Supporting Information

Electrochemical alkylation of C(sp^2)-H bonds *via* halogen atom transfer (XAT) from alkyl iodides

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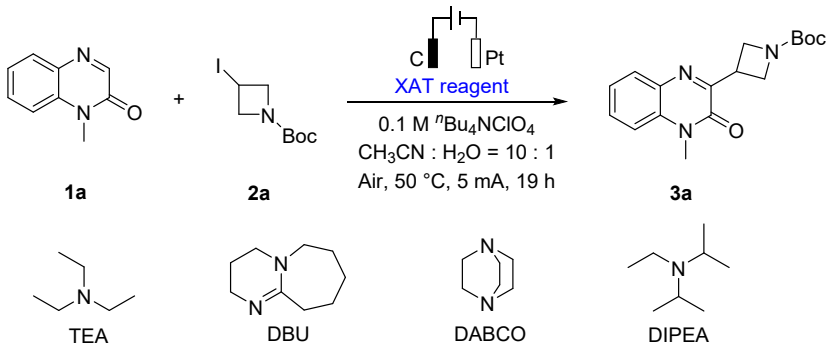
1. General considerations

General Information. All commercial reagents and solvent were purchased from Adamas, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated. All reactions were carried out under an air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods. NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C{1H} NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets), br (broad singlet) and m (multiplet). High-resolution mass spectrometry (HRMS) spectra were obtained on a micrTOF II Instrument. The electrochemical reactions were performed on IT6720 60V/5A/100W. Cyclic voltammograms were recorded on a CHI760E potentiostat

2. Optimization of reaction conditions

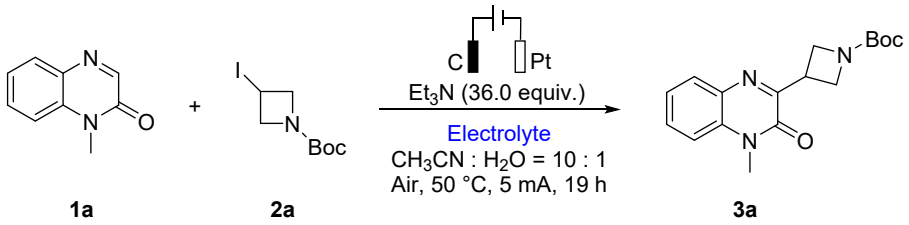
2.1 Optimization of (XAT) reagent[a].



Entry	XAT reagent	Yield (%)
1	DBU, 5.0 equiv.	51
2	DABCO, 5.0 equiv.	20
3	DIPEA, 5.0 equiv.	54
4	Et_3N, 5.0 equiv.	53
5	Et_3N, 10.0 equiv.	76
6	**Et_3N, 36.0 equiv.**	**90**

[a]Reaction conditions: C plate anode, Pt plate cathode, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), $^n Bu_4NClO_4$ (0.3 mmol, 0.1 M), XAT reagent, CH_3CN (3.0 mL), H_2O (0.3 mL), I = 5.0 mA, under air, 50 °C, 19 h; Isolated yields.

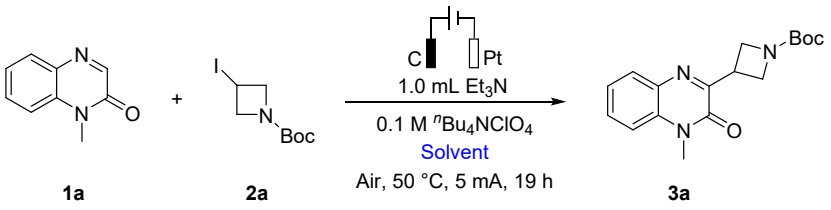
2.2 Optimization of electrolyte[a].



Entry	Electrolyte	Yield (%)
1	**$^n Bu_4NClO_4$**	**90**
2	$^n Bu_4NBF_4$	24
3	$^n Bu_4NBr$	58
4	$^n Bu_4NI$	65
5	$^n Bu_4NCl$	62
6	$^n Bu_4NPF_6$	31
7	Et_4NPF_6	22
8	Et_4NBF_4	84

[a]Reaction conditions: C plate anode, Pt plate cathode, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), Electrolyte (0.3 mmol, 0.1 M), Et_3N (36.0 equiv.), CH_3CN (3.0 mL), H_2O (0.3 mL), I = 5.0 mA, under air, 50 °C, 19 h; Isolated yields.

2.3 Optimization of solvent[a].

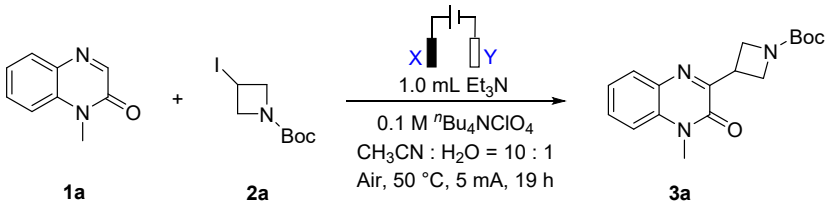


1a **2a** **3a**

Entry	Solvent (3.0 mL)	Yield (%)
1	CH_3CN	62
2	THF	29
3	H_2O	17
4	THF: H_2O = 10: 1	26
5	DMSO	63
6	NMP	trace
7	DMF	57
8	**CH_3CN: H_2O = 10: 1**	**90**

[a]Reaction conditions: C plate anode, Pt plate cathode, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), ^{n}Bu_4NClO_4 (0.3 mmol, 0.1 M), Et_3N (36.0 equiv.), Solvent (3.0 mL), I = 5.0 mA, under air, 50 °C, 19 h; Isolated yields.

2.4 Optimization of electrode[a].



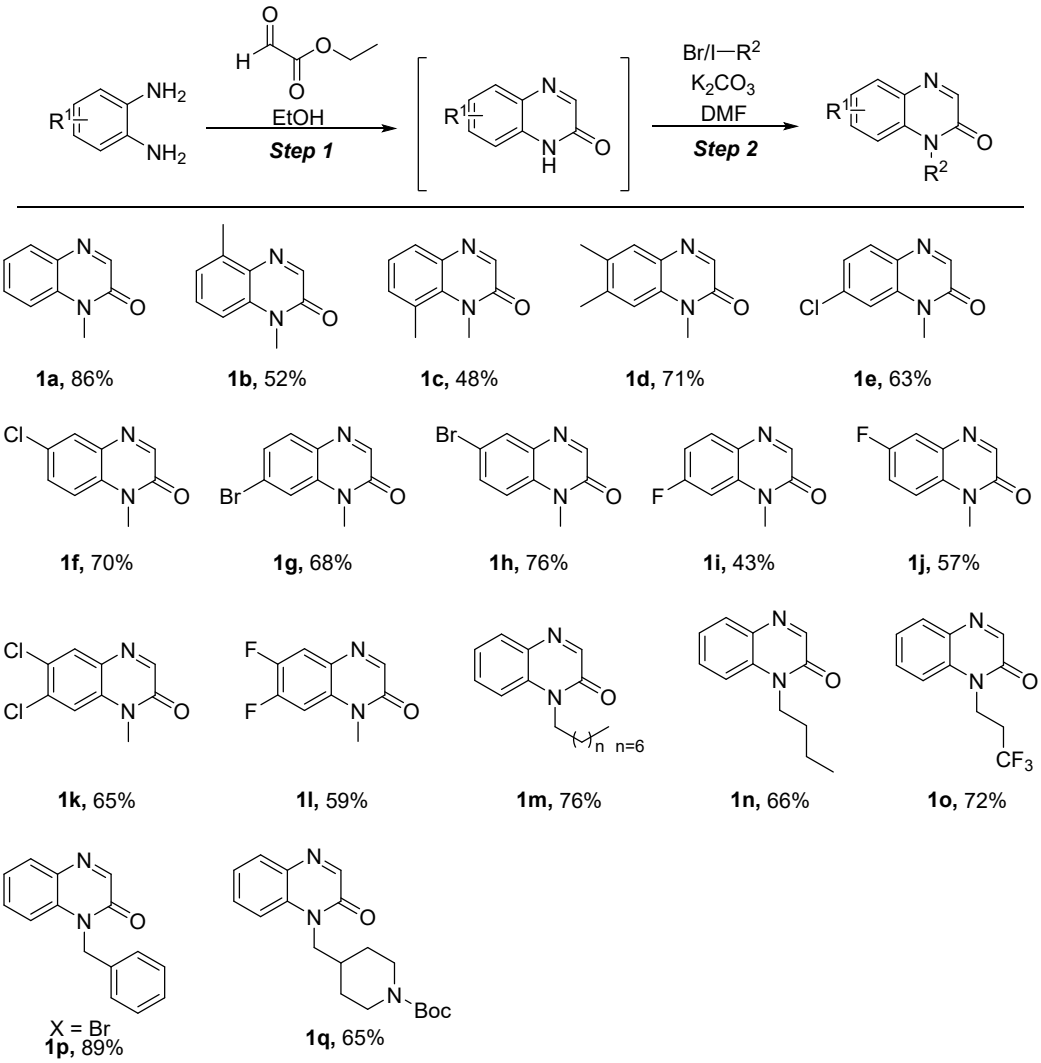
1a **2a** **3a**

Entry	Electrode	Yield (%)
1	**C (+) / Pt (-)**	**90**
2	Pt (+) / Pt (-)	trace
3	Pt (+) / C (-)	49
4	C (+) / C (-)	21
5	C (+) / Ni (-)	30
6	C (+) / Al (-)	31

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), ^{n}Bu_4NClO_4 (0.3 mmol, 0.1 M.), Et_3N (36.0 equiv.), CH_3CN (3.0 mL), H_2O (0.3 mL), I = 5.0 mA, under air, 50 °C, 19 h; Isolated yields.

3. General Procedure for Synthesis of substrates (1a-1r)

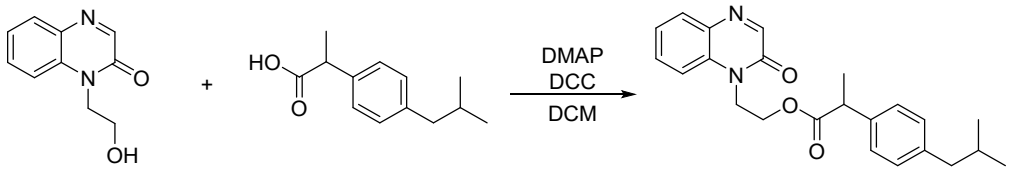
3.1 Preparation of substrates (1a-1q)



Step1: Anhydrous ethanol, benzene-1,2-diamine (1.0 equiv.), and ethyl glyoxalate (1.2 equiv.) were added to a dry 100 mL round-bottom flask at room temperature and stirred overnight. The crude quinoxaline derivative was obtained by filtration, without purification, for the next step.

Step2: The crude quinoxaline derivative (1.0 equiv.), R^2-X (1.5 equiv.) and K_2CO_3 (1.6 equiv.) were added to a dry 100 mL round-bottom flask, stirred in DMF solvent at room temperature overnight, and the mixture was extracted with ethyl acetate and concentrated to obtain the crude product, which was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate as the eluent to obtain the N-alkyl quinoxalin-2(1H)-one derivatives (**1a**-**1q**).

3.2 Preparation of drug molecule (1r)

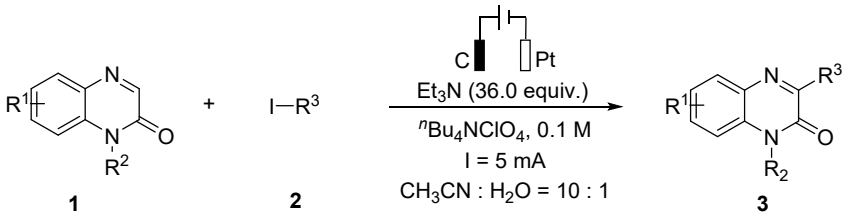


ibuprofen *from ibuprofen*

1r, 90%

1-(2-hydroxyethyl) quinoxalin-2(1H)-one (0.6 mmol, 1.0 equiv.), ibuprofen (0.72 mmol, 1.2 equiv.) and DMAP (0.03 mmol, 0.05 equiv.) were dissolved in 5.0 mL CH_2Cl_2, and the mixture was cooled to 0 °C. To this solution was added DCC (0.9 mmol, 1.5 equiv.) in 2.0 mL CH_2Cl_2. The reaction mixture was stirred vigorously for 16 h. After filtration, the solvent was evaporated, and the crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate as the eluent to obtain the 2-(2-oxoquinoxalin-1(2H)-yl) ethyl 2-(4-isobutylphenyl) propanoate (**1r**).

4. General procedure for the C(sp²)-H alkylation *via* electrochemical halogen-atom transfer



General Procedure A: Quinoxalin-2(1H)-one compounds **1** (0.2 mmol, 1.0 equiv.), alkyl iodide **2** (0.6 mmol, 3.0 equiv.), additive (Et_3N, 36.0 equiv.), solvent (CH_3CN: H_2O = 10: 1, 3.3 mL), and electrolyte ($^nBu_4NClO_4$, 0.3 mmol) were added to a dried 15 mL reaction vial. Then, the graphite electrode and platinum plates electrode (**Figure S1-a**, 10*10*0.2 mm) were immerged into the solution, as anode and cathode respectively. The electrodes were connected to a constant current power supply, and the current was set as 5 mA (**Figure S1-b**). The reaction mixture was stirred at 50 ℃ for 19 hours under air conditions (**Figure S1-c**). After the reaction, the mixture was concentrated and the crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate as the eluent to obtain the target product.

(a) **(b)** **(c)**

Figure S1. Electrocatalytic equipment. (a) Platinum electrode (10*10*0.2 mm); (b) Constant current power supply; (c) The reaction vial.

General Procedure B: Quinoxalin-2(1H)-one compounds **1** (0.2 mmol, 1.0 equiv.), alkyl iodide **2** (0.6 mmol, 3.0 equiv.), additive (Et_3N, 36.0 equiv.), solvent (CH_3CN: H_2O = 10: 1, 3.3 mL), and electrolyte ($^nBu_4NClO_4$, 0.3 mmol) were added to a dried 15 mL reaction vial. Then, the graphite electrode and platinum plates electrode were immerged into the solution, as anode and cathode respectively. The electrodes were connected to a constant current power supply, and the current was set as 5 mA. The reaction mixture was stirred at 50 ℃ for 24 hours under air conditions. After the reaction, the mixture was concentrated and the crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate as the eluent to obtain the target product.

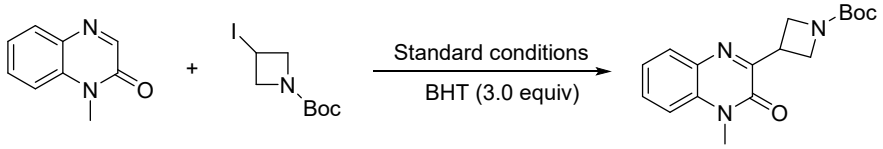
General Procedure C: Quinoxalin-2(1H)-one compounds **1** (0.2 mmol, 1.0 equiv.), alkyl iodide **2** (0.6 mmol, 3.0 equiv.), additive (Et_3N, 36.0 equiv.), solvent (CH_3CN: H_2O = 10: 1, 3.3 mL), and electrolyte

($^{n}Bu_4NClO_4$, 0.3 mmol) were added to a dried 15 mL reaction vial. Then, the graphite electrode and platinum plates electrode were immerged into the solution, as anode and cathode respectively. The electrodes were connected to a constant current power supply, and the current was set as 7 mA. The reaction mixture was stirred at 60 ℃ for 22 hours under air conditions. After the reaction, the mixture was concentrated and the crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate as the eluent to obtain the target product.

General Procedure D: Quinoxalin-2(1H)-one compounds **1** (0.2 mmol, 1.0 equiv.), alkyl iodide **2** (0.6 mmol, 3.0 equiv.), additive (Et_3N, 10.0 equiv.), solvent (CH_3CN: H_2O = 10: 1, 3.3 mL), and electrolyte ($^{n}Bu_4NClO_4$, 0.3 mmol) were added to a dried 15 mL reaction vial. Then, the graphite electrode and platinum plates electrode were immerged into the solution, as anode and cathode respectively. The electrodes were connected to a constant current power supply, and the current was set as 7 mA. The reaction mixture was stirred at 60 ℃ for 16 hours under air conditions. After the reaction, the mixture was concentrated and the crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate as the eluent to obtain the target product.

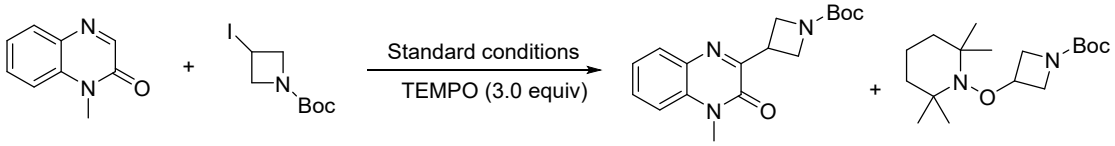
5. General procedure for the mechanism experiments

5.1 Radical trapping and inhibition experiments



1a **2a** **3a, 53%**

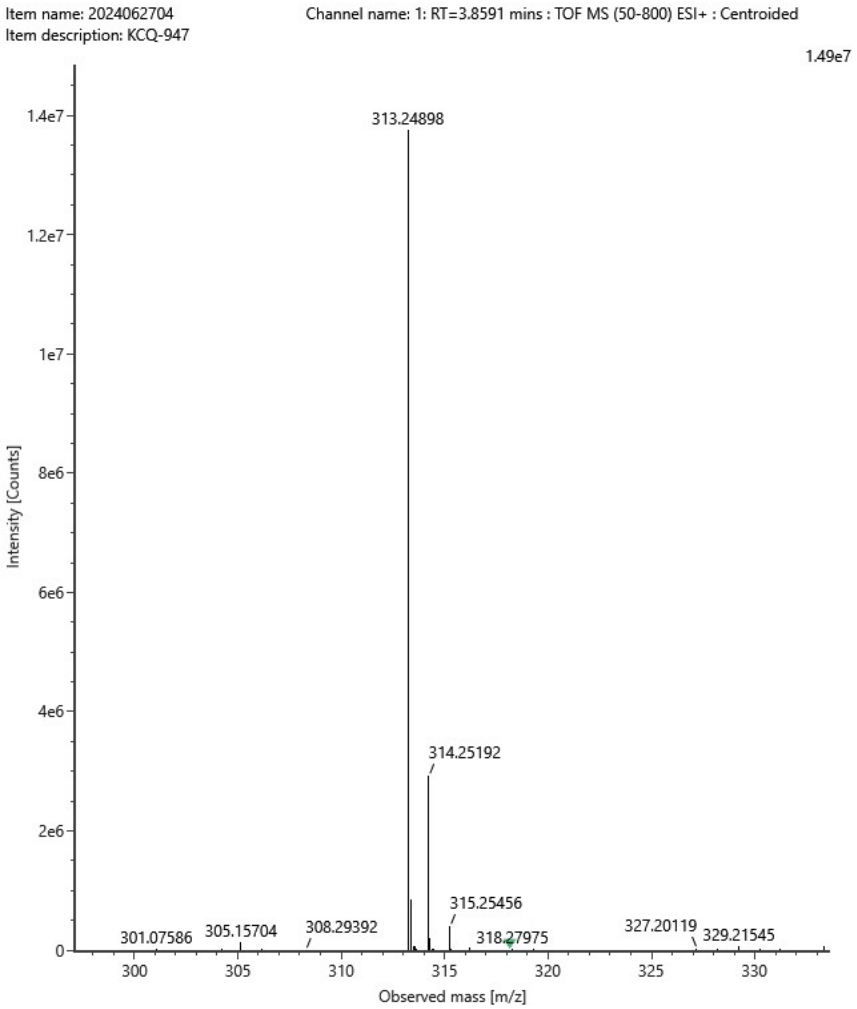
1-methylquinoxalin-2(1H)-one **1a** (0.2 mmol, 1.0 equiv.), tert-butyl 3-iodoazetidine-1-carboxylate **2a** (0.6 mmol, 3.0 equiv.), additive (Et_3N, 1.0 mL), BHT (0.6 mmol, 3.0 equiv.), solvent (CH_3CN: H_2O = 10: 1, 3.3 mL), and electrolyte ($^nBu_4NClO_4$, 0.3 mmol) were added to a dried 15 mL reaction vial. Then, the graphite electrode and platinum plates electrode were immerged into the solution, as anode and cathode respectively. After the reaction, the yield of **3a** was reduced to 53%. This result indicates that the reaction might proceed via a radical pathway.



1a **2a** **3a, n.d.** **5**

detected by HRMS
$[M+H]^+$:Calc. 313.2486
Fond: 313.2490

1-methylquinoxalin-2(1H)-one **1a** (0.2 mmol, 1.0 equiv.), tert-butyl 3-iodoazetidine-1-carboxylate **2a** (0.6 mmol, 3.0 equiv.), additive (Et_3N, 1.0 mL), TEMPO (0.6 mmol, 3.0 equiv.), solvent (CH_3CN: H_2O = 10: 1, 3.3 mL), and electrolyte ($^nBu_4NClO_4$, 0.3 mmol) were added to a dried 15 mL reaction vial. Then, the graphite electrode and platinum plates electrode were immerged into the solution, as anode and cathode respectively. The electrodes were connected to a constant current power supply, and the current was set as 5 mA. The reaction mixture was stirred at 50 ℃ for 19 hours under air conditions, After the reaction, the reaction was found to be completely inhibited and the TEMPO-adduct **5** was detected by HRMS. This result indicates that the reaction might proceed via a radical pathway.



5.2 Cyclic voltammetry experiment

The cyclic voltammograms were recorded in CH_3CN (5.0 mL) with $^{n}Bu_4NClO_4$ (0.1 M) as supporting electrolyte using a glassy carbon disk working electrode, a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 100 mV/s.

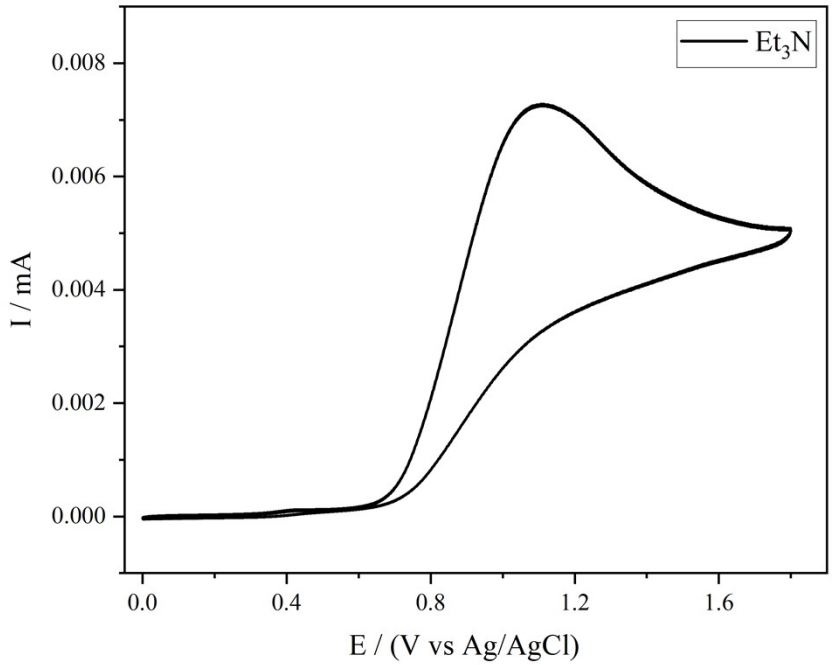


Figure S2. Cyclic voltammograms of Et_3N (0.1 mmol).

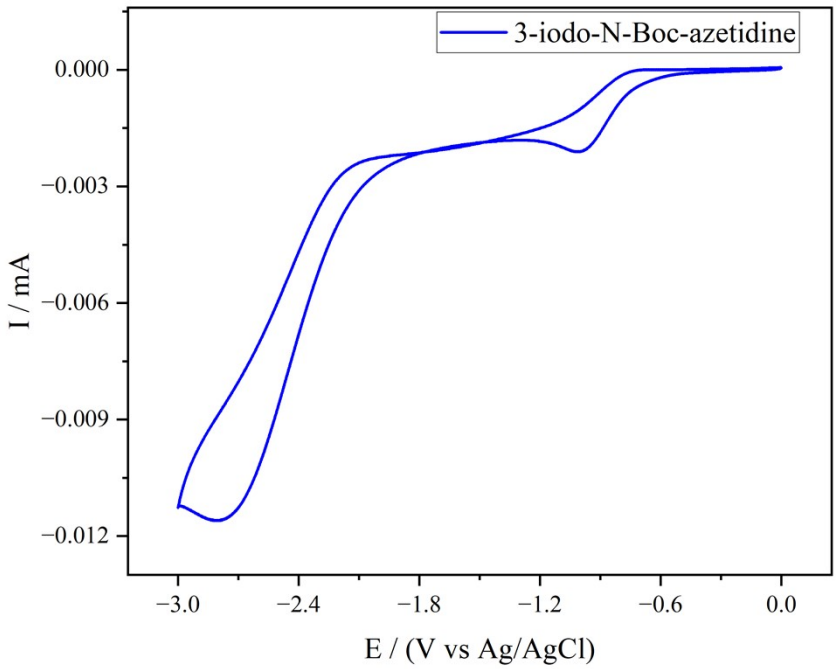


Figure S3. Cyclic voltammograms of alkyl iodides (0.1 mmol).

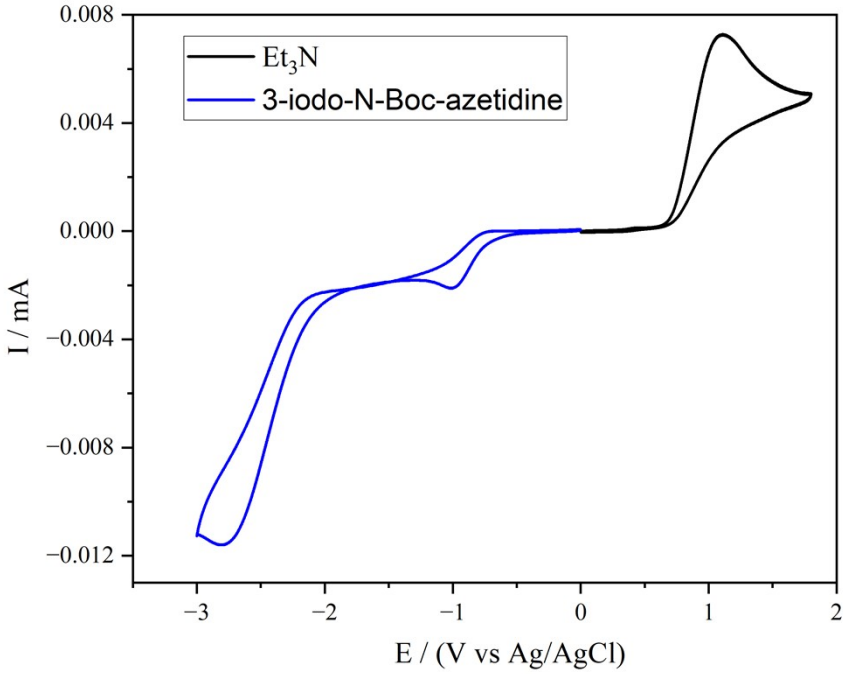
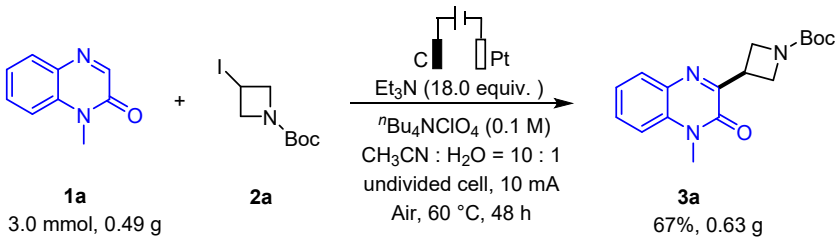


Figure S4. Cyclic voltammograms of alkyl iodides (0.1 mmol) and Et_3N (0.1 mmol).

5.3 Scale-up experiment



1a
3.0 mmol, 0.49 g

2a

3a
67%, 0.63 g

Quinoxalin-2(1H)-one compounds **1a** (3 mmol, 1.0 equiv. 0.49 g), alkyl iodide **2** (9 mmol, 3.0 equiv.), additive (Et_3N, 18.0 equiv.), solvent (CH_3CN: H_2O = 10: 1, 23.1 mL), and electrolyte ($^nBu_4NClO_4$, 2.1 mmol) were added to a dried 100 mL reaction vial (**Figure S5)**. Then, the graphite electrode and platinum plates electrode (**Figure S5**, 15*15*0.2 mm) were immerged into the solution, as anode and cathode respectively. The electrodes were connected to a constant current power supply, and the current was set as 10 mA. The reaction mixture was stirred at 60 ℃ for 48 hours under air conditions After the reaction, the mixture was concentrated and the crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate as the eluent to obtain the target product.

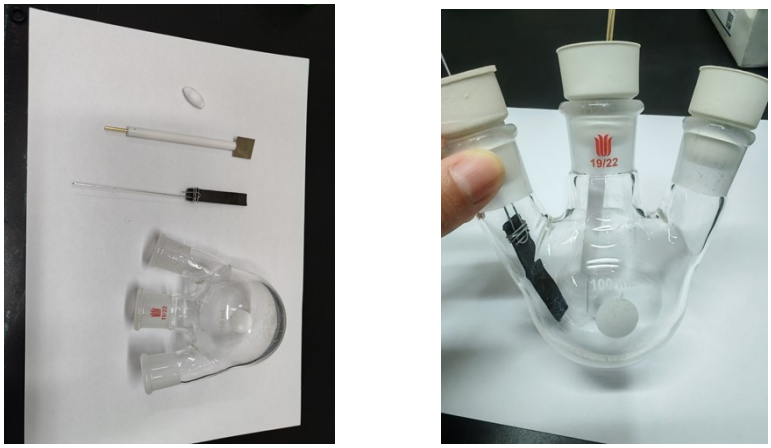
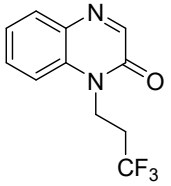


Figure S5. Electrocatalytic equipment.

6. Characterization data.

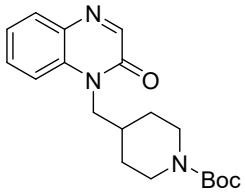
6.1 Characterization data of raw materials

(1o) 1-(3,3,3-Trifluoropropyl)quinoxalin-2(1H)-one



White solid; Mp (℃): 95.7 - 98.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.92 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.45 – 7.37 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 4.59 – 4.42 (m, 2H), 2.73 – 2.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 150.0, 133.7, 131.8, 131.5, 131.2, 127.0, 124.2, 112.8, 35.4 (q, *J* = 3.9 Hz), 31.3 (q, *J* = 29.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.43; IR (KBr, cm^{-1}) 2927, 1695, 1500, 1465, 1340, 1276, 1172, 1020, 997, 923, 862, 732, 615, 549; HRMS (ESI)m/z calcd for $C_{11}H_9F_3N_2O$ $[M+H]^+$ 243.0740, found 243.0736.

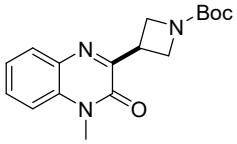
(1q) Tert-butyl 4-((2-oxoquinoxalin-1(2H)-yl)methyl)piperidine-1-carboxylate



White solid; Mp (℃): 103.9 - 105.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.01 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.82 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.59 – 7.53 (m, 1H), 4.34 (d, *J* = 6.4 Hz, 2H), 4.17 (s, 2H), 2.77 (t, *J* = 12.5 Hz, 2H), 2.10 – 2.00 (m, 1H), 1.86 (d, *J* = 12.8 Hz, 2H), 1.47 (s, 9H), 1.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 154.9, 140.3, 139.6, 138.9, 130.2, 129.0, 127.1, 126.6, 79.5, 70.5, 35.8, 28.5; IR (KBr, cm^{-1}) 2920, 1656, 1558, 1465, 1375, 1340, 1259, 1139, 1074, 1035, 937, 866, 783, 692, 536; HRMS (ESI) m/z calcd for $C_{19}H_{25}N_3O_3$ $[M+H]^+$ 344.1969, found 344.1962.

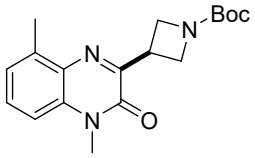
6.2 Characterization data of products

(3a) Tert-butyl 3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)azetidine-1-carboxylate



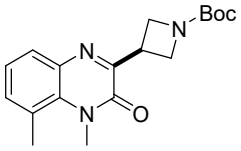
Following the General Procedure A with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3a** was obtained as yellow solid (56.5 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.41 – 7.32 (m, 2H), 4.31 (d, *J* = 7.6 Hz, 4H), 4.23 – 4.15 (m, 1H), 3.70 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 156.5, 154.4, 133.1, 132.6, 130.3, 130.2, 123.9, 113.7, 79.4, 52.3, 32.0, 29.0, 28.4.
The spectroscopic data match with the previously reported data[1].

(3b) Tert-butyl 3-(4,8-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)azetidine-1-carboxylate



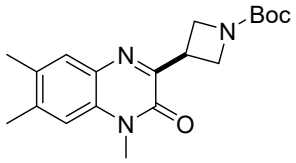
Following the General Procedure B with 1,5-dimethylquinoxalin-2(1H)-one (34.8 mg, 0.3 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3b** was obtained as white solid (46.3 mg, 70%); Mp (℃): 134.5 - 139.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.31 (d, *J* = 7.6 Hz, 4H), 4.23 – 4.15 (m, 1H), 3.69 (s, 3H), 2.71 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 156.5, 154.3, 139.1, 133.2, 131.0, 130.0, 125.2, 111.6, 79.4, 53.7, 32.3, 29.1, 28.4, 17.5; IR (KBr, cm^{-1}) 2933, 1704, 1654, 1598, 1479, 1349, 1251, 1170, 1060, 1004, 996, 889, 779, 648, 572; HRMS (APCI) m/z calcd for $C_{18}H_{23}N_3O_3$ $[M+e]^-$ 329.1745, found 329.1741.

(**3c**) **Tert-butyl 3-(4,5-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)azetidine-1-carboxylate**



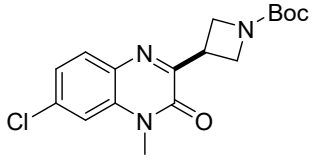
Following the General Procedure B with 1,8-dimethylquinoxalin-2(1H)-one (34.8 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3c** was obtained as white solid (47.8 mg, 73%); Mp (℃): 100.4 - 105.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 - 7.43 (m, 2H), 4.41 – 4.37 (m, 2H), 4.31 (t, *J* = 8.6 Hz, 2H), 4.18 – 4.10 (m, 1H), 4.09 (s, 3H), 2.68 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 155.0, 147.8, 138.8, 138.3, 135.2, 129.7, 126.3, 126.2, 79.4, 53.6, 52.6, 31.2, 28.5, 17.0; IR (KBr, cm^{-1}) 2962, 1706, 1610, 1585, 1448, 1396, 1215, 1159, 1014, 904, 852, 783, 636; HRMS (APCI) m/z calcd for $C_{18}H_{23}N_3O_3$ $[M-H]^-$ 328.1667, found 328.1663.

(**3d**) **Tert-butyl 3-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine -1-carboxylate**



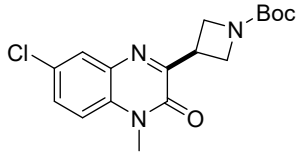
Following the General Procedure A with 1,6,7-trimethylquinoxalin-2(1H)-one (37.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3d** was obtained as white solid (59.3 mg, 86%); Mp (℃): 151.3 - 156.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.07 (s, 1H), 4.28 (d, *J* = 8.0 Hz, 4H), 4.17 – 4.13 (m, 1H), 3.65 (s, 3H), 2.41 (s, 3H), 2.35 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 156.5, 154.5, 140.1, 132.8, 131.0, 131.0, 130.2, 114.2, 79.4, 52.6, 31.9, 28.9, 28.4, 20.6, 19.2; IR (KBr, cm^{-1}) 2981, 1697, 1467, 1394, 1163, 1020, 1004, 943, 857, 777, 649, 580; HRMS (APCI) m/z calcd for $C_{19}H_{25}N_3O_3$ $[M-H]^-$ 342.1823, found 342.1819.

(**3e**) **Tert-butyl 3-(6-chloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate**



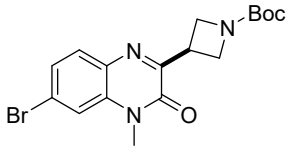
Following the General Procedure B with 7-chloro-1-methylquinoxalin-2(1H)-one (38.8 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3e** was obtained as yellow solid (39.5 mg, 57%); Mp (℃): 166.9 - 171.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.29 (m, 2H), 4.33 – 4.22 (m, 4H), 4.21 – 4.11 (m, 1H), 3.65 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 156.5, 154.1, 136.2, 134.0, 131.2, 131.0, 124.3, 113.8, 79.5, 52.7, 32.0, 29.1, 28.4; IR (KBr, cm^{-1}) 3107, 3082, 2956, 1685, 1598, 1471, 1392, 1294, 1251, 1159, 968, 881, 786, 688, 561; HRMS (APCI) m/z calcd for $C_{17}H_{20}ClN_3O_3$ $[M+e]^-$ 349.1199, found 349.1195.

(**3f**) **Tert-butyl 3-(7-chloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate**



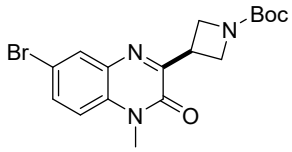
Following the General Procedure B with 6-chloro-1-methylquinoxalin-2(1H)-one (38.8 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3f** was obtained as white solid (29.6 mg, 42%); Mp (℃): 188.0 - 192.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 4.32 – 4.24 (m, 4H), 4.22 – 4.14 (m, 1H), 3.68 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 156.5, 154.0, 133.0, 131.8, 130.3, 129.5, 129.2, 114.8, 79.5, 52.2, 32.1, 29.2, 28.4; IR (KBr, cm^{-1}) 2931, 1695, 1585, 1461, 1355, 1255, 1163, 912, 869,779, 588; HRMS (APCI) m/z calcd for $C_{17}H_{20}ClN_3O_3$ $[M+e]^-$ 349.1199, found 349.1195.

(**3g**) **Tert-butyl 3-(6-bromo-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate**



Following the General Procedure B with 7-bromo-1-methylquinoxalin-2(1H)-one (47.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3g** was obtained as yellow solid (31.1 mg, 40%); Mp (℃): 150.6 - 155.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.49 – 7.46 (m, 2H), 4.33 – 4.22 (m, 4H), 4.19 – 4.11 (m, 1H), 3.66 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 156.5, 154.0, 134.1, 131.3, 127.2, 124.3, 116.8, 79.5, 52.6, 32.0, 29.1, 28.4; IR (KBr, cm^{-1}) 3095, 3079, 2972, 1697, 1650, 1593, 1471, 1392, 1352, 1259, 1163, 966, 881, 784, 669, 590; HRMS (APCI) m/z calcd for $C_{17}H_{20}BrN_3O_3$ $[M+e]^-$ 393.0694, found 393.0688.

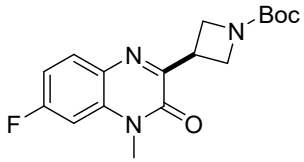
(**3h**) **Tert-butyl 3-(7-bromo-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate**



Following the General Procedure B with 6-bromo-1-methylquinoxalin-2(1H)-one (47.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3h** was obtained as white solid (31.8 mg, 40%); Mp (℃): 203.8 - 208.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.4 Hz, 1H), 7.65 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.20 (d, *J* = 9.2 Hz, 1H), 4.33 – 4.23 (m, 4H), 4.21– 4.16 (m, 1H), 3.67 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 156.5, 154.0, 133.3, 133.0, 132.5, 132.2, 116.5, 115.1, 79.5, 52.5, 32.1, 29.1, 28.4; IR (KBr, cm^{-1}) 2954, 2920, 1691, 1649, 1598, 1463, 1355, 1242, 1172, 869,

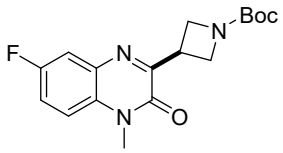
775, 568; HRMS (APCI) m/z calcd for $C_{17}H_{20}BrN_3O_3$ [M+e]$^-$ 393.0694, found 393.0690.

(**3i**) **Tert-butyl 3-(6-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate**



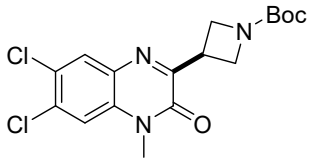
Following the General Procedure A with 7-fluoro-1-methylquinoxalin-2(1H)-one (35.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3i** was obtained as white solid (22.7 mg, 34%); Mp (℃): 145.4 - 150.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 1H), 7.12 – 7.05 (m, 1H), 7.00 (dd, *J* = 10.0, 2.8 Hz, 1H), 4.36 – 4.21 (m, 4H), 4.20 – 4.11 (m, 1H), 3.65 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 251.9 Hz), 157.2 (d, *J* = 3.4 Hz), 156.5, 154.3, 134.5 (d, *J* = 11.6 Hz), 132.1 (d, *J* = 10.5 Hz), 129.3 (d, *J* = 2.2 Hz), 111.7 (d, *J* = 23.5 Hz), 100.7 (d, *J* = 28.0 Hz), 79.4, 52.1, 31.9, 29.2, 28.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.05; IR (KBr, cm^{-1}) 3080, 2966, 2921, 1691, 1656, 1454, 1394, 1228, 1172, 987, 875, 784, 638, 563; HRMS（APCI）m/z calcd for $C_{17}H_{20}FN_3O_3$ [M+e]$^-$ 333.1494, found 333.1490.

(**3j**) **Tert-butyl 3-(7-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate**



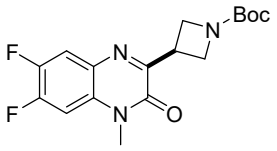
Following the General Procedure B with 6-fluoro-1-methylquinoxalin-2(1H)-one (35.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3j** was obtained as yellow solid (30.6 mg, 46%); Mp (℃): 146.0 - 151.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.35 – 7.27 (m, 2H), 4.33 – 4.25 (m, 4H), 4.23 – 4.15 (m, 1H), 3.69 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 157.6, 156.5, 154.0, 133.1 (d, *J* = 11.4 Hz), 129.7 (d, *J* = 2.1 Hz), 118.0 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 22.5 Hz), 114.8 (d, *J* = 8.9 Hz), 79.5, 52.4, 32.1, 29.3, 28.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.58; IR (KBr, cm^{-1}) 3091, 2981, 1701, 1600, 1502, 1461, 1386, 1272, 1122, 952, 862, 784, 613, 541; HRMS (APCI) m/z calcd for $C_{17}H_{20}FN_3O_3$ [M+e]$^-$ 333.1494, found 333.1489.

(**3k**) **Tert-butyl 3-(6,7-dichloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate**



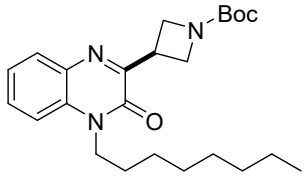
Following the General Procedure B with 6,7-dichloro-1-methylquinoxalin-2(1H)-one (45.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3k** was obtained as white solid (30.5 mg, 40%); Mp (℃): 184.9 - 189.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.41 (s, 1H), 4.33 – 4.22 (m, 4H), 4.21 – 4.14 (m, 1H), 3.65 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 156.4, 153.8, 134.4, 132.5, 131.6, 130.9, 127.7, 115.2, 79.6, 52.2, 32.1, 29.3, 28.4; IR (KBr, cm^{-1}) 2914, 1695, 1656, 1595, 1467, 1163, 1128, 973, 877, 779, 690, 572; HRMS (APCI) m/z calcd for $C_{17}H_{19}Cl_2N_3O_3$ [M+e]$^-$ 383.0809, found 383.0804.

(3l) Tert-butyl 3-(6,7-difluoro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate



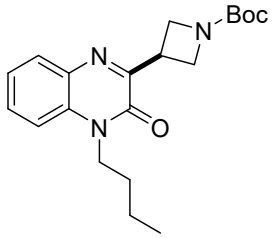
Following the General Procedure A with 6,7-difluoro-1-methylquinoxalin-2(1H)-one (39.1 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3l** was obtained as white solid (40.2 mg, 57%); Mp (℃): 180.3 - 185.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 10.0, 8.2 Hz, 1H), 7.12 (dd, *J* = 11.2, 7.2 Hz, 1H), 4.33 – 4.22 (m, 4H), 4.20 – 4.12 (m, 1H), 3.65 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (d, *J* = 3.4 Hz), 156.5, 153.9, 151.5 (q, *J* = 254.7 Hz), 146.8 (q, *J* = 248.5 Hz), 130.3 (dd, *J* = 8.9, 1.9 Hz), 128.8 (dd, *J* = 9.2, 3.0 Hz), 117.8 (dd, *J* = 18.2, 2.2 Hz), 102.4 (d, *J* = 23.2 Hz), 79.5, 52.4, 32.0, 29.5, 28.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.43 (d, *J* = 22.6 Hz), -141.60 (d, *J* = 14.7 Hz); IR (KBr, cm^{-1}) 3072, 2931, 1685, 1608, 1519, 1463, 1396, 1317, 1278, 1161, 1130, 950, 877, 775, 651, 572; HRMS (APCI) m/z calcd for $C_{17}H_{19}F_2N_3O_3$ $[M+e]^-$ 351.1400, found 351.1395.

(3m) Tert-butyl 3-(4-octyl-3-oxo-3,4-dihydroquinoxalin-2-yl)azetidine-1- carboxylate



Following the General Procedure A with 1-octylquinoxalin-2(1H)-one (51.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3m** was obtained as yellow liquid (49.7 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.39 – 7.27 (m, 2H), 4.30 (d, *J* = 7.6 Hz, 4H), 4.24 – 4.14 (m, 3H), 1.76 – 1.70 (m, 2H), 1.44 (s, 11H), 1.37 – 1.20 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 156.5, 154.1, 132.8, 132.3, 130.4, 130.2, 123.6, 113.7, 79.4, 53.3, 42.3, 32.0, 31.8, 29.2, 29.1, 28.4, 27.3, 27.0, 22.6, 14.1; IR (KBr, cm^{-1}) 2933, 2860, 1708, 1649, 1606, 1463, 1411, 1363, 1245, 1170, 1136, 1041, 950, 865, 761, 636, 568; HRMS (APCI) m/z calcd for $C_{24}H_{35}N_3O_3$ $[M+e]^-$ 413.2684, found 413.2678.

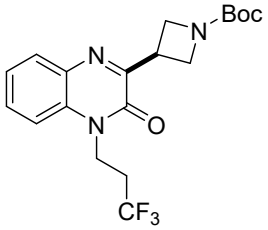
(3n) Tert-butyl 3-(4-butyl-3-oxo-3,4-dihydroquinoxalin-2-yl)azetidine- 1-carboxylate



Following the General Procedure A with 1-butylquinoxalin-2(1H)-one (40.4 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3n** was obtained as yellow liquid (46.3 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.38 – 7.32 (m, 2H), 4.31 (d, *J* = 7.6 Hz, 4H), 4.26 – 4.18 (m, 3H), 1.76 – 1.69 (m, 2H), 1.45 (s, 9H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.86 (dd, *J* = 12.0, 5.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 156.5, 154.1, 132.8, 132.3,

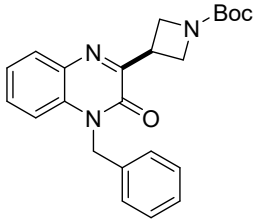
130.4, 130.2, 123.6, 113.7, 79.4, 52.7, 42.1, 32.0, 29.4, 28.4, 20.3, 13.8; IR (KBr, cm^{-1}) 2964, 2925, 1695, 1600, 1460, 1396, 1369, 1174, 1037, 941, 858, 759, 638, 565; HRMS (APCI) m/z calcd for $C_{20}H_{27}N_3O_3$ $[M+e]^-$ 357.2058, found 357.2054.

(3o) Tert-butyl 3-(3-oxo-4-(3,3,3-trifluoropropyl)-3,4-dihydroquinoxalin-2-yl) azetidine-1-carboxylate



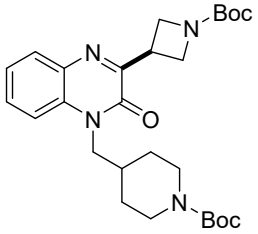
Following the General Procedure A with 1-(3,3,3-trifluoropropyl)quinoxalin-2(1H)-one (48.4 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3o** was obtained as yellow liquid (32.6 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 – 7.53 (m, 1H), 7.44 – 7.37 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 4.53 – 4.46 (m, 2H), 4.30 (d, *J* = 8.4 Hz, 4H), 4.23 – 4.13 (m, 1H), 2.66 – 2.51 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 156.5, 153.9, 132.8, 131.6, 130.8, 130.7, 124.3, 112.7, 79.5, 52.2, 35.7 (q, *J* = 3.9 Hz), 31.8, 31.5, 31.2, 28.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.48; IR (KBr, cm^{-1}) 2972, 1708, 1652, 1602, 1465, 1400, 1369, 1257, 1168, 1010, 956, 864, 759, 565; HRMS (APCI) m/z calcd for $C_{19}H_{22}F_3N_3O_3$ $[M+e]^-$ 397.1619, found 397.1612.

(3p) Tert-butyl 3-(4-benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1 -carboxylate



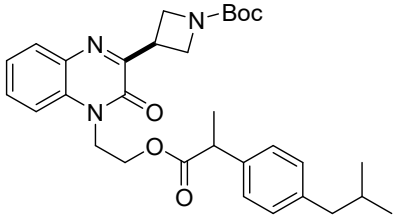
Following the General Procedure A with 1-benzylquinoxalin-2(1H)-one (47.2 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3p** was obtained as yellow solid (57.1 mg, 73%); Mp (℃): 124.8 - 129.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.36 – 7.19 (m, 7H), 5.48 (s, 2H), 4.35 (d, *J* = 7.2 Hz, 4H), 4.28 – 4.21 (m, 1H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 156.5, 154.5, 135.1, 132.8, 132.4, 130.3, 129.0, 127.8, 126.9, 123.9, 114.5, 79.4, 52.3, 45.8, 32.0, 28.5; IR (KBr, cm^{-1}) 2916, 1704, 1658, 1606, 1467, 1369, 1166, 1029, 919, 854, 752, 649, 557; HRMS (APCI) m/z calcd for $C_{23}H_{25}N_3O_3$ $[M-H]^-$ 390.1823, found 390.1818.

(3q) Tert-butyl 4-((3-(1-(tert-butoxycarbonyl) azetidin-3-yl)-2-oxoquinoxalin -1(2H)-yl) methyl) piperidine-1-carboxylate



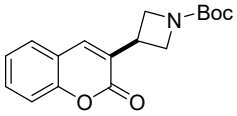
Following the General Procedure A with tert-butyl 4-((2-oxoquinoxalin-1(2H)-yl)methyl) piperidine-1-carboxylate (68.6 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3q** was obtained as white solid (50.9 mg, 51%); Mp (℃): 120.7 - 125.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.79 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.57 – 7.53 (m, 1H), 4.40 – 4.28 (m, 6H), 4.23 – 4.08 (m, 3H), 2.76 (t, *J* = 12.0 Hz, 2H), 2.07 – 1.96 (m, 1H), 1.86 – 1.72 (m, 3H), 1.47 (s, 9H), 1.45 (s, 9H), 1.38 – 1.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 155.5, 154.9, 148.4, 139.9, 138.3, 129.6, 128.7, 126.7, 126.7, 79.6, 79.5, 70.7, 60.4, 52.3, 35.8, 31.3, 28.5, 28.4; IR (KBr, cm^{-1}) 2979, 1706, 1587, 1417, 1361, 1323, 1226, 1172, 1020, 989, 871, 769, 605, 559; HRMS (APCI) m/z calcd for $C_{27}H_{38}N_4O_5$ $[M-H]^-$ 497.2769, found 497.2763.

(3r) Tert-butyl 3-(4-(2-((2-(4-isobutylphenyl) propanoyl) oxy) ethyl)-3-oxo-3,4 -dihydroquinoxalin-2-yl) azetidine-1-carboxylate



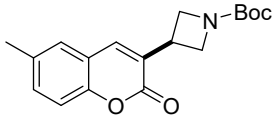
Following the General Procedure A with 2-(2-oxoquinoxalin-1(2H)-yl)ethyl 2-(4-isobutylphenyl) propanoate (42.0 mg, 0.1 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (85.0 mg, 0.3 mmol), **3r** was obtained as white solid (48.9 mg, 92%); Mp (℃): 70.3 - 74.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51 – 6.99 (m, 1H), 7.41 – 7.32 (m, 2H), 7.10 – 6.99 (m, 4H), 4.56 – 4.48 (m, 1H), 4.46 – 4.34 (m, 3H), 4.30 – 4.29 (m, 4H), 4.19 – 4.14 (m, 1H), 3.56 (q, *J* = 7.2 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.86 – 1.79 (m, 1H), 1.45 (s, 9H), 1.39 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 158.2, 156.5, 154.2, 140.7, 137.1, 132.7, 132.6, 130.4, 130.3, 129.4, 127.0, 123.9, 113.8, 79.4, 61.0, 52.7, 45.1, 45.0, 40.9, 31.8, 30.2, 28.4, 22.4, 18.4; IR (KBr, cm^{-1}) 2956, 2921, 1741, 1699, 1606, 1465, 1367, 1336, 1161, 1028, 864, 759, 638, 561; HRMS (APCI) m/z calcd for $C_{31}H_{39}N_3O_5$ $[M+e]^-$ 533.2895, found 533.2888.

(3s) Tert-butyl 3-(2-oxo-2H-chromen-3-yl) azetidine-1-carboxylate



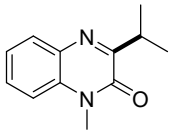
Following the General Procedure B with 2H-chromen-2-one (29.2 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3s** was obtained as white solid (13.5 mg, 22%); Mp (℃): 121.8 - 125.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 0.8 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 4.31 (t, *J* = 8.6 Hz, 2H), 4.02 – 3.99 (m, 2H), 3.91 – 3.78 (m, 1H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 156.4, 153.1, 137.7, 131.4, 129.0, 127.7, 124.6, 119.0, 116.6, 79.8, 53.6, 29.3, 28.4; IR (KBr, cm^{-1}) 3076, 2970, 1685, 1608, 1454, 1367, 1278, 1163, 1089, 943, 856, 777, 626, 567; HRMS (ESI) m/z calcd for $C_{17}H_{19}NO_4$ $[M+H]^+$ 302.1387, found 302.1392.

(3t) Tert-butyl 3-(6-methyl-2-oxo-2H-chromen-3-yl) azetidine-1-carboxylate



Following the General Procedure B with 6-methyl-2H-chromen-2-one (32.0 mg, 0.2 mmol), tert-butyl 3-iodoazetidine-1-carboxylate (169.9 mg, 0.6 mmol), **3t** was obtained as white solid (12.8 mg, 20%); Mp (°C): 107.3 - 110,3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.34 – 7.27 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 4.31 (t, *J* = 8.6 Hz, 2H), 3.99 (br, 2H), 3.89 – 3.78 (m, 1H), 2.41 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 156.4, 151.2, 137.7, 134.3, 132.4, 128.8, 127.5, 118.70, 116.3, 79.8, 53.0, 29.3, 28.4, 20.8; IR (KBr, cm^{-1}) 2974, 1720, 1697, 1583, 1492, 1369, 1230, 1191, 1137, 948, 815, 779, 572; HRMS (ESI) m/z calcd for $C_{18}H_{21}NO_4$ $[M+H]^+$ 316.1543, found 316.1542.

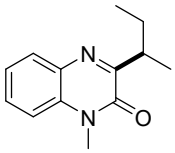
(4a) 3-isopropyl-1-methylquinoxalin-2(1H)-one



Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), 2-iodopropane (102.0 mg, 0.6 mmol), **4a** was obtained as white solid (19 mg, 47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.38 – 7.26 (m, 2H), 3.70 (s, 3H), 3.66 – 3.59 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 154.5, 133.0, 132.8, 129.8, 129.4, 123.4, 113.5, 31.2, 29.0, 20.2.

The spectroscopic data match with the previously reported data[2].

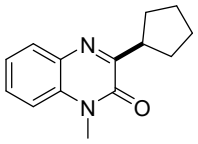
(4b) 3-(sec-butyl)-1-methylquinoxalin-2(1H)-one



Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), 2-iodobutane (110.4 mg, 0.6 mmol), **4b** was obtained as white solid (23.1 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.36 – 7.27 (m, 2H), 3.70 (s, 3H), 3.53 – 3.41 (m, 1H), 1.99 – 1.87 (m, 1H), 1.66 – 1.55 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 154.7, 132.9, 132.8, 129.8, 129.4, 123.4, 113.5, 37.8, 29.1, 27.6, 17.9, 12.1.

The spectroscopic data match with the previously reported data[1].

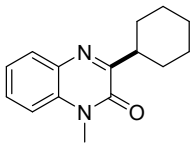
(4c) 3-cyclopentyl-1-methylquinoxalin-2(1H)-one



Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), iodocyclopentane (117.6 mg, 0.6 mmol), **4c** was obtained as yellow solid (20.1 mg, 44%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.35 – 7.25 (m, 2H), 3.76 – 3.71 (m, 1H), 3.70 (s, 3H), 2.10 – 2.02 (m, 2H), 1.97 – 1.88 (m, 2H), 1.87 – 1.78 (m, 2H), 1.75 – 1.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 155.0, 133.0, 132.7, 129.8, 129.3, 123.4, 113.4, 42.73, 30.9, 29.0, 25.9.

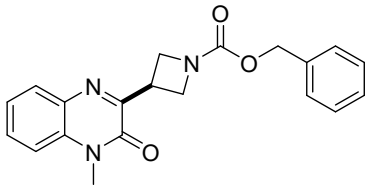
The spectroscopic data match with the previously reported data[1].

(4d) 3-cyclohexyl-1-methylquinoxalin-2(1H)-one



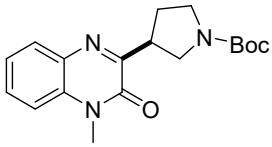
Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), iodocyclohexane (126.0 mg, 0.6 mmol), **4d** was obtained as yellow solid (27.2 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 – 7.45 (m, 1H), 7.35 – 7.26 (m, 2H), 3.69 (s, 3H), 3.38 – 3.30 (m, 1H), 2.00 – 1.91 (m, 2H), 1.91 – 1.82 (m, 2H), 1.81 – 1.72 (m, 1H), 1.62 – 1.40 (m, 4H), 1.37 – 1.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 154.6, 132.9, 132.9, 129.8, 129.4, 123.4, 113.5, 40.8, 30.5, 29.1, 26.3, 26.2.
The spectroscopic data match with the previously reported data[1].

(4e) Benzyl 3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) azetidine-1 -carboxylate



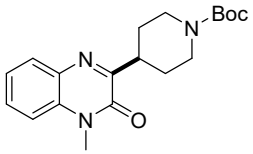
Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), benzyl 3-iodoazetidine-1-carboxylate (190.3 mg, 0.6 mmol), **4e** was obtained as yellow solid (46.4 mg, 66%); Mp (°C): 98.0 - 102.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.40 – 7.30 (m, 7H), 5.12 (s, 2H), 4.40 (d, *J* = 7.6 Hz, 4H), 4.28 – 4.22 (m, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.6, 154.4, 136.8, 133.1, 132.5, 130.4, 130.2, 128.5, 128.0, 127.9, 123.9, 113.7, 66.6, 61.8, 32.3, 29.0; IR (KBr, cm^{-1}) 3483, 2962, 2894, 1685, 1598, 1434, 1355, 1190, 1026, 950, 757, 605, 540; HRMS (APCI) m/z calcd for $C_{20}H_{19}N_3O_3$ $[M+e]^-$ 349.1432, found 349.1426.

(4f) Tert-butyl-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) pyrrolidine-1- carboxylate



Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), tert-butyl 3-iodopyrrolidine-1-carboxylate (178.3 mg, 0.6 mmol), **4f** was obtained as white solid (37.4 mg, 57%); Mp (°C): 148.9 - 153.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 6.6 Hz, 1H), 7.60 – 7.48 (m, 1H), 7.36 – 7.30 (m, 2H), 4.00 (p, *J* = 7.6 Hz, 1H), 3.79 (d, *J* = 7.4 Hz, 1H), 3.71 (s, 3H), 3.69 – 3.50 (m, 2H), 3.50 – 3.39 (m, 1H), 2.41 – 2.13 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 154.7, 133.1, 132.5, 130.1, 130.0, 123.7, 123.6, 113.6, 79.1, 49.3, 48.9, 45.5, 41.5, 29.1, 28.6; IR (KBr, cm^{-1}) 2954, 2891, 1699, 1602, 1477, 1396, 1253, 1168, 1060, 945, 879, 771, 692, 526; HRMS (APCI) m/z calcd for $C_{18}H_{23}N_3O_3$ $(M-H)^-$ 328.1667, found 328.1664.

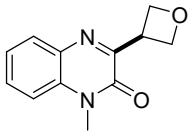
(4g) Tert-butyl 4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)piperidine-1- carboxylate



Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), tert-butyl 4-iodopiperidine-1-carboxylate (186.7 mg, 0.6 mmol), **4g** was obtained as yellow solid (23.7 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.36 – 7.29 (m, 2H), 4.24 (s, 2H), 3.70 (s, 3H), 3.51 – 3.43 (m, 1H), 2.91 (t, *J* = 10.0 Hz, 2H), 1.93 (d, *J* = 12.0 Hz, 2H), 1.76 (dd, *J* = 12.4, 4.0 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 154.8, 154.4, 132.9, 132.8, 130.0, 129.8, 123.6, 113.6, 79.3, 43.6, 39.0, 29.4, 29.1, 28.5.

The spectroscopic data match with the previously reported data[1].

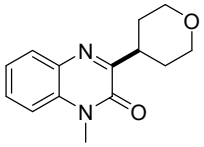
(4h) 1-methyl-3-(oxetan-3-yl) quinoxalin-2(1H)-one



Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), 3-iodooxetane (110.4 mg, 0.6 mmol), **4h** was obtained as yellow solid (29.8 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.43 – 7.29 (m, 2H), 5.11 – 5.01 (m, 4H), 4.71 – 4.64 (m, 1H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 154.4, 133.1, 132.7, 130.2, 130.1, 123.9, 113.7, 74.5, 38.3, 29.0.

The spectroscopic data match with the previously reported data[3].

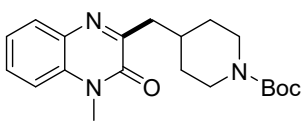
(4i) 1-methyl-3-(tetrahydro-2H-pyran-4-yl) quinoxalin-2(1H)-one



Following the General Procedure C with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), 4-iodotetrahydro-2H-pyran (127.2 mg, 0.6 mmol), **4i** was obtained as white solid (22.5 mg, 46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.40 – 7.27 (m, 2H), 4.12 – 4.08 (m, 2H), 3.70 (s, 3H), 3.65 – 3.59 (m, 2H), 3.57 – 3.52 (m, 1H), 2.02 – 1.85 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 154.5, 132.9, 132.8, 130.0, 129.8, 123.6, 113.5, 67.9, 38.1, 30.1, 29.1.

The spectroscopic data match with the previously reported data[1].

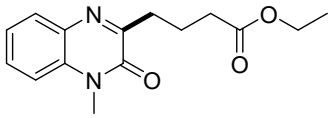
(4j) Tert-butyl 4-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)piperidine-1-carboxylate



Following the General Procedure D with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), tert-butyl 4-(iodomethyl)piperidine-1-carboxylate (195.1 mg, 0.6 mmol), **4j** was obtained as transparency liquid (36.1 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.39 – 7.27 (m, 2H), 4.12 – 4.06 (m, 2H), 3.69 (s, 3H), 2.88 (d, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 12.0 Hz, 2H), 2.22 – 2.11 (m, 2H), 1.71 (d, *J* = 12.4 Hz, 2H), 1.44 (s, 9H), 1.35 – 1.21 (m, 2H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 159.6, 155.0, 154.9, 133.1, 132.6, 129.8, 129.8, 123.6, 113.6, 79.2, 40.7, 34.3, 32.2, 29.1, 28.5; IR (KBr, cm^{-1}) 2931, 2248, 1658, 1415, 1245, 1164, 927, 757, 644; HRMS（ESI） m/z calcd for $C_{20}H_{28}N_3O_3$ $(M+H)^+$ 358.2125, found 358.2119.

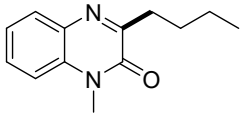
(4k) Ethyl 4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanoate



Following the General Procedure D with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), ethyl 4-iodobutanoate (242.1 mg, 1.0 mmol), **4k** was obtained as white solid (25.1 mg, 46%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 – 7.47 (m, 1H), 7.36 – 7.27 (m, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.69 (s, 3H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.15 (t, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 160.0, 154.9, 133.1, 132.7, 129.7, 129.7, 123.6, 113.6, 60.3, 33.9, 33.2, 29.0, 21.6, 14.2.

The spectroscopic data match with the previously reported data[3].

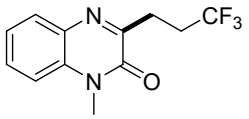
(4l) 3-butyl-1-methylquinoxalin-2(1H)-one



Following the General Procedure D with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), 1-iodobutane (110.4 mg, 0.6 mmol), **4l** was obtained as white solid (6.5 mg, 15%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 – 7.47 (m, 1H), 7.37 – 7.27 (m, 2H), 3.70 (s, 3H), 2.98 – 2.91 (m, 2H), 1.82 – 1.71 (m, 2H), 1.54 – 1.41 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 155.0, 133.1, 132.8, 129.6, 129.5, 123.5, 113.6, 34.1, 29.0, 29.0, 22.8, 14.0.

The spectroscopic data match with the previously reported data[2].

(4m) 1-methyl-3-(3,3,3-trifluoropropyl)quinoxalin-2(1H)-one



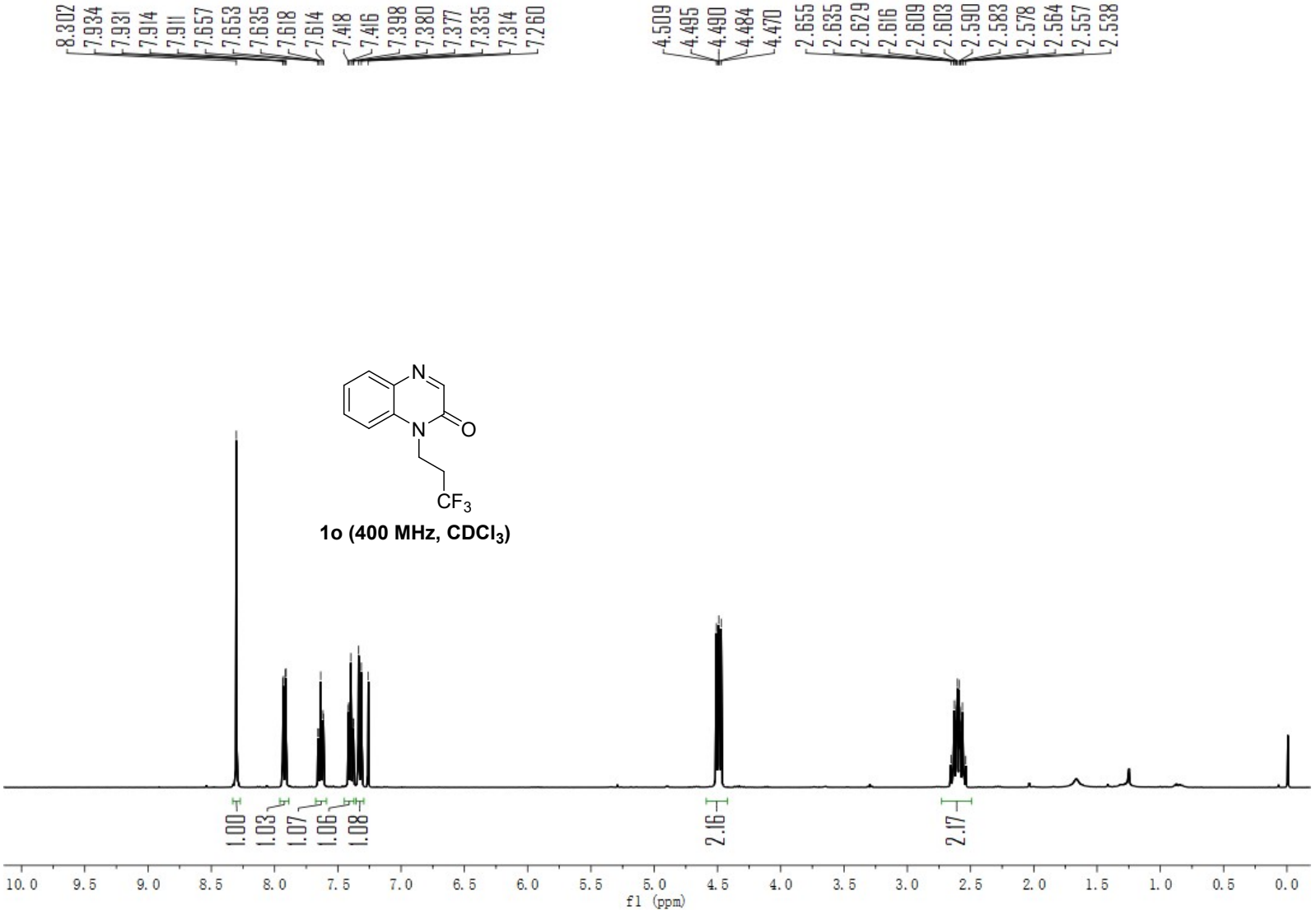
Following the General Procedure D with 1-methylquinoxalin-2(1H)-one (32.4 mg, 0.2 mmol), 1,1,1-trifluoro-3-iodopropane (134.4 mg, 0.6 mmol), **4m** was obtained as white solid (8.5 mg, 17%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.42 – 7.29 (m, 2H), 3.71 (s, 3H), 3.24 – 7.20 (m, 2H), 2.81 – 2.61 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 154.6, 133.1, 132.5, 130.1, 129.9, 127.2 (q, *J* = 276.2 Hz), 123.7, 113.7, 30.2 (q, *J* = 29.6 Hz), 29.0, 26.6 (q, *J* = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3.

The spectroscopic data match with the previously reported data[4].

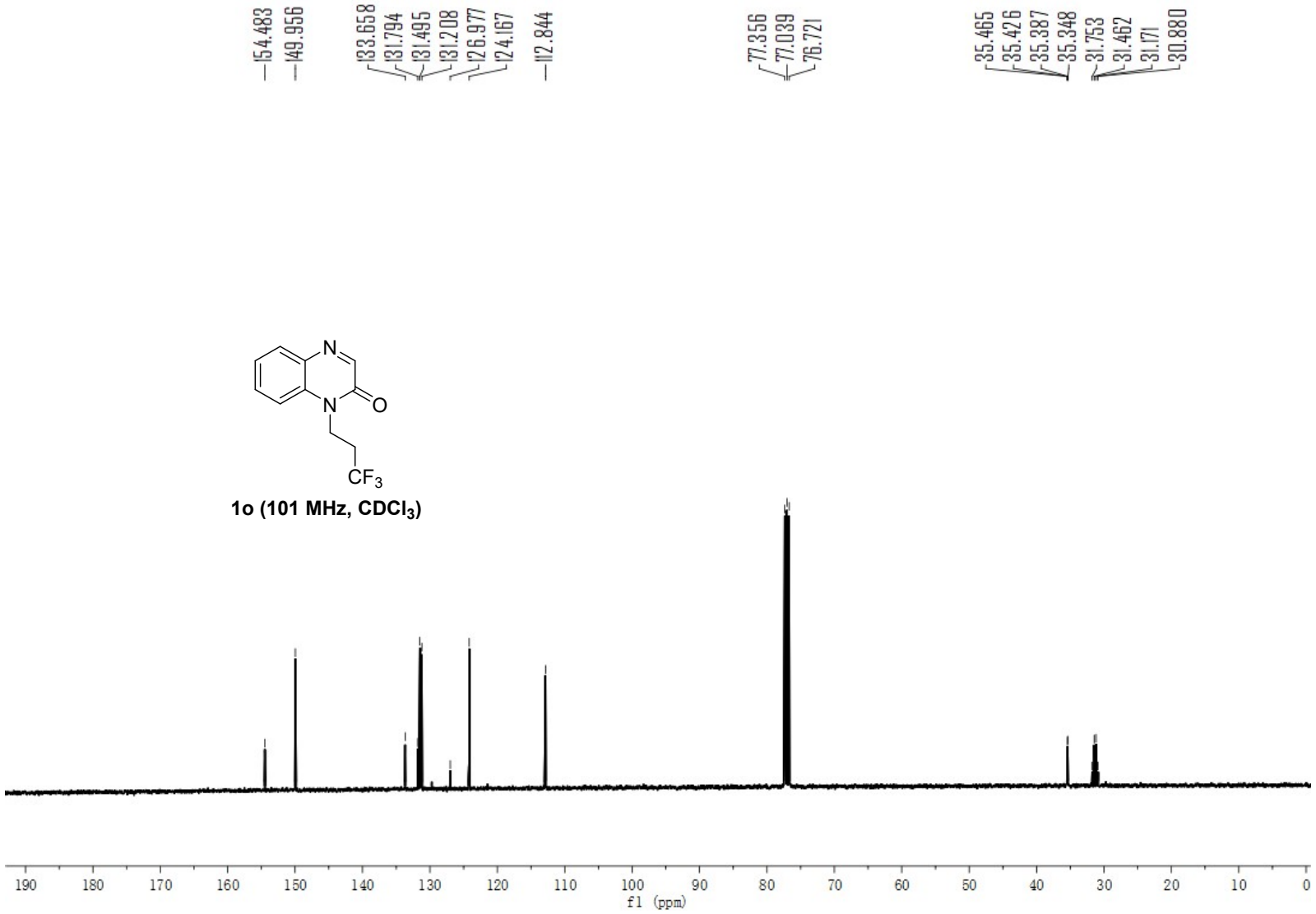
7. References

1. J. Xu, C. F. Liang, J. B. Shen, Q. Chen, W. M. Li and P. F. Zhang, Photoinduced, metal- and photosensitizer-free decarboxylative C-H (amino)alkylation of heteroarenes in a sustainable solvent. *Green Chem*., 2023, **25**, 1975-1981.
2. L. L. Wang, P. Y. Yang, J. W. Yuan, W. Lian, S. Y. Zhang, L. R. Yang and D. L. Xing, Visible-Light-Promoted Deoxygenative Alkylation of Quinoxalin-2(1H)-ones with Activated Alcohols. *J. Org. Chem*., 2024, **89**, 6334-6344.
3. J. Sun, H. Yang and B. Zhang, Metal-free visible-light-initiated direct C3 alkylation of quinoxalin-2(1H)-ones and coumarins with unactivated alkyl iodides. *Green Chem*., 2022, **24**, 858-863.
4. F. K. Cheng, L. L. Fan, Q. Y. Lv, X. L. Chen and B. Yu, Alkyl radicals from diacyl peroxides: Metal-/base-/additive-free photocatalytic alkylation of N-heteroaromatics. *Green Chem*., 2023, **25**, 7971-7977.

8. Copies of NMR spectra



1o (400 MHz, $CDCl_3$)



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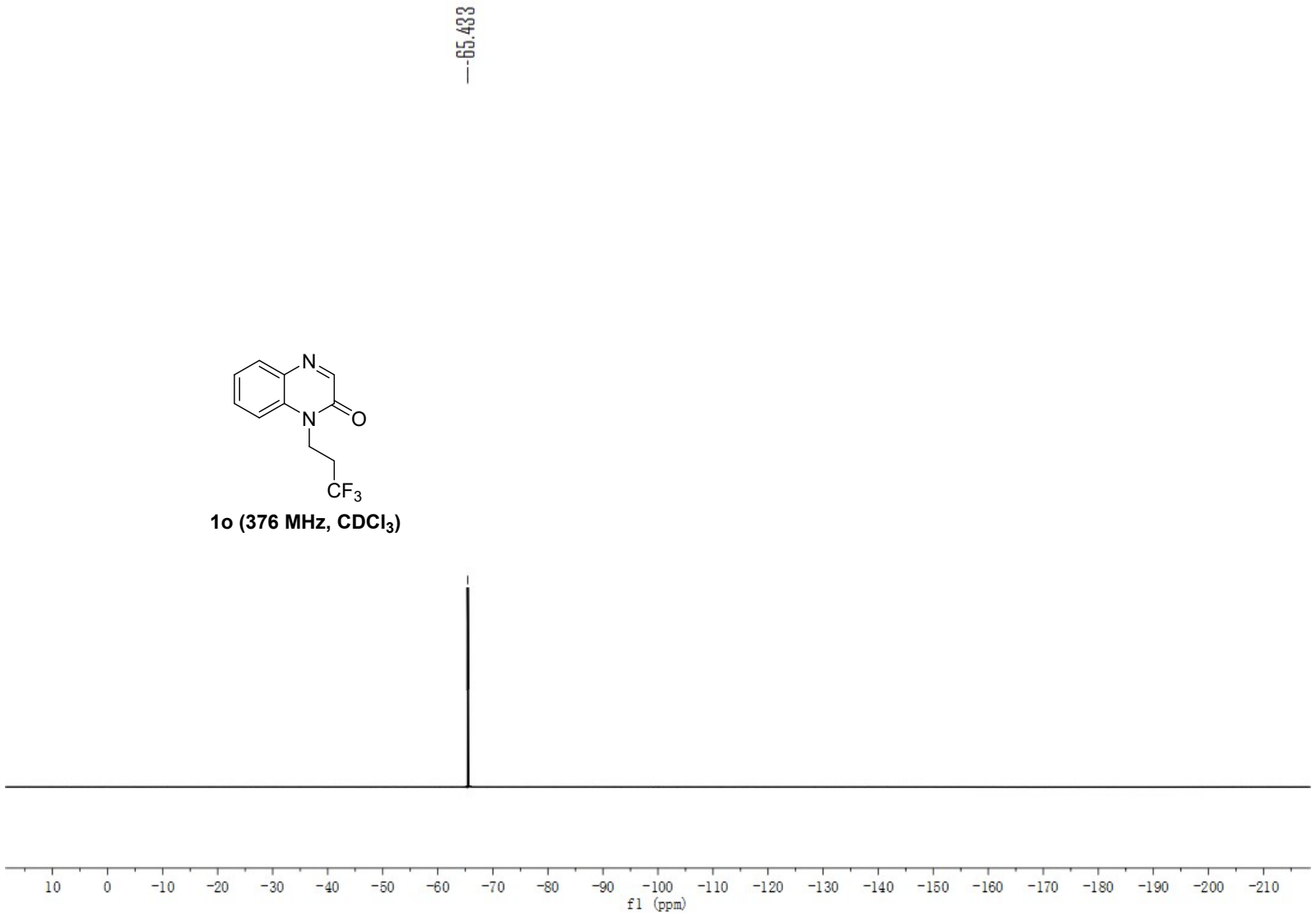
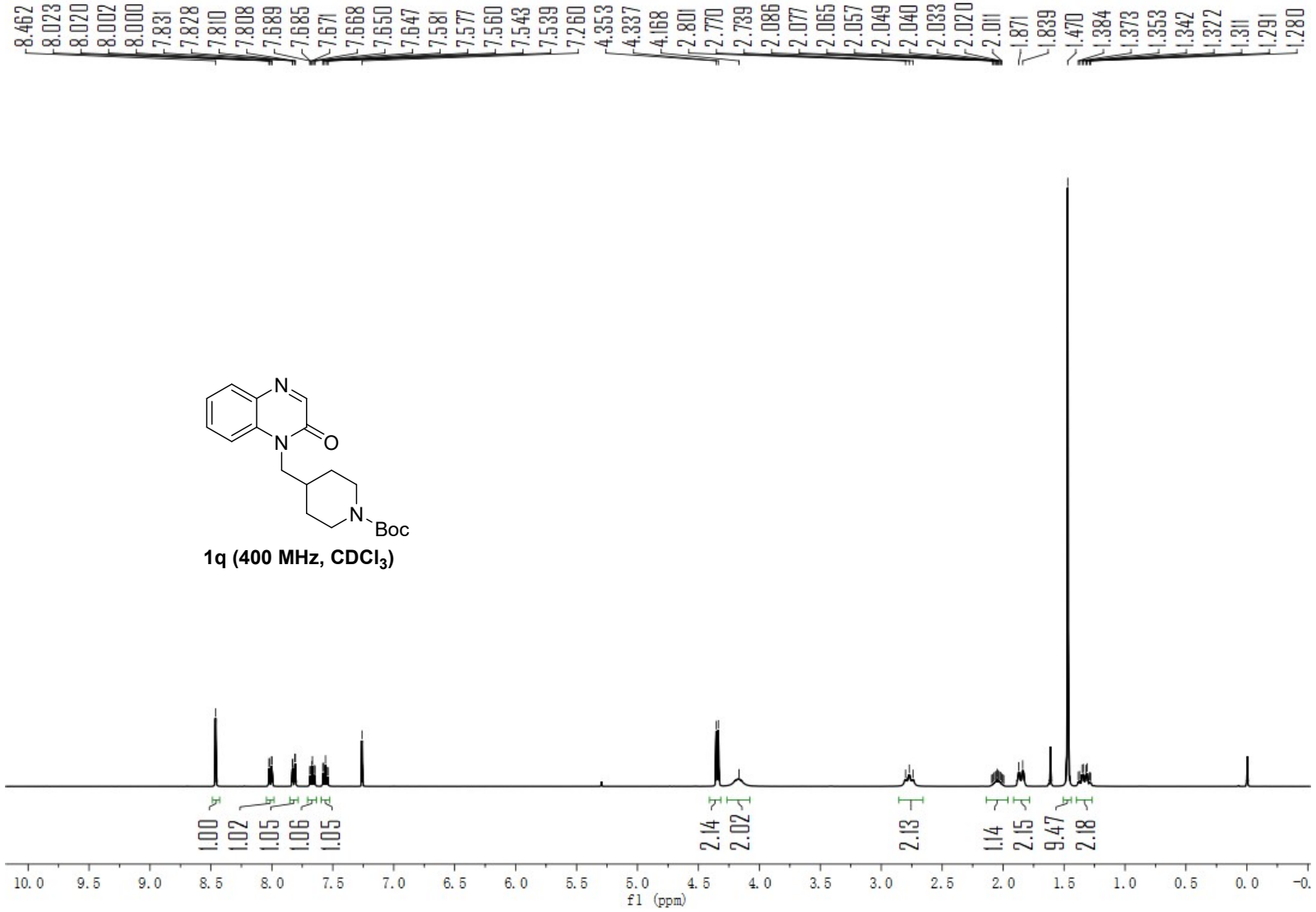


1o (376 MHz, $CDCl_3$)



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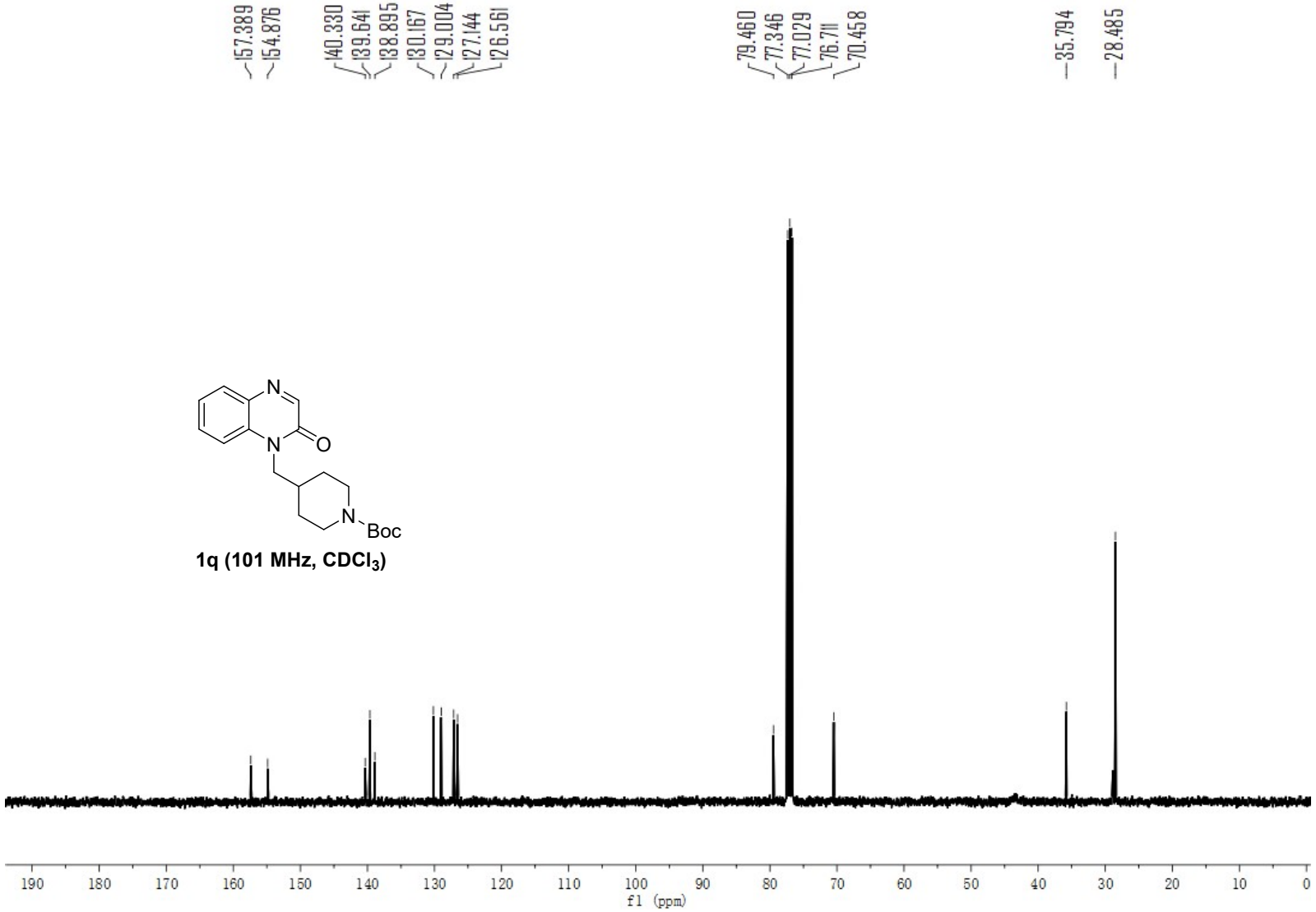

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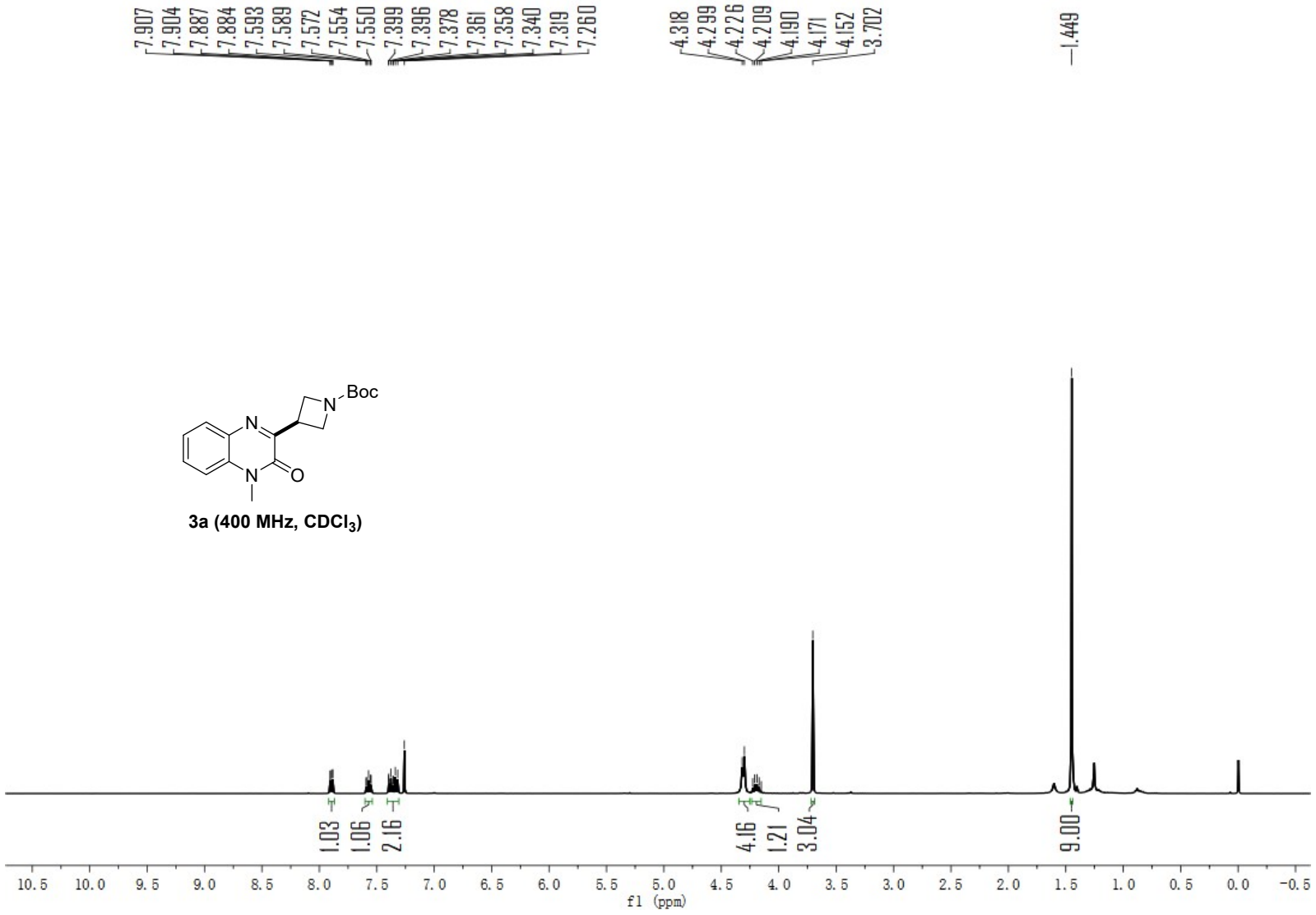
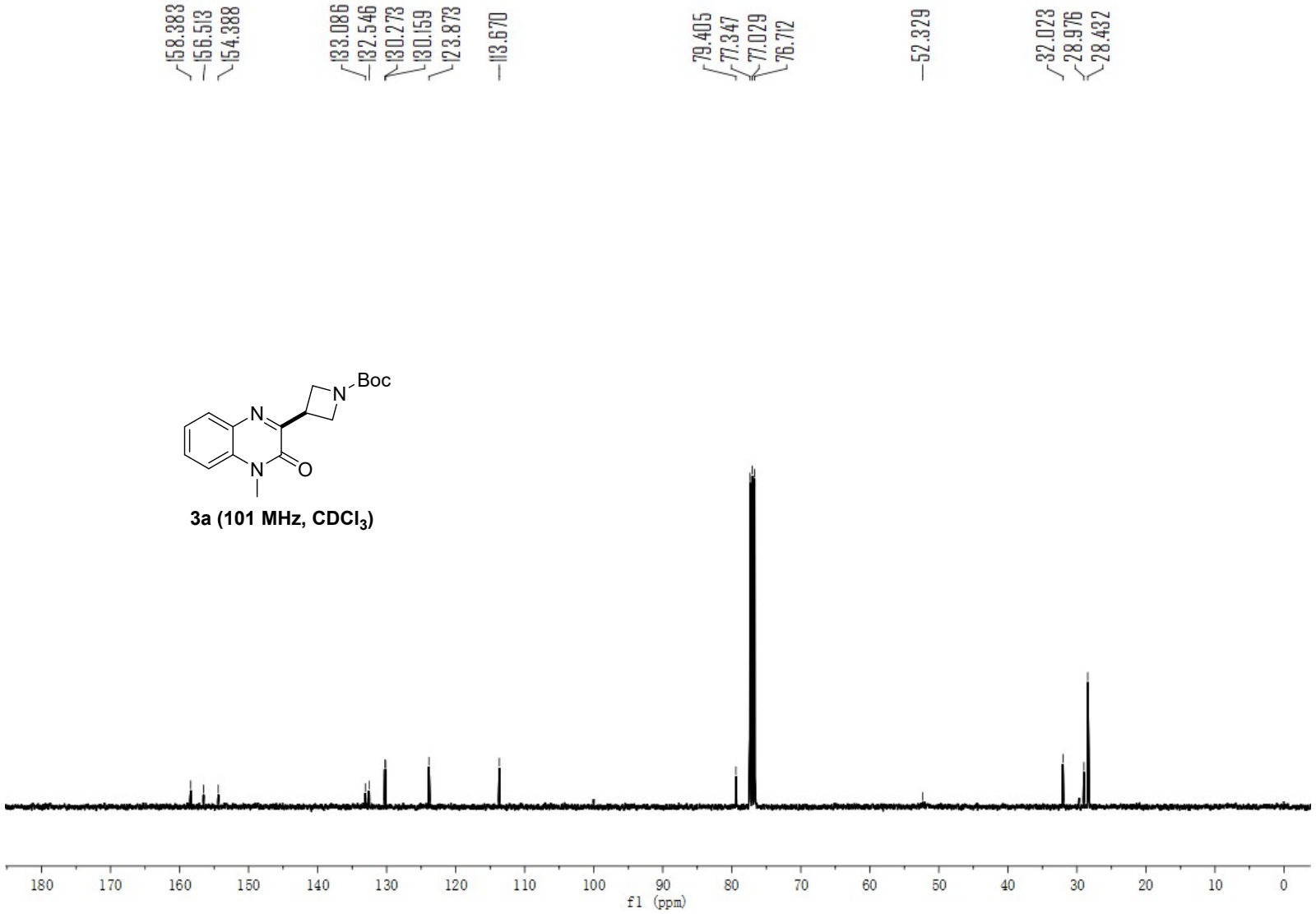


3a (400 MHz, $CDCl_3$)



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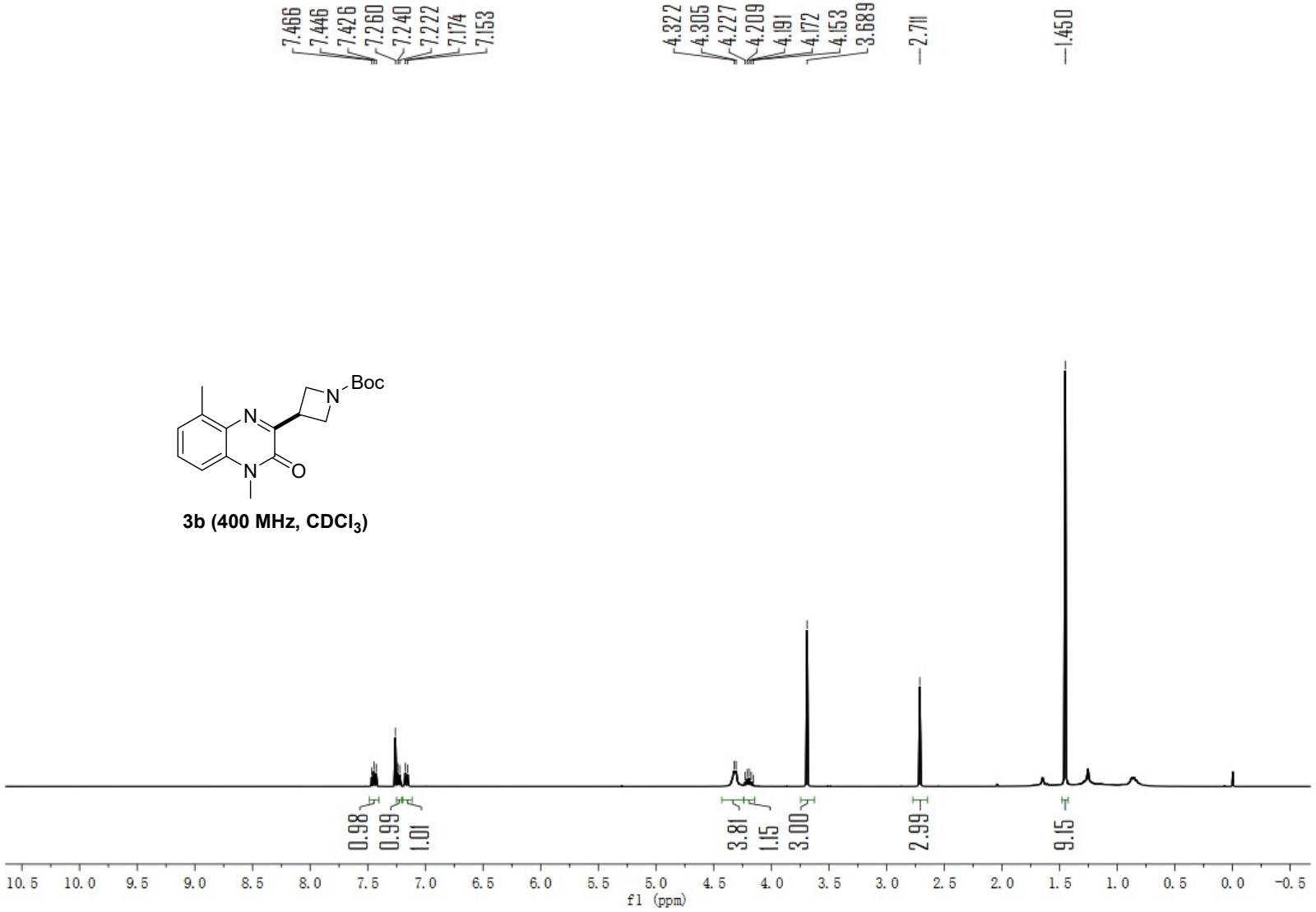

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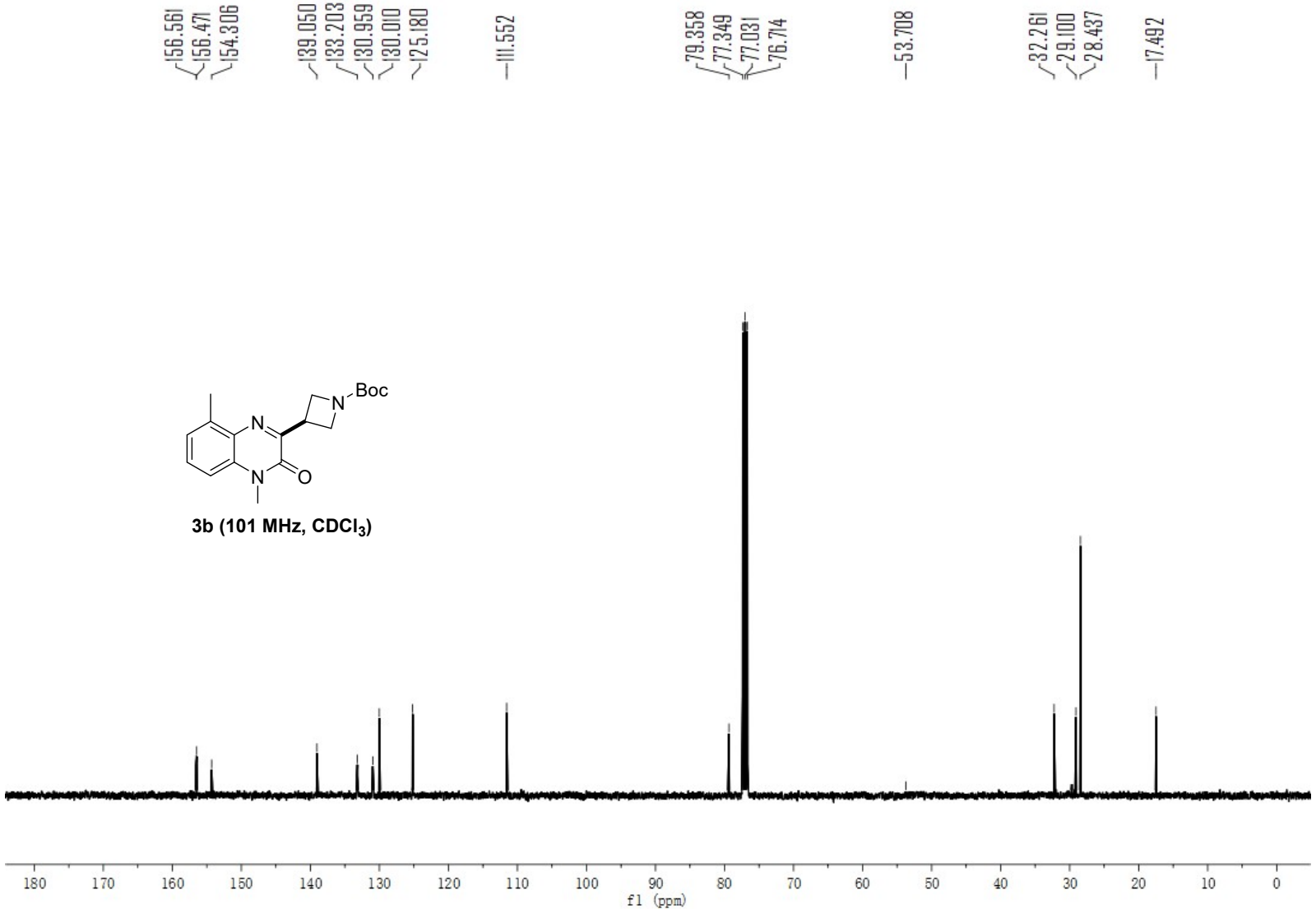

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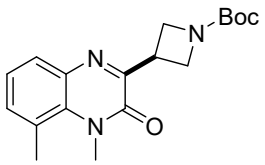

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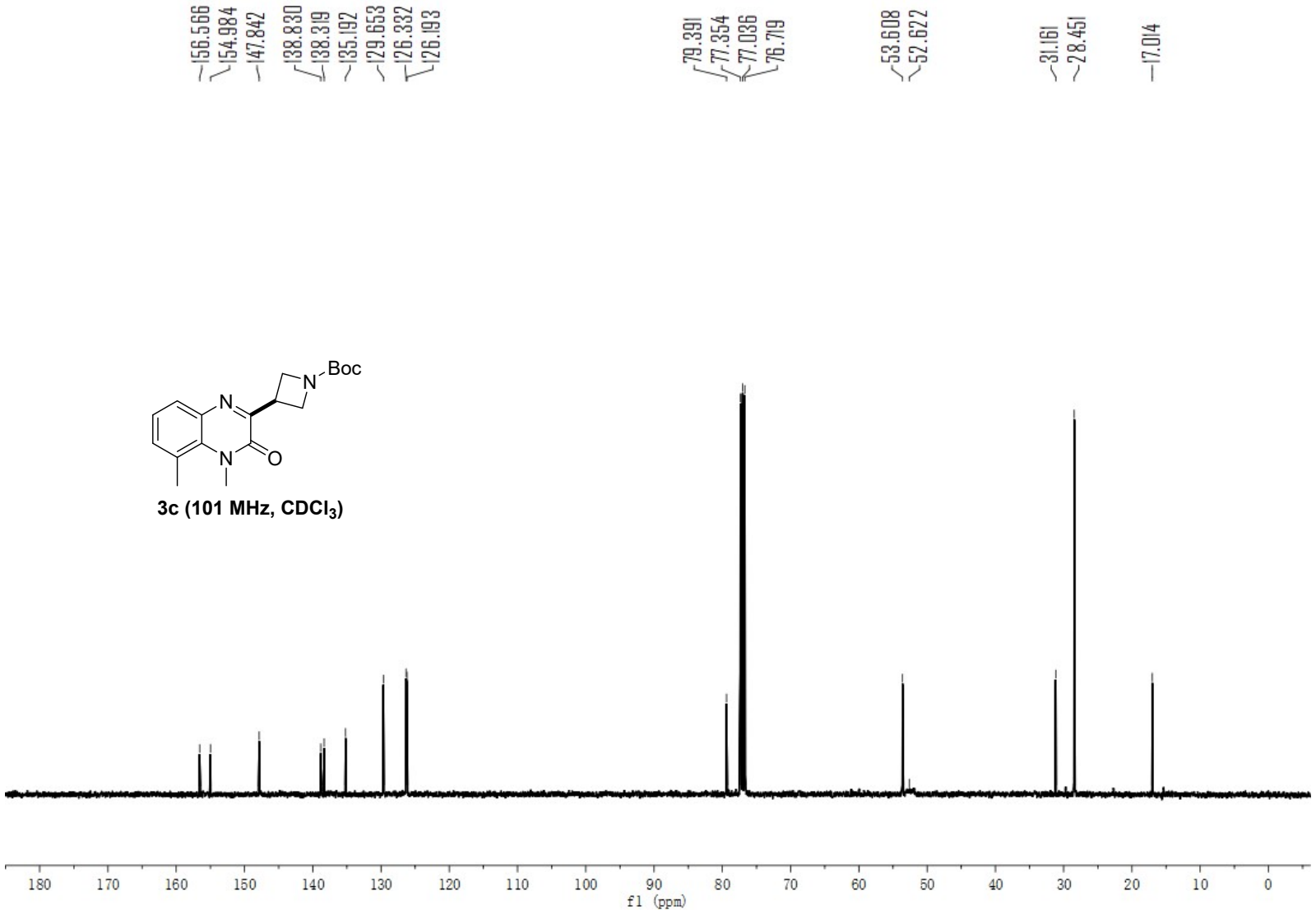

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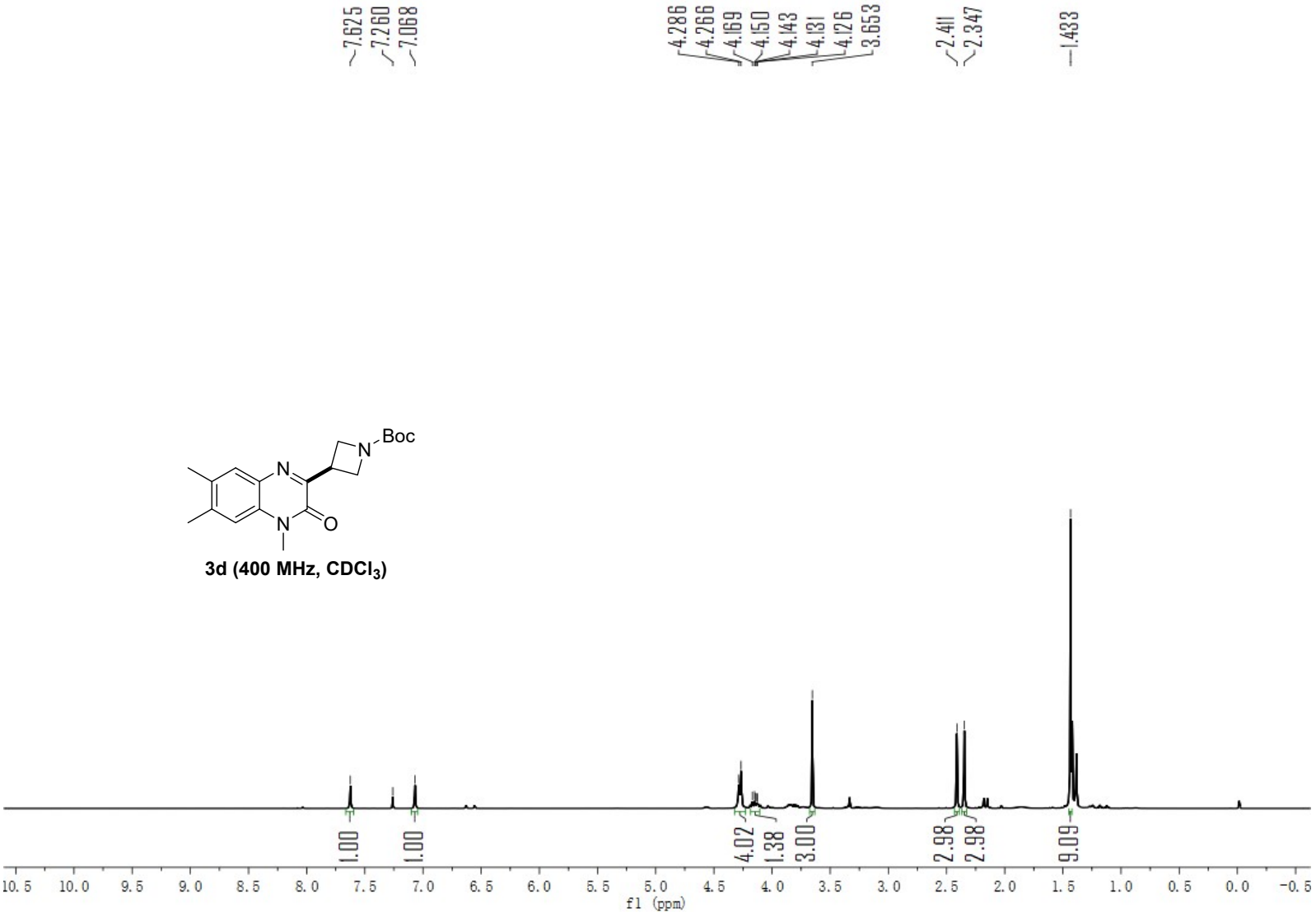

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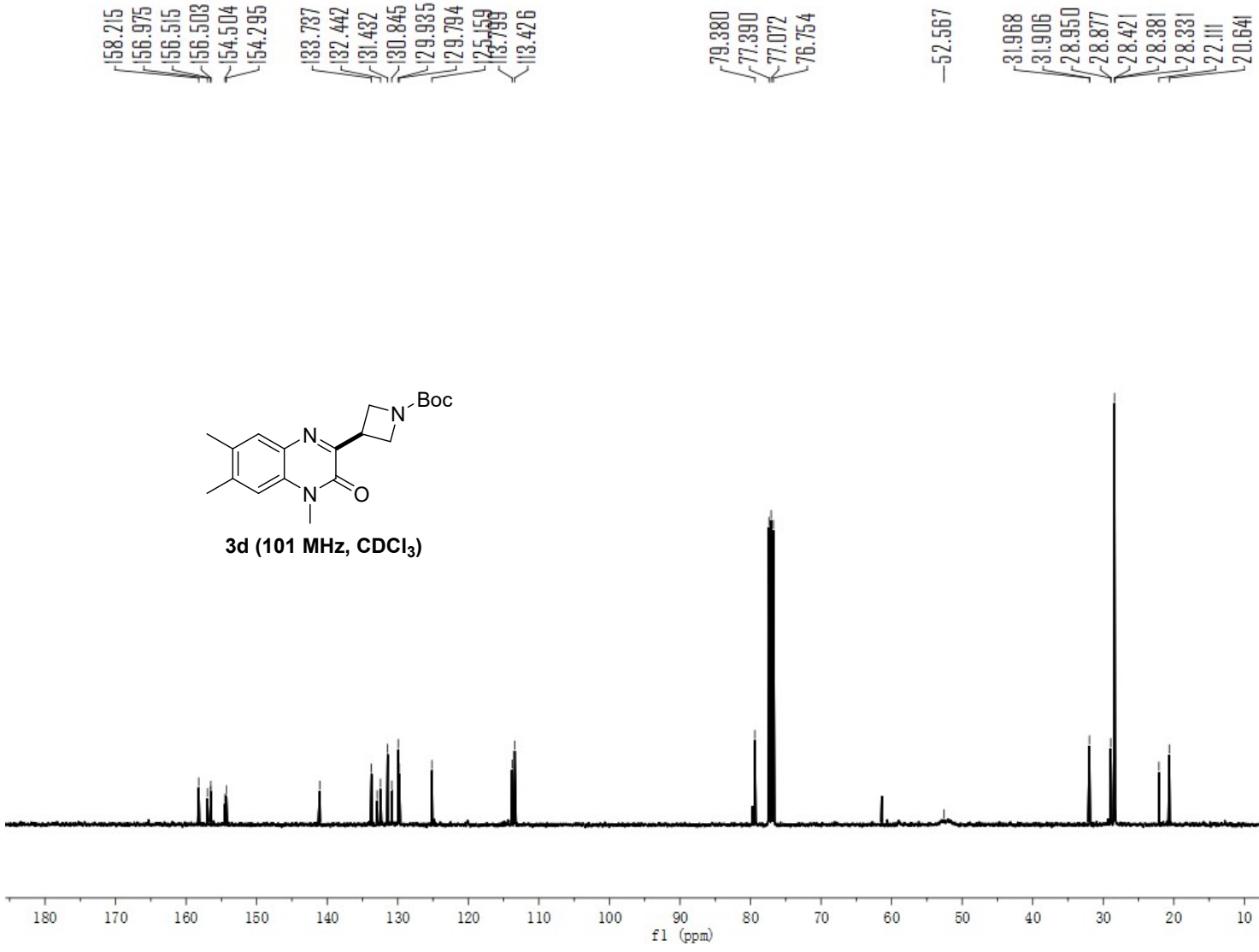

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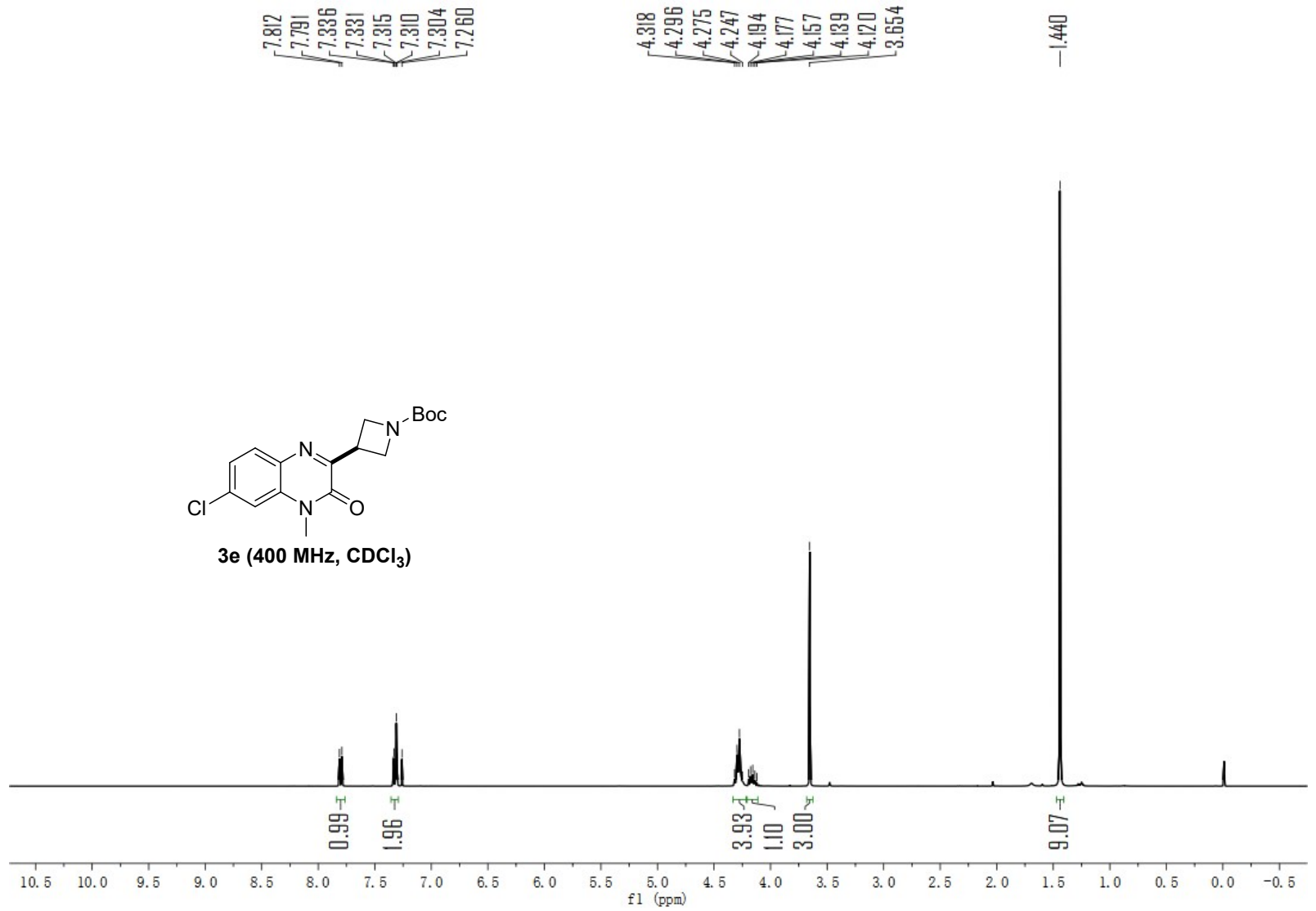

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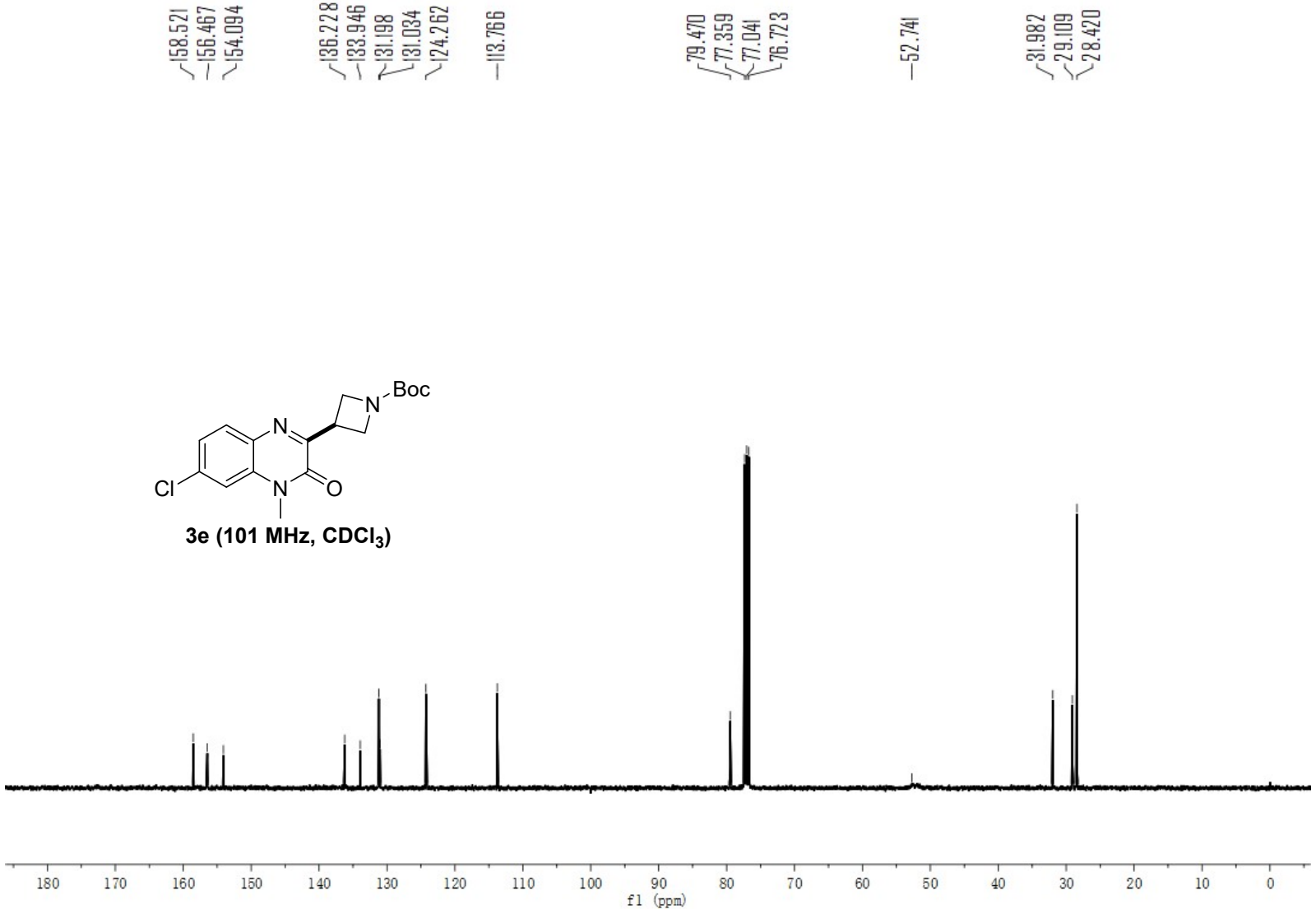

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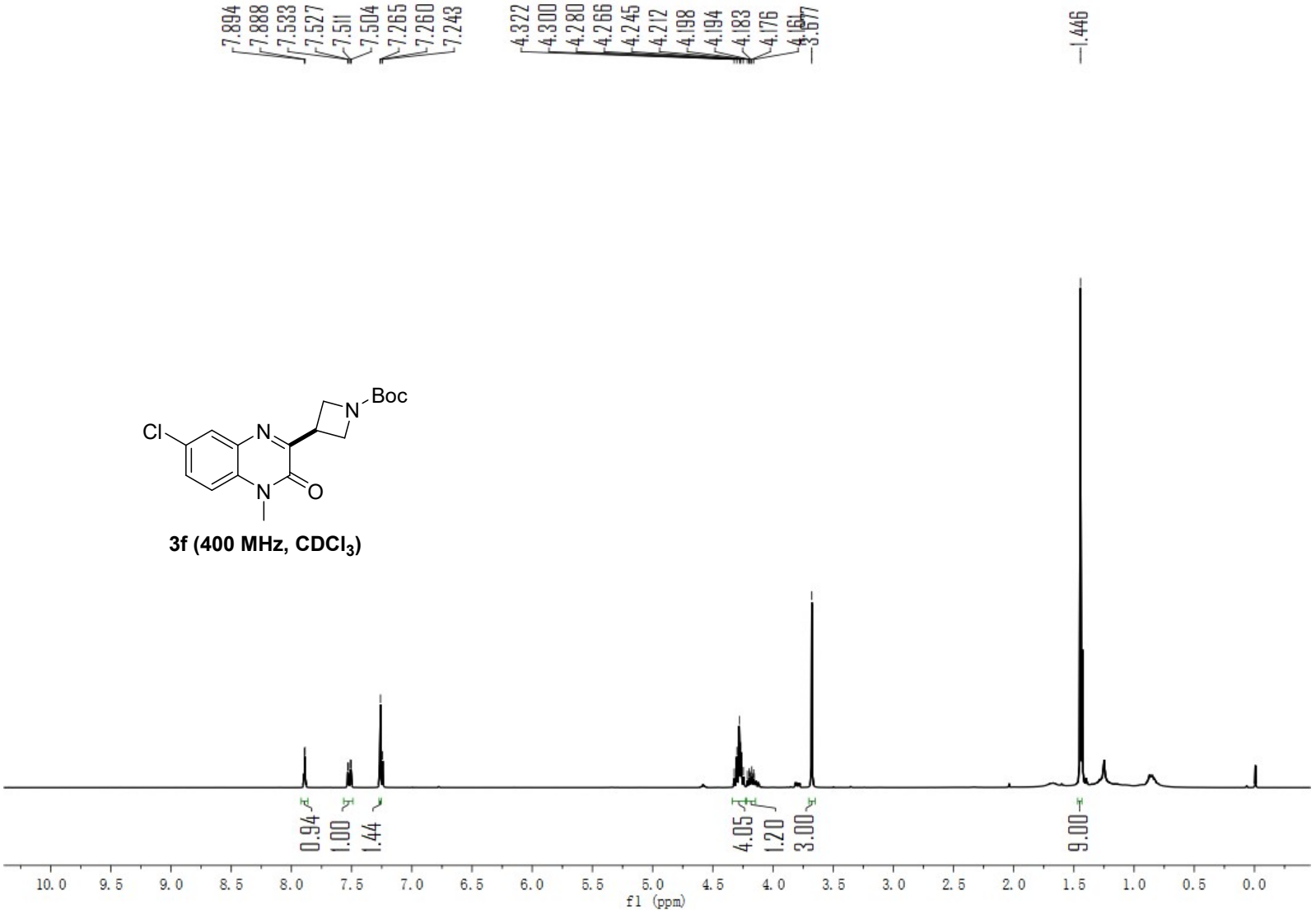

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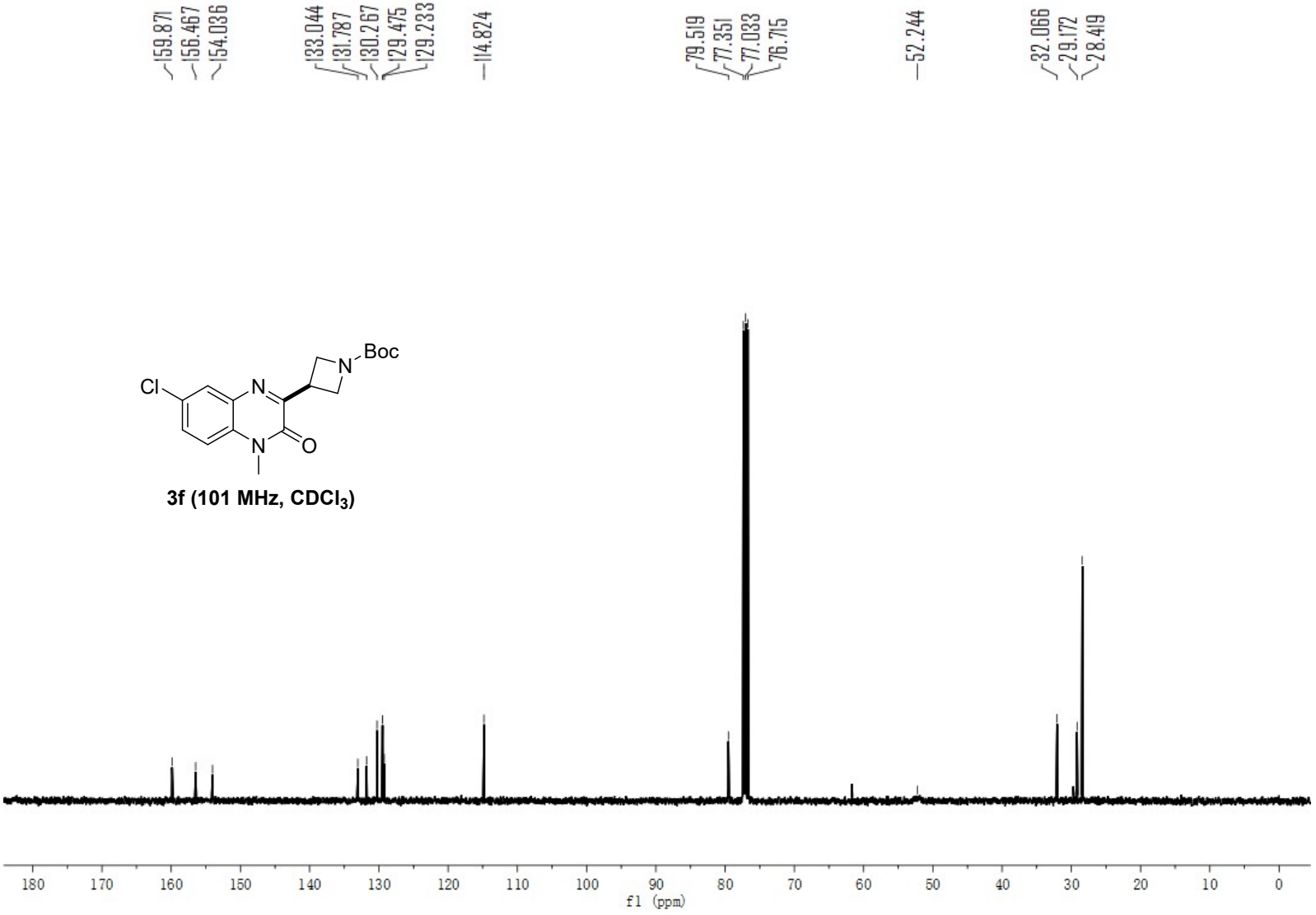

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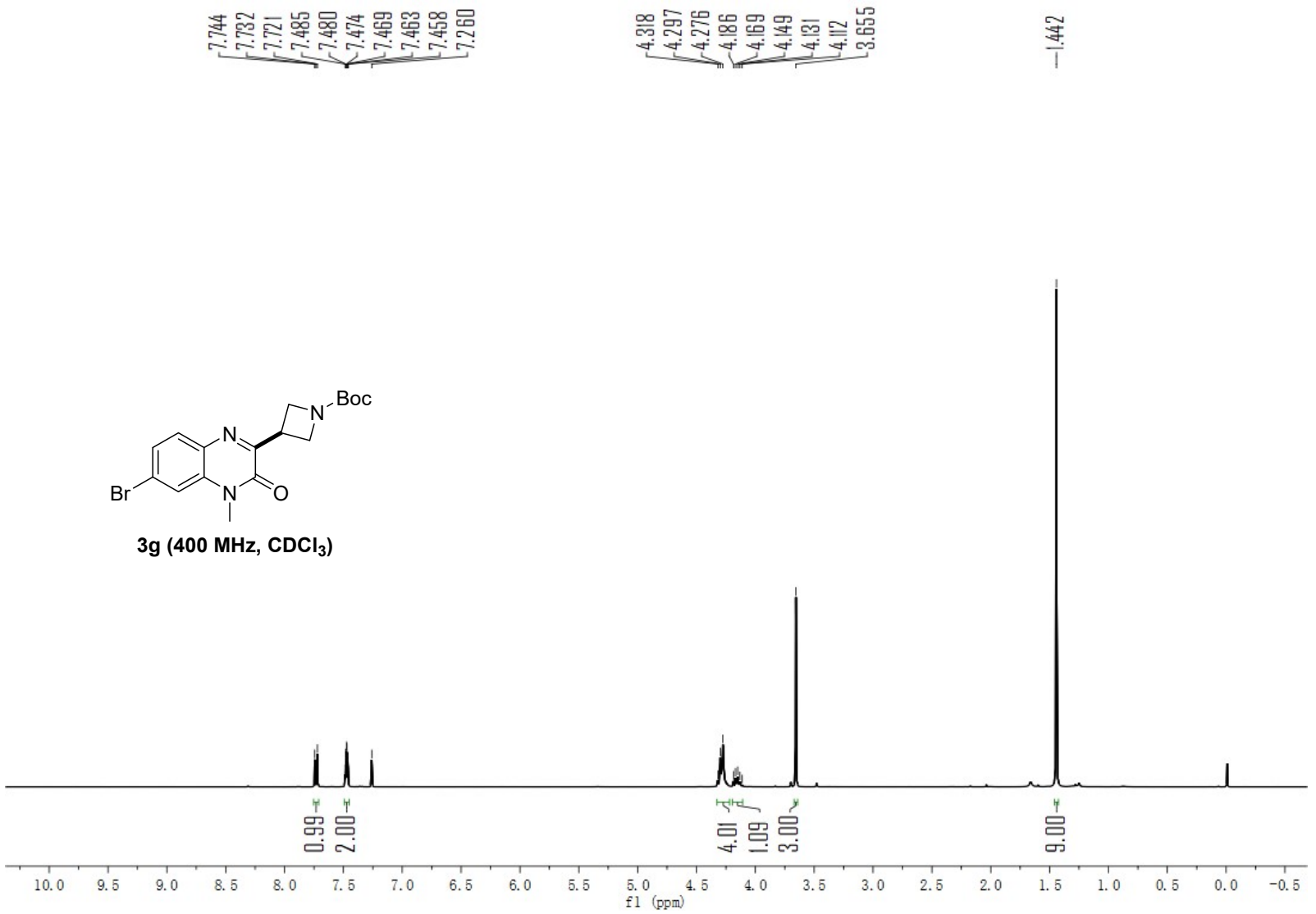

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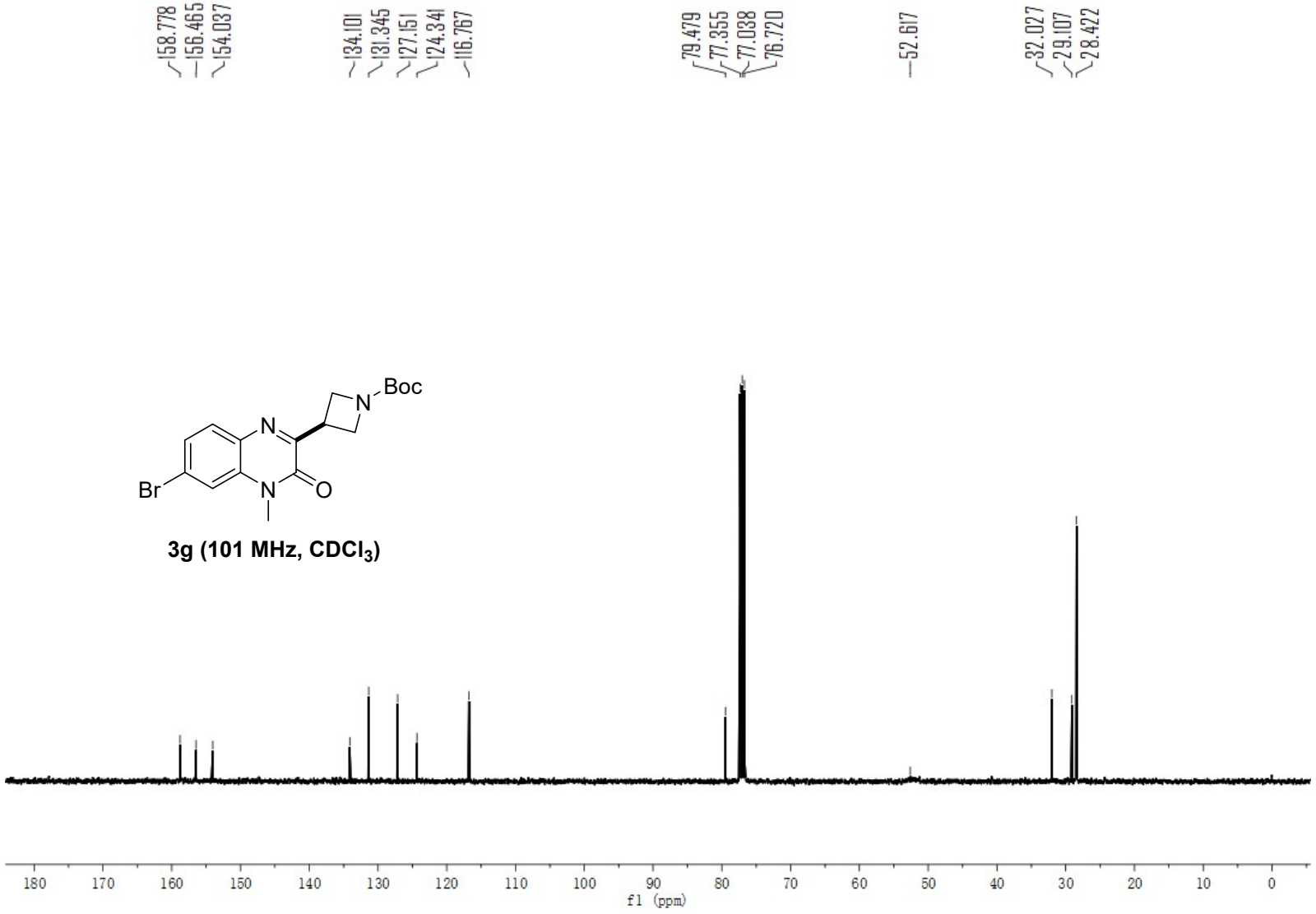

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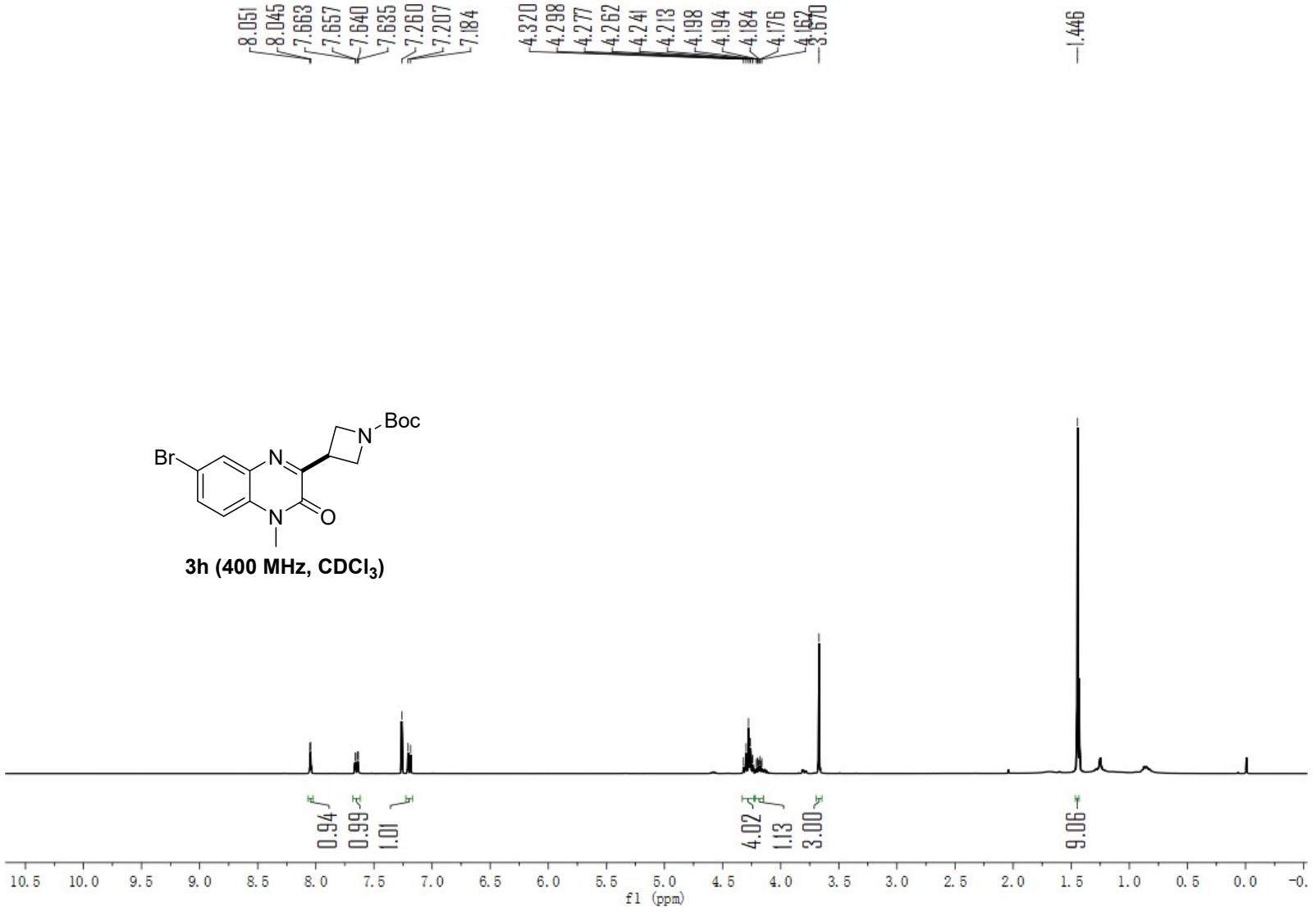

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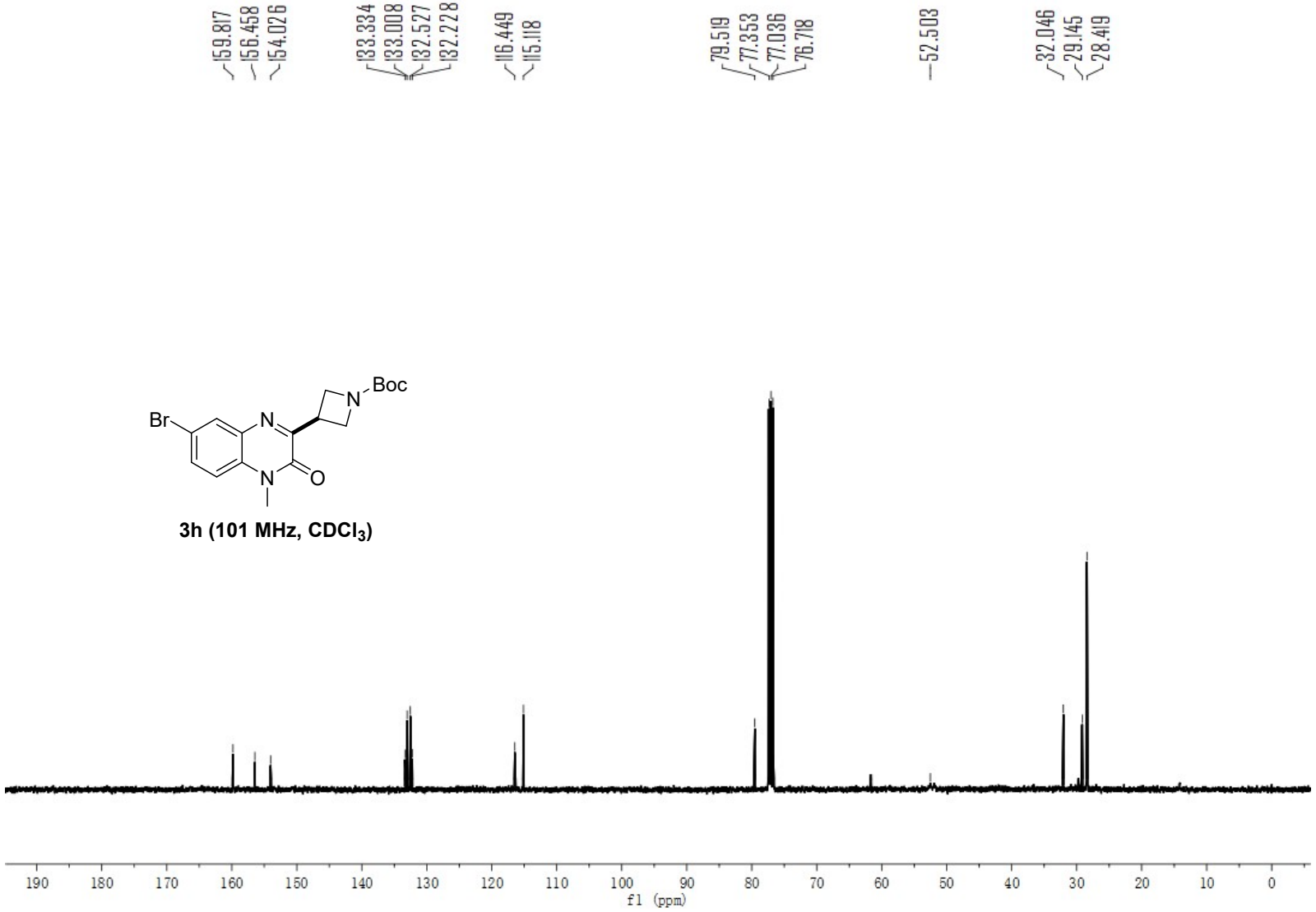

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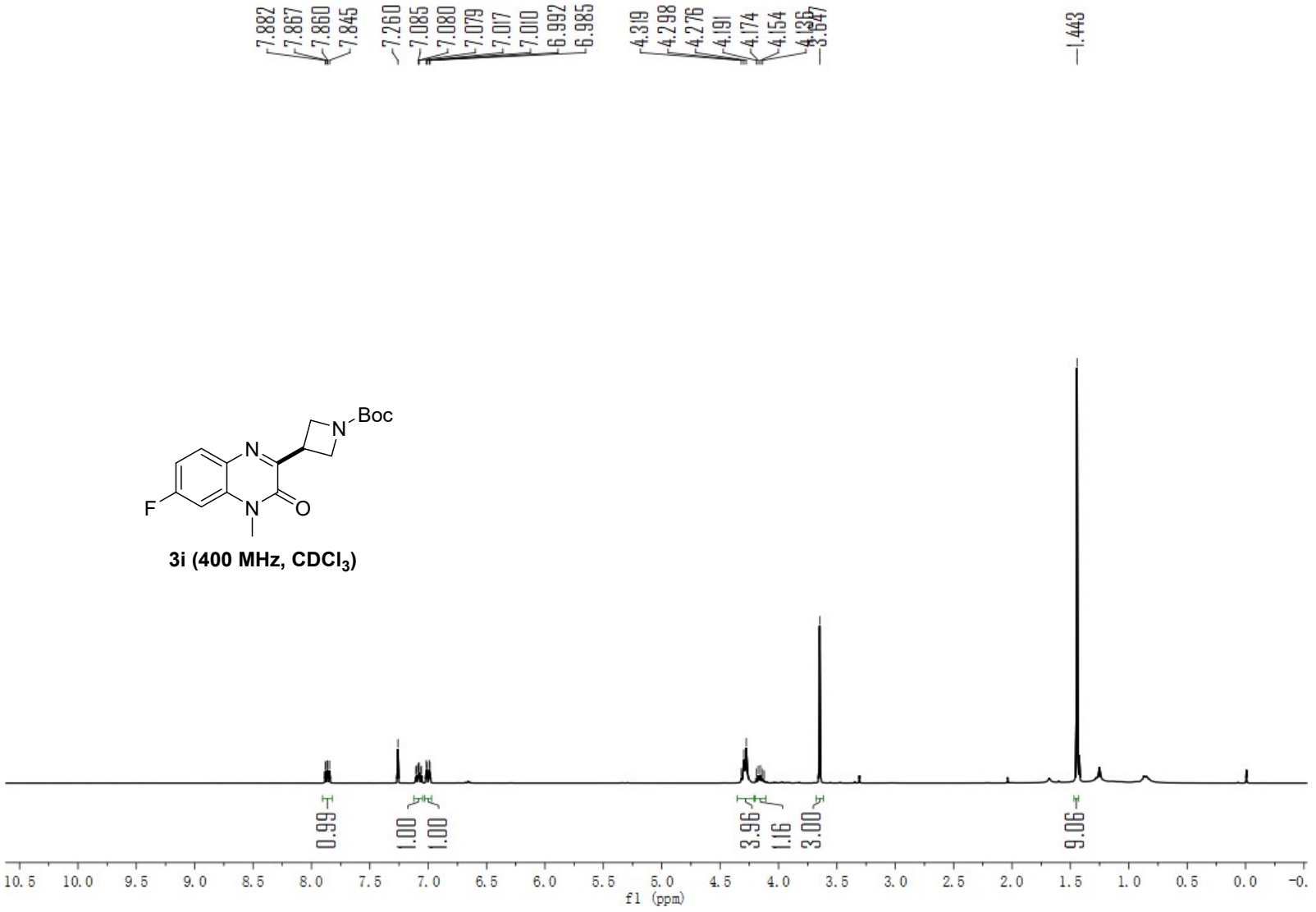

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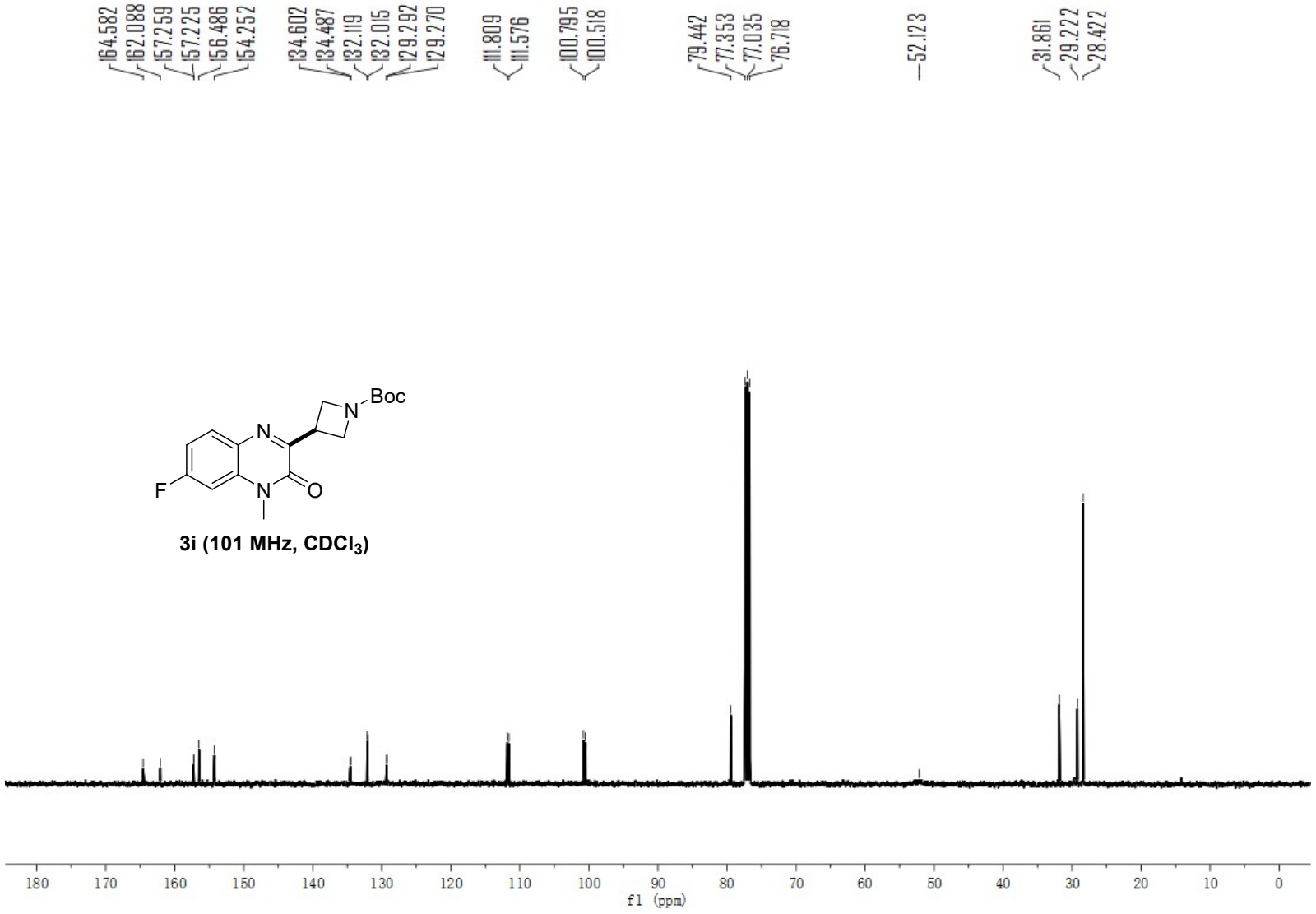

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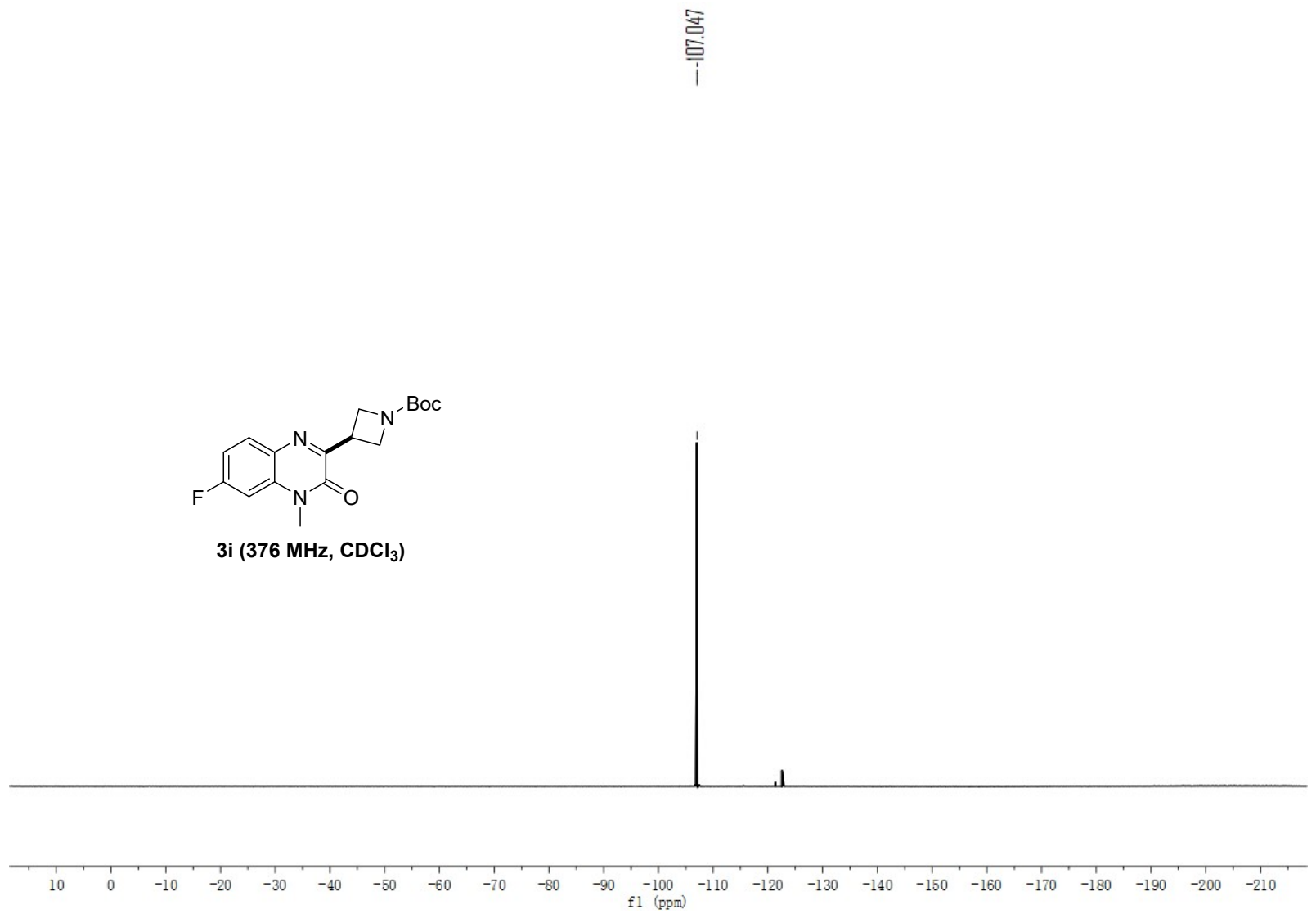

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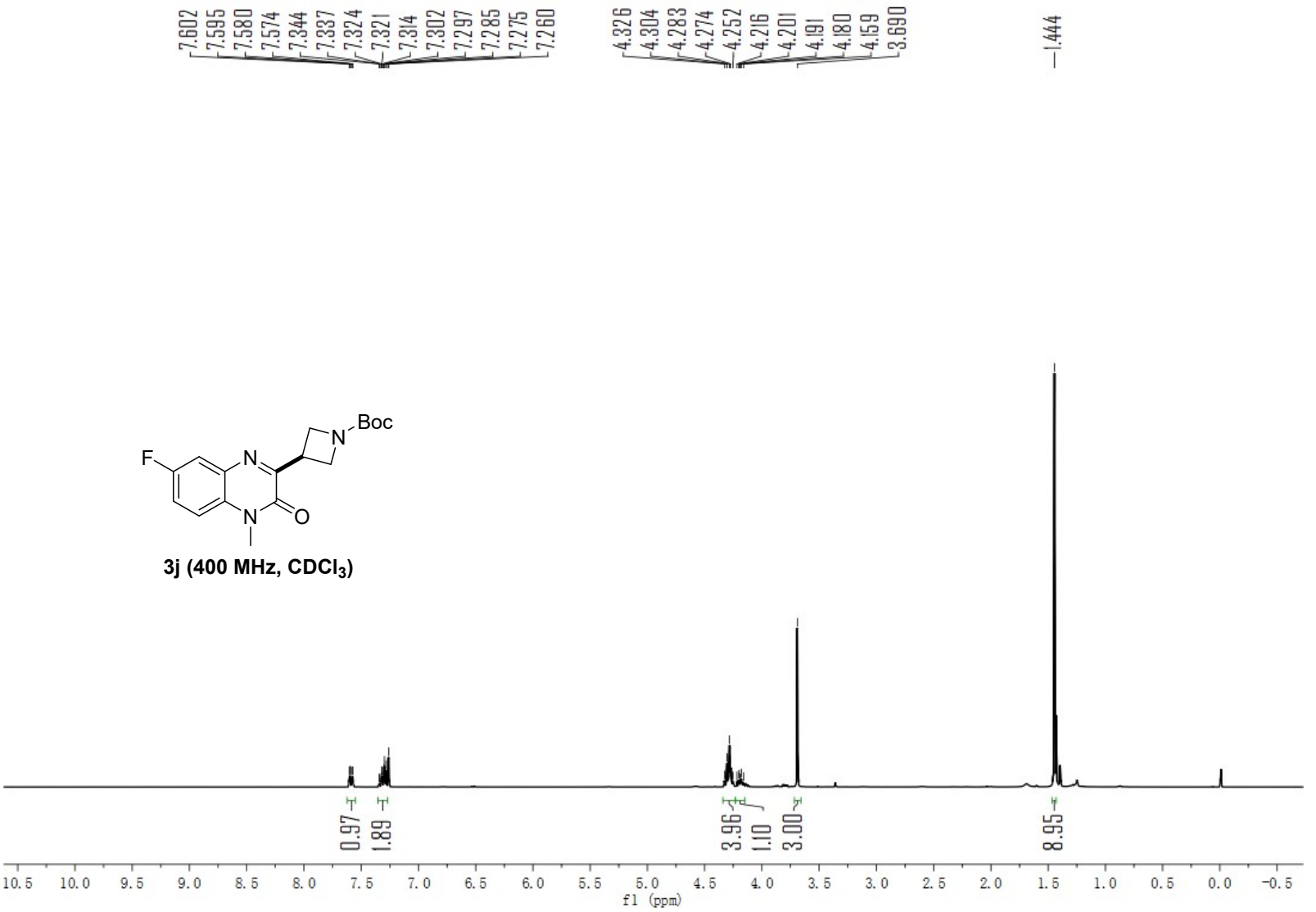

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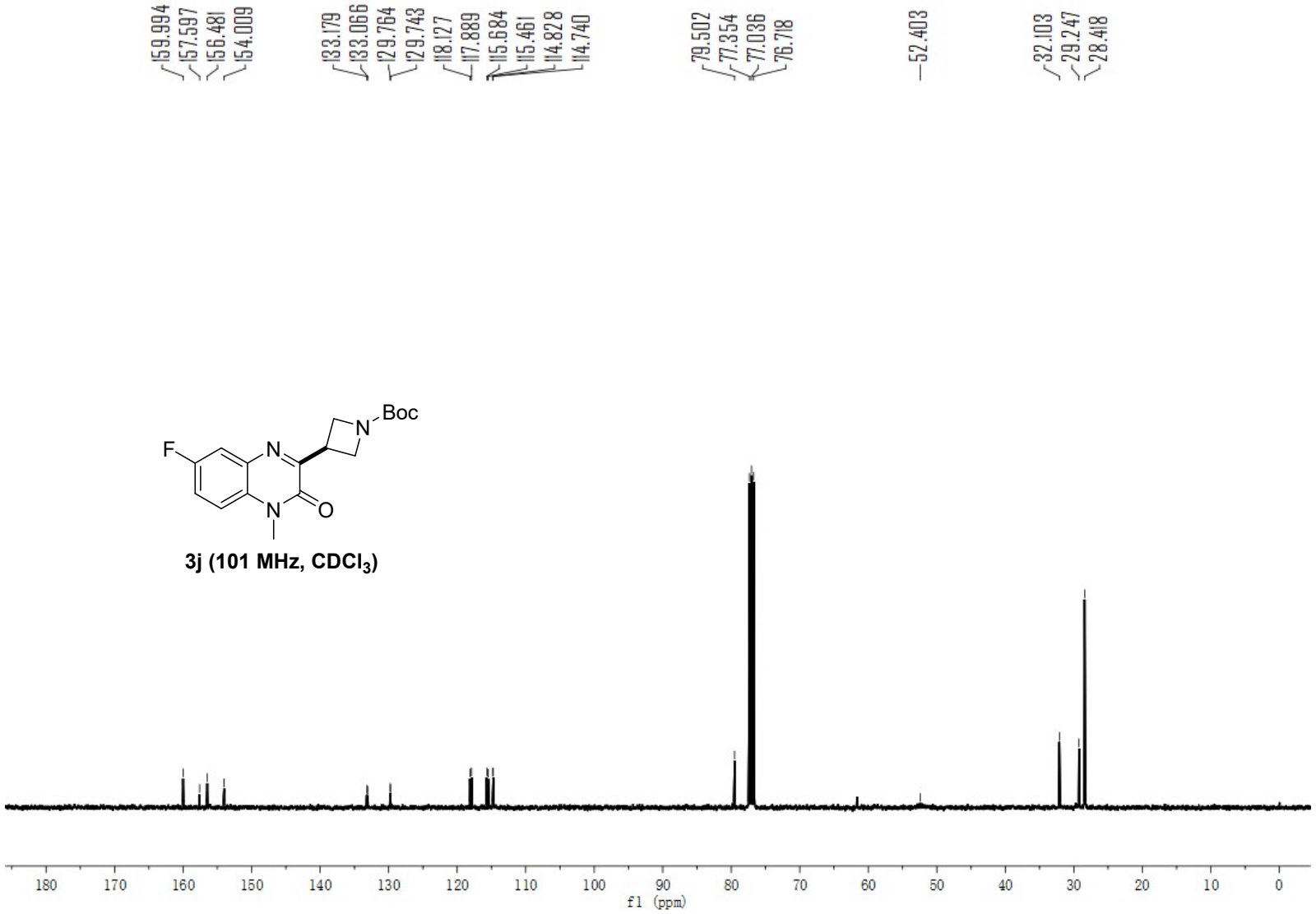

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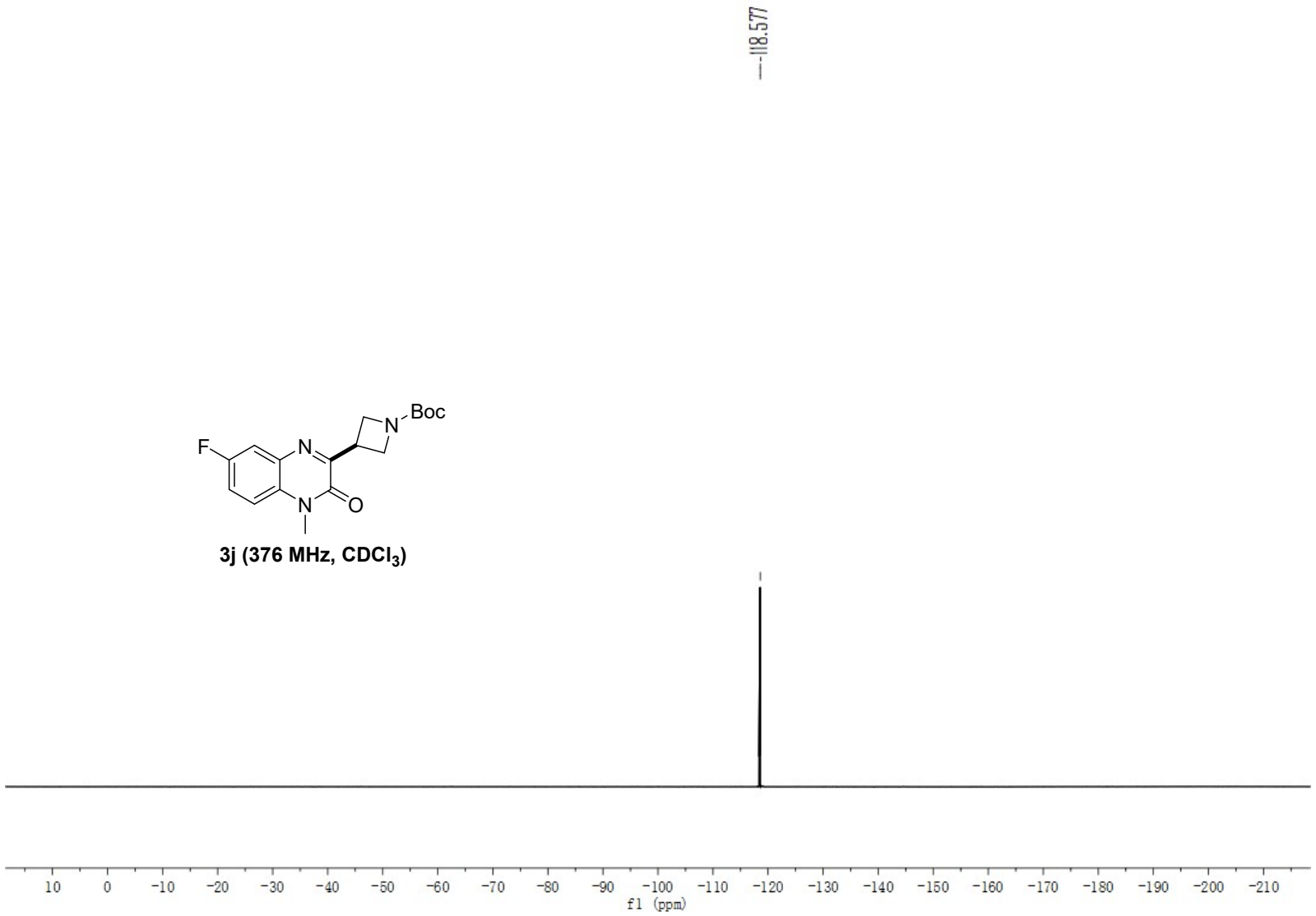

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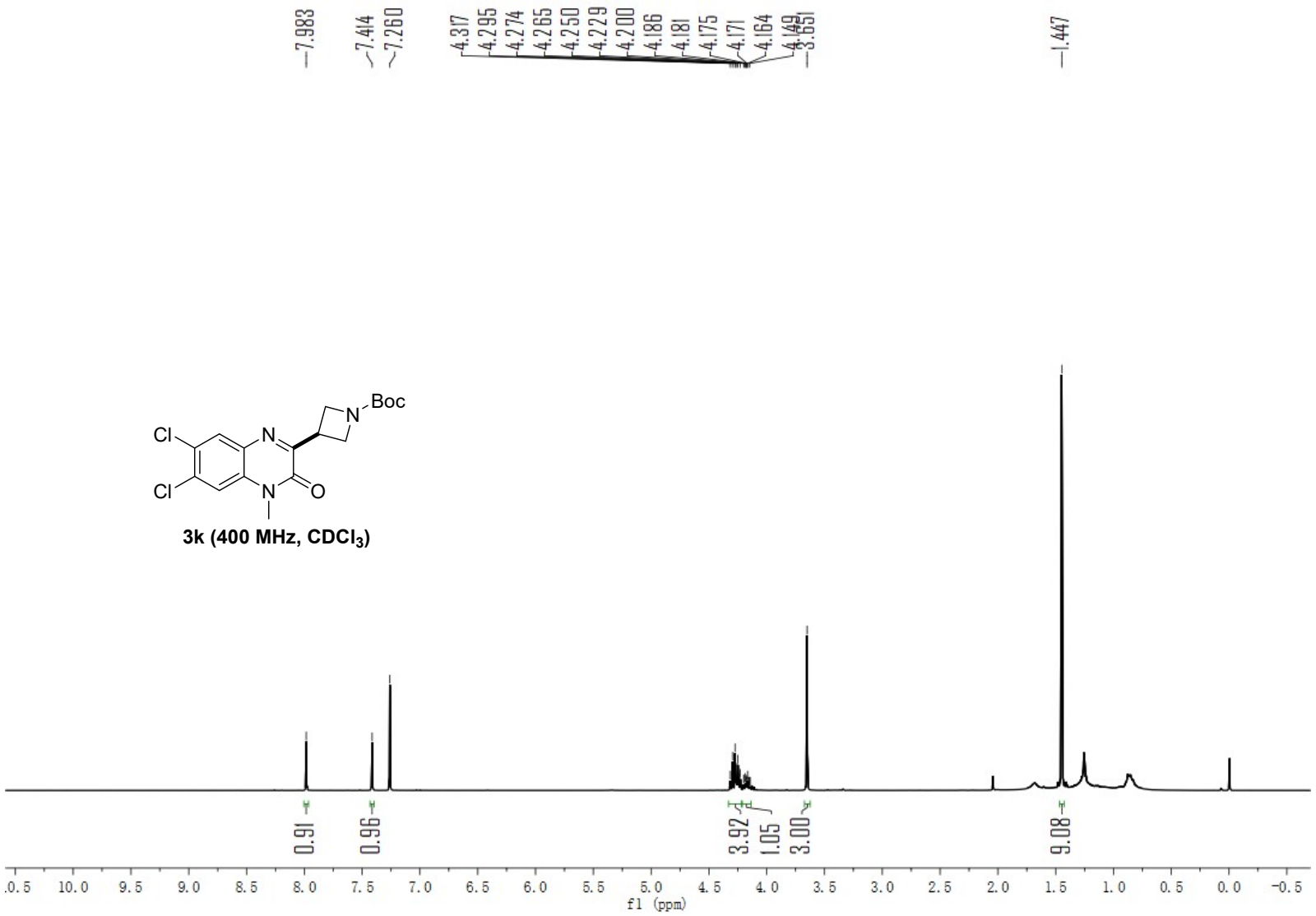

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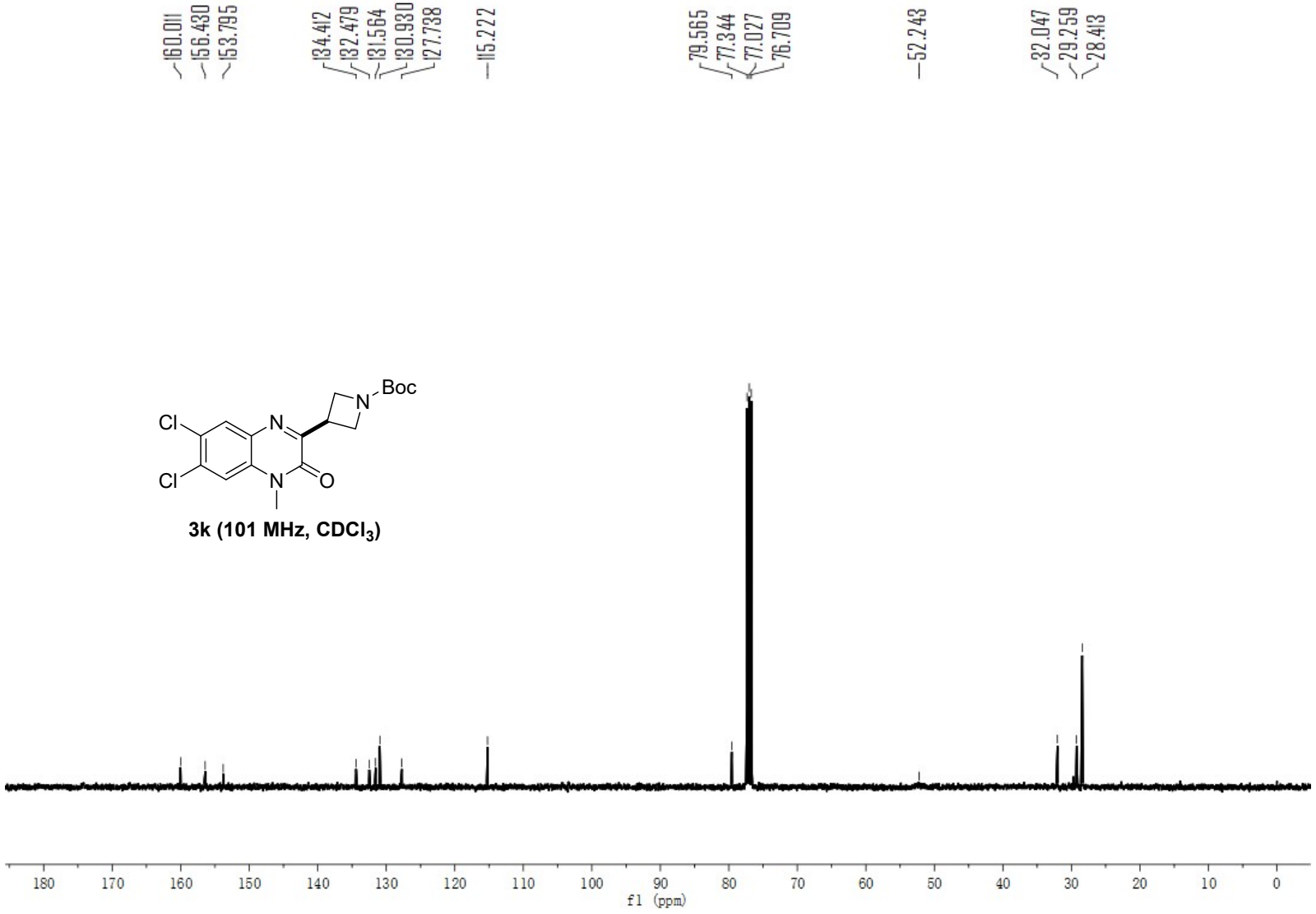

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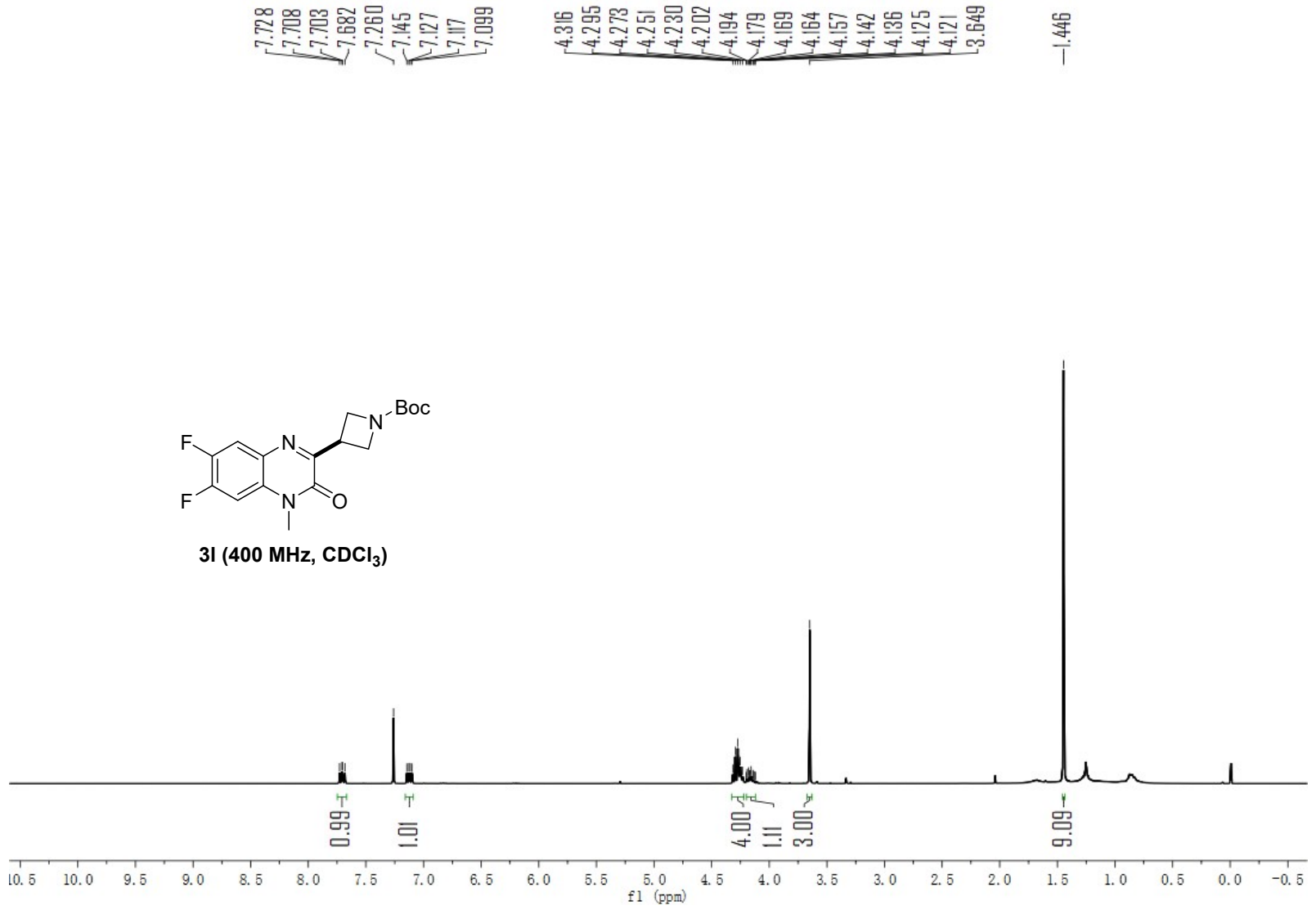

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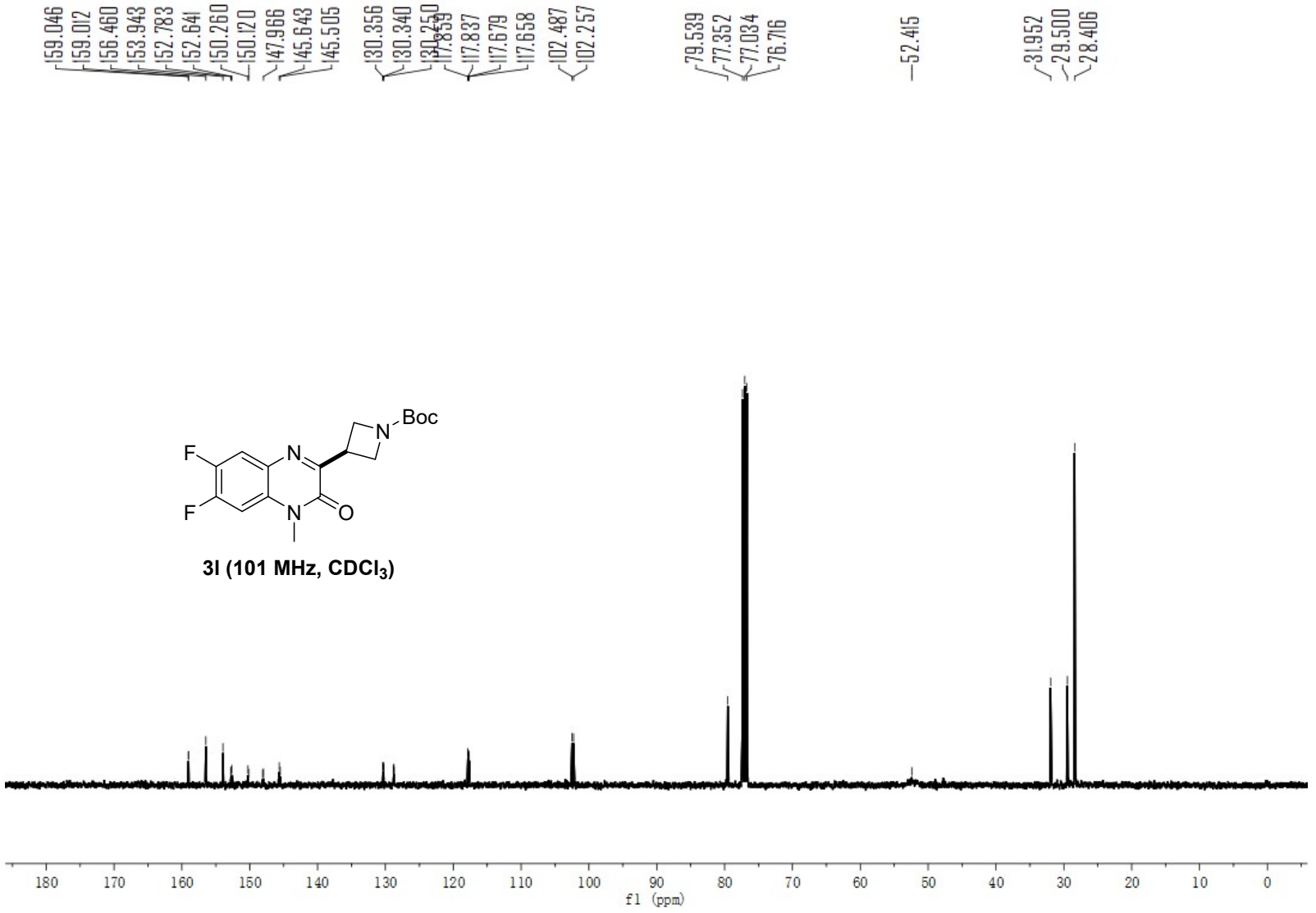

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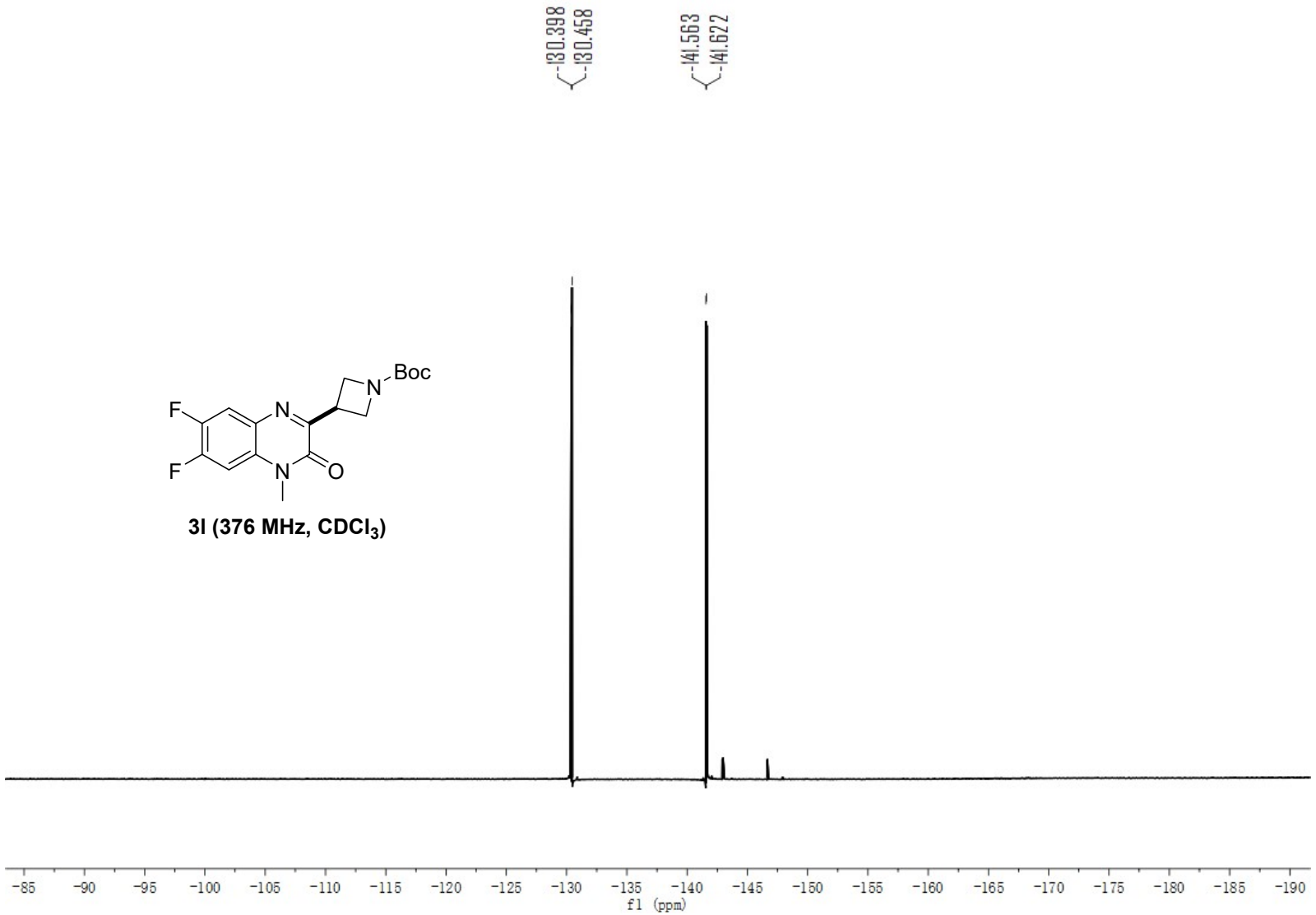

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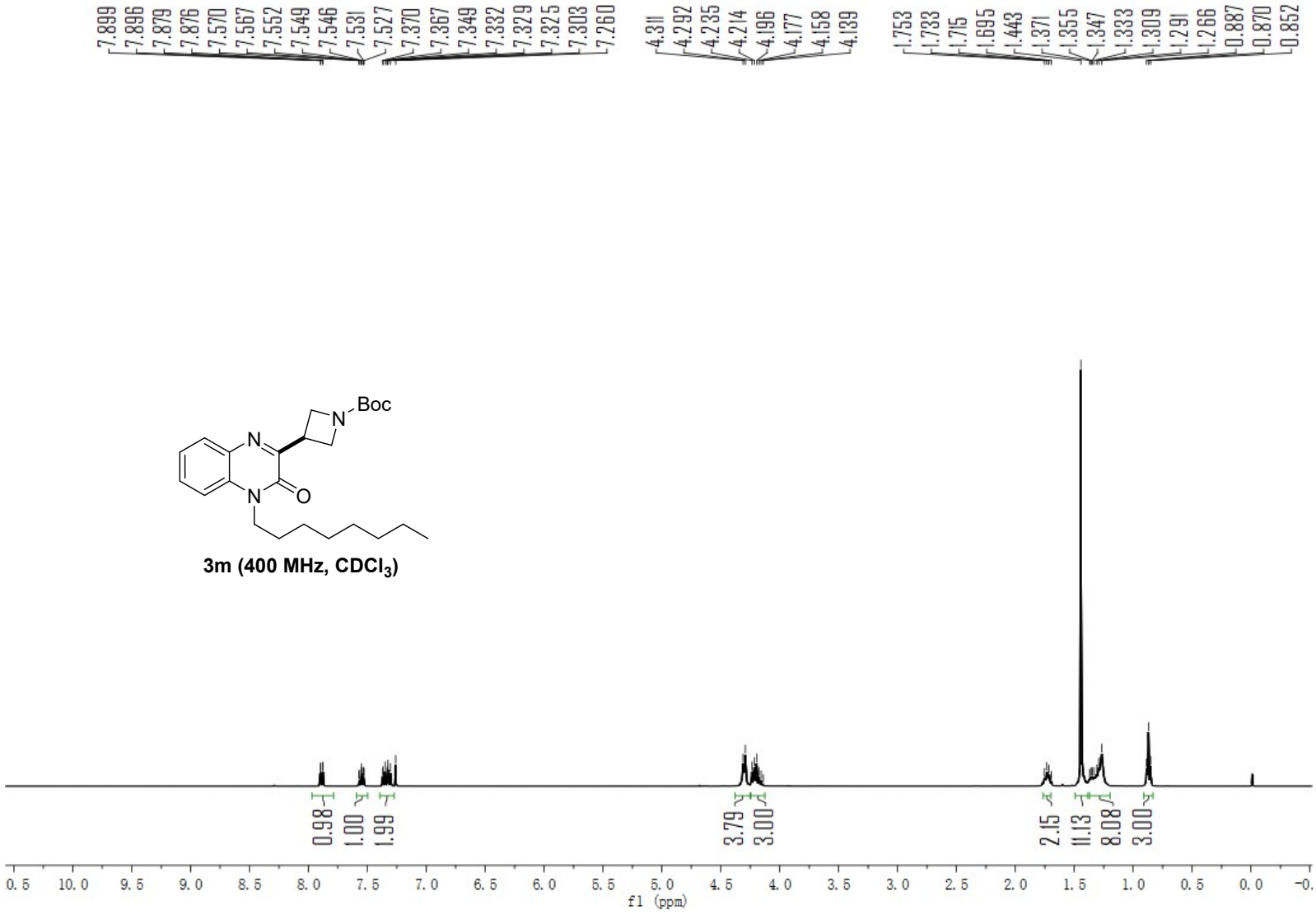

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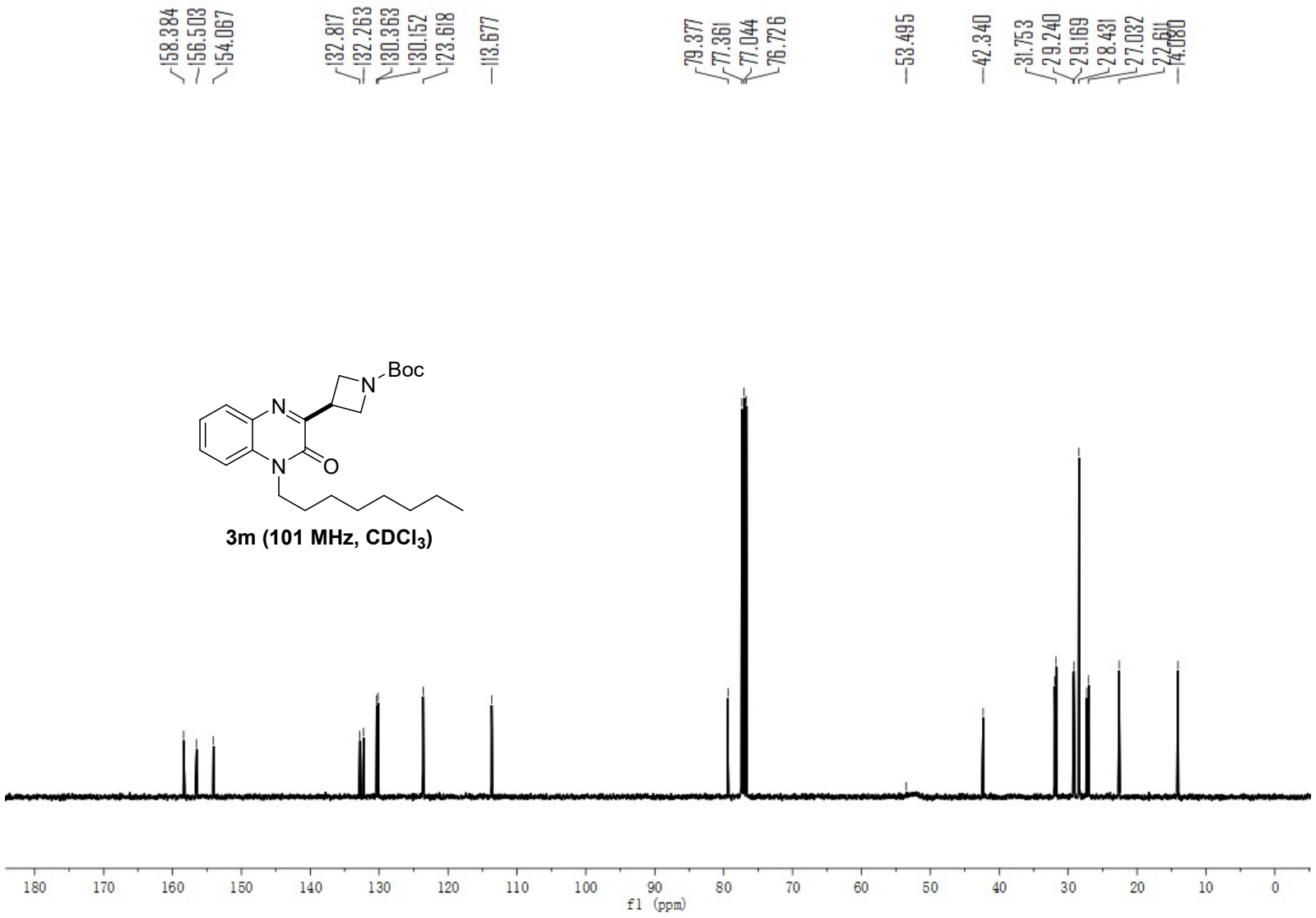

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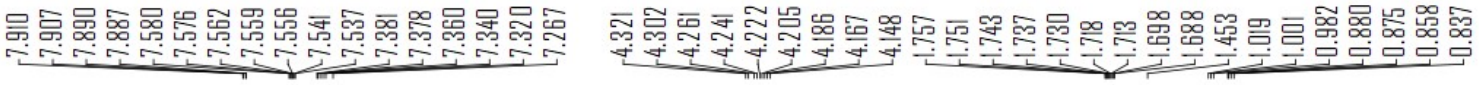

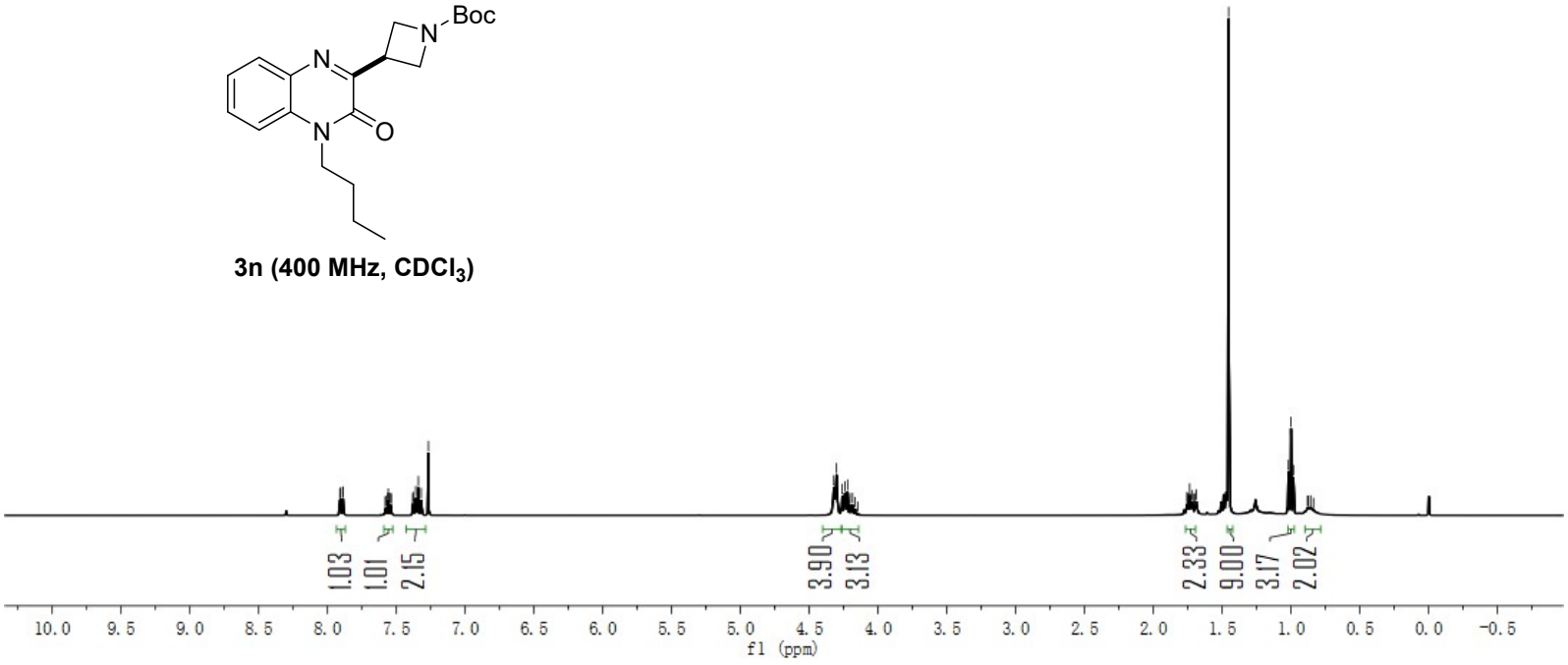

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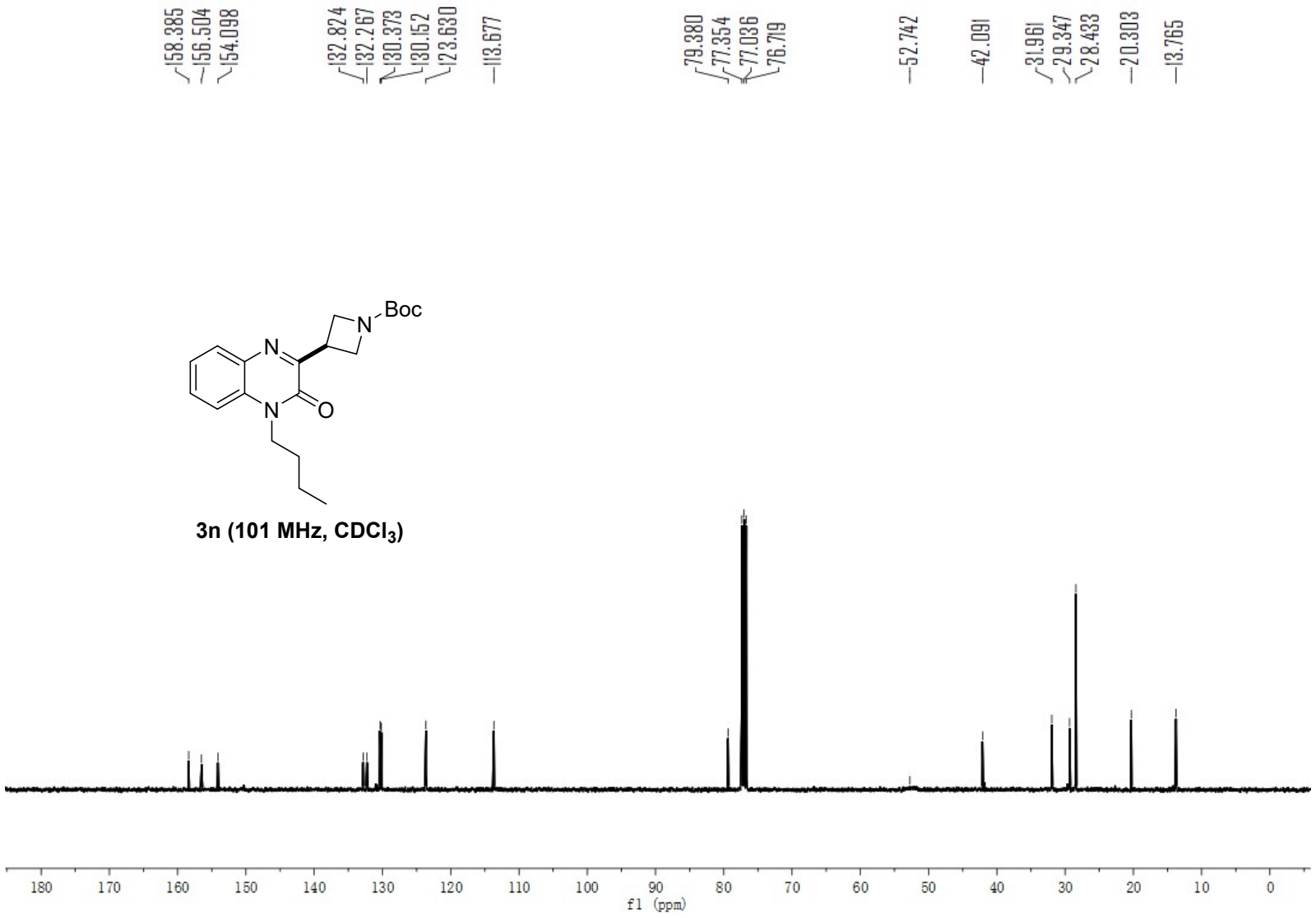

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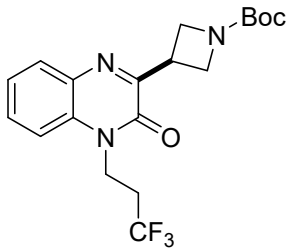

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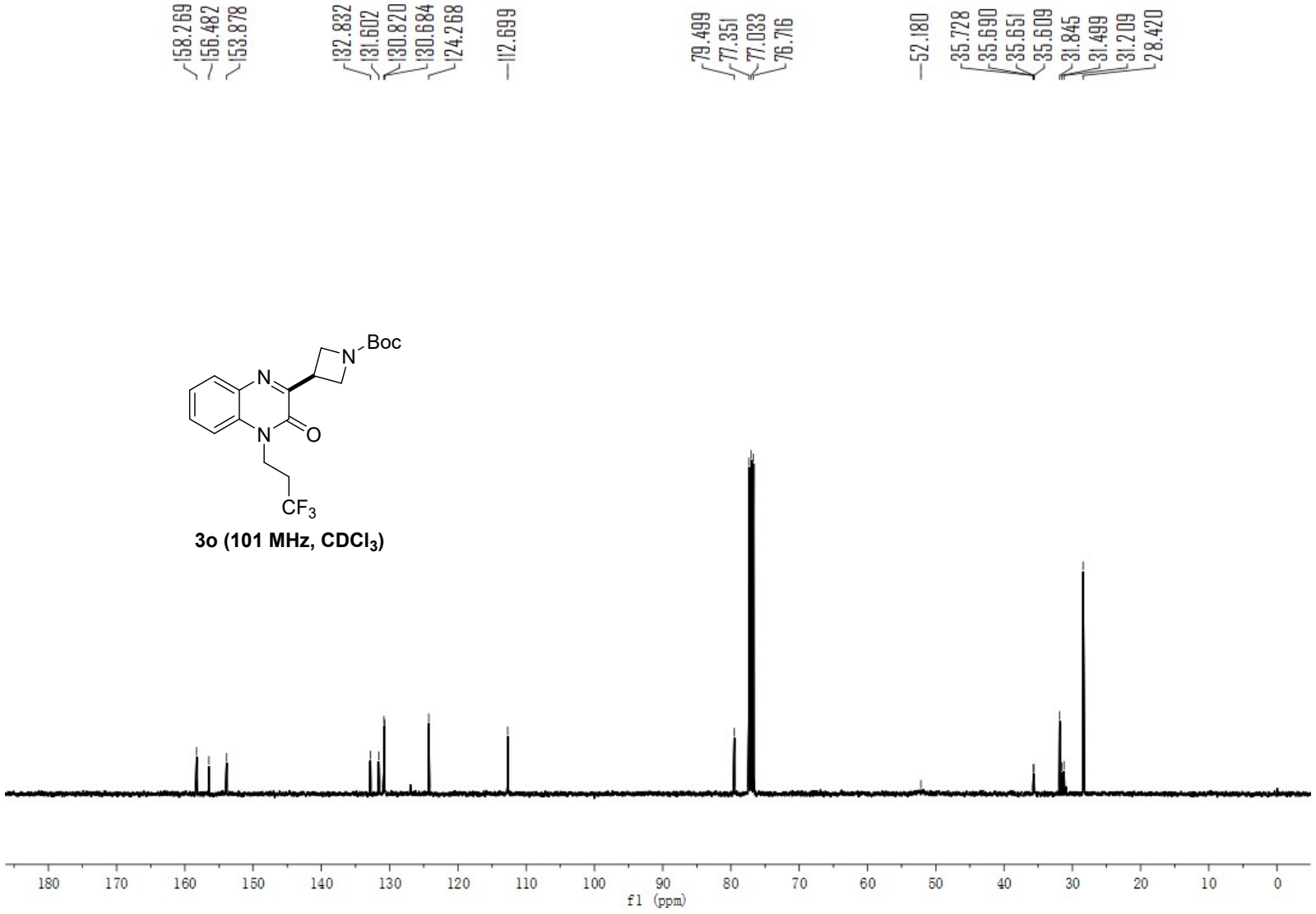

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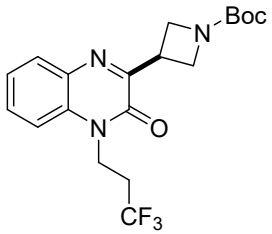

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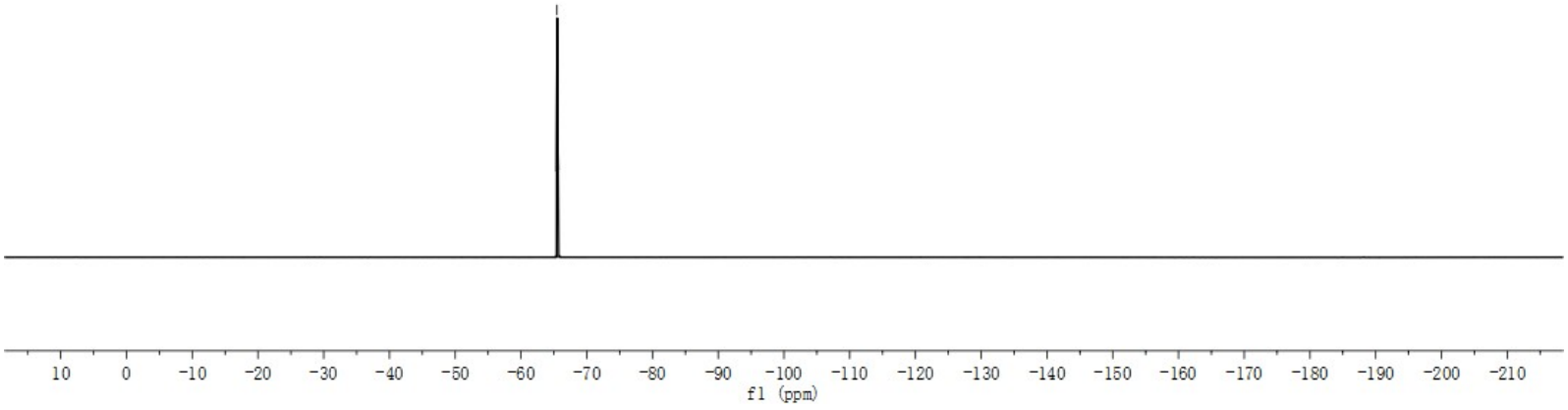

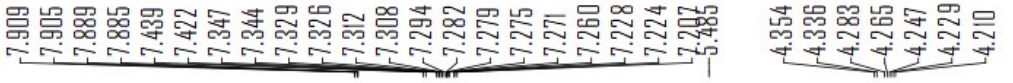

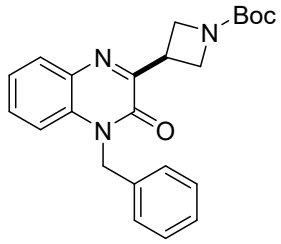

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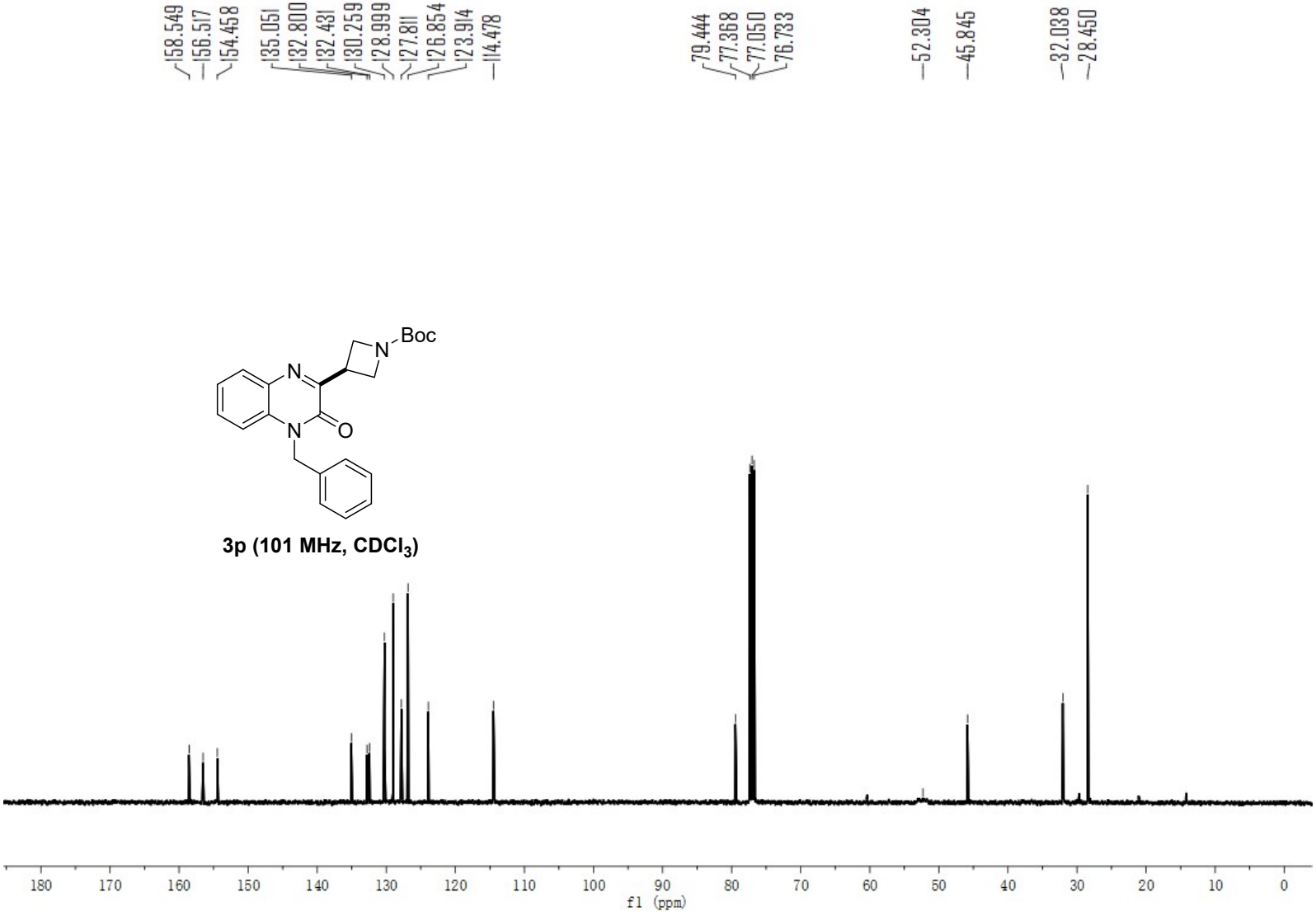

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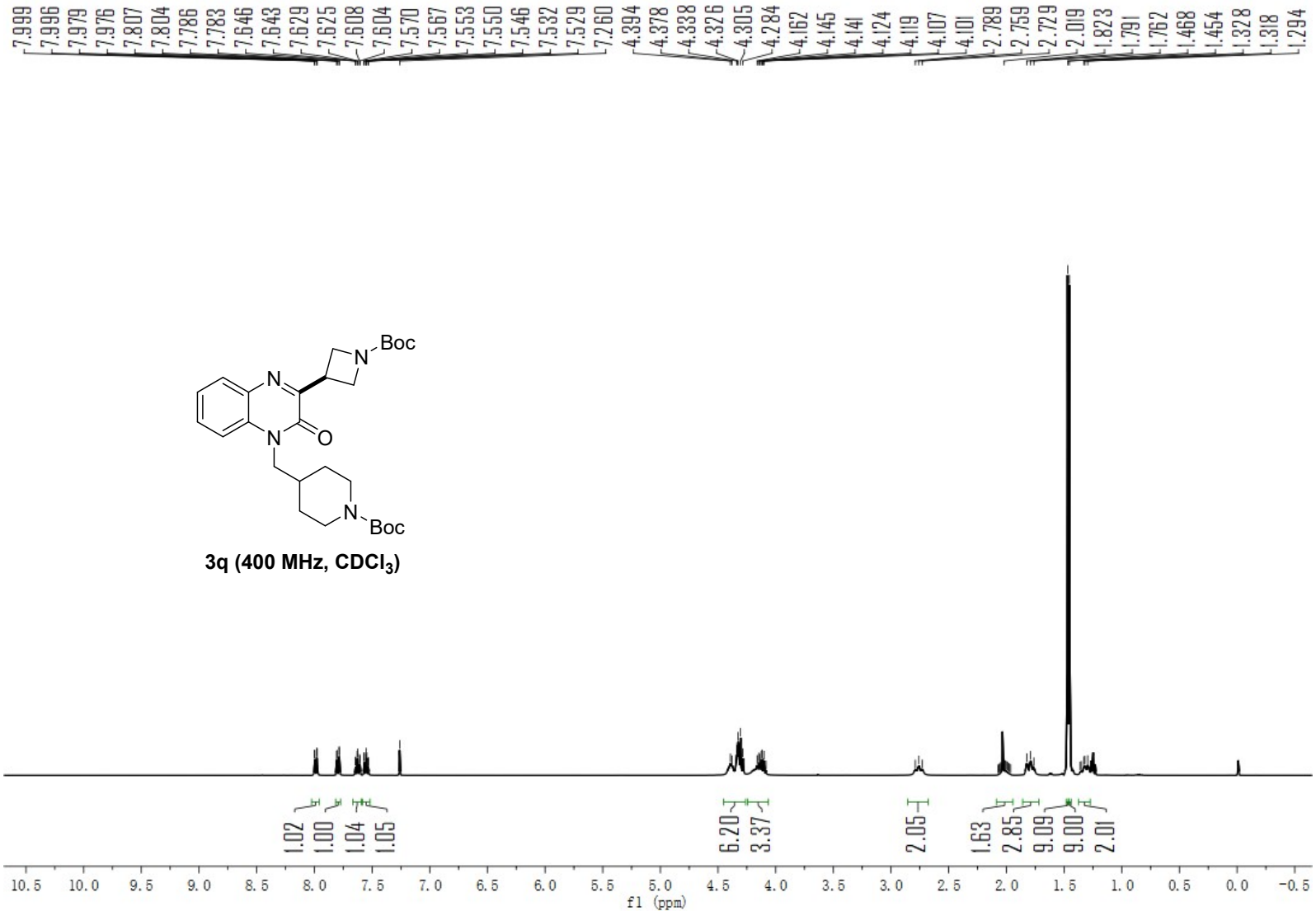

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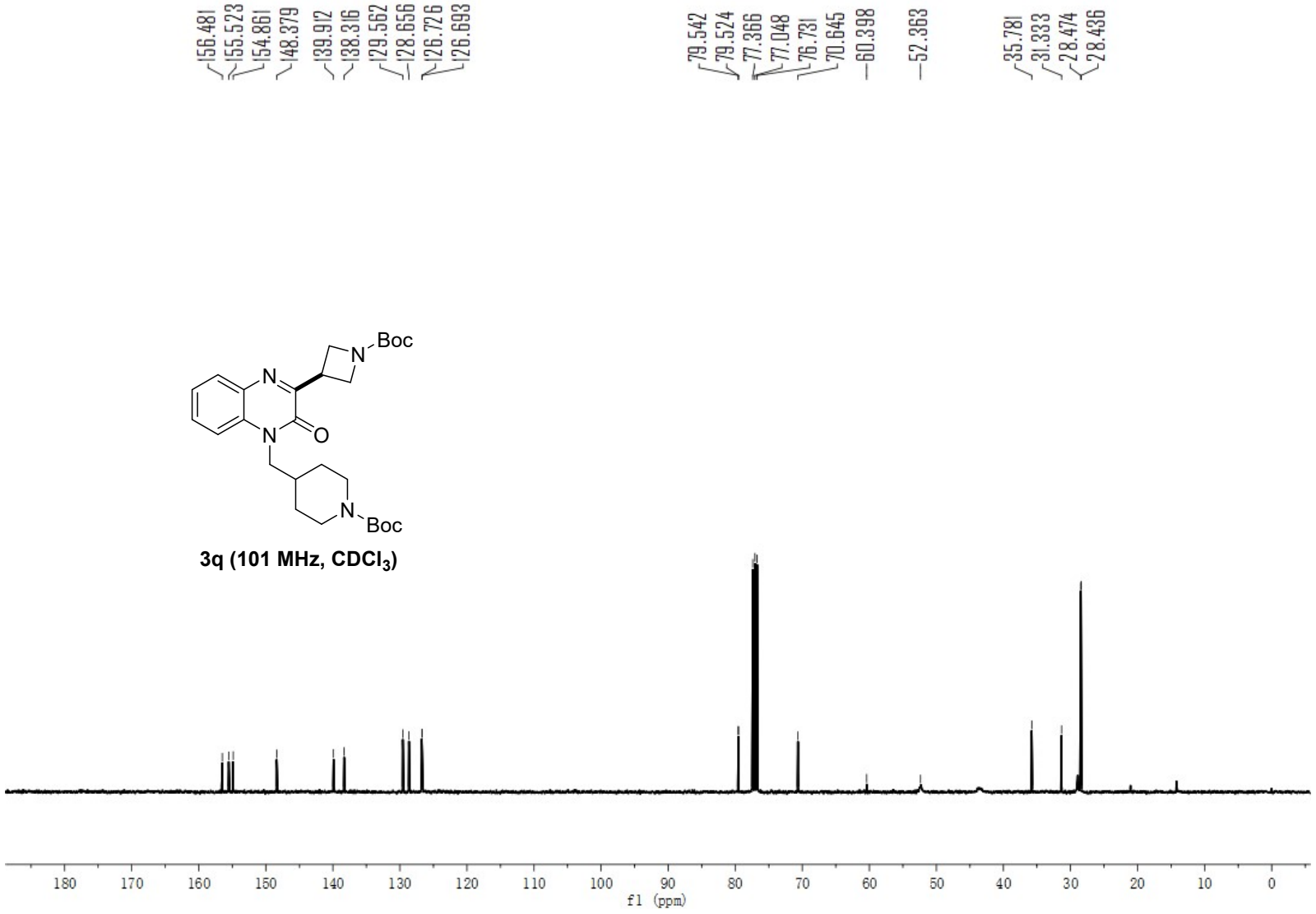

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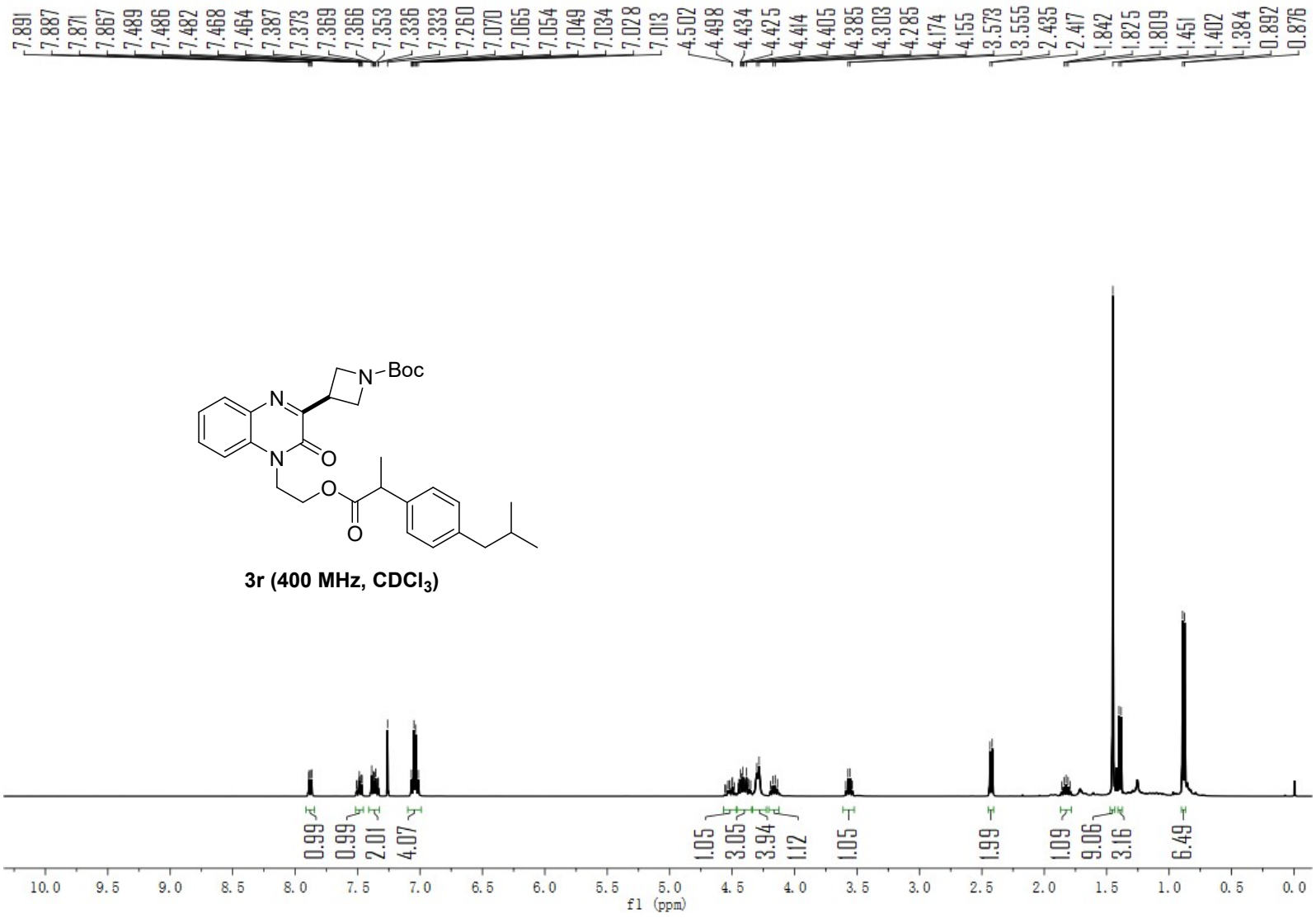
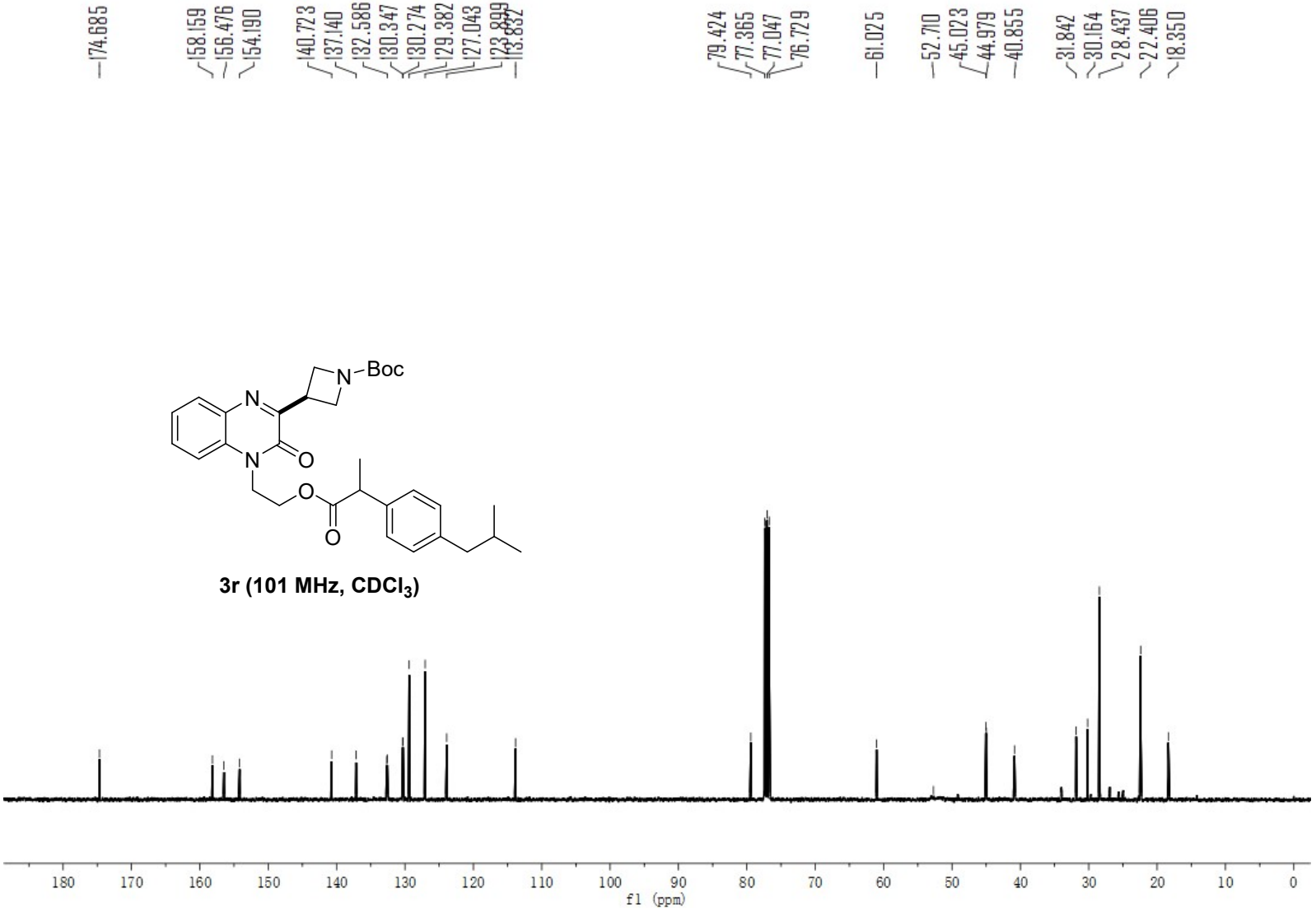
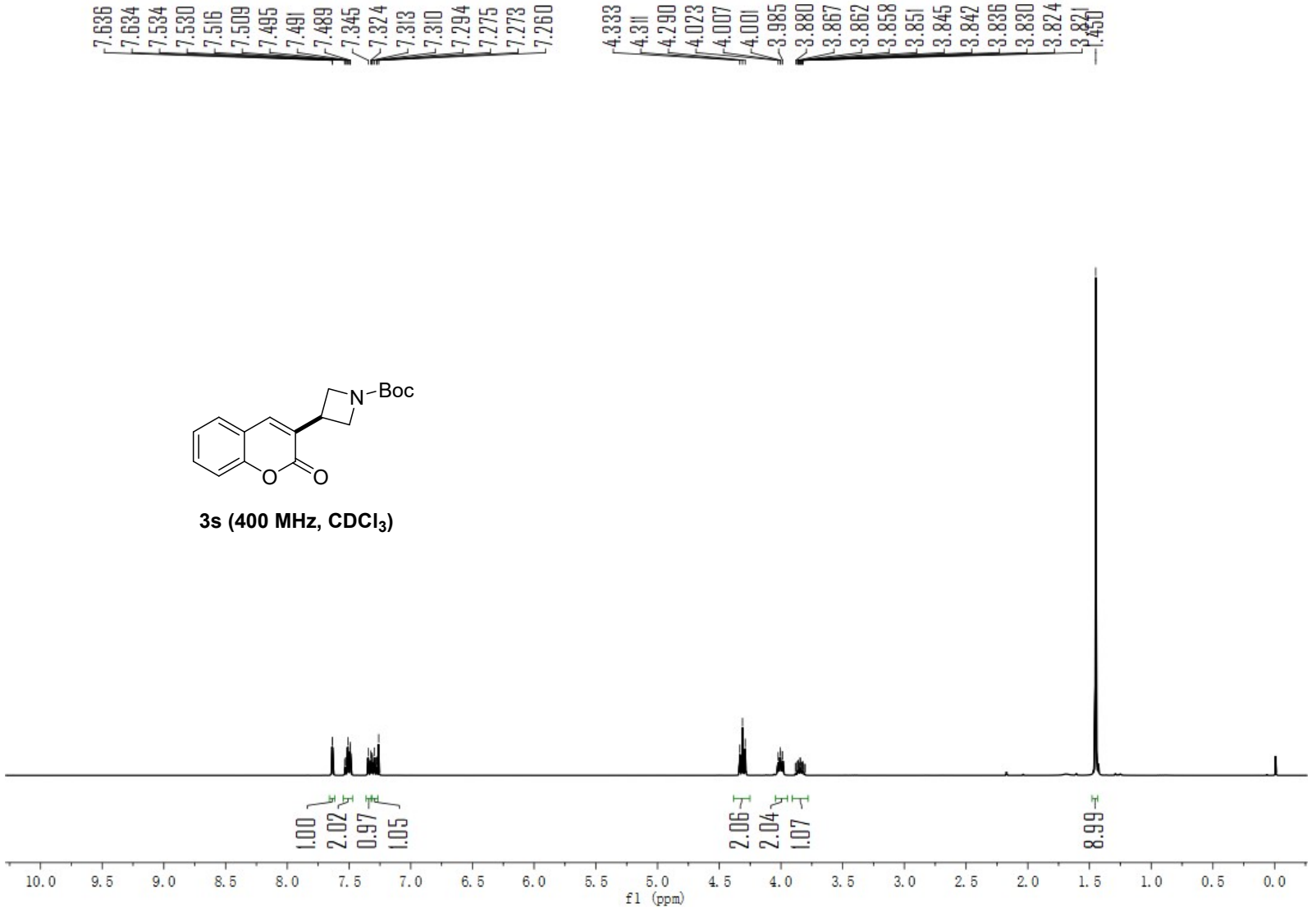


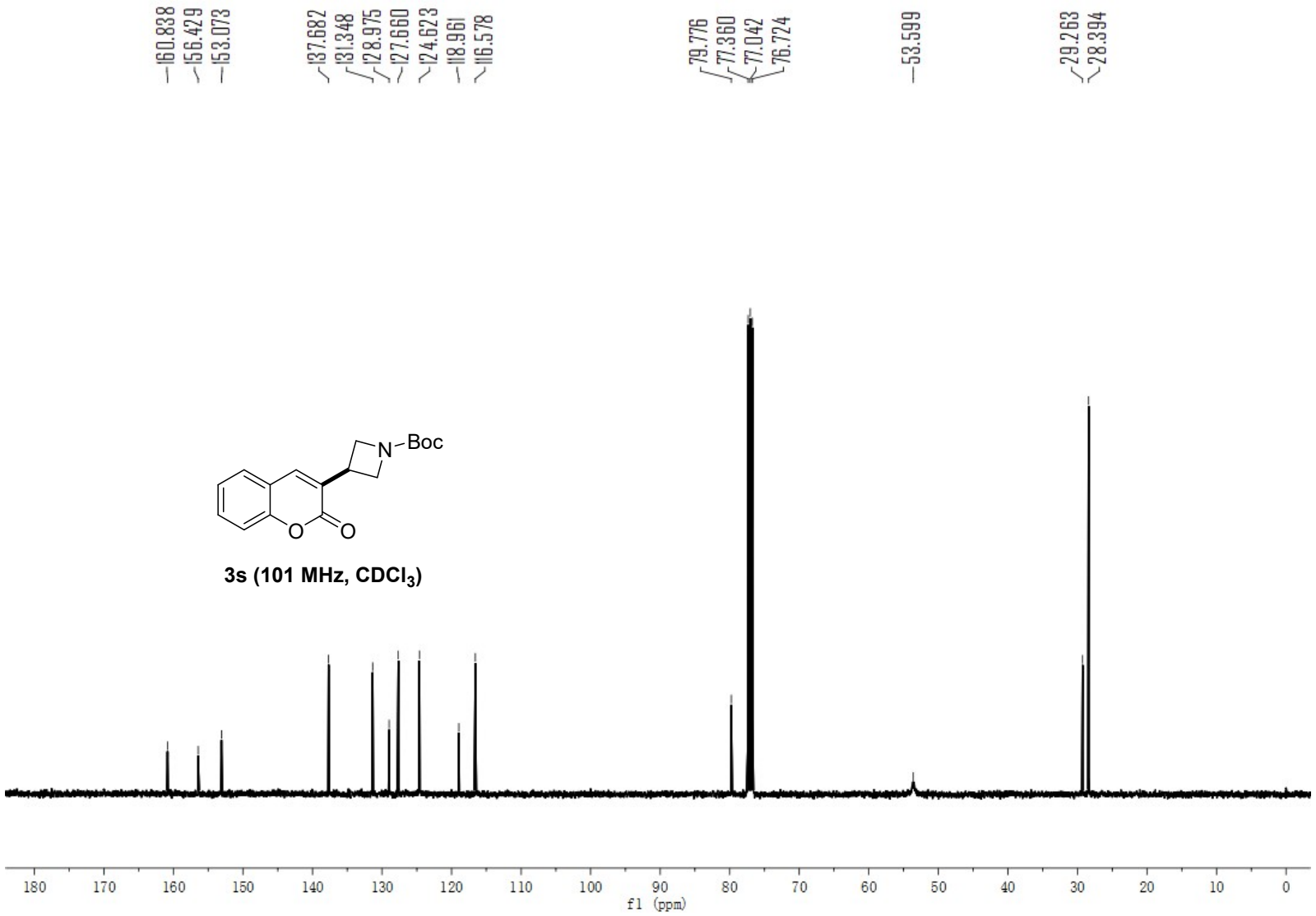
3r (400 MHz, $CDCl_3$)



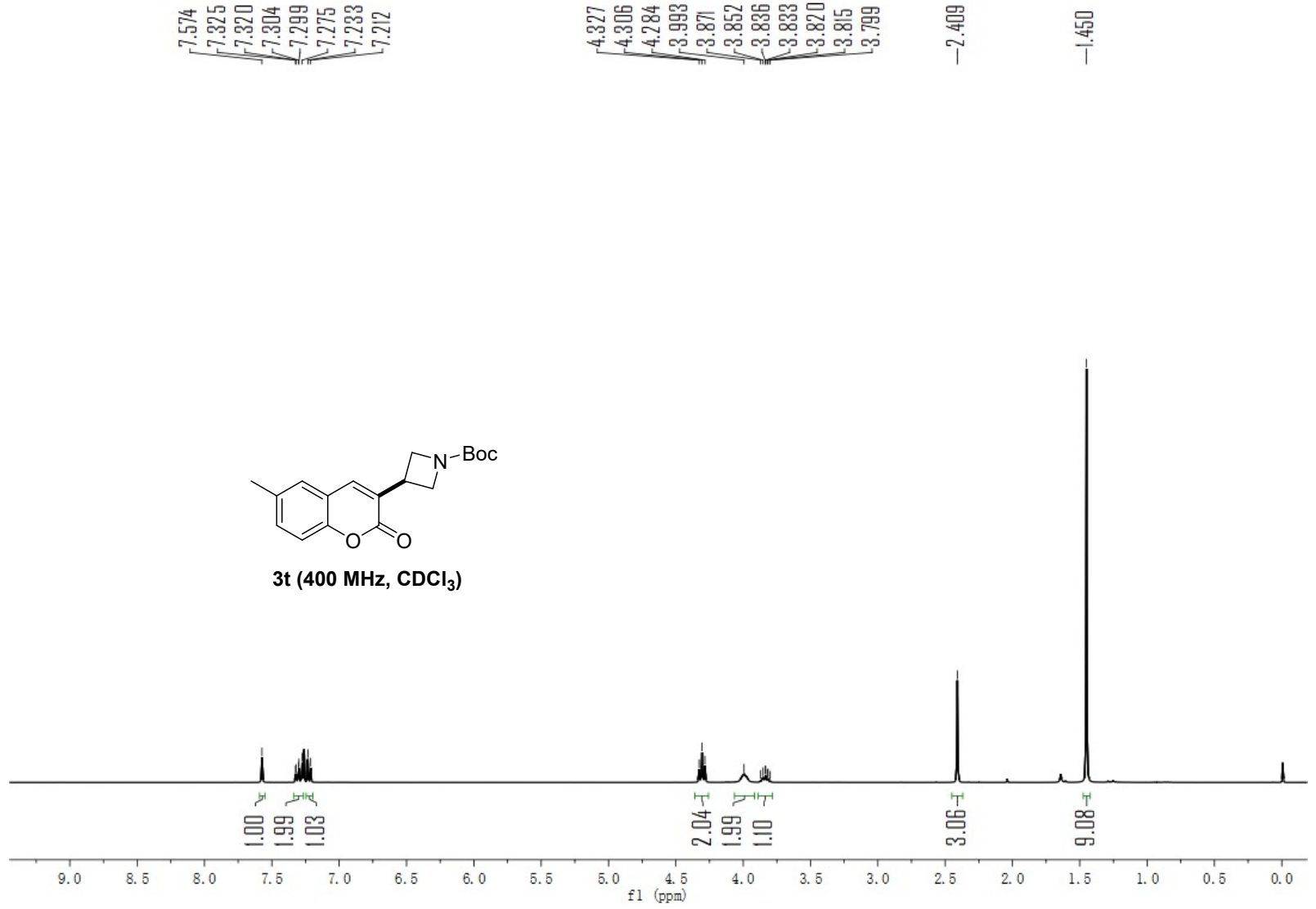
3r (101 MHz, $CDCl_3$)



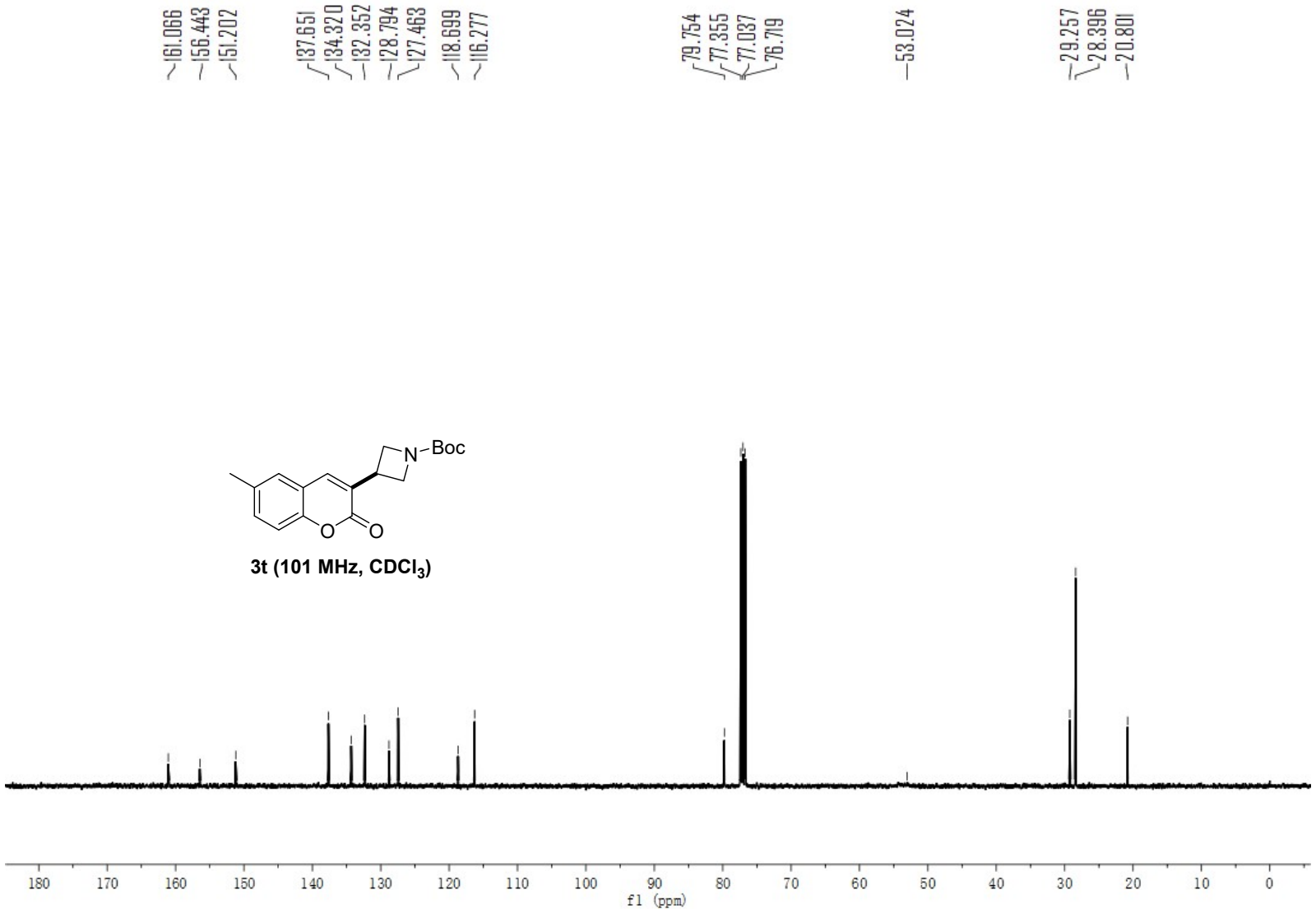
3s (400 MHz, $CDCl_3$)



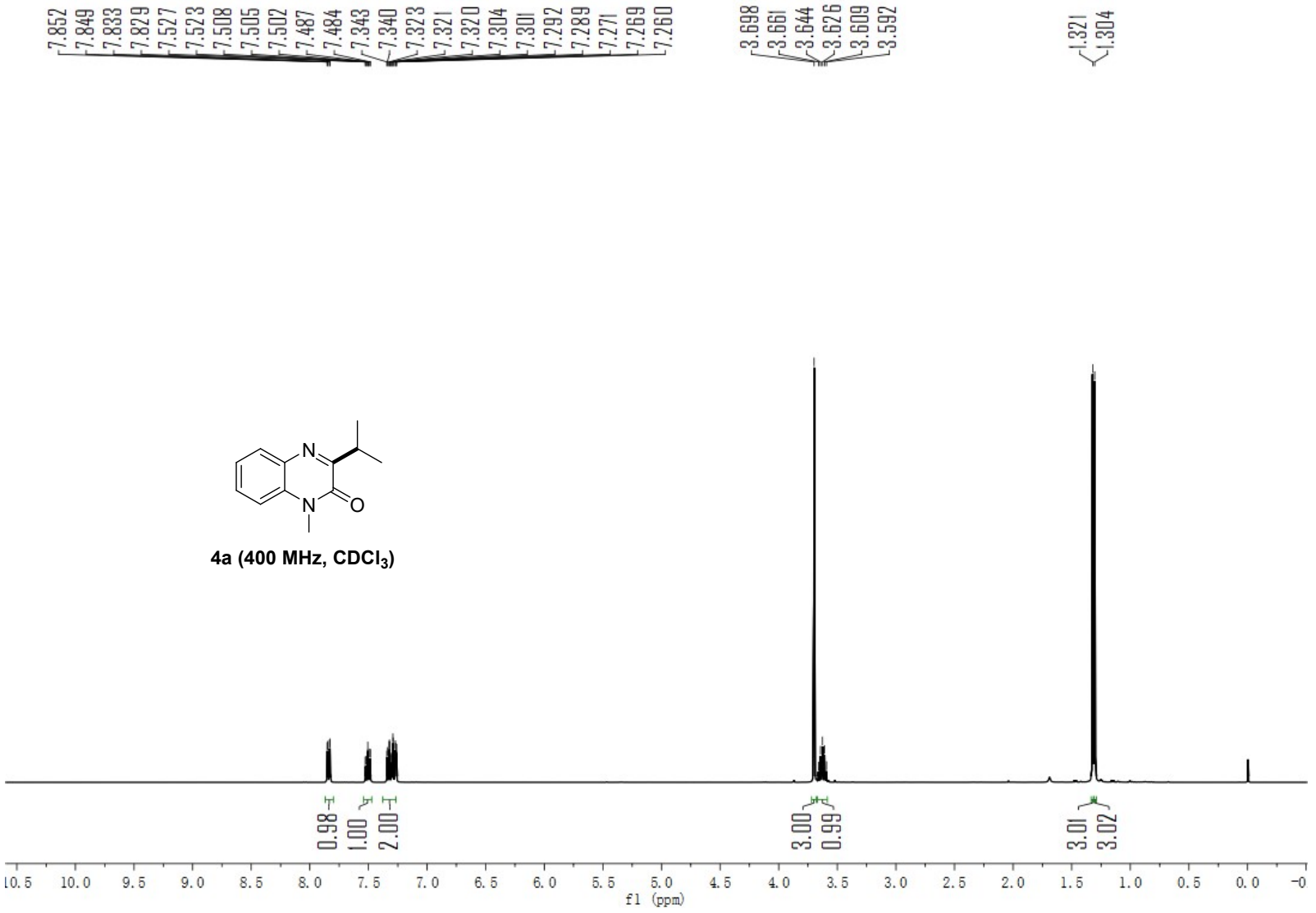
3s (101 MHz, $CDCl_3$)



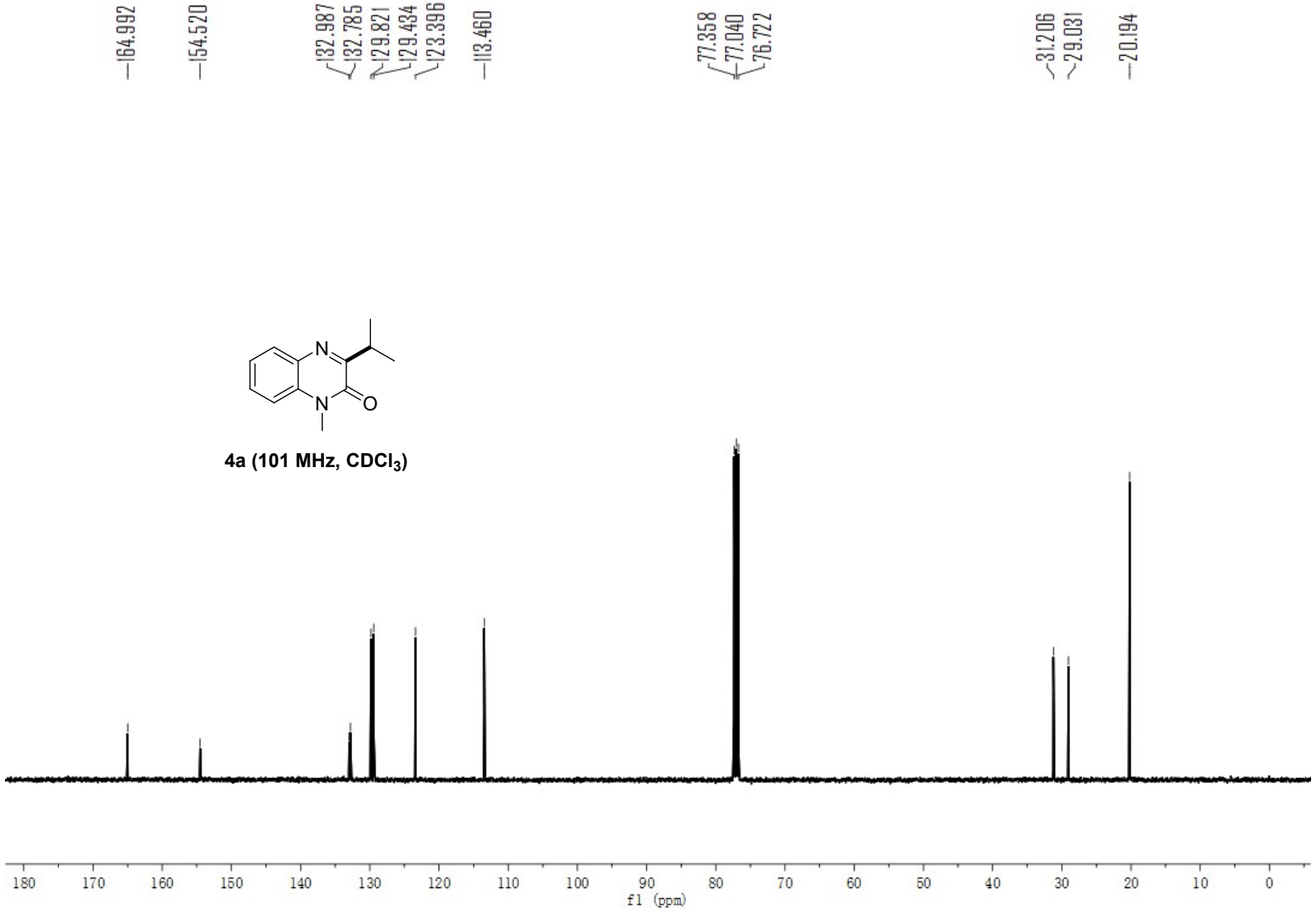
3t (400 MHz, $CDCl_3$)



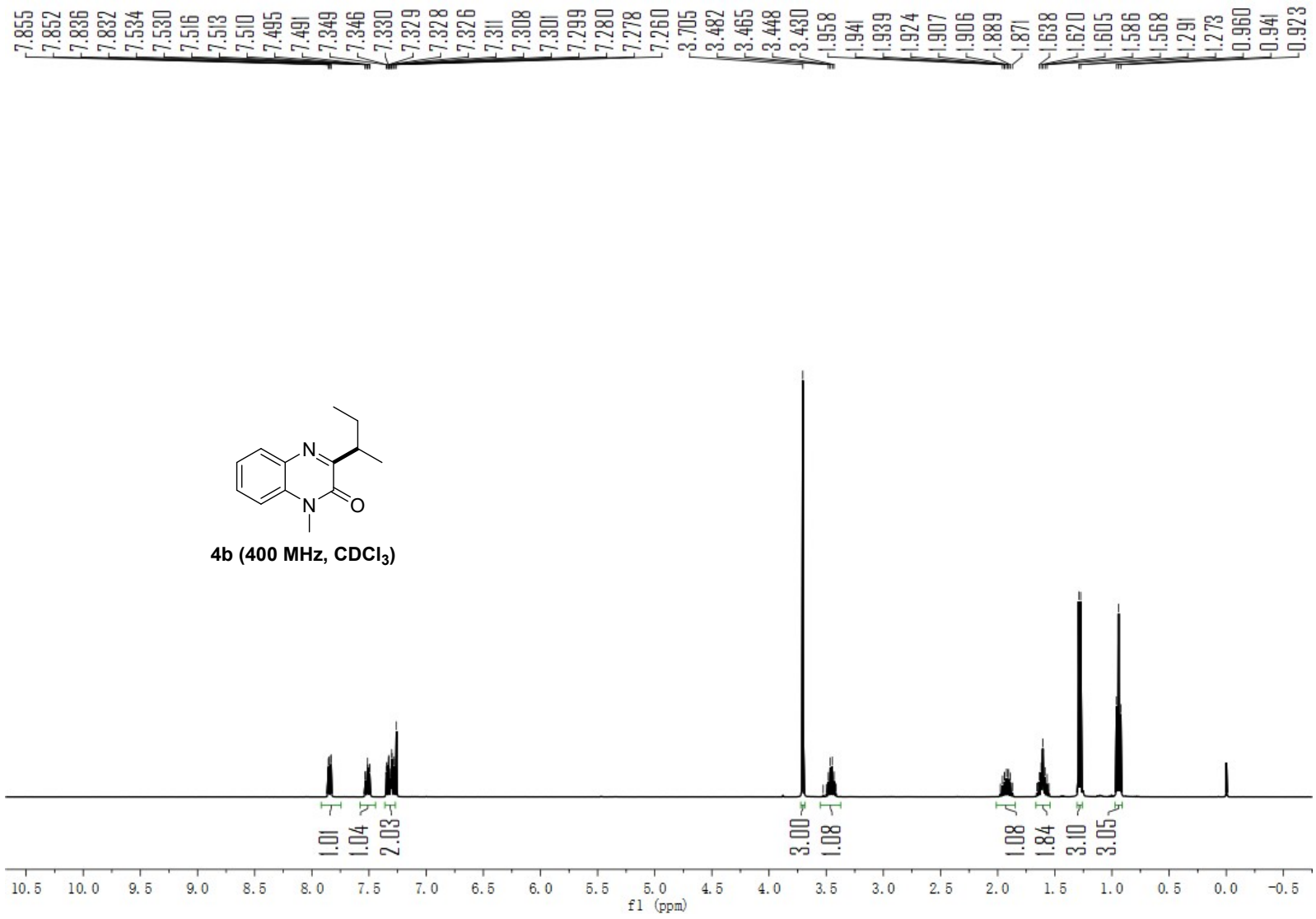
3t (101 MHz, $CDCl_3$)

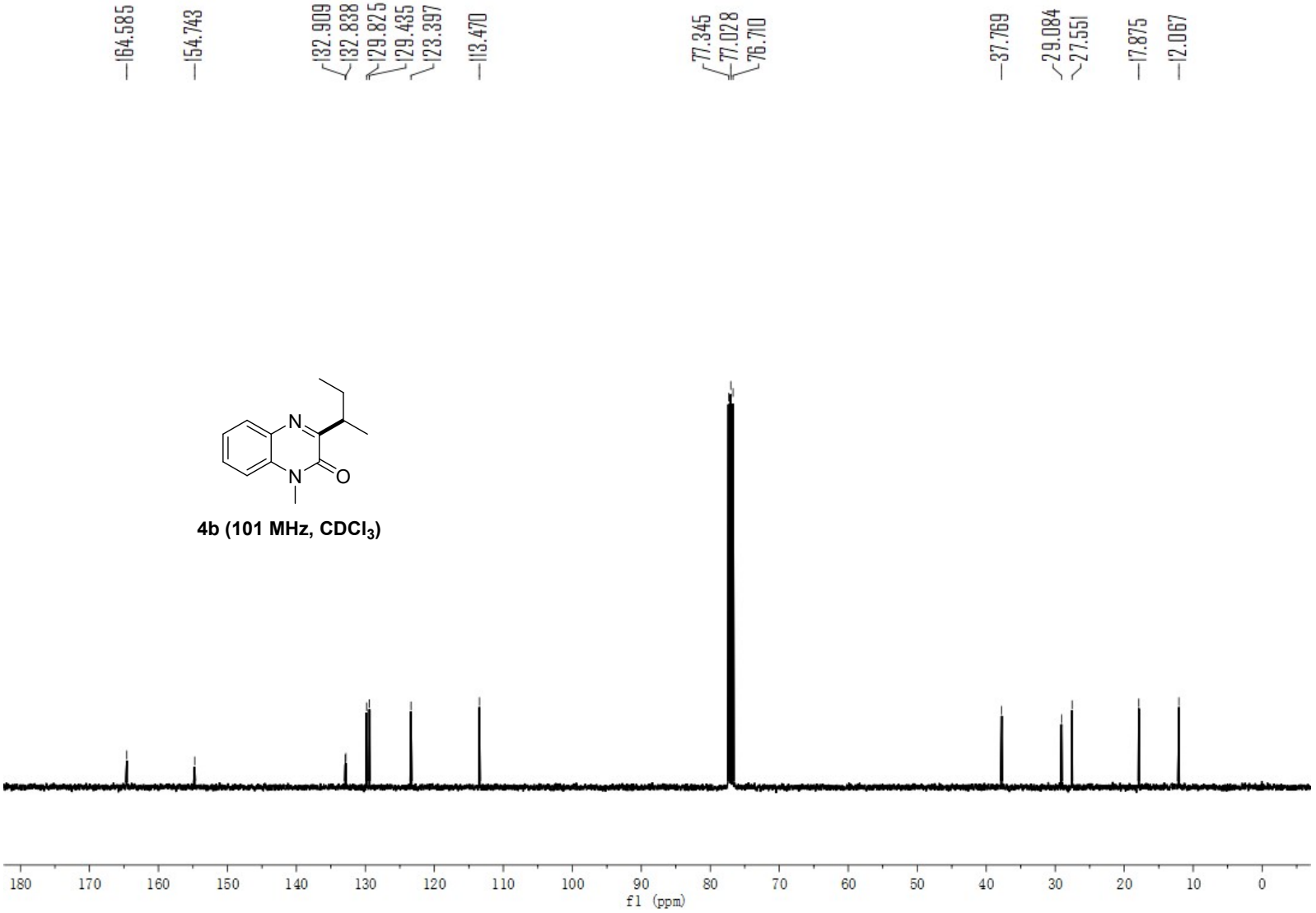


4a (400 MHz, $CDCl_3$)

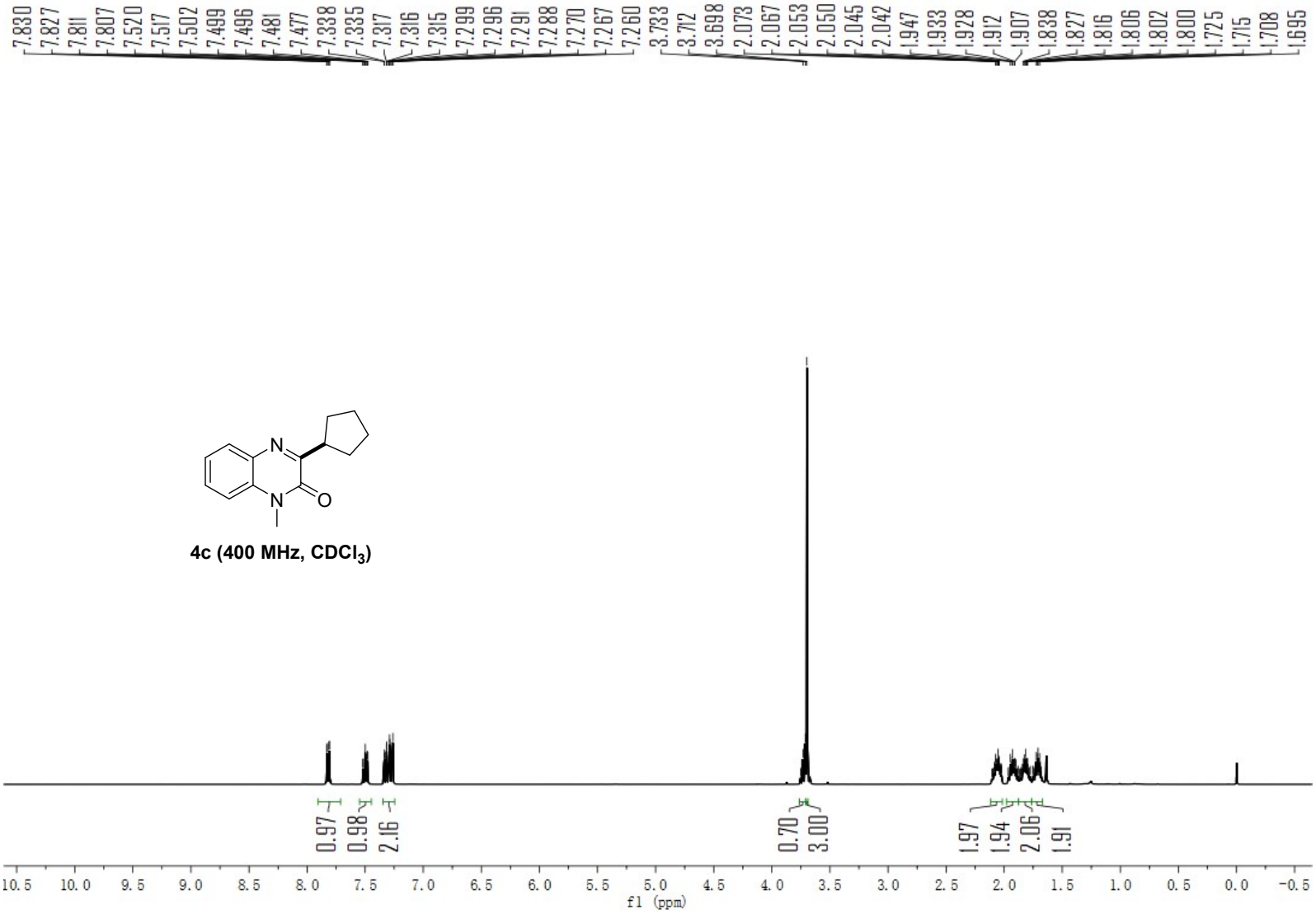


4a (101 MHz, $CDCl_3$)

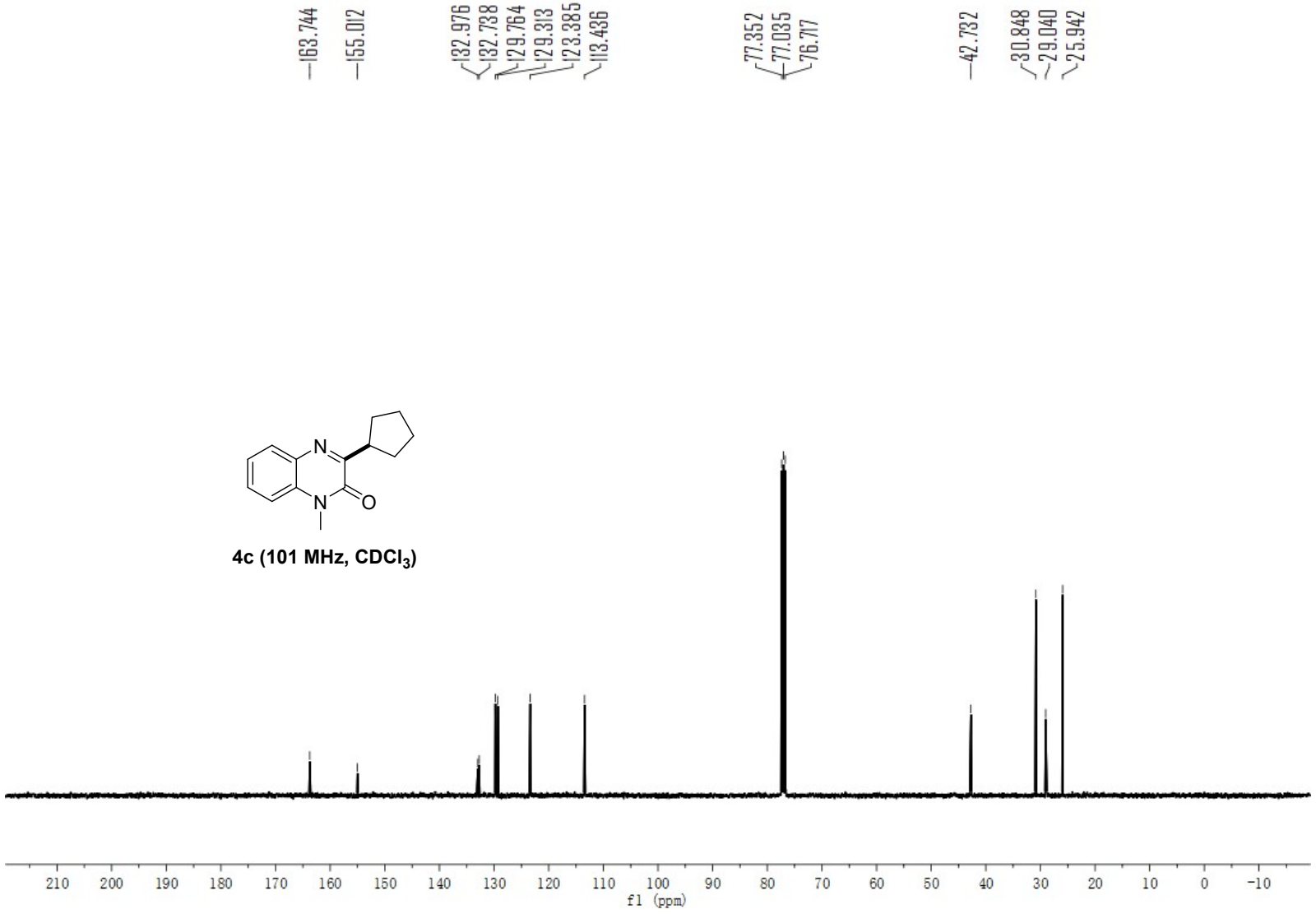

7.855
7.852
7.836
7.832
7.534
7.530
7.516
7.513
7.510
7.495
7.491
7.349
7.346
7.330
7.329
7.328
7.326
7.311
7.308
7.301
7.299
7.280
7.278
7.260
3.705
3.482
3.465
3.448
3.430
1.958
1.941
1.939
1.924
1.907
1.906
1.889
1.871
1.638
1.620
1.605
1.586
1.568
1.291
1.273
0.960
0.941
0.923
N
N
O
4b (400 MHz, CDCl3)
1.01
1.04
2.03
3.00
1.08
1.08
1.84
3.10
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)



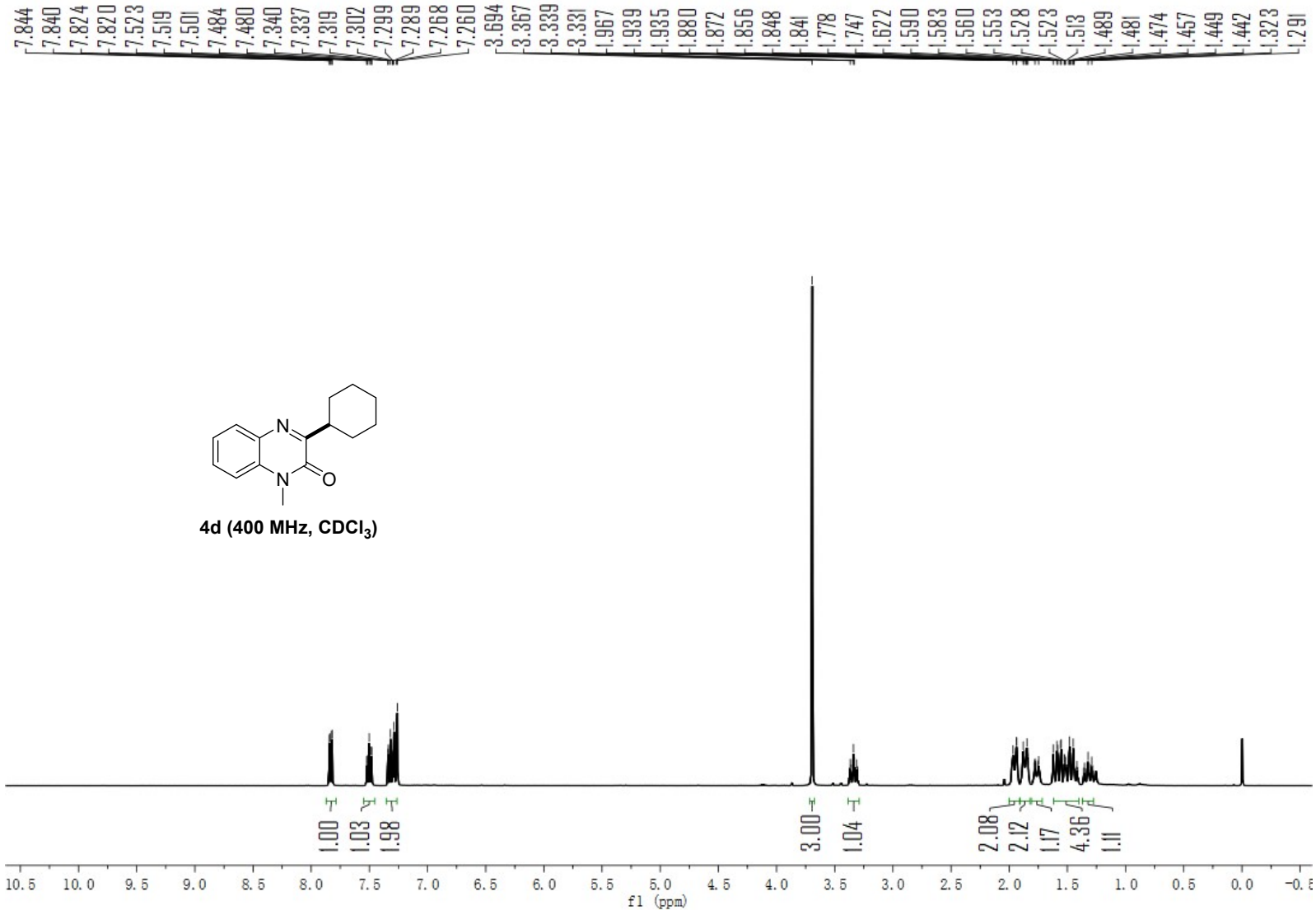
4b (101 MHz, $CDCl_3$)



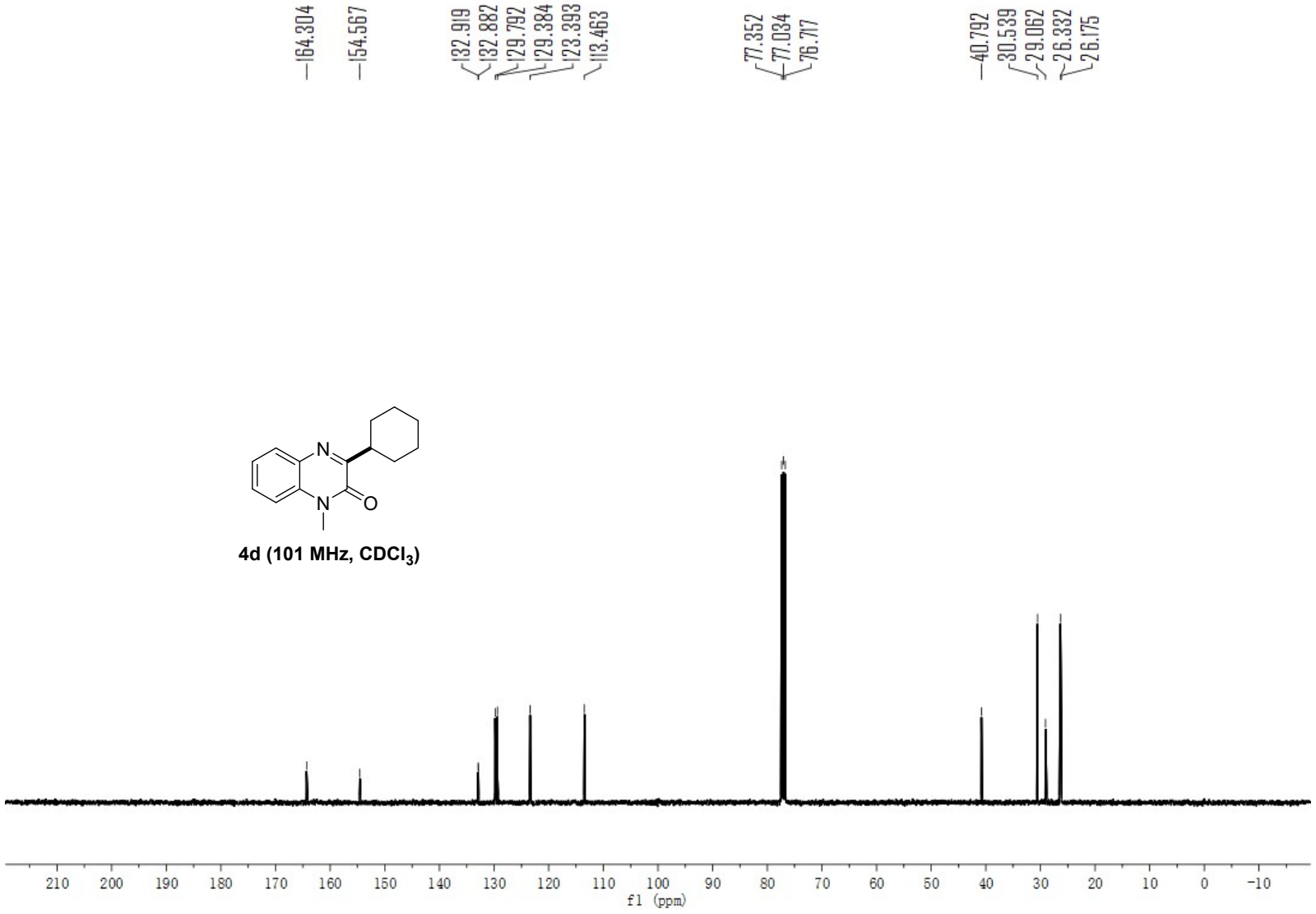
4c (400 MHz, $CDCl_3$)



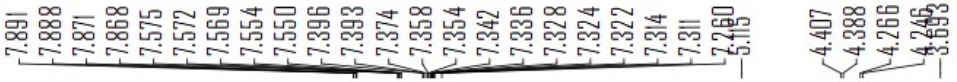
4c (101 MHz, $CDCl_3$)

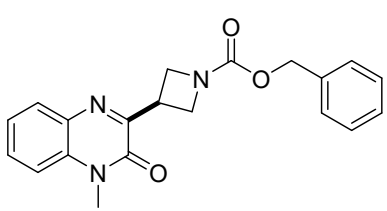


4d (400 MHz, $CDCl_3$)

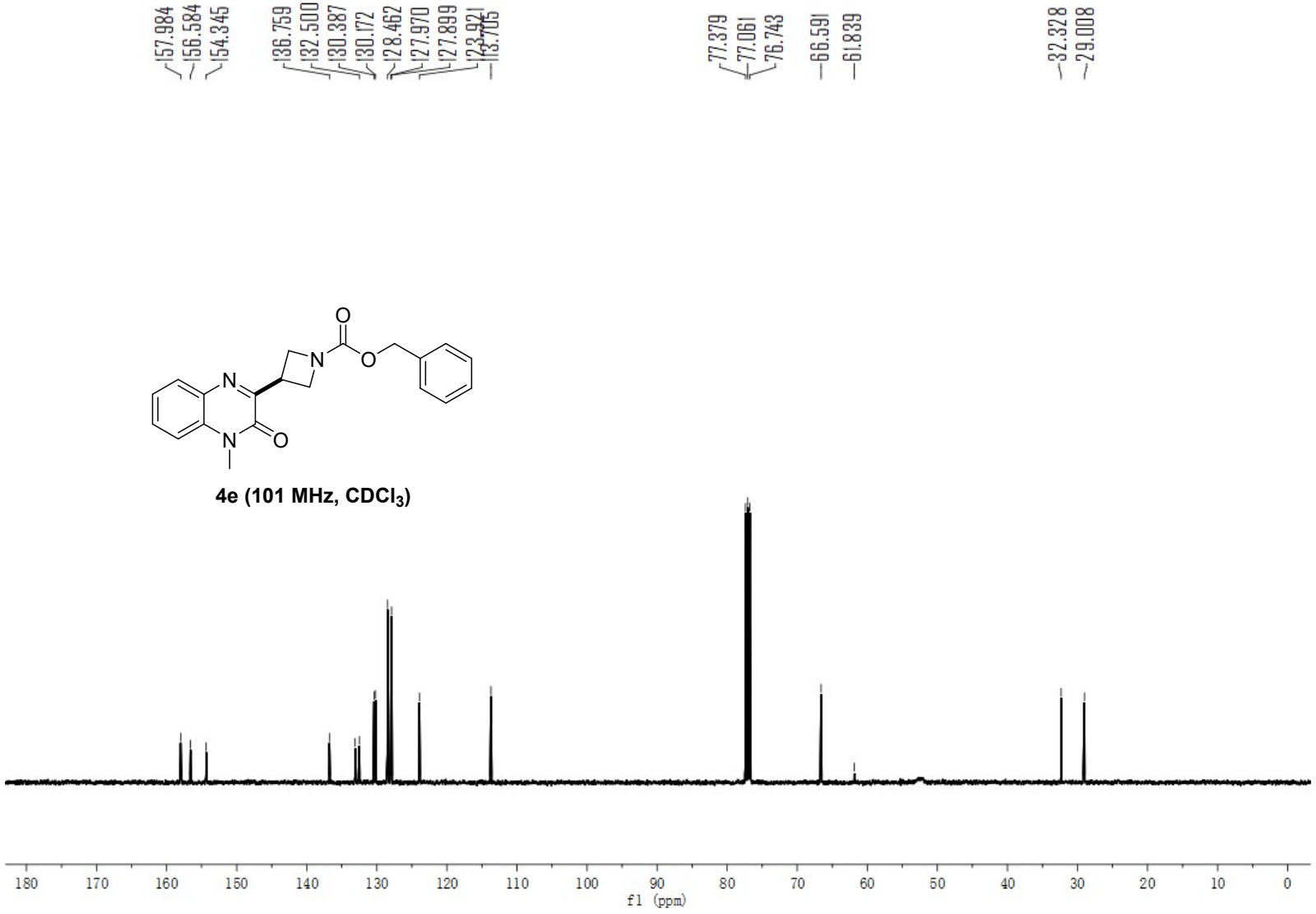


4d (101 MHz, $CDCl_3$)

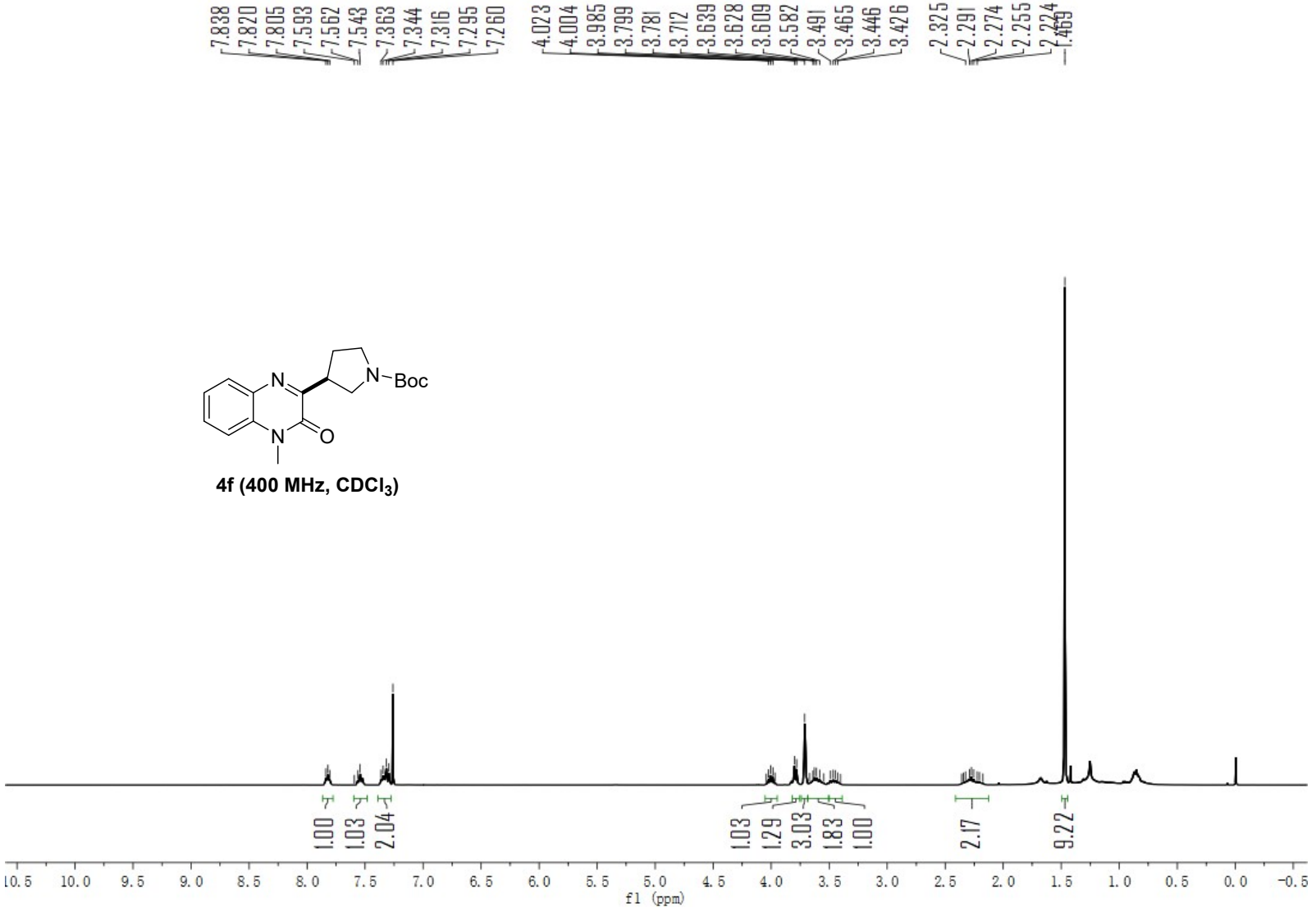




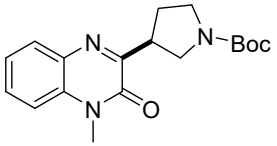
4e (400 MHz, $CDCl_3$)



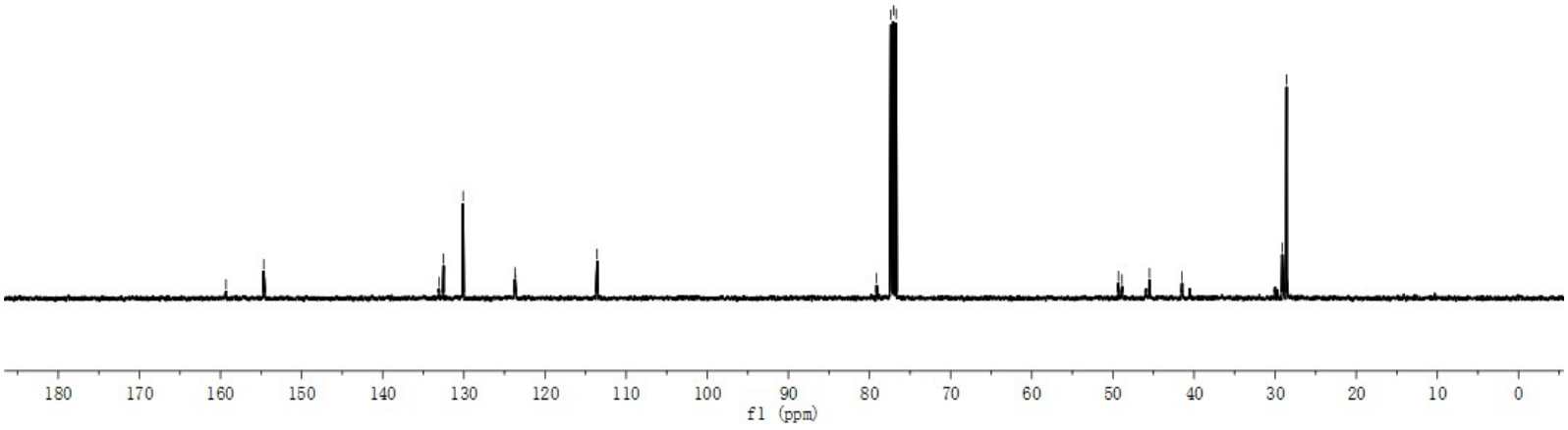
4e (101 MHz, $CDCl_3$)

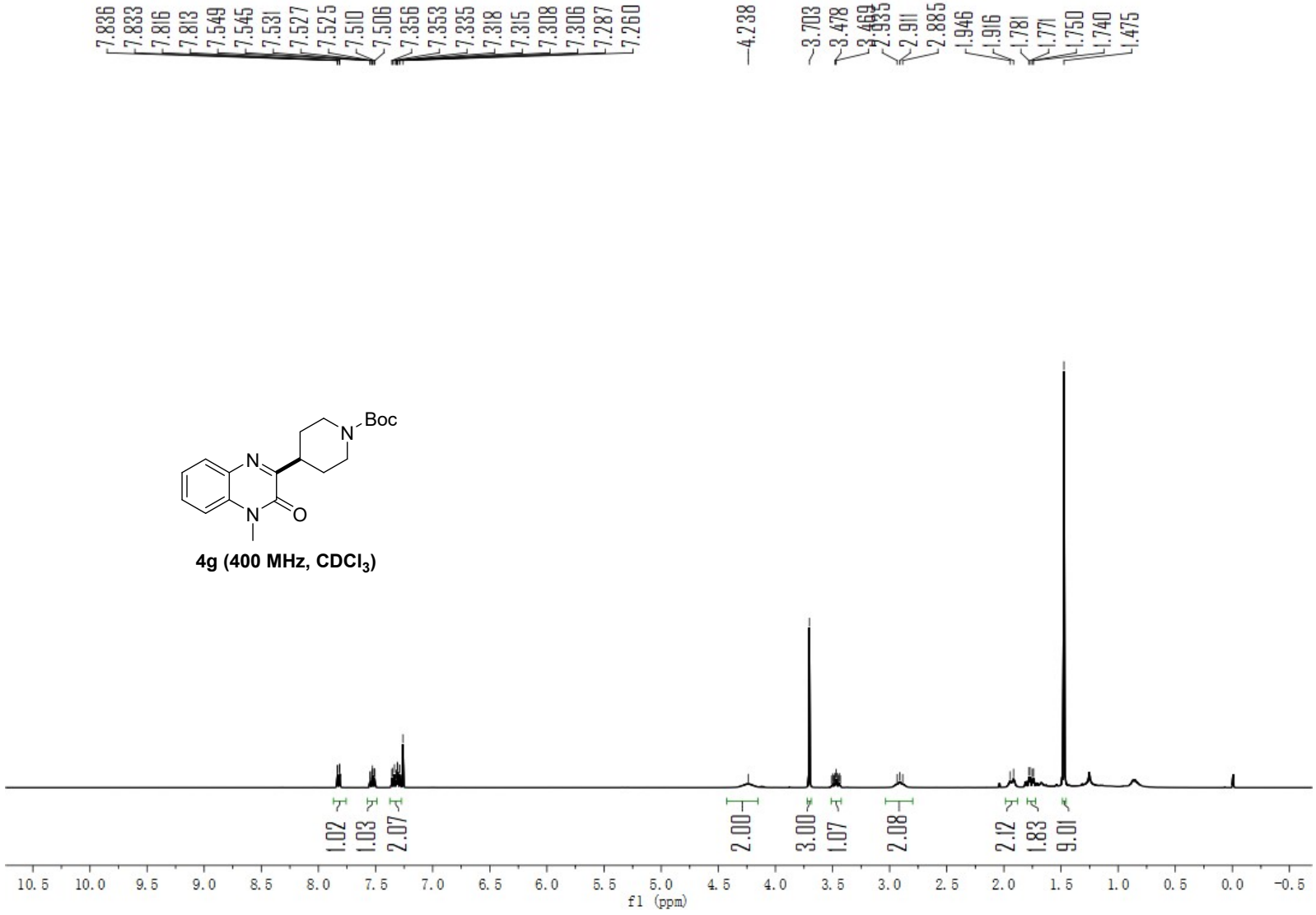


4f (400 MHz, $CDCl_3$)

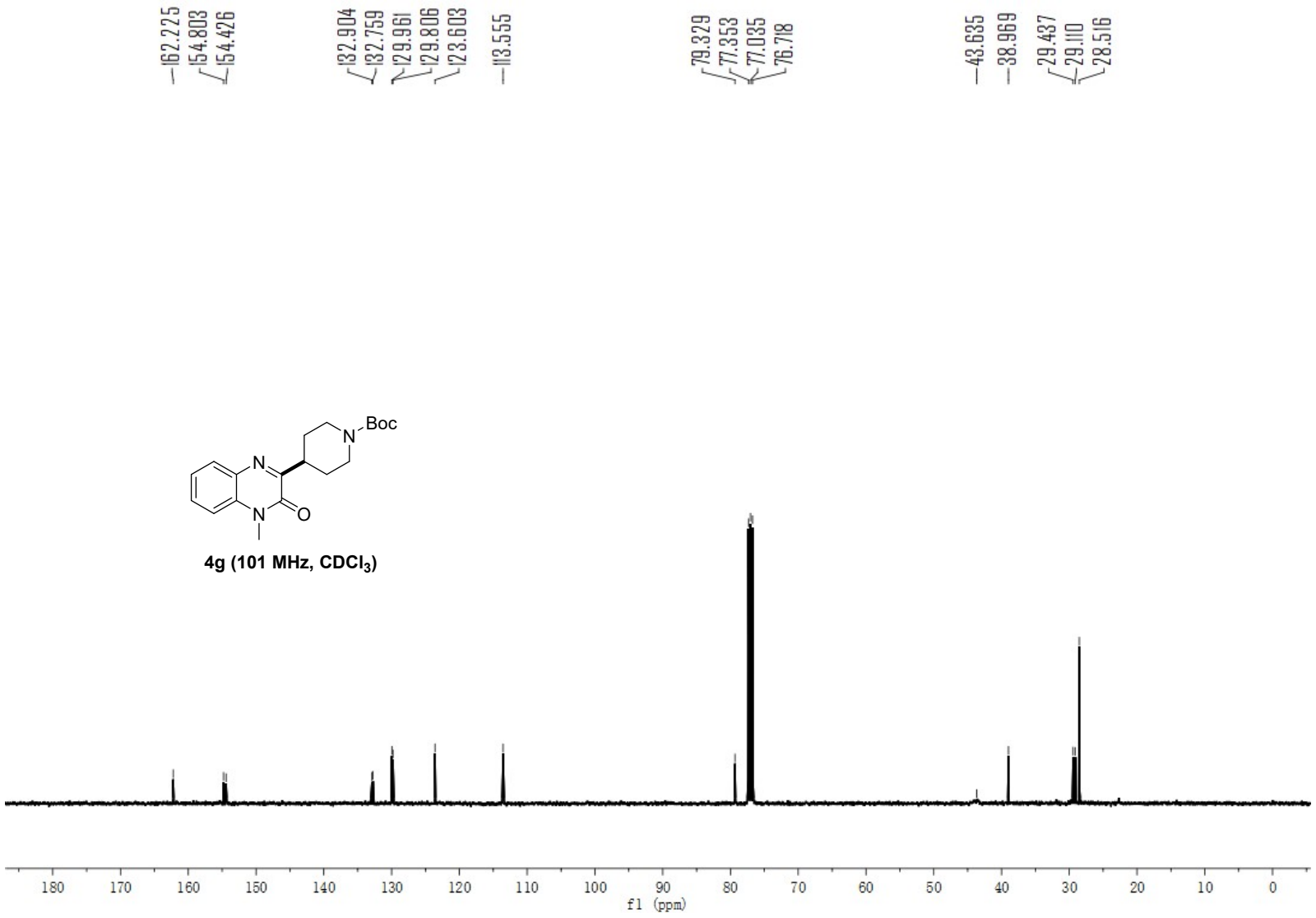


4f (101 MHz, $CDCl_3$)

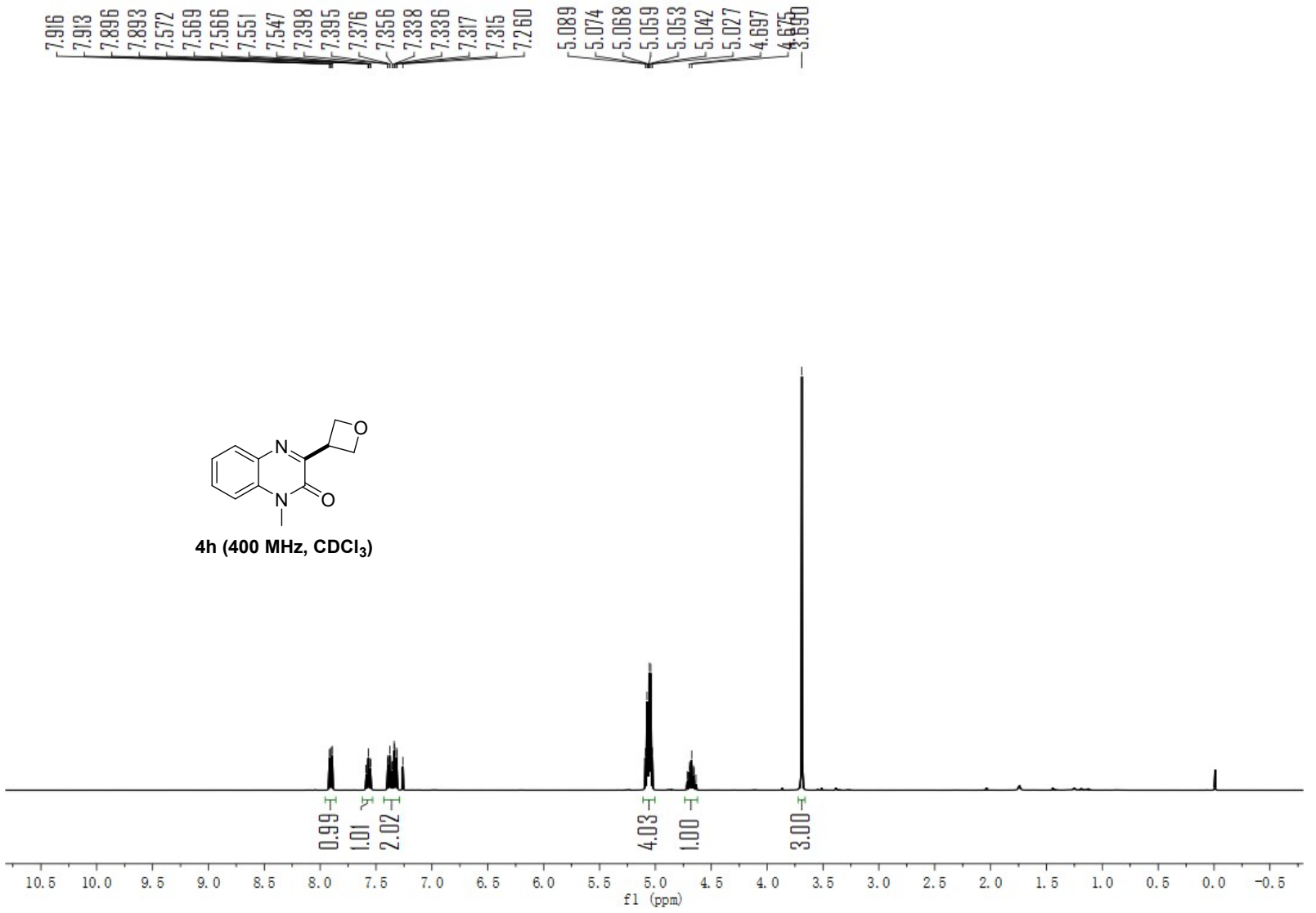




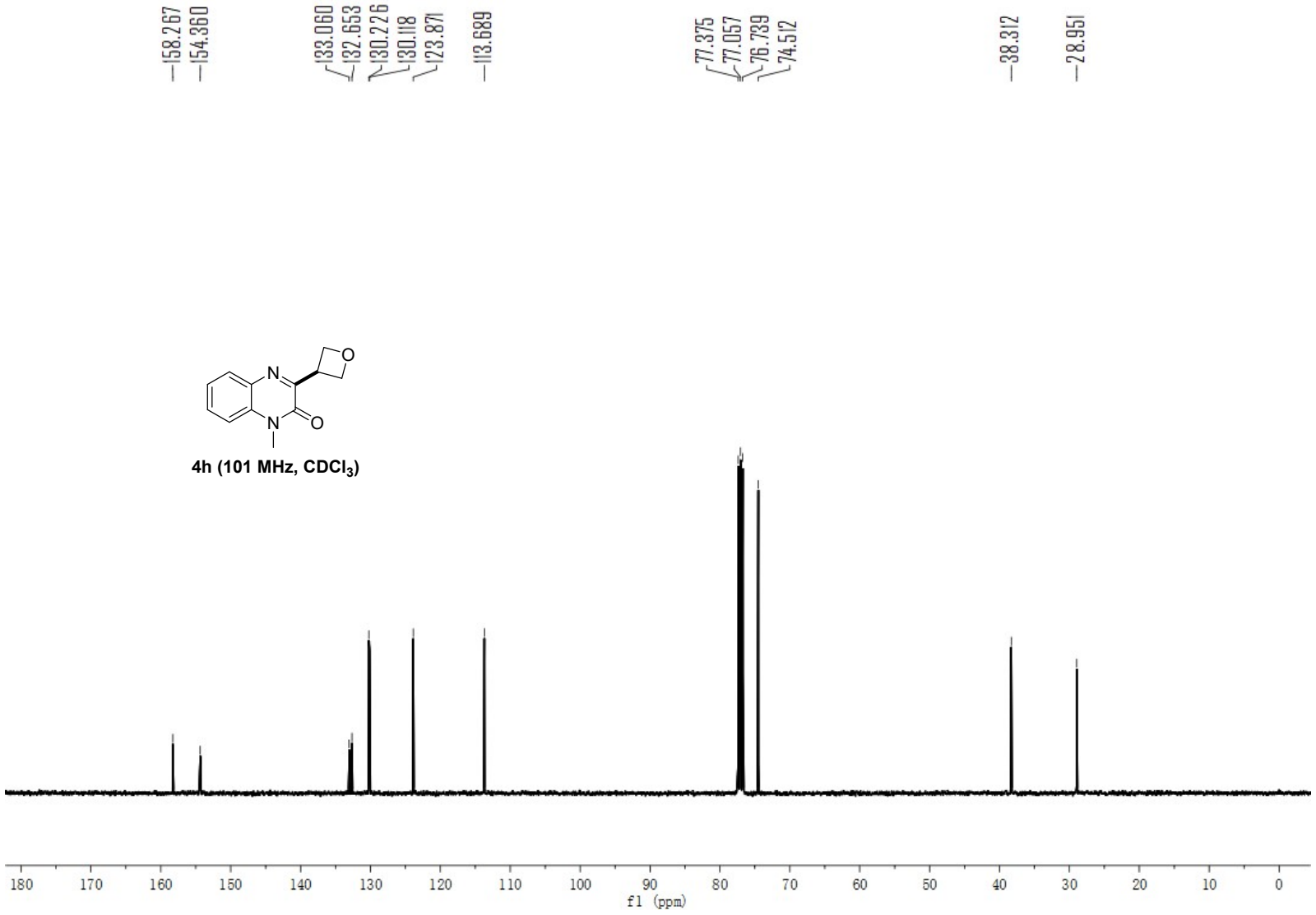
4g (400 MHz, $CDCl_3$)



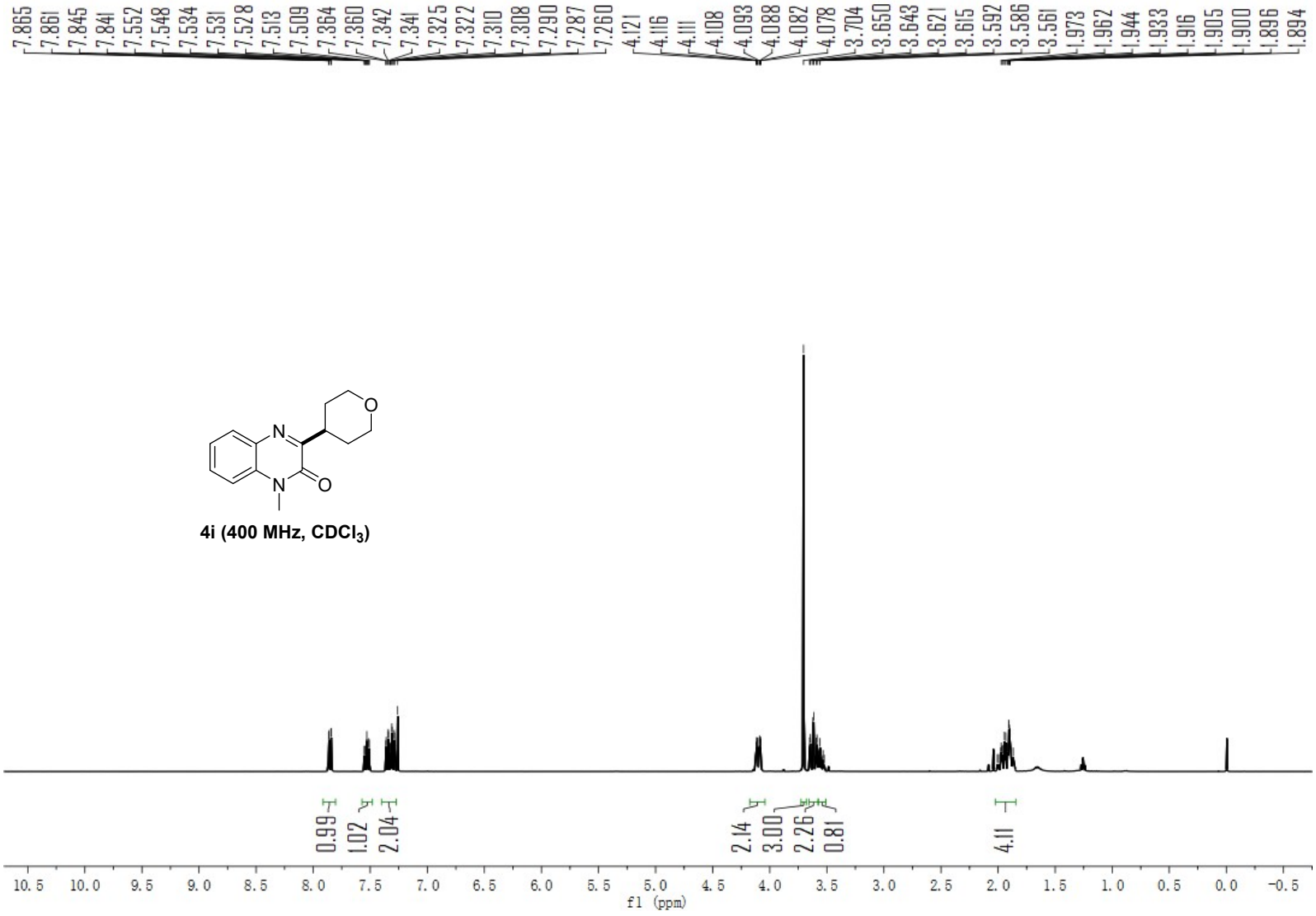
4g (101 MHz, $CDCl_3$)



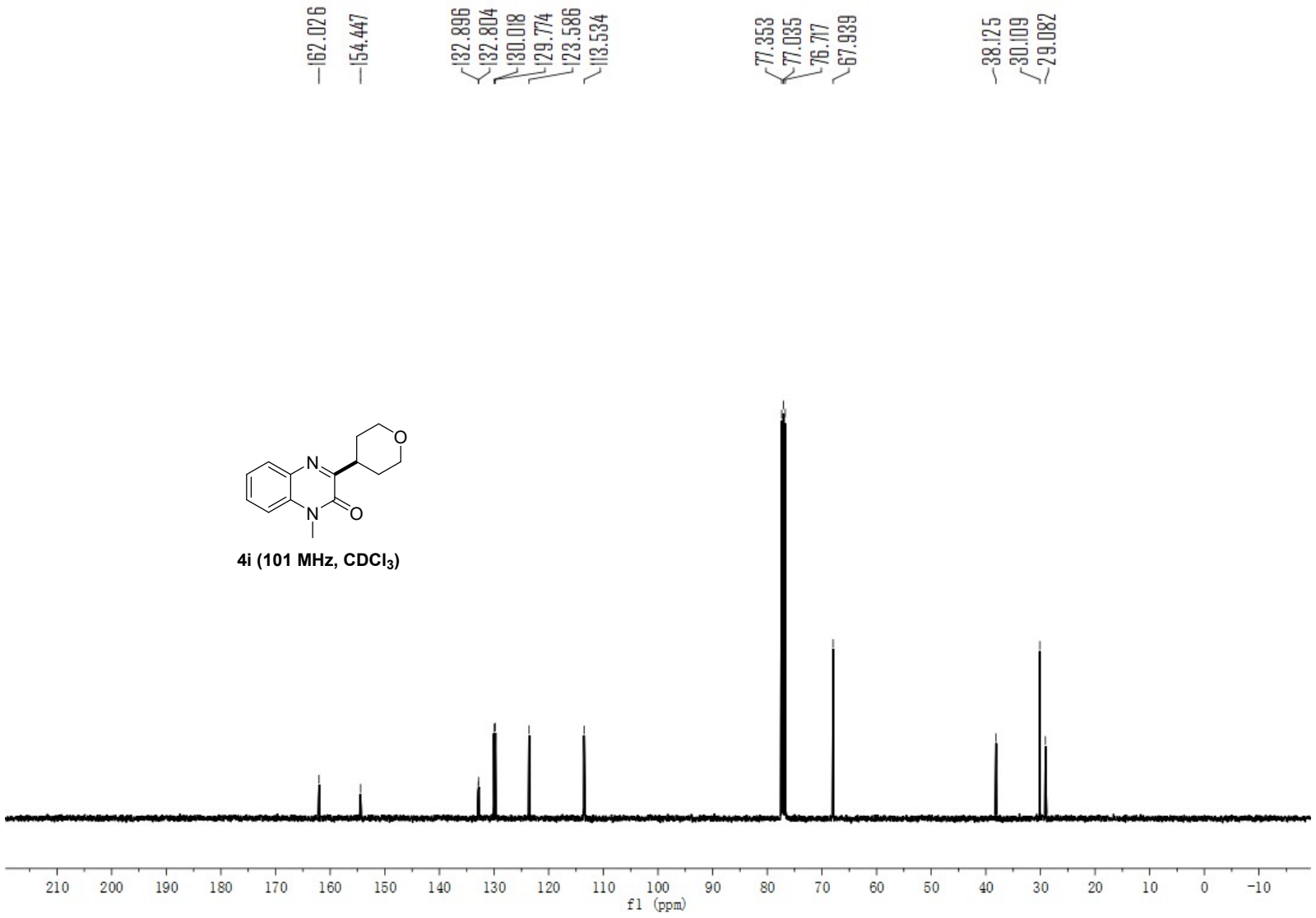
4h (400 MHz, $CDCl_3$)



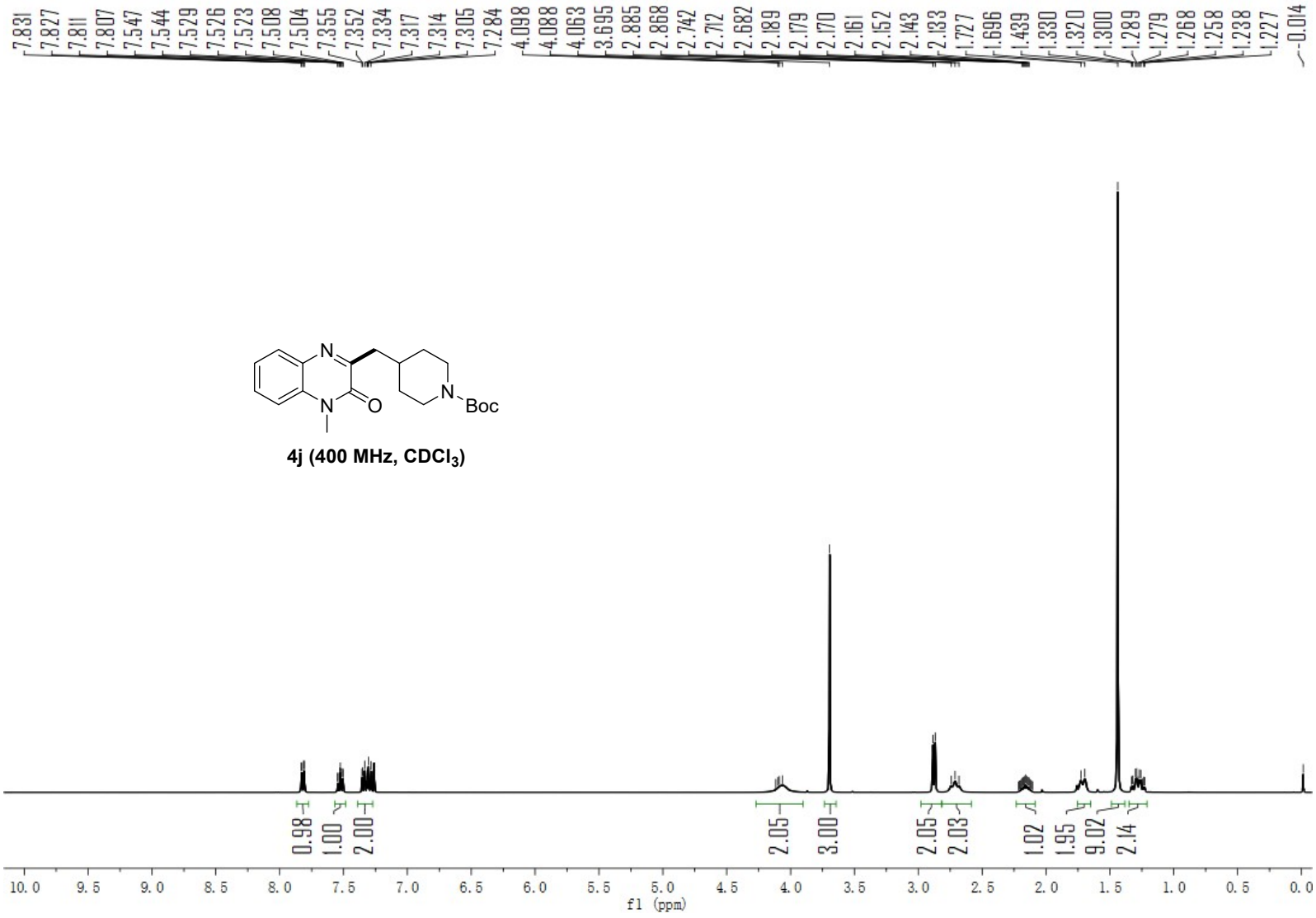
4h (101 MHz, $CDCl_3$)



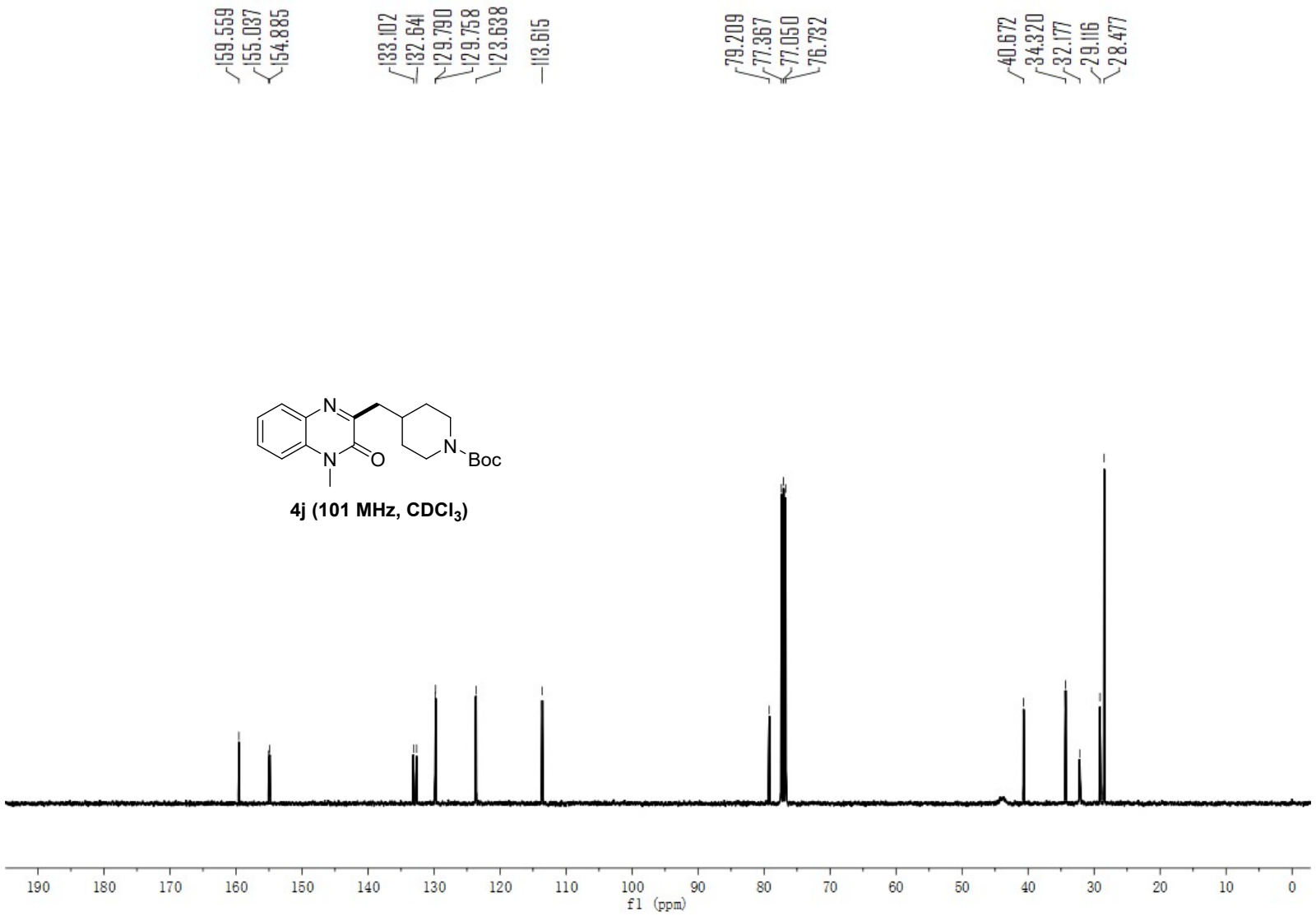
4i (400 MHz, $CDCl_3$)



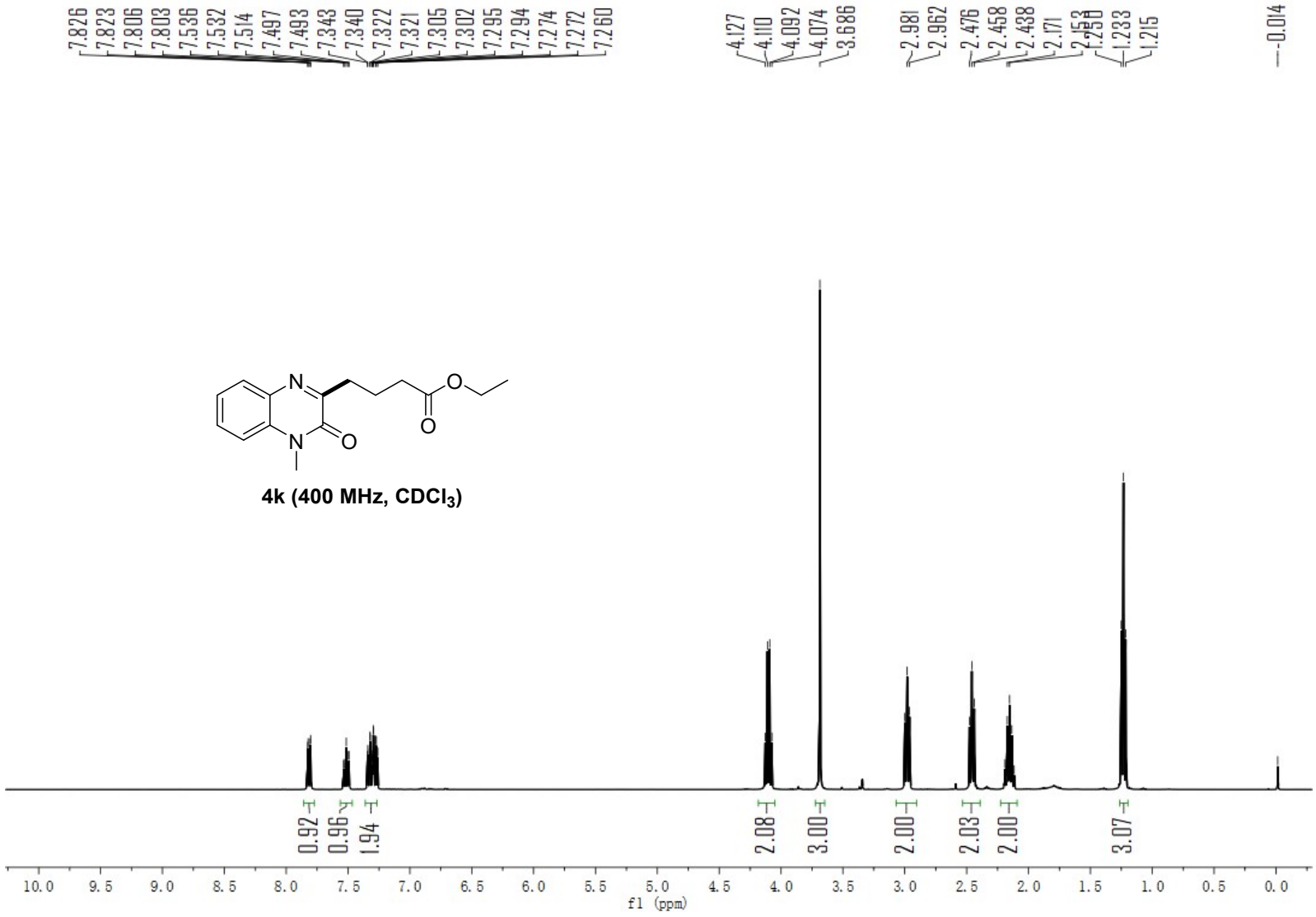
4i (101 MHz, $CDCl_3$)



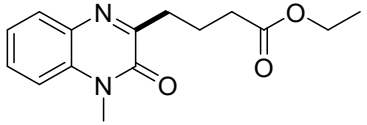
4j (400 MHz, $CDCl_3$)



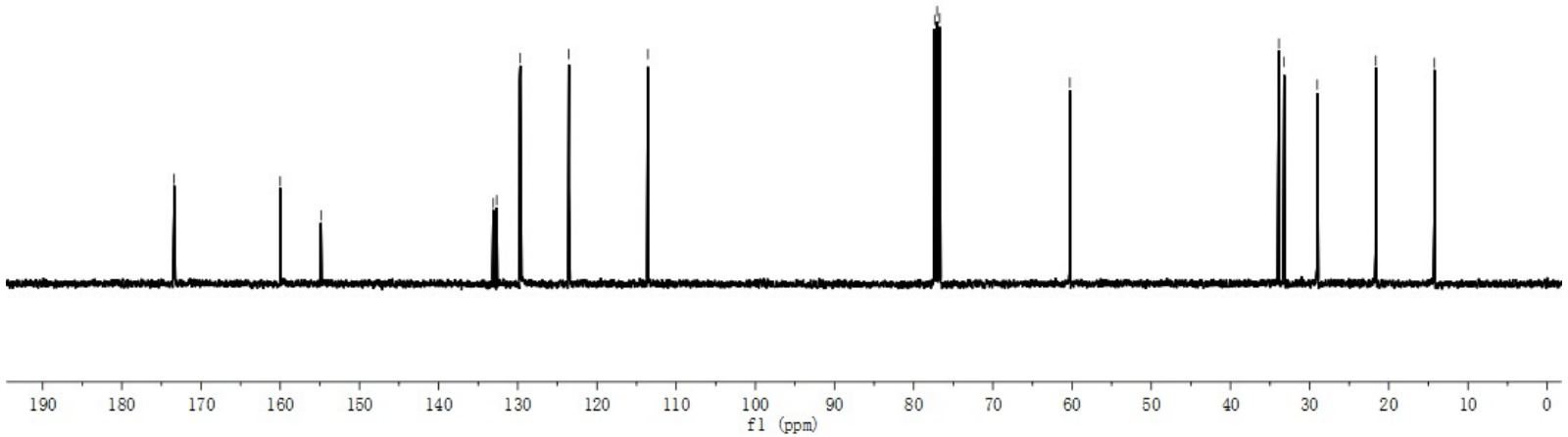
4j (101 MHz, $CDCl_3$)

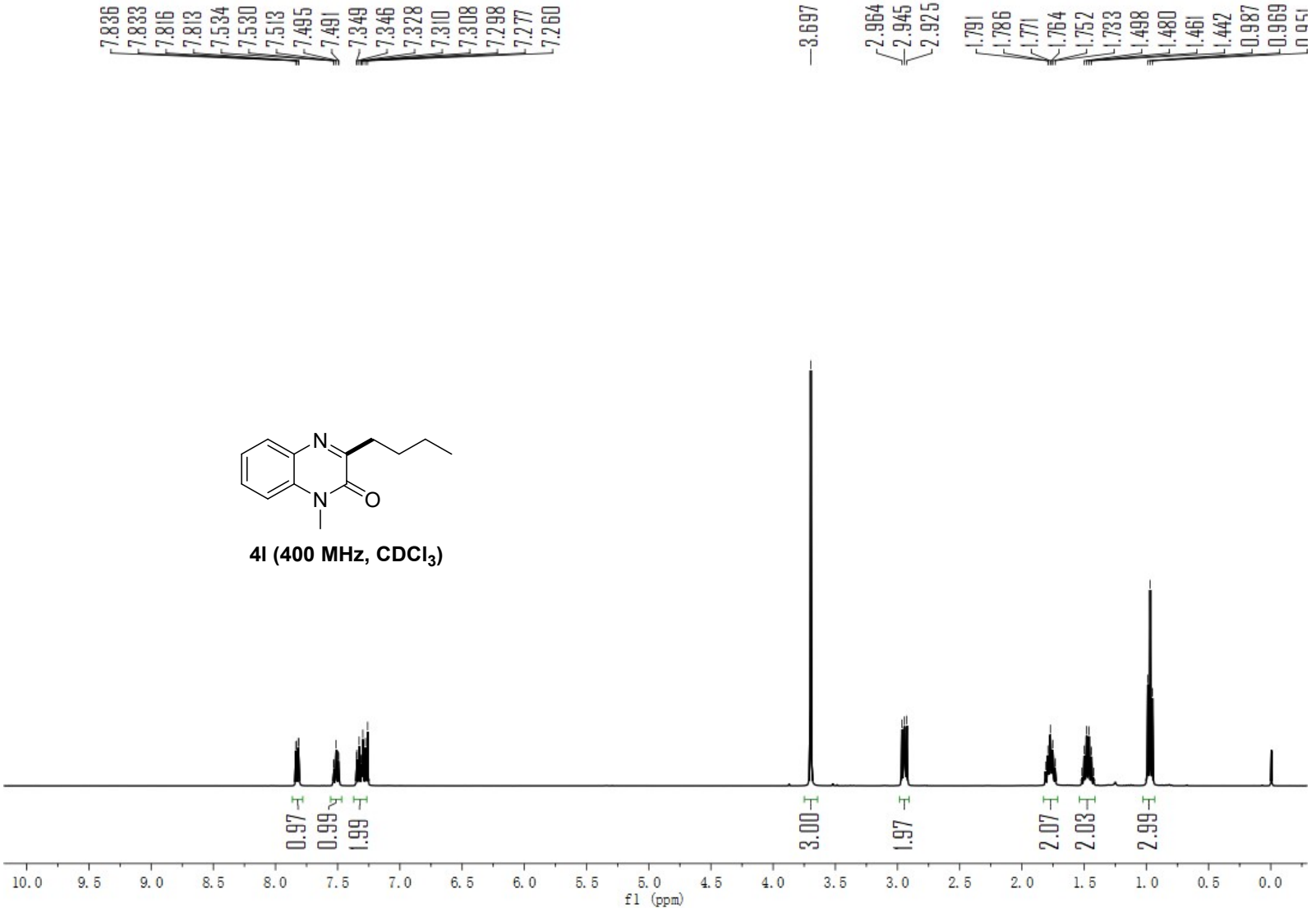


4k (400 MHz, $CDCl_3$)

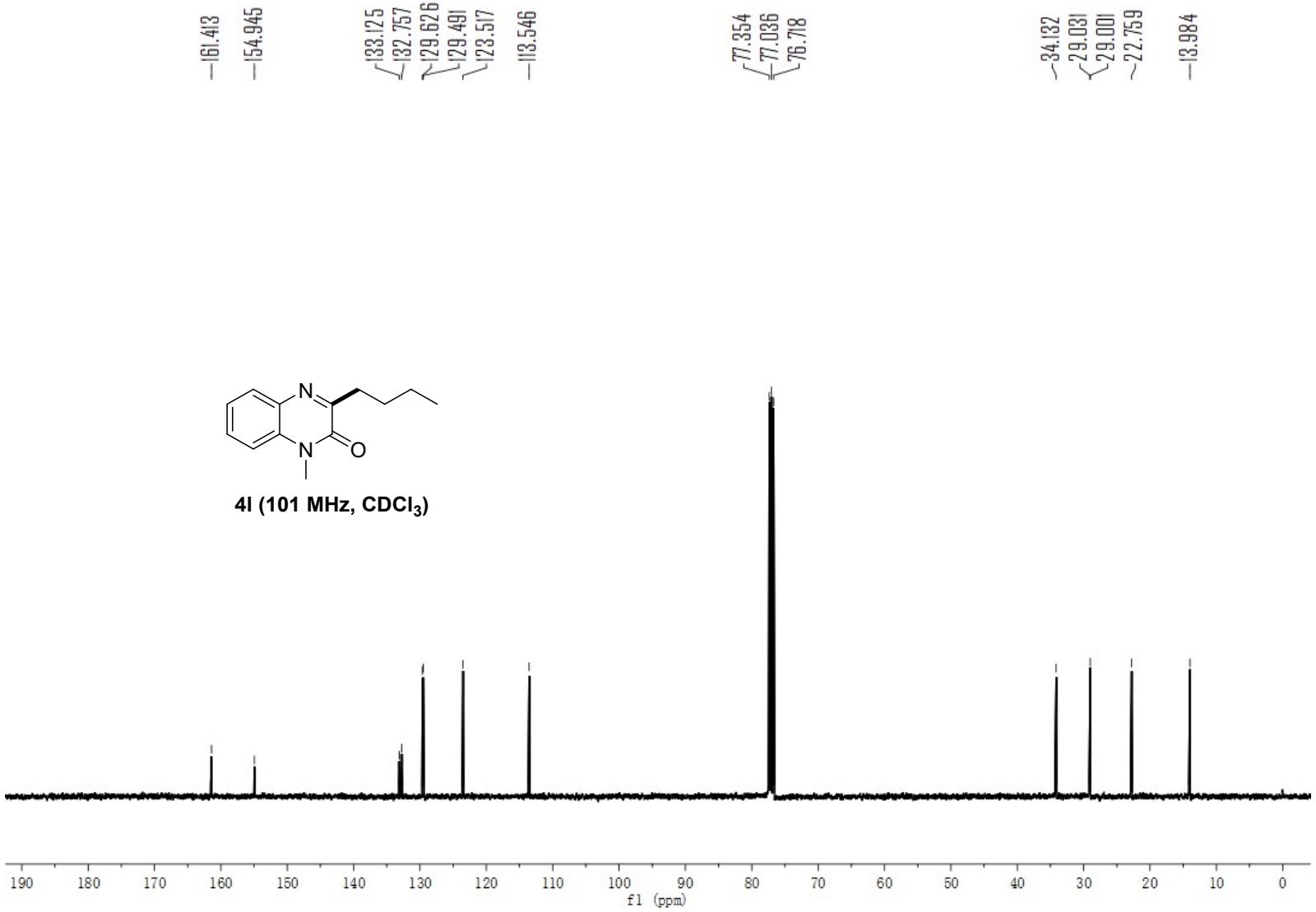


4k (101 MHz, $CDCl_3$)

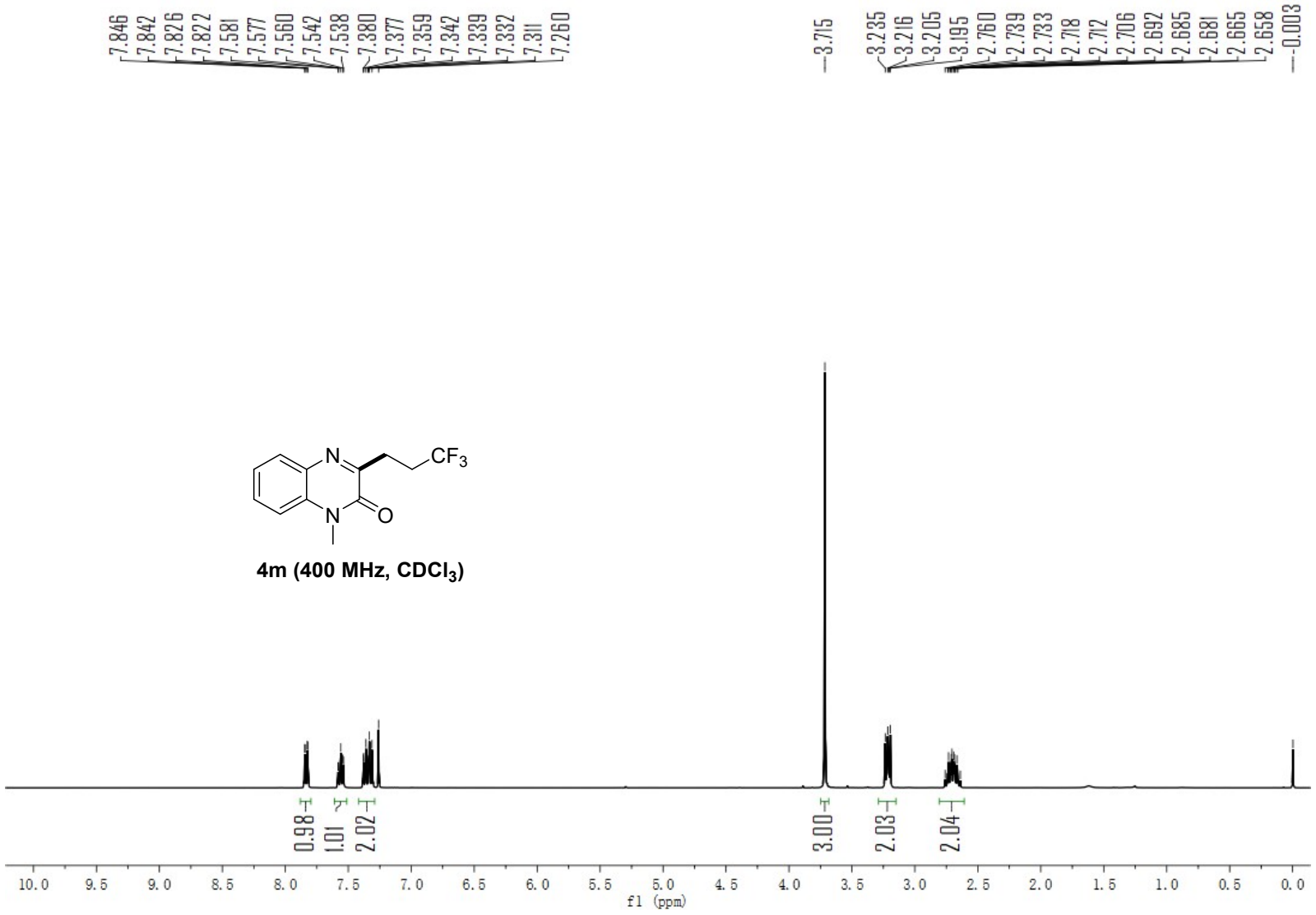




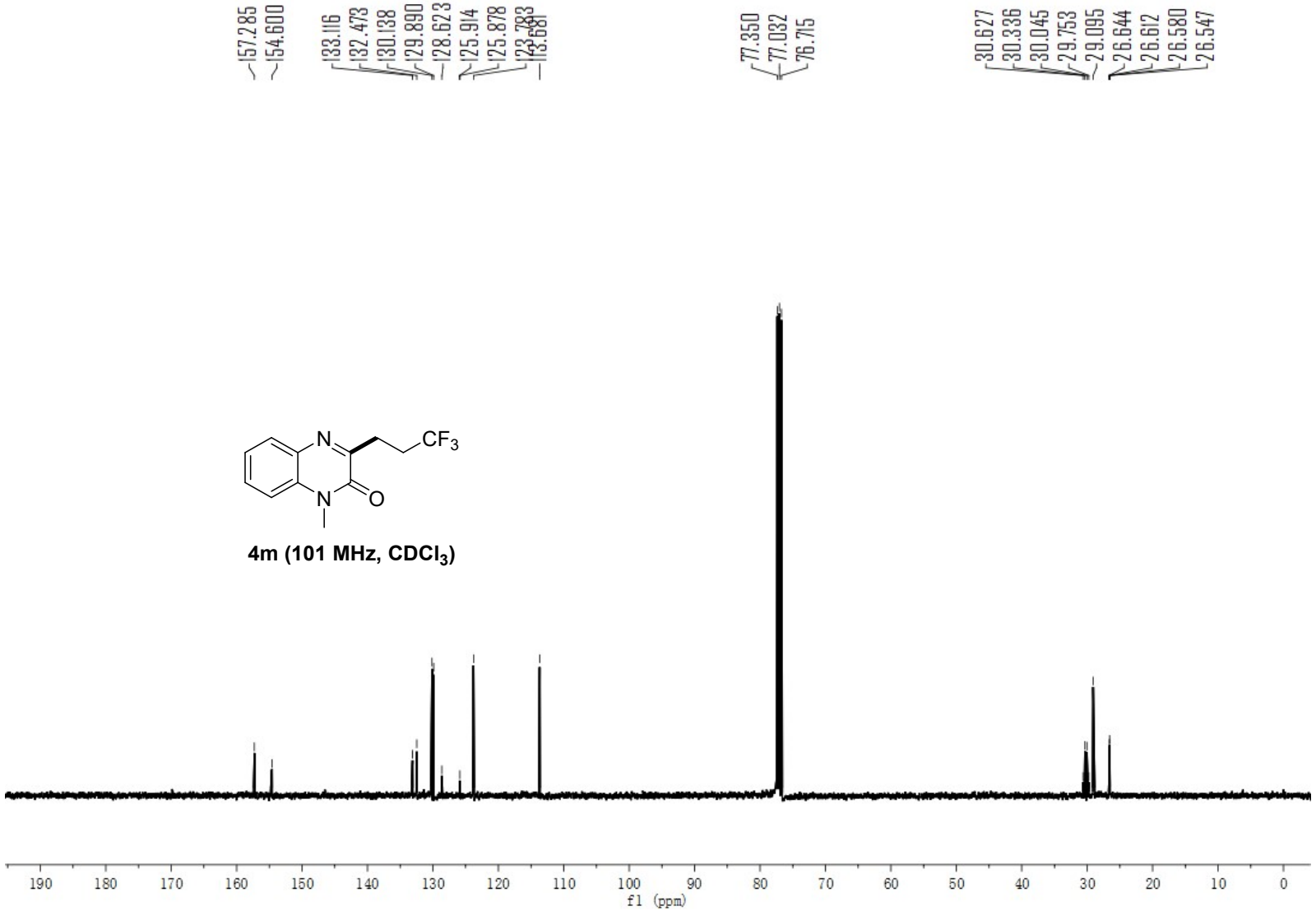
4l (400 MHz, $CDCl_3$)



4l (101 MHz, $CDCl_3$)



4m (400 MHz, $CDCl_3$)



4m (101 MHz, $CDCl_3$)

4m (376 MHz, $CDCl_3$)