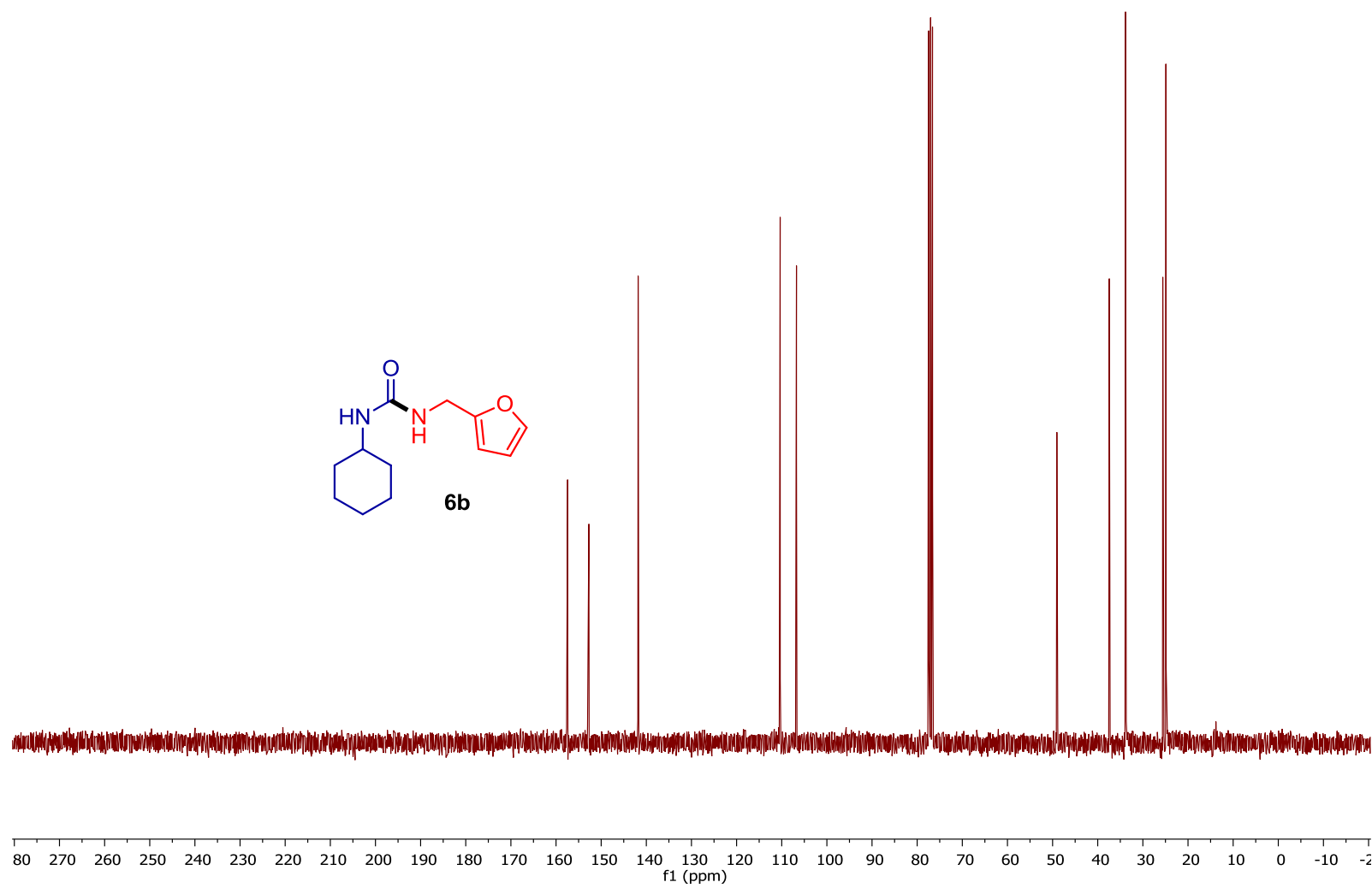


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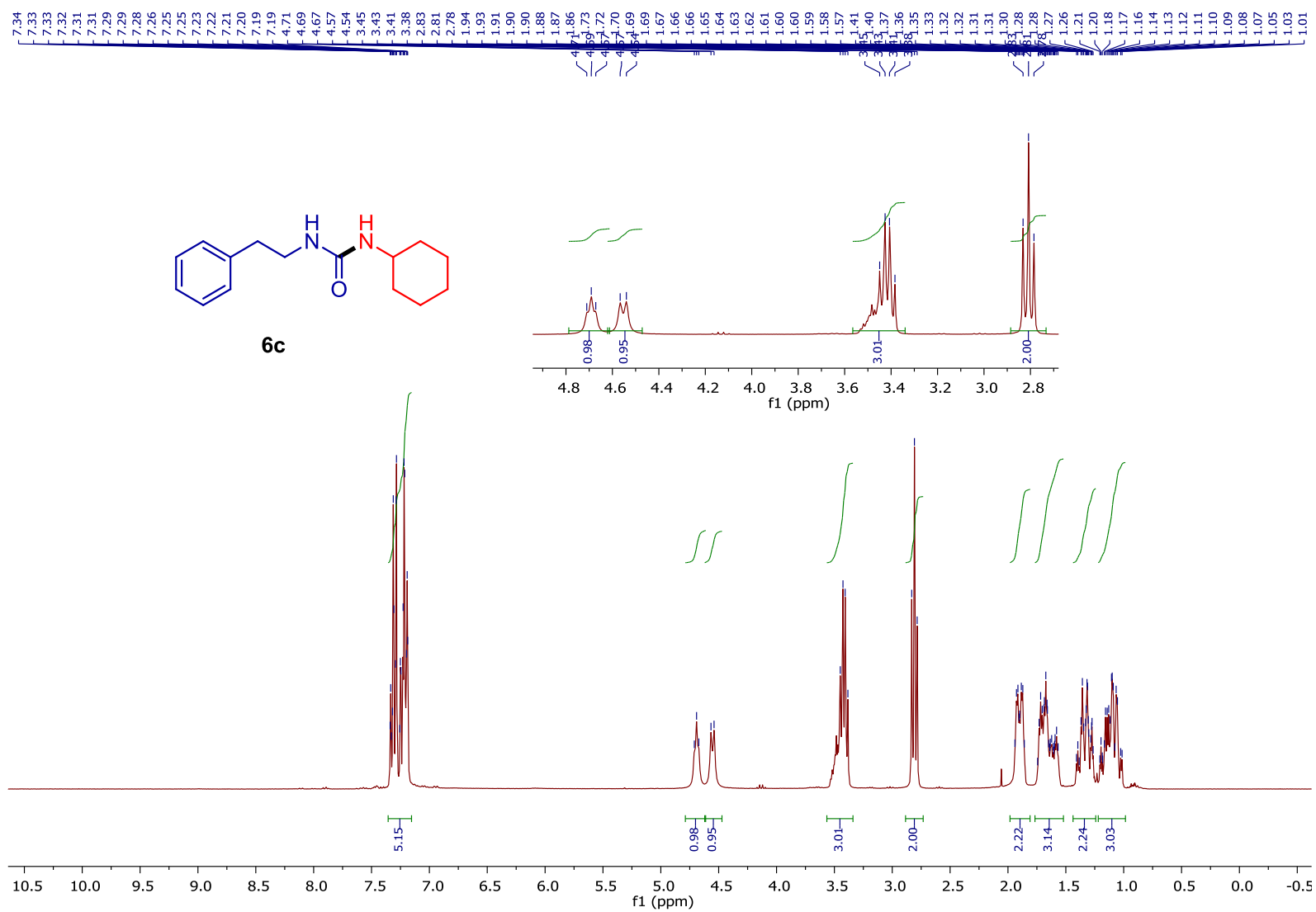


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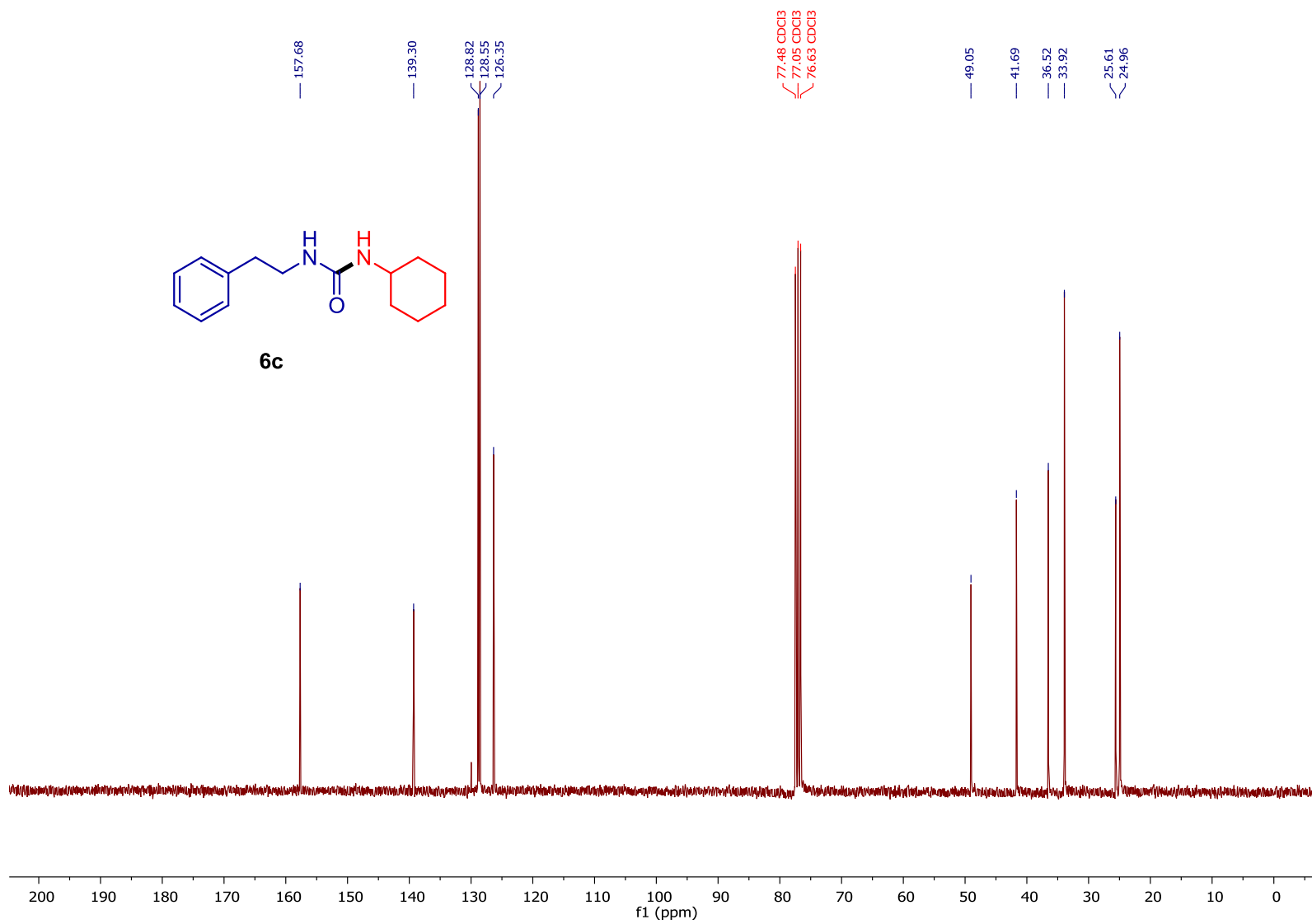




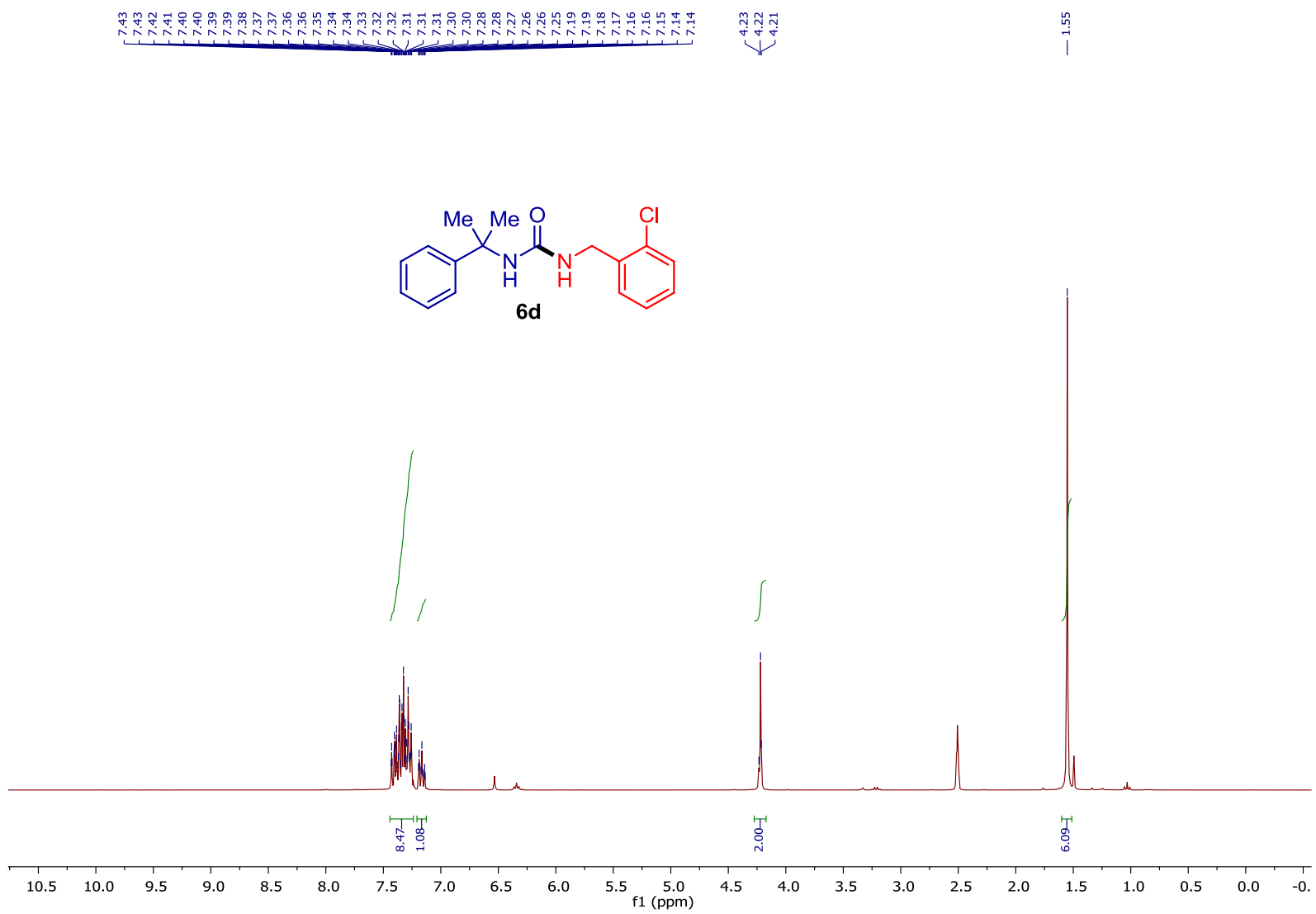
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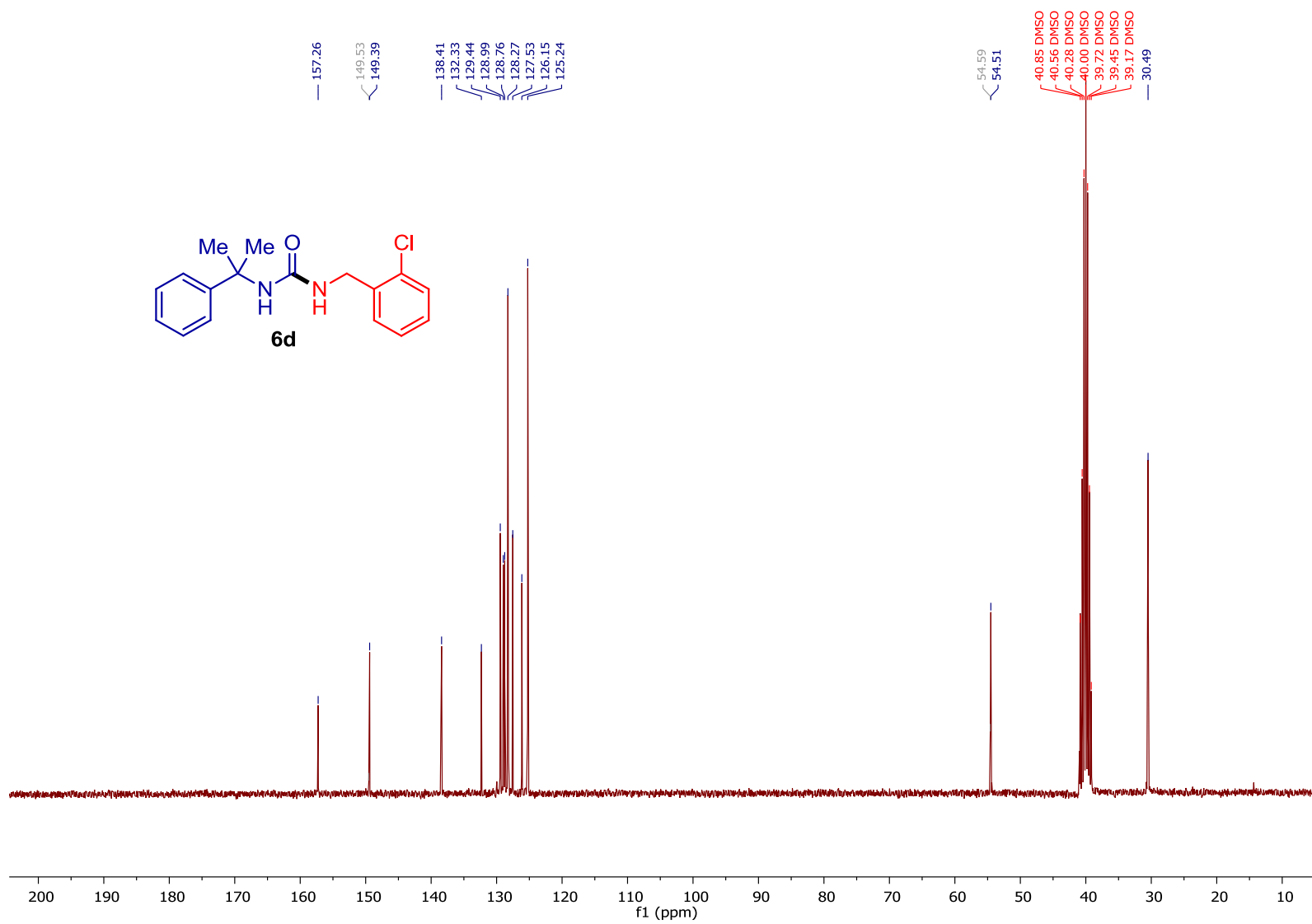
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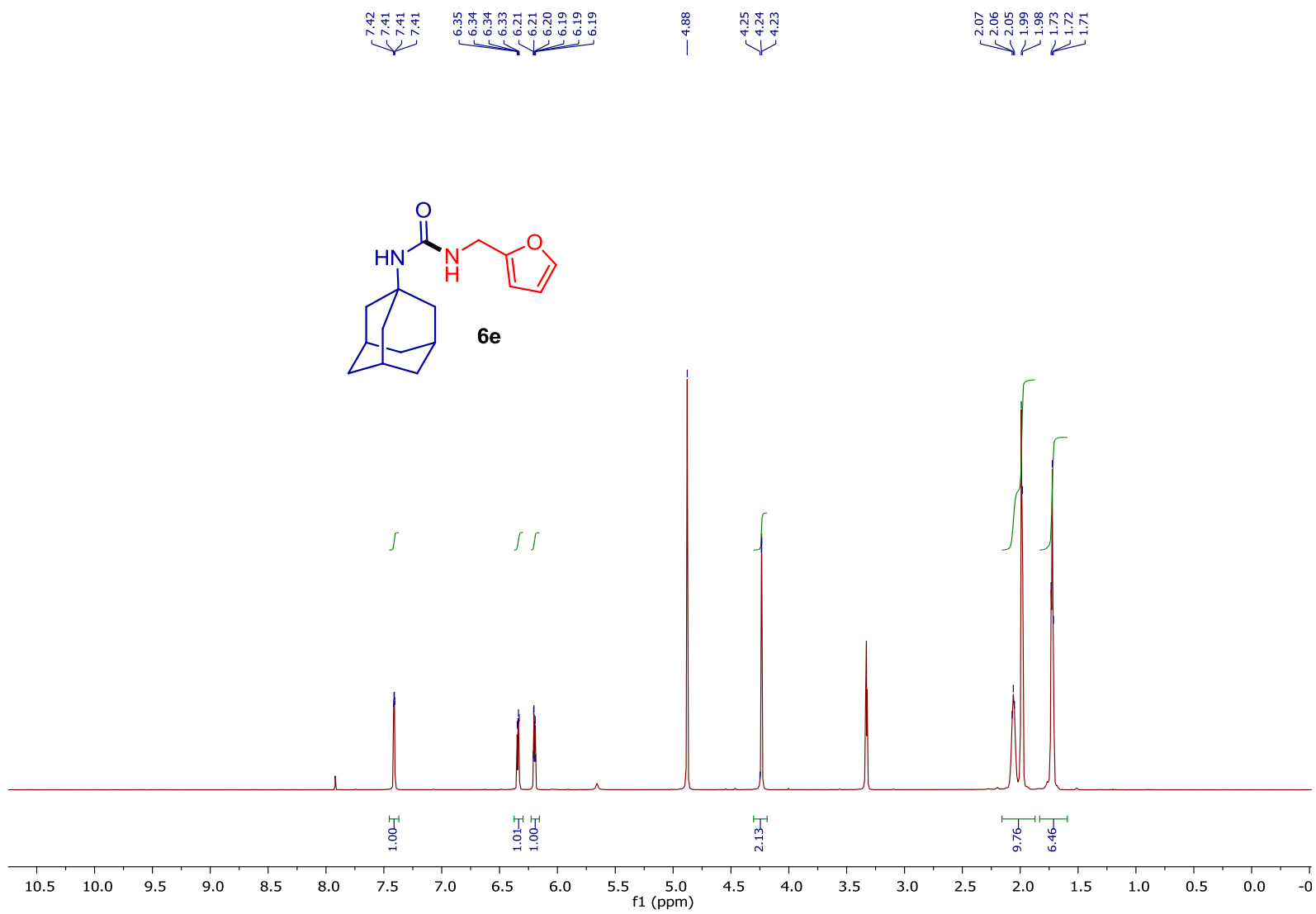
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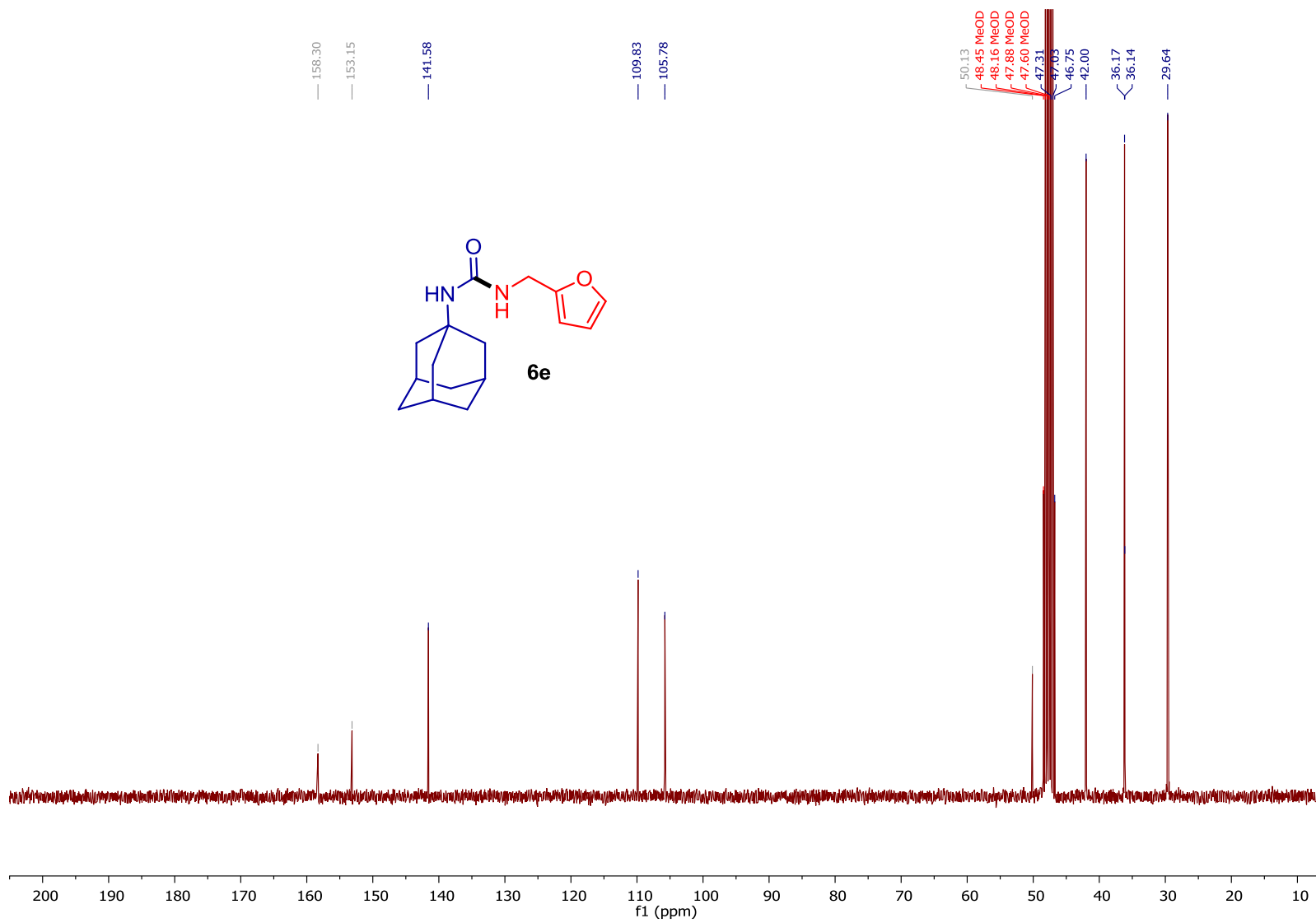
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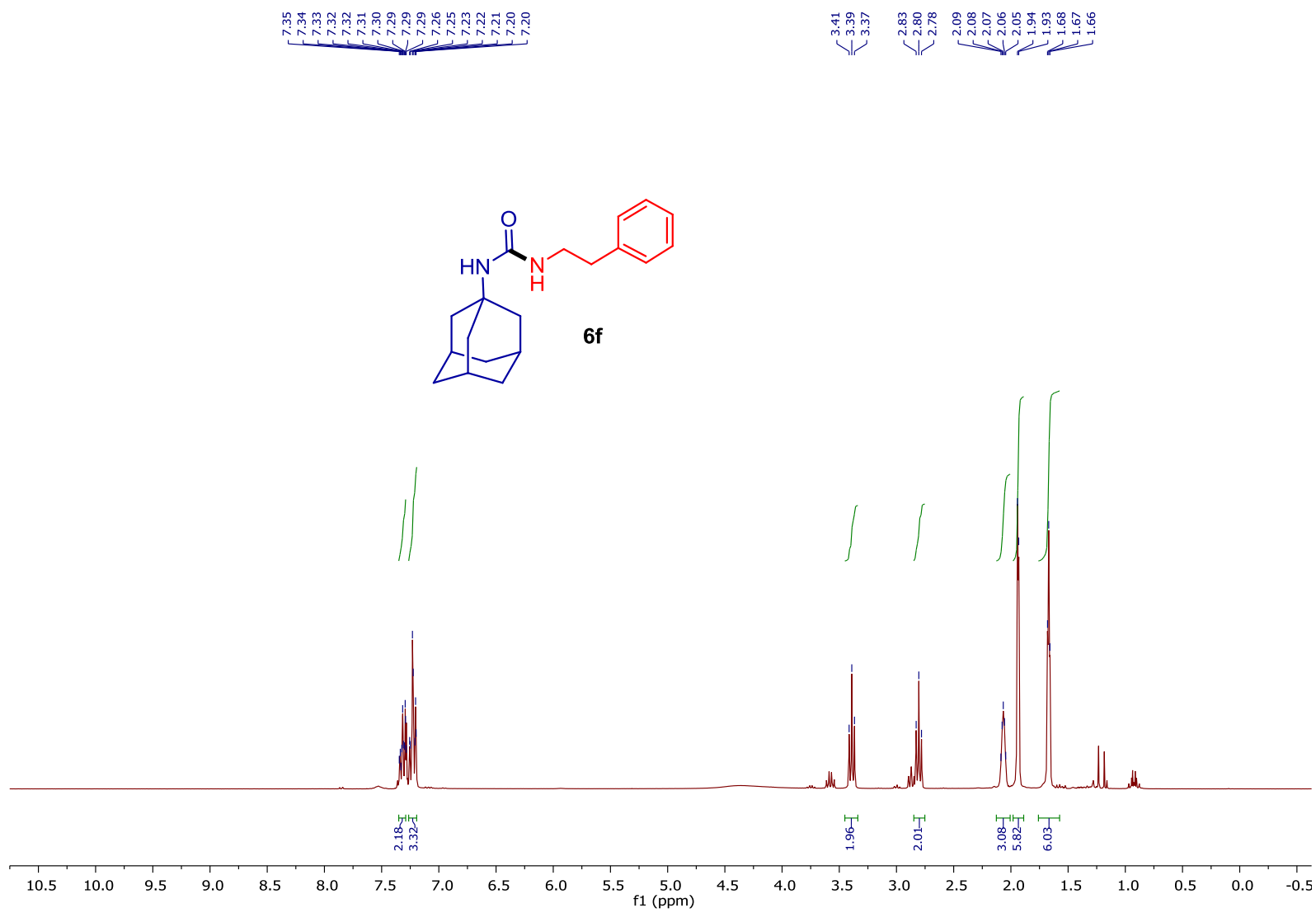
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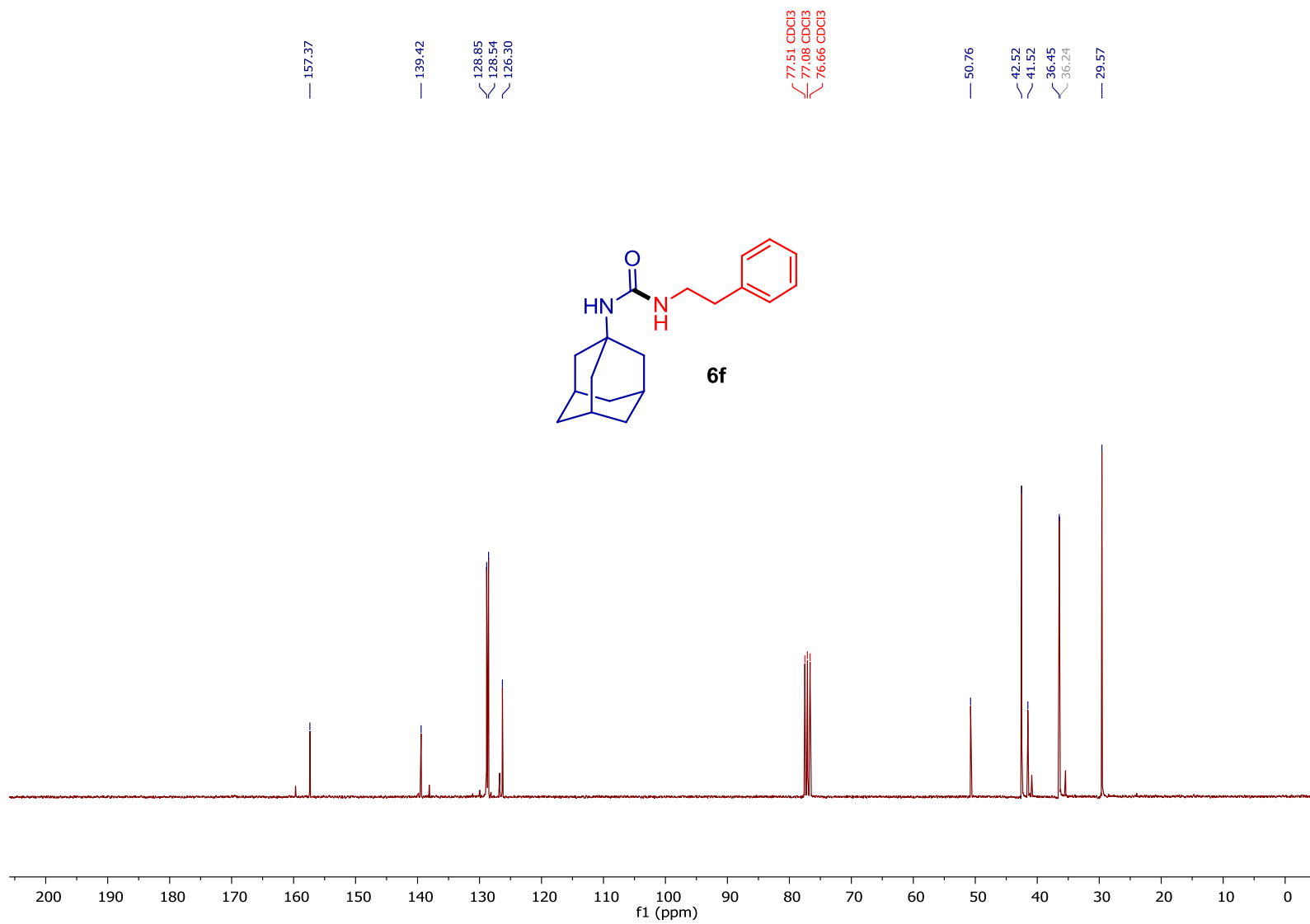
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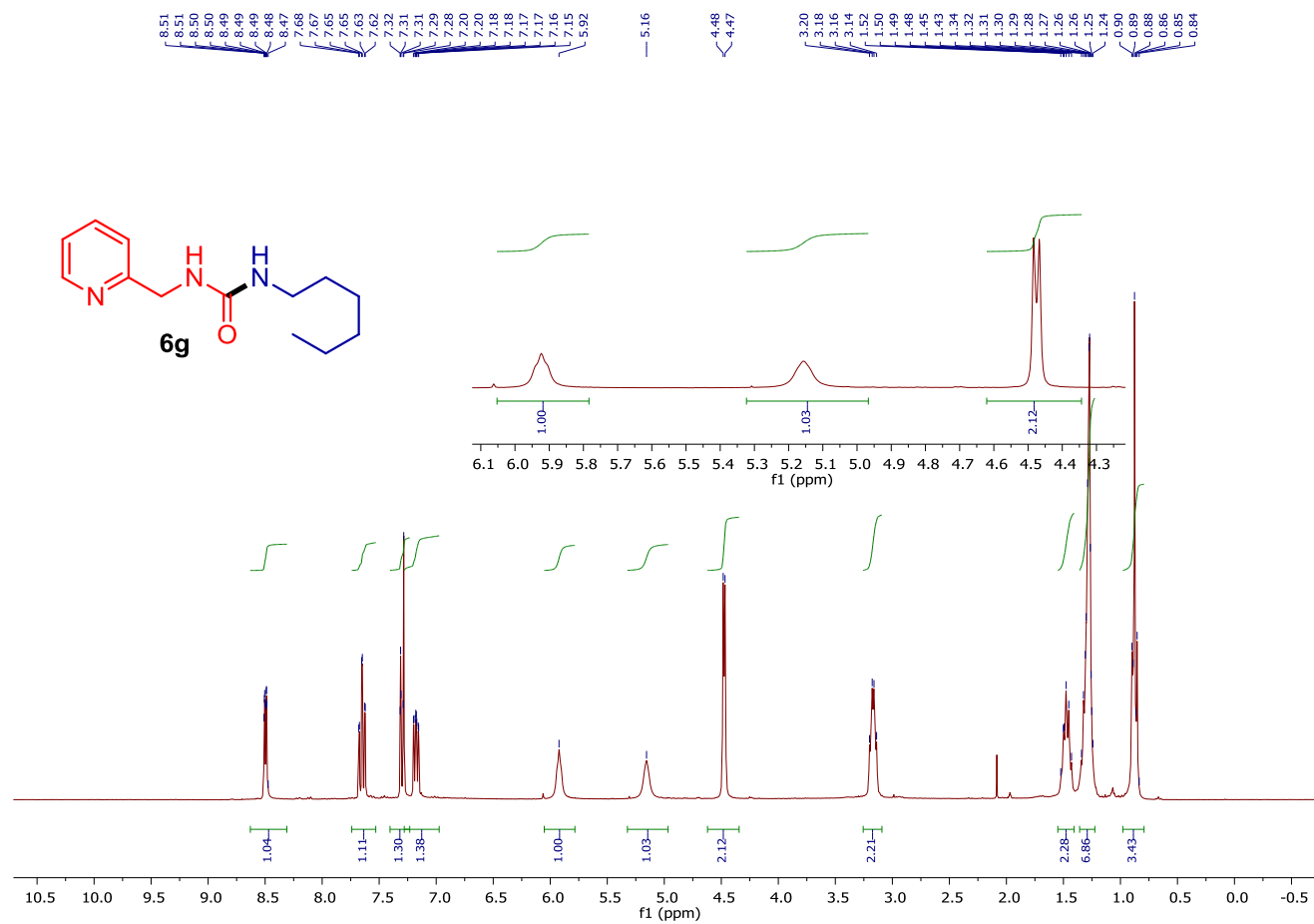
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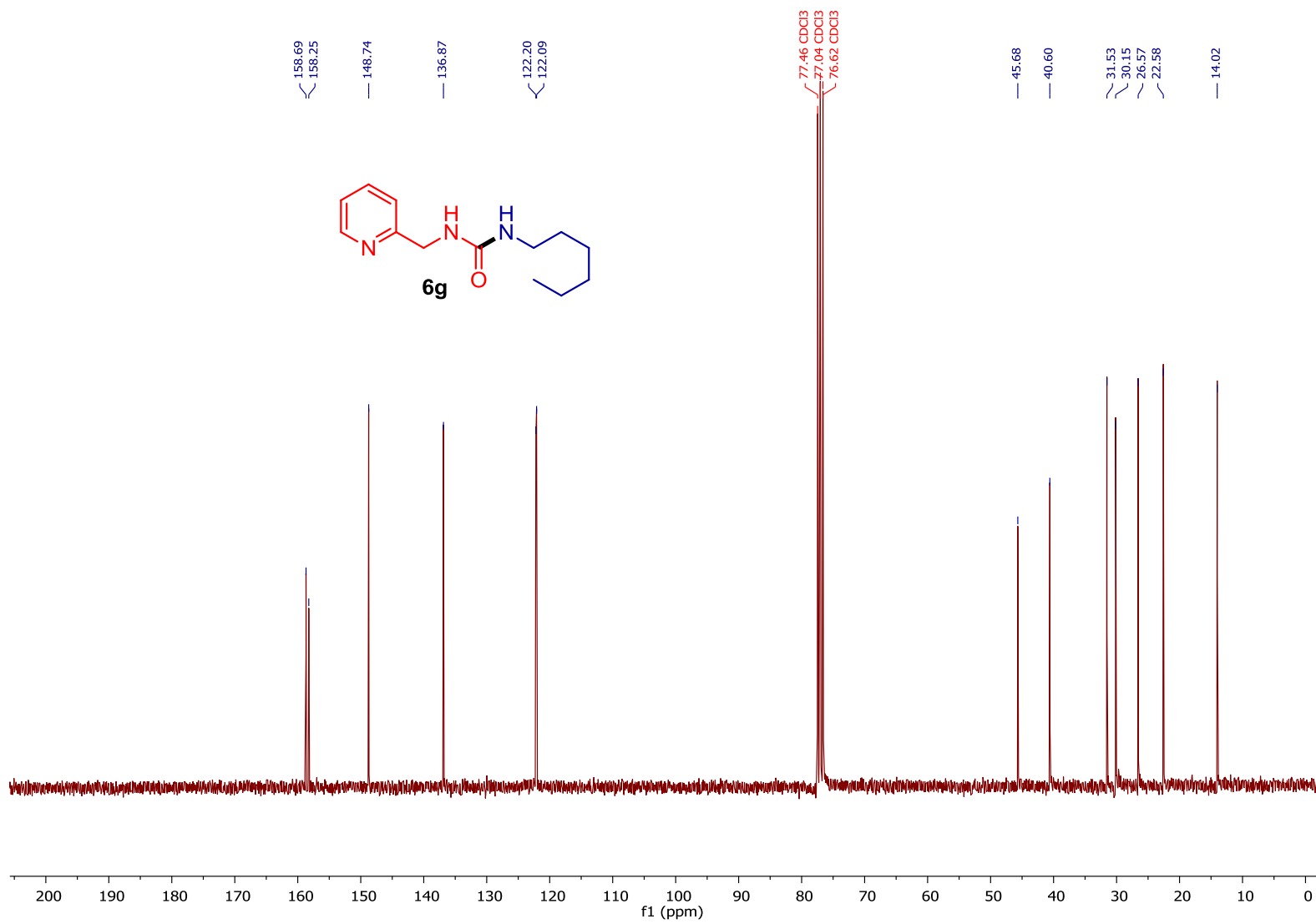
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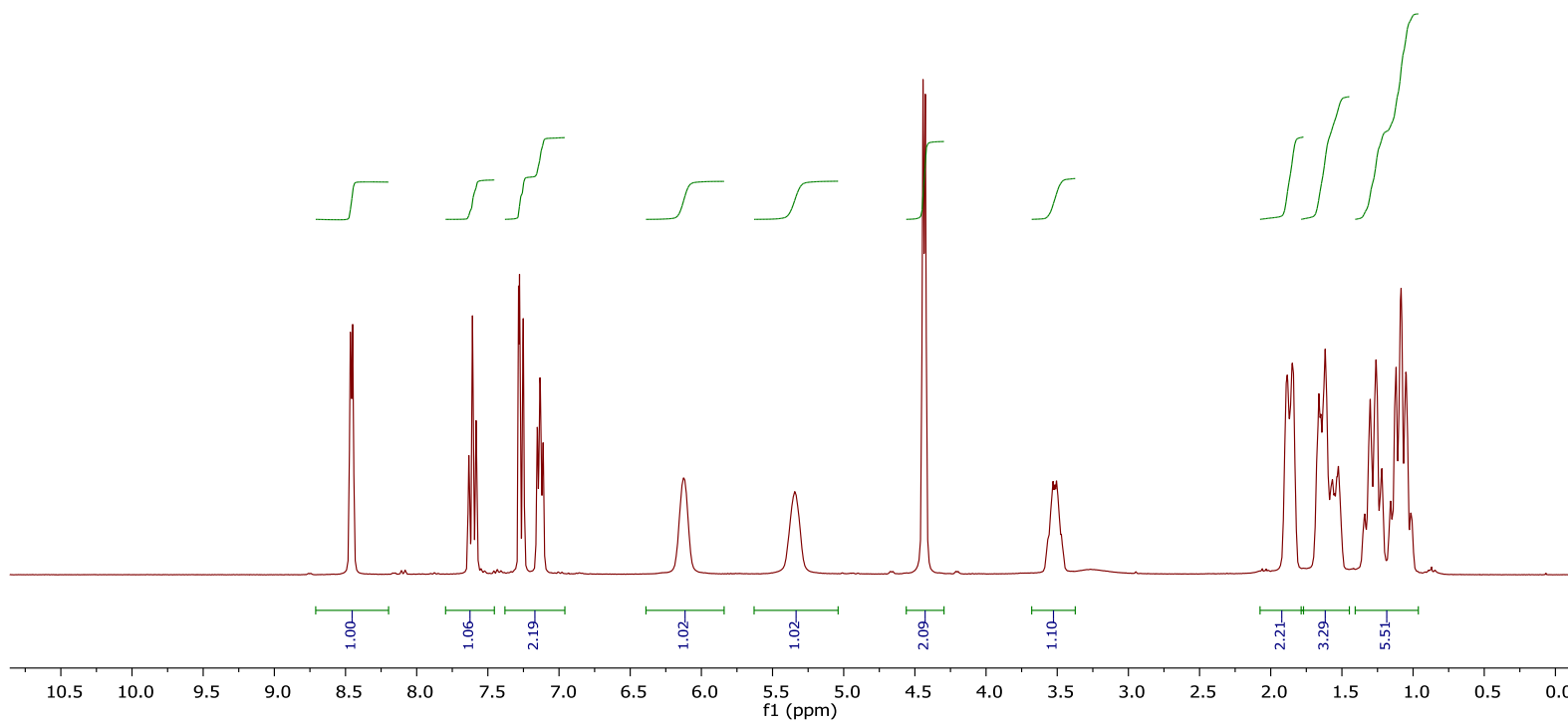
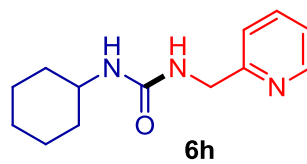
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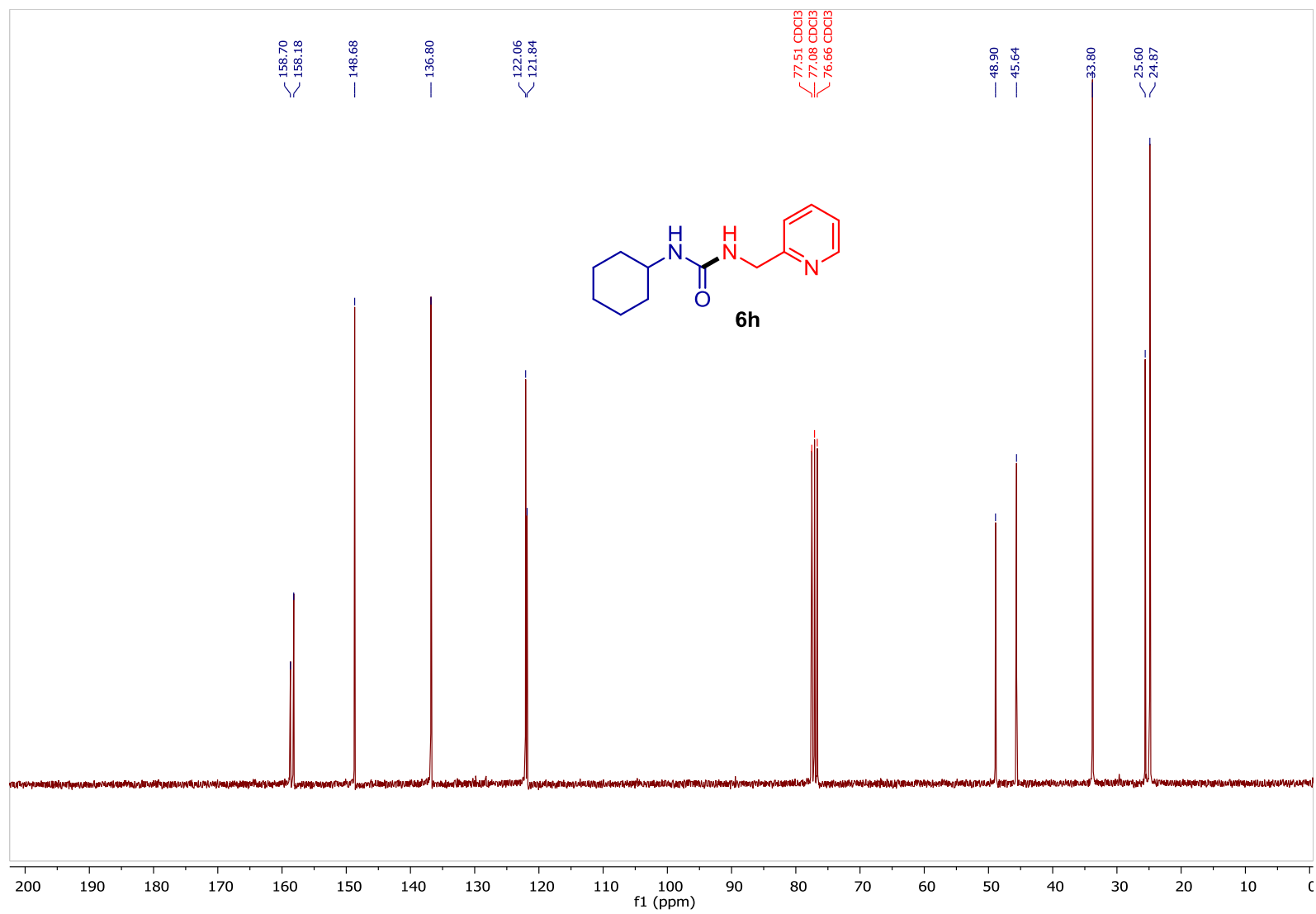
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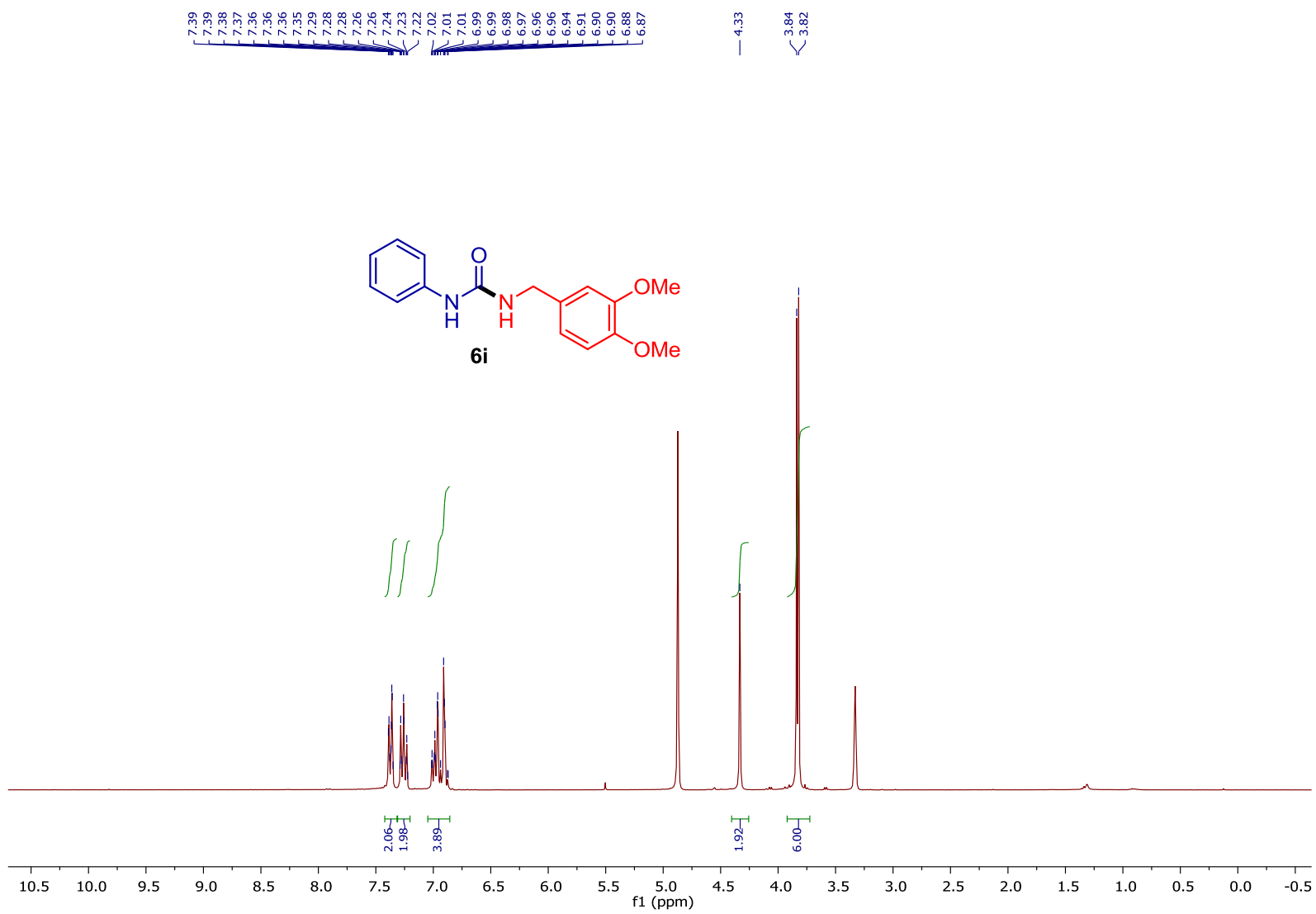
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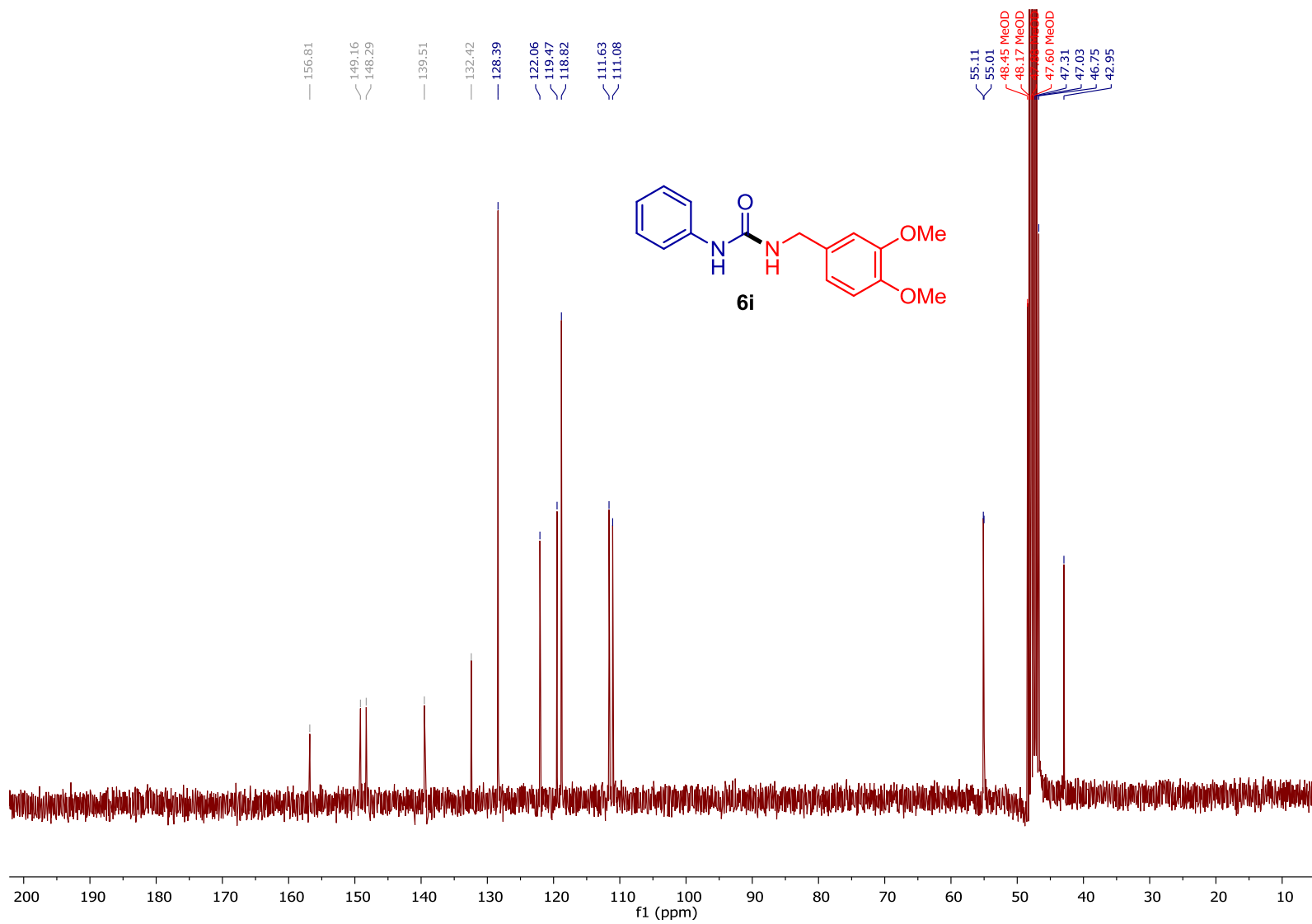
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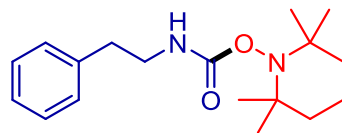
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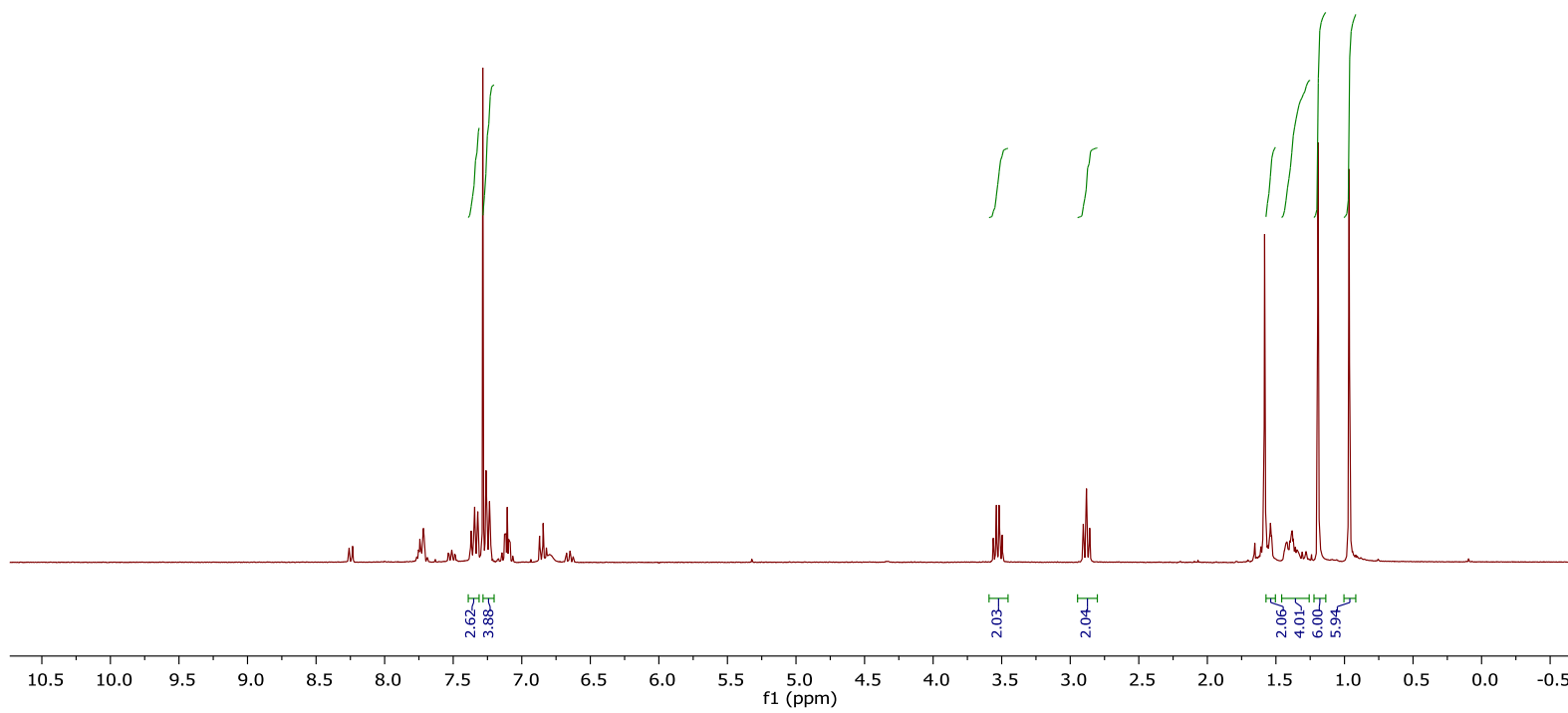
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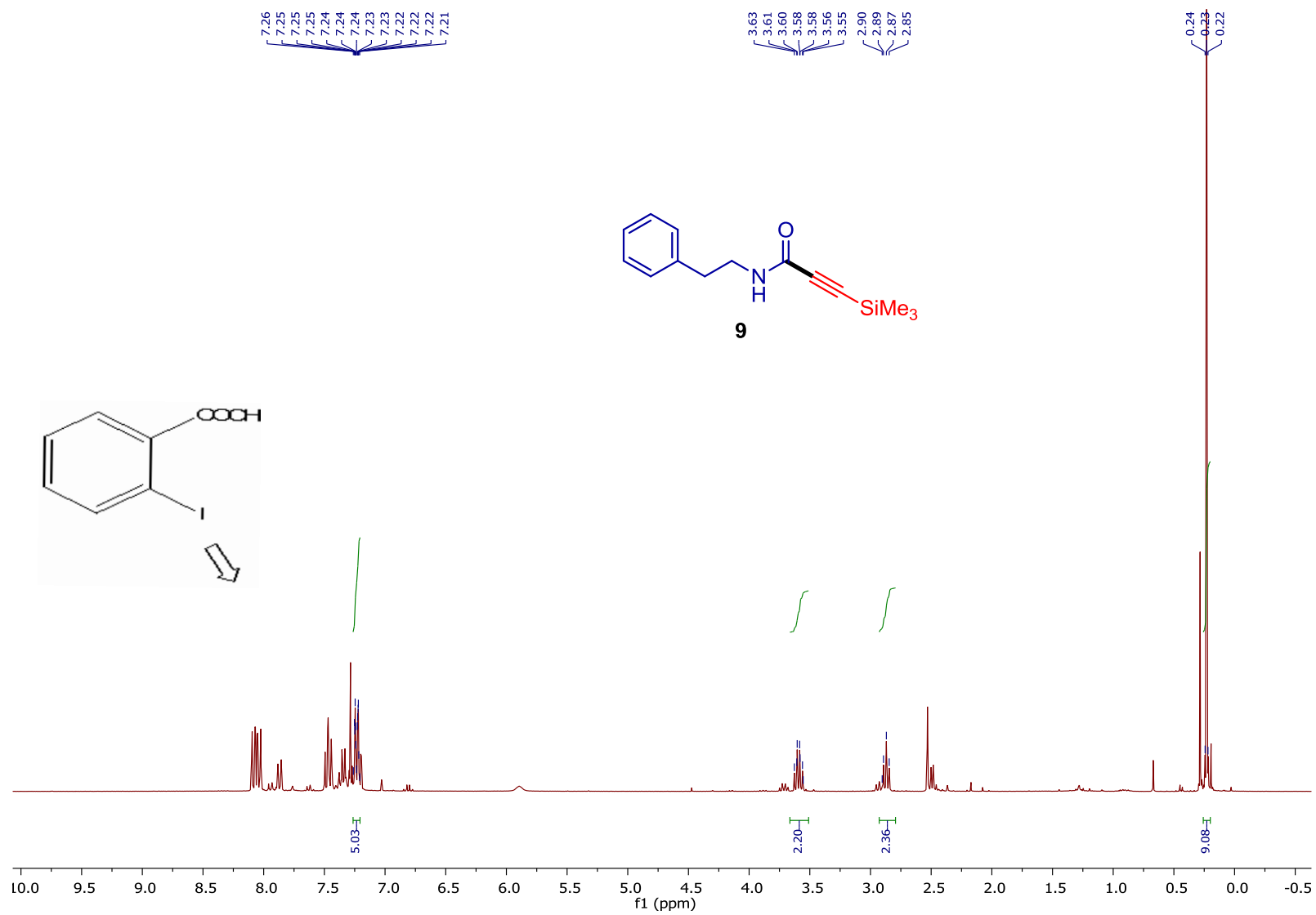


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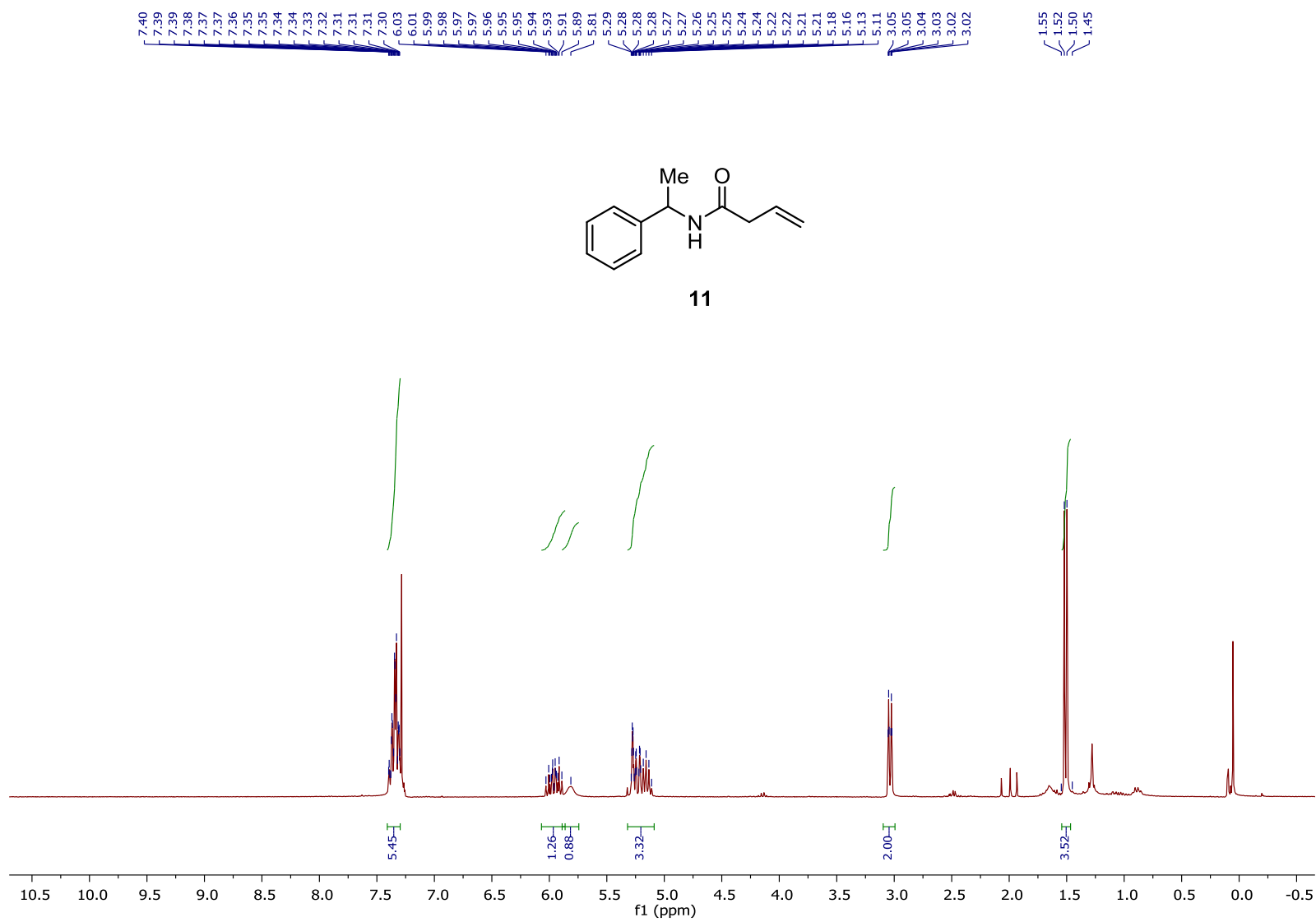


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Supporting Information



Supporting Information



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