Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photoredox-catalysed chlorination of quinoxalin-2(1*H*)-ones enabled by using $CHCl_3$ as chlorine source

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1. General Experimental Information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES^{+} mass spectrometer and acetonitrile was used to dissolve the sample. UV-Vis spectra were recorded using a shimadzu UV-26000 instrument. Column chromatography was carried out on silica gel (200-300 mesh). Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected. The light source for the photocatalytic reaction is manufactured by XINNENGYUAN with power of 30 W (450 nm), and the reaction is carried out in a borosilicate glass vessel without use of filters. The light source used for illuminating the reaction vessel consists of blue LEDs (λ_{max} = 450 nm) purchased from Taobao (https://gpiled.taobao.com/).

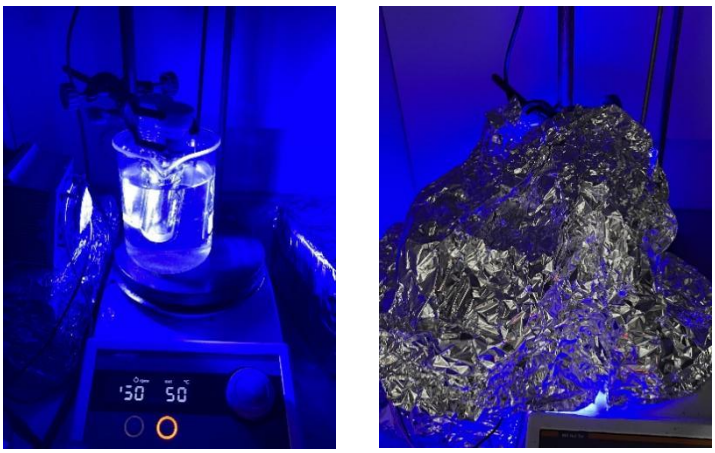
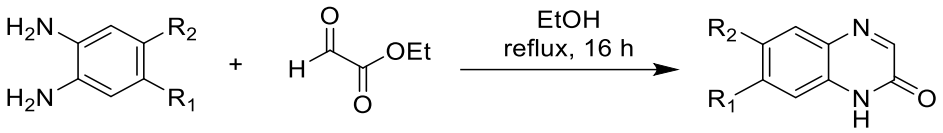
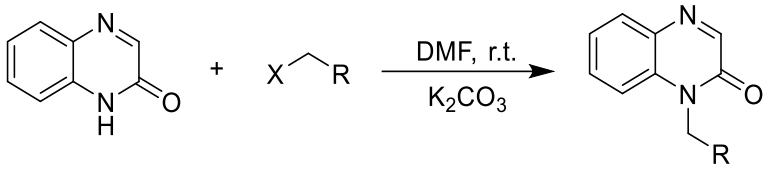


Figure S1. The Set-up for the Reaction (photographed by M.-Z. Li)

2. General procedures for the synthesis of starting materials 1a-1q



Starting materials **1a-1q** were synthesized according to the literature procedures.[1-5] To the solution of *o*-arylenediamine (5 mmol) in ethanol (20 mL) was added ethyl 2-oxoacetate (1.0 equiv.). The reaction mixture was stirred and heated to reflux for 16 h. After the reaction was completed (as monitored by TLC), the precipitate was filtered and washed with cooled ethanol, and finally dried to give the Ph-substituted quinoxalinones.



To a 50 mL round-bottom flask was added with the starting material 2-quinoxalinone (5 mmol) in DMF (20 mL), and then the corresponding halide (1.6 equiv.) and potassium carbonate (1.2 equiv.) were added into the reaction mixture. The reaction solution was stirred at room temperature overnight. After the reaction completed, water (10 mL) was added to the reaction mixture, and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with water, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain the *N*-substituted quinoxalinones. All the substrates **1a-1q** are known compounds.[1-5]

3. General Procedures for the Preparation of Compounds 2a-2q

To a 15 mL reaction tube equipped with a magnetic stirring bar, quinoxalin-2(1*H*)-one **1a**−**1q** (0.2 mmol, 1.0 equiv), $AlCl_3$ (0.1 mmol, 0.5 equiv), $[Ir(dF(CF_3)ppy)_2(4,4'\text{-}dCF_3bpy)]PF_6$ (5 mol%), and $CHCl_3$ (2 mL) were added. The tube screw-capped was under irradiation of 30 W blue LEDs (distance app. 5 cm, without filters) and heating by an oil bath at 50 ℃ for 48 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EtOAc = 100:10 to 100:30) to afford the desired product **2a**−**2q**.

4. General Procedures for the Preparation of Compounds 5a

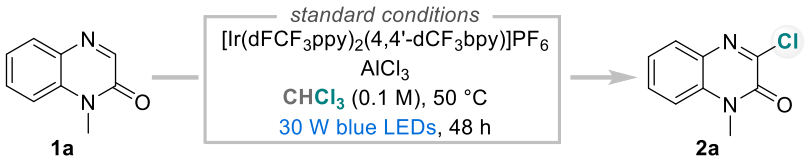
To a 15 mL reaction tube equipped with a magnetic stirring bar was added quinoxalin-2(1*H*)-one **2a** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.5 mol%), Xantphos (5 mol%), K_2CO_3 (0.3 mol, 1.5 equiv),

benzamide (0.22 mmol) and 1,4-dioxane (2 mL). The Schlenk tube was screw-capped, evacuated and backfilled with argon. Then, the mixture was stirred at 90 ℃ for 30 min. After the reaction completed, the resulting suspension was cooled to room temperature, filtered through celite, and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. Finally, purification of the residue by silica gel column chromatography gave the desired product.[6]

5.General Procedures for the Preparation of Compounds 6a

To a 15 mL reaction tube equipped with a magnetic stirring bar was added quinoxalin-2(1*H*)-one **2a** (0.2 mmol, 1.0 equiv), and ethyl carbazate (0.22 mmol) in 2 mL of acetonitrile. The reaction mixture was heated at 120 ℃ for 2 h. After the reaction completed, the resulting suspension was cooled to room temperature, filtered through a pad of celite, and eluted with ethyl acetate. The filtrate was concentrated and purification of the residue by silica gel column chromatography gave the desired product.[7]

6. Optimization of reaction conditions



6.1 Screening of photocatalyst

Entry	Catalyst	Yield (%)
1	$Ir(ppy)_3$	n.r.
2	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	52
3	$[Ir(ppy)_2(dtbpy)]PF_6$	trace
4	$[Ir(dF(CF_3)ppy)_2(4,4'\text{-}CF_3bpy)]PF_6$	56
5	$Ru(bpy)_3(PF_6)_2$	n.r.
6	4CzIPN	trace
7	Eosin Y	28
8	Rhodamine B	44
9	Rose Bengal	50
10	Riboflavin	55

The reaction was carried out on a 0.2 mmol scale in $CHCl_3$ (2 mL) with photocatalyst (5 mol%), $AlCl_3$ (0.5 equiv.), irradiating with 30 W blue LEDs for 24 h, at room temperature, under air atmosphere.

6.2 Screening of temperature

Entry	temp. (℃)	time (h)	Yield (%)
1	r.t.	24	56
2	r.t.	48	65
3	40	48	73
4	50	48	86
5	60	48	60
6	50	72	78

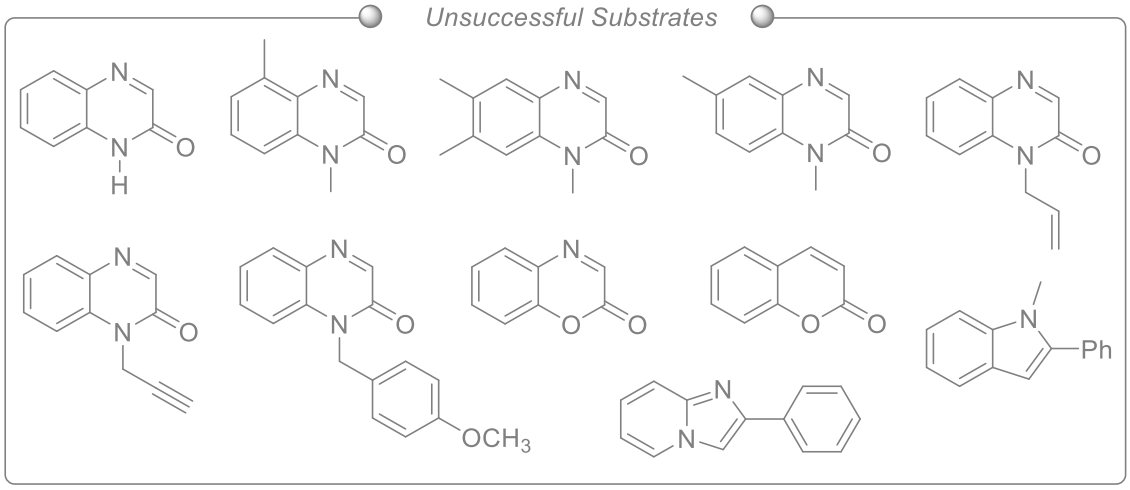
The reaction was carried out on a 0.2 mmol scale in $CHCl_3$ (2 mL) with $[Ir(dF(CF_3)ppy)_2(4,4'\text{-}CF_3bpy)]PF_6$ (5 mol%), $AlCl_3$ (0.5 equiv.), irradiating with 30 W blue LEDs for specified time, under air atmosphere.

6.3 Amount of $AlCl_3$

Entry	$AlCl_3$ (equiv.)	yield
1	0	52%
2	0.2	70%
3	0.5	86%
4	1.0	75%

The reaction was carried out on a 0.2 mmol scale in $CHCl_3$ (2 mL) with $[Ir(dF(CF_3)ppy)_2(4,4'\text{-}CF_3bpy)]PF_6$ (5 mol%), $AlCl_3$ (0-1.0 equiv.), irradiating with 30 W blue LEDs for 48 h, at 50 ℃, under air atmosphere.

6.4 Unsuccessful substrates



7. Mechanistic studies

7.1 Emission Quenching Experiments (Stern-Volmer Studies) [8, 9]

All fluorescence measurements were recorded by a Hitachi FL-7000 Fluorometer. Quenching experiments were conducted in MeCN solution (Figure S2).

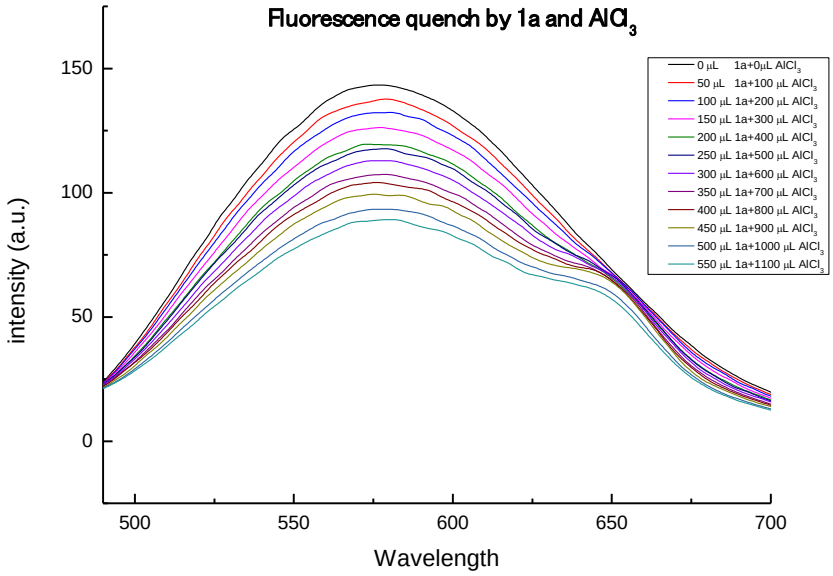


Figure S2. Stern-Volmer experiments in MeCN

7.2 Trapping Experiment

In order to confirm whether the putative radical was trapped by ethene-1,1-diyldibenzene, ESI-MS analysis of the crude reaction mixture was performed. The resulting mass spectrum clearly shows a peak corresponding to the coupled product between ethene-1,1-diyldibenzene radical and quinoxalinone **1a**. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}N_2O_2^+$ 339.1492, Found 339.1492.

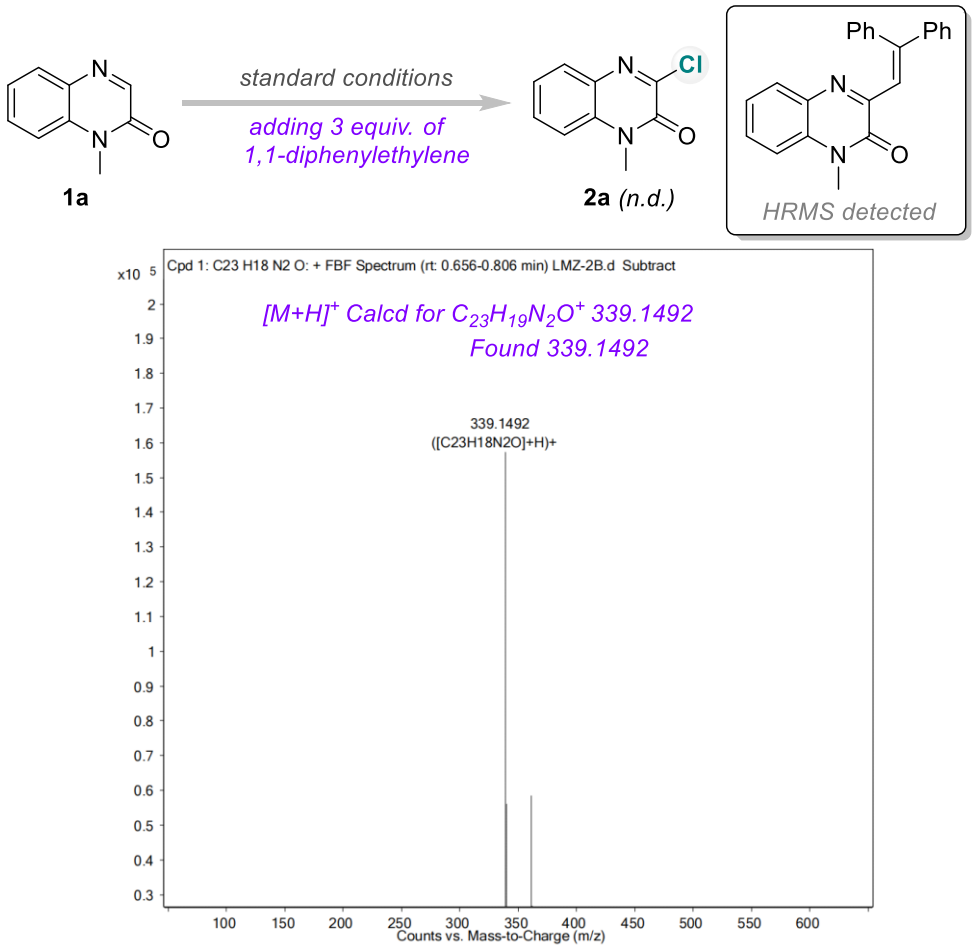


Figure S3. Crude **ESI-MS** of the ethene-1,1-diyldibenzene -trapping experiments

7.3 Calculation of Quantum Yield

The quantum yield was calculated following the method reported by Yoon group.[10, 11] First, standard ferrioxalate actinometry was used to calculate the intensity of LED light used in the experiment, and then the quantum yield of the reaction was calculated.

A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4 and stored in the dark. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4 and stored in the dark. 2 mL of 0.15 M ferrioxalate solution were put into a 15 mL sealed

tube under the protection of argon. After 90 s irradiation by 450 nm LED lamp with an emission slit width at 10.0 nm, 0.35 mL of the phenanthroline solution was added immediately, and the solution was stirred in the dark for 1 h to achieve complete coordination. In addition, 0.35 mL phenphenline solution was added to 2 mL 0.15 M ferrioxalate solution and stirred in the dark for 1 h to serve as blank control. 3 mL of distilled water was put into a colorimetric dish, and 30 μL of blank and experimental solution were added respectively. The absorption value at 510 nm was scanned with UV spectrophotometer and repeated three times to give the average. The conversion was calculated as eq (1):

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A \cdot 100}{l \cdot \varepsilon} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol $^{-1}$ cm $^{-1}$).[12] The photon flux can be calculated as eq (2).

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.767 for a 0.15 M solution at λ = 452 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 452 nm (0.99289, *vide infra*). Sample calculation as follows:

$$\text{mol } Fe^{2+} = \frac{0.00235 \text{ L} \cdot 1.64 \cdot 100}{1.000 \text{ cm} \cdot 11{,}100 \text{ L mol}^{-1}\text{cm}^{-1}} = 3.47 \times 10^{-5} \text{ mol}$$

$$\text{photon flux} = \frac{3.47 \times 10^{-5} \text{ mol}}{0.767 \cdot 90.0 \text{ S} \cdot 0.99289} = 5.06 \times 10^{-7} \text{einstein s}^{-1}$$

The absorbance of the above ferrioxalate solution at 452 nm was measured to be 2.148. The fraction of light absorbed (f) by this solution was calculated using eq (3), where A is the measured absorbance at 452 nm.

$$f = 1 - 10^{-A} \quad (3)$$

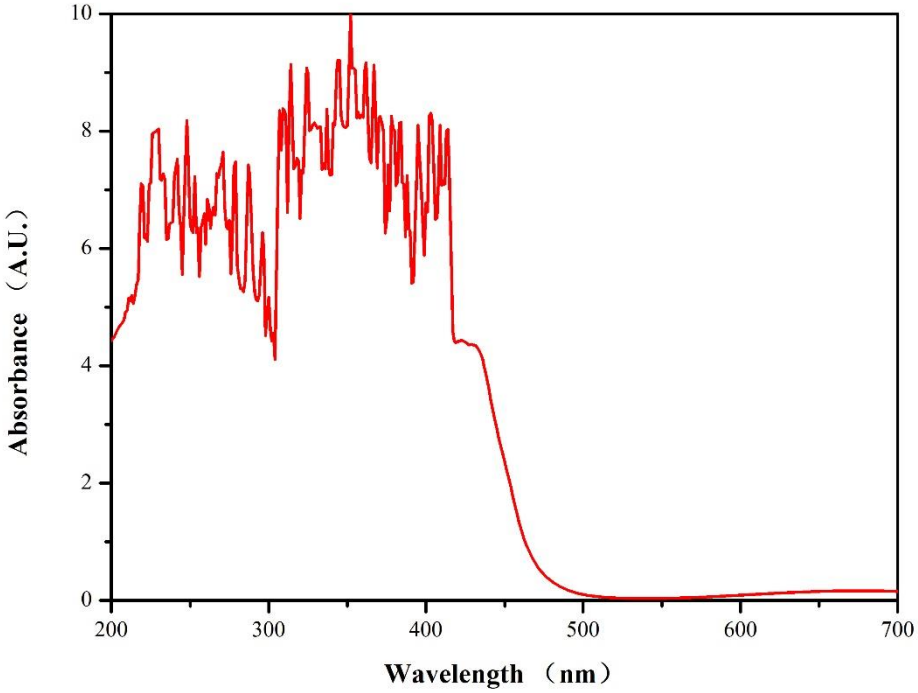


Figure S4. Absorbance of the ferrioxalate actinometer solution.

Under the condition of air atmosphere, 1-methylquinoxalin-2(1*H*)-one (**1a,** 0.2 mmol, 1.0 equiv.), $AlCl_3$ (0.1 mmol, 0.5 equiv.), $[Ir(dF(CF_3)ppy)_2(4,4'\text{-}dCF_3bpy)]PF_6$ and $CHCl_3$ (2.0 mL) were added into the 15 mL sealing tube. The reaction was stirred and irradiated ((λ = 452 nm, 3 cm distance) for 12 h. Then, the organic phase was removed by rotary evaporation under reduced pressure. Finally, the target product was separated by rapid column chromatography. This reaction was repeated three times, and the yield was calculated as 27.2%, 29.0% and 29.6%, respectively. The final average yield was 28.6%. The quantum yield was determined using eq(4):

$$\Phi = \frac{\text{moles of product formed}}{\text{photo flux}\cdot t\cdot f} \quad (4)$$

Where t is the reaction time (43200 s) and f is the fraction of light absorbed by $[Ir(dF(CF_3)ppy)_2(4,4'\text{-}dCF_3bpy)]PF_6$ at λ = 452 nm (0.233, *vide infra*). The photon flux was calculated (average of three experiments) to be 5.06×10^{-7} einstein s^{-1}. Sample quantum yield calculation as follows:

$$\Phi = \frac{5.72 \times 10^{-5}\text{mol}}{5.06 \times 10^{-7}\text{einstein s}^{-1} \cdot 43200\ \text{S} \cdot 0.233} = 0.01123$$

The absorbance of $[Ir(dF(CF_3)ppy)_2(4,4'\text{-}dCF_3bpy)]PF_6$ in MeCN was measured at the reaction concentration of 2×10^{-3} M. Calculated by eq (3), the absorbance at 452 nm is

0.23264.

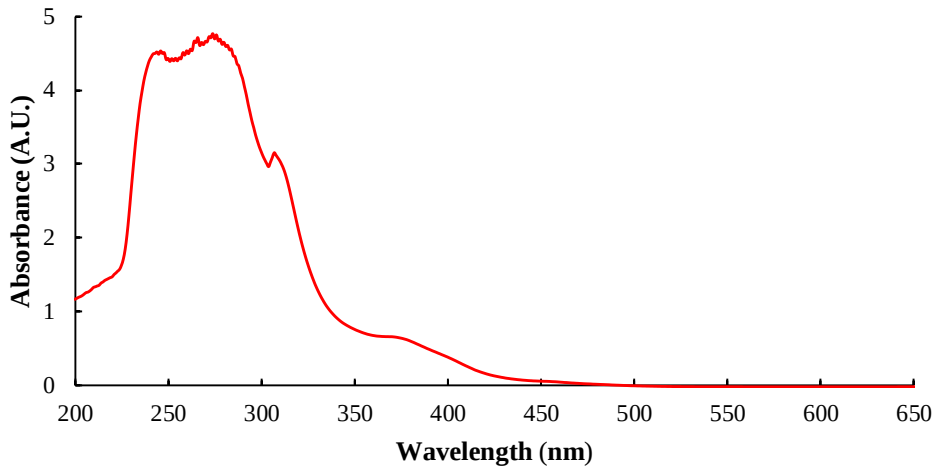
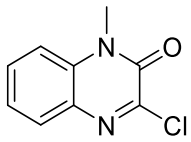


Figure S5. Absorbance of a 2 × 10^{-3} M solution of [Ir(dF(CF$_3$)ppy)$_2$(4,4'-dCF$_3$bpy)]PF$_6$ in MeCN

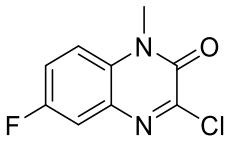
8. Characterization Data of Compounds



2a

This is a known compound reported in the literature.[13]

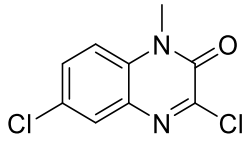
3-Chloro-1-methylquinoxalin-2(1*H*)-one (**2a**)**:** 33.4 mg, yield 86%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p**. 126 - 128 ℃. **IR** (neat) *v* 2918, 1651, 1602, 1160, 1076, 750 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.62 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.40 (td, *J* = 8.0, 7.5, 1.2 Hz, 1H), 7.35 (dd, *J* =8.4 Hz, 0.8Hz, 1H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-d) δ 151.72, 148.79, 133.26, 131.68, 131.07, 129.66, 124.45, 113.99, 30.57. **HRMS** (ESI) m/z [M+H]$^+$ Calcd for $C_9H_8ClN_2O^+$ 195.0320, Found 195.0322.



2b

3-Chloro-6-fluoro-1-methylquinoxalin-2(1*H*)-one (**2b**): 33.1 mg, yield 78%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 105 - 107. **IR** (neat) *v* 2918, 1152, 1078, 959, 865, 821 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.33 – 7.29 (m, 1H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 158.98 (d, $^1J_{C\text{-}F}$ = 244.0 Hz), 151.32, 150.51, 132.16 (d, $^3J_{C\text{-}F}$ = 11.5 Hz), 129.99, 118.90 (d, $^2J_{C\text{-}F}$ = 23.9 Hz) 115.31 (d, $^2J_{C\text{-}F}$ =

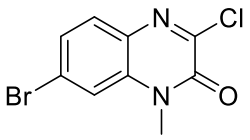
13.9 Hz), 115.17, 30.85. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_9H_7ClFN_2O^+$ 213.0225 Found 213.0237.



2c

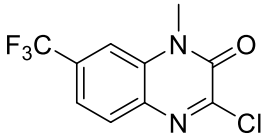
This is a known compound reported in the literature. [13]

3,6-Dichloro-1-methylquinoxalin-2(1*H*)-one (**2c**): 40.3 mg, yield 88%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 131 - 133. **IR** (neat) *v* 2919, 1659, 1470, 1095, 819 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.81 (d, *J* = 2.3 Hz, 1H), 7.58 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.36, 150.28, 132.09, 131.95, 131.07, 129.87, 128.94, 115.10, 30.75. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_9H_6Cl_2N_2NaO^+$ 250.9749, Found 250.9762.



2d

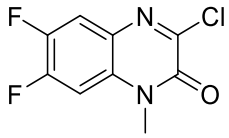
7-Bromo-3-chloro-1-methylquinoxalin-2(1*H*)-one (**2d**): 34.8 mg, yield 64%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 172 - 174 °C. **IR** (neat) *v* 2920, 1666, 1456, 1162, 1095, 1067, 803 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 2.2 Hz, 1H), 7.54 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 3.73 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.36, 150.29, 132.09, 131.95, 131.07, 129.87, 128.95, 115.09, 30.75. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_9H_6BrClN_2NaO^+$ 294.9244, Found 294.9237.



2e

3-Chloro-1-methyl-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (**2e**): 32.5 mg, yield 62%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 129 - 131 °C. **IR** (neat) *v* 2920, 1661, 1118, 1071, 898, 850 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 3.82 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.51, 151.38, 133.32, 133.29, 132.57 (q, $^2J_{C-F}$ = 33.0 Hz), 130.44, 123.36 (q, $^1J_{C-F}$ = 271.4 Hz) 120.96 (q, $^3J_{C-F}$ = 3.5 Hz), 111.49 (q, $^3J_{C-F}$ = 4.0 Hz), 30.76. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_{10}H_6ClF_3N_2NaO^+$ 285.0013, Found

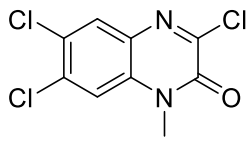
285.0021.



2f

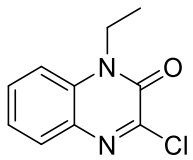
This is a known compound reported in the literature.[13]

3-Chloro-6,7-difluoro-1-methylquinoxalin-2(1*H*)-one (**2f**): 40.1 mg, yield 87%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 219 - 221 °C. **IR** (neat) *v* 3064, 2919, 1660, 1509, 1068, 640 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 1H), 7.18 – 7.13 (m, 1H), 3.74 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.92 (dd, *J* = 253.9, 14.3 Hz), 151.29, 149.41 (d, *J* = 3.7 Hz), 147.11 (dd, *J* = 247.6, 13.9 Hz), 130.61 (dd, *J* = 8.9, 1.8 Hz), 127.77 (dd, *J* = 9.6, 2.9 Hz), 117.37 (dd, *J* = 18.6, 2.2 Hz), 102.80 (d, *J* = 23.2 Hz), 31.11. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_9H_5ClF_2N_2NaO^+$ 252.9951, Found 252.9976.



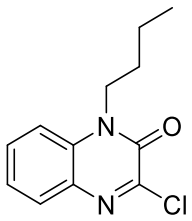
2g

3,6,7-Trichloro-1-methylquinoxalin-2(1*H*)-one (**2g**): 43.5 mg, yield 83%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 108 - 110 °C. **IR** (neat) *v* 2921, 2851, 1660, 1455, 1083, 799 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.44 (s, 1H), 3.73 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.12, 150.30, 135.39, 132.57, 130.56, 130.36, 128.47, 115.50, 30.83. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_9H_5Cl_3N_2NaO^+$ 284.9360, Found 284.9399.



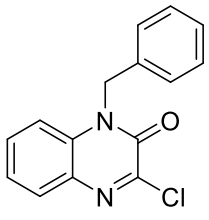
2h

3-Chloro-1-ethylquinoxalin-2(1H)-one (**2h**): 29.9 mg, yield 77%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 112 - 114 °C. **IR** (neat) *v* 2920, 1661, 1464, 1072, 833, 760 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.62 (td, *J* = 7.8, 1.4 Hz, 1H), 7.42 – 7.34 (m, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.19, 148.83, 132.22, 132.01, 131.05, 129.93, 124.26, 113.83, 38.92, 12.34. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_{10}H_{10}ClN_2O^+$ 209.0476, Found 209.0478.



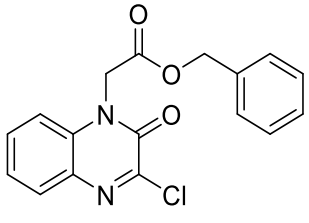
2i

1-*Butyl*-3-chloroquinoxalin-2(1*H*)-one (**2i**): 37.8 mg, yield 80%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 77 - 79 °C. **IR** (neat) *v* 2956, 2929, 1651, 1464, 1153, 1079, 764 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.40 – 7.34 (m, 2H), 4.30 (t, *J* = 7.8 Hz, 2H), 1.77 (p, *J* = 7.7 Hz, 2H), 1.50 (m, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.44, 148.85, 132.50, 131.98, 130.96, 129.89, 124.23, 114.00, 43.64, 29.22, 20.21, 13.75. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_{12}H_{14}ClN_2O^+$ 237.0789, Found 237.0808.



2j

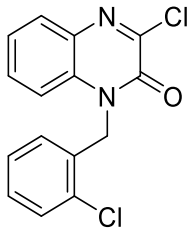
1-Benzyl-3-chloroquinoxalin-2(1*H*)-one (**2j**): 43.2 mg, yield 80%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 122 - 124 °C. **IR** (neat) *v* 921, 1666, 1601, 1089, 952, 750 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 1H), 7.51 – 7.47 (m, 1H), 7.37 – 7.26 (m, 7H), 5.54 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.93, 148.86, 134.52, 132.64, 131.97, 131.03, 129.79, 129.06, 128.04, 126.99, 124.49, 114.79, 47.39. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_{15}H_{11}ClN_2NaO^+$ 293.0452, Found 293.0453.



2k

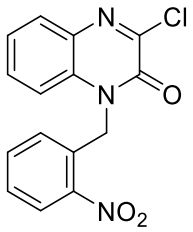
Benzyl 2-(3-chloro-2-oxoquinoxalin-1(2*H*)-yl)acetate (**2k**): 42.6 mg, yield 65%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 177 - 179 °C. **IR** (neat) *v* 2919, 1667, 1190, 756, 739 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.41 –

7.34 (m, 4H), 7.31 – 7.28 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 5.22 (s, 2H), 5.11 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 166.41, 151.41, 148.42, 134.68, 132.37, 131.75, 131.21, 129.99, 128.75, 128.71, 128.44, 124.75, 113.45, 67.95, 44.70，29.71. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_{17}H_{14}ClN_2O_3^+$ 329.0687, Found 329.0693.



2l

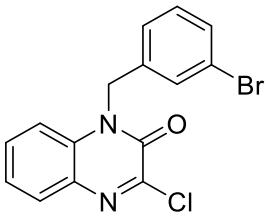
3-Chloro-1-(2-chlorobenzyl)quinoxalin-2(1*H*)-one (**2l**): 54.7 mg, yield 90%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 178 - 180 °C. **IR** (neat) *v* 2919, 1666, 1036, 935, 751 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 1H), 7.52 – 7.45 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.63 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.92, 148.73, 132.62, 132.36, 131.92, 131.58, 131.29, 129.90, 129.78, 129.14, 127.46, 126.89, 124.71, 114.71, 44.94. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_{15}H_{11}Cl_2N_2O^+$ 305.0243, Found 305.0261.



2m

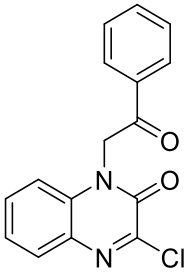
This is a known compound reported in the literature. [14]

3-Chloro-1-(2-nitrobenzyl)quinoxalin-2(1*H*)-one (**2m**): 36.5 mg, yield 58%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 198 - 200 °C. **IR** (neat) *v* 2919, 1669, 1518, 1330, 758, 728 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27 – 8.25 (m, 1H), 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.45 – 7.36 (m, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.87 – 6.84 (m, 1H), 5.94 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.75, 148.79, 147.73, 134.37, 132.40, 131.95, 131.43, 130.03, 129.98, 128.86, 126.96, 125.99, 124.97, 114.33, 45.40. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_{15}H_{10}ClN_3NaO_3^+$ 338.0303, Found 338.0335.



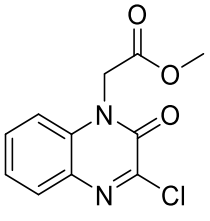
2n

1-(3-Bromobenzyl)-3-chloroquinoxalin-2(1*H*)-one (**2n**): 56.3 mg, yield 81%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 168 - 170 °C. **IR** (neat) *v* 2918, 1664, 1089, 1024, 937, 760, 641 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.42 (s, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.19 (m, 3H), 5.50 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 151.84, 148.76, 136.79, 132.43, 131.97, 131.32, 131.18, 130.63, 129.98, 125.60, 124.69, 123.17, 114.48, 46.79. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_{15}H_{10}BrClN_2NaO^+$ 370.9557, Found 370.9567.



2o

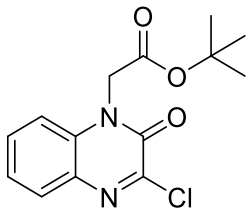
3-Chloro-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (**2o**): 50.7 mg, yield 85%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 196 - 198 °C. **IR** (neat) *v* 2920, 1656, 1227, 1094, 999, 753 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.79 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 190.27, 151.60, 148.39, 144.68, 134.56, 134.33, 132.75, 131.07, 129.93, 129.16, 128.20, 124.56, 113.85, 49.60, 29.70. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_{16}H_{11}ClN_2NaO_2^+$ 321.0401, Found 321.0410.



2p

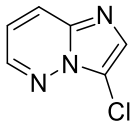
Methyl 2-(3-chloro-2-oxoquinoxalin-1(2*H*)-yl)acetate (**2p**): 36.3 mg, yield 72%, (Petroleum

ether/EtOAc = 3:1), a white solid. **m.p.** 117 - 119 °C. **IR** (neat) *v* 2958, 1754, 1432, 1219, 1086, 1043 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 5.13 (s, 2H), 3.80 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 168.24, 151.86, 138.97, 138.88, 130.42, 128.02, 126.92, 63.41, 52.42, 29.72. **HRMS** (ESI) m/z $[M+Na]^+$ Calcd for $C_{11}H_9ClN_2NaO_3^+$ 275.0194, Found 275.0218.



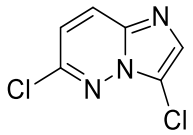
2q

Tert-*butyl* 2-(3-chloro-2-oxoquinoxalin-1(2*H*)-yl)acetate (**2q**): 37.6 mg, yield 64%, (Petroleum ether/EtOAc = 3:1), a white solid. **m.p.** 149 - 151 °C. **IR** (neat) *v* 2919, 1671, 1237, 1147, 1091, 763 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.41 – 7.37 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.97 (s, 2H), 1.47 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 165.43, 151.40, 148.51, 132.56, 131.74, 131.09, 129.93, 124.60, 113.48, 83.66, 45.39, 27.97. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_{14}H_{16}ClN_2O_3^+$ 295.0844, Found 295.0858.



4a

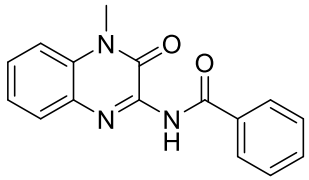
3-Chloroimidazo[1,2-*b*]pyridazine (**4a**): 13.2 mg, yield 43%, (Petroleum ether/EtOAc = 1:1), a white solid. **m.p.** 240 °C. **IR** (neat) *v* 2922, 1061, 789, 753, 449 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 4.4 Hz, 1H), 7.98 (dd, *J* = 9.2, 1.5 Hz, 1H), 7.75 (s, 1H), 7.10 (dd, *J* = 9.2, 4.4 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, Chloroform-*d*) δ 143.76, 131.03, 126.13, 116.63, 29.70. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_6H_5ClN_3^+$ 154.0167, Found 154.0178.



4b

3,6-Dichloroimidazo[1,2-*b*]pyridazine (**4b**): 11.7 mg, yield 31%, (Petroleum ether/EtOAc = 1:1), a white solid. **m.p.** 69 - 71 °C. **IR** (neat) *v* 2922, 536, 503, 457, 472, 429 cm^{-1}. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.30 (d, *J* = 9.5 Hz, 1H), 8.00 (s, 1H), 7.47 (d, *J* = 9.5 Hz, 1H). **^{13}C{^{1}H} NMR** (100

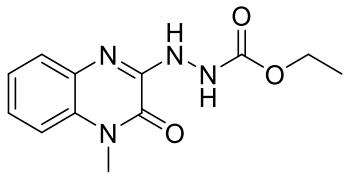
MHz, DMSO-d_6) δ 148.11, 137.71, 131.98, 130.09, 128.81, 119.97. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_6H_4Cl_2N_3^+$ 187.9777, Found 187.9796.



5a

This is a known compound reported in the literature.[15]

N-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)benzamide (**5a**): 34.5 mg, yield 62%, (Petroleum ether/EtOAc = 1:1), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.03 – 7.98 (m, 2H), 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.48 – 7.46 (m, 1H), 7.40 – 7.35 (m, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 3.79 (s, 3H).

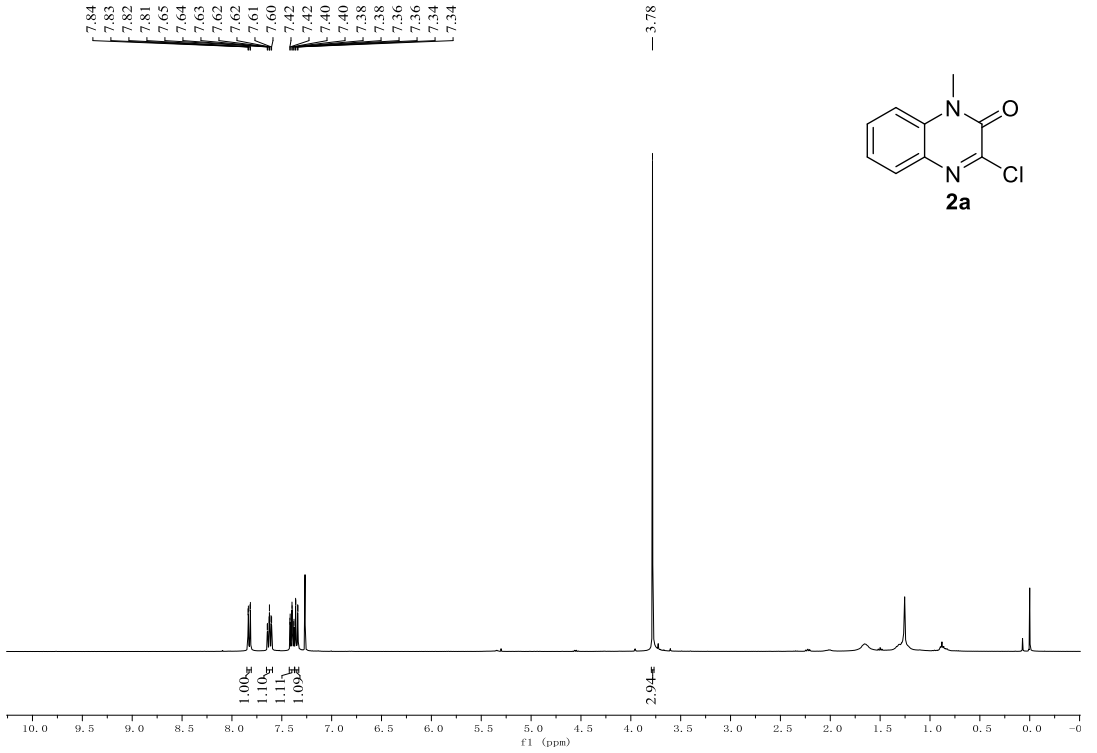


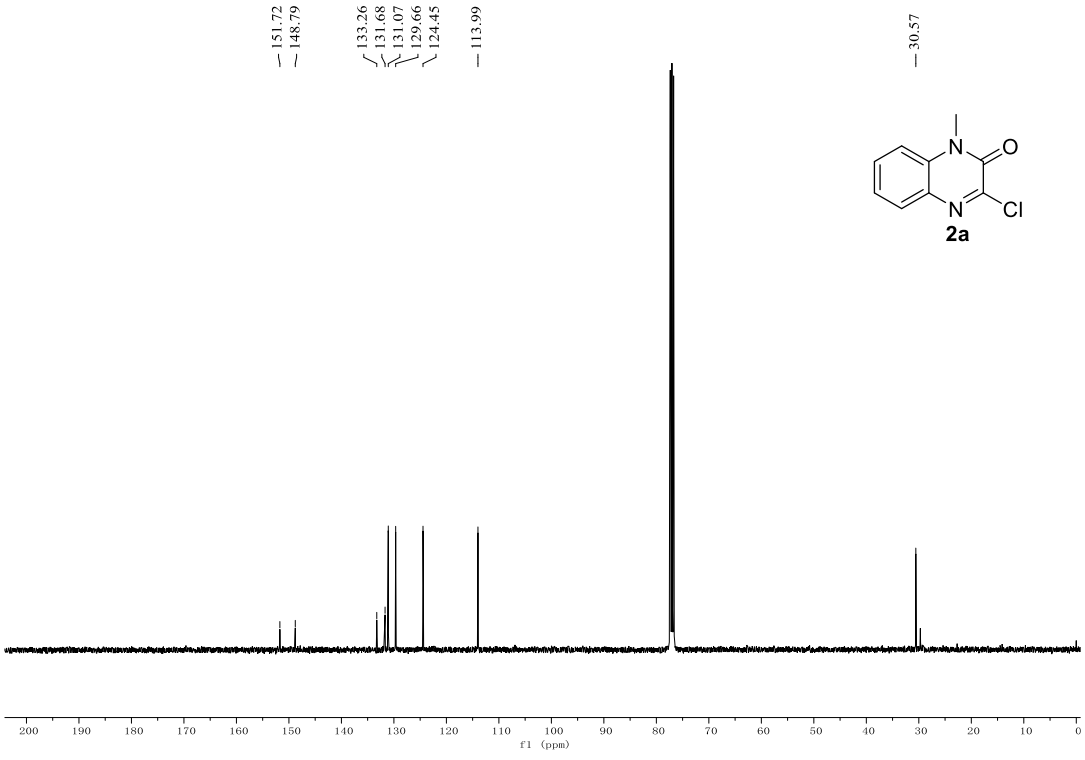
6a

Ethyl 2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)hydrazine-1-carboxylate (**6a**): 16.9 mg, yield 32%, (Petroleum ether/EtOAc = 1:1), a white solid. **m.p.** 189 - 191 °C. **IR** (neat) *v* 2919, 1738, 1654, 1469, 1288, 1044 cm^{-1}. **^{1}H NMR** (400 MHz, DMSO-d_6) δ9.17 (s, 1H), 7.46 – 7.43 (m, 2H), 7.34 – 7.30 (m, 1H), 7.25 (td, *J* = 7.7, 1.3 Hz, 1H), 4.12 – 4.09 (m, 2H), 3.67 (s, 3H), 1.27 – 1.21 (m, 3H). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ206.34, 156.24, 150.30, 132.67, 130.03, 125.63, 124.69, 123.62, 114.34, 60.39, 28.73, 14.41. **HRMS** (ESI) m/z $[M+H]^+$ Calcd for $C_{12}H_{15}N_4O_3^+$ 263.1139, Found 263.1140.

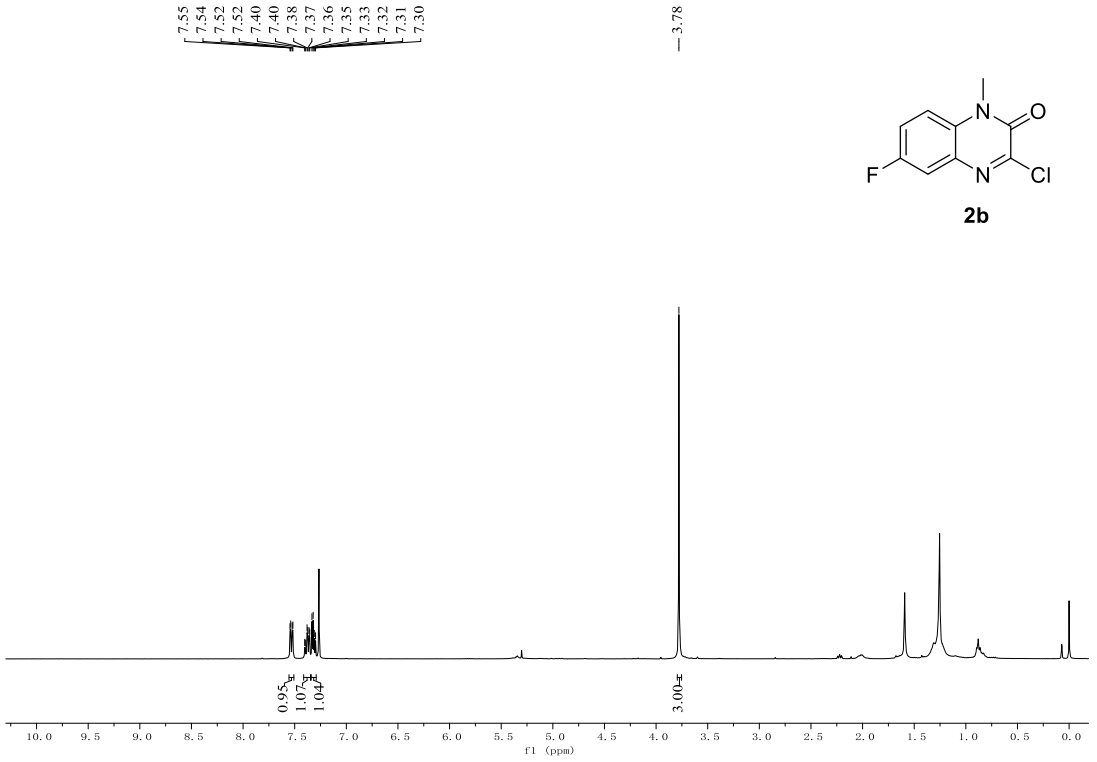
9. NMR spectra of 2a-2q, 4a-4b, 5a, 6a

Compound **2a:** **^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

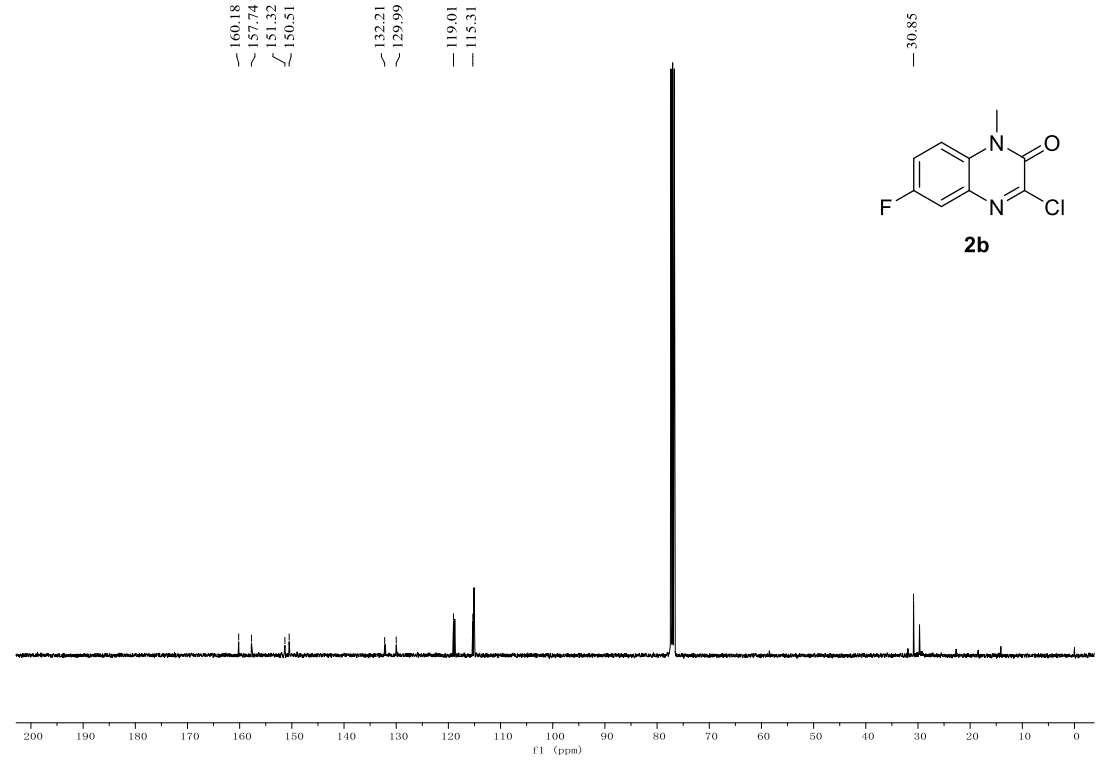




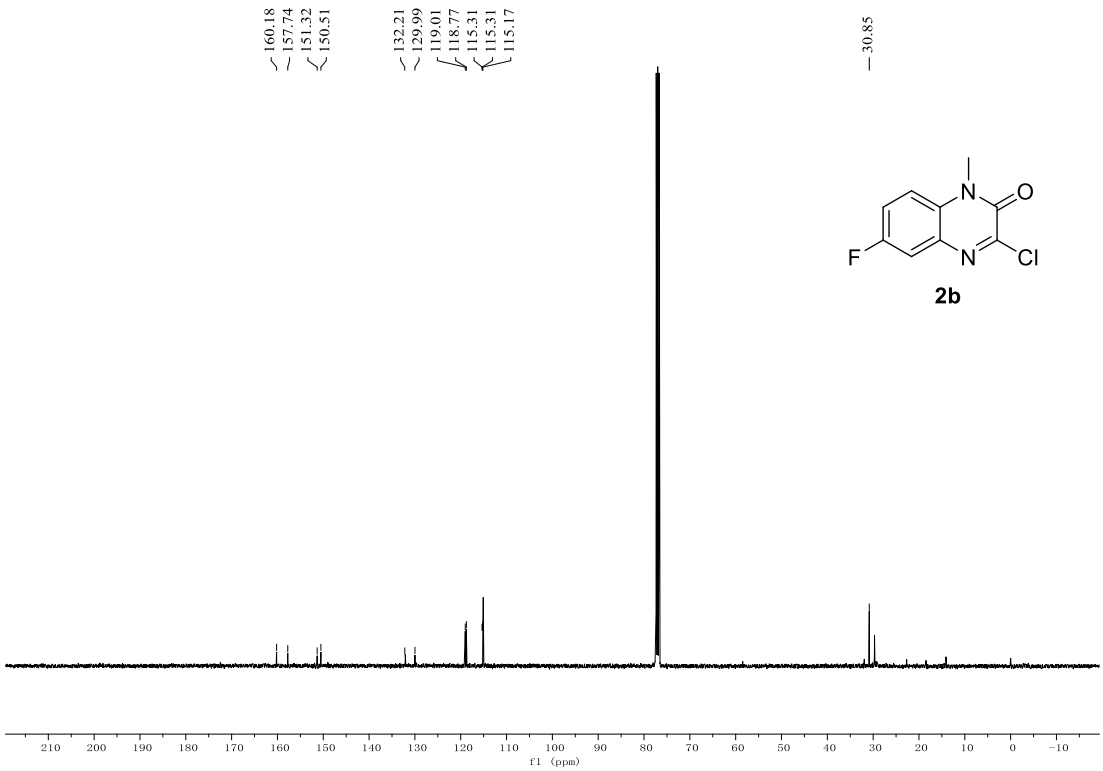
Compound **2b: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



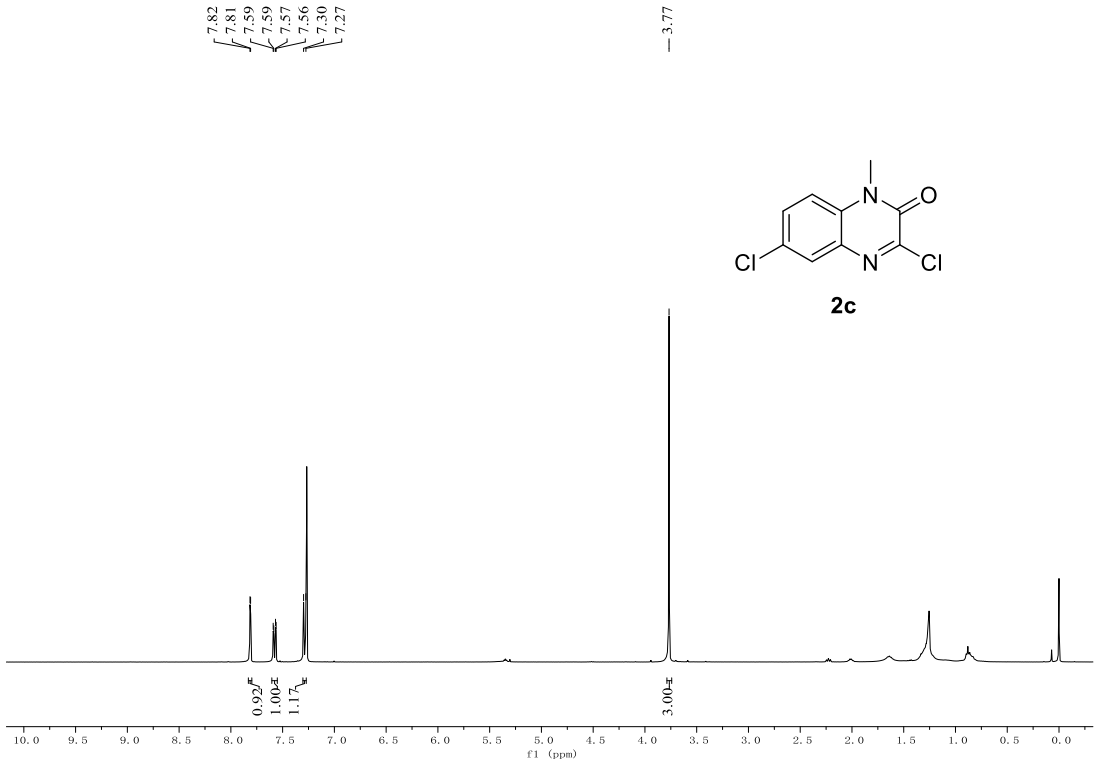
2b

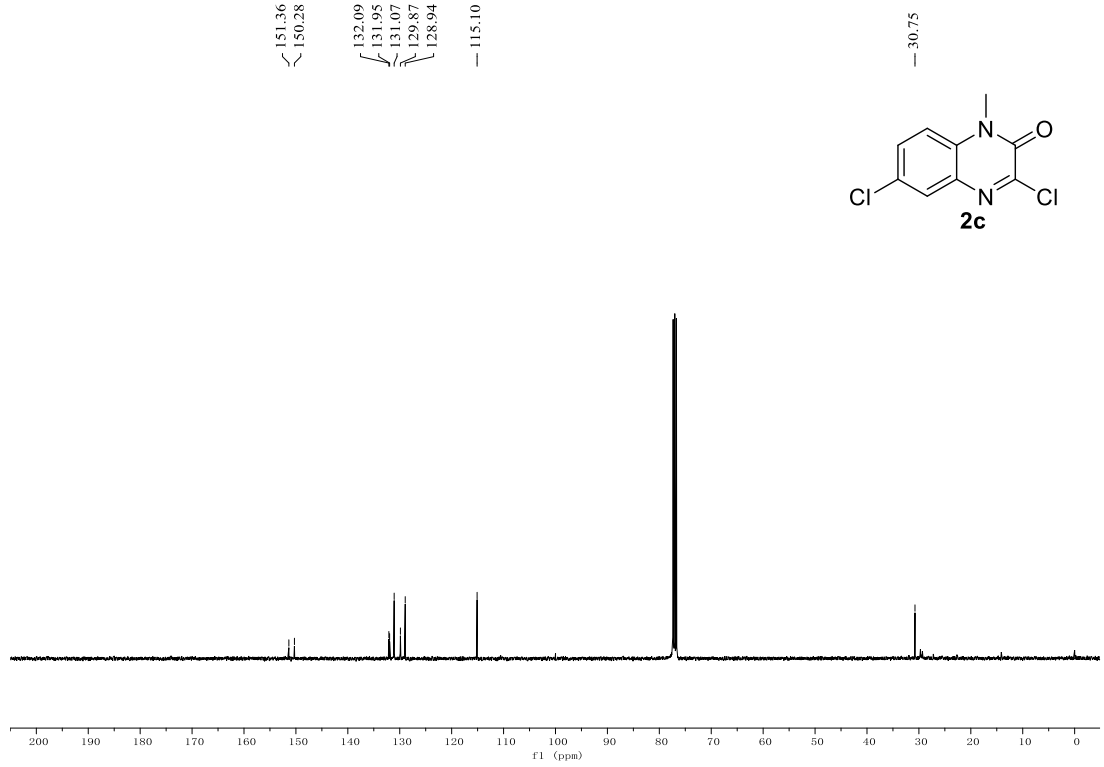


2b

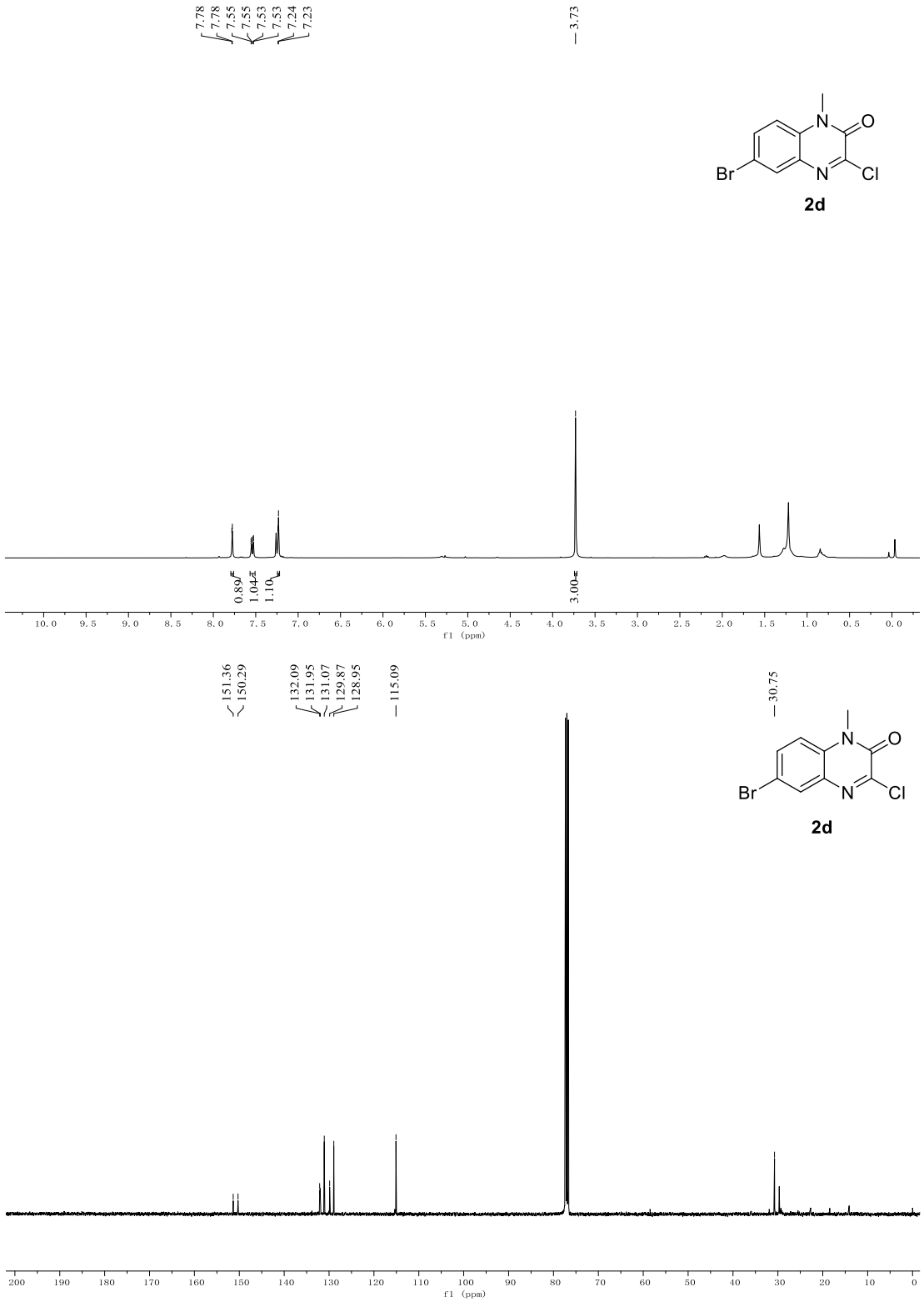

160.18
157.74
151.32
150.51
132.21
129.99
119.01
118.77
115.31
115.31
115.17
30.85
N
O
F
N
Cl
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

Compound **2c: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

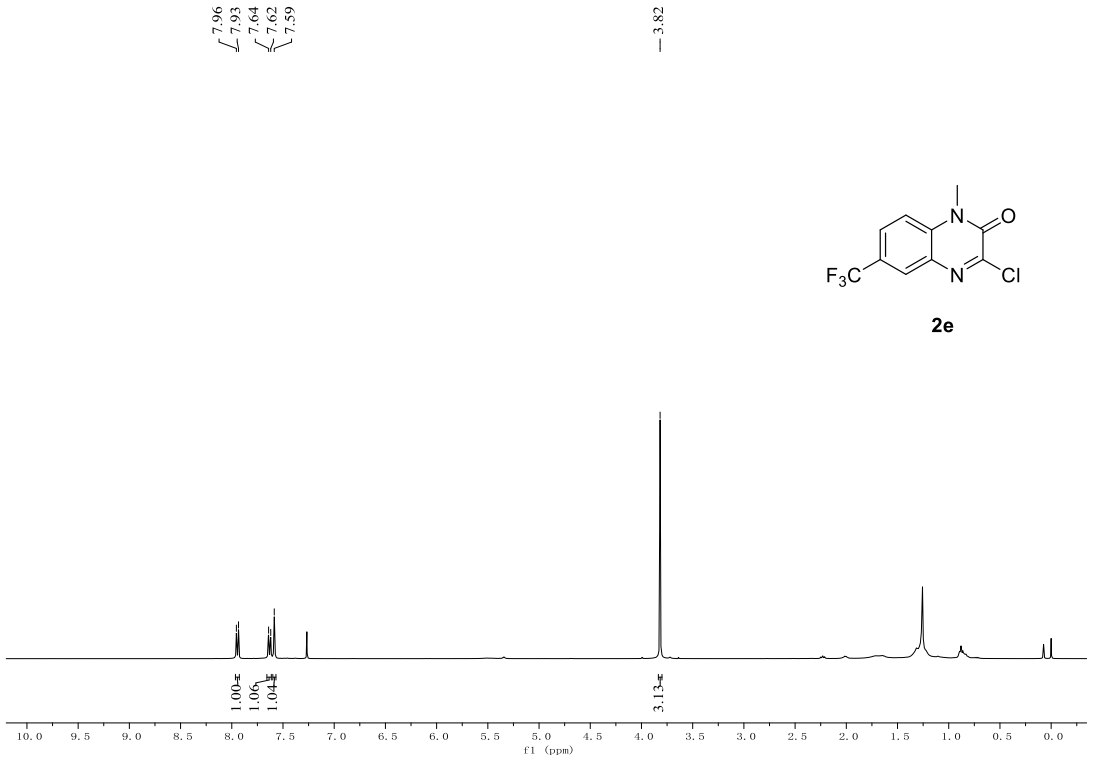


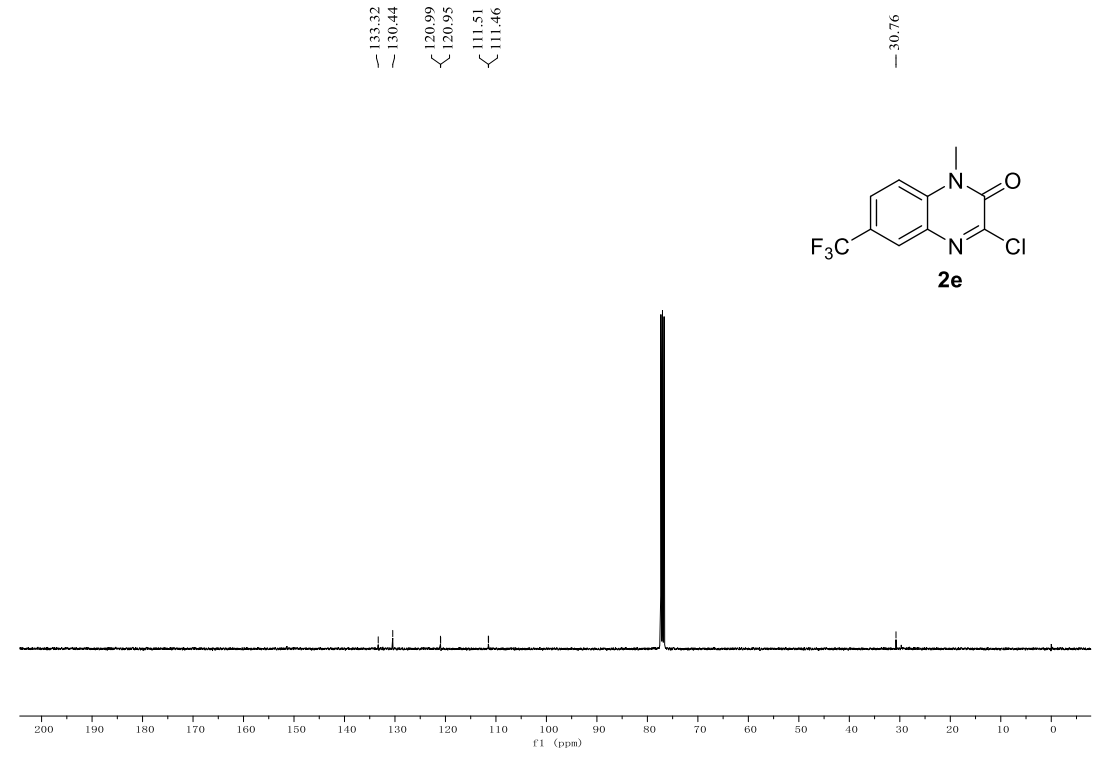


Compound **2d: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

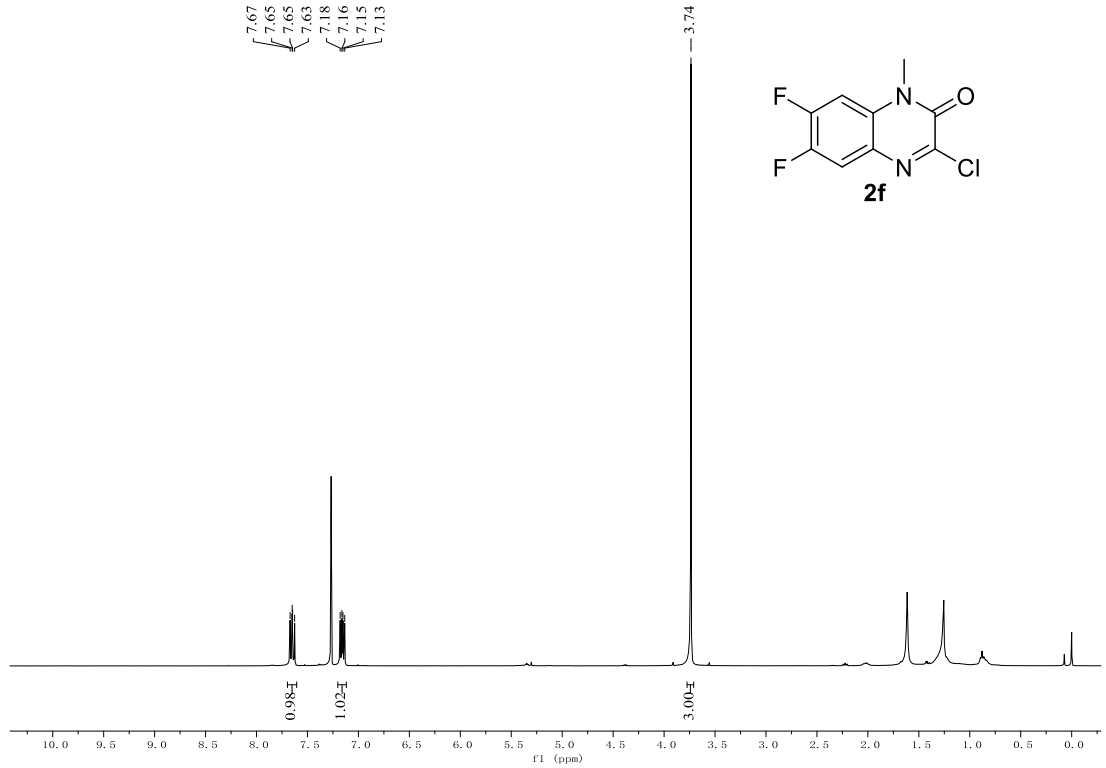


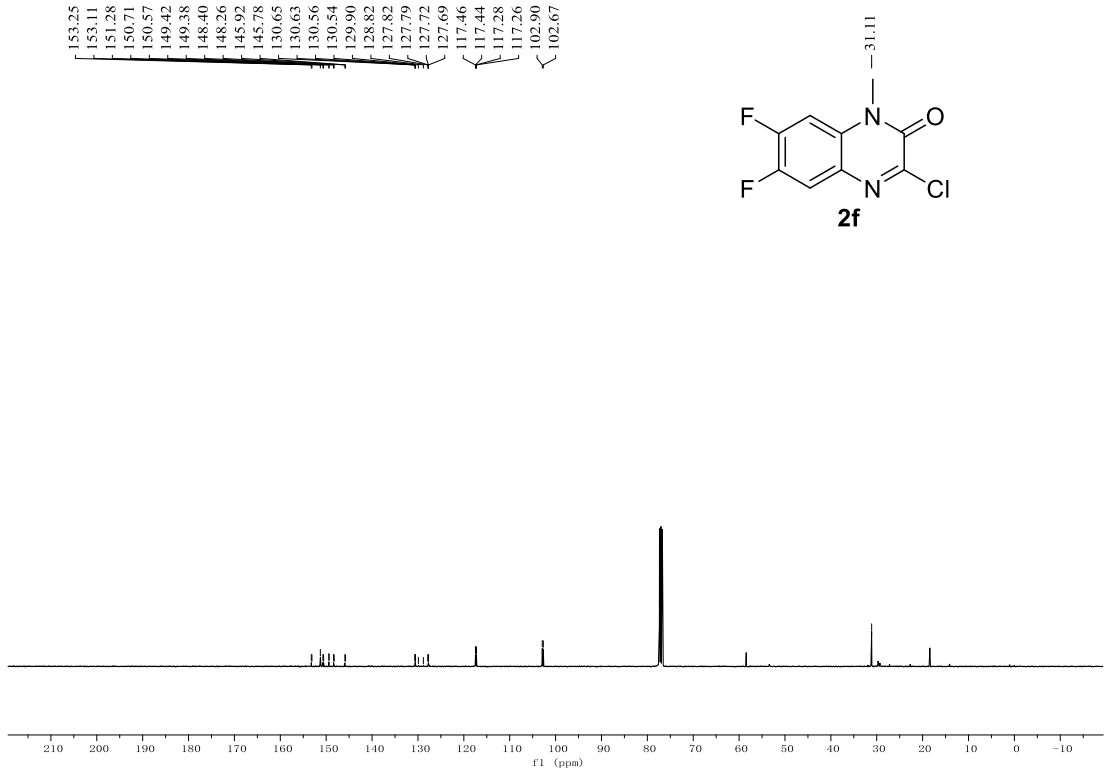
Compound **2e: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



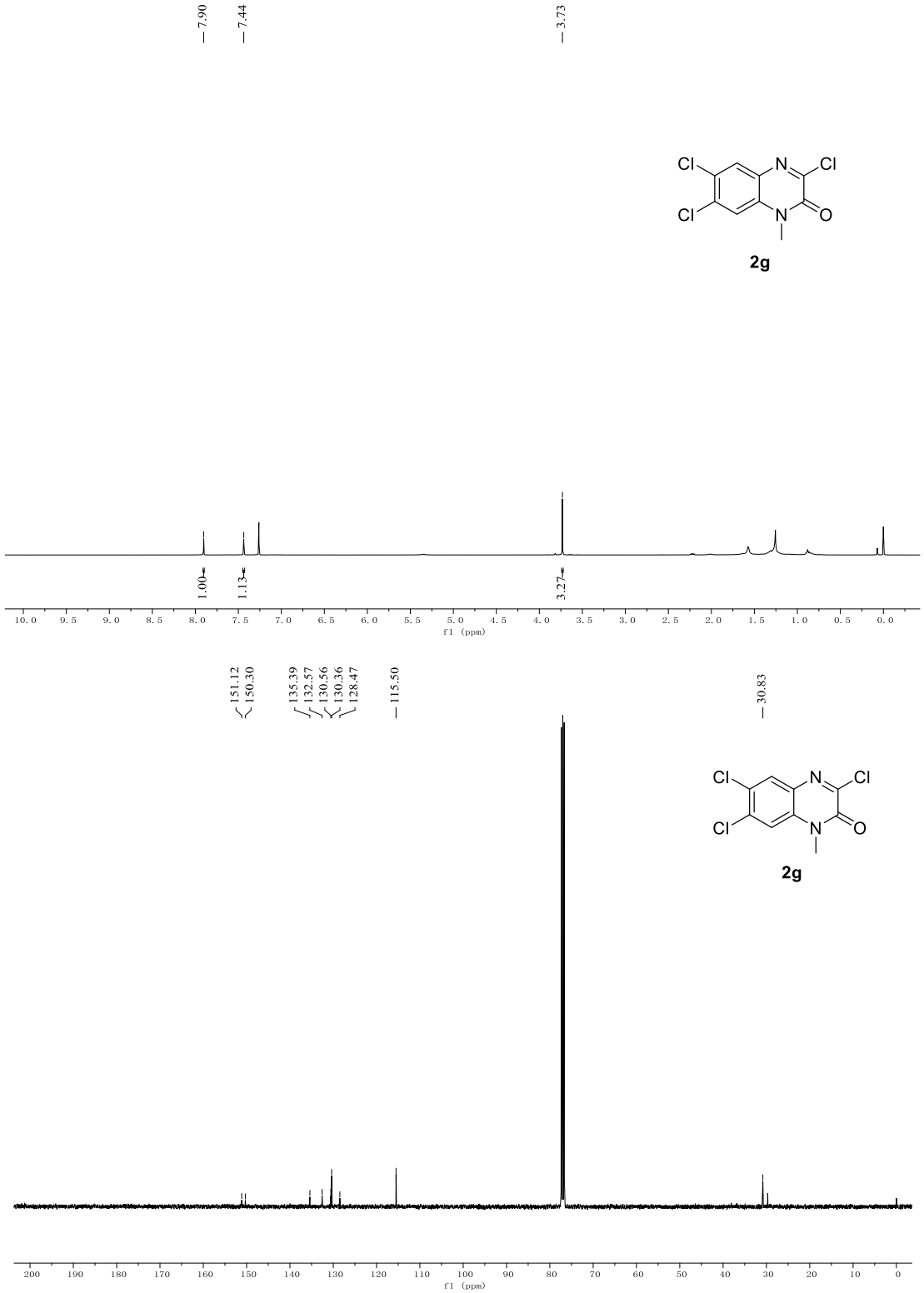


Compound **2f: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

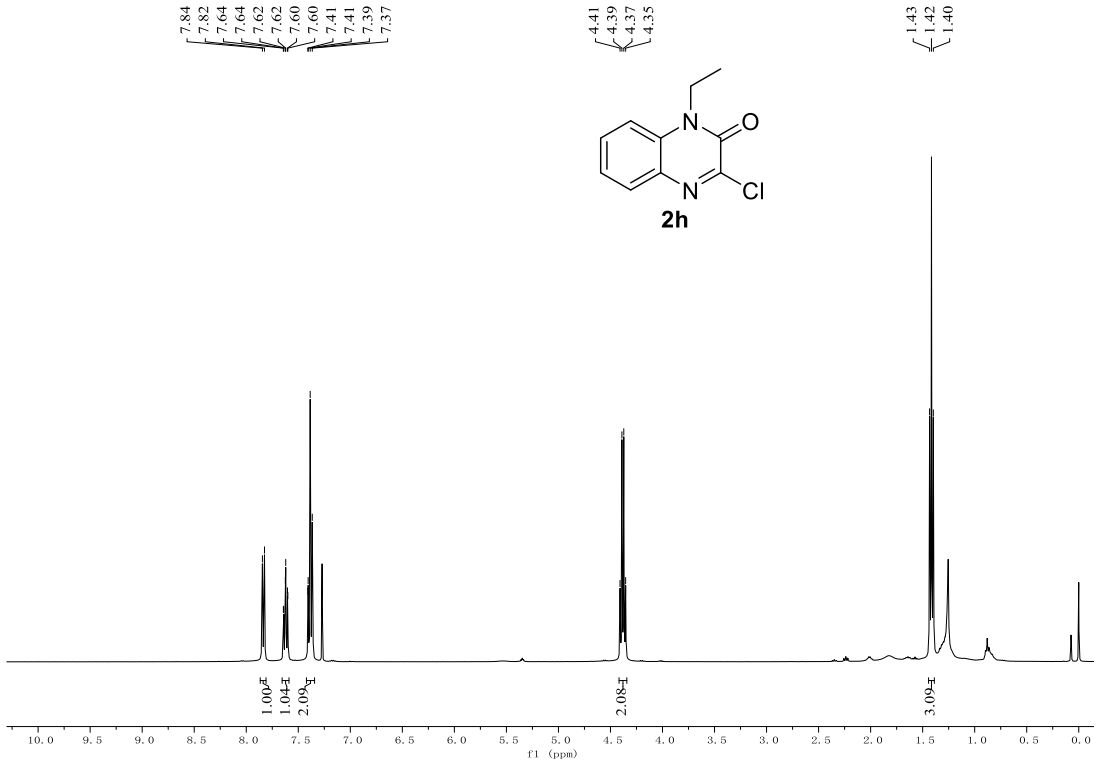


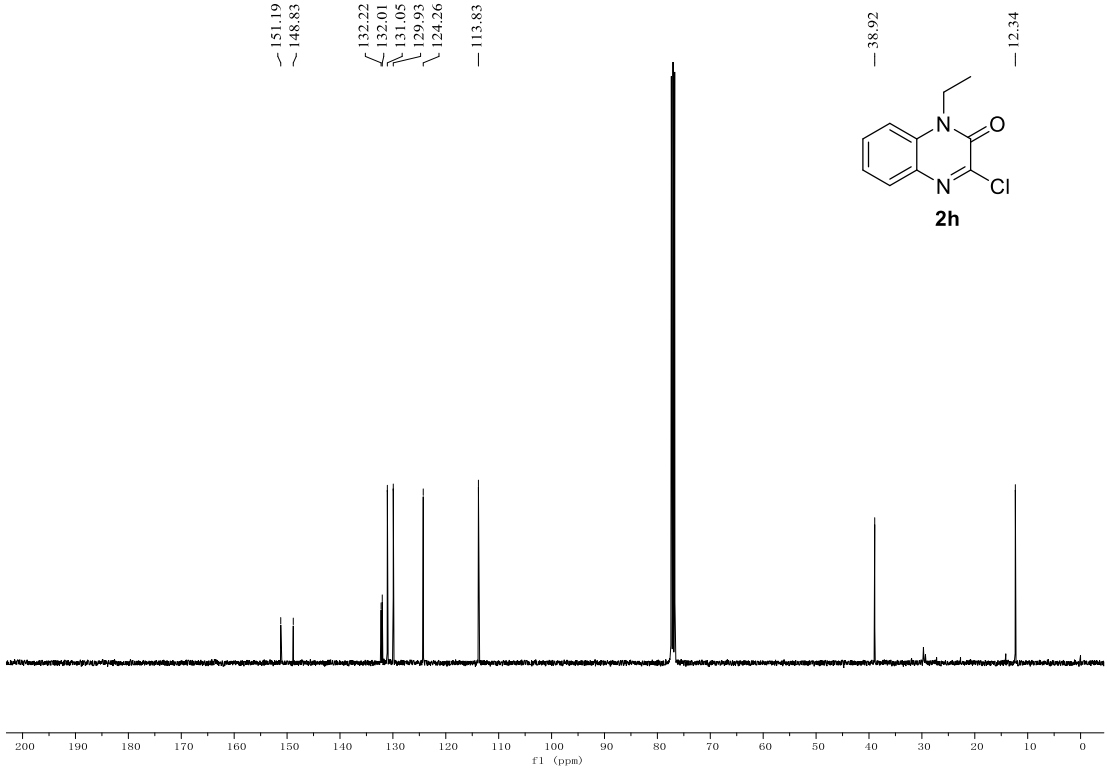


Compound **2g: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

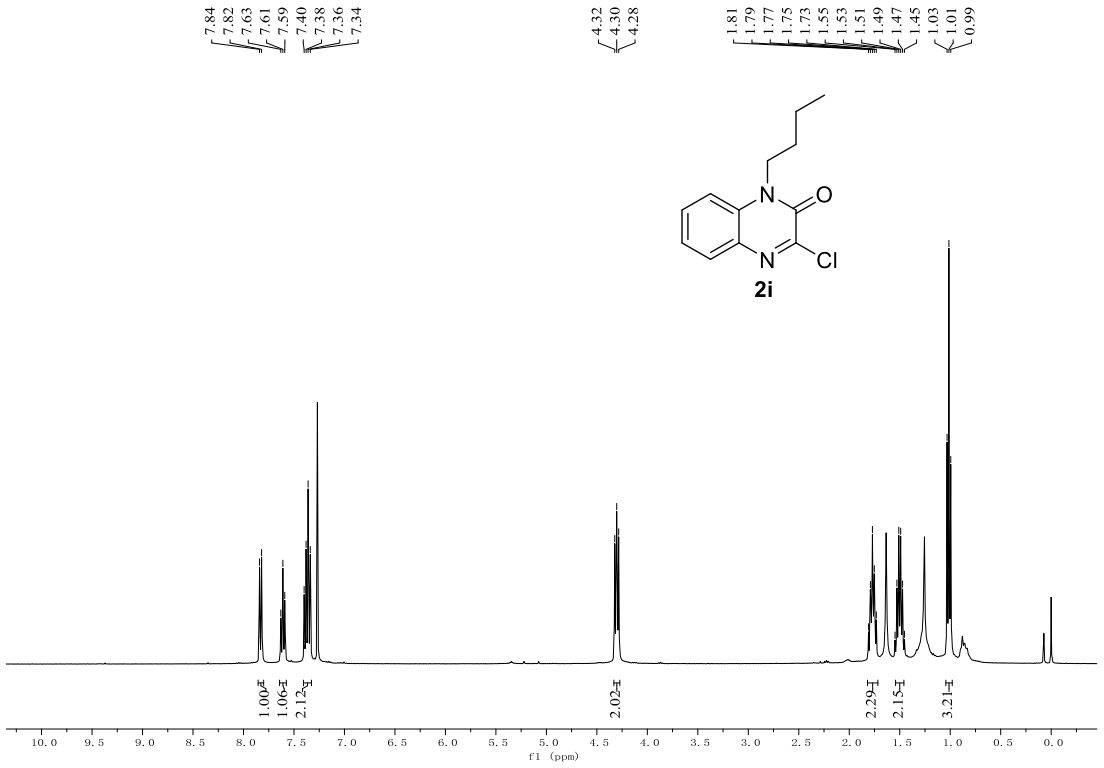


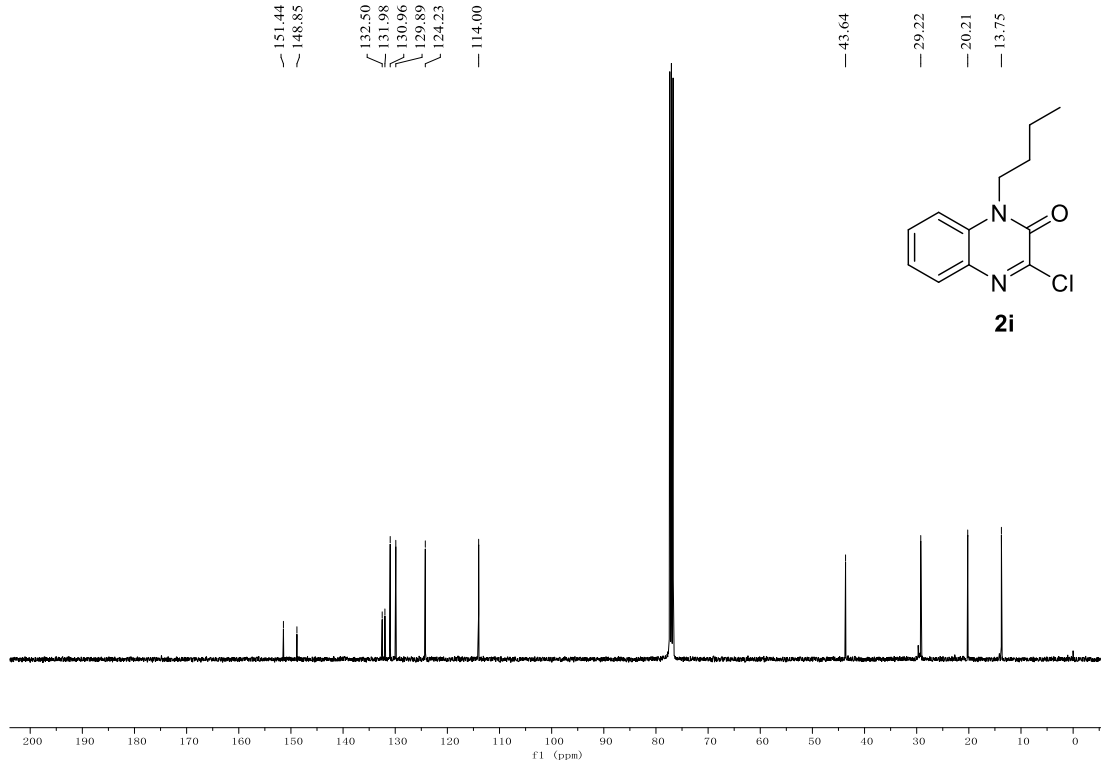
Compound **2h: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



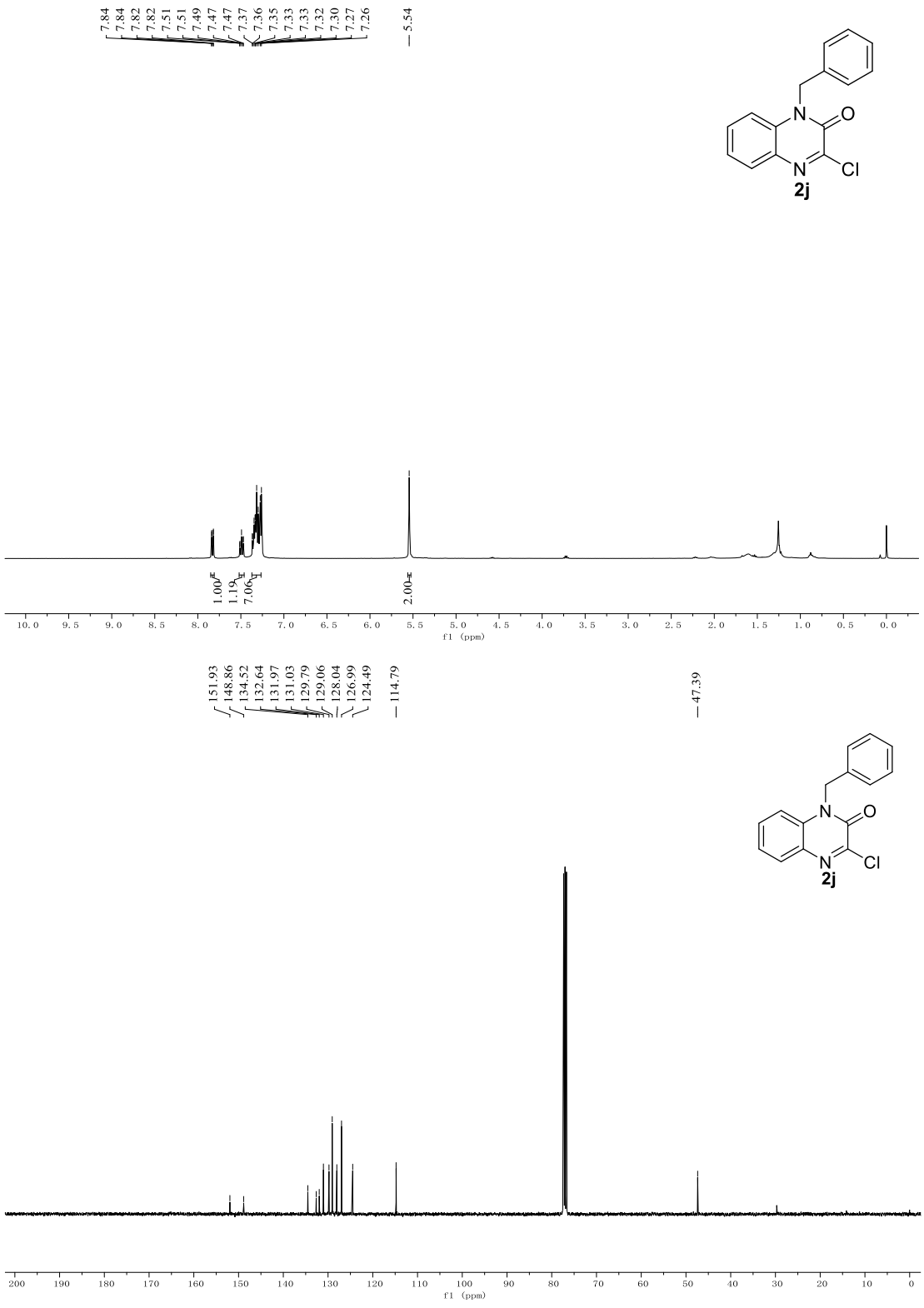


Compound **2i: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

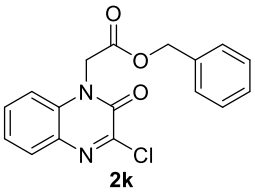


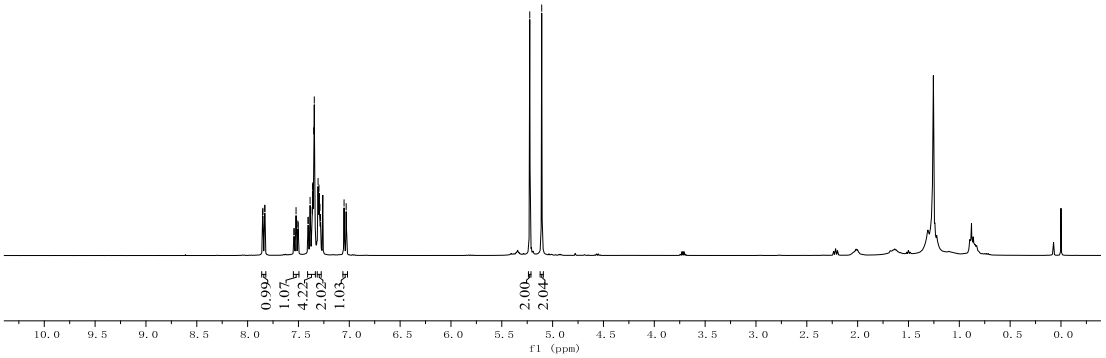


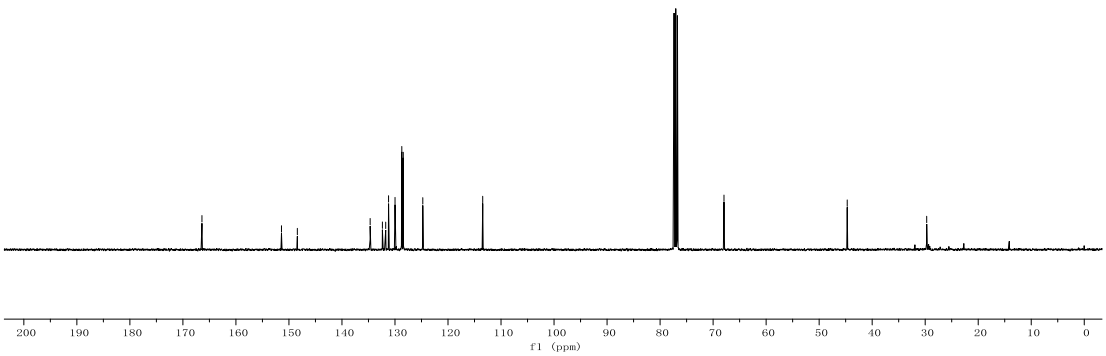
Compound **2j: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



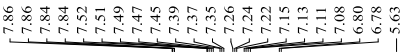
Compound **2k: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

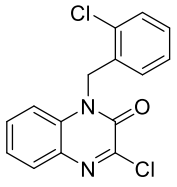




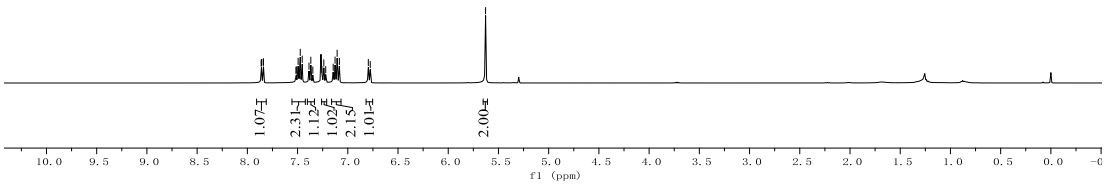


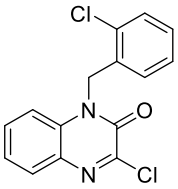
Compound **2l: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



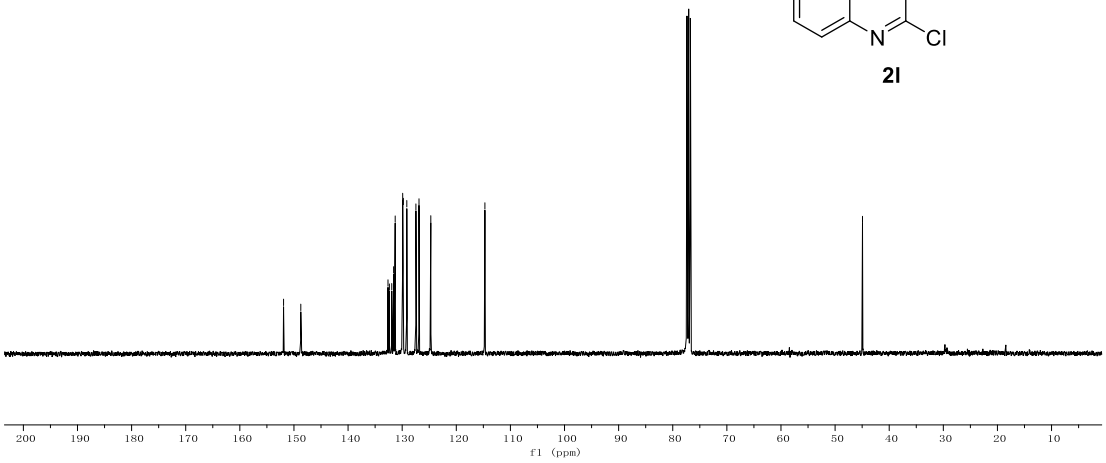


2l

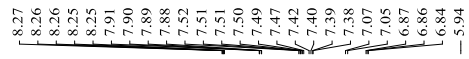


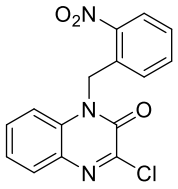


2l

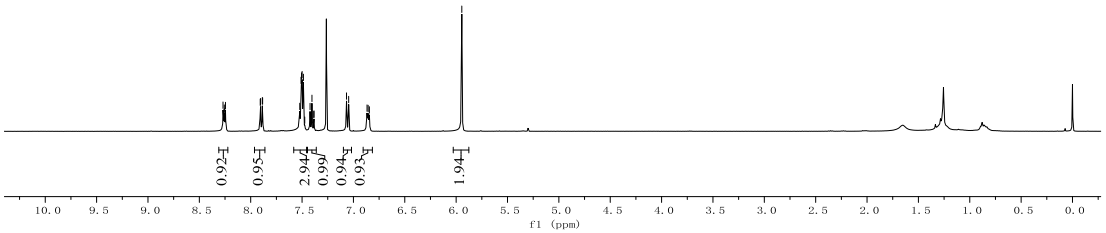


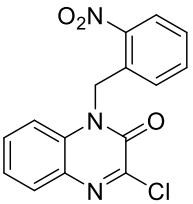
Compound **2m: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



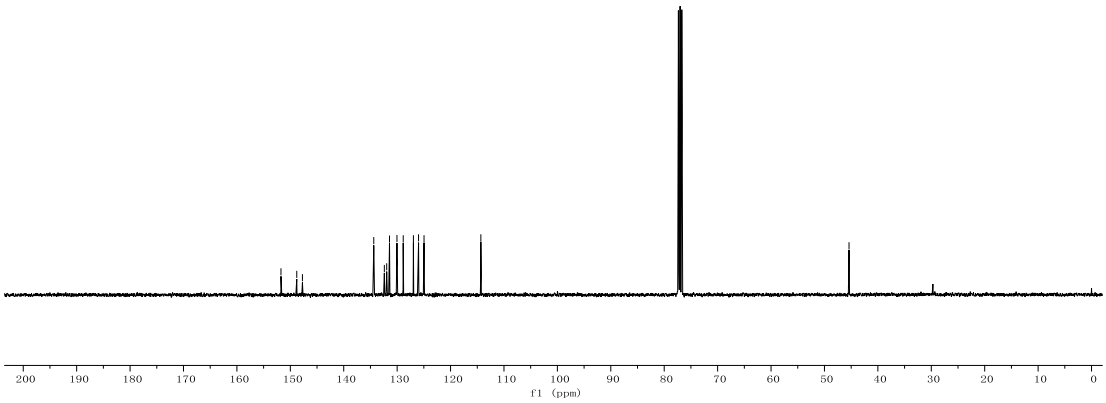


2m

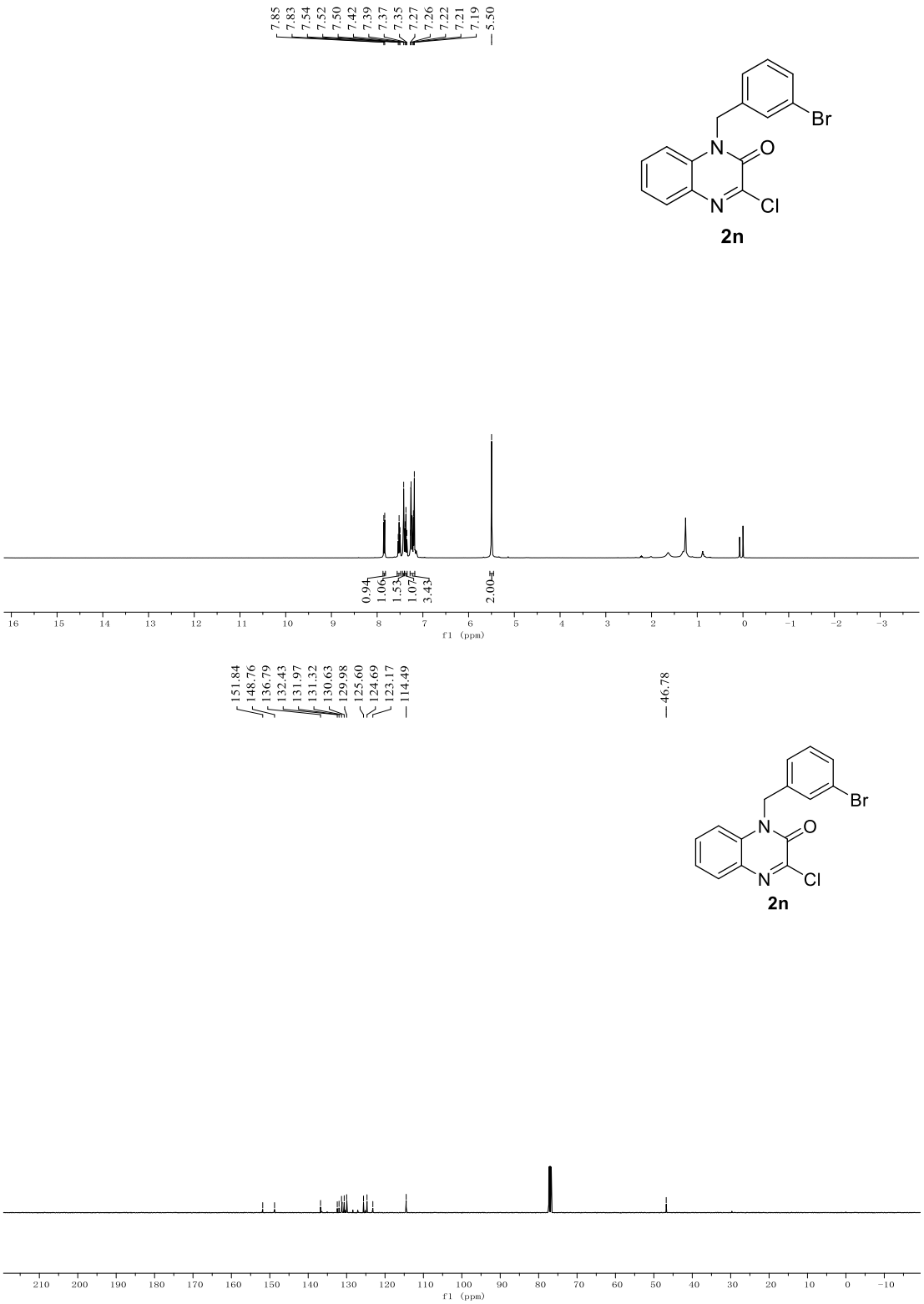




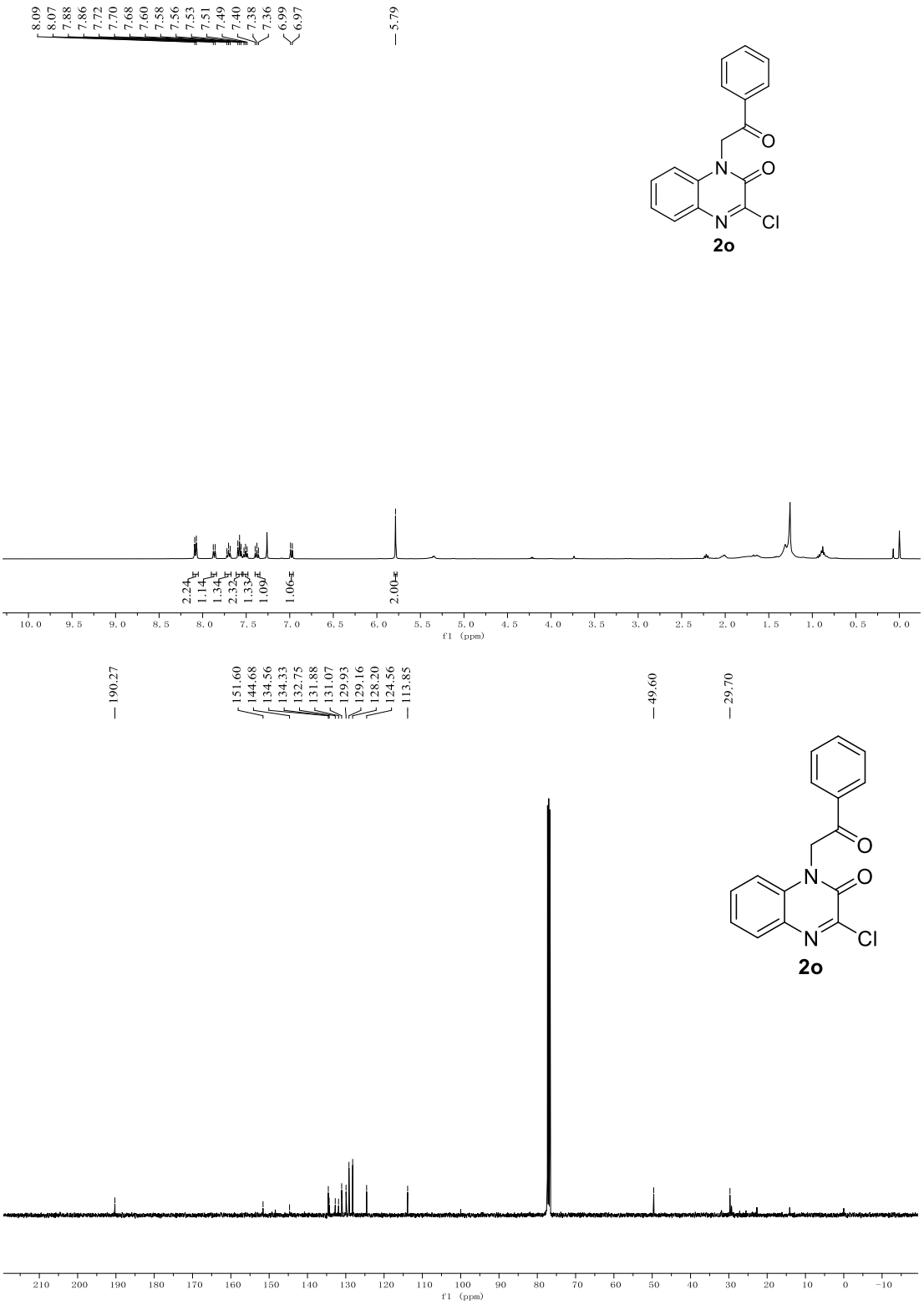
2m



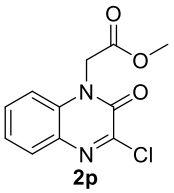
Compound **2n: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



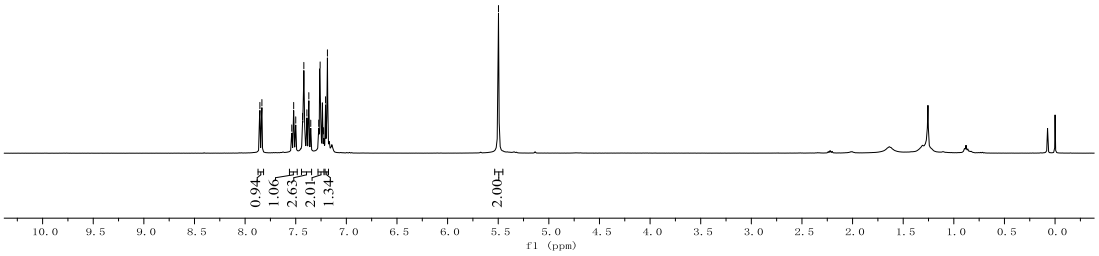
Compound **2o: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

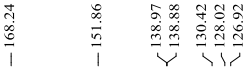


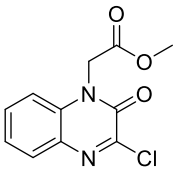
Compound **2p: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



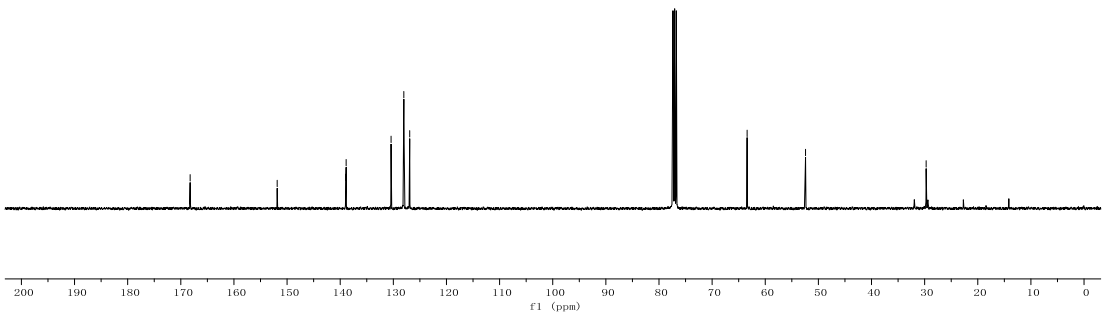
2p



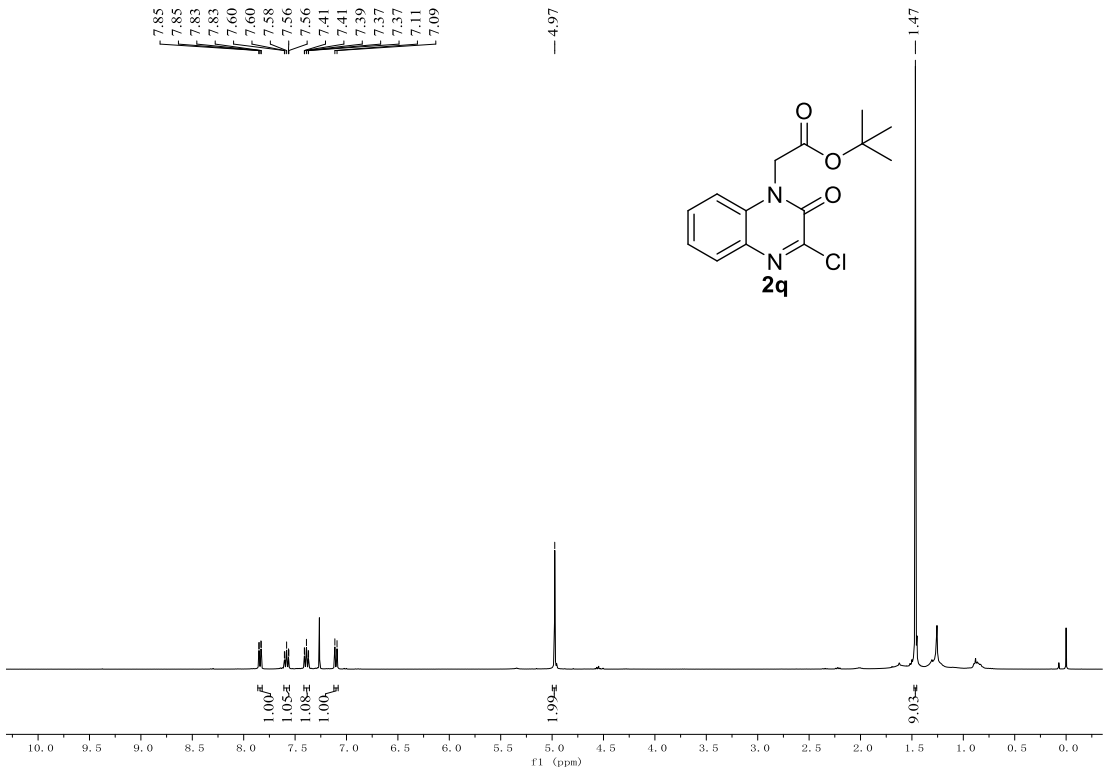


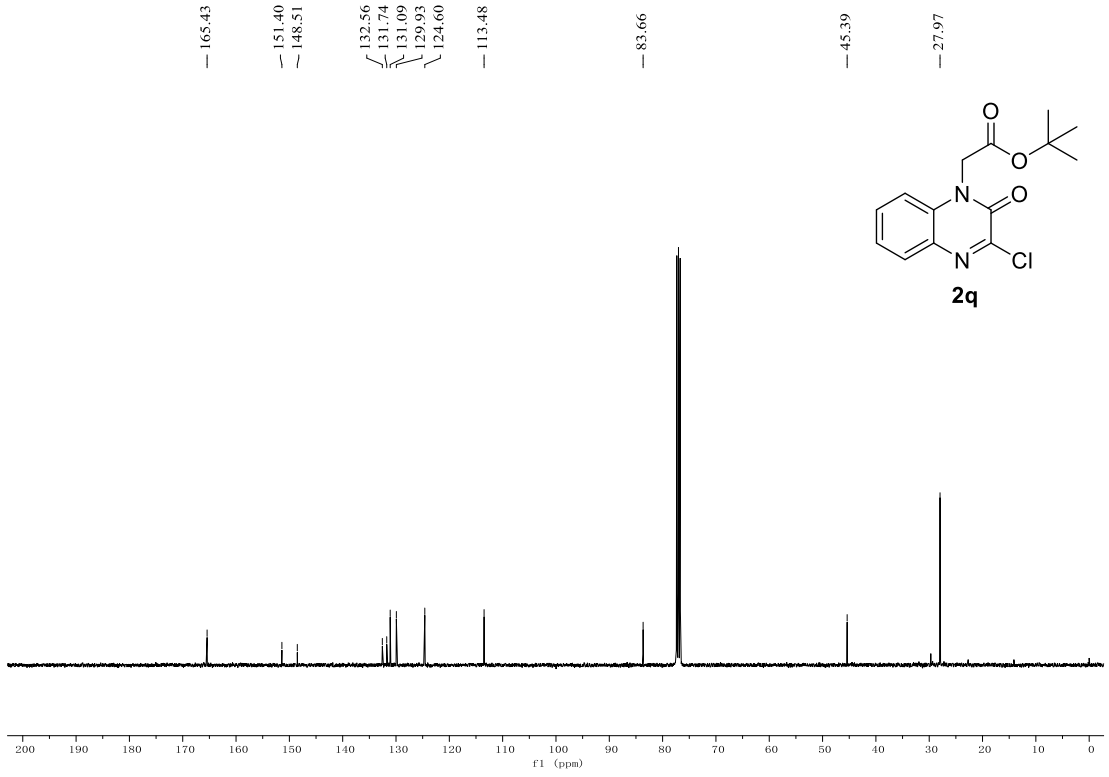


2p

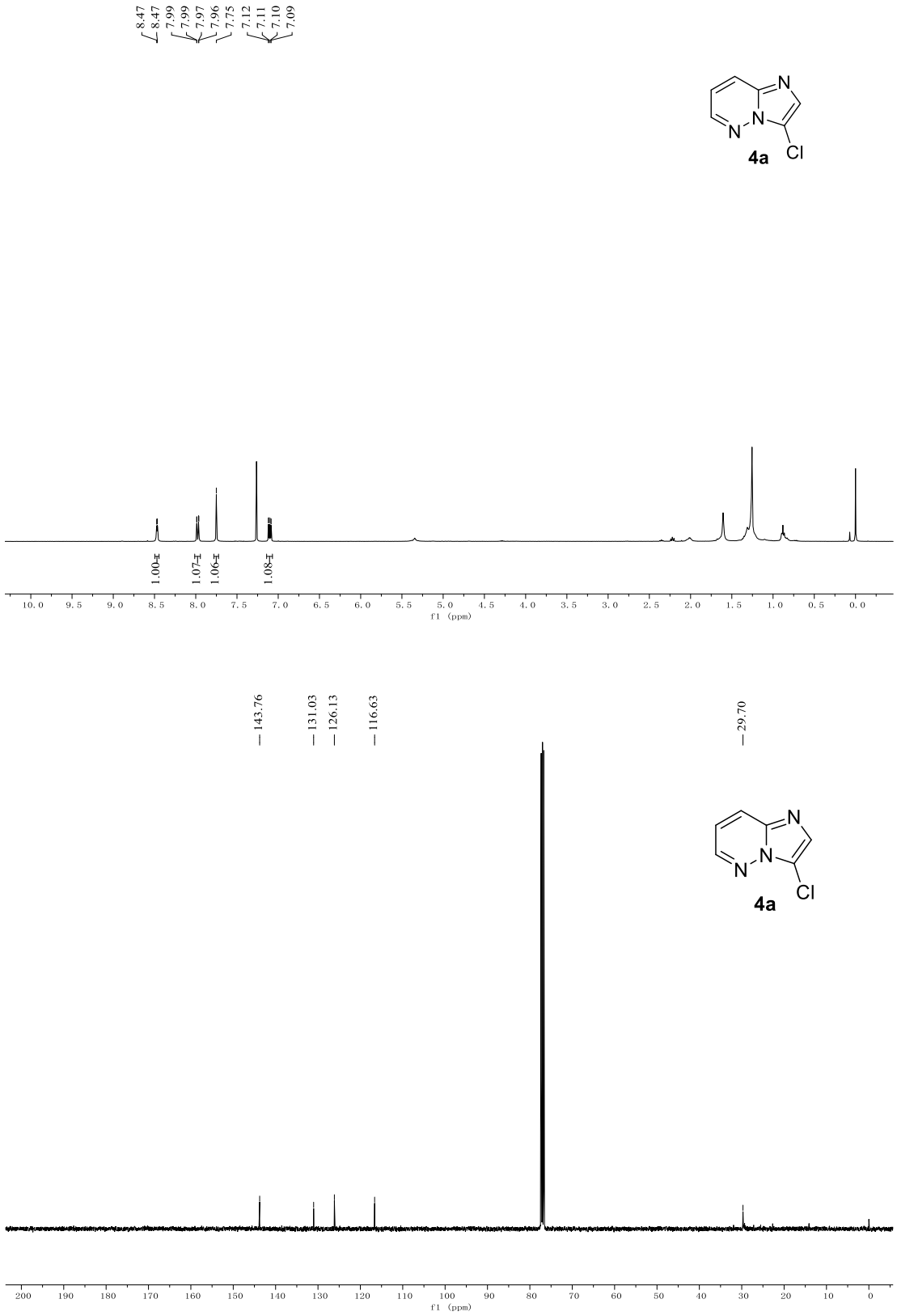


Compound **2q: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)

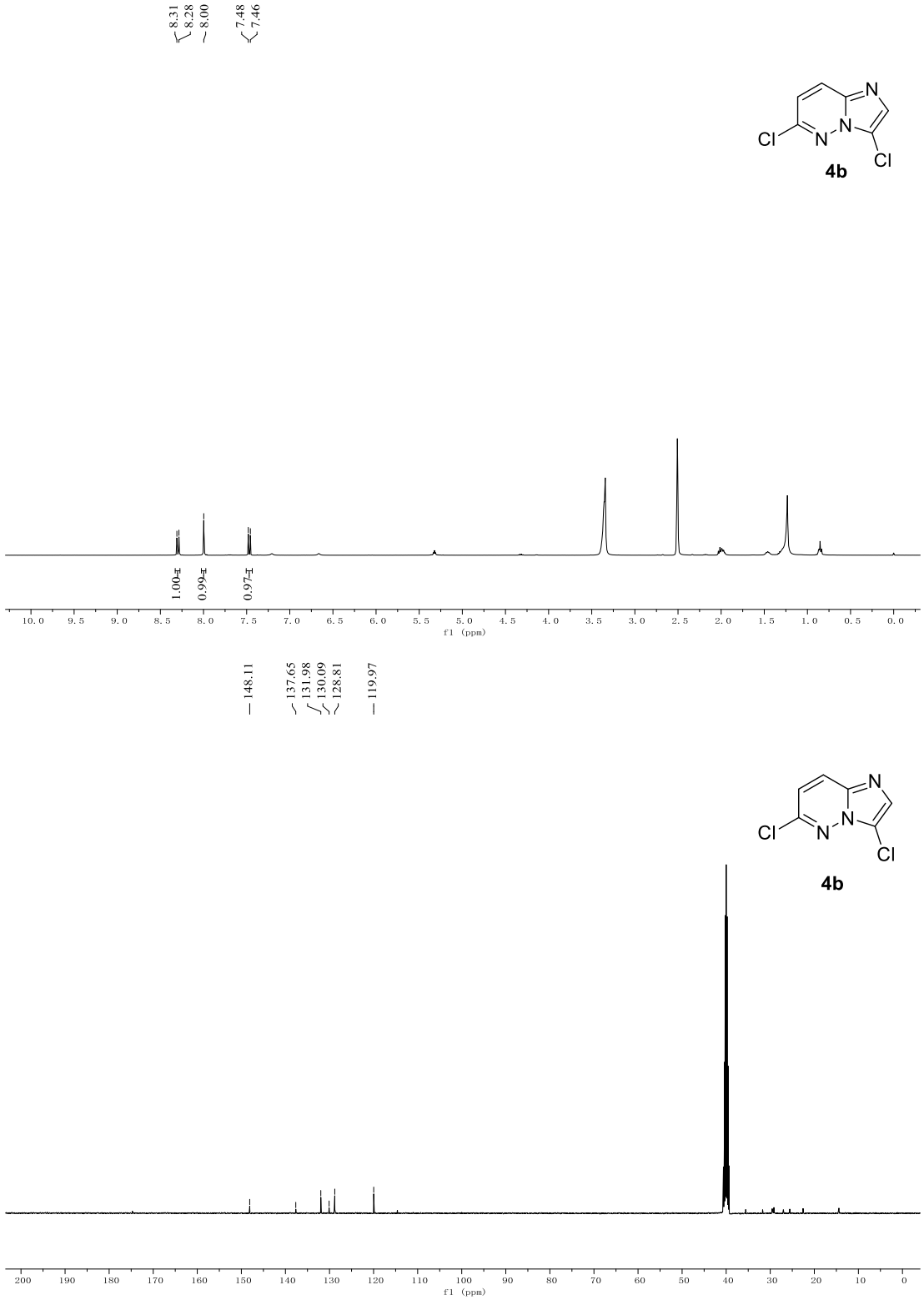




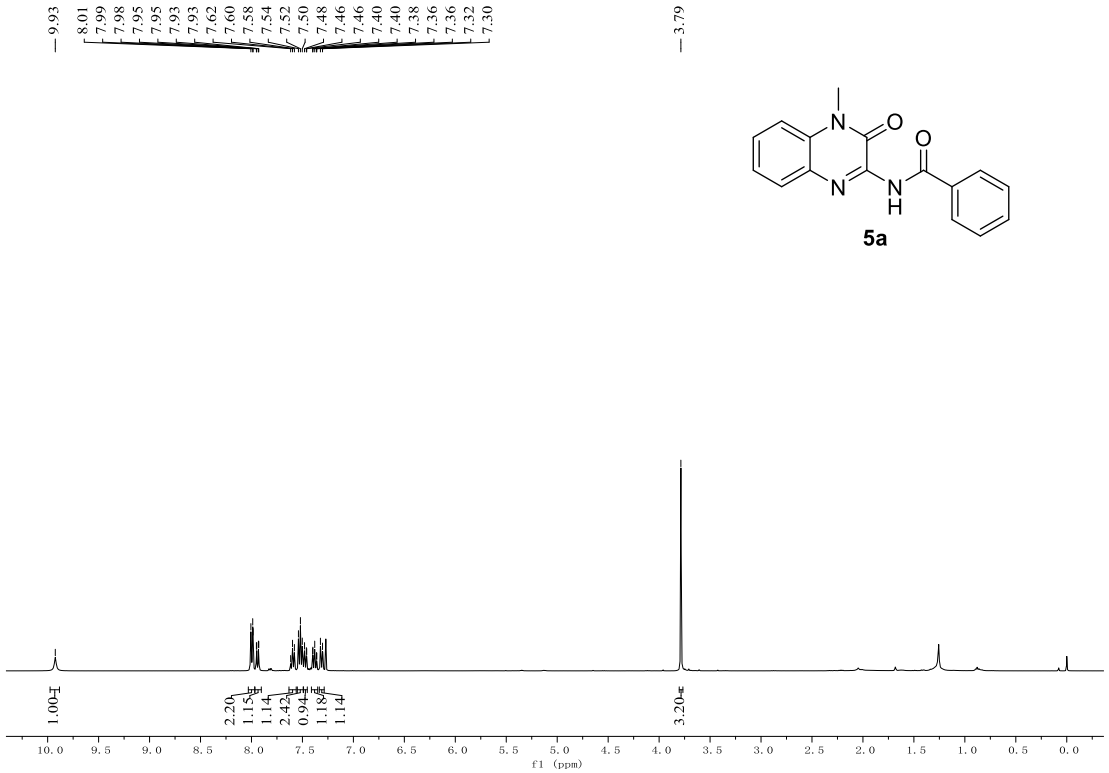
Compound **4a: ^{1}H NMR** ($CDCl_3$, 400 MHz), **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz)



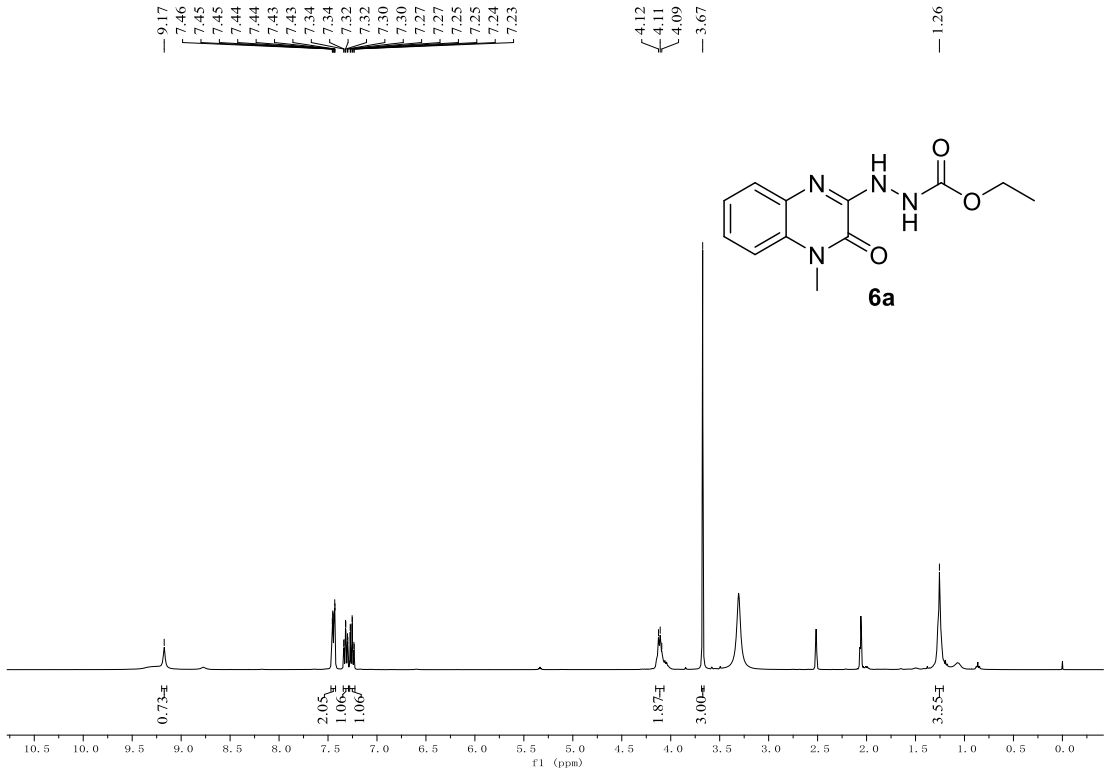
Compound **4b:** **^{1}H NMR** (DMSO-d_6, 400 MHz), **^{13}C{^{1}H} NMR** (DMSO-d_6, 100 MHz)

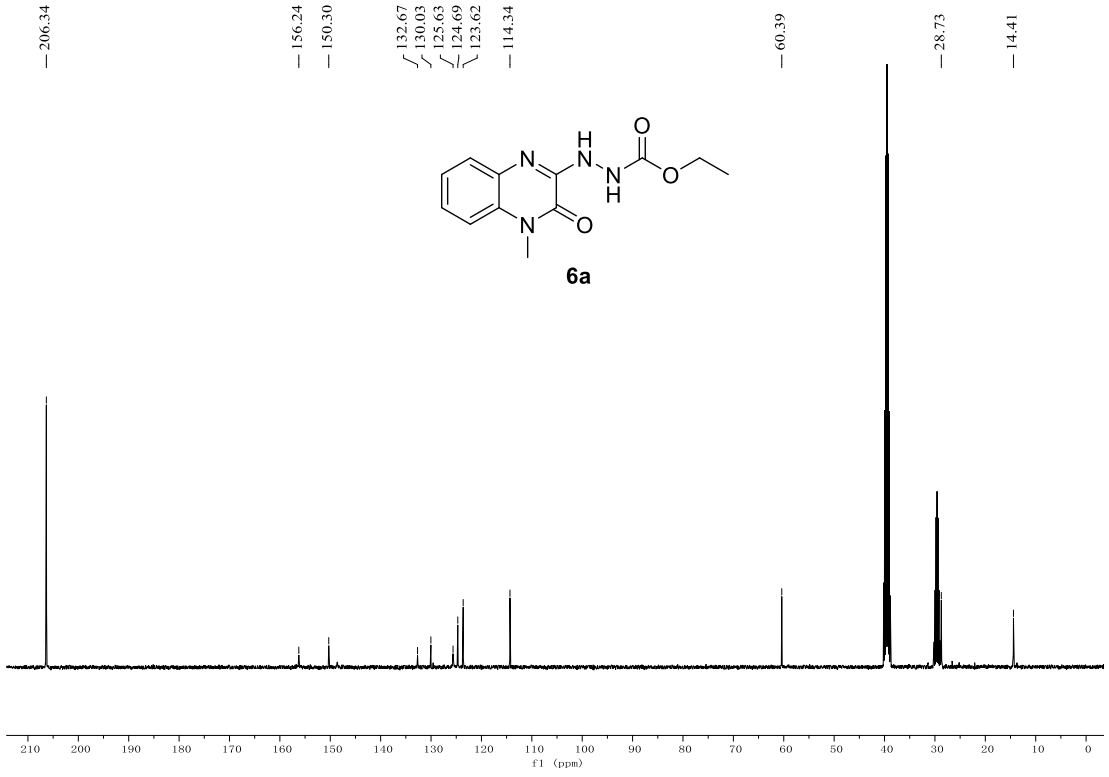


Compound **5a: ^{1}H NMR** ($CDCl_3$, 400 MHz)



Compound **6a:** **^{1}H NMR** (DMSO-d_6, 400 MHz), **^{13}C{^{1}H} NMR** (DMSO-d_6, 100 MHz)





10. X-ray Crystallographic Data of Compound 2h (CCDC: 2182535)

Crystal of compound **2h** was prepared in a solvent mixture of DCM and *n*-hexane (v/v = 1/1.5). First, **2h** (~50 mg) was dissolved in DCM (~1 mL) in a vial, then *n*-hexane (~1.5 mL) was added dropwise. The sample was stored in the screw cap vial and carefully setting in room temperature. To our delight, the crystal was obtained in about 48 h.

All the measurements were performed on a BRUKER Single Crystal X-Ray diffractometer, Germany (model of the instrument –AXS D8 Quest System).

Specification: D8 QUEST, Photon 100 CMOS Detector, Horizontal Goniometer, Fixed Chi stage, Goniometer headmanual, Ceramic Tube KFF Mo-2K-90c, two pinhole collimator (0.3/17 mrad, 0.6/17 mrad), Head turned by 90 ℃, APEX2 w.SHELXTL S/W, Video microscope SCD, Cryostream-700plus extended range low temperature.

X-Ray crystallographic analysis of 3-chloro-1-ethylquinoxalin-2(1*H*)-one **2h** (CCDC 2182535) showing the thermal ellipsoids at 50% probability level.

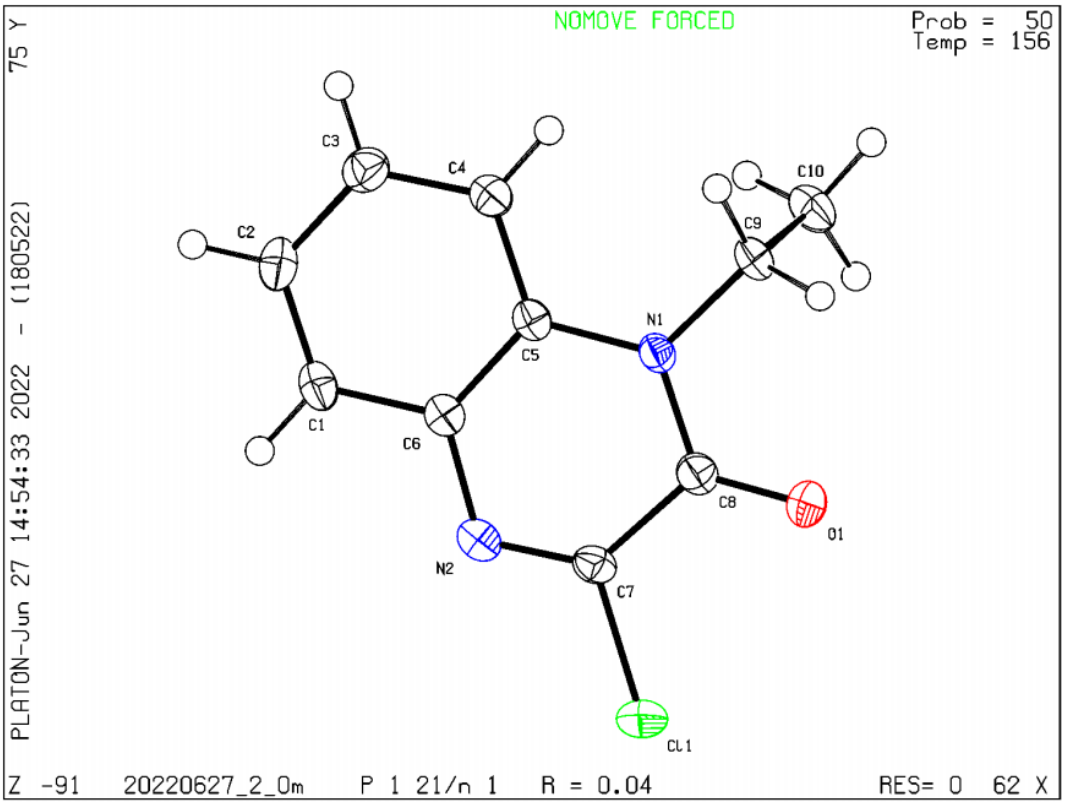


Figure S6. Single-crystal X-ray structure of 2h

Bond precision: C-C = 0.0020 A Wavelength=1.34138

Cell: a=7.3980(3) b=10.9637(4) c=11.9743(4)
alpha=90 beta=101.8516(14) gamma=90
Temperature: 156 K

	Calculated	Reported
Volume	950.53(6)	950.52(6)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C10 H9 Cl N2 O	4(C10 H9 Cl N2 O)
Sum formula	C10 H9 Cl N2 O	C40 H36 Cl4 N8 O4
Mr	208.64	834.57
Dx,g cm-3	1.458	1.458
Z	4	1
Mu (mm-1)	2.168	2.139
F000	432.0	432.0
F000'	434.14	
h,k,lmax	9,13,14	9,13,14
Nref	1941	1920
Tmin,Tmax	0.628,0.652	0.563,0.751
Tmin'	0.501	

Correction method= # Reported T Limits: Tmin=0.563 Tmax=0.751
AbsCorr = MULTI-SCAN

Data completeness= 0.989 Theta(max)= 56.990

R(reflections)= 0.0357(1788) wR2(reflections)= 0.1058(1920)

S = 1.075 Npar= 128

11. References

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