Electronic supplementary information for

Minisci Reaction of Heteroarenes and Unactivated C(sp^3)−H Alkanes via Photogenerated Chlorine Radical

Zi-Tong Pan, Li-Miao Shen, Fentahun Wondu Dagnaw, Jian-Ji Zhong, Jing-Xin Jian* and Qing-Xiao Tong*

[a]College of Chemistry and Chemical Engineering, Key Laboratory for Preparation and Application of Ordered Structural Material of Guangdong Province, and Guangdong Provincial Key Laboratory of Marine Disaster Prediction and Prevention, Shantou University, Shantou, Guangdong, 515063, P. R. China.

E-mail: jxjian@stu.edu.cn, qxtong@stu.edu.cn

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1. Experimental section

1) General information

All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. Unless stated otherwise, all reactions were carried out under air atmosphere. The substrates were synthesized according to the literature methods[1]. Irradiation with visible light was performed using blue LEDs (λ = 385 ± 10 nm) illumination instruments (The instruments were designed by ourselves and the actual output power density of the LEDs at 0.5 cm distance is 33.70 mW/cm^2 detected by CEL-NP2000-10 (Beijing Ceau Light Co. Ltd., China) light power meter). For irradiation, the material of the reaction vessel is quartz; the distance from the light source is about 0.5 cm.

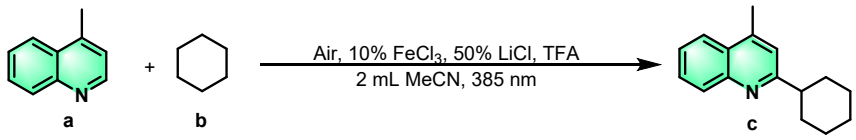
The nuclear magnetic resonance spectra were recorded on the Bruker Ascend^{TM} 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA).

2) General procedure for the reactions

The 4-methylquinoline substrates (0.2 mmol, 1.0 equiv.), cyclohexane (20.0 equiv.), 10 mol% $FeCl_3$, 50 mol% LiCl and TFA (1.5 eq.) were dissolved in 2.0 mL CH_3CN in a 15 mL reaction tube equipped with magnetic stirring bar, and let it open, then the reaction tube was irradiated by LEDs (λ = 385 ± 10 nm) at room temperature for 6-24 h. After reaction, DCM and $NaHCO_3$ saturated solution are used for extraction, and then the organic phase is separated. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (200:3) as the eluent.

3) Optimization of the reaction conditions

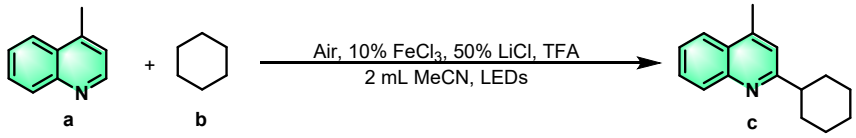
Table S1. Substrate ratio effect



Entry	**a** / **b** (equiv.)	Yield (%)
1	1/5	trace
2	1/10	37
3	1/20	82

Yields of isolated products.

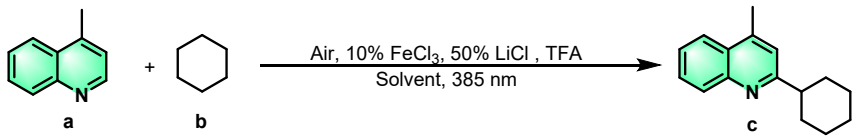
Table S2. LED light effect



Entry	LED light	Yield (%)
1	3W 365 nm	71
2	3W 385 nm	82
3	3W 410 nm	51
4	3W 450 nm	12
5	3W 510 nm	trace

Yields of isolated products.

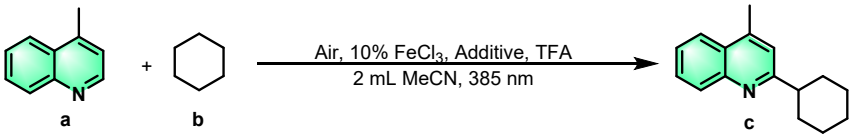
Table S3. Solvent effect



Entry	Solvent (2 mL)	Yield (%)
1	MeCN	82
2	DCE	54
3	DMSO	31
4	DCM	11
5	DMF	0
6	MeCN:Seawater (1.75:0.25)	65
7	MeCN:Seawater (1:1)	28
6	Seawater	Trace

Yields of isolated products.

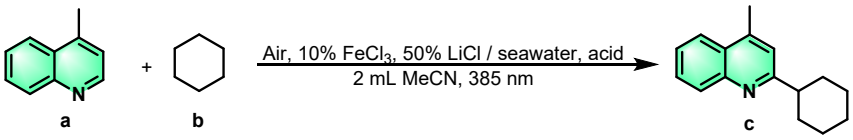
Table S4. Additive effect



Entry	Additive	Yield (%)
1	LiCl (50%)	82
2	NaCl (50%)	63
3	Seawater (0.25 mL)	65

Yields of isolated products.

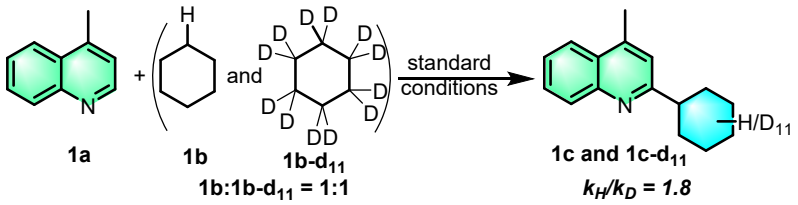
Table S5. Acid effect



Entry	Acid	Yield (%)
1	TFA (0.5 equiv.)	43
2	TFA (1.0 equiv.)	73
3	TFA (1.5 equiv.)	82
4	TFA (2.0 equiv.)	66
5	H_2SO_4 (1.5 equiv.)	52
6	HFIP (1.5 equiv.)	trace

Yields of isolated products.

4) Kinetic isotope effect experiment



The preparation of 1c-d_{11} followed the general procedure using heteroarene 1a and deuterated cyclohexane 2b-d_{12} as the starting materials. The isolated product was obtained by column chromatography. Prominent isotope effect (k_H/k_D = 1.8) indicates that C−H homocleavage of cyclohexane is the rate-determine-step.

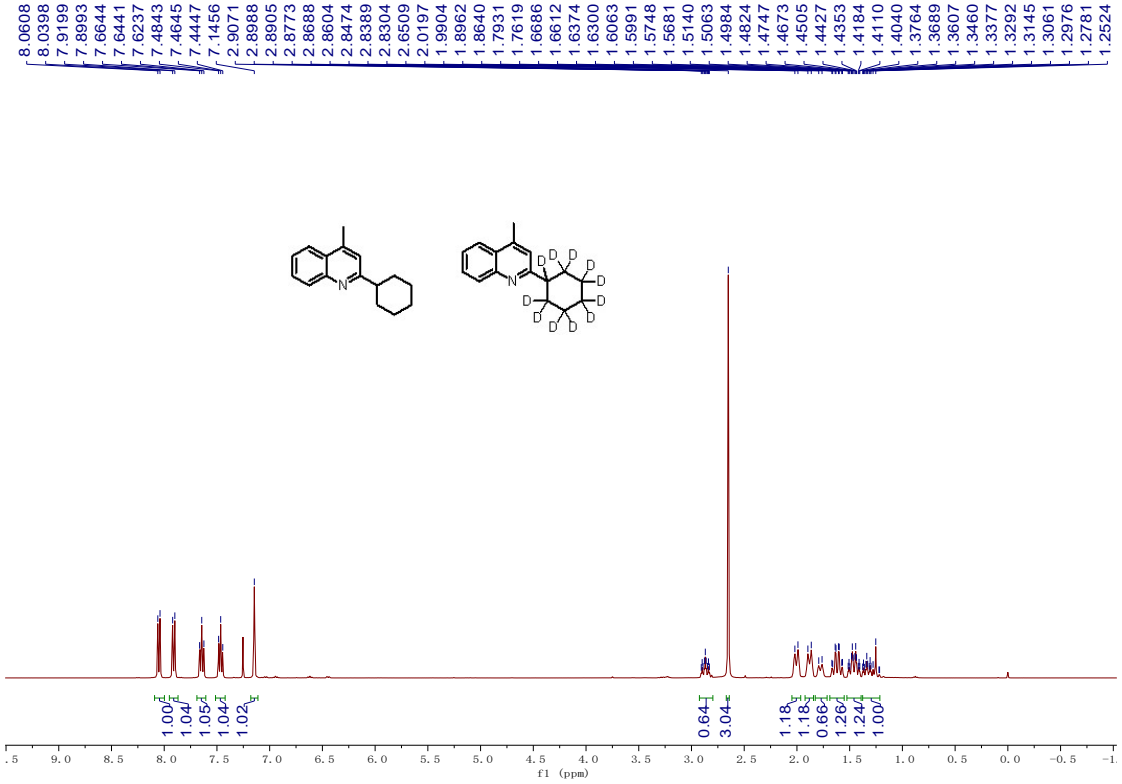
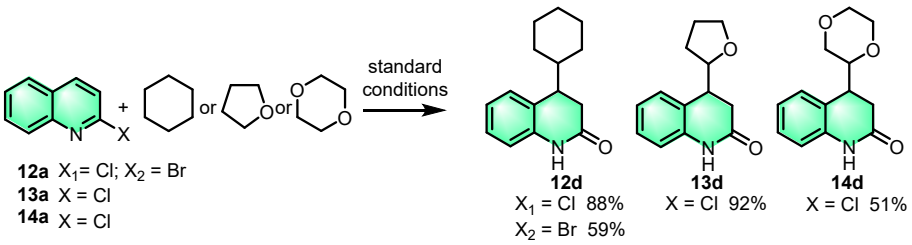


Figure S1. Purified isotope mixtures of 1a and 1c-d_{11}

5) Confirmation experiment



when 2-chloroquinoline (0.2 mmol) or 2-bromoquinoline (0.2 mmol) was coupled with cyclohexane under the application of optimized reaction conditions, 4-cyclohexyl-3,4-dihydroquinolin-2(1H)-one (**12d**) was obtained. Similarly, replacing cyclohexane with tetrahydrofuran or 1,4-dioxane gave similar products (**13d**-**14d**).

6) Reaction quantum yield

The reaction quantum yield (Φ) is given by the following equation:

$$\Phi = \frac{mol\ of\ products}{photon\ flux\ \times\ f\ \times\ t} = \frac{mol\ of\ products}{\frac{light\ intensity}{\frac{hc}{\lambda} \times N_A} \times \left(1 - 10^{-A}\right) \times t}$$

Under the optimal conditions, a yield of 82% product (1.64×10^{-4} mol) is achieved under 6 hours of illumination. A 3 W 385-nm LED was used as the light source, which has a photo flux of 3.21×10^{-8} mol s^{-1} (light intensity: ~100 mW cm^{-2}; h: 6.63×10^{-34} J s; *c*: 3.00×10^{5} m s^{-1}; λ: 385 nm; N_A: 6.022×10^{23} mol). UV-vis absorption spectrum exhibits that the A value of the reaction mixture is over 5.1 at 385 nm (Figure R2). Herein, the Φ of this reaction is calculated to be 23.6%.

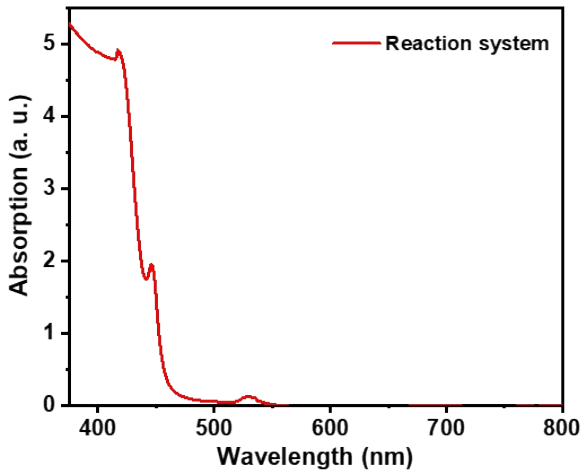
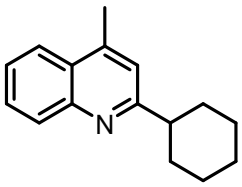


Figure S2. Absorption spectrum of the reaction system.

7) References

1. Q. Q. Zhao, M. Li, X. S. Xue, J. R. Chen and W. J. Xiao, *Org. Lett.*, 2019, **21**, 3861.
2. (a) L. Capaldo, L. L. Quadri, D. Merli and D. Ravelli, *Chem. Commun.*, 2021, **57**, 4424; (b) X. S. Ning, X. Liang, K. F. Hu, C. Z. Yao, J. P. Qu and Y. B. Kang, *Adv. Synth. Cat.*, 2018, **360**, 1590.

2. Characterization data of the products

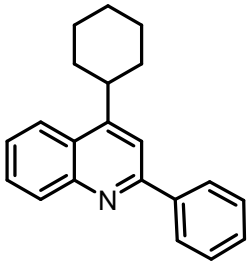


2-cyclohexyl-4-methylquinoline (1c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.05 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 2.87 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.67 (s, 3H), 2.01 (d, *J* = 11.9 Hz, 2H), 1.89 (d, *J* = 12.9 Hz, 2H), 1.78 (d, *J* = 12.5 Hz, 1H), 1.62 (qd, *J* = 12.4, 2.8 Hz, 2H), 1.51 – 1.41 (m, 2H), 1.34 (ddd, *J* = 16.0, 7.9, 3.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 166.51, 147.62, 144.26, 129.49, 128.94, 127.05, 125.37, 123.56, 120.25, 47.60, 26.58, 26.14, 18.84.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{16}H_{20}N$: 226.1590, found: 226.1592.

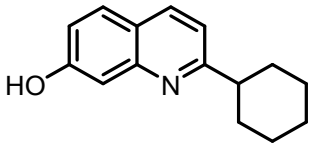


4-cyclohexyl-2-phenylquinoline (2c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.15 (s, 2H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 10.5 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.52 (s, 3H), 7.46 (d, *J* = 5.3 Hz, 1H), 3.36 (t, *J* = 11.2 Hz, 1H), 2.07 (d, *J* = 10.3 Hz, 2H), 1.95 (d, *J* = 9.9 Hz, 2H), 1.86 (d, *J* = 13.0 Hz, 1H), 1.59 (q, *J* = 12.2 Hz, 4H), 1.39 (dd, *J* = 12.7, 3.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 157.37, 153.99, 148.57, 140.25, 139.70, 136.76, 130.68, 129.31, 128.77, 127.64, 125.89, 122.85, 115.51, 39.15, 33.69, 26.99, 26.35.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{21}H_{22}N$: 288.1747, found: 288.1747.

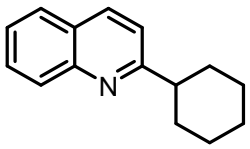


2-cyclohexylquinolin-7-ol (3c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.06 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 2.88 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.02 (d, *J* = 12.1 Hz, 2H), 1.92 – 1.88 (m, 2H), 1.80 (d, *J* = 12.5 Hz, 1H), 1.70 – 1.61 (m, 2H), 1.46 (dt, *J* = 12.8, 3.1 Hz, 2H), 1.33 (td, *J* = 9.2, 4.6 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 164.57, 151.87, 137.50, 136.27, 126.95, 126.63, 121.06, 117.46, 109.54, 46.64, 32.71, 26.52, 26.12.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{15}H_{18}NO$: 228.1383, found: 228.1383.

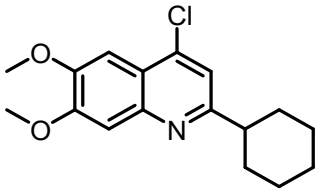


2-cyclohexylquinoline (4c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.07 (t, *J* = 9.2 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 2.95 (dd, *J* = 7.6, 4.3 Hz, 1H), 2.03 (d, *J* = 11.8 Hz, 2H), 1.90 (d, *J* = 12.9 Hz, 2H), 1.79 (d, *J* = 12.6 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.47 (dddd, *J* = 15.5, 12.5, 7.7, 3.0 Hz, 2H), 1.33 (dt, *J* = 12.6, 3.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 166.84, 147.74, 136.36, 128.92, 127.44, 126.96, 125.62, 119.57, 47.63, 32.85, 26.55, 26.10.3

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{15}H_{18}N$: 212.1434, found: 212.1425.

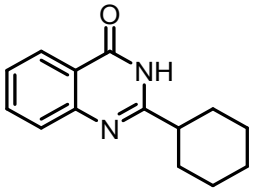


4-chloro-2-cyclohexyl-6,7-dimethoxyquinoline (5c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.38 (d, *J* = 14.6 Hz, 2H), 7.28 (s, 1H), 4.04 (d, *J* = 3.4 Hz, 6H), 2.83 (tt, *J* = 11.9, 3.3 Hz, 1H), 2.02 (d, *J* = 11.8 Hz, 2H), 1.89 (d, *J* = 12.8 Hz, 2H), 1.78 (d, *J* = 12.6 Hz, 1H), 1.58 (qd, *J* = 12.2, 2.3 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.33 (ddt, *J* = 16.0, 12.7, 6.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 164.71, 150.00, 140.68, 120.34, 117.79, 101.70, 56.23, 56.12, 47.13, 32.90, 26.51, 26.02.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{17}H_{21}ClNO_2$: 306.1255, found: 306.1249.

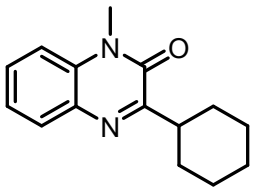


2-cyclohexylquinazolin-4(3H)-one (6c)

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm = 12.07 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 2.60 – 2.50 (m, 1H), 1.89 (d, *J* = 12.4 Hz, 1H), 1.75 (s, 1H), 1.60 (dt, *J* = 36.9, 11.8 Hz, 3H), 1.26 (dq, *J* = 23.4, 12.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ ppm = 162.43, 161.23, 149.37, 127.40, 126.34, 126.10, 43.29, 30.64, 25.94, 25.78.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{17}N_2O$: 229.1335, found: 229.1330.

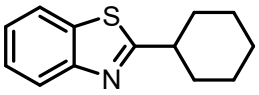


3-cyclohexyl-1-methylquinoxalin-2(1H)-one (7c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.83 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.4, 1.5 Hz, 1H), 7.34 – 7.27 (m, 2H), 3.69 (s, 3H), 3.34 (tt, *J* = 11.6, 3.2 Hz, 1H), 1.96 (d, *J* = 13.6 Hz, 2H), 1.87 (dt, *J* = 12.7, 2.9 Hz, 2H), 1.76 (d, *J* = 12.6 Hz, 1H), 1.59 (td, *J* = 12.2, 2.8 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.31 (dtd, *J* = 12.7, 9.1, 3.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 164.24, 154.52, 132.89, 129.75, 129.34, 123.34, 113.41, 40.79, 30.52, 29.02, 26.32, 26.17.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{15}H_{19}N_2O$: 243.1492, found: 243.1498.

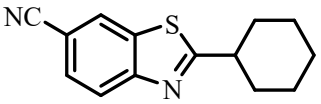


2-cyclohexylbenzo[d]thiazole (8c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.98 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.11 (tt, *J* = 11.7, 3.5 Hz, 1H), 2.21 (d, *J* = 11.6 Hz, 2H), 1.89 (dt, *J* = 12.7, 3.1 Hz, 2H), 1.77 (d, *J* = 12.6 Hz, 1H), 1.68 – 1.60 (m, 2H), 1.44 (ddd, *J* = 15.7, 8.0, 3.1 Hz, 2H), 1.35 – 1.28 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 134.52, 124.50, 122.54, 121.55, 43.45, 33.44, 26.08, 25.79.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{13}H_{17}NS$: 218.1003, found: 218.1002.

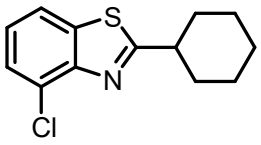


2-cyclohexylbenzo[d]thiazole-6-carbonitrile (9c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.19 (d, *J* = 1.2 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.14 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.25 – 2.19 (m, 2H), 1.91 (dt, *J* = 13.0, 3.3 Hz, 2H), 1.82 – 1.76 (m, 1H), 1.71 – 1.63 (m, 2H), 1.52 – 1.41 (m, 2H), 1.34 (tt, *J* = 12.3, 3.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 182.29, 155.65, 135.21, 129.13, 126.42, 123.39, 118.89, 108.05, 43.69, 33.32, 25.97, 25.71.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{15}N_2S$: 243.0951, found: 243.0951.

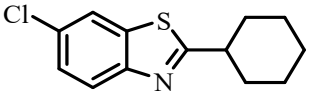


4-chloro-2-cyclohexylbenzo[d]thiazole (10c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.74 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.25 (m, 1H), 3.22 (tt, *J* = 11.7, 3.5 Hz, 1H), 2.23 (d, *J* = 13.2 Hz, 2H), 1.89 (dt, *J* = 12.6, 3.0 Hz, 2H), 1.78 (d, *J* = 12.5 Hz, 1H), 1.63 – 1.56 (m, 2H), 1.45 (dtd, *J* = 12.6, 9.5, 3.1 Hz, 2H), 1.32 (dt, *J* = 12.4, 3.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 179.13, 150.05, 136.13, 127.37, 126.12, 125.06, 120.19, 43.75, 33.77, 26.07, 25.75.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{13}H_{15}ClNS$: 252.0608, found: 252.0608.

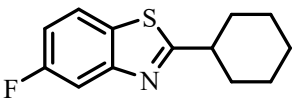


6-chloro-2-cyclohexylbenzo[d]thiazole (11c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.86 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 1.9 Hz, 1H), 7.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.08 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.19 (d, *J* = 11.2 Hz, 2H), 1.89 (dt, *J* = 12.8, 3.1 Hz, 2H), 1.77 (dt, *J* = 12.6, 3.1 Hz, 1H), 1.67 – 1.58 (m, 2H), 1.44 (dtd, *J* = 12.6, 9.4, 3.2 Hz, 2H), 1.30 (ddd, *J* = 16.0, 7.9, 3.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 178.15, 151.74, 135.83, 130.42, 126.59, 123.33, 121.20, 43.45, 33.37, 26.05, 25.79.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{13}H_{15}ClNS$: 252.0608, found: 252.0608.



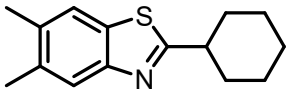
2-cyclohexyl-5-fluorobenzo[d]thiazole (12c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.76 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.65 (dd, *J* = 9.6, 2.5 Hz, 1H), 7.11 (td, *J* = 8.8, 2.5 Hz, 1H), 3.10 (tt, *J* = 11.7, 3.6 Hz, 1H), 2.20 (d, *J* = 11.3 Hz, 2H), 1.89 (dt, *J* = 12.8, 3.2 Hz, 2H), 1.79 – 1.75 (m, 1H), 1.68 – 1.58 (m, 2H), 1.44 (ddd, *J* = 15.8, 8.0, 3.2 Hz, 2H), 1.36 – 1.28 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 180.28, 162.89, 160.48, 154.08, 153.96, 129.91, 122.18, 122.08, 113.25, 113.00, 108.91, 108.68, 43.55, 33.36, 26.02, 25.75.

^{19}F NMR (376 MHz, Chloroform-*d*) δ ppm = -116.54.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{13}H_{15}FNS$: 236.0904, found: 236.0904.

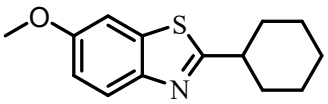


2-cyclohexyl-5,6-dimethylbenzo[d]thiazole (13c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.73 (s, 1H), 7.58 (s, 1H), 3.06 (tt, *J* = 11.7, 3.6 Hz, 1H), 2.36 (d, *J* = 5.6 Hz, 6H), 2.18 (d, *J* = 11.8 Hz, 2H), 1.90 – 1.84 (m, 2H), 1.77 – 1.73 (m, 1H), 1.66 – 1.55 (m, 2H), 1.48 – 1.37 (m, 2H), 1.35 – 1.25 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 176.51, 151.90, 134.93, 133.82, 131.93, 122.81, 43.42, 33.50, 26.15, 25.88, 20.22, 20.11.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{15}H_{20}NS$: 246.1311, found: 246.1314.

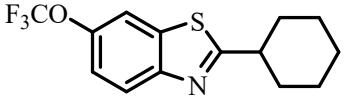


2-cyclohexyl-6-methoxybenzo[d]thiazole (14c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.86 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.87 (s, 3H), 3.07 (tt, *J* = 11.7, 3.6 Hz, 1H), 2.20 (d, *J* = 15.4 Hz, 2H), 1.89 (dt, *J* = 12.8, 3.2 Hz, 2H), 1.77 (dt, *J* = 14.4, 3.2 Hz, 1H), 1.68 – 1.57 (m, 2H), 1.44 (dtd, *J* = 12.6, 9.4, 3.3 Hz, 2H), 1.33 (ddd, *J* = 15.8, 7.9, 3.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 175.07, 157.24, 147.47, 135.73, 122.94, 114.93, 104.31, 55.80, 43.29, 33.42, 26.08, 25.80.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{18}NOS$: 248.1104, found: 248.1101.



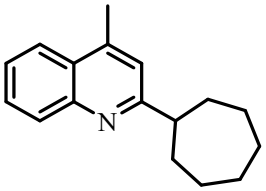
2-cyclohexyl-6-(trifluoromethoxy)benzo[d]thiazole (15c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.95 (d, *J* = 8.9 Hz, 1H), 7.71 (s, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 3.10 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.23 – 2.17 (m, 2H), 1.89 (dt, *J* = 12.8, 3.2 Hz, 2H), 1.79 – 1.73 (m, 1H), 1.68 – 1.56 (m, 2H), 1.45 (dtd, *J* = 12.6, 9.4, 3.2 Hz, 2H), 1.33 (tt, *J* = 12.3, 3.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 178.92, 151.71, 146.06, 135.43, 123.34, 119.79, 114.26, 43.52, 33.38, 26.04, 25.77.

^{19}F NMR (376 MHz, Chloroform-*d*) δ ppm = -58.06.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{15}F_3NOS$: 302.0821, found: 302.0820.

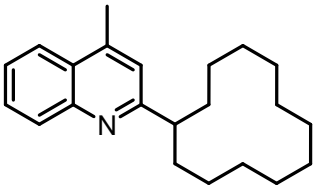


2-cycloheptyl-4-methylquinoline (1d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.05 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.14 (s, 1H), 3.07 – 3.00 (m, 1H), 2.68 (s, 3H), 2.07 – 2.00 (m, 2H), 1.87 – 1.59 (m, 10H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 135.98, 129.30, 129.09, 126.88, 125.73, 123.61, 122.14, 45.03, 29.71, 21.05, 18.71.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{17}H_{22}N$: 240.1747, found: 240.1741.

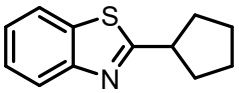


2-cyclododecyl-4-methylquinoline (2d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.07 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.13 (s, 1H), 3.10 (p, *J* = 6.5 Hz, 1H), 2.68 (s, 3H), 1.91 (dd, *J* = 13.0, 6.0 Hz, 2H), 1.75 – 1.70 (m, 2H), 1.53 – 1.30 (m, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 166.71, 128.79, 126.98, 125.29, 123.52, 121.42, 30.18, 23.98, 23.74, 22.94, 22.58, 18.81.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{22}H_{32}N$: 310.2529, found: 310.2530.

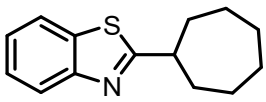


2-cyclopentylbenzo[d]thiazole (3d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 3.56 (p, *J* = 8.4 Hz, 1H), 2.30 – 2.21 (m, 2H), 1.94 (ddd, *J* = 28.5, 14.3, 7.9 Hz, 4H), 1.79 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 177.29, 153.14, 134.80, 125.90, 124.61, 122.51, 121.55, 44.83, 34.14, 25.66.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{12}H_{14}NS$: 218.1003, found: 218.1002.

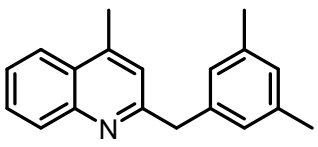


2-cycloheptylbenzo[d]thiazole (4d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 7.96 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 8.1 Hz, 1H), 3.29 (ddd, *J* = 14.1, 9.9, 4.1 Hz, 1H), 2.27 – 2.18 (m, 2H), 1.87 (ddd, *J* = 17.4, 8.4, 4.9 Hz, 4H), 1.72 – 1.57 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 178.69, 153.01, 134.68, 125.77, 124.48, 122.53, 121.50, 45.51, 35.36, 28.08, 26.54.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{19}NS$: 232.1160, found: 232.1165.

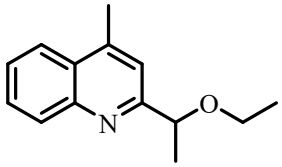


2-(3,5-dimethylbenzyl)-4-methylquinoline (5d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.13 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 6.96 (s, 2H), 6.89 (s, 1H), 4.24 (s, 2H), 2.63 (s, 3H), 2.30 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 161.11, 144.52, 139.16, 138.09, 128.11, 127.06, 125.68, 123.61, 122.23, 45.40, 18.70.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{19}H_{20}N$: 262.1590, found: 262.1591.

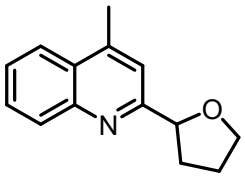


2-(1-ethoxyethyl)-4-methylquinoline (6d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.07 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.70 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.55 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.45 (s, 1H), 4.68 (q, *J* = 6.6 Hz, 1H), 3.55 – 3.47 (m, 1H), 3.41 (dd, *J* = 16.3, 7.0 Hz, 1H), 2.73 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 163.99, 129.53, 129.15, 127.66, 125.97, 123.69, 118.30, 79.70, 64.64, 22.67, 18.99, 15.48.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{18}NO$: 216.1383, found: 216.1383.

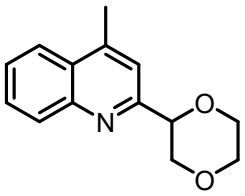


4-methyl-2-(tetrahydrofuran-2-yl)quinoline (7d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.05 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.44 (s, 1H), 5.14 (t, *J* = 6.9 Hz, 1H), 4.22 – 4.15 (m, 1H), 4.04 (q, *J* = 7.0 Hz, 1H), 2.71 (s, 3H), 2.55 – 2.46 (m, 1H), 2.11 – 1.98 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 163.09, 147.36, 144.91, 129.57, 129.11, 127.47, 125.81, 123.68, 118.61, 82.08, 69.24, 33.28, 25.98, 18.87.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{16}NO$: 214.1226, found: 214.1232.

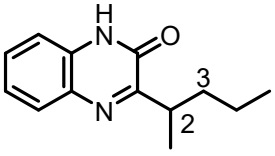


2-(1,4-dioxan-2-yl)-4-methylquinoline (8d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.07 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 4.90 (dd, *J* = 10.1, 2.8 Hz, 1H), 4.23 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.01 (dd, *J* = 9.9, 2.8 Hz, 2H), 3.87 – 3.77 (m, 2H), 3.69 – 3.59 (m, 1H), 2.72 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 157.84 , 129.82 , 129.38 , 126.30 , 123.76 , 119.16 , 78.84 , 71.16 , 67.14 , 66.48 , 18.95.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{16}NO_2$: 230.1176, found: 230.1168.

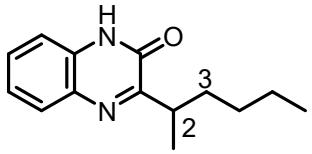


C2/C3 = 3:1, **1-methyl-3-(pentan-2-yl)quinoxalin-2(1H)-one (9d)**

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 12.46 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.29 (m, 2H), 3.69 – 3.29 (m, 1H), 1.94 – 1.74 (m, 2H), 1.69 – 1.52 (m, 1H), 1.41 – 1.32 (m, 4H), 0.98 – 0.91 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 165.37, 133.02 , 130.76 , 129.57 , 128.90 , 124.02 , 115.60 , 44.14, 37.05 , 35.38 , 25.92 , 20.79 , 18.37 , 14.33 , 12.06 .

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{13}H_{17}N_2O$: 217.1335, found: 217.1337.

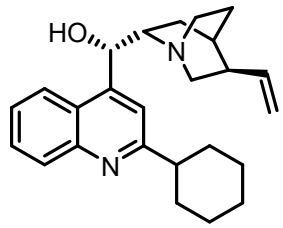


C2/C3 = 3:2, **3-(hexan-2-yl)-1-methylquinoxalin-2(1H)-one (10d)**

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 12.24 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 3.62 – 3.42 (m, 1H), 1.99 – 1.57 (m, 4H), 1.34 (t, *J* = 8.2 Hz, 5H), 0.90 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 165.35 , 164.72, 156.78, 156.40 , 133.10, 132.97, 130.73 , 129.51 , 128.90 , 123.96 , 115.49 , 42.34, 35.56 , 34.48 , 29.80 , 28.18, 26.37, 22.86 , 20.77 , 18.34 , 14.37 , 14.11 , 12.07 .

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{14}H_{19}N_2O$: 231.1492, found: 231.1490.

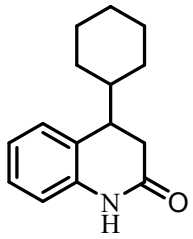


(1S)-(2-cyclohexylquinolin-4-yl)((2S)-5-vinylquinuclidin-2-yl)methanol (11d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.01 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.48 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.16 – 6.00 (m, 1H), 5.85 (s, 1H), 5.40 (s, 1H), 5.13 – 5.02 (m, 2H), 3.61 (dd, *J* = 12.5, 8.0 Hz, 1H), 3.04 – 2.69 (m, 5H), 2.28 – 2.09 (m, 2H), 1.92 – 1.69 (m, 6H), 1.55 (q, *J* = 12.3 Hz, 3H), 1.44 – 1.25 (m, 4H), 0.98 (t, *J* = 8.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 166.53, 149.00, 147.72, 140.13 , 129.68, 128.80 , 125.81, 124.19, 122.45 , 116.73 , 115.10 , 70.94 , 60.00 , 50.01 , 49.46 , 47.73 , 39.84 , 32.83 , 32.72 , 28.36 , 26.49 , 26.02 , 25.90 , 19.93 .

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{25}H_{33}N_2O$: 377.2587, found: 377.2593.

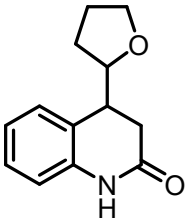


4-cyclohexyl-3,4-dihydroquinolin-2(1H)-one (12d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 9.39 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 2.79 – 2.61 (m, 3H), 1.82 (d, *J* = 12.4 Hz, 1H), 1.70 (t, *J* = 11.0 Hz, 2H), 1.60 – 1.50 (m, 2H), 1.12 (p, *J* = 12.6 Hz, 3H), 0.98 (d, *J* = 12.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 172.28, 136.98, 129.14, 127.45, 126.31, 122.57, 115.79, 42.27, 41.55, 33.57, 30.84, 29.70, 29.56, 26.35, 26.21.

HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{15}H_{20}NO$: 230.1539, found: 230.1540.

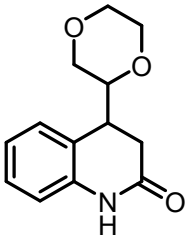


4-(tetrahydrofuran-2-yl)-3,4-dihydroquinolin-2(1H)-one (13d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.87 (d, *J* = 20.1 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.00 (q, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.86 – 3.71 (m, 2H), 3.09 – 2.98 (m, 1H), 2.92 – 2.62 (m, 2H), 1.99 (dt, *J* = 12.2, 6.2 Hz, 1H), 1.86 – 1.80 (m, 2H), 1.69 – 1.59 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 171.50, 171.36, 137.42, 136.94, 129.51, 128.96, 128.12, 124.23, 123.03, 115.81, 81.15, 80.43, 68.30, 68.25, 41.46, 41.13, 33.06, 32.69, 29.41, 28.91, 25.89, 25.78.

HRMS (ESI-TOF) (m/z) for $[M+Na]^+$ calculated for $C_{13}H_{15}NO_2Na$: 240.0995, found: 240.0995.



4-(1,4-dioxan-2-yl)-3,4-dihydroquinolin-2(1H)-one (14d)

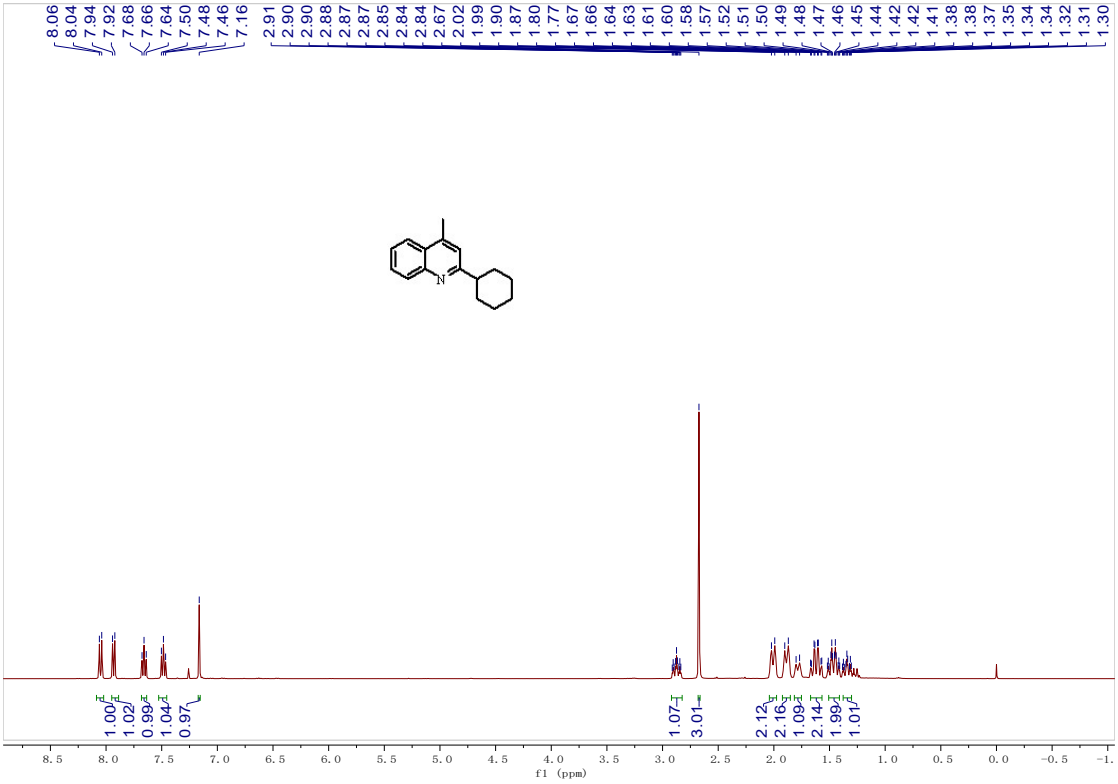
^{1}H NMR (400 MHz, Chloroform-*d*) δ ppm = 8.63 (s, 1H), 7.22 (t, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 3.81 (d, *J* = 11.1 Hz, 1H), 3.72 – 3.65 (m, 2H), 3.62 – 3.54 (m, 3H), 3.45 – 3.35 (m, 1H), 3.08 – 2.92 (m, 2H), 2.64 (dd, *J* = 16.3, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ ppm = 137.20, 128.98, 128.57, 123.13, 122.64, 116.06, 74.69, 69.78, 66.96, 66.40, 38.99.

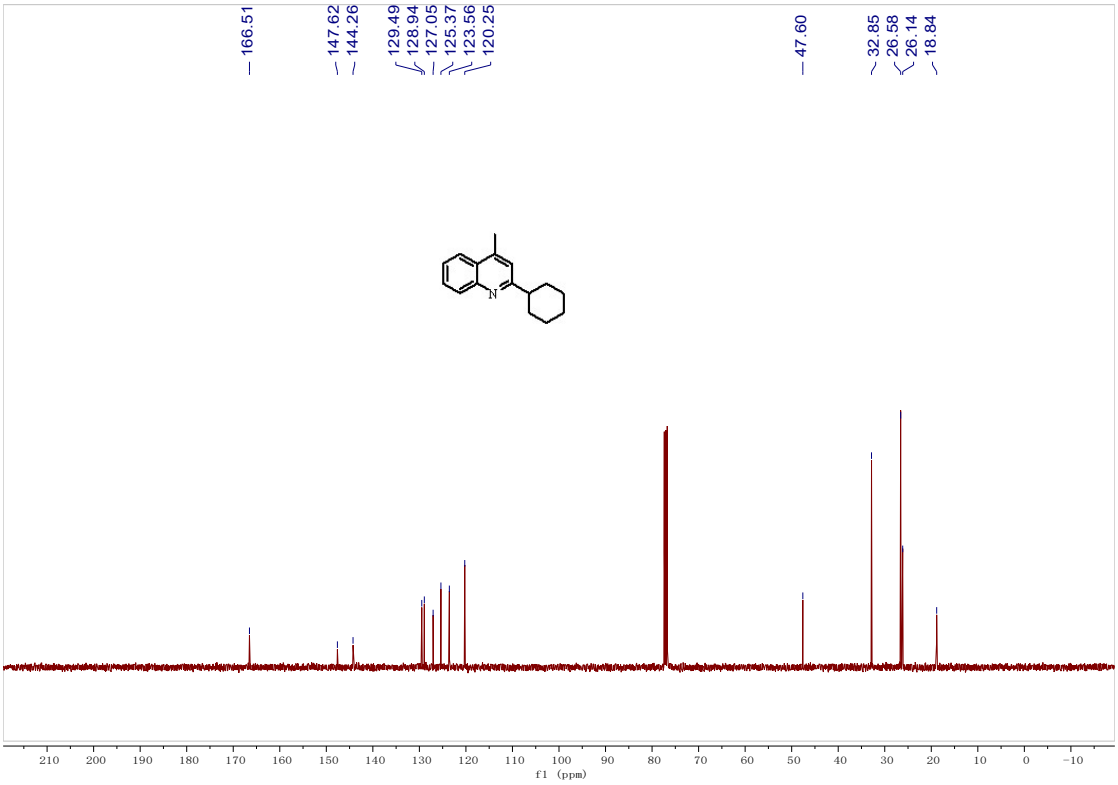
HRMS (ESI-TOF) (m/z) for $[M+H]^+$ calculated for $C_{13}H_{16}NO_2$: 234.1125, found: 234.1128.

3. NMR spectra for the products

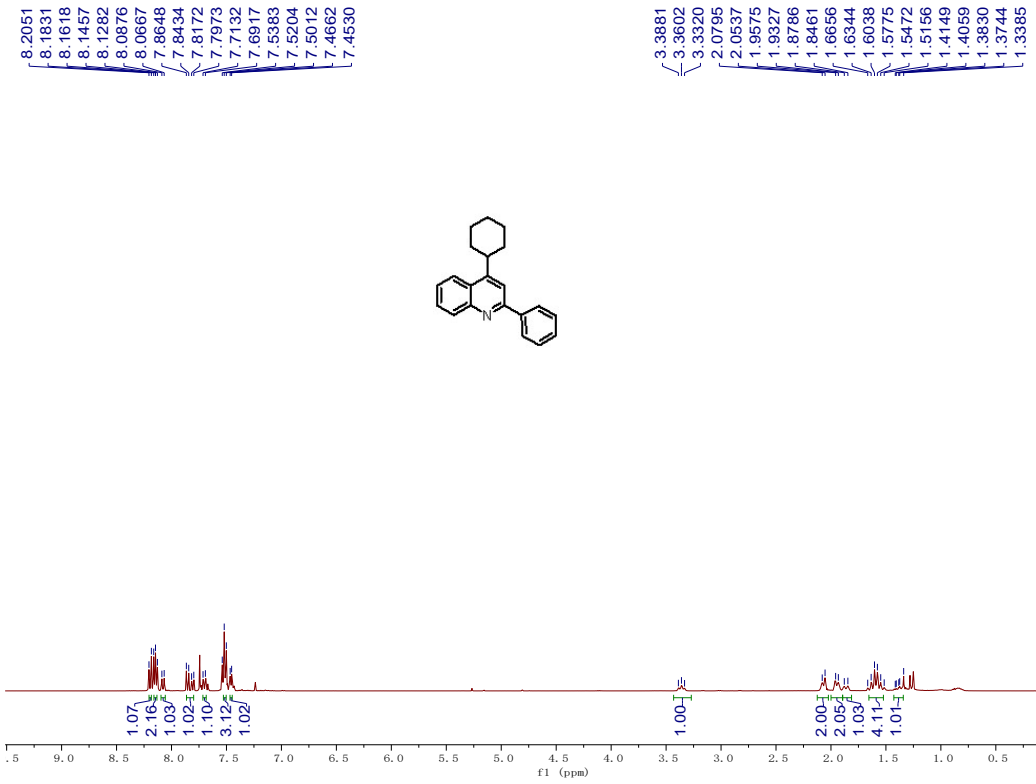
^{1}H NMR spectrum of compound **1c** in $CDCl_3$ (400 MHz):



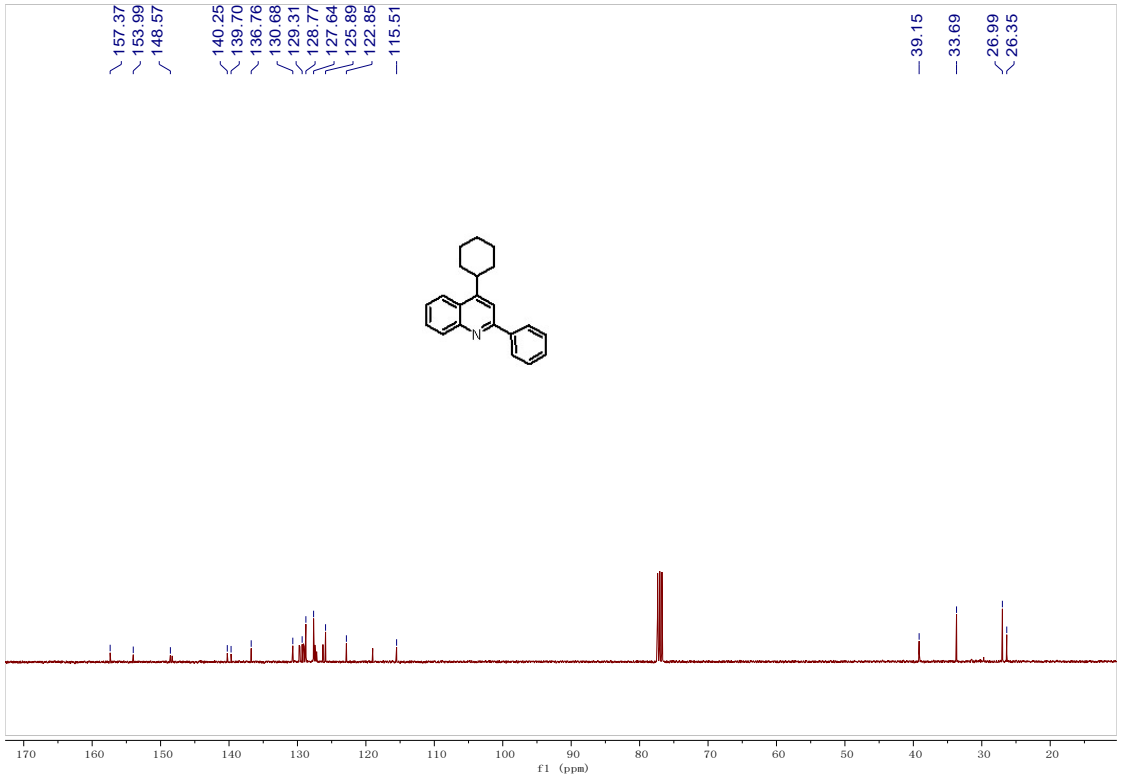
^{13}C NMR spectrum of compound **1c** in $CDCl_3$ (101 MHz):



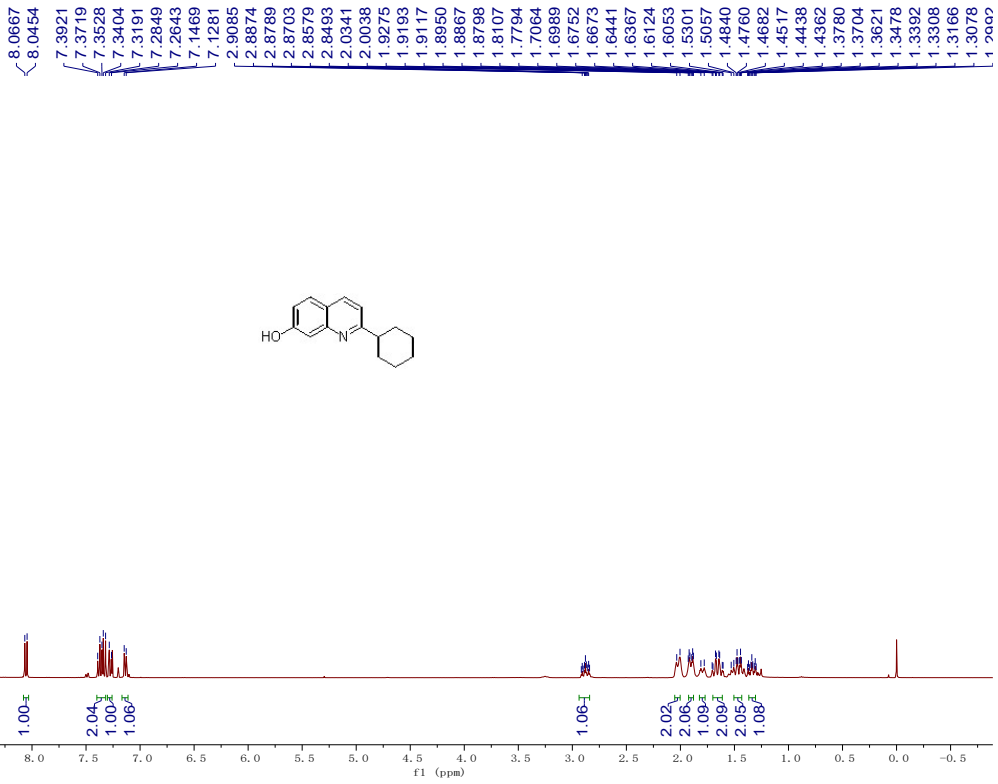
^{1}H NMR spectrum of compound **2c** in $CDCl_3$ (400 MHz):



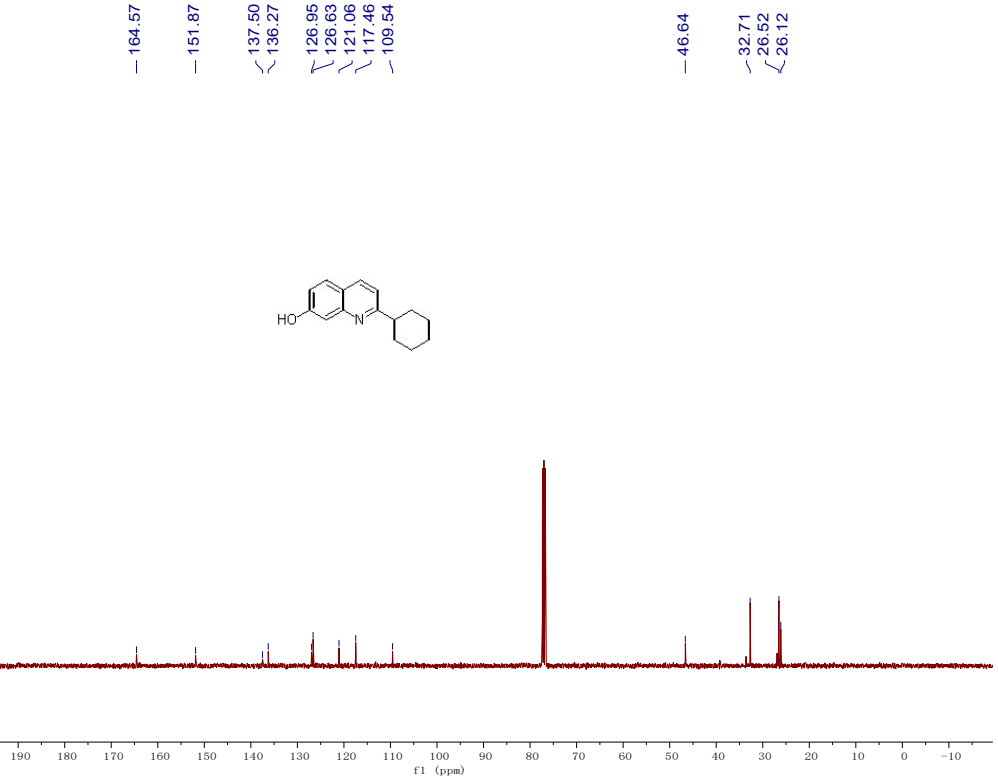
^{13}C NMR spectrum of compound **2c** in $CDCl_3$ (101 MHz):



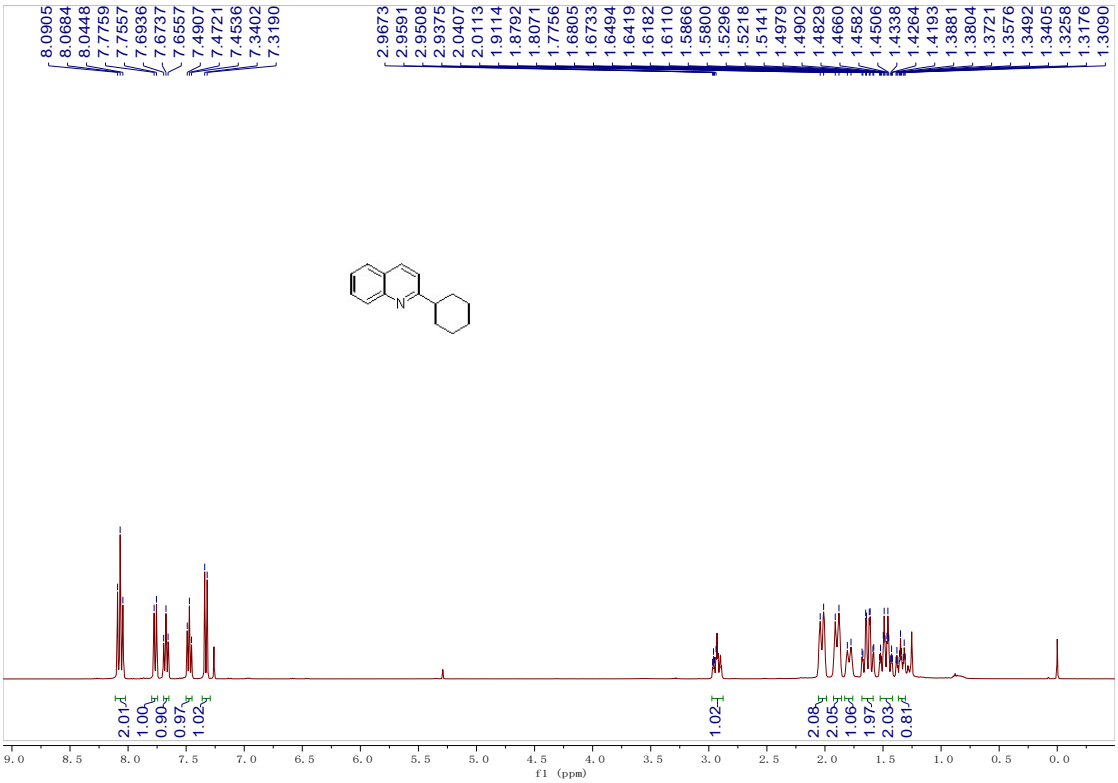
^{1}H NMR spectrum of compound **3c** in $CDCl_3$ (400 MHz):



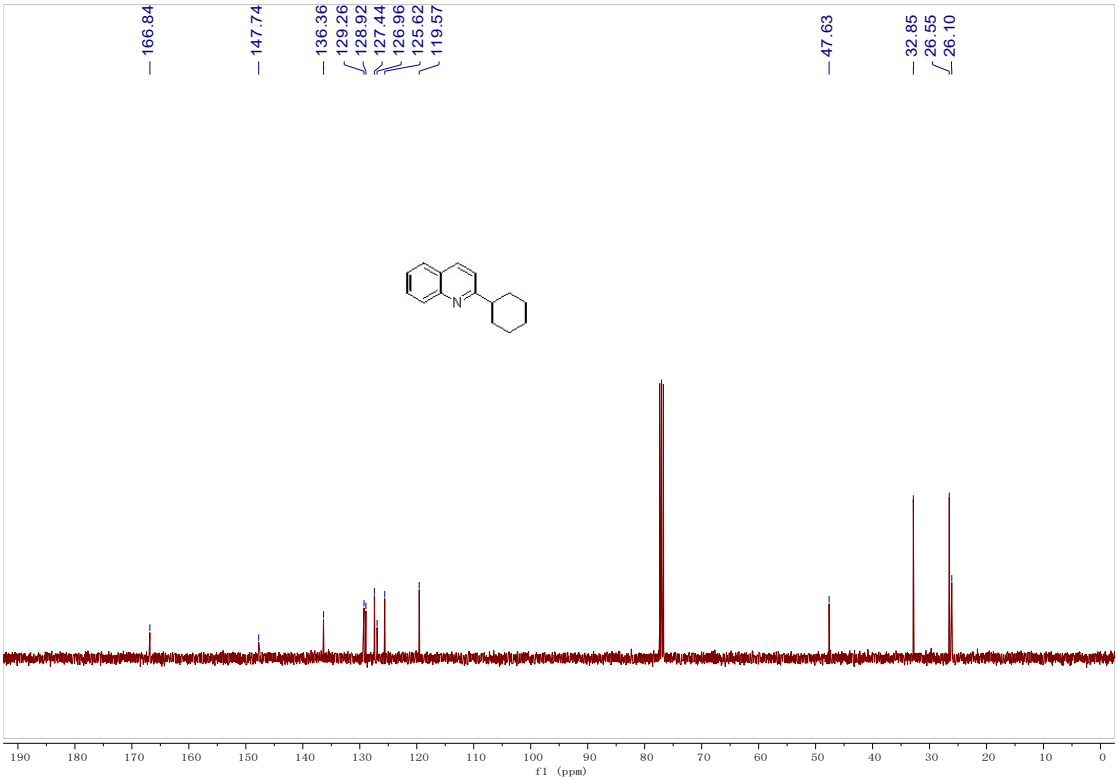
^{13}C NMR spectrum of compound **3c** in $CDCl_3$ (101 MHz):



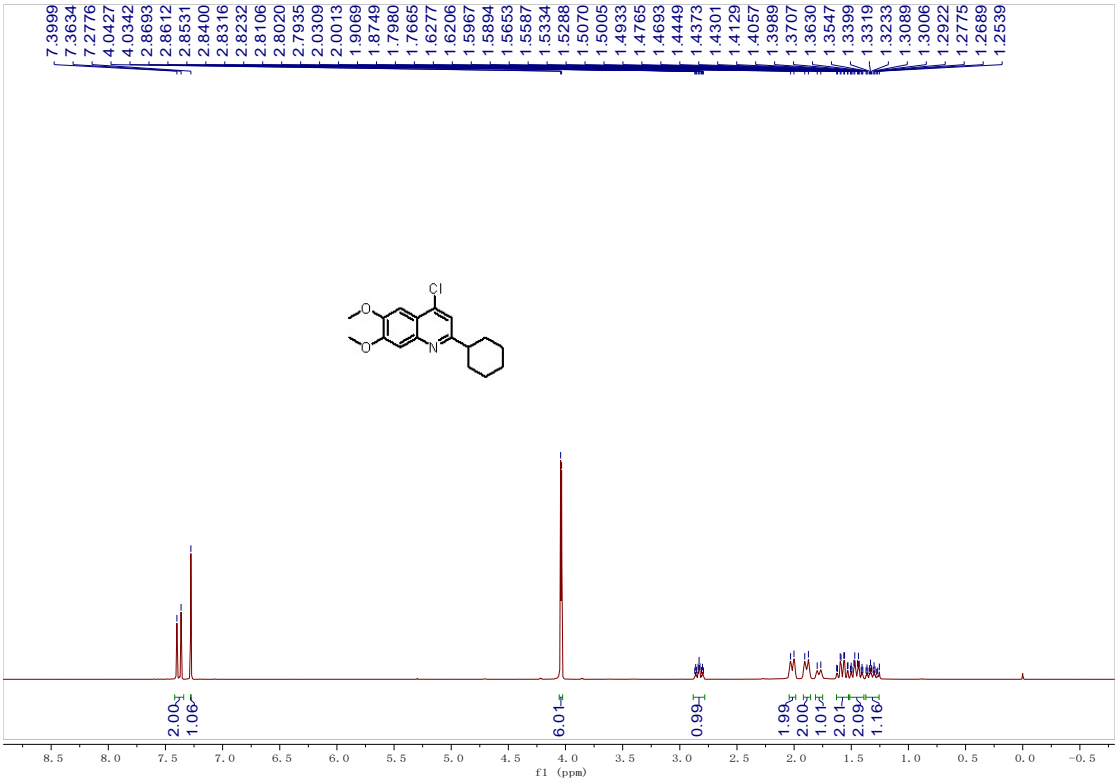
^{1}H NMR spectrum of compound **4c** in $CDCl_3$ (400 MHz):



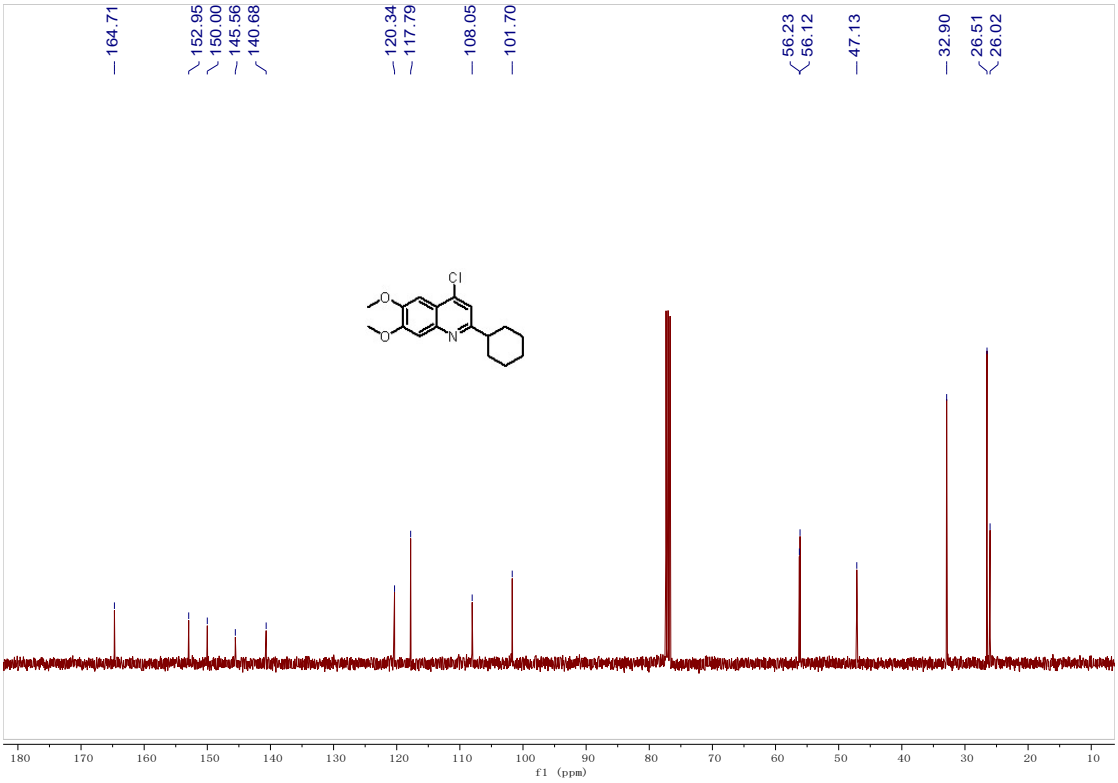
^{13}C NMR spectrum of compound **4c** in $CDCl_3$ (101 MHz):



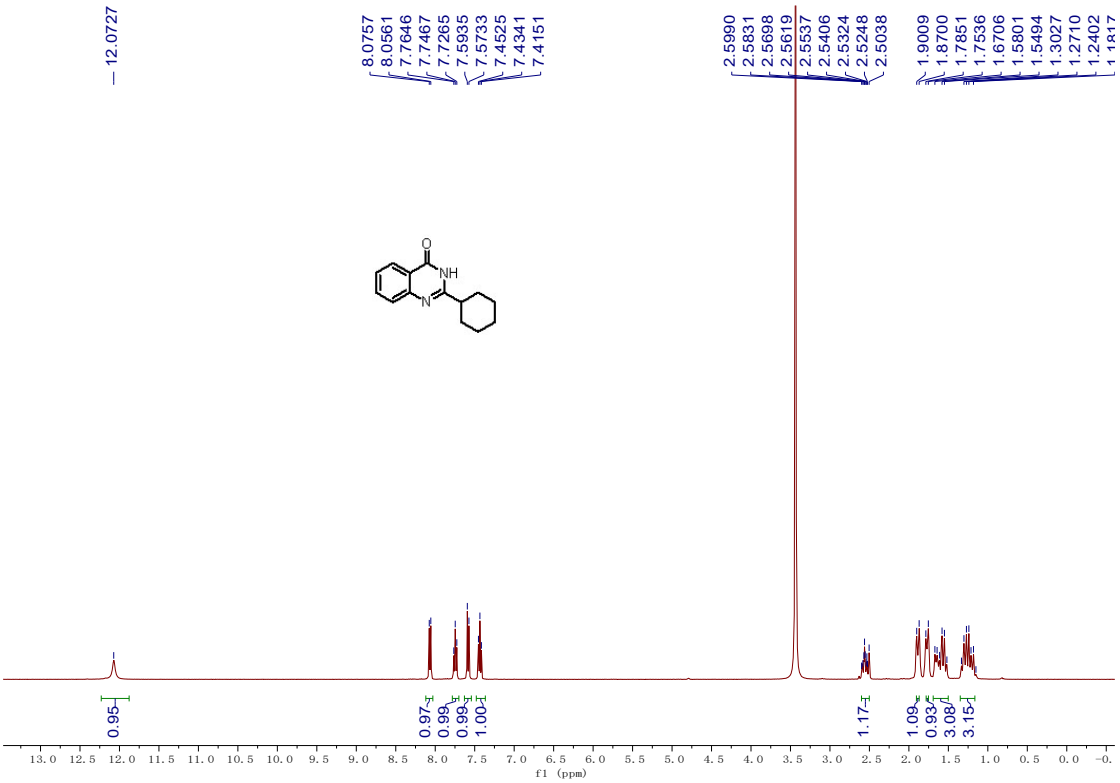
^{1}H NMR spectrum of compound **5c** in $CDCl_3$ (400 MHz):



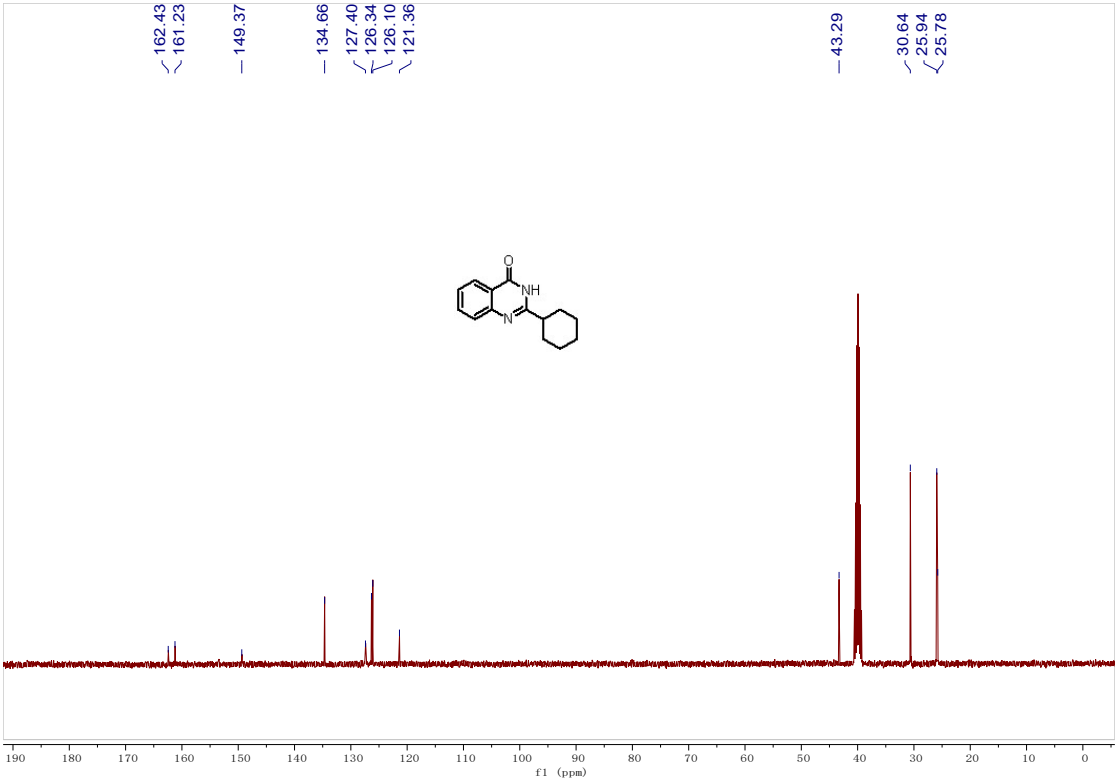
^{13}C NMR spectrum of compound **5c** in $CDCl_3$ (101 MHz):



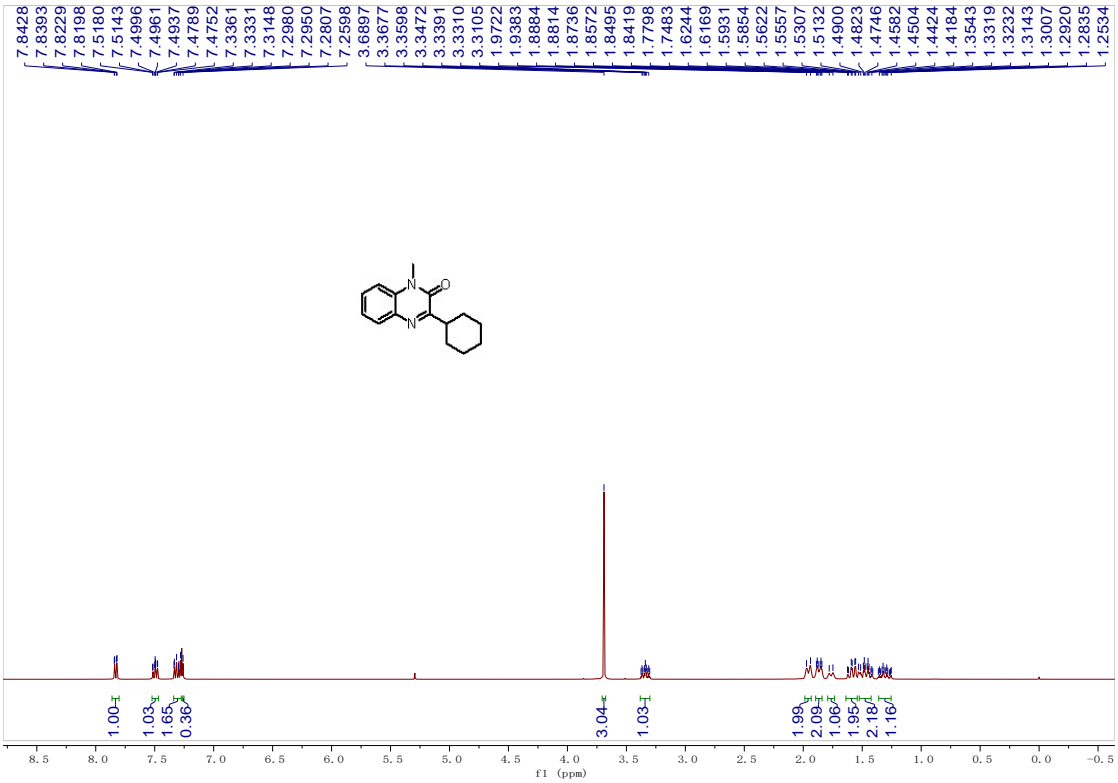
^{1}H NMR spectrum of compound **6c** in DMSO (400 MHz):



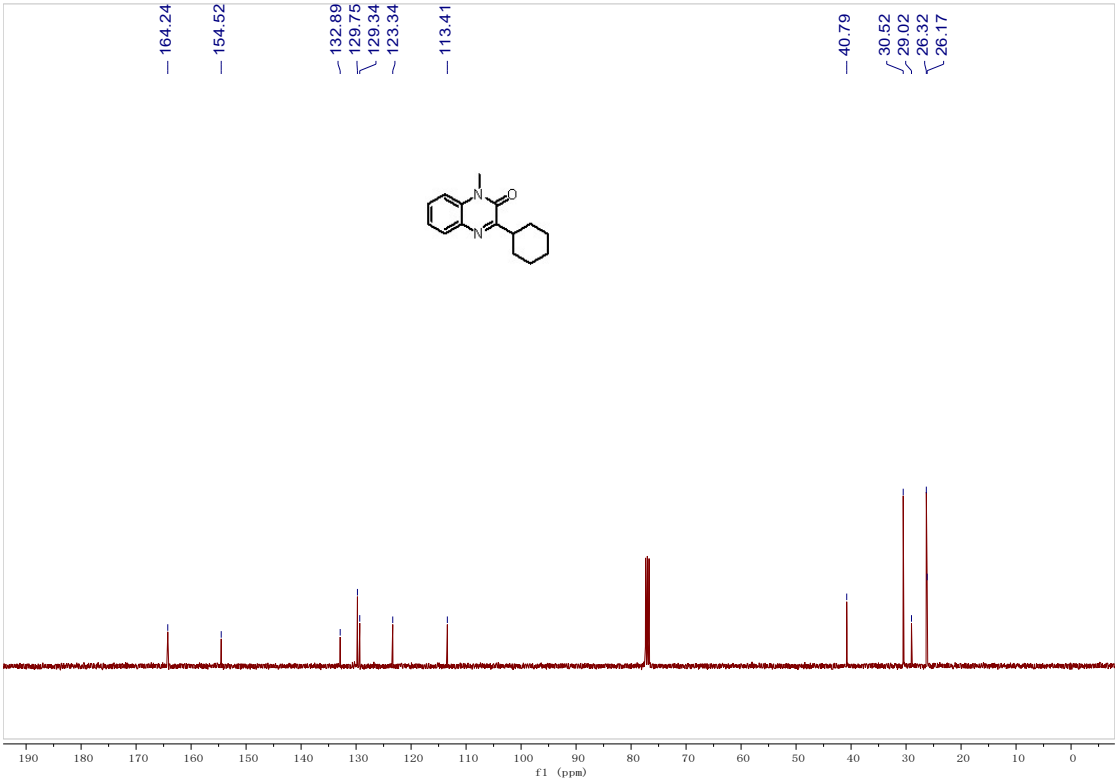
^{13}C NMR spectrum of compound **6c** in DMSO (101 MHz):



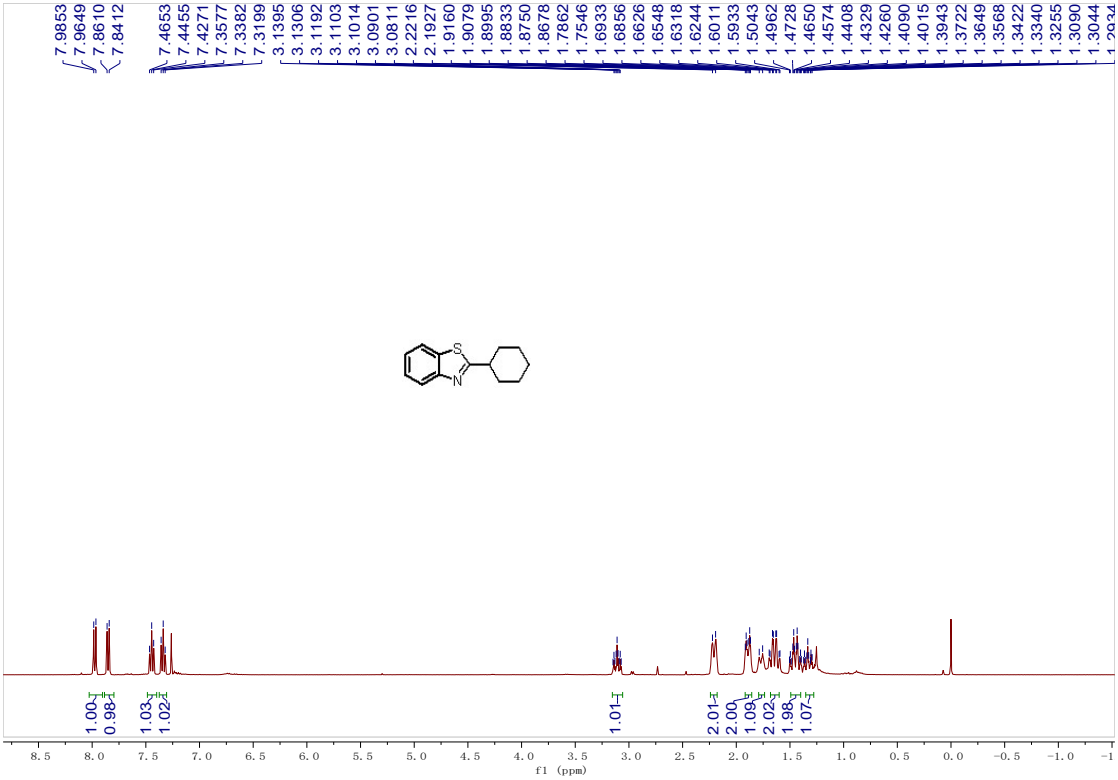
^{1}H NMR spectrum of compound **7c** in $CDCl_3$ (400 MHz):



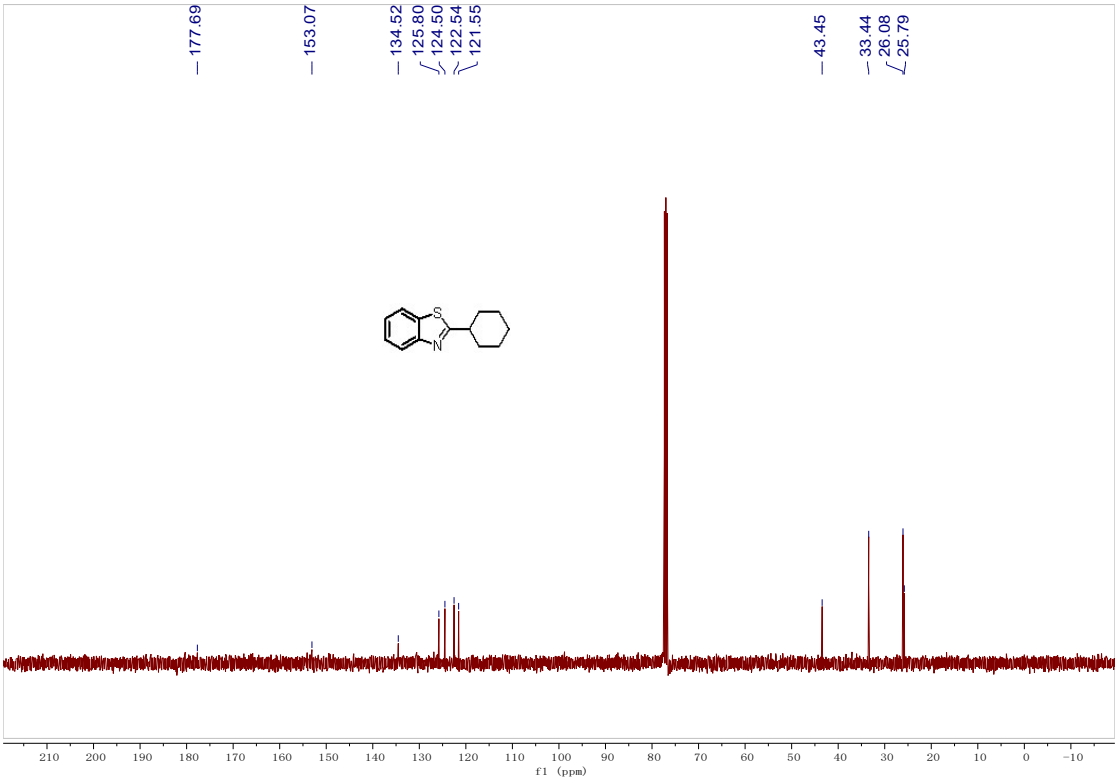
^{13}C NMR spectrum of compound **7c** in $CDCl_3$ (101 MHz):



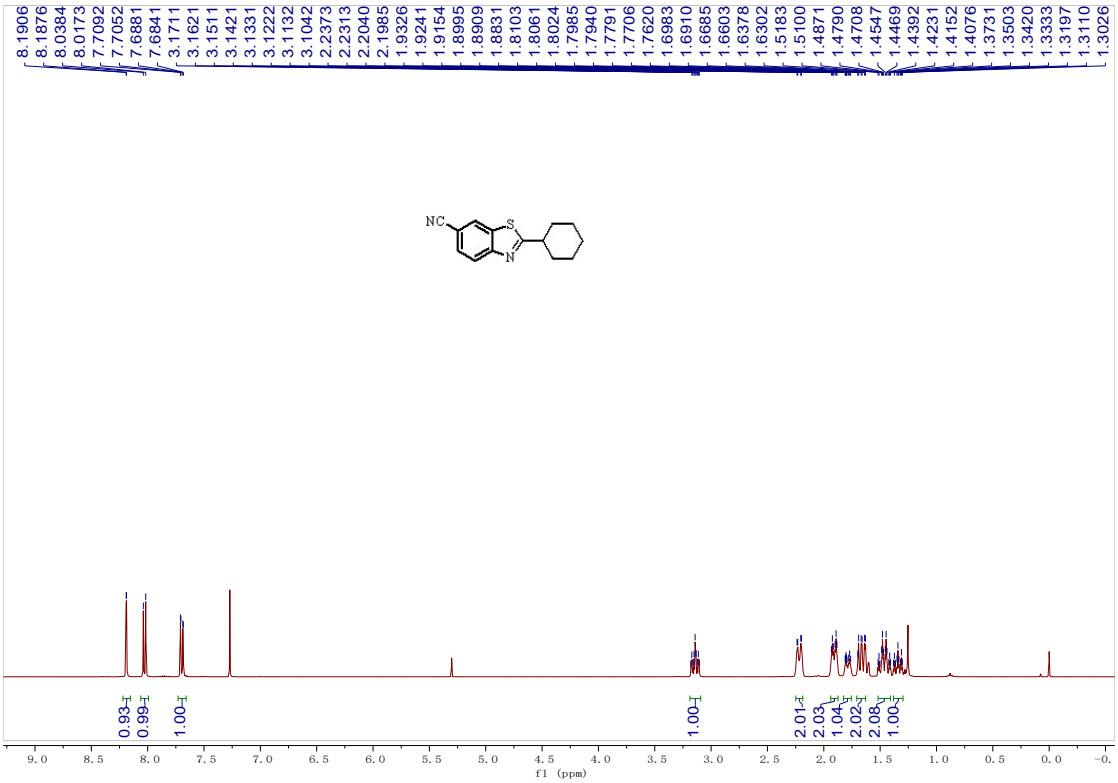
^{1}H NMR spectrum of compound **8c** in $CDCl_3$ (400 MHz):



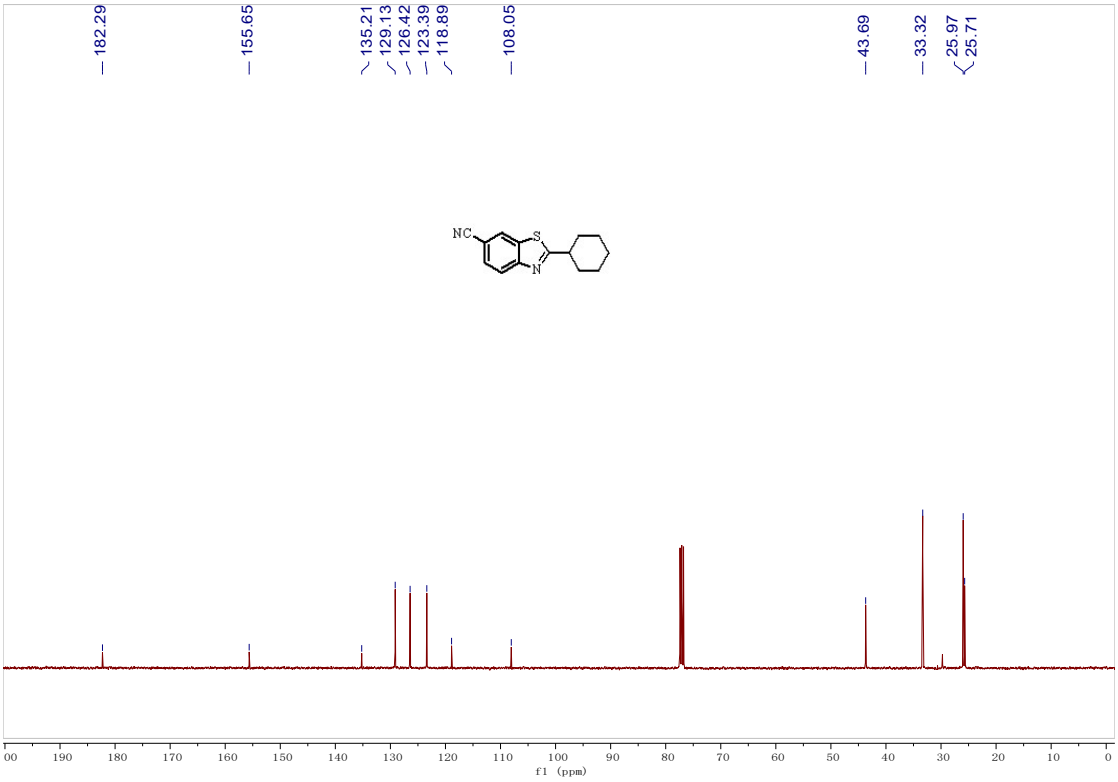
^{13}C NMR spectrum of compound **8c** in $CDCl_3$ (101 MHz):



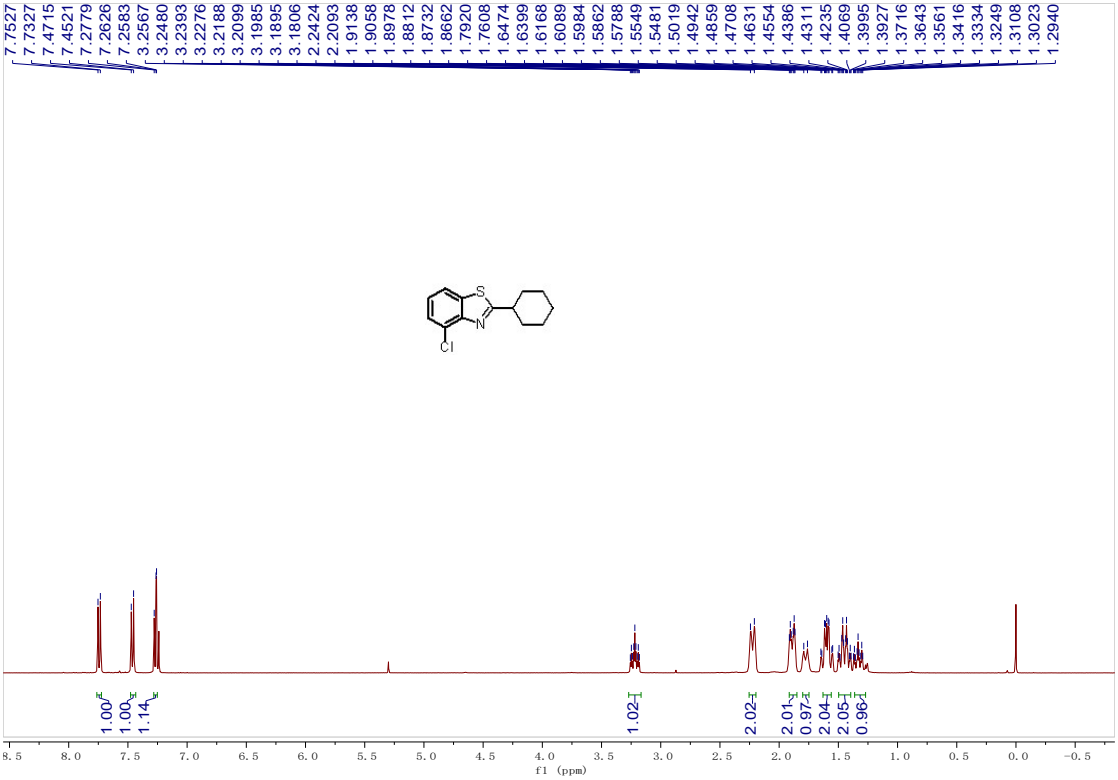
^{1}H NMR spectrum of compound **9c** in $CDCl_3$ (400 MHz):



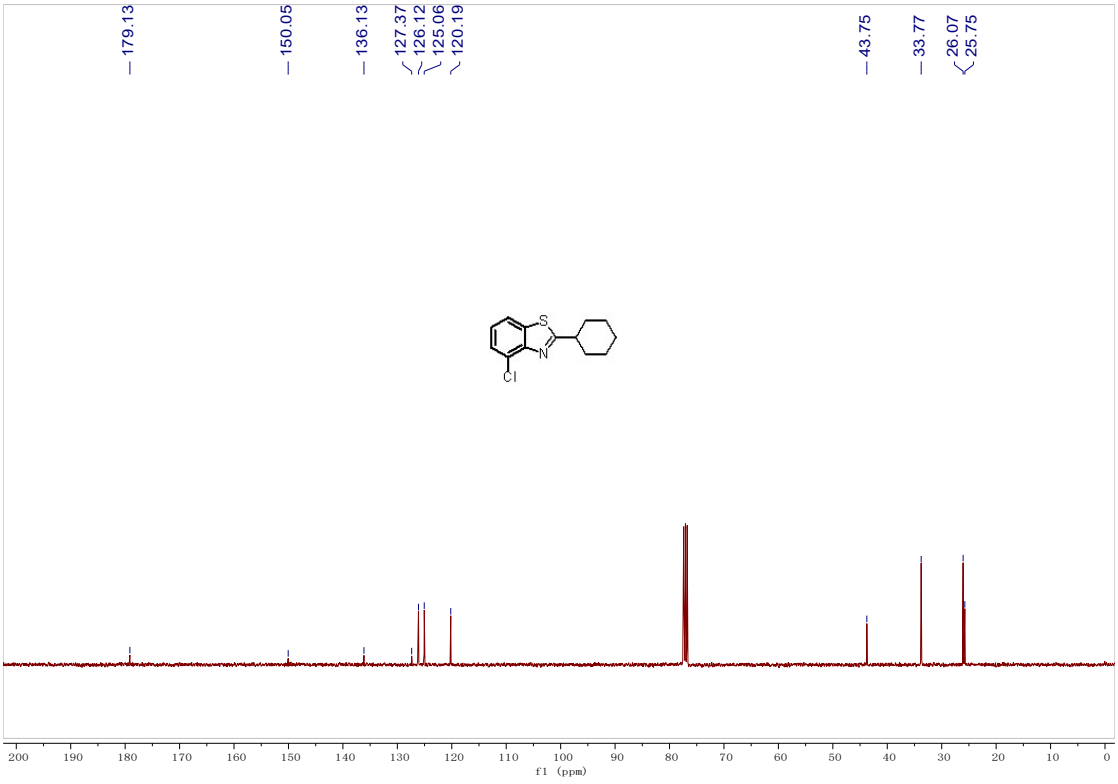
^{13}C NMR spectrum of compound **9c** in $CDCl_3$ (101 MHz):



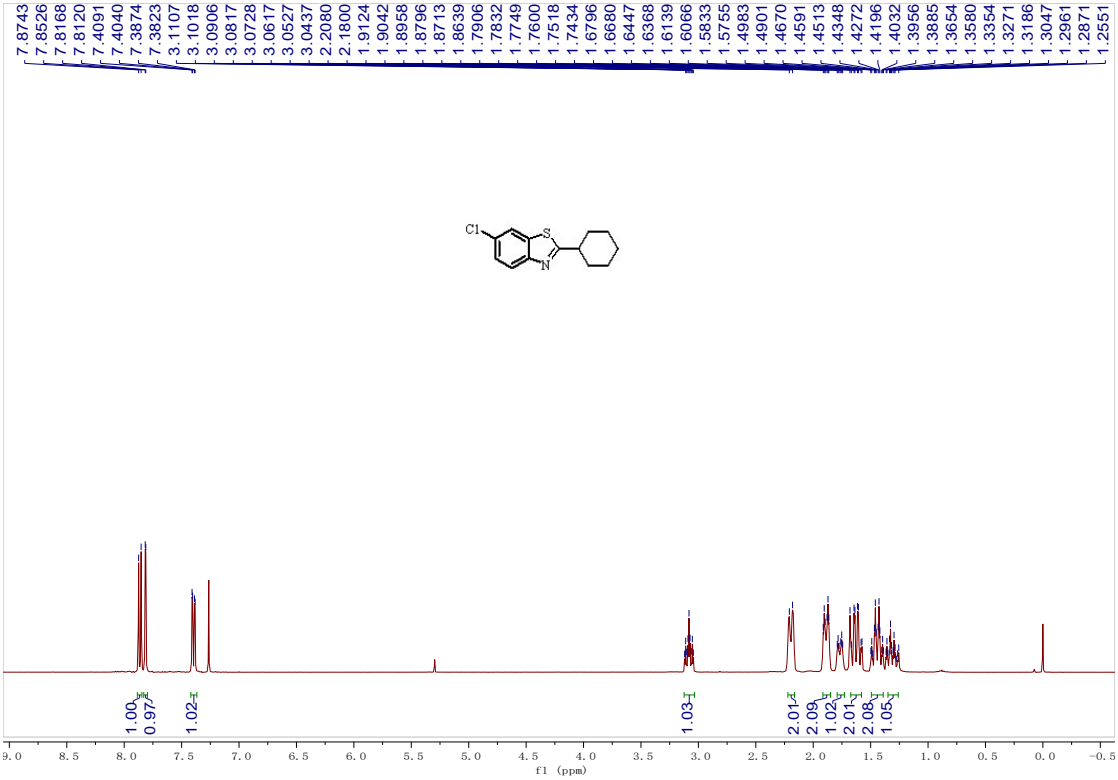
^{1}H NMR spectrum of compound **10c** in $CDCl_3$ (400 MHz):



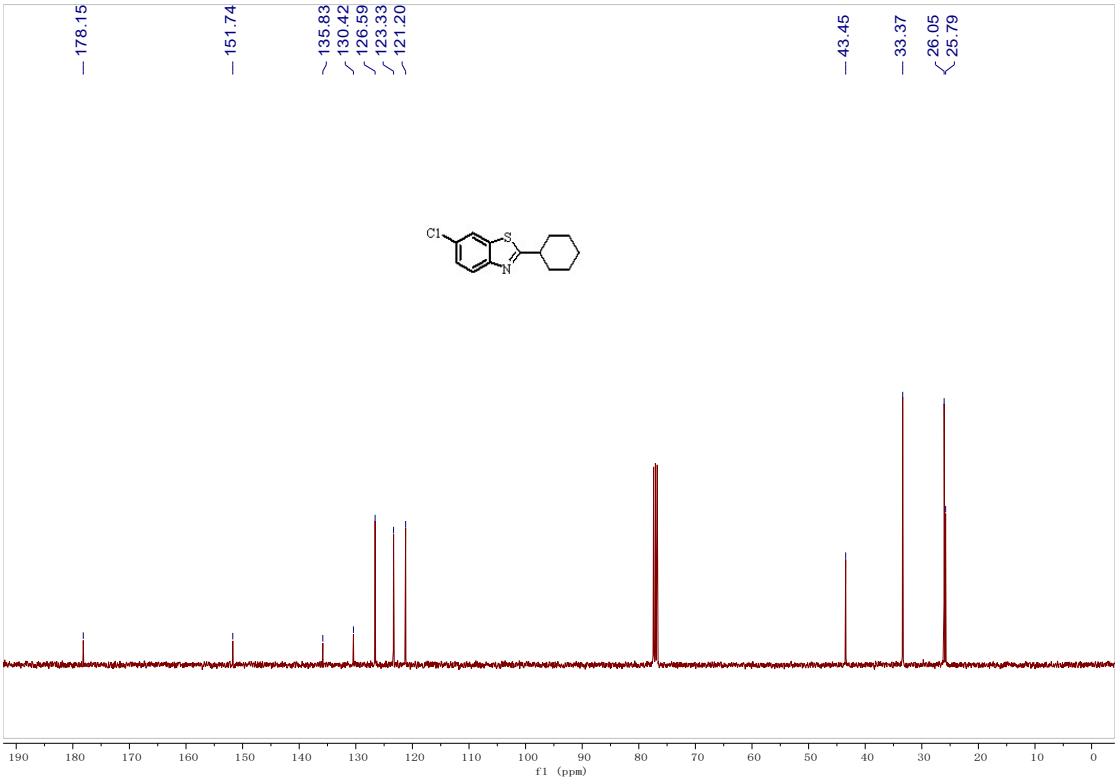
^{13}C NMR spectrum of compound **10c** in $CDCl_3$ (101 MHz):



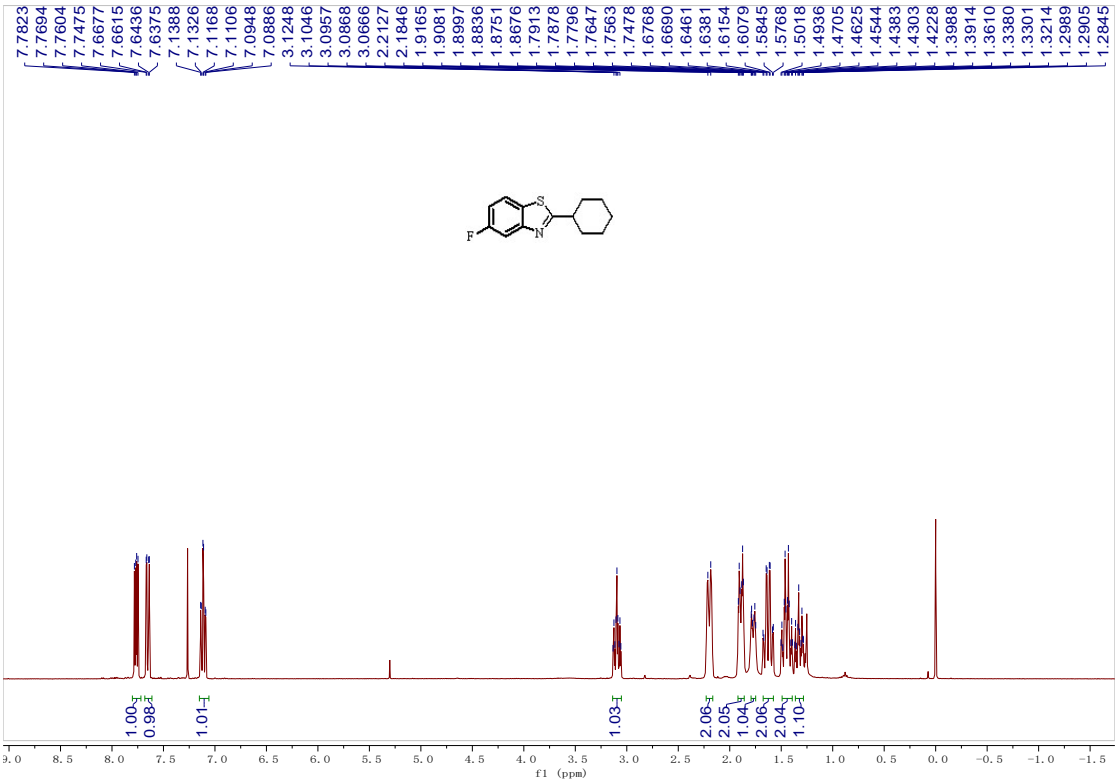
^{1}H NMR spectrum of compound **11c** in $CDCl_3$ (400 MHz):



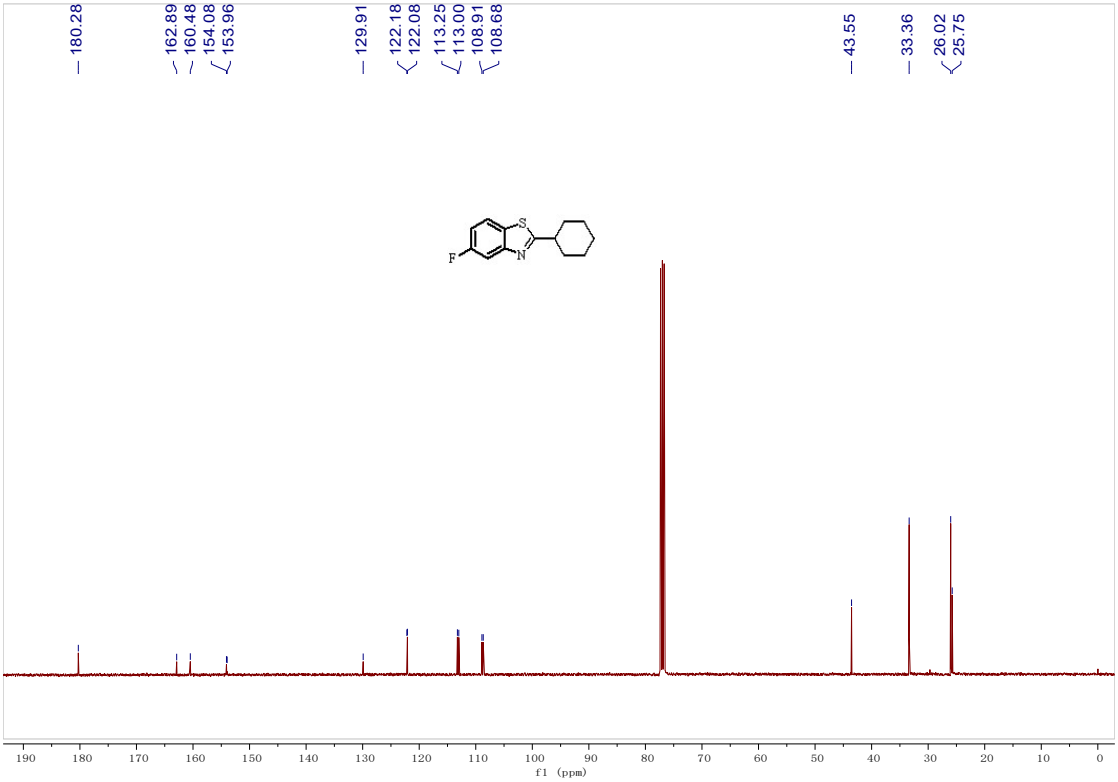
^{13}C NMR spectrum of compound **11c** in $CDCl_3$ (101 MHz):



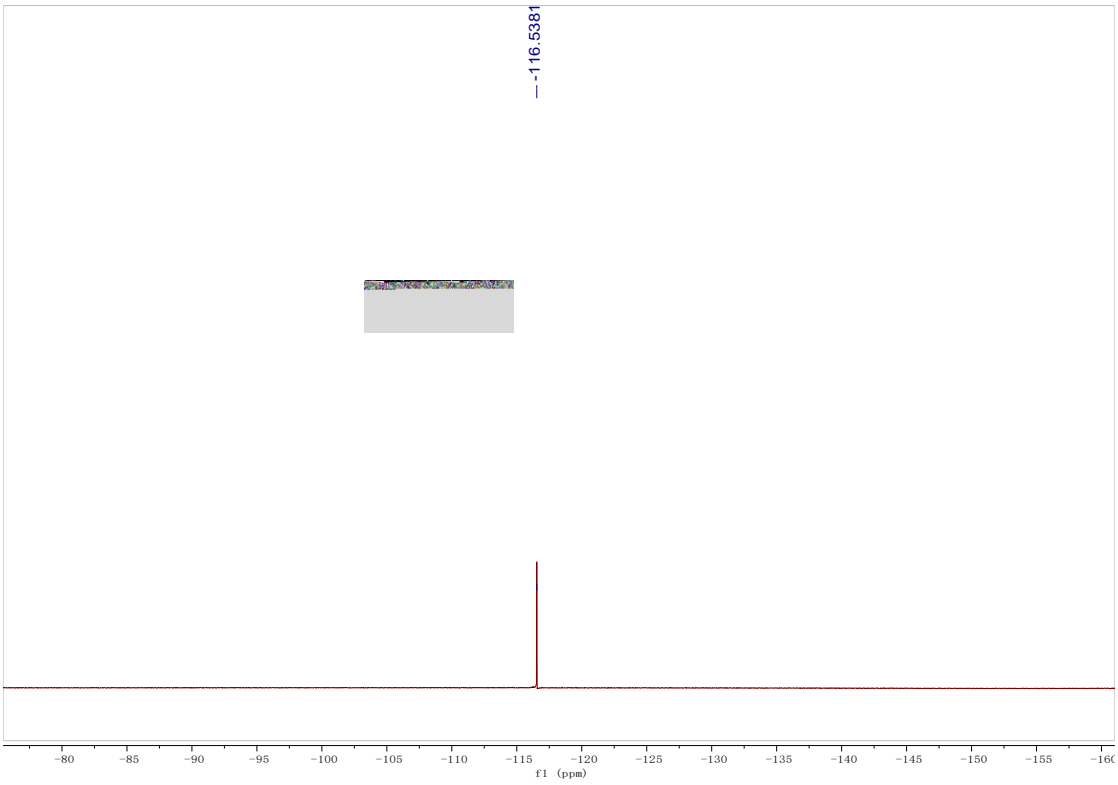
^{1}H NMR spectrum of compound **12c** in $CDCl_3$ (400 MHz):



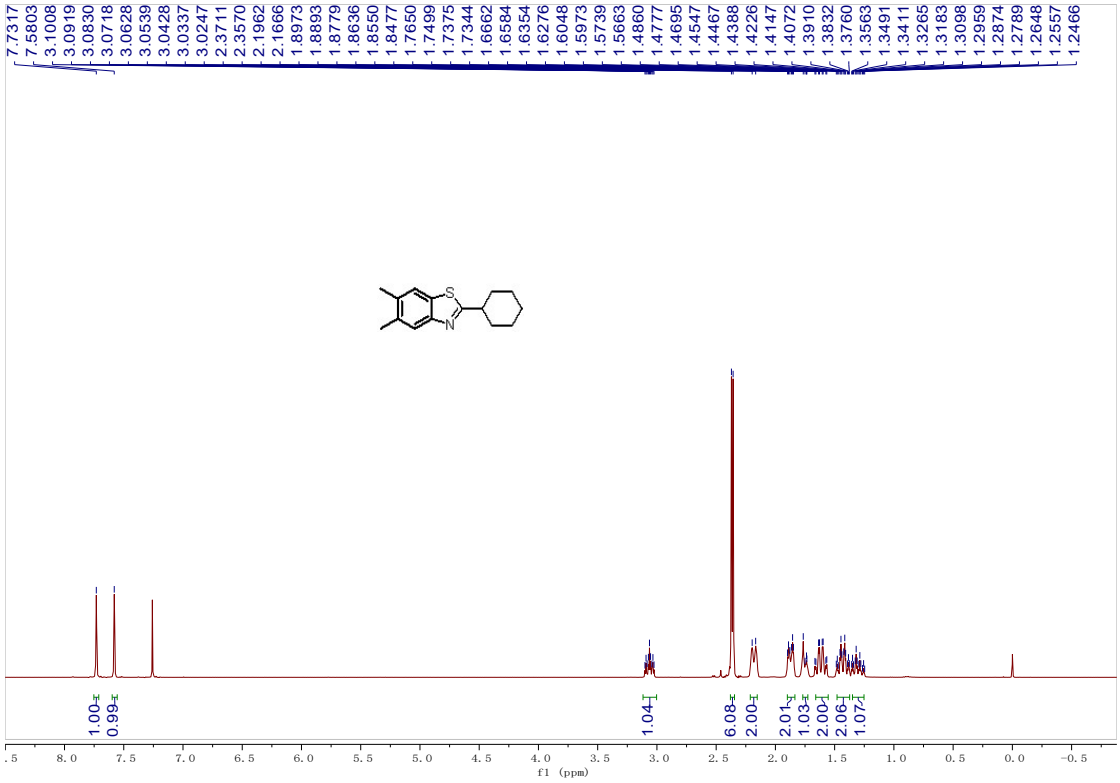
^{13}C NMR spectrum of compound **12c** in $CDCl_3$ (101 MHz):



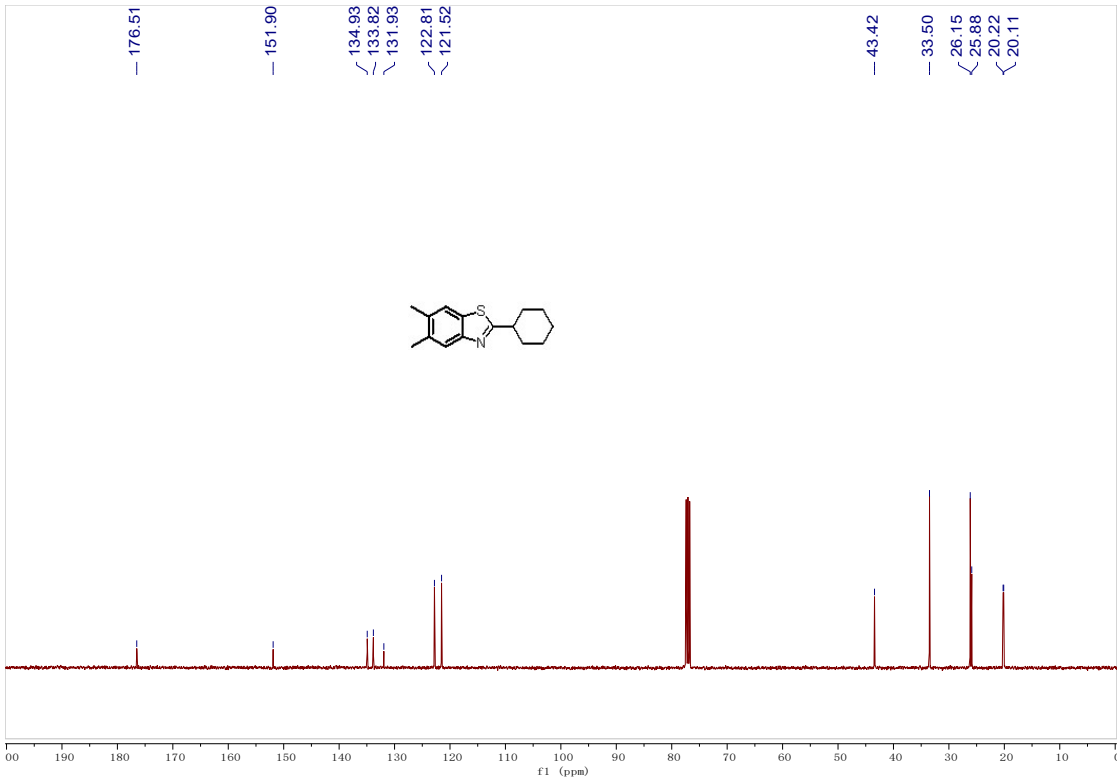
^{19}F NMR spectrum of compound **12c** in $CDCl_3$ (376 MHz):



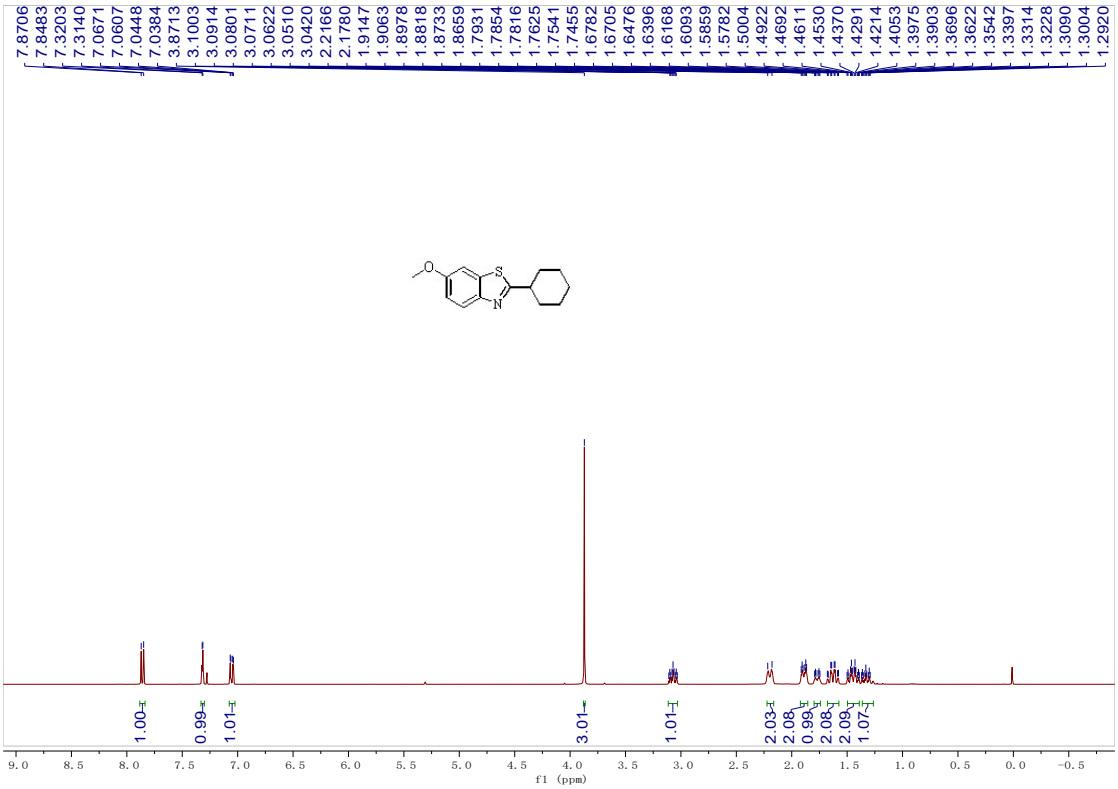
^{1}H NMR spectrum of compound **13c** in $CDCl_3$ (400 MHz):



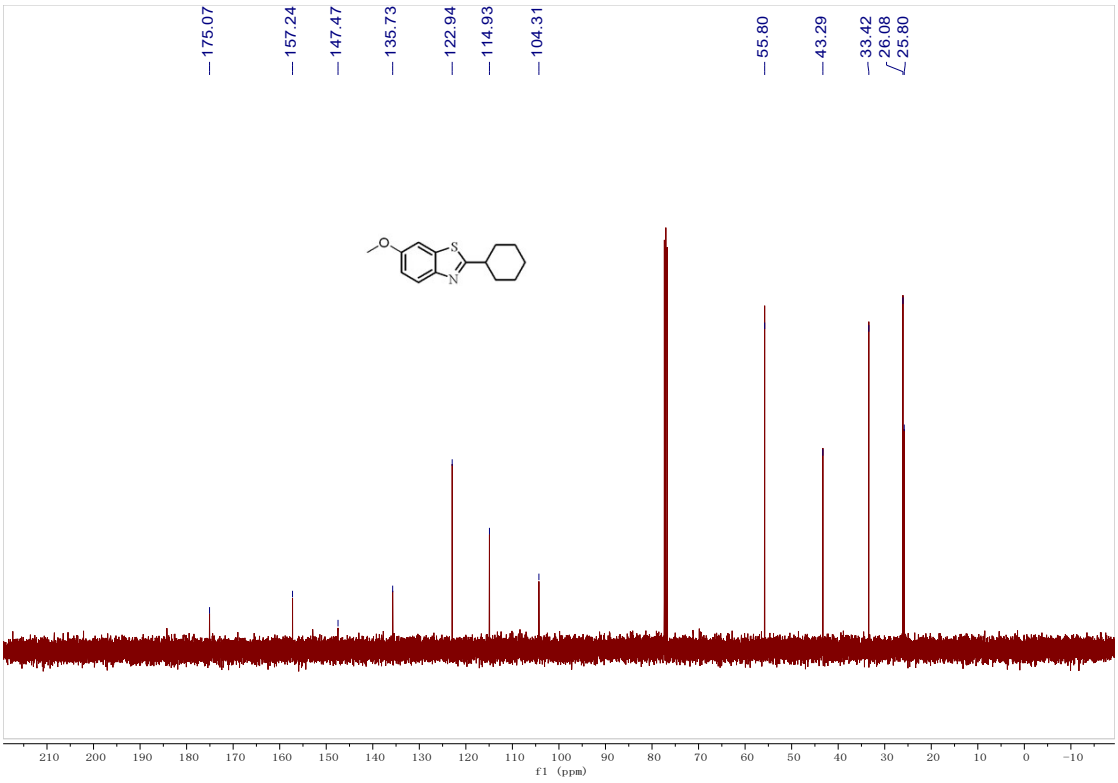
^{13}C NMR spectrum of compound **13c** in $CDCl_3$ (101 MHz):



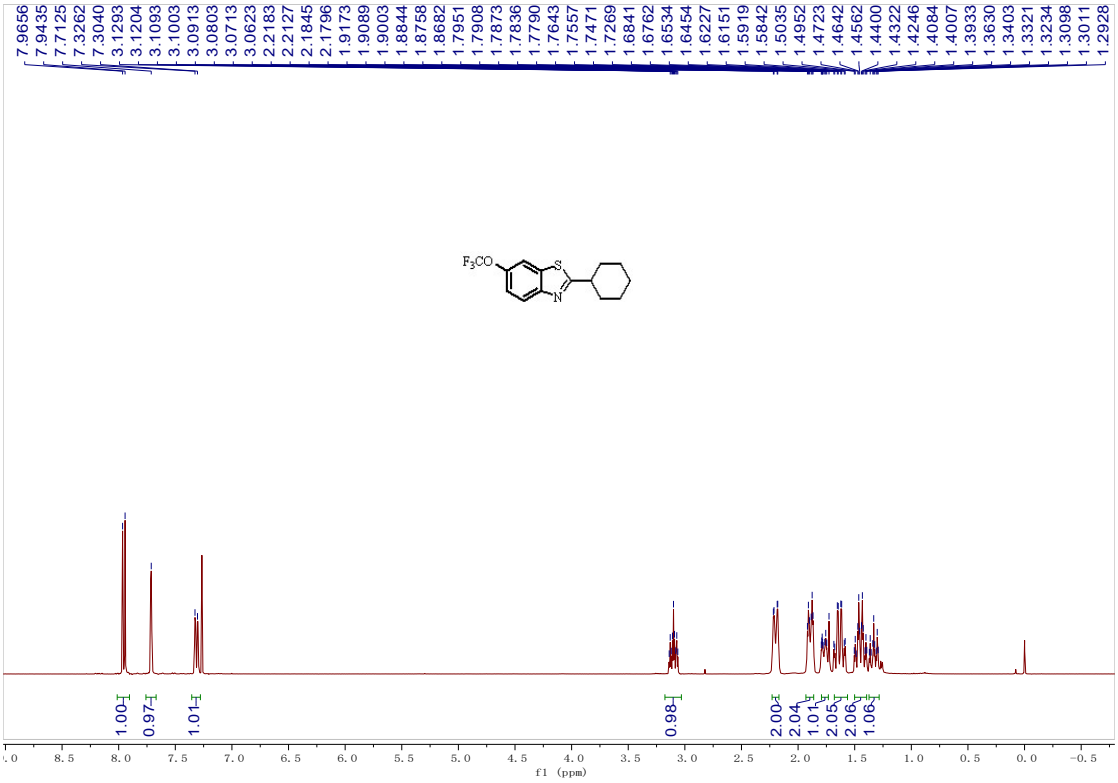
^{1}H NMR spectrum of compound **14c** in $CDCl_3$ (400 MHz):



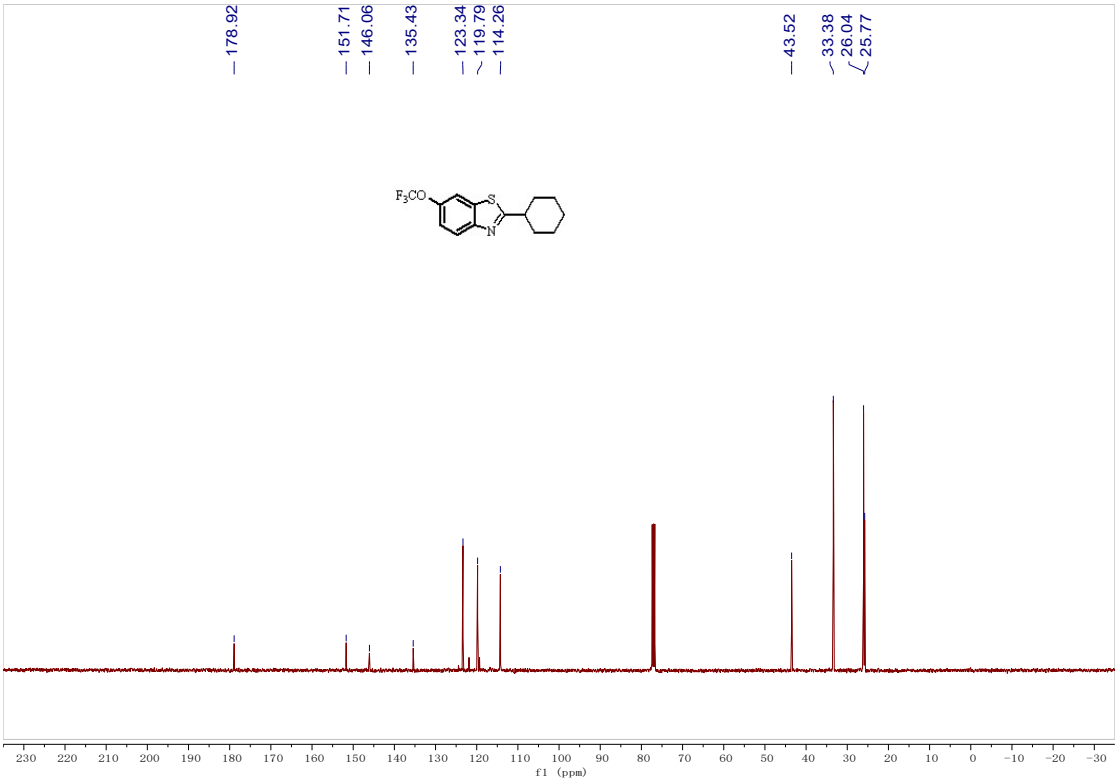
^{13}C NMR spectrum of compound **14c** in $CDCl_3$ (101 MHz):



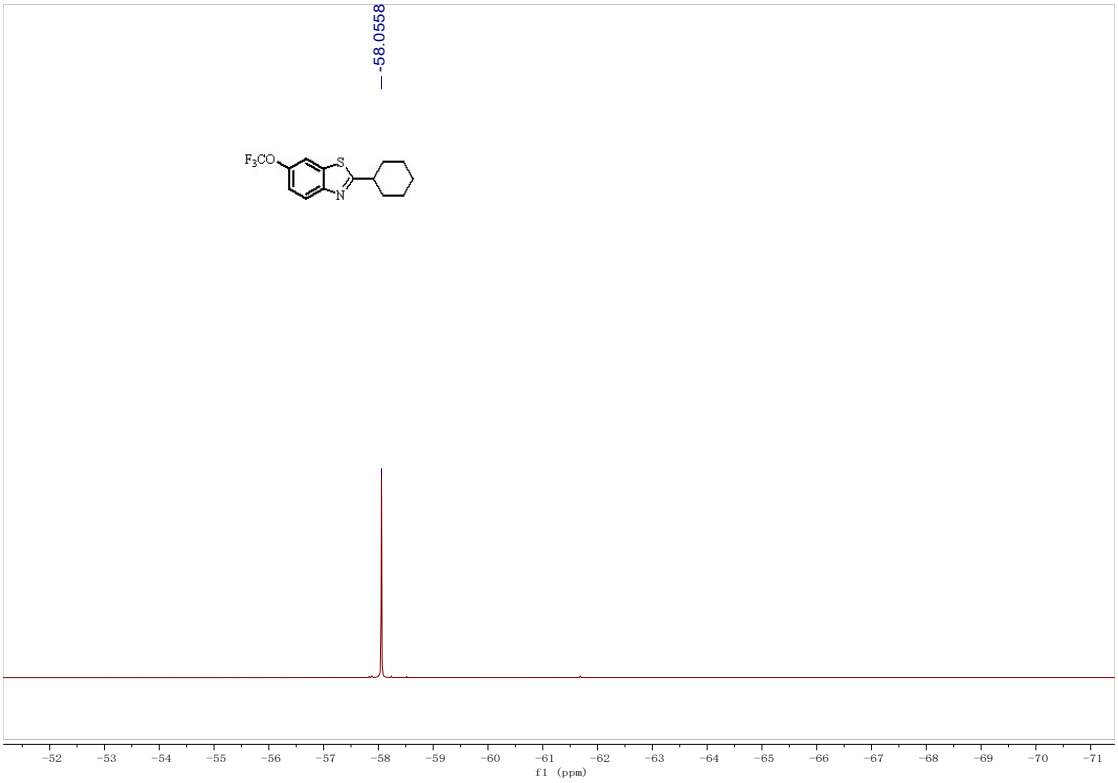
^{1}H NMR spectrum of compound **15c** in $CDCl_3$ (400 MHz):



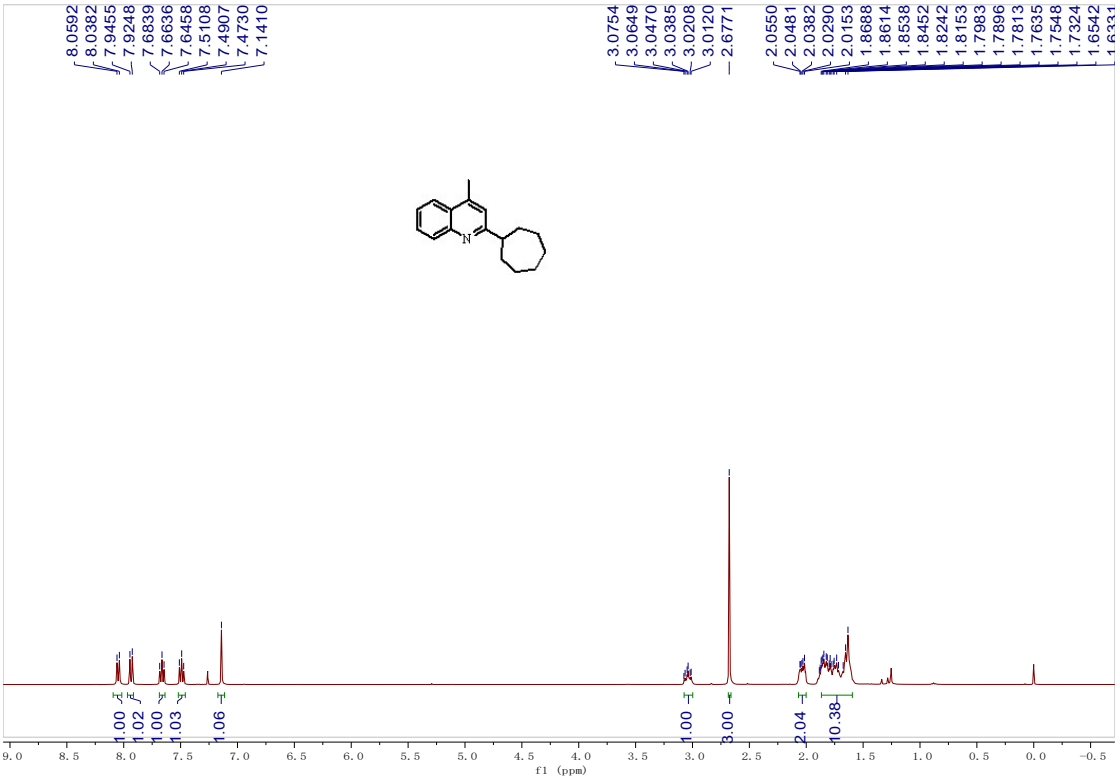
^{13}C NMR spectrum of compound **15c** in $CDCl_3$ (101 MHz):



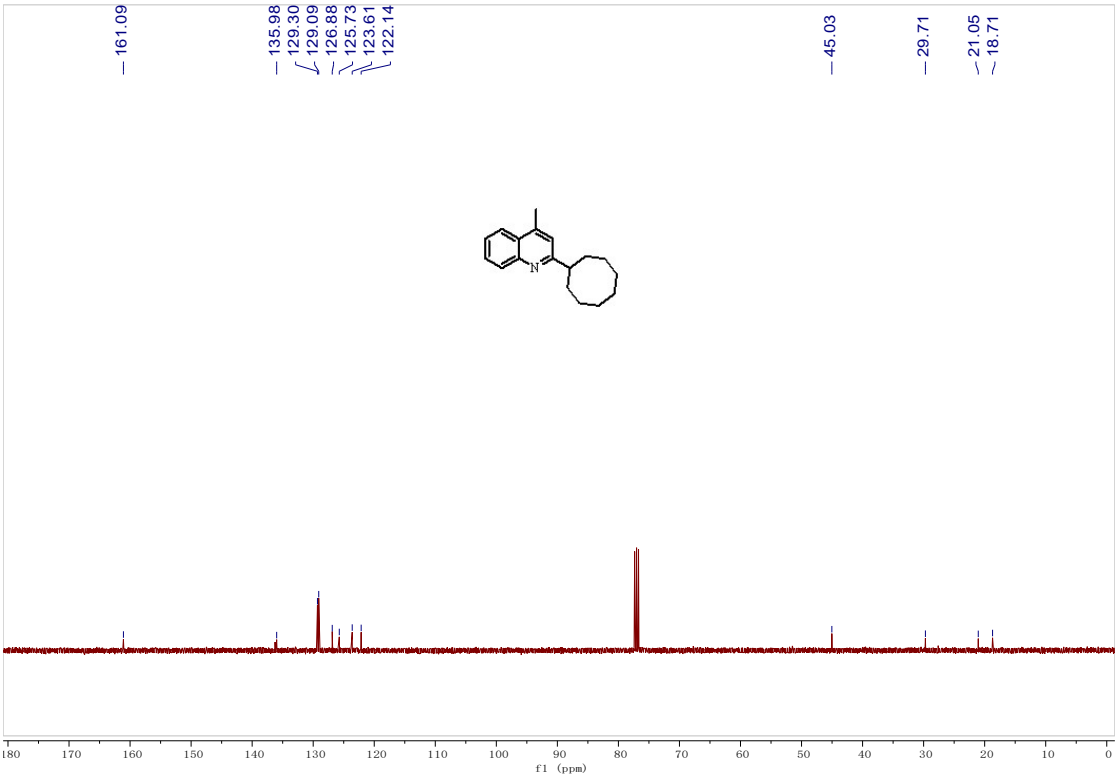
^{19}F NMR spectrum of compound **15c** in $CDCl_3$ (376 MHz):



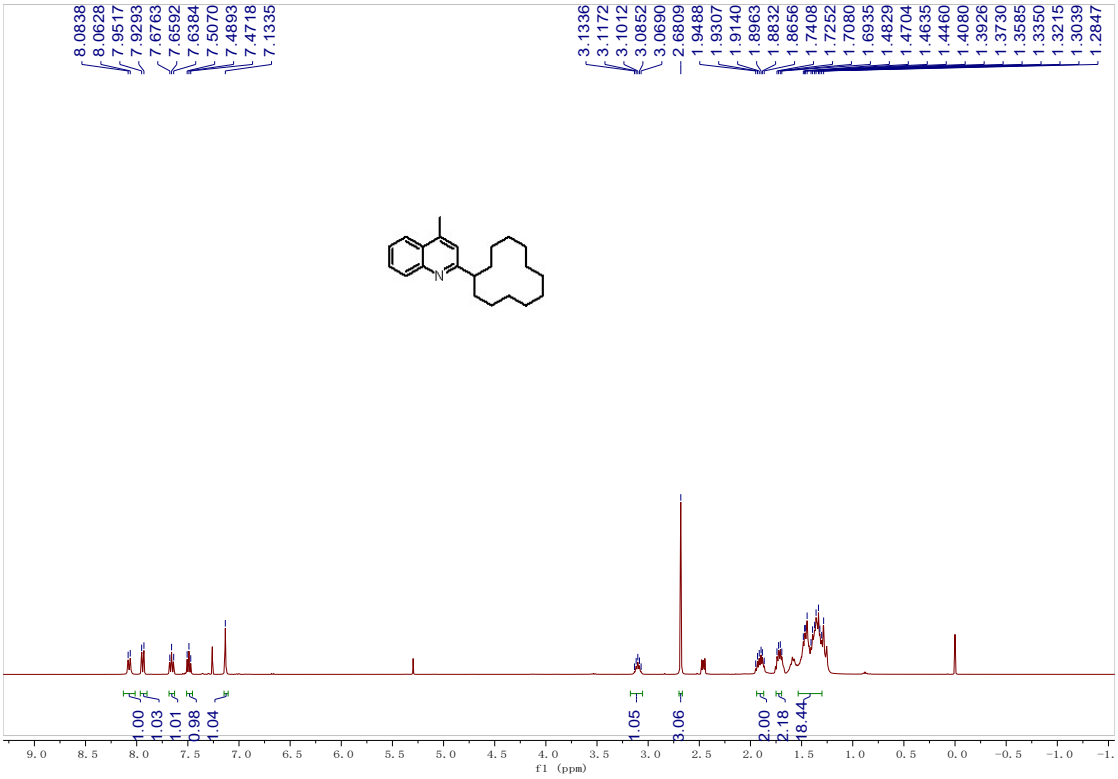
^{1}H NMR spectrum of compound **1d** in $CDCl_3$ (400 MHz):



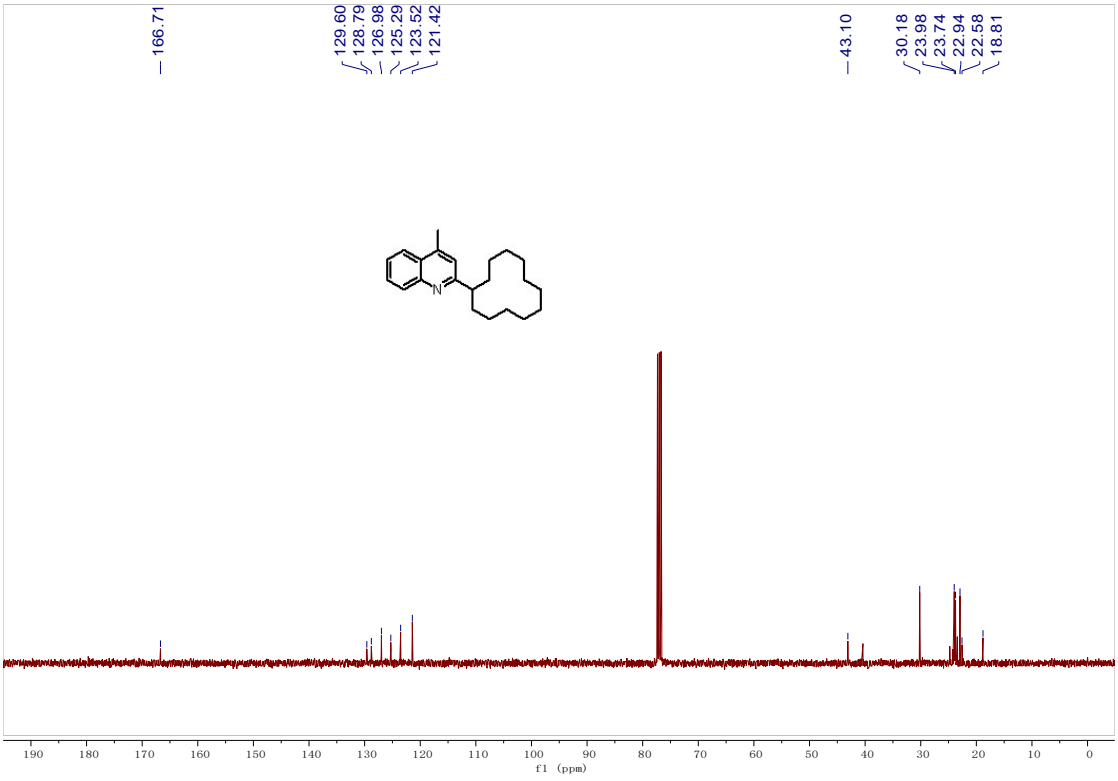
^{13}C NMR spectrum of compound **1d** in $CDCl_3$ (101 MHz):



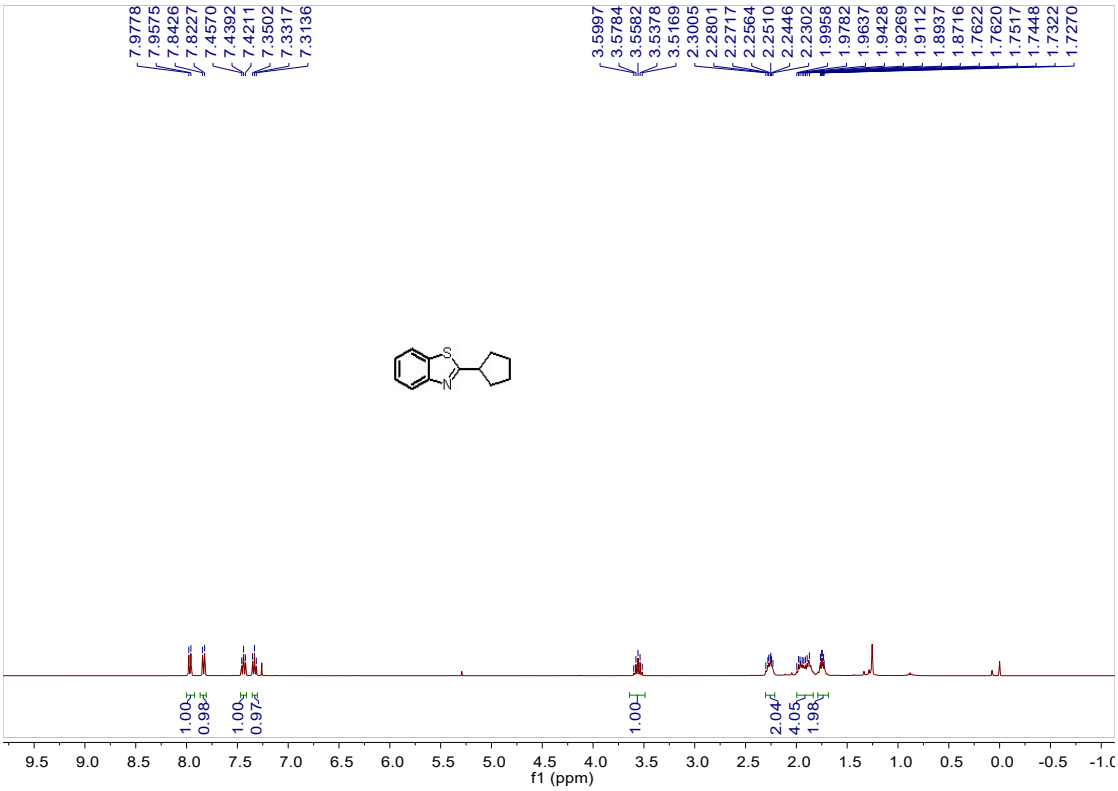
^{1}H NMR spectrum of compound **2d** in $CDCl_3$ (400 MHz):



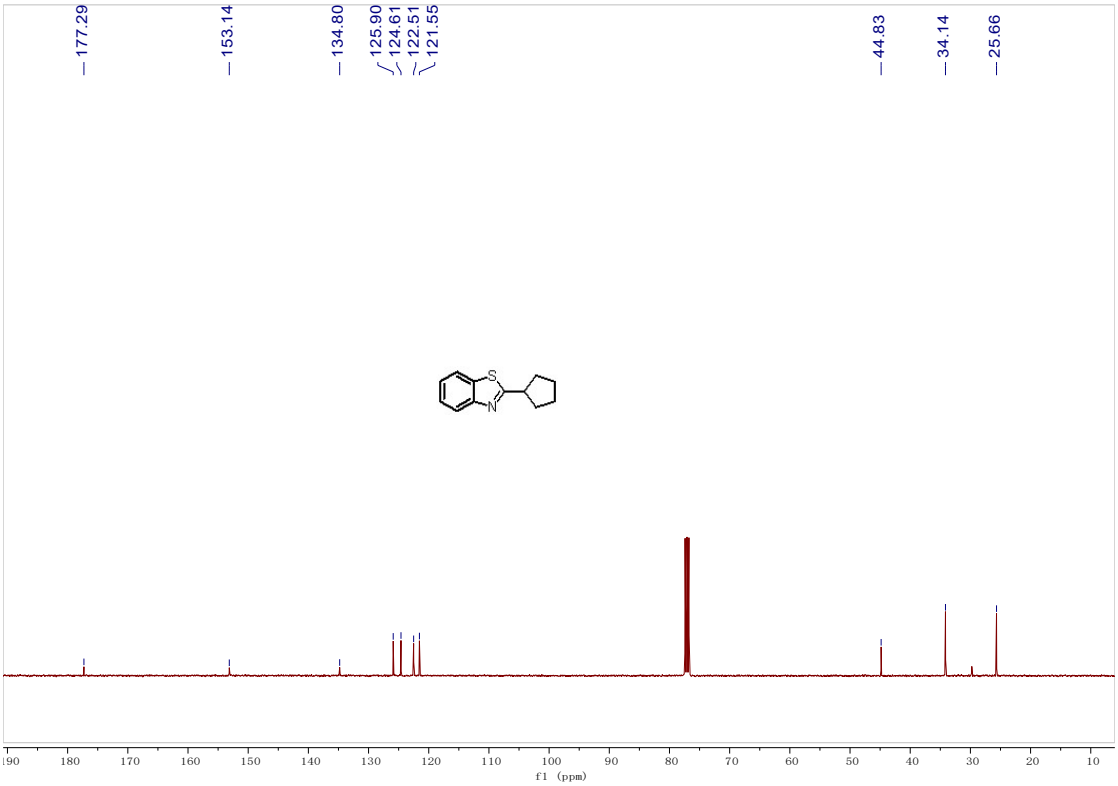
^{13}C NMR spectrum of compound **2d** in $CDCl_3$ (101 MHz):



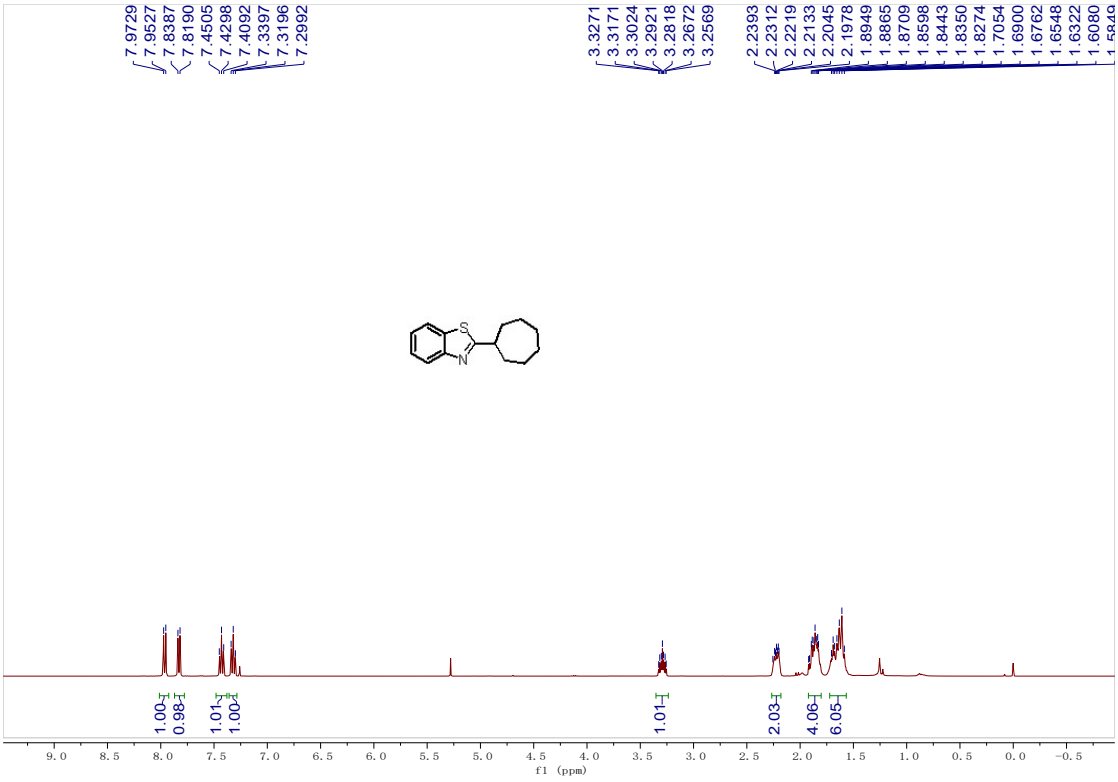
^{1}H NMR spectrum of compound **3d** in $CDCl_3$ (400 MHz):



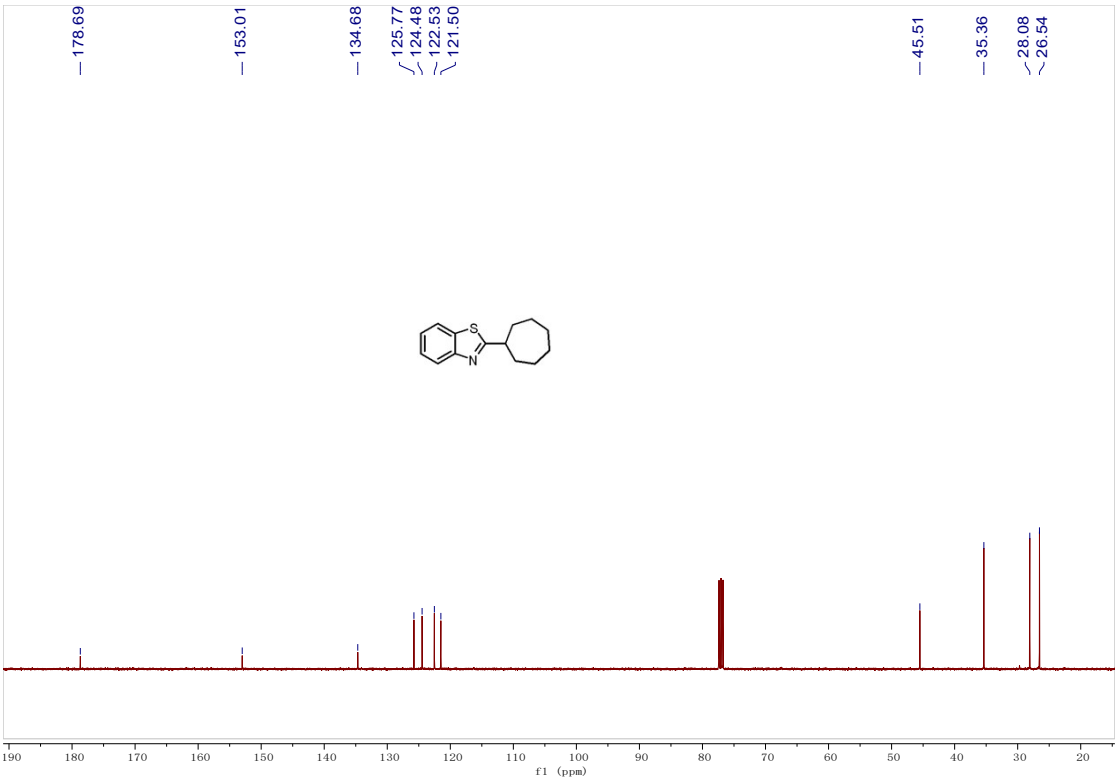
^{13}C NMR spectrum of compound **3d** in $CDCl_3$ (101 MHz):



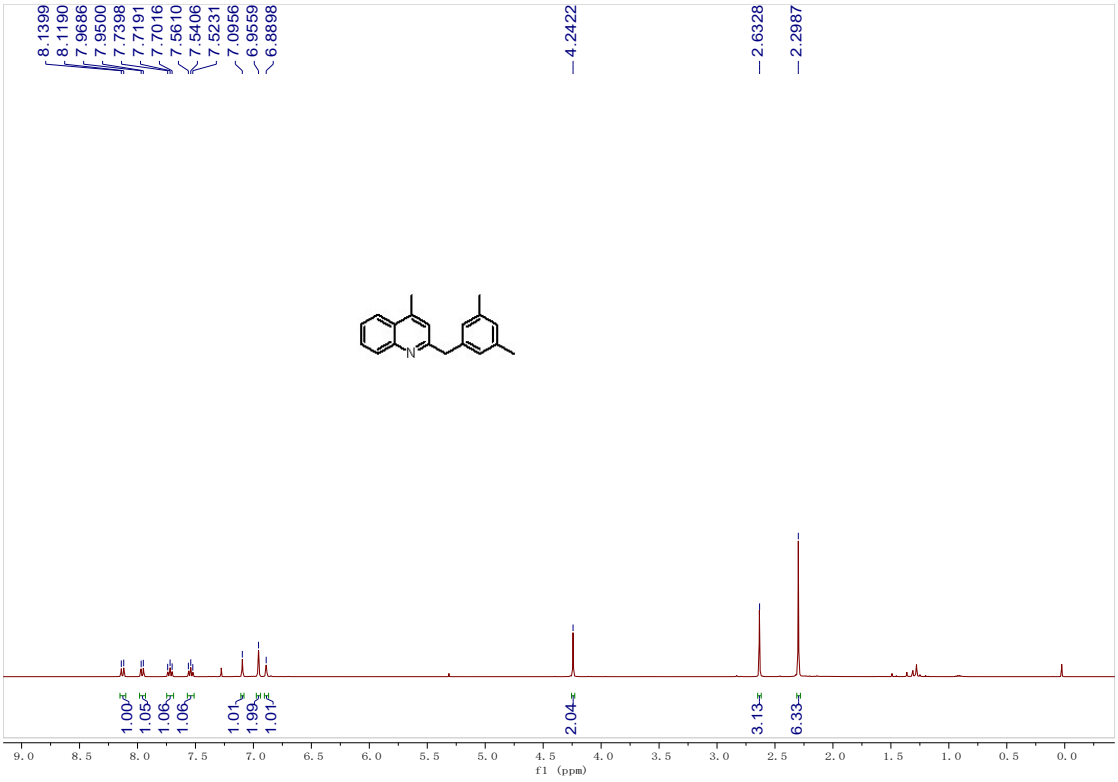
^{1}H NMR spectrum of compound **4d** in $CDCl_3$ (400 MHz):



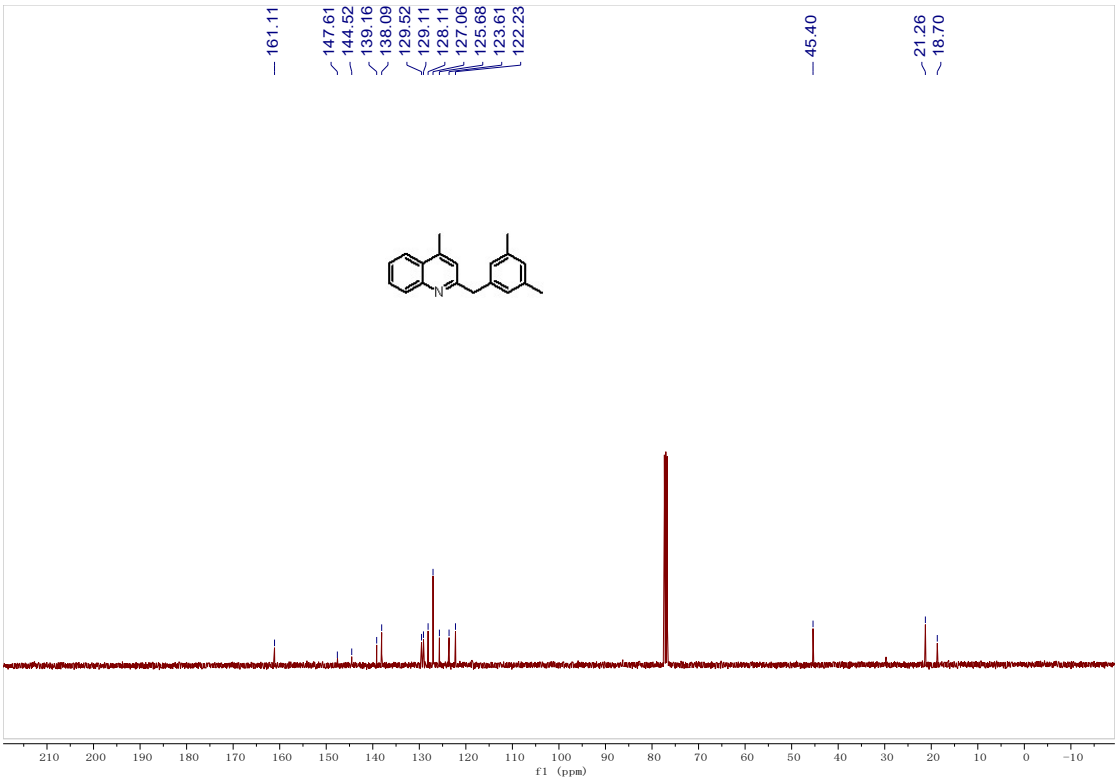
^{13}C NMR spectrum of compound **4d** in $CDCl_3$ (101 MHz):



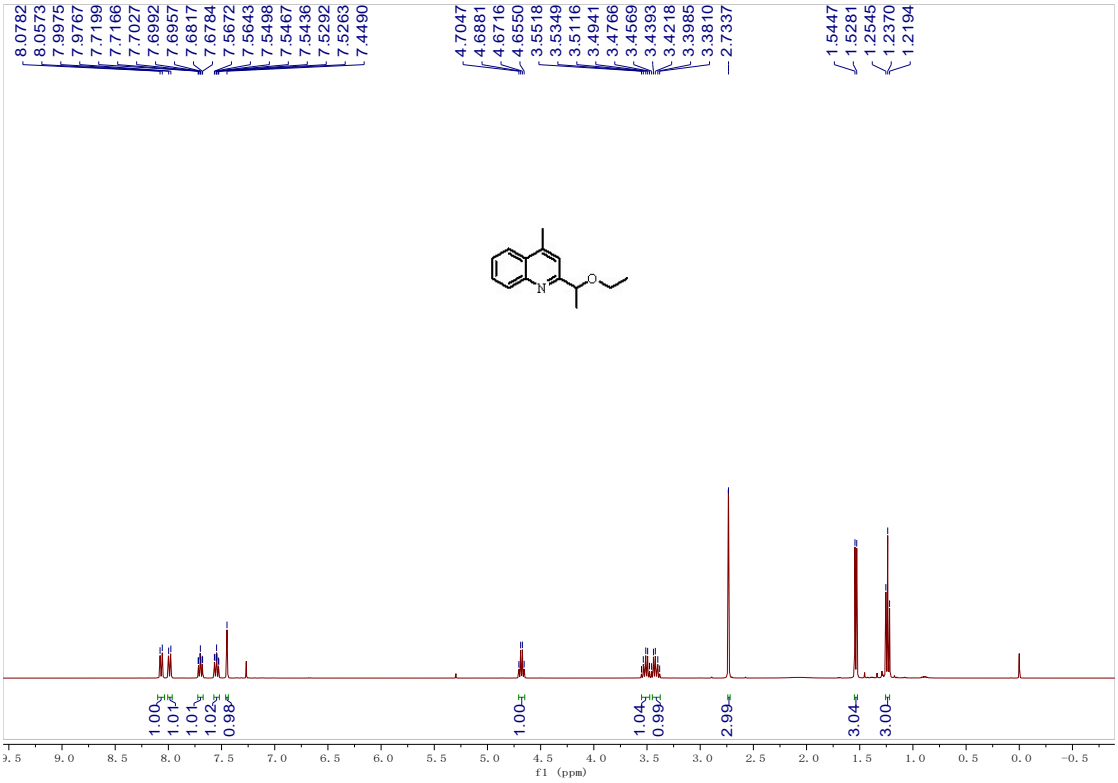
^{1}H NMR spectrum of compound **5d** in $CDCl_3$ (400 MHz):



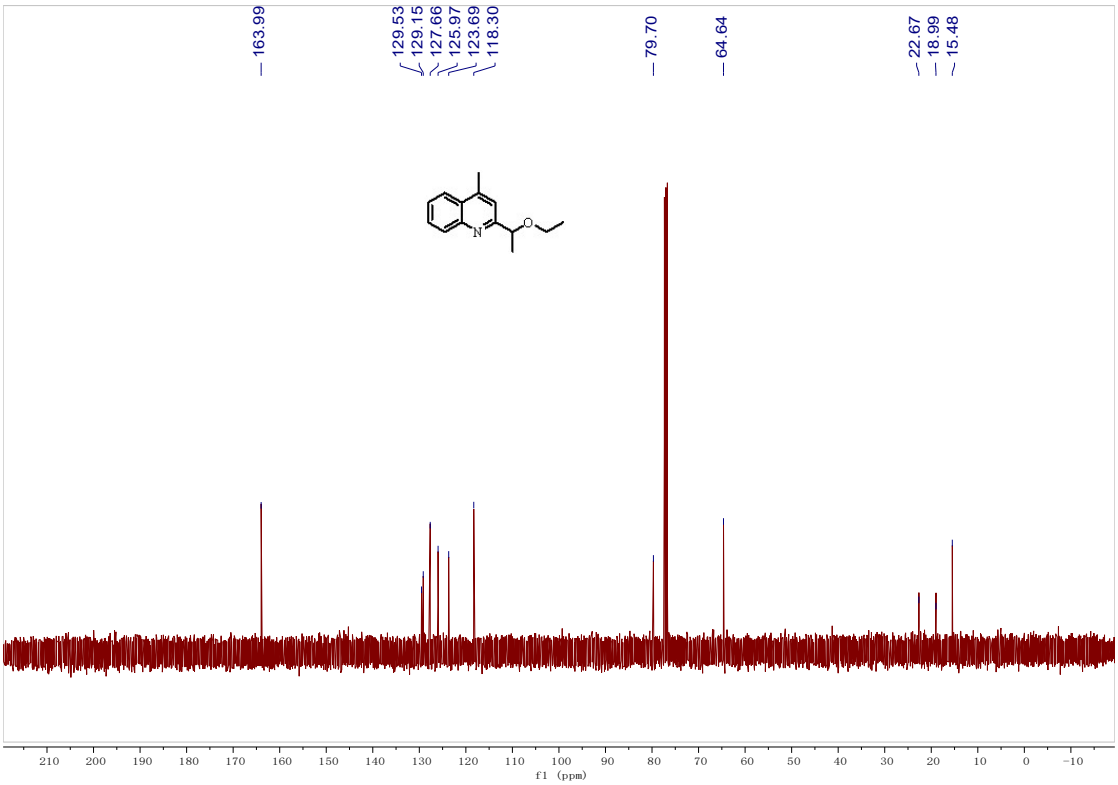
^{13}C NMR spectrum of compound **5d** in $CDCl_3$ (101 MHz):



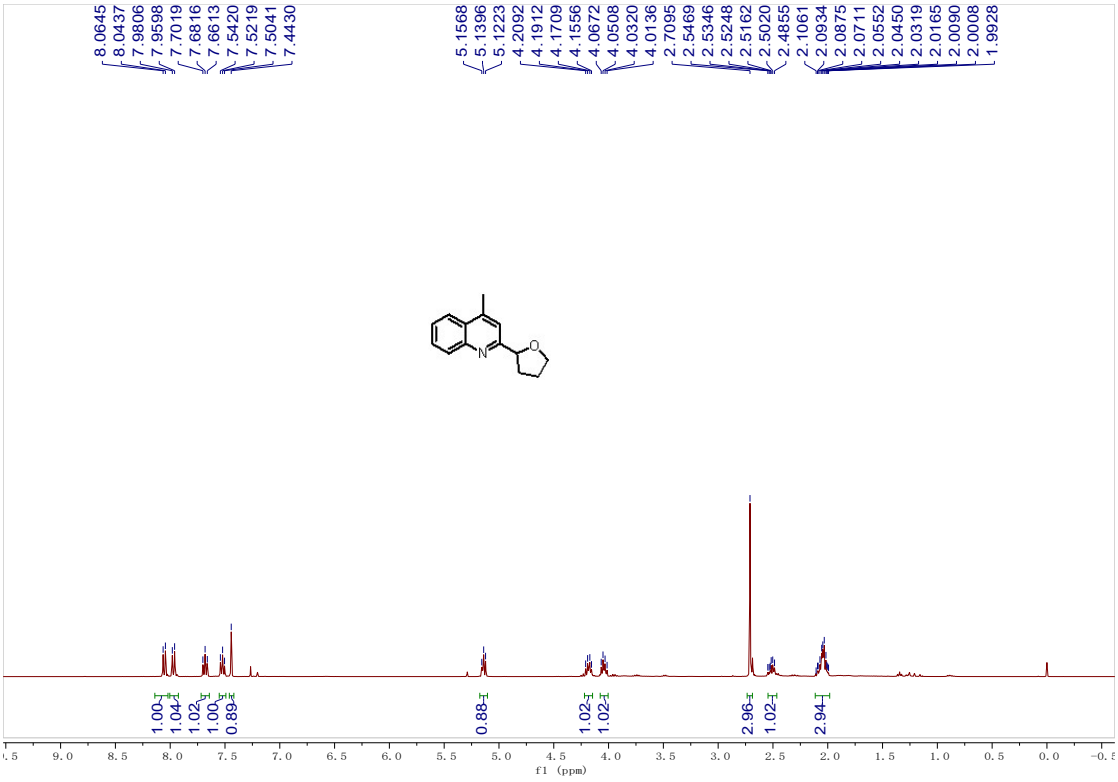
^{1}H NMR spectrum of compound **6d** in $CDCl_3$ (400 MHz):



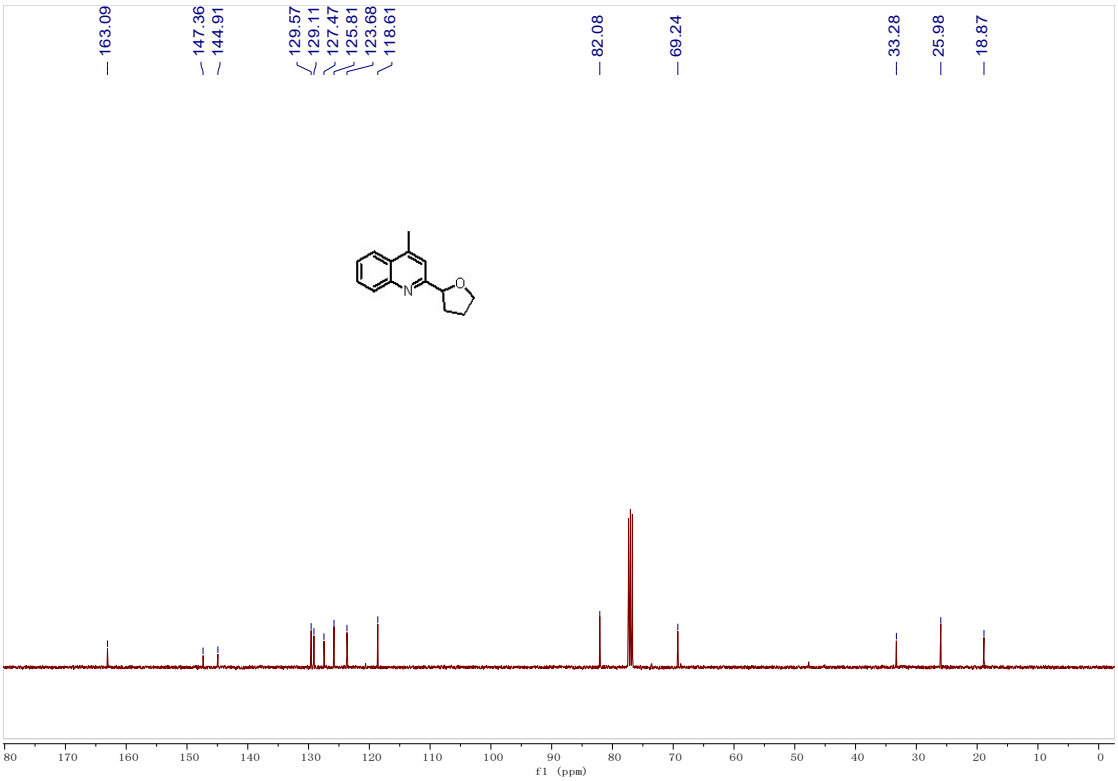
^{13}C NMR spectrum of compound **6d** in $CDCl_3$ (101 MHz):



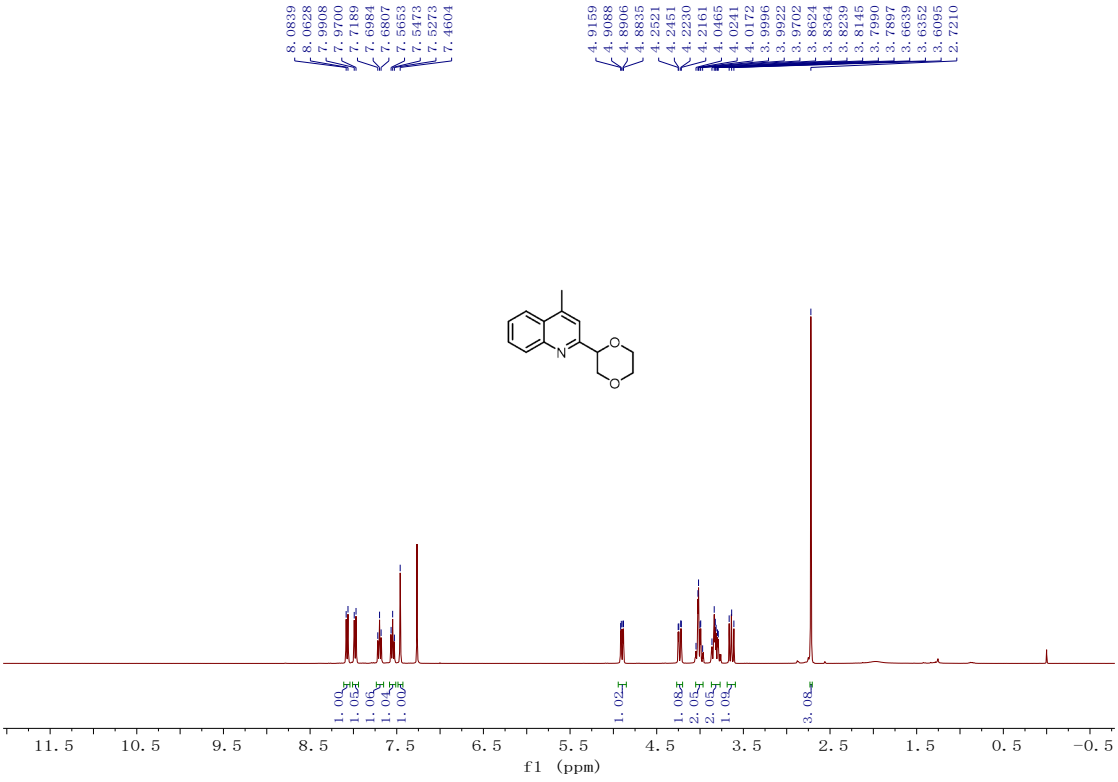
^{1}H NMR spectrum of compound **7d** in $CDCl_3$ (400 MHz):



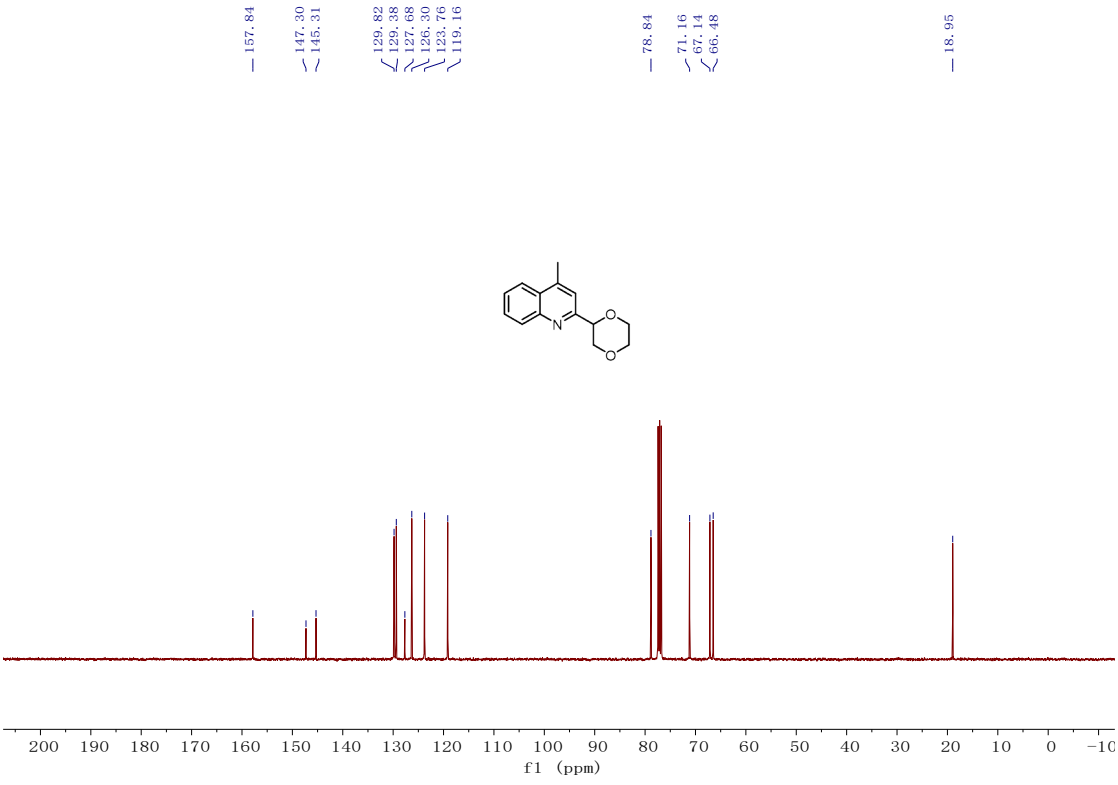
^{13}C NMR spectrum of compound **7d** in $CDCl_3$ (101 MHz):



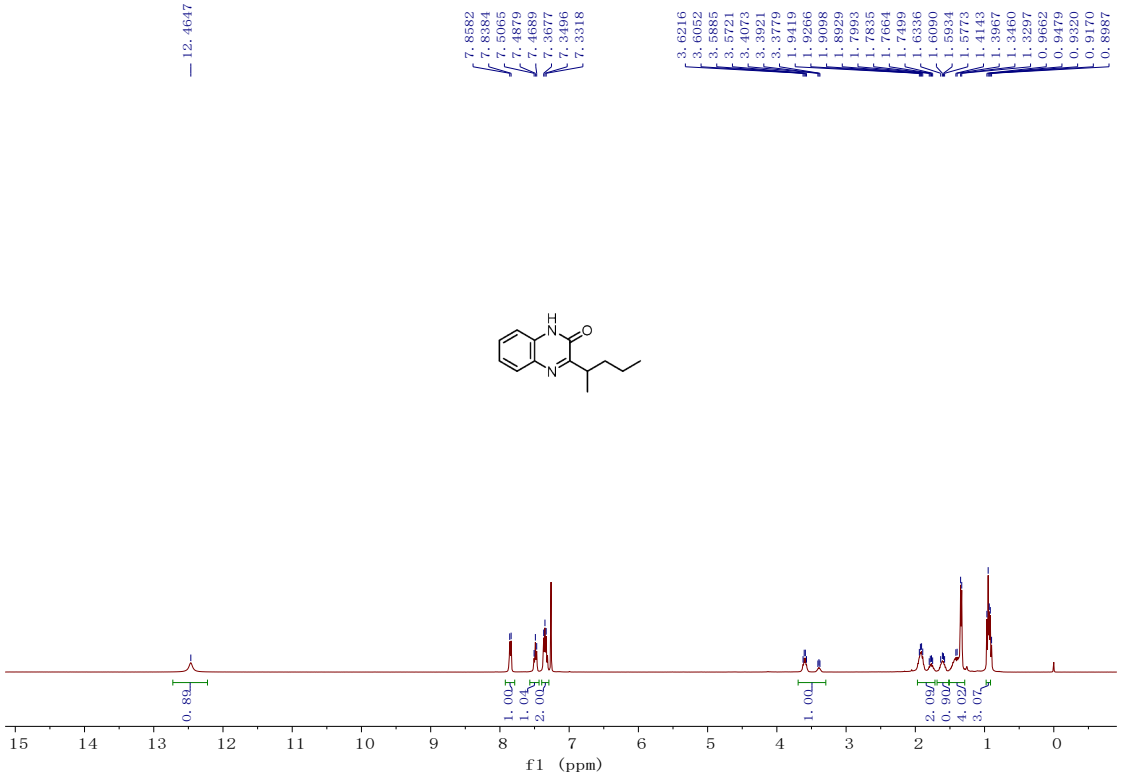
^{1}H NMR spectrum of compound **8d** in $CDCl_3$ (400 MHz):



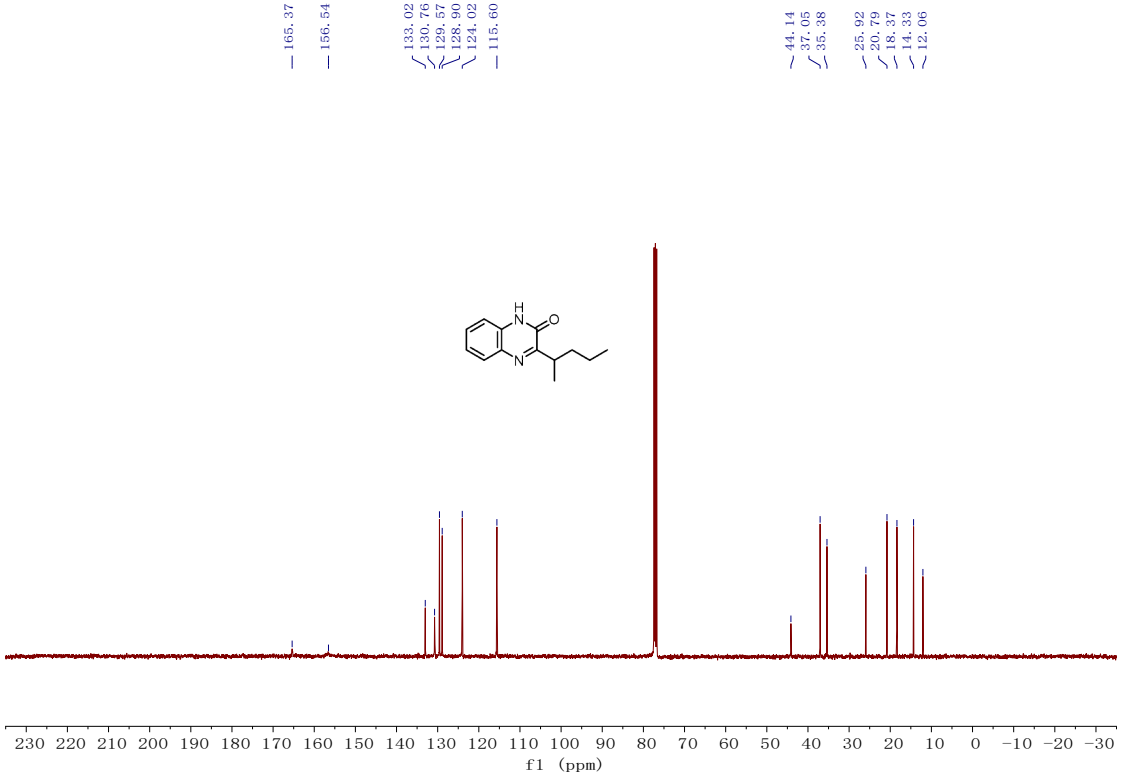
^{13}C NMR spectrum of compound **8d** in $CDCl_3$ (101 MHz):



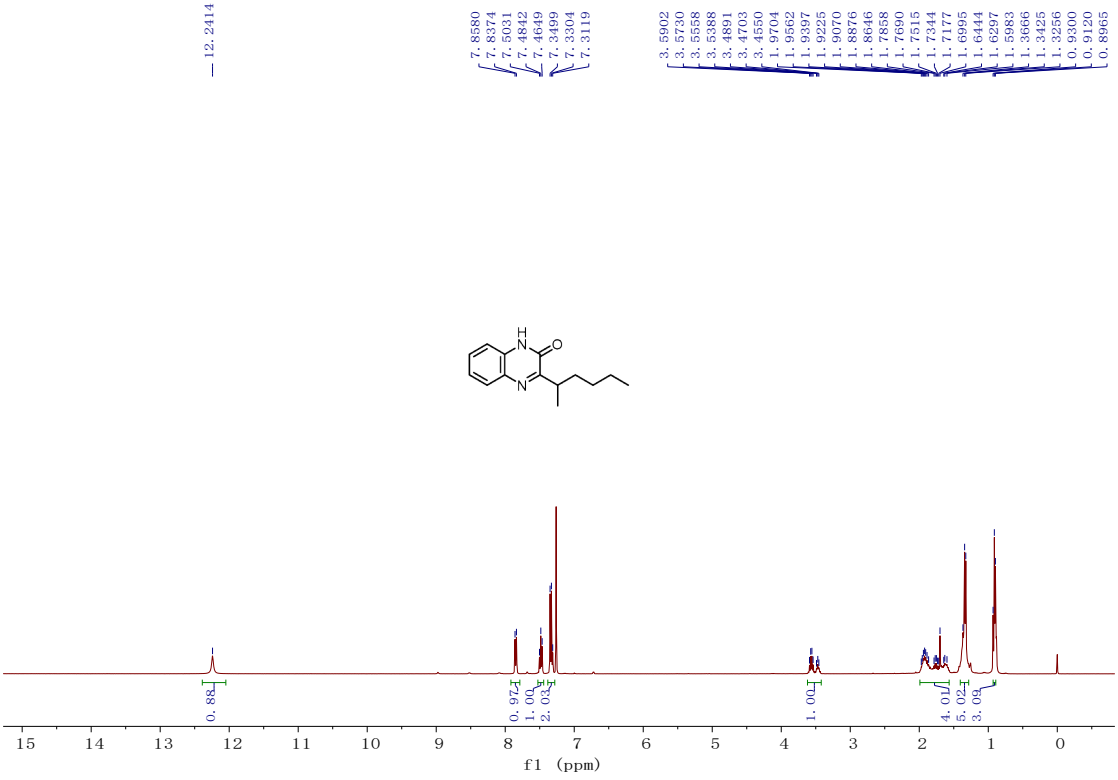
^{1}H NMR spectrum of compound **9d** in $CDCl_3$ (400 MHz):



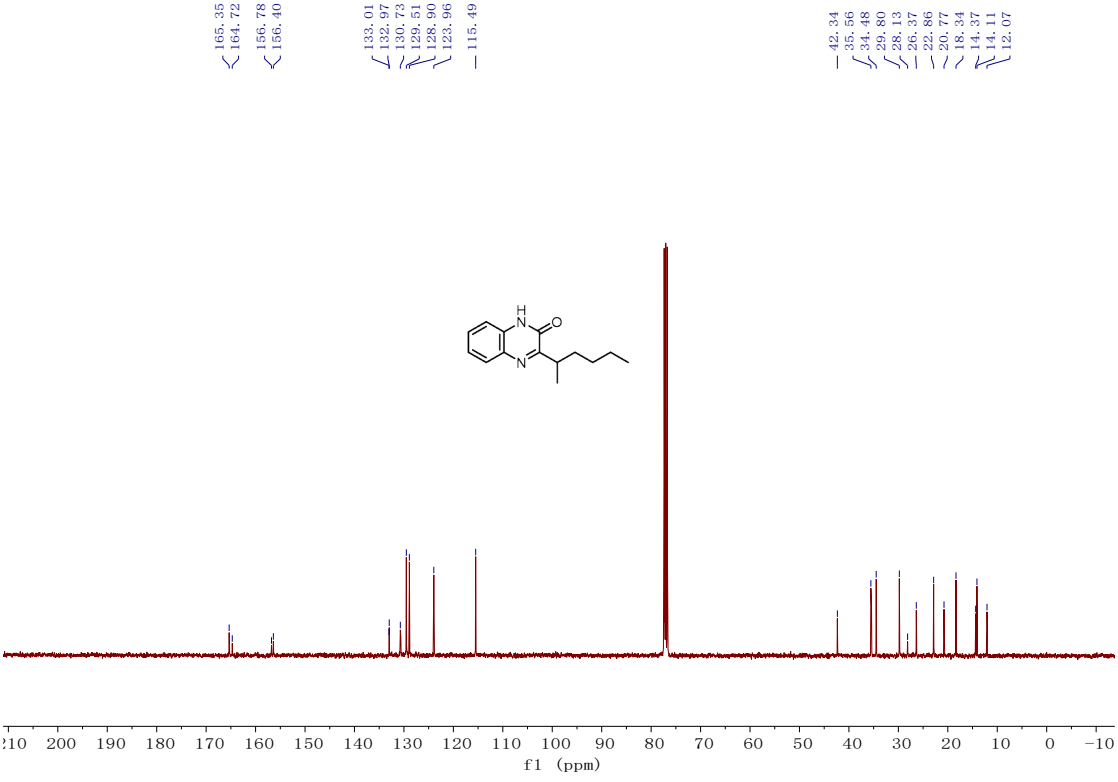
^{13}C NMR spectrum of compound **9d** in $CDCl_3$ (101 MHz):



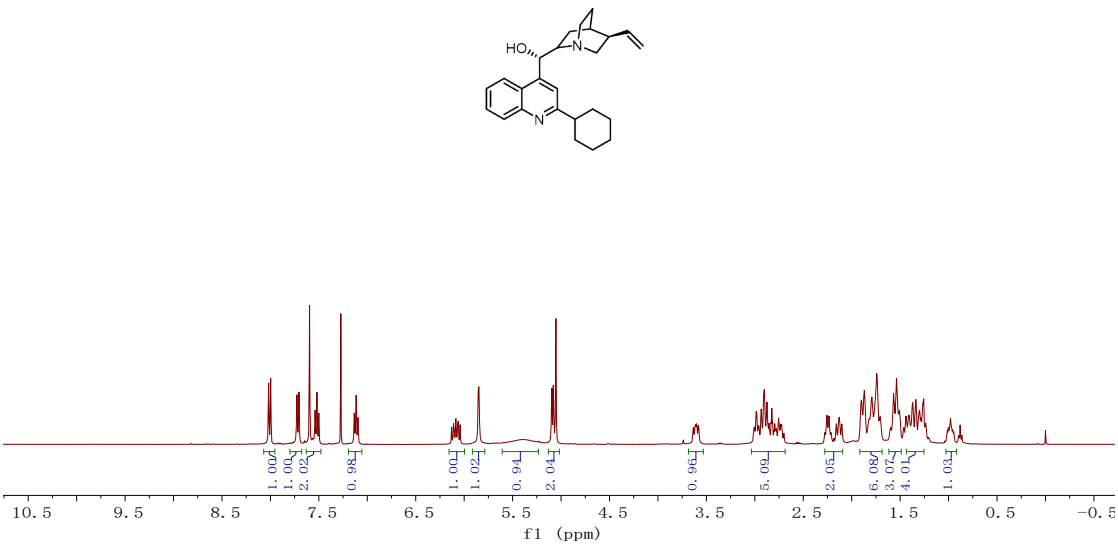
^{1}H NMR spectrum of compound **10d** in $CDCl_3$ (400 MHz):



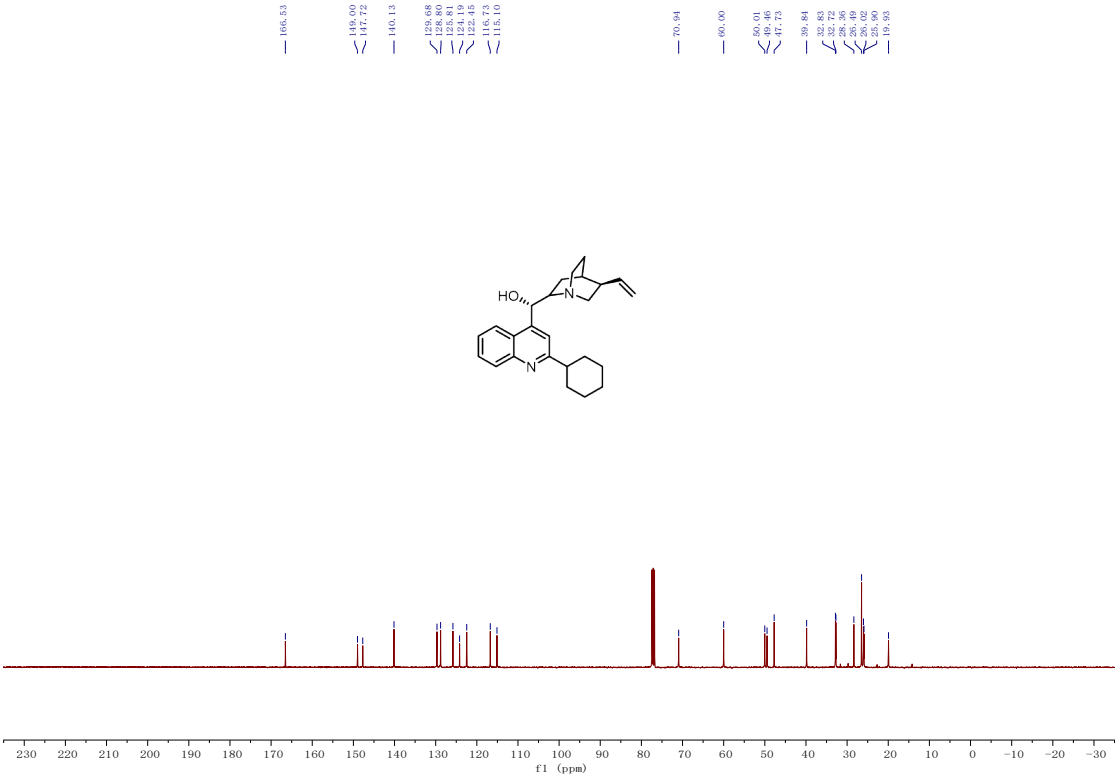
^{13}C NMR spectrum of compound **10d** in $CDCl_3$ (101 MHz):



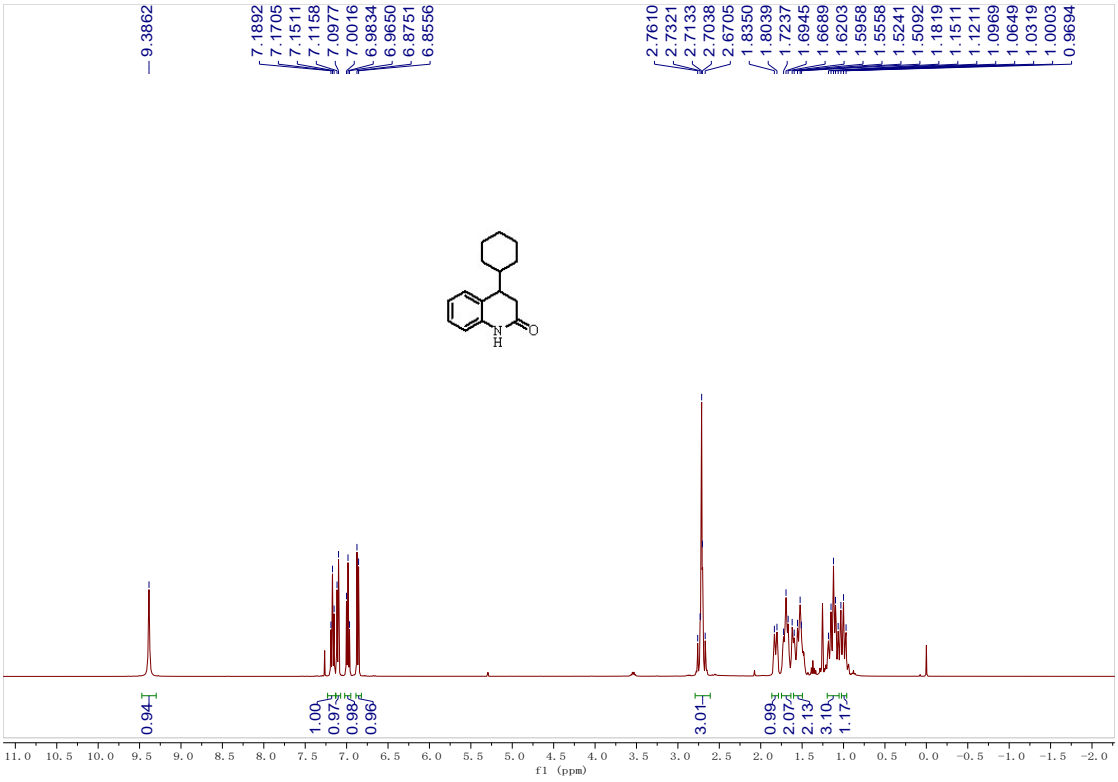
^{1}H NMR spectrum of compound **11d** in $CDCl_3$ (400 MHz):



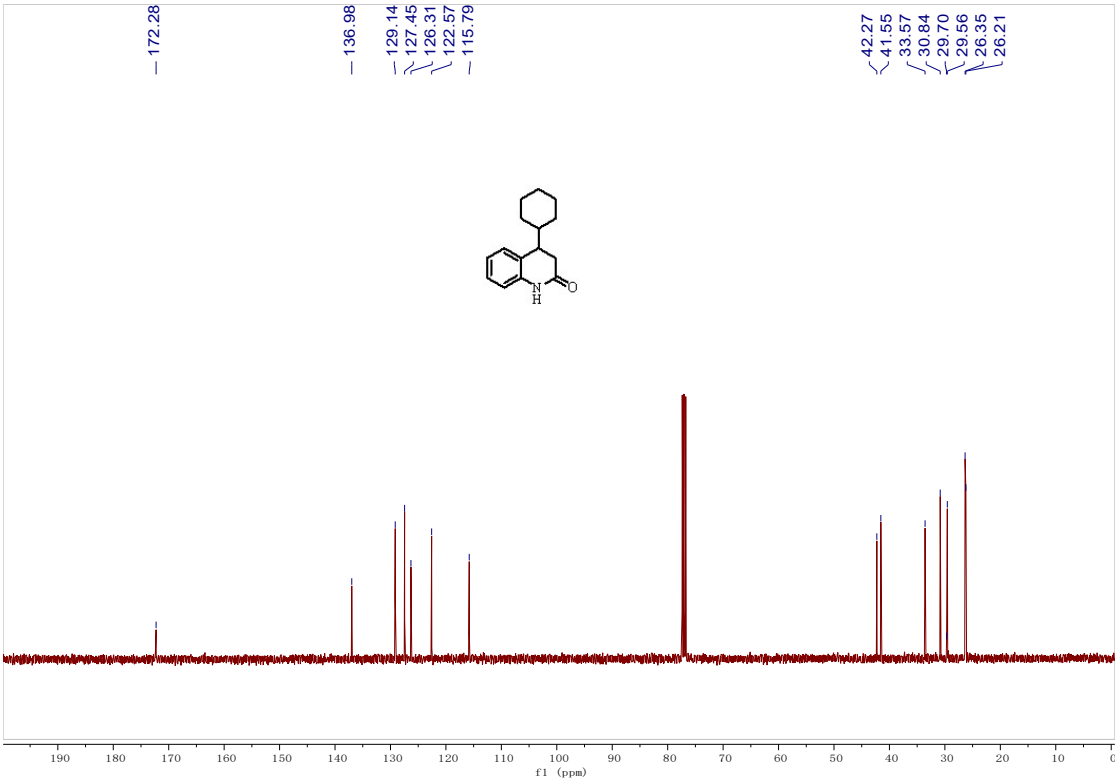
^{13}C NMR spectrum of compound **11d** in $CDCl_3$ (101 MHz):



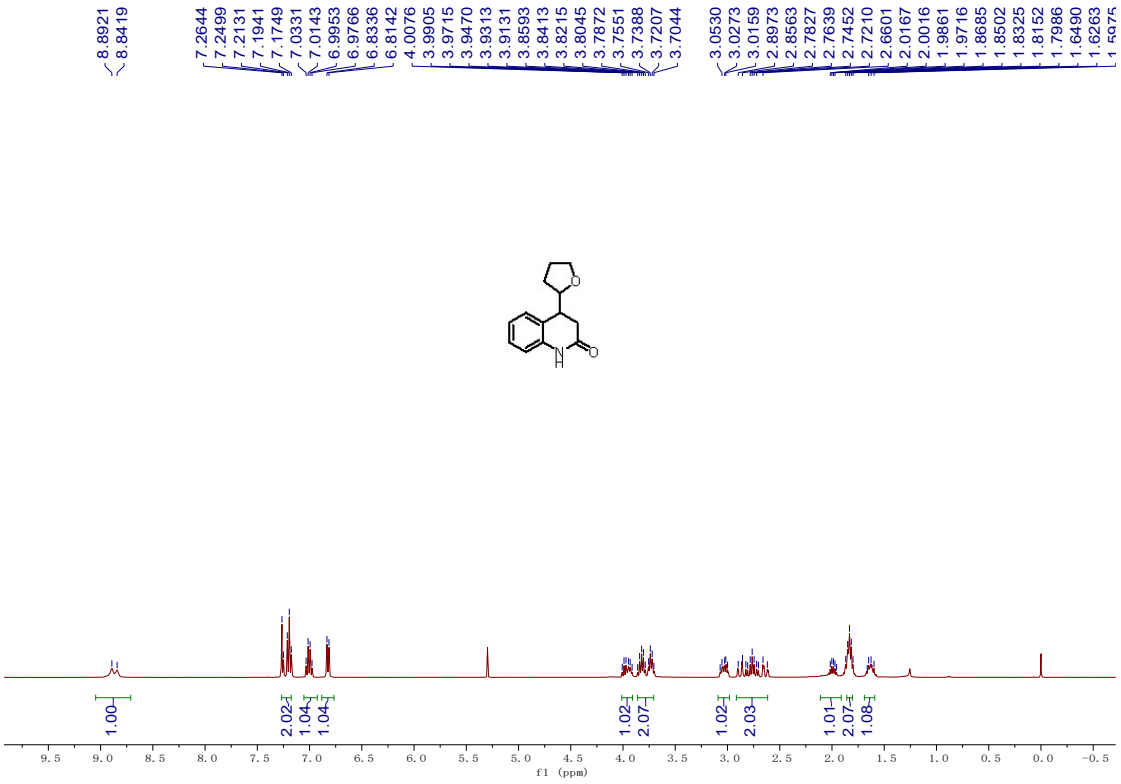
^{1}H NMR spectrum of compound **12d** in $CDCl_3$ (400 MHz):



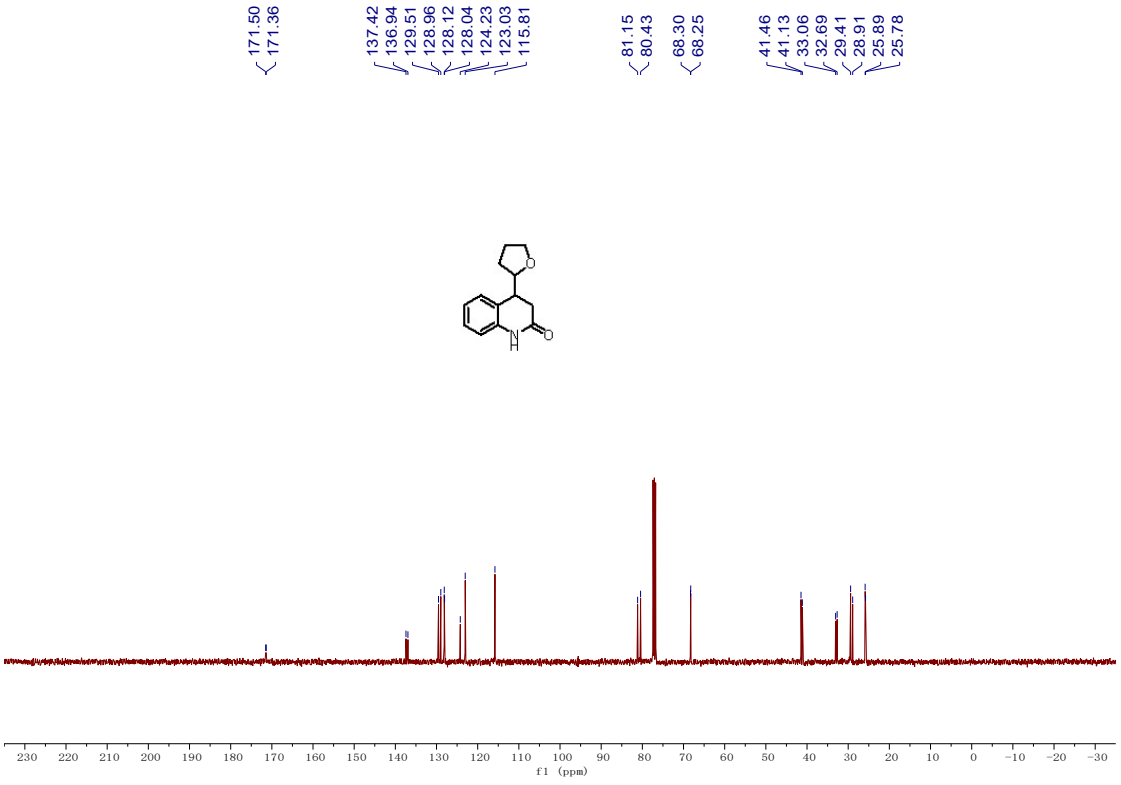
^{13}C NMR spectrum of compound **12d** in $CDCl_3$ (101 MHz):



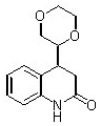
^{1}H NMR spectrum of compound **13d** in $CDCl_3$ (400 MHz):

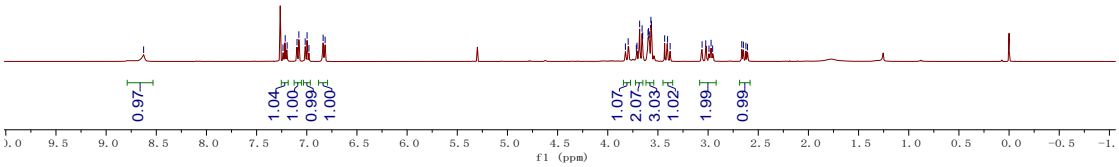


^{13}C NMR spectrum of compound **13d** in $CDCl_3$ (101 MHz):



^{1}H NMR spectrum of compound **14d** in $CDCl_3$ (400 MHz):





^{13}C NMR spectrum of compound **14d** in $CDCl_3$ (101 MHz):