Supporting Information

Visible-Light Mediated Carbamoyl Radical Addition to Heteroarenes

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Supporting Information

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Supporting Information

1. General Information

Reagents

All reagent-grade chemicals were obtained from commercial suppliers and were used as received unless otherwise noted. CH_2Cl_2 and THF were dried over activated alumina columns on MBraun Solvent Purification System (SPS-800). DCE and MeCN were distilled from CaH_2 and anhydrous dimethylformamide and dimethylsulfoxide was purchased from Sigma Aldrich. Triethylamine (reagent grade, ≥98%, Sigma Aldrich) and DMSO (anhydrous, ≥99.9%, 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* micro-syringe or plastic syringe (fitted with metal needle) into the reaction test tubes under a positive argon pressure.

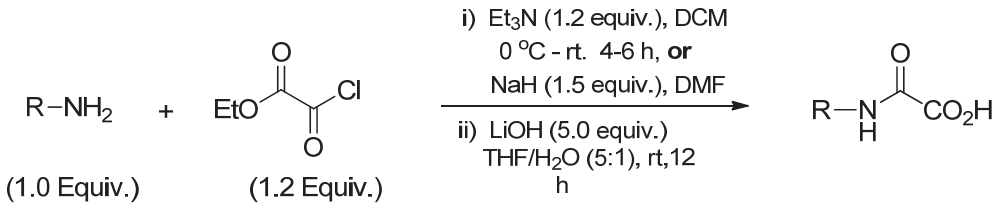
Photochemical reactions were performed with 455 nm (Castorama-blue LEDs (λ = 455 nm (± 15 nm), 12 V, 500 mA).

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 (^{1}H-NMR) homogeneous materials, unless otherwise stated.

Instruments

^{1}H-NMR and ^{13}C-NMR were recorded on various spectrometers: a Brüker DPX 200 (^{1}H: 200 MHz, ^{13}C: 50.25 MHz), a Brüker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75.46 MHz), a using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplets. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 using a thin film between KBr plates. HRMS were recorded with a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mode.

2. A. General procedure for the preparation of Oxamic Acids

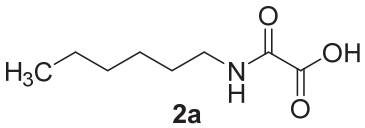


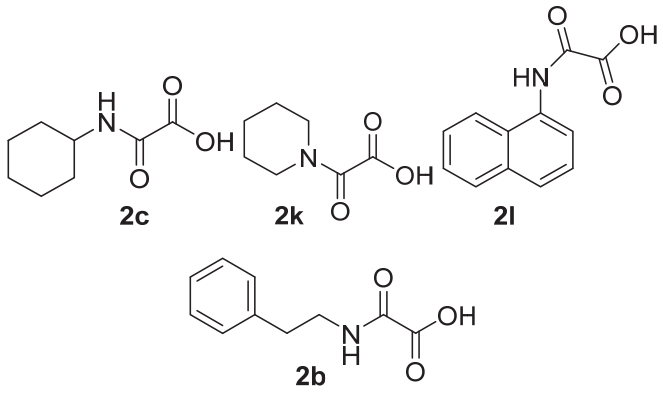
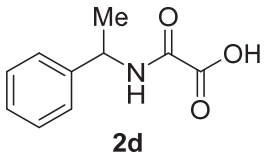
Scheme 1. Preparation of oxamic acids

To a solution of the corresponding aniline or amine (10 mmol) in CH_2Cl_2 (0.3 M) was added Et_3N (11 mmol), oxalyl chloride (11 mmol) was then added to the solution slowly at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 - 6 h. The reaction mixture was then treated with 1 M HCl (20 mL) and extracted with dichloromethane (3 x 20 mL). The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, directly subjected to hydrolysis.

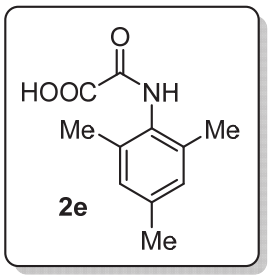
The residue was dissolved in 15 mL THF and 5 mL H_2O, and LiOH (50 mmol) was added. After stirring for 6 - 8 h at room temperature, the basic reaction mixture was washed with dichloromethane (3 x 30 mL). The aqueous phase was separated and acidified with 1M aqueous HCl solution. The resulting mixture was extracted with ethyl acetate (3 x 30 mL) and the combined organic layers were washed with brine (30 mL) and dried over Na_2SO_4. The solvent was evaporated and the residue was recrystallized by CH_2Cl_2/hexanes.

Table 1. Previously reported Oxamic acids

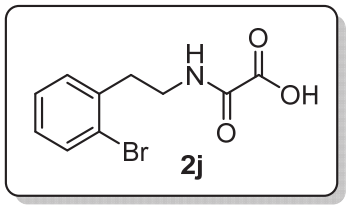
Oxamic Acids	References
 **2a**	1. N. S. Vujicic, Z. Glasovac, N. Zweep, J. H. van Esch, M. Vinkovic, J. Popovic, M. Zinic *Chem. Eur. J.* **2013**, *19*, 8558-8572.

	2. S. D. Linton et. al. *J. Med. Chem.* **2005**, *48*, 6779-6782.
	3. J. Bálint, G. Egri, M. Czugler, J. Schindler, V. Kiss, Z. Juvancz, E. Fogassy, *Tetrahedron: Asymmetry* **2001**, *12*, 1511–1518.

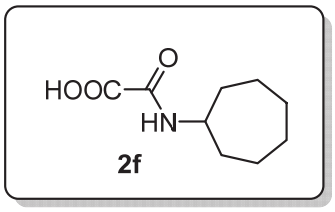
2-(Mesitylamino)-2-oxoacetic acid: 2e (1.2 g) was obtained through the general procedure A in 58 % yield as a white solid; mp 105-108 ^{o}C; **^{1}H NMR (300 MHz, CDCl$_3$)** δ (ppm) 8.49 (s, 1H), 6.94 (s, 2H), 2.29 (s, 3H), 2.19 (s, 6H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ (ppm) 160.0, 138.5, 134.6, 129.4, 128.9, 21.1, 18.4. **IR (neat) υ_{max} (cm^{-1})** = 3250, 2922, 1883, 1668. **HRMS (ESI):** Calcd. For $C_{11}H_{11}NO_3$ $[M-H]^+$ 206.0817, found 206.0821.



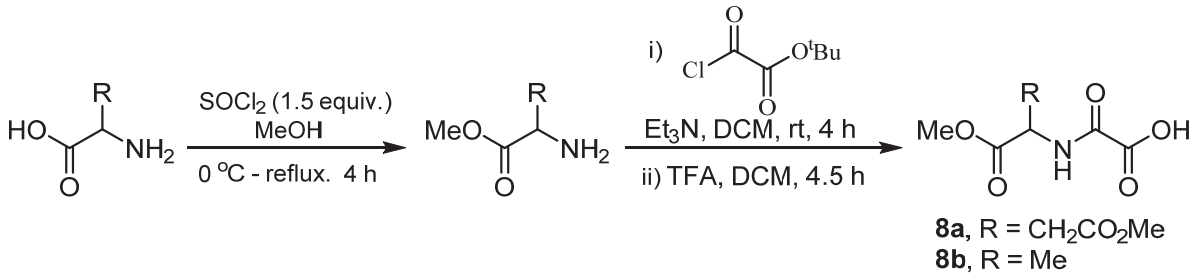
2-((2-Bromophenethyl)amino)-2-oxoacetic acid: 2j (1.4 g) was obtained through the general procedure A in 52 % yield as a white solid; mp 137-140 ^{o}C; **^{1}H NMR (300 MHz, CDCl$_3$)** δ (ppm) 7.59 (dd, J = 8.0, 1.3 Hz, 1H), 7.45 (s, 1H), 7.35 – 7.20 (m, 2H), 7.19 – 7.10 (m, 1H), 3.68 (q, J = 7.2 Hz, 1H), 3.07 (t, J = 7.2 Hz, 1H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ (ppm) 159.6, 157.5, 137.0, 133.2, 130.8, 128.8, 127.9, 124.5, 40.2, 35.3. **IR (neat) υ_{max} (cm^{-1})** = 3282, 2938, 1769, 17672. **HRMS (ESI):** Calcd. For $C_{10}H_9NO_3Br$ $[M-H]^+$ 269.9771, found 269.9770.



2-(Cycloheptylamino)-2-oxoacetic acid: 2f (1.0 g) was obtained through the general procedure A in 54 % yield as a white solid; mp 158-63 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.26 (s, 1H), 4.07-3.67 (m, 1H), 2.08 – 1.86 (m, 2H), 1.81 – 1.41 (m, 10H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 160.2, 156.3, 52.3, 34.6, 29.0, 24.0. **IR (neat) υ_{max} (cm^{-1})** = 3293, 2923, 1767, 1674. **HRMS (ESI):** Calcd. For $C_9H_{14}NO_3$ $[M-H]^+$, 184.0979, found 184.0982.



2. B. General procedure for the preparation of Oxamic Acids[1]



Scheme 2. Preparation of Oxamic acids

To a solution of the corresponding amino acid (30.07 mmol) in MeOH (25 mL) at 0 °C under nitrogen, thionyl chloride (3.2 mL, 45.11 mmol) was added dropwise over 15 mins. The reaction mixture was warmed to room temperature and then refluxed for 4 h. The solution was concentrated in vacuo to afford colorless oil. Hexane was added to this crude oil and was stirred for 10 min. Hexane was decanted and this procedure was repeated twice to obtain a solid compound.[4a] This solid compound was dissolved in DCM (60 mL) and *tert*-butyl 2-chloro-2-oxoacetate was added dropwise at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 4 h. The resulting mixture was washed with water (100 mL), and brine (100 mL) then dried over sodium sulfate, concentrated under reduced pressure to obtain a crude solid compound.[4b] The crude product was then treated with TFA in dichloromethane for 4 h at room temperature[4b] and then mixture was concentrated under reduced pressure to give the desired oxamic acid product as a colorless oil.

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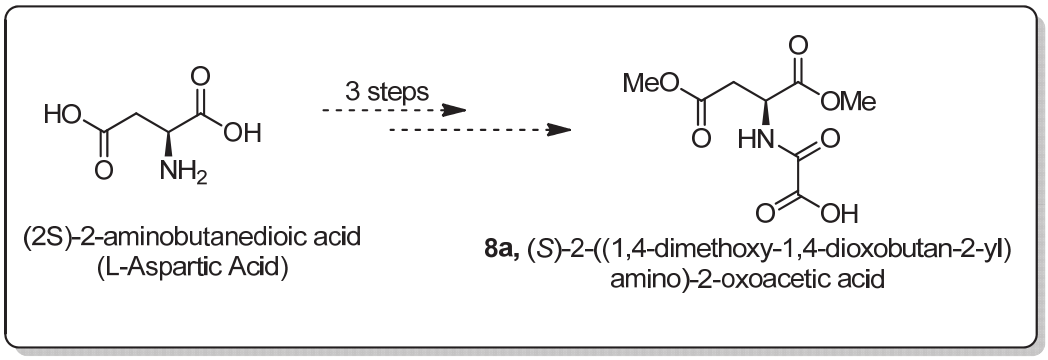
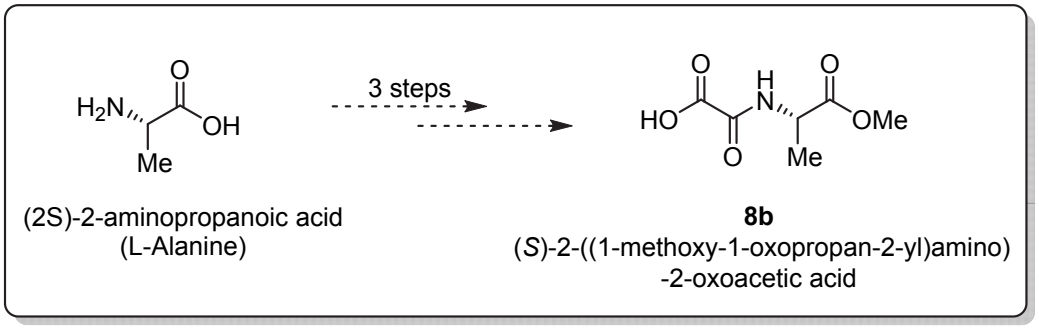
1 (a) C. R. Reddy; M. D. Reddy; U. Dilipkumar. *Eur. J. Org. Chem*. **2014**, 6310-6313. (b) Y. Seki, K. Tanabe, D. Sasaki, Y. Sohma, K. Oisaki, M. Kanai, *Angew. Chem. Int. Ed*. **2014**, *53*, 6501-6505.

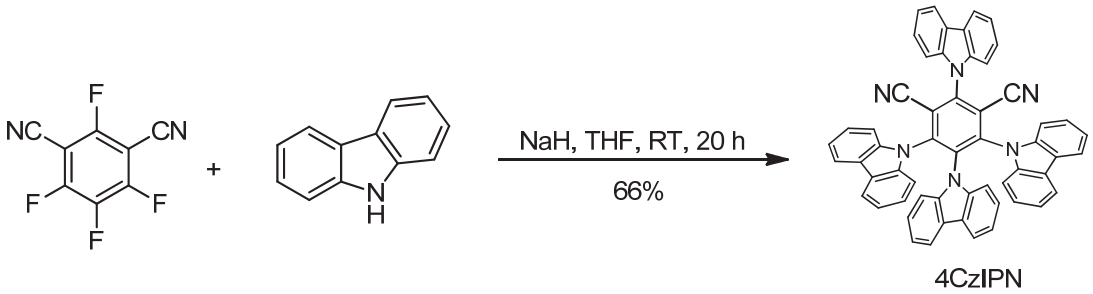


(*S*)-2-((1,4-Ddimethoxy-1,4-dioxobutan-2-yl)amino)-2-oxoacetic acid: 8a (4.5 g) was obtained through the general procedure B in 64 % yield as a colorless oil; **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.48 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 4.94 – 4.78 (m, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.11 (dd, *J* = 17.4, 5.0 Hz, 1H), 2.92 (dd, *J* = 17.4, 4.5 Hz, 1H). **^{13}C NMR (76 MHz, $CDCl_3$)** δ (ppm) 171.0, 169.7, 159.5, 157.5, 53.4, 52.5, 49.5, 35.6. **IR (neat) υ_{max} (cm^{-1})** = 3355, 2959, 1739, 1696. **HRMS (ESI):** Calcd. For $C_8H_{10}NO_7$ $[M-H]^+$ 232.0457, found 232.0462. $[\alpha]_D^{25}$ +80.76 (c 1.8, $CHCl_3$).



(*S*)-2-((1-Methoxy-1-oxopropan-2-yl) amino)-2-oxoacetic acid: 8b (3.1 g) was obtained through the general procedure B in 59 % yield as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.69 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 4.57 (p, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 1.47 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 172.0, 160.1, 157.5, 52.9, 49.0, 17.5. **IR (neat) υ_{max} (cm^{-1})** = 3290, 2958, 1739, 1692. **HRMS (ESI):** Calcd. For $C_6H_7NO_5$ $[M-H]^+$ 174.0402, found 174.0406. $[\alpha]_D^{25}$ +9.32 (c 4.0, $CHCl_3$).

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



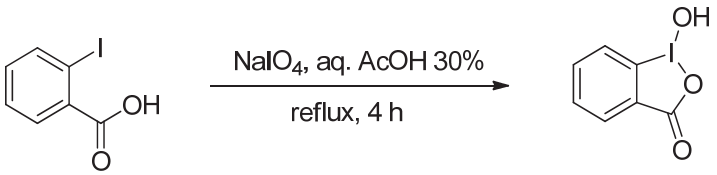
Scheme 3. Synthesis of 4CzIPN

The 4CzIPN was synthesized according to the following reported procedure.[5] 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 a minimum quantity of CH_2Cl_2 and crystallized by addition of pentane to give the pure 4CzIPN (2.21 g, 66%) as a yellow solid; **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 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 (ppm) 145.2, 144.6, 140.0, 138.2, 137.0, 134.8, 127.0, 125.8, 125.0, 124.8, 124.5, 123.9, 122.4, 121.9, 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.[2]

[2] Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234-238.

4. Hypervalent Iodine Reagents (HIR)

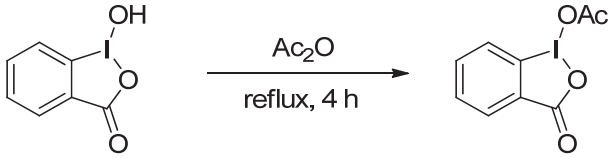
(a) 1-Hydroxy-1,2-benziodoxol-3(1H)-one (CAS: 131-62-4):



Scheme 4. Preparation of BI-OH

Following a reported procedure,[3] $NaIO_4$ (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 reaction 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 to give the pure compound **BI-OH** (6.8 g, 86%) as a white solid; **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ (ppm) 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 (ppm) 168.2, 134.9, 132.0, 131.6, 130.8, 126.7, 120.9. Spectroscopic data were in good agreement with literature.

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



Scheme 4. Preparation of BI-OAc

Following a reported procedure,[4] BI-OH (6.00 g, 22.7 mmol) was heated in Ac_2O (20 mL) to 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. Crystals were then collected and dried overnight under high vacuum to give compound **BI-OAc** (6.1 g, 88%) as a white solid; **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 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). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 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.

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3 Fernández González, D.; Brand, J. P.; Waser, J. *Chem. Eur. J.* **2010**, *16*, 9457-9461.
4 Eisenberger, P.; Gischig, S.; Togni, A. *Chem. Eur. J.* **2006**, *12*, 2579-2586.

5. General procedure for the Visible-Light Mediated Carbamoyl Radical Addition to Heteroarenes

Reaction Setup:

Photochemical reactions were performed with 455 nm (Castorama-blue LEDs (λ = 455 nm (± 15 nm), 12 V, 500 mA).

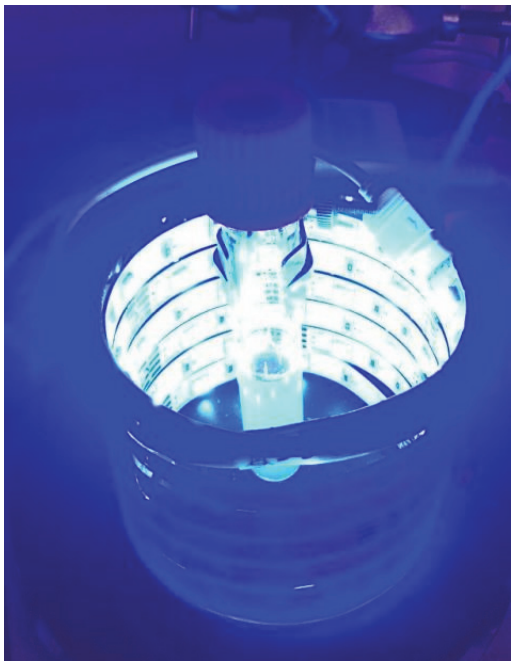
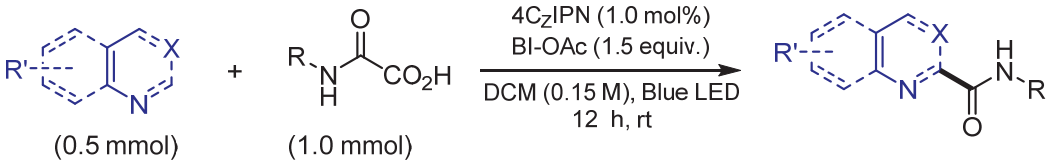


Figure 1. Reaction Setup

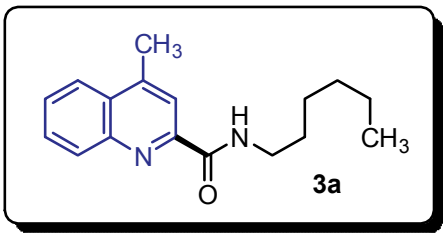


Scheme 5. Carbamoyl addition to Heteroarenes

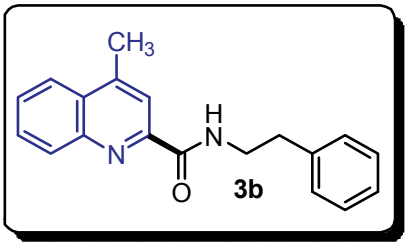
The *N*-Heterocycle (1.0 equiv., 0.5 mmol), Oxamic Acid (1.5 equiv., 0.75 mmol), 4CzIPN (1.0 mol%, 0.005 mmol), and BIOAc (1.5 equiv., 0.75 mmol) were placed into a re-sealable test-tube with Teflon septa (10 mL) and a magnetic stir bar. Air was removed from the reaction vessel, which was then backfilled with argon three times, and DCM (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 12 h. The reaction mixture was concentrated and purified directly by column chromatography to afford the product. (Eluting with ethyl acetate/hexanes).

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

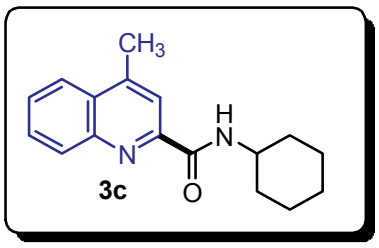
***N*-Hexyl-4-methylquinoline-3-carboxamide: 3a** (122 mg) was obtained through the general procedure in 90 % yield as a white solid, m.p. 60-63 °C. R_f = 0.84 (EtOAc-Hexane 10/90).**^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.29 (s, 1H), 8.13 (d, *J* = 0.8 Hz, 1H), 8.10 – 8.02 (m, 1H), 7.98 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.75 – 7.65 (m, 1H), 7.62 – 7.51 (m, 1H), 3.59 – 3.41 (m, 2H), 2.71 (d, *J* = 1.0 Hz, 3H), 1.72 – 1.56 (m, 2H), 1.48 – 1.22 (m, 6H), 0.96 – 0.77 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.7, 149.6, 146.4, 146.0, 130.3, 129.6, 129.2, 127.5, 123.9, 119.5, 39.6, 31.6, 29.7, 26.8, 22.6, 18.9, 14.1. **IR (neat) υ_{max} (cm^{-1})** = 3373, 2928, 1672, 1528. **HRMS (ESI):** Calcd. For $C_{17}H_{22}N_2O$, $[M+H]^+$ 271.1804, found 271.1809.



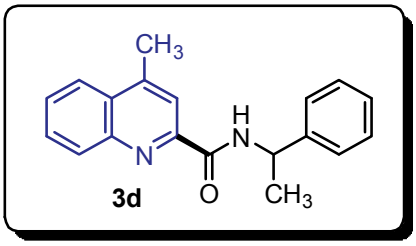
4-Methyl-N-phenethylquinoline-2-carboxamide: 3b (121 mg) was obtained through the general procedure in 83 % yield as a yellow gel. R_f = 0.62 (EtOAc-Hexane 15/85).**^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.42 (s, 1H), 8.19 – 8.12 (m, 1H), 8.09 – 7.95 (m, 3H), 7.73 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.61 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.42 – 7.26 (m, 5H), 3.88 – 3.73 (m, 2H), 3.01 (t, *J* = 7.3 Hz, 2H), 2.75 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.7, 149.4, 146.3, 146.0, 139.1, 130.3, 129.7, 129.2, 128.9, 128.6, 127.6, 126.5, 123.9, 119.4, 40.9, 36.1, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3383, 2928, 1672, 1526. **HRMS (APCI):** Calcd. For $C_{19}H_{18}N_2O$, $[M+H]^+$ 291.1491, found 291.1493.



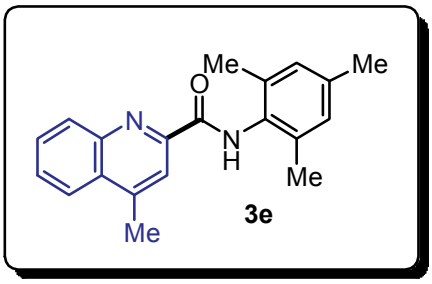
***N*-Cyclohexyl-4-methylquinoline-2-carboxamide: 3c** (131 mg) was obtained through the general procedure in 86 % yield as a yellow gel. R_f = 0.72 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.13 (d, *J* = 0.8 Hz, 1H), 8.11 – 8.05 (m, 1H), 8.00 – 7.94 (m, 1H), 7.74 – 7.66 (m, 1H), 7.61 – 7.52 (m, 1H), 4.10 – 3.91 (m, 1H), 2.71 (d, *J* = 0.8 Hz, 3H), 2.12 – 1.96 (m, 2H), 1.86 – 1.71 (m, 2H), 1.72 – 1.57 (m, 1H), 1.51 – 1.13 (m, 5H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.7, 149.7, 146.3, 146.0, 130.2, 129.6, 129.2, 127.5, 123.9, 119.5, 48.4, 33.2, 25.7, 25.0, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3378, 2930, 1669, 1550. **HRMS (APCI):** Calcd. For $C_{17}H_{20}N_2O$, $[M+H]^+$ 269.1648, found 269.1641.



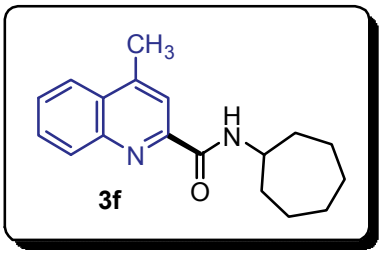
4-Methyl-N-(1-phenylethyl) quinoline-2-carboxamide: 3d (120 mg) was obtained through the general procedure in 83 % yield as a yellow gel. R_f = 0.86 (EtOAc-Hexane 10/90). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.62 (d, *J* = 8.2 Hz, 1H), 8.24 – 8.17 (m, 1H), 8.17 – 8.09 (m, 1H), 8.07 – 7.97 (m, 1H), 7.79 – 7.69 (m, 1H), 7.67 – 7.57 (m, 1H), 7.54 – 7.45 (m, 2H), 7.44 – 7.36 (m, 2H), 7.34 – 7.30 (m, 1H), 5.44 (p, *J* = 7.0 Hz, 1H), 2.75 (s, 3H), 1.71 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.9, 149.3, 146.3, 146.1, 143.4, 130.3, 129.7, 129.2, 128.7, 127.6, 127.3, 126.3, 123.9, 119.5, 48.9, 22.1, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3380, 2975, 1670, 1550. **HRMS (APCI):** Calcd, For $C_{19}H_{18}N_2O$, $[M+H]^+$ 291.1491, found, 291.1503.



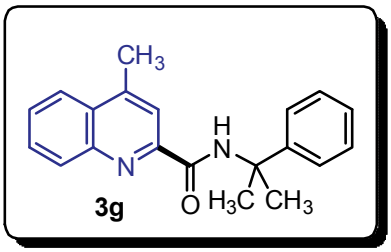
***N*-Mesitylquinoline-2-carboxamide: 3e** (65 mg) was obtained through the general procedure in 43 % yield as a brown solid; m.p., 198-201 °C. R_f = 0.77 (EtOAc-Hexane 10/90). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.66 (s, 1H), 8.25 (d, *J* = 0.7 Hz, 1H), 8.17 (s, *J* = 8.4, 0.7 Hz, 1H), 8.08 (m, *J* = 8.4, 0.9 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.70 – 7.63 (m, 1H), 6.97 (s, 2H), 2.81 (d, *J* = 0.8 Hz, 3H), 2.31 (d, *J* = 6.9 Hz, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.1, 149.4, 146.5, 136.9, 135.3, 131.4, 130.5, 129.9, 129.5, 129.1, 127.9, 124.1, 119.8, 21.1, 19.0, 18.7. **IR (neat) υ_{max} (cm^{-1})** = 3348, 2920, 1686, 1559. **HRMS (ESI):** Calcd. For $C_{20}H_{20}N_2O$ $[M+Na]^+$, 327.1473, found 327.1469.



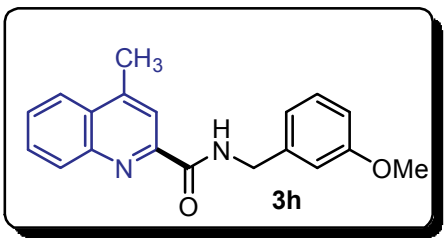
***N*-Cycloheptyl-4-methylquinoline-2-carboxamide: 3f** (120 mg) was obtained through the general procedure in 85 % yield as a white solid; m.p. 102-105 °C. R_f = 0.88 (EtOAc-Hexane 20/80). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.23 (d, *J* = 8.4 Hz, 1H), 8.14 – 8.03 (m, 2H), 7.95 (dd, *J* = 1.0, 8.2 Hz, 1H), 7.68 (dt, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.55 (dt, *J* = 8.2, 6.8, 1.4 Hz, 1H), 4.29 – 4.04 (m, 1H), 2.70 (d, *J* = 1.0 Hz, 3H), 2.14 – 1.93 (m, 2H), 1.80 – 1.40 (m, 10H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.4, 149.7, 146.3, 145.9, 130.2, 129.6, 129.1, 127.4, 123.8, 119.4, 50.6, 35.1, 28.1, 24.2, 18.8. **IR (neat) υ_{max} (cm^{-1})** = 3380, 2926, 1669, 1522. **HRMS (ESI):** Calcd. For $C_{18}H_{22}N_2O$ $[M+Na]^+$, 305.1630, found 305.1624.



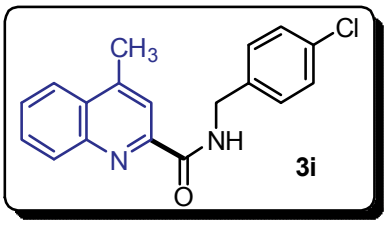
4-Methyl-N-(2-phenylpropan-2-yl) quinoline-2-carboxamide: 3g (131 mg) was obtained through the general procedure in 86 % yield as a yellow gel. R_f = 0.85 (EtOAc-Hexane 10/90). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.79 (s, 1H), 8.24 – 8.13 (m, 2H), 8.05 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.78 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.71 – 7.54 (m, 3H), 7.45 – 7.36 (m, 2H), 7.34 – 7.24 (m, 1H), 2.75 (d, *J* = 0.8 Hz, 3H), 1.95 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.7, 149.9, 147.0, 146.3, 146.0, 130.3, 129.7, 129.2, 128.8, 128.5, 127.6, 126.7, 124.9, 123.9, 119.3, 55.8, 29.3, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3372, 2976, 1677, 1503. **HRMS (ESI):** Calcd. For $C_{20}H_{20}N_2O$ $[M+Na]^+$, 327.1467, found 327.1474.



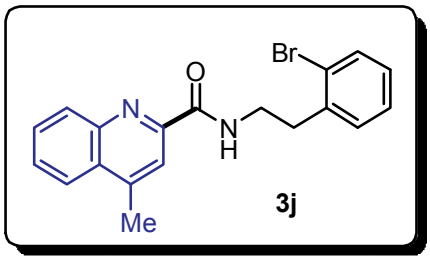
N-(3-Methoxybenzyl)-4-methylquinoline-2-carboxamide: 3h (115 mg) was obtained through the general procedure in 66 % yield as a brown gel. R_f = 0.88 (EtOAc-Hexane 10/90). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.67 (s, 1H), 8.25 – 8.17 (m, 1H), 8.13 – 7.98 (m, 2H), 7.80 – 7.68 (m, 1H), 7.68 – 7.57 (m, 1H), 7.34 – 7.24 (m, 1H), 7.06 – 6.94 (m, 2H), 6.85 (dd, *J* = 8.0, 2.2 Hz, 1H), 4.73 (d, *J* = 6.2 Hz, 2H), 3.81 (s, 3H), 2.78 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.7, 160.0, 149.2, 146.3, 146.3, 140.0, 130.3, 129.8, 129.3, 127.7, 123.9, 120.2, 119.6, 113.5, 113.0, 55.3, 43.6, 19.0. **IR (neat) υ_{max} (cm^{-1})** = 3381, 2936, 1672, 1527. **HRMS (ESI):** Calcd.For $C_{19}H_{18}N_2O_2$ $[M+Na]^+$, 329.1260, found 329.1267.



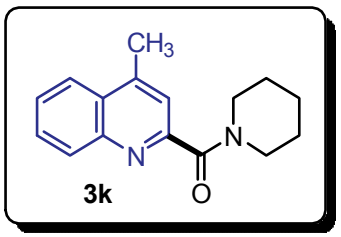
***N*-(4-Chlorobenzyl)-4-methylquinoline-2-carboxamide: 3i** (132 mg) was obtained through the general procedure in 77 % yield as a yellow gel. R_f = 0.61 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.68 (s, 1H), 8.24 – 8.16 (m, 1H), 8.13 – 8.01 (m, 1H), 7.82 – 7.59 (m, 3H), 7.39 – 7.30 (m, 4H), 7.16 – 7.05 (m, 1H), 4.71 (d, *J* = 6.2 Hz, 1H), 2.80 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.8, 149.0, 146.3, 136.9, 133.1, 130.2, 129.7, 129.2, 128.7, 127.7, 123.9, 119.5, 42.8, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3379, 2924, 1685, 1526. **HRMS (ESI):** Calcd. For $C_{18}H_{15}N_2OCl$, $[M+H]^+$, 311.0945, found 311.0939.



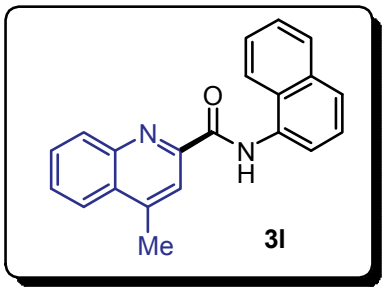
***N*-(2-Bromophenethyl)-4-methylquinoline-2-carboxamide: 3j** (135 mg) was obtained through the general procedure in 73 % yield as a yellow solid; m.p. 245-249 °C. R_f = 0.69 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.45 (s, 1H), 8.19 (d, *J* = 0.8 Hz, 1H), 8.12 – 8.03 (m, 2H), 7.80 – 7.74 (m, 1H), 7.69 – 7.58 (m, 2H), 7.35 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.31 – 7.28 (m, 1H) 7.17 – 7.11 (m, 1H), 3.84 (dt, *J* = 7.4, 6.5 Hz, 2H), 3.18 (t, *J* = 7.3 Hz, 2H), 2.79 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.9, 149.3, 146.4, 146.1, 138.4, 133.0, 131.1, 130.3, 129.7, 129.3, 128.3, 127.7, 124.7, 123.96, 119.4, 39.4, 36.2, 19.0. **IR (neat) υ_{max} (cm^{-1})** = 3379, 2930, 1672, 1525. **HRMS (ESI):** Calcd. For $C_{19}H_{17}N_2OBr$, $[M+H]^+$, 369.0597, found 369.0594.



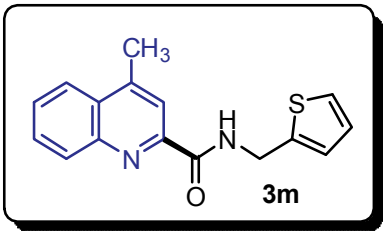
(4-Methylquinoline-2-yl)(piperidin-1-yl)methanone: 3k (103 mg) was obtained through the general procedure in 81 % yield as a brown gel, R_f = 0.74 (EtOAc-Hexane 10/90). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.16 – 8.09 (m, 1H), 8.00 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.77-7.70 (m, 1H), 7.64-7.57 (m, 1H), 7.51 – 7.45 (m, 1H), 3.78 (t, *J* = 4.8 Hz, 2H), 3.55 – 3.39 (m, 2H), 2.73 (d, *J* = 0.8 Hz, 3H), 1.82 – 1.46 (m, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 167.5, 153.8, 146.6, 146.1, 130.1, 129.8, 128.1, 127.4, 123.8, 121.0, 48.4, 43.4, 26.6, 25.6, 24.6, 19.0. **IR (neat) υ_{max} (cm^{-1})** = 3344, 2937, 1669, 1557. **HRMS (APCI):** Calcd. For $C_{16}H_{19}N_2O$, $[M+H]^+$, 255.1491, found 255.1492.



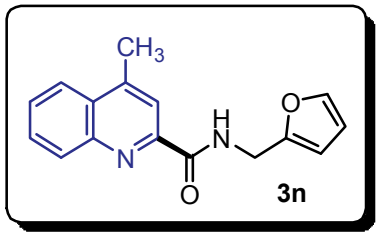
4-Methyl-*N*-(naphthalen-1yl) quinolone-2-carboxamide: 3l (91 mg) was obtained through the general procedure in 58 % yield as a brown gel. R_f = 0.66 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 11.01 (s, 1H), 8.47 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.33 – 8.26 (m, 2H), 8.24 – 8.18 (m, 1H), 8.11 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.93 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.77 – 7.53 (m, 6H), 2.85 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 162.8, 149.5, 146.8, 146.3, 134.3, 132.7, 130.6, 130.1, 129.6, 129.0, 128.0, 126.3, 125.1, 124.1, 120.7, 119.5, 118.76, 19.2. **IR (neat) υ_{max} (cm^{-1})** = 3331, 2926, 1691, 1542. **HRMS (ESI):** Calcd. For $C_{21}H_{16}N_2O$, $[M+H]^+$, 313.1335, found 313.1345.



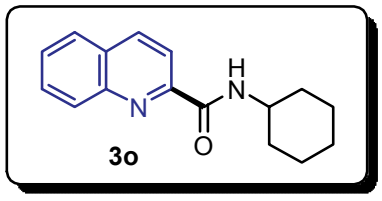
4-Methyl-N-(thiophen-2-ylmethyl) quinoline-2-carboxamide: 3m (113 mg) was obtained through the general procedure in 80 % yield as a white solid, m.p. 145-148 °C. R_f = 0.41 (EtOAc-Hexane 20/80). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.71 (s, 1H), 8.19 (d, *J* = 0.9 Hz, 1H), 8.12 – 7.97 (m, 2H), 7.77 – 7.67 (m, 1H), 7.66 – 7.56 (m, 1H), 7.25 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.14 – 7.05 (m, 1H), 6.99 (dd, *J* = 5.2, 3.4 Hz, 1H), 4.91 (dd, *J* = 6.0, 0.8 Hz, 2H), 2.75 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.5, 149.0, 146.3, 146.2, 141.0, 130.2, 129.7, 129.3, 127.7, 126.9, 126.1, 125.2, 123.9, 119.5, 38.3, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3381, 2924, 1671, 1596. **HRMS (ESI):** Calcd. For $C_{16}H_{14}N_2OS$ $[M+Na]^+$, 305.0719, found 305.0714.



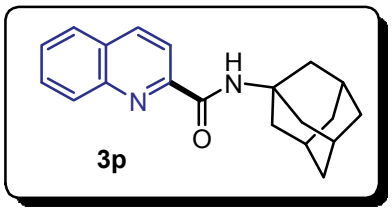
***N*-(Furan-2-ylmethyl)-4-methylquinoline-2-carboxamide: 3n** (111 mg) was obtained through the general procedure in 71 % yield as a white solid; m.p. 145-148 °C. R_f = 0.40 (EtOAc-Hexane 20/80). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.59 (s, 1H), 8.18 (d, *J* = 1.0 Hz, 1H), 8.13 – 8.01 (m, 2H), 7.80-7.72 (m, 1H), 7.68-7.61 (m, 1H), 7.42 (dd, *J* = 1.8, 1.0 Hz, 1H), 6.41 – 6.32 (m, 2H), 4.74 (d, *J* = 6.0 Hz, 2H), 2.79 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.6, 151.4, 149.0, 146.4, 146.1, 142.3, 130.3, 129.7, 127.7, 123.9, 119.5, 110.4, 107.5, 36.5, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3382, 2923, 1673, 1596.



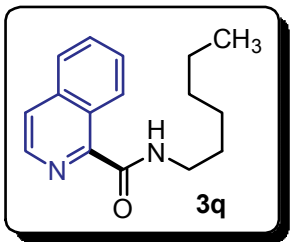
***N*-Cyclohexylquinoline-2-carboxamide: 3o** (101 mg) was obtained through the general procedure in 80 % yield as a yellow solid; m.p. 92-94 °C. R_f = 0.57 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.34 – 8.22 (m, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.12 – 8.05 (m, 1H), 7.83 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.72 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 4.12 – 3.89 (m, 1H), 2.12 – 1.95 (m, 2H), 1.85 – 1.58 (m, 3H), 1.52 – 1.30 (m, 5H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.5, 150.2, 146.5, 137.4, 130.0, 129.7, 129.3, 127.8, 127.8, 118.9, 48.4, 33.2, 25.7, 25.0. **IR (neat) υ_{max} (cm^{-1})** = 3381, 2931, 1671, 1526. **HRMS (ESI):** Calcd. For $C_{16}H_{18}N_2O$, $[M+H]^+$, 255.1491, found 255.1499.



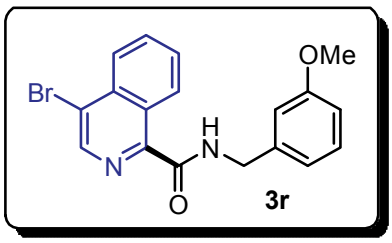
***N*-((1s, 3s)-Adamantan-1-yl) quinoline-2-carboxamide: 3p** (111 mg) was obtained through the general procedure in 72 % yield as a white gel. R_f = 0.56 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.30 (s, 2H), 8.20 – 8.07 (m, 2H), 7.87 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.75 (dtd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.61 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 2.33 – 2.10 (m, 9H), 1.87 – 1.67 (m, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.4, 150.9, 146.4, 137.5, 130.0, 129.7, 129.2, 127.8, 127.7, 118.6, 51.8, 41.6, 36.6, 29.6. **IR (neat) υ_{max} (cm^{-1})** = 3364, 2908, 1676, 1527. **HRMS (ESI):** Calcd.For $C_{20}H_{22}N_2O$ $[M+Na]^+$, 329.1624, found 329.1625.



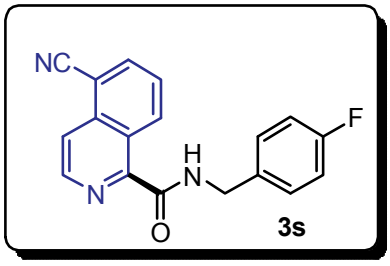
***N*-Hexylisoquinoline-3-carboxamide: 3q** (99 mg) was obtained through the general procedure in 77 % yield as a yellow gel. R_f = 0.60 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.65 – 9.52 (m, 1H), 8.41 (d, *J* = 5.5 Hz, 1H), 8.21 (s, 1H), 7.86 – 7.55 (m, 4H), 3.58 – 3.39 (m, 2H), 1.64 (q, *J* = 7.8 Hz, 2H), 1.50 – 1.23 (m, 6H), 0.96 – 0.80 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 166.1, 148.6, 140.2, 137.4, 130.5, 128.6, 128.0, 127.0, 126.8, 124.2, 39.6, 31.6, 29.7, 26.8, 22.6, 14.1. **IR (neat) υ_{max} (cm^{-1})** = 3381, 2929, 1666, 1518. HRMS (ESI): Calcd. $C_{16}H_{21}N_2O$, $[M+H]^+$, 257.1648, found, 257.1651.



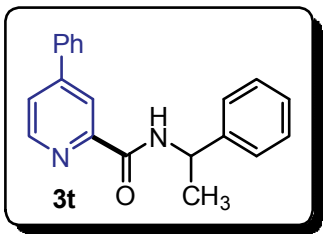
4-Bromo-N-(3-methoxybenzyl) isoquinoline-1-carboxamide: 3r (131 mg) was obtained through the general procedure in 70 % yield as a yellow gel. R_f = 0.61 (EtOAc-Hexane 15/85). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.68 (d, *J* = 8.4 Hz, 1H), 8.61 (bs,1H), 8.49 (bs, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.66 (m, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.07 – 6.92 (m, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.70 (d, *J* = 6.0 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 165.4, 159.9, 147.4, 142.1, 139.8, 135.9, 131.8, 129.8, 129.5, 128.4, 126.1, 123.5, 123.3, 120.1, 113.5, 113.0, 55.5, 55.3, 43.6. **IR (neat) υ_{max} (cm^{-1})** = 3378, 2929, 1668, 1516. **HRMS (ESI):** Calcd. For, $C_{18}H_{16}N_2O_2Br$, $[M+H]^+$, 371.0389, found 371.0392.



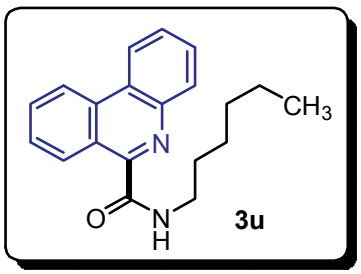
Cyano-N-(4-fluorobenzyl)isoquinoline-1-carboxamide : 3s (107 mg) was obtained through the general procedure in 70 % yield as a yellow gel. R_f = 0.30 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, CDCl3)** δ (ppm) 10.06 (dt, *J* = 8.9, 1.1 Hz, 1H), 8.78 – 8.55 (m, 2H), 8.29 – 8.11 (m, 2H), 7.79 (dd, *J* = 8.8, 7.2 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.15 – 7.00 (m, 2H), 4.71 (d, *J* = 6.1 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 165.2, 164.0, 148.6, 142.7, 137.0, 133.7, 129.7, 129.6, 127.9, 126.7, 121.6, 116.7, 115.9, 115.6, 109.9, 43.1. **IR (neat) υ_{max} (cm^{-1})** = 3381, 2929, 1666, 1518. **HRMS (ESI):** Calcd. For $C_{16}H_{21}N_2O$, $[M+Na]^+$, 328.0856, found, 328.0855.



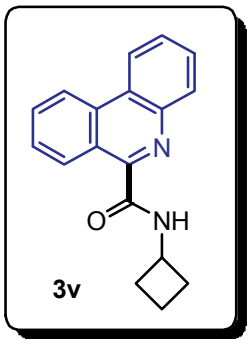
4-Phenyl-*N* (1-phenylethyl) picolinamide: 3t (86 mg) was obtained through the general procedure in 57 % yield as a yellow gel. R_f = 0.53 (EtOAc-Hexane 20/80). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.58 (dd, *J* = 5.1, 0.7 Hz, 1H), 8.52 – 8.30 (m, 2H), 7.73 – 7.68 (m, 2H), 7.64 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.54 – 7.42 (m, 5H), 7.40 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 5.45 – 5.25 (m, 1H), 1.65 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.6, 150.6, 150.0, 148.7, 143.4, 137.5, 129.4, 128.8, 127.3, 126.4, 123.9, 120.3, 49.0, 22.2. **IR (neat) υ_{max} (cm^{-1})** = 3378, 2974, 1670, 1515. **HRMS (ESI):** Calcd. For, $C_{20}H_{18}N_2O$ $[M+Na]^+$, 325.1311, found 325.1325.



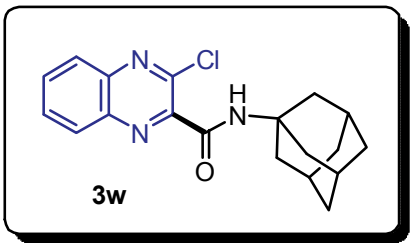
***N*-Hexylphenanthridine-6-carboxamide: 3u** (142 mg) was obtained through the general procedure in 93 % yield as a yellow solid; m.p. 91-95 ºC. R_f = 0.61 (EtOAc-Hexane 10/90). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.59 – 9.48 (m, 1H), 8.55 – 8.39 (m, 2H), 8.20 (s, 1H), 8.12 – 8.03 (m, 1H), 7.81 – 7.72 (m, 1H), 7.71 – 7.57 (m, 3H), 3.61 – 3.45 (m, 2H), 1.79 – 1.60 (m, 2H), 1.51 – 1.24 (m, 6H), 0.99 – 0.79 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 166.1, 149.8, 141.8, 133.6, 130.8, 130.3, 129.0, 128.7, 128.3, 127.8, 125.3, 124.2, 122.0, 121.7, 39.8, 31.6, 29.6, 26.8, 22.6, 14.1. **IR (neat) υ_{max} (cm^{-1})** = 3295, 2928, 1653, 1522. **HRMS (ESI):** Calcd. For, $C_{20}H_{23}N_2O$, $[M+H]^+$, 307.1804, found 307.1810.



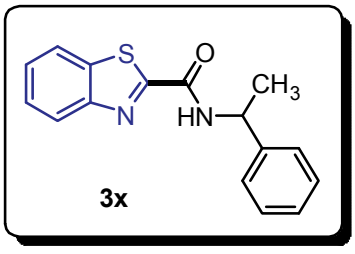
***N*-Cyclobutylphenanthridine-6-carboxamide: 3v** (110 mg) was obtained through the general procedure in 79 % yield as a yellow gel. R_f = 0.53 (EtOAc-Hexane 10/90). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.66 – 9.49 (m, 1H), 8.65 – 8.55 (m, 2H), 8.31 (d, *J* = 7.4 Hz, 1H), 8.22 – 8.12 (m, 1H), 7.85 (td, *J* = 7.0, 3.5 Hz, 1H), 7.80 – 7.69 (m, 3H), 4.67 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.59 – 2.43 (m, 2H), 2.19 – 2.09 (m, 2H), 1.89 – 1.79 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 165.2, 149.5, 141.9, 133.8, 131.1, 130.5, 129.2, 128.9, 128.5, 128.0, 125.6, 124.4, 122.2, 121.9, 45.06, 31.3, 15.5, 8.8. **IR (neat) υ_{max} (cm^{-1})** = 3372, 2976, 1678, 1520. **HRMS (ESI):** Calcd. For, $C_{18}H_{16}N_2O$, $[M+H]^+$, 277.1335, found 277.1340.



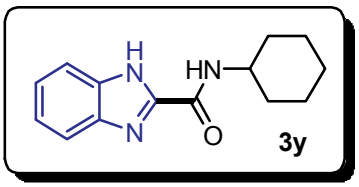
***N*-((3s, 5s, 7s)-Adamantan-1-yl)-3-chloroquinoxaline-2-carboxamide: 3w** (120 mg) was obtained through the general procedure in 71 % yield as a yellow solid; m.p. 198-203 °C. R_f = 0.30 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.11 – 7.96 (m, 2H), 7.89 – 7.72 (m, 2H), 7.15 (s, 1H), 2.28 – 2.07 (m, 9H), 1.73 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 161.8, 145.1, 144.2, 142.4, 138.9, 132.4, 130.9, 129.2, 128.3, 52.8, 41.6, 41.4, 36.4, 29.7, 29.6. **IR (neat) υ_{max} (cm^{-1})** = 3294, 2909, 1665, 1563. **HRMS (ESI):** Calcd. For, $C_{19}H_{21}N_3OCl$, $[M+H]^+$, 342.1367, found 342.1362.



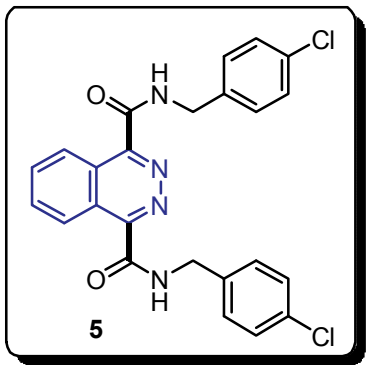
***N*-(1-Phenylethyl) benzo[d]thiazole-2-carboxamide: 3x** (58 mg) was obtained through the general procedure in 41 % yield as a yellow solid; m.p. 145-148 °C. R_f = 0.50 (EtOAc-Hexane 20/80). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.11 – 8.04 (m, 1H), 8.02 – 7.94 (m, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.29 (m, 6H), 5.48 – 5.27 (m, 1H), 1.70 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.1, 159.1, 152.9, 142.5, 137.2, 128.9, 127.7, 126.9, 126.8, 126.4, 124.3, 122.5, 49.6, 21.9. **IR (neat) υ_{max} (cm^{-1})** = 3392, 2976, 1667, 1524. **HRMS (ESI):** Calcd. For $C_{16}H_{14}N_2OS$ $[M+Na]^+$, 305.0719, found 305.0717.



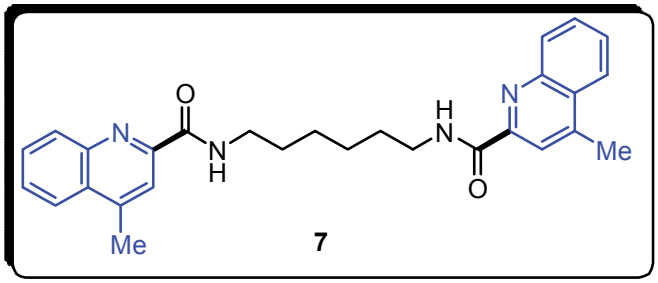
***N*-Cyclohexyl-1*H*- benzo[d]thiazole-2-carboxamide: 3y** (71 mg) was obtained through the general procedure in 59 % yield as a white solid; m.p. 153-156 °C. R_f = 0.50 (EtOAc-Hexane 20/80). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.71 (s, 3H), 7.41 – 7.31 (m, 2H), 4.17 – 3.92 (m, 1H), 2.08 (d, *J* = 9.9 Hz, 2H), 1.83 (dd, *J* = 9.2, 3.5 Hz, 2H), 1.69 (d, *J* = 12.6 Hz, 1H), 1.51 – 1.35 (m, 4H), 1.33 – 1.14 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 159.1, 158.3, 145.3, 142.9, 134.1, 124.9, 123.3, 120.4, 112.2, 48.9, 32.9, 32.6, 25.4, 24.8. **IR (neat) υ_{max} (cm^{-1})** = 3379, 2971, 1658, 1541. **HRMS (ESI):** Calcd. For $C_{14}H_{17}N_3O$ $[M+Na]^+$, 266.1263, found 266.1270.



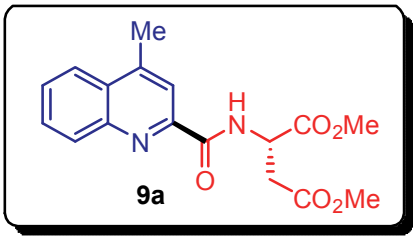
***N1,N4*-Bis(4-chlorobenzyl)phthalazine-1,4-dicarboxamide: 5** (188 mg) was obtained through the general procedure in 81 % yield as a yellow solid, m.p. 170-73 °C. R_f = 0.31 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.65 – 9.42 (m, 2H), 8.46 (s, 2H), 8.14 – 7.91 (m, 2H), 7.40 – 7.28 (m, 8H), 4.71 (dd, *J* = 6.2, 1.8 Hz, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 163.8, 150.4, 136.1, 134.0, 133.5, 129.2, 129.0, 126.8, 126.4, 43.1. **IR (neat) υ_{max} (cm^{-1})** = 3288, 2922, 1640, 1530. **HRMS (ESI):** Calcd. For, $C_{24}H_{18}N_4O_2Cl_2$ $[M+Na]^+$, 487.0699, found 487.0713.



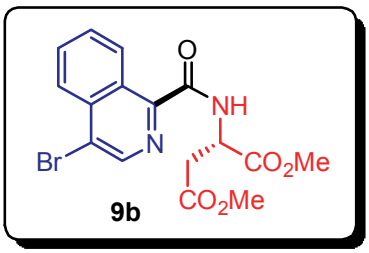
***N, N'*-(Hexane-1,6-diyl)bis(4-methylquinoline-2-carboxamide) : 7** (115 mg) was obtained through the general procedure, in 51 % yield as a yellow gel. R_f = 0.51 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.31 (t, *J* = 5.2 Hz, 2H), 8.15 (d, *J* = 0.8 Hz, 2H), 8.09 (dd, *J* = 8.4, 0.8 Hz, 2H), 8.02 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.77-7.70 (m, 2H), 7.65 – 7.56 (m, 2H), 3.58 – 3.49 (m, 4H), 2.76 (d, *J* = 0.8 Hz, 6H), 1.78 – 1.67 (m, 4H), 1.57 – 1.48 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 164.7, 149.5, 146.3, 146.0, 130.3, 129.6, 129.2, 127.5, 123.9, 119.4, 39.5, 29.7, 26.8, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3380, 2929, 1667, 1531. **HRMS (ESI):** Calcd. For $C_{28}H_{30}N_4O_2$ $[M+Na]^+$, 477.2266, found 477.2260.



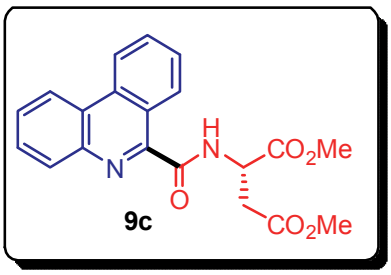
(*S*)-Dimethyl 2-(4-methylquinoline-2-carboxamido) succinate: 9a (144 mg) was obtained through the general procedure, in 87 % yield as a yellow gel. R_f = 0.43 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.04 (d, *J* = 8.4 Hz, 1H), 8.14 – 8.06 (m, 2H), 7.97 (d, *J* = 8.4, 0.9 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.61 – 7.45 (m, 1H), 5.16 – 5.08 (m, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.15 (dd, *J* = 17.0, 4.8 Hz, 1H), 3.01 (dd, *J* = 17.0, 4.8 Hz, 1H), 2.71 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 171.3, 164.7, 148.5, 146.4, 146.0, 130.6, 129.7, 129.3, 127.8, 123.8, 119.3, 52.9, 52.1, 48.8, 36.4, 18.9. **IR (neat) υ_{max} (cm^{-1})** = 3383, 2954, 1677, 1504. **HRMS (ESI):** Calcd. For $C_{17}H_{18}N_2O_5$ $[M+Na]^+$, 353.1113, found 353.1111. $[\alpha]_D^{25}$ +31.75 (c 1.8, $CHCl_3$).



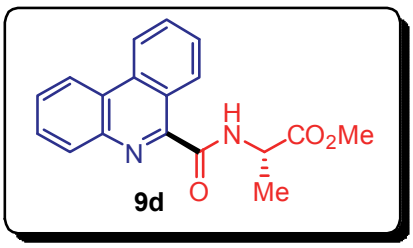
(*S*)-Dimethyl 2-(4-bromoisoquinoline-1-carboxamido) succinate: 9b (169 mg) was obtained through the general procedure, in 86 % yield as a yellow gel. R_f = 0.41 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.56 – 9.51 (m, 1H), 8.95 (d, *J* = 8.2 Hz, 1H), 8.65 (s, 1H), 8.21 – 8.08 (m, 1H), 7.81 – 7.74 (m, 1H), 7.72 – 7.65 (m, 1H), 5.14 – 5.06 (m, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.16 (dd, *J* = 17.0, 4.8 Hz, 1H), 3.02 (dd, *J* = 17.0, 4.8 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 171.2, 165.2, 146.5, 142.4, 135.8, 131.8, 129.6, 128.1, 126.1, 123.8, 53.0, 52.2, 48.8, 36.3. **IR (neat) υ_{max} (cm^{-1})** = 3383, 2953, 1673, 1507. **HRMS (ESI):** Calcd. For $C_{16}H_{15}BrN_2O_5$ $[M+Na]^+$, 417.0062, found 417.0057. $[\alpha]_D^{25}$ +29.38 (c 2.0, $CHCl_3$).



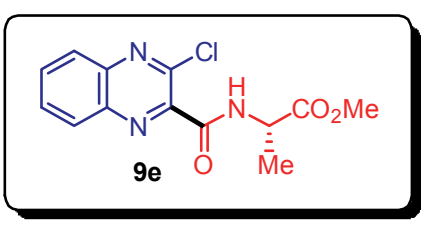
(*S*)-Dimethyl 2-(4-phenanthridine-6-carboxamido) succinate: 9c (163 mg) was obtained through the general procedure, in 89 % yield as a yellow gel. R_f = 0.44 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.57 – 5.52 (m, 1H), 9.09 (d, *J* = 8.2 Hz, 1H), 8.55 – 8.43 (m, 2H), 8.17 – 8.12 (m, 1H), 7.78 (m, 1H), 7.73 – 7.65 (s, 3H), 5.22 - 515 (m, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 3.21 (dd, *J* = 17.0, 4.8 Hz, 1H), 3.09 (dd, *J* = 17.0, 4.8 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 171.3, 165.8, 148.1, 141.7, 133.6, 130.8, 128.7, 127.9, 125.4, 124.2, 121.9, 52.9, 52.1, 48.9, 36.4. **IR (neat) υ_{max} (cm^{-1})** = 3379, 2954, 1674, 1505. $[\alpha]_D^{25}$ +71.80 (c 1.8, $CHCl_3$).



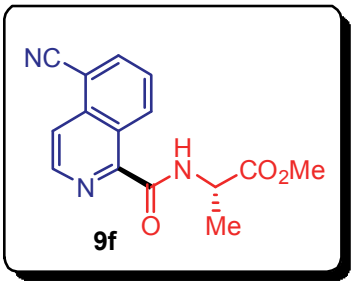
(*S*)-Methyl 2-(phenanthridine-6-carboxamido) propanoate: 9d (140 mg) was obtained through the general procedure, in 91 % yield as a white solid. m.p. 149-152 °C. R_f = 0.47 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.54 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.73 (d, *J* = 7.4 Hz, 1H), 8.60 – 8.37 (m, 2H), 8.22 – 8.06 (m, 1H), 7.86 – 7.59 (m, 4H), 4.92 - 4.81 (m, 1H), 3.84 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 173.4, 165.6, 153.2, 148.5, 141.7, 133.6, 130.8, 130.5, 128.8, 128.5, 127.9, 125.4, 124.1, 122.0, 121.7, 52.5, 48.4, 18.3. **IR (neat) υ_{max} (cm^{-1})** = 3328, 2924, 1743, 1525. **HRMS (ESI):** Calcd. For $C_{18}H_{16}N_2O_3$ $[M+Na]^+$, 331.1058, found 331.1054. $[\alpha]_D^{25}$ +94.70 (c 2.3, $CHCl_3$).



(*S*)-Methyl 2-(3-chloroquinoxaline-2-carboxamido) propanoate: 9e (102 mg) was obtained through the general procedure, in 69 % yield as a yellow gel. R_f = 0.39 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.22 – 8.16 (m, 1H), 8.13 – 8.08 (m, 1H), 7.98 – 7.83 (m, 2H), 4.94 – 4.80 (m, 1H), 3.85 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 173.1, 161.9, 145.2, 142.7, 142.2, 138.9, 132.9, 131.0, 129.4, 128.3, 52.7, 48.5, 18.4. **IR (neat) υ_{max} (cm^{-1})** = 3331, 2924, 1741, 1680, 1530. **HRMS (ESI):** Calcd. For $C_{13}H_{12}ClN_3O_3$ $[M+Na]^+$, 316.0464, found 316.0458. $[\alpha]_D^{25}$ +39.33 (c 1.7, $CHCl_3$).

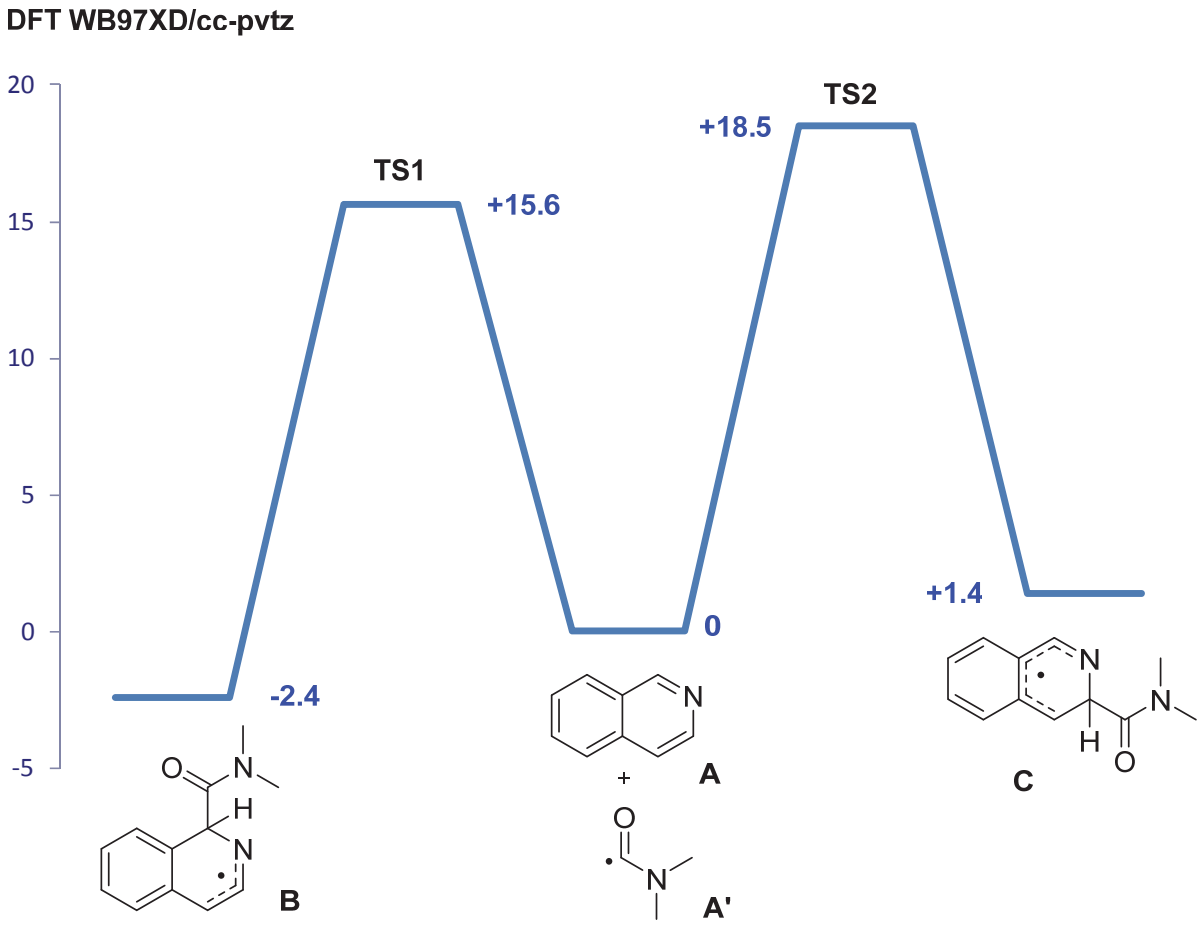


(*S*)-Methyl 2-(5-cyanoisoquinoline-1-carboxamido) propanoate: 9f (104 mg) was obtained through the general procedure, in 74 % yield as a white solid; m.p. 123-126 °C. R_f = 0.51 (EtOAc-Hexane 30/70). **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 9.94 (dt, *J* = 8.8, 1.2 Hz, 1H), 8.74 (s, 1H), 8.72 (d, *J* = 5.6 Hz, 2H), 8.23 (dd, *J* = 5.6, 1.2 Hz, 1H), 8.16 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.75 (dd, *J* = 8.8, 7.2 Hz, 1H), 4.90 – 4.77 (m, 1H), 3.83 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 173.1, 164.7, 148.1, 142.7, 136.8, 133.3, 127.8, 126.5, 121.5, 116.5, 109.8, 52.6, 48.3, 27.7, 18.3. **IR (neat) υ_{max} (cm^{-1})** = 3377, 2929, 1743, 1671, 1513. **HRMS (ESI):** Calcd. For $C_{15}H_{13}N_3O_3$ $[M+Na]^+$, 306.0854, found 306.0849. $[\alpha]_D^{25}$ +167.66 (c 1.4, $CHCl_3$).



7. DFT calculations

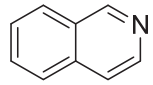
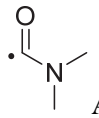
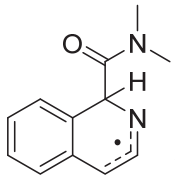
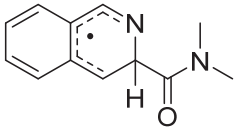
All DFT calculations were performed with the Gaussian16 software package.[5] Frequency calculations were performed to insure that there is no imaginary frequencies for local minima and only one for transition states. All calculations were performed at the WB97XD/cc-pvtz level.
All these computed structures are available on request. This Supporting information contains free Gibbs energies and cartesian coordinates of all structures computed.



[5] **Gaussian 16, Revision A.03**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Supporting Information

Free Gibbs energies at WB97XD/cc-pvtz level

Compounds	Sum of electronic and thermal Free Energies (Hartrees)	Energy difference (kcal/mol)
 **A**	-401.807061	-
 **A'**	-247.799614	-
A + A'	-649.606675	0
TS1	-649.581789	+15.6
TS2	-649.577183	+18.5
 **B**	-649.610476	-2.4
 **C**	-649.604367	+1.4

Compound **A**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.399307	-0.707492	0.000001
2	6	0	1.226812	-1.406049	-0.000009
3	6	0	-0.009814	-0.720189	-0.000001
4	6	0	-0.008492	0.691340	-0.000005
5	6	0	1.219334	1.390109	-0.000000
6	6	0	2.398703	0.704171	0.000007
7	1	0	-1.320845	-2.446562	-0.000012
8	1	0	3.342792	-1.236453	0.000006
9	1	0	1.228753	-2.488271	-0.000010
10	6	0	-1.266237	-1.366115	0.000002
11	6	0	-1.261649	1.350784	-0.000009
12	1	0	1.208577	2.472617	0.000001
13	1	0	3.339453	1.237162	0.000015
14	6	0	-2.404003	-0.615563	0.000019
15	1	0	-1.281442	2.437460	0.000007
16	1	0	-3.378255	-1.088314	-0.000004
17	7	0	-2.414684	0.740911	-0.000005

Compound **A'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.834256	-0.692394	-0.000016
2	8	0	-1.945125	-0.252429	-0.000049
3	7	0	0.327712	-0.041518	-0.000001
4	6	0	1.583793	-0.760055	0.000061
5	1	0	2.171240	-0.514683	-0.886768
6	1	0	2.171165	-0.514667	0.886935
7	1	0	1.375225	-1.826590	0.000062
8	6	0	0.337084	1.417898	-0.000009
9	1	0	-0.169089	1.804431	-0.884248
10	1	0	-0.168983	1.804448	0.884283
11	1	0	1.367725	1.764419	-0.000074

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.068023	-0.041326	0.059340
2	6	0	1.436184	0.011345	0.072999
3	6	0	2.100819	1.252358	0.005286
4	6	0	1.336156	2.431374	-0.071739
5	6	0	-0.062577	2.355461	-0.079450
6	6	0	-0.690334	1.138107	-0.019911
7	1	0	4.140852	0.505604	0.046899
8	1	0	-0.435950	-0.997002	0.111651
9	1	0	2.021417	-0.897080	0.134941
10	6	0	3.512755	1.383738	-0.015593
11	6	0	2.039907	3.686021	-0.091869
12	1	0	-0.641408	3.269470	-0.123299
13	1	0	-1.770069	1.081987	-0.026515
14	6	0	4.070872	2.625767	-0.178111
15	1	0	1.474189	4.569762	-0.375678
16	1	0	5.146136	2.732391	-0.262525
17	7	0	3.367037	3.763069	-0.273140
18	6	0	1.810979	4.256010	2.001926
19	8	0	1.255428	3.449260	2.681197
20	7	0	2.316552	5.442761	2.338643
21	6	0	2.917161	6.368574	1.399048
22	1	0	2.226953	7.181872	1.160824
23	1	0	3.810102	6.800736	1.852721
24	1	0	3.218802	5.846556	0.496280
25	6	0	2.172259	5.916594	3.708477
26	1	0	1.690336	5.146951	4.303017
27	1	0	3.153755	6.140780	4.129307
28	1	0	1.566368	6.824816	3.731205

TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.004828	0.011649	0.027405
2	6	0	1.361728	-0.019770	0.038488
3	6	0	2.105151	1.183180	-0.014345
4	6	0	1.401140	2.409616	-0.092329
5	6	0	-0.002648	2.413895	-0.106537
6	6	0	-0.698732	1.235156	-0.043624
7	1	0	4.084228	0.322459	0.049878
8	1	0	-0.564191	-0.913040	0.076211
9	1	0	1.891086	-0.961559	0.099419
10	6	0	3.506157	1.234230	-0.004177
11	6	0	2.170591	3.606473	-0.204242
12	1	0	-0.526331	3.359815	-0.168353
13	1	0	-1.779797	1.238604	-0.051226
14	6	0	4.149307	2.473240	0.052243
15	1	0	1.645421	4.547381	-0.349906
16	1	0	5.208033	2.519783	-0.178057
17	7	0	3.462056	3.656234	-0.173683
18	6	0	4.598721	2.661465	2.132463
19	8	0	4.121750	1.819902	2.830985
20	7	0	5.418578	3.662955	2.464600
21	6	0	5.935062	4.635070	1.522852
22	1	0	5.890528	5.625462	1.978300
23	1	0	6.977423	4.422026	1.271718
24	1	0	5.324531	4.652398	0.625332
25	6	0	5.888076	3.779084	3.837619
26	1	0	5.582871	4.738657	4.259068
27	1	0	5.461783	2.973989	4.427789
28	1	0	6.977759	3.714951	3.868586

Compound **B**

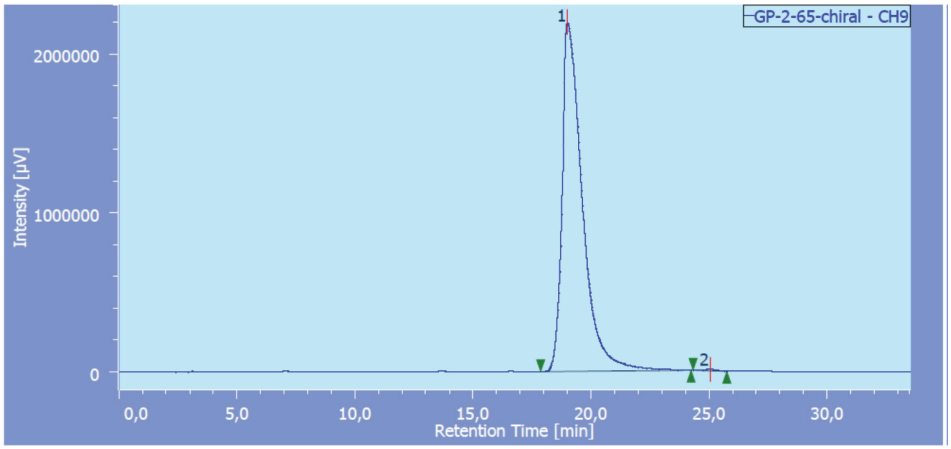
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.019558	0.028165	0.020690
2	6	0	1.389207	0.058374	0.154736
3	6	0	2.081122	1.279176	0.106779
4	6	0	1.361722	2.471342	-0.068839
5	6	0	-0.014054	2.423910	-0.211957
6	6	0	-0.686442	1.214237	-0.168404
7	1	0	4.088027	0.470963	0.344986
8	1	0	-0.508511	-0.914618	0.059502
9	1	0	1.947658	-0.858349	0.294196
10	6	0	3.496692	1.362560	0.190476
11	6	0	2.098687	3.782325	-0.073887
12	1	0	-0.569890	3.344092	-0.343110
13	1	0	-1.762180	1.191196	-0.275440
14	6	0	4.136472	2.600660	-0.010391
15	1	0	1.723892	4.386996	-0.905672
16	1	0	5.222119	2.623252	-0.046366
17	7	0	3.541213	3.738614	-0.190750
18	6	0	1.792967	4.567658	1.240552
19	8	0	1.390174	3.978497	2.221885
20	7	0	2.008546	5.906079	1.210045
21	6	0	2.507984	6.638916	0.064233
22	1	0	1.693571	7.057431	-0.534824
23	1	0	3.120259	7.466480	0.422758
24	1	0	3.142615	6.009292	-0.551240
25	6	0	1.692254	6.694909	2.382398
26	1	0	1.263070	6.046772	3.138900
27	1	0	2.593778	7.165962	2.780688
28	1	0	0.976335	7.479483	2.126548

Compound **C**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.057260	0.003451	-0.035566
2	6	0	1.429668	0.012055	-0.079188
3	6	0	2.141163	1.236269	-0.041211
4	6	0	1.393715	2.441642	0.042353
5	6	0	0.009202	2.408904	0.085041
6	6	0	-0.665777	1.199456	0.046748
7	1	0	4.127114	0.422491	-0.100536
8	1	0	-0.473457	-0.938761	-0.062514
9	1	0	1.984289	-0.915206	-0.136925
10	6	0	3.526047	1.320084	-0.072764
11	6	0	2.133370	3.691642	0.071185
12	1	0	-0.542199	3.339017	0.150043
13	1	0	-1.745735	1.177509	0.081464
14	6	0	4.231087	2.630624	-0.016831
15	1	0	1.550210	4.610689	0.119950
16	1	0	4.863410	2.729551	-0.910521
17	7	0	3.397104	3.821505	0.031418
18	6	0	5.196566	2.650108	1.203107
19	8	0	5.087856	1.800099	2.065769
20	7	0	6.137287	3.625822	1.238644
21	6	0	6.348787	4.616327	0.203435
22	1	0	6.639353	5.556560	0.673402
23	1	0	7.151910	4.317204	-0.477238
24	1	0	5.434610	4.799331	-0.350369
25	6	0	7.090675	3.641456	2.328308
26	1	0	7.044294	4.596047	2.856556
27	1	0	6.855116	2.835978	3.015423
28	1	0	8.106194	3.506521	1.947171

8. HPLC Data for (*S*)-Dimethyl 2-(4-phenanthridine-6-carboxamido) succinate (9c)

Chromatogram



Chromatogram Information

User Name	Administrator
Date Modified	05/10/2018 15:53:15
Description	
HPLC System Name	Orga
Injection Date	05/10/2018 15:19:40
Volume	20,00 [μL]
Sample Number	32
Project Name	Test
Acquisition Time	59,0 [min]
Acquisition Sequence	GP-2-65-Chiral-85-Hx-15-EtOH 1mL-min 20° C IA
Control Method	85A-Hx 15D-EtOH 60Min-1ml-min 20° C
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

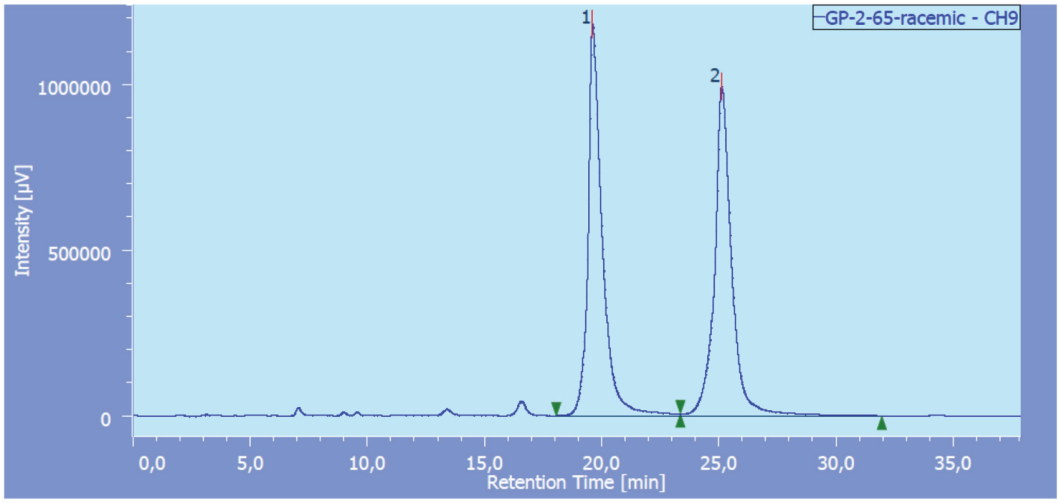
Chromatogram Name	GP-2-65-chiral-CH9
Sample Name	
Channel Name	252,5nm
Sampling Interval	100 [msec]
Peak Method	IT (Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	18,993	131633855	2193708	99,762	99,599	N/A	2838	5,103	1,928	
2	Unknown	9	25,023	313987	8828	0,238	0,401	N/A	11256	N/A	0,945	

Supporting Information

HPLC Data for Dimethyl 2-(4-phenanthridine-6-carboxamido) succinate (rac-9c)

Chromatogram



Chromatogram Information	
User Name	Administrator
Date Modified	05/10/2018 12:21:01
Description	
HPLC System Name	Orga
Injection Date	05/10/2018 11:43:07
Volume	20,00 [µL]
Sample Number	31
Project Name	Test
Acquisition Time	59,0 [min]
Acquisition Sequence	GP-2-65-Racemic-85-Hx-15-EtOH 1mL-min 20° C IA
Control Method	85A-Hx 15D-EtOH 60Min-1ml-min 20° C
Peak ID Table	
Calibration Method	
Additional Information	

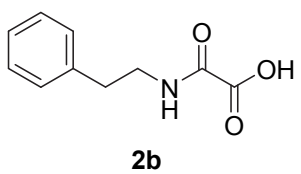
Channel & Peak Information Table

Chromatogram Name	GP-2-65-racemic-CH9
Sample Name	
Channel Name	252,5nm
Sampling Interval	100 [msec]
Peak Method	IT (Manual)
Formula	
Decision	

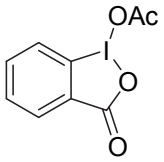
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	19,608	49926380	1179801	49,688	54,319	N/A	7055	5,384	1,455	
2	Unknown	9	25,113	50554084	992200	50,312	45,681	N/A	8094	N/A	1,093	

9. Fluorescence quenching experiments

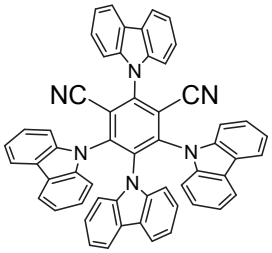
Fluorescence decay profiles were collected on aerated samples in dichloromethane solution at 530 nm using the single photon counting technique on a Horiba Jobin-Yvon Fluorolog 211 instrument using a 370-nm pulsed LED excitation source operated at 250 kHz and a cooled Hammamatsu 928P single photon counting photomultiplier. The data was deconvoluted from the IRF using a multi-exponential function and the goodness-of-fit judged by the χ^2 parameter, randomness of the residuals, and Durbin-Watson (D-W) test statistic. 4-CzIPN exhibited a bi-exponential decay in which the short component is assigned to the decay of the singlet excited state. The longer component is instead attributed to delayed fluorescence. The decay rates are only slightly shortened in the presence of oxamic acid **2b** or BIOAc (100 mM concentration) (**Figures 1-2**), indicating that they do not quench the catalyst in its excited singlet or triplet state. Instead, a 1:1 mixture of **2b** and BIOAc quenches more efficiently both the excited singlet and triplet state of 4-CzIPN (**Figures 1-4**). The rate constants can be calculated according to $k_{obs} = \tau^{-1} - \tau_0^{-1}$, where τ_0 and τ are the decay parameters in the absence and presence of quencher, respectively (Table 1).



2b



BIOAc



4CzIPN

Table 1. Decay parameters and calculated quenching rates for 4-CzIPN in aerated DCM solutions.

Quencher[a]	τ_1 (ns)	τ_2 (ns)	χ^2	$k_{obs}(S_1)$ (s^{-1})	$k_{obs}(T_1)$ (s^{-1})
None	20.4	742	1.19		
2b	19.7	634	1.05	1.8×10^6	2.3×10^5
BIOAc	19.3	647	1.22	2.9×10^6	2.0×10^5
2b + BIOAc	16.9	101	1.21	1.02×10^7	8.6×10^6

[a] 100m M concentration

Figure 1. Fluorescence decay of 4-CzIPN in the presence of oxamic acid **2b**.

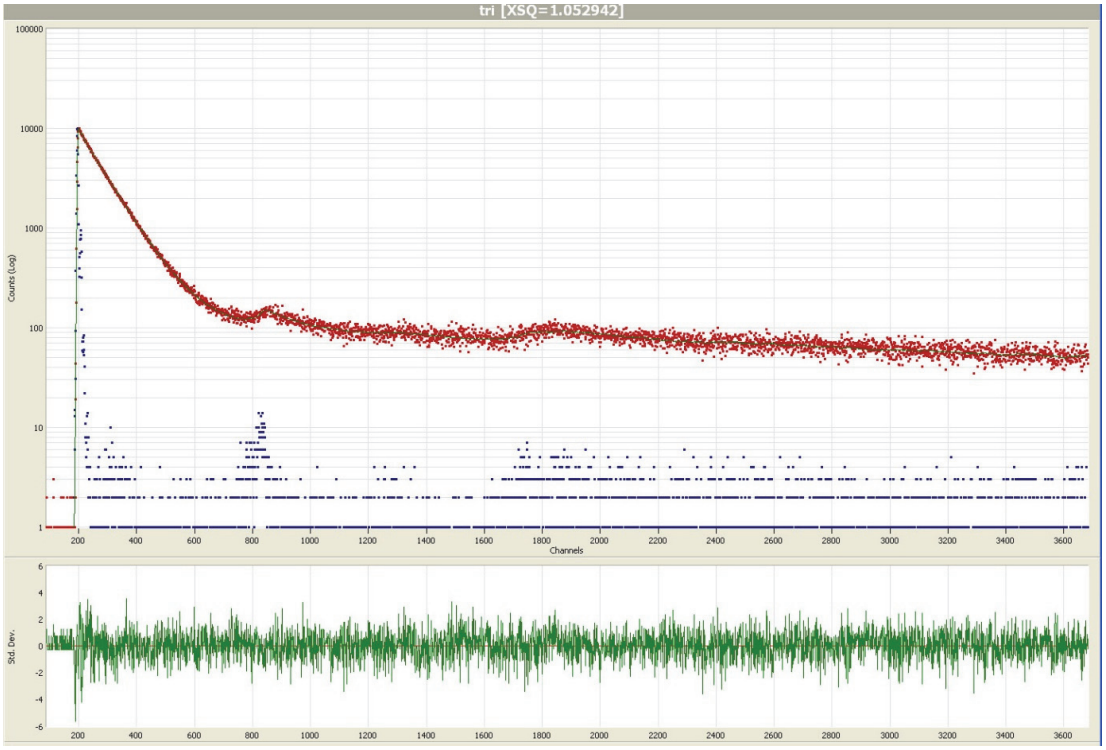


Figure 2. Fluorescence decay of 4-CzIPN in the presence of BIOAc.

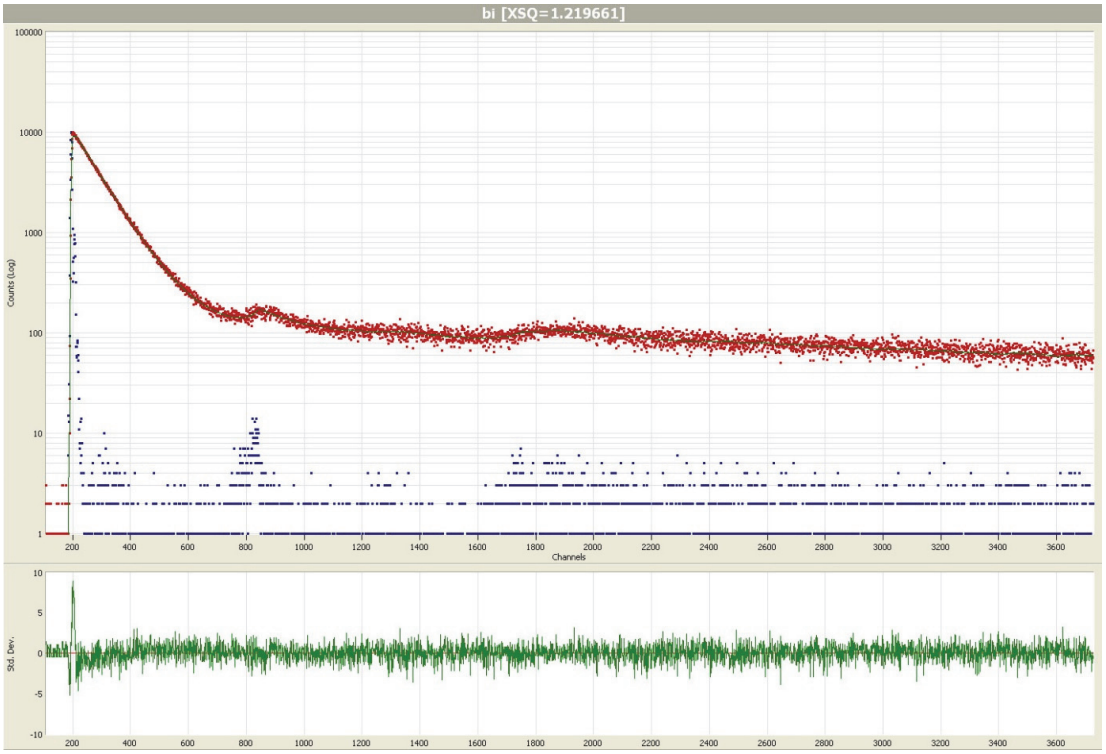


Figure 3. Fluorescence decay of 4-CzIPN in the presence of oxamic acid **2b** and BIOAc.

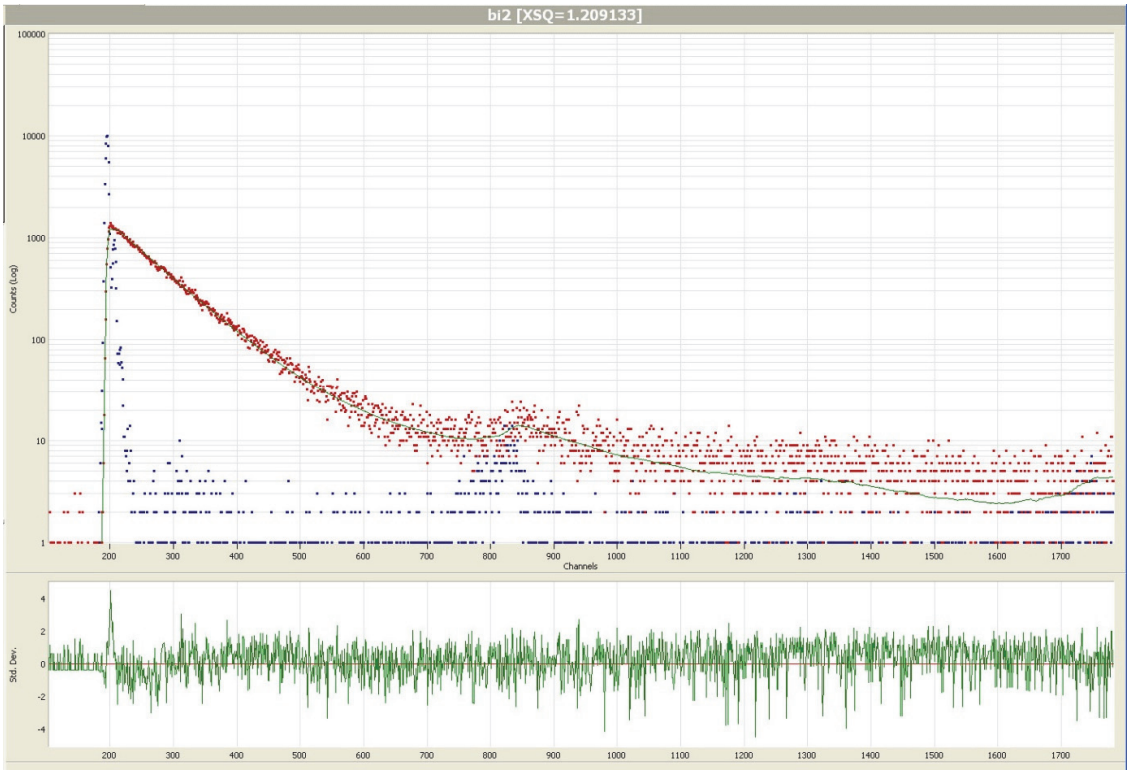
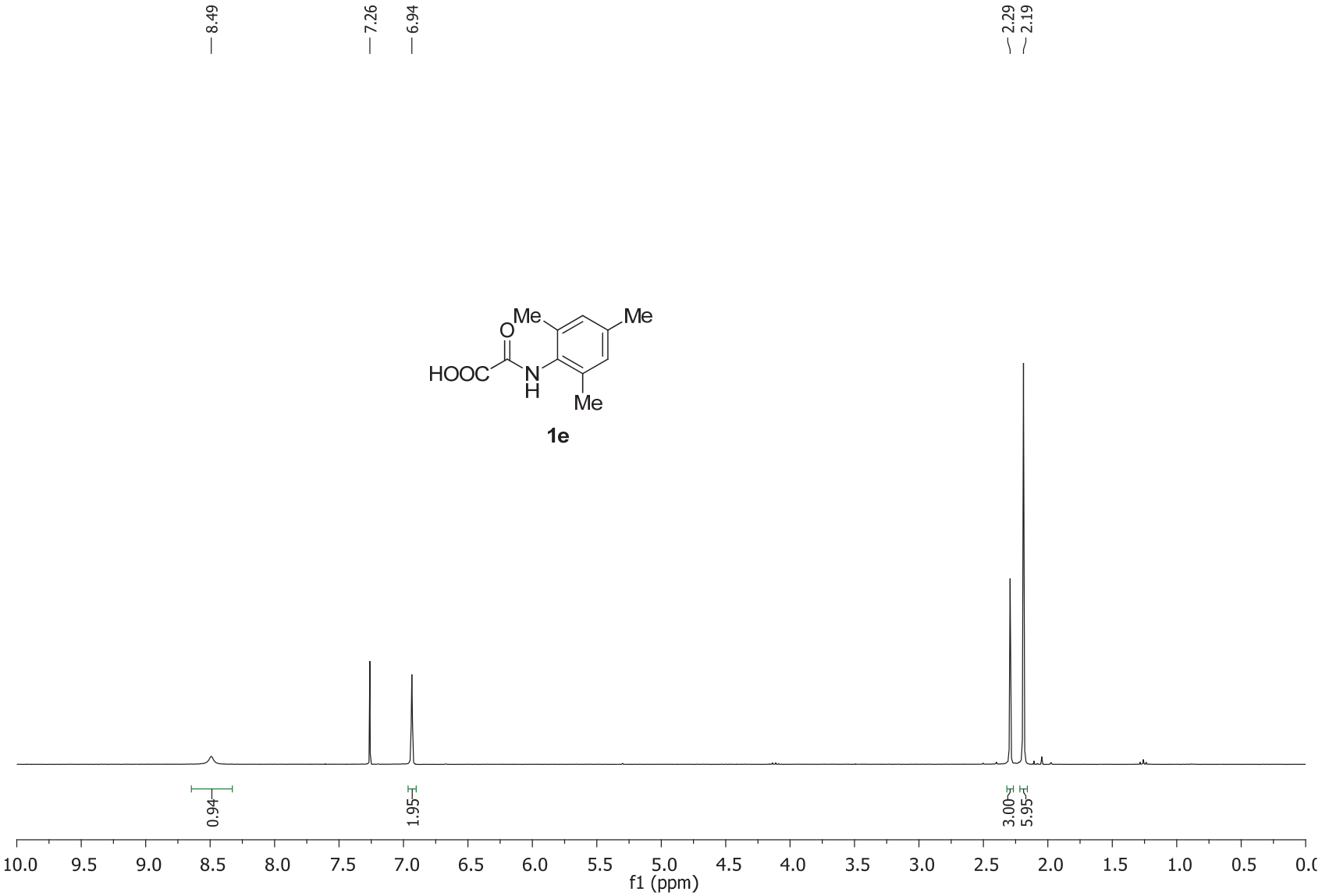
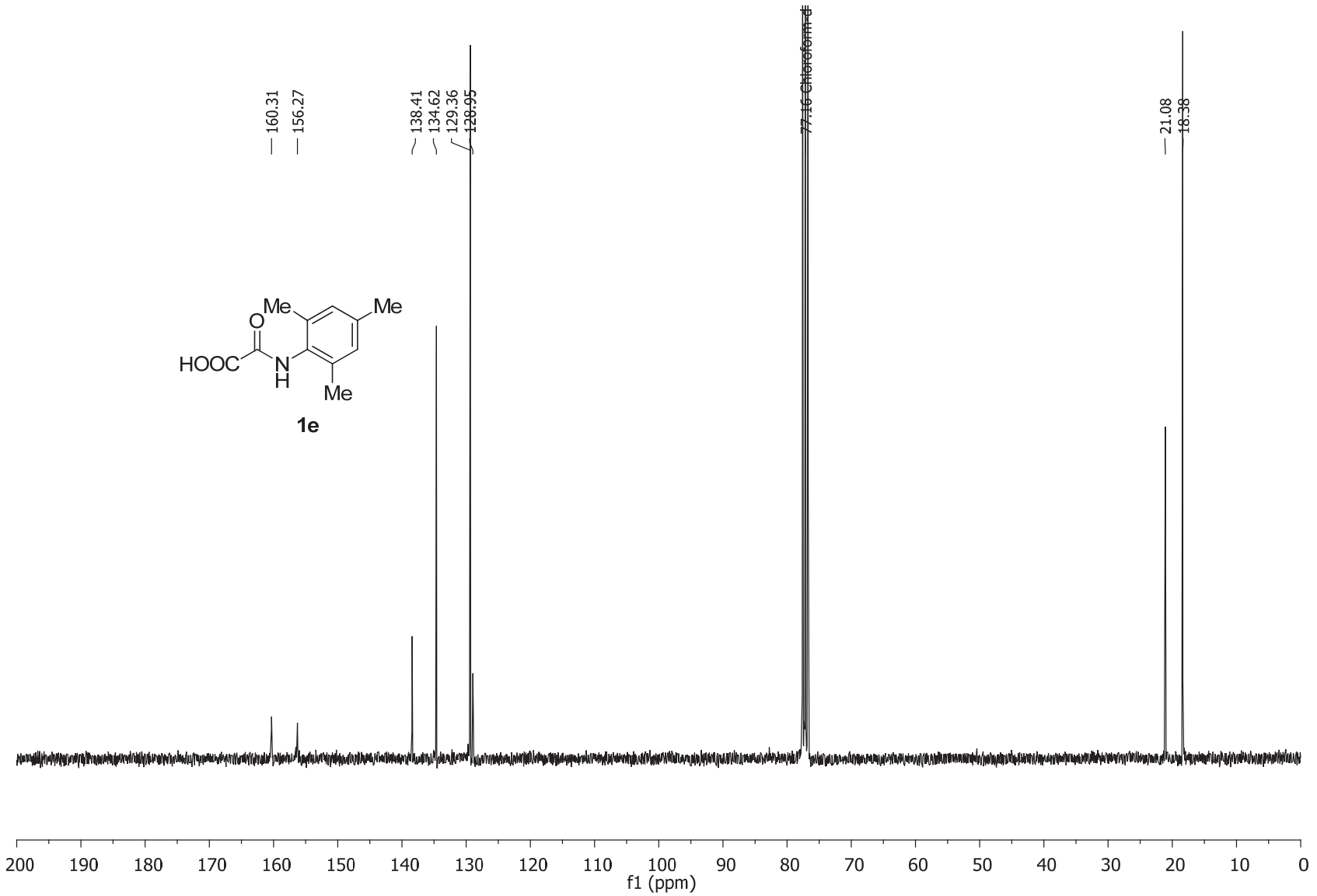
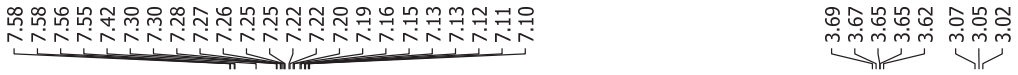


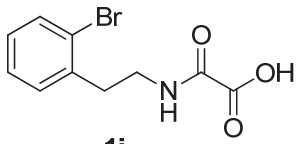
Figure 4. Fluorescence decay of 4-CzIPN.


8.49
7.26
6.94
2.29
2.19
Me
Me
O
HOOC
N
H
Me
0.94
1.95
3.00
5.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

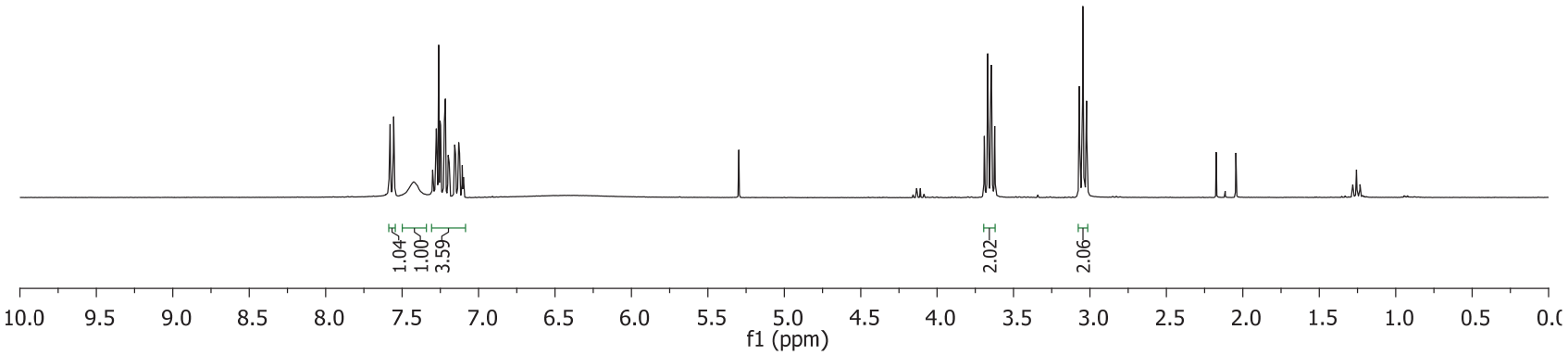
1e

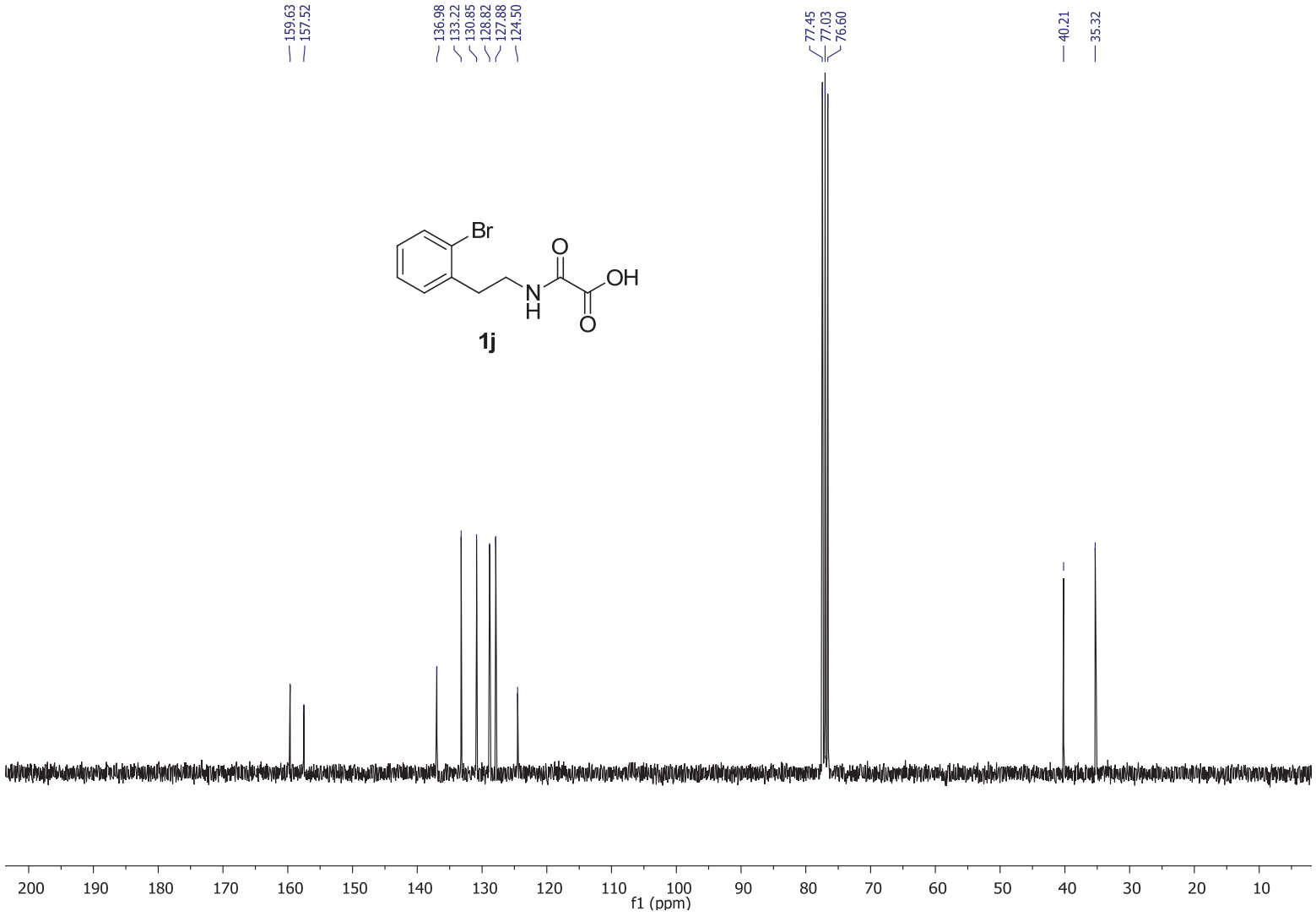

160.31
156.27
138.41
134.62
129.36
128.95
77.16 Chloroform-d
21.08
18.38
Me
Me
O
HOOC
N
H
Me
1e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

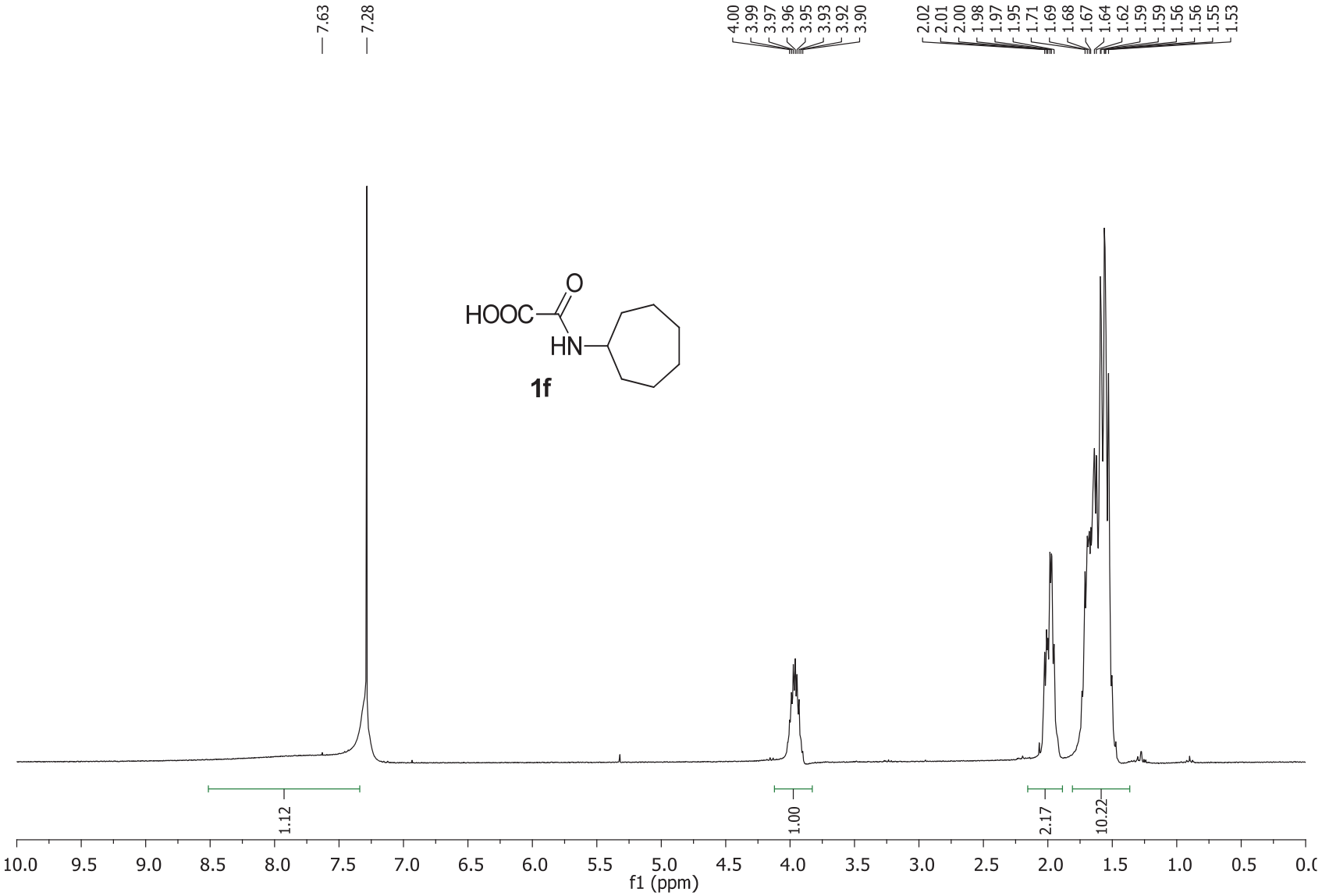

7.58
7.58
7.56
7.55
7.42
7.30
7.30
7.28
7.27
7.26
7.25
7.25
7.22
7.22
7.20
7.19
7.16
7.15
7.13
7.13
7.12
7.11
7.10
3.69
3.67
3.65
3.65
3.62
3.07
3.05
3.02

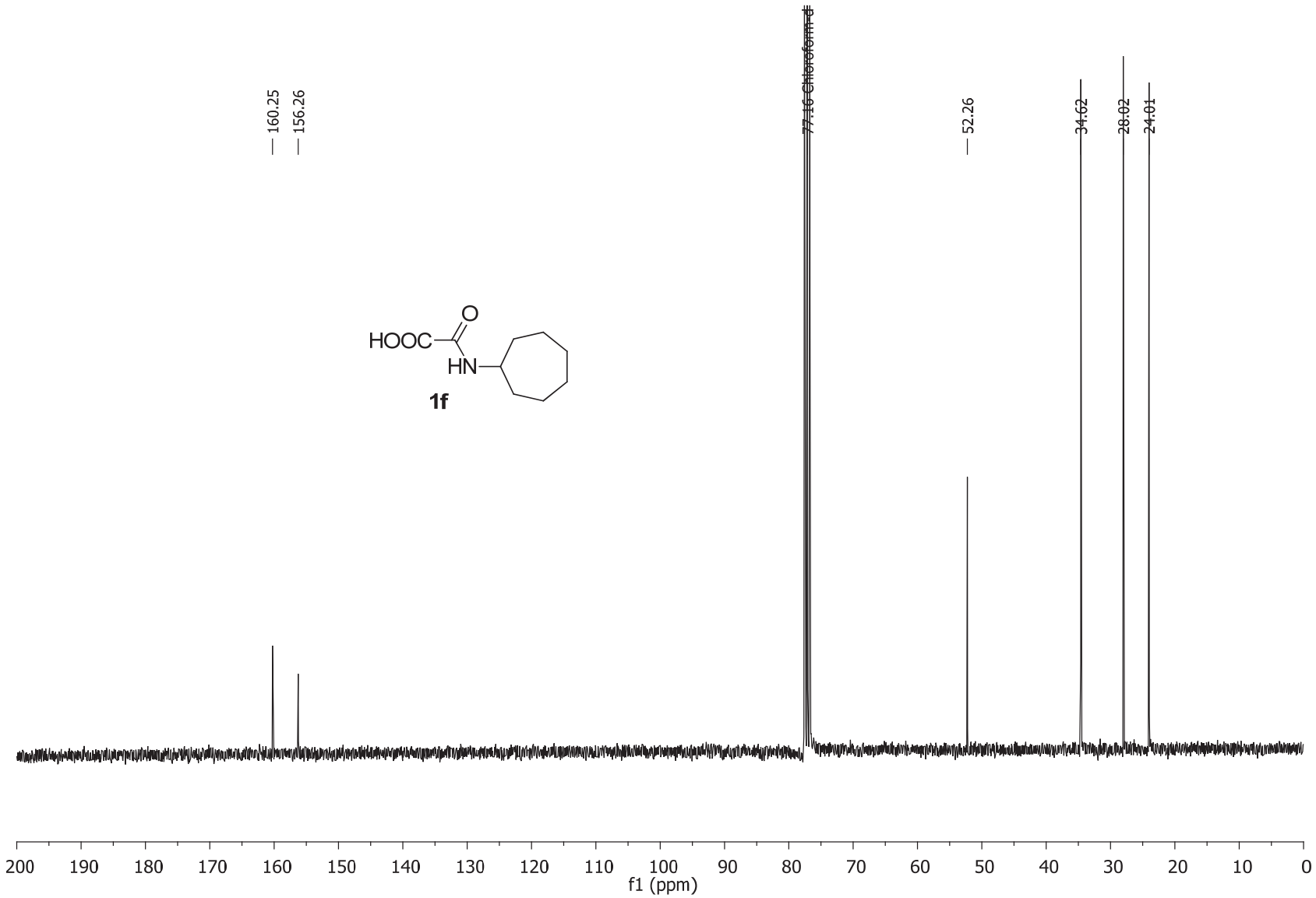

Br
O
OH
N
H
O

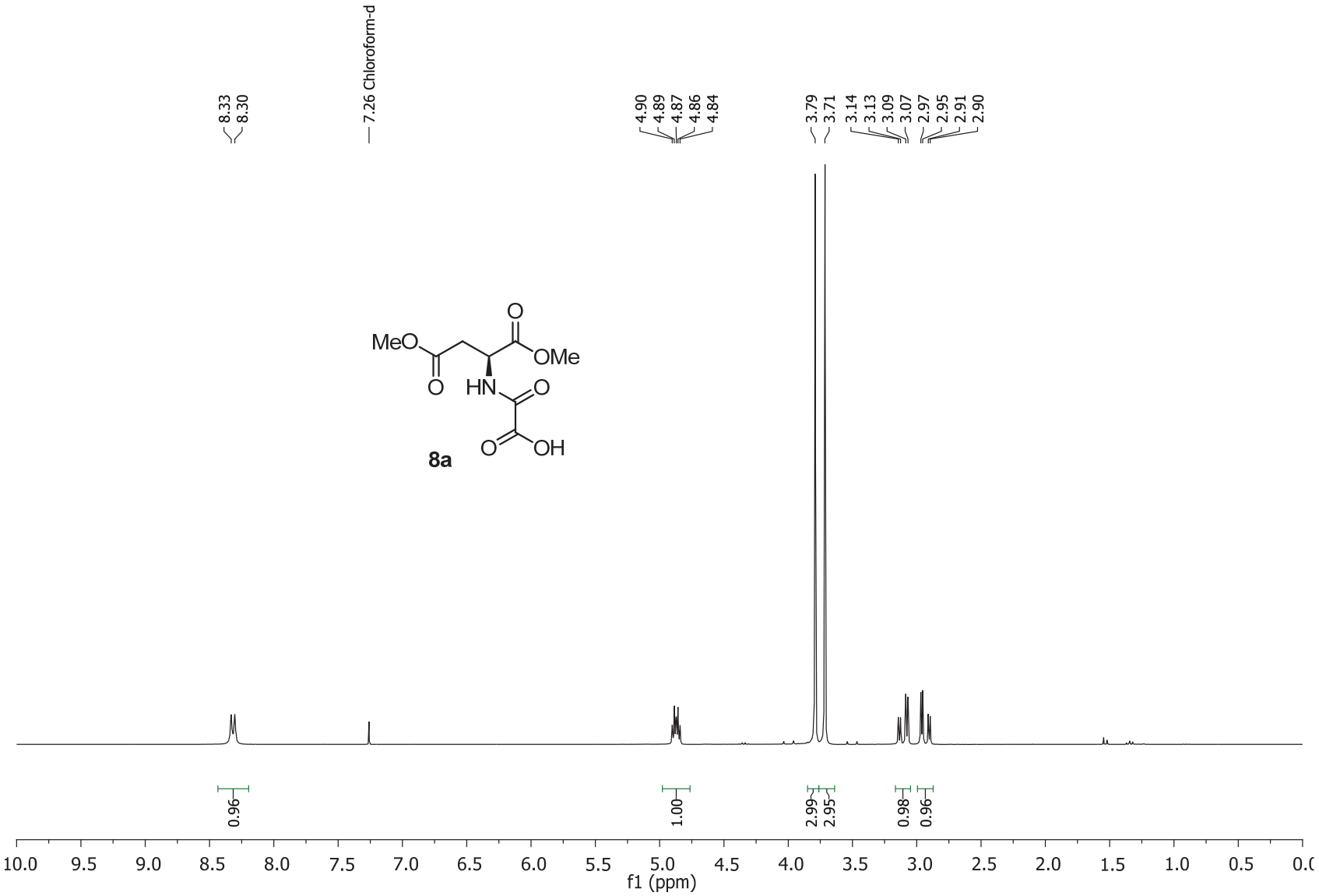
1j

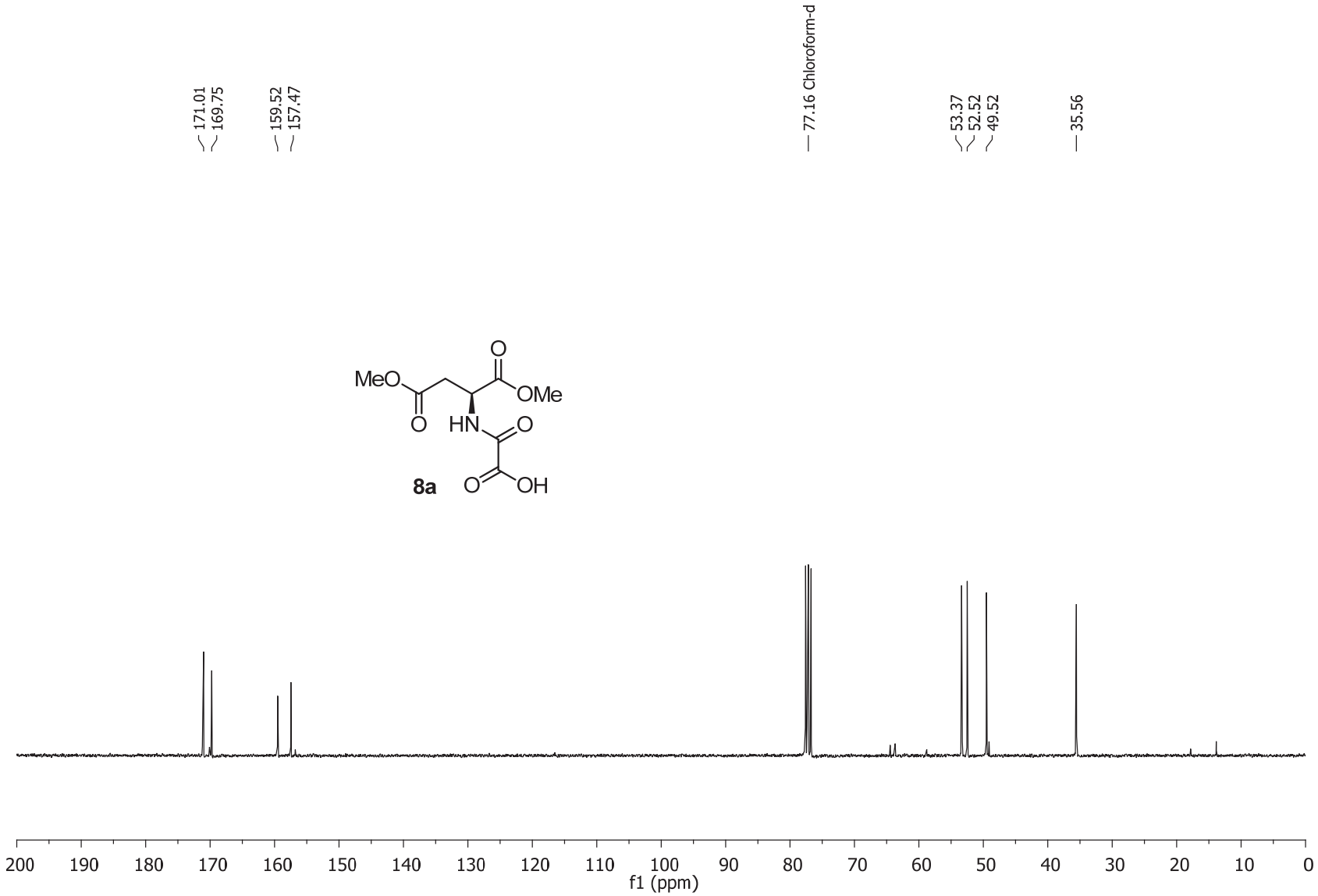

1.04
1.00
3.59
2.02
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

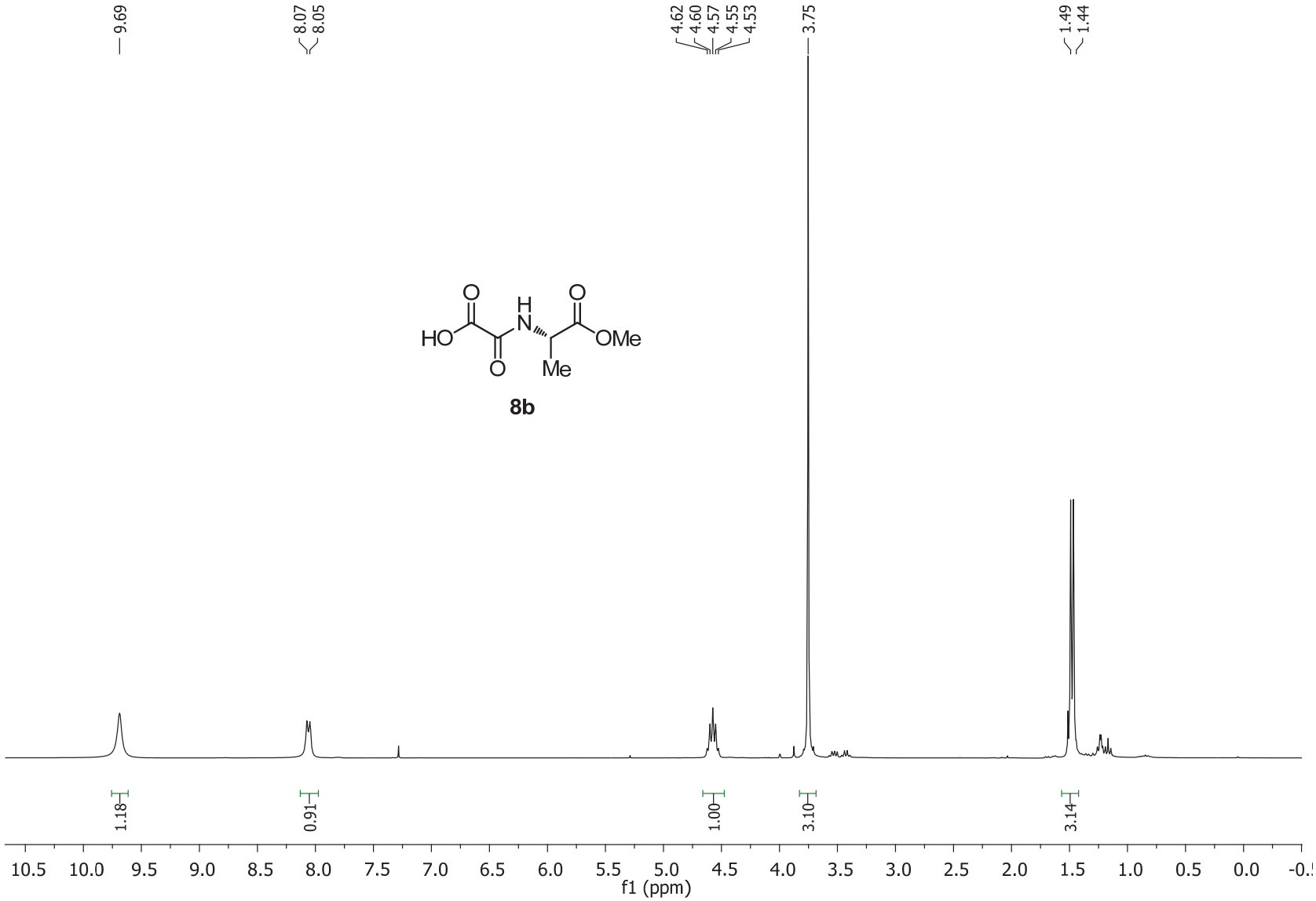

159.63
157.52
136.98
133.22
130.85
128.82
127.88
124.50
77.45
77.03
76.60
40.21
35.32
Br
O
OH
N
H
O
1j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.63
7.28
4.00
3.99
3.97
3.96
3.95
3.93
3.92
3.90
2.02
2.01
2.00
1.98
1.97
1.95
1.71
1.69
1.68
1.67
1.64
1.62
1.59
1.59
1.56
1.56
1.55
1.53
HOOC
O
HN
1f
1.12
1.00
2.17
10.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

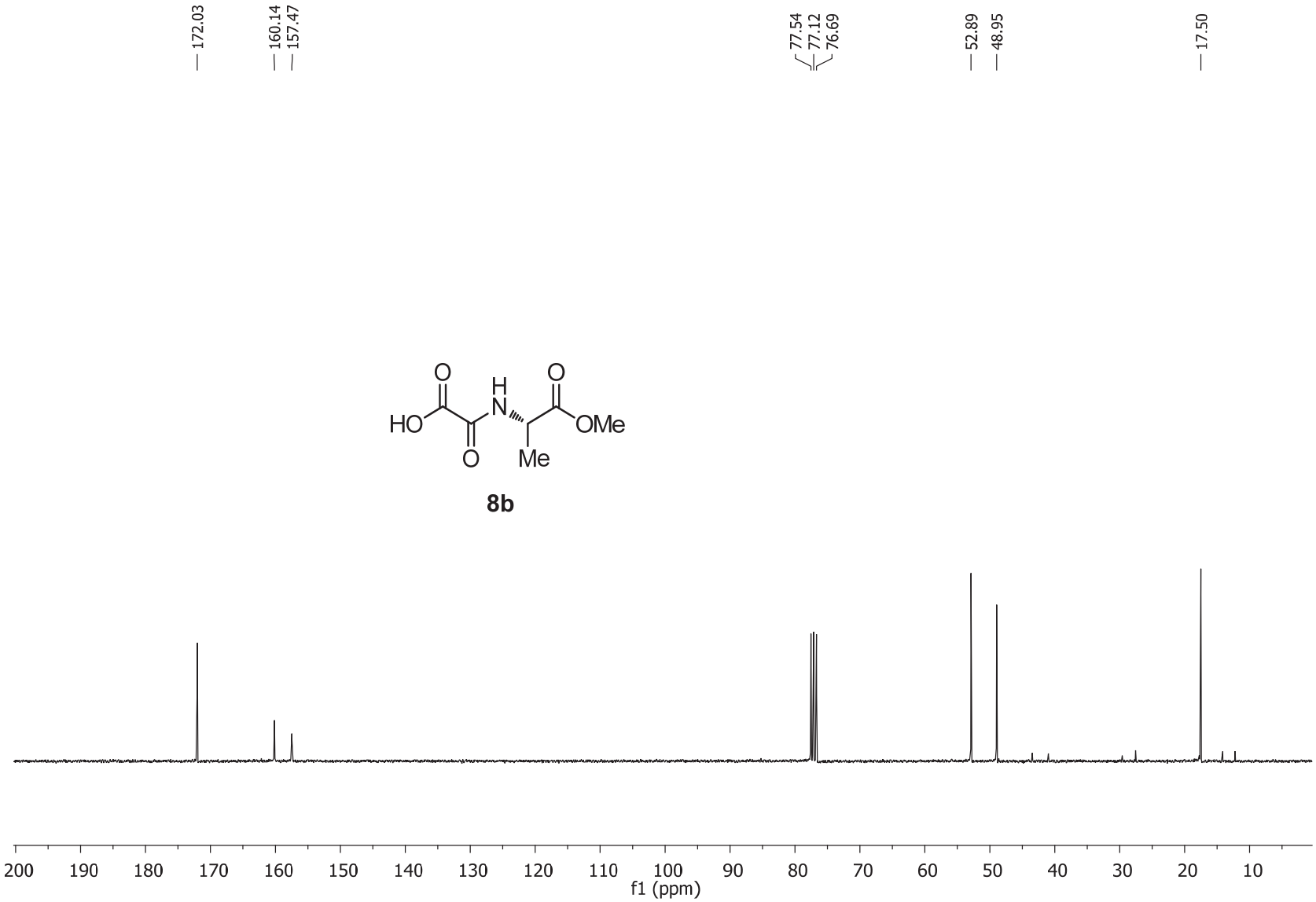

160.25
156.26
77.16 Chloroform-d
52.26
34.62
28.02
24.01
HOOC
O
HN
1f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.33
8.30
7.26 Chloroform-d
4.90
4.89
4.87
4.86
4.84
3.79
3.71
3.14
3.13
3.09
3.07
2.97
2.95
2.91
2.90
MeO
O
OMe
O
HN
O
O
OH
8a
0.96
1.00
2.99
2.95
0.98
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

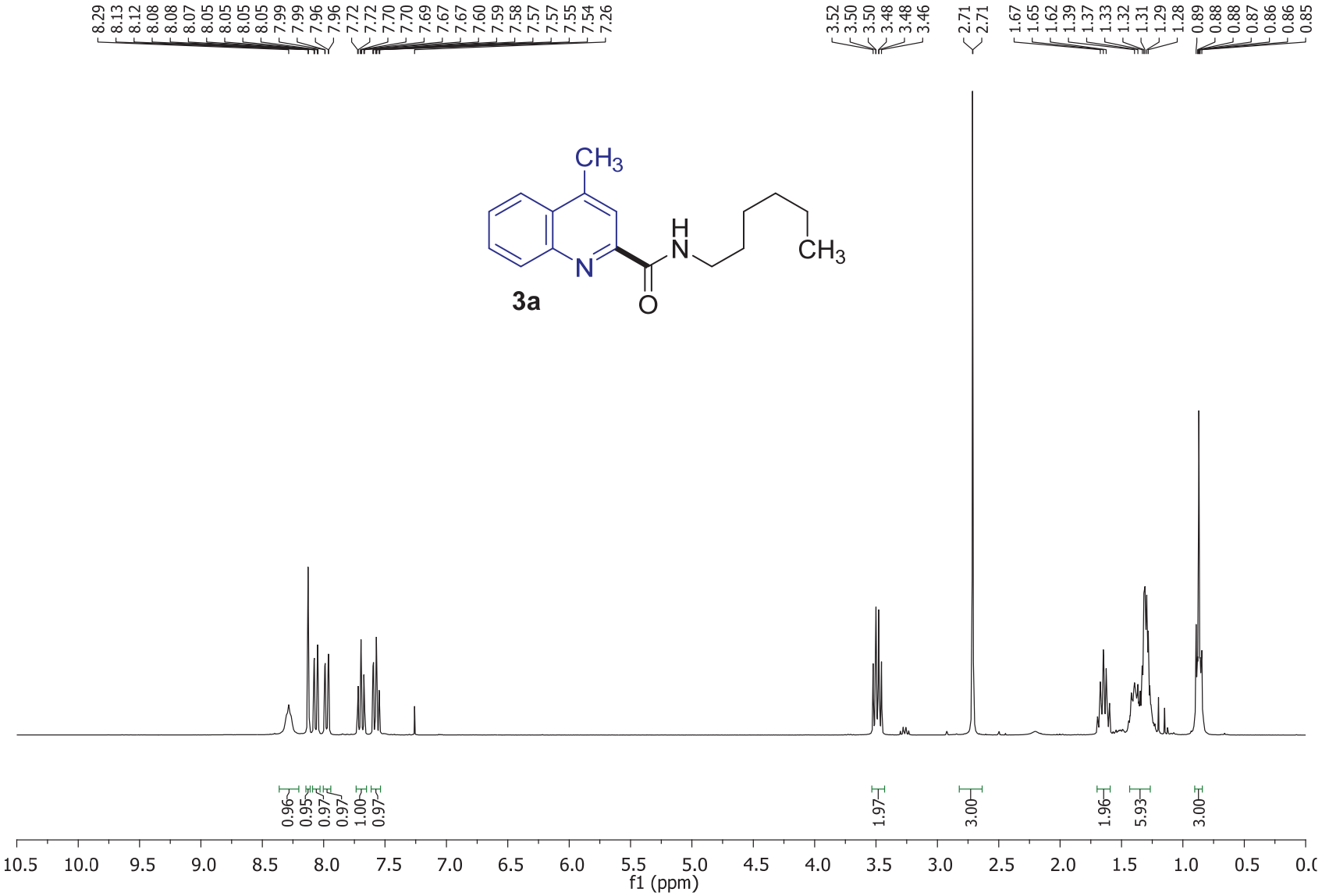

171.01
169.75
159.52
157.47
77.16 Chloroform-d
53.37
52.52
49.52
35.56
MeO
O
OMe
O
HN
O
O
OH
8a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

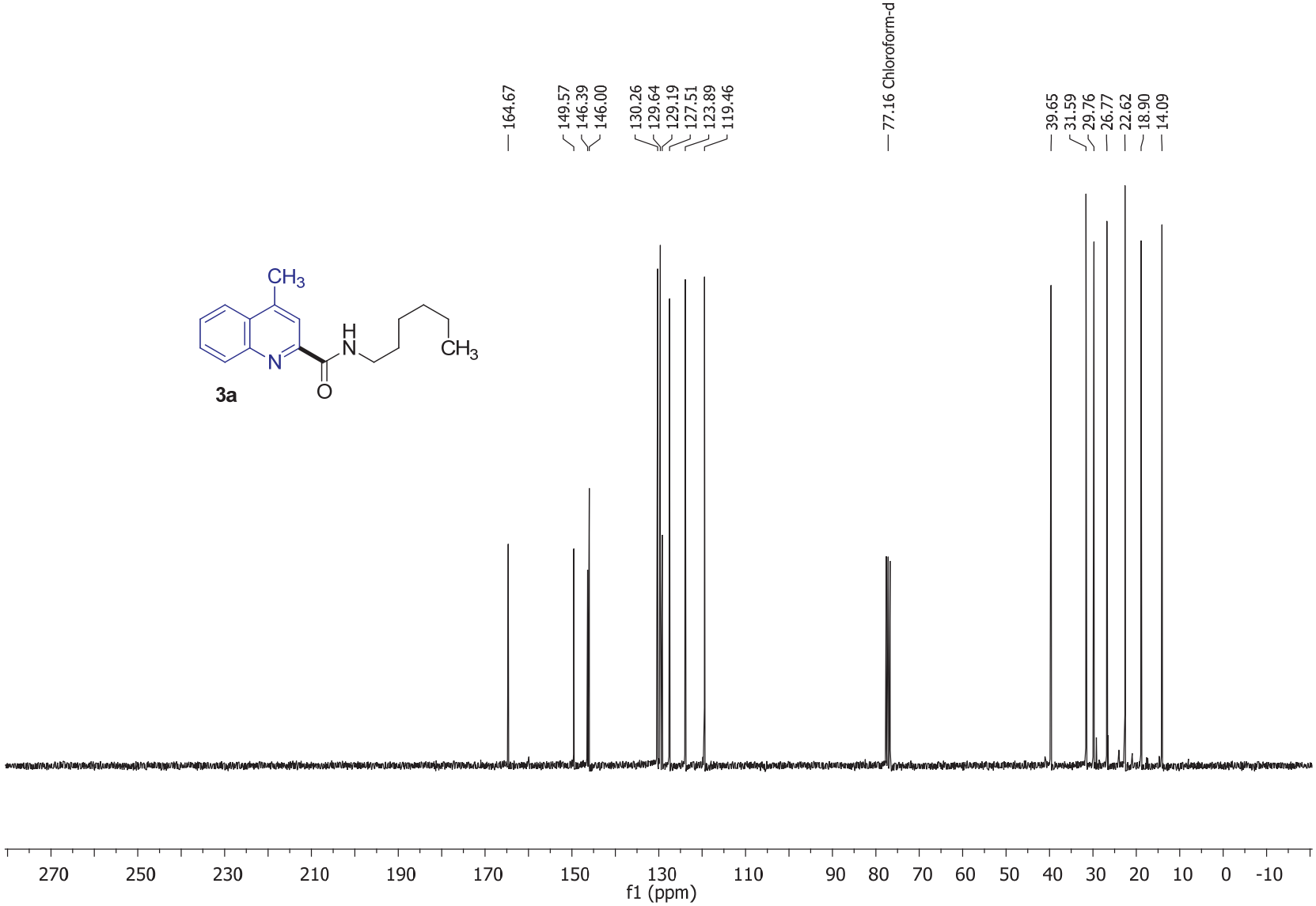

9.69
8.07
8.05
4.62
4.60
4.57
4.55
4.53
3.75
1.49
1.44
HO
O
O
H
N
O
OMe
Me
1.18
0.91
1.00
3.10
3.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

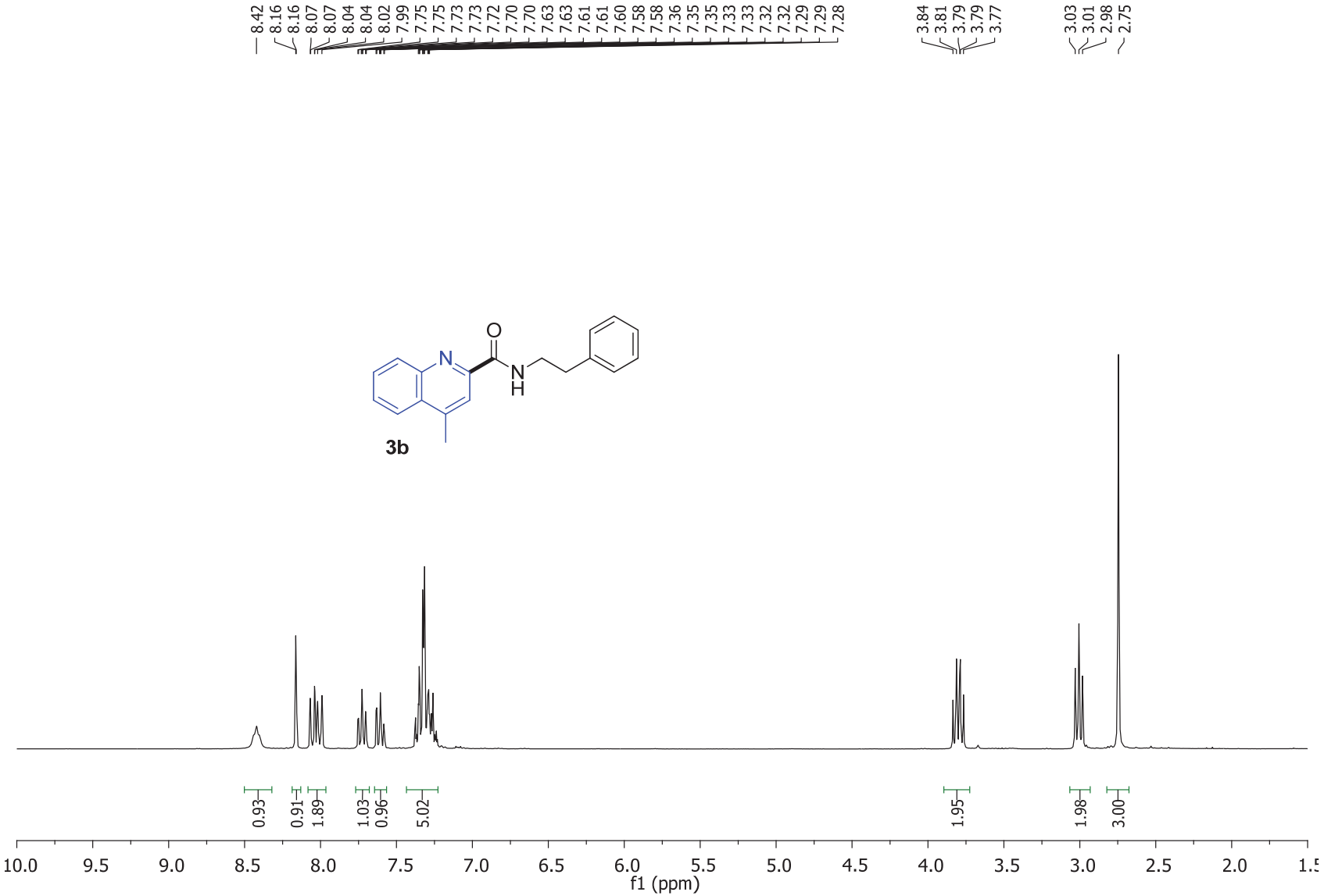
8b

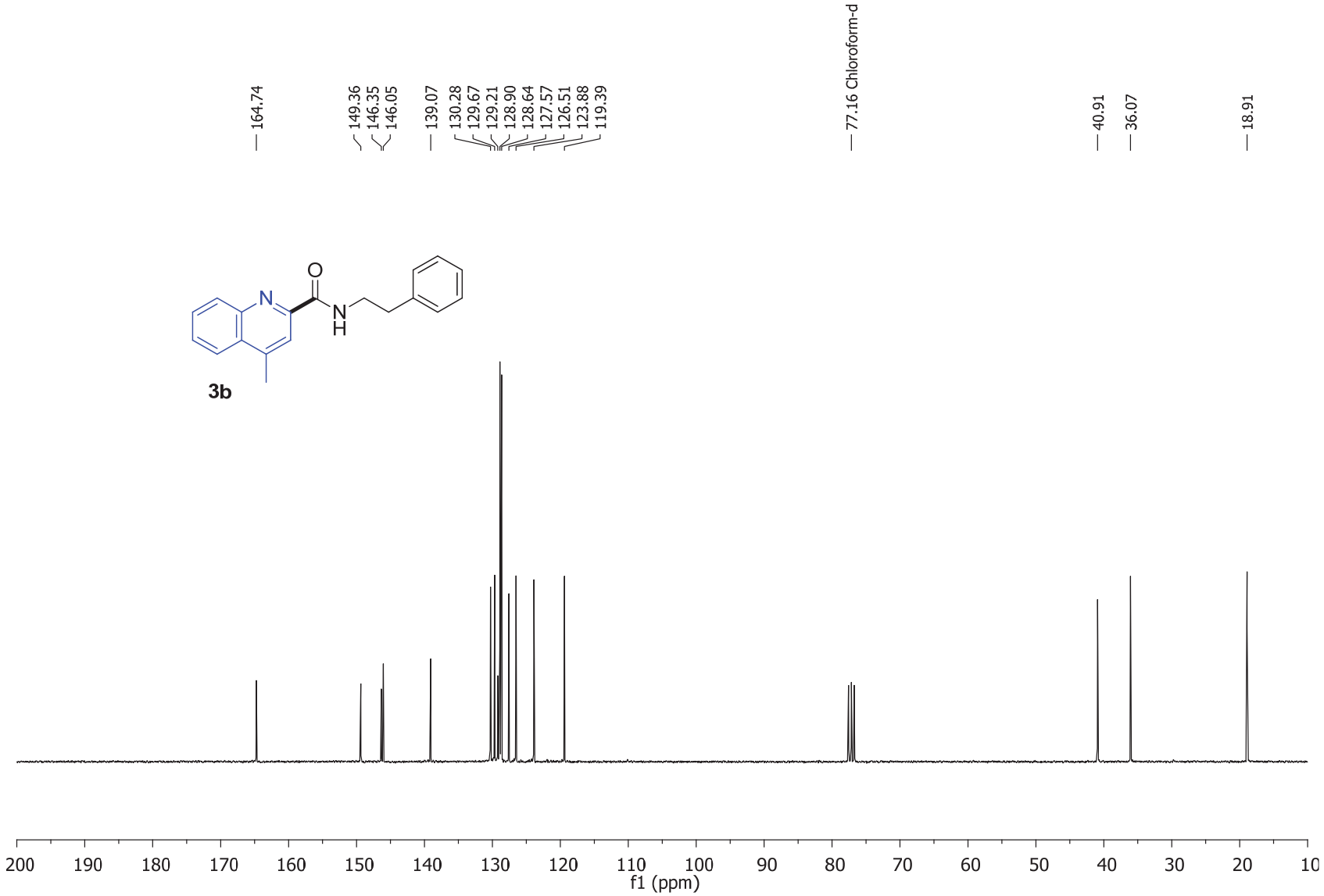

172.03
160.14
157.47
77.54
77.12
76.69
52.89
48.95
17.50
HO
O
O
H
N
O
OMe
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

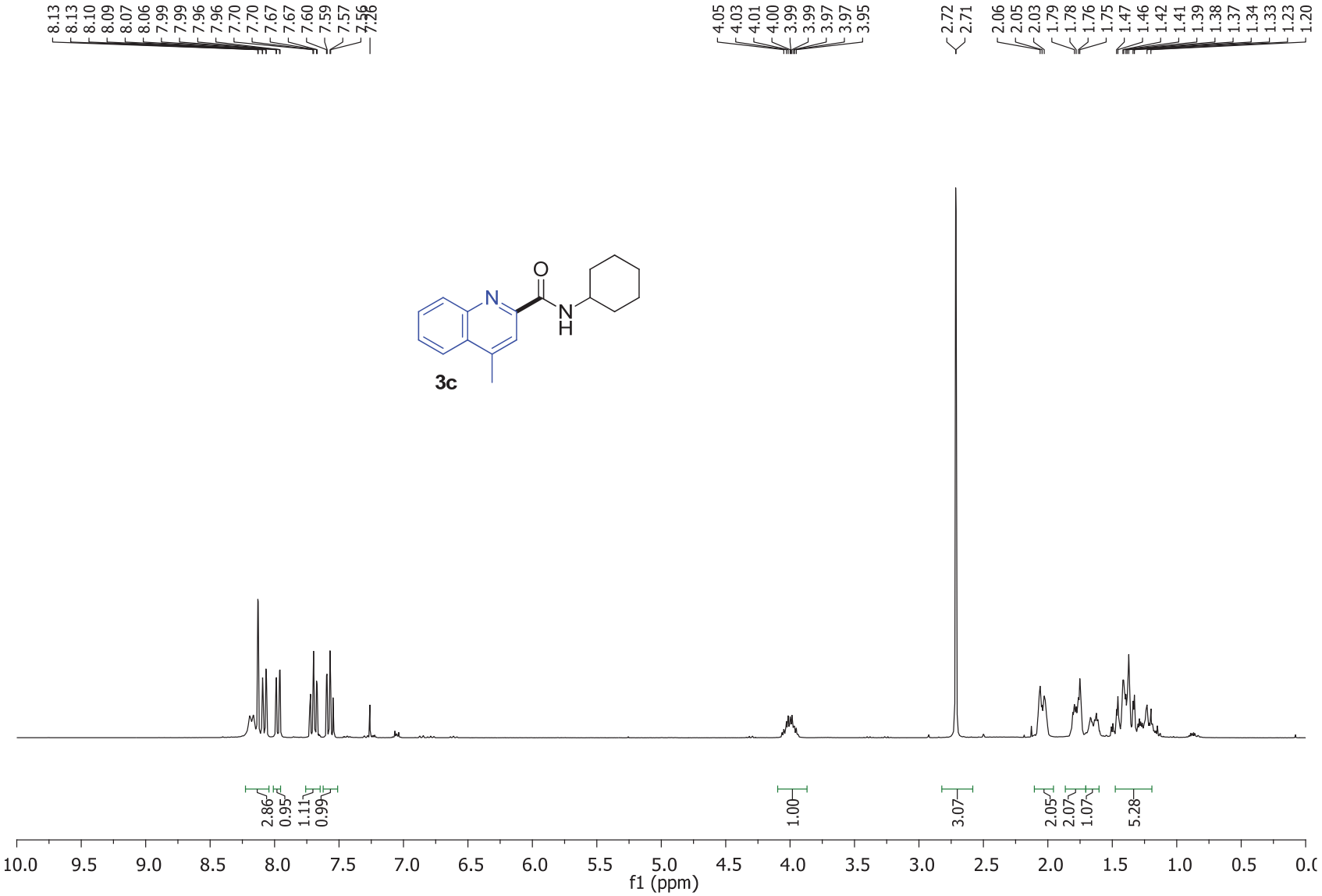
8b

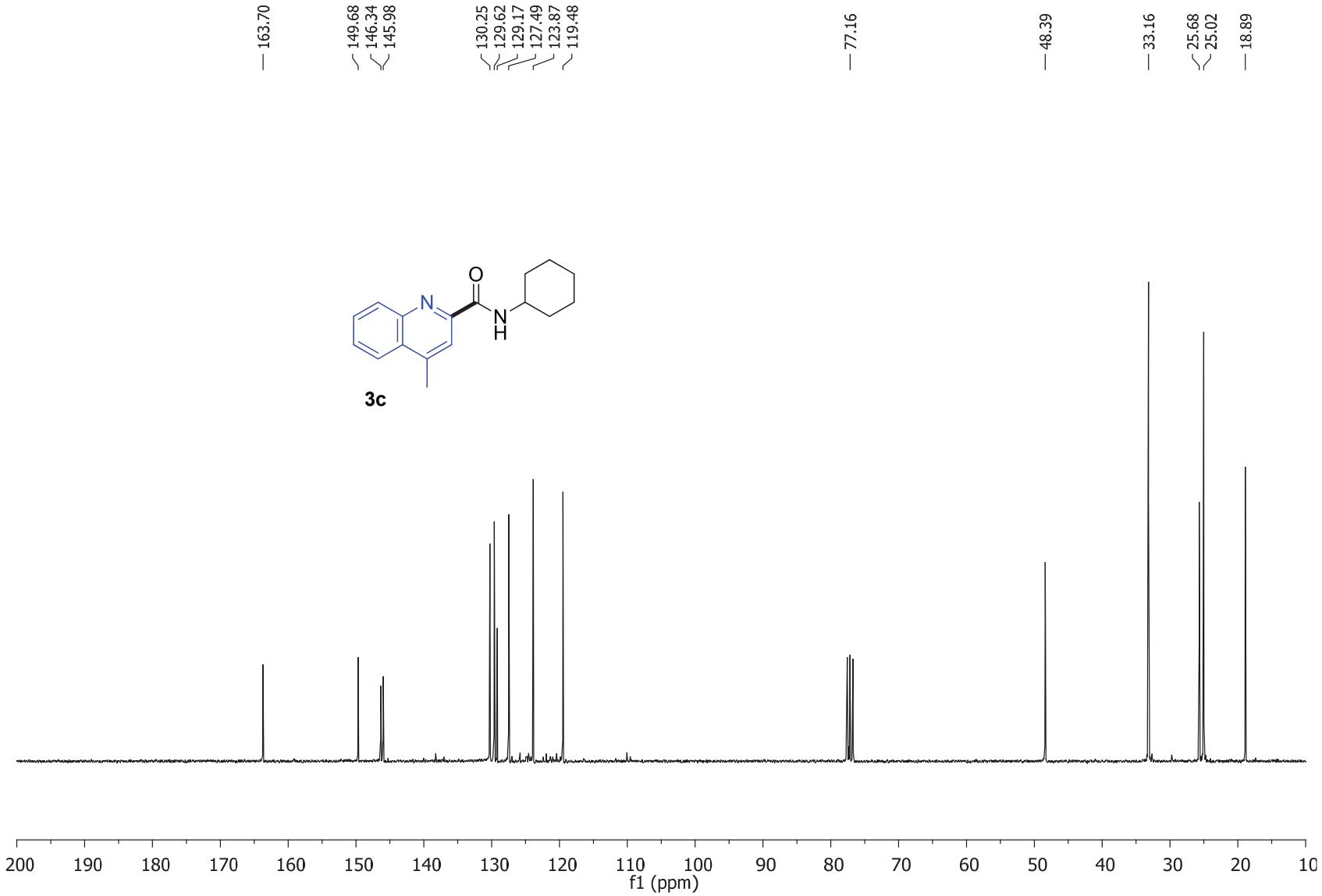

8.29
8.13
8.12
8.08
8.08
8.07
8.05
8.05
8.05
8.05
7.99
7.99
7.96
7.96
7.72
7.72
7.70
7.70
7.69
7.67
7.67
7.60
7.59
7.58
7.57
7.57
7.55
7.54
7.26
3.52
3.50
3.50
3.48
3.48
3.46
2.71
2.71
1.67
1.65
1.62
1.39
1.37
1.33
1.32
1.31
1.29
1.28
0.89
0.88
0.88
0.87
0.86
0.86
0.85
CH3
H
N
N
CH3
O
3a
0.96
0.95
0.97
0.97
1.00
0.97
1.97
3.00
1.96
5.93
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

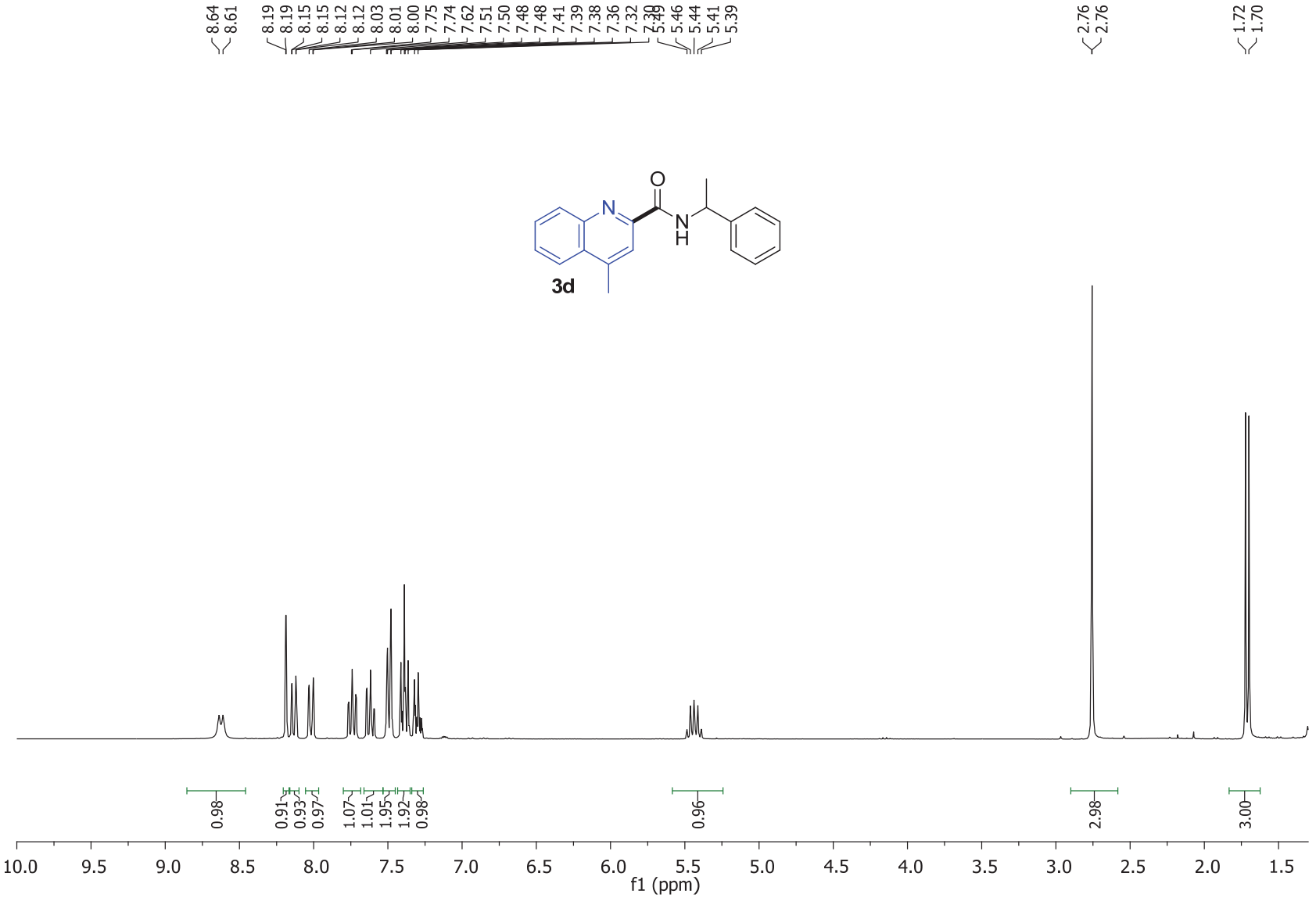

164.67
149.57
146.39
146.00
130.26
129.64
129.19
127.51
123.89
119.46
77.16 Chloroform-d
39.65
31.59
29.76
26.77
22.62
18.90
14.09
CH3
N
H
N
CH3
O
3a
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.42
8.16
8.16
8.07
8.07
8.04
8.04
8.02
7.99
7.75
7.75
7.73
7.73
7.72
7.70
7.70
7.63
7.63
7.61
7.61
7.60
7.58
7.58
7.36
7.35
7.35
7.33
7.33
7.32
7.32
7.29
7.29
7.28
3.84
3.81
3.79
3.79
3.77
3.03
3.01
2.98
2.75
O
N
N
H
3b
0.93
0.91
1.89
1.03
0.96
5.02
1.95
1.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


164.74
149.36
146.35
146.05
139.07
130.28
129.67
129.21
128.90
128.64
127.57
126.51
123.88
119.39
77.16 Chloroform-d
40.91
36.07
18.91
O
N
N
H
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.13
8.13
8.10
8.09
8.07
8.06
7.99
7.99
7.96
7.96
7.70
7.70
7.67
7.67
7.60
7.59
7.57
7.56
7.26
4.05
4.03
4.01
4.00
3.99
3.99
3.97
3.97
3.95
2.72
2.71
2.06
2.05
2.03
1.79
1.78
1.76
1.75
1.47
1.46
1.42
1.41
1.39
1.38
1.37
1.34
1.33
1.23
1.20
O
N
N
H
3c
2.86
0.95
1.11
0.99
1.00
3.07
2.05
2.07
1.07
5.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


163.70
149.68
146.34
145.98
130.25
129.62
129.17
127.49
123.87
119.48
77.16
48.39
33.16
25.68
25.02
18.89
O
N
N
H
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.64
8.61
8.19
8.19
8.15
8.15
8.12
8.12
8.03
8.01
8.00
7.75
7.74
7.62
7.51
7.50
7.48
7.48
7.41
7.39
7.38
7.36
7.32
5.46
5.44
5.41
5.39
2.76
2.76
1.72
1.70
O
N
N
H
3d
0.98
0.91
0.93
0.97
1.07
1.01
1.95
1.92
0.98
0.96
2.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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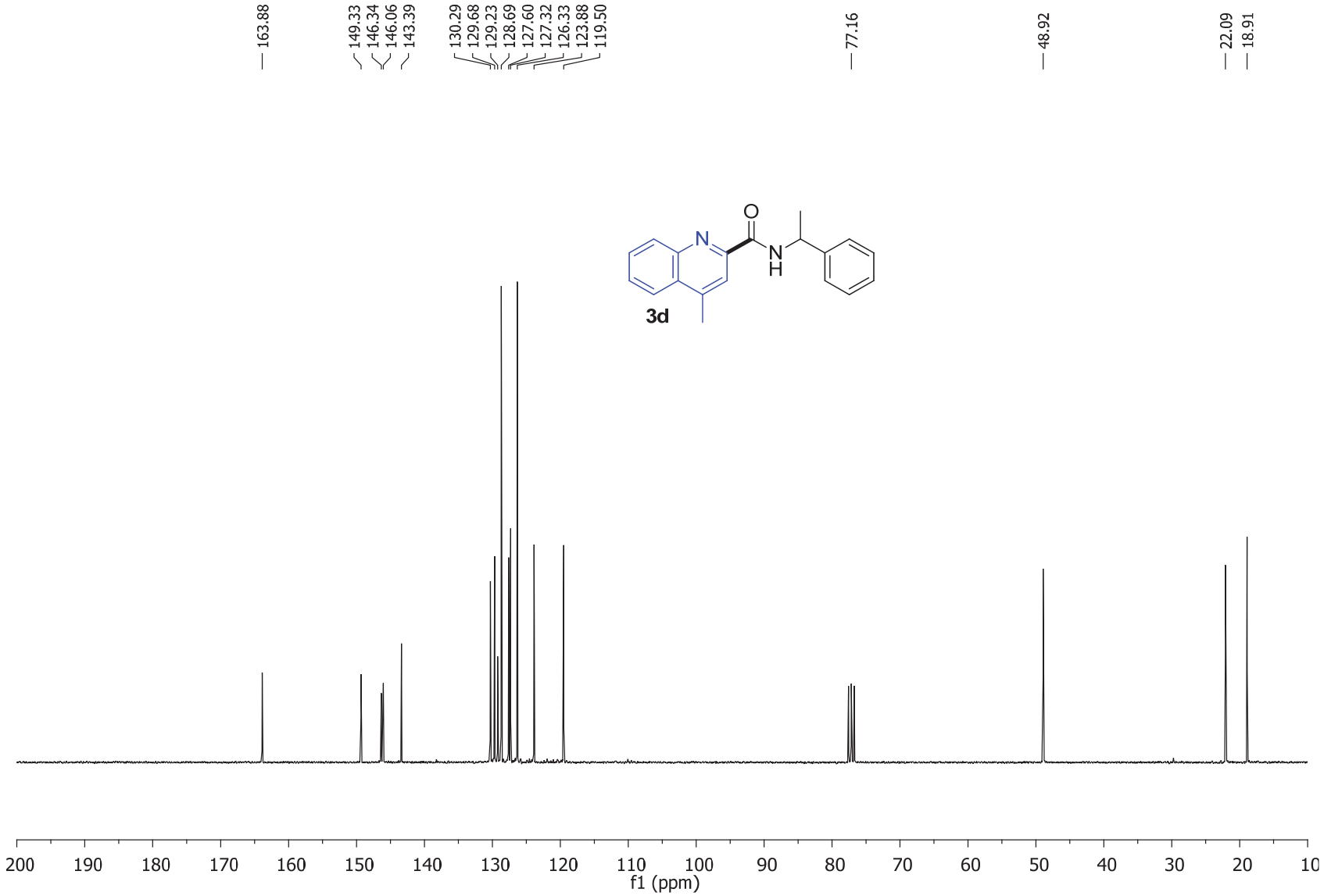
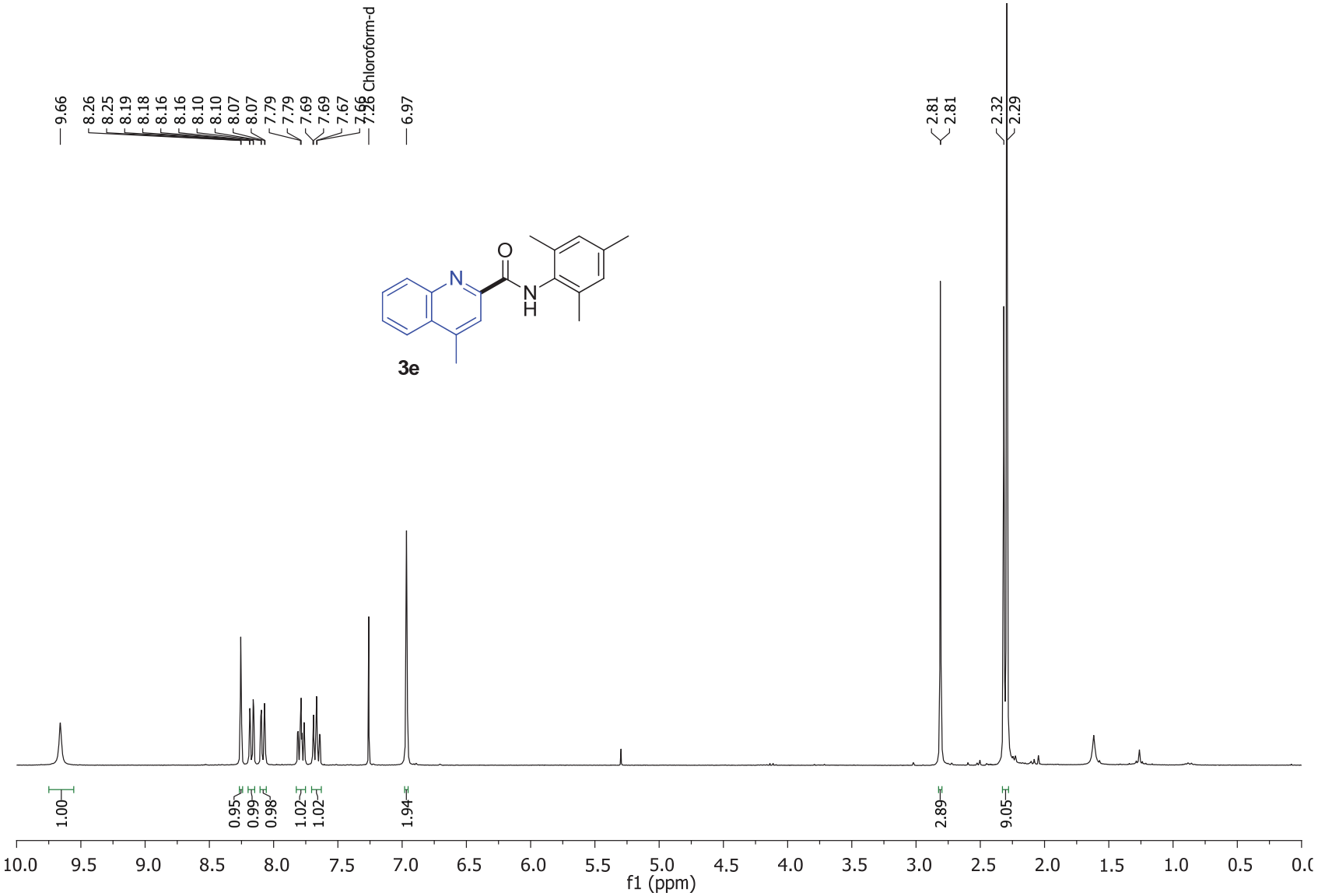
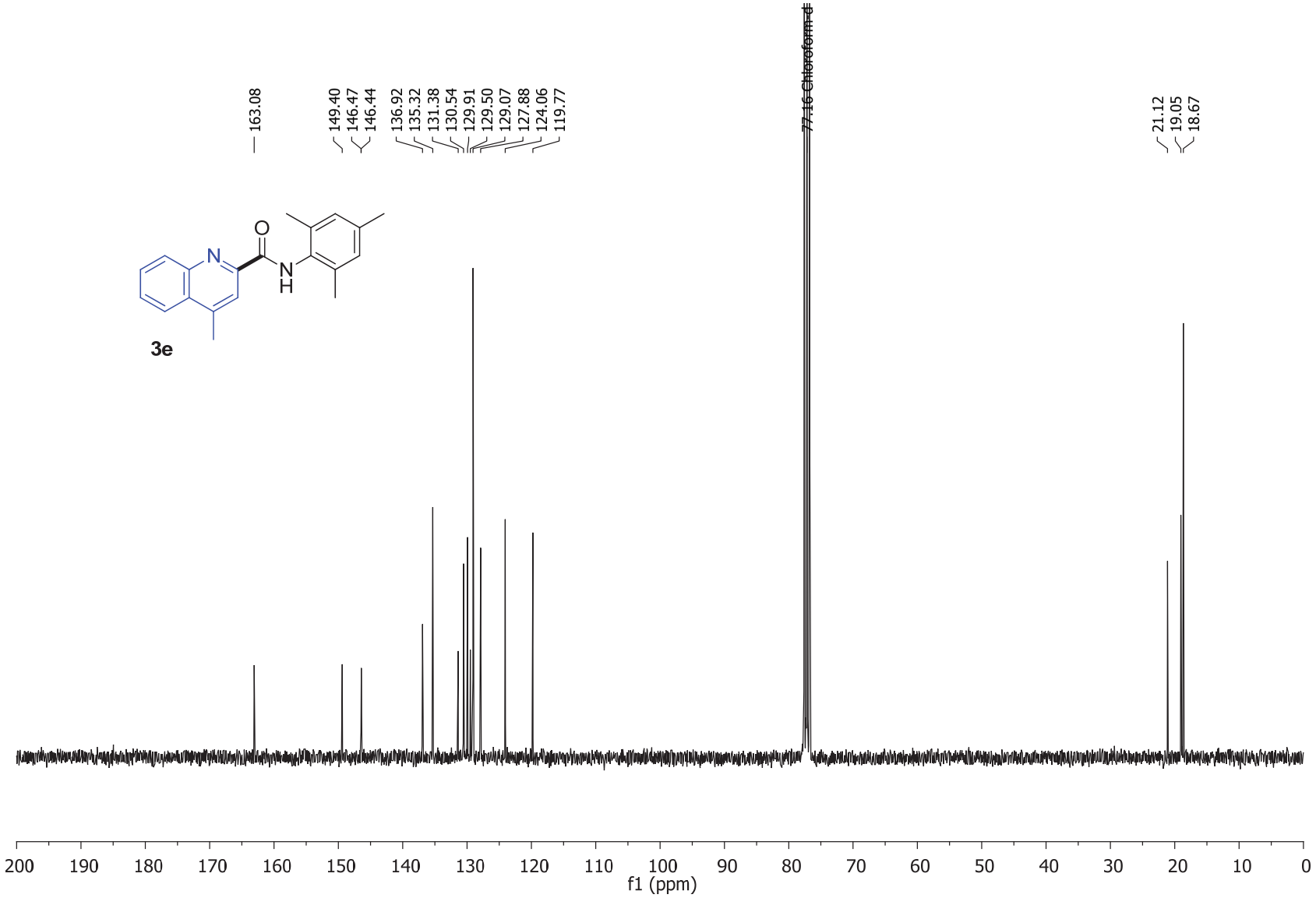
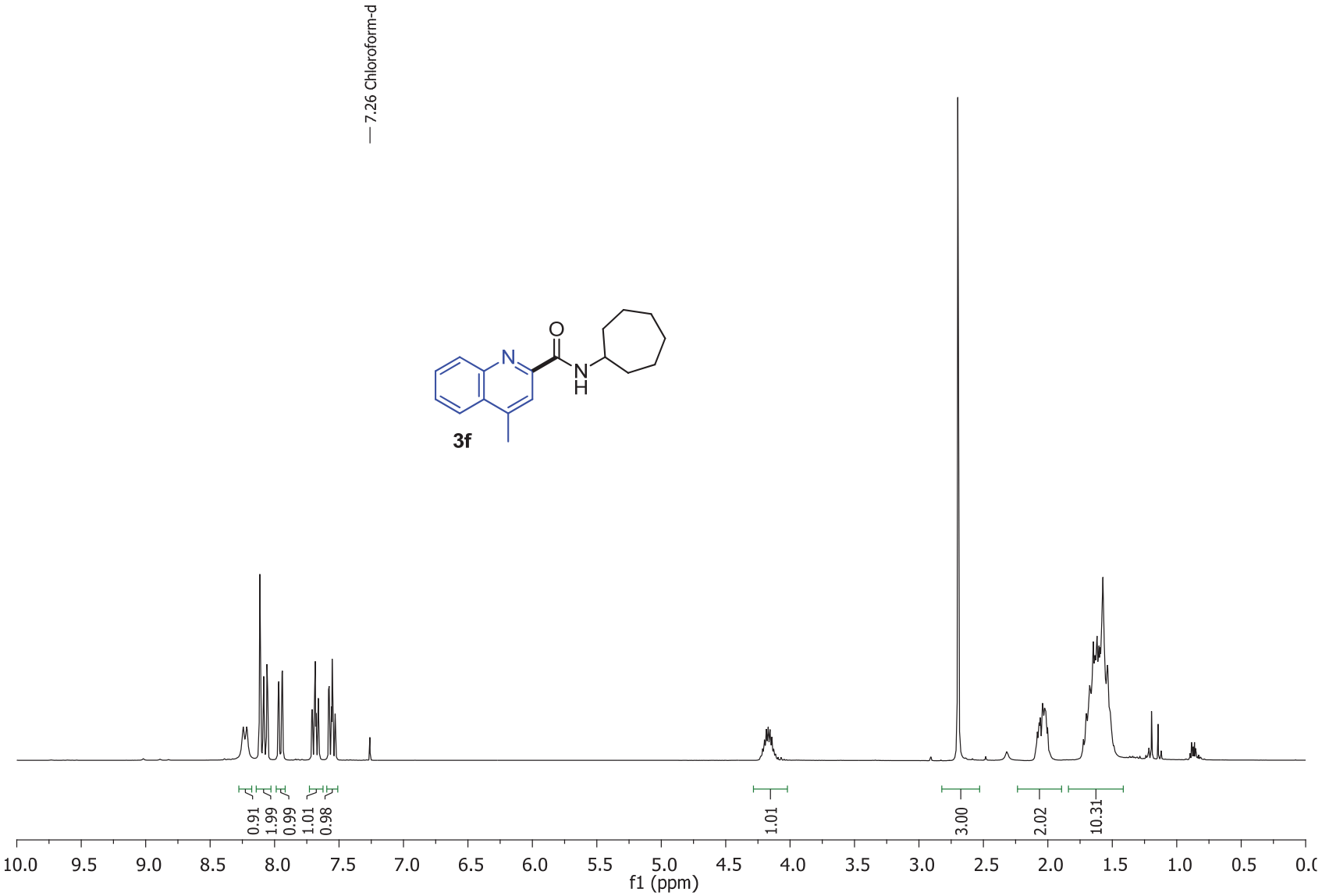
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


163.88
149.33
146.34
146.06
143.39
130.29
129.68
129.23
128.69
127.60
127.32
126.33
123.88
119.50
77.16
48.92
22.09
18.91
O
N
N
H
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9.66
8.26
8.25
8.19
8.18
8.16
8.16
8.10
8.10
8.07
8.07
7.79
7.79
7.69
7.69
7.67
7.66
7.26 Chloroform-d
6.97
2.81
2.81
2.32
2.29
O
N
N
H
3e
1.00
0.95
0.99
0.98
1.02
1.02
1.94
2.89
9.05
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)


163.08
149.40
146.47
146.44
136.92
135.32
131.38
130.54
129.91
129.50
129.07
127.88
124.06
119.77
77.16 Chloroform-d
21.12
19.05
18.67
O
N
N
H
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


— 7.26 Chloroform-d
O
N
N
H
3f
0.91
1.99
0.99
1.01
0.98
1.01
3.00
2.02
10.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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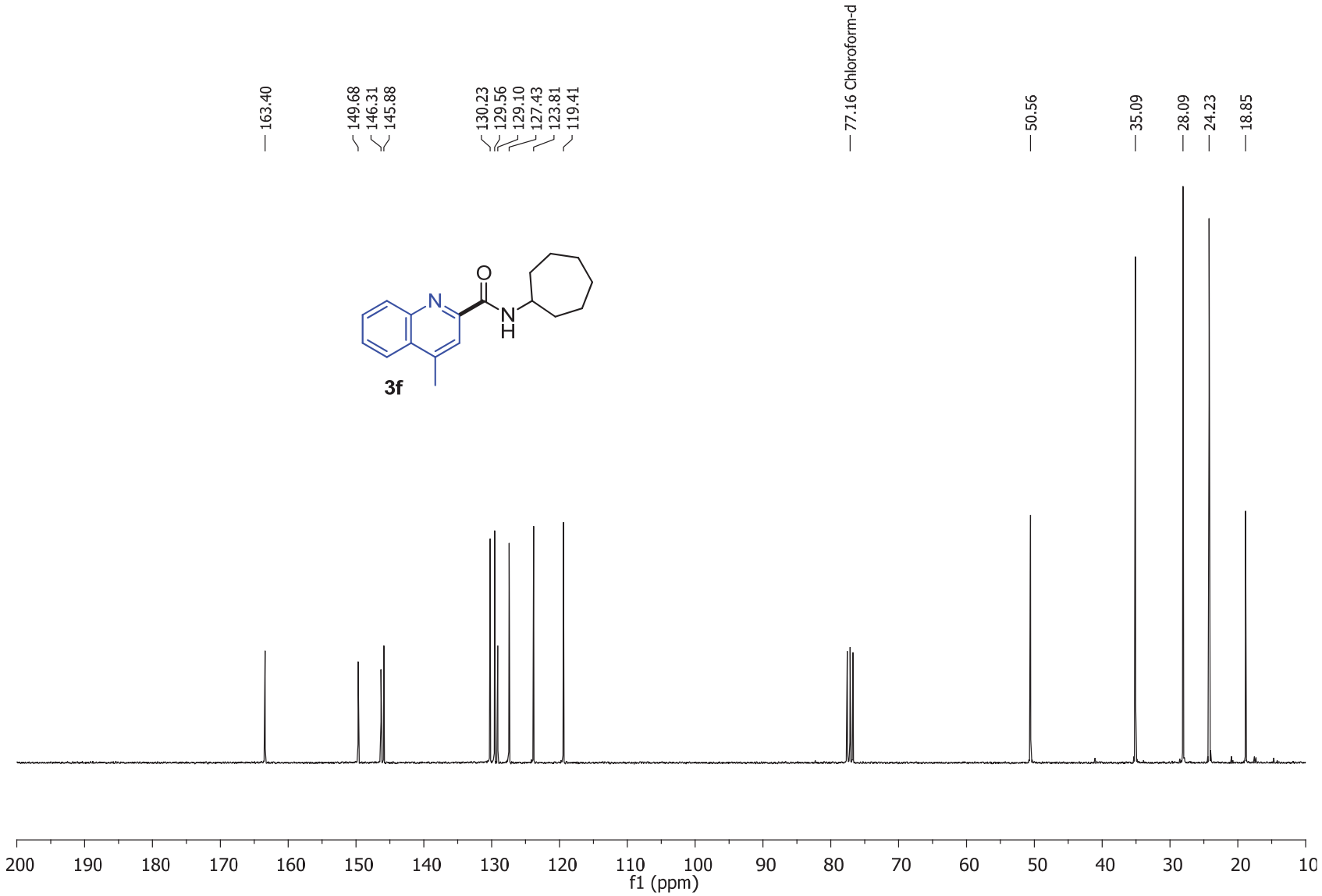
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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145.88
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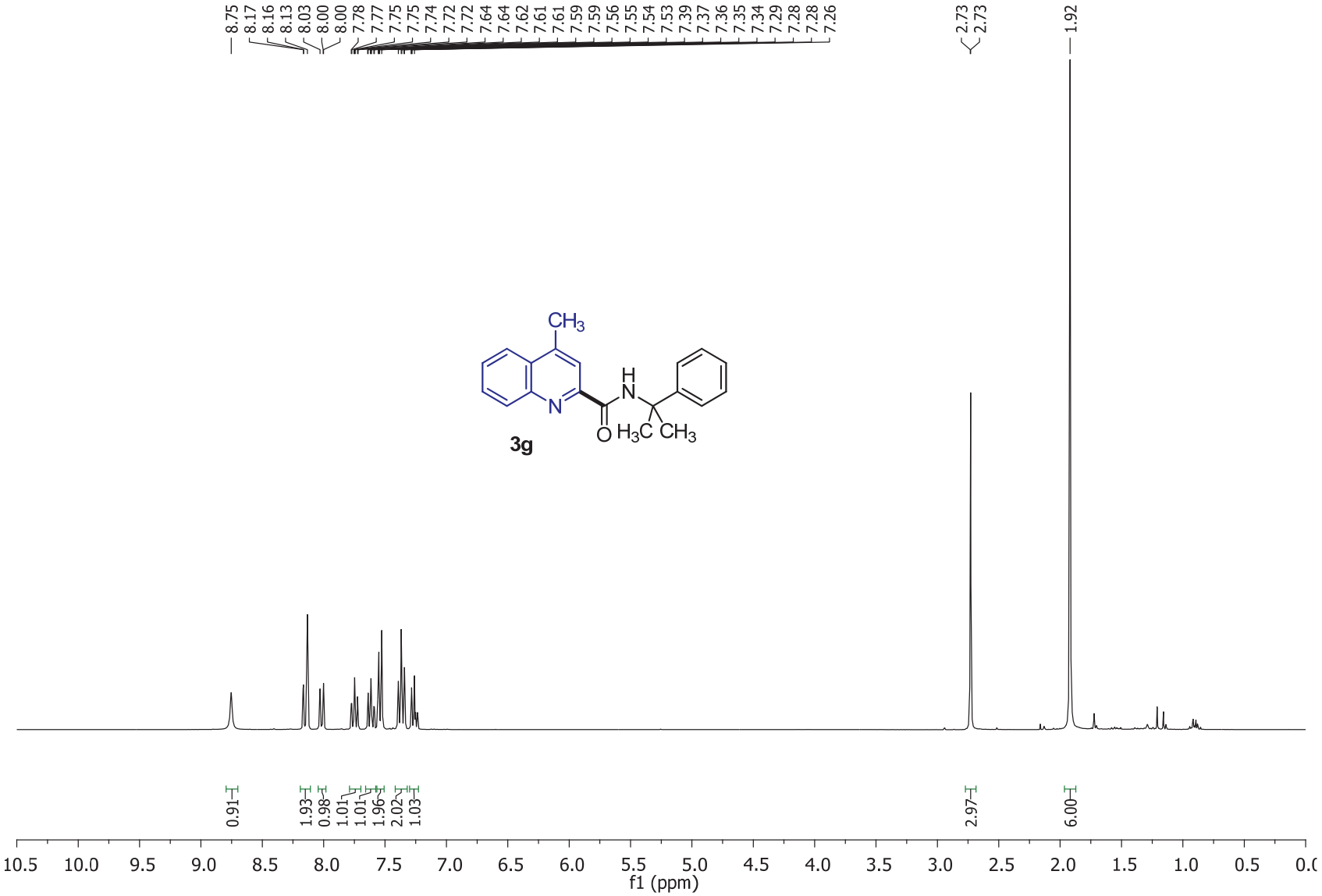
129.10
127.43
123.81
119.41
77.16 Chloroform-d
50.56
35.09
28.09
24.23
18.85
O
N
N
H
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.78
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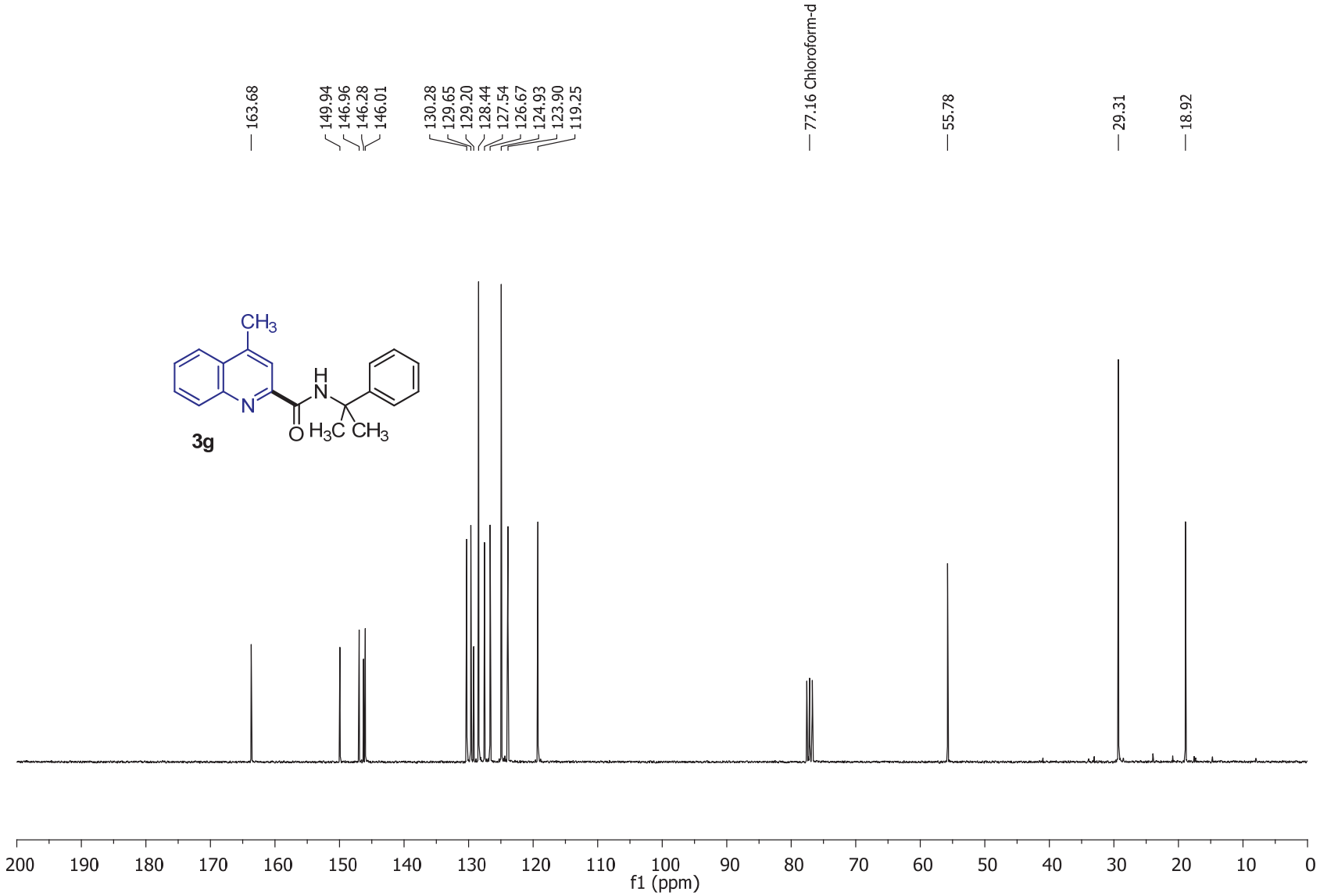
7.75
7.74
7.72
7.72
7.64
7.64
7.62
7.61
7.61
7.59
7.59
7.56
7.55
7.54
7.53
7.39
7.37
7.36
7.35
7.34
7.29
7.28
7.28
7.26
2.73
2.73
1.92
CH3
H
N
N
O H3C CH3
3g
0.91
1.93
0.98
1.01
1.01
1.96
2.02
1.03
2.97
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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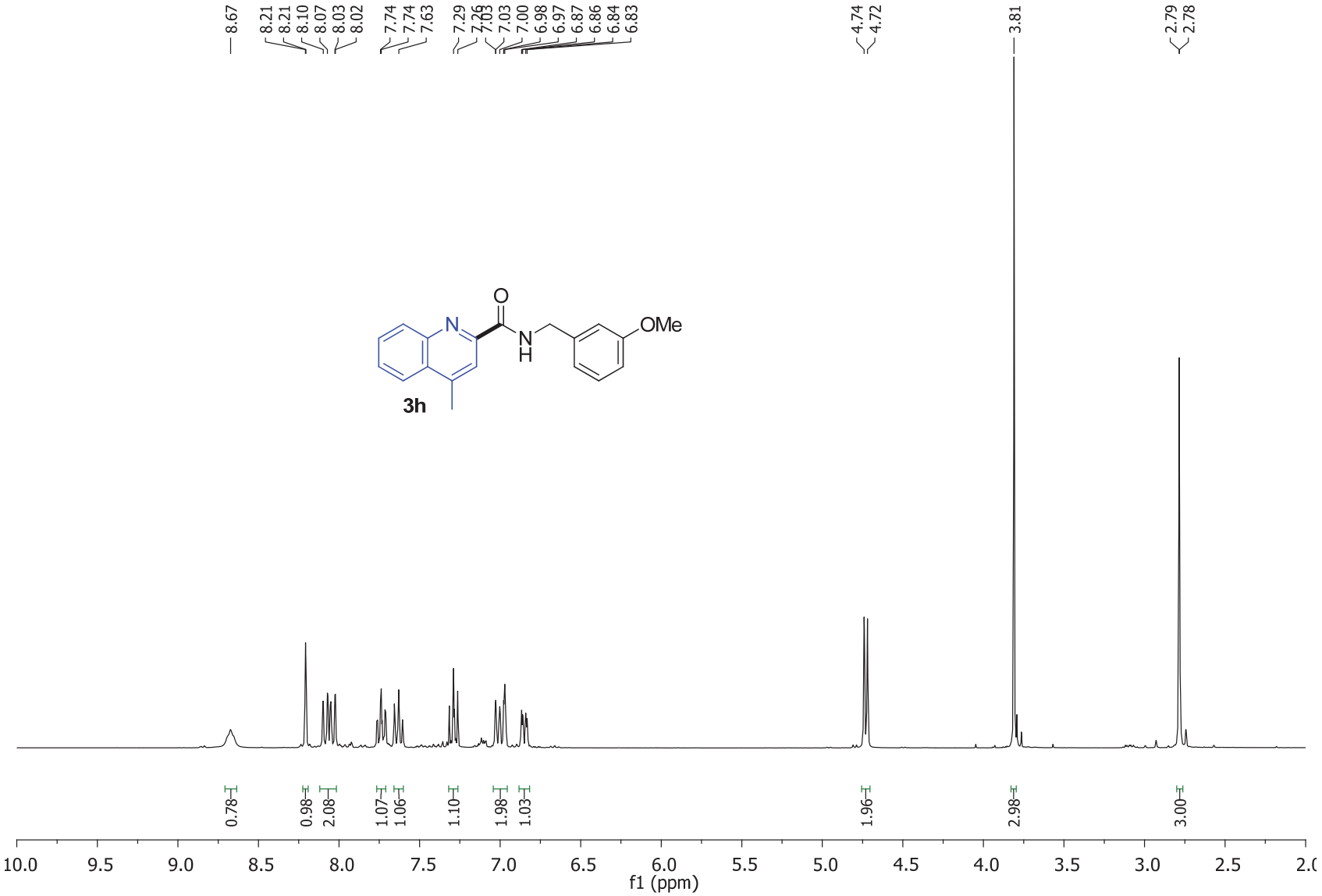
130.28
129.65
129.20
128.44
127.54
126.67
124.93
123.90
119.25
77.16 Chloroform-d
55.78
29.31
18.92
CH3
N
H
N
O H3C CH3
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.02
7.74
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7.63
7.29
7.26
7.03
7.03
7.00
6.98
6.97
6.87
6.86
6.84
6.83
4.74
4.72
3.81
2.79
2.78
O
N
H
N
OMe
3h
0.78
0.98
2.08
1.07
1.06
1.10
1.98
1.03
1.96
2.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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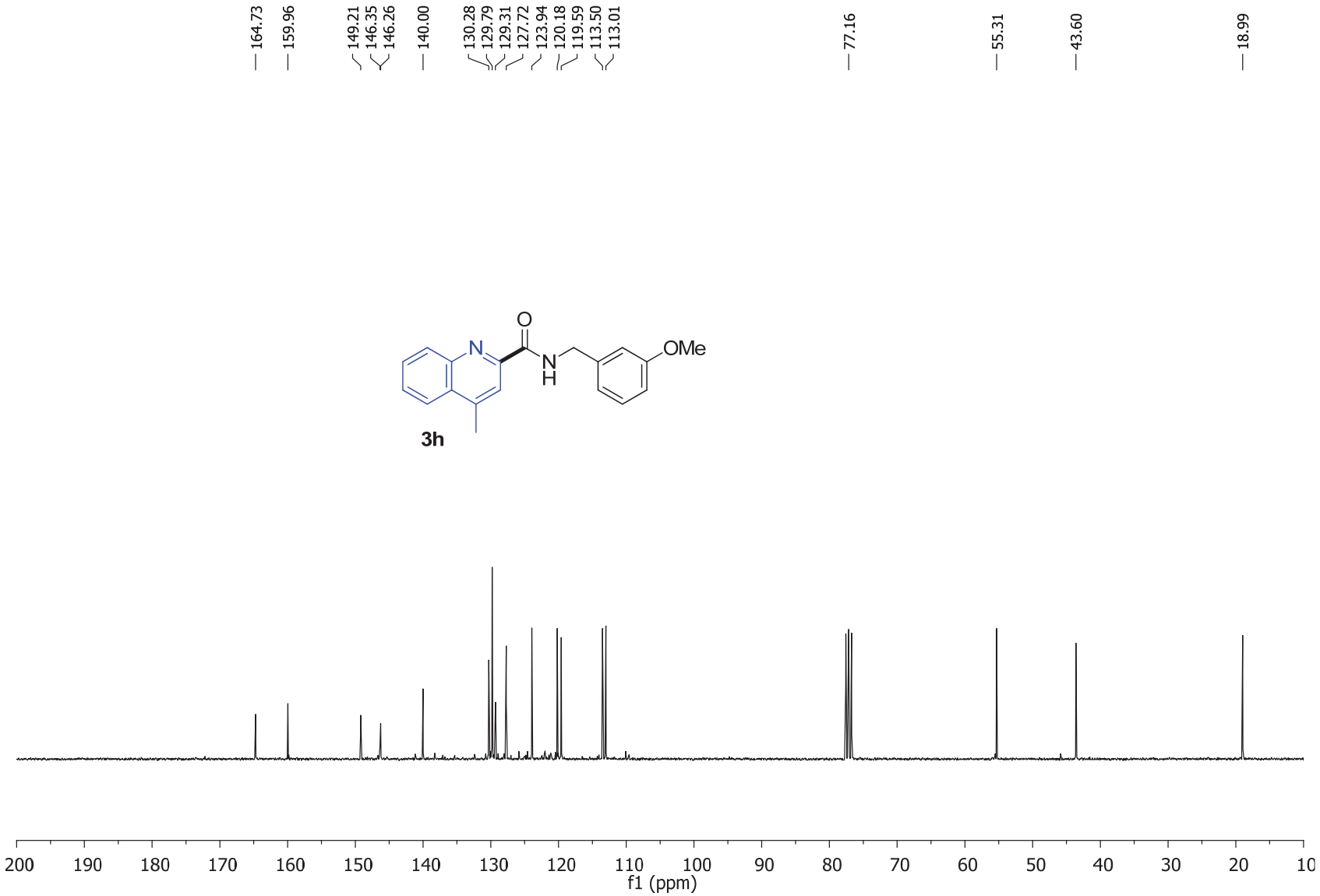
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)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146.26
140.00
130.28
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127.72
123.94
120.18
119.59
113.50
113.01
77.16
55.31
43.60
18.99
O
N
N
H
OMe
3h
200
190
180
170
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150
140
130
120
110
100
90
80
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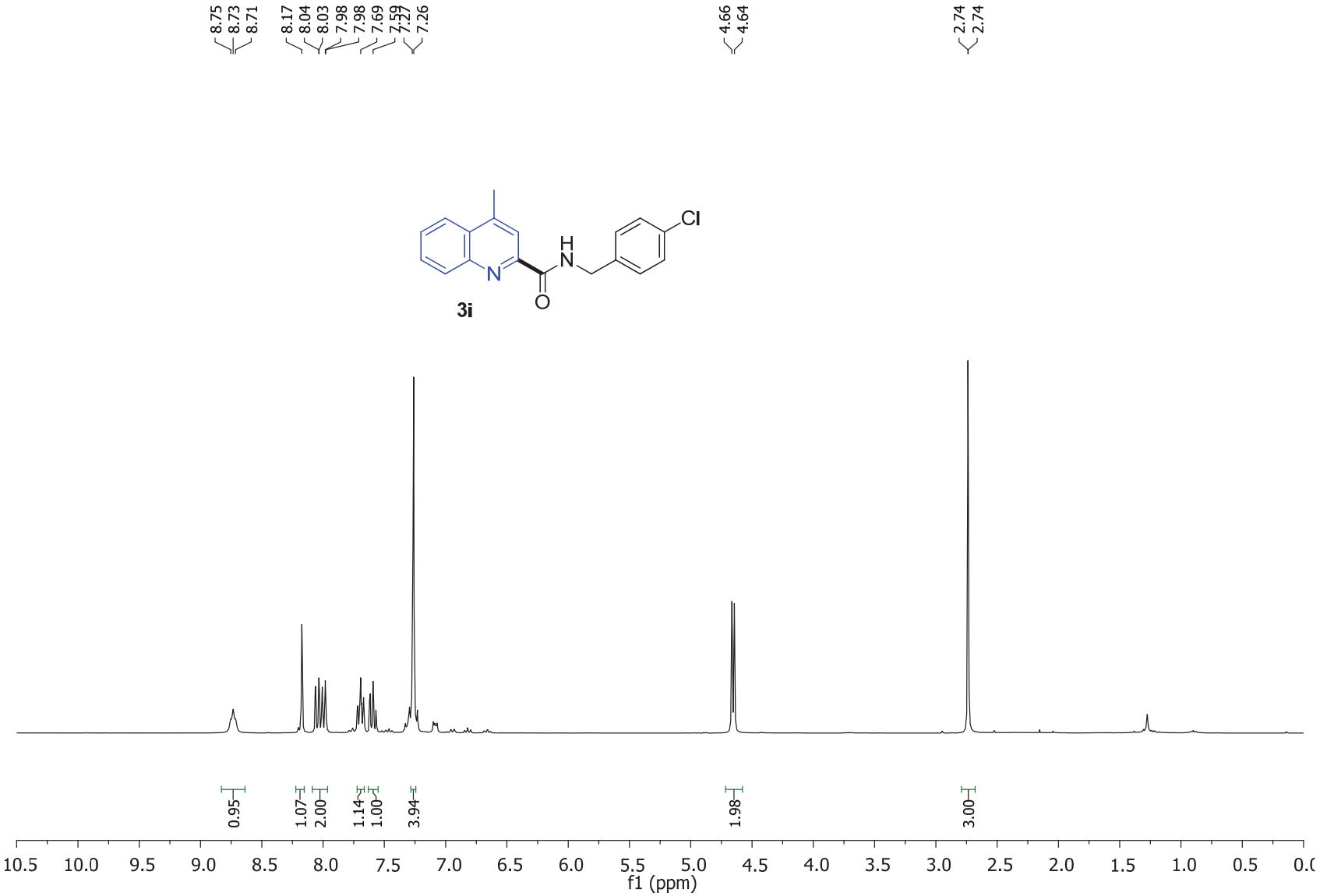
60
50
40
30
20
10
f1 (ppm)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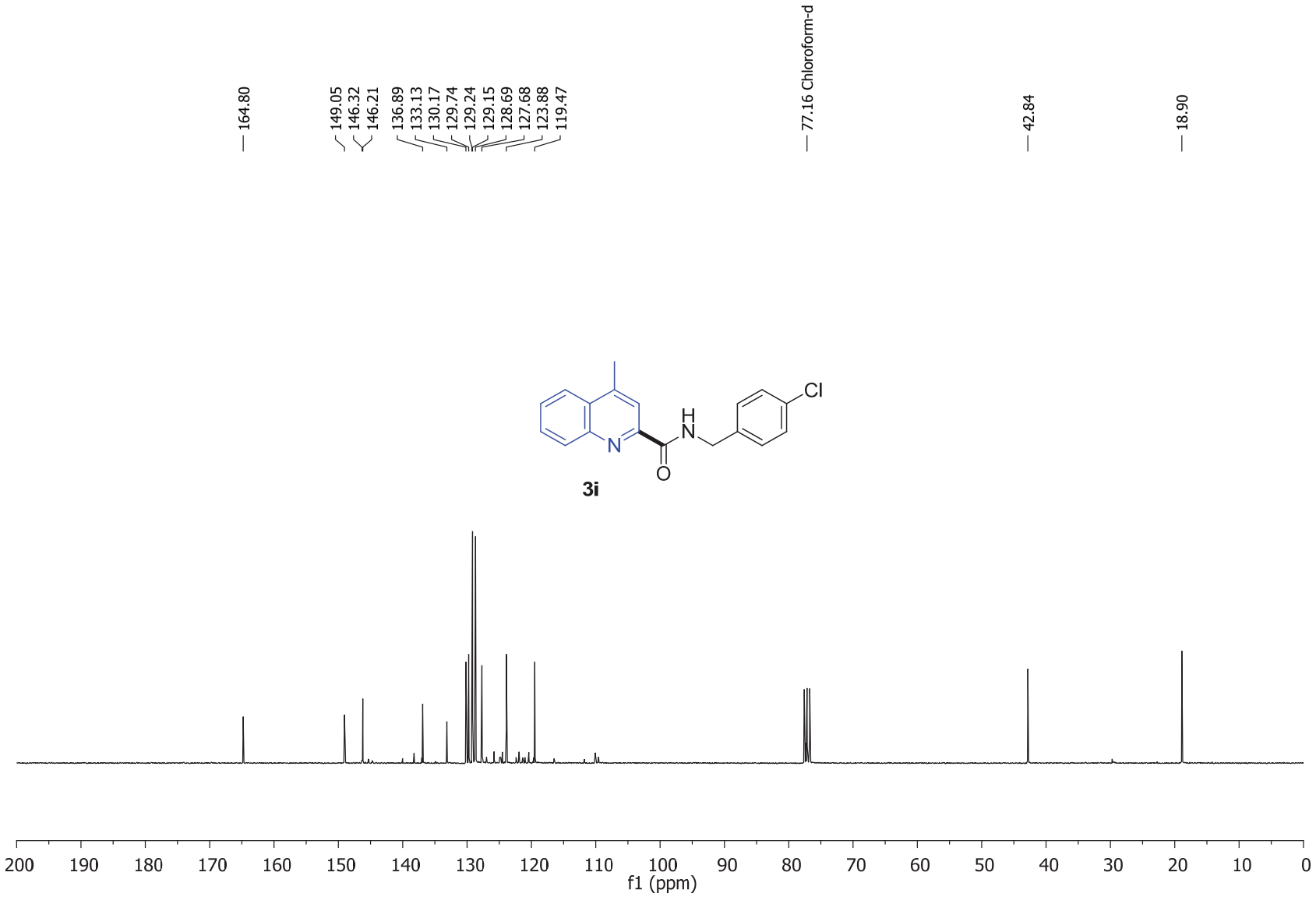
8.73
8.71
8.17
8.04
8.03
7.98
7.98
7.69
7.59
7.27
7.26
4.66
4.64
2.74
2.74
Cl
H
N
N
O
3i
0.95
1.07
2.00
1.14
1.00
3.94
1.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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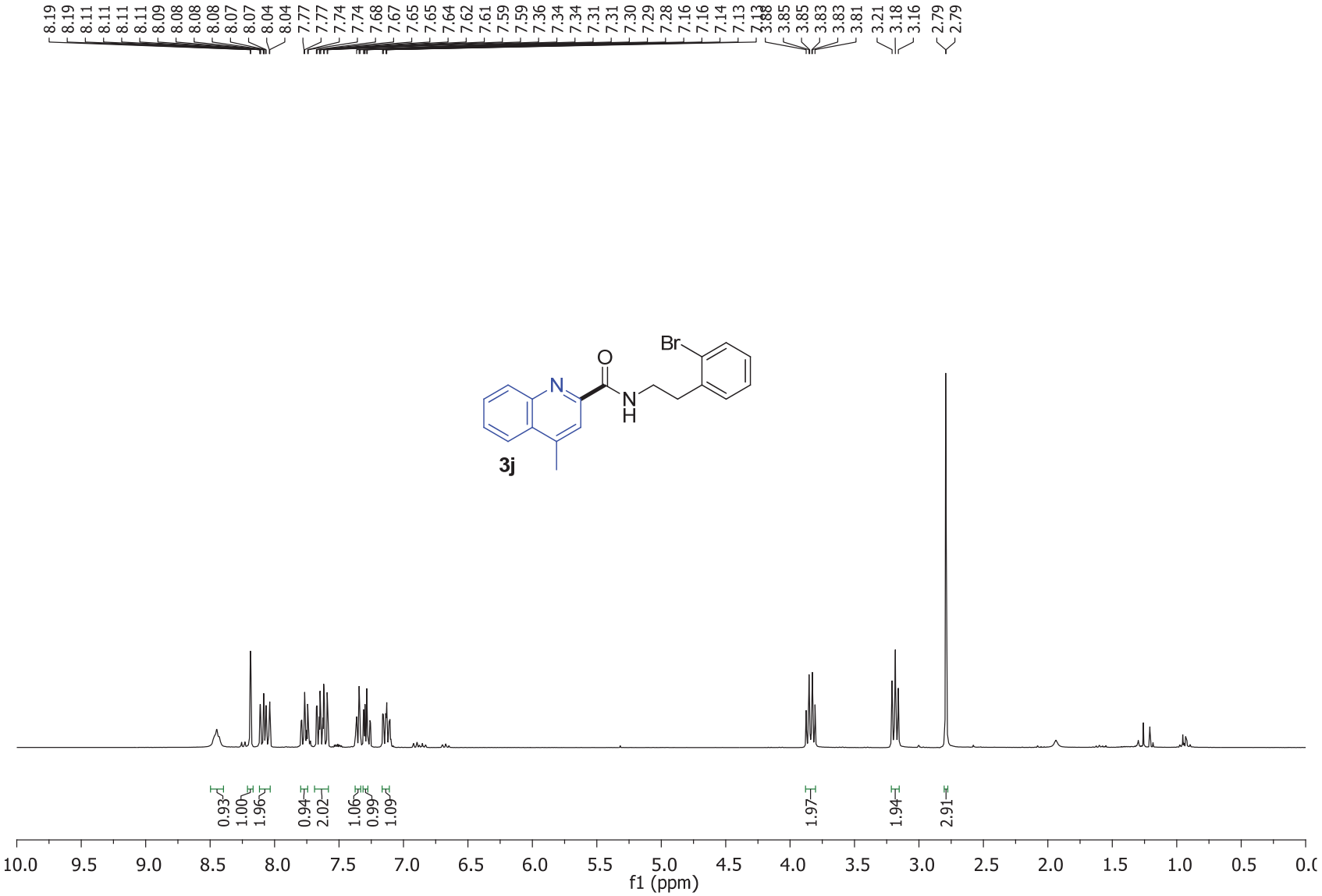
129.24
129.15
128.69
127.68
123.88
119.47
77.16 Chloroform-d
42.84
18.90
Cl
N
H
N
O
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.19
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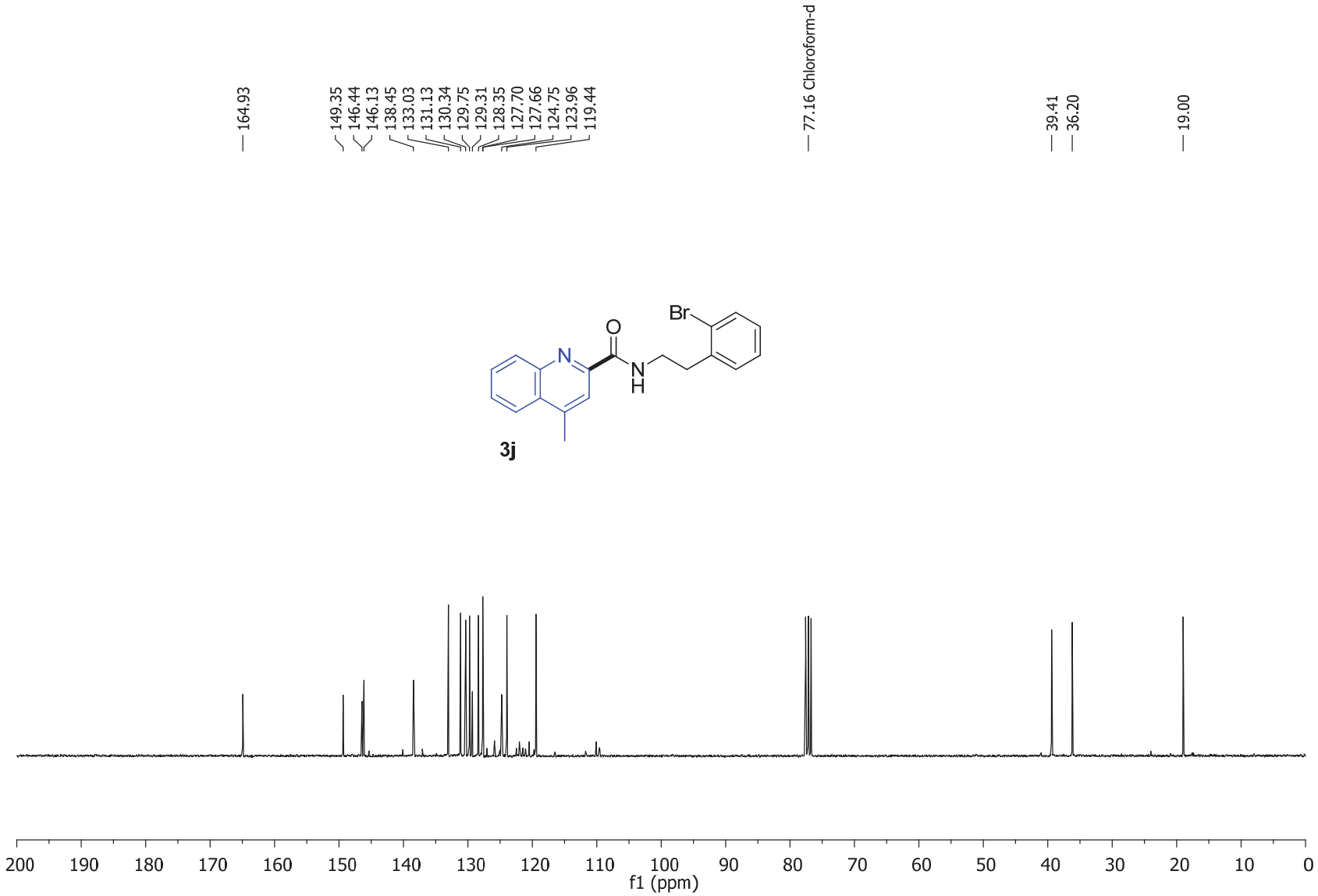
8.11
8.11
8.11
8.09
8.08
8.08
8.08
8.07
8.07
8.04
8.04
7.77
7.77
7.74
7.74
7.68
7.67
7.65
7.65
7.64
7.62
7.61
7.59
7.59
7.36
7.34
7.34
7.31
7.31
7.30
7.29
7.28
7.16
7.16
7.14
7.13
3.88
3.85
3.85
3.83
3.83
3.81
3.21
3.18
3.16
2.79
2.79
Br
O
N
N
H
3j
0.93
1.00
1.96
0.94
2.02
1.06
0.99
1.09
1.97
1.94
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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133.03
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130.34
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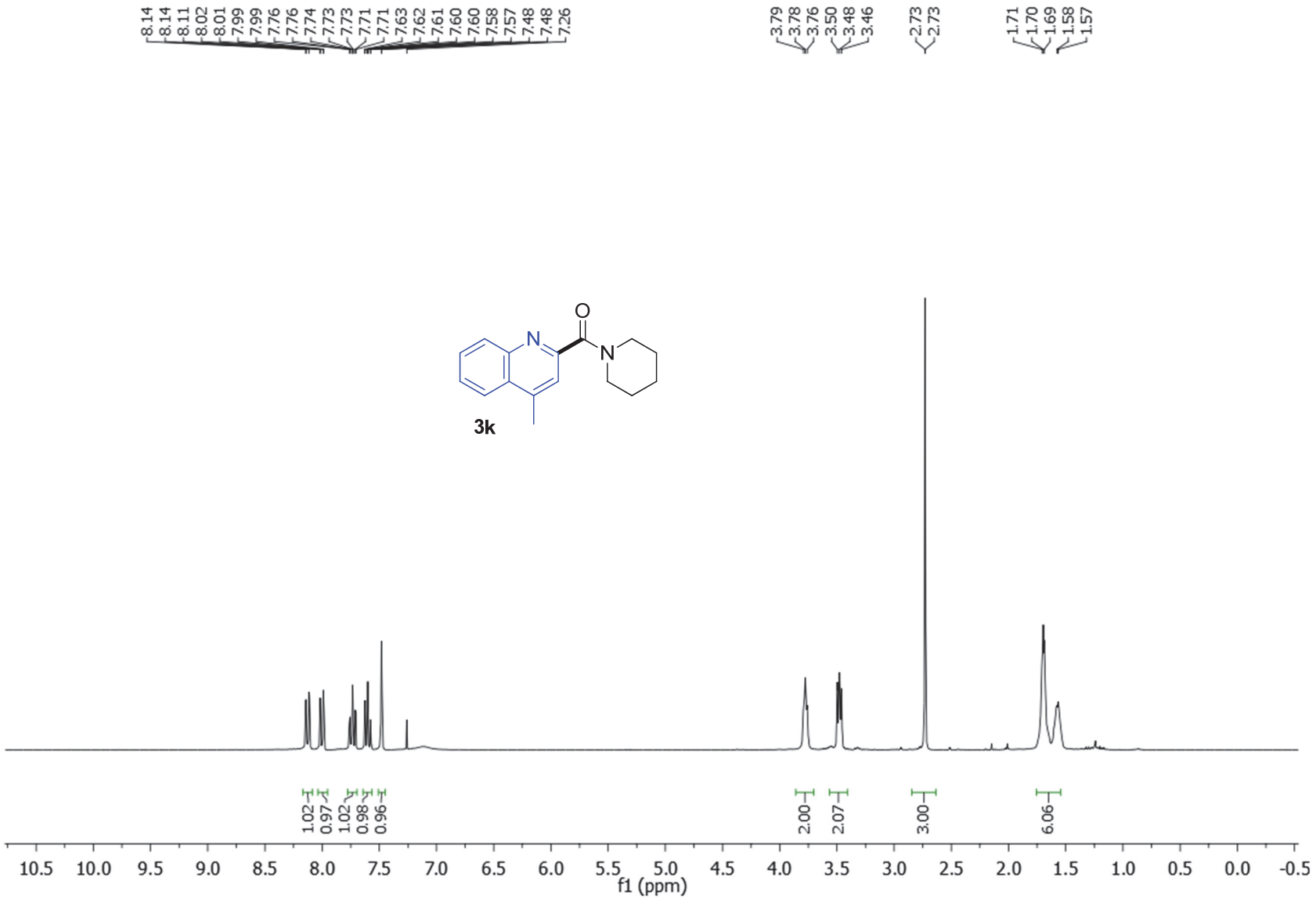
129.31
128.35
127.70
127.66
124.75
123.96
119.44
77.16 Chloroform-d
39.41
36.20
19.00
Br
O
N
N
H
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.14
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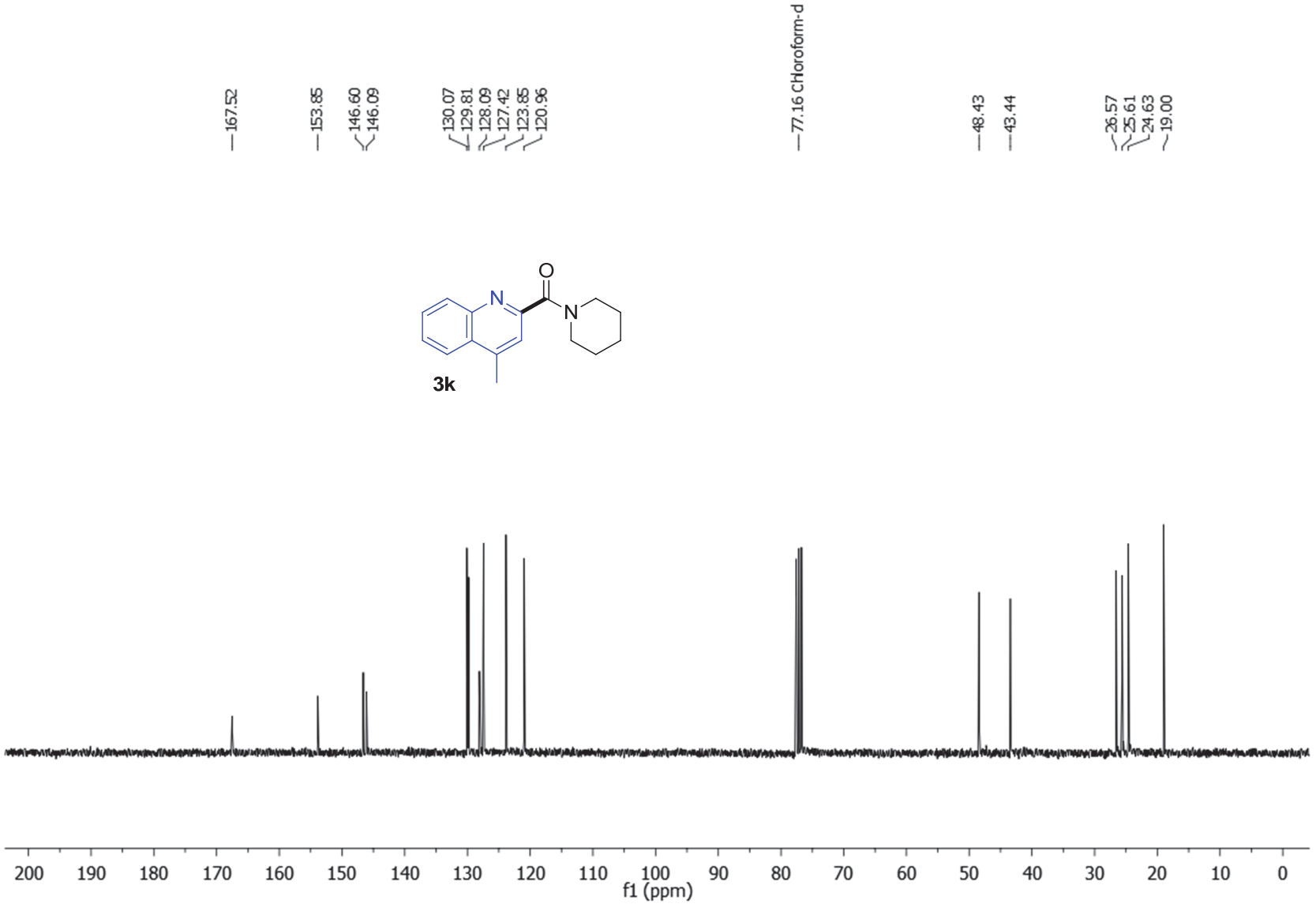
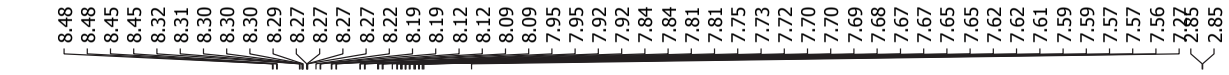
7.99
7.76
7.76
7.74
7.73
7.73
7.71
7.71
7.63
7.62
7.61
7.60
7.60
7.58
7.57
7.48
7.48
7.26
3.79
3.78
3.76
3.50
3.48
3.46
2.73
2.73
1.71
1.70
1.69
1.58
1.57
O
N
N
3k
1.02
0.97
1.02
0.98
0.96
2.00
2.07
3.00
6.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.52
153.85
146.60
146.09
130.07
129.81
128.09
127.42
123.85
120.96
77.16 Chloroform-d
48.43
43.44
26.57
25.61
24.63
19.00
O
N
N
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.27
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8.27
8.27
8.22
8.19
8.19
8.12
8.12
8.09
8.09
7.95
7.95
7.92
7.92
7.84
7.84
7.81
7.81
7.75
7.73
7.72
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7.70
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7.68
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7.57
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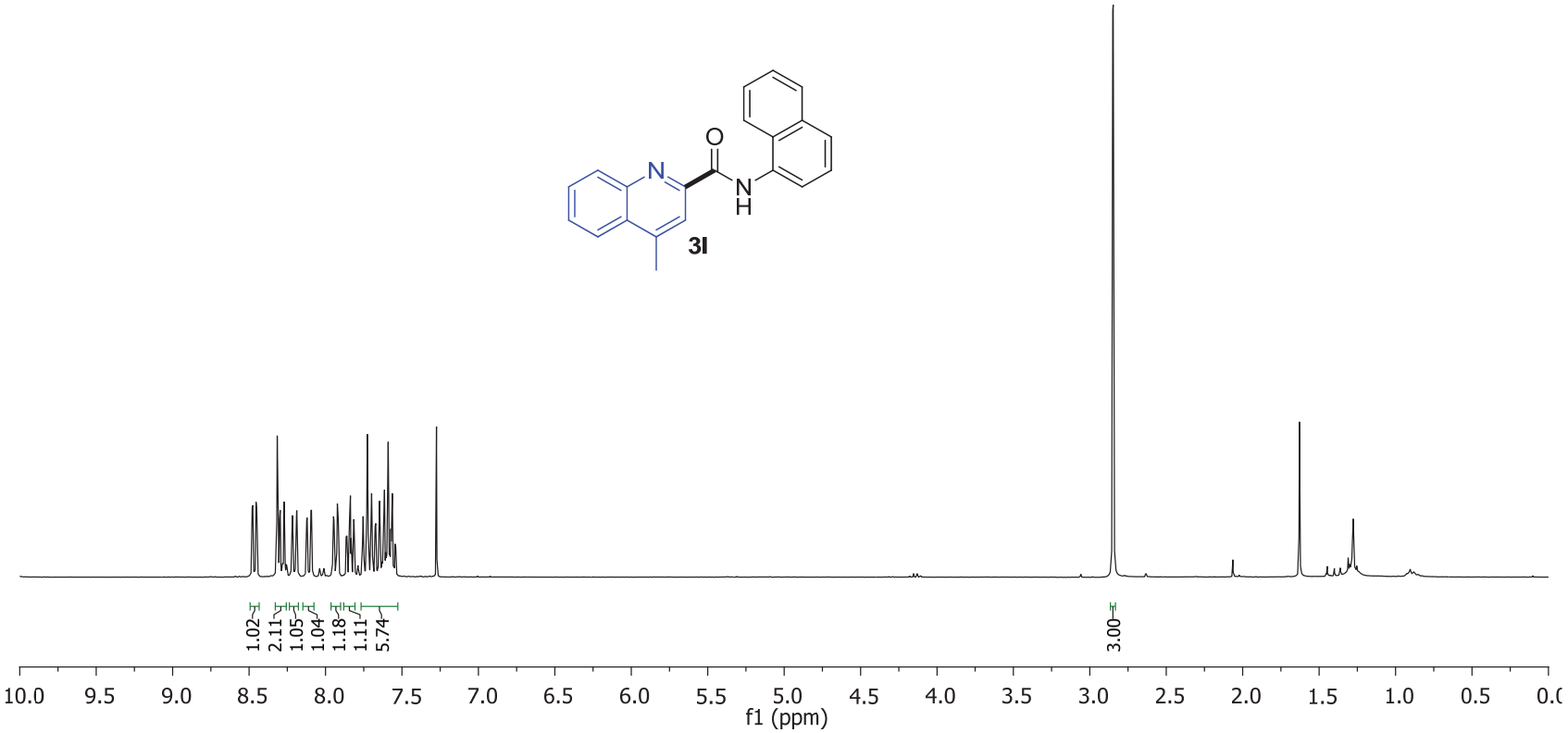
7.56
2.85
2.85


O
N
H
N
3l
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2.11
1.05
1.04
1.18
1.11
5.74
3.00
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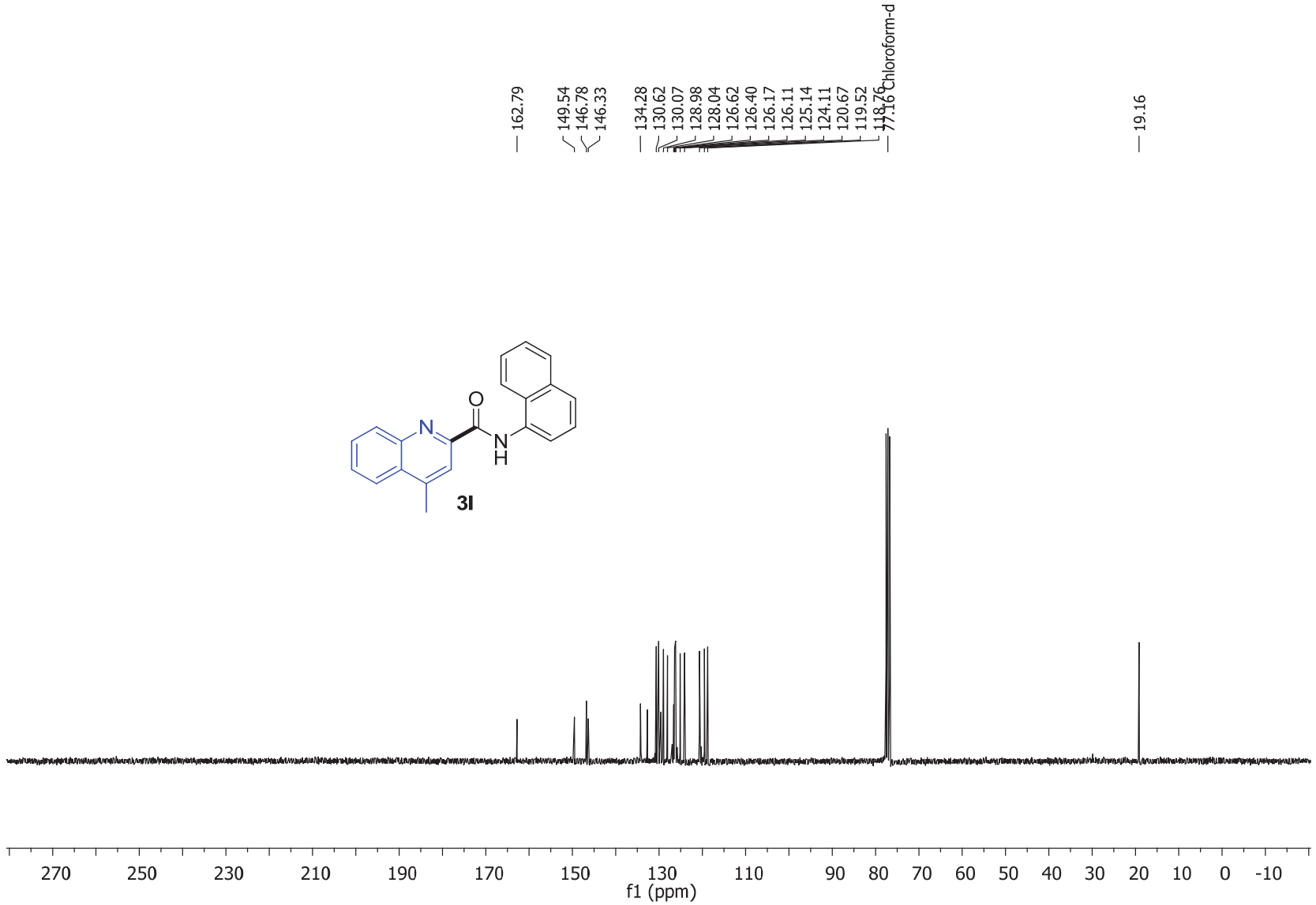
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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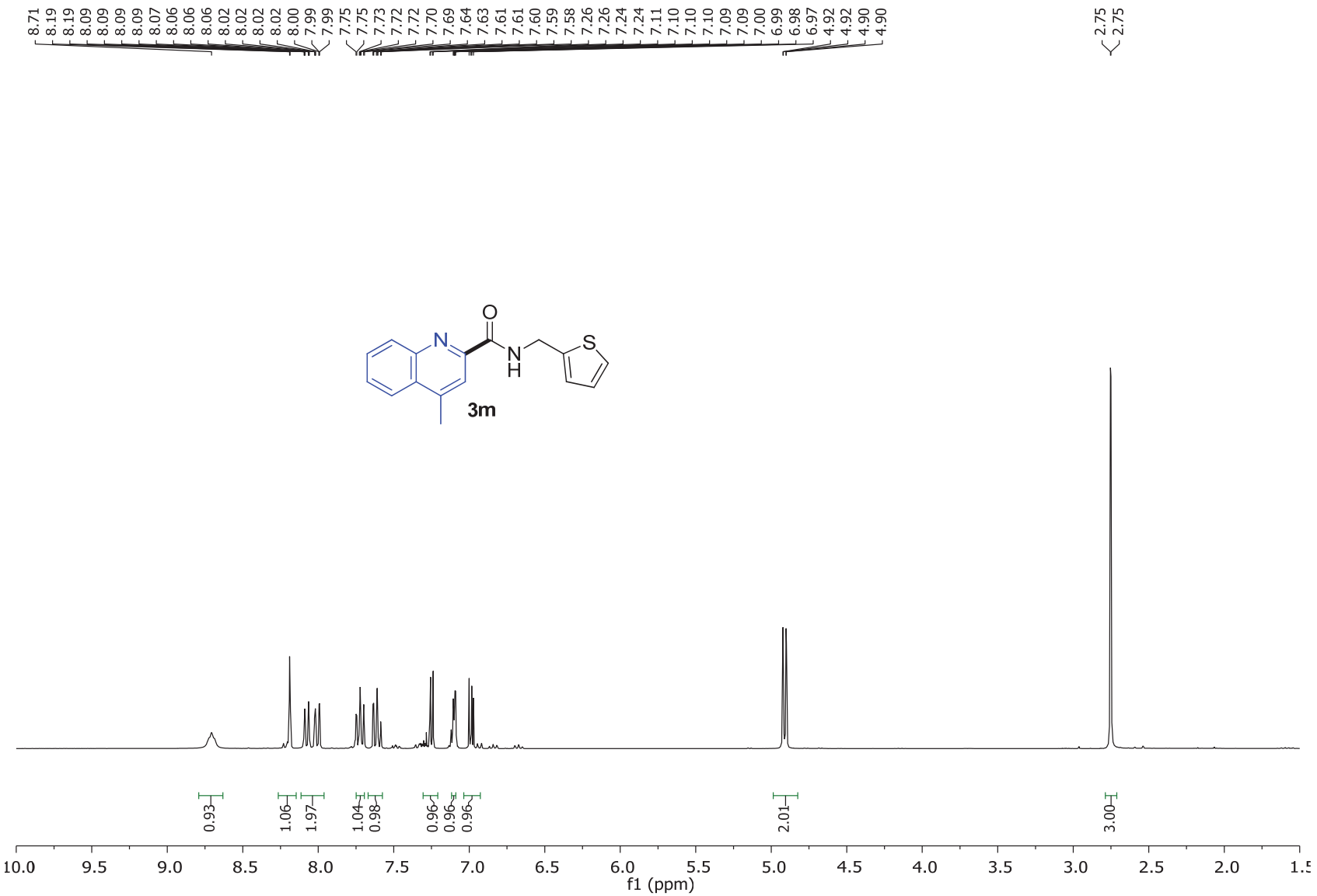
128.98
128.04
126.62
126.40
126.17
126.11
125.14
124.11
120.67
119.52
118.76
77.16 Chloroform-d
19.16
O
N
N
H
3l
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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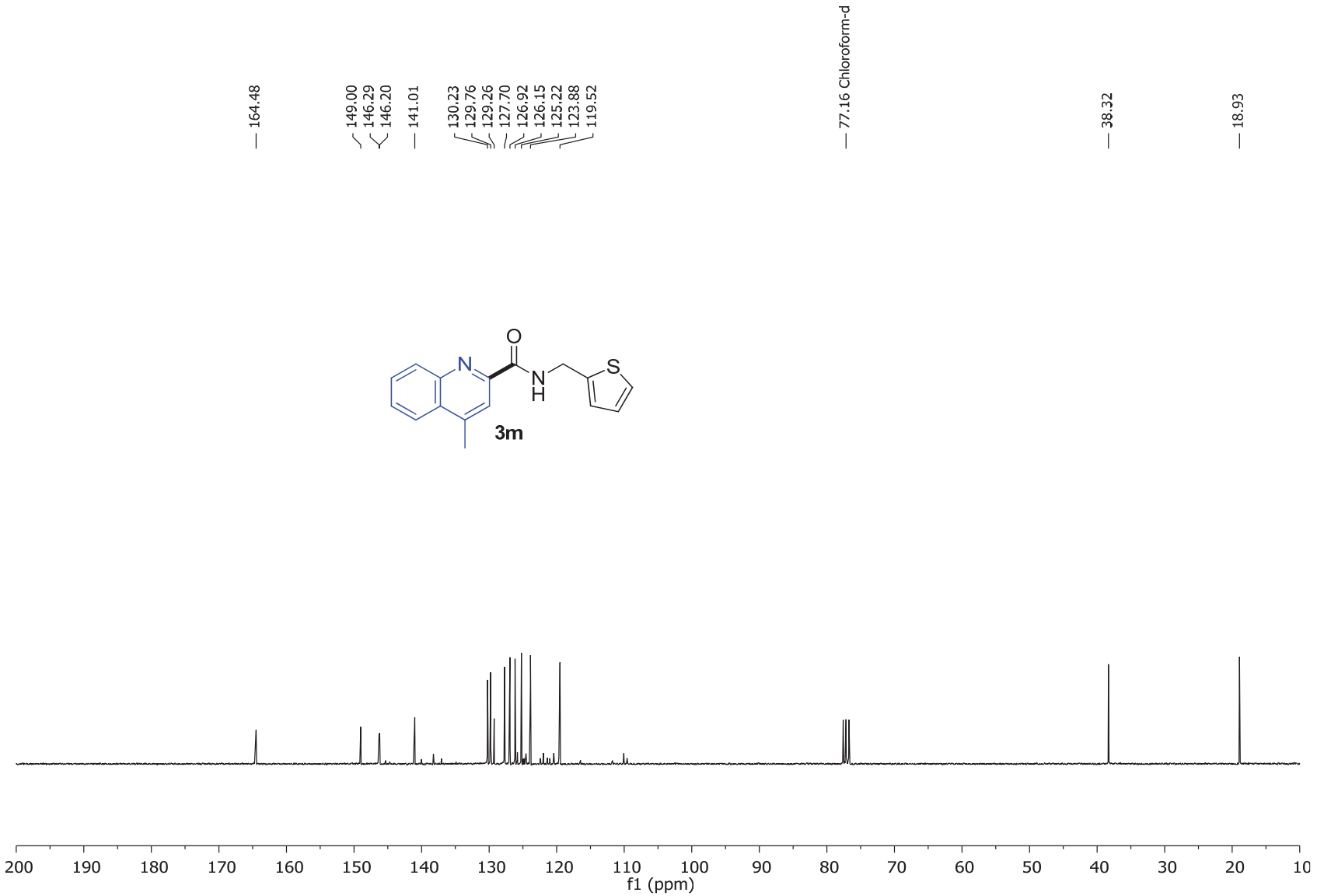
8.09
8.09
8.07
8.06
8.06
8.06
8.02
8.02
8.02
8.00
7.99
7.99
7.75
7.75
7.73
7.72
7.72
7.70
7.69
7.64
7.63
7.61
7.61
7.60
7.59
7.58
7.26
7.26
7.24
7.24
7.11
7.10
7.10
7.10
7.09
7.09
7.00
6.99
6.98
6.97
4.92
4.92
4.90
4.90
2.75
2.75
O
N
N
H
S
3m
0.93
1.06
1.97
1.04
0.98
0.96
0.96
0.96
2.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)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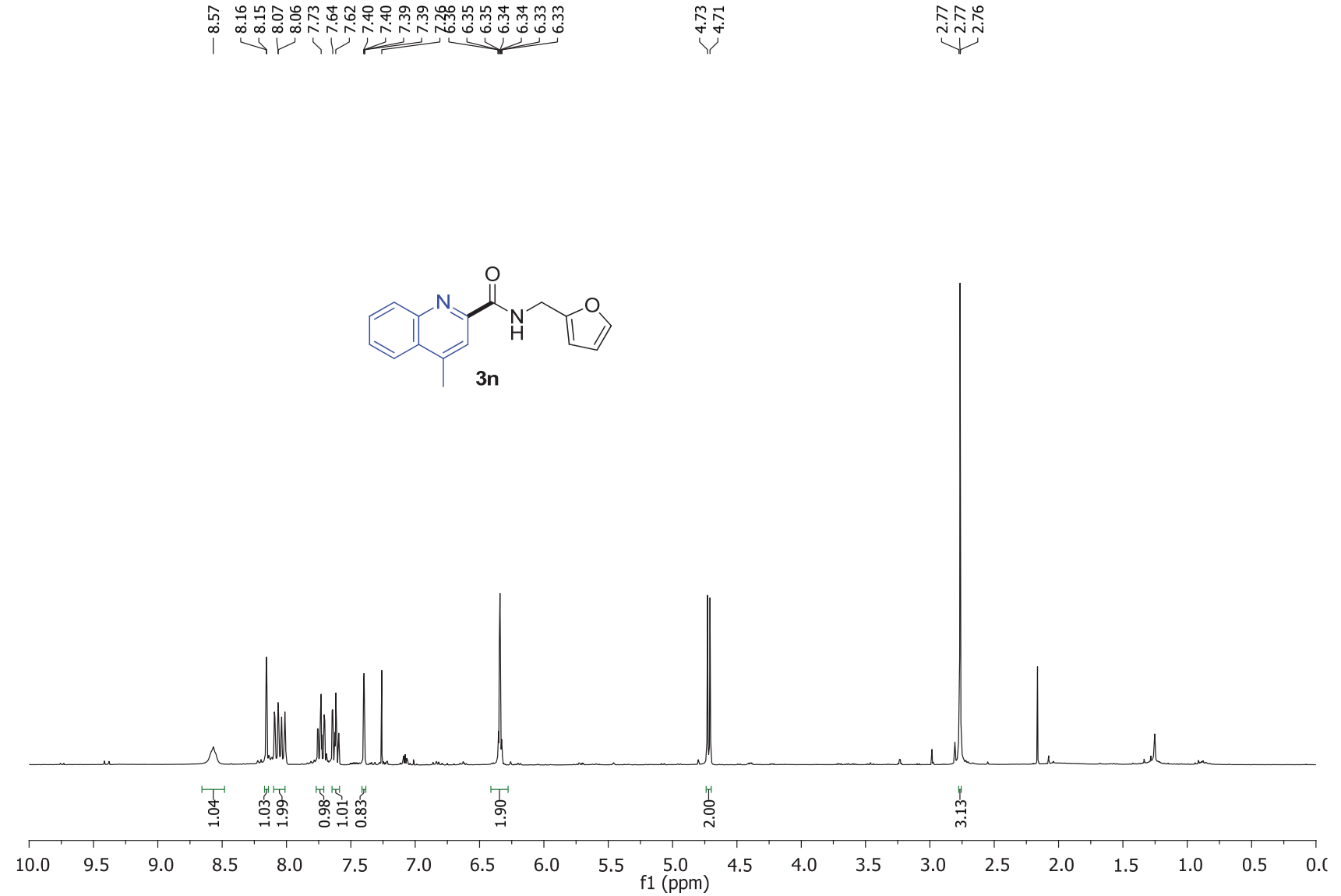
129.26
127.70
126.92
126.15
125.22
123.88
119.52
77.16 Chloroform-d
38.32
18.93
O
N
N
H
S
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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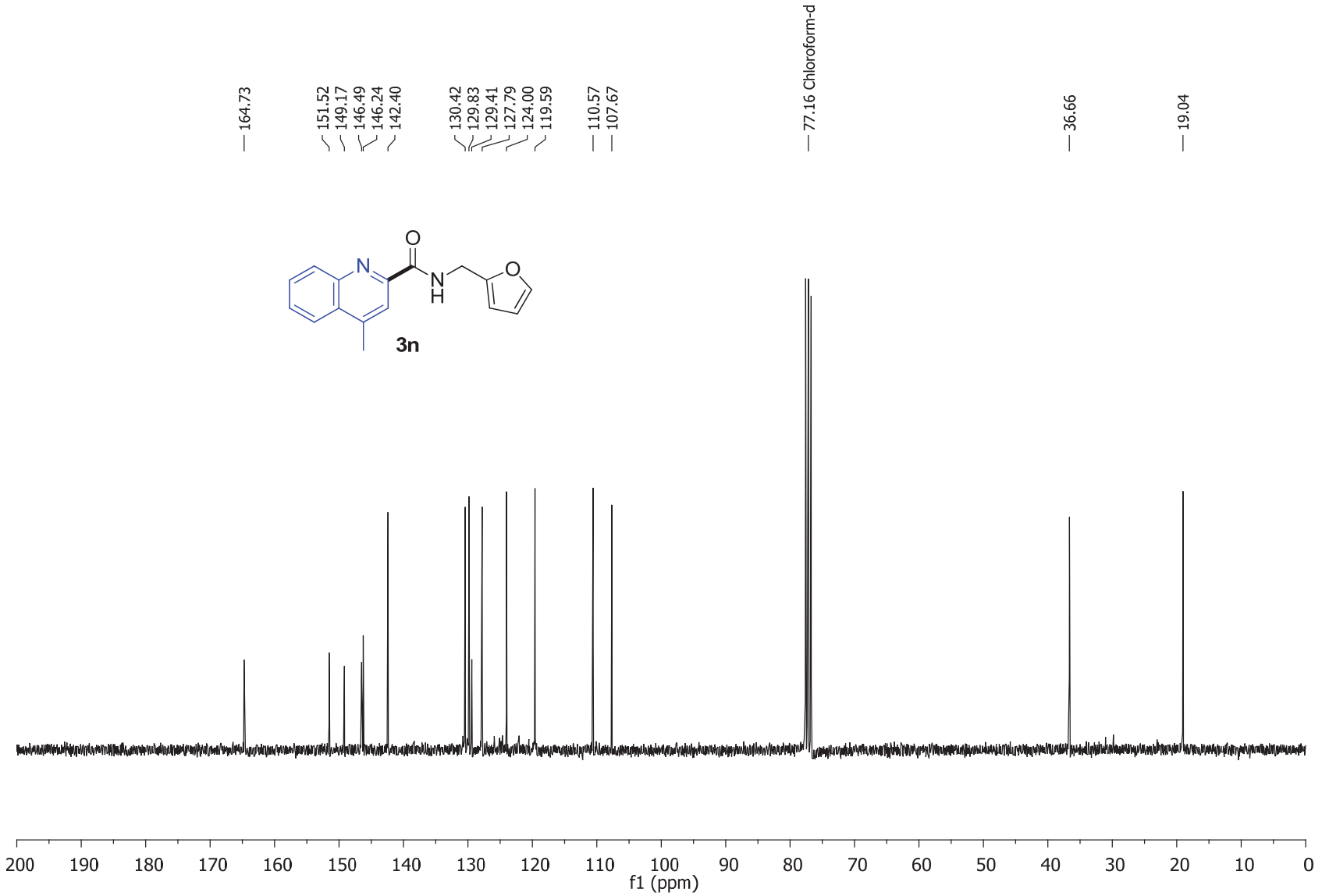
7.40
7.39
7.39
7.26
6.36
6.35
6.35
6.34
6.34
6.33
6.33
4.73
4.71
2.77
2.77
2.76
O
N
N
H
O
3n
1.04
1.03
1.99
0.98
1.01
0.83
1.90
2.00
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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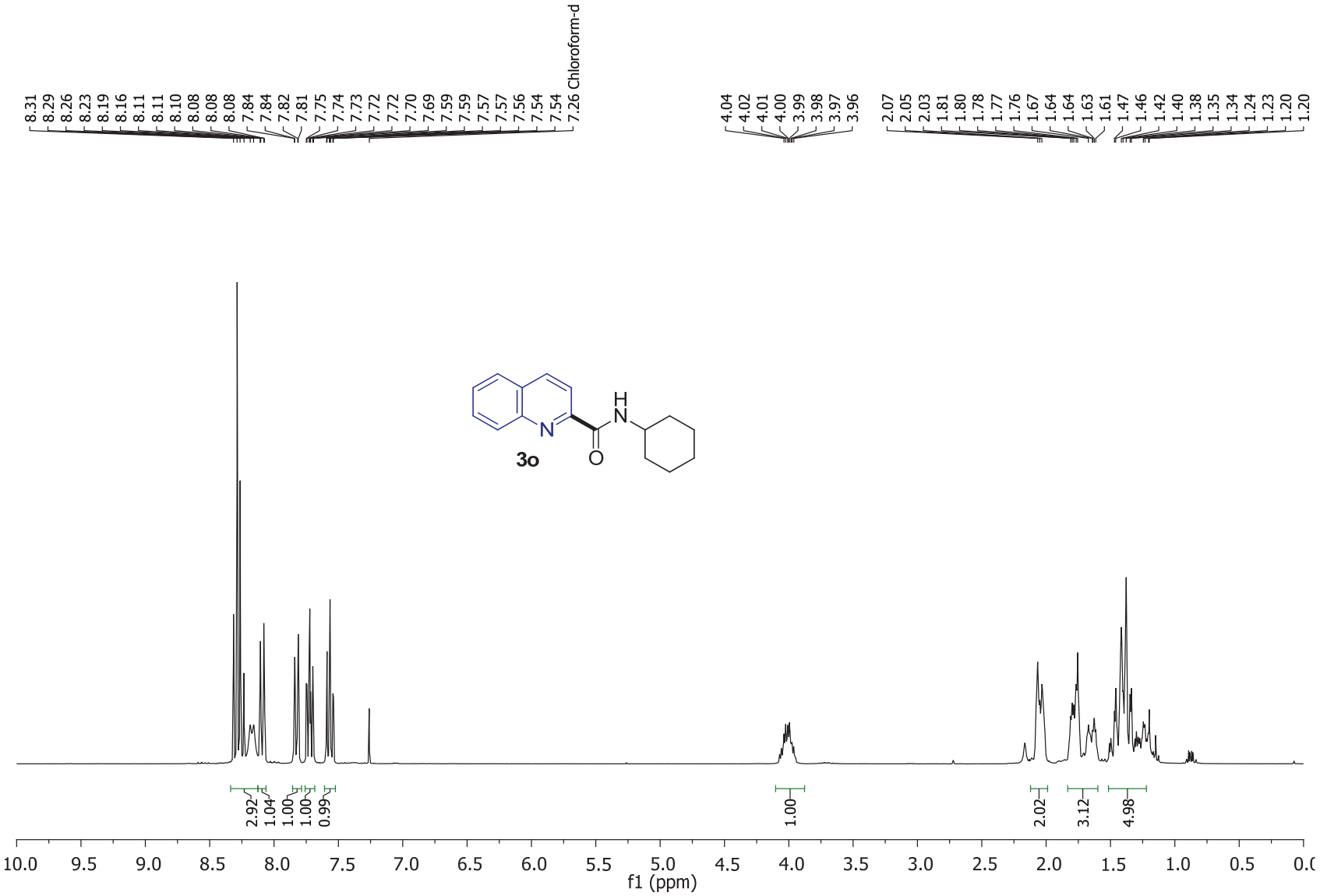
146.24
142.40
130.42
129.83
129.41
127.79
124.00
119.59
110.57
107.67
77.16 Chloroform-d
36.66
19.04
O
N
H
N
O
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.16
8.11
8.11
8.10
8.08
8.08
8.08
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7.84
7.82
7.81
7.75
7.74
7.73
7.72
7.72
7.70
7.69
7.59
7.59
7.57
7.57
7.56
7.54
7.54
7.26 Chloroform-d
4.04
4.02
4.01
4.00
3.99
3.98
3.97
3.96
2.07
2.05
2.03
1.81
1.80
1.78
1.77
1.76
1.67
1.64
1.64
1.63
1.61
1.47
1.46
1.42
1.40
1.38
1.35
1.34
1.24
1.23
1.20
1.20
3o
2.92
1.04
1.00
1.00
0.99
1.00
2.02
3.12
4.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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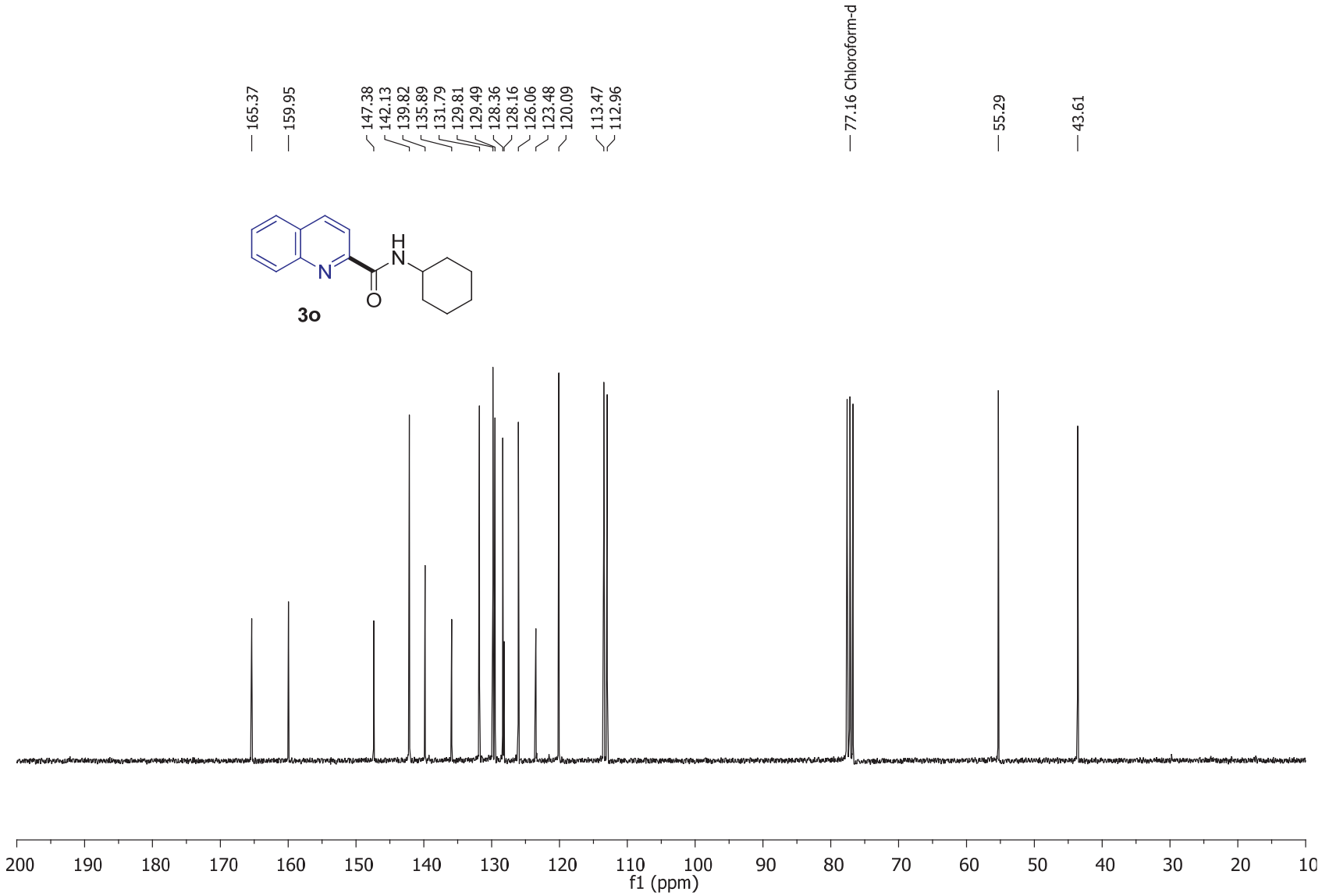
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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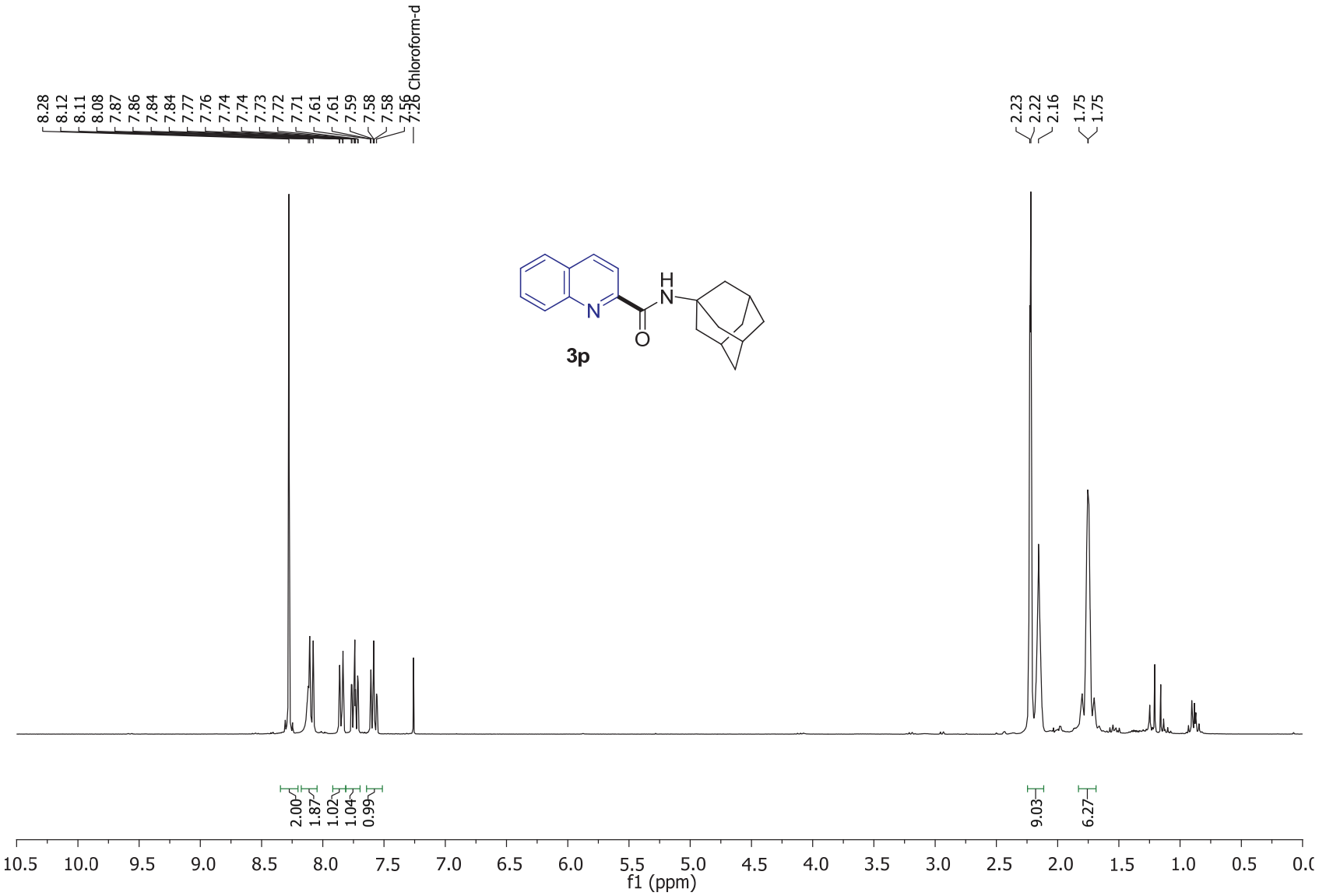
129.81
129.49
128.36
128.16
126.06
123.48
120.09
113.47
112.96
77.16 Chloroform-d
55.29
43.61
H
N
N
O
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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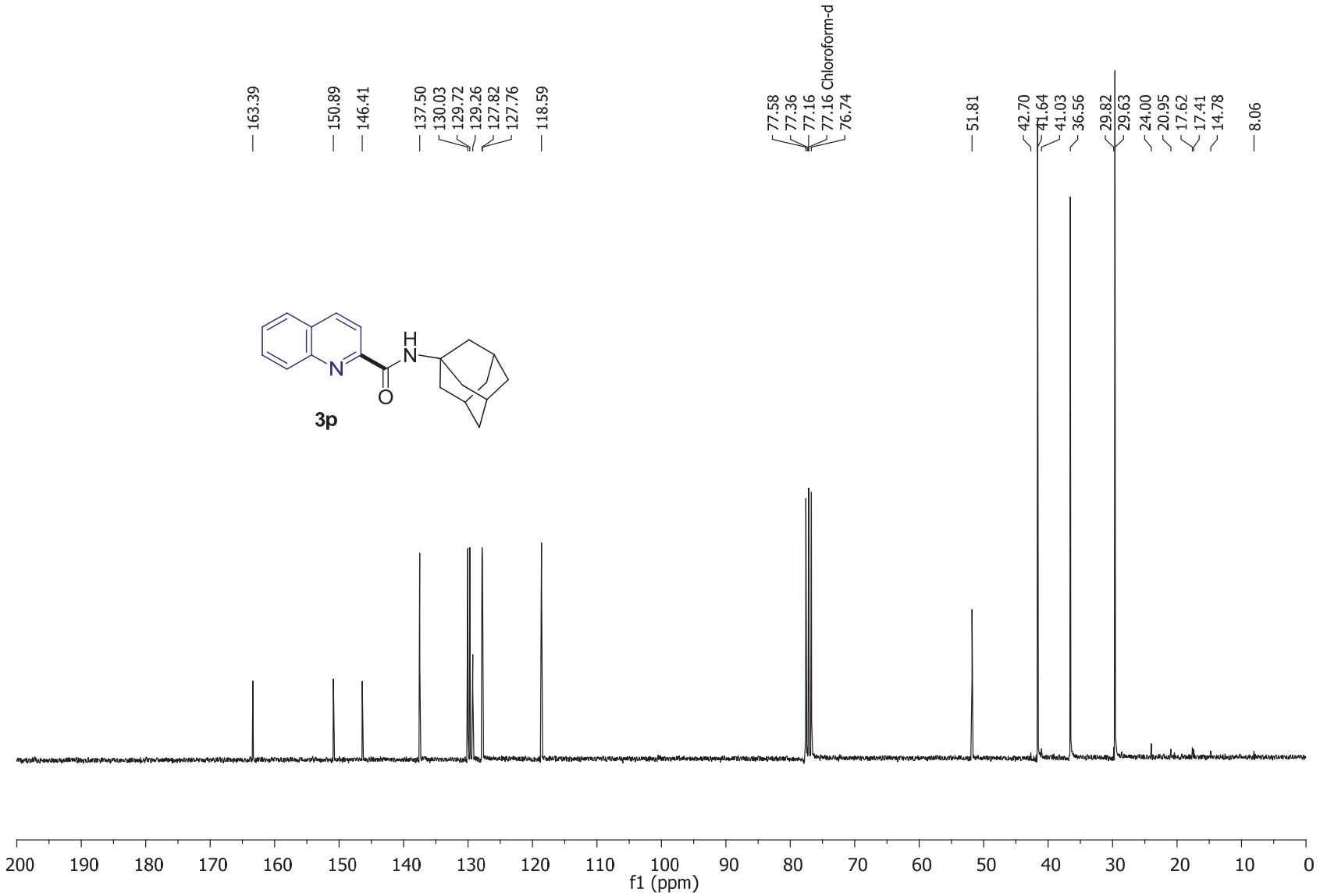
7.76
7.74
7.74
7.73
7.72
7.71
7.61
7.61
7.59
7.58
7.58
7.56
7.26 Chloroform-d
2.23
2.22
2.16
1.75
1.75
H
N
N
O
3p
2.00
1.87
1.02
1.04
0.99
9.03
6.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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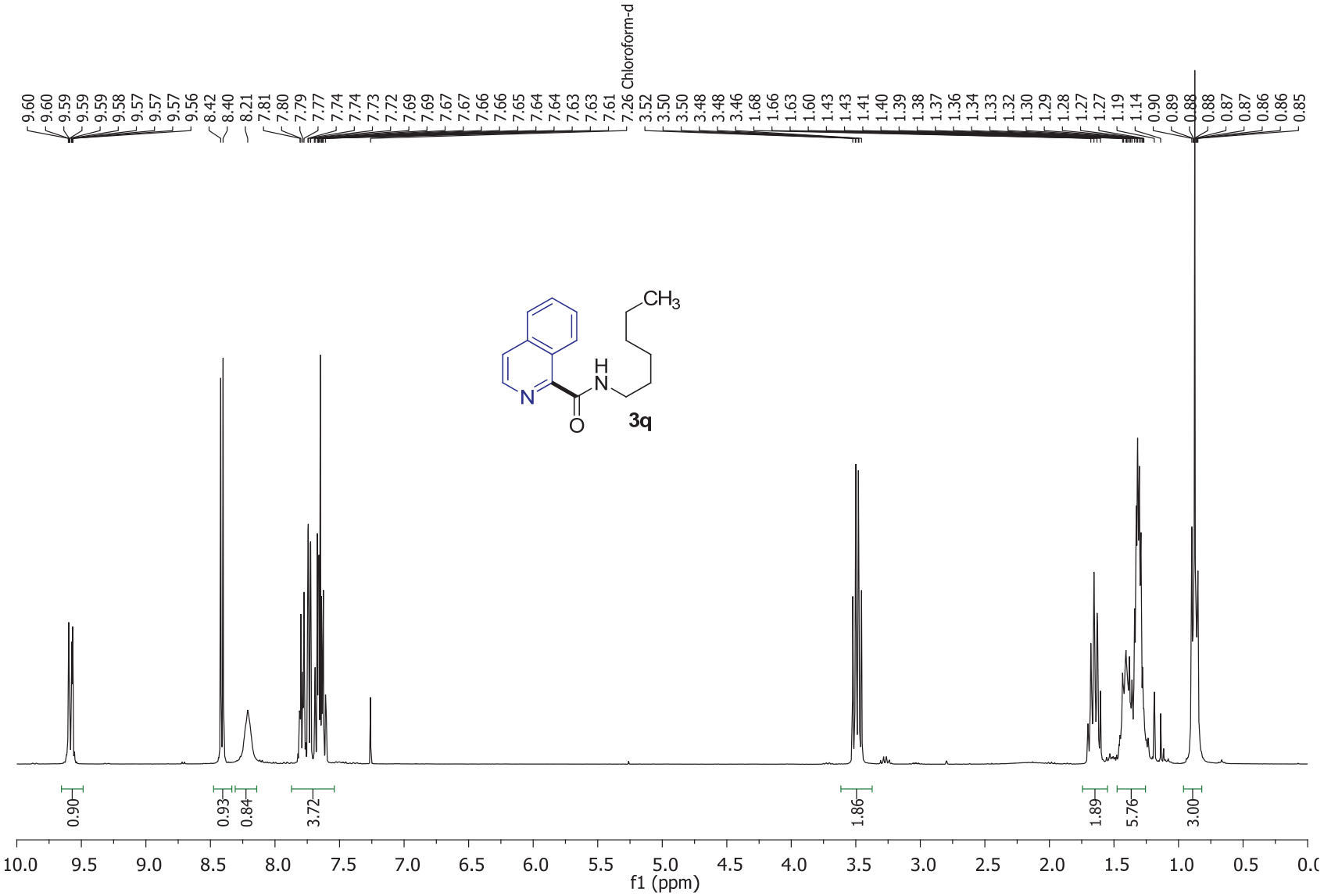
137.50
130.03
129.72
129.26
127.82
127.76
118.59
77.58
77.36
77.16
77.16 Chloroform-d
76.74
51.81
42.70
41.64
41.03
36.56
29.82
29.63
24.00
20.95
17.62
17.41
14.78
8.06
H
N
N
O
3p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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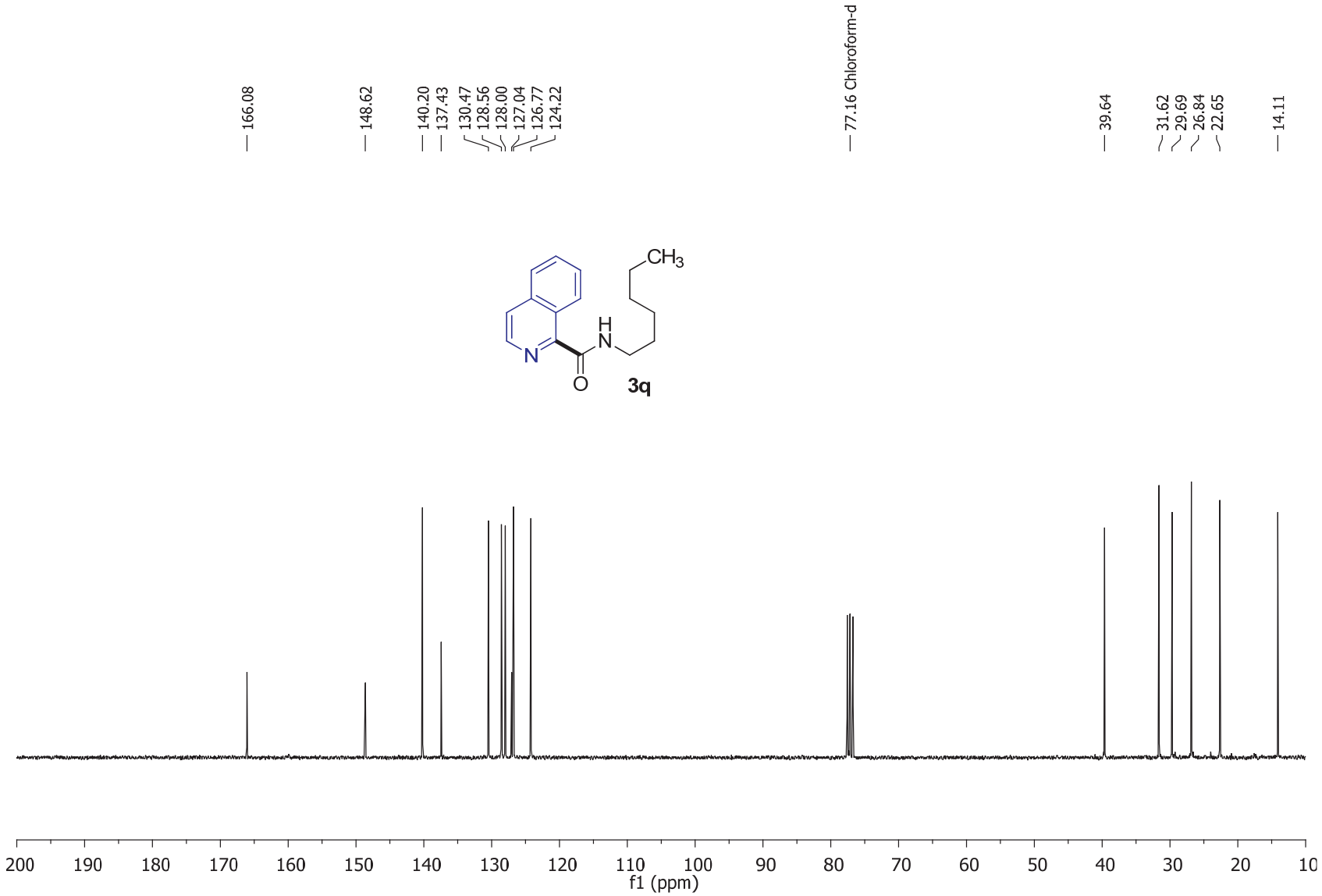
CH3
H
N
N
O
3q
0.90 0.93 0.84 3.72 1.86 1.89 5.76 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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148.62
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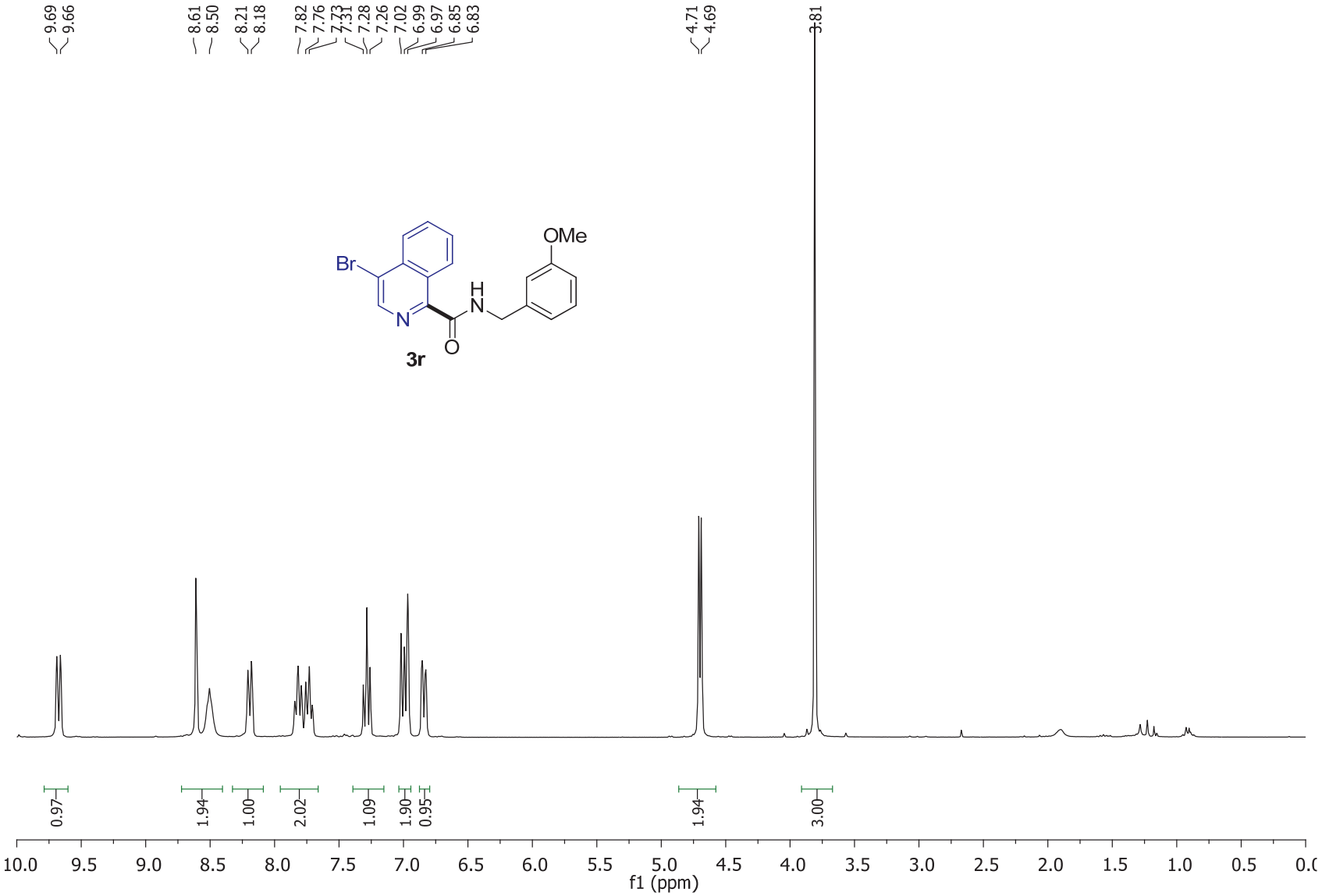
128.56
128.00
127.04
126.77
124.22
77.16 Chloroform-d
39.64
31.62
29.69
26.84
22.65
14.11
CH3
H
N
N
O
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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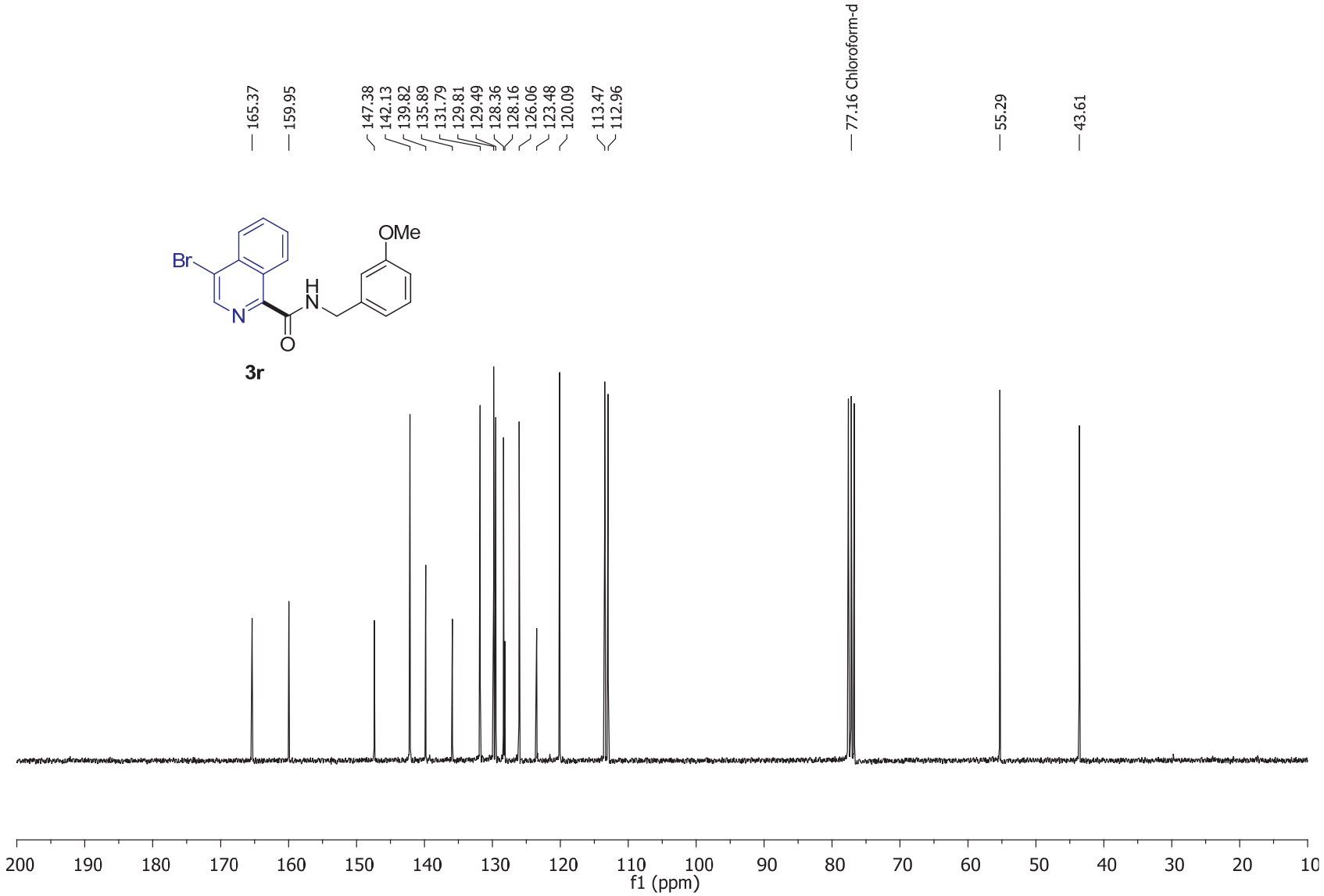
8.18
7.82
7.76
7.73
7.31
7.28
7.26
7.02
6.99
6.97
6.85
6.83
4.71
4.69
3.81
Br
N
H
N
O
OMe
3r
0.97
1.94
1.00
2.02
1.09
1.90
0.95
1.94
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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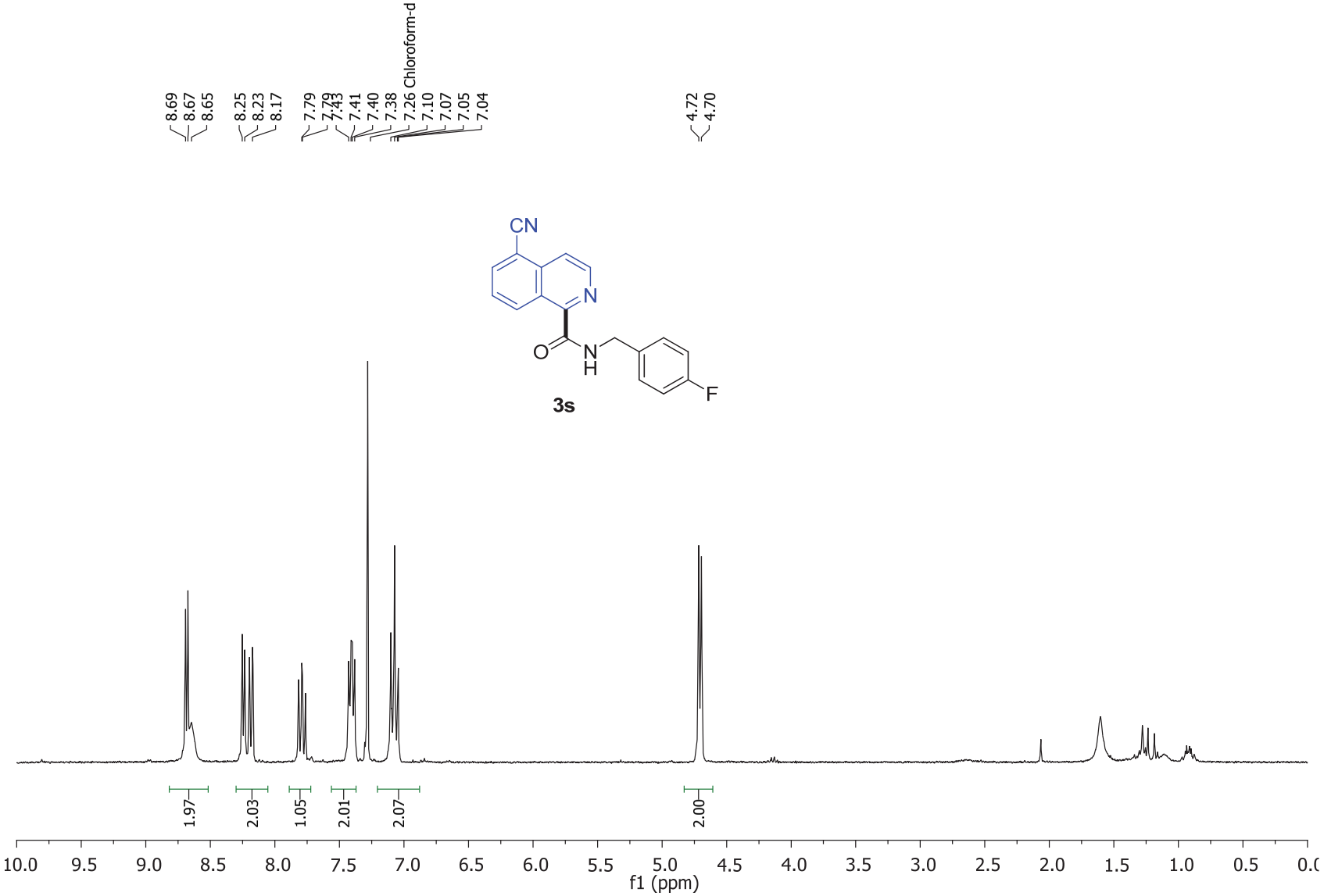
159.95
147.38
142.13
139.82
135.89
131.79
129.81
129.49
128.36
128.16
126.06
123.48
120.09
113.47
112.96
77.16 Chloroform-d
55.29
43.61
Br
N
H
N
O
OMe
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.69
8.67
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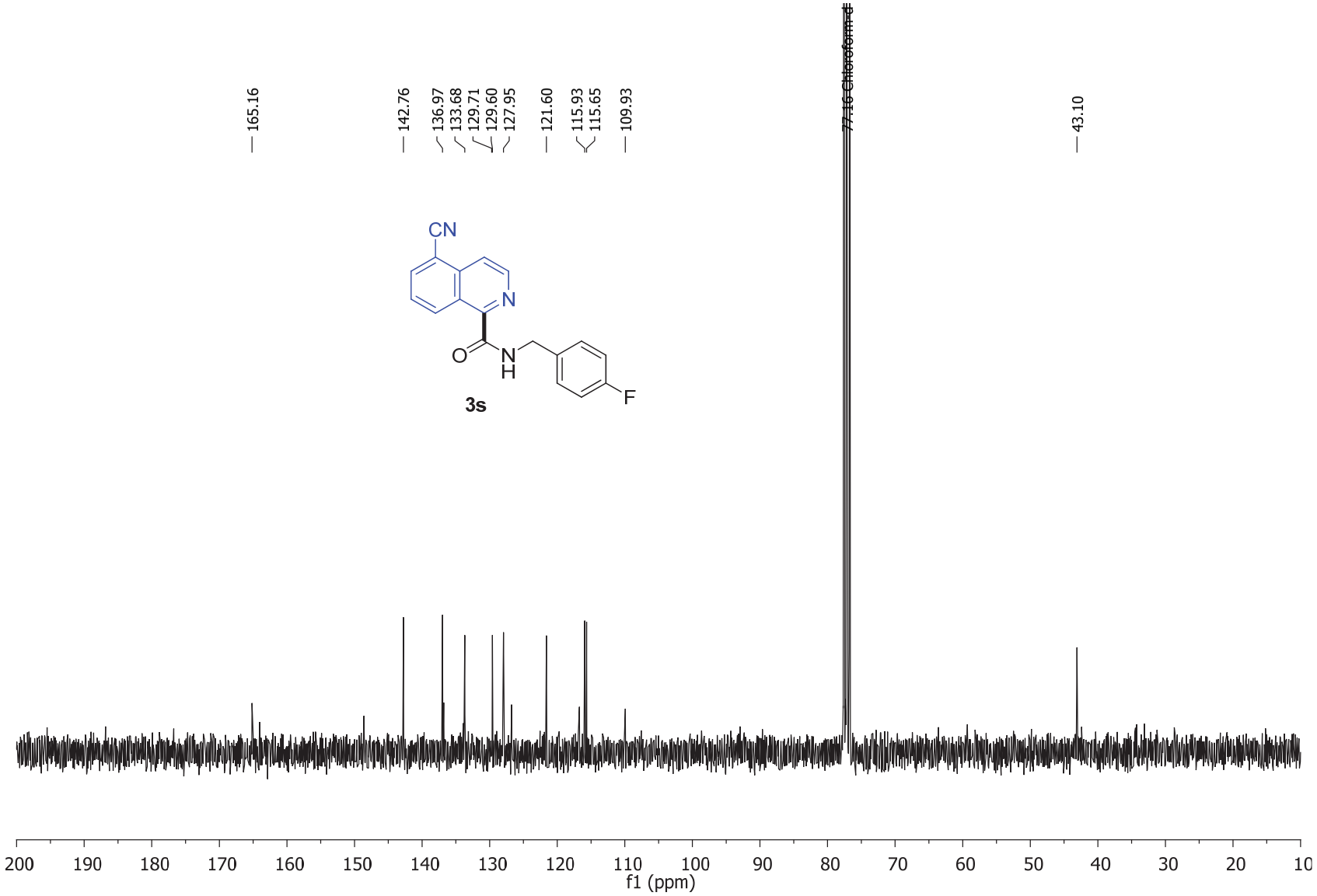
8.25
8.23
8.17
7.79
7.79
7.43
7.41
7.40
7.38
7.26 Chloroform-d
7.10
7.07
7.05
7.04
4.72
4.70
CN
N
O
N
H
F
3s
1.97
2.03
1.05
2.01
2.07
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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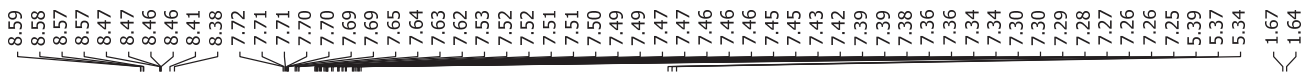
142.76
136.97
133.68
129.71
129.60
127.95
121.60
115.93
115.65
109.93
77.16 Chloroform-d
43.10
CN
N
O
N
H
F
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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8.57
8.57
8.47
8.47
8.46
8.46
8.41
8.38
7.72
7.71
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7.70
7.70
7.69
7.69
7.65
7.64
7.63
7.62
7.53
7.52
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7.51
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7.47
7.47
7.46
7.46
7.46
7.45
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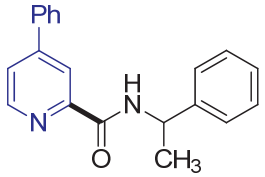
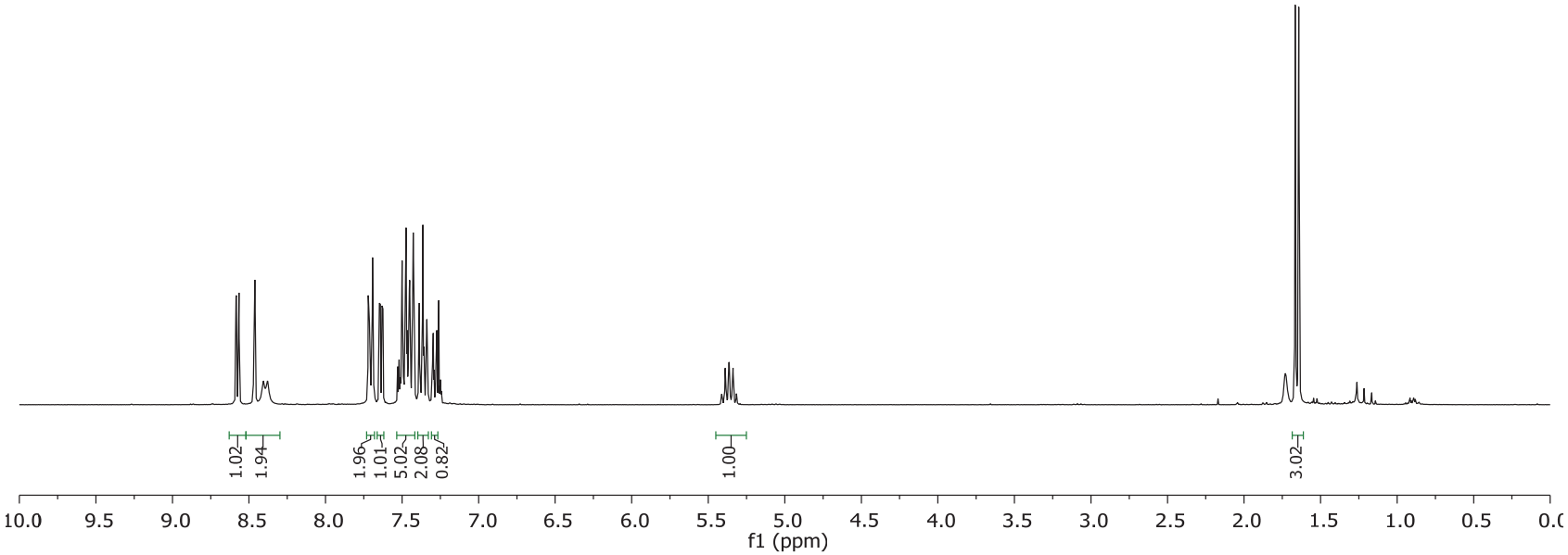
7.25
5.39
5.37
5.34
1.67
1.64


Ph
N
H
N
O
CH3

3t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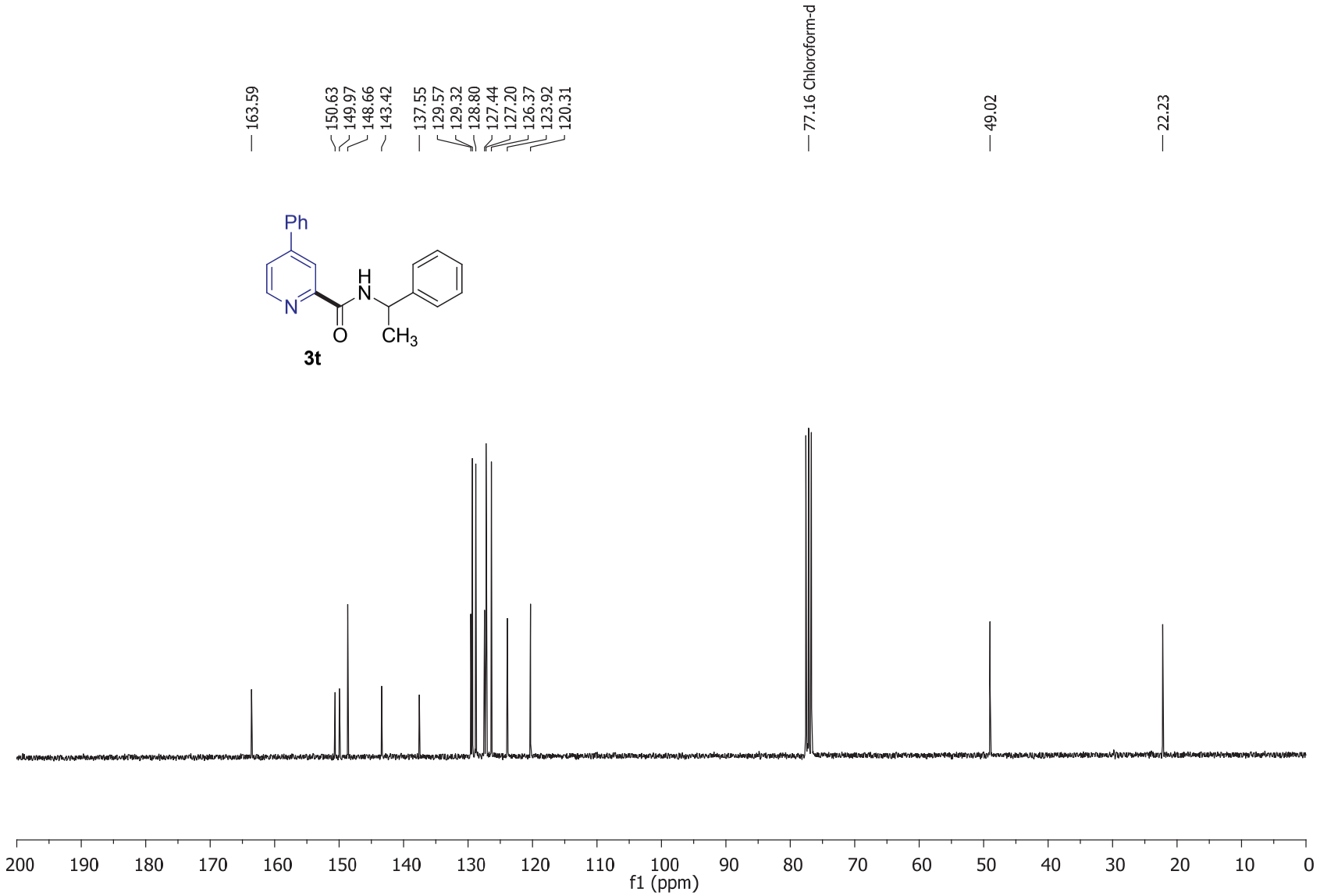
1.94
1.96
1.01
5.02
2.08
0.82
1.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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150.63
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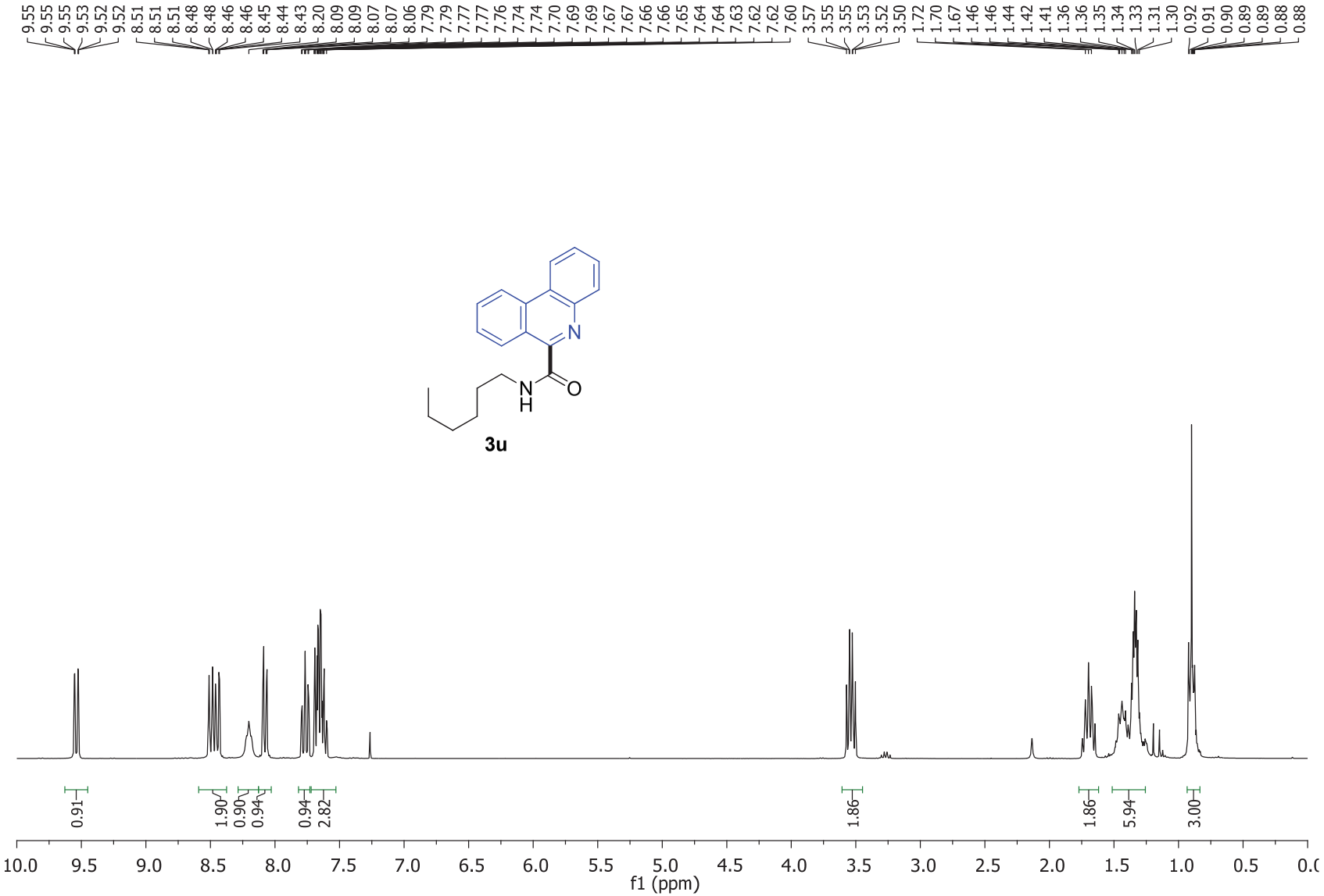
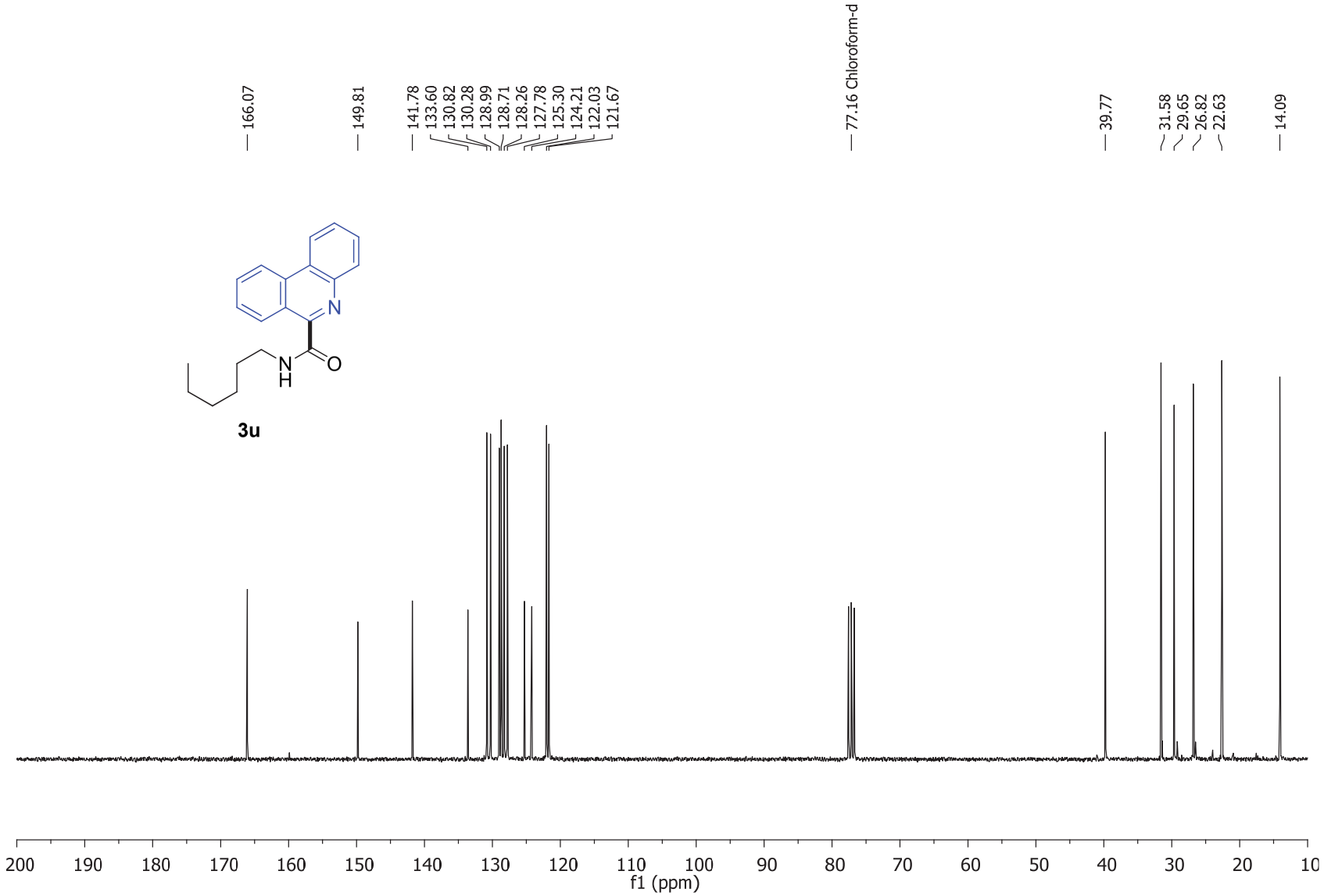
148.66
143.42
137.55
129.57
129.32
128.80
127.44
127.20
126.37
123.92
120.31
77.16 Chloroform-d
49.02
22.23
Ph
N
H
N
O
CH3
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.55 9.55 9.55 9.53 9.52 9.52 8.51 8.51 8.51 8.48 8.48 8.46 8.46 8.45 8.44 8.43 8.20 8.09 8.09 8.07 8.07 8.06 7.79 7.79 7.77 7.77 7.76 7.74 7.74 7.70 7.69 7.69 7.67 7.67 7.66 7.66 7.65 7.64 7.64 7.63 7.62 7.62 7.60 3.57 3.55 3.55 3.53 3.52 3.50 1.72 1.70 1.67 1.46 1.46 1.44 1.42 1.41 1.36 1.35 1.34 1.33 1.31 1.30 0.92 0.91 0.90 0.89 0.89 0.88 0.88
N
N
H
O
3u
0.91
1.90
0.90
0.94
0.94
2.82
1.86
1.86
5.94
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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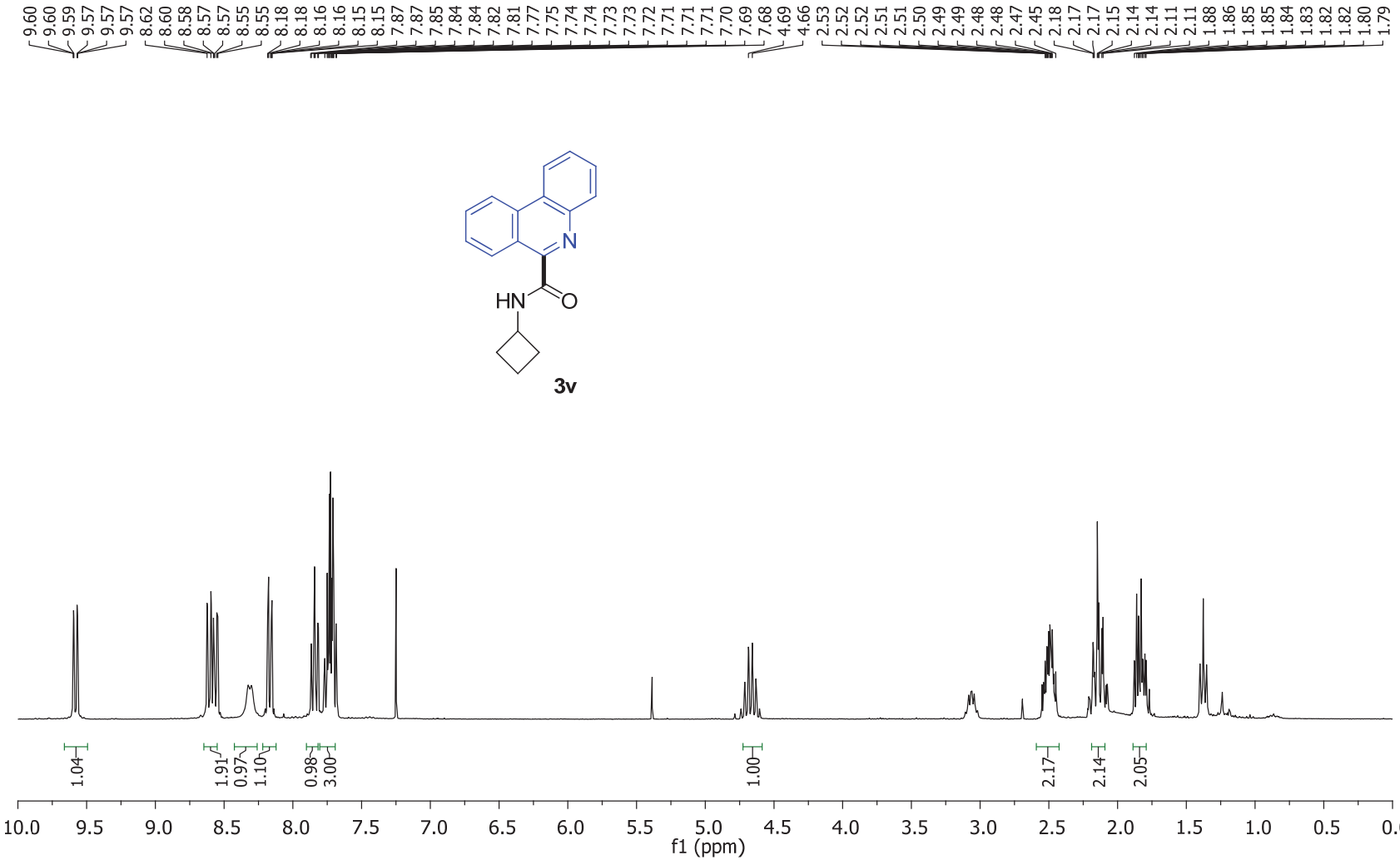
130.28
128.99
128.71
128.26
127.78
125.30
124.21
122.03
121.67
77.16 Chloroform-d
39.77
31.58
29.65
26.82
22.63
14.09
N
N
H
O
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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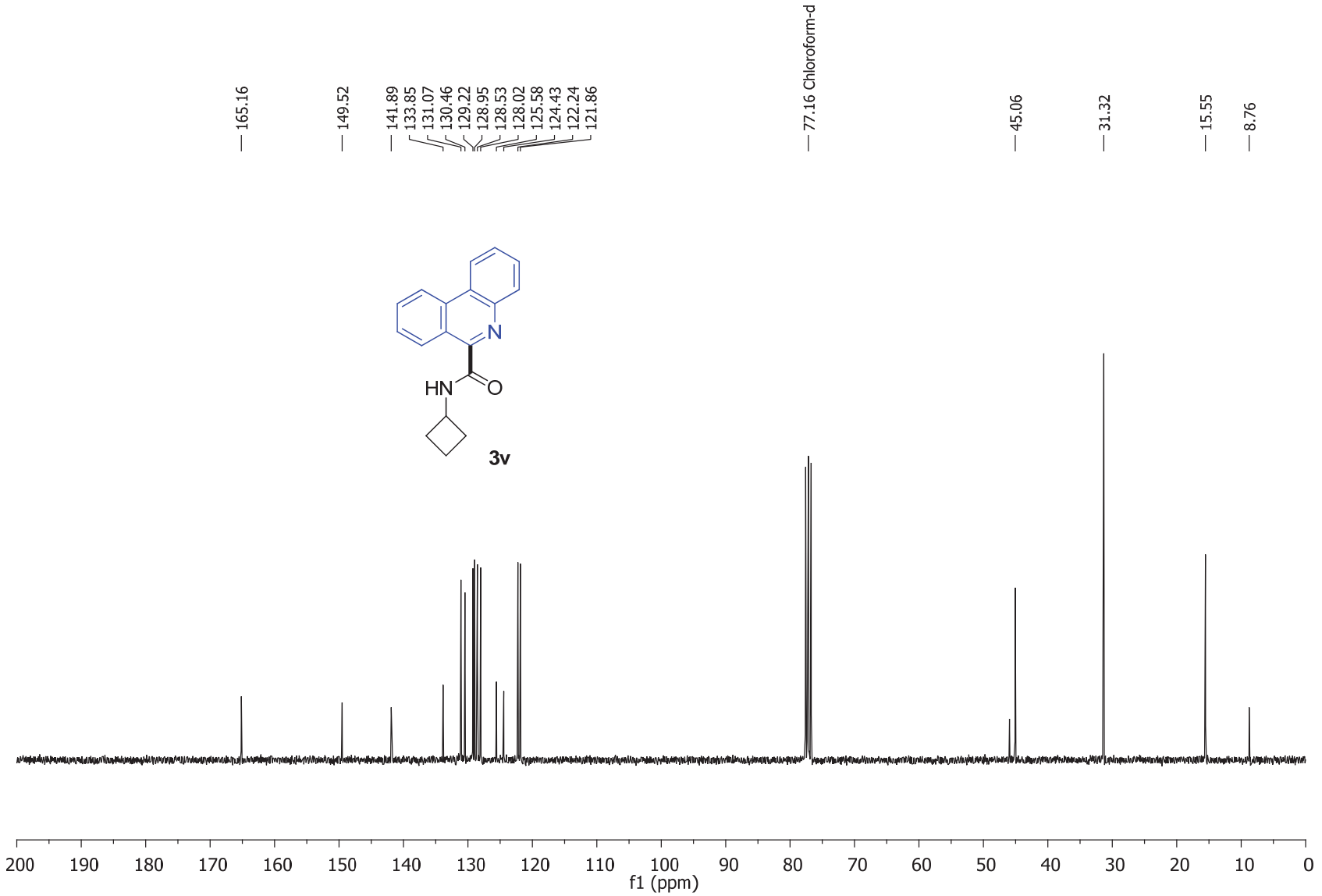
N
HN
O
3v
1.04
1.91
0.97
1.10
0.98
3.00
1.00
2.17
2.14
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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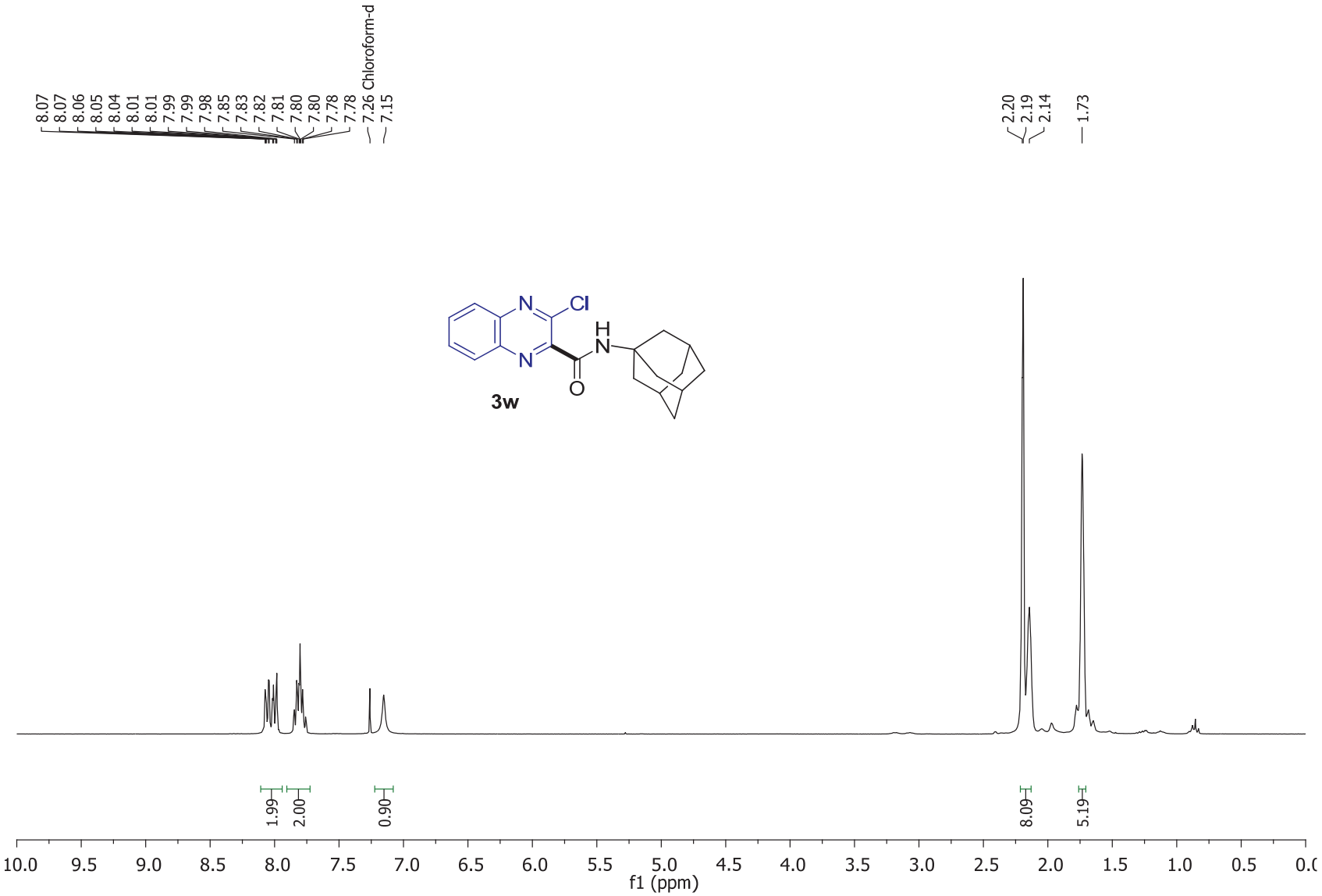
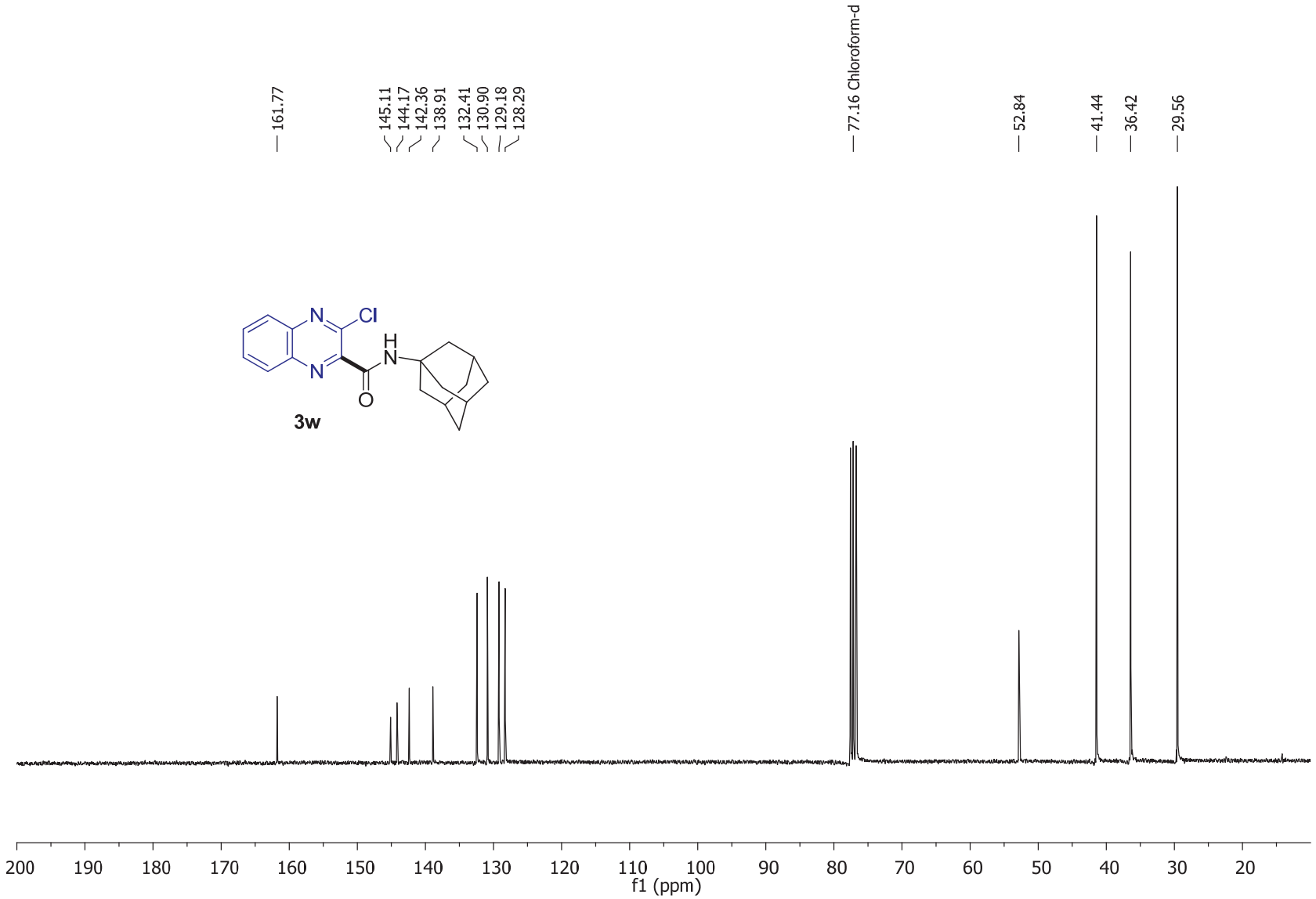
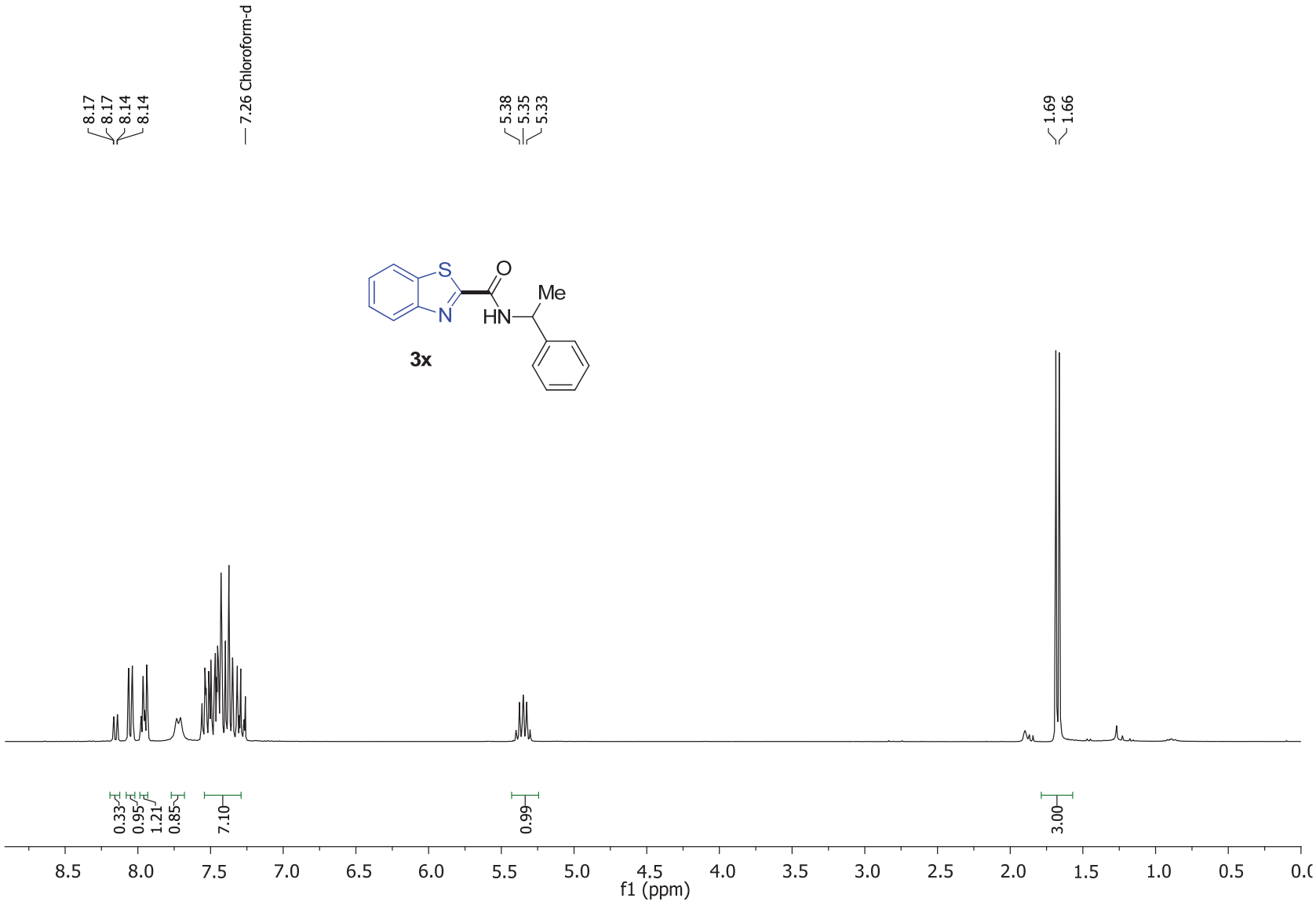
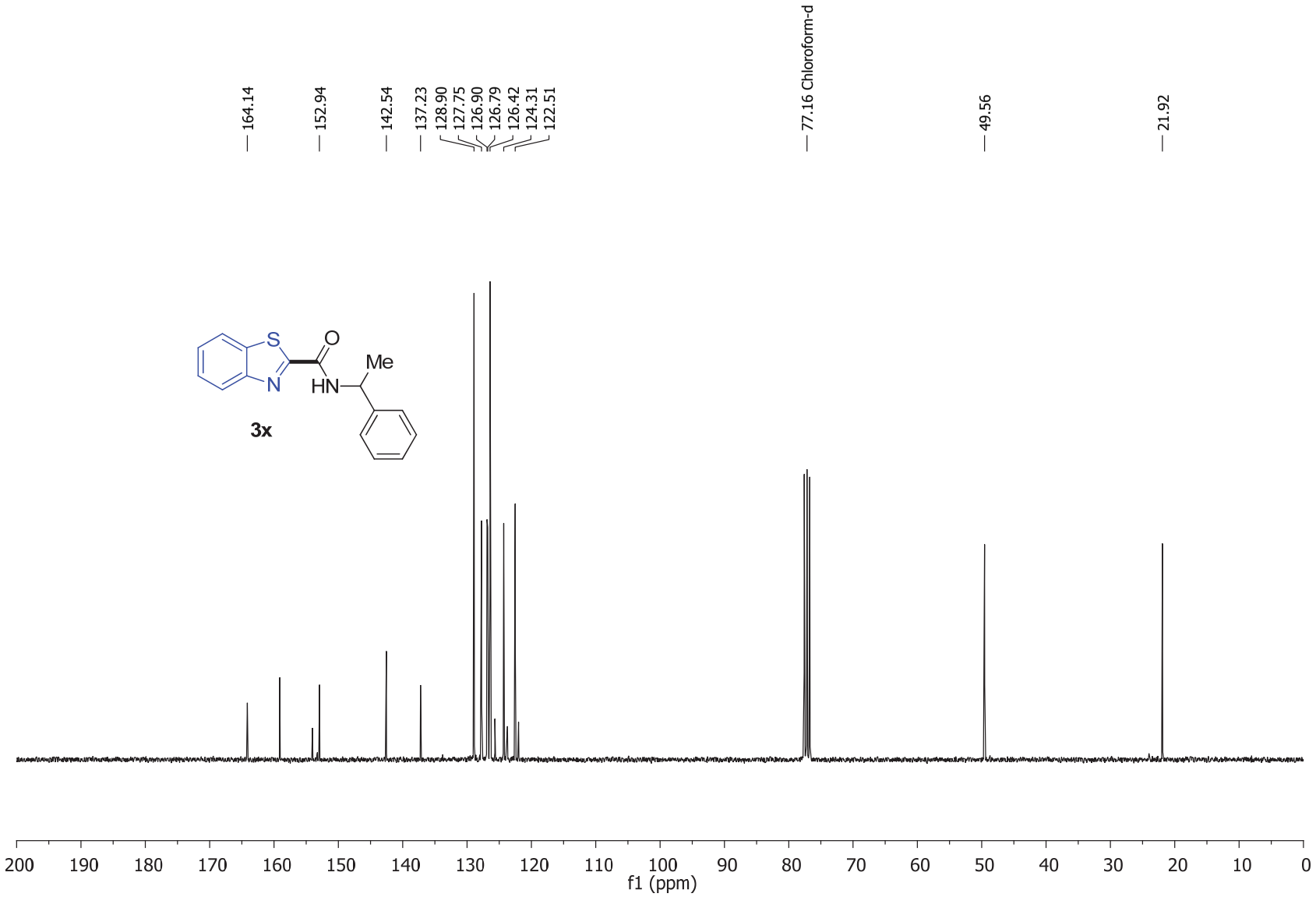
141.89
133.85
131.07
130.46
129.22
128.95
128.53
128.02
125.58
124.43
122.24
121.86
77.16 Chloroform-d
45.06
31.32
15.55
8.76
N
HN
O
3v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.07
8.07
8.06
8.05
8.04
8.01
8.01
7.99
7.99
7.98
7.85
7.83
7.82
7.81
7.80
7.80
7.78
7.78
7.26 Chloroform-d
7.15
2.20
2.19
2.14
1.73
N
Cl
H
N
N
O
3w
1.99
2.00
0.90
8.09
5.19
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
f1 (ppm)


161.77
145.11
144.17
142.36
138.91
132.41
130.90
129.18
128.29
77.16 Chloroform-d
52.84
41.44
36.42
29.56
N
Cl
H
N
O
3w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.17
8.17
8.14
8.14
7.26 Chloroform-d
5.38
5.35
5.33
1.69
1.66
S
O
N
HN
Me
3x
0.33
0.95
1.21
0.85
7.10
0.99
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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152.94
142.54
137.23
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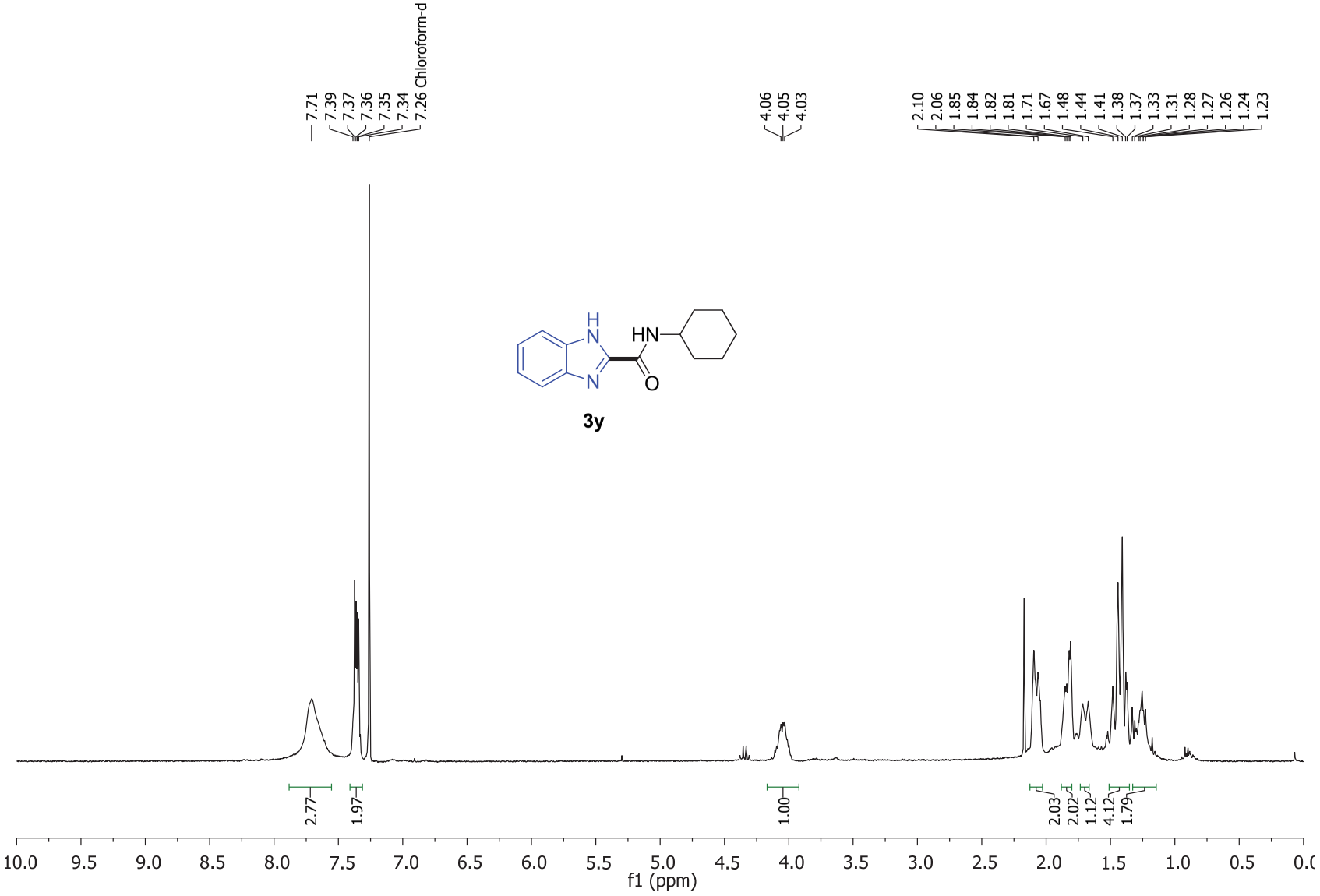
127.75
126.90
126.79
126.42
124.31
122.51
77.16 Chloroform-d
49.56
21.92
S
O
N
HN
Me
3x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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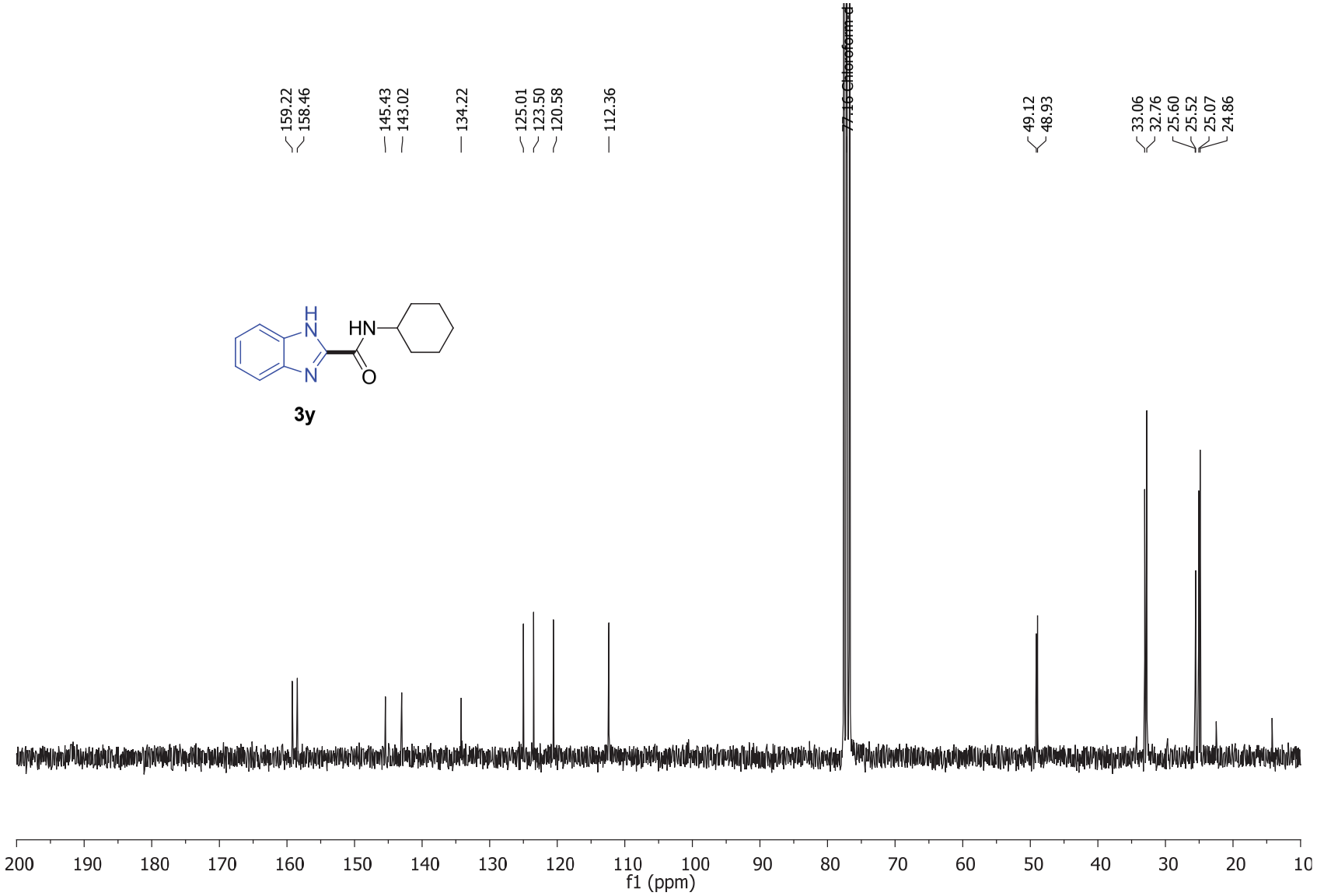
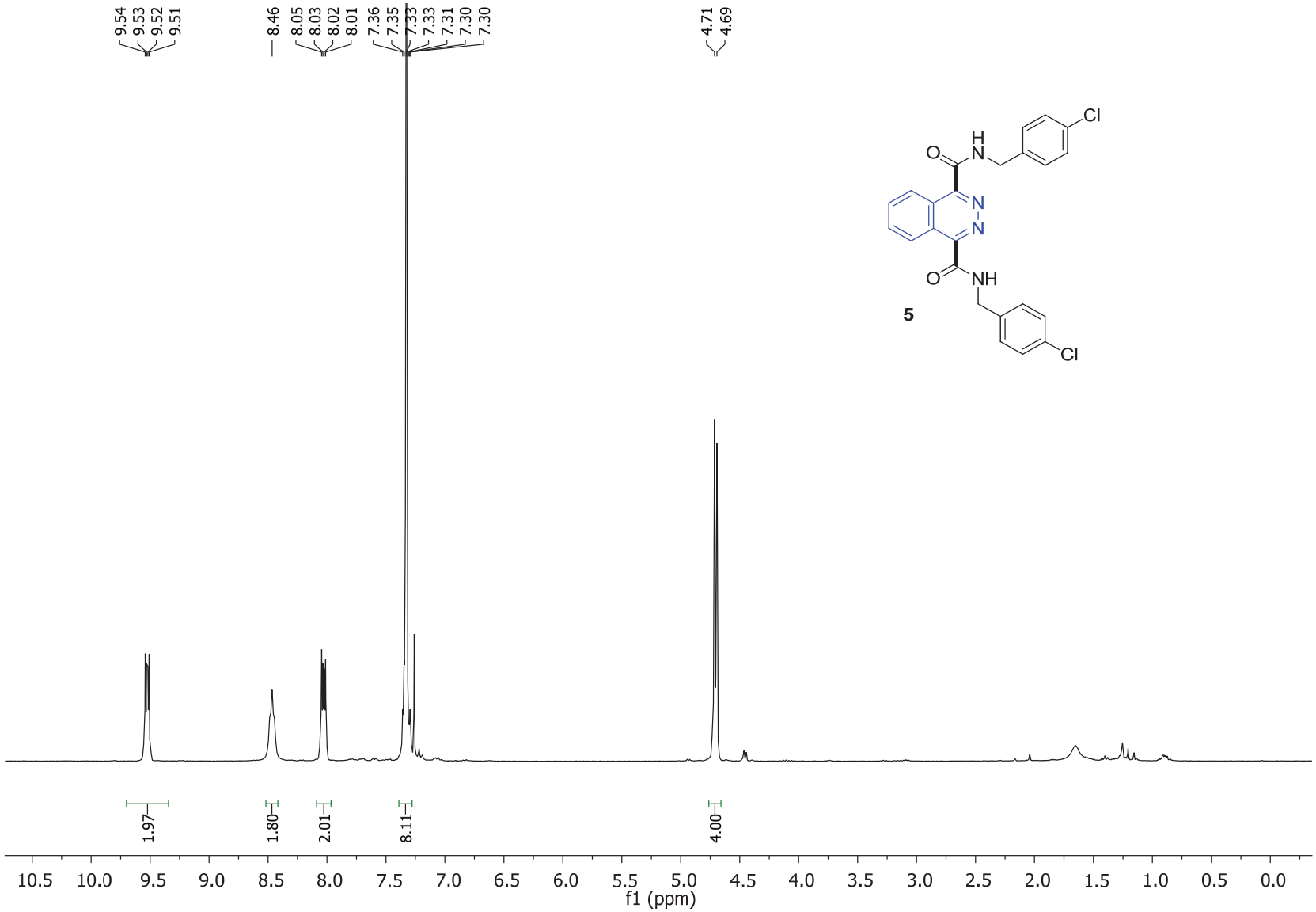
7.37
7.36
7.35
7.34
7.26 Chloroform-d
4.06
4.05
4.03
2.10
2.06
1.85
1.84
1.82
1.81
1.71
1.67
1.48
1.44
1.41
1.38
1.37
1.33
1.31
1.28
1.27
1.26
1.24
1.23
H
N
HN
N
O
2.77
1.97
1.00
2.03
2.02
1.12
4.12
1.79
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3y


159.22
158.46
145.43
143.02
134.22
125.01
123.50
120.58
112.36
77.16 Chloroform-d
49.12
48.93
33.06
32.76
25.60
25.52
25.07
24.86
H
N
HN
N
O
3y
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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9.52
9.51
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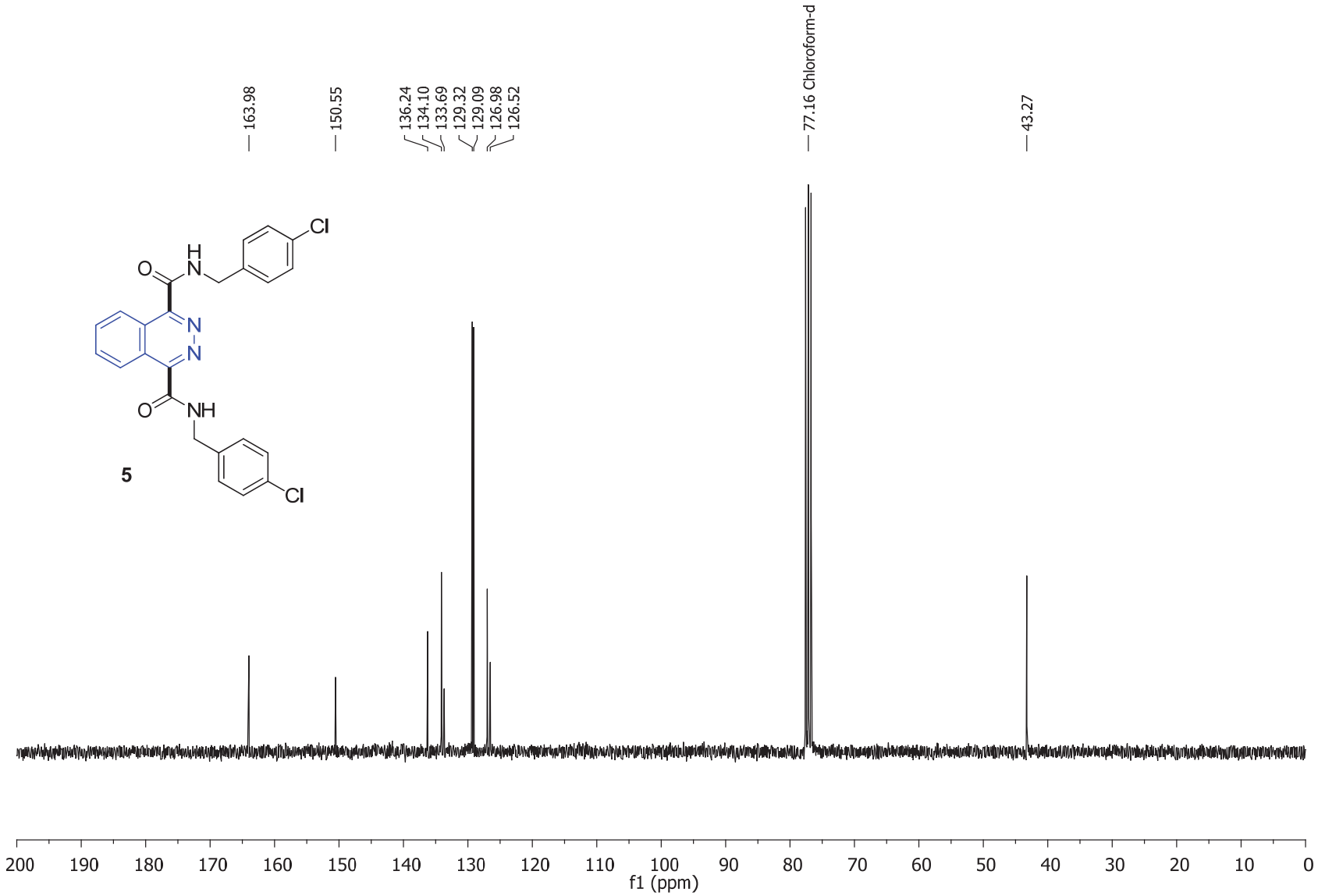
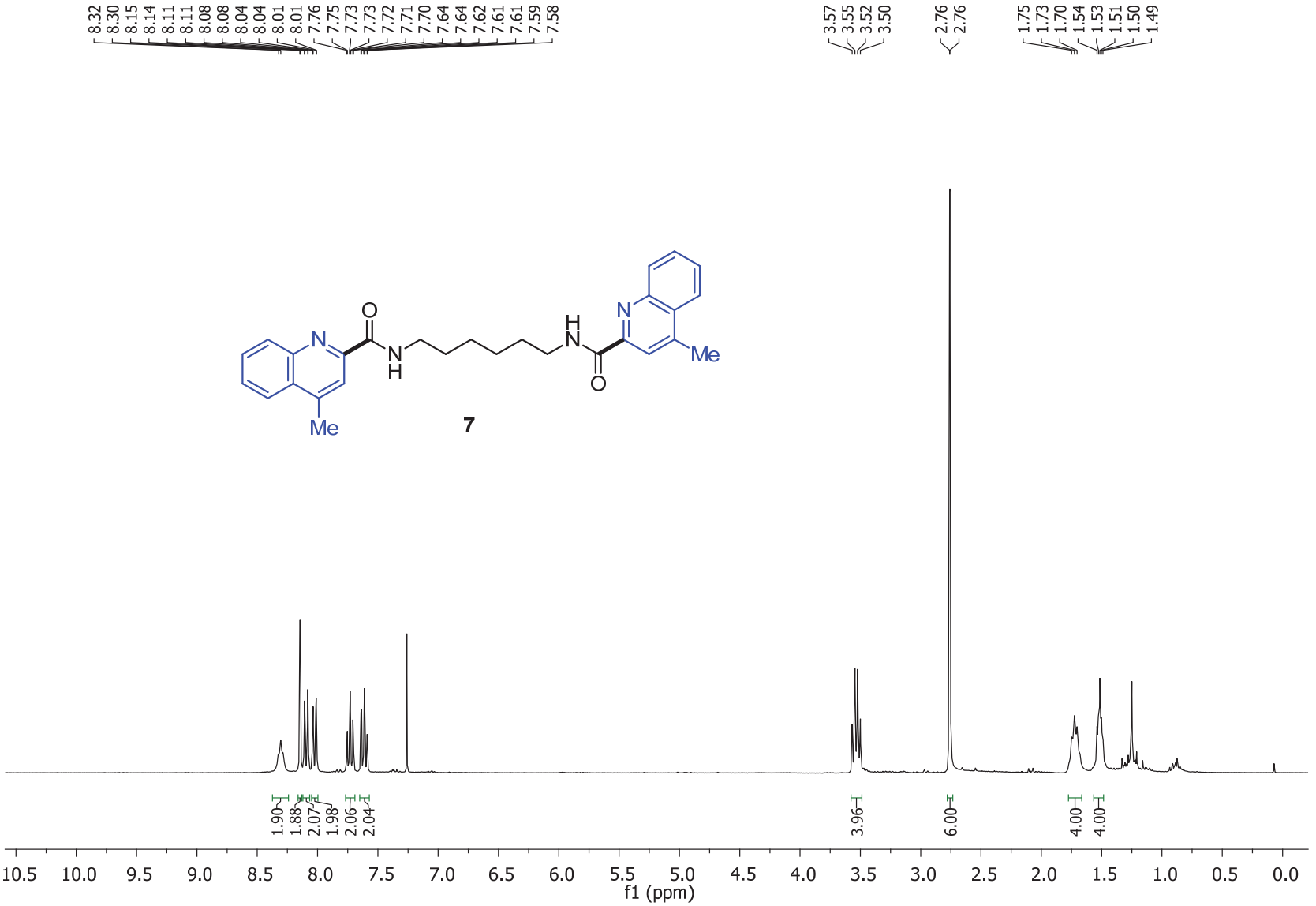
8.05
8.03
8.02
8.01
7.36
7.35
7.33
7.33
7.31
7.30
7.30
4.71
4.69
Cl
H
N
O
N
N
O
NH
Cl
5
1.97
1.80
2.01
8.11
4.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.98
150.55
136.24
134.10
133.69
129.32
129.09
126.98
126.52
77.16 Chloroform-d
43.27
Cl
H
N
O
N
N
O
NH
Cl
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.15
8.14
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8.11
8.08
8.08
8.04
8.04
8.01
8.01
7.76
7.75
7.73
7.73
7.72
7.71
7.70
7.64
7.64
7.62
7.61
7.61
7.59
7.58
3.57
3.55
3.52
3.50
2.76
2.76
1.75
1.73
1.70
1.54
1.53
1.51
1.50
1.49
N
O
N
H
N
H
O
N
Me
Me
1.90
1.88
2.07
1.98
2.06
2.04
3.96
6.00
4.00
4.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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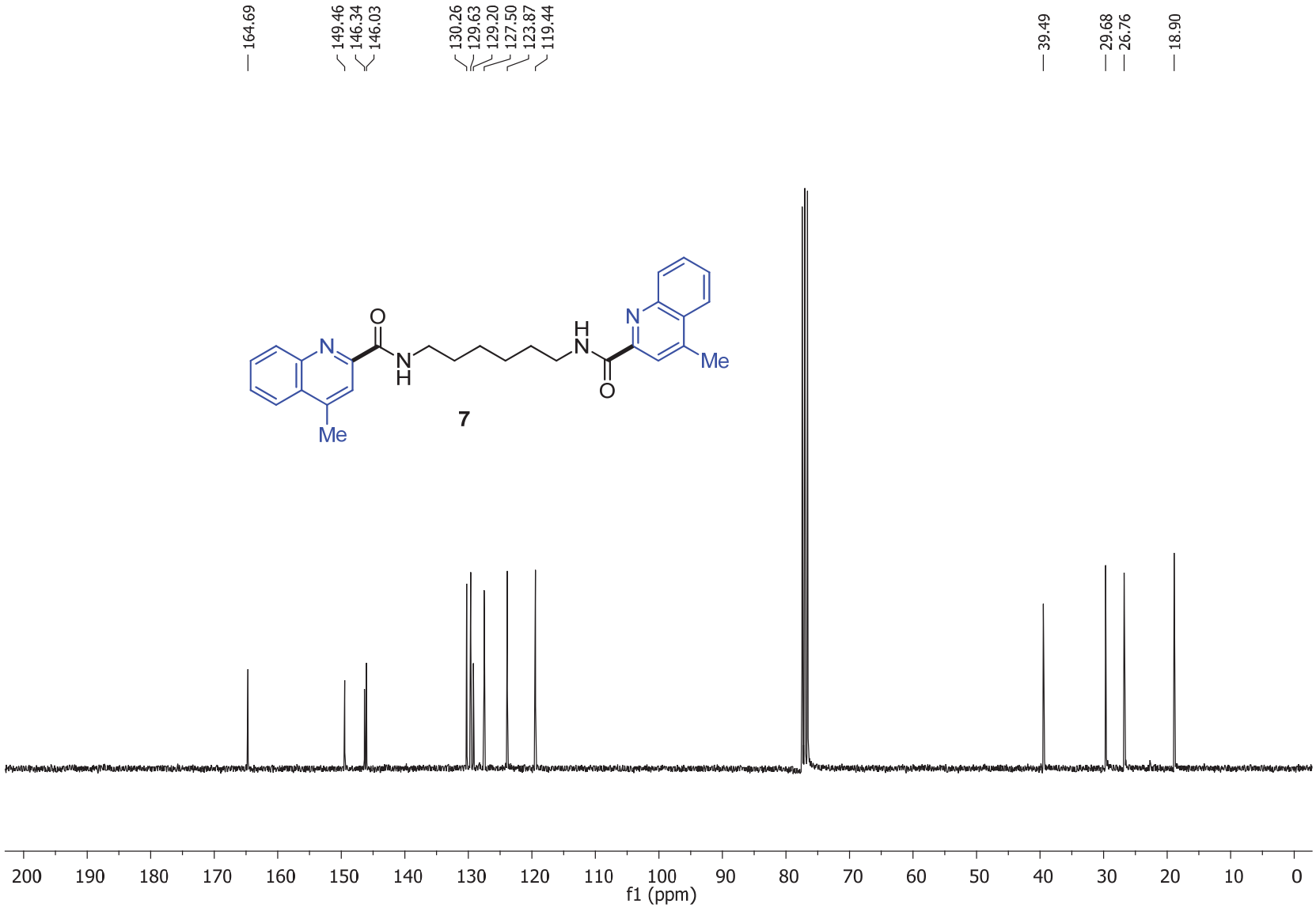
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

7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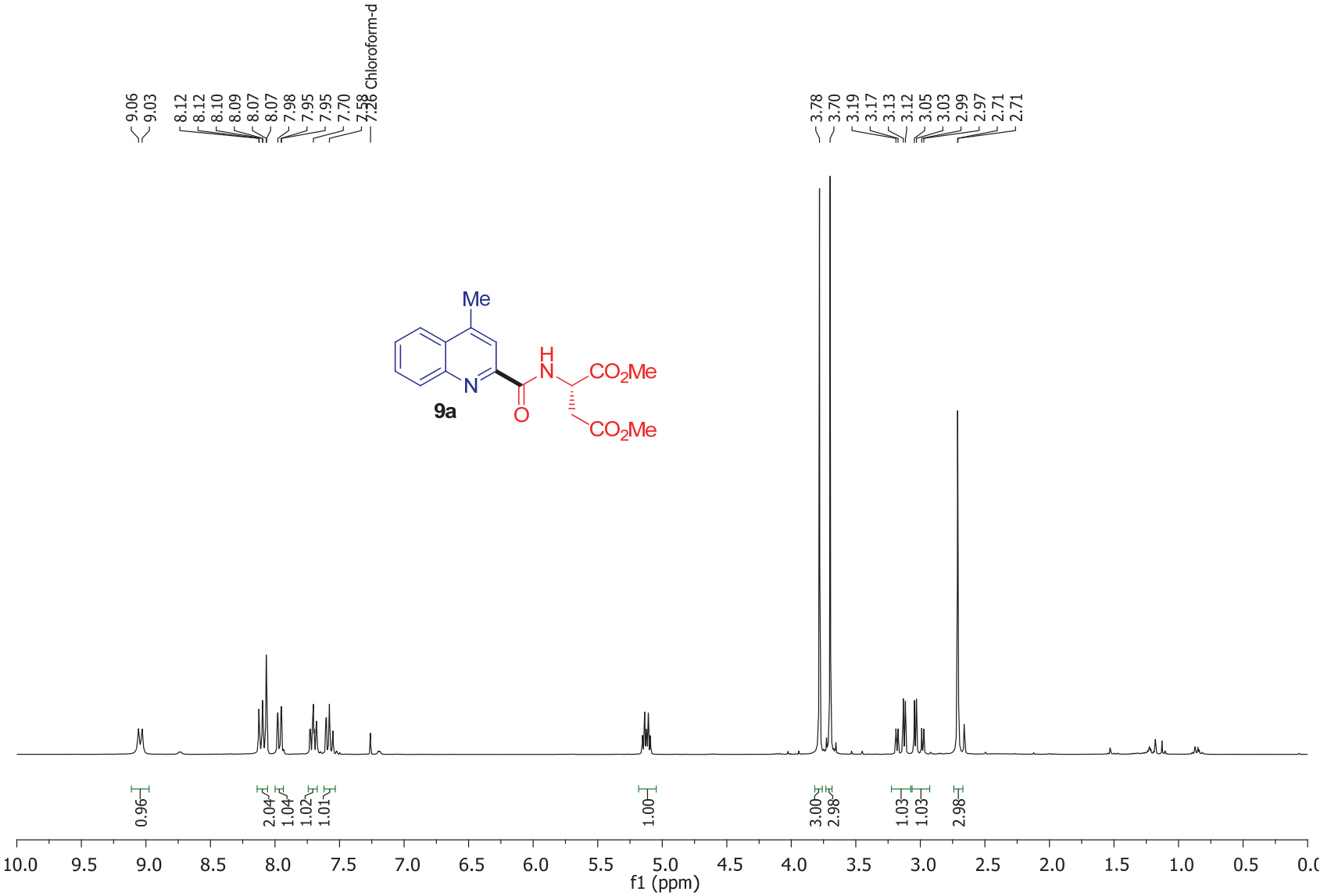
146.34
146.03
130.26
129.63
129.20
127.50
123.87
119.44
39.49
29.68
26.76
18.90
O
N
H
N
H
N
O
Me
Me
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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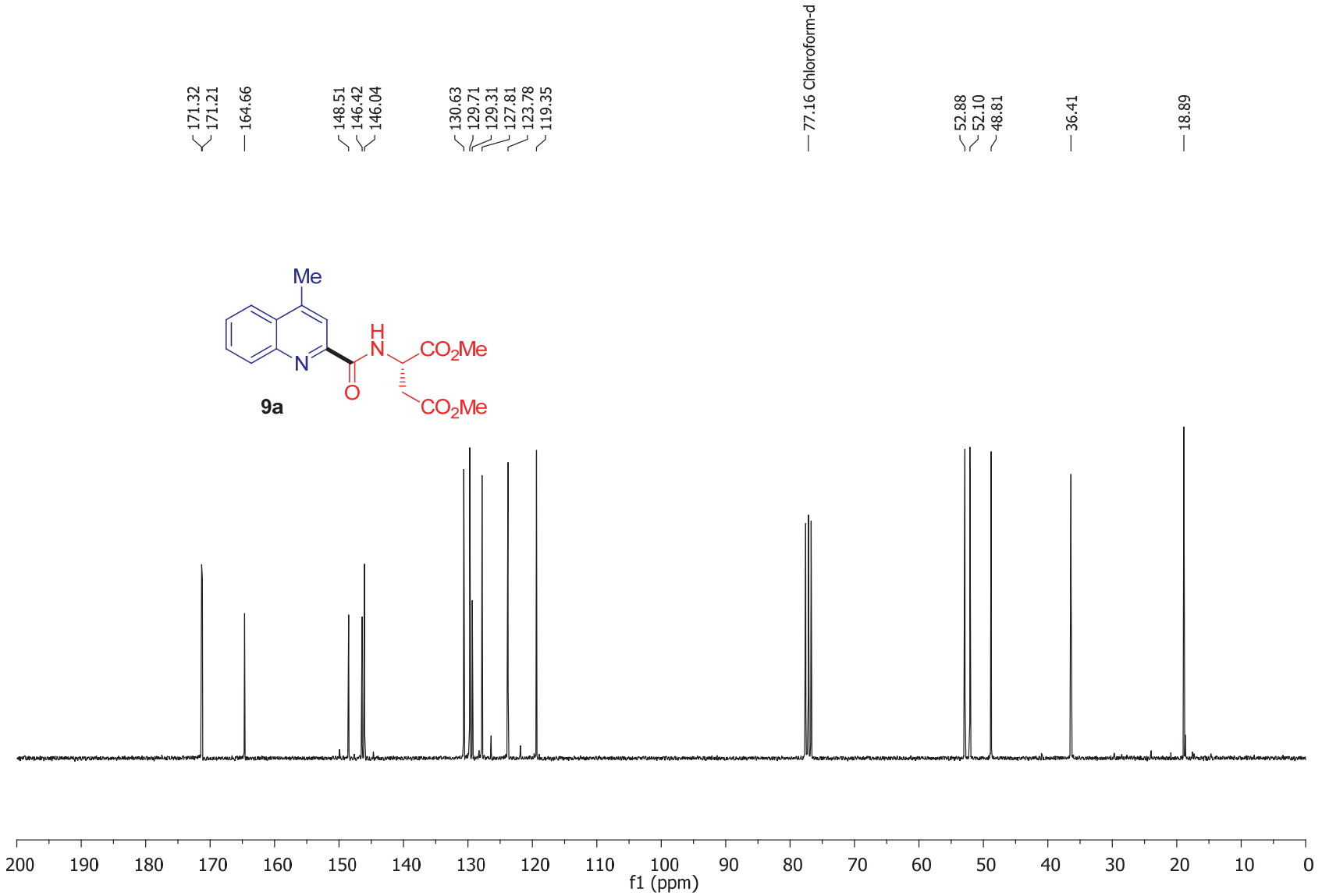
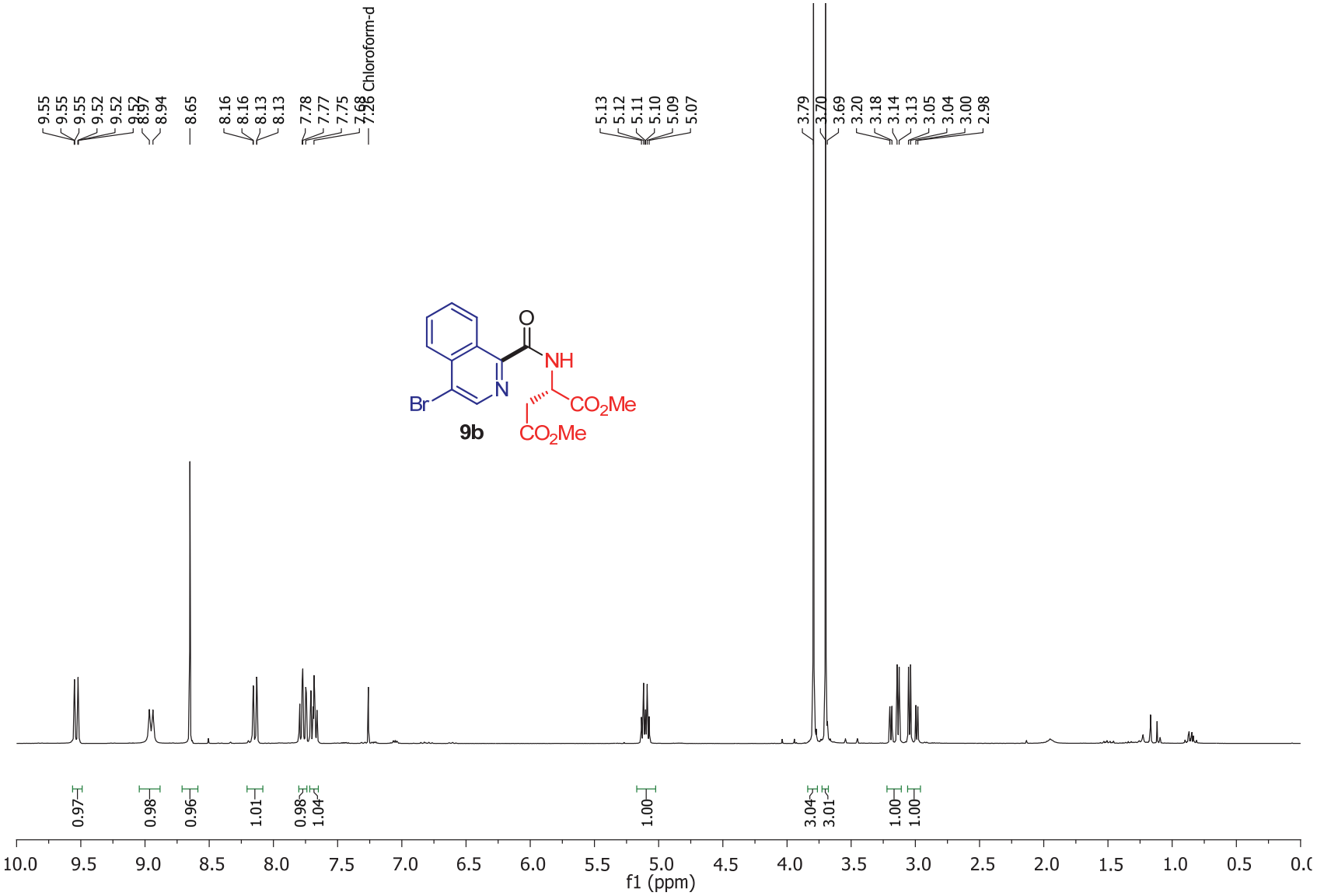
9.03
8.12
8.12
8.10
8.09
8.07
8.07
7.98
7.95
7.95
7.70
7.58
7.26 Chloroform-d
3.78
3.70
3.19
3.17
3.13
3.12
3.05
3.03
2.99
2.97
2.71
2.71
Me
N
H
N
CO2Me
CO2Me
O
9a
0.96
2.04
1.04
1.02
1.01
1.00
3.00
2.98
1.03
1.03
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


171.32
171.21
164.66
148.51
146.42
146.04
130.63
129.71
129.31
127.81
123.78
119.35
77.16 Chloroform-d
52.88
52.10
48.81
36.41
18.89
Me
N
H
N
CO2Me
O
CO2Me
9a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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9.55
9.55
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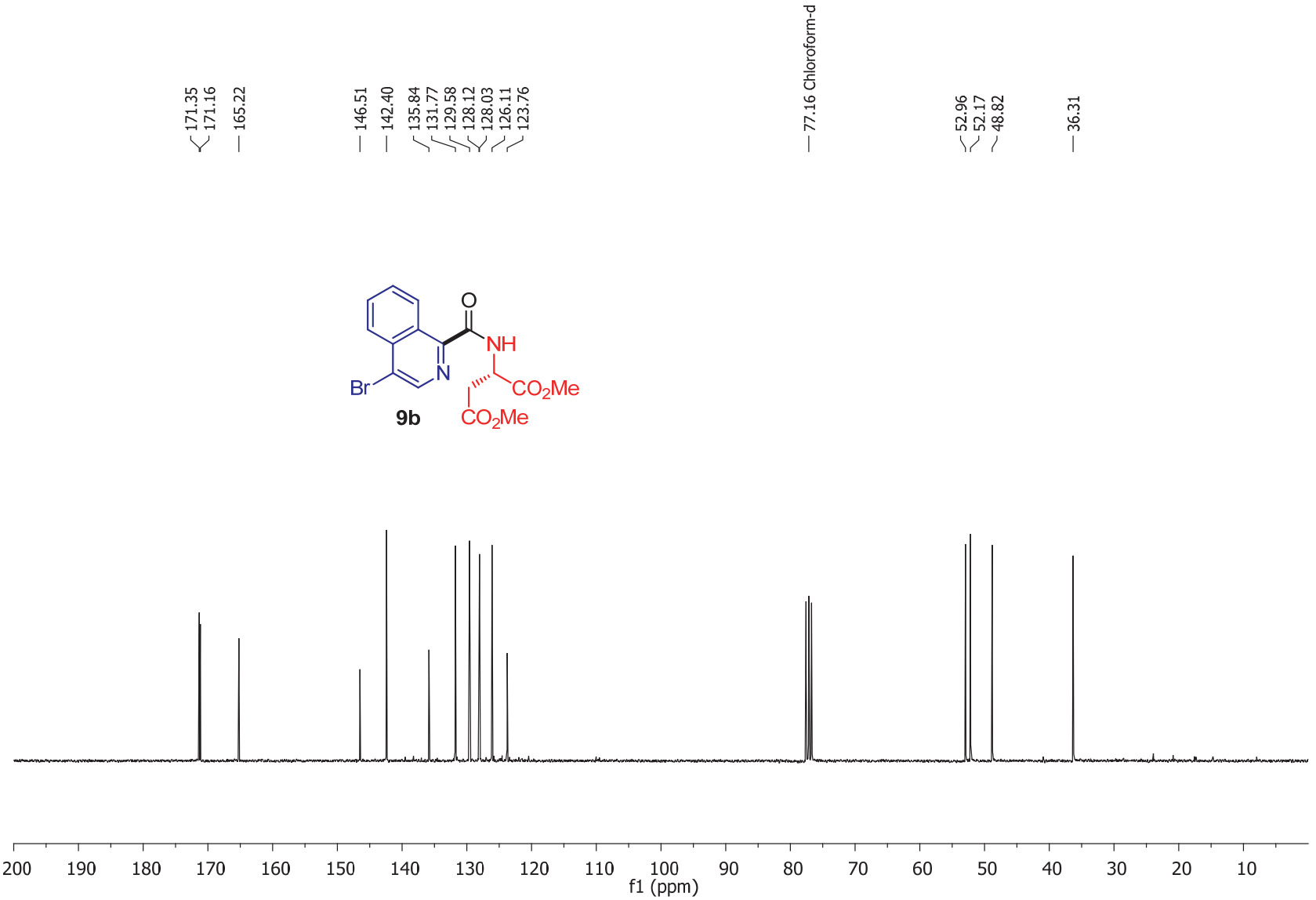
9.52
8.97
8.94
8.65
8.16
8.16
8.13
8.13
7.78
7.77
7.75
7.68
Chloroform-d
5.13
5.12
5.11
5.10
5.09
5.07
3.79
3.70
3.69
3.20
3.18
3.14
3.13
3.05
3.04
3.00
2.98
O
NH
N
Br
CO2Me
CO2Me
9b
0.97
0.98
0.96
1.01
0.98
1.04
1.00
3.04
3.01
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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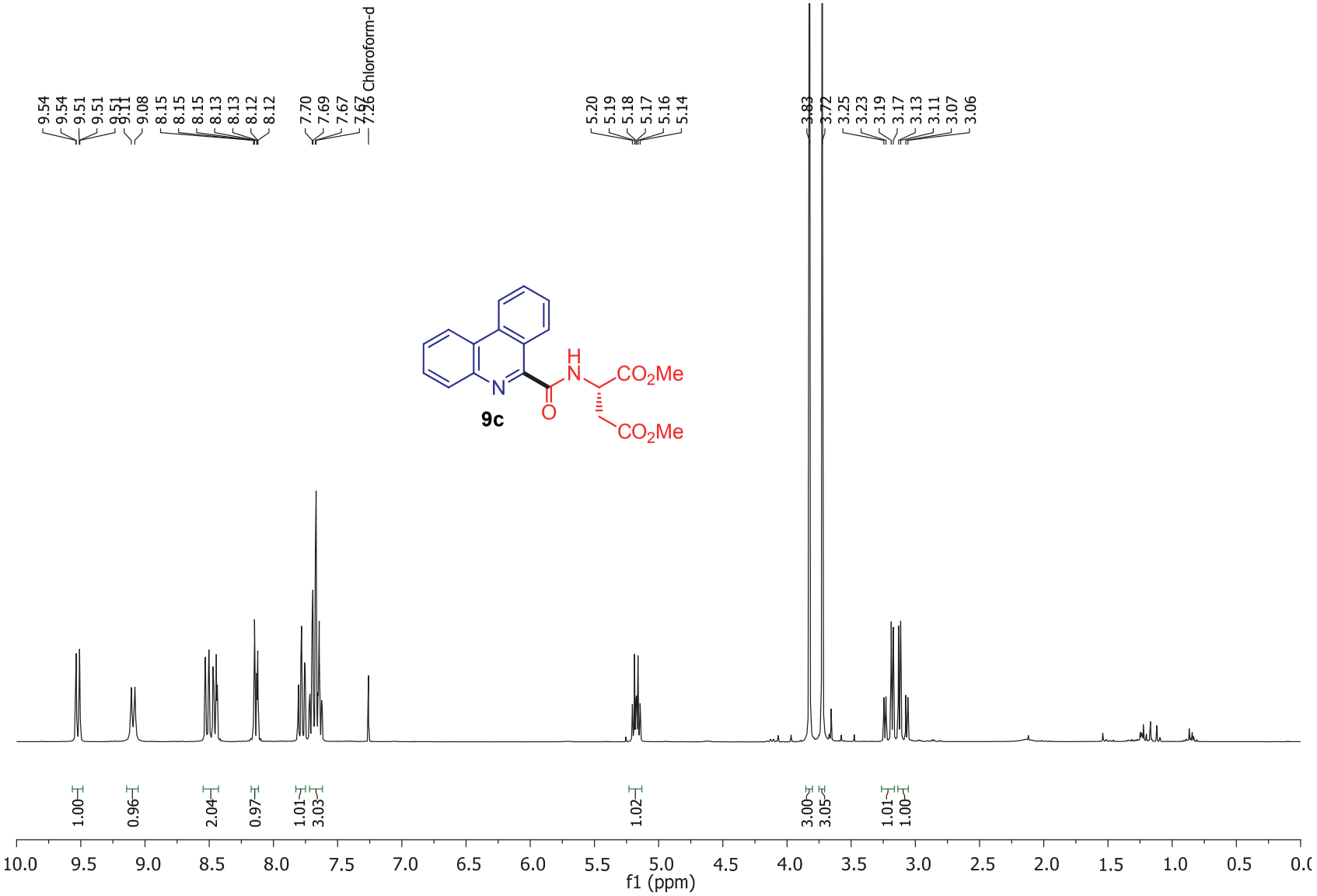
165.22
146.51
142.40
135.84
131.77
129.58
128.12
128.03
126.11
123.76
77.16 Chloroform-d
52.96
52.17
48.82
36.31
O
NH
N
Br
CO2Me
CO2Me
9b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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9.51
9.51
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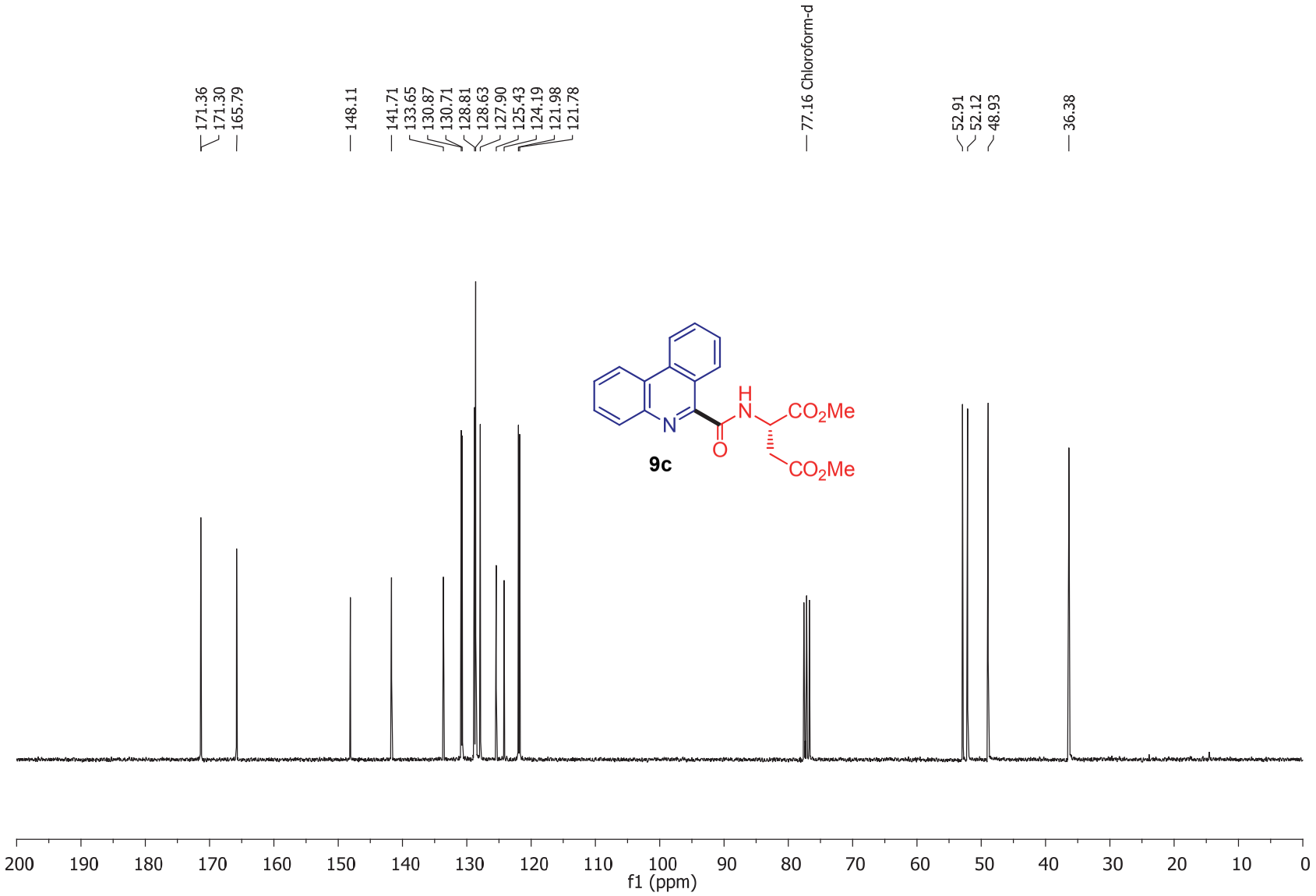
9.08
8.15
8.15
8.15
8.13
8.13
8.12
8.12
7.70
7.69
7.67
7.26 Chloroform-d
5.20
5.19
5.18
5.17
5.16
5.14
3.83
3.72
3.25
3.23
3.19
3.17
3.13
3.11
3.07
3.06
H
N
CO2Me
CO2Me
N
O
9c
1.00
0.96
2.04
0.97
1.01
3.03
1.02
3.00
3.05
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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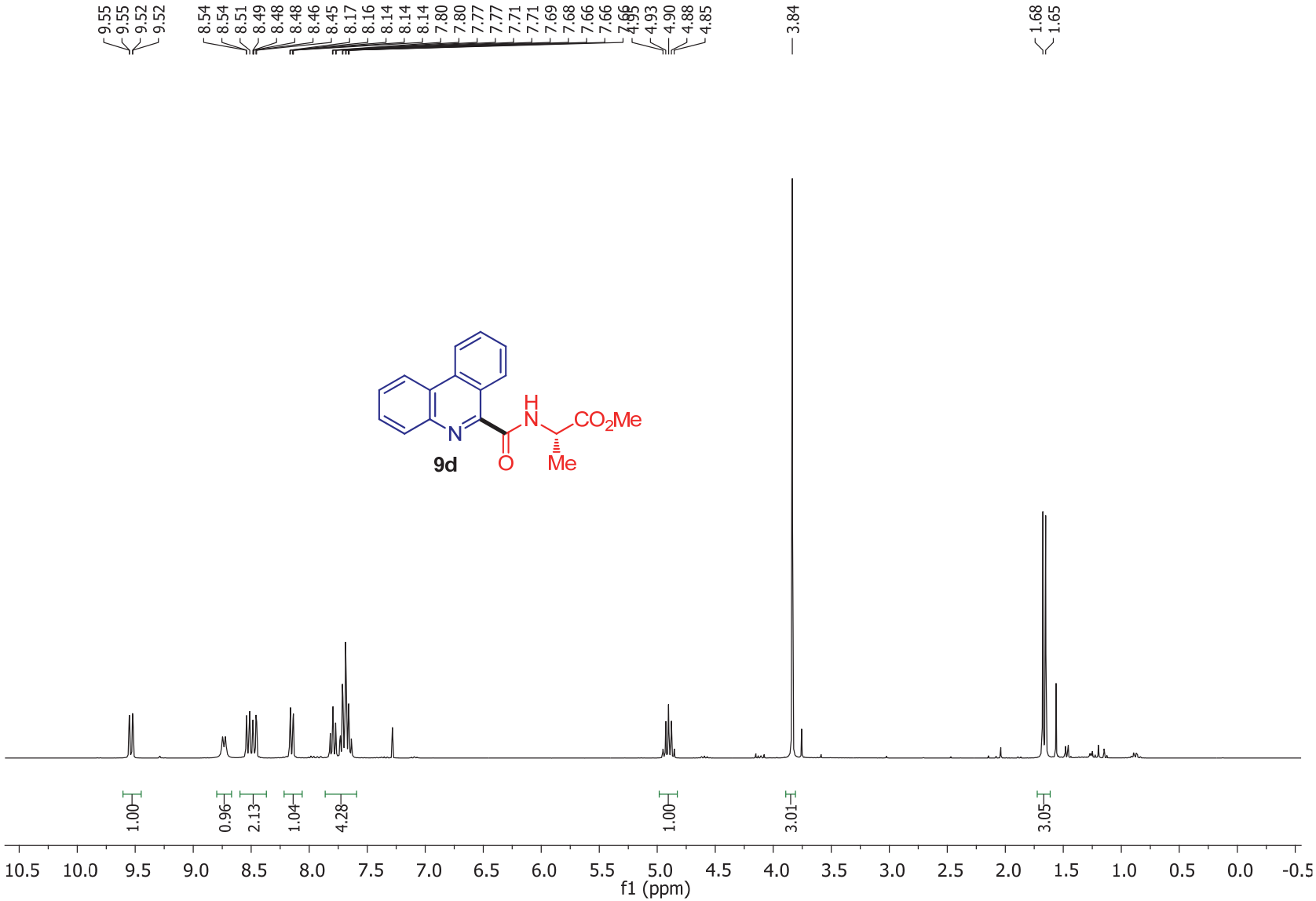
133.65
130.87
130.71
128.81
128.63
127.90
125.43
124.19
121.98
121.78
77.16 Chloroform-d
52.91
52.12
48.93
36.38
H
N
O
CO2Me
CO2Me
9c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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9.52
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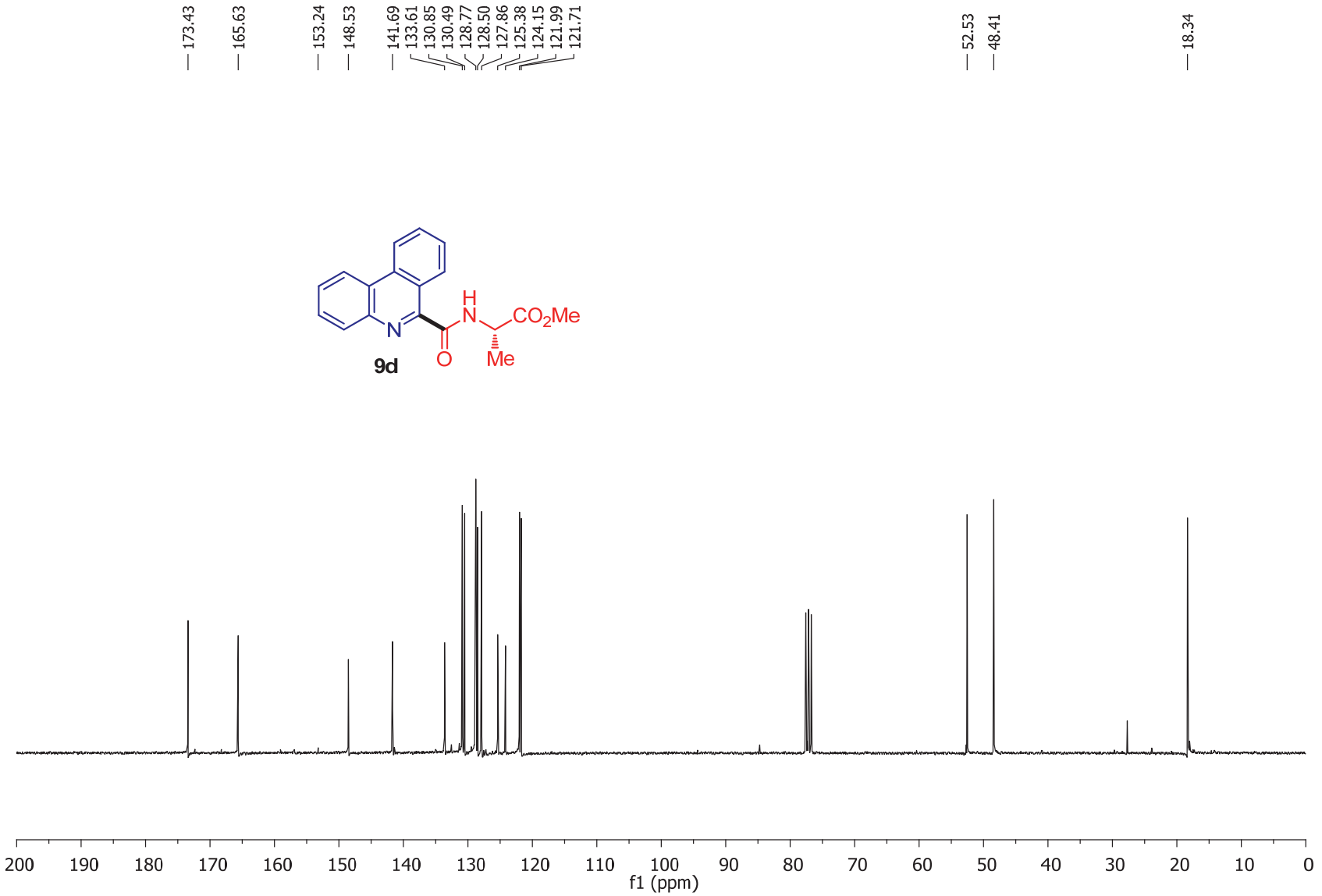
8.54
8.51
8.49
8.48
8.48
8.46
8.45
8.17
8.16
8.14
8.14
8.14
7.80
7.77
7.77
7.71
7.71
7.69
7.68
7.66
7.66
7.66
4.93
4.90
4.88
4.85
3.84
1.68
1.65
9d
H
N
CO2Me
N
O
Me
1.00
0.96
2.13
1.04
4.28
1.00
3.01
3.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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130.49
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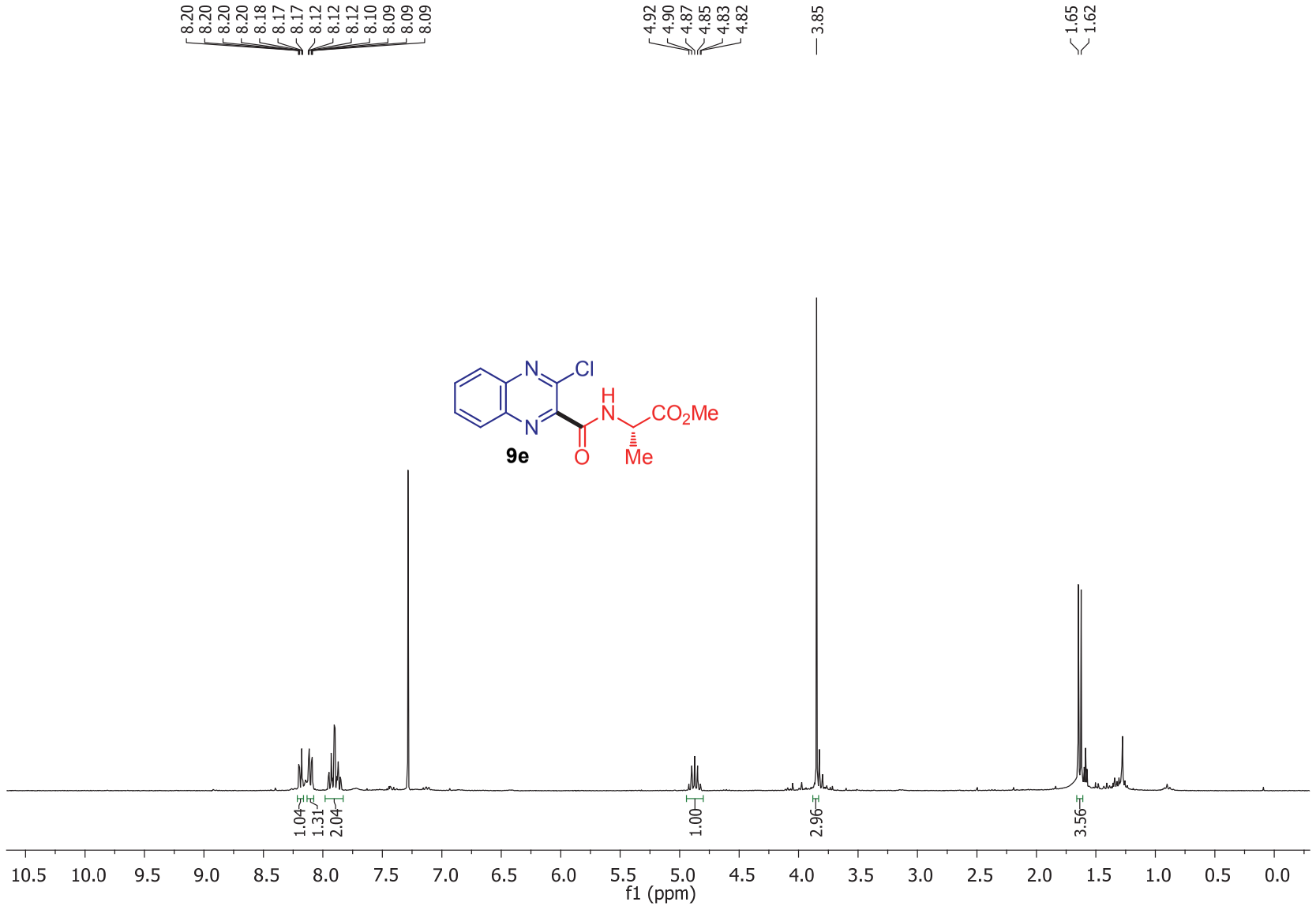
128.50
127.86
125.38
124.15
121.99
121.71
52.53
48.41
18.34
H
N
CO2Me
N
O
Me
9d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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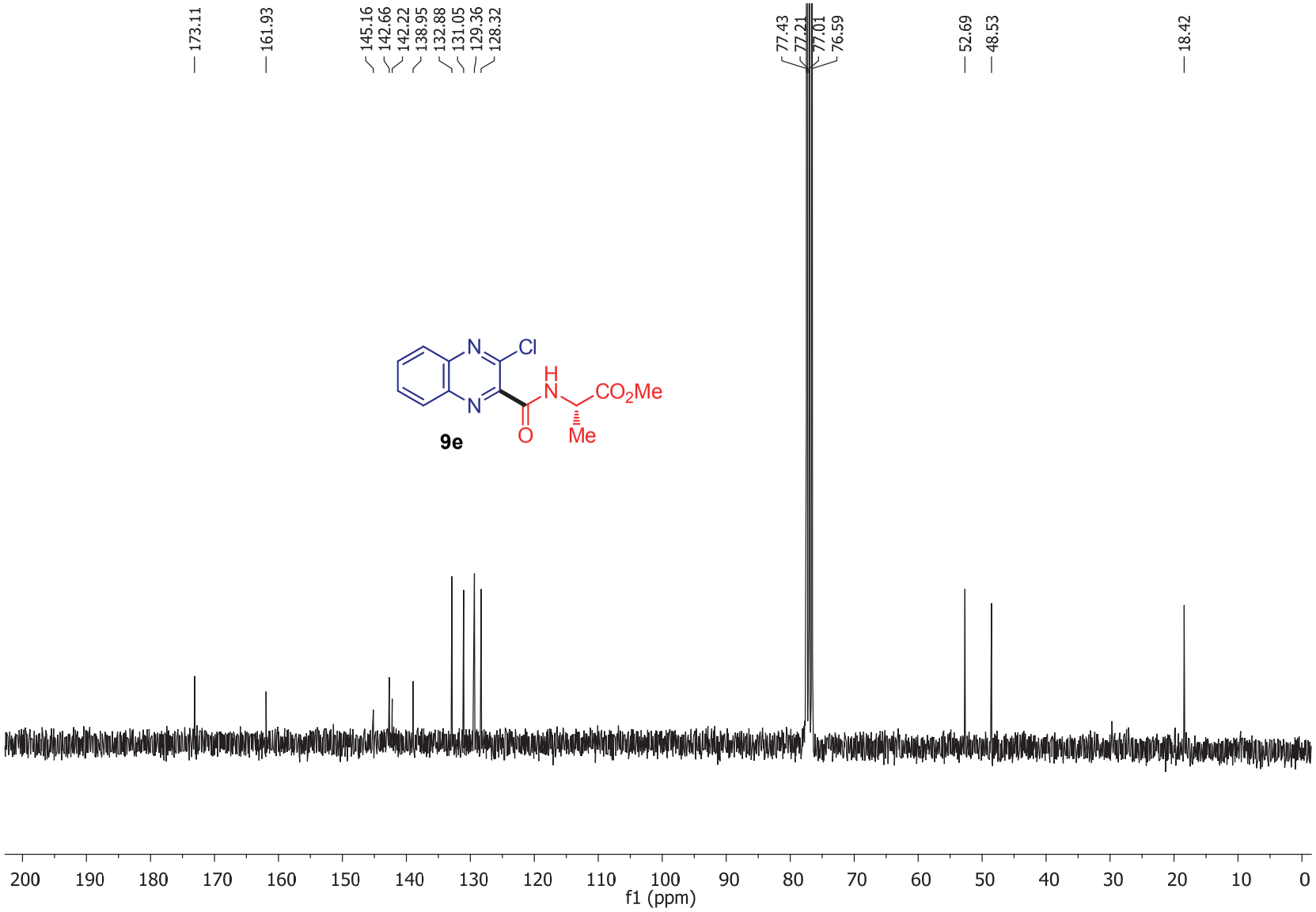
8.18
8.17
8.17
8.12
8.12
8.12
8.10
8.09
8.09
8.09
4.92
4.90
4.87
4.85
4.83
4.82
3.85
1.65
1.62
N
Cl
H
N
CO2Me
N
O
Me
9e
1.04
1.31
2.04
1.00
2.96
3.56
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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161.93
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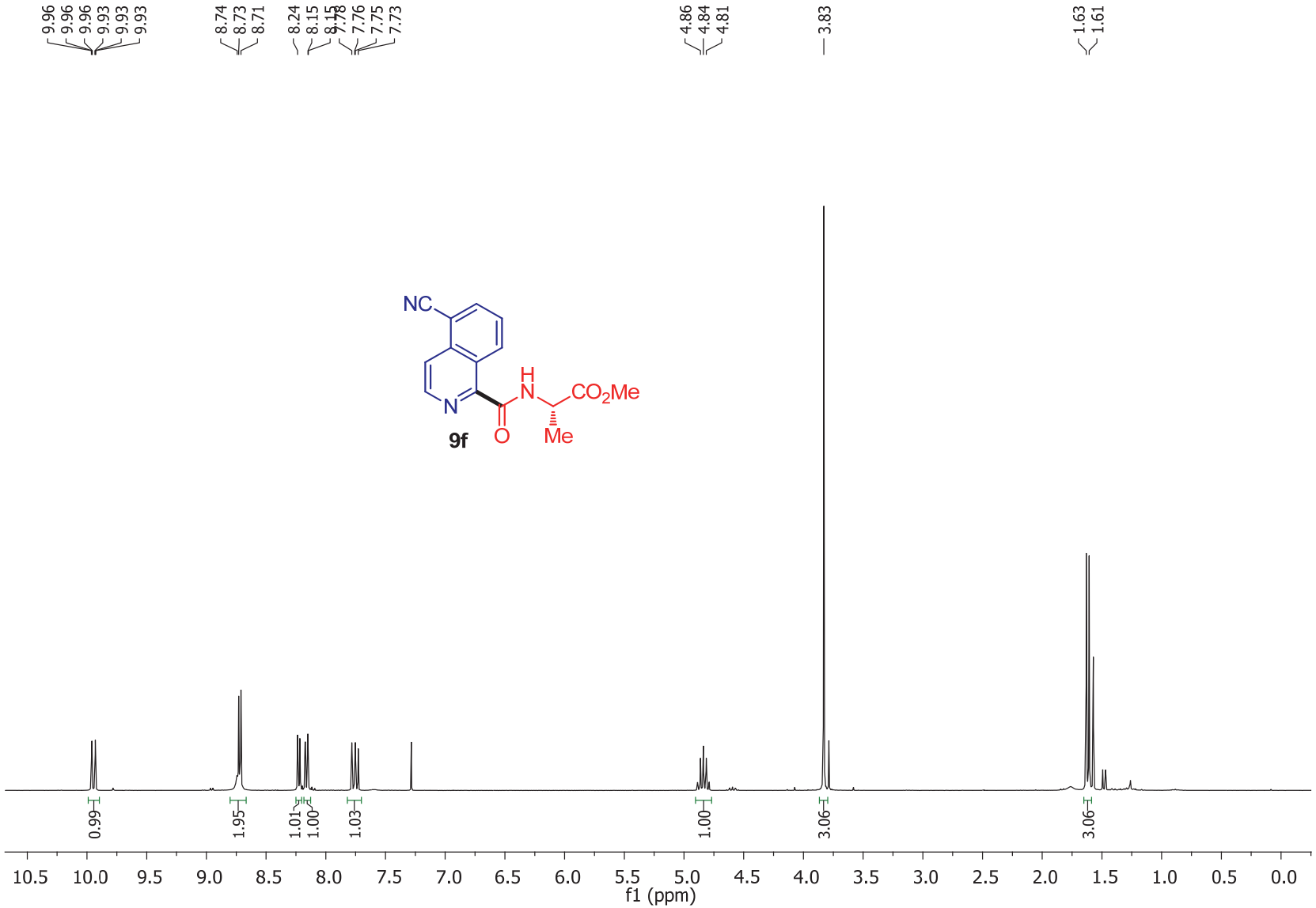
142.66
142.22
138.95
132.88
131.05
129.36
128.32
77.43
77.21
77.01
76.59
52.69
48.53
18.42
N
Cl
H
N
CO2Me
N
O
Me
9e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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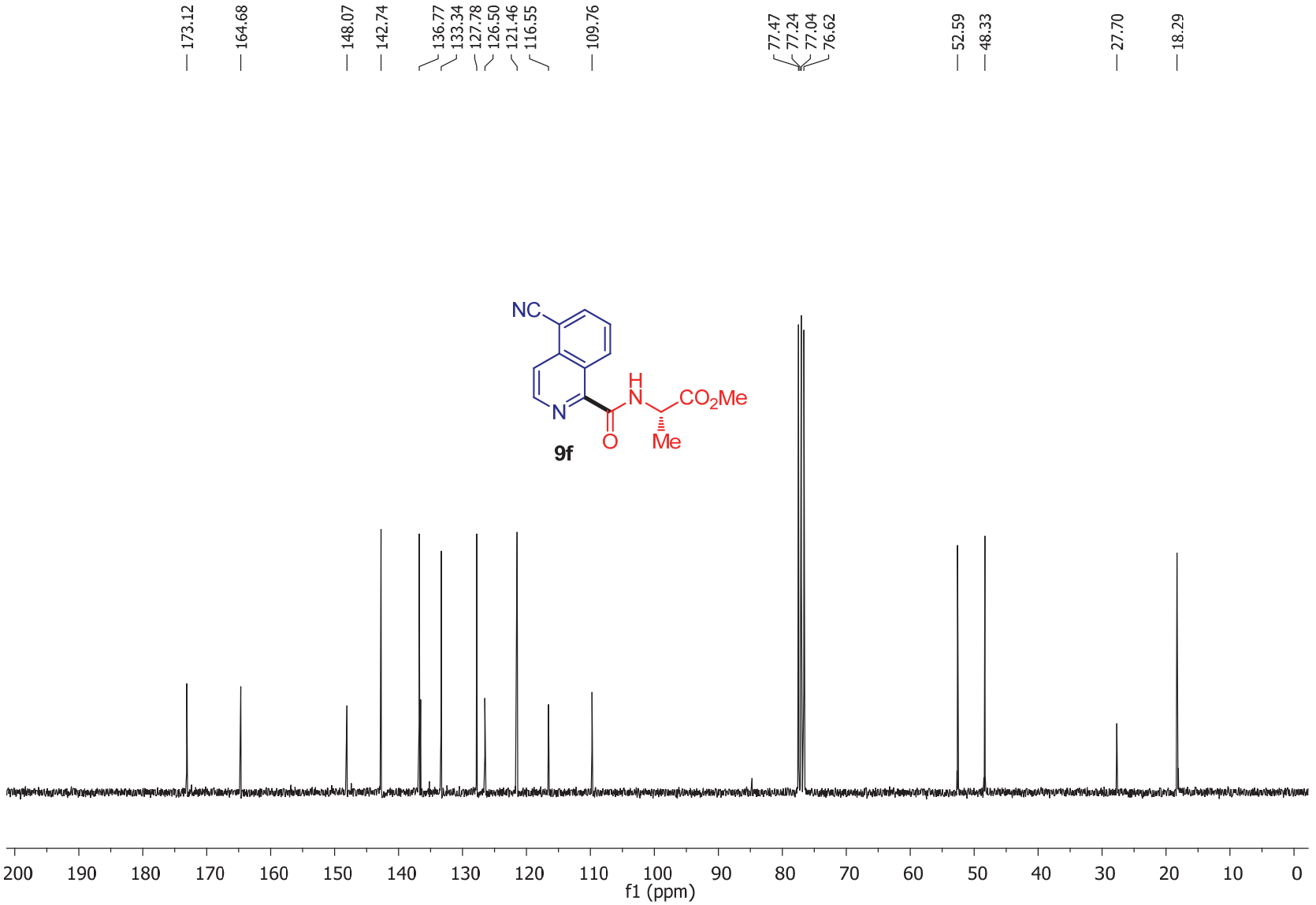
9.96
9.96
9.93
9.93
9.93
8.74
8.73
8.71
8.24
8.15
7.78
7.76
7.75
7.73
4.86
4.84
4.81
3.83
1.63
1.61
NC
N
H
N
CO2Me
O
Me
9f
0.99
1.95
1.01
1.00
1.03
1.00
3.06
3.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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142.74
136.77
133.34
127.78
126.50
121.46
116.55
109.76
77.47
77.24
77.04
76.62
52.59
48.33
27.70
18.29
NC
N
H
N
CO2Me
O
Me
9f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)