Photoelectrochemical upcycling of PVC plastic waste for the synthesis of chlorinated quinolinone derivatives

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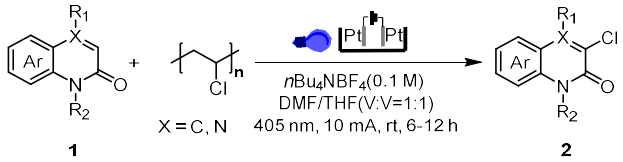
1. General Information

All the chemicals were purchased from Aladdin reagent and used without any prior purification. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90°C) and ethyl acetate unless otherwise noted. ^{1}H, and ^{13}C spectras were recorded on a Bruker Advance 500 and 400 spectrometer at ambient temperature with Chloroform-*d* or DMSO-d_6 solvent and tetramethylsilane (TMS) as the internal standard. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6530 QTOF mass spectrometer.

2. Experimental Section

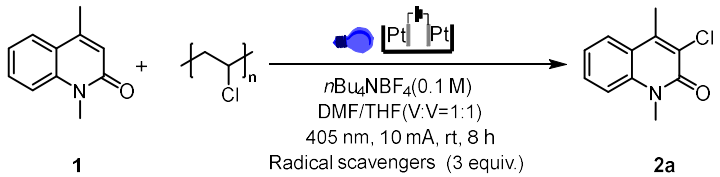
2.1 General procedures for photoelectricalchemical reaction properties



1 **2**

To a 25 mL tube was added quinolinone (**1**) (0.2 mmol), PVC (3.0 equiv. (repeat unit)), nBu$_4$NBF$_4$ (0.1 M), *N*, *N*-dimethylformamide/THF (6 mL) were added, respectively. Under blue (405 nm) LED irradiation, the reaction mixture was subjected to constant current electrolysis (platinum plate (1 cm × 1 cm) as anode and cathode). After the completion (as indicated by TLC), the water 30 mL was added. Then extracted with ethyl acetate and the collected organic layer was washed with brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure and further purified by flash chromatography (neutral alumina, petroleum ether/ethyl acetate = 5:1–3:1) to give the desired product.

2.2 Radical inhibition experiment

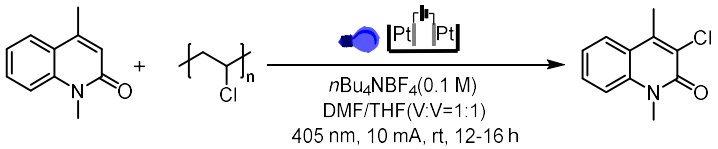


1 **2a**

To a 25 mL tube was added quinolin-2(1*H*)-one (**1**) (0.2 mmol), PVC (3.0 equiv. (repeat unit)), nBu$_4$NBF$_4$ (0.1 M), *N*,*N*-dimethylformamide/THF (6 mL) were added, respectively. Under blue (405 nm) LED irradiation, the reaction mixture was subjected to constant current electrolysis (platinum plate (1 cm × 1 cm) as anode and cathode). No target product **2a** was obtained in the presence of the radical scavengers TEMPO, DPE, or BHT, which showed that a radical pathway should be

involved.

2.3 Gram-scale experiment



1 **2a**

To a 250 mL tube was added quinolin-2(1*H*)-one (**1**) (8.0 mmol), PVC (3.0 equiv. (repeat unit)), *n*Bu_4NBF_4 (0.1 M), *N*, *N*-dimethylformamide/THF (30 mL) were added, respectively. Under blue (405 nm) LED irradiation, the reaction mixture was subjected to constant current electrolysis (platinum plate (8 cm × 6 cm) as anode and cathode). After the completion (as indicated by TLC), the water 150 mL was added. Then extracted with ethyl acetate and the collected organic layer was washed with brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure and further purified by flash chromatography (neutral alumina, petroleum ether/ethyl acetate = 5:1–3:1) to give the desired product.

2.4 Isolation of dechlorinated PVC (dPVC) under extended conditions

After electrolysis, dPVC was recovered using the following protocol. The reaction mixture was poured into 200 mL H_2O while stirring to precipitate the polymer. The polymer was collected by filtration and then redissolved in 5 mL THF. The solution was poured into 200 mL methanol while stirring to precipitate the polymer, again. The polymer was collected by filtration, and the dissolution and precipitation processes were repeated one more time. The polymer was collected by filtration and dried under vacuum overnight.

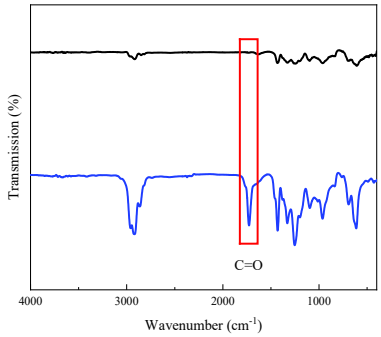


Figure S1 IR spectra of PVC (black), dPVC recovered from reactions (blue)

After the chlorination reaction, an amount of dechlorinated PVC (dPVC) remains in the reaction solution. The FTIR spectra of PVC and dPVC are shown in Figure S1. A new peak was observed at 1725 cm^{-1}, which was due to C=O stretching vibration. According to literature reports,[1] the carbonyl group was formed during the photodegradation of PVC under air atmosphere. Fourier transform infrared spectroscopy could prove this result.

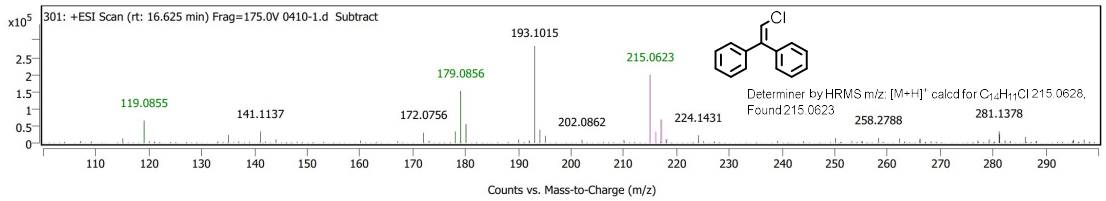
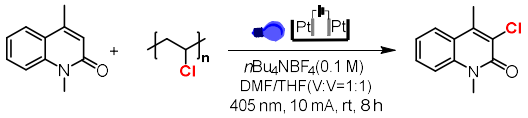


Figure S2 HRMS analysis of DPE adduct

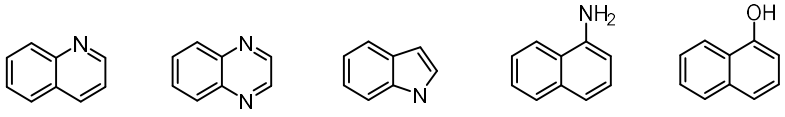
Table S1 Optimization of chlorine source.[a]



1a 2a

Entry	Chlorine source	Yield [%][b]
1	PVC	71
2[c]	NaCl	84
3[c]	NH_4Cl	81
4[c]	DCE	78
5[c]	DCM	69
6[d]	NCS	0

[a] Reaction conditions: **1a** (0.2 mmol), PVC (3.0 equiv.), nBu_4NBF_4 (0.1 M), DMF/THF (3 mL), rt, in air, undivided cell, Pt (+)/Pt (−), constant current = 10 mA, 405 nm LEDs, 8 h. [b] Isolated yields. [c] **1a** (0.2 mmol), chlorine source (3.0 equiv.), nBu_4NBF_4 (0.1 M), DMF (3 mL), rt, in air, undivided cell, Pt (+)/Pt (−), constant current = 10 mA. [d] **1a** (0.2 mmol), NCS (1.5 equiv.), DMF (3 mL), rt, in air.



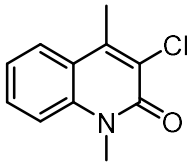
1ae **1af** **1ah** **1ai** **1aj**

Scheme S2 Ineffective arenes for the photoelectricalchemical reaction

To expand the substrate scope, we tested some other arenes, such as quinoline (**1ae**), quinoxaline (**1af**), indole (**1ah**), naphthyl amine (**1ai**), and naphthol (**1aj**).Unfortunately, the substrates above were not compatible with this method.

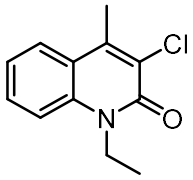
3. Characterization of Products

3-Chloro-1,4-dimethylquinolin-2(1*H*)-one (2a)



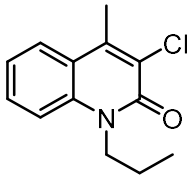
Obtained as a yellow solid in 71% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.58 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.31 – 7.28 (m, 1H), 3.77 (s, 3H), 2.63 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.05, 142.58, 137.97, 130.53, 126.34, 125.51, 122.69, 120.66, 114.59, 30.81, 16.53. **HRMS** (ESI+): Calculated for $C_{11}H_{11}ClNO$: $[M+H]^+$ 208.0529, Found 208.0523.

3-Chloro-1-ethyl-4-methylquinolin-2(1*H*)-one (2b)



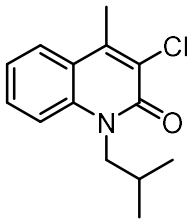
Obtained as a yellow solid in 70% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.56 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.29 – 7.25 (m, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.17, 143.09, 137.58, 131.07, 127.01, 126.37, 123.08, 121.63, 115.06, 39.32, 17.16, 13.35. **HRMS** (ESI+): Calculated for $C_{12}H_{13}ClNO$: $[M+H]^+$ 222.0686, Found 222.0681.

3-Chloro-4-methyl-1-propylquinolin-2(1*H*)-one (2c)



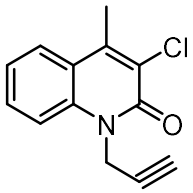
Obtained as a yellow solid in 69% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 4.30 – 4.23 (m, 2H), 2.59 (s, 3H), 1.74 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.22, 142.96, 137.65, 130.90, 126.79, 126.17, 122.95, 121.36, 115.10, 45.62, 21.34, 17.03, 11.88. **HRMS** (ESI+): Calculated for $C_{13}H_{15}ClNO$: $[M+H]^+$ 236.0842, Found 236.0836.

3-Chloro-1-isobutyl-4-methylquinolin-2(1*H*)-one (2d)



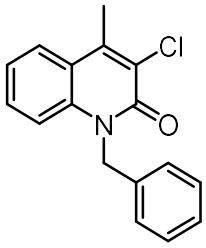
Obtained as a yellow solid in 71% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.39 – 7.35 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 4.25 (d, *J* = 7.0 Hz, 2H), 2.65 (s, 3H), 2.26 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.77, 143.00, 138.00, 130.76, 126.91, 126.19, 122.97, 121.39, 115.57, 50.62, 27.92, 20.75, 17.14. **HRMS** (ESI+): Calculated for $C_{14}H_{17}ClNNaO$: $[M+H]^+$ 250.0999, Found 250.0992.

3-Chloro-4-methyl-1-(prop-2-yn-1-yl) quinolin-2(1*H*)-one (2e)



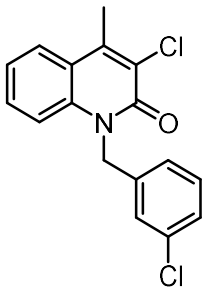
Obtained as a yellow solid in 60% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 1H), 7.69 – 7.62 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 5.20 (d, *J* = 2.3 Hz, 2H), 2.67 (s, 3H), 2.30 – 2.26 (t, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.24, 143.43, 136.56, 130.64, 125.98, 125.68, 123.10, 120.94, 115.07, 77.69, 72.90, 32.96, 16.62. **HRMS** (ESI+): Calculated for $C_{13}H_{11}ClNO$: $[M+H]^+$ 232.0529, Found 232.0522.

1-Benzyl-3-chloro-4-methylquinolin-2(1*H*)-one (2f)



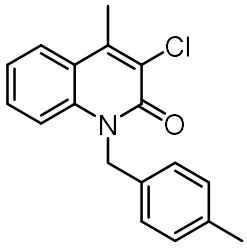
Obtained as a yellow solid in 57% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.34 – 7.25 (m, 7H), 5.64 (s, 2H), 2.71 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.94, 143.83, 138.04, 136.75, 131.11, 129.50, 128.08, 127.38, 126.91, 126.20, 123.37, 121.57, 116.09, 47.95, 17.30. **HRMS** (ESI+): Calculated for $C_{17}H_{15}ClNO$: $[M+H]^+$ 284.0842, Found 284.0837.

3-Chloro-1-(3-chlorobenzyl)-4-methylquinolin-2(1*H*)-one (2g)



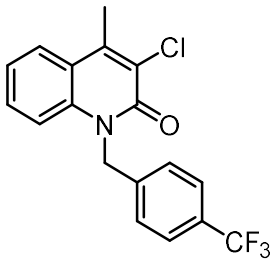
Obtained as a yellow solid in 60% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.11 (m, 5H), 7.09 (d, *J* = 5.5 Hz, 1H), 5.55 (s, 2H), 2.67 – 2.65 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.90, 142.50, 137.82, 135.73, 135.02, 130.61, 130.33, 128.70, 128.01, 127.50, 126.78, 125.23, 124.90, 122.16, 116.63, 47.01, 16.78. **HRMS** (ESI+): Calculated for $C_{17}H_{14}Cl_2NO$: $[M+H]^+$ 318.0452, Found 318.0446.

3-Chloro-4-methyl-1-(4-methylbenzyl) quinolin-2(1*H*)-one (2h)



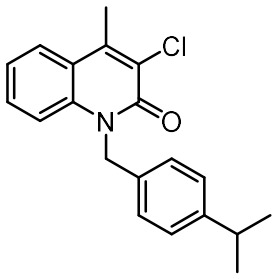
Obtained as a yellow solid in 58% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 2.2 Hz, 1H), 7.38 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.29 (d, *J* = 3.8 Hz, 1H), 7.12 (s, 5H), 5.55 (s, 2H), 2.65 (t, *J* = 2.0 Hz, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.77, 142.02, 137.23, 135.77, 132.60, 130.28, 129.52, 128.23, 127.40, 126.64, 124.82, 121.91, 116.84, 77.48, 76.84, 47.13, 21.03, 16.57. **HRMS** (ESI+): Calculated for $C_{18}H_{17}ClNO$: $[M+H]^+$ 298.0999, Found 298.0993.

3-Chloro-4-methyl-1-(4-(trifluoromethyl)benzyl)quinolin-2(1*H*)-one (2i)



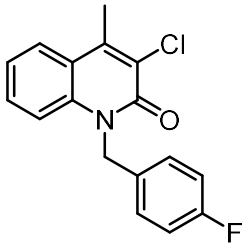
Obtained as a yellow solid in 56% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.73 (m, 1H), 7.55 (d, *J* = 6.0 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.28 (dd, *J* = 19.9, 5.1 Hz, 3H), 7.13 (dd, *J* = 8.9, 3.3 Hz, 1H), 5.62 (s, 2H), 2.67 – 2.65 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.52, 143.17, 140.36, 136.23, 131.24, 129.38, 128.07, 127.62, 126.81, 126.63, 126.60, 125.90, 122.76, 117.09, 47.70, 17.37. **HRMS** (ESI+): Calculated for $C_{18}H_{14}ClF_3NO$: $[M+H]^+$ 352.0716, Found 352.0711.

3-Chloro-1-(4-isopropylbenzyl)-4-methylquinolin-2(1*H*)-one (2j)



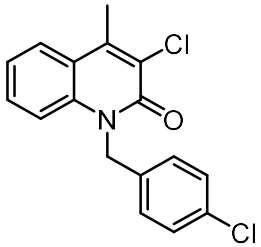
Obtained as a yellow solid in 55% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.3 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.26 (s, 5H), 5.89 (d, *J* = 185.8 Hz, 2H), 2.97 (p, *J* = 6.8 Hz, 1H), 2.75 (s, 3H), 1.32 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.94, 148.37, 142.10, 135.99, 133.01, 130.44, 128.38, 127.05, 126.86, 126.79, 124.97, 122.08, 116.99, 47.31, 33.82, 24.00, 16.72. **HRMS** (ESI+): Calculated for $C_{20}H_{21}ClNO$: $[M+H]^+$ 326.1312, Found 326.1307.

3-Chloro-1-(4-fluorobenzyl)-4-methylquinolin-2(1*H*)-one (2k)



Obtained as a yellow solid in 56% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.73 (m, 1H), 7.50 – 7.42 (m, 1H), 7.39 – 7.09 (m, 4H), 7.05 (t, *J* = 8.2 Hz, 2H), 5.60 (s, 2H), 2.71 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.47, 161.02, 157.93, 142.36, 135.77, 131.48, 130.52, 128.60, 128.52, 127.55, 125.17, 122.15, 116.69, 116.06, 115.84, 46.85, 16.74. **HRMS** (ESI+): Calculated for $C_{17}H_{14}ClFNO$: $[M+H]^+$ 302.0748, Found 302.0743.

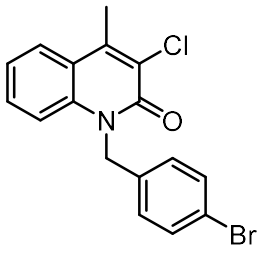
3-Chloro-1-(4-chlorobenzyl)-4-methylquinolin-2(1*H*)-one (2l)



Obtained as a yellow solid in 61% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.69 (m, 1H), 7.43 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.35 – 7.14 (m, 6H), 5.57 (s, 2H), 2.69 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.95, 142.44, 135.76, 134.28, 133.62, 130.58, 129.23,

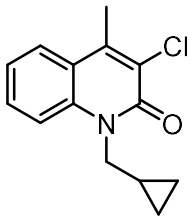
128.69, 128.22, 127.57, 125.24, 122.19, 116.67, 46.95, 16.79. **HRMS** (ESI+): Calculated for $C_{17}H_{14}Cl_2NO$: $[M+H]^+$ 318.0452, Found 318.0446.

1-(4-Bromobenzyl)-3-chloro-4-methylquinolin-2(1*H*)-one (2m)



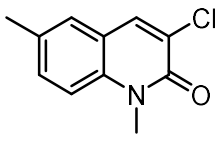
Obtained as a yellow solid in 62% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.56 – 7.26 (m, 4H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 5.56 (s, 2H), 2.69 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.92, 142.46, 135.67, 134.77, 132.13, 130.57, 128.66, 128.52, 127.48, 125.21, 122.13, 121.62, 116.65, 46.95, 16.78. **HRMS** (ESI+): Calculated for $C_{17}H_{14}BrClNO$: $[M+H]^+$ 361.9947, Found 361.9941.

3-Chloro-1-(cyclopropylmethyl)-4-methylquinolin-2(1*H*)-one (2n)



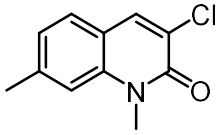
Obtained as a yellow solid in 45% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.19 (d, *J* = 6.9 Hz, 2H), 2.52 (s, 3H), 0.79 – 0.73 (m, 1H), 0.51 – 0.39 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.59, 143.07, 137.95, 130.90, 127.00, 126.18, 122.99, 121.38, 115.41, 78.02, 17.11, 10.39, 4.67. **HRMS** (ESI+): Calculated for $C_{14}H_{15}ClNO$: $[M+H]^+$ 248.0842, Found 248.0836.

3-Chloro-1,6-dimethylquinolin-2(1*H*)-one (2o)



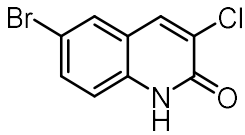
Obtained as a yellow solid in 58% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.17 (m, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 3.75 (d, *J* = 2.9 Hz, 3H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.56, 138.87, 133.63, 133.23, 132.41, 131.59, 128.68, 118.58, 113.31, 31.85, 20.68. **HRMS** (ESI+): Calculated for $C_{11}H_{11}ClNO$: $[M+H]^+$ 208.0529, Found 208.0523.

3-Chloro-1,7-dimethylquinolin-2(1*H*)-one (2p)



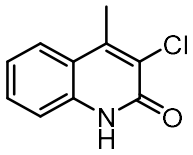
Obtained as a yellow solid in 56% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.43 – 7.22 (m, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 3.80 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 157.89, 138.20, 132.96, 132.55, 131.73, 130.92, 128.01, 117.91, 112.64, 31.18, 20.13. **HRMS** (ESI+): Calculated for $C_{11}H_{11}ClNO$: $[M+H]^+$ 208.0529, Found 208.0521.

6-Bromo-3-chloro-1-methylquinolin-2(1*H*)-one (2q)



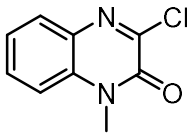
Obtained as a yellow solid in 43% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.40 (s, 1H), 8.23 (s, 1H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.64 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 157.28, 136.66, 136.51, 132.99, 129.25, 127.01, 120.38, 117.29, 113.92. **HRMS** (ESI+): Calculated for $C_9H_6BrClNO$: $[M+H]^+$ 257.9321, Found 257.9315.

3-Chloro-4-methylquinolin-2(1*H*)-one (2r)



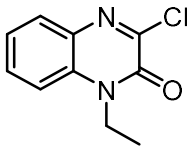
Obtained as a yellow solid in 41% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.18 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 2.59 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.95, 143.98, 136.62, 130.42, 125.17, 125.05, 122.30, 119.04, 115.51, 16.09. **HRMS** (ESI+): Calculated for $C_{10}H_9ClNO$: $[M+H]^+$ 194.0373, Found 194.0365.

3-Chloro-1-methylquinoxalin-2(1*H*)-one (2s)[2]



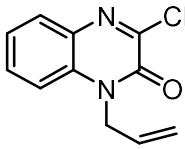
Obtained as a white solid in 51% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.62 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.40 (td, *J* = 8.0, 7.5, 1.2 Hz, 1H), 7.35 (dd, *J* =8.4 Hz, 0.8Hz, 1H), 3.78 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.72, 148.79, 133.26, 131.68, 131.07, 129.66, 124.45, 113.99, 30.57. **HRMS** (ESI+): Calculated for $C_9H_8ClN_2O$: $[M+H]^+$ 195.0320, Found 195.0322.

3-Chloro-1-ethyquinoxalin-2(1*H*)-one (2t)[2]



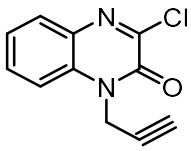
Obtained as a white solid in 47% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.62 (td, *J* = 7.8, 1.4 Hz, 1H), 7.42 – 7.34 (m, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.19, 148.83, 132.22, 132.01, 131.05, 129.93, 124.26, 113.83, 38.92, 12.34. **HRMS** (ESI+): Calculated for $C_{10}H_{10}ClN_2O$: $[M+H]^+$ 209.0476, Found 209.0471.

3-Chloro-1-vinylquinoxalin-2(1*H*)-one (2u)[3]



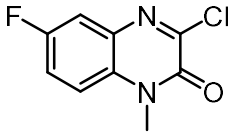
Obtained as a brown solid in 41% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.40 – 7.34 (m, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 5.92 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 5.2 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 151.29, 148.76, 132.51, 131.84, 130.97, 129.93, 129.73, 124.41, 118.82, 114.54, 45.93. **HRMS** (ESI+): Calculated for $C_{11}H_9ClN_2O$: $[M+H]^+$ 221.0476, Found 221.0472.

3-Chloro-1-ethynylquinoxalin-2(1*H*)-one (2v)[3]



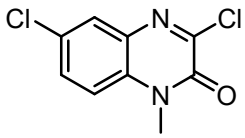
Obtained as a white solid in 49% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.50 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.44 – 7.39 (m, 1H), 5.09 (d, *J* = 2.5 Hz, 2H), 2.33 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.81, 148.44, 131.81, 131.16, 129.78, 124.80, 114.53, 76.02, 73.99, 32.97. **HRMS** (ESI+): Calculated for $C_{11}H_7ClN_2O$: $[M+H]^+$ 219.0320, Found 219.0315.

3-Chloro-6-fluoro-1-methylquinoxalin-2(1*H*)-one (2w)[2]



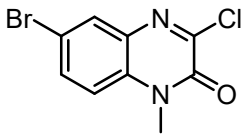
Obtained as a white solid in 46% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.33 – 7.29 (m, 1H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 158.98, 151.32, 150.51, 132.16, 129.99, 118.90, 115.31, 115.17, 30.85. **HRMS** (ESI+): Calculated for $C_9H_7ClFN_2O$: $[M+H]^+$ 213.0225, Found 213.21.

3,6-Dichloro-1-methylquinoxalin-2(1*H*)-one (2x)[2]



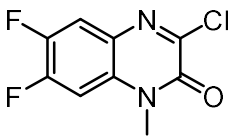
Obtained as a white solid in 45% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.3 Hz 1H), 7.58 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.36, 150.28, 150.51, 132.09, 131.95, 131.07, 129.87, 128.94, 115.10, 30.75. **HRMS** (ESI+): Calculated for $C_9H_6Cl_2N_2NaO$: $[M+Na]^+$ 250.9749, Found 250.9762.

6-Bromo-3-chloro-1-methylquinoxalin-2(1*H*)-one (2y)[2]



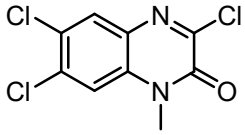
Obtained as a white solid in 43% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 2.2 Hz, 1H), 7.54 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.36, 150.29, 132.09, 131.95, 131.07, 129.87, 128.95, 115.09, 30.75. **HRMS** (ESI+): Calculated for $C_9H_6BrClN_2NaO$: $[M+Na]^+$ 294.9244, Found 294.9237.

3-Chloro-6,7-difluoro-1-methylquinoxalin-2(1*H*)-one (2z)[2]



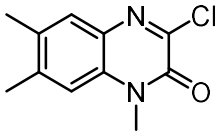
Obtained as a white solid in 42% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 1H), 7.18 - 7.13 (m, 1H), 3.74 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.92, 151.29, 149.41, 147.11, 130.61, 127.77, 117.37, 102.80, 31.11. **HRMS** (ESI+): Calculated for $C_9H_5ClF_2N_2NaO$: $[M+Na]^+$ 252.9951, Found 252.9976.

3,6,7-Trichloro-1-methylquinoxalin-2(1*H*)-one (2aa)[2]



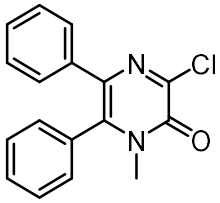
Obtained as a white solid in 41% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.44 (s, 1H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 151.12, 150.30, 135.39, 132.57, 130.56, 130.36, 128.47, 115.50, 30.83. **HRMS** (ESI+): Calculated for $C_9H_5Cl_3N_2NaO$: $[M+Na]^+$ 284.9360, Found 284.9399.

3-Chloro-1,6,7-trimethylquinoxalin-2(1*H*)-one (2ab)



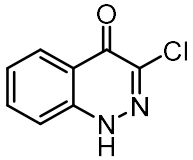
Obtained as a yellow solid in 47% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (s, 1H), 7.09 (s, 1H), 3.74 (d, *J* = 2.42 Hz, 3H), 2.44 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 151.77, 147.41, 141.25, 133.62, 131.27, 130.04, 129.52, 114.48, 30.48, 20.75, 19.27. **HRMS** (ESI+): Calculated for $C_{11}H_{11}ClN_2O$: $[M+Na]^+$ 223.0633, Found 223.0637.

3-Chloro-1-methyl-5,6-diphenylpyrazin-2(1*H*)-one (2ac)



Obtained as a yellow solid in 56% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 3H), 7.24 – 7.18 (m, 2H), 7.15 – 7.07 (m, 5H), 3.37 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.88, 145.84, 138.53, 136.37, 132.14, 131.77, 130.02, 129.98, 129.37, 129.27, 127.98, 127.53, 35.54. **HRMS** (ESI+): Calculated for $C_{17}H_{14}ClN_2O$: $[M+H]^+$ 297.0795, Found 297.0791.

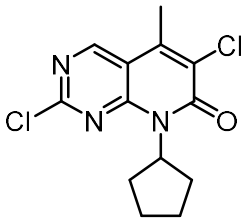
3-Chlorocinnolin-4(1*H*)-one (2ad)



Obtained as a white solid in 40% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.05 (q, J = 8.95 Hz), 7.92 – 7.75 (m), 7.60 (q, *J* = 9.42 Hz), 7.46 (t, *J* = 9.51 Hz). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.86, 141.68, 141.21, 134.83, 126.12, 124.97, 117.24. **HRMS** (ESI+): Calculated for $C_8H_6ClN_2O$:

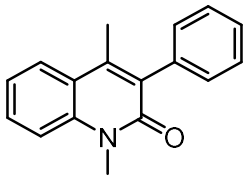
$[M+H]^+$ 181.0169, Found 181.0167.

2,6-Dichloro-8-cyclopentyl-5-methylpyrido[2,3-d]pyrimidin-7(8*H*)-one (2ag)



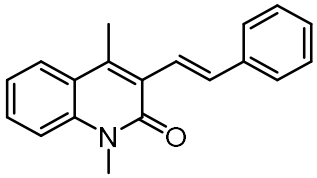
Obtained as a white solid in 51% yield.**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 6.23 – 5.69 (m, 1H), 2.65 (s, 3H), 2.33 – 2.12 (m, 4H), 1.97 (m, *J* = 10.68, 6.68 Hz, 2H), 1.82 – 1.60 (m, 2H). **HRMS** (ESI+): Calculated for $C_{13}H_{14}Cl_2N_3O$: $[M+H]^+$ 299.1750, Found 299.1746.

1,4-Dimethyl-3-phenylquinolin-2(1*H*)-one (3a)



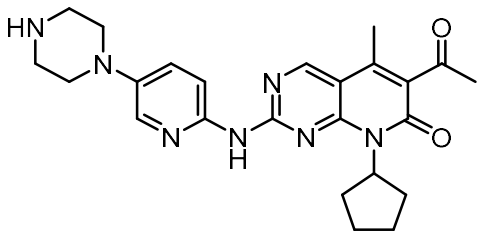
Obtained as a yellow solid in 91% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 2.0 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.47 – 7.37 (m, 3H), 7.34 – 7.25 (m, 3H), 3.76 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.67, 140.94, 138.29, 138.05, 137.28, 133.10, 129.30, 129.12, 128.77, 128.70, 127.46, 124.11, 123.51, 116.51, 115.80, 30.54, 16.82. **HRMS** (ESI+): Calculated for $C_{17}H_{16}NO$: $[M+H]^+$ 250.1232, Found 250.1238.

(E)-1,4-Dimethyl-3-styrylquinolin-2(1*H*)-one (4a)



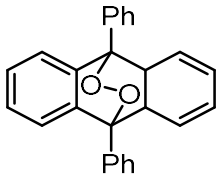
Obtained as a yellow solid in 85% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 – 7.98 (m, 1H), 7.82 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.48 (dt, *J* = 10.4, 7.2 Hz, 5H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.32 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.20, 142.98, 140.90, 139.07, 137.39, 135.65, 133.46, 130.66, 129.68, 129.58, 128.82, 128.10, 127.99, 127.64, 124.57, 122.45, 115.34, 30.52, 17.56. **HRMS** (ESI+): Calculated for $C_{19}H_{18}NO$: $[M+H]^+$ 276.1388, Found 276.1384.

Palbociclib



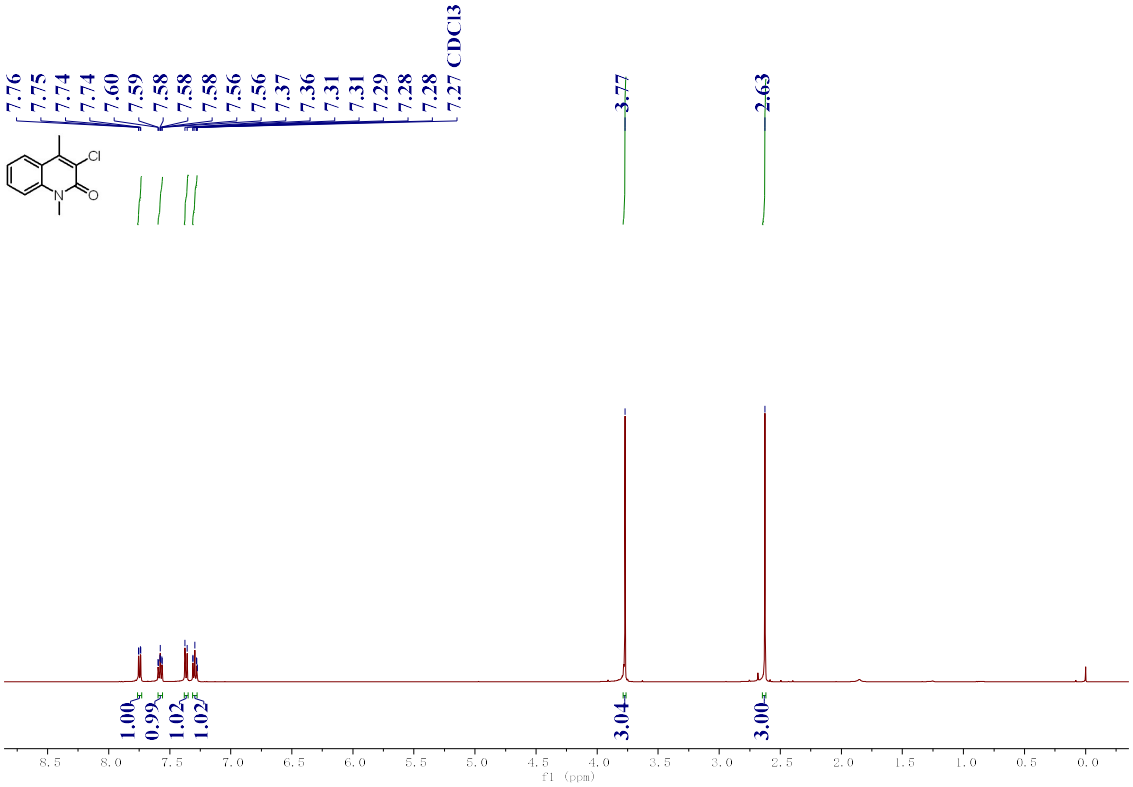
Obtained as a white solid in 75% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.14 (s, 1H), 8.91 (s, 1H), 8.17 (d, *J* = 9.1 Hz, 1H), 8.11 (d, *J* = 2.8 Hz, 1H), 7.33 (dd, *J* = 9.1, 3.0 Hz, 1H), 5.93 – 5.86 (m, 1H), 3.16 (dd, J = 6.2, 3.6 Hz, 4H), 3.08 (dd, *J* = 6.2, 3.7 Hz, 4H), 2.55 (s, 3H), 2.39 (s, 3H), 2.36 (dd, *J* = 14.0, 6.0 Hz, 2H), 2.07 (dq, *J* = 13.2, 7.4 Hz, 2H), 1.92 – 1.86 (m, 2H), 1.79 (s, 1H), 1.70 (dt, *J* = 10.3, 4.7 Hz, 2H). **HRMS** (ESI+): Calculated for $C_{24}H_{30}N_7O_2$: $[M+H]^+$ 448.2461, Found 448.2453.

9,10-Diphenyl-9,10-dihydro-9,10-epidioxyanthracene (5a)[4]

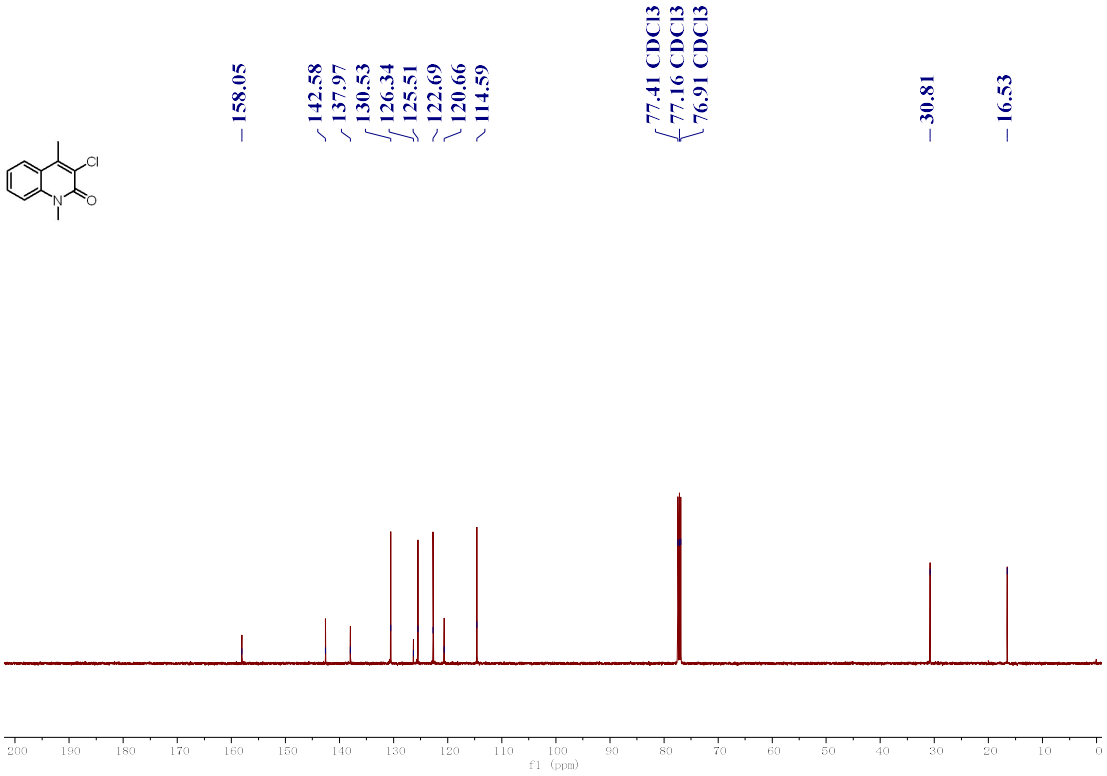


Obtained as a white solid in 18% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.3 Hz, 4H), 7.63 (t, *J* = 7.6 Hz, 4H), 7.19 (ddt, *J* = 9.1, 6.2, 3.2 Hz, 8H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.27, 133.03, 128.38, 128.30, 127.68, 127.56, 123.54, 84.12.

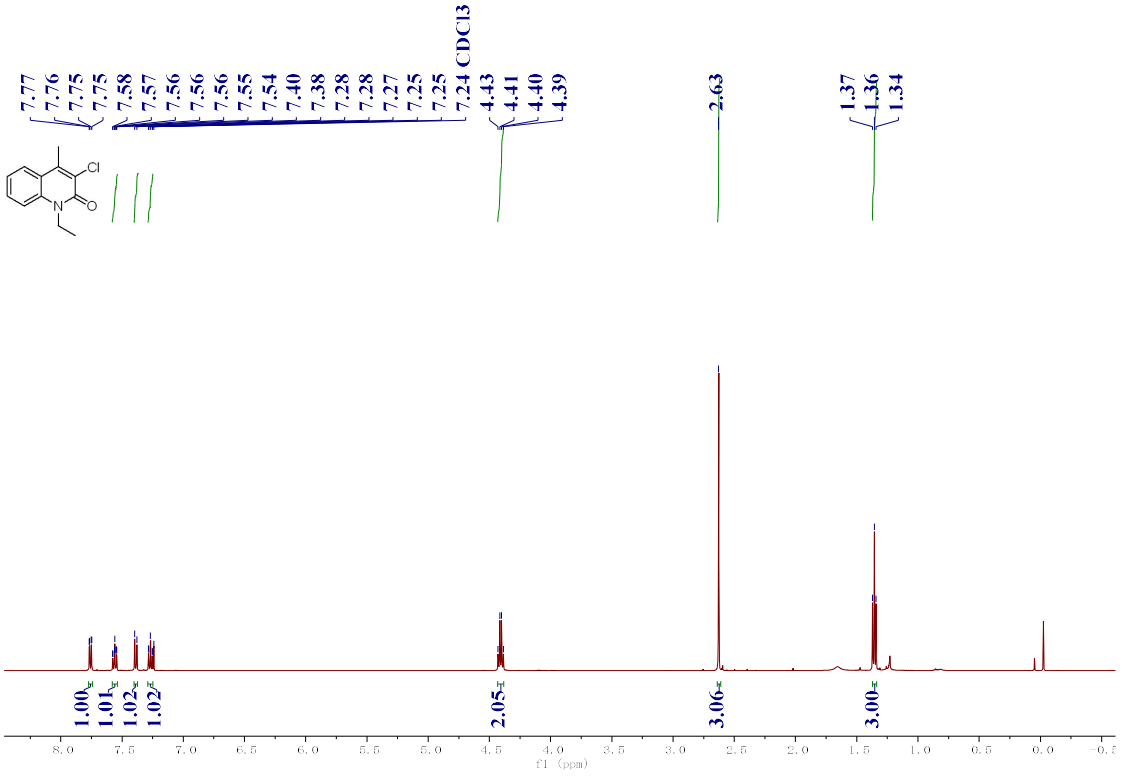
4. ^{1}H and ^{13}C NMR Spectra of These Compounds



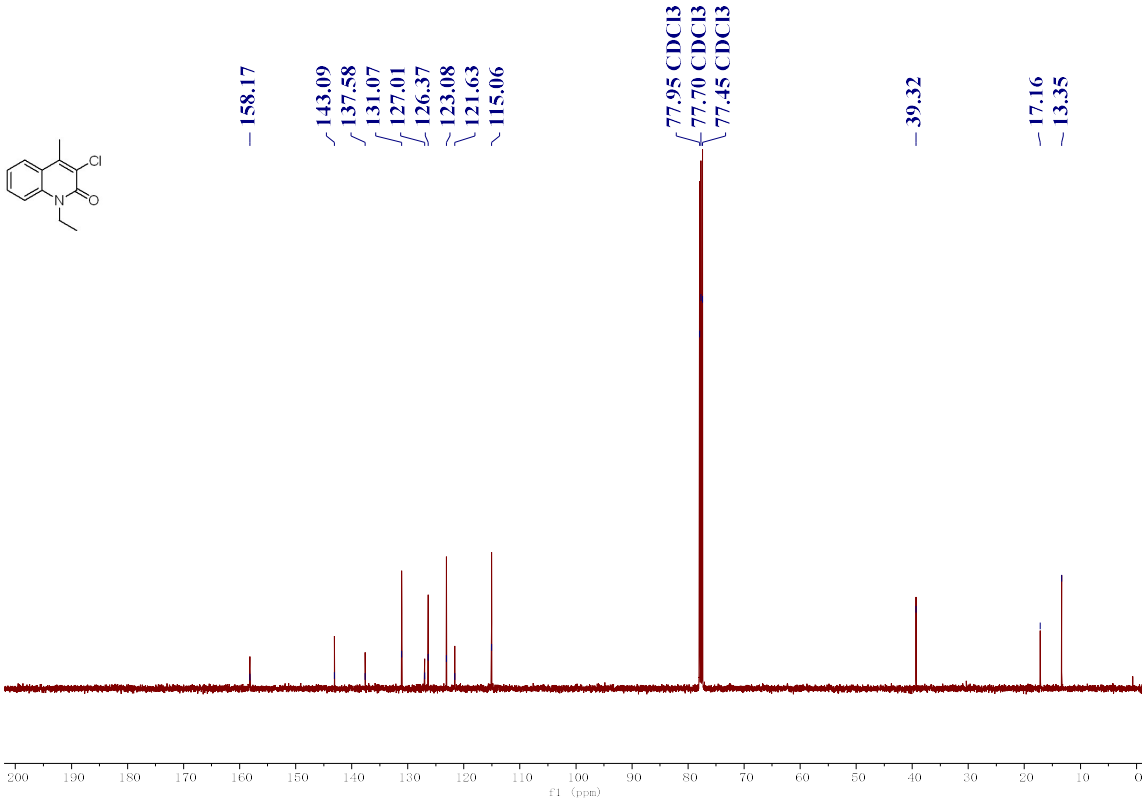
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **2a**



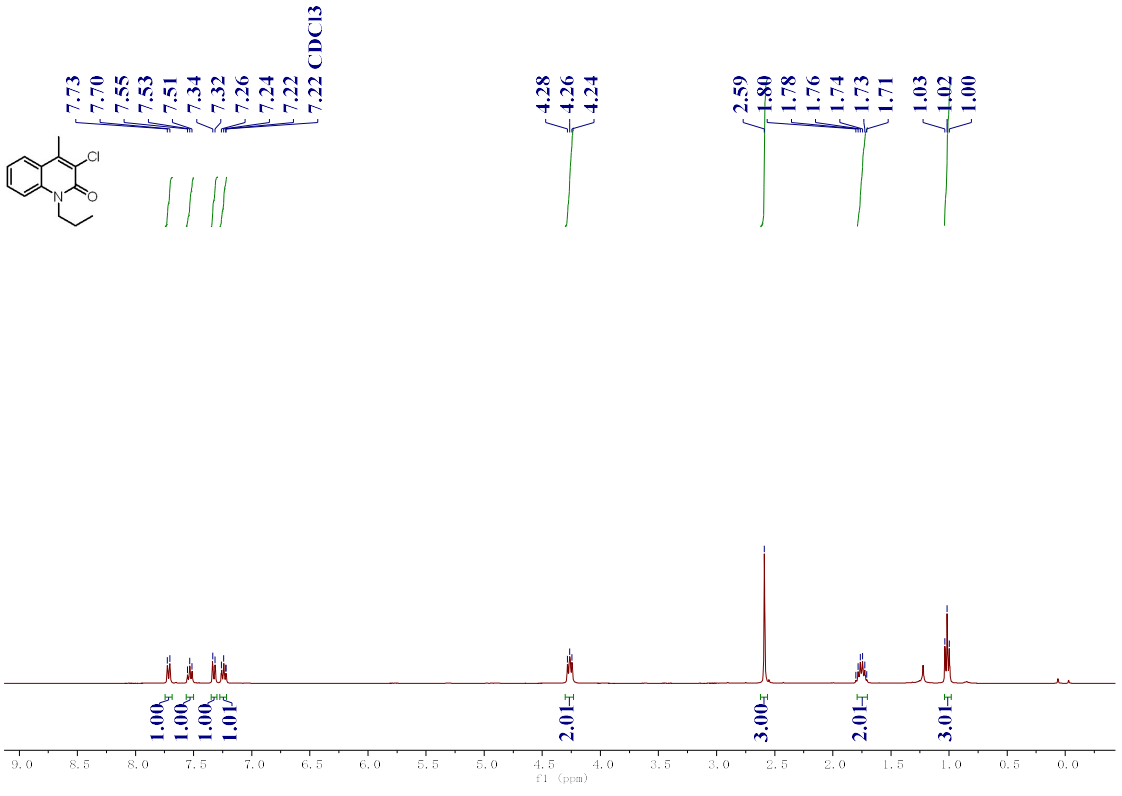
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **2a**



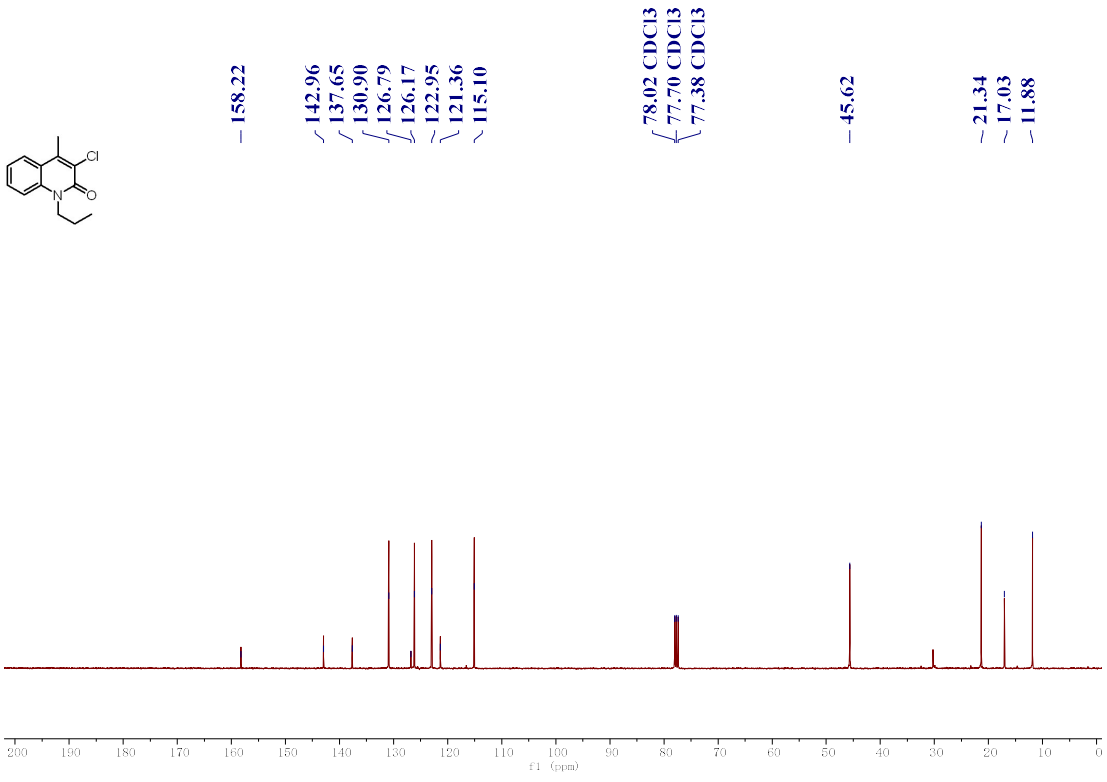
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **2b**



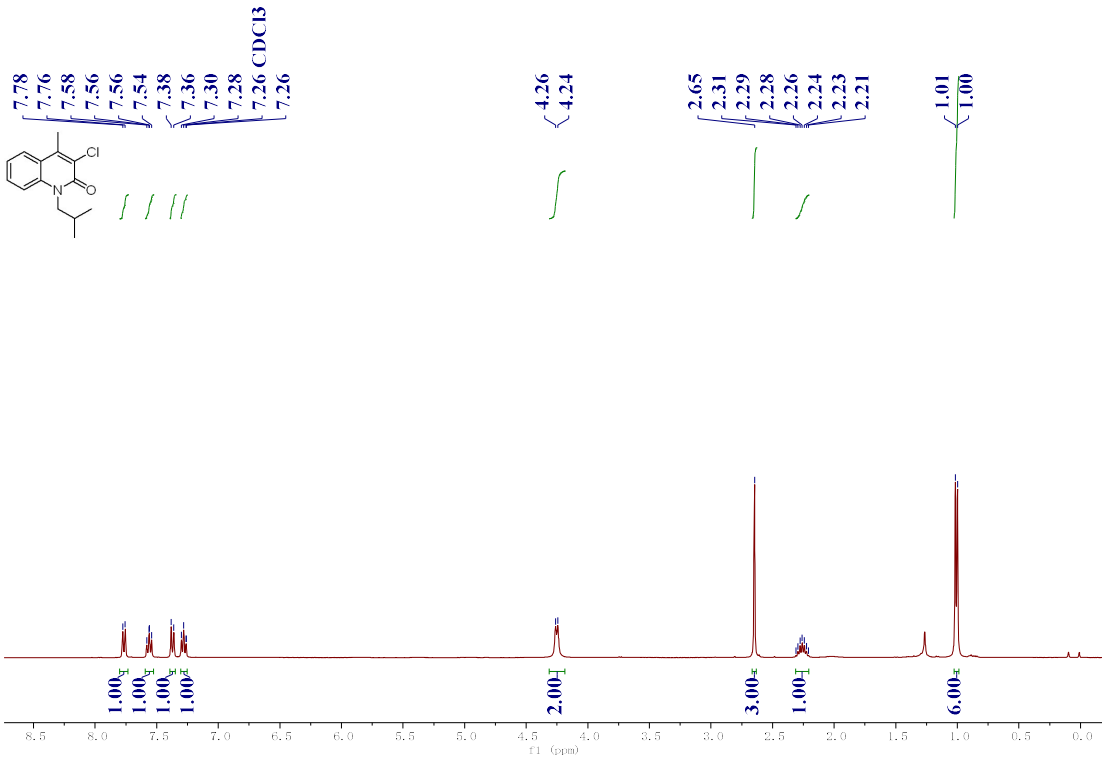
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **2b**



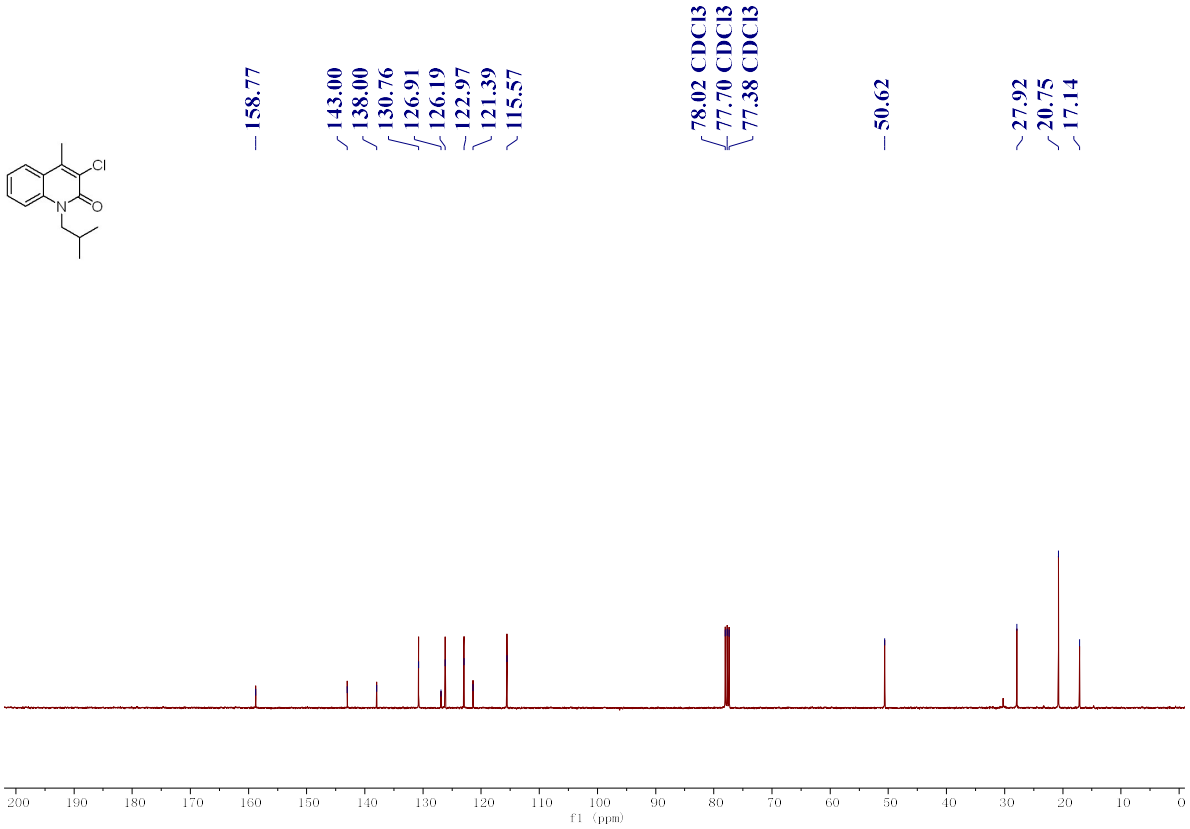
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2c**



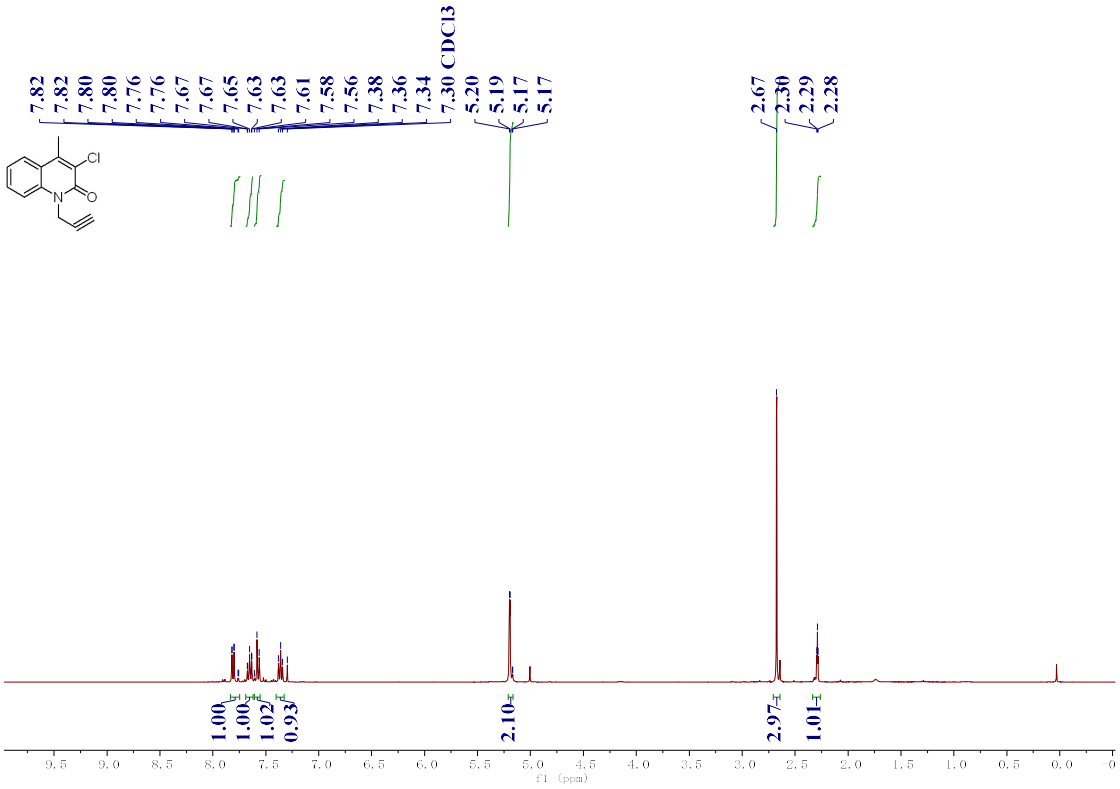
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2c**



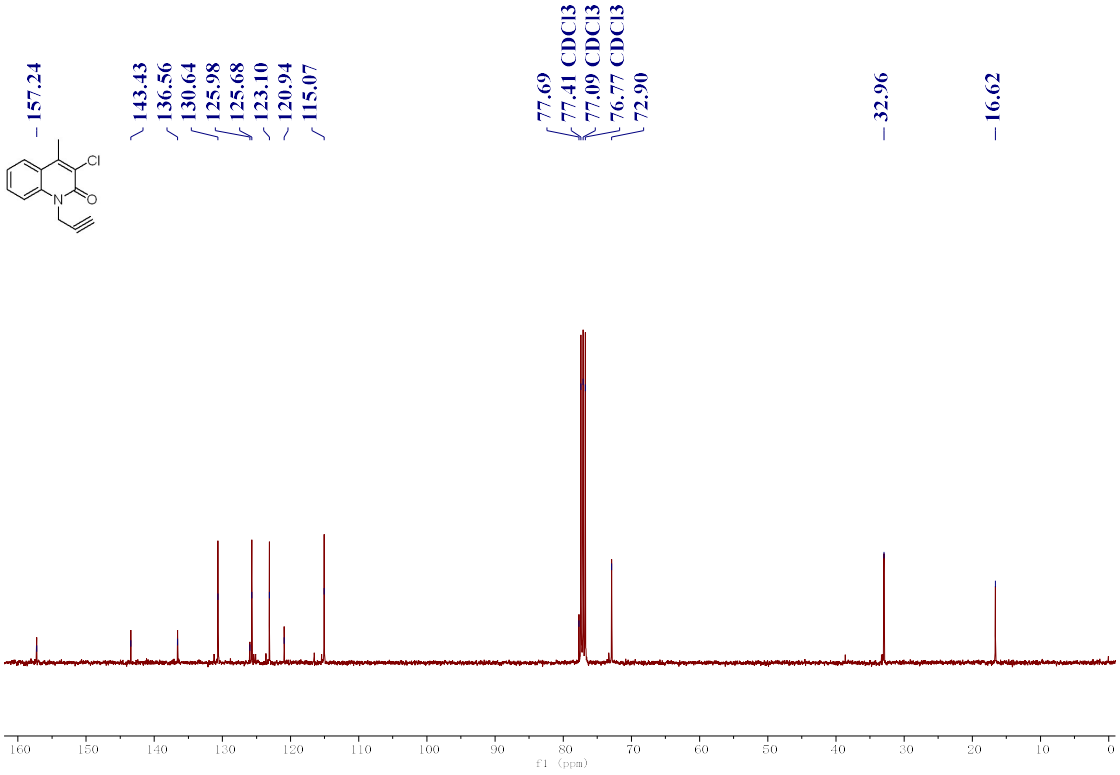
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2d**



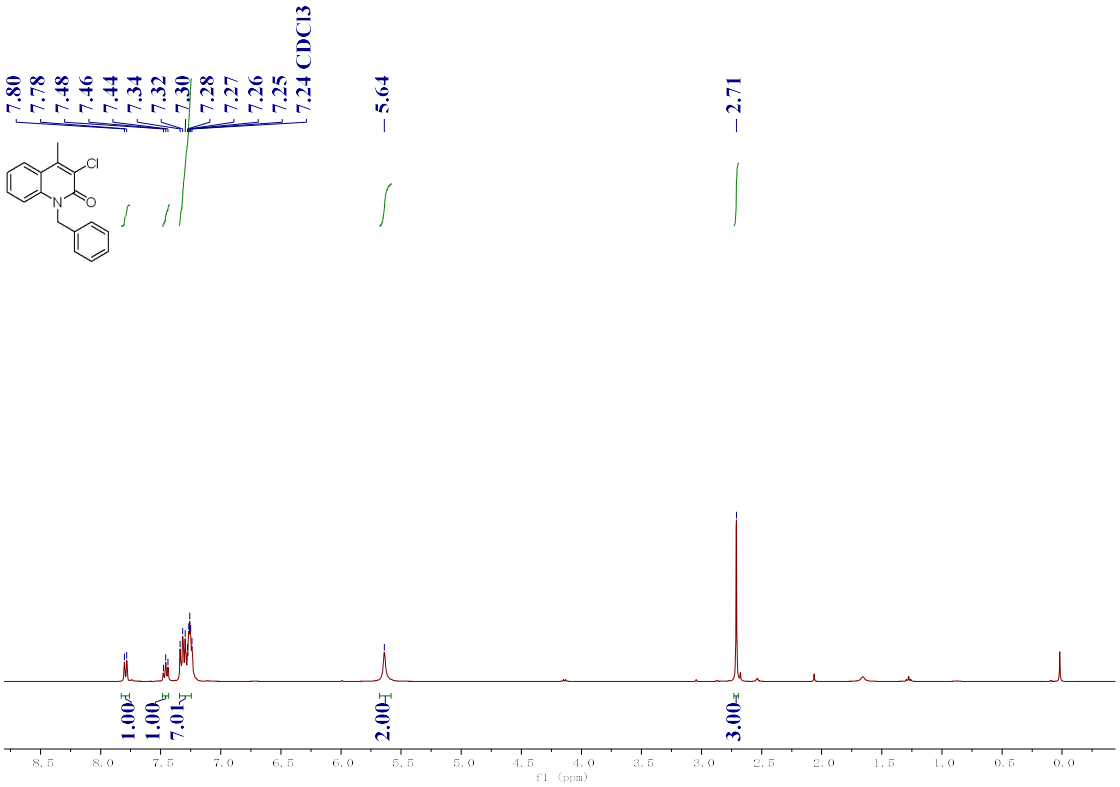
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2d**



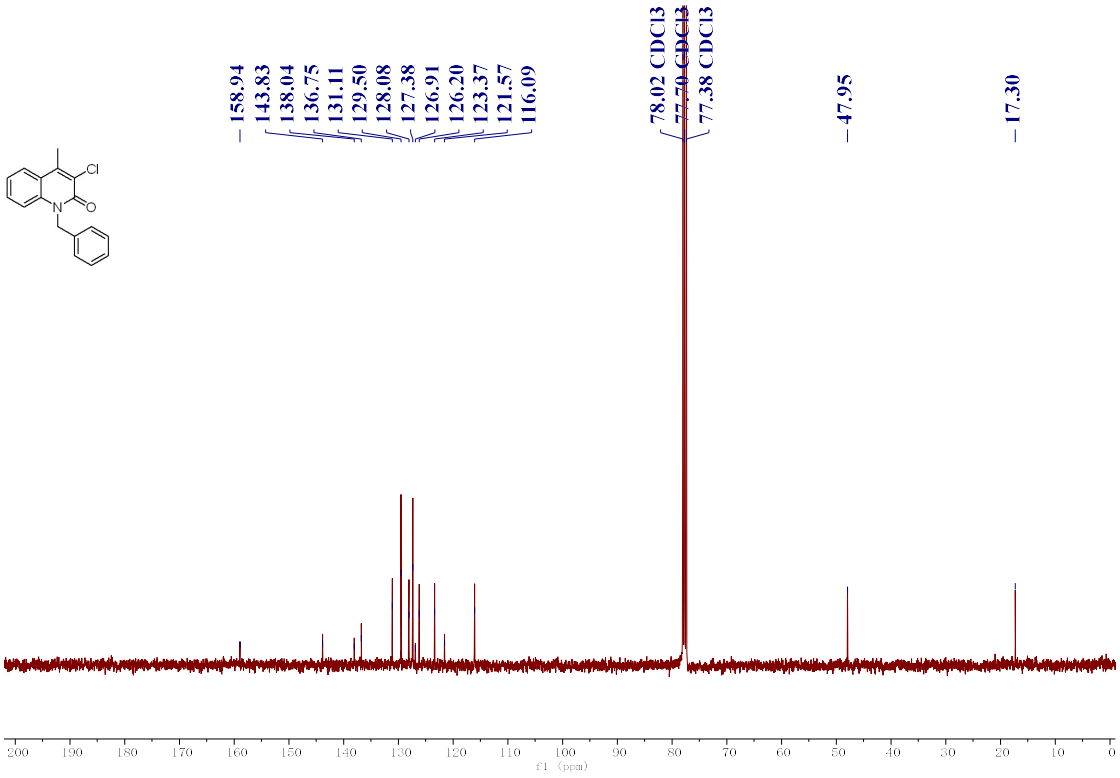
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2e**



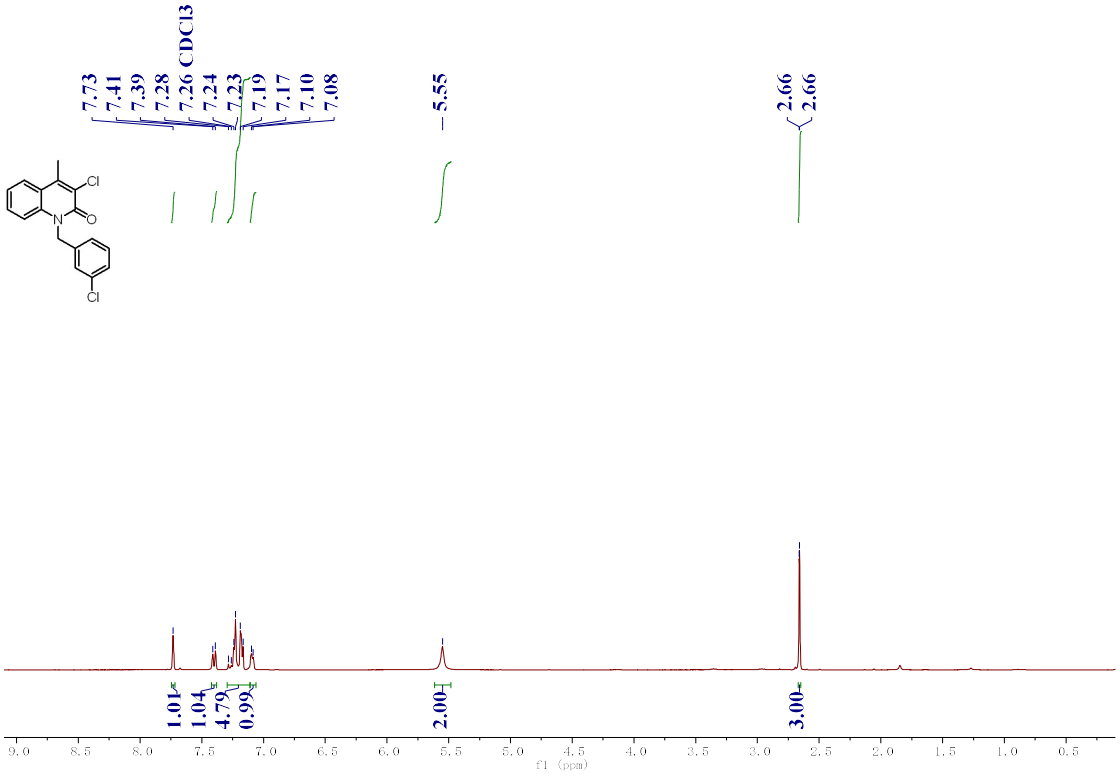
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2e**



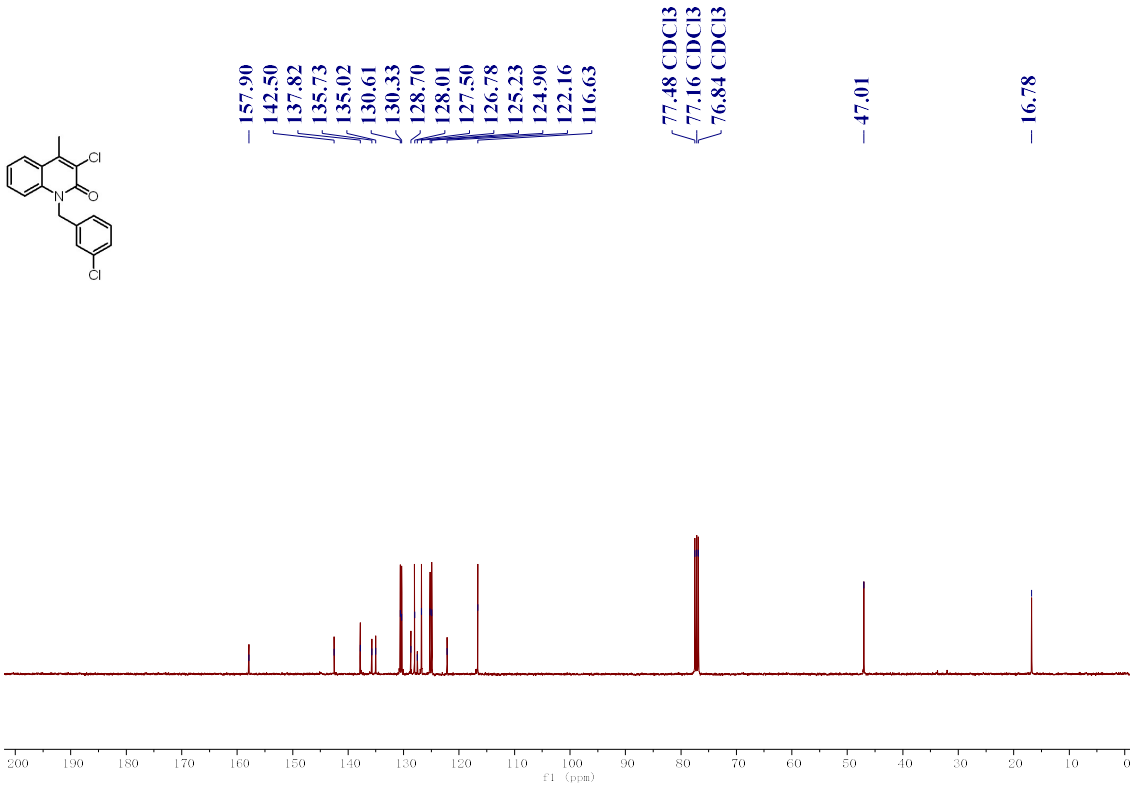
[1]H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2f**



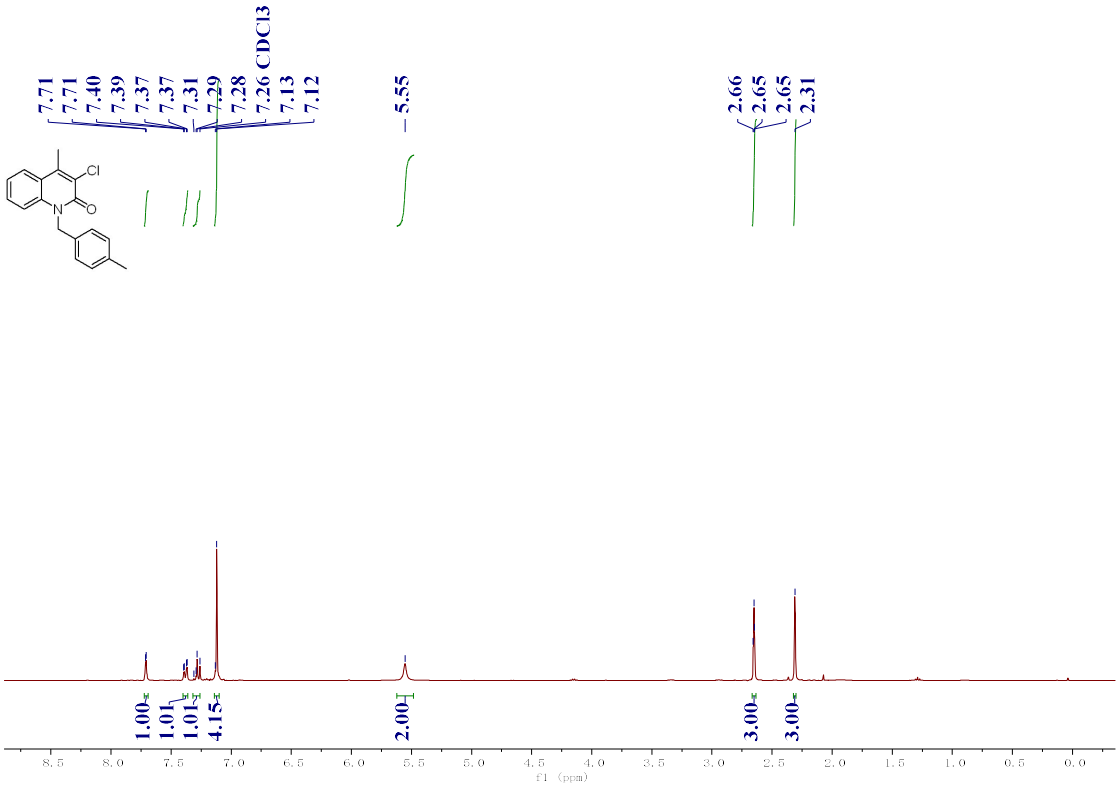
[13]C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2f**



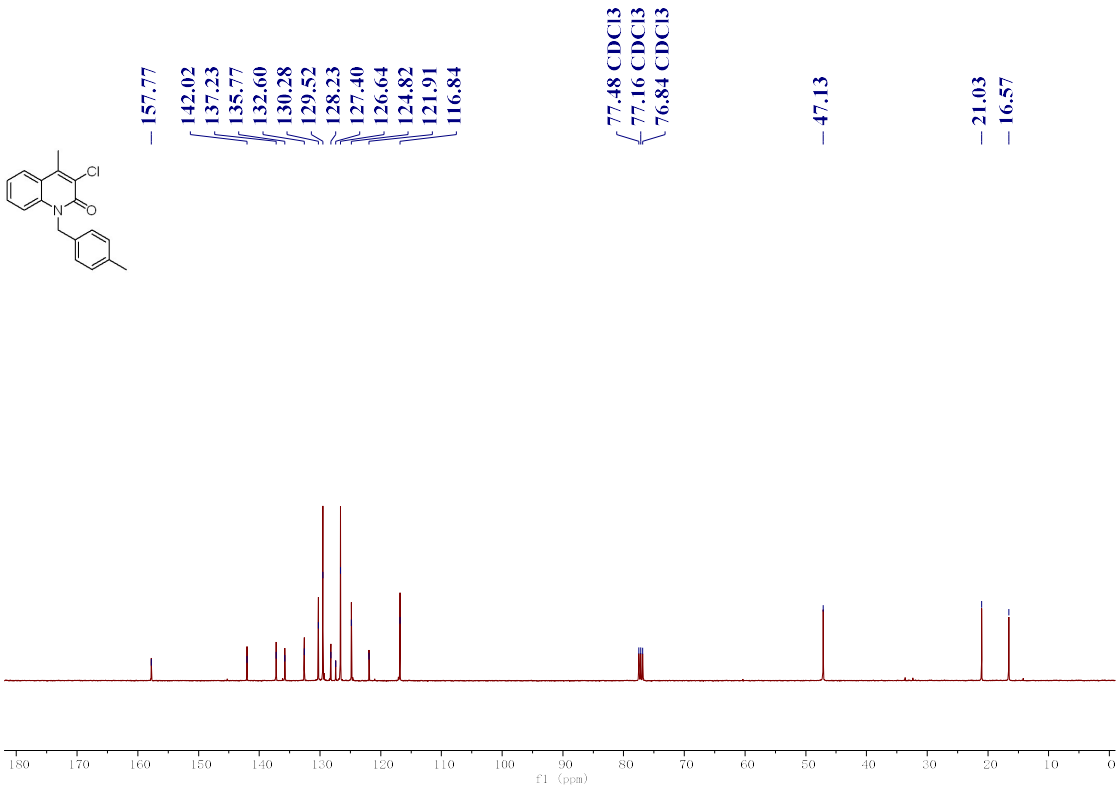
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2g**



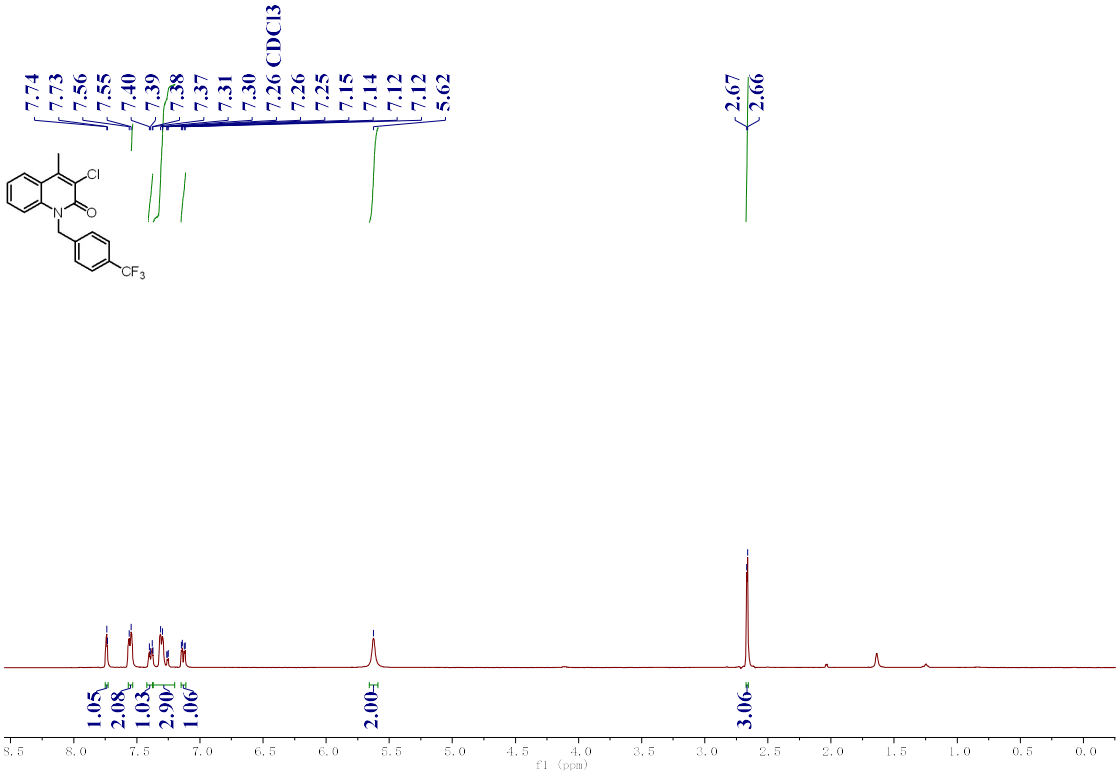
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **2g**



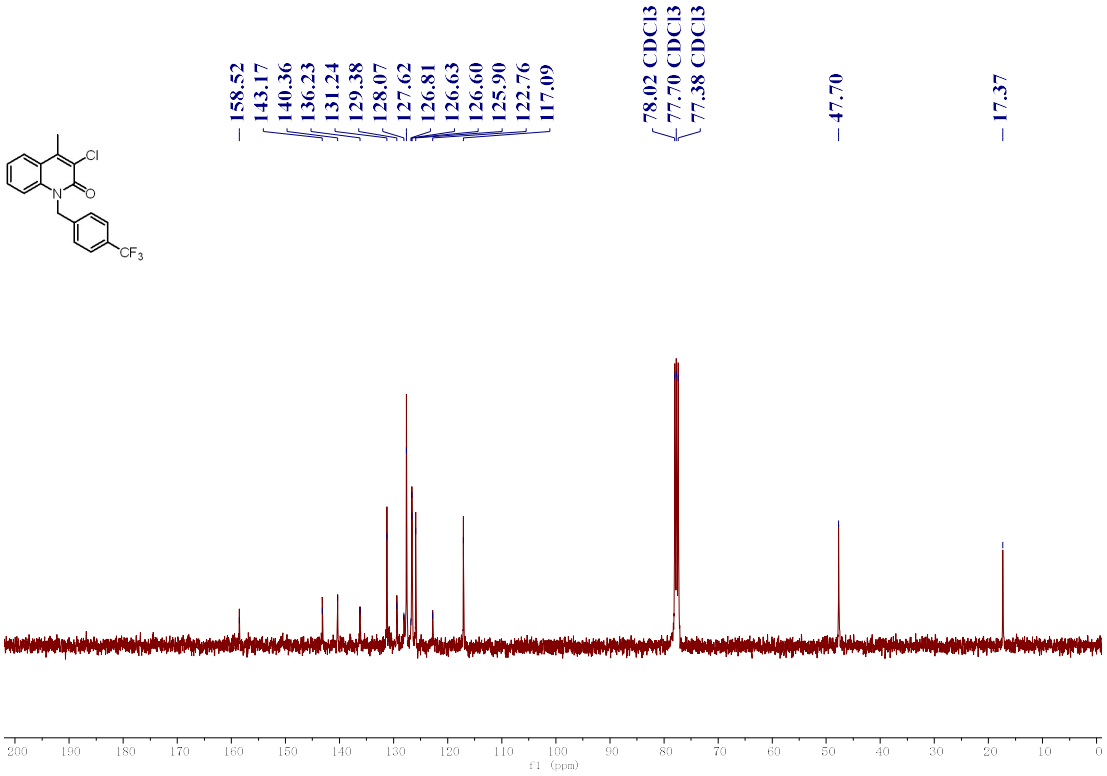
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2h**



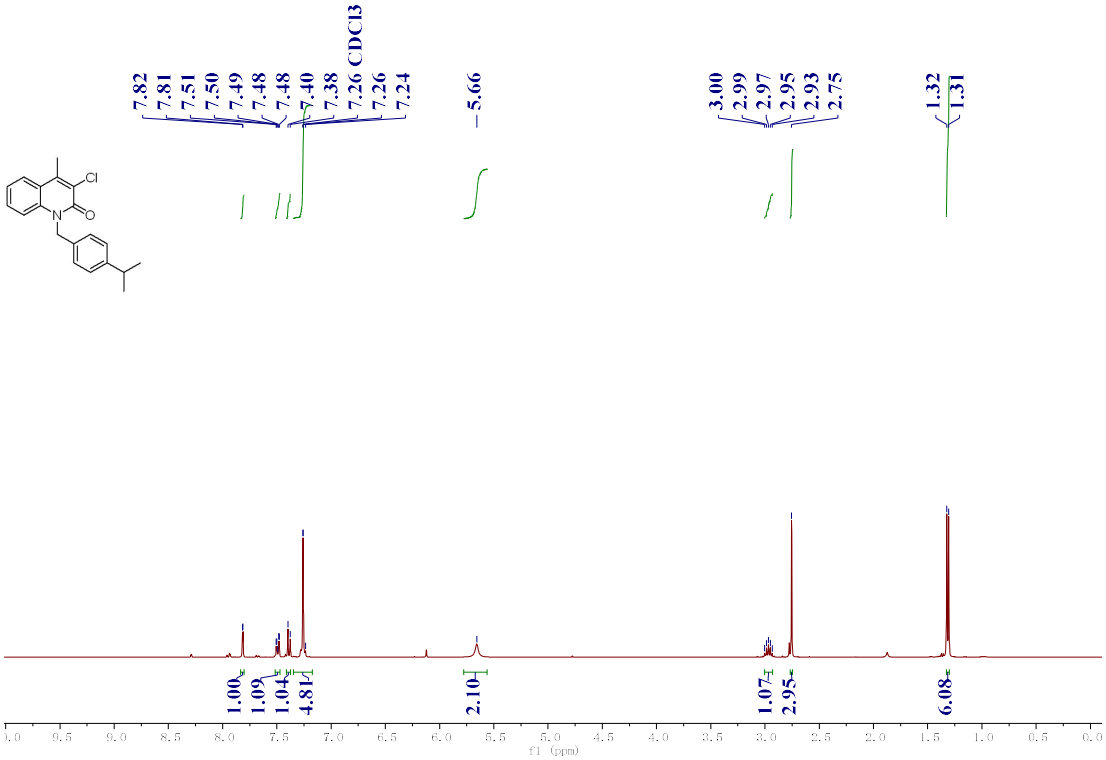
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2h**



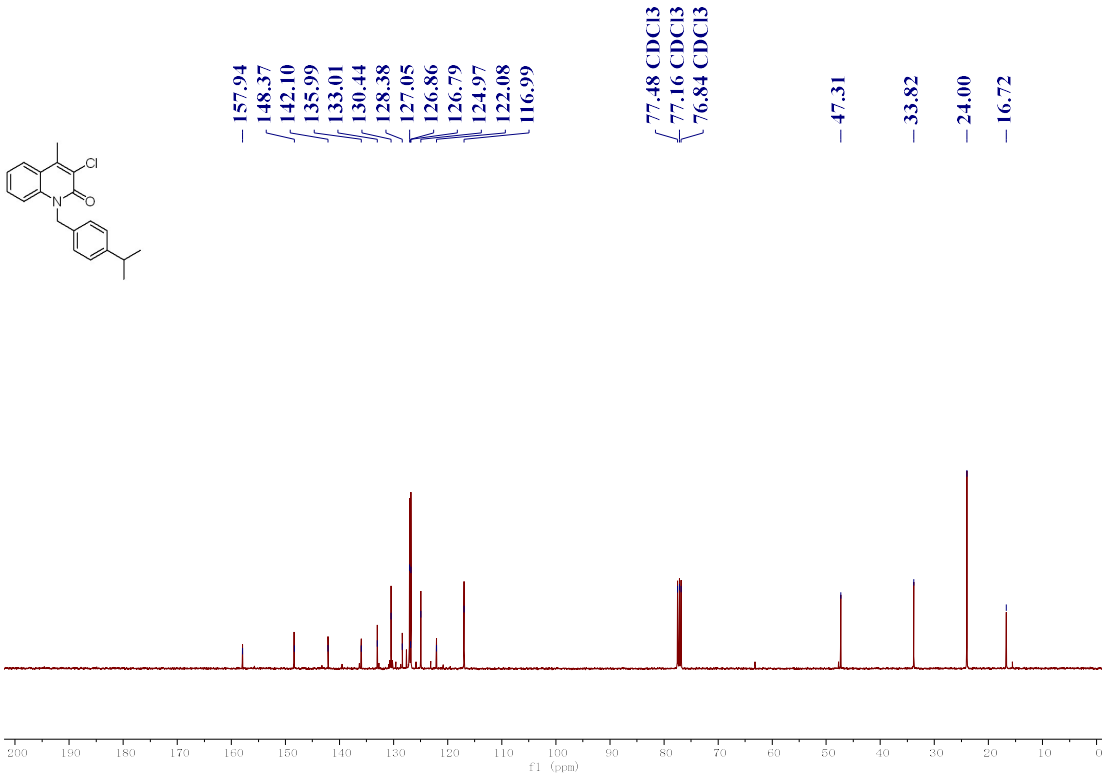
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2i**



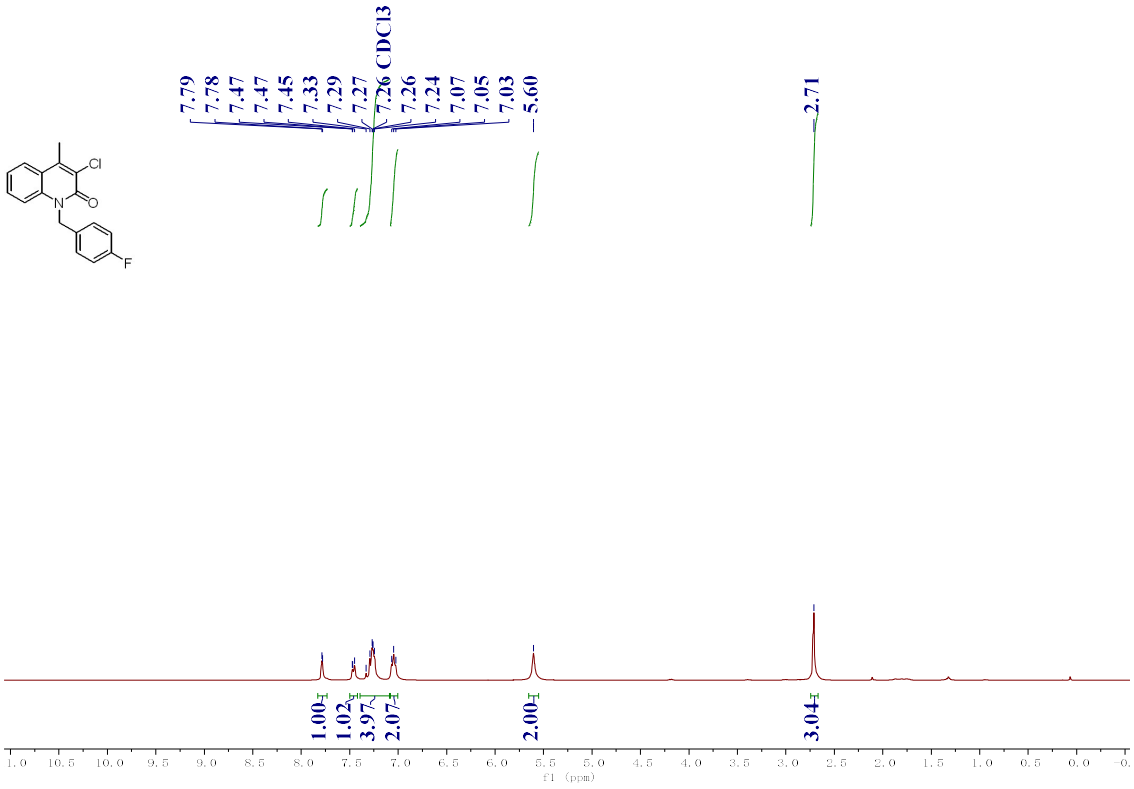
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2i**



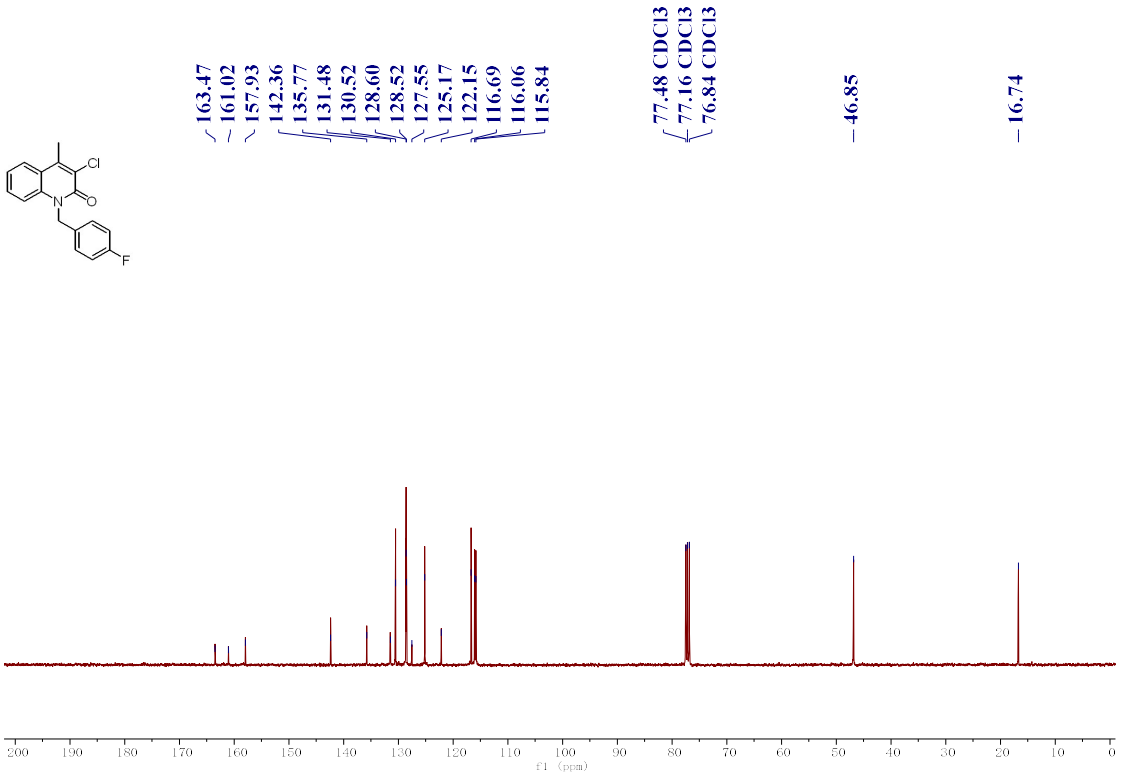
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2j**



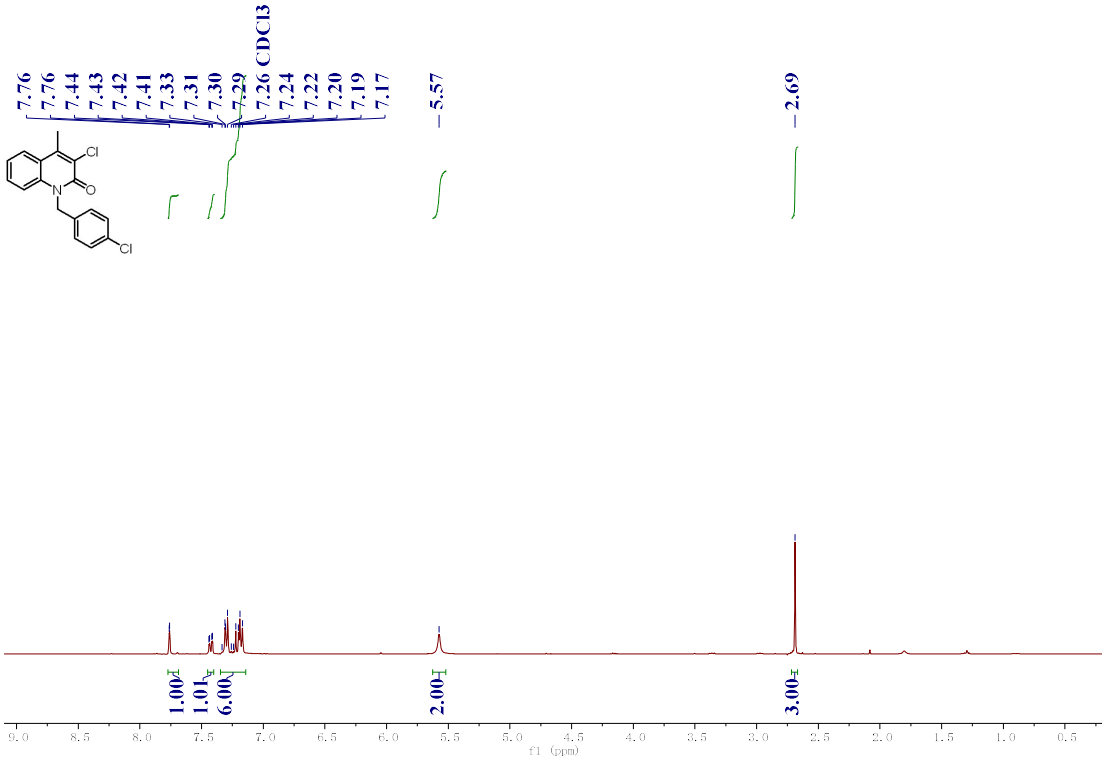
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2j**



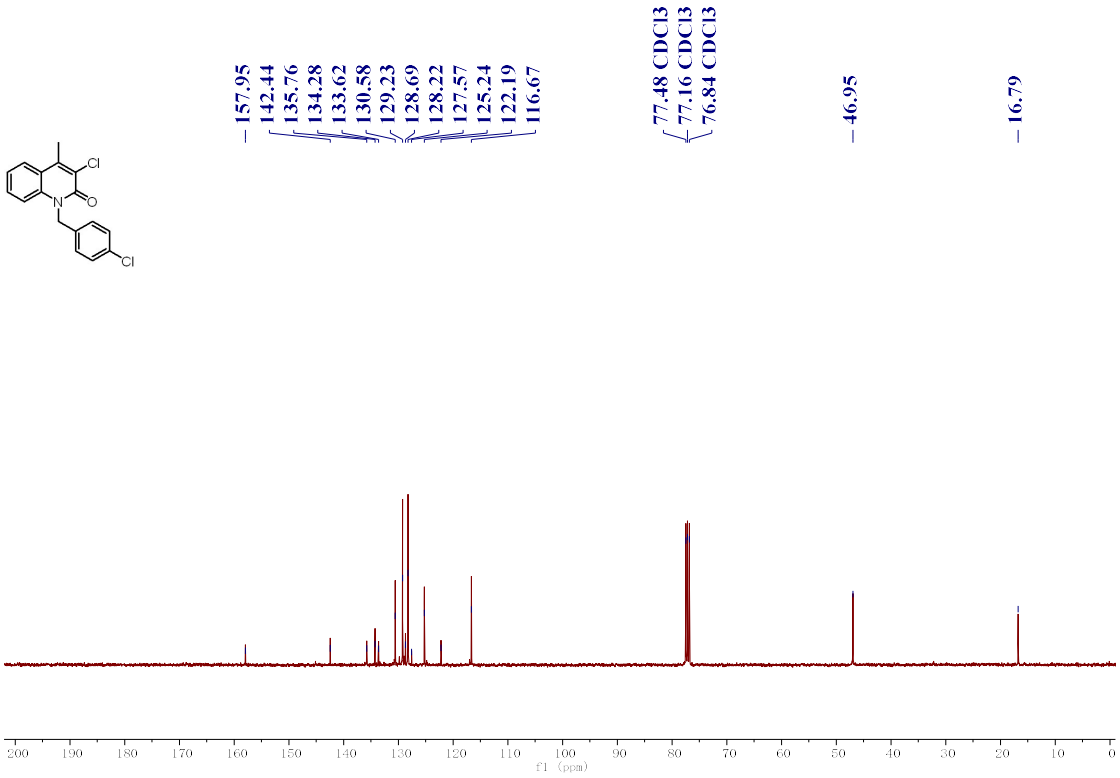
[1]H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2k**



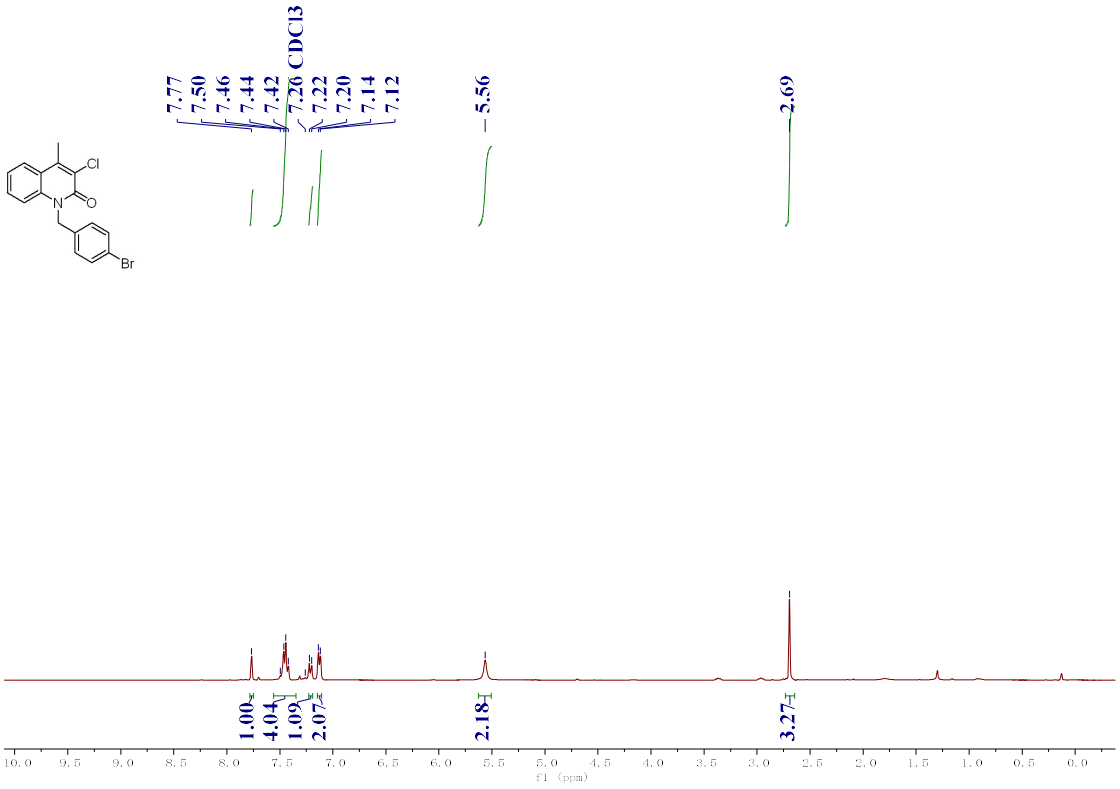
[13]C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2k**



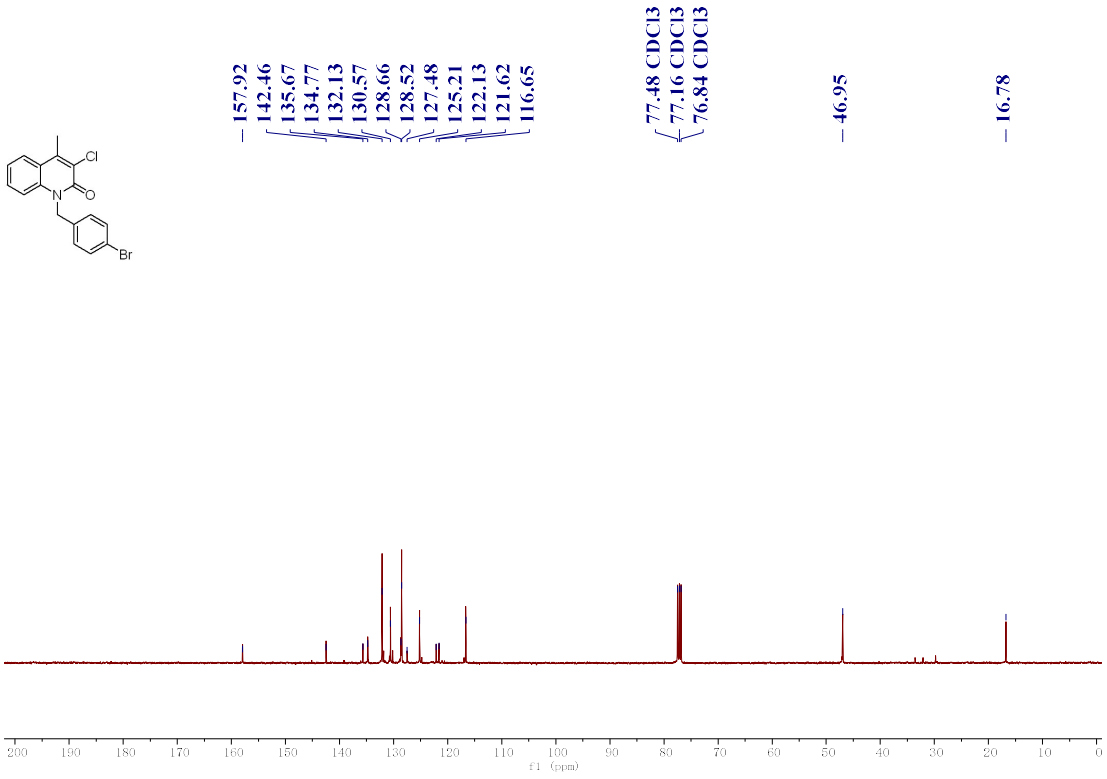
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2l**



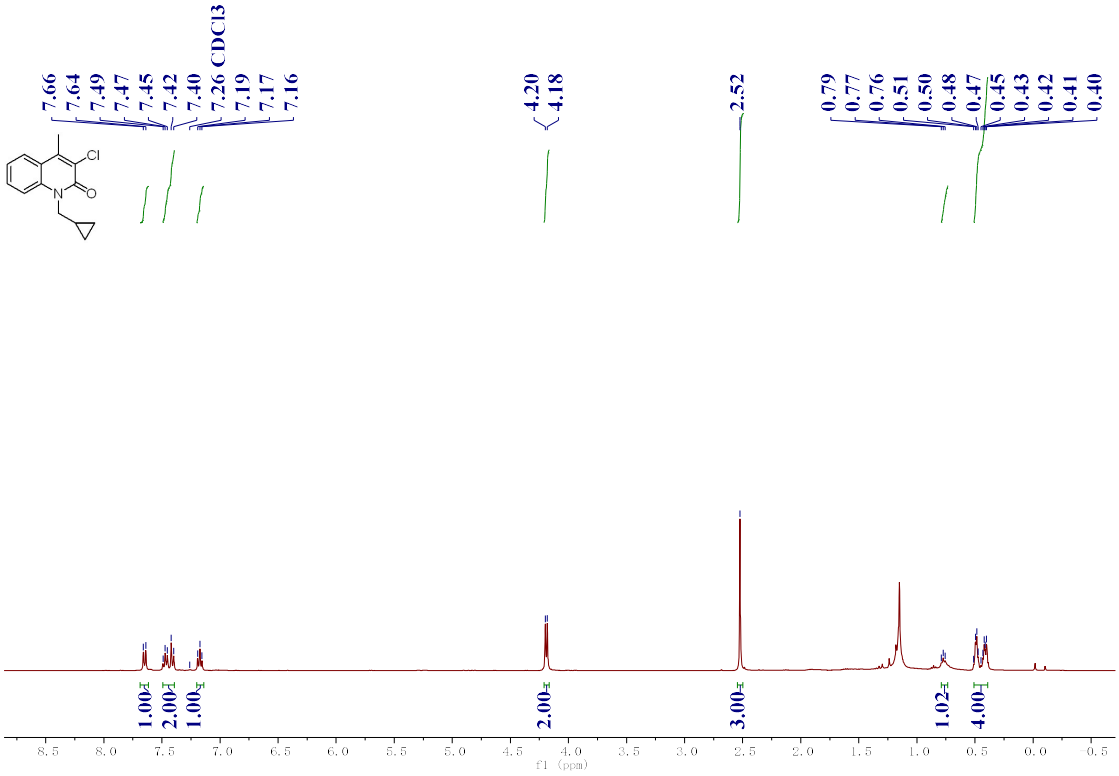
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2l**



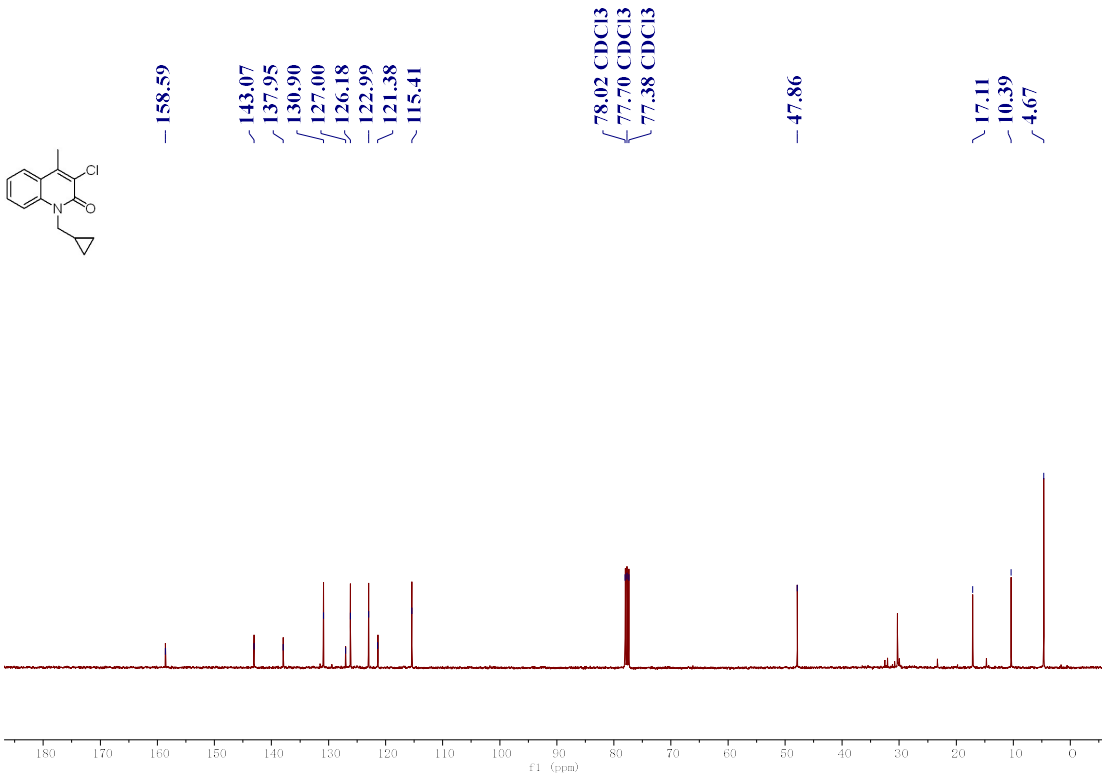
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2m**



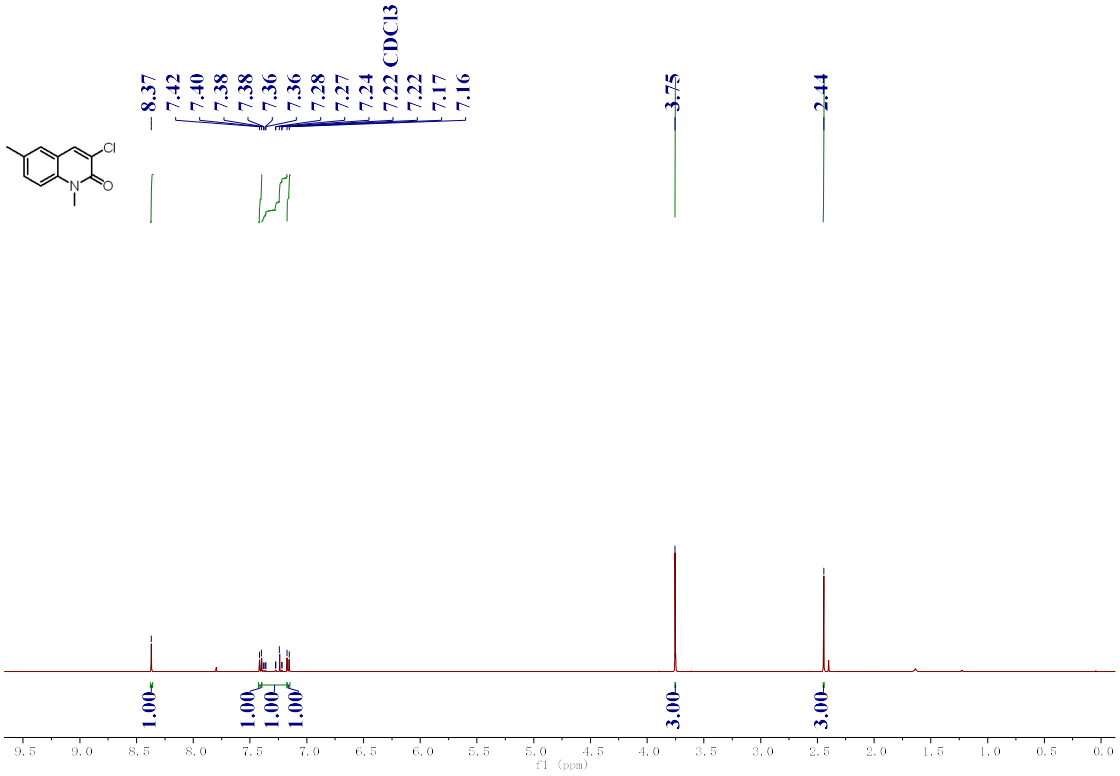
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2m**



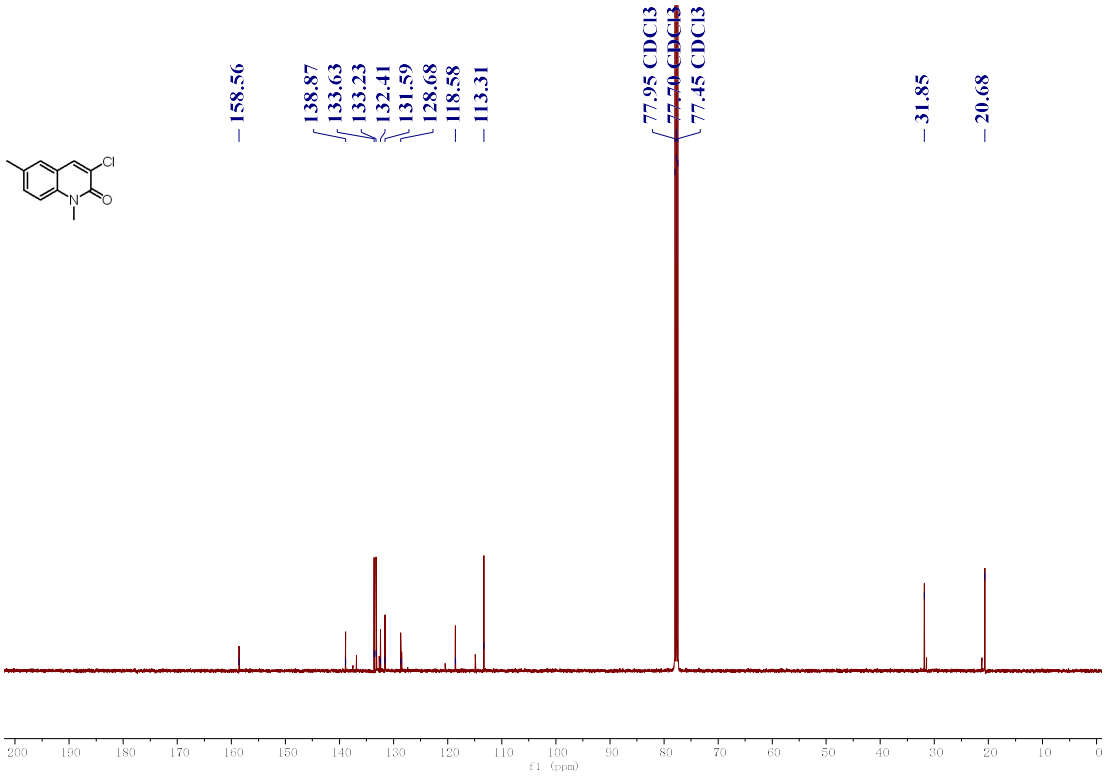
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2n**



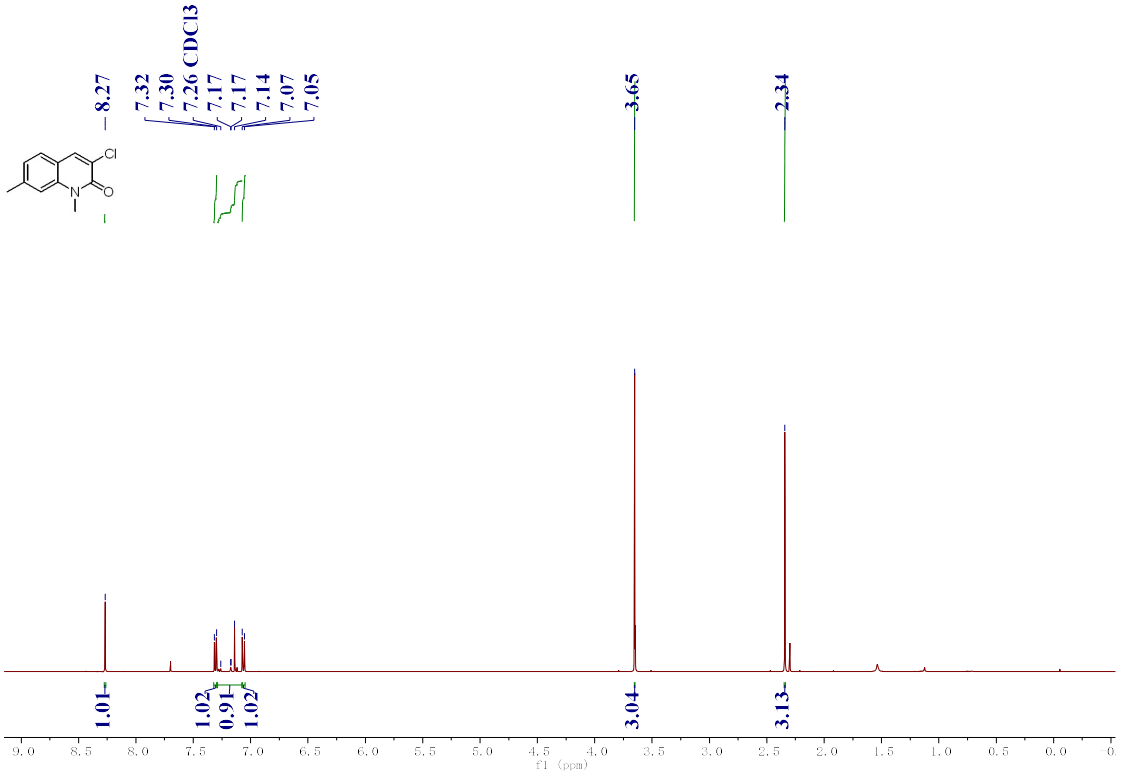
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2n**



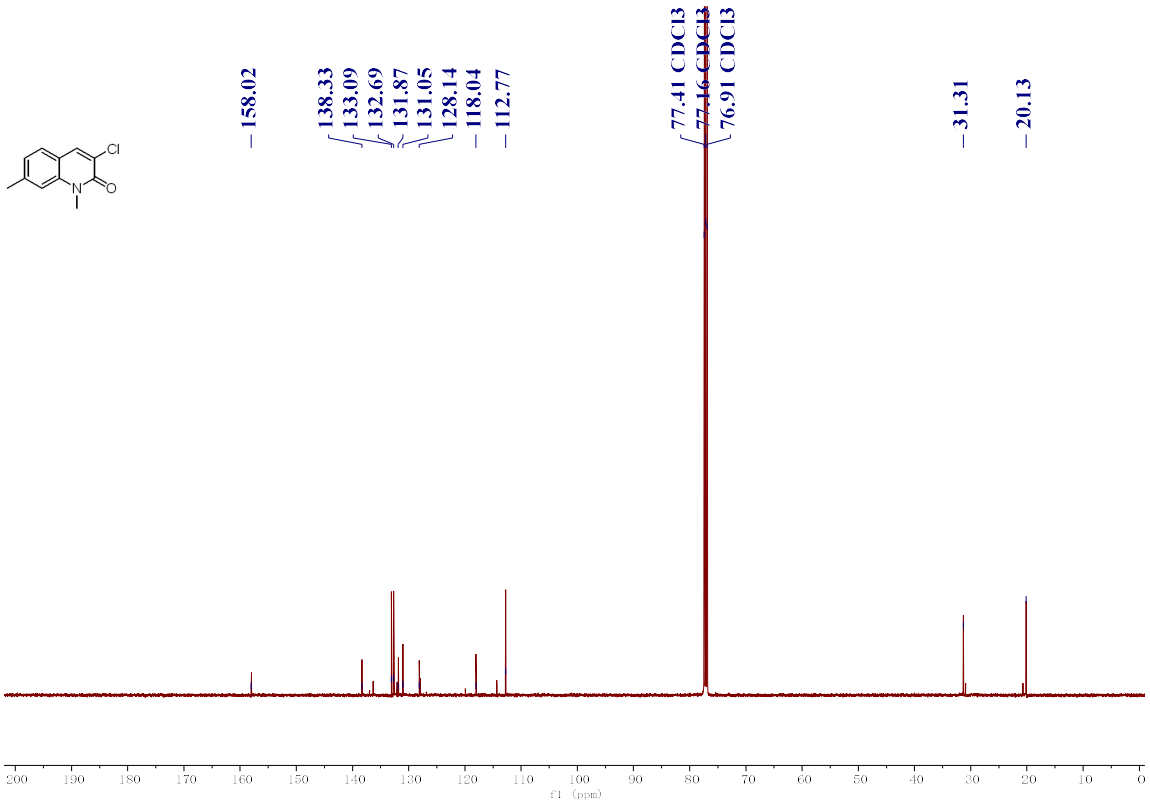
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **2o**



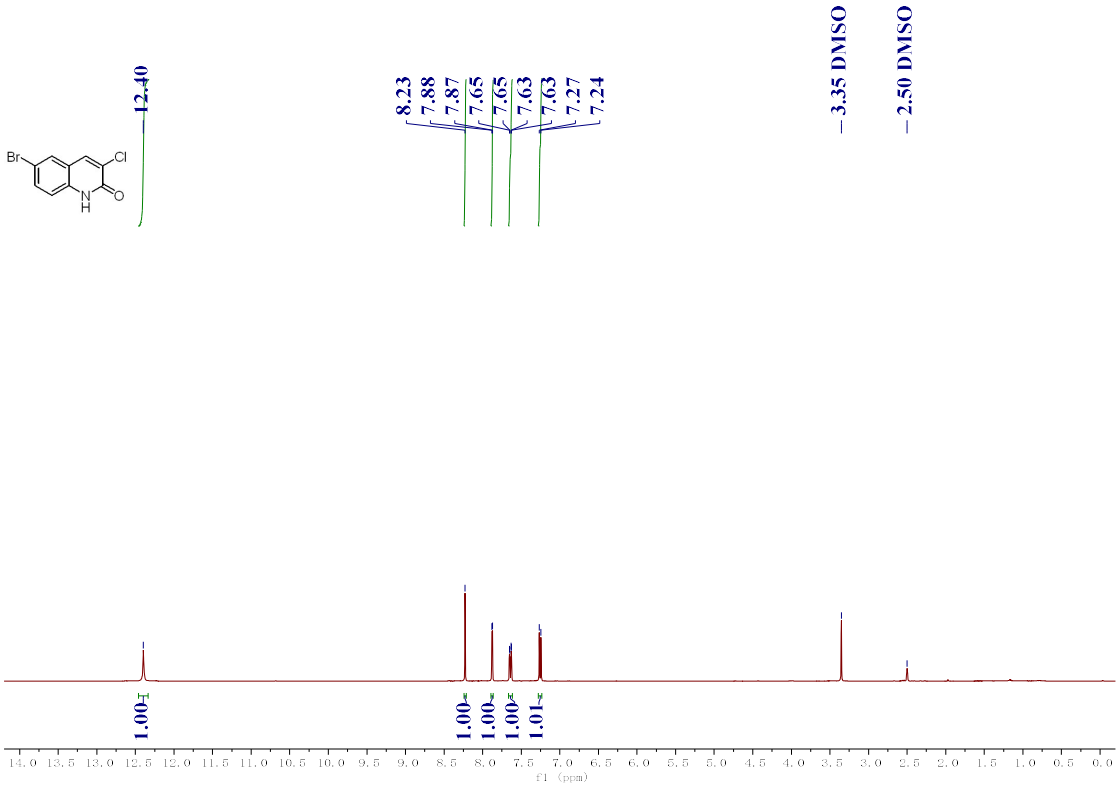
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **2o**



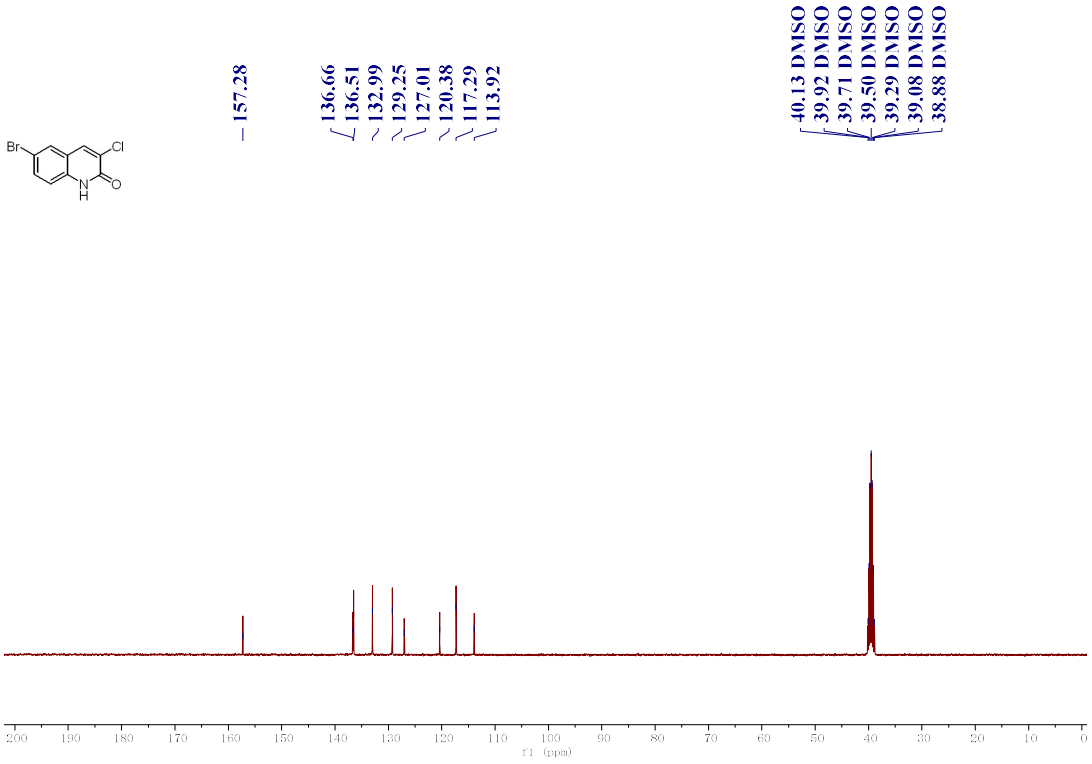
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **2p**



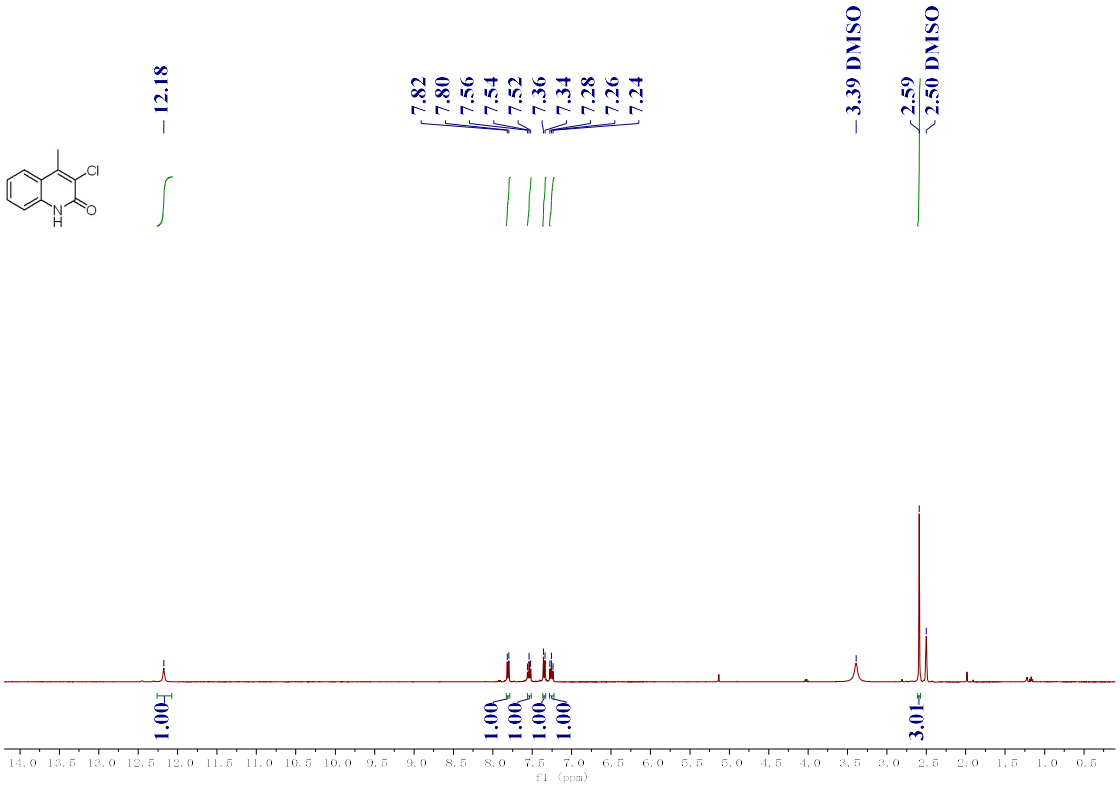
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **2p**



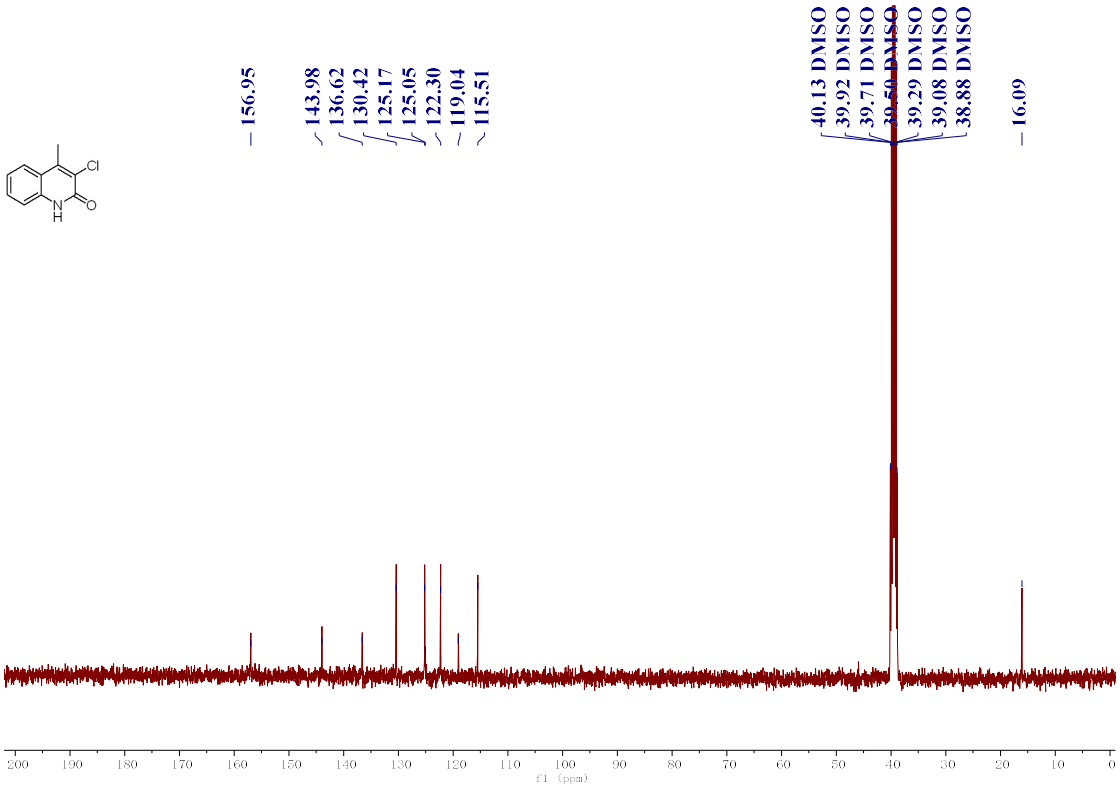
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2q**



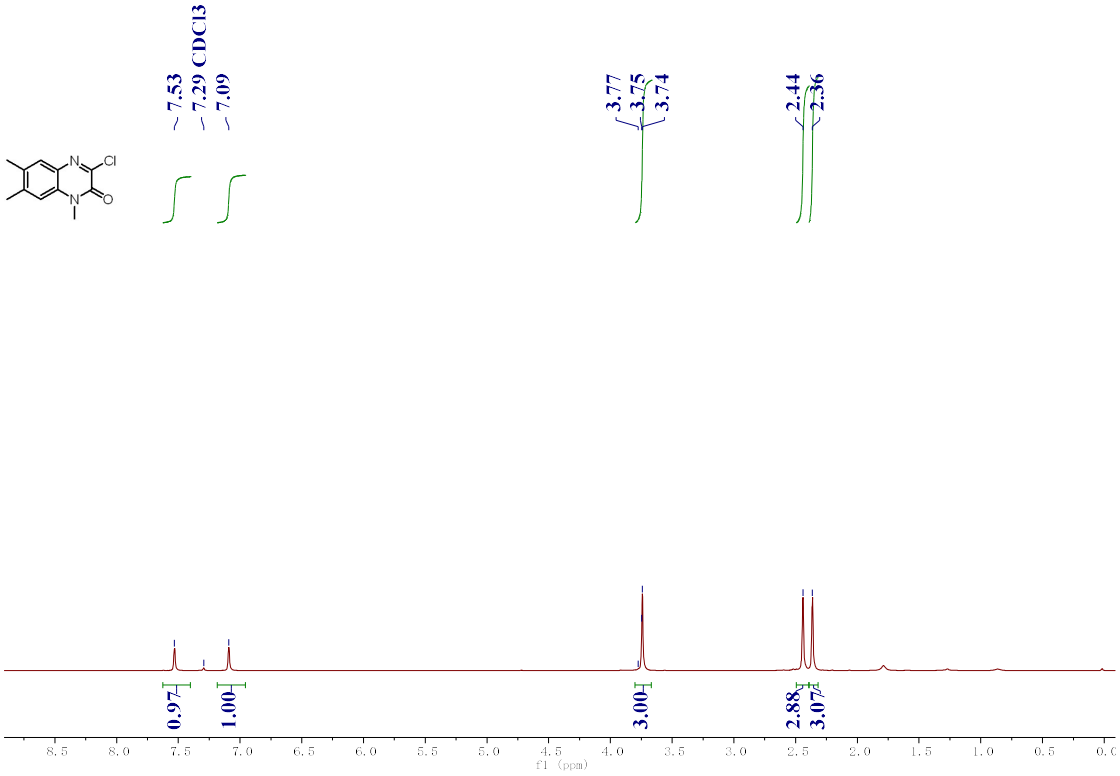
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **2q**



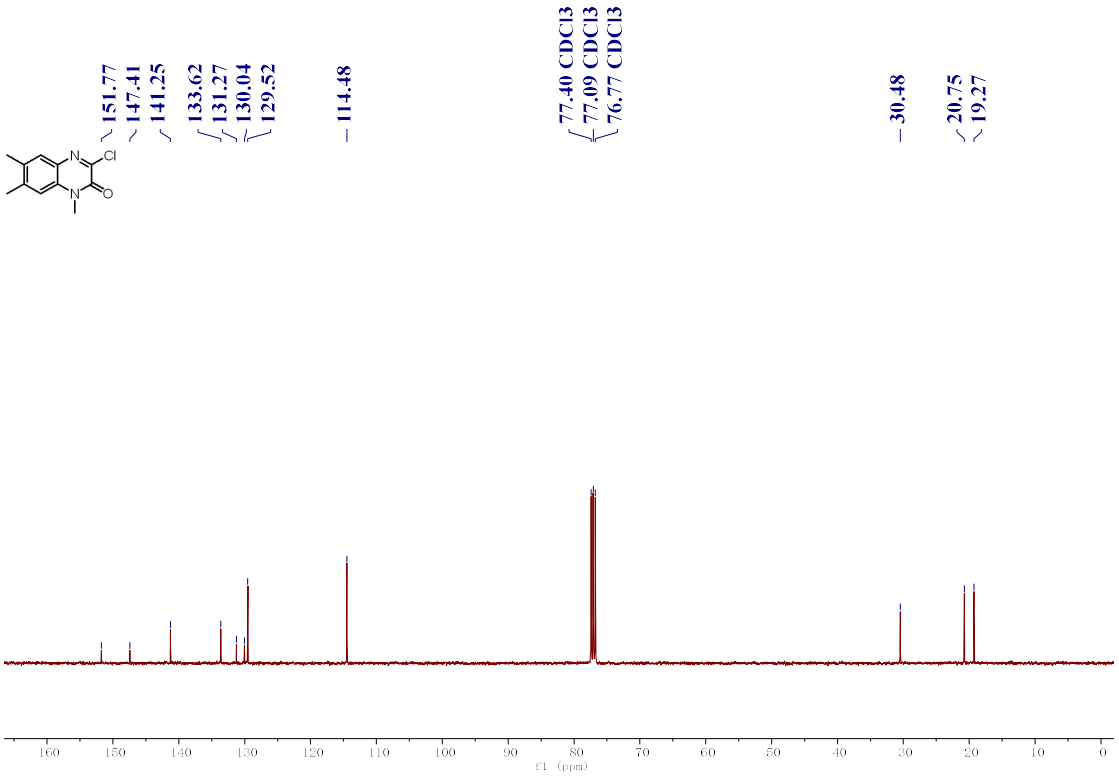
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2r**



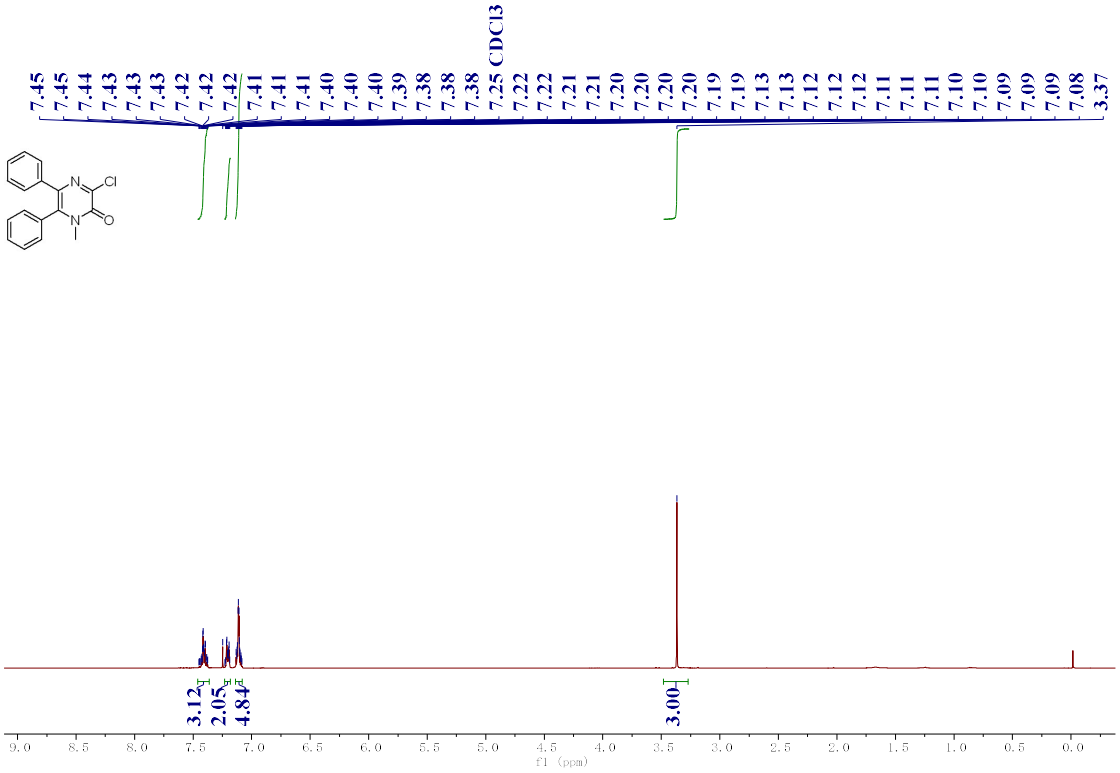
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **2r**



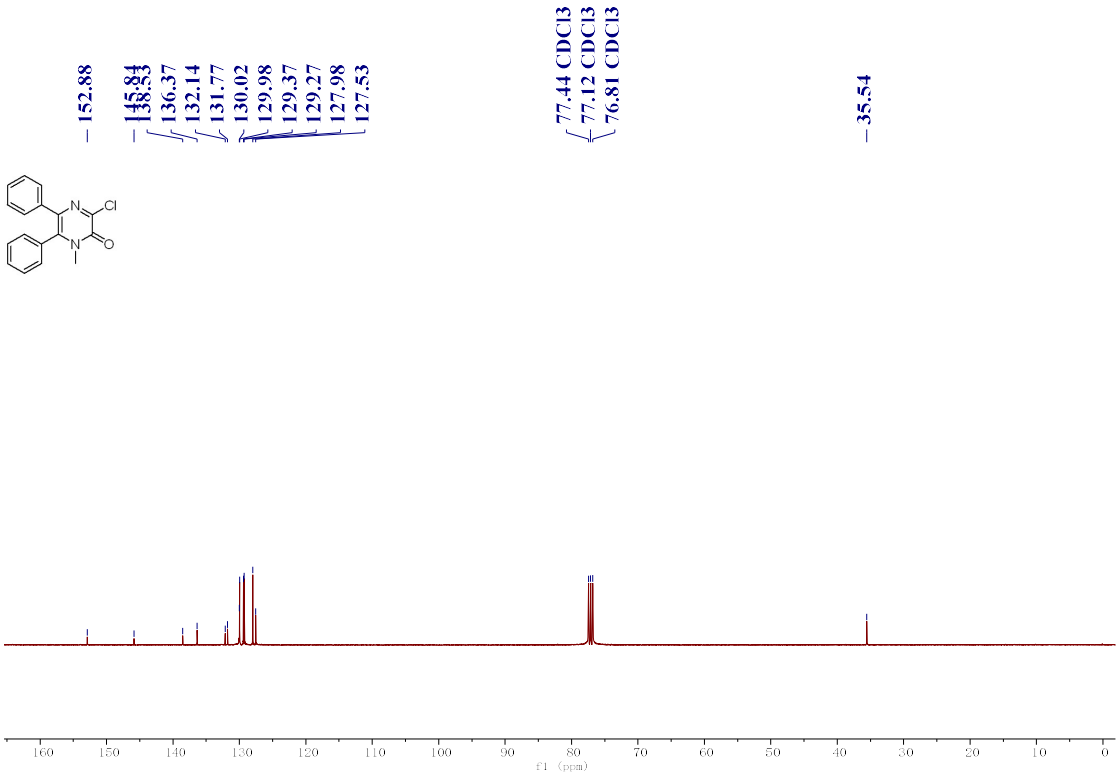
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2ab**



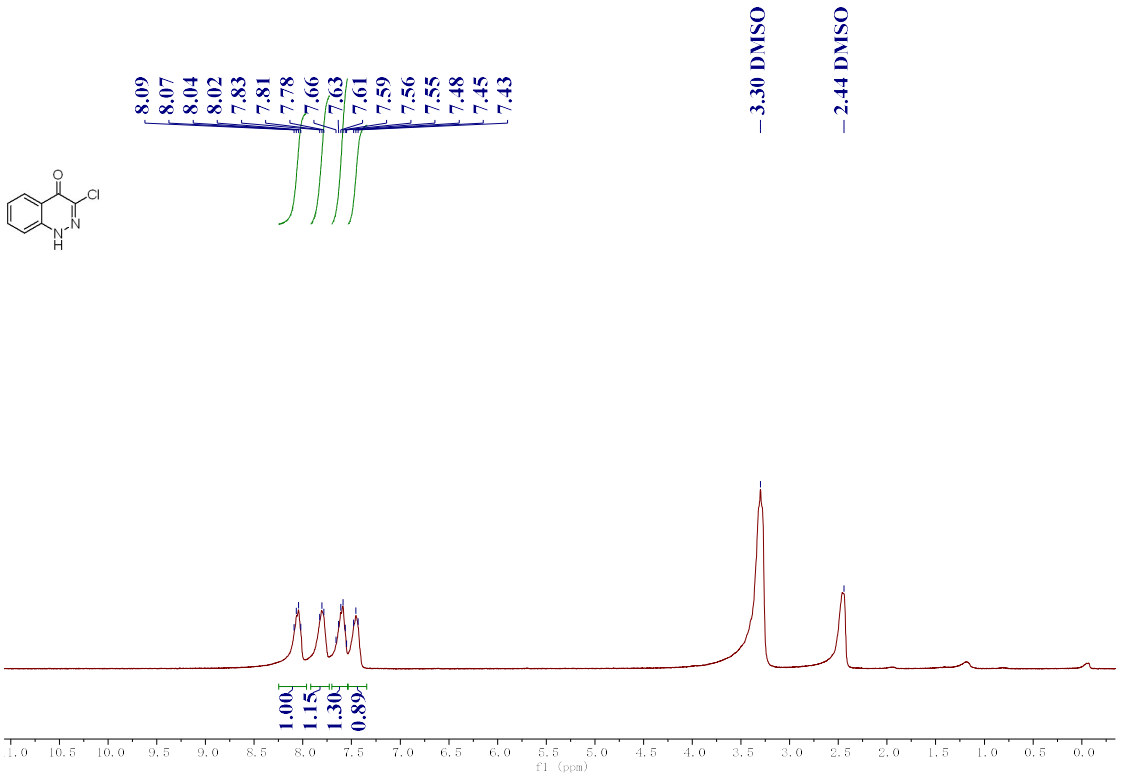
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2ab**



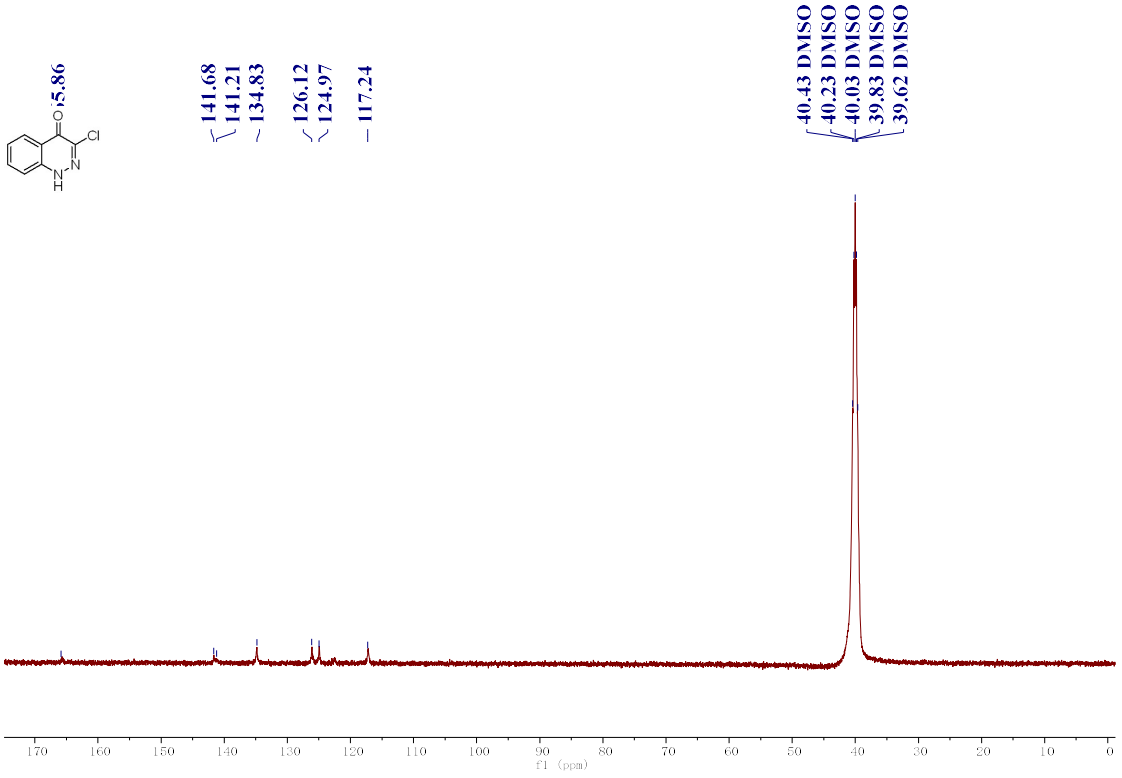
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2ac**



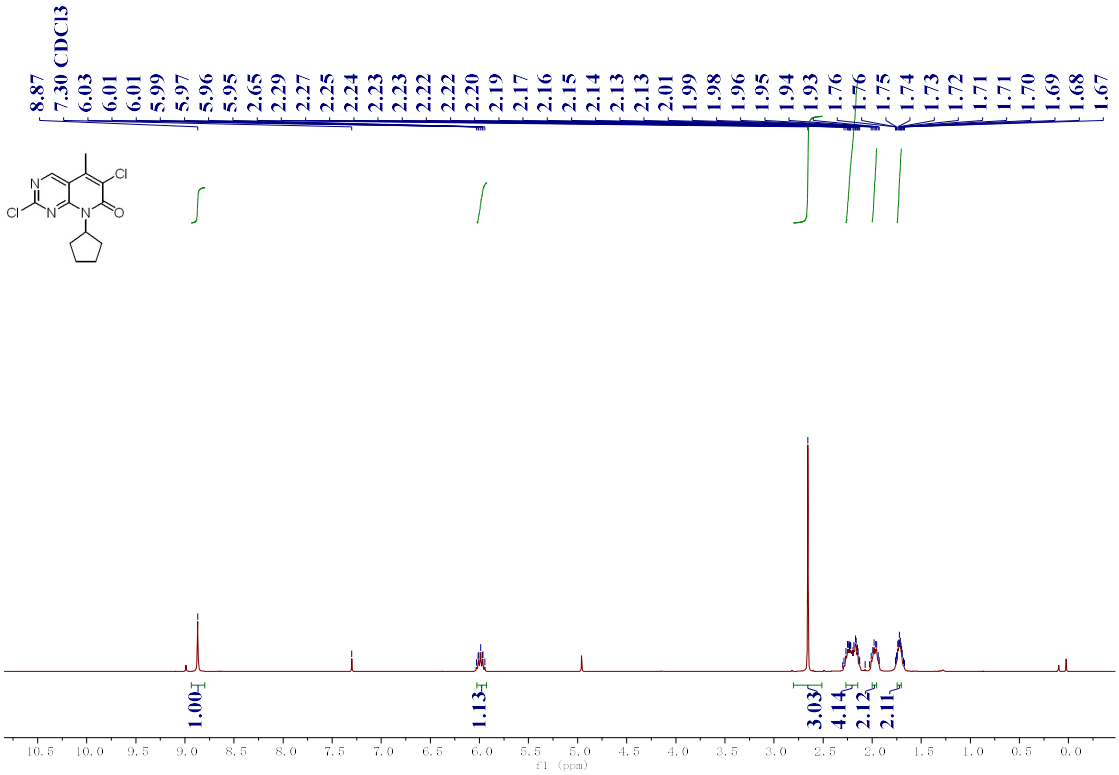
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2ac**



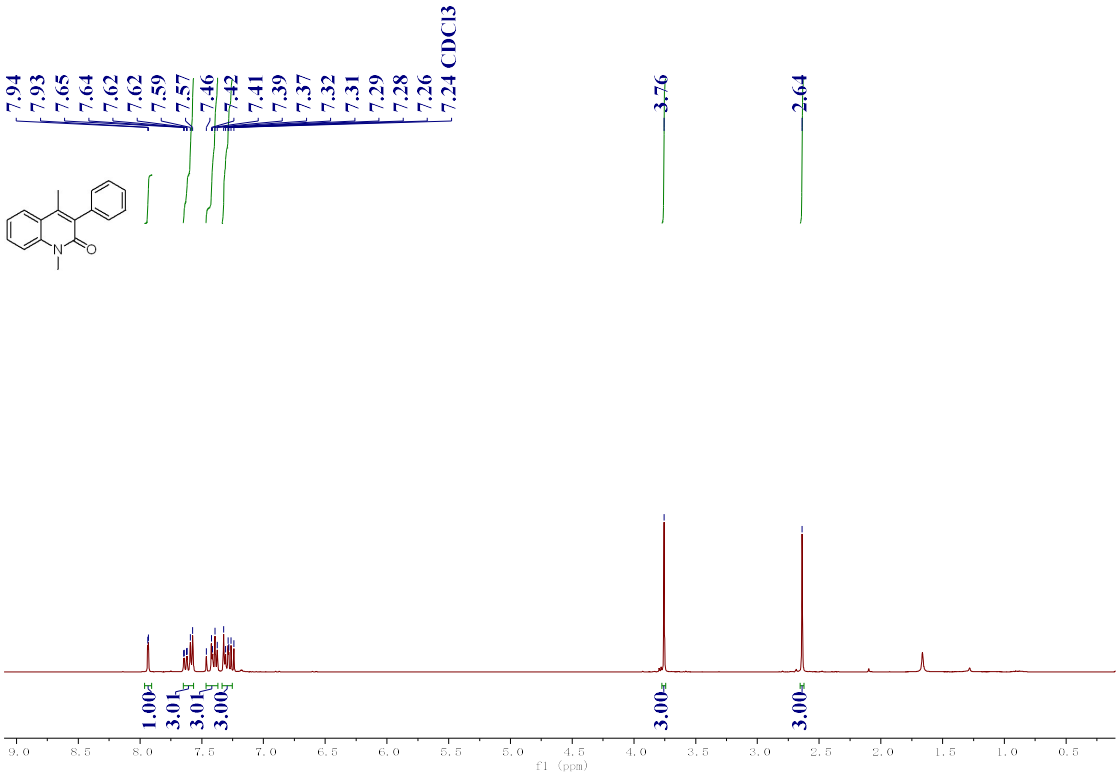
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2ad**



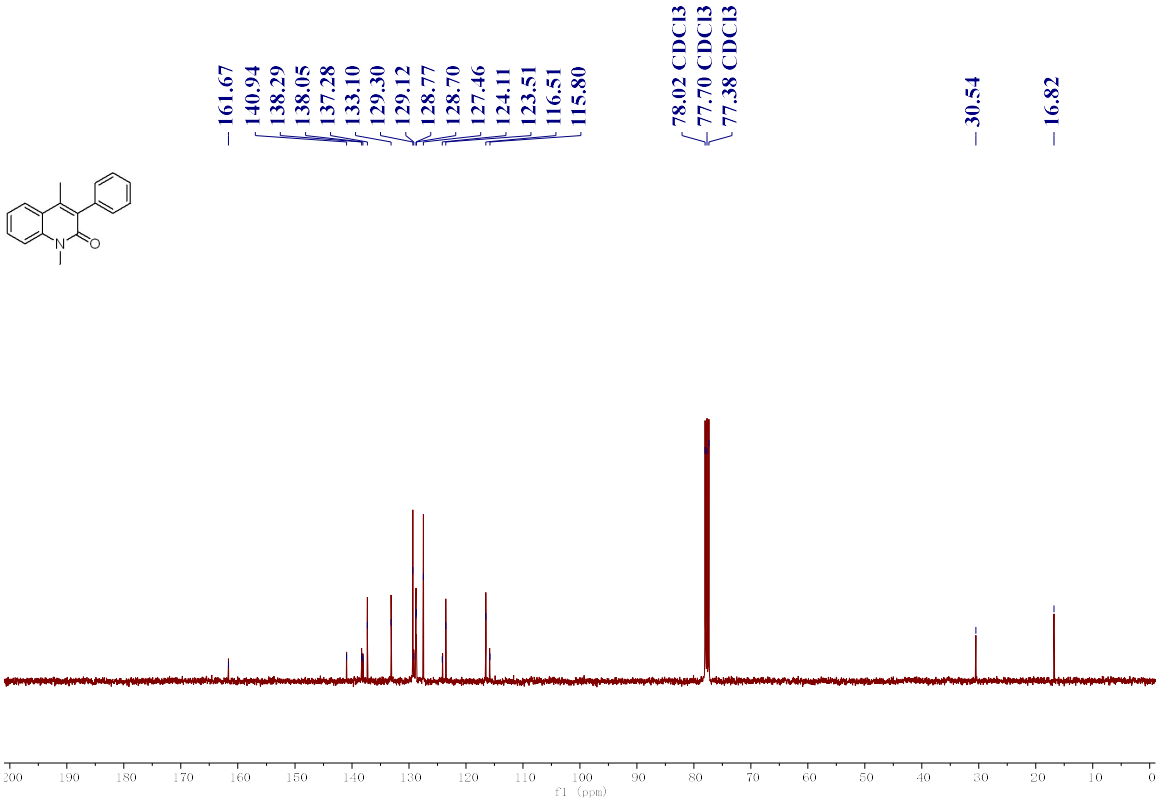
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **2ad**



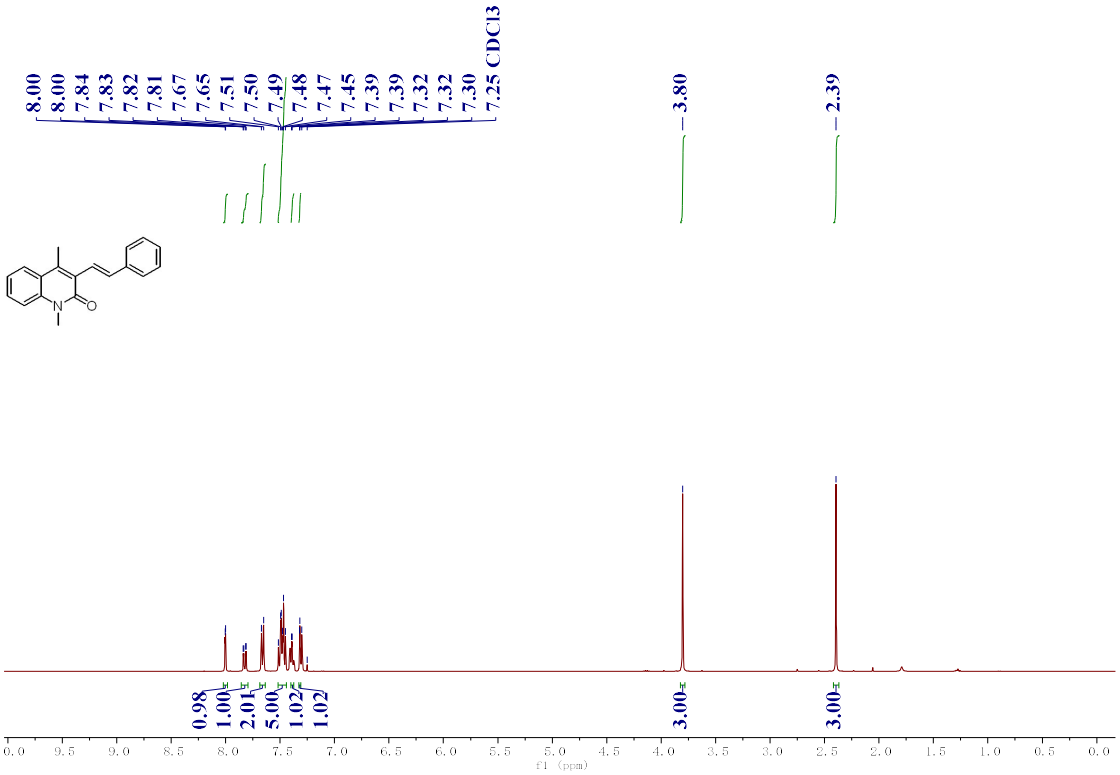
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2ag**



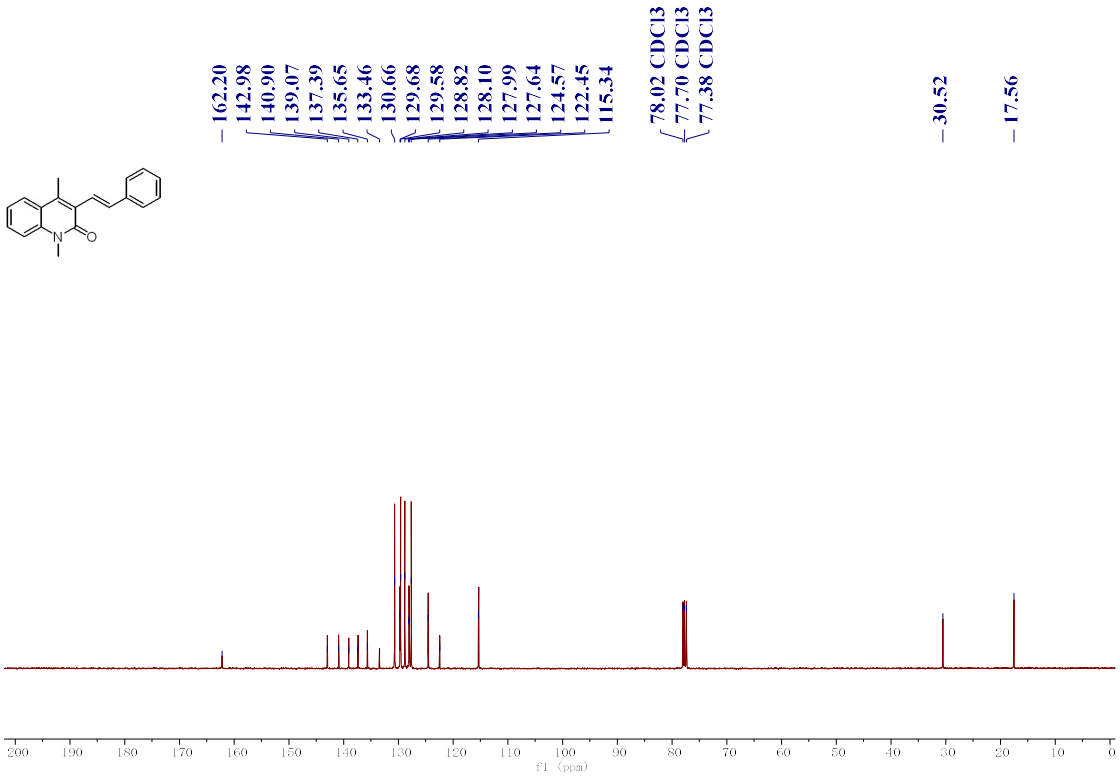
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3a**



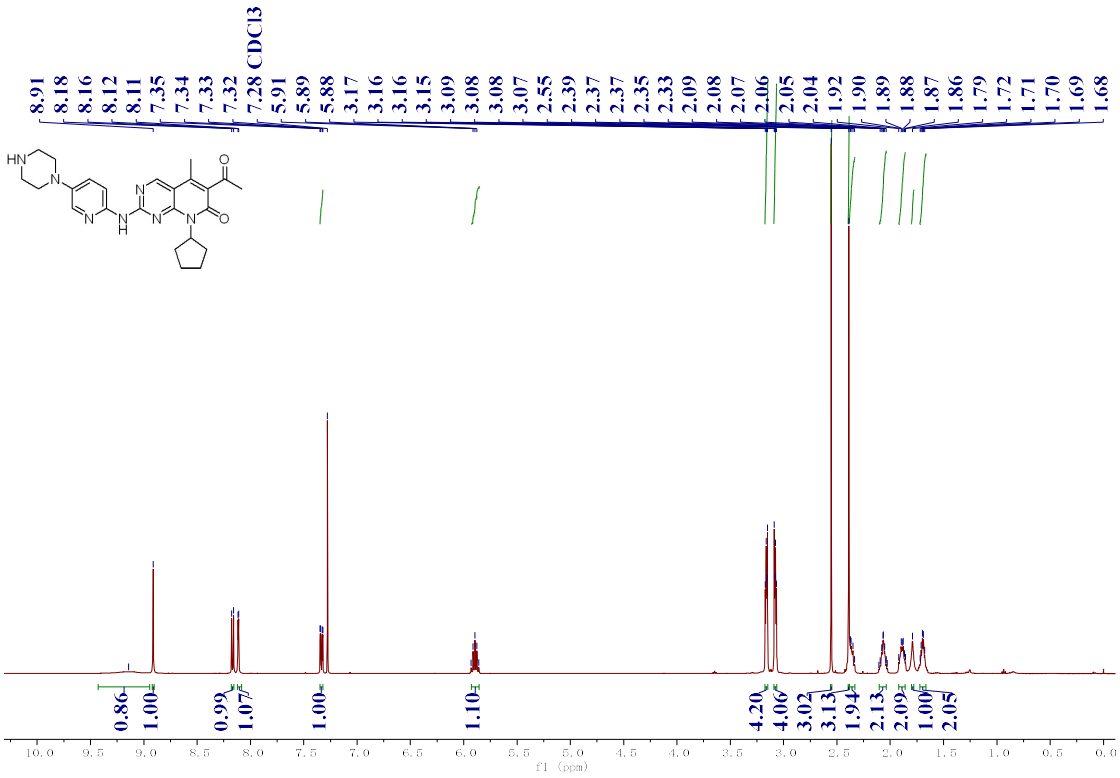
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3a**



^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **4a**



^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **4a**



^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **Palbociclib**

5. References

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