

SUPPLEMENTARY INFORMATION

Supplementary Information

Zwitterions as catalytic electron donor species for visible light-induced photoactivation of oxime esters and direct C3-alkylation of quinoxalin-2(1*H*)-ones

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Table of Contents

1. General Information	S2
2. Reaction Investigation and Condition Optimization	S2
2.1 Screening of catalysts	S2
2.2 Screening of Base and Solvent	S3
2.3 Control Experiments	S3
3. Synthesis Procedures and Characterization of Products	S4
3.1 Synthesis Procedure and Characterization of Product 3	S4
3.2 Synthesis Procedure and Characterization of Product 5	S14
3.3 Synthesis Procedure and Characterization of Product 7	S15
3.4 Gram Scale Synthesis Procedure of Product 3aa and 3aj	S16
3. Mechanisms Study Experiments	S17
4.1 Radical Trap Experiment	S17
4.2 Radical Clock Experiment	S18
4.3 UV-Vis Absorption Spectroscopic Measurements	S19
4.4 Job's Plot Experiment	S20
4.5 On-Off-On Experiment	S20
References	S21
NMR Spectra	S22

1. General Information

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under nitrogen (N_2) atmosphere using standard *Schlenk* techniques. All reactions under irradiation were conducted in front of a 20 W white LED (400-800 nm) bulb. All commercially available reagents were purchased and used directly without further purification. Thin layer chromatography (TLC) was performed on silica gel plates and visualized by fluorescence quenching under UV light or staining with the standard solution of Phosphomolybdic acid. Flash chromatography was carried out using silica gel (200-300 mesh) under a light positive pressure, eluting with the specified solvent system. Organic solutions were concentrated under reduced pressure on a rotatory evaporator. Isolated yields refer to materials of >95% purity as determined by 1H NMR.

1H NMR spectra were recorded on Bruker Bruker 400 MHz and 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26ppm, singlet). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($^{13}CDCl_3$: 77.16ppm). Data are reported as follows: chemical shift δ /ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants J in Hz, and integration (1H only). ^{19}F NMR spectra were recorded on the same Spectrometers.

High Resolution Mass Spectrometry (HRMS) were all recorded on an ABI/Sciex QStar Mass Spectrometer using a positive electrospray ionization (ESI+). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

The starting materials, including oxime esters¹⁻³, quinoxalin-2(1*H*)-ones^{4,5}, and heterocycles⁶, were synthesized according to previously reported methods. Zwitterions **Z1**^{7,8} and **Z4**⁹ were also prepared following established protocols. The photocatalyst fac-Ir(ppy)₃, 4CzIPN, and zwitterions **Z2** and **Z3** were purchased and used as received, without further purification.

2. Reaction Investigation and Condition Optimization

2.1 Screening of catalysts

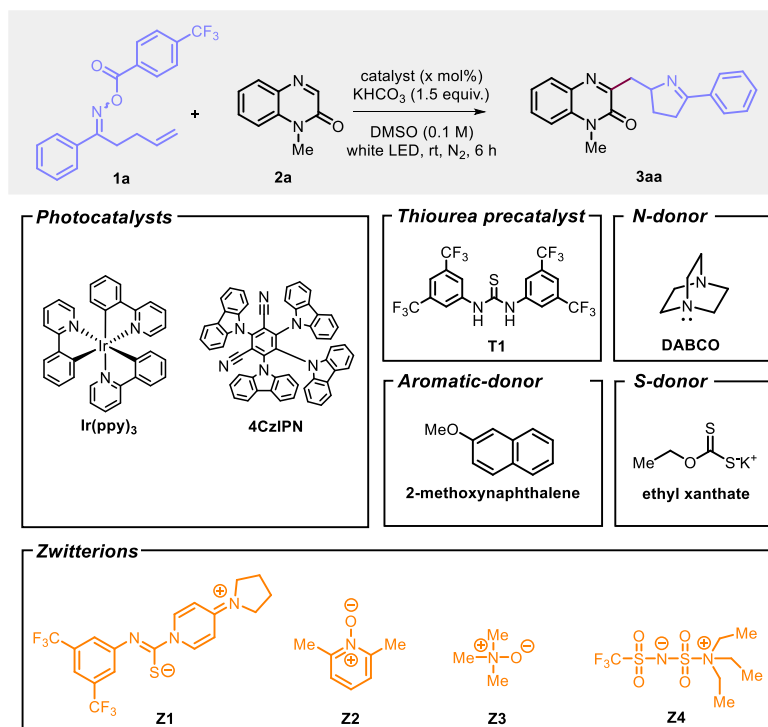


Table S1. Screening of photocatalyst ^[a].

entry	catalyst	x	yield of 3aa (%) ^[b]
1	none	-	8

SUPPLEMENTARY INFORMATION

2	fac-Ir(ppy) ₃	2	93
3	4CzIPN	2	83
4	T1	5	89
5	DABCO	5	8
6	2-methoxynaphthalene	5	29
7	potassium ethyl xanthate	5	80
8	Z1	5	96
9	Z2	5	7
10	Z3	5	75
11	Z4	5	51
12	Z1	10	95
13	Z1	2	43

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), photocatalyst (x mmol), KHCO₃ (0.30 mmol), DMSO (2.0 mL), under the irradiation of 20 W white LED for 6 h at room temperature in a sealed tube under N₂ atmosphere. [b] Yield of the isolated product **3aa**.

2.2 Screening of Base and Solvent

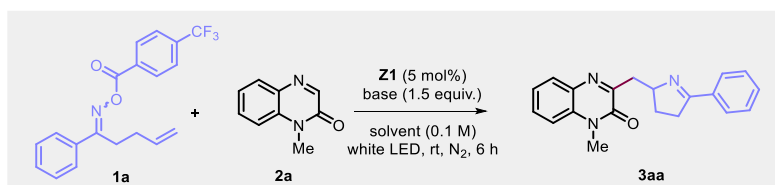


Table S2. Screening of base and solvent ^[a].

Entry	base	solvent	Yield of 3aa (%) ^[b]
1	K ₂ CO ₃	DMSO	90
2	Na ₂ CO ₃	DMSO	88
3	K ₃ PO ₄	DMSO	89
4	KHCO₃	DMSO	96
5	Et ₃ N	DMSO	15
6	DMAP	DMSO	32
7	KHCO ₃	DMF	90
8	KHCO ₃	DMAc	90
9	KHCO ₃	MeCN	75
10	KHCO ₃	THF	10
11	KHCO ₃	DCM	NR

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), **Z1** (5 mmol), base (0.30 mmol), solvent (2.0 mL), under the irradiation of 20 W white LED for 6 h at room temperature in a sealed tube under N₂ atmosphere. [b] Yield of the isolated product **3aa**.

2.3 Control Experiments

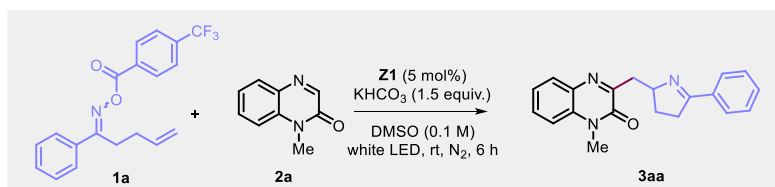


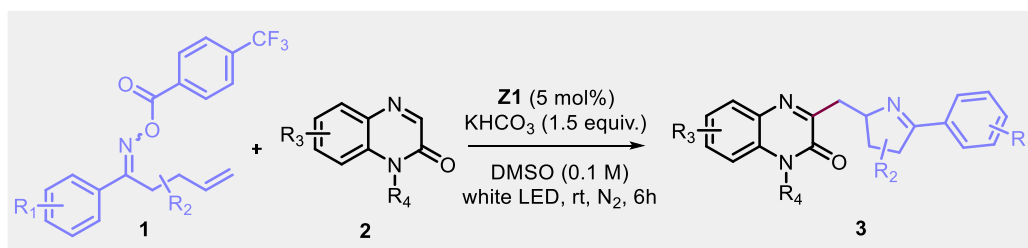
Table S3. Control experiments ^[a].

Entry	variations	Yield of 3aa (%) ^[b]
1	without Z1	8
2	without KHCO ₃	NR
3	without irradiation	NR
4	under air	trace
5	under sunlight	90

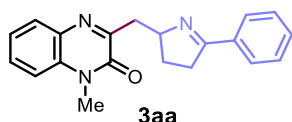
[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), **Z1** (5 mmol), KHCO₃ (0.30 mmol), solvent (2.0 mL), under the irradiation of 20 W white LED for 6 h at room temperature in a sealed tube under N₂ atmosphere. [b] Yield of the isolated product **3aa**.

3. Synthesis Procedures and Characterization of Products

3.1 Synthesis Procedure and Characterization of Product 3



An oven-dried Schlenk tube equipped with a stirring bar was charged with **1** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), **Z1** (0.01 mmol, 4.19 mg, 5 mol%) and KHCO₃ (0.3 mmol, 30.0 mg, 1.5 equiv.). After refilling with N₂ repeated three times, DMSO (2.0 mL) was added through syringe. The mixture was stirred at room temperature for 6 h in front of a 20 W white LED bulb. Water and EtOAc were added and the mixture was stirred for 10 min. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were then washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product.

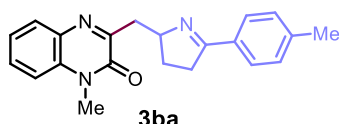


1-Methyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3aa): 60.9 mg, 96% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 – 7.82 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 4.97 – 4.92 (m, 1H), 3.70 (s, 3H), 3.52 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.10 (dd, *J* = 11.4, 8.4 Hz, 1H), 3.09 – 3.04 (m, 1H), 2.96 – 2.91 (m, 1H), 2.32 (dddd, *J* = 12.7, 9.6, 7.7, 4.9 Hz, 1H), 1.78 (ddt, *J* = 13.3, 9.7, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.74, 159.11, 155.16, 134.82, 133.31, 132.93, 130.39, 129.96, 129.78, 128.42, 127.88, 123.58, 113.66, 70.95, 41.13, 35.14, 29.17, 29.00;

HRMS (ESI) m/z: calculated for C₂₀H₂₀N₃O [M+H]⁺: 318.1601, found: 318.1597.

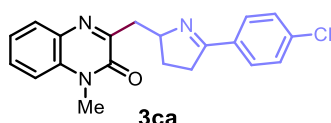


1-Methyl-3-((5-(*p*-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ba): 59.7 mg, 90% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.52 (ddd, *J* = 8.5, 7.3, 1.5 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.92 (tt, *J* = 8.2, 6.2 Hz, 1H), 3.69 (s, 3H), 3.12 – 3.01 (m, 2H), 2.91 (dddd, *J* = 17.0, 9.5, 7.4, 1.8 Hz, 1H), 2.36 (s, 3H), 2.30 (dddd, *J* = 12.8, 9.9, 7.8, 5.0 Hz, 1H), 1.76 (ddt, *J* = 13.2, 10.0, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.63, 159.14, 155.13, 140.56, 133.29, 132.91, 132.08, 129.93, 129.74, 129.12, 127.85, 123.55, 113.64, 70.79, 41.14, 35.09, 29.15, 28.94, 21.53;

HRMS (ESI) m/z: calculated for C₂₁H₂₂N₃O [M+H]⁺: 332.1757, found: 332.1754.



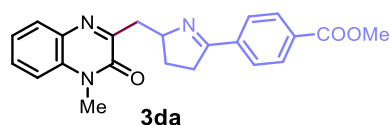
3-((5-(4-Chlorophenyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ca): 62.6 mg, 89% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.84 (ddd, *J* = 16.4, 8.0, 1.7 Hz, 3H), 7.55 – 7.49 (m, 1H), 7.39 (dq, *J* = 8.7, 6.7 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 4.94 (tt, *J* = 8.1, 6.3 Hz, 1H), 3.70 (s, 3H), 3.52 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.15 – 3.02 (m, 2H), 2.94 (dddd, *J* = 17.2, 9.7, 7.5, 1.8 Hz, 1H), 2.32 (dddd, *J* = 12.7, 9.6, 7.7, 4.9 Hz, 1H), 1.78 (ddt, *J* = 13.4, 9.8, 7.0 Hz, 1H);

SUPPLEMENTARY INFORMATION

¹³C NMR (151 MHz, CDCl₃): δ 172.73, 159.10, 155.15, 134.82, 133.31, 132.92, 130.39, 129.96, 129.78, 128.42, 127.87, 123.58, 113.65, 70.95, 41.13, 35.14, 29.16, 29.00;

HRMS (ESI) m/z: calculated for C₂₀H₁₉ClN₃O [M+H]⁺: 352.1211, found: 352.1210.

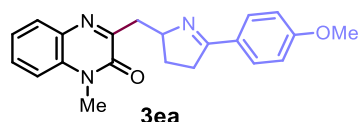


Methyl 4-(2-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)-3,4-dihydro-2H-pyrrol-5-yl)benzoate (3da): 69.1 mg, 92% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 8.04 – 8.02 (m, 2H), 7.8–7.83 (m, 2H), 7.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.96 (tt, *J* = 8.1, 6.2 Hz, 1H), 3.91 (s, 3H), 3.70 (s, 3H), 3.50 (dd, *J* = 14.9, 6.4 Hz, 1H), 3.17 – 3.02 (m, 2H), 2.95 (dddd, *J* = 17.1, 9.7, 7.4, 1.9 Hz, 1H), 2.35 (dddd, *J* = 12.8, 9.9, 7.8, 5.1 Hz, 1H), 1.79 (ddt, *J* = 13.0, 10.1, 7.1 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.03, 166.80, 158.90, 155.14, 138.80, 133.31, 132.89, 131.57, 129.94, 129.84, 129.68, 127.82, 123.62, 113.67, 71.26, 52.29, 40.98, 35.25, 29.17, 29.03;

HRMS (ESI) m/z: calculated for C₂₂H₂₂N₃O₃ [M+H]⁺: 376.1656, found: 376.1653.

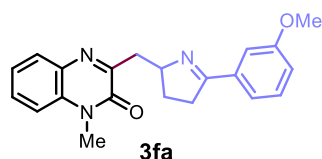


3-((5-(4-Methoxyphenyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ea): 63.7 mg, 92% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.52 (td, *J* = 7.9, 1.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.95 – 4.86 (m, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 3.50 (dd, *J* = 14.8, 6.1 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.95 – 2.85 (m, 1H), 2.29 (dddd, *J* = 12.8, 9.7, 7.7, 5.0 Hz, 1H), 1.76 (ddt, *J* = 13.2, 9.9, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.07, 161.43, 159.19, 155.16, 133.31, 132.92, 129.95, 129.75, 129.50, 127.62, 123.56, 113.73, 113.64, 70.71, 55.40, 41.22, 35.03, 29.16, 29.02;

HRMS (ESI) m/z: calculated for C₂₁H₂₂N₃O₂ [M+H]⁺: 348.1707, found: 348.1704.



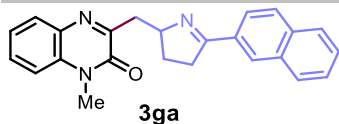
3-((5-(3-Methoxyphenyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-methylquinoxalin-2(1H)-one (3fa): 65.3 mg, 94% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.43 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.34 (tdd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 7.32 – 7.26 (m, 2H), 6.96 (ddd, *J* = 8.1, 2.7, 1.0 Hz, 1H), 5.00 – 4.90 (m, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.52 (dd, *J* = 14.9, 6.1 Hz, 1H), 3.14 – 3.01 (m, 2H), 2.93 (dddd, *J* = 17.0, 9.6, 7.4, 1.8 Hz, 1H), 2.32 (dddd, *J* = 12.8, 9.9, 7.8, 5.0 Hz, 1H), 1.78 (dddd, *J* = 12.8, 9.9, 7.3, 6.4 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.73, 159.68, 159.06, 155.15, 136.19, 133.30, 132.92, 129.95, 129.79, 129.40, 123.59, 120.63, 116.90, 113.67, 112.28, 70.89, 55.46, 41.08, 35.26, 29.17, 28.97;

HRMS (ESI) m/z: calculated for C₂₁H₂₂N₃O₂ [M+H]⁺: 348.1707, found: 348.1706.

SUPPLEMENTARY INFORMATION

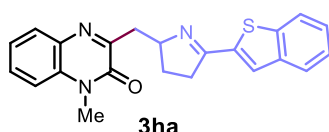


1-Methyl-3-((5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ga): 67.6 mg, 92% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 8.16 (d, *J* = 1.7 Hz, 1H), 8.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.83 (dd, *J* = 7.8, 2.7 Hz, 2H), 7.55 – 7.45 (m, 3H), 7.37 – 7.32 (m, 1H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.00 (dtdd, *J* = 8.2, 6.3, 3.8, 2.0 Hz, 1H), 3.70 (s, 3H), 3.57 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.25 – 3.12 (m, 2H), 3.06 (dddd, *J* = 16.8, 9.6, 7.5, 1.8 Hz, 1H), 2.38 (dddd, *J* = 12.7, 9.9, 7.7, 4.9 Hz, 1H), 1.84 (dddd, *J* = 12.7, 9.9, 7.4, 6.4 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.77, 159.09, 155.17, 134.47, 133.32, 133.06, 132.93, 132.30, 129.97, 129.80, 128.81, 128.34, 128.11, 127.83, 127.07, 126.39, 124.92, 123.60, 113.67, 71.04, 41.17, 35.16, 29.17, 29.07;

HRMS (ESI) m/z: calculated for C₂₄H₂₂N₃O [M+H]⁺: 368.1757, found: 368.1754.

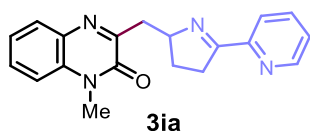


3-((5-(Benzo[b]thiophen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ha): 60.7 mg, 81% yield as a light yellow solid.

¹H NMR (600 MHz, CDCl₃): δ 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.79 – 7.75 (m, 1H), 7.57 – 7.49 (m, 2H), 7.40 – 7.32 (m, 3H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.04 – 4.93 (m, 1H), 3.70 (s, 3H), 3.57 (dd, *J* = 15.2, 5.8 Hz, 1H), 3.19 – 3.07 (m, 2H), 3.01 (dddd, *J* = 16.8, 9.8, 7.2, 1.7 Hz, 1H), 2.37 (dddd, *J* = 12.8, 9.9, 7.7, 5.1 Hz, 1H), 1.84 (dddd, *J* = 13.2, 10.0, 7.2, 6.2 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 167.94, 158.84, 155.13, 141.20, 139.81, 139.67, 133.30, 132.90, 129.98, 129.83, 126.42, 125.89, 124.54, 124.51, 123.61, 122.71, 113.68, 71.07, 40.79, 35.59, 29.29, 29.19;

HRMS (ESI) m/z: calculated for C₂₂H₂₀N₃OS [M+H]⁺: 374.1322, found: 374.1314.

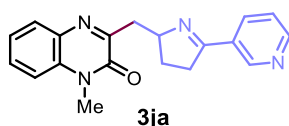


1-Methyl-3-((5-(pyridin-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ia): 33.7 mg, 53% yield as a yellow solid.

¹H NMR (600 MHz, CDCl₃): δ 8.65 (d, *J* = 4.7 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.93 (s, 1H), 7.75 (s, 1H), 7.53 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.41 – 7.27 (m, 3H), 5.01 (p, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 3.49 (dd, *J* = 15.7, 6.7 Hz, 1H), 3.31 – 3.02 (m, 3H), 2.39 (s, 1H), 1.83 (s, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 174.76, 158.72, 155.14, 149.26, 136.69, 133.30, 132.87, 130.15, 129.94, 123.70, 122.75, 113.67, 70.85, 40.73, 34.80, 29.24, 29.00 (*one aromatic carbon signal is not observed due to signal weakness*);

HRMS (ESI) m/z: calculated for C₁₉H₁₈N₄NaO [M+Na]⁺: 341.1373, found: 341.1369.



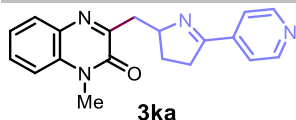
1-Methyl-3-((5-(pyridin-3-yl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ja): 46.9 mg, 74% yield as a yellow solid.

¹H NMR (600 MHz, CDCl₃): δ 8.95 (s, 1H), 8.62 (d, *J* = 4.7 Hz, 1H), 8.15 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.35 – 7.27 (m, 3H), 4.94 (tt, *J* = 8.1, 6.4 Hz, 1H), 3.69 (s, 3H), 3.47 (dd, *J* = 14.9, 6.6 Hz, 1H), 3.16 – 3.01 (m, 2H), 2.94 (dddd, *J* = 17.1, 9.6, 7.4, 1.9 Hz, 1H), 2.35 (dddd, *J* = 12.8, 9.9, 7.8, 4.9 Hz, 1H), 1.80 (ddt, *J* = 13.3, 10.0, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 170.48, 158.82, 155.12, 151.26, 149.25, 135.04, 133.28, 132.85, 130.40, 129.92, 129.87, 123.64, 123.46, 113.68, 71.13, 40.96, 35.01, 29.18, 28.89;

HRMS (ESI) m/z: calculated for C₁₉H₁₈N₄NaO [M+Na]⁺: 341.1373, found: 341.1366.

SUPPLEMENTARY INFORMATION

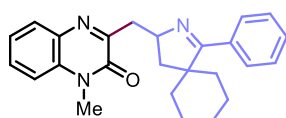


1-Methyl-3-((5-(pyridin-4-yl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ka): 52.6 mg, 83% yield as a light yellow solid.

¹H NMR (600 MHz, CDCl₃): δ 8.65 (d, *J* = 5.1 Hz, 2H), 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.52 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.36 – 7.27 (m, 2H), 4.97 (qdd, *J* = 8.6, 6.6, 2.2 Hz, 1H), 3.70 (s, 3H), 3.48 (dd, *J* = 15.0, 6.5 Hz, 1H), 3.10 (dd, *J* = 14.9, 8.2 Hz, 1H), 3.04 (dddd, *J* = 17.2, 10.1, 4.9, 2.4 Hz, 1H), 2.91 (dddd, *J* = 17.2, 9.7, 7.5, 2.0 Hz, 1H), 2.36 (dddd, *J* = 12.8, 9.9, 7.8, 4.8 Hz, 1H), 1.80 (ddt, *J* = 13.0, 10.1, 7.1 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 171.29, 158.68, 155.11, 150.28, 141.62, 133.29, 132.85, 129.93, 123.67, 121.87, 113.70, 71.45, 40.81, 34.96, 29.19, 28.89;

HRMS (ESI) *m/z*: calculated for C₁₉H₁₈N₄NaO [M+Na]⁺: 341.1373, found: 341.1370.

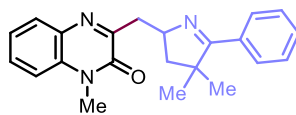


1-Methyl-3-(((1-phenyl-2-azaspiro[4.5]dec-1-en-3-yl)methyl)quinoxalin-2(1H)-one (3la): 74.4 mg, 96% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.56 – 7.48 (m, 3H), 7.36 – 7.30 (m, 4H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.85 – 4.74 (m, 1H), 3.69 (s, 3H), 3.56 (dd, *J* = 14.7, 6.8 Hz, 1H), 3.11 (dd, *J* = 14.8, 8.1 Hz, 1H), 2.45 (dd, *J* = 12.8, 7.2 Hz, 1H), 1.77 (td, *J* = 13.1, 3.7 Hz, 1H), 1.73 – 1.59 (m, 5H), 1.59 – 1.49 (m, 2H), 1.43 (qt, *J* = 13.9, 4.9 Hz, 1H), 1.29 (tt, *J* = 13.1, 3.6 Hz, 1H), 1.14 (qt, *J* = 13.9, 3.8 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 180.62, 159.18, 155.16, 136.07, 133.30, 132.93, 129.94, 129.76, 128.88, 128.24, 128.03, 123.54, 113.62, 66.83, 56.62, 41.87, 41.33, 35.78, 32.17, 29.15, 25.68, 23.47, 23.23;

HRMS (ESI) *m/z*: calculated for C₂₅H₂₈N₃O [M+H]⁺: 386.2227, found: 386.2224.

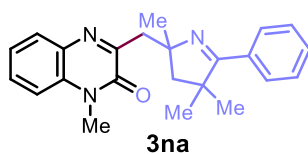


3-((4,4-Dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ma): 65.2 mg, 94% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.51 (ddd, *J* = 8.5, 7.3, 1.5 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.77 (tt, *J* = 8.4, 6.8 Hz, 1H), 3.70 (s, 3H), 3.56 (dd, *J* = 14.7, 6.8 Hz, 1H), 3.11 (dd, *J* = 14.7, 8.0 Hz, 1H), 2.20 (dd, *J* = 12.6, 6.7 Hz, 1H), 1.72 (dd, *J* = 12.5, 8.7 Hz, 1H), 1.37 (s, 3H), 1.34 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 179.80, 159.19, 155.17, 135.03, 133.30, 132.91, 129.92, 129.78, 129.42, 128.19, 128.07, 123.57, 113.63, 66.09, 50.62, 48.42, 41.50, 29.17, 27.34, 26.21;

HRMS (ESI) *m/z*: calculated for C₂₂H₂₄N₃O [M+H]⁺: 346.1914, found: 346.1913.



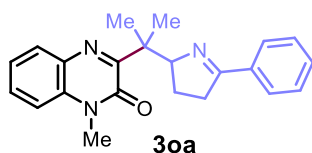
1-Methyl-3-((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3na): 59.2 mg, 82% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.50 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.36 – 7.28 (m, 4H), 7.28 – 7.24 (m, 1H), 3.69 (s, 3H), 3.54 (d, *J* = 14.0 Hz, 1H), 3.18 (d, *J* = 13.9 Hz, 1H), 2.40 (d, *J* = 13.2 Hz, 1H), 1.89 (d, *J* = 13.2 Hz, 1H), 1.54 (s, 3H), 1.43 (s, 3H), 1.27 (s, 3H);

SUPPLEMENTARY INFORMATION

¹³C NMR (151 MHz, CDCl₃): δ 177.34, 158.92, 155.53, 135.49, 133.26, 132.72, 129.96, 129.79, 129.10, 128.24, 128.11, 123.49, 113.60, 72.81, 51.98, 51.81, 44.85, 29.35, 29.30, 28.19 (one alkyl carbon signal is overlapped);

HRMS (ESI) m/z: calculated for C₂₃H₂₆N₃O [M+H]⁺: 360.2070, found: 360.2067.

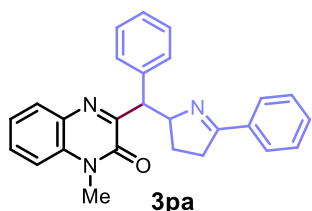


1-methyl-3-(2-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-2-yl)quinoxalin-2(1H)-one (3oa): 44.8 mg, 65% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.52 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 (dd, *J* = 8.3, 1.2 Hz, 1H), 5.53 (ddt, *J* = 9.3, 7.5, 2.3 Hz, 1H), 3.70 (s, 3H), 2.92 (td, *J* = 8.1, 7.5, 2.2 Hz, 2H), 2.06 – 1.96 (m, 1H), 1.72 – 1.67 (m, 1H), 1.65 (s, 3H), 1.35 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 171.86, 163.94, 154.18, 135.16, 133.45, 132.42, 130.39, 130.16, 129.73, 128.40, 127.83, 123.32, 113.43, 47.60, 35.76, 29.01, 24.50, 23.30, 20.93;

HRMS (ESI) m/z: calculated for C₂₂H₂₄N₃O [M+H]⁺: 346.1914, found: 346.1911.

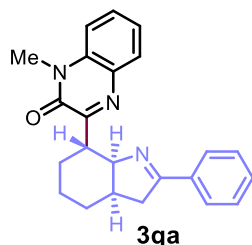


1-Methyl-3-(phenyl(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3pa): 59.8 mg, d.r. = 5:1, 76% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): (**major**) δ 7.97 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.61 – 7.56 (m, 2H), 7.50 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.38 – 7.24 (m, 7H), 7.23 – 7.19 (m, 1H), 5.52 – 5.42 (m, 1H), 4.80 (d, *J* = 10.3 Hz, 1H), 3.65 (s, 3H), 2.87 (ddd, *J* = 9.2, 6.8, 2.0 Hz, 2H), 2.12 – 2.03 (m, 1H), 1.71 (dtd, *J* = 13.1, 8.8, 7.0 Hz, 1H); (**minor**) δ 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.62 – 7.56 (m, 2H), 7.54 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.40 – 7.26 (m, 7H), 7.24 – 7.20 (m, 1H), 5.33 (dddt, *J* = 10.1, 8.5, 6.7, 2.1 Hz, 1H), 4.75 (d, *J* = 10.3 Hz, 1H), 3.64 (s, 3H), 3.04 – 2.91 (m, 2H), 2.39 (dddd, *J* = 13.0, 9.5, 7.7, 5.3 Hz, 1H), 1.68 (dddd, *J* = 13.0, 9.8, 7.7, 6.5 Hz, 2H);

¹³C NMR (151 MHz, CDCl₃): (**major**) δ 173.22, 161.11, 154.85, 139.35, 134.98, 133.23, 133.10, 130.41, 130.25, 129.71, 129.54, 128.44, 128.28, 127.91, 127.00, 123.39, 113.57, 75.99, 53.42, 34.99, 29.29, 27.77; (**minor**) δ 172.90, 160.34, 154.68, 140.22, 134.96, 133.16, 132.84, 130.39, 130.33, 130.04, 129.54, 128.36, 128.31, 127.95, 126.80, 123.64, 113.69, 54.51, 35.12, 29.32, 28.62;

HRMS (ESI) m/z: calculated for C₂₆H₂₄N₃O [M+H]⁺: 394.1914, found: 394.1910.



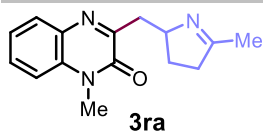
1-Methyl-3-(2-phenyl-3a,4,5,6,7,7a-hexahydro-3H-indol-7-yl)quinoxalin-2(1H)-one (3qa): 47.1 mg, 66% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.90 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.51 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.28 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.84 (dd, *J* = 8.9, 6.9 Hz, 1H), 3.67 (s, 3H), 3.46 (td, *J* = 9.5, 4.0 Hz, 1H), 3.01 (dd, *J* = 15.8, 7.8 Hz, 1H), 2.88 – 2.73 (m, 2H), 1.90 (dt, *J* = 8.8, 5.1 Hz, 1H), 1.83 – 1.71 (m, 2H), 1.68 – 1.52 (m, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 173.62, 162.91, 154.77, 135.36, 133.18, 133.03, 130.28, 130.08, 129.63, 128.35, 127.75, 123.43, 113.57, 72.32, 42.92, 39.58, 37.05, 29.24, 28.31, 26.26, 20.73;

HRMS (ESI) m/z: calculated for C₂₃H₂₄N₃O [M+H]⁺: 358.1914, found: 358.1911.

SUPPLEMENTARY INFORMATION

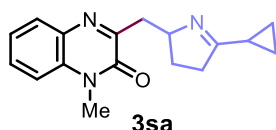


1-methyl-3-((5-methyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ra): 35.7 mg, 70% yield as a yellow solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 – 7.80 (m, 1H), 7.50 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.28 – 7.26 (m, 1H), 4.79 – 4.62 (m, 1H), 3.68 (s, 3H), 3.30 (dd, *J* = 14.9, 7.3 Hz, 1H), 3.04 (dd, *J* = 14.9, 7.4 Hz, 1H), 2.60 (dddd, *J* = 17.2, 10.2, 5.0, 2.0 Hz, 1H), 2.49 (dt, *J* = 17.5, 8.8 Hz, 1H), 2.18 (dddd, *J* = 12.9, 9.9, 7.8, 4.9 Hz, 1H), 2.04 (d, *J* = 1.8 Hz, 3H), 1.62 (ddt, *J* = 13.2, 10.1, 7.1 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 158.87, 155.10, 133.26, 132.74, 129.90, 129.85, 123.58, 113.61, 69.89, 53.53, 40.83, 38.97, 29.15, 29.09, 19.78;

HRMS (ESI) *m/z*: calculated for C₁₅H₁₈N₃O [M+H]⁺: 256.1444, found: 256.1441.

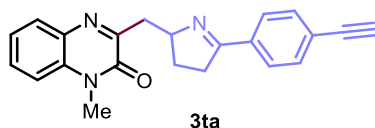


3-((5-cyclopropyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-methylquinoxalin-2(1H)-one (3sa): 47.5 mg, 84% yield as a yellow solid.

¹H NMR (600 MHz, CDCl₃): δ 7.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.28 – 7.26 (m, 1H), 4.66 (tt, *J* = 8.0, 6.4 Hz, 1H), 3.67 (s, 3H), 3.33 (dd, *J* = 14.9, 6.6 Hz, 1H), 2.97 (dd, *J* = 14.9, 8.0 Hz, 1H), 2.39 (dddd, *J* = 16.8, 9.8, 5.0, 1.9 Hz, 1H), 2.28 (dddd, *J* = 17.0, 9.3, 7.5, 1.6 Hz, 1H), 2.11 (dddd, *J* = 12.8, 9.7, 7.6, 5.0 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.56 (ddt, *J* = 13.2, 9.8, 7.0 Hz, 1H), 0.87 – 0.73 (m, 4H);

¹³C NMR (151 MHz, CDCl₃): δ 179.16, 159.17, 155.13, 133.28, 132.90, 129.94, 129.73, 123.54, 113.60, 69.91, 41.03, 34.02, 29.14, 28.63, 14.60, 7.22, 7.01;

HRMS (ESI) *m/z*: calculated for C₁₇H₂₀N₃O [M+H]⁺: 282.1601, found: 282.1598.

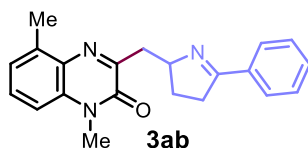


3-((5-(4-ethynylphenyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-methylquinoxalin-2(1H)-one (3ta): 55.2 mg, 81% yield as a white solid after 24 h irradiation.

¹H NMR (600 MHz, CDCl₃): δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.52 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.35 – 7.31 (m, 1H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.94 (tddd, *J* = 8.3, 6.3, 4.2, 2.0 Hz, 1H), 3.70 (s, 3H), 3.49 (dd, *J* = 14.9, 6.3 Hz, 1H), 3.16 (s, 1H), 3.13 – 2.99 (m, 2H), 2.91 (dddd, *J* = 17.1, 9.7, 7.5, 1.9 Hz, 1H), 2.33 (dddd, *J* = 12.8, 9.9, 7.8, 4.8 Hz, 1H), 1.84 – 1.72 (m, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.03, 158.97, 155.14, 134.99, 133.31, 132.90, 132.18, 129.95, 129.84, 127.78, 124.01, 123.62, 113.68, 83.47, 78.89, 71.09, 41.05, 35.10, 29.19, 29.01;

HRMS (ESI) *m/z*: calculated for C₂₂H₂₀N₃O [M+H]⁺: 342.1601, found: 342.1598.



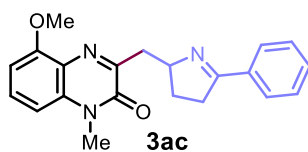
1,5-Dimethyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ab): 54.5 mg, 82% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.89 – 7.80 (m, 2H), 7.40 (qd, *J* = 5.7, 3.1 Hz, 4H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 4.96 (dtd, *J* = 9.4, 7.1, 4.8 Hz, 1H), 3.69 (s, 3H), 3.62 (dd, *J* = 16.0, 4.9 Hz, 1H), 3.13 – 3.03 (m, 2H), 2.95 (dddd, *J* = 17.1, 9.5, 7.3, 1.8 Hz, 1H), 2.68 (s, 3H), 2.38 (dddd, *J* = 12.9, 9.9, 7.7, 5.0 Hz, 1H), 1.79 (ddt, *J* = 13.3, 10.0, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.66, 157.00, 155.06, 138.66, 134.84, 133.26, 131.38, 130.40, 129.48, 128.46, 127.84, 124.88, 111.58, 71.05, 40.67, 35.14, 29.29, 29.00, 17.69;

SUPPLEMENTARY INFORMATION

HRMS (ESI) m/z: calculated for $C_{21}H_{22}N_3O$ $[M+H]^+$: 332.1757, found: 332.1754.

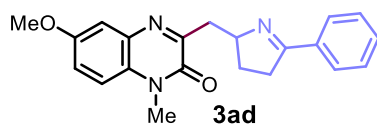


5-Methoxy-1-methyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ac): 63.3 mg, 91% yield as a white solid.

1H NMR (600 MHz, $CDCl_3$): δ 7.83 – 7.81 (m, 2H), 7.45 (dd, J = 8.1, 1.4 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.21 (t, J = 8.1 Hz, 1H), 7.01 (dd, J = 8.2, 1.4 Hz, 1H), 4.96 – 4.87 (m, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.51 (dd, J = 14.9, 6.0 Hz, 1H), 3.11 – 3.01 (m, 2H), 2.92 (dddd, J = 17.1, 9.5, 7.4, 1.8 Hz, 1H), 2.30 (dddd, J = 12.7, 9.8, 7.7, 4.9 Hz, 1H), 1.76 (dddd, J = 12.9, 10.0, 7.4, 6.5 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.67, 158.85, 156.28, 148.20, 134.81, 134.79, 130.35, 128.39, 127.85, 124.27, 123.43, 122.92, 112.62, 70.90, 56.74, 40.98, 35.11, 34.77, 28.94;

HRMS (ESI) m/z: calculated for $C_{21}H_{22}N_3O_2$ $[M+H]^+$: 348.1707, found: 348.1704.

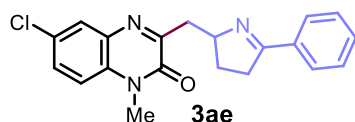


6-Methoxy-1-methyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ad): 65.4 mg, 94% yield as a white solid.

1H NMR (600 MHz, $CDCl_3$): δ 7.84 – 7.77 (m, 2H), 7.41 – 7.33 (m, 3H), 7.32 (d, J = 2.9 Hz, 1H), 7.19 (d, J = 9.1 Hz, 1H), 7.13 (dd, J = 9.1, 2.9 Hz, 1H), 4.99 – 4.86 (m, 1H), 3.86 (s, 3H), 3.67 (s, 3H), 3.49 (dd, J = 14.8, 6.3 Hz, 1H), 3.14 – 3.00 (m, 2H), 2.92 (dddd, J = 17.1, 9.5, 7.4, 1.8 Hz, 1H), 2.31 (dddd, J = 12.7, 9.8, 7.7, 4.9 Hz, 1H), 1.77 (dddd, J = 12.8, 9.9, 7.4, 6.4 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.69, 159.61, 155.96, 154.77, 134.77, 133.59, 130.35, 128.38, 127.84, 127.50, 118.80, 114.53, 111.46, 70.90, 55.82, 41.23, 35.08, 29.25, 28.98;

HRMS (ESI) m/z: calculated for $C_{21}H_{22}N_3O_2$ $[M+H]^+$: 348.1707, found: 348.1702.

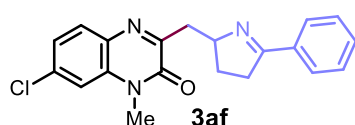


6-Chloro-1-methyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ae): 66.0 mg, 94% yield as a white solid.

1H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, J = 2.4 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.49 (dd, J = 8.9, 2.4 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.23 (d, J = 8.9 Hz, 1H), 4.92 (qdd, J = 8.1, 6.2, 1.9 Hz, 1H), 3.69 (s, 3H), 3.49 (dd, J = 15.1, 6.3 Hz, 1H), 3.15 – 3.03 (m, 2H), 2.95 (dddd, J = 17.1, 9.6, 7.5, 1.8 Hz, 1H), 2.34 (dddd, J = 12.7, 9.8, 7.8, 4.9 Hz, 1H), 1.81 – 1.71 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.87, 160.60, 154.78, 134.71, 133.40, 132.00, 130.46, 129.71, 129.29, 128.85, 128.44, 127.85, 114.80, 70.76, 41.16, 35.13, 29.34, 29.05;

HRMS (ESI) m/z: calculated for $C_{20}H_{19}ClN_3O$ $[M+H]^+$: 352.1211, found: 352.1202.



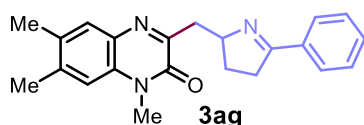
7-Chloro-1-methyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3af): 64.5 mg, 92% yield as a white solid.

1H NMR (600 MHz, $CDCl_3$): δ 7.84 – 7.79 (m, 2H), 7.76 (d, J = 9.1 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.28 (dq, J = 3.7, 2.1 Hz, 2H), 4.91 (tt, J = 8.0, 6.3 Hz, 1H), 3.66 (s, 3H), 3.46 (dd, J = 15.0, 6.4 Hz, 1H), 3.13 – 3.01 (m, 2H), 2.94 (dddd, J = 17.1, 9.5, 7.4, 1.8 Hz, 1H), 2.32 (dddd, J = 12.8, 9.9, 7.7, 4.9 Hz, 1H), 1.76 (dddd, J = 12.8, 9.9, 7.4, 6.4 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.86, 159.27, 154.85, 135.63, 134.71, 134.17, 131.42, 131.00, 130.46, 128.44, 127.86, 123.94, 113.71, 70.82, 41.10, 35.14, 29.30, 29.03;

SUPPLEMENTARY INFORMATION

HRMS (ESI) m/z: calculated for C₂₀H₁₉ClN₃O [M+H]⁺: 352.1211, found: 352.1205.

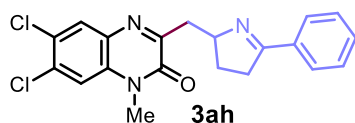


1,6,7-Trimethyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ag): 56.5 mg, 82% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 – 7.79 (m, 2H), 7.60 (s, 1H), 7.42 – 7.34 (m, 3H), 7.05 (s, 1H), 4.92 (ddd, *J* = 8.3, 6.2, 2.0 Hz, 1H), 3.67 (s, 3H), 3.51 (dd, *J* = 14.9, 6.0 Hz, 1H), 3.09 – 3.00 (m, 2H), 2.92 (dddd, *J* = 17.0, 9.6, 7.4, 1.8 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 2.29 (dddd, *J* = 12.7, 9.8, 7.7, 4.9 Hz, 1H), 1.76 (dddd, *J* = 12.9, 9.9, 7.4, 6.4 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.64, 157.70, 155.21, 139.45, 134.83, 132.40, 131.32, 131.27, 130.34, 130.03, 128.39, 127.86, 114.23, 70.98, 41.02, 35.08, 29.06, 28.91, 20.59, 19.24;

HRMS (ESI) m/z: calculated for C₂₂H₂₄N₃O [M+H]⁺: 346.1914, found: 346.1911.

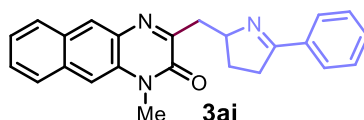


6,7-Dichloro-1-methyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3ah): 66.5 mg, 86% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.92 (s, 1H), 7.84 – 7.78 (m, 2H), 7.43 – 7.34 (m, 4H), 4.89 (qdd, *J* = 8.4, 5.2, 2.1 Hz, 1H), 3.64 (s, 3H), 3.45 (dd, *J* = 15.2, 6.5 Hz, 1H), 3.13 – 3.02 (m, 2H), 2.94 (dddd, *J* = 17.1, 9.6, 7.5, 1.8 Hz, 1H), 2.33 (dddd, *J* = 12.7, 9.9, 7.7, 4.9 Hz, 1H), 1.74 (ddt, *J* = 12.9, 10.0, 7.1 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.92, 160.80, 154.54, 134.68, 133.74, 132.74, 131.97, 130.77, 130.50, 128.46, 127.86, 127.29, 115.17, 70.71, 41.17, 35.15, 29.43, 29.09;

HRMS (ESI) m/z: calculated for C₂₀H₁₈Cl₂N₃O [M+H]⁺: 386.0821, found: 386.0815.

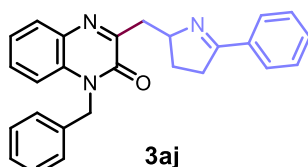


1-Methyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)benzo[g]quinoxalin-2(1H)-one (3ai): 48.6 mg, 66% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 8.32 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.58 – 7.51 (m, 2H), 7.46 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 7.43 – 7.35 (m, 3H), 5.04 – 4.93 (m, 1H), 3.72 (s, 3H), 3.56 (dd, *J* = 15.0, 6.2 Hz, 1H), 3.17 – 3.04 (m, 2H), 2.95 (dddd, *J* = 17.0, 9.6, 7.5, 1.8 Hz, 1H), 2.37 (dddd, *J* = 12.8, 9.9, 7.8, 4.9 Hz, 1H), 1.81 (ddt, *J* = 12.9, 9.9, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.83, 159.61, 154.93, 134.75, 133.46, 132.22, 131.92, 130.43, 129.77, 128.86, 128.48, 128.43, 127.88, 127.70, 127.23, 125.25, 109.91, 70.95, 41.22, 35.13, 29.12, 29.05;

HRMS (ESI) m/z: calculated for C₂₂H₂₄N₃O [M+H]⁺: 368.1757, found: 368.1756.



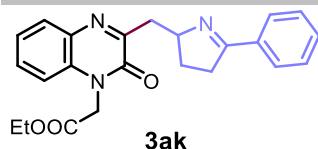
1-Benzyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3aj): 74.5 mg, 94% yield as a pale yellow solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.43 – 7.35 (m, 4H), 7.33 – 7.19 (m, 7H), 5.62 – 5.38 (m, 2H), 4.97 (dtdd, *J* = 8.4, 6.6, 4.1, 1.9 Hz, 1H), 3.57 (dd, *J* = 14.8, 6.5 Hz, 1H), 3.18 (dd, *J* = 14.9, 8.2 Hz, 1H), 3.08 (dddd, *J* = 17.0, 10.0, 4.9, 2.2 Hz, 1H), 2.95 (dddd, *J* = 17.1, 9.6, 7.5, 1.8 Hz, 1H), 2.36 (dddd, *J* = 12.7, 9.9, 7.7, 4.8 Hz, 1H), 1.82 (ddt, *J* = 12.9, 10.0, 7.1 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.74, 159.37, 155.25, 135.49, 134.82, 133.18, 132.63, 130.38, 130.06, 129.74, 129.01, 128.42, 127.88, 127.72, 126.99, 123.61, 114.47, 71.20, 45.98, 40.99, 35.15, 29.07;

HRMS (ESI) m/z: calculated for C₂₆H₂₄N₃O [M+H]⁺: 394.1914, found: 394.1911.

SUPPLEMENTARY INFORMATION

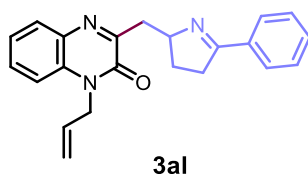


Ethyl 2-(2-oxo-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-1(2H)-yl)acetate (3ak): 73.2 mg, 94% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.49 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.35 – 7.31 (m, 1H), 7.06 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.03 (s, 2H), 4.97 – 4.89 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.55 (dd, *J* = 15.1, 6.0 Hz, 1H), 3.14 – 3.03 (m, 2H), 2.94 (dddd, *J* = 17.0, 9.7, 7.5, 1.8 Hz, 1H), 2.33 (dddd, *J* = 12.7, 9.9, 7.7, 4.9 Hz, 1H), 1.79 (ddt, *J* = 12.9, 10.0, 7.1 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 172.86, 167.30, 158.93, 154.72, 134.76, 132.98, 132.43, 130.44, 130.30, 129.95, 128.44, 127.90, 123.90, 113.12, 70.88, 62.13, 43.65, 40.85, 35.15, 28.96, 14.21;

HRMS (ESI) m/z: calculated for C₂₃H₂₄N₃O₃ [M+H]⁺: 390.1812, found: 390.1804.

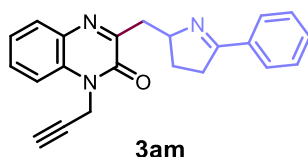


1-Allyl-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-2(1H)-one (3al): 63.2 mg, 92% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.38 (dq, *J* = 13.9, 6.9 Hz, 3H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 5.94 (ddt, *J* = 15.9, 10.3, 5.1 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 5.01 – 4.84 (m, 3H), 3.52 (dd, *J* = 15.0, 6.3 Hz, 1H), 3.18 – 3.01 (m, 2H), 2.94 (ddd, *J* = 17.1, 9.7, 7.7 Hz, 1H), 2.41 – 2.27 (m, 1H), 1.79 (ddt, *J* = 13.4, 9.9, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.74, 159.20, 154.71, 134.79, 133.08, 132.51, 130.87, 130.39, 130.04, 129.67, 128.41, 127.87, 123.55, 118.11, 114.21, 71.00, 44.58, 40.92, 35.13, 29.01;

HRMS (ESI) m/z: calculated for C₂₂H₂₂N₃O [M+H]⁺: 344.1757, found: 344.1750.



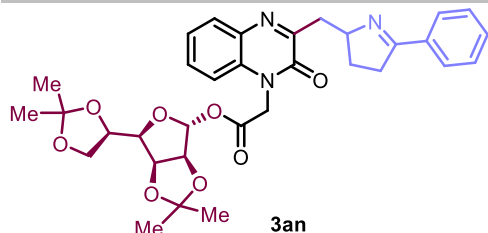
3-((5-Phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (3am): 63.4 mg, 93% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.87 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.56 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.43 – 7.33 (m, 4H), 5.06 (d, *J* = 2.6 Hz, 2H), 4.93 (tt, *J* = 8.2, 6.3 Hz, 1H), 3.51 (dd, *J* = 15.0, 6.3 Hz, 1H), 3.16 – 3.03 (m, 2H), 2.94 (dddd, *J* = 17.0, 9.6, 7.5, 1.8 Hz, 1H), 2.34 (dddd, *J* = 12.8, 9.8, 7.7, 4.9 Hz, 1H), 2.29 (t, *J* = 2.5 Hz, 1H), 1.78 (ddt, *J* = 12.8, 9.9, 7.0 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 172.84, 159.01, 154.11, 134.75, 133.10, 131.77, 130.42, 130.11, 129.88, 128.43, 127.88, 123.96, 114.16, 77.02, 73.28, 70.87, 41.00, 35.13, 31.57, 29.03;

HRMS (ESI) m/z: calculated for C₂₂H₂₀N₃O [M+H]⁺: 342.1601, found: 342.1595.

SUPPLEMENTARY INFORMATION



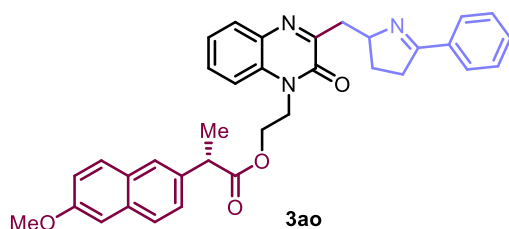
3an

(3aS,4R,6R,6aS)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl 2-(2-oxo-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-1(2H)-yl)acetate (3an): 114.6 mg, 95% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.86 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.50 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.41 – 7.29 (m, 4H), 7.03 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.19 (d, *J* = 1.3 Hz, 1H), 5.08 – 4.97 (m, 2H), 4.96 – 4.86 (m, 1H), 4.78 (td, *J* = 6.2, 3.5 Hz, 1H), 4.69 (d, *J* = 5.8 Hz, 1H), 4.35 (dddd, *J* = 8.9, 6.9, 4.2, 2.8 Hz, 1H), 4.06 (ddd, *J* = 8.0, 6.2, 1.7 Hz, 1H), 3.96 (dt, *J* = 8.9, 4.4 Hz, 1H), 3.89 (ddd, *J* = 9.4, 7.9, 3.6 Hz, 1H), 3.51 (ddd, *J* = 14.9, 6.2, 3.1 Hz, 1H), 3.15 – 3.00 (m, 2H), 2.92 (dddd, *J* = 17.0, 9.6, 7.4, 1.8 Hz, 1H), 2.31 (dddt, *J* = 12.6, 9.6, 7.7, 4.7 Hz, 1H), 1.77 (ddt, *J* = 12.9, 10.0, 7.1 Hz, 1H), 1.44 (d, *J* = 1.3 Hz, 3H), 1.42 (d, *J* = 2.0 Hz, 3H), 1.36 (s, 3H), 1.29 (d, *J* = 2.0 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 172.80, 172.77, 165.92, 165.91, 158.83, 158.81, 154.56, 134.69, 132.88, 132.16, 132.14, 130.38, 130.33, 130.07, 128.39, 127.82, 124.07, 113.45, 112.92, 109.47, 102.12, 102.09, 84.95, 82.79, 79.13, 72.73, 70.86, 70.81, 66.79, 43.51, 40.92, 40.78, 35.10, 28.95, 28.93, 27.03, 25.93, 25.19, 24.63;

HRMS (ESI) m/z: calculated for C₃₃H₃₈N₃O₈ [M+H]⁺: 604.2653, found: 604.2645.



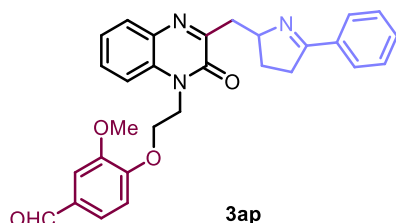
3ao

2-(2-Oxo-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-1(2H)-yl)ethyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate (3ao): 99.5 mg, 89% yield as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.79 (tt, *J* = 8.4, 1.6 Hz, 3H), 7.61 (ddd, *J* = 8.8, 5.5, 3.8 Hz, 2H), 7.51 (t, *J* = 2.5 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.29 – 7.18 (m, 4H), 7.11 (ddd, *J* = 8.9, 2.5, 1.4 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 4.89 (qdd, *J* = 8.2, 6.2, 2.0 Hz, 1H), 4.53 – 4.32 (m, 4H), 3.86 (s, 3H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.48 (ddd, *J* = 15.0, 6.2, 1.7 Hz, 1H), 3.09 – 2.97 (m, 2H), 2.88 (dddt, *J* = 17.0, 9.5, 7.4, 1.9 Hz, 1H), 2.26 (dddd, *J* = 12.7, 9.8, 7.7, 4.8 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.48 (dd, *J* = 7.2, 1.3 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 174.61, 172.66, 158.76, 157.72, 154.83, 135.14, 134.70, 133.75, 132.90, 132.68, 130.33, 130.00, 129.63, 129.28, 128.88, 128.35, 127.78, 127.24, 126.02, 125.99, 123.47, 119.05, 113.64, 105.61, 70.88, 61.30, 55.31, 45.31, 40.93, 40.77, 35.03, 28.90, 18.38;

HRMS (ESI) m/z: calculated for C₃₅H₃₄N₃O₄ [M+H]⁺: 560.2544, found: 560.2539.



3ap

3-Methoxy-4-(2-(2-oxo-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)quinoxalin-1(2H)-yl)ethoxy)benzaldehyde (3ap): 78.9 mg, 82% yield as a white solid.

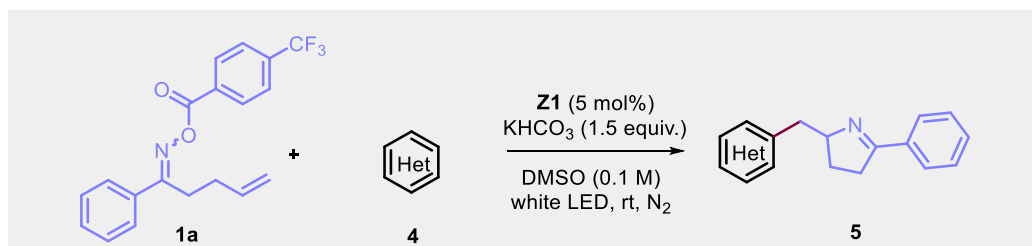
¹H NMR (600 MHz, CDCl₃): δ 9.80 (s, 1H), 7.99 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.80 (dt, *J* = 8.5, 1.7 Hz, 3H), 7.62 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.3, 7.0, 1.5 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.08 (d, *J* = 8.2 Hz, 1H), 4.94 (dd, *J* = 5.7, 4.4 Hz, 2H), 4.89 (dddd, *J* = 11.9, 7.7, 4.7, 2.8 Hz, 1H), 4.54 (t, *J* = 5.1 Hz, 2H), 3.83 (s, 3H), 3.65 (dd, *J* = 14.2, 5.7 Hz, 1H), 3.07 – 2.95 (m, 2H), 2.93 – 2.81 (m, 1H), 2.17 (dddd, *J* = 12.8, 9.9, 7.7, 5.1 Hz, 1H), 1.78 (dddd, *J* = 13.2, 9.9, 7.2, 6.2 Hz, 1H);

SUPPLEMENTARY INFORMATION

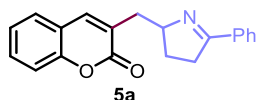
^{13}C NMR (151 MHz, CDCl_3): δ 190.97, 172.70, 155.82, 153.76, 150.11, 149.14, 139.66, 139.01, 134.66, 130.58, 130.53, 129.24, 128.59, 128.51, 127.80, 126.87, 126.71, 126.64, 112.31, 109.63, 71.38, 67.09, 64.43, 56.02, 40.18, 35.01, 28.55;

HRMS (ESI) m/z : calculated for $\text{C}_{29}\text{H}_{28}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$: 482.2074, found: 482.2071.

3.2 Synthesis Procedure and Characterization of Product 5



An oven-dried Schlenk tube equipped with a stirring bar was charged with **1** (0.2 mmol, 69.47 mg, 1.0 equiv.), **4** (0.3 mmol, 1.5 equiv.), **Z1** (0.01 mmol, 4.19 mg, 5 mol%) and KHCO_3 (0.3 mmol, 30.0 mg, 1.5 equiv.). After refilling with N_2 repeated three times, DMSO (2.0 mL) was added through syringe. The mixture was stirred at room temperature in front of a 20 W white light LED bulb. Upon completion, water and EtOAc were added and the mixture was stirred for 10 min. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were then washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product.

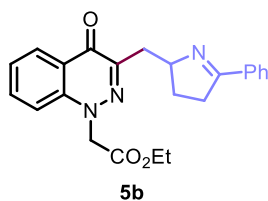


3-((5-Phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-2H-chromen-2-one (5a): 49.7 mg, 82% yield as a white solid after 24 h irradiation.

^1H NMR (600 MHz, CDCl_3): δ 7.84 – 7.75 (m, 2H), 7.75 (s, 1H), 7.49 – 7.44 (m, 2H), 7.44 – 7.37 (m, 3H), 7.32 (dd, J = 8.3, 1.0 Hz, 1H), 7.26 – 7.22 (m, 1H), 4.59 (pt, J = 7.0, 2.0 Hz, 1H), 3.03 (dddd, J = 16.8, 9.9, 4.6, 2.1 Hz, 1H), 2.96 – 2.85 (m, 3H), 2.28 (dddd, J = 12.5, 9.8, 7.7, 4.6 Hz, 1H), 1.72 (dddd, J = 12.8, 9.9, 7.8, 6.8 Hz, 1H);

^{13}C NMR (151 MHz, CDCl_3): δ 172.99, 162.29, 153.40, 140.79, 134.62, 130.77, 130.60, 128.54, 127.81, 127.53, 127.42, 124.34, 119.79, 116.52, 71.59, 37.54, 35.16, 28.88;

HRMS (ESI) m/z : calculated for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 304.1332, found: 304.1329.



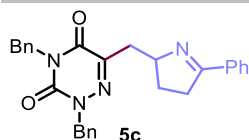
Ethyl 2-(4-oxo-3-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)cinnolin-1(4H)-yl)acetate (5b): 73.9 mg, 95% yield as a yellow solid after 12 h irradiation.

^1H NMR (600 MHz, CDCl_3): δ 8.35 (dd, J = 8.1, 1.5 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.67 (ddd, J = 8.7, 7.0, 1.6 Hz, 1H), 7.42 – 7.34 (m, 4H), 7.17 (d, J = 8.7 Hz, 1H), 5.10 (s, 2H), 4.78 (tt, J = 7.9, 6.0 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.40 (dd, J = 14.2, 5.8 Hz, 1H), 3.06 – 2.93 (m, 2H), 2.88 (dddd, J = 17.1, 9.6, 7.3, 1.8 Hz, 1H), 2.18 (dddd, J = 12.8, 9.9, 7.8, 5.0 Hz, 1H), 1.76 (ddt, J = 13.3, 9.9, 7.0 Hz, 1H), 1.24 (t, J = 7.1 Hz, 4H);

^{13}C NMR (151 MHz, CDCl_3): δ 172.57, 170.98, 167.55, 149.64, 141.40, 134.86, 133.82, 130.34, 128.41, 127.84, 126.51, 124.43, 123.08, 114.07, 71.16, 62.15, 56.78, 36.65, 35.09, 28.53, 14.19;

HRMS (ESI) m/z : calculated for $\text{C}_{23}\text{H}_{23}\text{N}_3\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 412.1632, found: 412.1627.

SUPPLEMENTARY INFORMATION



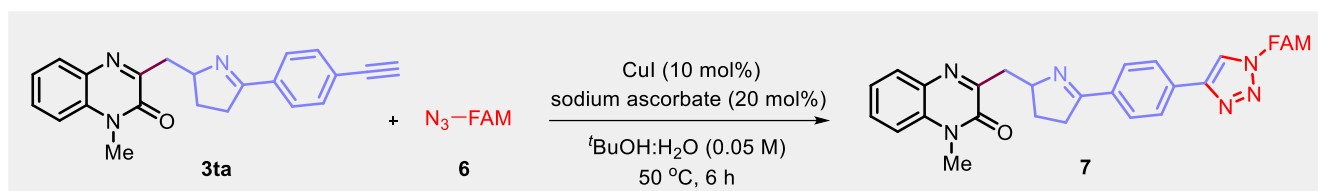
2,4-Dibenzyl-6-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (5c): 81.0 mg, 90% yield as a white solid after 24 h irradiation.

¹H NMR (600 MHz, CDCl₃): δ 7.81 – 7.80 (m, 2H), 7.51 – 7.50 (m, 2H), 7.41 (ddd, *J* = 14.7, 7.9, 6.1 Hz, 5H), 7.36 – 7.27 (m, 6H), 5.20 – 5.04 (m, 4H), 4.67 (tdd, *J* = 9.3, 7.1, 3.5 Hz, 1H), 3.11 – 2.98 (m, 2H), 2.92 (dddd, *J* = 17.1, 9.7, 7.6, 1.8 Hz, 1H), 2.85 (dd, *J* = 14.8, 7.5 Hz, 1H), 2.25 (dddd, *J* = 12.7, 9.8, 7.8, 4.8 Hz, 1H), 1.67 (ddt, *J* = 12.9, 10.0, 7.2 Hz, 1H);

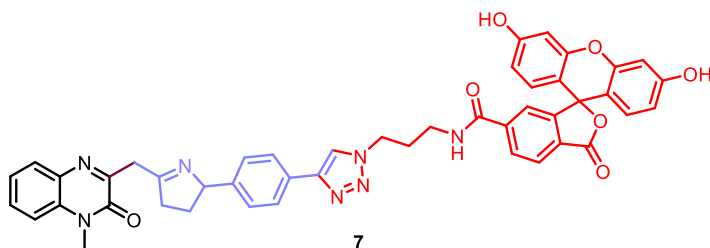
¹³C NMR (151 MHz, CDCl₃): δ 172.89, 156.27, 149.12, 143.97, 135.98, 135.81, 134.60, 130.57, 129.55, 128.78, 128.76, 128.66, 128.51, 128.22, 128.11, 127.86, 70.54, 55.39, 44.32, 37.27, 35.12, 28.81;

HRMS (ESI) *m/z*: calculated for C₂₈H₂₇N₄O₂ [M+H]⁺: 451.2129, found: 451.2127.

3.3 Synthesis Procedure and Characterization of Product 7

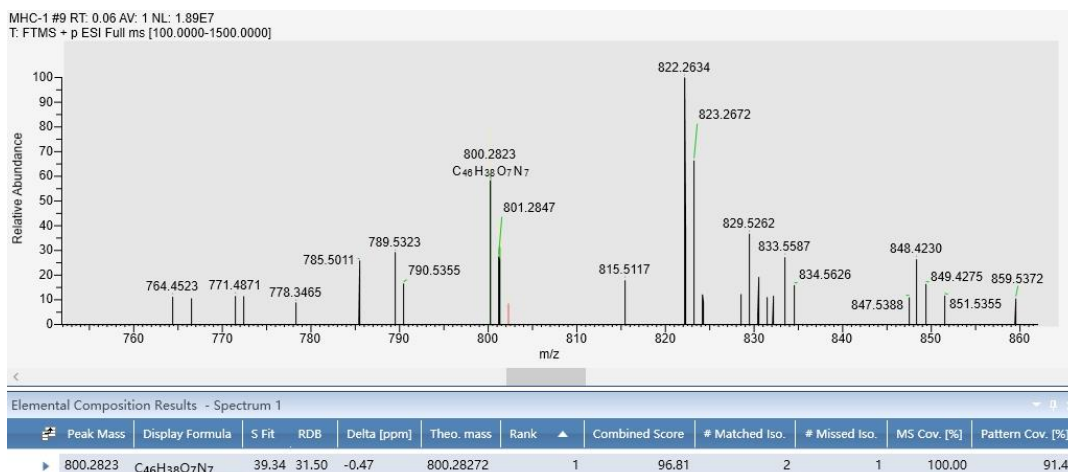


FAM azide **6** (cas: 1386385-76-7, 5.0 nmol, 2.29 mg, 1.0 equiv.) was mixed with **3ta** (5.0 nmol, 1.71 mg, 1.0 equiv.) in 1:1 mixture of *t*BuOH:H₂O (100 μL). To this mixture was added CuSO₄·5H₂O (0.50 nmol, 0.12 mg, 10 mol%) and sodium ascorbate (1.0 nmol, 0.20 mg, 20 mol%). The reaction was stirred at 50 °C for 6 h, then extracted with ethyl acetate, washed twice with dilute aqueous ammonium hydroxide and once with brine. The aqueous layer was back extracted once into ethyl acetate. The organic layers were combined, dried over Na₂SO₄, and evaporated to dryness. Then the product **7** was validated by HRMS.



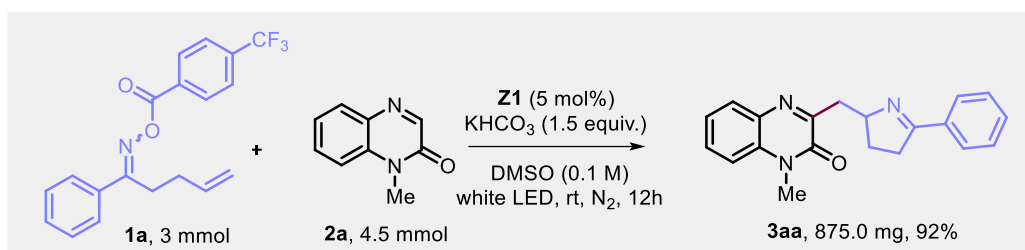
3',6'-Dihydroxy-N-(3-(4-(4-(5-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)-3,4-dihydro-2H-pyrrol-2-yl)phenyl)-1H-1,2,3-triazol-1-yl)propyl)-3-oxo-3H-spiro[isobenzofuran-1,9'-xanthene]-6-carboxamide (7).

HRMS (ESI) *m/z*: calculated for C₄₆H₃₈N₇O₇ [M+H]⁺: 800.2827, found: 800.2823.

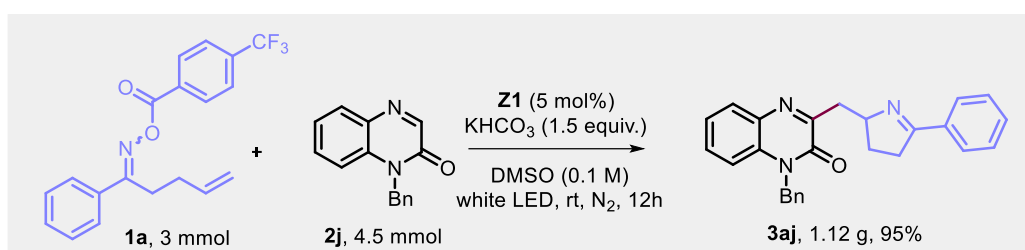


SUPPLEMENTARY INFORMATION

3.4 Gram Scale Synthesis Procedure of Product 3aa and 3aj



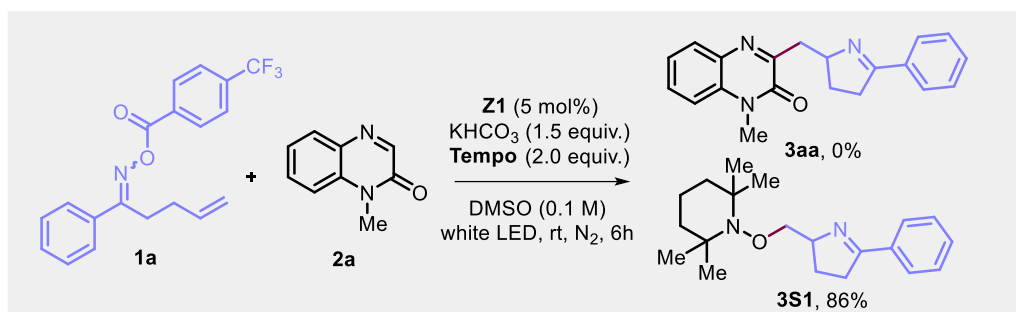
An oven-dried 100 mL Schlenk tube equipped with a stirring bar was charged with **1a** (3.0 mmol, 1.04 g, 1.0 equiv.), **2a** (4.5 mmol, 720.80 mg, 1.5 equiv.), **Z1** (0.15 mmol, 62.91 mg, 5 mol%) and KHCO_3 (4.5 mmol, 450.51 mg, 1.5 equiv.). After refilling with N_2 repeated three times, DMSO (30.0 mL) was added through syringe. The mixture was stirred at room temperature for 12 h in front of a 20 W white LED bulb. Water and EtOAc were added and the mixture was stirred for 20 min. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were then washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product **3aa** (875.0 mg, 92%).



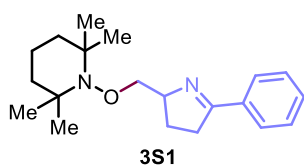
An oven-dried 100 mL Schlenk tube equipped with a stirring bar was charged with **1a** (3.0 mmol, 1.04 g, 1.0 equiv.), **2j** (4.5 mmol, 1.06 g, 1.5 equiv.), **Z1** (0.15 mmol, 62.91 mg, 5 mol%) and KHCO_3 (4.5 mmol, 450.51 mg, 1.5 equiv.). After refilling with N_2 repeated three times, DMSO (30.0 mL) was added through syringe. The mixture was stirred at room temperature for 12 h in front of a 20 W white LED bulb. Water and EtOAc were added and the mixture was stirred for 20 min. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were then washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product **3aj** (1.12 g, 95%).

3. Mechanisms Study Experiments

4.1 Radical Trap Experiment



An oven-dried Schlenk tube equipped with a stirring bar was charged with **1a** (0.2 mmol, 69.47 mg, 1.0 equiv.), **2a** (0.3 mmol, 48.05 mg, 1.5 equiv.), **Z1** (0.01 mmol, 4.19 mg, 5 mol%), KHCO_3 (0.3 mmol, 30.0 mg, 1.5 equiv.) and **Tempo** (0.4 mmol, 62.50 mg, 2.0 equiv.). After refilling with N_2 repeated three times, DMSO (2.0 mL) was added through syringe. The mixture was stirred at room temperature for 6 h in front of a 20 W white LED bulb. Water and EtOAc were added and the mixture was stirred for 10 min. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were then washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product.



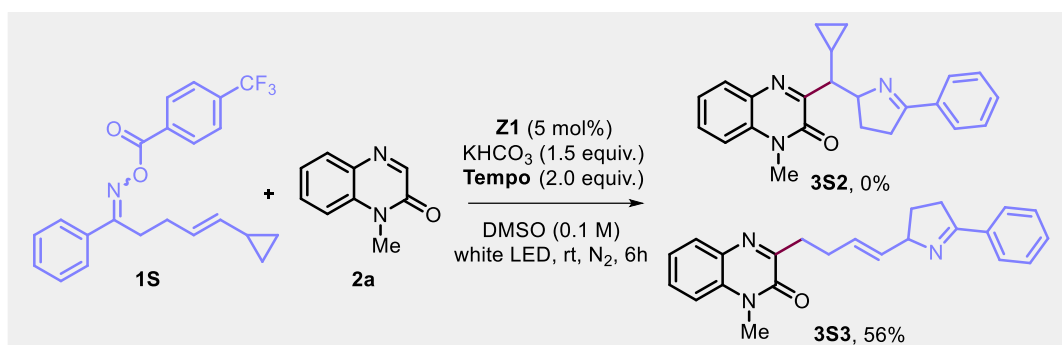
2,2,6,6-Tetramethyl-1-((5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine (3S1): 54.0 mg, 86% yield as a pale yellow solid. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.89 – 7.82 (m, 2H), 7.46 – 7.37 (m, 3H), 4.45 (dq, J = 10.8, 5.2 Hz, 1H), 4.09 (dd, J = 8.7, 4.2 Hz, 1H), 3.97 (dd, J = 8.7, 5.2 Hz, 1H), 3.10 – 2.90 (m, 2H), 2.16 (dtd, J = 12.6, 9.4, 7.0 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.60 – 1.27 (m, 7H), 1.23 (s, 3H), 1.17 (s, 3H), 1.12 (s, 3H), 0.96 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 173.21, 134.52, 130.05, 128.13, 127.49, 78.90, 72.12, 59.65, 39.40, 35.17, 33.00, 32.79, 25.68, 20.02, 19.77, 16.86

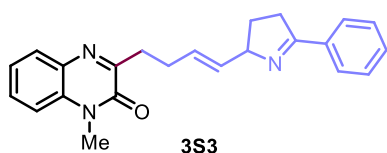
HRMS (ESI) m/z : calculated for $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 315.2431, found: 315.2428.

SUPPLEMENTARY INFORMATION

4.2 Radical Clock Experiment



An oven-dried Schlenk tube equipped with a stirring bar was charged with **5** (0.2 mmol, 91.03 mg, 1.0 equiv.), **T4** (0.01 mmol, 5.0 mg, 5 mol%) and K_2CO_3 (0.2 mmol, 27.60 mg, 1.0 equiv.). After refilling with N_2 repeated three times, MeCN (1.0 mL) and **2a** (0.6 mmol, 140.65 mg, 3.0 equiv.) was added through syringe. The mixture was stirred at 10 °C in a freezer for 24 h in front of a 20 W white LED bulb. Saturated NaHCO_3 aqueous solution and EtOAc were added and the mixture was stirred for 10 min. The layers were separated and the aqueous layer was extracted with EtOAc . The combined organic layers were then washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product.



(E)-1-Phenyl-6-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)hex-5-en-1-one (8): 39.8 mg, 56% yield as a white solid.

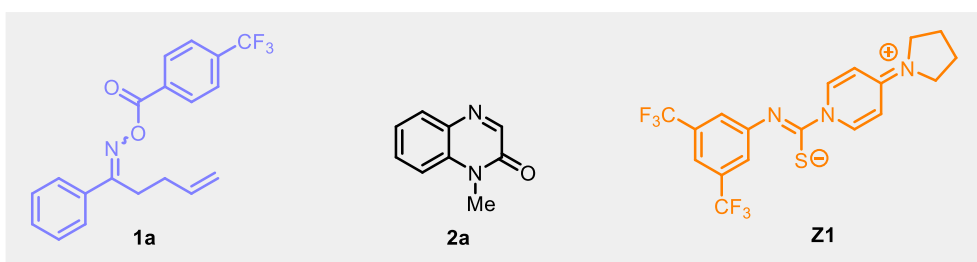
$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.95 (d, $J = 7.2$ Hz, 2H), 7.86 – 7.82 (m, 2H), 7.81 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.50 (ddd, $J = 8.5, 7.2, 1.5$ Hz, 1H), 7.42 – 7.35 (m, 3H), 7.31 (ddd, $J = 8.3, 7.3, 1.2$ Hz, 1H), 7.27 – 7.25 (m, 1H), 5.83 (dtd, $J = 14.6, 6.7, 1.1$ Hz, 1H), 5.66 (ddt, $J = 15.2, 7.2, 1.5$ Hz, 1H), 4.68 (q, $J = 7.0$ Hz, 1H), 3.67 (s, 4H), 3.07 – 2.96 (m, 3H), 2.87 (dddd, $J = 16.9, 9.4, 7.5, 1.8$ Hz, 1H), 2.61 – 2.52 (m, 2H), 2.24 (dddd, $J = 12.8, 9.6, 7.9, 5.0$ Hz, 1H), 1.76 – 1.65 (m, 1H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 173.13, 160.47, 154.94, 134.54, 133.19, 132.79, 130.56, 130.13, 129.76, 129.68, 128.46, 127.89, 123.61, 113.65, 74.39, 35.11, 33.94, 29.73, 29.46, 29.11;

HRMS (ESI) m/z : calculated for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 358.1914, found: 358.1910.

SUPPLEMENTARY INFORMATION

4.3 UV-Vis Absorption Spectroscopic Measurements



0.1M stock solutions of different starting materials were prepared using DMSO as solvent for measurements. The solutions with KHCO_3 was stirred under N_2 for 1 h in dark and the supernatant was separated for measurement.

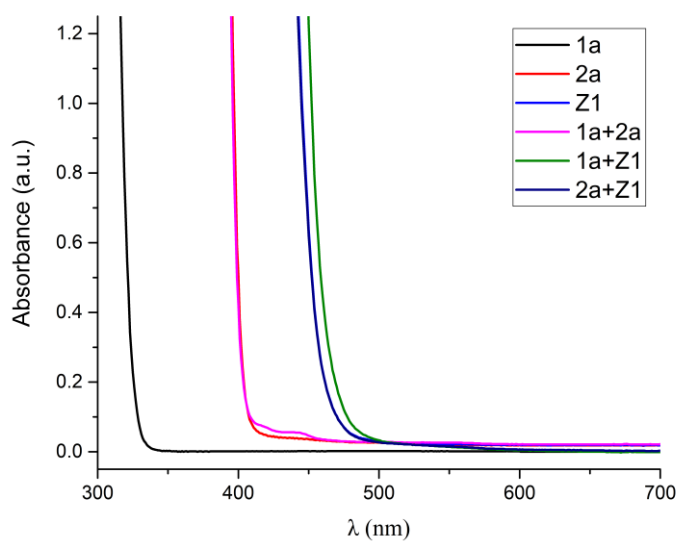


Figure S1: UV/vis absorption spectra of the combination between **1a**, **2a**, and **Z1**.

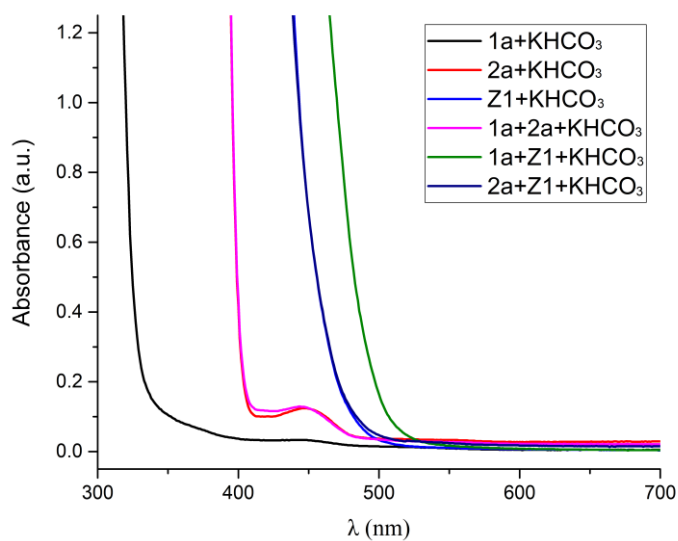


Figure S2: UV/vis absorption spectra of the combination between **1a**, **2a**, and **Z1** with KHCO_3 .

SUPPLEMENTARY INFORMATION

4.4 Job's Plot Experiment

Eleven measurements with **Z1** molar fraction of 0, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100% of the combination of **1a** and **Z1** were recorded in the solution with KHCO_3 . The absorbance obtained at 480 nm was selected and plotted.

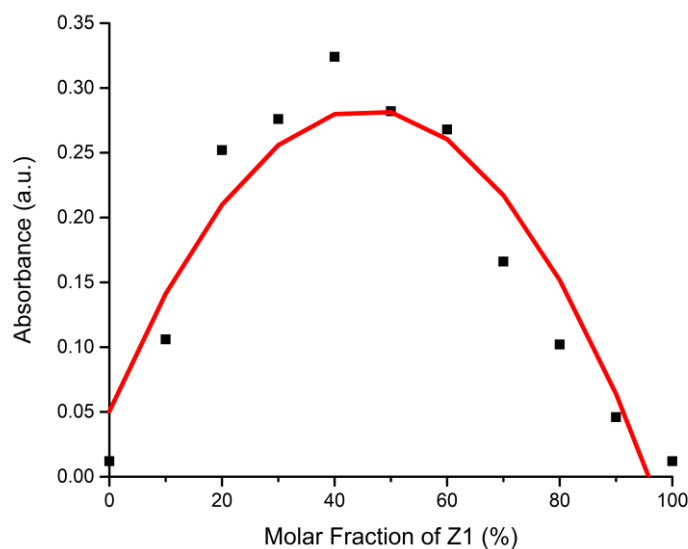


Figure S3: Job's plot of the EDA complexes with UV-Vis absorption spectrometry.

4.5 On-Off-On Experiment

A series of identical reactions between **1a** and **2a** were conducted under the standard conditions on a 0.2 mmol scale, using DMSO as the solvent, and employing 5 mol% of **Z1** with 1.5 equiv. of KHCO_3 . The mixture was subjected to sequential periods of stirring under 20 W white LED irradiation followed by stirring in the absence of light. At each time point (0.5 h, 1.0 h, 1.5 h, ..., 7 h, 8 h, 10 h), one of the reactions was terminated and separated, and the yields of **3aa** were recorded.

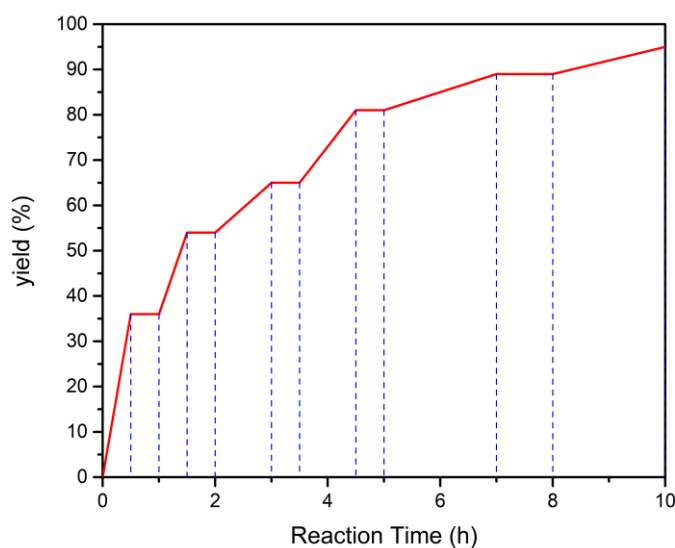


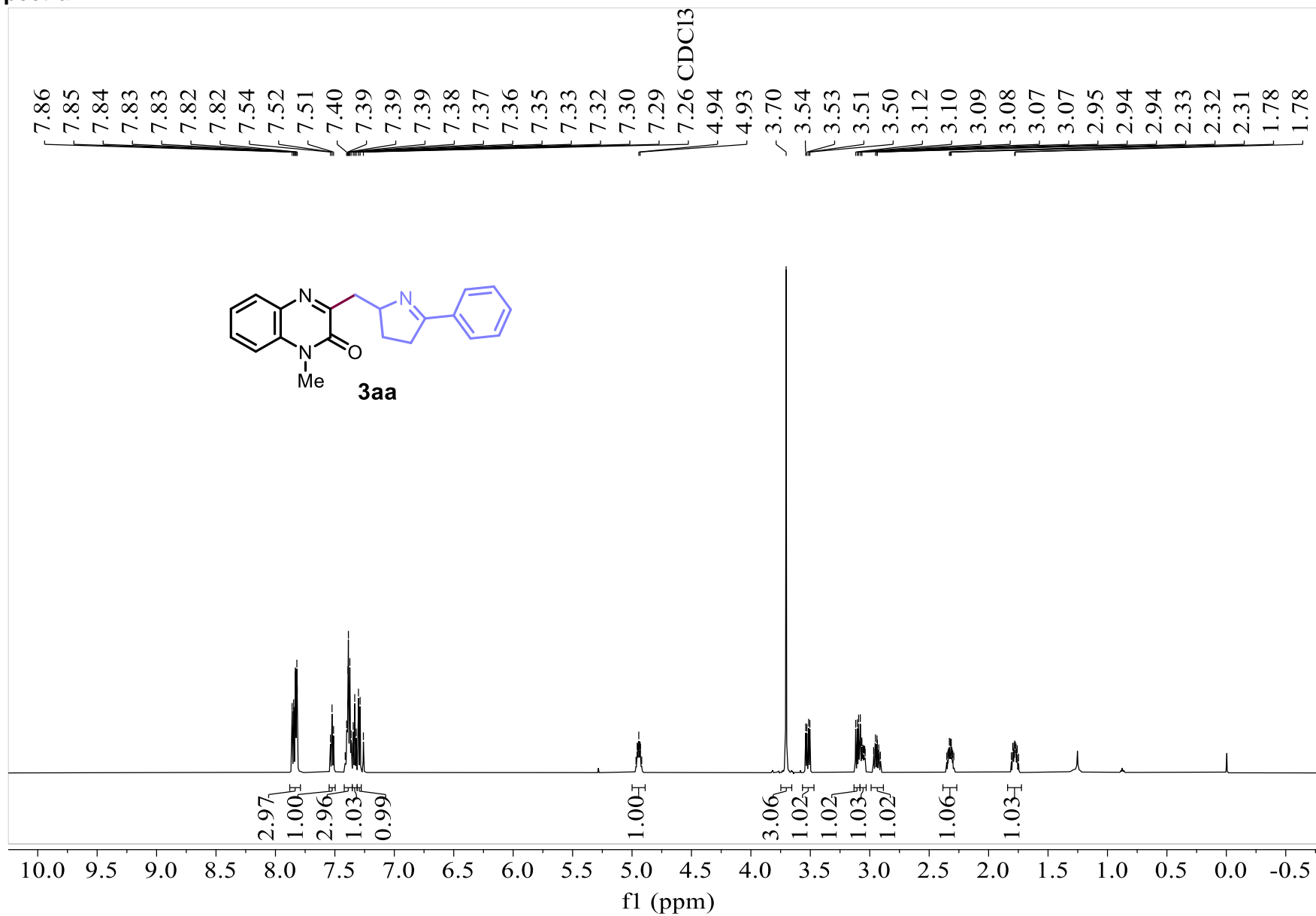
Figure S4: On-Off-On experiment over the time.

References

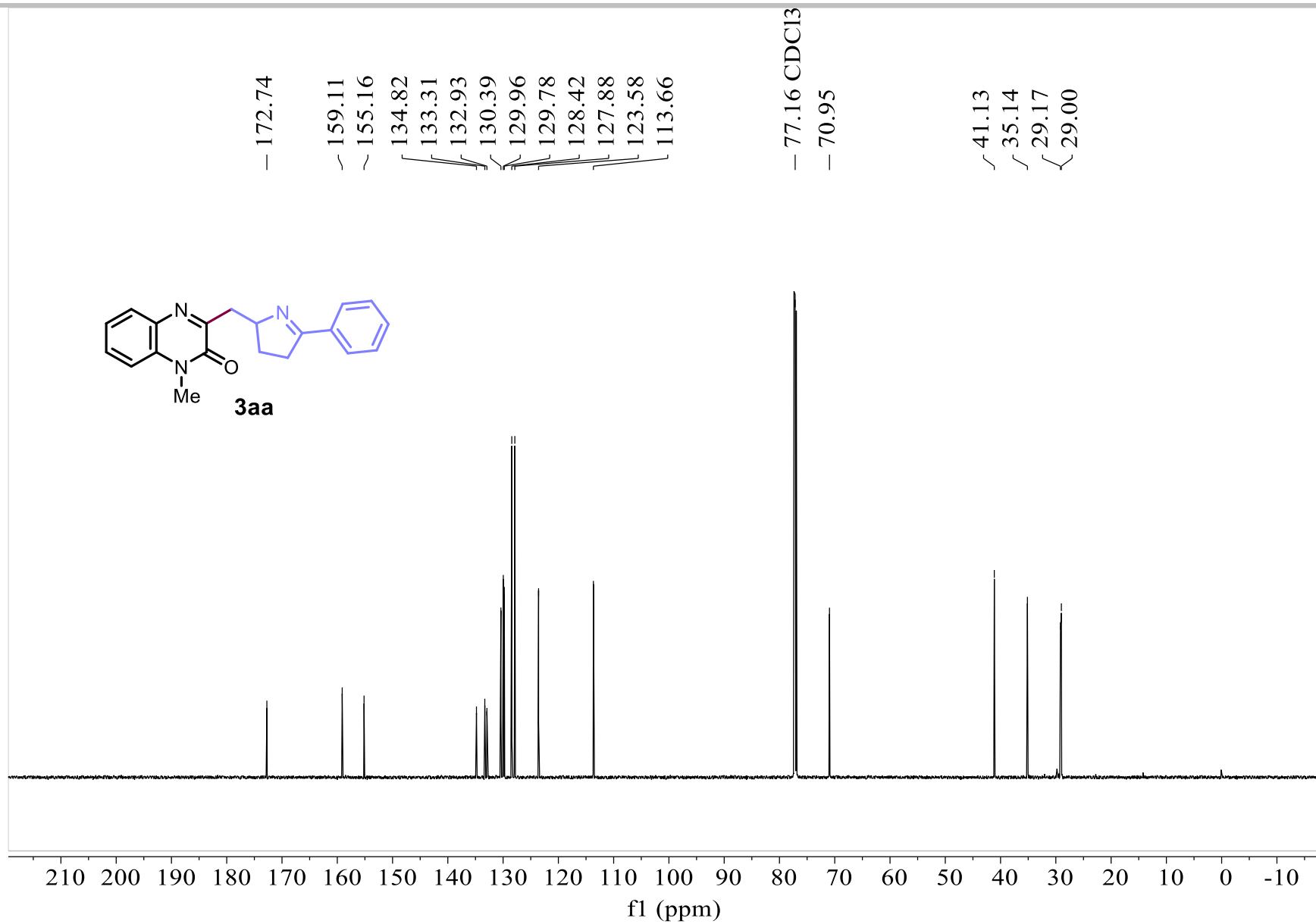
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SUPPLEMENTARY INFORMATION

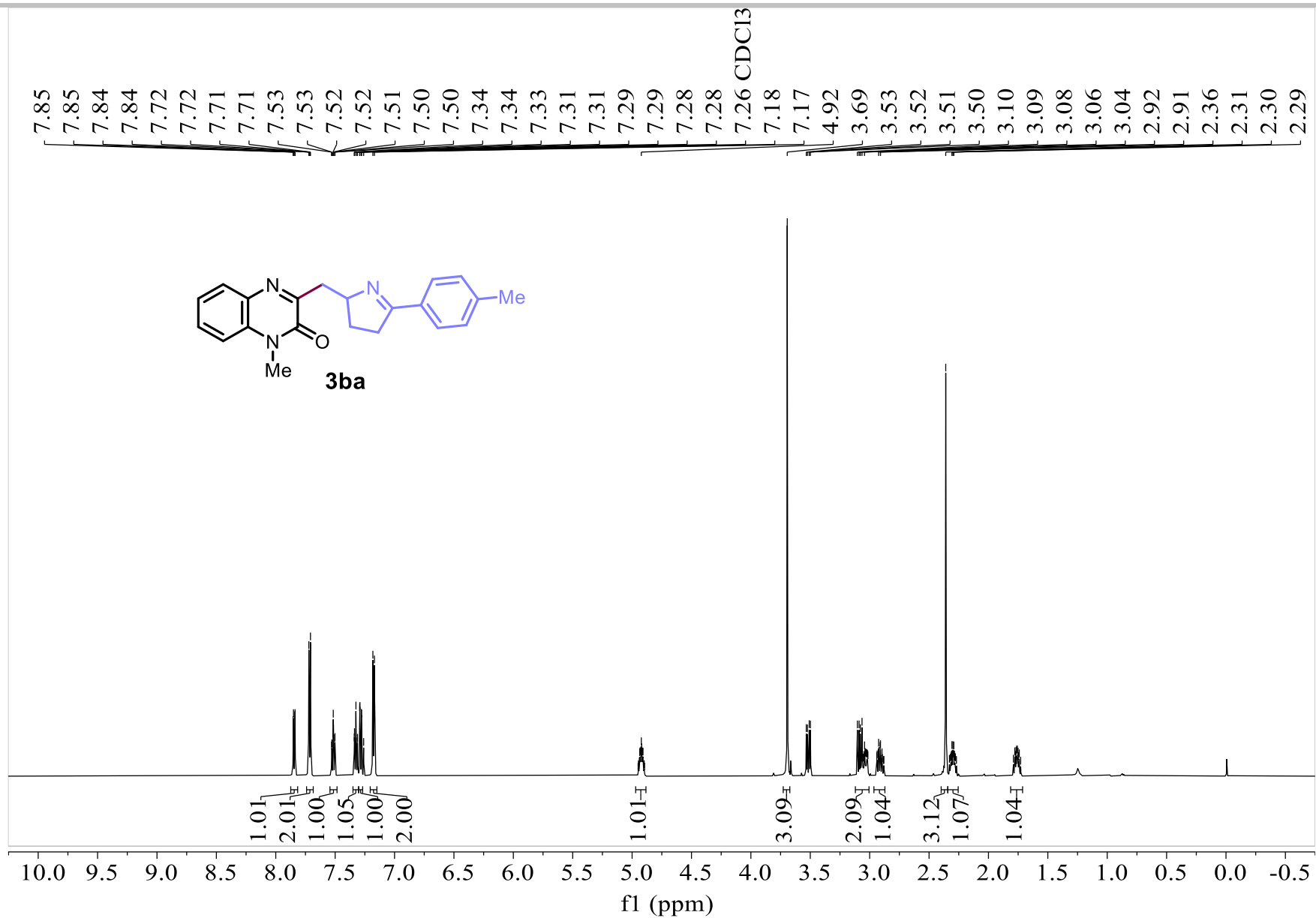
NMR Spectra



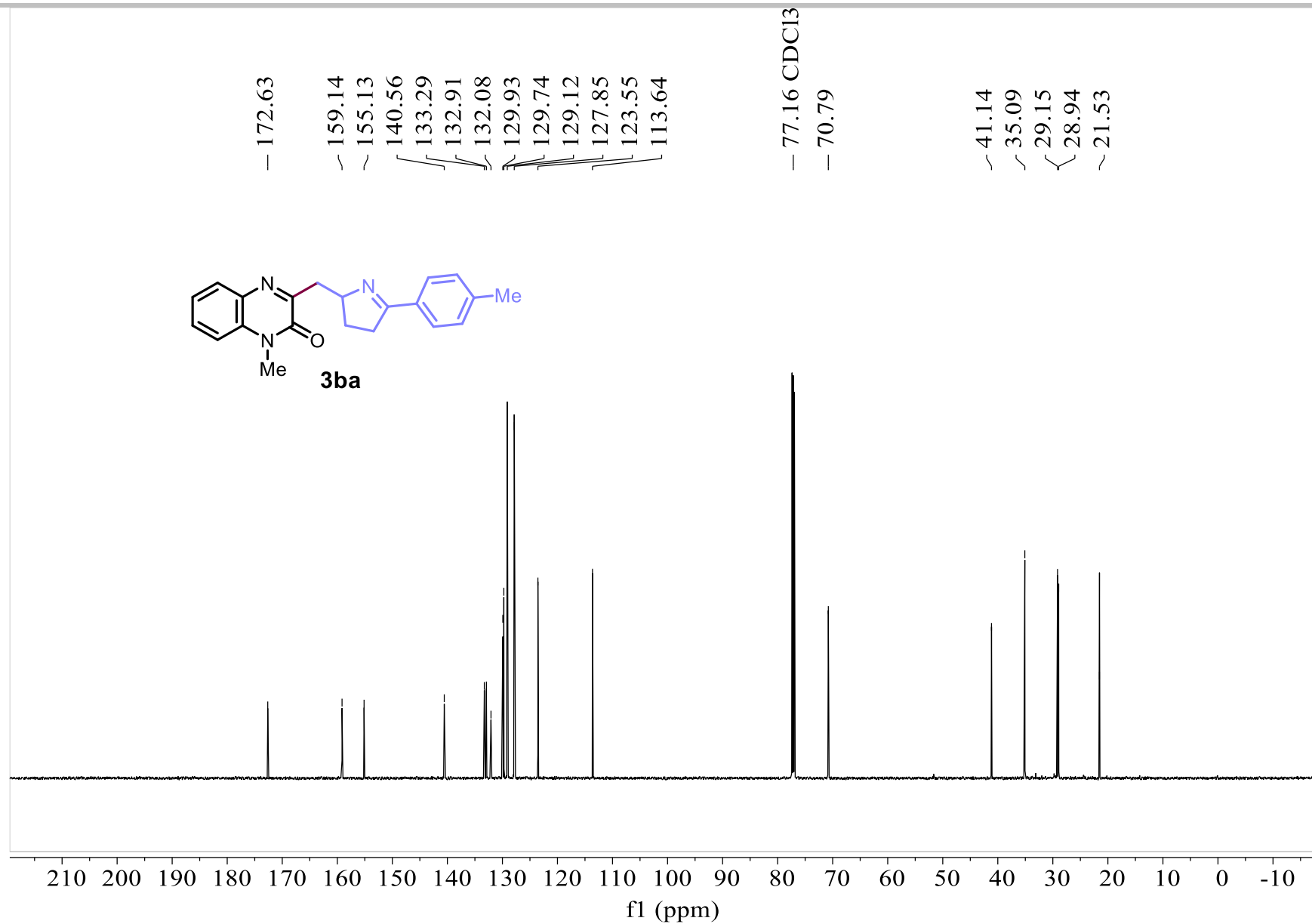
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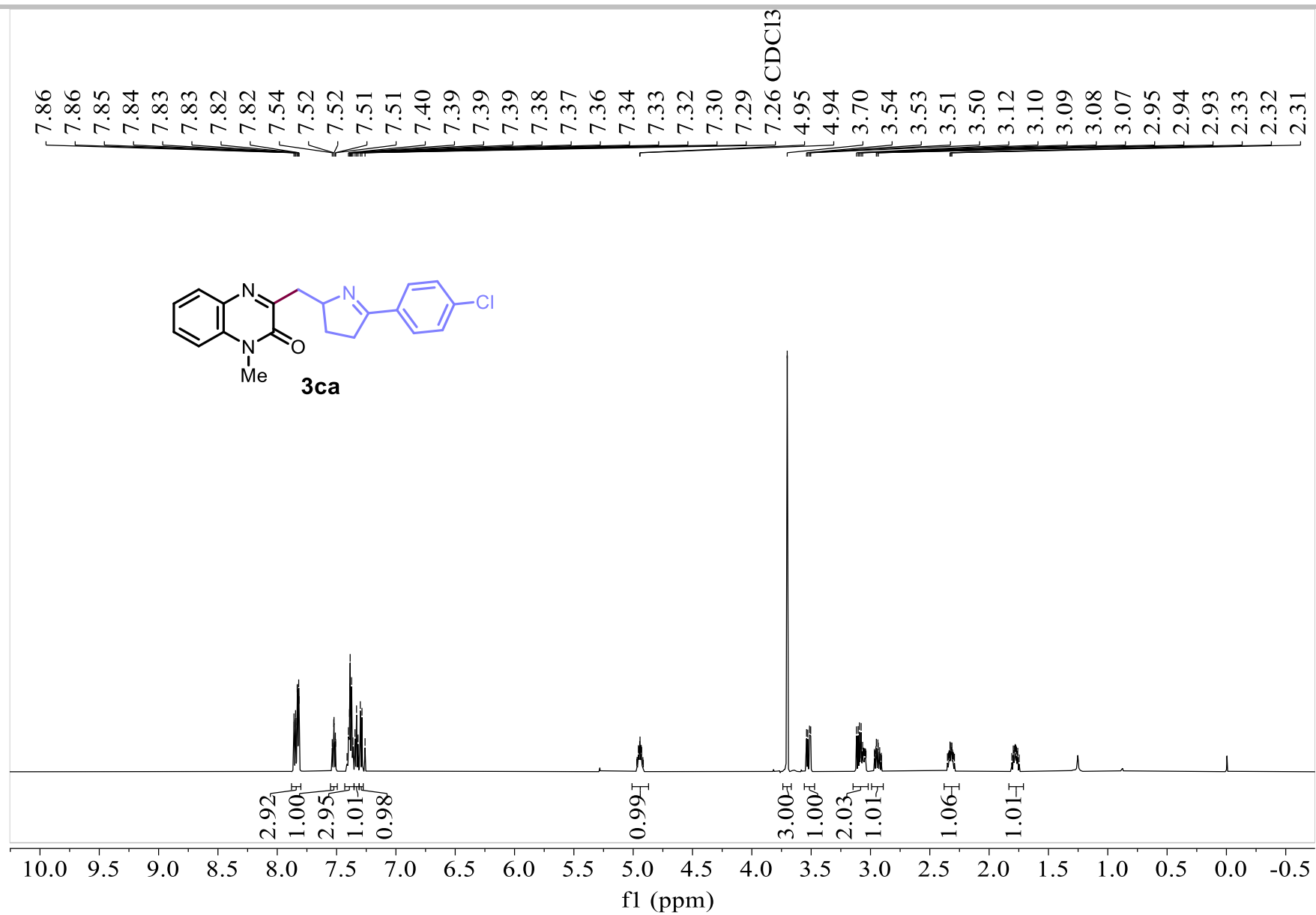
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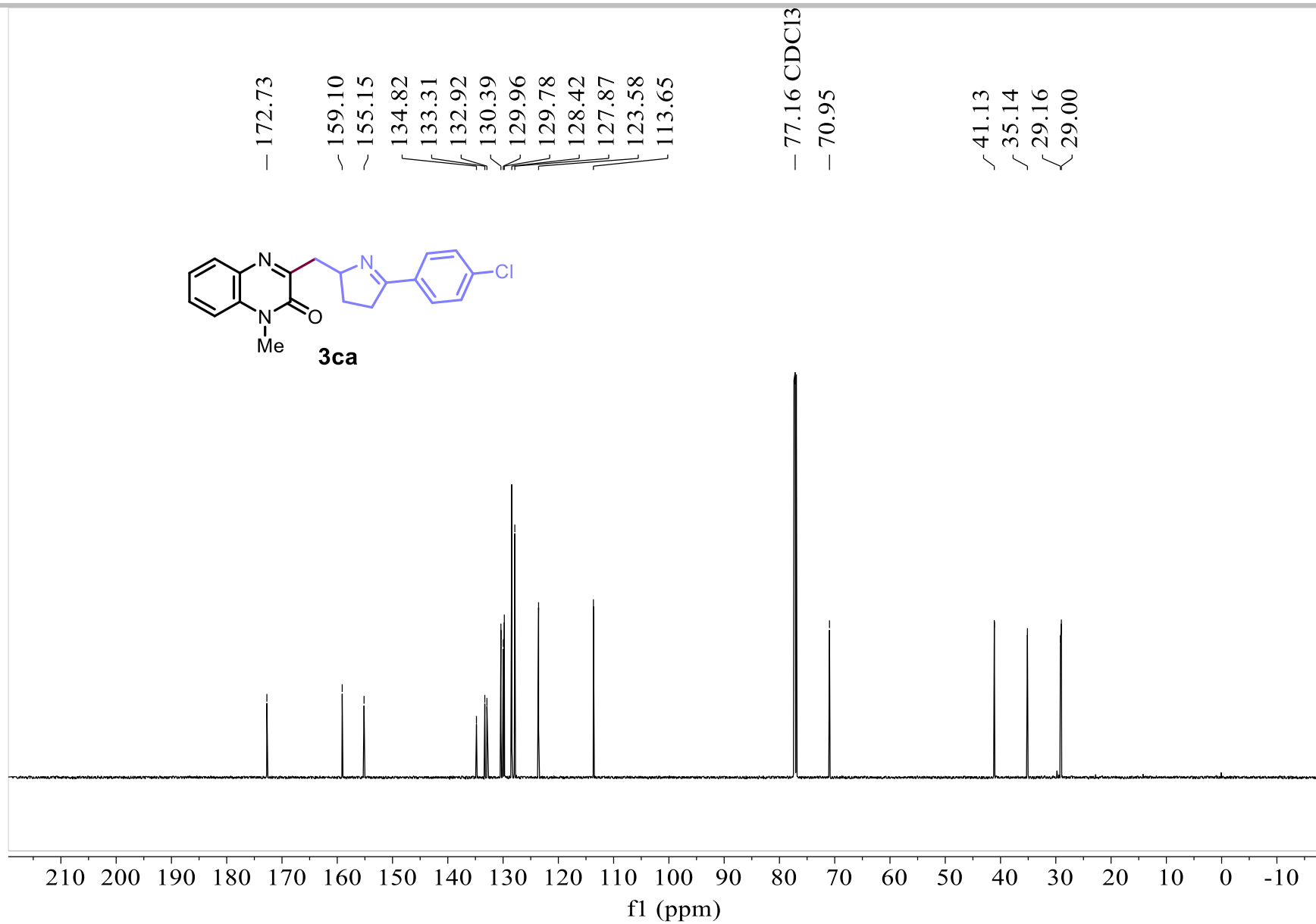
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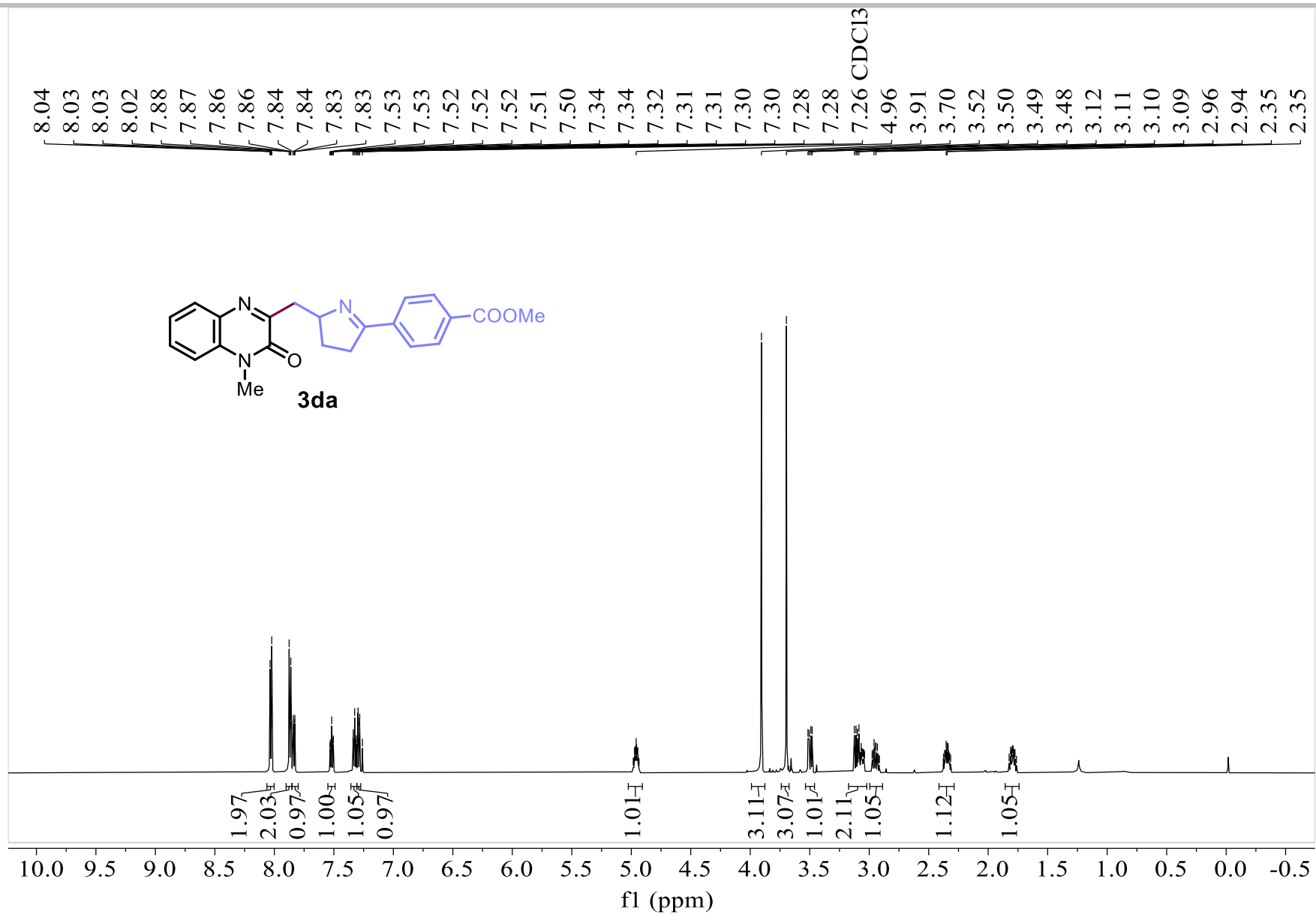
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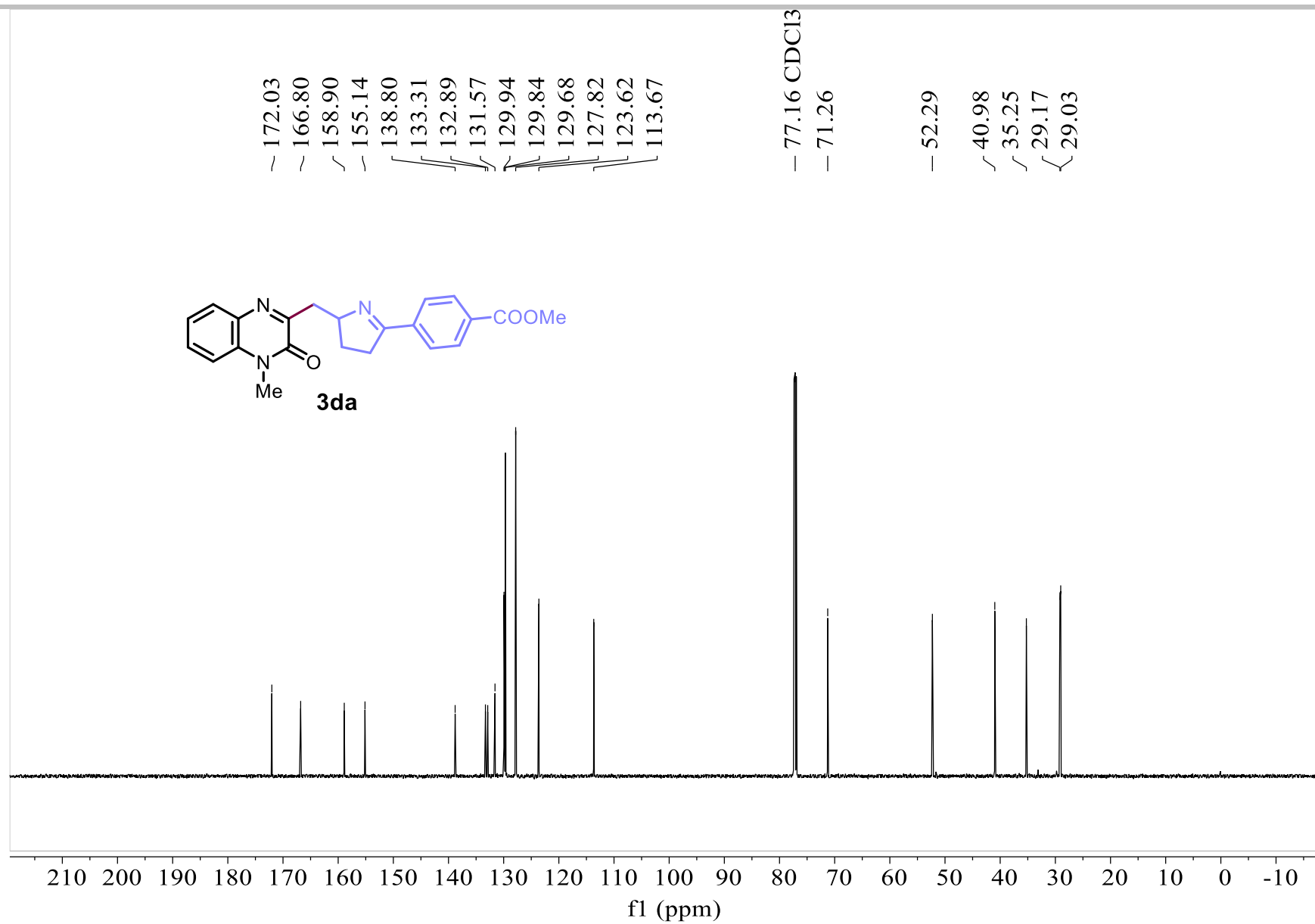
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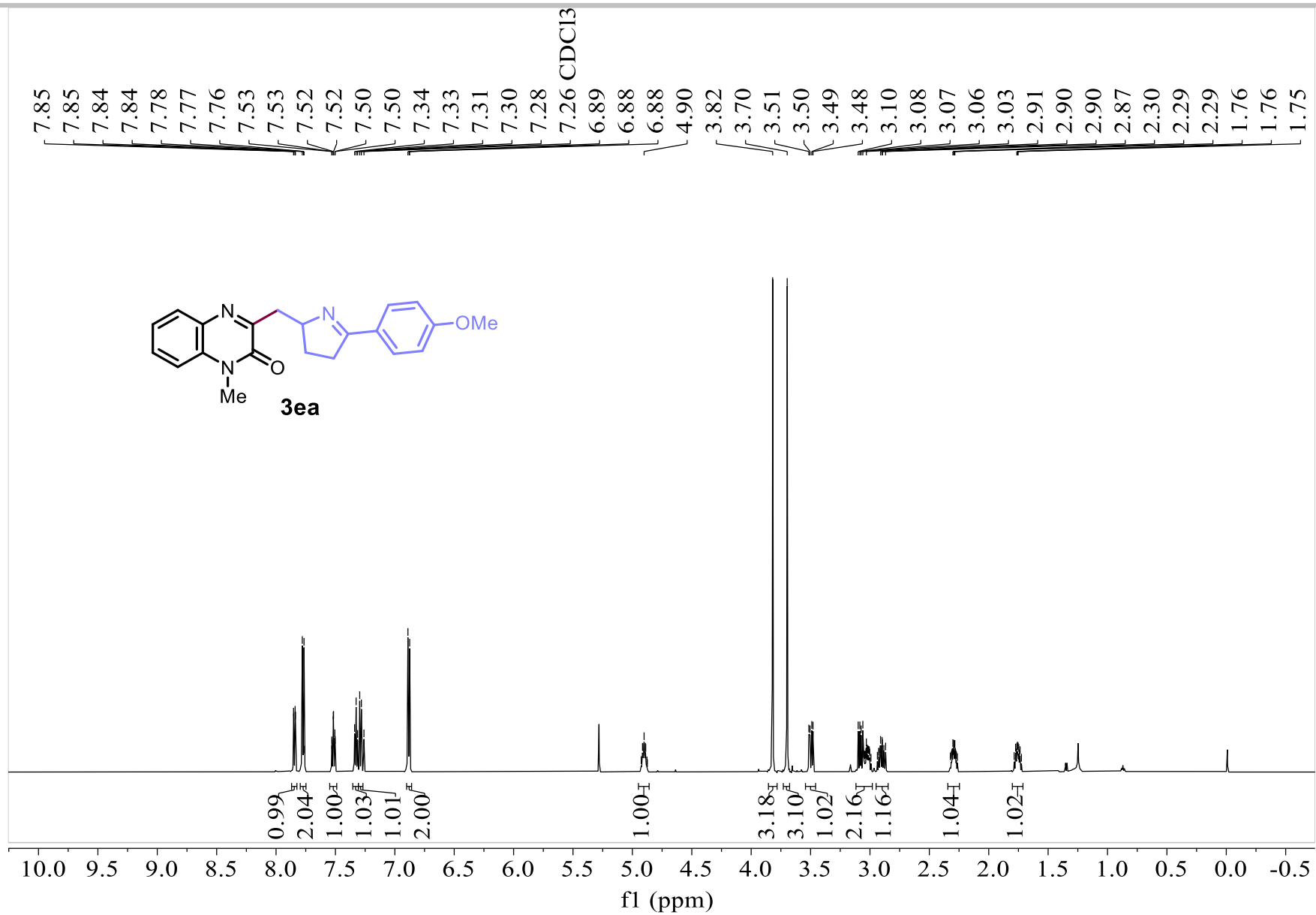
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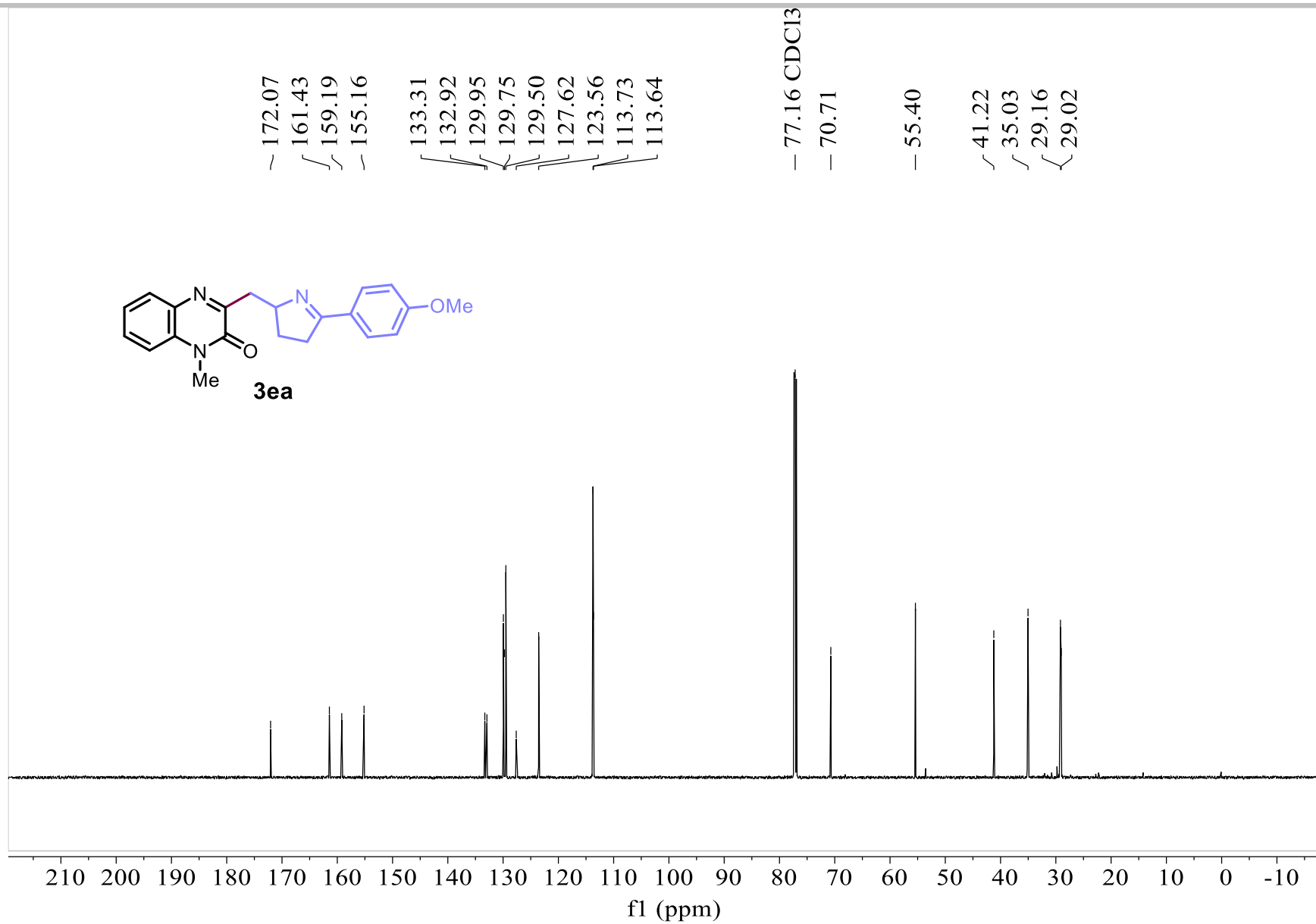
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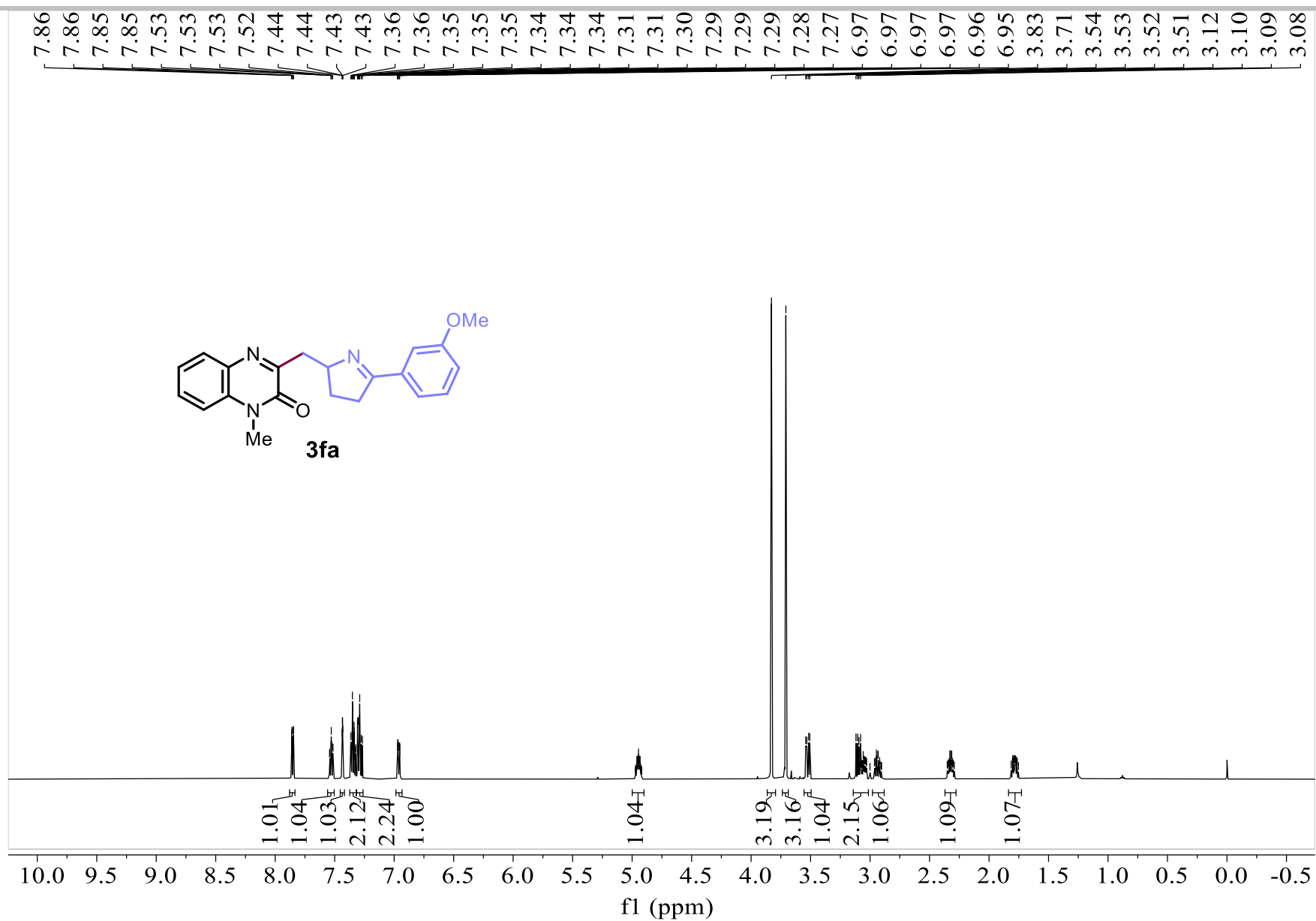
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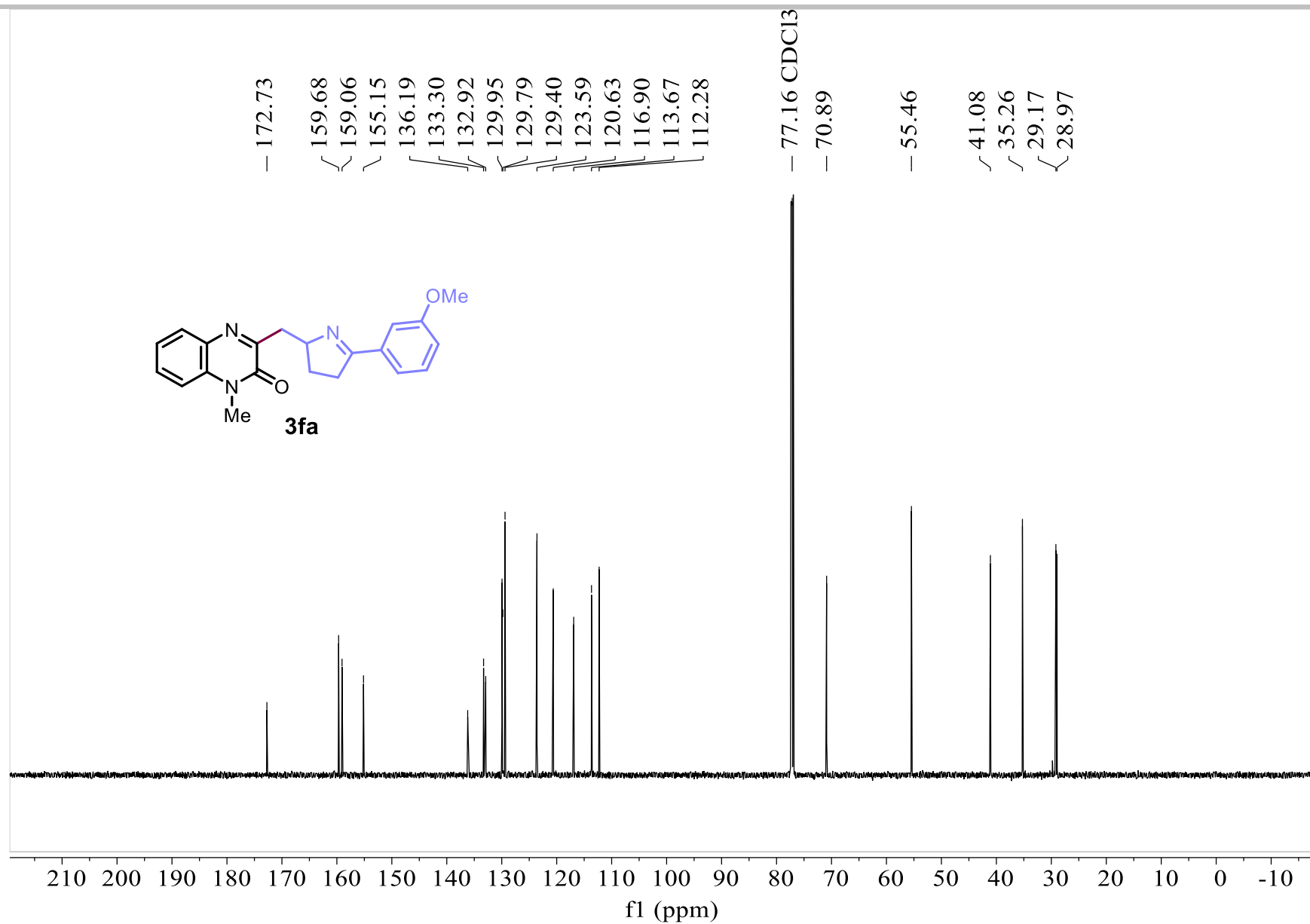
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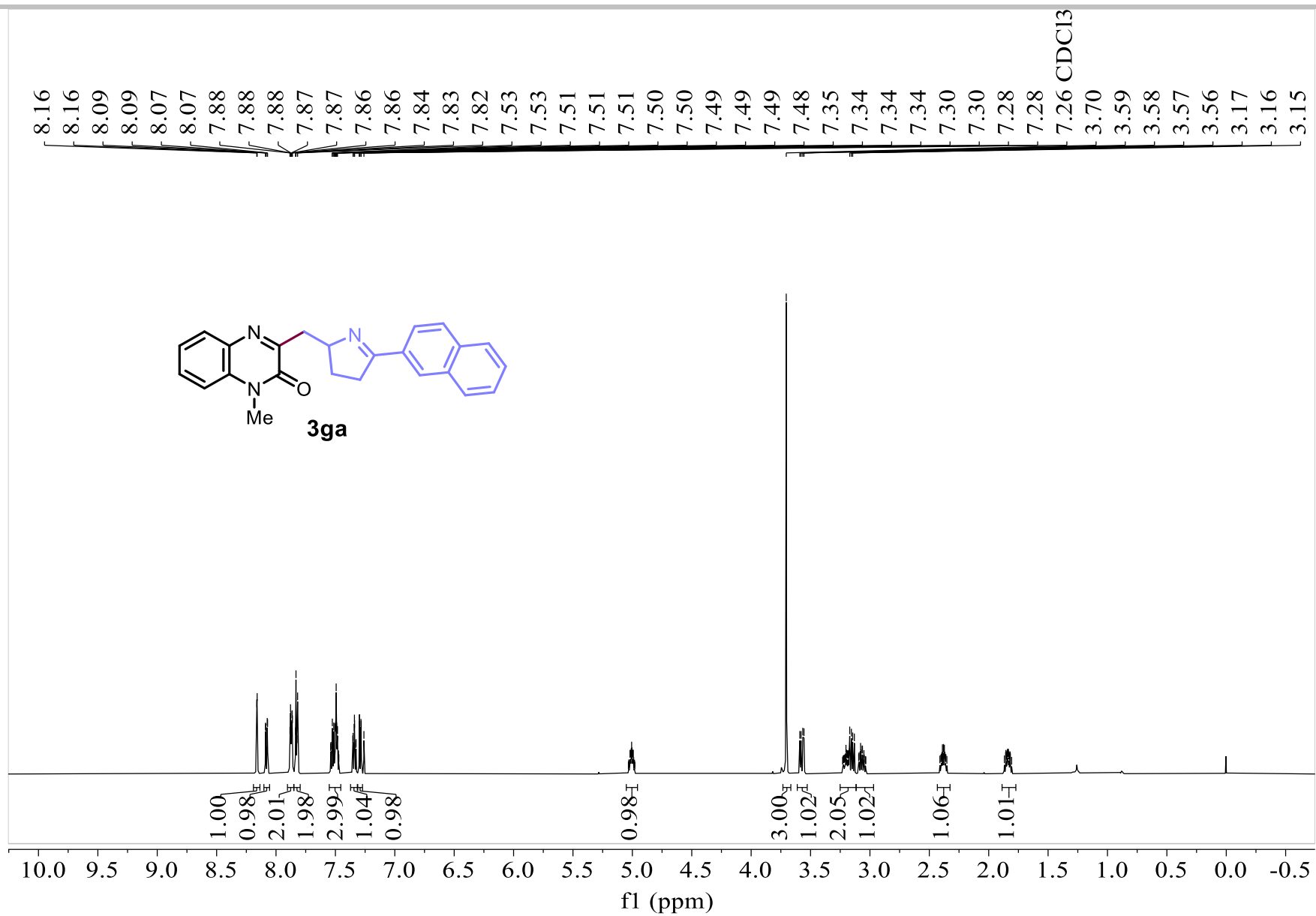
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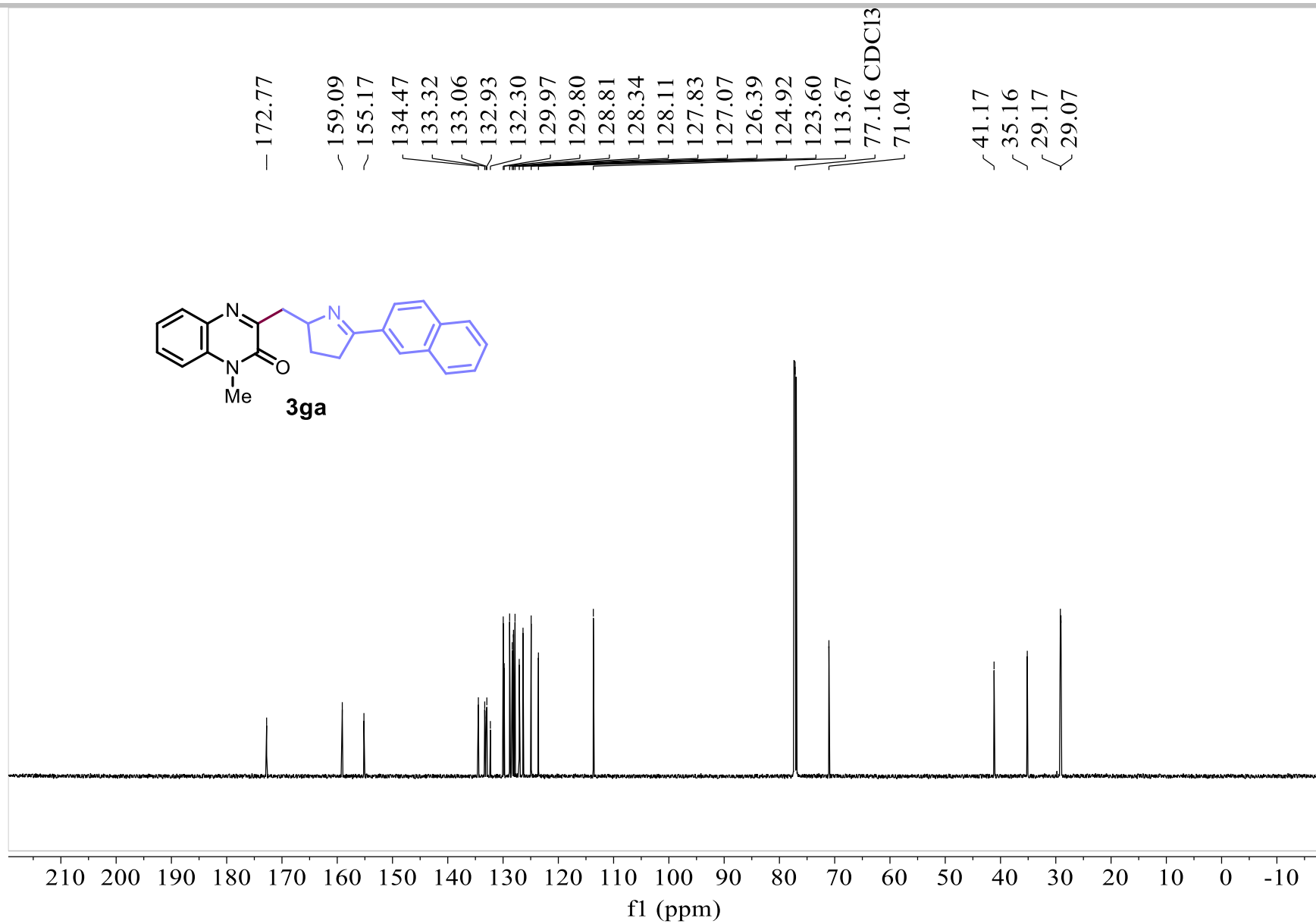
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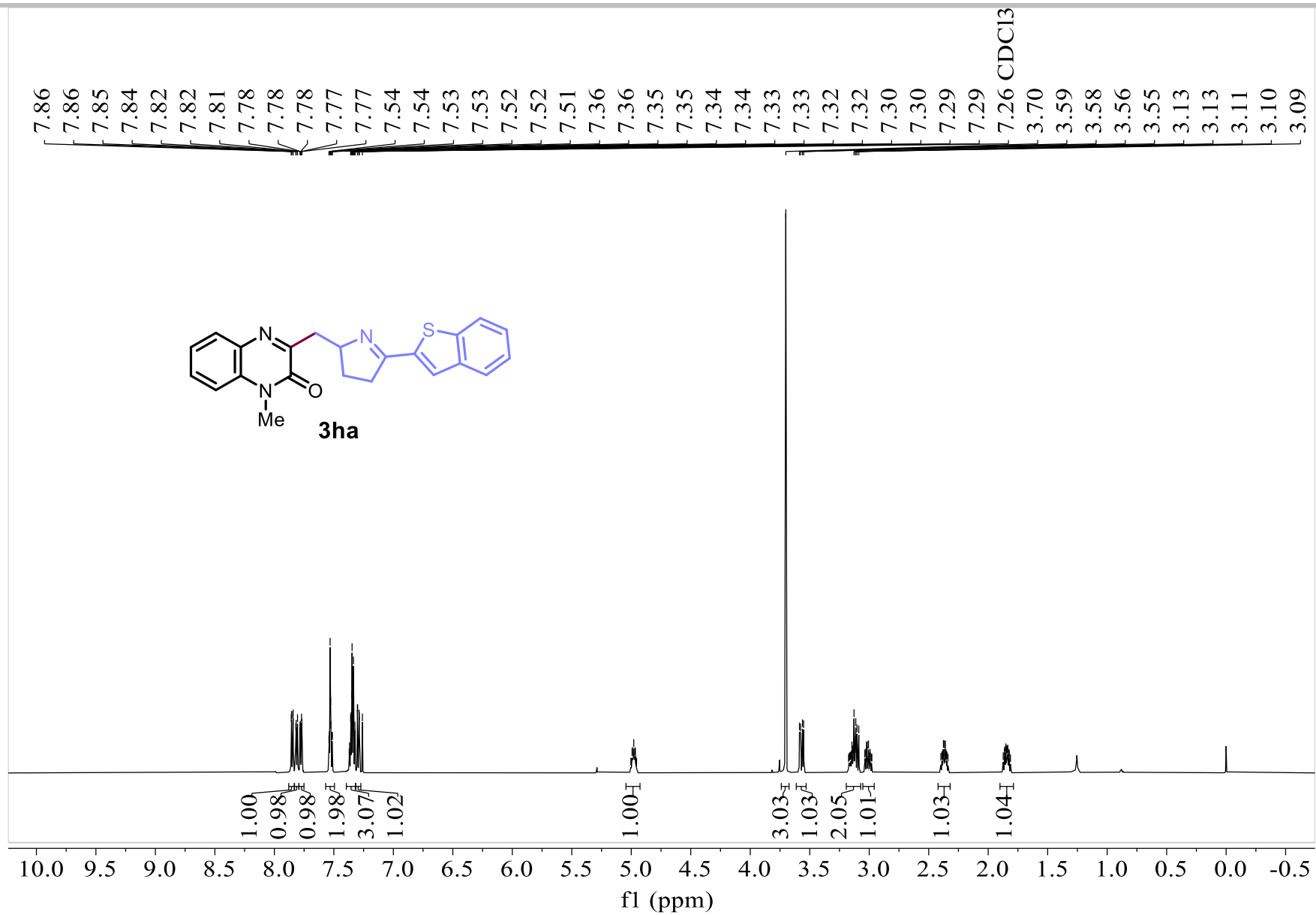
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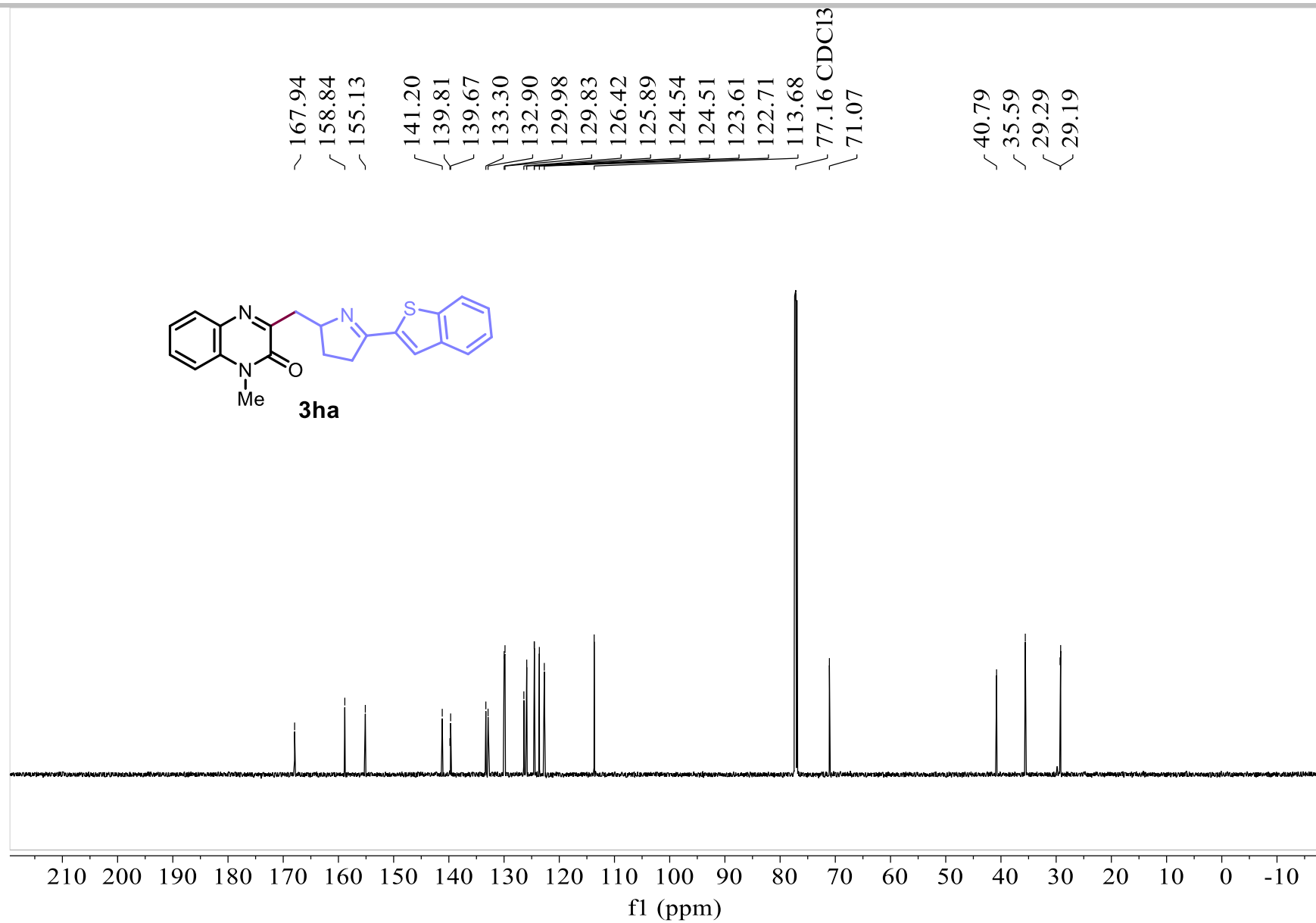
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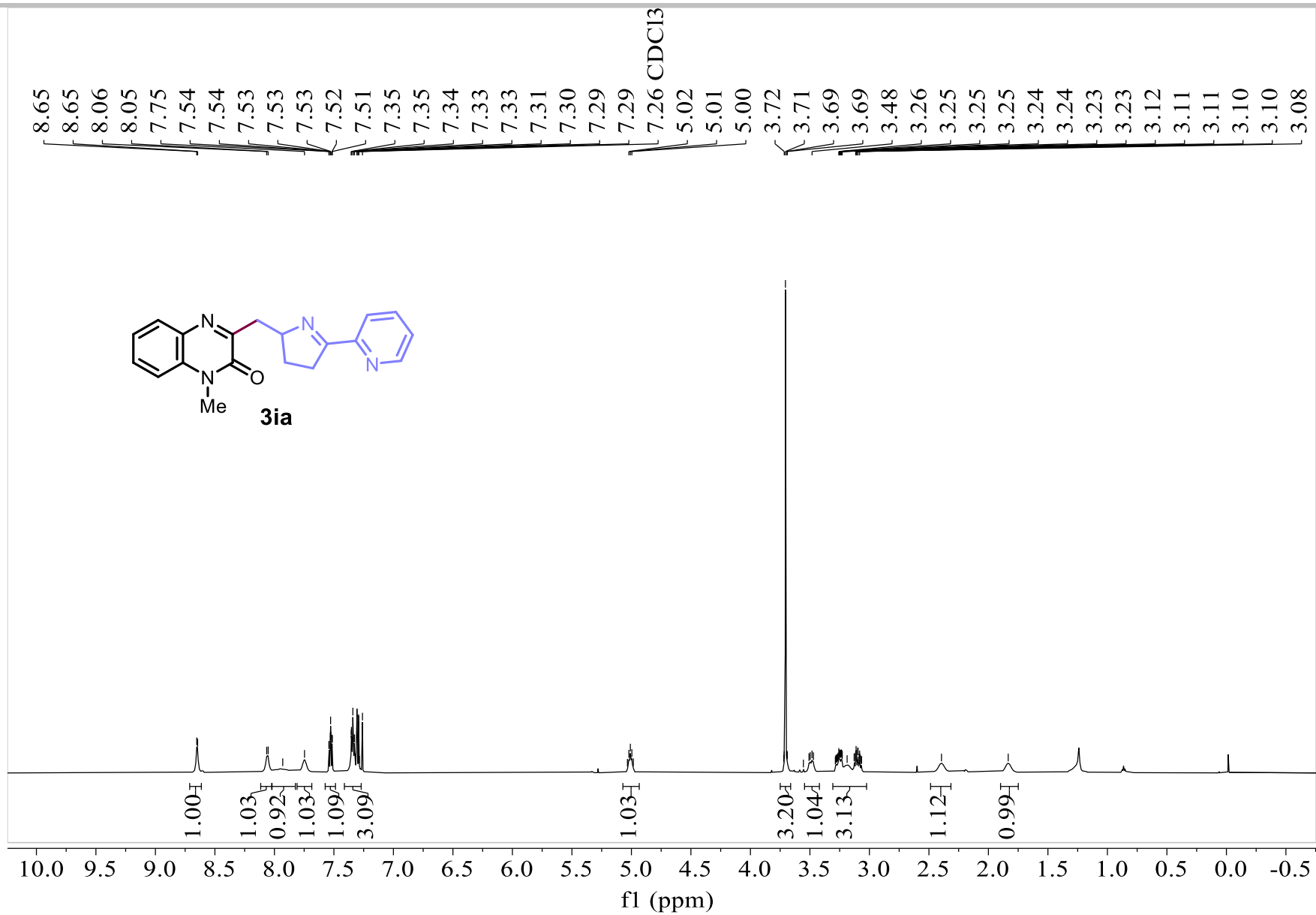
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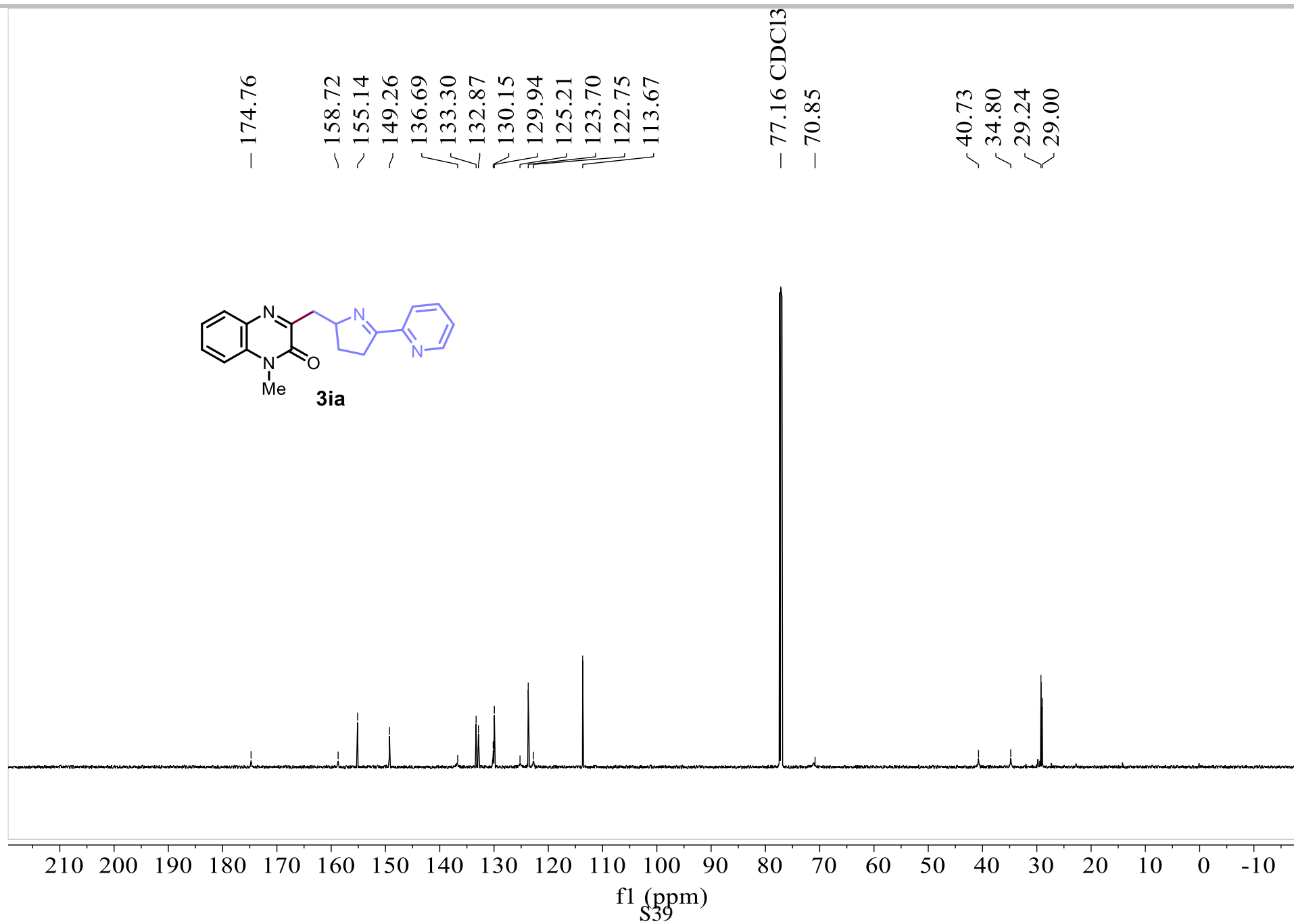
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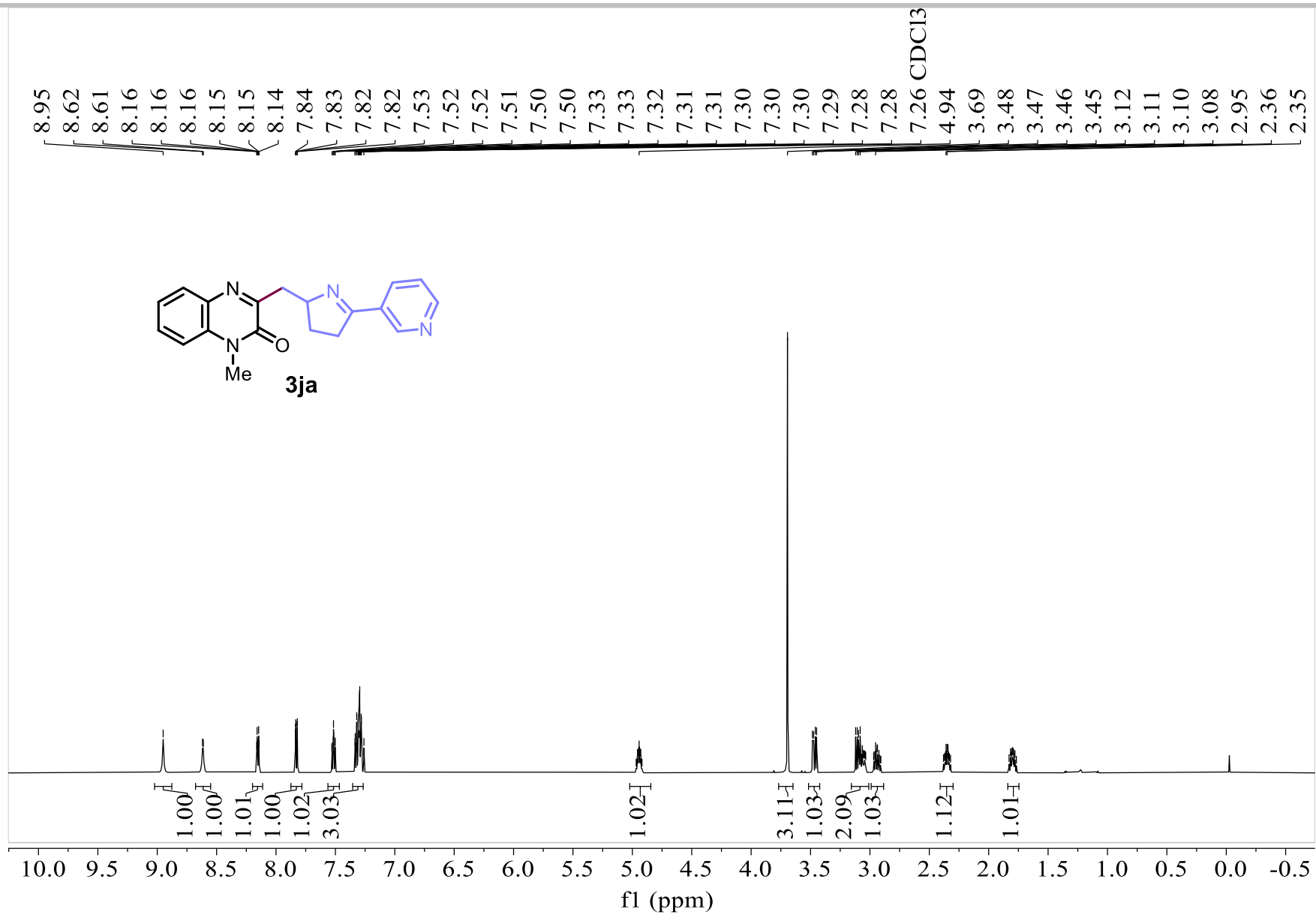
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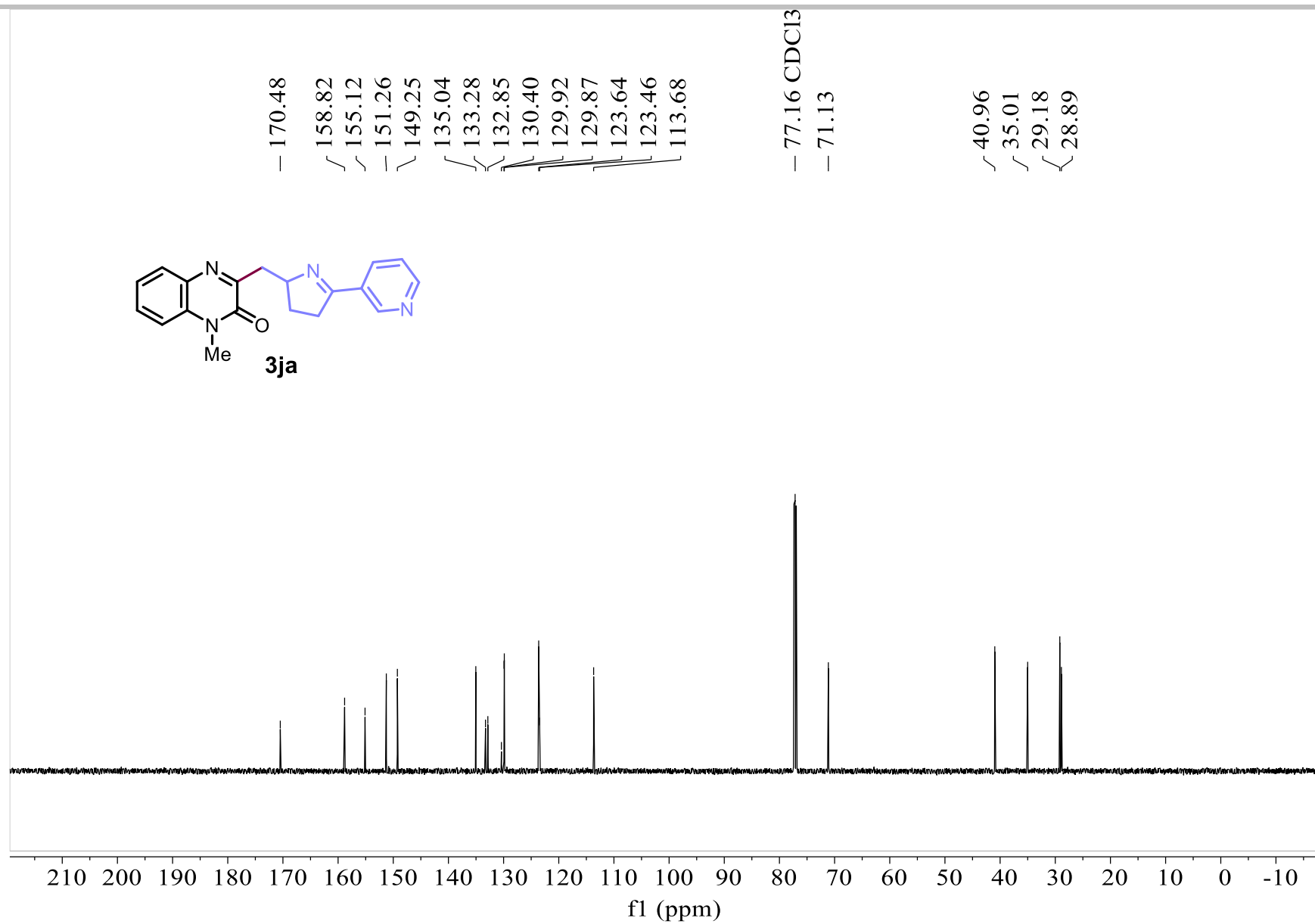
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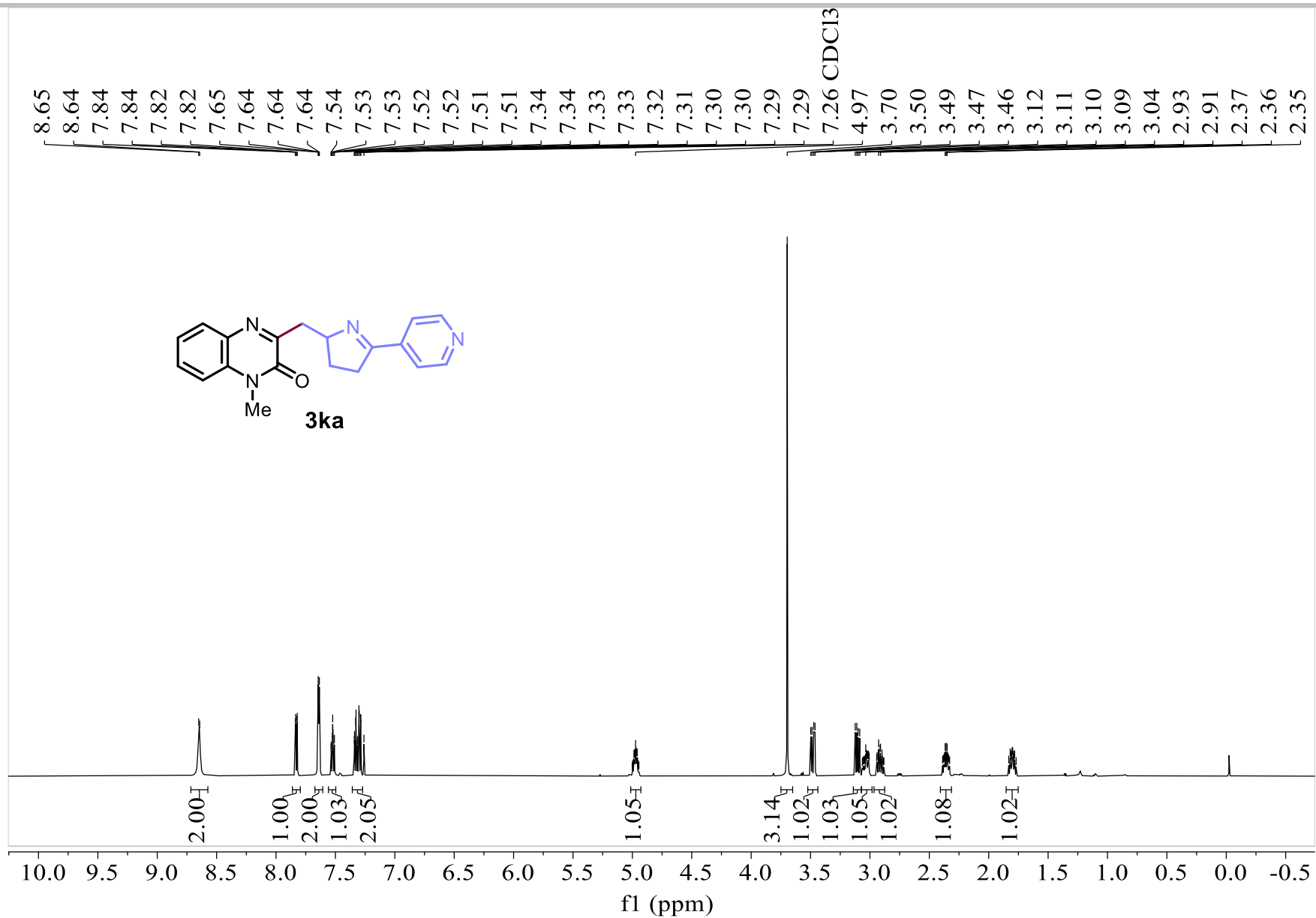
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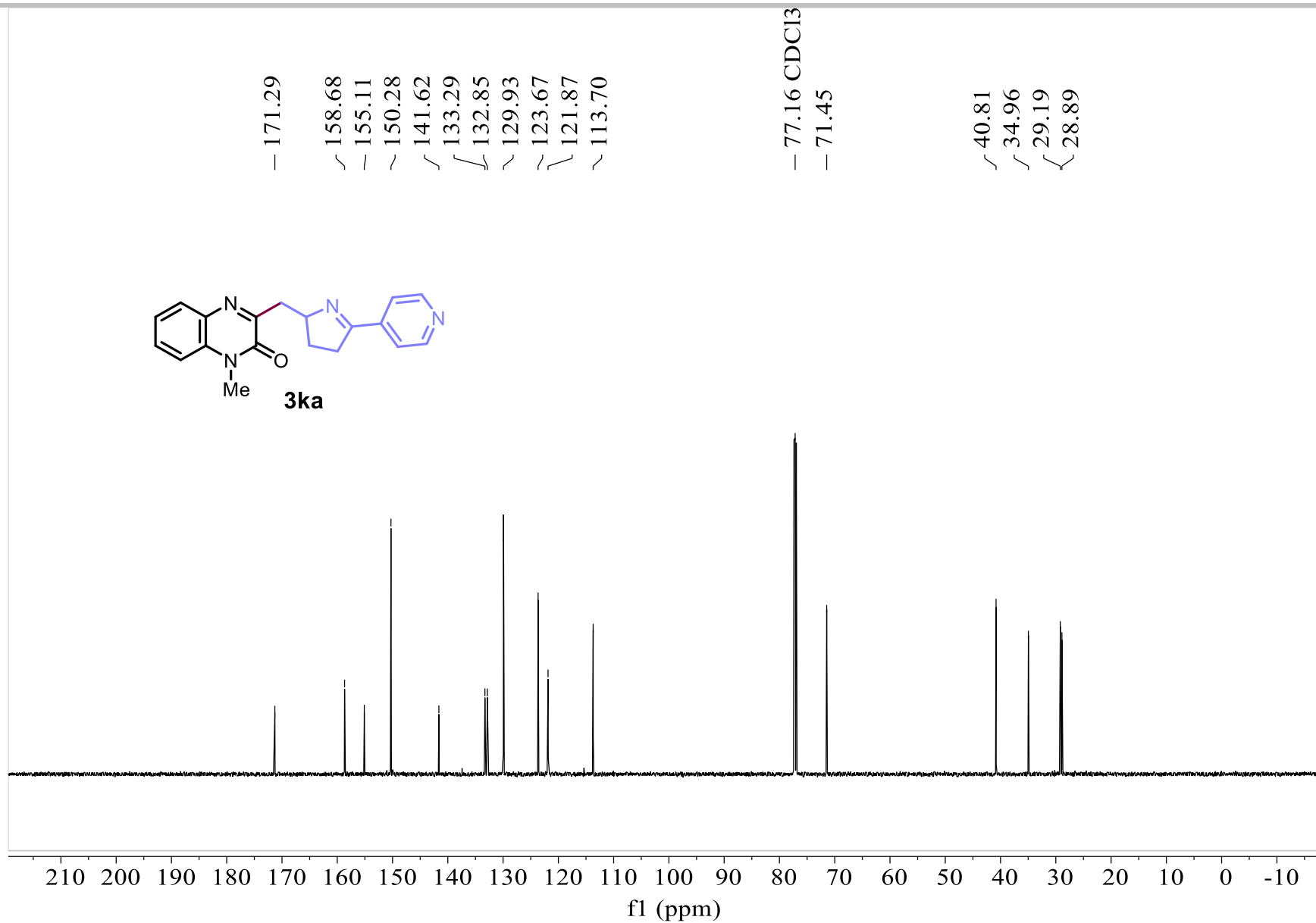
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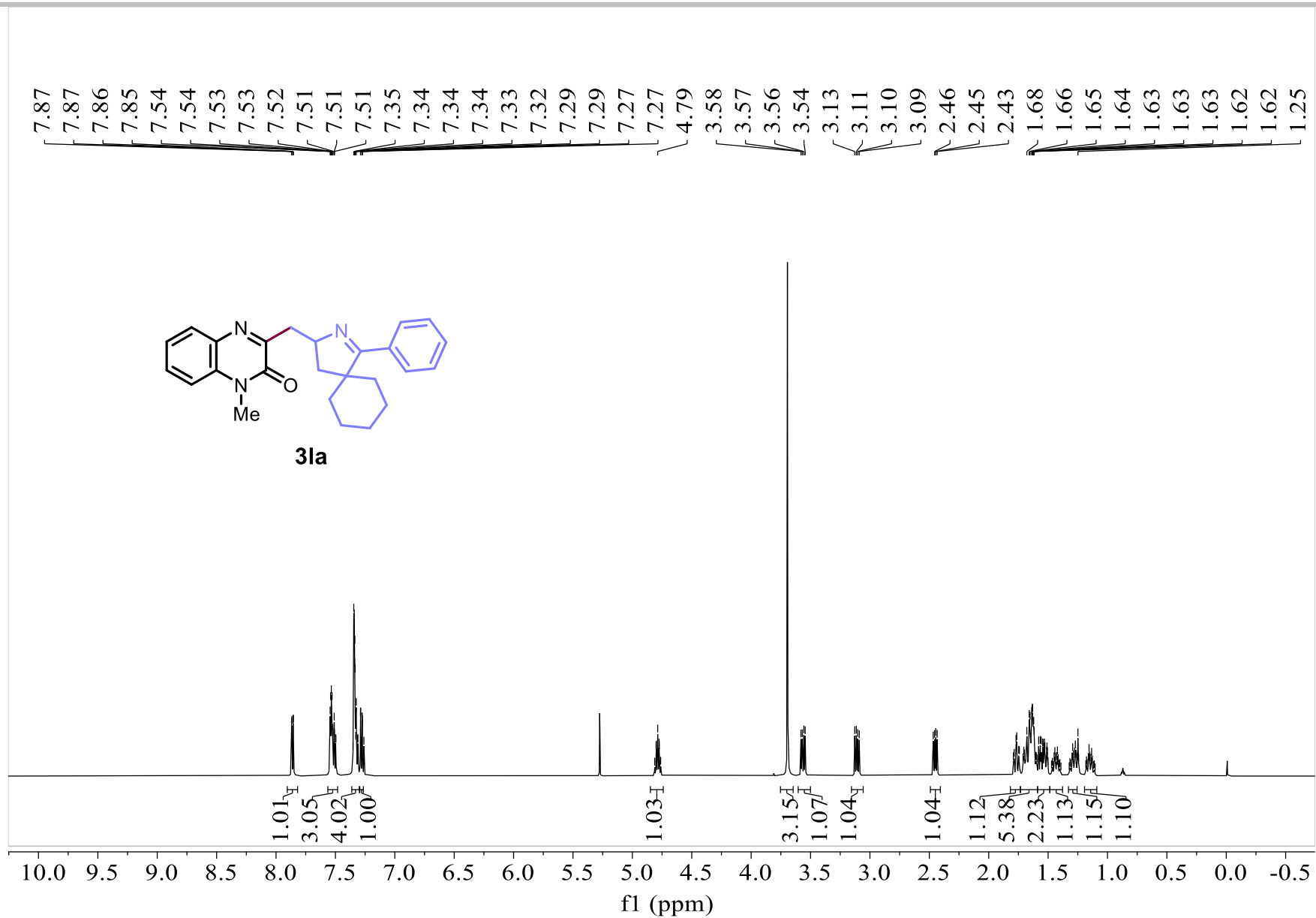
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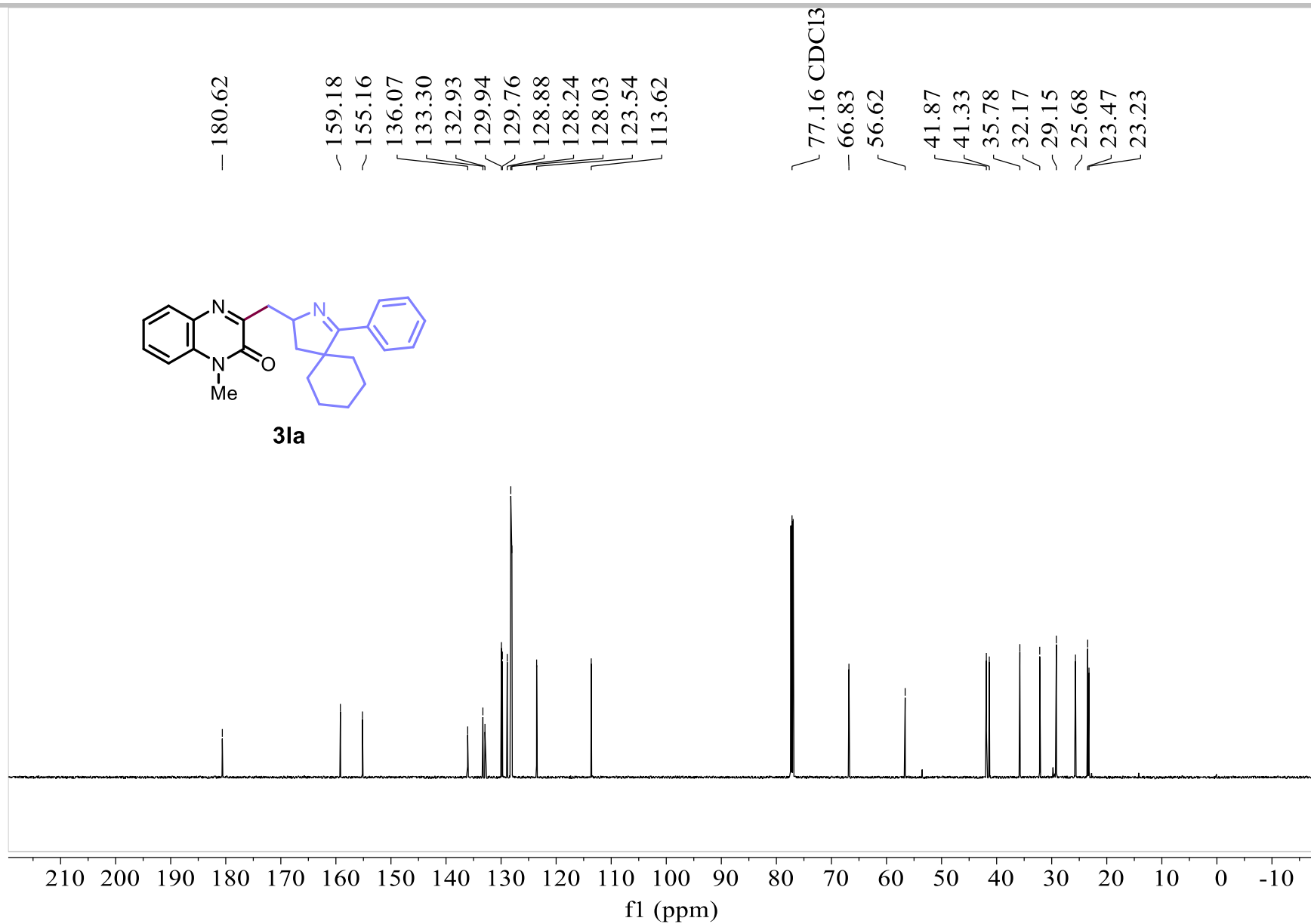
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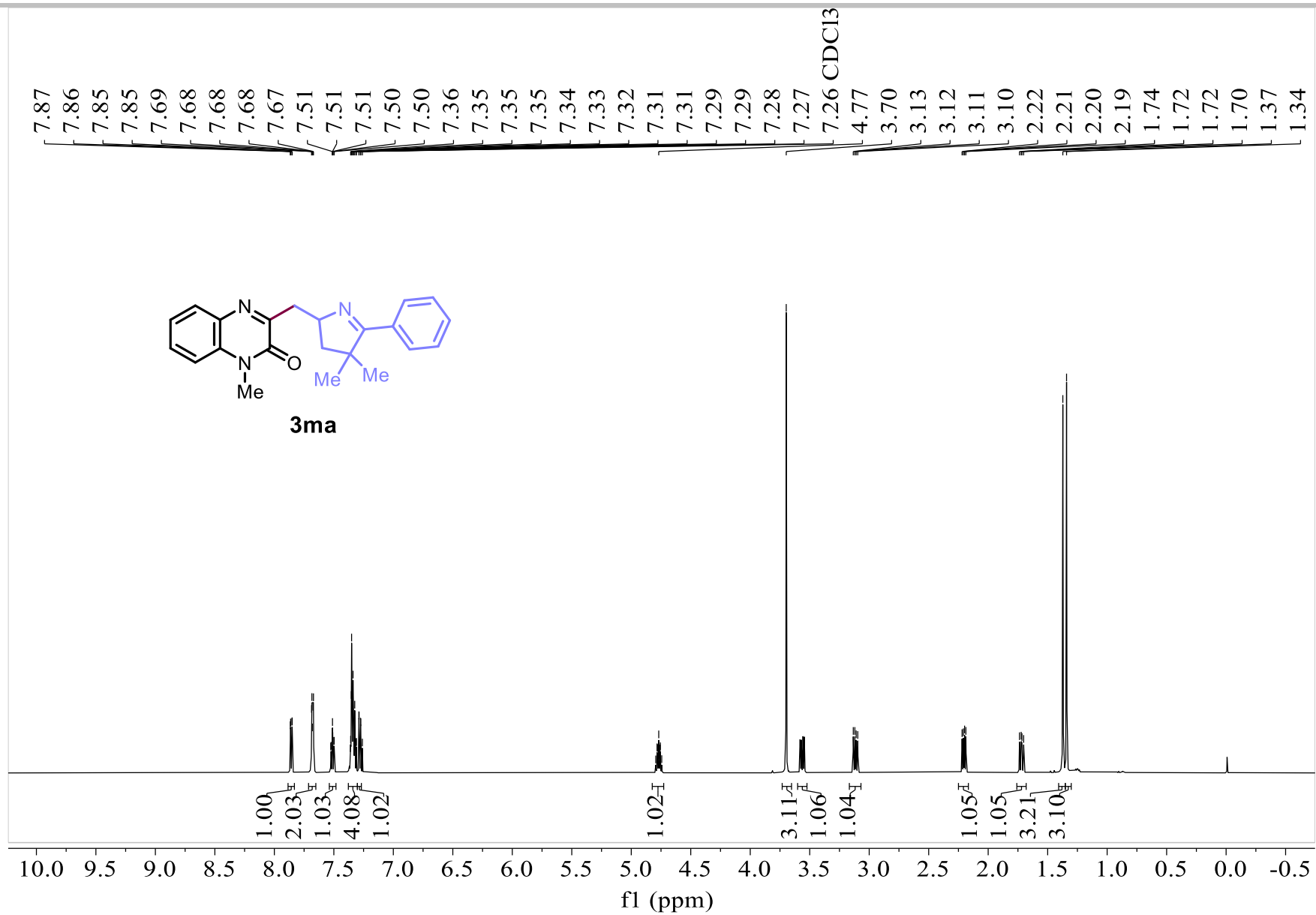
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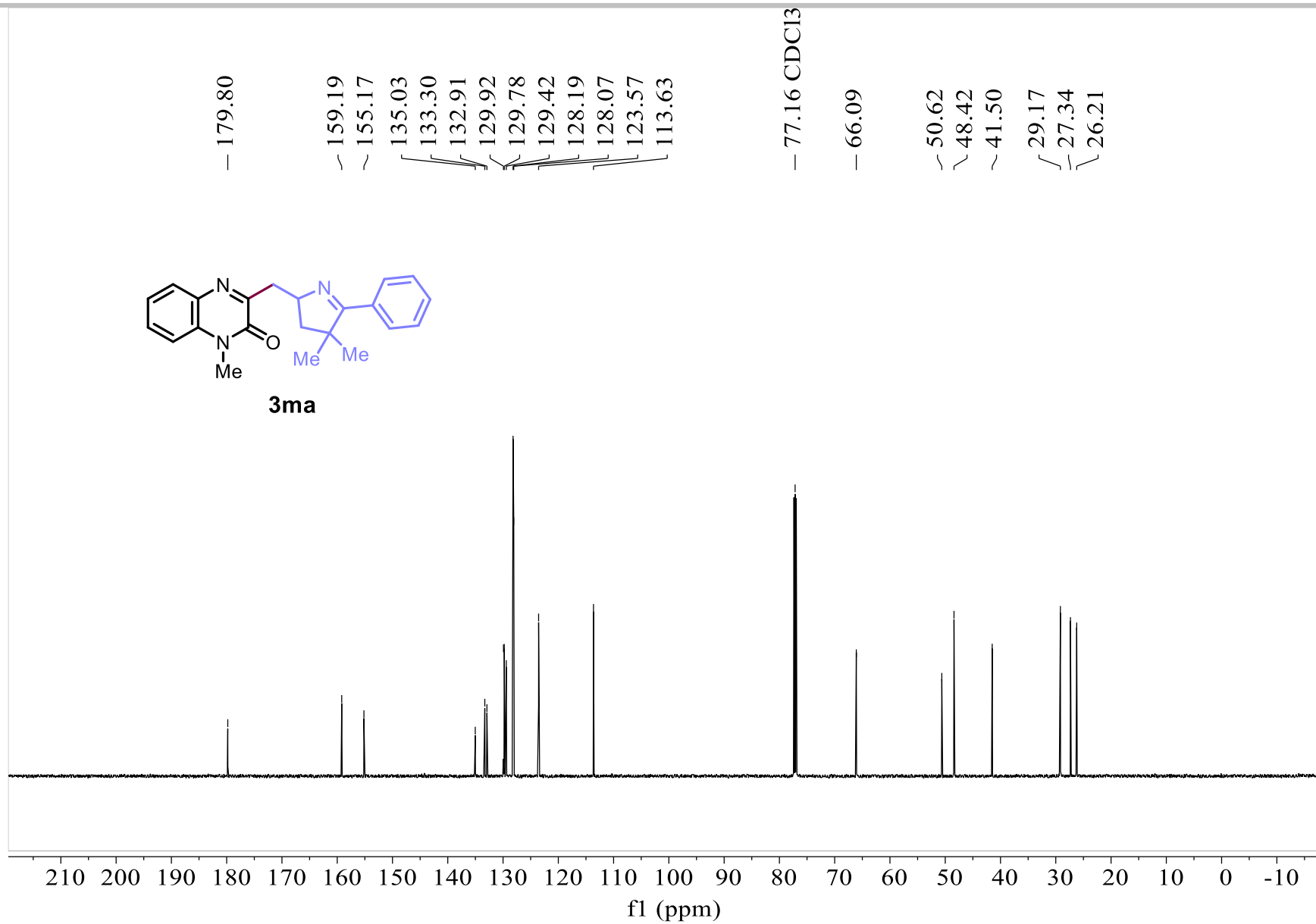
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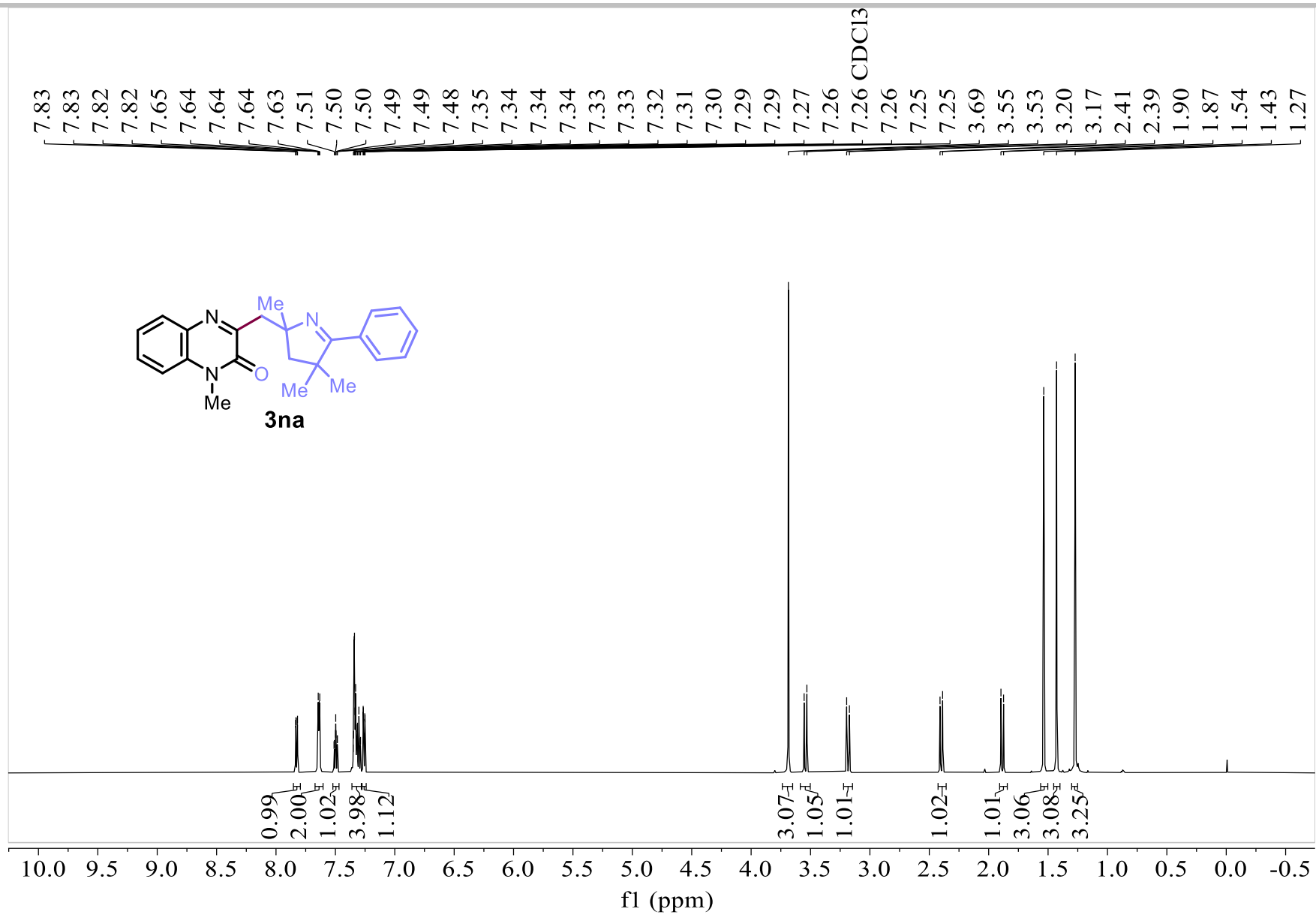
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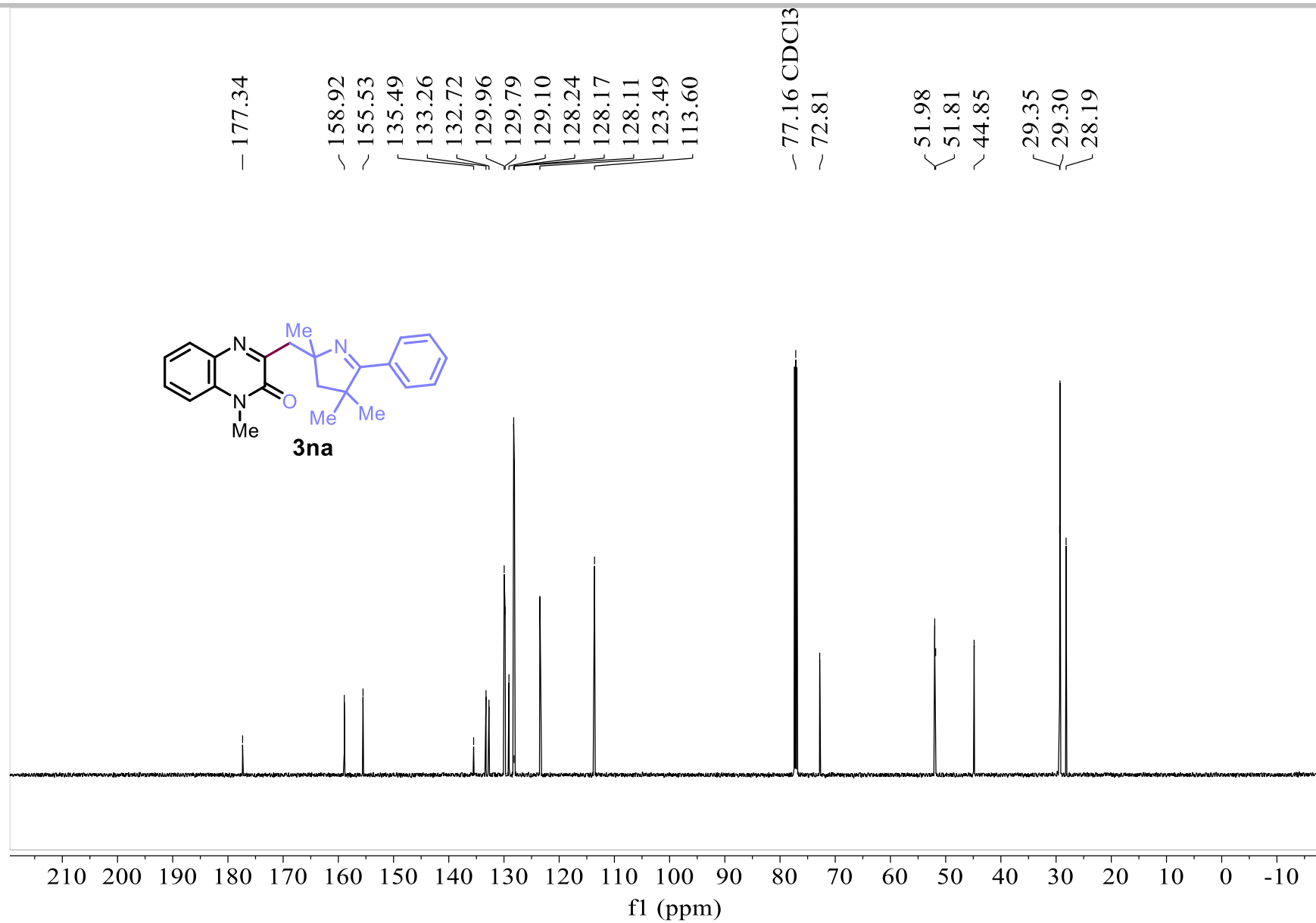
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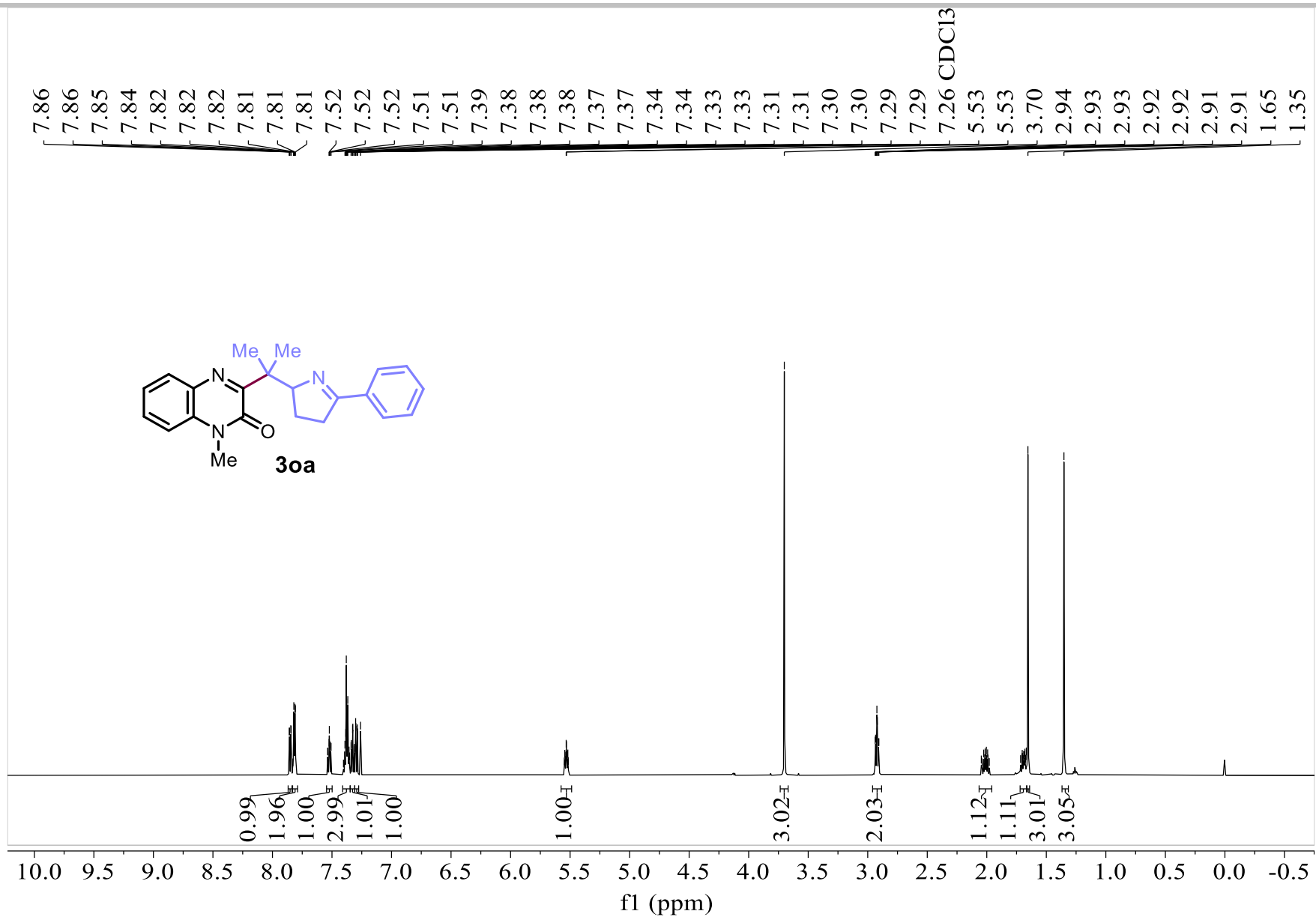
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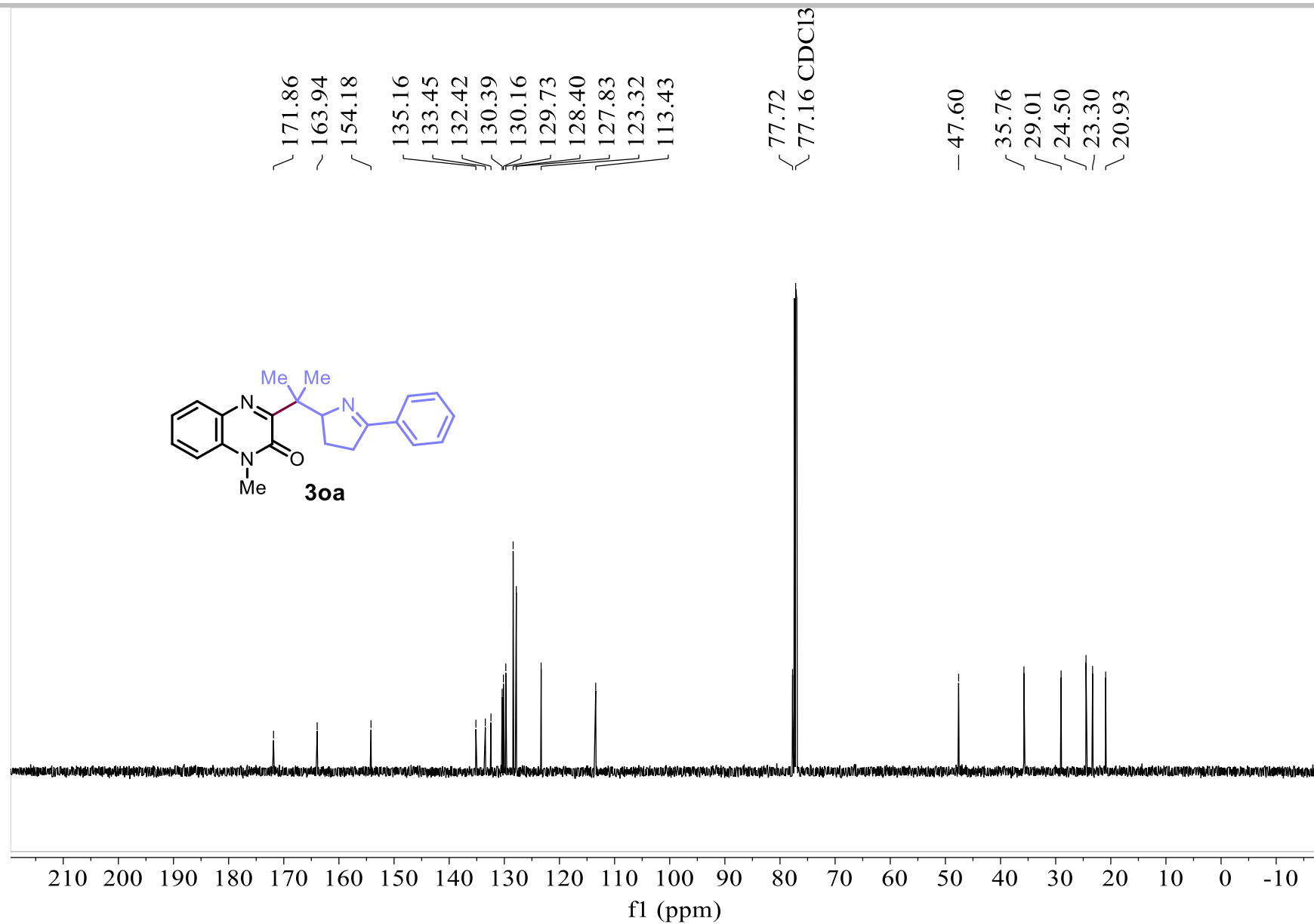
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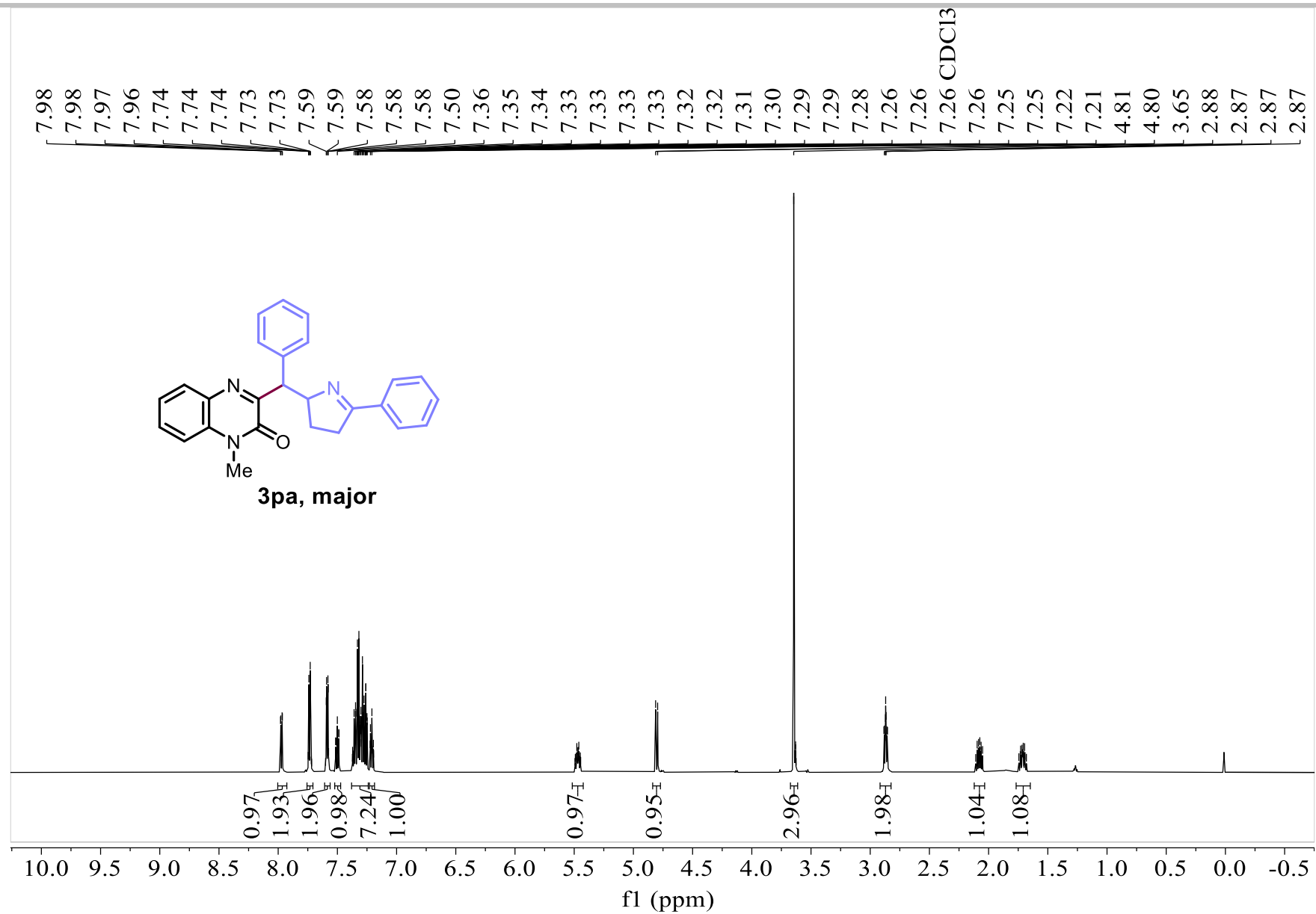
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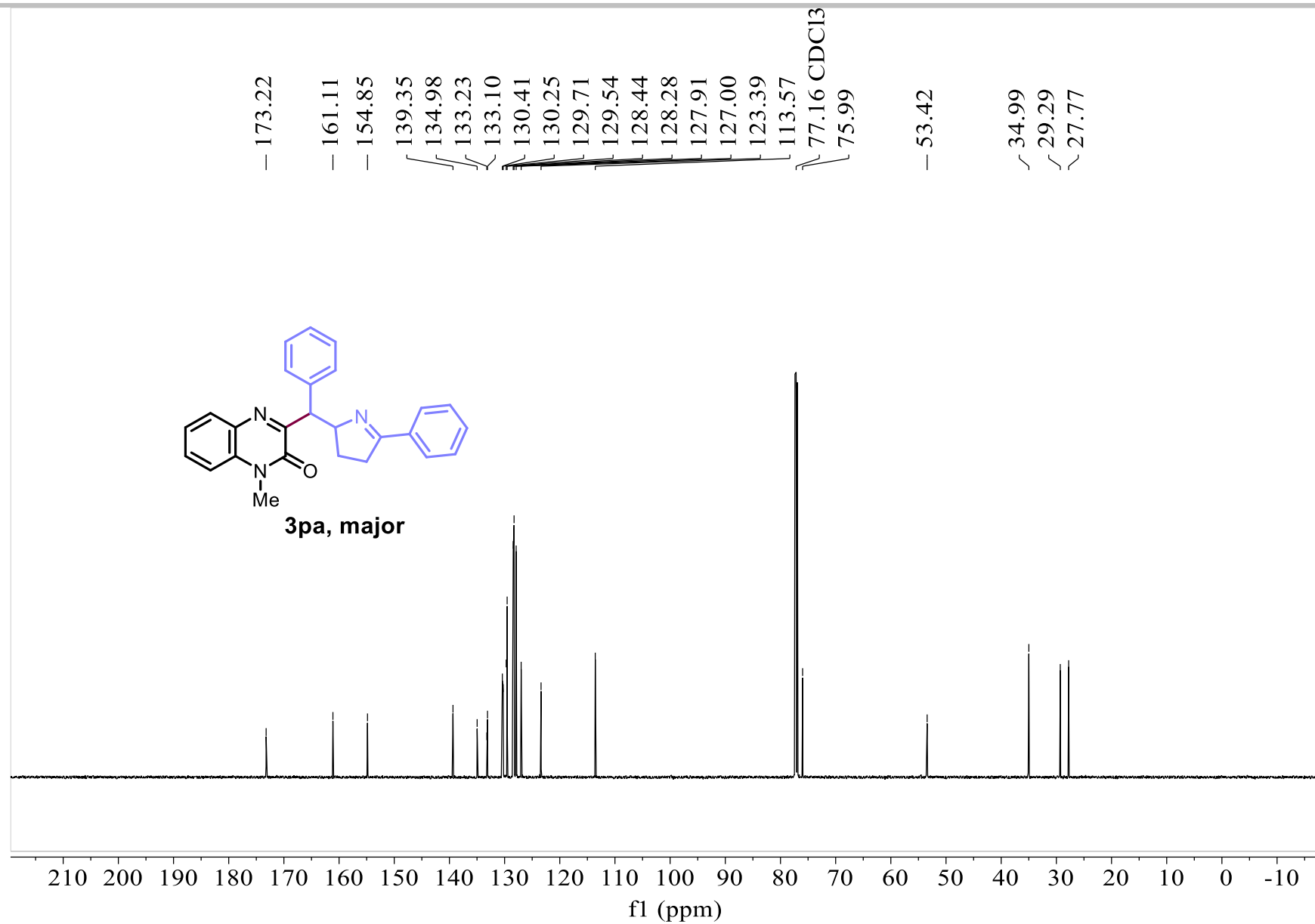
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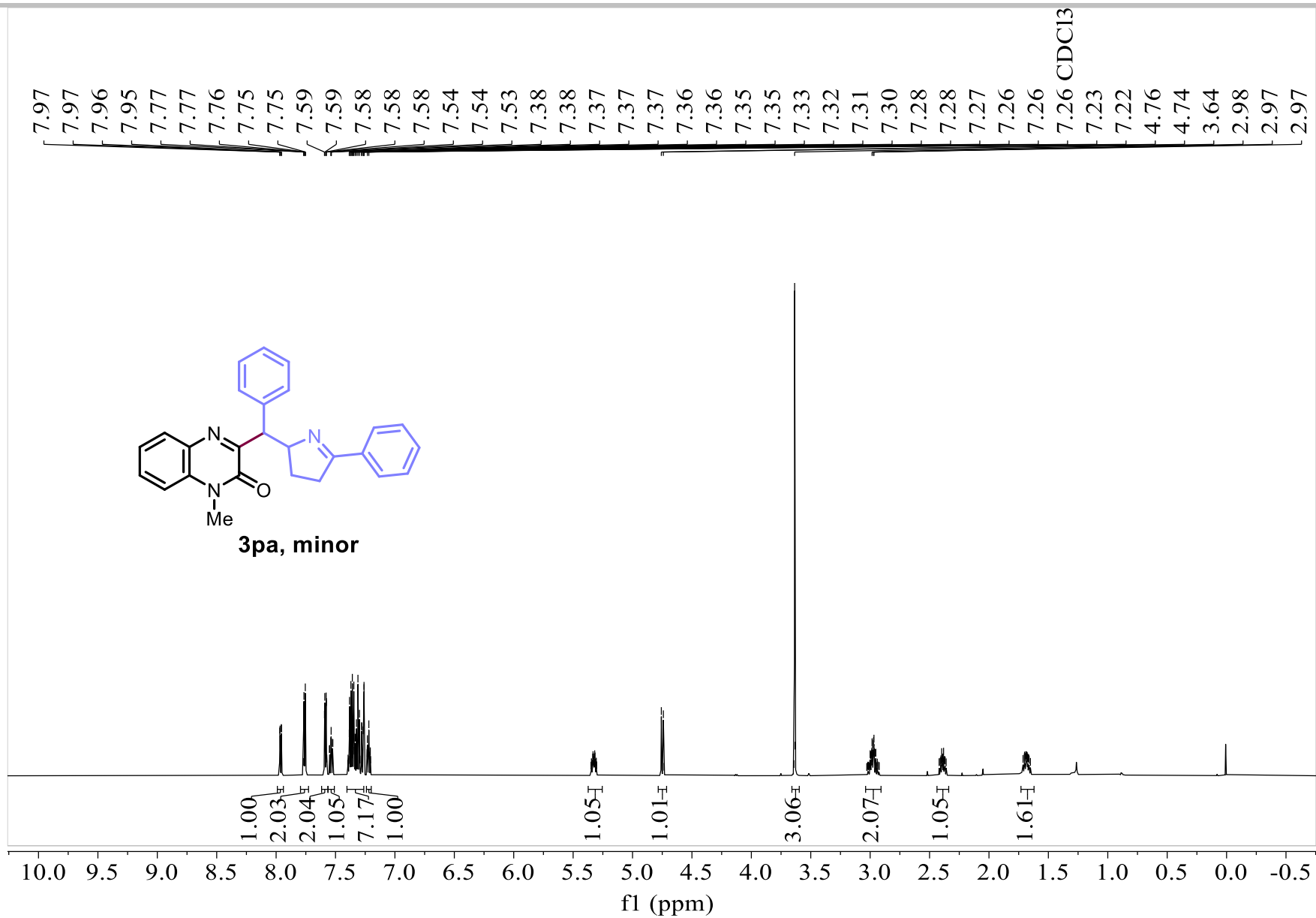
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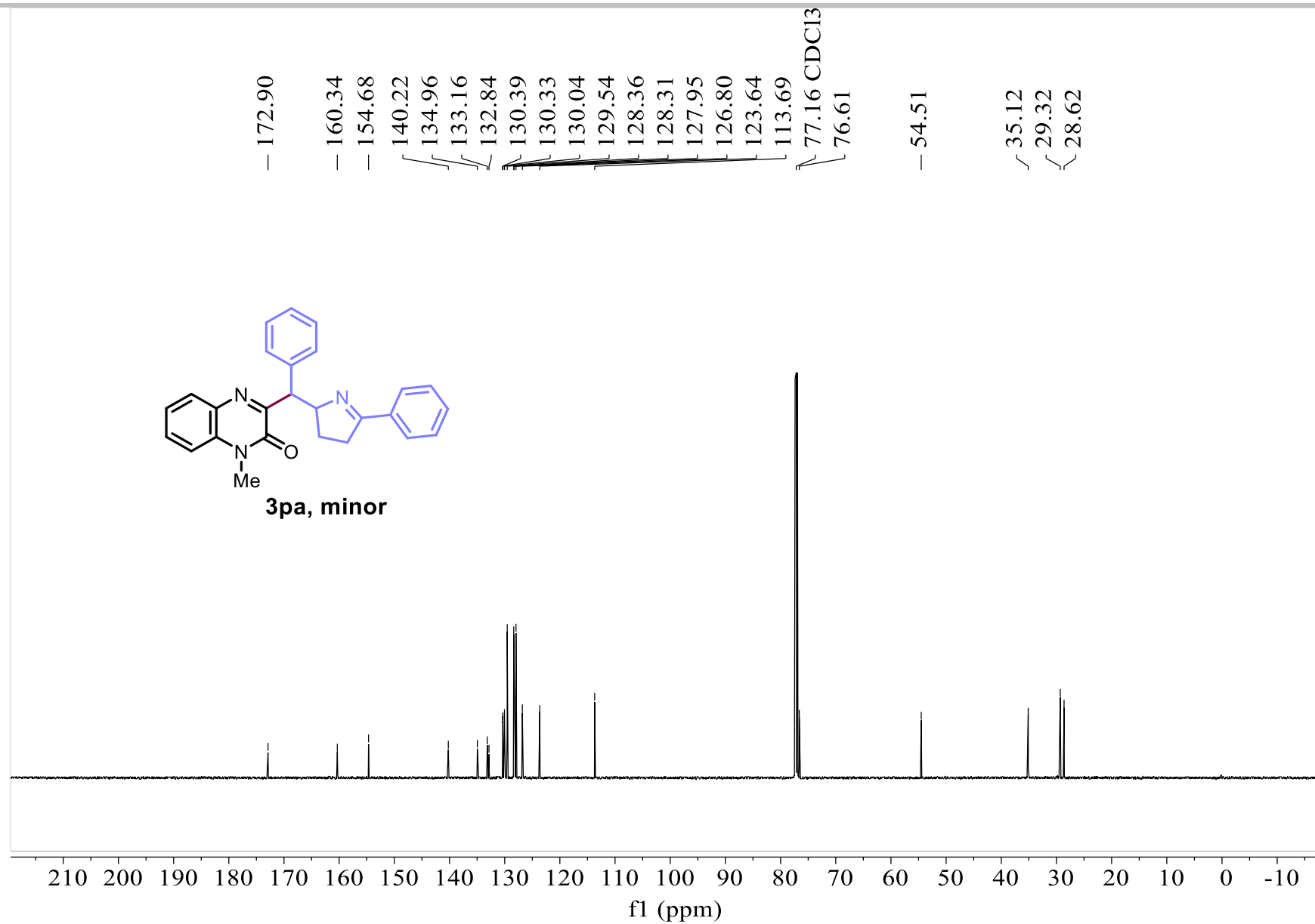
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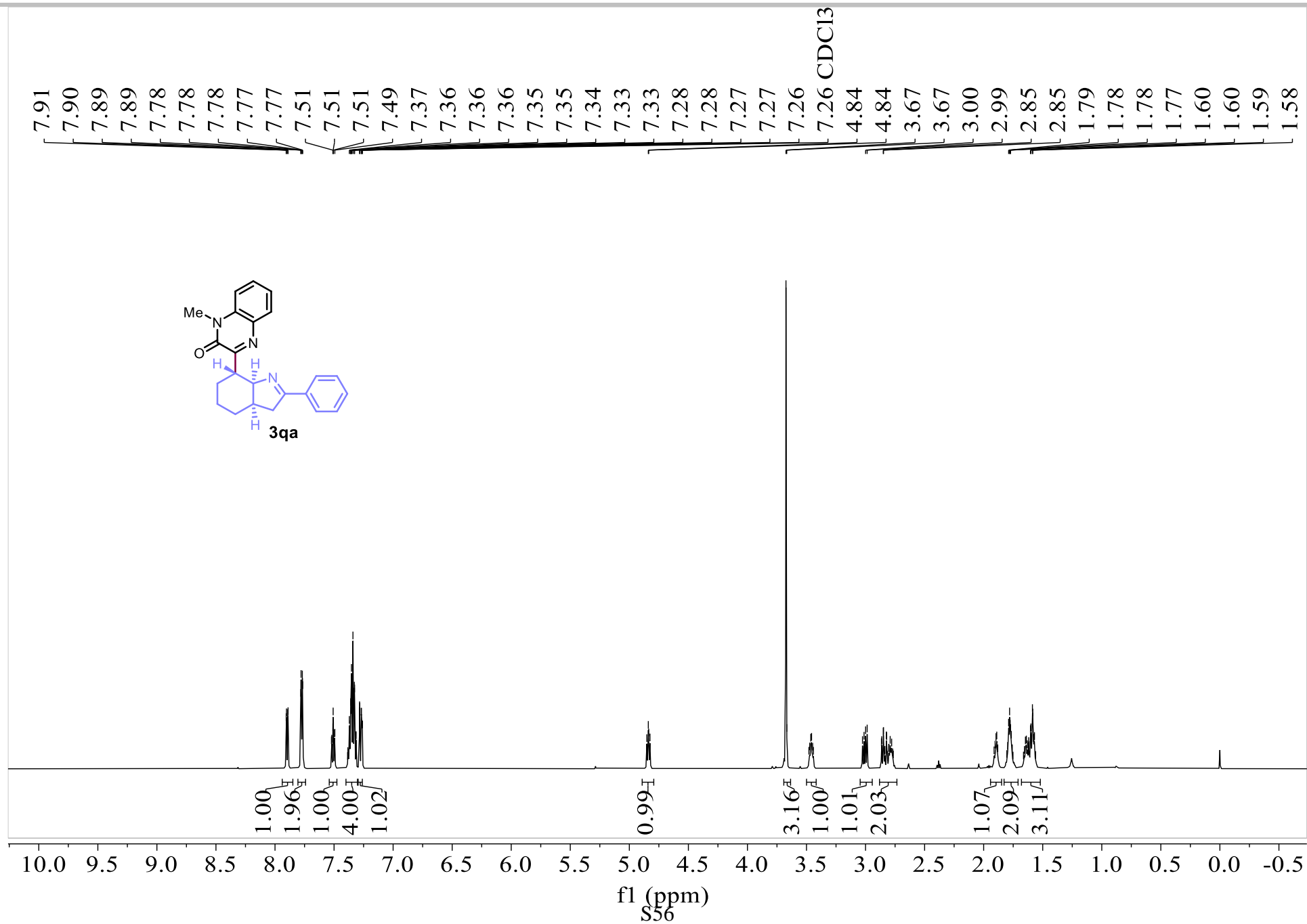
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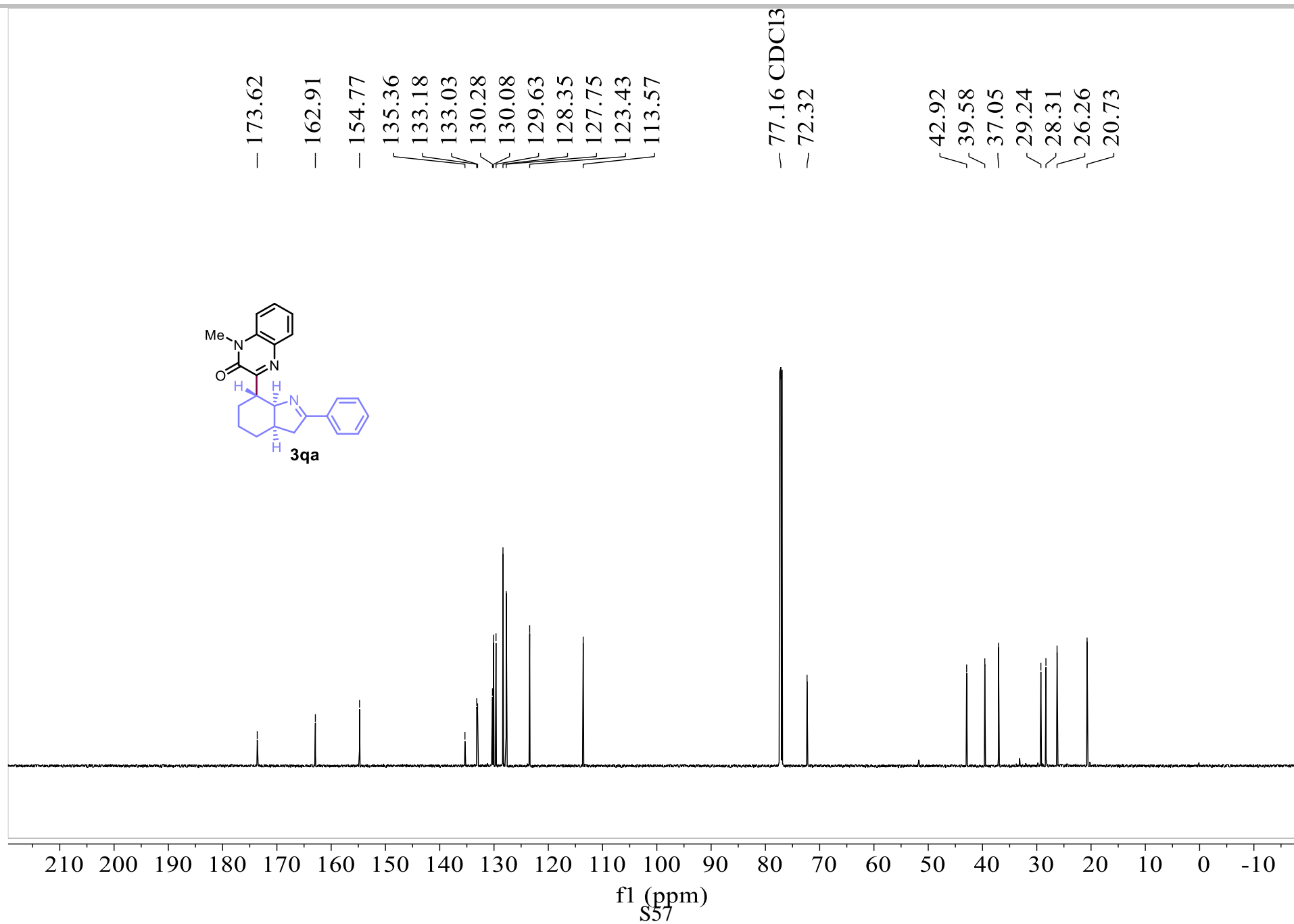
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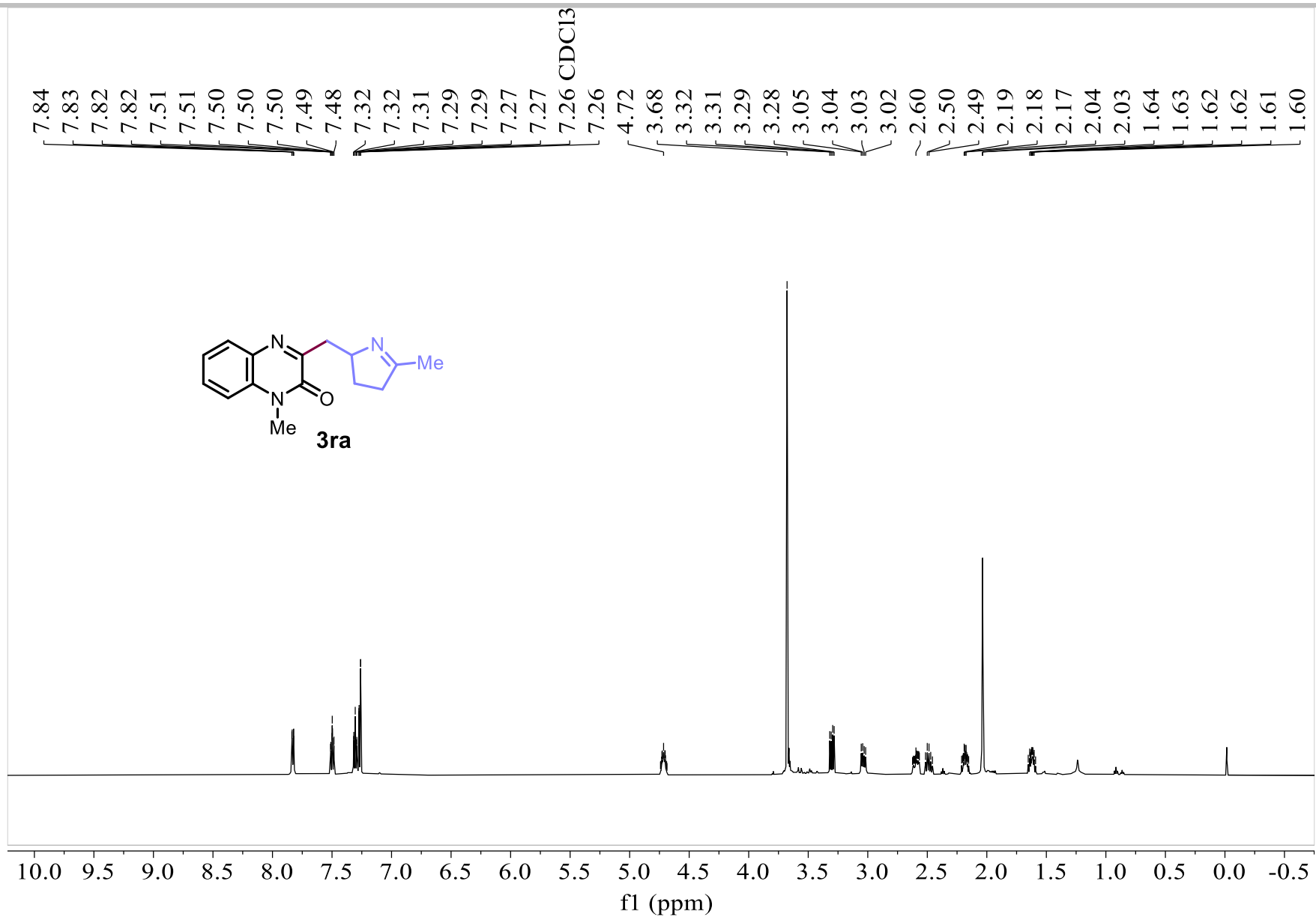
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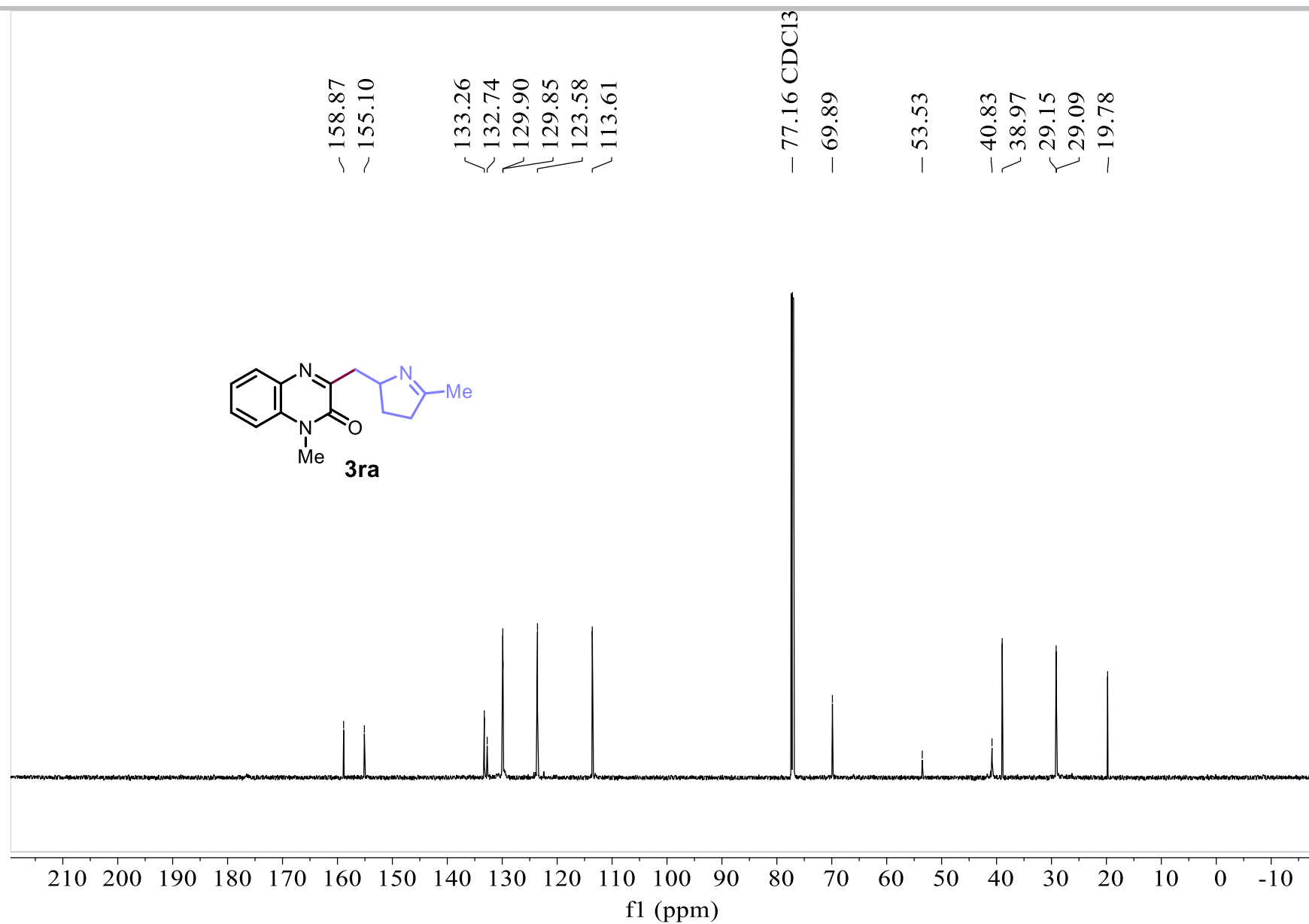
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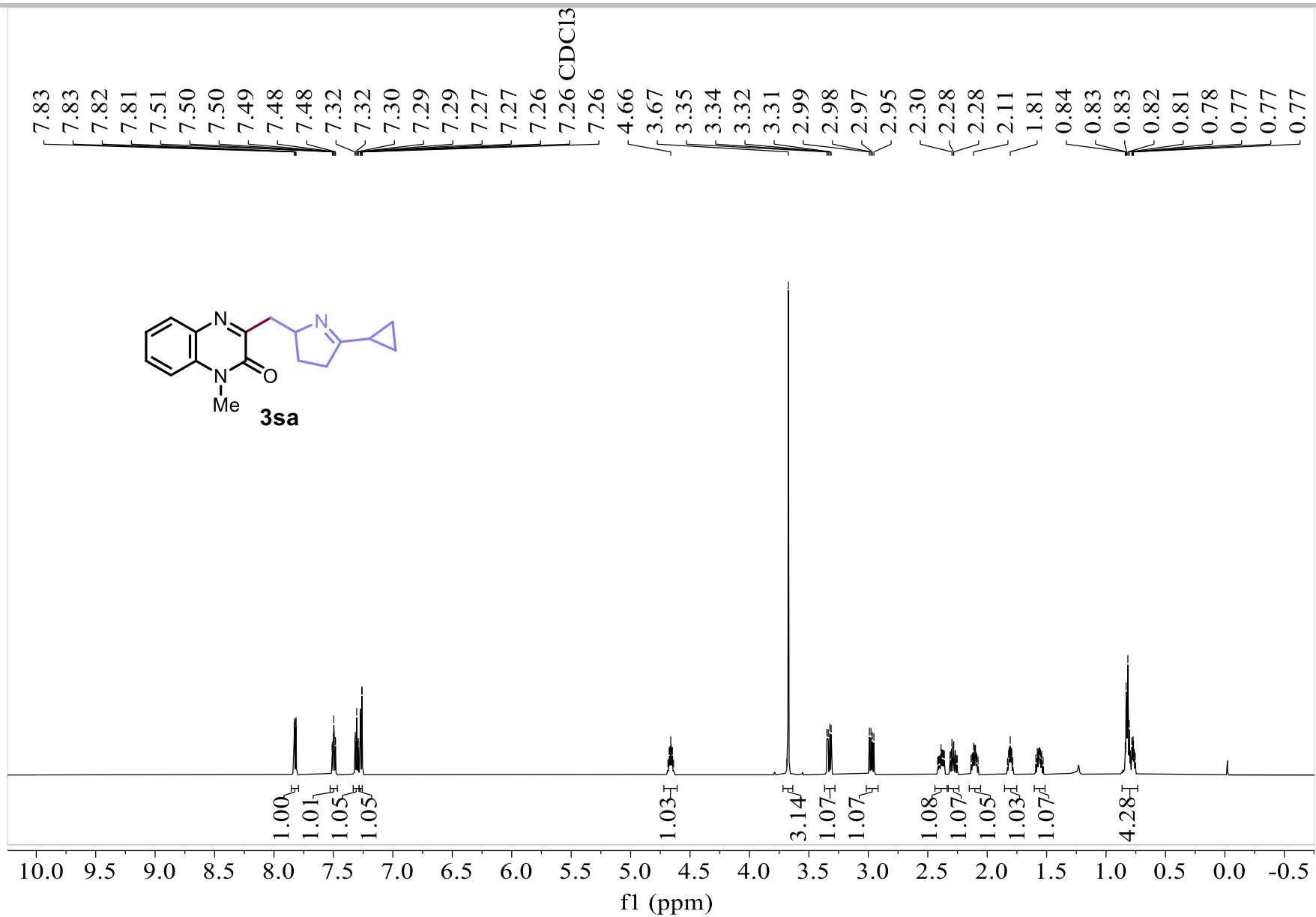
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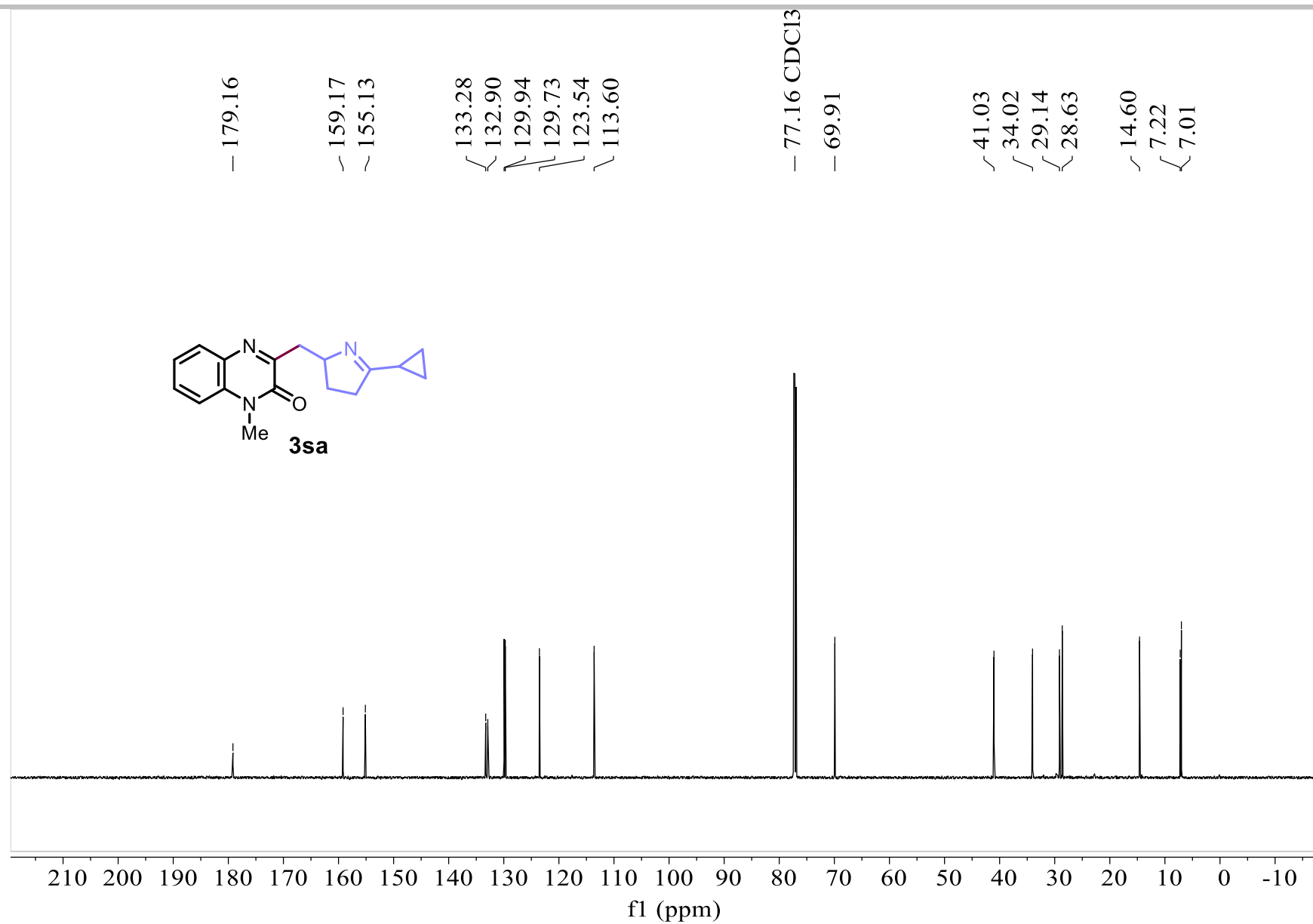
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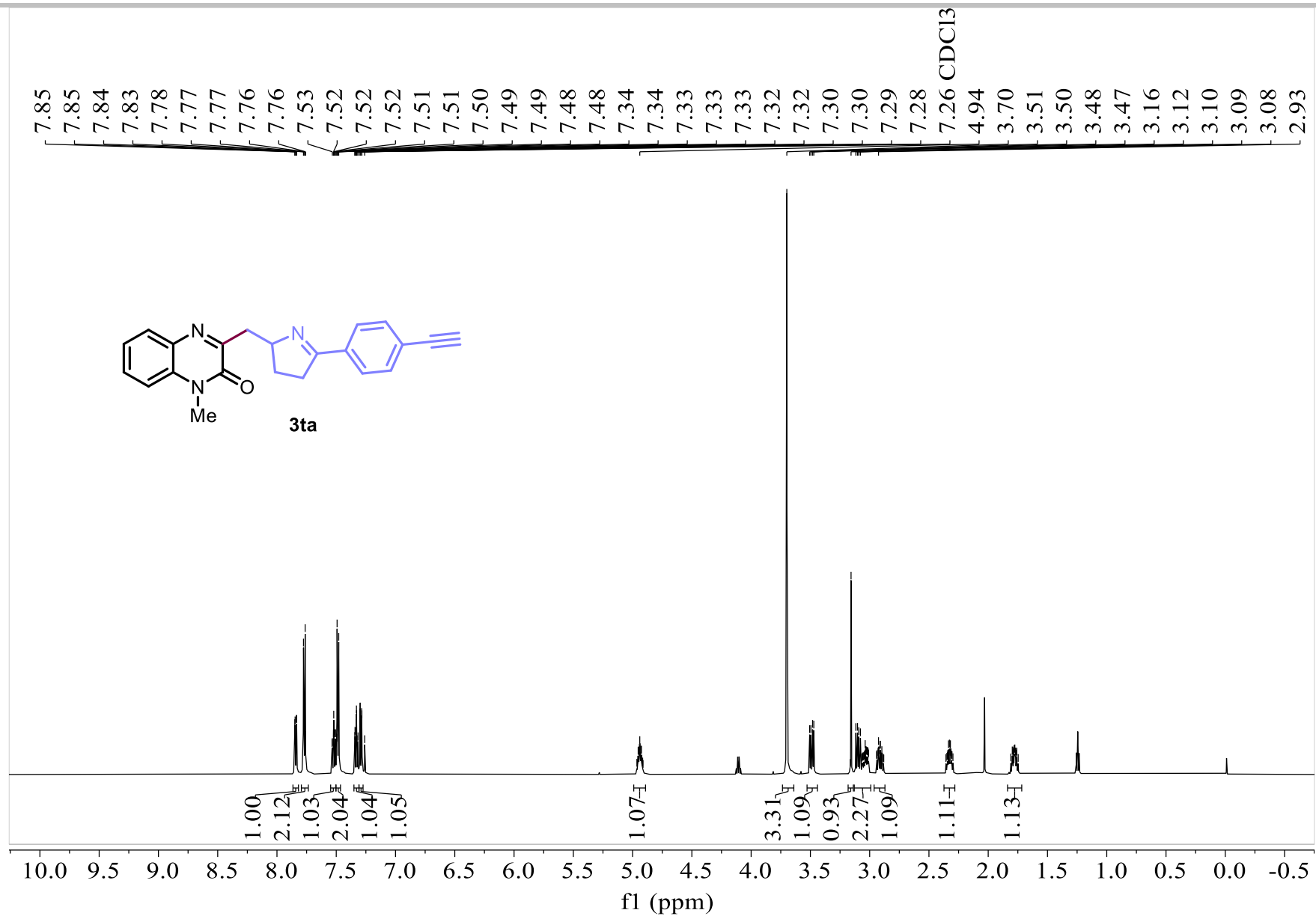
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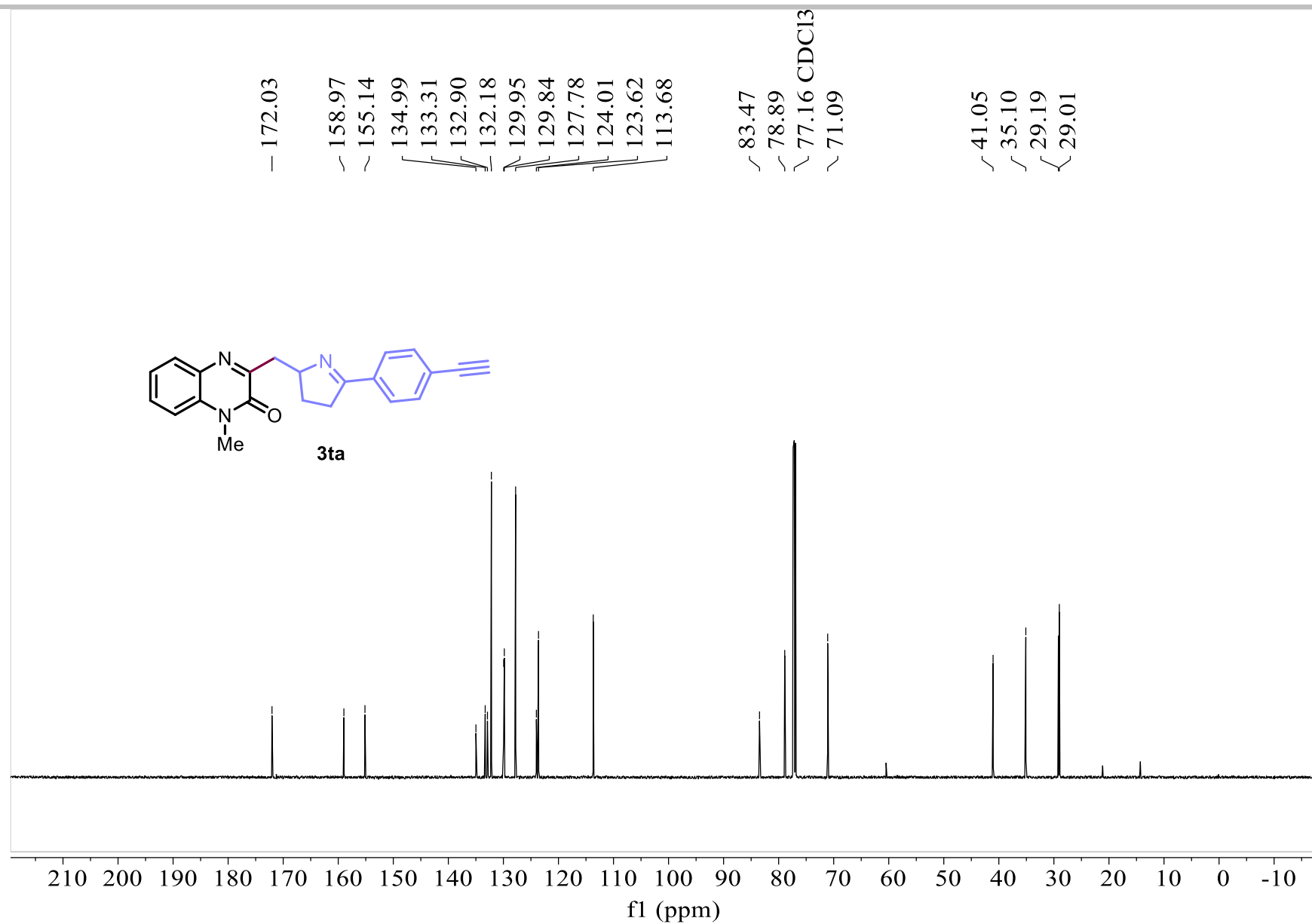
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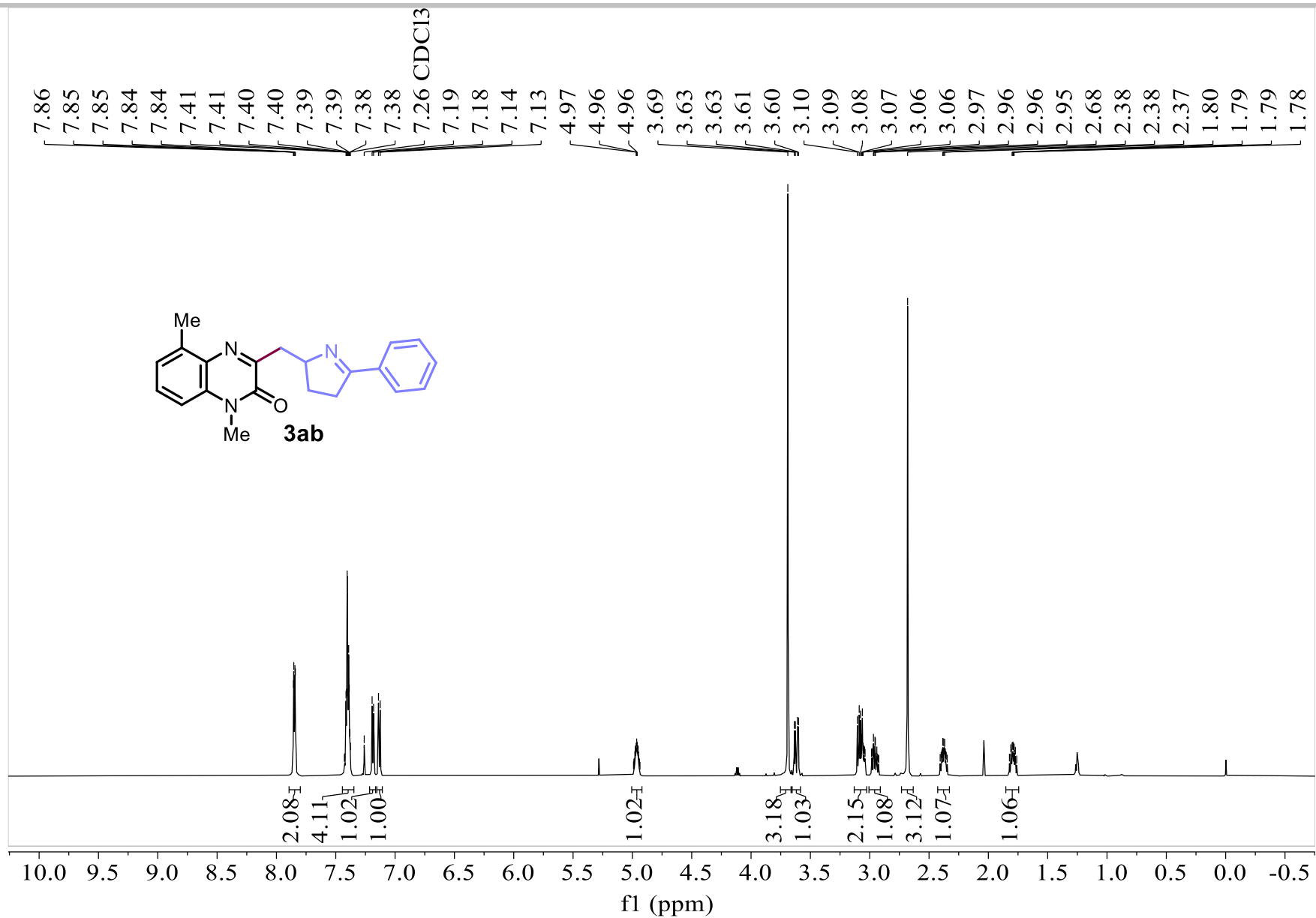
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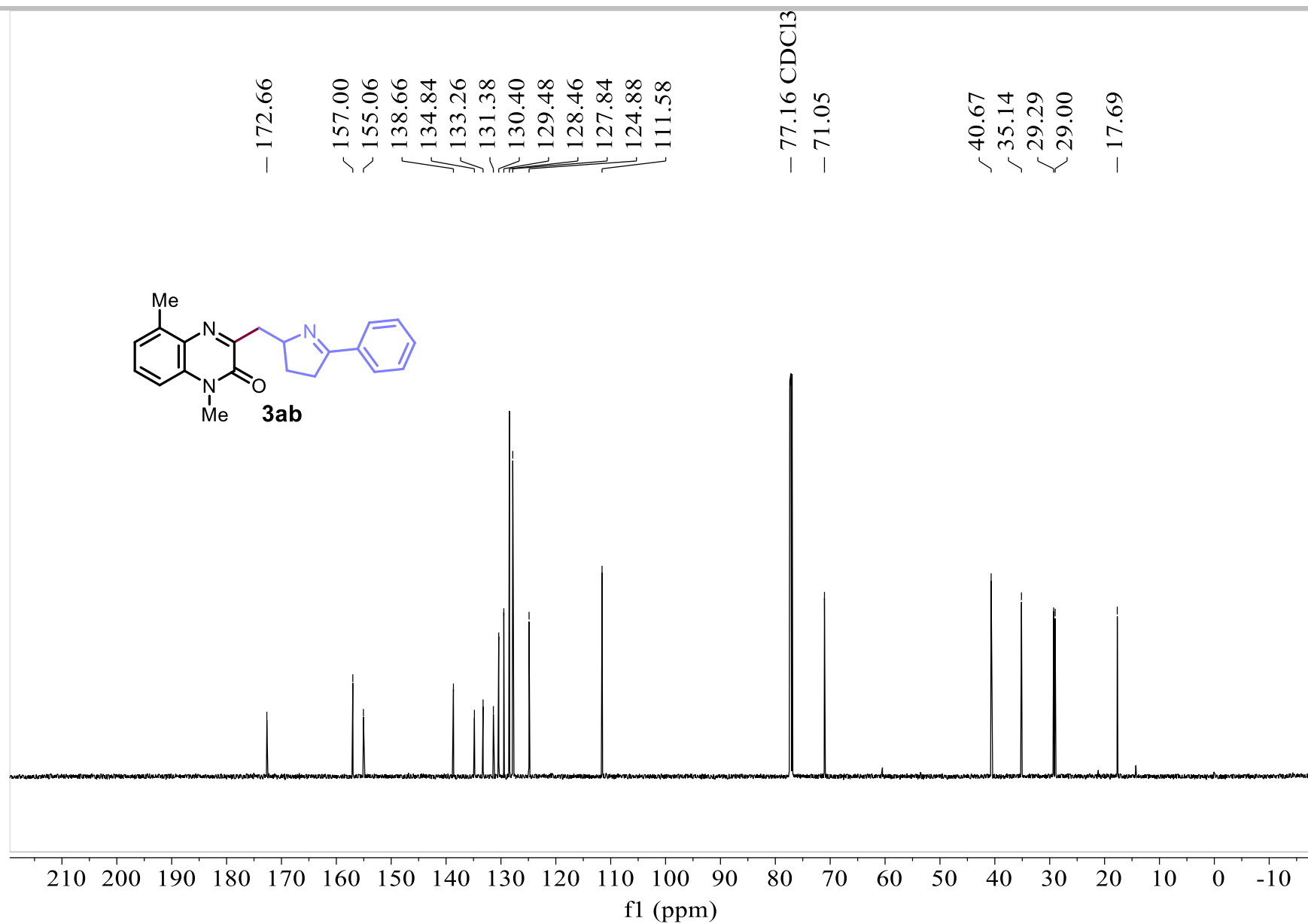
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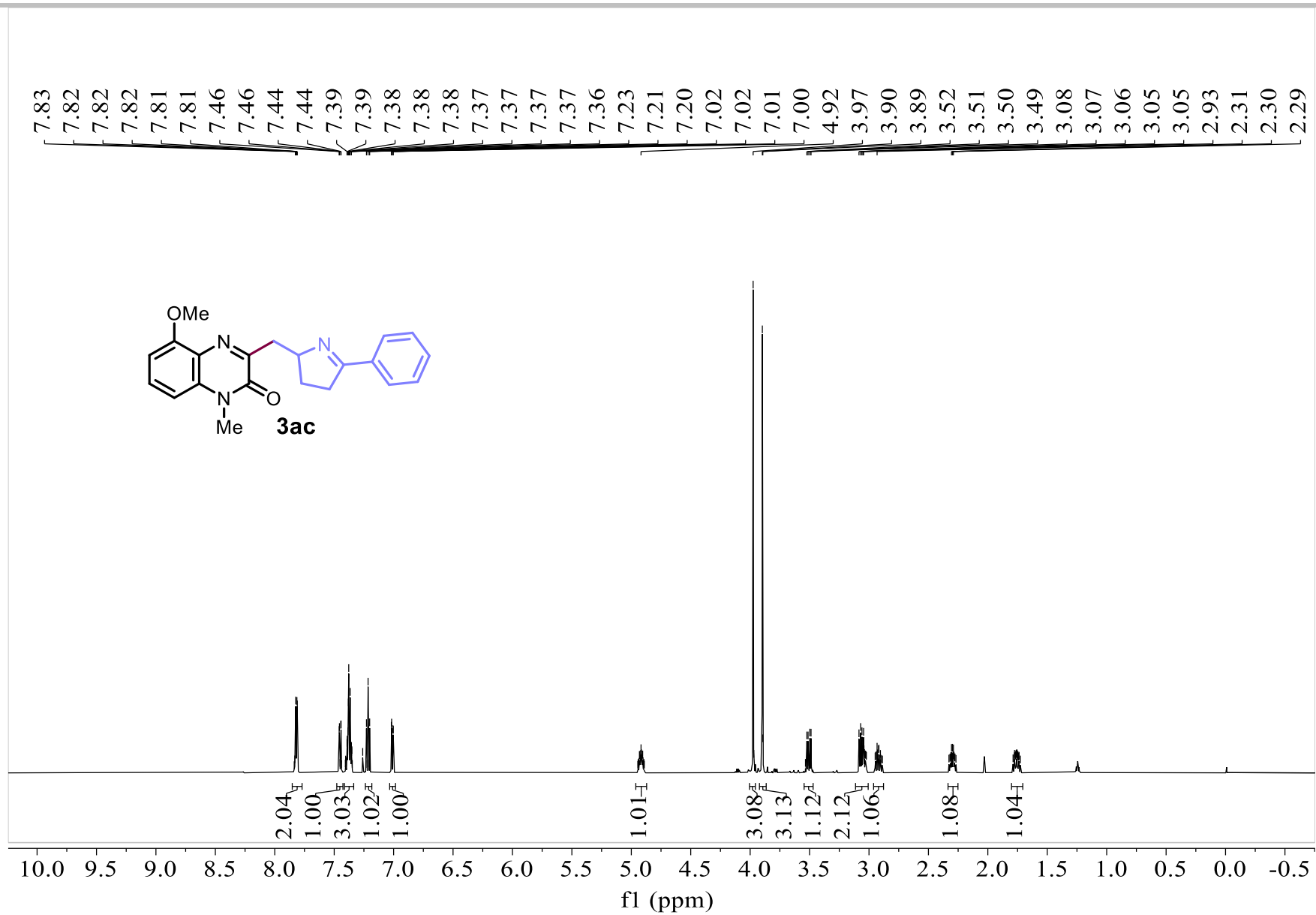
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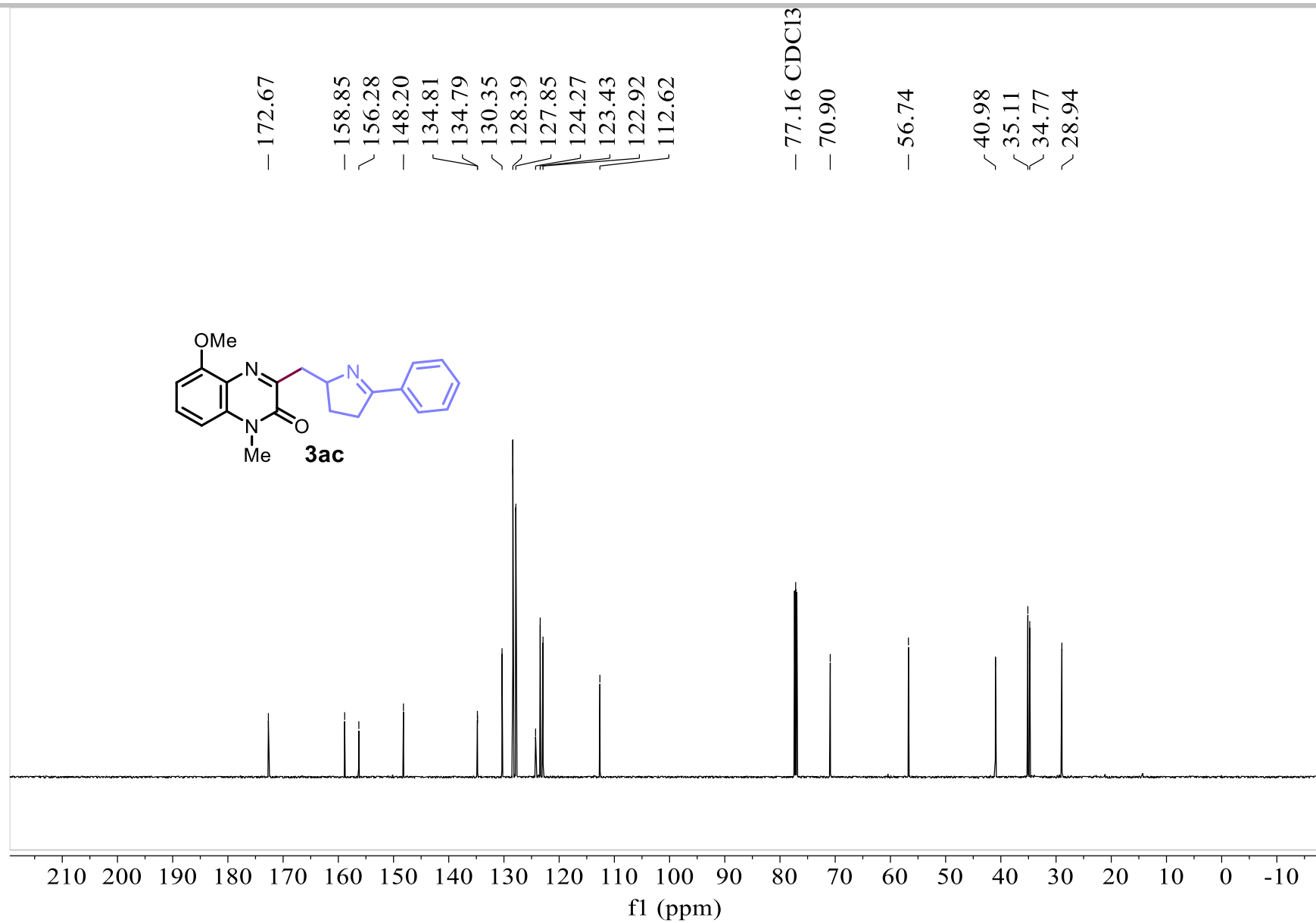
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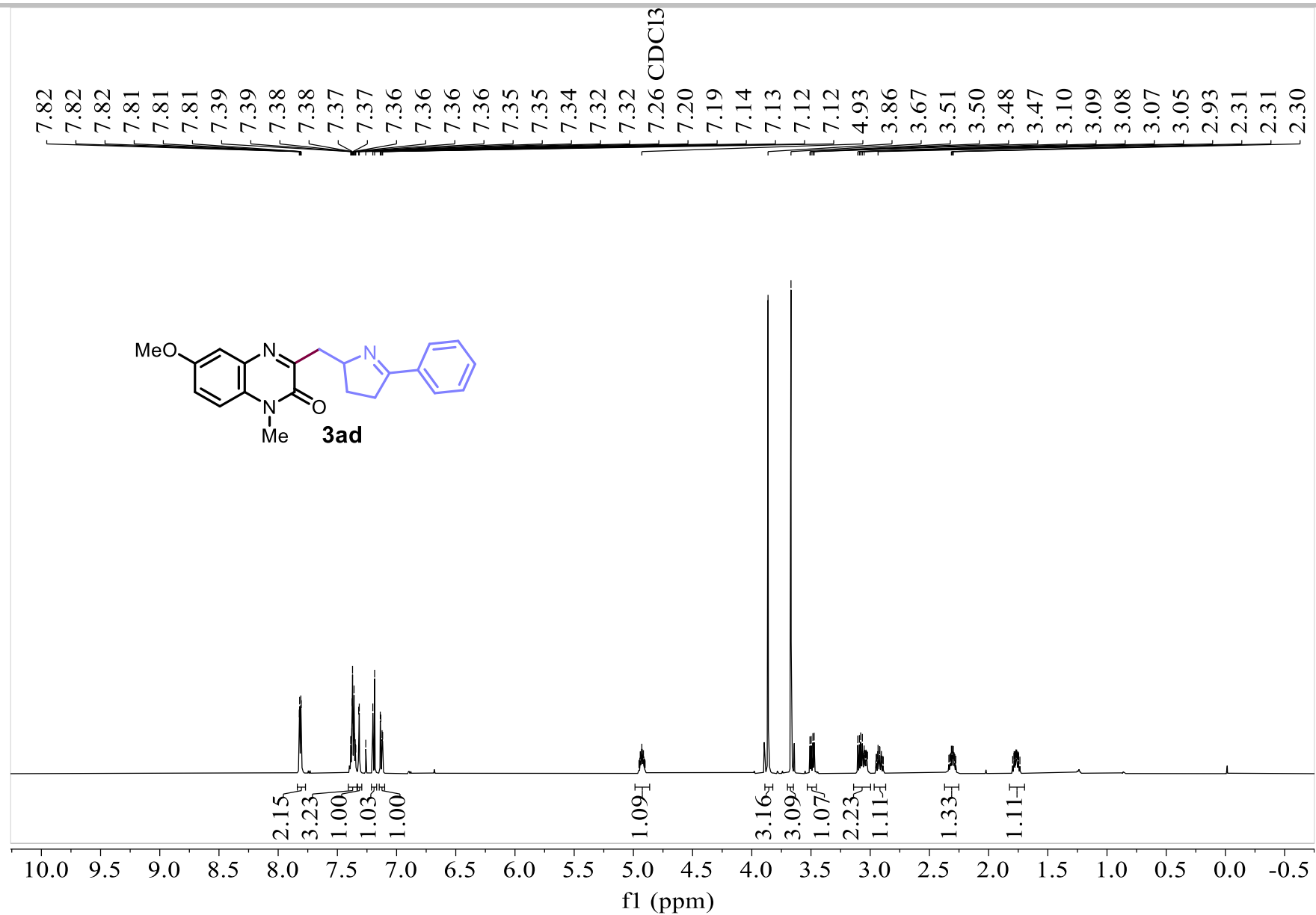
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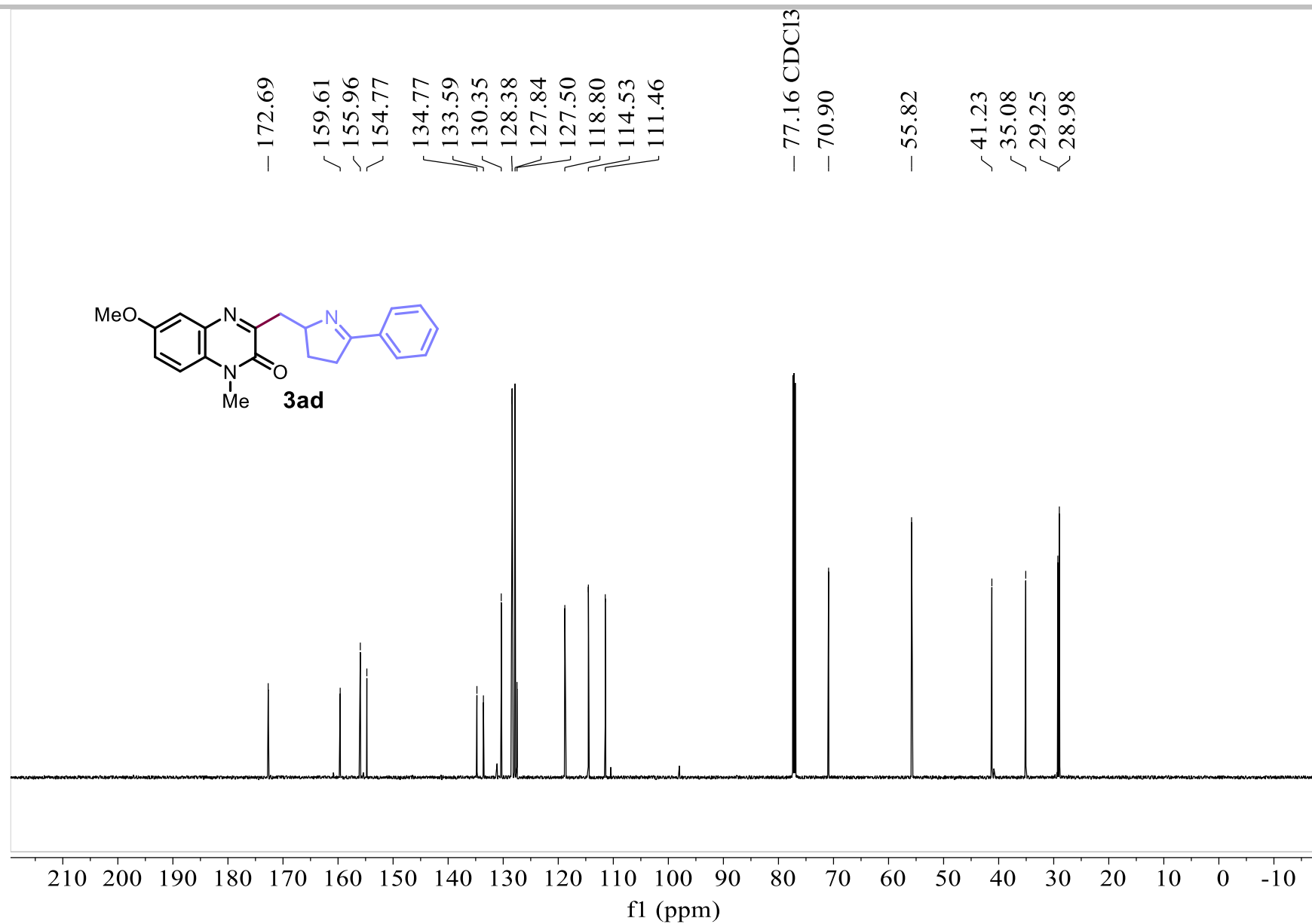
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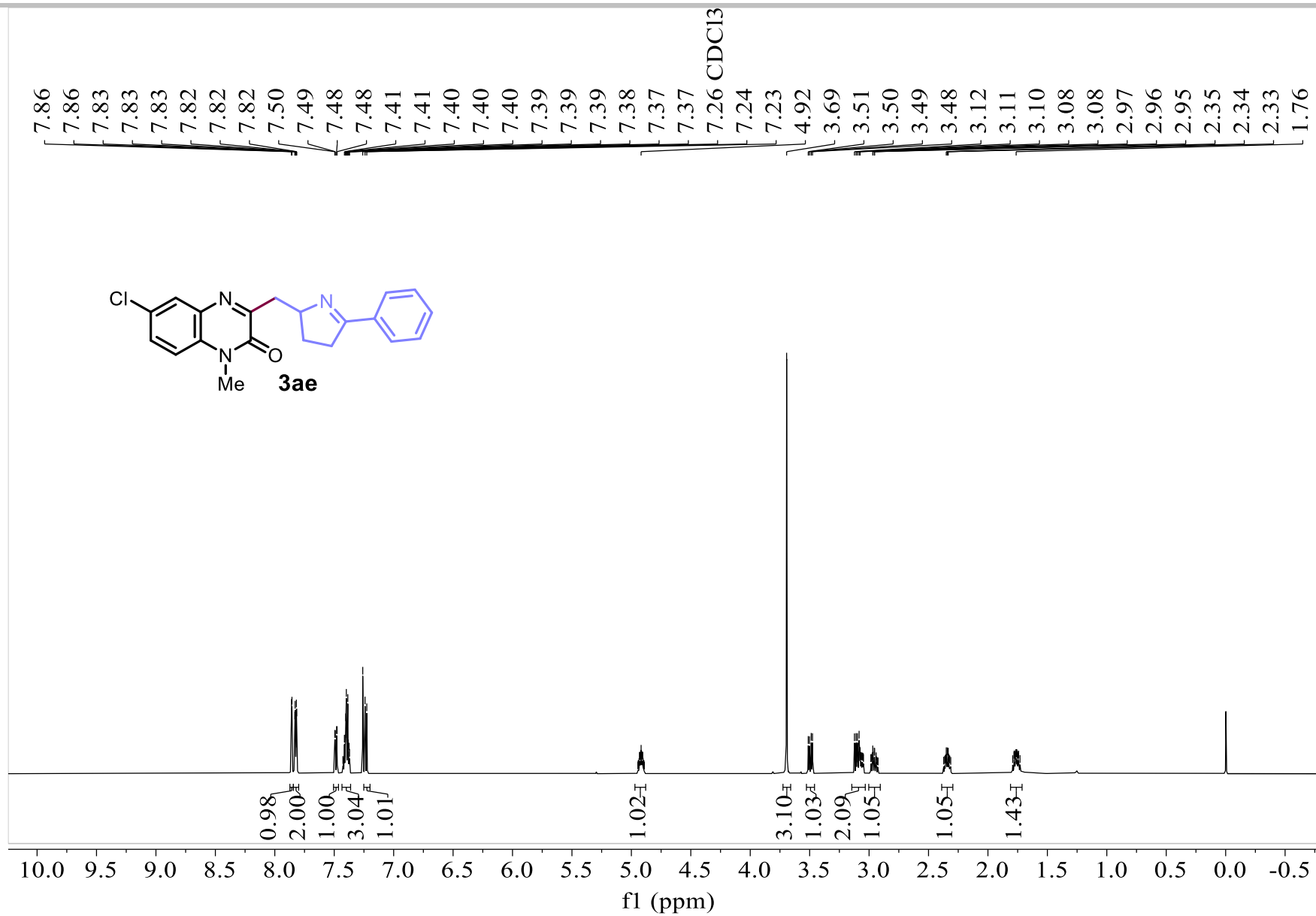
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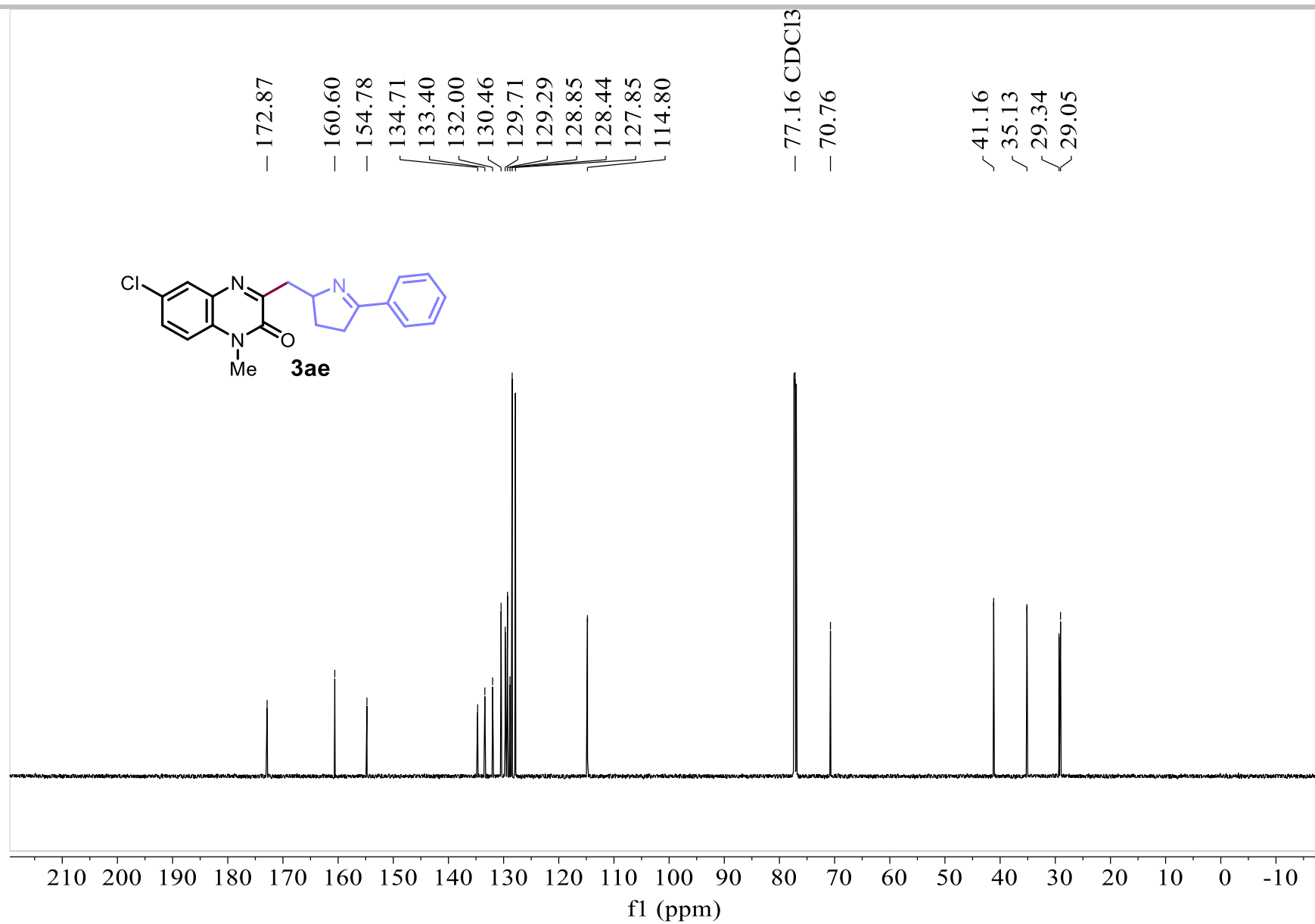
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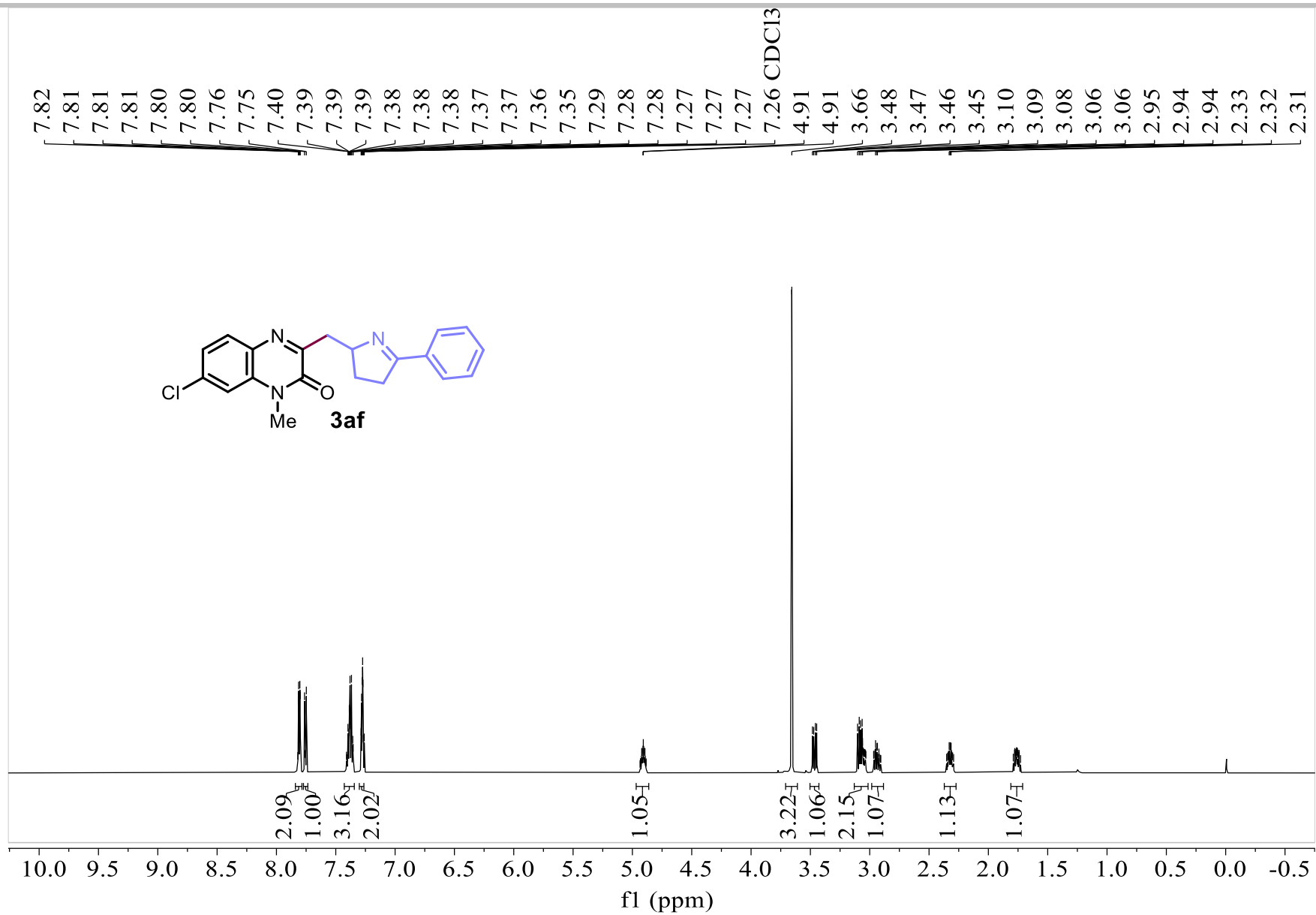
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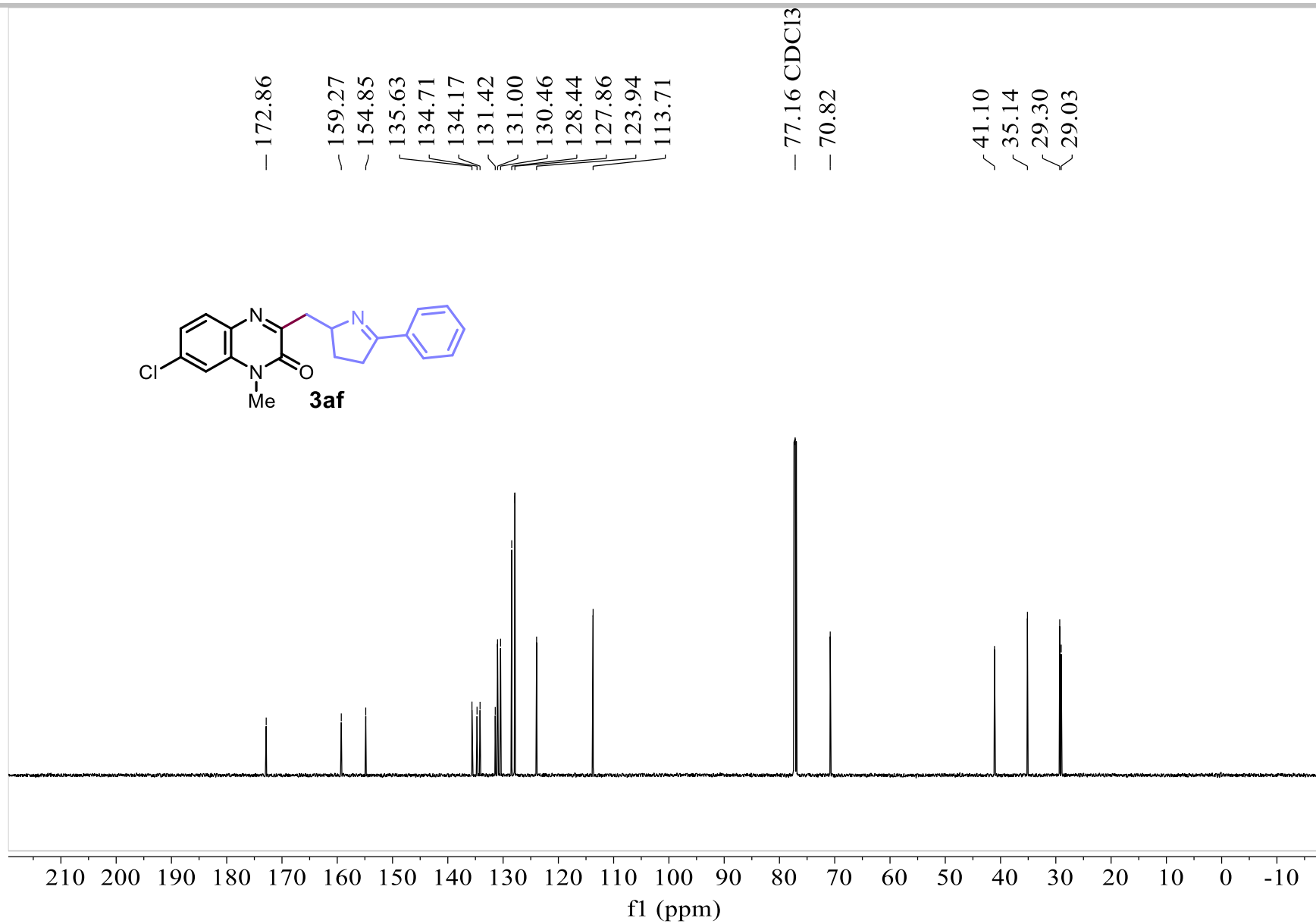
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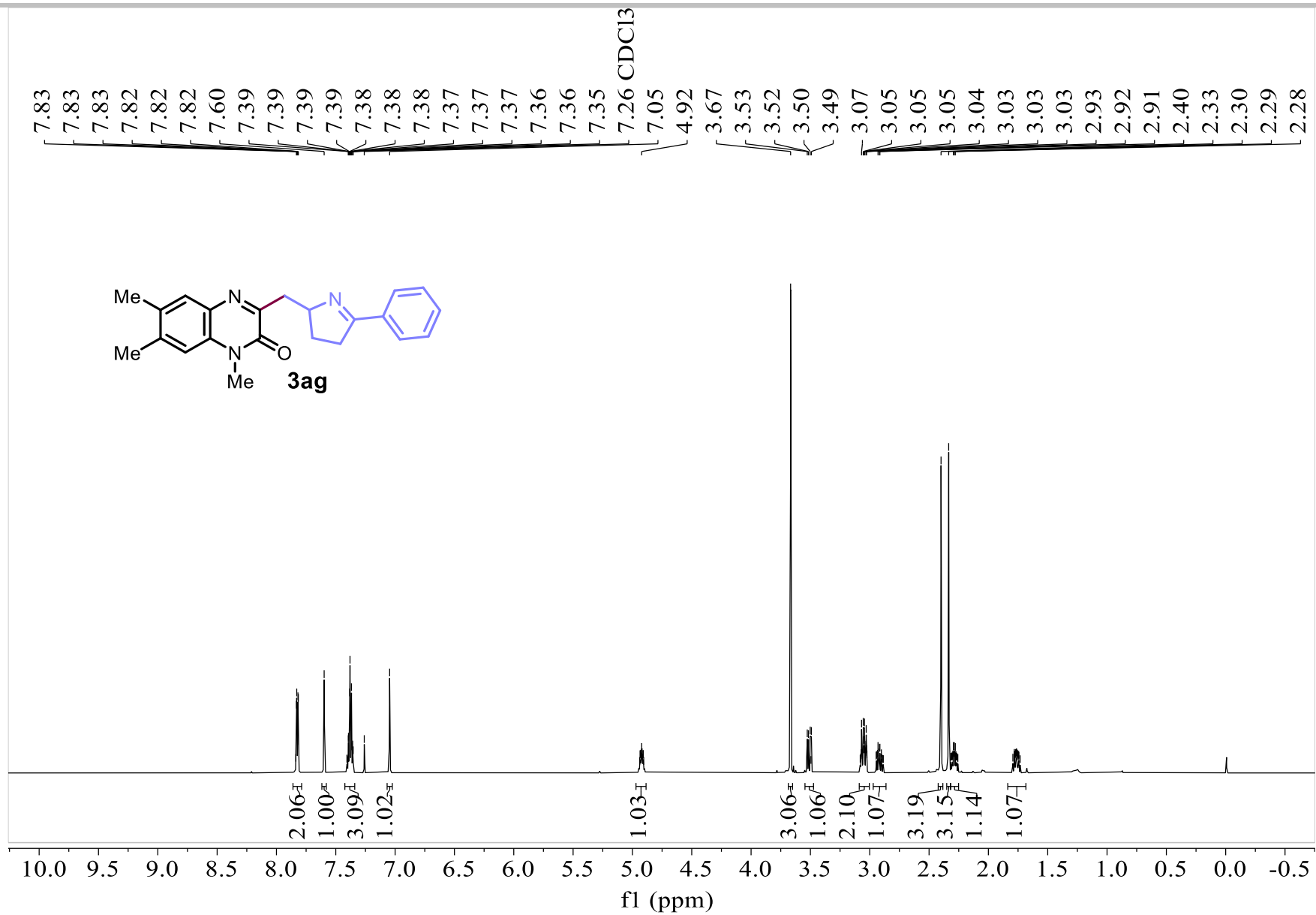
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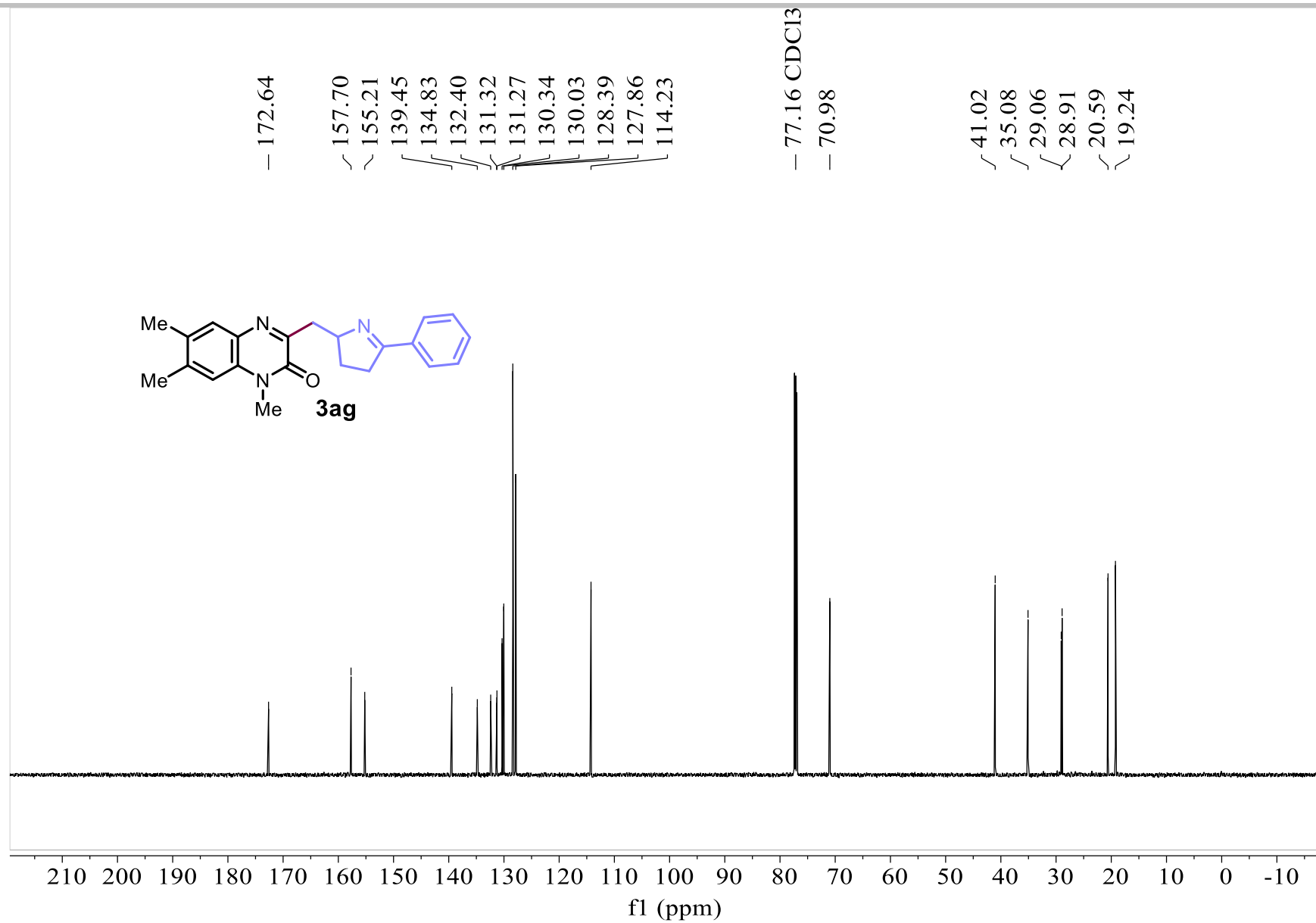
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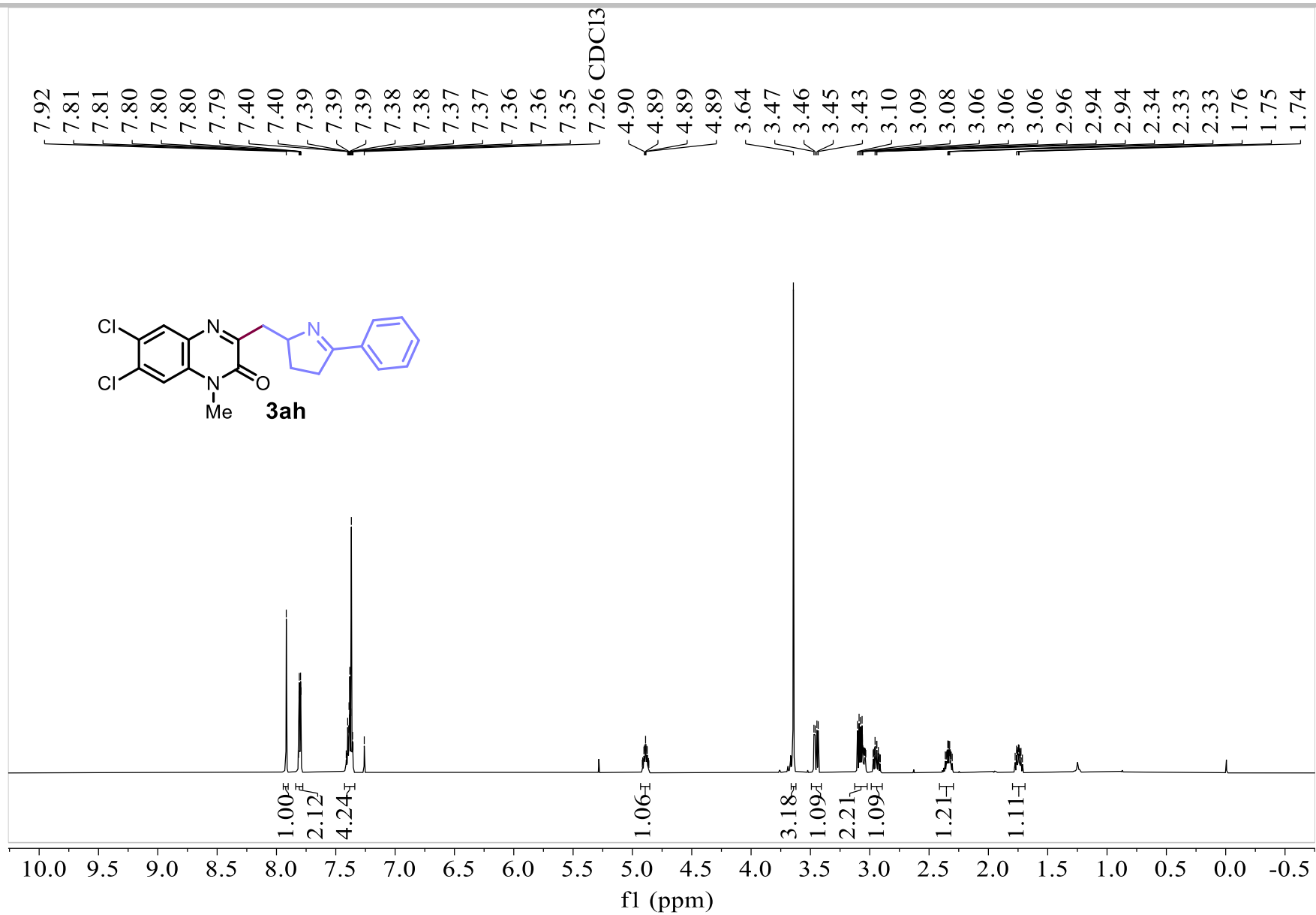
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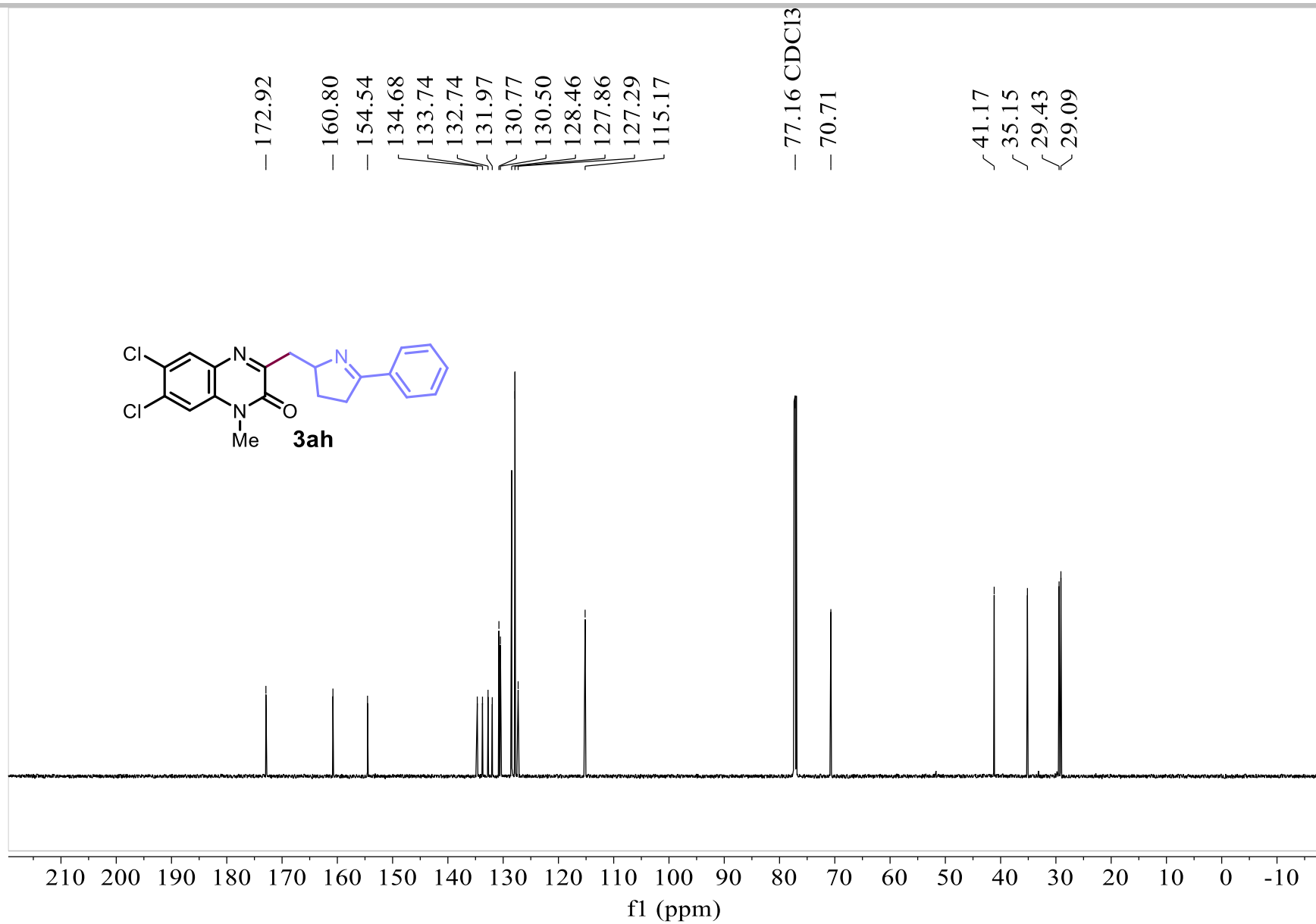
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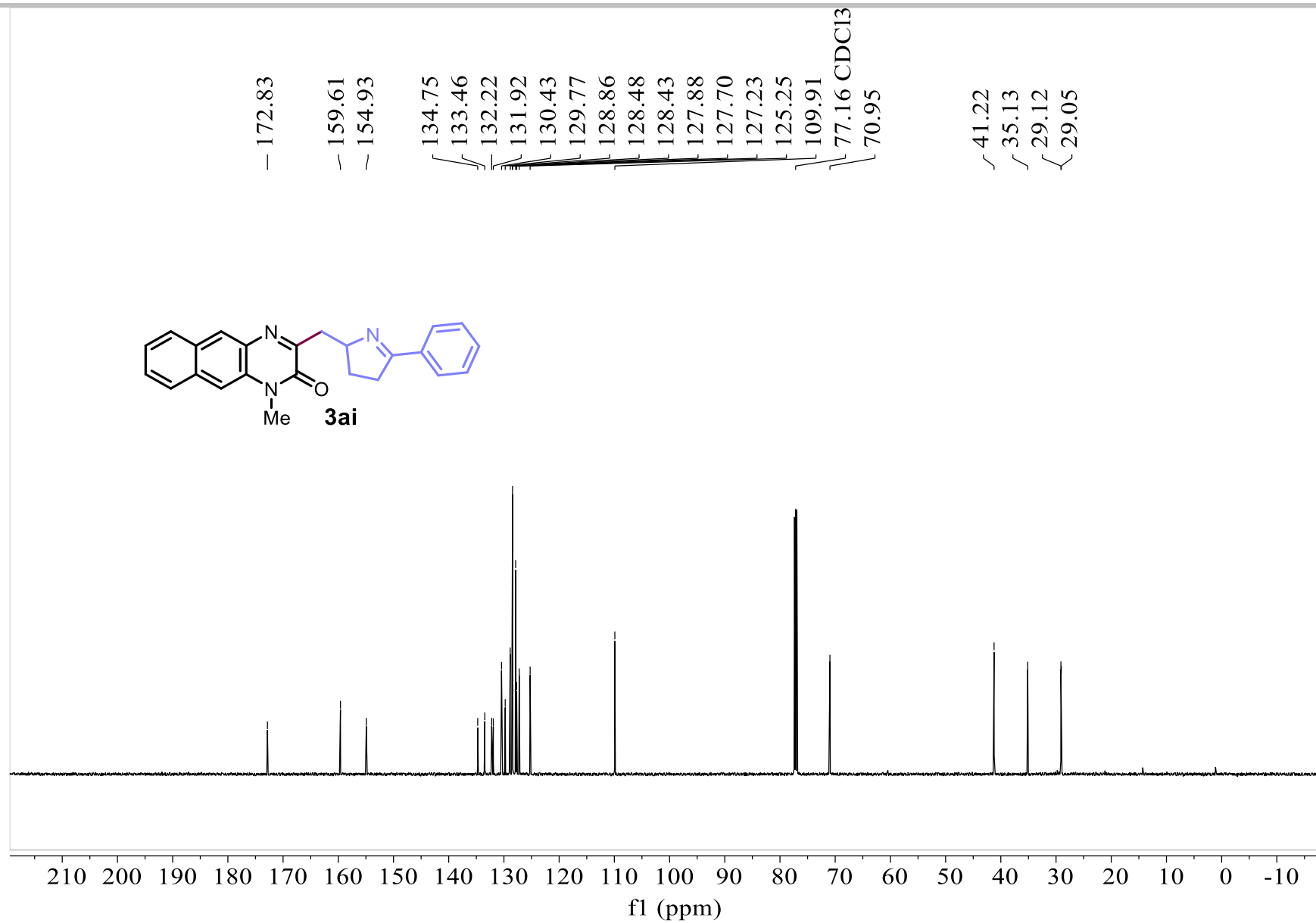
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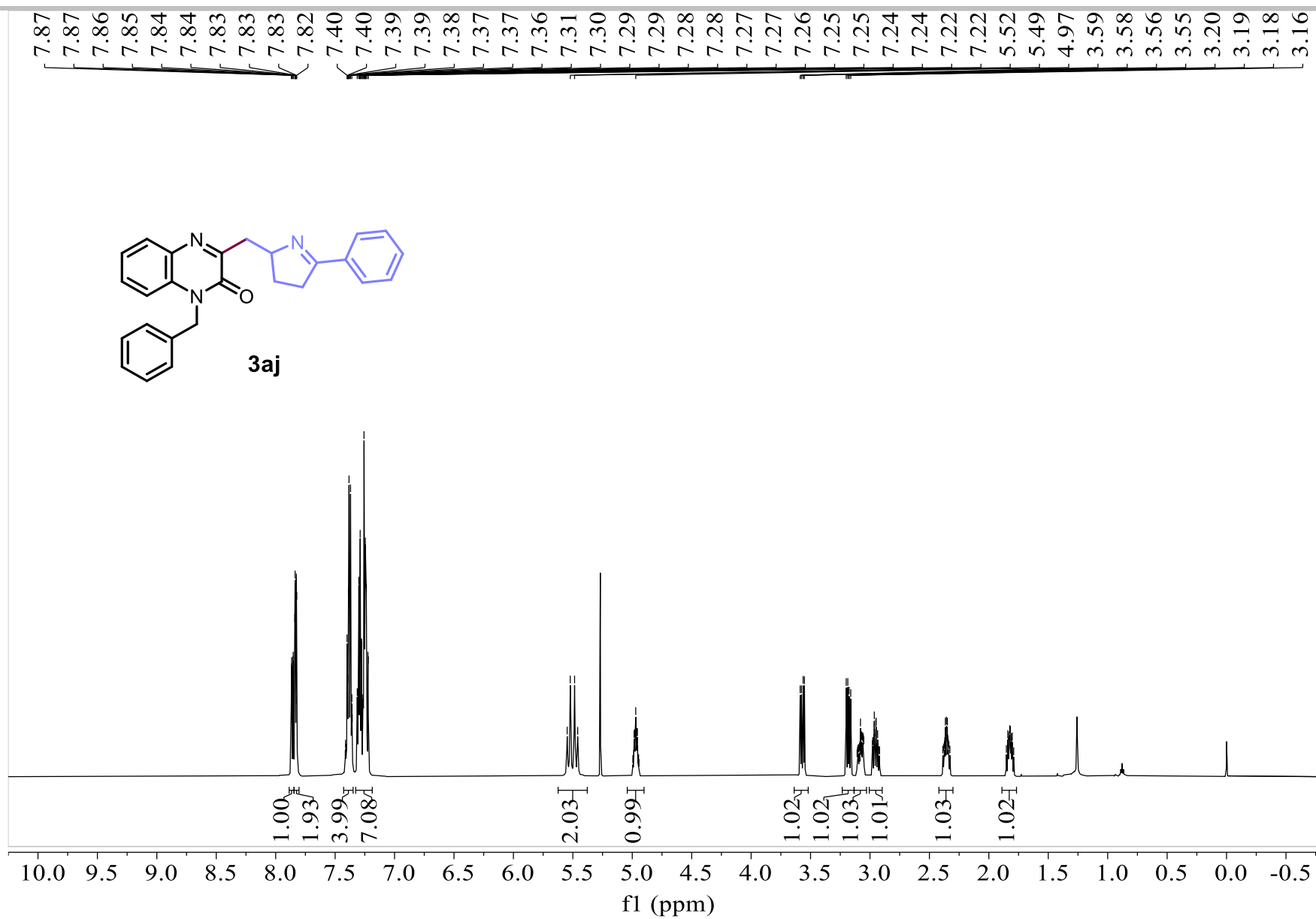
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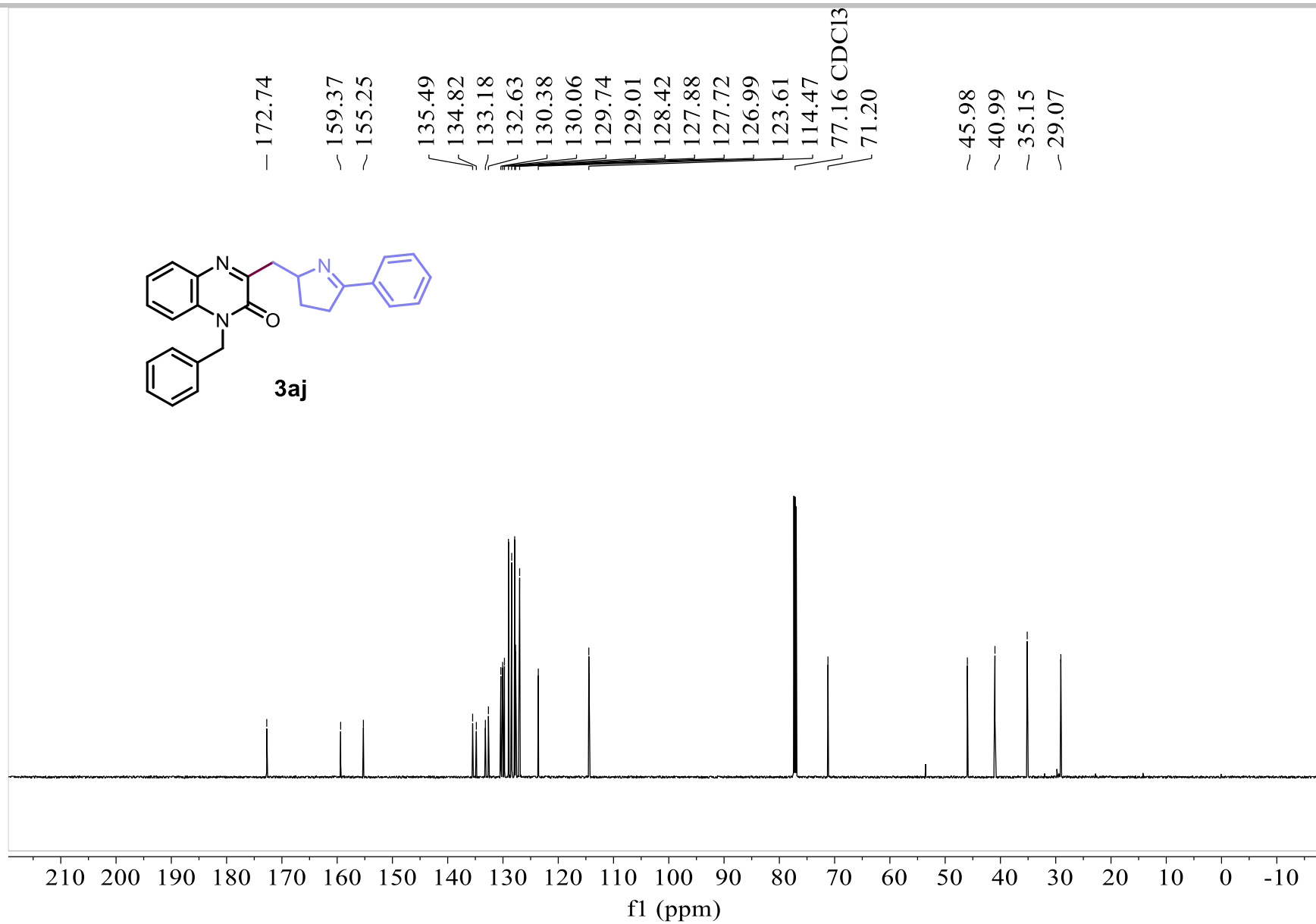
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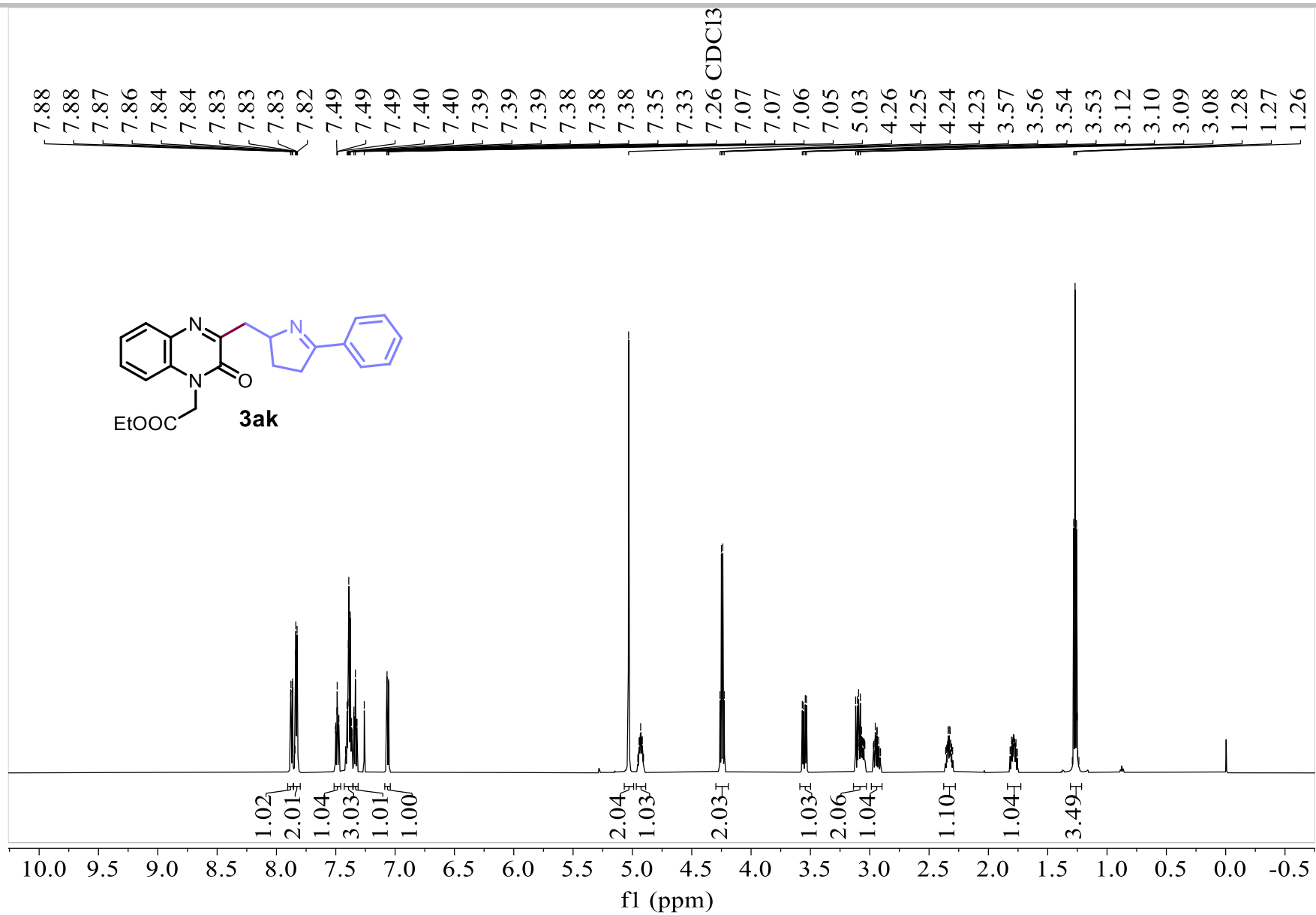
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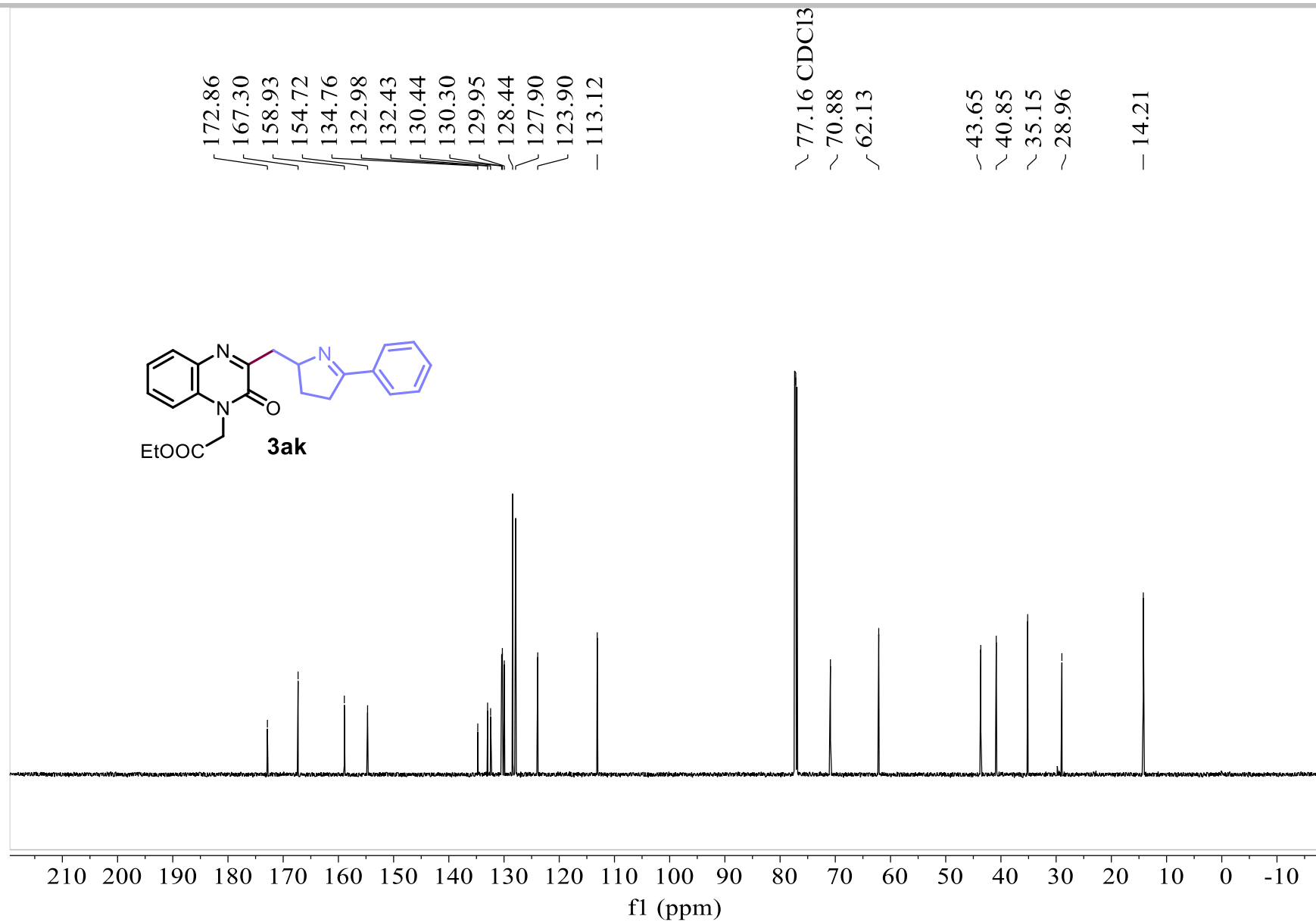
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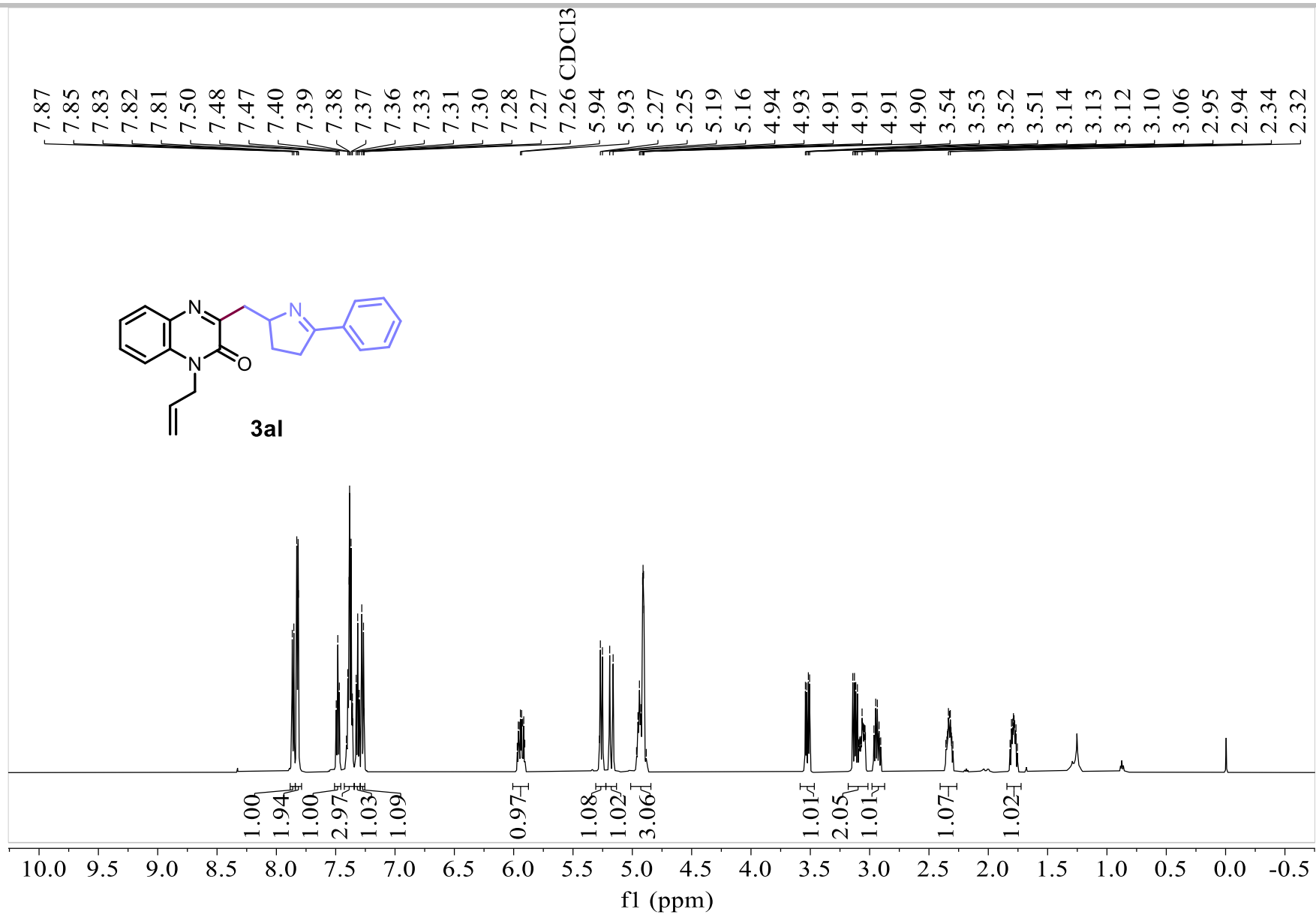
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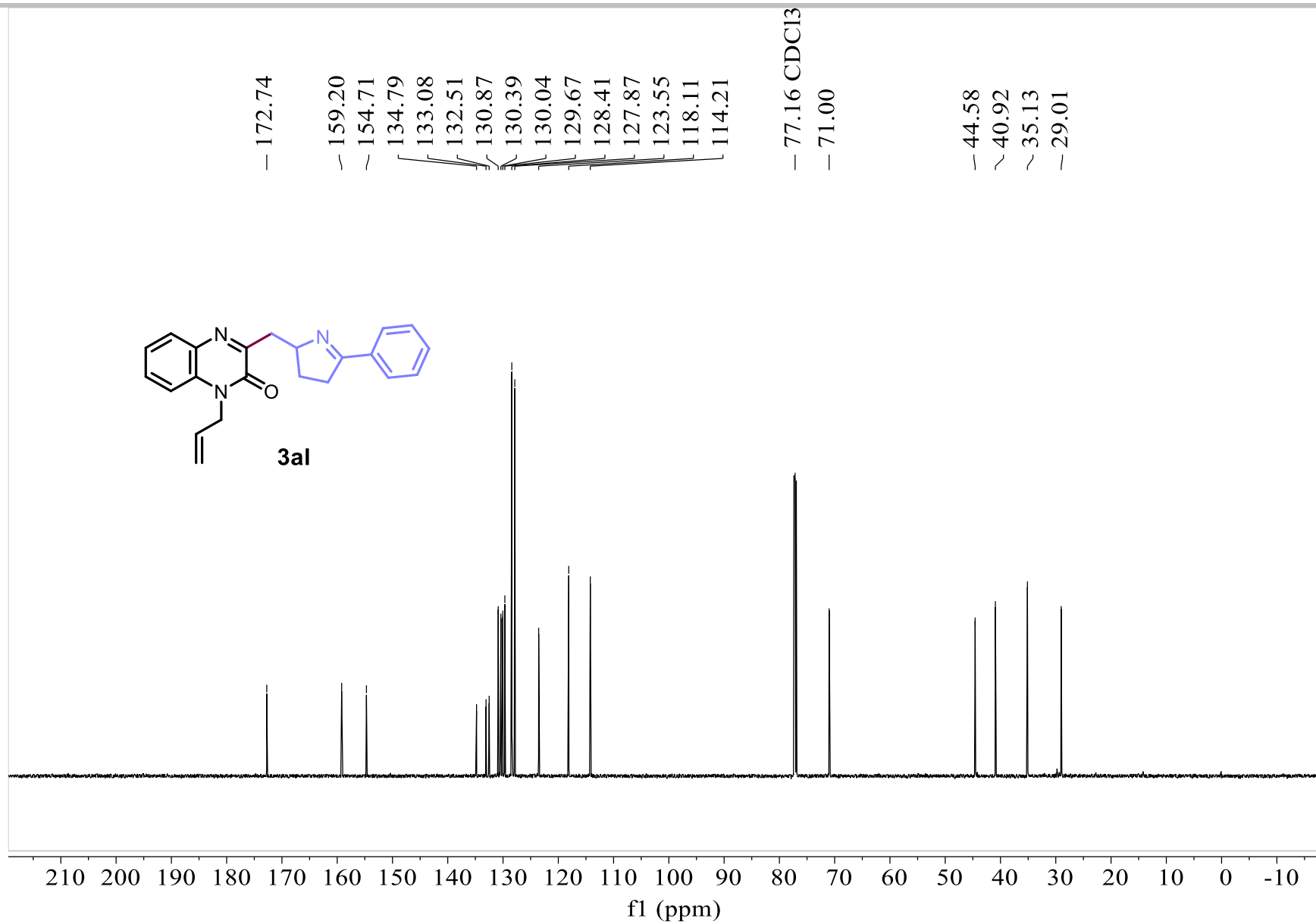
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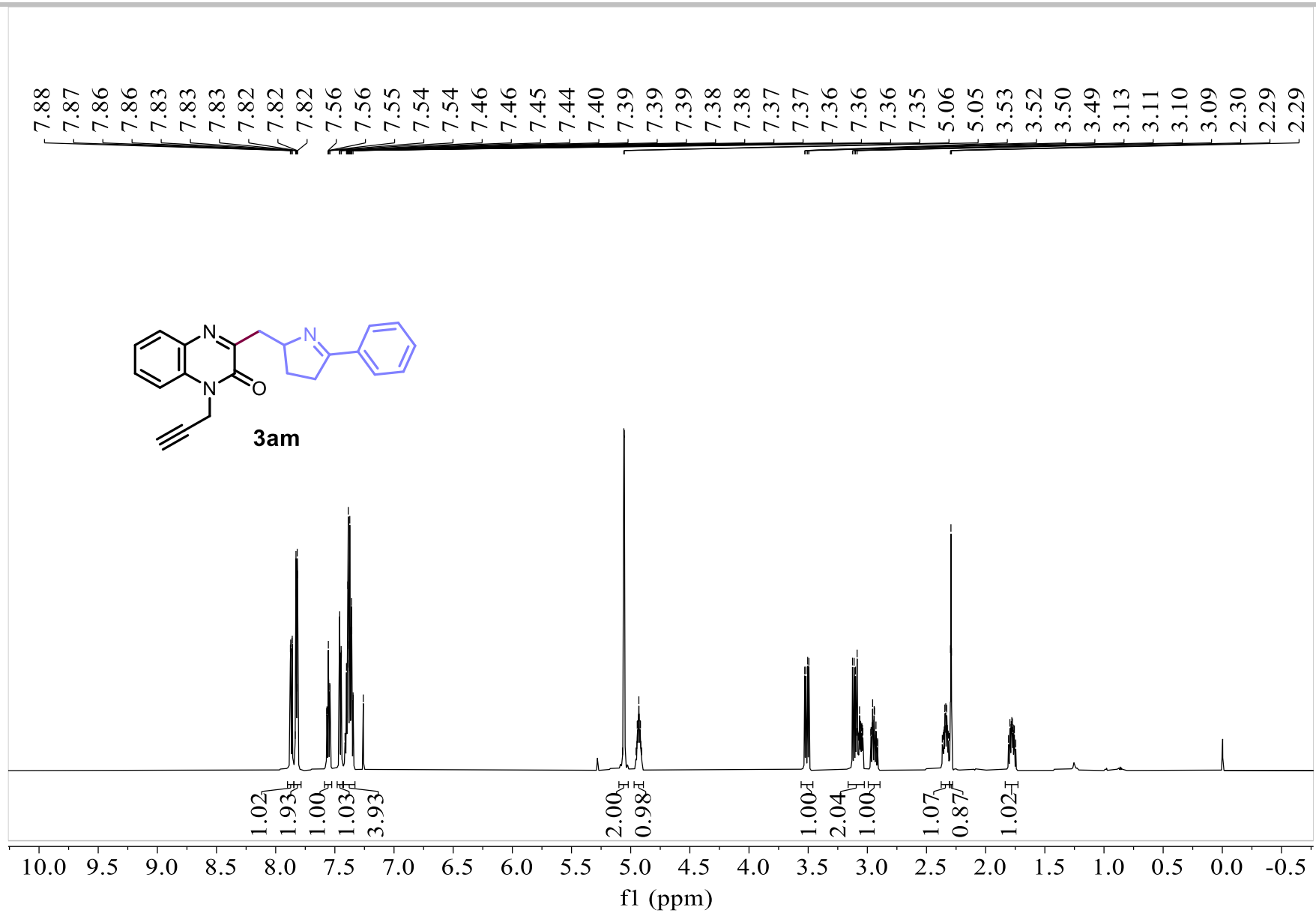
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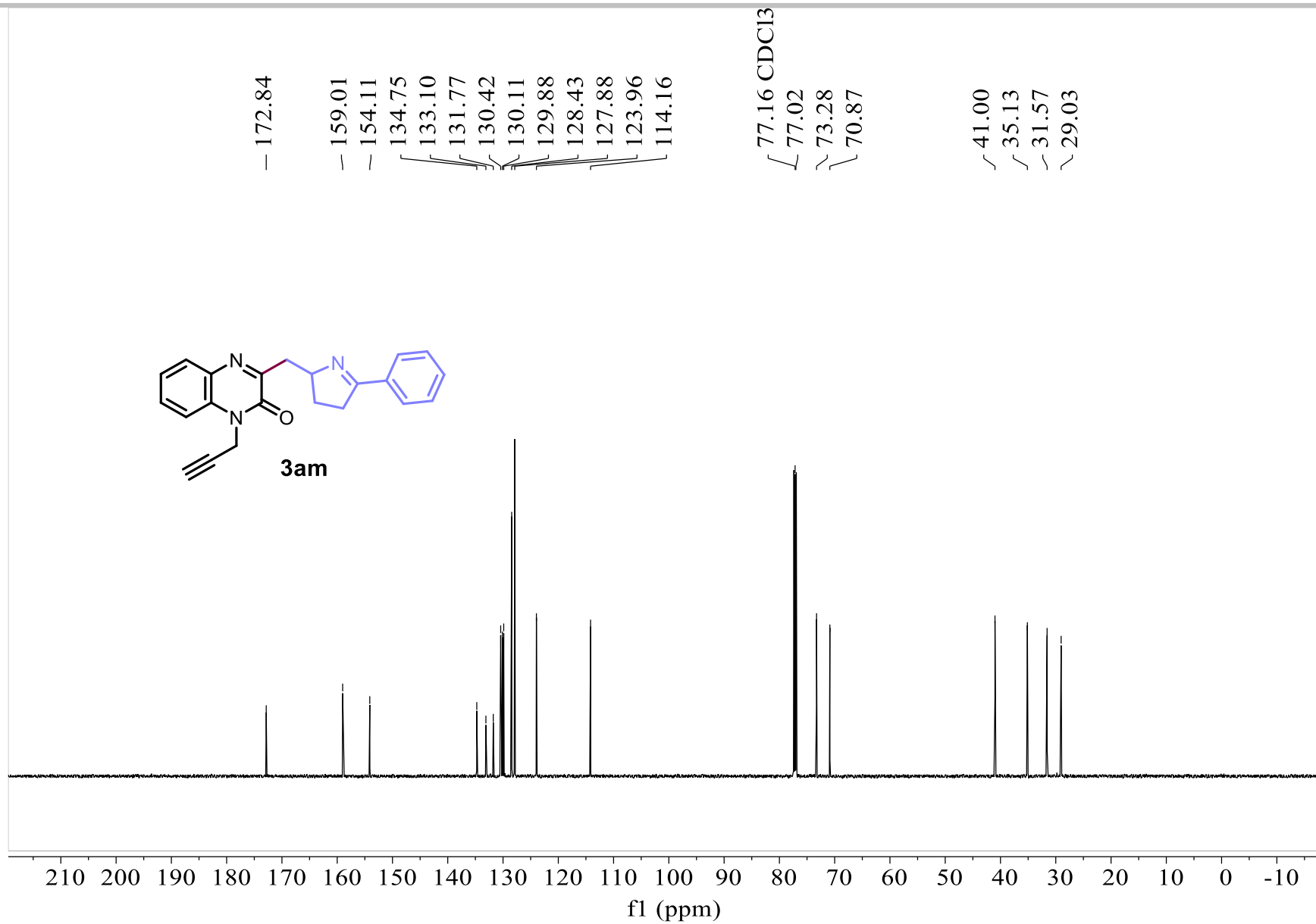
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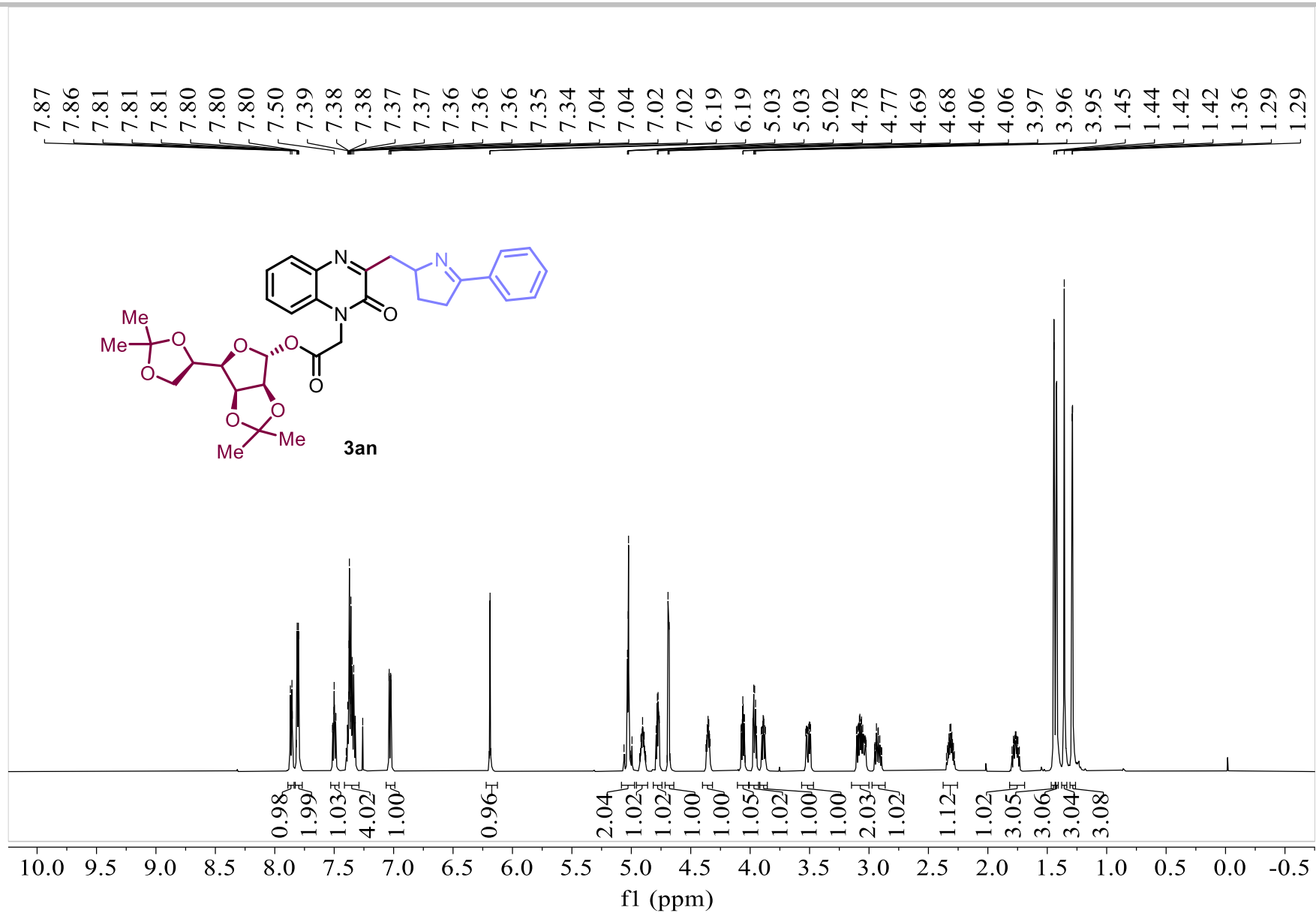
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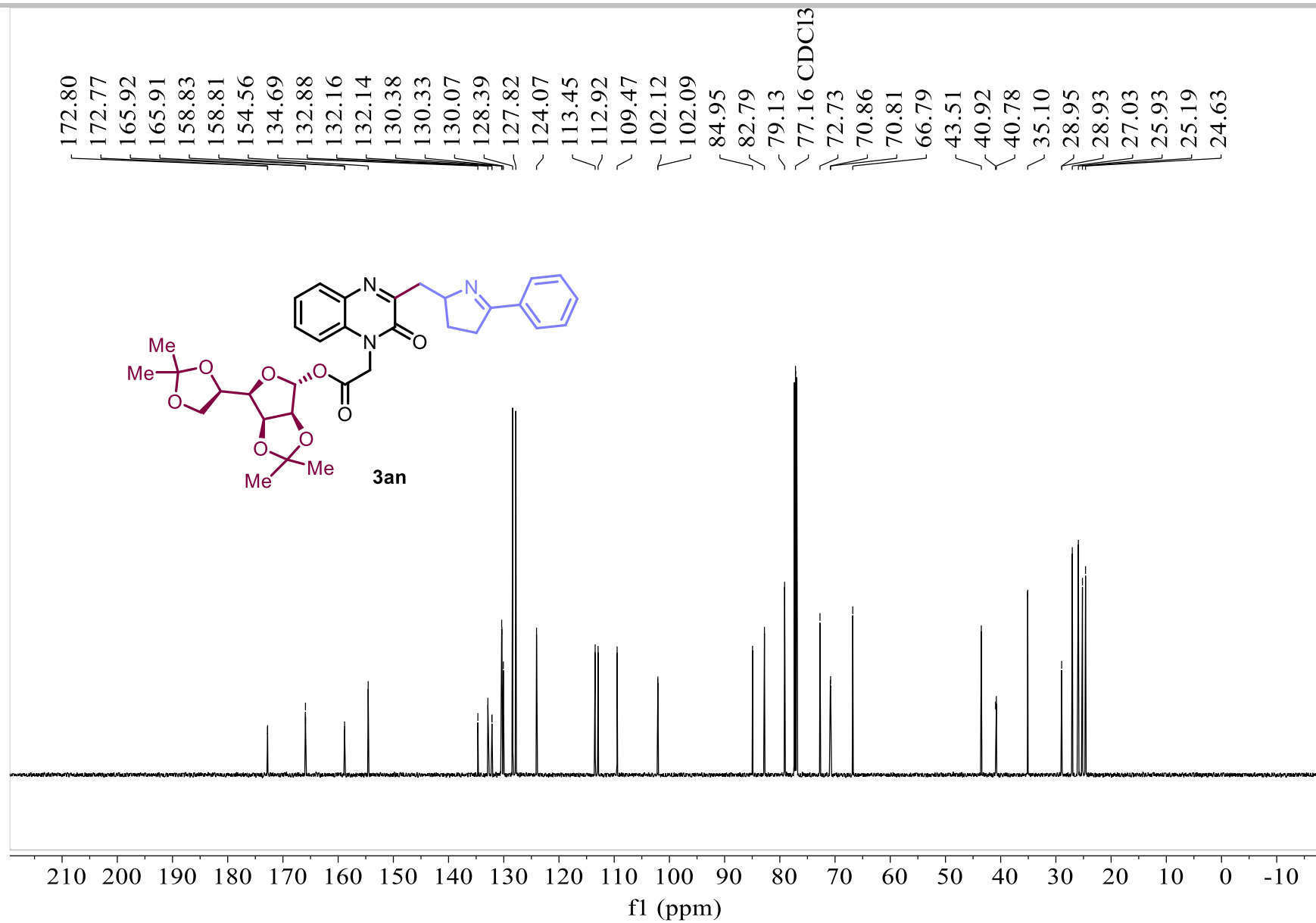
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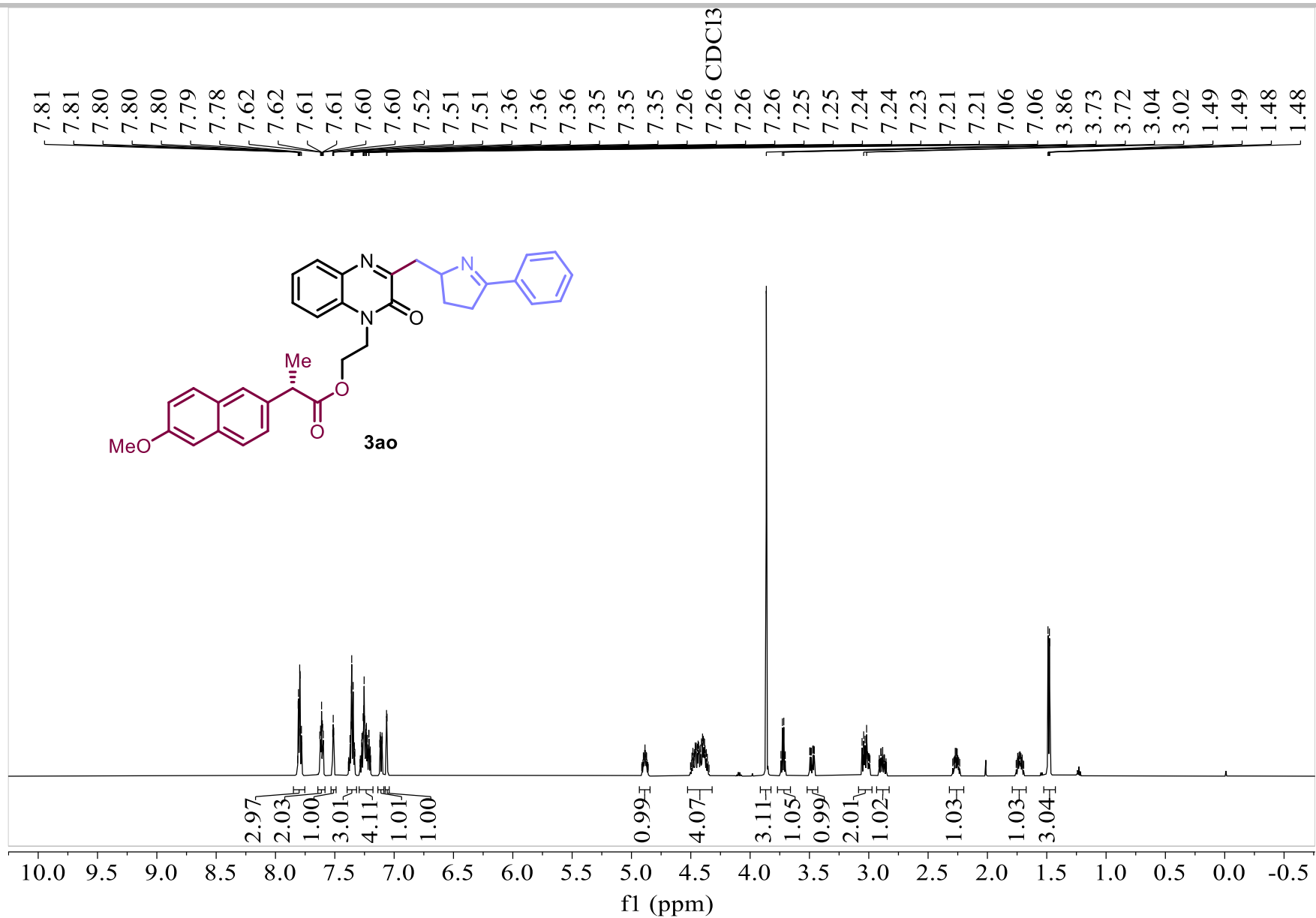
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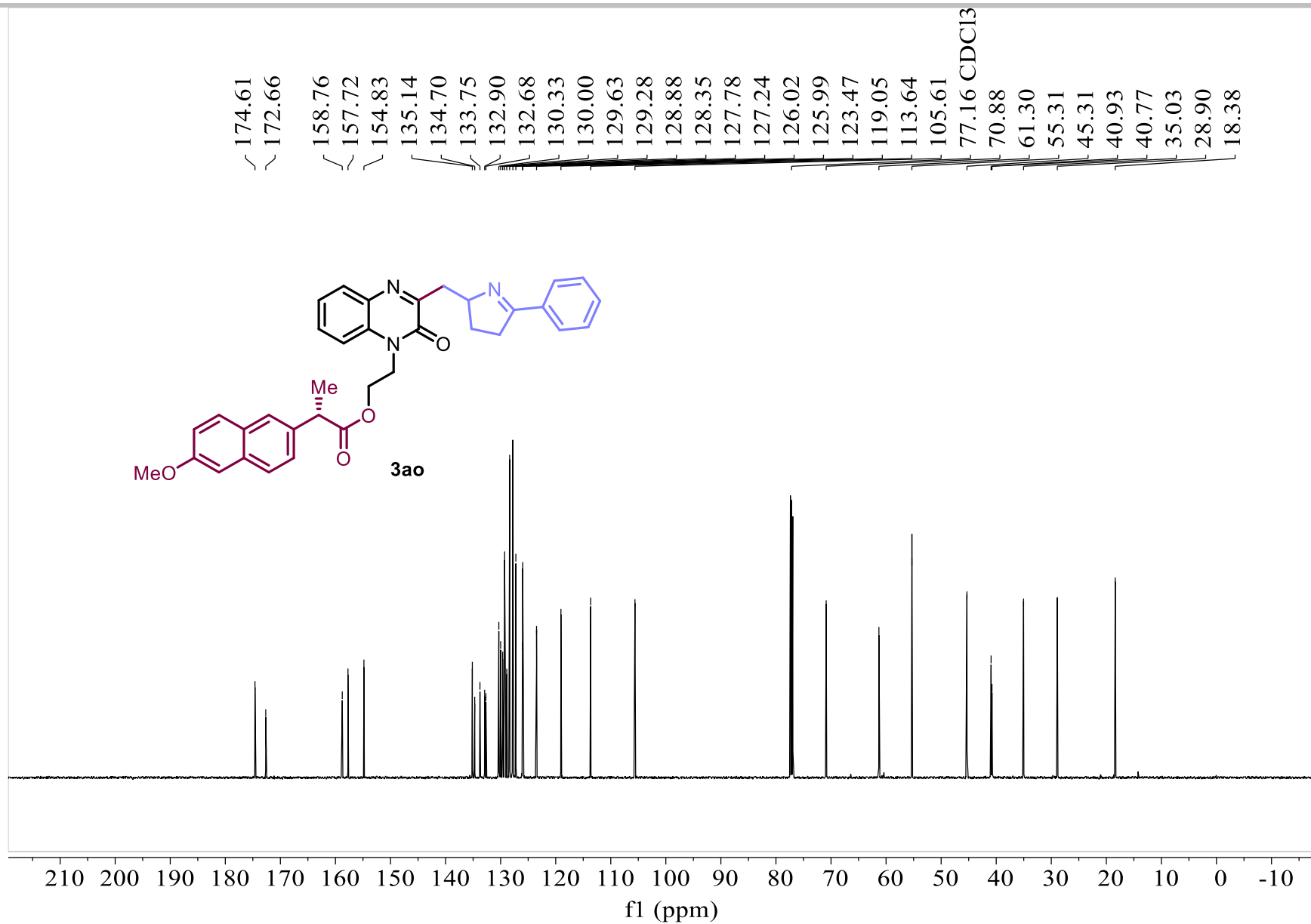
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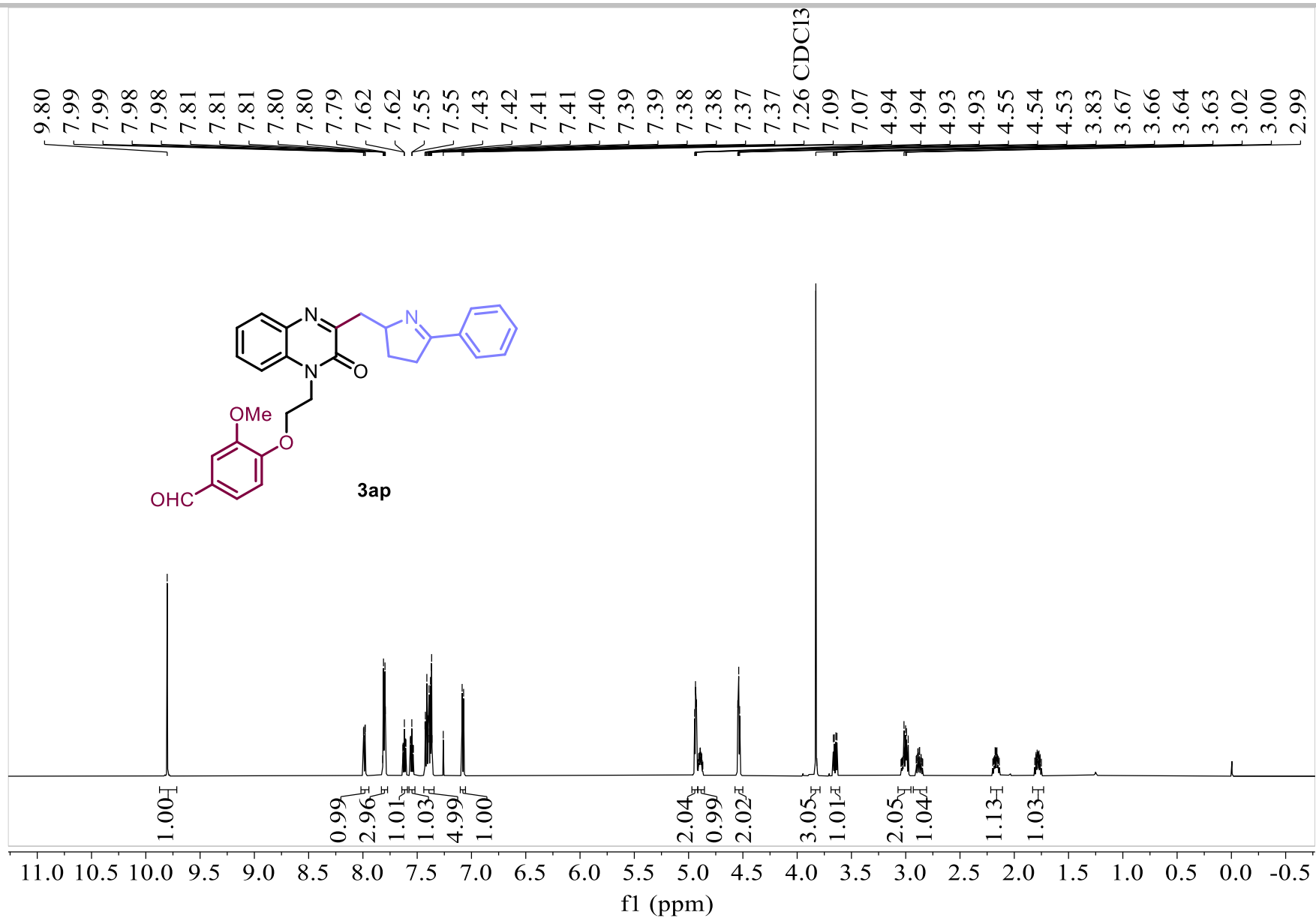
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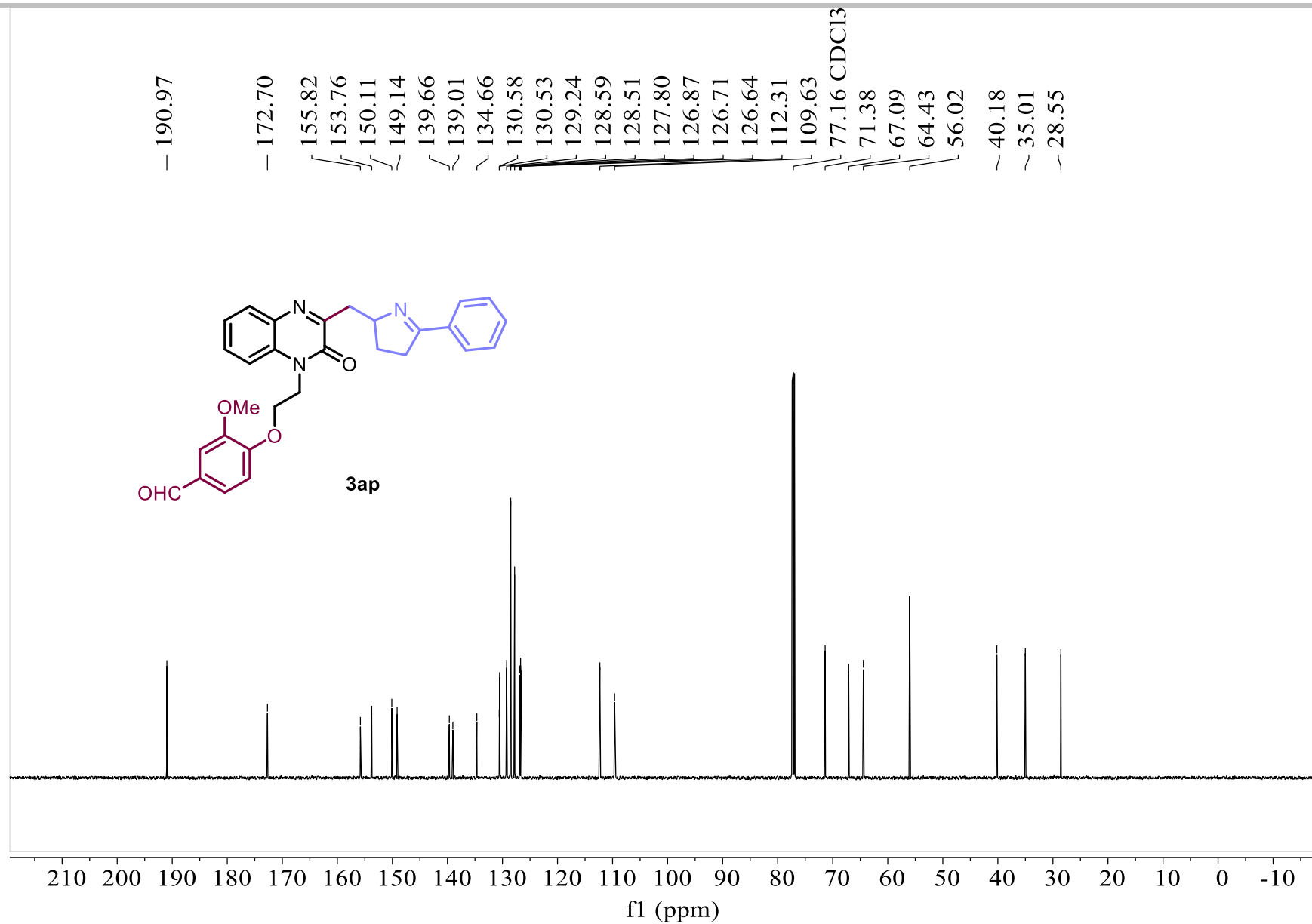
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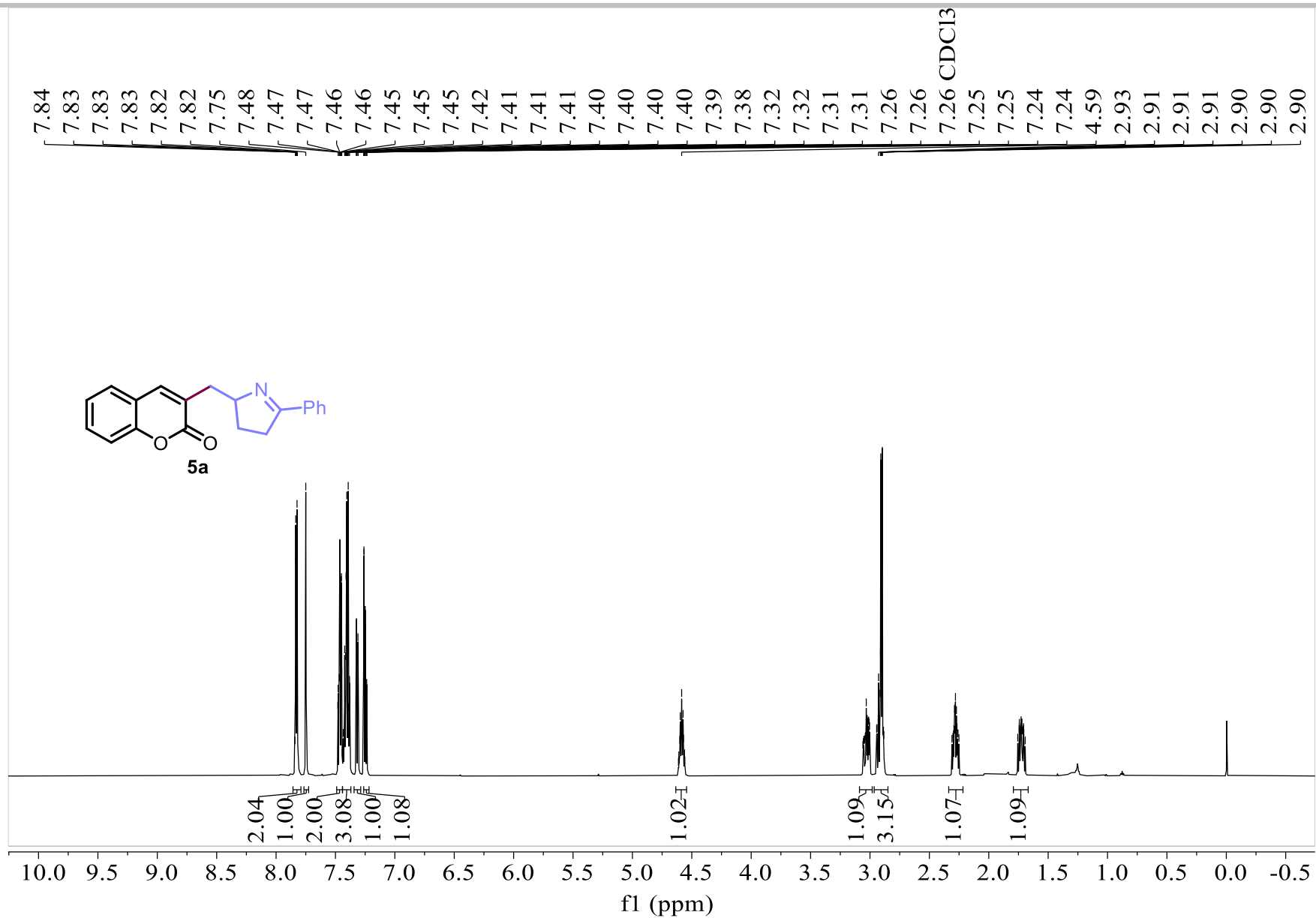
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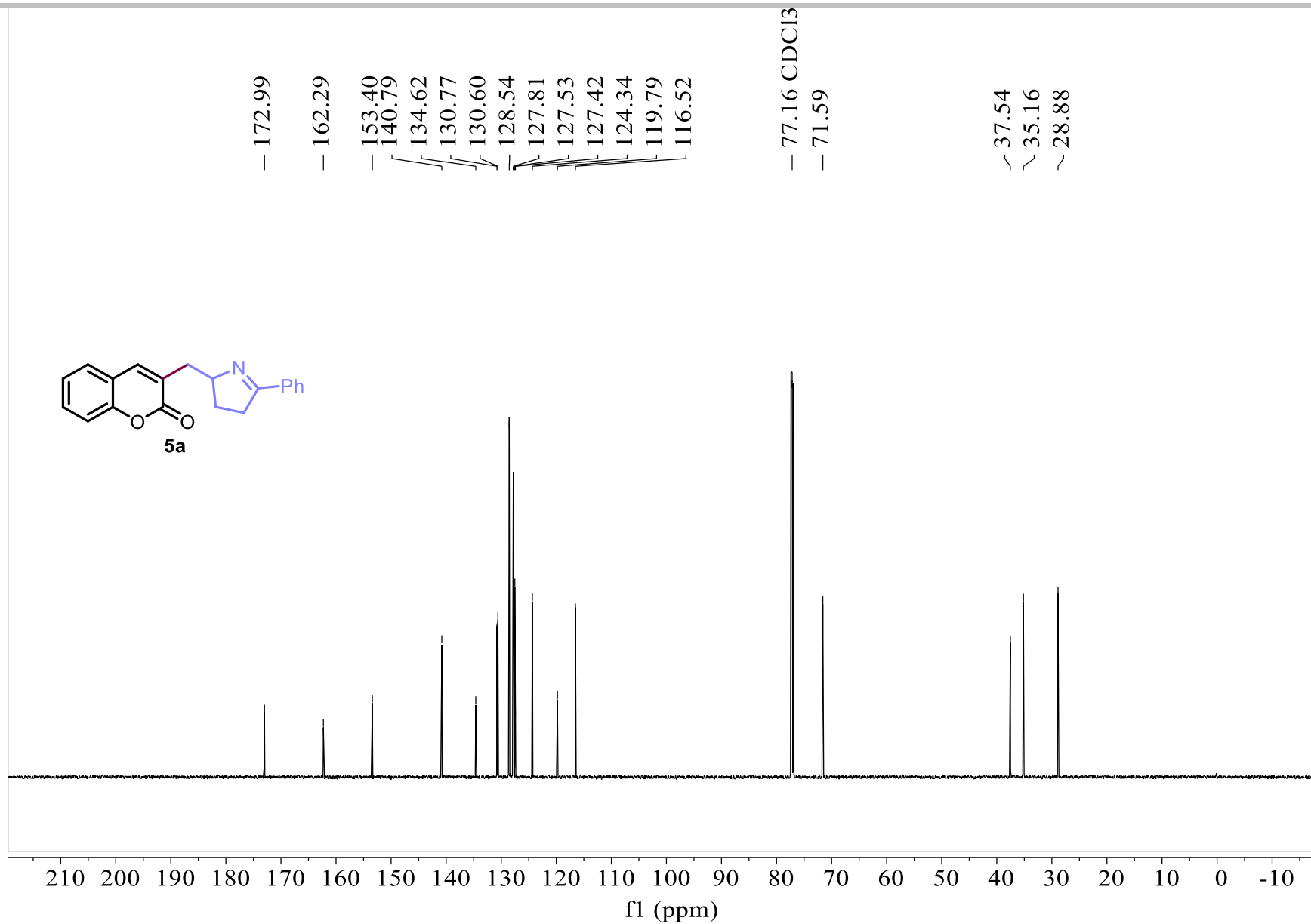
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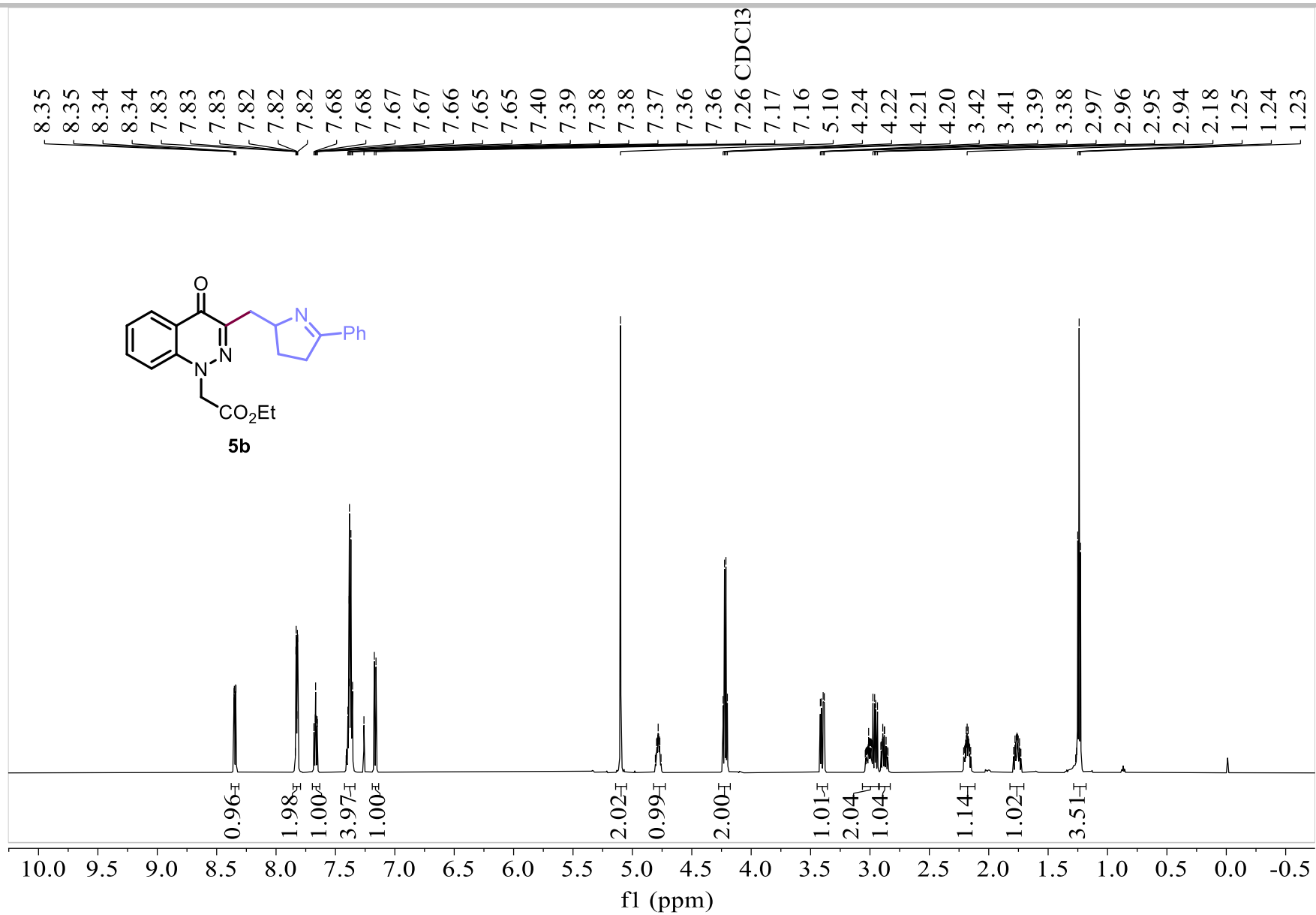
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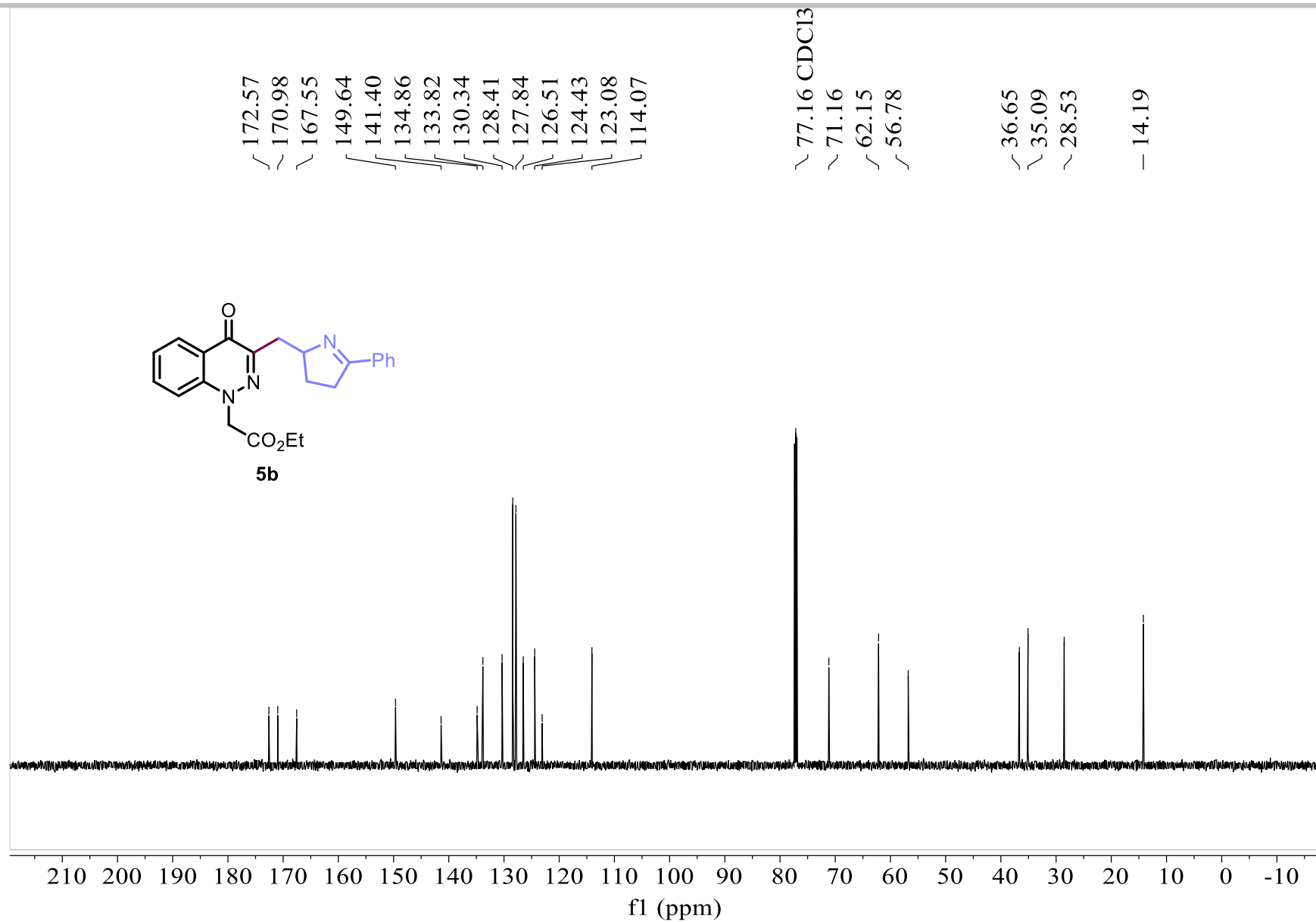
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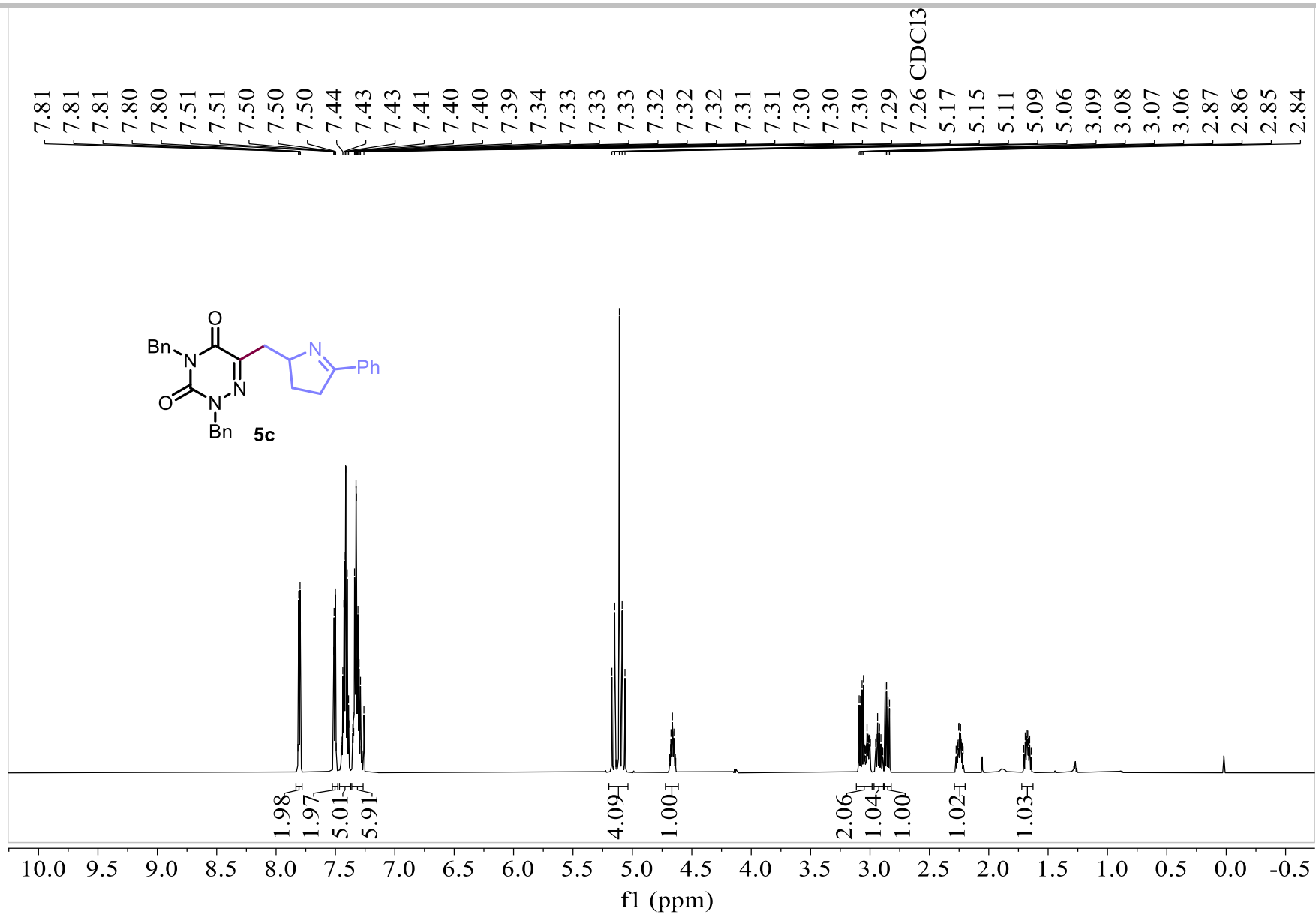
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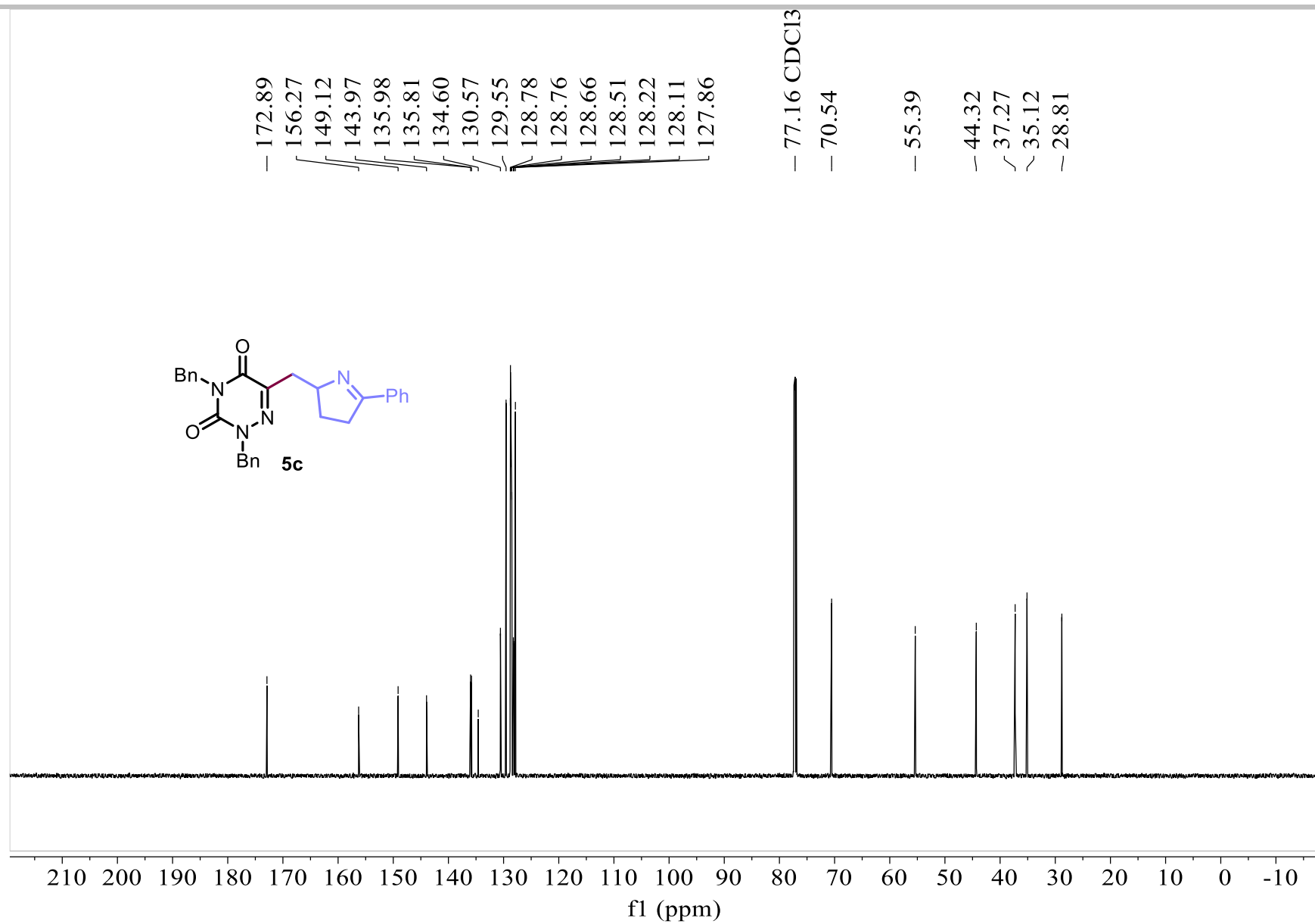
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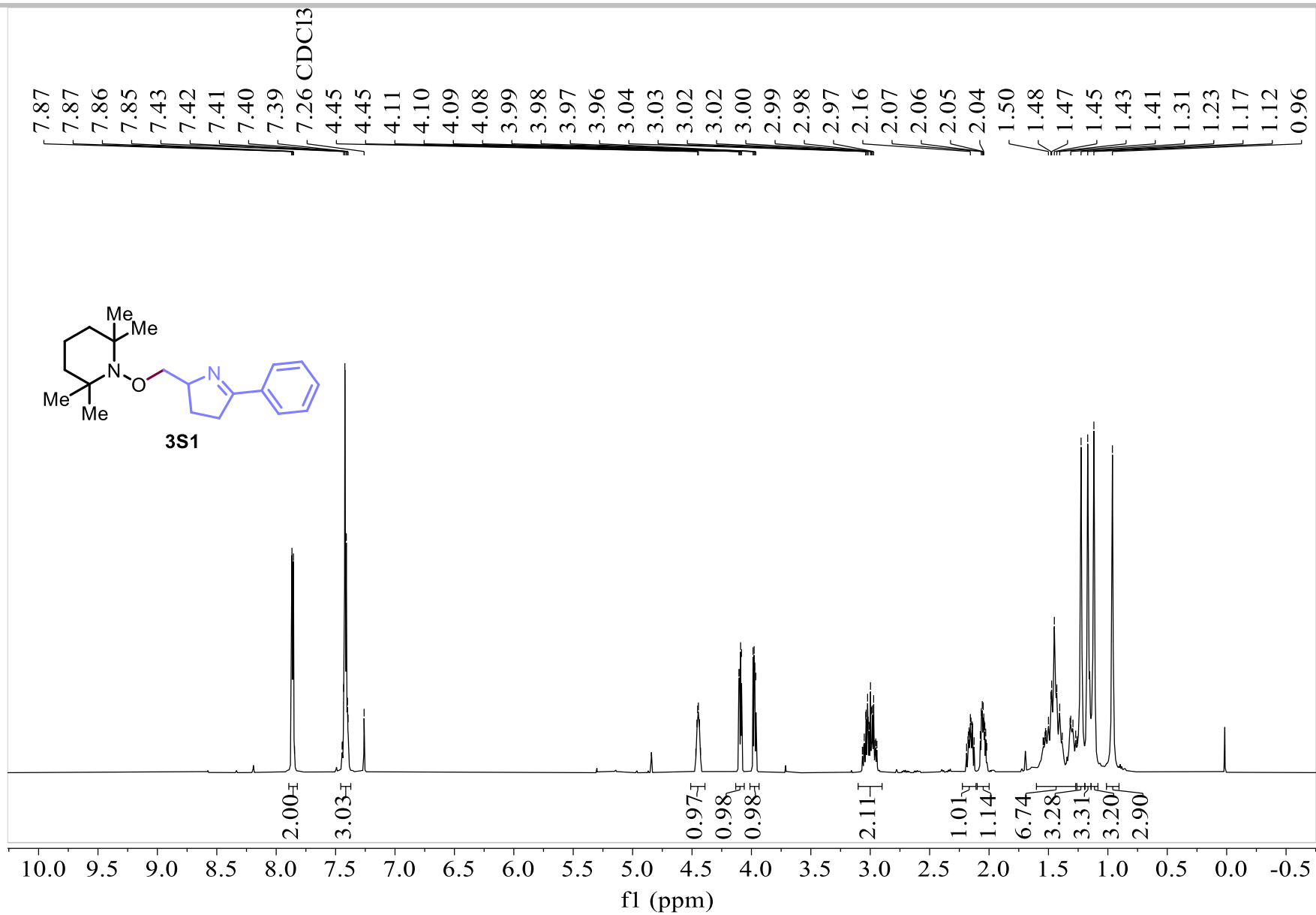
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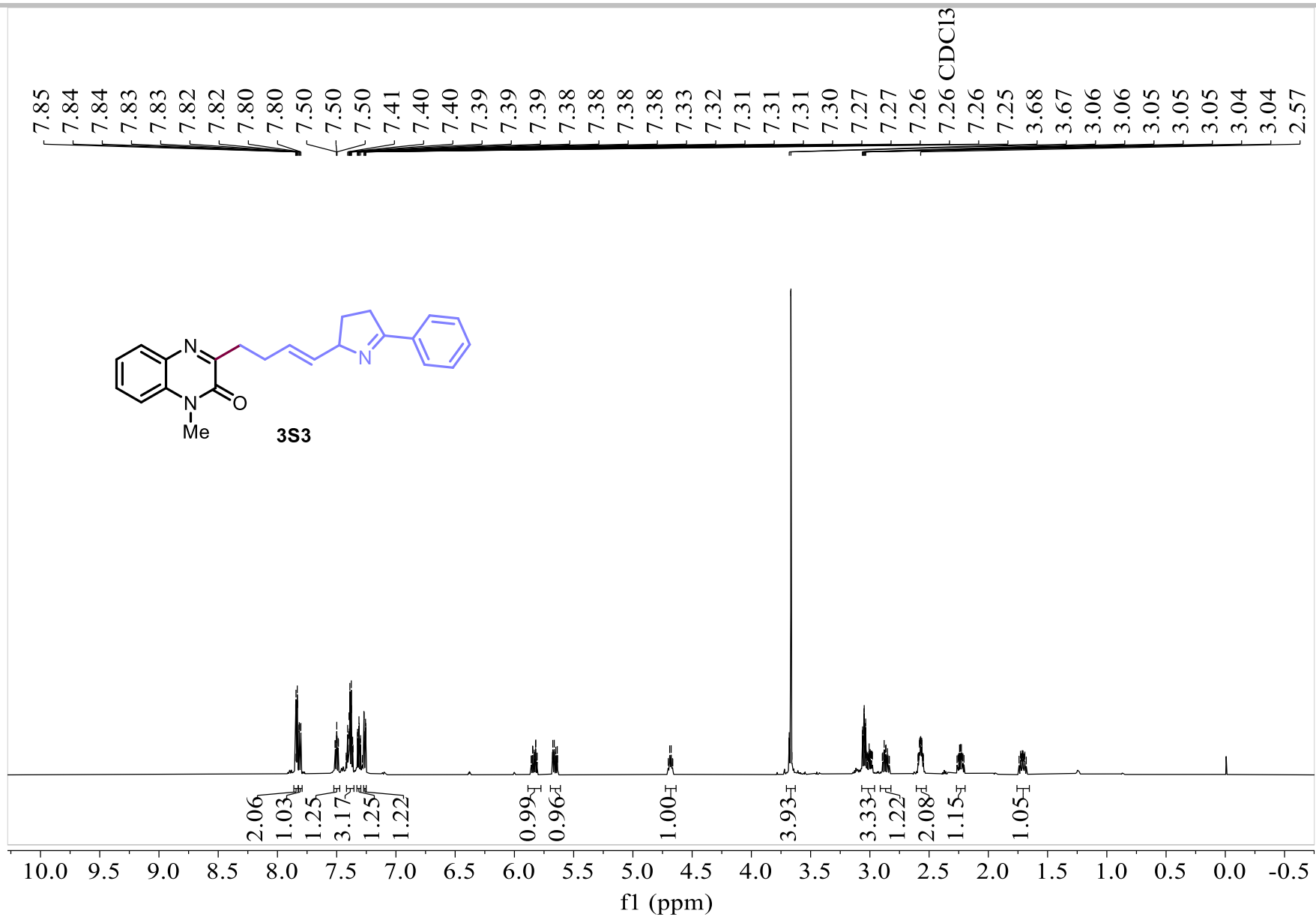
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