Supporting Information

For

Photoinduced Regioselective Halogenation of 1-Alkyl/Benzyl-3-Phenylquinoxalin-2(1*H*)-ones in Water

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Content

1. General Consideration

All photoredox reactions were carried out in oven-dried a screw capped reaction vial with magnetic stirring under the irradiation of blue light. A Kessil LED PhotoReaction lighting photoreactor equipped with a blue LED light of 456nm wavelength and an attached cooling fan was employed for all photoreactions. The light source was positioned 2 cm away from the reaction vessel. All chemicals and solvents were purchased from Alfa-Aesar by Thermo Fischer Scientific, India Pvt. Limited, Sigma-Aldrich Chemicals Pvt. Limited India and from local commercial sources, and were used without any further purification unless otherwise specified. Solvents for column chromatography were dried and distilled prior to use. Solvents were removed under reduced pressure using rotary evaporator, followed by further removal of the residual solvent under high vacuum. Column chromatography was performed on silica gel (100-200 mesh). Melting points were determined on Buchi M-560 instrument and are uncorrected. HRMS analysis was carried out using Agilent G6530AA LC Q-TOF mass spectrometer using ESI method. The ^{1}H- and the ^{13}C-NMR spectra were recorded on Bruker-Avance Neo 400 FT-NMR spectrometers by using tetramethyl silane (TMS) as internal standard. The chemical shift values are on δ scale and the coupling constant (J) are in Hz. All the chemicals and reagents were purchased from commercial sources and used as received. 1-alkyl/benzyl-3-phenylquinoxalin-2(1*H*)-ones derivatives were well known compounds and were prepared according to literature[1-4].

2. Reaction Setup

A Kessil LED PhotoReaction lighting PR160L photoreactor (Figure **S1**) equipped with a blue LED light of λ_{max} = 456nm wavelength (24W), along with a built-in cooling fan was employed. The temperature of the reaction was maintained approximately 28-30°C during the course of reaction.

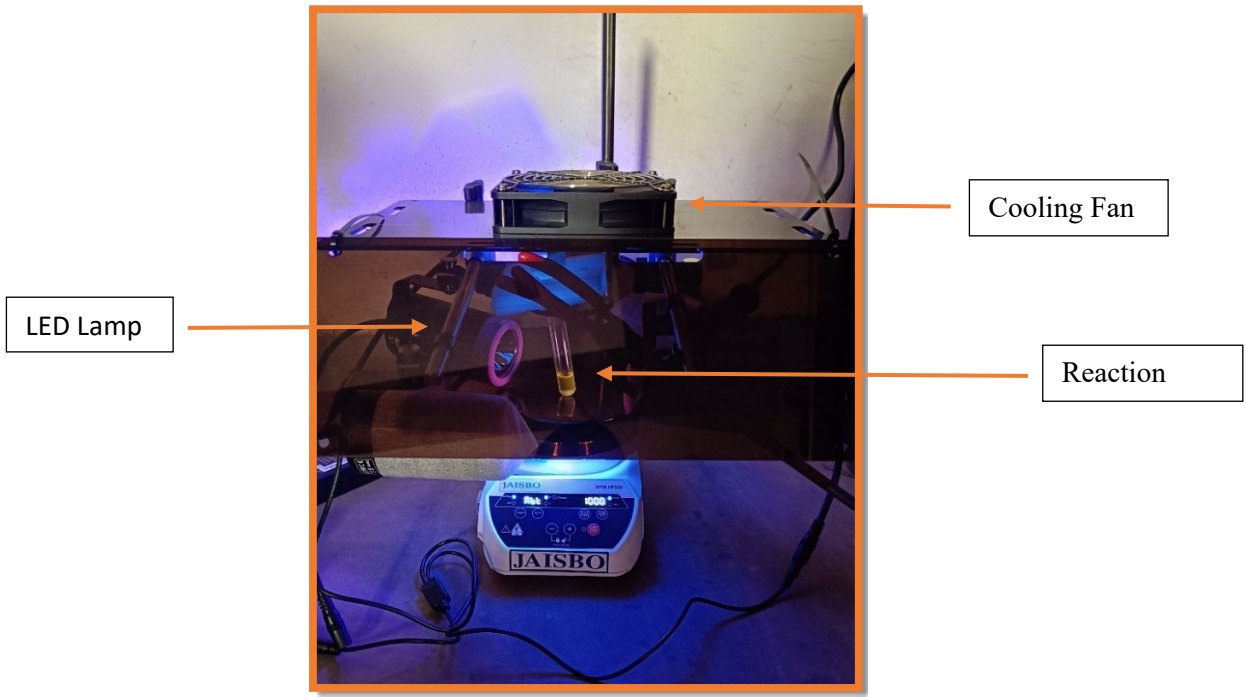
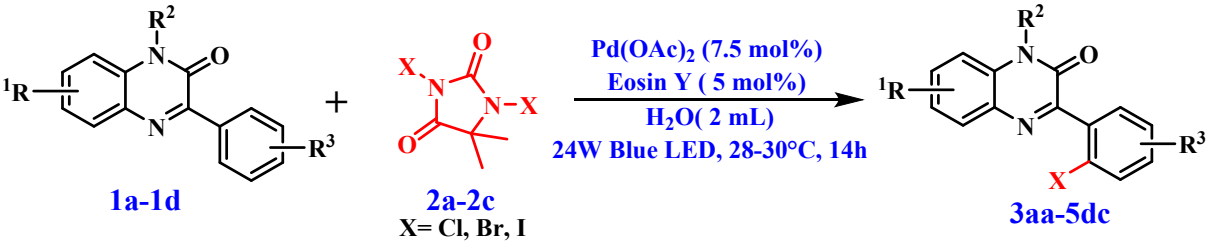


Figure S1: Photo-reaction setup

3. General procedure for the synthesis of compounds 3aa-5dc



An oven dried 10 mL screw capped reaction vial with a small stirring bar was charged with a mixture of 1-alkyl/benzyl-3-phenylquinoxalin-2(1*H*)-ones **1a-1d** (0.4 mmol), DXDMH **2a-2c** (0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 7.5 mol%), water-soluble disodium salt of Eosin Y (13.8 mg, 5 mol%) and H_2O (2mL). The resulting mixture was irradiated under 24W blue LED light at room temperature for 14h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with water and extracted with EtOAc (3×10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain the crude product. The crude product thus obtained was further purified on a silica gel column using hexane/ethyl acetate (7:3) as eluent to afford the pure targeted products.

4. References

1. Xue, Z.-Y.; Jiang, Y.; Peng, X.-Z.; Yuan, W.-C.; Zhang, X.-M., *Adv. Synth. Catal.* **2010**, *352*, 2132-2136.
2. Núñez-Rico, J. L.; Vidal-Ferran, A., *Org. Lett.* **2013**, *15*, 2066-2069.
3. Carrër, A.; Brion, J.-D.; Messaoudi, S.; Alami, M., *Org. Lett.* **2013**, *15*, 5606-5609.
4. Zhang, Y.; Huang, T.; Li, X.; Zhang, M.; Song, Y.; Huang, K.; Su, W. *RSC Advances* **2020**, *10*, 22216-22221.

5. Important Crystal Data of Compound 4bb

CCDC deposition number	2487347
Empirical Formula	$C_{15}H_9BrCl_2N_2O$
Formula weight	384.05
Temperature (K)	293(2)
Crystal System	monoclinic
Space Group	Ia
Unit Cell Dimension	a/Å = 6.8975(7) b/Å = 31.1454(18) c/Å = 7.4421(7) α/° = 90 β/° = 111.773(11) γ/° = 90
Volume Å^3	1484.7(2)
Z	4
Density Calculated g/cm^3	1.718
Absorption coefficient (μ) mm^{-1}	3.127
F (000)	760.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.232 to 62.152
Index ranges	$-9 \leq h \leq 9$ $-43 \leq k \leq 42$ $-10 \leq l \leq 10$
Reflection Collected	32431
Independent Reflections	4106 [R_{int} = 0.1559, R_{sigma} = 0.1073]
Data/Restraints/parameter s	4106/2/191
Goodness of fit on F^2	0.989
Final R indices [I>=2sigma(I)]	R_1 = 0.0501, wR_2 = 0.0988
R indices (all data)	R_1 = 0.1270, wR_2 = 0.1185
Largest difference peak and hole [e Å^{-3}]	0.26/-0.29

Important Crystal Data of Compound 5aa

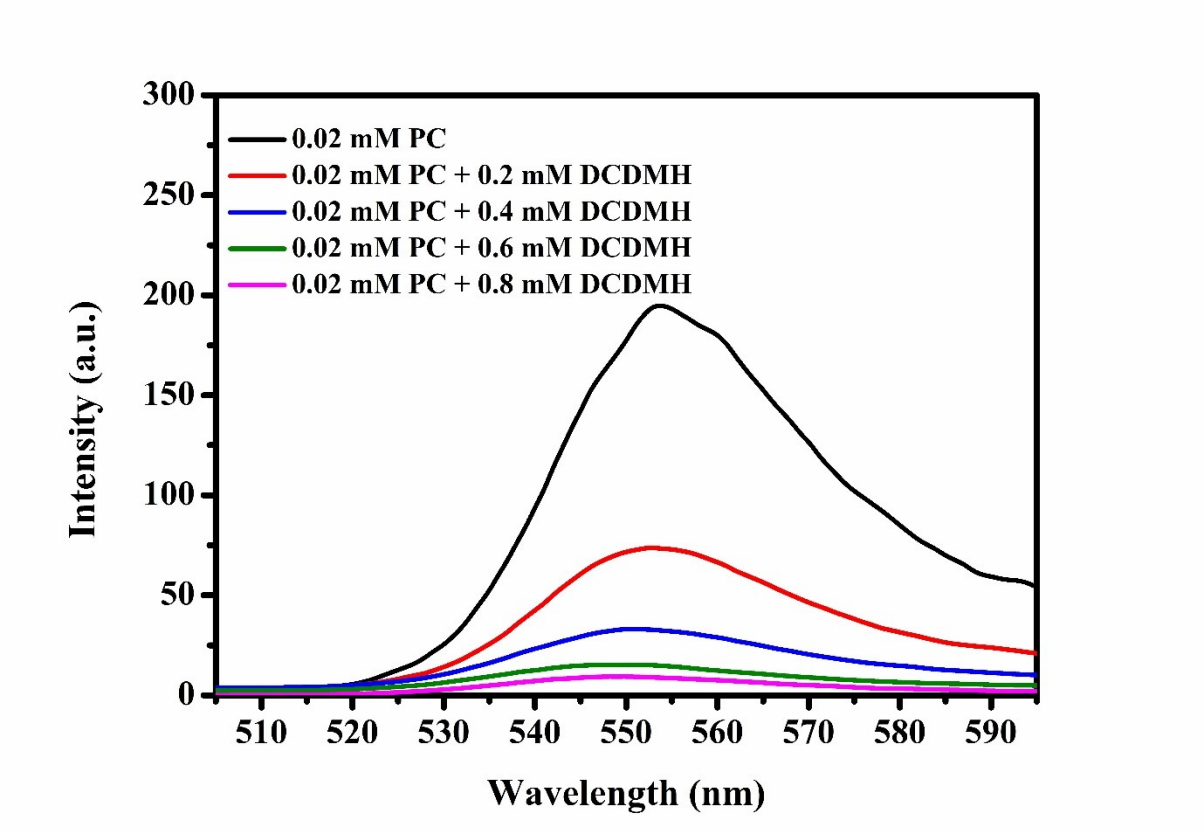
CCDC deposition number	2487225
Empirical Formula	$C_{15}H_{10}ClFN_2O$
Formula weight	288.70
Temperature (K)	293(2)
Crystal System	triclinic
Space Group	P-1
Unit Cell Dimension	a/Å = 7.4093(3) b/Å = 7.4847(4) c/Å = 12.1426(7) α/° = 89.291(4) β/° = 78.306(4) γ/° = 87.354(4)
Volume $Å^3$	658.70(6)
Z	2
Density Calculated g/cm^3	1.456
Absorption coefficient (μ) mm^{-1}	1.456
F (000)	296.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.426 to 61.61
Index ranges	$-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $-17 \leq l \leq 15$
Reflection Collected	9662
Independent Reflections	3334 [R_{int} = 0.0306, R_{sigma} = 0.0382]
Data/Restraints/parameter s	3334/0/182
Goodness of fit on F^2	1.107
Final R indices [I>=2sigma(I)]	R_1 = 0.0578, wR_2 = 0.1686
R indices (all data)	R_1 = 0.0862, wR_2 = 0.1867
Largest difference peak and hole [e $Å^{-3}$]	0.64/-0.31

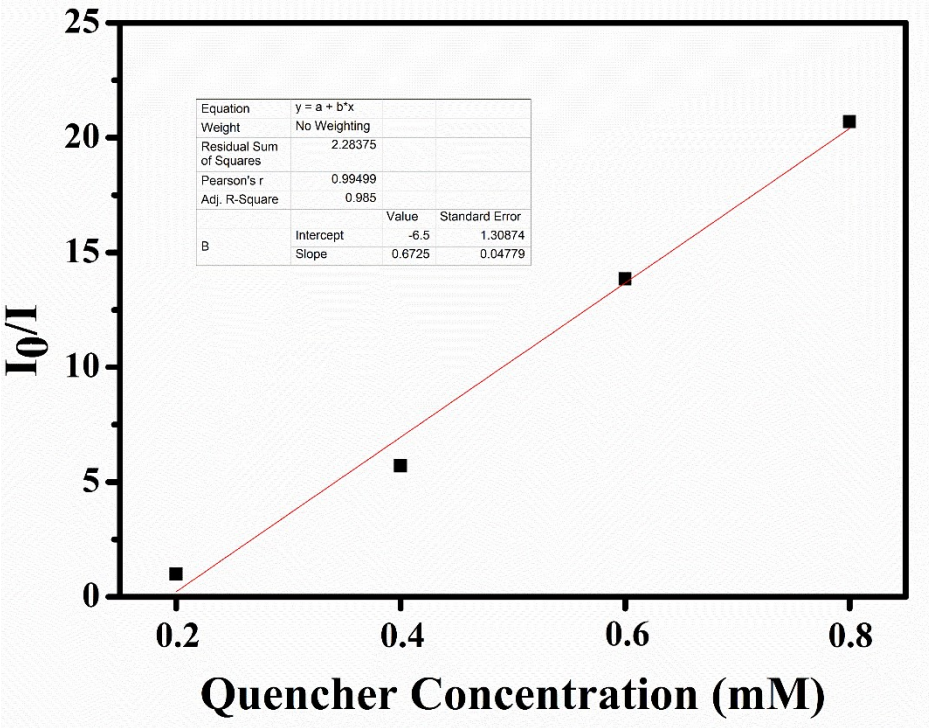
6. Fluorescence Quenching Experiments and Stern-Volmer Plot

Fluorescence quenching studies were carried out using a Cary Eclipse fluorescence spectrofluorometer (Varian optical spectroscopy instruments, Mulgrave, Victoria, Australia). A 0.02 mM stock solution of the photocatalyst Eosin Y was prepared by dissolving 0.138 mg of it in 10 mL of spectroscopic-grade acetonitrile. To a quartz cuvette 500 μL stock solution was added. The sample was irradiated at 440 nm and emission was detected at 548 nm. The emission intensity was recorded in the range of 500-600 nm. For the quenching experiments, an appropriate aliquot of this stock solution was combined with varying concentrations of the quencher (0.2, 0.4, 0.6 and 0.8 mM DCDMH). Upon successive increases in the quencher

concentration, the fluorescence intensity of the photocatalyst progressively decreased, confirming that the halogen source efficiently quenches the excited state of the photocatalyst.

Fluorescence Quenching and Stern-Volmer plot of Eosin Y vs DCDMH(2a)





7. Determination of Quantum Yield

Using the Hammond adaptation of the Hatchard and Parker method outlined in the *Handbook of Photochemistry*, a ferrioxalate actinometer solution was prepared. The actinometer operates by quantifying the photoreduction of ferric ions (Fe^{3+}) to ferrous ions (Fe^{2+}). The concentration of Fe^{2+} generated is then determined by UV-Vis spectroscopy through measurement of the absorbance of its complex with 9,10-phenanthroline. To perform the experiment, following three solutions were prepared and stored in dark:

1) Potassium ferrioxalate solution: A 50 mL volumetric flask was charged with 294.8 mg of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and 139 µl of H_2SO_4, and the solution was made up to volume with distilled water.

2) An aqueous solution was prepared by dissolving NaOAc (4.94 g) and sulfuric acid (0.5 mL) in a 50 mL volumetric flask, followed by dilution to the mark with water.

3) Phenanthroline solution: In a 50 mL volumetric flask, 100 mg of 1,10-phenanthroline was added to the ferrioxalate solution, and the volume was adjusted to the mark with distilled water.

The photon flux of the spectrophotometer was determined using the following procedure:

A 1 mL solution of the ferrioxalate solution was transferred into a cuvette (path length =10 mm) and irradiated at 440 nm for 90.0 seconds. After irradiation, the solution was quantitatively transferred to a 10 mL volumetric flask. Subsequently, 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution were added, and the volume was adjusted to the mark with distilled water. The resulting mixture was allowed to stand for 1 h to ensure complete complexation of ferrous ions with phenanthroline. The absorbance of the irradiated sample was then recorded at 510 nm. For comparison, the absorbance of a non-irradiated sample was also measured at the same wavelength.

The conversion of ferrioxalate was calculated using eq. 1:

$$\textbf{Moles of } Fe^{2+} = \frac{V_1\, V_3\, \Delta A}{10^3\, V_2\, l\, \varepsilon} \quad \text{.....(1)}$$

V_1 represents the volume of the irradiated solution (1 mL).
V_2 corresponds to the portion of the irradiated solution used for ferrous ion analysis (1 mL).
V_3 denotes the total volume after complexation with phenanthroline (10 mL).
l is the optical path length of the irradiation cell (1 cm).
ΔA (510 nm) is the difference in absorbance between the irradiated sample and the dark (non-irradiated) sample, calculated as 1.638 - 0.142 = 1.496.
ε (510 nm) refers to the molar extinction coefficient of the $Fe(phen)_3^{2+}$ complex, which is 11100 L mol^{-1} cm^{-1}.

$$Fe^{2+} = \frac{1\ ml \times 10ml \times 1.496}{10^3 \times 1\ ml \times 1cm \times 11100\ L\ mol^{-1}cm^{-1}} = 1.347 \times 10^{-6}$$

Absorbance of ferrioxalate solution at 440nm = 1.637

Fraction of light absorbed (*f*) by ferrioxalate actinometer at 440 nm is calculated using eq. 2:

$f = 1 - 10^{-A}$ …… (2)

$f = 1 - 10^{-1.637} = 0.9769$

The photon flux was calculated using eq. 3:

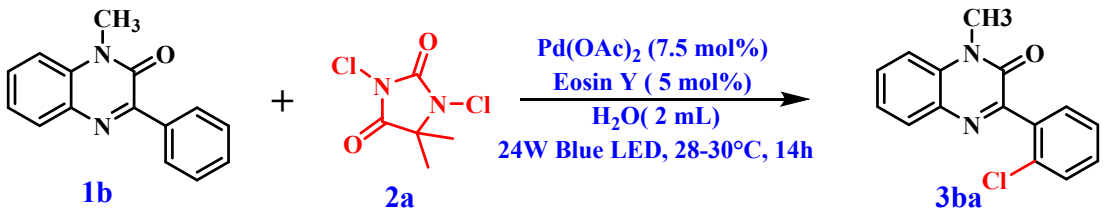
$$F = \frac{\text{mol } Fe^{+2}}{\Phi \times t \times f} \quad \text{……..(3)}$$

Moles (Fe^{+2}) = 1.347×10^{-6}

Φ is the quantum yield for the ferrioxalate actinometer at 440nm (0.9431), t is the time = 90 seconds and *f* is the fraction of light absorbed by ferrioxalate actinometer solution.

$$F = \frac{1.347 \times 10^{-6}\ \text{mol}}{0.9431 \times 90\ \text{sec} \times 0.976} = 1.62 \times 10^{-8}\ \text{einstein sec}^{-1}$$

Determination of Quantum Yield:



The parent reaction was done in 10 mL reaction tube at optimal reaction condition at 0.2 mmol scale for 2 hours and the isolated yield was 18% calculated.

The quantum yield (Φ) is calculated using eq. 4

$$\Phi = \frac{\text{moles of product}}{F \times t \times f} \quad \text{.....(4)}$$

Fraction of light absorbed (*f*) at 456 nm for the photocatalytic reaction

$$f = 1 - 10^{-A}$$

Determination of fraction of light absorbed by photocatalyst at λ = 456 nm:

A 1×10^{-3} M solution of photocatalyst was prepared by dissolving 2.77 mg of Eosin Y in 4 mL spectroscopic grade acetonitrile and by taking 1 mL out of this solution, UV- Visible spectra was recorded. The absorbance (A)of photocatalytic solution was measure at 456 nm was found to be 0.540. The fraction of light absorbed (*f*) by this solution is then calculated.

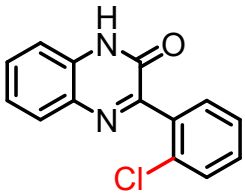
$f = 1 - 10^{-0.540} = 0.7116$

$$\Phi = \frac{1.8 \times 10^{-5}}{1.62 \times 10^{-8} \times 7200 \text{ sec} \times 0.7116} = 0.2168$$

Inference: A measured quantum yield significantly lower than unity, indicates that each absorbed photon leads to less than one product-forming event. This observation strongly suggests that the reaction does not proceed via a radical chain propagation mechanism. Instead, it is consistent with a predominantly closed catalytic cycle, where each turnover requires continuous photoexcitation rather than chain amplification.

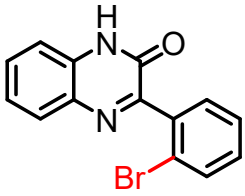
8. Analytical Data

4.1) 3-(2-chlorophenyl)quinoxalin-2(1H)-one (3aa)



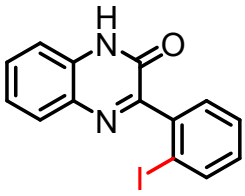
It was obtained as **White solid** having melting point **238-240 °C** with **84%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.36 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 6.7, 2.5 Hz, 1H), 7.54 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.51-7.42 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.93, 155.75, 135.60, 133.73, 133.05, 131.83, 131.19, 130.95, 130.79, 129.98, 129.69, 127.08,124.56,116.22.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{14}H_{10}ClN_2O^+$: 257.0473; found: 257.0492.

4.2) 3-(2-bromophenyl)quinoxalin-2(1H)-one (3ab)



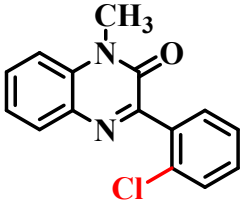
It was obtained as **White solid** having melting point **251-253 °C** with **82%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.40 (s, 1H), 7.92 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.57 (ddd, *J* = 13.3, 8.0, 4.8 Hz, 2H), 7.53 – 7.43 (m, 3H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.97, 155.53, 137.48, 133.12, 132.98, 131.80, 131.22, 130.92, 129.73, 127.69, 124.62, 122.81, 116.20.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{14}H_{10}BrN_2O^+$: 300.9971; found: 300.9988.

4.3) 3-(2-iodophenyl)quinoxalin-2(1H)-one (3ac)



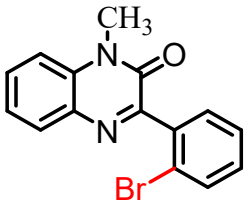
It was obtained as **White solid** having melting point **136-138 °C** with **64%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.13 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.55-7.51 (m, 3H), 7.40-7.32 (m, 2H), 7.23-7.19 (m, 1H).
.**^{13}C NMR (100 MHz, Chloroform-*d*)** δ 159.75, 155.27, 141.05, 139.54, 132.93, 131.83, 131.21, 130.85, 130.29, 129.74, 128.41, 124.66, 116.24, 96.74.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{14}H_{10}IN_2O^+$: 348.9832; found: 348.9844.

4.4) 3-(2-chlorophenyl)-1-methylquinoxalin-2(1H)-one (3ba)



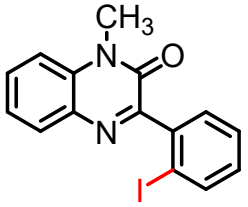
It was obtained as **Yellow solid** having melting point **120-122 °C** with **82%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.68-7.60 (m, 2H), 7.50-7.43 (m, 2H), 7.41-7.37 (m, 2H), 7.34-7.29 (m, 1H), 3.77 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.48, 154.18, 135.98, 133.91, 133.39, 132.90, 131.13, 130.74, 130.62, 129.89, 126.92, 123.97, 113.93, 29.53.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{12}ClN_2O^+$: 271.0633; found: 271.0633.

4.5) 3-(2-bromophenyl)-1-methylquinoxalin-2(1H)-one (3bb)



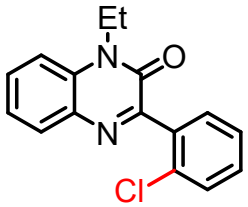
It was obtained as **White solid** having melting point **134-136 °C** with **85%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.3 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.65-7.61 (m, 1H), 7.50-7.47 (m, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34-7.30 (m, 1H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.53, 154.07, 137.93, 133.98, 133.04, 132.88, 131.14, 130.78, 130.73, 130.62, 127.51, 123.98, 122.54, 113.95, 29.54.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{12}BrN_2O^+$: 315.0128; found: 315.0127.

4.6) 3-(2-iodophenyl)-1-methylquinoxalin-2(1H)-one (3bc)



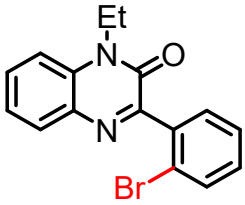
It was obtained as **Pale-yellow solid** having melting point **121-123 °C** with **76%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96-7.94 (m, 2H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 4.2 Hz, 2H), 7.42-7.39 (m, 2H), 7.17-7.13 (m, 1H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.25, 153.84, 141.46, 139.46, 133.99, 132.79, 131.14, 130.74, 130.67, 129.98, 128.25, 124.03, 113.98, 96.49, 29.58.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{12}IN_2O^+$: 362.9989; found: 362.9999.

4.7) 3-(2-chlorophenyl)-1-ethylquinoxalin-2(1H)-one (3ca)



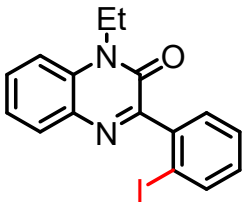
It was obtained as **Pale-yellow solid** having melting point **111-113 °C** with **84%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97-7.93 (m, 2H), 7.65-7.61 (m, 1H), 7.50-7.45 (m, 2H), 7.40 (q, *J* = 7.5 Hz, 2H), 7.17-7.12 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.54, 153.68, 135.99, 133.48, 133.25, 132.92, 131.10, 131.06, 130.73, 130.62, 129.91, 126.94, 113.77, 37.79, 12.58.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}ClN_2O^+$: 285.0789; found: 285.0803.

4.8) 3-(2-bromophenyl)-1-ethylquinoxalin-2(1H)-one (3cb)



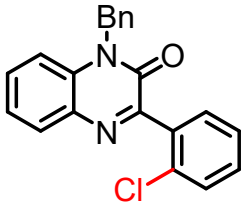
It was obtained as **White solid** having melting point **118-120 °C** with **81%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.68-7.61 (m, 2H), 7.51 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.46-7.37 (m, 3H), 7.34-7.30 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.54, 153.52, 137.90, 133.17, 133.01, 132.92, 131.08, 131.03, 130.69, 127.51, 123.76, 122.60, 113.76, 37.75, 12.56.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}BrN_2O^+$: 329.0284; found: 329.0297.

4.9) 1-ethyl-3-(2-iodophenyl)quinoxalin-2(1H)-one (3cc)



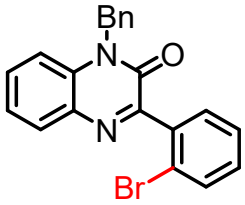
It was obtained as **White solid** having melting point **108-110 °C** with **77%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (t, *J* = 7.6 Hz, 2H), 7.65-7.61 (m, 1H), 7.51-7.45 (m, 2H), 7.40 (dd, *J* = 15.5, 7.4 Hz, 2H), 7.17-7.12 (m, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.27, 153.26, 141.47, 139.40, 133.09, 132.93, 131.07, 131.00, 130.61, 130.05, 128.24, 123.78, 113.77, 96.59, 37.74, 12.53.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}IN_2O^+$: 377.0145; found: 377.0161.

4.10) 1-benzyl-3-(2-chlorophenyl)quinoxalin-2(1H)-one (3da)



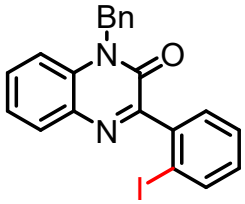
It was obtained as **White solid** having melting point **128-130 °C** with **79%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96-7.94 (m, 1H), 7.59-7.57 (m, 1H), 7.52-7.48 (m, 2H), 7.45-7.40 (m, 2H), 7.37-7.31 (m, 6H), 7.29-7.27 (m, 1H), 5.57 (s, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.68, 154.31, 136.01, 135.40, 133.53, 133.28, 133.23, 131.10, 130.90, 130.74, 130.70, 129.93, 129.13, 127.93, 127.21, 127.03, 124.03, 114.73, 46.29.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{21}H_{16}ClN_2O^+$: 347.0946; found: 347.0956.

4.11) 1-benzyl-3-(2-bromophenyl)quinoxalin-2(1H)-one (3db)



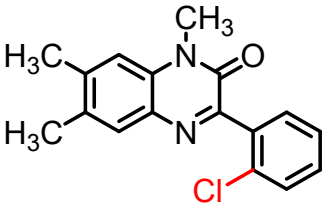
It was obtained as **White solid** having melting point **131-133 °C** with **89%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.58-7.53 (m, 1H), 7.50-7.39 (m, 3H), 7.35-7.31 (m, 6H), 7.26 (dd, *J* = 9.1, 4.8 Hz, 1H), 5.56 (s, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.67, 154.30, 136.00, 135.39, 133.52, 133.26, 133.22, 131.10, 130.89, 130.73, 130.69, 129.92, 129.12, 127.92, 127.20, 127.03, 124.03, 114.72, 46.28.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{21}H_{16}BrN_2O^+$: 391.0441; found: 391.0453.

4.12) 1-benzyl-3-(2-iodophenyl)quinoxalin-2(1H)-one (3dc)



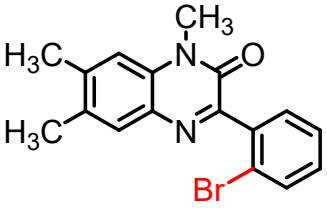
It was obtained as **Pale-yellow solid** having melting point **134-136 °C** with **85%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98-7.95 (m, 2H), 7.54-7.48 (m, 3H), 7.37-7.31 (m, 6H), 7.29-7.27 (m, 1H), 7.19-7.15 (m, 1H), 5.58 (s, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.53, 153.91, 141.54, 139.39, 135.37, 133.34, 133.10, 131.09, 130.86, 130.73, 130.03, 129.09, 128.35, 127.90, 127.25, 124.04, 114.78, 96.66, 46.28.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{21}H_{16}IN_2O^+$: 439.0302; found: 439.0292.

4.13) 3-(2-chlorophenyl)-1,6,7-trimethylquinoxalin-2(1H)-one (4aa)



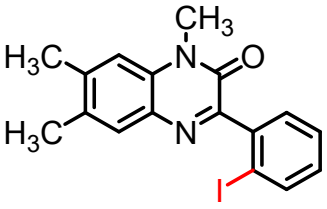
It was obtained as **Yellow solid** having melting point **184-186 °C** with **79%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.50-7.47 (m, 2H), 7.41-7.35 (m, 2H), 7.15 (s, 1H), 3.75 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.19, 154.30, 141.18, 136.27, 133.47, 132.96, 131.99, 131.40, 130.77, 130.69, 130.43, 129.87, 126.88, 114.49, 29.44, 20.80, 19.33.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{17}H_{16}ClN_2O^+$: 299.0946; found: 299.0951.

4.14) 3-(2-bromophenyl)-1,6,7-trimethylquinoxalin-2(1H)-one (4ab)



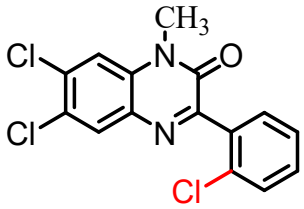
It was obtained as **Yellow solid** having melting point **207-209 °C** with **82%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.30 (td, *J* = 7.6, 1.8 Hz, 1H), 7.15 (s, 1H), 3.75 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.23, 154.16, 141.18, 138.18, 132.99, 132.01, 131.31, 130.75, 130.65, 130.52, 127.45, 122.66, 114.50, 29.44, 20.80, 19.32.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{17}H_{16}BrN_2O^+$: 343.0441; found: 343.0444.

4.15) 3-(2-iodophenyl)-1,6,7-trimethylquinoxalin-2(1H)-one (4ac)



It was obtained as **Pale-yellow solid** having melting point **201-203 °C** with **76%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.45 (d, *J* = 4.5 Hz, 2H), 7.16 (s, 1H), 7.15-7.11 (m, 1H), 3.75 (s, 3H), 2.46 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.01, 153.93, 141.69, 141.22, 139.40, 133.04, 132.02, 131.21, 130.71, 130.50, 129.99, 128.21, 114.55, 96.75, 29.49, 20.85, 19.37.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{17}H_{16}IN_2O^+$: 391.0302; found: 391.0301.

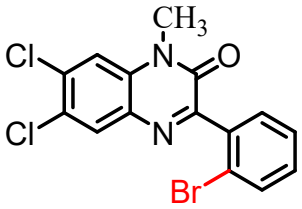
4.16) 6,7-dichloro-3-(2-chlorophenyl)-1-methylquinoxalin-2(1H)-one (4ba)



It was obtained as **White solid** having melting point **161-163 °C** with **68%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.50-7.47 (m, 3H), 7.44-7.36 (m, 2H), 3.73 (s, 3H).

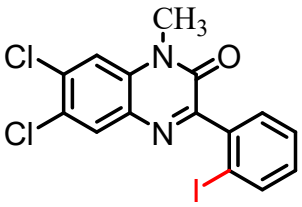
^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.75, 153.60, 135.37, 135.33, 133.33, 133.30, 131.95, 131.50, 131.01, 130.56, 130.03, 127.87, 126.97, 115.48, 29.83.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{10}Cl_3N_2O^+$: 338.9853; found: 338.9852.

4.17) 3-(2-bromophenyl)-6,7-dichloro-1-methylquinoxalin-2(1H)-one (4bb)



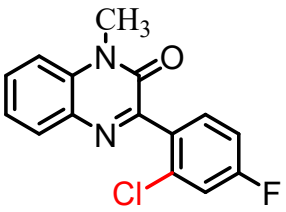
It was obtained as **White solid** having melting point **167-169 °C** with **74%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 2.6 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 1H), 3.72 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.74, 153.48, 137.24, 135.37, 133.33, 133.14, 131.89, 131.48, 131.09, 130.53, 127.88, 127.55, 122.36, 115.51, 29.84.
HRMS (ESI^{+}): m/z $[M+H]^{+}$ calculated for $C_{15}H_{10}BrCl_2N_2O^{+}$: 382.9348; found: 382.9350.

4.18) 6,7-dichloro-3-(2-iodophenyl)-1-methylquinoxalin-2(1H)-one (4bc)



It was obtained as **Pale-yellow solid** having melting point **180-182 °C** with **75%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.95 (d, *J* = 6.9 Hz, 1H), 7.50-7.48 (m, 1H), 7.45 (dt, *J* = 7.7, 3.4 Hz, 1H), 7.26 (s, 1H), 7.19-7.15 (m, 1H), 3.73 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.43, 153.29, 140.72, 139.58, 135.40, 133.33, 131.81, 131.45, 131.04, 129.90, 128.30, 127.96, 115.55, 96.19, 29.86.
HRMS (ESI^{+}): m/z $[M+H]^{+}$ calculated for $C_{15}H_{10}ICl_2N_2O^{+}$: 430.9209; found: 430.9210.

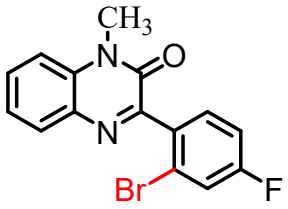
4.19) 3-(2-chloro-4-fluorophenyl)-1-methylquinoxalin-2(1H)-one (5aa)



It was obtained as **White solid** having melting point **160-162 °C** with **66%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.51 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.40 (t, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.11 (td, *J* = 8.3, 2.5 Hz, 1H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.88, 155.52, 154.19, 134.72, 133.92, 132.87, 132.13, 132.03, 131.34, 130.78, 124.11, 117.37, 114.44, 113.99, 29.91.
^{19}F NMR (377 MHz, Chloroform-*d*) δ -109.81.

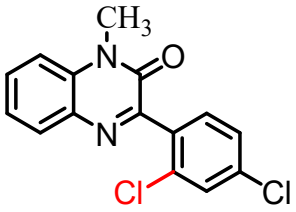
HRMS (ESI^{+}): m/z $[M+H]^{+}$ calculated for $C_{15}H_{11}ClFN_2O^{+}$: 289.0538; found: 289.0545.

4.20) 3-(2-bromo-4-fluorophenyl)-1-methylquinoxalin-2(1H)-one (5ab)



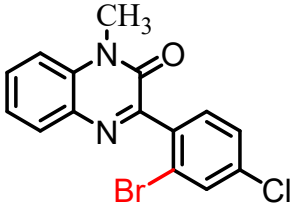
It was obtained as **White solid** having melting point **140-142°C** with **80%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.49 (dd, *J* = 8.5, 5.9 Hz, 1H), 7.44-7.38 (m, 3H), 7.15 (td, *J* = 8.3, 2.5 Hz, 1H), 3.77 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.64, 156.56, 154.07, 133.96, 132.80, 132.02, 131.93, 131.34, 130.78, 124.13, 123.20, 120.41, 114.75, 114.01, 29.63.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{11}BrFN_2O^+$: 333.0033; found: 333.0033.
^{19}F NMR (377 MHz, Chloroform-*d*) δ -109.95.

4.21) 3-(2,4-dichlorophenyl)-1-methylquinoxalin-2(1H)-one (5ba)



It was obtained as **White solid** having melting point **153-155°C** with **82%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.43-7.36 (m, 3H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.43, 154.08, 136.03, 134.51, 134.43, 133.96, 132.91, 131.66, 131.41, 130.85, 129.89, 127.31, 124.13, 114.00, 29.61.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{11}Cl_2N_2O^+$: 305.0243; found: 305.0259.

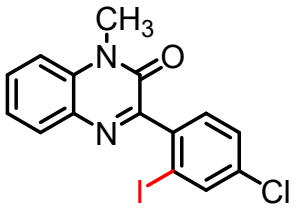
4.22) 3-(2-bromo-4-chlorophenyl)-1-methylquinoxalin-2(1H)-one (5bb)



It was obtained as **White solid** having melting point **123-125 °C** with **88%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 1.7 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.43-7.42 (m, 2H), 7.41-7.38 (m, 2H), 3.78 (s, 3H).

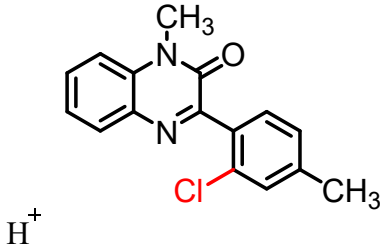
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.44, 153.94, 136.40, 135.96, 133.98, 132.83, 131.56, 131.39, 130.83, 127.83, 124.12, 123.15, 114.00, 29.60.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{11}BrClN_2O^+$: 348.9738; found: 348.9734.

4.23) 3-(4-chloro-2-iodophenyl)-1-methylquinoxalin-2(1H)-one (5bc)



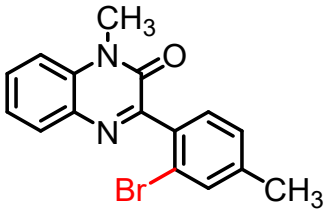
It was obtained as **White solid** having melting point **123-125°C** with **70%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.8 Hz, 2H), 7.68-7.64 (m, 1H), 7.47-7.39 (m, 4H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.14, 153.73, 139.85, 138.96, 135.65, 133.97, 132.72, 131.42, 130.80, 130.76, 128.53, 124.19, 114.05, 96.69, 29.65.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{15}H_{11}ClIN_2O^+$: 396.9599; found: 396.9598.

4.24) 3-(2-chloro-4-methylphenyl)-1-methylquinoxalin-2(1H)-one(5ca)



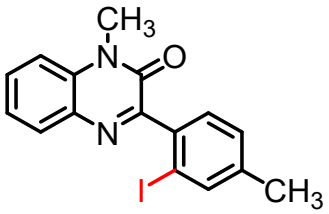
It was obtained as **White solid** having melting point **146-148 °C** with **82%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.41-7.36 (m, 3H), 7.31 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.52, 154.26, 141.08, 133.87, 133.04, 133.01, 132.91, 130.95, 130.66, 130.40, 130.37, 127.68, 123.86, 113.87, 29.50, 21.23.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}ClN_2O^+$: 285.0789; found: 285.0791.

4.25) 3-(2-bromo-4-methylphenyl)-1-methylquinoxalin-2(1H)-one (5cb)



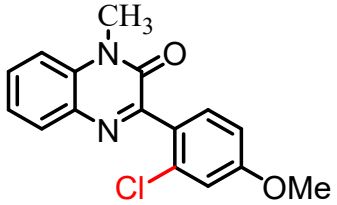
It was obtained as **White solid** having melting point **145-147 °C** with **83%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.4 Hz, 1H), 7.63 (t, *J* = 7.1 Hz, 1H), 7.51 (s, 1H), 7.41-7.36 (m, 3H), 7.23 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 2.39 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.50, 154.26, 141.10, 133.83, 133.01, 132.97, 132.88, 130.98, 130.64, 130.38, 130.37, 127.69, 123.89, 113.89, 29.52, 21.25.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}BrN_2O^+$: 329.0284; found: 329.0282.

4.26) 3-(2-iodo-4-methylphenyl)-1-methylquinoxalin-2(1H)-one (5cc)



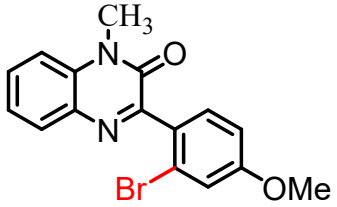
It was obtained as **White solid** having melting point **122-124 °C** with **79%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.64-7.60 (m, 1H), 7.41-7.34 (m, 3H), 7.27 (d, *J* = 7.1 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.20, 153.96, 141.01, 140.01, 138.50, 133.96, 132.81, 130.99, 130.69, 129.69, 129.04, 123.95, 113.92, 96.40, 29.57, 20.92.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}IN_2O^+$: 377.0145; found: 377.0163.

4.27) 3-(2-chloro-4-methoxyphenyl)-1-methylquinoxalin-2(1H)-one (5da)



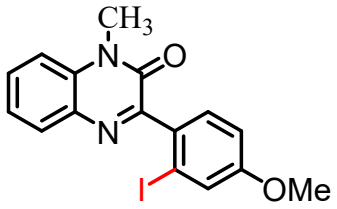
It was obtained as **Pale-yellow solid** having melting point **129-131 °C** with **72%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.3 Hz, 1H), 7.64-7.60 (m, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.39 (t, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.11, 156.20, 154.44, 134.39, 133.90, 132.99, 131.66, 130.92, 130.70, 128.30, 123.93, 115.45, 113.89, 113.09, 55.82, 29.58.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}ClN_2O_2^+$: 301.0738; found: 301.0741.

4.28) 3-(2-bromo-4-methoxyphenyl)-1-methylquinoxalin-2(1H)-one (5db)



It was obtained as **Pale-yellow solid** having melting point **138-140 °C** with **80%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.4 Hz, 1H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.41-7.36 (m, 2H), 7.22 (d, *J* = 2.5 Hz, 1H), 6.96 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.90, 157.16, 153.32, 133.92, 132.91, 131.54, 130.93, 130.68, 130.18, 123.93, 123.19, 118.54, 113.89, 113.62, 55.82, 29.58.
HRMS (ESI$^+$): m/z $[M+H]^+$ calculated for $C_{16}H_{14}BrN_2O_2^+$: 345.0233; found: 345.0234.

4.29) 3-(2-iodo-4-methoxyphenyl)-1-methylquinoxalin-2(1H)-one (5dc)



It was obtained as **White solid** having melting point **240-242 °C** with **70%** yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.64-7.59 (m, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.42-7.36 (m, 3H), 6.99 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.42, 158.68, 154.11, 133.92, 133.66, 132.78, 130.93, 130.77, 130.61, 124.99, 123.96, 114.24, 113.91, 96.83, 55.75, 29.59.
HRMS (ESI^{+}): m/z $[M+H]^{+}$ calculated for $C_{16}H_{14}IN_2O_2^{+}$: 393.0094; found: 393.0091.

9. Copies of ^{1}H NMR and ^{13}C NMR Spectra

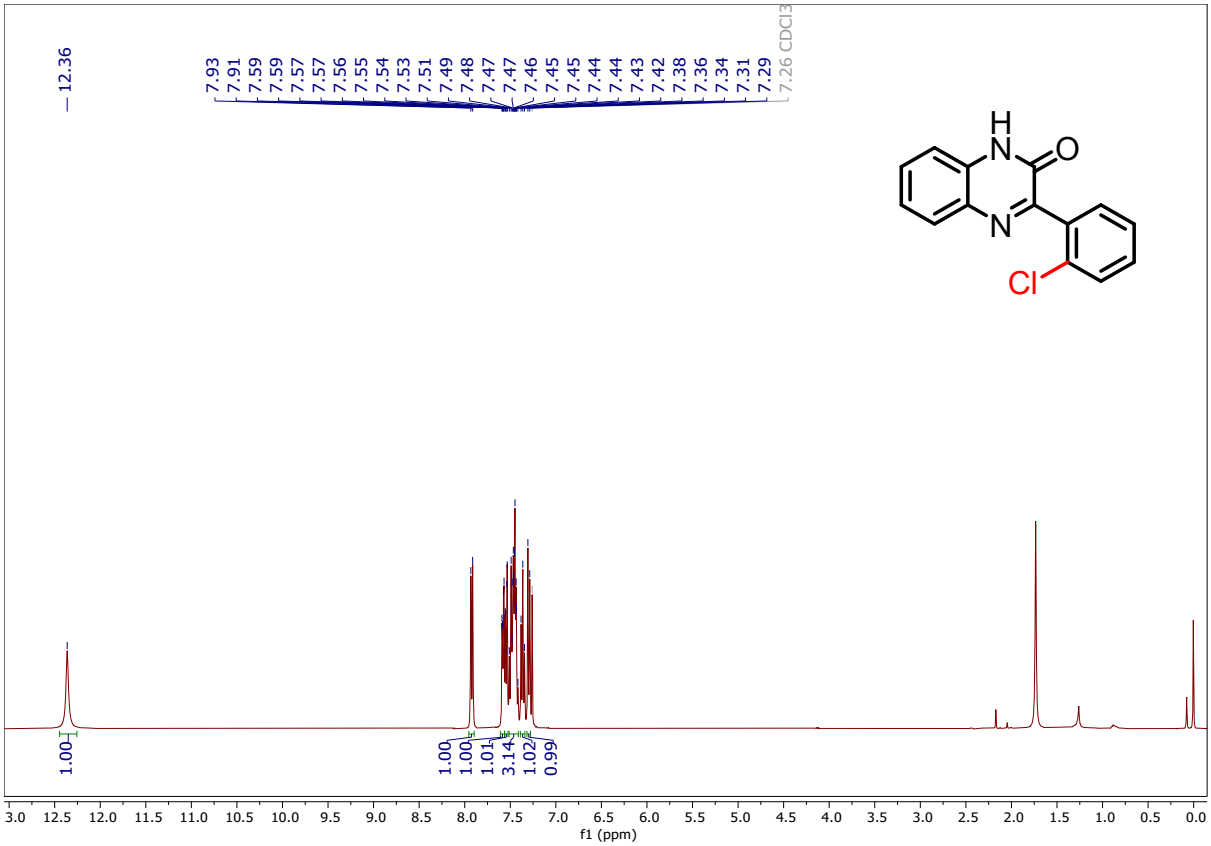


Figure 1: ^{1}H NMR spectrum of compound **3aa** (400 MHz, $CDCl_3$).

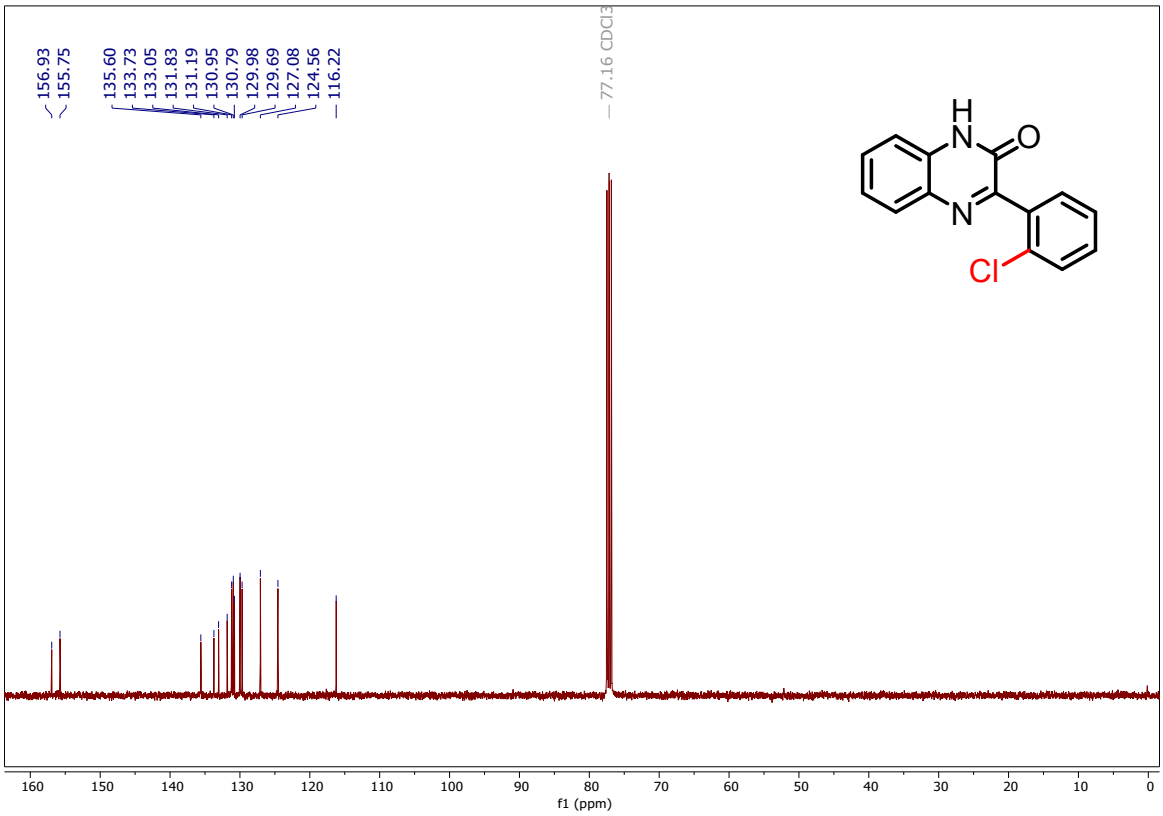


Figure 2: ^{13}C NMR spectrum of compound **3aa** (100 MHz, $CDCl_3$).

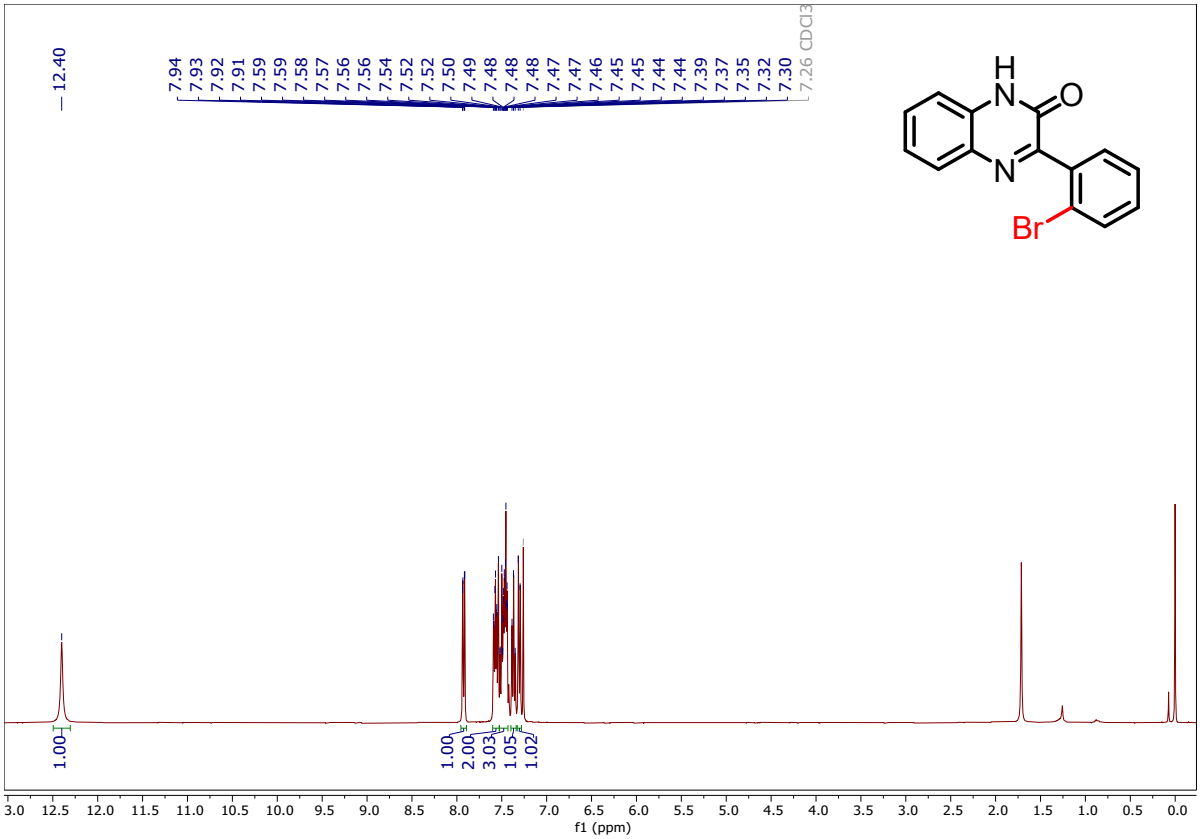


Figure 3: ^{1}H NMR spectrum of compound **3ab** (400 MHz, $CDCl_3$).

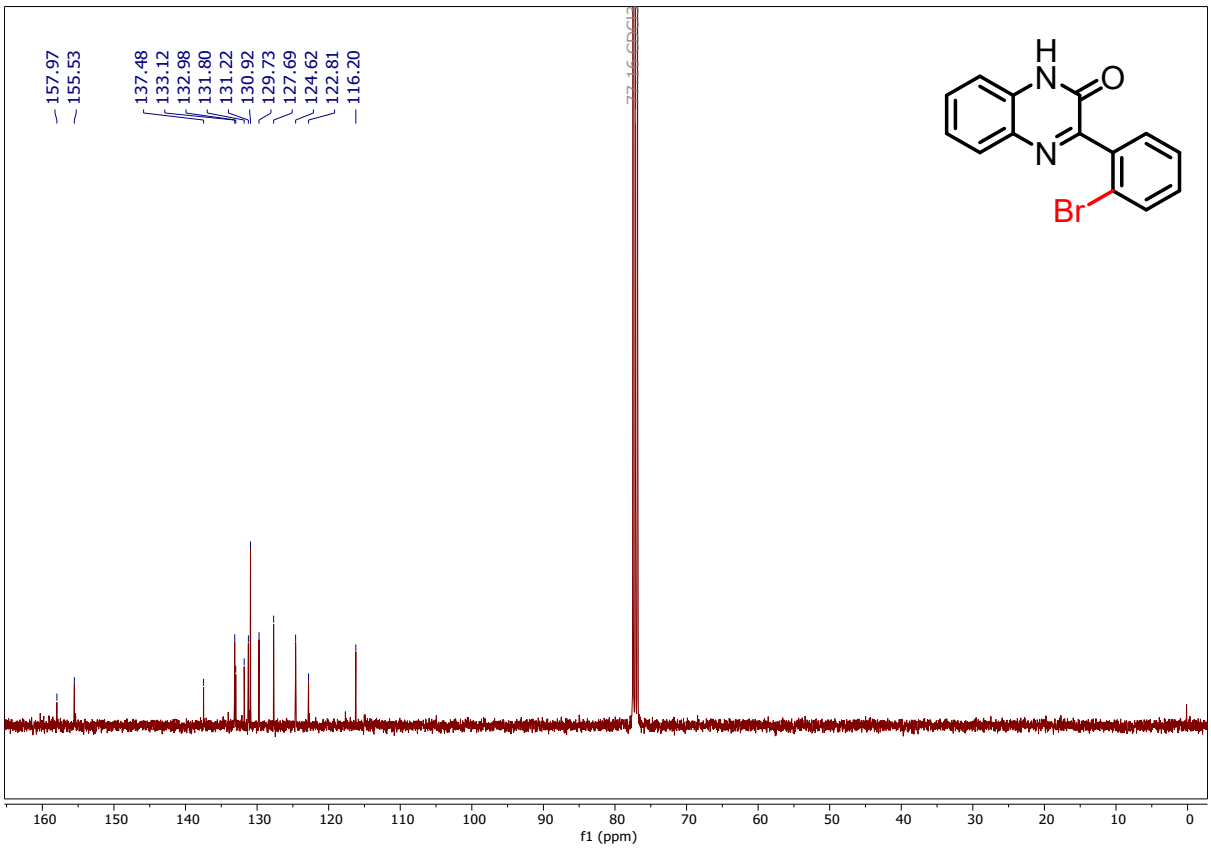


Figure 4: ^{13}C NMR spectrum of compound **3ab** (100 MHz, $CDCl_3$).

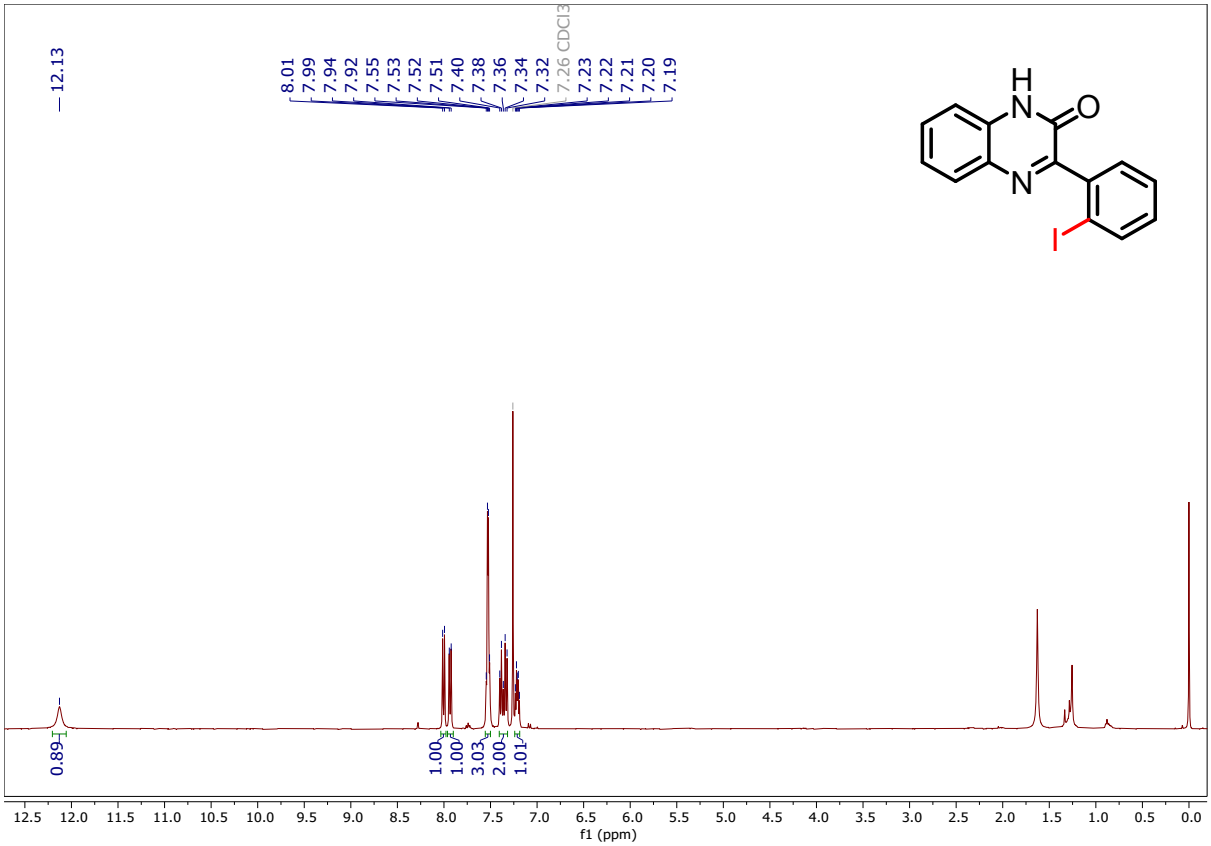


Figure 5: ^{1}H NMR spectrum of compound **3ac** (400 MHz, $CDCl_3$).

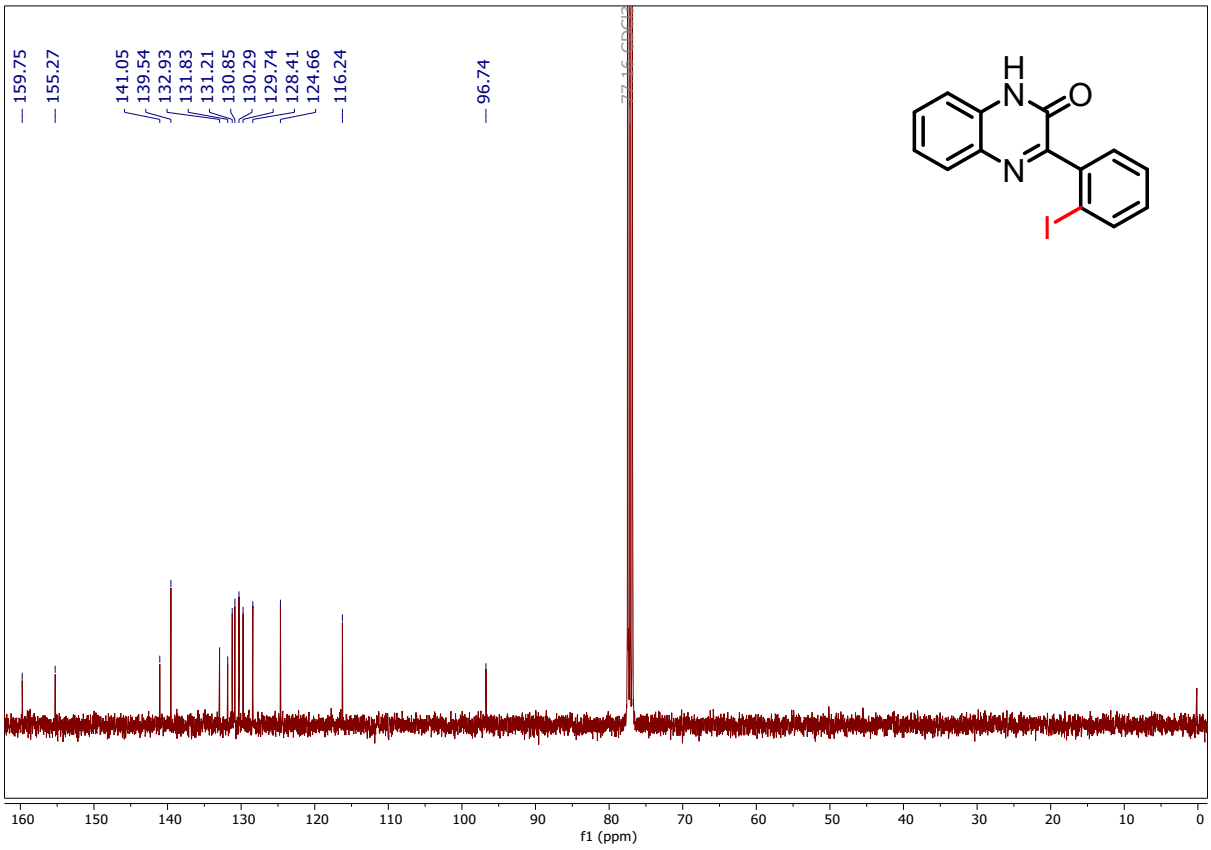


Figure 6: ^{13}C NMR spectrum of compound **3ac** (100 MHz, $CDCl_3$).

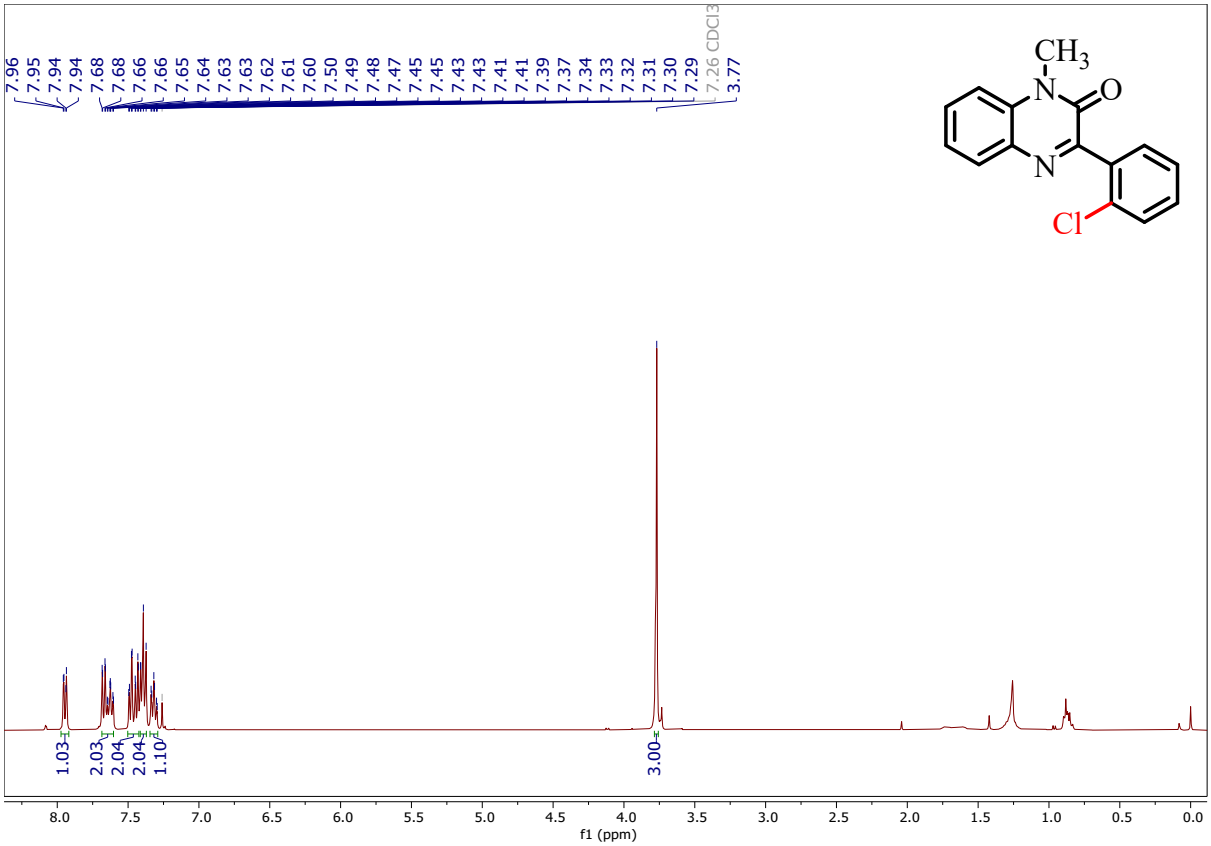


Figure 7: ^{1}H NMR spectrum of compound **3ba** (400 MHz, $CDCl_3$).

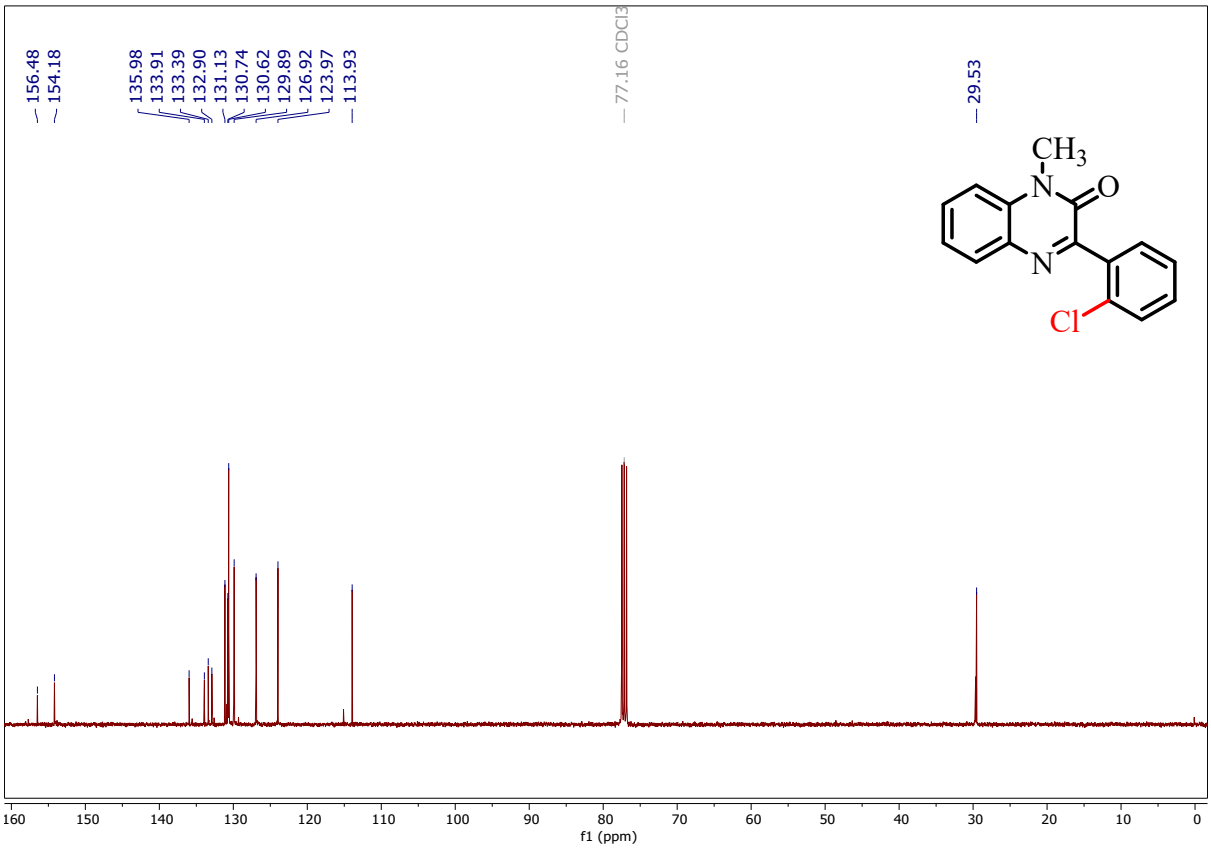


Figure 8: ^{13}C NMR spectrum of compound **3ba** (100 MHz, $CDCl_3$).

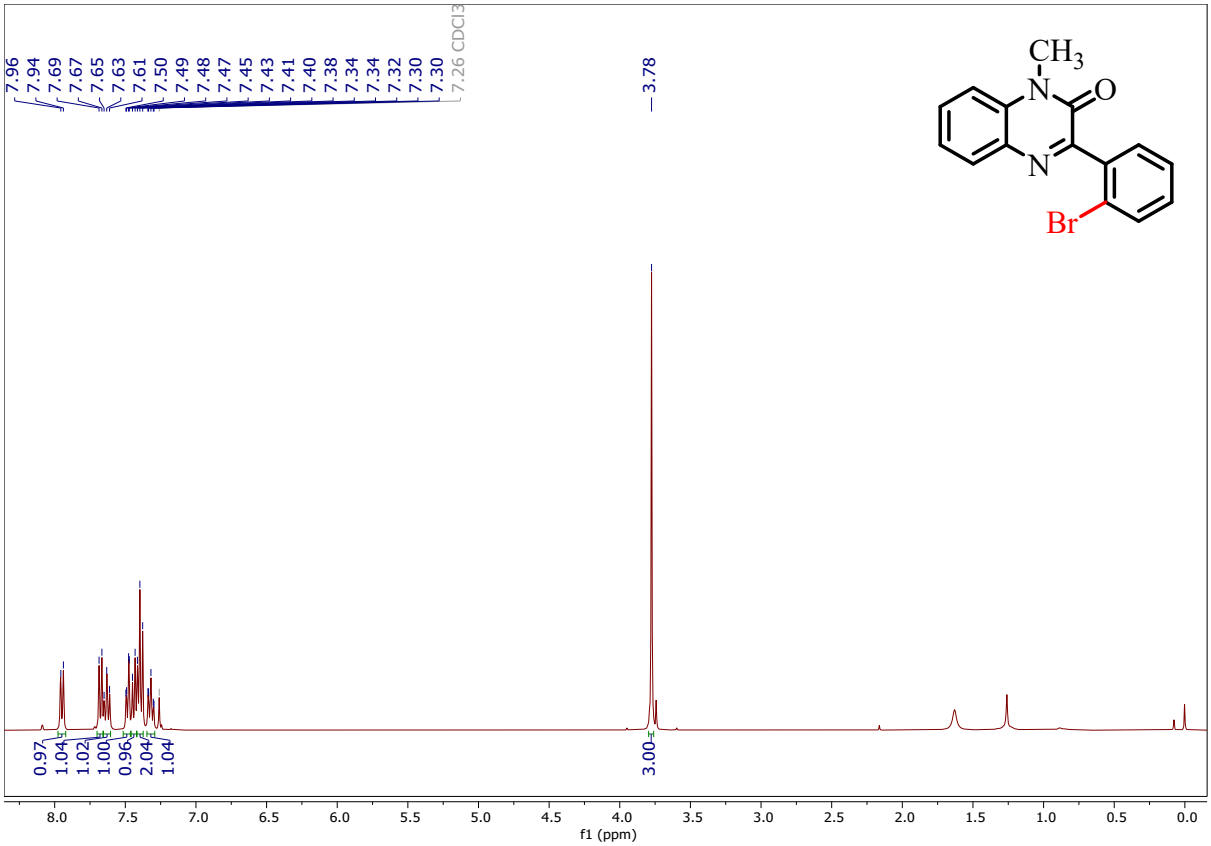


Figure 9: ^{1}H NMR spectrum of compound **3bb** (400 MHz, $CDCl_3$).

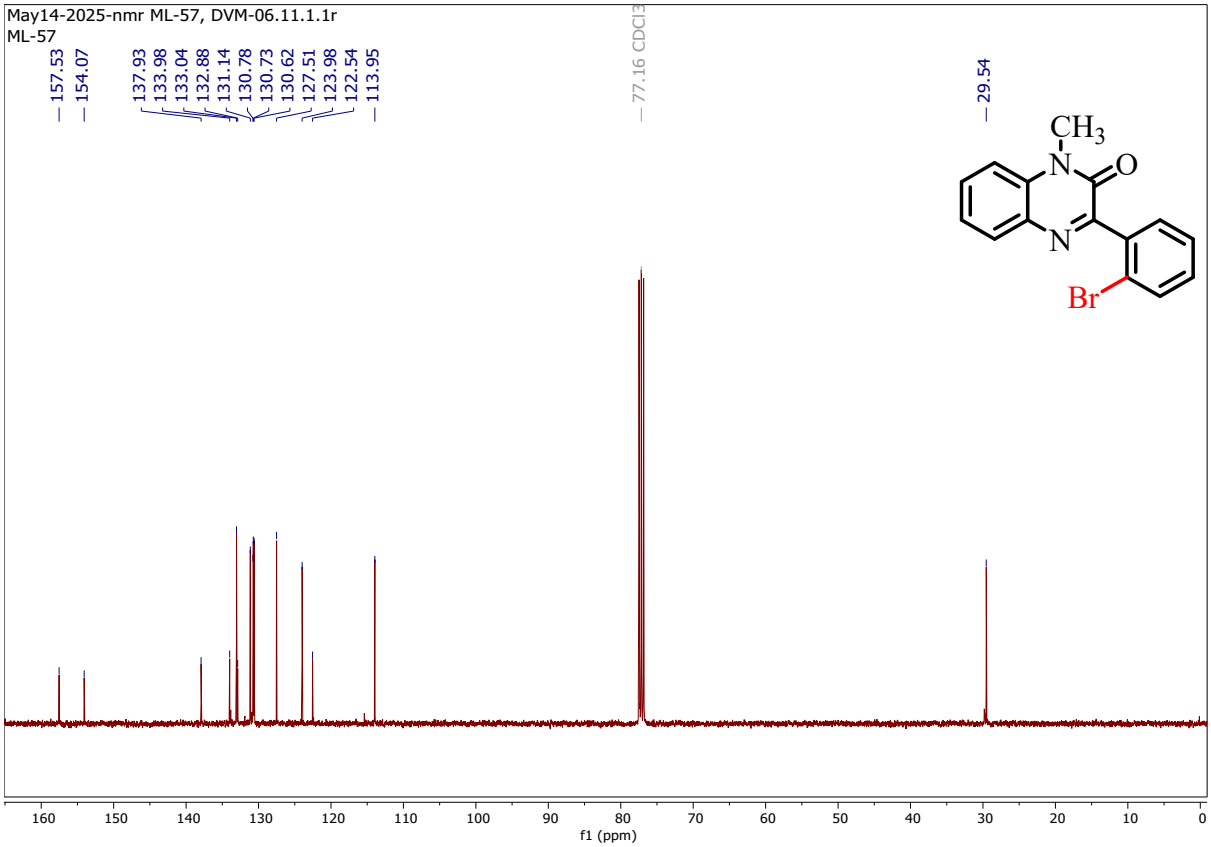


Figure 10: ^{13}C NMR spectrum of compound **3bb** (100 MHz, $CDCl_3$).

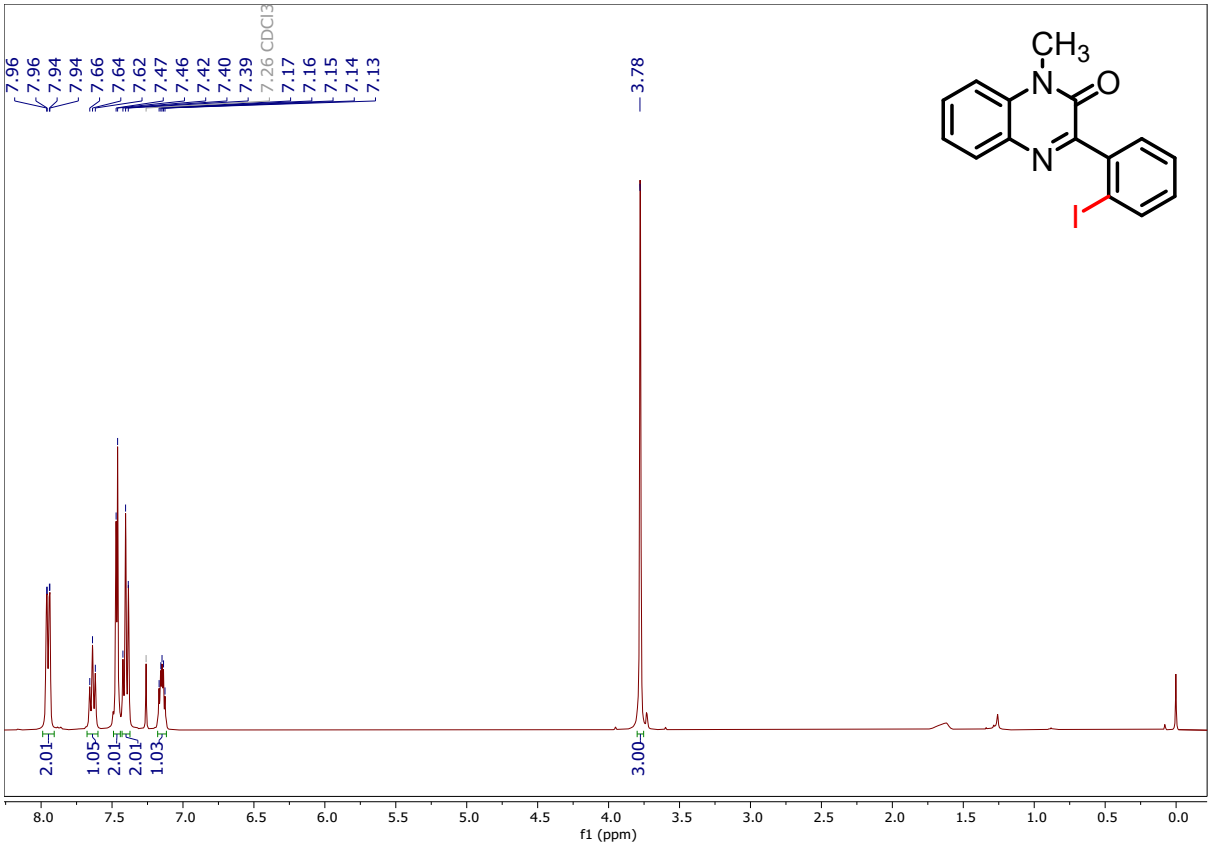


Figure 11: ^{1}H NMR spectrum of compound **3bc** (400 MHz, $CDCl_3$).

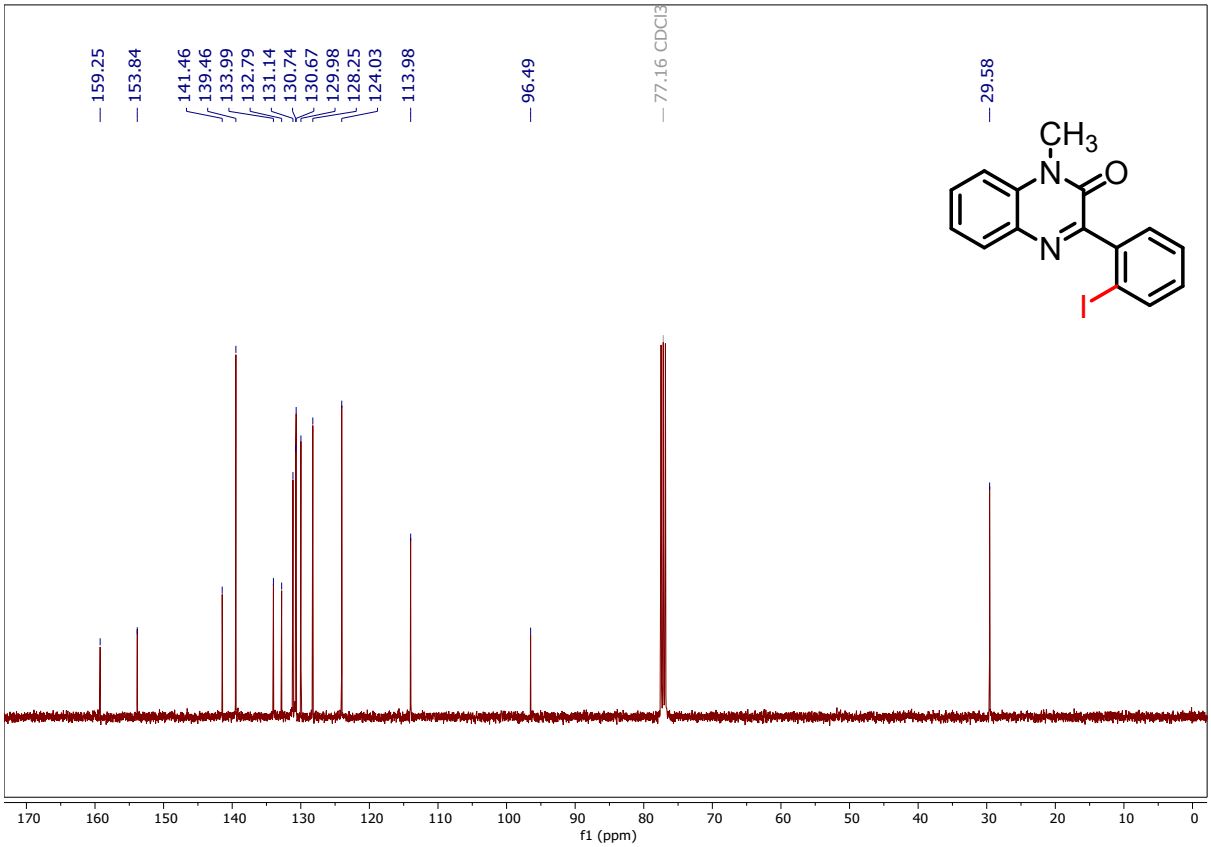


Figure12: ^{13}C NMR spectrum of compound **3bc** (100 MHz, $CDCl_3$).

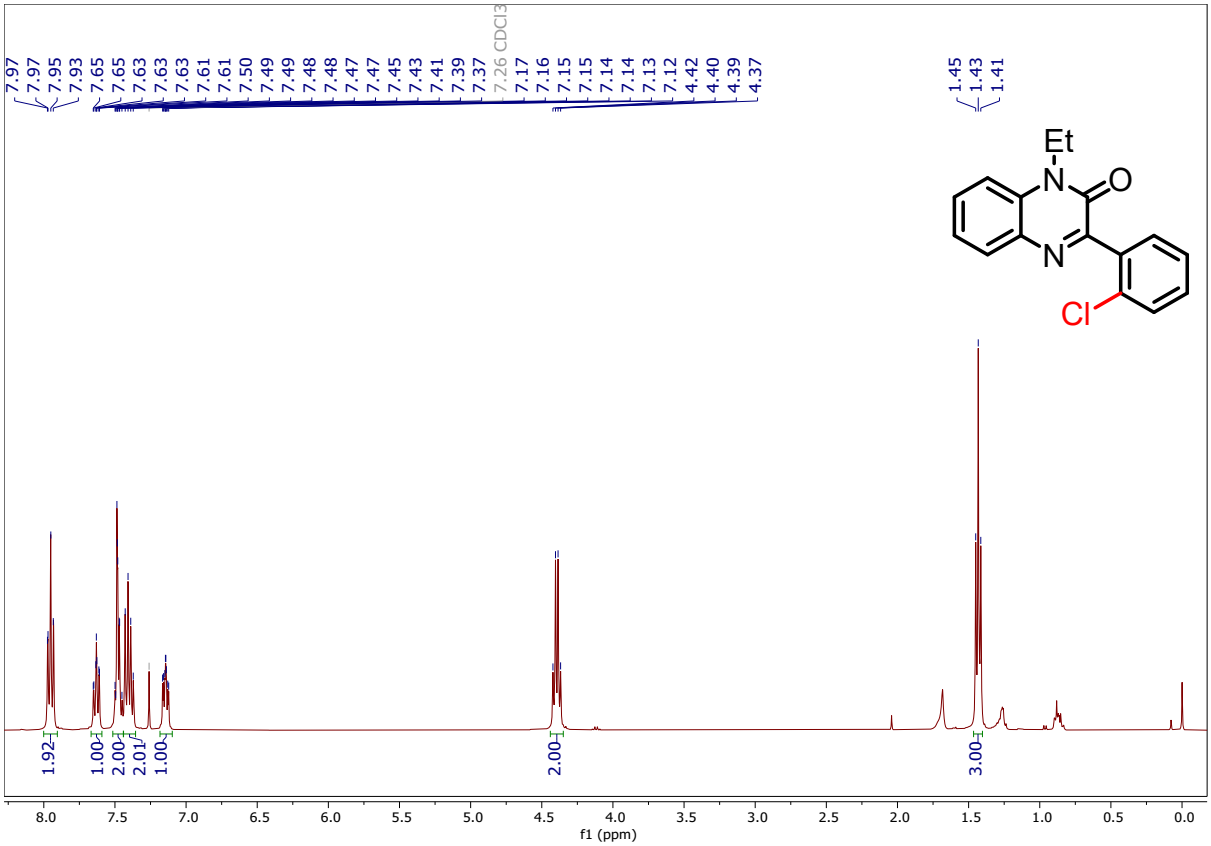


Figure 13: ^{1}H NMR spectrum of compound **3ca** (400 MHz, $CDCl_3$).

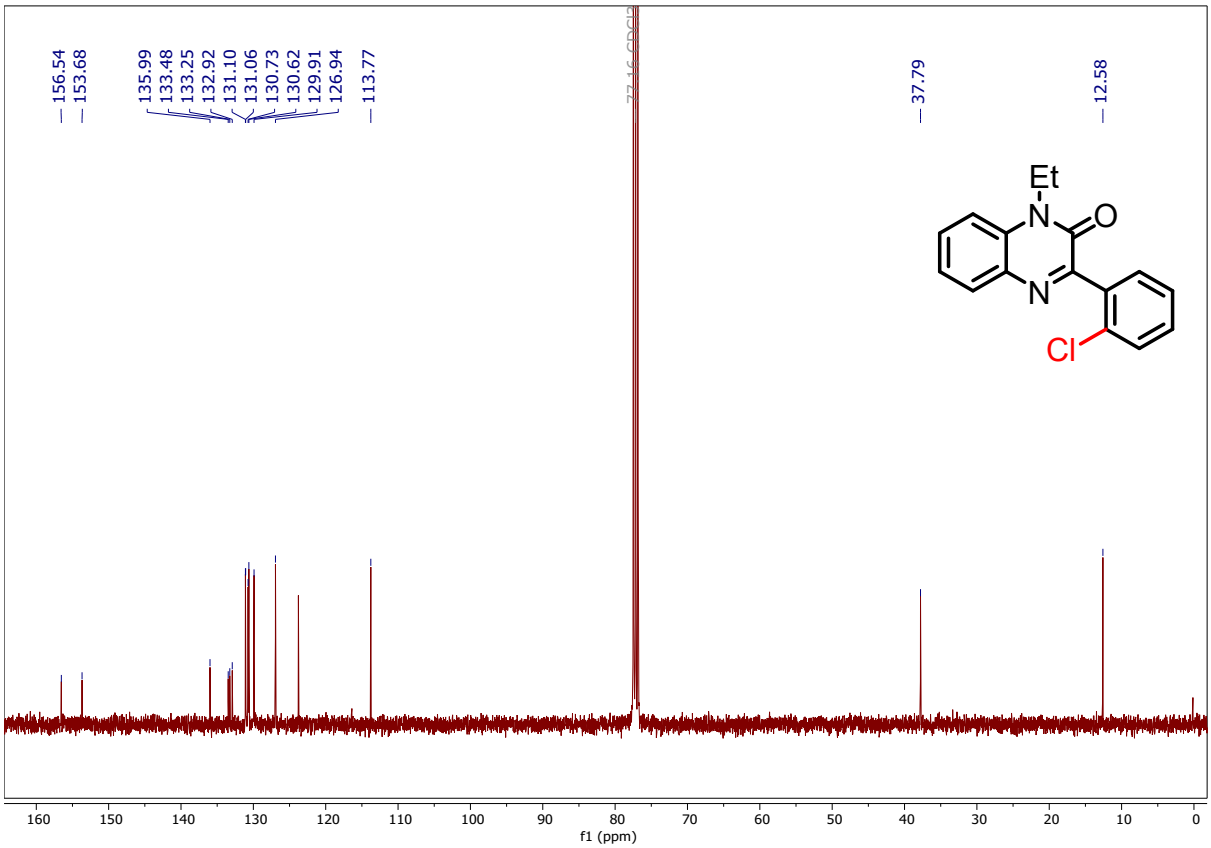


Figure 14: ^{13}C NMR spectrum of compound **3ca** (100 MHz, $CDCl_3$).

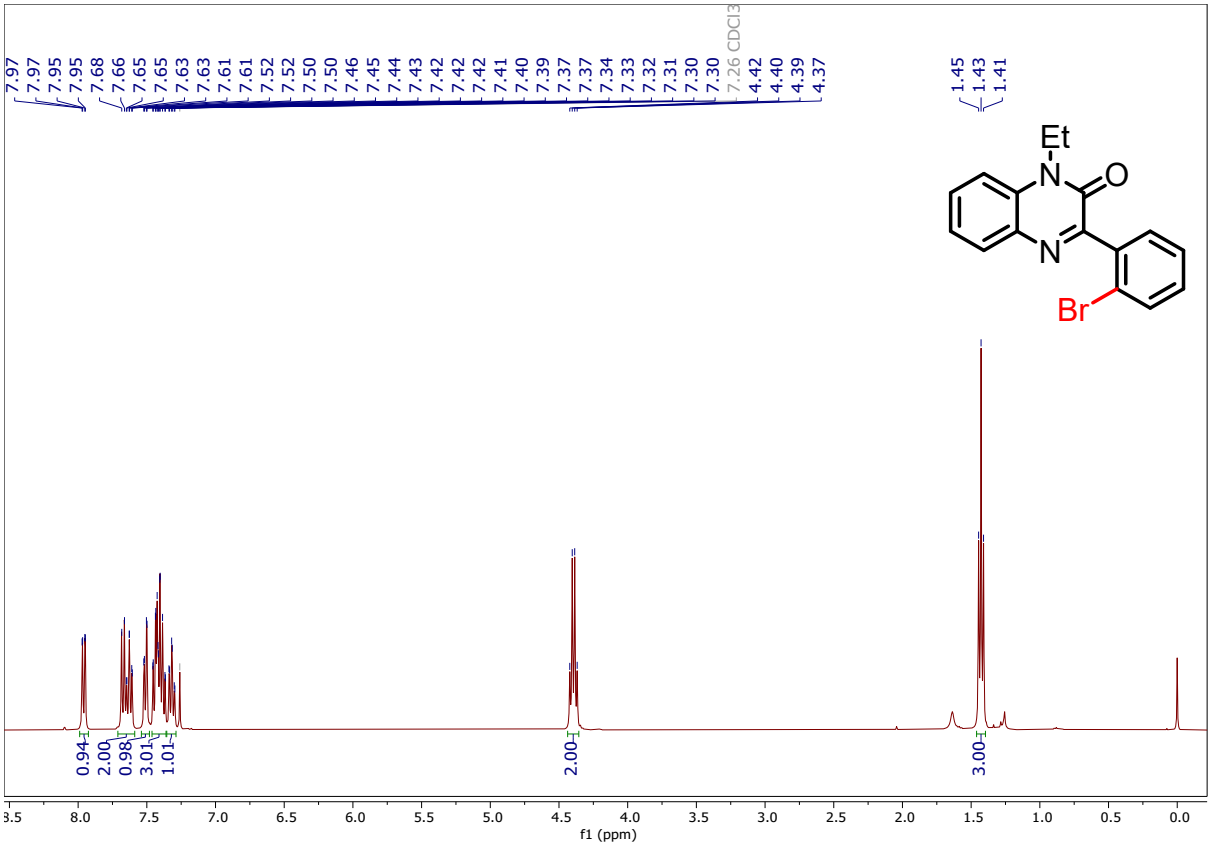


Figure 15: ^{1}H NMR spectrum of compound **3cb** (400 MHz, $CDCl_3$).

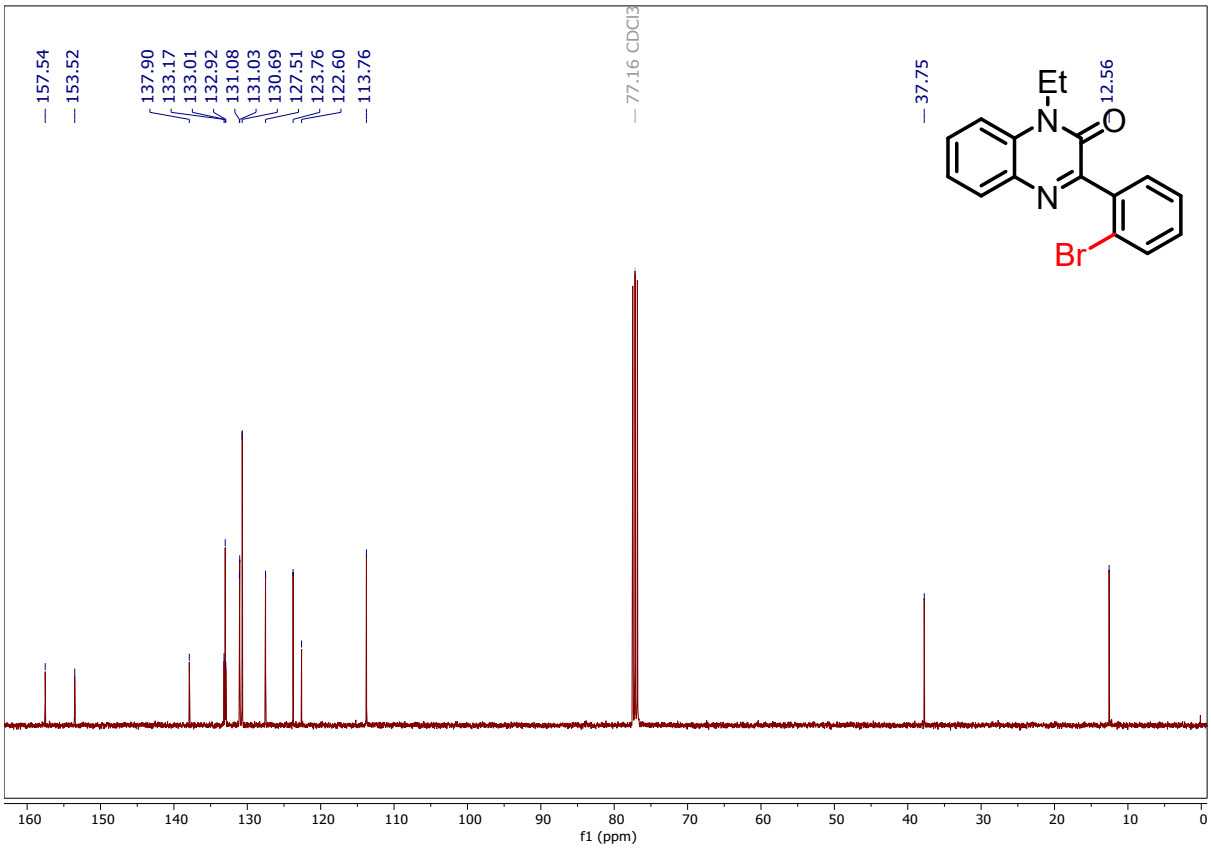


Figure 16: ^{13}C NMR spectrum of compound **3cb** (100 MHz, $CDCl_3$).

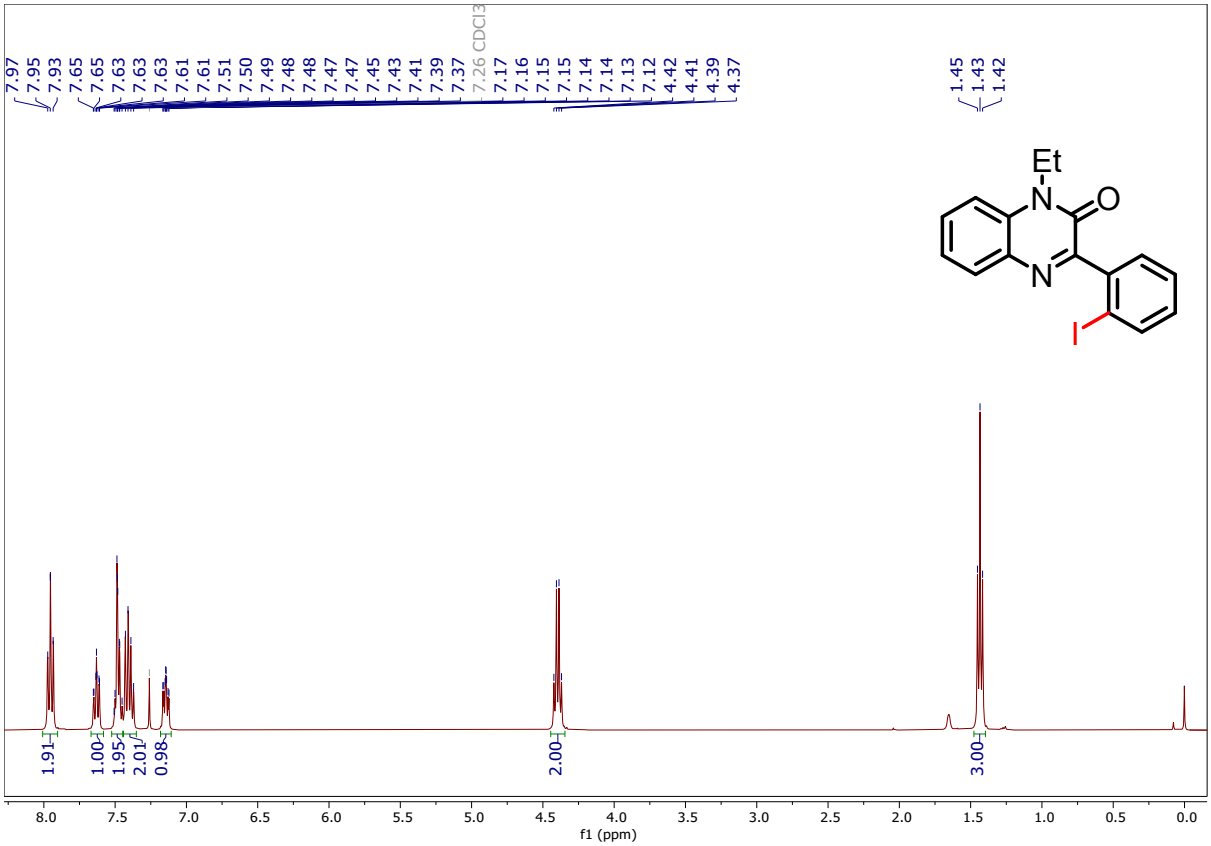


Figure 17: ^{1}H NMR spectrum of compound **3cc** (400 MHz, $CDCl_3$).

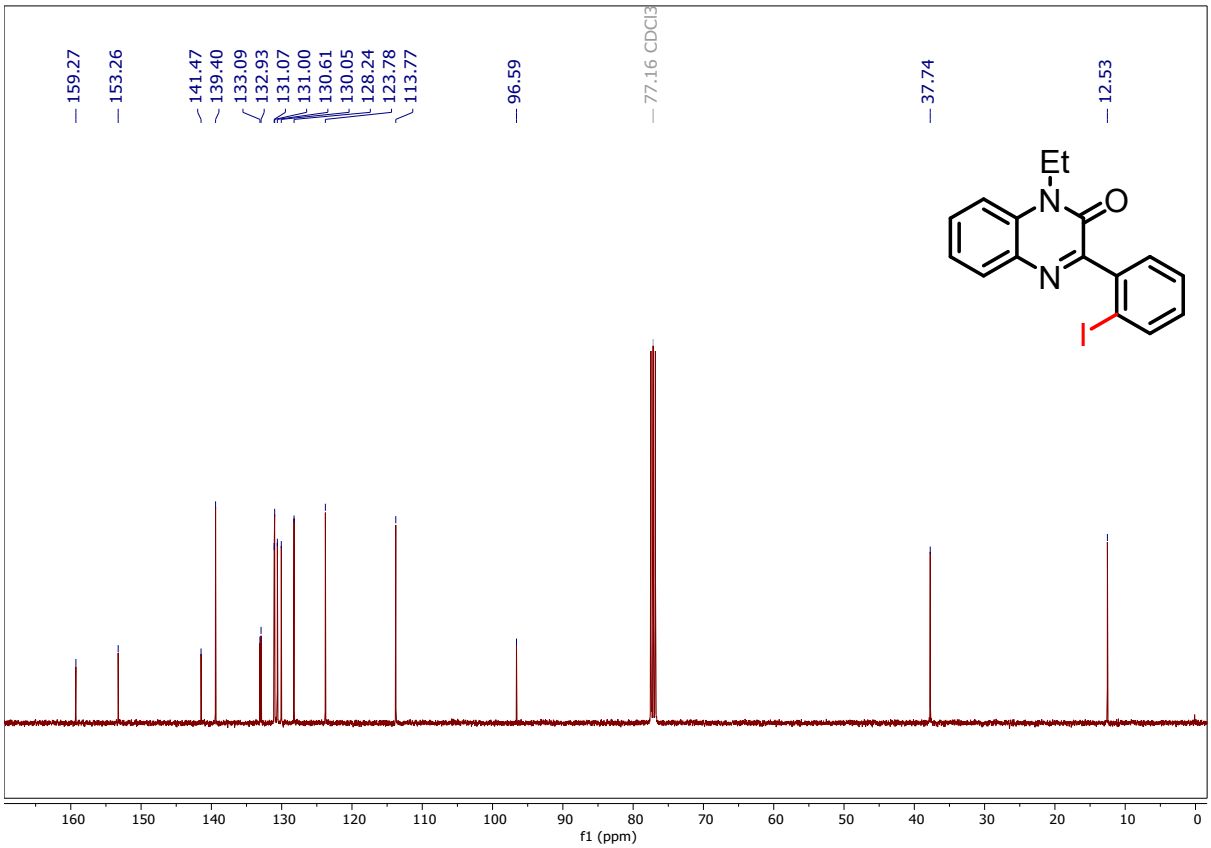


Figure 18: ^{13}C NMR spectrum of compound **3cc** (100 MHz, $CDCl_3$).

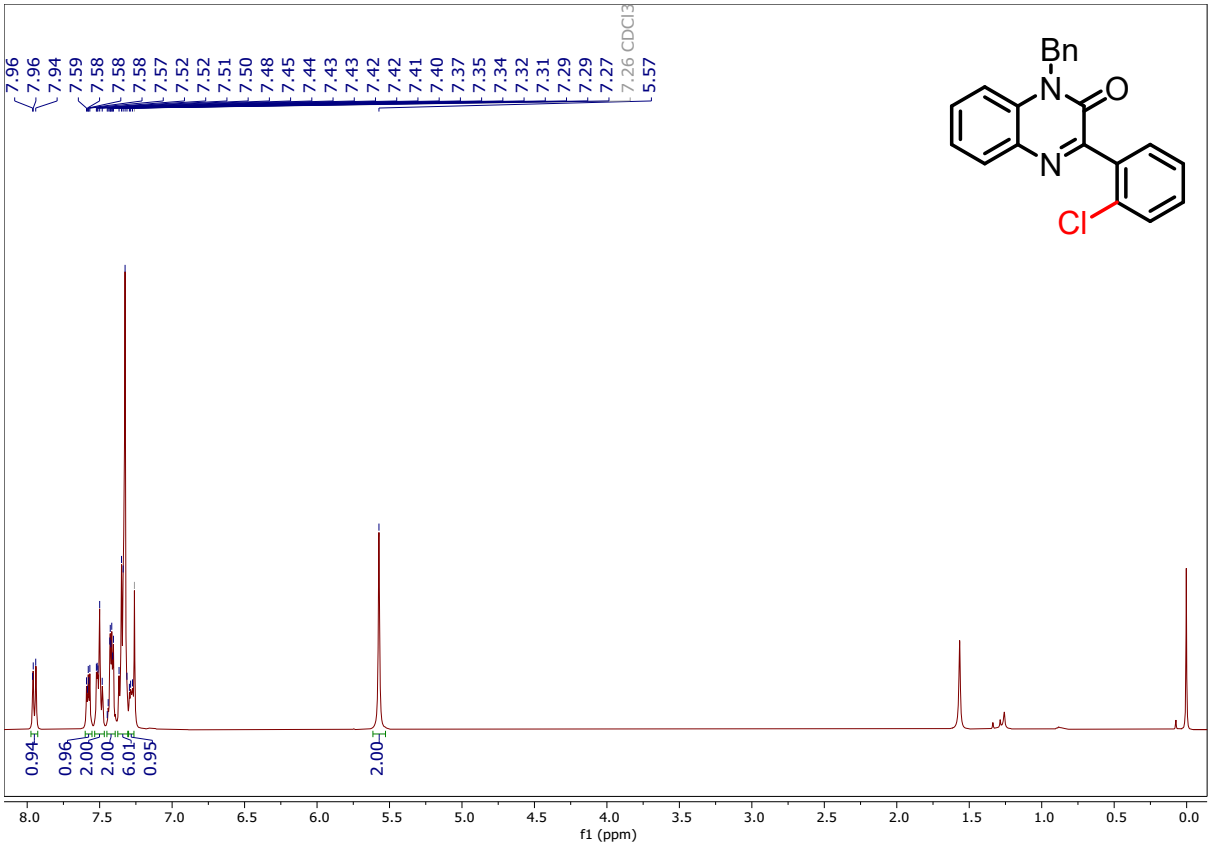


Figure 19: ^{1}H NMR spectrum of compound **3da** (400 MHz, $CDCl_3$).

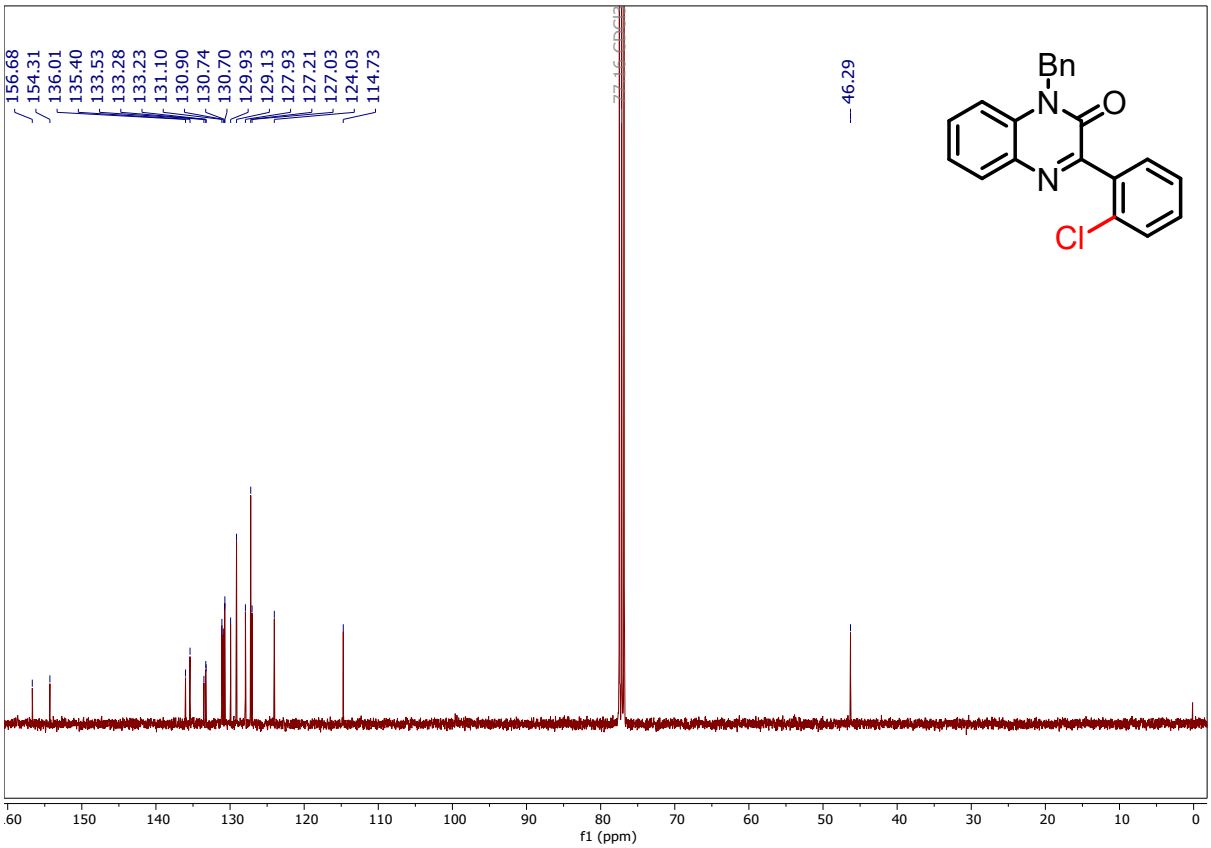


Figure 20: ^{13}C NMR spectrum of compound **3da** (100 MHz, $CDCl_3$).

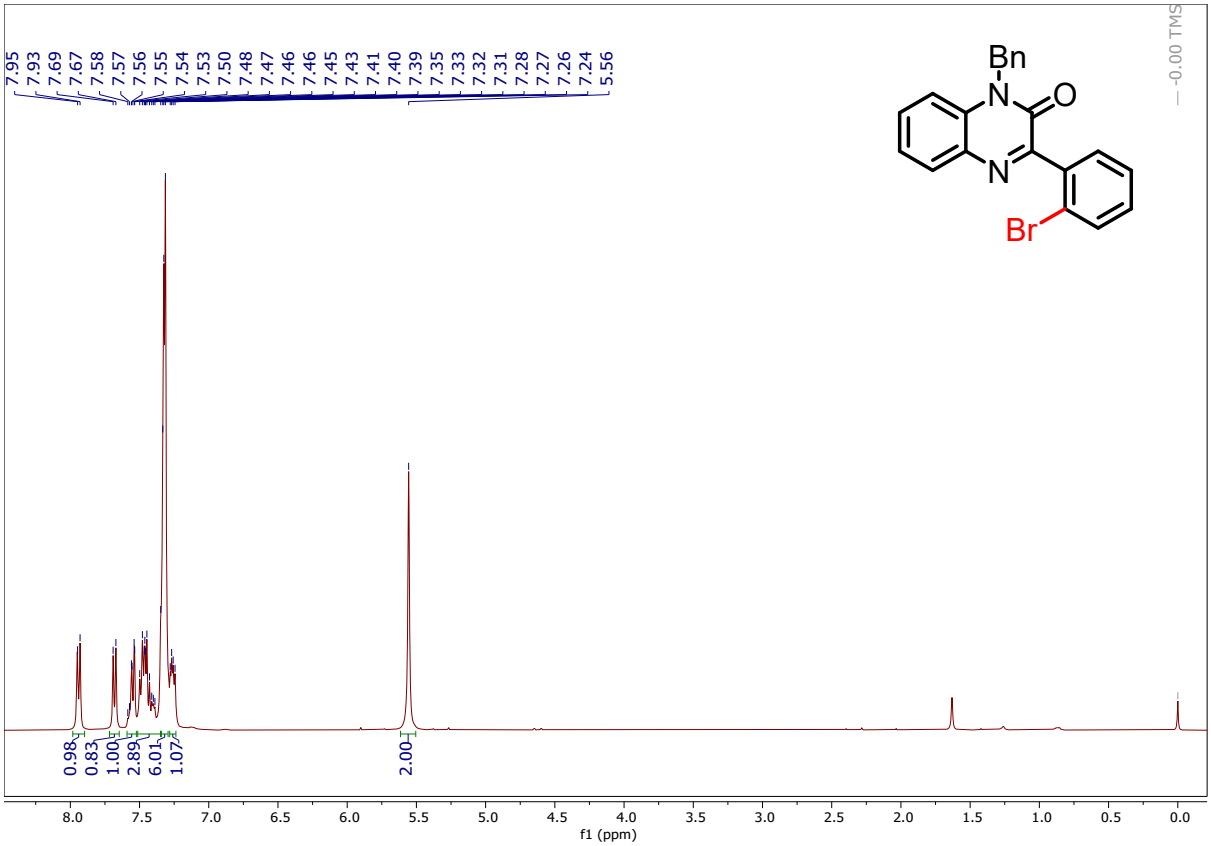


Figure 21: ^{1}H NMR spectrum of compound **3db** (400 MHz, $CDCl_3$).

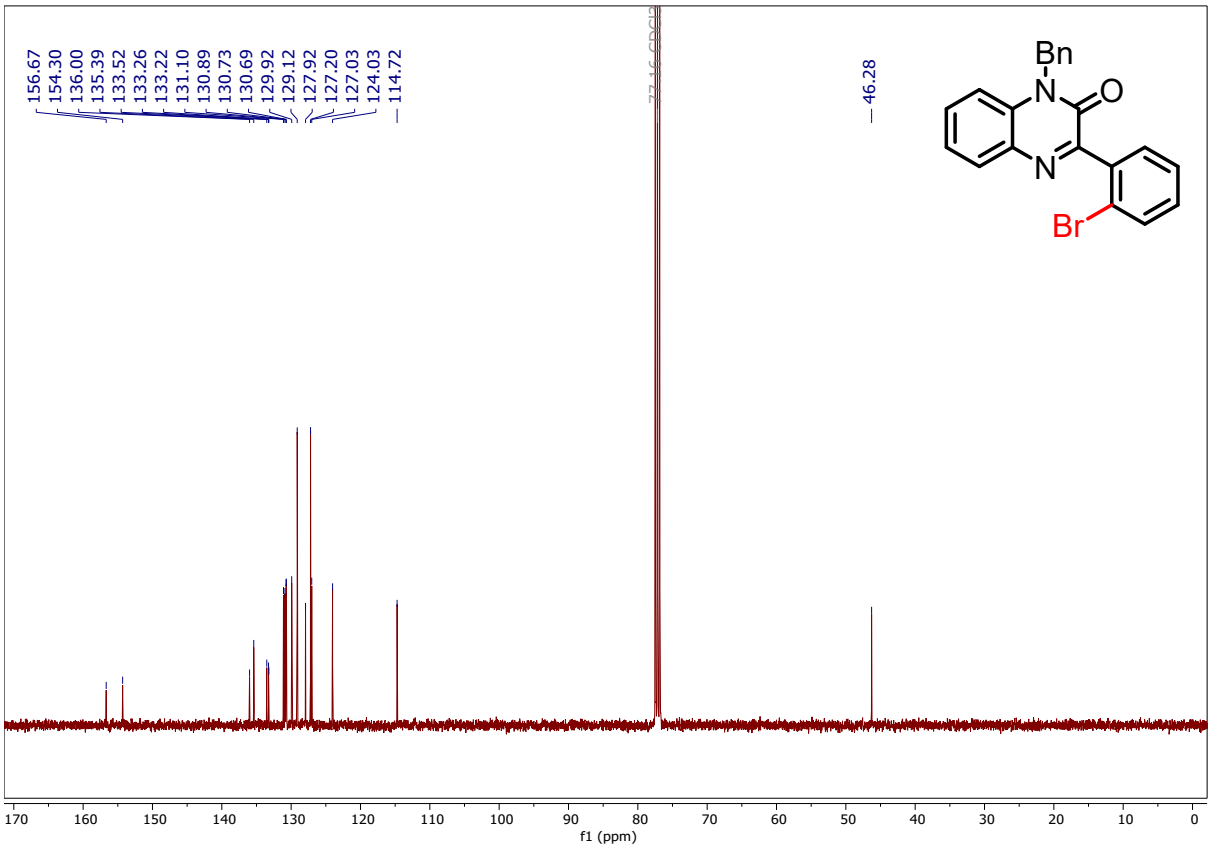


Figure 22: ^{13}C NMR spectrum of compound **3db** (100 MHz, $CDCl_3$).

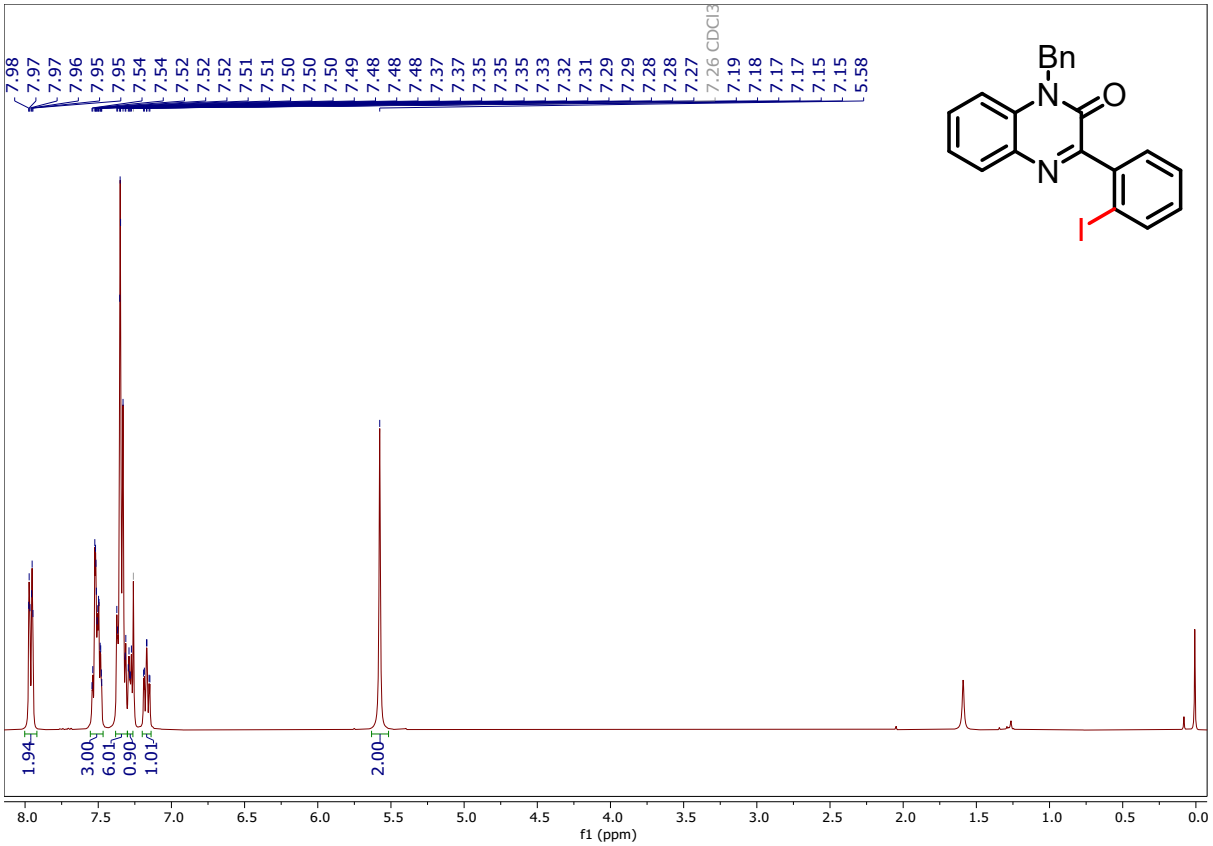


Figure 23: ^{1}H NMR spectrum of compound **3dc** (400 MHz, $CDCl_3$).

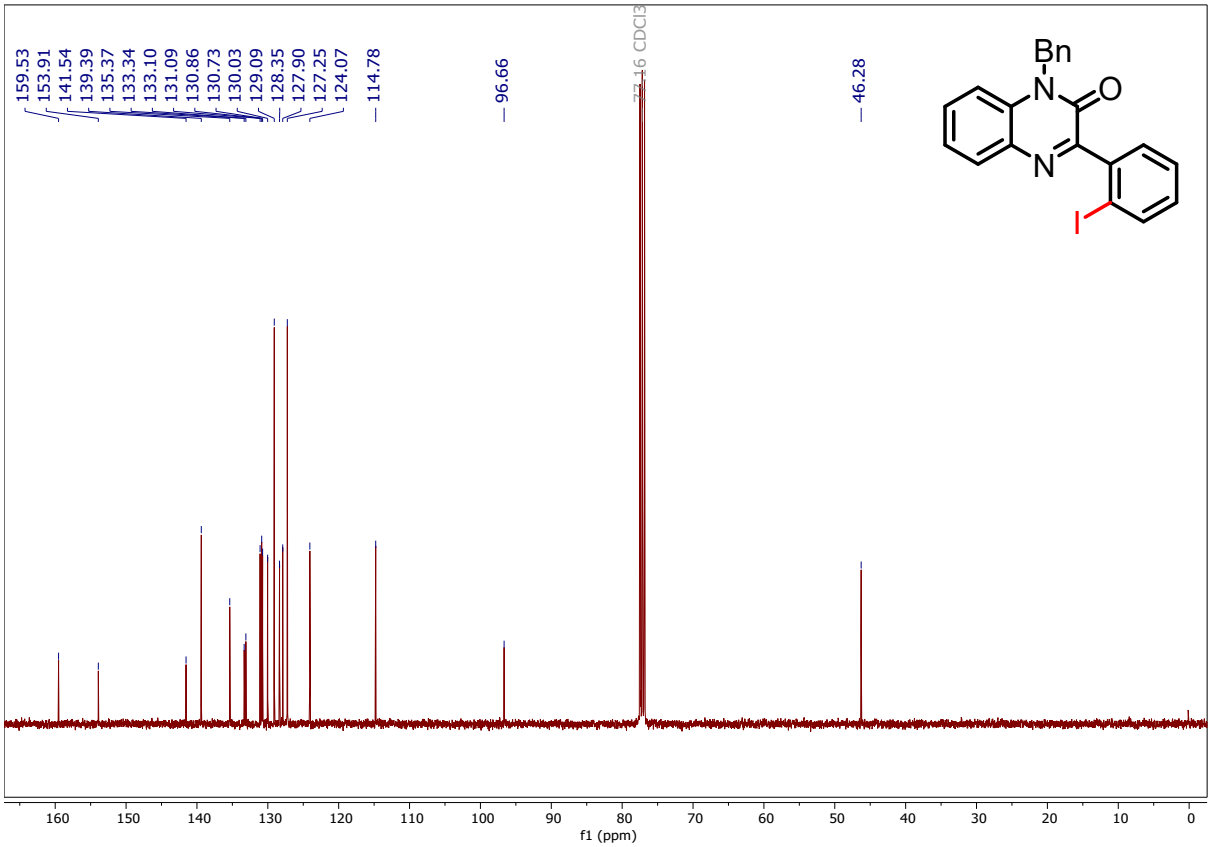


Figure 24: ^{13}C NMR spectrum of compound **3dc** (100 MHz, $CDCl_3$).

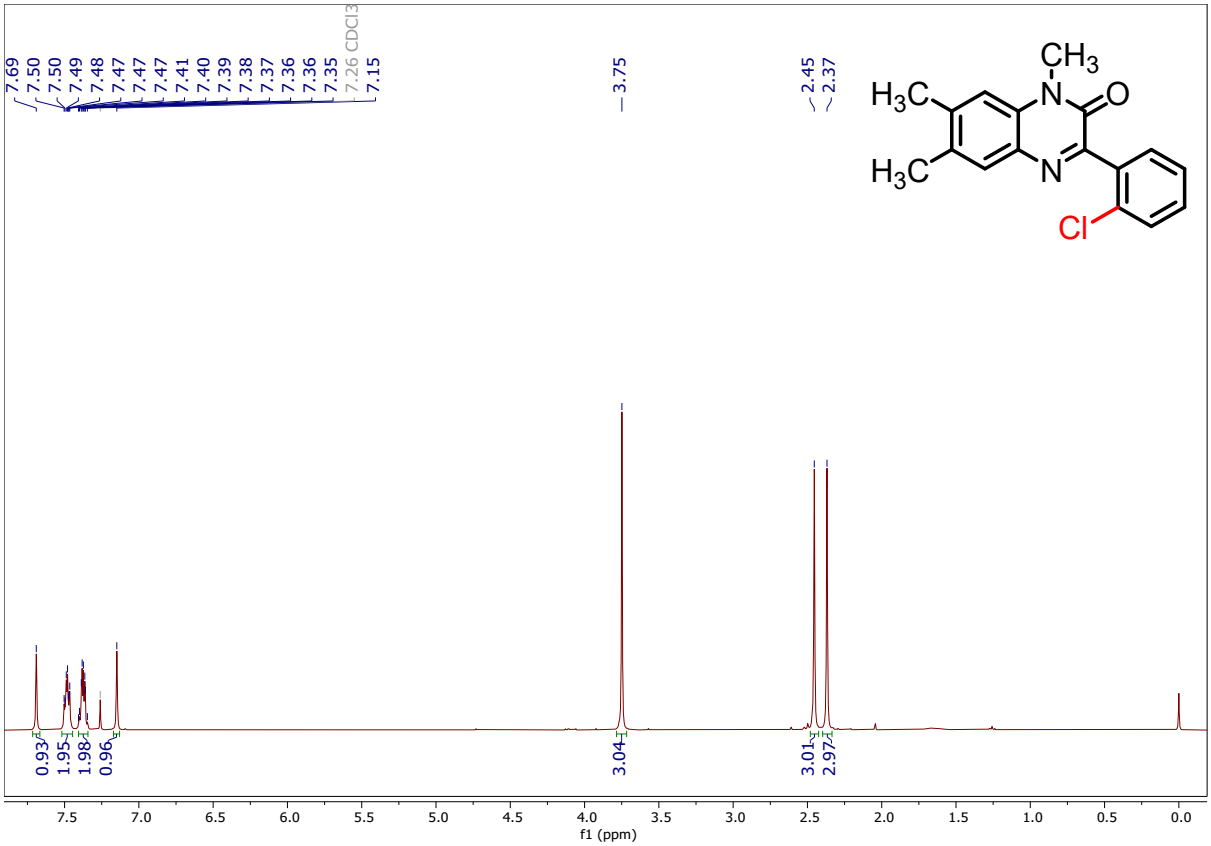


Figure 25: ^{1}H NMR spectrum of compound **4aa** (400 MHz, $CDCl_3$).

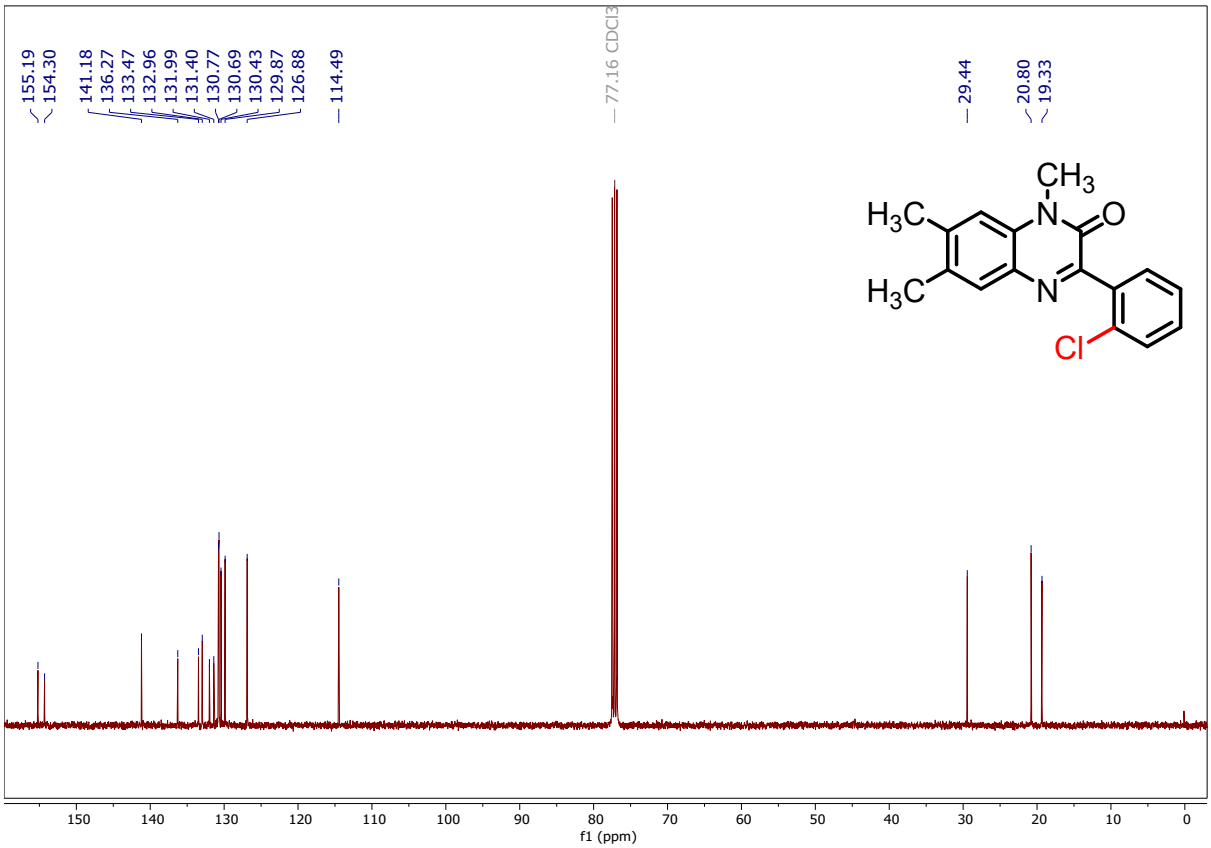


Figure 26: ^{13}C NMR spectrum of compound **4aa** (100 MHz, $CDCl_3$).

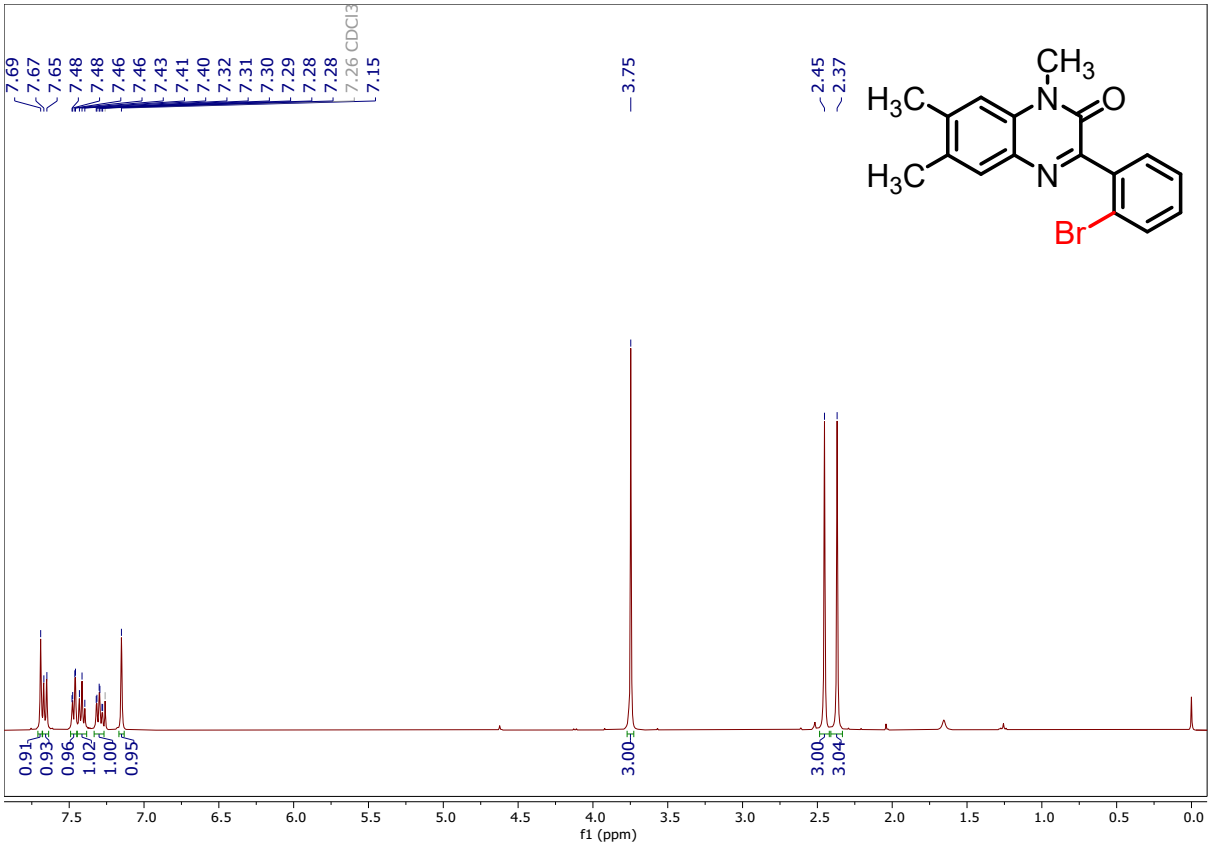


Figure 27: ^{1}H NMR spectrum of compound **4ab** (400 MHz, $CDCl_3$).

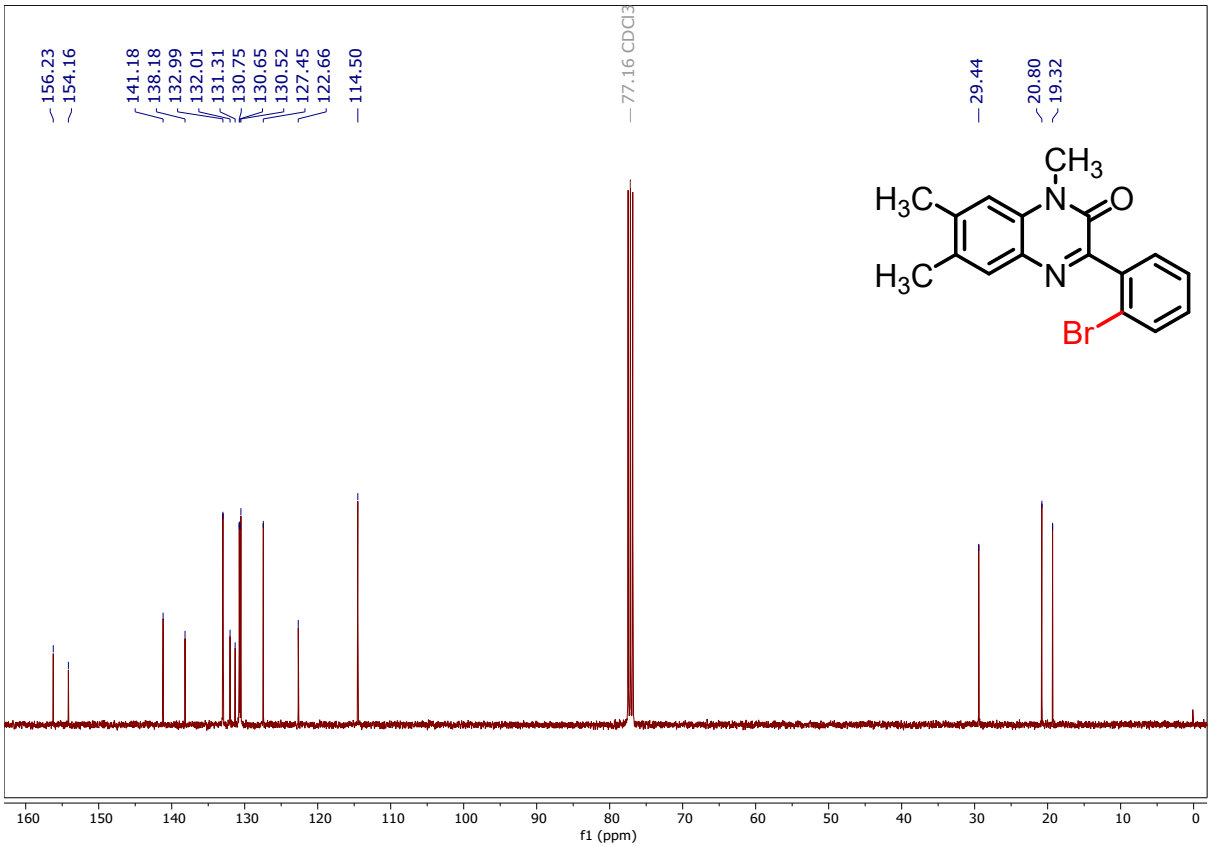


Figure 28: ^{13}C NMR spectrum of compound **4ab** (100 MHz, $CDCl_3$).

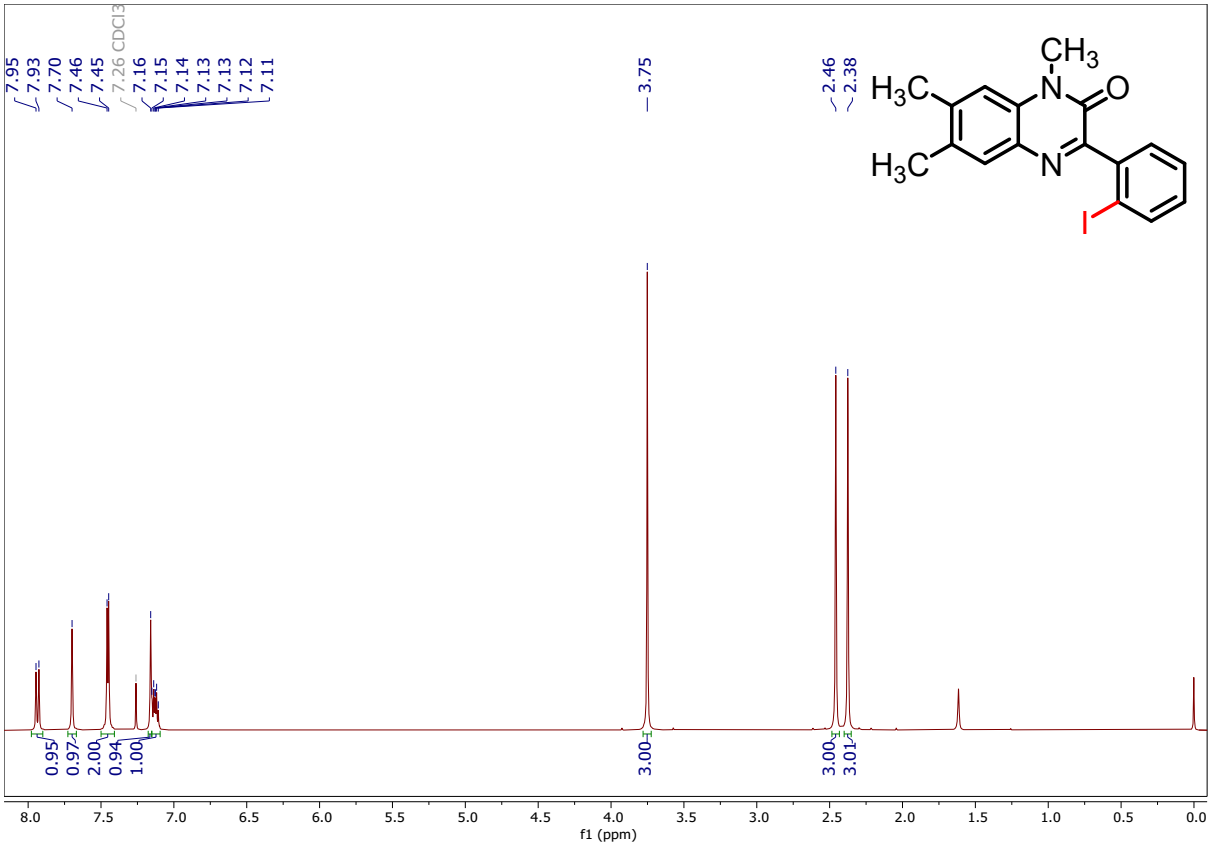


Figure 29: ^{1}H NMR spectrum of compound 4**ac** (400 MHz, $CDCl_3$).

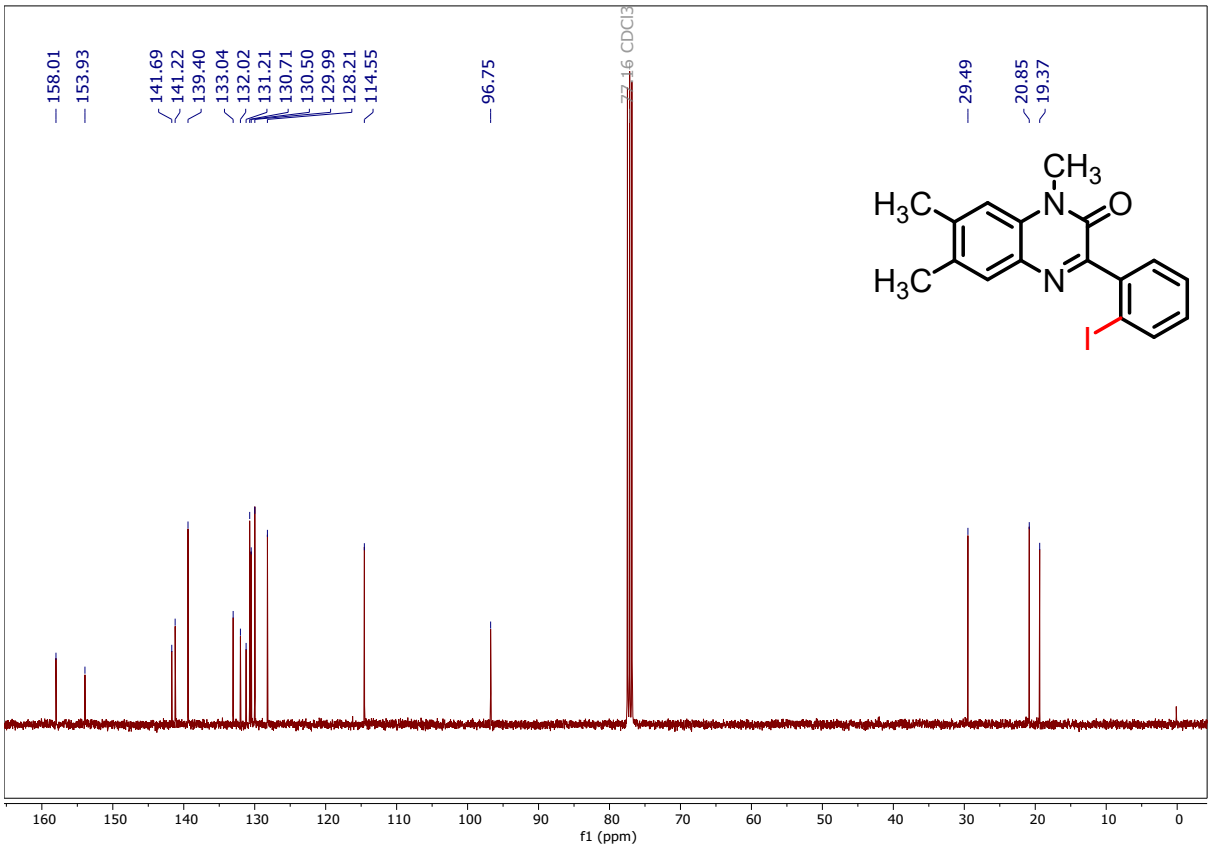


Figure 30: ^{13}C NMR spectrum of compound 4**ac** (100 MHz, $CDCl_3$).

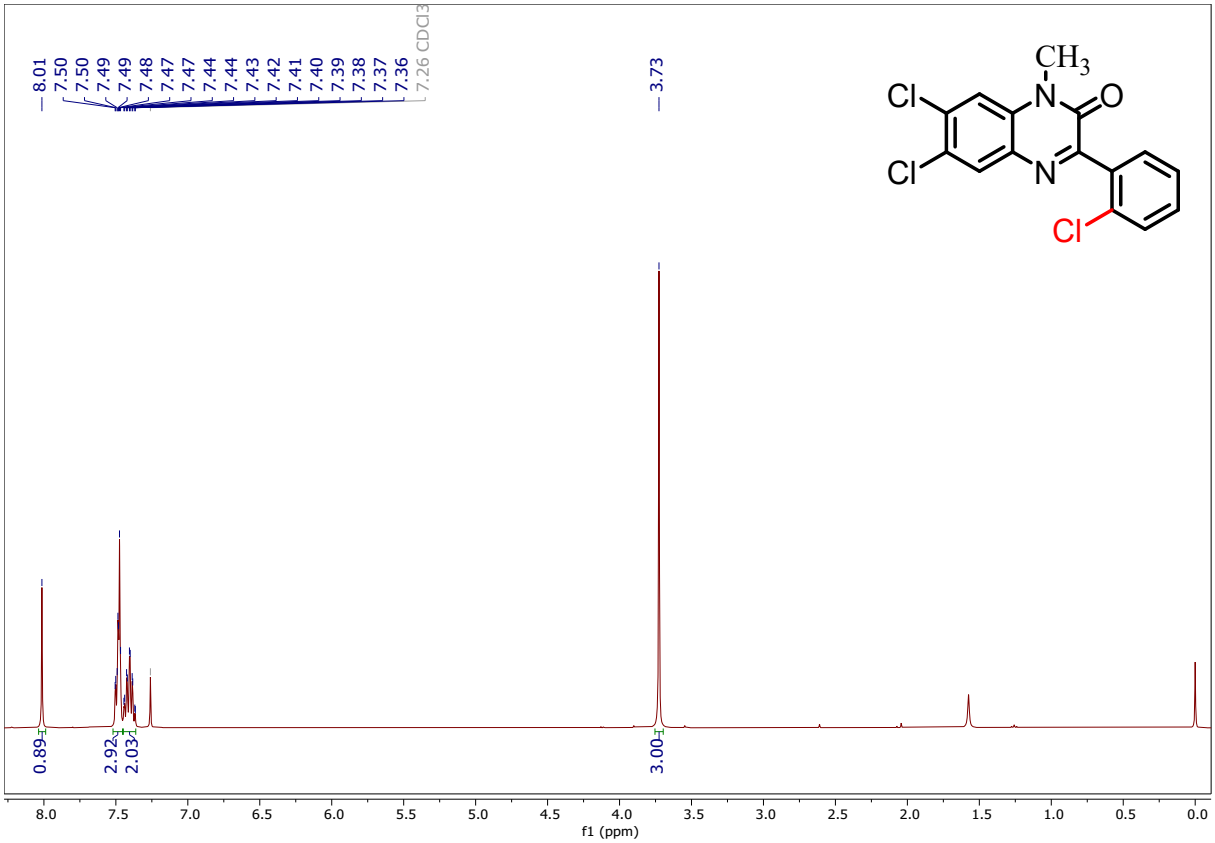


Figure 31: ^{1}H NMR spectrum of compound **4ba** (400 MHz, $CDCl_3$).

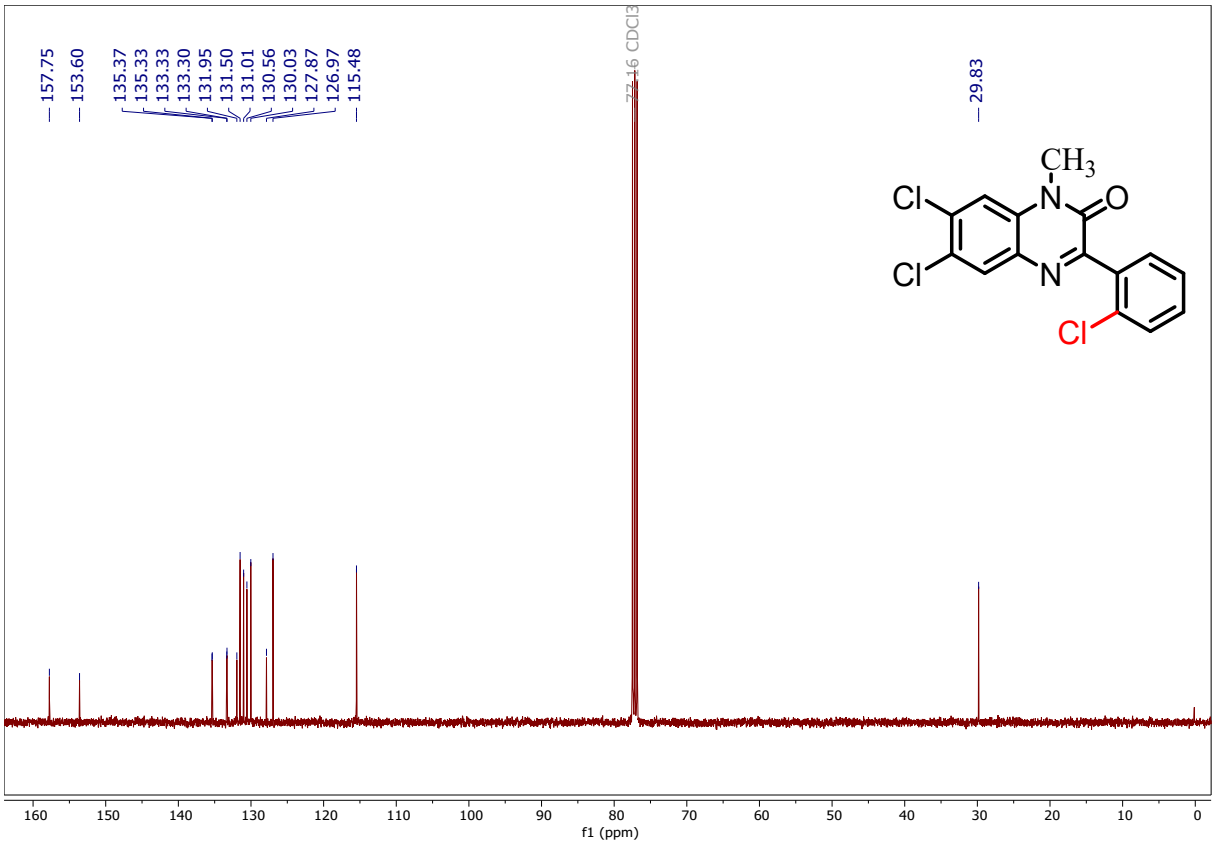


Figure 32: ^{13}C NMR spectrum of compound **4ba** (100 MHz, $CDCl_3$).

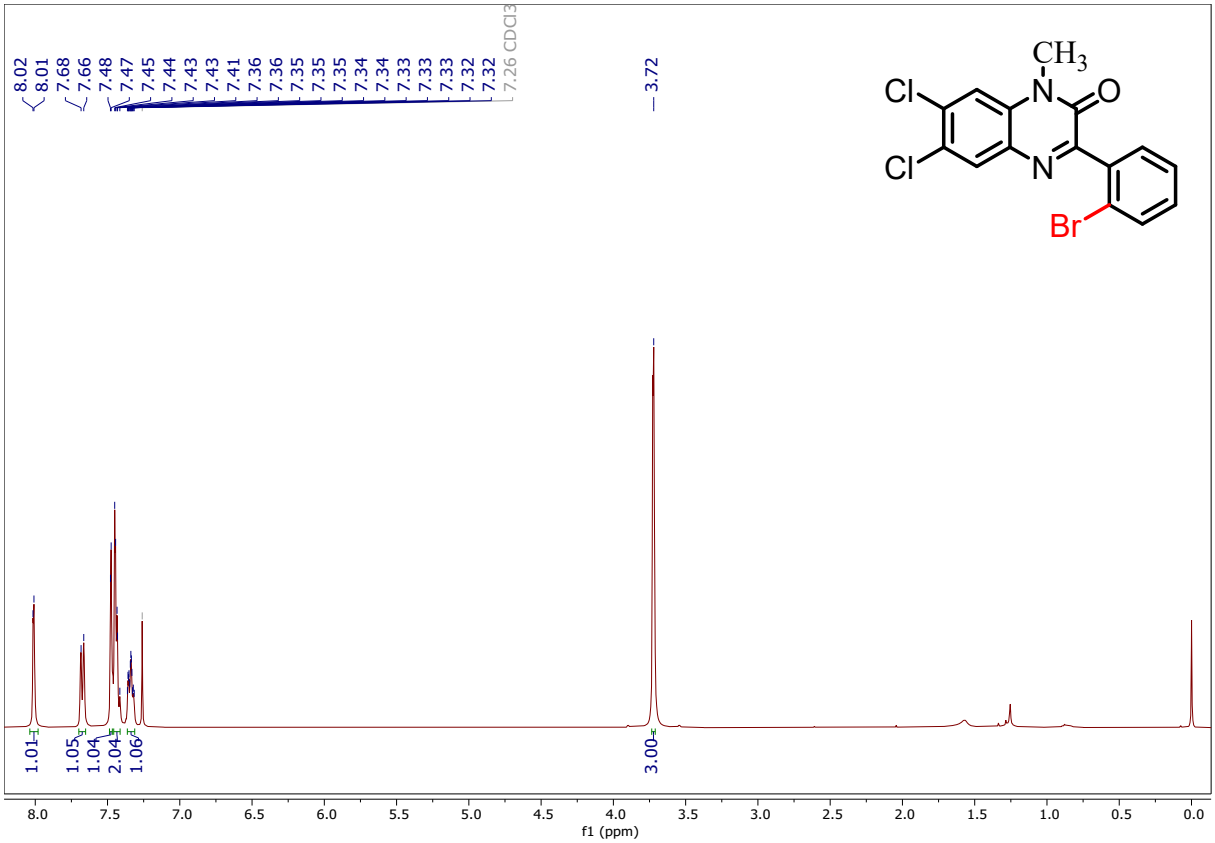


Figure 33: ^{1}H NMR spectrum of compound **4bb** (400 MHz, $CDCl_3$).

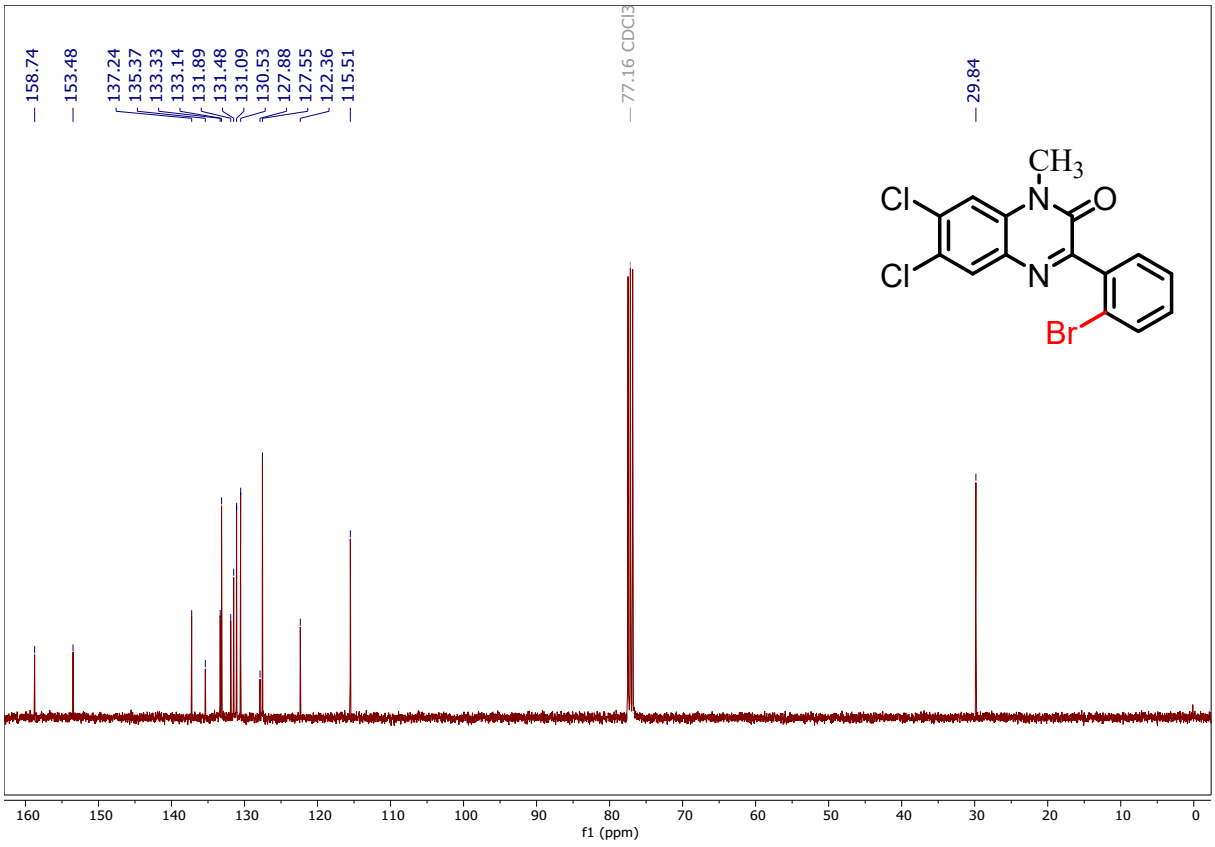


Figure 34: ^{13}C NMR spectrum of compound **4bb** (100 MHz, $CDCl_3$).

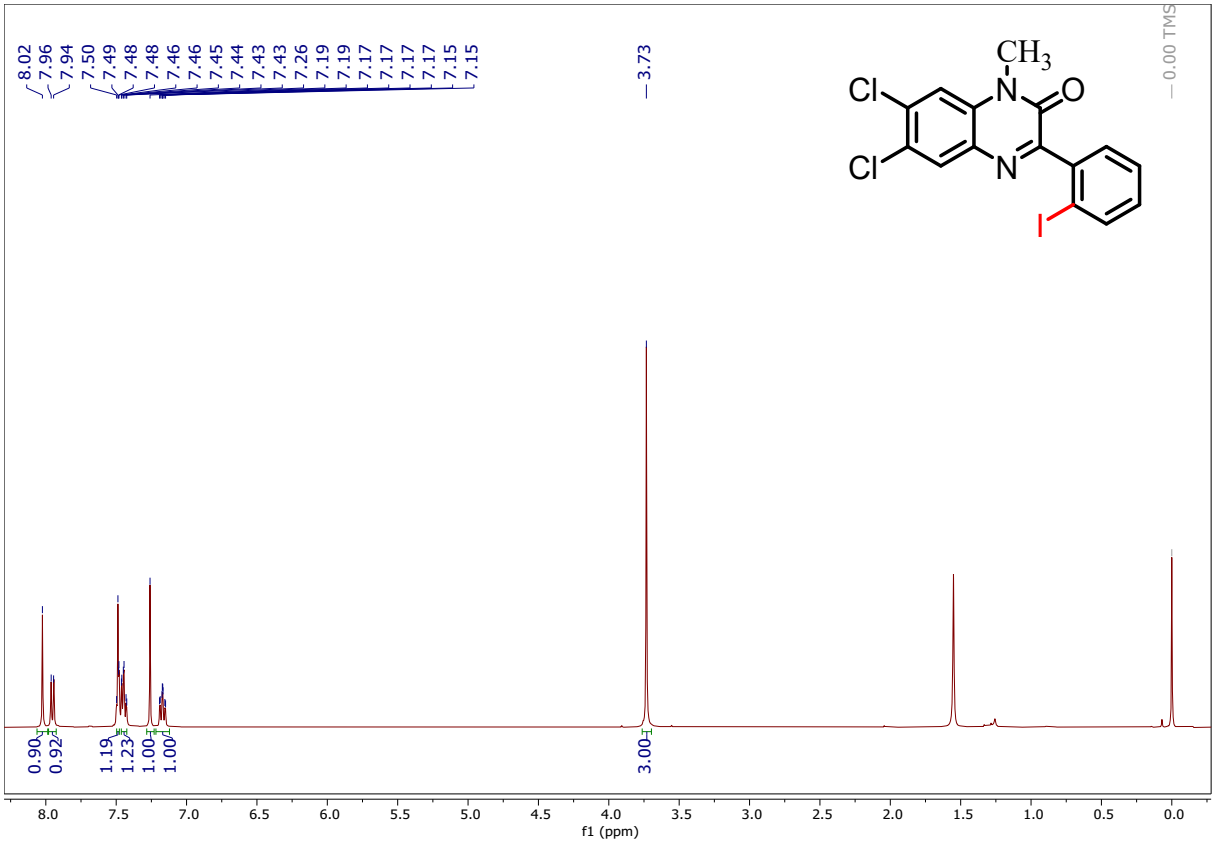


Figure 35: ^{1}H NMR spectrum of compound **4bc** (400 MHz, $CDCl_3$).

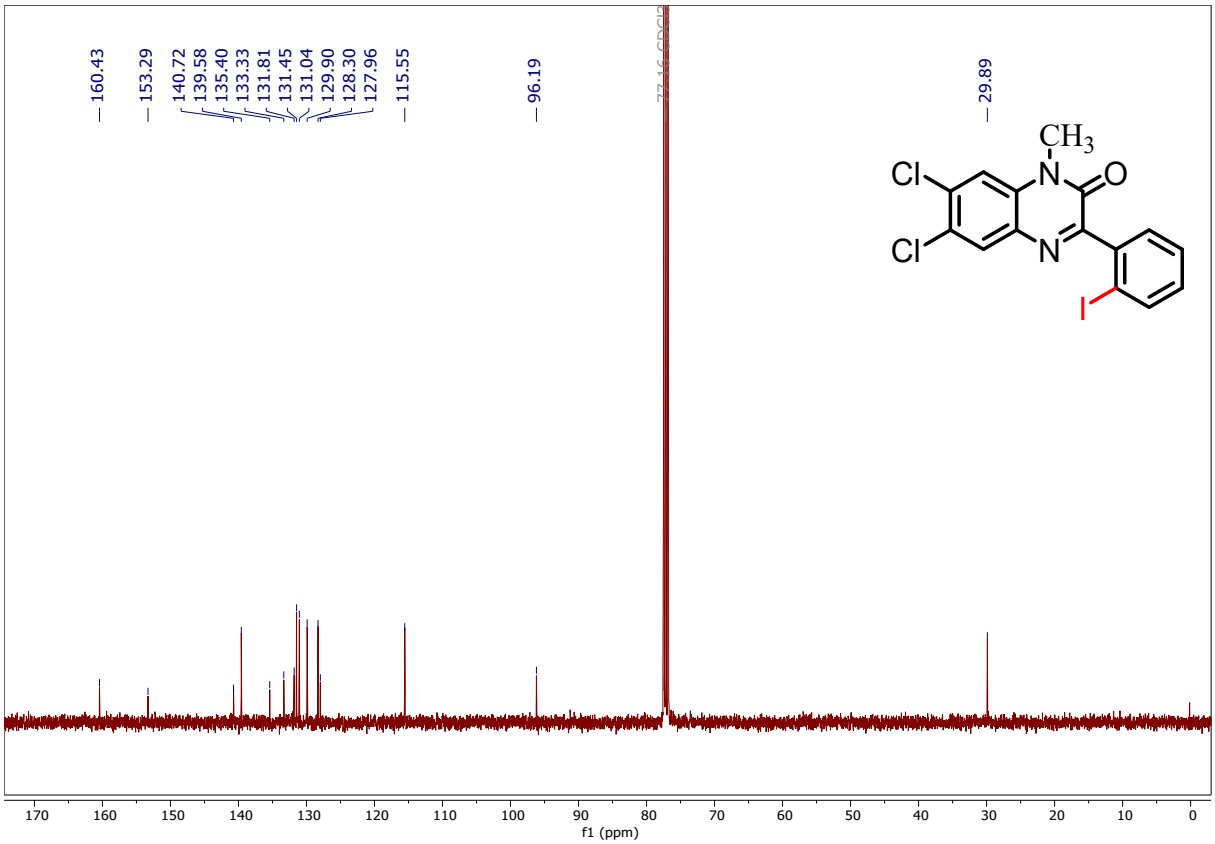


Figure 36: ^{13}C NMR spectrum of compound **4bc** (100 MHz, $CDCl_3$).

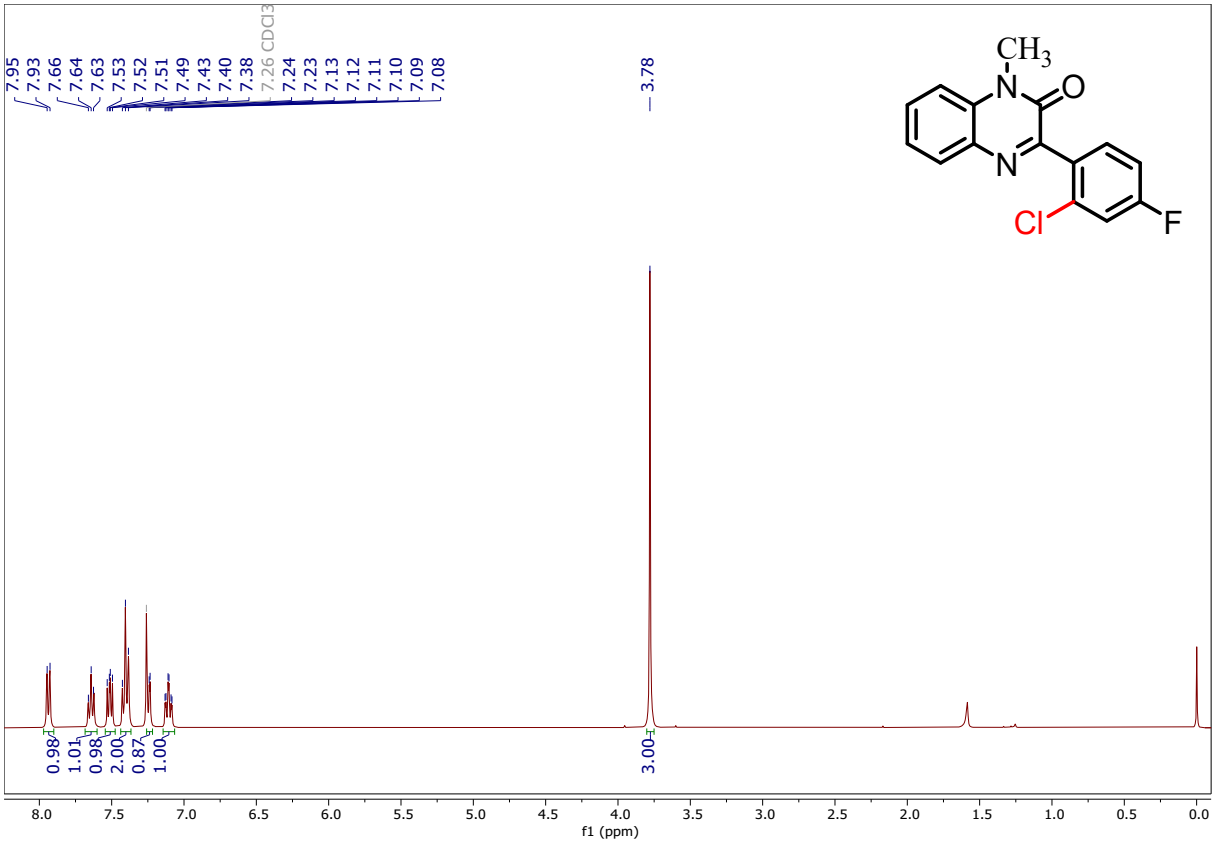


Figure 37: ^{1}H NMR spectrum of compound **5aa** (400 MHz, $CDCl_3$).

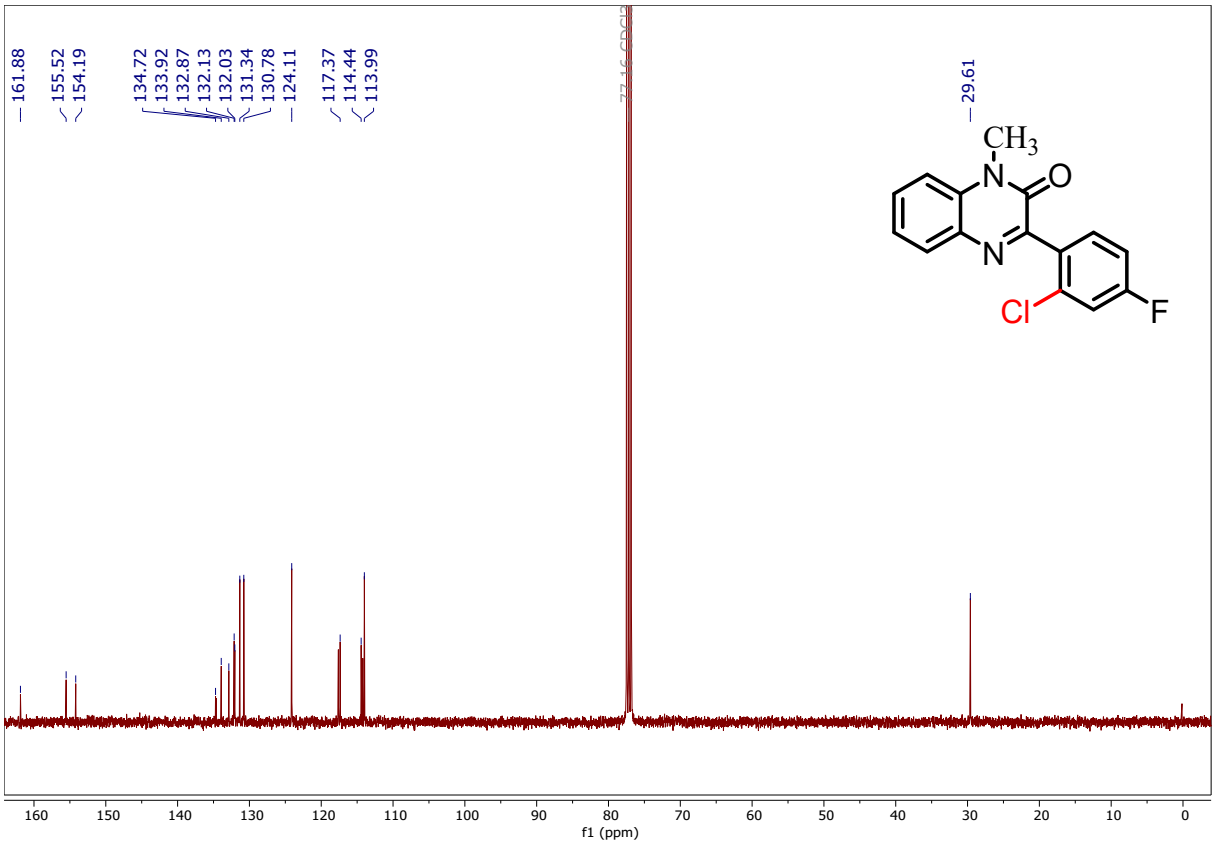


Figure 38: ^{13}C NMR spectrum of compound **5aa** (100 MHz, $CDCl_3$).

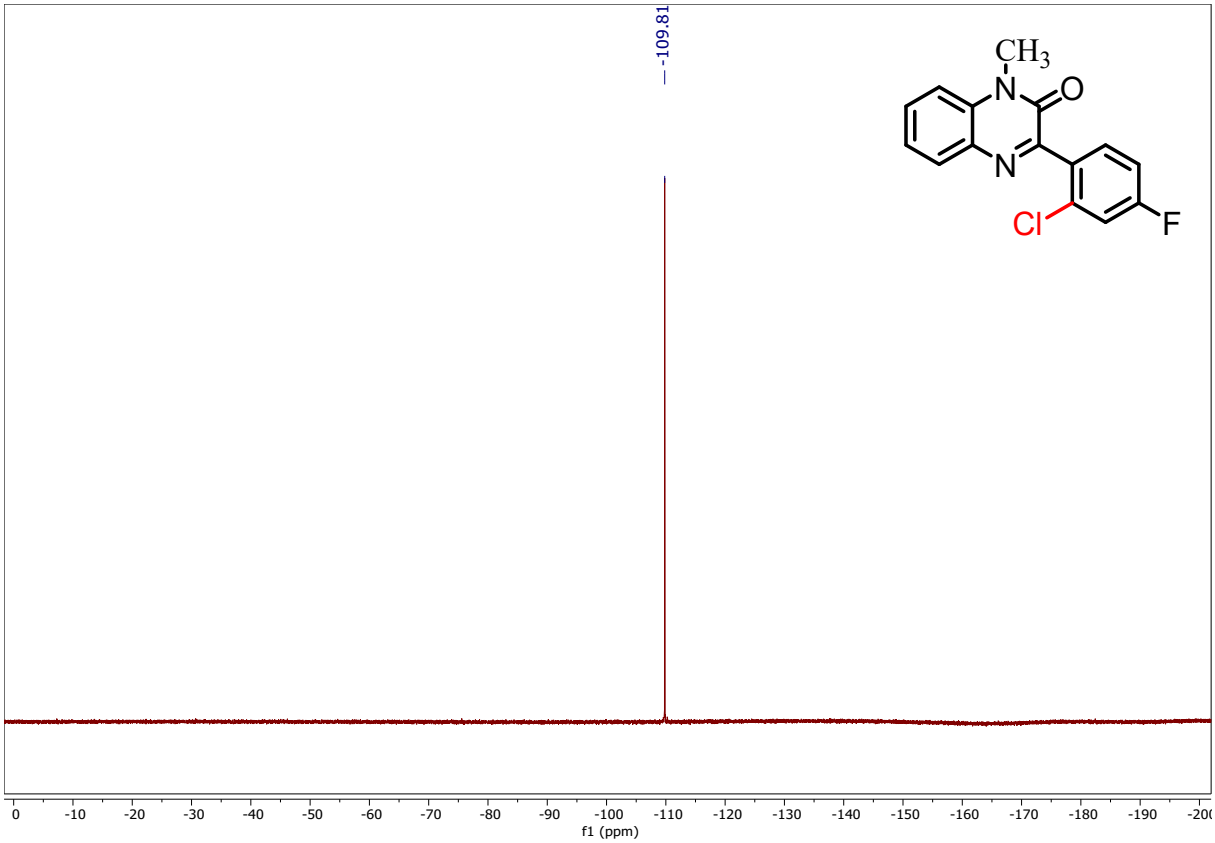


Figure 39: ^{19}F NMR spectrum of compound **5aa** (377 MHz, $CDCl_3$).

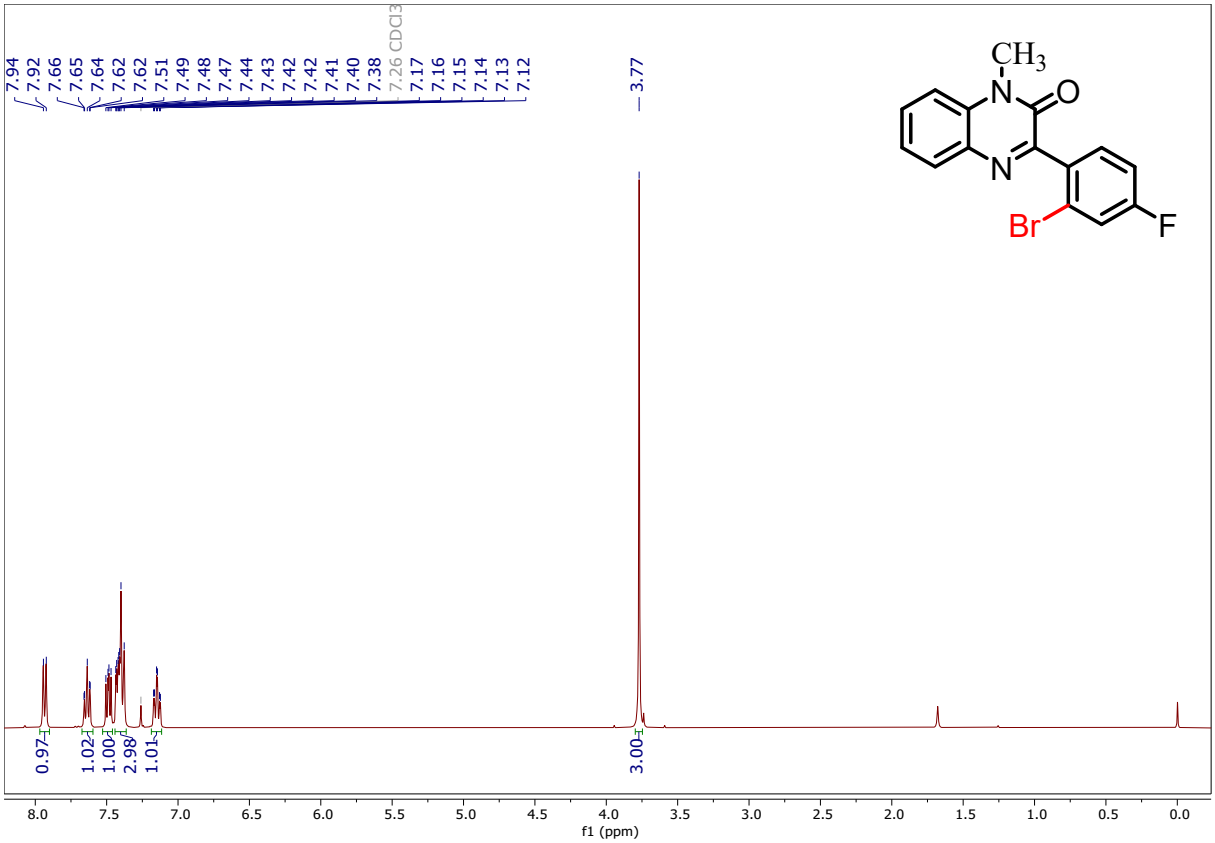


Figure 40: ^{1}H NMR spectrum of compound **5ab** (400 MHz, $CDCl_3$).

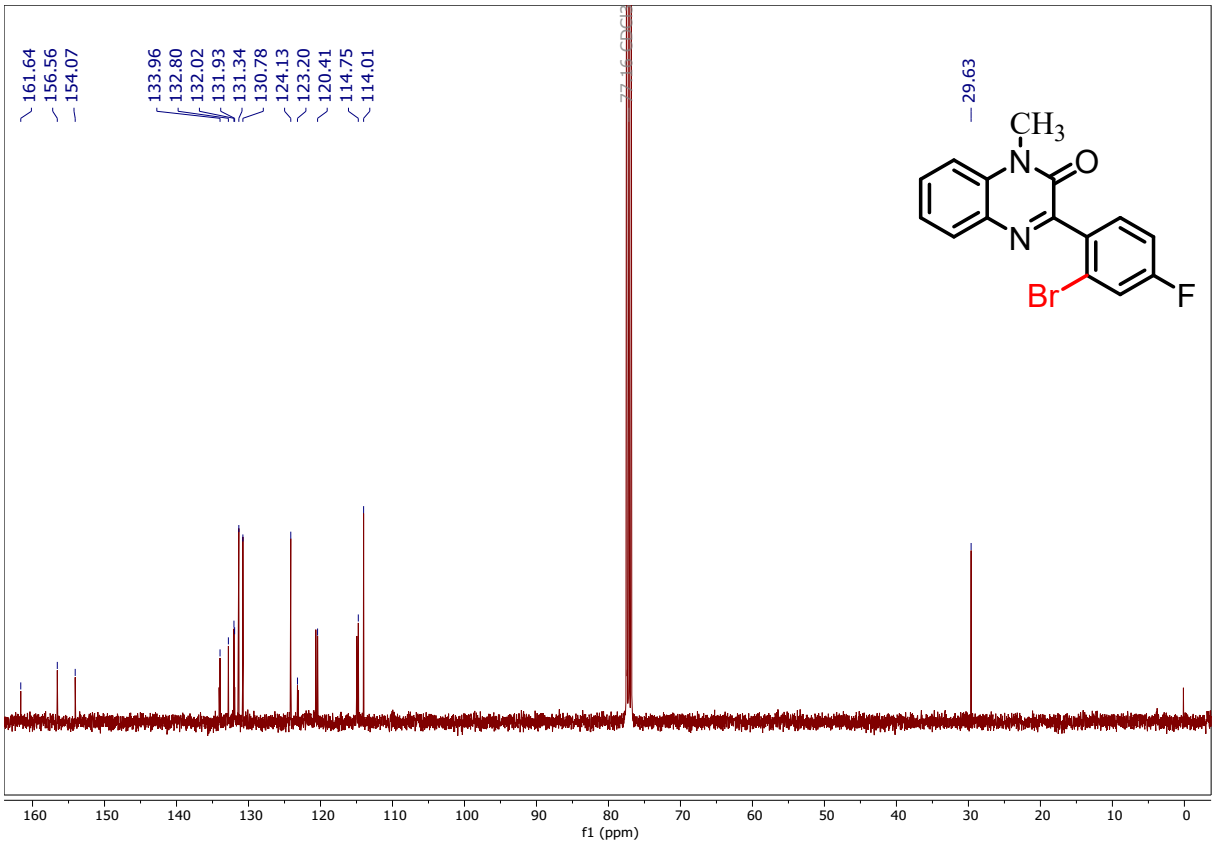


Figure 41: ^{13}C NMR spectrum of compound **5ab** (100 MHz, $CDCl_3$).

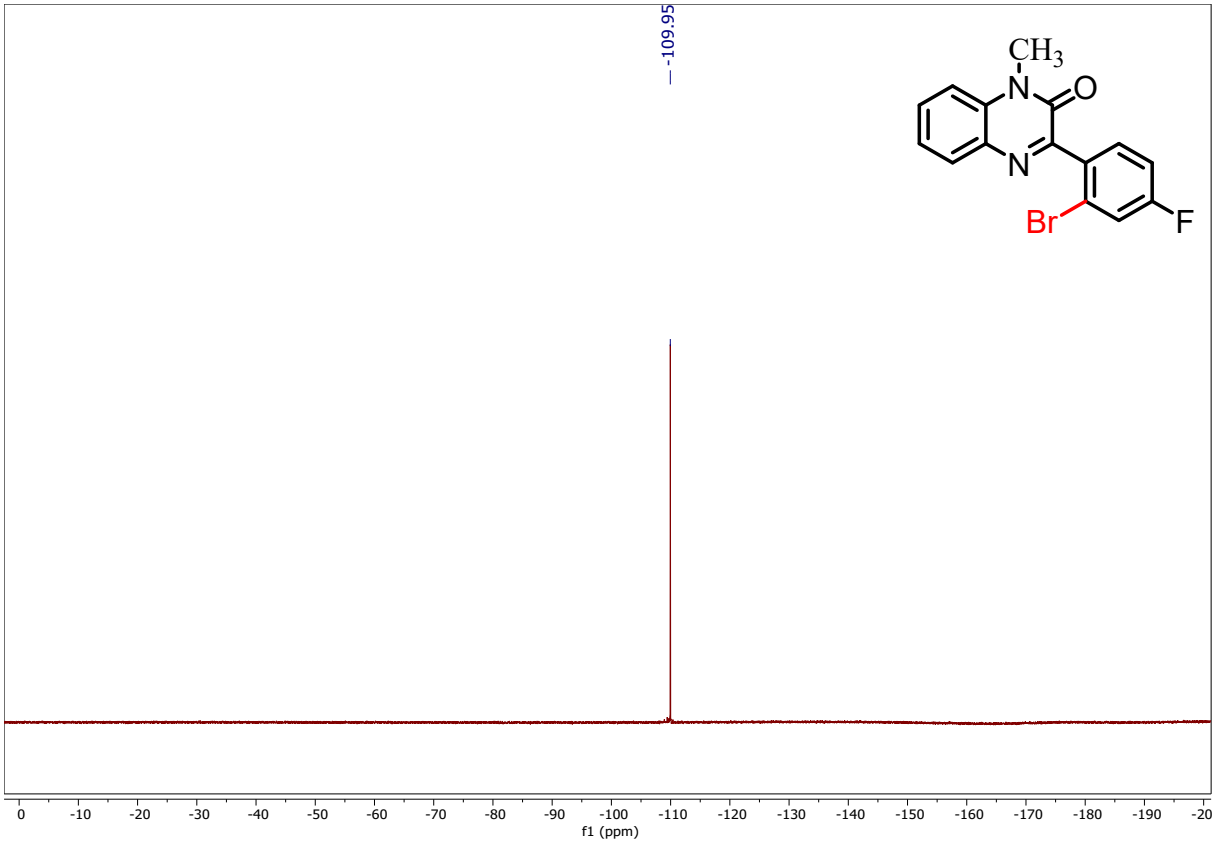


Figure 42: ^{19}F NMR spectrum of compound **5ab** (377 MHz, $CDCl_3$).

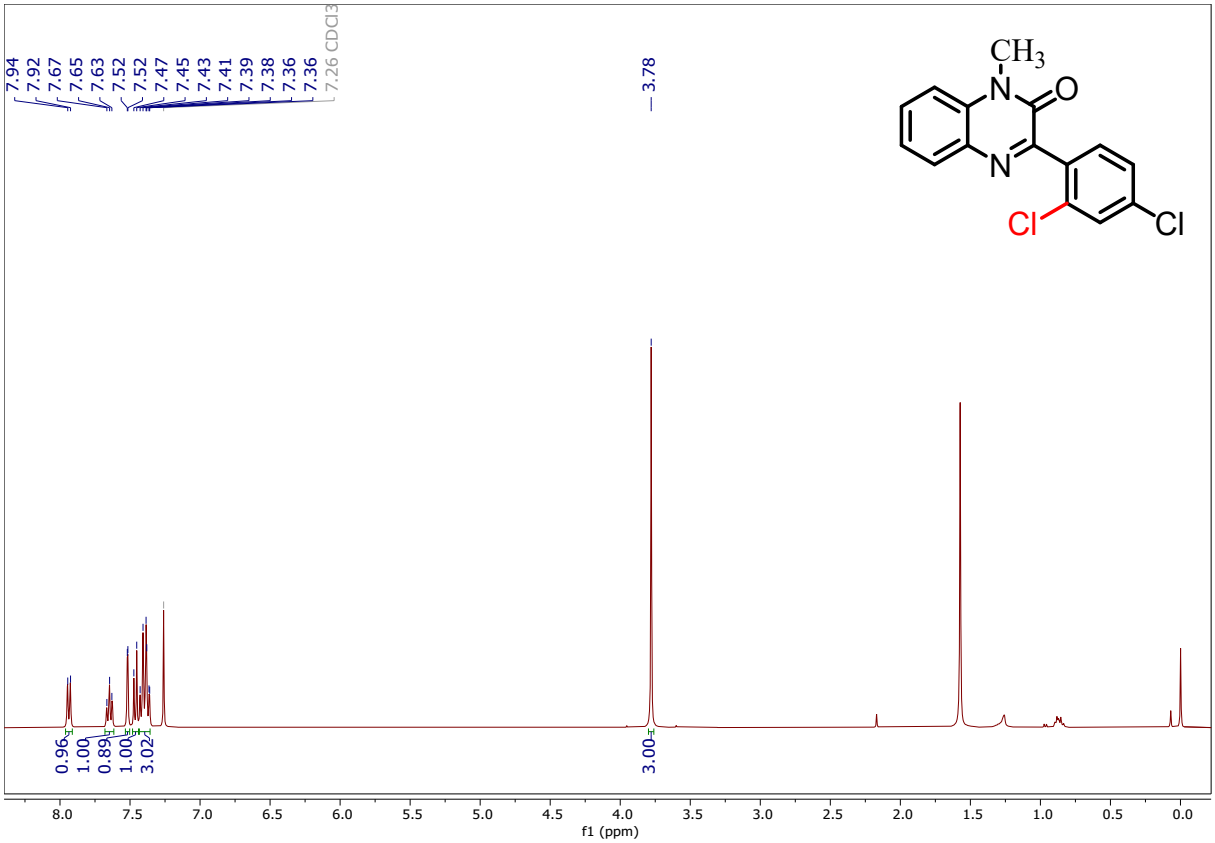


Figure 43: ^{1}H NMR spectrum of compound **5ba** (400 MHz, $CDCl_3$).

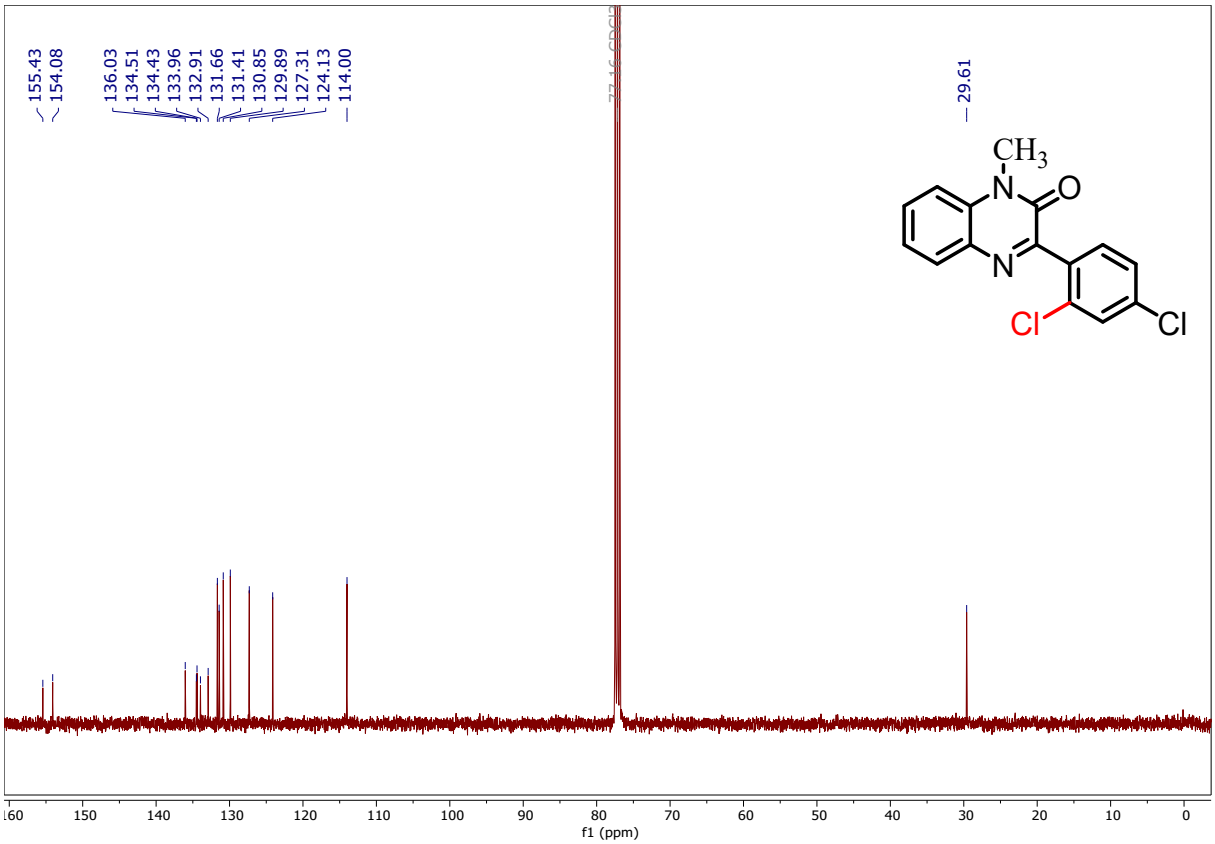


Figure 44: ^{13}C NMR spectrum of compound **5ba** (100 MHz, $CDCl_3$).

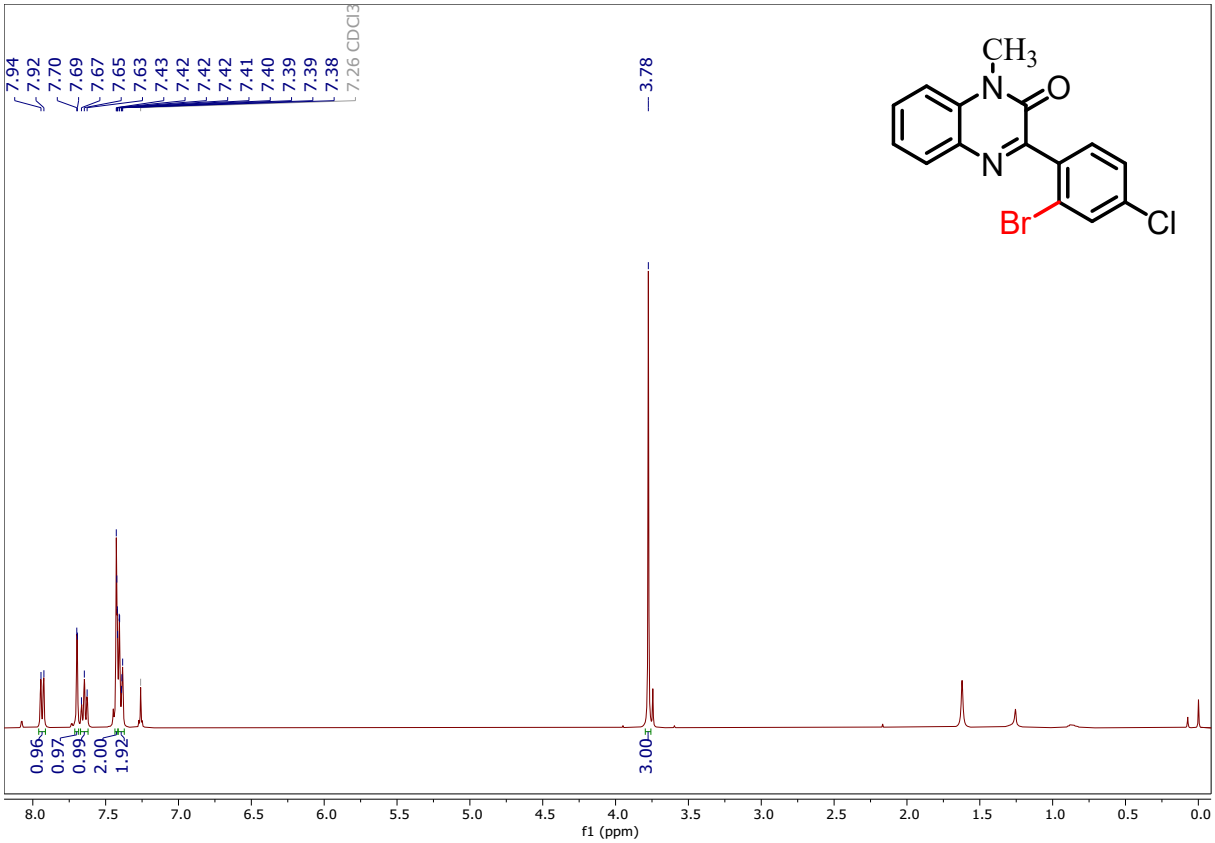


Figure 45: ^{1}H NMR spectrum of compound **5bb** (400 MHz, $CDCl_3$).

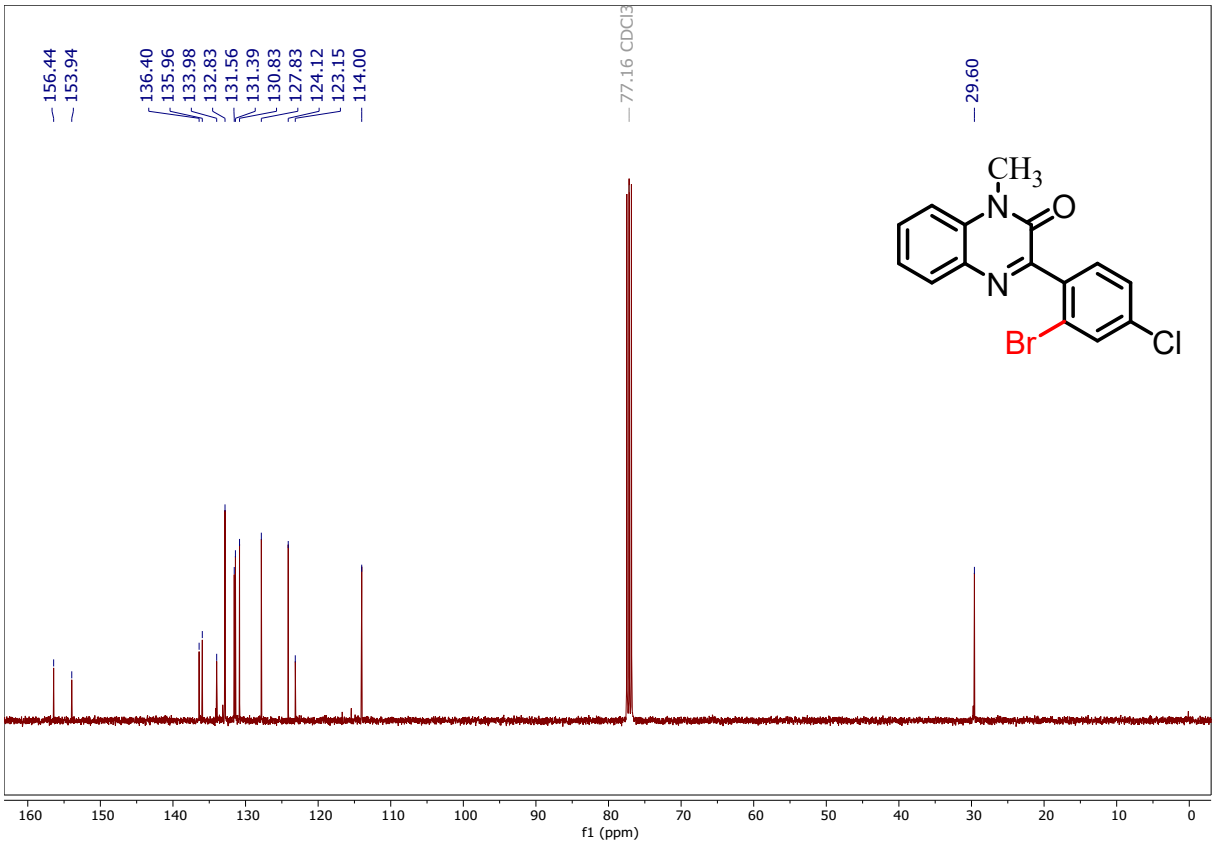


Figure 46: ^{13}C NMR spectrum of compound **5bb** (100 MHz, $CDCl_3$).

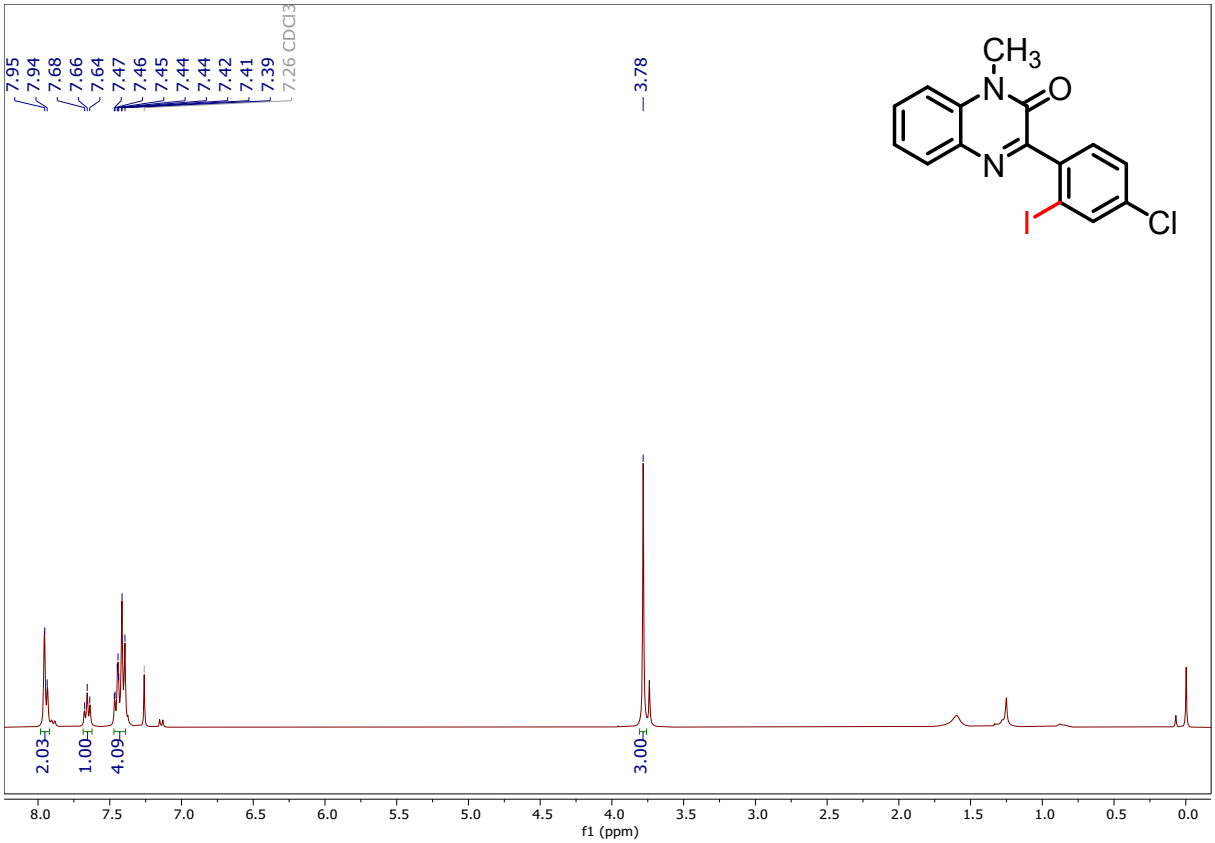


Figure 47: ^{1}H NMR spectrum of compound **5bc** (400 MHz, $CDCl_3$).

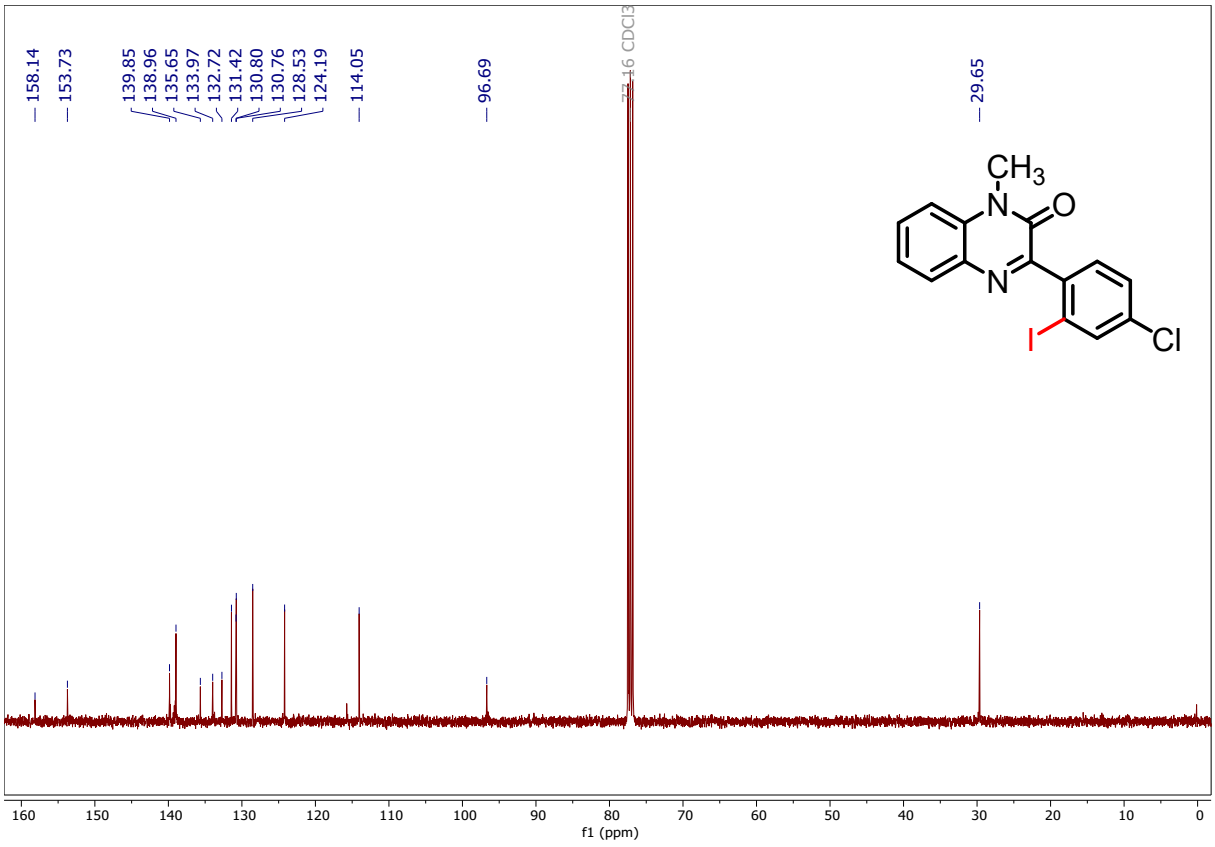


Figure 48: ^{13}C NMR spectrum of compound **5bc** (100 MHz, $CDCl_3$).

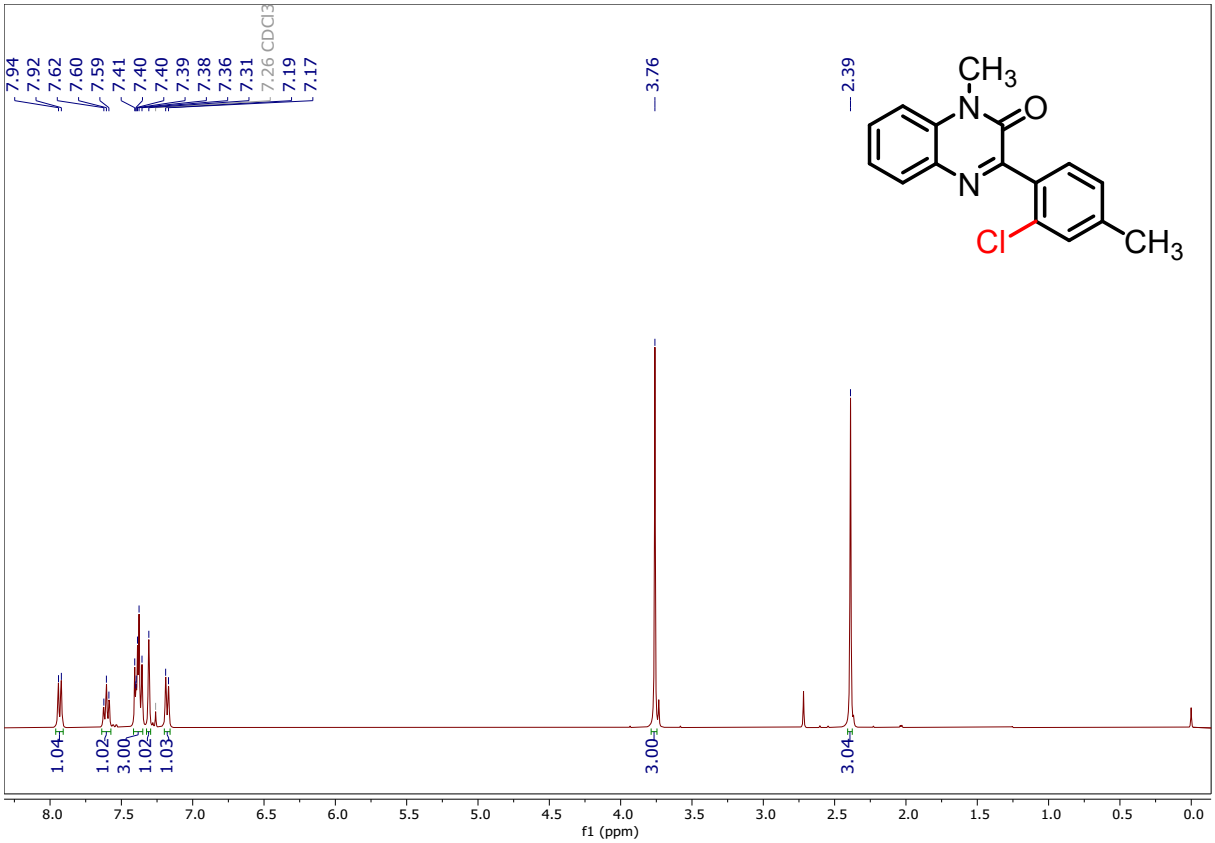


Figure 49: ^{1}H NMR spectrum of compound **5ca** (400 MHz, $CDCl_3$).

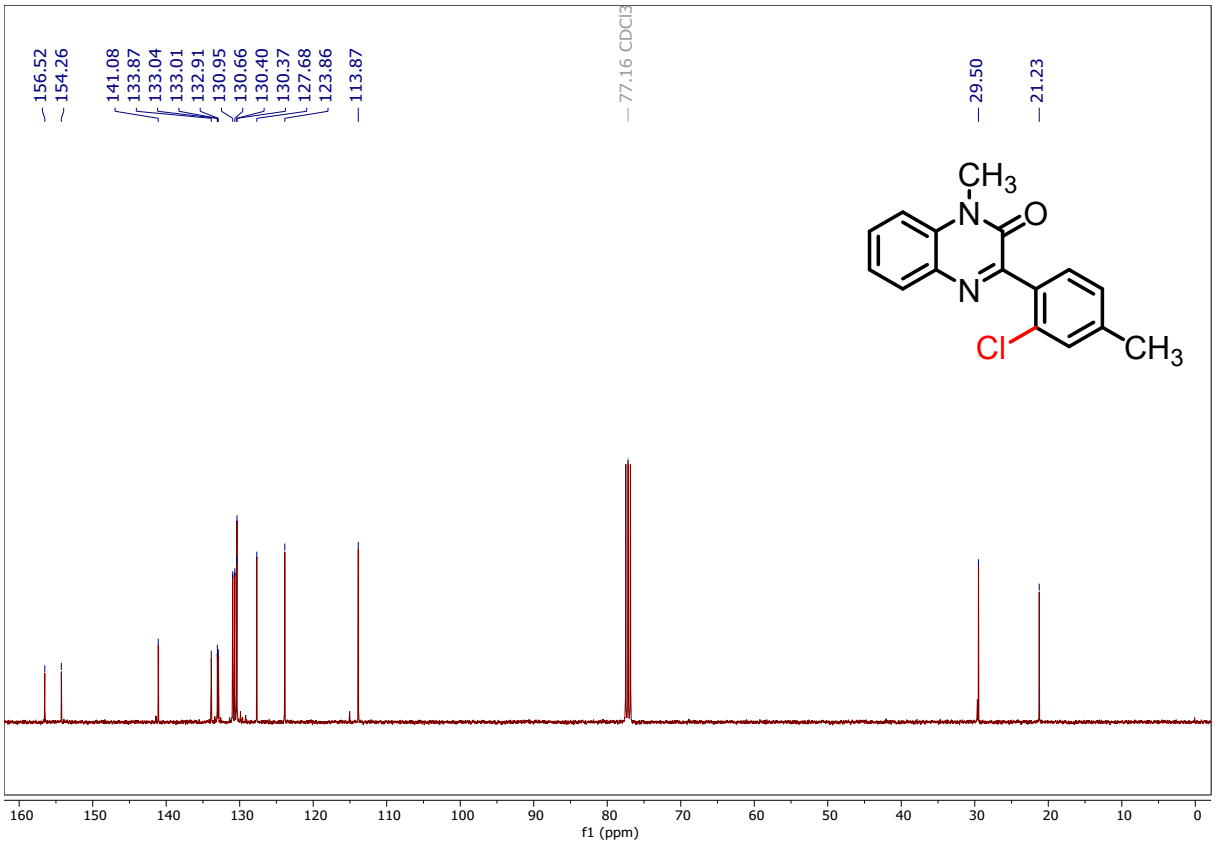


Figure 50: ^{13}C NMR spectrum of compound **5ca** (100 MHz, $CDCl_3$).

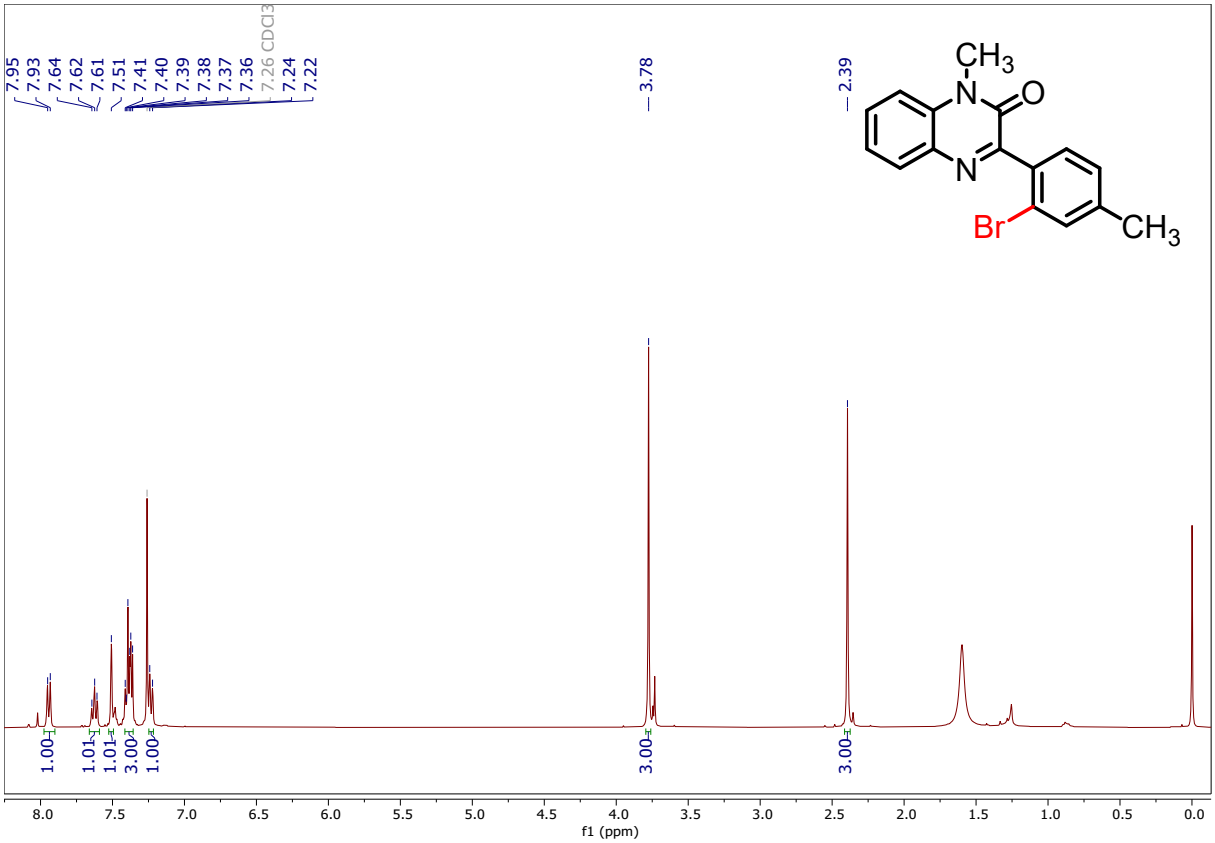


Figure 51: ^{1}H NMR spectrum of compound **5cb** (400 MHz, $CDCl_3$).

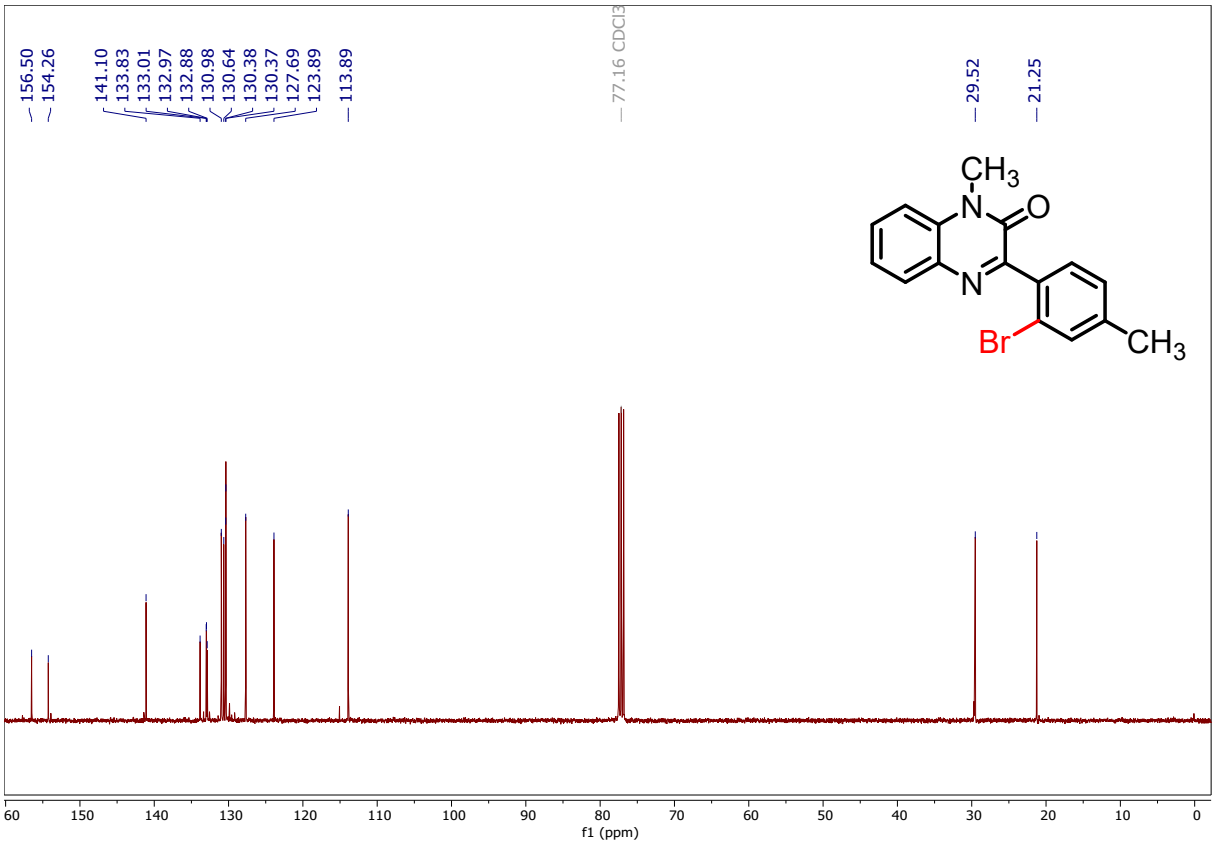


Figure 52: ^{13}C NMR spectrum of compound **5cb** (100 MHz, $CDCl_3$).

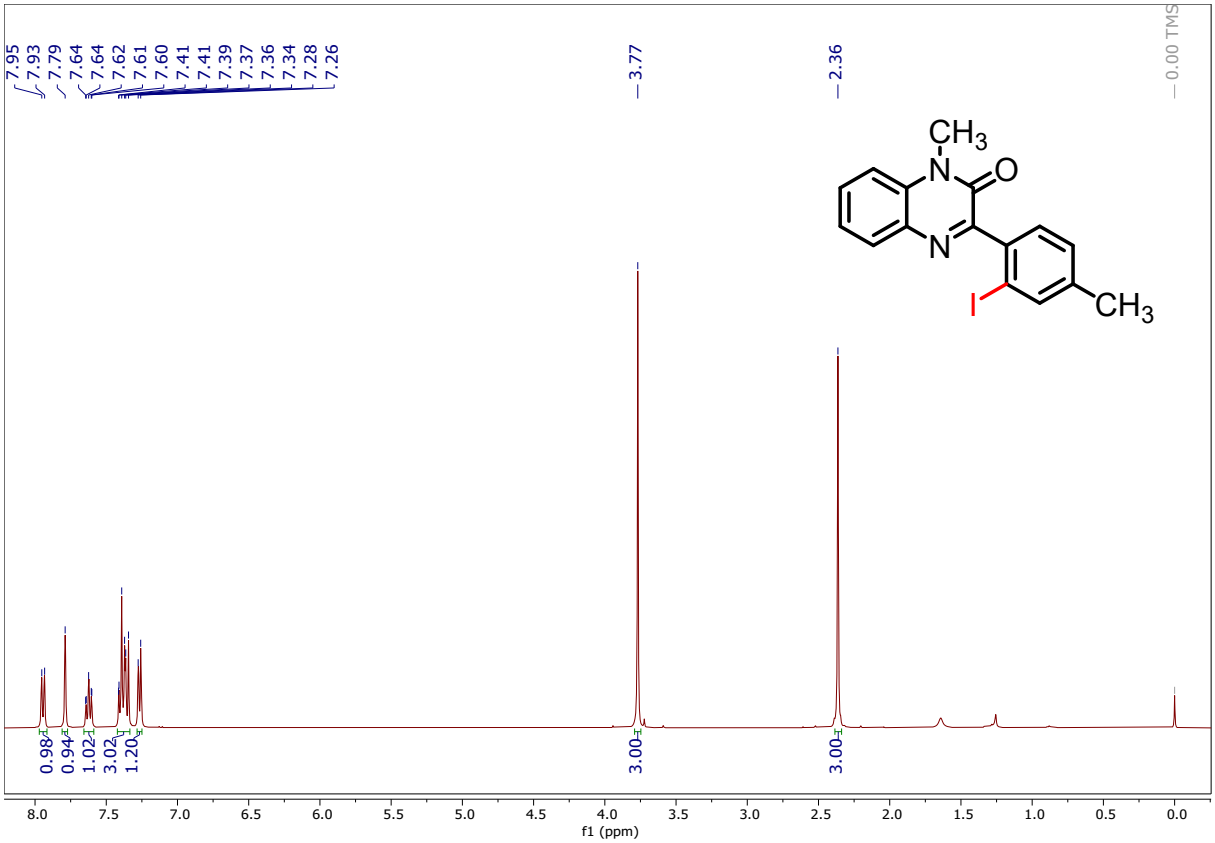


Figure 53: ^{1}H NMR spectrum of compound **5cc** (400 MHz, $CDCl_3$).

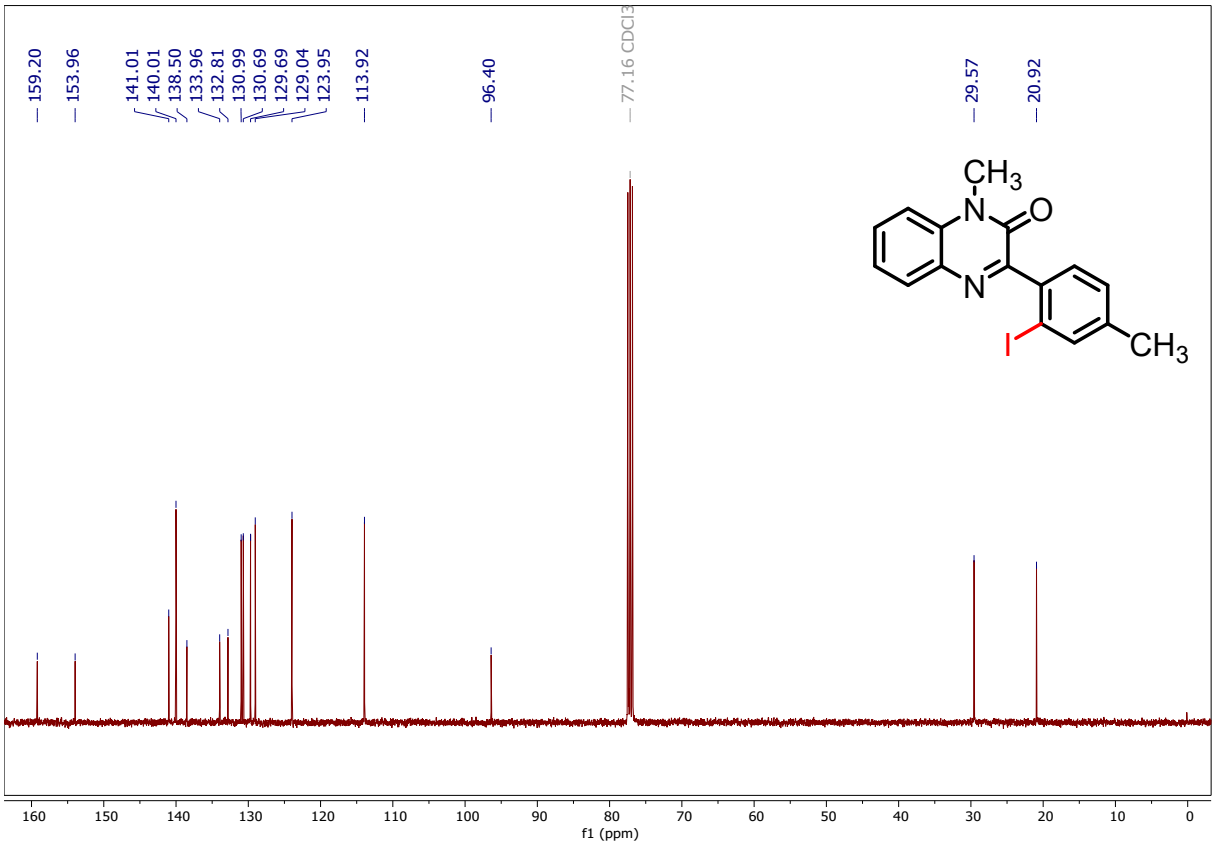


Figure 54: ^{13}C NMR spectrum of compound **5cc** (100 MHz, $CDCl_3$).

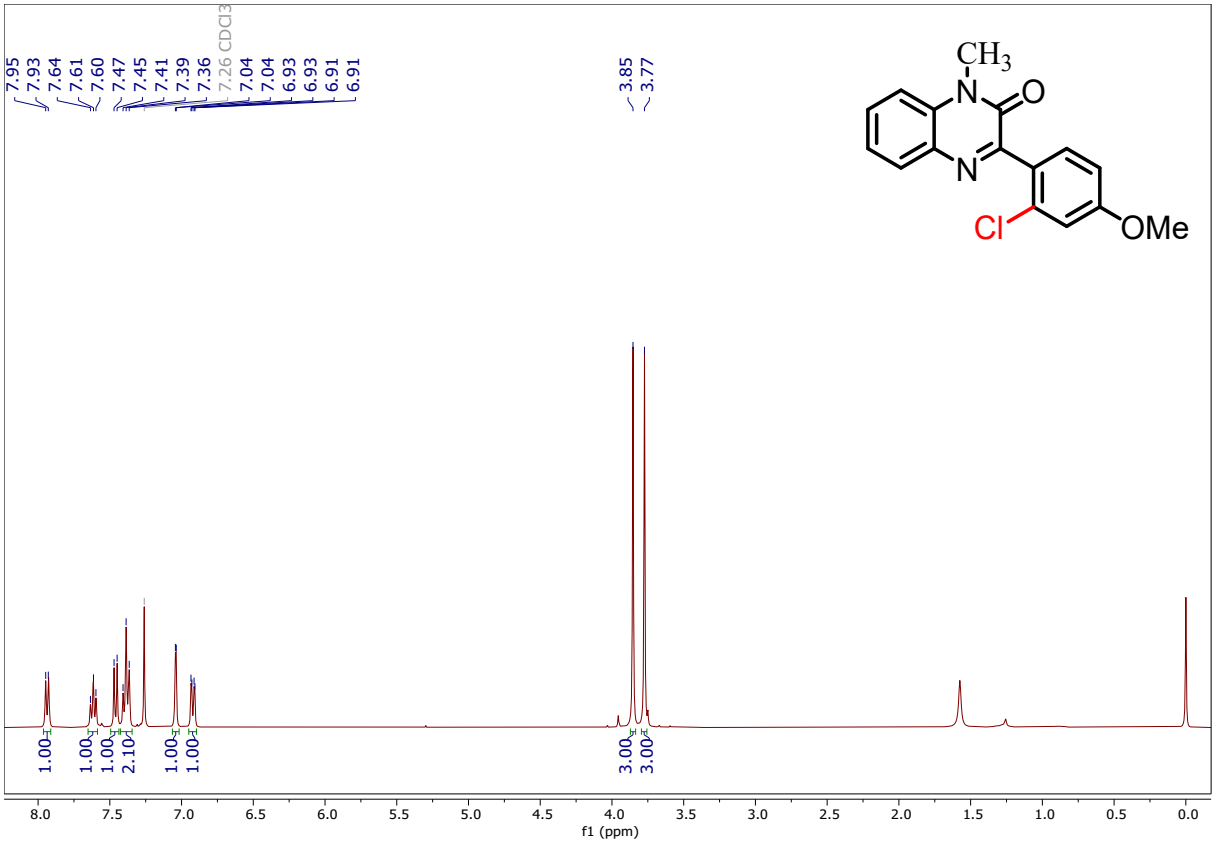


Figure 55: ^{1}H NMR spectrum of compound **5da** (400 MHz, $CDCl_3$).

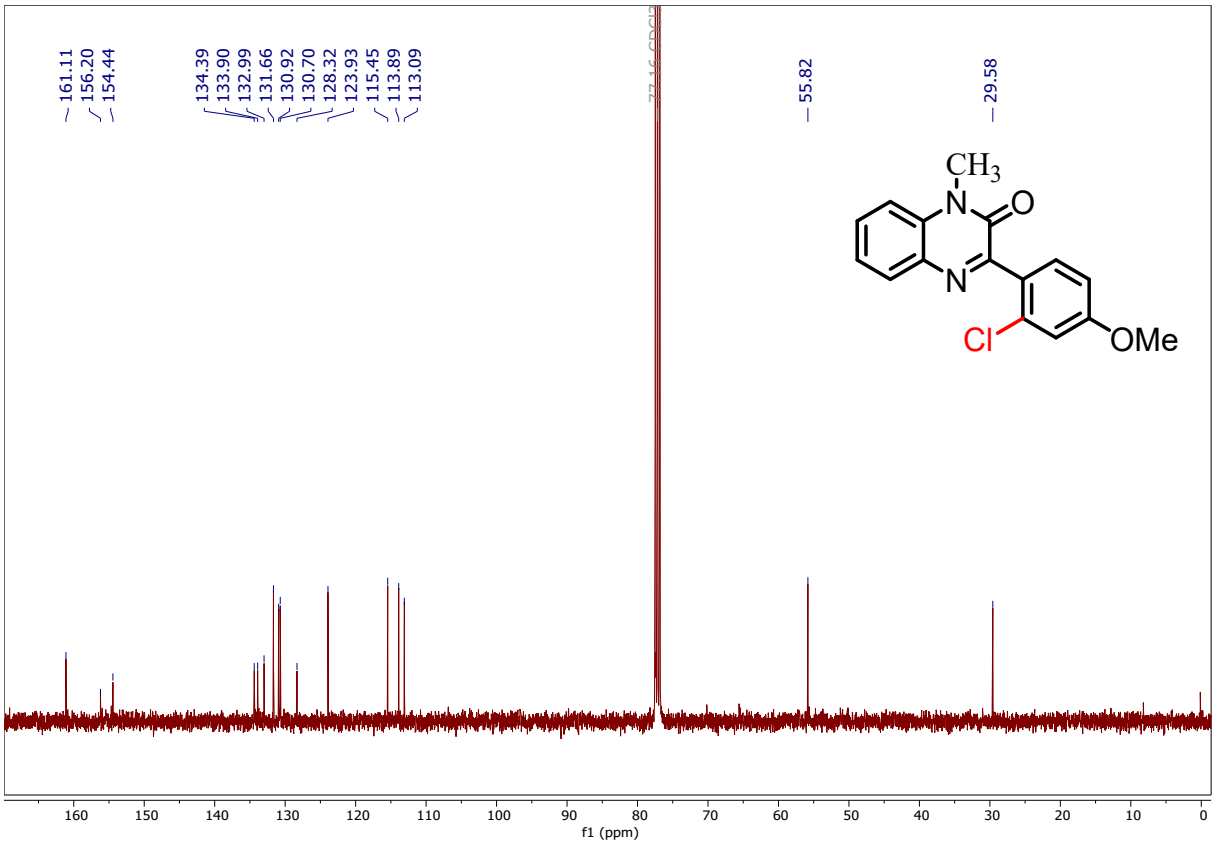


Figure 56: ^{13}C NMR spectrum of compound **5da** (100 MHz, $CDCl_3$).

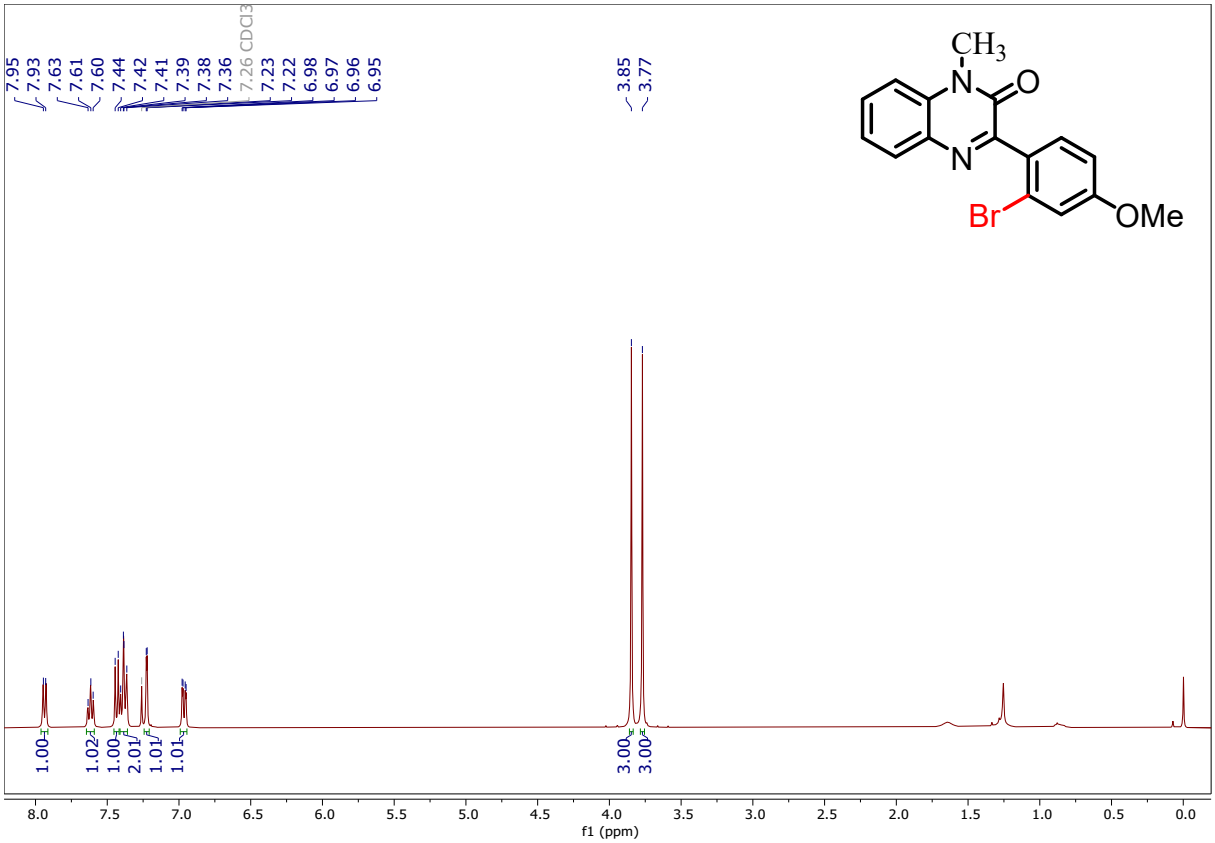


Figure 57: ^{1}H NMR spectrum of compound **5db** (400 MHz, $CDCl_3$).

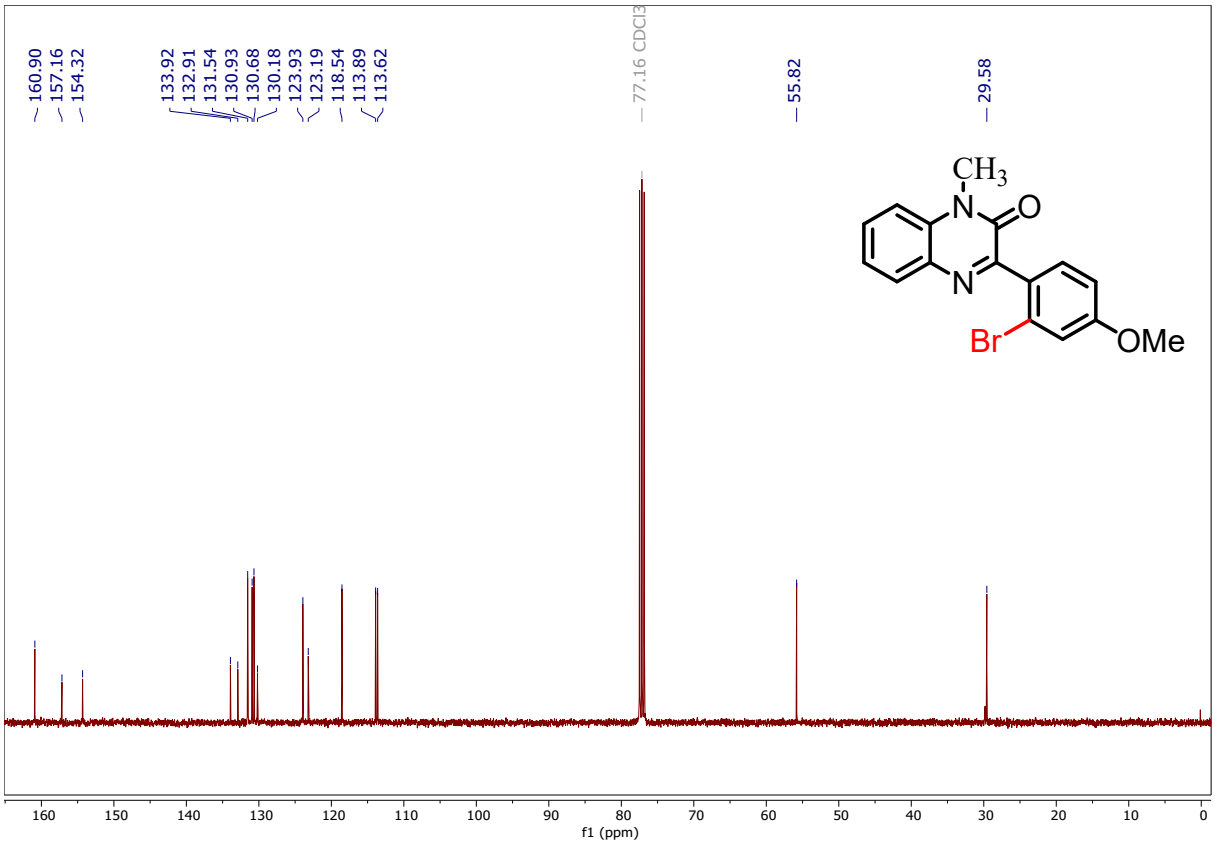


Figure 58: ^{13}C NMR spectrum of compound **5bd** (100 MHz, $CDCl_3$).

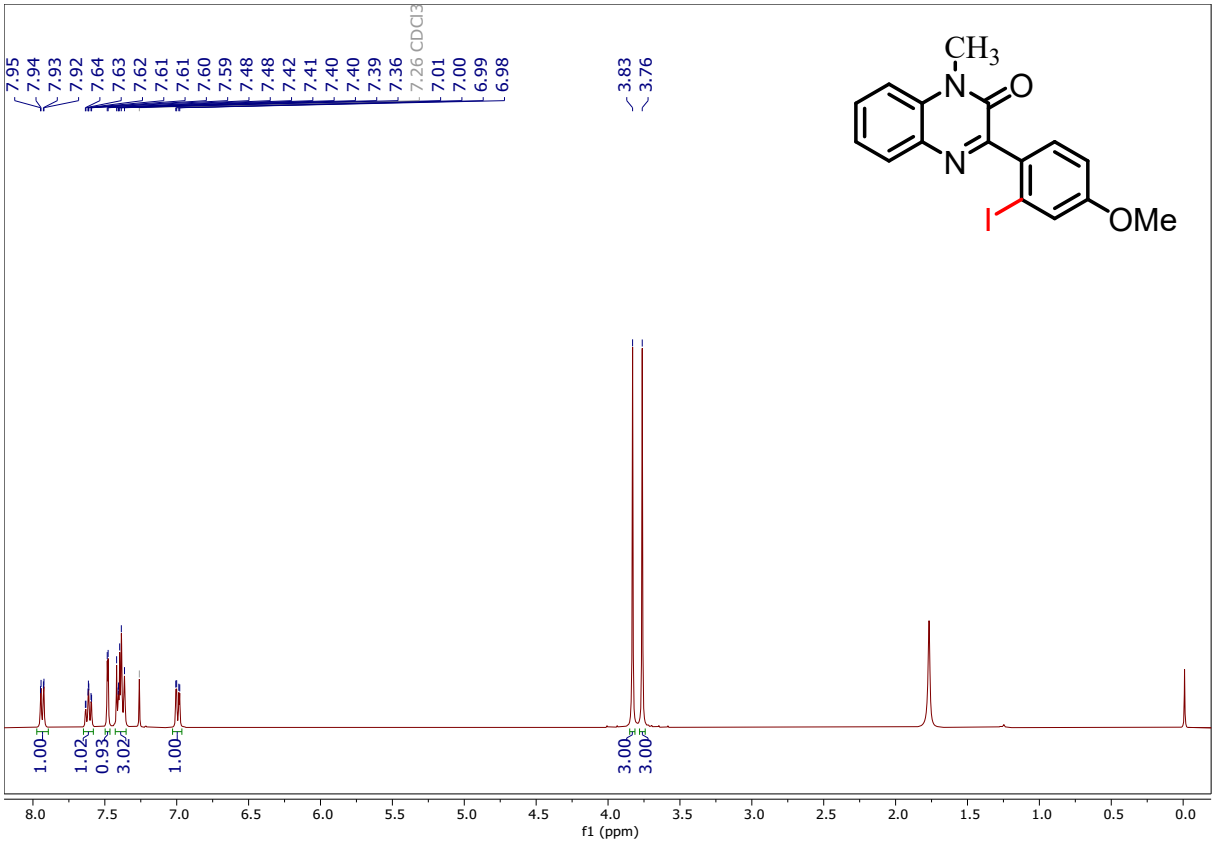


Figure 59: ^{1}H NMR spectrum of compound **5dc** (400 MHz, $CDCl_3$).

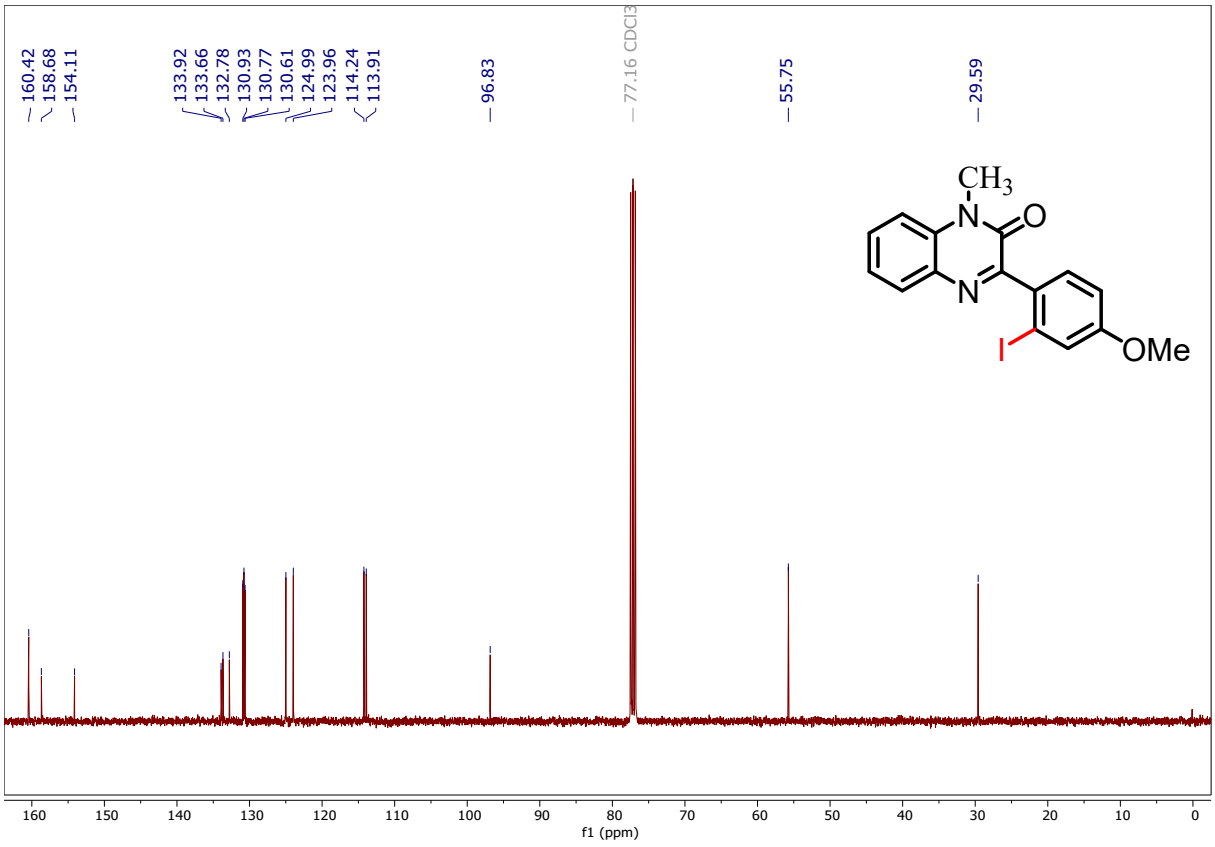


Figure 60: ^{13}C NMR spectrum of compound **5dc** (100 MHz, $CDCl_3$).

10. HRMS data of Radical adducts

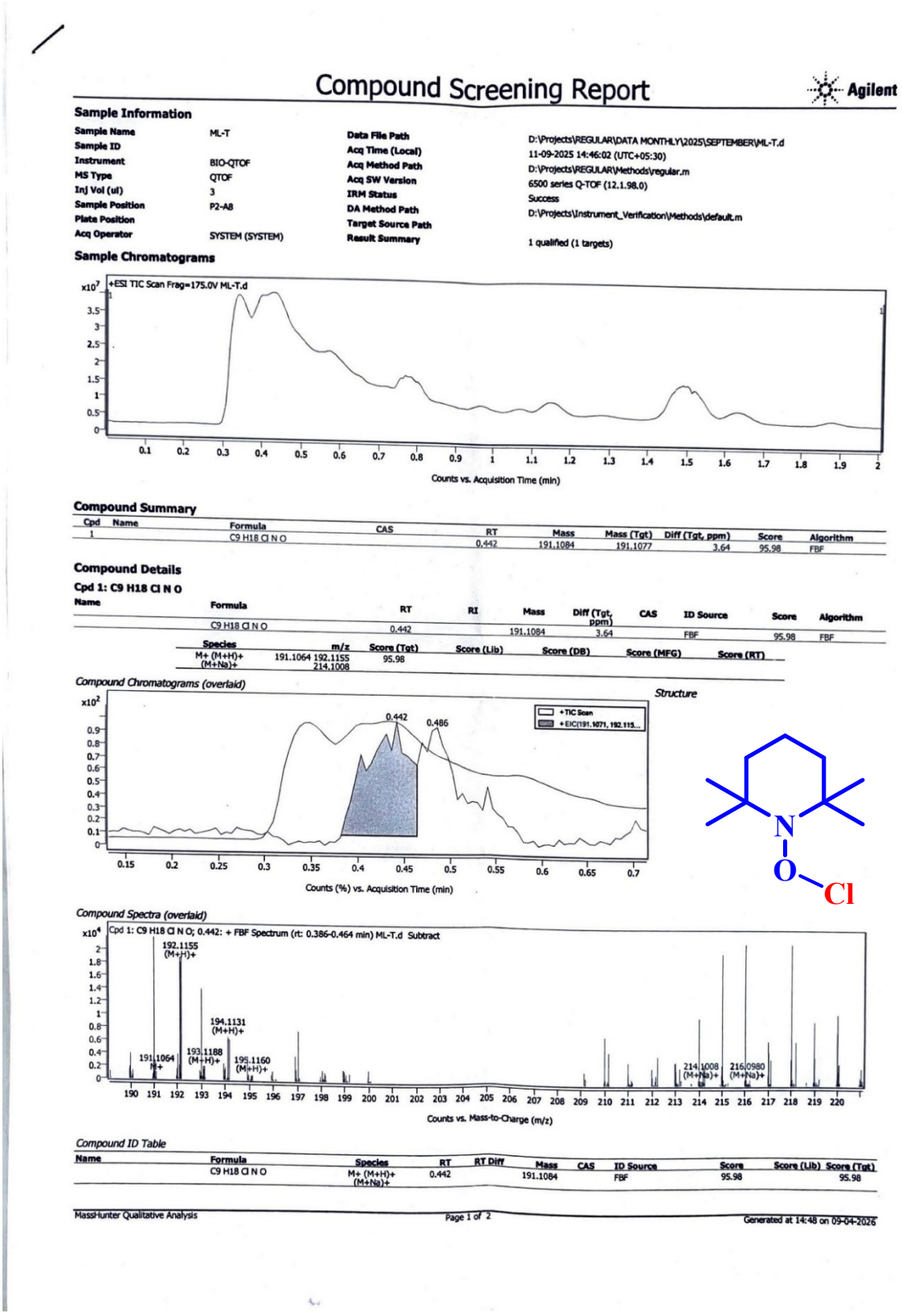


Figure 61: HRMS spectrum of radical adduct **6**.

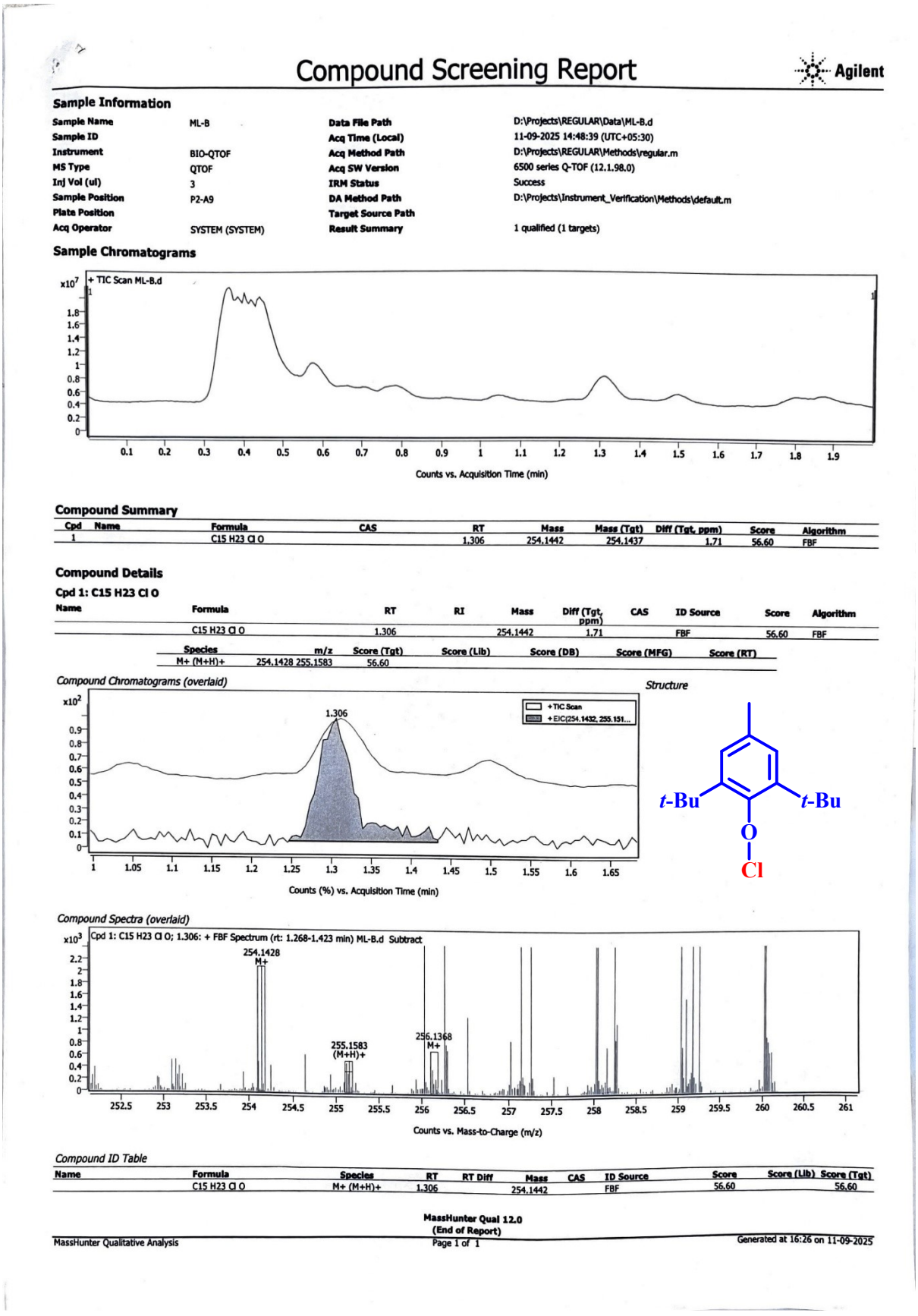


Figure 62: HRMS spectrum of radical adduct **7**.

11. Table T1: Comparison of the Previous (2023) and Present Halogenation Protocols

Parameter	2023 Method (Microwave Pd-Catalyzed)	Present Work (Photocatalytic Protocol)	Remark
Catalyst	$Pd(OAc)_2$ (10 mol%)	$Pd(OAc)_2$ (7.5 mol%)	Reduced catalyst loading enhances cost-efficiency and sustainability
Halogen Source	NXS (NCS/NBS/NIS)	DXDMH (DCDMH/ DBDMH/ DIDMH)	Less/ non-hazardous reagents required
Oxidant / Additive	*p*-TSA required	No additive / oxidant	Oxidant/ Additive-free conditions improve atom economy and simplify the protocol
Solvent	Organic solvent (DCE)	Water (aqueous medium)	Use of green solvent improves environmental compatibility
Energy Input	Microwave irradiation	Visible light (photocatalysis)	Avoids specialized equipment; utilizes sustainable energy source
Temperature	Elevated (microwave conditions)	Room temperature	Mild reaction conditions reduce energy consumption
Atmosphere	Air / controlled	Air (open flask)	Operationally simple; no need for inert or controlled atmosphere
Operational Simplicity	Requires microwave setup	Simple LED setup	More practical and accessible setup for routine laboratory use