Photocatalyzed Decarboxylation of Oxamic acids Under Near- Infrared Conditions.

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Supporting Information

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1. General Information:

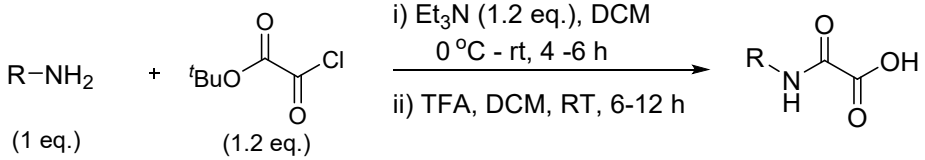
1,2-Dichloroethane (DCE) and acetonitrile (MeCN) were distilled using calcium hydride. Dichloromethane (DCM), tetrahydrofuran (THF) and methanol were dried over activated alumina columns on MBraun Solvent Purification System (SPS-800). Haemoglobin bovine (lyophilized powder, CAS Number: 9008-02-0) was procured from Sigma Aldrich company and the solution was made by dissolving the powder in water (17.0 g/L). All other reagent-grade chemicals including alcohols were purchased from commercial suppliers and were directly used without further purification unless

otherwise indicated. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous material unless otherwise stated.

^{1}H-NMR and ^{13}C-NMR were performed using Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), $CDCl_3$ was used as an internal reference. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively unless otherwise indicated. The following notations were used for the multiplicity: broad singlet = bs, singlet = s, doublet = d, triplet = t, quartet = q, doublet of doublets = dd and multiplets = m. High-resolution mass spectra (HRMS) analysis was performed using a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mode. FTIR analysis was performed using a Perkin-Elmer Spectrum 100 using a KBr disc or pellet. Optical rotation of the chiral compounds were determined using a Rudolph Research Analytical Autopol III Automatic Polarimeter. Melting point (m.p.) determination was done using Stuart melting point apparatus. Thin layer chromatography (TLC) was done using silica gel 60 F254 pre-coated plates (Merck) and visualized with potassium permanganate, ceric ammonium molybdate or UV light. Flash chromatography was performed using silica gel (0.043-0.063 mm).

2. General procedure for preparation of oxamic acids

Method A: [1,2,3,4,5,6.]



Anhydrous CH_2Cl_2 (0.3 M), corresponding amine (20 mmol, 1.0 eq.) and Et_3N (1.2 eq.) were charged into a dry two-neck round-bottom flask equipped with magnetic stirrer and under argon atm, using syringe fitted with metal needle. Note: solid amines were first weighed into the flask, flushed with argon before the other liquid reaction components were added *via* syringe. The resulted solution was brought to 0^{o}C using ice. Then, *t*-butyl-2-chloro-2-oxo acetate (1.2 eq.) was added to the mixture dropwise over 10 min under constant stirring. The mixture was thereafter warmed to room temperature and allowed to stir for 4–6 h. The mixture was washed with 1M HCl (50 mL) and the aqueous layer was further extracted with DCM (2 x 30 mL). The combined organic layer was washed with brine, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The obtained gel/solid (oxamate ester) was dissolved in DCM (0.3 M), TFA (5.0 eq.) was added into the mixture and was stirred at room temperature for 6 to 12h. The mixture was concentrated in vacuo to deliver the oxamic acids as milky to white solids.

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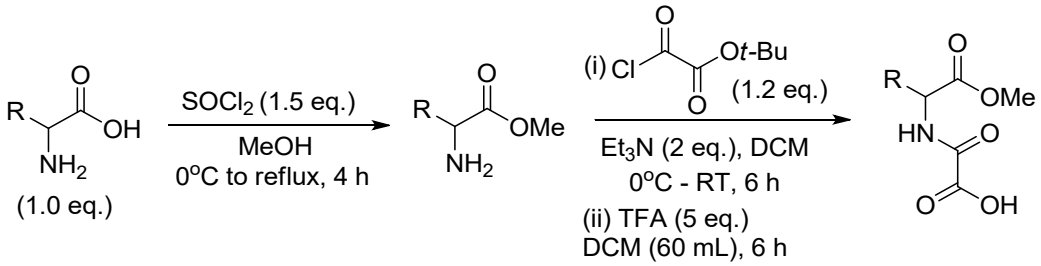
1 I. M. Ogbu, J. Lusseau, G. Kurtay, F. Robert, Y. Landais, *Chem. Commun*., **2020**, *56*, 12226-12229.
2 G. G. Pawar, F. Robert, E. Grau, H. Cramail, Y. Landais, *Chem. Commun*., **2018**, *54*, 9337-9340.
3 A. H. Jatoi, G. G. Pawar, F. Robert, Y. Landais, *Chem. Commun*., **2019**, *55*, 466-469.
4 a) S. D. Linton *et. al. J. Med. Chem*. **2005**, *48*, 6779-6782. b) H. Hanchu, J. Kunfang, C. Yiyun, *Angew. Chem. Int. Ed.* **2015**, *54*, 1881-1884.
5 J. Bálint, G. Egri, M. Czugler, J. Schindler, V. Kiss, Z. Juvancz, E. Fogassy, *Tetrahedron: Asymmetry* **2001**, *12*, 1511–1518.
6 N. S. Vujicic, Z. Glasovac, N. Zweep, J. H. van Esch, M. Vinkovic, J. Popovic, M. Zinic, *Chem. Eur. J*. **2013**, *19*, 8558-8572

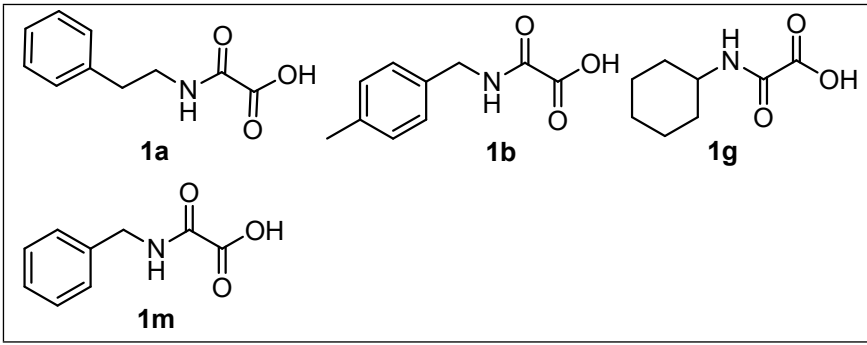
Mono-oxamic acids can further be recrystallized by dissolving it in minimum quantity of ether and adding hexane. Bis-oxamic acids can be purified further by washing with ether.

Method B: Preparation of chiral oxamic acids.[1,3]

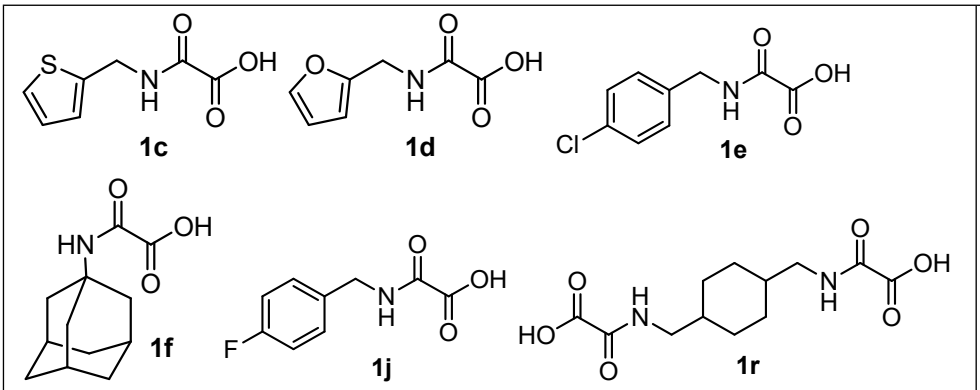
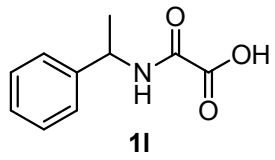
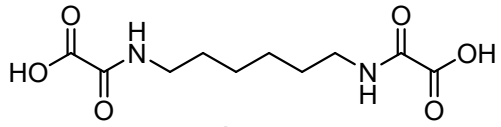
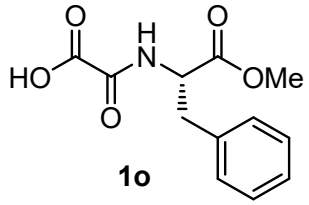


Amino acid (30.0 mmol, 1.0 eq.) was weighed into a dry two-neck round-bottom flask equipped with a reflux condenser. The content was flushed with argon, methanol (25 mL) was added under argon. The flask was cooled to 0°C, then thionyl chloride (45.11 mmol, 1.5 eq.) was added to the heterogeneous mixture dropwise over 15 min under constant stirring during which a homogeneous solution was obtained. The mixture was then warmed to room temperature and then refluxed for 4 h. The reaction mixture was concentrated under reduced pressure resulting in a gel. The product was washed with *n*-hexane by stirring it in the solvent for 10 min, then decanting the solvent. This was repeated twice to give a solid product. The solid was dissolved in DCM (60 mL) under argon atm, cooled to 0°C. Et_3N (60.15 mmol, 2 eq.) was added into the mixture followed by a dropwise addition of *t*-butyl-2-chloro-2-oxo acetate (36.08 mmol, 1.2 eq.) over 10 min under constant stirring. The mixture was warmed to room temperature and allowed to stir for 6h. The mixture was washed successively with water (100 mL) and brine (100 mL), dried over sodium sulfate and concentrated under reduced pressure to give a solid product. The crude product was dissolved in DCM (60 mL) and treated with TFA (11.5 mL, 150 mmol, 5 eq.) at room temperature for 6 h. The resulted solution was concentrated in vacuo to give the desired chiral oxamic acid.

Table S1: Oxamic acids substrates used for the reactions.

 **1a** **1b** **1g** **1m**	**Method A** Ref. [7]

[7] S. D. Linton *et. al. J. Med. Chem*. **2005**, *48*, 6779-6782; (b) H. Hanchu, J. Kunfang, C. Yiyun *Angew. Chem. Int. Ed.* **2015**, *54*, 1881-1884.

	Ref. [2]
	Ref. [8]
	Ref. [9]
	**Method B** Ref. [1]

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

4-CzIPN was synthesized following previously reported procedure.[10] Carbazole (4.18 g, 25 mmol) was dissolved in dry THF (100 mL) in a two-neck round-bottom flask under an argon atm, at room temperature. NaH (60% in oil, 1.4 g, 60 mmol) was added slowly under stirring. The mixture was stirred for 30 min, thereafter tetrafluoroisophthalonitrile (1.0 g, 5 mmol) was added and the mixture was stirred further for 12h. The reaction was quenched with water (5 mL) and concentrated in vacuo. The mixture was washed successively with water and EtOH to afford yellow solid product. This crude 4-CzIPN was recrystallized by dissolving it in minimum quantity of CH_2Cl_2 and adding pentane to give the pure 4-CzIPN (3.1 g, 79%) as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) 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). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 145.2, 144.6, 140.0, 138.2, 137.0, 134.8, 127.0, 125.79, 125.0, 124.8, 124.6, 123.9, 122.4, 122.0, 121.4, 121.0, 120.4, 119.7, 116.4, 111.6, 110.0, 109.5, 109.4. Spectroscopic data were in good agreement with literature.[10]

[8] J. Bálint, G. Egri, M. Czugler, J. Schindler, V. Kiss, Z. Juvancz, E. Fogassy, *Tetrahedron: Asymmetry* **2001**, *12,* 1511–1518.
[9] N. S. Vujicic, Z. Glasovac, N. Zweep, J. H. van Esch, M. Vinkovic, J. Popovic, M. Zinic, *Chem. Eur. J.* **2013**, *19,* 8558-8572.
[10] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, *492*, 234-238.

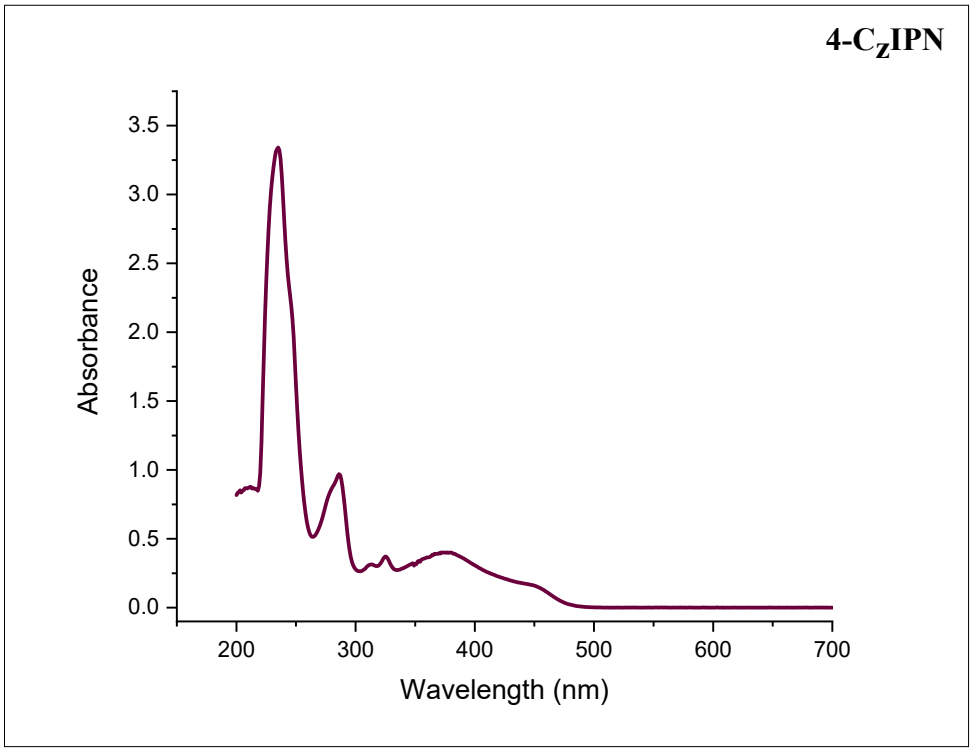
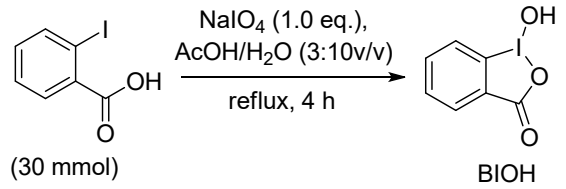


Figure S1: UV-visible absorption of 4-CzIPN in DCE

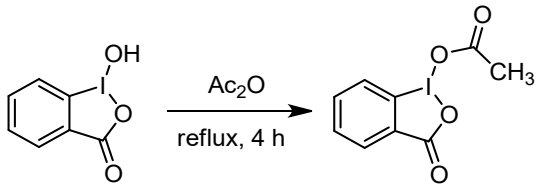
4. Synthesis of 1-Hydroxy-1,2-benziodoxol-3(1*H*)-one



2-iodobenzoic acid (BI-OH), was prepared following a reported procedure.[11] 2-iodobenzoic acid (7.4 g, 30.0 mmol, 1.0 eq.) and sodium periodate (6.7 g, 31.0 mmol, 1.0 eq.) were weighed into a 100 mL round-bottom flask. A mixture of 13.5 mL acetic acid and 31.5 mL of water was added. The reaction mixture was refluxed for 4 h under constant stirring and protection from light using aluminum foil. Thereafter, 120 mL of cold water was added, and the mixture was allowed to cool to room temperature. The white solid product was obtained by filtration and was successively washed with ice-cold water (3x30 mL), acetone (3x30 mL) and then, air dried in the dark overnight. 1-Hydroxy-1,2-benziodoxol-3(1H)-one (6.6 g, 84%) was obtained as a white solid compound. ^{1}H NMR (300 MHz, DMSO-d) 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, DMSO-d^{6}) δ : 168.2, 134.9, 132.0, 131.6, 130.8, 126.7, 120.9. Spectroscopic data were in good agreement with literature.[11]

[11] Fernández González, D.; Brand, J. P.; Waser, *J. Chem. Eur. J.* **2010**, *16*, 9457-9461.

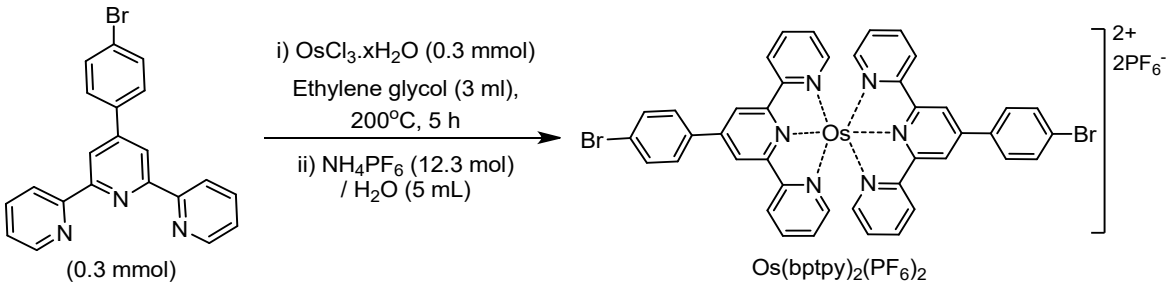
5. Synthesis of 1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one



BI-OAc

1-Acetoxy-1,2-benziodoxol-3-(1H)-one (BI-OAc) was acetylated following previously reported procedure.[12] BI-OH (6.0 g, 22.7 mmol) was treated with acetic anhydride (20 mL) in a round-bottom flask equipped with reflux condenser. The mixture was refluxed until BI-OH completely dissolved. The solution was allowed to cool to room temperature, and thereafter further cooled to -20°C using dry ice/acetone. BI-OAc was obtained as white crystals and was dried under vacuum for 12 h after separation by filtration. BI-OAc (6.1 g, 88%, m.p. : 171-173°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.23 (dt, J = 7.6, 1.4 Hz, 1H), 7.99 (ddt, J = 8.3, 1.2, 0.5 Hz, 1H), 7.91 (ddd, J = 8.4, 7.0, 1.6 Hz, 1H), 7.70 (ddt, J = 7.6, 7.0, 0.9 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 176.4, 168.2, 136.1, 133.2, 131.3, 129.3, 129.0, 118.3, 20.3. Spectroscopic data were in good agreement with literature.[12]

6. Synthesis of $Os(bptpy)_2(PF_6)_2$



(0.3 mmol)

$Os(bptpy)_2(PF_6)_2$

$Os(bptpy)_2(PF_6)_2$ complex was synthesized according to reported literature[13] with some modifications. Osmium (III) chloride hydrate (89.4 mg, 0.30 mmol) and 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (CAS: 89972-76-9, 234.6 mg, 0.60 mmol) were mixed in ethylene glycol (3 mL) in a round bottom flask equipped with magnetic stirrer and reflux condenser. The mixture was degassed, heated under argon atm and continuous stirring in a 200°C pre-heated hotplate (fitted with heat-on block) for 5 h. Thereafter, the dark mixture was directly transferred into 5 mL saturated solution of NH_4PF_6 (2 g in 5 mL of deionized water). The resulted dark purple precipitates were collected by filtration, purified using column chromatography (alumina, toluene/CH_3CN 1:1) to obtain the desired complex as a dark purple solid 298 mg, 79%. ^{1}H NMR (300 MHz, DMSO) δ : 9.53 (s, 4H), 9.11 (d, J = 8.1 Hz, 4H), 8.40 (d, J = 8.4 Hz, 4H), 8.10 - 7.86 (m, 8H), 7.44 (d, J = 5.4 Hz, 4H), 7.22 (t, J = 6.5 Hz, 4H). ^{13}C NMR (76 MHz, DMSO) δ : 160.1, 155.2, 152.7, 145.2, 138.3, 135.1, 132.6, 130.4, 128.5, 125.4, 124.6, 120.1. MS (MALDI-TOF) : m/z = 965 $[M - (2PF_6^-) - H]^+$, 887 $[M - (2PF_6^-) - Br]^+$. Spectroscopic data were in good agreement with literature.[13,14]

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12 P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579-2586.

13 Y. Sasaki, S. Amemori, H. Kouno, N. Yanai, N. Kimizuka, *J. Mater. Chem. C*, **2017**, *5,* 5063-5067.

14 B.D. Ravetz, N.E.S. Tay, C.L. Joe, M. Sezen-Edmonds, M.A. Schmidt, Y. Tan, J.M. Janey, M.D. Eastgate, T. Rovis, *ACS Cent. Sci.* **2020**, *6*, 2053–2059.

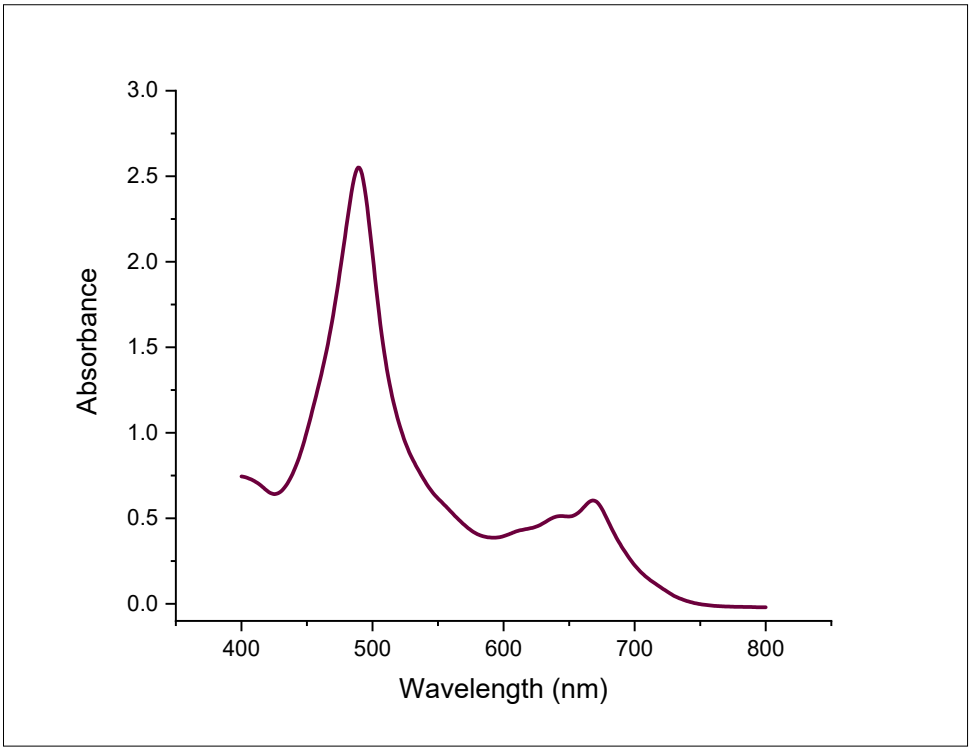
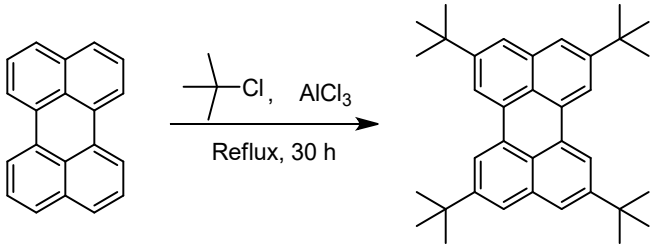


Figure S2: UV-visible absorption of $Os(bptpy)_2(PF_6)_2$ complex in CH_3CN

7. Synthesis of 2,5,8,11-Tetra(*tert*-butyl)perylene (TTBP)

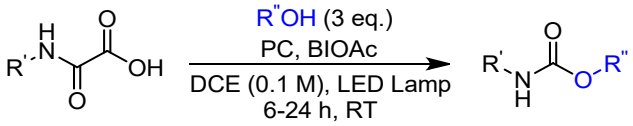


2,5,8,11-Tetra(*tert*-butyl) perylene (TTBP) was synthesized following a reported literature.[15] Perylene (0.5 g, 1.98 mmol) was weighed into a dry two-neck round bottom flask equipped with reflux condenser and magnetic bar. The content was flushed with argon and dry *tert*-butyl chloride (50 mL) was added into the flask under argon atm, followed by the addition of anhydrous aluminum trichloride (1.0 g). The mixture was then refluxed for 6 h. Additional *tert*-butyl chloride (30 mL) was added, and the reaction mixture was allowed to reflux overnight. Thereafter, additional 20 mL of *tert*-butyl chloride and 1.0 g anhydrous aluminum trichloride were added to the mixture and allowed to reflux for additional 24h. After cooling to room temperature, the mixture was extracted with 100 mL of brine in a separatory funnel. The aqueous layer was further extracted with DCM (3x50 mL). The combined organic layer including the *tert*-butyl chloride portion was dried with anhydrous Na_2SO_4 and concentrated in vacuo initially at 40°C and then at 80°C. The product obtained (viscous liquid) was further baked in a petri-dish at 170°C for 30h using a hot plate until smoke evolution stopped. Dark brown solid obtained was dissolved in a mixture of petroleum ether and chloroform (2:1). The mixture was purified by column chromatography (silica, petroleum ether/chloroform). The product was obtained as a yellow crystal (0.75 g, 80%), Rf : 9.2 ($CHCl_3$/petroleum ether, 1:1). ^1H NMR (300 MHz, $CDCl_3$) δ : 8.27 (d, J = 1.7

[15] S. H. C. Askes, W. Pomp, S. L. Hopkins, A. Kros, S. Wu, T. Schmidt, S. Bonnet, *small* **2016**, *12*, 40, 5579–5590.

Hz, 4H), 7.65 (d, J = 1.6 Hz, 4H), 1.53 (s, 36H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 148.7, 134.9, 130.8, 125.8, 123.3, 117.7, 34.9, 31.4. Spectroscopic data were in good agreement with literature.[15,16]

8. General procedures for urethane synthesis from oxamic acids under red/NIR light conditions



All the reactions were carried out in a re-sealable test tube using LED red/NIR light source, 660 or 780 nm. Oxamic acid (0.25 mmol, 1.0 eq.), BI-OAc (0.375 mmol, 1.5 eq.) and the photocatalyst PC were weighed into a dry re-sealable test-tube equipped with a magnetic bar. The tube was sealed with Teflon septum and degassed for 5 min using Schlenk line and then back filled with argon. Dry CH_2Cl_2 (0.1 M) and the corresponding alcohol (0.75 mmol, 3.0 eq.) were added into the tube under argon atm using syringe-needle. Note: For solid alcohol, it was added alongside oxamic acid before degassing process. The tube was then place in the NIR LED light at room temperature under constant stirring for 6-24h (Figure S3). Completion of conversion of oxamic acid was monitored by TLC. The reaction mixture was diluted with DCM (10 mL) and was washed successively with $NaHCO_3$ and brine, dried with Na_2SO_4 and concentrated using rotavap. The crude mixture was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether 5/95 to 20/80) to obtain the pure urethane.

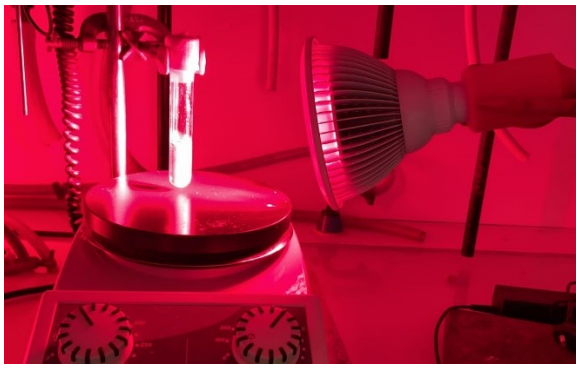
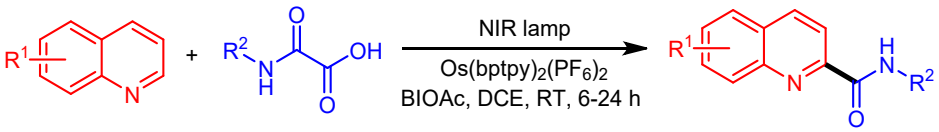


Figure S3: Experimental Setup NIR light reactions

9. General procedures for carbamoyl radical addition to heteroarenes under red/NIR light conditions



Oxamic acid (0.25 mmol, 2.0 eq.), heteroarene (1.0 eq.), BI-OAc (2.0 eq.) and $Os(bptpy)_2(PF_6)_2$ (0.3 mol%) were weighed into a dry re-sealable test-tube equipped with a magnetic bar. The tube was sealed with Teflon septum and was degassed and backfilled with argon. Dry DCE (0.1 M) was added into the tube under argon atm. The tube was placed in the NIR light at room temperature under constant stirring

[16] R. O. Al-Kaysi, T. Sang Ahn, A. M. Muller, C. J. Bardeen, *Phys. Chem. Chem. Phys*. **2006**, *8*, 3453.

for 6 to 24h depending on the substrate. The reaction mixture was directly washed successively with sodium bicarbonate (10 mL) and brine, dried using sodium sulfate and then concentrated using rotavap. The crude mixture was purified by flash column chromatography (silica gel, petroleum/ethyl acetate 90/10 to 70/30) to obtain the pure amide.

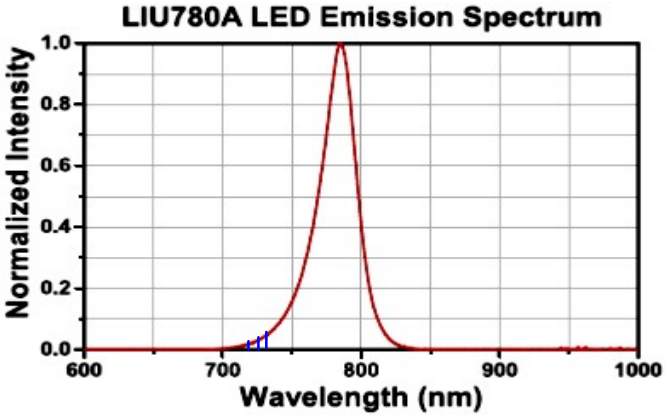
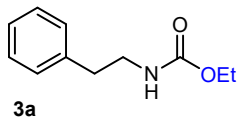


Figure S4: Emission spectrum of 780 nm LED lamp (NIR). Intensity = 3.7 mW/cm^2 (determined 100 mm from the LED along the emission axis)

10. Spectroscopic data of the urethanes.

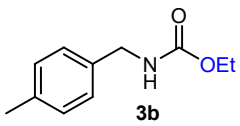
Ethyl phenethylcarbamate (3a)



3a

Following the general procedure and the corresponding oxamic acid (0.5 mmol), **3a** (84 mg, 88%) was obtained as a colorless gel within 24h. Rf : 0.43 (EtOAc/petroleum ether 20/90). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.40 – 7.16 (m, 5H), 4.69 (s, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.46 (q, J = 6.8 Hz, 2H), 2.84 (t, J = 7.0 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ : 156.6, 138.8, 130.0, 128.8, 128.7, 128.6, 126.5, 60.7, 42.1, 36.2, 14.6. Spectroscopic data were in good agreement with literature.[2]

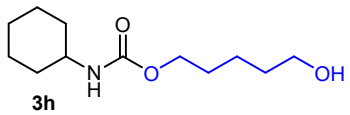
Ethyl 4-methylbenzylcarbamate (3b)



3b

Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3b** (38 mg, 78%) was obtained as white solid within 6h, m.p. : 57-59°C. Rf = 0.43 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.18 (q, J = 8.2 Hz, 4H), 4.98 (s, 1H), 4.34 (d, J = 5.6 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 1.33 – 1.22 (t, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.7, 137.1, 135.6, 129.3, 128.9, 127.5, 60.9, 44.8, 21.1, 14.7.

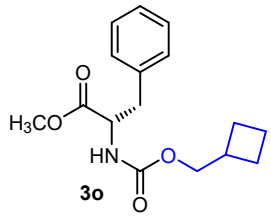
5-Hydroxypentyl cyclohexylcarbamate (3h)



3h

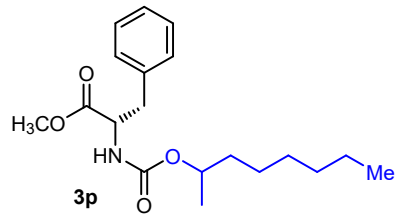
Following the general procedure and the corresponding oxamic acid (0.5 mmol), **3h** (100 mg, 87%) was obtained as white solid within 24h, m.p. : 78-79°C. Rf = 0.23 (AcOEt/petroleum ether 40/60). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.63 (s, 1H), 4.05 (dd, J = 11.8, 5.8 Hz, 2H), 3.64 (t, J = 6.4 Hz, 2H), 3.44 (s, 1H), 1.98 – 1.83 (m, 2H), 1.78 – 1.53 (m, 8H), 1.49 – 1.28 (m, 4H), 1.22 – 1.02 (m, 4H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 155.9, 64.5, 62.6, 49.7, 33.4, 32.3, 28.9, 25.5, 24.8, 22.2. IR (neat) υ_{max} (cm^{-1}): 3319, 2939, 2862, 1693, 1533, 1449. HRMS (ESI): Calcd. for $C_{19}H_{29}O_4N$ $[M+H]^+$ 230.1751, found 230.1741.

(*S*)-Methyl 2-(((cyclobutylmethoxy)carbonyl)amino)-3-phenylpropanoate (3o)



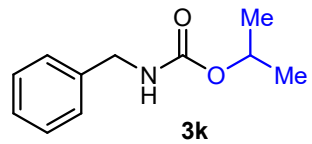
Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3o** (54 mg, 73%) was obtained as colorless gel within 24h. Rf : 0.52 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.39 – 7.21 (m, 3H), 7.15 (m, 2H), 5.15 (d, J = 7.3 Hz, 1H), 4.67 (dd, J = 13.8, 6.0 Hz, 1H), 4.05 (d, J = 6.8 Hz, 2H), 3.74 (s, 1H), 3.23 – 3.01 (m, 2H), 2.70 – 2.47 (m, 1H), 2.15 – 1.67 (m, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 172.1, 156.1, 135.8, 134.3, 129.3, 128.6, 127.1, 69.0, 54.7, 52.3, 38.3, 34.3, 24.6, 18.4. IR (neat) υ_{max} (cm^{-1}) = 3341, 3034, 2953, 2862, 1720, 1604, 1521. HRMS (ESI): Calcd. for $C_{16}H_{22}O_4N$ $[M+H]^+$ 292.1543, found 292.1543. $[\alpha]_D^{25}$ +49.17 (c 0.53, $CHCl_3$).

(2*S*)-Methyl 2-(((octan-2-yloxy)carbonyl)amino)-3-phenylpropanoate (3p)



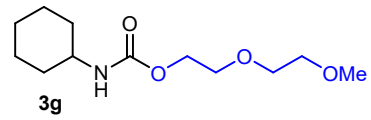
Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3p** was obtained as a colorless gel (61 mg, 73%) within 24h. Rf : 0.43 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.29 (m, 3H), 7.18–7.06 (m, 2H), 5.08 (d, *J* = 7.7 Hz, 1H), 4.79 (dq, *J* = 12.3, 6.2 Hz, 1H), 4.67 (d, *J* = 6.2 Hz, 1H), 3.74 (d, *J* = 0.8 Hz, 3H), 3.13 (qd, *J* = 13.8, 5.9 Hz, 2H), 1.69 – 1.39 (m, 2H), 1.30 (d, *J* = 3.7 Hz, 8H), 1.20 (d, *J* = 6.2 Hz, 3H), 0.90 (q, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 172.1, 155.7, 135.9, 129.3, 128.5, 127.1, 72.0, 54.6, 52.2, 38.3, 36.2, 31.8, 29.2, 25.3, 22.6, 20.3, 14.1. IR (neat) υ_{max} (cm^{-1}): 3345, 3026, 2927, 2849, 1746, 1720, 1606, 1501. HRMS (ESI): Calcd. for $C_{19}H_{29}O_4NNa$ $[M+Na]^+$ 358.1988, found 358.1986. $[\alpha]_D^{25}$ +43.41 (c 0.49, $CHCl_3$).

Isopropyl benzylcarbamate (3k)



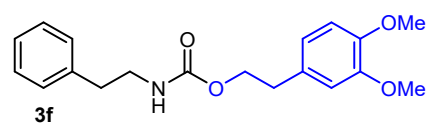
Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3k** was obtained as a colorless gel (36 mg, 75%) within 24h. Rf : 0.42 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.46 – 7.16 (m, 5H), 4.97 (m, 2H), 4.38 (d, J = 5.2 Hz, 2H), 1.26 (d, J = 6.3 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.3, 138.7, 128.6, 127.5, 127.4, 68.3, 45.0, 22.2. IR (neat) υ_{max} (cm^{-1}) : 3332, 3030, 2983, 2931, 1693, 1533, 1454. Spectroscopic data were in good agreement with literature.[2]

2-(2-Methoxyethoxy)ethyl cyclohexylcarbamate (3g)



Following the general procedure and the corresponding oxamic acid (0.5 mmol), **3g** was obtained as a colorless gel (86 mg, 70%) within 24h. Rf : 0.46 (AcOEt/petroleum ether 40/60). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.65 (s, 1H), 4.24 – 4.15 (m, 2H), 3.70 – 3.60 (m, 4H), 3.55 (m, J = 6.8, 3.2 Hz, 2H), 3.44 (s, 1H), 3.37 (s, 3H), 1.96 – 1.83 (m, 2H), 1.73 – 1.51 (m, 3H), 1.40 – 1.00 (m, 5H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 155.5, 71.9, 70.4, 69.7, 63.6, 59.1, 49.8, 33.4, 25.5, 24.7. IR (neat) υ_{max} (cm^{-1}) : 3328, 2935, 2858, 1699, 1536, 1452. HRMS (ESI): Calcd. for $C_{12}H_{24}O_4N$ $[M+H]^+$ 246.1699, found 246.1700.

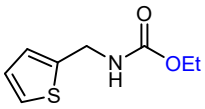
3,4-dimethoxyphenethyl phenethylcarbamate (3f)



Following the general procedure and the corresponding oxamic acid (0.5 mmol), **3f** was obtained as white solid (65 mg, 40%) within

24h, m.p. : 87-89°C. Rf : 0.37 (AcOEt/cyclohexane 40/60). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.35 – 7.12 (m, 5H), 6.84 – 6.68 (m, 3H), 4.67 (s, 1H), 4.25 (t, J = 7.1 Hz, 2H), 3.87 (s, Hz, 6H), 3.44 (d, J = 6.2 Hz, 2H), 2.83 (dt, J = 11.2, 6.9 Hz, 4H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.4, 148.9, 147.7, 130.5, 128.8, 128.6, 126.5, 120.8, 112.1, 111.3, 65.4, 55.9, 55.8, 42.1, 36.1, 35.1. IR (neat) υ_{max} (cm^{-1}) : 3323. 2935, 2836, 1688, 1591. HRMS (ESI): Calcd. for $C_{19}H_{24}O_4N$ $[M+H]^+$ 330.1699, found 330.1701.

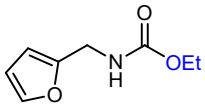
Ethyl (thiophen-2-ylmethyl)carbamate (3c)



3c

Following the general procedure and the corresponding oxamic acid (0.3 mmol), **3c** was obtained as light brown gel (30 mg, 54%) within 24h. Rf : 0.43 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.24 (dd, J = 4.8, 1.6 Hz, 1H), 6.96 (dd, J = 4.8, 3.5 Hz, 2H), 5.08 (s, 1H), 4.54 (d, J = 5.4 Hz, 2H), 4.17 (q, J = 7.0 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.3, 141.5, 126.9, 125.7, 125.1, 61.1, 39.8, 14.6. IR (neat) υ_{max} (cm^{-1}): 3319, 3103, 3069, 2978, 2927, 1693, 1527. Spectroscopic data were in good agreement with literature.[2]

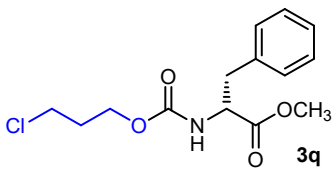
Ethyl (furan-2-ylmethyl)carbamate (3d)



3d

Following the general procedure and the corresponding oxamic acid (0.3 mmol), **3d** was obtained as light brown gel (21 mg, 41%) within 24h. Rf : 0.39 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.37 (dd, J = 1.8, 0.8 Hz, 1H), 6.33 (dd, J = 3.2, 1.9 Hz, 1H), 6.24 (d, J = 2.9 Hz, 1H), 5.02 (s, 1H), 4.36 (d, J = 5.6 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.4, 151.7, 142.1, 110.4, 107.1, 61.1, 38.0, 14.6. IR (neat) υ_{max} (cm^{-1}): 3328, 3121, 2989, 2935, 1703, 1527.

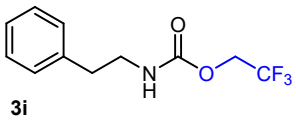
(*R*)-methyl 2-(((3-chloropropoxy)carbonyl)amino)-3-phenylpropanoate (3q)



3q

Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3q** was obtained as light brown gel (60 mg, 80%) within 24h. Rf : 0.36 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.36 – 7.25 (m, 3H), 7.17 – 7.10 (m, 2H), 5.18 (s, 1H), 4.66 (dd, J = 14.1, 6.0 Hz, 1H), 4.22 (t, J = 6.0 Hz, 2H), 3.75 (s, 3H), 3.59 (t, J = 6.4 Hz, 2H), 3.13 (qd, J = 13.9, 6.0 Hz, 2H), 2.14 – 1.99 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 172.0, 155.5, 135.7, 129.2, 128.6, 127.2, 61.9, 54.7, 52.4, 41.2, 38.2, 31.9. IR (neat) υ_{max} (cm^{-1}): 3336. 3025, 2956, 1722, 1604, 1520. HRMS (ESI): Calcd. for $C_{14}H_{18}O_4NClNa$ $[M+Na]^+$ 322.08167, found 322.0809. $[\alpha]_D^{25}$ +47.22 (c 0.73, $CHCl_3$).

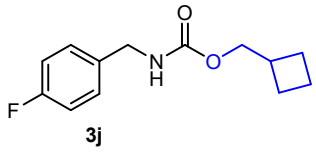
2,2,2-Trifluoroethyl phenethylcarbamate (3i)



3i

Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3i** was obtained as light brown gel (38 mg, 61%) within 24h. Rf : 0.74 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.44 – 7.05 (m, 5H), 4.93 (s, 1H), 4.47 (q, J = 8.5 Hz, 2H), 3.51 (dd, J = 13.1, 6.8 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 154.5, 138.4, 123.3 (q, $^1J_{CF}$ = 277.5 Hz), 60.9 (q, $^2J_{CF}$ = 36.4 Hz), 42.6, 36.0. IR (neat) υ_{max} (cm^{-1}): 3345, 3064, 3030, 2945, 1730, 1604, 1604, 1526. Spectroscopic data were in good agreement with literature.[1,2]

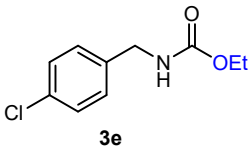
Cyclobutylmethyl 4-fluorobenzylcarbamate (3j)



3j

Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3j** was obtained as white solid (30 mg, 50%) within 24h, m.p. : 58-60°C. Rf : 0.48 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.28 (dd, J = 8.7, 5.1 Hz, 2H), 7.13 – 6.94 (m, 2H), 5.01 (s, 1H), 4.35 (d, J = 5.4 Hz, 2H), 4.08 (d, J = 6.8 Hz, 2H), 2.71 – 2.44 (m, 1H), 2.06 (ddd, J = 13.7, 8.7, 4.8 Hz, 2H), 1.99 – 1.71 (m, 4H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 162.2 (d, $^{1}J_{CF}$ = 245.6 Hz), 156.8, 134.4 (d, $^{3}J_{CF}$ = 3.2 Hz), 129.2, 115.5 (d, $^{2}J_{CF}$ = 21.5 Hz), 68.9, 44.4, 34.4, 24.6, 18.4. IR (neat) υ_{max} (cm^{-1}): 3336, 3065, 2969, 2931, 1699, 1607, 1512. Spectroscopic data were in good agreement with literature.[2]

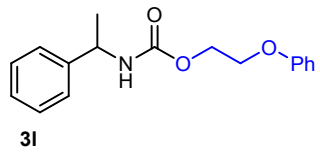
Ethyl 4-chlorobenzylcarbamate (3e)



3e

Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3e** was obtained as white solid (38 mg, 72%) within 24h, m.p. : 60-61°C. Rf : 0.31 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.29 (ddd, J = 22.0, 12.3, 5.2 Hz, 4H), 5.04 (s, 1H), 4.34 (d, J = 6.0 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.6, 137.2, 133.2, 128.8, 61.1, 44.3, 14.6. IR (neat) υ_{max} (cm^{-1}): 3310, 3051, 2982, 2870, 2784, 1696, 1544, 1407. Spectroscopic data were in good agreement with literature.[1]

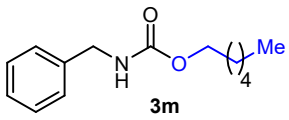
2-Phenoxyethyl (1-phenylethyl)carbamate (3l)



3l

Following the general procedure and the corresponding oxamic acid (0.5 mmol), **3l** was obtained as white solid (110 mg, 78%) within 24h, m.p. : 88-90°C. Rf : 0.43 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.31 (dd, J = 8.6, 7.5 Hz, 7H), 7.07 – 6.85 (m, 3H), 5.11 (s, 1H), 4.98 – 4.78 (m, 1H), 4.53 – 4.32 (m, 2H), 4.17 (d, J = 4.1 Hz, 2H), 1.53 (t, J = 10.9 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 158.5, 155.4, 143.4, 129.5, 128.7, 127.4, 125.9, 121.1, 114.6, 66.4, 63.3, 50.8, 22.5. IR (neat) υ_{max} (cm^{-1}): 3332, 3060, 3030, 2978, 2922, 2871, 1690, 1583, 1596, 1533, 1497, 1452. HRMS (ESI): Calcd. for $C_{17}H_{19}O_3NNa$ $[M+Na]^+$ 308.1257, found 308.1249.

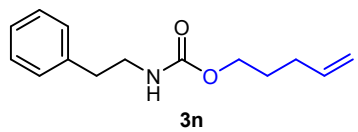
Hexyl benzylcarbamate (3m)



3m

Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3m** was obtained as colorless gel (41 mg, 71%) within 24h. Rf : 0.7 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.42 – 7.20 (m, 5H), 5.05 (s, 1H), 4.38 (d, J = 5.5 Hz, 2H), 4.11 (t, J = 6.7 Hz, 2H), 1.70 – 1.54 (m, 2H), 1.28 (d, J = 28.6 Hz, 6H), 0.92 (dd, J = 8.8, 4.7 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.8, 138.7, 128.6, 127.5, 127.4, 65.2, 45.0, 31.5, 29.0, 25.5, 22.6, 14.0. IR (neat) υ_{max} (cm^{-1}): 3332, 3030, 2961, 2927, 2858, 1697, 1533. Spectroscopic data were in good agreement with literature.[2]

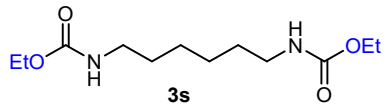
Pent-4-en-1-yl phenethylcarbamate (3n)



3n

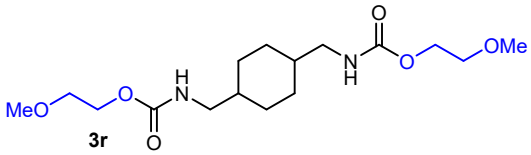
Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3n** was obtained as colorless gel (33 mg, 30%) within 24h. Rf : 0.46 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.49 – 6.99 (m, 5H), 5.83 (m, J = 16.9, 10.2, 6.6 Hz, 1H), 5.01 (d, J = 10.2 Hz, 2H), 4.68 (s, 1H), 4.09 (t, J = 6.6 Hz, 2H), 3.47 (dd, J = 13.0, 6.5 Hz, 2H), 2.84 (t, J = 7.0 Hz, 2H), 2.13 (dd, J = 13.9, 6.8 Hz, 2H), 1.81 – 1.62 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.6, 138.8, 137.6, 128.8, 128.6, 126.5, 115.1, 64.3, 42.1, 36.2, 30.0, 28.3. IR (neat) υ_{max} (cm^{-1}) = 3335, 3065, 3028, 2940, 1703, 1641, 1531. Spectroscopic data were in good agreement with literature.[1]

Diethyl hexane-1,6-diyldicarbamate (3s)



Following the general procedure and the corresponding oxamic acid (0.25 mmol), **3s** was obtained as white solid (54 mg, 82%) after 24 h, m.p. : 71-73°C. Rf : 0.46 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 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 : 156.72, 60.64, 40.72, 29.93, 26.26, 14.66. IR (neat) υ_{max} (cm^{-1}): 3314, 2984, 2936, 1685. Spectroscopic data were in good agreement with literature.[1,2]

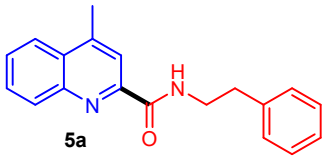
Bis(2-methoxyethyl) (cyclohexane-1,4-diylbis(methylene))dicarbamate (3r)



Following the general procedure with the corresponding oxamic acid (0.25 mmol), **3r** was obtained as white solid (60.6 mg, 70%) after 24h, m.p. : 114-117°C. Rf : 0.5 (AcOEt/petroleum ether 50/50). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 4.84 (s, 2H), 4.31 – 4.15 (m, 4H), 3.63 – 3.54 (m, 4H), 3.40 (s, 6H), 3.14 (dd, J = 13.2, 6.4 Hz, 1H), 3.04 (t, J = 6.4 Hz, 3H), 1.79 (d, J = 7.0 Hz, 3H), 1.57 – 1.27 (m, 4H), 1.03 – 0.82 (m, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 156.5, 71.0, 63.8, 58.9, 47.1, 38.2, 29.9, 26.1. IR (neat) υ_{max} (cm^{-1}): 3315, 2905, 2841, 1688, 1538, 1449. HRMS (ESI): Calcd. for $C_{16}H_{31}O_6N_2$ $[M+H]^+$ 347.2177, found 347.2177.

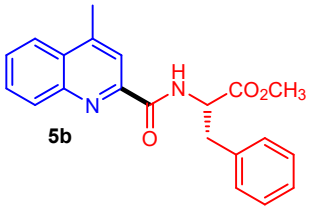
11. Spectroscopic data of the amides

4-Methyl-*N*-phenethylquinoline-2-carboxamide (5a)



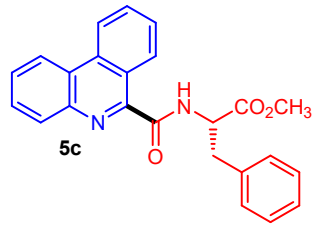
Following the general procedure and the corresponding heteroarene (0.125 mmol), **5a** was obtained as milky solid (27.0 mg, 75%) within 6h, mp. : 98–101°C. Rf : 0.53 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.36 (d, J = 23.8 Hz, 1H), 8.18 (s, 1H), 8.06 (dd, J = 7.7, 4.4 Hz, 2H), 7.76 (t, J = 7.1 Hz, 1H), 7.64 (t, J = 7.1 Hz, 1H), 7.46 – 7.18 (m, 5H), 3.81 (dd, J = 13.8, 6.8 Hz, 2H), 3.02 (t, J = 7.2 Hz, 2H), 2.79 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 164.8, 149.5, 146.5, 146.2, 139.2, 130.4, 129.8, 129.3, 129.0, 128.7, 127.7, 126.6, 124.0, 119.5, 41.0, 36.2, 19.0. Spectroscopic data were in good agreement with literature.[3]

(*S*)-Methyl 2-(4-methylquinoline-2-carboxamido)-3-phenylpropanoate (5b)



Following the general procedure and the corresponding heteroarene (0.125 mmol), **5b** was obtained as white solid (38mg, 86%) within 12h, mp°C. 116-118 °C, Rf : 0.4 (AcOEt/petroleum ether 30/70). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.73 (d, J = 8.3 Hz, 1H), 8.16 – 8.02 (m, 3H), 7.77 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.65 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.37 – 7.21 (m, 5H), 5.14 (dt, J = 8.4, 6.1 Hz, 1H), 3.77 (s, 3H), 3.32 (d, J = 6.2 Hz, 2H), 2.79 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 171.9, 164.4, 148.6, 146.4, 146.0, 136.1, 130.6, 129.7, 129.4, 129.3, 128.6, 127.7, 127.1, 123.8, 119.3, 53.5, 52.3, 38.4, 18.9. IR (neat) υ_{max} (cm^{-1}): 3379, 3064, 2952, 1744, 1675. HRMS (ESI): Calcd. for $C_{21}H_{21}O_3N_2$ $[M+H]^+$ 349.1547, found 349.1538. $[\alpha]_D^{25}$ +22.32 (c 0.48, $CHCl_3$).

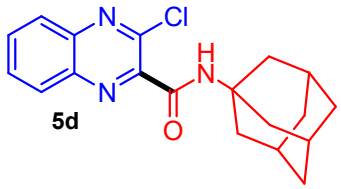
(*S*)-Methyl 2-(phenanthridine-6-carboxamido)-3-phenylpropanoate (5c)



Following the general procedure and the corresponding heteroarene (0.25 mmol), **5c** was obtained as white solid (80 mg, 83%) within 12h, mp. 107-110°C. Rf : 0.51 (AcOEt/petroleum ether 30/70). ^{1}H NMR (300 MHz,

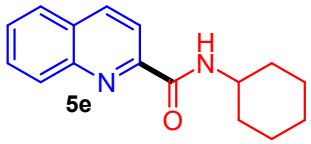
$CDCl_3$) δ : 9.57 (d, J = 8.5, 0.7 Hz, 1H), 8.75 – 8.57 (m, 3H), 8.21 – 8.13 (m, 1H), 7.89 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.83 – 7.71 (m, 3H), 7.41 – 7.24 (m, 5H), 5.19 (dt, J = 8.2, 6.0 Hz, 1H), 3.81 (s, 3H), 3.46 – 3.28 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 172.0, 165.6, 148.5, 141.9, 136.1, 133.8, 130.9, 130.7, 129.5, 128.8, 128.8, 128.6, 128.6, 128.0, 127.2, 125.5, 124.3, 122.1, 121.8, 53.6, 53.4, 52.4, 38.3. IR (neat) υ_{max} (cm^{-1}): 3370, 3064, 3034, 2948, 1744, 1673. HRMS (ESI): Calcd. for $C_{24}H_{21}O_3N_2$ $[M+H]^+$ 385.1547, found 385.1534. $[\alpha]_D^{25}$ +41.52 (c 0.53, $CHCl_3$).

_N_-(3-Chloroquinoxalin-2-yl)adamantane-1-carboxamide (5d)



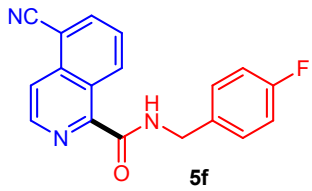
Following the general procedure and the corresponding heteroarene (0.25 mmol), **5d** was obtained as white solid (58 mg, 68%) within 12h, mp.: 197-200°C. Rf : 0.4 (AcOEt/petroleum ether 30/70). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.16 – 8.04 (m, 2H), 7.94 – 7.79 (m, 2H), 7.17 (s, 1H), 2.22 (t, J = 7.9 Hz, 9H), 1.86 – 1.71 (m, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 161.7, 145.1, 144.1, 142.3, 138, 132.3, 130.8, 129.1, 128.2, 52.8, 41.4, 36.3, 29.7, 29.5. IR (neat) υ_{max} (cm^{-1}): 3288, 3064, 2909, 2849, 1662. Spectroscopic data were in good agreement with literature.[3]

_N_-cyclohexylquinoline-2-carboxamide (5e)



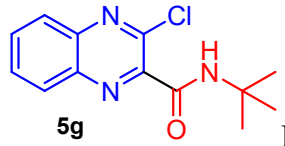
Following the general procedure and the corresponding heteroarene (0.25 mmol), **5e** was obtained as white solid (48 mg, 76%) within 12h, mp. : 92-95°C. Rf : 0.38 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.38 – 8.28 (m, 2H), 8.17 (m, 2H), 7.89 (d, J = 8.2 Hz, 1H), 7.78 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.63 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 4.06 (qd, J = 10.2, 4.0 Hz, 1H), 2.15 – 2.03 (m, 2H), 1.89 – 1.59 (m, 3H), 1.59 – 1.21 (m, 5H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 163.4, 150.1, 137.4, 130.0, 129.7, 129.2, 127.7, 118.9, 48.4, 33.1, 25.6, 25.0. IR (neat) υ_{max} (cm^{-1}): 3375, 3056, 2935, 2835, 2849, 1674. Spectroscopic data were in good agreement with literature.[3]

5-Cyano-N-(4-fluorobenzyl)isoquinoline-1-carboxamide (5f)



Following the general procedure and the corresponding heteroarene (0.125 mmol), **5f** was obtained as white solid (30.5 mg, 80%) within 12h, mp. 159–162°C. Rf : 0.28 (AcOEt/petroleum ether 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 10.04 (dd, J = 8.8, 0.9 Hz, 1H), 8.67 (d, J = 5.7 Hz, 2H), 8.20 (ddd, J = 8.3, 6.4, 1.0 Hz, 2H), 7.78 (dd, J = 8.8, 7.2 Hz, 1H), 7.49 – 7.33 (m, 2H), 7.18 – 6.98 (m, 2H), 4.70 (d, J = 6.1 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 165.0, 162.3 (d, $^1J_{CF}$ = 245.8 Hz), 148.5, 142.6, 136.8, 136.6, 133.8, 133.5, 129.5 (d, $^3J_{CF}$ = 8.1 Hz), 127.8, 126.6, 121.4, 116.6, 115.6 (d, $^2J_{CF}$ = 21.5 Hz), 109.8, 42.9. IR (neat) υ_{max} (cm^{-1}): 3362, 3051, 2922, 2225, 16668. Spectroscopic data were in good agreement with literature.[3]

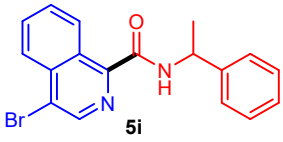
_N_-(*tert*-butyl)-3-chloroquinoxaline-2-carboxamide (5g)



5g

Following the general procedure and the corresponding heteroarene (0.125 mmol), **5g** was obtained as light-yellow solid (20.9mg, 61%) within 12h, mp. : 145-149°C. Rf : 0.57 (AcOEt/petroleum ether 30/70). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.19 – 8.00 (m, 2H), 7.95 – 7.77 (m, 2H), 7.28 (s, 1H), 1.56 (s, 9H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 162.0, 145.0, 144.1, 142.4, 138.9, 132.4, 130.8, 129.1, 128.3, 52.0, 28.7. IR (neat) υ_{max} (cm^{-1}): 3267, 3077, 2969, 2926, 1647. HRMS (ESI): Calcd. for $C_{17}H_{19}O_3NNa$ $[M+Na]^+$ 286.0717, found 286.0714.

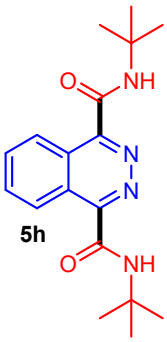
4-Bromo-N-(1-phenylethyl)-1-naphthamide (5i)



5i

Following the general procedure, **75i** was obtained as pale yellow gel (24 mg, 56%). Rf : 0.32 (AcOEt/petroleum ether 10/90) within 12h. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 9.74 – 9.63 (m, 1H), 8.68 (s, 1H), 8.47 (d, J = 7.8 Hz, 1H), 8.29 – 8.19 (m, 1H), 7.80 (dddd, J = 30.9, 8.3, 6.9, 1.3 Hz, 2H), 7.52 – 7.25 (m, 5H), 5.46 – 5.27 (m, 1H), 1.69 (d, J = 6.9 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 164.3, 147.3, 143.3, 141.7, 136.0, 132.0, 129.5, 128.7, 128.5, 128.2, 127.4, 126.2, 126.1, 123.5, 49.2, 22.2. IR (neat) υ_{max} (cm^{-1}) : 3379, 3064, 3064, 3021, 2974, 2926, 1664, 1559. Spectroscopic data were in good agreement with literature.[3]

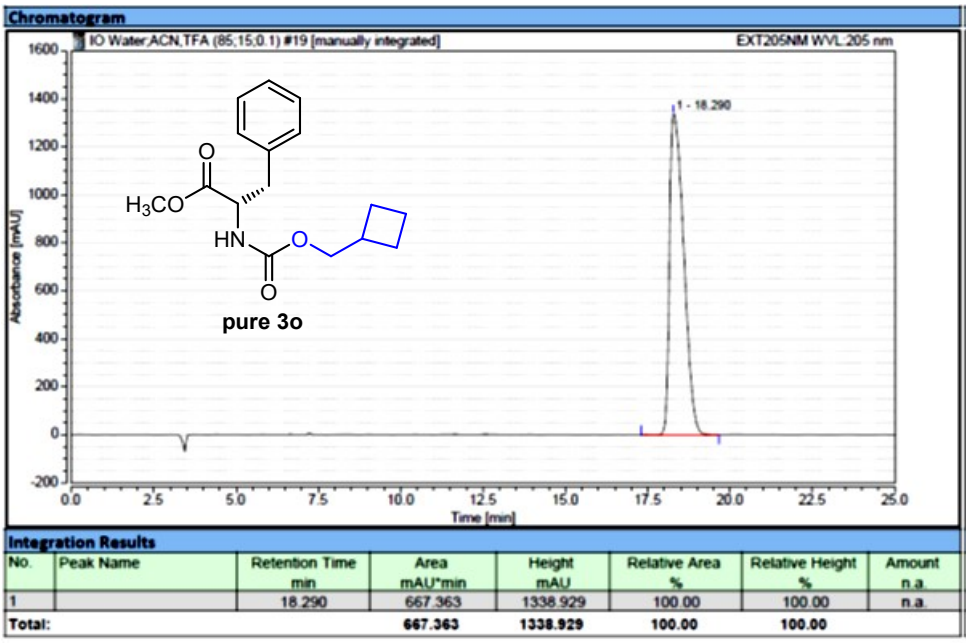
N^1,N^4-Di-tert-butylphthalazine-1,4-dicarboxamide (5h)



5h

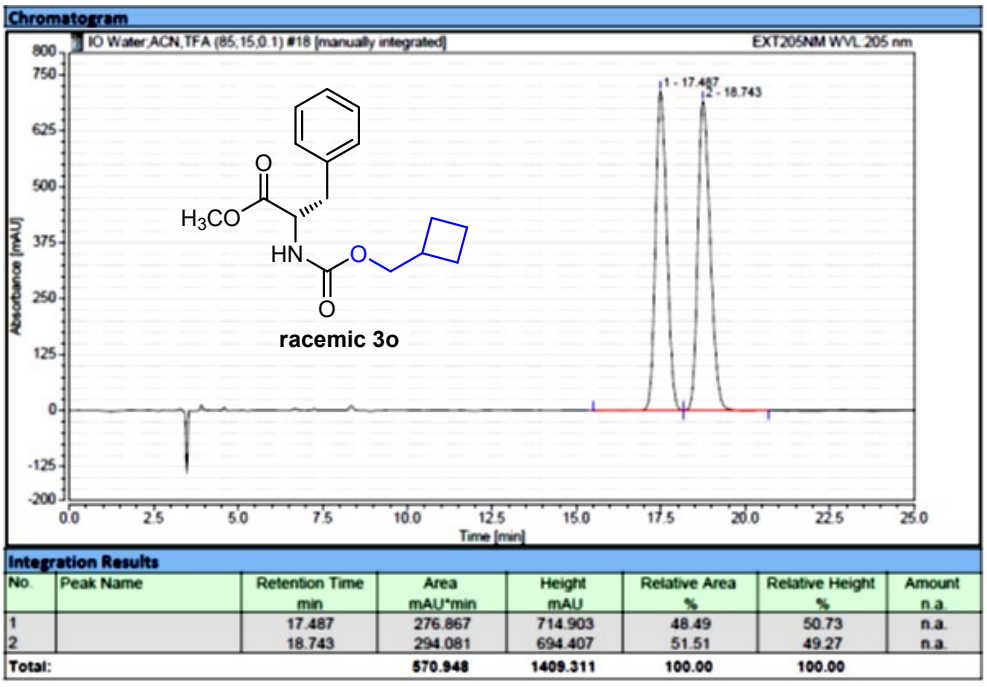
Following the general procedure and the corresponding heteroarene (0.125 mmol), **5h** was obtained as pale yellow solid (31 mg, 76%) within 24h, mp : 126-131°C. Rf : 0.6 (AcOEt/DCM 20/80). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 9.50 (dd, J = 6.5, 3.4 Hz, 2H), 8.10 – 7.88 (m, 4H), 1.58 (s, 18H). ^{13}C NMR (76 MHz, $CDCl_3$) δ : 163.3, 151.3, 133.5, 127.0, 126.3, 51.9, 28.7. IR (neat) υ_{max} (cm^{-1}) : 3262, 3051, 2951, 2969, 1668. HRMS (ESI): Calcd. for $C_{18}H_{24}O_2N_4Na$ $[M+Na]^+$ 351.1792, found 351.1787.

12. Chiral HPLC of the chiral urethane and amide



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.290	667.363	1338.929	100.00	100.00	n.a.
Total:			667.363	1338.929	100.00	100.00	

Figure 5: HPLC Data for (*S*)-methyl 2-(((cyclobutylmethoxy)carbonyl)amino)-3-phenylpropanoate (pure **3o**). UltiMate-3000 (Water:CH_3CN:TFA (65:35:0.1).



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.487	276.867	714.903	48.49	50.73	n.a.
2		18.743	294.081	694.407	51.51	49.27	n.a.
Total:			570.948	1409.311	100.00	100.00	

Figure 6: HPLC Data for (*S*)-methyl 2-(((cyclobutylmethoxy)carbonyl)amino)-3-phenylpropanoate (racemic **3o**). UltiMate-3000 (Water:CH_3CN:TFA (65:35:0.1).

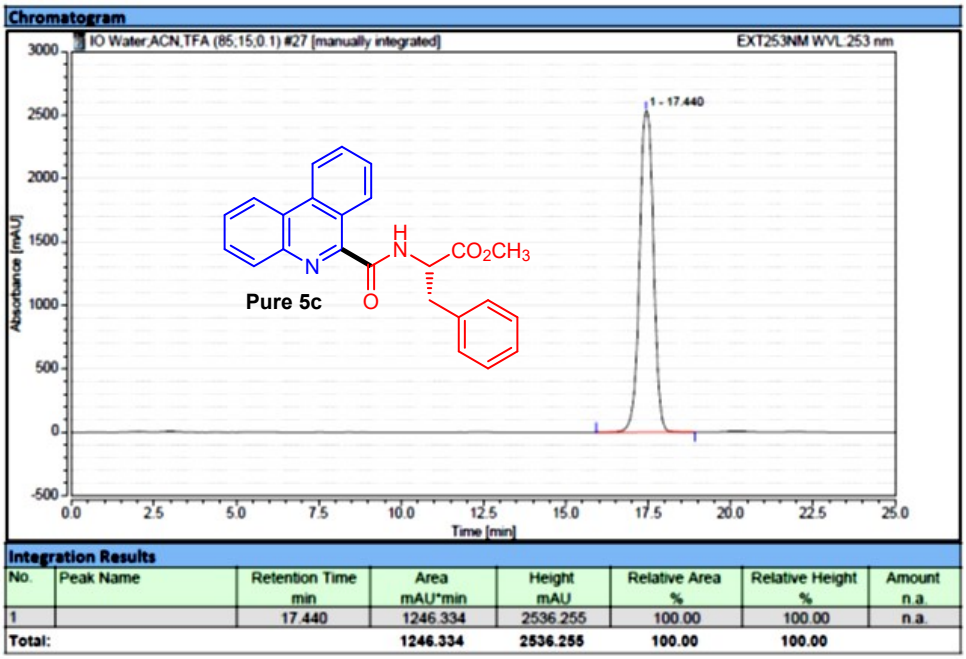


Figure 7: HPLC Data for (*S*)-methyl 2-(phenanthridine-6-carboxamido)-3-phenylpropanoate (pure **5c**). UltiMate-3000 (Water:CH_3CN:TFA (85:15:0.1).

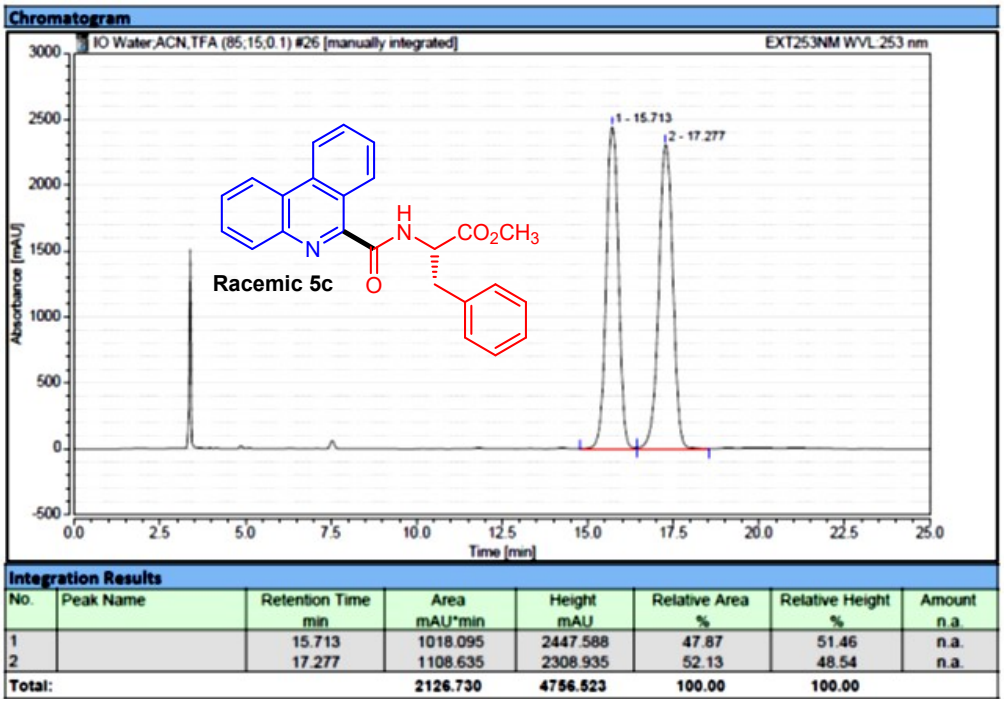


Figure 8: HPLC Data for (*S*)-methyl 2-(phenanthridine-6-carboxamido)-3-phenylpropanoate (racemic **5c**). UltiMate-3000 (Water:CH_3CN:TFA (85:15:0.1).

13. Comparing the penetration depth of the NIR light and blue LED light

The penetration depth of the optimal NIR light photocatalytic procedure was compared with that of the visible light process developed earlier.[2] The light source was placed 13cm behind the barrier (Figure 9) and the reaction was performed using the optimized conditions.

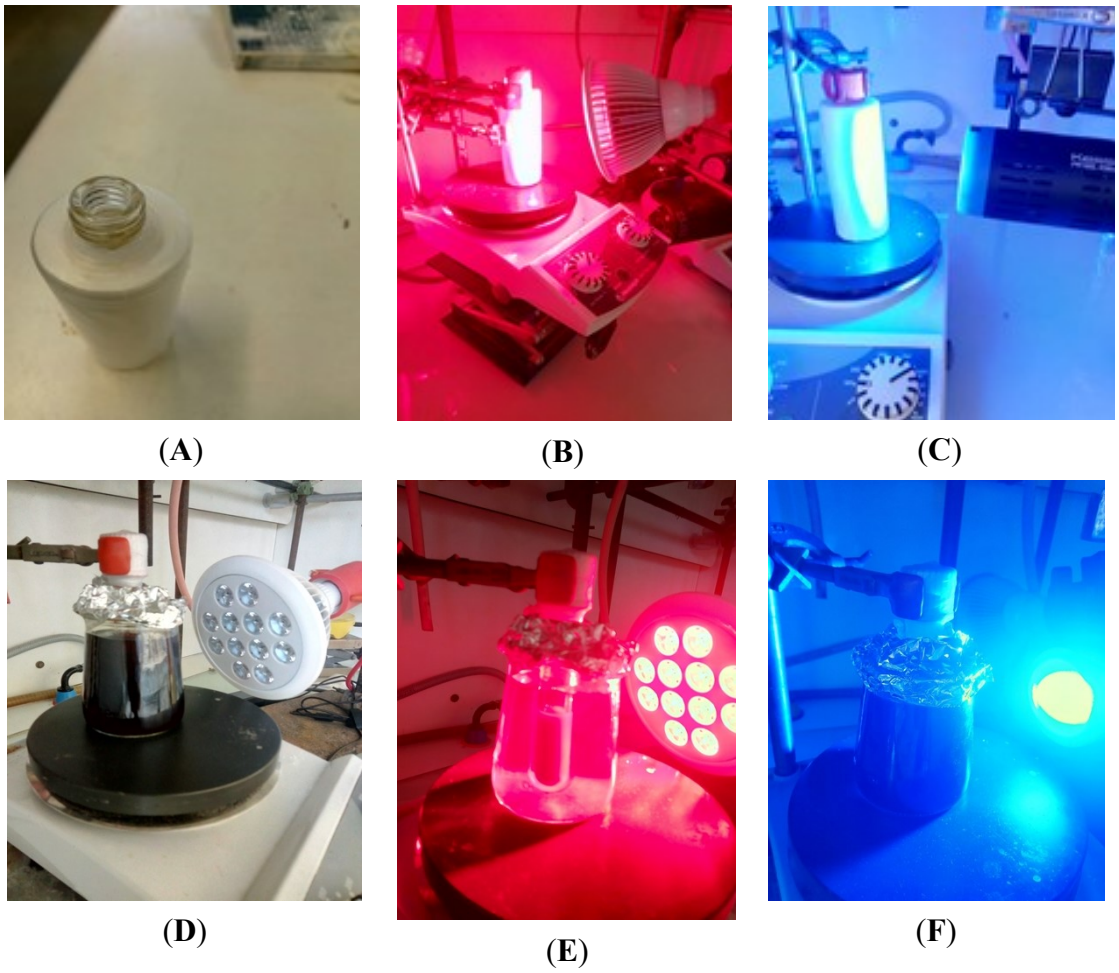


Figure 9: Paraffin barricade (1.5cm) used for the reaction (**A**); reaction using red light (**B**); reaction using blue light (**C**). Reaction setup using hemoglobin solution as barricade (**D**); reaction under red light irradiation, indicating penetration of the red light into the solution (**E**), reaction using blue light which was completely blocked by the hemoglobin solution (**F**).

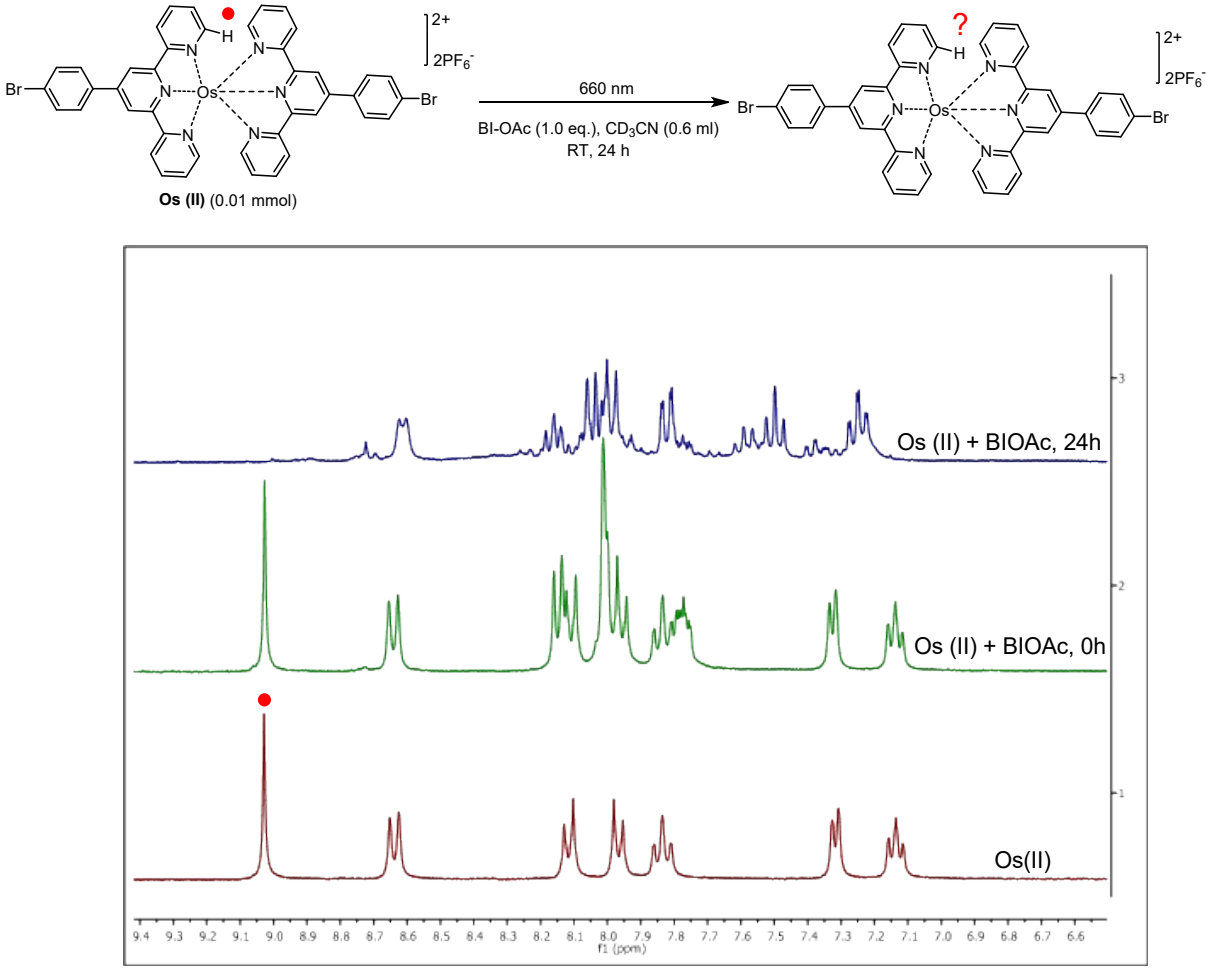


Figure S10: Disappearance of *ter*-pyridine 6,6" protons of the $Os(bptpy)_2(PF_6)_2$ in the presence of BI-OAc. MS (MALDI) of the mixture after the irridiation indicated that the molecular wieght of the photocatalyst was still not altered, suggesting that the observed change in th ^{1}H-NMR could probably be due to a weak interaction between the photocatalyst and BI-OAc.

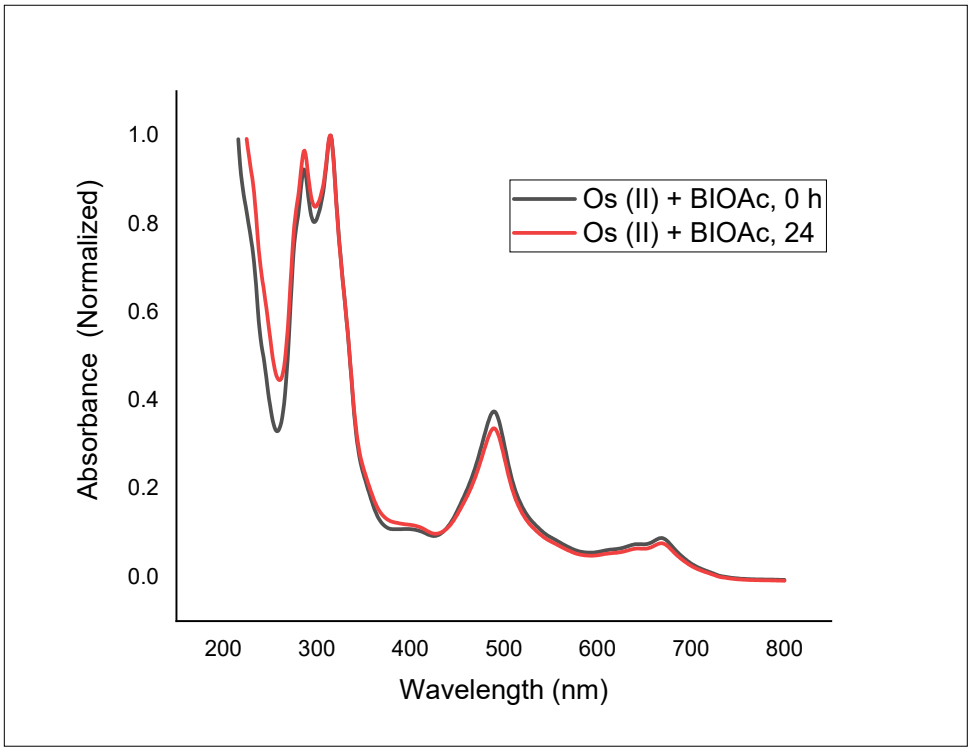


Figure S11: UV-visible absorption showed that the absorption profile of $Os(bptpy)_2(PF_6)_2$ was not altered by BI-OAc after the irradiation for 24 h.

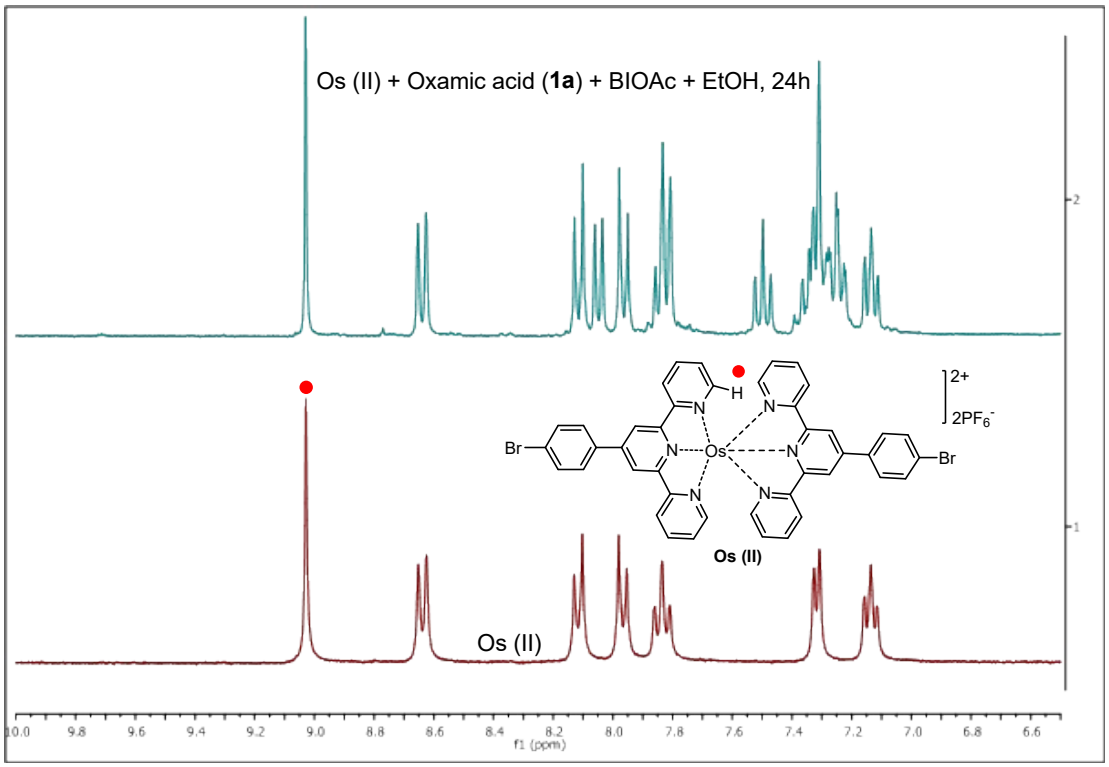
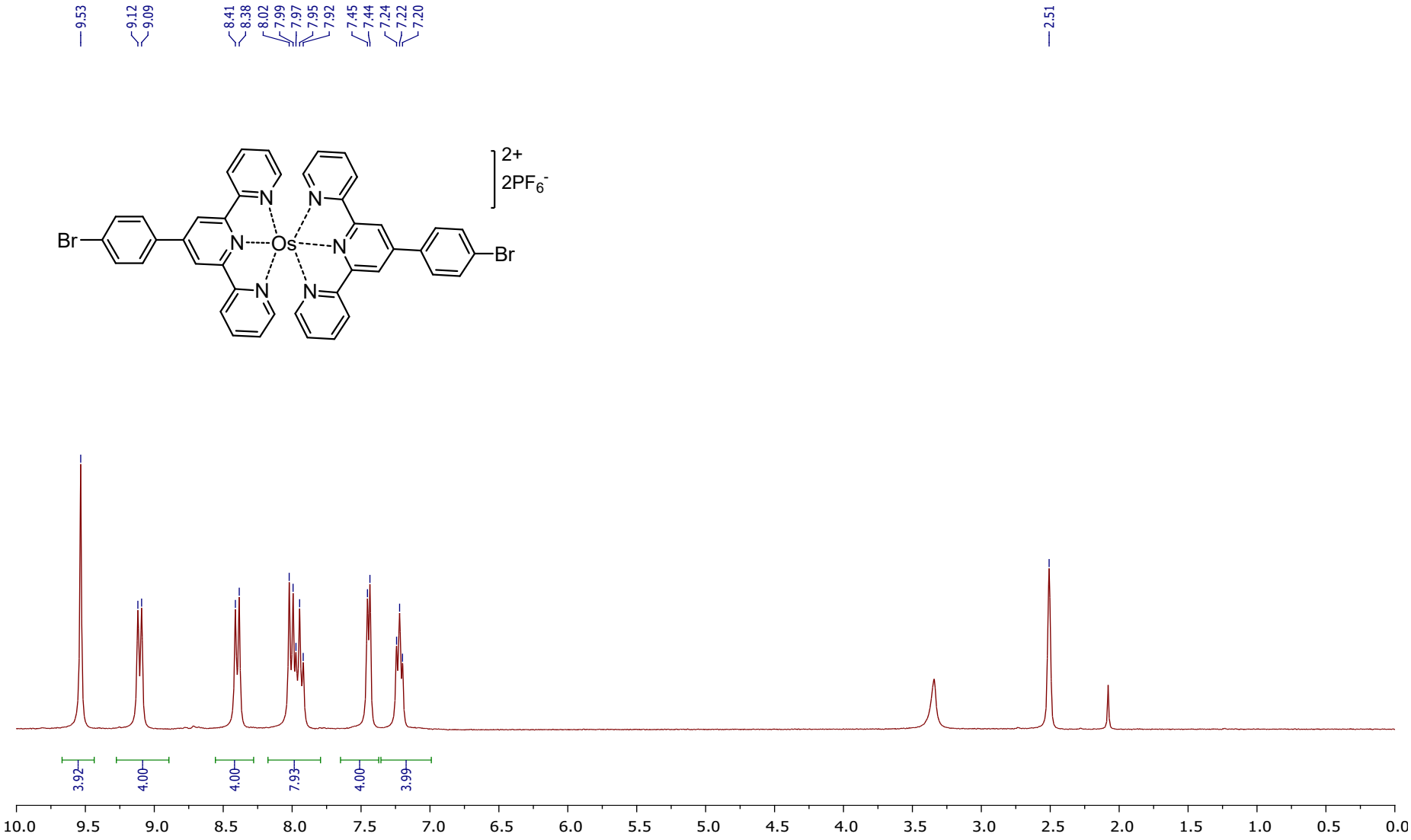
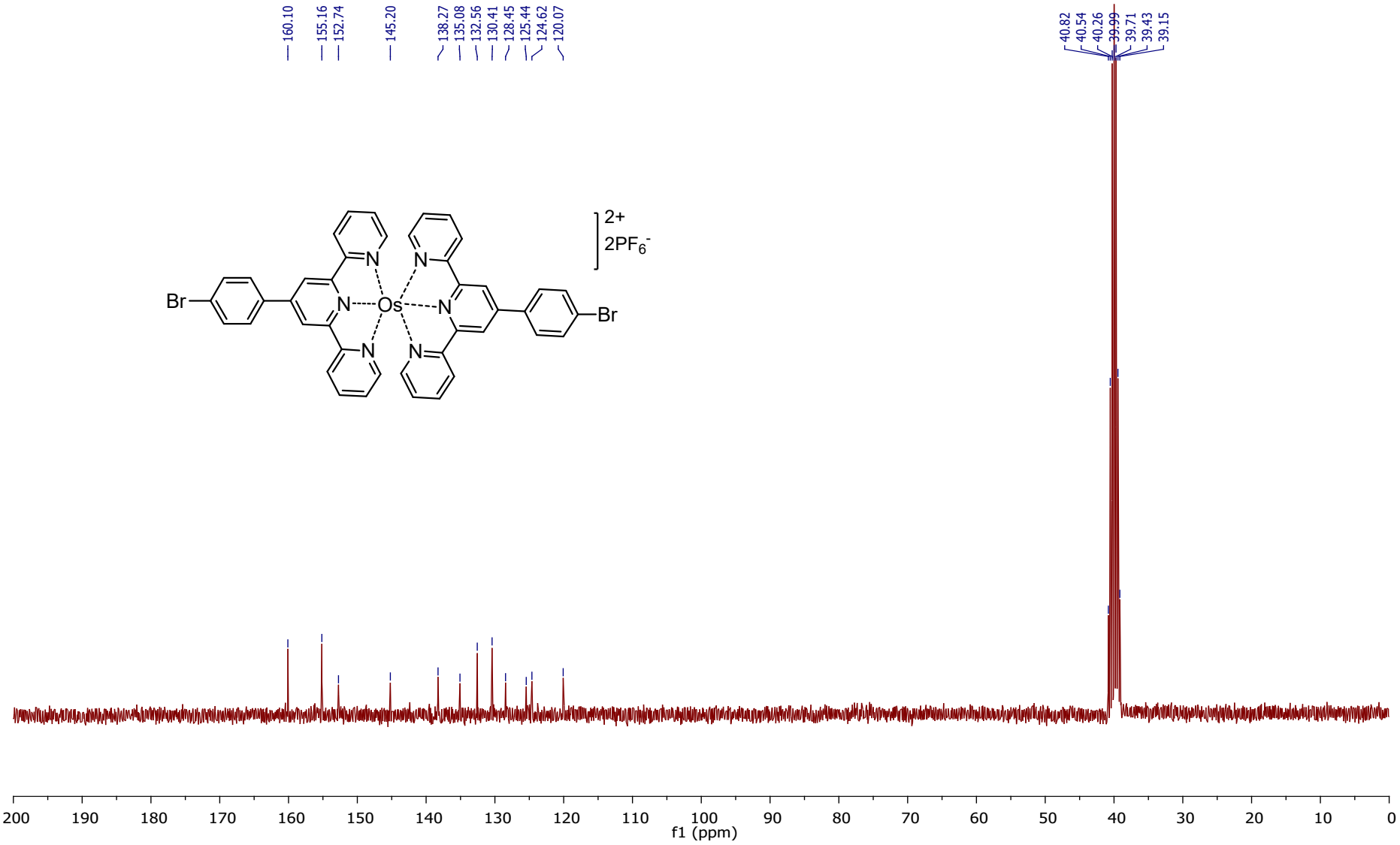
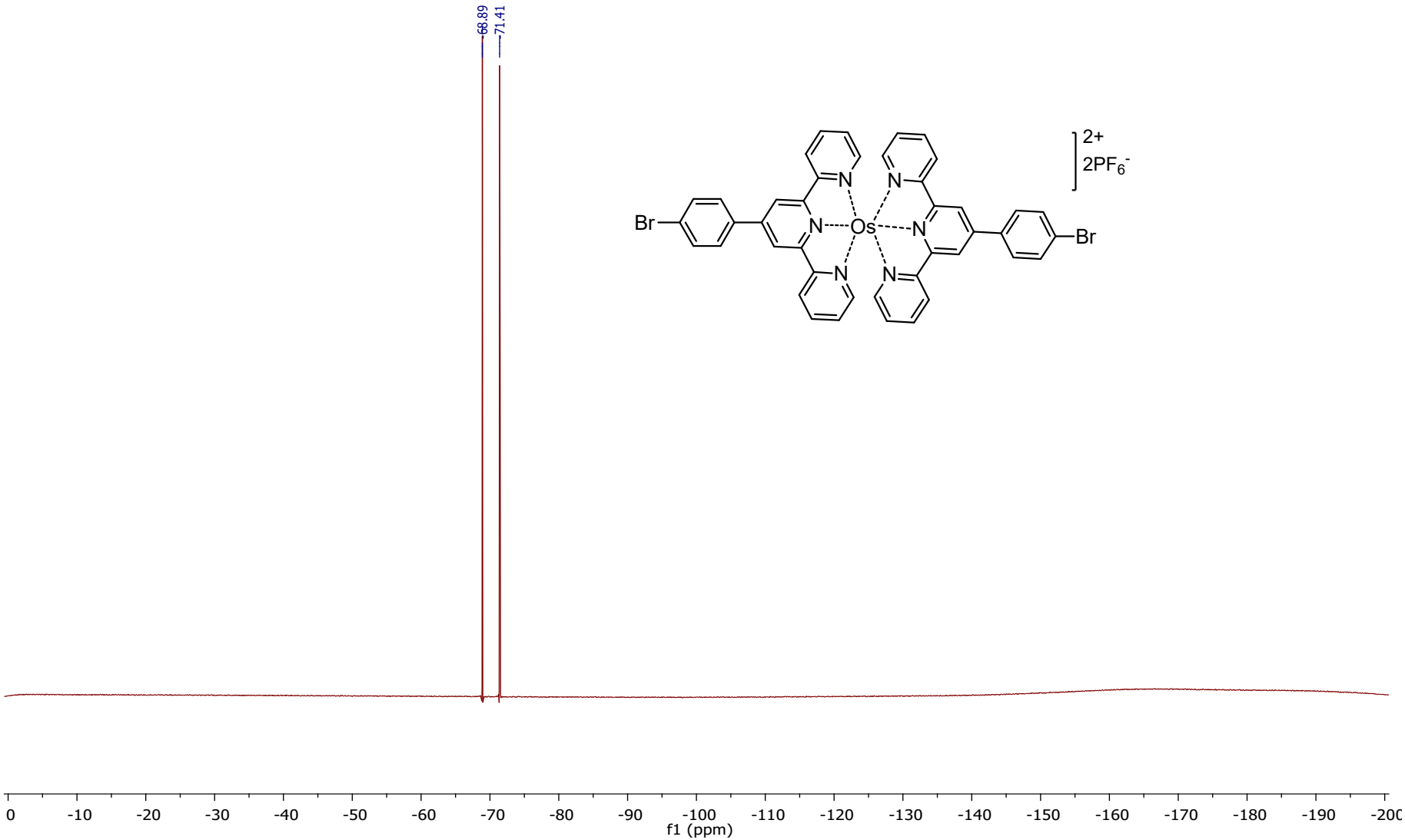


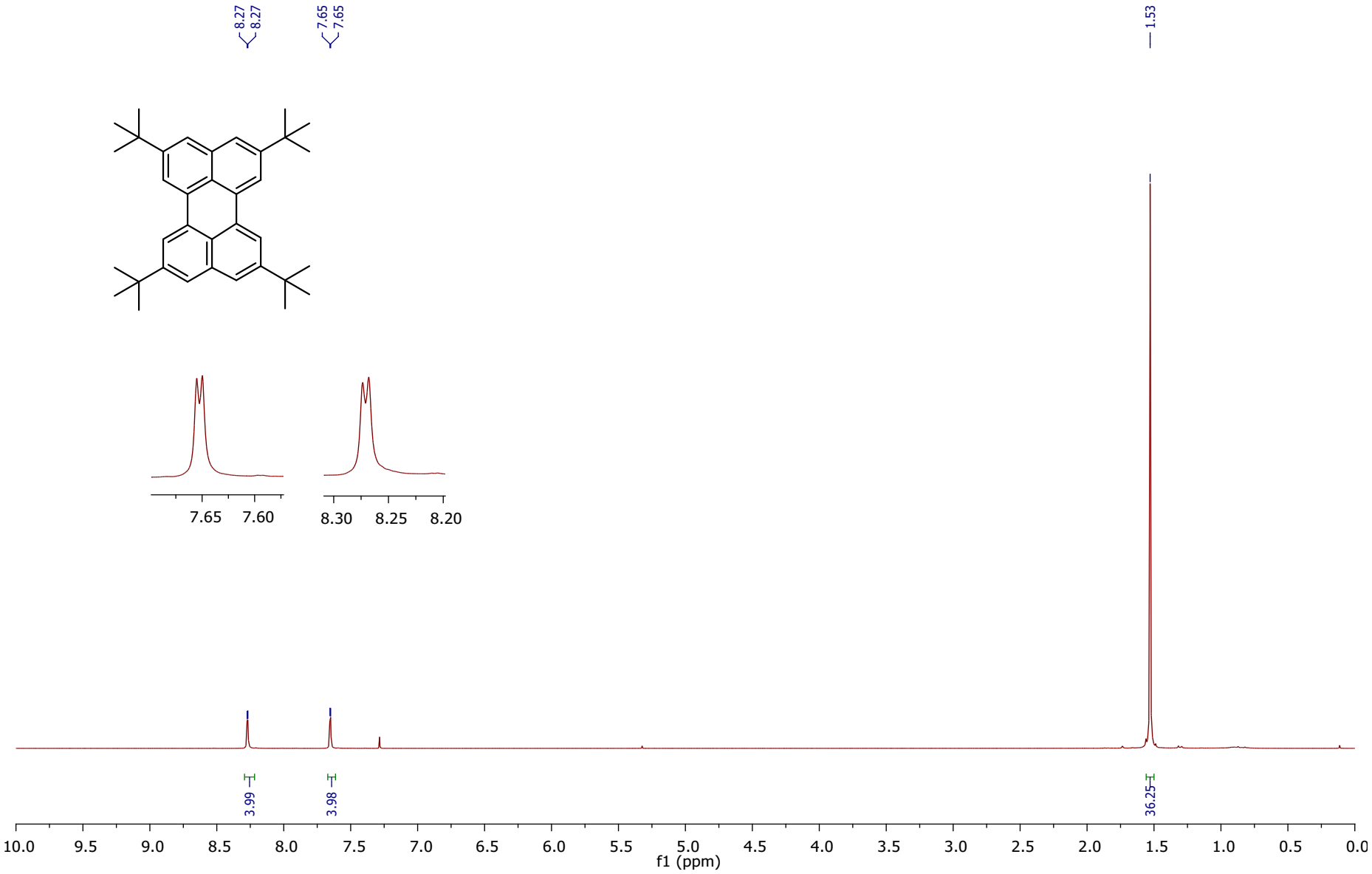
Figure 12: In the presence of oxamic acid and ethanol, BI-OAc did not affect the *ter*-pyridine 6,6" protons in the $Os(bptpy)_2(PF_6)_2$.

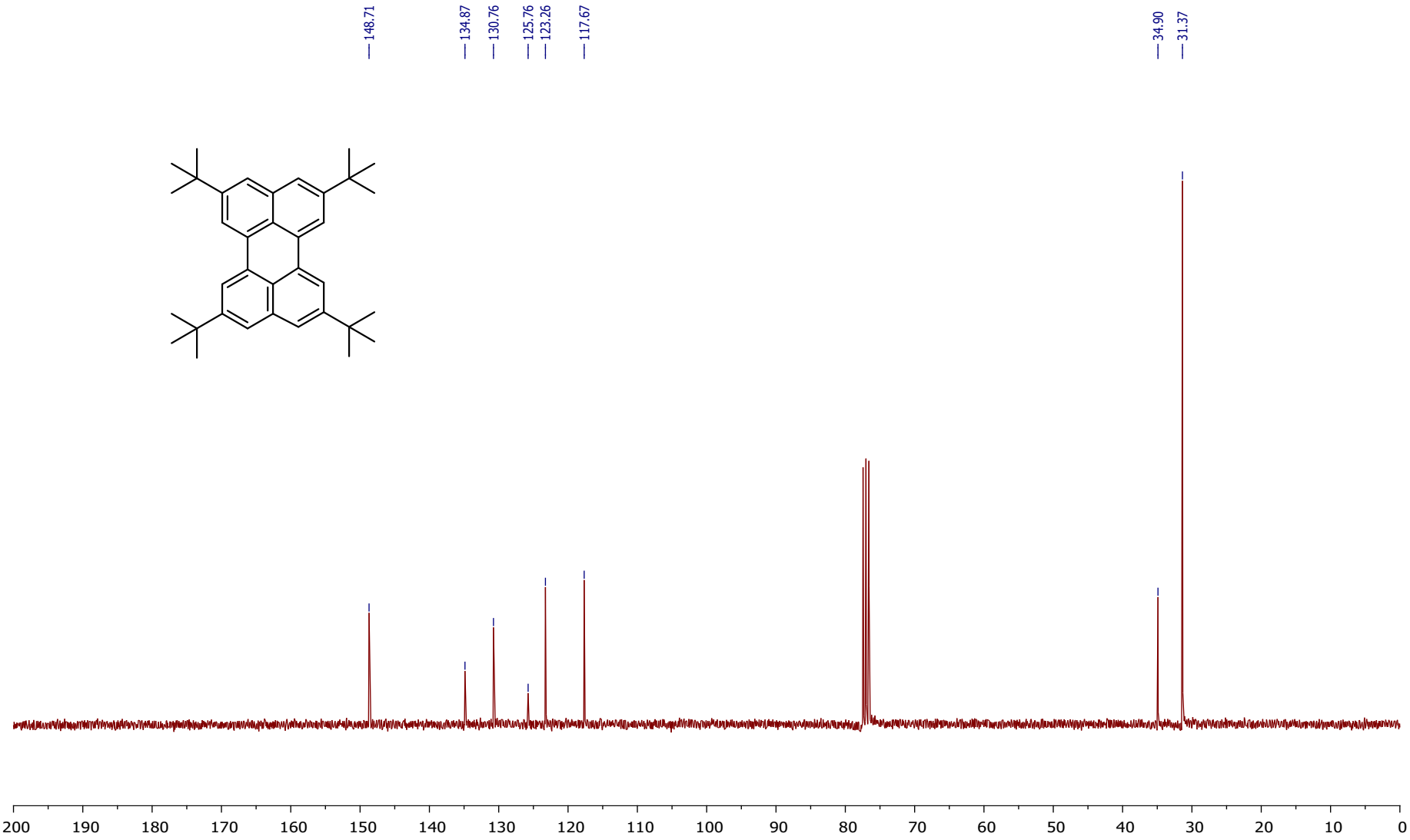
14. NMR Spectra

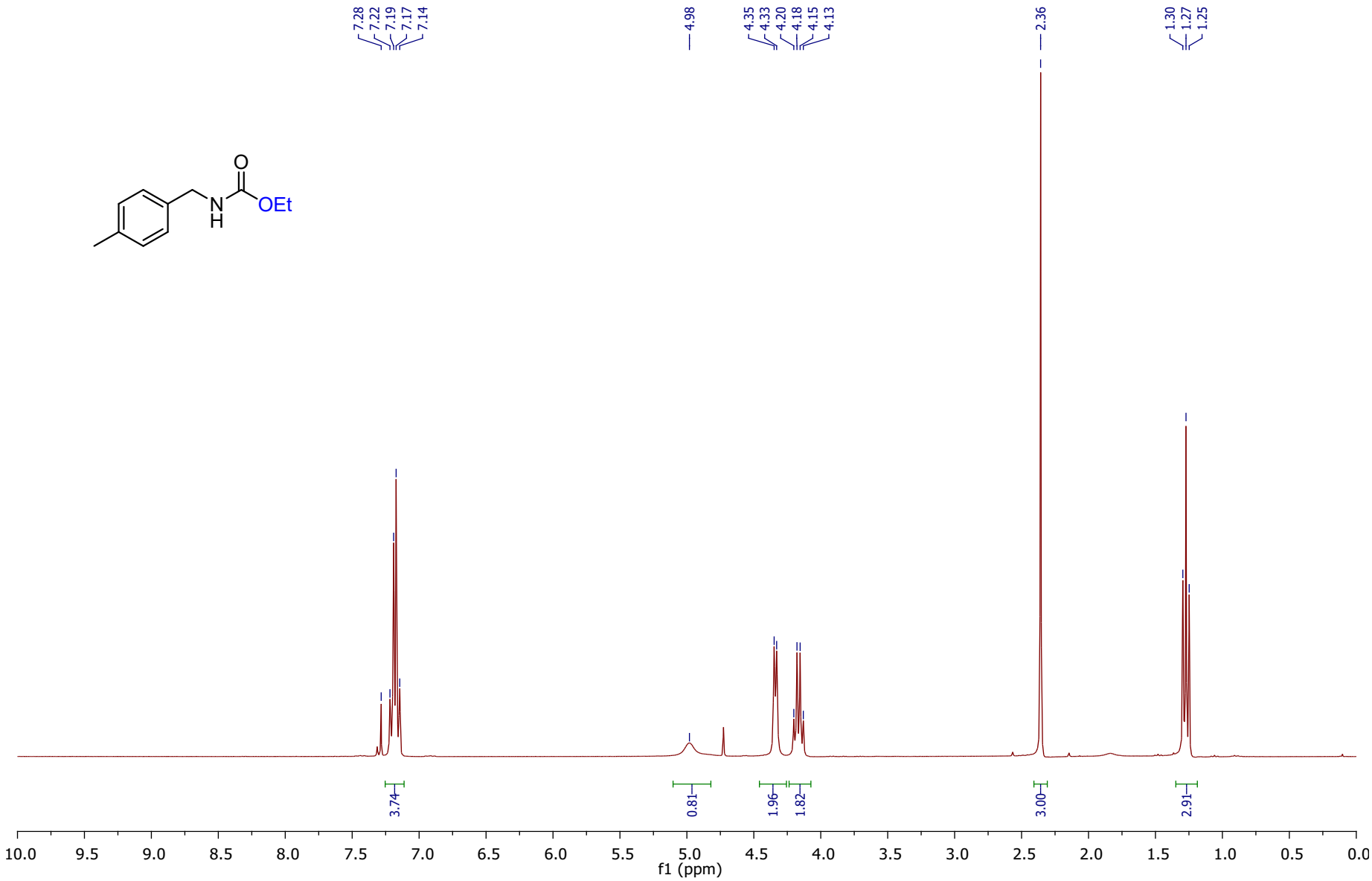



160.10
155.16
152.74
145.20
138.27
135.08
132.56
130.41
128.45
125.44
124.62
120.07
40.82
40.54
40.26
39.99
39.71
39.43
39.15
2+
2PF6-
Br
Br
N
N
Os
N
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


68.89
71.41
Br
N
N
Os
N
N
N
N
Br
2+
2PF6-
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


8.27
8.27
7.65
7.65
1.53
7.65
7.60
8.30
8.25
8.20
3.99
3.98
36.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.71
134.87
130.76
125.76
123.26
117.67
34.90
31.37
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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4.13
2.36
1.30
1.27
1.25
O
N
H
OEt
3.74
0.81
1.96
1.82
3.00
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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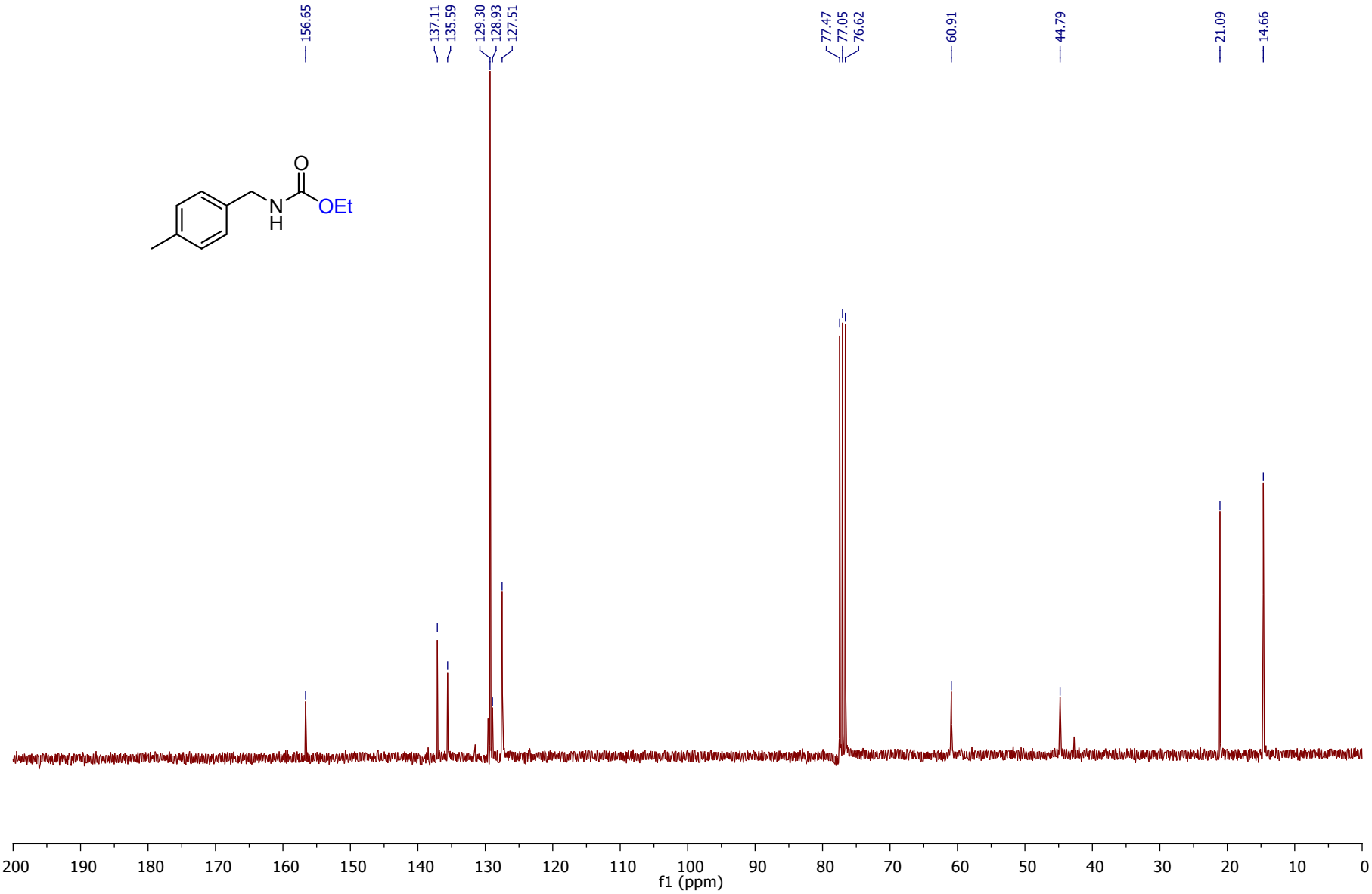
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127.51
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77.05
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60.91
44.79
21.09
14.66
O
N
H
OEt
200
190
180
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130
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110
100
90
80
70
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50
40
30
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10
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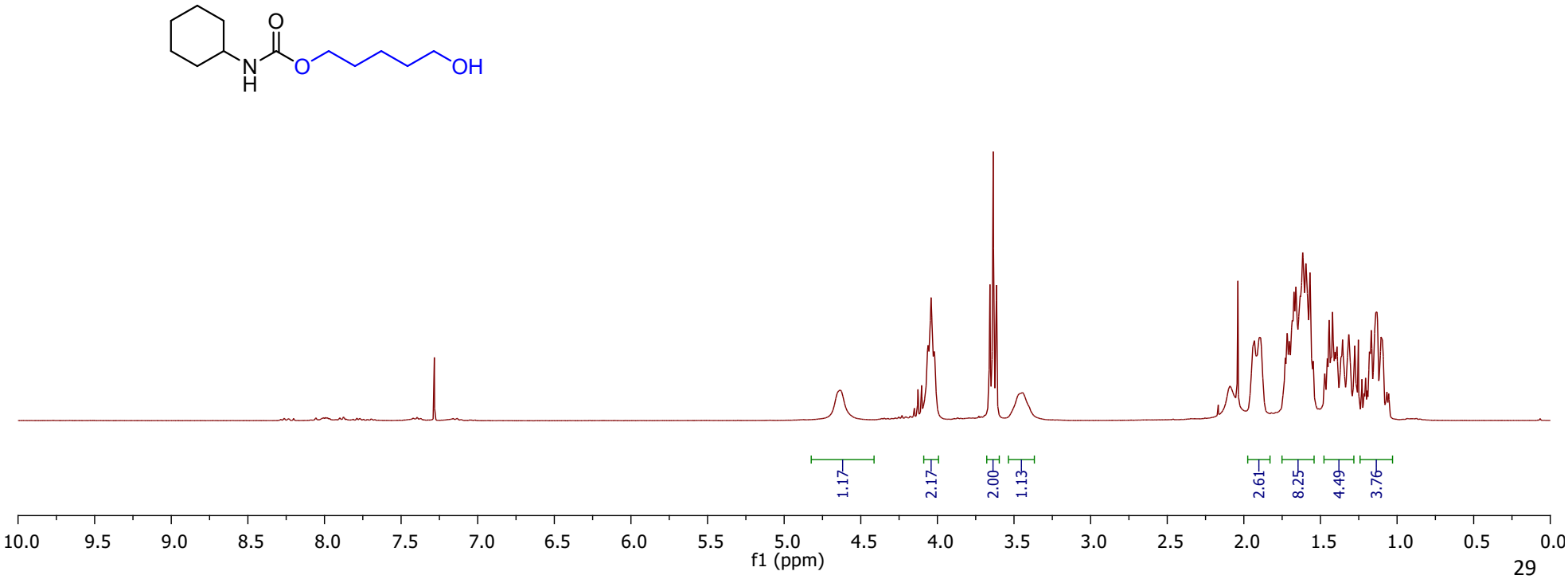
f1 (ppm)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OH
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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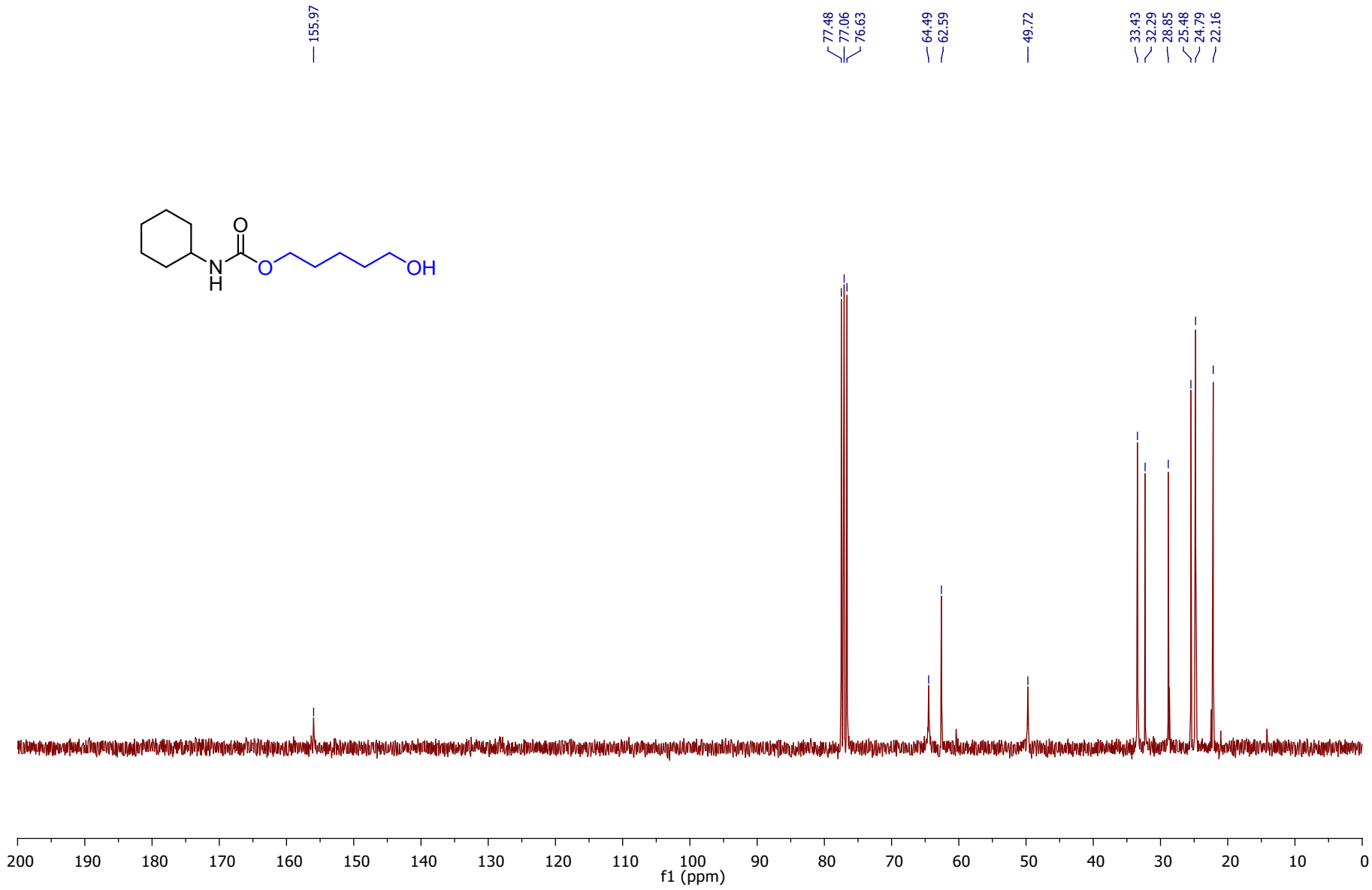
0.0
f1 (ppm)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33.43
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28.85
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24.79
22.16
O
N
H
O
OH
200
190
180
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50
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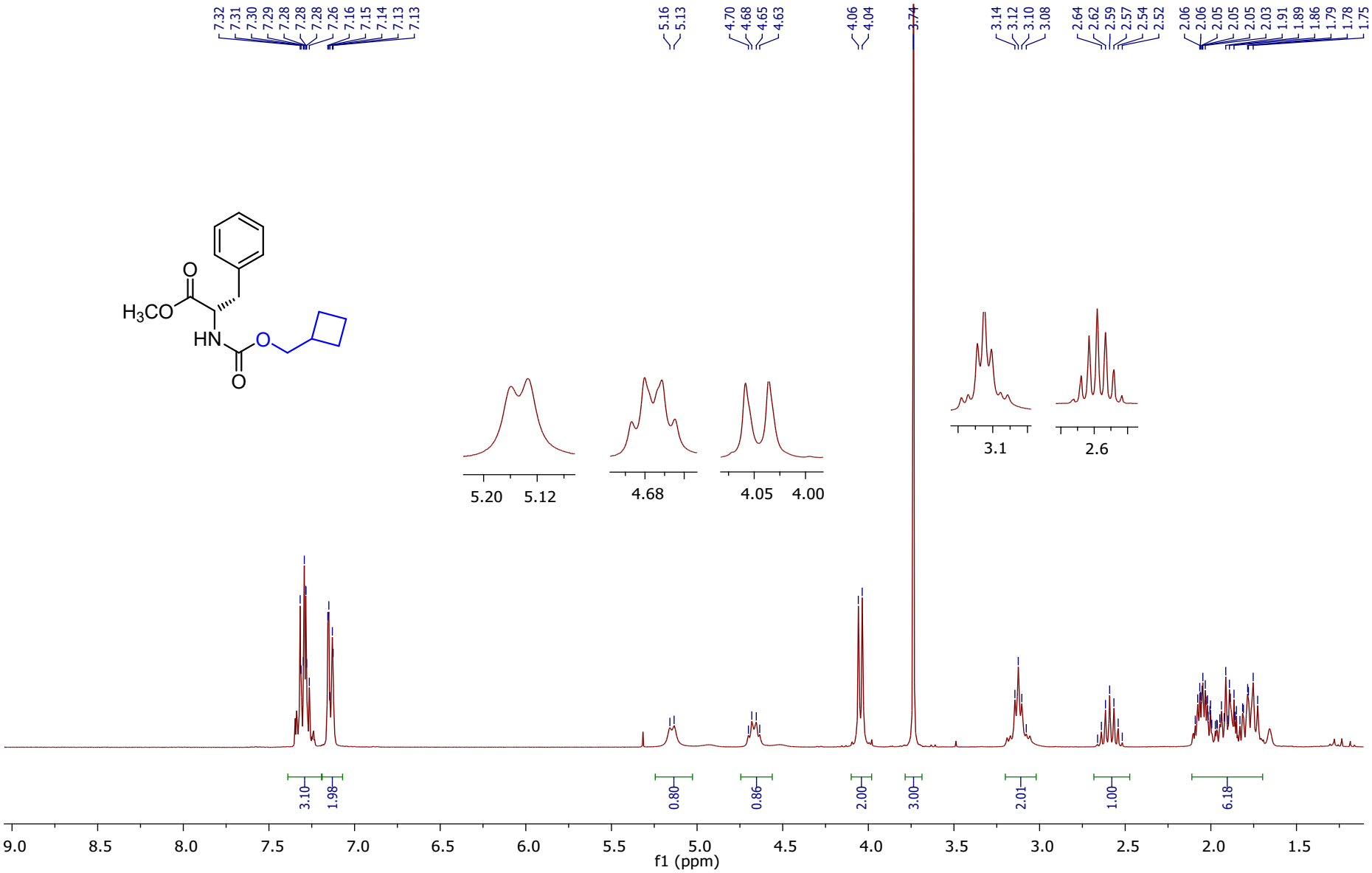
f1 (ppm)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5.16 5.13
4.70 4.68 4.65 4.63
4.06 4.04
3.74
3.14 3.12 3.10 3.08
2.64 2.62 2.59 2.57 2.54 2.52
2.06 2.06 2.05 2.05 2.05 2.03 1.91 1.89 1.86 1.79 1.78 1.75
H3CO
O
HN
O
O
5.20 5.12
4.68
4.05 4.00
3.1
2.6
3.10 1.98 0.80 0.86 2.00 3.00 2.01 1.00 6.18
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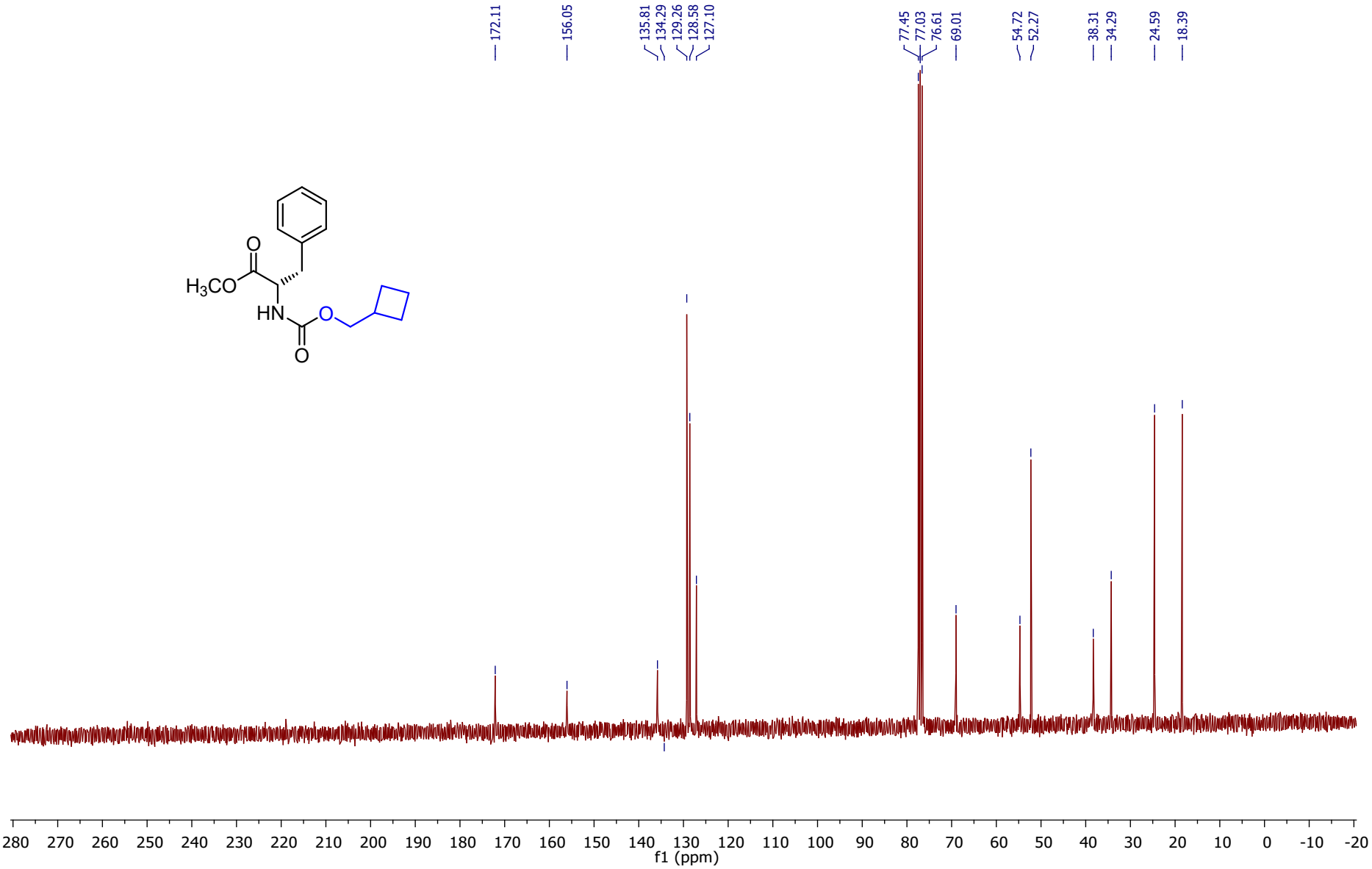
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76.61
69.01
54.72
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34.29
24.59
18.39
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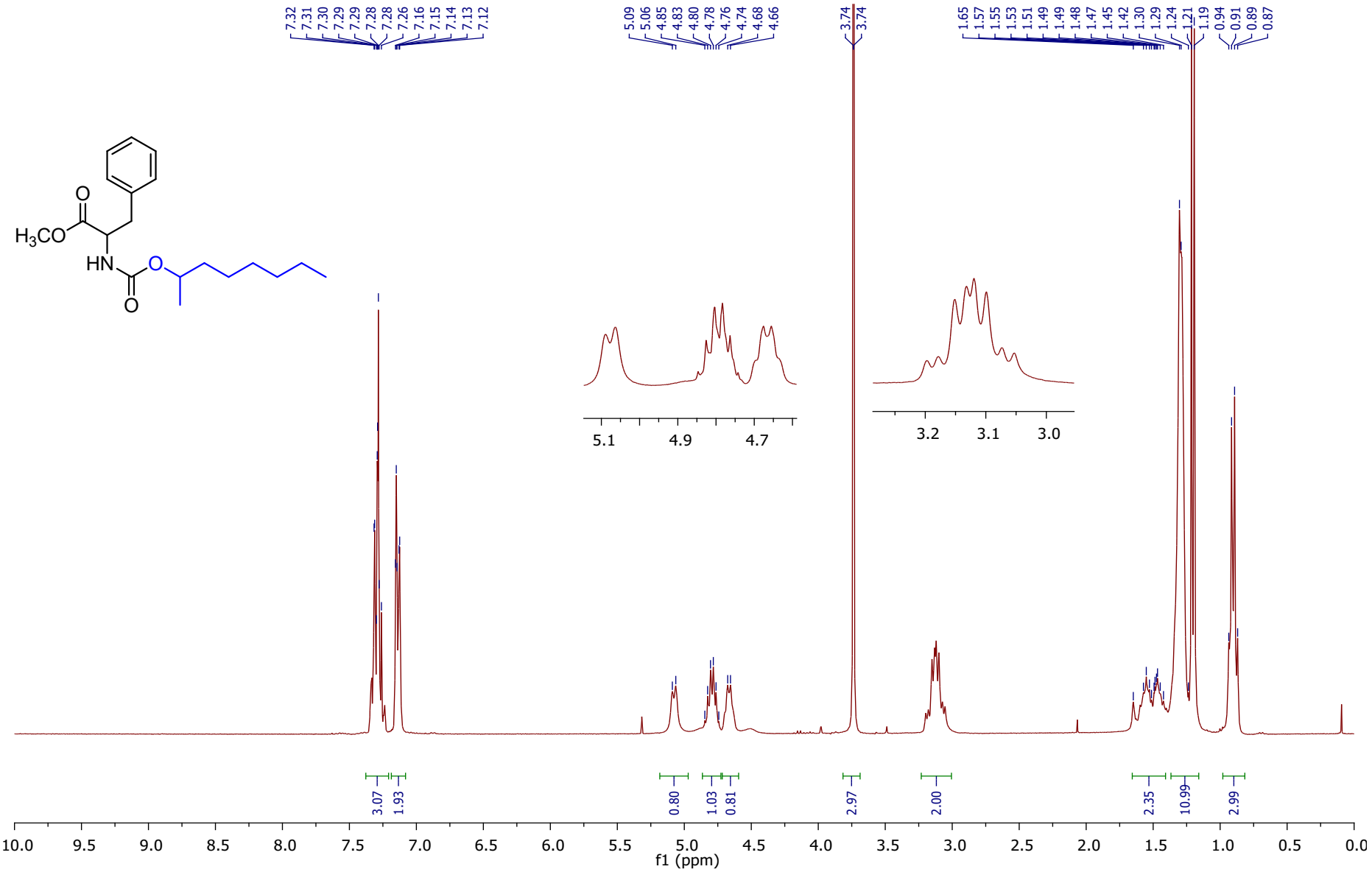
H3CO
HN
O
O
280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.15
7.14
7.13
7.12
5.09
5.06
4.85
4.83
4.80
4.78
4.76
4.74
4.68
4.66
3.74
3.74
1.65
1.57
1.55
1.53
1.51
1.49
1.49
1.48
1.47
1.45
1.42
1.30
1.29
1.24
1.21
1.19
0.94
0.91
0.89
0.87
O
H3CO
HN
O
O
5.1
4.9
4.7
3.2
3.1
3.0
3.07
1.93
0.80
1.03
0.81
2.97
2.00
2.35
10.99
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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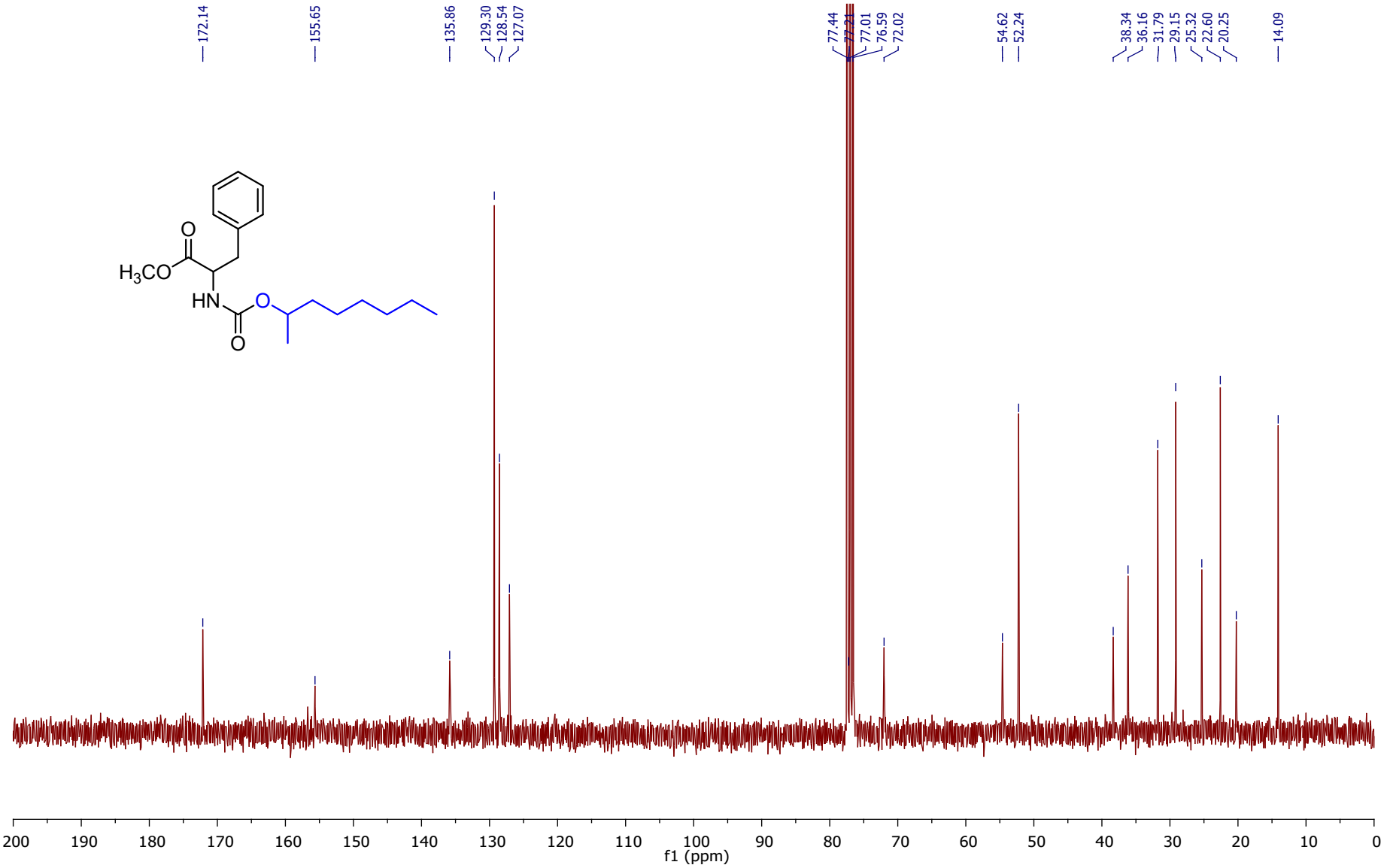
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.07
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77.21
77.01
76.59
72.02
54.62
52.24
38.34
36.16
31.79
29.15
25.32
22.60
20.25
14.09
O
H3CO
HN
O
O
200
190
180
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130
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110
100
90
80
70
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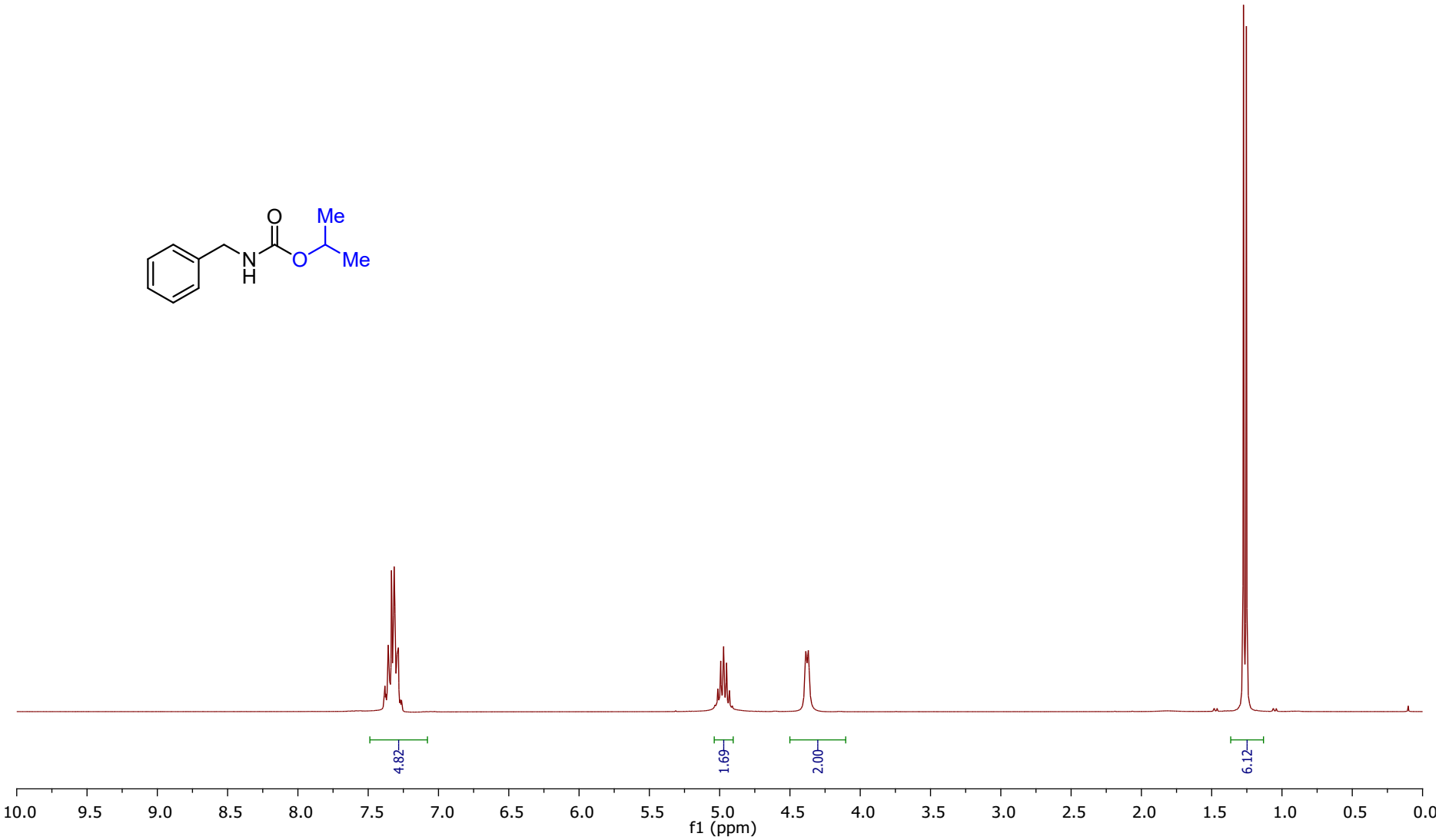
50
40
30
20
10
0
f1 (ppm)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N
H
O
Me
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1.69
2.00
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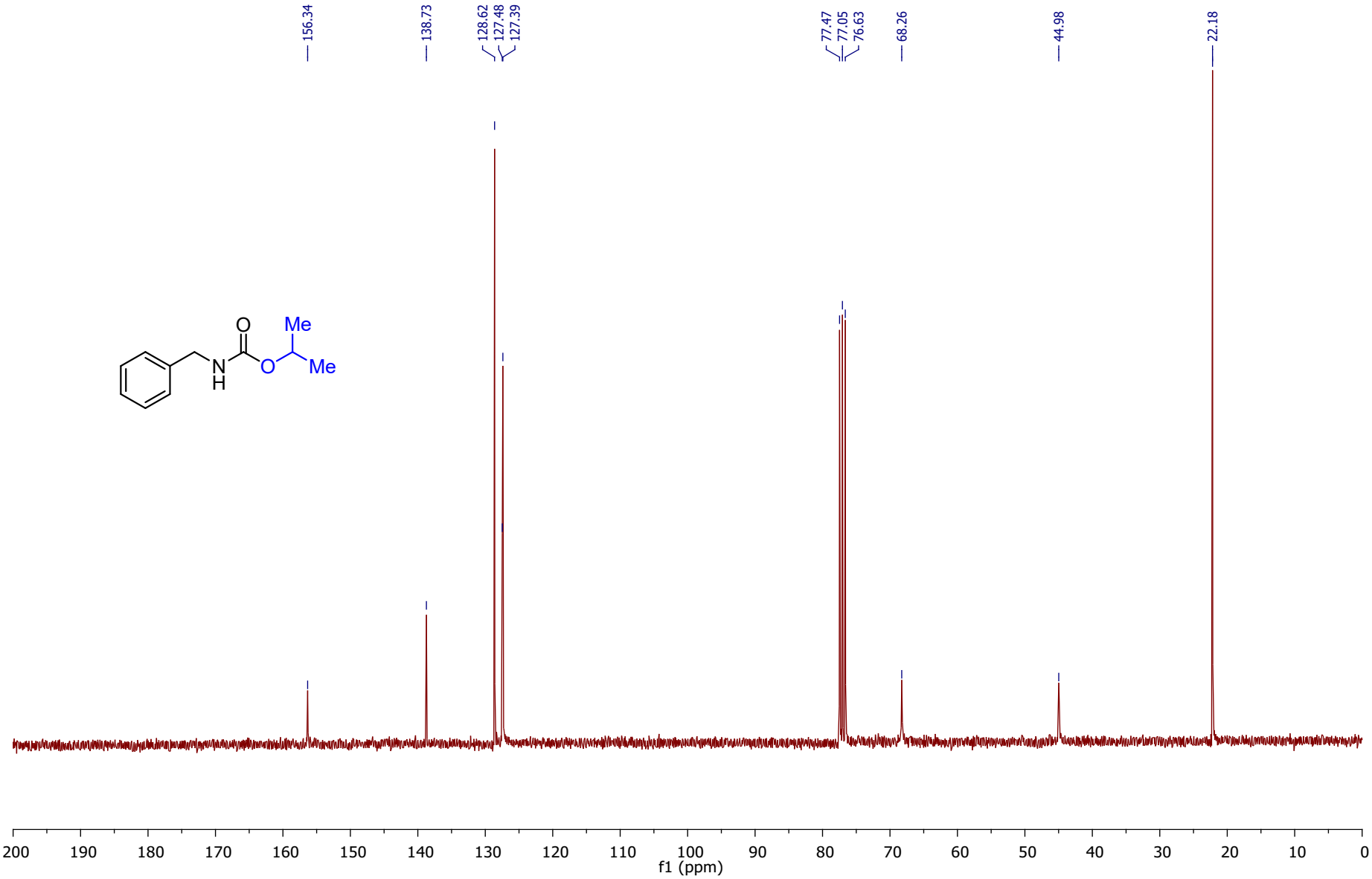
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.39
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76.63
68.26
44.98
22.18
O
Me
N
H
O
Me
200
190
180
170
160
150
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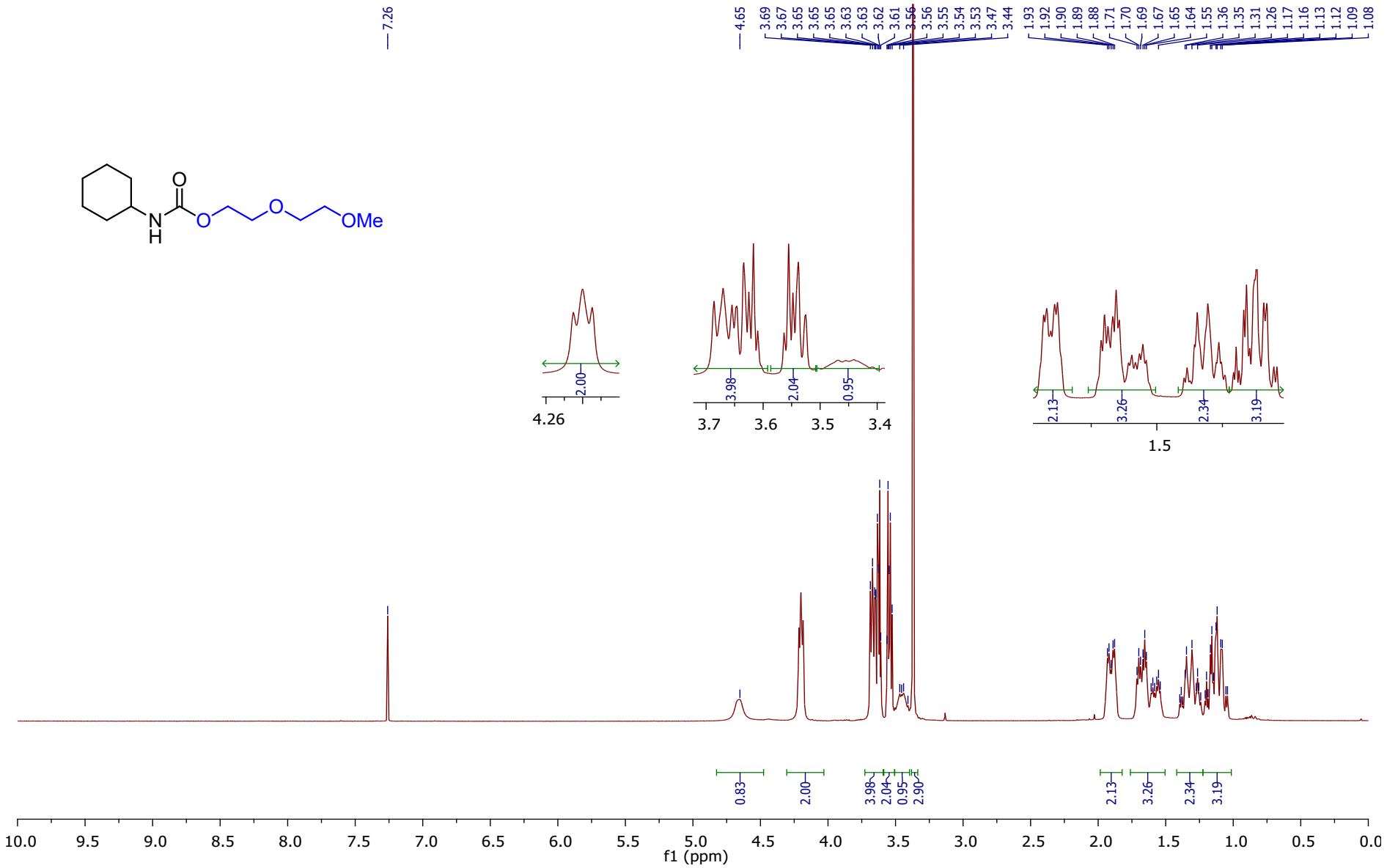
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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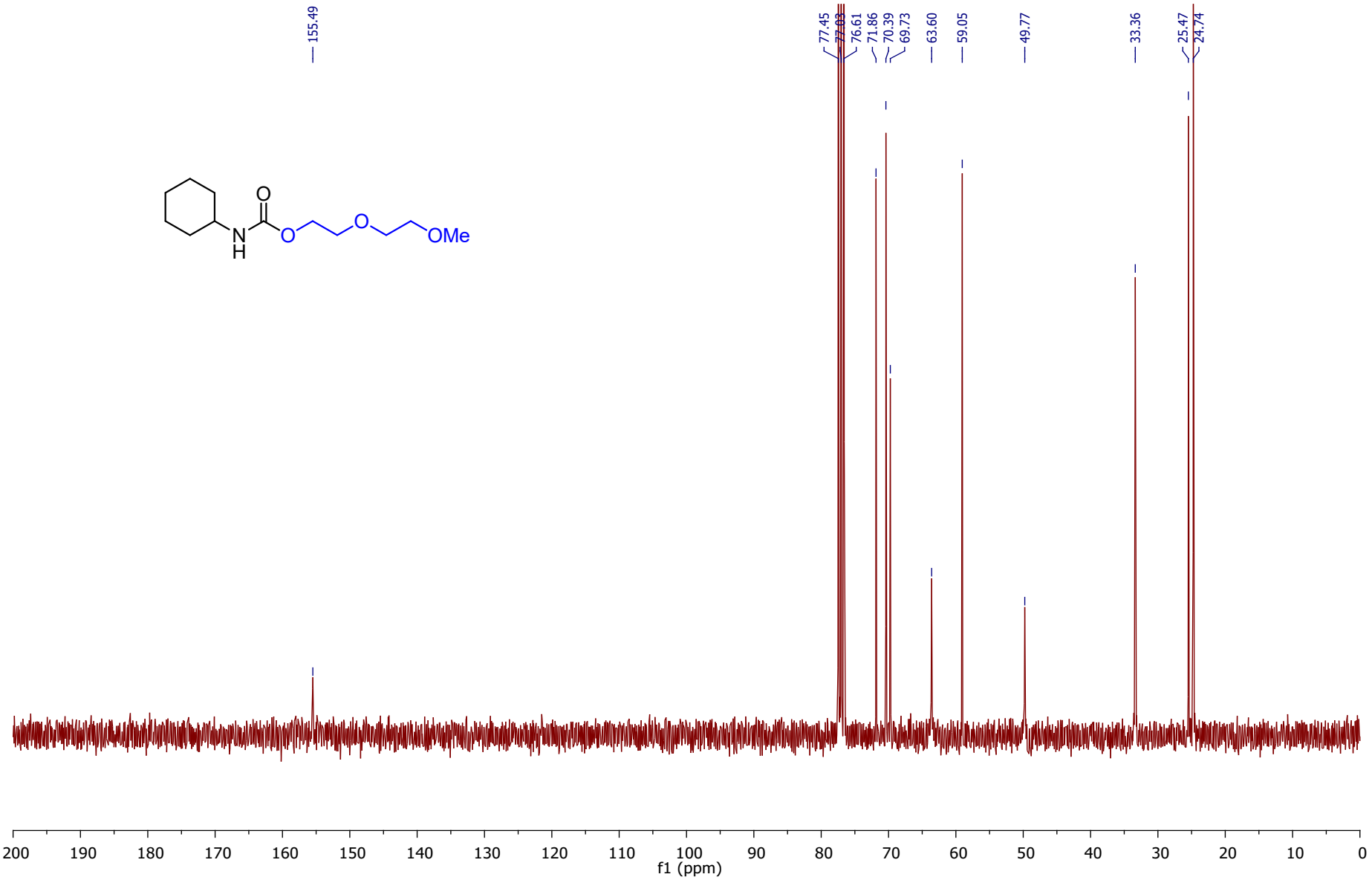
3.63
3.63
3.62
3.61
3.56
3.56
3.55
3.54
3.53
3.47
3.44
1.93
1.92
1.90
1.89
1.88
1.71
1.70
1.69
1.67
1.65
1.64
1.55
1.36
1.35
1.31
1.26
1.17
1.16
1.13
1.12
1.09
1.08
O
N
H
O
O
O
OMe
2.00
4.26
3.98
2.04
0.95
3.7
3.6
3.5
3.4
2.13
3.26
2.34
3.19
1.5
0.83
2.00
3.98
2.04
0.95
2.90
2.13
3.26
2.34
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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69.73
63.60
59.05
49.77
33.36
25.47
24.74
O
N
H
O
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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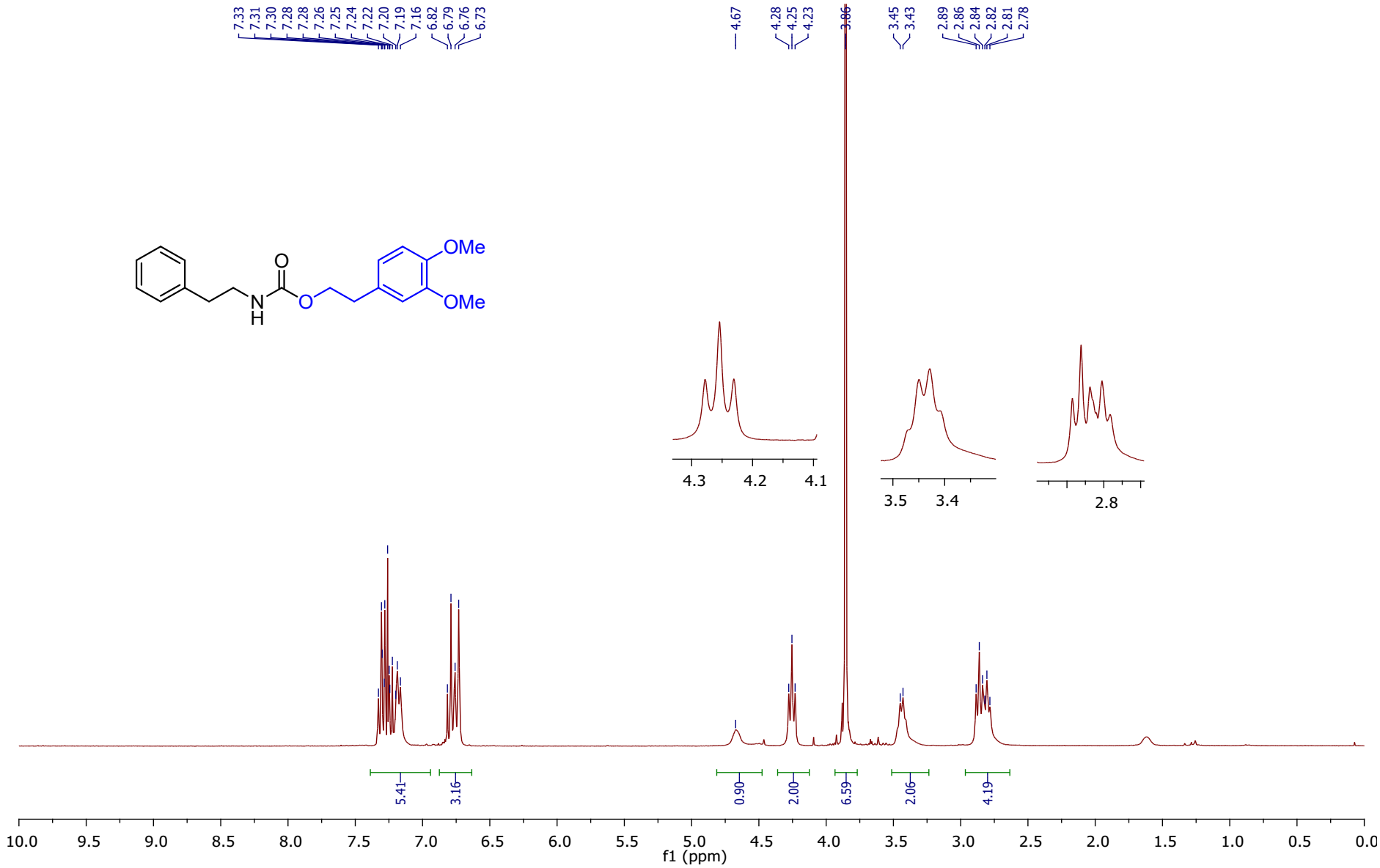
50
40
30
20
10
0
f1 (ppm)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7.24
7.22
7.20
7.19
7.16
6.82
6.79
6.76
6.73
4.67
4.28
4.25
4.23
3.86
3.45
3.43
2.89
2.86
2.84
2.82
2.81
2.78
OMe
OMe
O
N
H
O
4.3
4.2
4.1
3.5
3.4
2.8
5.41
3.16
0.90
2.00
6.59
2.06
4.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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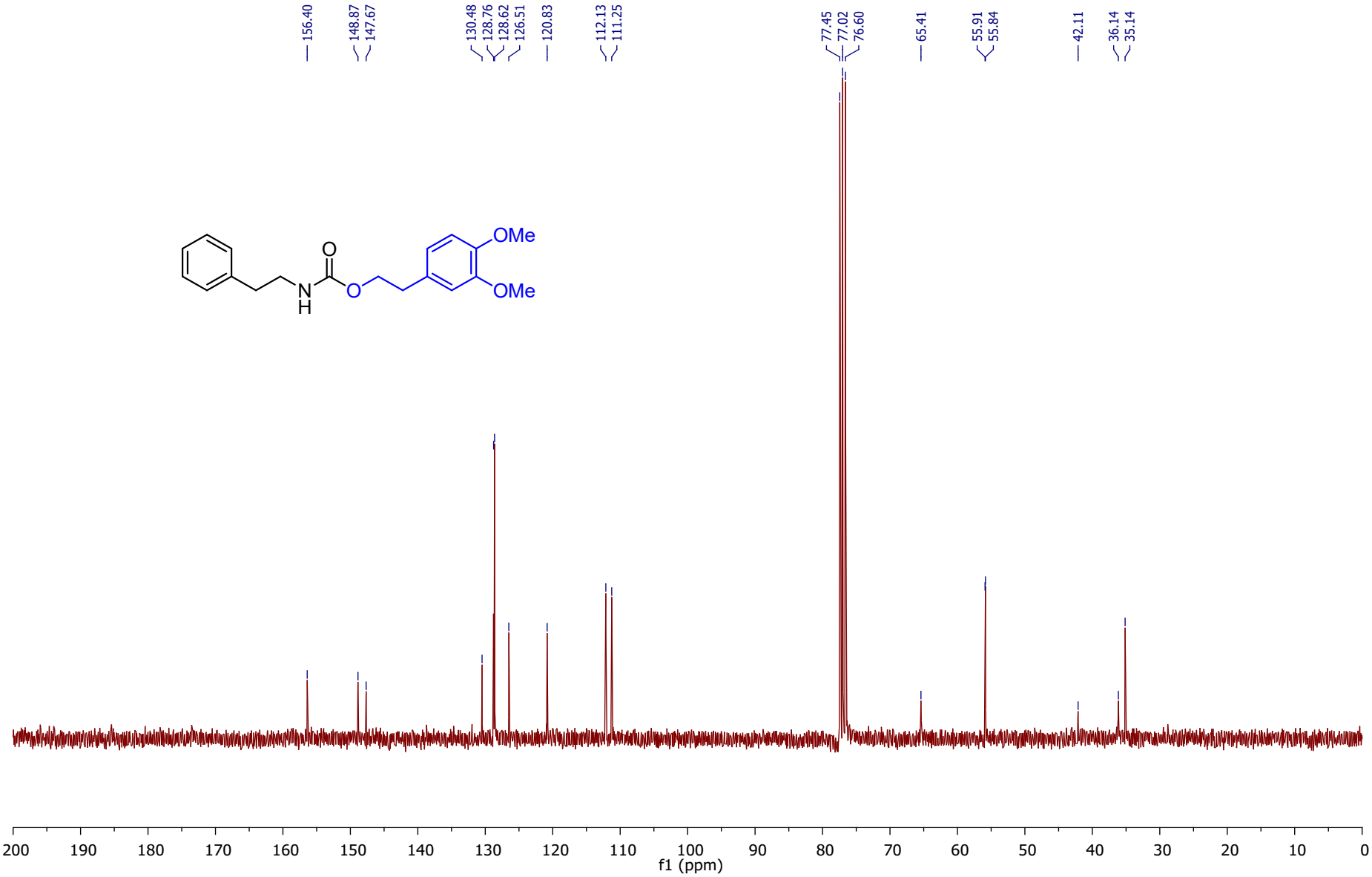
f1 (ppm)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111.25
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77.02
76.60
65.41
55.91
55.84
42.11
36.14
35.14
O
N
H
O
OMe
OMe
200
190
180
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110
100
90
80
70
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50
40
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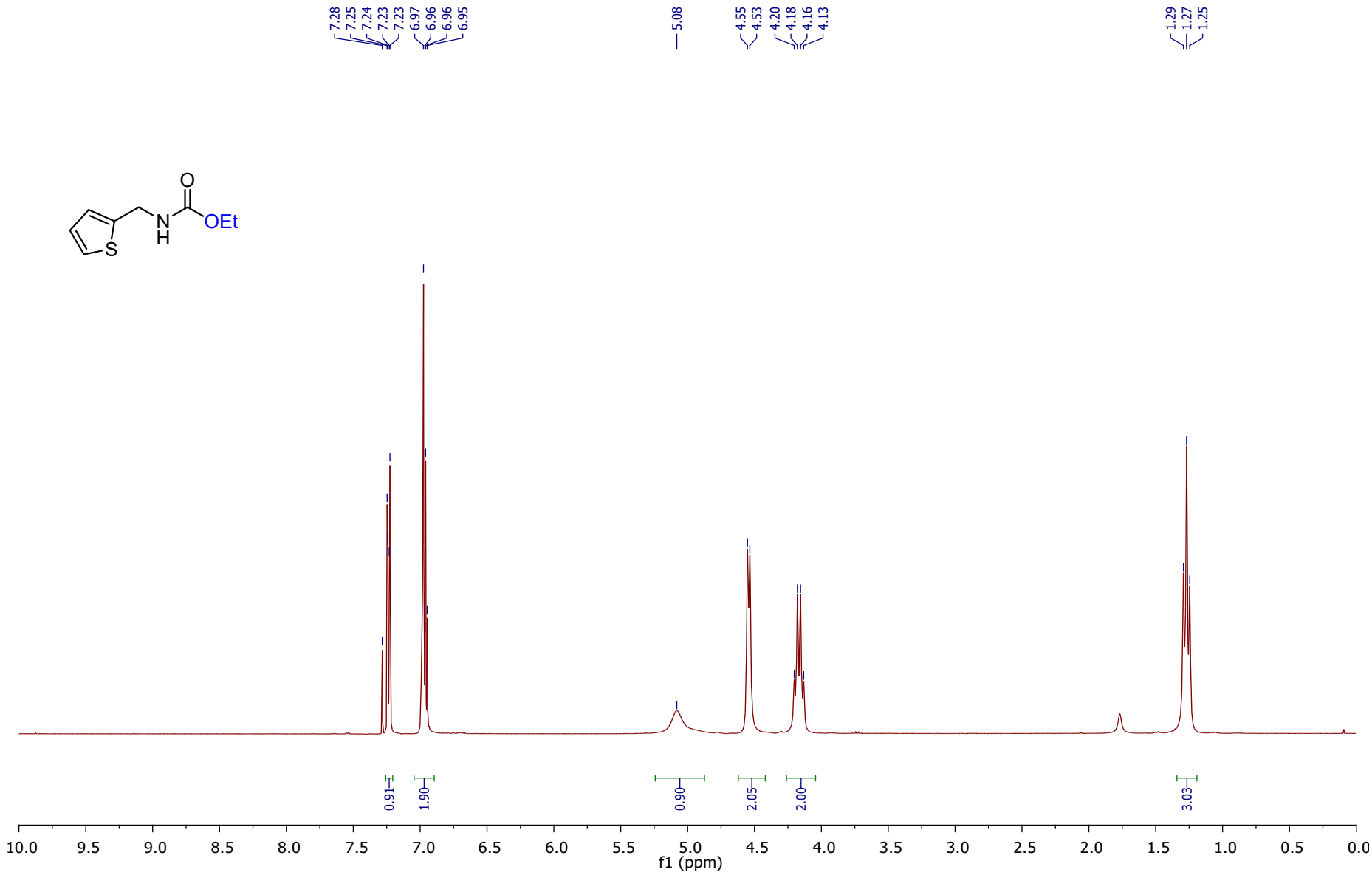
20
10
0
f1 (ppm)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4.20
4.18
4.16
4.13
1.29
1.27
1.25
O
N
H
S
OEt
0.91
1.90
0.90
2.05
2.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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0.0
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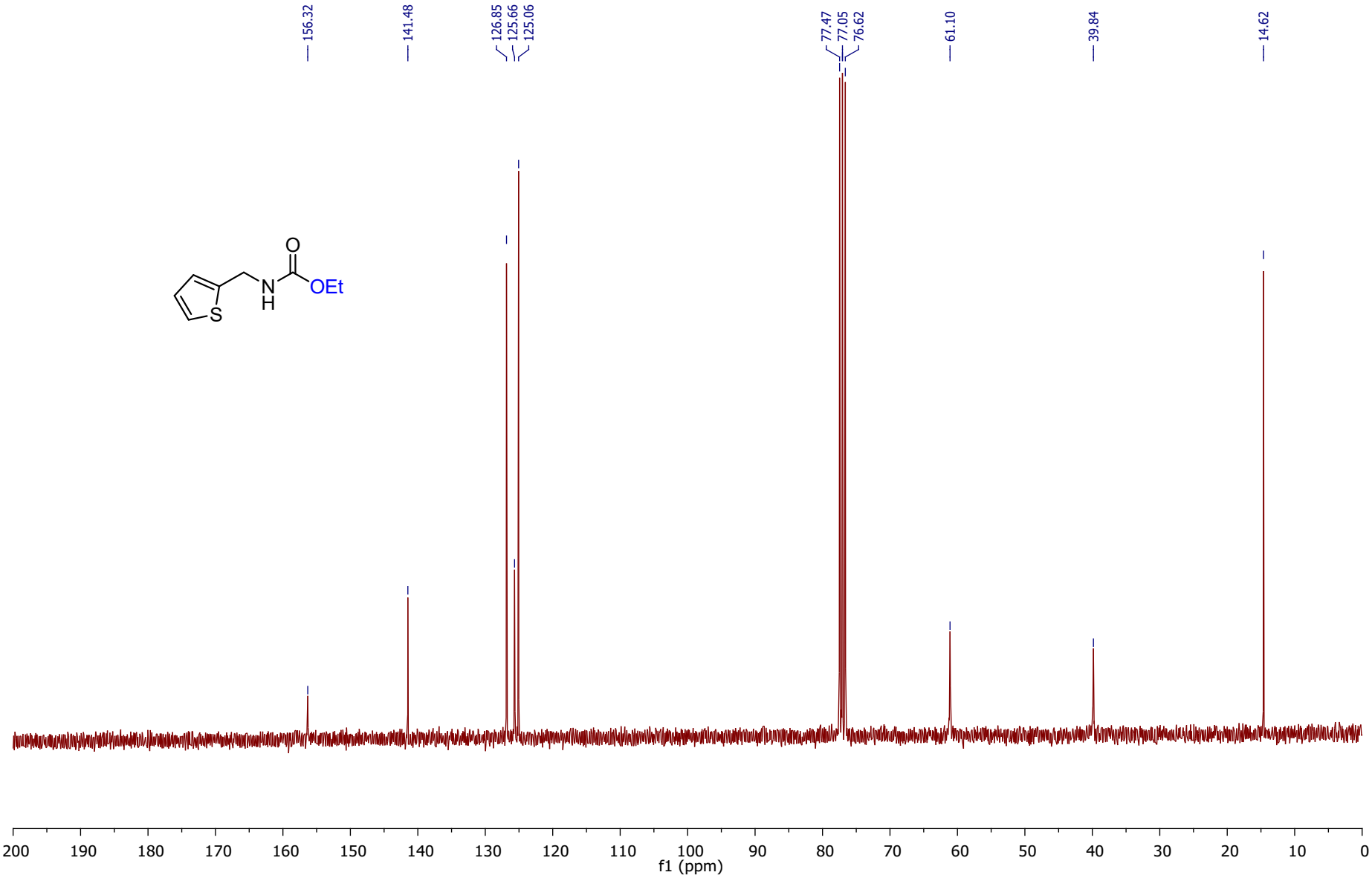
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76.62
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39.84
14.62
O
N
H
OEt
S
200
190
180
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130
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110
100
90
80
70
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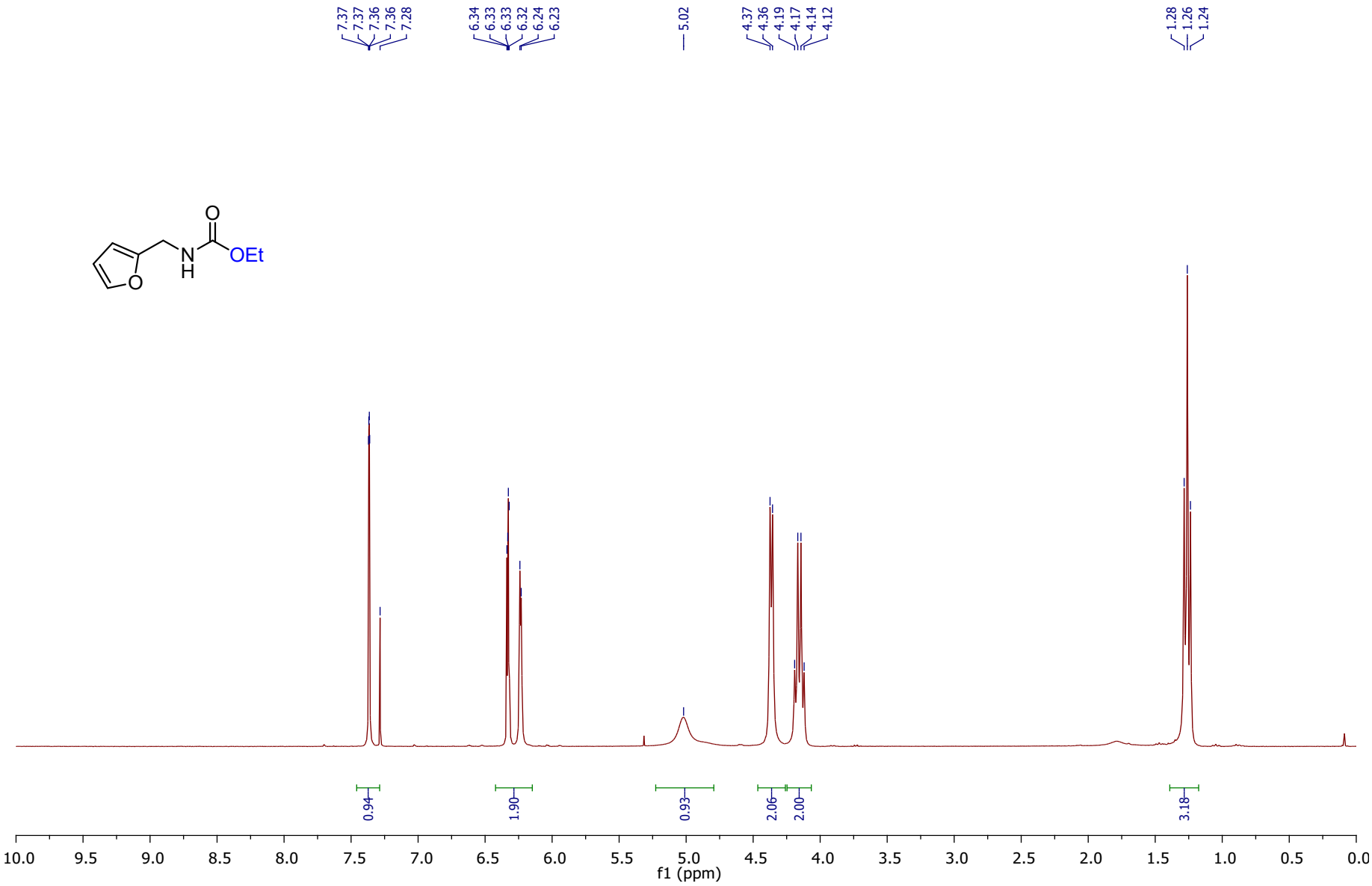
50
40
30
20
10
0
f1 (ppm)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6.23
5.02
4.37
4.36
4.19
4.17
4.14
4.12
1.28
1.26
1.24
O
N
H
O
OEt
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0.93
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2.00
3.18
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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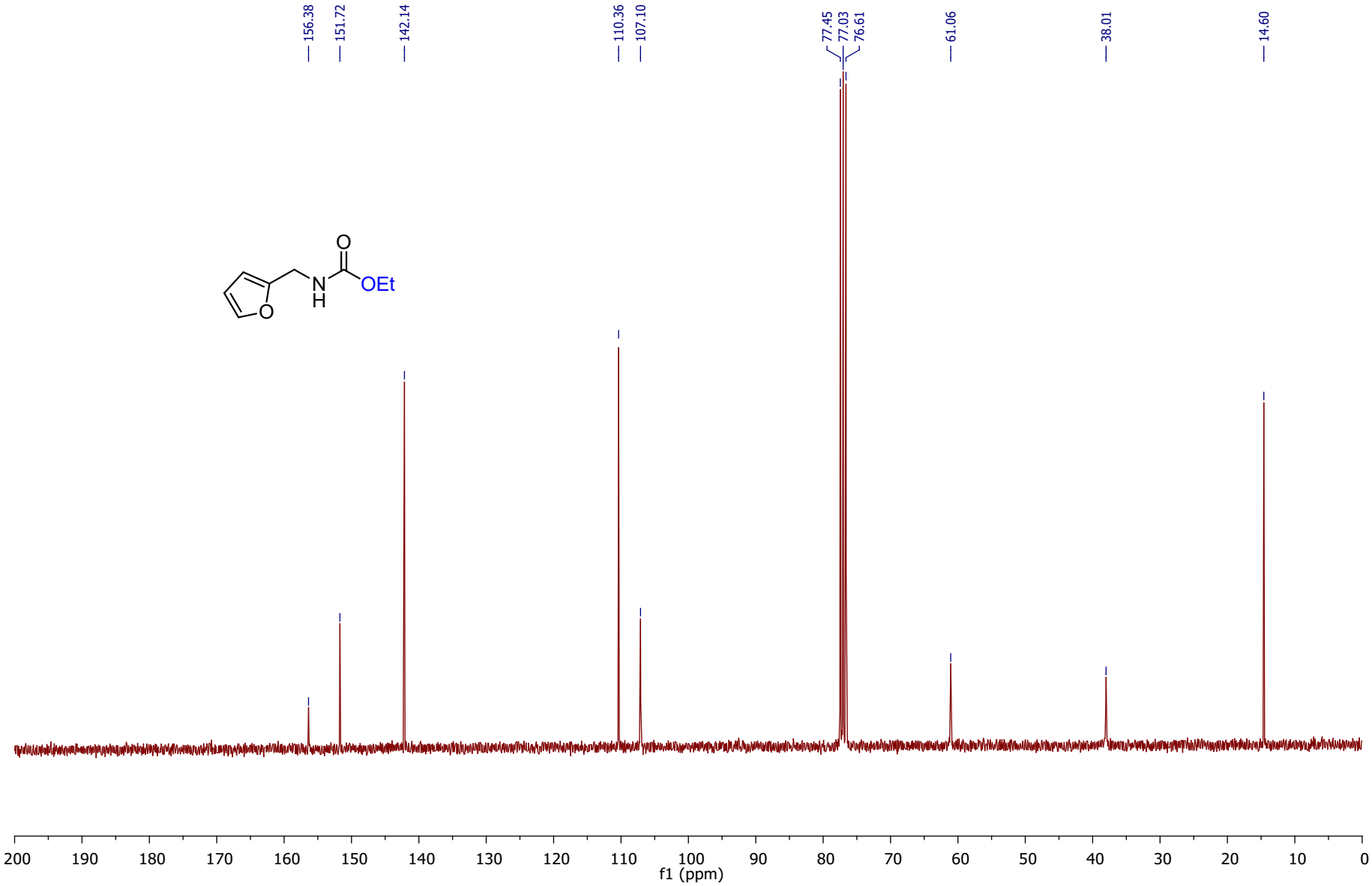
1.0
0.5
0.0
f1 (ppm)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76.61
61.06
38.01
14.60
O
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H
O
OEt
200
190
180
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90
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70
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50
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10
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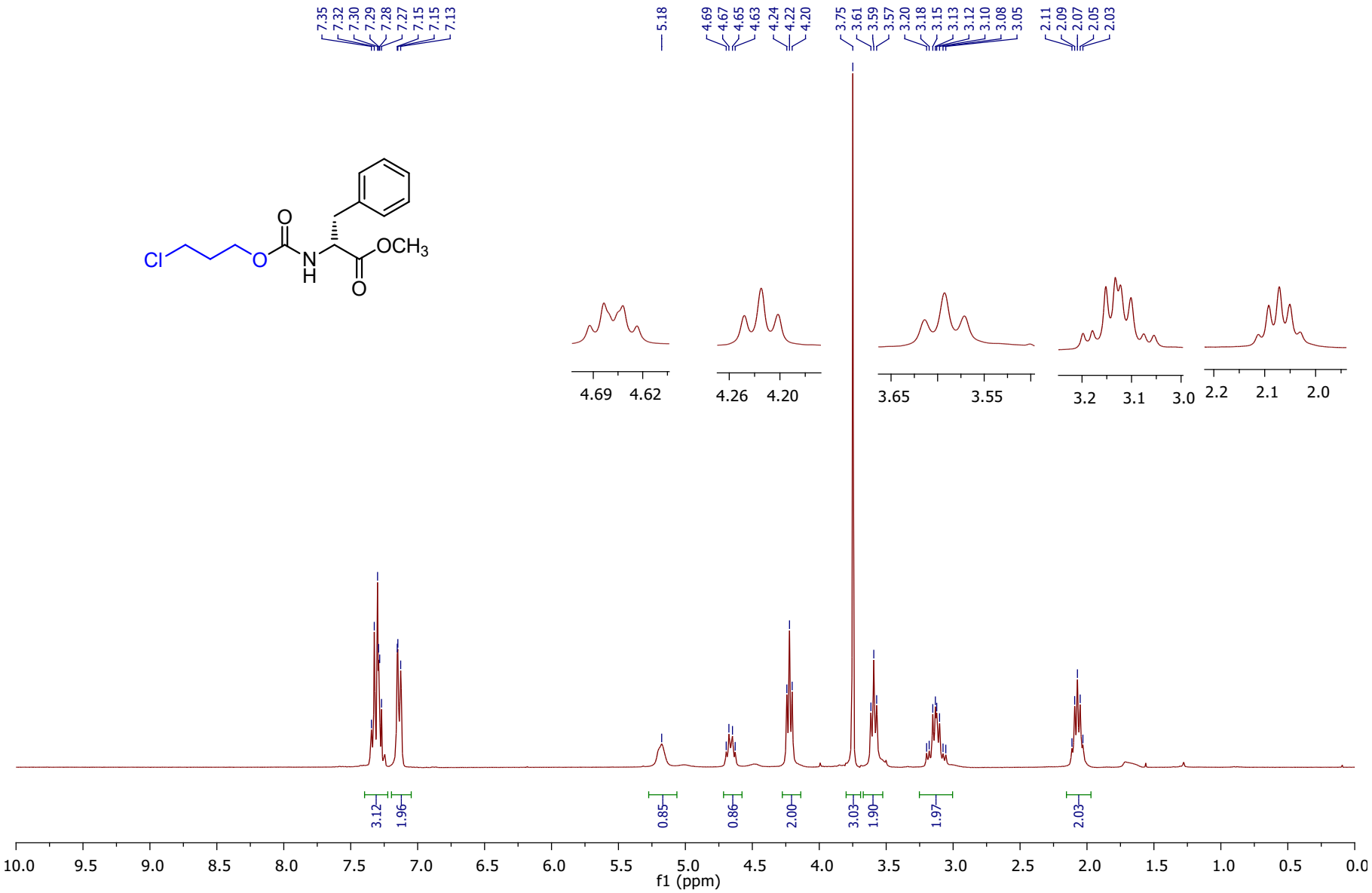
f1 (ppm)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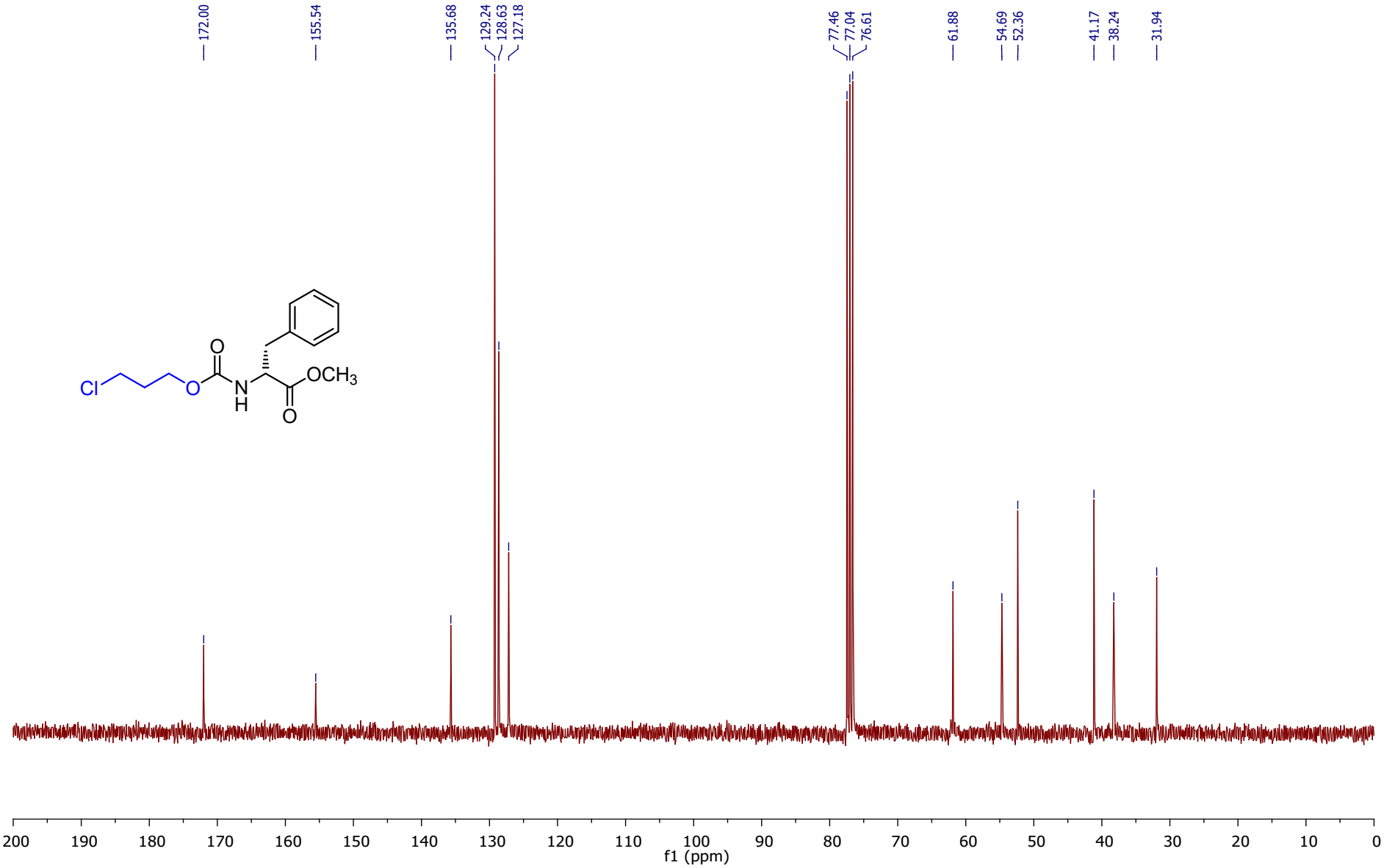
4.63
4.24
4.22
4.20
3.75
3.61
3.59
3.57
3.20
3.18
3.15
3.13
3.12
3.10
3.08
3.05
2.11
2.09
2.07
2.05
2.03
Cl
O
O
N
H
O
OCH3
4.69 4.62
4.26 4.20
3.65 3.55
3.2 3.1 3.0
2.2 2.1 2.0
3.12
1.96
0.85
0.86
2.00
3.03
1.90
1.97
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.04
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61.88
54.69
52.36
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38.24
31.94
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N
H
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200
190
180
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160
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130
120
110
100
90
80
70
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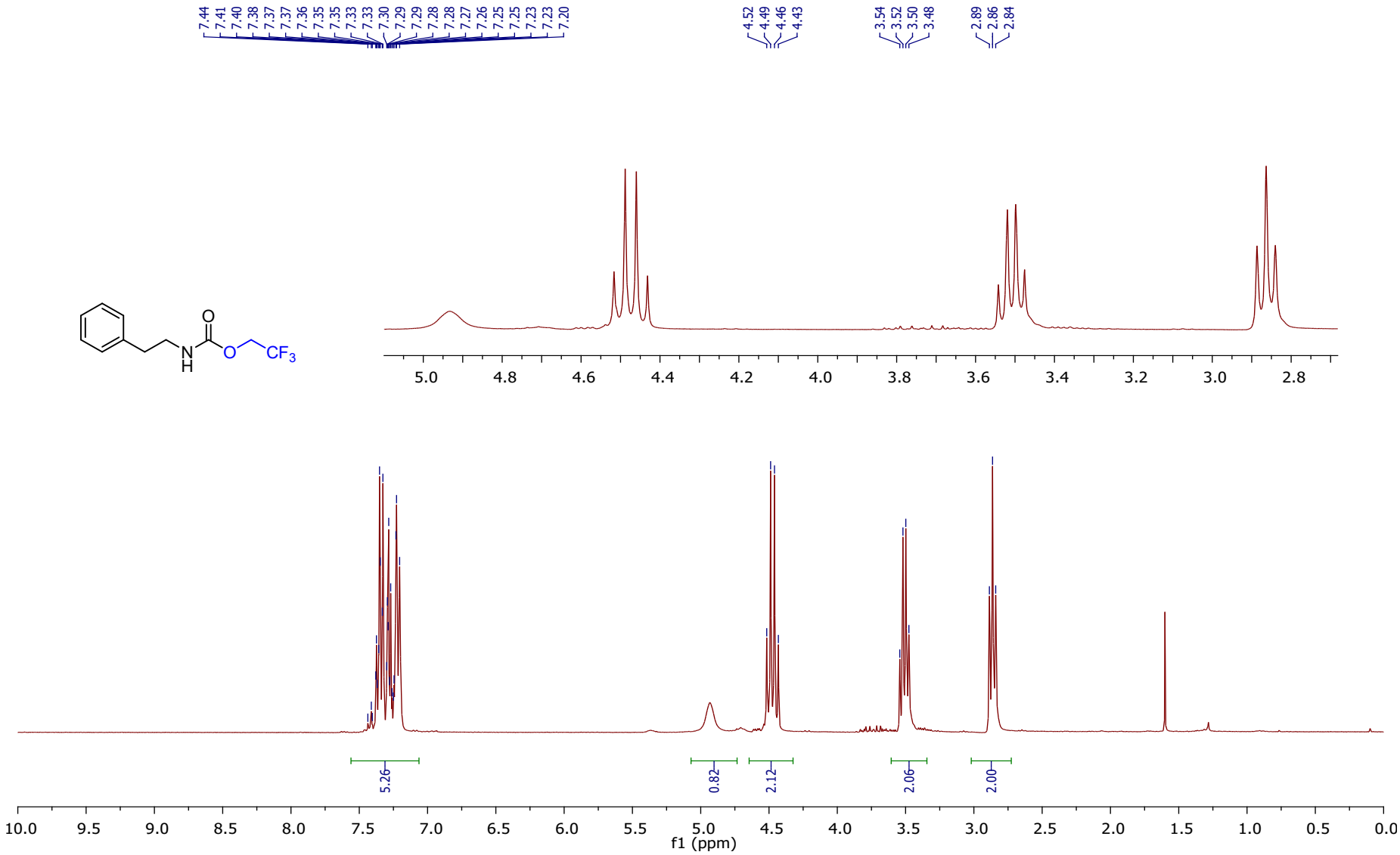
50
40
30
20
10
0
f1 (ppm)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7.29
7.28
7.28
7.27
7.26
7.25
7.25
7.23
7.23
7.20
4.52
4.49
4.46
4.43
3.54
3.52
3.50
3.48
2.89
2.86
2.84
O
N
H
O
CF3
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4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
5.26
0.82
2.12
2.06
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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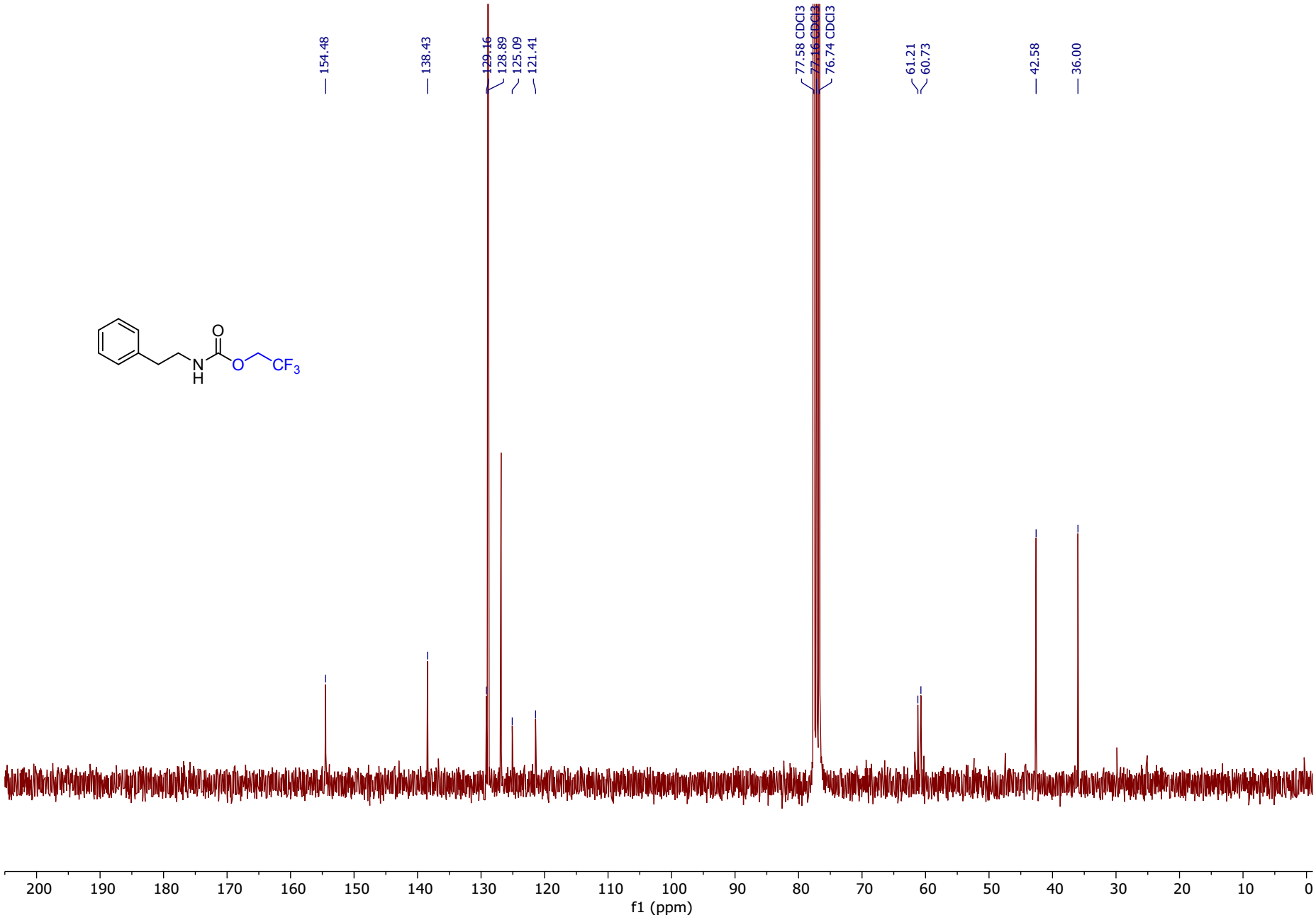
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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125.09
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77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
61.21
60.73
42.58
36.00
O
N
H
O
CF3
200
190
180
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160
150
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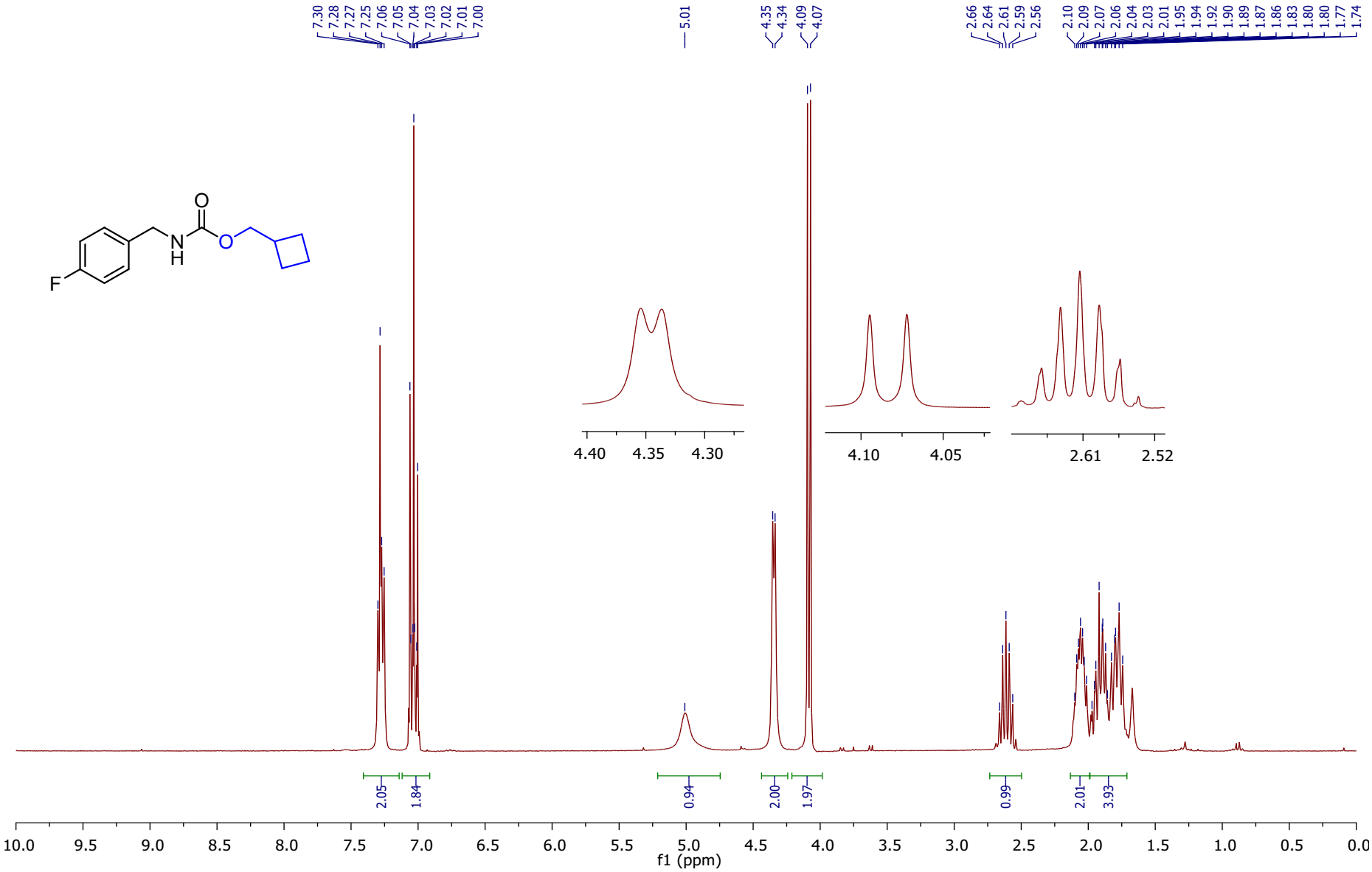
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.35
4.34
4.09
4.07
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2.64
2.61
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2.56
2.10
2.09
2.07
2.06
2.04
2.03
2.01
1.95
1.94
1.92
1.90
1.89
1.87
1.86
1.83
1.80
1.80
1.77
1.74
O
N
H
O
F
4.40
4.35
4.30
4.10
4.05
2.61
2.52
2.05
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0.94
2.00
1.97
0.99
2.01
3.93
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9.0
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8.0
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7.0
6.5
6.0
5.5
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1.0
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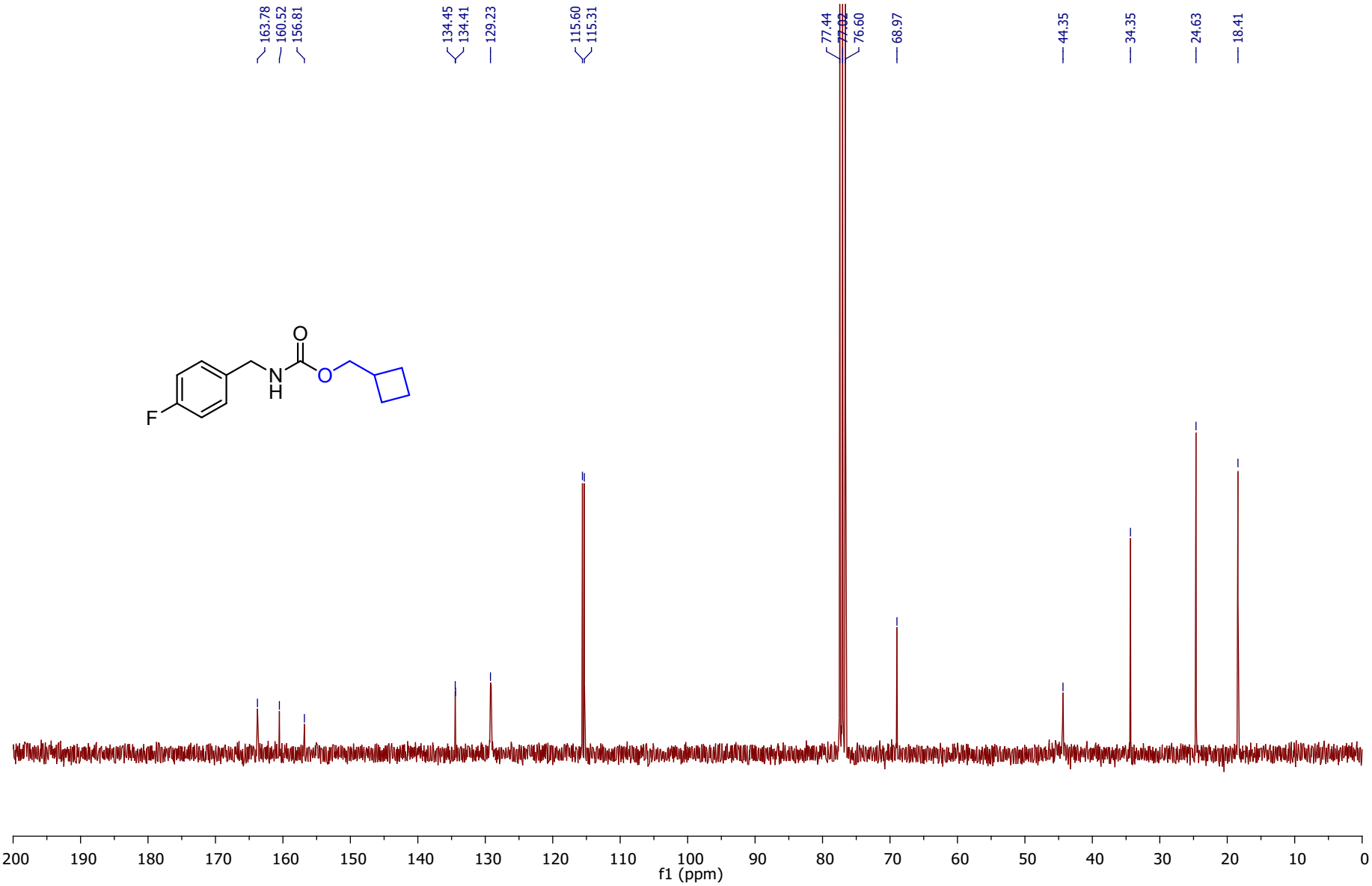
f1 (ppm)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115.31
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77.02
76.60
68.97
44.35
34.35
24.63
18.41
O
N
H
O
F
200
190
180
170
160
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130
120
110
100
90
80
70
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50
40
30
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10
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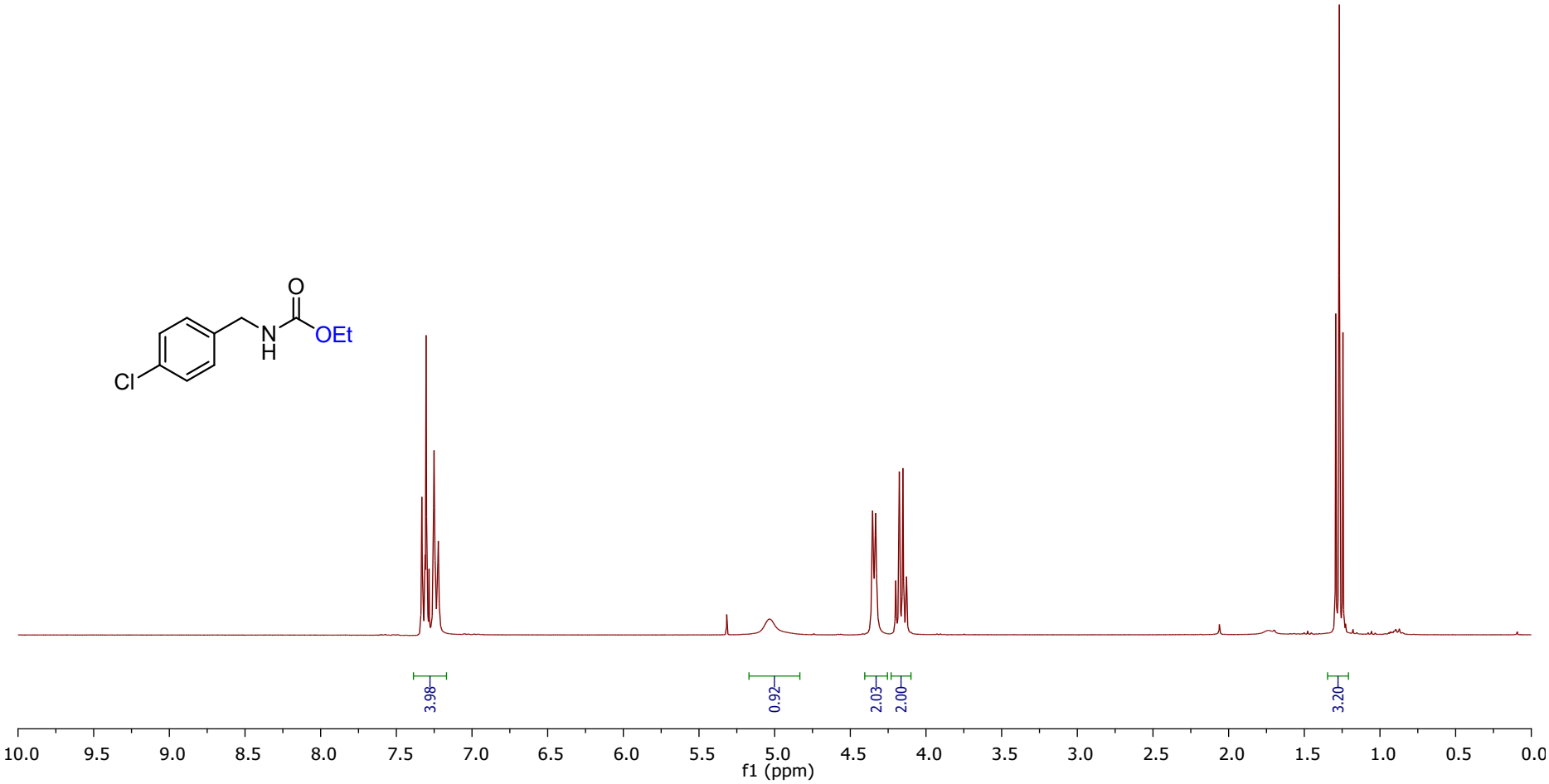
f1 (ppm)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H
OEt
Cl
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8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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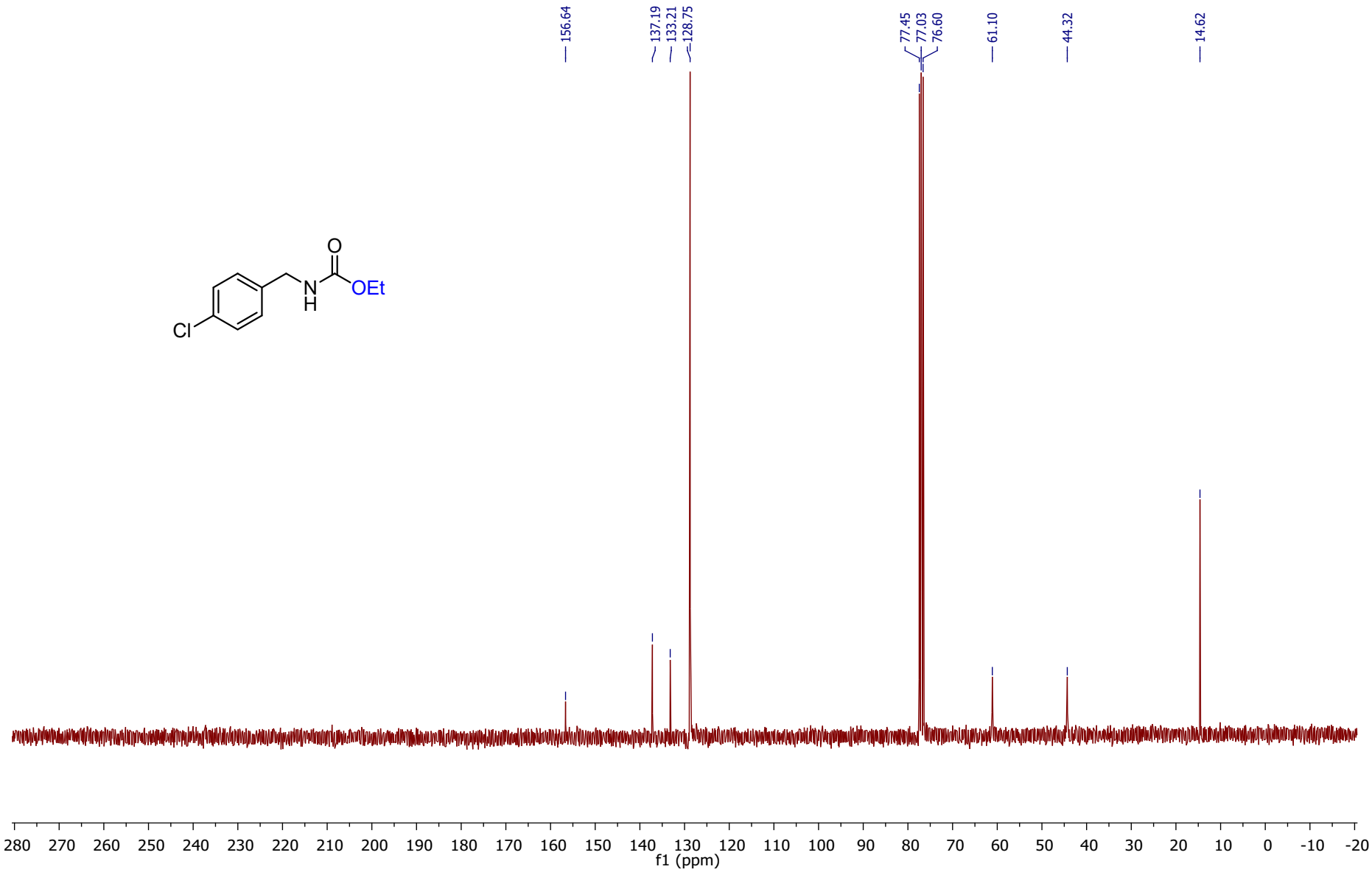
0.0
f1 (ppm)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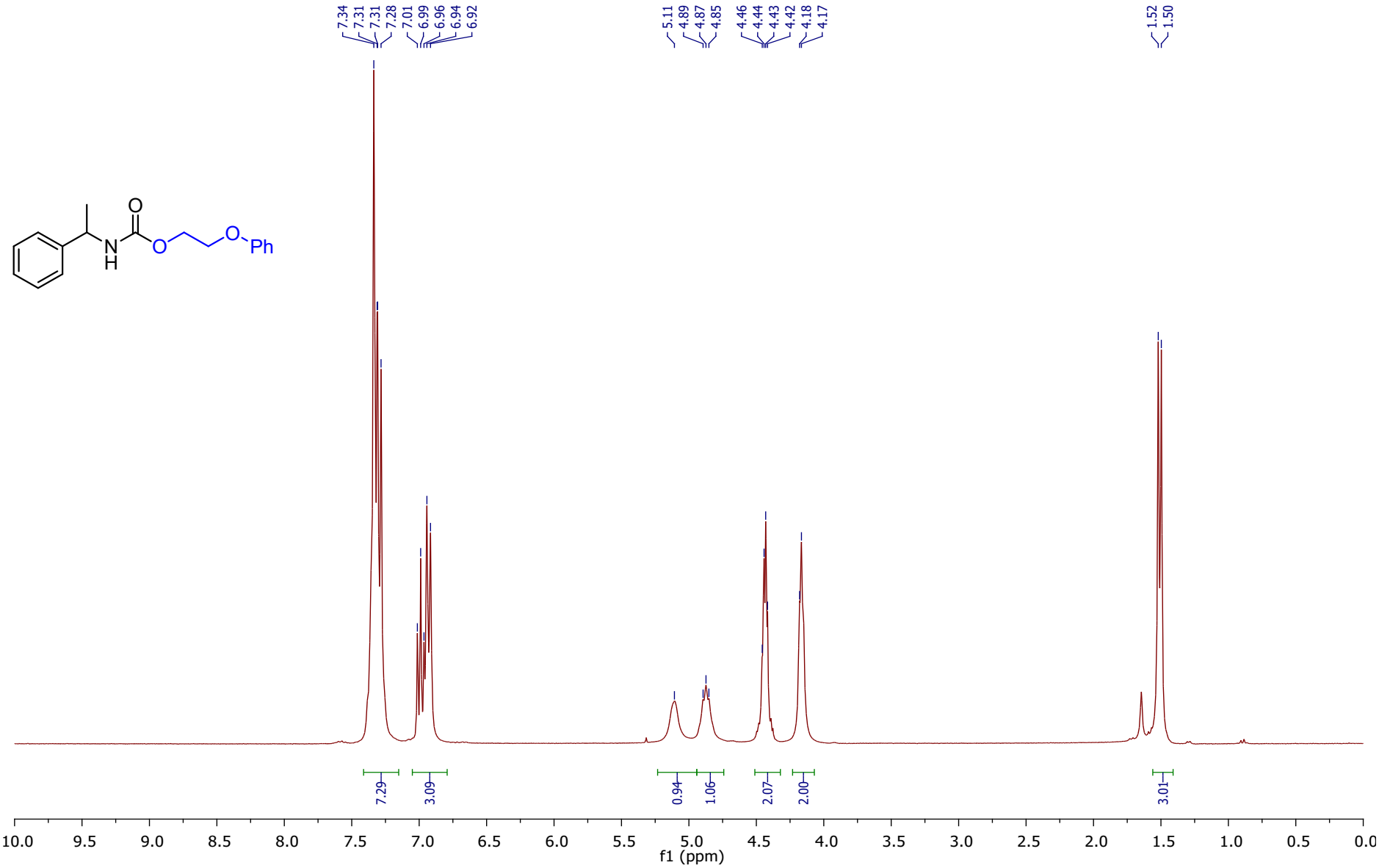
76.60
61.10
44.32
14.62
O
N
H
OEt
Cl
280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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6.94
6.92
5.11
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4.85
4.46
4.44
4.43
4.42
4.18
4.17
1.52
1.50
O
N
H
O
O
Ph
7.29
3.09
0.94
1.06
2.07
2.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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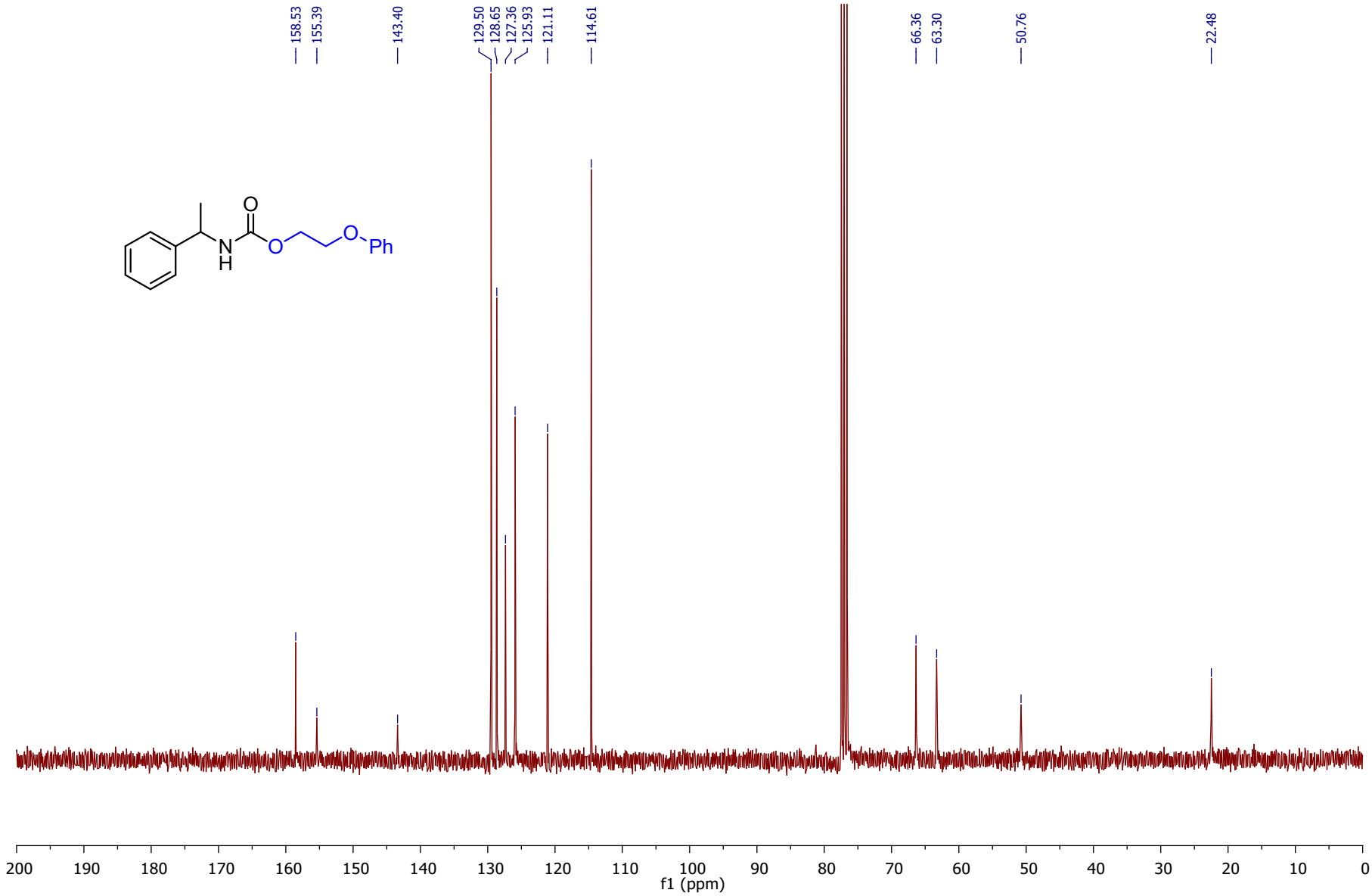
f1 (ppm)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128.65
127.36
125.93
121.11
114.61
66.36
63.30
50.76
22.48
O
N
H
O
O
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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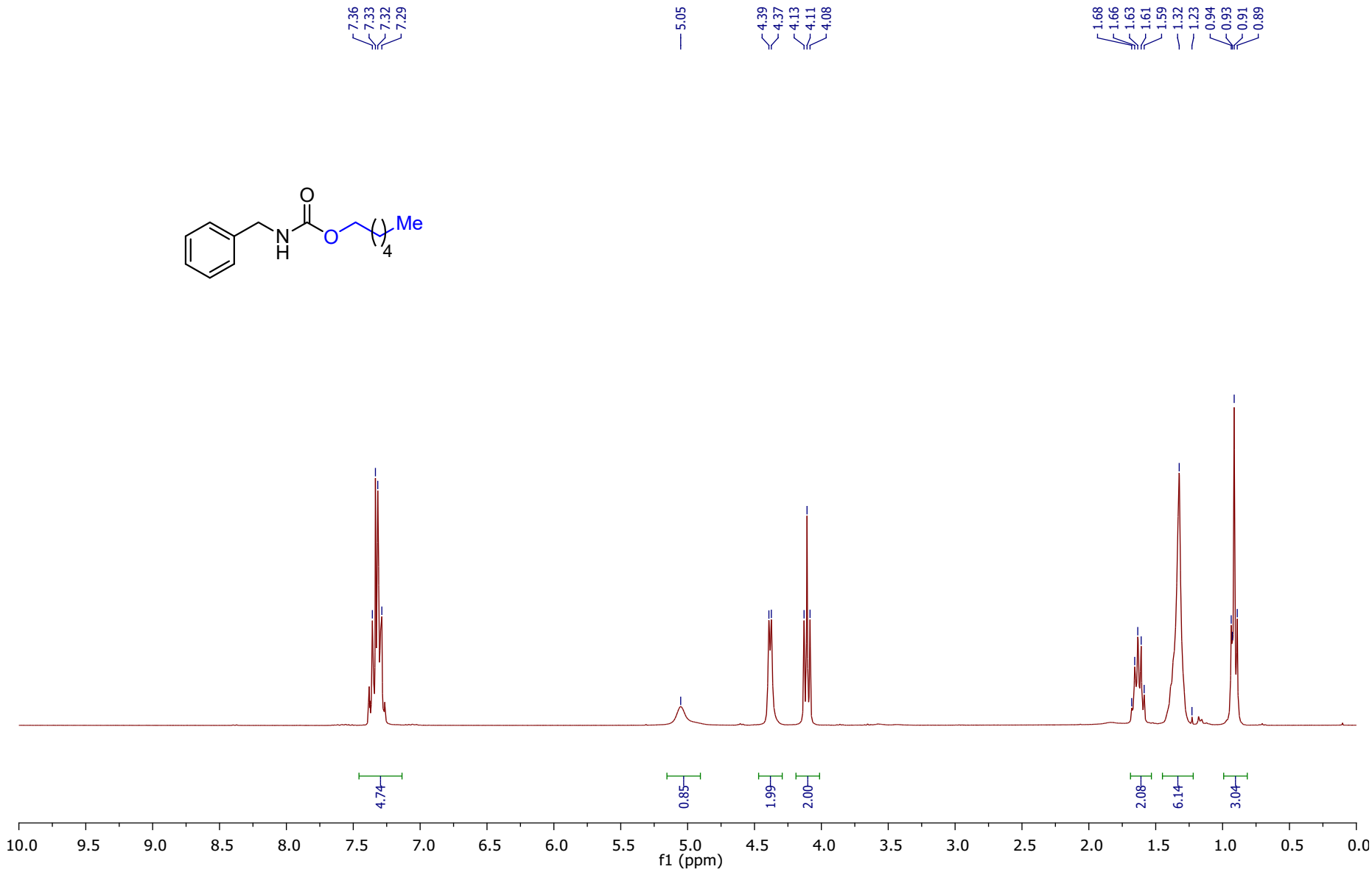
50
40
30
20
10
0
f1 (ppm)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4.37
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4.08
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1.66
1.63
1.61
1.59
1.32
1.23
0.94
0.93
0.91
0.89
O
N
H
O
Me
4
4.74
0.85
1.99
2.00
2.08
6.14
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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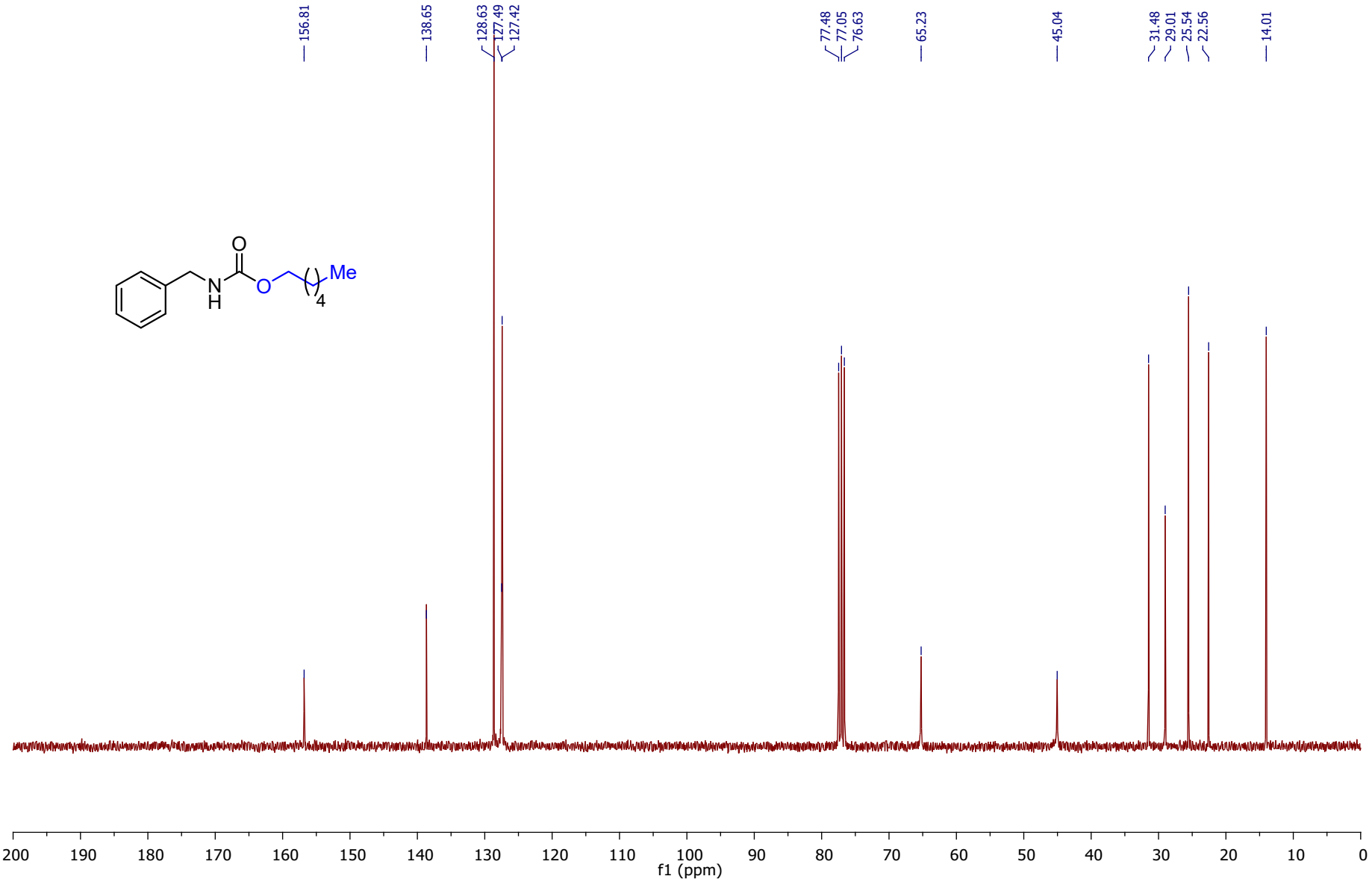
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.42
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77.05
76.63
65.23
45.04
31.48
29.01
25.54
22.56
14.01
O
N
H
O
Me
4
200
190
180
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130
120
110
100
90
80
70
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50
40
30
20
10
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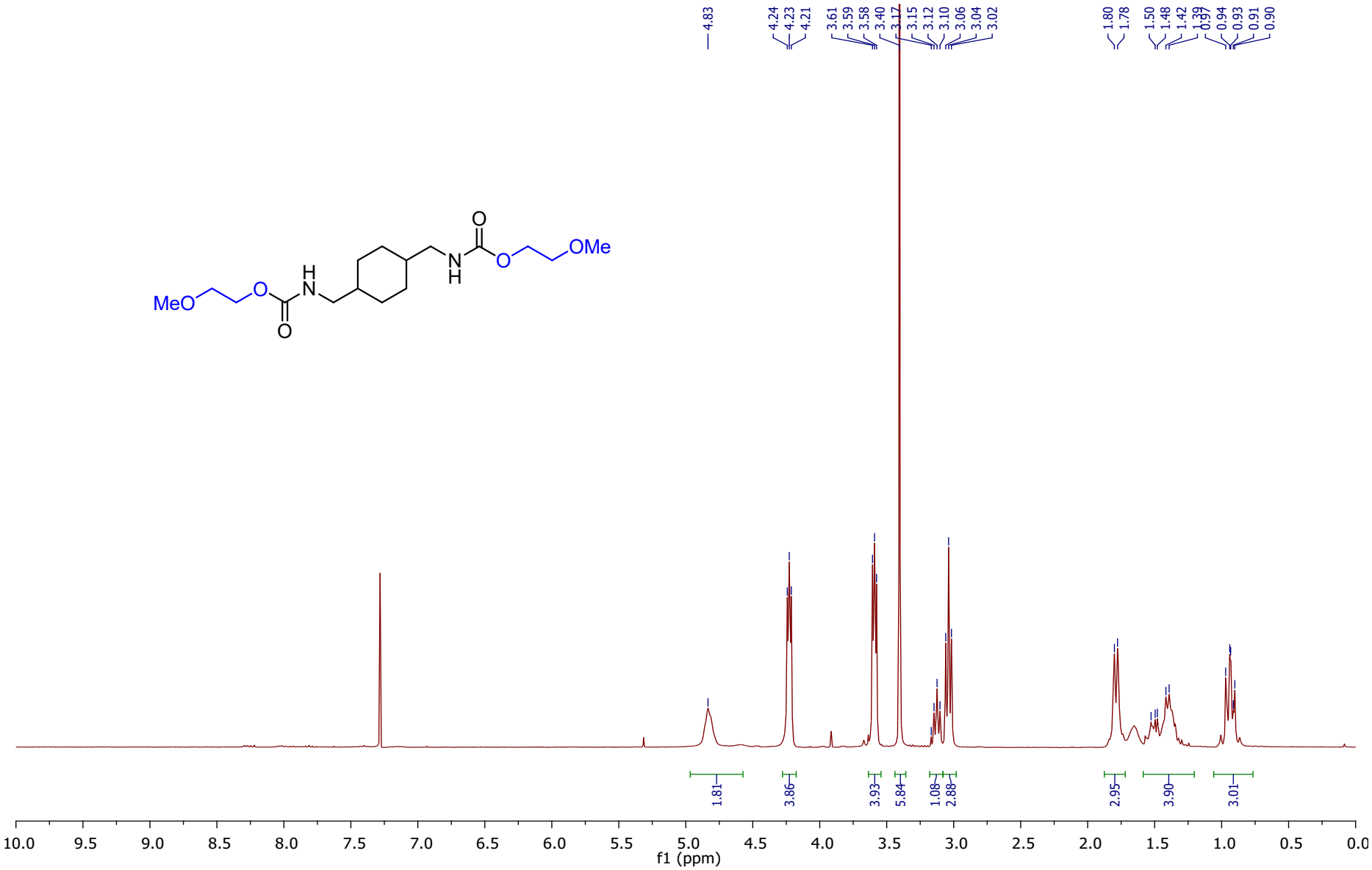
f1 (ppm)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4.23
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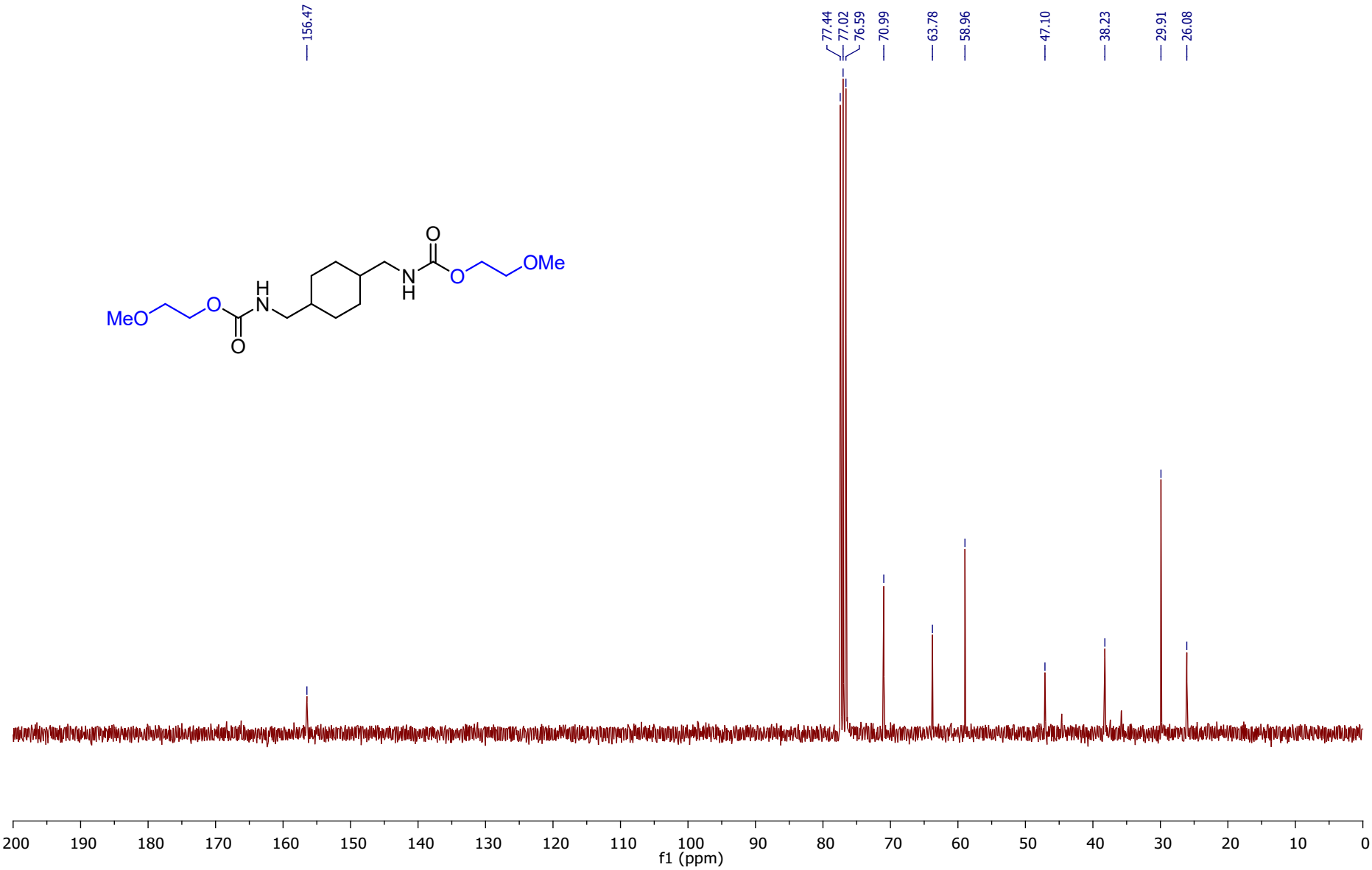
3.59
3.58
3.40
3.17
3.15
3.12
3.10
3.06
3.04
3.02
1.80
1.78
1.50
1.48
1.42
0.97
0.94
0.93
0.91
0.90
MeO
O
H
N
O
N
H
O
O
OMe
1.81
3.86
3.93
5.84
1.08
2.88
2.95
3.90
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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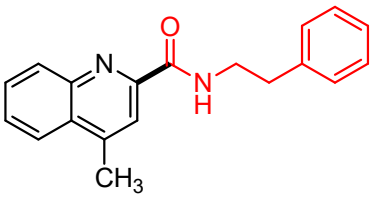
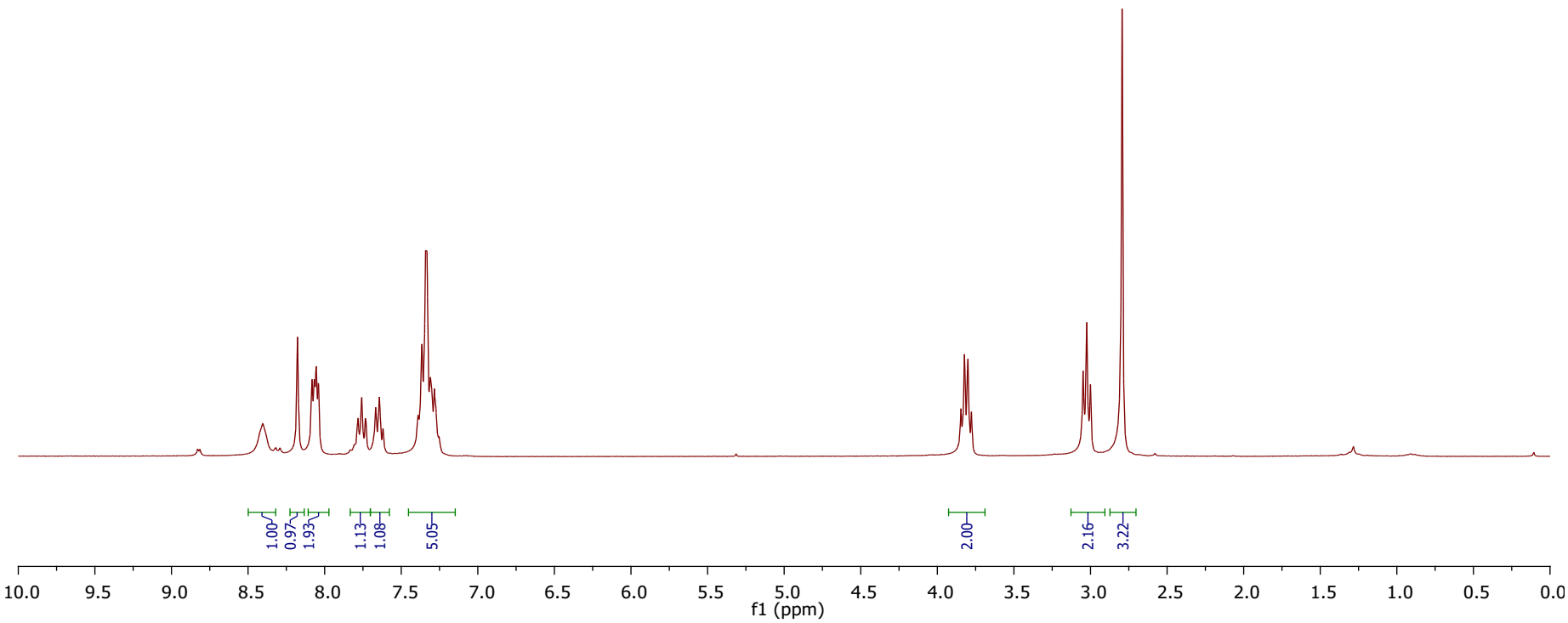
70.99
63.78
58.96
47.10
38.23
29.91
26.08
MeO
O
O
H
N
O
N
H
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
H
CH3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5.05
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2.16
3.22
10.0
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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1.0
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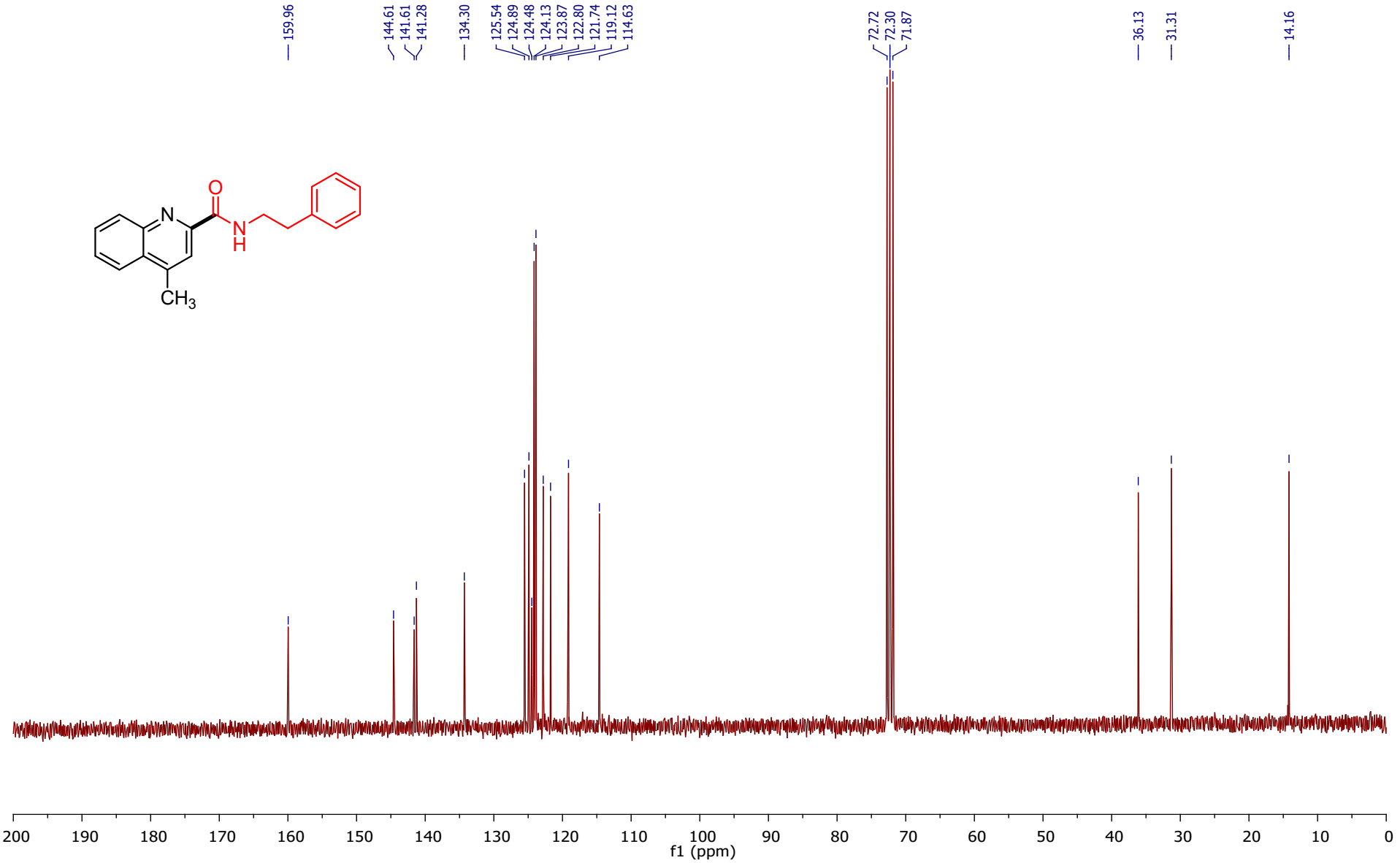
0.0
f1 (ppm)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124.48
124.13
123.87
122.80
121.74
119.12
114.63
72.72
72.30
71.87
36.13
31.31
14.16
O
N
N
H
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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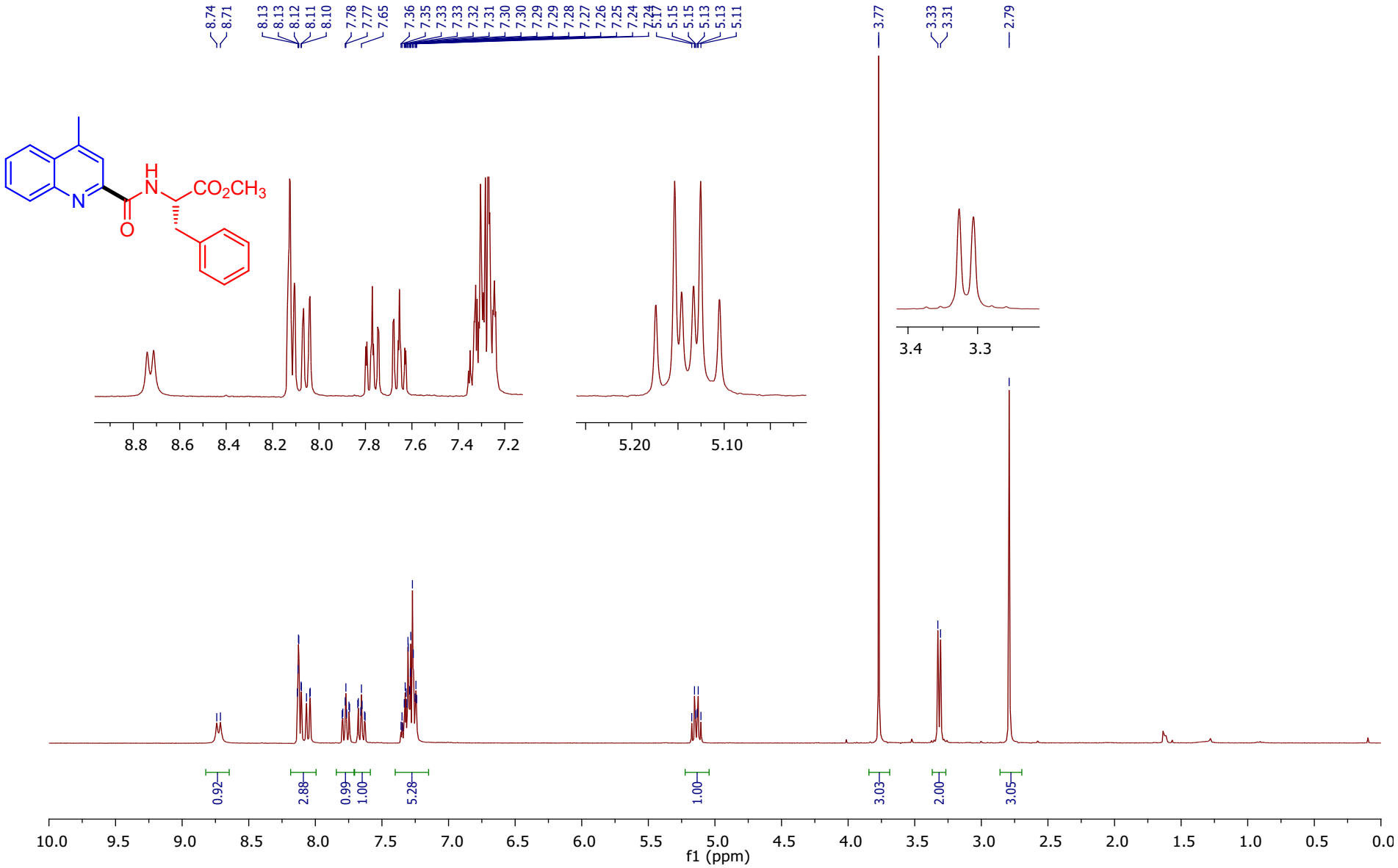
50
40
30
20
10
0
f1 (ppm)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7.65
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7.35
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.24
5.15
5.15
5.13
5.13
5.11
3.77
3.33
3.31
2.79
H
N
CO2CH3
N
O
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
5.20
5.10
3.4
3.3
0.92
2.88
0.99
1.00
5.28
1.00
3.03
2.00
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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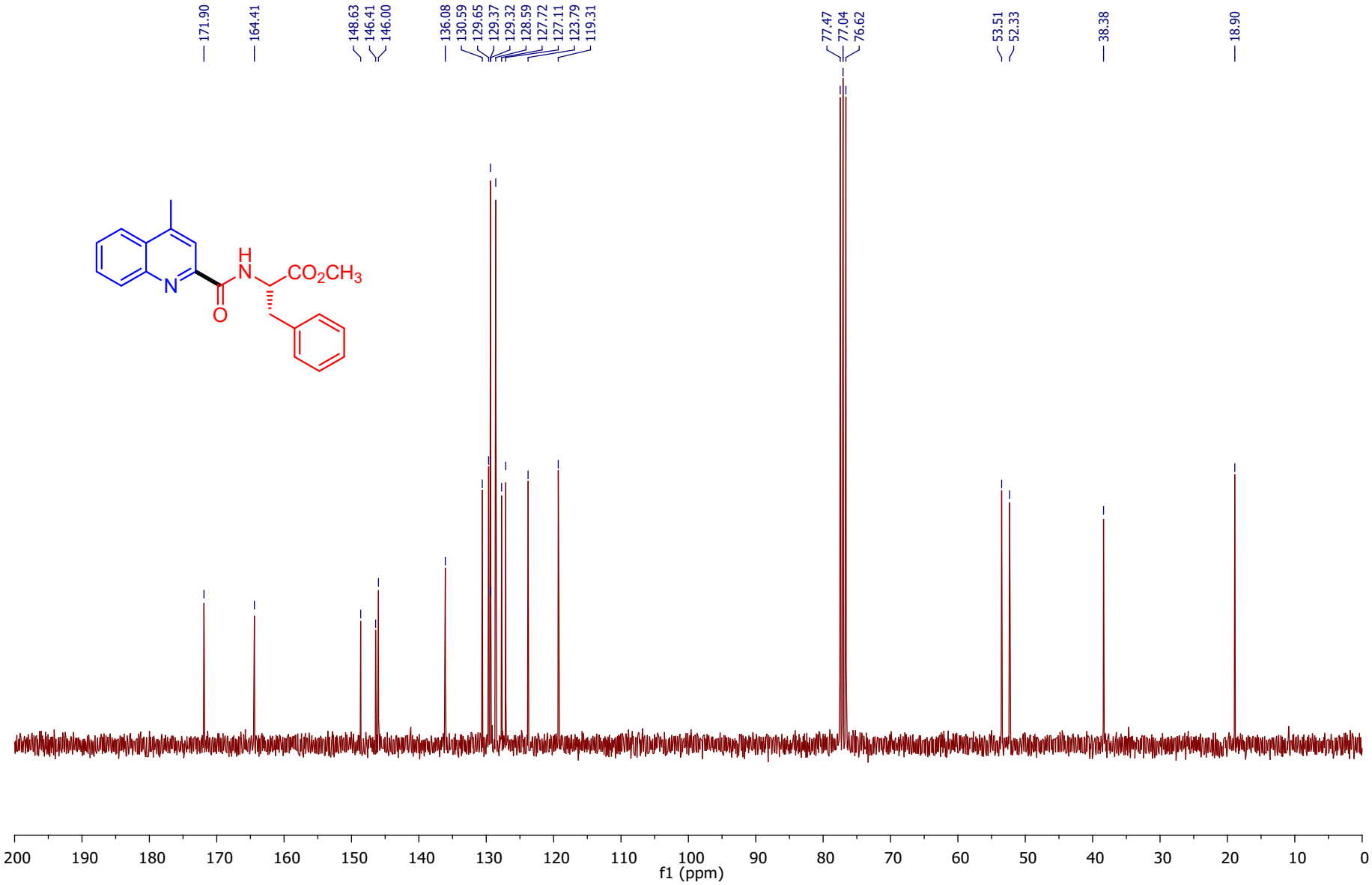
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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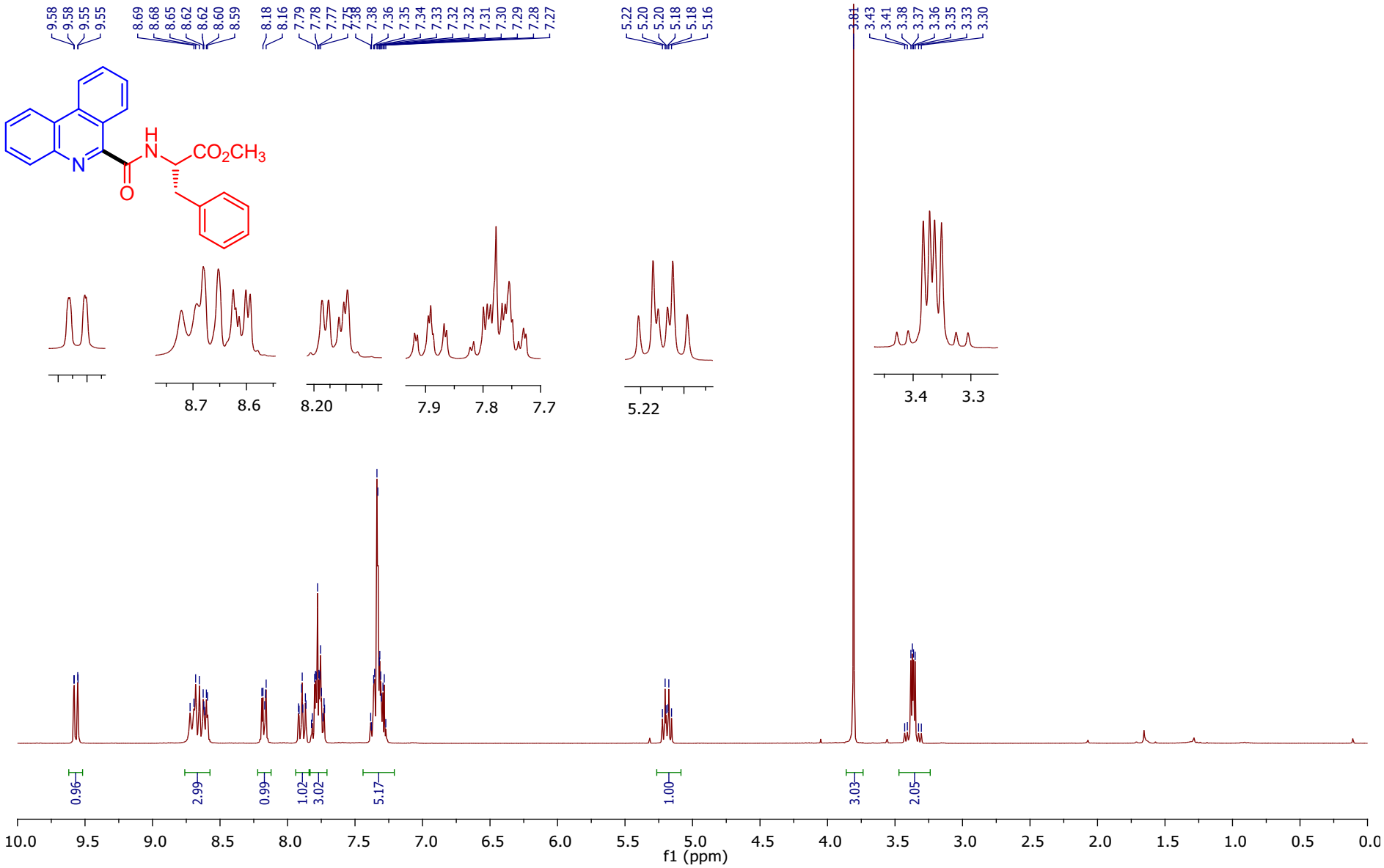
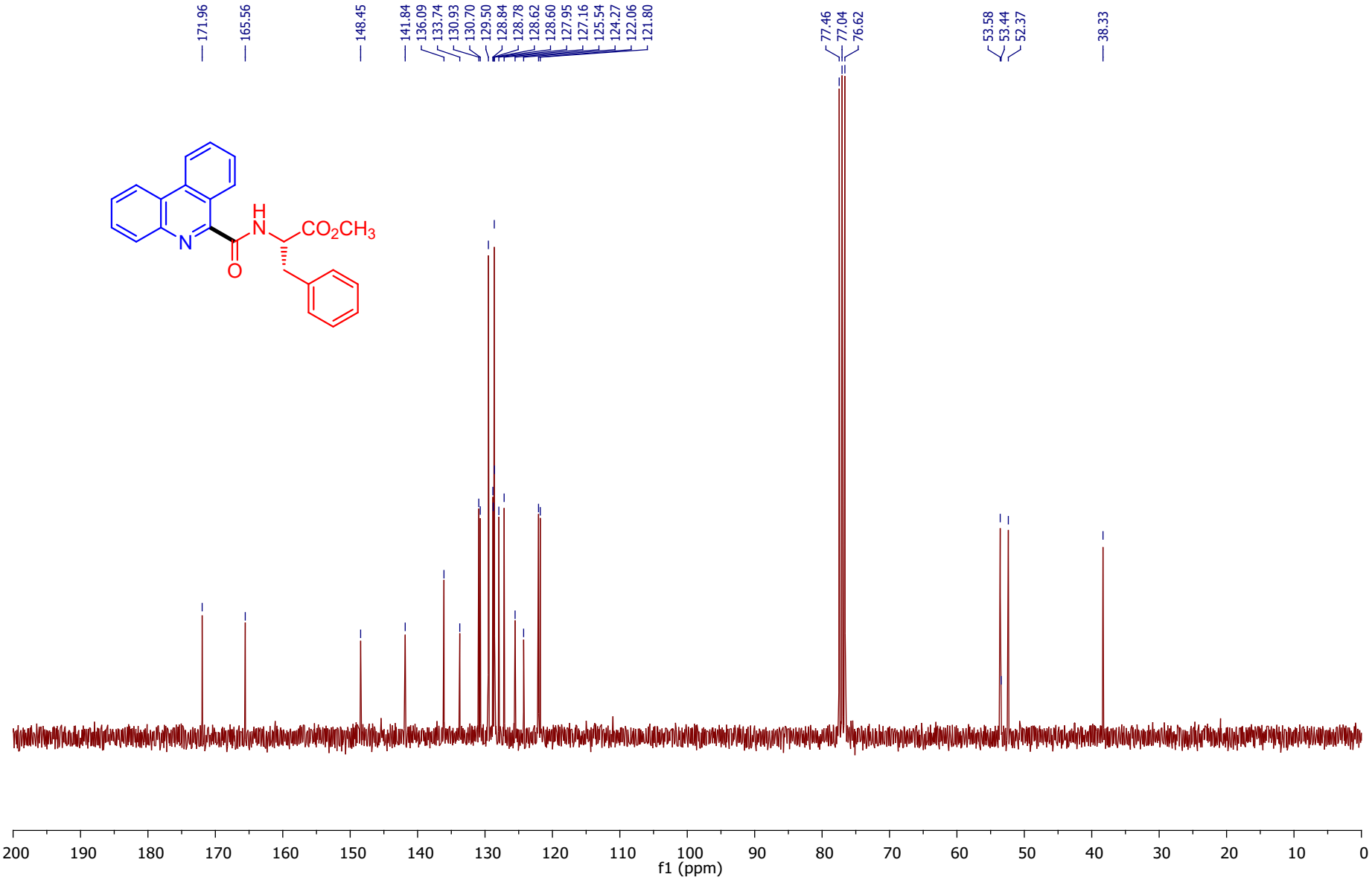
129.32
128.59
127.72
127.11
123.79
119.31
77.47
77.04
76.62
53.51
52.33
38.38
18.90
H
N
CO2CH3
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.58 9.58 9.55 9.55
8.69 8.68 8.65 8.62 8.62 8.60 8.59
8.18 8.16
7.79 7.78 7.77 7.75 7.38 7.38 7.36 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.28 7.27
5.22 5.20 5.20 5.18 5.16
3.81
3.43 3.41 3.38 3.37 3.36 3.35 3.33 3.30
H
N
CO2CH3
N
O
8.7 8.6
8.20
7.9 7.8 7.7
5.22
3.4 3.3
0.96 2.99 0.99 1.02 3.02 5.17 1.00 3.03 2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.78
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128.60
127.95
127.16
125.54
124.27
122.06
121.80
77.46
77.04
76.62
53.58
53.44
52.37
38.33
H
N
CO2CH3
N
O
200
190
180
170
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150
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130
120
110
100
90
80
70
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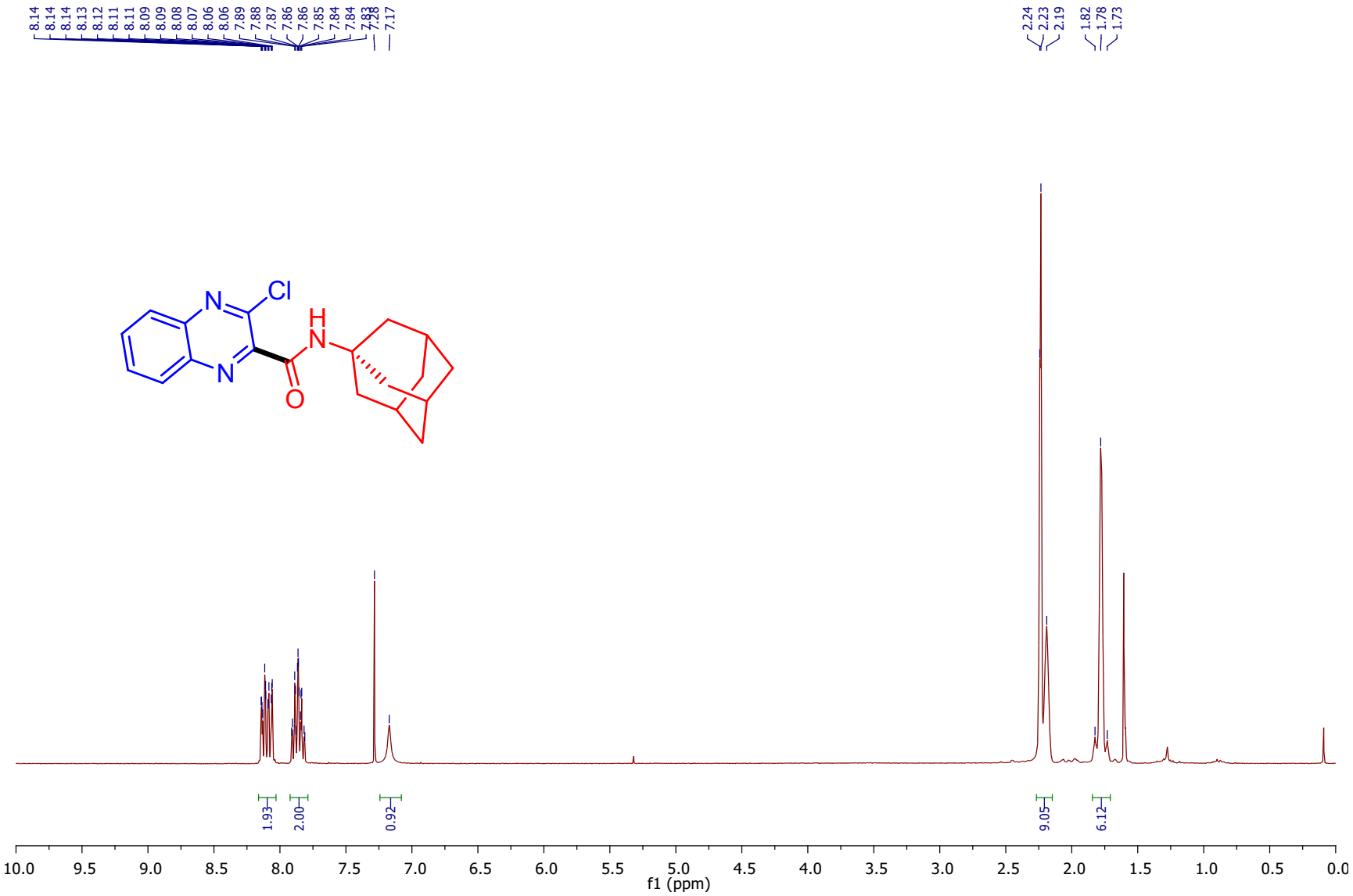
50
40
30
20
10
0
f1 (ppm)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8.08
8.07
8.06
8.06
7.89
7.88
7.87
7.86
7.86
7.85
7.84
7.84
7.28
7.17
2.24
2.23
2.19
1.82
1.78
1.73
Cl
N
N
H
N
O
1.93
2.00
0.92
9.05
6.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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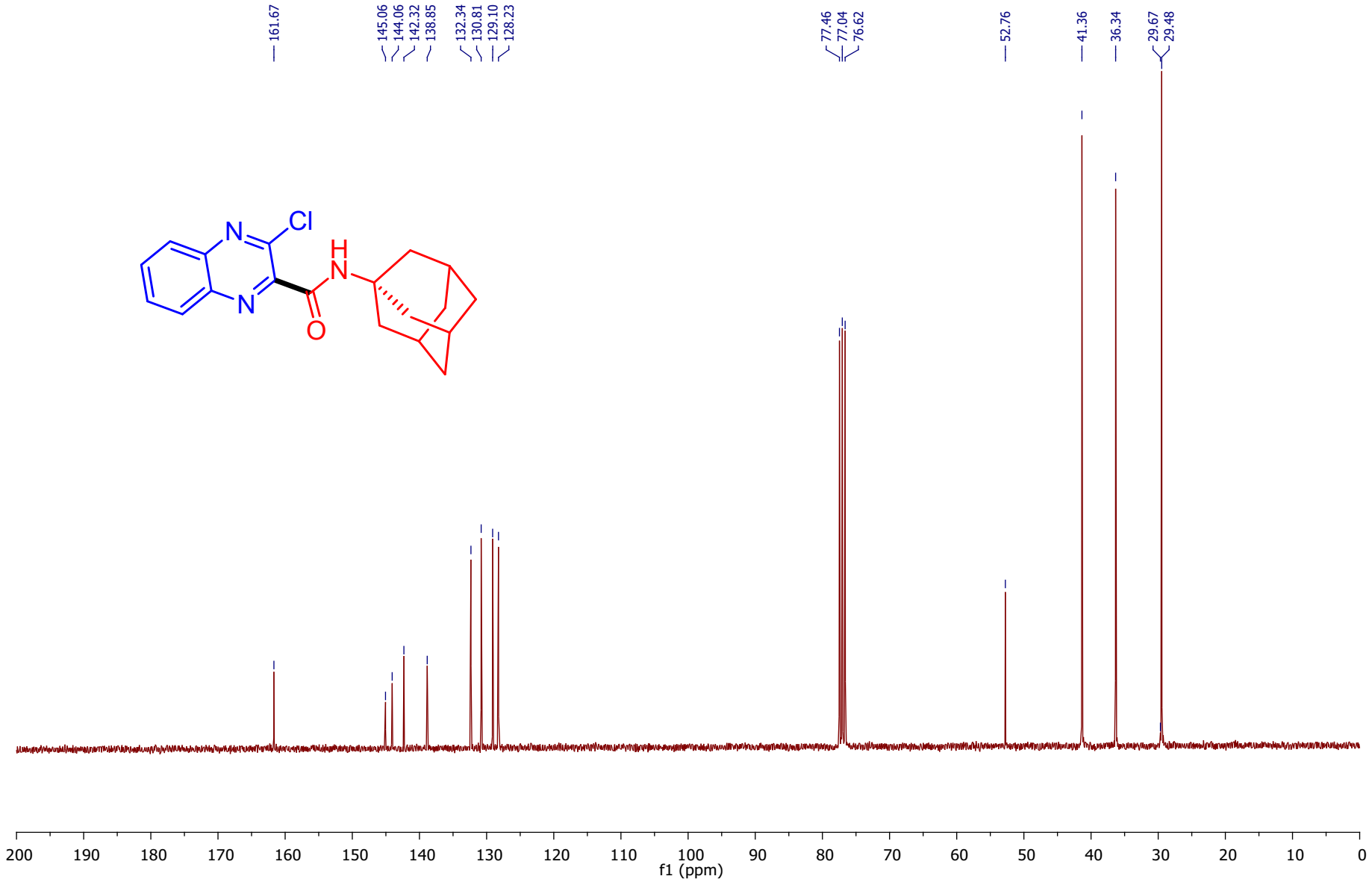
0.0
f1 (ppm)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77.46
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52.76
41.36
36.34
29.67
29.48
Cl
N
N
H
N
O
200
190
180
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130
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110
100
90
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70
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50
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30
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10
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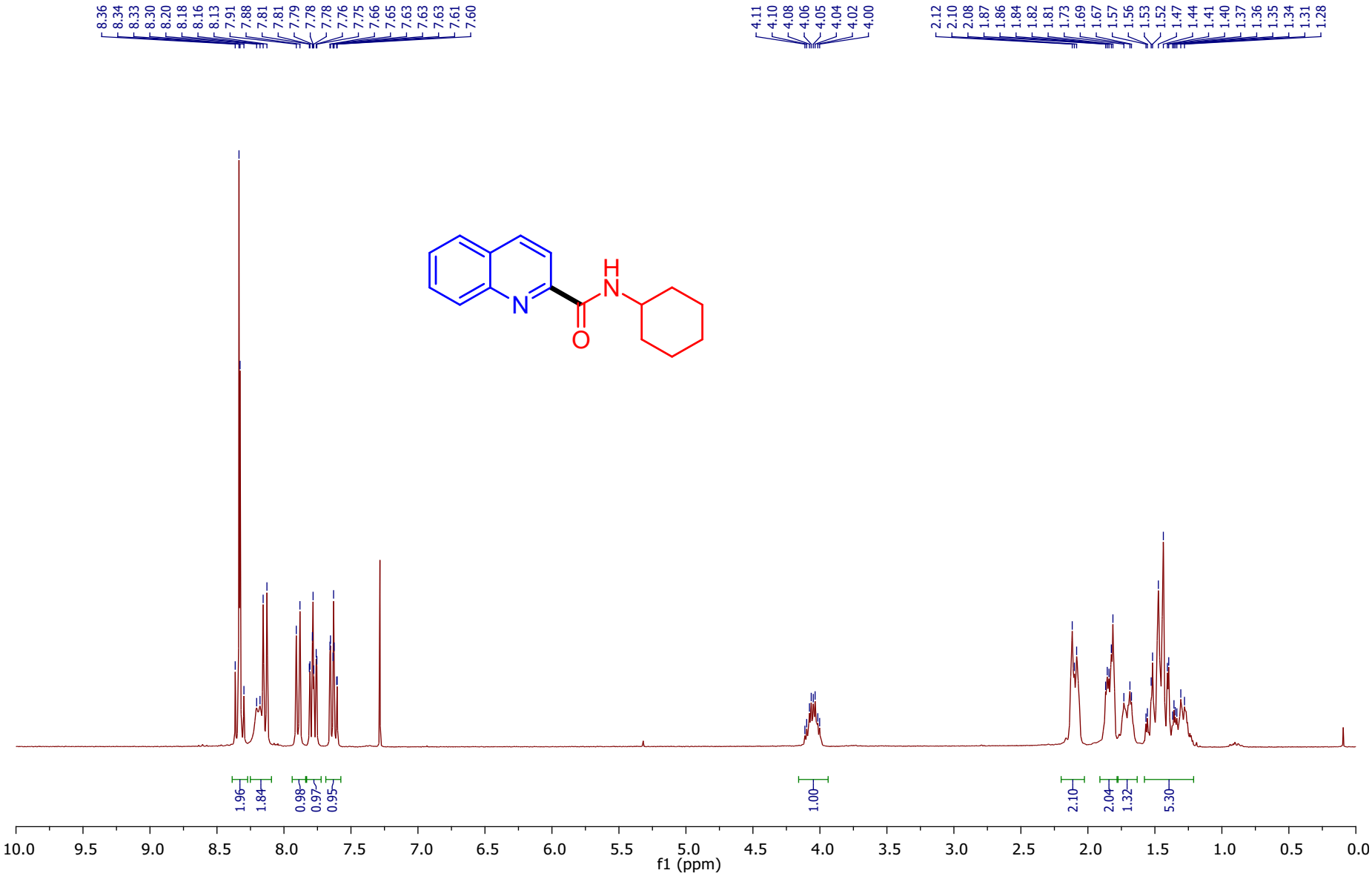
f1 (ppm)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7.78
7.78
7.76
7.75
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7.65
7.63
7.63
7.63
7.61
7.60
4.11
4.10
4.08
4.06
4.05
4.04
4.02
4.00
2.12
2.10
2.08
1.87
1.86
1.84
1.82
1.81
1.73
1.69
1.67
1.57
1.56
1.53
1.52
1.47
1.44
1.41
1.40
1.37
1.36
1.35
1.34
1.31
1.28
H
N
N
O
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0.95
1.00
2.10
2.04
1.32
5.30
10.0
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9.0
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7.0
6.5
6.0
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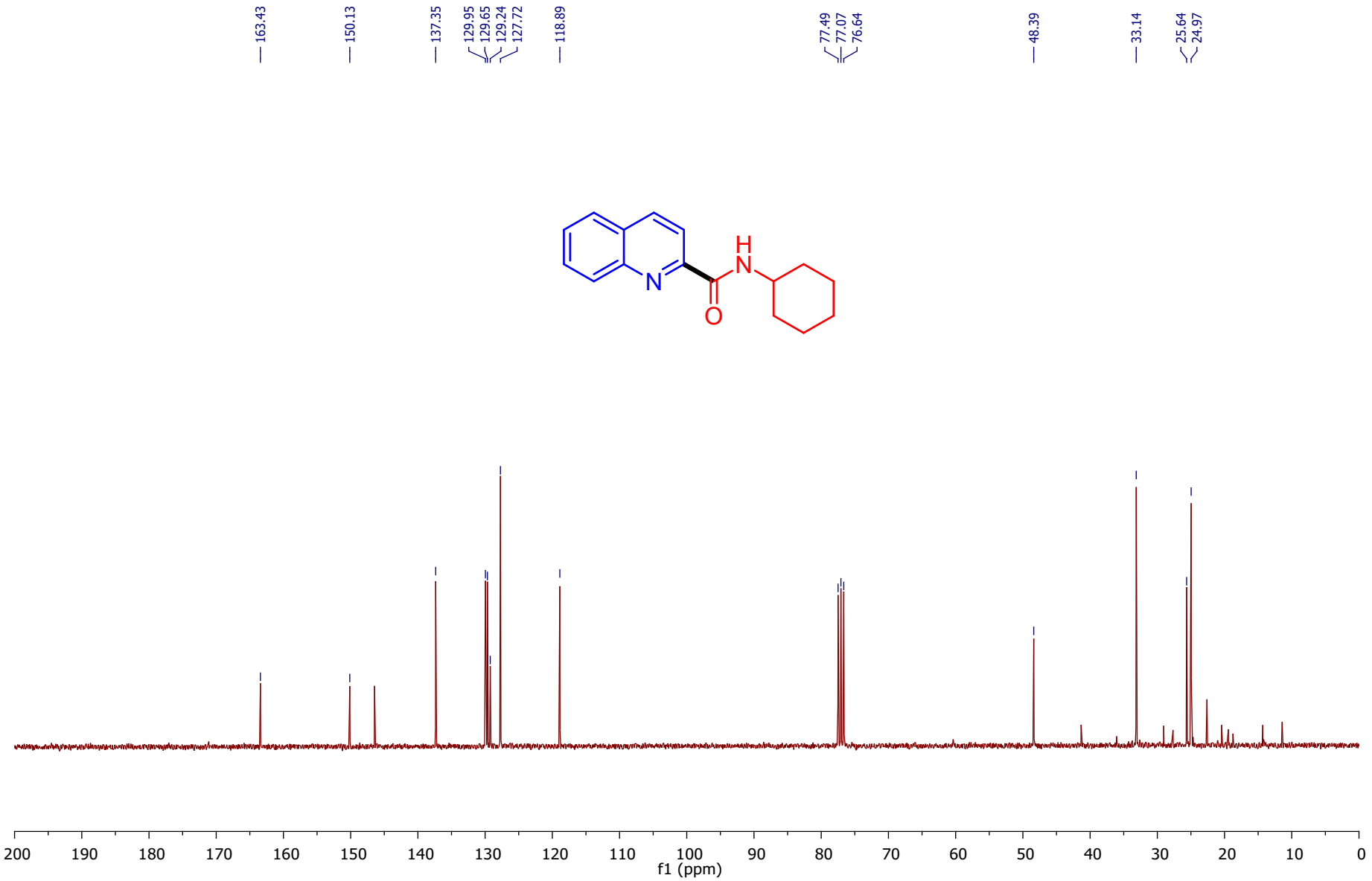
0.0
f1 (ppm)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77.07
76.64
48.39
33.14
25.64
24.97
H
N
N
O
200
190
180
170
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130
120
110
100
90
80
70
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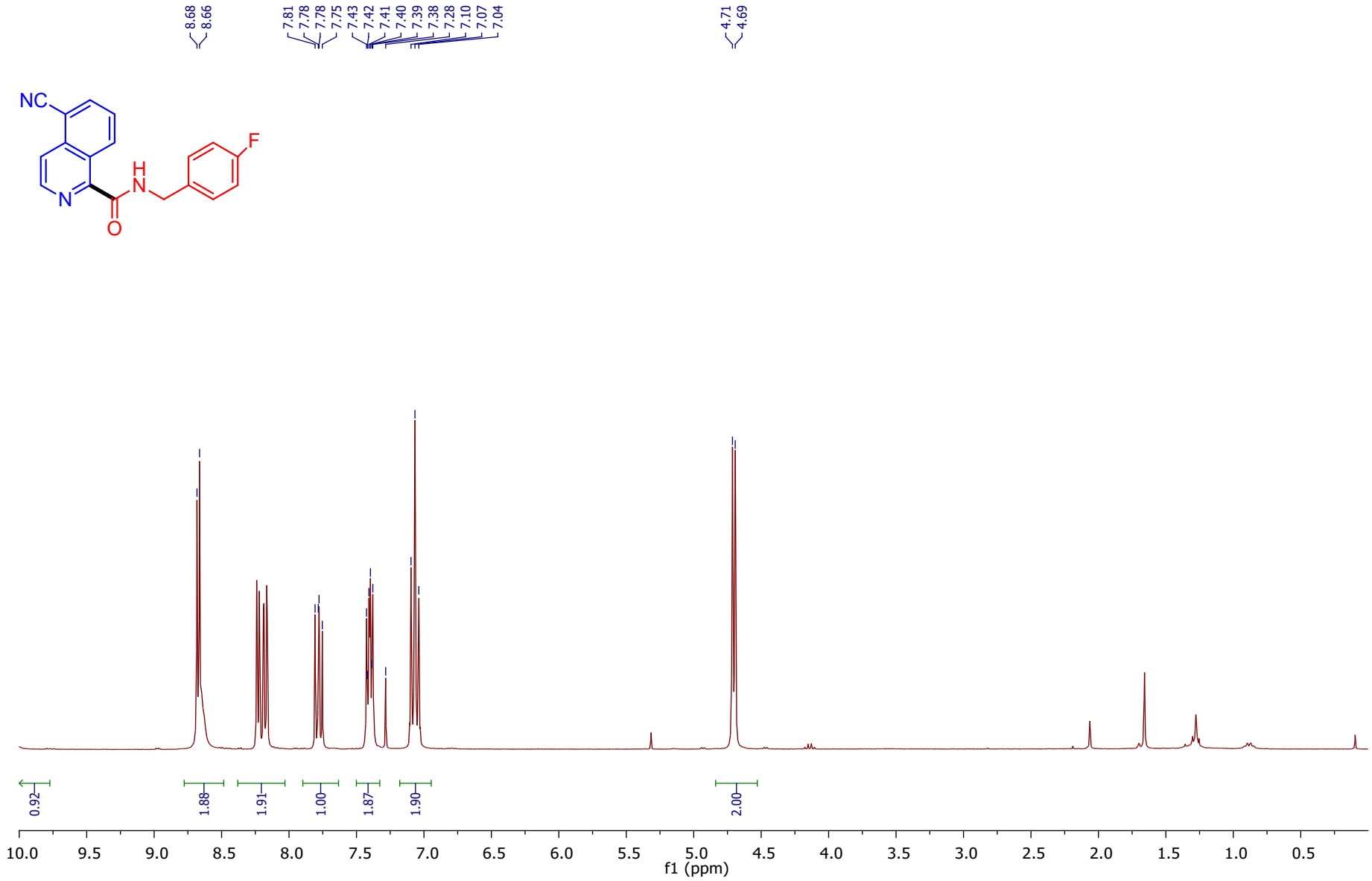
50
40
30
20
10
0
f1 (ppm)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7.39
7.38
7.28
7.10
7.07
7.04
4.71
4.69
NC
F
H
N
N
O
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1.88
1.91
1.00
1.87
1.90
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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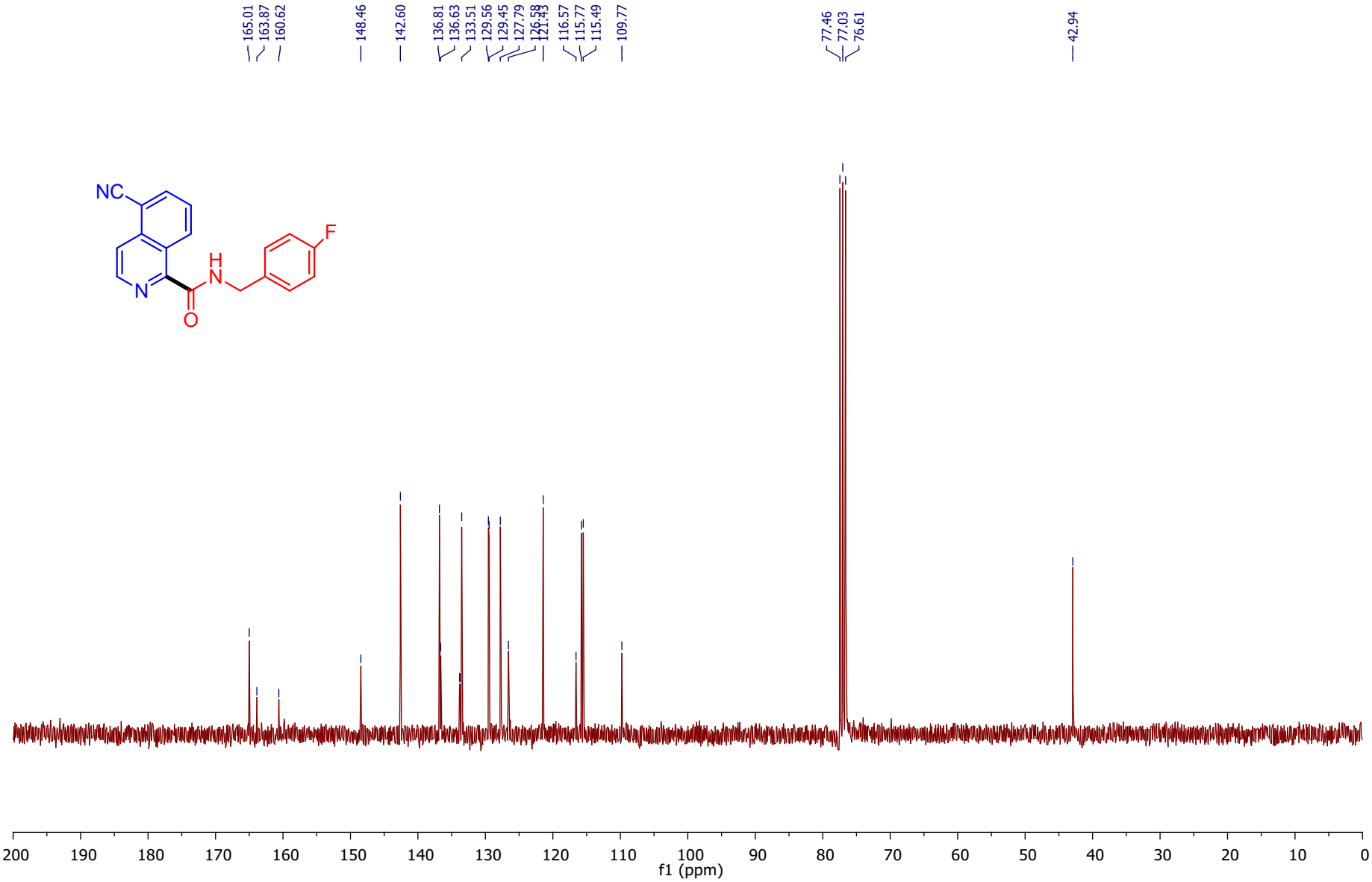
f1 (ppm)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129.45
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115.77
115.49
109.77
77.46
77.03
76.61
42.94
NC
F
H
N
N
O
200
190
180
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110
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90
80
70
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50
40
30
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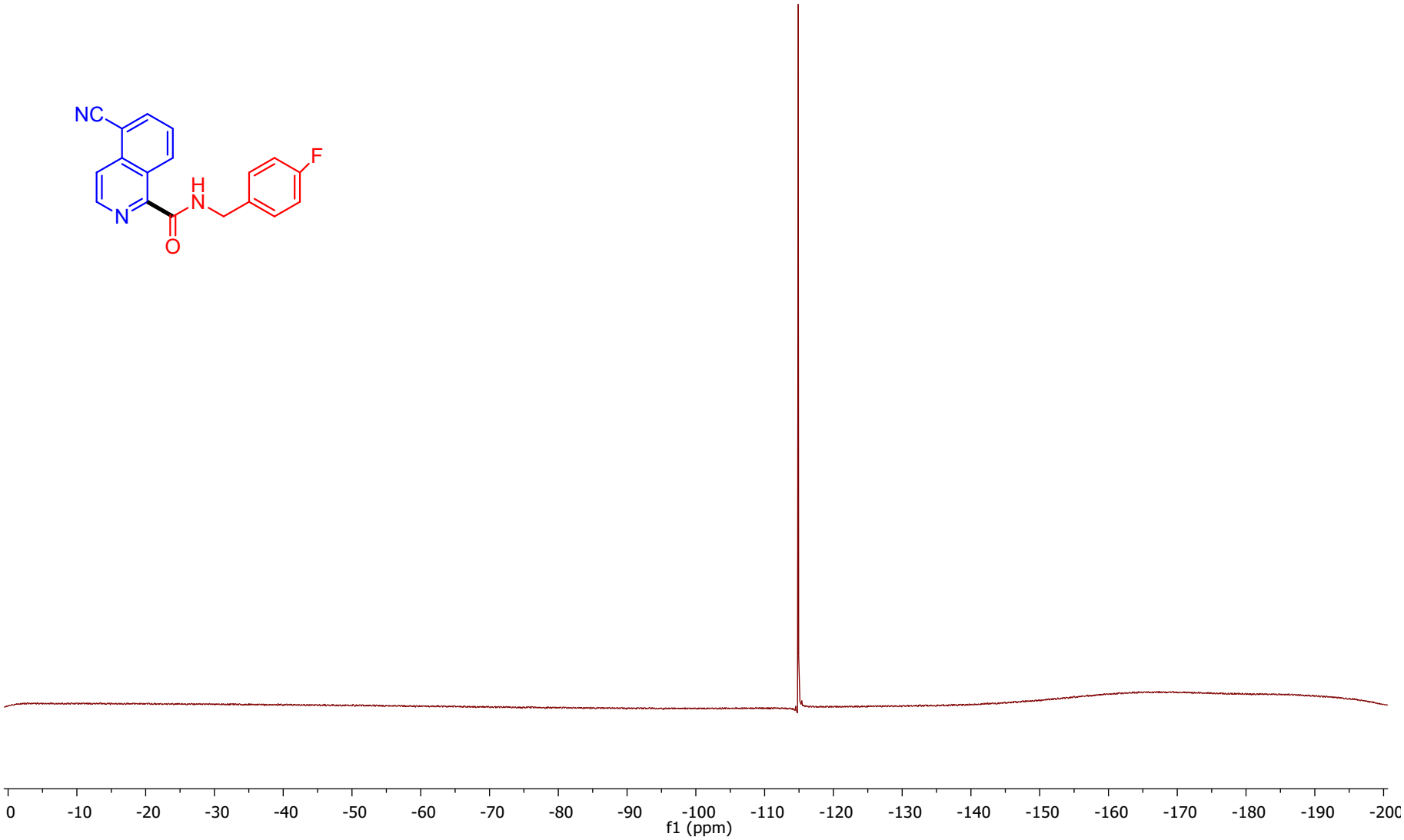
10
0
f1 (ppm)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H
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O
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-10
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-50
-60
-70
-80
-90
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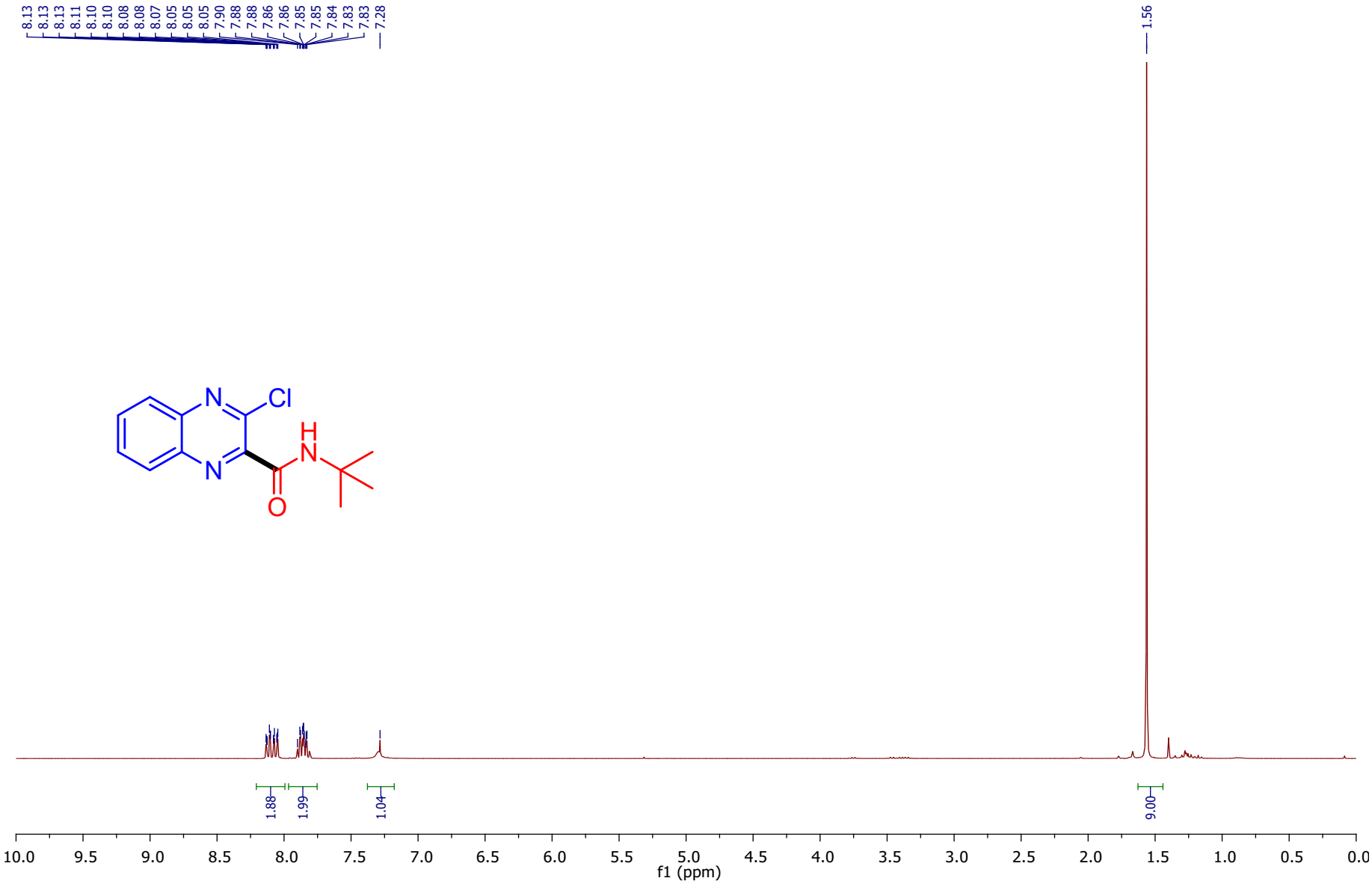
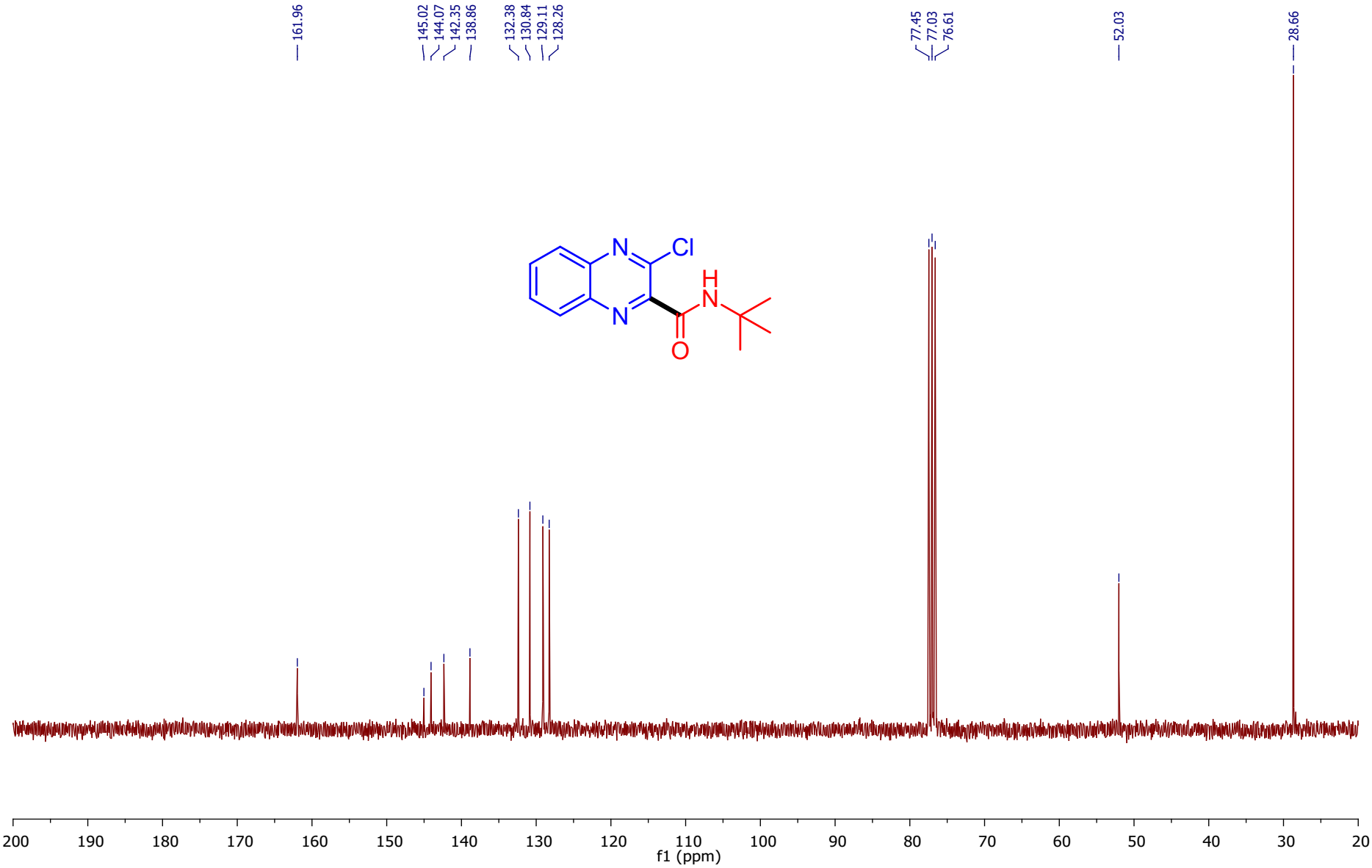
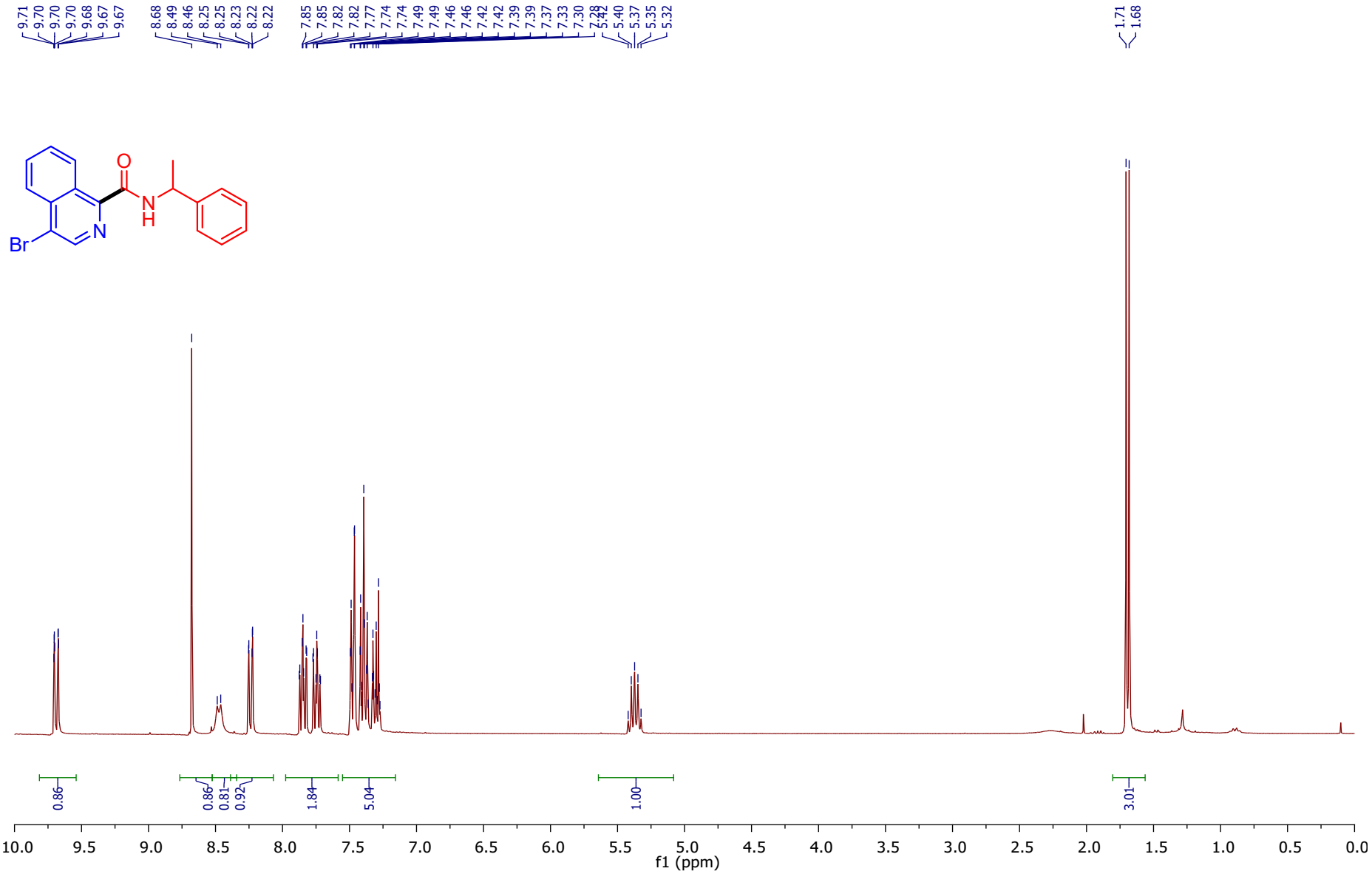
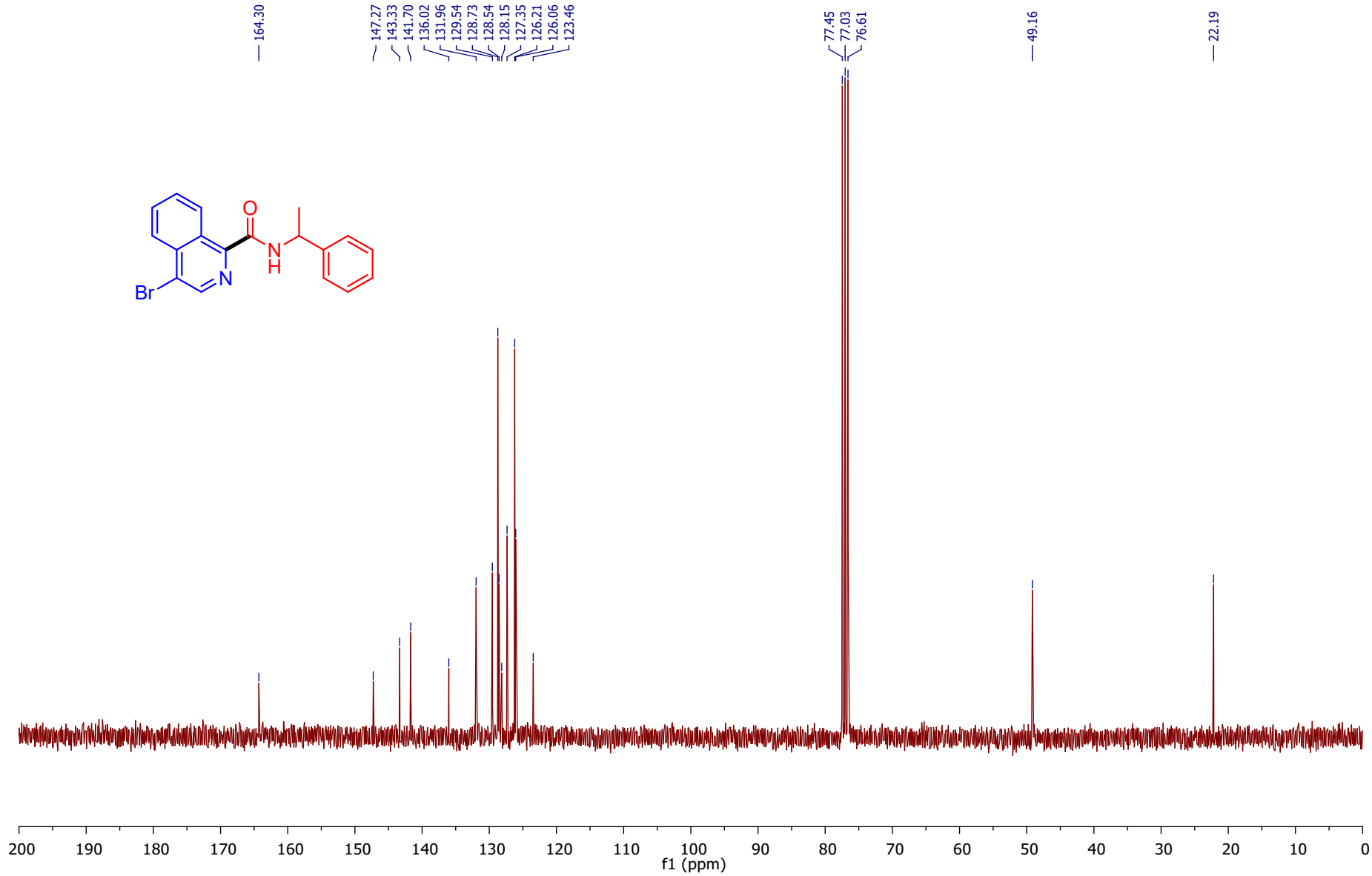
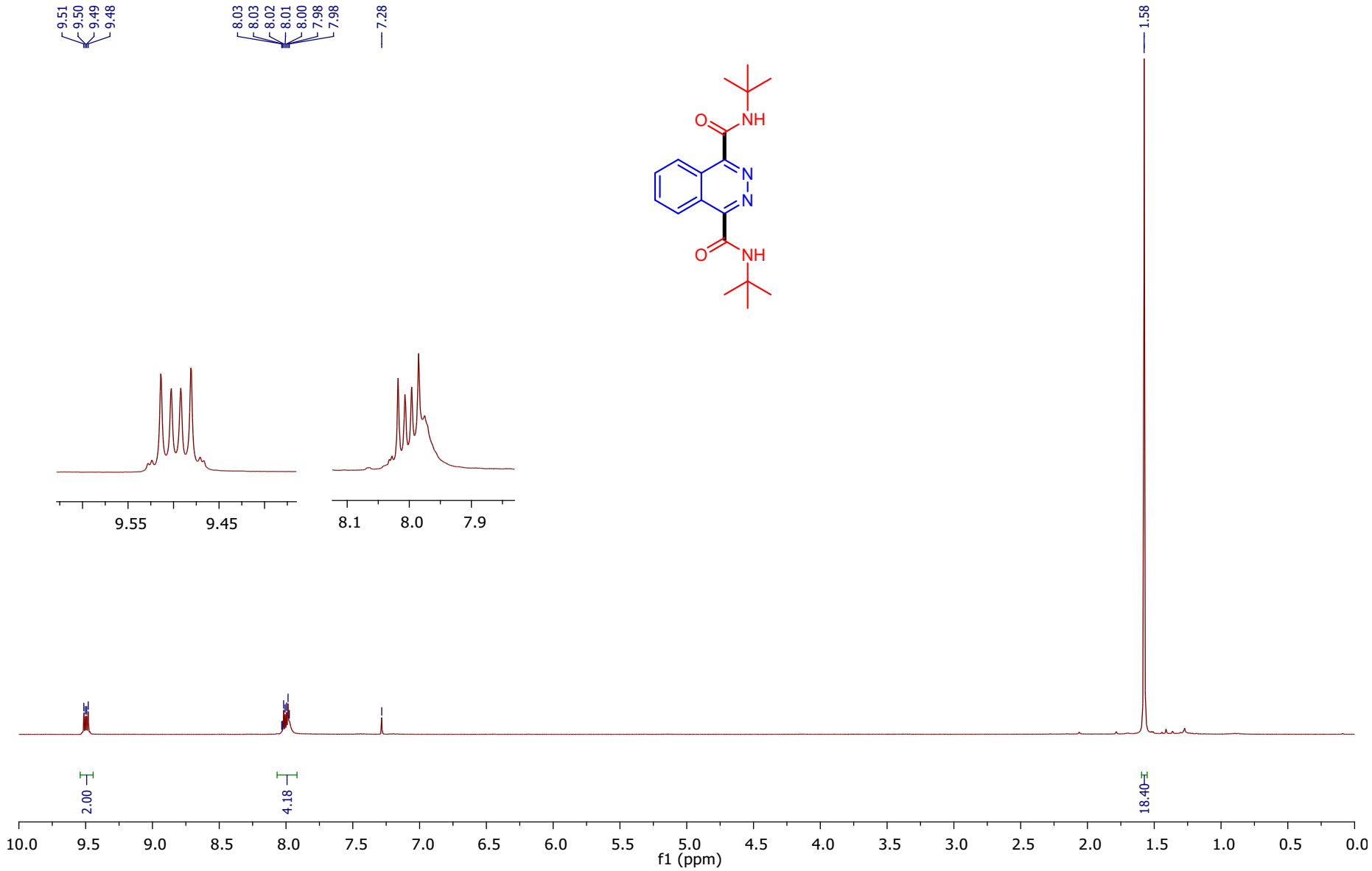
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

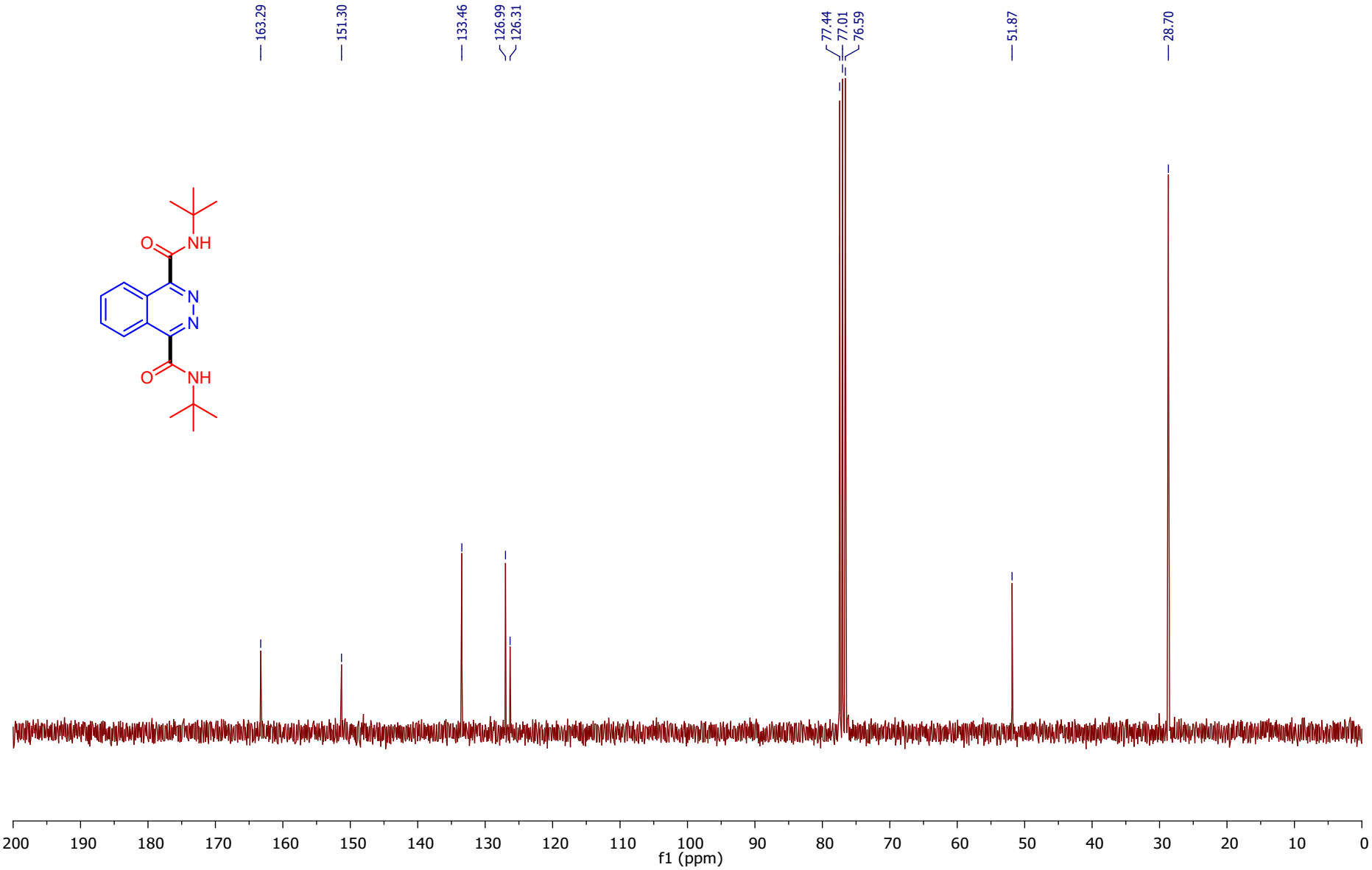

8.13
8.13
8.13
8.11
8.10
8.10
8.08
8.08
8.07
8.05
8.05
8.05
7.90
7.88
7.88
7.86
7.86
7.85
7.85
7.84
7.83
7.83
7.28
1.56
N
Cl
H
N
N
O
1.88
1.99
1.04
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


161.96
145.02
144.07
142.35
138.86
132.38
130.84
129.11
128.26
77.45
77.03
76.61
52.03
28.66
N
Cl
H
N
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


9.71
9.70
9.70
9.70
9.68
9.67
9.67
8.68
8.49
8.46
8.25
8.25
8.23
8.22
8.22
7.85
7.85
7.82
7.82
7.77
7.74
7.74
7.49
7.49
7.46
7.46
7.42
7.42
7.39
7.39
7.37
7.33
7.30
5.42
5.40
5.37
5.35
5.32
1.71
1.68
O
N
H
N
Br
0.86
0.86
0.81
0.92
1.84
5.04
1.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.30
147.27
143.33
141.70
136.02
131.96
129.54
128.73
128.54
128.15
127.35
126.21
126.06
123.46
77.45
77.03
76.61
49.16
22.19
O
N
H
N
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.51
9.50
9.49
9.48
8.03
8.03
8.02
8.01
8.00
7.98
7.98
7.28
1.58
NH
N
N
NH
9.55
9.45
8.1
8.0
7.9
2.00
4.18
18.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.29
151.30
133.46
126.99
126.31
77.44
77.01
76.59
51.87
28.70
O
NH
N
N
O
NH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)