Visible-Light-Mediated Minisci C–H Alkylation of Heteroarenes with Unactivated Alkyl Halides Using O_2 as an Oxidant

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Supporting Information

1. General Information

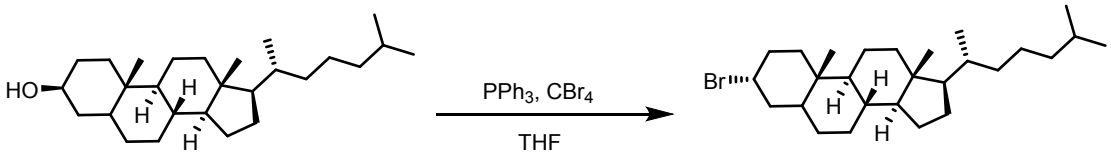
Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane.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

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

2. Preparation of photocatalyst Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$

The photocatalyst was synthesized according to literature report.[1] The spectral Data of the photocatalyst is consistent with the literature data. The other photocatalysts (Eosin Y, Fluorescein, [Ru(bpy)$_3$]Cl$_2$·6H$_2$O, Ru(bpy)$_3$(PF$_6$)$_2$, Ir(ppy)$_3$ and Mes-Acr) are commercially available.

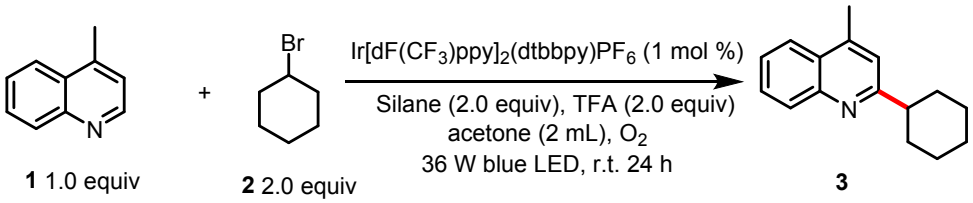
3. Preparation of 3R-Bromo-5R-cholestane



3R-Bromo-5R-cholestane was synthesized according to literature report.[2] The spectral Data is consistent with the literature data.

4. Investigation of the Key Reaction Parameters.

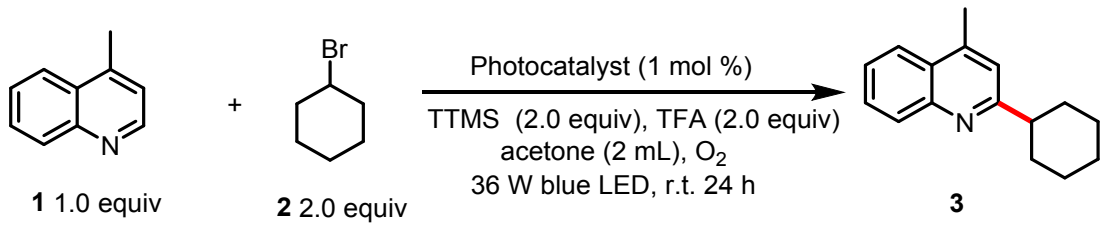
Table S1: Screening of different silanes[a]



entry	silanes	yield (%)[b]
1	TTMS	82
2	Ph_3SiH	NR
3	Et_3SiH	NR
5	Cl_3SiH	NR

[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol), Silane (0.4 mmol), TFA (0.4 mmol) and acetone (2 mL) under O_2 atmosphere. [b]Isolated yield. NR = no reaction.

Table S2: Screening of photocatalysts[a]

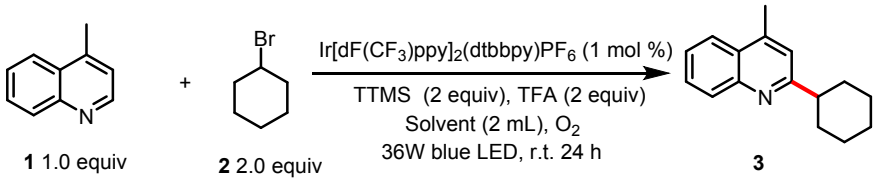


entry	photocatalyst	yield (%)[b]
1	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	82
2	Ir(ppy)$_3$	trace
3	[Ru(bpy)$_3$]Cl$_2$·6H$_2$O	NR
4	[Ru(bpy)$_3$](PF$_6$)$_2$	NR
5	Fluorescein	trace[c]

6	(Mes-Acr)ClO_4	NR[c]
7	Eosin-Y	trace [c]

[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol), photocatalyst (0.002 mmol), TTMS (0.4 mmol), TFA (0.4 mmol) and acetone (2 mL) under O_2 atmosphere. [b]Isolated yield. [c]Photocatalyst (0.004 mmol). NR = no reaction.

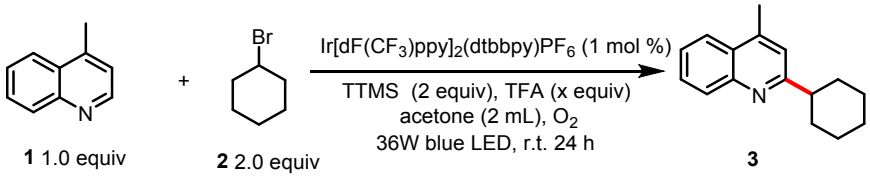
Table S3: Screening of different solvents[a]



entry	solvent	yield (%)[b]
1	acetone	82
2	MeOH	52
3	dioxane	20
4	DMF	23
5	CH_3CN	68

[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.002 mmol), TTMS (0.4 mmol), TFA (0.4 mmol) and Solvent (2 mL) under O_2 atmosphere. [b]Isolated yield.

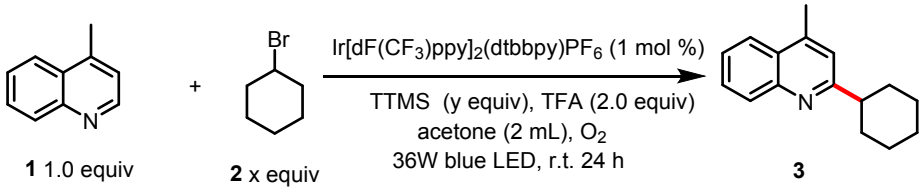
Table S4: Screening of the amount of TFA[a]



entry	x eq. TFA	yield (%)[b]
1	0	28
2	1	74
3	2	82
4	4	81

[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.002 mmol), TTMS (0.4 mmol), TFA (0.2x mmol) and acetone (2 mL) under O_2 atmosphere. [b]Isolated yield.

Table S5: Screening of the amount of bromocyclohexane and TTMS[a]



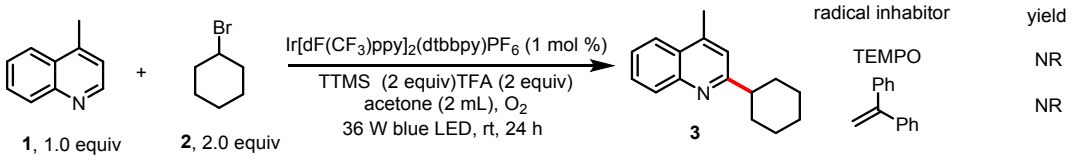
entry	x eq. **2**	y eq. TTMS	yield (%)[b]
1	2	2	82
2	1.5	2	71

3	1.2	2	52
4	2	1.5	73
6	2	1.2	49

[a]General conditions: **1** (0.2 mmol), **2** (0.2x mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.002 mmol), TTMS (0.2y mmol), TFA (0.4 mmol) and acetone (2 mL) under O_2 atmosphere. [b]Isolated yield.

5. Investigation of the mechamism.

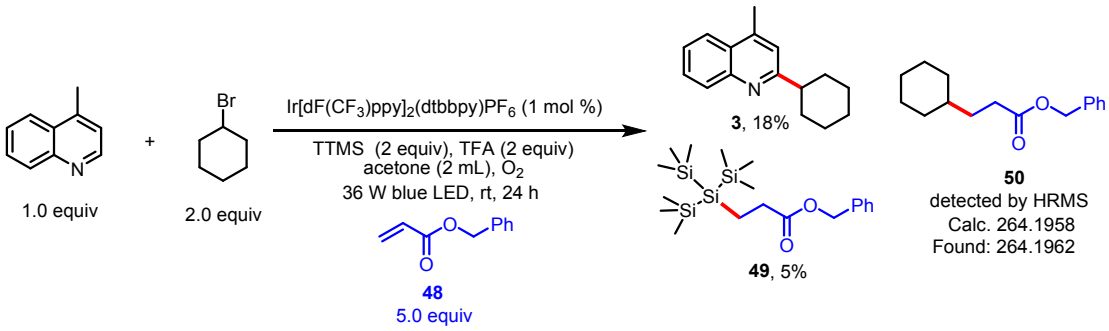
5.1 TEMPO and BHT were used as radical scavengers.



Scheme S1

To a 10 mL glass vial was added Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.24mg, 0.002 mmol, 1 mol %), **1** (0.2 mmol, 1.0 equiv), TTMS (123 μL, 0.4 mmol, 2.0 equiv), **2** (0.4 mmol, 2.0 equiv), TEMPO (78.1 mg, 0.5 mmol, 2.5 equiv) or BHT (110 mg, 0.5 mmol, 2.5 equiv), TFA (30 μL, 0.4 mmol, 2.0 equiv) and 2.0 mL of acetone. The reaction mixture was degassed by bubbling with O_2 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 corresponding alkylated product **3** was not observed based on ^{1}H NMR analysis.

5.2 Benzyl acrylate 48 was used as radical scavengers.



Scheme S2

To a 10 mL glass vial was added Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.24 mg, 0.002 mmol, 1 mol %), **1** (0.2 mmol, 1.0 equiv), TTMS (123 μL, 0.4 mmol, 2.0 equiv), **2** (0.4 mmol, 2.0 equiv), benzyl acrylate **48** (1.0 mmol, 5.0 equiv), TFA (30 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of acetone. The reaction mixture was degassed by bubbling with O_2 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 products **3** and **49**. The corresponding product of cyclohexyl radical trapping, benzyl 3-cyclohexylpropanoate **50** can be observed by HR-MS (positive mode ESI).

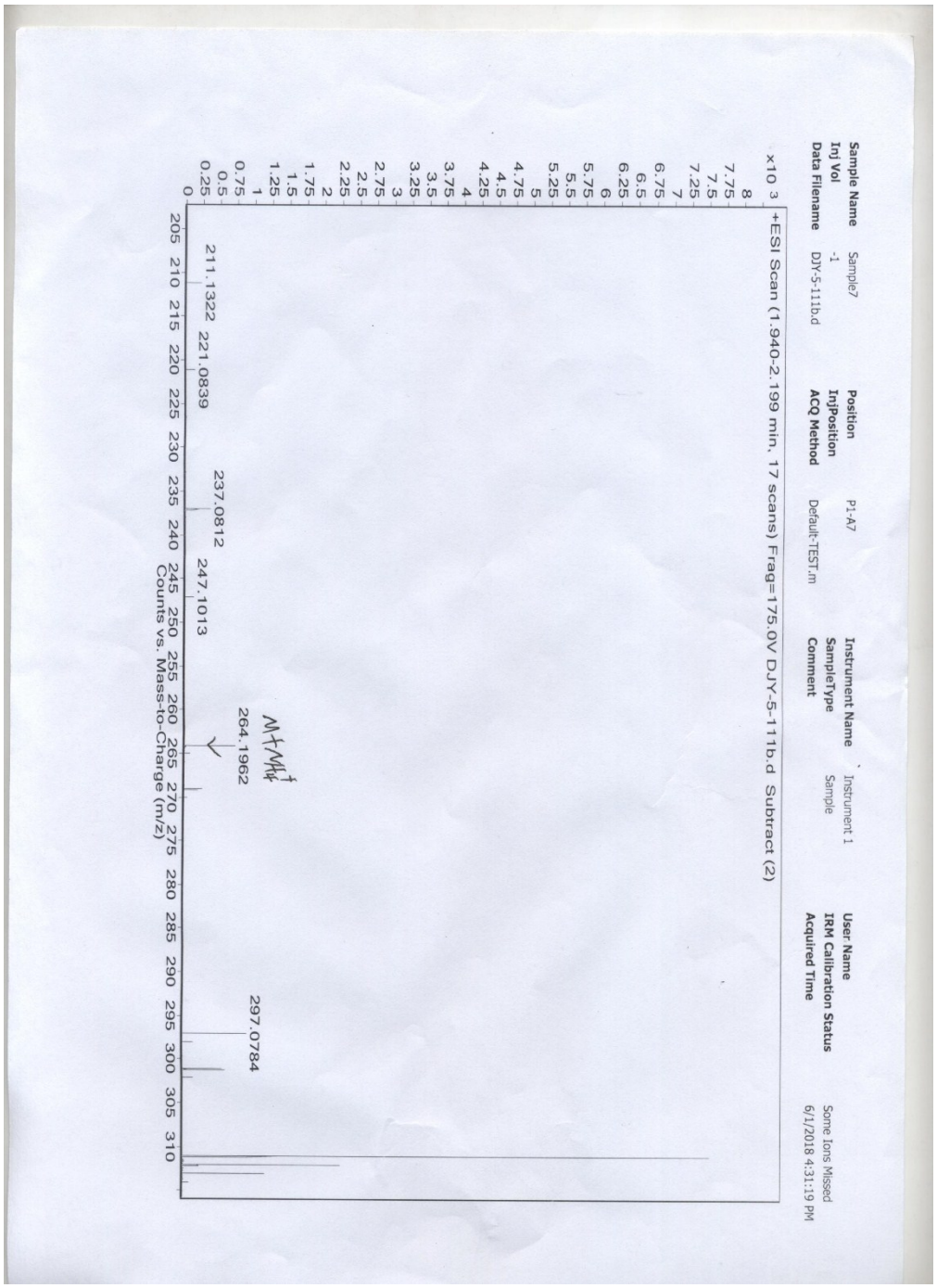
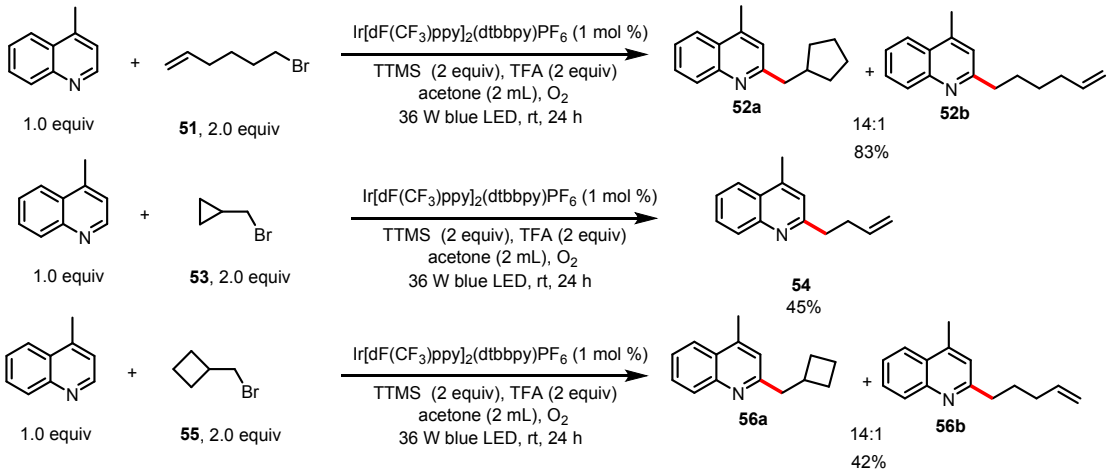


Figure S2 HR-ESI mass spectra of benzyl 3-cyclohexylpropanoate (**50)**

5.3 Radical clock experiment.



Scheme S3

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 %), 1 (0.3 mmol, 1.0 equiv), TTMS (185 µL, 0.6 mmol, 2.0 equiv), bromoalkane (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 O_2 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.

5.4 Light/dark experiment.

Eight standard reaction mixtures in 10 mL glass vials were charged with Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (2.24 mg, 0.002 mmol, 1 mol %), **1** (0.2 mmol, 1.0 equiv), TTMS (123 µL, 0.4 mmol, 2.0 equiv), **2** (0.4 mmol, 2.0 equiv), TFA (30 µL, 0.4 mmol, 2.0 equiv) and 2.0 mL of acetone. The reaction mixtures were degassed by bubbling with O_2 for 15 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 2 h, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 2 h of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h, then, a vial was removed for analysis and the Blue LED was turned back on to

irradiate the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 2 h, and then it was analyzed. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.

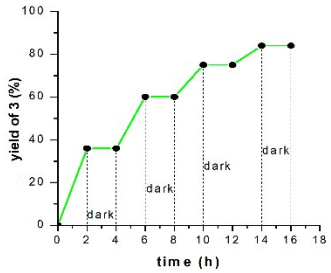


Figure S3 Light/dark experiment.

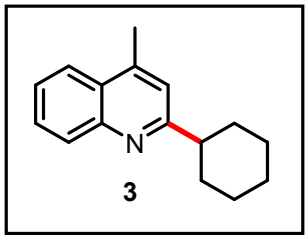
6. Experimental Procedures and Product Characterization

6.1 General Procedure 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), TTMS (185 μL, 0.6 mmol, 2.0 equiv), bromoalkane (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 O_2 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.

6.2. Product Characterization

2-cyclohexyl-4-methylquinoline (3).

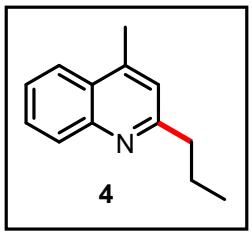


According to the *general procedure*. The spectral Data is consistent with the literature data.[3]
Yellow oil (55.4 mg, 82%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.16 (s, 1H), 3.02 – 2.80 (m, 1H), 2.67 (s, 3H), 2.01 (d, J = 12.0 Hz, 2H), 1.89 (d, J = 12.8 Hz, 2H), 1.79 (d, J = 12.4 Hz, 1H), 1.62 (ddd, J = 24.8, 12.4, 2.4 Hz, 2H), 1.46 (dd, J = 25.2, 12.4 Hz, 2H), 1.40 – 1.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 147.7, 144.4, 129.5,

129.0, 127.1, 125.5, 123.7, 120.3, 47.7, 32.9, 26.7, 26.2, 19.0.

HRMS (ESI) calcd for $C_{16}H_{20}N$ $[M + H]^+$ 226.1590, found 226.1595.

4-methyl-2-propylquinoline (4).



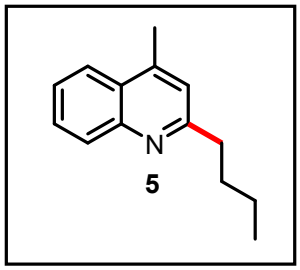
According to the *general procedure*. Yellow oil (27.8 mg, 50%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.4, 0.8 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.50 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.15 (s, 1H), 2.96 – 2.84 (m, 2H), 2.68 (d, J = 0.8 Hz, 3H), 1.83 (dq, J = 14.8, 7.6 Hz, 2H), 1.02 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 147.8, 144.4, 129.4, 129.2, 126.9, 125.6, 123.7, 122.3, 41.3, 23.5, 18.9, 14.2.

HRMS (ESI) calcd for $C_{13}H_{16}N$ $[M + H]^+$ 186.1277, 186.1280.

2-butyl-4-methylquinoline (5).



According to the *general procedure*. The spectral Data is consistent with the literature data.[4]

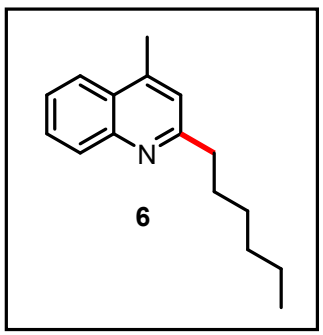
Yellow oil (36.4 mg, 61%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.4, 0.8 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.50 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.14 (s, 1H), 2.98 – 2.85 (m, 2H), 2.67 (d, J = 0.8 Hz, 3H), 1.83 – 1.71 (m, 2H), 1.43 (dt, J = 14.8, 7.2 Hz, 2H), 0.96 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 147.8, 144.3, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 39.1, 32.4, 22.9, 18.8, 14.1.

HRMS (ESI) calcd for $C_{14}H_{18}N$ $[M + H]^+$ 200.1434, found 200.1438.

2-hexyl-4-methylquinoline (6).



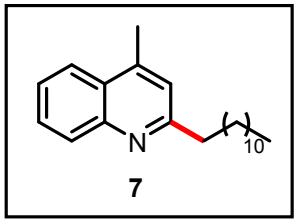
According to the *general procedure*. Yellow oil (57.2 mg, 84%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.14 (s, 1H), 2.96 – 2.86 (m, 2H), 2.67 (s, 3H), 1.86 – 1.71 (m, 2H), 1.50 – 1.20 (m, 6H), 0.88 (t, J = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 147.8, 144.3, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 39.4, 31.9, 30.2, 29.4, 22.7, 18.8, 14.2.

HRMS (ESI) calcd for $C_{16}H_{22}N$ $[M + H]^+$ 228.1747, found 228.1748.

2-dodecyl-4-methylquinoline (7).



7

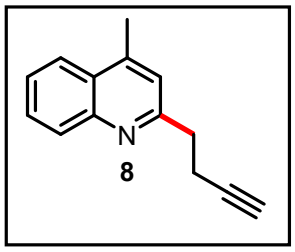
According to the *general procedure*. Yellow oil (42.0 mg, 45%).

R_f 0.50 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.55 – 7.47 (m, 1H), 7.15 (s, 1H), 3.00 – 2.84 (m, 2H), 2.68 (s, 3H), 1.79 (dt, J = 15.6, 7.6 Hz, 2H), 1.42 – 1.19 (m, 18H), 0.87 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 147.3, 129.4, 129.1, 126.9, 125.7, 123.7, 122.2, 119.8, 39.2, 32.0, 30.2, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 22.8, 22.6, 18.9, 14.2.

HRMS (ESI) calcd for $C_{22}H_{34}N$ $[M + H]^+$ 312.2686, found 312.2689.

2-(but-3-yn-1-yl)-4-methylquinoline (8).



8

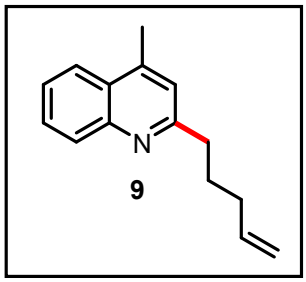
According to the *general procedure*. Yellow oil (43.9 mg, 75%).

R_f 0.30 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.71 – 7.61 (m, 1H), 7.49 (dd, J = 11.2, 4.0 Hz, 1H), 7.17 (s, 1H), 3.13 (t, J = 7.6 Hz, 2H), 2.71 (td, J = 7.6, 2.4 Hz, 2H), 2.66 (s, 3H), 1.93 (t, J = 2.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 147.9, 144.6, 129.6, 129.3, 127.1, 125.8, 123.8, 122.3, 83.9, 69.0, 37.8, 18.9, 18.6.

HRMS (ESI) calcd for $C_{14}H_{14}N$ $[M + H]^+$ 196.1121, found 196.1126.

4-methyl-2-(pent-4-en-1-yl)quinoline (9).



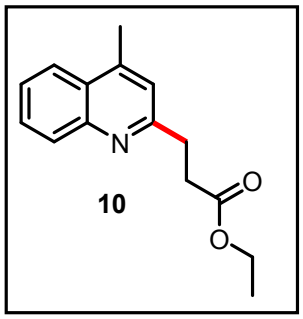
According to the *general procedure*. Yellow oil (51.3 mg, 81%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.57 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.40 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.04 (s, 1H), 5.77 (ddt, J = 16.8, 10.0, 6.4 Hz, 1H), 5.01 – 4.83 (m, 2H), 2.91 – 2.79 (m, 2H), 2.58 (s, 3H), 2.08 (dd, J = 14.4, 7.6 Hz, 2H), 1.81 (dt, J = 15.2, 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 147.8, 144.4, 138.6, 129.4, 129.2, 126.9, 125.6, 123.7, 122.2, 115.0, 38.7, 33.7, 29.3, 18.8.

HRMS (ESI) calcd for $C_{15}H_{18}N$ $[M + H]^+$ 212.1434, found 212.1436.

ethyl 3-(4-methylquinolin-2-yl)propanoate (10).



According to the *general procedure*. The spectral Data is consistent with the literature data.[5]

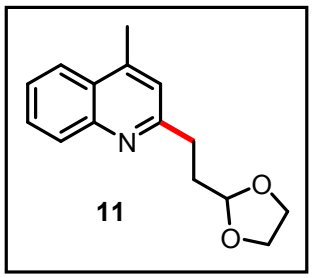
Yellow oil (40.8 mg, 56%).

R_f 0.40 (Petroleum ether/EtOAc, 7/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.4, 0.8 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.50 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.17 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.25 (t, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.67 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 160.3, 147.8, 144.5, 129.5, 129.2, 127.0, 125.7, 123.7, 122.3, 60.5, 33.6, 33.4, 18.8, 14.4.

HRMS (ESI) calcd for $C_{15}H_{18}NO_2$ $[M + H]^+$ 244.1332, found 244.1334.

2-(2-(1,3-dioxolan-2-yl)ethyl)-4-methylquinoline (11).



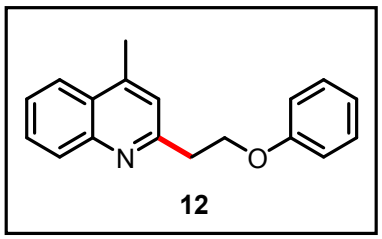
According to the *general procedure*. Yellow oil (32.1 mg, 44%).

R_f 0.30 (Petroleum ether/EtOAc, 7/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.50 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.17 (s, 1H), 5.00 (t, J = 4.8 Hz, 1H), 4.04 – 3.97 (m, 2H), 3.91 – 3.84 (m, 2H), 3.13 – 3.02 (m, 2H), 2.67 (d, J = 0.8 Hz, 3H), 2.26 – 2.16 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 147.7, 144.7, 129.4, 129.3, 127.0, 125.7, 123.7, 122.3, 104.0, 65.1, 33.8, 33.3, 18.8.

HRMS (ESI) calcd for $C_{15}H_{18}NO_2$ $[M + H]^+$ 244.1332, found 244.1336.

4-methyl-2-(2-phenoxyethyl)quinoline (12).



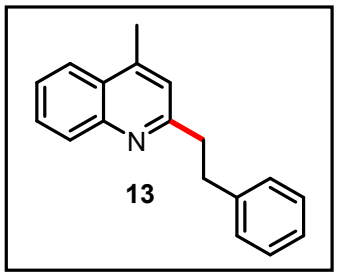
According to the *general procedure*. Yellow oil (35.5 mg, 45%).

R_f 0.40 (Petroleum ether/EtOAc, 7/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.96 (dd, J = 8.4, 0.8 Hz, 1H), 7.69 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.52 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.34 – 7.21 (m, 3H), 7.00 – 6.88 (m, 3H), 4.45 (t, J = 6.8 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 2.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 158.9, 147.8, 144.7, 129.5, 129.4, 129.3, 127.1, 125.9, 123.8, 122.9, 120.9, 114.8, 67.3, 38.8, 18.9.

HRMS (ESI) calcd for $C_{18}H_{18}NO$ $[M + H]^+$ 264.1383, found 264.1388.

4-methyl-2-phenethylquinoline (13).



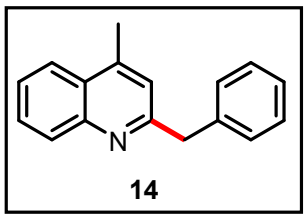
According to the *general procedure*. Yellow oil (57.8 mg, 78%).

R_f 0.40 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.33 – 7.22 (m, 4H), 7.23 – 7.16 (m, 1H), 7.09 (s, 1H), 3.29 – 3.20 (m, 2H), 3.18 – 3.09 (m, 2H), 2.65 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 147.8, 144.5, 141.8, 129.4, 129.3, 128.6, 128.5, 127.0, 126.1, 125.7, 123.8, 122.4, 41.0, 36.0, 18.8.

HRMS (ESI) calcd for $C_{18}H_{18}N$ $[M + H]^+$ 248.1434, found 248.1436.

4-methyl-2-(2-phenoxyethyl)quinoline (14).



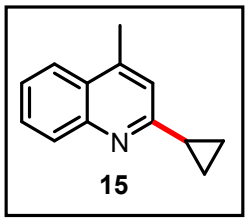
According to the *general procedure*. Yellow oil (59.4 mg, 85%).

R_f 0.30 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.4, 0.8 Hz, 1H), 7.68 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.50 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 7.05 (s, 1H), 4.29 (s, 2H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0, 147.7, 144.8, 139.5, 129.6, 129.3, 129.3, 128.7, 127.0, 126.6, 125.9, 123.7, 122.3, 45.6, 18.8.

HRMS (ESI) calcd for $C_{17}H_{16}N$ $[M + H]^+$ 234.1277, found 234.1278.

2-cyclopropyl-4-methylquinoline (15).



According to the *general procedure*. The spectral Data is consistent with the literature data.[4]

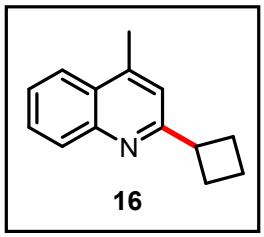
Yellow oil (32.4 mg, 59%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 6.98 (s, 1H), 2.64 (s, 3H), 2.26 – 2.11 (m, 1H), 1.16 – 1.02 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 147.9, 143.9, 129.3, 129.1, 126.9, 125.1, 123.7, 119.9, 18.8, 18.1, 10.1.

HRMS (ESI) calcd for $C_{13}H_{14}N$ $[M + H]^+$ 184.1121, found 184.1122.

2-cyclobutyl-4-methylquinoline (16).



According to the *general procedure*. The spectral Data is consistent with the literature data.[5]

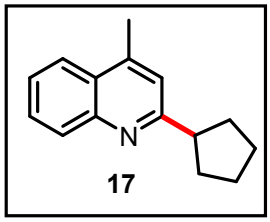
Yellow oil (39.6 mg, 67%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.53 – 7.44 (m, 1H), 7.19 (s, 1H), 3.83 (p, J = 8.8 Hz, 1H), 2.67 (s, 3H), 2.50 – 2.35 (m, 4H), 2.21 – 2.05 (m, 1H), 2.00 – 1.87 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 147.7, 144.2, 129.6, 129.0, 127.0, 125.5, 123.6, 120.3, 42.8, 28.3, 18.9, 18.5.

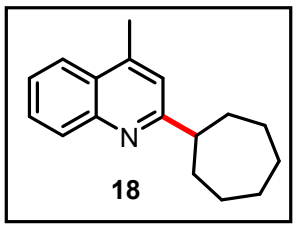
HRMS (ESI) calcd for $C_{14}H_{16}N$ $[M + H]^+$ 198.1277, found 198.1279.

2-cyclopentyl-4-methylquinoline (17).



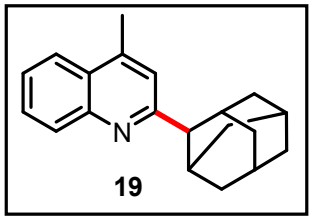
According to the *general procedure*. The spectral Data is consistent with the literature data.[3]
Yellow oil (45.6 mg, 72%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.70 – 7.61 (m, 1H), 7.52 – 7.44 (m, 1H), 7.17 (s, 1H), 3.41 – 3.27 (m, 1H), 2.67 (s, 3H), 2.17 (ddd, J = 10.8, 9.2, 2.4 Hz, 2H), 1.97 – 1.81 (m, 4H), 1.81 – 1.66 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 147.6, 144.2, 129.5, 129.0, 127.1, 125.4, 123.6, 120.7, 48.9, 33.7, 26.1, 18.9.
HRMS (ESI) calcd for $C_{15}H_{18}N$ $[M + H]^+$ 212.1434, found 212.1436.

2-cycloheptyl-4-methylquinoline (18).



According to the *general procedure*. Yellow oil (55.9 mg, 78%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.4, 0.8 Hz, 1H), 7.65 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.47 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.13 (s, 1H), 3.03 (tt, J = 10.4, 3.6 Hz, 1H), 2.66 (s, 3H), 2.12 – 1.98 (m, 2H), 1.93 – 1.52 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 147.5, 144.5, 129.5, 129.0, 127.0, 125.4, 123.6, 120.4, 49.7, 35.2, 28.0, 27.6, 18.9.
HRMS (ESI) calcd for $C_{17}H_{22}N$ $[M + H]^+$ 240.1747, found 240.1750.

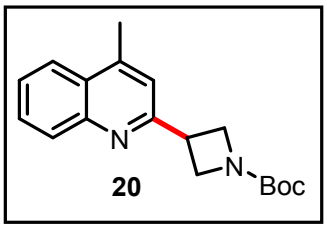
2-(adamantan-2-yl)-4-methylquinoline (19).



According to the *general procedure*. The spectral Data is consistent with the literature data.[5]
White solid (49.9 mg, 60%). M.p. = 89 – 90 °C.
R_f 0.80 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.4, 0.8 Hz, 1H), 7.66 (ddd, J =

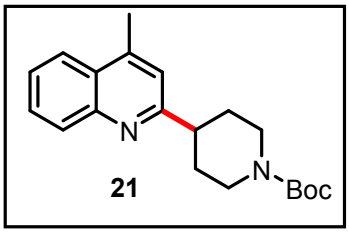
8.4, 6.8, 1.2 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.28 (d, J = 8.8 Hz, 1H), 3.20 (s, 1H), 2.78 (s, 2H), 2.69 (s, 3H), 2.07 – 1.94 (m, 7H), 1.81 (s, 3H), 1.63 (d, J = 12.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 147.8, 143.5, 129.9, 128.7, 126.6, 125.4, 123.6, 120.6, 50.5, 39.3, 38.0, 32.7, 31.0, 28.2, 28.1, 19.0.
HRMS (ESI) calcd for $C_{20}H_{24}N$ $[M + H]^+$ 278.1903, found 278.1906.

***tert*-butyl 3-(4-methylquinolin-2-yl)azetidine-1-carboxylate (20).**



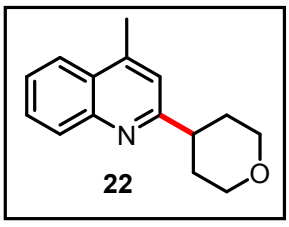
According to the *general procedure*. The spectral Data is consistent with the literature data.[4]
Yellow oil (41.1 mg, 46%).
R_f 0.20 (Petroleum ether/EtOAc, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.70 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.55 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.28 (s, 1H), 4.39 (t, J = 8.8 Hz, 2H), 4.28 (dd, J = 8.4, 6.0 Hz, 2H), 4.01 (tt, J = 8.8, 6.0 Hz, 1H), 2.72 (s, 3H), 1.48 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 156.7, 147.6, 145.4, 129.7, 129.5, 127.3, 126.2, 123.8, 120.1, 79.7, 54.6, 35.9, 28.6, 19.0.
HRMS (ESI) calcd for $C_{18}H_{23}N_2O_2$ $[M + H]^+$ 299.1754, found 299.1759.

***tert*-butyl 4-(4-methylquinolin-2-yl)piperidine-1-carboxylate (21).**



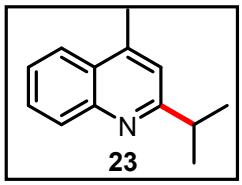
According to the *general procedure*. The spectral Data is consistent with the literature data.[4]
Yellow oil (44.0 mg, 45%).
R_f 0.20 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.54 – 7.47 (m, 1H), 7.14 (s, 1H), 4.28 (s, 2H), 3.71 (t, J = 6.0 Hz, 1H), 3.01 (tt, J = 12.0, 3.6 Hz, 1H), 2.68 (s, 3H), 2.43 (t, J = 6.0 Hz, 1H), 1.97 (d, J = 12.0 Hz, 2H), 1.84 (td, J = 12.4, 4.0 Hz, 2H), 1.49 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 155.0, 147.7, 144.8, 129.6, 129.3, 127.2, 125.8, 123.8, 120.1, 79.5, 45.6, 44.4, 31.7, 28.6, 19.0.
HRMS (ESI) calcd for $C_{20}H_{27}N_2O_2$ $[M + H]^+$ 327.2067, 327.2072.

4-methyl-2-(tetrahydro-2*H*-pyran-4-yl)quinoline (22).



According to the *general procedure*. The spectral Data is consistent with the literature data.[3]
White solid (44.9 mg, 66%). M.p. = 107 – 108 °C.
R_f 0.20 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.17 (s, 1H), 4.12 (dd, J = 11.2, 3.6 Hz, 2H), 3.59 (td, J = 11.6, 1.6 Hz, 2H), 3.12 (tt, J = 11.6, 3.6 Hz, 1H), 2.69 (s, 3H), 2.14 – 1.85 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 147.7, 144.8, 129.6, 129.2, 127.2, 125.8, 123.7, 120.0, 68.2, 44.5, 32.4, 19.0.
HRMS (ESI) calcd for $C_{15}H_{18}NO$ $[M + H]^+$ 228.1383, 228.1386.

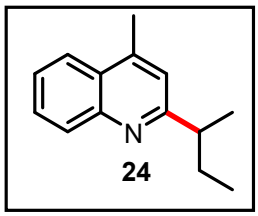
2-isopropyl-4-methylquinoline (23).



23

According to the *general procedure*. The spectral Data is consistent with the literature data.[5]
Yellow oil (52.7 mg, 95%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.72 – 7.62 (m, 1H), 7.55 – 7.44 (m, 1H), 7.18 (s, 1H), 3.30 – 3.11 (m, 1H), 2.68 (s, 3H), 1.39 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 147.6, 144.5, 129.6, 129.1, 127.1, 125.5, 123.7, 119.9, 37.4, 22.7, 19.0.
HRMS (ESI) calcd for $C_{13}H_{16}N$ $[M + H]^+$ 186.1277, found 186.1280.

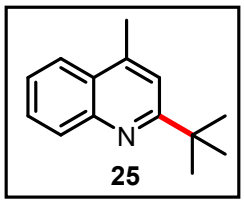
(S)-2-(*sec*-butyl)-4-methylquinoline (24).



24

According to the *general procedure*. The spectral Data is consistent with the literature data.[4]
Yellow oil (44.2 mg, 74%).
R_f 0.50 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.13 (s, 1H), 3.06 – 2.87 (m, 1H), 2.68 (s, 3H), 1.92 – 1.77 (m, 1H), 1.76 – 1.63 (m, 1H), 1.35 (d, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 147.8, 144.3, 129.7, 129.0, 127.2, 125.5, 123.7, 120.3, 44.7, 30.1, 20.5, 18.9, 12.4.
HRMS (ESI) calcd for $C_{14}H_{18}N$ $[M + H]^+$ 200.1434, found 200.1436.

2-(*tert*-butyl)-4-methylquinoline (25).



According to the *general procedure*. The spectral Data is consistent with the literature data.[5]

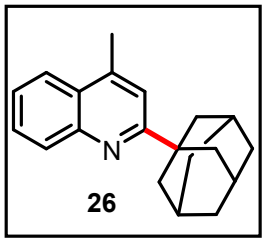
Colorless oil (48.8 mg, 81%).

R_f 0.35 (Petroleum ether/EtOAc, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.4, 0.8 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.50 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.37 (s, 1H), 2.70 (s, 3H), 1.48 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 147.4, 143.8, 130.0, 128.8, 126.7, 125.5, 123.5, 119.0, 38.0, 30.2, 19.1.

HRMS (ESI) calcd for $C_{14}H_{18}N$ $[M + H]^+$ 200.1434, found 200.1436.

2-(adamantan-1-yl)-4-methylquinoline (26).



According to the *general procedure*. The spectral Data is consistent with the literature data.[3]

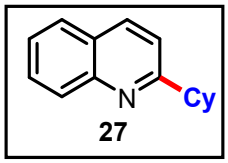
White solid (73.9 mg, 89%). M.p. = 105 – 106 °C.

R_f 0.40 (Petroleum ether/EtOAc, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.32 (s, 1H), 2.68 (s, 3H), 2.19 – 2.05 (m, 9H), 1.82 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 147.7, 143.7, 130.1, 128.7, 126.8, 125.5, 123.5, 118.6, 41.9, 39.7, 37.0, 29.0, 19.1.

HRMS (ESI) calcd for $C_{20}H_{24}N$ $[M + H]^+$ 278.1903, found 278.1906.

2-cyclohexylquinoline (27).



According to the *general procedure*. The spectral Data is consistent with the literature data.[3]

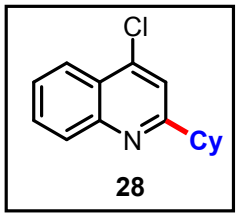
Yellow oil (28.5 mg, 45%).

R_f 0.50 (Petroleum ether/EtOAc, 60/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 12.4, 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 2.93 (tt, J = 12.0, 3.2 Hz, 1H), 2.03 (d, J = 12.4 Hz, 2H), 1.90 (d, J = 12.8 Hz, 2H), 1.79 (d, J = 12.8 Hz, 1H), 1.63 (dd, J = 12.4, 3.2 Hz, 2H), 1.48 (ddd, J = 15.6, 12.8, 6.4 Hz, 2H), 1.40 – 1.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 148.0, 136.4, 129.3, 129.1, 127.6, 127.1, 125.7, 119.7, 47.8, 33.0, 26.7, 26.3.

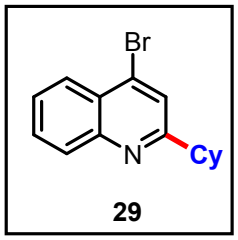
HRMS (ESI) calcd for $C_{15}H_{18}N$ $[M + H]^+$ 212.1434, found 212.1436.

4-chloro-2-cyclohexylquinoline (28).



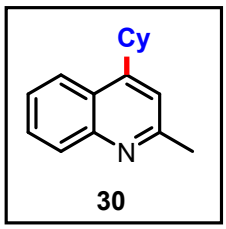
According to the *general procedure*. The spectral Data is consistent with the literature data.[3]
Yellow oil (61.7 mg, 84%).
R_f 0.70 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.4, 0.8 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.56 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.42 (s, 1H), 2.89 (tt, J = 12.0, 3.2 Hz, 1H), 2.02 (dd, J = 13.2, 1.6 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.79 (ddd, J = 12.8, 4.8, 2.4 Hz, 1H), 1.60 (ddd, J = 24.8, 12.4, 2.8 Hz, 2H), 1.53 – 1.39 (m, 2H), 1.38 – 1.28 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 148.8, 142.7, 130.3, 129.4, 126.7, 125.2, 124.0, 119.9, 47.5, 32.8, 26.5, 26.1.
HRMS (ESI) calcd for $C_{15}H_{17}ClN$ $[M + H]^+$ 246.1044, found 246.1048.

4-bromo-2-cyclohexylquinoline (29).



According to the *general procedure*. The spectral Data is consistent with the literature data.[3]
Yellow oil (35.5 mg, 41%).
R_f 0.70 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.63 (s, 1H), 7.57 (t, J = 7.6 Hz, 1H), 2.88 (tt, J = 12.0, 3.2 Hz, 1H), 2.02 (d, J = 12.8 Hz, 2H), 1.95 – 1.85 (m, 2H), 1.79 (d, J = 12.8 Hz, 1H), 1.61 (ddd, J = 24.8, 12.4, 2.8 Hz, 2H), 1.52 – 1.39 (m, 2H), 1.39 – 1.29 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 148.6, 134.4, 130.3, 129.5, 127.0, 126.7, 126.6, 123.8, 47.4, 32.8, 26.6, 26.1.
HRMS (ESI) calcd for $C_{15}H_{17}BrN$ $[M + H]^+$ 290.0539, found 290.0542.

4-cyclohexyl-2-methylquinoline (30).

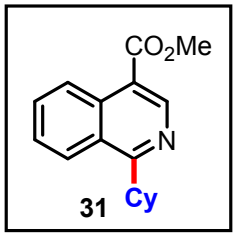


According to the *general procedure*. The spectral Data is consistent with the literature data.[3]
Yellow oil (54.7 mg, 81%).
R_f 0.30 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 2H), 7.63 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.47 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.15 (s, 1H), 3.36 – 3.20 (m, 1H), 2.71 (s, 3H), 2.10 – 1.78 (m, 5H), 1.63 – 1.44 (m, 4H), 1.40 – 1.21 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 153.4, 148.2, 129.5, 128.9, 125.3, 125.2, 122.9, 118.4, 38.8, 33.6, 27.0, 26.4, 25.6.

HRMS (ESI) calcd for $C_{16}H_{20}N$ $[M + H]^+$ 226.1590, found 226.1593.

methyl 1-cyclohexylisoquinoline-4-carboxylate (31).



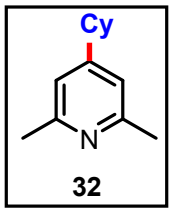
According to the *general procedure*. Colorless oil (65.4 mg, 81%).

R_f 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.96 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 3.99 (s, 3H), 3.59 (t, J = 11.2 Hz, 1H), 1.94 (t, J = 11.2 Hz, 4H), 1.89 – 1.75 (m, 3H), 1.59 – 1.45 (m, 2H), 1.44 – 1.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 167.4, 146.0, 134.4, 131.3, 127.2, 126.0, 125.8, 125.1, 118.7, 52.2, 42.2, 32.6, 26.8, 26.2.

HRMS (ESI) calcd for $C_{17}H_{20}NO_2$ $[M + H]^+$ 270.1489, found 270.1492.

4-cyclohexyl-2,6-dimethylpyridine (32).



According to the *general procedure*. The spectral Data is consistent with the literature data.[3]

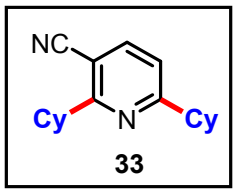
Yellow oil (28.4 mg, 50%).

R_f 0.30 (Petroleum ether/EtOAc, 7/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 2.50 (s, 6H), 2.45 – 2.37 (m, 1H), 1.84 (d, J = 8.4 Hz, 4H), 1.75 (d, J = 12.4 Hz, 2H), 1.38 (t, J = 10.8 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 157.5, 119.2, 44.0, 33.7, 26.7, 26.1, 24.4.

HRMS (ESI) calcd for $C_{13}H_{20}N$ $[M + H]^+$ 190.1590, found 190.1593.

2,6-dicyclohexylnicotinonitrile (33).



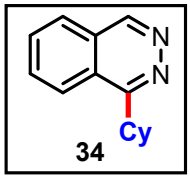
According to the *general procedure*. Colorless oil (32.2 mg, 40%).

R_f 0.70 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 1H), 7.08 – 6.99 (m, 1H), 3.19 – 2.97 (m, 1H), 2.71 (tt, J = 11.6, 3.2 Hz, 1H), 1.96 – 1.79 (m, 7H), 1.72 (ddd, J = 25.6, 12.8, 3.2 Hz, 4H), 1.54 – 1.31 (m, 6H), 1.28 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 168.4, 140.5, 118.2, 117.9, 104.9, 46.9, 44.9, 32.6, 32.0, 26.4, 26.3, 26.1, 25.9.

HRMS (ESI) calcd for $C_{18}H_{25}N_2$ $[M + H]^+$ 269.2012, found 269.2015.

1-cyclohexylphthalazine (34).



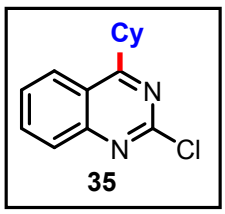
According to the *general procedure*. Yellow oil (29.3 mg, 46%).

R_f 0.50 (CH_2Cl_2/MeOH, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.90 (dddd, J = 14.4, 8.4, 7.2, 1.2 Hz, 3H), 3.63 – 3.39 (m, 1H), 2.09 – 2.01 (m, 2H), 1.99 – 1.93 (m, 3H), 1.86 – 1.79 (m, 2H), 1.62 – 1.46 (m, 2H), 1.46 – 1.37 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.4, 131.8, 127.3, 125.1, 123.6, 40.8, 32.4, 27.0, 26.2.

HRMS (ESI) calcd for $C_{14}H_{17}N_2$ $[M + H]^+$ 213.1386, found 213.1389

2-chloro-4-cyclohexylquinazoline (35).



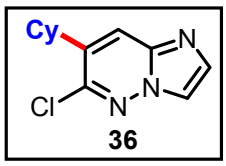
According to the *general procedure*. Colorless oil (41.3 mg, 56%).

R_f 0.70 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 3.53 (t, J = 11.6 Hz, 1H), 2.01 – 1.90 (m, 4H), 1.89 – 1.77 (m, 3H), 1.54 – 1.45 (m, 2H), 1.44 – 1.35 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.2, 157.6, 152.2, 134.6, 128.6, 127.7, 124.6, 121.8, 41.8, 32.0, 26.5, 25.9.

HRMS (ESI) calcd for $C_{14}H_{16}ClN_2$ $[M + H]^+$ 247.0997, found 247.0999.

6-chloro-7-cyclohexylimidazo[1,2-*b*]pyridazine (36).



According to the *general procedure*. The spectral Data is consistent with the literature data.[3]

Yellow oil (33.8 mg, 48%).

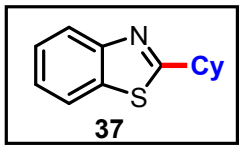
R_f 0.70 (Petroleum ether/EtOAc, 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 1.2 Hz, 1H), 7.72 (d, J = 1.2 Hz, 1H), 6.86 (s, 1H), 3.42 –

3.27 (m, 1H), 2.13 – 2.04 (m, 2H), 1.96 – 1.87 (m, 2H), 1.82 (d, J = 17.2 Hz, 2H), 1.55 – 1.50 (m, 3H), 1.32 (ddd, J = 12.4, 8.0, 3.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 147.5, 138.1, 133.3, 117.4, 114.7, 38.9, 32.2, 26.4, 26.1.

HRMS (ESI) calcd for $C_{12}H_{15}ClN_3$ $[M + H]^+$ 236.0949, found 236.0951.

2-cyclohexylbenzo[*d*]thiazole (37).



37

According to the *general procedure*. The spectral Data is consistent with the literature data.[3]

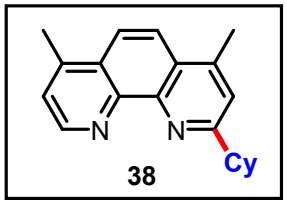
Yellow oil (28.6 mg, 44%).

R_f 0.70 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.37 – 7.29 (m, 1H), 3.11 (tt, J = 11.6, 3.6 Hz, 1H), 2.21 (dd, J = 13.2, 2.0 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.77 (ddd, J = 12.4, 4.8, 2.4 Hz, 1H), 1.64 (ddd, J = 24.8, 12.4, 3.2 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.37 – 1.28 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 153.2, 134.7, 125.9, 124.6, 122.7, 121.7, 43.6, 33.6, 26.2, 25.9.

HRMS (ESI) calcd for $C_{13}H_{16}NS$ $[M + H]^+$ 218.0998, found 218.1001.

2-cyclohexyl-4,7-dimethyl-1,10-phenanthroline (38).



38

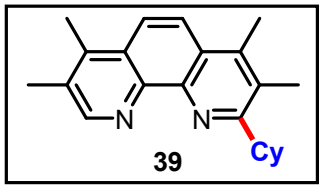
According to the *general procedure*. White solid (40.9 mg, 47%). M.p. = 62 – 63 °C.

R_f 0.70 (CH_2Cl_2/MeOH, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, J = 4.4 Hz, 1H), 7.96 (q, J = 9.2 Hz, 2H), 7.40 (d, J = 4.4 Hz, 1H), 7.38 (s, 1H), 3.27 (tt, J = 12.0, 3.2 Hz, 1H), 2.76 (d, J = 4.4 Hz, 6H), 2.08 (d, J = 12.4 Hz, 2H), 1.86 (d, J = 12.8 Hz, 2H), 1.65 – 1.53 (m, 3H), 1.50 – 1.42 (m, 2H), 1.39 – 1.31 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 150.0, 146.3, 145.6, 144.4, 144.3, 128.1, 126.6, 123.8, 122.2, 121.7, 121.1, 48.0, 33.6, 26.6, 26.3, 19.5, 19.3.

HRMS (ESI) calcd for $C_{20}H_{23}N_2$ $[M + H]^+$ 291.1856, found 291.1858.

2-cyclohexyl-3,4,7,8-tetramethyl-1,10-phenanthroline (39).



39

According to the *general procedure*. White solid (63.9 mg, 67%). M.p. = 89 – 90 °C.

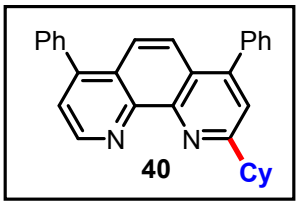
R_f 0.50 (CH_2Cl_2/MeOH, 80/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.99 (dd, J = 22.8, 9.6 Hz, 2H), 3.17 (tt, J = 11.2, 3.6 Hz,

1H), 2.68 (s, 6H), 2.51 (s, 6H), 2.04 – 1.84 (m, 7H), 1.44 (td, *J* = 12.8, 6.4 Hz, 2H), 1.33 (dd, *J* = 12.8, 3.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 151.3, 144.5, 143.4, 142.2, 141.4, 130.2, 128.9, 127.2, 125.6, 122.7, 120.9, 44.2, 31.8, 27.0, 26.0, 17.6, 15.4, 15.2, 14.8.

HRMS (ESI) calcd for $C_{22}H_{27}N_2$ $[M + H]^+$ 319.2169, found 319.2173.

2-cyclohexyl-4,7-diphenyl-1,10-phenanthroline (40).



40

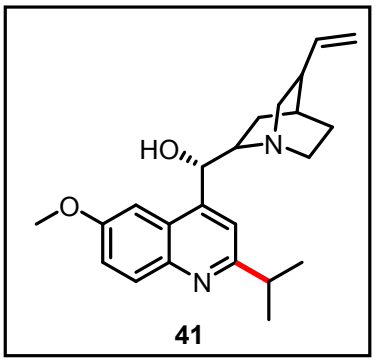
According to the *general procedure*. White solid (72.0 mg, 58%). M.p. = 103 – 104 °C.

R_f 0.50 (CH_2Cl_2/MeOH, 80/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 4.4 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.57 – 7.50 (m, 12H), 3.41 (tt, *J* = 12.0, 3.2 Hz, 1H), 2.19 (d, *J* = 12.4 Hz, 2H), 1.94 – 1.87 (m, 2H), 1.84 (s, 1H), 1.66 (dd, *J* = 12.4, 3.2 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.40 – 1.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 149.9, 148.9, 148.5, 146.9, 146.2, 138.7, 138.3, 129.9, 129.8, 128.7, 128.6, 128.5, 128.4, 126.7, 125.2, 124.2, 123.3, 123.1, 121.3, 48.1, 33.6, 26.6, 26.3.

HRMS (ESI) calcd for $C_{30}H_{27}N_2$ $[M + H]^+$ 415.2169, found 415.2173.

(1S)-(2-isopropyl-6-methoxyquinolin-4-yl)((1S,4S)-5-vinylquinuclidin-2-yl)methanol (41).



41

According to the *general procedure*. The spectral Data is consistent with the literature data.[6]

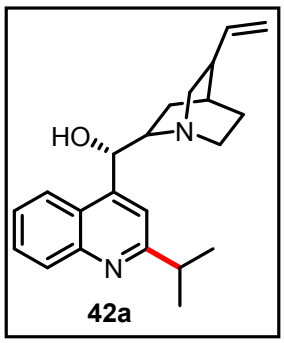
White solid (73.6 mg, 67%). M.p. = 144 – 145 °C.

R_f 0.50 (CH_2Cl_2/MeOH, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 1H), 7.52 (s, 1H), 7.21 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 5.75 (d, *J* = 2.8 Hz, 1H), 5.67 (ddd, *J* = 17.6, 10.4, 7.6 Hz, 1H), 4.94 (t, *J* = 14.0 Hz, 2H), 3.79 (s, 3H), 3.72 (t, *J* = 6.4 Hz, 1H), 3.21 – 3.11 (m, 3H), 2.82 – 2.69 (m, 2H), 2.36 (s, 1H), 1.90 – 1.79 (m, 3H), 1.57 (t, *J* = 10.0 Hz, 1H), 1.48 – 1.40 (m, 1H), 1.34 (dd, *J* = 6.8, 2.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 157.4, 147.1, 143.7, 141.0, 131.2, 124.8, 121.3, 116.4, 115.2, 101.0, 71.0, 60.0, 56.7, 55.9, 43.6, 39.5, 37.2, 27.9, 27.0, 22.7, 20.6.

HRMS (ESI) calcd for $C_{23}H_{31}N_2O_2$ $[M + H]^+$ 367.2380, found 367.2383.

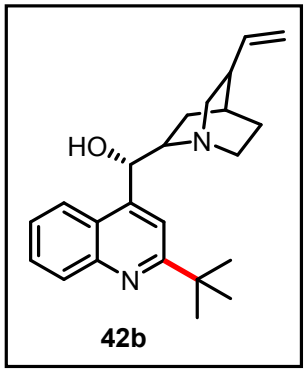
(1S)-(2-isopropylquinolin-4-yl)((1S,4S)-5-vinylquinuclidin-2-yl)methanol (42a).



42a

According to the *general procedure*. White solid (53.4 mg, 53%). M.p. = 168 – 169 °C.
R_f 0.50 (CH_2Cl_2/MeOH, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.14 – 5.94 (m, 1H), 5.84 (d, J = 3.2 Hz, 1H), 5.15 – 4.98 (m, 2H), 3.50 (dd, J = 12.0, 8.0 Hz, 1H), 3.23 (dp, J = 14.0, 6.8 Hz, 1H), 3.03 (dd, J = 9.2, 6.4 Hz, 1H), 2.91 (dd, J = 16.4, 6.8 Hz, 2H), 2.76 (dt, J = 13.2, 9.2 Hz, 1H), 2.24 (dd, J = 16.8, 8.2 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.75 (s, 1H), 1.59 – 1.44 (m, 2H), 1.36 (d, J = 6.8 Hz, 6H), 1.13 – 1.00 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 149.0, 147.8, 140.2, 129.9, 128.9, 125.9, 124.3, 122.6, 116.4, 115.0, 71.3, 60.0, 50.1, 49.6, 39.9, 37.5, 28.4, 26.1, 22.7, 22.6, 20.4.
HRMS (ESI) calcd for $C_{22}H_{29}N_2O$ $[M + H]^+$ 337.2274, found 337.2278.

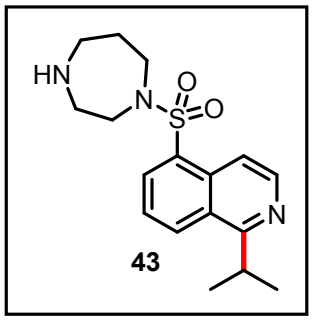
(1S)-(2-(*tert*-butyl)quinolin-4-yl)((1S,4S)-5-vinylquinuclidin-2-yl)methanol (42b).



42b

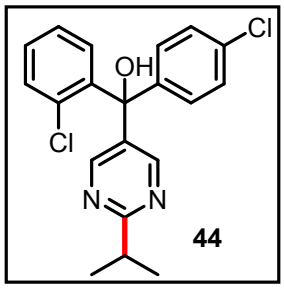
According to the *general procedure*. White solid (69.3 mg, 66%). M.p. = 172 – 173 °C.
R_f 0.50 (CH_2Cl_2/MeOH, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.4, 0.8 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.65 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.49 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.36 (s, 1H), 5.99 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 5.21 – 5.05 (m, 2H), 3.44 (dd, J = 13.2, 4.4 Hz, 1H), 3.20 – 3.10 (m, 1H), 3.10 – 2.85 (m, 5H), 2.31 (dd, J = 16.4, 8.0 Hz, 1H), 1.60 – 1.49 (m, 3H), 1.46 (s, 9H), 1.37 – 1.28 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 147.8, 144.8, 140.7, 130.4, 128.7, 126.2, 125.7, 123.3, 118.8, 114.8, 56.0, 49.4, 47.8, 40.0, 38.1, 37.9, 30.2, 28.1, 28.0, 26.6.
HRMS (ESI) calcd for $C_{23}H_{31}N_2O$ $[M + H]^+$ 351.2431, found 351.2432.

5-((1,4-diazepan-1-yl)sulfonyl)-1-isopropylisoquinoline (43).



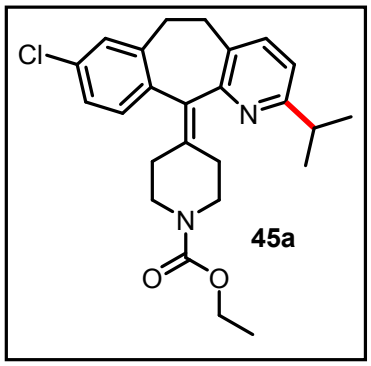
According to the *general procedure*. The spectral Data is consistent with the literature data.[4]
Yellow oil (42.0 mg, 42%).
R_f 0.50 (CH_2Cl_2/MeOH, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 6.0 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.35 – 8.26 (m, 2H), 7.66 (dd, J = 8.4, 7.6 Hz, 1H), 4.06 – 3.91 (m, 1H), 3.55 – 3.48 (m, 2H), 3.48 – 3.43 (m, 2H), 3.03 – 2.93 (m, 4H), 2.11 (s, 1H), 1.86 (dt, J = 12.0, 6.0 Hz, 2H), 1.45 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 143.9, 135.3, 132.4, 132.4, 130.4, 127.0, 125.3, 115.7, 51.2, 50.4, 47.8, 47.5, 31.6, 31.3, 22.4.
HRMS (ESI) calcd for $C_{17}H_{24}N_3O_2S$ $[M + H]^+$ 334.1584, found 334.1587.

(2-chlorophenyl)(4-chlorophenyl)(2-isopropylpyrimidin-5-yl)methanol (44).



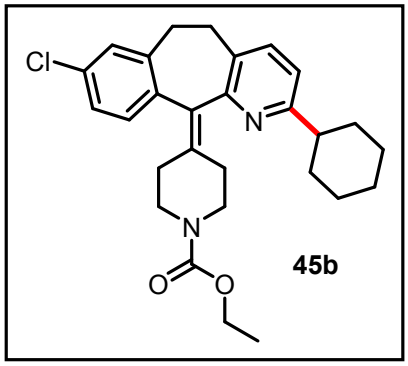
According to the *general procedure*. Yellow oil (69.2 mg, 62%).
R_f 0.50 (CH_2Cl_2/MeOH, 80/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 2H), 7.44 (dd, J = 8.0, 1.2 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.22 – 7.16 (m, 3H), 6.76 (dd, J = 8.0, 1.6 Hz, 1H), 4.42 (s, 1H), 3.30 – 3.19 (m, 1H), 1.37 (d, J = 6.8 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 156.5, 142.6, 141.5, 135.2, 134.2, 132.9, 132.0, 130.8, 130.2, 128.9, 128.8, 127.1, 79.9, 37.4, 21.9, 21.8.
HRMS (ESI) calcd for $C_{20}H_{19}Cl_2N_2O$ $[M + H]^+$ 373.0869, found 373.0873.

ethyl 4-(8-chloro-2-isopropyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (45a).



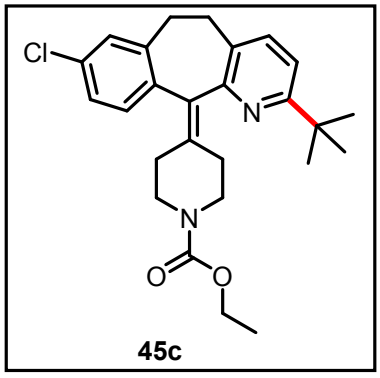
According to the *general procedure*. White solid (105.6 mg, 83%). M.p. = 99 – 100 °C.
R_f 0.70 (CH_2Cl_2/MeOH, 80/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 1H), 7.23 – 7.08 (m, 3H), 6.98 (d, J = 8.0 Hz, 1H), 4.22 – 4.06 (m, 2H), 3.96 – 3.66 (m, 2H), 3.33 (tdd, J = 16.4, 20.0, 5.6 Hz, 2H), 3.21 – 3.10 (m, 2H), 3.03 (dt, J = 13.6, 6.8 Hz, 1H), 2.88 – 2.71 (m, 2H), 2.58 – 2.44 (m, 1H), 2.44 – 2.25 (m, 3H), 1.29 – 1.22 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 155.8, 155.6, 140.0, 138.2, 138.1, 137.4, 134.6, 132.8, 130.7, 130.3, 128.9, 126.1, 118.5, 61.4, 45.0, 36.0, 31.9, 31.5, 31.0, 30.7, 23.5, 22.2, 14.8.
HRMS (ESI) calcd for $C_{25}H_{30}ClN_2O_2$ $[M + H]^+$ 425.1990, found 425.1993.

ethyl 4-(8-chloro-2-cyclohexyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (45b).



According to the *general procedure*. White solid (58.5 mg, 42%). M.p. = 105 – 106 °C.
R_f 0.30 (CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 1H), 7.20 – 7.09 (m, 3H), 6.95 (d, J = 8.0 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.83 (s, 2H), 3.43 – 3.22 (m, 2H), 3.10 (t, J = 9.6 Hz, 2H), 2.88 – 2.73 (m, 2H), 2.68 (t, J = 11.6 Hz, 1H), 2.49 (s, 1H), 2.34 (dd, J = 9.2, 4.5 Hz, 3H), 1.85 (ddd, J = 46.4, 28.8, 11.6 Hz, 6H), 1.44 – 1.34 (m, 3H), 1.26 (t, J = 7.2 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 155.9, 155.7, 140.1, 138.3, 138.1, 137.4, 134.7, 132.9, 130.7, 130.3, 128.9, 126.2, 118.9, 61.4, 46.2, 45.0, 34.0, 32.5, 31.9, 31.5, 31.1, 30.8, 26.8, 26.6, 26.2, 14.8.
HRMS (ESI) calcd for $C_{28}H_{34}ClN_2O_2$ $[M + H]^+$ 465.2303, found 465.2307.

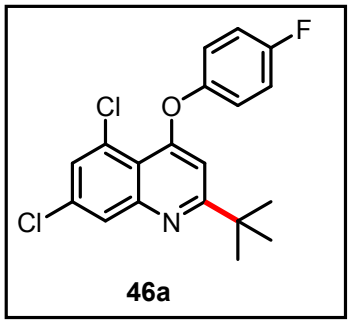
ethyl 4-(2-*(tert*-butyl)-8-chloro-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (45c).



45c

According to the *general procedure*. White solid (80.2 mg, 61%). M.p. = 102 – 103 °C.
R_f 0.50 (CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 1H), 7.18 (s, 1H), 7.16 – 7.07 (m, 3H), 4.15 (q, J = 7.2 Hz, 2H), 3.77 – 3.56 (m, 3H), 3.42 – 3.36 (m, 2H), 3.32 – 3.18 (m, 1H), 2.89 – 2.68 (m, 2H), 2.61 (d, J = 4.8 Hz, 1H), 2.45 – 2.31 (m, 1H), 2.30 – 2.15 (m, 2H), 1.31 (s, 9H), 1.27 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 155.7, 154.7, 140.4, 139.0, 138.1, 137.24, 134.7, 132.7, 130.5, 129.7, 128.5, 126.1, 117.2, 62.9, 61.5, 45.4, 37.3, 31.8, 31.7, 30.8, 30.3, 15.2, 14.9.
HRMS (ESI) calcd for $C_{26}H_{32}ClN_2O_2$ $[M + H]^+$ 439.2147, found 439.2149.

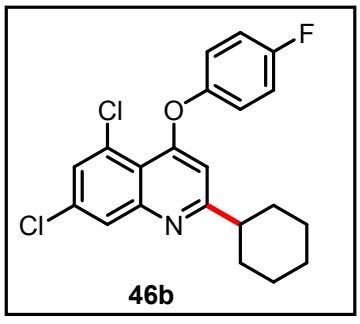
2-(*tert*-butyl)-5,7-dichloro-4-(4-fluorophenoxy)quinoline (46a).



46a

According to the *general procedure*. White solid (82.8 mg, 76%). M.p. = 86 – 87 °C.
R_f 0.50 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 2.0 Hz, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.20 – 7.02 (m, 4H), 6.76 (s, 1H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 162.1, 159.8 (d, J = 244 Hz), 151.2, 150.8, 134.71, 129.8, 128.8, 128.0, 121.8, 121.7, 117.2, 116.9, 116.8, 104.9, 38.4, 29.8.
HRMS (ESI) calcd for $C_{19}H_{17}Cl_2FNO$ $[M + H]^+$ 364.0666, found 364.0671.

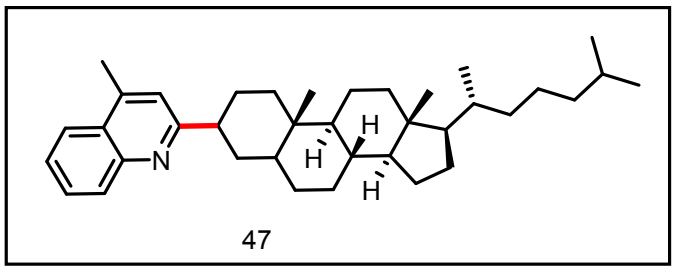
5,7-dichloro-2-cyclohexyl-4-(4-fluorophenoxy)quinoline (46b).



46b

According to the *general procedure*. The spectral Data is consistent with the literature data.[7]
White solid (80.5 mg, 69%). M.p. = 92 – 93 °C.
R_f 0.60 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.20 – 7.06 (m, 4H), 6.52 (s, 1H), 2.68 (tt, J = 11.6, 3.2 Hz, 1H), 1.85 (dd, J = 23.2, 12.4 Hz, 4H), 1.72 (d, J = 12.4 Hz, 1H), 1.40 (ddd, J = 15.6, 9.6, 2.8 Hz, 4H), 1.26 (ddd, J = 12.0, 5.6, 3.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 162.45, 159.0 (d, J = 244 Hz), 151.5, 150.5, 134.9, 130.0, 128.7, 127.6, 122.1, 122.0, 117.2, 117.1, 117.0, 105.8, 47.4, 32.5, 26.4, 26.0.
HRMS (ESI) calcd for $C_{21}H_{19}Cl_2FNO$ $[M + H]^+$ 390.0822, found 390.0824.

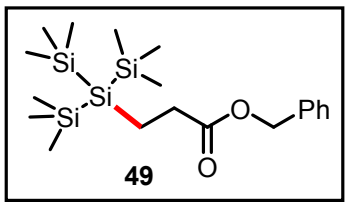
2-((3S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)-4-methylquinoline (47).



47

According to the *general procedure*. Steride (0.2 mmol) and lepidine (0.4 mmol) $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2.24 mg, 0.002 mmol, 1 mol %), TTMS (123 μL, 0.4 mmol, 2.0 equiv), TFA (30 μL, 0.4 mmol, 2.0 equiv) and 2.0 mL of acetone.
White solid (72.8 mg, 71%). M.p. = 180 – 181 °C.
R_f 0.68 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.18 (s, 1H), 3.00 – 2.84 (m, 1H), 2.68 (s, 3H), 2.02 – 1.95 (m, 1H), 1.90 – 1.78 (m, 4H), 1.68 (d, J = 11.6 Hz, 2H), 1.63 – 1.51 (m, 4H), 1.39 – 1.21 (m, 9H), 1.13 (ddd, J = 18.8, 9.6, 4.0 Hz, 7H), 1.01 (dd, J = 12.4, 9.6 Hz, 3H), 0.97 – 0.90 (m, 7H), 0.87 (dd, J = 6.8, 1.6 Hz, 6H), 0.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 147.8, 144.3, 129.6, 129.0, 127.2, 125.5, 123.7, 120.3, 56.7, 56.4, 54.7, 48.1, 46.9, 42.8, 40.2, 39.7, 38.8, 36.3, 36.0, 35.9, 35.7, 35.1, 32.3, 29.0, 28.5, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.0, 18.8, 12.8, 12.2.
HRMS (ESI) calcd for $C_{37}H_{56}N$ $[M + H]^+$ 514.4407, found 514.4412.

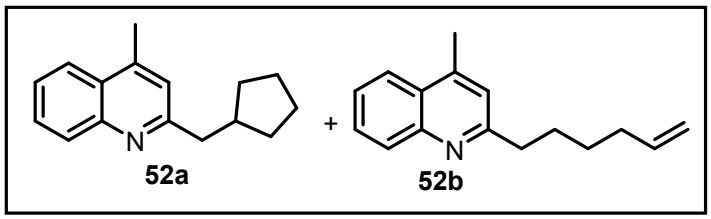
benzyl 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (49).



49

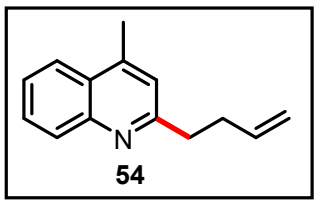
According to the *general procedure*. Colorless oil.
R_f 0.60 (Petroleum ether/EtOAc, 200/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 4H), 5.12 (s, 2H), 2.46 – 2.32 (m, 2H), 1.19 – 1.07 (m, 2H), 0.17 (s, 27H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 136.2, 128.7, 128.4, 128.3, 66.4, 33.3, 2.9, 1.2.
HRMS (ESI) calcd for $C_{19}H_{42}NO_2Si_4$ $[M + NH_4]^+$ 428.2287, found 428.2283.

2-(cyclopentylmethyl)-4-methylquinoline and 2-(hex-5-en-1-yl)-4-methylquinoline (52).



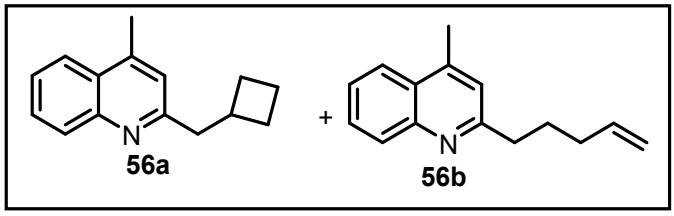
According to the *general procedure*. The spectral Data is consistent with the literature data.[5]
Yellow oil (56.0 mg, 83%).
R_f 0.35 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.72 – 7.63 (m, 1H), 7.55 – 7.44 (m, 1H), 7.13 (s, 1H), 5.81 (ddt, J = 16.8, 10.0, 6.8 Hz, 0.05H), 5.04 – 4.92 (m, 0.1H), 2.93 (d, J = 7.6 Hz, 2H), 2.67 (s, 3H), 2.43 – 2.28 (m, 1H), 1.87 – 1.61 (m, 4H), 1.60 – 1.46 (m, 2H), 1.33 – 1.24 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 147.8, 144.1, 129.5, 129.1, 126.9, 125.5, 123.7, 122.6, 45.2, 40.9, 32.7, 25.1, 18.9.
HRMS (ESI) calcd for $C_{16}H_{20}N$ $[M + H]^+$ 226.1590, found 226.1593.

2-(but-3-en-1-yl)-4-methylquinoline (54).



According to the *general procedure*. The spectral Data is consistent with the literature data.[5]
Yellow oil (26.6 mg, 45%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.68 (dd, J = 8.4, 6.8 Hz, 1H), 7.51 (dd, J = 8.4, 6.8 Hz, 1H), 7.15 (s, 1H), 5.93 (ddt, J = 16.8, 10.4, 6.4 Hz, 1H), 5.09 (dd, J = 16.8, 1.2 Hz, 1H), 4.99 (d, J = 10.4 Hz, 1H), 3.10 – 2.97 (m, 2H), 2.68 (s, 3H), 2.58 (td, J = 7.6, 1.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 147.8, 144.4, 137.9, 129.4, 129.2, 127.0, 125.6, 123.76, 122.3, 115.3, 38.6, 34.0, 18.9.
HRMS (ESI) calcd for $C_{14}H_{16}N$ $[M + H]^+$ 198.1277, found 198.1279.

2-(cyclobutylmethyl)-4-methylquinoline and 4-methyl-2-(pent-4-en-1-yl)quinoline (56).

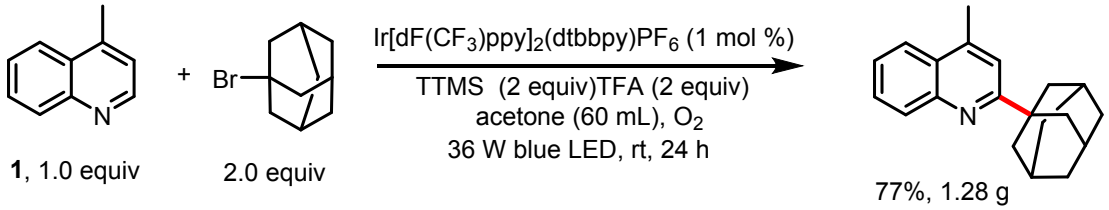


According to the *general procedure*. The spectral Data is consistent with the literature data.[5]
Yellow oil (26.6 mg, 42%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.4, 0.8 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.08 (s, 1H), 5.87 (ddt, J = 16.8, 10.4, 6.8 Hz, 0.08H), 5.11 – 4.93 (m, 0.16H), 3.02 (d, J = 7.6 Hz, 2H), 2.81 (dt, J = 15.6, 7.6 Hz, 1H), 2.66 (s, 3H), 2.12 – 2.00 (m, 2H), 1.95 – 1.77 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5, 147.8, 144.2, 129.5, 129.1, 126.9, 125.5, 123.7, 122.3, 46.1, 36.4, 28.5, 18.9, 18.7.

HRMS (ESI) calcd for $C_{15}H_{18}N$ $[M + H]^+$ 212.1434, found 212.1436.

7. Gram-scale Reaction



Scheme S4

To an oven dried Schlenk tube was added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (67.3 mg, 0.06 mmol, 1 mol %), lepidine (0.8 mL, 6.0 mmol, 1.0 equiv), TTMS (3.7 mL, 12 mmol, 2.0 equiv), bromoalkane (2.6 g, 12 mmol, 2.0 equiv), TFA (0.9 mL, 12 mmol, 2.0 equiv) and 60 mL of acetone. The tube was evacuated and backfilled with O_2 (this process was repeated three times). 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 60 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na_2SO_4, and concentrated in vacuo. After purification by flash column chromatography on silica gel, the product was obtained in 77% yield.

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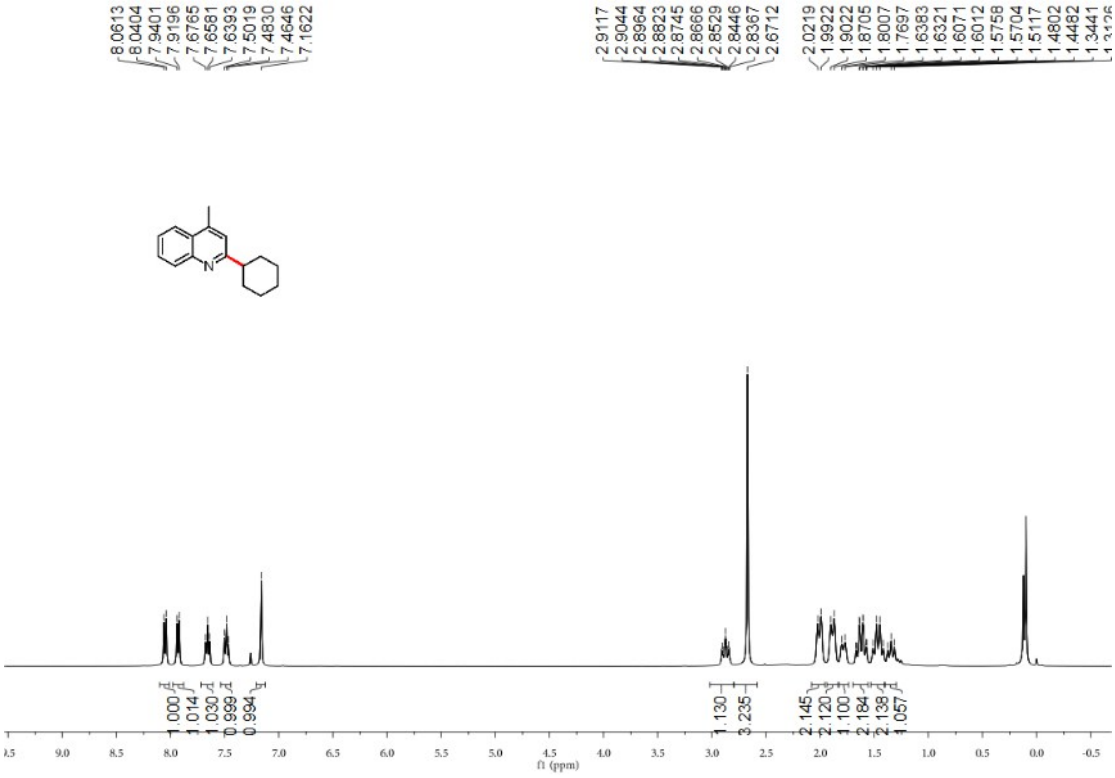
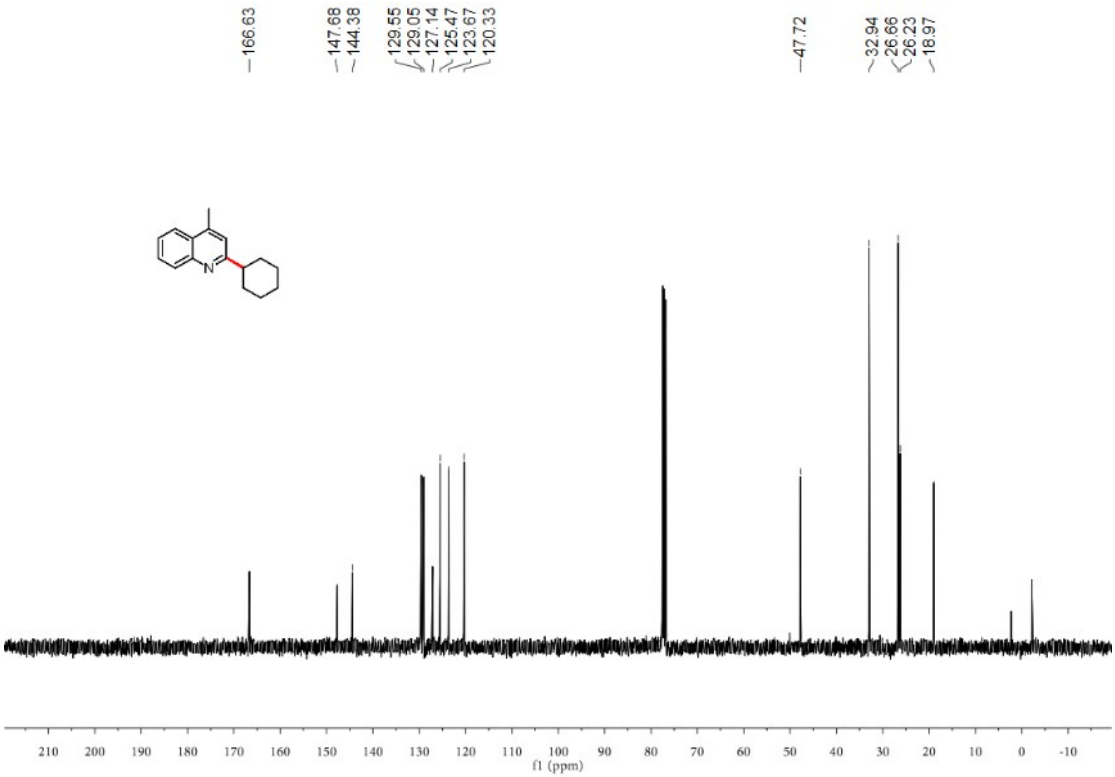
NMR Spectra

^{1}H NMR spectrum of compound **3**



^{13}C NMR spectrum of compound **3**



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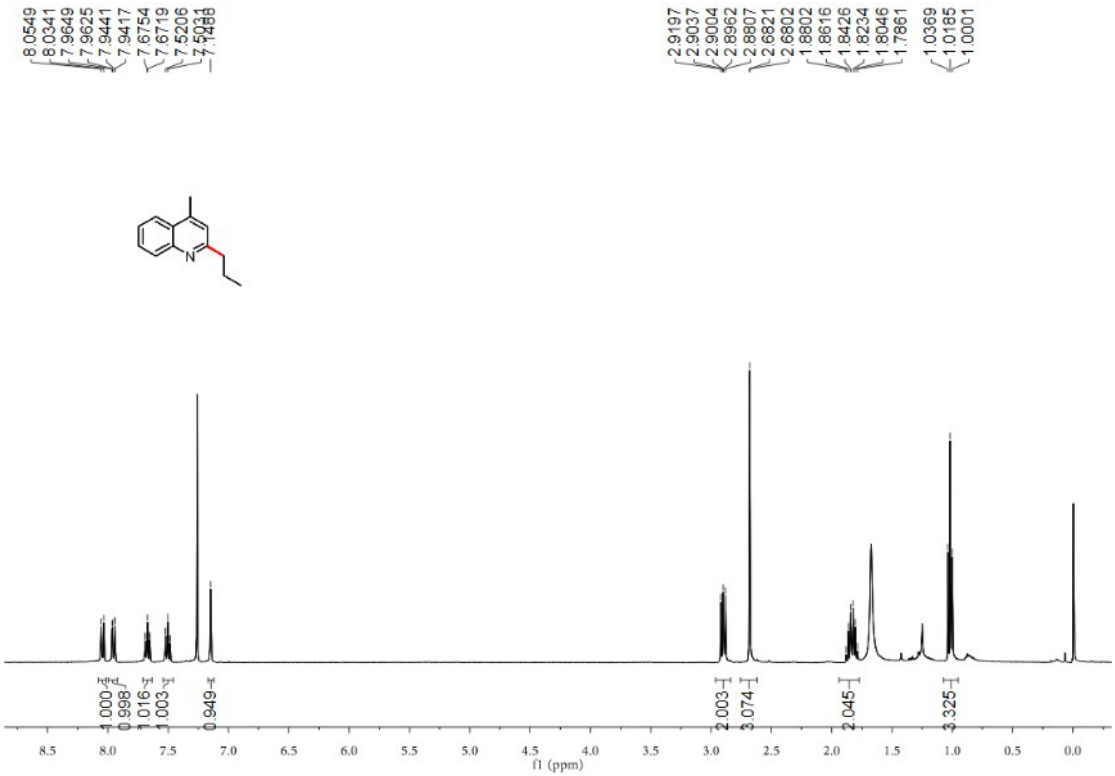
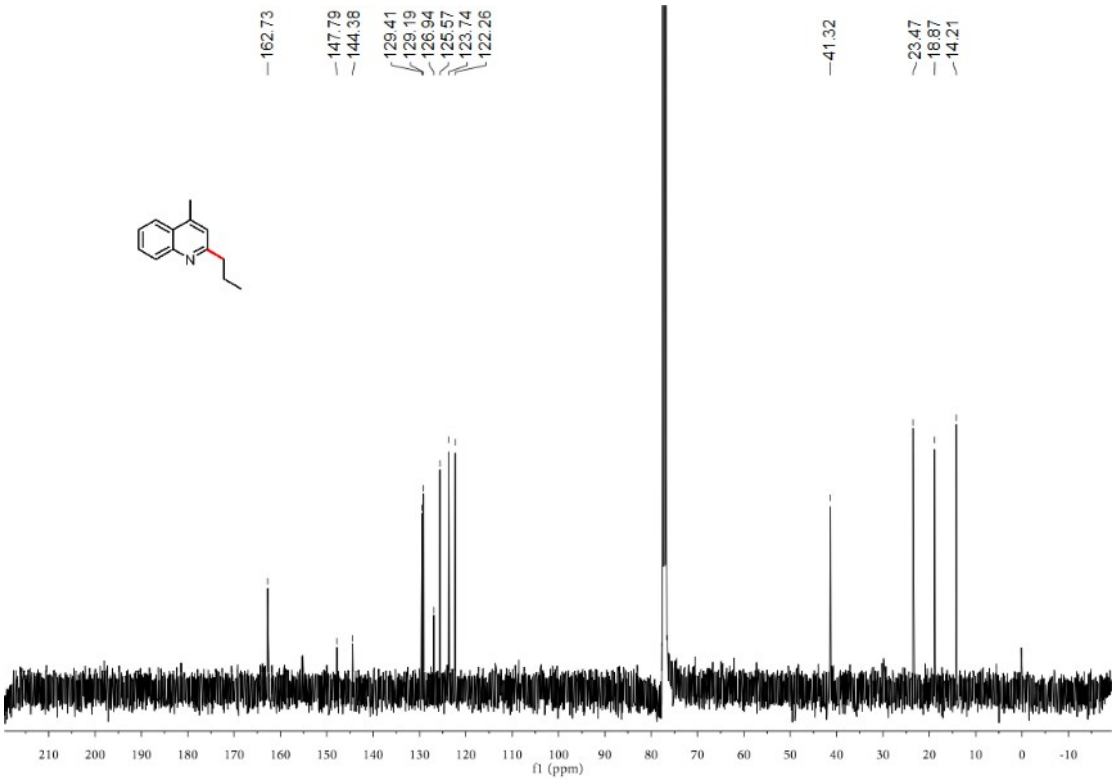
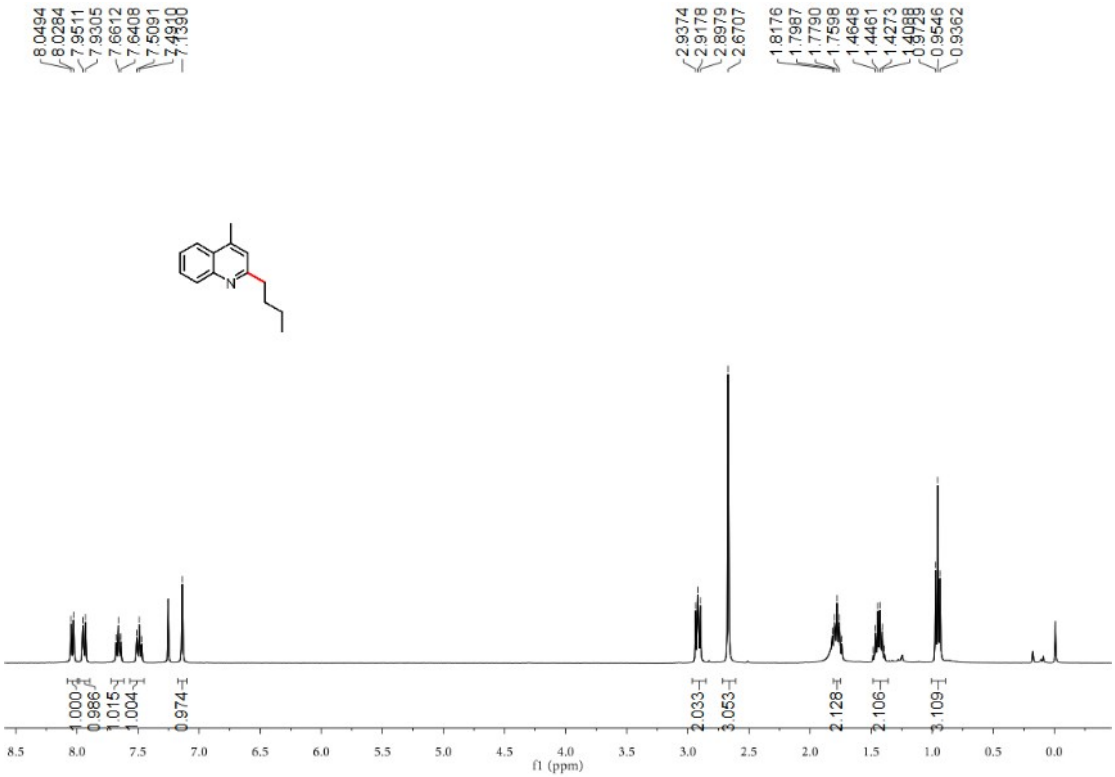


^{13}C NMR spectrum of compound **4**



[1]H NMR spectrum of compound **5**



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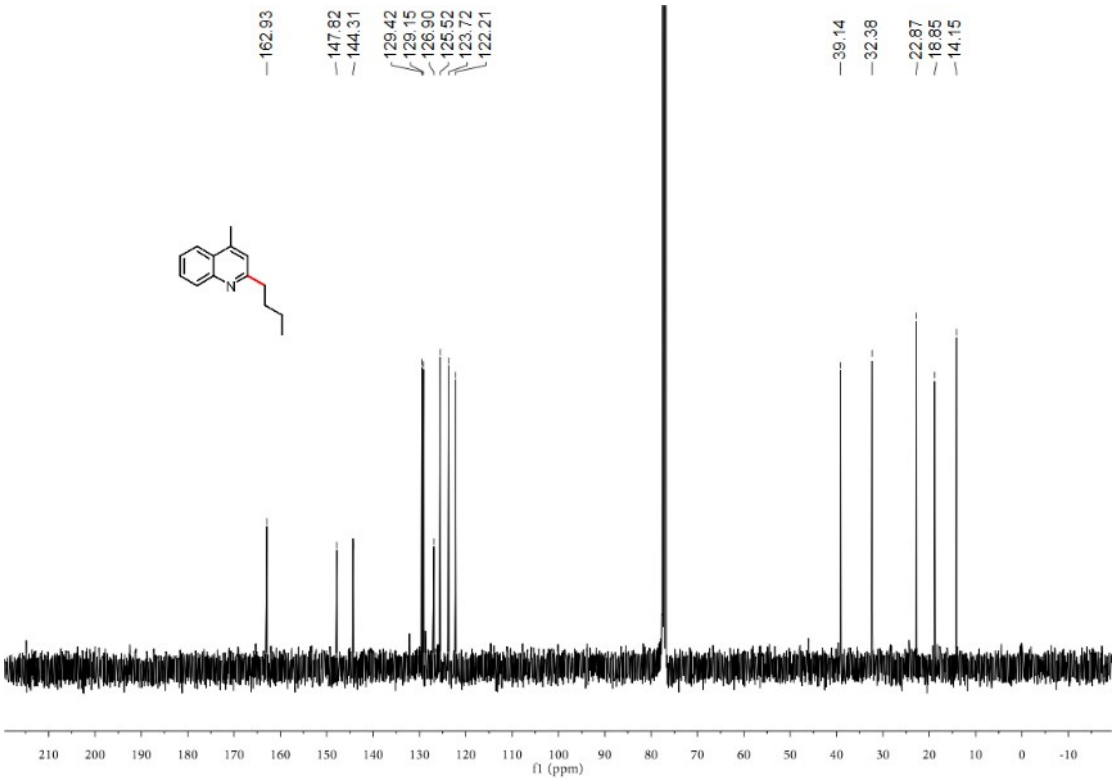

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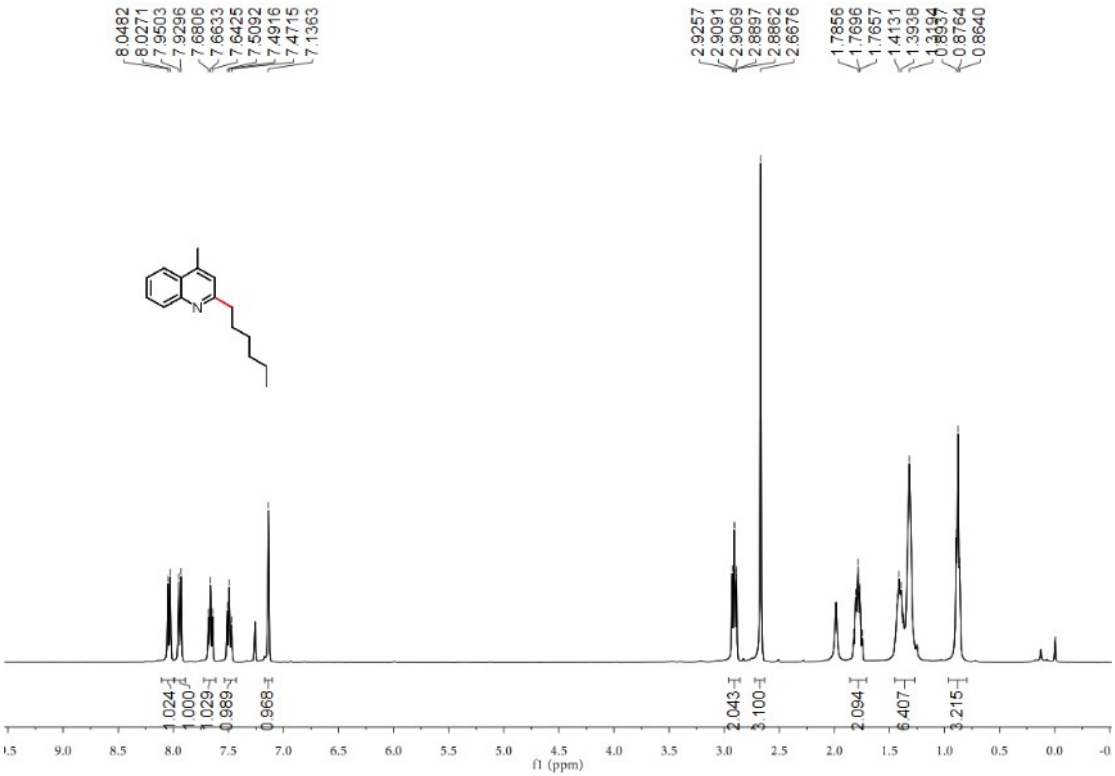

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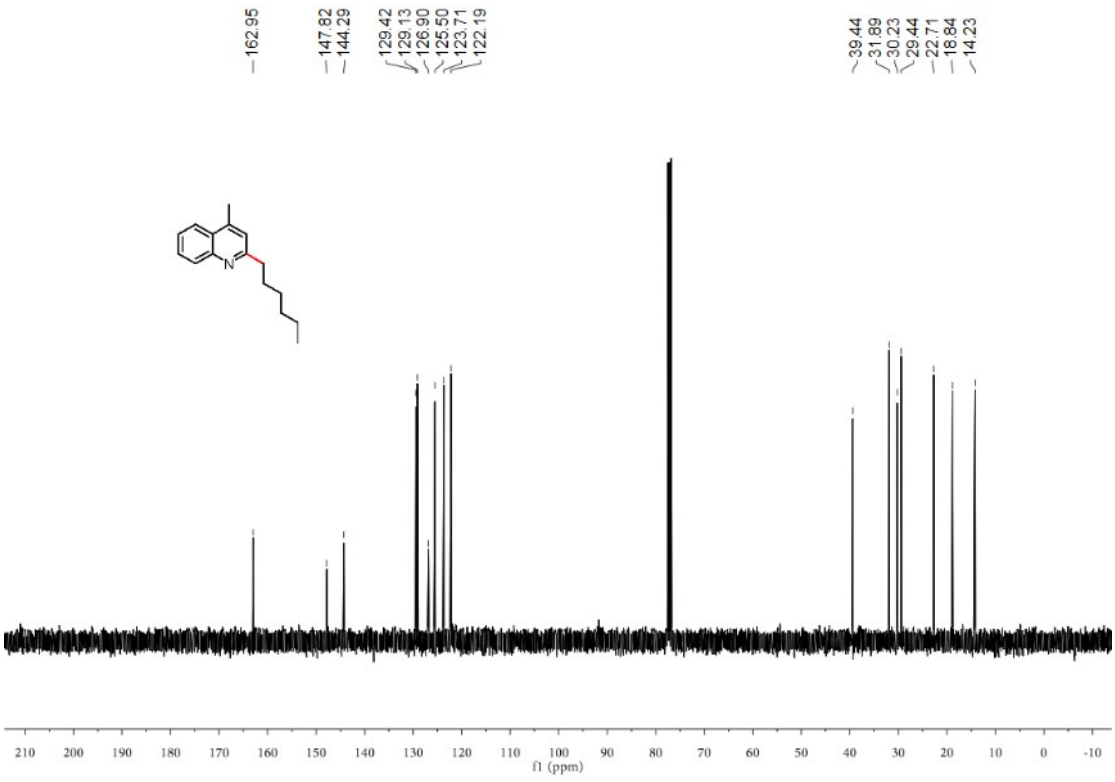

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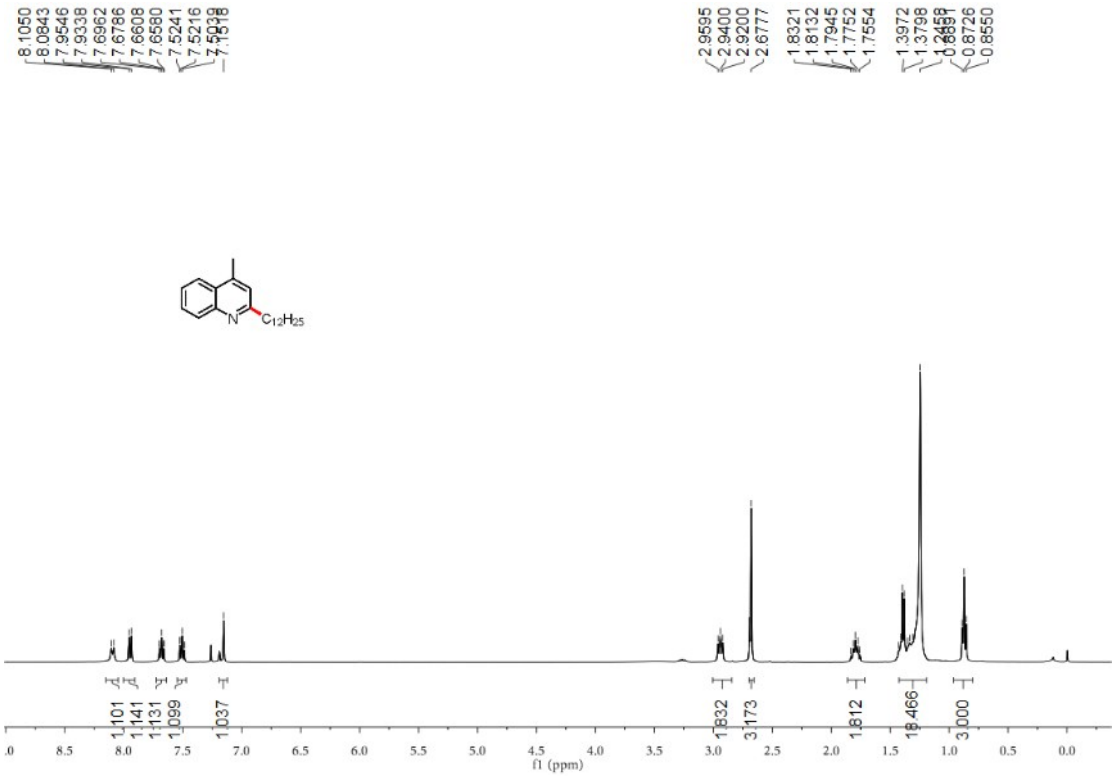

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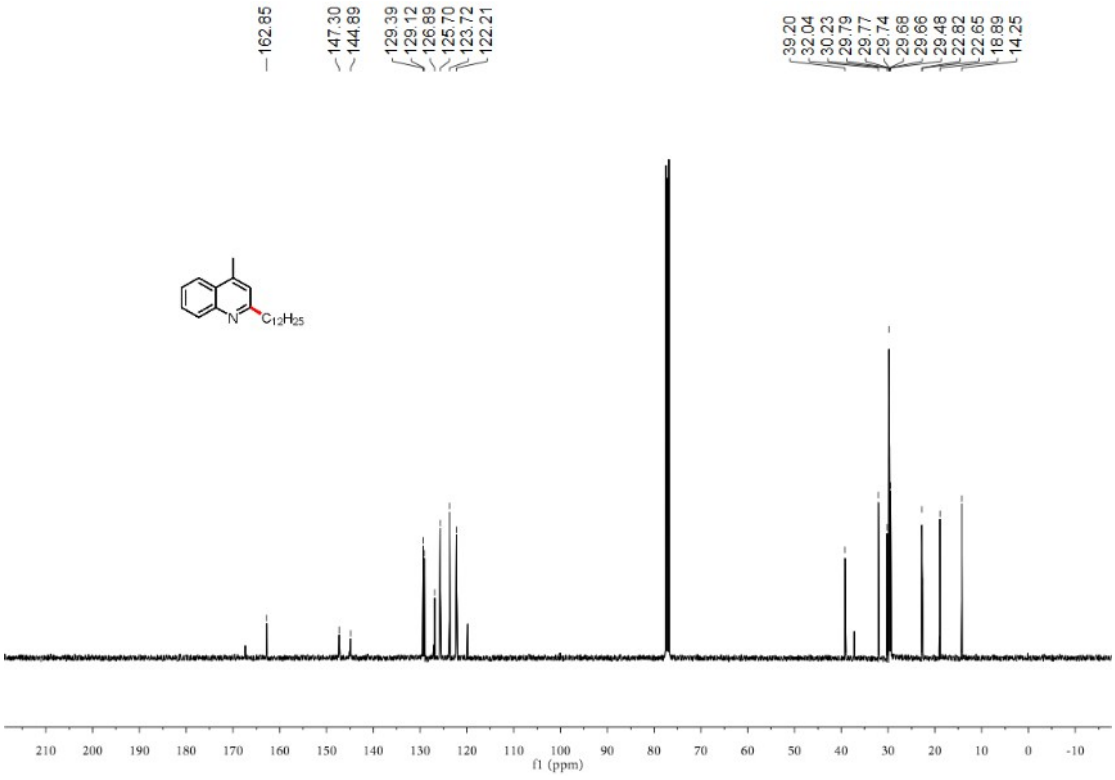

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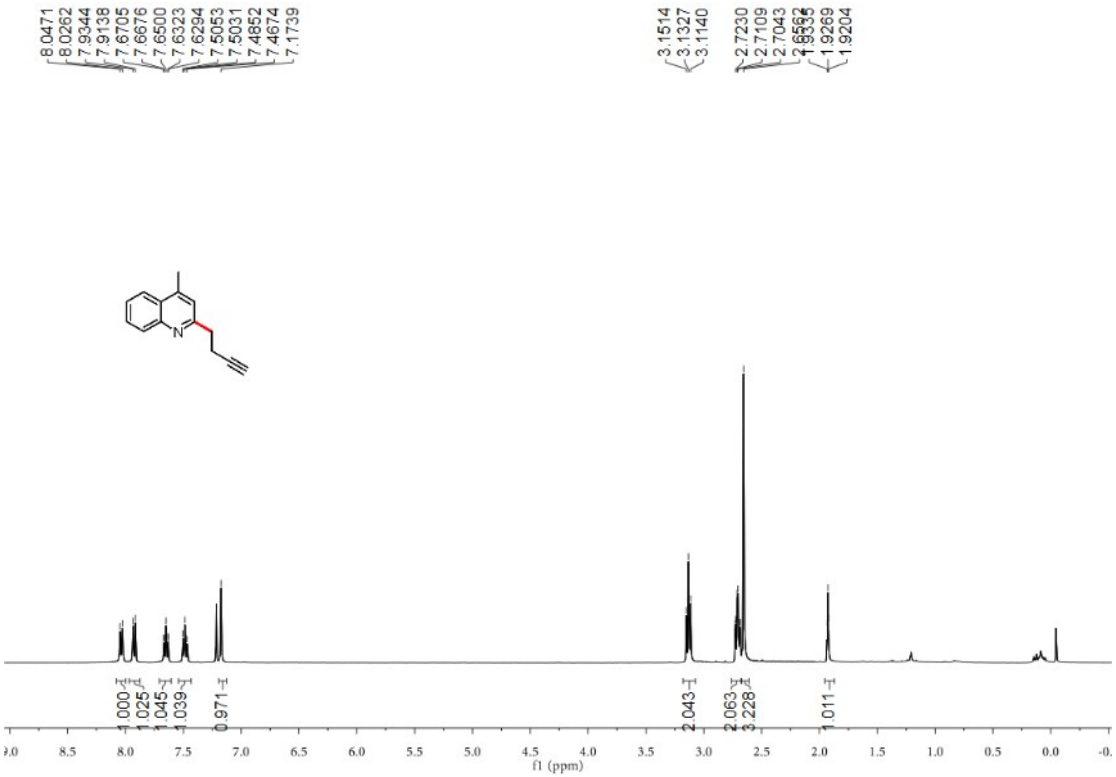

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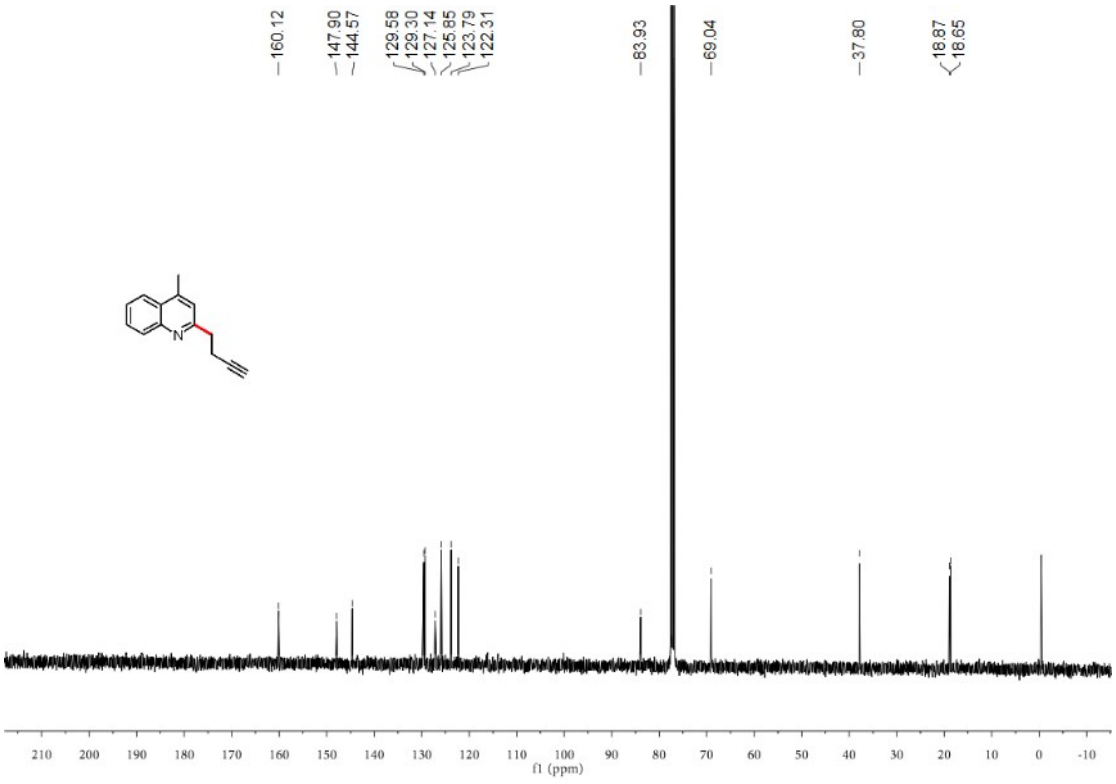

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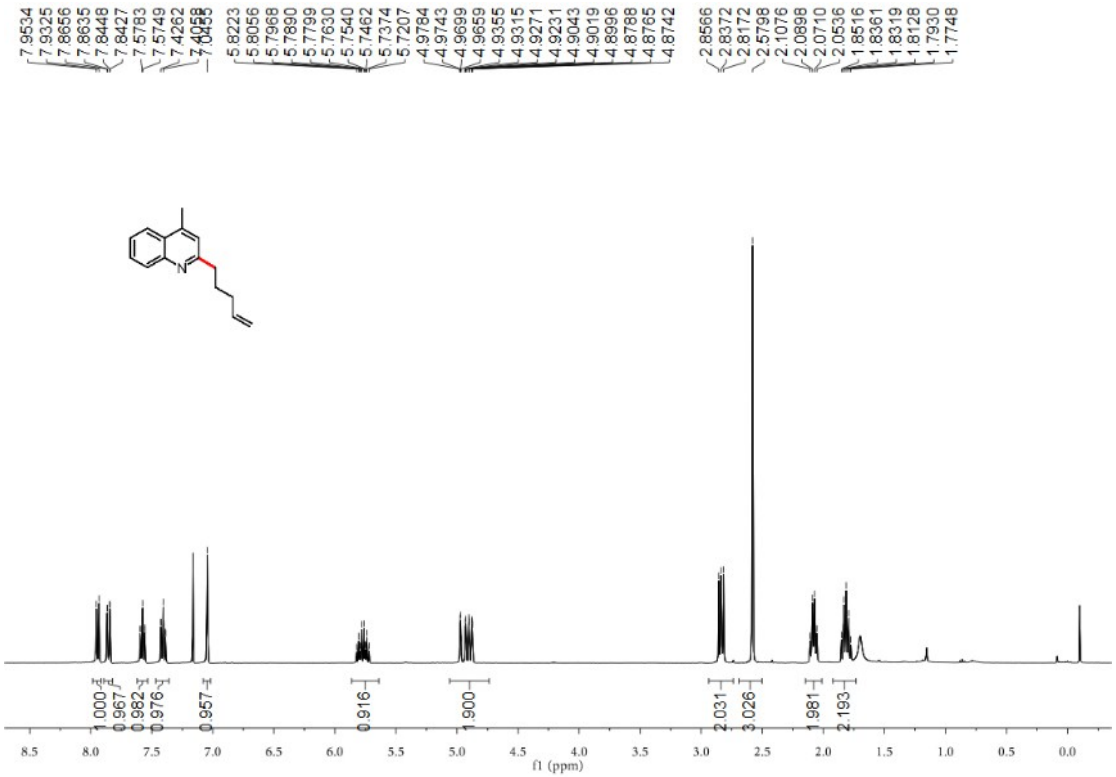

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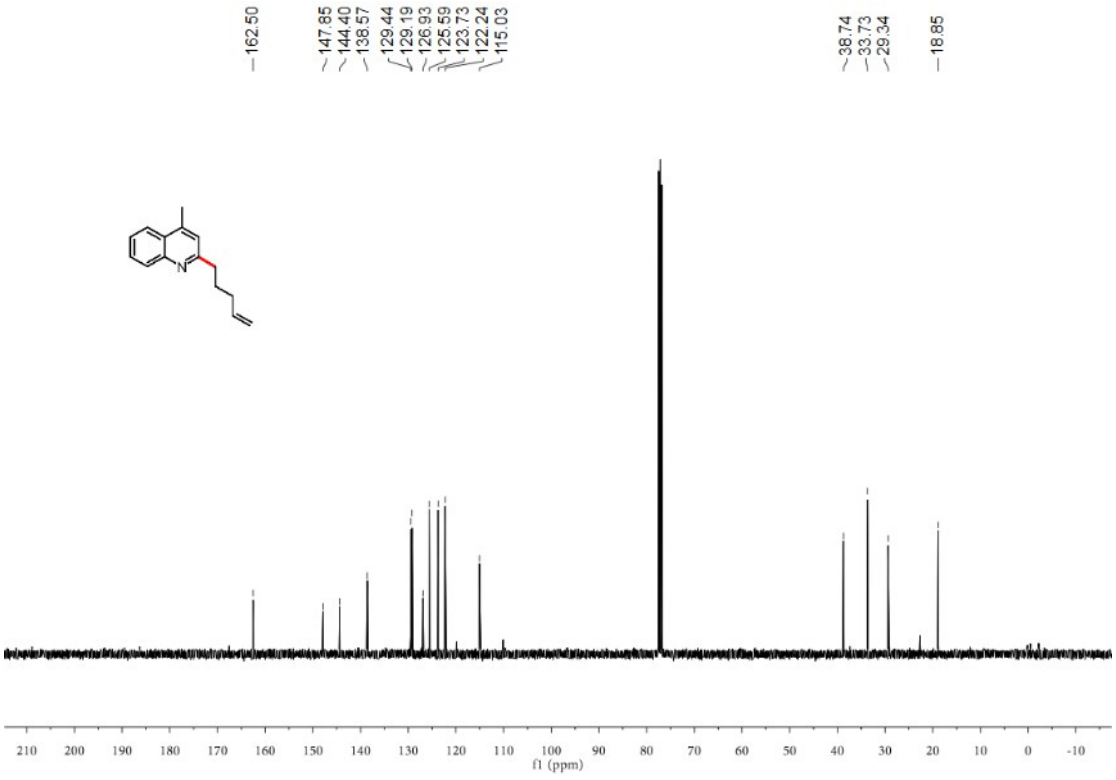

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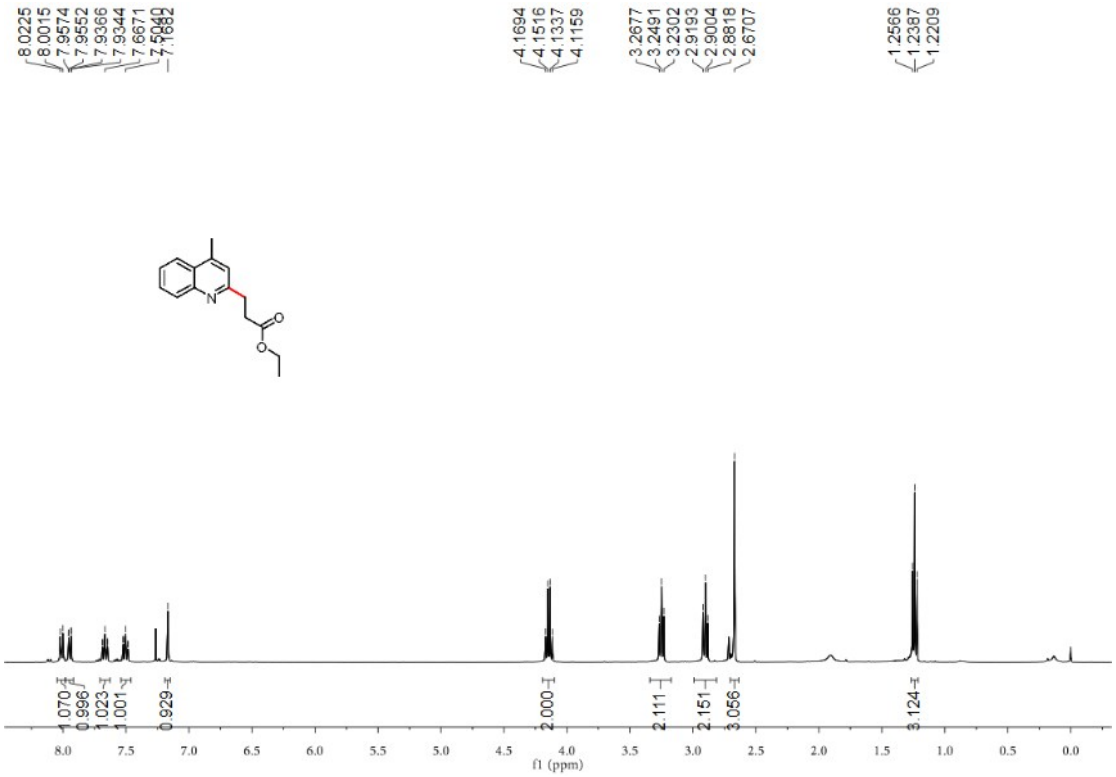

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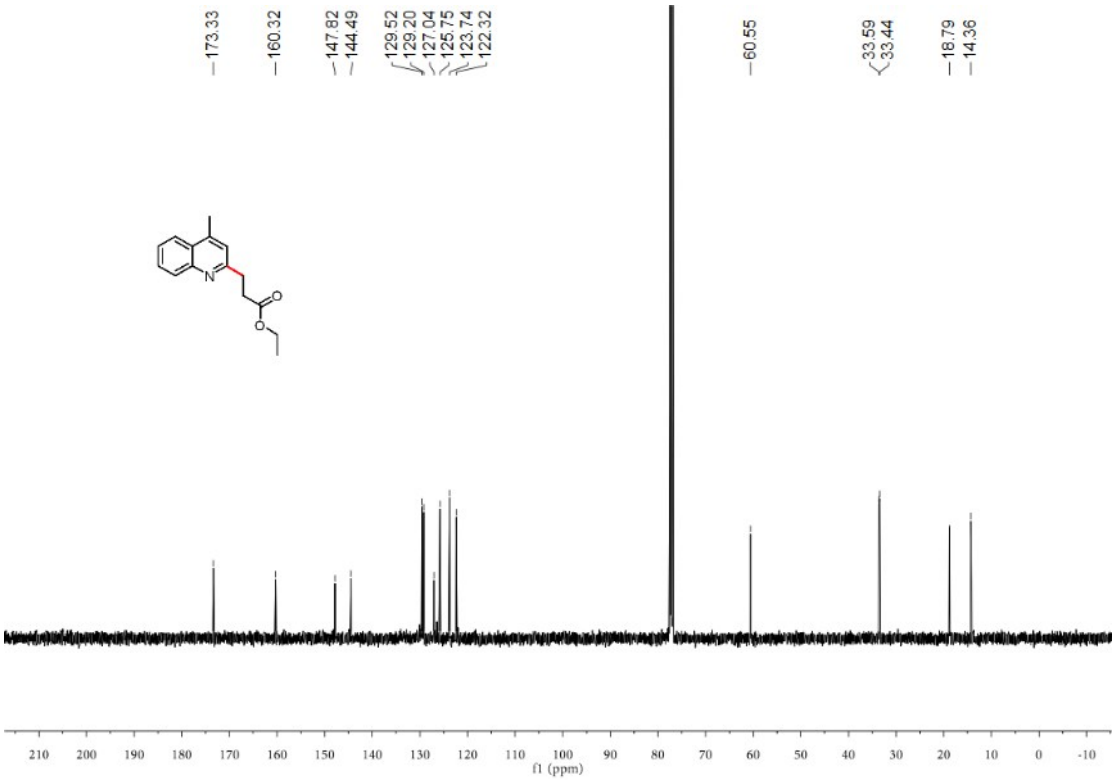

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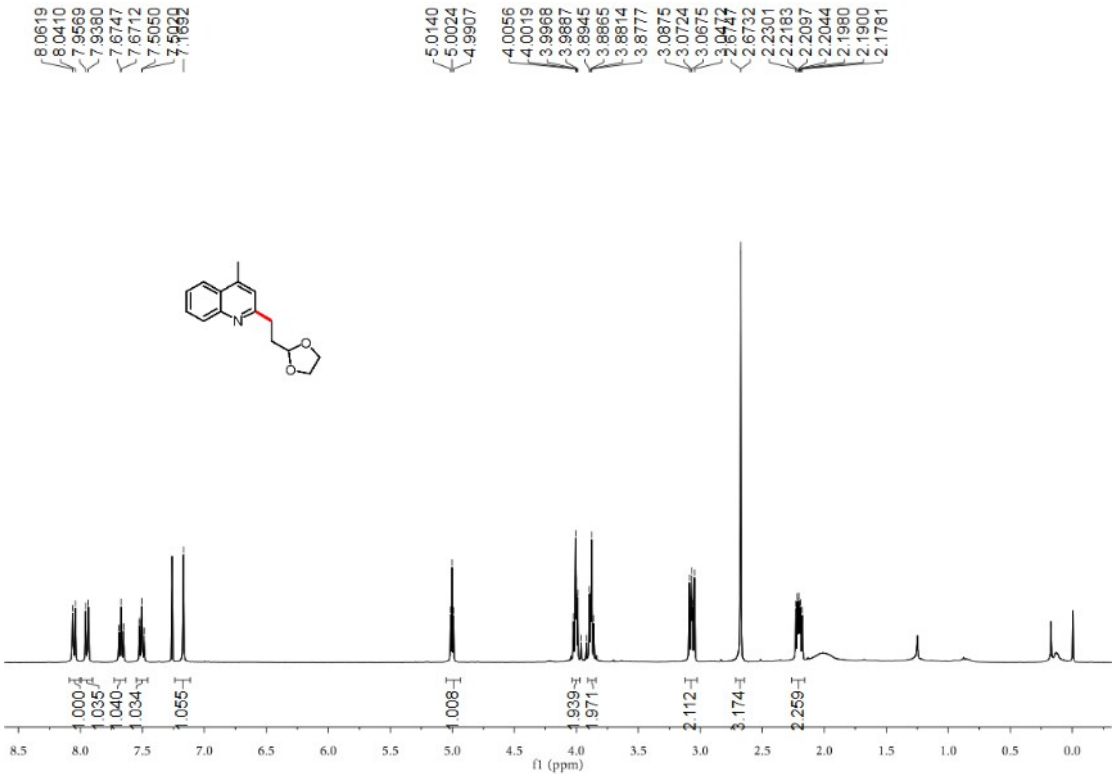

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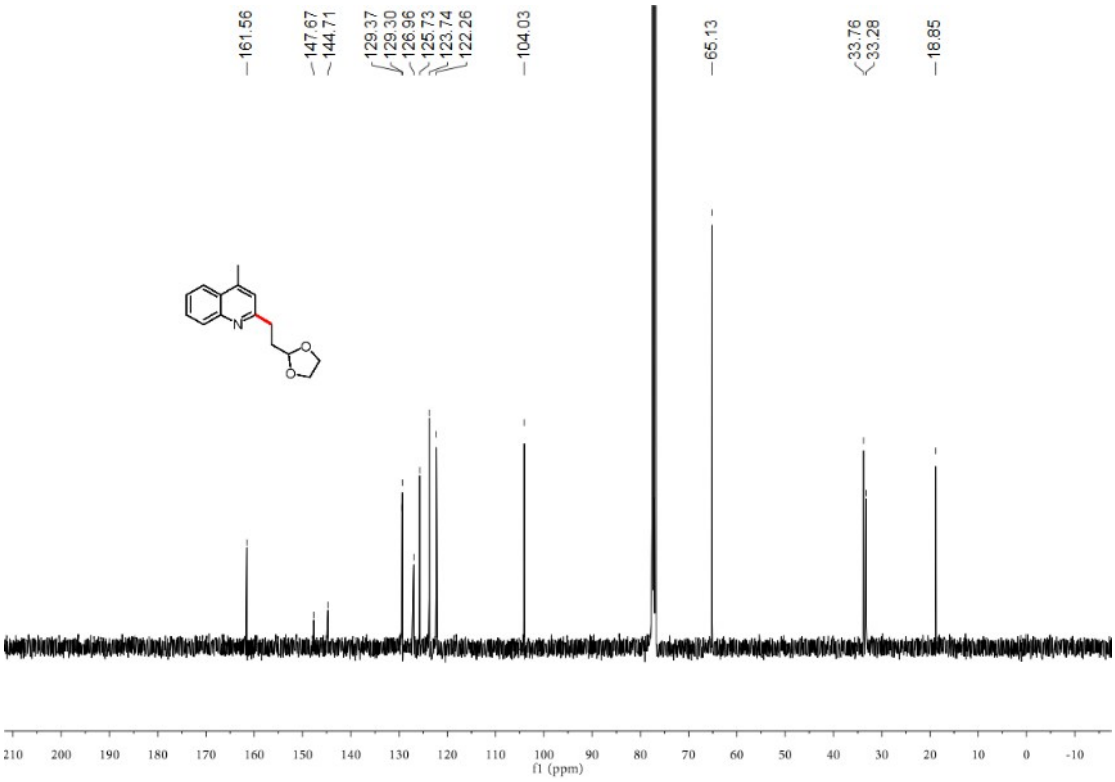

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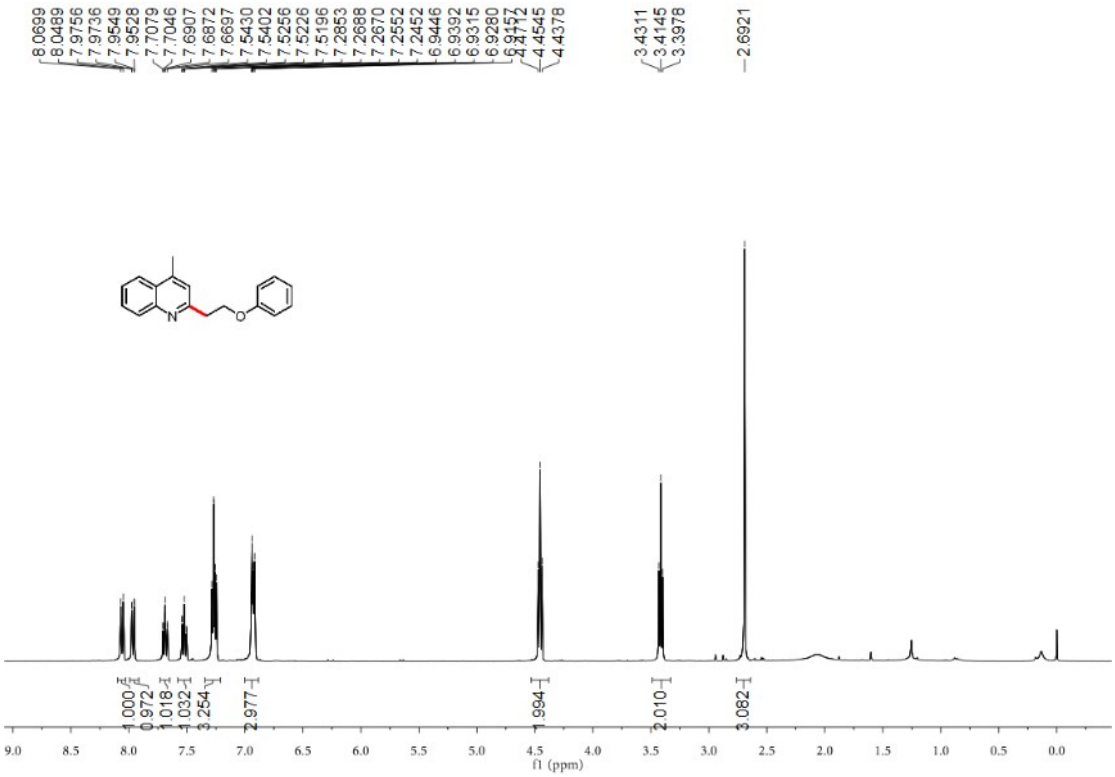

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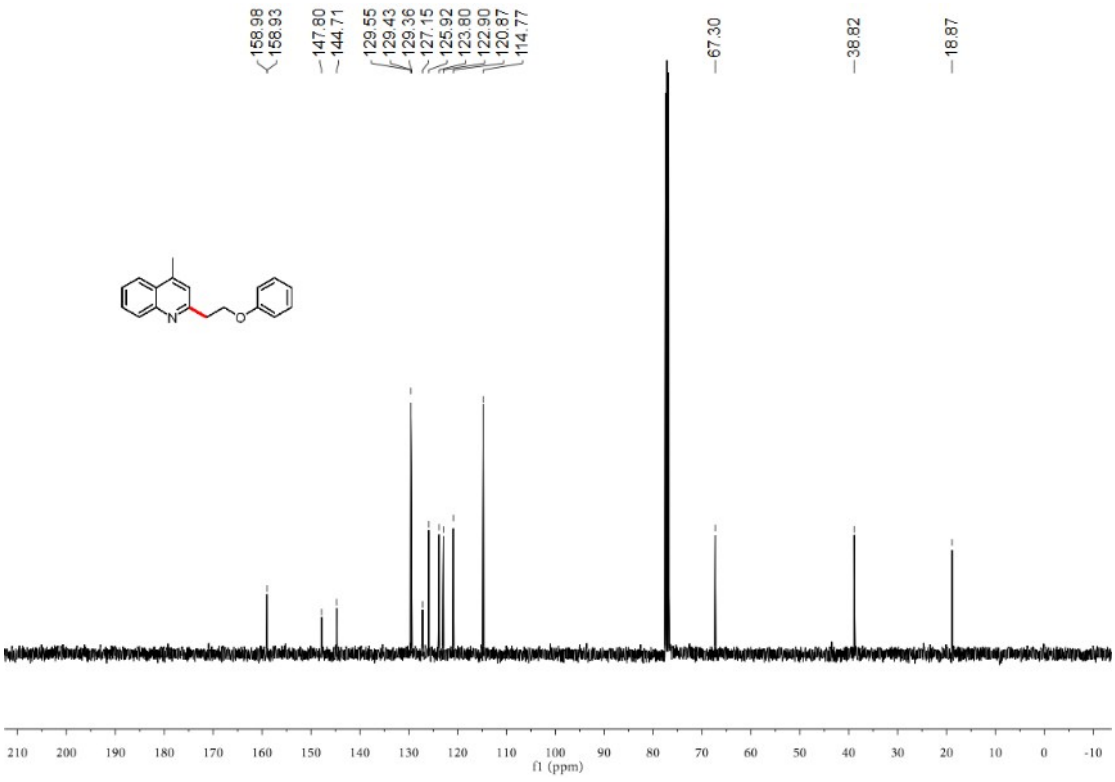

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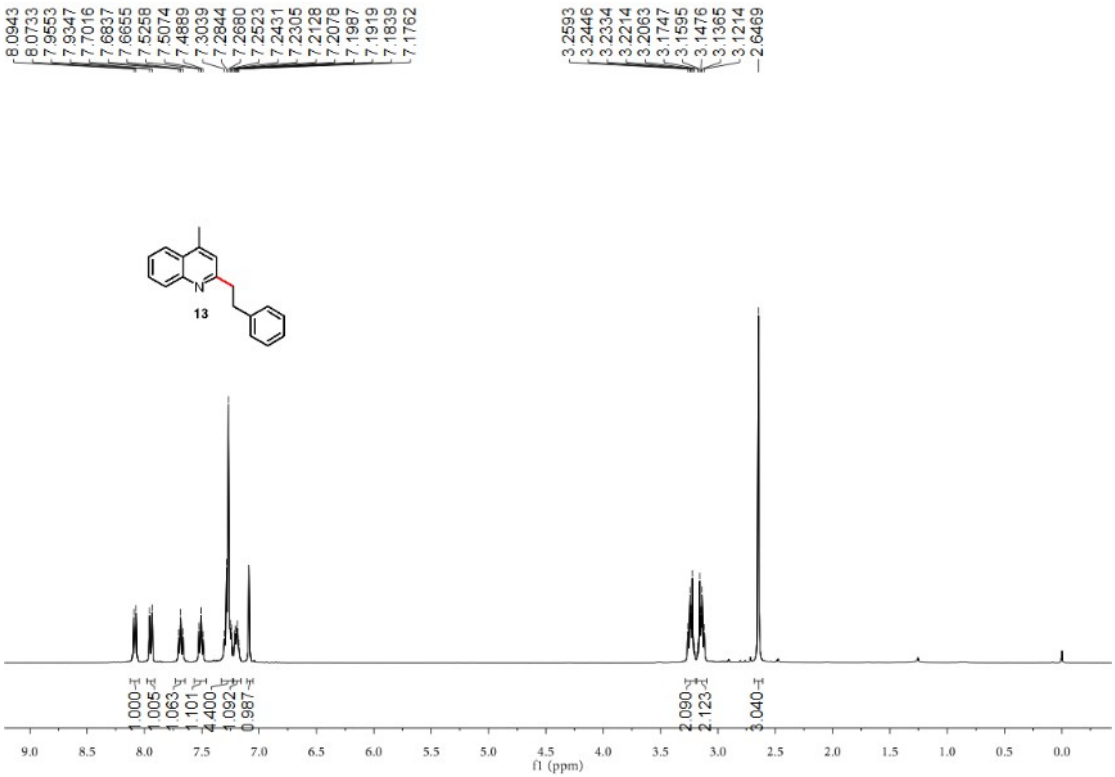

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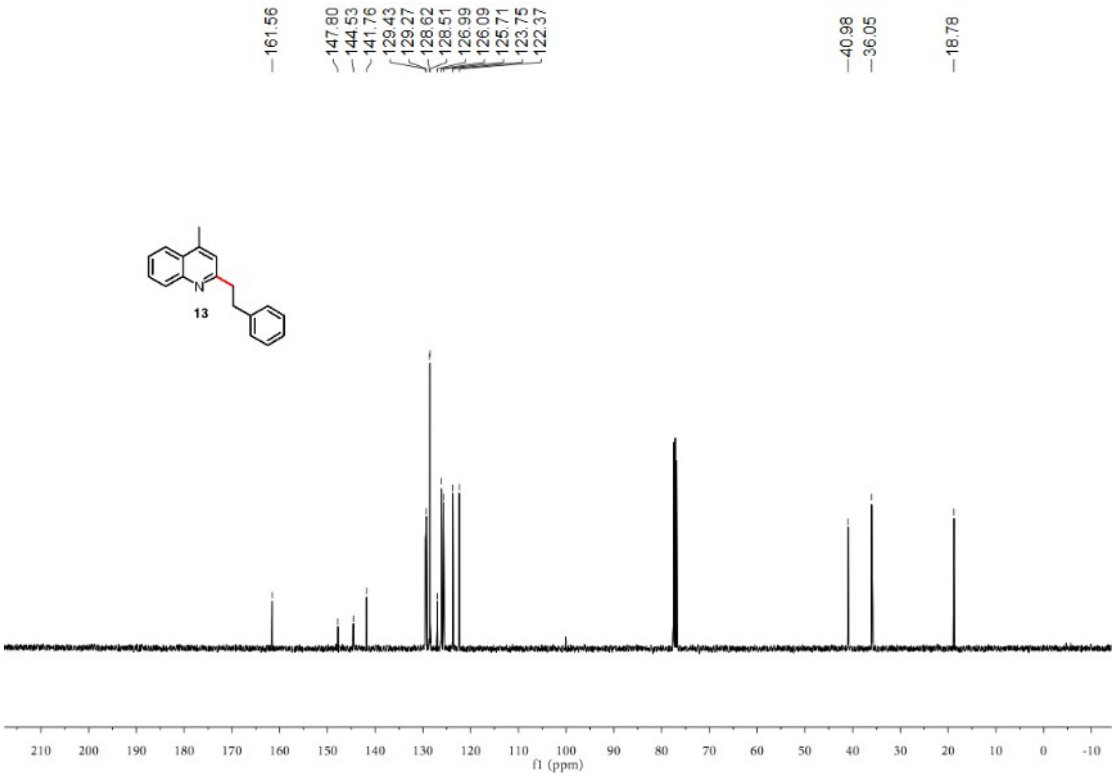

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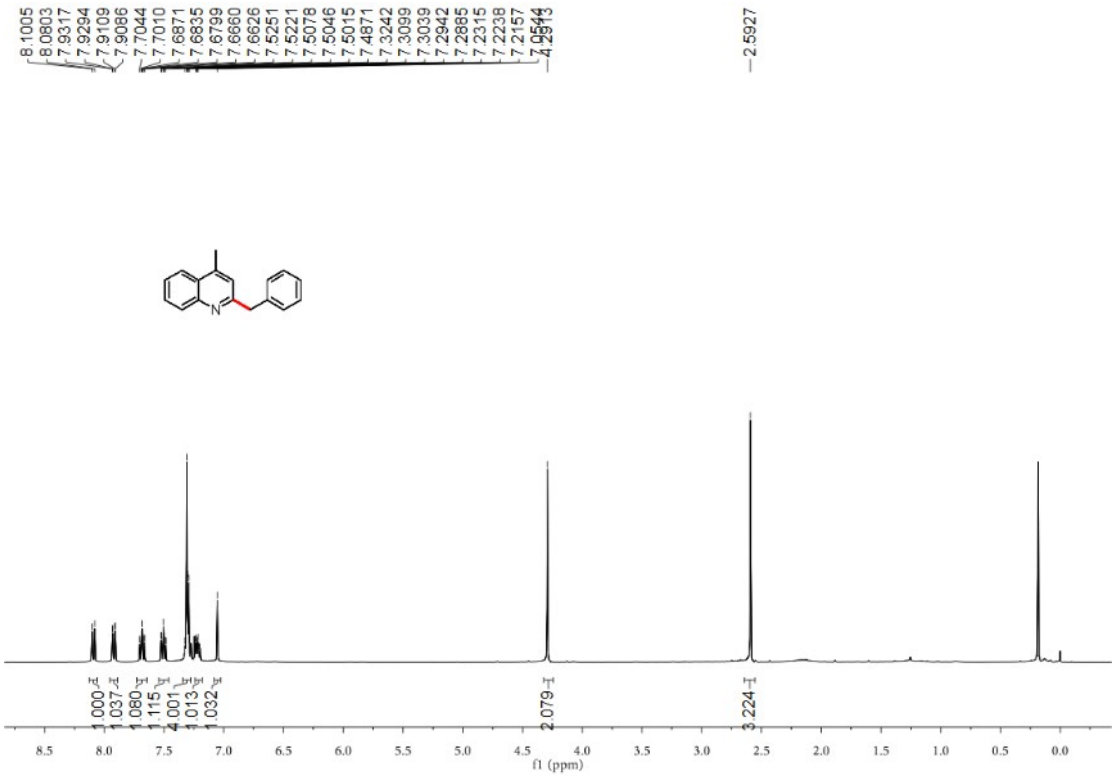

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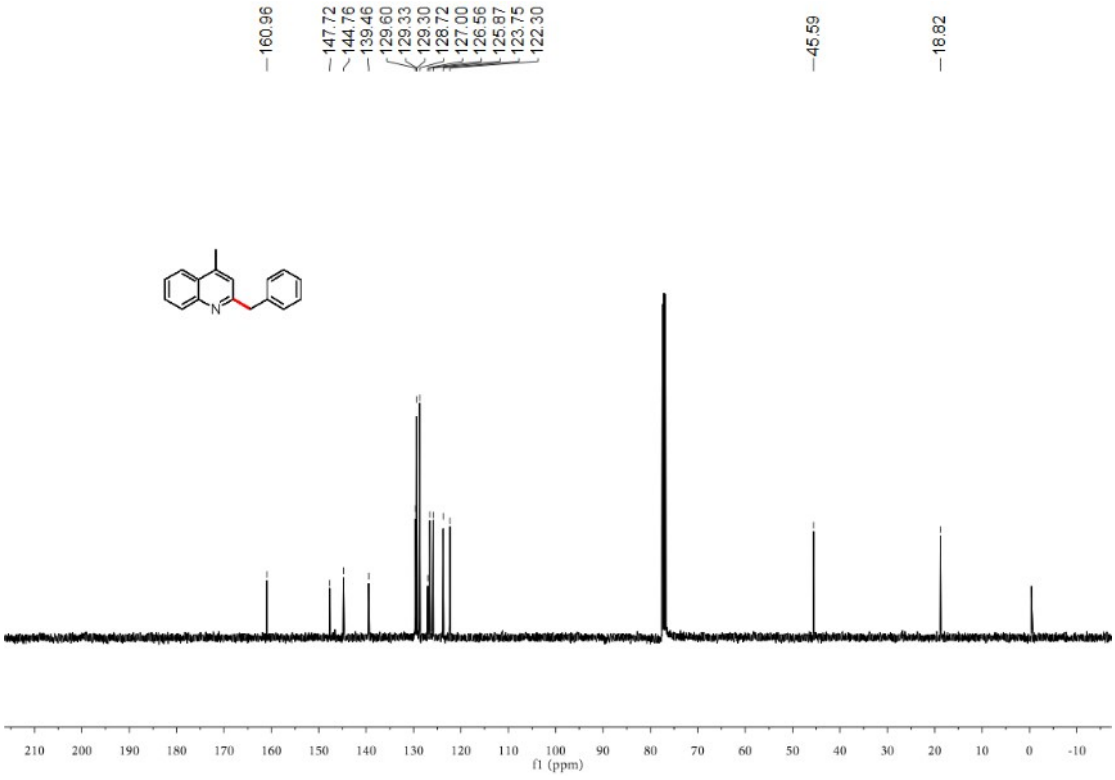

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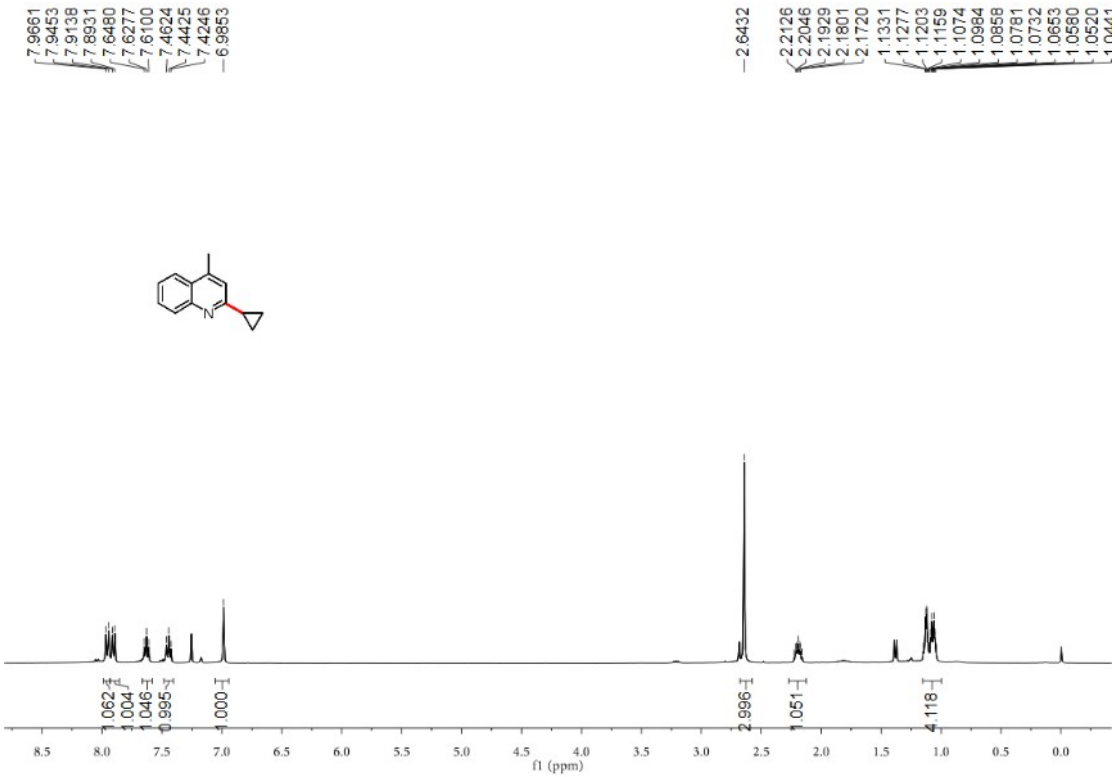

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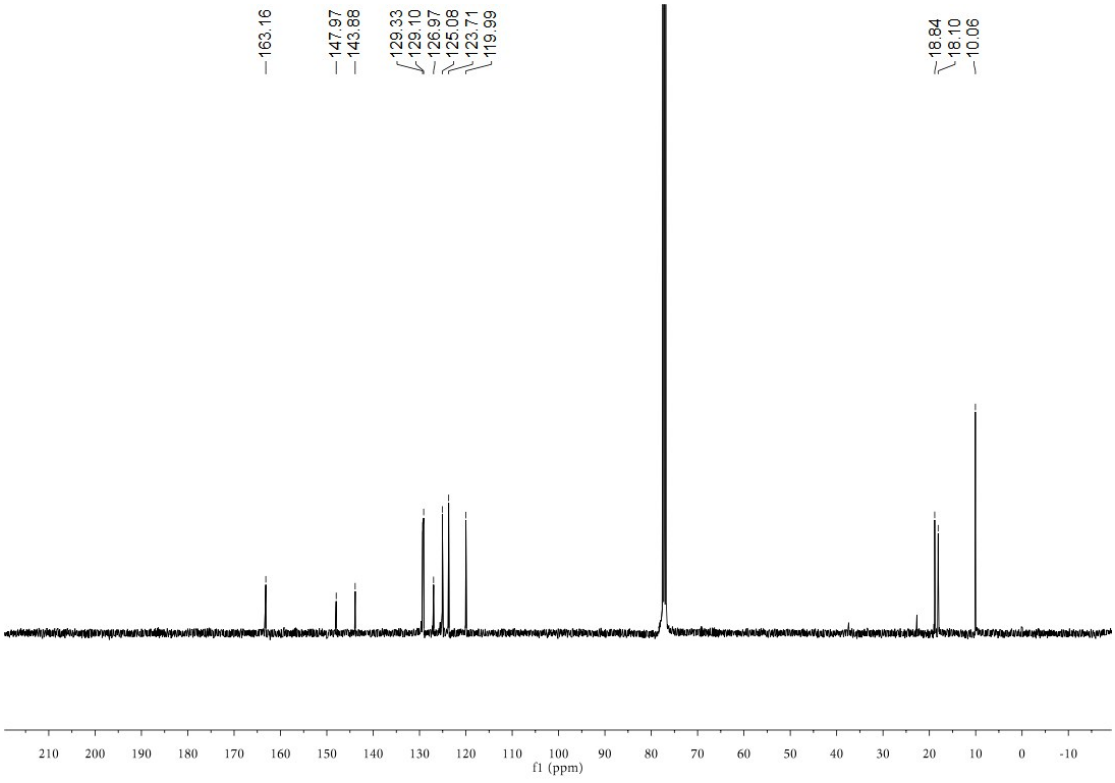

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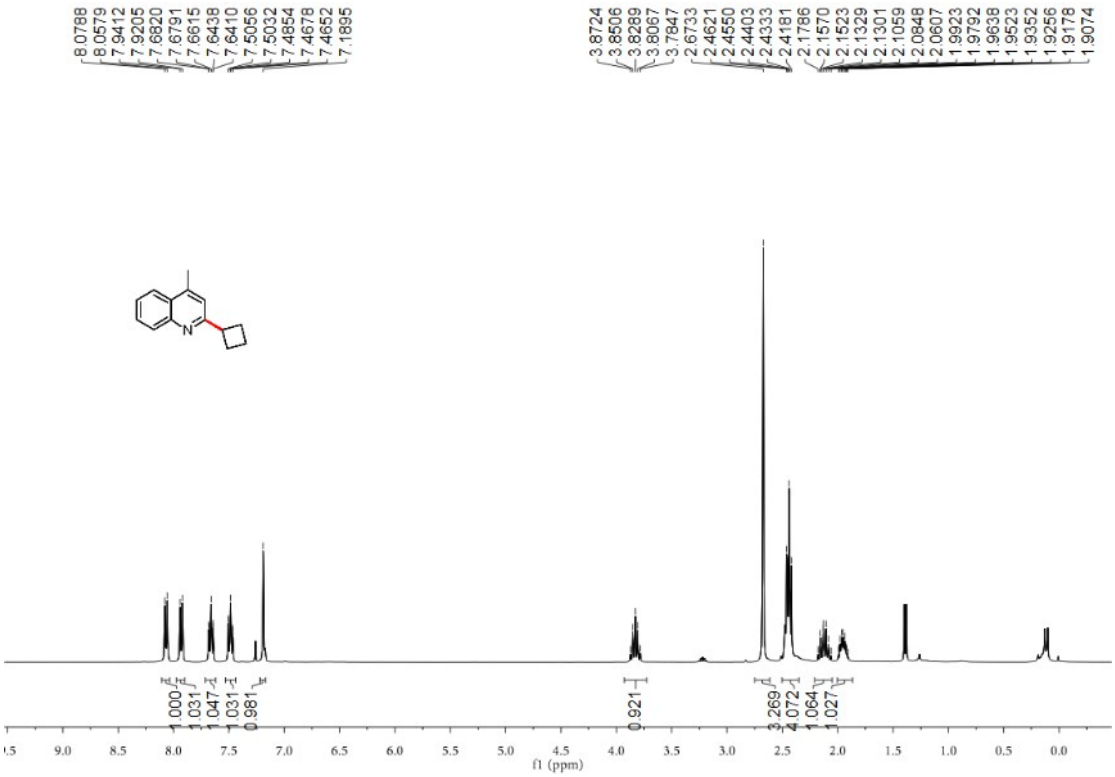

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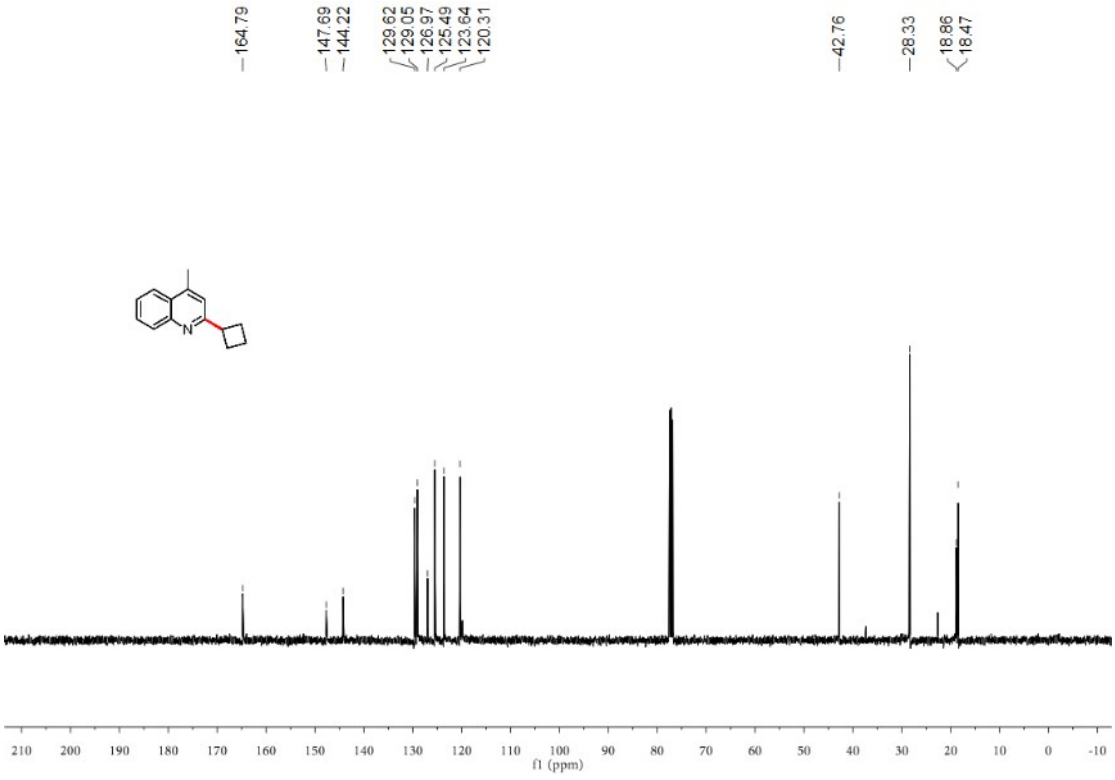

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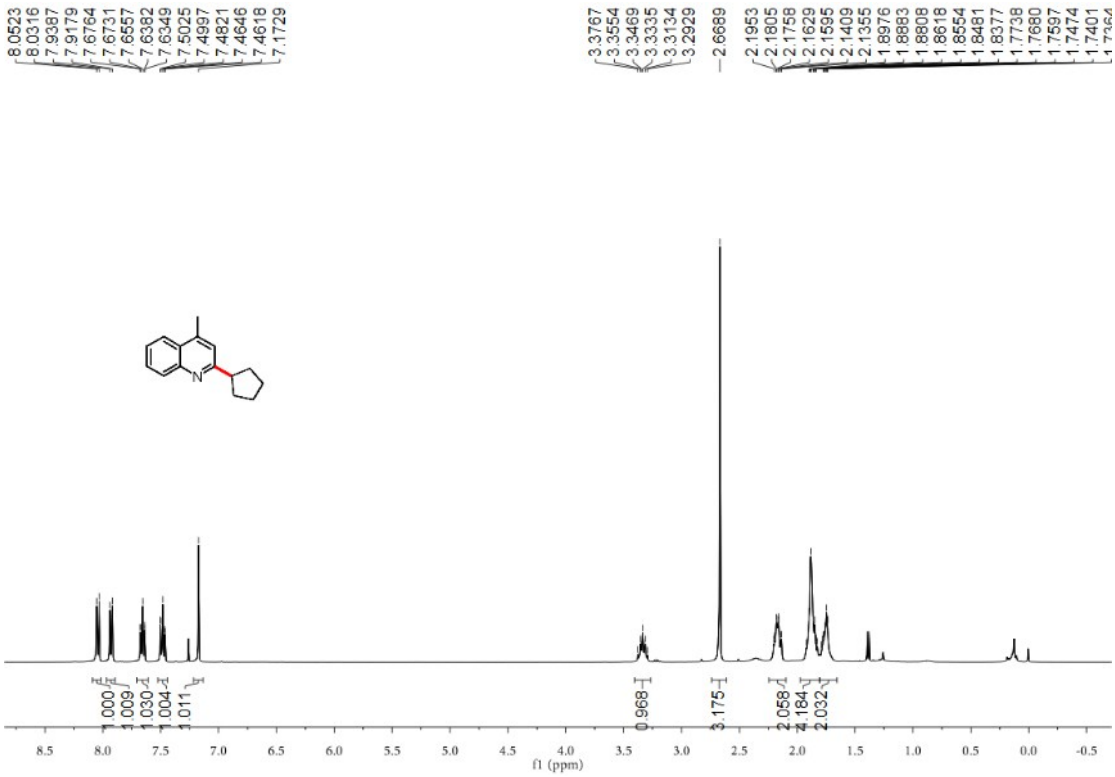

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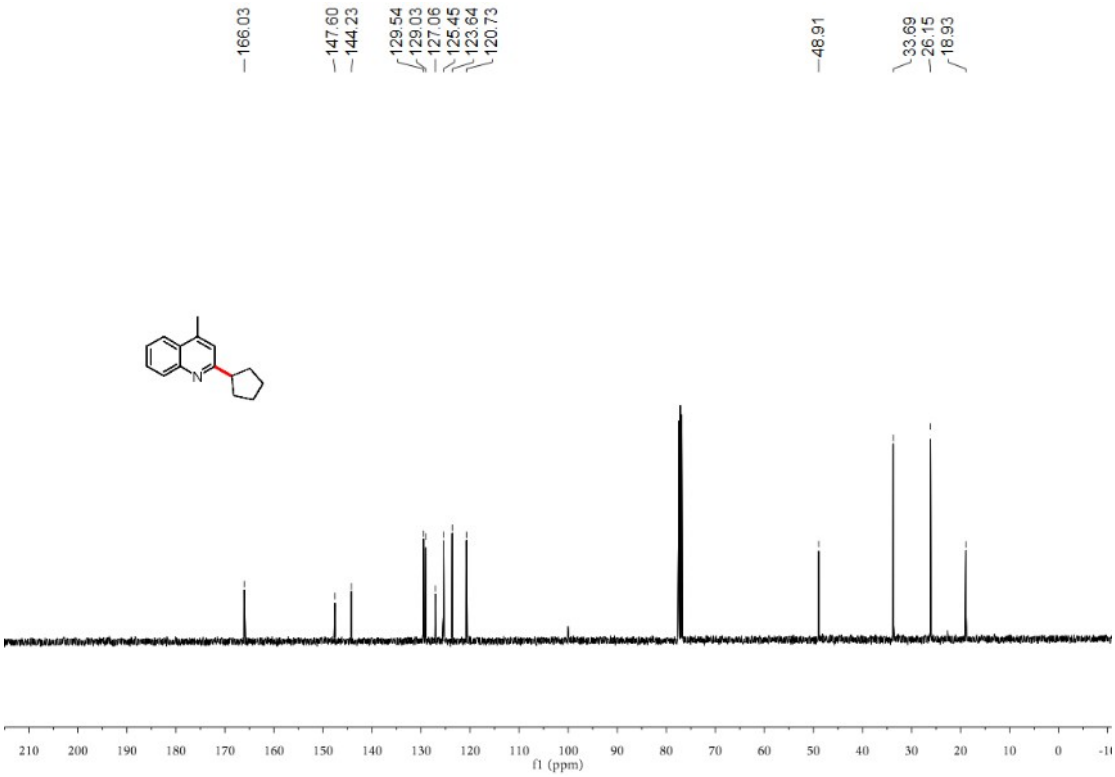

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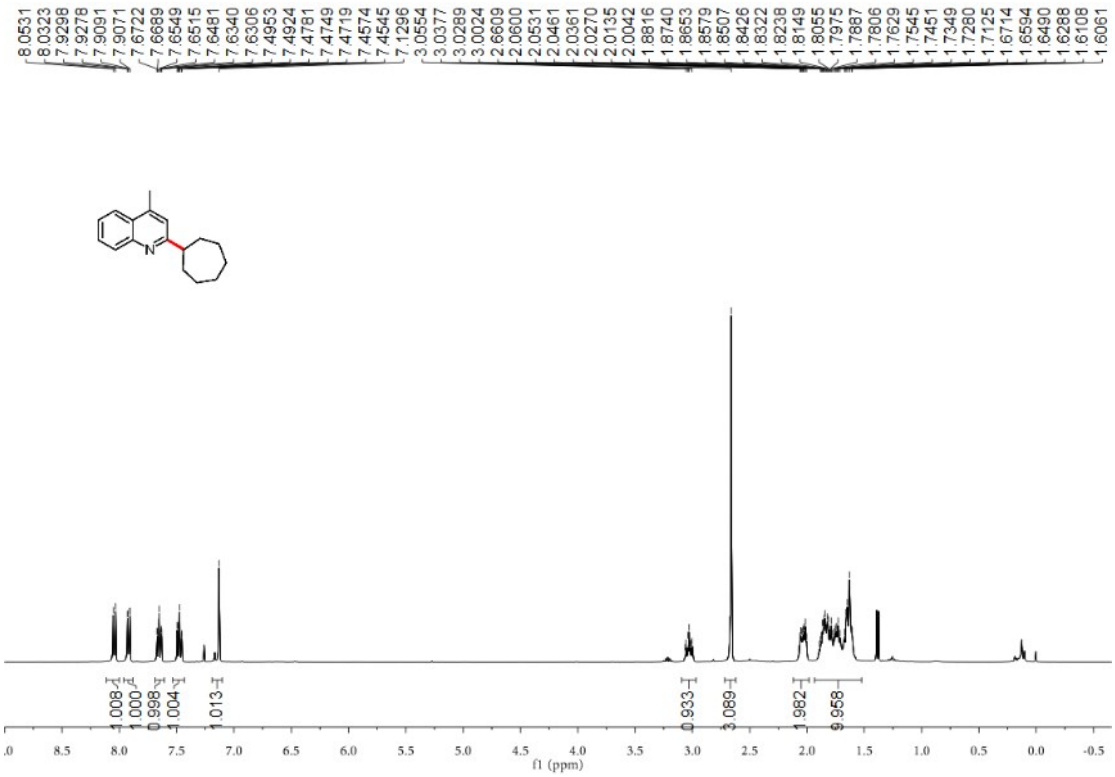

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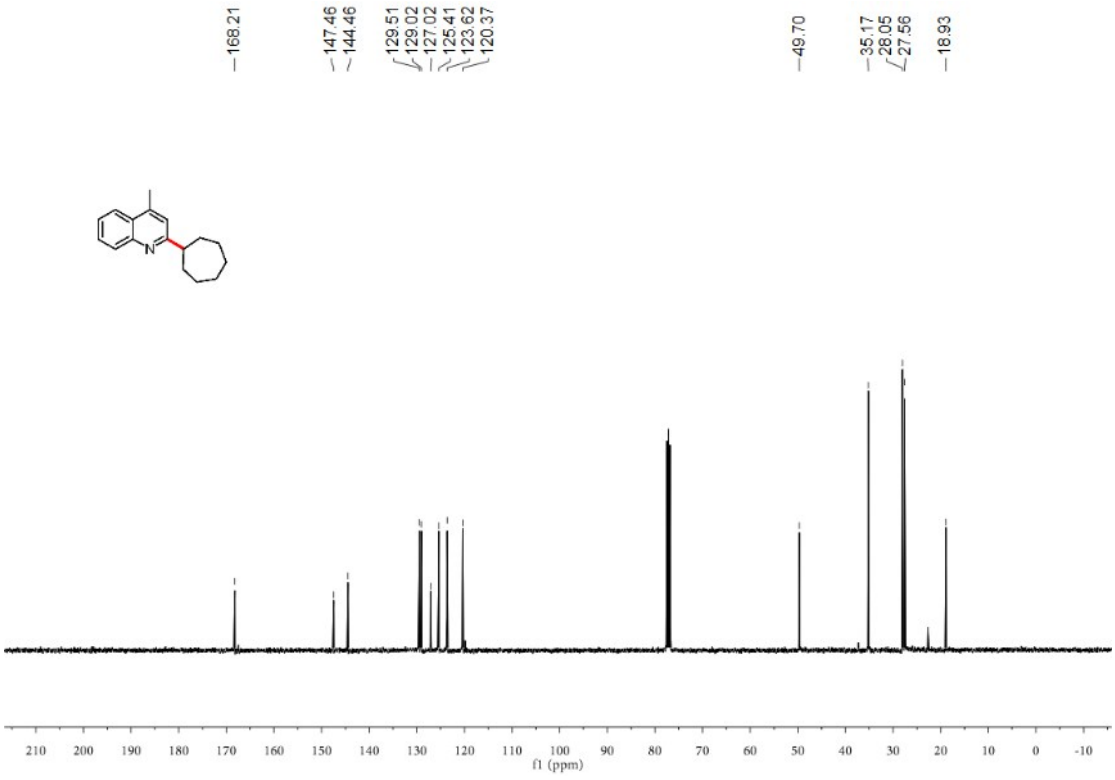

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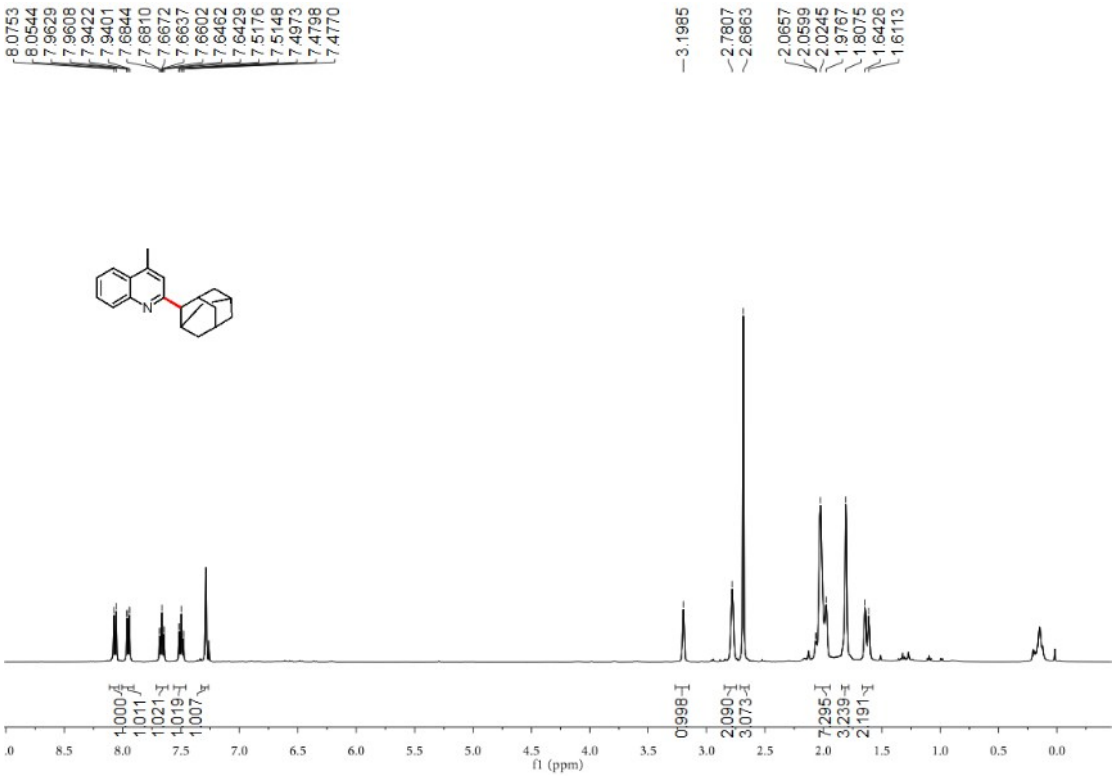

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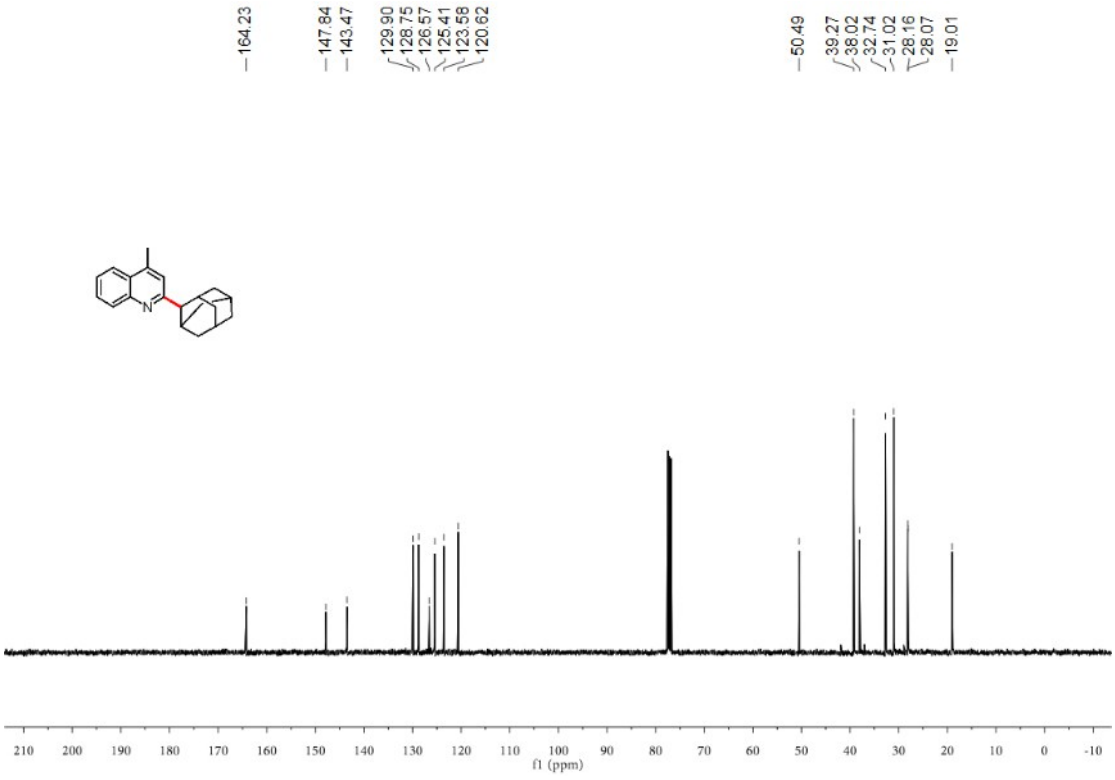

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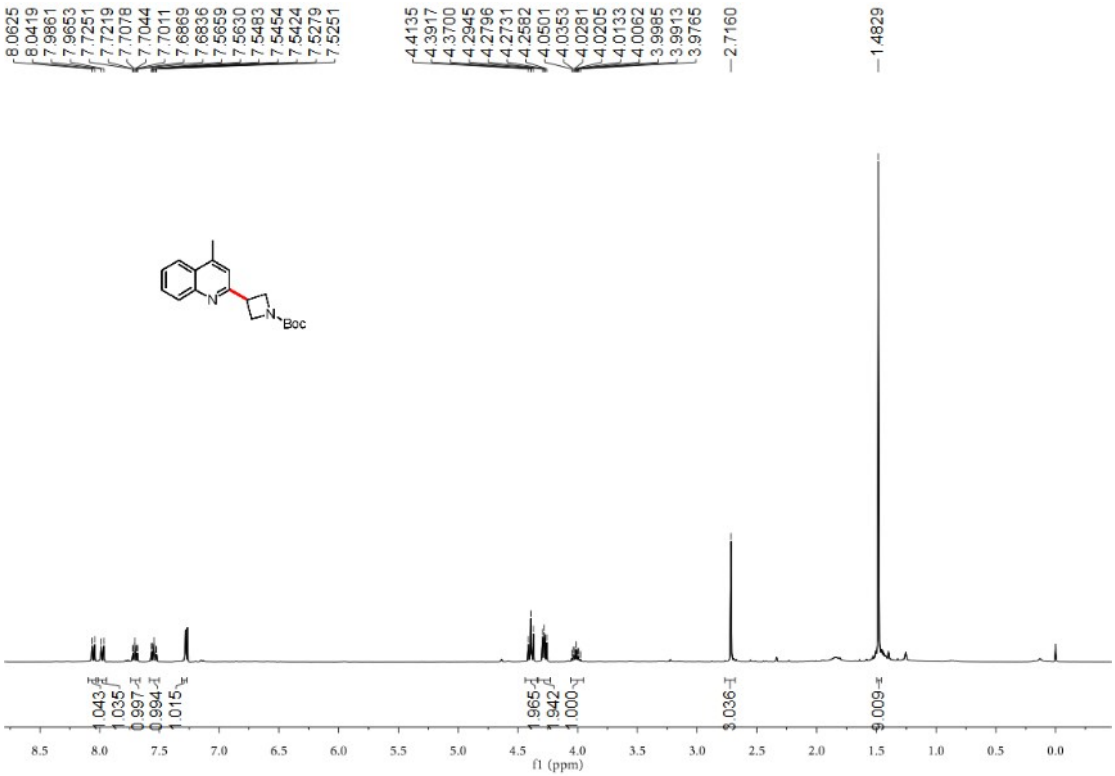

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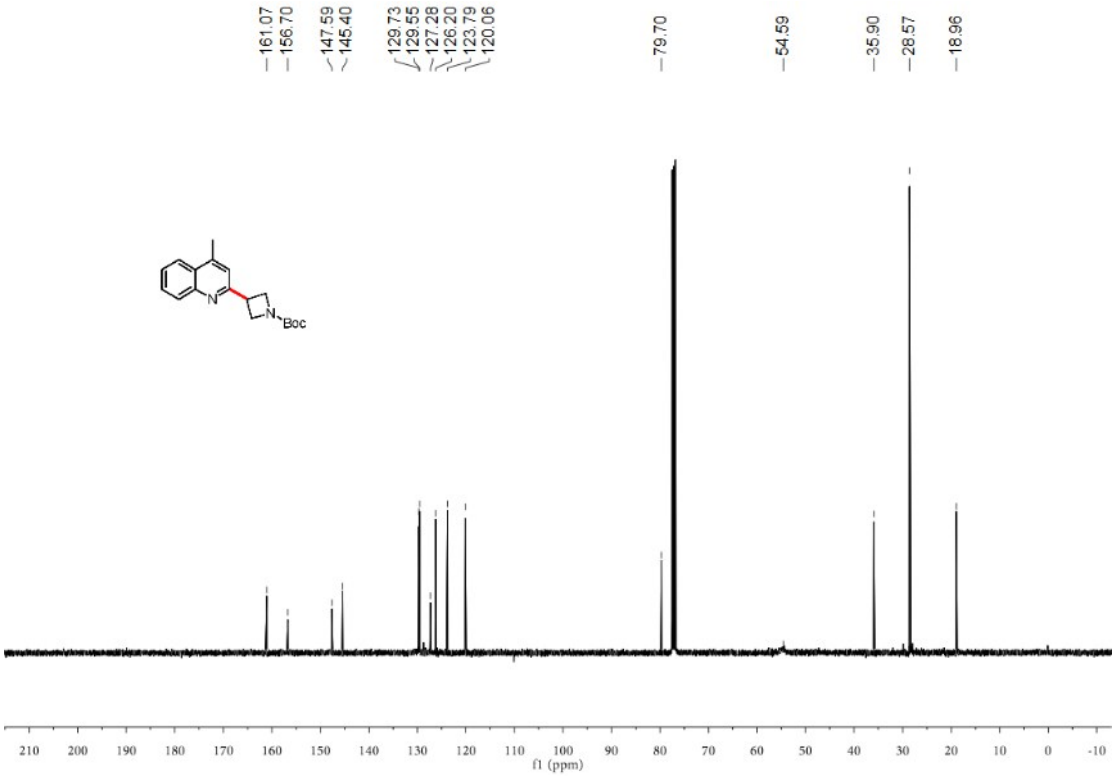

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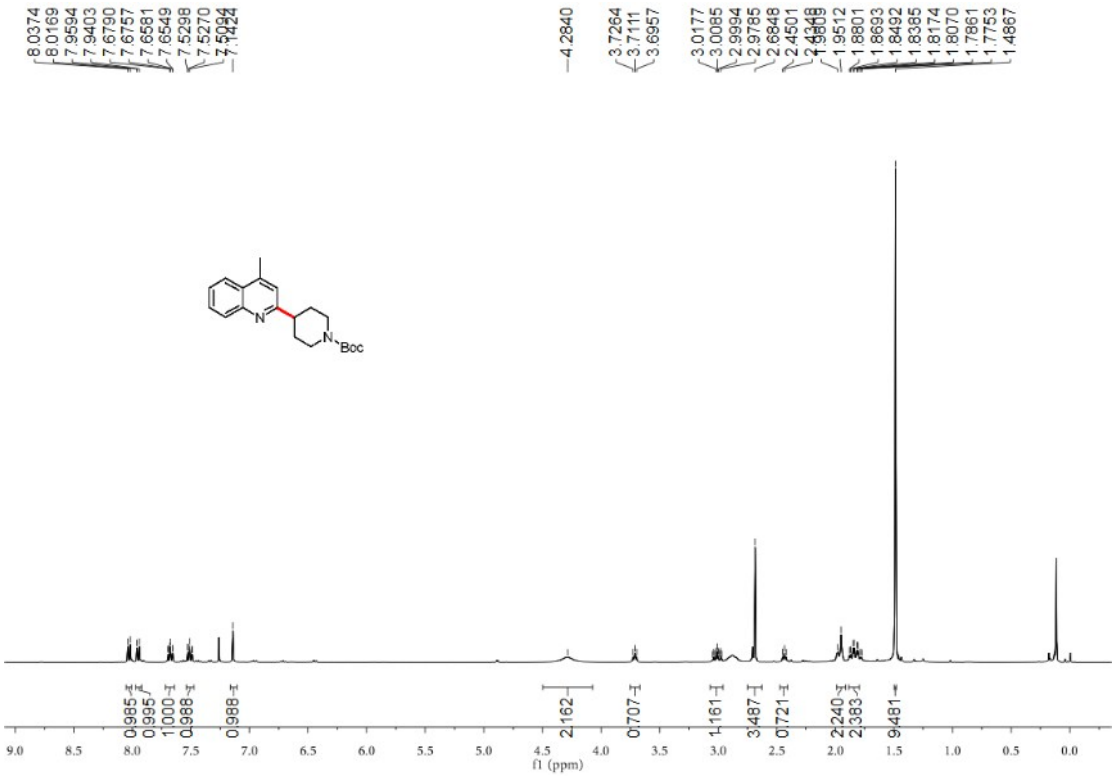

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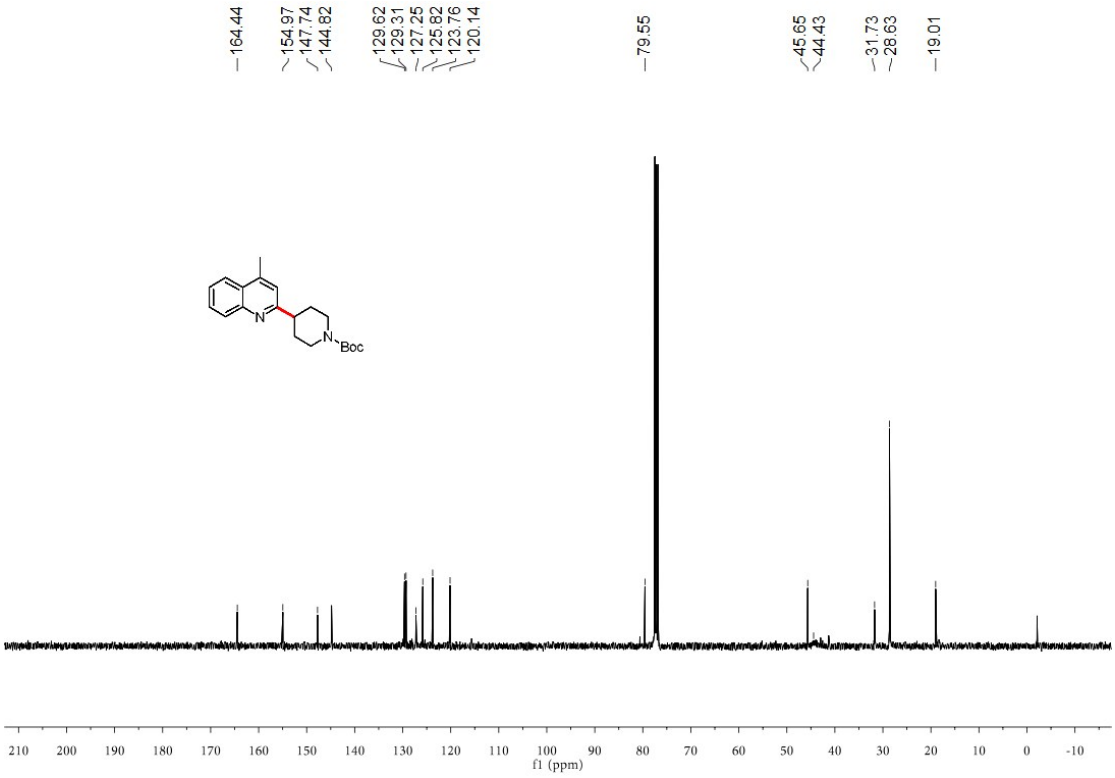

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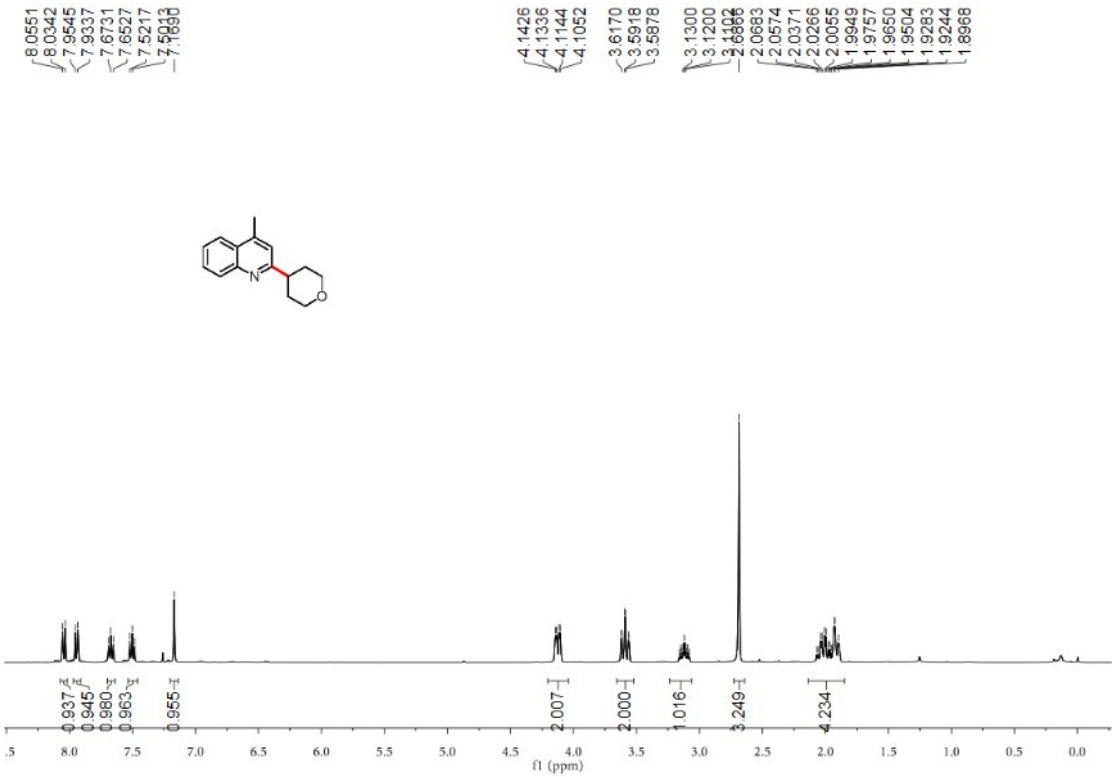

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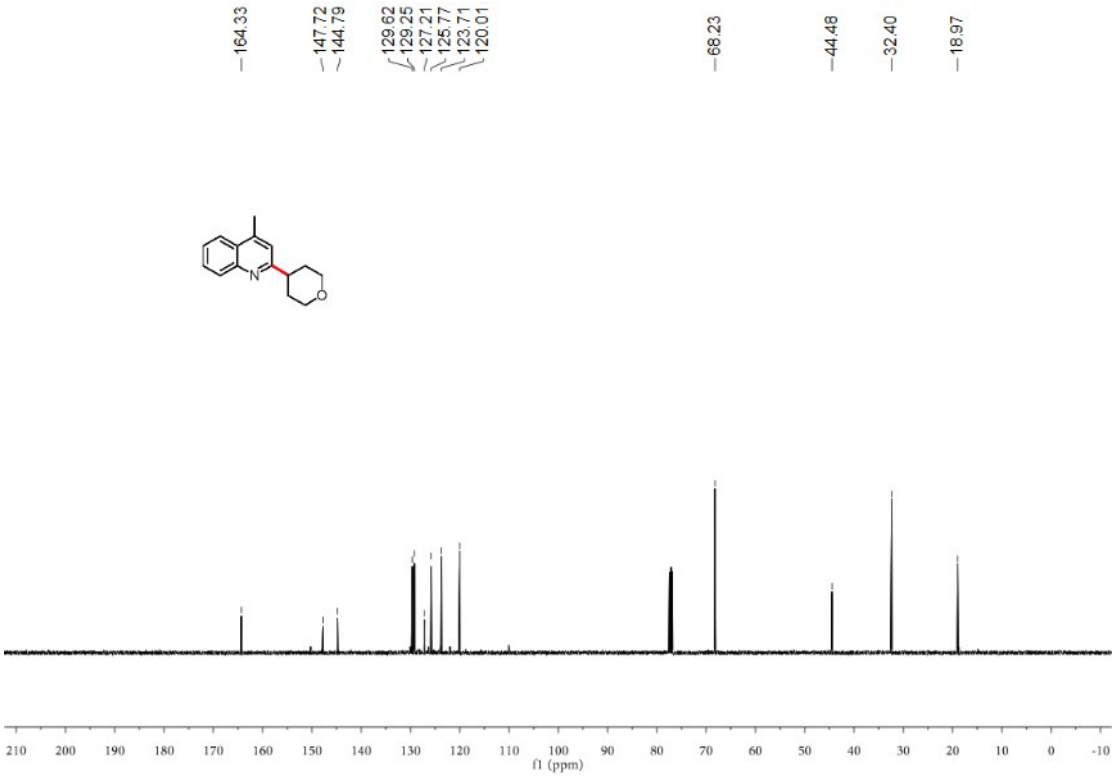

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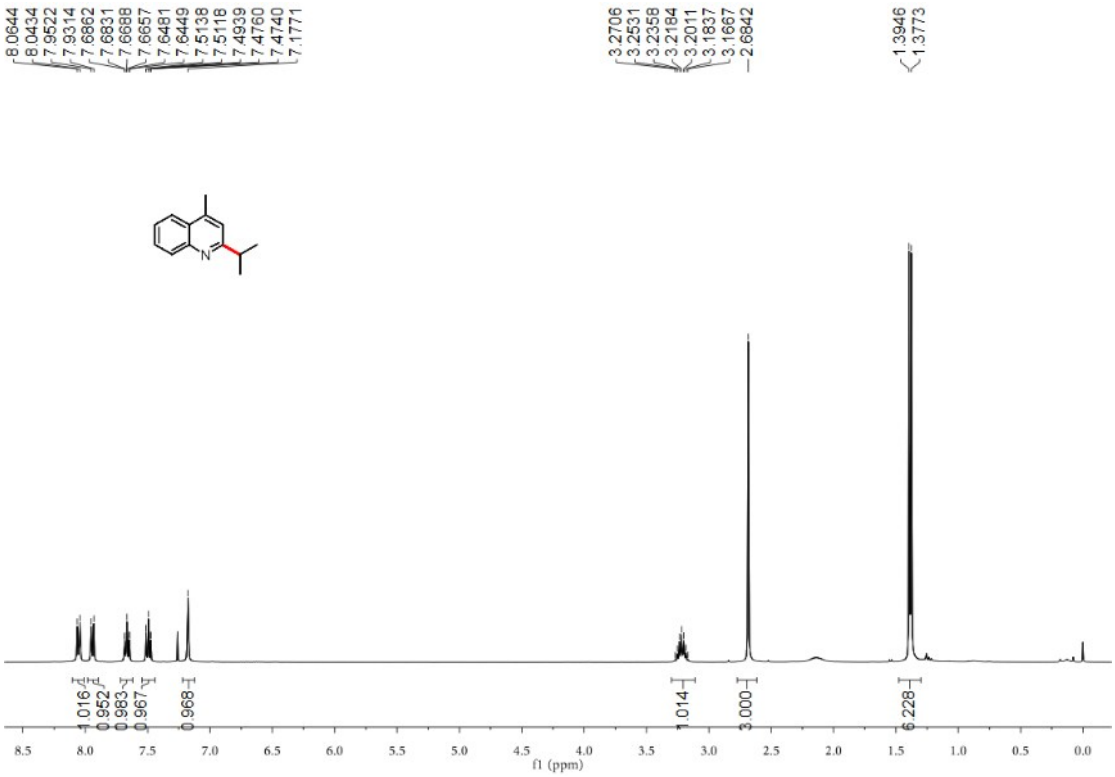

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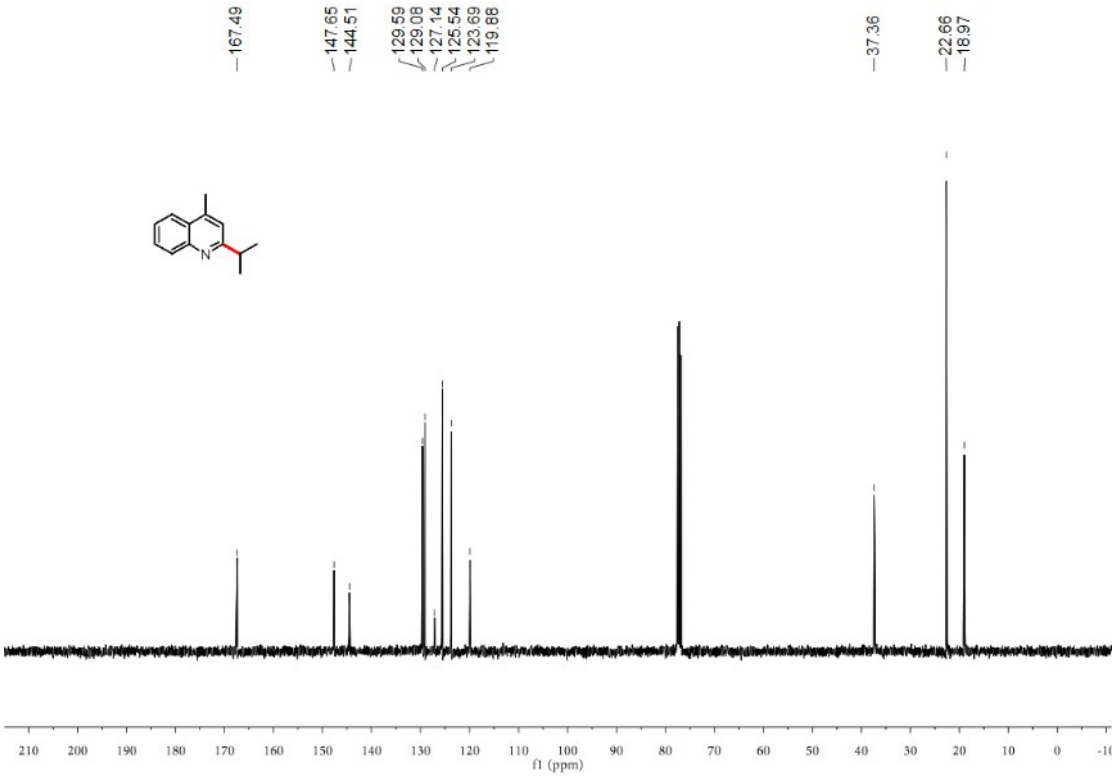

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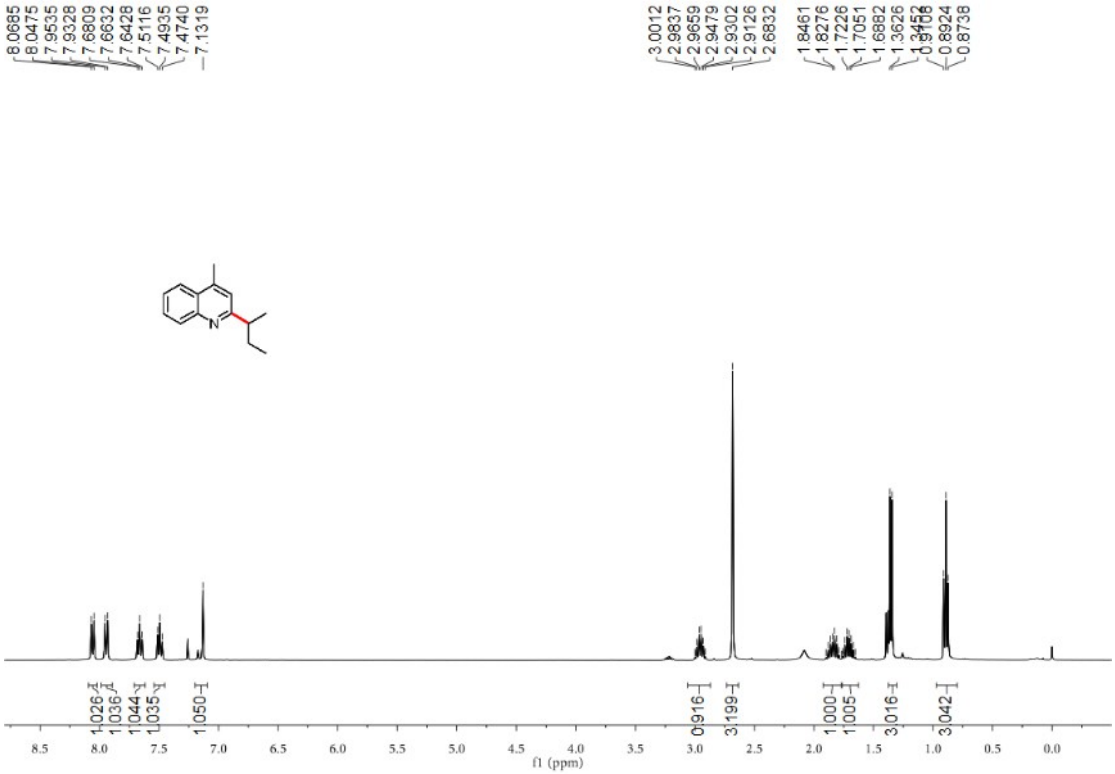

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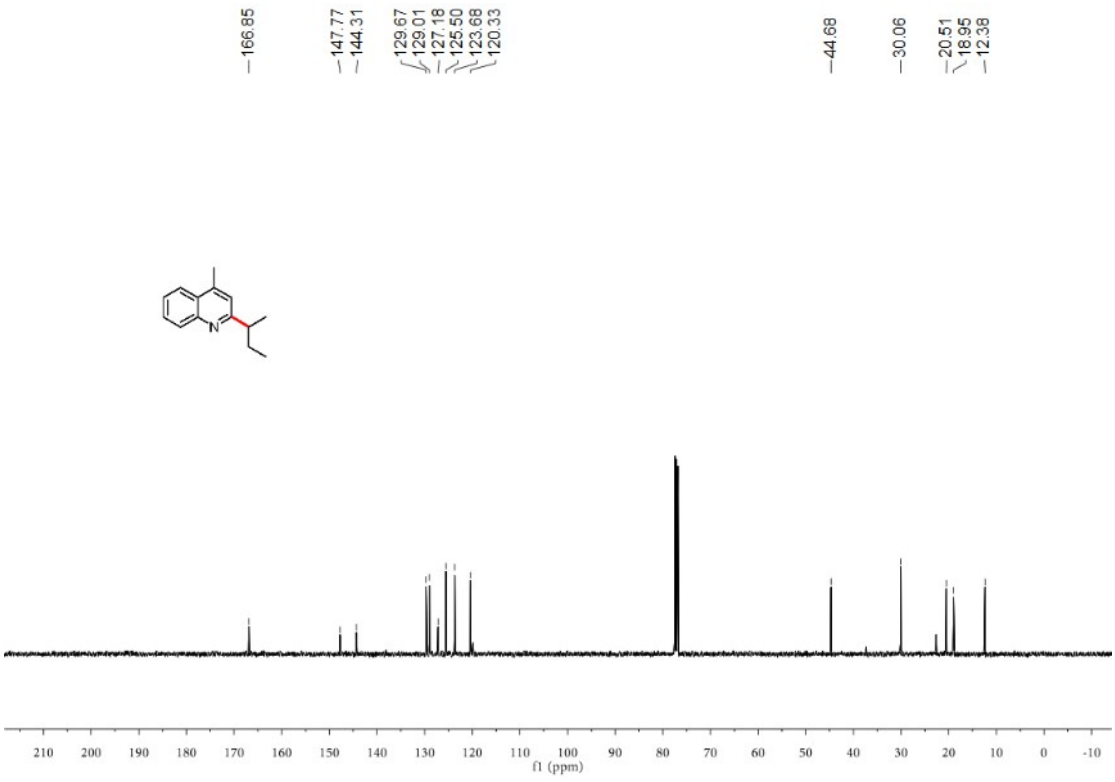

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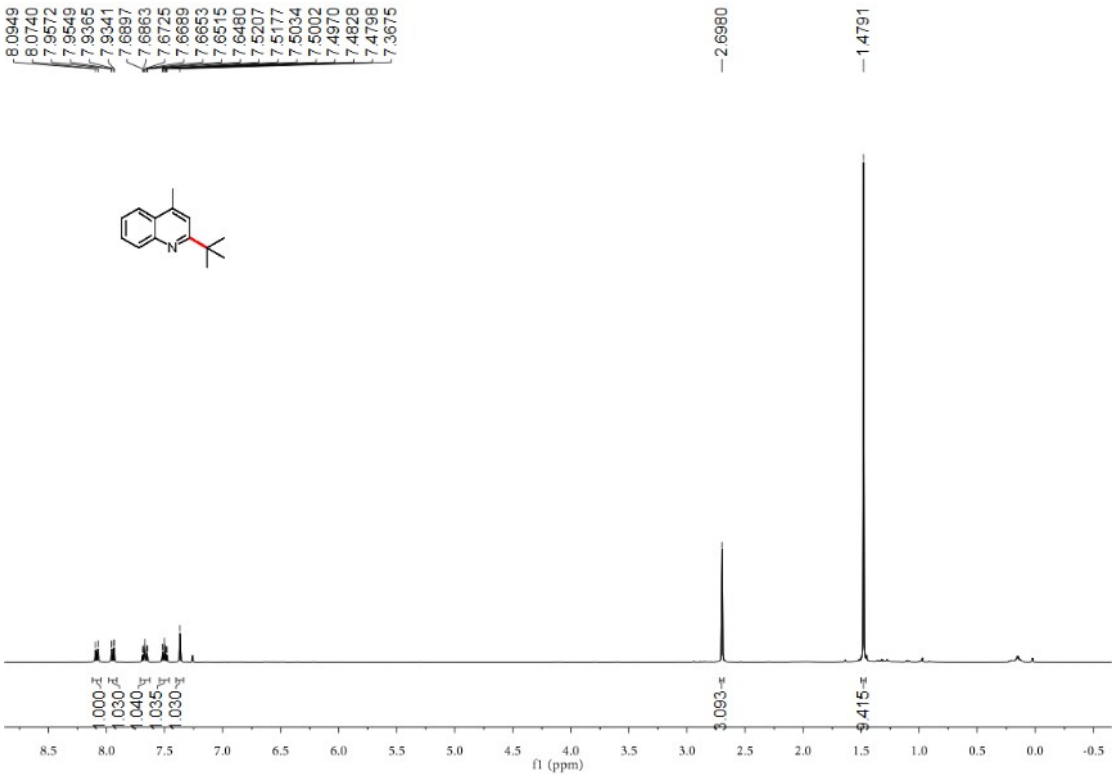

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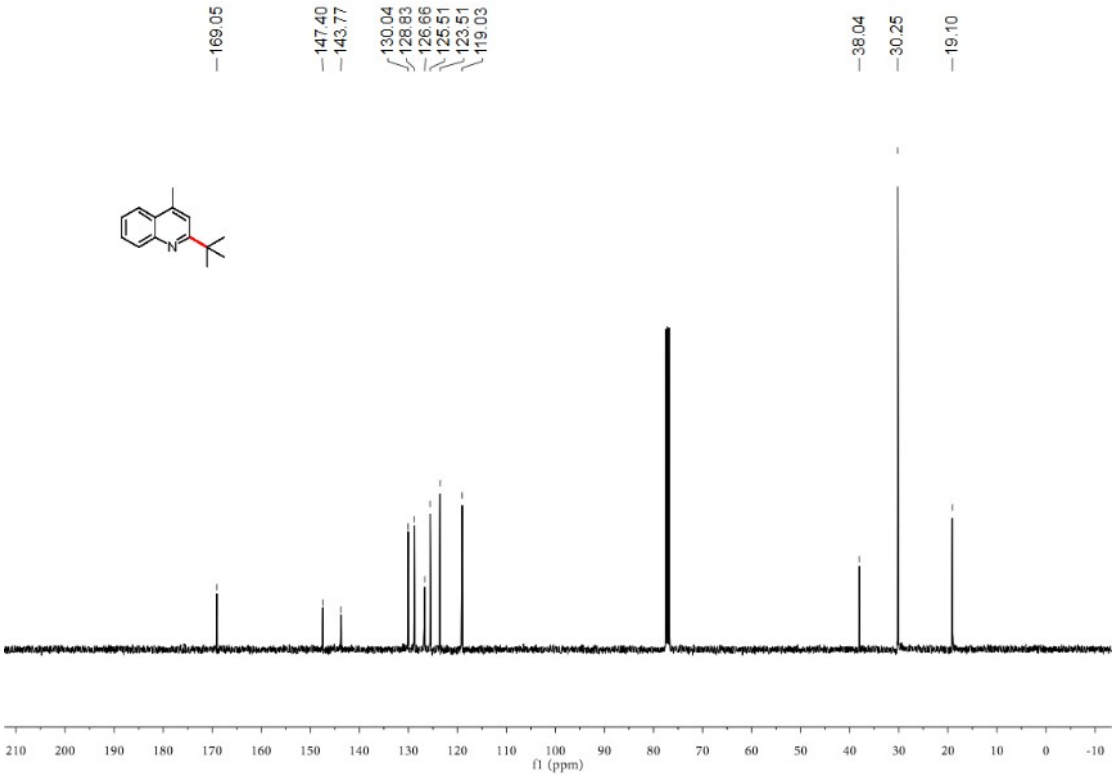

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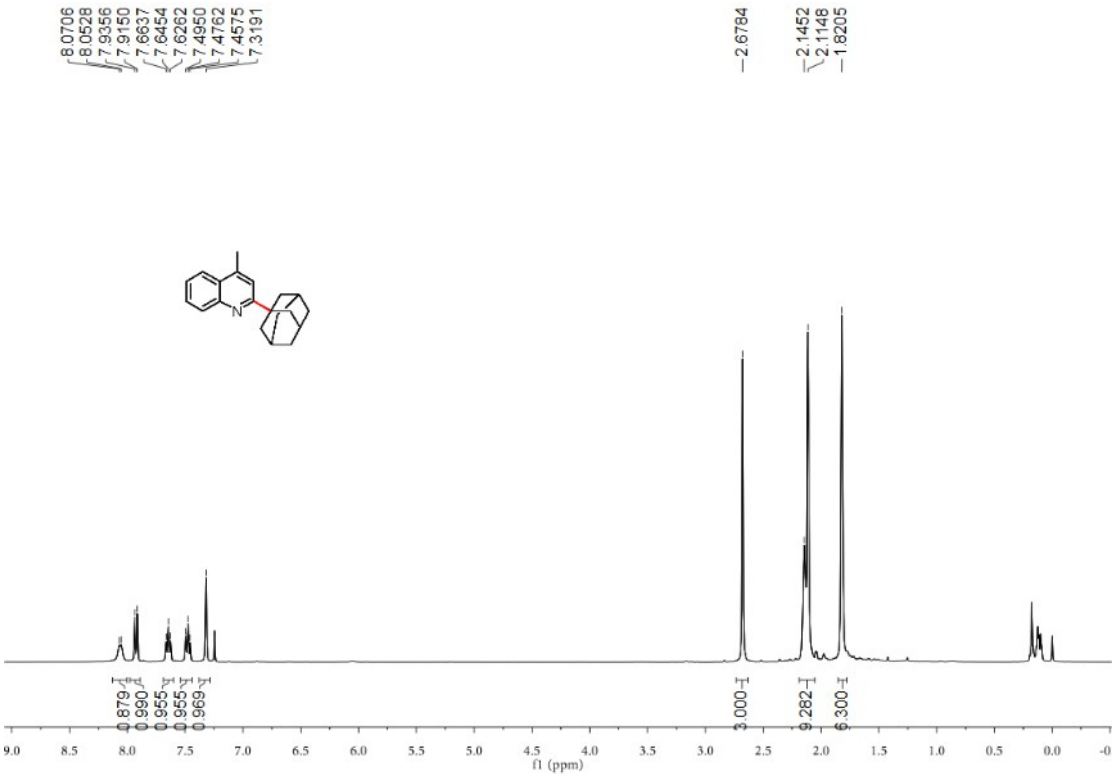

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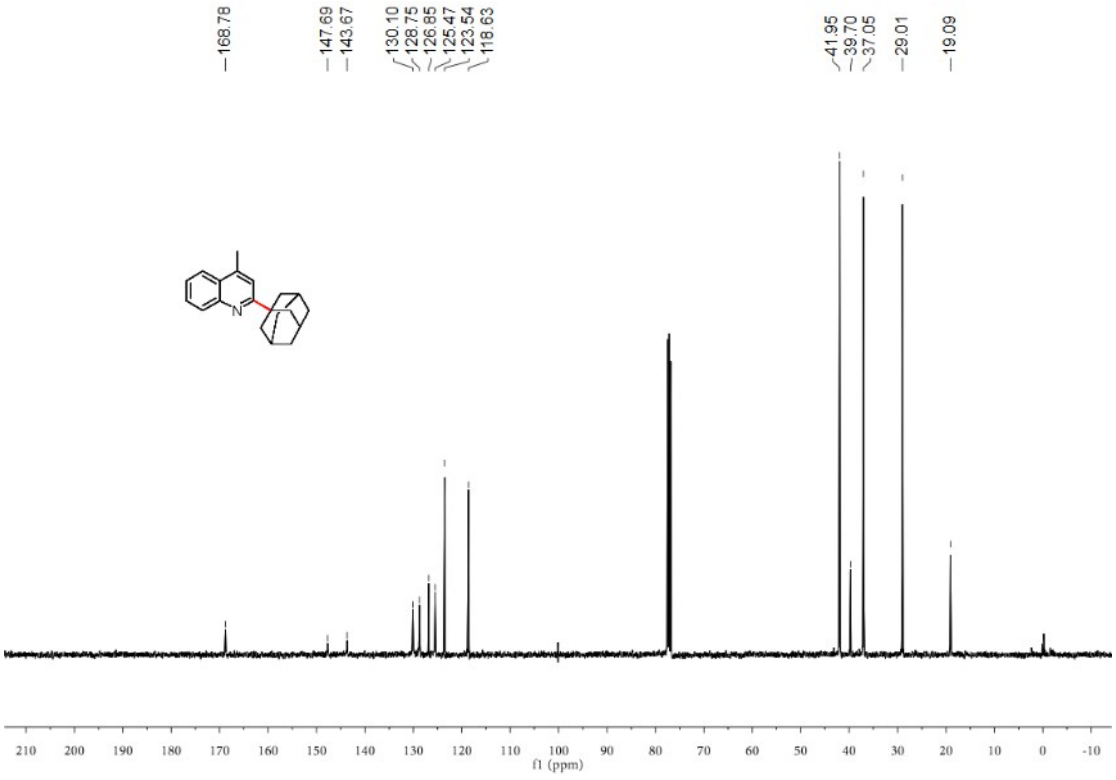

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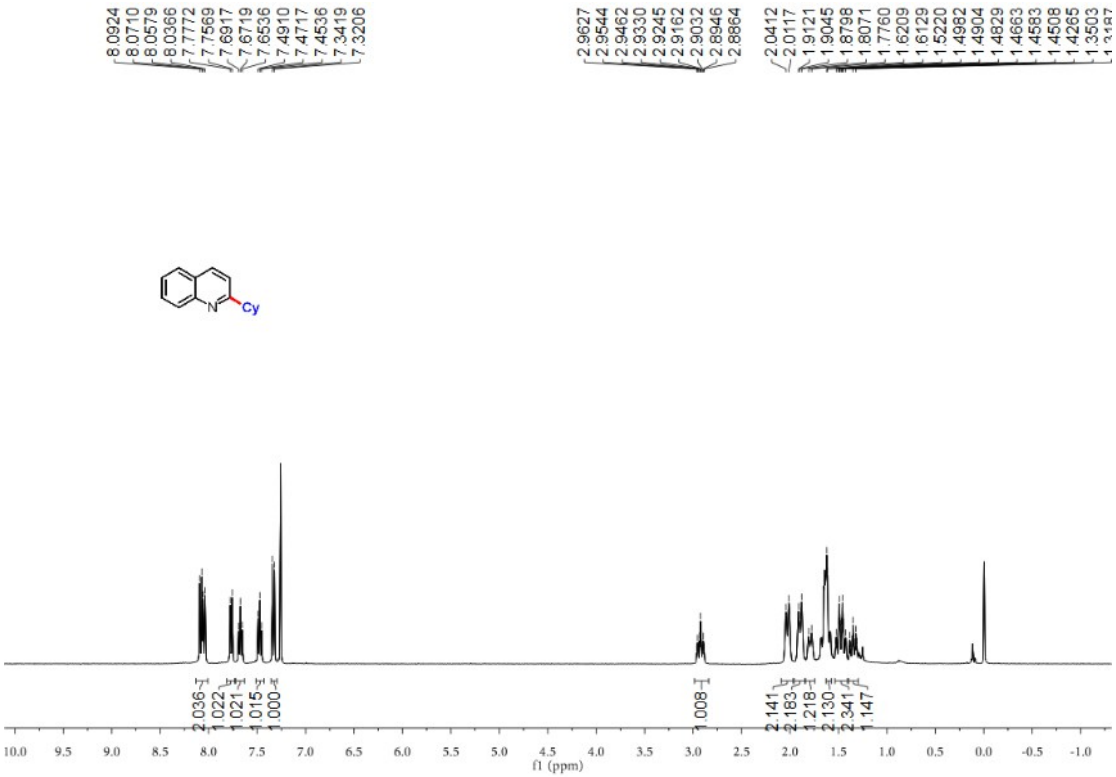
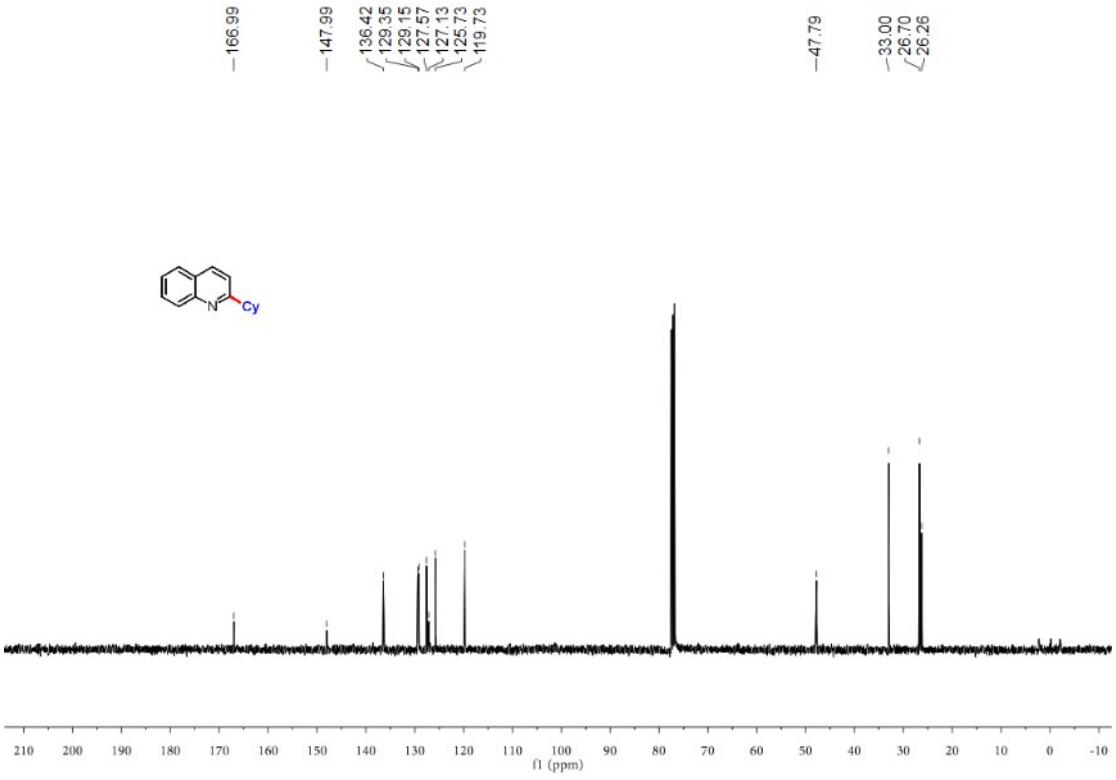
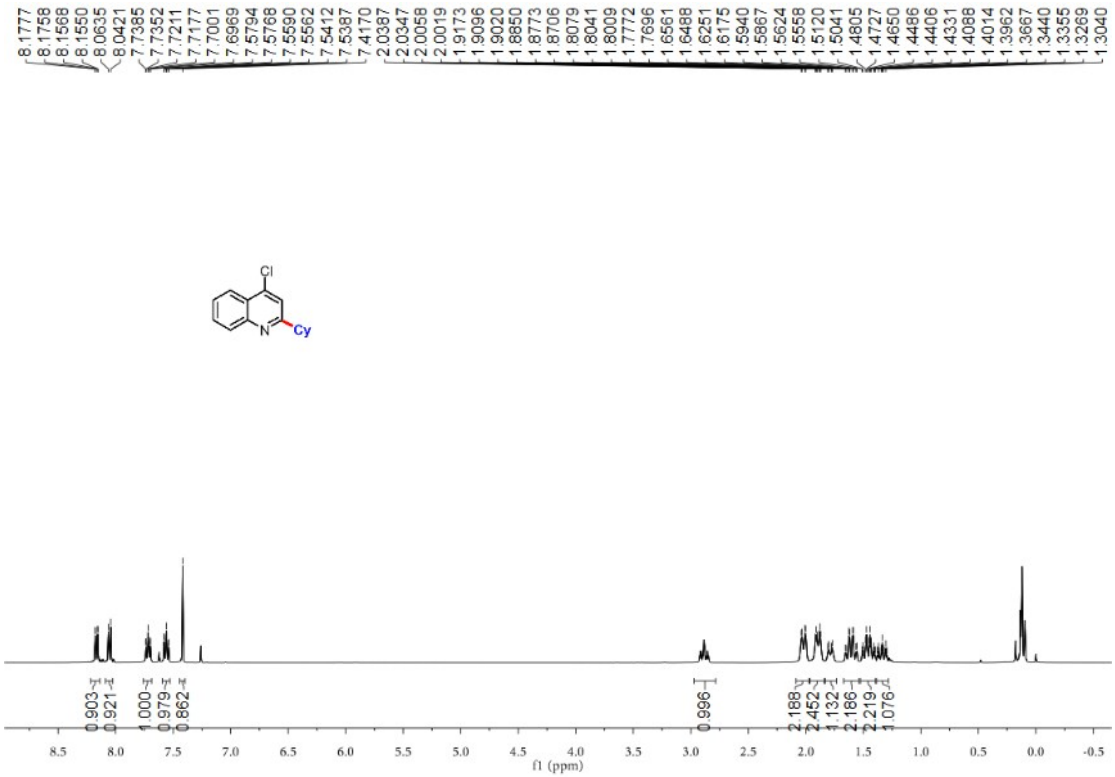


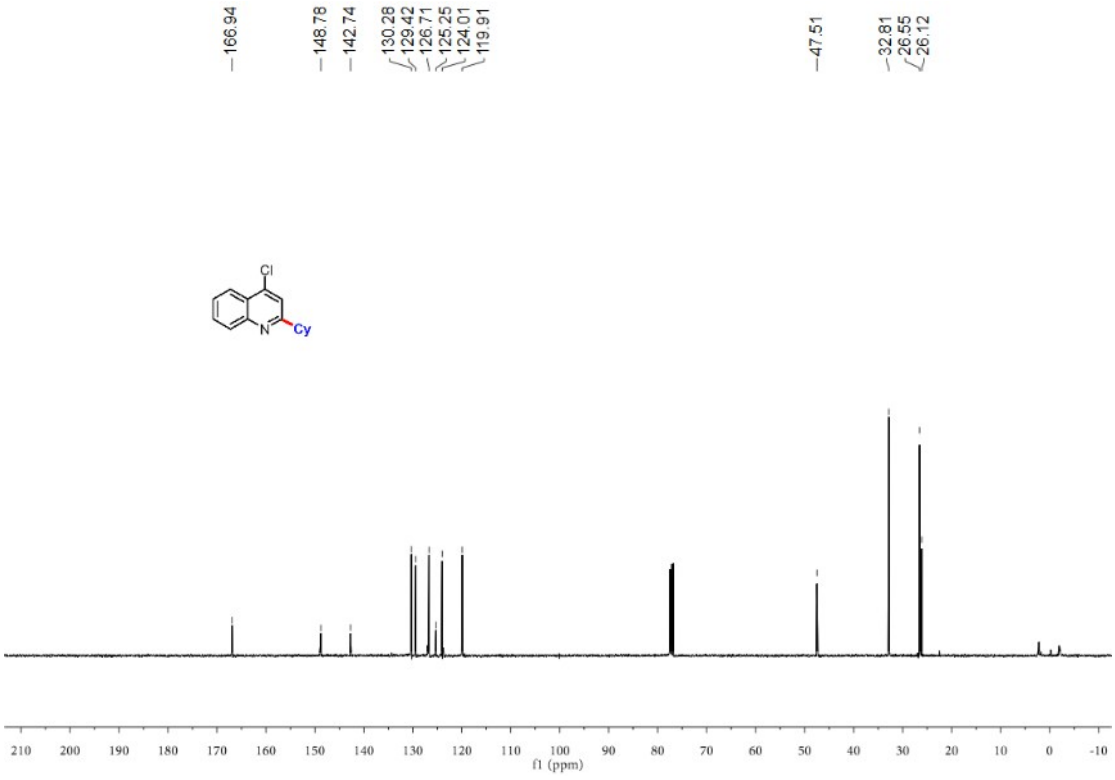
^{13}C NMR spectrum of compound **27**



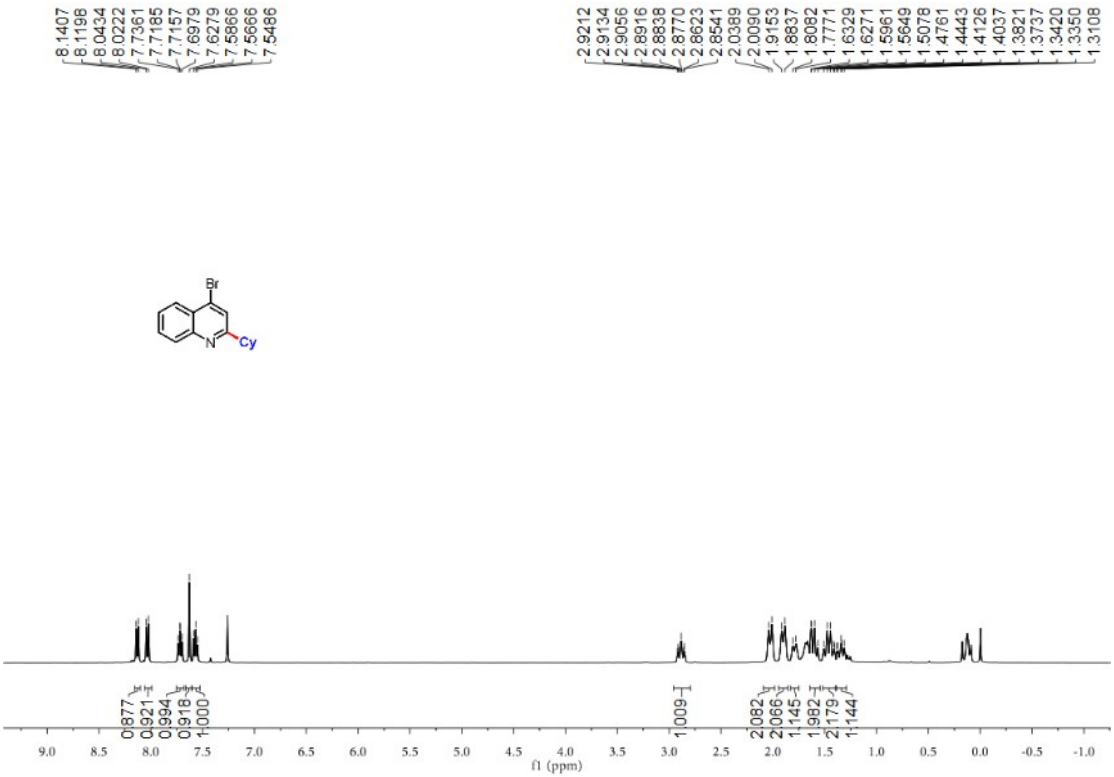
[1]H NMR spectrum of compound **28**



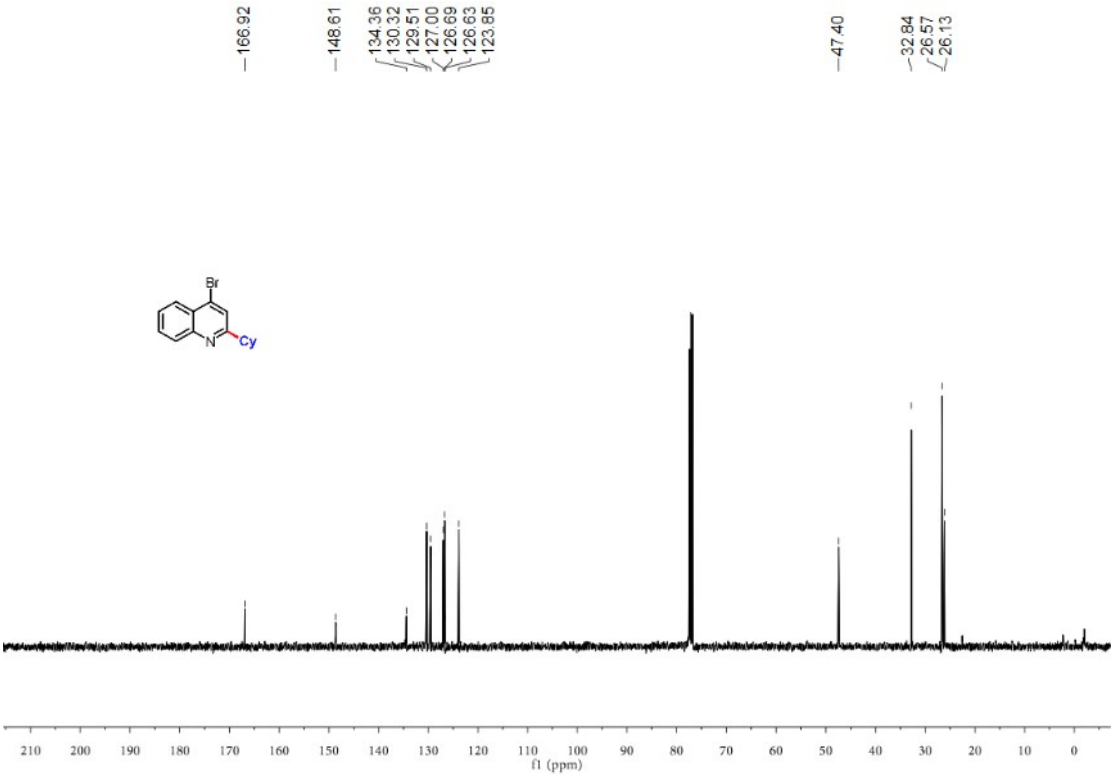
[13]C NMR spectrum of compound **28**



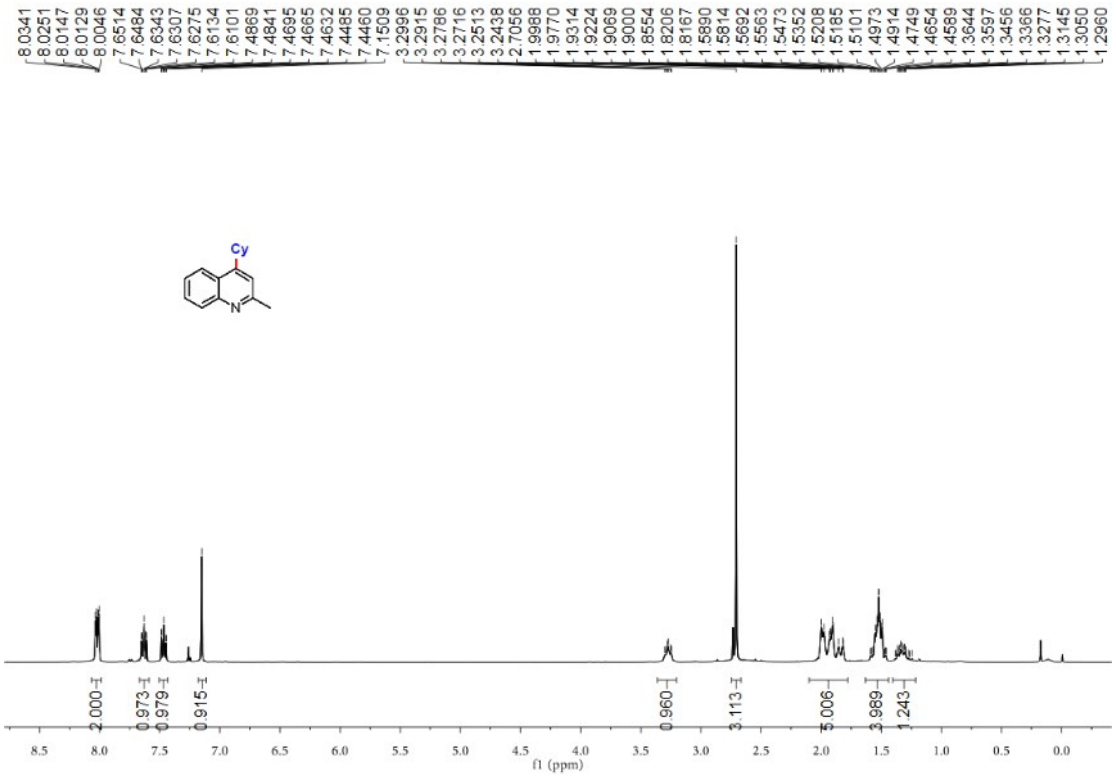
[1]H NMR spectrum of compound **29**



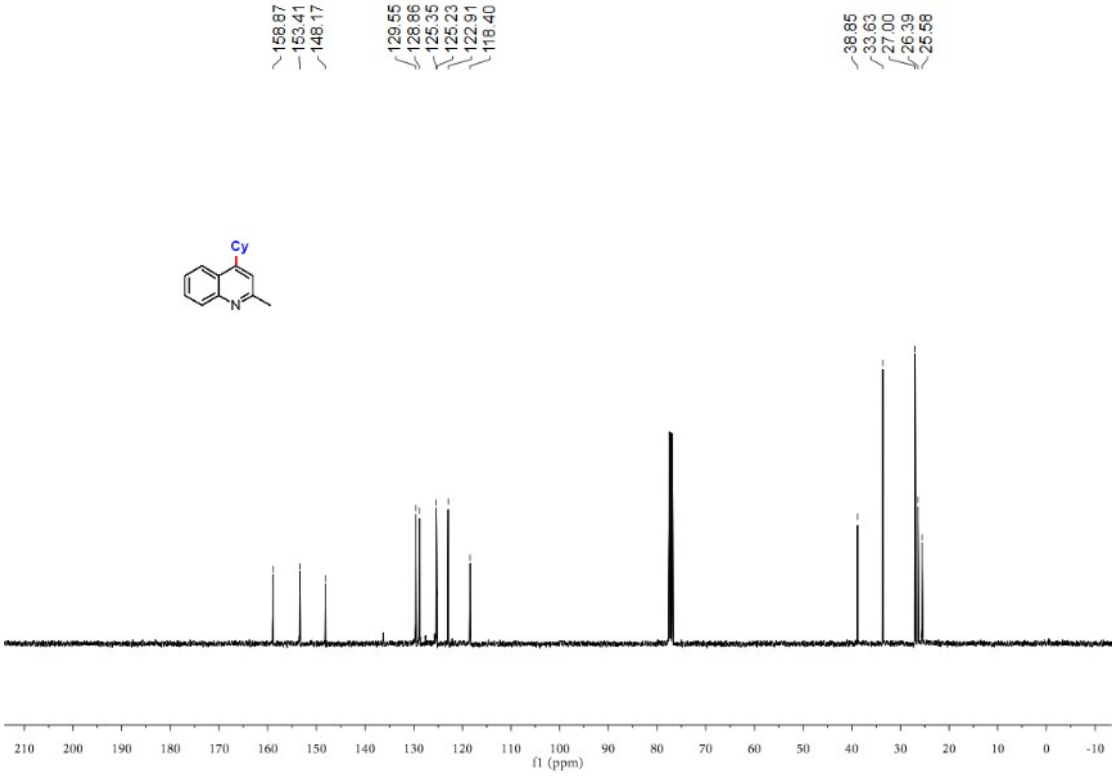
[13]C NMR spectrum of compound **29**



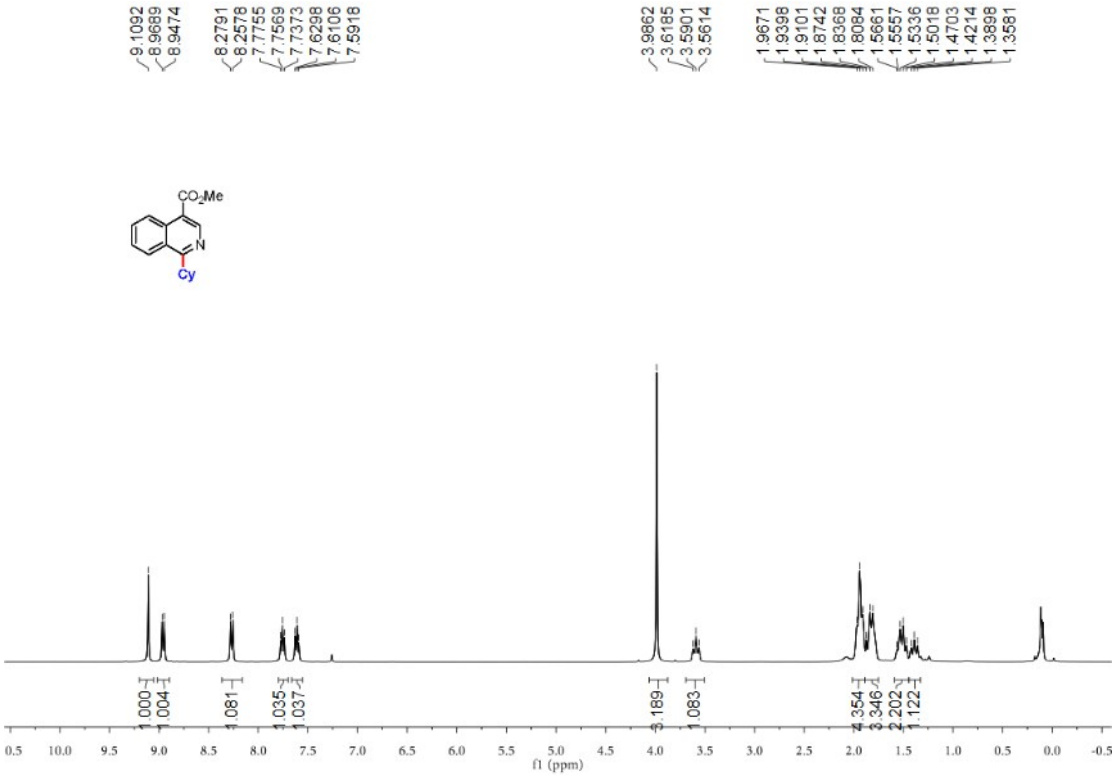
^{1}H NMR spectrum of compound **30**



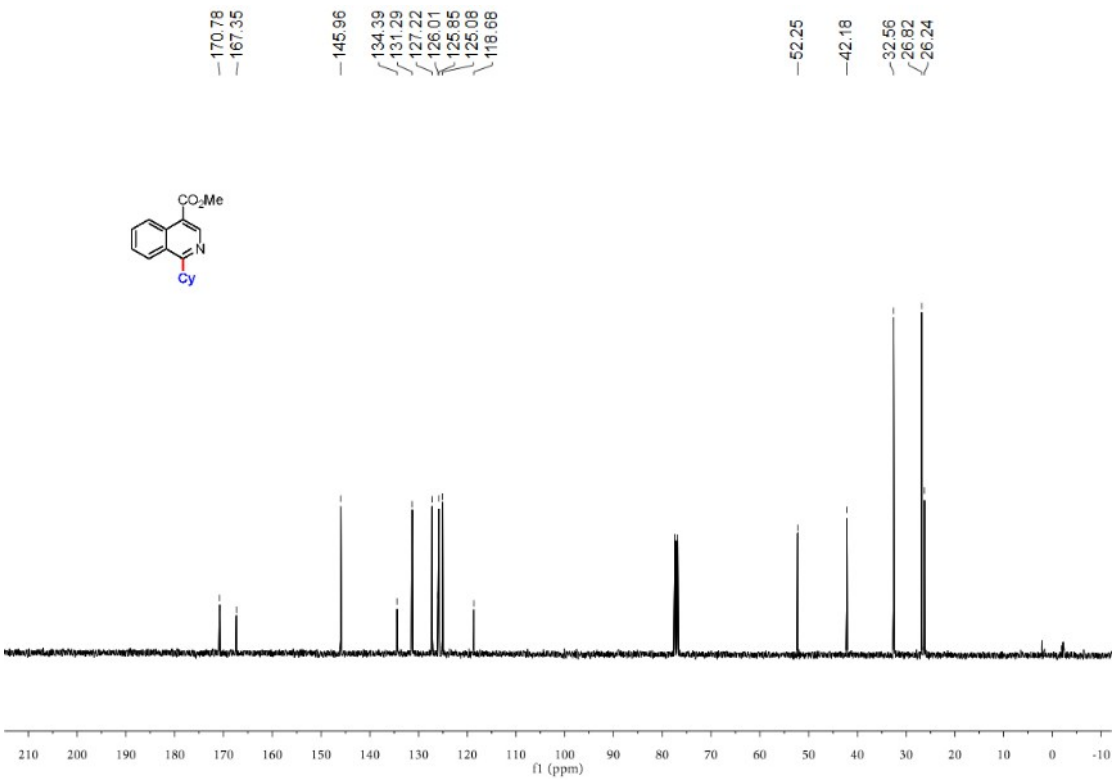
^{13}C NMR spectrum of compound **30**



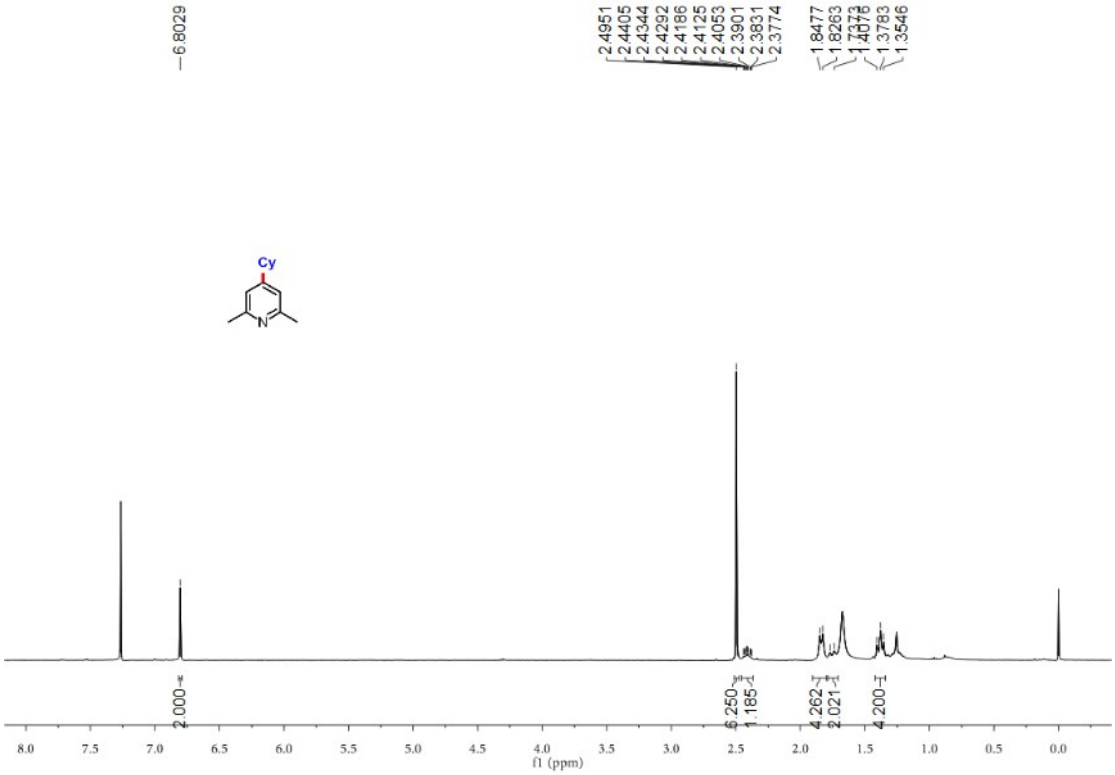
[1]H NMR spectrum of compound **31**



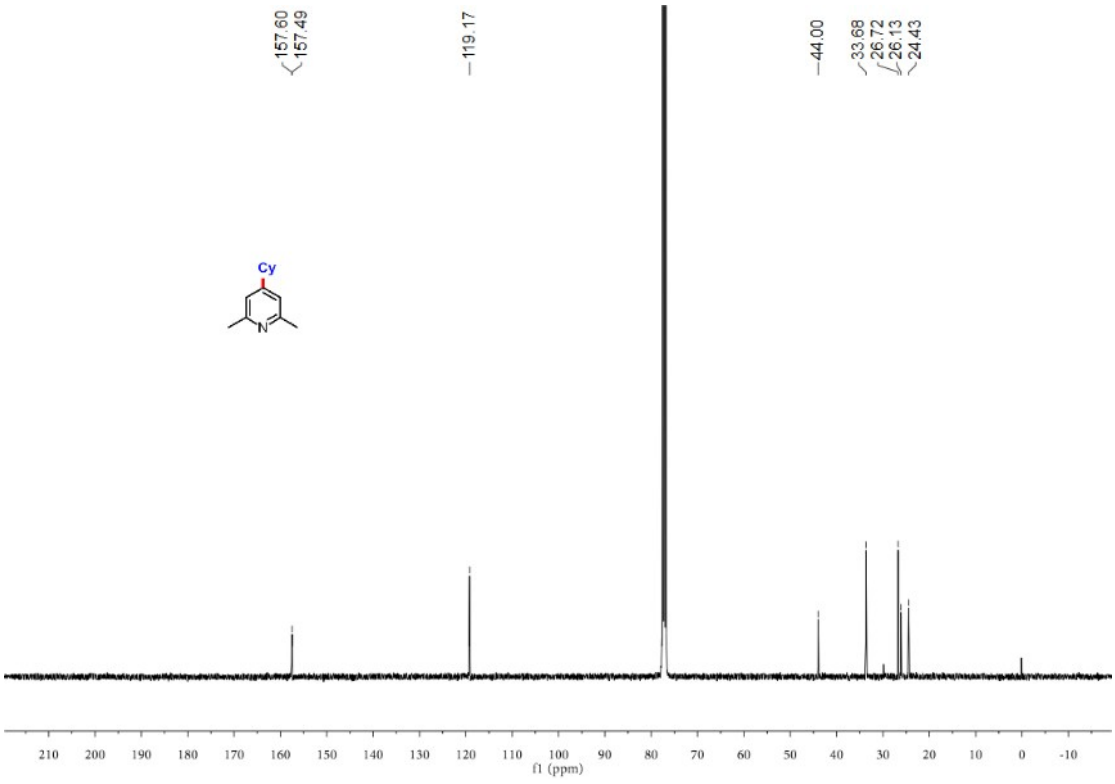
[13]C NMR spectrum of compound **31**



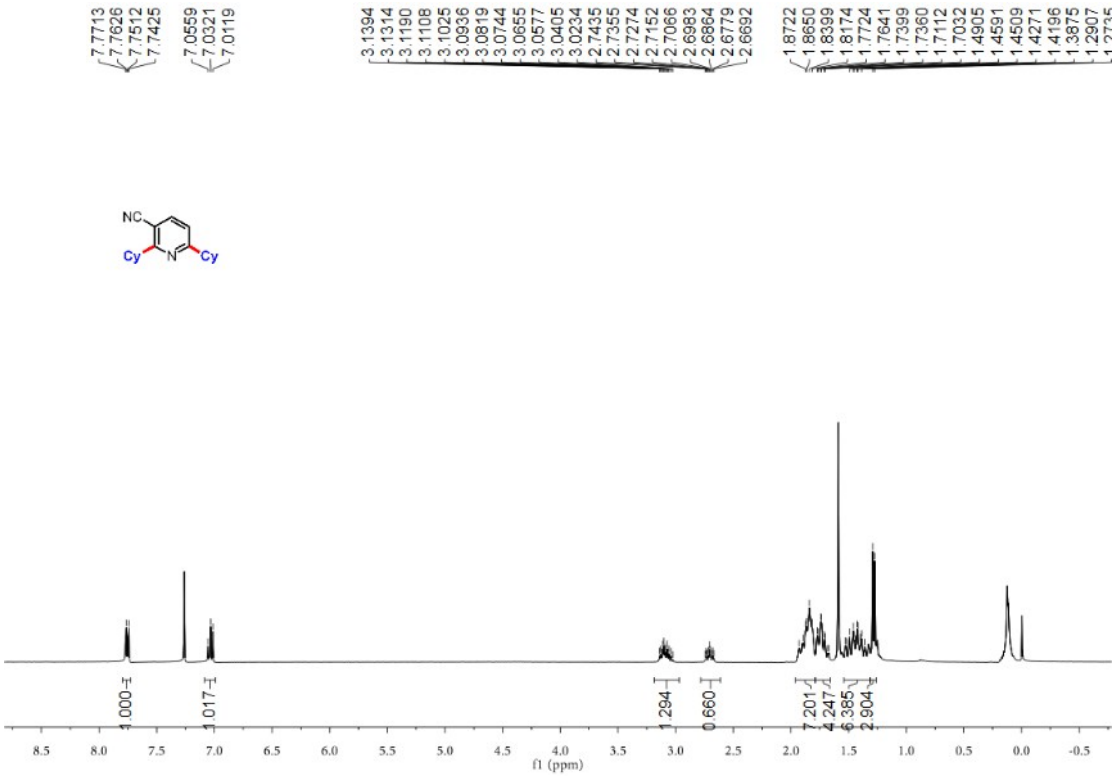
^{1}H NMR spectrum of compound **32**



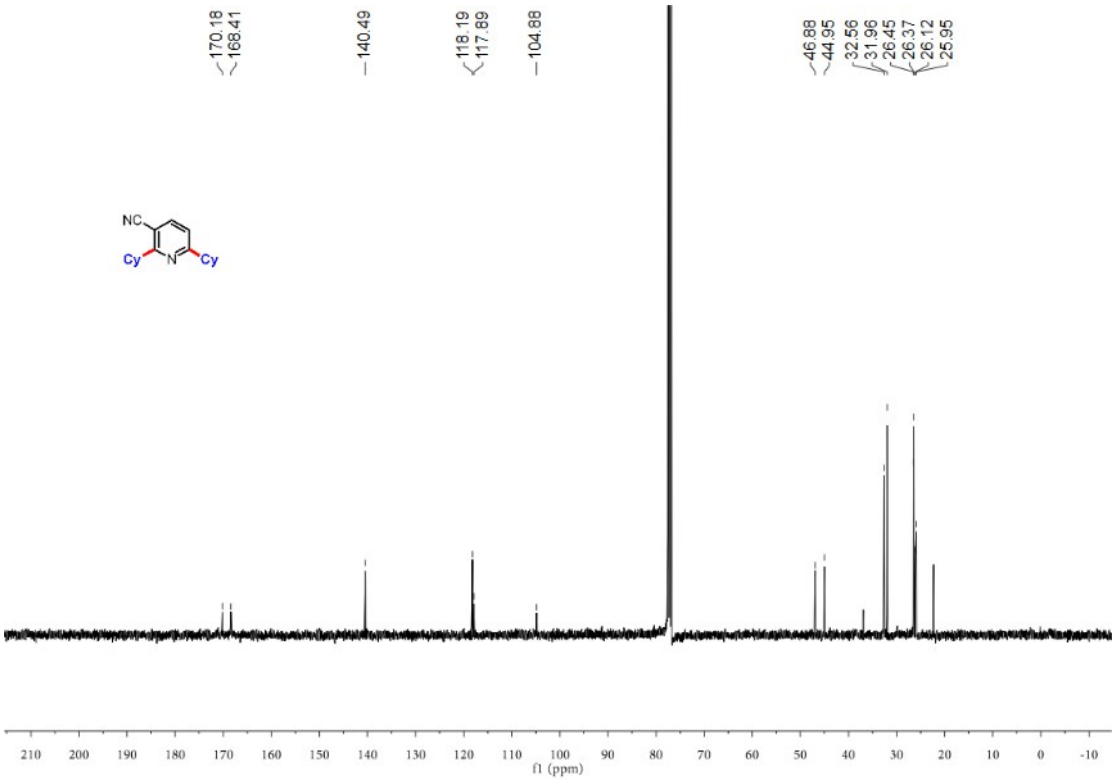
^{13}C NMR spectrum of compound **32**



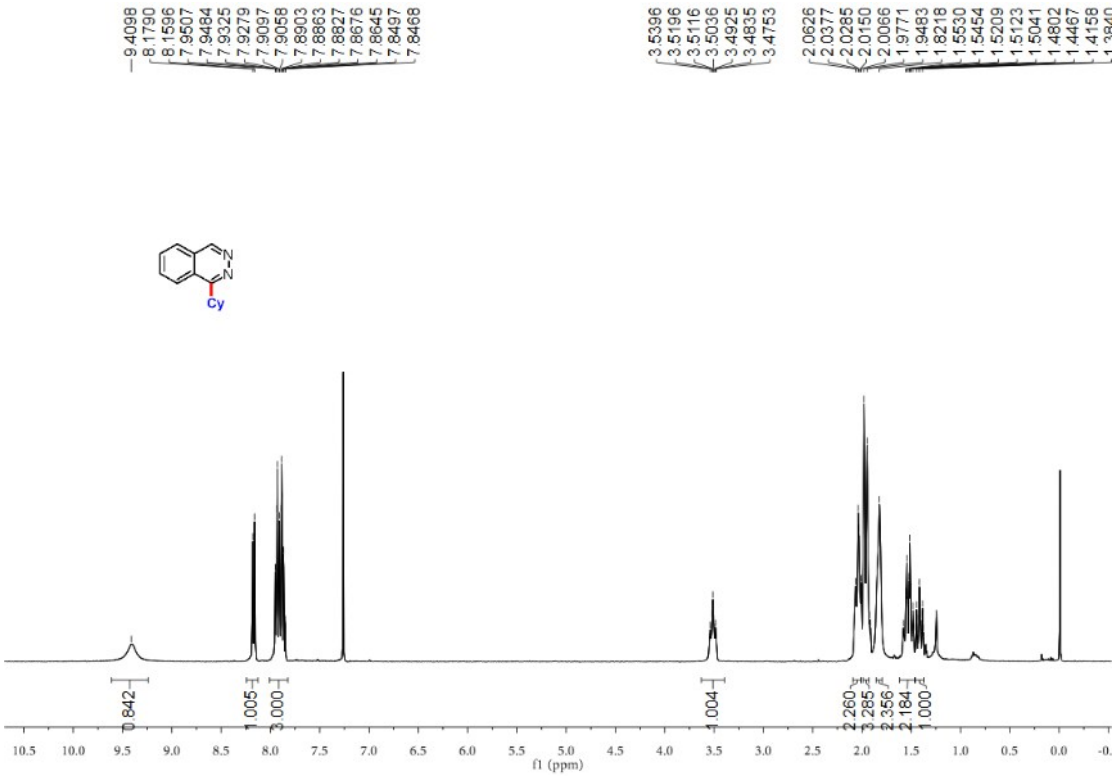
^{1}H NMR spectrum of compound **33**



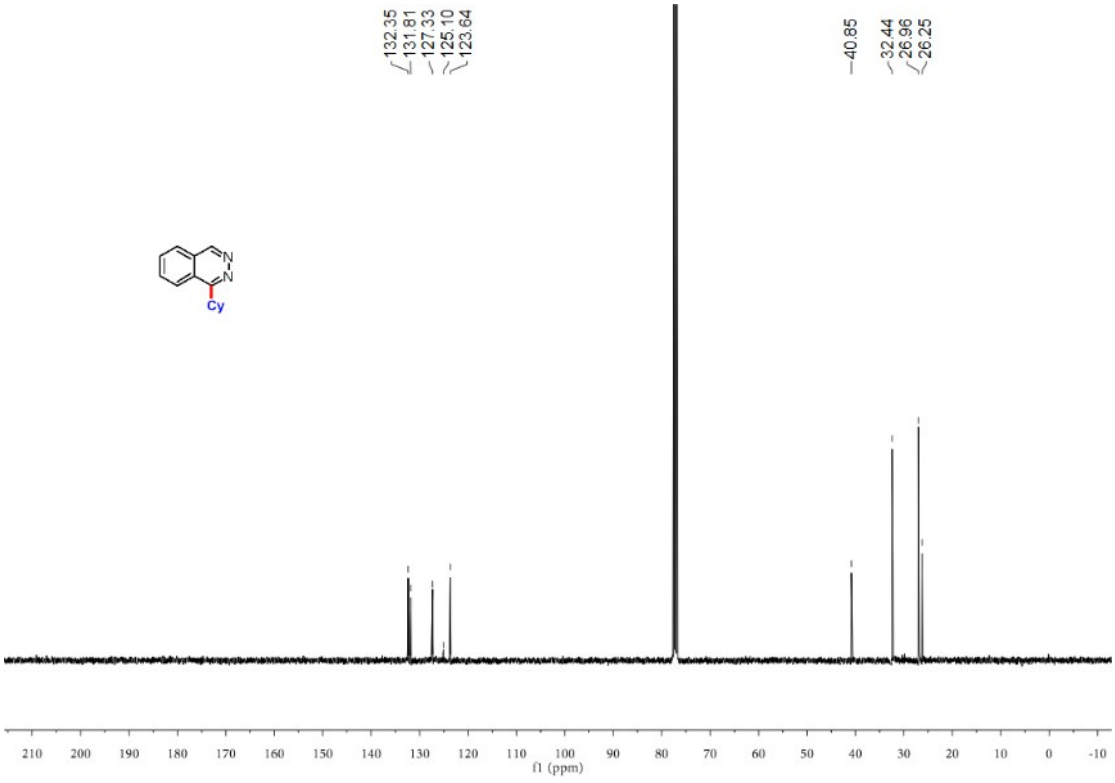
^{13}C NMR spectrum of compound **33**



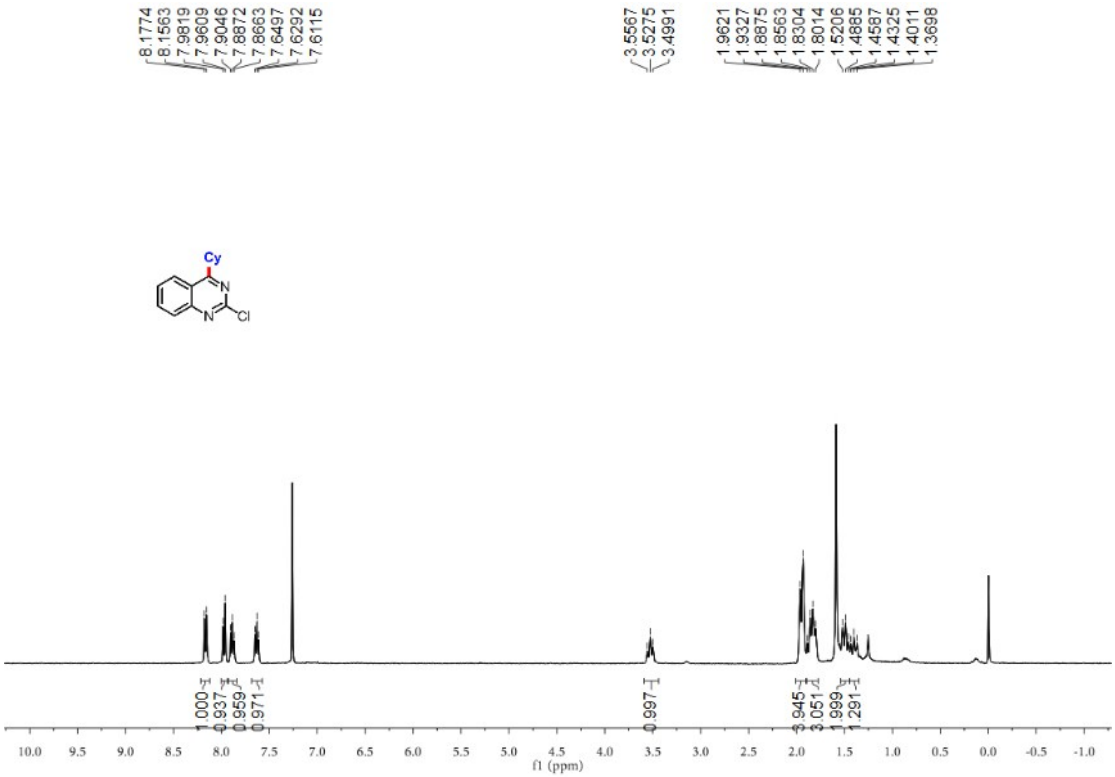
^{1}H NMR spectrum of compound **34**



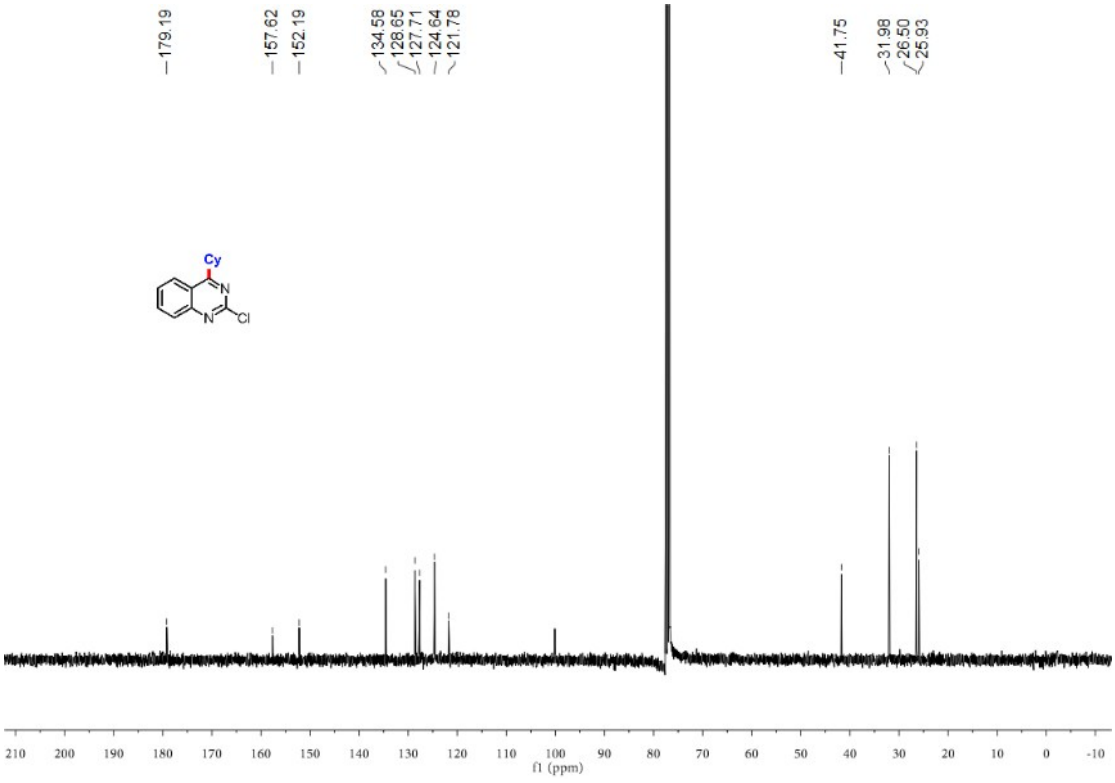
^{13}C NMR spectrum of compound **34**



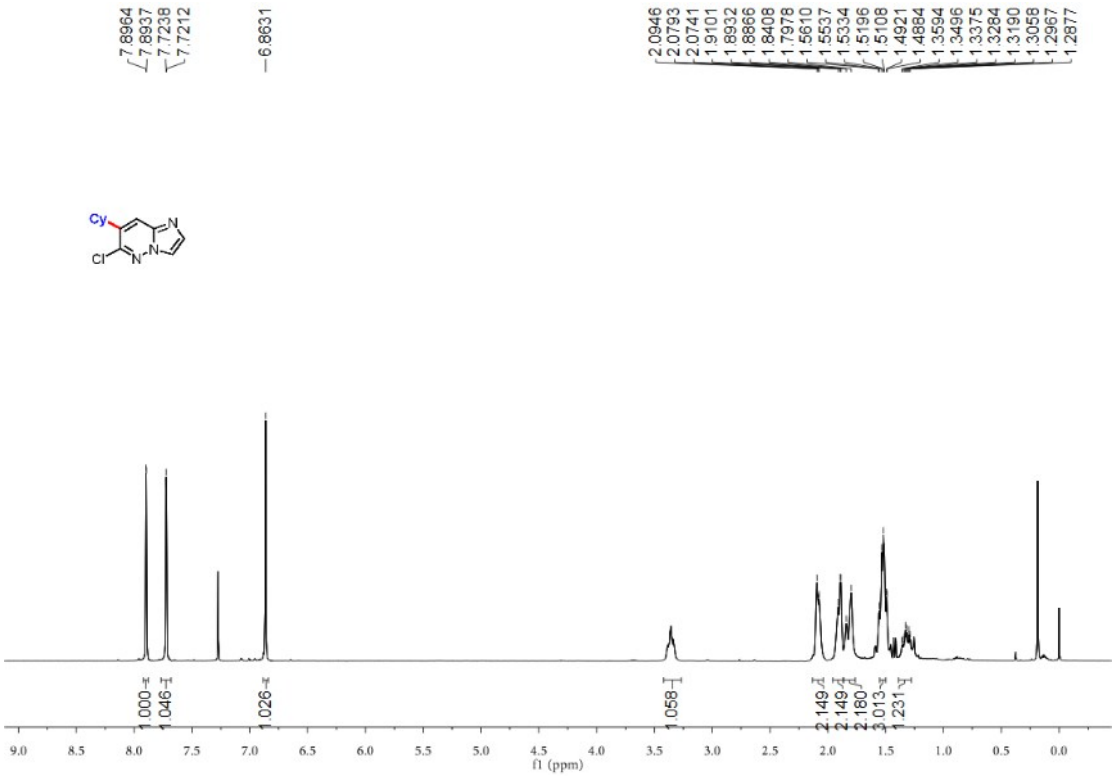
^{1}H NMR spectrum of compound **35**



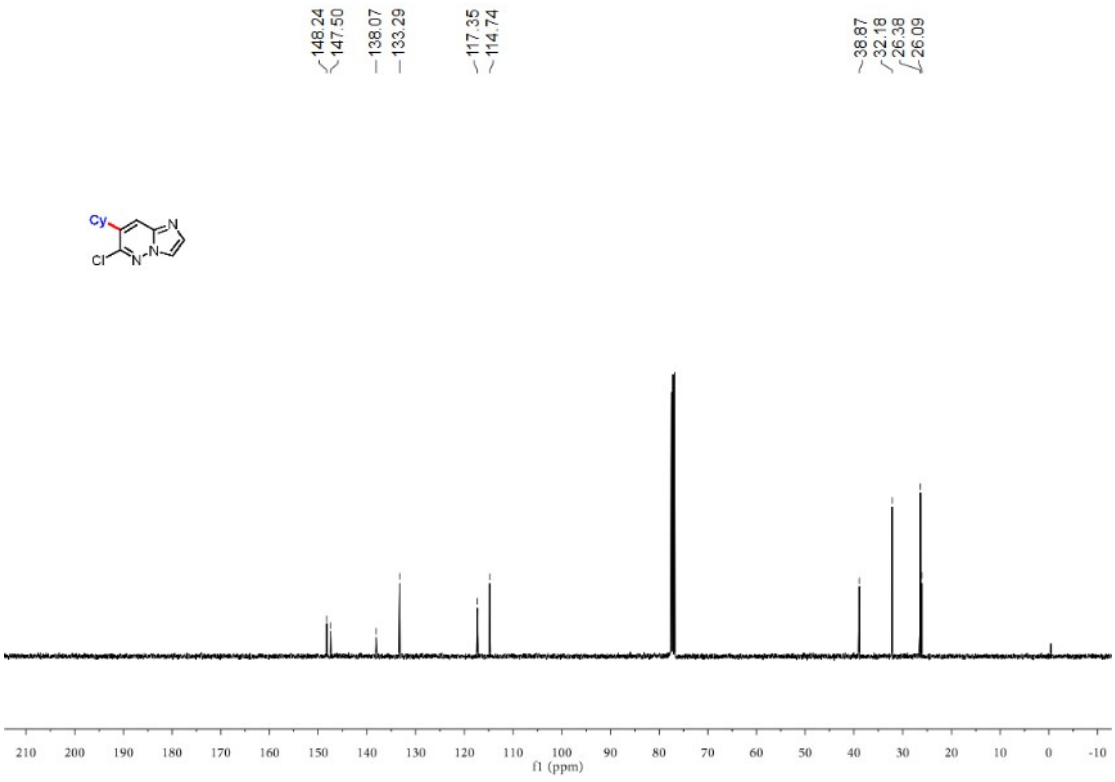
^{13}C NMR spectrum of compound **35**



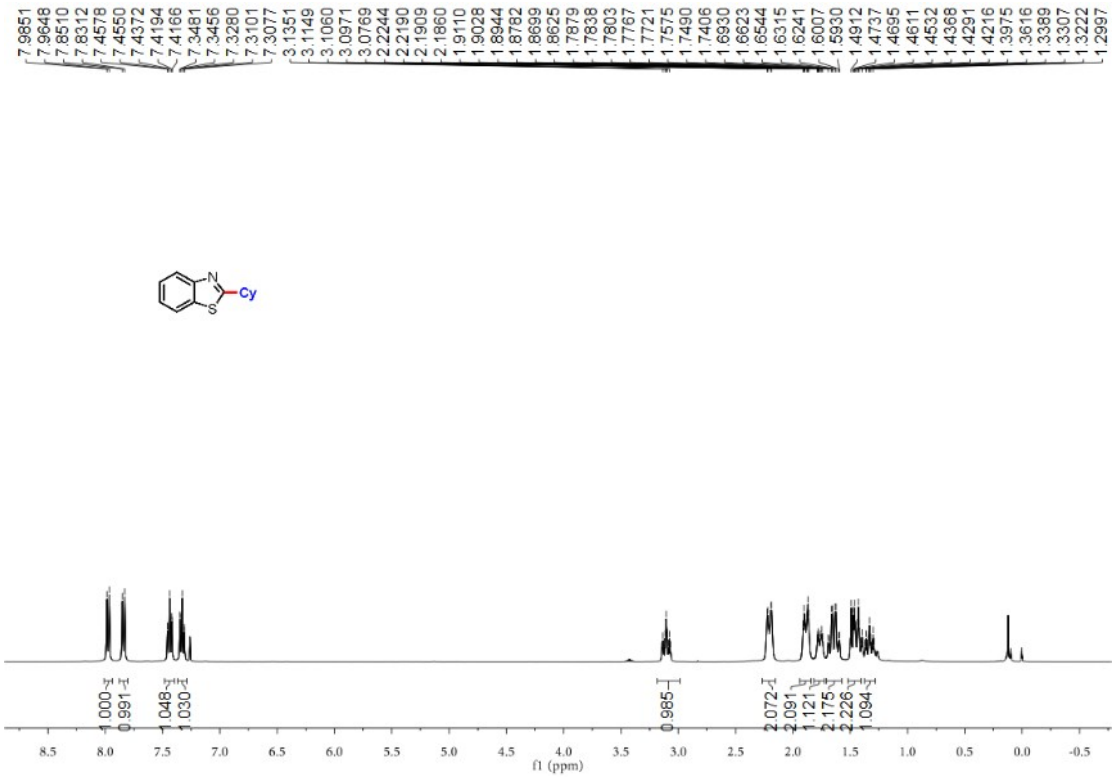
[1]H NMR spectrum of compound **36**



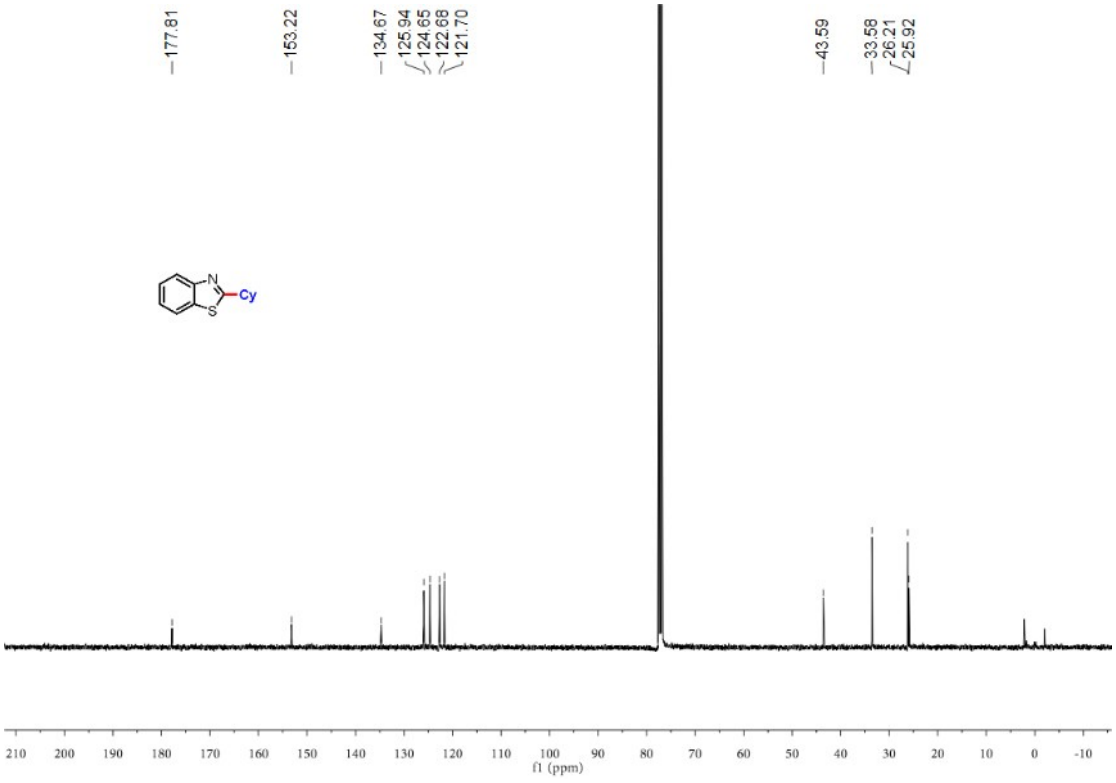
[13]C NMR spectrum of compound **36**



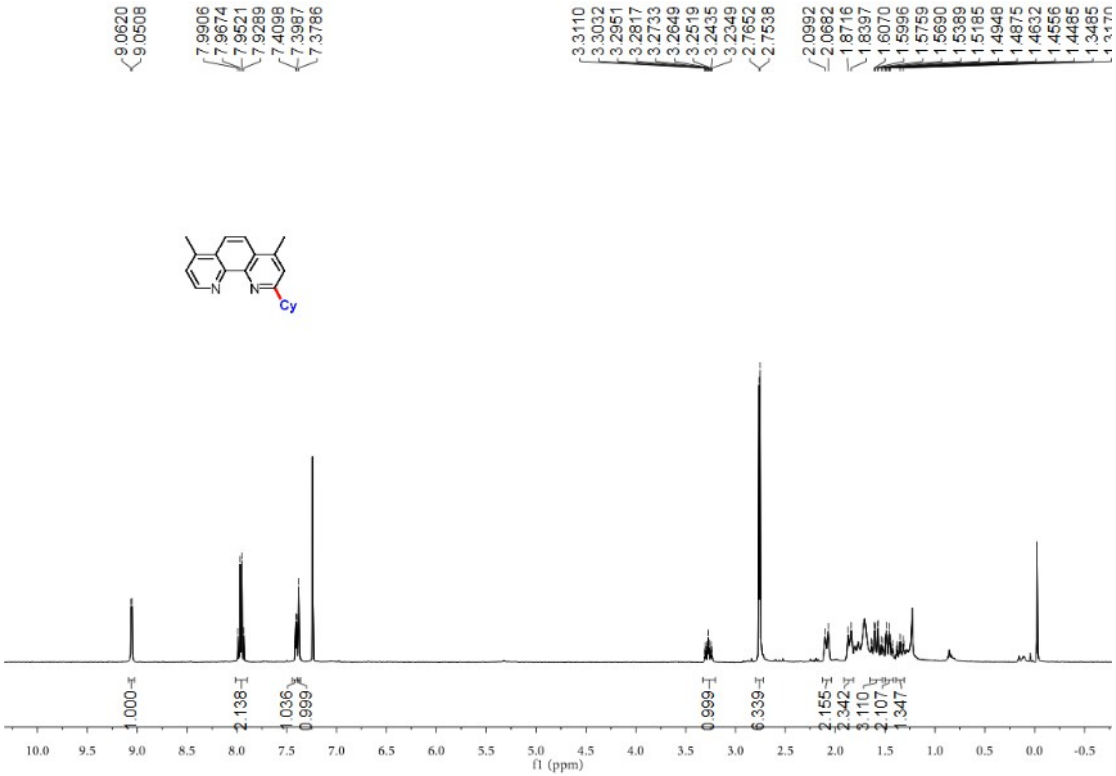
^{1}H NMR spectrum of compound **37**



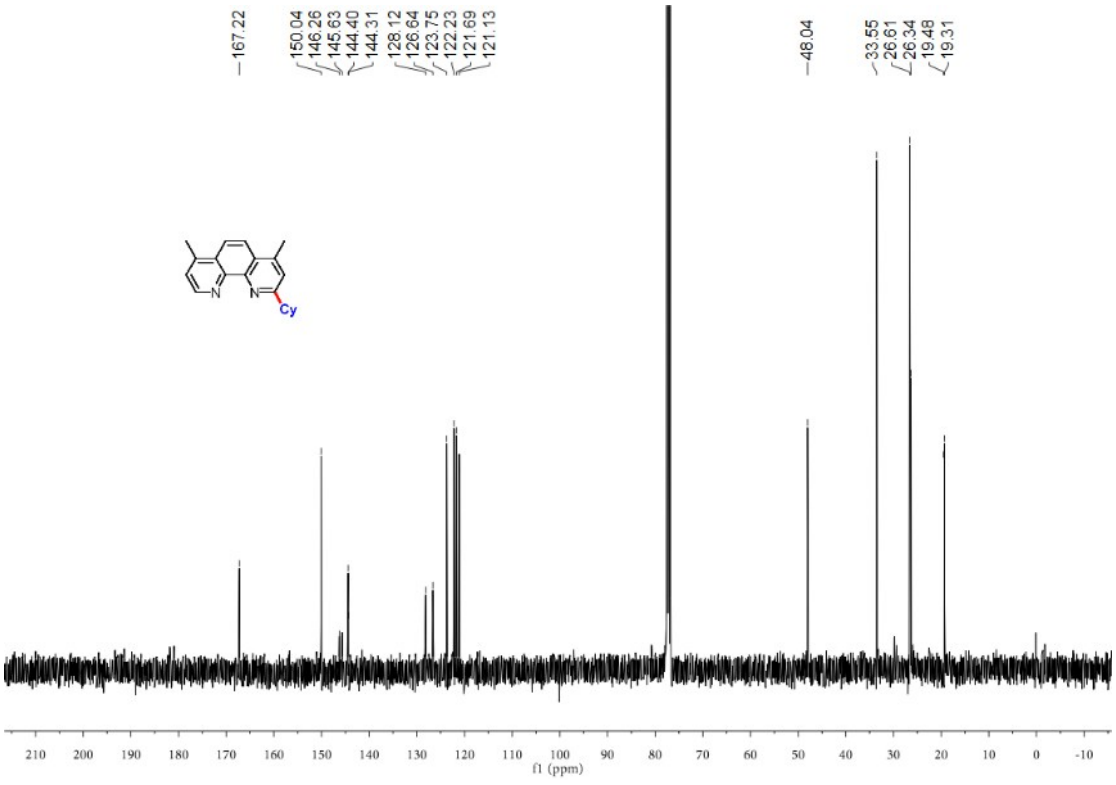
^{13}C NMR spectrum of compound **37**



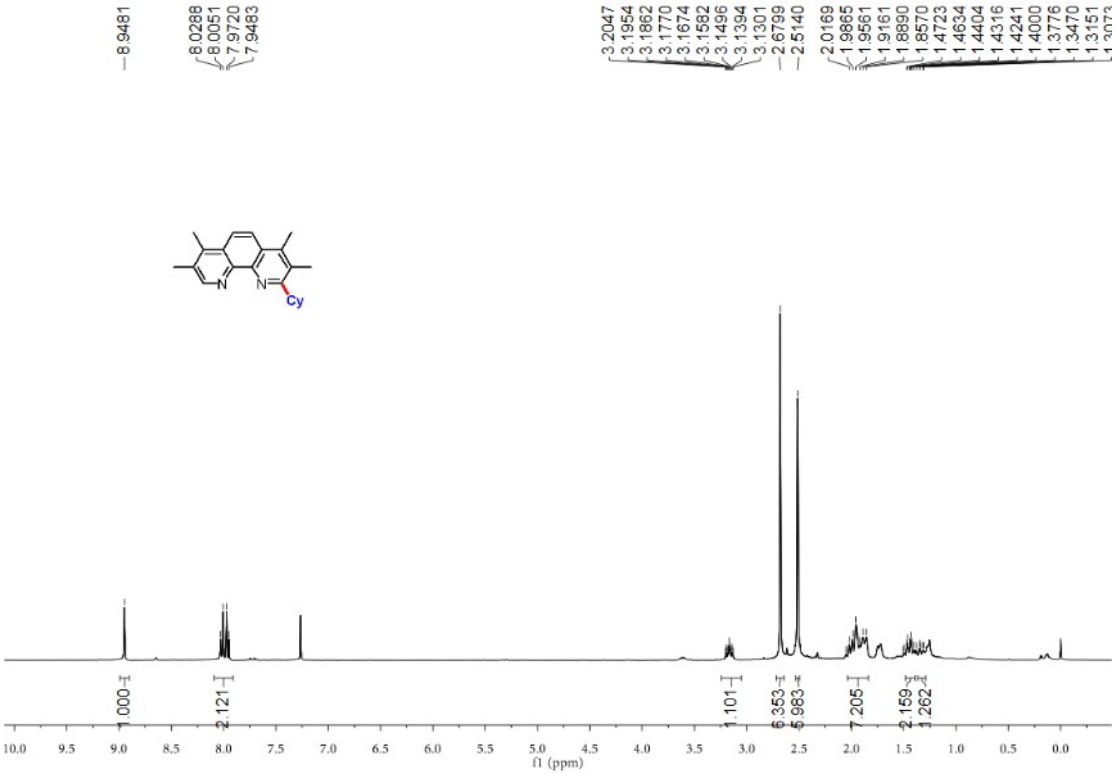
^{1}H NMR spectrum of compound **38**



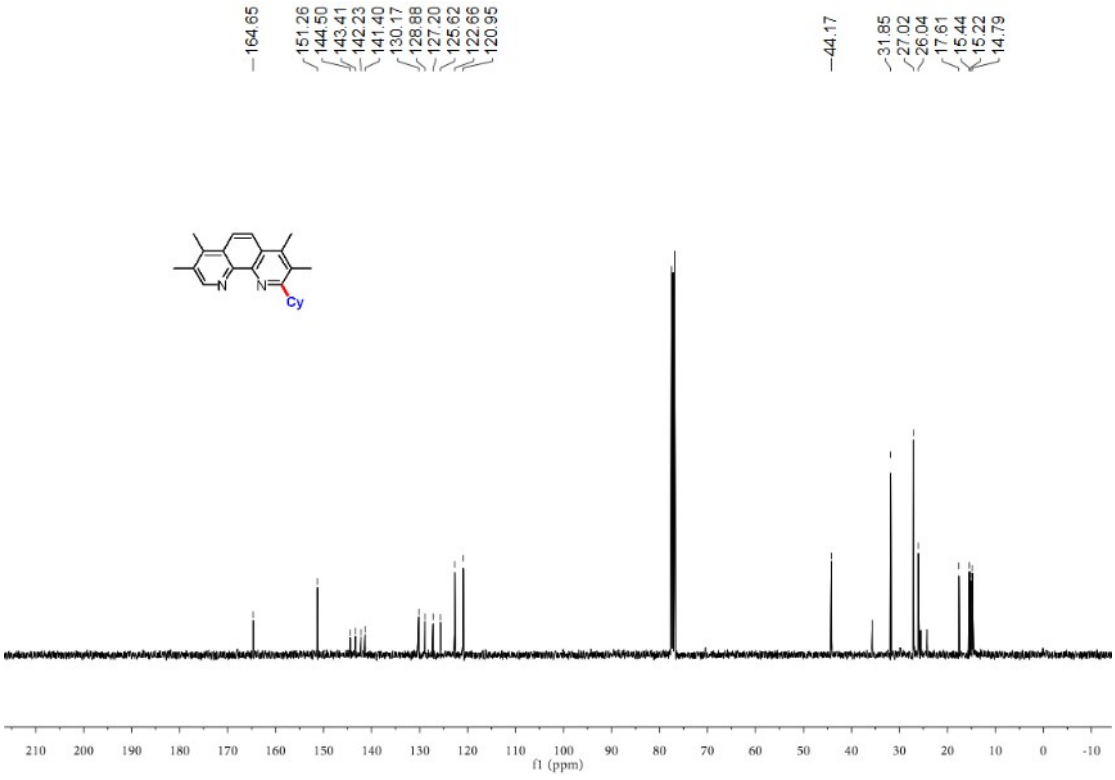
^{13}C NMR spectrum of compound **38**



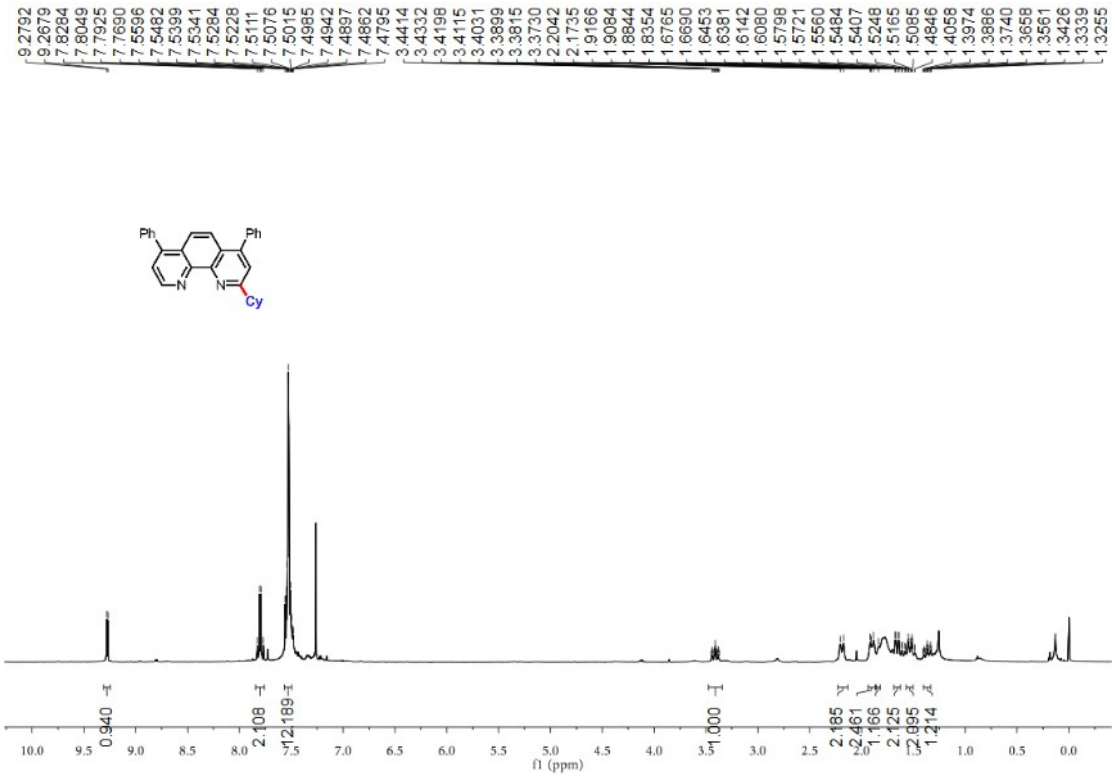
^{1}H NMR spectrum of compound **39**



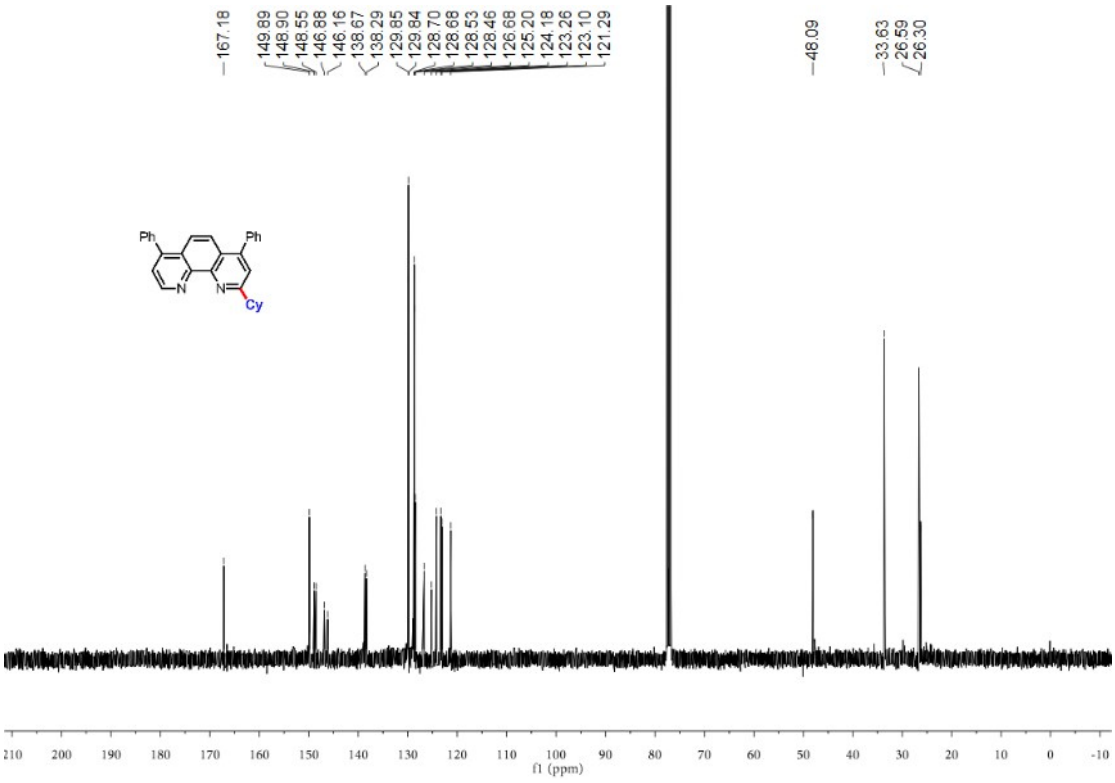
^{13}C NMR spectrum of compound **39**



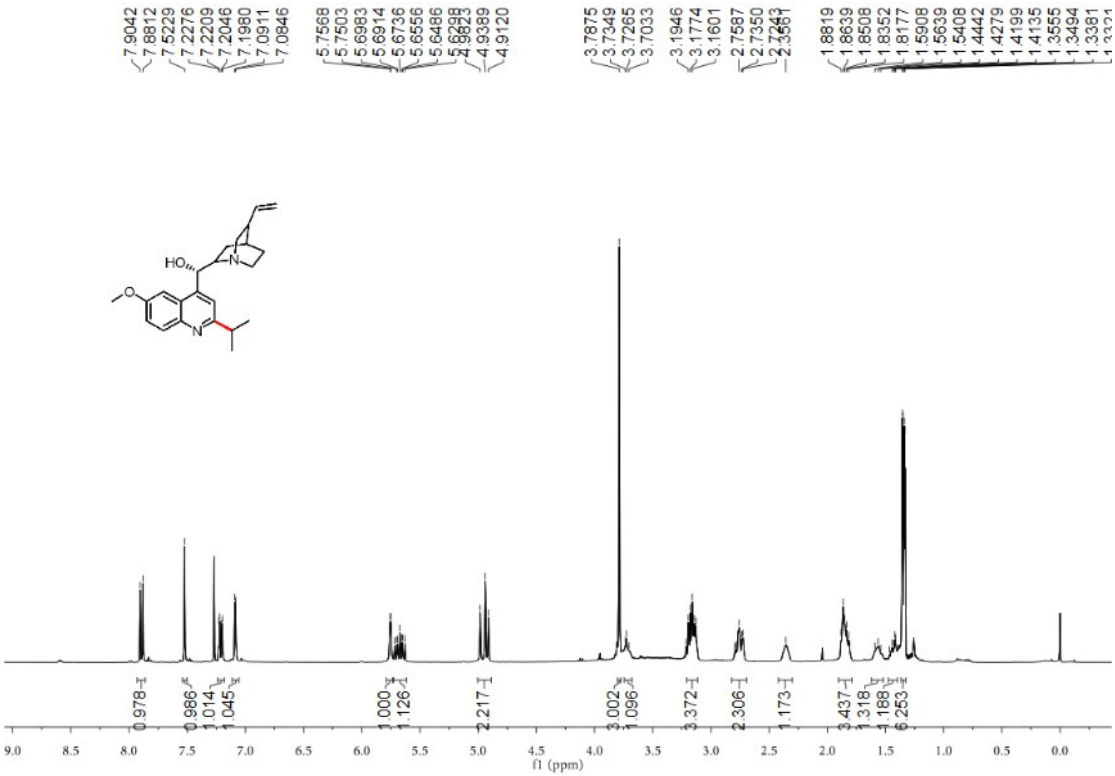
^{1}H NMR spectrum of compound **40**



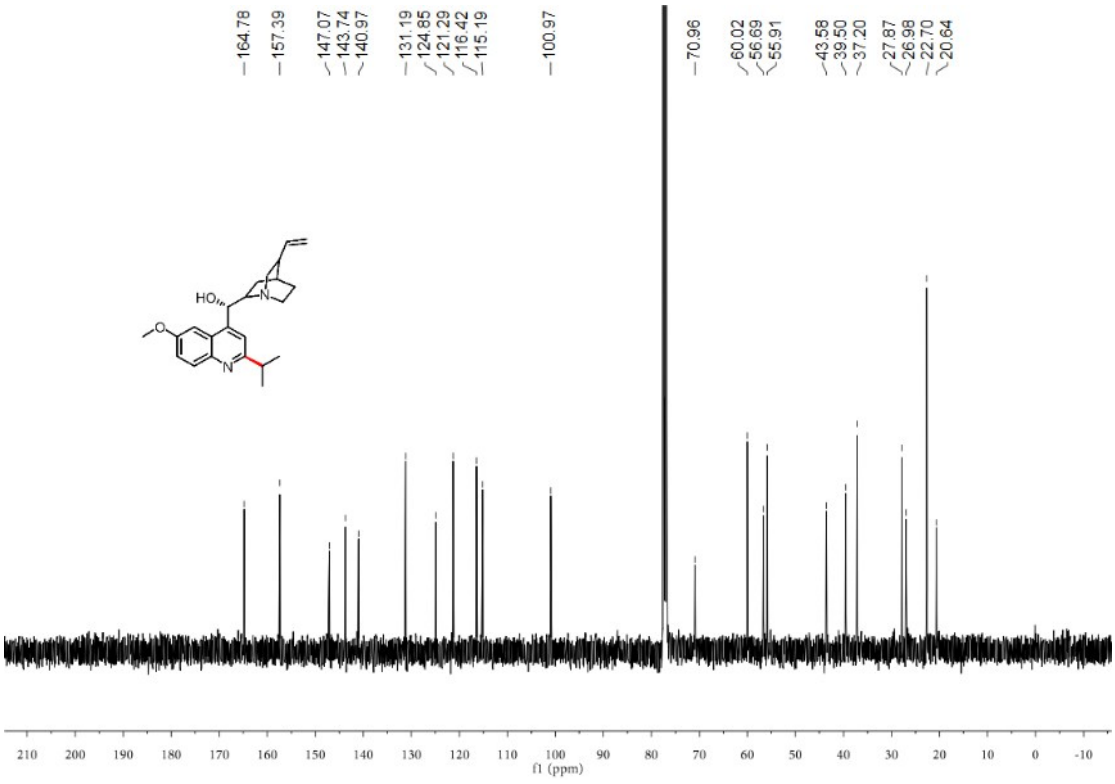
^{13}C NMR spectrum of compound **40**



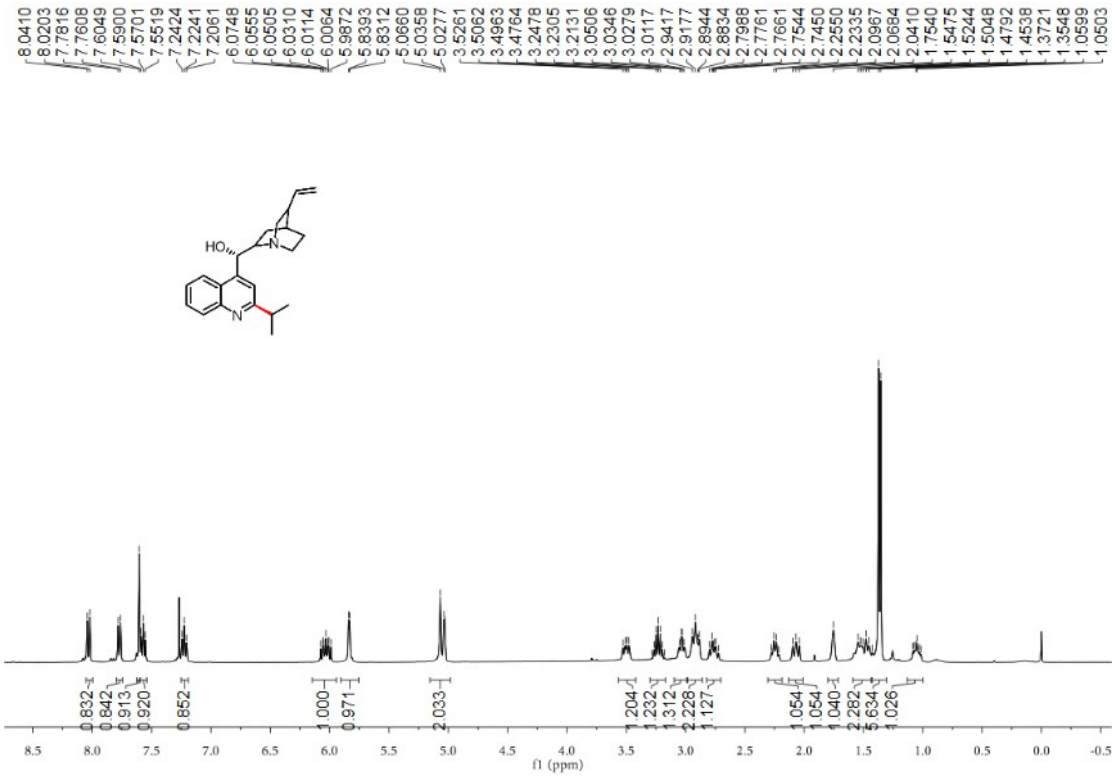
^{1}H NMR spectrum of compound **41**



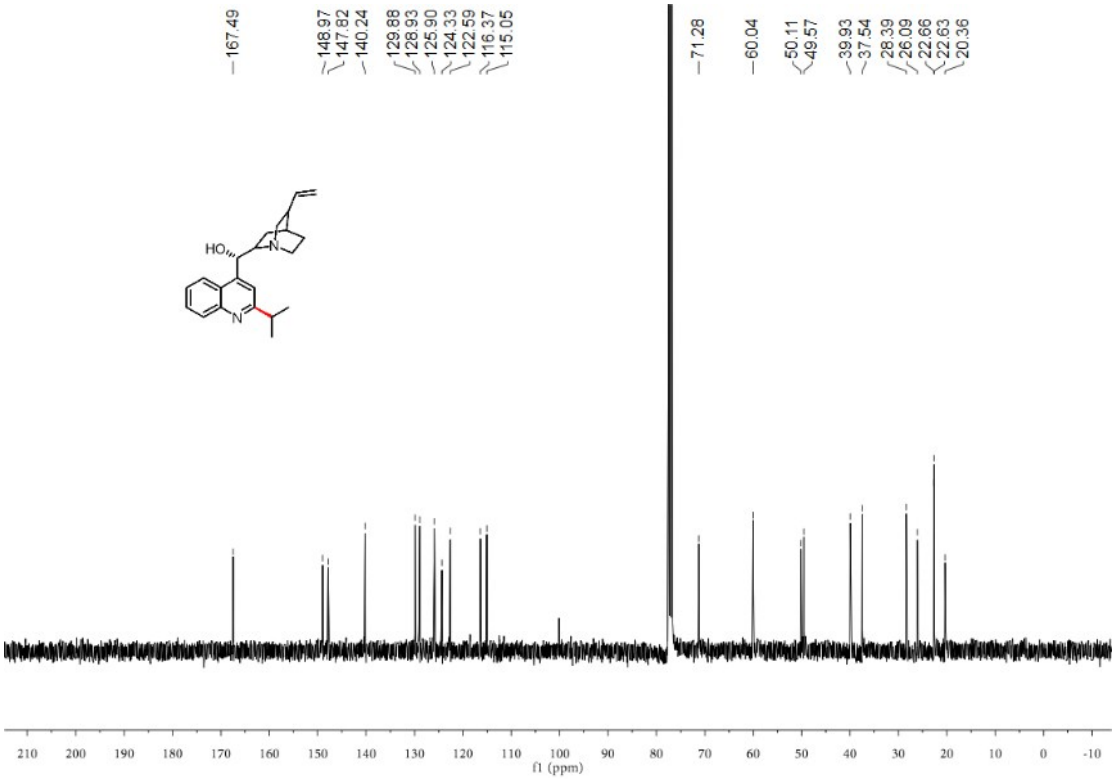
^{13}C NMR spectrum of compound **41**



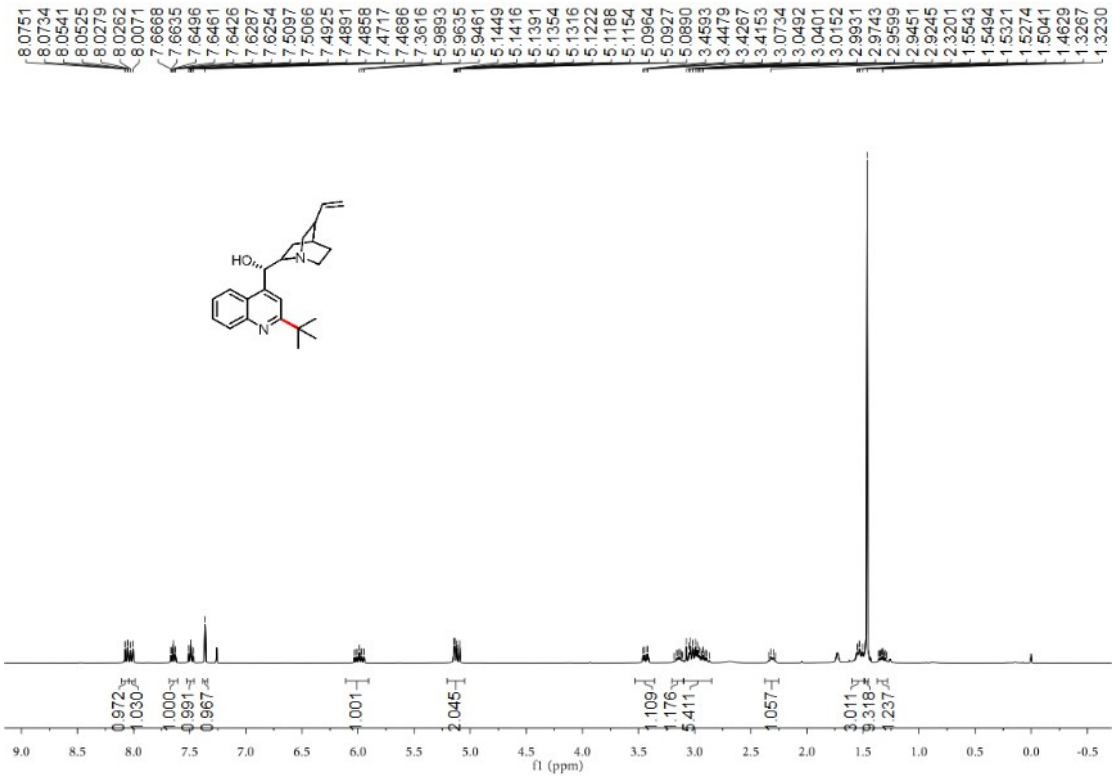
^{1}H NMR spectrum of compound **42a**



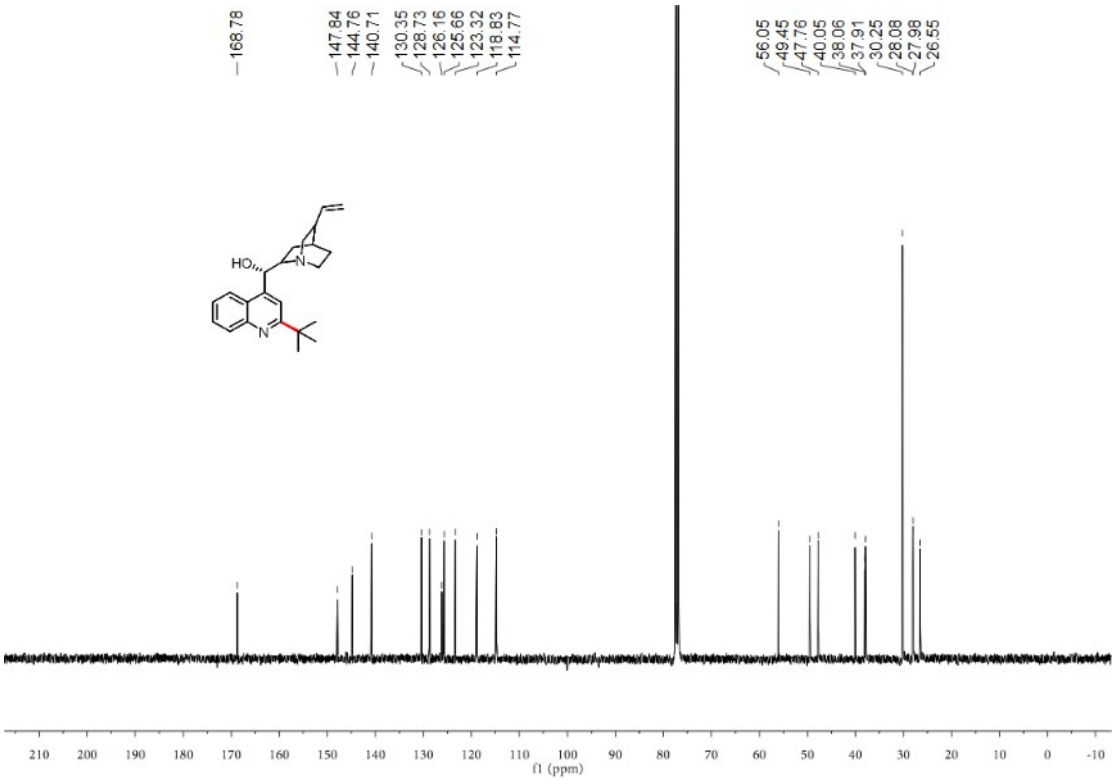
^{13}C NMR spectrum of compound **42a**



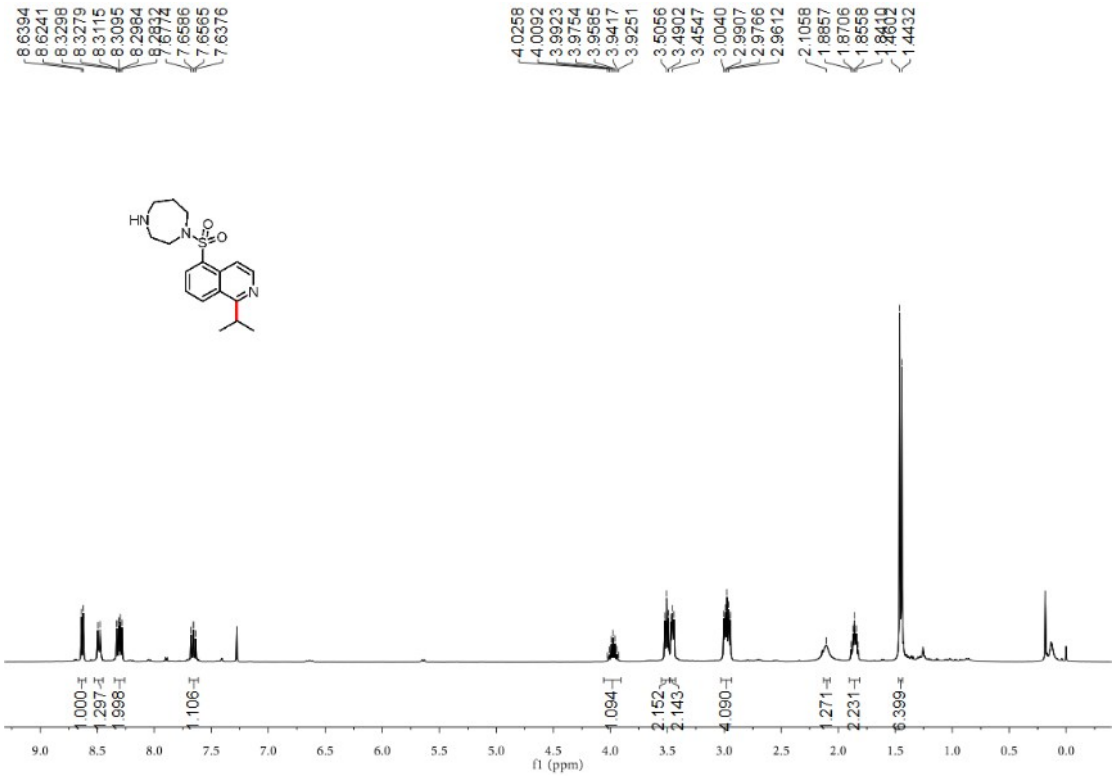
^{1}H NMR spectrum of compound **42b**



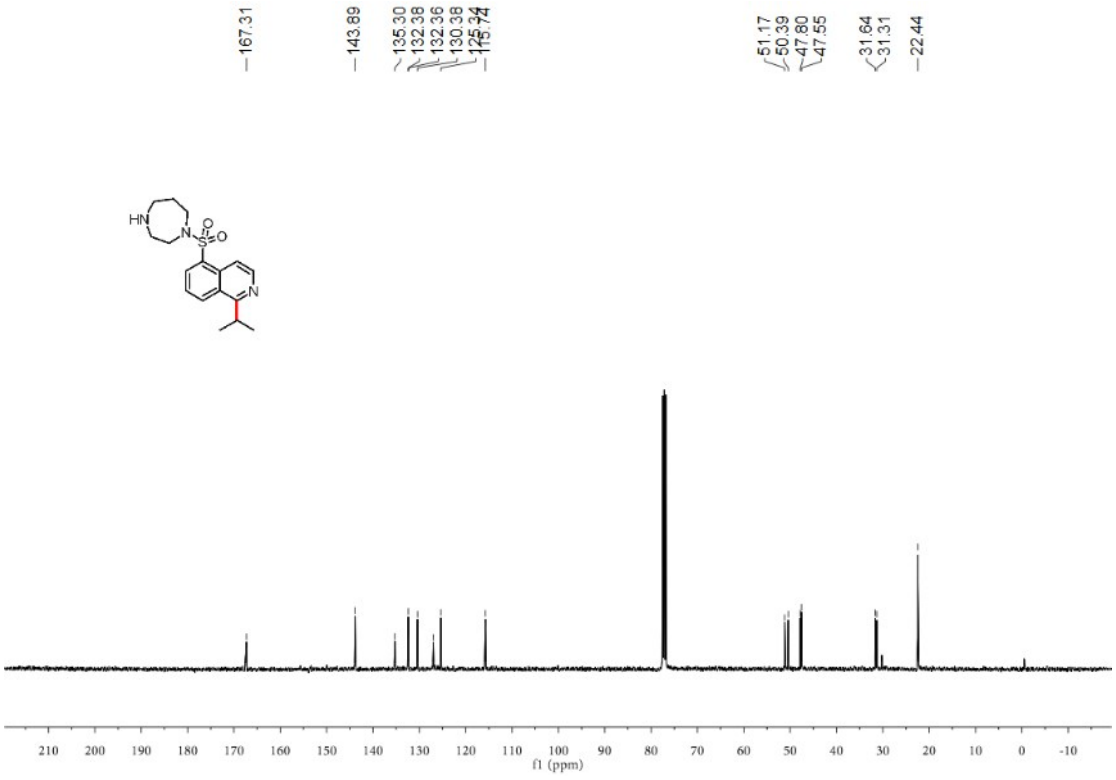
^{13}C NMR spectrum of compound **42b**



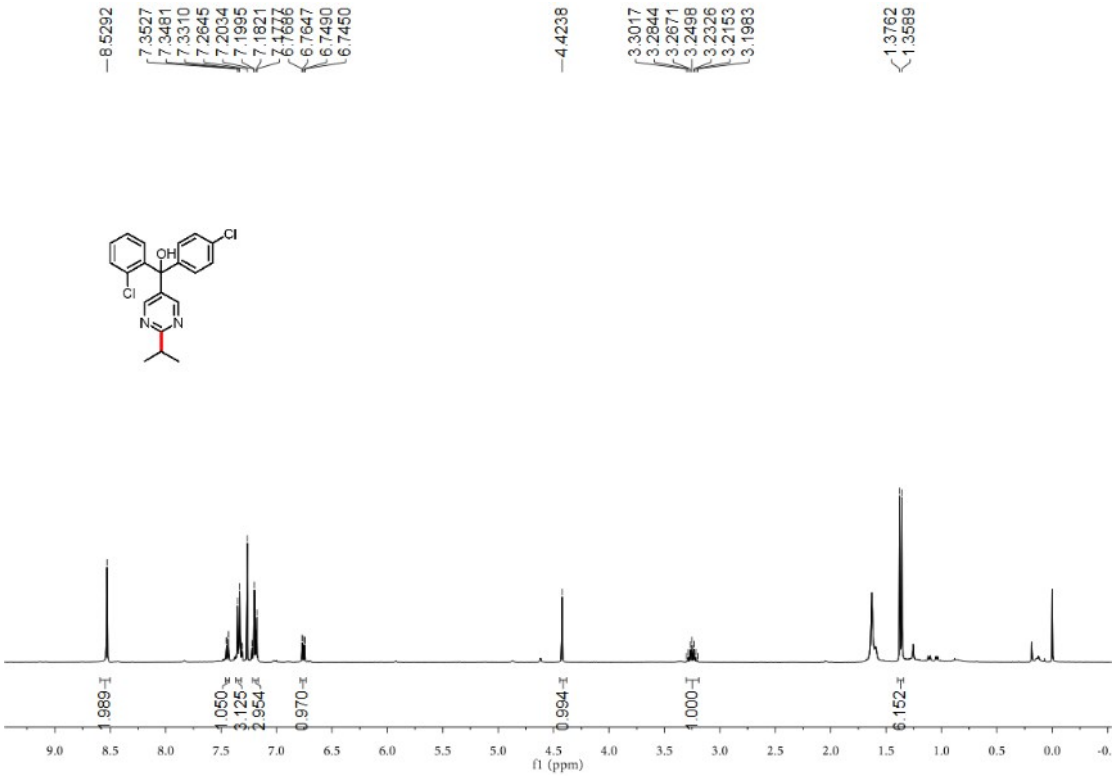
^{1}H NMR spectrum of compound **43**



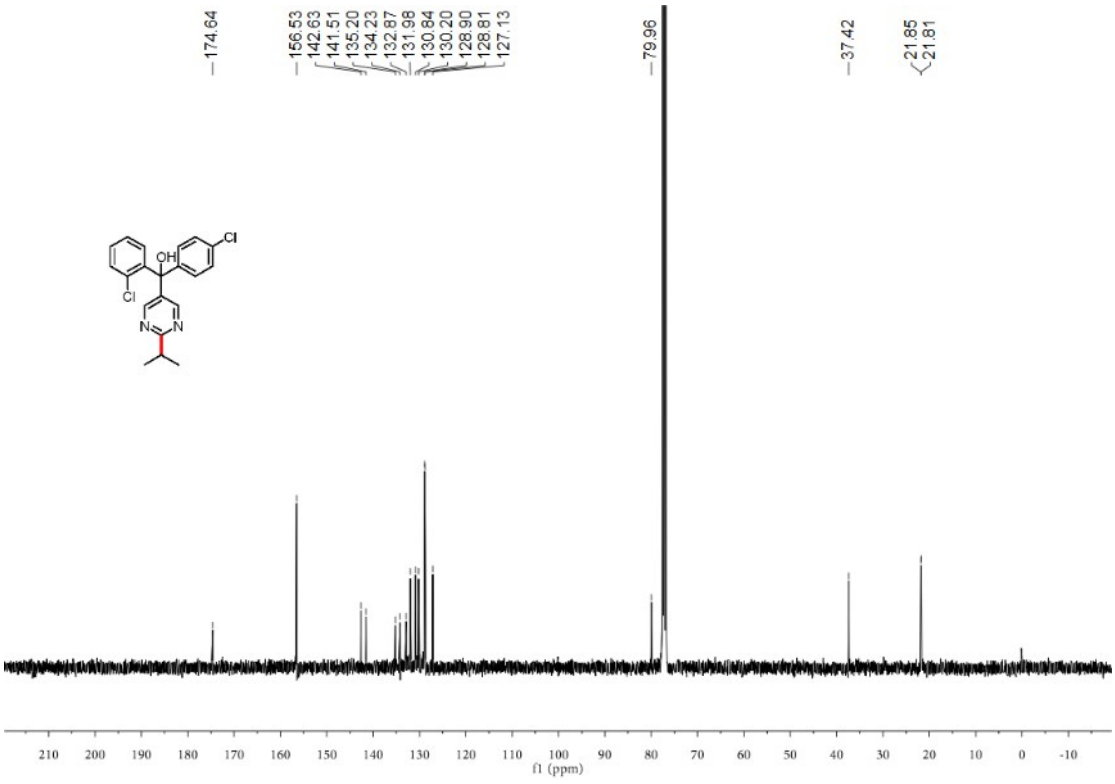
^{13}C NMR spectrum of compound **43**



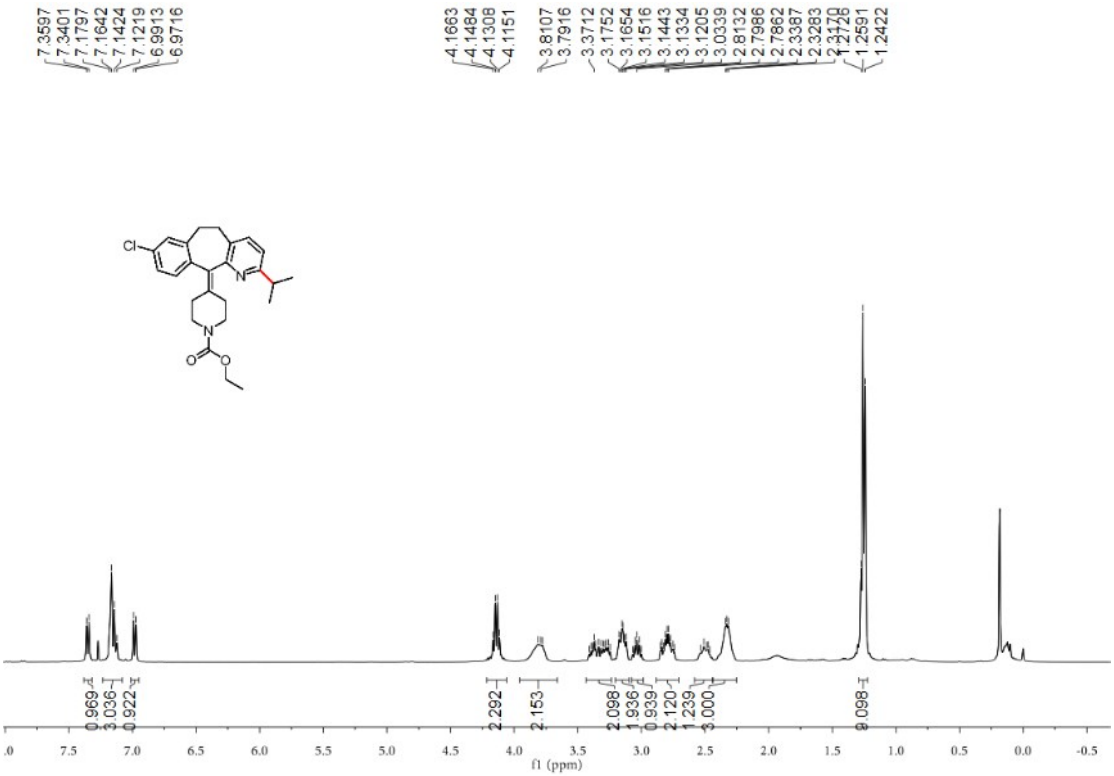
^{1}H NMR spectrum of compound **44**



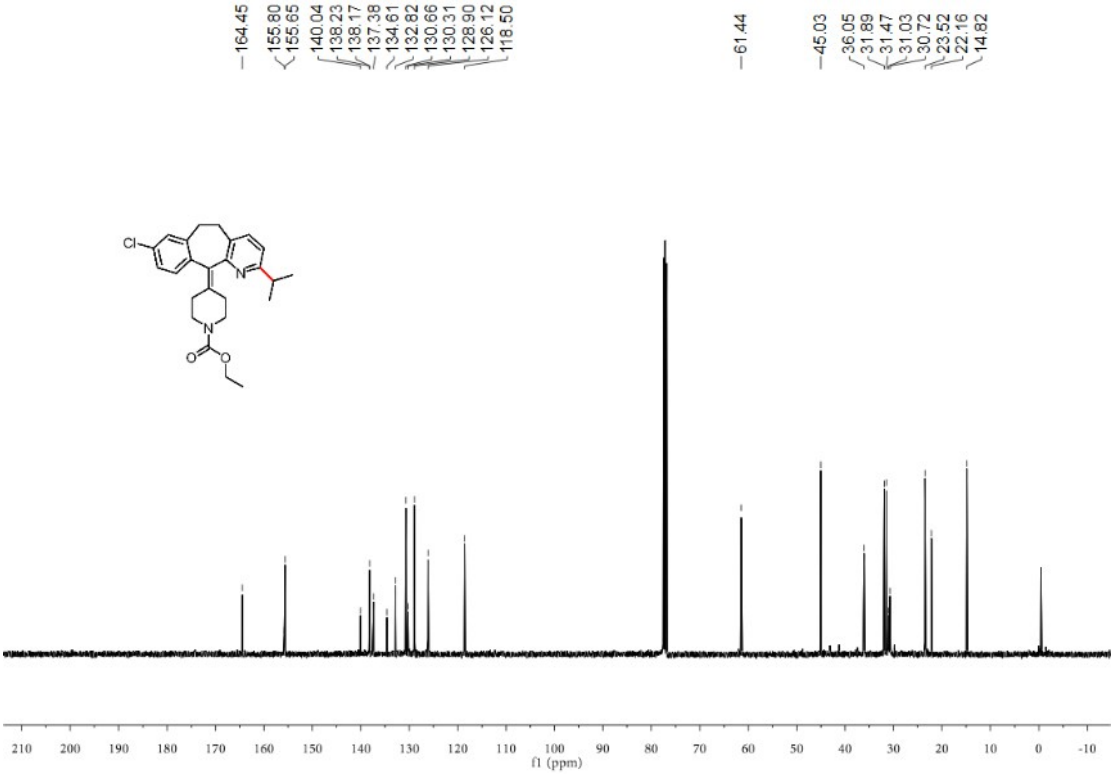
^{13}C NMR spectrum of compound **44**



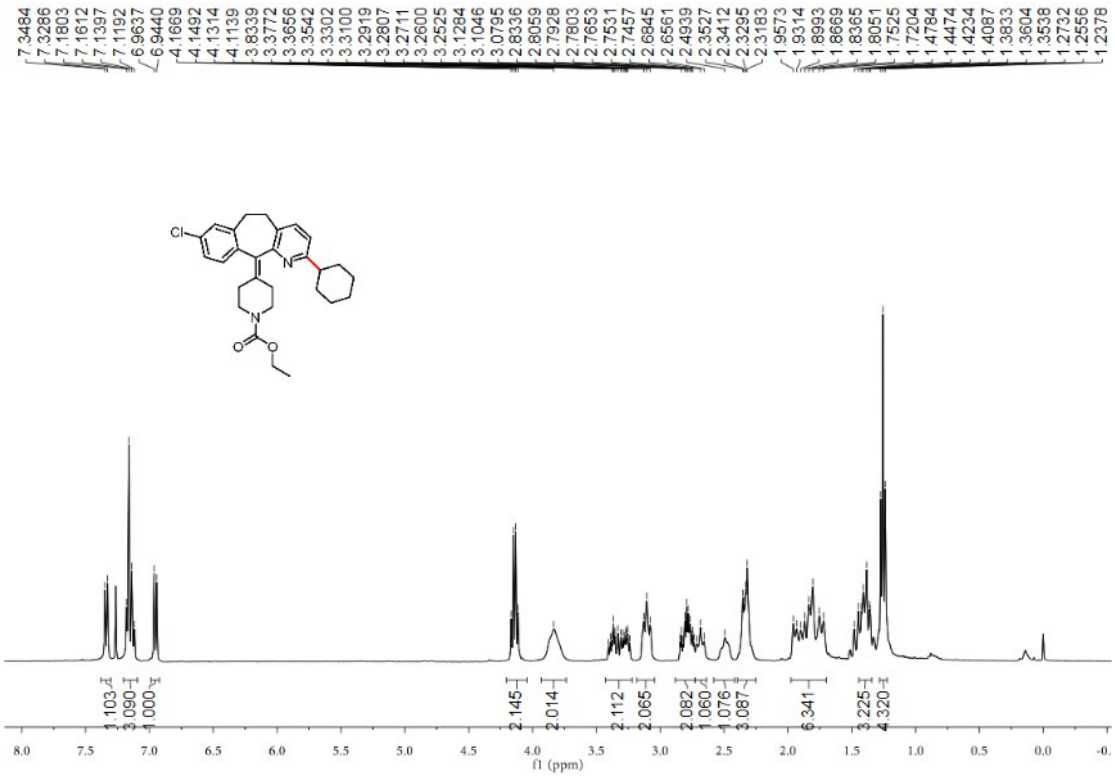
^{1}H NMR spectrum of compound **45a**



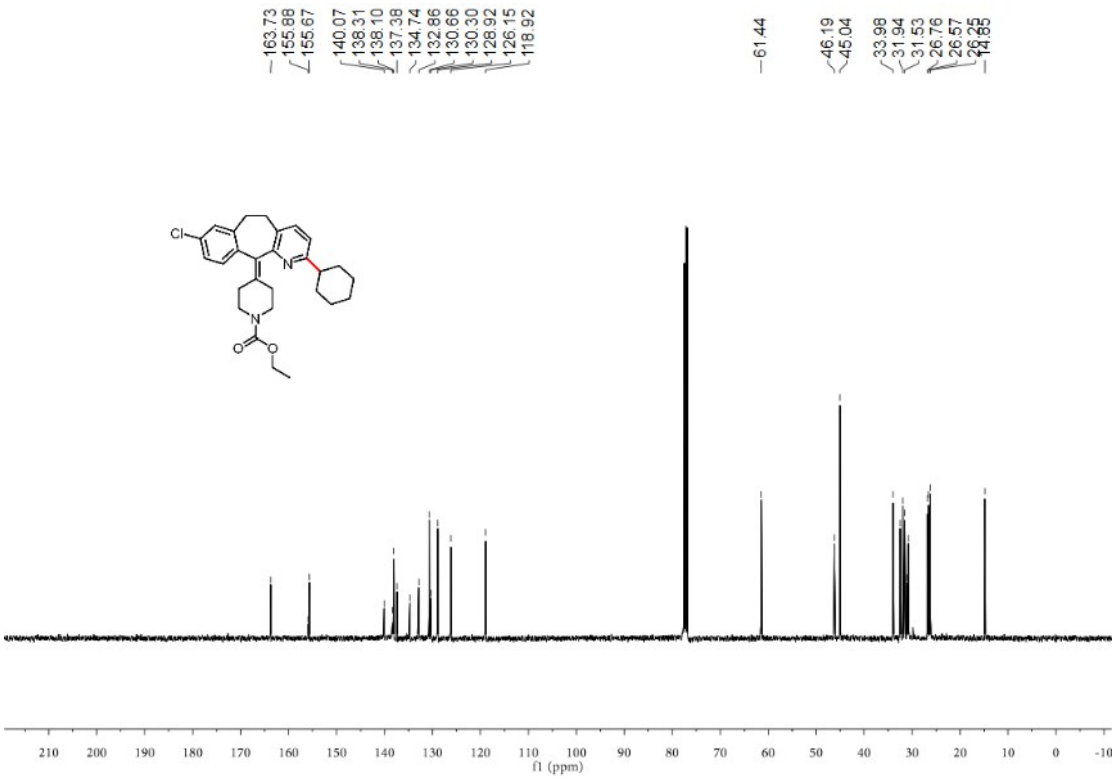
^{13}C NMR spectrum of compound **45a**



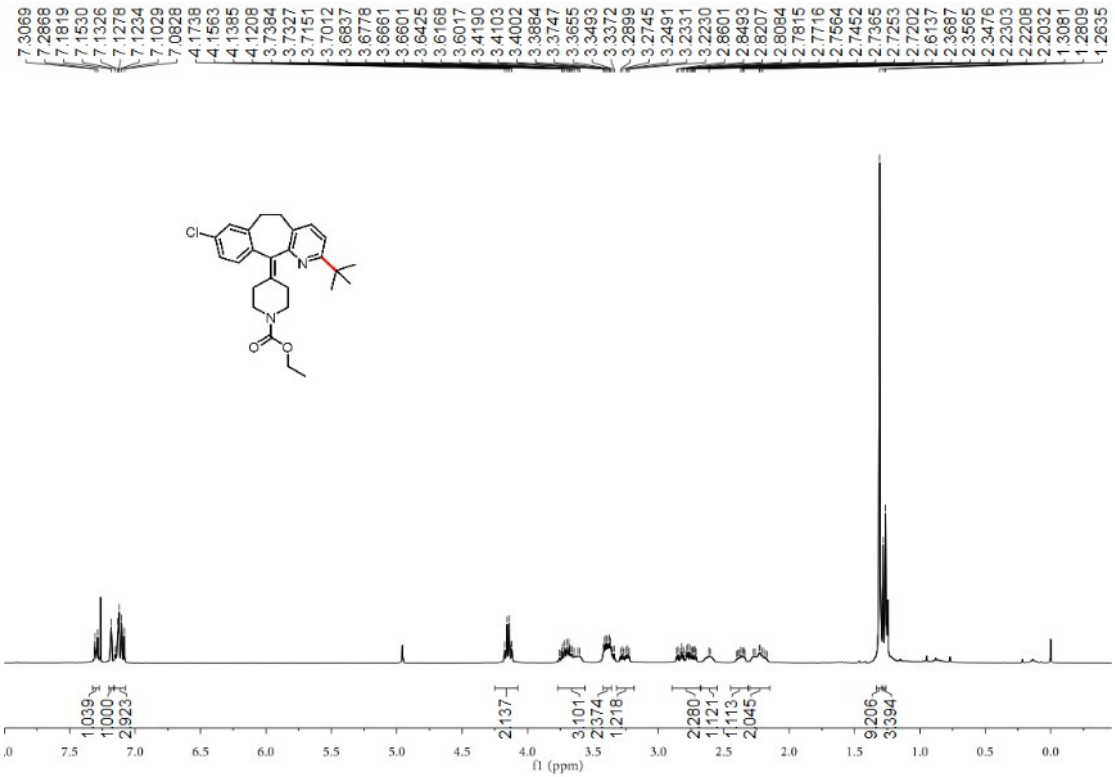
^{1}H NMR spectrum of compound **45b**



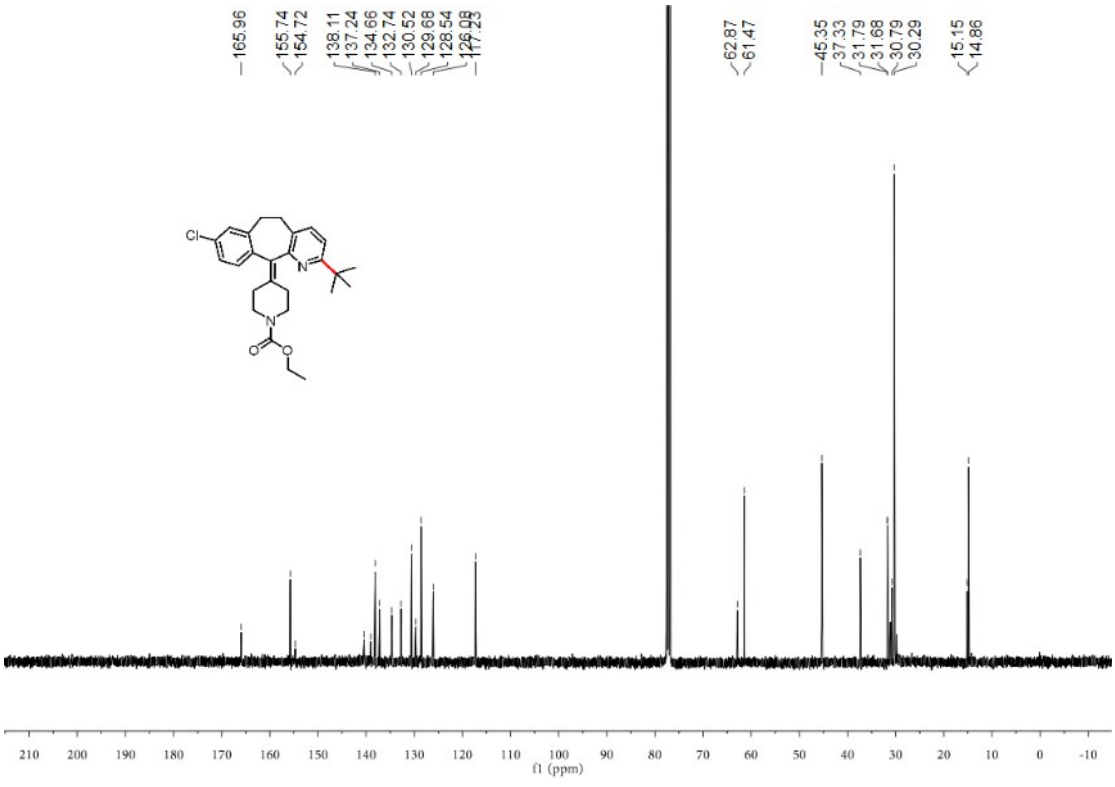
^{13}C NMR spectrum of compound **45b**



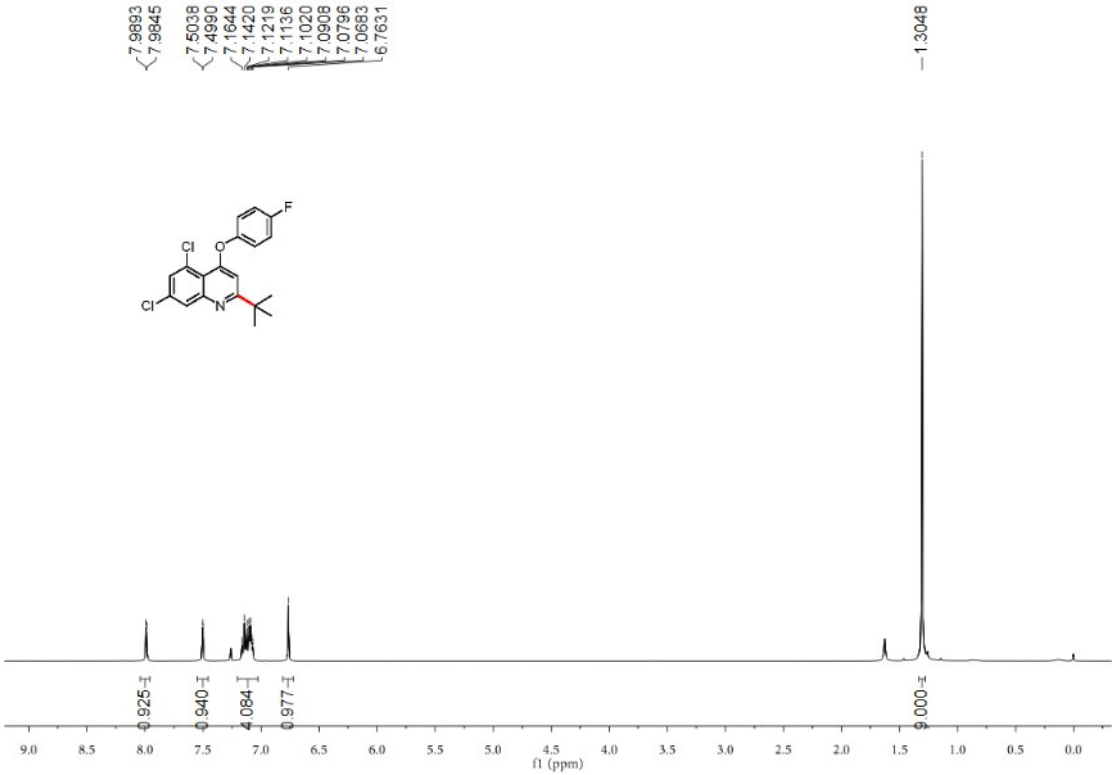
[1]H NMR spectrum of compound **45c**



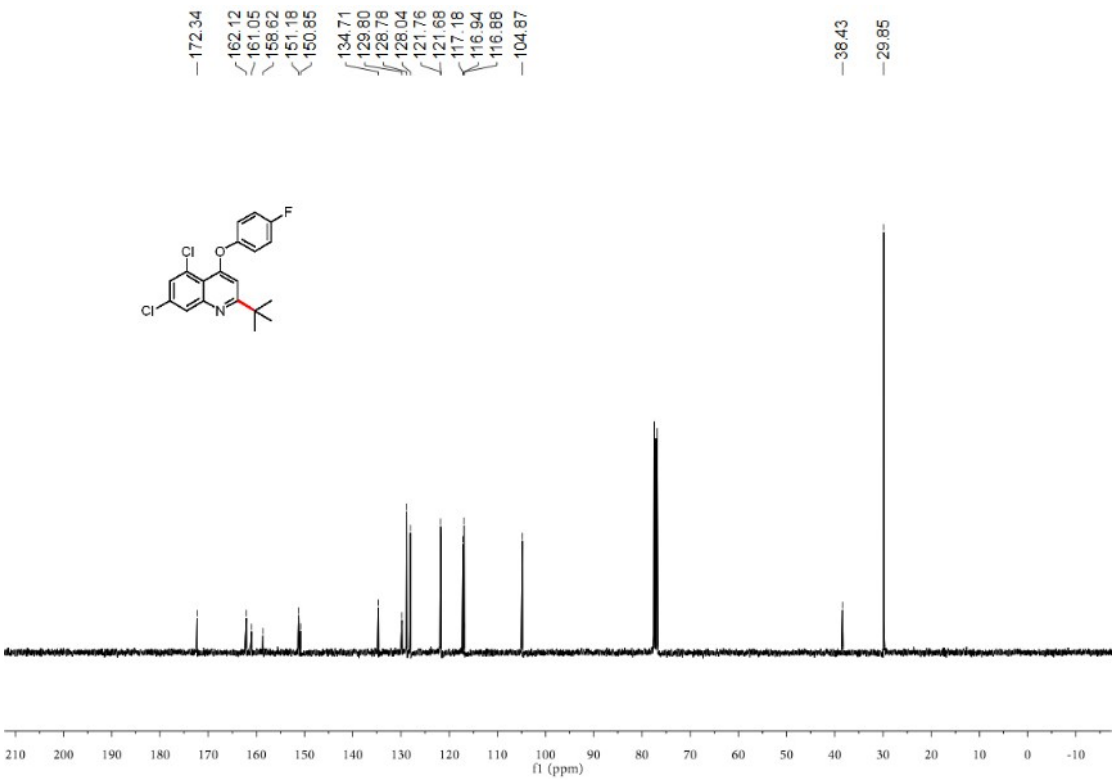
[13]C NMR spectrum of compound **45c**



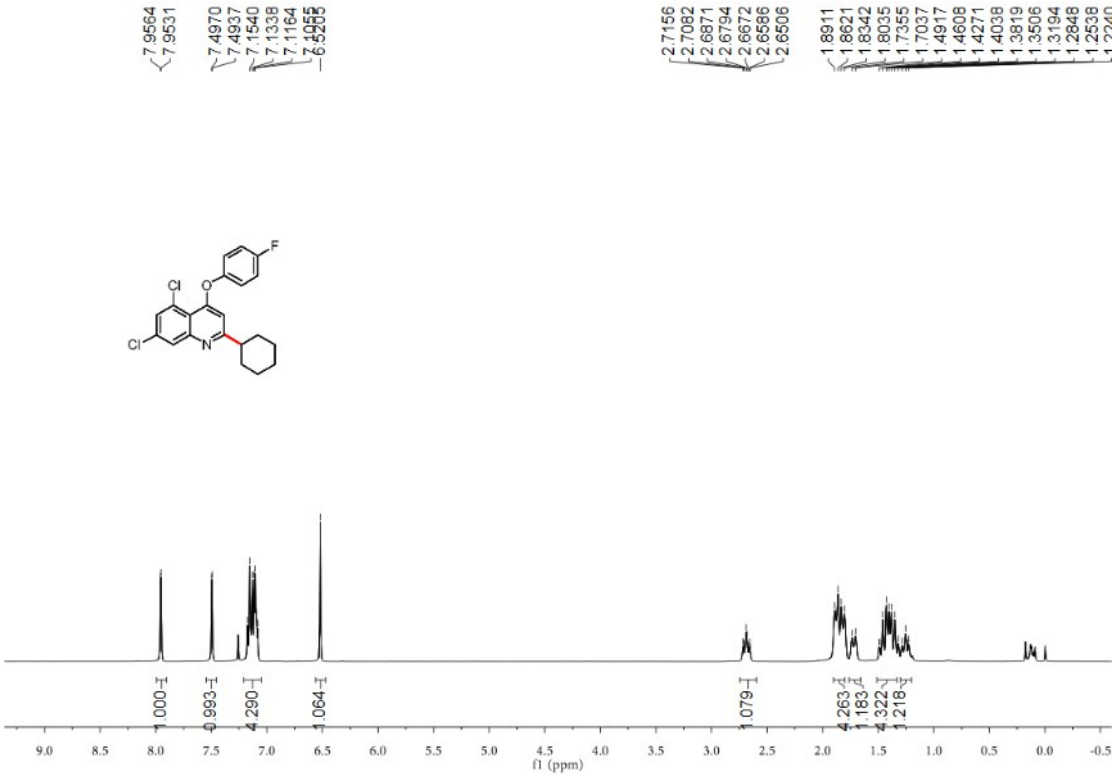
^{1}H NMR spectrum of compound **46a**



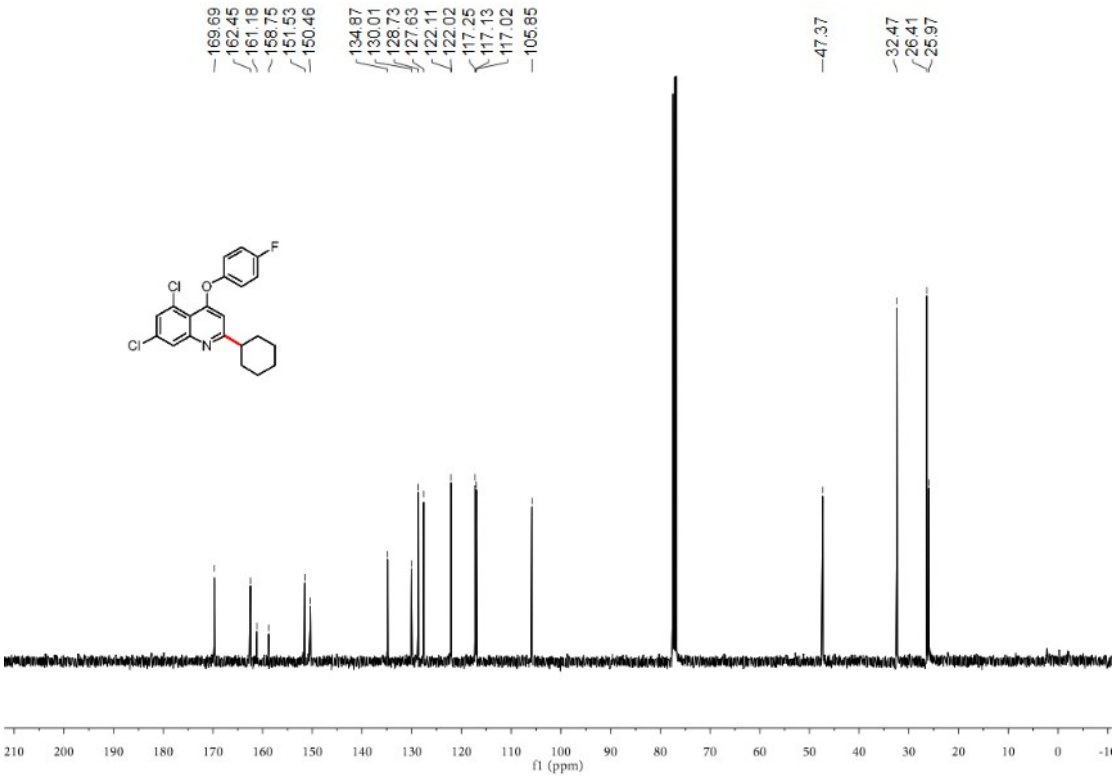
^{13}C NMR spectrum of compound **46a**



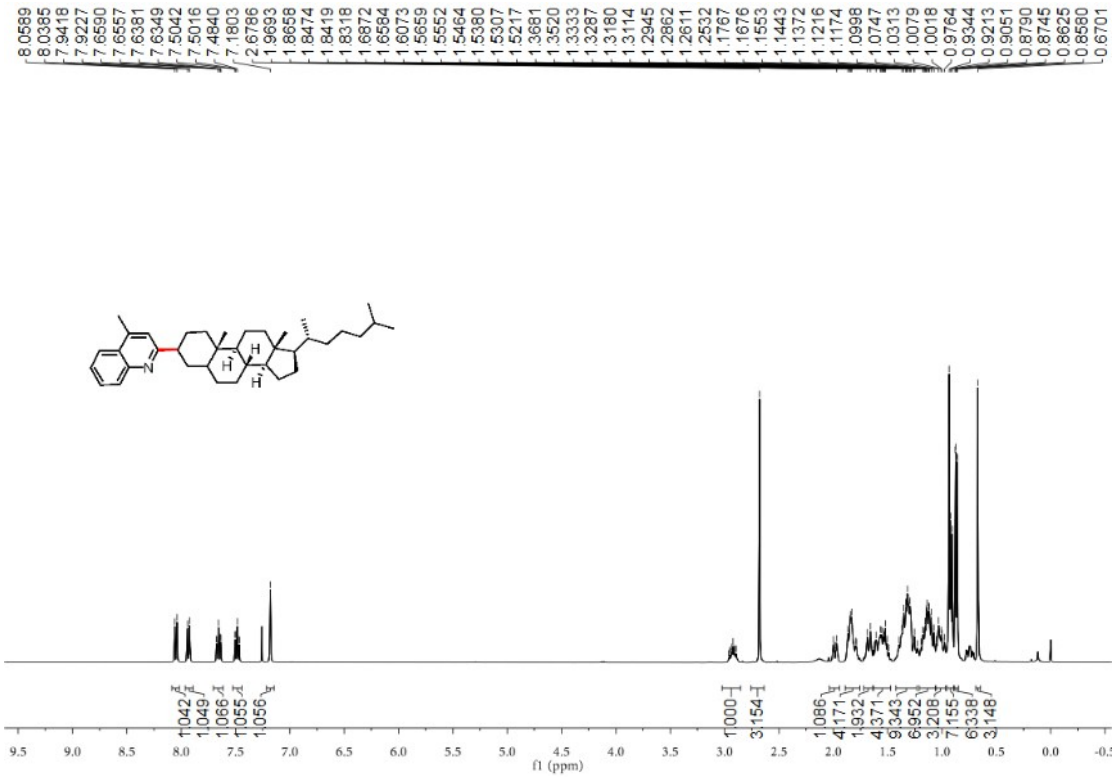
^{1}H NMR spectrum of compound **46b**



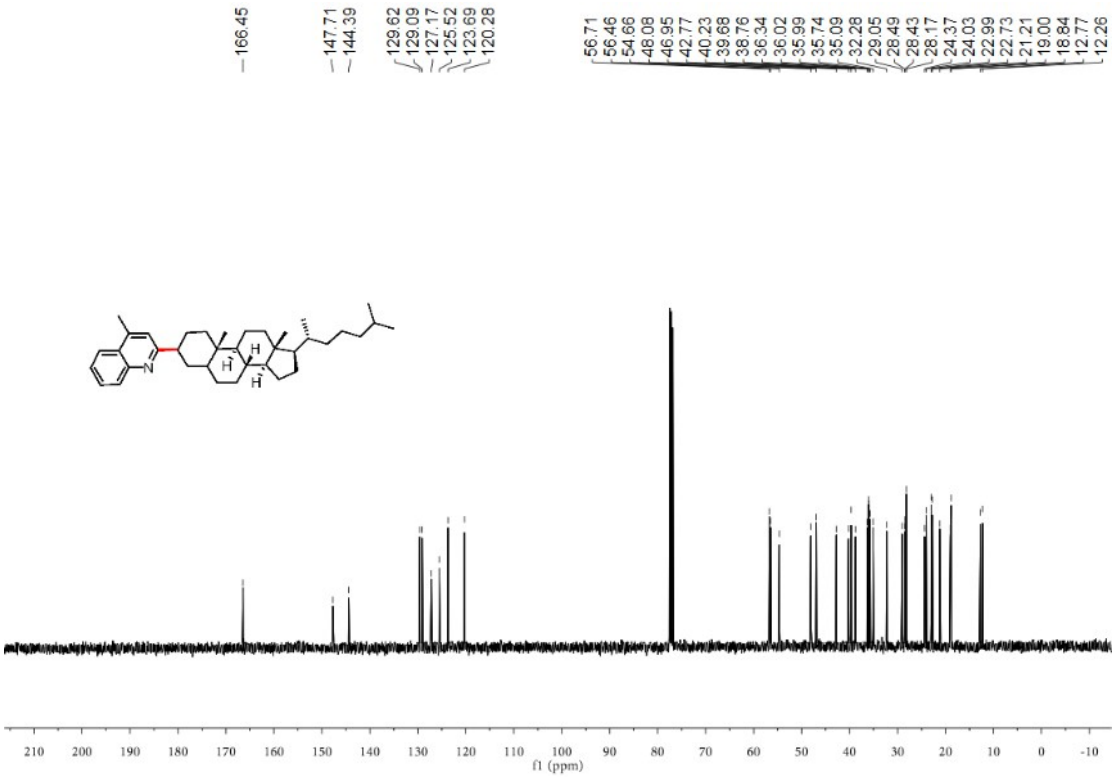
^{13}C NMR spectrum of compound **46b**



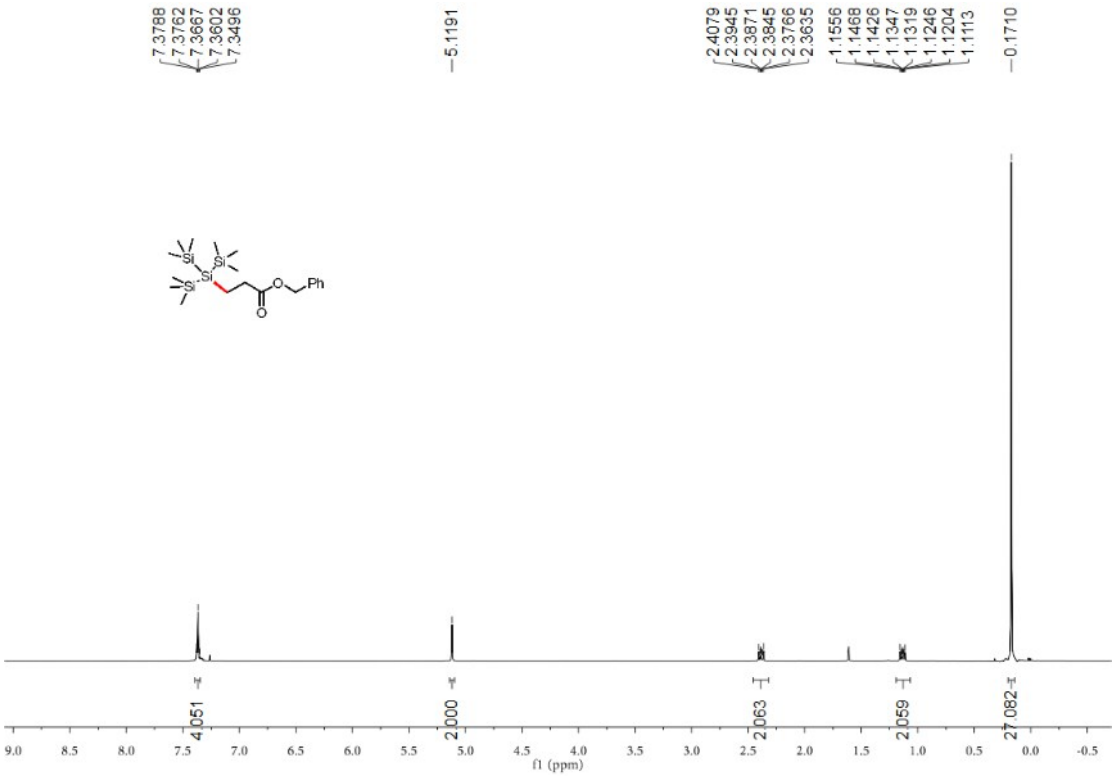
^{1}H NMR spectrum of compound **47**



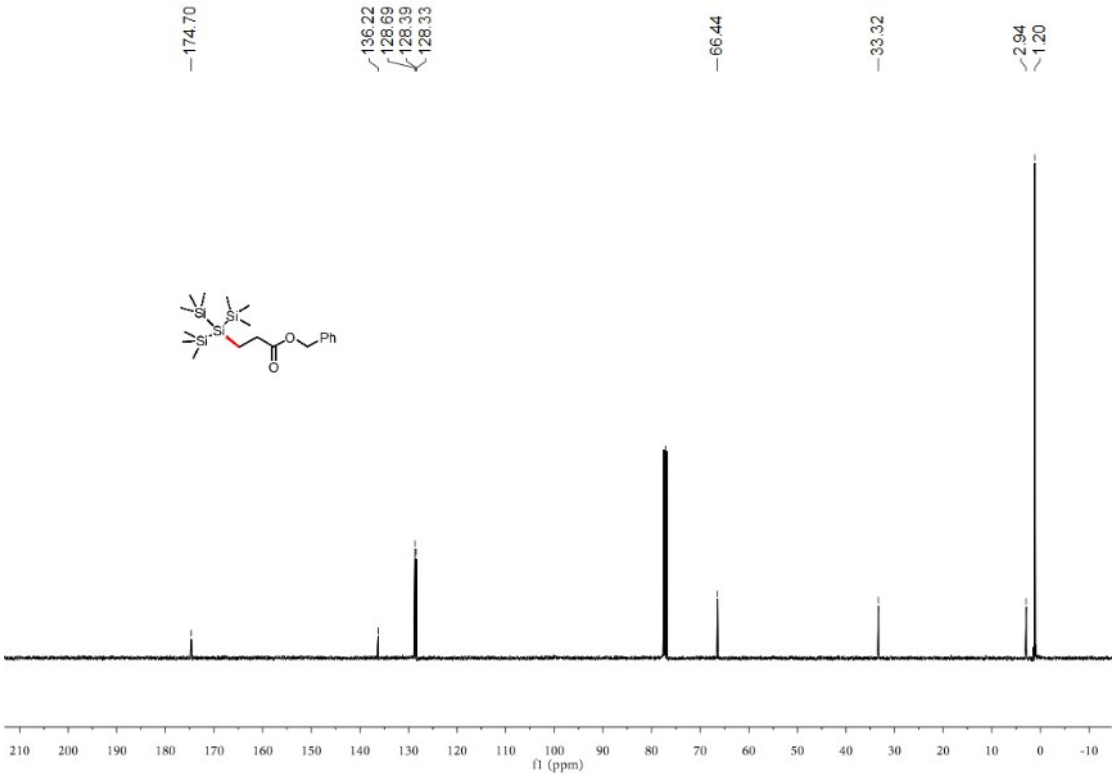
^{13}C NMR spectrum of compound **47**



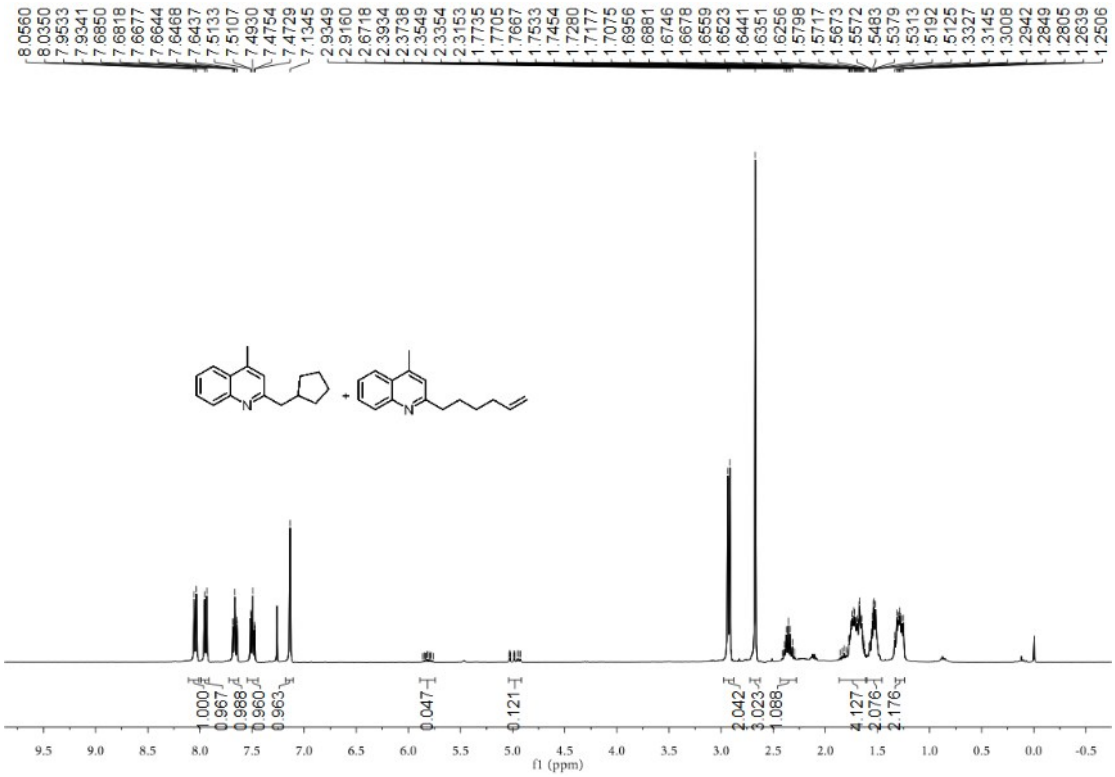
^{1}H NMR spectrum of compound **49**



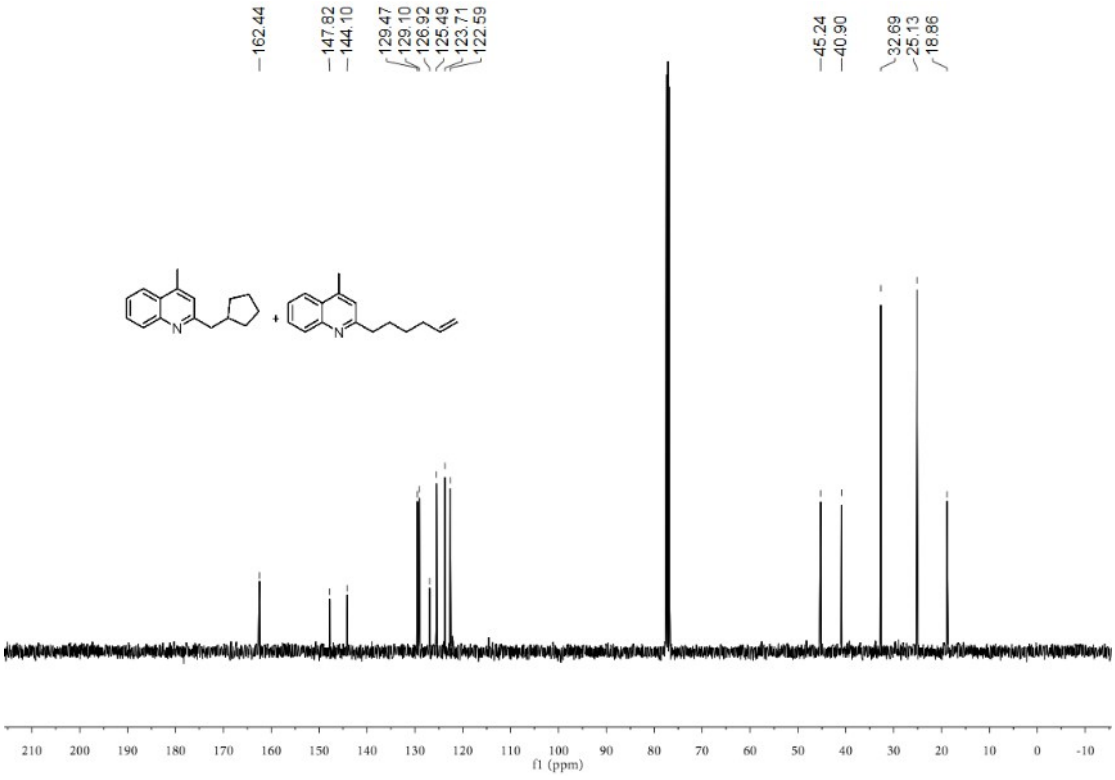
^{13}C NMR spectrum of compound **49**



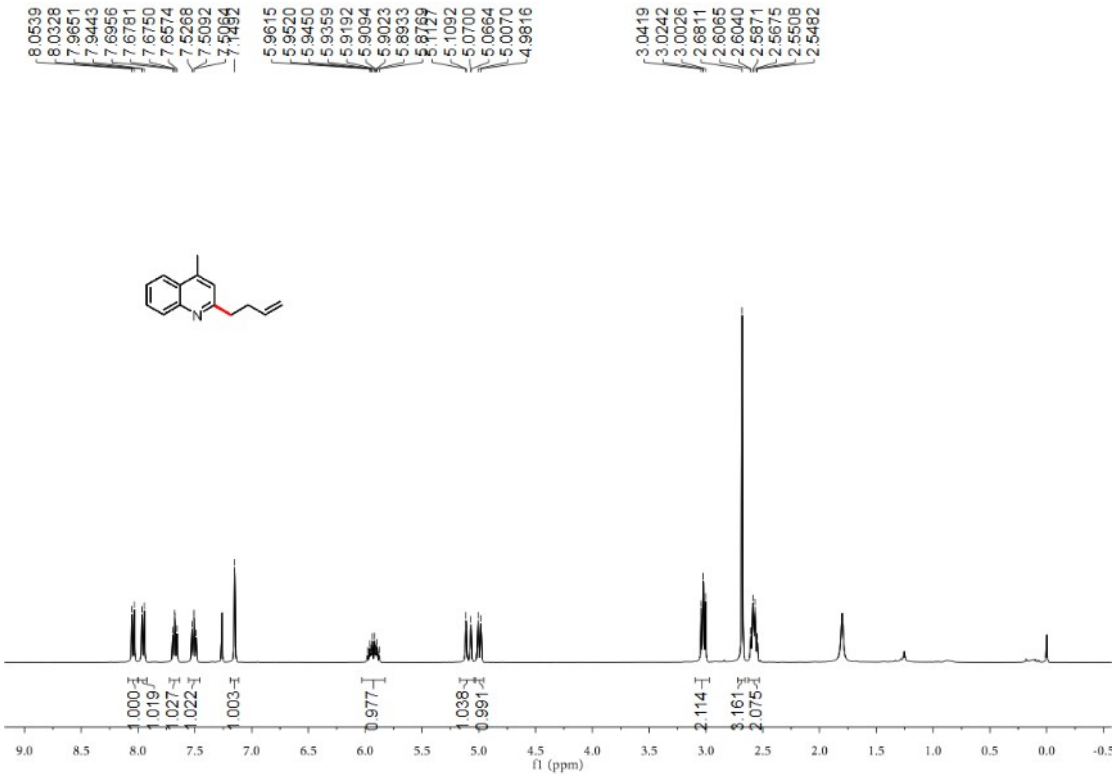
^{1}H NMR spectrum of compound **52**



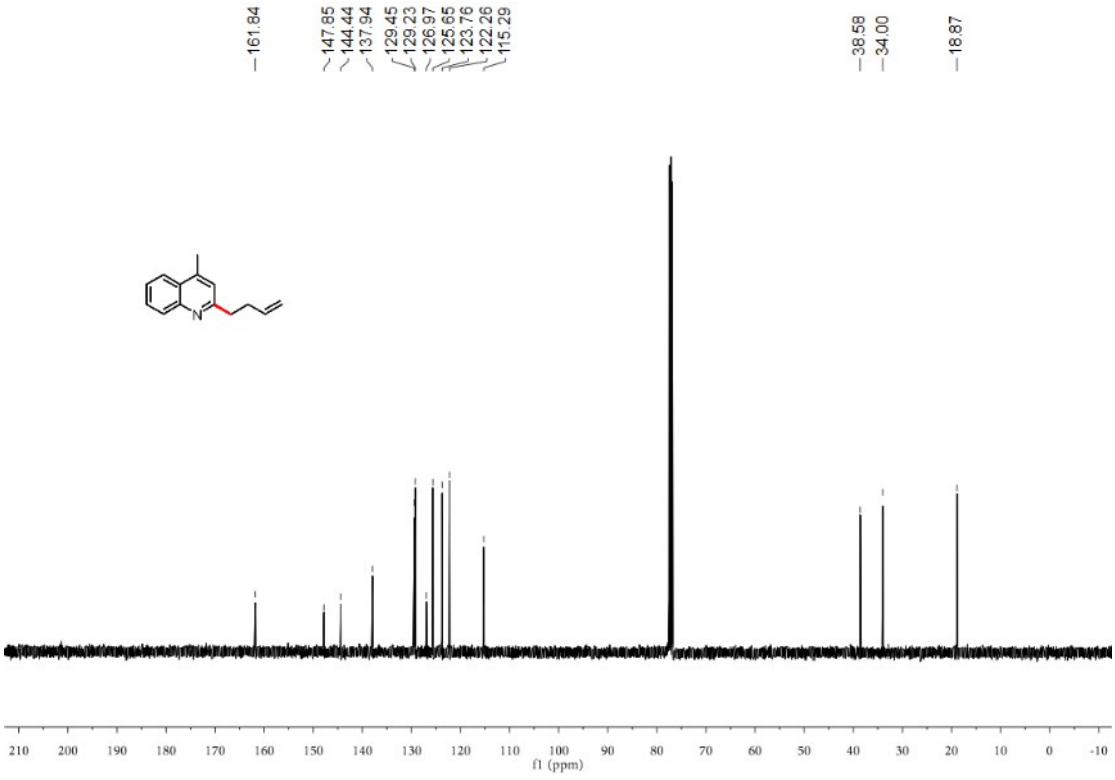
^{13}C NMR spectrum of compound **52**



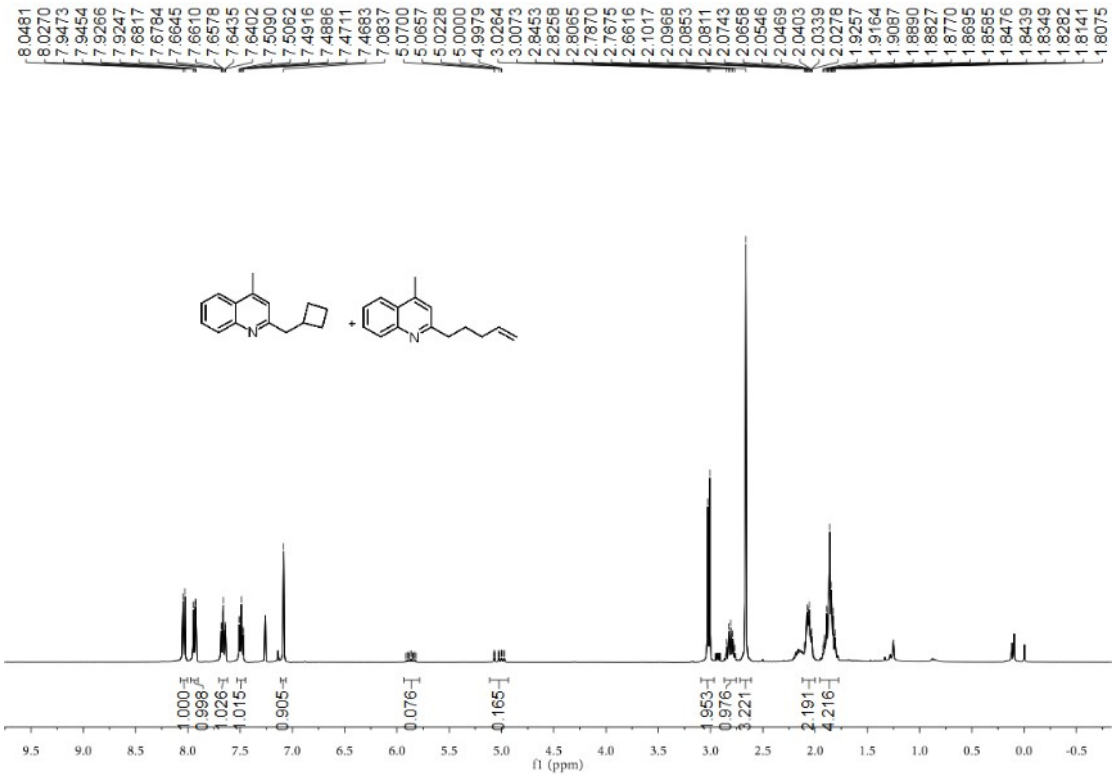
^{1}H NMR spectrum of compound **54**



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



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



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