Visible-Light-Mediated Three-Component Minisci Reaction for Heteroarylethyl Alcohols Synthesis

Jianyang Dong, Fuyang Yue, Jianhua Liu, Hongjian Song, Yuxiu Liu and Qingmin Wang*

State Key Laboratory of Elemento-Organic Chemistry, Research Institute of Elemento-Organic Chemistry, College of Chemistry, Frontiers Science Center for New Organic Matter, Nankai University, Tianjin 300071, People's Republic of China

E-mail: wangqm@nankai.edu.cn

Supporting Information

1. General information

Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (36 W, λ_{max} = 470 nm) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature, the internal temperature is 30 ℃.

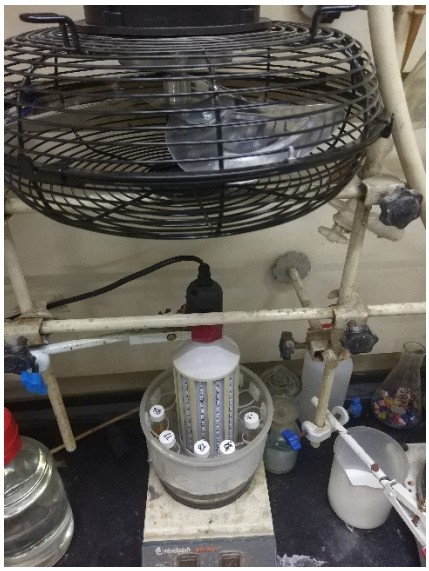


Figure S1 Photograph of the Photocatalytic reactor used for reactions conducted under blue LED irradiation.

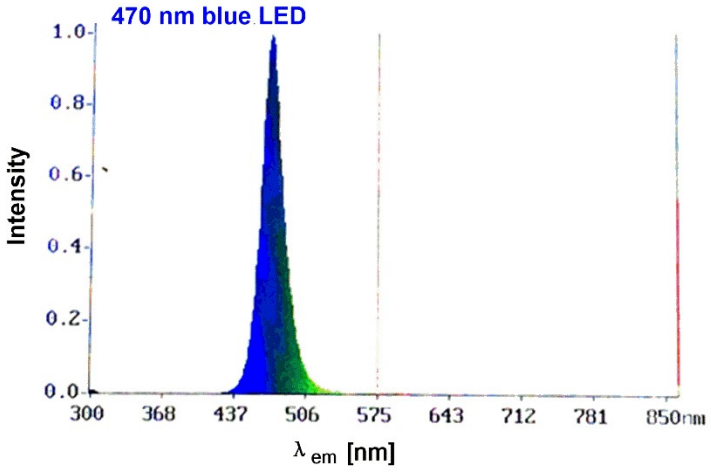


Figure S2 Emission spectra of the used light sources.

2. Preparation of photocatalyst

The photocatalyst was synthesized according to literature report.[1] The spectral data of the photocatalyst is consistent with the literature data. The other photocatalysts (Eosin Y, Fluorescein, $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$, $Ru(bpy)_3(PF_6)_2$, $Ir(ppy)_3$ and Mes-Acr) are commercially available.

3. Investigation of the key reaction parameters

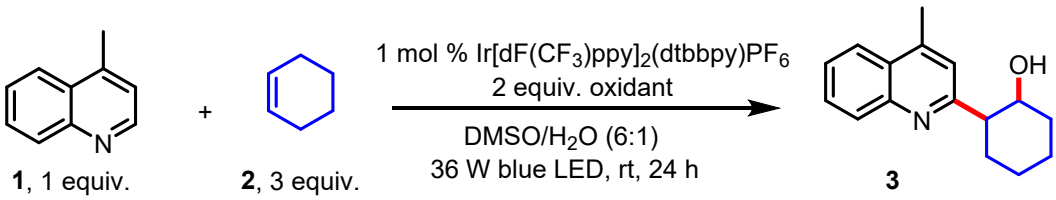
Table S1: Screening of photocatalysts[a]

1, 1 equiv. + **2**, 3 equiv. → **3**

entry	photocatalyst	yield (%)[b]
1	$[Ir(dtbbpy)(ppy)_2][PF_6]$	13
2	$[Ru(bpy)_3](PF_6)_2$	8
3	$[Ru(bpy)_3]$ $6H_2O$	12
4[c]	4CzIPN	NR
5[c]	Eosin-Y	NR
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	94

[a]Reaction conditions, unless otherwise noted: **1** (0.2 mmol), **2** (0.6 mmol), photocatalyst (0.002 mmol), $K_2S_2O_8$ (0.4 mmol), DMSO (2.0 mL), H_2O (333 μL), rt, air atmosphere, 24 h. [b]Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction. [c]The amount of photocatalyst was 0.01 mmol.

Table S2: Screening of oxidants[a]



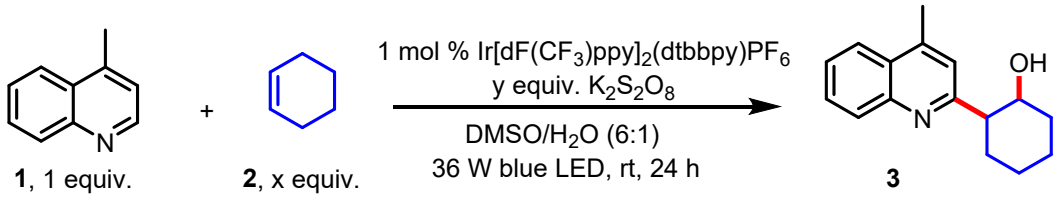
1, 1 equiv. + **2**, 3 equiv. → **3**

entry	oxidant	yield (%)[b]
1	$K_2S_2O_8$	94
2	$Na_2S_2O_8$	87%
3	$(NH_4)_2S_2O_8$	88%
4	TBHP	<5
5	t-BPA	<5
6	H_2O_2	<5
7	1 atm O_2	<5

[a]Reaction conditions, unless otherwise noted: **1** (0.2 mmol), **2** (0.6 mmol),

$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol), oxidant (0.4 mmol), DMSO (2.0 mL), H_2O (333 μL), rt, air atmosphere, 24 h. [b]Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard.

Table S3: Screening of the amount of cyclohexene (2) and oxidant[a]



1, 1 equiv. + **2**, x equiv. → **3**

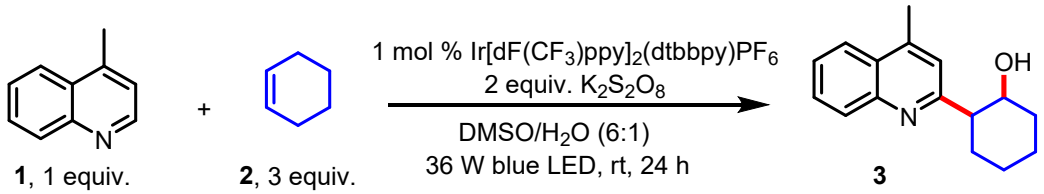
entry	x eq. **2**	y eq. $K_2S_2O_8$	yield (%)[b]
1	3	2	94
2	2	2	85
3	1.5	2	77
4	3	1.5	82
5	3	1.2	73

[a]Reaction conditions, unless otherwise noted: **1** (0.2 mmol), **2** (0.2x mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol), $K_2S_2O_8$ (0.2y mmol), DMSO (2.0 mL), H_2O (333 μL), rt, air atmosphere, 24 h. [b]Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard.

4. Investigation of the mechamism

4.1 Control experiments

Table S4

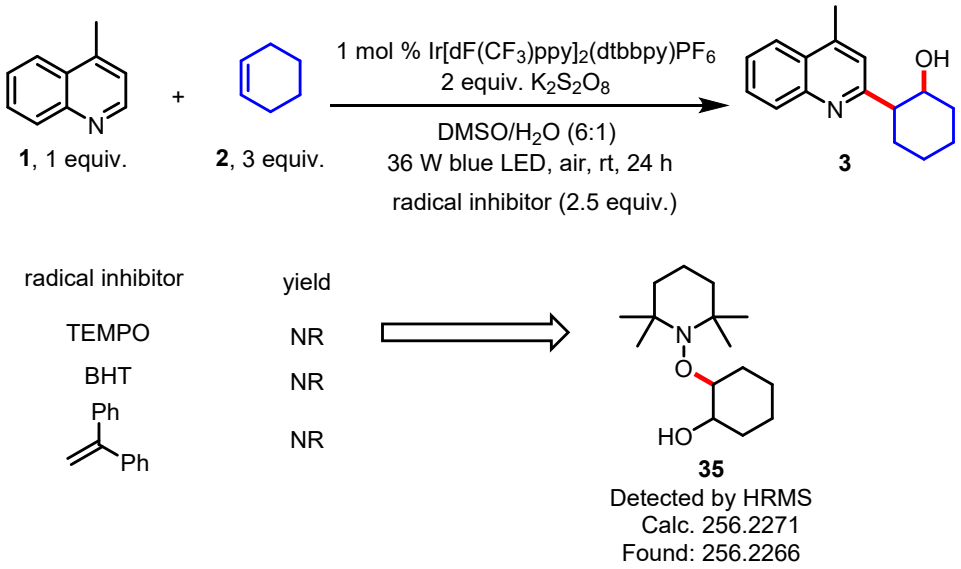


1, 1 equiv. + **2**, 3 equiv. → **3**

entry	control conditions	yield (%)
1	w/o photocatalyst	<5
2	w/o light	NR
3	w/o $K_2S_2O_8$	<5
4	standard conditions, w/all	94

Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard.

4.2 TEMPO, BHT and 1,1-diphenylethylene were used as radical scavengers



Scheme S1

To a 10 mL glass vial was added Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (2.24 mg, 0.002 mmol, 1 mol %), **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3 equiv), TEMPO (78 mg, 0.5 mmol, 2.5 equiv), BHT (110 mg, 0.5 mmol, 2.5 equiv), or 1,1-diphenylethylene (90 mg, 0.5 mmol, 2.5 equiv), $K_2S_2O_8$ (0.4 mmol, 2 equiv), 333 uL of H_2O and 2.0 mL of DMSO. The vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The corresponding heteroarylethyl alcohol **3** was not observed based on ^{1}H NMR analysis, and instead the corresponding product of radical trapping, 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)cyclohexan-1-ol (**35**), was detected by HR-MS (positive mode ESI).

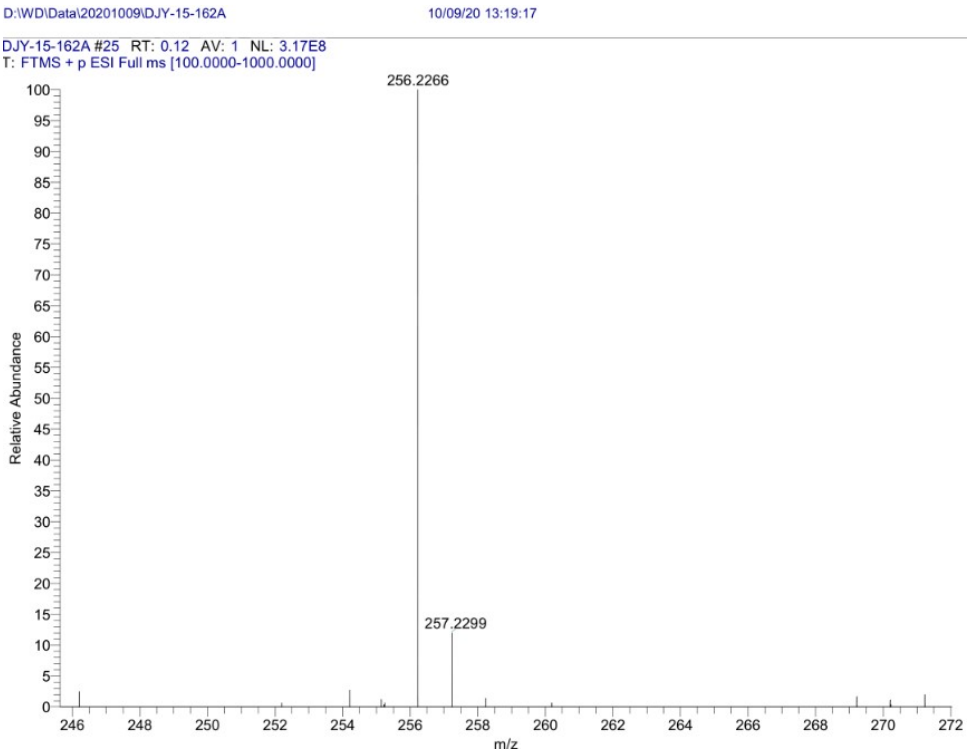
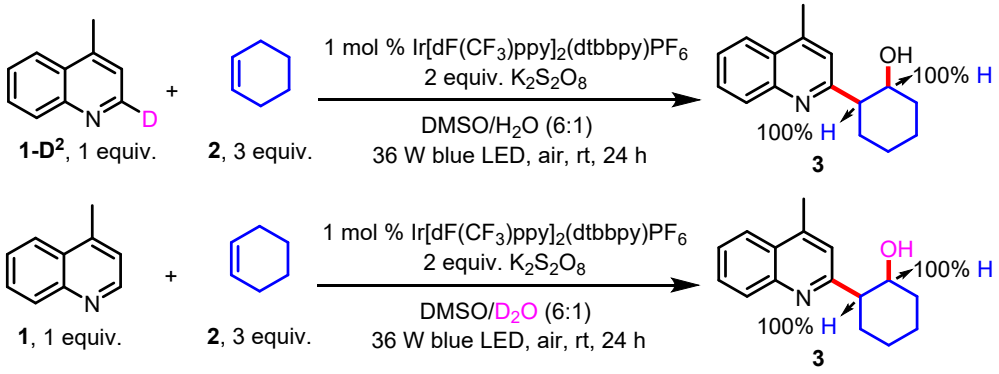


Figure S3 HR-ESI mass spectra of 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)cyclohexan-1-ol (**35**)

4.3 Deuterium-labelling experiments



Scheme S2

To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.24 mg, 0.002 mmol, 1 mol %), **1** or **1-D²** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3 equiv), $K_2S_2O_8$ (0.4 mmol, 2 equiv), 333 uL of H_2O or D_2O, 2.0 mL of DMSO. The vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reactions did not result in incorporation of deuterium into the α-hydroxyl and benzyl positions of product **3** based on ^1H NMR analysis.

4.4 Light/dark experiment

Eight standard reaction mixtures in 10 mL glass vials were charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.24 mg, 0.002 mmol, 1 mol %), **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3 equiv), $K_2S_2O_8$ (0.4 mmol, 2 equiv), 333 uL of H_2O and 2.0 mL of DMSO. The vial was sealed with PTFE cap. The mixtures were then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 2 h, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 2 h of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h, then, a vial was removed for analysis and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 2 h, and then it was analyzed. The yield was determined by ^1H NMR spectroscopy using dibromomethane as the internal standard.

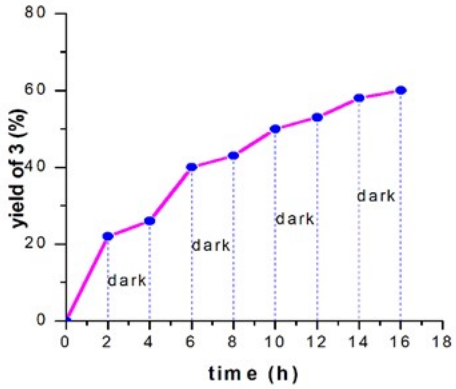


Figure S4 Light/dark experiment.

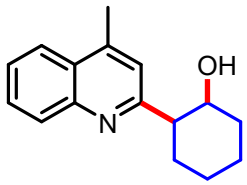
5. Experimental Procedures and Product Characterization

5.1 General procedure for the hydroxy-heteroarylation of unactivated alkenes.

To a 10 mL glass vial was added Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (2.24 mg, 0.002 mmol, 1 mol %), *N*-heteroarene (0.2 mmol, 1.0 equiv), alkene (0.6 mmol, 3.0 equiv), $K_2S_2O_8$ (0.4 mmol, 2 equiv), 333 uL of H_2O and 2.0 mL of DMSO. The vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with 20 mL of aqueous 1 M $NaHCO_3$ solution and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

5.2. Product characterization

(1*S*,2*S*)-2-(4-methylquinolin-2-yl)cyclohexan-1-ol (3).



According to the *general procedure*.

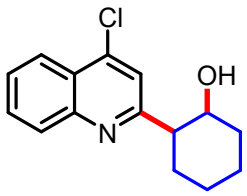
White solid (42.4mg, 88%). M.p. = 105 – 106 °C.

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.57 – 7.47 (m, 1H), 7.22 (s, 1H), 4.64 (s, 1H), 4.12 (td, J = 10.4, 4.4 Hz, 1H), 2.87 – 2.77 (m, 1H), 2.69 (s, 3H), 2.27 – 2.08 (m, 2H), 1.90 – 1.81 (m, 2H), 1.57 – 1.39 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 147.0, 145.2, 129.6, 129.4, 127.1, 126.0, 123.8, 121.1, 72.8, 52.7, 34.2, 31.5, 26.3, 25.0, 19.0.

HRMS (ESI) calcd for $C_{16}H_{20}NO$ $[M + H]^+$ 242.1539, found 242.1542.

(1*S*,2*S*)-2-(4-chloroquinolin-2-yl)cyclohexan-1-ol (4).



According to the *general procedure*.

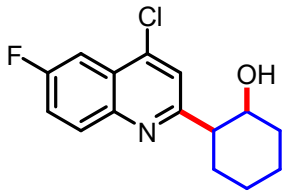
Yellow solid (29.2 mg, 56%). M.p. = 115 – 116 °C.

R_f 0.40 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.80 – 7.69 (m, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.47 (s, 1H), 4.21 (s, 1H), 4.15 – 3.96 (m, 1H), 2.91 – 2.75 (m, 1H), 2.16 (dd, J = 11.6, 9.2 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.57 – 1.40 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 148.1, 143.3, 130.6, 129.4, 127.2, 125.2, 124.1, 120.8, 72.6, 53.0, 34.3, 31.6, 26.1, 24.9.

HRMS (ESI) calcd for $C_{15}H_{17}ClNO$ $[M + H]^+$ 262.0993, found 262.0992.

(1*S*,2*S*)-2-(4-chloro-6-fluoroquinolin-2-yl)cyclohexan-1-ol (5).



According to the *general procedure*.

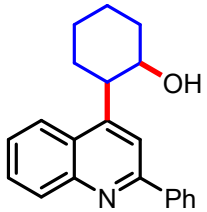
White solid (25.9 mg, 46%). M.p. = 154 – 155 °C.

R_f 0.40 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 9.2, 5.4 Hz, 1H), 7.78 (dd, J = 9.2, 2.8 Hz, 1H), 7.58 – 7.45 (m, 2H), 4.10 (td, J = 10.0, 4.4 Hz, 1H), 3.94 (s, 1H), 2.87 – 2.75 (m, 1H), 2.18 – 2.09 (m, 2H), 1.89 – 1.80 (m, 2H), 1.53 – 1.39 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 161.0 (d, J = 248.8 Hz), 145.2, 142.4, 132.0 (d, J = 9.0 Hz), 126.2 (d, J = 10.2 Hz), 121.5 (d, J = 25.8 Hz), 108.9 (d, J = 24.3 Hz), 72.7, 53.1, 34.3, 31.7, 26.0, 24.9.

HRMS (ESI) calcd for $C_{15}H_{16}ClFNO$ $[M + H]^+$ 280.0899, found 280.0900.

(1*R*,2*R*)-2-(2-phenylquinolin-4-yl)cyclohexan-1-ol (6).



According to the *general procedure*.

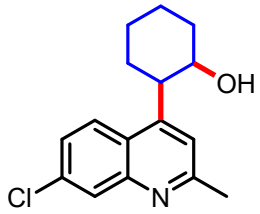
White solid (36.4 mg, 60%). M.p. = 106 – 107 °C.

R_f 0.30 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 1H), 8.07 (dd, J = 5.2, 3.2 Hz, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.69 (s, 1H), 7.62 – 7.55 (m, 1H), 7.54 – 7.42 (m, 4H), 3.87 (t, J = 7.6 Hz, 1H), 3.37 (t, J = 9.2 Hz, 1H), 2.54 (s, 1H), 2.19 (dd, J = 10.4, 3.6 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.80 (d,

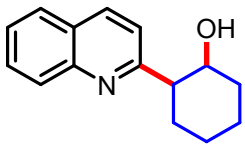
J = 7.6 Hz, 1H), 1.61 – 1.38 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 151.0, 148.4, 139.7, 130.3, 129.4, 129.3, 128.8, 127.8, 127.0, 126.2, 123.2, 115.8, 74.0, 46.4, 35.2, 33.4, 26.1, 25.1.
HRMS (ESI) calcd for $C_{21}H_{22}NO$ $[M + H]^+$ 304.1696, found 304.1699.

(1*R*,2*R*)-2-(7-chloro-2-methylquinolin-4-yl)cyclohexan-1-ol (7).



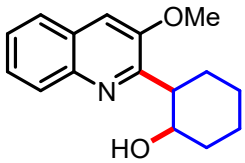
According to the *general procedure*.
Yellow solid (37.4 mg, 68%). M.p. = 145 – 146 °C.
R_f 0.20 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 9.2 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.41 (dd, J = 9.2, 2.0 Hz, 1H), 7.12 (s, 1H), 3.92 (s, 1H), 3.29 (t, J = 9.2 Hz, 1H), 2.47 (s, 3H), 2.31 – 2.20 (m, 1H), 1.97 (d, J = 12.0 Hz, 1H), 1.86 (t, J = 13.6 Hz, 2H), 1.66 – 1.42 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 151.3, 148.1, 135.1, 127.9, 126.5, 124.9, 124.8, 118.9, 74.5, 46.6, 35.4, 33.1, 26.1, 25.2, 25.2.
HRMS (ESI) calcd for $C_{16}H_{19}ClNO$ $[M + H]^+$ 276.1150, found 276.1151.

(1*S*,2*S*)-2-(quinolin-2-yl)cyclohexan-1-ol (8).



According to the *general procedure*.
White solid (27.7 mg, 61%). M.p. = 115 – 116 °C.
R_f 0.40 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 4.14 (t, J = 8.4 Hz, 1H), 2.87 (t, J = 11.2 Hz, 1H), 2.19 (d, J = 11.6 Hz, 2H), 1.87 (dd, J = 13.6, 5.2 Hz, 2H), 1.58 – 1.42 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 147.2, 137.0, 129.8, 129.0, 127.6, 127.0, 126.3, 120.5, 72.8, 52.9, 34.2, 31.6, 26.3, 25.0.
HRMS (ESI) calcd for $C_{15}H_{18}NO$ $[M + H]^+$ 228.1383, found 228.1385.

(1*R*,2*R*)-2-(3-methoxyquinolin-2-yl)cyclohexan-1-ol (9).



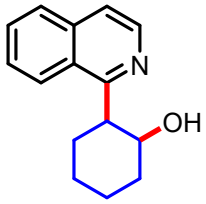
According to the *general procedure*.
White solid (29.3 mg, 57%). M.p. = 100 – 101 °C.

R_f 0.50 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.45 (ddd, J = 8.4, 2.8, 1.2 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 4.54 – 4.39 (m, 1H), 3.94 (s, 3H), 3.31 (s, 1H), 3.27 – 3.11 (m, 1H), 2.17 (dd, J = 7.2, 4.8 Hz, 2H), 1.90 – 1.75 (m, 2H), 1.57 – 1.44 (m, 3H), 1.34 – 1.25 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 152.2, 142.5, 128.8, 128.2, 126.7, 126.5, 126.4, 111.9, 71.5, 55.4, 49.0, 33.7, 30.5, 26.3, 25.3.

HRMS (ESI) calcd for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1489, found 258.1490.

(1*S*,2*S*)-2-(isoquinolin-1-yl)cyclohexan-1-ol (10).



According to the *general procedure*.

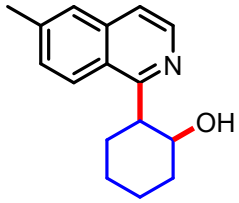
White solid (31.8 mg, 70%). M.p. = 86 – 87 °C.

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 5.6 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 5.6 Hz, 1H), 4.52 – 4.37 (m, 1H), 3.53 (t, J = 10.0 Hz, 1H), 3.03 (s, 1H), 2.21 (d, J = 12.4 Hz, 1H), 2.10 (d, J = 11.2 Hz, 1H), 1.92 (d, J = 6.6 Hz, 1H), 1.80 (s, 1H), 1.67 – 1.41 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 141.7, 136.7, 130.0, 127.7, 127.4, 127.2, 125.0, 119.6, 71.9, 50.0, 33.8, 32.9, 26.4, 25.2.

HRMS (ESI) calcd for $C_{15}H_{18}NO$ $[M + H]^+$ 228.1383, found 228.1385.

(1*S*,2*S*)-2-(6-methylisoquinolin-1-yl)cyclohexan-1-ol (11).



According to the *general procedure*.

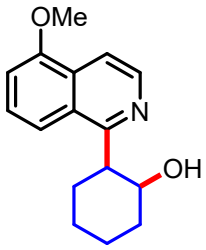
White solid (38.1 mg, 79%). M.p. = 98 – 99 °C.

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 5.6 Hz, 1H), 8.07 (d, J = 8.8 Hz, 1H), 7.58 (s, 1H), 7.51 – 7.38 (m, 2H), 4.44 (td, J = 10.4, 4.0 Hz, 1H), 3.49 (dd, J = 14.4, 6.4 Hz, 1H), 3.05 (s, 1H), 2.53 (s, 3H), 2.21 (d, J = 12.0 Hz, 1H), 2.08 (d, J = 10.8 Hz, 1H), 1.92 (dd, J = 5.6, 2.8 Hz, 1H), 1.80 (d, J = 7.6 Hz, 1H), 1.63 – 1.44 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 141.8, 140.3, 137.1, 129.4, 126.6, 125.8, 124.9, 119.1, 71.9, 50.0, 33.8, 32.9, 26.4, 25.2, 21.9.

HRMS (ESI) calcd for $C_{16}H_{20}NO$ $[M + H]^+$ 242.1539, found 242.1541.

(1*S*,2*S*)-2-(5-methoxyisoquinolin-1-yl)cyclohexan-1-ol (12).



According to the *general procedure*.

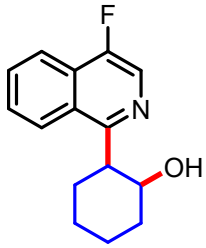
White solid (42.7 mg, 83%). M.p. = 105 – 106 °C.

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 5.6 Hz, 1H), 7.93 (d, J = 5.6 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 4.46 (td, J = 10.4, 4.0 Hz, 1H), 4.01 (s, 3H), 3.50 (dd, J = 14.8, 6.2 Hz, 1H), 3.04 (s, 1H), 2.22 (d, J = 12.4 Hz, 1H), 2.11 (d, J = 13.2 Hz, 1H), 1.93 (d, J = 6.4 Hz, 1H), 1.80 (s, 1H), 1.62 – 1.44 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 155.2, 141.3, 129.4, 128.1, 127.2, 116.8, 113.8, 107.4, 71.9, 55.8, 50.3, 33.8, 32.9, 26.4, 25.2.

HRMS (ESI) calcd for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1489, found 258.1491.

(1*S*,2*S*)-2-(4-fluoroisoquinolin-1-yl)cyclohexan-1-ol (13).



According to the *general procedure*.

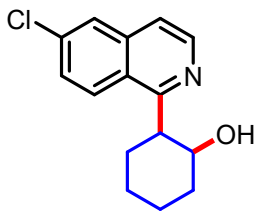
Yellow solid (39.2 mg, 80%). M.p. = 122 – 123 °C.

R_f 0.60 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 4.41 (t, J = 10.0 Hz, 1H), 3.46 (t, J = 10.0 Hz, 1H), 2.86 (s, 1H), 2.20 (d, J = 12.0 Hz, 1H), 2.04 (d, J = 10.8 Hz, 1H), 1.92 (d, J = 4.8 Hz, 1H), 1.79 (s, 1H), 1.52 (dt, J = 20.0, 12.0 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 154.2 (d, J = 257.8 Hz), 130.2, 128.5 (d, J = 1.6 Hz), 128.0, 127.4 (d, J = 15.0 Hz), 126.6 (d, J = 22.7 Hz), 125.0, 120.4 (d, J = 4.5 Hz), 71.9, 49.8, 33.9, 32.9, 26.3, 25.2.

HRMS (ESI) calcd for $C_{15}H_{17}FNO$ $[M + H]^+$ 246.1289, found 246.1289.

(1*S*,2*S*)-2-(6-chloroisoquinolin-1-yl)cyclohexan-1-ol (14).



According to the *general procedure*.

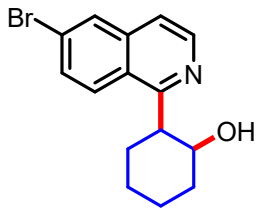
White solid (29.8 mg, 57%). M.p. = 114 – 115 °C.

R_f 0.35 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 5.6 Hz, 1H), 8.13 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 2.0 Hz, 1H), 7.52 (dd, J = 9.2, 2.0 Hz, 1H), 7.42 (d, J = 5.6 Hz, 1H), 4.53 – 4.34 (m, 1H), 3.54 – 3.35 (m, 1H), 2.95 (s, 1H), 2.20 (d, J = 12.0 Hz, 1H), 2.11 – 1.99 (m, 1H), 1.92 (dd, J = 5.6, 2.8 Hz, 1H), 1.81 (d, J = 5.6 Hz, 1H), 1.62 – 1.45 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 142.8, 137.6, 136.2, 128.1, 126.9, 126.4, 125.6, 118.6, 71.9, 50.0, 33.9, 32.9, 26.3, 25.1.

HRMS (ESI) calcd for $C_{15}H_{17}ClNO$ $[M + H]^+$ 262.0993, found 262.0994.

(1*S*,2*S*)-2-(6-bromoisoquinolin-1-yl)cyclohexan-1-ol (15).



According to the *general procedure*.

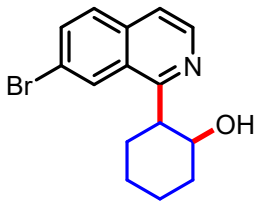
Yellow solid (42.1 mg, 69%). M.p. = 126 – 127 °C.

R_f 0.40 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 5.6 Hz, 1H), 8.03 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 1.2 Hz, 1H), 7.63 (dd, J = 9.2, 1.6 Hz, 1H), 7.40 (d, J = 5.6 Hz, 1H), 4.40 (td, J = 10.0, 4.0 Hz, 1H), 3.44 (dd, J = 14.4, 6.4 Hz, 1H), 2.89 (s, 1H), 2.18 (d, J = 12.0 Hz, 1H), 2.00 (d, J = 10.4 Hz, 1H), 1.93 – 1.87 (m, 1H), 1.78 (s, 1H), 1.58 – 1.42 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 142.8, 137.9, 130.7, 129.8, 126.9, 125.8, 124.8, 118.5, 71.8, 50.0, 33.8, 32.9, 26.3, 25.1.

HRMS (ESI) calcd for $C_{15}H_{17}BrNO$ $[M + H]^+$ 306.0488, found 306.0490.

(1*S*,2*S*)-2-(7-bromoisoquinolin-1-yl)cyclohexan-1-ol (16).



According to the *general procedure*.

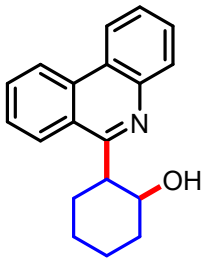
Yellow solid (42.7 mg, 70%). M.p. = 119 – 120 °C.

R_f 0.40 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, J = 5.6, 2.0 Hz, 1H), 8.33 (s, 1H), 7.72 (dt, J = 8.8, 5.2 Hz, 2H), 7.60 – 7.46 (m, 1H), 4.43 (dd, J = 13.6, 6.8 Hz, 1H), 3.43 (t, J = 10.4 Hz, 1H), 2.81 (s, 1H), 2.21 (d, J = 12.0 Hz, 1H), 2.05 (d, J = 10.8 Hz, 1H), 1.97 – 1.89 (m, 1H), 1.82 (d, J = 8.8 Hz, 1H), 1.54 (ddd, J = 21.2, 17.6, 7.6 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 142.2, 135.2, 133.5, 129.4, 128.4, 127.4, 121.1, 119.2, 71.9, 49.9, 33.9, 32.9, 26.3, 25.2.

HRMS (ESI) calcd for $C_{15}H_{17}BrNO$ $[M + H]^+$ 306.0488, found 306.0490.

(1*S*,2*S*)-2-(phenanthridin-6-yl)cyclohexan-1-ol (17).



According to the *general procedure*.

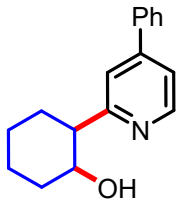
Yellow solid (27.7 mg, 50%). M.p. = 64 – 65 °C.

R_f 0.60 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.4 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 4.57 (s, 1H), 3.61 (d, J = 11.6 Hz, 1H), 2.19 – 2.06 (m, 2H), 1.99 – 1.85 (m, 3H), 1.67 – 1.60 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 142.2, 133.3, 130.9, 129.6, 129.0, 127.6, 126.9, 125.9, 124.6, 123.6, 122.9, 122.1, 68.3, 43.8, 33.1, 27.8, 26.7, 20.0.

HRMS (ESI) calcd for $C_{19}H_{20}NO$ $[M + H]^+$ 278.1539, found 278.1539.

(1*S*,2*S*)-2-(4-phenylpyridin-2-yl)cyclohexan-1-ol (18).



According to the *general procedure*.

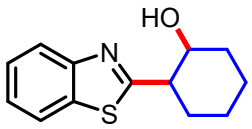
Yellow oil (20.7 mg, 41%).

R_f 0.30 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 4.4 Hz, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.55 – 7.41 (m, 4H), 7.39 (d, J = 4.8 Hz, 1H), 3.95 (t, J = 9.6 Hz, 1H), 2.74 (t, J = 11.2 Hz, 1H), 2.20 – 2.03 (m, 2H), 1.89 – 1.78 (m, 2H), 1.64 – 1.38 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 149.6, 149.0, 138.5, 129.2, 127.2, 120.5, 119.9, 73.3, 52.2, 34.7, 31.4, 26.0, 24.9.

HRMS (ESI) calcd for $C_{17}H_{20}NO$ $[M + H]^+$ 254.1539, found 254.1539.

(1*S*,2*R*)-2-(benzo[d]thiazol-2-yl)cyclohexan-1-ol (19).



According to the *general procedure*.

Yellow solid (20.5 mg, 44%). M.p. = 85 – 86 °C.

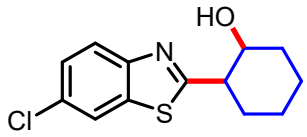
R_f 0.40 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.41 – 7.34 (m, 1H), 4.49 (s, 1H), 3.93 (td, J = 10.0, 4.4 Hz, 1H), 3.03 – 2.89 (m, 1H), 2.31 – 2.22 (m, 1H), 2.18 (dd, J = 9.2, 2.8 Hz, 1H), 1.89 – 1.82 (m, 2H), 1.64 (ddd, J = 25.2, 12.6, 3.4 Hz, 2H), 1.44 (ddd, J = 13.6, 7.2, 2.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7, 152.7, 134.3,

126.2, 125.0, 122.8, 121.7, 73.3, 50.2, 33.9, 31.7, 25.7, 24.4.

HRMS (ESI) calcd for $C_{13}H_{16}NOS$ $[M + H]^+$ 234.0947, found 234.0949.

(1*S*,2*R*)-2-(6-chlorobenzo[d]thiazol-2-yl)cyclohexan-1-ol (20).



According to the *general procedure*.

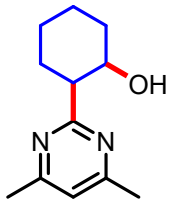
Yellow solid (20.3 mg, 38%). M.p. = 87 – 88 °C.

R_f 0.40 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 3.91 (t, J = 9.6 Hz, 1H), 2.98 (t, J = 11.2 Hz, 1H), 2.21 (dd, J = 28.4, 11.6 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.63 (dd, J = 22.8, 10.8 Hz, 2H), 1.43 (t, J = 10.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 153.6, 132.6, 132.3, 125.6, 122.7, 122.4, 73.2, 50.3, 34.0, 31.8, 25.7, 24.4.

HRMS (ESI) calcd for $C_{13}H_{15}ClNOS$ $[M + H]^+$ 268.0557, found 268.0561.

(1*R*,2*R*)-2-(4,6-dimethylpyrimidin-2-yl)cyclohexan-1-ol (21).



According to the *general procedure*.

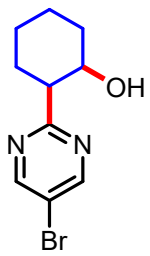
White solid (16.5 mg, 40%). M.p. = 63– 64 °C.

R_f 0.35 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 4.58 (s, 1H), 3.97 (td, J = 10.0, 4.4 Hz, 1H), 2.82 – 2.65 (m, 1H), 2.46 (s, 6H), 2.32 (dd, J = 8.0, 5.2 Hz, 1H), 2.12 (d, J = 10.8 Hz, 1H), 1.84 – 1.78 (m, 2H), 1.46 – 1.34 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 166.6, 117.9, 72.5, 53.2, 34.2, 30.7, 26.0, 25.0, 24.2.

HRMS (ESI) calcd for $C_{12}H_{19}N_2O$ $[M + H]^+$ 207.1492, found 207.1493.

(1*R*,2*R*)-2-(5-bromopyrimidin-2-yl)cyclohexan-1-ol (22).



According to the *general procedure*.

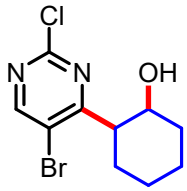
Yellow oil (22.0 mg, 43%).

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.76 (s, 1H), 4.24 (t, J = 7.6 Hz, 1H), 3.20 – 3.05 (m,

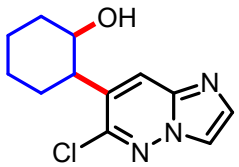
1H), 2.14 (d, J = 10.0 Hz, 1H), 2.00 – 1.94 (m, 1H), 1.91 – 1.85 (m, 1H), 1.79 (d, J = 8.4 Hz, 1H), 1.46 (dd, J = 8.4, 2.4 Hz, 2H), 1.41 – 1.33 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 159.0, 156.9, 71.7, 52.0, 34.5, 30.7, 25.7, 24.9.
HRMS (ESI) calcd for $C_{10}H_{14}BrN_2O$ $[M + H]^+$ 257.0284, found 257.0288.

(1*S*,2*S*)-2-(5-bromo-2-chloropyrimidin-4-yl)cyclohexan-1-ol (23).



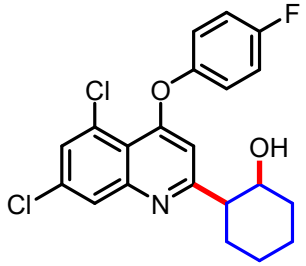
According to the *general procedure*.
White solid (19.7 mg, 34%). M.p. = 126 – 127 °C.
R_f 0.40 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 4.20 (td, J = 10.0, 4.4 Hz, 1H), 3.19 – 3.03 (m, 1H), 2.12 (dt, J = 5.6, 4.4 Hz, 1H), 1.94 – 1.89 (m, 1H), 1.80 (dd, J = 12.8, 2.4 Hz, 2H), 1.48 – 1.36 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 160.9, 159.8, 120.6, 71.7, 52.1, 34.7, 30.6, 25.5, 24.8.
HRMS (ESI) calcd for $C_{10}H_{13}BrClN_2O$ $[M + H]^+$ 290.9894, found 290.9898.

(1*R*,2*R*)-2-(6-chloroimidazo[1,2-b]pyridazin-7-yl)cyclohexan-1-ol (24).



According to the *general procedure*.
Yellow solid (34.6 mg, 69%). M.p. = 140 – 141 °C.
R_f 0.30 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 0.8 Hz, 1H), 7.71 (d, J = 0.8 Hz, 1H), 6.96 (s, 1H), 3.94 (td, J = 10.0, 4.4 Hz, 1H), 3.34 – 3.20 (m, 1H), 2.19 (dd, J = 9.2, 4.4 Hz, 1H), 2.03 – 1.97 (m, 1H), 1.93 – 1.87 (m, 1H), 1.86 – 1.80 (m, 1H), 1.73 (dd, J = 12.4, 3.2 Hz, 1H), 1.52 – 1.41 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 145.3, 138.9, 133.3, 117.5, 116.3, 73.8, 47.8, 36.2, 31.3, 25.5, 24.9.
HRMS (ESI) calcd for $C_{12}H_{15}ClN_3O$ $[M + H]^+$ 252.0898, found 252.0902.

(1*S*,2*S*)-2-(5,7-dichloro-4-(4-fluorophenoxy)quinolin-2-yl)cyclohexan-1-ol (25).



According to the *general procedure*.

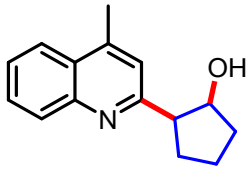
White solid (38.3 mg, 47%). M.p. = 120 – 121 °C.

R_f 0.40 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.54 (s, 1H), 7.22 – 7.01 (m, 4H), 6.53 (s, 1H), 4.16 – 4.01 (m, 1H), 3.91 (s, 1H), 2.62 (dd, J = 13.6, 7.6 Hz, 1H), 2.12 (d, J = 2.4 Hz, 1H), 1.88 – 1.80 (m, 2H), 1.46 – 1.35 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 163.1, 160.2 (d, J = 245.0 Hz), 150.4 (d, J = 83.2 Hz), 135.4, 130.3, 129.2, 127.4, 122.4 (d, J = 8.4 Hz), 117.3 (d, J = 23.6 Hz), 116.4 (d, J = 7.9 Hz), 116.0 (d, J = 23.1 Hz), 106.3, 72.5, 53.1, 34.1, 31.5, 26.0, 24.8.

HRMS (ESI) calcd for $C_{21}H_{19}Cl_2FNO_2$ $[M + H]^+$ 406.0771, found 406.0777.

(1*S*,2*S*)-2-(4-methylquinolin-2-yl)cyclopentan-1-ol (26).



According to the *general procedure*.

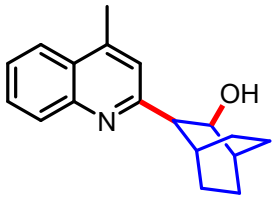
White solid (23.2 mg, 51%). M.p. = 97– 98 °C.

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.14 (s, 1H), 4.41 (q, J = 7.6 Hz, 1H), 3.14 (dd, J = 17.2, 8.8 Hz, 1H), 2.68 (s, 3H), 2.34 (t, J = 9.2 Hz, 1H), 2.18 (dd, J = 14.0, 8.0 Hz, 1H), 1.87 (ddd, J = 32.0, 14.2, 6.8 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 147.1, 144.9, 129.5, 129.4, 127.0, 125.8, 123.7, 120.9, 78.1, 53.5, 32.6, 28.4, 20.7, 18.9.

HRMS (ESI) calcd for $C_{15}H_{18}NO$ $[M + H]^+$ 228.1383, found 228.1385.

(3*S*)-3-(4-methylquinolin-2-yl)bicyclo[2.2.2]octan-2-ol (27).



According to the *general procedure*.

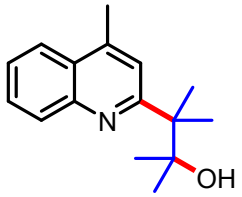
Yellow oil (24.6 mg, 46%).

R_f 0.50 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.16 (s, 1H), 4.23 (d, J = 6.8 Hz, 1H), 3.07 (d, J = 6.8 Hz, 1H), 2.66 (s, 3H), 2.29 (t, J = 13.2 Hz, 3H), 1.69 – 1.45 (m, 3H), 1.34 (d, J = 11.2 Hz, 1H), 1.22 (dd, J = 31.2, 10.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 146.2, 145.3, 129.5, 129.3, 126.6, 126.0, 123.7, 123.5, 78.9, 53.6, 45.0, 44.1, 33.3, 30.4, 24.8, 18.9.

HRMS (ESI) calcd for $C_{18}H_{22}NO$ $[M + H]^+$ 268.1696, found 268.1699.

2,3-dimethyl-3-(4-methylquinolin-2-yl)butan-2-ol (28).



According to the *general procedure*.

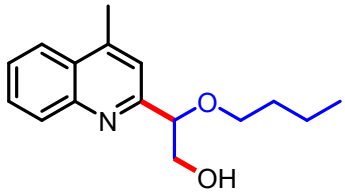
Yellow oil (17.0 mg, 35%).

R_f 0.70 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, J = 9.2 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.38 (s, 1H), 2.73 (s, 3H), 1.49 (s, 6H), 1.15 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 146.0, 145.4, 129.6, 129.5, 126.4, 126.1, 123.6, 119.4, 75.6, 46.6, 26.0, 24.5, 19.3.

HRMS (ESI) calcd for $C_{16}H_{22}NO$ $[M + H]^+$ 244.1696, found 244.1699.

(*R*)-2-butoxy-2-(4-methylquinolin-2-yl)ethan-1-ol (29).



According to the *general procedure*.

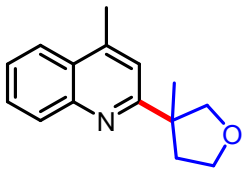
Yellow solid (43.0 mg, 83%). M.p. = 60 – 61 °C.

R_f 0.30 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.43 (s, 1H), 4.64 (t, J = 5.6 Hz, 1H), 3.91 (d, J = 5.6 Hz, 2H), 3.56 (t, J = 6.4 Hz, 2H), 3.25 (s, 1H), 2.74 (s, 3H), 1.65 (dt, J = 13.2, 6.4 Hz, 2H), 1.44 (dt, J = 12.4, 7.2 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 147.3, 145.5, 129.7, 129.5, 127.8, 126.4, 123.9, 119.5, 83.1, 70.1, 65.7, 32.1, 19.5, 19.1, 14.0.

HRMS (ESI) calcd for $C_{16}H_{22}NO_2$ $[M + H]^+$ 260.1645, found 260.1646.

(*S*)-4-methyl-2-(3-methyltetrahydrofuran-3-yl)quinoline (30).



According to the *general procedure*.

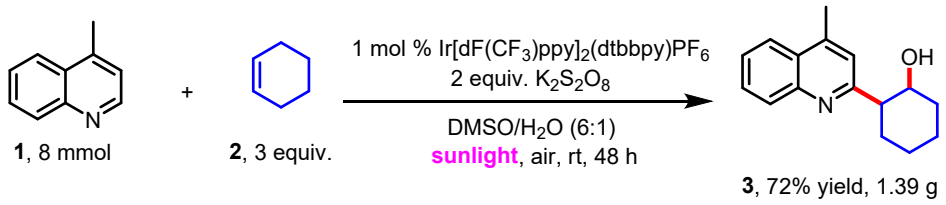
Yellow oil (32.2 mg, 71%).

R_f 0.60 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, J = 7.6 Hz, 2H), 7.76 – 7.68 (m, 1H), 7.60 – 7.54 (m, 1H), 7.22 (s, 1H), 4.30 (dd, J = 11.6, 1.2 Hz, 1H), 3.75 (d, J = 11.6 Hz, 1H), 3.57 (ddd, J = 12.0, 5.6, 3.6 Hz, 1H), 3.34 (ddd, J = 12.0, 9.4, 2.8 Hz, 1H), 2.72 (s, 3H), 2.24 – 2.15 (m, 1H), 2.06 (ddd, J = 14.8, 9.2, 3.6 Hz, 1H), 1.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 145.9, 145.8, 129.8, 129.3, 126.9, 126.5, 123.8, 119.9, 70.5, 59.1, 44.9, 44.6, 25.5, 19.2.

HRMS (ESI) calcd for $C_{15}H_{18}NO$ $[M + H]^+$ 228.1383, found 228.1386.

6. Gram-scale reaction



Scheme S3

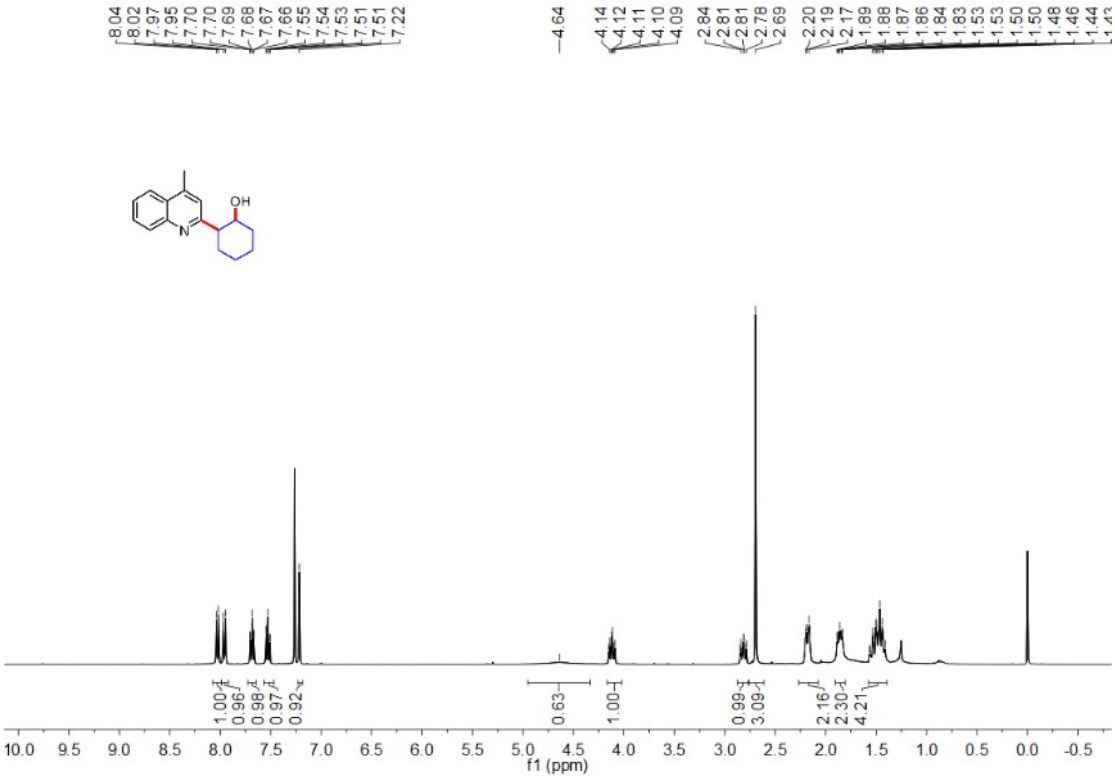
To an oven dried Schlenk tube was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (90 mg, 0.08 mmol, 1 mol %), **1** (1.17 g, 8.0 mmol, 1.0 equiv), **2** (1.97 g ,24 mmol, 3 equiv), $K_2S_2O_8$ (4.32 g , 16 mmol, 2 equiv), 13.3 mL of H_2O and 80 mL of DMSO. The mixture was then stirred rapidly under sunlight irradiation at room temperature for 48 h. The reaction mixture was diluted with 60 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (3 × 200 mL), dried over Na_2SO_4, and concentrated in vacuo. After purification by flash column chromatography on silica gel, the product was obtained in 72% yield (1.39 g).

References

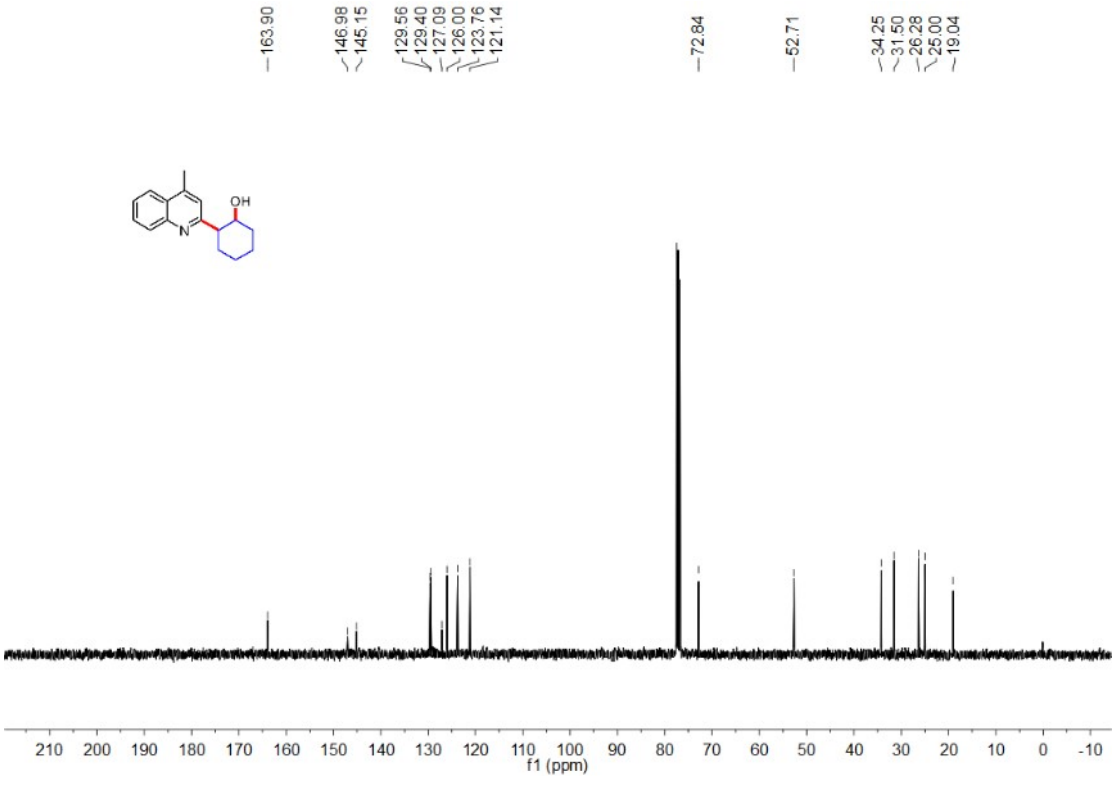
[1] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.***2005**, *17*, 5712.

NMR Spectra

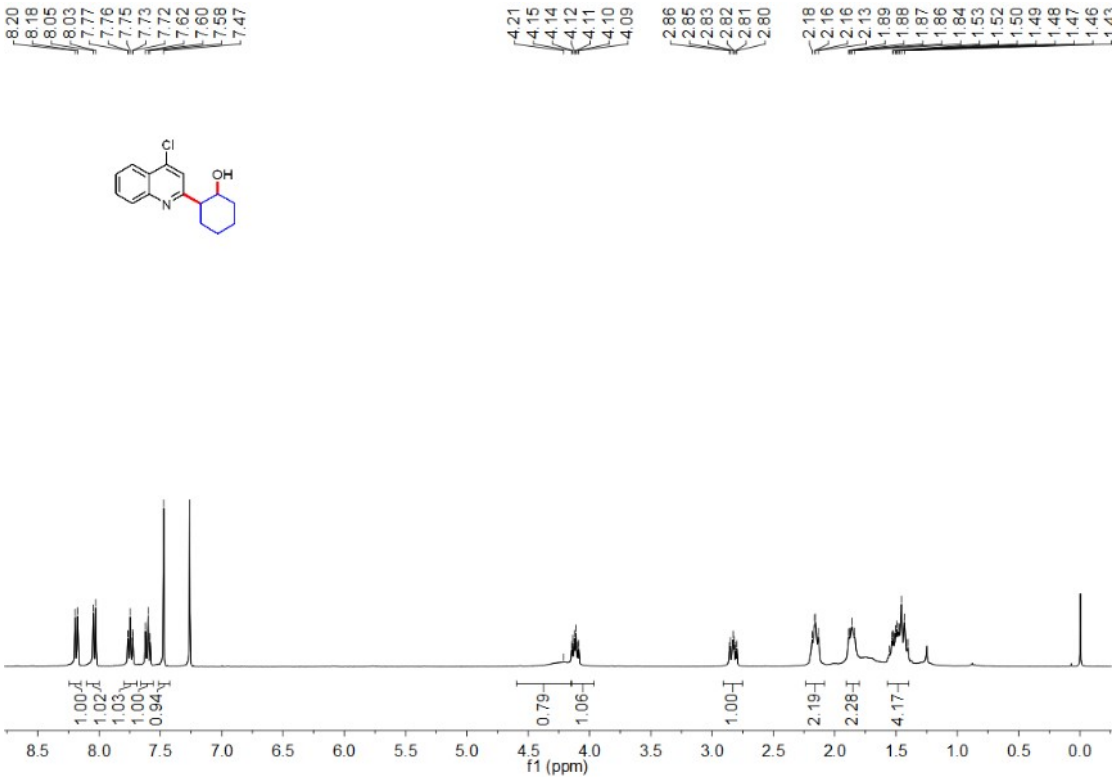
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3**



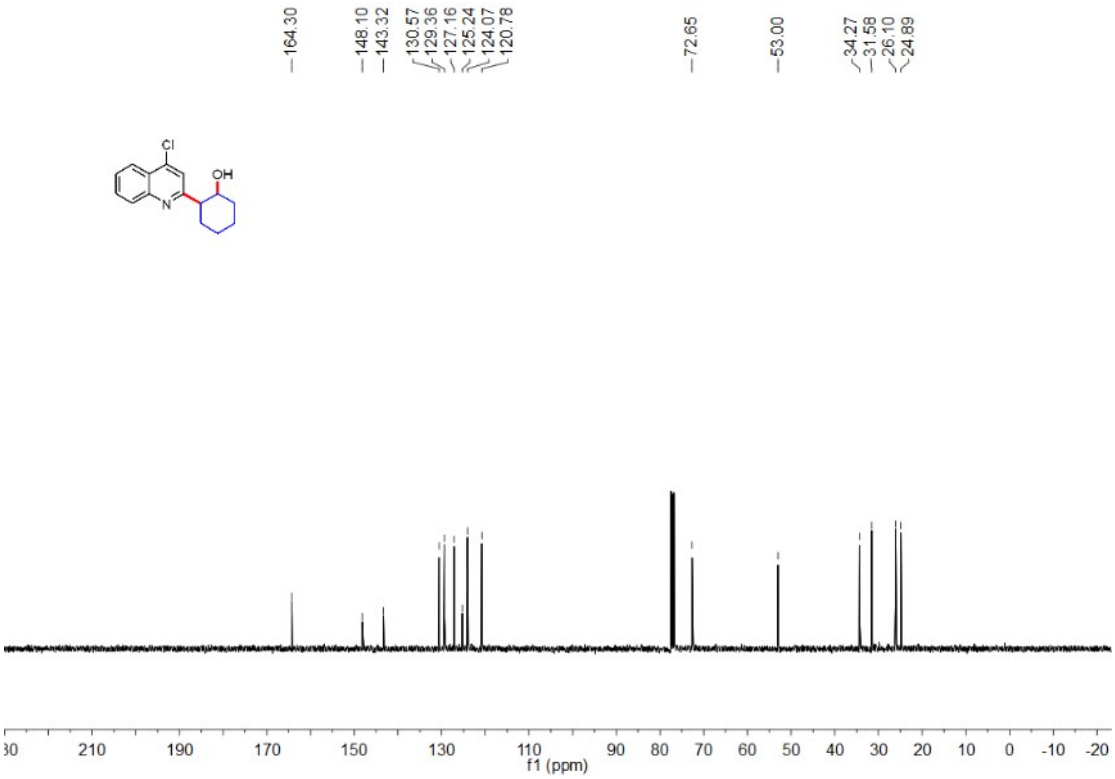
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3**



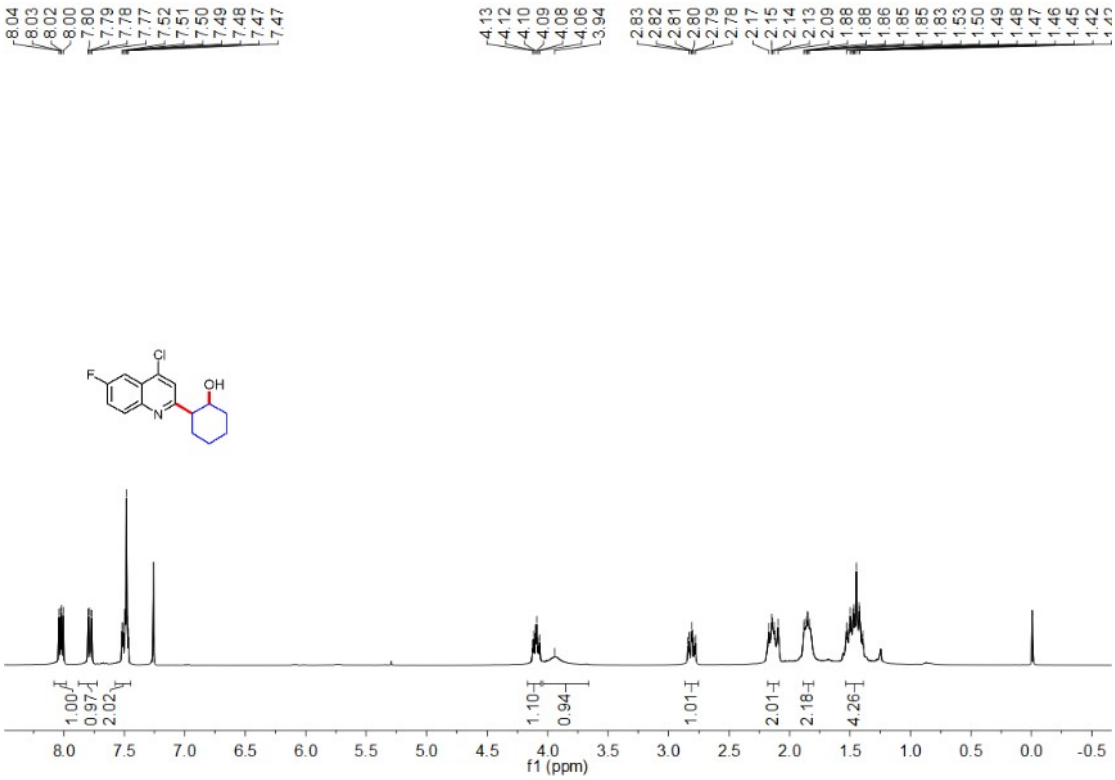
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**



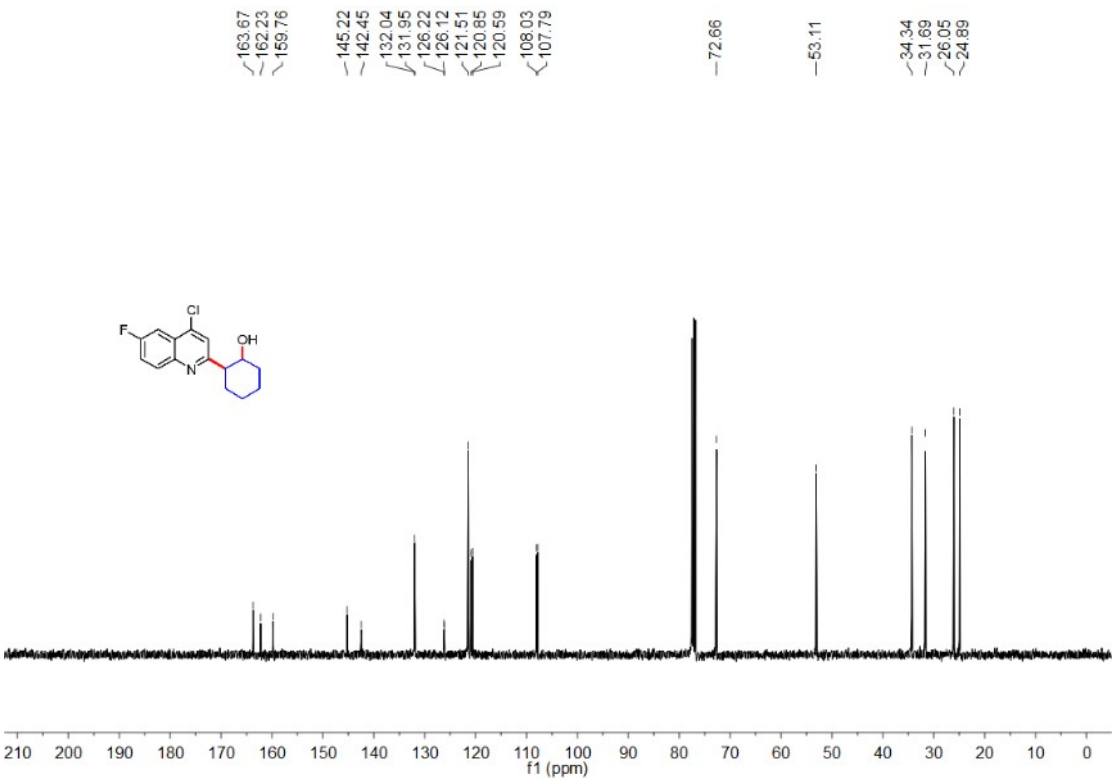
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4**



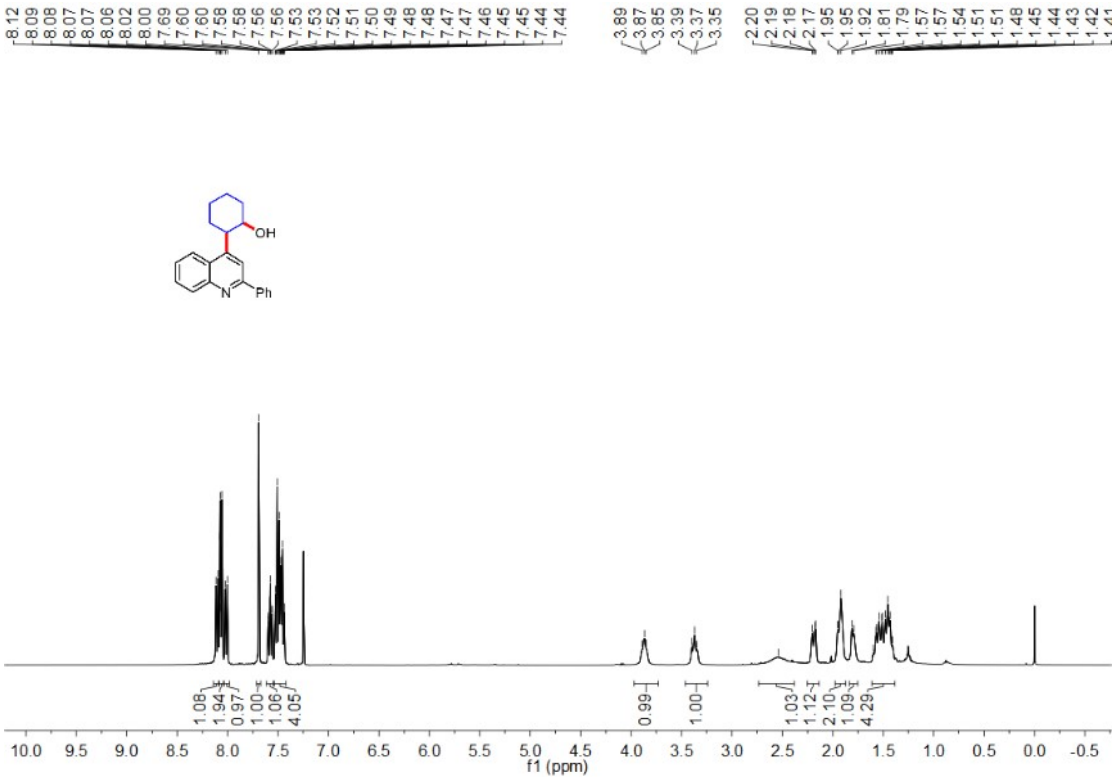
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5**



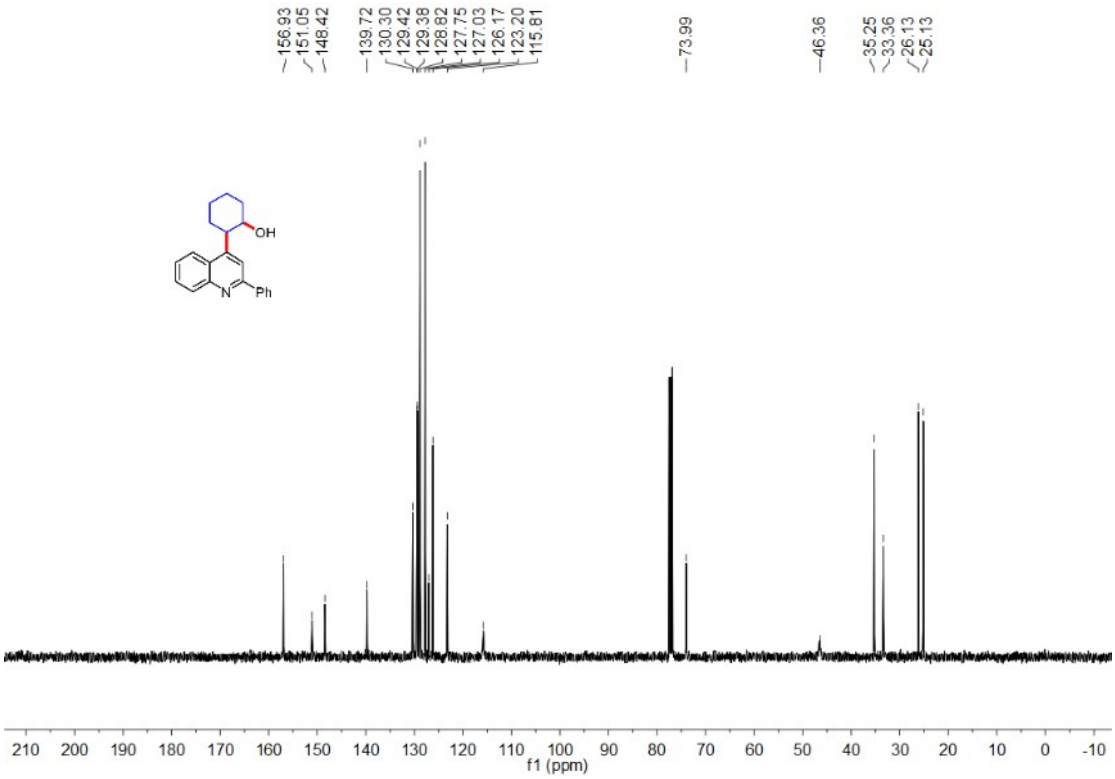
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5**



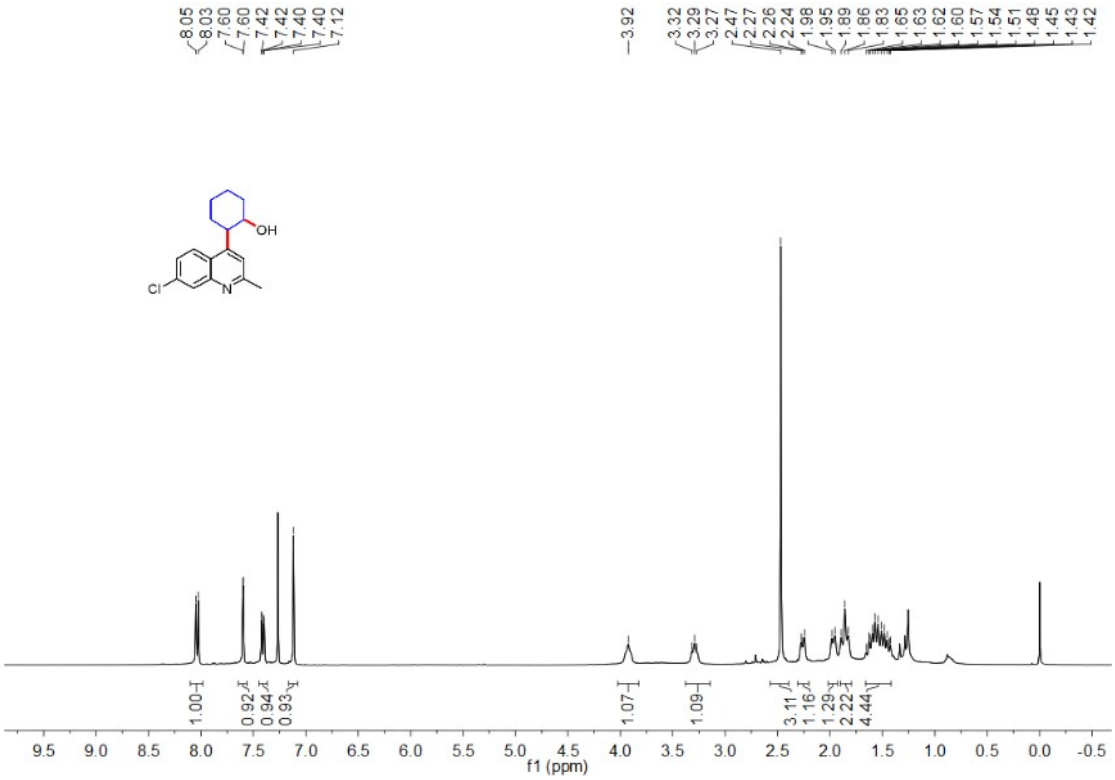
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**



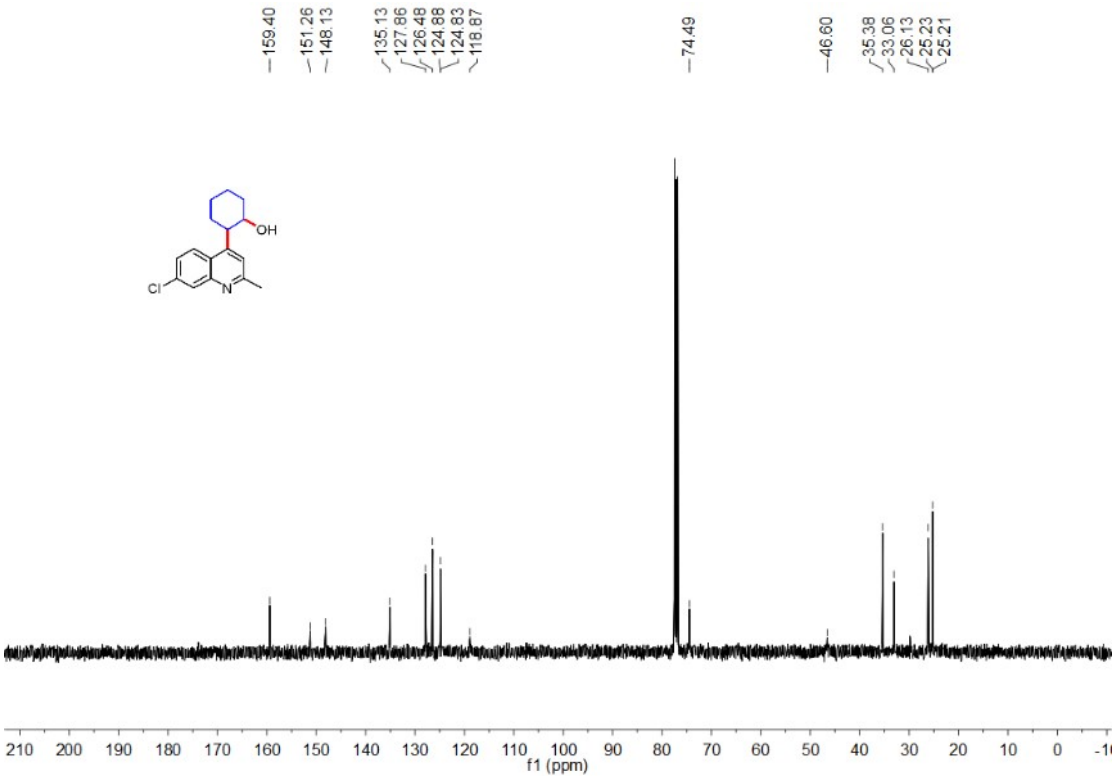
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **6**



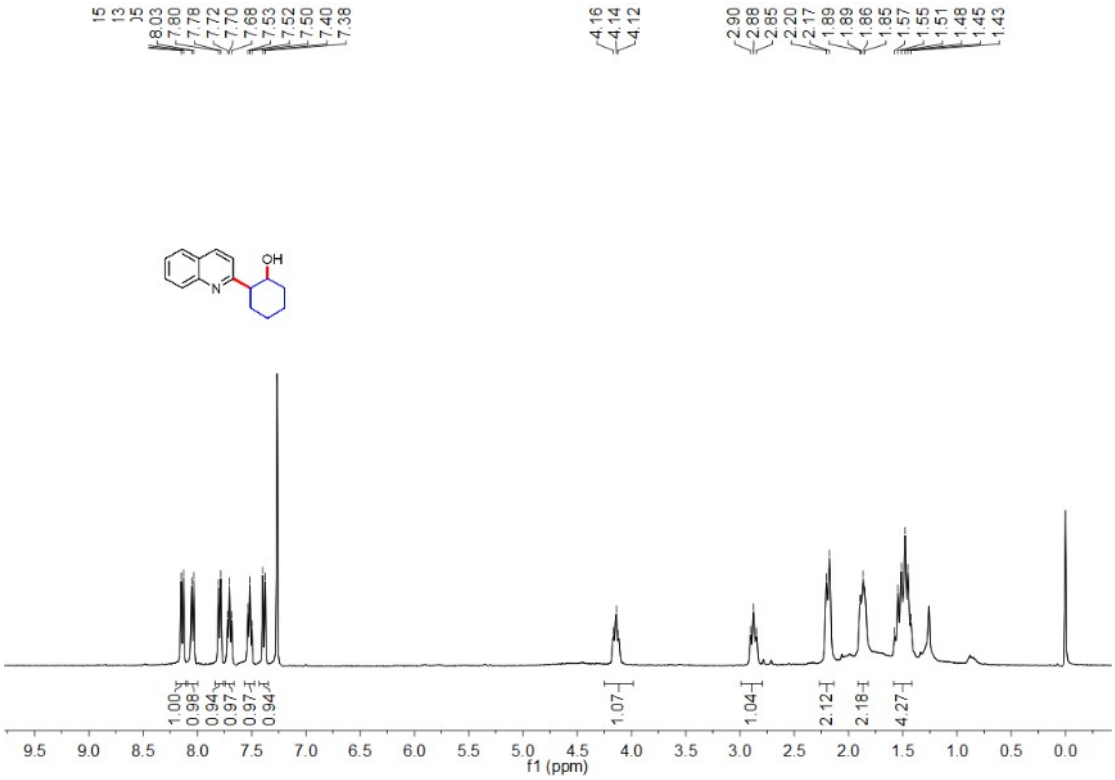
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**



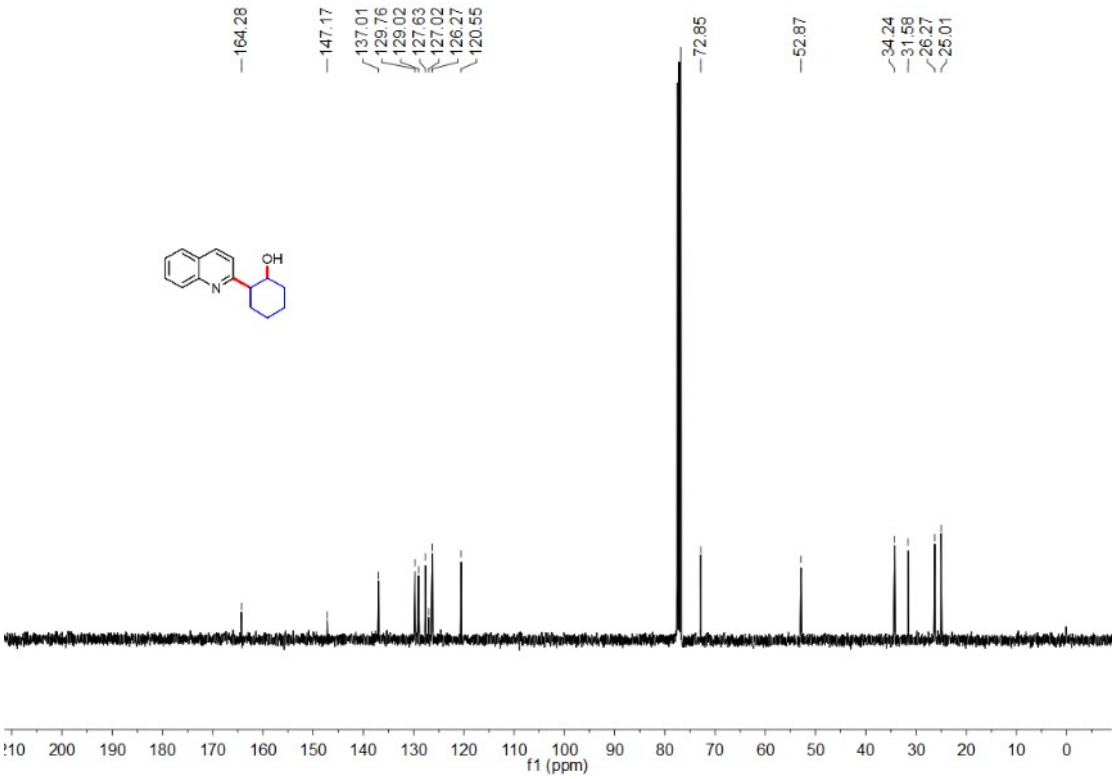
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **7**



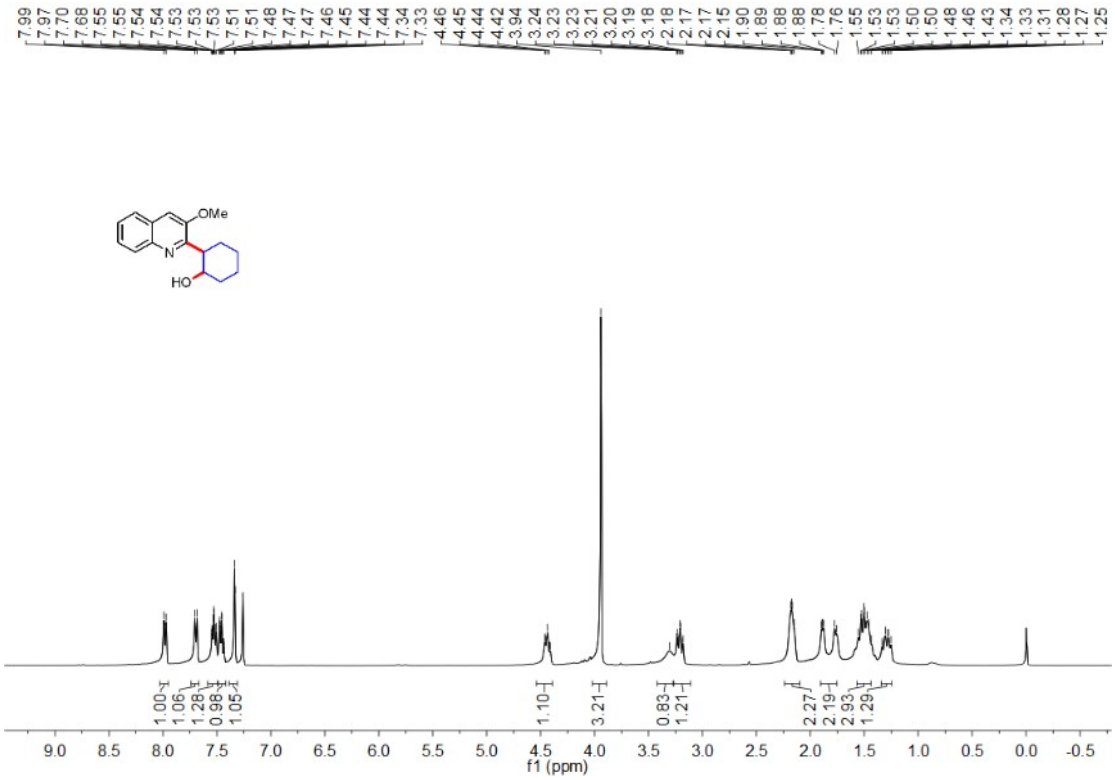
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8**



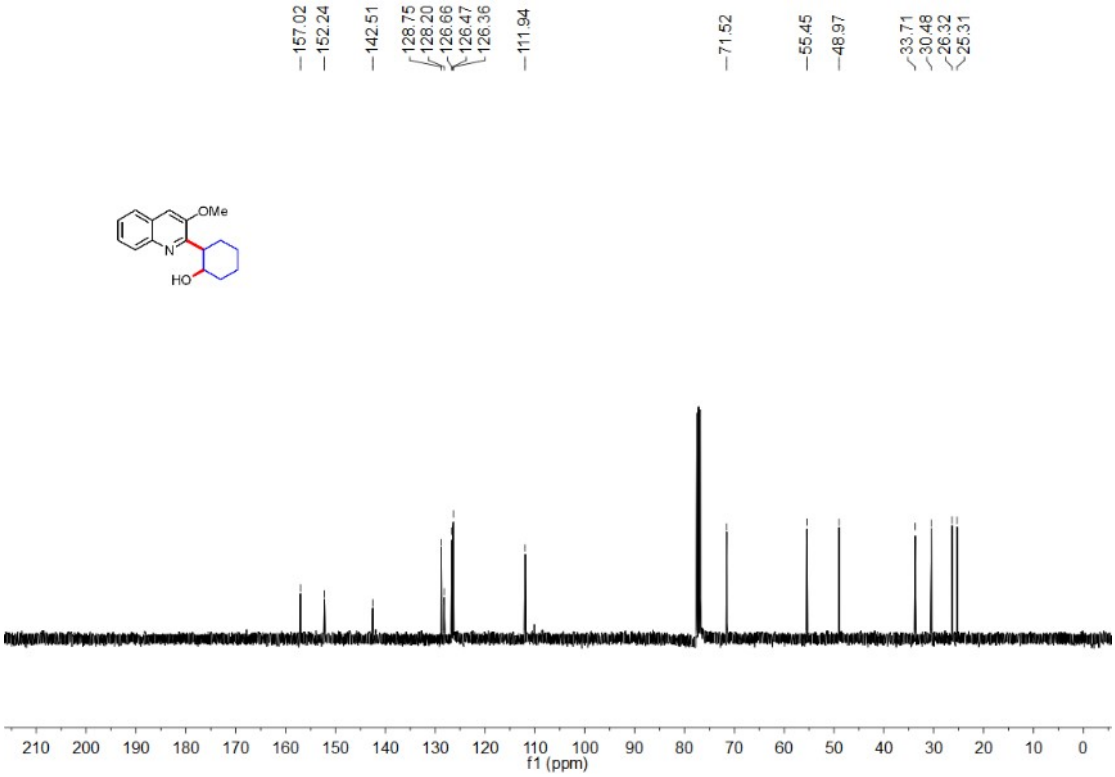
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8**



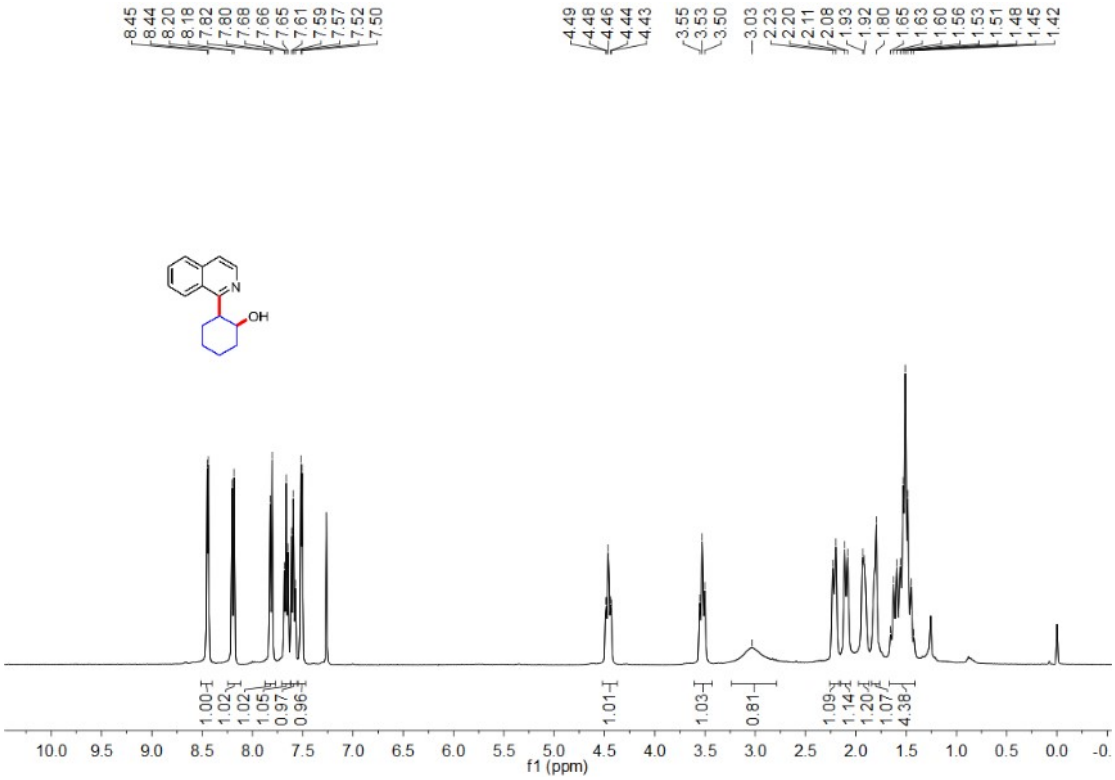
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **9**



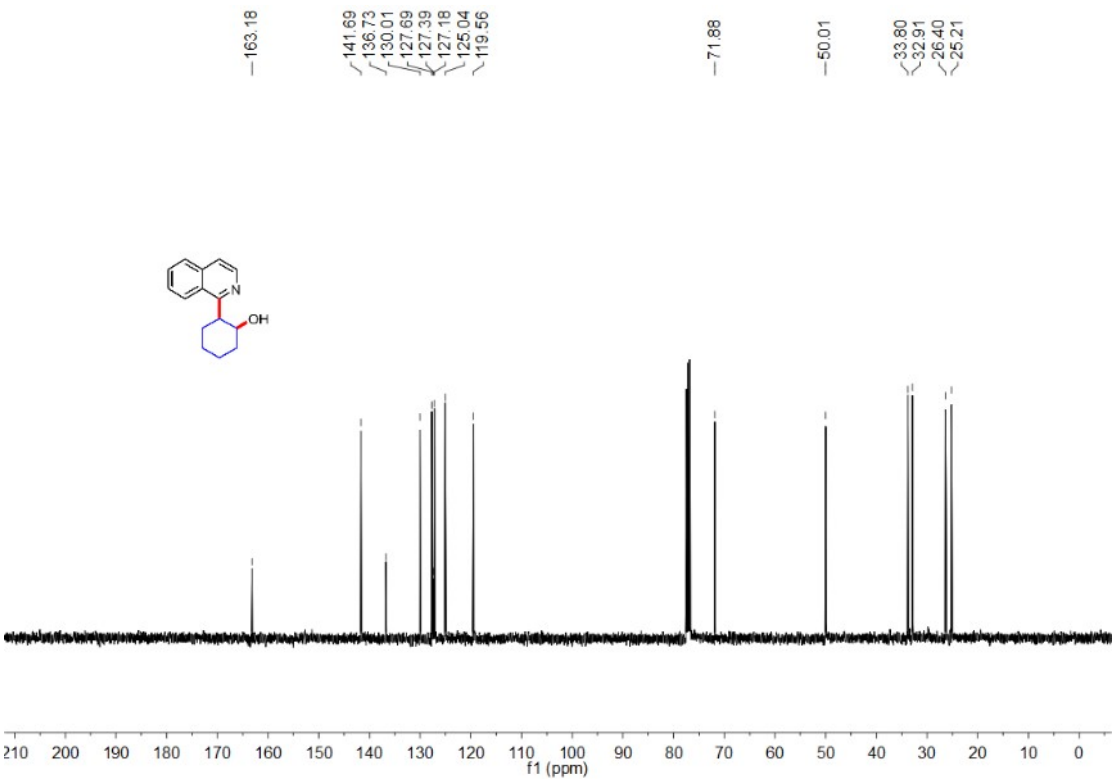
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **9**



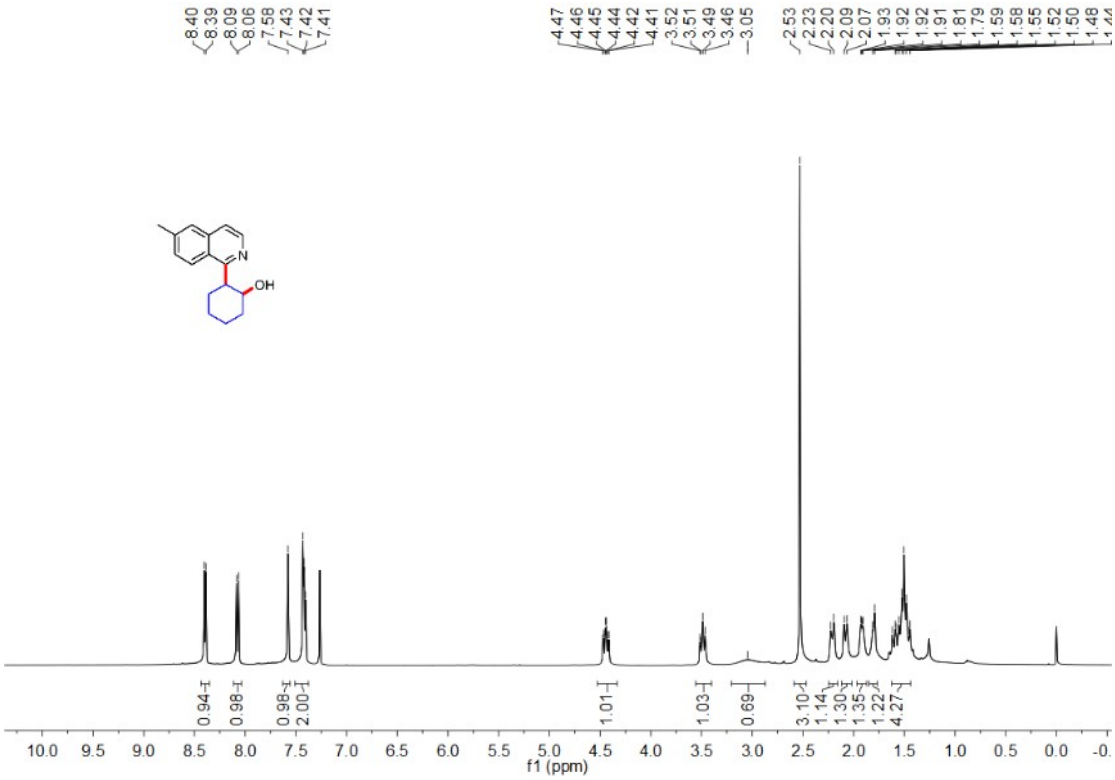
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**



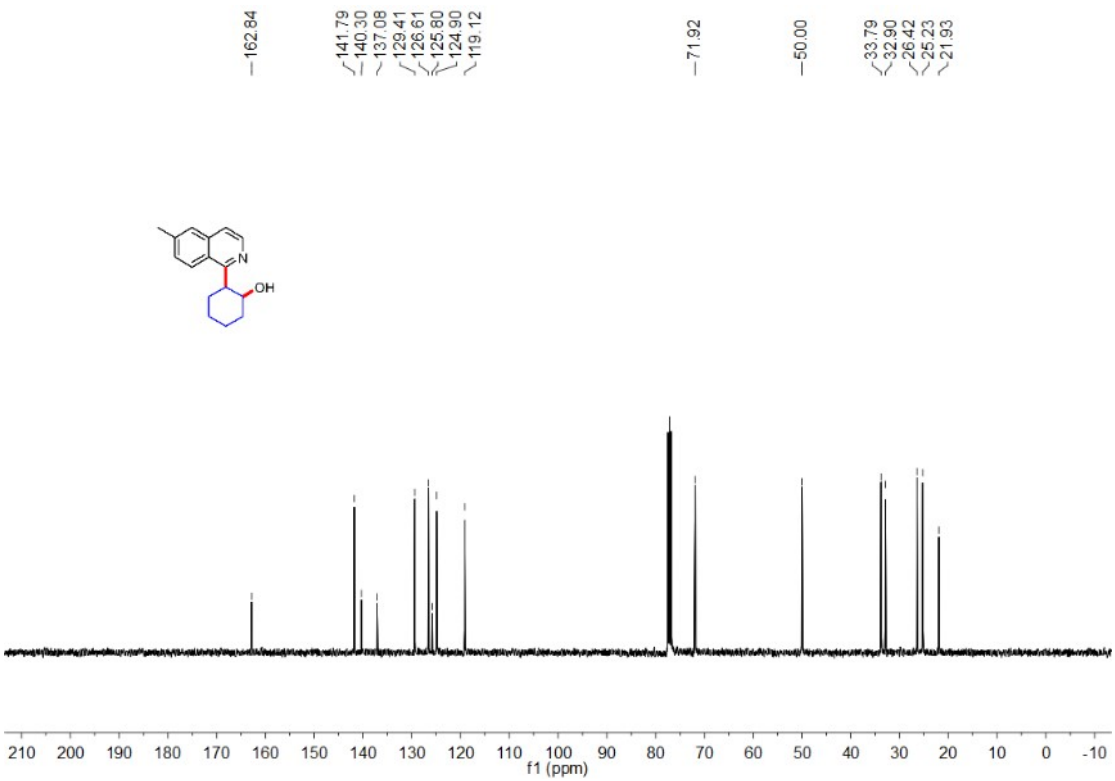
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **10**



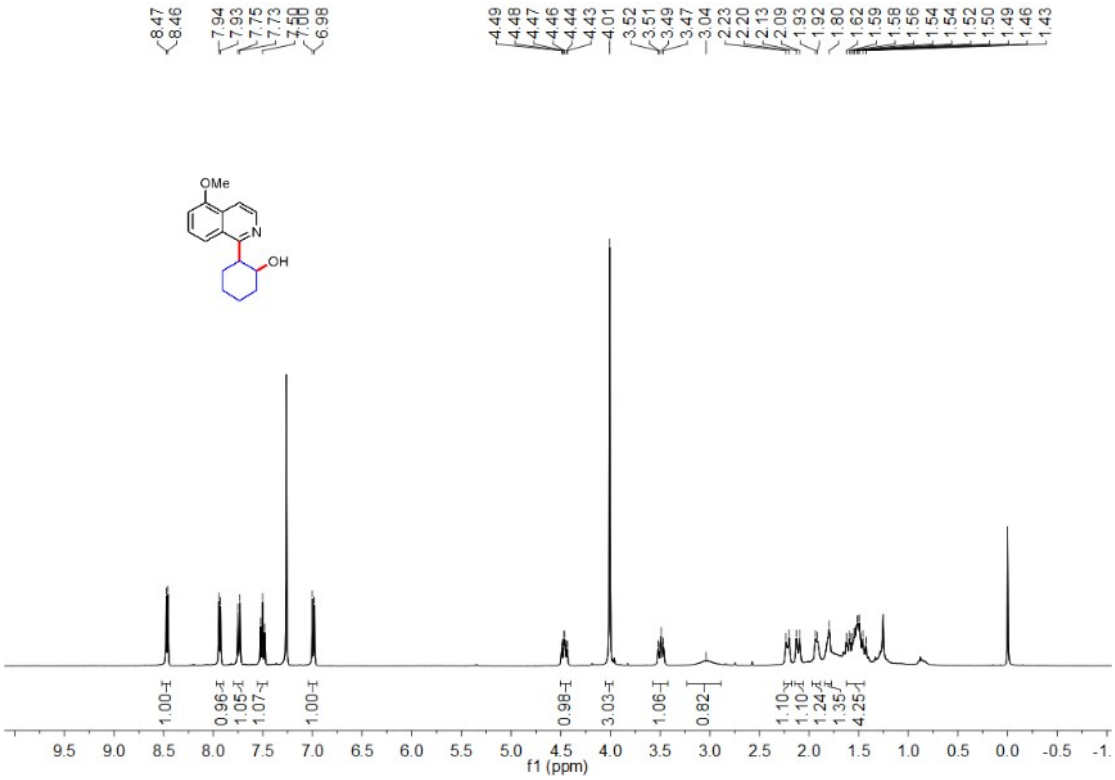
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **11**



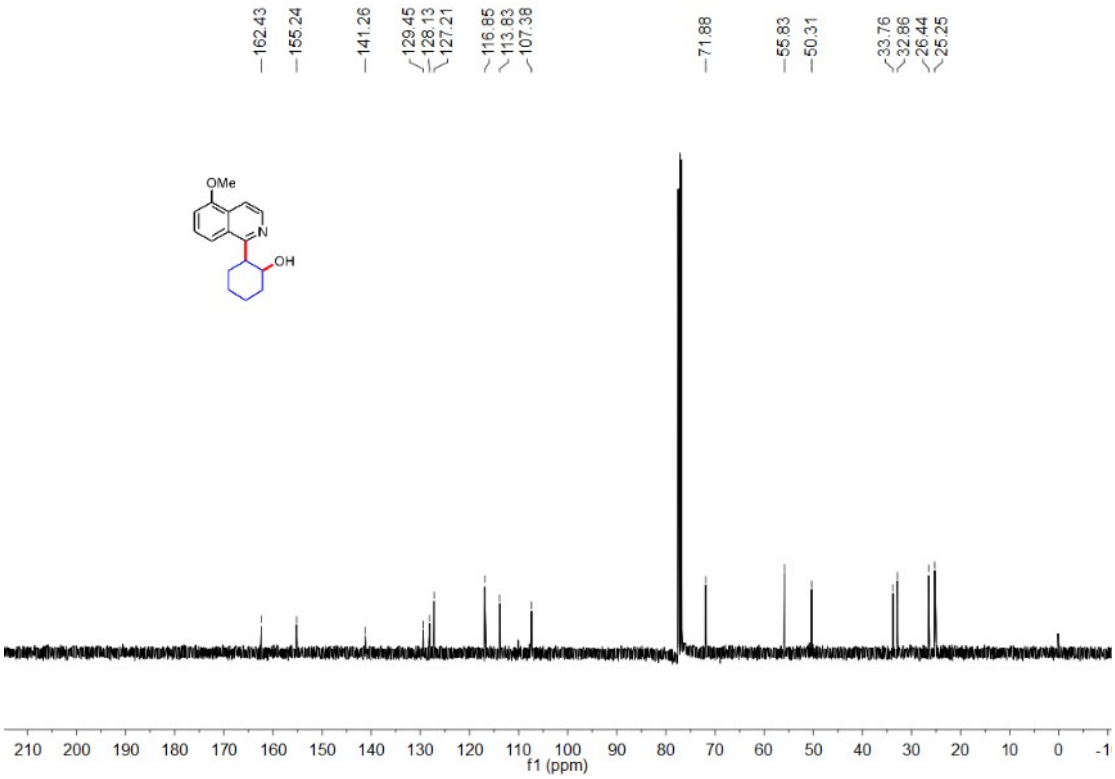
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound**11**



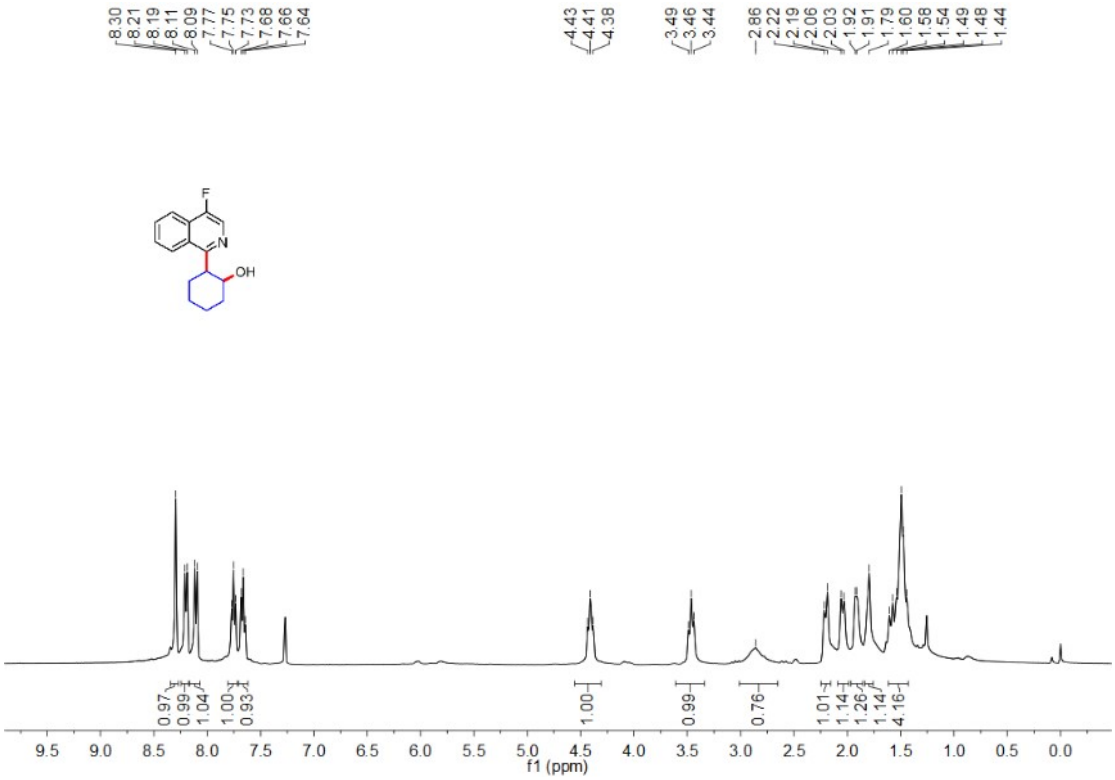
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **12**



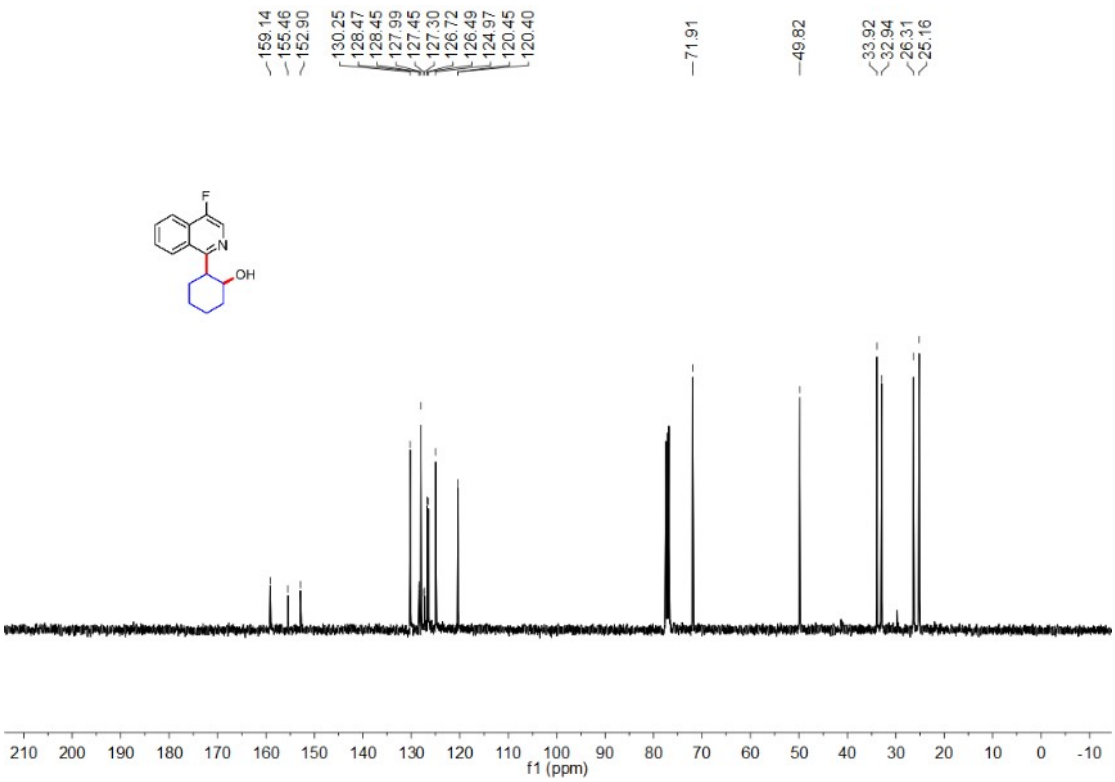
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **12**



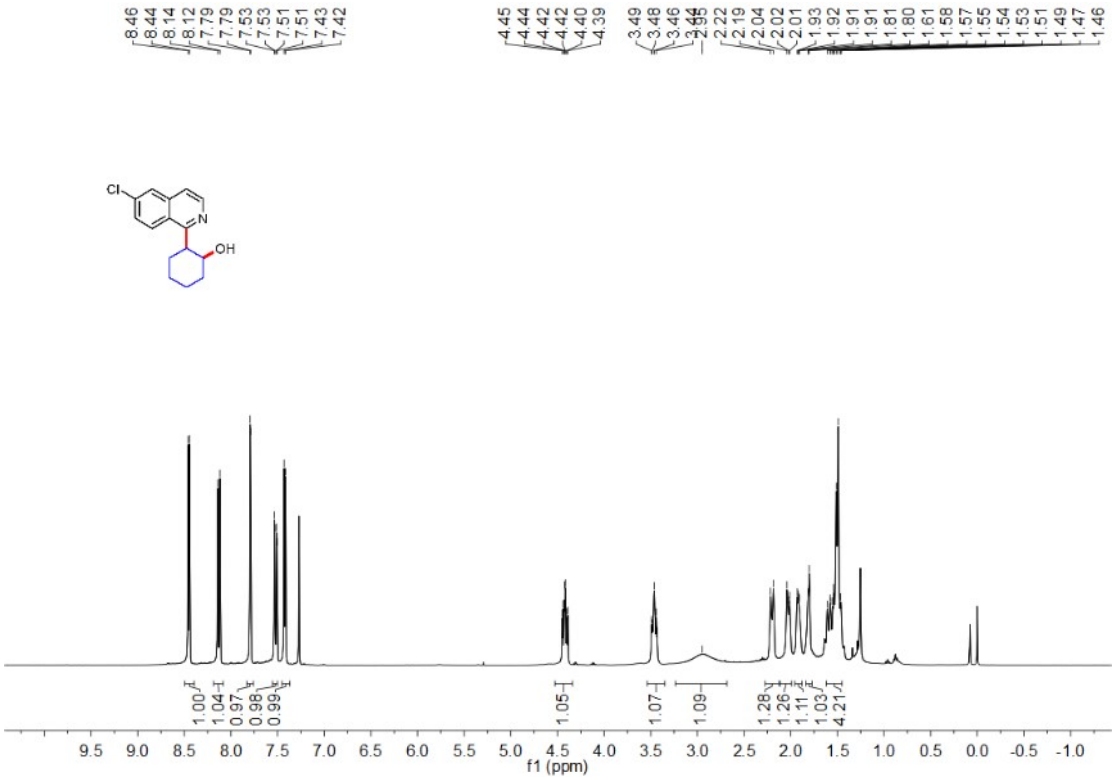
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **13**



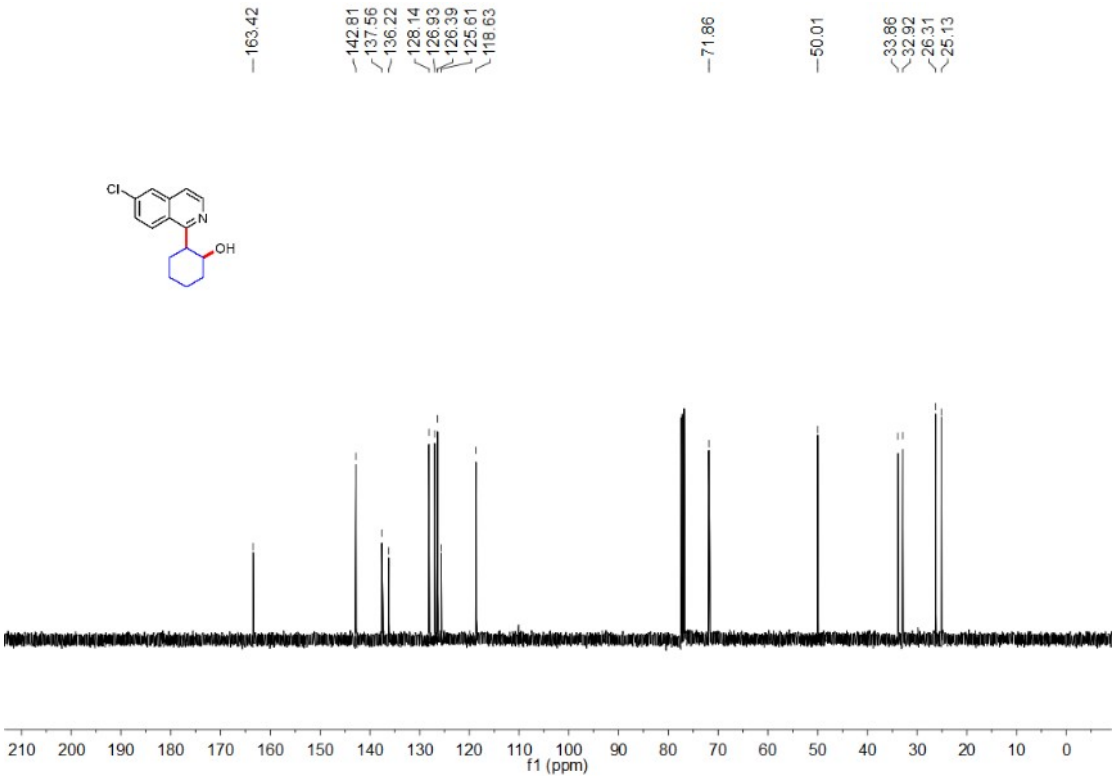
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **13**



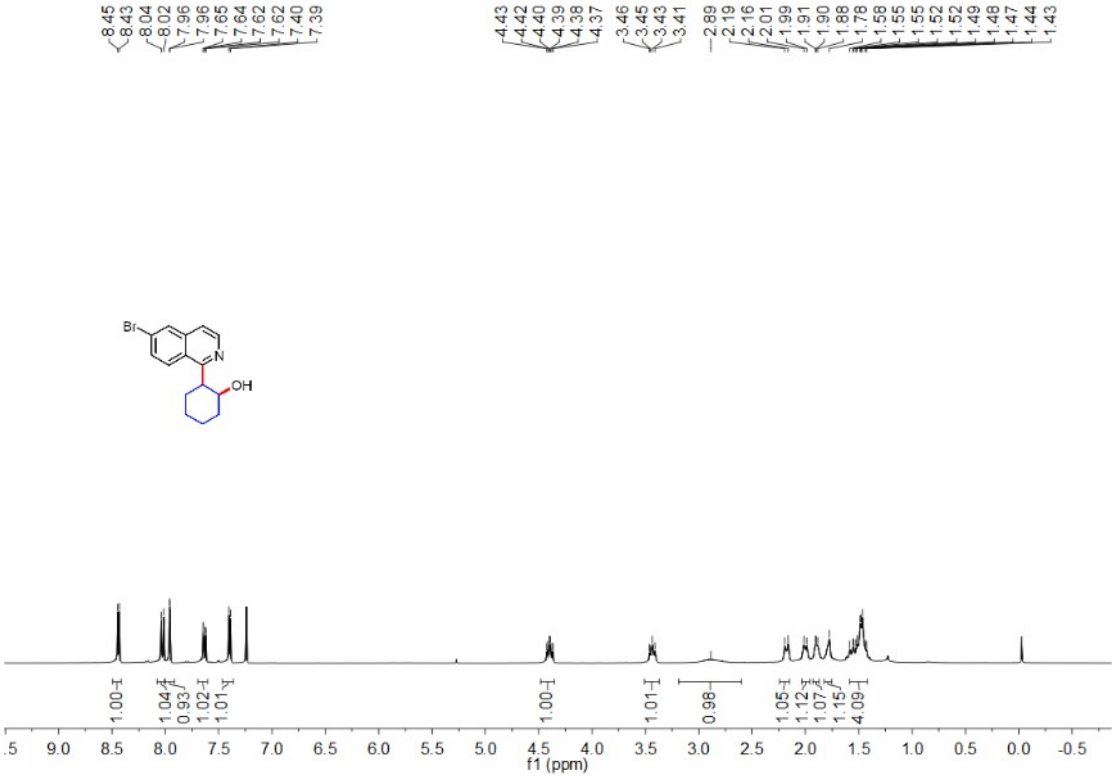
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **14**



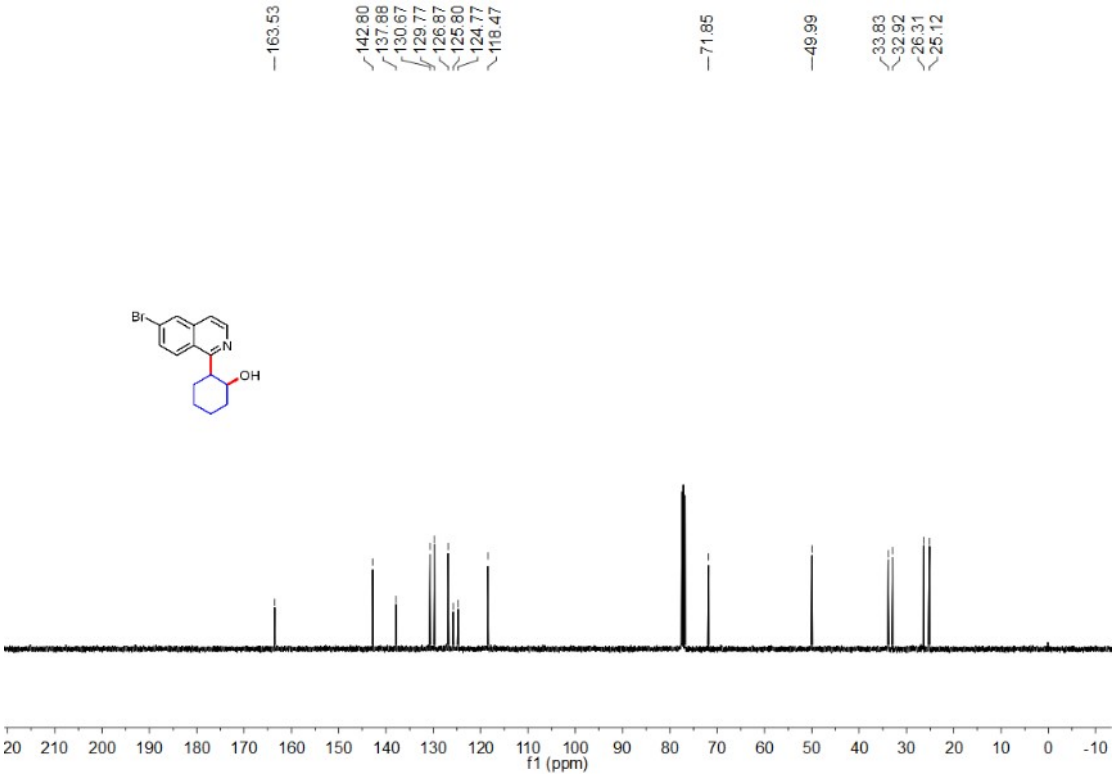
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **14**



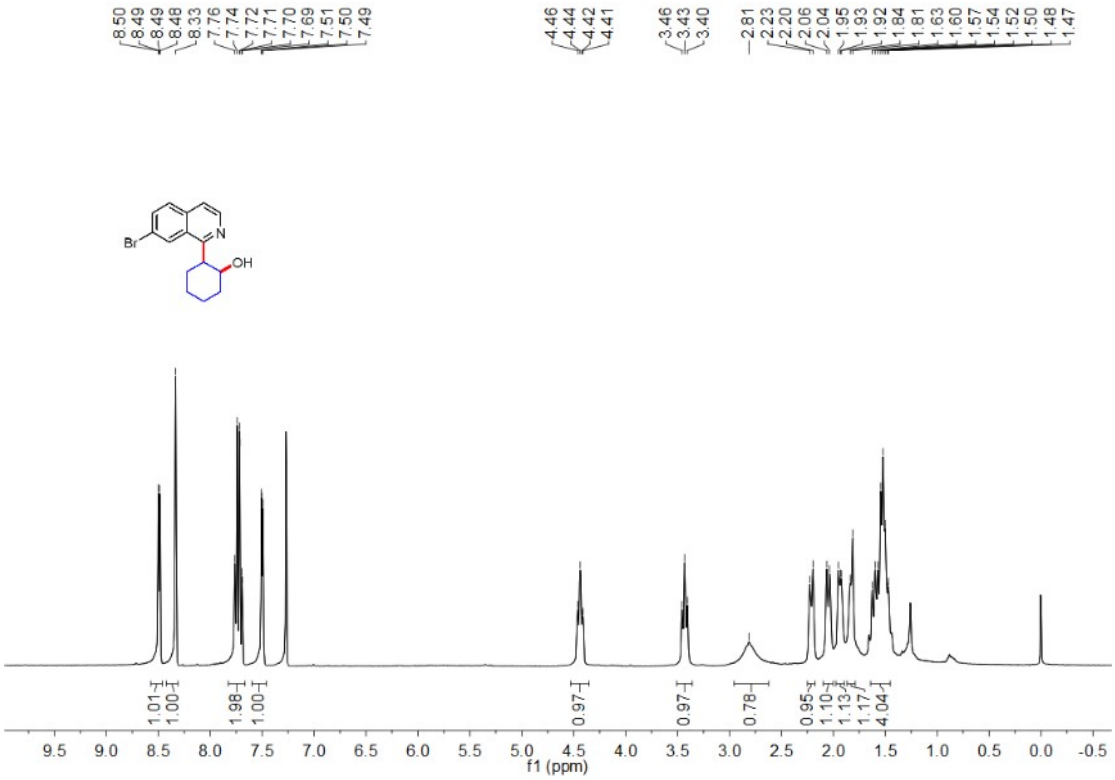
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **15**



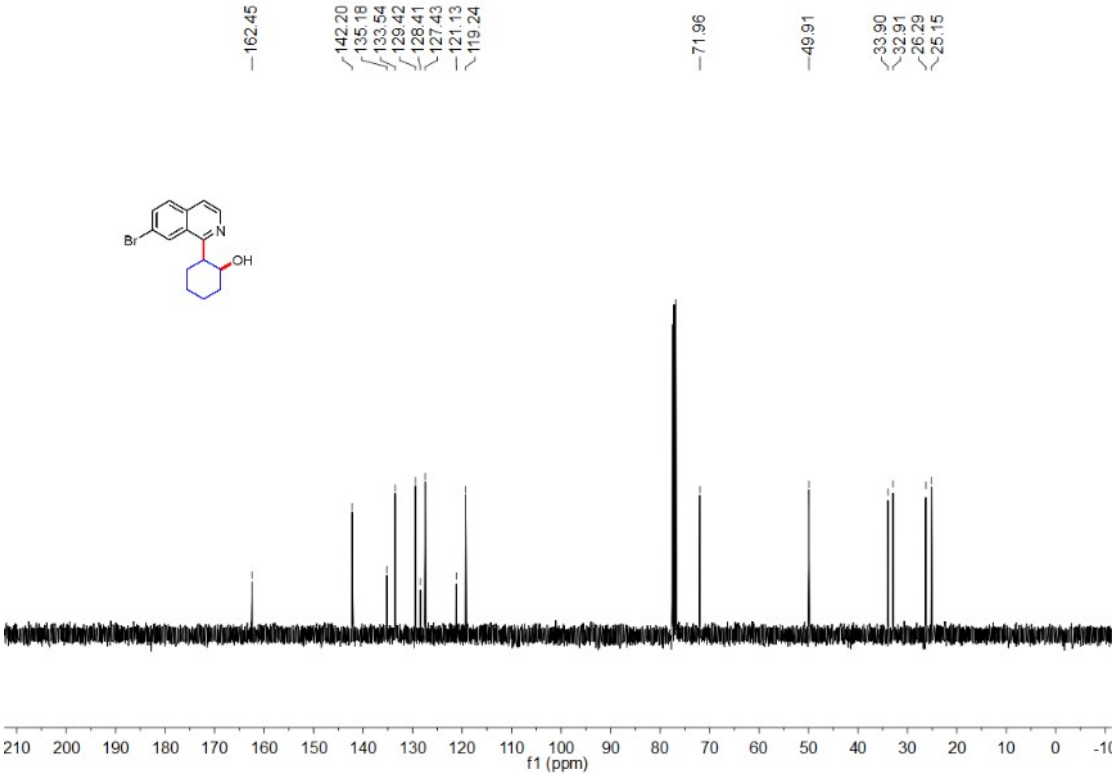
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **15**



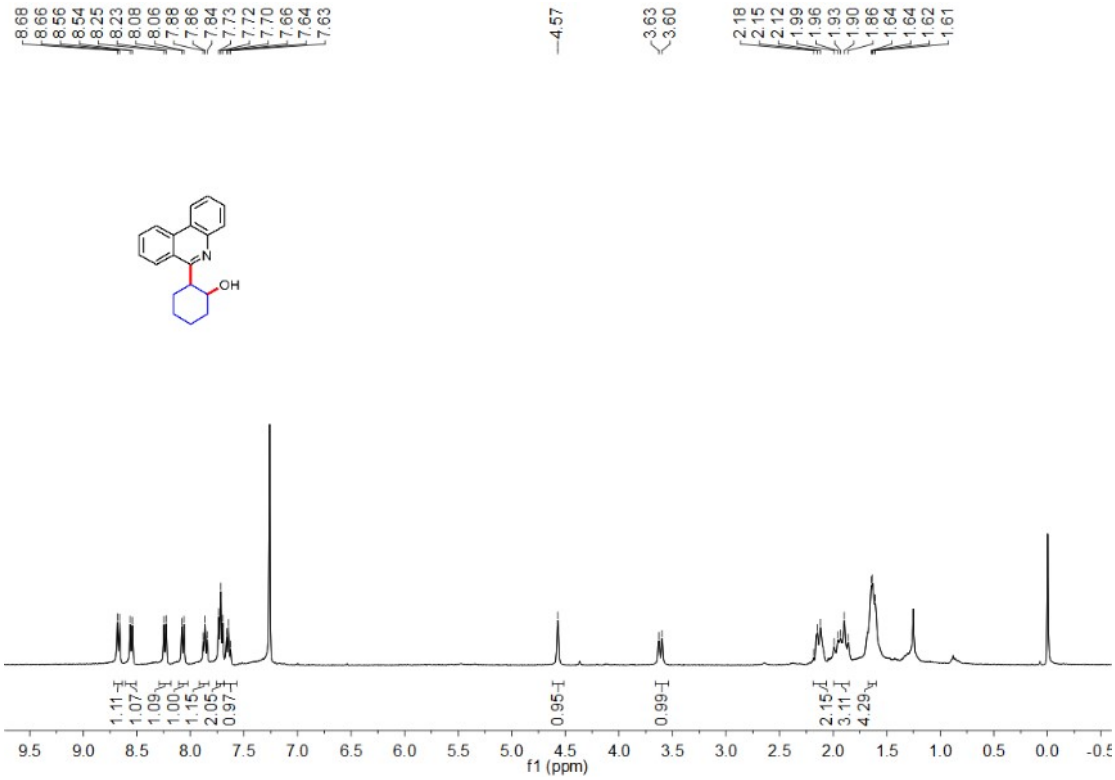
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16**



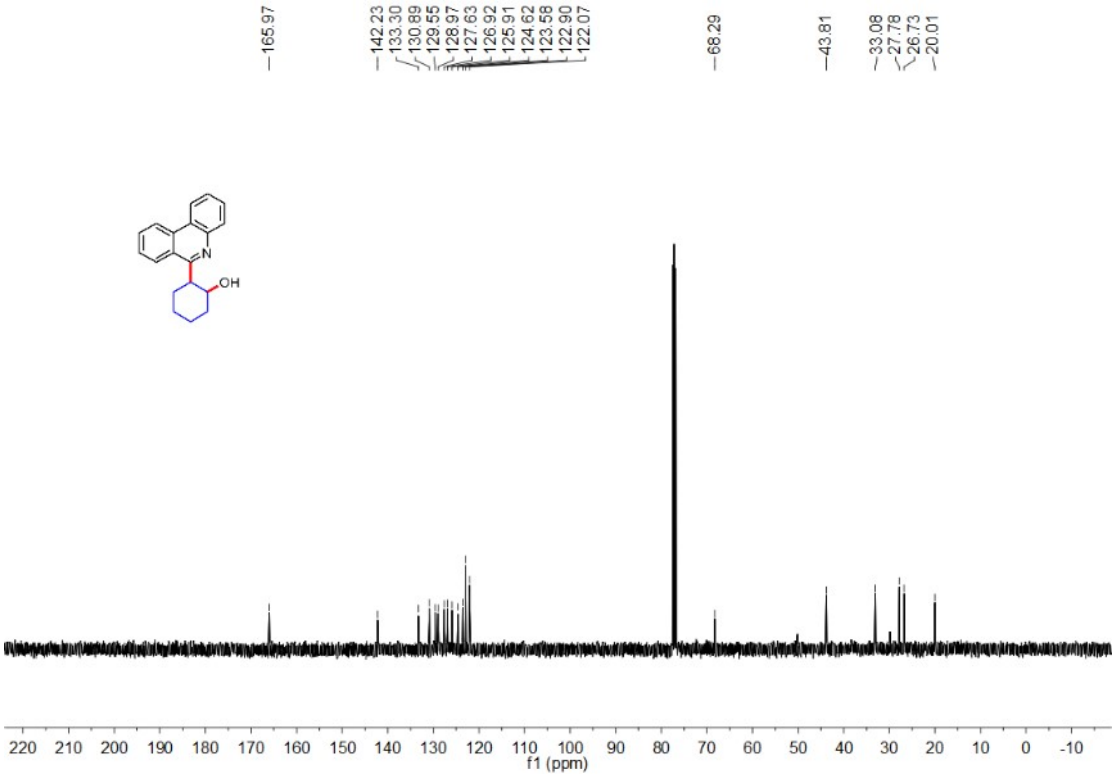
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **16**



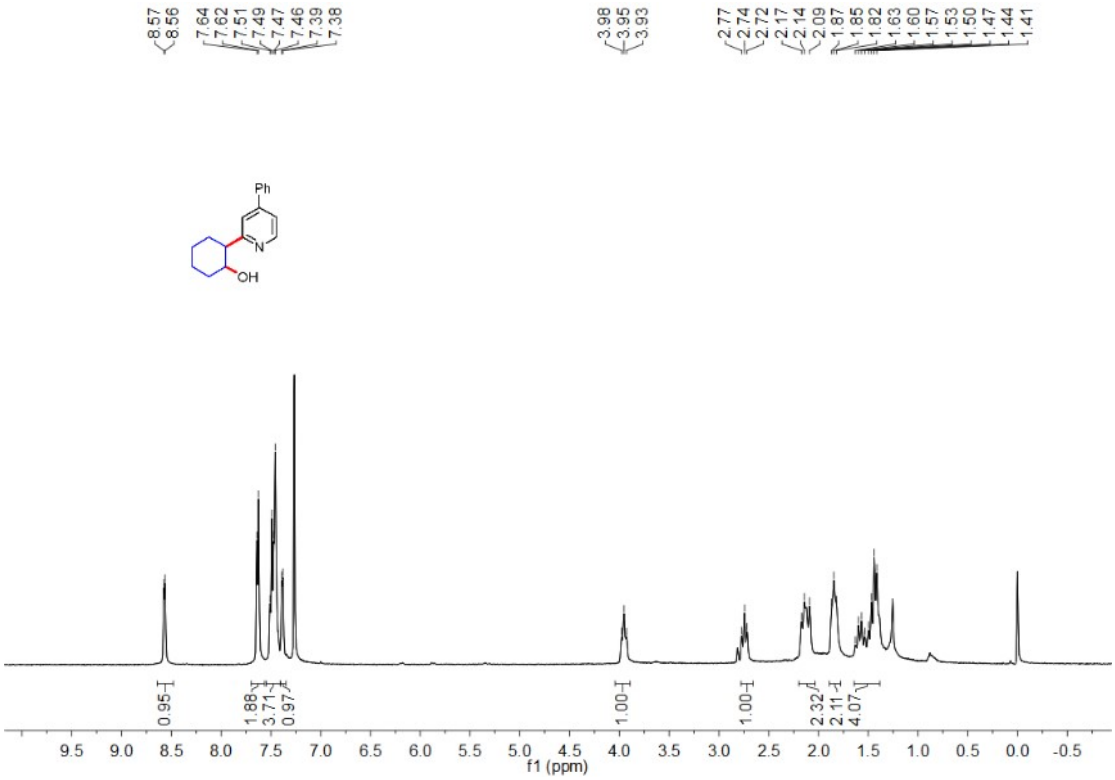
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **17**



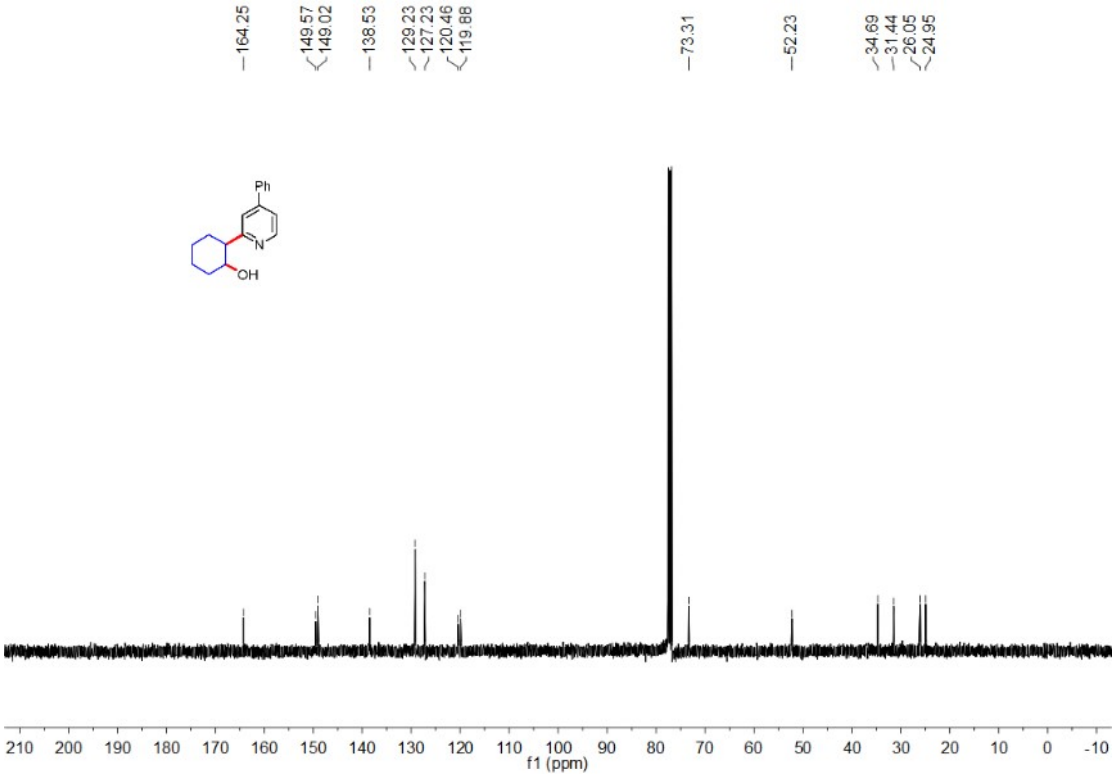
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **17**



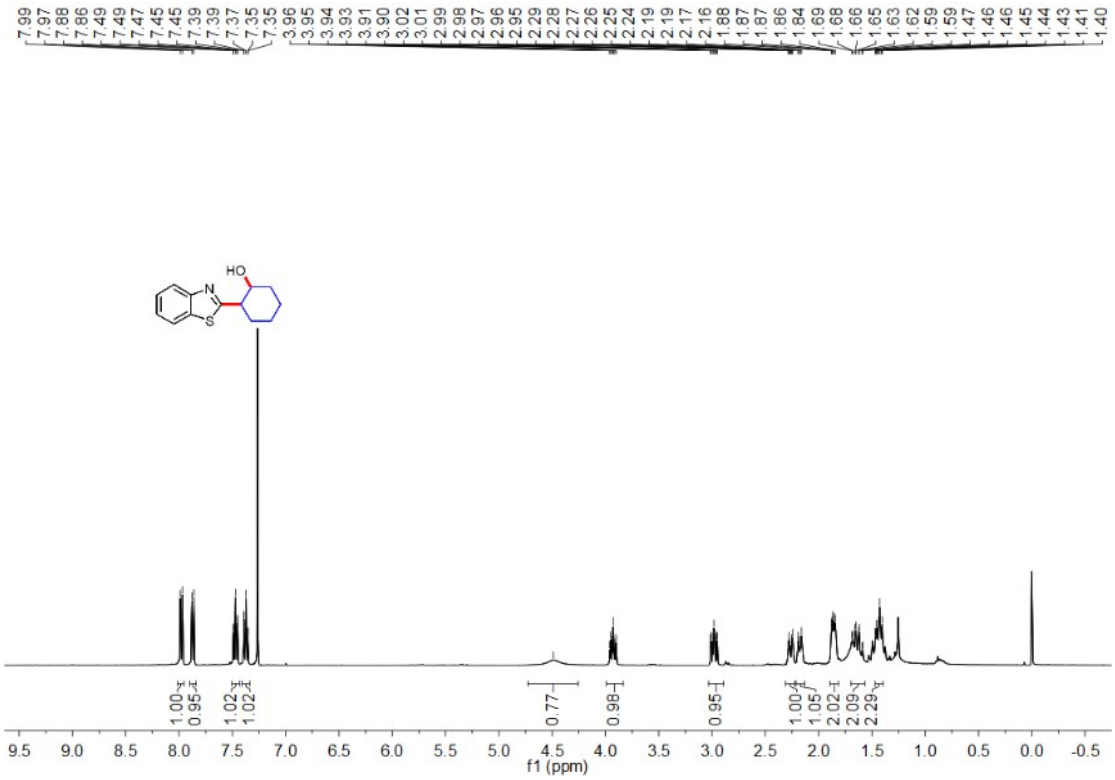
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **18**



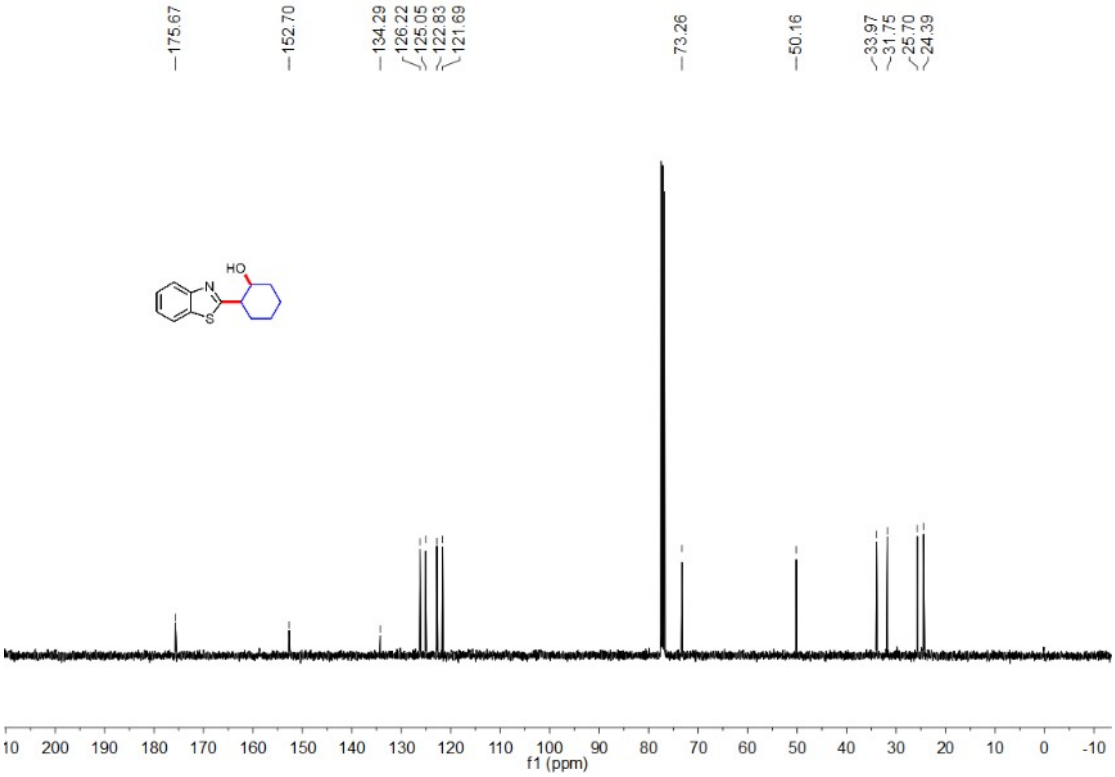
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **18**



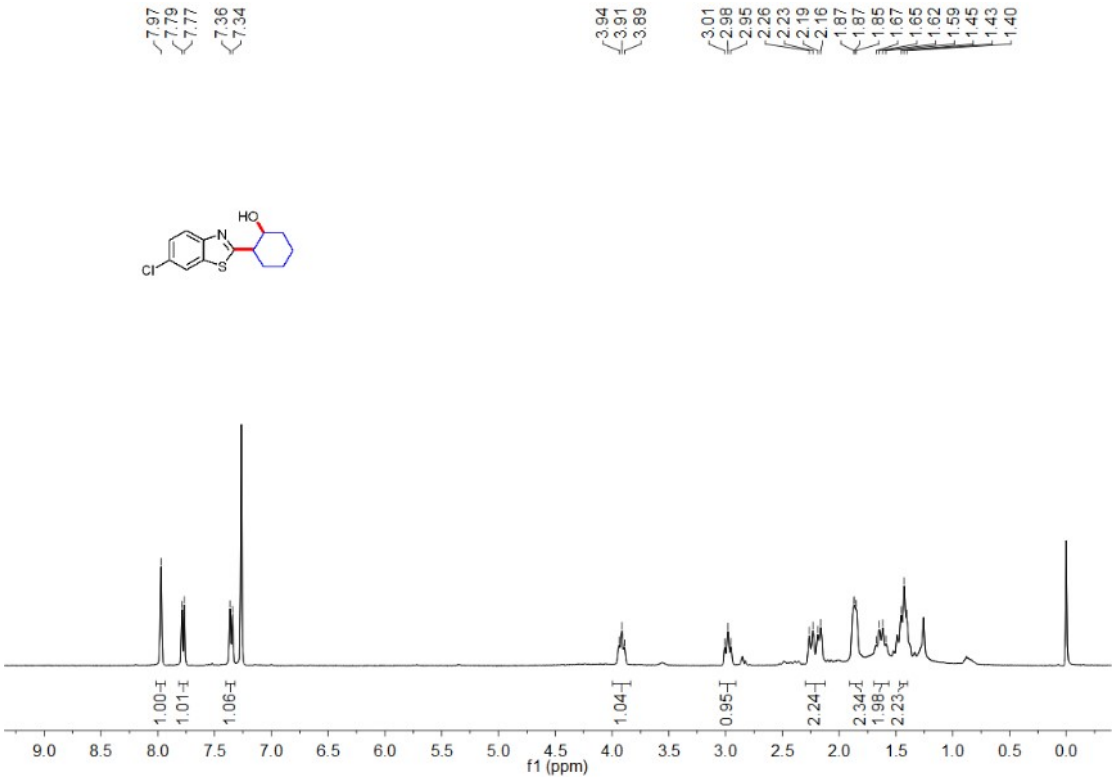
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **19**



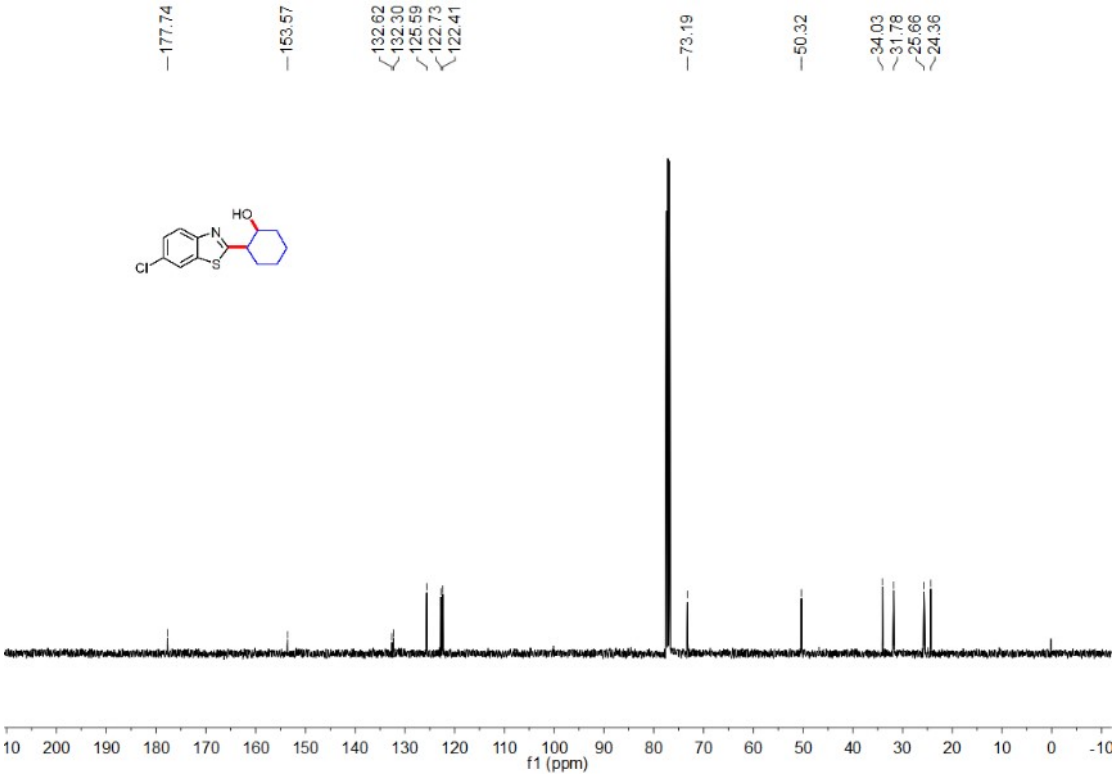
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **19**



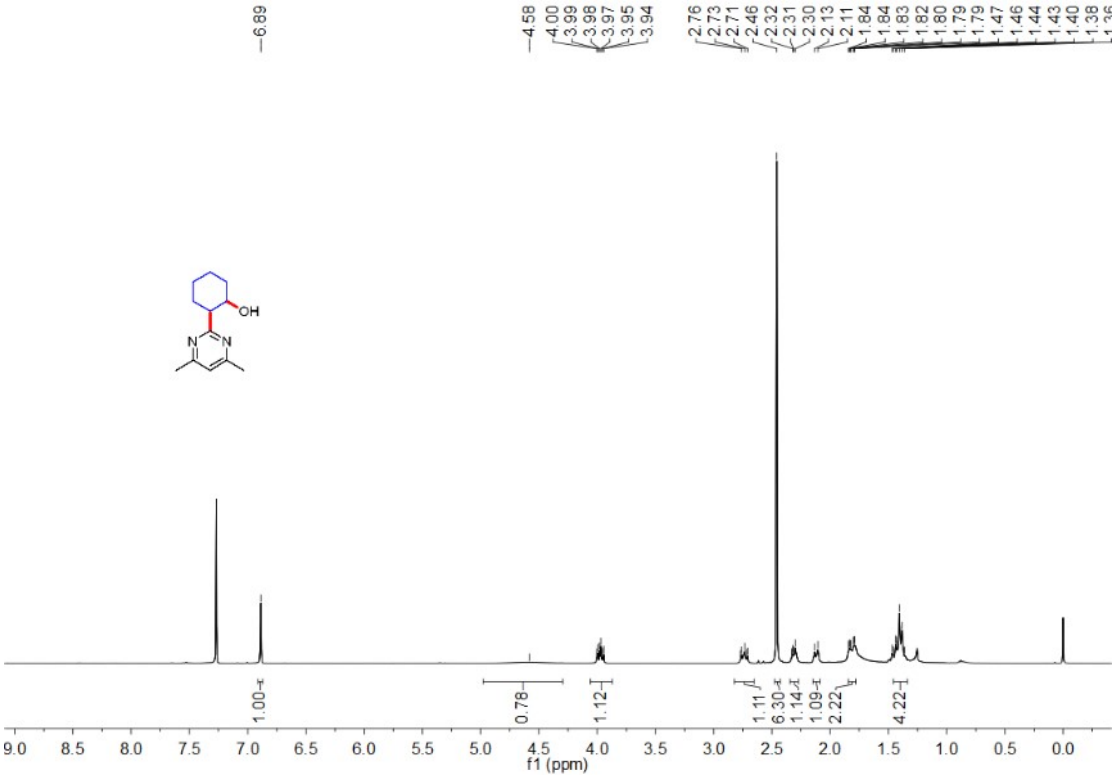
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20**



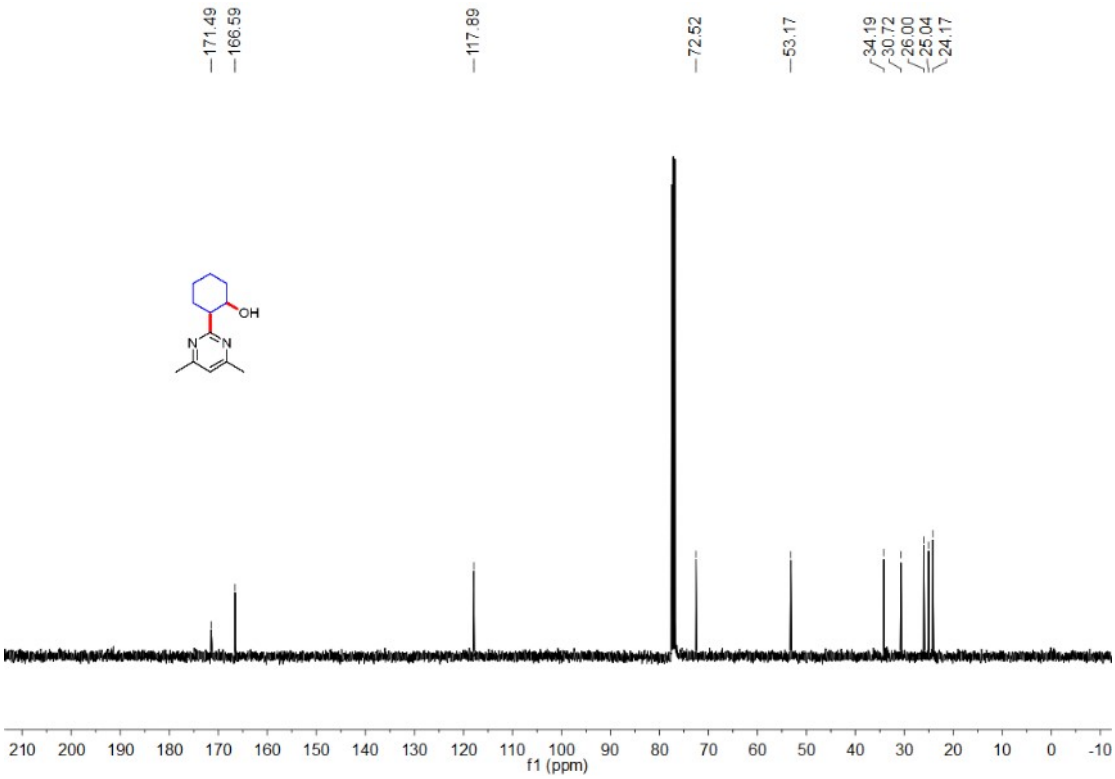
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20**



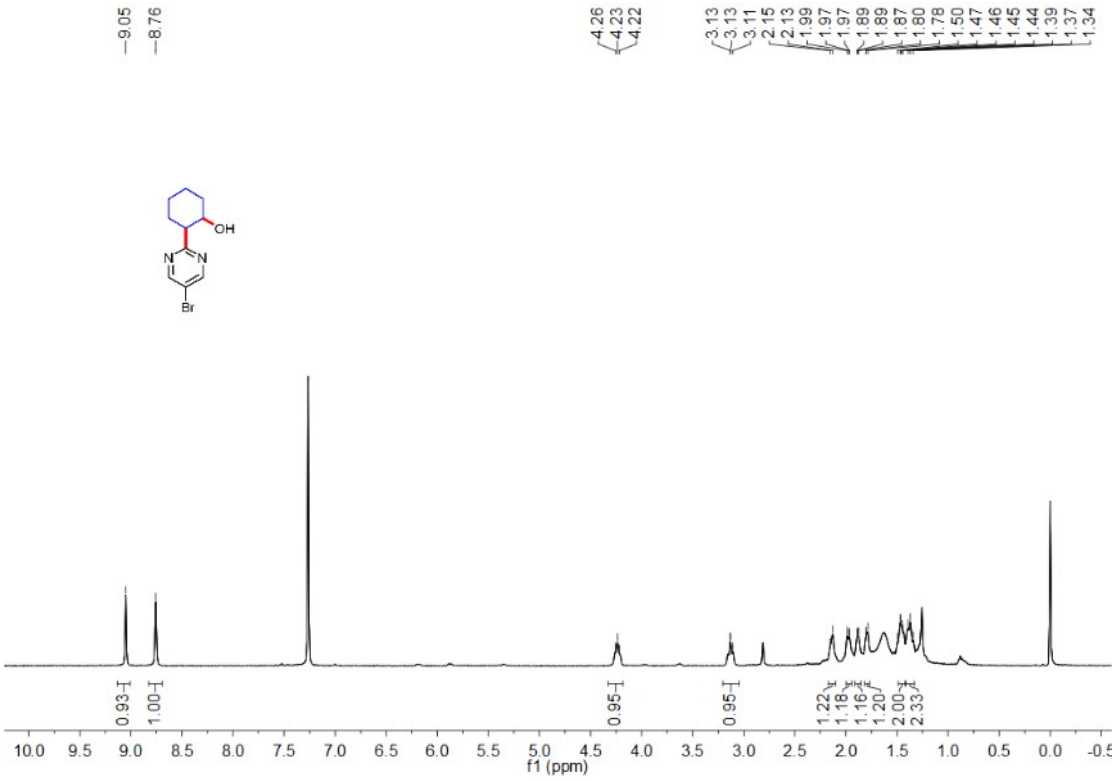
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **21**



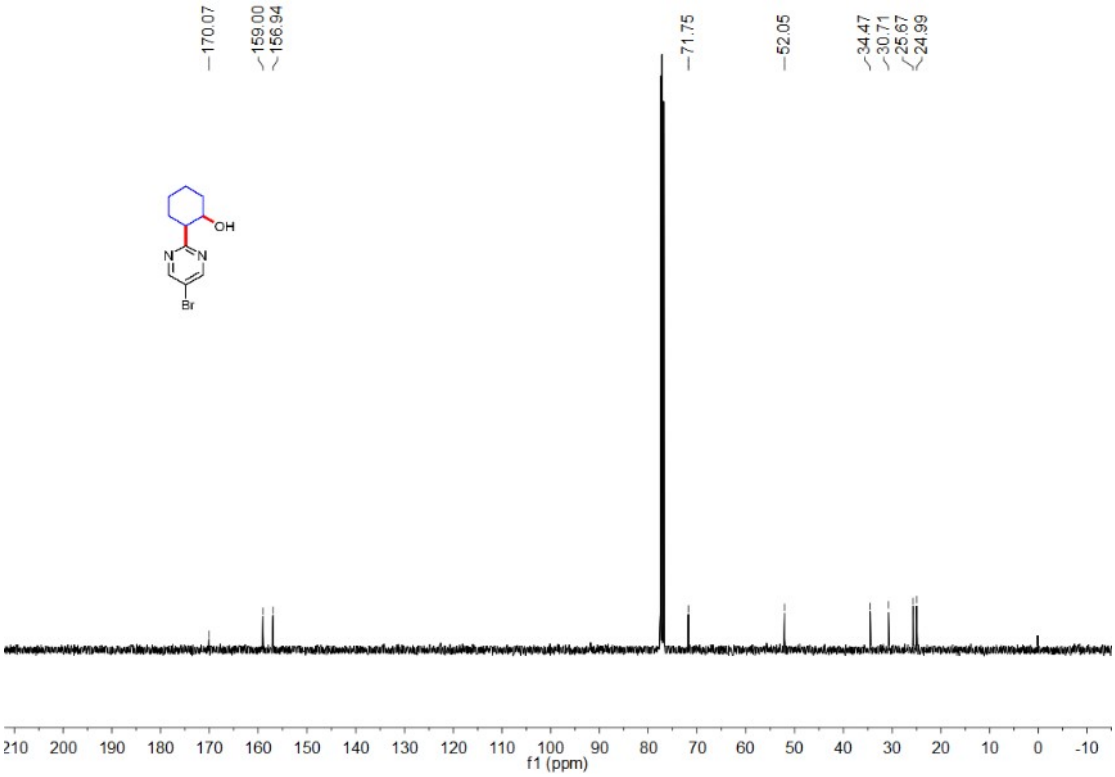
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **21**



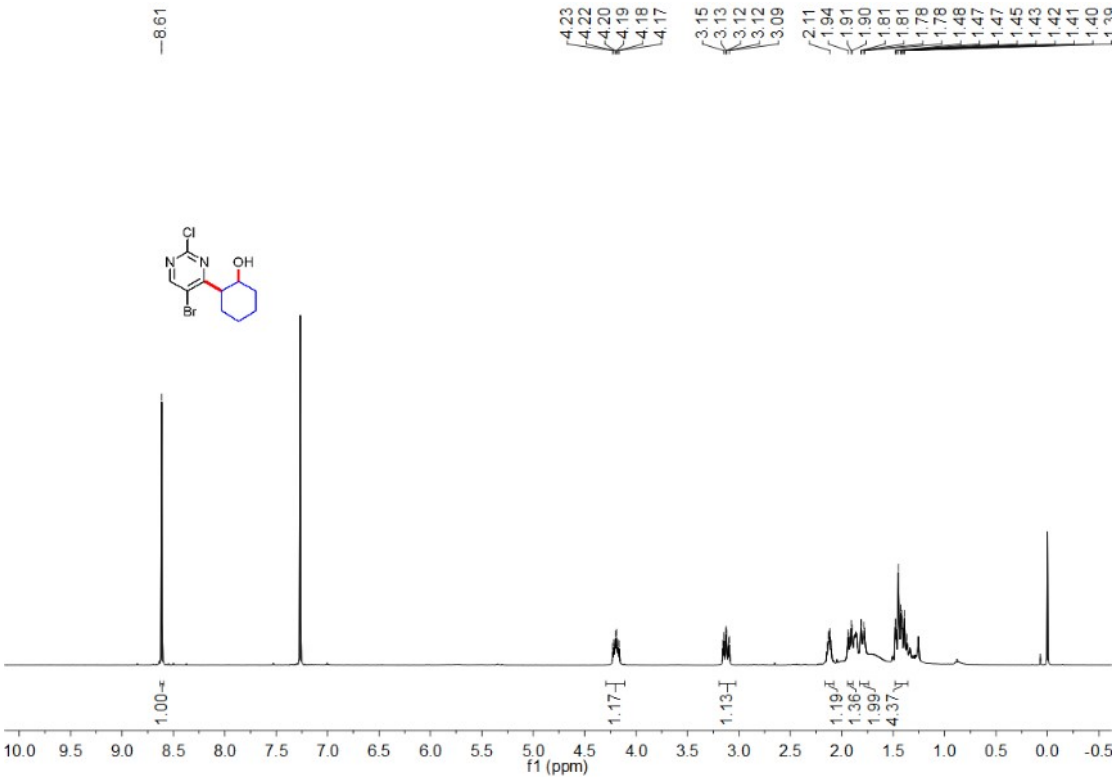
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **22**



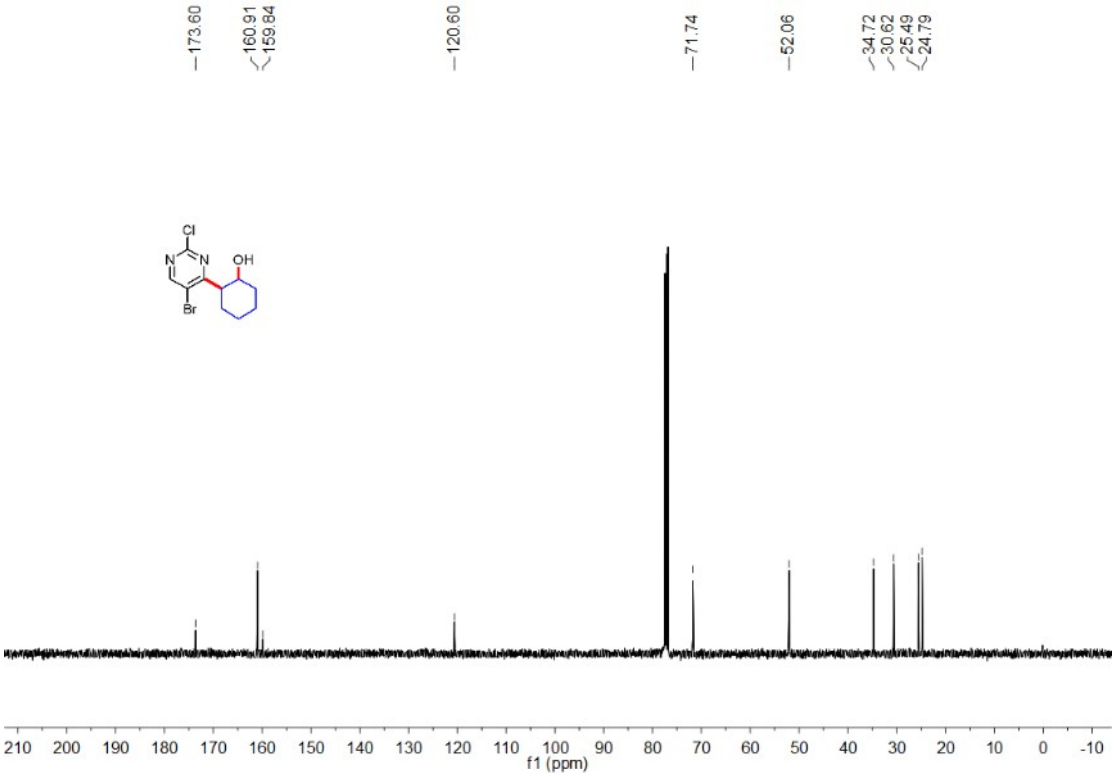
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **22**



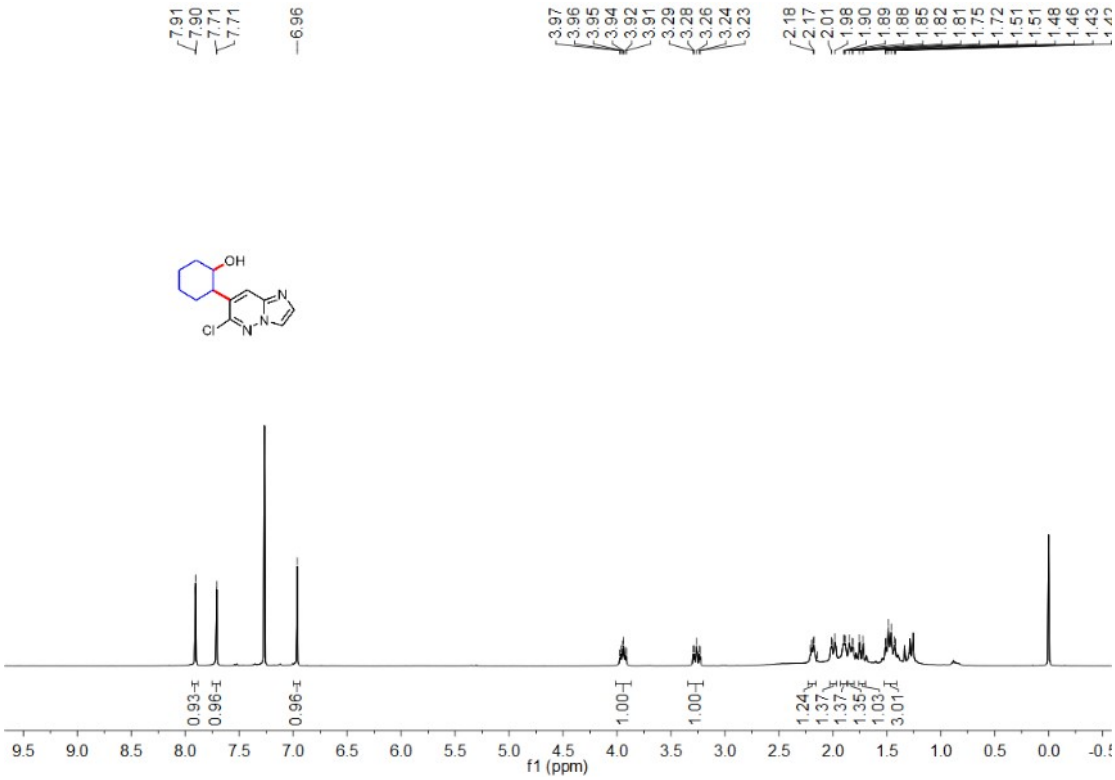
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **23**



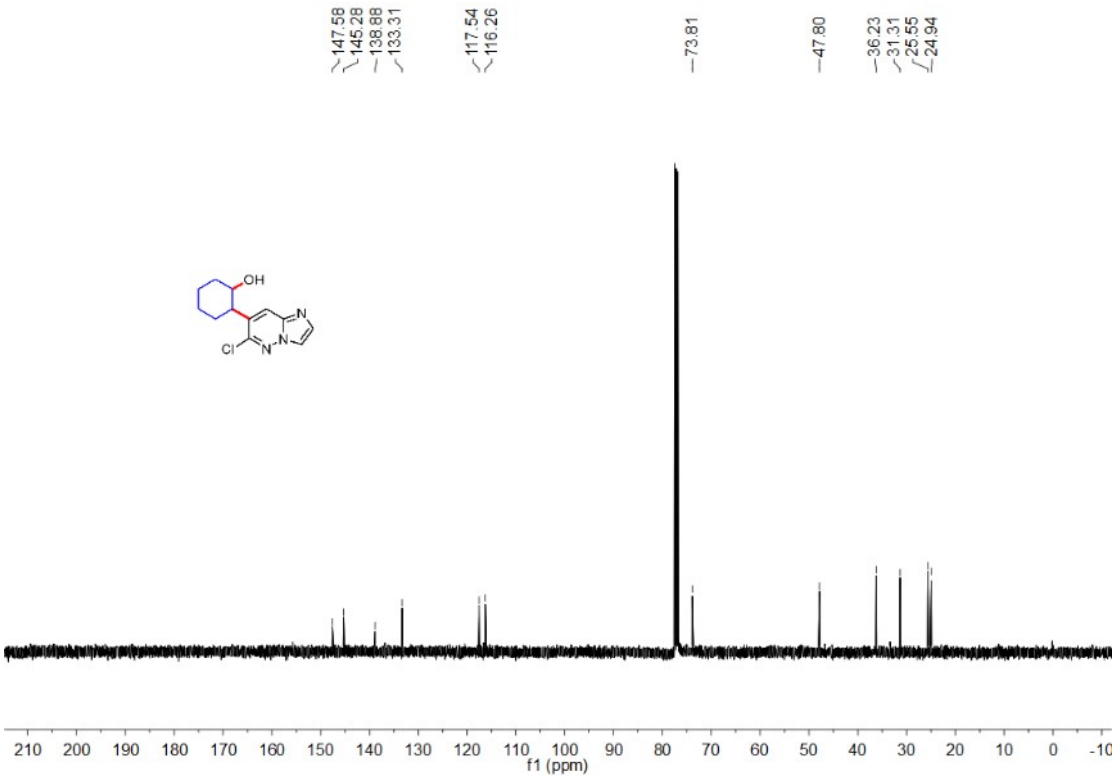
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **23**



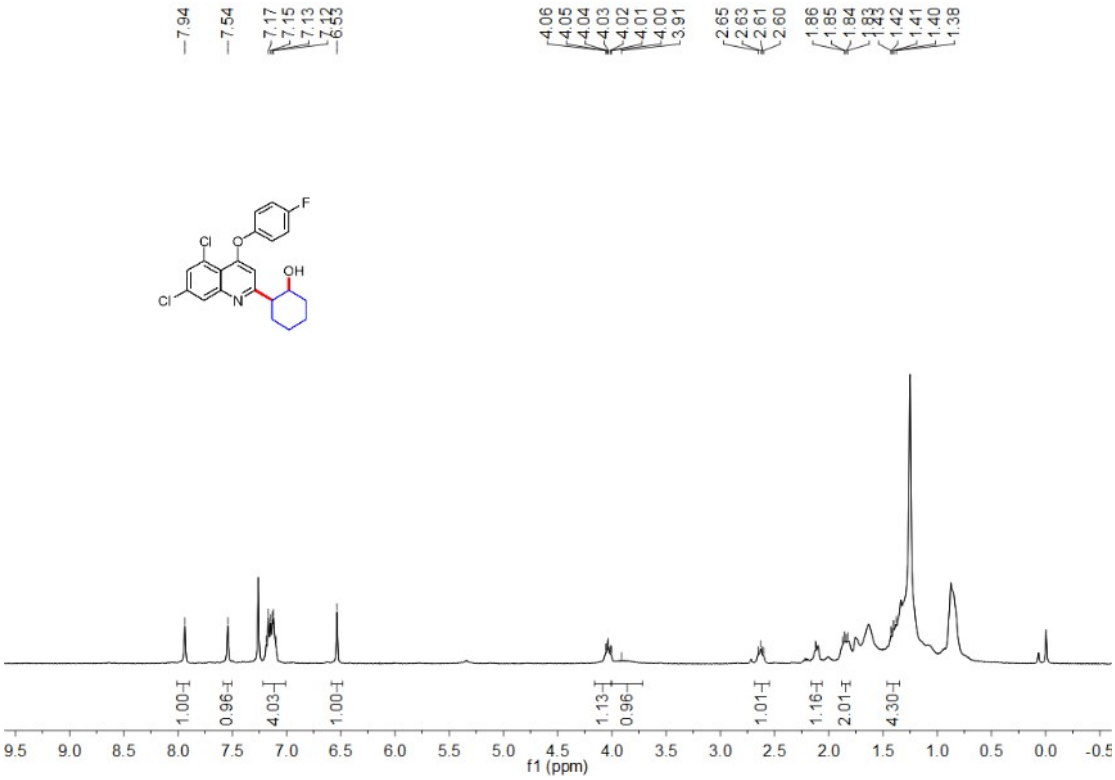
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **24**



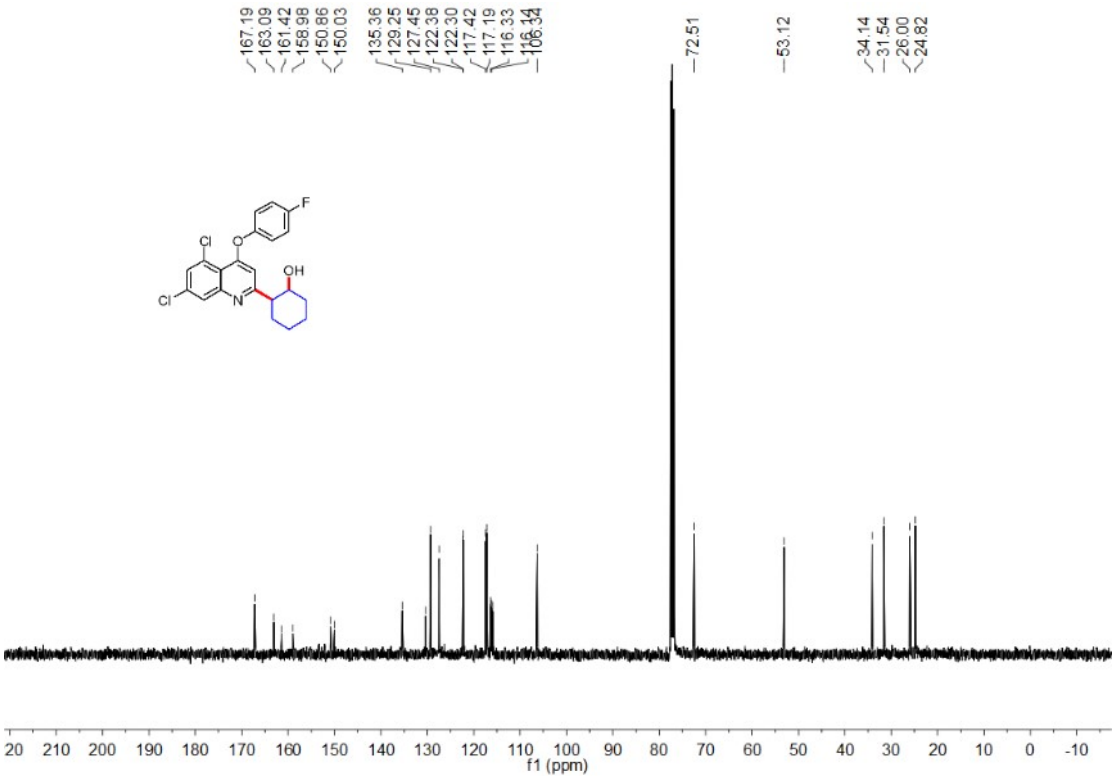
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **24**



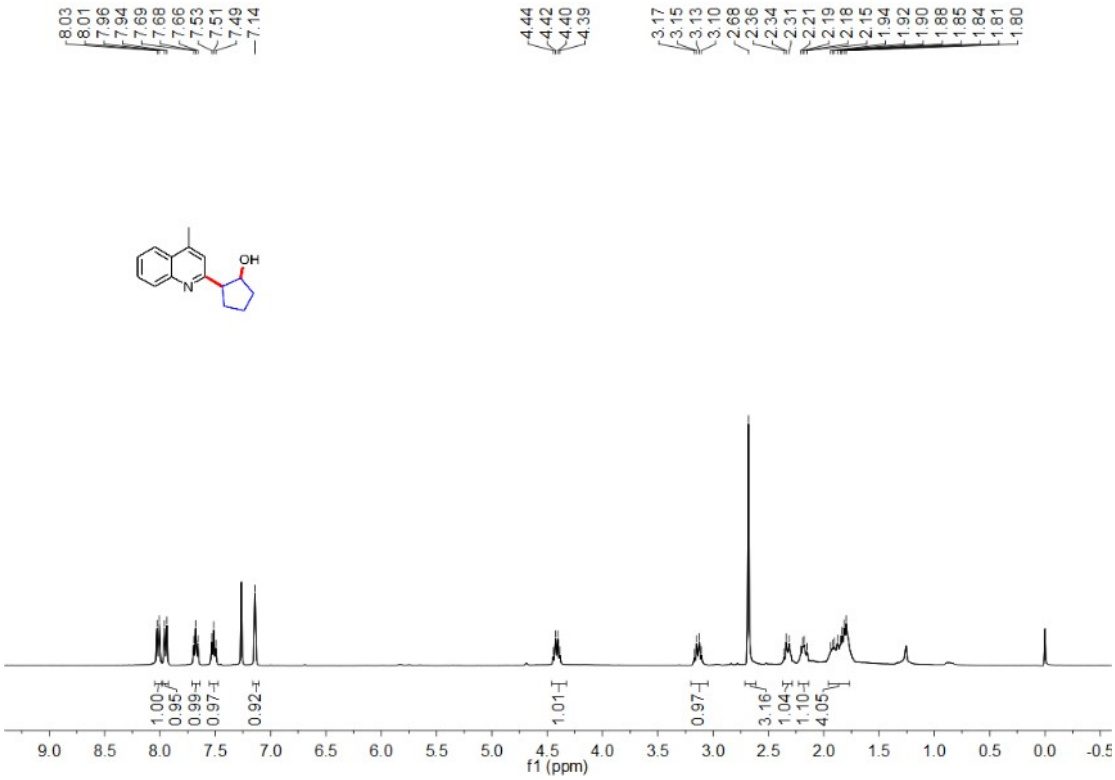
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25**



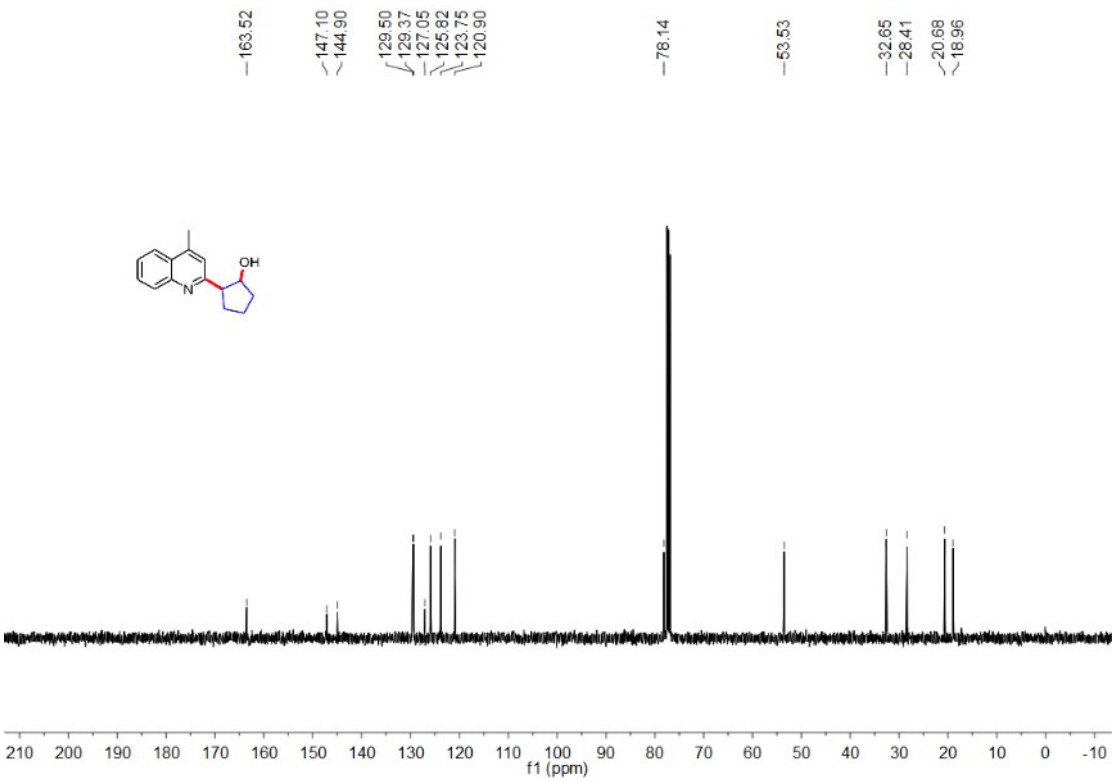
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25**



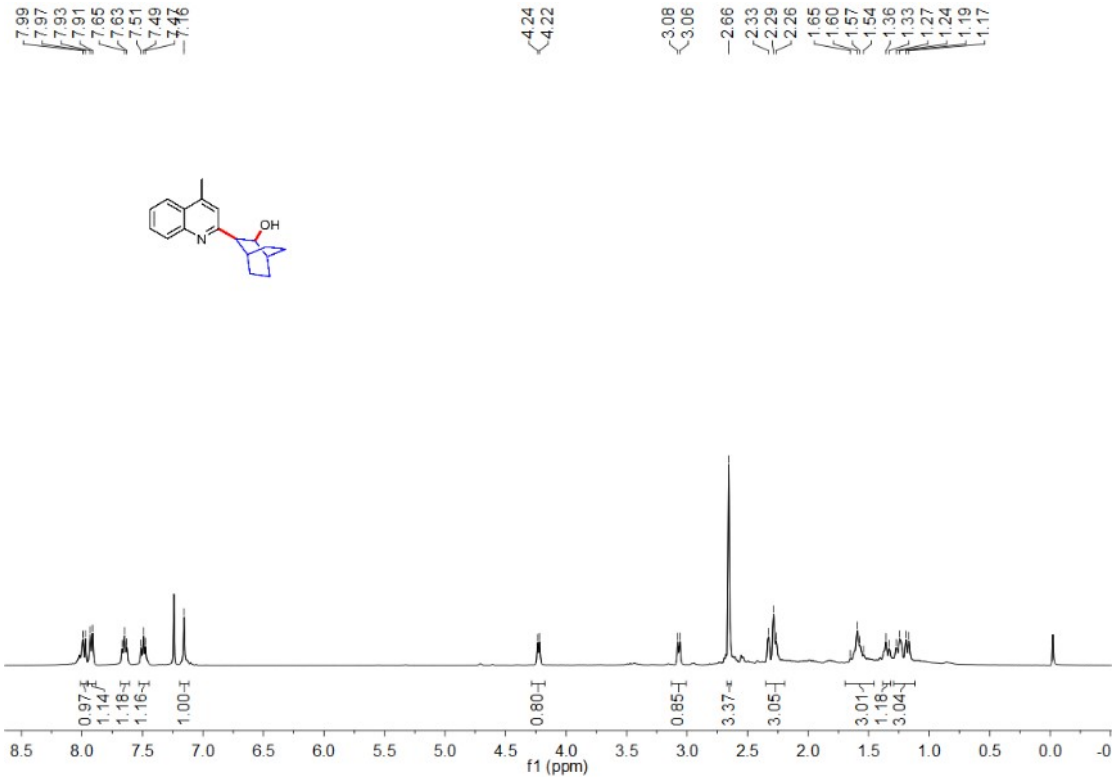
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **26**



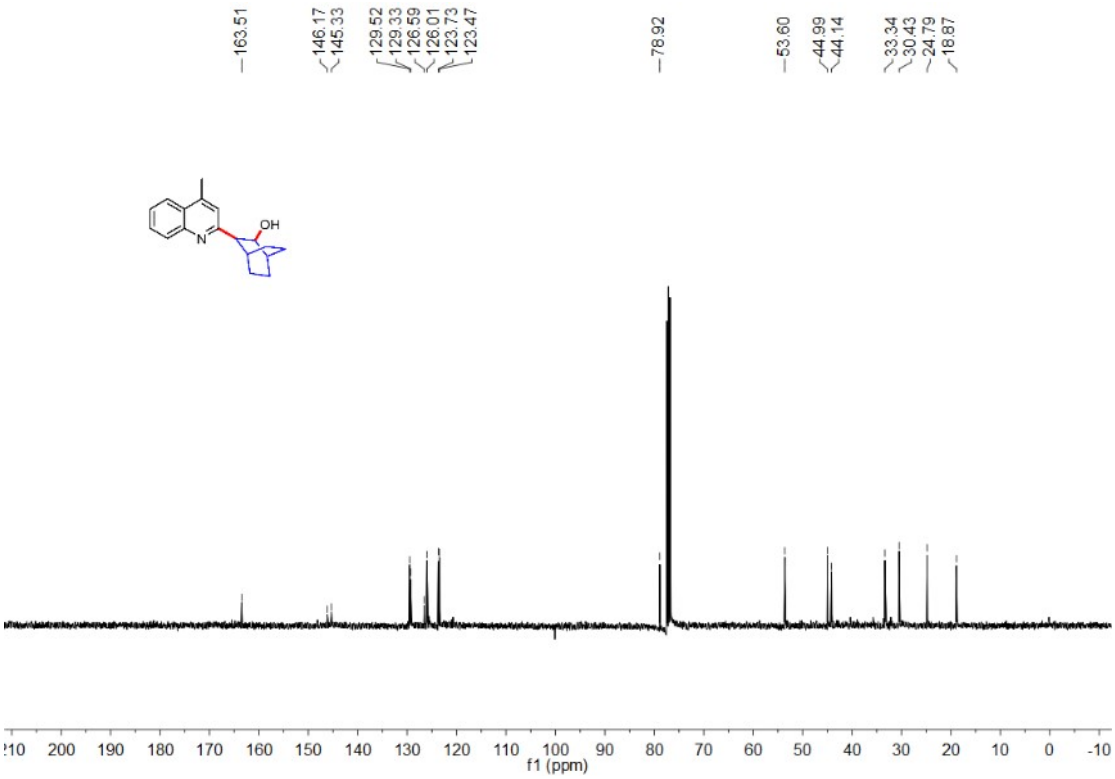
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **26**



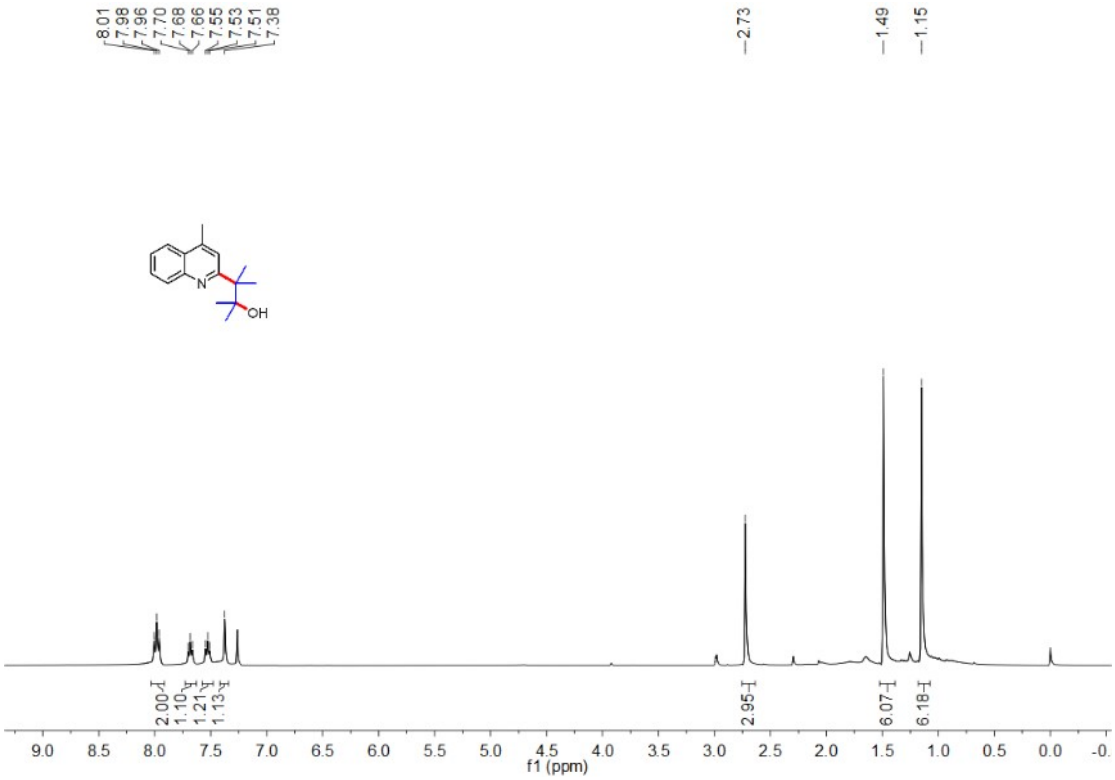
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **27**



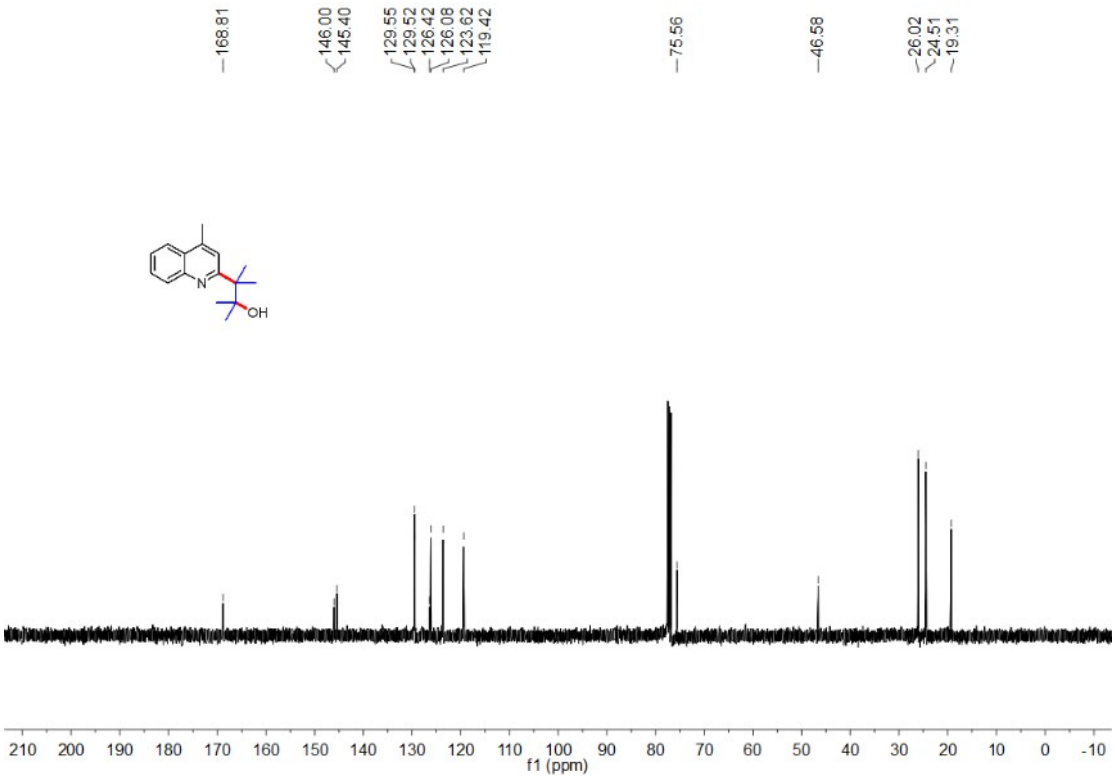
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **27**



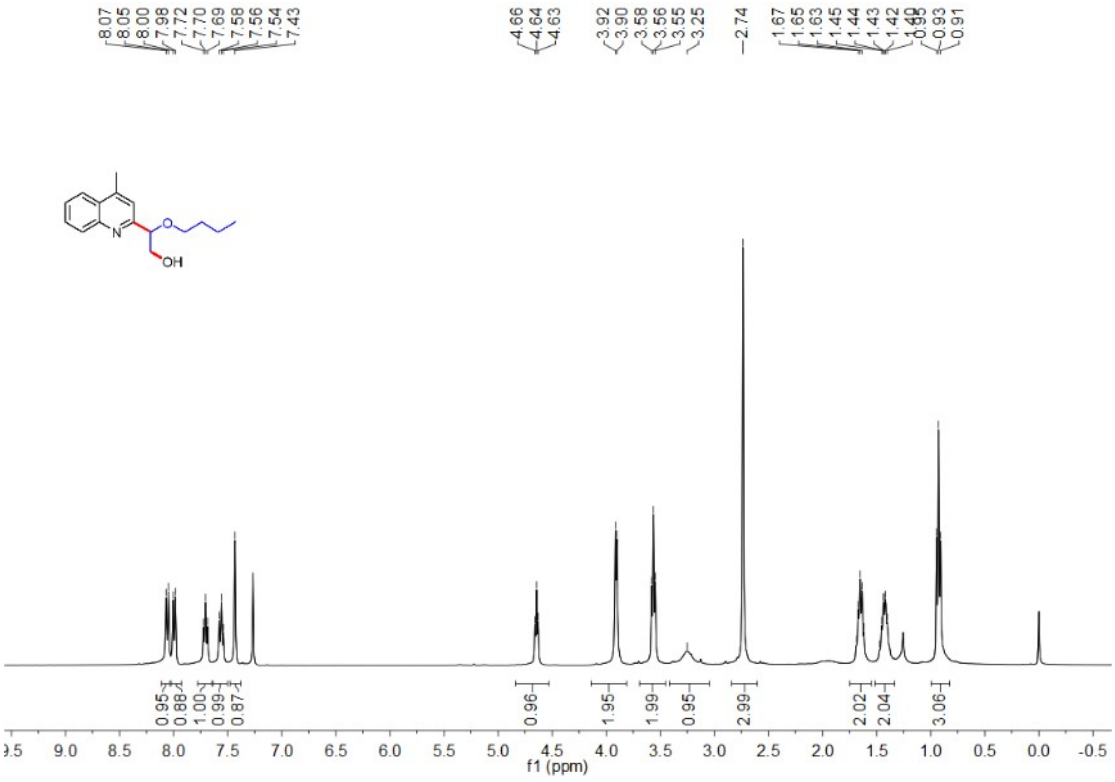
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28**



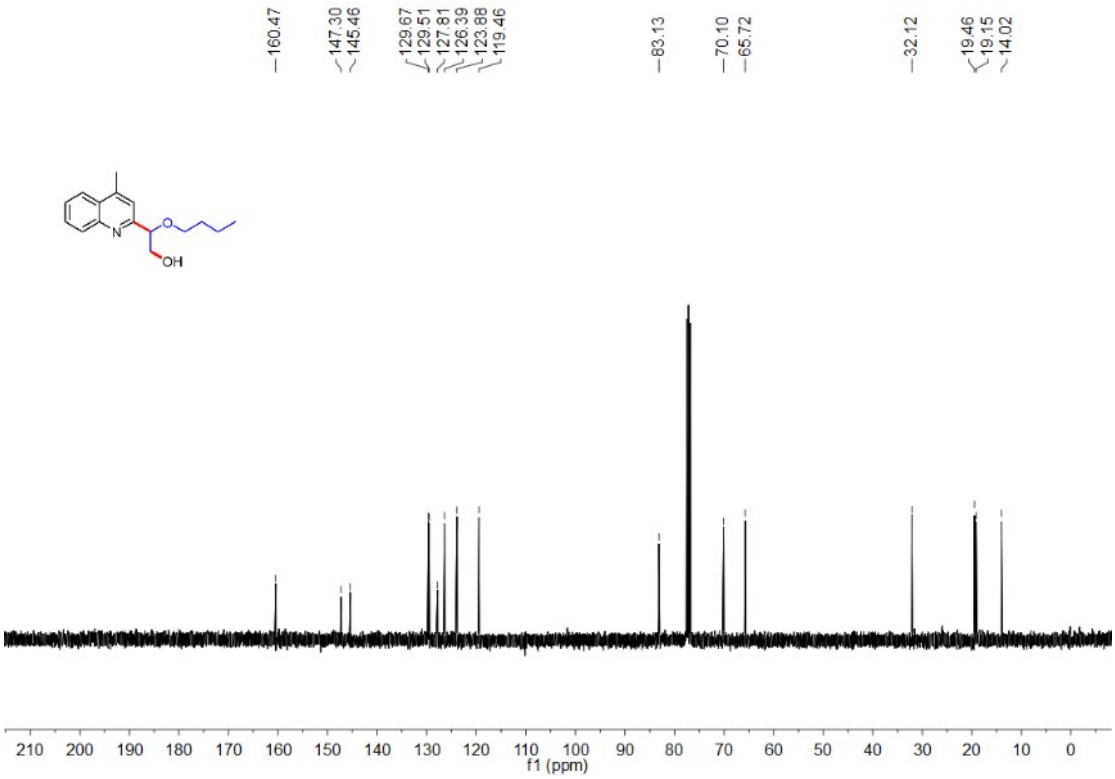
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **28**



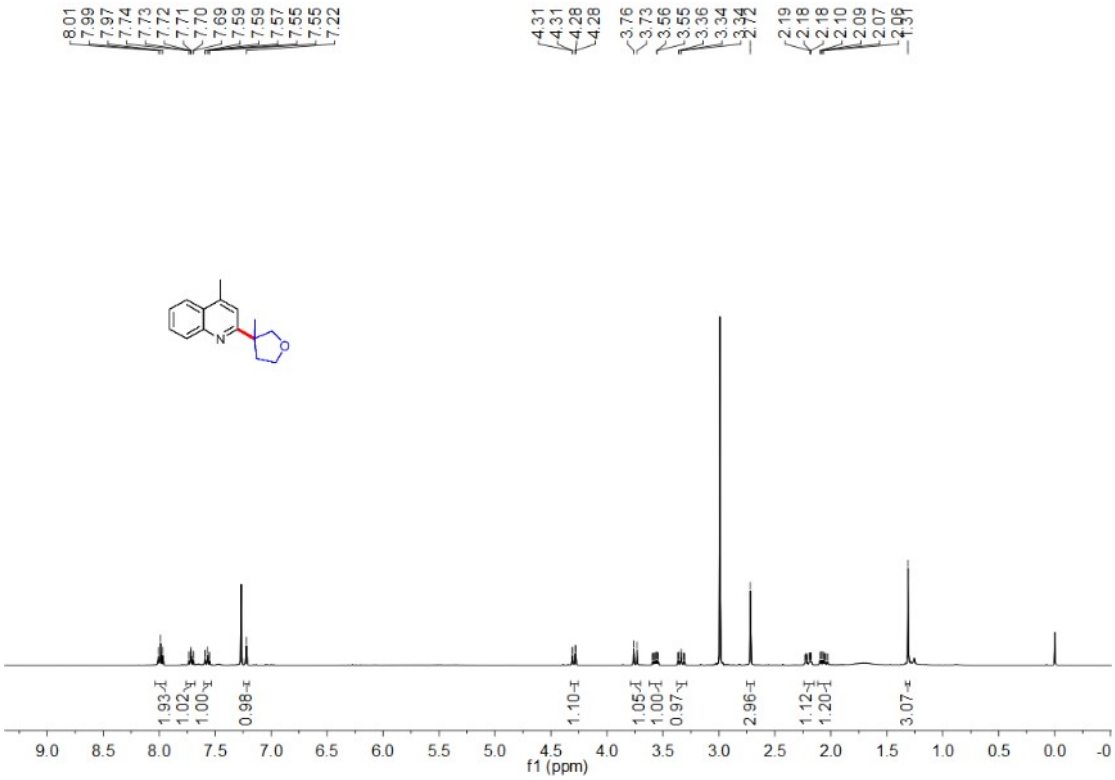
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **29**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **29**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **30**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **30**