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Supplementary Materials for

Ketones and aldehydes as alkyl radical equivalents for C─H functionalization of heteroarenes

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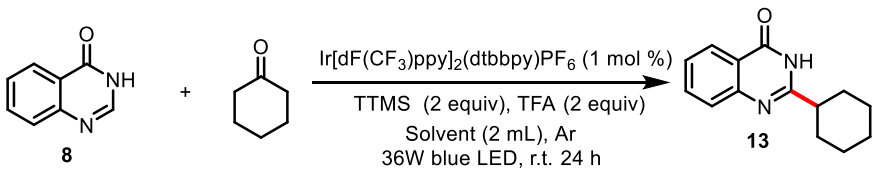
This PDF file includes:

Section S1. 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.

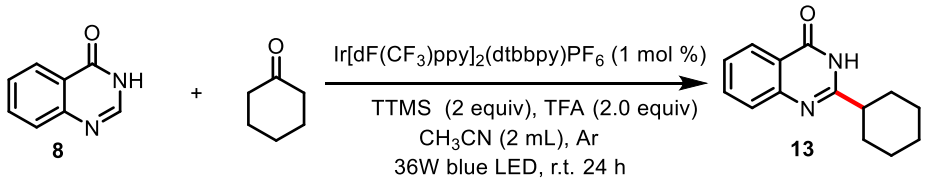
Section S2. Reaction optimization

Table S1. Screening of different solvents. Reaction conditions: 4-hydroxyquinazoline (0.3 mmol), cyclohexanone (9.0 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), TTMS (0.6 mmol), TFA (0.6 mmol) and solvent (2 mL) under Ar atmosphere. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.



entry	solvent	yield (%)
1	CH_3CN	92
2	MeOH	83
3	EtOH	30
4	isopropyl alcohol	62
5	EA	50
6	DMF	<10
7	DMA	<10
8	HFIP	<10

Table S2. Screening of the amount of cyclohexanone. Reaction conditions: 4-hydroxyquinazoline (0.3 mmol), cyclohexanone (0.3x mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), TTMS (0.6 mmol), TFA (0.6 mmol) and CH_3CN (2 mL) under Ar atmosphere. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.



entry	x eq. cyclohexanone	yield (%)[b]
1	10	76
2	20	85
3	30	92
4	40	88
5	50	85

Section S3. Investigation of the mechanism

Fig. S1. Control experiments. To a 10 mL glass vial was added Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (3.36mg, 0.003 mmol, 1 mol %), 4-hydroxyquinazoline (0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), radical inhabitor (0.75 mmol, 2.5 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and 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 yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.

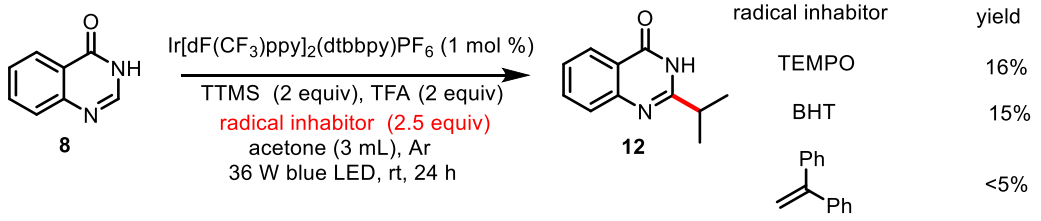
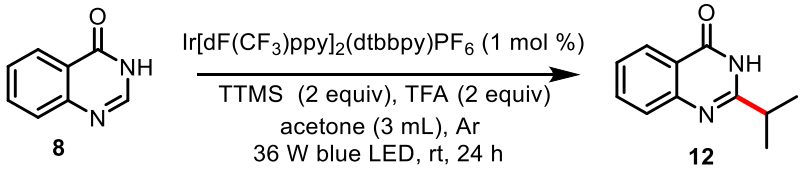


Table S3. Light on and off experiments. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.



entry	light on and off conditions	yield (%)
1	on 1 h	12
2	on 1h, off 23 h	14
3	on 24 h	96

Fig. S2. Emission quenching experiments (Stern-Volmer studies). (**a**) UV-vis absorption spectra. (**b**) Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 emission quenching with TTMS. Emission intensities were recorded using a CARY VARIAN luminescence spectrophotometer. All Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 solutions were excited at 350 nm and the emission intensity was collected at 475 nm. In a typical experiment, to a 3×10^{-5} M solution of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 in acetone was added the appropriate amount of TTMS in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.

(a) (b)

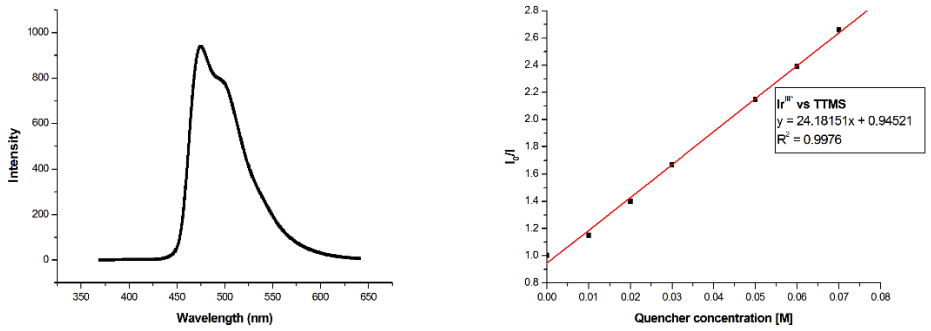
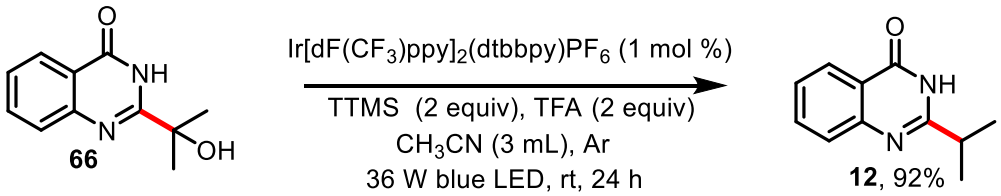


Table S4. Control experiments of intermediate 66. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.



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

Section S4. Experimental procedures and product characterization

4.1 General procedure A for the isopropylation of N-heteroarenes.

To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), heteroarene (0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and 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 concentrated in vacuum to remove the acetone. The mixture was diluted with 10 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.

4.2 General procedure B for the isopropylation of N-heteroarenes.

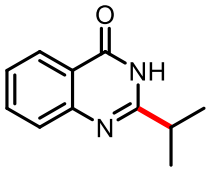
To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), heteroarene (0.3 mmol, 1.0 equiv), HEH (155 mg, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and 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 concentrated in vacuum to remove the acetone. The mixture was diluted with 10 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.

4.3 General procedure C for the alkylation of N-heteroarenes.

To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), heteroarene (0.3 mmol, 1.0 equiv), ketones or aldehydes (9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and 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 concentrated in vacuum to remove the CH_3CN. The mixture was diluted with 10 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.

4.4. Product characterization

2-isopropylquinazolin-4(3*H*)-one (12).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone. The spectral data is consistent with the literature data (*33*).

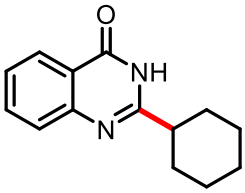
White solid (51.9 mg, 92%). M.p. = 190 – 191 °C.

R_f 0.40 (Petroleum ether/EtOAc, 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.82 – 7.66 (m, 2H), 7.54 – 7.41 (m, 1H), 3.13 – 3.00 (m, 1H), 1.46 (d, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 161.0, 149.6, 134.8, 127.5, 126.4, 126.3, 120.9, 35.1, 20.6.

HRMS (ESI) calcd for $C_{11}H_{13}N_2O$ $[M + H]^+$ 189.1022, found 189.1024.

2-cyclohexylquinazolin-4(3*H*)-one (13).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), cyclohexanone (0.93 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN. The spectral data is consistent with the literature data (*33*).

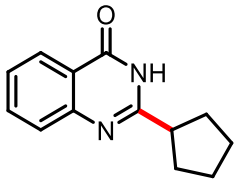
White solid (61.6 mg, 90%). M.p. = 189 – 190 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.92 (s, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.88 – 7.66 (m, 2H), 7.47 (t, J = 6.8 Hz, 1H), 2.75 (t, J = 11.6 Hz, 1H), 2.06 (d, J = 11.6 Hz, 2H), 1.93 (d, J = 9.6 Hz, 2H), 1.85 – 1.75 (m, 3H), 1.52 – 1.38 m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 160.4, 149.7, 134.8, 127.5, 126.4, 126.3, 120.8, 45.0, 30.6, 26.1, 25.8.

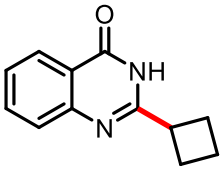
HRMS (ESI) calcd for $C_{14}H_{17}N_2O$ $[M + H]^+$ 229.1335, found 229.1339.

2-cyclopentylquinazolin-4(3*H*)-one (14).



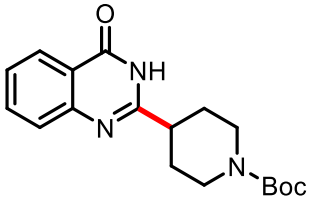
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), cyclopentanone (0.80 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (54.6 mg, 85%). M.p. = 188 – 189 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.27 (d, J = 7.6 Hz, 1H), 7.83 – 7.66 (m, 2H), 7.46 (t, J = 7.6 Hz, 1H), 3.16 (p, J = 8.6 Hz, 1H), 2.25 – 2.11 (m, 2H), 2.09 – 1.98 (m, 2H), 1.96 – 1.85 (m, 2H), 1.77 – 1.70 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 159.8, 149.6, 134.8, 127.5, 126.3, 120.8, 45.7, 31.5, 26.0.
HRMS (ESI) calcd for $C_{13}H_{15}N_2O$ $[M + H]^+$ 215.1179, found 215.1180.

2-cyclobutylquinazolin-4(3*H*)-one (15).



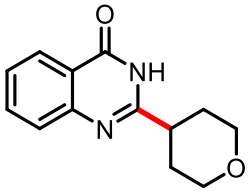
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), cyclobutanone (0.67 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (32.4 mg, 54%). M.p. = 177 – 178 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.83 – 7.69 (m, 2H), 7.47 (t, J = 6.4 Hz, 1H), 3.68 (p, J = 8.8 Hz, 1H), 2.67 – 2.52 (m, 2H), 2.46 (dd, J = 17.6, 8.8 Hz, 2H), 2.25 – 2.09 (m, 1H), 2.02 (dd, J = 19.2, 9.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 158.8, 149.5, 134.8, 127.4, 126.4, 126.3, 120.7, 39.3, 26.6, 18.3.
HRMS (ESI) calcd for $C_{12}H_{13}N_2O$ $[M + H]^+$ 201.1022, found 201.1025.

***tert*-butyl 4-(4-oxo-3,4-dihydroquinazolin-2-yl)piperidine-1-carboxylate (16).**



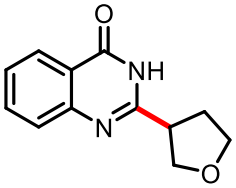
According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), N-(tert-butoxycarbonyl)-4-piperidone (1.80 g, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH$_3$CN.
White solid (71.1 mg, 72%). M.p. = 198 – 199 °C.
R_f 0.75 (EtOAc).
^{1}H NMR (400 MHz, CDCl$_3$) δ 11.82 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 4.30 (s, 2H), 3.01 – 2.76 (m, 3H), 2.12 – 1.84 (m, 4H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.4, 158.3, 154.8, 149.5, 135.0, 127.6, 126.8, 126.4, 120.9, 79.8, 43.9, 42.7, 29.7, 28.6.
HRMS (ESI) calcd for C$_{18}$H$_{24}$N$_3$O$_3$ [M + H]$^+$ 330.1812, found 330.1808.

2-(tetrahydro-2H-pyran-4-yl)quinazolin-4(3*H*)-one (17).



According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), tetrahydrohpyranone (0.83 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH$_3$CN. The spectral data is consistent with the literature data (*33*).
White solid (33.8 mg, 49%). M.p. = 193 – 194 °C.
R_f 0.50 (EtOAc).
^{1}H NMR (400 MHz, CDCl$_3$) δ 11.96 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.88 – 7.68 (m, 2H), 7.50 (t, J = 7.6 Hz, 1H), 4.16 (d, J = 9.2 Hz, 2H), 3.61 (t, J = 11.6 Hz, 2H), 3.01 (t, J = 11.6 Hz, 1H), 2.13 (qd, J = 12.4, 4.0 Hz, 2H), 2.06 – 1.94 (m, 2H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 164.3, 158.2, 149.4, 135.0, 127.6, 126.8, 126.4, 120.9, 67.6, 41.5, 30.3.
HRMS (ESI) calcd for C$_{13}$H$_{15}$N$_2$O$_2$ [M + H]$^+$ 231.1128, found 231.1126.

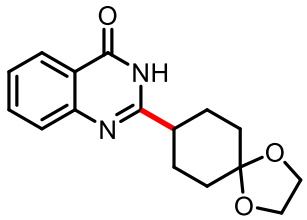
(*R*)-2-(tetrahydrofuran-3-yl)quinazolin-4(3*H*)-one (18).



According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), dihydrofuran-3(2*H*)-one (0.77 g, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH$_3$CN.

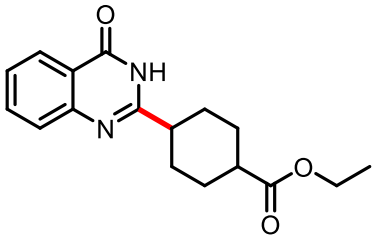
White solid (40.8 mg, 63%). M.p. = 192 – 193 °C.
R_f 0.40 (EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 4.25 – 4.06 (m, 3H), 3.94 (dd, J = 15.6, 8.0 Hz, 1H), 3.57 (dt, J = 12.4, 5.6 Hz, 1H), 2.59 – 2.27 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 157.0, 149.2, 135.0, 127.6, 126.9, 126.4, 120.9, 71.6, 68.4, 44.7, 31.3.
HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2$ $[M + H]^+$ 217.0972, found 217.0967.

2-(1,4-dioxaspiro[4.5]decan-8-yl)quinazolin-4(3*H*)-one (19).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), 1,4-dioxaspiro[4.5]decan-8-one (1.4 g, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (78.9 mg, 92%). M.p. = 202 – 203 °C.
R_f 0.25 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.37 – 8.29 (m, 1H), 7.83 – 7.74 (m, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.53 – 7.42 (m, 1H), 4.02 (s, 4H), 2.87 – 2.71 (m, 1H), 2.16 – 2.08 (m, 4H), 2.00 – 1.92 (m, 2H), 1.81 – 1.70 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 159.1, 149.6, 134.8, 127.6, 126.5, 126.4, 120.9, 108.2, 64.6, 64.5, 43.2, 34.4, 28.1.
HRMS (ESI) calcd for $C_{16}H_{19}N_2O_3$ $[M + H]^+$ 287.1390, found 287.1393.

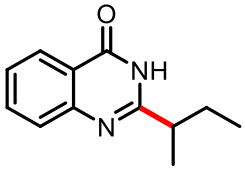
ethyl 4-(4-oxo-3,4-dihydroquinazolin-2-yl)cyclohexane-1-carboxylate (20).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), ethyl 4-oxocyclohexanecarboxylate (1.43 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (83.7 mg, 93%). M.p. = 196 – 197 °C.
R_f 0.35 (Petroleum ether/EtOAc, 2/1).

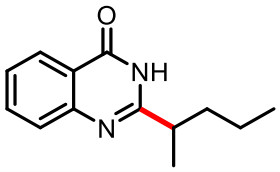
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.74 (ddd, J = 12.4, 7.6, 3.2 Hz, 1H), 2.46 (ddd, J = 12.4, 7.6, 3.2 Hz, 1H), 2.20 (dd, J = 10.8, 6.8 Hz, 4H), 1.91 – 1.77 (m, 2H), 1.72 – 1.63 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 164.3, 159.4, 149.6, 134.9, 127.6, 126.6, 126.4, 120.9, 60.5, 43.9, 42.7, 29.7, 28.6, 14.4.
HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3$ $[M + H]^+$ 301.1547, found 301.1550.

(*R*)-2-(sec-butyl)quinazolin-4(3*H*)-one (21).



According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), 2-butanone (0.80 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (28.5 mg, 47%). M.p. = 173 – 174 °C.
R_f 0.80 (Petroleum ether/EtOAc, 1/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.83 – 7.67 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 2.86 – 2.74 (m, 1H), 1.95 (dt, J = 14.4, 7.6 Hz, 1H), 1.81 – 1.71 (m, 1H), 1.42 (d, J = 6.8 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 160.3, 149.6, 134.8, 127.6, 126.4, 126.4, 121.0, 42.4, 28.3, 18.4, 12.1.
HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1183.

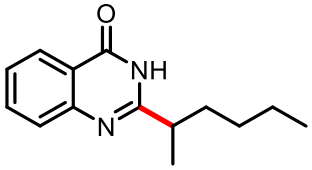
(*R*)-2-(pentan-2-yl)quinazolin-4(3*H*)-one (22).



According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), 2-pentanone (0.96 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (26.6 mg, 41%). M.p. = 134 – 135 °C.
R_f 0.35 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 8.30 (dd, J = 7.6, 1.2 Hz, 1H), 7.80 – 7.69 (m, 2H), 7.50 – 7.43 (m, 1H), 2.91 (h, J = 7.6 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.75 – 1.61 (m, 1H), 1.50 – 1.41 (m, 4H), 1.39 – 1.32 (m, 1H), 0.94 (t, J = 7.6 Hz, 3H). **^{13}C**

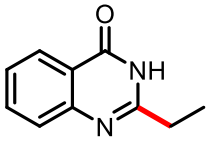
NMR (100 MHz, $CDCl_3$) δ 164.3, 160.7, 149.6, 134.8, 127.5, 126.4, 120.9, 40.5, 37.3, 20.7, 18.6, 14.1.
HRMS (ESI) calcd for $C_{12}H_{17}N_2O$ $[M + H]^+$ 217.1335, found 217.1338.

(*R*)-2-(hexan-2-yl)quinazolin-4(3*H*)-one (23).



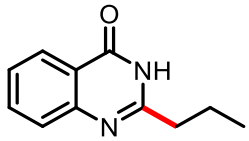
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), 2-hexanone (1.1 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (24.8 mg, 36%). M.p. = 136 – 138 °C.
R_f 0.50 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 2.86 (h, *J* = 7.2 Hz, 1H), 1.95 – 1.83 (m, 1H), 1.77 – 1.69 (m, 1H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.38 – 1.24 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 160.4, 149.6, 134.8, 127.5, 126.4, 126.4, 120.9, 40.8, 34.9, 29.7, 22.7, 18.8, 14.1.
HRMS (ESI) calcd for $C_{14}H_{19}N_2O$ $[M + H]^+$ 231.1492, found 231.1493.

2-ethylquinazolin-4(3*H*)-one (24).



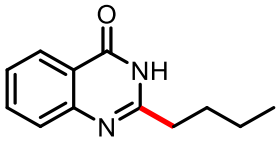
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetaldehyde (40% aq in H_2O).
White solid (26.3 mg, 50%). M.p. = 142 – 143 °C.
R_f 0.15 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.15 (s, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.65 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 2.86 (q, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 157.9, 149.6, 134.9, 127.3, 126.4, 126.3, 120.6, 29.3, 11.7.
HRMS (ESI) calcd for $C_{10}H_{11}N_2O$ $[M + H]^+$ 175.0866, found 175.0863.

2-propylquinazolin-4(3*H*)-one (25).



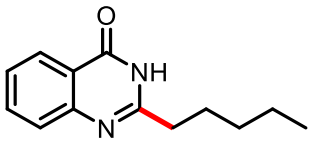
According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), propionaldehyde (0.65 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH$_3$CN.
White solid (50.2 mg, 89%). M.p. = 189 – 190 °C.
R_f 0.45 (Petroleum ether/EtOAc, 1/1).
^{1}H NMR (400 MHz, CDCl$_3$) δ 12.10 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 2.80 (t, J = 7.6 Hz, 2H), 2.01 – 1.87 (m, 2H), 1.09 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 164.5, 156.9, 149.6, 134.9, 127.4, 126.5, 126.3, 120.6, 37.9, 21.1, 13.9.
HRMS (ESI) calcd for $C_{11}H_{13}N_2O$ $[M + H]^+$ 189.1022, found 189.1024

2-butylquinazolin-4(3*H*)-one (26).



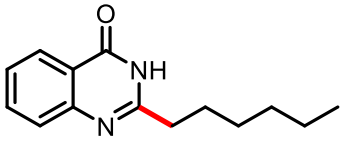
According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), butyraldehyde (0.79 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH$_3$CN.
White solid (49.7 mg, 82%). M.p. = 191 – 192 °C.
R_f 0.30 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, CDCl$_3$) δ 12.29 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 2.89 – 2.75 (m, 2H), 1.97 – 1.80 (m, 2H), 1.51 (dq, J = 14.4, 7.2 Hz, 2H), 1.01 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 164.7, 157.3, 149.7, 134.9, 127.3, 126.4, 126.3, 120.6, 35.8, 29.8, 22.5, 13.9.
HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1183.

2-pentylquinazolin-4(3*H*)-one (27).



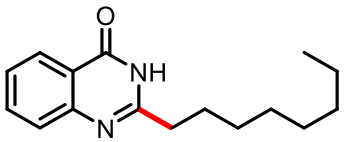
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), valeraldehyde (0.96 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (51.8 mg, 80%). M.p. = 189 – 191 °C.
R_f 0.50 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 8.34 – 8.25 (m, 1H), 7.82 – 7.74 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 2.88 – 2.72 (m, 2H), 1.90 (dt, J = 15.6, 7.6 Hz, 2H), 1.47 – 1.39 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 157.3, 149.7, 134.9, 127.4, 126.5, 126.4, 120.7, 36.2, 31.6, 27.5, 22.5, 14.2.
HRMS (ESI) calcd for $C_{13}H_{17}N_2O$ $[M + H]^+$ 217.1335, found 217.1338.

2-hexylquinazolin-4(3*H*)-one (28).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), hexanal (1.10 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (51.1 mg, 74%). M.p. = 196 – 197 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.34 (s, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.85 – 7.66 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 2.89 – 2.74 (m, 2H), 1.90 (dt, J = 15.6, 7.6 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.39 – 1.31 (m, 4H), 0.89 (t, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 157.3, 149.7, 134.9, 127.3, 126.4, 126.3, 120.6, 36.1, 31.6, 29.0, 27.7, 22.6, 14.2.
HRMS (ESI) calcd for $C_{14}H_{19}N_2O$ $[M + H]^+$ 231.1492, found 231.1492.

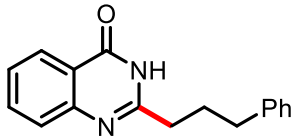
2-octylquinazolin-4(3*H*)-one (29).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), octanal (1.40 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (55.7 mg, 72%). M.p. = 199 – 200 °C.
R_f 0.60 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.43 (s, 1H), 8.27 (d, J = 7.6 Hz, 1H), 7.83 – 7.65 (m,

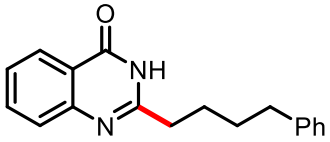
2H), 7.44 (t, *J* = 7.6 Hz, 1H), 2.88 – 2.72 (m, 2H), 1.88 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.38 – 1.25 (m, 8H), 0.87 – 0.82 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 157.3, 149.6, 134.9, 127.3, 126.4, 126.3, 120.5, 36.0, 31.9, 29.4, 29.3, 29.2, 27.7, 22.7, 14.2.
HRMS (ESI) calcd for $C_{16}H_{23}N_2O$ $[M + H]^+$ 259.1805, found 259.1806.

2-(3-phenylpropyl)quinazolin-4(3*H*)-one (30).



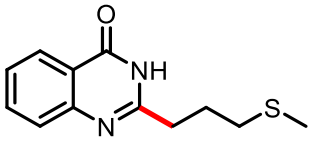
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), phenylpropyl aldehyde (1.18 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (40.4 mg, 51%). M.p. = 166 – 167 °C.
R_f 0.20 (Petroleum ether/EtOAc, 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.34 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.19 – 7.12 (m, 1H), 2.92 – 2.75 (m, 4H), 2.32 – 2.18 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 156.7, 149.6, 141.4, 135.0, 128.6, 128.5, 127.3, 126.5, 126.3, 126.1, 120.5, 35.5, 29.0.
HRMS (ESI) calcd for $C_{17}H_{17}N_2O$ $[M + H]^+$ 265.1335, found 265.1339.

2-(4-phenylbutyl)quinazolin-4(3*H*)-one (31).



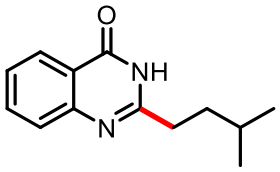
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), 4-phenylbutanal (1.33 g, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (57.5 mg, 69%). M.p. = 162 – 163 °C.
R_f 0.30 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.36 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.20 (m, 3H), 7.17 – 7.11 (m, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.99 – 1.90 (m, 2H), 1.86 – 1.74 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 156.9, 149.6, 142.2, 135.0, 128.5, 128.4, 127.3, 126.5, 126.3, 125.9, 120.5, 35.7, 35.6, 31.0, 27.2.
HRMS (ESI) calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492, found 279.1487.

2-(3-(methylthio)propyl)quinazolin-4(3*H*)-one (32).



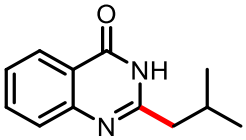
According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), 3-(methylthio)propionaldehyde (0.90 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (28.8 mg, 41%). M.p. = 172 – 173 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.83 – 7.74 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 3.00 – 2.90 (m, 2H), 2.68 (t, J = 7.2 Hz, 2H), 2.28 – 2.17 (m, 2H), 2.15 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 156.1, 149.6, 134.9, 127.4, 126.6, 126.4, 120.6, 34.6, 33.6, 26.6, 15.5.
HRMS (ESI) calcd for $C_{12}H_{15}N_2OS$ $[M + H]^+$ 235.0900, found 235.0899.

2-isopentylquinazolin-4(3*H*)-one (33).



According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), isovaleraldehyde (0.96 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (44.1 mg, 68%). M.p. = 176 – 177 °C.
R_f 0.50 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.43 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.82 – 7.74 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 2.90 – 2.75 (m, 2H), 1.86 – 1.68 (m, 3H), 1.03 (d, J = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 157.6, 149.7, 134.9, 127.3, 126.4, 126.3, 120.6, 36.7, 34.2, 28.2, 22.5.
HRMS (ESI) calcd for $C_{13}H_{17}N_2O$ $[M + H]^+$ 217.1335, found 217.1337.

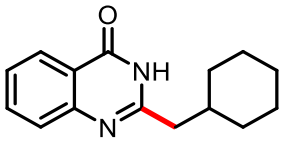
2-isobutylquinazolin-4(3*H*)-one (34).



According to the *general procedure C*. To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-on

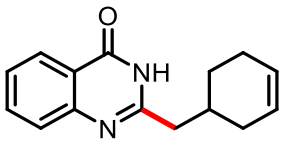
e (43.8 mg, 0.3 mmol, 1.0 equiv), isobutyraldehyde (0.82 mL, 9.0 mmol, 30 e quiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equi v) and 2.0 mL of CH_3CN.
White solid (44.2 mg, 73%). M.p. = 169 – 170 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.77 – 7.59 (m, 2H), 7.40 (t, J = 7.2 Hz, 1H), 2.62 (d, J = 7.2 Hz, 2H), 2.28 (tt, J = 12.4, 6.4 Hz, 1H), 1.00 (d, J = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 156.6, 149.6, 134.9, 127.4, 126.4, 126.3, 120.6, 44.8, 28.1, 22.5.
HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1180.

2-(cyclohexylmethyl)quinazolin-4(3*H*)-one (35).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), cyclohexanecarboxaldehyde (1.09 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (60.3 mg, 83%). M.p. = 195 – 196 °C.
R_f 0.50 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.29 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.84 – 7.65 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 2.70 (d, J = 7.2 Hz, 2H), 2.09 – 1.94 (m, 1H), 1.86 – 1.77 (m, 2H), 1.68 – 1.55 (m, 2H), 1.30 – 1.10 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 156.4, 149.6, 134.8, 127.3, 126.4, 126.3, 120.5, 43.7, 37.3, 33.1, 26.3, 26.2.
HRMS (ESI) calcd for $C_{15}H_{19}N_2O$ $[M + H]^+$ 243.1492, found 243.1495.

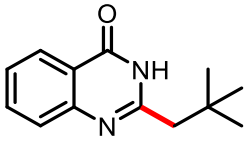
2-(cyclohex-3-en-1-ylmethyl)quinazolin-4(3*H*)-one (36).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), 3-cyclohexene-1-carboxaldehyde (1.05 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (41.8 mg, 58%). M.p. = 176 – 177 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.37 (s, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.83 – 7.66 (m, 2H), 7.48 (t, J = 7.2 Hz, 1H), 5.67 (s, 2H), 2.79 (d, J = 7.2 Hz, 2H), 2.45 – 2.28 (m, 1H), 2.26 – 2.16 (m, 1H), 2.15 – 2.06 (m, 2H), 1.96 – 1.84 (m, 2H), 1.54 – 1.42 (m,

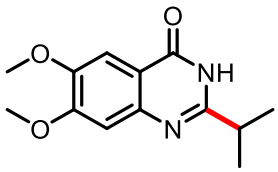
1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 156.1, 149.6, 134.9, 127.4, 127.1, 126.5, 126.3, 125.8, 120.6, 42.6, 33.2, 31.4, 28.6, 25.0.
HRMS (ESI) calcd for $C_{15}H_{17}N_2O$ $[M + H]^+$ 241.1335, found 241.1337.

2-neopentylquinazolin-4(3*H*)-one (37).



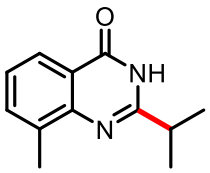
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), pivaldehyde (0.98 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (31.8 mg, 49%). M.p. = 169 – 170 °C.
R_f 0.70 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.16 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.83 – 7.67 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 2.71 (s, 2H), 1.13 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 155.3, 149.6, 134.8, 127.5, 126.4, 126.2, 120.5, 49.3, 32.6, 29.8.
HRMS (ESI) calcd for $C_{13}H_{17}N_2O$ $[M + H]^+$ 217.1335, found 217.1338.

2-isopropyl-6,7-dimethoxyquinazolin-4(3*H*)-one (38).



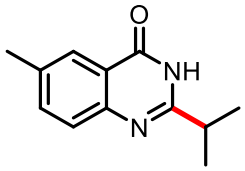
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 6,7-dimethoxyquinazolin-4(3*H*)-one (61.8 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (67.0 mg, 90%). M.p. = 193 – 194 °C.
R_f 0.28 (Petroleum ether/EtOAc, 1/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H), 7.58 (s, 1H), 7.13 (s, 1H), 4.02 (s, 6H), 3.18 – 2.89 (m, 1H), 1.42 (d, J = 4.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 159.6, 155.4, 148.8, 145.9, 113.8, 107.8, 105.1, 56.3, 34.6, 20.6.
HRMS (ESI) calcd for $C_{13}H_{17}N_2O_3$ $[M + H]^+$ 249.1234, found 249.1238.

2-isopropyl-8-methylquinazolin-4(3*H*)-one (39).



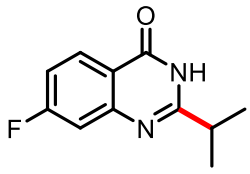
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 8-methylquinazolin-4(3*H*)-one (48.0 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (49.7 mg, 82%). M.p. = 188 – 189 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 3.05 (hept, J = 6.8 Hz, 1H), 2.63 (s, 3H), 1.44 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 159.4, 148.2, 136.2, 135.3, 125.8, 123.9, 120.7, 34.9, 20.7, 17.6.
HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1180.

2-isopropyl-6-methylquinazolin-4(3*H*)-one (40).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 6-methylquinazolin-4(3*H*)-one (48.0 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (47.3 mg, 78%). M.p. = 220 – 221 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 8.06 (s, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 3.29 – 3.11 (m, 1H), 2.51 (s, 3H), 1.50 (d, J = 6.8 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.3, 145.4, 137.5, 136.9, 126.1, 125.9, 120.1, 34.5, 21.4, 20.4.
HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1182.

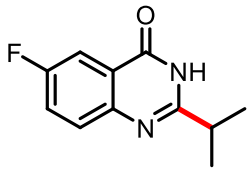
7-fluoro-2-isopropylquinazolin-4(3*H*)-one (41).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 7-fluoroquinazolin-4(3*H*)-one (49.2 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (60.6 mg, 98%). M.p. = 172 – 173 °C.
R_f 0.75 (Petroleum ether/EtOAc, 1/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 8.39 – 8.23 (m, 1H), 7.37 (d, J = 9.6 Hz, 1H), 7.18 (t, J = 8.4 Hz, 1H), 3.15 – 2.95 (m, 1H), 1.45 (d, J = 6.8 Hz, 6H). **^{13}C NMR**

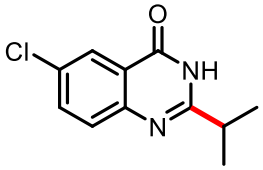
(100 MHz, $CDCl_3$) δ 166.9 (d, J = 254.2 Hz), 163.9, 162.5, 152.0 (d, J = 13.4 Hz), 129.0 (d, J = 10.8 Hz), 117.5, 115.3 (d, J = 23.5 Hz), 112.9 (d, J = 21.6 Hz), 35.0, 20.5.
HRMS (ESI) calcd for $C_{11}H_{12}FN_2O$ $[M + H]^+$ 207.0928, found 207.0930.

6-fluoro-2-isopropylquinazolin-4(3*H*)-one (42).



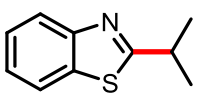
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 6-fluoroquinazolin-4(3*H*)-one (49.2 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (38.9 mg, 63%). M.p. = 164 – 165 °C.
R_f 0.60 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 7.91 (dd, J = 8.4, 2.8 Hz, 1H), 7.72 (dd, J = 8.8, 4.8 Hz, 1H), 7.49 (td, J = 8.4, 2.8 Hz, 1H), 3.09 – 2.95 (m, 1H), 1.44 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, J = 162.9 Hz), 160.1, 159.5, 146.3, 129.9 (d, J = 8.0 Hz), 123.4 (d, J = 24.0 Hz), 122.1, 111.2 (d, J = 23.6 Hz), 35.0, 20.5.
HRMS (ESI) calcd for $C_{11}H_{12}FN_2O$ $[M + H]^+$ 207.0928, found 207.0927.

6-chloro-2-isopropylquinazolin-4(3*H*)-one (43).



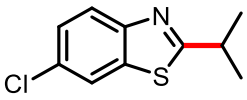
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 6-chloroquinazolin-4(3*H*)-one (54.0 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (57.3 mg, 86%). M.p. = 198 – 199 °C.
R_f 0.40 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (s, 1H), 8.24 (d, J = 2.0 Hz, 1H), 7.75 – 7.62 (m, 2H), 3.14 – 2.95 (m, 1H), 1.44 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 159.4, 148.2, 136.2, 135.3, 125.8, 123.9, 120.7, 34.9, 20.7.
HRMS (ESI) calcd for $C_{11}H_{12}ClN_2O$ $[M + H]^+$ 223.0633, found 223.0632.

2-isopropylbenzo[*d*]thiazole (44).



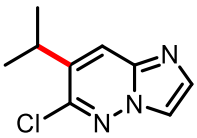
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), benzo[*d*]thiazole (40.5 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (27.2 mg, 51%).
R_f 0.60 (Petroleum ether/EtOAc, 15/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.39 – 7.30 (m, 1H), 3.49 – 3.34 (m, 1H), 1.49 (d, J = 6.8 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 153.3, 134.8, 126.0, 124.7, 122.7, 121.7, 34.2, 23.0.
HRMS (ESI) calcd for $C_{10}H_{12}NS$ $[M + H]^+$ 178.0685, found 178.0683.

6-chloro-2-isopropylbenzo[*d*]thiazole (45).



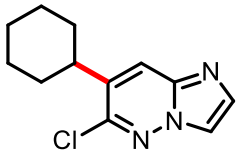
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 6-chlorobenzo[*d*]thiazole (50.4 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (25.3 mg, 40%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.40 (dd, J = 8.8, 2.0 Hz, 1H), 3.40 (hept, J = 6.8 Hz, 1H), 1.48 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 151.9, 136.1, 130.6, 126.7, 123.5, 121.3, 34.2, 22.9.
HRMS (ESI) calcd for $C_{10}H_{10}ClNS$ $[M + H]^+$ 212.0295, found 212.0293.

6-chloro-7-isopropylimidazo[1,2-*b*]pyridazine (46a).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 6-chloroimidazo[1,2-*b*]pyridazine (45.9 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (33.3 mg, 57%).
R_f 0.75 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.73 (s, 1H), 6.88 (s, 1H), 3.75 – 3.62 (m, 1H), 1.42 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 147.4, 137.9, 133.3, 117.3, 114.3, 29.2, 21.6.
HRMS (ESI) calcd for $C_9H_{11}ClN_3$ $[M + H]^+$ 196.0636, found 196.0638.

6-chloro-7-cyclohexylimidazo[1,2-*b*]pyridazine (46b).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 6-chloroimidazo[1,2-*b*]pyridazine (45.9 mg, 0.3 mmol, 1.0 equiv), cyclohexanone (0.93 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN. The spectral data is consistent with the literature data (*34*).

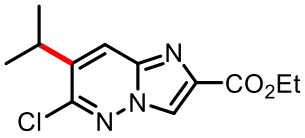
White solid (23.3 mg, 33%). M.p. = 70 – 71 °C.

R_f 0.75 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 (s, 1H), 6.86 (s, 1H), 3.41 – 3.27 (m, 1H), 2.16 – 2.03 (m, 2H), 1.89 (s, 2H), 1.82 (d, J = 13.2 Hz, 1H), 1.59 – 1.44 (m, 4H), 1.31 (d, J = 11.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 147.4, 138.0, 133.2, 117.3, 114.6, 38.8, 32.1, 26.3, 26.0.

HRMS (ESI) calcd for $C_{12}H_{15}ClN_3$ $[M + H]^+$ 236.0949, found 236.0952.

ethyl 6-chloro-7-isopropylimidazo[1,2-*b*]pyridazine-2-carboxylate (47).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), ethyl 6-chloroimidazo[1,2-*b*]pyridazine-2-carboxylate (67.5 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.

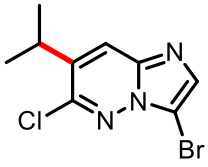
Colorless oil (32.0 mg, 40%).

R_f 0.75 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 6.95 (s, 1H), 4.48 (q, J = 7.2 Hz, 2H), 3.90 – 3.78 (m, 1H), 1.46 – 1.39 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 150.9, 149.2, 138.4, 136.1, 121.3, 116.1, 61.4, 28.6, 21.8, 14.5.

HRMS (ESI) calcd for $C_{12}H_{15}ClN_3O_2$ $[M + H]^+$ 268.0847, found 268.0852.

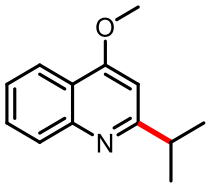
3-bromo-6-chloro-7-isopropylimidazo[1,2-*b*]pyridazine (48).



According to the *general procedure B*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 3-bromo-6-chloroimidazo[1,2-*b*]pyridazine (69.0 mg, 0.3 mmol, 1.0 equiv), hantzsch

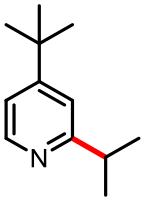
dihydropyridine (155.0 mg, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (31.0 mg, 38%).
R_f 0.80 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 6.94 (s, 1H), 3.68 (hept, J = 6.8 Hz, 1H), 1.42 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 148.5, 138.6, 133.7, 114.7, 101.3, 28.9, 21.7.
HRMS (ESI) calcd for $C_9H_{10}BrClN_3$ $[M + H]^+$ 273.9741, found 273.9741.

2-isopropyl-4-methoxyquinoline (49).



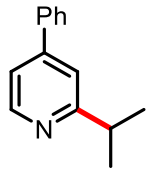
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 4-methoxyquinoline (47.7 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (23.6 mg, 39%).
R_f 0.30 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.4, 1.2 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.48 – 7.41 (m, 1H), 6.67 (s, 1H), 4.06 (s, 3H), 3.30 – 3.14 (m, 1H), 1.40 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 162.7, 148.8, 129.8, 128.6, 124.9, 121.7, 120.4, 97.5, 55.6, 38.0, 22.8.
HRMS (ESI) calcd for $C_{13}H_{16}NO$ $[M + H]^+$ 202.1226, found 202.1227.

4-(*tert*-butyl)-2-isopropylpyridine (50).



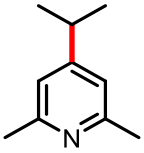
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 4-(*tert*-butyl)pyridine (40.5 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (33.5 mg, 63%).
R_f 0.32 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 5.2 Hz, 1H), 6.95 (s, 1H), 6.89 (dd, J = 5.2, 1.6 Hz, 1H), 2.93 – 2.78 (m, 1H), 1.17 – 1.07 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 160.3, 148.9, 118.2, 117.6, 36.5, 34.7, 30.6, 22.8.
HRMS (ESI) calcd for $C_{12}H_{20}N$ $[M + H]^+$ 178.1590, found 178.1592.

2-isopropyl-4-phenylpyridine (51).



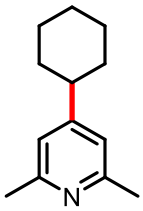
According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 4-phenylpyridine (46.5 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (33.1 mg, 56%).
R_f 0.50 (Petroleum ether/EtOAc, 7/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 5.2 Hz, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.54 – 7.42 (m, 3H), 7.40 (s, 1H), 7.34 (d, J = 5.2 Hz, 1H), 3.25 – 3.07 (m, 1H), 1.37 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 149.6, 149.0, 138.9, 129.2, 128.9, 127.2, 119.4, 118.8, 36.6, 22.8.
HRMS (ESI) calcd for $C_{11}H_{13}N_2O$ $[M + H]^+$ 198.1277, found 198.1278.

4-isopropyl-2,6-dimethylpyridine (52a).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 2,6-dimethylpyridine (32.1 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (40.2 mg, 90%).
R_f 0.30 (Petroleum ether/EtOAc, 7/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.86 – 2.73 (m, 1H), 2.50 (s, 6H), 1.22 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3, 157.7, 118.7, 33.6, 24.6, 23.3.
HRMS (ESI) calcd for $C_{10}H_{16}N$ $[M + H]^+$ 150.1277, found 150.1278.

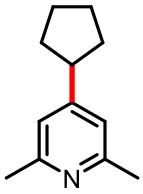
4-cyclohexyl-2,6-dimethylpyridine (52b).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 2,6-dimethylpyridine (32.1 mg, 0.3 mmol, 1.0 equiv), cyclohexanone (0.93 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL

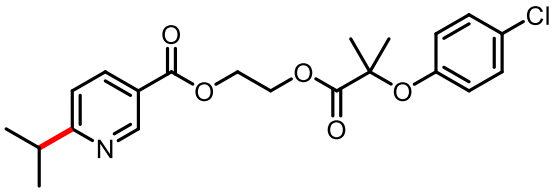
of CH_3CN. The spectral data is consistent with the literature data (*34*).
Colorless oil (52.2 mg, 92%).
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 2H), 2.49 (s, 6H), 2.41 (s, 1H), 1.84 (d, J = 8.0 Hz, 4H), 1.75 (d, J = 12.0 Hz, 1H), 1.46 – 1.29 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 157.2, 118.9, 43.8, 33.5, 26.6, 26.0, 24.4.
HRMS (ESI) calcd for $C_{13}H_{20}N$ $[M + H]^+$ 190.1590, found 190.1596.

4-cyclopentyl-2,6-dimethylpyridine (52c).



According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 2,6-dimethylpyridine (32.1 mg, 0.3 mmol, 1.0 equiv), cyclopentanone (0.80 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
Colorless oil (40.4 mg, 77%).
R_f 0.40 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 2.97 – 2.81 (m, 1H), 2.49 (s, 6H), 2.13 – 1.97 (m, 2H), 1.85 – 1.75 (m, 2H), 1.74 – 1.69 (m, 2H), 1.62 – 1.52 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 156.2, 119.2, 45.1, 33.9, 25.6, 24.4.
HRMS (ESI) calcd for $C_{11}H_{18}N$ $[M + H]^+$ 176.1434, found 176.1436.

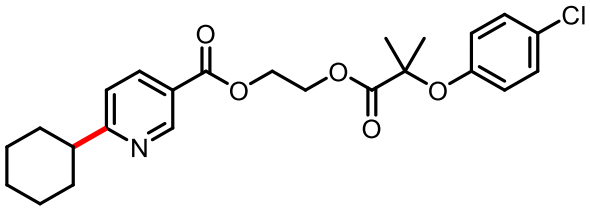
2-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)ethyl 6-isopropylnicotinate (53a).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 2-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)ethyl nicotinate (108.9 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
Colorless oil (46.3 mg, 38%).
R_f 0.40 (Petroleum ether/EtOAc, 4/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 1.6 Hz, 1H), 8.04 (dd, J = 8.0, 2.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 4.56 – 4.49 (m, 4H), 3.21 – 3.04 (m, 1H), 1.59 (s, 6H), 1.33 (d, J = 6.8 Hz, 6H). **^{13}C NMR**

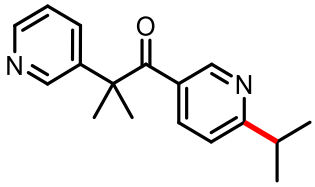
(100 MHz, $CDCl_3$) δ 174.0, 172.5, 165.2, 154.1, 150.6, 137.6, 129.3, 127.4, 123.1, 120.5, 120.4, 79.5, 63.2, 62.6, 36.8, 25.4, 22.4.
HRMS (ESI) calcd for $C_{21}H_{24}ClNO_5$ $[M + H]^+$ 406.1416, found 406.1412.

2-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)ethyl 6-cyclohexylnicotinate (53b).
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 2-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)ethyl nicotinate (108.9 mg, 0.3 mmol, 1.0 equiv), cyclohexanone (0.93 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
Yellow oil (66.8 mg, 50%).
R_f 0.40 (Petroleum ether/EtOAc, 4/1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 4.53 (s, 4H), 2.78 (t, J = 11.6 Hz, 1H), 1.97 (d, J = 12.0 Hz, 2H), 1.88 (d, J = 12.4 Hz, 2H), 1.77 (d, J = 12.0 Hz, 1H), 1.59 (s, 6H), 1.56 – 1.49 (m, 2H), 1.43 (dd, J = 25.2, 12.4 Hz, 2H), 1.35 – 1.29 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 171.5, 165.2, 153.9, 150.5, 137.5, 129.2, 127.2, 122.9, 120.8, 120.2, 79.3, 63.1, 62.5, 46.8, 32.7, 26.4, 26.0, 25.3.
HRMS (ESI) calcd for $C_{24}H_{29}ClNO_5$ $[M + H]^+$ 446.1729, found 446.1730.

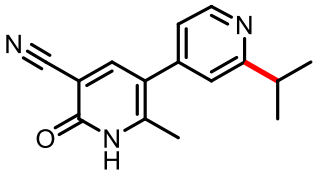
1-(6-isopropylpyridin-3-yl)-2-methyl-2-(pyridin-3-yl)propan-1-one (54).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 2-methyl-1,2-di(pyridin-3-yl)propan-1-one (67.8 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (28.1 mg, 35%). M.p. = 60 – 61 °C.
R_f 0.50 (CH_2Cl_2/MeOH, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 20.0 Hz, 3H), 7.80 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.30 (dd, J = 7.6, 5.2 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 3.11 – 2.95 (m, 1H), 1.66 (s, 6H), 1.25 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ

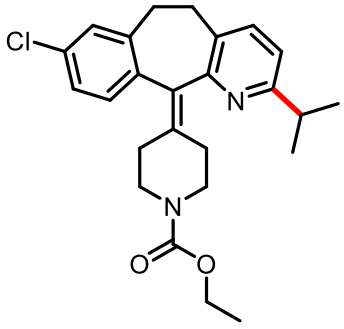
201.1, 171.0, 150.8, 148.6, 147.6, 137.8, 133.9, 133.5, 128.6, 124.0, 120.5, 50.3, 36.5, 27.6, 22.3.
HRMS (ESI) calcd for $C_{17}H_{21}N_2O$ $[M + H]^+$ 269.1648, found 269.1650.

2'-isopropyl-2-methyl-6-oxo-1,6-dihydro-[3,4'-bipyridine]-5-carbonitrile (55).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 2-methyl-6-oxo-1,6-dihydro-[3,4'-bipyridine]-5-carbonitrile (63.3 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone.
White solid (31.1 mg, 41%). M.p. = 63 – 64 °C.
R_f 0.40 (CH_2Cl_2/MeOH, 20/1).
^{1}H NMR (400 MHz, MeOD) δ 8.50 (d, *J* = 5.2 Hz, 1H), 8.08 (s, 1H), 7.34 (s, 1H), 7.26 (dd, *J* = 5.2, 1.6 Hz, 1H), 3.12 (dp, *J* = 13.6, 6.8 Hz, 1H), 2.38 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, MeOD) δ 167.7, 161.1, 151.0, 149.6, 148.5, 145.6, 121.9, 121.5, 117.6, 115.1, 101.4, 36.0, 21.4, 17.1.
HRMS (ESI) calcd for $C_{15}H_{16}N_3O$ $[M + H]^+$ 254.1288, found 254.1286.

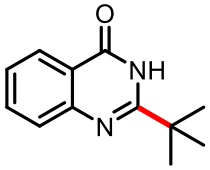
ethyl 4-(8-chloro-2-isopropyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (56).



According to the *general procedure A*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), ethyl 4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (114.6 mg, 0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone. The spectral data is consistent with the literature data (*25*).
White solid (58.5 mg, 46%). M.p. = 99 – 100 °C.
R_f 0.35 (CH_2Cl_2/MeOH, 80/1).
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.10 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.93 – 3.69 (m, 2H), 3.42 – 3.23 (m, 2H),

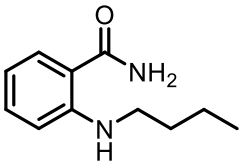
3.22 – 3.12 (m, 2H), 3.02 (td, *J* = 14.0, 7.2 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.58 – 2.47 (m, 1H), 2.41 – 2.26 (m, 3H), 1.27 – 1.22 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 155.7, 155.5, 140.0, 138.2, 138.0, 137.3, 134.6, 132.7, 130.6, 130.2, 128.8, 126.0, 118.4, 61.3, 45.0, 36.0, 31.8, 31.4, 31.0, 30.7, 23.4, 22.1, 14.7.
HRMS (ESI) calcd for $C_{25}H_{30}ClN_2O_2$ $[M + H]^+$ 425.1990, found 425.1988.

2-(*tert*-butyl)quinazolin-4(3*H*)-one (58).



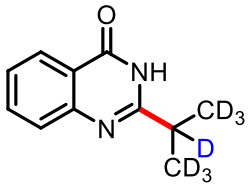
According to the *general procedure C*. To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), quinazolin-4(3*H*)-one (43.8 mg, 0.3 mmol, 1.0 equiv), pivaldehyde (0.98 mL, 9.0 mmol, 30 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of CH_3CN.
White solid (27.3 mg, 45%). M.p. = 150 – 151 °C.
R_f 0.50 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.46 (dd, *J* = 8.0, 6.4 Hz, 1H), 1.51 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 162.4, 149.3, 134.6, 127.8, 126.4, 126.3, 120.7, 37.6, 28.4.
HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1187.

2-(butylamino)benzamide (61).



White solid (49.9 mg, 59%). M.p. = 89 – 90 °C.
R_f 0.50 (Petroleum ether/EtOAc, 2/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.59 – 6.50 (m, 1H), 5.71 (s, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 1.66 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.45 (dq, *J* = 14.4, 7.2 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 150.6, 133.7, 128.4, 114.2, 112.7, 111.9, 42.8, 31.4, 20.5, 14.0.
HRMS (ESI) calcd for $C_{11}H_{15}N_2O$ $[M - H]^-$ 191.1190, found 191.1190.

2-(propan-2-yl-d7)quinazolin-4(3*H*)-one (70).



White solid (49.9 mg, 60%). M.p. = 189 – 190 °C.

R_f 0.40 (Petroleum ether/EtOAc, 2/1).

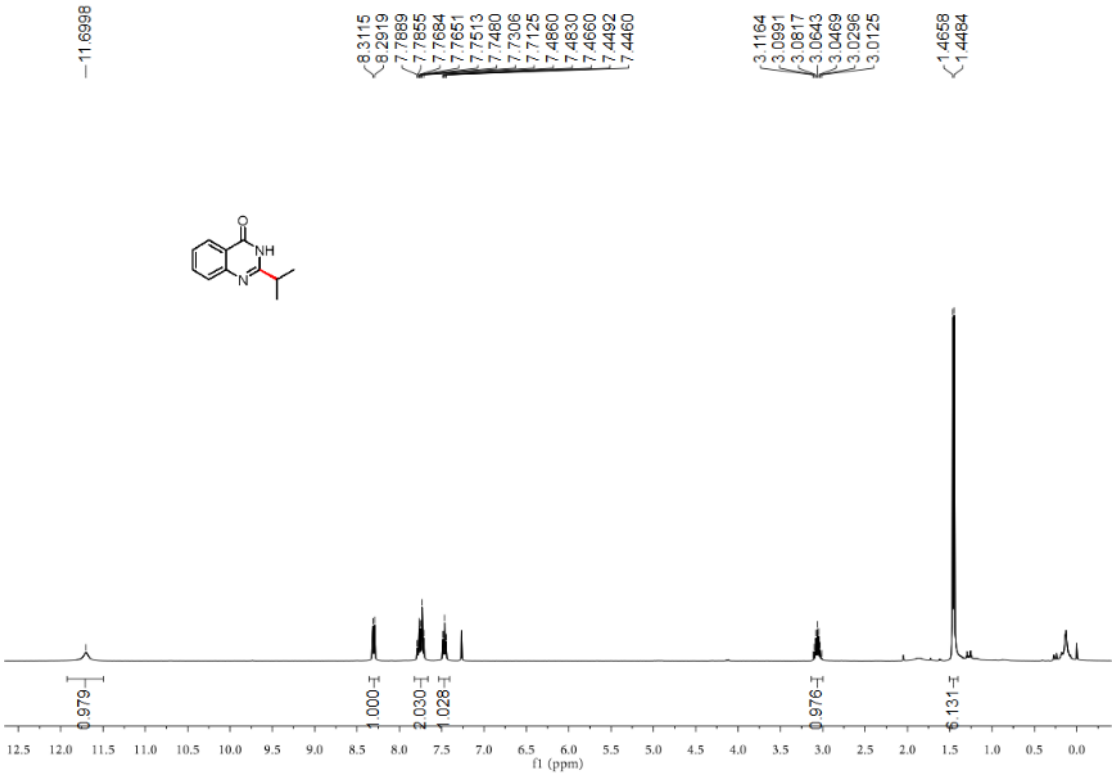
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.84 – 7.68 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 161.1, 149.6, 134.8, 127.5, 126.4, 126.4, 120.9.

HRMS (ESI) calcd for $C_{11}H_6D_7N_2O$ $[M + H]^+$ 196.1462, found 196.1464.

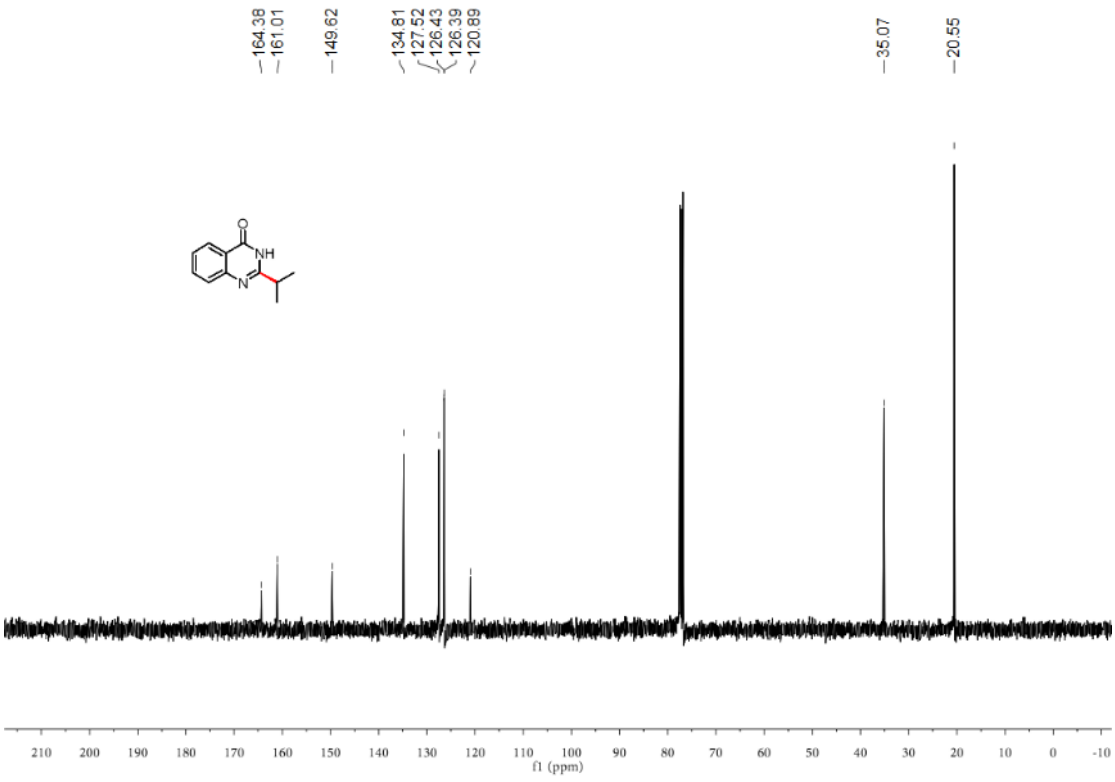
Section S5. Copies of ^{1}H NMR and ^{13}C NMR spectra for new compounds

NMR Spectra

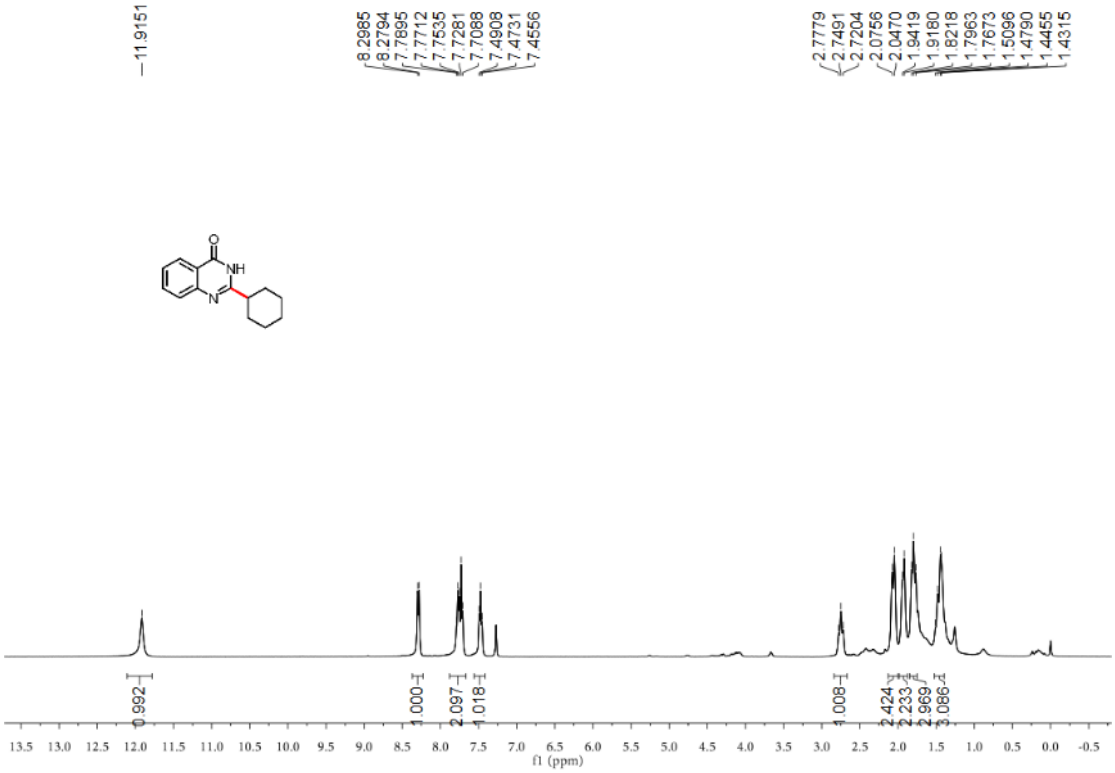
^{1}H NMR spectrum of compound **12**



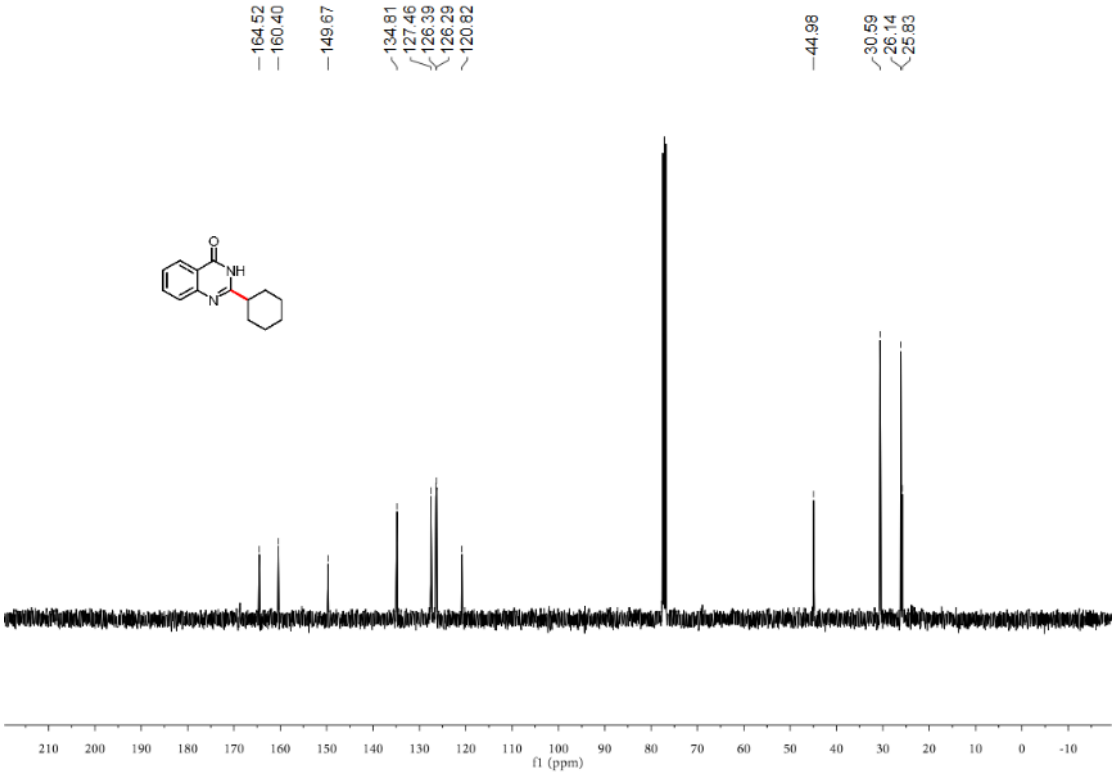
^{13}C NMR spectrum of compound **12**



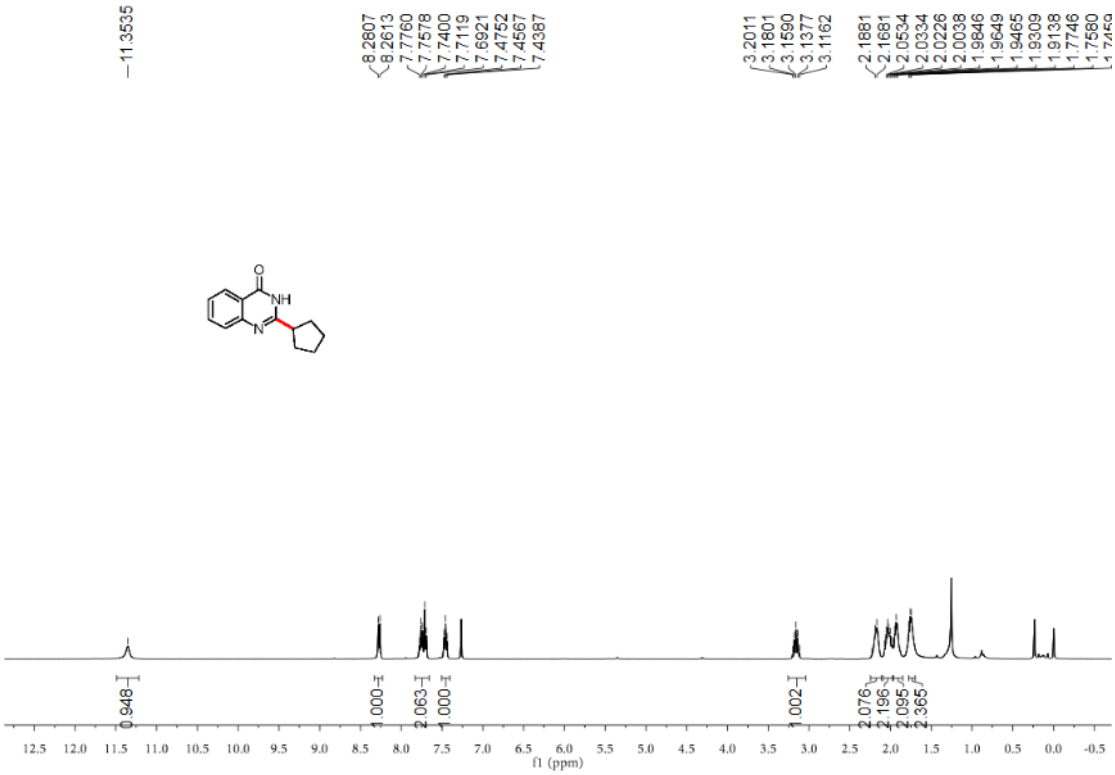
^{1}H NMR spectrum of compound **13**



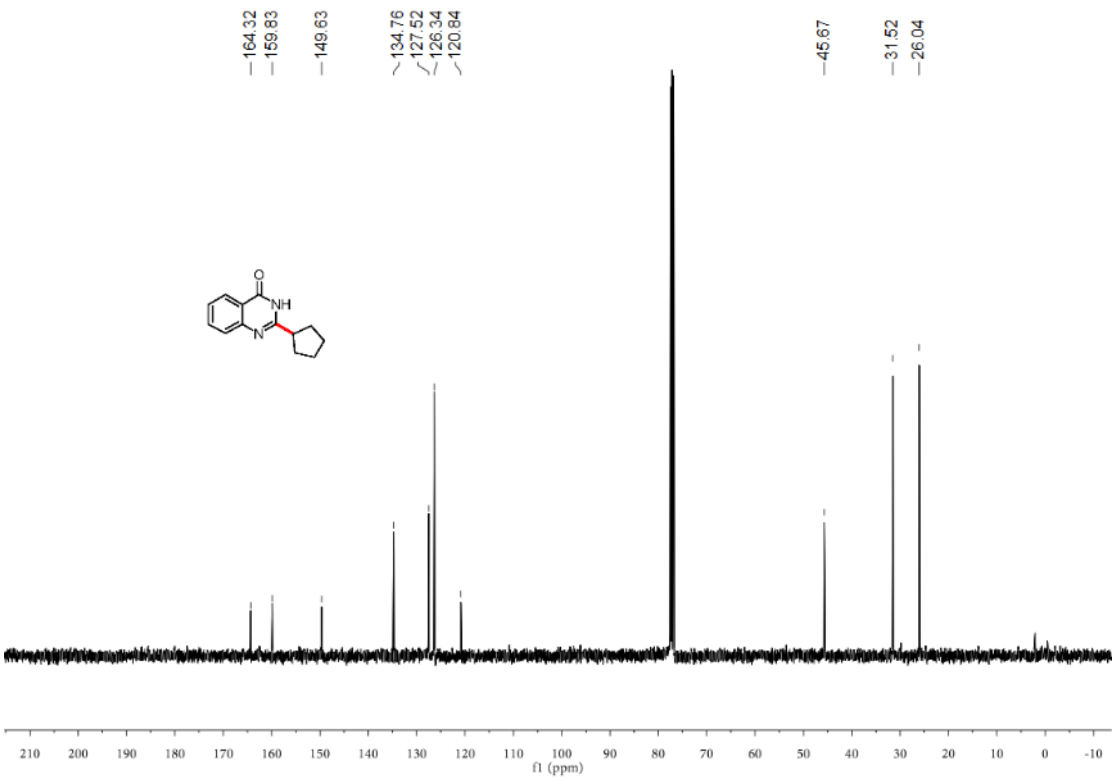
^{13}C NMR spectrum of compound **13**



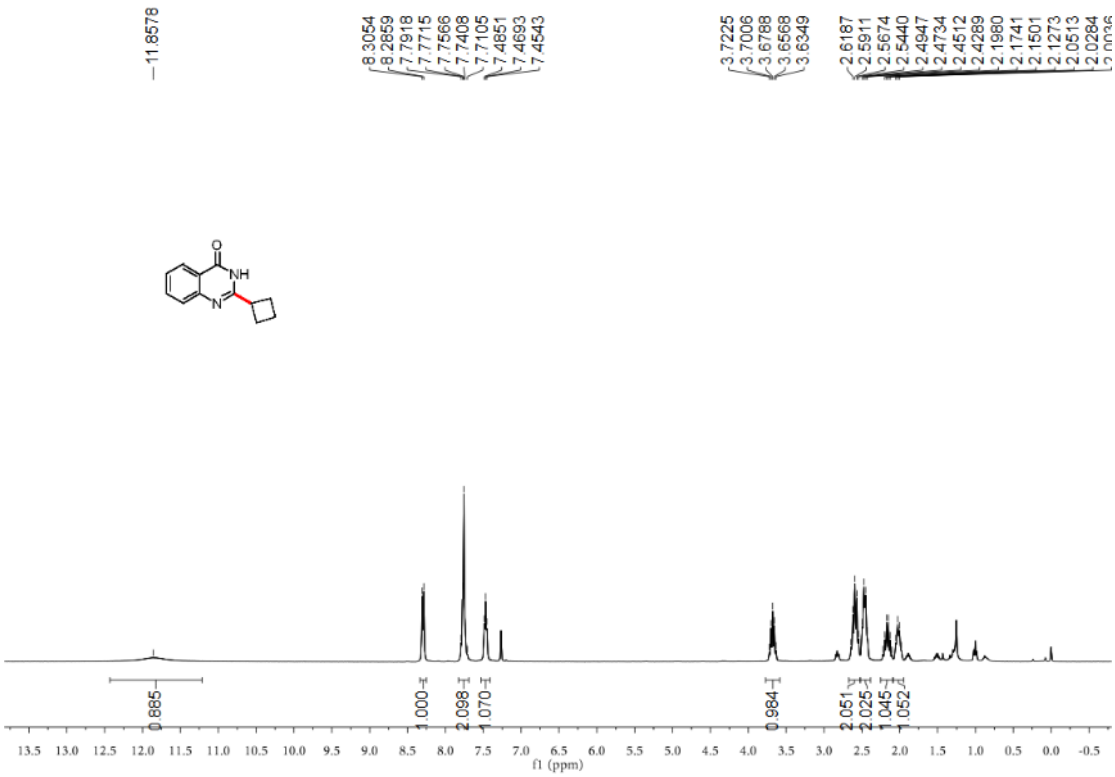
^{1}H NMR spectrum of compound **14**



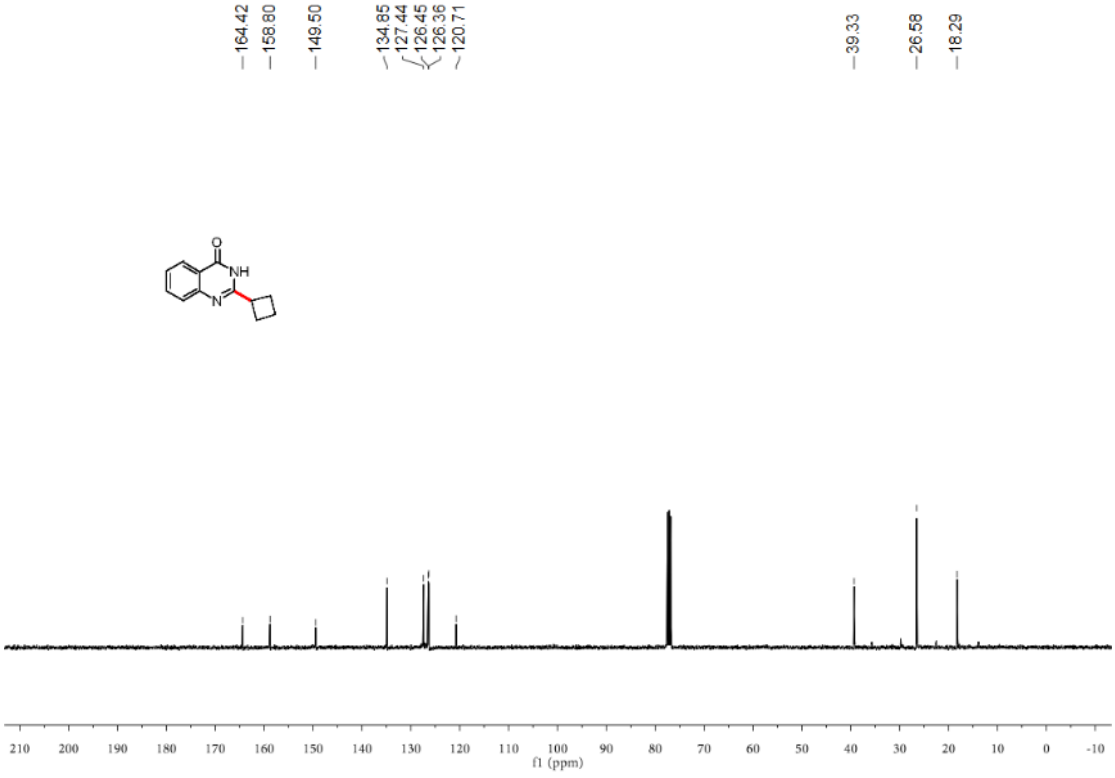
^{13}C NMR spectrum of compound **14**



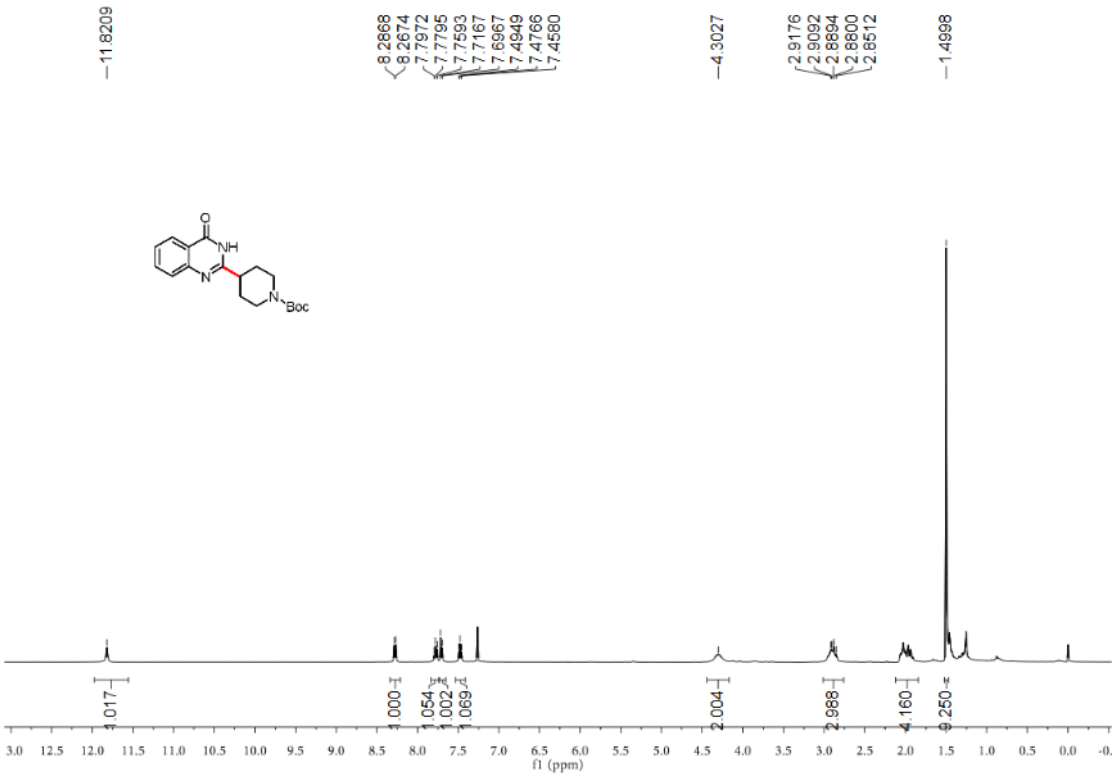
^{1}H NMR spectrum of compound **15**



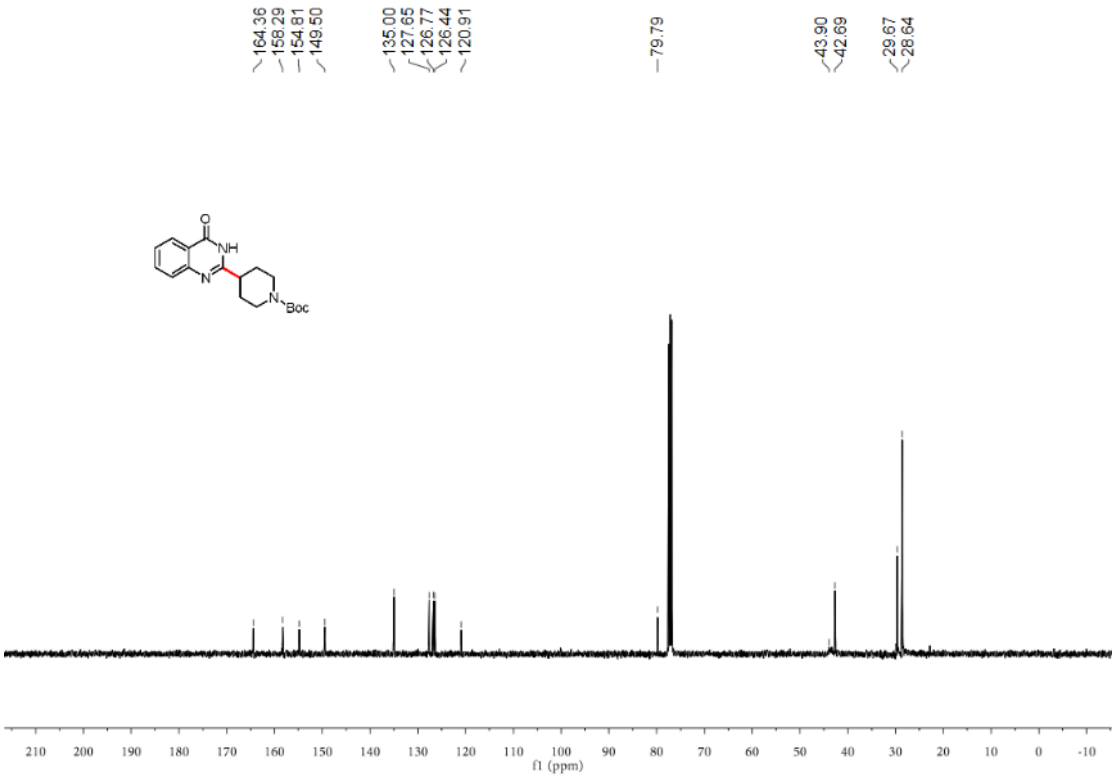
^{13}C NMR spectrum of compound **15**



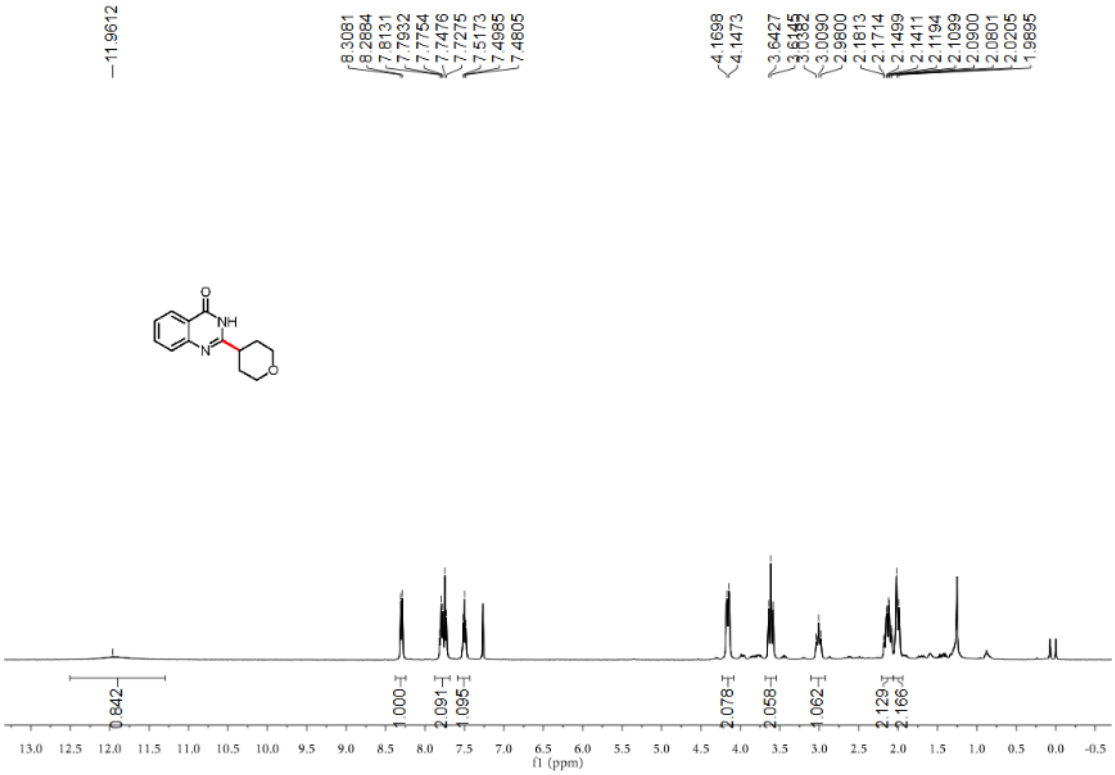
^{1}H NMR spectrum of compound **16**



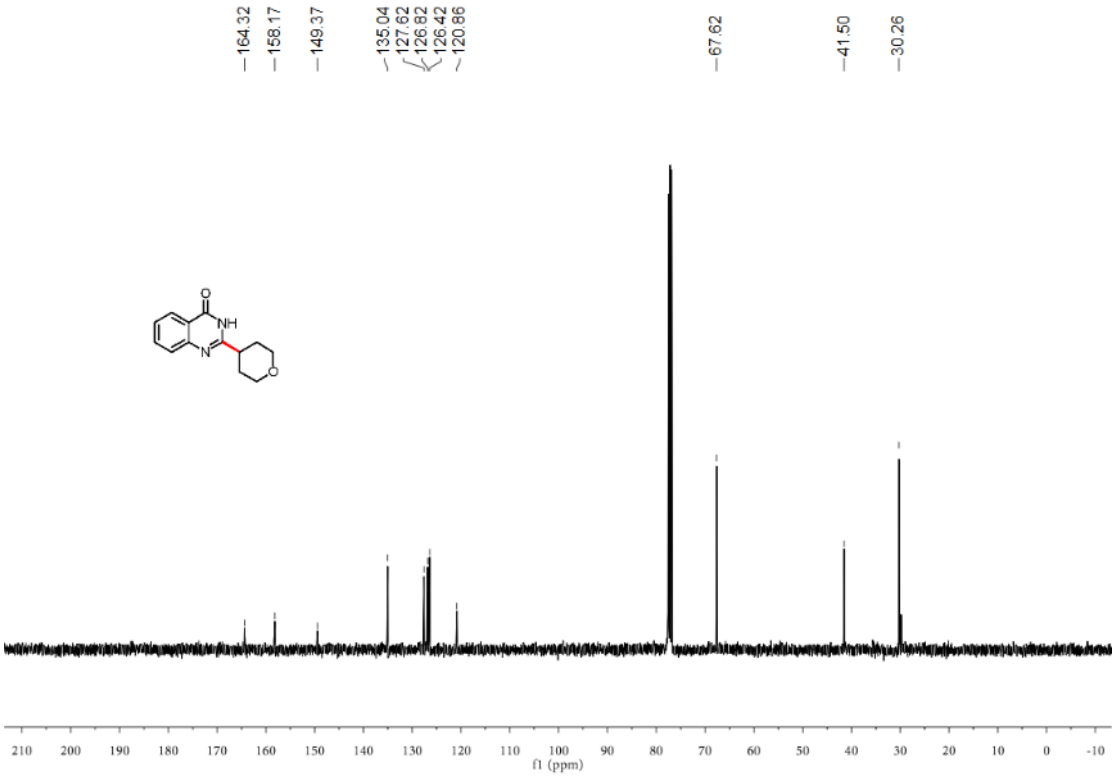
^{13}C NMR spectrum of compound **16**



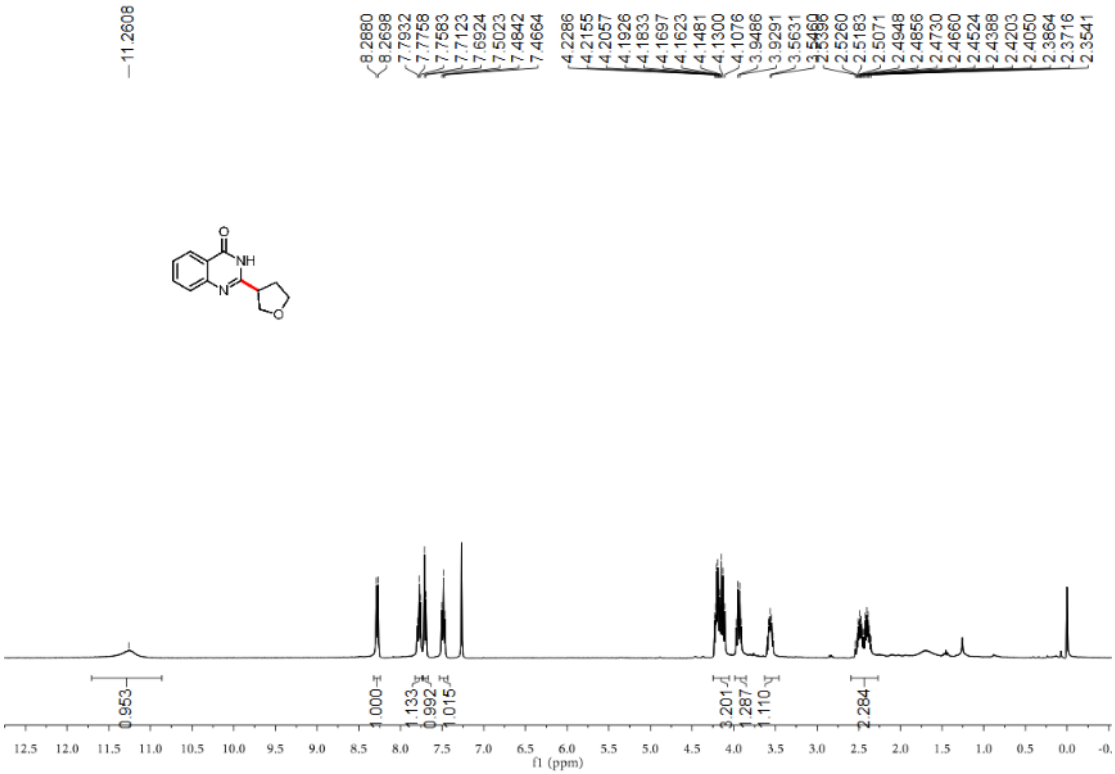
^{1}H NMR spectrum of compound **17**



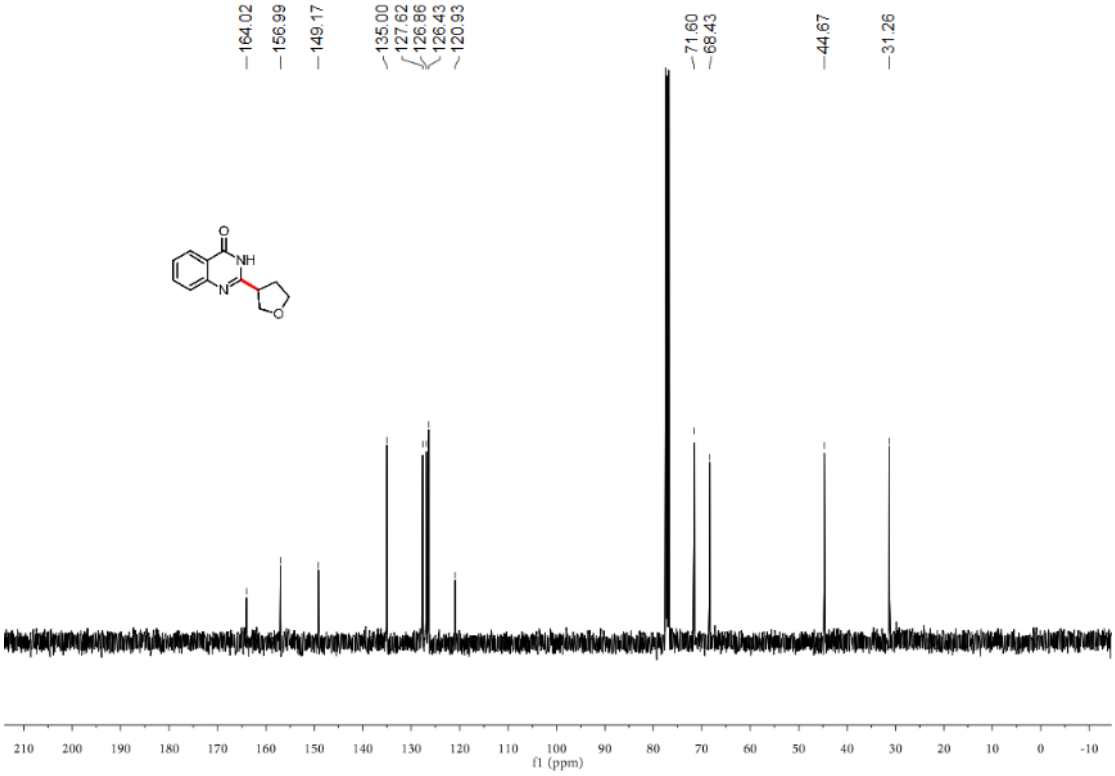
^{13}C NMR spectrum of compound **17**



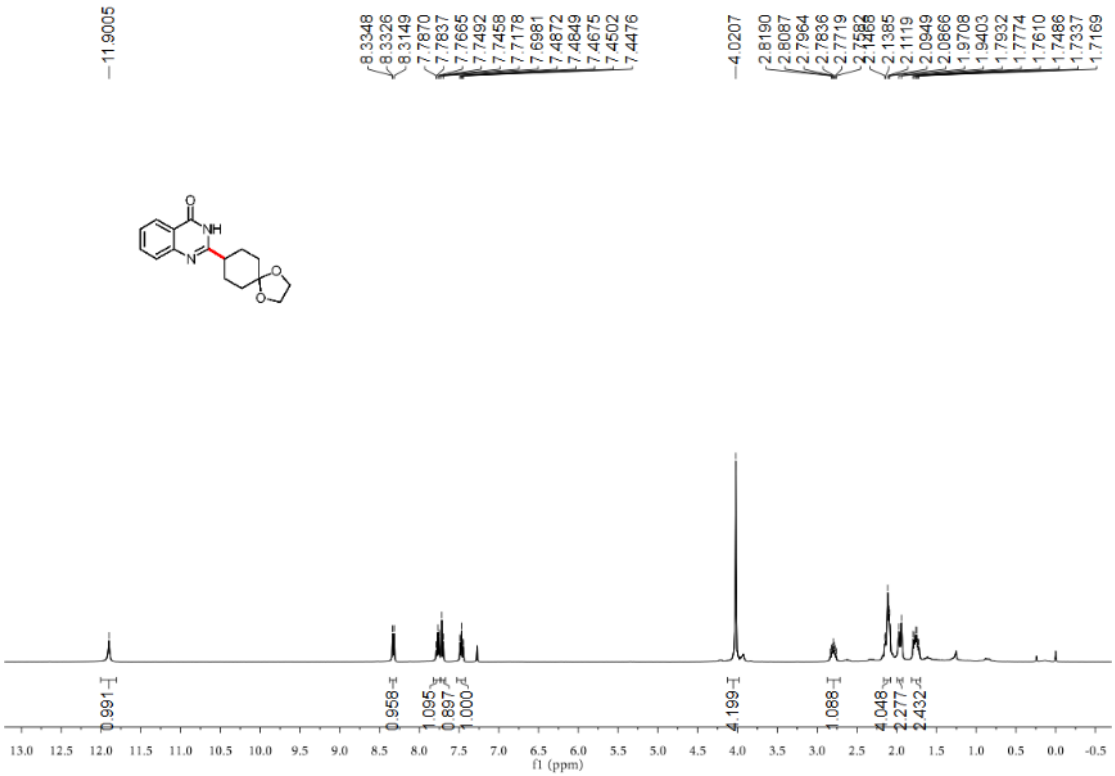
^{1}H NMR spectrum of compound **18**



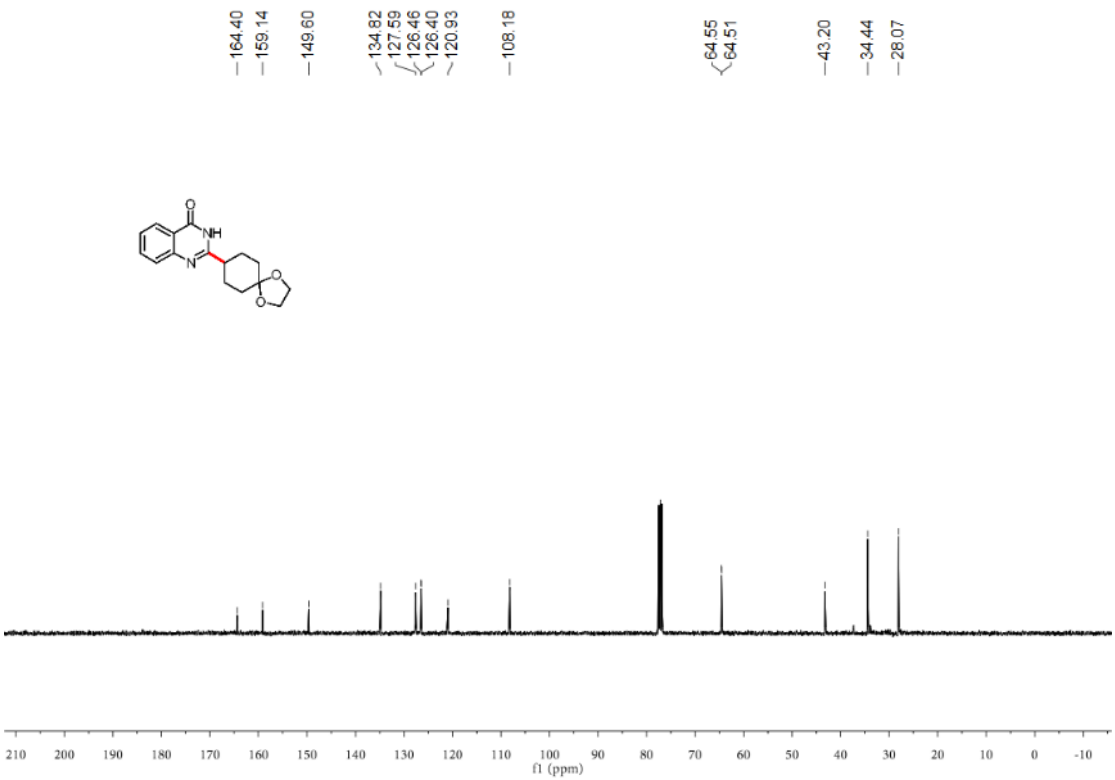
^{13}C NMR spectrum of compound **18**



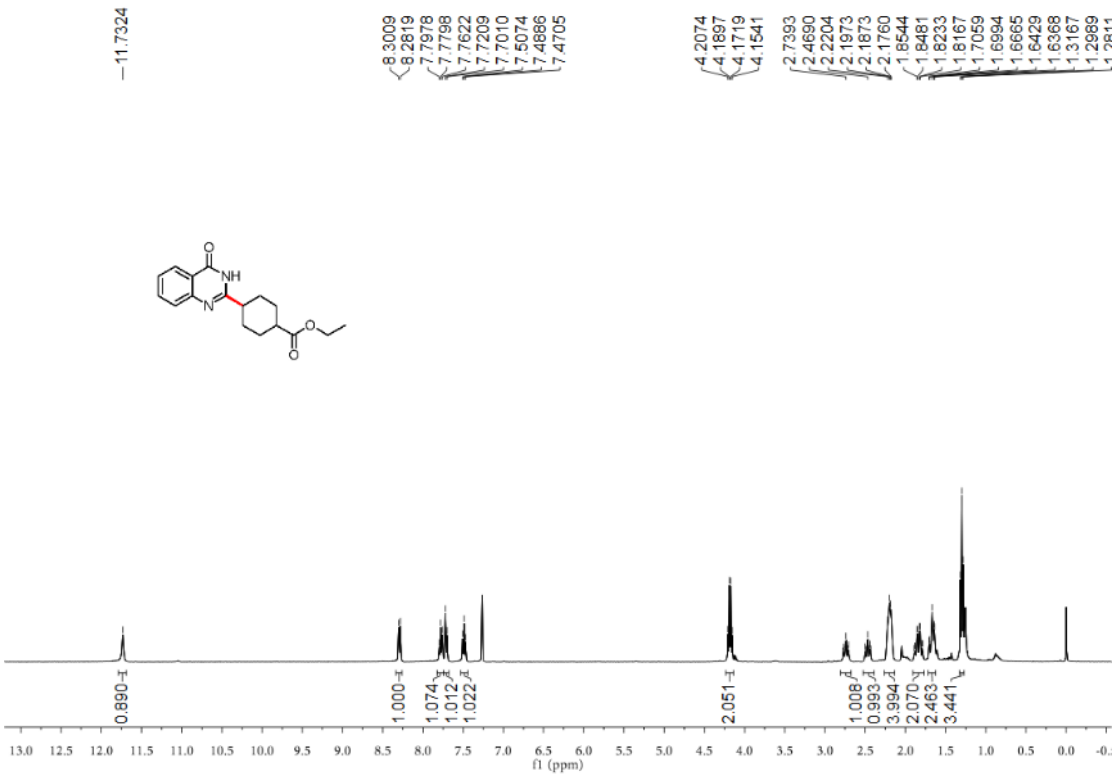
^{1}H NMR spectrum of compound **19**



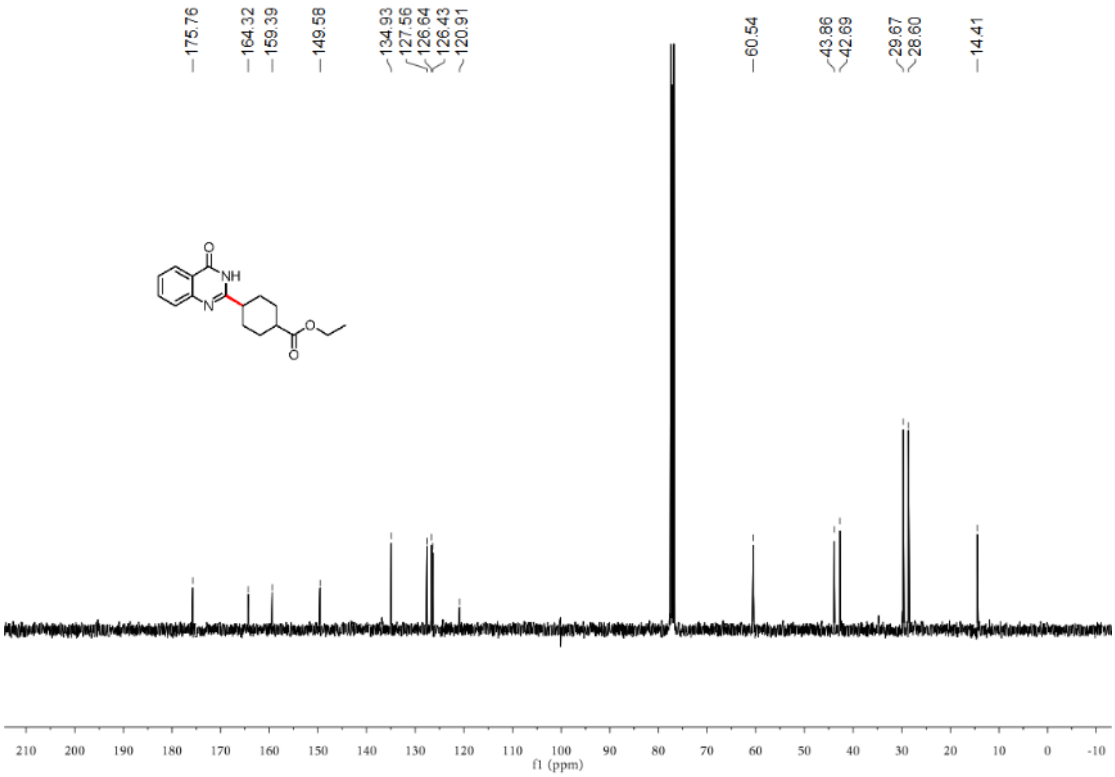
^{13}C NMR spectrum of compound **19**



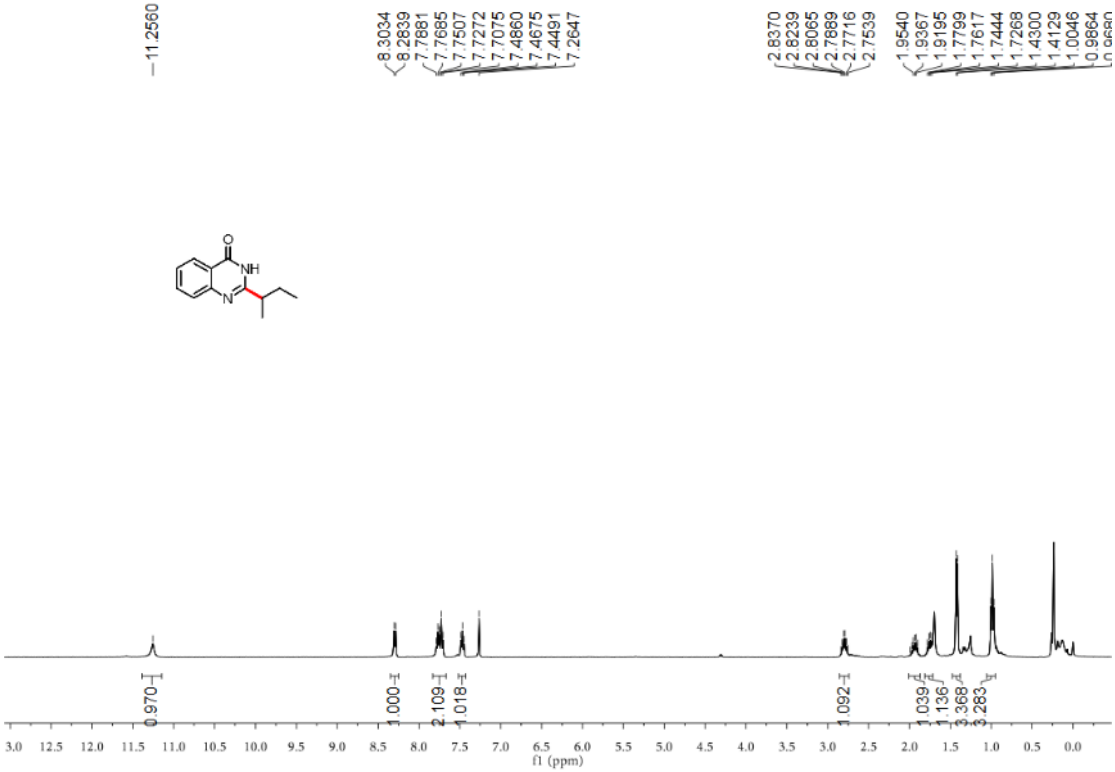
^{1}H NMR spectrum of compound **20**



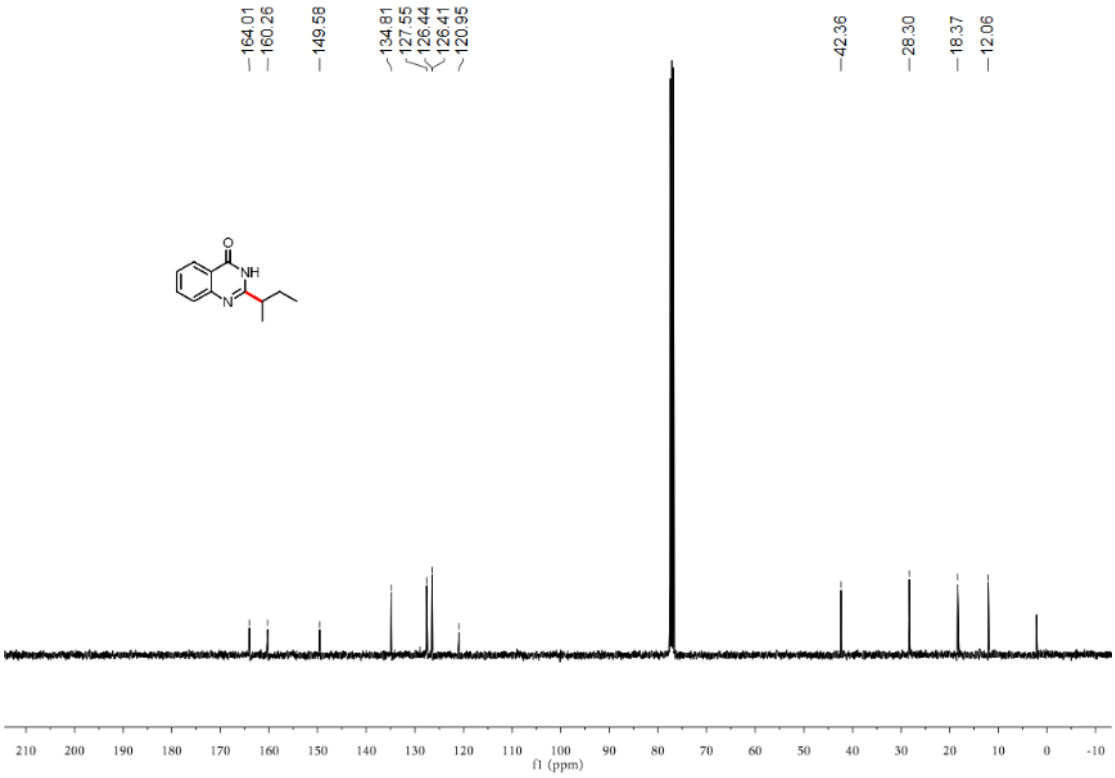
^{13}C NMR spectrum of compound **20**



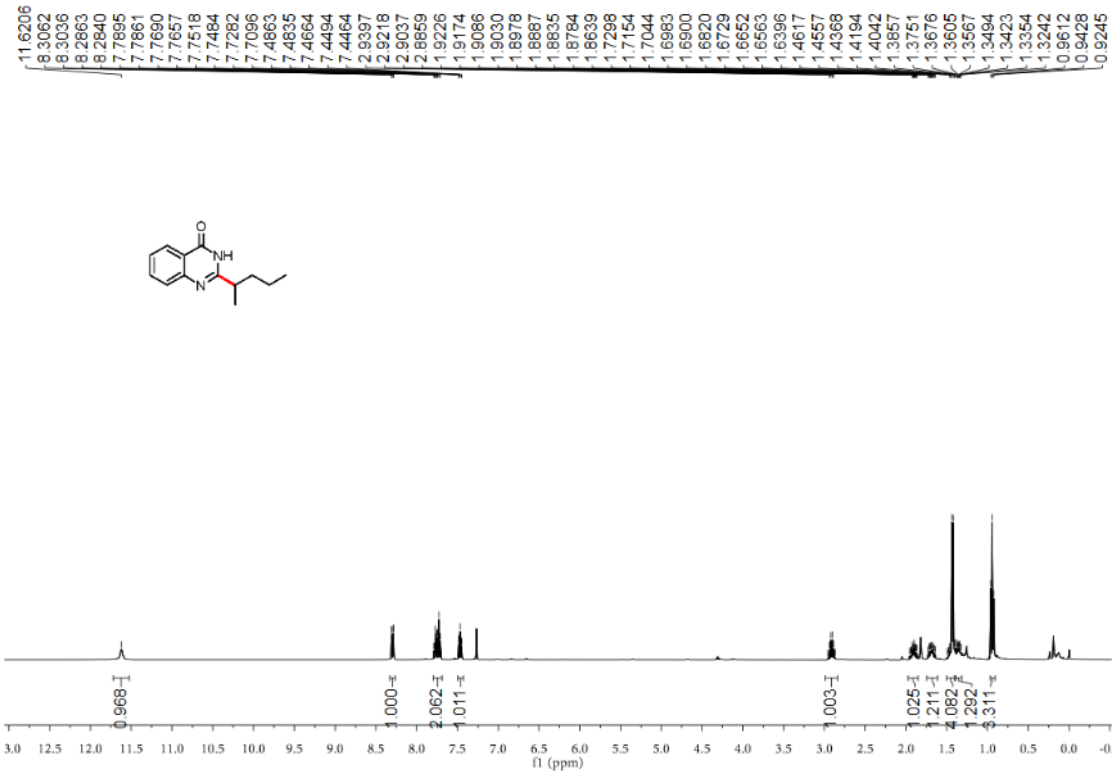
^{1}H NMR spectrum of compound **21**



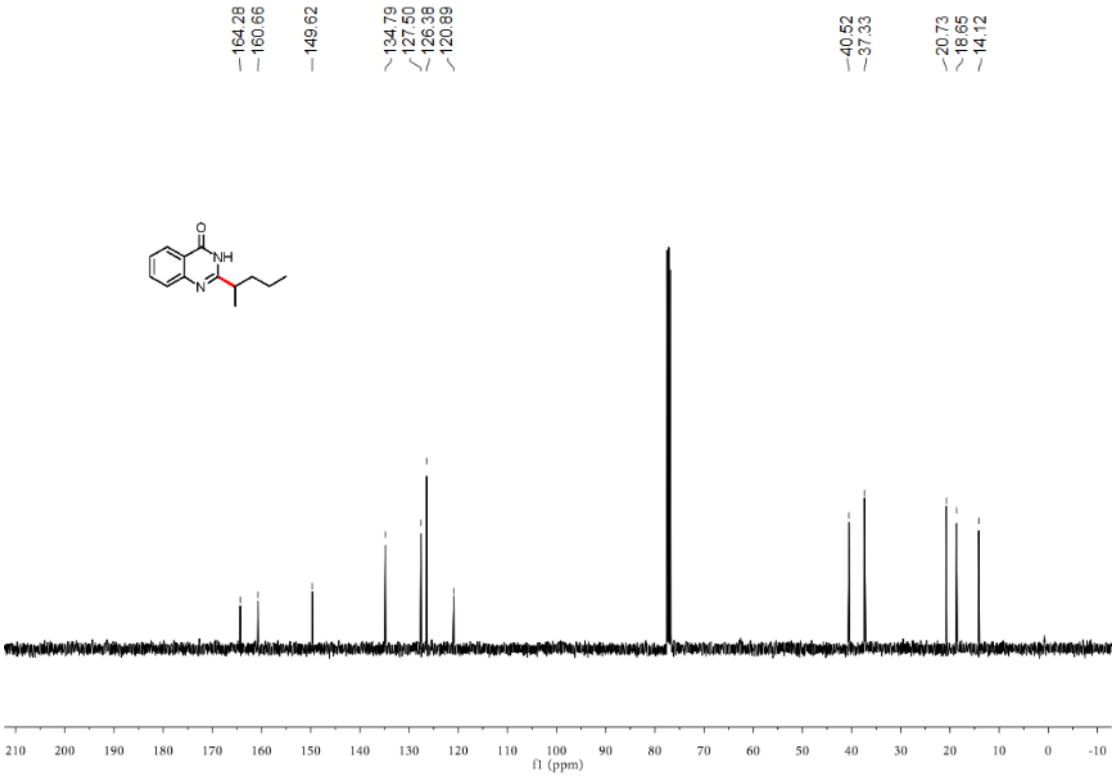
^{13}C NMR spectrum of compound **21**



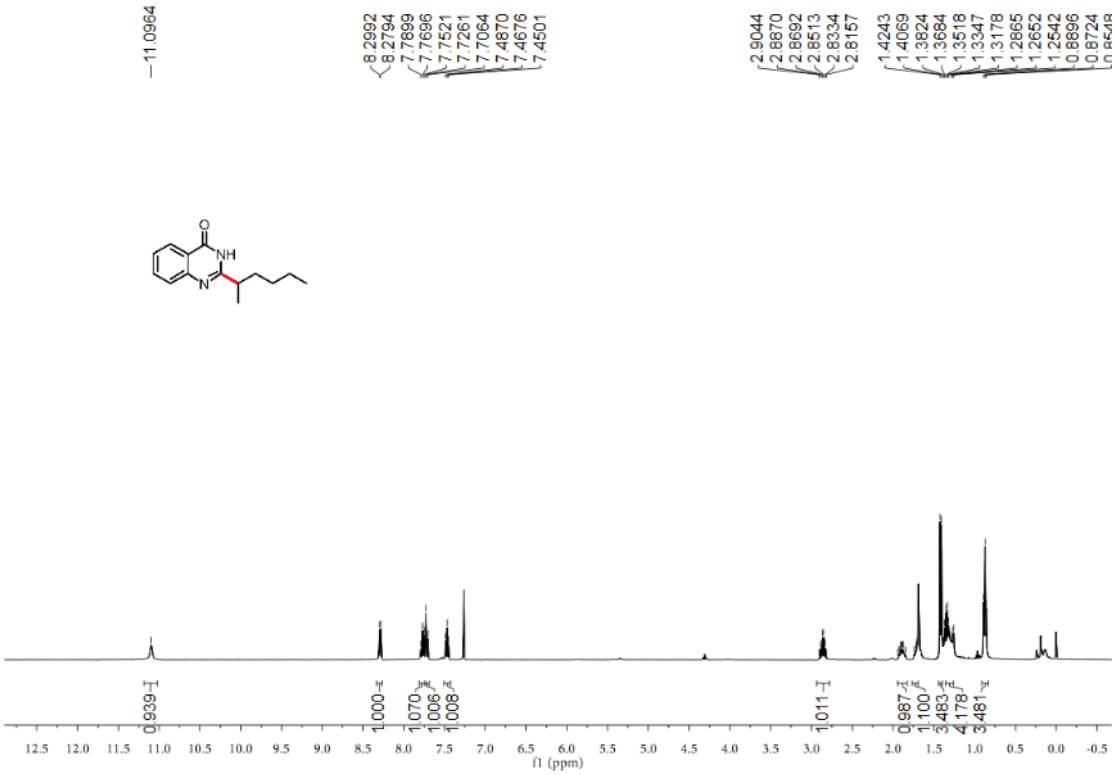
^{1}H NMR spectrum of compound **22**



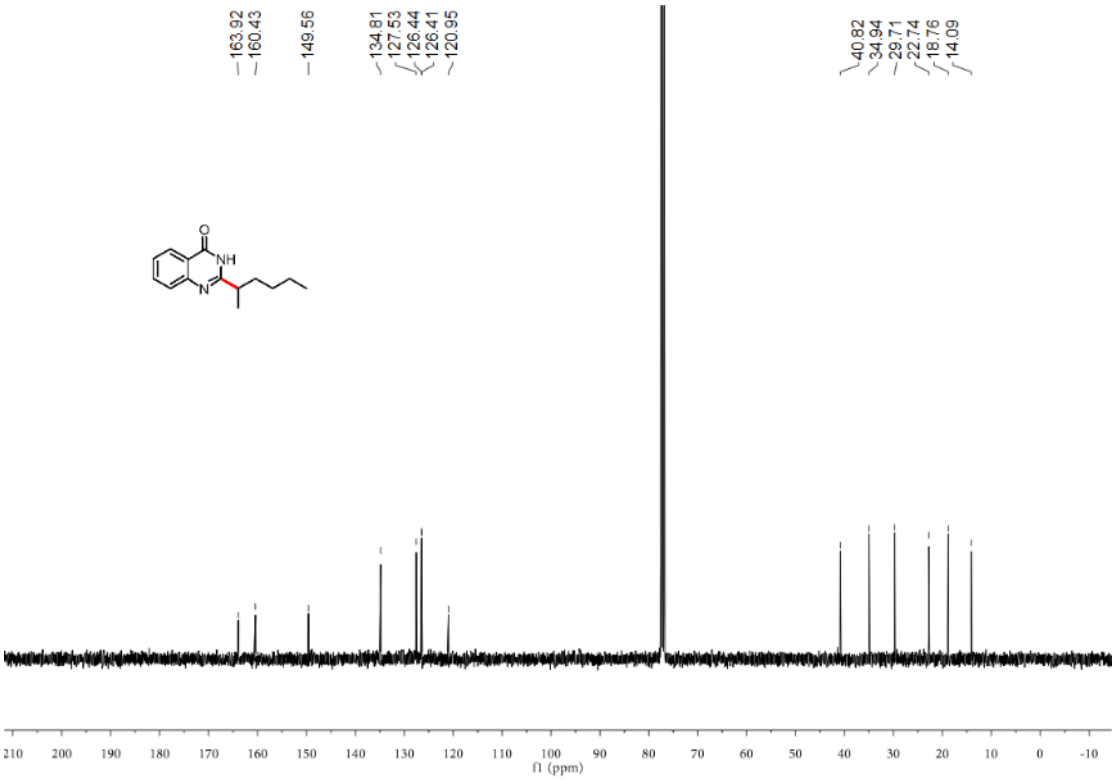
^{13}C NMR spectrum of compound **22**



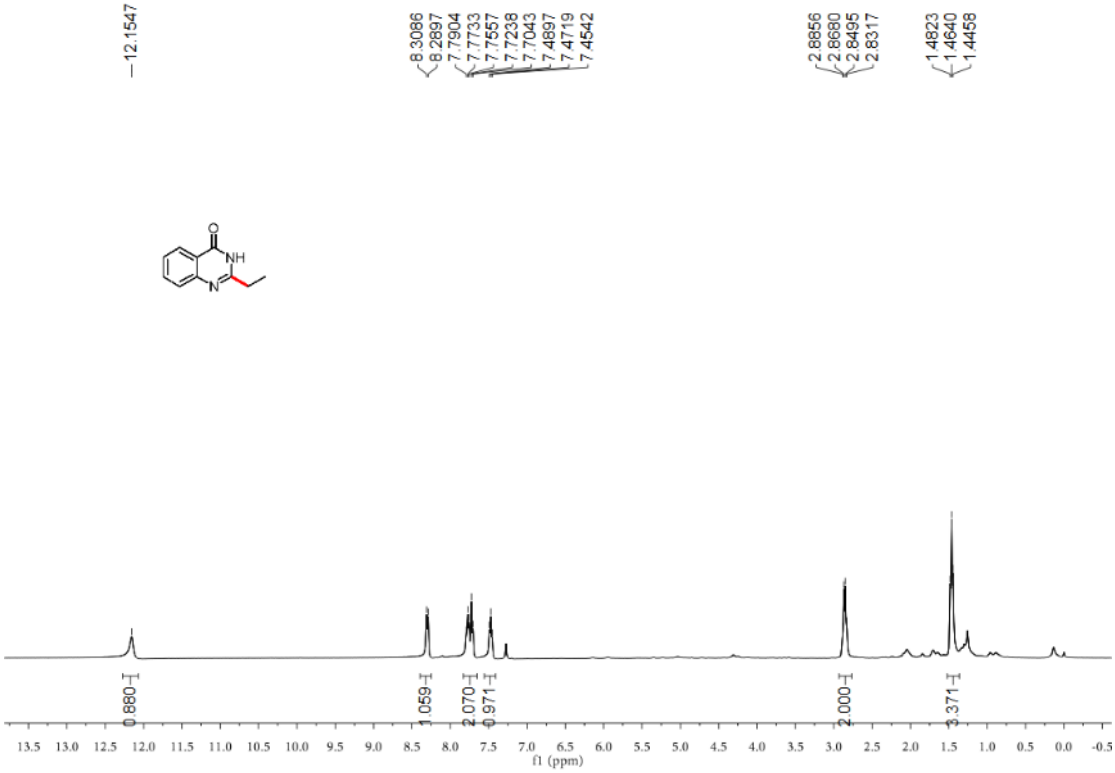
^{1}H NMR spectrum of compound **23**



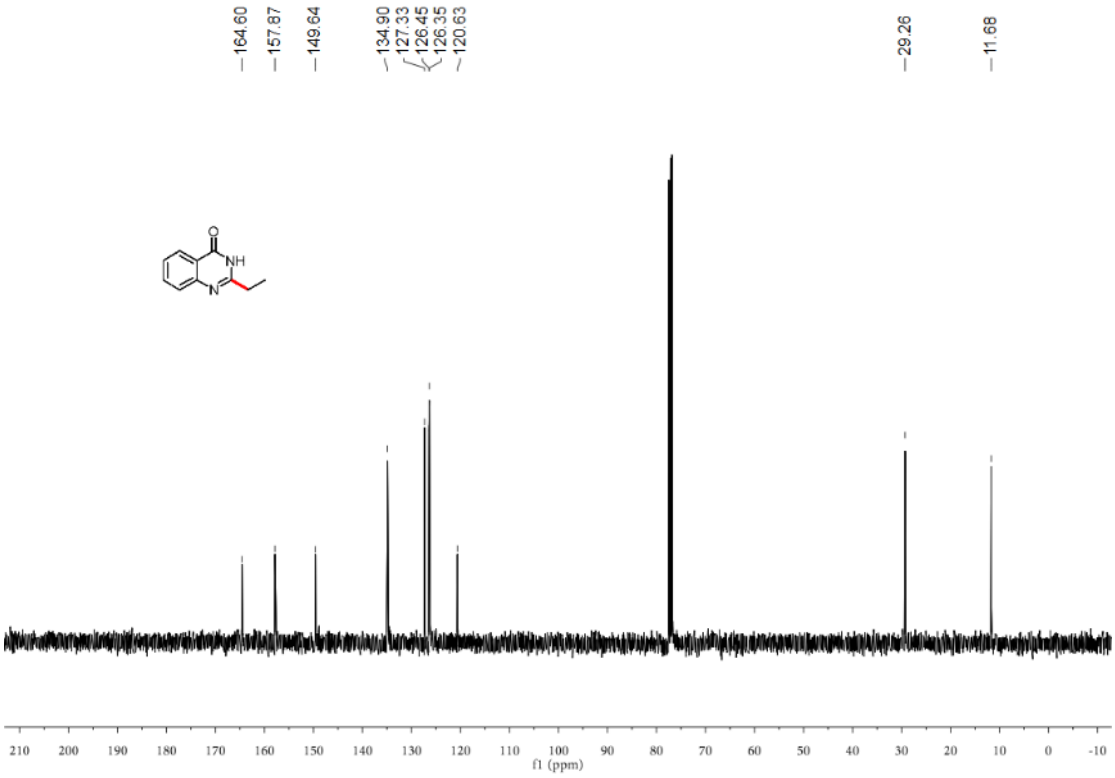
^{13}C NMR spectrum of compound **23**



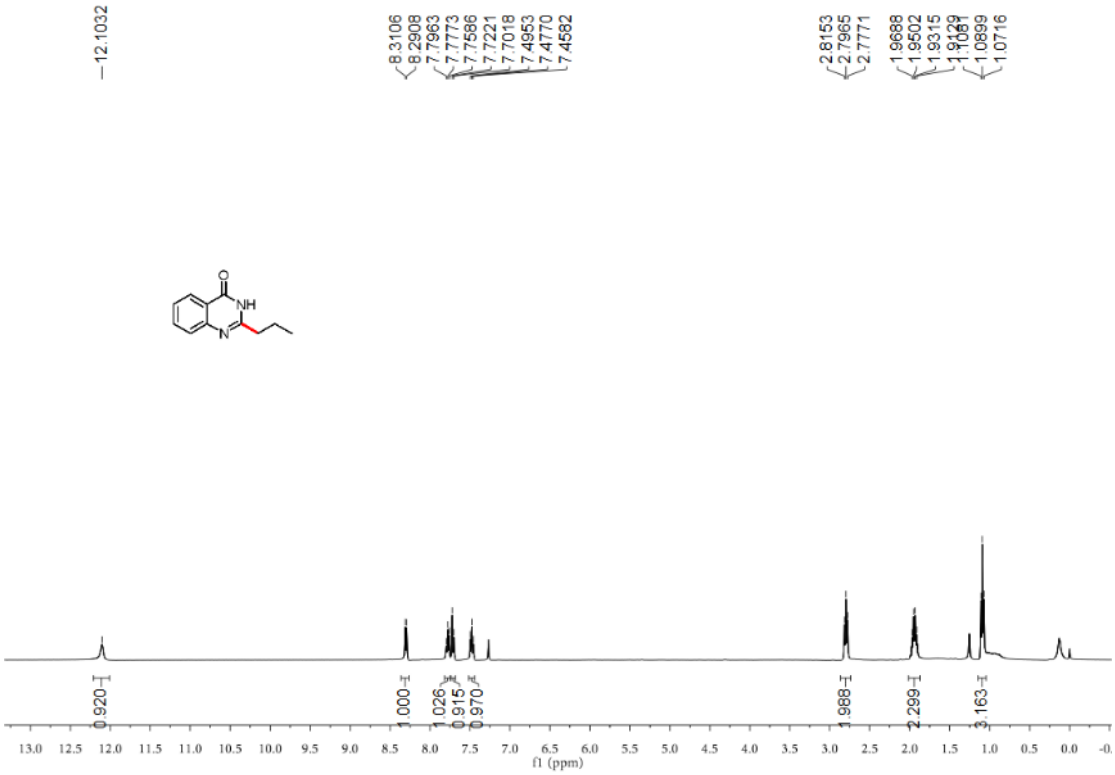
^{1}H NMR spectrum of compound **24**



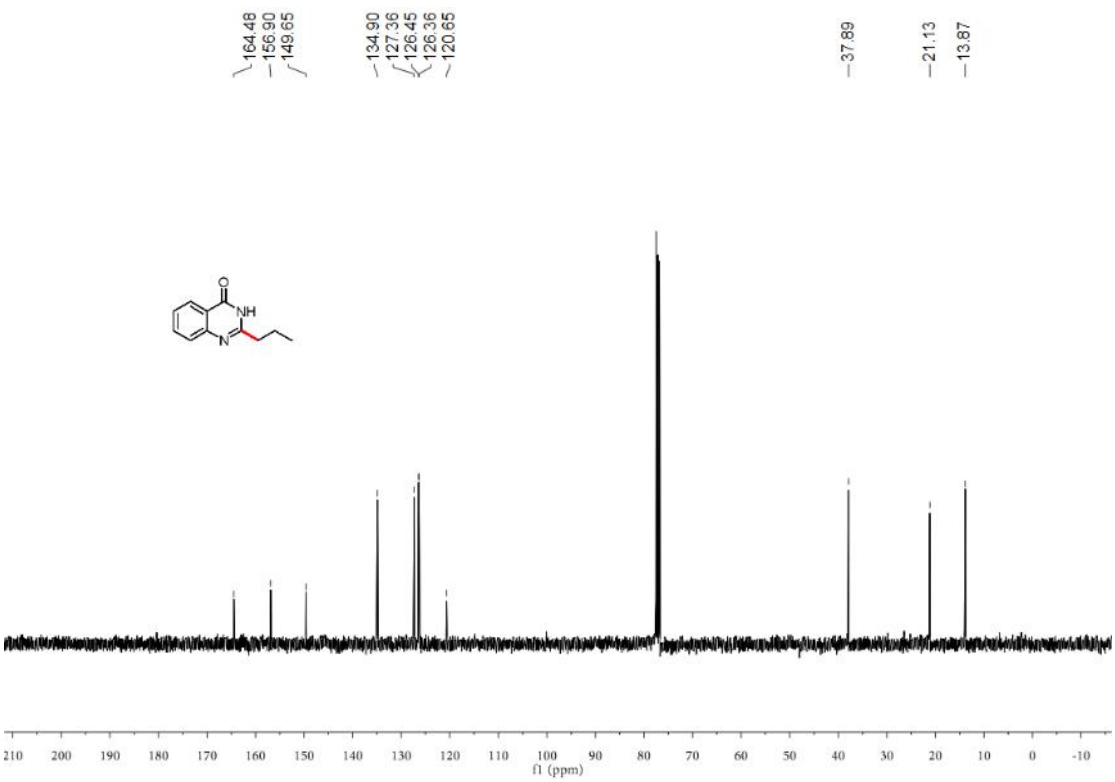
^{13}C NMR spectrum of compound **24**



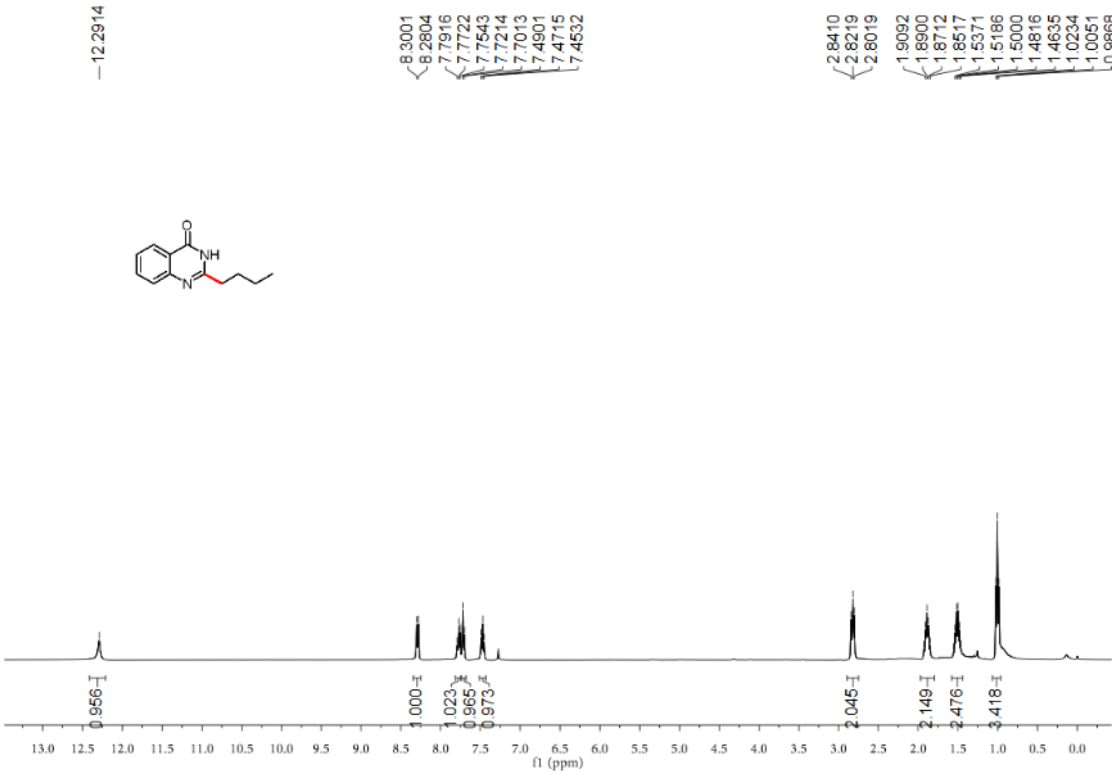
^{1}H NMR spectrum of compound **25**



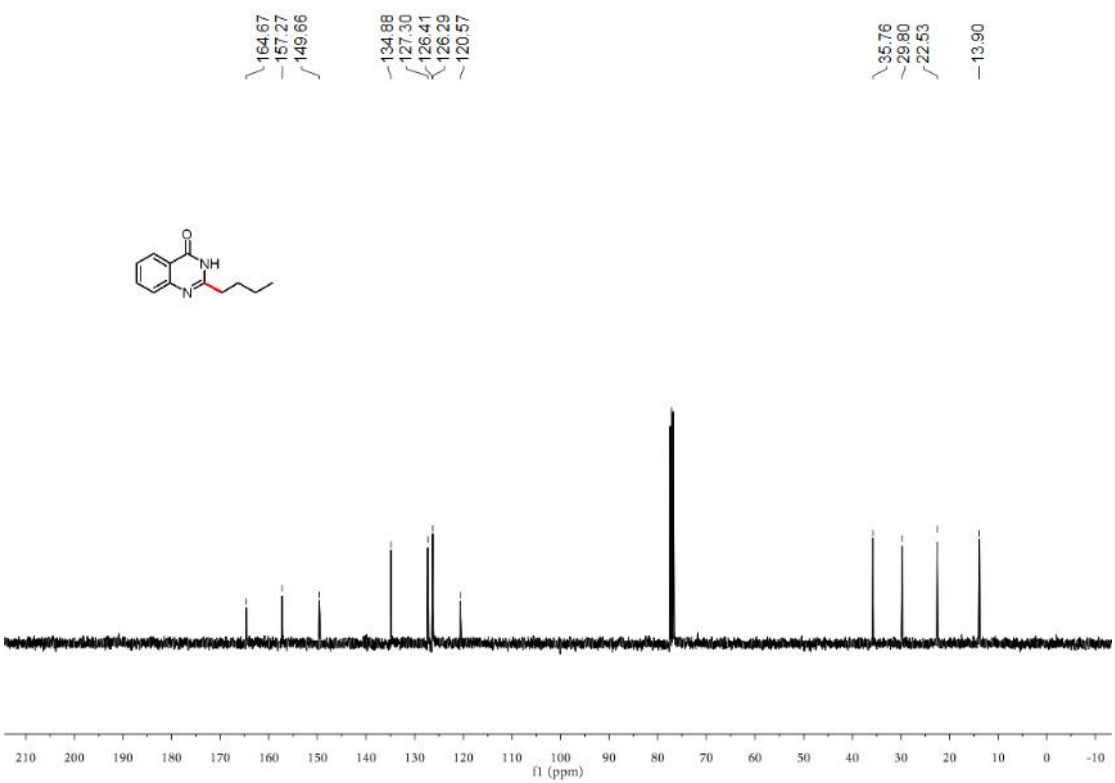
^{13}C NMR spectrum of compound **25**



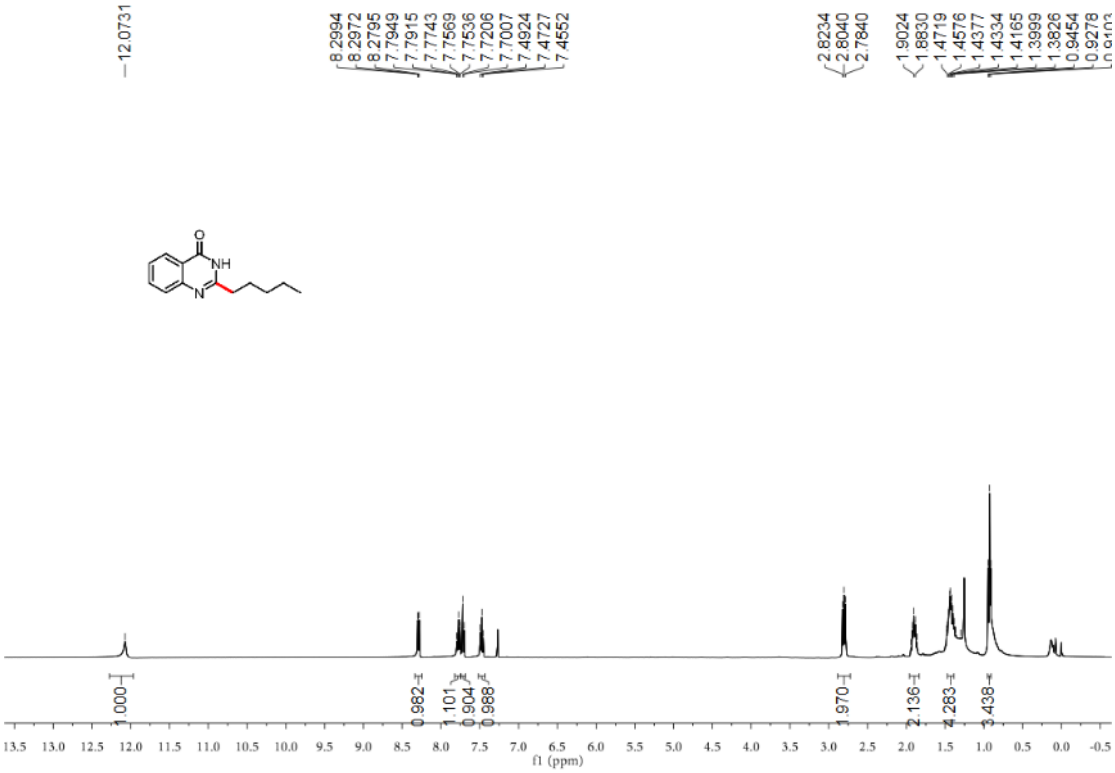
^{1}H NMR spectrum of compound **26**



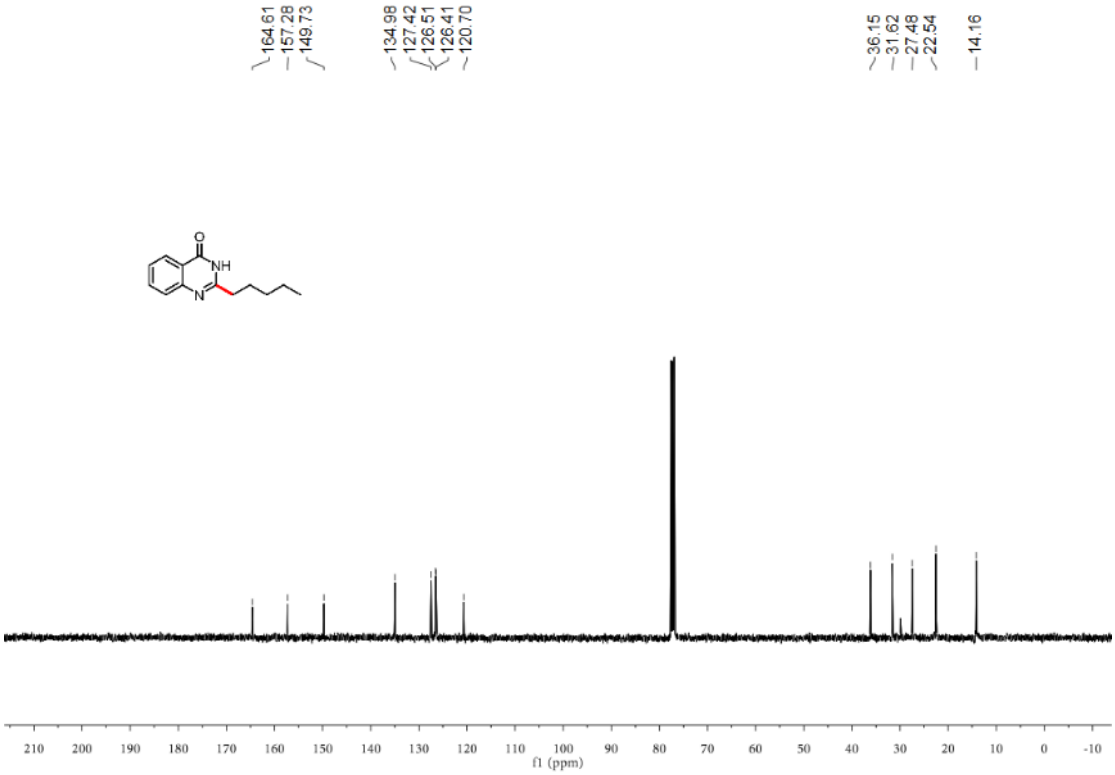
^{13}C NMR spectrum of compound **26**



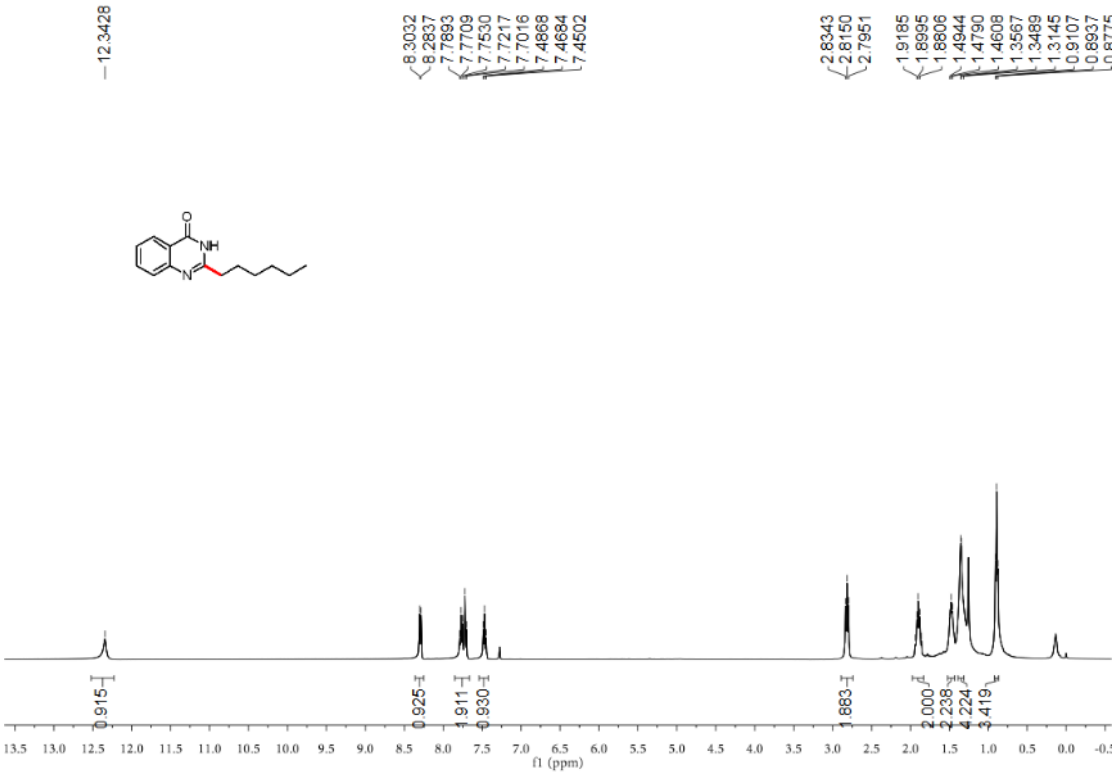
^{1}H NMR spectrum of compound **27**



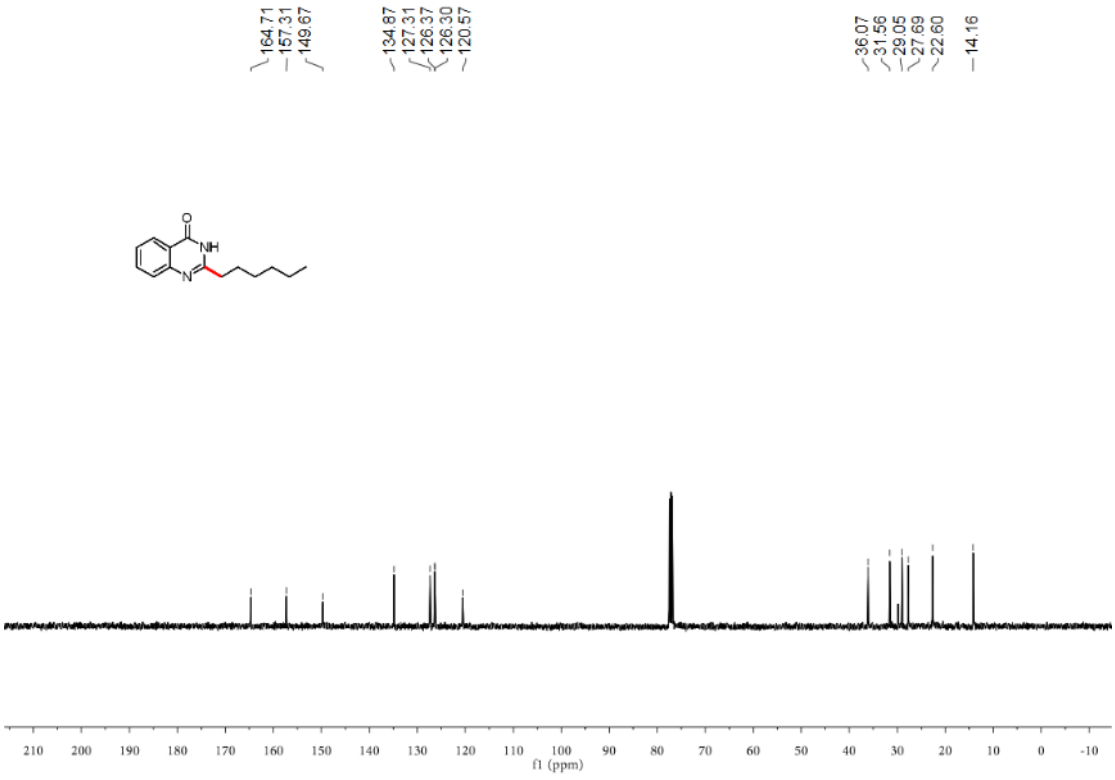
^{13}C NMR spectrum of compound **27**



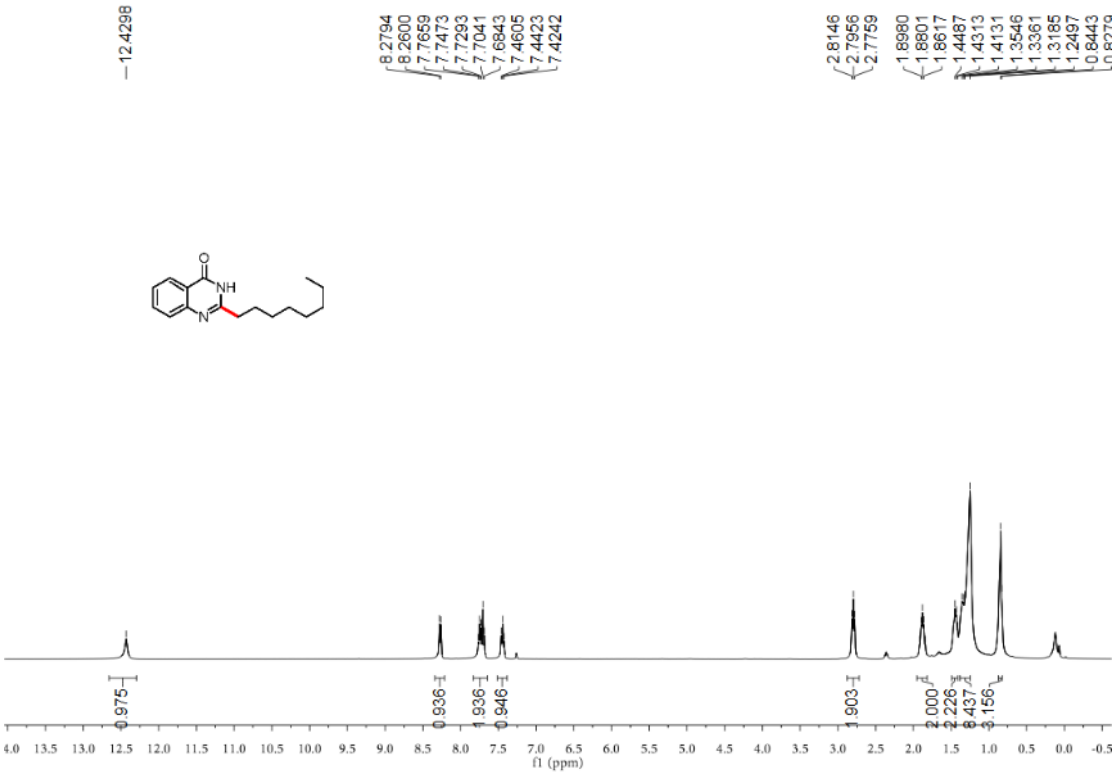
^{1}H NMR spectrum of compound **28**



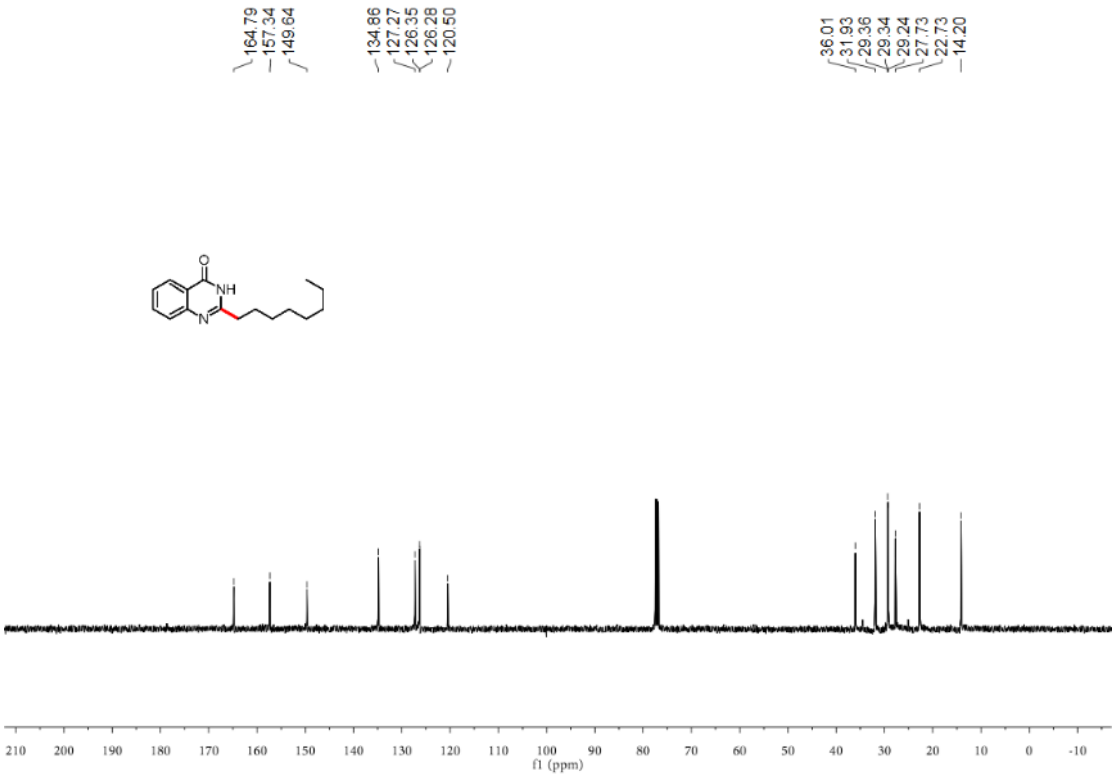
^{13}C NMR spectrum of compound **28**



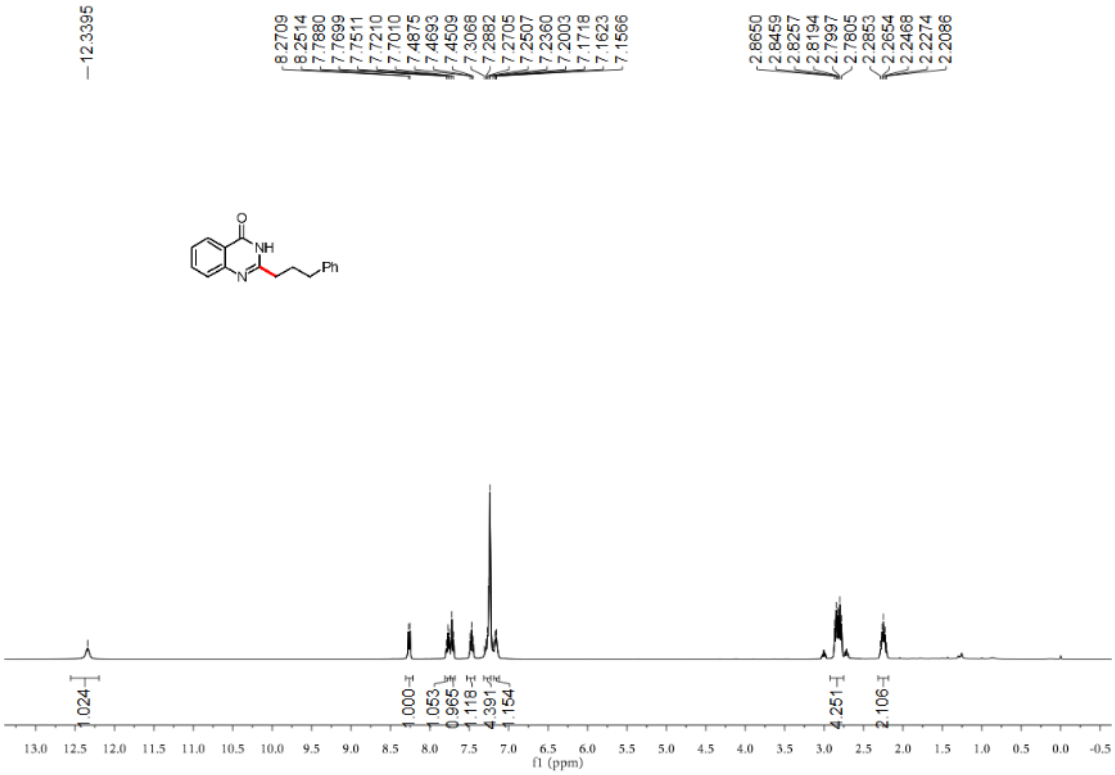
^{1}H NMR spectrum of compound **29**



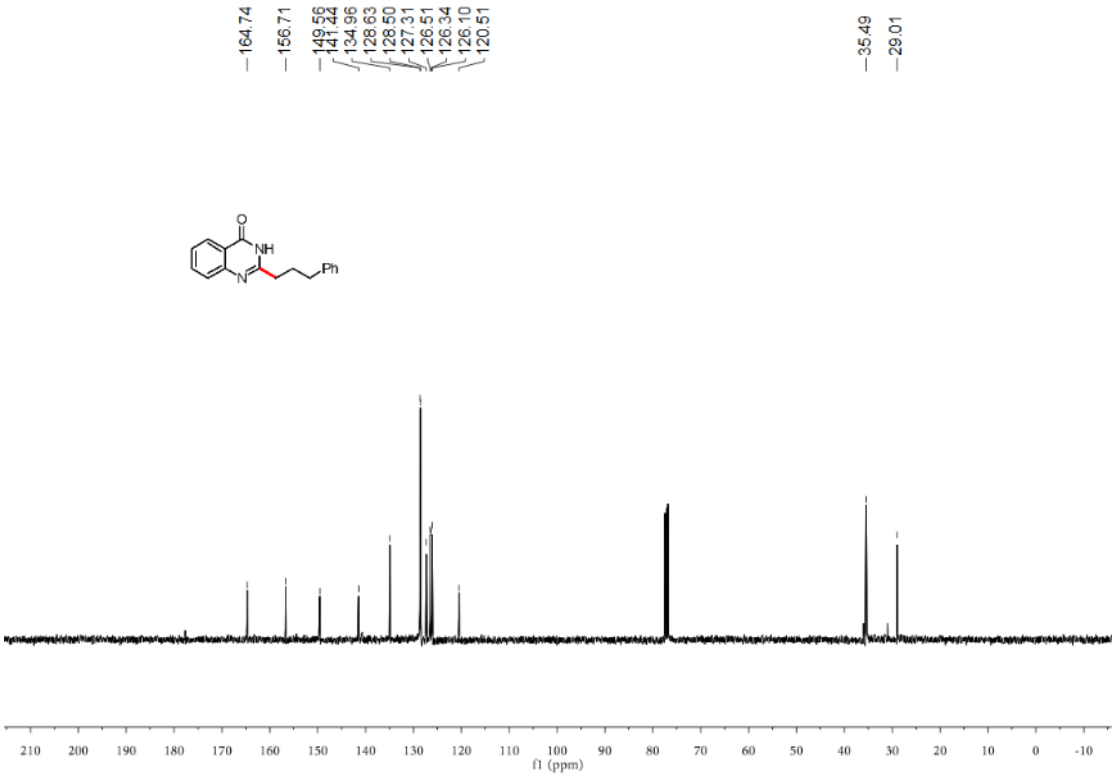
^{13}C NMR spectrum of compound **29**



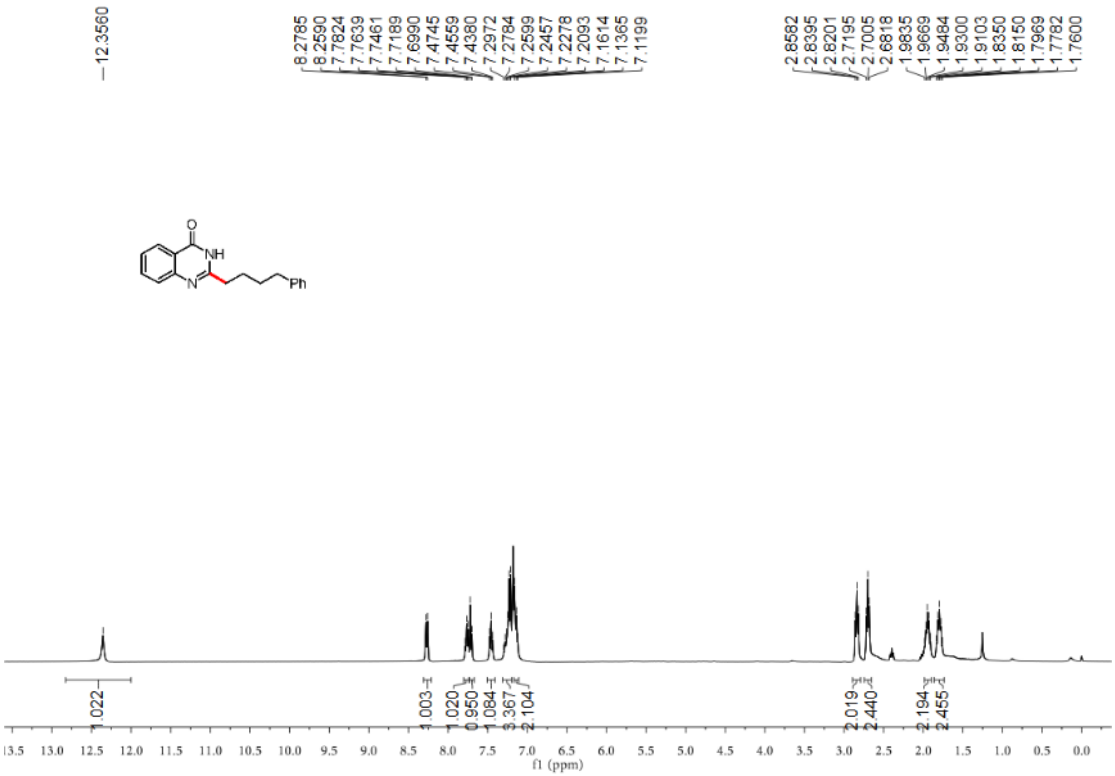
^{1}H NMR spectrum of compound **30**



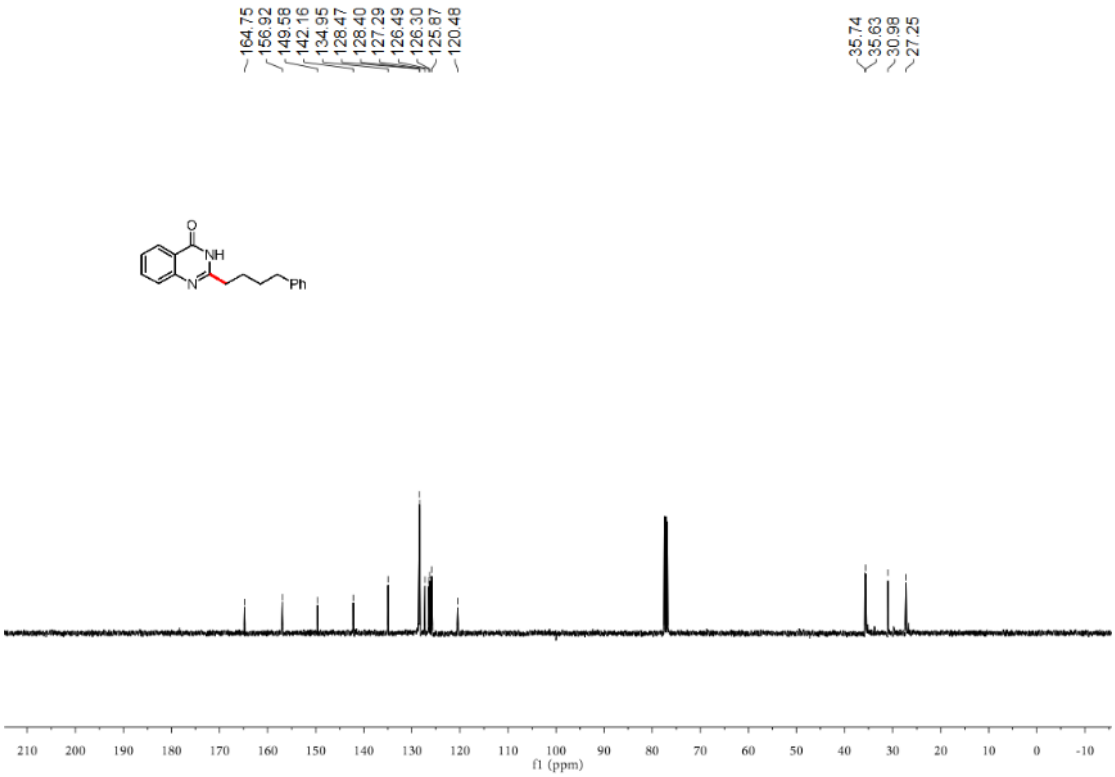
^{13}C NMR spectrum of compound **30**



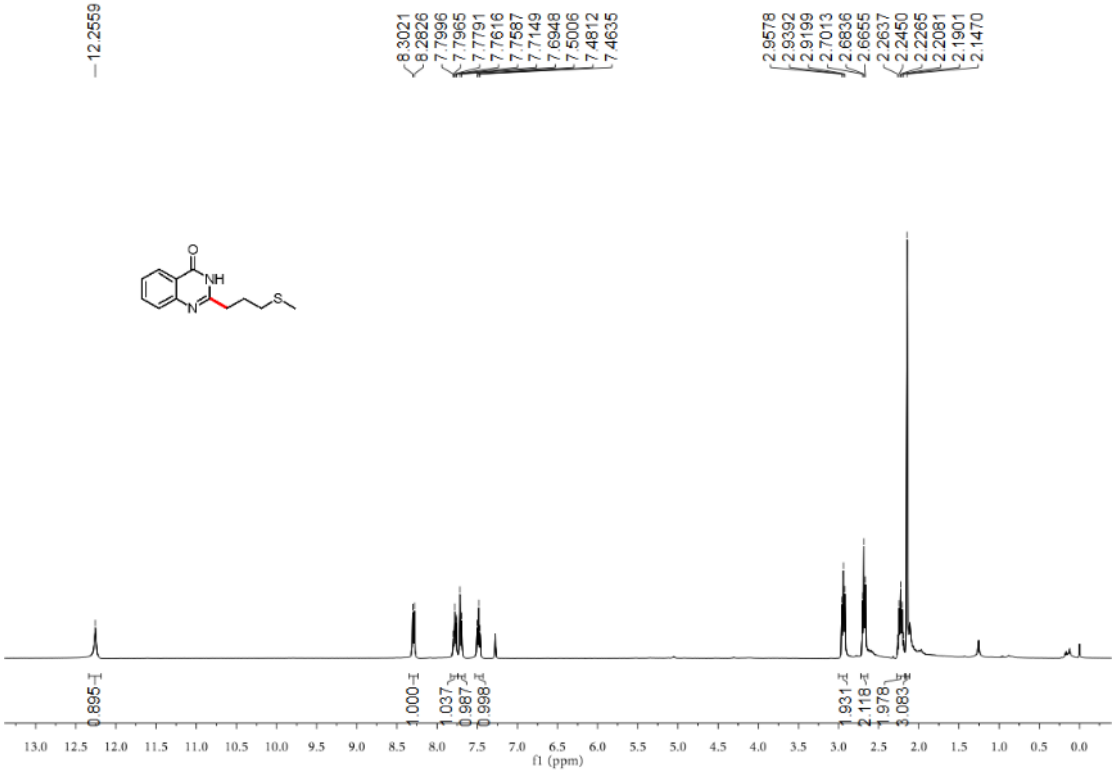
^{1}H NMR spectrum of compound **31**



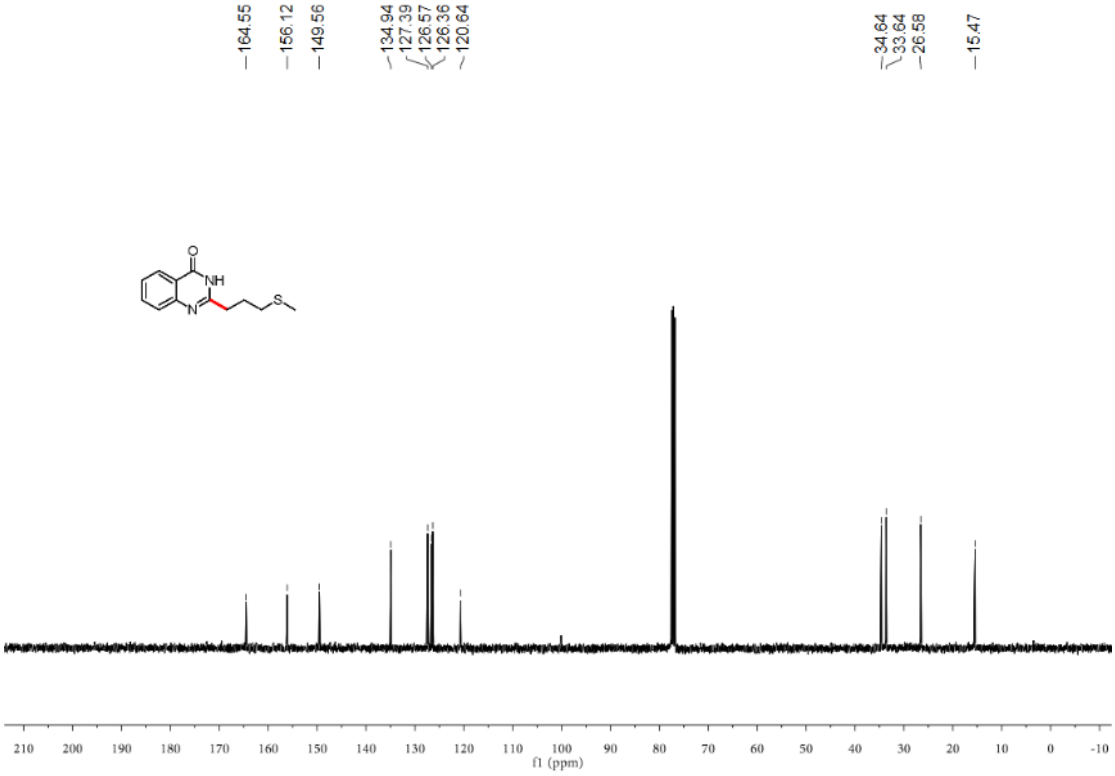
^{13}C NMR spectrum of compound **31**



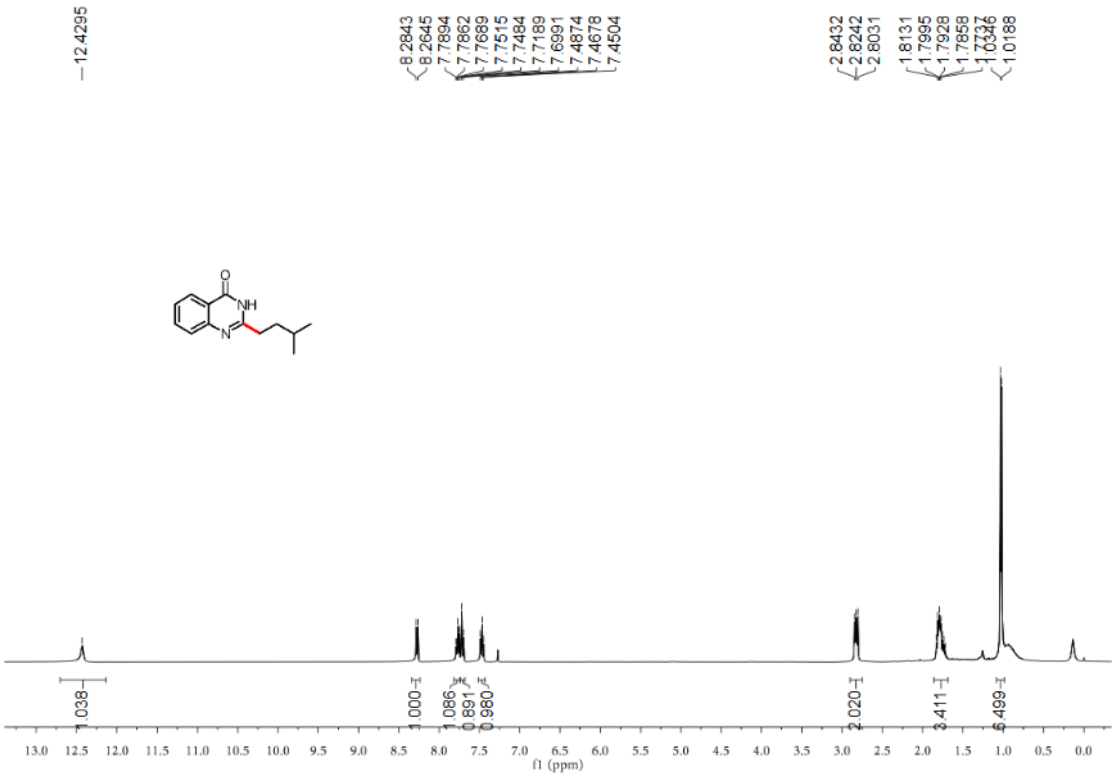
^{1}H NMR spectrum of compound **32**



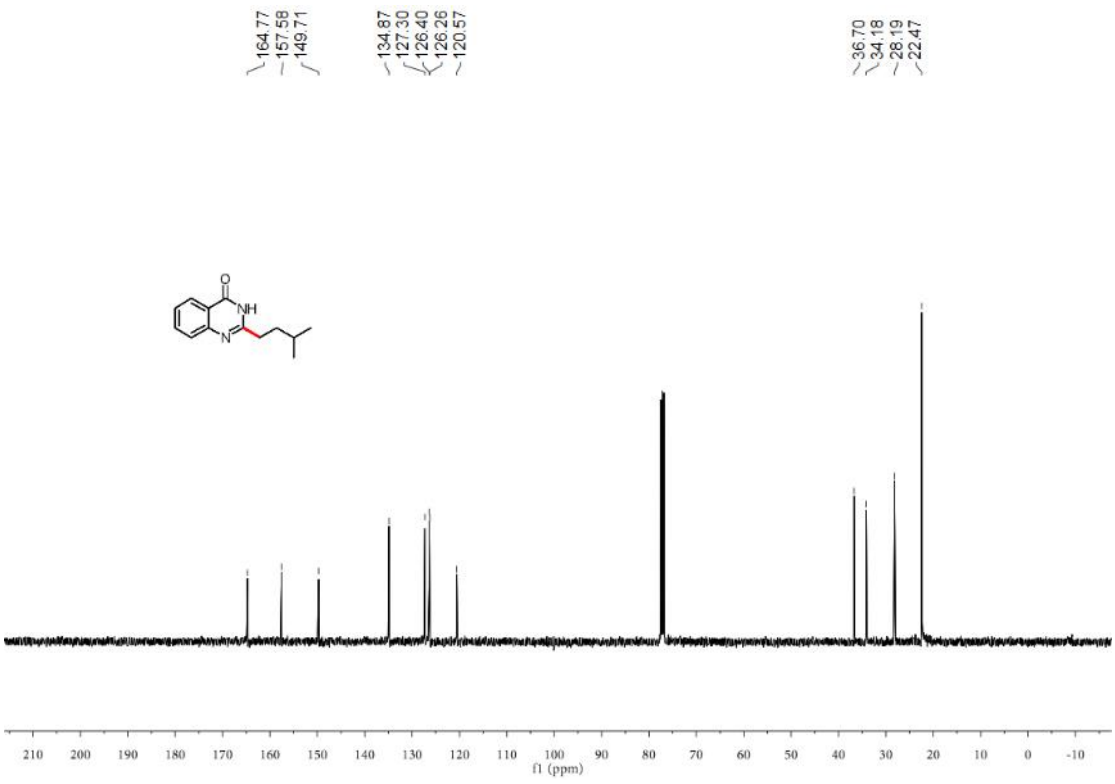
^{13}C NMR spectrum of compound **32**



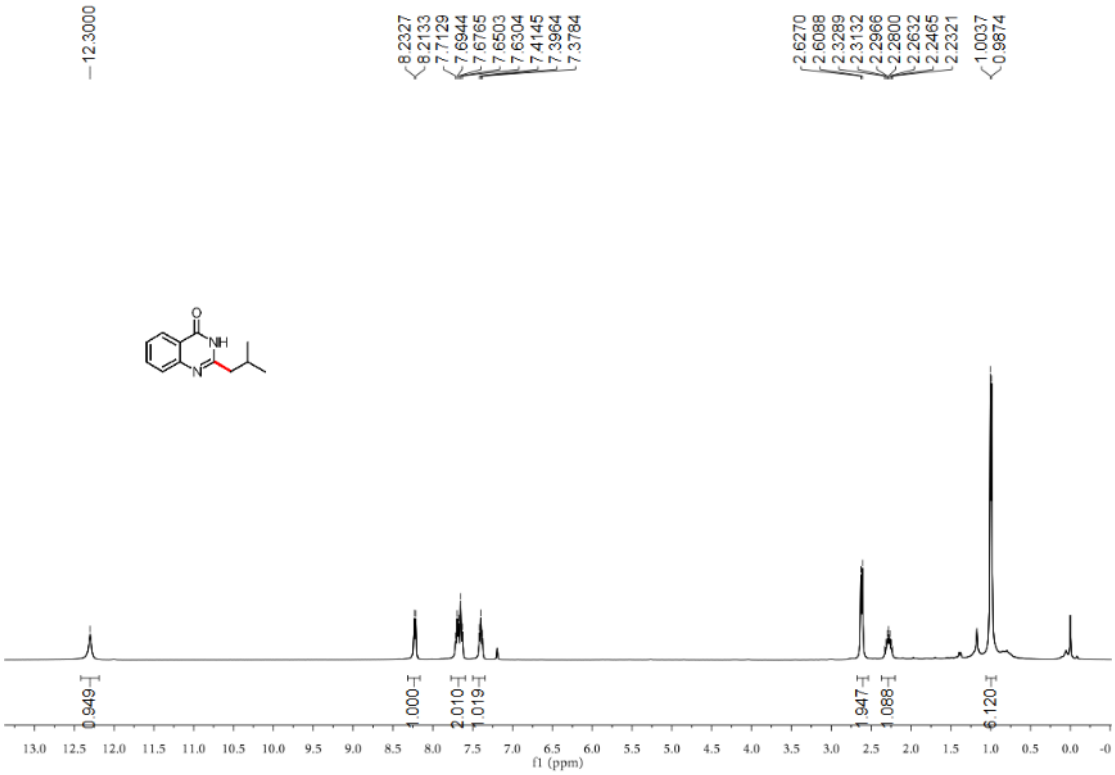
^{1}H NMR spectrum of compound **33**



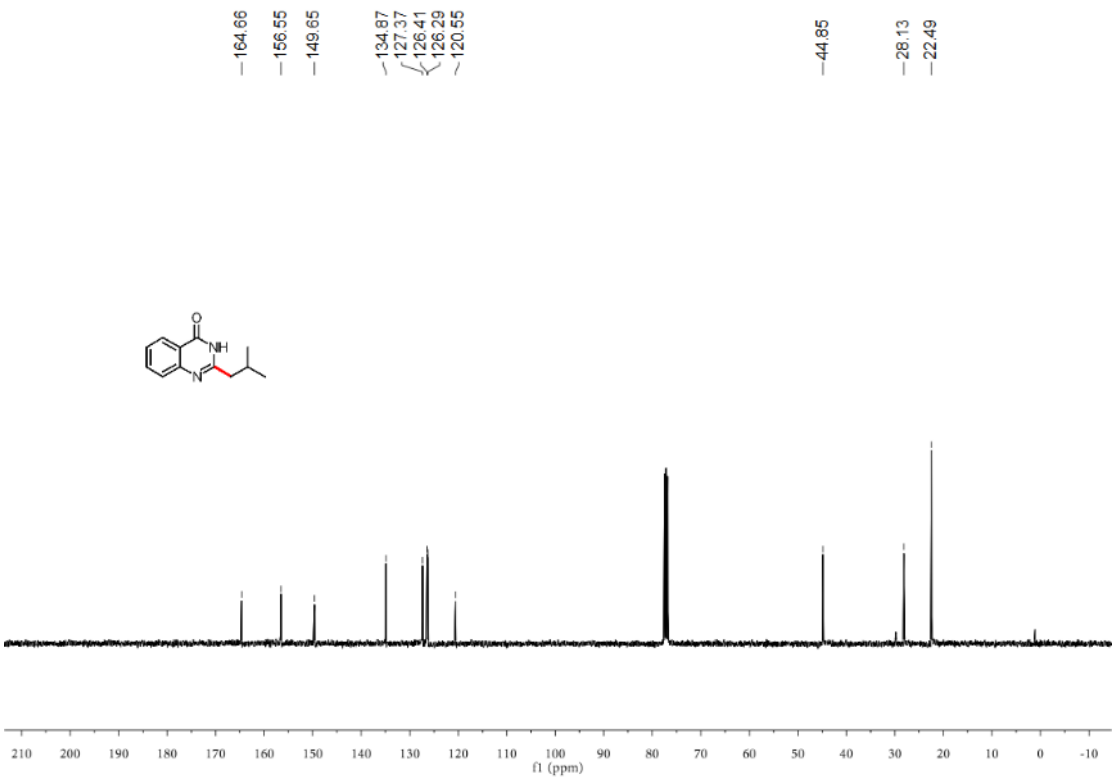
^{13}C NMR spectrum of compound **33**



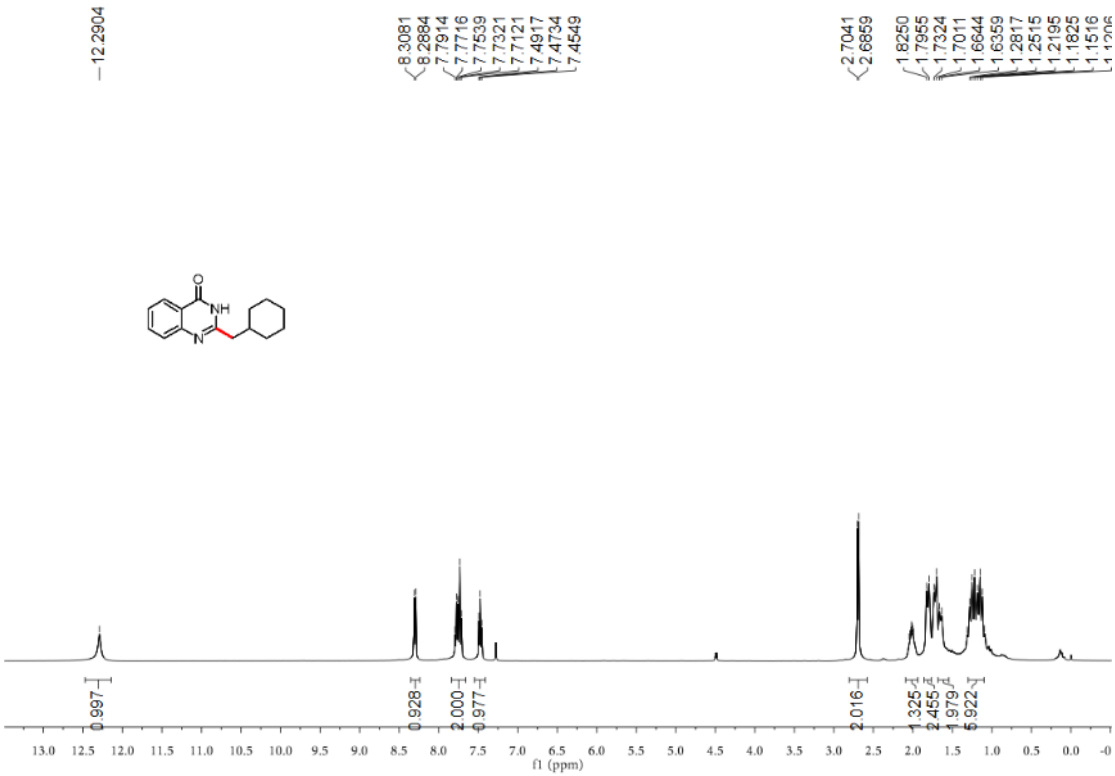
^{1}H NMR spectrum of compound **34**



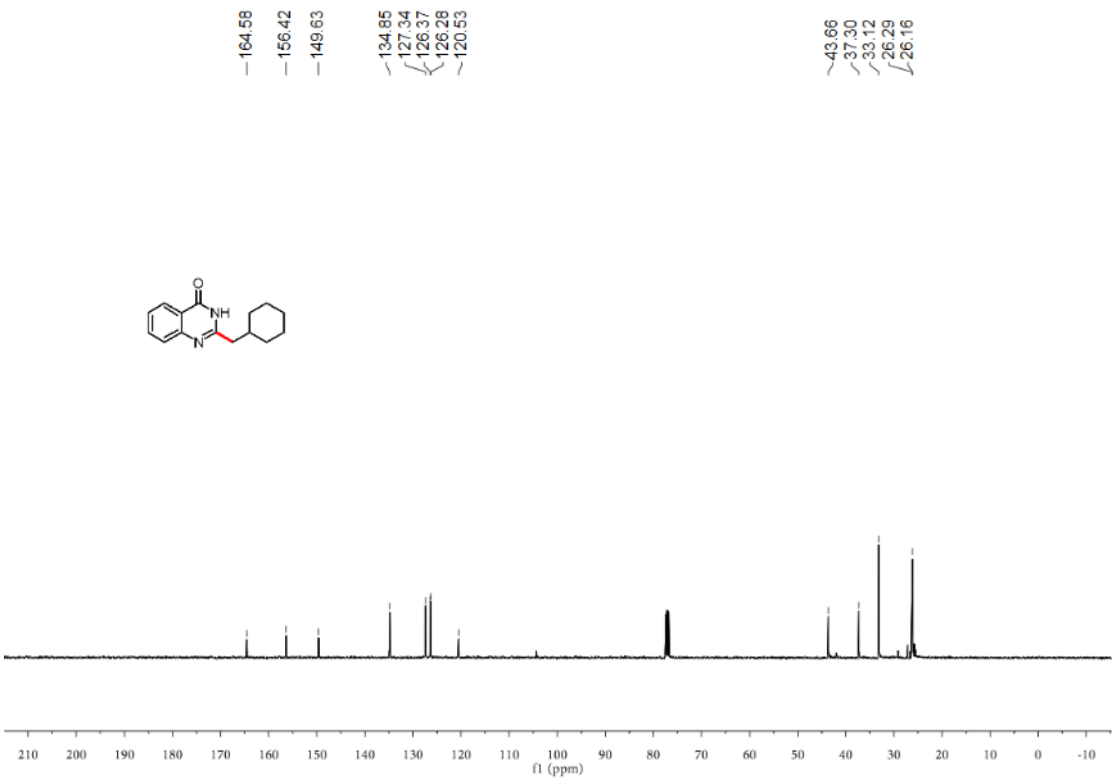
^{13}C NMR spectrum of compound **34**



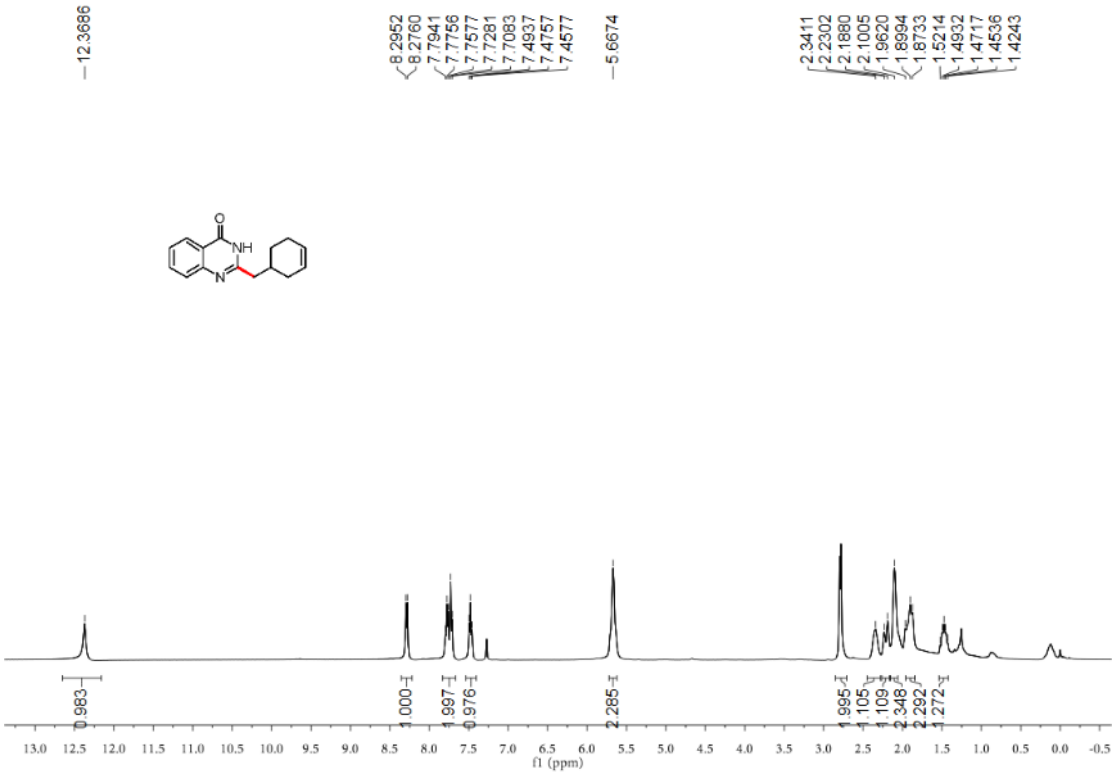
^{1}H NMR spectrum of compound **35**



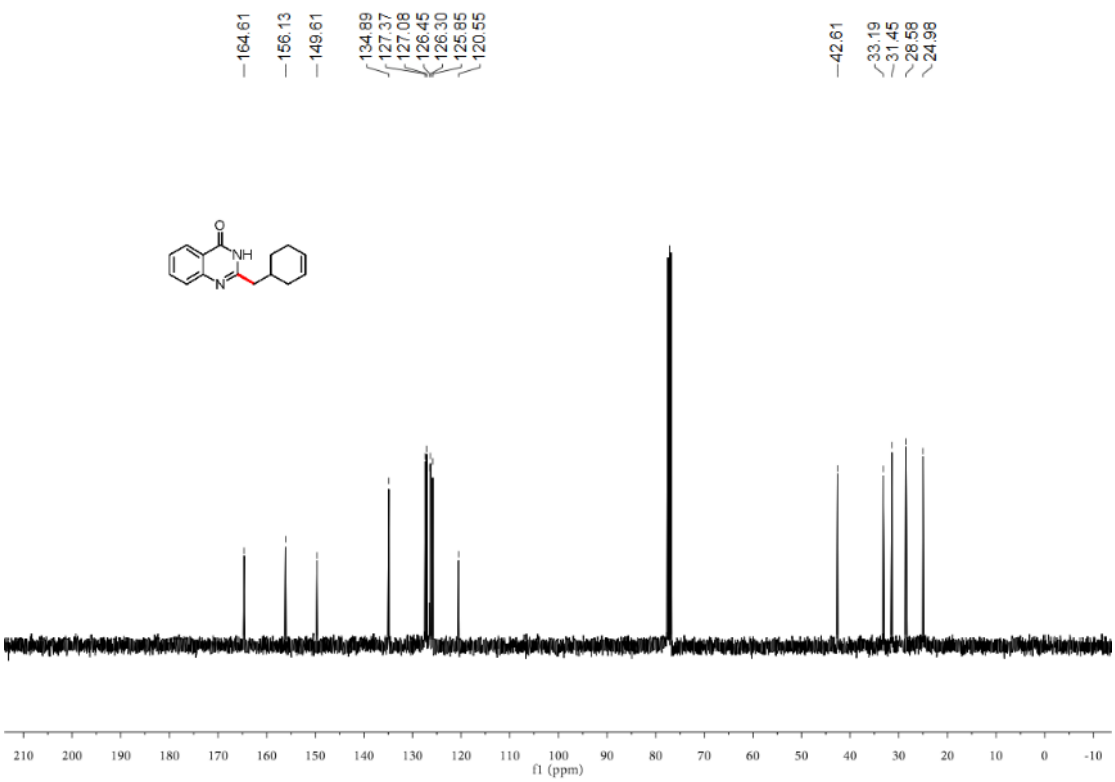
^{13}C NMR spectrum of compound **35**



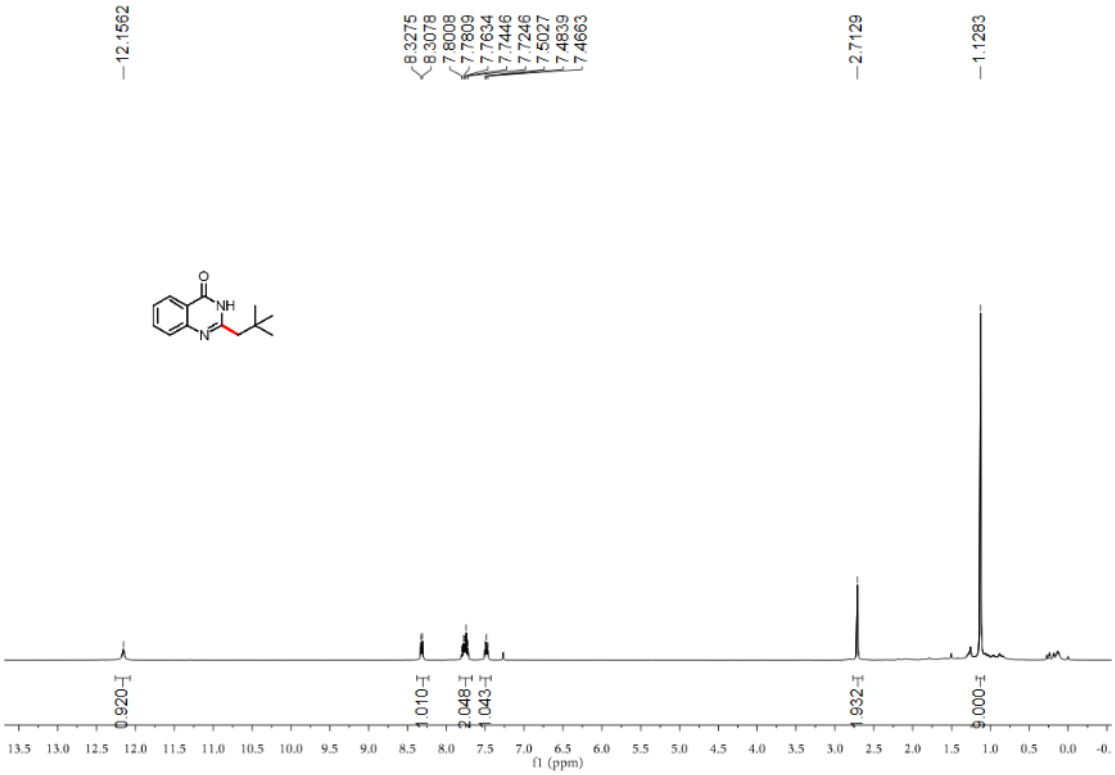
^{1}H NMR spectrum of compound **36**



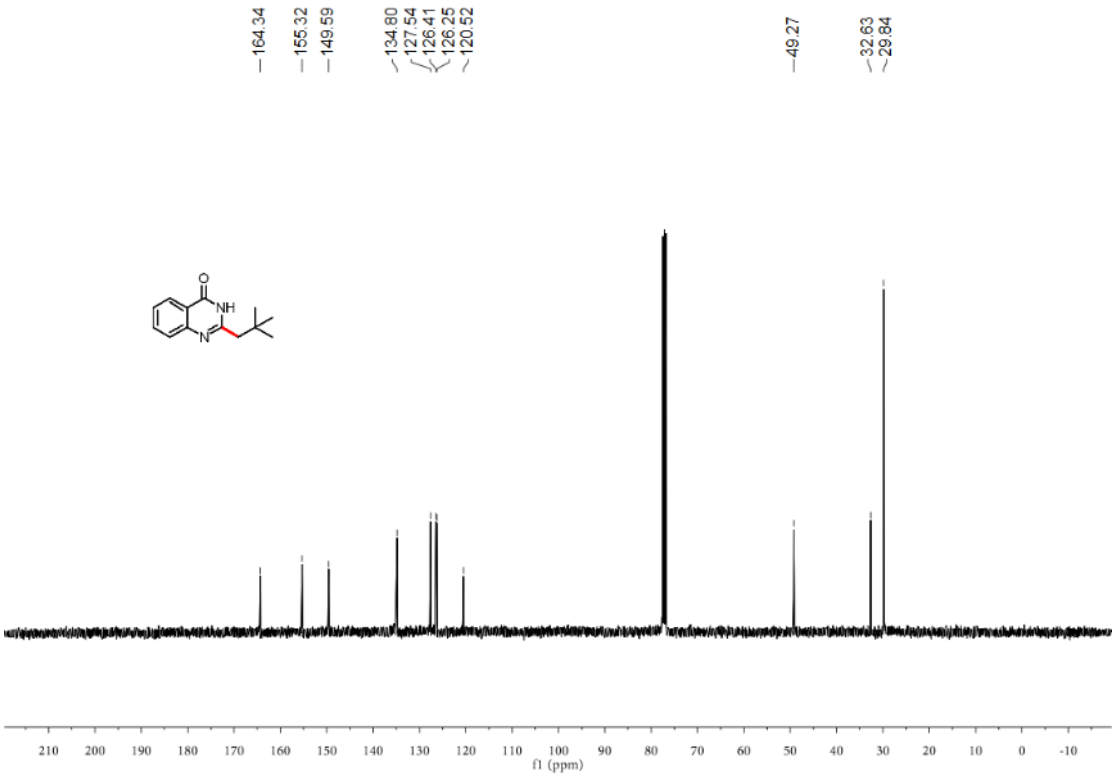
^{13}C NMR spectrum of compound **36**



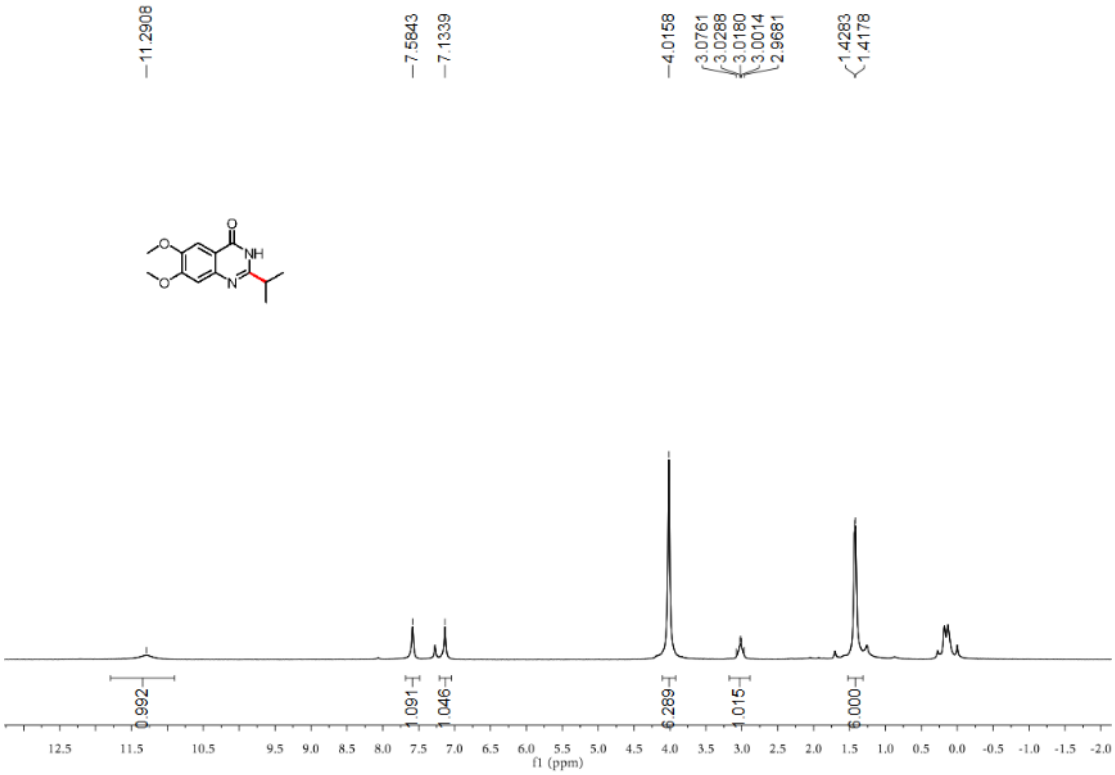
^{1}H NMR spectrum of compound **37**



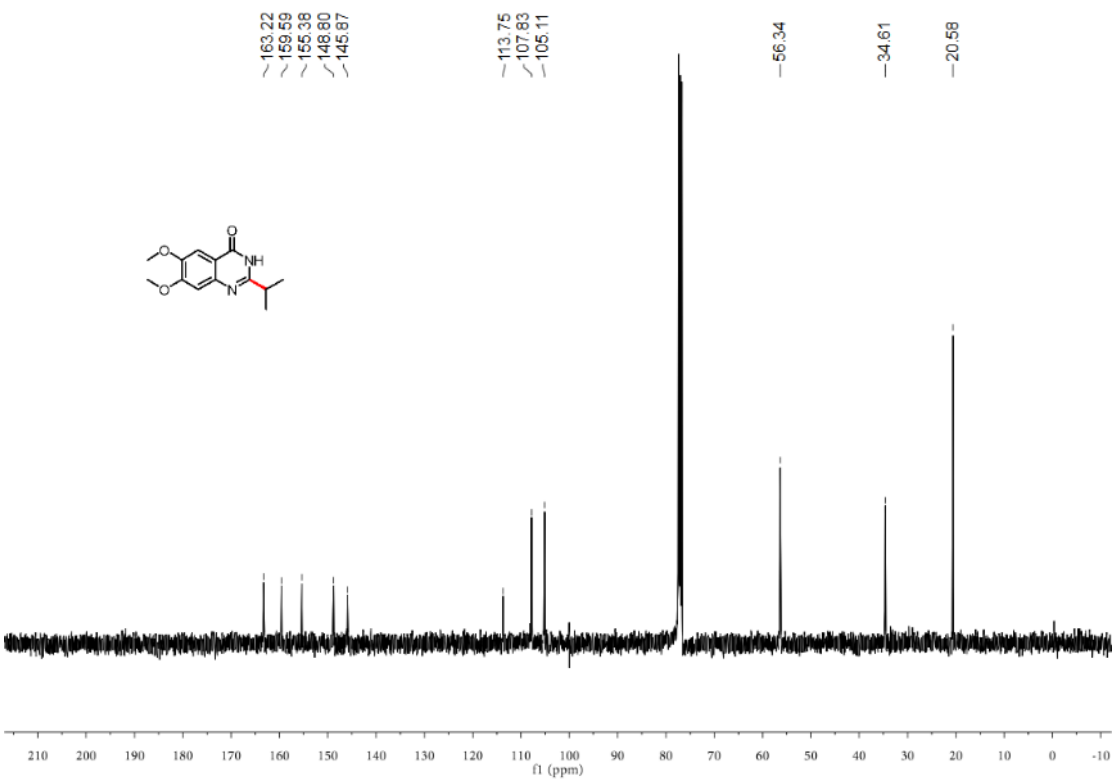
^{13}C NMR spectrum of compound **37**



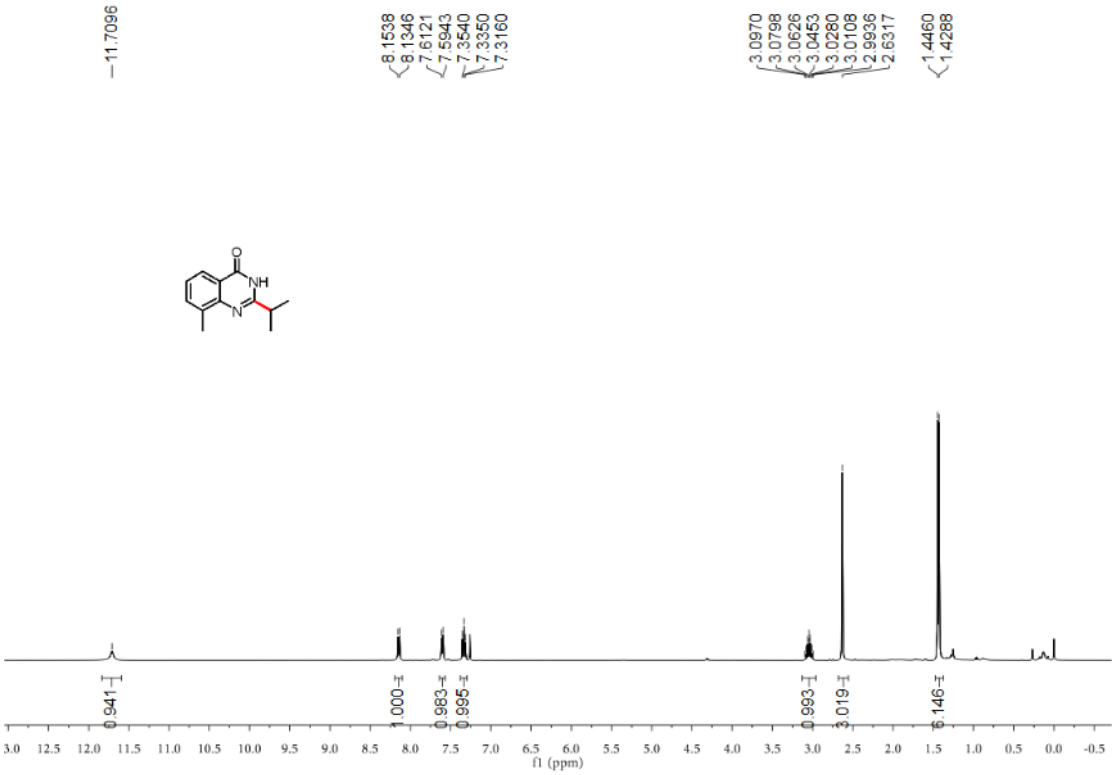
^{1}H NMR spectrum of compound **38**



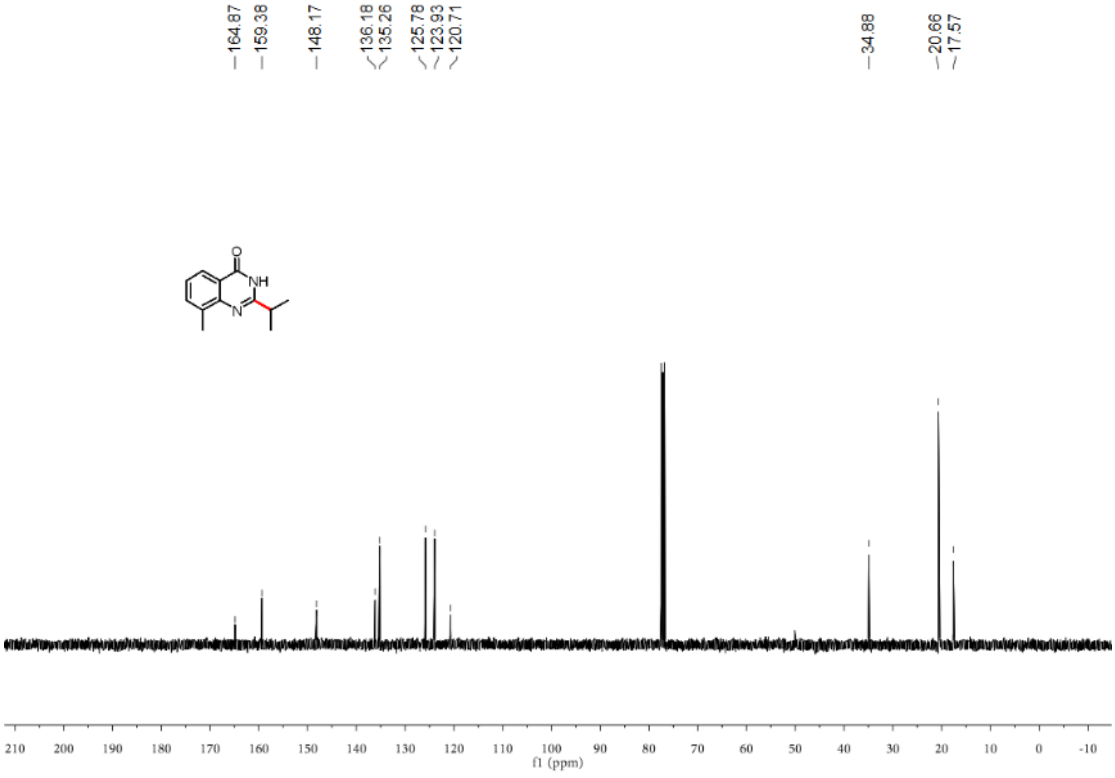
^{13}C NMR spectrum of compound **38**



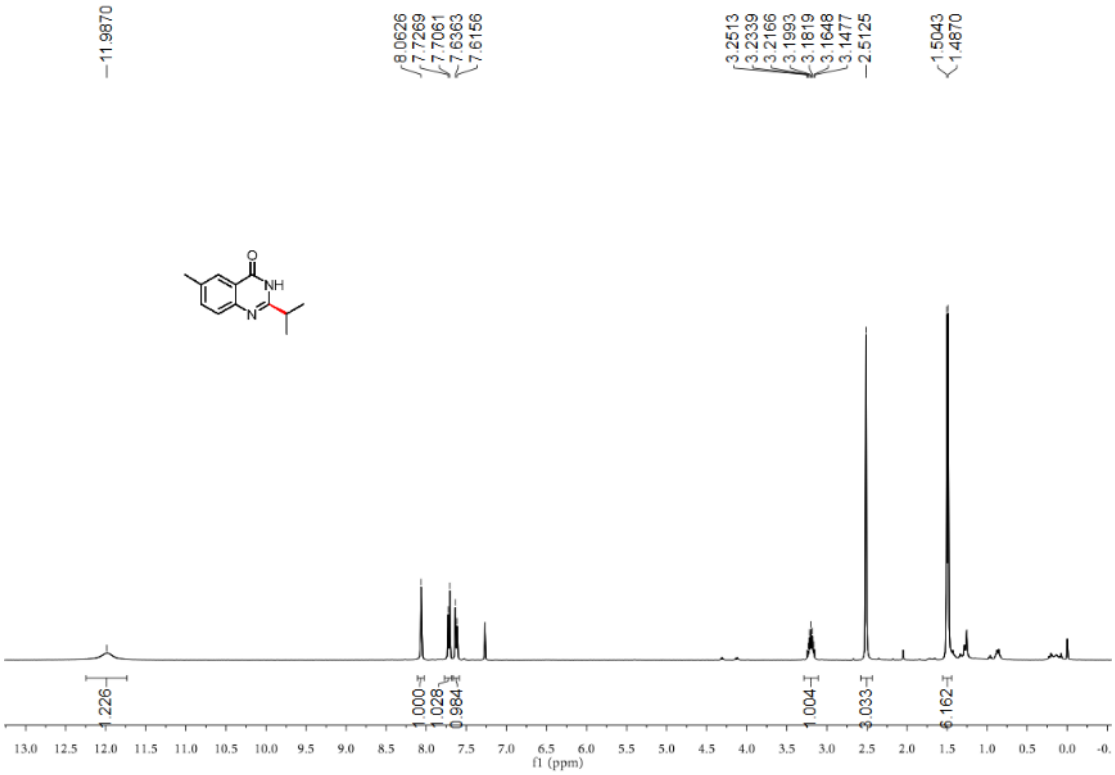
^{1}H NMR spectrum of compound **39**



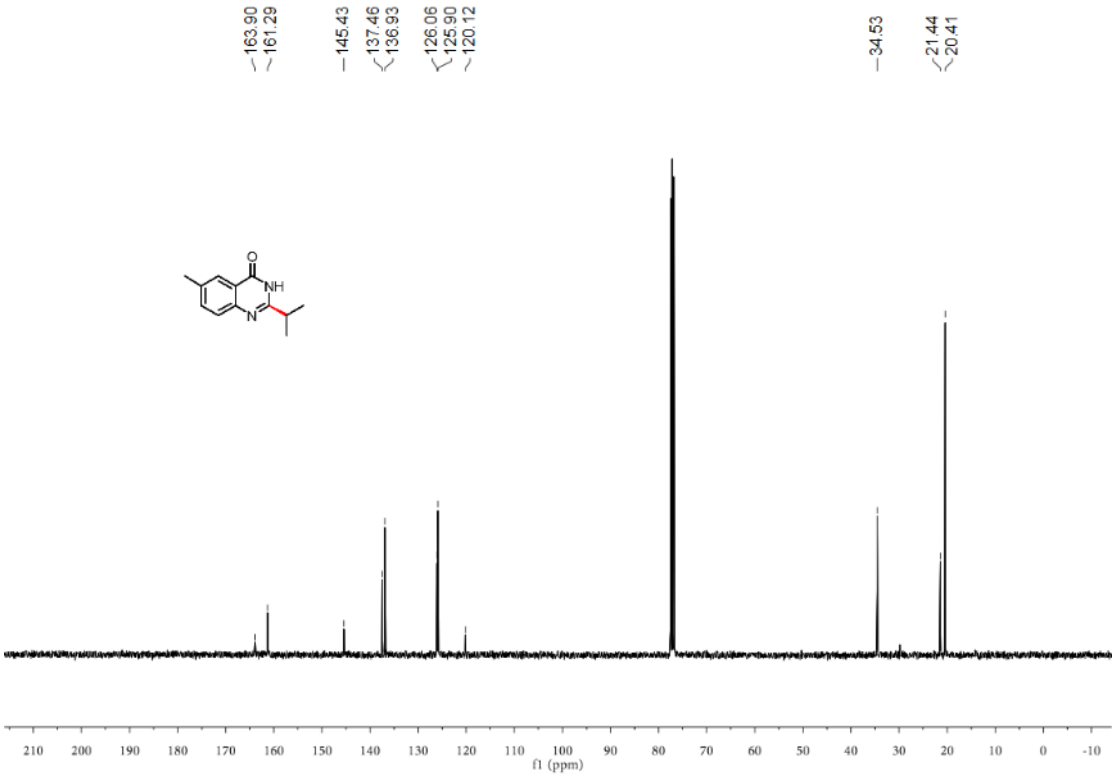
^{13}C NMR spectrum of compound **39**



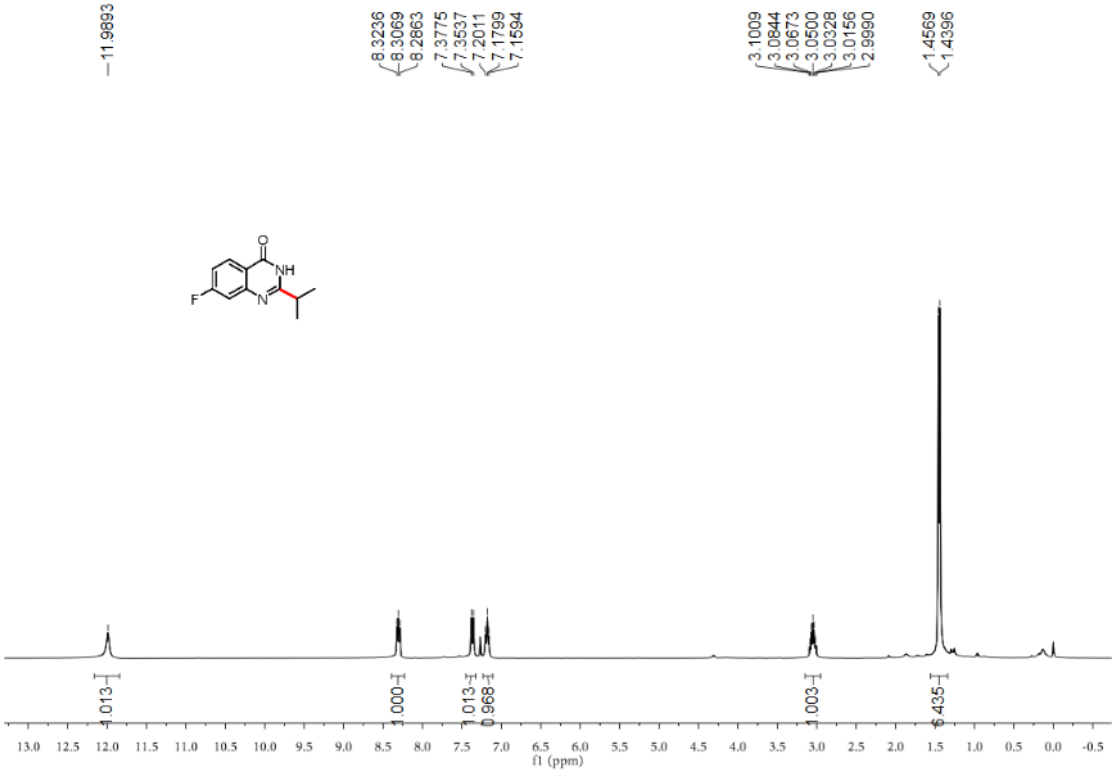
^{1}H NMR spectrum of compound **40**



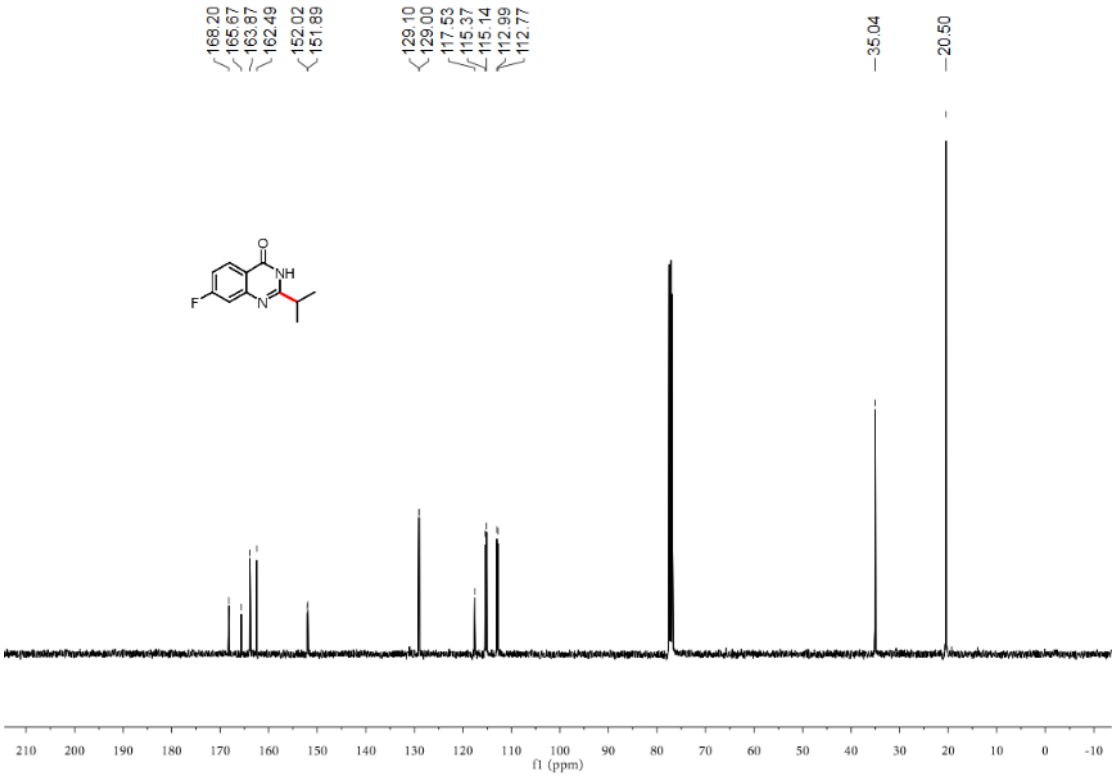
^{13}C NMR spectrum of compound **40**



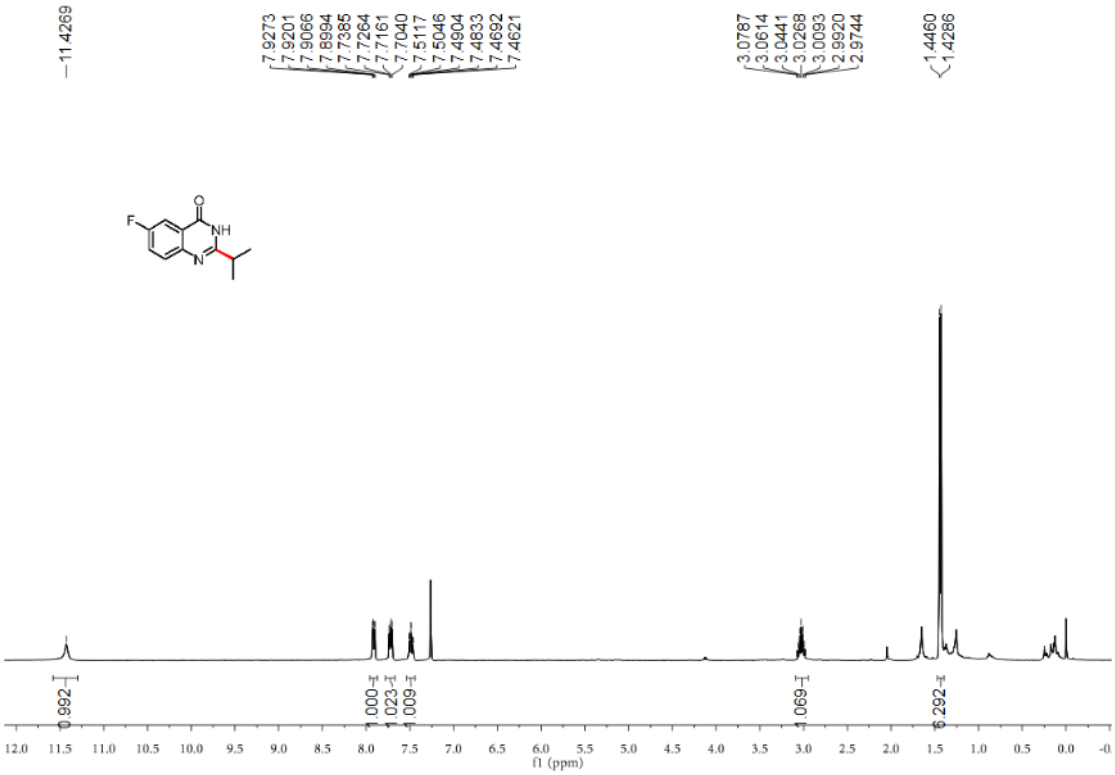
^{1}H NMR spectrum of compound **41**



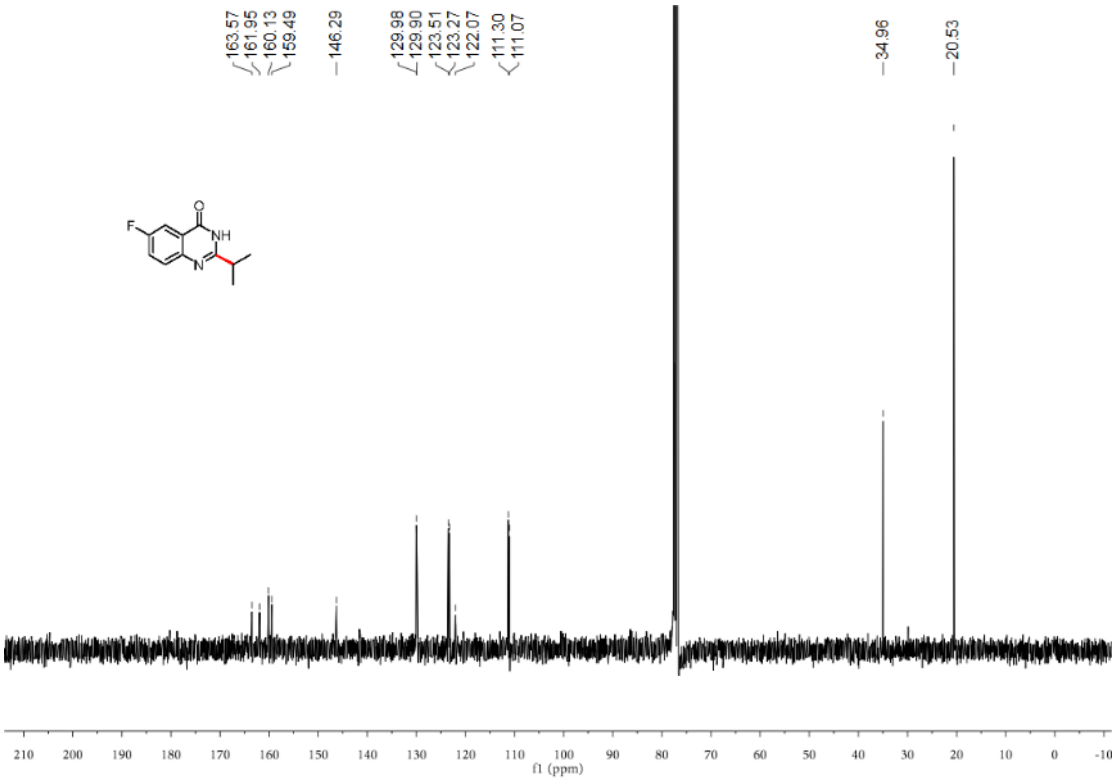
^{13}C NMR spectrum of compound **41**



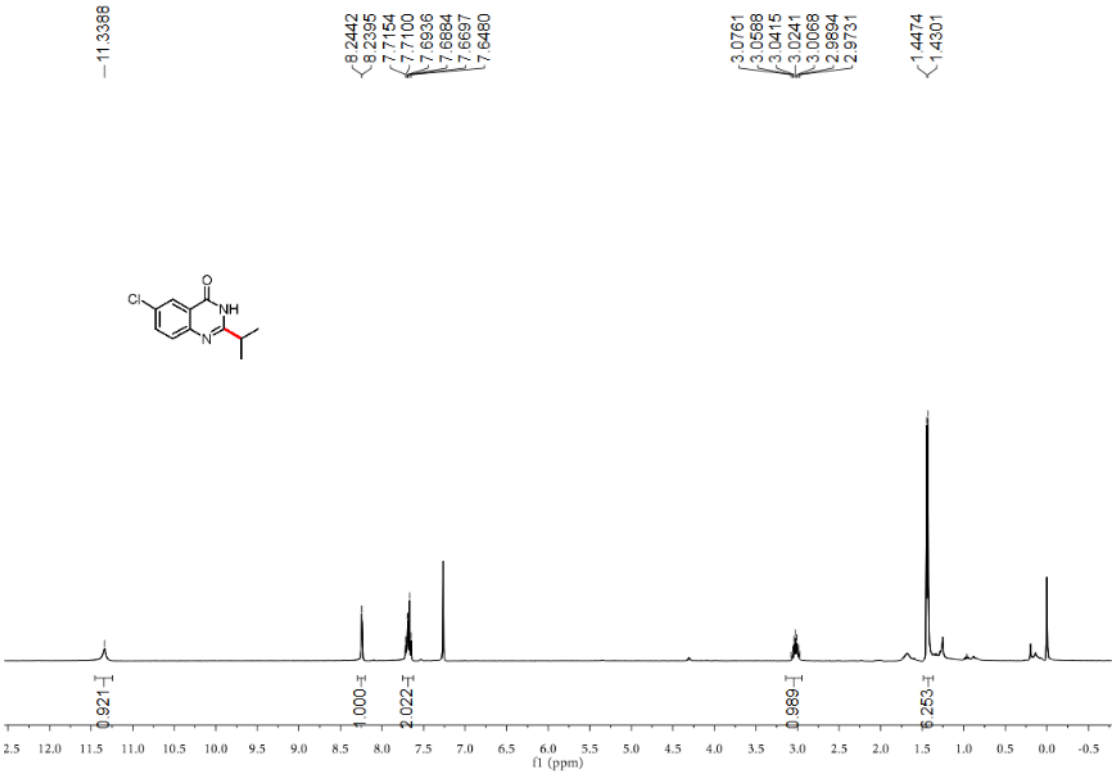
^{1}H NMR spectrum of compound **42**



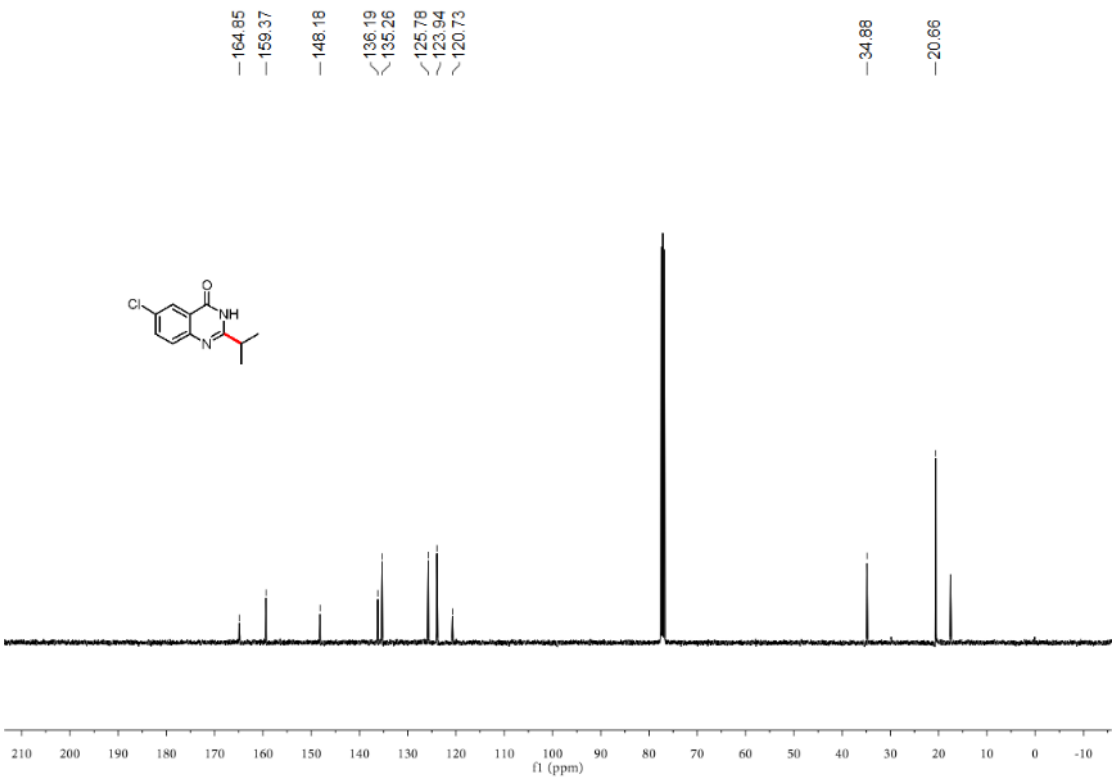
^{13}C NMR spectrum of compound **42**



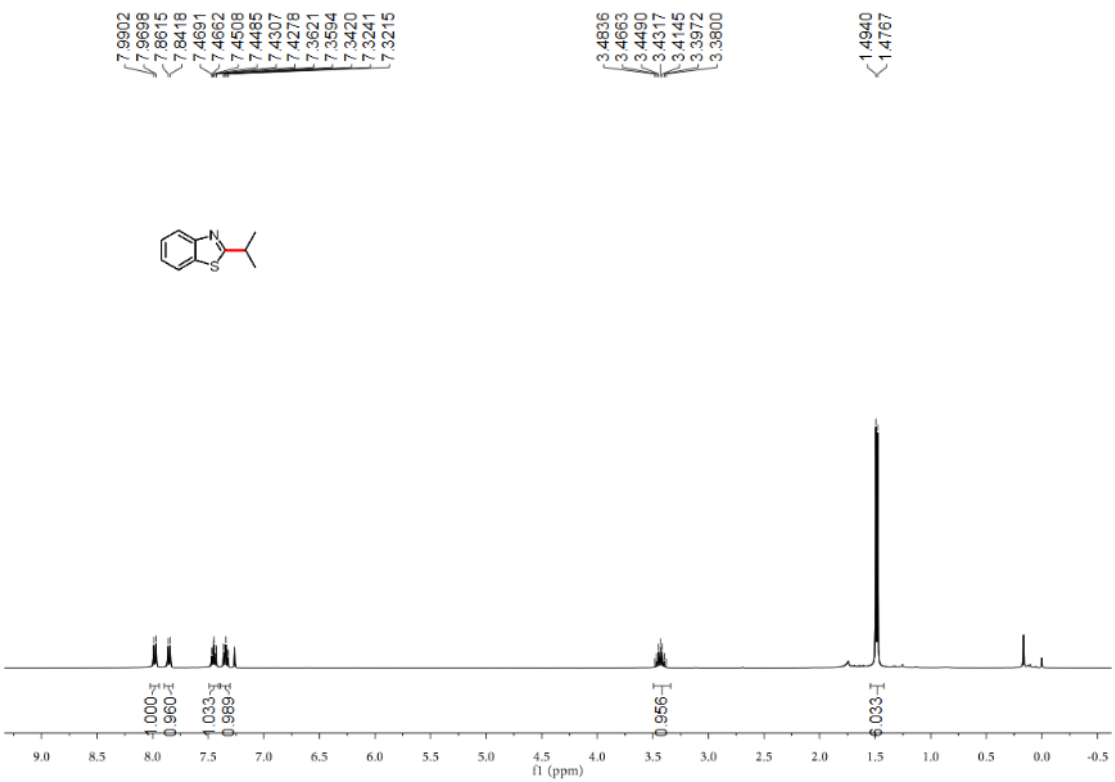
^{1}H NMR spectrum of compound **43**



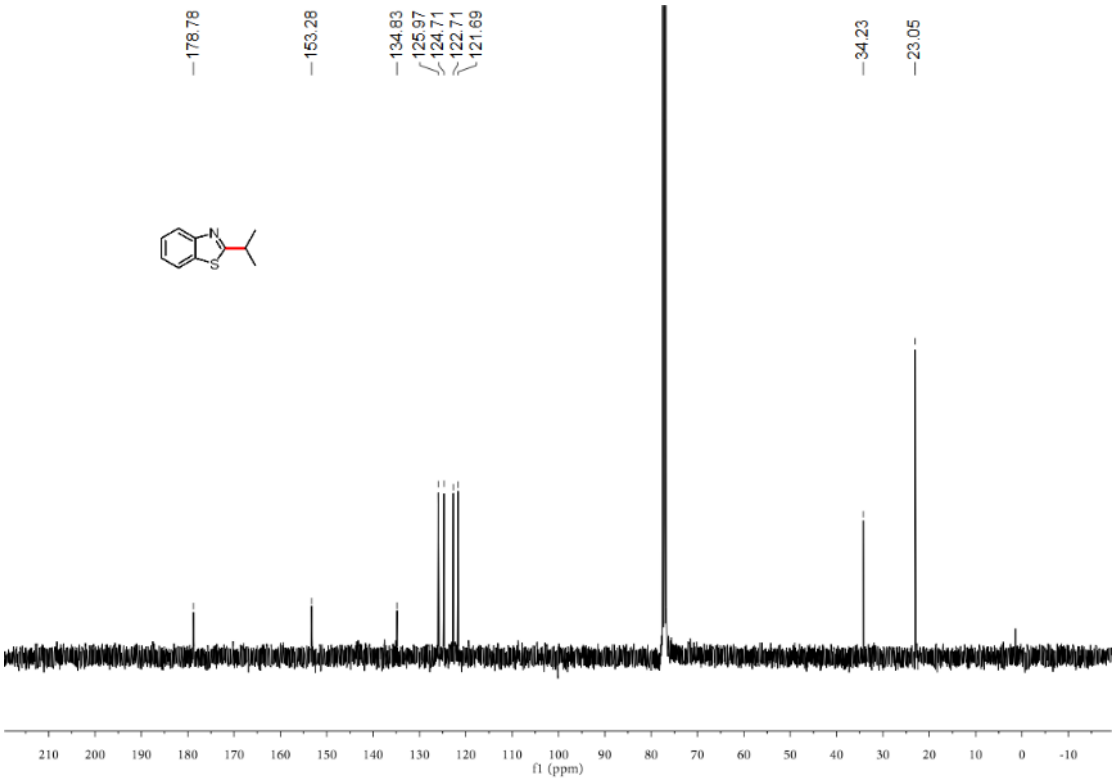
^{13}C NMR spectrum of compound **43**



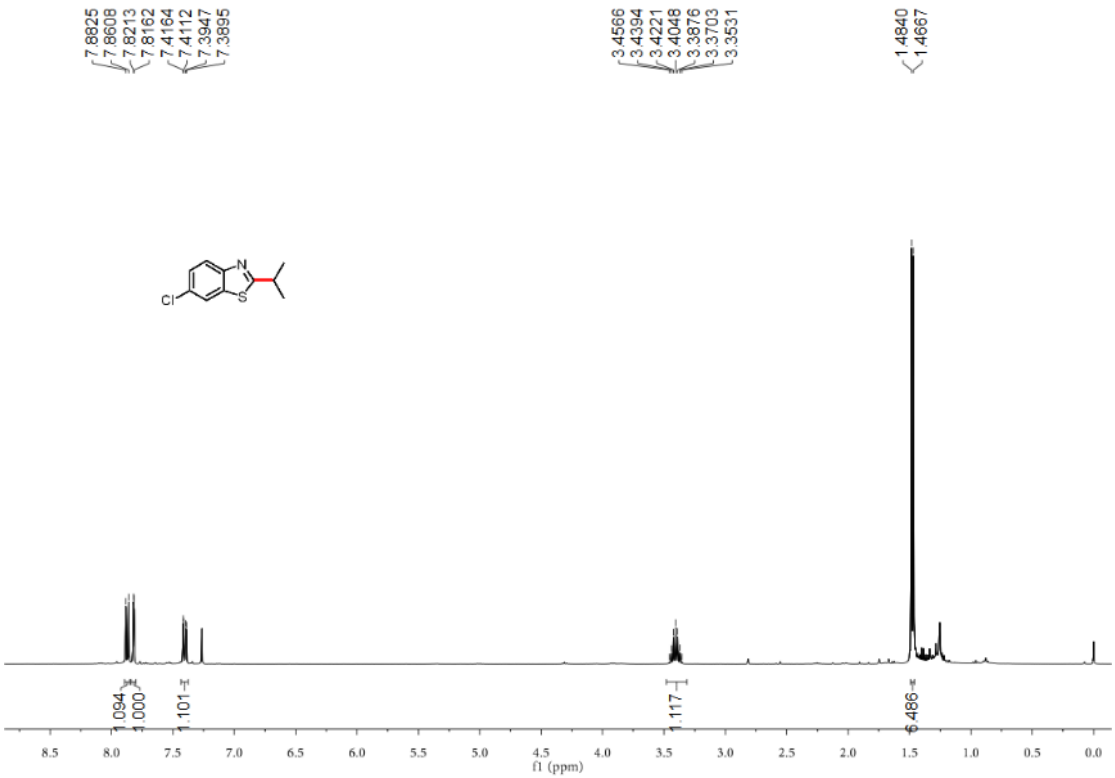
^{1}H NMR spectrum of compound **44**



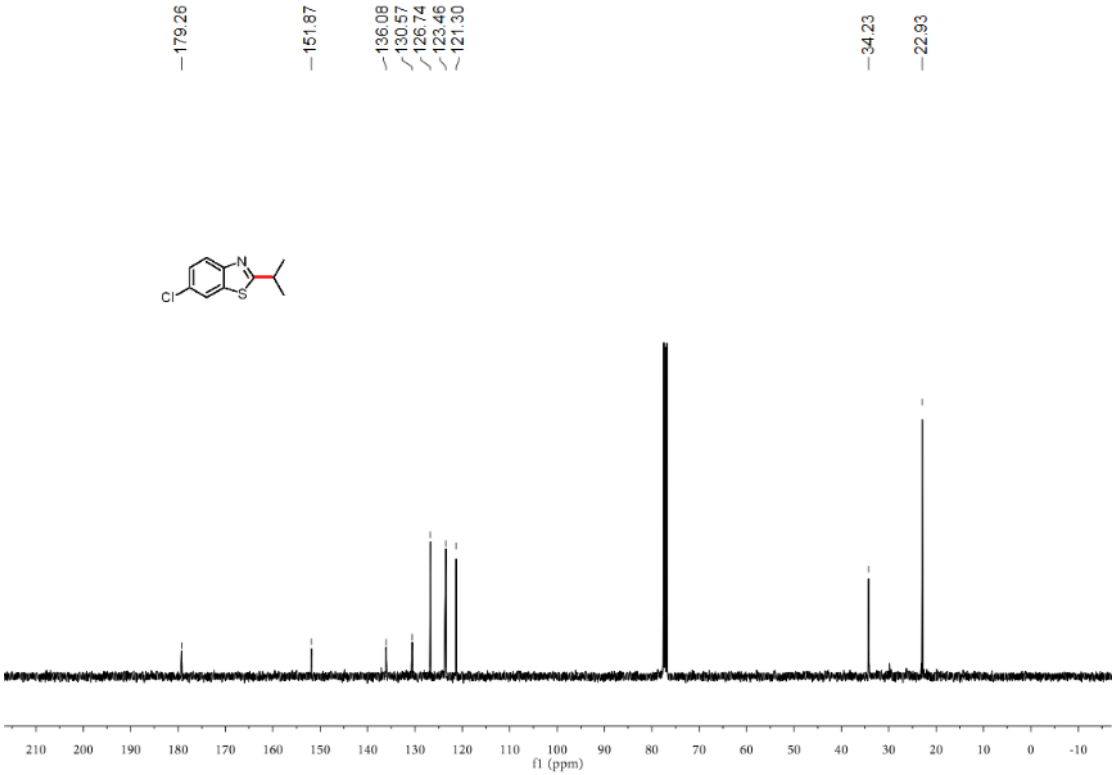
^{13}C NMR spectrum of compound **44**



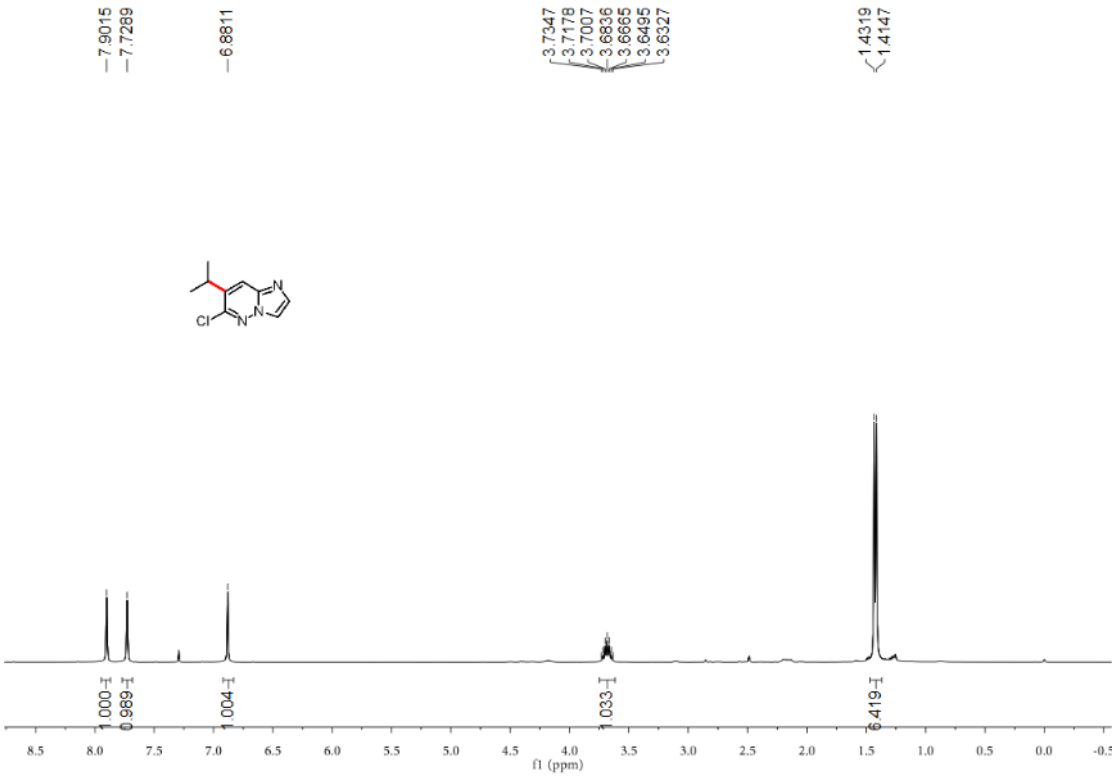
^{1}H NMR spectrum of compound **45**



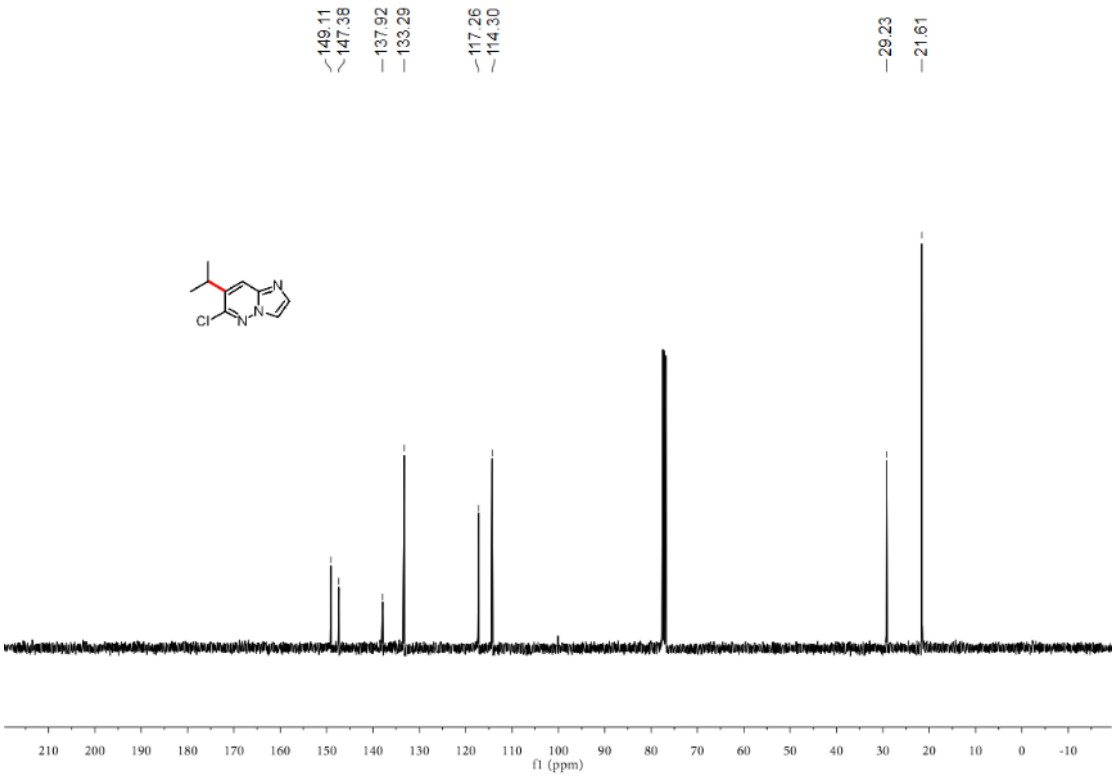
^{13}C NMR spectrum of compound **45**



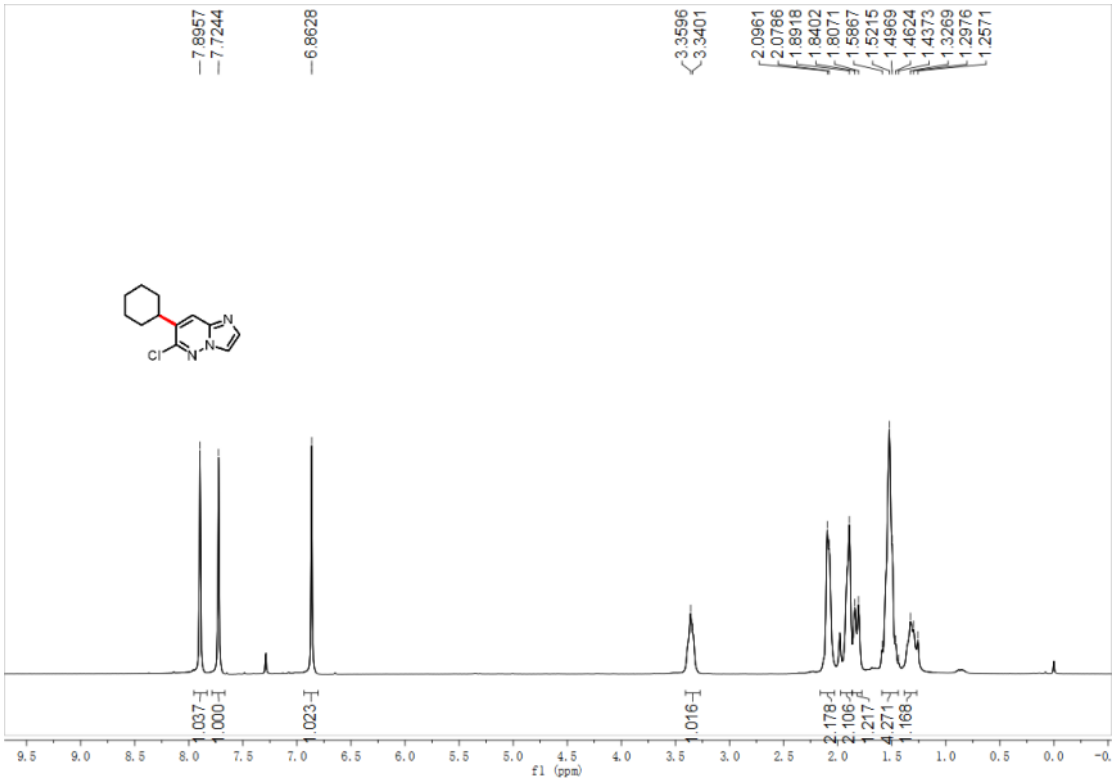
^{1}H NMR spectrum of compound **46a**



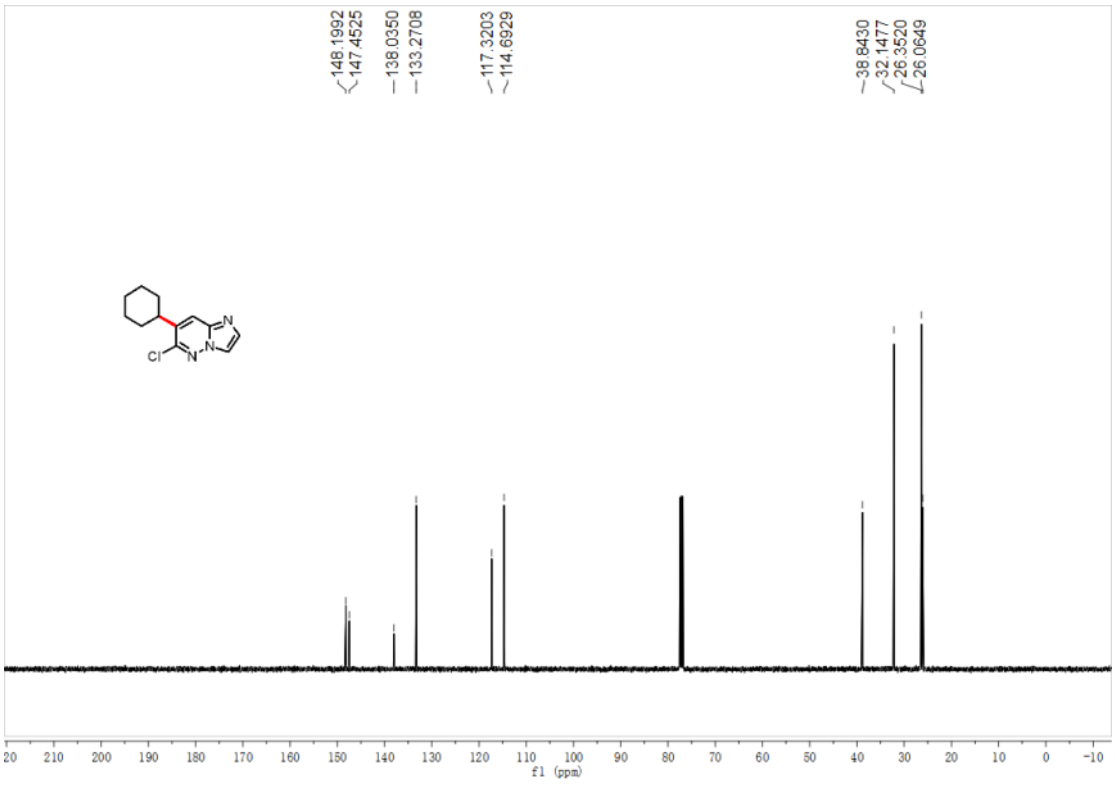
^{13}C NMR spectrum of compound **46a**



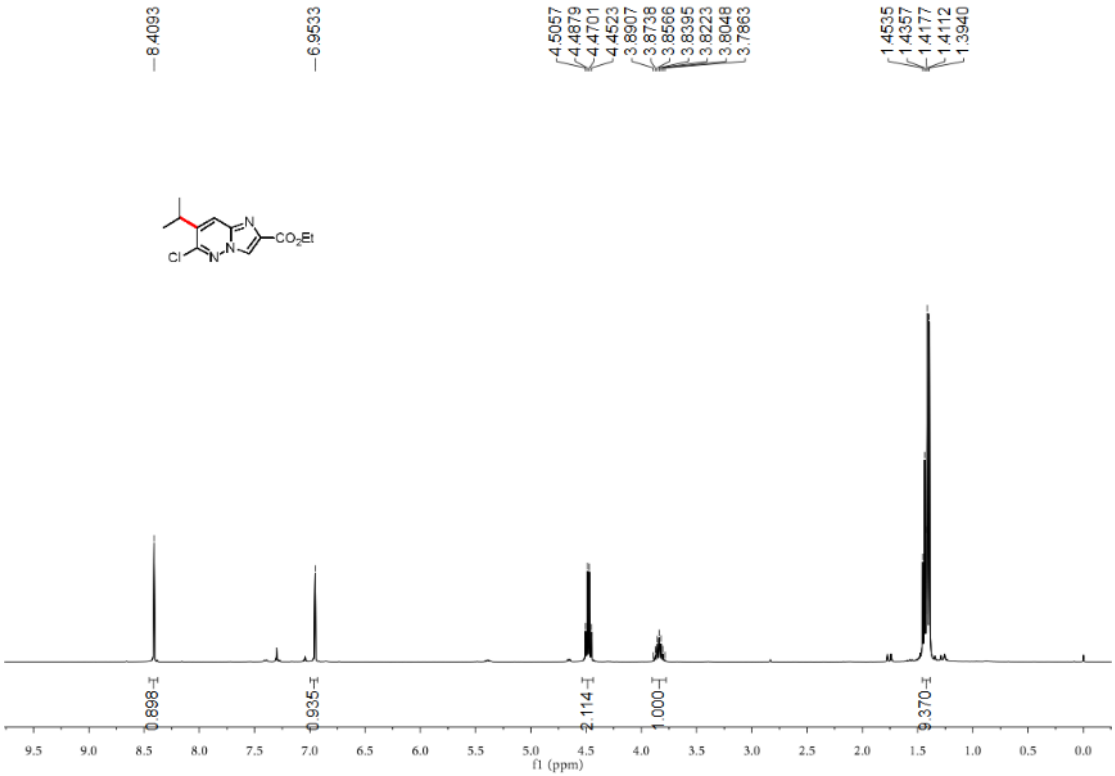
^{1}H NMR spectrum of compound **46b**



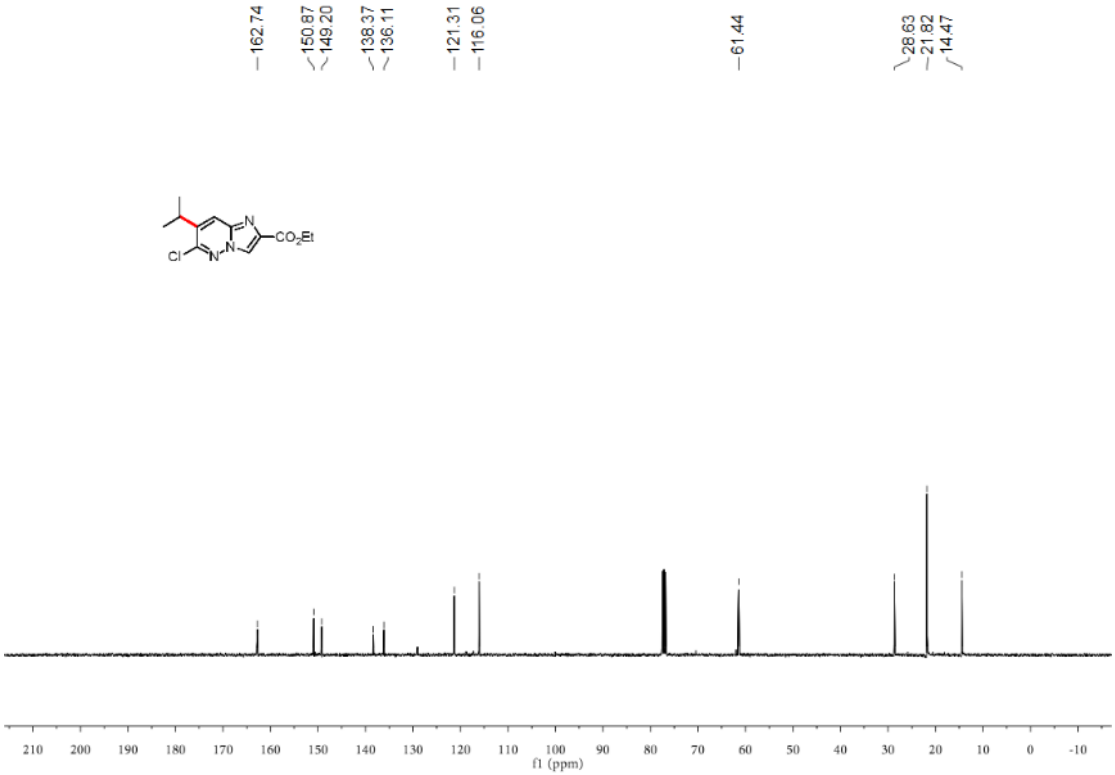
^{13}C NMR spectrum of compound **46b**



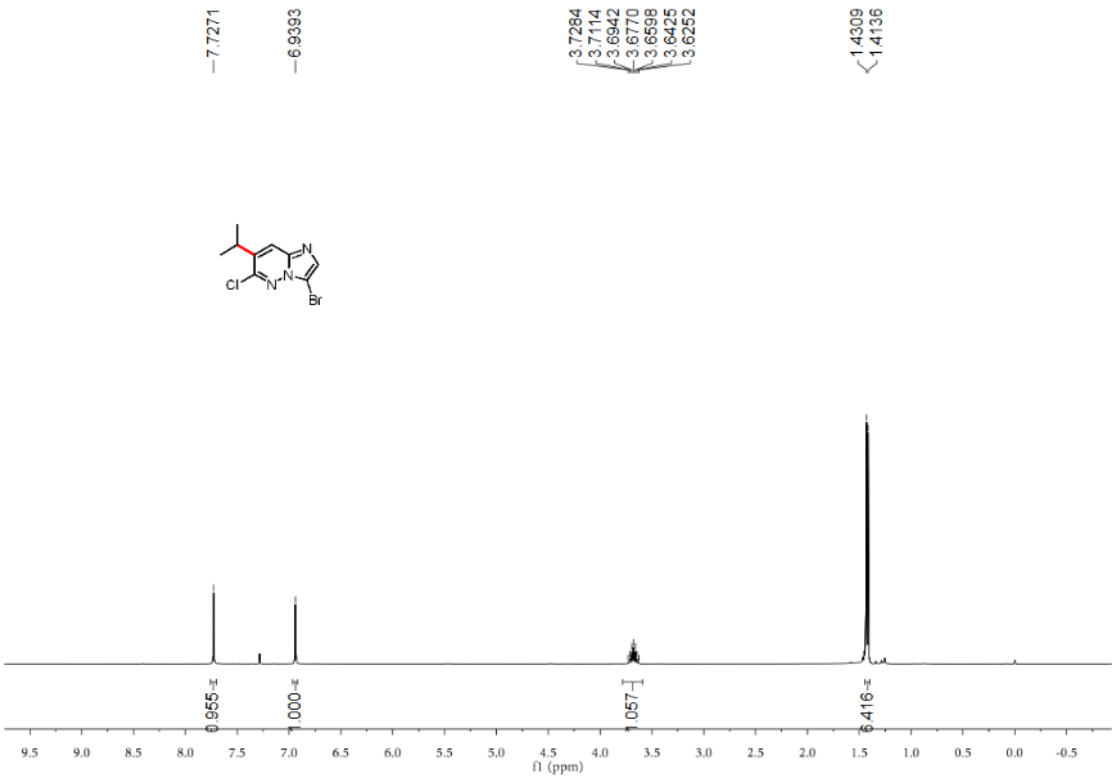
^{1}H NMR spectrum of compound **47**



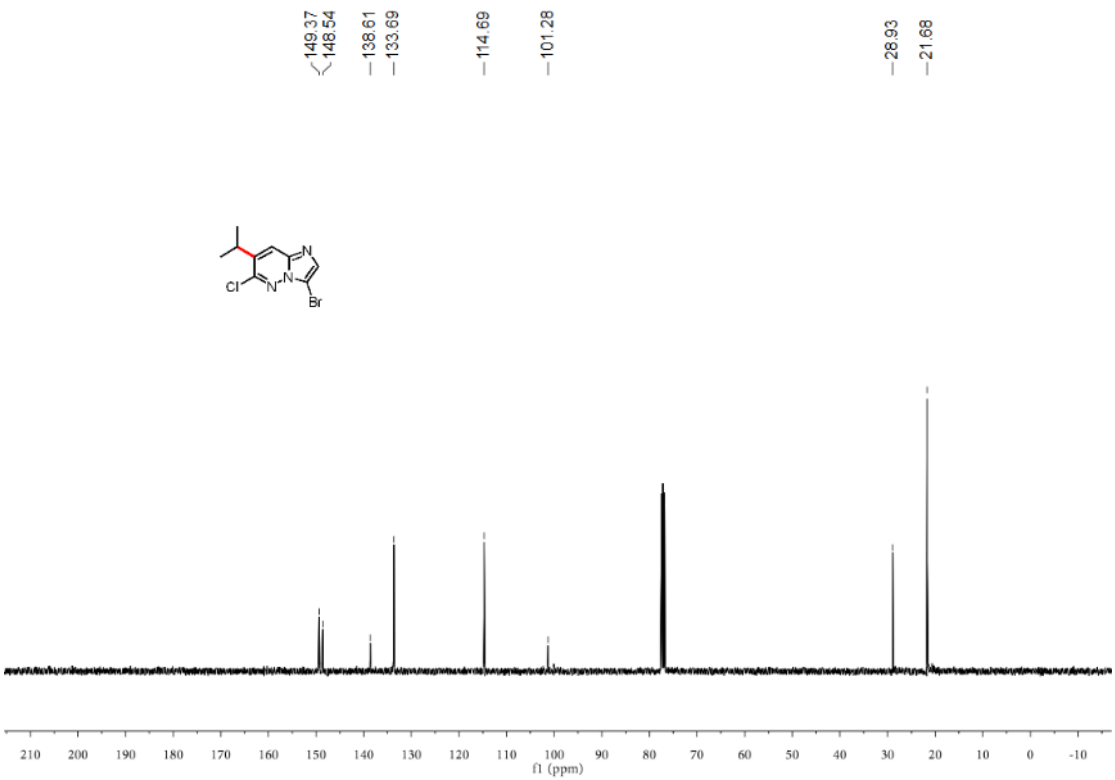
^{13}C NMR spectrum of compound **47**



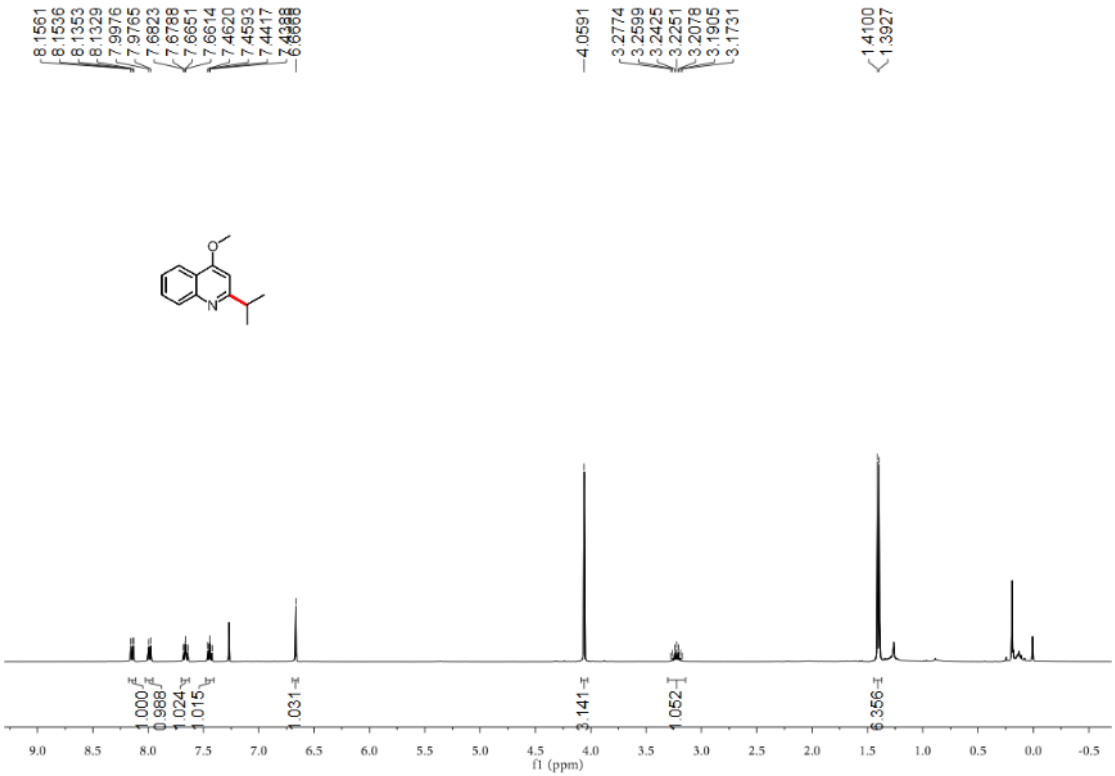
^{1}H NMR spectrum of compound **48**



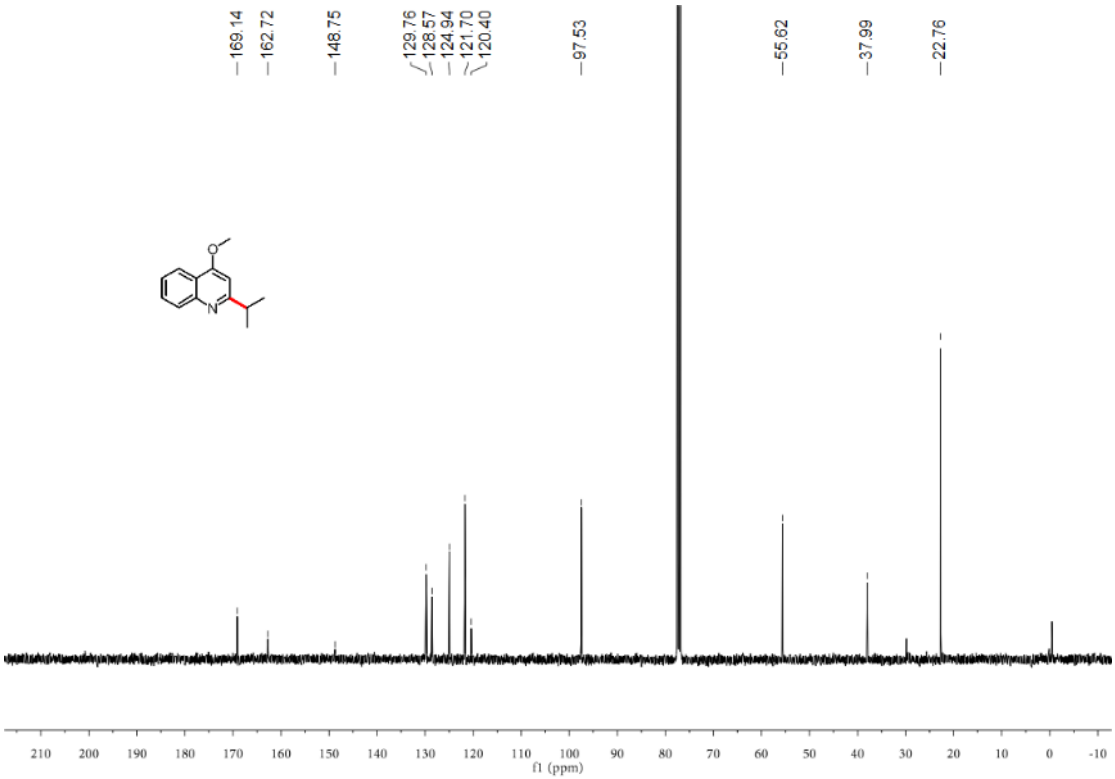
^{13}C NMR spectrum of compound **48**



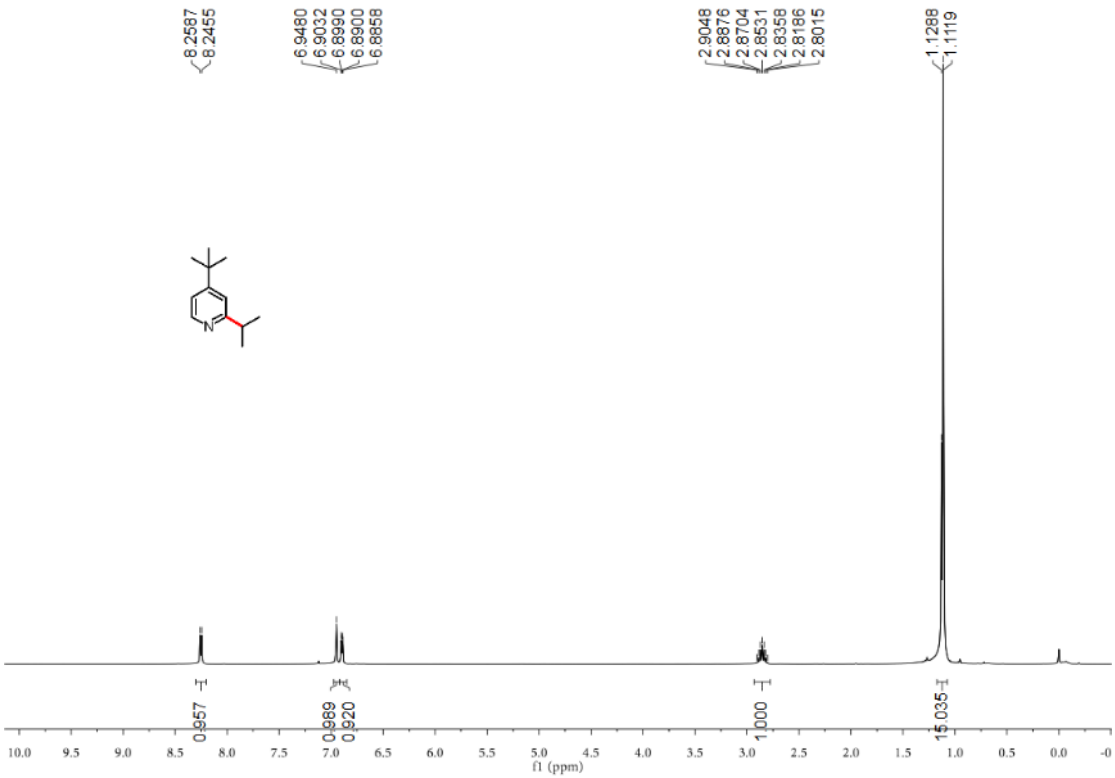
^{1}H NMR spectrum of compound **49**



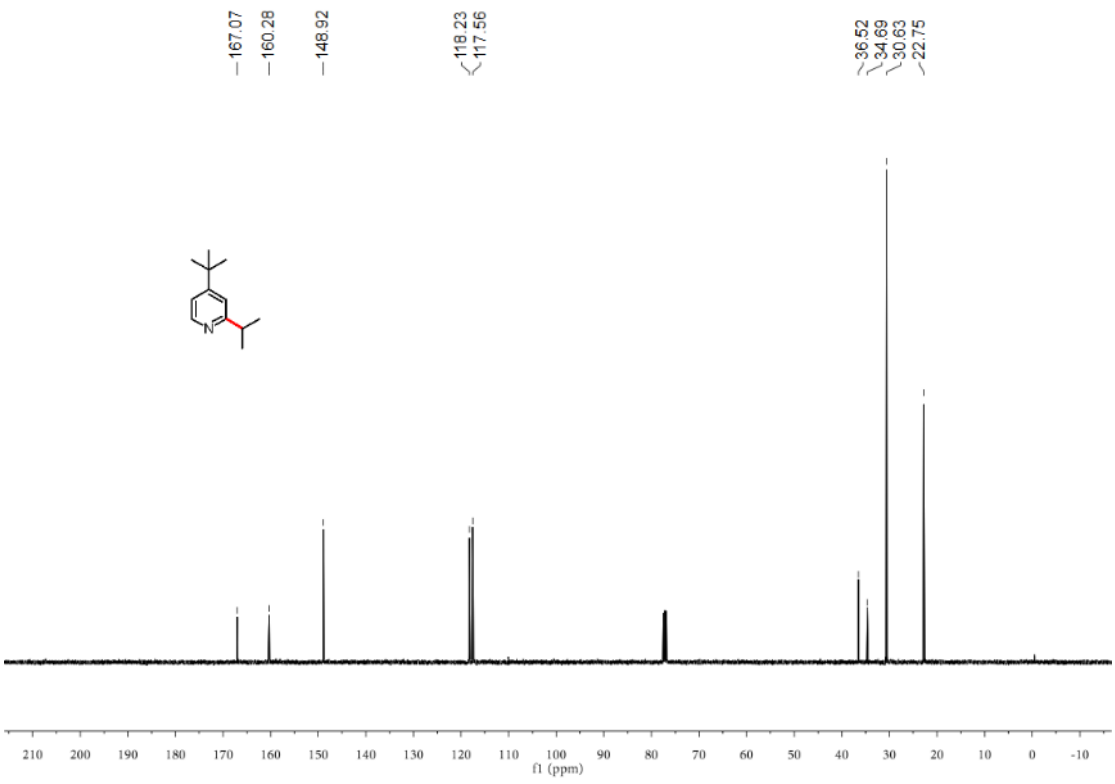
^{13}C NMR spectrum of compound **49**



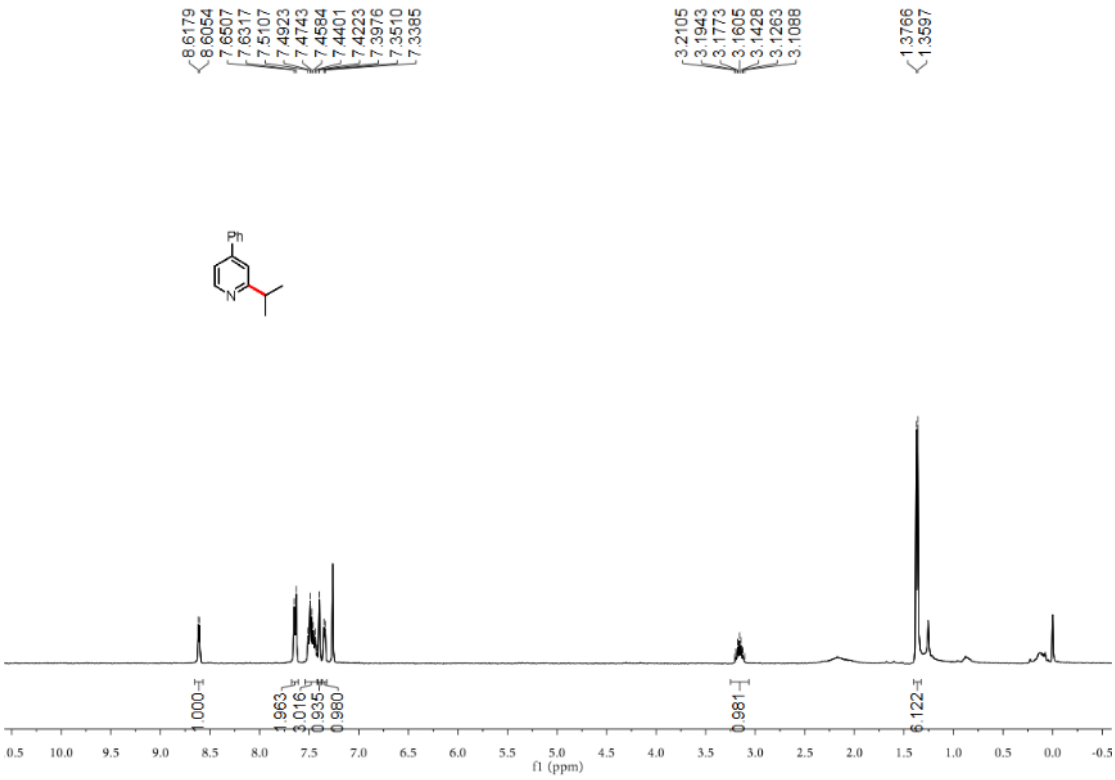
^{1}H NMR spectrum of compound **50**



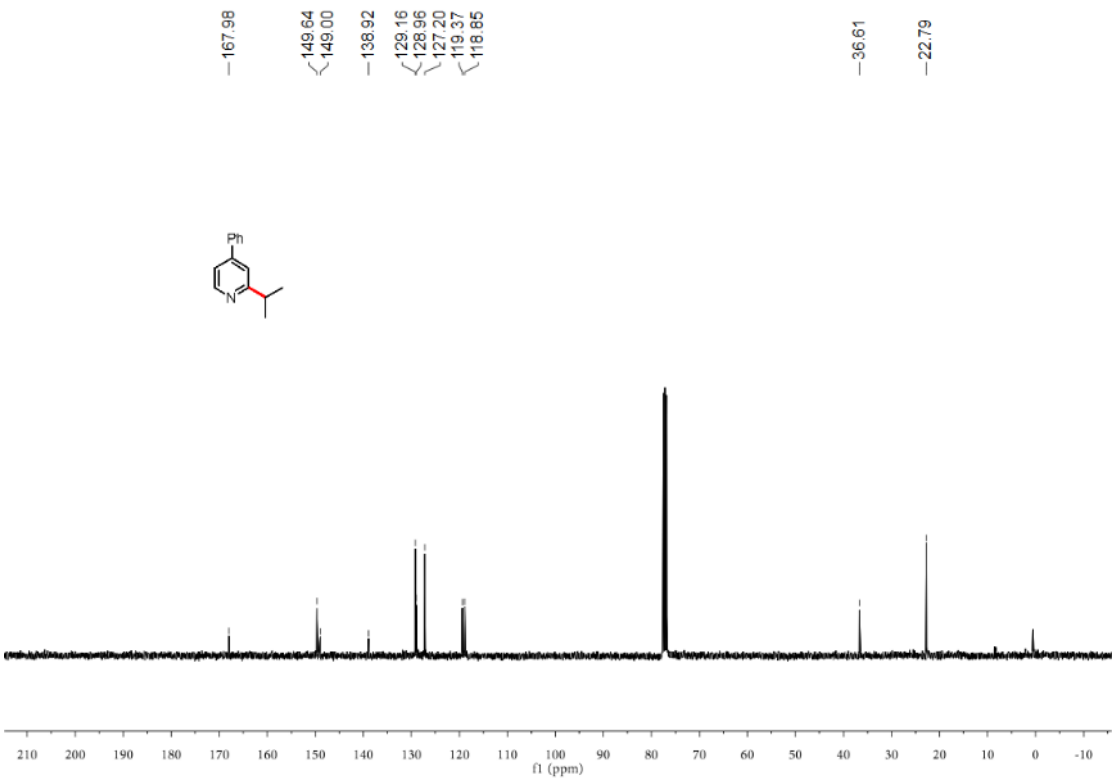
^{13}C NMR spectrum of compound **50**



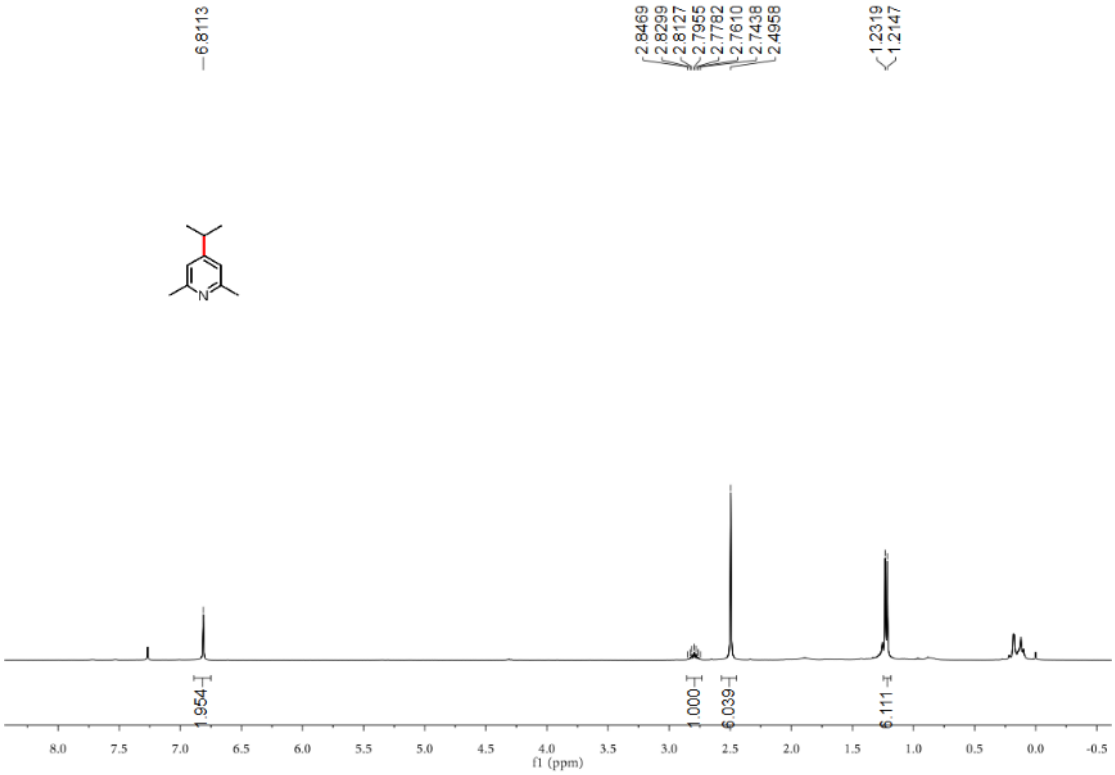
^{1}H NMR spectrum of compound **51**



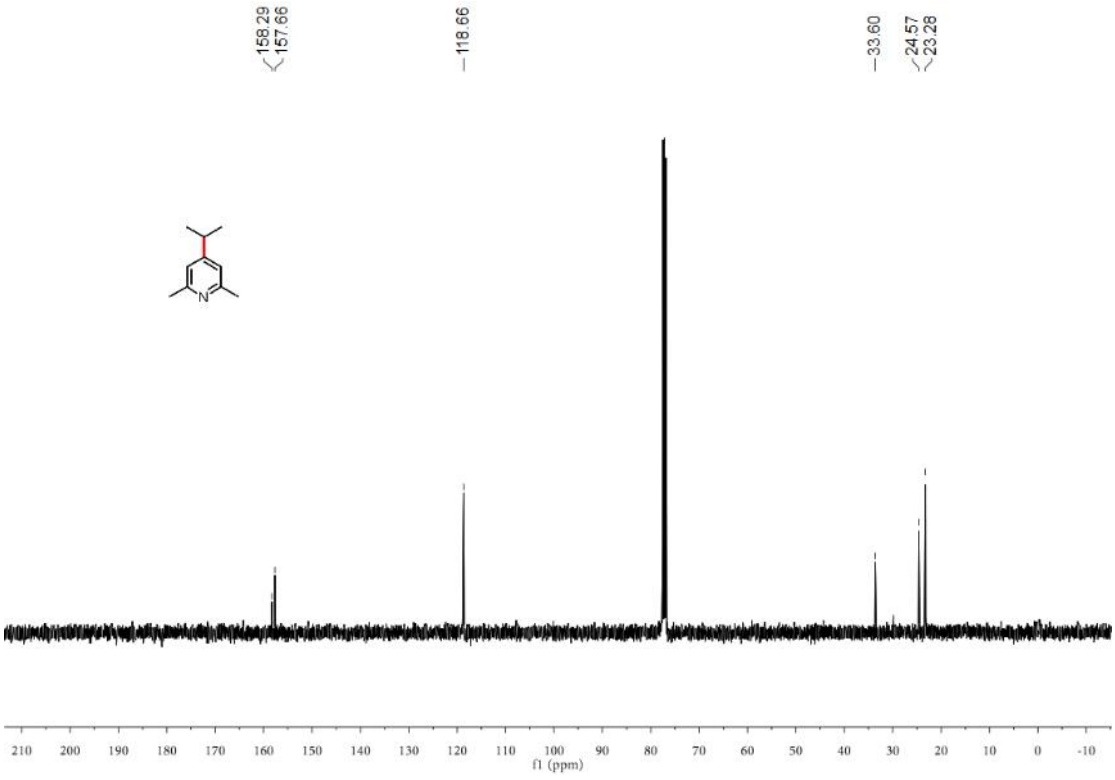
^{13}C NMR spectrum of compound **51**



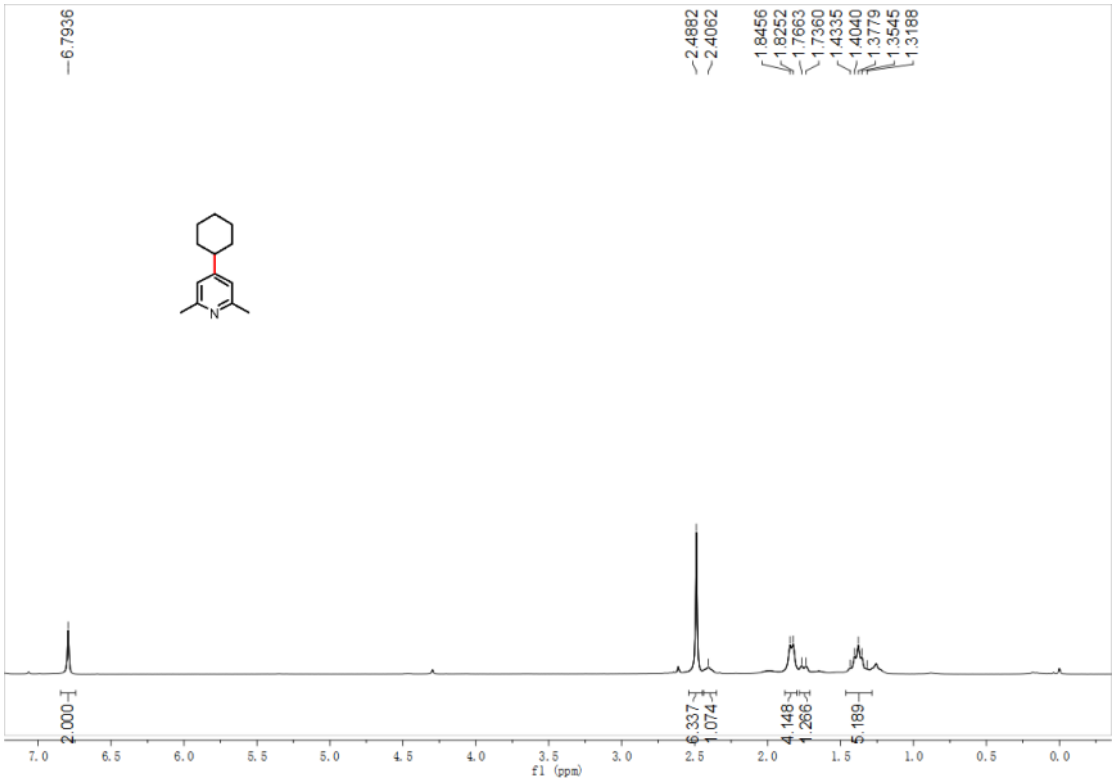
^{1}H NMR spectrum of compound **52a**



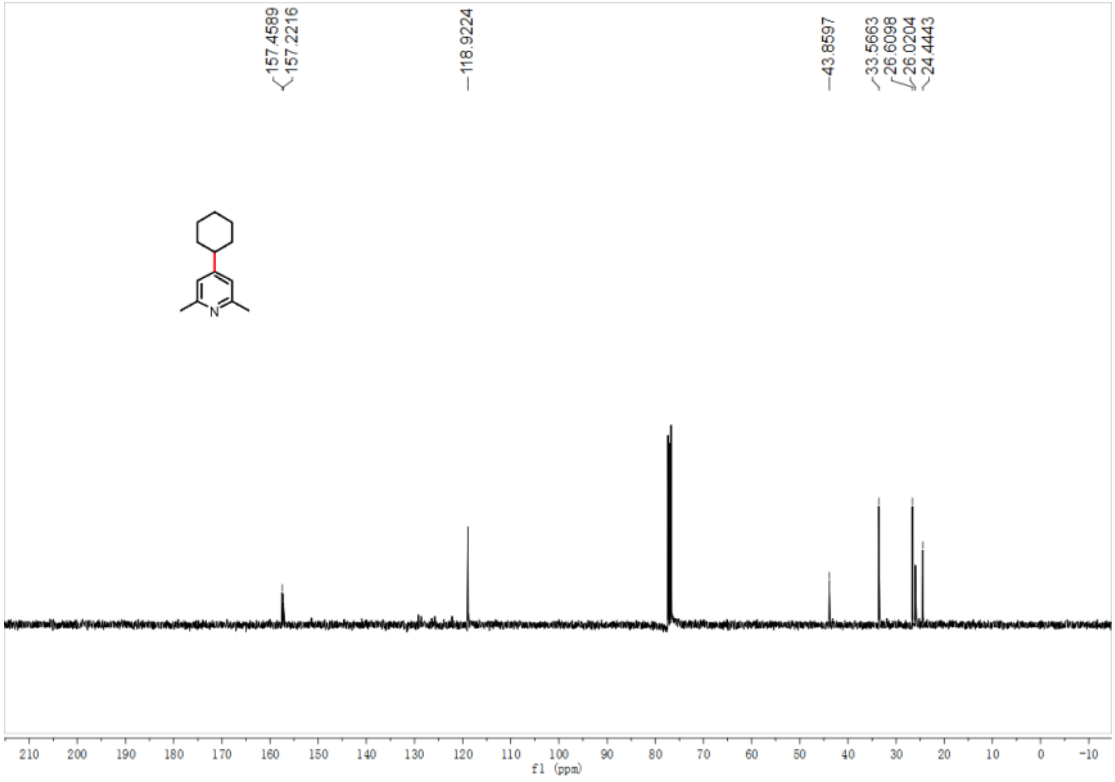
^{13}C NMR spectrum of compound **52a**



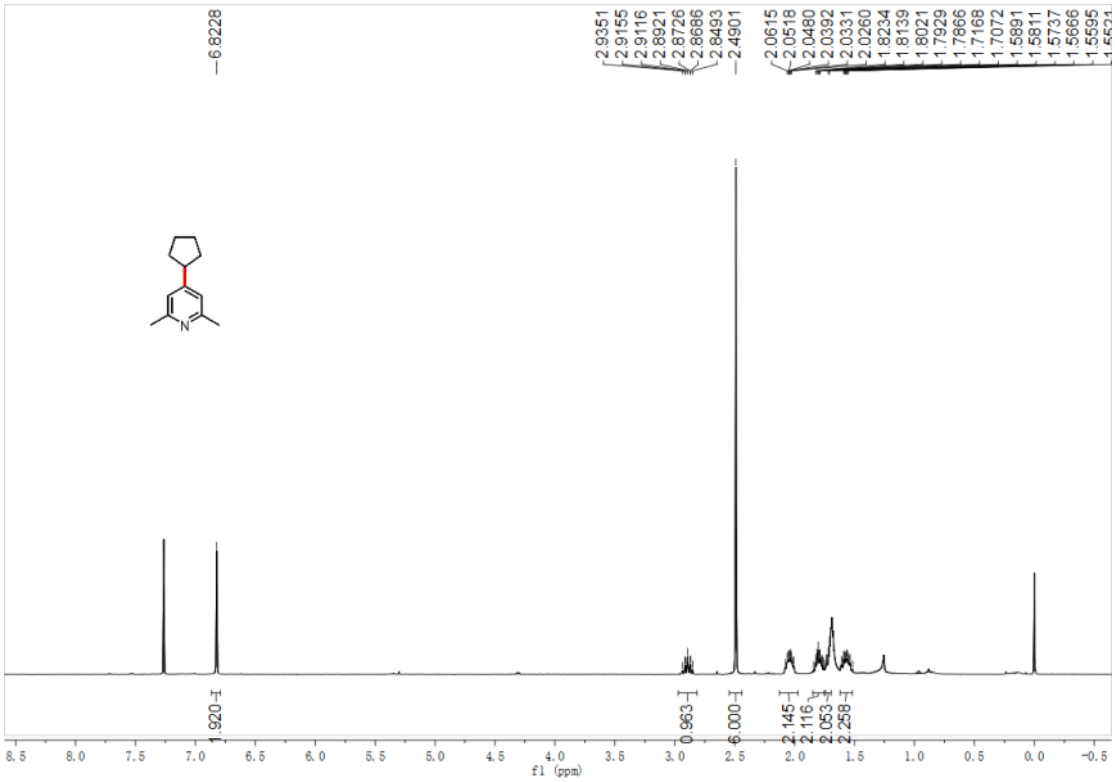
^{1}H NMR spectrum of compound **52b**



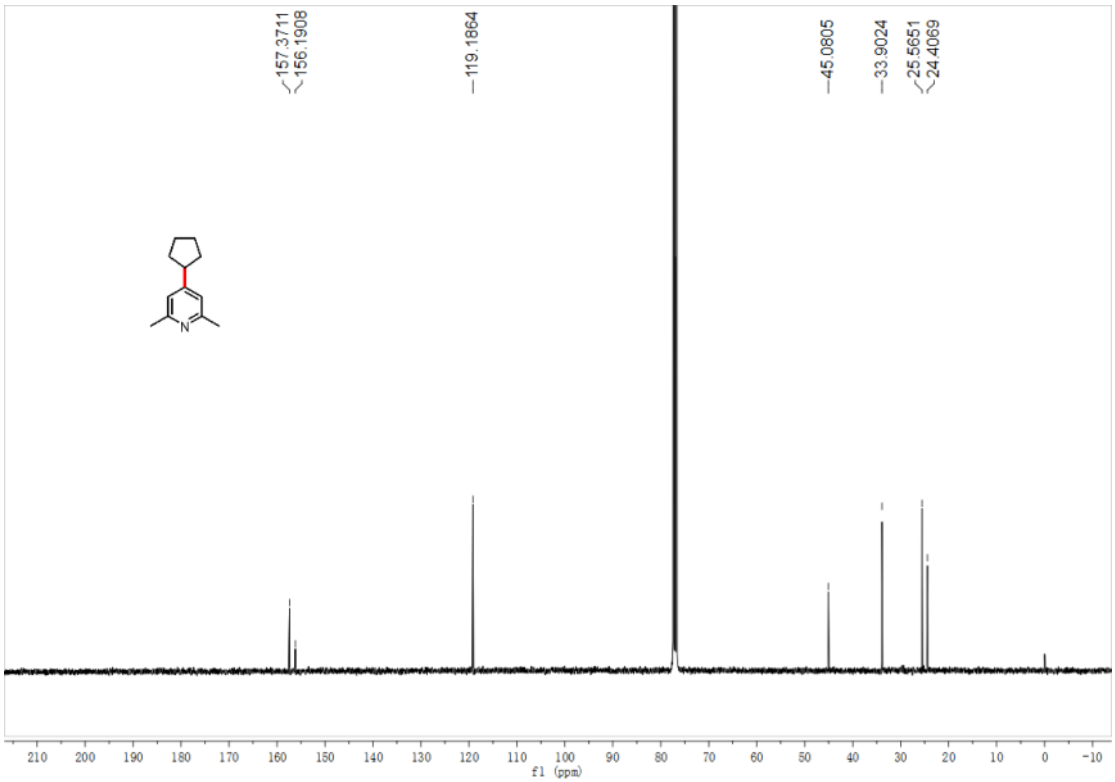
^{13}C NMR spectrum of compound **52b**



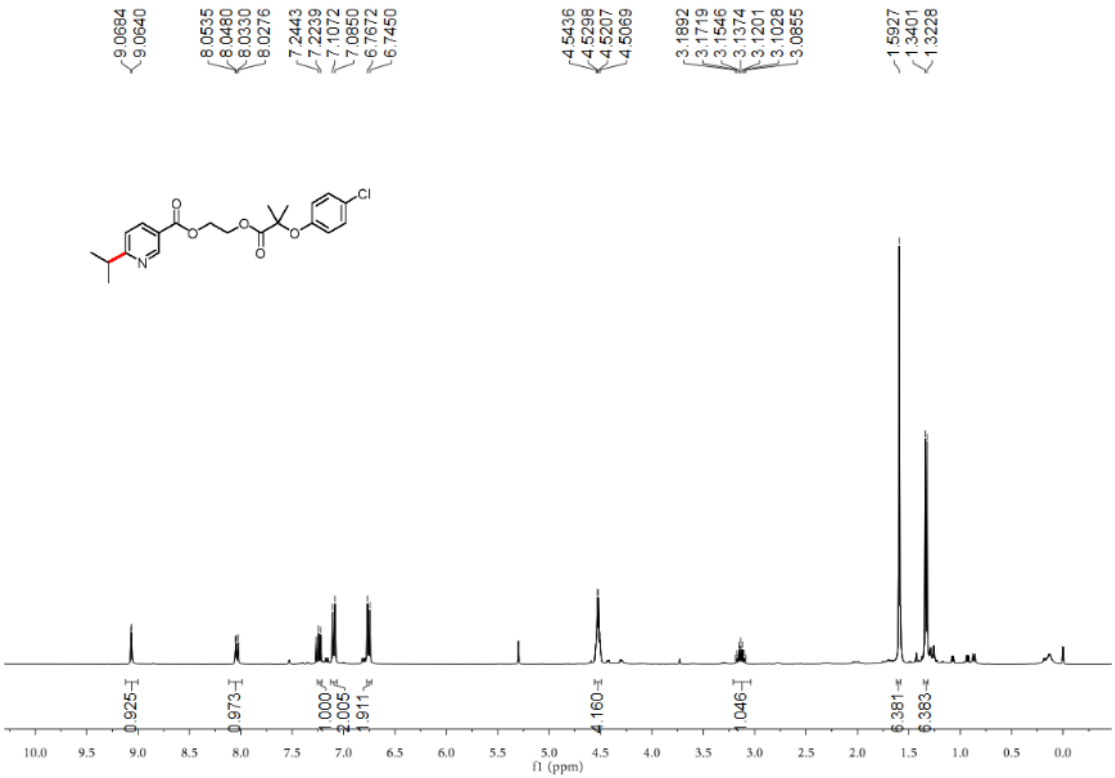
^{1}H NMR spectrum of compound **52c**



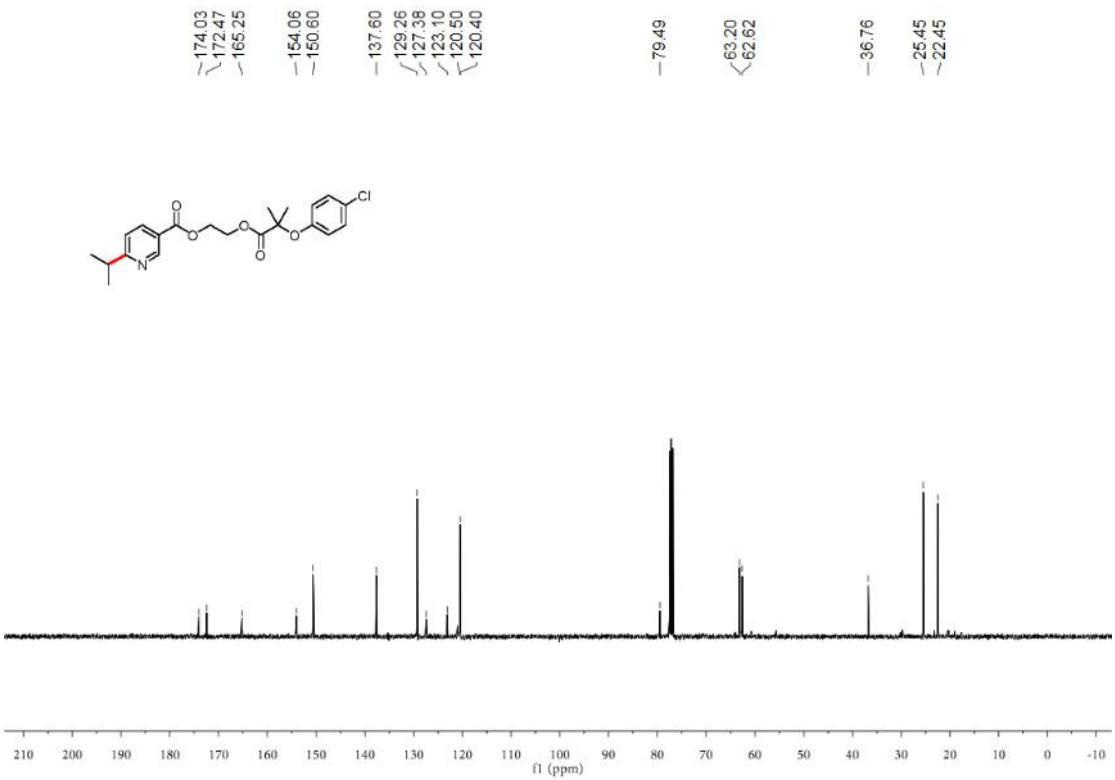
^{13}C NMR spectrum of compound **52c**



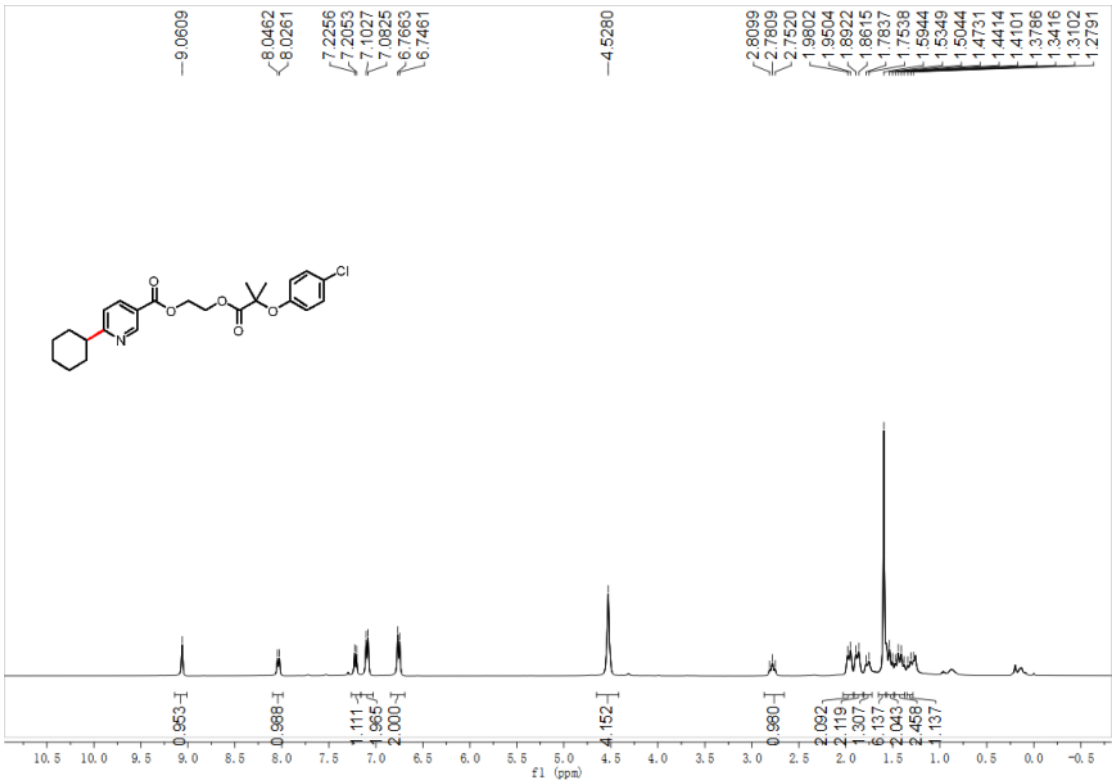
^{1}H NMR spectrum of compound **53a**



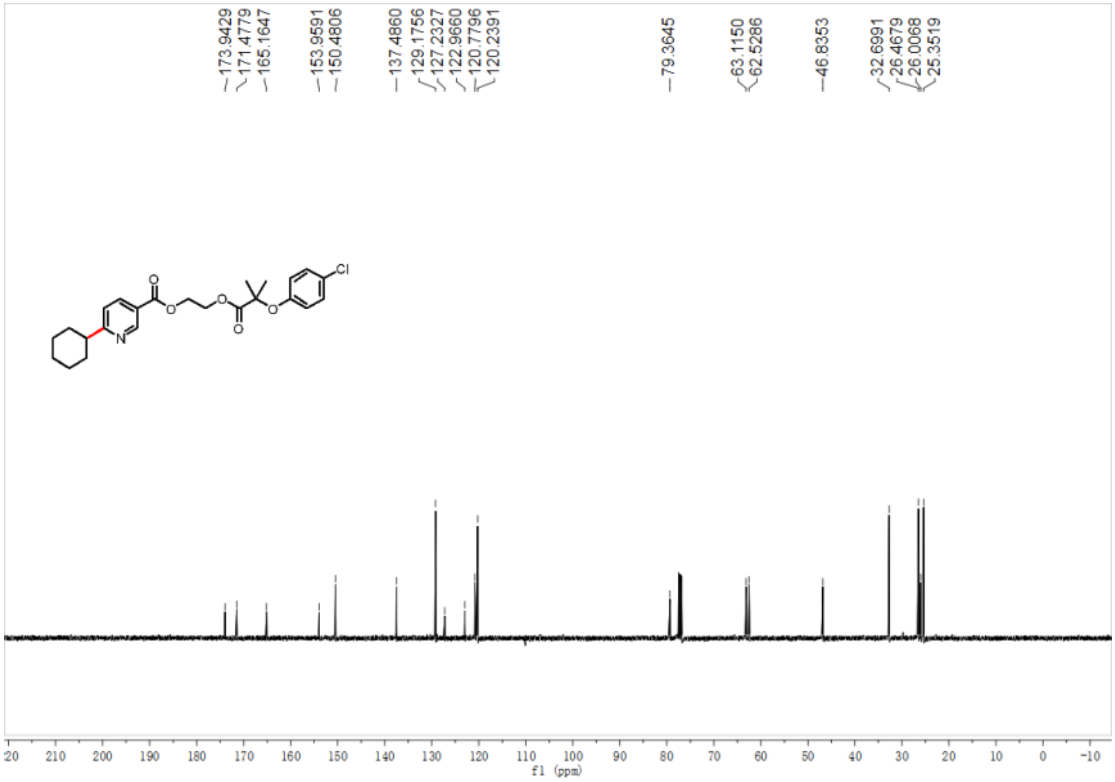
^{13}C NMR spectrum of compound **53a**



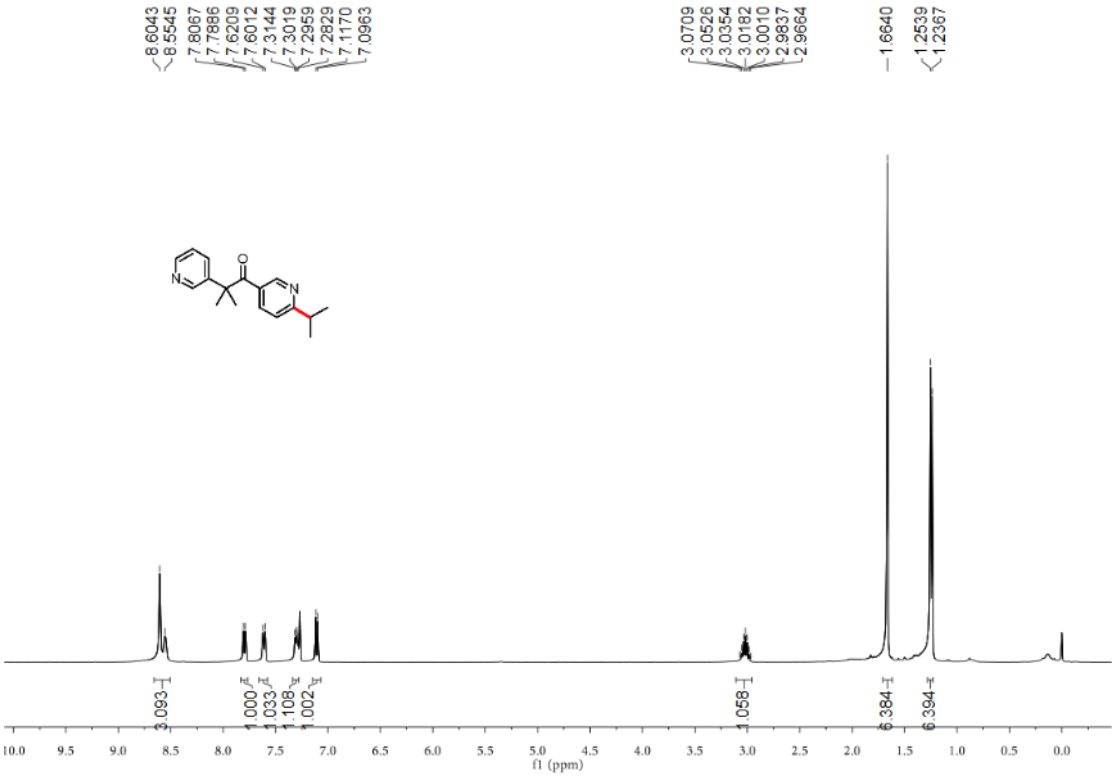
^{1}H NMR spectrum of compound **53b**



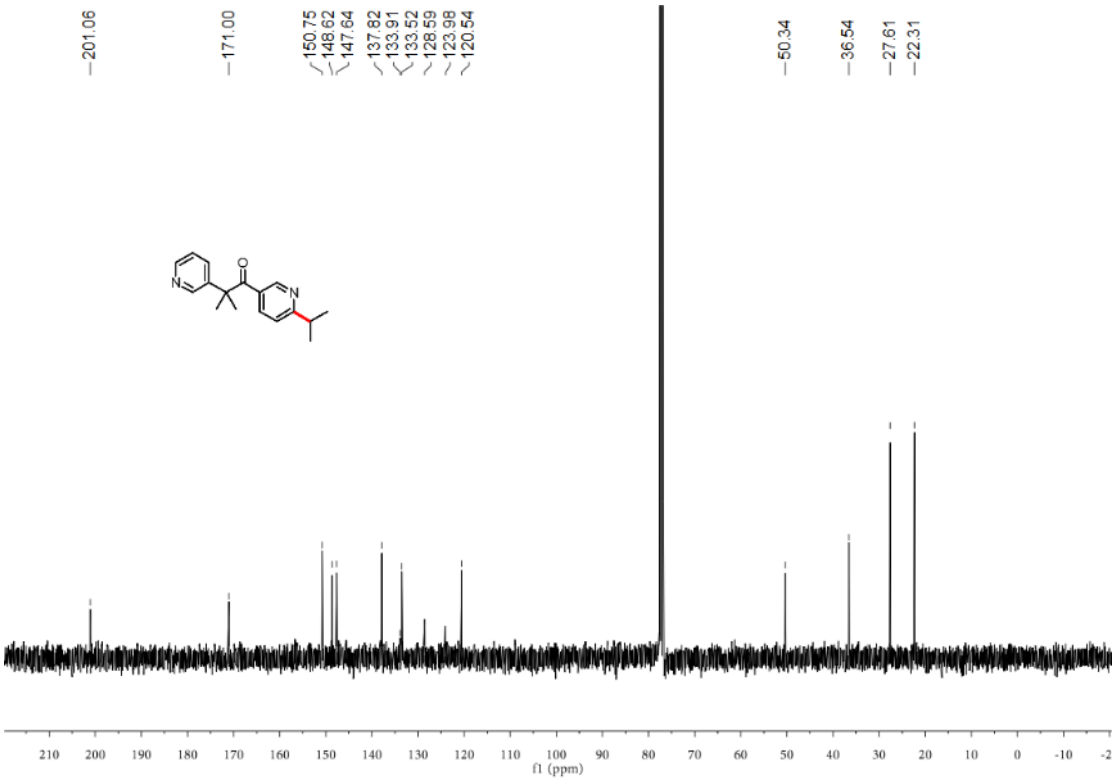
^{13}C NMR spectrum of compound **53b**



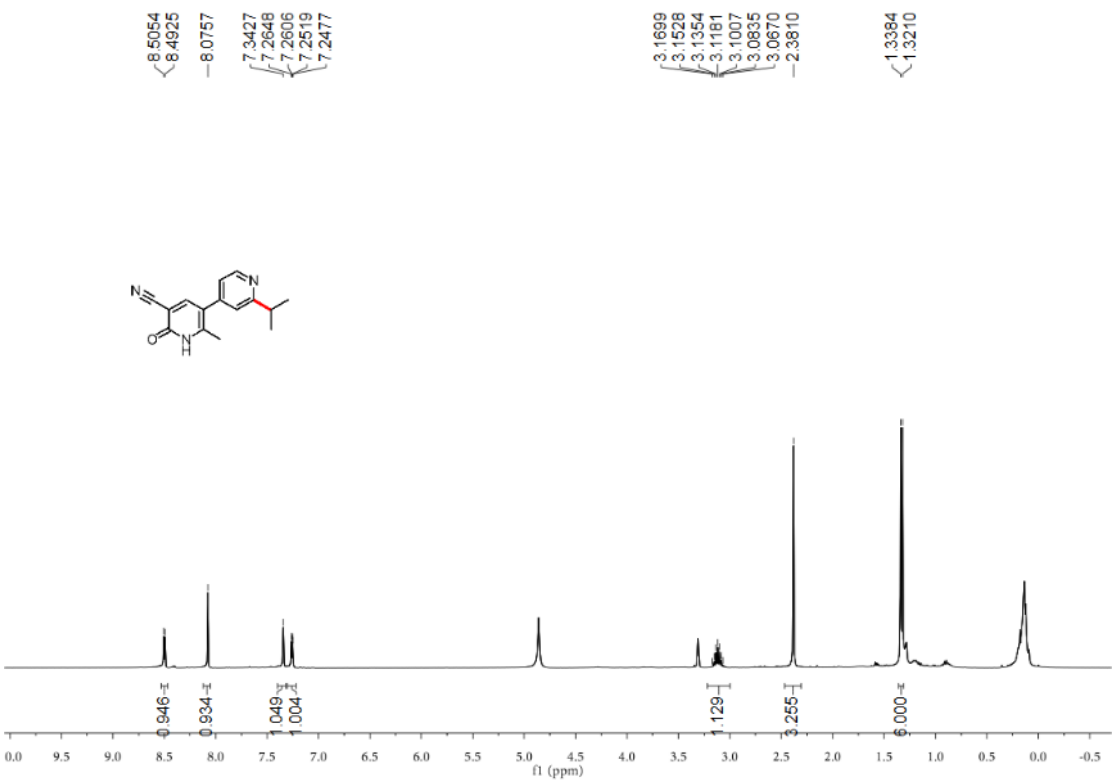
^{1}H NMR spectrum of compound **54**



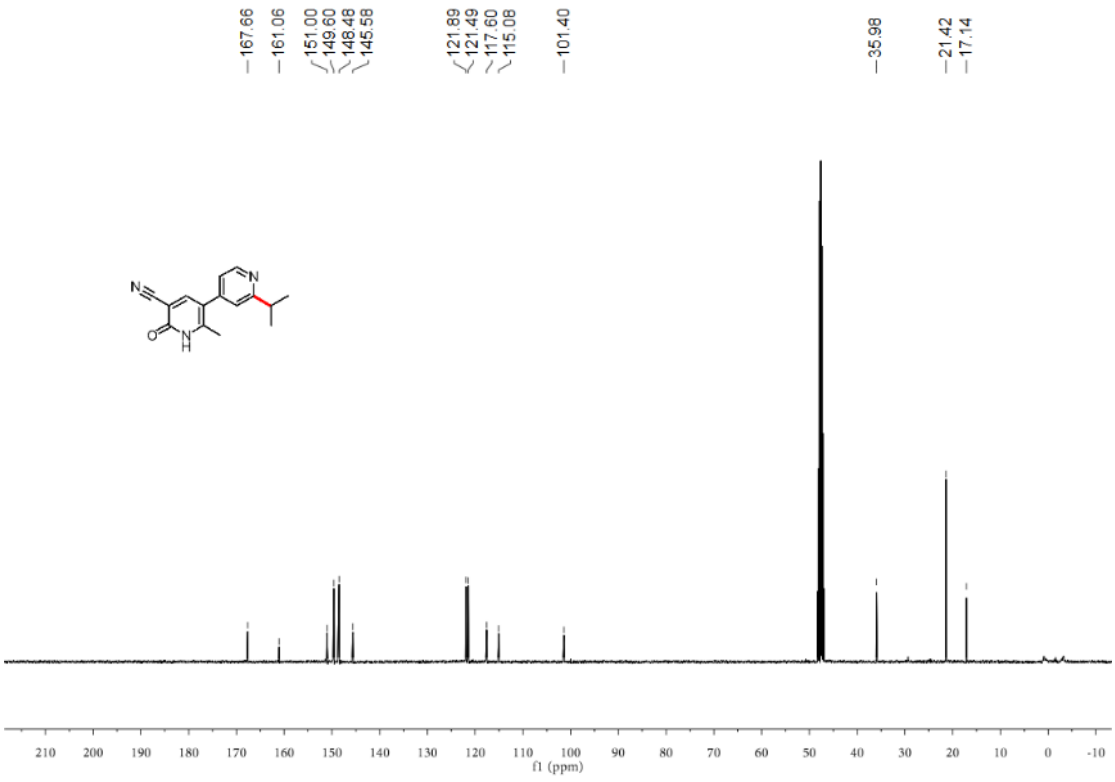
^{13}C NMR spectrum of compound **54**



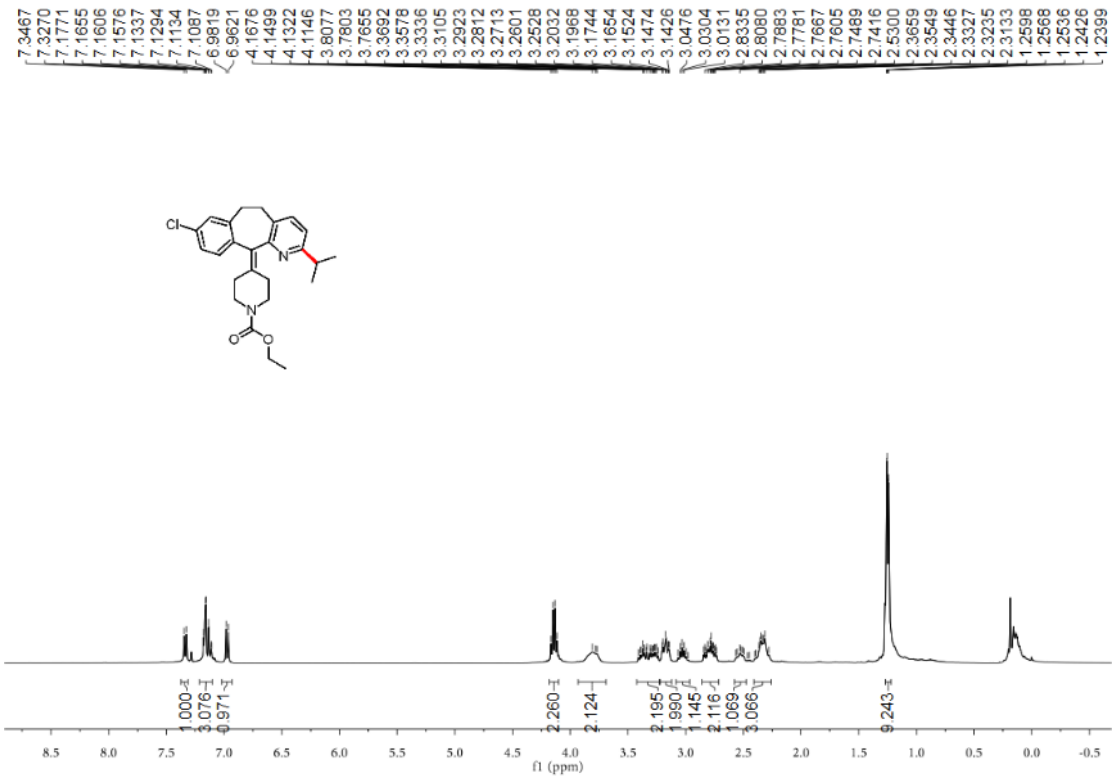
^{1}H NMR spectrum of compound **55**



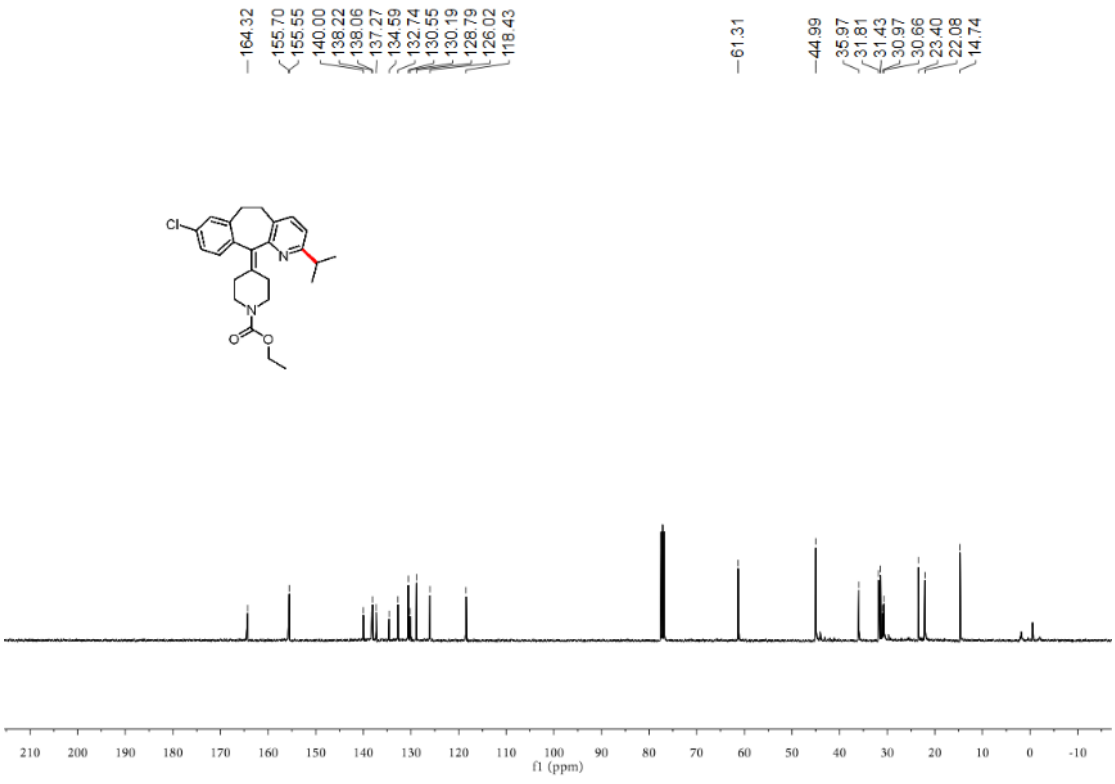
^{13}C NMR spectrum of compound **55**



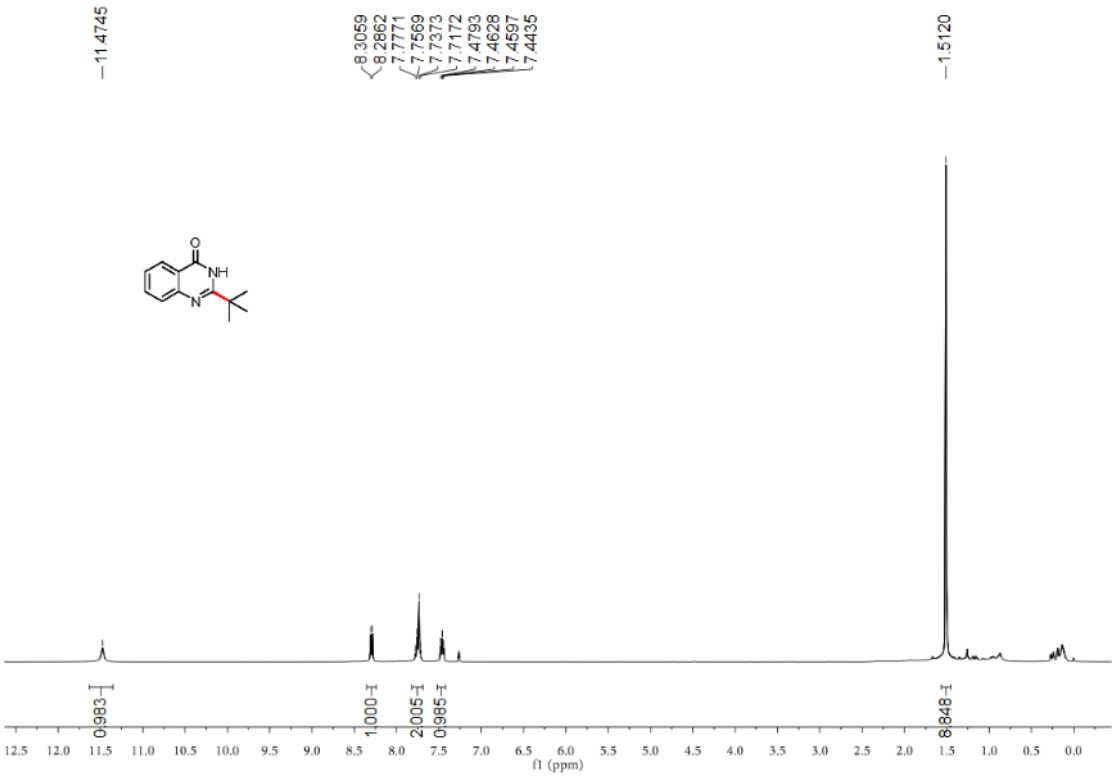
^{1}H NMR spectrum of compound **56**



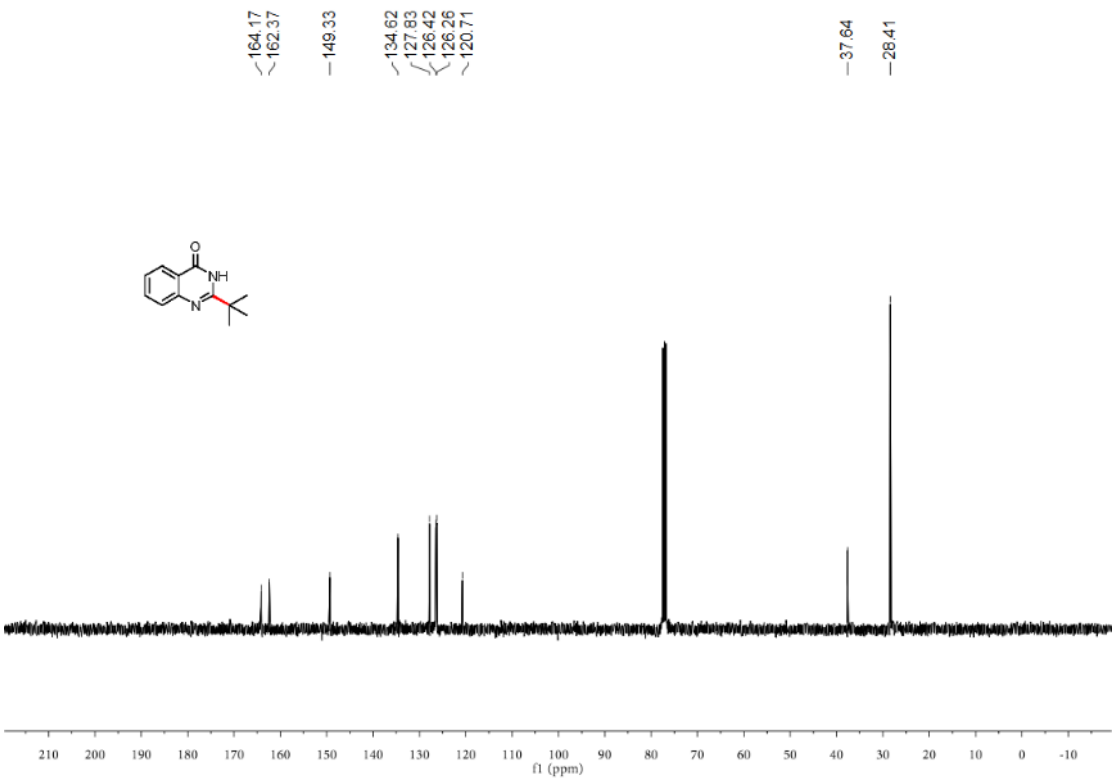
^{13}C NMR spectrum of compound **56**



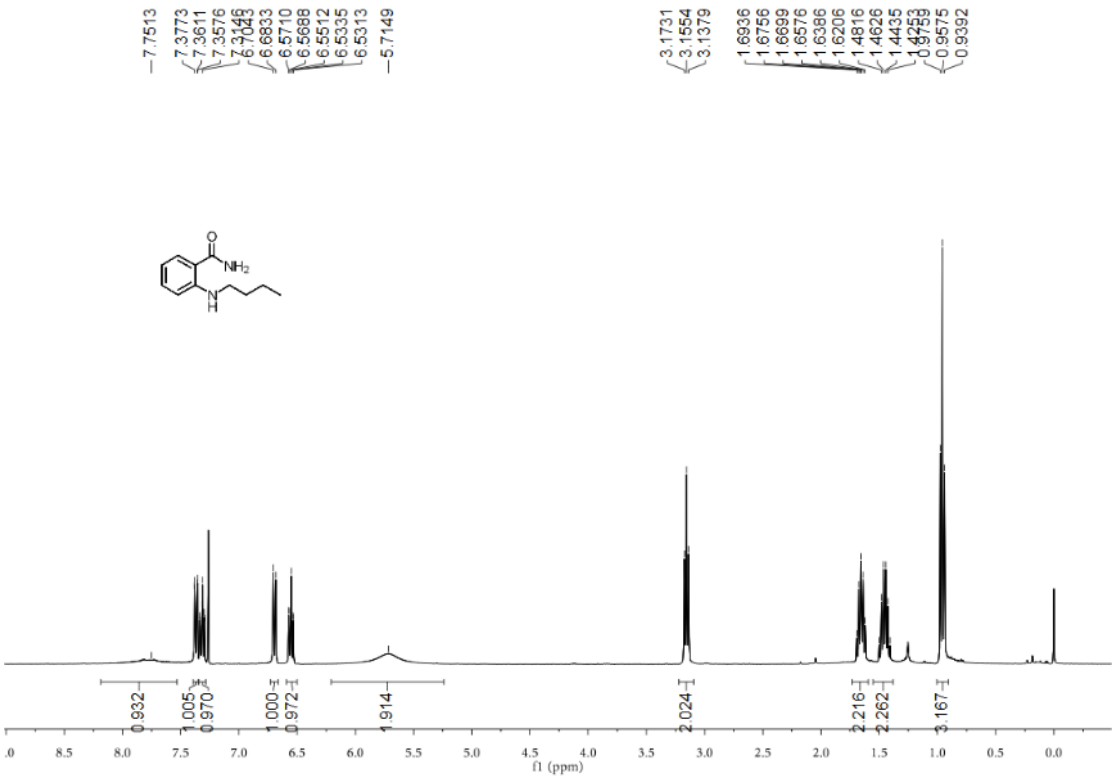
^{1}H NMR spectrum of compound **58**



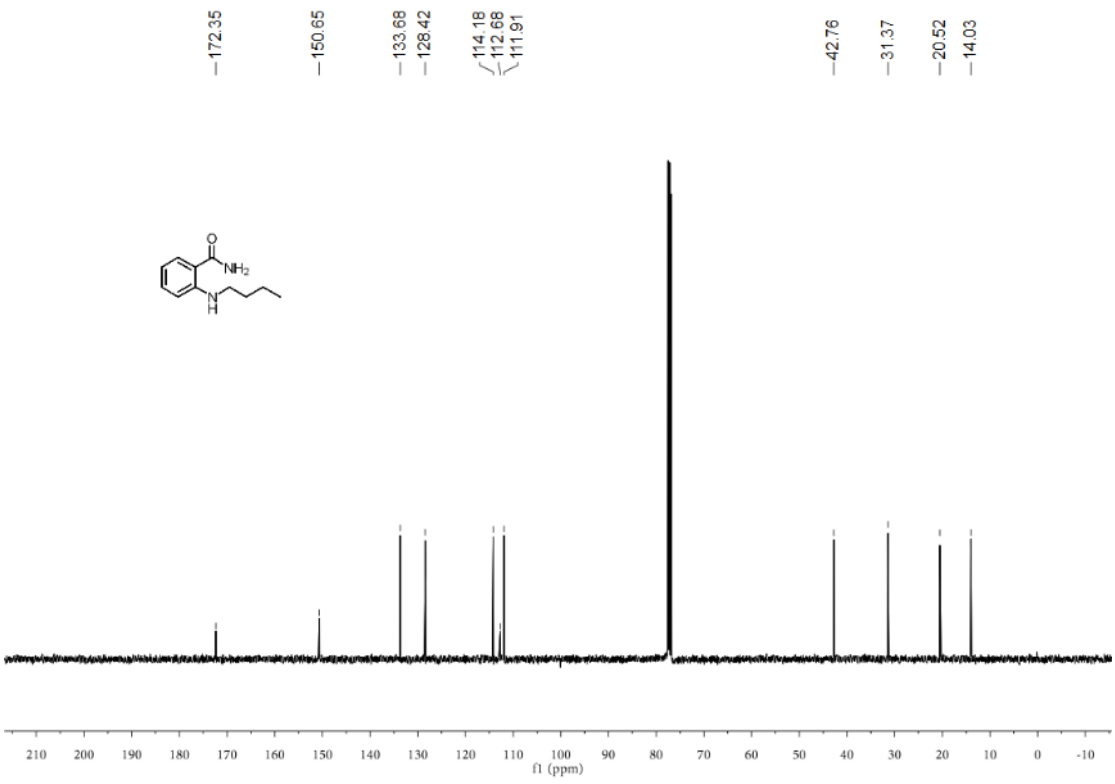
^{13}C NMR spectrum of compound **58**



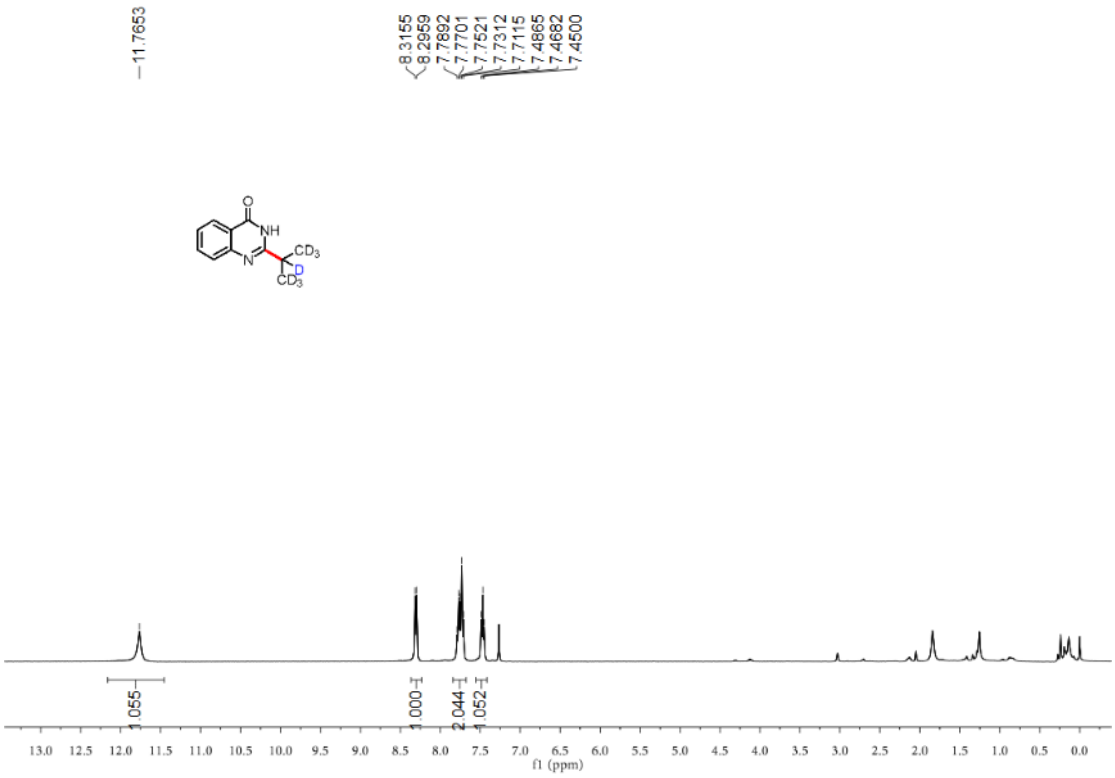
^{1}H NMR spectrum of compound **61**



^{13}C NMR spectrum of compound **61**



^{1}H NMR spectrum of compound **70**



^{13}C NMR spectrum of compound **70**