Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Metal-, Photocatalyst-, and Light-Free Late-Stage C–H Alkylation of N-Heteroarenes with Organotrimethylsilanes using Persulfate as a Stoichiometric Oxidant

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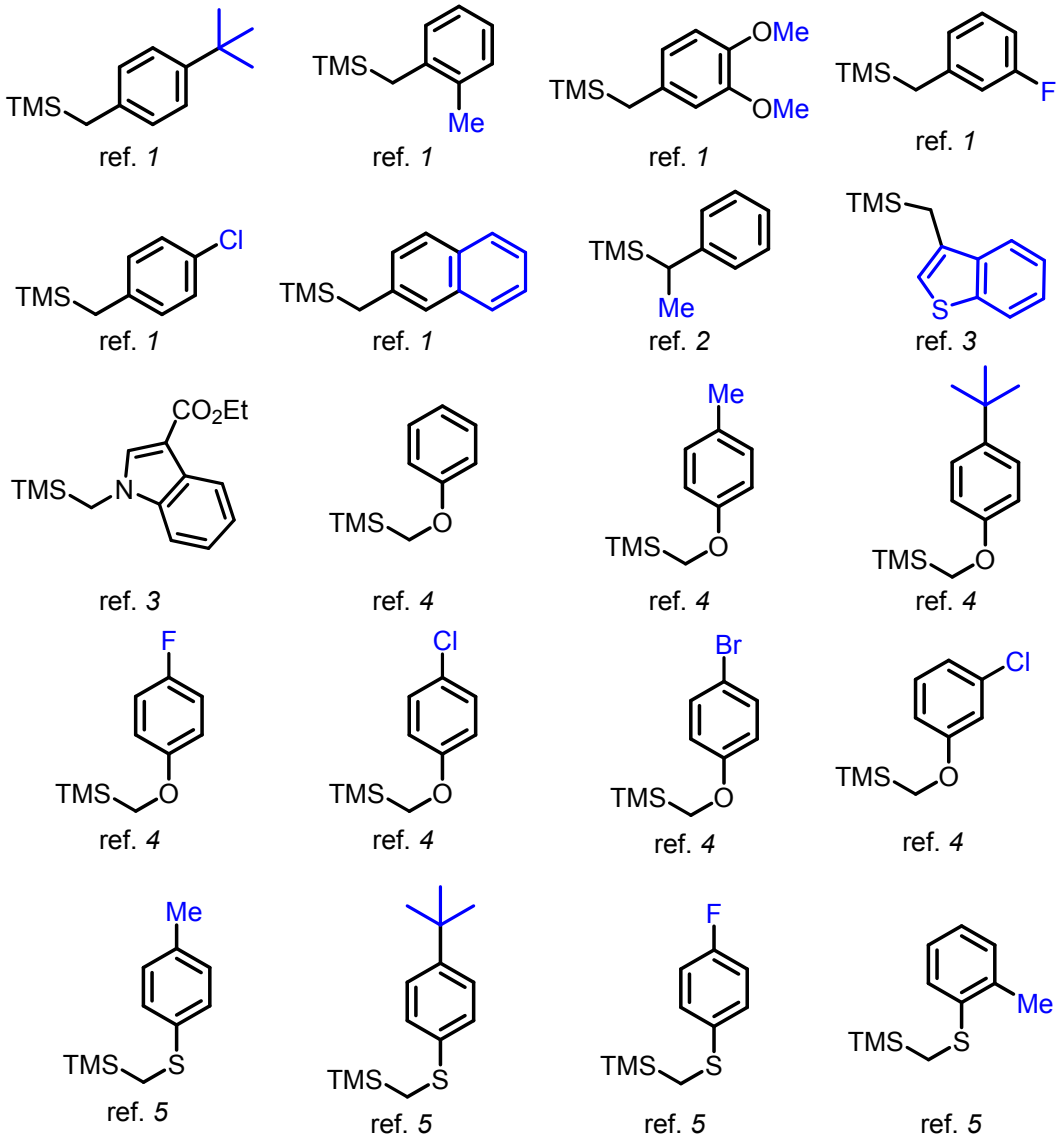
Supporting Information

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).

2. Synthesis of alkyl-trimethyl-silanes.

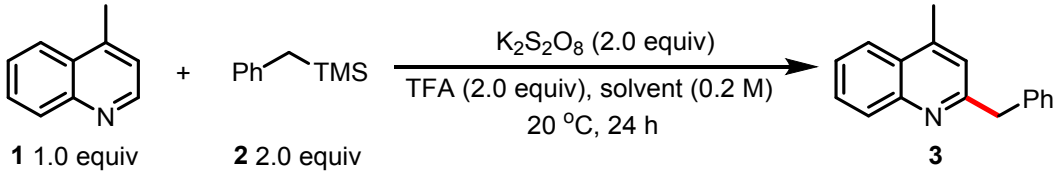
Many alkyl-trimethyl-silanes (except for commercially available benzyltrimethylsilane **2**) were synthesized using procedures reported in the literature. **Scheme S1** depicts the silanes that have been prepared and the corresponding literature references.



Scheme S1. The alkyl-trimethyl-silanes synthesized according to procedure reported in the literature.

3. Investigation of the key reaction parameters.

Table S1: Screening of different solvents[a]

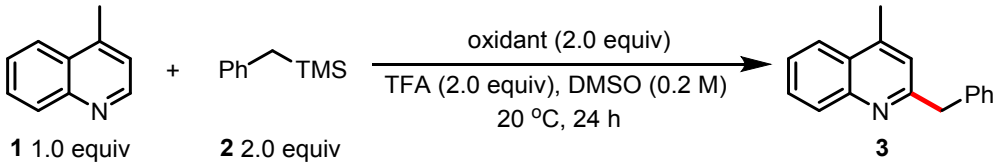


entry	solvent	yield (%)[b]
1	CH_3CN	18
2	CH_3CN:H_2O=1:1	6

3	**DMSO**	**38**
4	HCl_3	8
5	H_2O	NR

[a]General conditions: **1** (0.3 mmol), **2** (0.6 mmol), $K_2S_2O_8$ (0.6 mmol) and solvent (1.5 mL) under Ar atmosphere. [b]NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard; NR, no reaction.

Table S2: Screening of oxidants.[a]

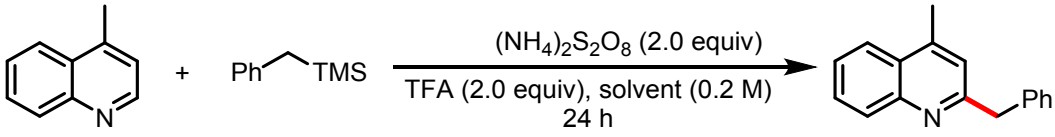


1 1.0 equiv **2** 2.0 equiv **3**

entry	oxidant	yield (%)[b]
1	$K_2S_2O_8$	38
2	$Na_2S_2O_8$	60
3	**$(NH_4)_2S_2O_8$**	**67**
4	*t*-BPA	7
5	*t*-BHP	5

[a]General conditions: **1** (0.3 mmol), **2** (0.6 mmol), oxidant (0.6 mmol) and DMSO (1.5 mL) under Ar atmosphere. [b]NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard.

Table S3: Screening of different temperature.[a]

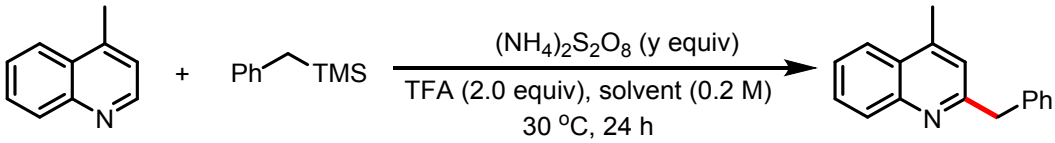


1 1.0 equiv **2** 2.0 equiv **3**

entry	temperature/°C	yield (%)[b]
1	20	67
2	**30**	**84**
3	40	85
4	50	85
5	60	86

[a]General conditions: **1** (0.3 mmol), **2** (0.6 mmol), $(NH_4)_2S_2O_8$ (0.6 mmol) and DMSO (1.5 mL) under Ar atmosphere. [b]NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard;

Table S4: Screening of the amount of benzyltrimethylsilane and oxidant.[a]

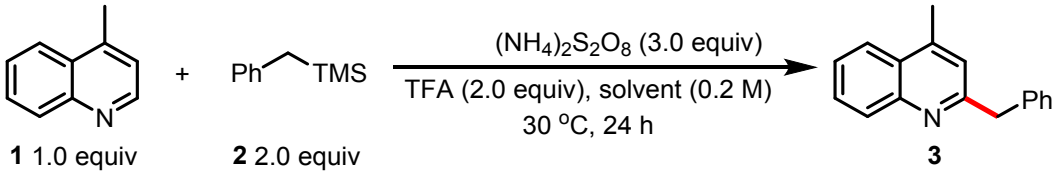


1 1.0 equiv **2** x equiv **3**

Entry	x eq. **2**	y eq. $(NH_4)_2S_2O_8$	Yield (%)[b]
1	2.0	2.0	84
2	1.5	2.0	67
3	3.0	2.0	86
4	2.0	1.5	62
5	**2.0**	**3.0**	**93 (91%)[c]**

[a]General conditions: **1** (0.3 mmol), **2** (0.3x mmol), $(NH_4)_2S_2O_8$ (0.3y mmol) and DMSO (1.5 mL) under Ar atmosphere. [b]NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard; [c]Isolated yield.

Table S5 Control experiments



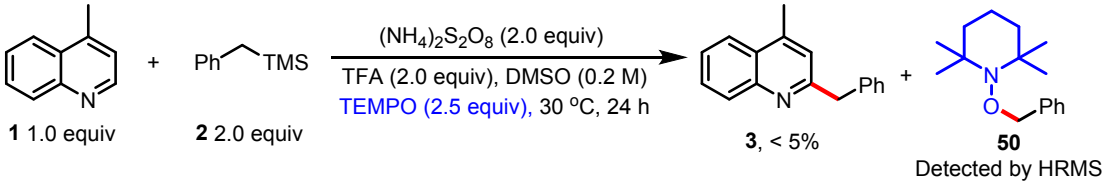
1 1.0 equiv **2** 2.0 equiv **3**

entry	control conditions	yield (%)
1	w/o $(NH_4)_2S_2O_8$	NR
2	w/o TFA	13
3	standard conditions, w/all	93

The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.

4. Investigation of the mechamism.

4.1 TEMPO was used as radical scavengers.

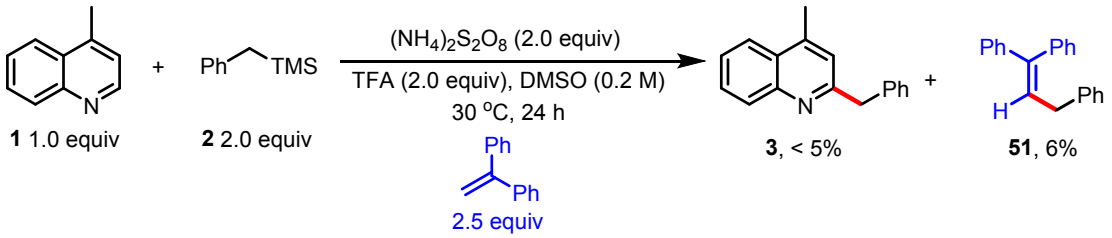


1 1.0 equiv **2** 2.0 equiv **3**, < 5% **50** Detected by HRMS

Scheme S2

To a 8 mL glass vial was added **1** (40 µL, 0.3 mmol, 1.0 equiv), **2** (114 μL, 0.6 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (205 mg, 0.9 mmol, 2.0 equiv), TEMPO (117 mg, 0.75 mmol, 2.5 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 30 °C for 24 h. The product **3** was obtained in less than 5% yield; and instead the corresponding product of radical trapping, 1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (**50**), was observed by mass spectrometry.

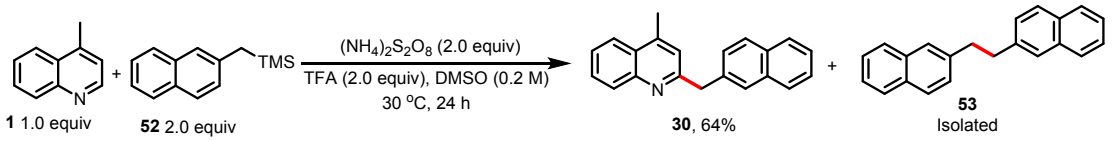
4.2 1,1-diphenylethylene was used as radical scavengers.



Scheme S3

To a 8 mL glass vial was added **1** (40 µL, 0.3 mmol, 1.0 equiv), **2** (114 μL, 0.6 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (205 mg, 0.9 mmol, 2.0 equiv), 1,1-diphenylethylene (117 mg, 0.75 mmol, 2.5 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 30 °C for 24 h. The product **3** was obtained in less than 5% yield; and instead a 6% yield of compound **51**, was isolated from the reaction.

4.3 Detection of by-product 53



To a 8 mL glass vial was added **1** (40 µL, 0.3 mmol, 1.0 equiv), **46** (128.4 mg, 0.6 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (205 mg, 0.9 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 30 °C for 24 h. The byproduct of radical coupling **53** was isolated from the reaction in 15% yield.

5. Experimental procedures and product characterization

5.1 General procedure A for the alkylation of N-heteroarenes.

To a 8 mL glass vial was added heteroarene (0.3 mmol, 1.0 equiv), alkyl-trimethyl-silanes (0.6 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (205 mg, 0.9 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 30 °C for 24 h. The mixture was diluted with 20 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

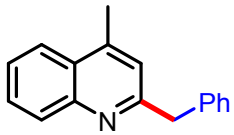
5.2 General procedure B for the alkylation of N-heteroarenes.

To a 8 mL glass vial was added heteroarene (0.3 mmol, 1.0 equiv), alkyl-trimethyl-silanes (0.6 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (205 mg, 0.9 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 60 °C for 24 h. The mixture was diluted with 20 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried

over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

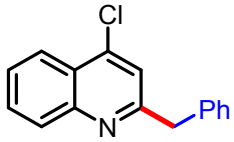
5.3. Product characterization

2-benzyl-4-methylquinoline (3).



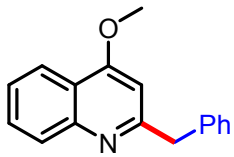
According to the *general procedure A*. The spectral data is consistent with the literature data.[6]
Brown solid (63.9 mg, 91%). M.p. = 64 – 65 °C.
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 7.06 (s, 1H), 4.29 (s, 2H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0, 147.8, 144.7, 139.5, 129.7, 129.4, 129.3, 128.7, 127.0, 126.6, 125.9, 123.8, 122.3, 45.7, 18.8.
HRMS (ESI) calcd for $C_{17}H_{16}N$ $[M + H]^+$ 234.1277, found 234.1279.

2-benzyl-4-chloroquinoline (4).



According to the *general procedure A*.
Yellow oil (30.4 mg, 40%).
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.38 – 7.28 (m, 5H), 7.26 (s, 1H), 4.31 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3, 148.8, 143.0, 138.6, 130.6, 129.5, 129.4, 128.9, 127.1, 126.9, 125.2, 124.1, 121.6, 45.5.
HRMS (ESI) calcd for $C_{16}H_{13}ClN$ $[M + H]^+$ 254.0731, found 254.0731.

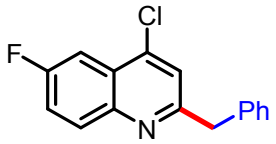
2-benzyl-4-methoxyquinoline (5).



According to the *general procedure A*.
Yellow solid (35.9 mg, 48%). M.p. = 71 – 72 °C.
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.4, 0.8 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.68 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.35 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 6.54 (s, 1H), 4.29 (s, 2H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 162.5, 148.8, 139.5, 129.9, 129.3, 128.7, 128.6, 126.6, 125.2, 121.8, 120.3, 100.2, 55.6, 46.2.

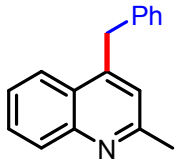
HRMS (ESI) calcd for $C_{17}H_{16}NO$ $[M + H]^+$ 250.1226, found 250.1231.

2-benzyl-4-chloro-6-fluoroquinoline (6).



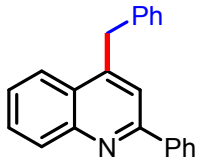
According to the *general procedure A*.
Yellow solid (34.1 mg, 42%). M.p. = 72 – 73 °C.
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 9.1, 5.2 Hz, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.51 (t, J = 8.4 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.28 – 7.22 (m, 1H), 4.29 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0 (d, J = 247.2 Hz), 160.7 (d, J = 2.9 Hz), 145.8, 142.2 (d, J = 5.5 Hz), 138.5, 132.1 (d, J = 9.0 Hz), 129.3, 128.9, 126.1 (d, J = 10.3 Hz), 126.0, 122.2, 120.7 (d, J = 25.8 Hz), 107.9 (d, J = 24.3 Hz), 45.3.
HRMS (ESI) calcd for $C_{16}H_{12}ClFN$ $[M + H]^+$ 272.0637, found 272.0637.

4-benzyl-2-methylquinoline (7).



According to the *general procedure A*.
Yellow oil (60.1 mg, 86%).
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.2 Hz, 2H), 7.22 (d, J = 6.8 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 6.99 (s, 1H), 4.34 (s, 2H), 2.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 148.1, 146.4, 138.7, 129.4, 129.2, 128.9, 128.7, 126.6, 125.9, 125.7, 123.7, 122.7, 38.1, 25.4.
HRMS (ESI) calcd for $C_{17}H_{16}N$ $[M + H]^+$ 234.1277, found 234.1280.

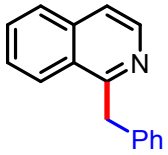
4-benzyl-2-phenylquinoline (8).



According to the *general procedure A*.
Yellow oil (81.4 mg, 92%).
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1H), 8.12 – 8.05 (m, 2H), 7.98 – 7.90 (m, 1H), 7.64 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.59 (s, 1H), 7.49 – 7.36 (m, 4H), 7.30 – 7.22 (m, 2H), 7.22 – 7.14 (m, 3H), 4.40 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.2, 148.7, 147.1, 139.8, 138.9, 130.6, 129.5, 129.4, 129.0, 128.9, 128.8, 127.6, 126.7, 126.4, 123.9, 119.9, 38.6.

HRMS (ESI) calcd for $C_{22}H_{18}N$ $[M + H]^+$ 296.1434, found 296.1436.

1-benzylisoquinoline (9).



According to the *general procedure A*.

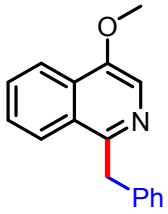
Yellow oil (57.3 mg, 96%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 5.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.30 – 7.19 (m, 4H), 7.13 (t, J = 7.2 Hz, 1H), 4.65 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2, 142.1, 139.5, 136.6, 129.9, 128.6, 128.55, 127.4, 127.2, 126.3, 125.8, 119.8, 42.1.

HRMS (ESI) calcd for $C_{16}H_{14}N$ $[M + H]^+$ 200.1121, found 200.1123.

1-benzyl-4-methoxyisoquinoline (10).



According to the *general procedure A*.

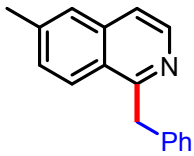
Yellow solid (61.3 mg, 82%). M.p. = 67 – 68 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.8 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.43 (m, 1H), 7.28 – 7.18 (m, 4H), 7.16 – 7.09 (m, 1H), 4.57 (s, 2H), 4.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5, 149.7, 139.9, 129.0, 128.9, 128.6, 128.5, 127.5, 127.4, 126.2, 125.5, 121.8, 121.7, 55.9, 41.7.

HRMS (ESI) calcd for $C_{17}H_{26}NO$ $[M + H]^+$ 250.1226, found 250.1223.

1-benzyl-6-methylisoquinoline (11).



According to the *general procedure A*.

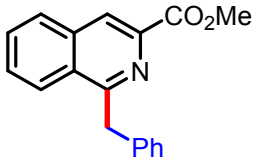
Gray oil (66.4 mg, 95%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 5.6 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.45 (d, J = 5.6 Hz, 1H), 7.33 (dd, J = 8.4, 1.6 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.18 – 7.11 (m, 1H), 4.63 (s, 2H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 142.2, 140.2, 139.7, 137.0, 129.5, 128.69, 128.6, 126.4, 126.3, 125.8, 125.7, 119.5, 42.1, 21.9.

HRMS (ESI) calcd for $C_{17}H_{16}N$ $[M + H]^+$ 234.1277, found 234.1281.

methyl 1-benzylisoquinoline-3-carboxylate (12).



According to the *general procedure A*.

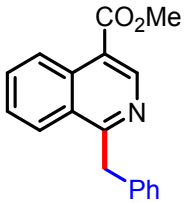
Yellow solid (70.6 mg, 85%). M.p. = 110 – 111 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.13 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.60 – 7.53 (m, 1H), 7.30 – 7.17 (m, 4H), 7.13 (t, J = 7.0 Hz, 1H), 4.76 (s, 2H), 4.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.51, 160.69, 140.57, 139.04, 136.14, 130.52, 129.46, 128.77, 128.58, 128.49, 126.31, 126.13, 123.55, 52.83, 42.41.

HRMS (ESI) calcd for $C_{18}H_{16}NO_2$ $[M + H]^+$ 278.1176, found 278.1181.

methyl 1-benzylisoquinoline-4-carboxylate (13).



According to the *general procedure A*.

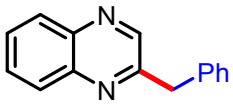
Yellow solid (56.5 mg, 68%). M.p. = 77 – 78 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.95 (d, J = 8.8 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 4.4 Hz, 4H), 7.17 (dd, J = 8.4, 4.4 Hz, 1H), 4.71 (s, 2H), 4.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 165.2, 145.9, 138.8, 134.6, 131.6, 128.7, 128.7, 127.6, 126.9, 126.6, 126.3, 125.8, 119.7, 52.4, 42.6.

HRMS (ESI) calcd for $C_{18}H_{16}NO_2$ $[M + H]^+$ 278.1176, found 278.1178.

2-benzylquinoxaline (14).



According to the *general procedure A*.

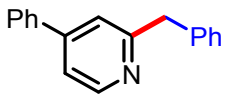
Red oil (30.4 mg, 46%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.07 (ddd, J = 7.6, 6.0, 1.6 Hz, 2H), 7.81 – 7.67 (m, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.21 (m, 1H), 4.38 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.9, 146.1, 142.2, 141.3, 138.0, 130.2, 129.4, 129.3, 129.2, 129.2, 129.0, 127.0, 43.1.

HRMS (ESI) calcd for $C_{15}H_{13}N_2$ $[M + H]^+$ 221.1073, found 221.1076.

2-benzyl-4-phenylpyridine (15).



According to the *general procedure B*.

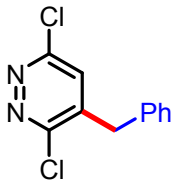
Yellow oil (33.1 mg, 45%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 4.8 Hz, 1H), 7.57 (d, J = 7.2 Hz, 2H), 7.44 (dd, J = 16.0, 8.4 Hz, 3H), 7.35 – 7.27 (m, 6H), 7.23 – 7.15 (m, 1H), 4.22 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 149.9, 149.1, 139.6, 138.5, 129.2, 129.2, 129.0, 128.8, 127.2, 126.6, 121.2, 119.5, 44.9.

HRMS (ESI) calcd for $C_{18}H_{16}N$ $[M + H]^+$ 246.1277, found 246.1280.

4-benzyl-3,6-dichloropyridazine (16).



According to the *general procedure B*.

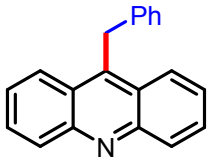
Yellow oil (30.7 mg, 43%)..

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.31 (m, 3H), 7.19 (d, J = 7.2 Hz, 2H), 7.08 (s, 1H), 4.06 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 156.3, 143.7, 134.6, 129.6, 129.5, 127.9, 38.4.

HRMS (ESI) calcd for $C_{11}H_9Cl_2N_2$ $[M + H]^+$ 239.0137, found 239.0135.

9-benzylacridine (17).



According to the *general procedure A*.

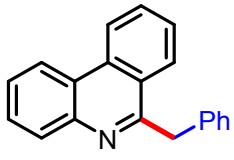
Brown solid (50.8 mg, 63%). M.p. = 163 – 164 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.8 Hz, 2H), 7.78 – 7.67 (m, 2H), 7.47 (ddd, J = 8.8, 6.4, 1.0 Hz, 2H), 7.22 – 7.10 (m, 3H), 7.07 (d, J = 7.2 Hz, 2H), 4.95 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.9, 143.5, 139.4, 130.4, 129.9, 128.8, 128.2, 126.5, 126.1, 125.7, 124.8, 33.2.

HRMS (ESI) calcd for $C_{20}H_{16}N$ $[M + H]^+$ 270.1277, found 270.1281.

6-benzylphenanthridine (18).



According to the *general procedure A*.

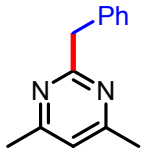
Yellow solid (76.7 mg, 95%). M.p. = 103 – 104 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 7.6 Hz, 1H), 8.19 (dd, J = 8.0, 0.7 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.74 – 7.61 (m, 2H), 7.61 – 7.54 (m, 1H), 7.51 – 7.44 (m, 1H), 7.29 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.2 Hz, 1H), 4.72 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 143.8, 139.2, 133.2, 130.3, 129.9, 128.7, 128.6, 128.6, 127.3, 127.0, 126.7, 126.4, 125.4, 123.9, 122.4, 122.0, 43.1.

HRMS (ESI) calcd for $C_{20}H_{16}N$ $[M + H]^+$ 270.1277, found 270.1282.

2-benzyl-4,6-dimethylpyrimidine (19).



According to the *general procedure B*.

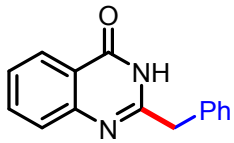
Yellow solid (30.9 mg, 52%). M.p. = 68 – 69 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 6.8 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.85 (s, 1H), 4.21 (s, 2H), 2.44 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 166.9, 138.8, 129.2, 128.4, 126.4, 117.7, 46.1, 24.2.

HRMS (ESI) calcd for $C_{13}H_{15}N_2$ $[M + H]^+$ 199.1230, found 199.1233.

2-benzylquinazolin-4(3*H*)-one (20).



According to the *general procedure B*.

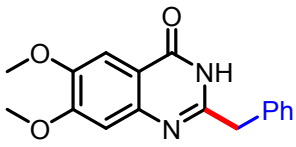
White solid (38.9 mg, 55%). M.p. = 249 – 250 °C.

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

^{1}H NMR (400 MHz, DMSO) δ 12.43 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 3.94 (s, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 162.3, 156.4, 149.4, 137.04, 134.9, 129.4, 129.0, 127.4, 127.3, 126.7, 126.2, 121.2, 41.2.

HRMS (ESI) calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$ 237.1022, found 237.1022.

2-benzyl-6,7-dimethoxyquinazolin-4(3*H*)-one (21).



According to the *general procedure B*.

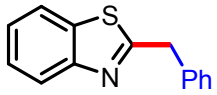
White solid (42.6 mg, 48%). M.p. = 66 – 67 °C.

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

^{1}H NMR (400 MHz, DMSO) δ 12.34 (s, 1H), 7.48 – 7.36 (m, 5H), 7.30 (t, J = 7.2 Hz, 1H), 7.14 (s, 1H), 3.96 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 161.2, 154.5, 154.4, 148.2, 145.0, 136.8, 128.8, 128.4, 126.7, 113.5, 107.8, 104.8, 55.9, 55.6, 40.6.

HRMS (ESI) calcd for $C_{17}H_{17}N_2O_3$ $[M + H]^+$ 297.1234, found 297.1236.

2-benzylbenzo[*d*]thiazole (22).



According to the *general procedure B*.

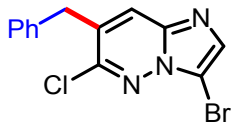
Yellow oil (54.7 mg, 81%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.40 – 7.32 (m, 5H), 7.32 – 7.28 (m, 1H), 4.44 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 153.4, 137.3, 135.8, 129.3, 129.0, 127.5, 126.1, 124.9, 122.9, 121.7, 40.8.

HRMS (ESI) calcd for $C_{14}H_{12}NS$ $[M + H]^+$ 226.0685, found 226.0685.

7-benzyl-3-bromo-6-chloroimidazo[1,2-*b*]pyridazine (23).



According to the *general procedure B*.

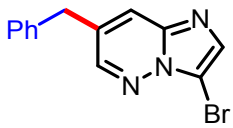
Yellow solid (39.5 mg, 41%). M.p. = 60 – 61 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.41 – 7.27 (m, 5H), 6.72 (s, 1H), 4.37 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 142.5, 139.0, 136.2, 134.2, 129.6, 129.2, 127.5, 117.62, 101.7, 35.7.

HRMS (ESI) calcd for $C_{13}H_{10}BrClN_3$ $[M + H]^+$ 321.9741, found 321.9739.

7-benzyl-3-bromoimidazo[1,2-*b*]pyridazine (24).



According to the *general procedure B*.

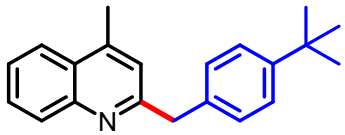
Yellow solid (42.2 mg, 49%). M.p. = 70 – 71 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 4.4 Hz, 1H), 7.79 (s, 1H), 7.39 – 7.27 (m, 5H), 6.71 (d, J = 4.4 Hz, 1H), 4.41 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.1, 140.8, 140.4, 136.9, 133.6, 129.6, 129.0, 127.3, 115.6, 101.0, 35.6.

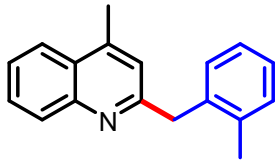
HRMS (ESI) calcd for $C_{13}H_{11}BrN_3$ $[M + H]^+$ 288.0131, found 288.0132.

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



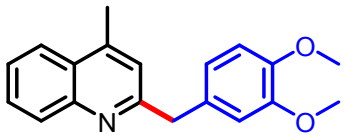
According to the *general procedure A*.
Yellow solid (72.8 mg, 84%). M.p. = 63 – 64 °C.
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.71 – 7.60 (m, 1H), 7.54 – 7.43 (m, 1H), 7.32 (dd, J = 8.4, 2.0 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.06 (s, 1H), 4.25 (s, 2H), 2.56 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 149.2, 147.7, 144.5, 136.3, 129.6, 129.2, 128.9, 126.9, 125.7, 125.6, 123.7, 122.3, 45.1, 34.5, 31.4, 18.8.
HRMS (ESI) calcd for $C_{21}H_{24}N$ $[M + H]^+$ 290.1903, found 290.1909.

4-methyl-2-(2-methylbenzyl)quinolone (26).



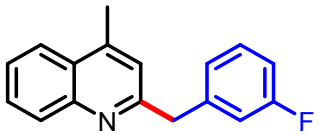
According to the *general procedure A*.
Yellow solid (47.4 mg, 64%). M.p. = 55 – 56 °C.
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.91 (dd, J = 8.4, 0.8 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.56 – 7.46 (m, 1H), 7.22 – 7.12 (m, 4H), 6.93 (s, 1H), 4.31 (s, 2H), 2.56 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 147.7, 144.6, 137.6, 137.2, 130.5, 130.3, 129.5, 129.2, 126.9, 126.8, 126.2, 125.8, 123.7, 121.7, 43.3, 20.0, 18.8.
HRMS (ESI) calcd for $C_{18}H_{18}N$ $[M + H]^+$ 248.1434, found 248.1437.

2-(3,4-dimethoxybenzyl)-4-methylquinoline (27).



According to the *general procedure A*.
Yellow oil (80.9 mg, 92%).
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.05 (s, 1H), 6.90 – 6.83 (m, 2H), 6.82 – 6.75 (m, 1H), 4.22 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 2.58 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 149.0, 147.6, 147.5, 144.6, 131.9, 129.4, 129.1, 126.8, 125.7, 123.6, 122.0, 121.2, 112.4, 111.2, 55.8, 45.1, 18.7.
HRMS (ESI) calcd for $C_{19}H_{20}NO_2$ $[M + H]^+$ 294.1489, found 294.1489.

2-(3-fluorobenzyl)-4-methylquinoline (28).



According to the *general procedure A*.

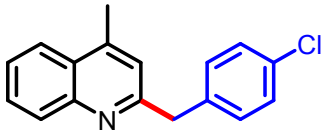
Brown solid (27.1 mg, 36%). M.p. = 50 – 51 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.32 – 7.21 (m, 1H), 7.13 – 6.97 (m, 3H), 6.91 (t, J = 8.4 Hz, 1H), 4.28 (s, 2H), 2.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ163.1 (d, J = 245.8 Hz), 160.1, 147.8, 145.0, 141.9 (d, J = 7.3 Hz), 130.1 (d, J = 8.4 Hz), 129.5 (d, J = 25.5 Hz), 127.0, 126.0, 125.0, 124.9, 123.8, 122.2, 116.2 (d, J = 21.2 Hz), 113.5 (d, J = 21.0 Hz), 45.2 (d, J = 1.5 Hz), 18.8.

HRMS (ESI) calcd for $C_{17}H_{15}FN$ $[M + H]^+$ 252.1183, found 252.1187.

2-(4-chlorobenzyl)-4-methylquinoline (29).



According to the *general procedure A*.

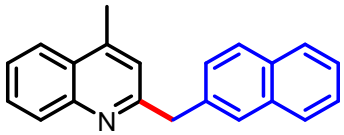
Yellow solid (36.8 mg, 46%). M.p. = 41 – 42 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.30 – 7.19 (m, 4H), 7.02 (s, 1H), 4.24 (s, 2H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3, 147.8, 144.9, 137.9, 132.4, 130.6, 129.6, 129.3, 128.8, 127.0, 126.0, 123.8, 122.1, 44.9, 18.8.

HRMS (ESI) calcd for $C_{17}H_{15}ClN$ $[M + H]^+$ 268.0888, found 268.0891.

4-methyl-2-(naphthalen-2-ylmethyl)quinolone (30).



According to the *general procedure A*.

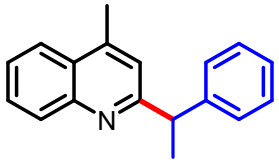
Yellow solid (53.3 mg, 64%). M.p. = 48 – 49 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.75 (dd, J = 11.6, 4.8 Hz, 4H), 7.70 – 7.62 (m, 1H), 7.46 (dd, J = 11.2, 4.0 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.03 (s, 1H), 4.43 (s, 2H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 147.7, 144.7, 137.0, 133.7, 132.3, 129.6, 129.2, 128.3, 127.8, 127.7, 127.6, 127.5, 126.9, 126.1, 125.8, 125.6, 123.7, 122.3, 45.7, 18.7.

HRMS (ESI) calcd for $C_{21}H_{18}N$ $[M + H]^+$ 284.1434, found 284.1438.

(*R*)-4-methyl-2-(1-phenylethyl)quinolone (31).



According to the *general procedure A*.

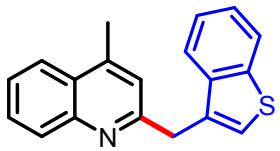
Red solid (38.5 mg, 52%). M.p. = 63 – 64 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.51 (dd, J = 11.2, 4.0 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.02 (s, 1H), 4.45 (q, J = 7.2 Hz, 1H), 2.59 (s, 3H), 1.78 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 147.6, 144.9, 144.5, 129.9, 129.1, 128.6, 127.9, 127.1, 126.5, 125.8, 123.7, 121.4, 48.1, 20.5, 18.9.

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

2-(benzo[b]thiophen-3-ylmethyl)-4-methylquinoline (32).



According to the *general procedure A*.

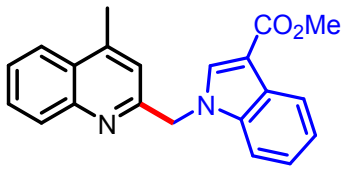
Yellow solid (63.3 mg, 73%). M.p. = 77 – 78 °C.

R_f 0.50 (Petroleum ether/EtOAc, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.19 (s, 1H), 7.07 (s, 1H), 4.51 (s, 2H), 2.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 147.8, 144.9, 140.6, 139.1, 133.9, 129.6, 129.4, 127.1, 125.9, 124.4, 124.2, 123.8, 123.7, 122.9, 122.4, 121.9, 38.9, 18.8.

HRMS (ESI) calcd for $C_{19}H_{16}NS$ $[M + H]^+$ 290.0998, found 290.0998.

methyl 1-((4-methylquinolin-2-yl)methyl)-1*H*-indole-3-carboxylate (33).



According to the *general procedure A*.

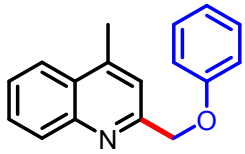
Yellow solid (68.5 mg, 84%). M.p. = 145 – 146 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.98 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.31 – 7.16 (m, 2H), 6.75 (s, 1H), 5.56 (s, 2H), 3.92 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 155.9, 147.5, 146.2, 136.9, 134.9, 129.8, 129.7, 127.5, 126.9, 126.7, 123.9, 123.2, 122.2, 121.8, 119.1, 110.6, 108.0, 53.5, 51.1, 18.9.

HRMS (ESI) calcd for $C_{21}H_{19}N_2O_2$ $[M + H]^+$ 331.1441, found 331.1442.

4-methyl-2-(phenoxymethyl)quinolone (34).



According to the *general procedure A*.

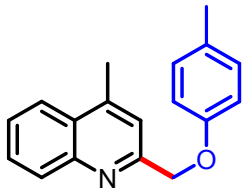
Yellow oil (47.1 mg, 63%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.99 (dd, J = 8.4, 0.8 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.56 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.52 (s, 1H), 7.36 – 7.25 (m, 2H), 7.03 (dd, J = 8.8, 0.8 Hz, 2H), 6.96 (t, J = 7.2 Hz, 1H), 5.34 (s, 2H), 2.71 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6, 157.7, 147.5, 145.5, 129.7, 129.6, 127.8, 126.4, 123.9, 121.3, 119.9, 115.0, 71.4, 19.1.

HRMS (ESI) calcd for $C_{17}H_{16}NO$ $[M + H]^+$ 250.1226, found 250.1226.

4-methyl-2-((*p*-tolyloxy)methyl)quinolone (35).



According to the *general procedure A*.

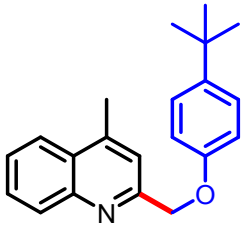
Yellow oil (40.2 mg, 51%).

R_f 0.50 (Petroleum ether/EtOAc, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.96 (dd, J = 8.4, 0.4 Hz, 1H), 7.75 – 7.66 (m, 1H), 7.60 – 7.45 (m, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 5.30 (s, 2H), 2.68 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 156.5, 147.4, 145.4, 130.4, 130.1, 129.6, 129.5, 127.7, 126.3, 123.9, 119.8, 114.8, 71.5, 20.6, 19.0.

HRMS (ESI) calcd for $C_{18}H_{18}NO$ $[M + H]^+$ 264.1383, found 264.1386.

2-((4-(*tert*-butyl)phenoxy)methyl)-4-methylquinoline (36).



According to the *general procedure A*.

Brown solid (60.4 mg, 66%). M.p. = 35 – 36 °C.

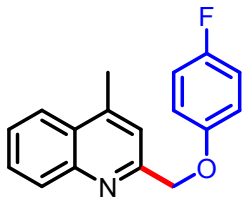
R_f 0.30 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.60 – 7.45 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 5.32 (s, 2H), 2.69 (s, 3H),

1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 156.4, 147.5, 145.4, 143.9, 129.6, 129.5, 127.7, 126.4, 126.3, 123.9, 119.9, 114.4, 71.5, 34.2, 31.6, 19.0.

HRMS (ESI) calcd for $C_{21}H_{24}NO$ $[M + H]^+$ 306.1852, found 306.1856.

2-((4-fluorophenoxy)methyl)-4-methylquinoline (37).



According to the *general procedure A*.

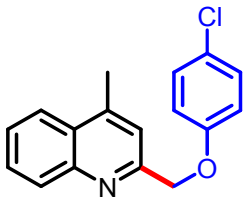
Yellow solid (50.5 mg, 63%). M.p. = 54 – 55 °C.

R_f 0.50 (Petroleum ether/EtOAc, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.97 (dd, J = 8.4, 0.8 Hz, 1H), 7.71 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.55 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.48 (s, 1H), 6.96 (d, J = 6.4 Hz, 4H), 5.28 (s, 2H), 2.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6 (d, J =240 Hz), 157.4, 154.7, 147.5, 145.5, 129.6 (d, J =2.5 Hz), 127.7, 126.4, 123.9, 119.8, 116.1, 116.0, 115.9, 72.0, 19.0.

HRMS (ESI) calcd for $C_{17}H_{15}FNO$ $[M + H]^+$ 268.1132, found 268.1136.

2-((4-chlorophenoxy)methyl)-4-methylquinoline (38).



According to the *general procedure A*.

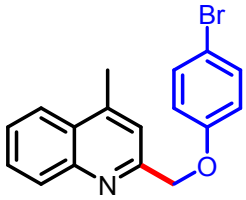
Yellow solid (54.3 mg, 64%). M.p. = 77 – 78 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.49 (s, 1H), 7.25 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 5.32 (s, 2H), 2.72 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.2, 157.1, 147.5, 145.6, 129.6, 129.5, 127.7, 126.5, 126.1, 123.9, 119.8, 116.3, 71.7, 19.0.

HRMS (ESI) calcd for $C_{17}H_{15}ClNO$ $[M + H]^+$ 284.0837, found 284.0839.

2-((4-bromophenoxy)methyl)-4-methylquinoline (39).



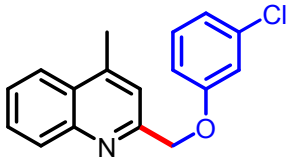
According to the *general procedure A*.

Yellow solid (54.0 mg, 55%). M.p. = 72 – 73 °C.

R_f 0.50 (Petroleum ether/EtOAc, 10/1).

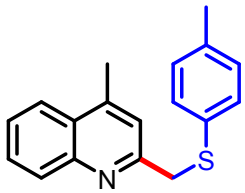
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.97 (dd, J = 8.4, 0.8 Hz, 1H), 7.71 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.55 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.45 (s, 1H), 7.41 – 7.32 (m, 2H), 6.94 – 6.85 (m, 2H), 5.28 (s, 2H), 2.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 157.0, 147.5, 145.6, 132.5, 129.6, 129.6, 127.7, 126.5, 123.9, 119.8, 116.8, 113.5, 71.6, 19.0.
HRMS (ESI) calcd for $C_{17}H_{15}BrNO$ $[M + H]^+$ 328.0332, found 328.0334.

2-((3-chlorophenoxy)methyl)-4-methylquinoline (40).



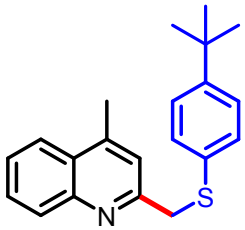
According to the *general procedure A*.
Yellow oil (34.8 mg, 41%).
R_f 0.50 (Petroleum ether/EtOAc, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 6.8 Hz, 1H), 7.56 (t, J = 6.8 Hz, 1H), 7.46 (s, 1H), 7.19 (td, J = 8.0, 2.4 Hz, 1H), 7.06 (d, J = 1.6 Hz, 1H), 7.00 – 6.83 (m, 2H), 5.30 (d, J = 2.4 Hz, 2H), 2.71 (d, J = 2.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 156.9, 147.4, 145.6, 135.1, 130.4, 129.7, 129.6, 127.8, 126.5, 123.9, 121.5, 119.8, 115.7, 113.2, 71.6, 19.0.
HRMS (ESI) calcd for $C_{17}H_{15}ClNO$ $[M + H]^+$ 284.0837, found 284.0838.

4-methyl-2-((*p*-tolylthio)methyl)quinolone (41).



According to the *general procedure A*.
Brown oil (31.8 mg, 38%).
R_f 0.50 (Petroleum ether/EtOAc, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.59 – 7.47 (m, 1H), 7.34 (s, 1H), 7.26 (t, J = 5.2 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 4.35 (s, 2H), 2.64 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 147.5, 145.0, 136.5, 132.2, 130.3, 129.8, 129.7, 129.4, 127.3, 126.2, 123.7, 121.8, 41.8, 21.1, 18.9.
HRMS (ESI) calcd for $C_{18}H_{18}NS$ $[M + H]^+$ 280.1154, found 280.1156.

2-(((4-(*tert*-butyl)phenyl)thio)methyl)-4-methylquinoline (42).



According to the *general procedure A*.

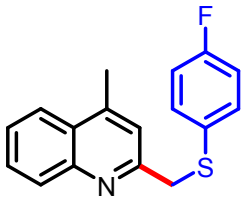
Yellow solid (34.7 mg, 36%). M.p. = 40 – 41 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.27 – 7.22 (m, 2H), 4.36 (s, 2H), 2.64 (s, 3H), 1.26 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 149.7, 147.6, 145.0, 132.5, 129.8, 129.7, 129.3, 127.3, 126.2, 126.0, 123.7, 121.8, 41.7, 34.6, 31.4, 18.9.

HRMS (ESI) calcd for $C_{21}H_{24}NS$ $[M + H]^+$ 322.1624, found 322.1620.

2-(((4-fluorophenyl)thio)methyl)-4-methylquinoline (43).



According to the *general procedure A*.

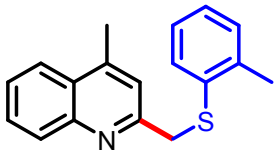
Yellow oil (28.0 mg, 33%).

R_f 0.50 (Petroleum ether/EtOAc, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.4, 0.8 Hz, 1H), 7.68 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.53 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.33 (ddd, J = 12.4, 7.2, 4.4 Hz, 3H), 6.98 – 6.87 (m, 2H), 4.31 (s, 2H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J = 248 Hz), 157.7, 147.5, 145.1, 132.8 (d, J = 8.0 Hz), 130.6 (d, J = 3.2 Hz), 129.7, 129.5, 127.3, 126.3, 123.7, 121.7, 116.0 (d, J = 22.0 Hz), 42.4, 18.9.

HRMS (ESI) calcd for $C_{17}H_{15}FNS$ $[M + H]^+$ 284.0904, found 284.0906.

4-methyl-2-((*o*-tolylthio)methyl)quinolone (44).



According to the *general procedure A*.

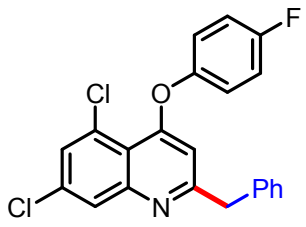
Brown solid (48.5 mg, 58%). M.p. = 58 – 59 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.69 (dd, J = 11.2, 4.0 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.34 (s, 1H), 7.17 – 7.02 (m, 3H), 4.37 (s, 2H), 2.65 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 147.6, 145.1, 137.6, 135.5, 130.1, 129.7, 129.4, 128.6, 127.3, 126.6, 126.2, 126.0, 123.7, 121.7, 40.5, 20.4, 18.9.

HRMS (ESI) calcd for $C_{18}H_{18}NS$ $[M + H]^+$ 280.1154, found 280.1156.

2-benzyl-5,7-dichloro-4-(4-fluorophenoxy)quinolone (45).



According to the *general procedure A*.

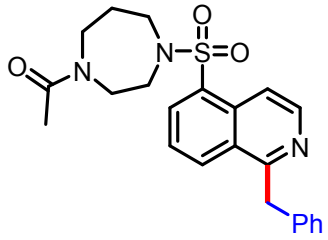
Yellow solid (35.7 mg, 30%). M.p. = 112 – 113 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.22 – 7.15 (m, 3H), 7.12 – 7.05 (m, 2H), 7.04 – 6.98 (m, 2H), 6.46 (s, 1H), 4.12 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 162.6, 160.0 (d, J = 244.3 Hz), 151.5, 150.1 (d, J = 2.7 Hz), 138.4, 135.2, 130.2, 129.1, 129.0, 128.8, 127.7, 126.8, 122.1, 122.0, 117.1 (d, J = 23.4 Hz), 117.0, 107.4, 45.3.

HRMS (ESI) calcd for $C_{22}H_{15}Cl_2FNO$ $[M + H]^+$ 398.0509, found 398.0504.

1-(4-((1-benzylisoquinolin-5-yl)sulfonyl)-1,4-diazepan-1-yl)ethan-1-one (46).



According to the *general procedure A*.

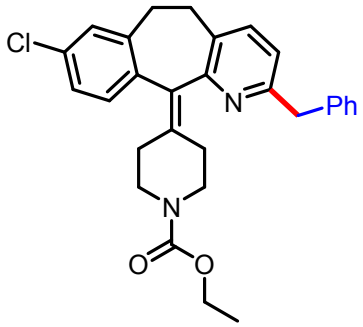
Yellow oil (103.6 mg, 82%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 6.4, 2.8 Hz, 1H), 8.41 (dd, J = 8.4, 4.4 Hz, 1H), 8.31 (d, J = 6.4 Hz, 1H), 8.28 – 8.20 (m, 1H), 7.65 – 7.52 (m, 1H), 7.29 – 7.22 (m, 4H), 7.21 – 7.16 (m, 1H), 4.71 (s, 2H), 3.76 – 3.69 (m, 1H), 3.62 (ddd, J = 13.2, 11.2, 6.4 Hz, 3H), 3.52 – 3.47 (m, 1H), 3.43 (dd, J = 11.6, 6.4 Hz, 2H), 3.37 (t, J = 6.0 Hz, 1H), 2.05 (s, 3H), 2.01 – 1.92 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 170.1, 161.3, 161.2, 144.2, 144.1, 138.9, 134.8, 132.6, 132.4, 131.7, 128.8, 128.6, 127.9, 126.6, 125.7, 116.4, 116.3, 50.8, 50.1, 49.2, 48.4, 48.0, 47.7, 46.9, 44.5, 42.7, 29.0, 27.7, 21.6, 21.1.

HRMS (ESI) calcd for $C_{23}H_{26}N_3O_3S$ $[M + H]^+$ 424.1689, found 424.1693.

ethyl 4-(2-benzyl-8-chloro-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (47).



According to the *general procedure A*.

Red solid (48.1 mg, 34%). M.p. = 119 – 120 °C.

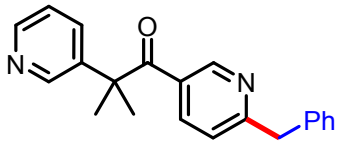
R_f 0.30 (Petroleum ether/EtOAc, 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.14 (m, 9H), 6.88 (d, J = 7.6 Hz, 1H), 4.23 – 4.02 (m, 4H), 3.79 (s, 2H), 3.41 – 3.21 (m, 2H), 3.19 – 3.03 (m, 2H), 2.87 – 2.70 (m, 2H), 2.53 – 2.21 (m, 4H), 1.26 (t, J =

7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 156.3, 155.6, 139.9, 138.3, 138.0, 137.6, 134.4, 132.9, 130.7, 129.2, 129.0, 128.6, 126.4, 126.2, 121.7, 61.4, 44.9, 44.4, 31.8, 31.4, 31.0, 30.7, 29.8, 14.8.

HRMS (ESI) calcd for $C_{29}H_{30}ClN_2O_2$ $[M + H]^+$ 473.1990, found 473.1993.

1-(6-benzylpyridin-3-yl)-2-methyl-2-(pyridin-3-yl)propan-1-one (48).



According to the *general procedure A*.

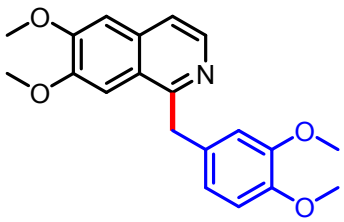
Yellow oil (31.3 mg, 33%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.47 (m, 3H), 7.74 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 7.2 Hz, 3H), 7.24 – 7.16 (m, 3H), 7.03 (d, J = 8.4 Hz, 1H), 4.10 (s, 2H), 1.65 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 164.6, 150.9, 148.6, 147.5, 140.2, 138.4, 137.8, 133.5, 129.2, 128.8, 128.7, 126.8, 124.0, 122.7, 50.3, 44.7, 27.5.

HRMS (ESI) calcd for $C_{21}H_{21}N_2O$ $[M + H]^+$ 317.1648, found 317.1650.

1-(3,4-dimethoxybenzyl)-6,7-dimethoxyisoquinoline (49).



According to the *general procedure A*.

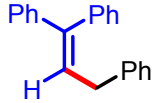
Yellow solid (89.5 mg, 88%). M.p. = 138 – 139 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 5.6 Hz, 1H), 7.42 (d, J = 5.6 Hz, 1H), 7.33 (s, 1H), 7.03 (s, 1H), 6.82 (d, J = 7.2 Hz, 2H), 6.76 (d, J = 8.4 Hz, 1H), 4.53 (s, 2H), 3.98 (s, 3H), 3.90 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 152.3, 149.7, 148.9, 147.4, 140.9, 133.4, 132.2, 122.8, 120.4, 118.7, 111.8, 111.1, 105.2, 104.1, 55.9, 55.8, 55.7, 42.2.

HRMS (ESI) calcd for $C_{20}H_{22}NO_4$ $[M + H]^+$ 340.1543, found 340.1545.

prop-1-ene-1,1,3-triyltribenzene (51).



The spectral data is consistent with the literature data.[7]

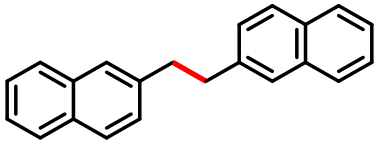
Yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 7.2 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.23 (m, 8H), 7.20 (d, J = 5.6 Hz, 3H), 6.27 (t, J = 7.6 Hz, 1H), 3.47 (d, J = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

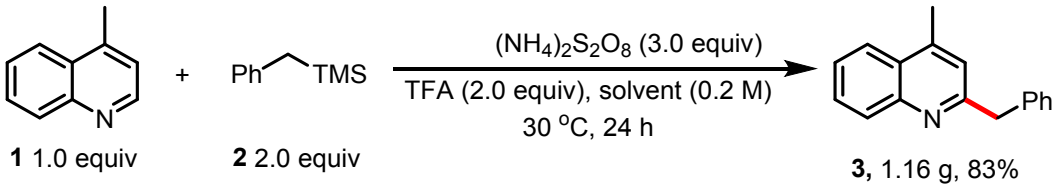
142.6, 142.6, 141.1, 139.9, 130.1, 128.9, 128.6, 128.6, 128.4, 128.2, 127.9, 127.5, 127.3, 127.2, 126.1, 125.9, 36.1.

1,2-di(naphthalen-2-yl)ethane (53).



According to the *general procedure A*. The spectral data is consistent with the literature data.[8]
Yellow solid. M.p. = 164 – 165 °C.
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 15.4, 8.0 Hz, 6H), 7.63 (s, 2H), 7.47 – 7.37 (m, 4H), 7.33 (d, J = 8.4 Hz, 2H), 3.15 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.4, 133.8, 132.2, 128.0, 127.8, 127.6, 127.5, 126.6, 126.0, 125.3, 38.1.

6. Gram-scale Reaction



To a 250 mL glass vial was added lepidine **1** (0.8 mL, 6 mmol, 1.0 equiv), benzyltrimethylsilane **2** (2.0 g, 12 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (4.0 g, 18 mmol, 3.0 equiv), TFA (0.9 mL, 12 mmol, 2.0 equiv) and 30 mL of DMSO. The reaction mixture was stirred rapidly at 30 °C for 24 h. The mixture was diluted with 100 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 83% yield.

References

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(5) H. Ishibashi, H. Nakatani, Y. Umei, W. Yamamoto, M. Ikeda, *J. Chem. Soc. Perkin Trans*. **1987**, *1*, 589.
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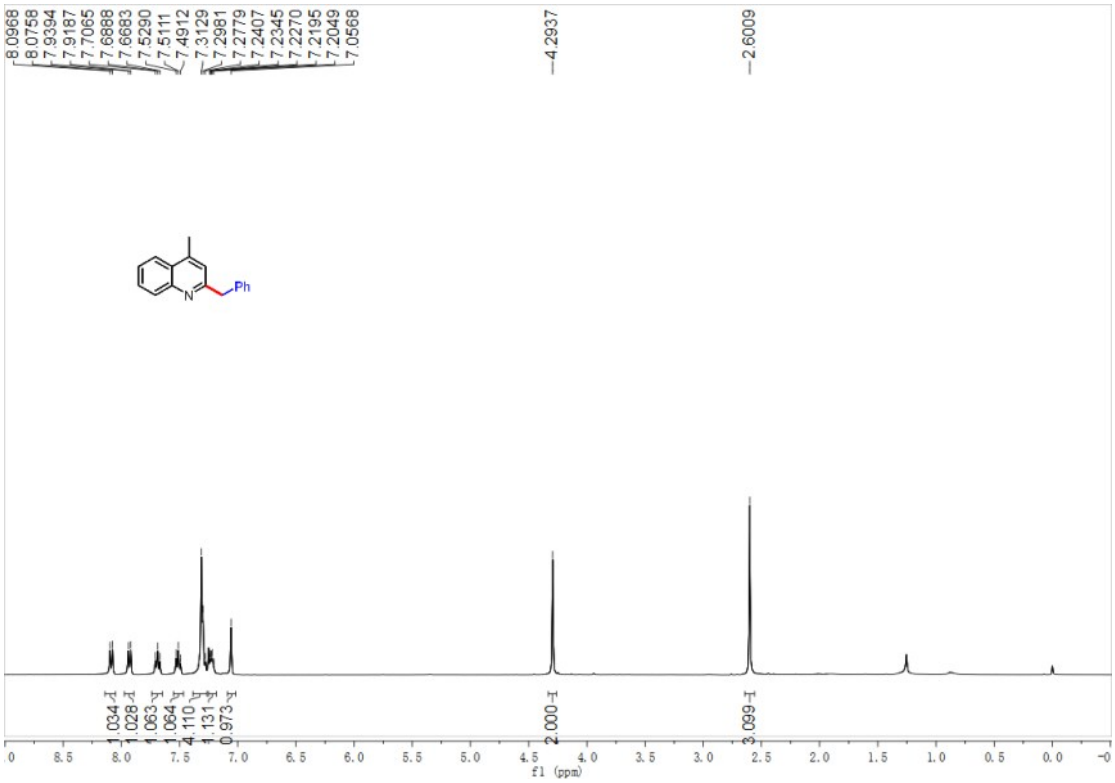
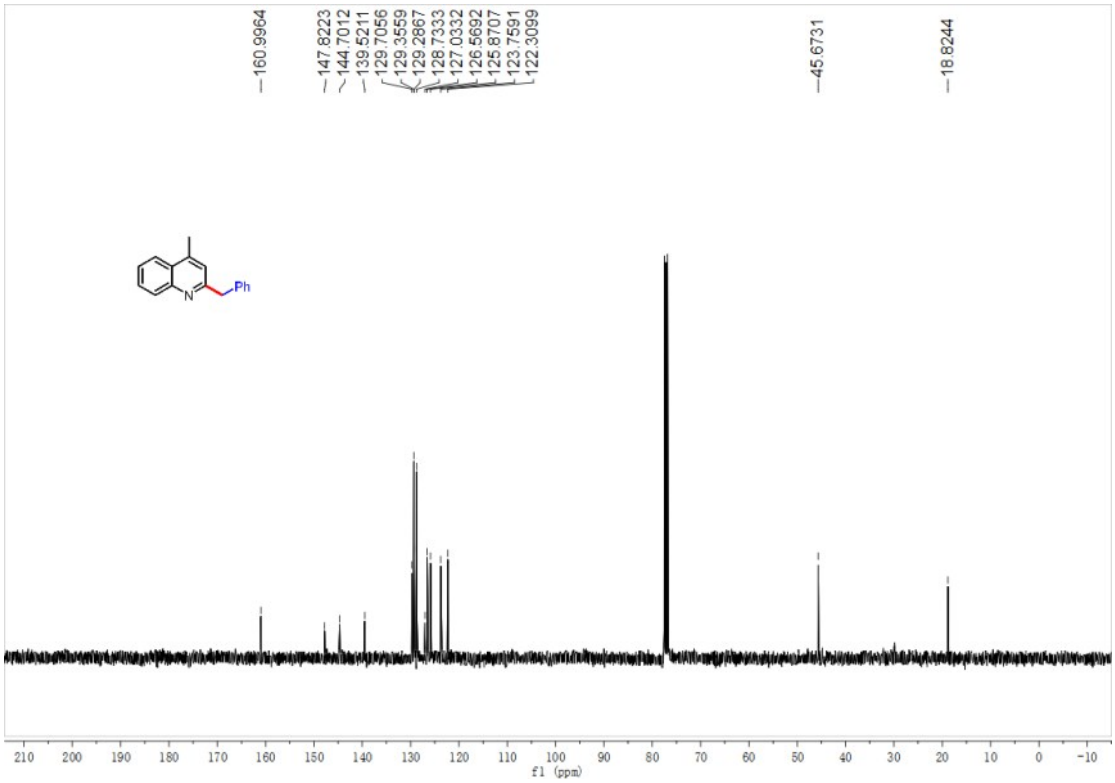
(7) H. Yu, B. Hu, H. Huang, *J. Org. Chem*. **2018**, *83*, 13922.
(8) Z.-C. Cao, Z.-J. Shi, *J. Am. Chem. Soc*. **2017**, *139*, 6546.

NMR Spectra

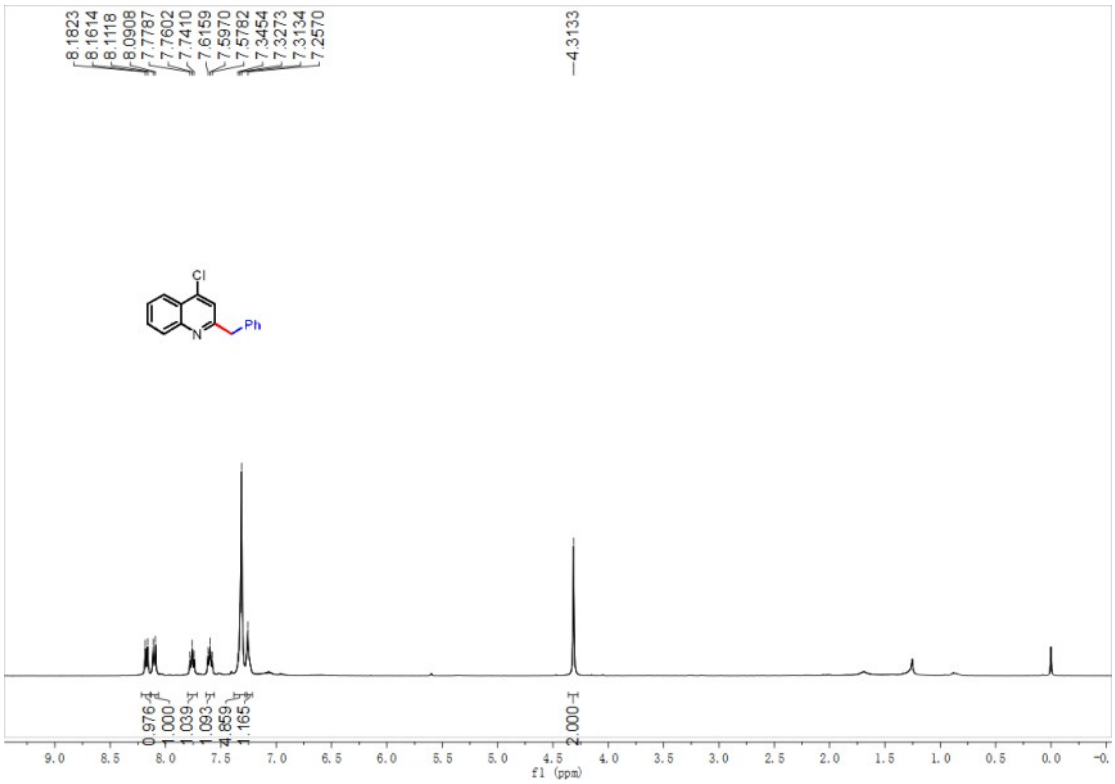
^{1}H NMR spectrum of compound **3**



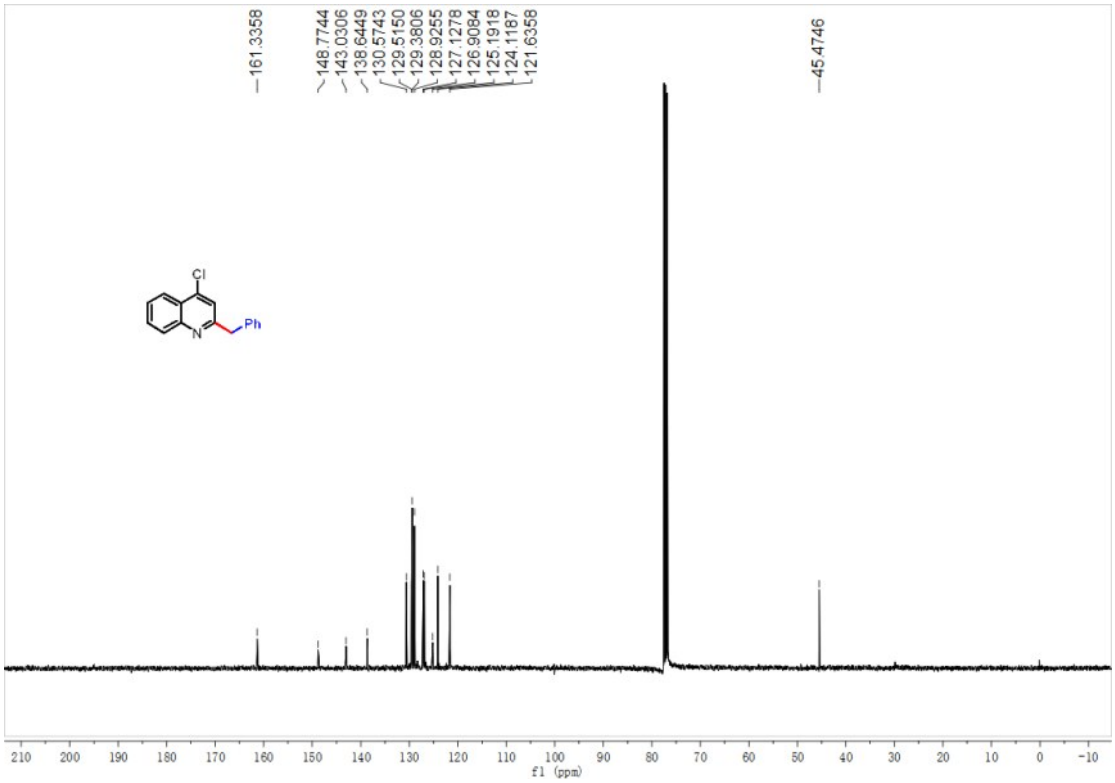
^{13}C NMR spectrum of compound **3**



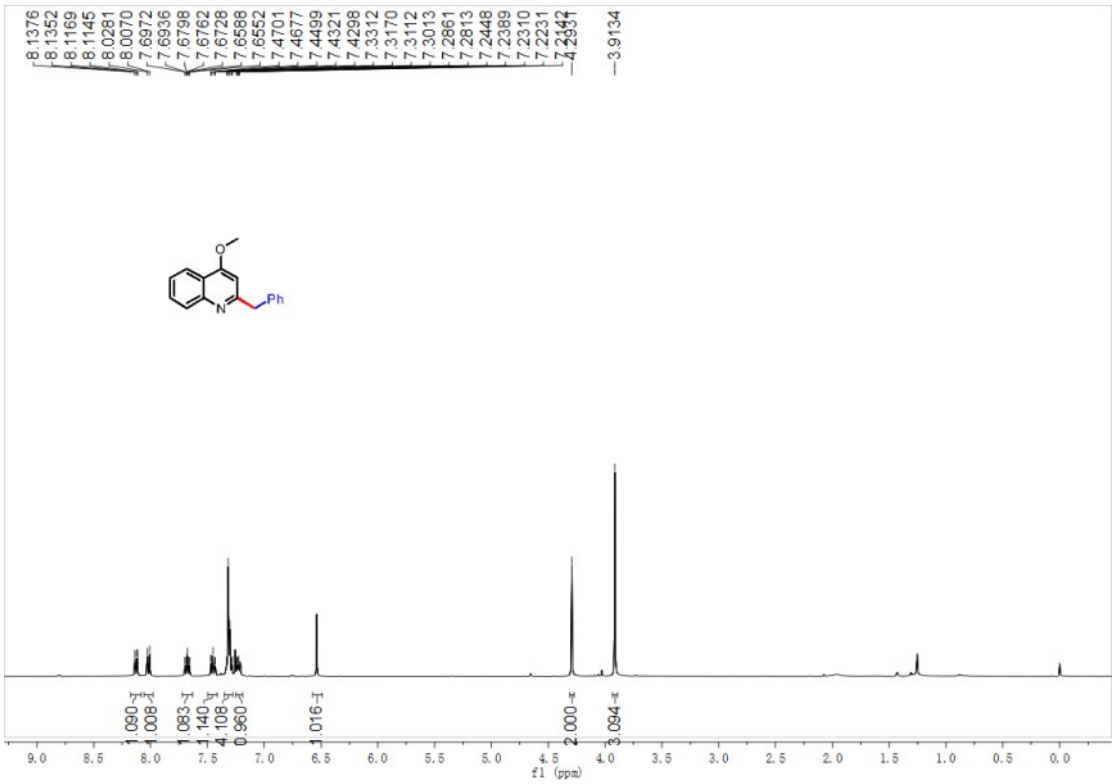
^{1}H NMR spectrum of compound **4**



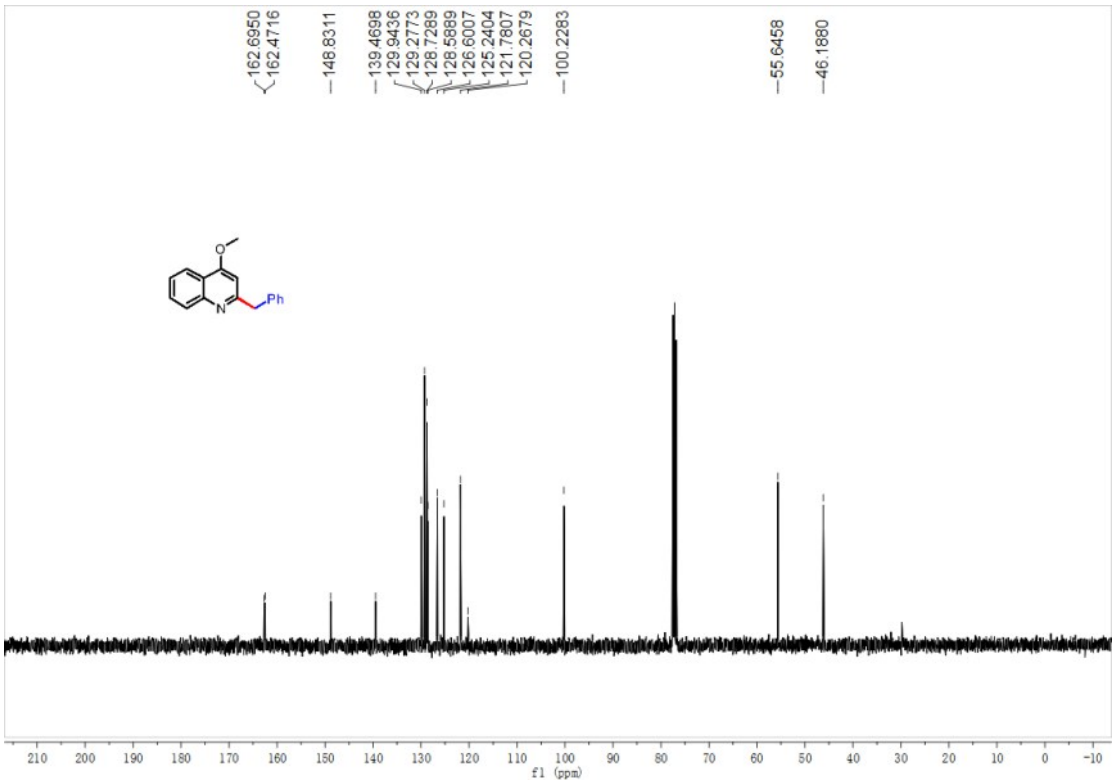
^{13}C NMR spectrum of compound **4**



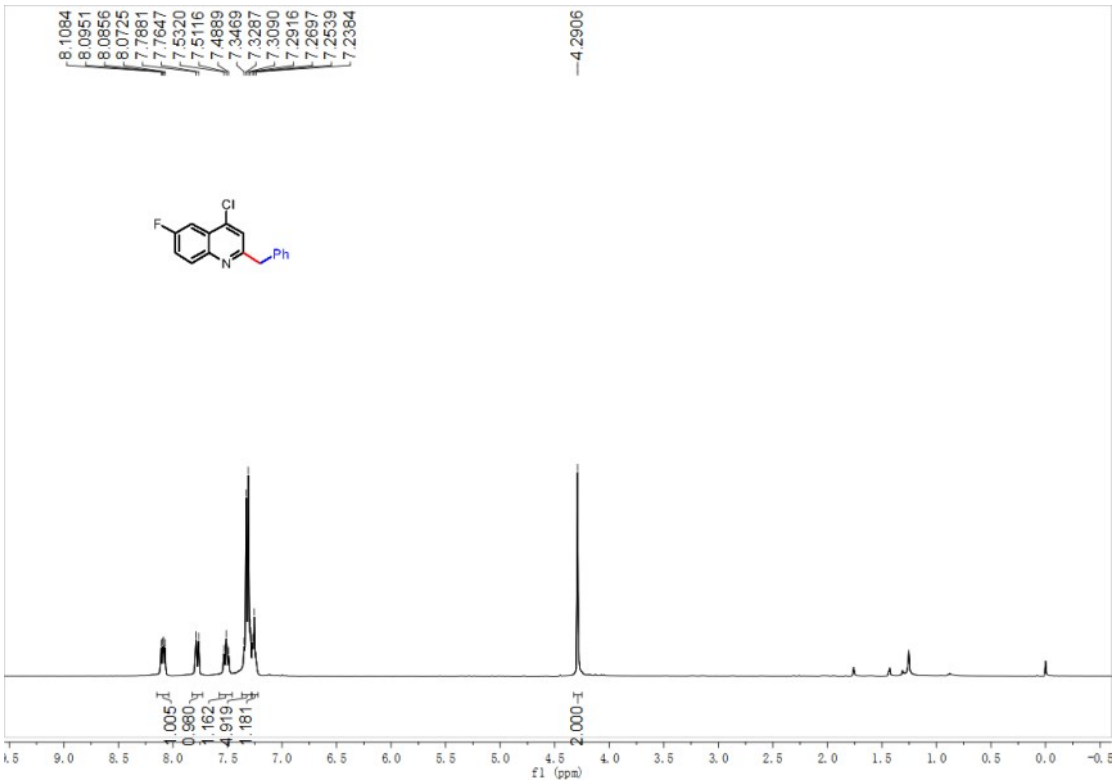
^{1}H NMR spectrum of compound **5**



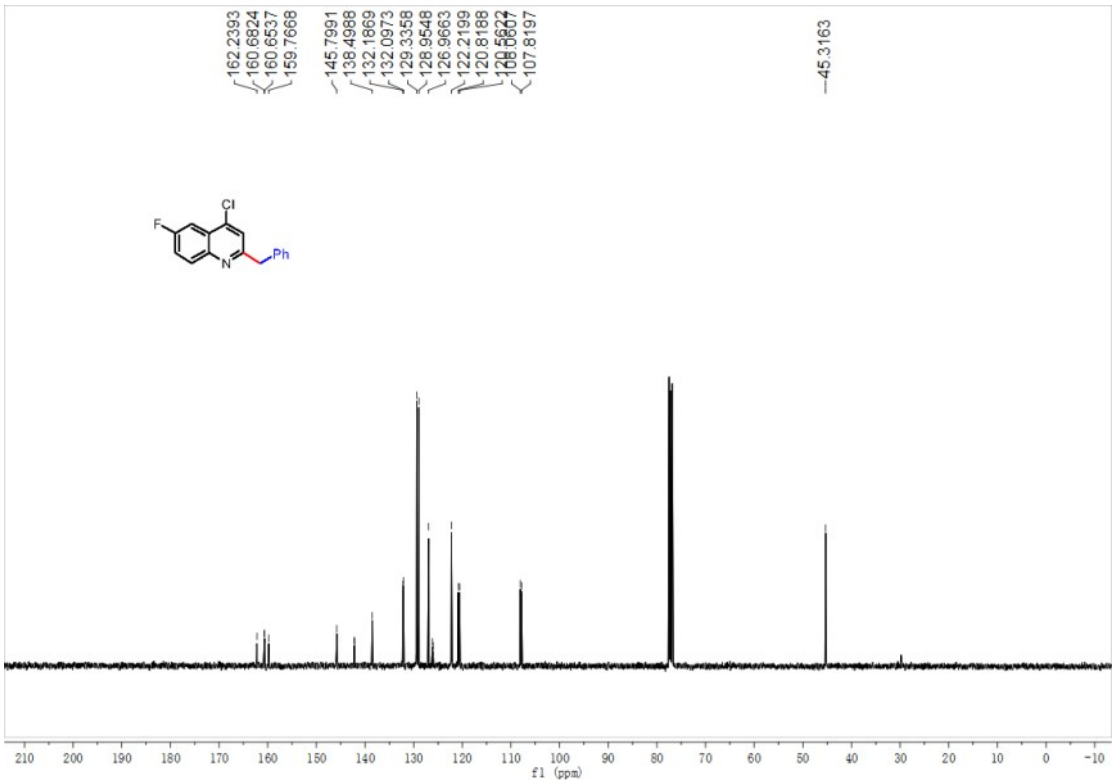
^{13}C NMR spectrum of compound **5**



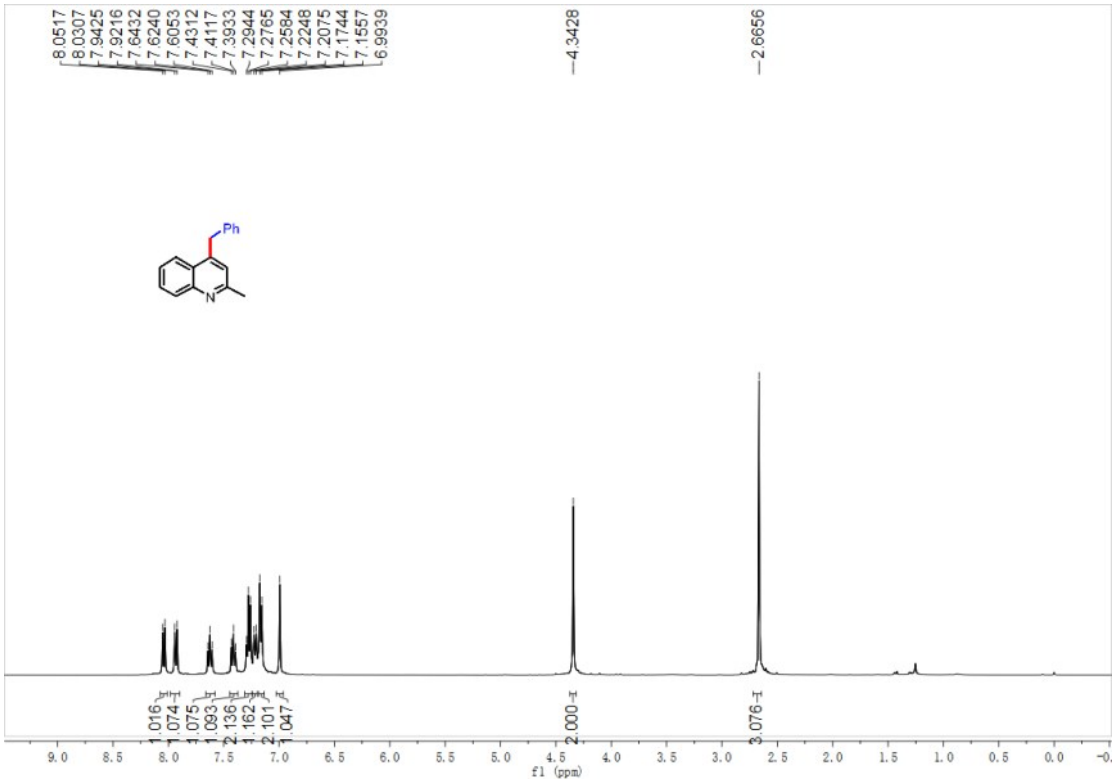
^{1}H NMR spectrum of compound **6**



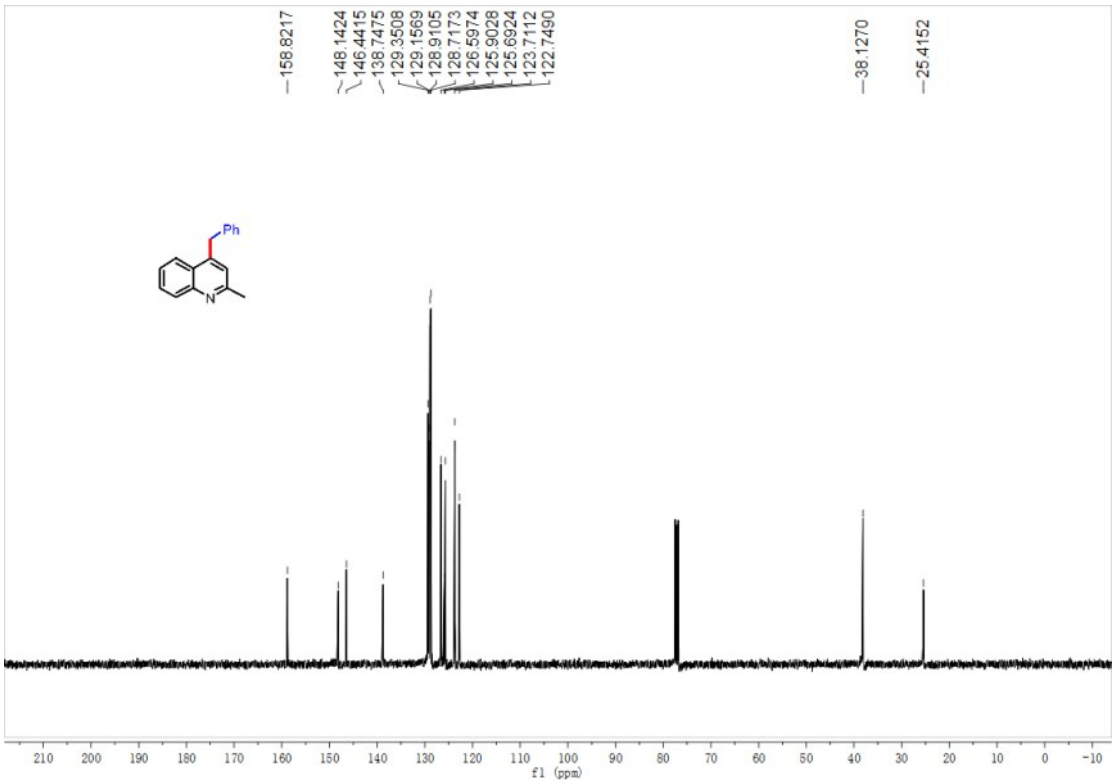
^{13}C NMR spectrum of compound **6**



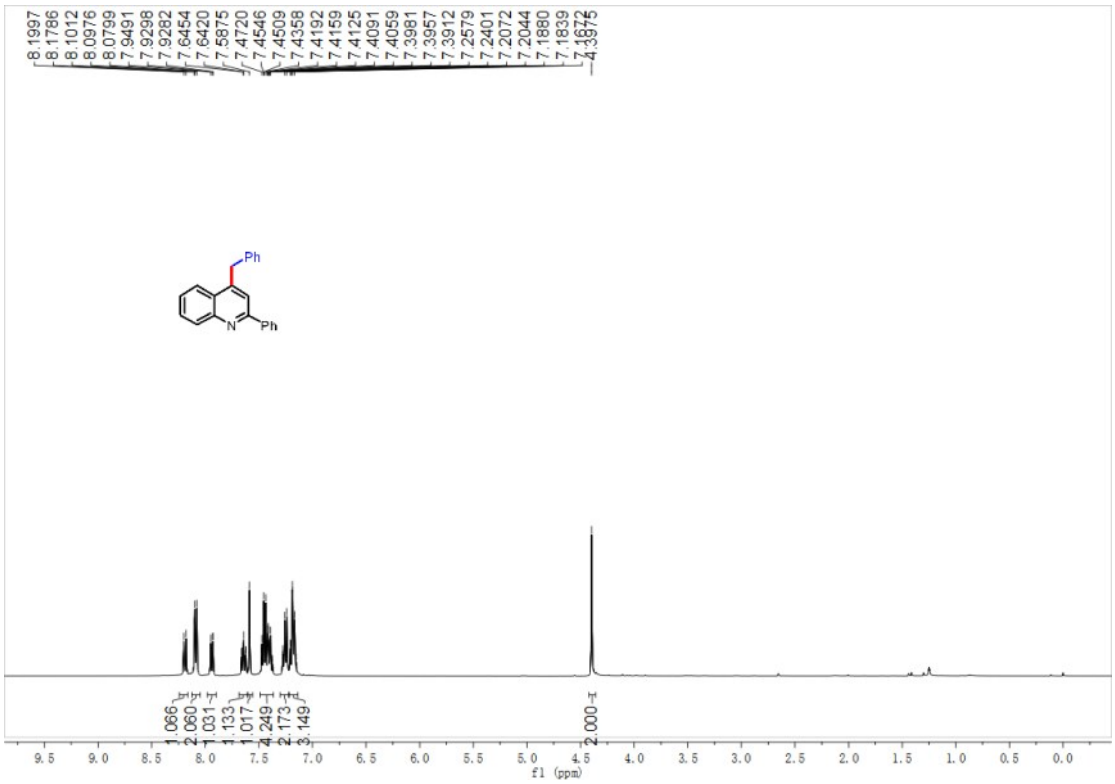
^{1}H NMR spectrum of compound **7**



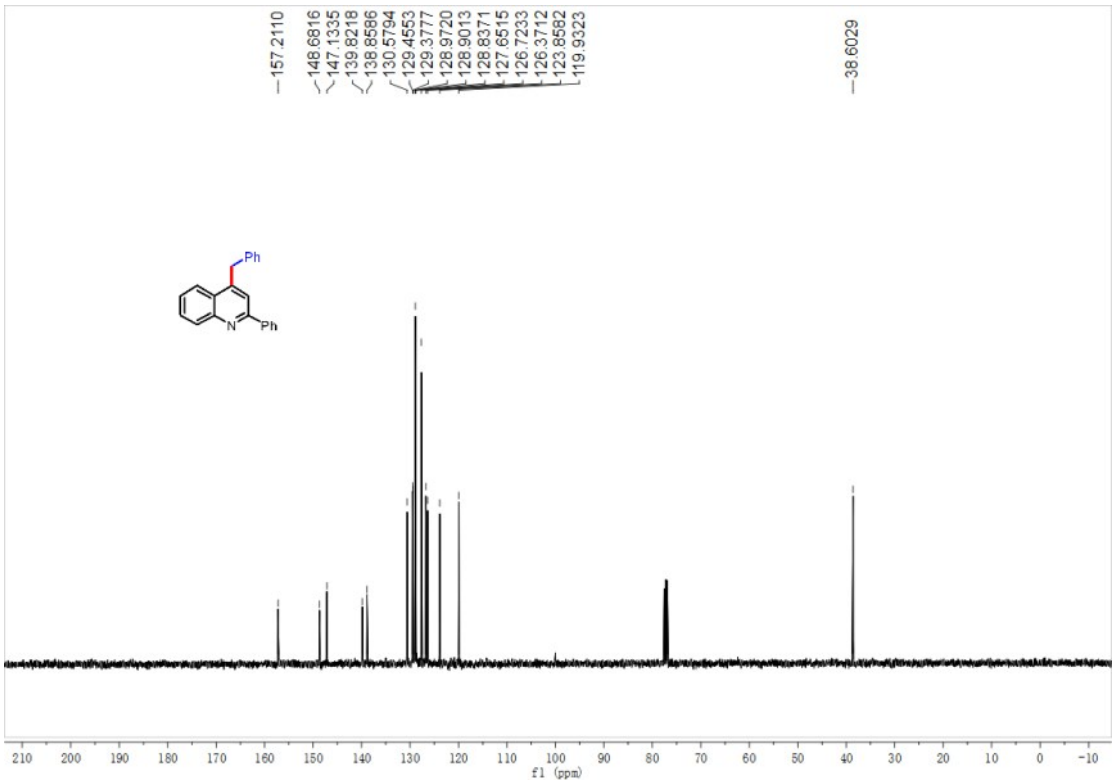
^{13}C NMR spectrum of compound **7**



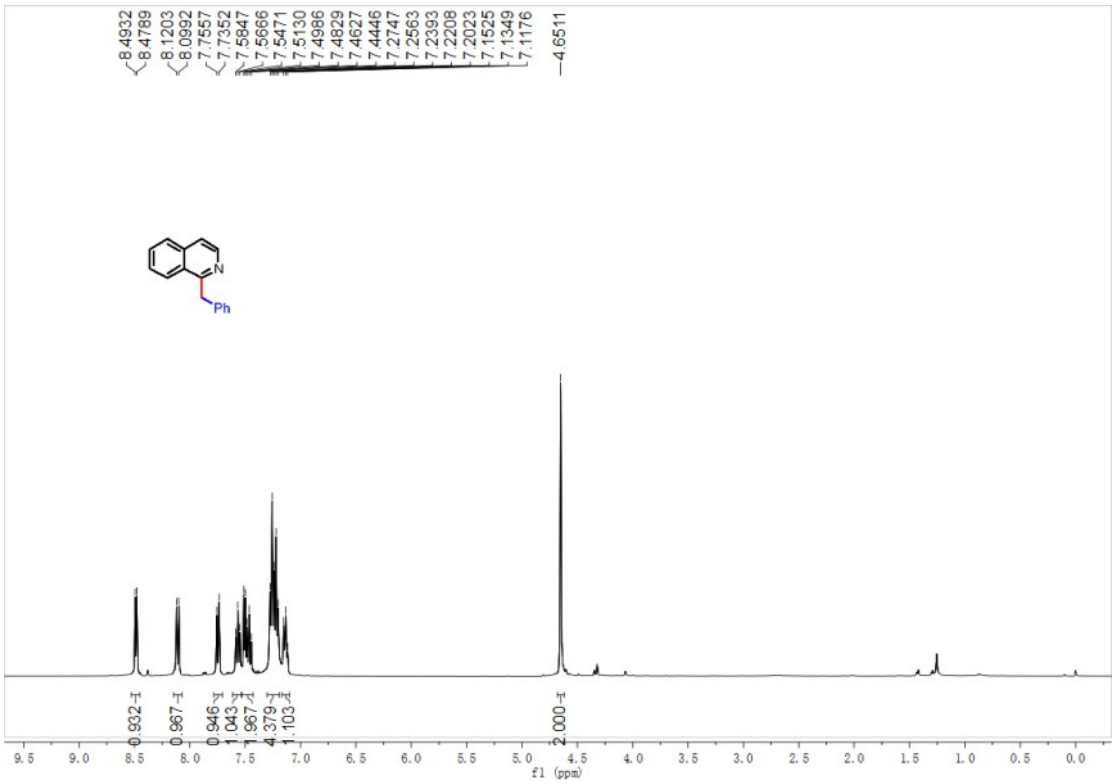
^{1}H NMR spectrum of compound **8**



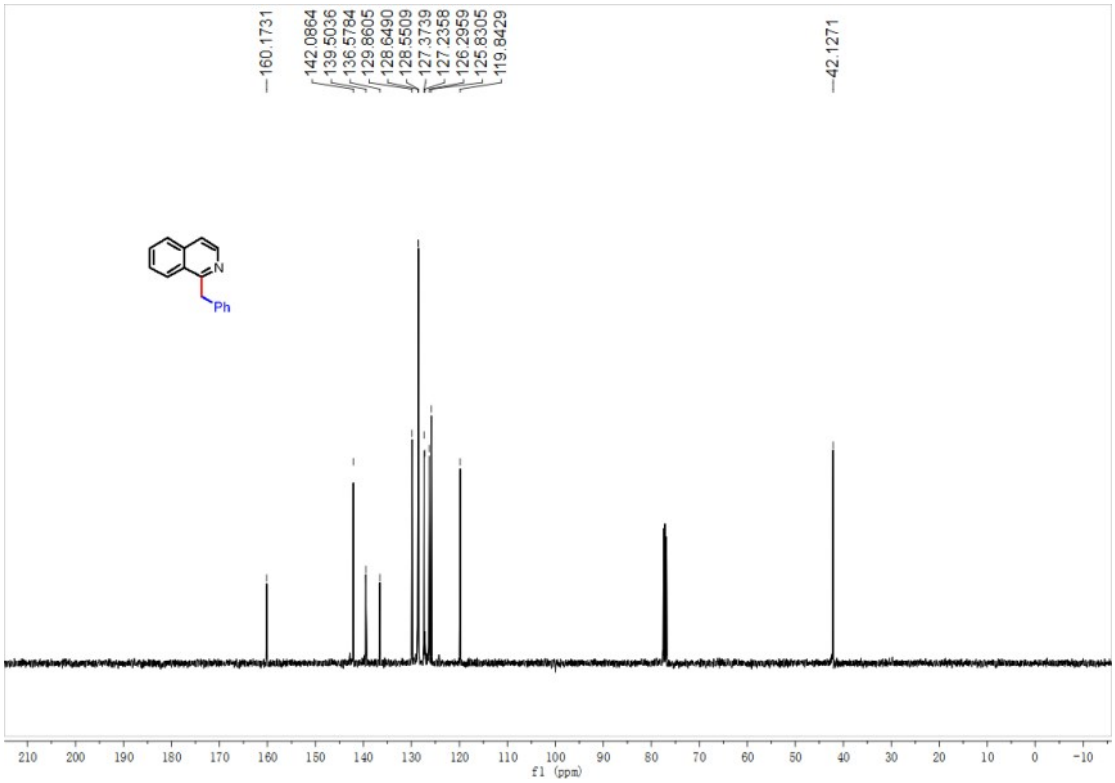
^{13}C NMR spectrum of compound **8**



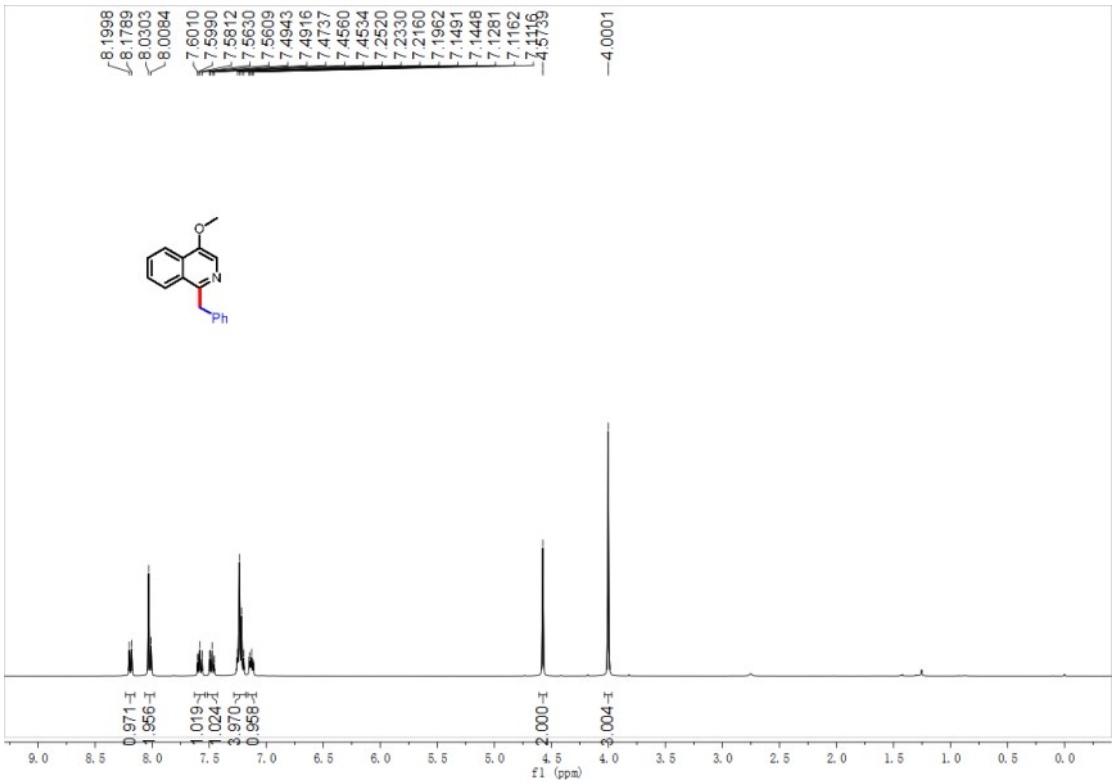
^{1}H NMR spectrum of compound **9**



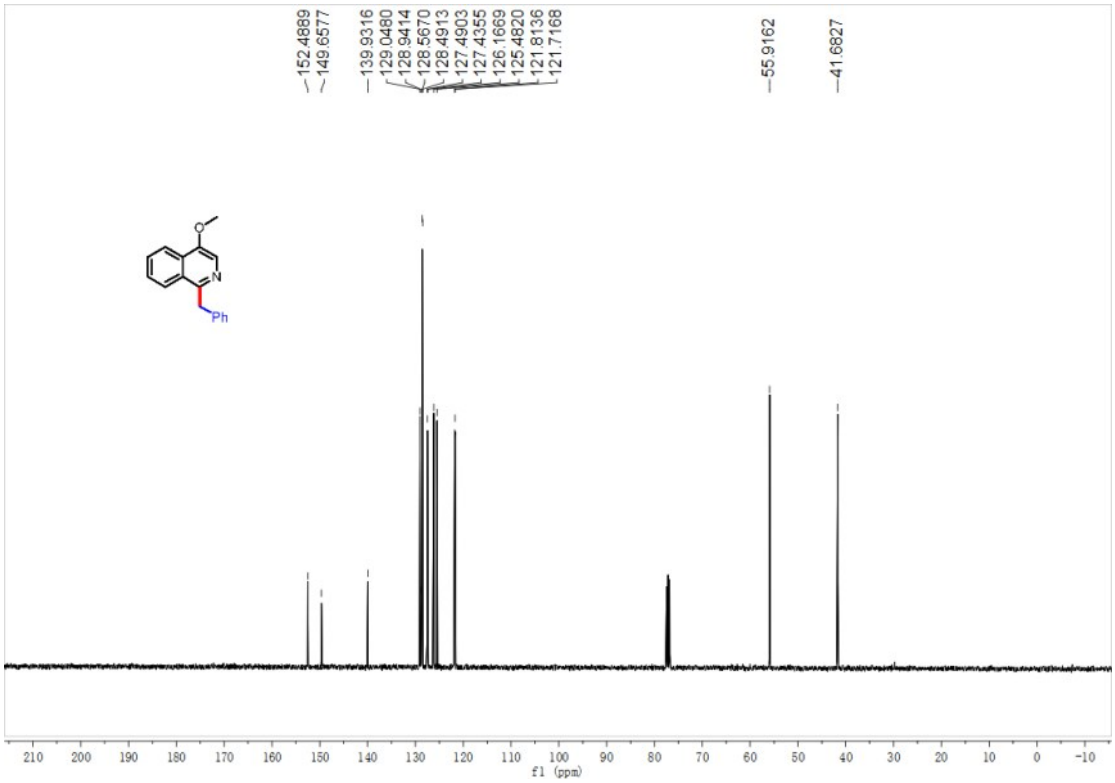
^{13}C NMR spectrum of compound **9**



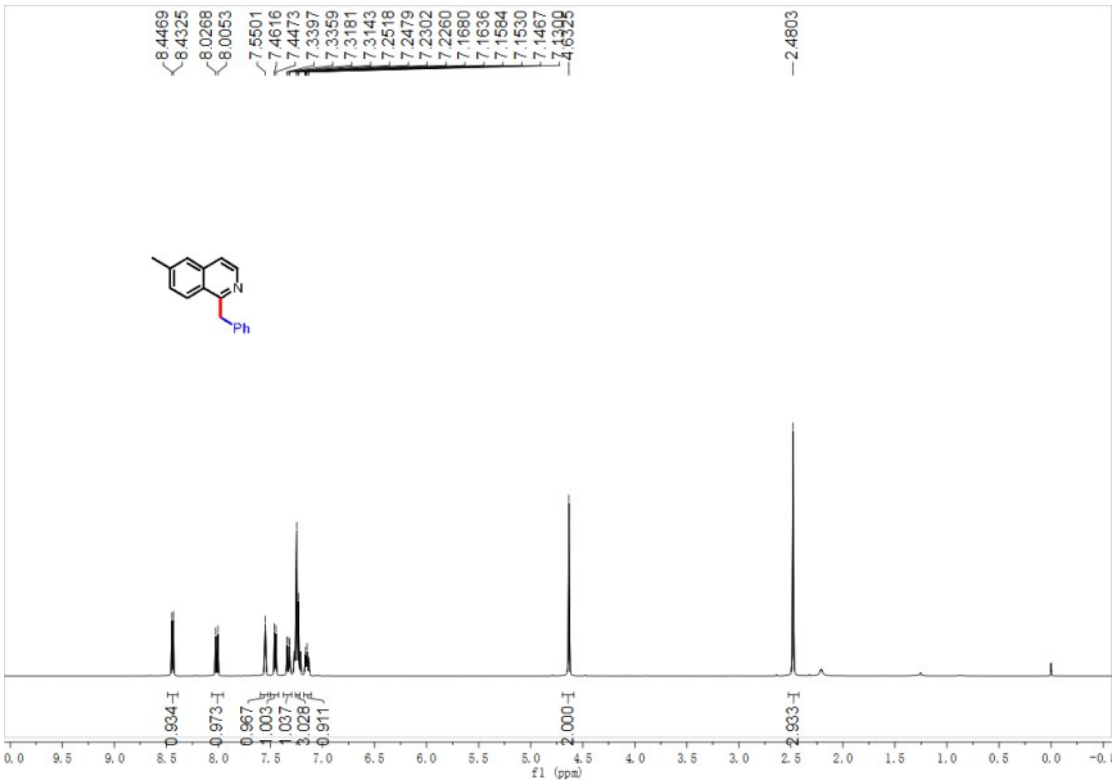
^{1}H NMR spectrum of compound **10**



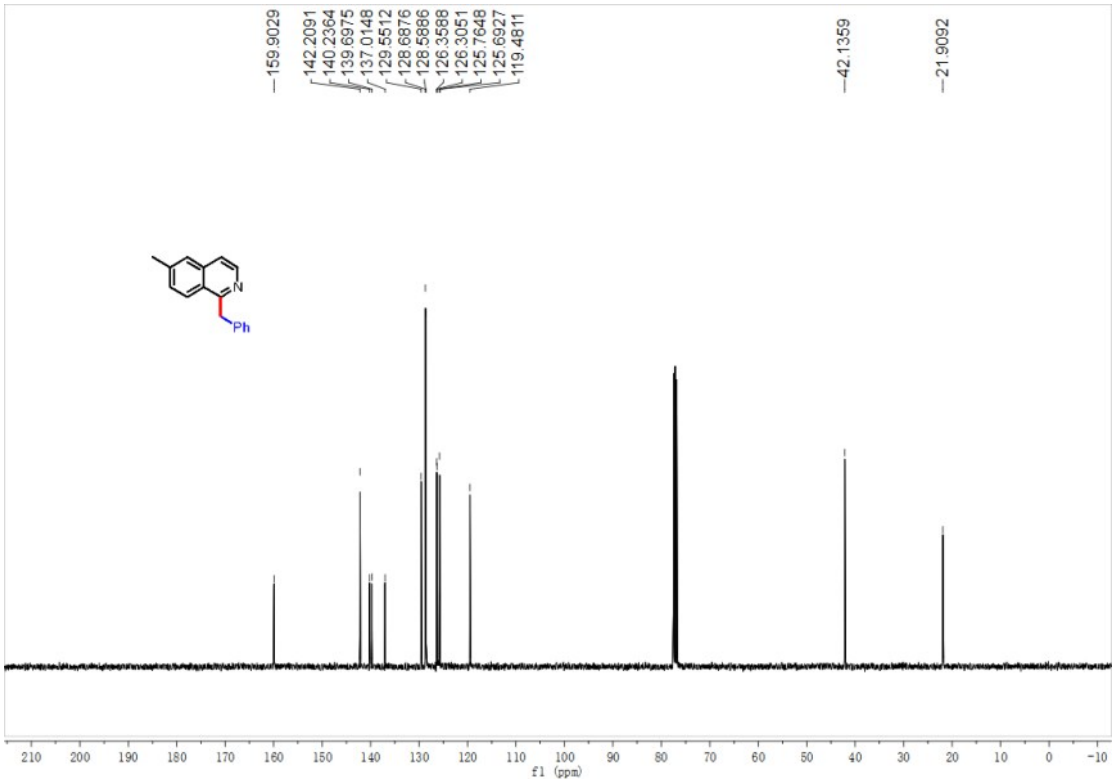
^{13}C NMR spectrum of compound **10**



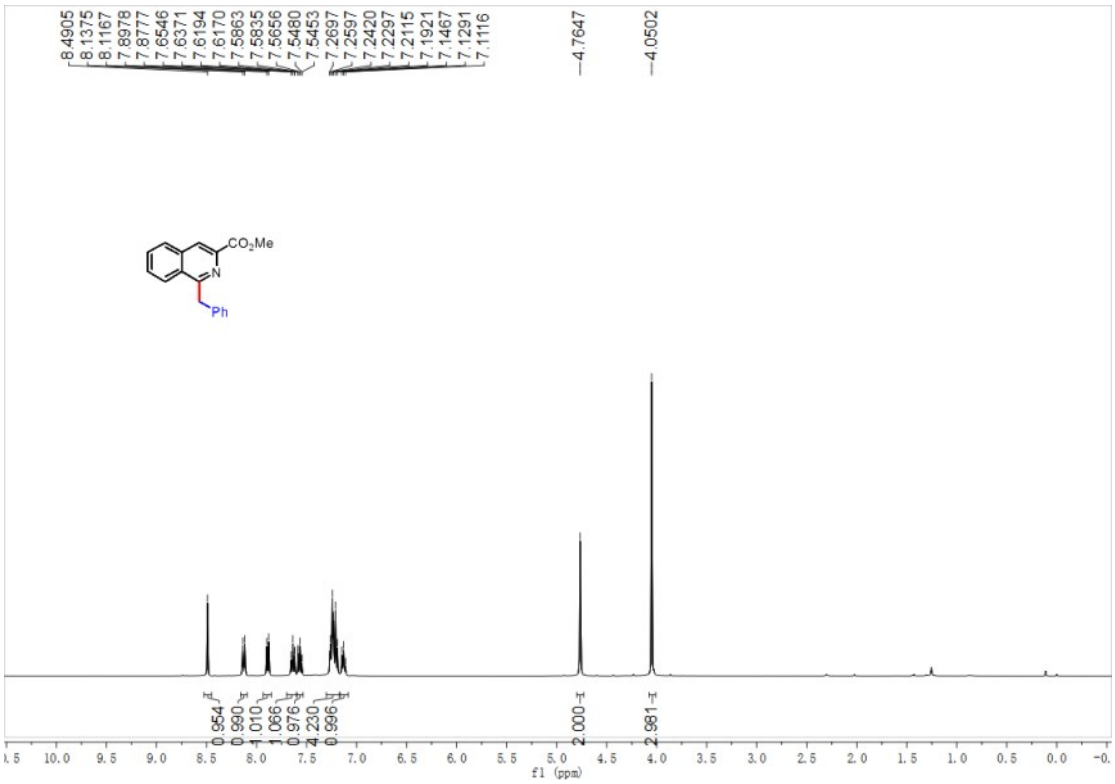
^{1}H NMR spectrum of compound **11**



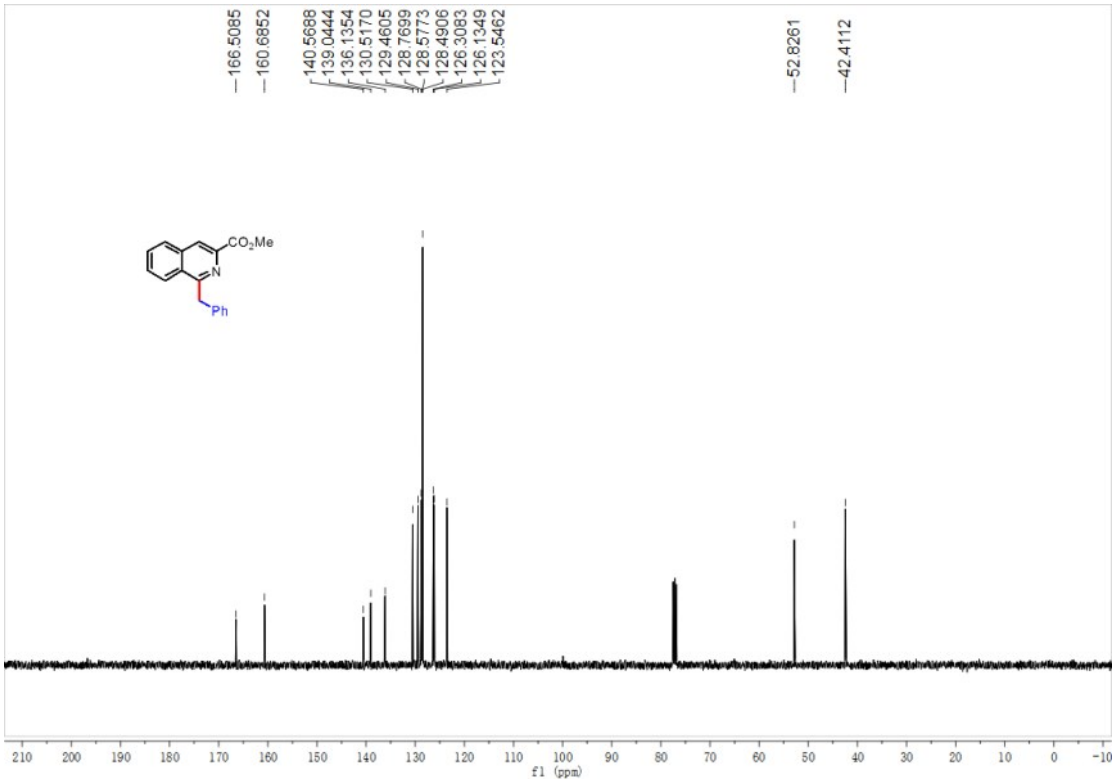
^{13}C NMR spectrum of compound **11**



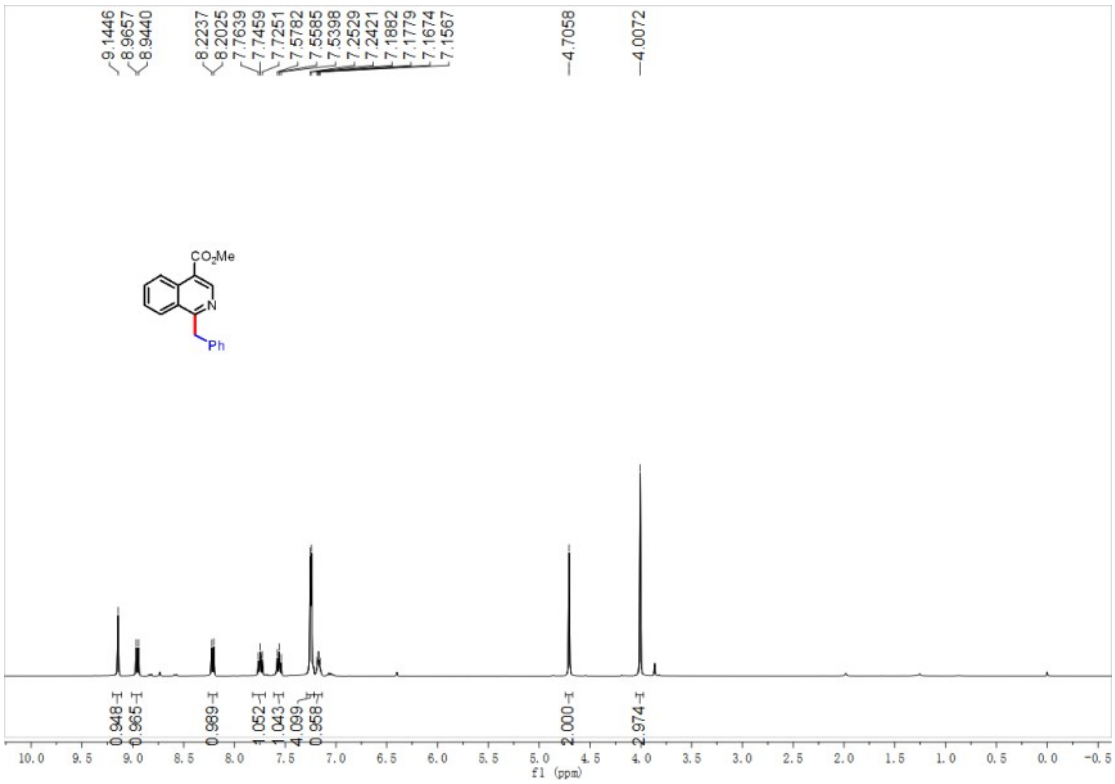
^{1}H NMR spectrum of compound **12**



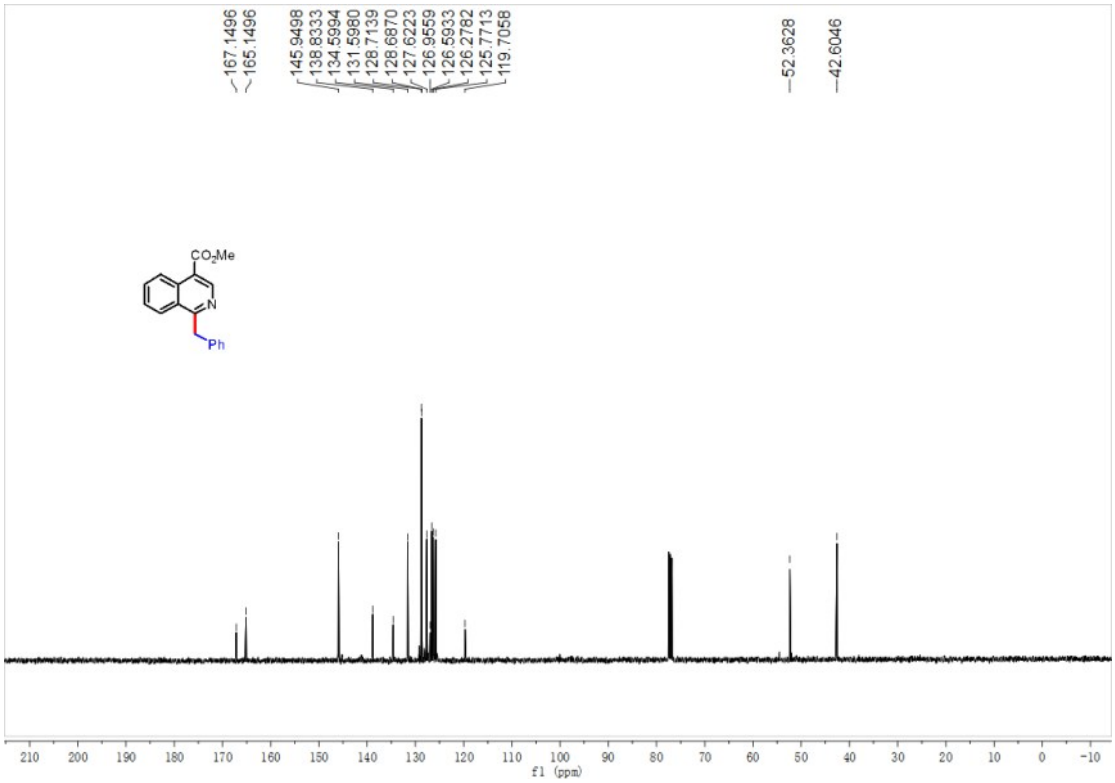
^{13}C NMR spectrum of compound **12**



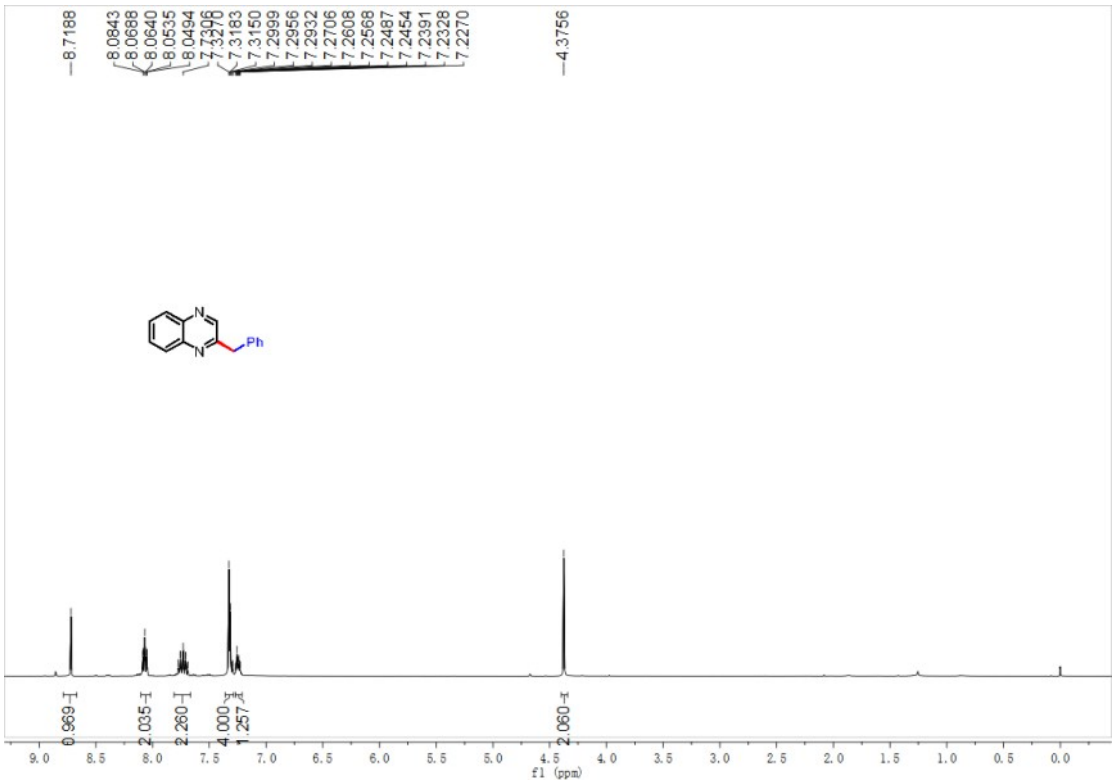
^{1}H NMR spectrum of compound **13**



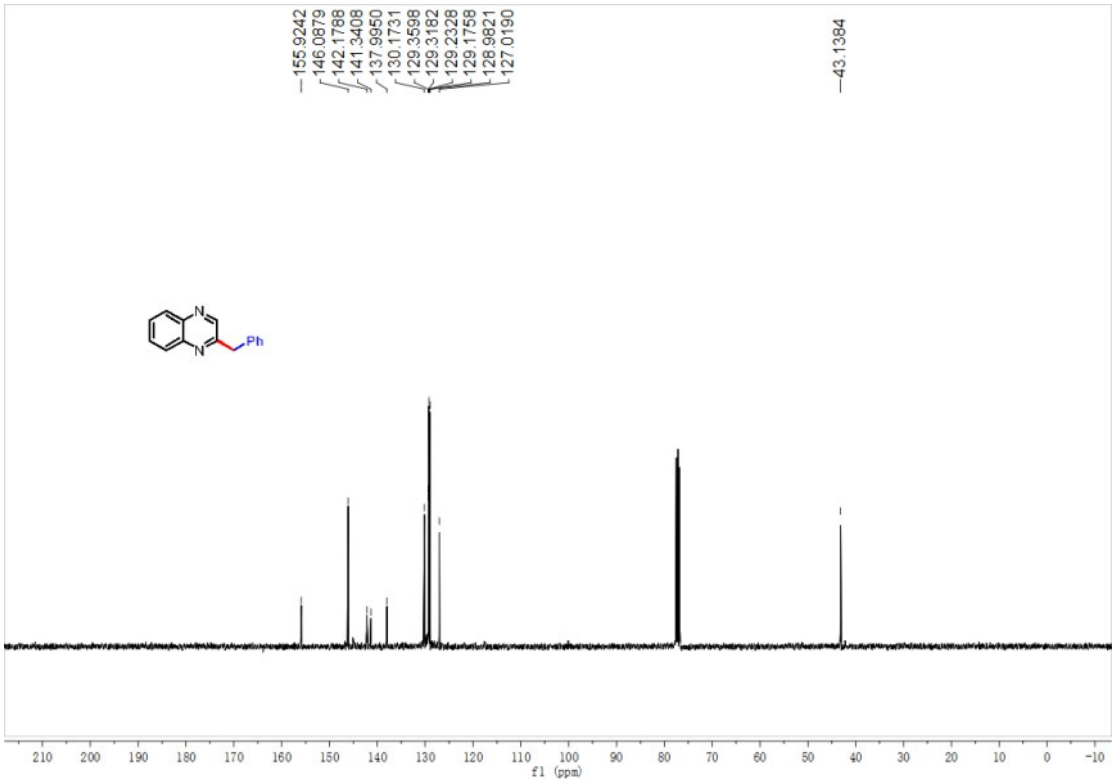
^{13}C NMR spectrum of compound **13**



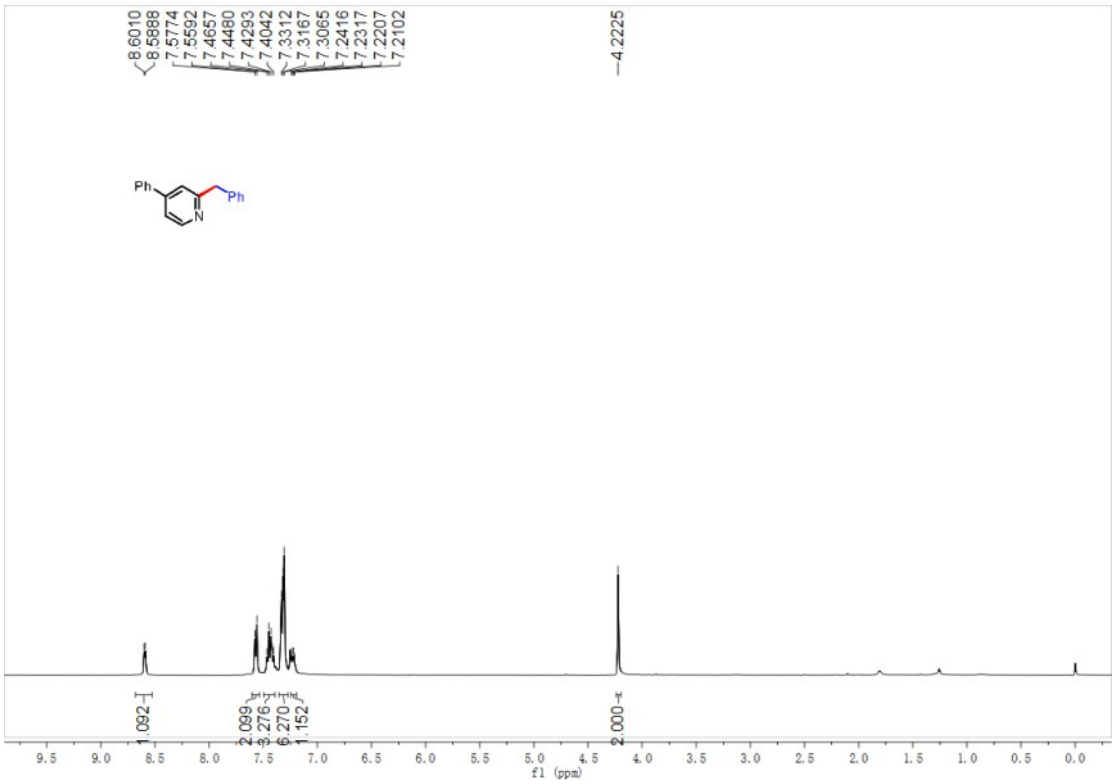
^{1}H NMR spectrum of compound **14**



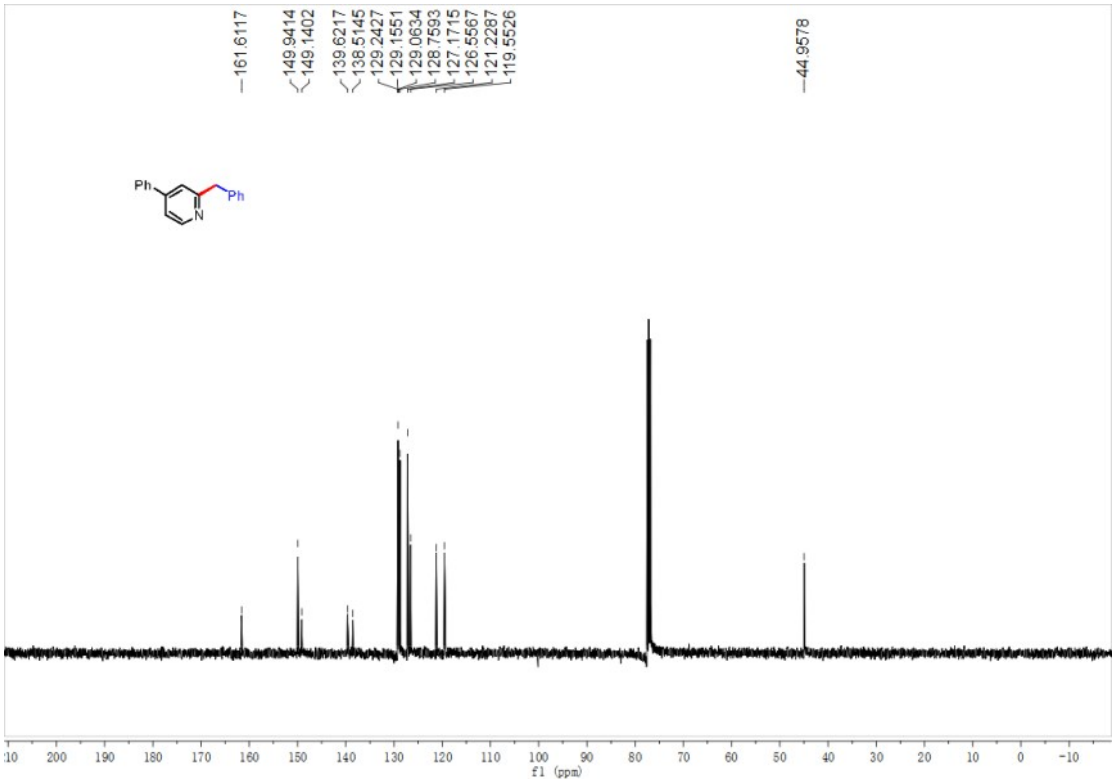
^{13}C NMR spectrum of compound **14**



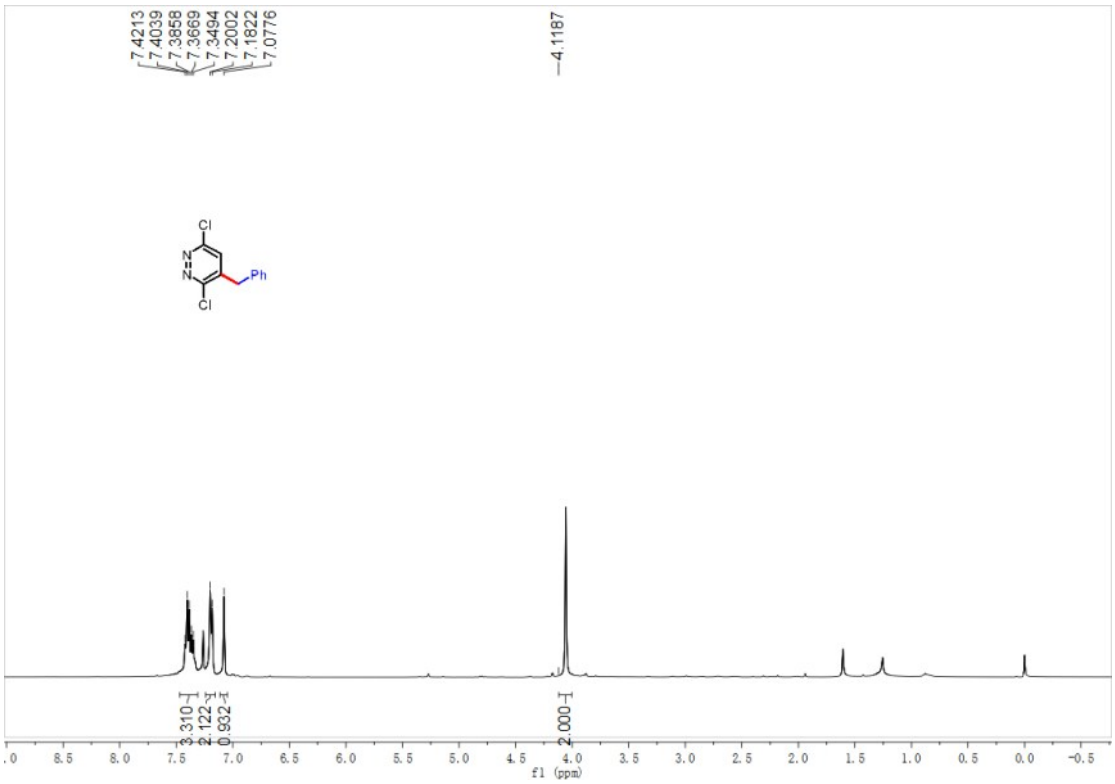
^{1}H NMR spectrum of compound **15**



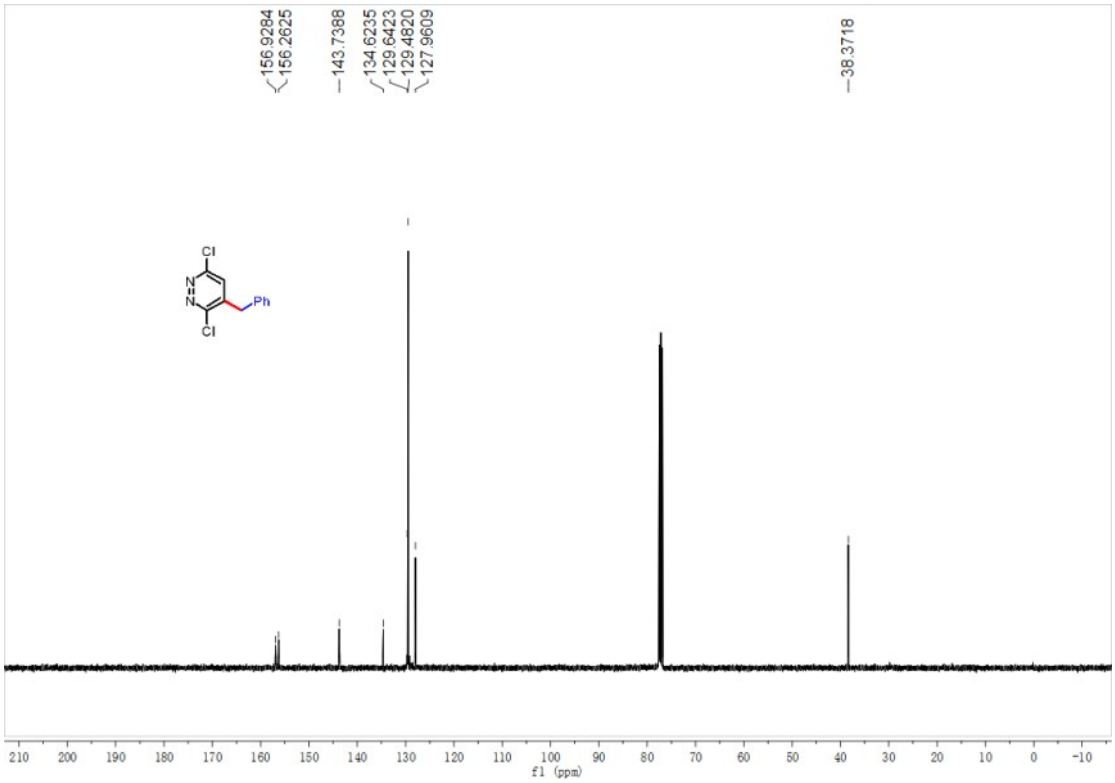
^{13}C NMR spectrum of compound **15**



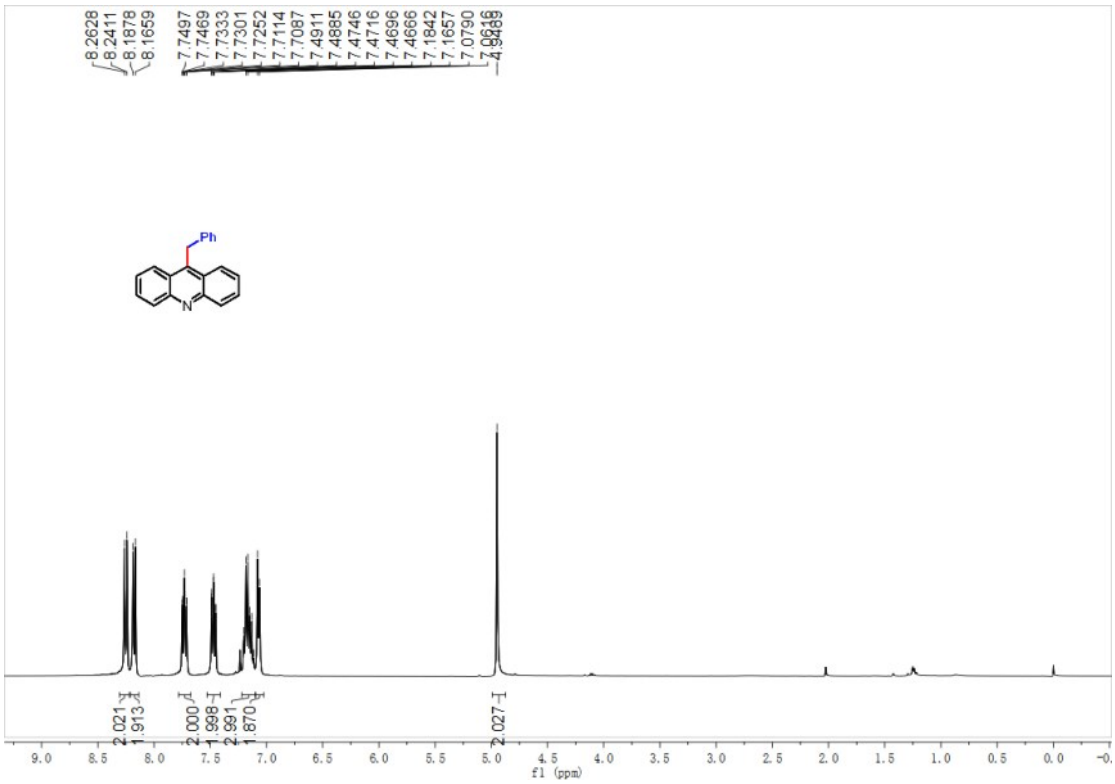
^{1}H NMR spectrum of compound **16**



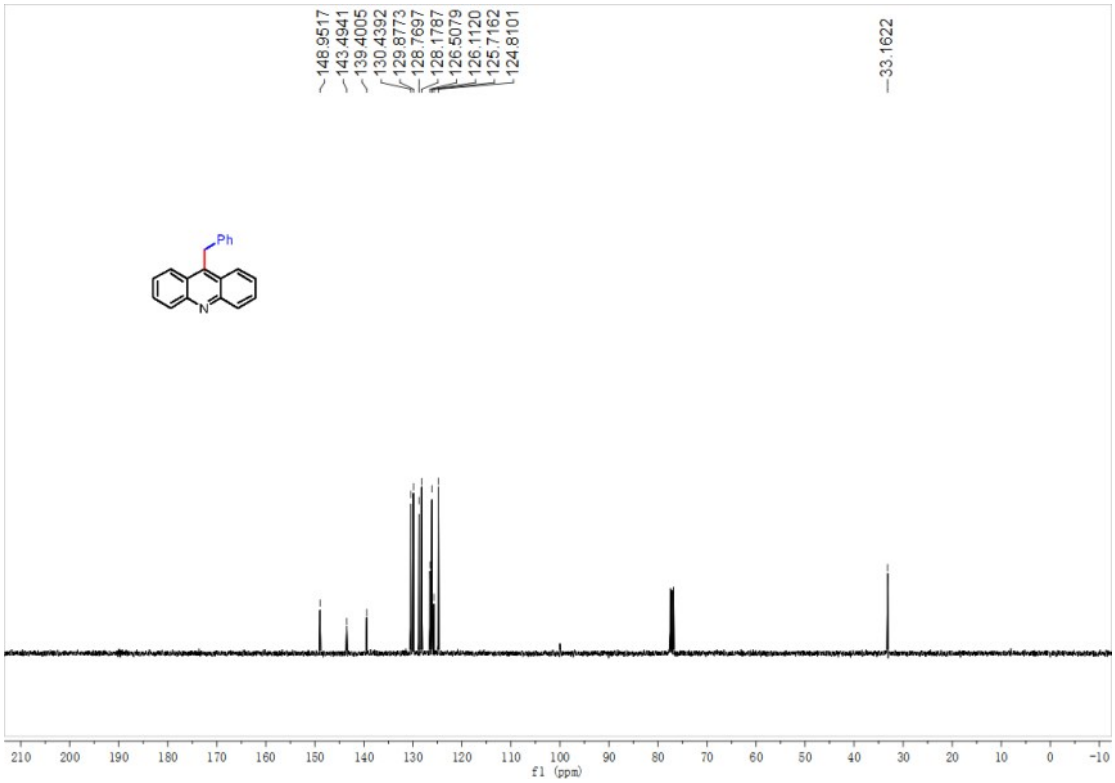
^{13}C NMR spectrum of compound **16**



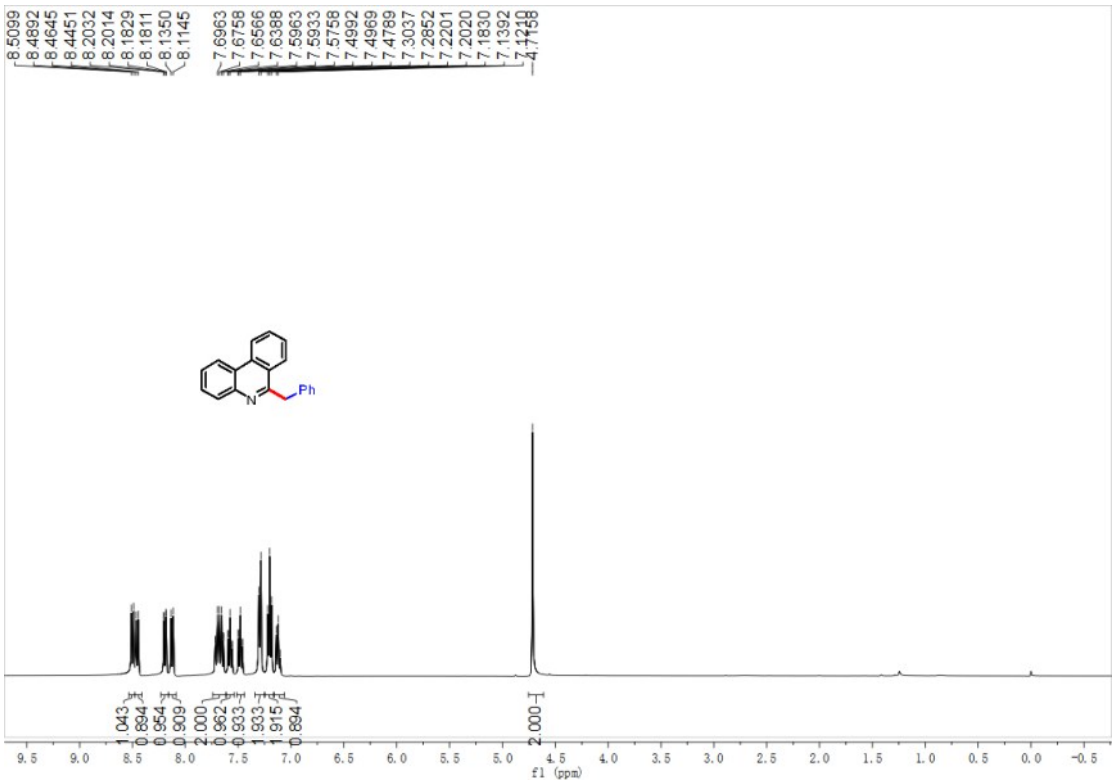
^{1}H NMR spectrum of compound **17**



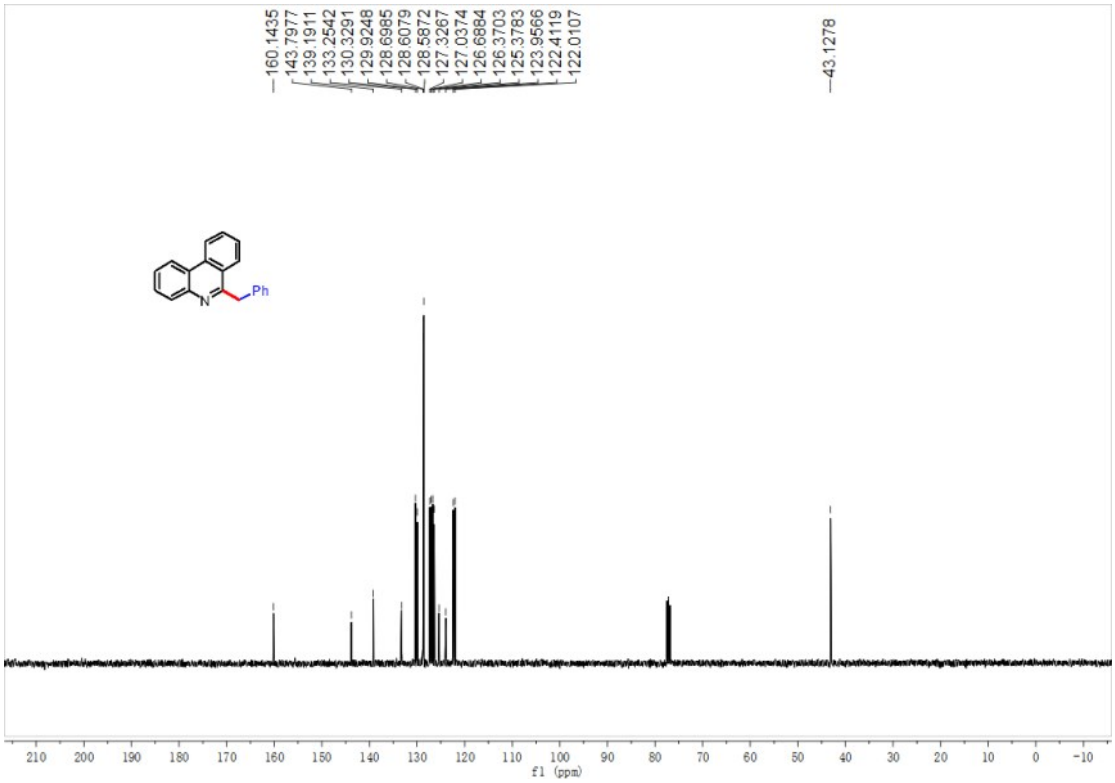
^{13}C NMR spectrum of compound **17**



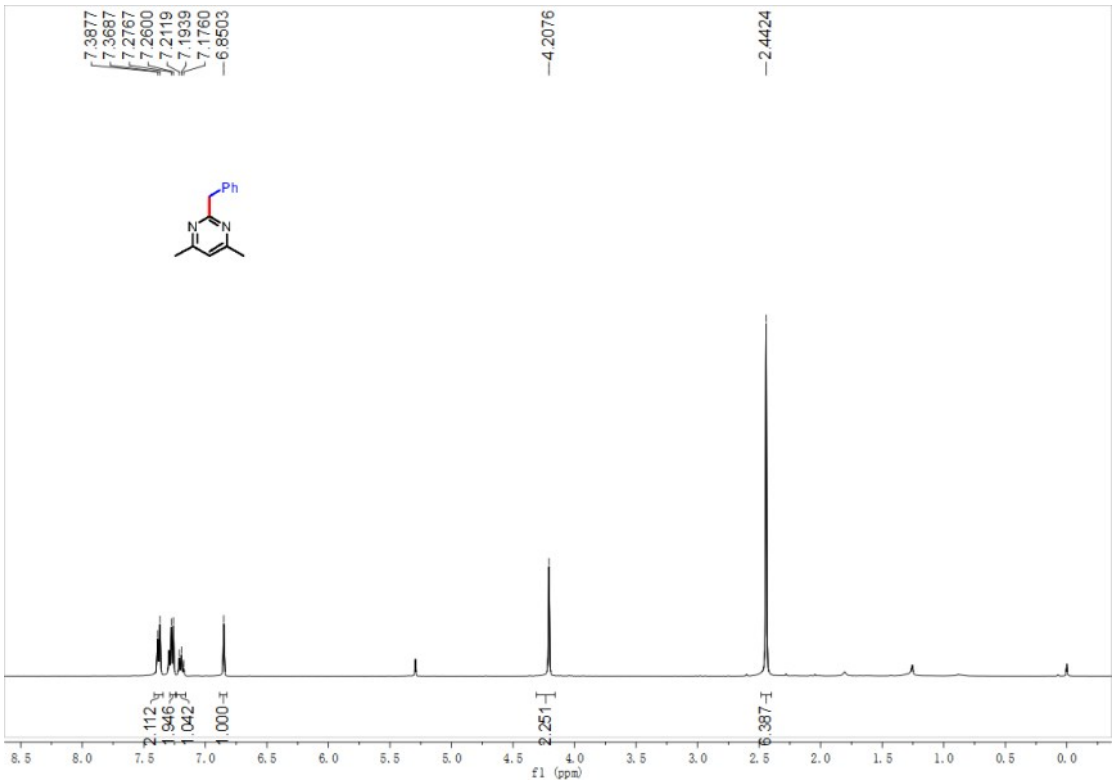
^{1}H NMR spectrum of compound **18**



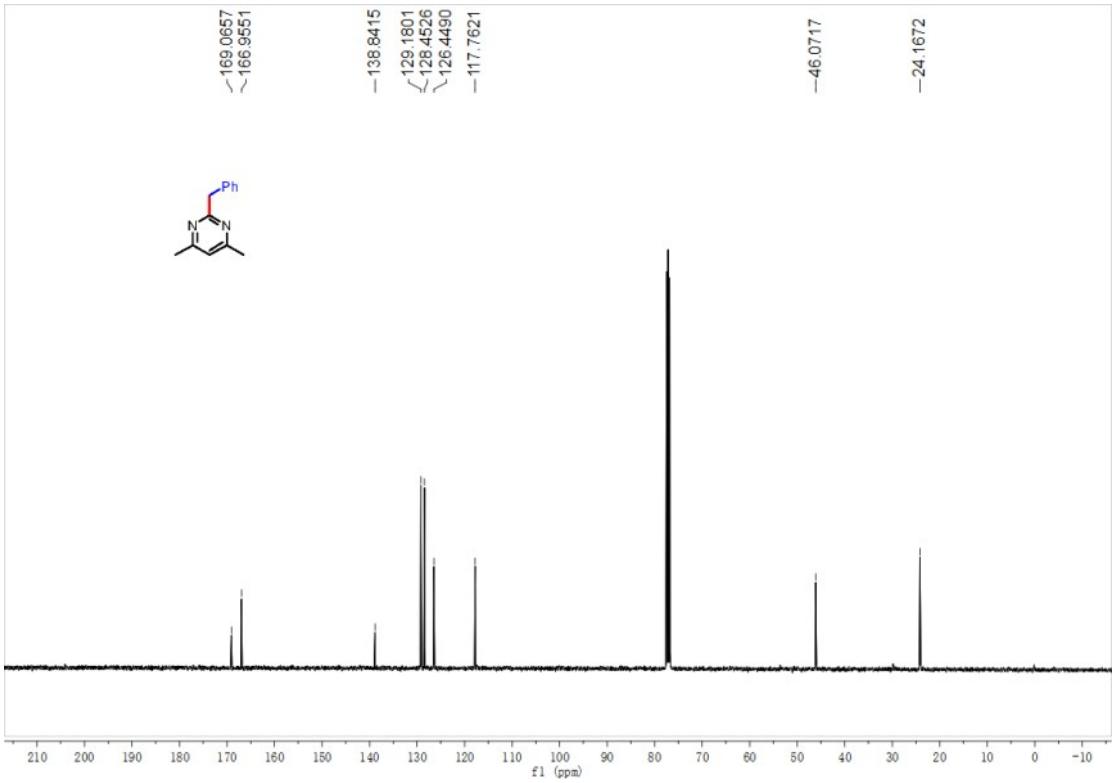
^{13}C NMR spectrum of compound **18**



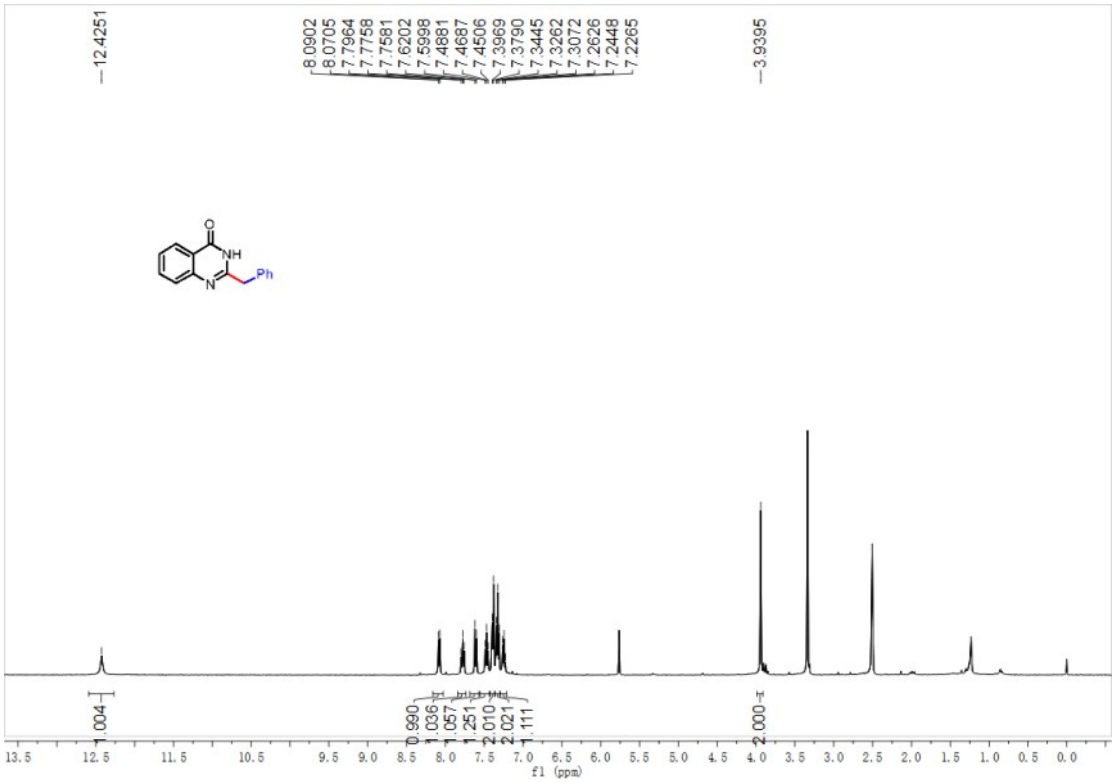
^{1}H NMR spectrum of compound **19**



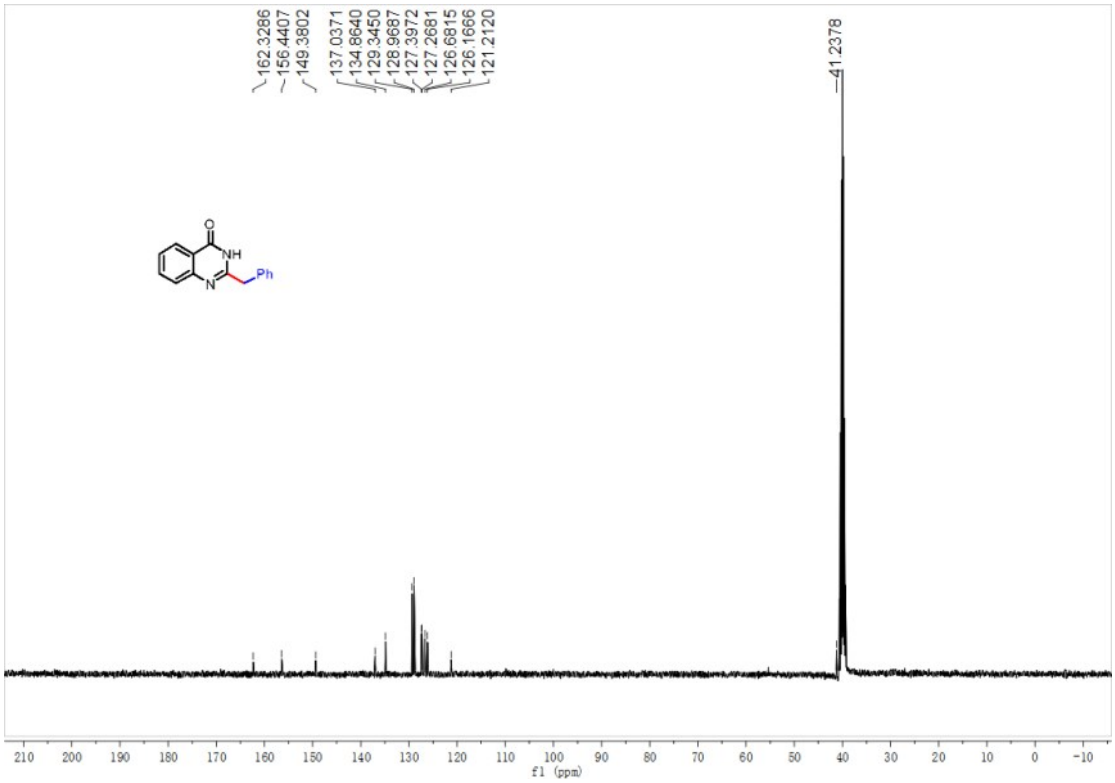
^{13}C NMR spectrum of compound **19**



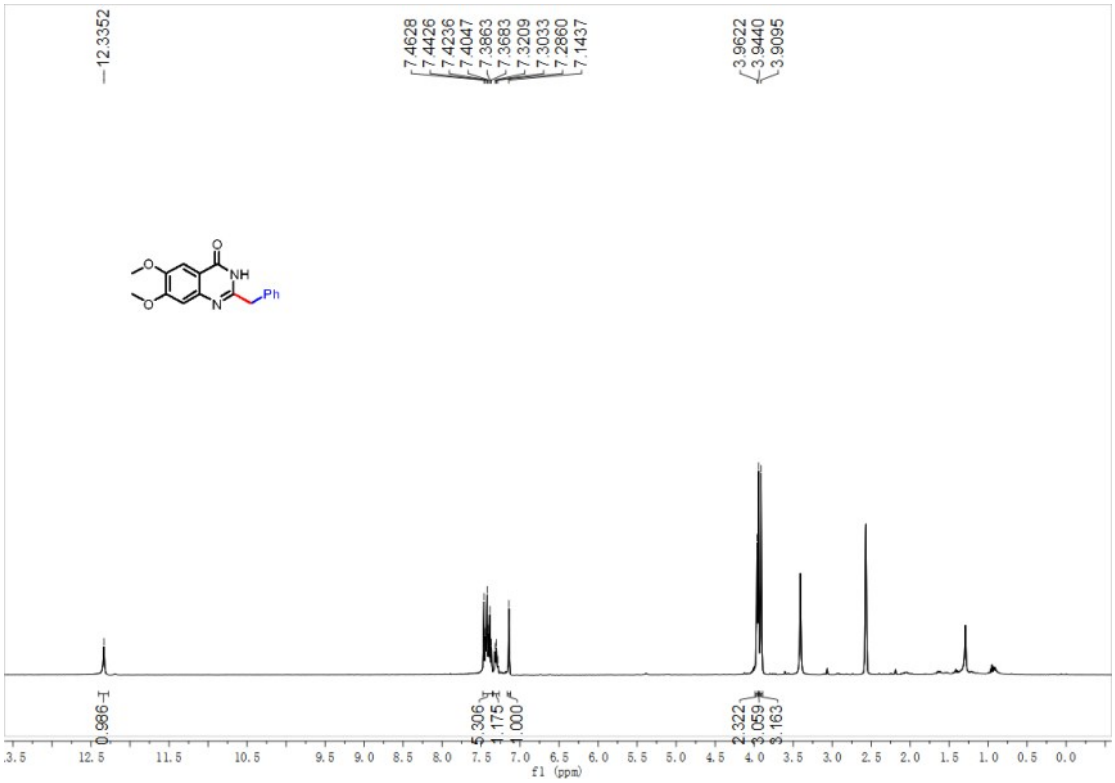
^{1}H NMR spectrum of compound **20**



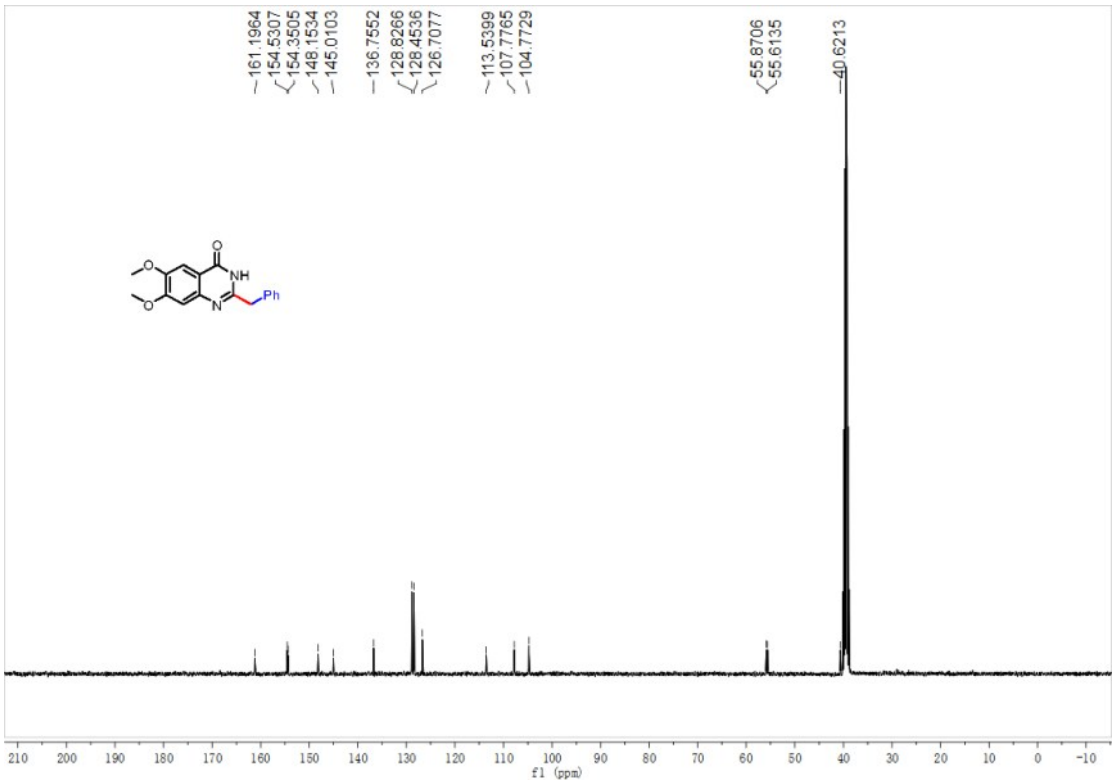
^{13}C NMR spectrum of compound **20**



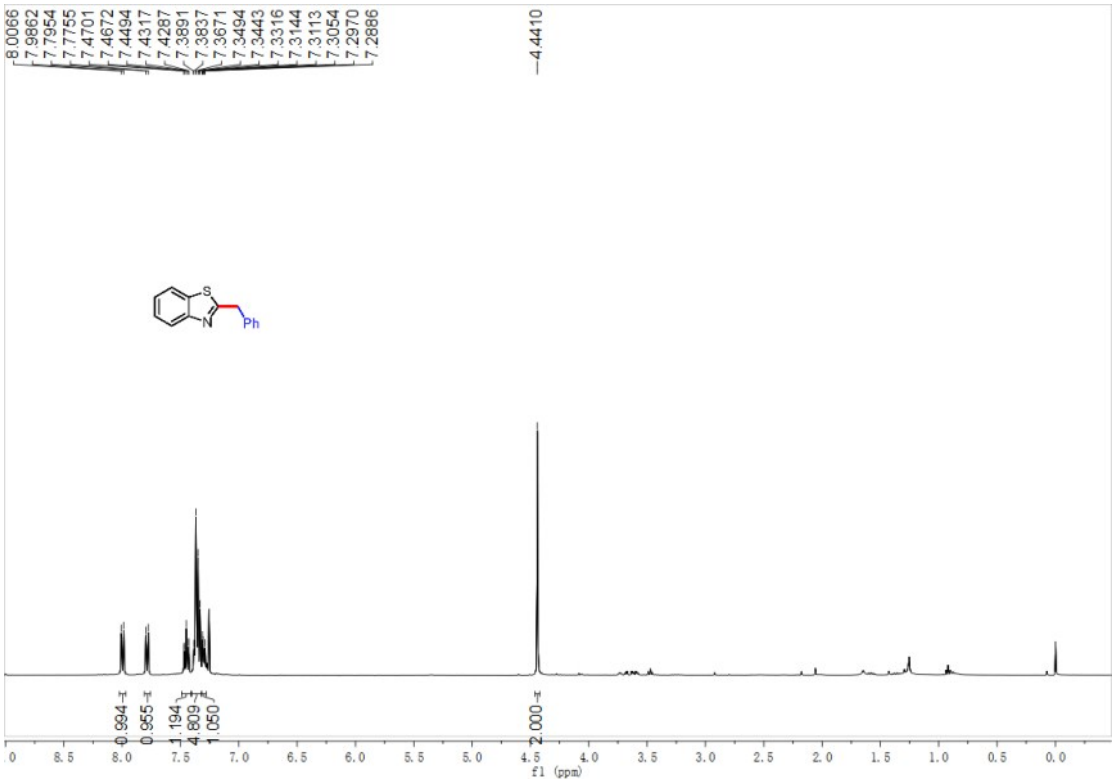
^{1}H NMR spectrum of compound **21**



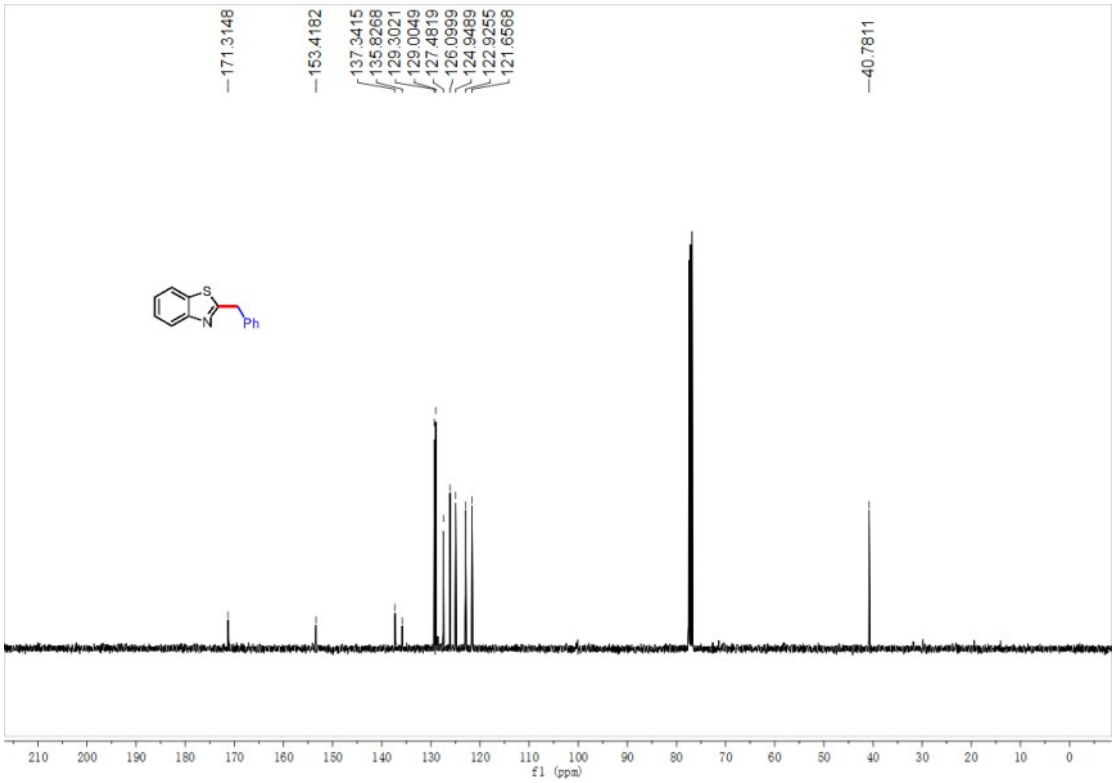
^{13}C NMR spectrum of compound **21**



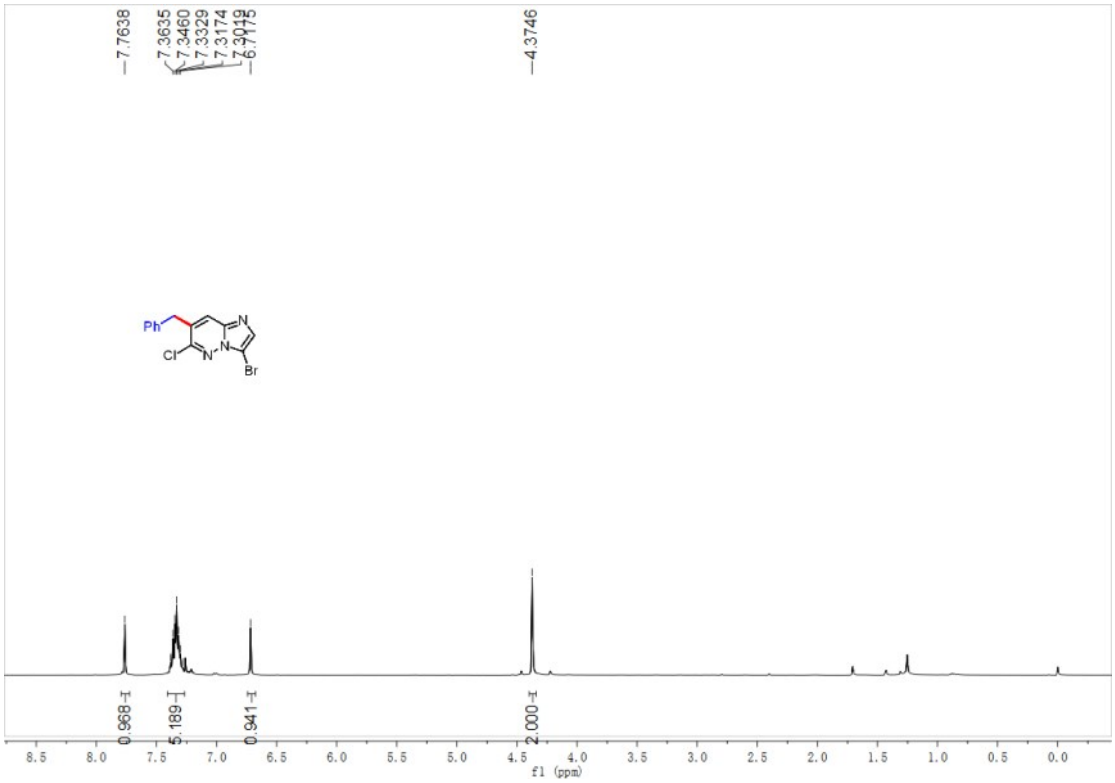
^{1}H NMR spectrum of compound **22**



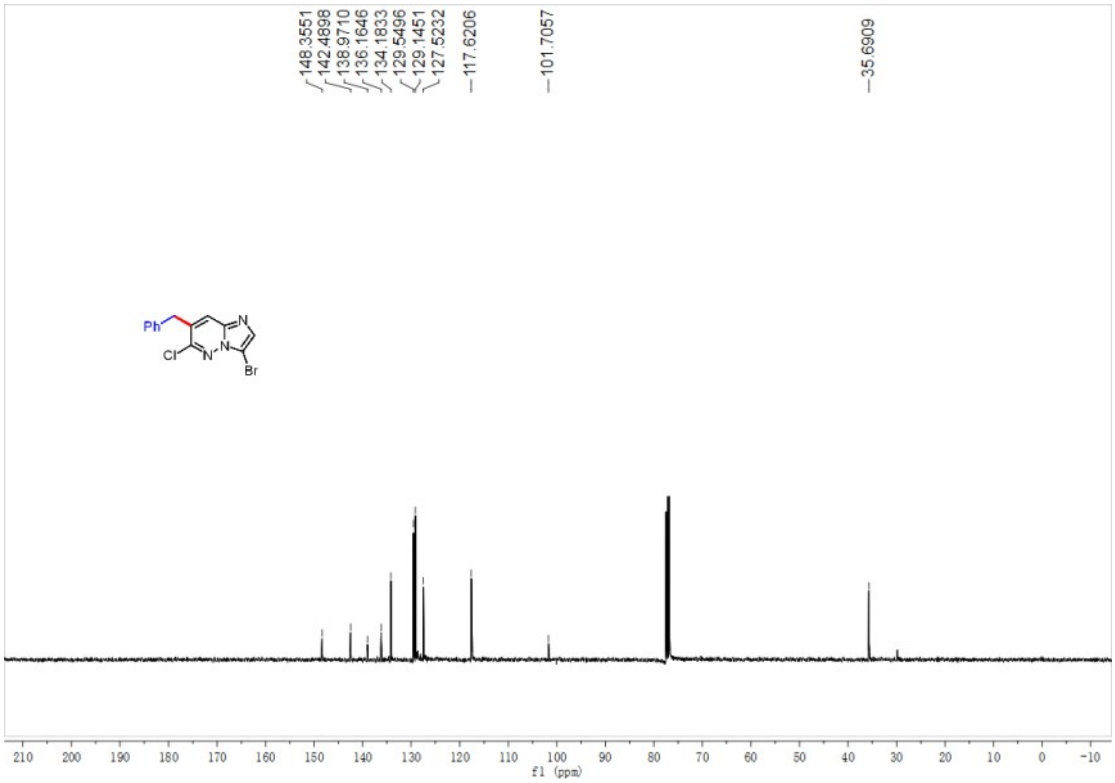
^{13}C NMR spectrum of compound **22**



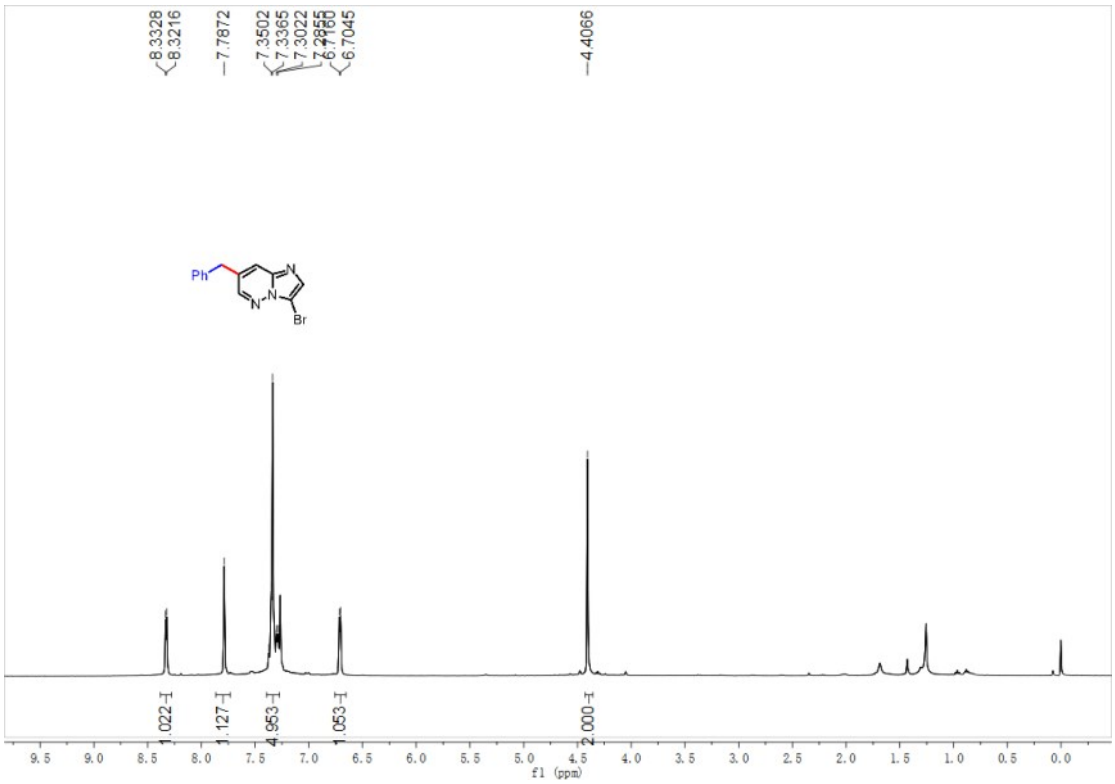
^{1}H NMR spectrum of compound **23**



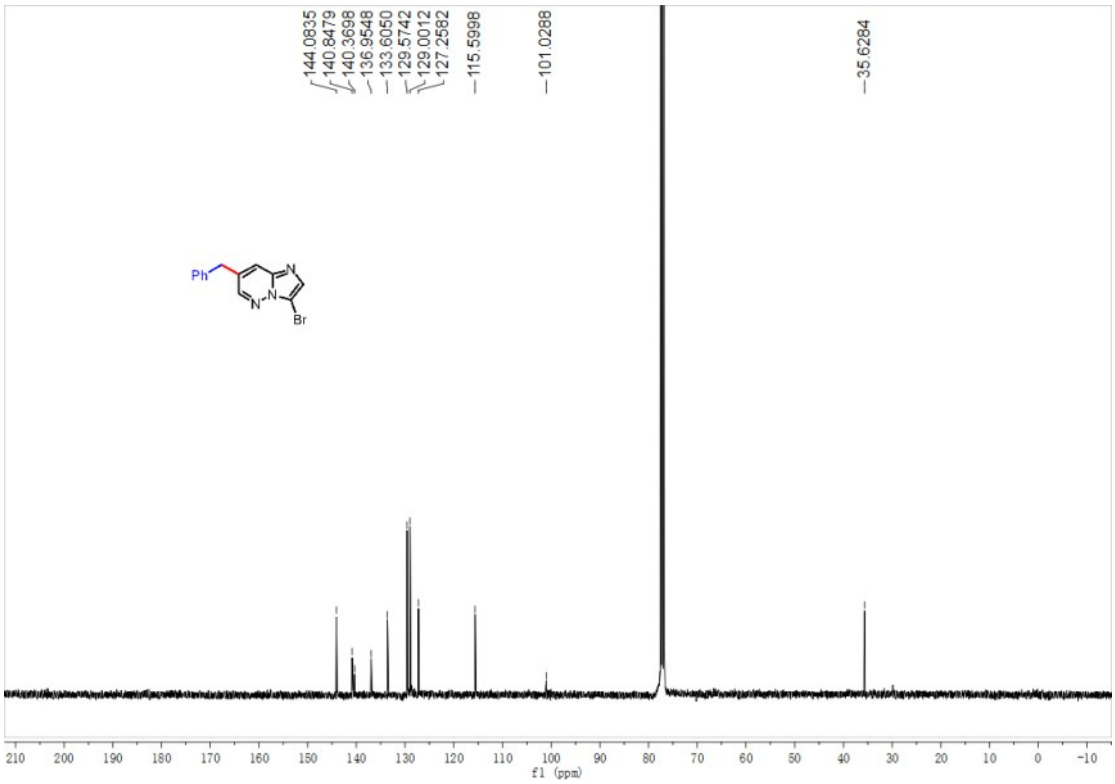
^{13}C NMR spectrum of compound **23**



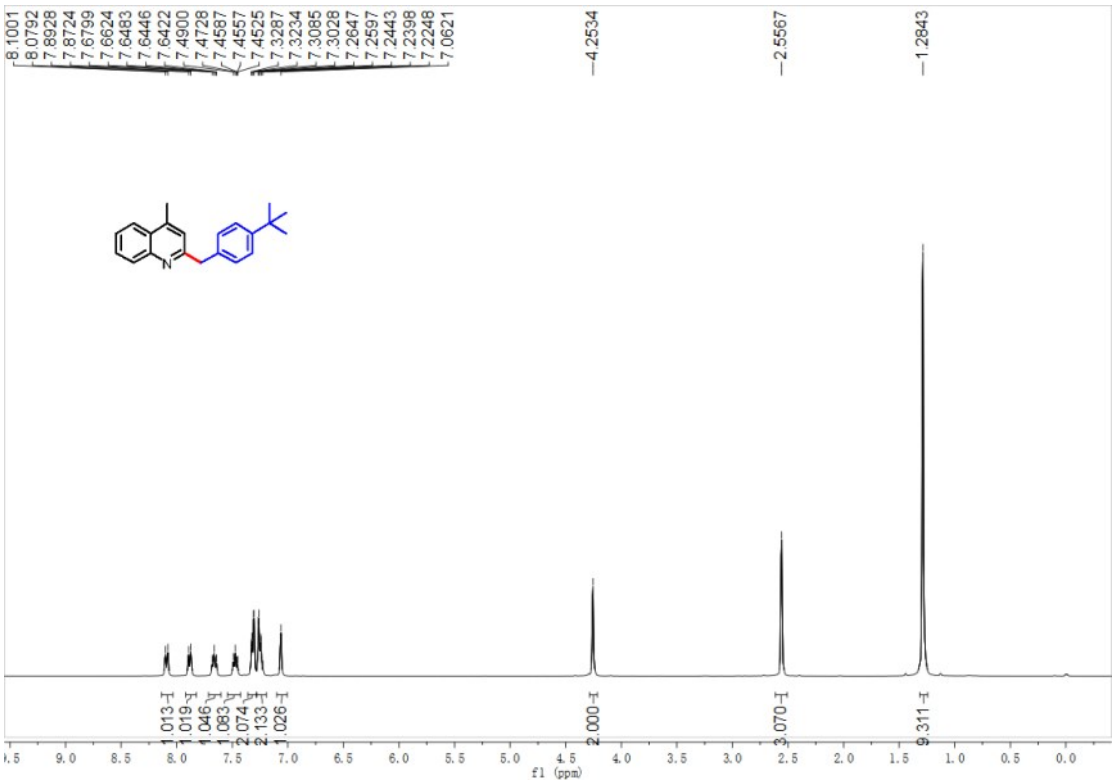
^{1}H NMR spectrum of compound **24**



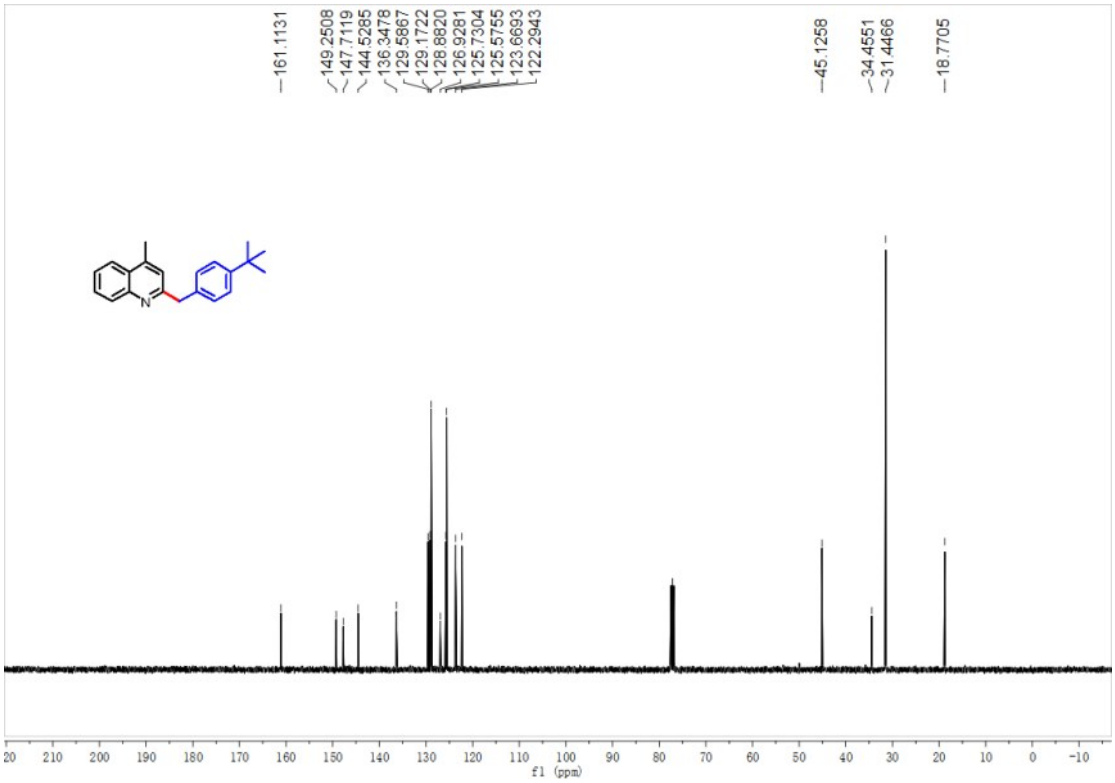
^{13}C NMR spectrum of compound **24**



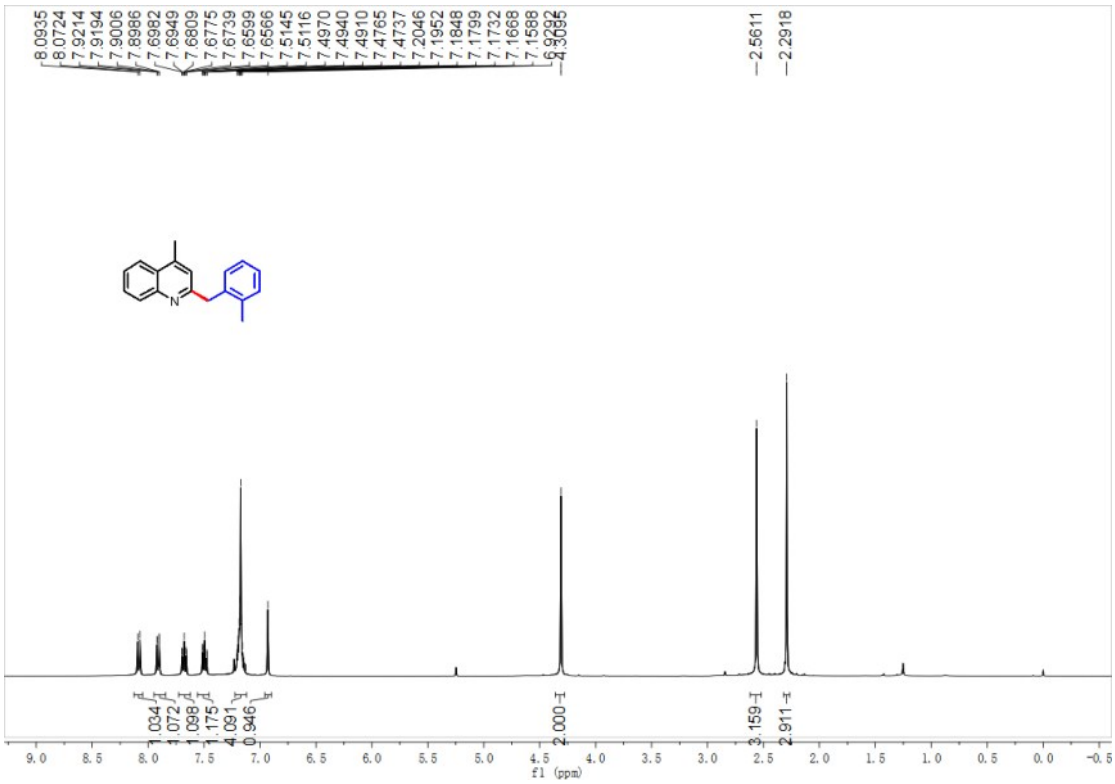
^{1}H NMR spectrum of compound **25**



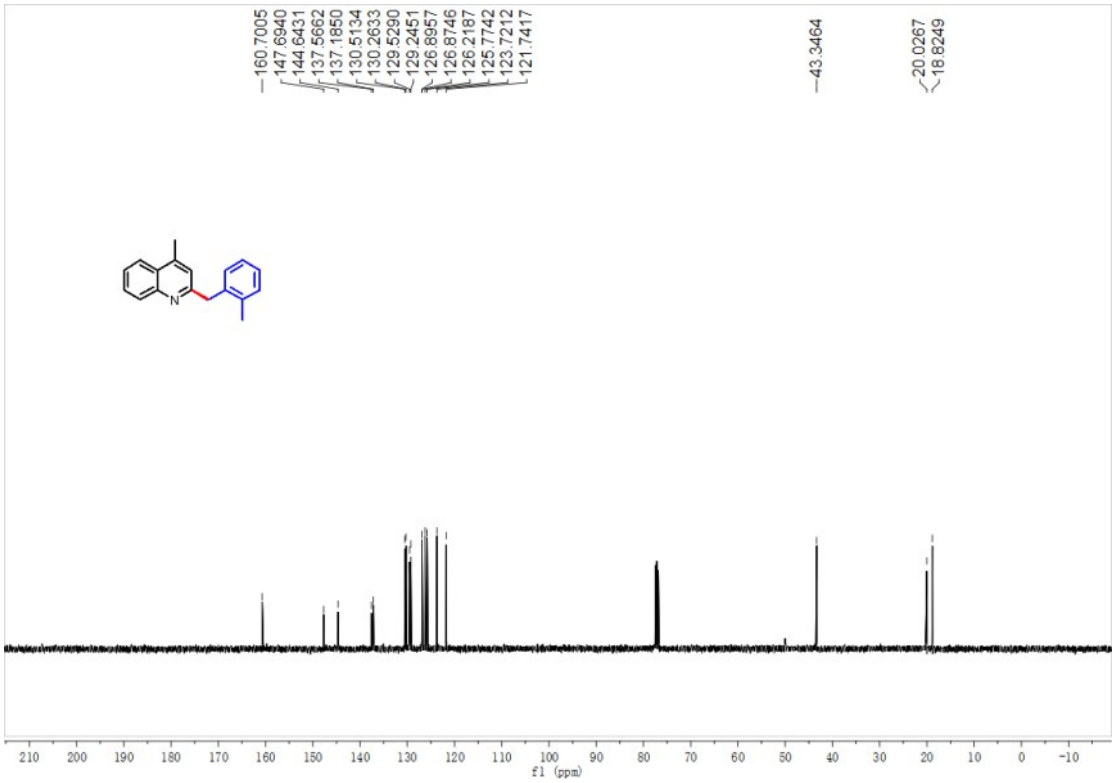
^{13}C NMR spectrum of compound **25**



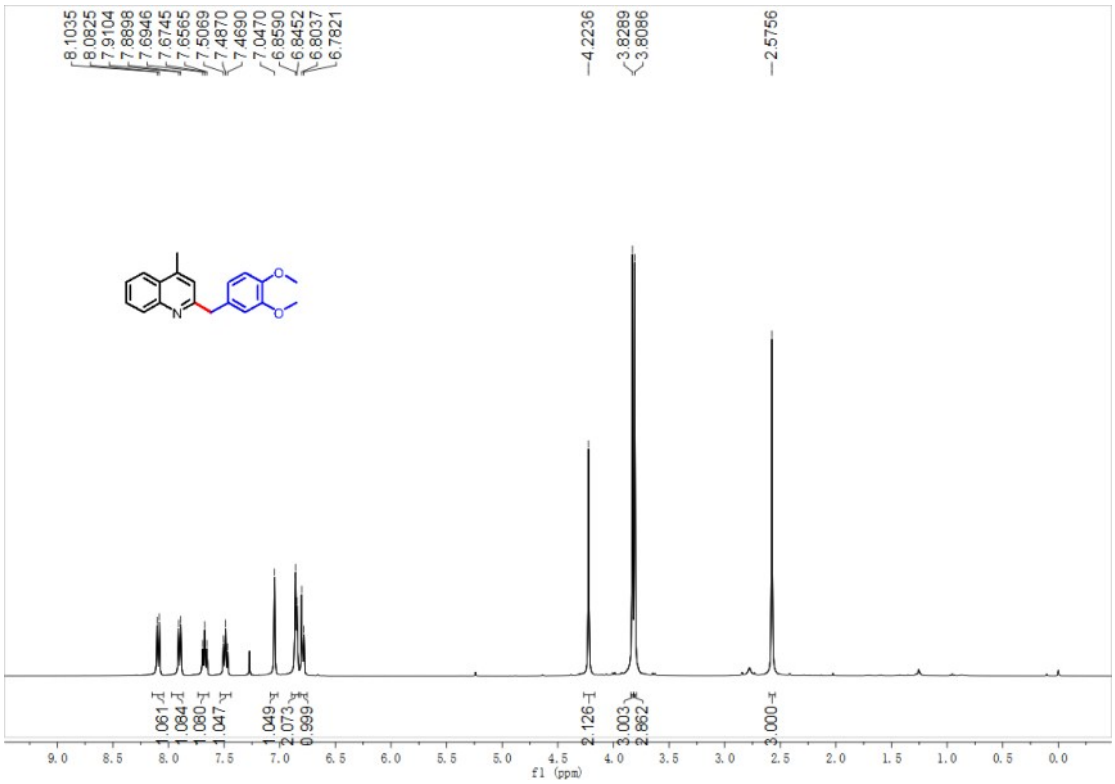
^{1}H NMR spectrum of compound **26**



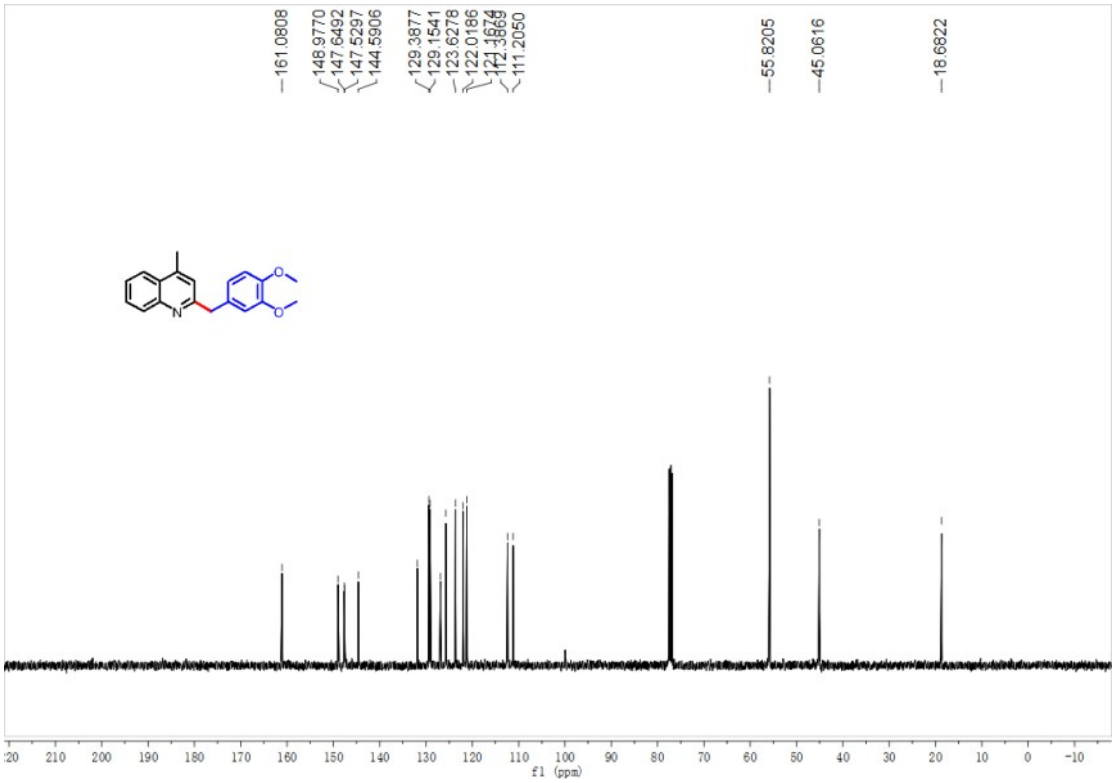
^{13}C NMR spectrum of compound **26**



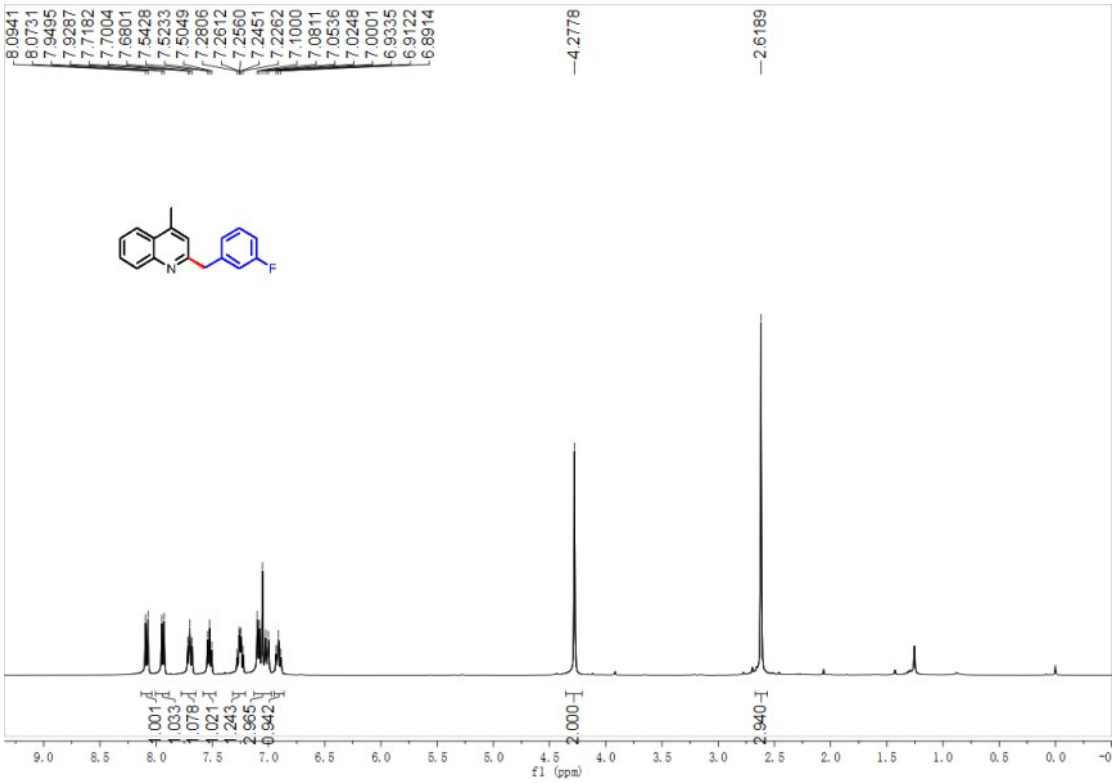
^{1}H NMR spectrum of compound **27**



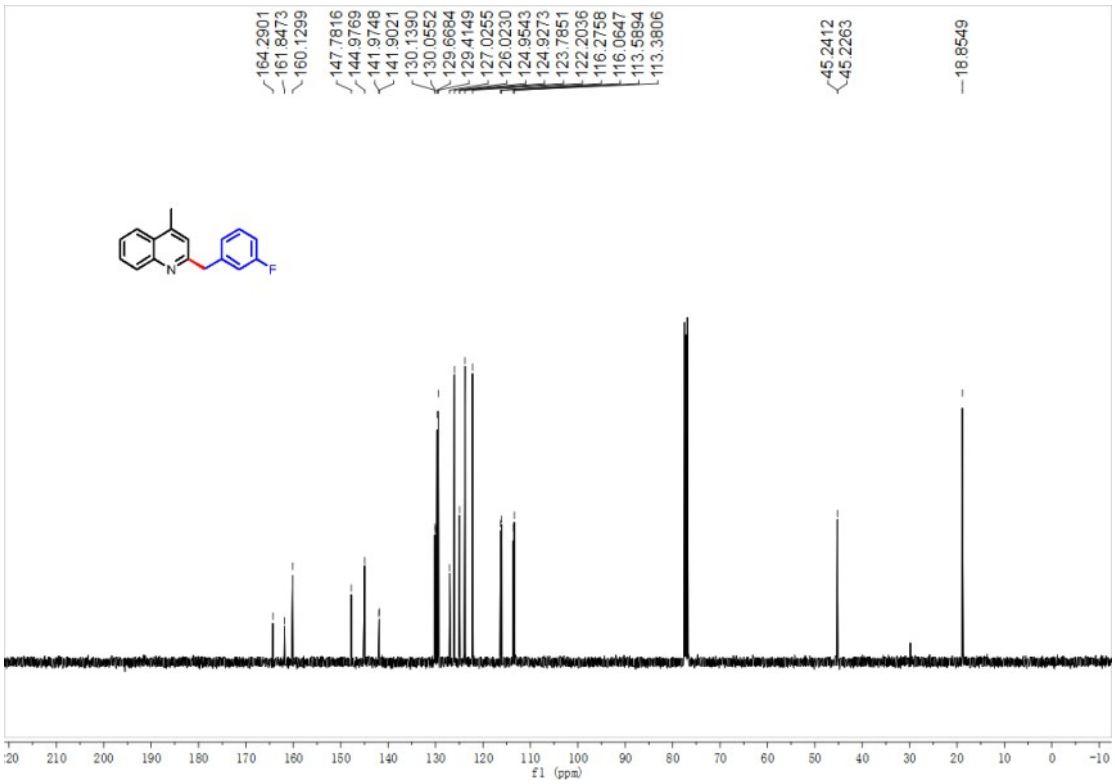
^{13}C NMR spectrum of compound **27**



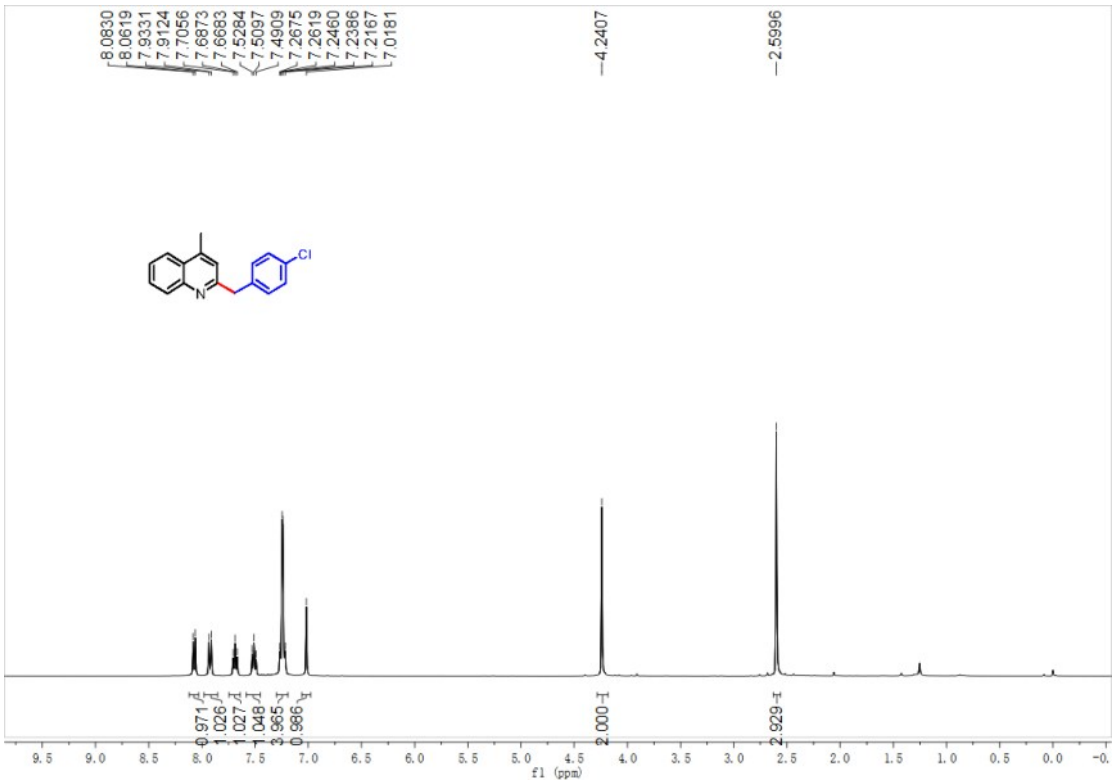
^{1}H NMR spectrum of compound **28**



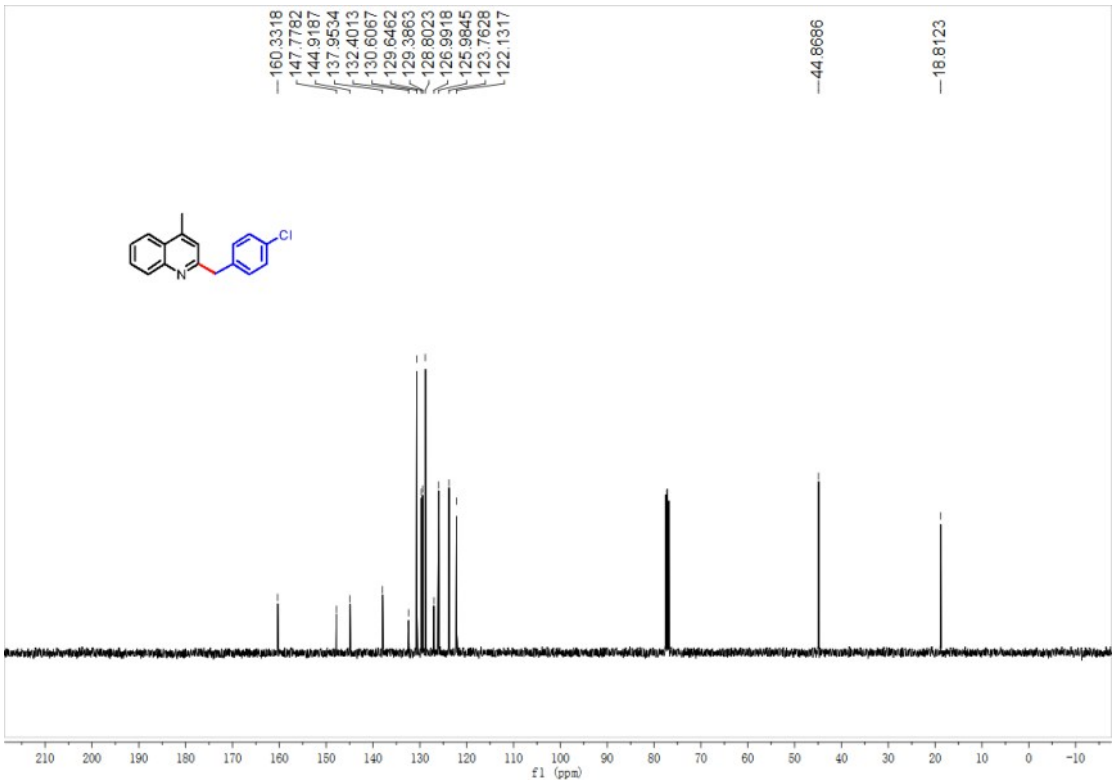
^{13}C NMR spectrum of compound **28**



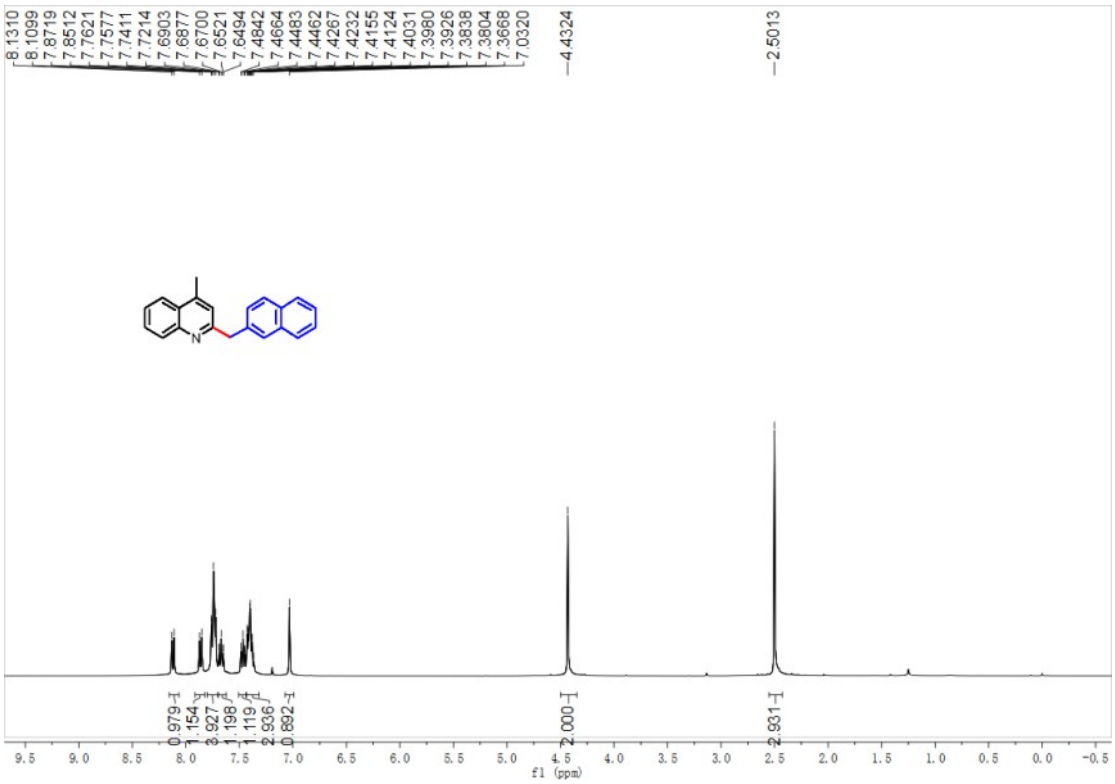
^{1}H NMR spectrum of compound **29**



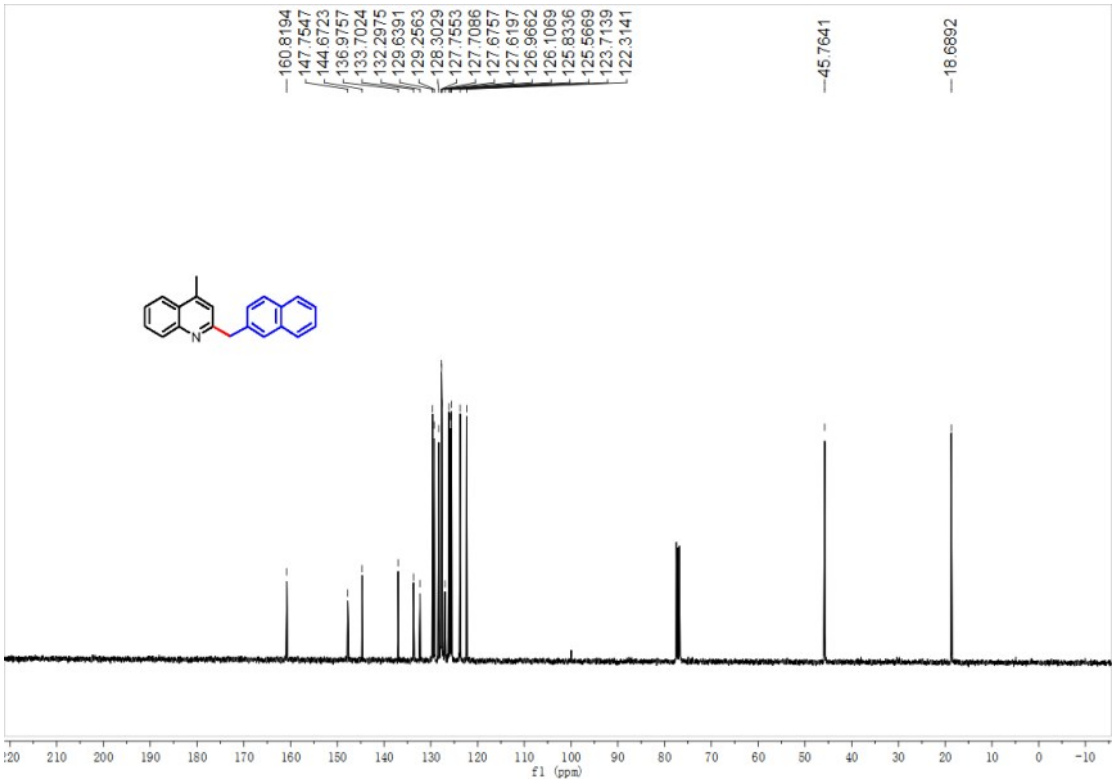
^{13}C NMR spectrum of compound **29**



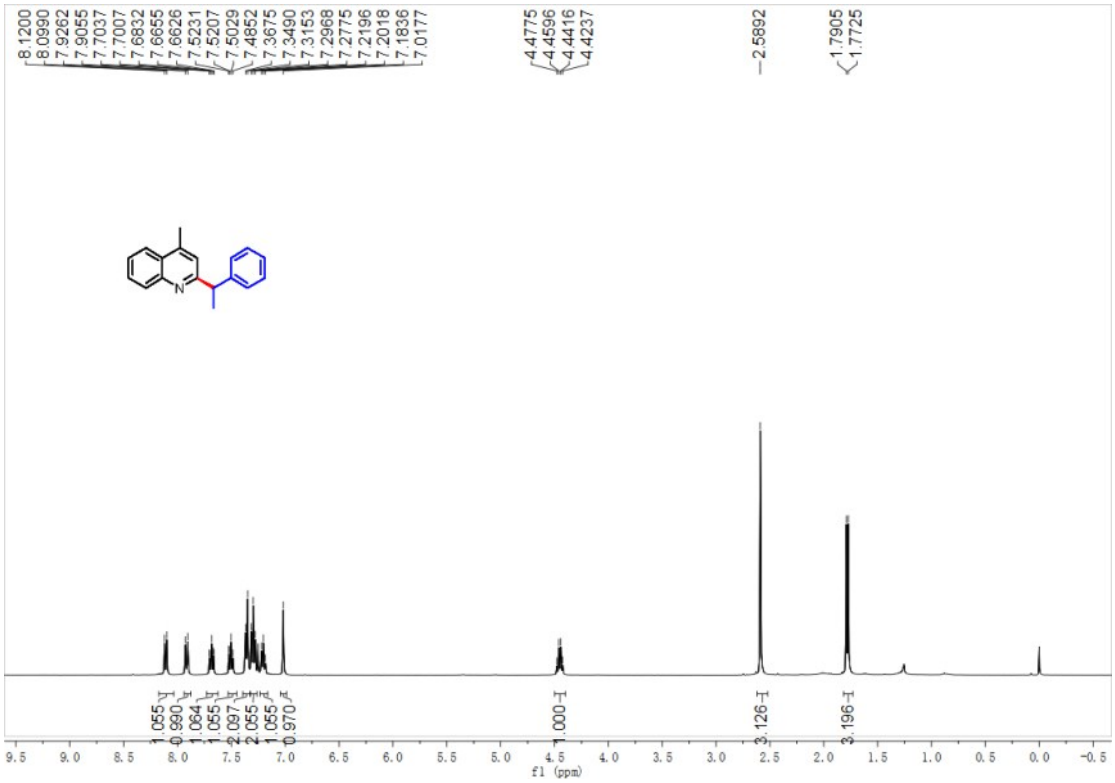
^{1}H NMR spectrum of compound **30**



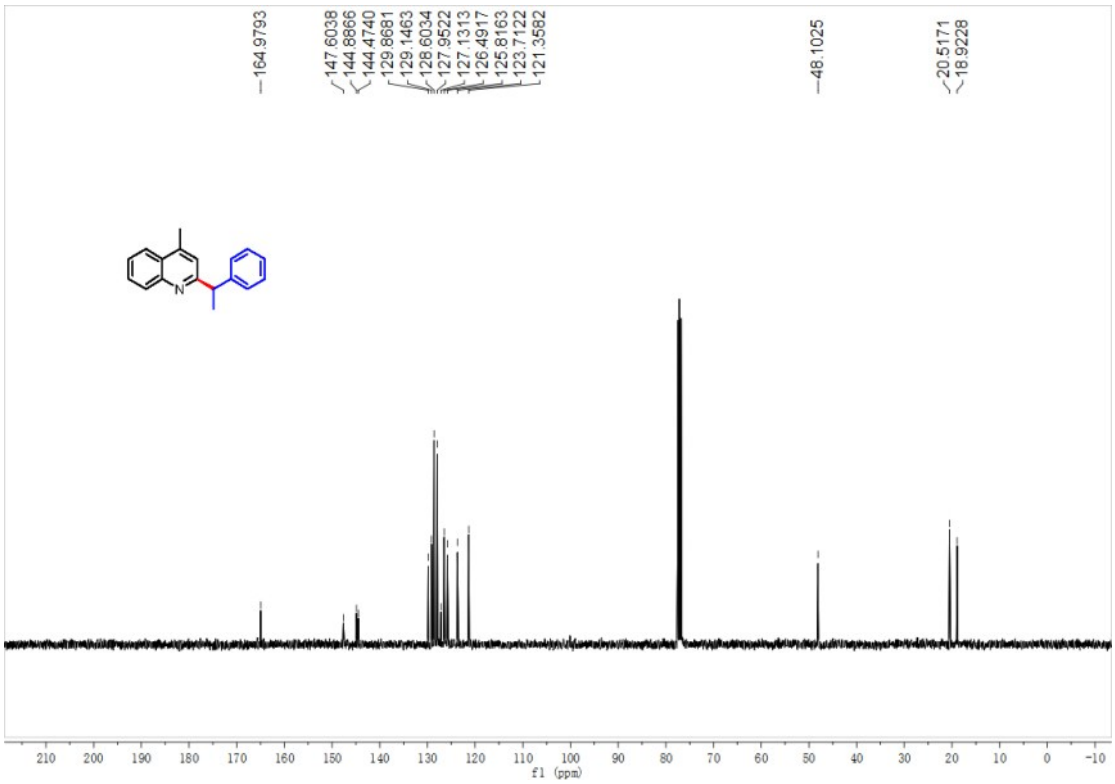
^{13}C NMR spectrum of compound **30**



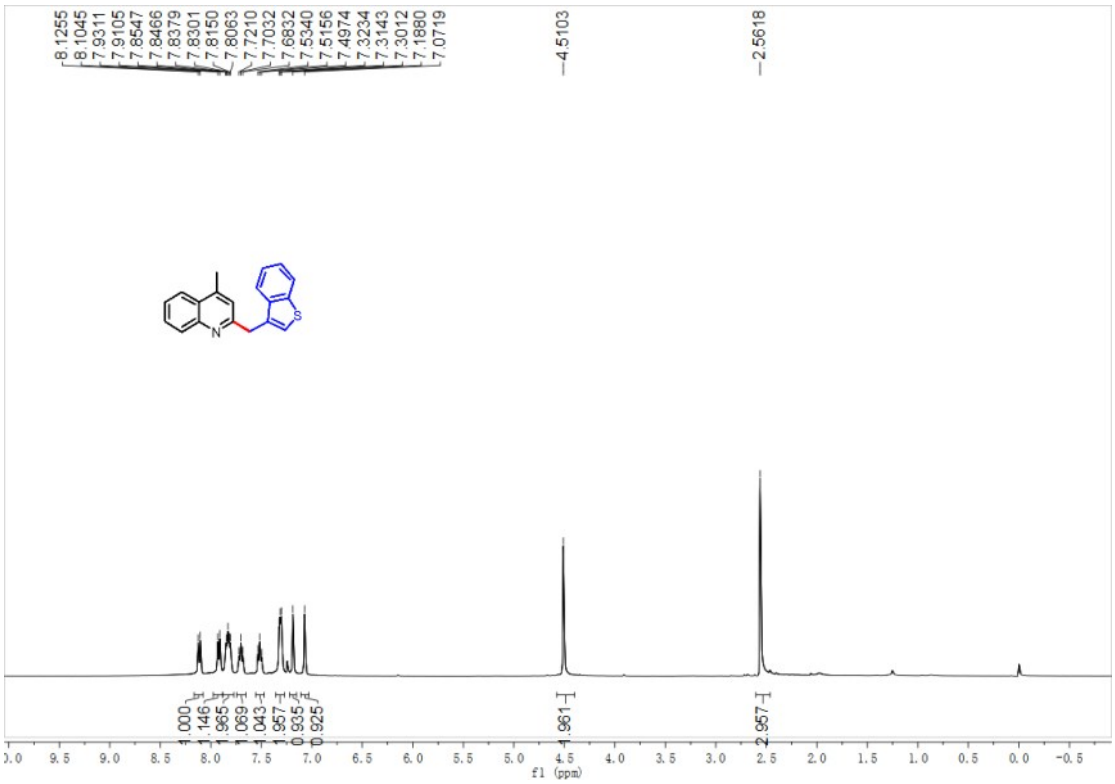
^{1}H NMR spectrum of compound **31**



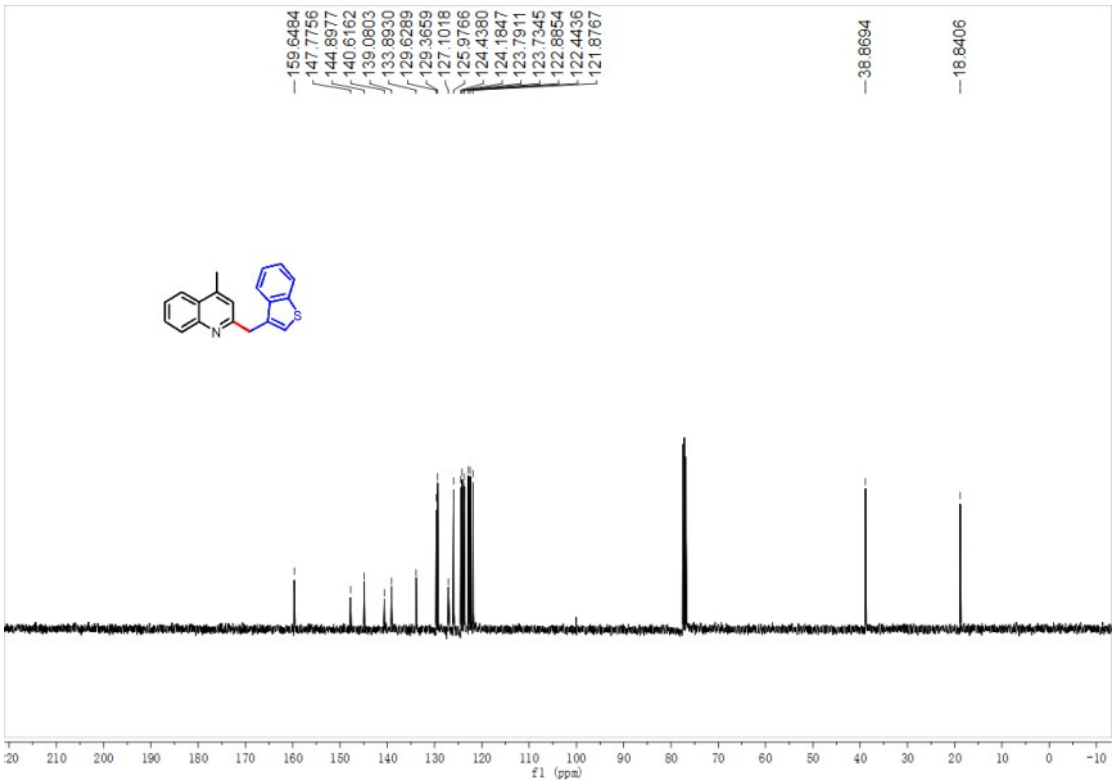
^{13}C NMR spectrum of compound **31**



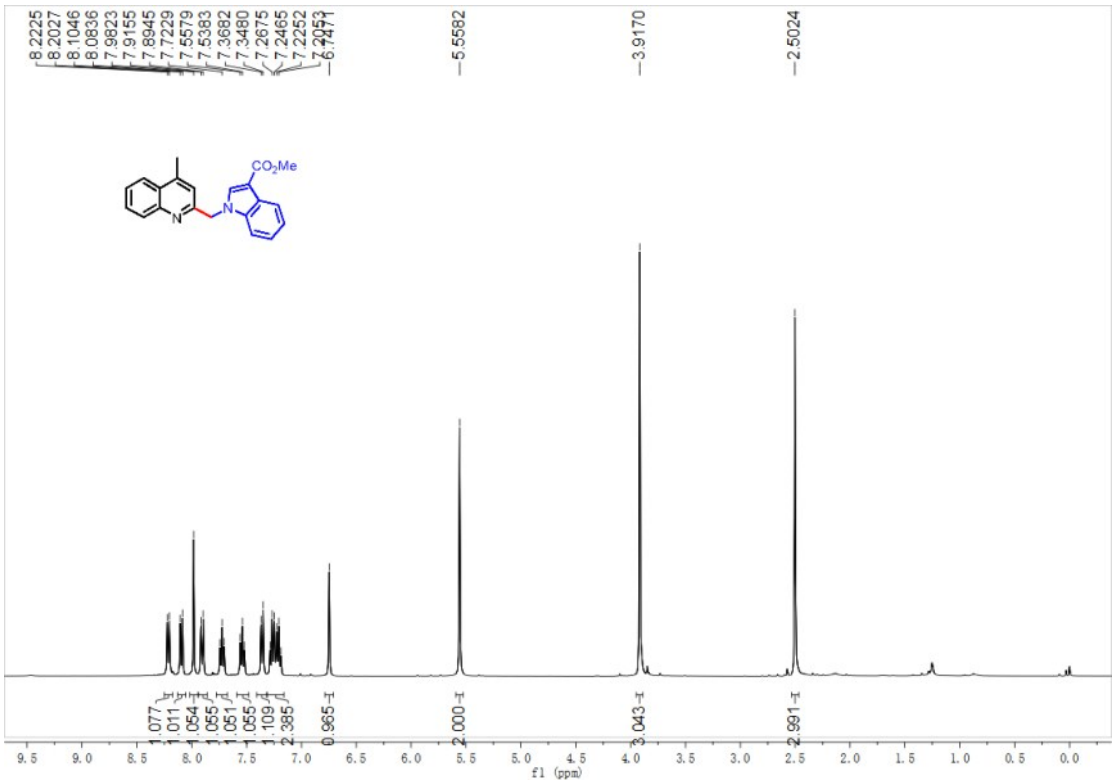
^{1}H NMR spectrum of compound **32**



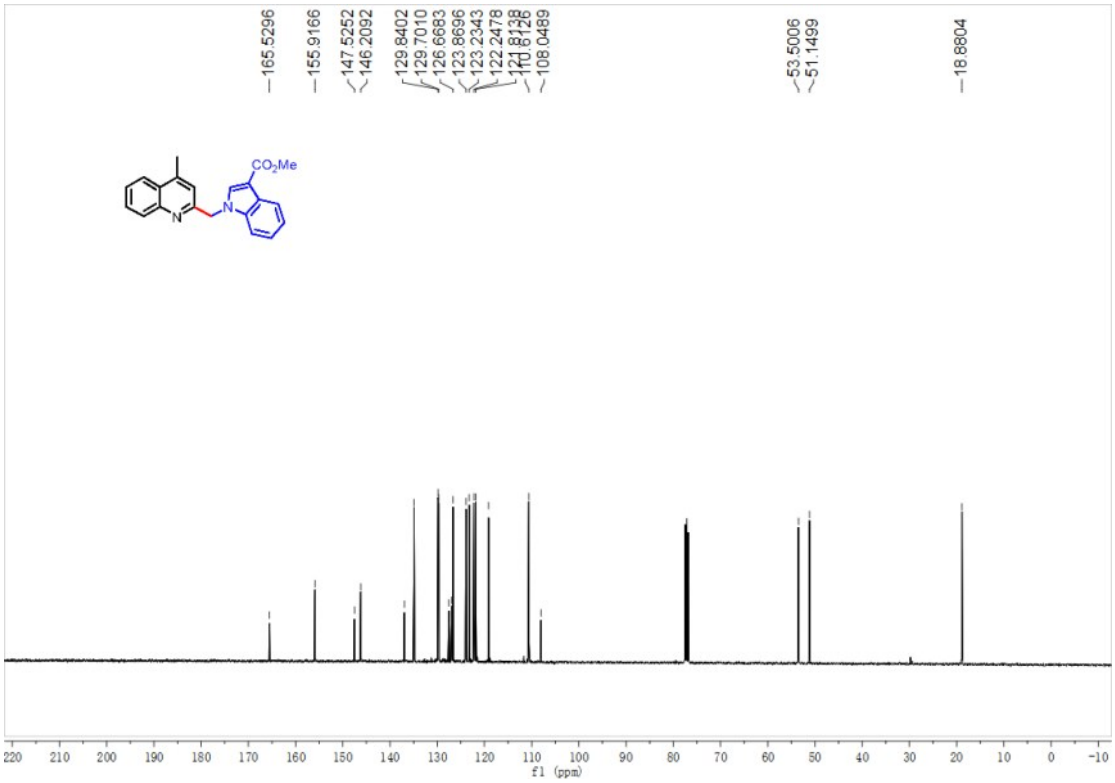
^{13}C NMR spectrum of compound **32**



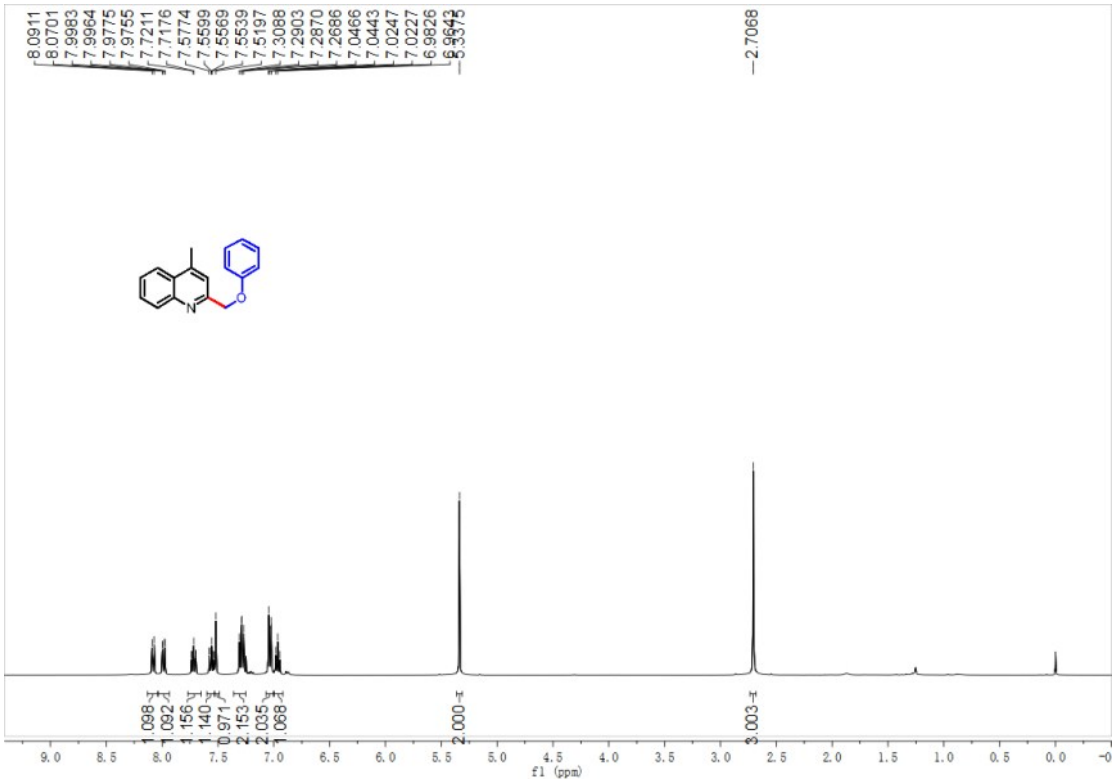
^{1}H NMR spectrum of compound **33**



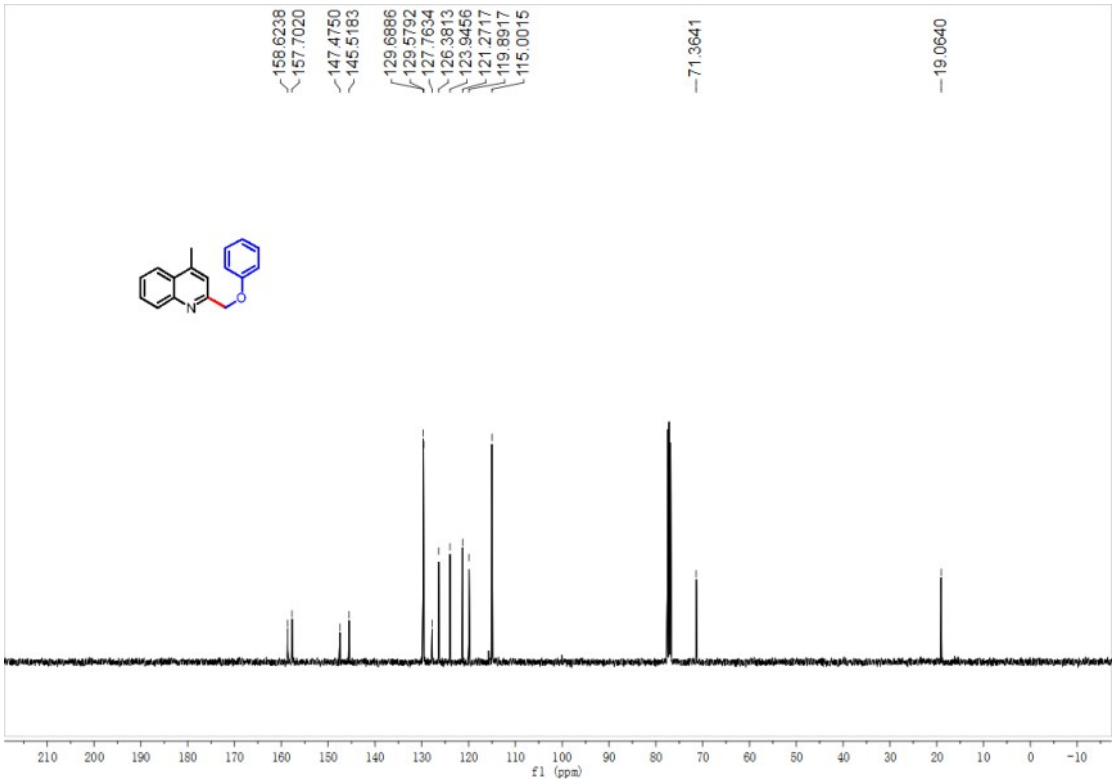
^{13}C NMR spectrum of compound **33**



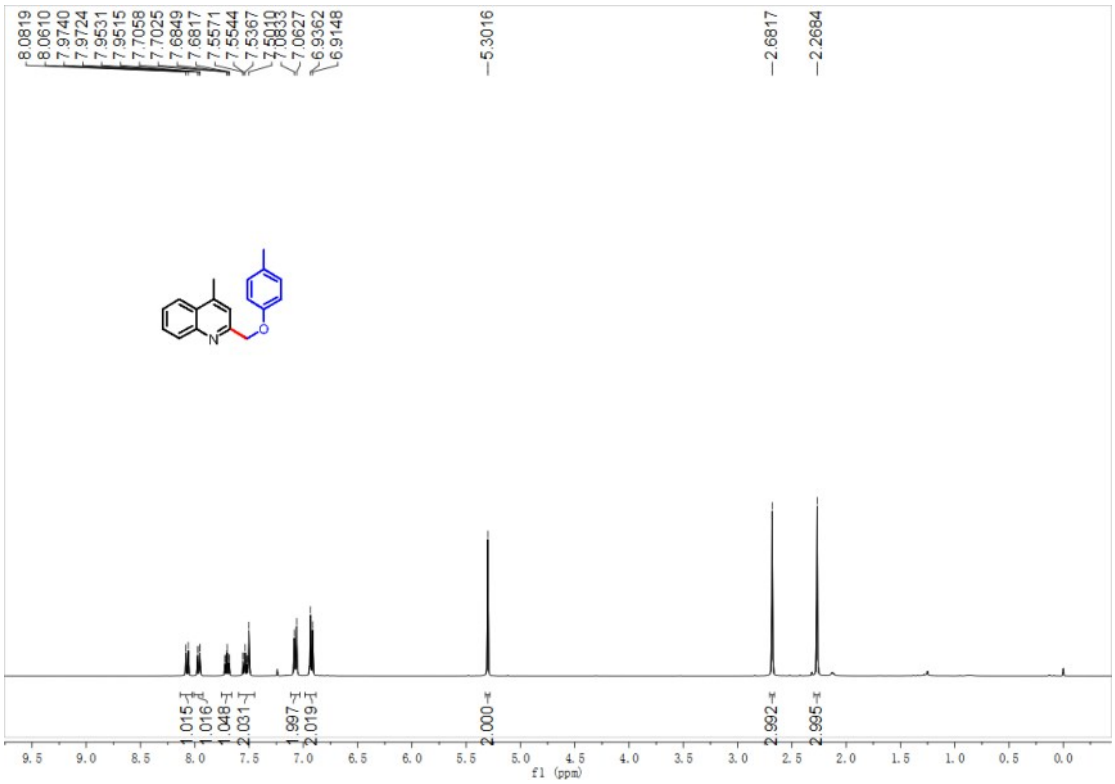
^{1}H NMR spectrum of compound **34**



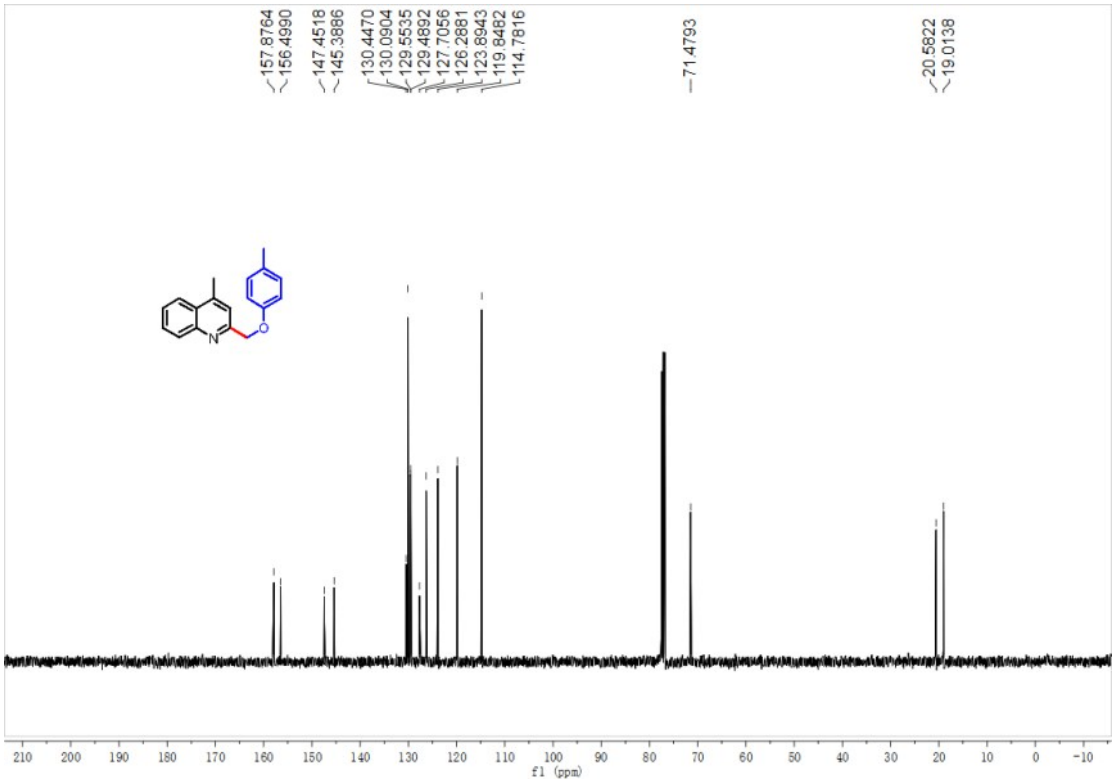
^{13}C NMR spectrum of compound **34**



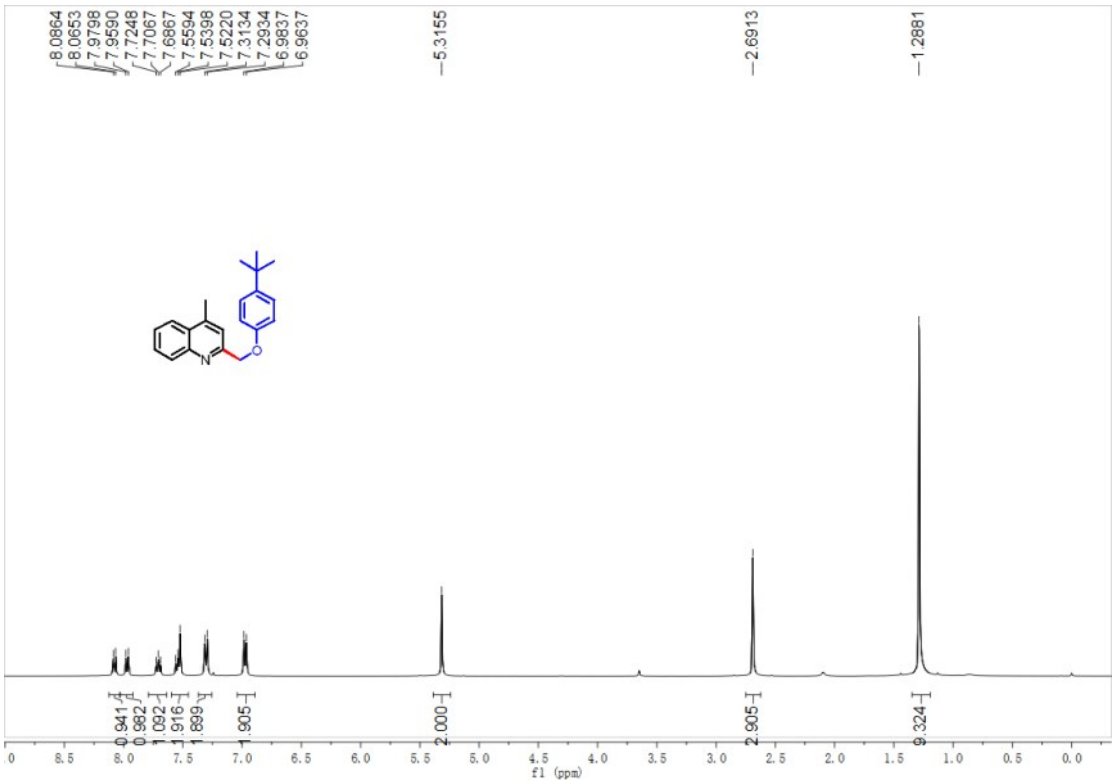
^{1}H NMR spectrum of compound **35**



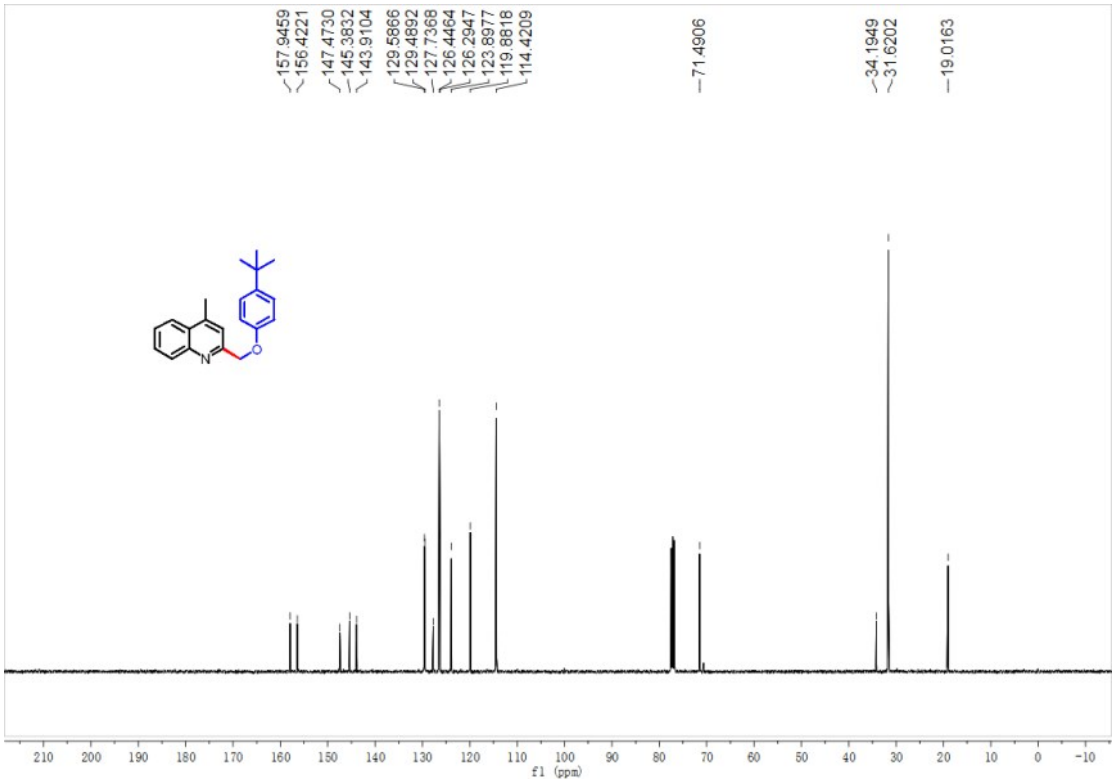
^{13}C NMR spectrum of compound **35**



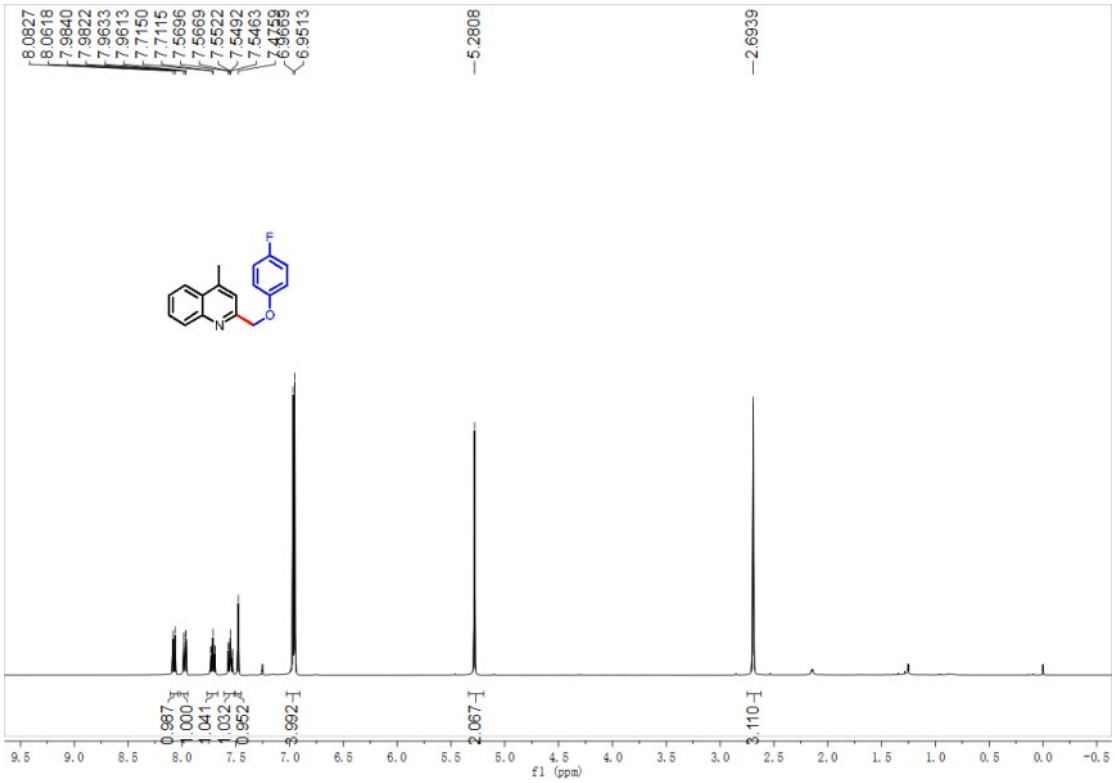
^{1}H NMR spectrum of compound **36**



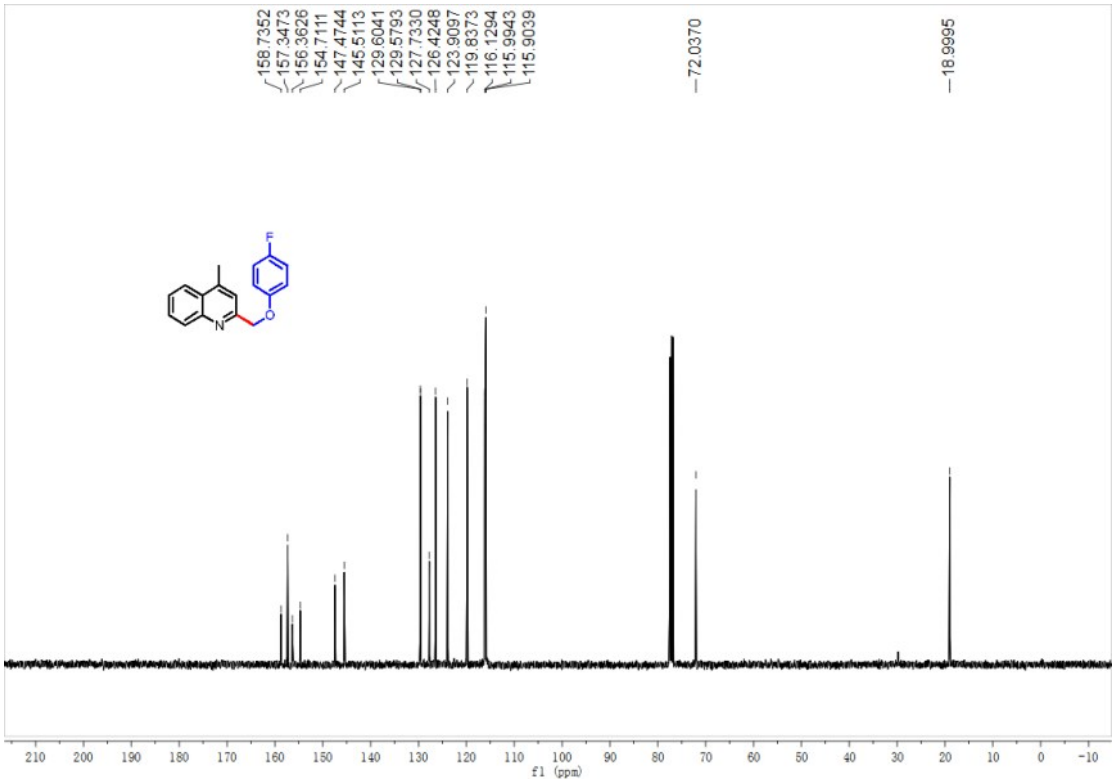
^{13}C NMR spectrum of compound **36**



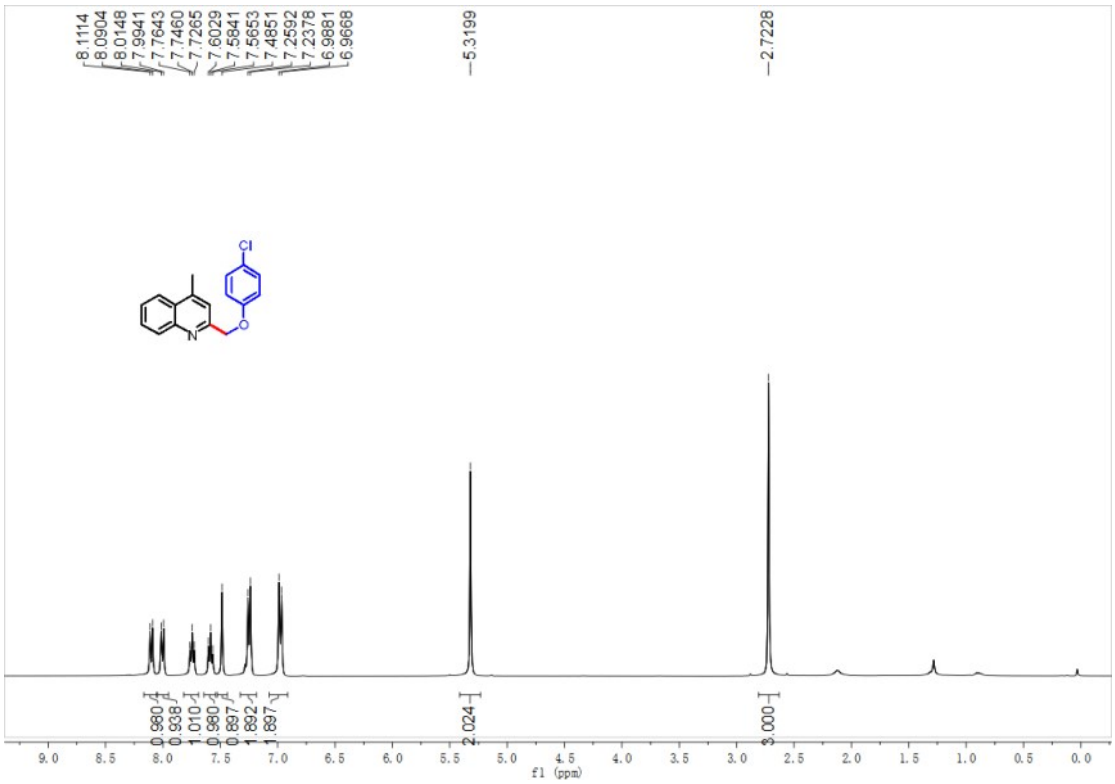
^{1}H NMR spectrum of compound **37**



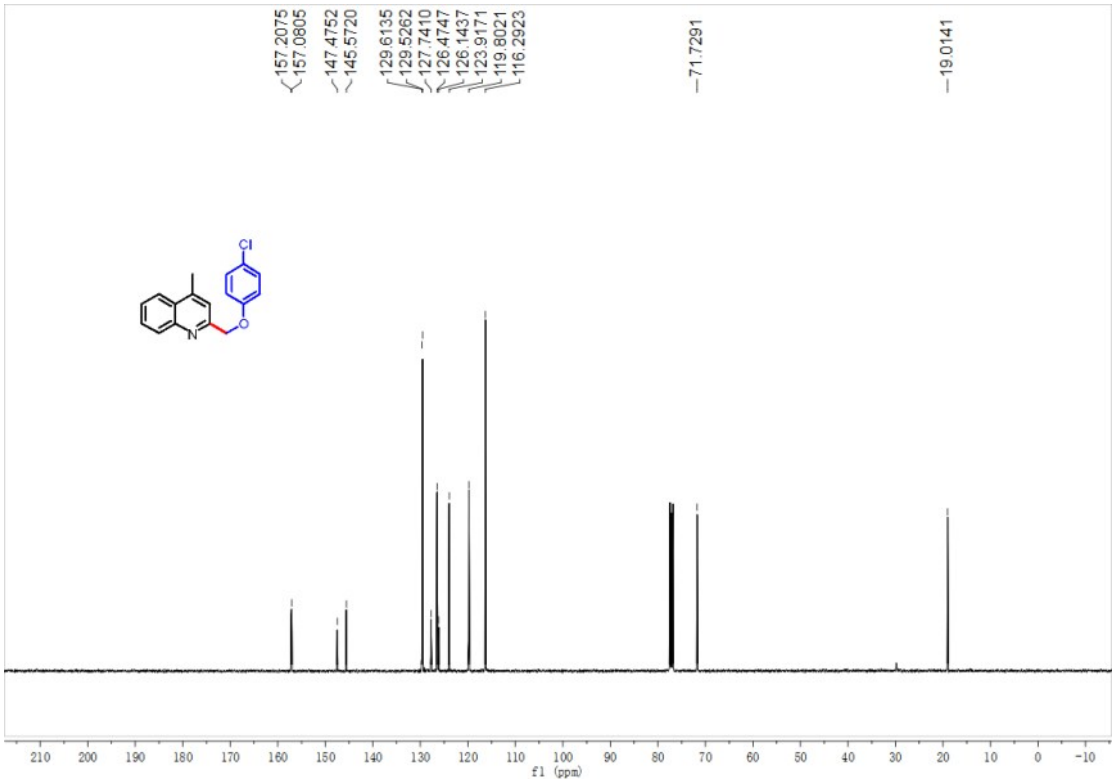
^{13}C NMR spectrum of compound **37**



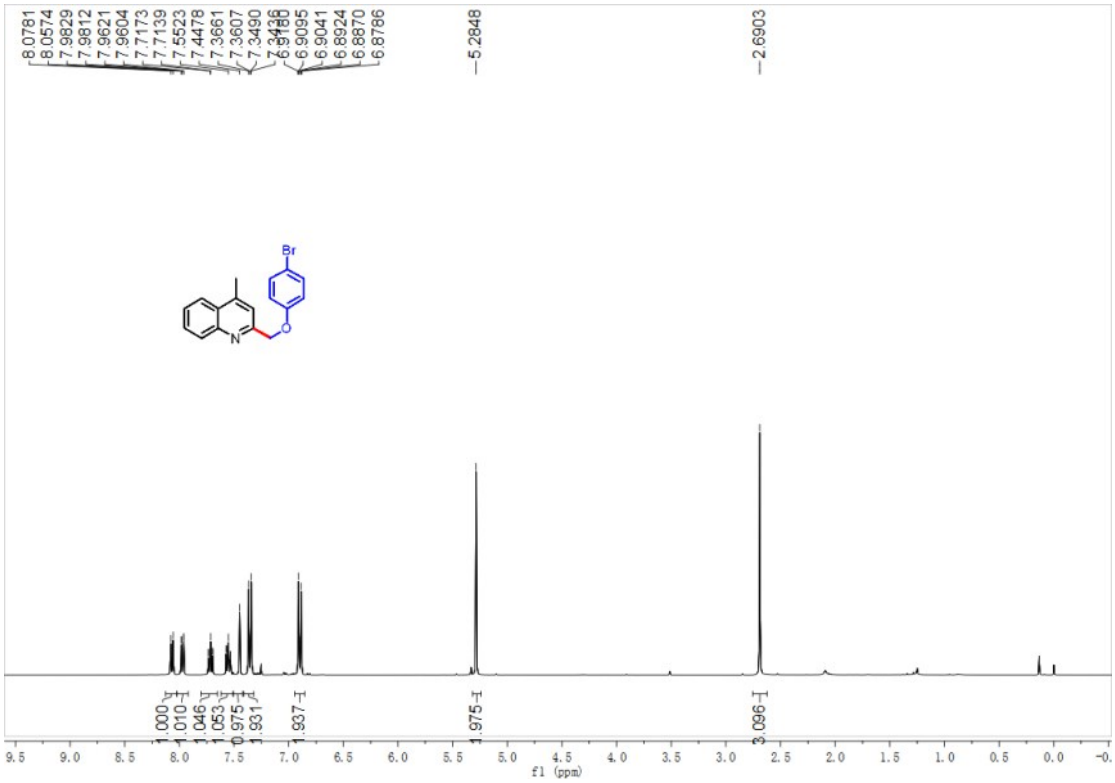
^{1}H NMR spectrum of compound **38**



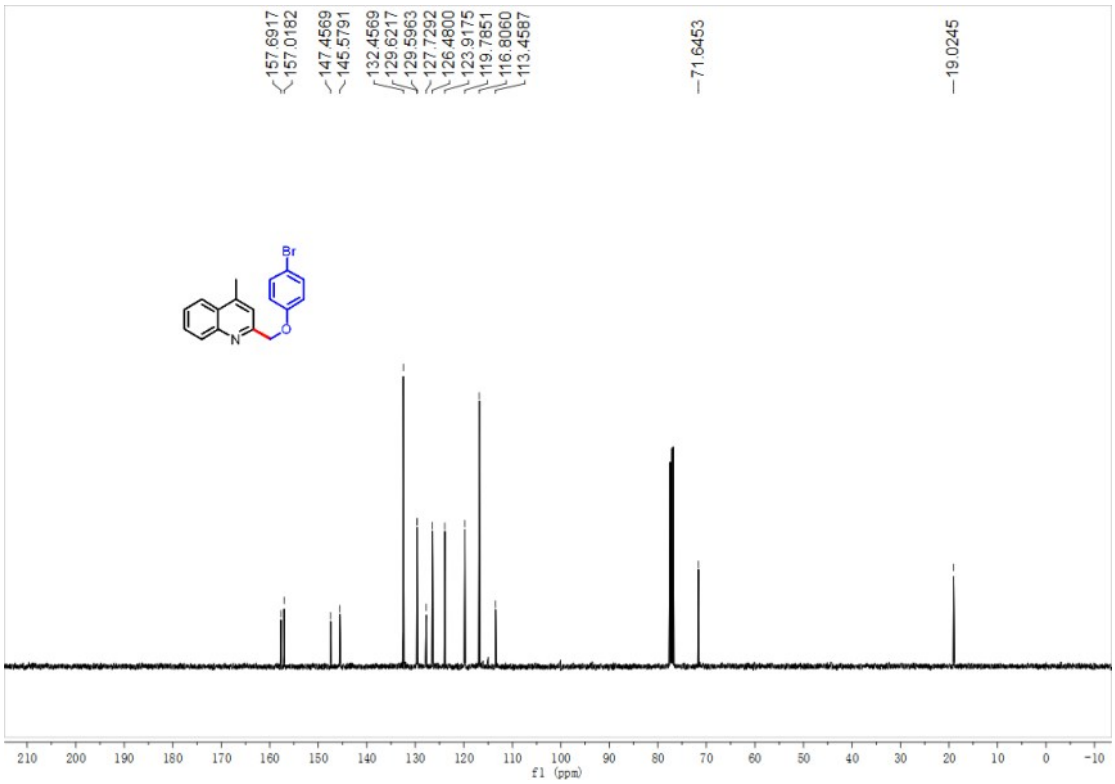
^{13}C NMR spectrum of compound **38**



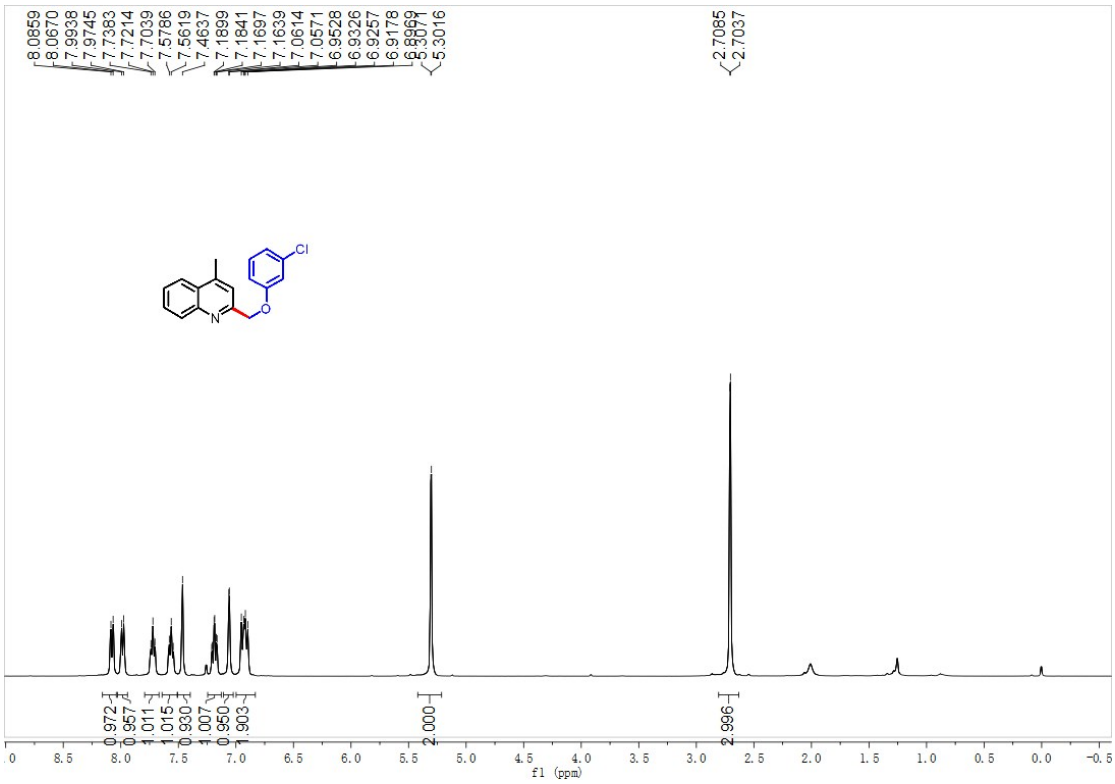
^{1}H NMR spectrum of compound **39**



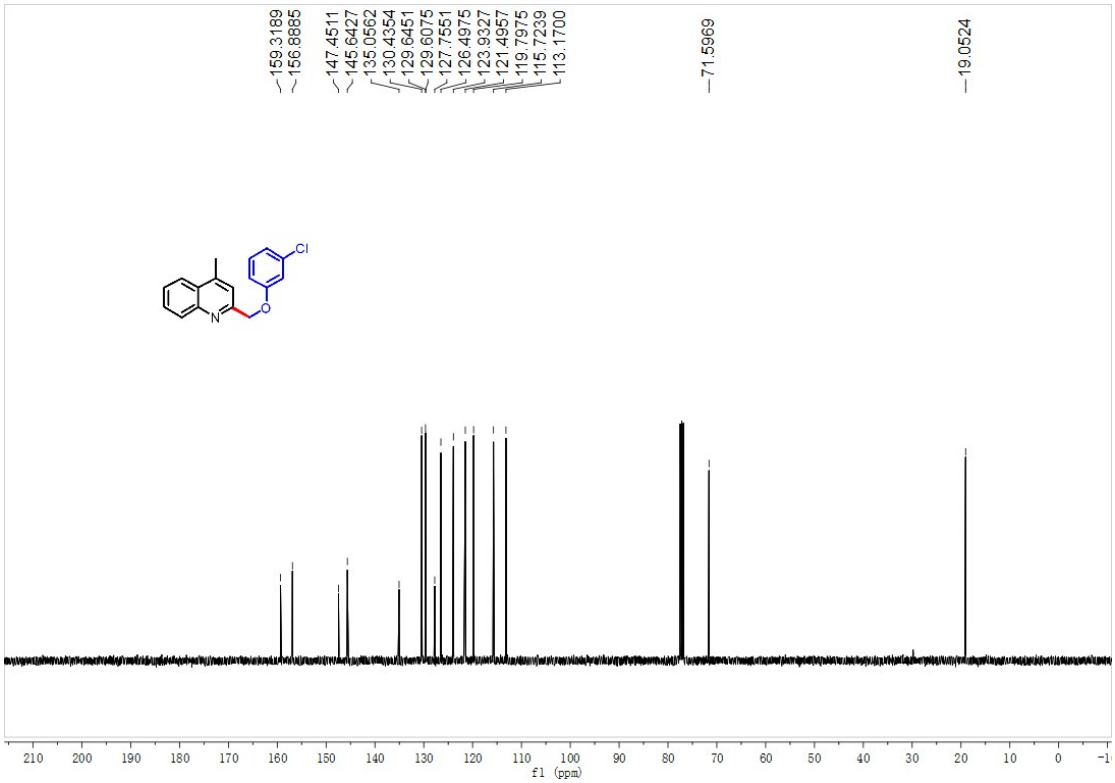
^{13}C NMR spectrum of compound **39**



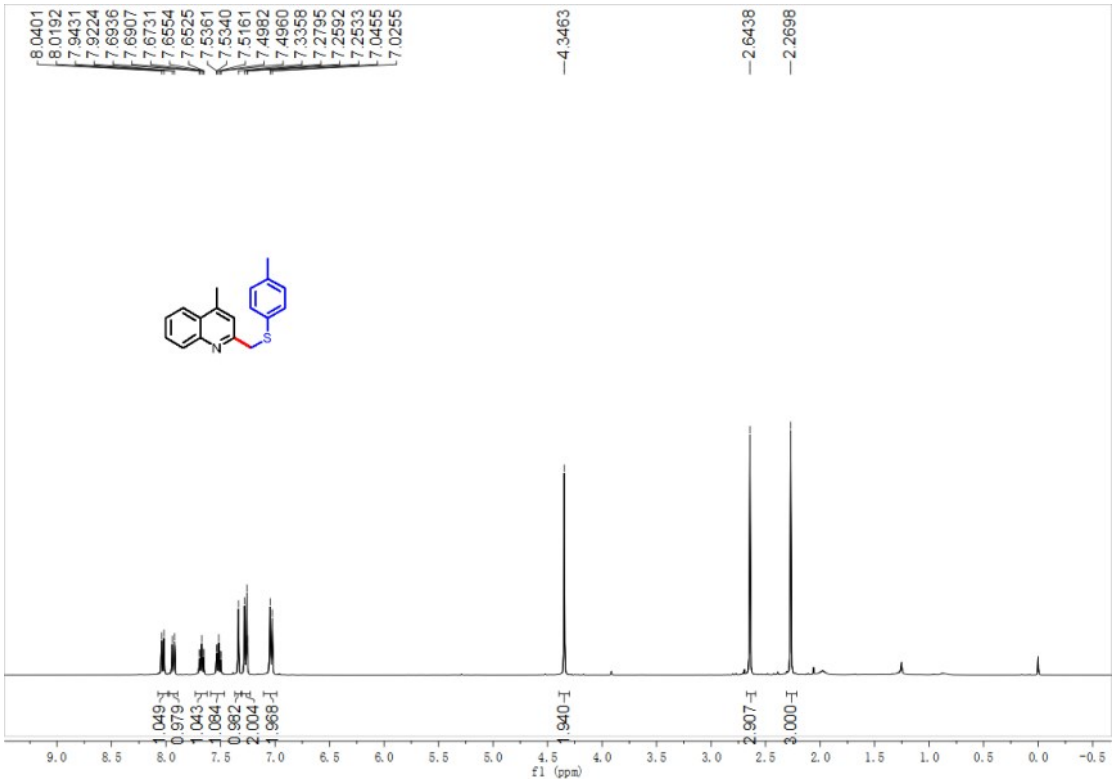
^{1}H NMR spectrum of compound **40**



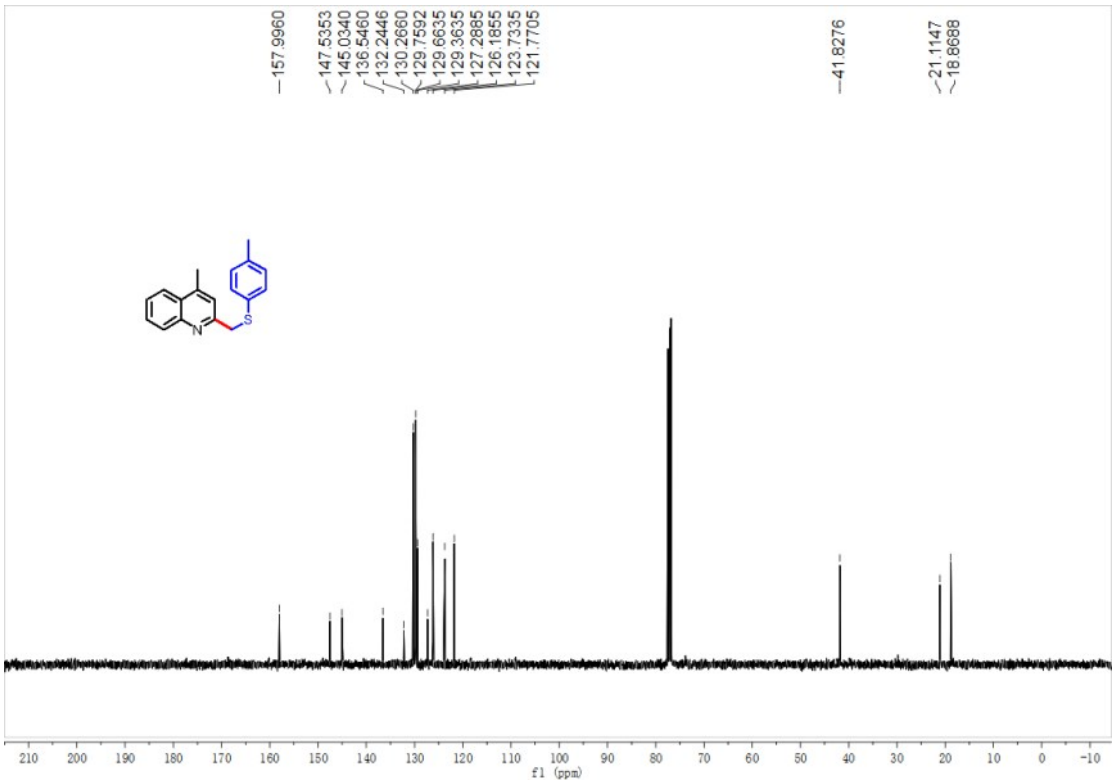
^{13}C NMR spectrum of compound **40**



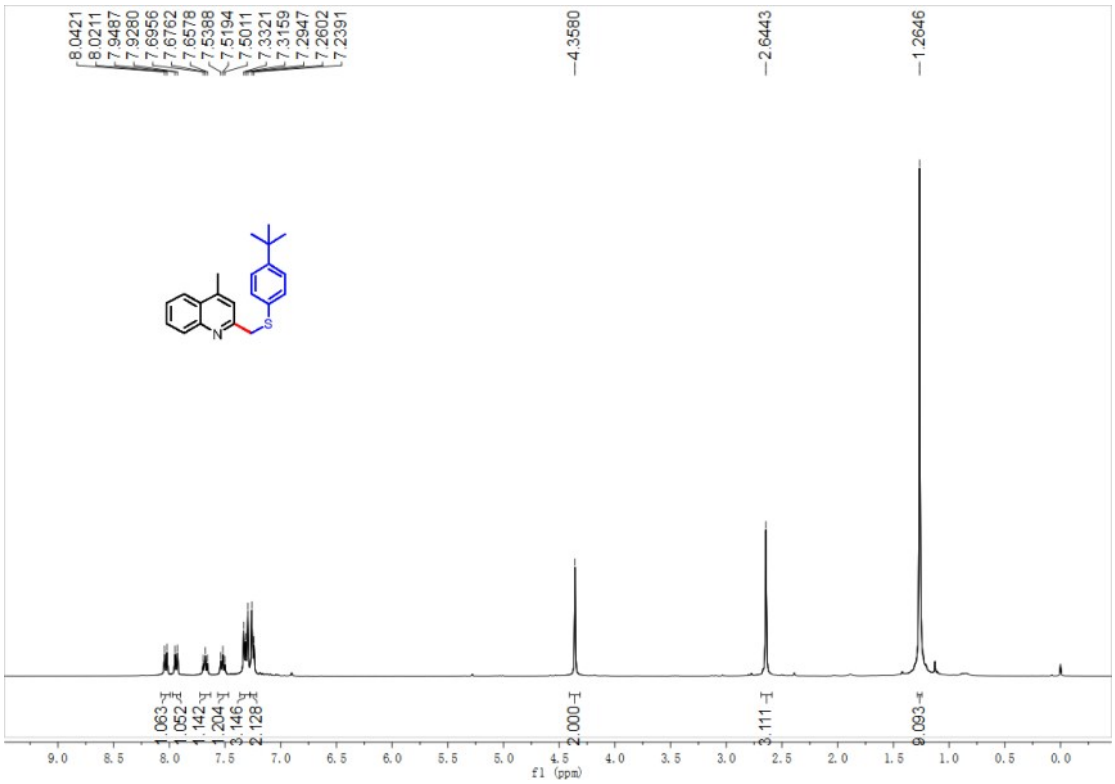
^{1}H NMR spectrum of compound **41**



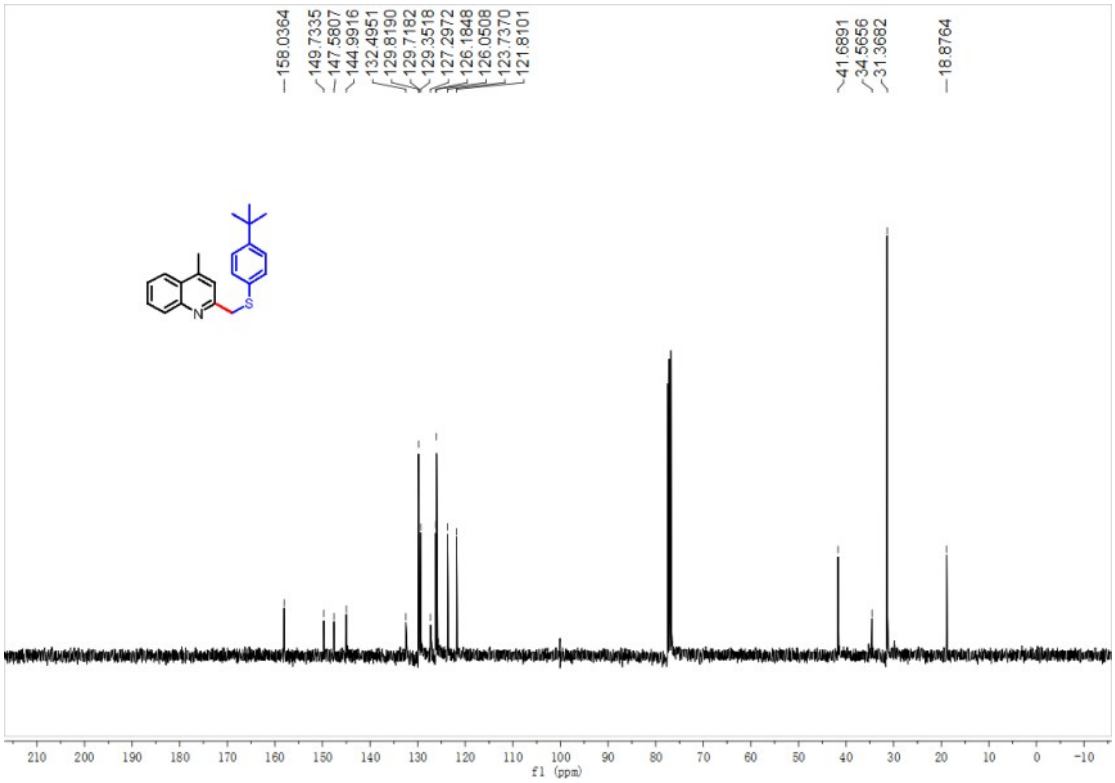
^{13}C NMR spectrum of compound **41**



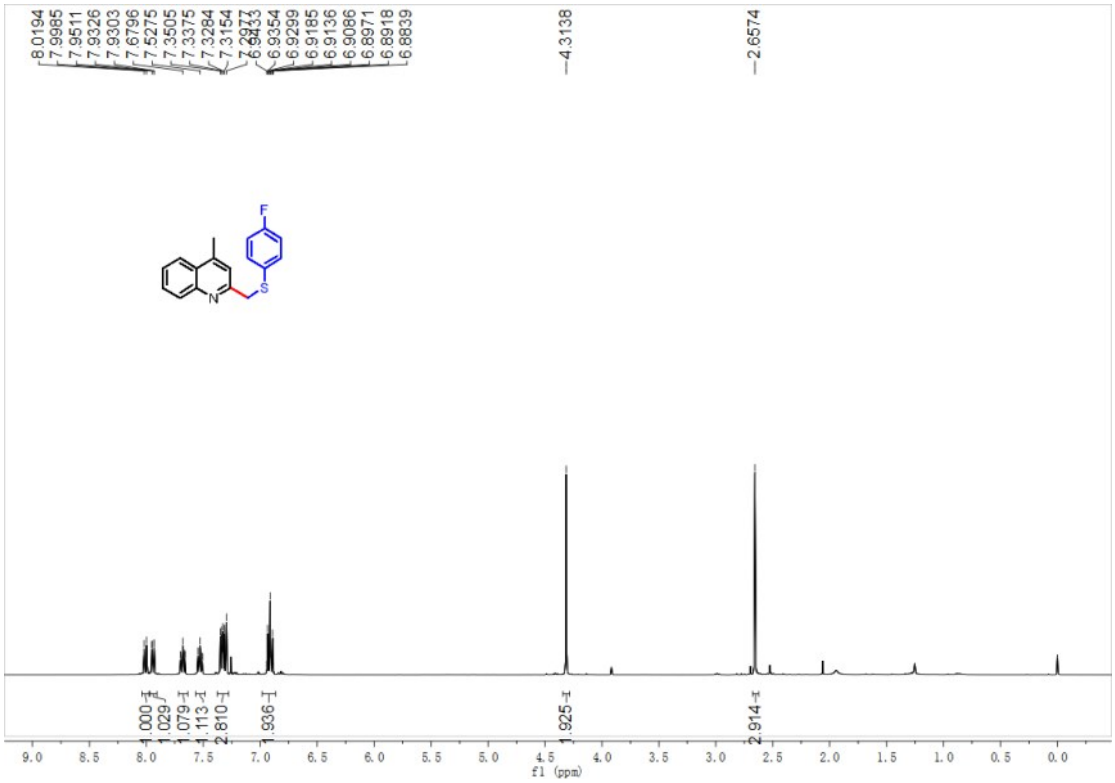
^{1}H NMR spectrum of compound **42**



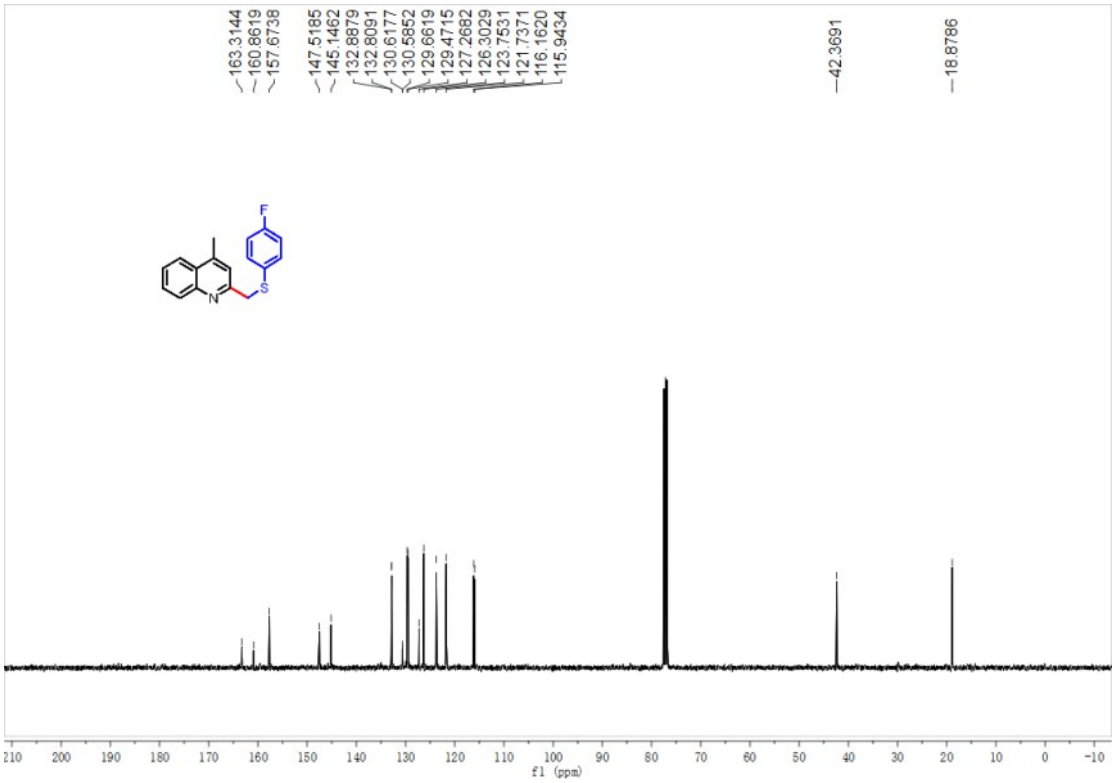
^{13}C NMR spectrum of compound **42**



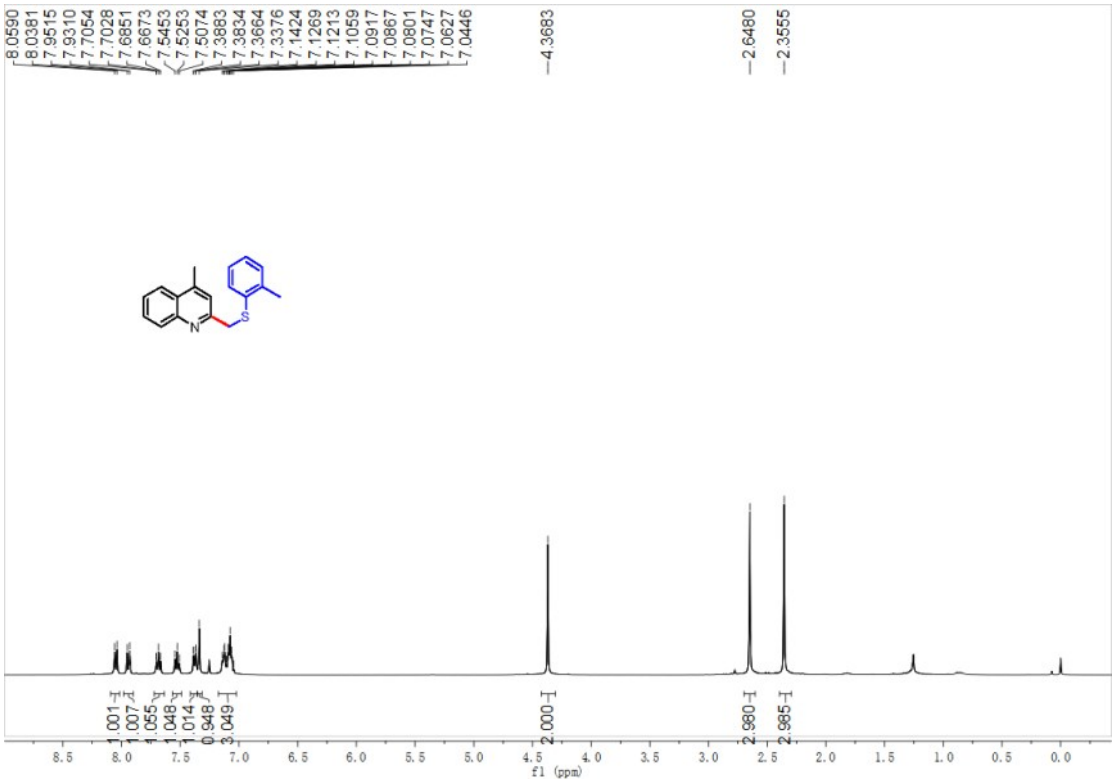
^{1}H NMR spectrum of compound **43**



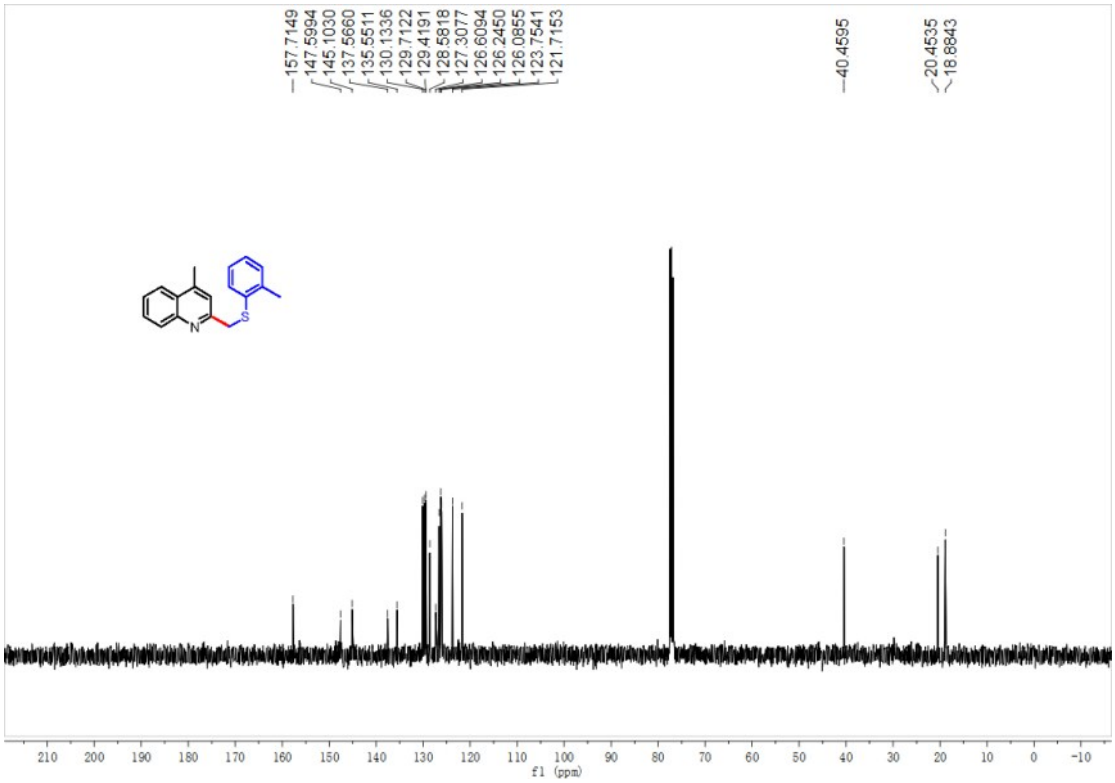
^{13}C NMR spectrum of compound **43**



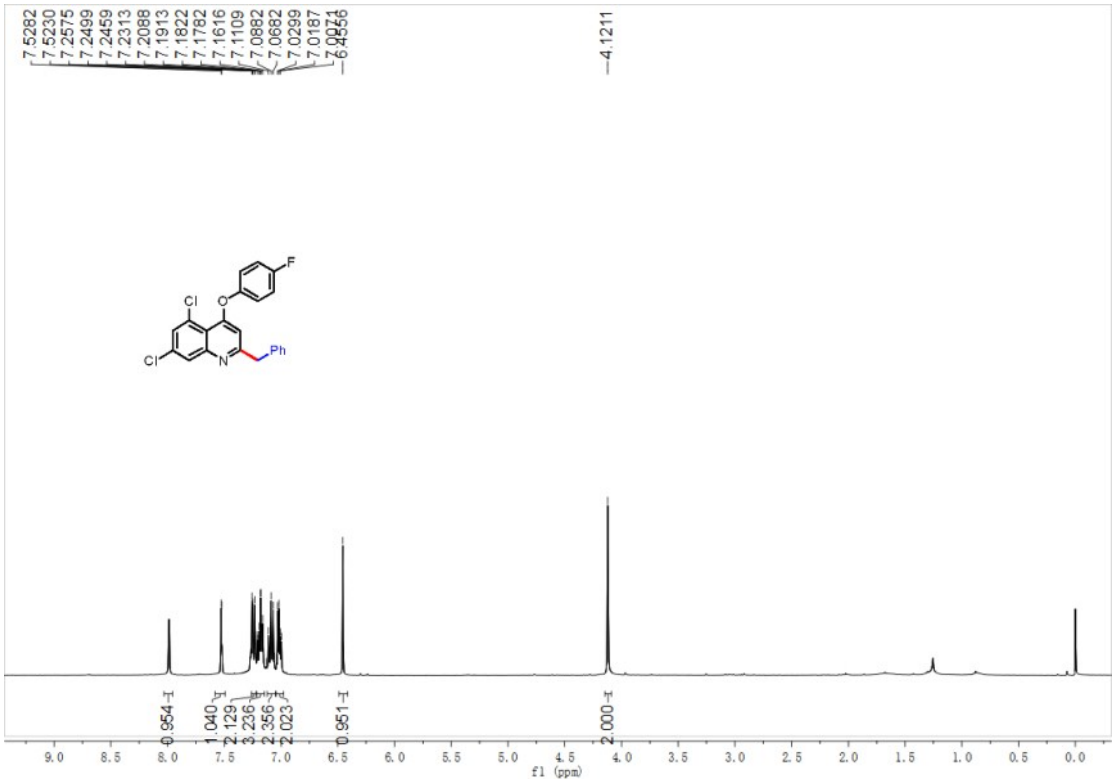
^{1}H NMR spectrum of compound **44**



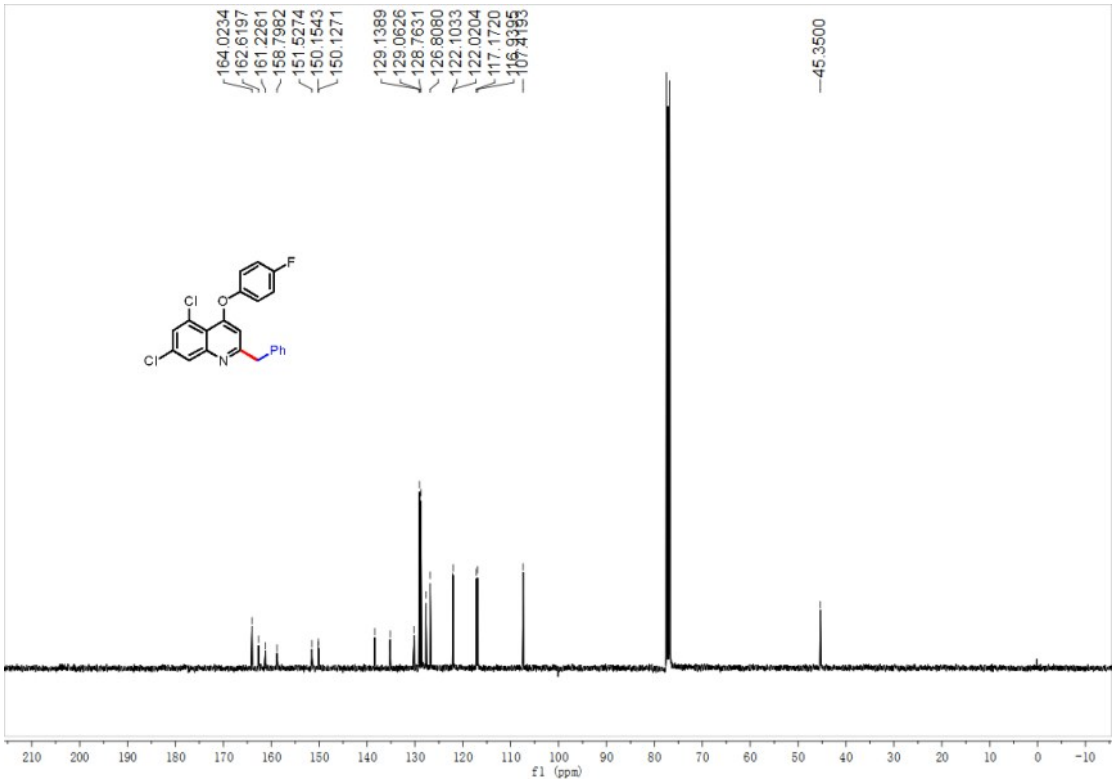
^{13}C NMR spectrum of compound **44**



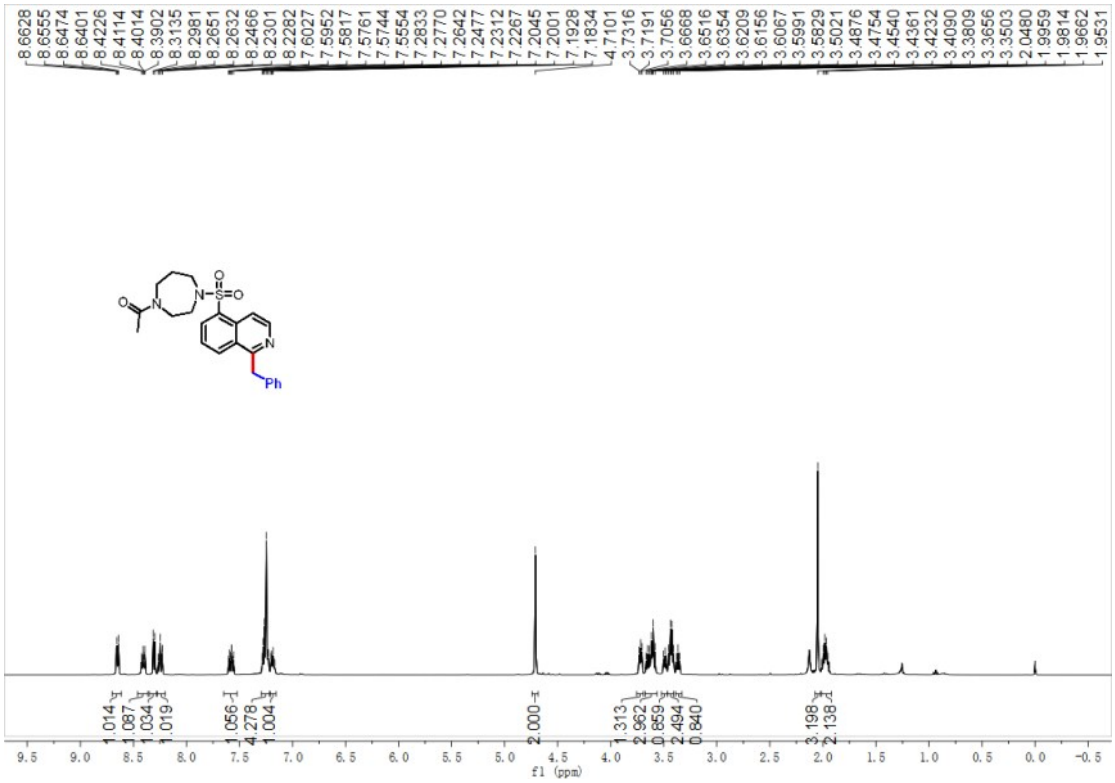
^{1}H NMR spectrum of compound **45**



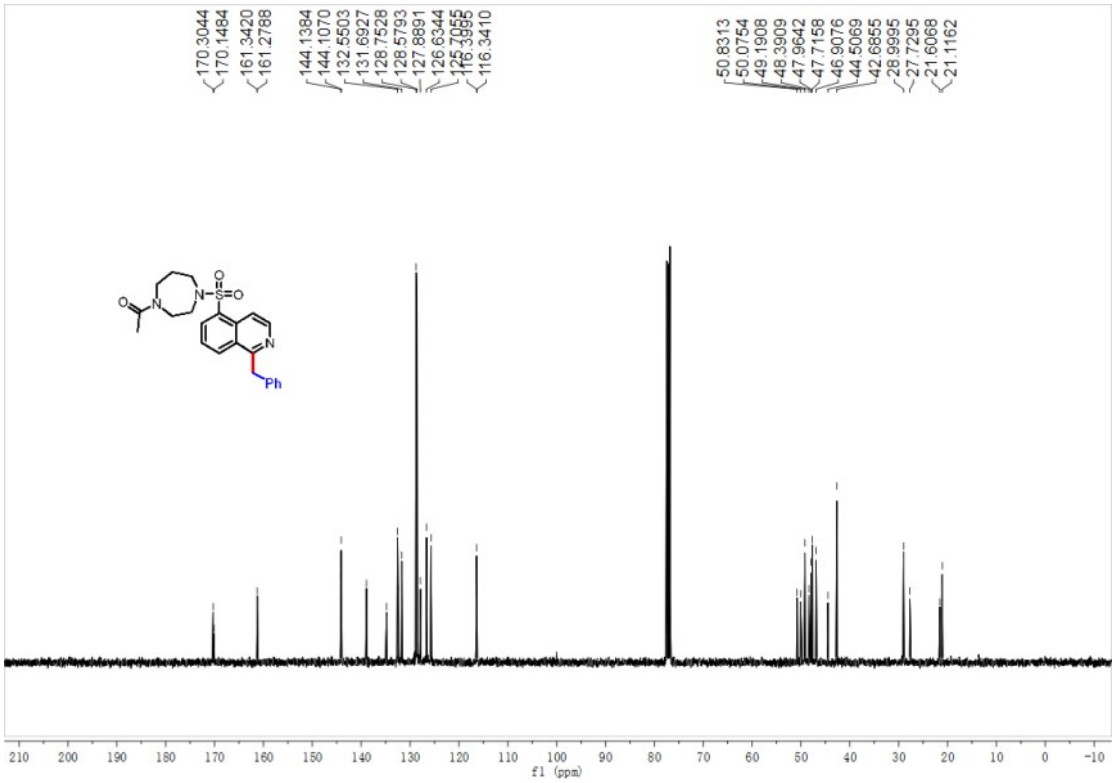
^{13}C NMR spectrum of compound **45**



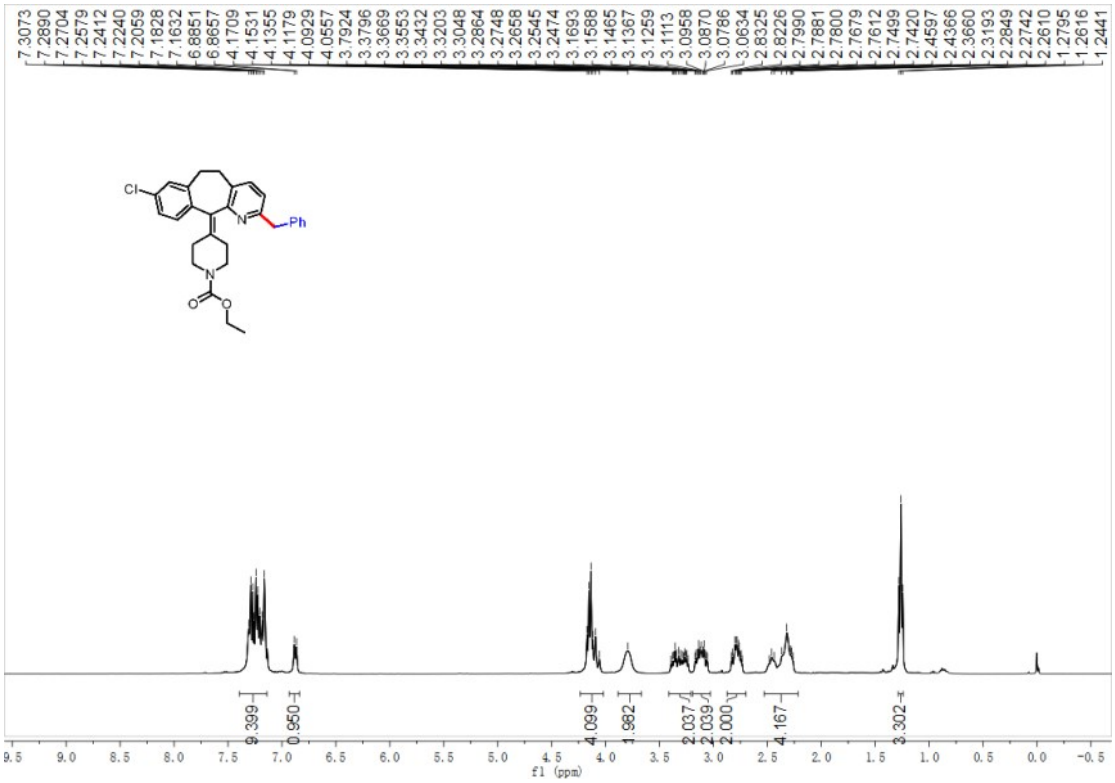
^{1}H NMR spectrum of compound **46**



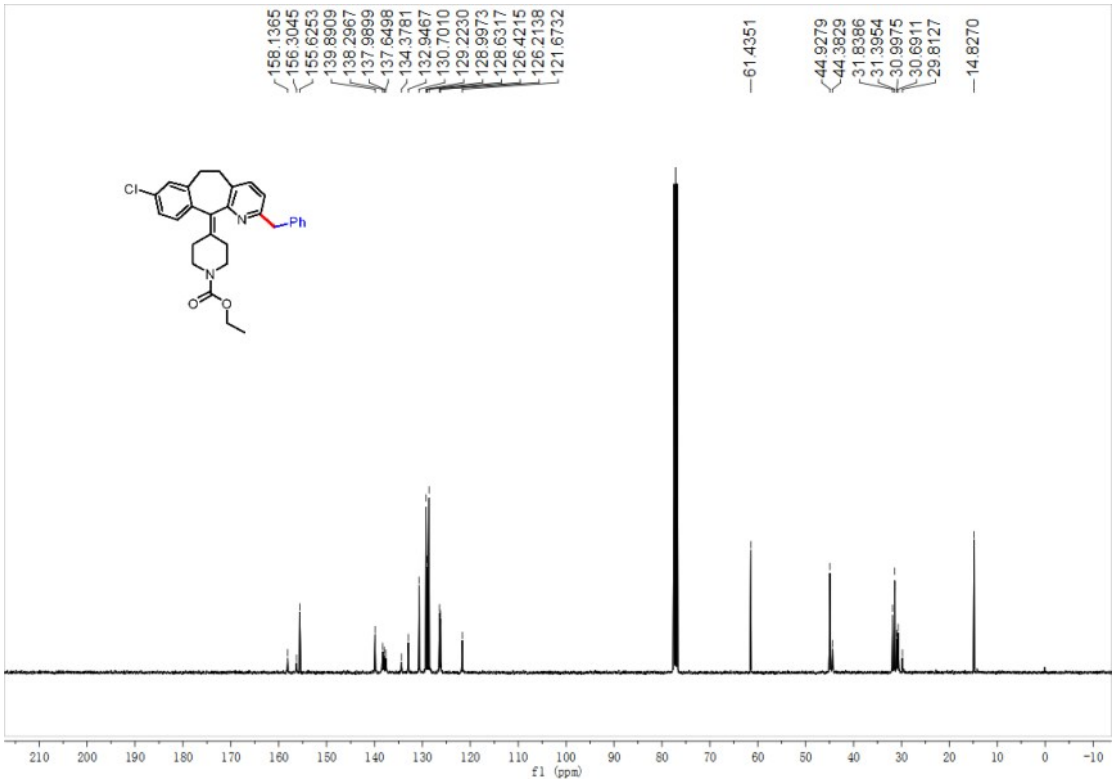
^{13}C NMR spectrum of compound **46**



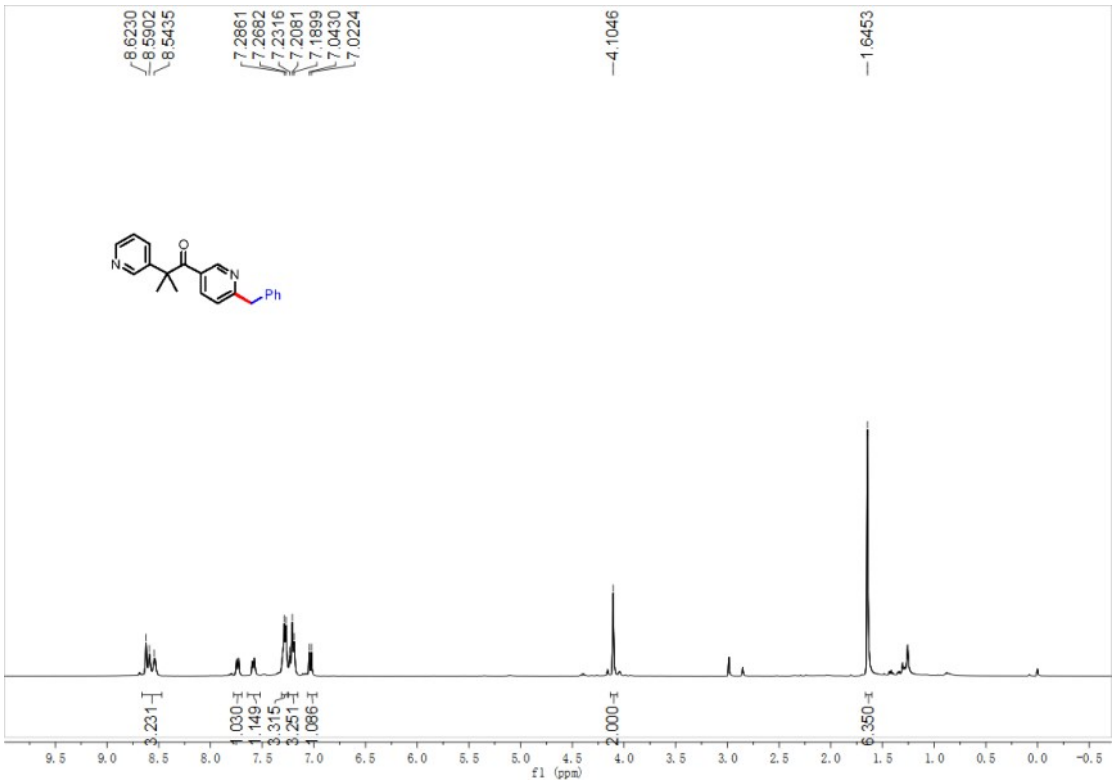
^{1}H NMR spectrum of compound **47**



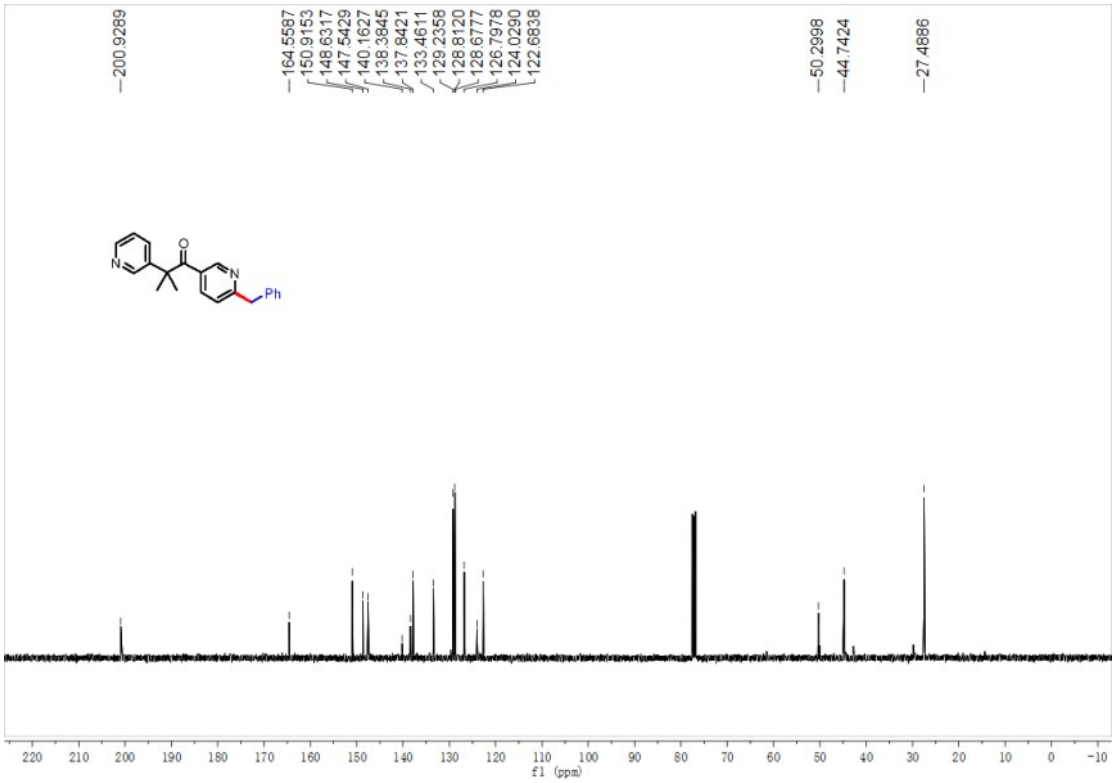
^{13}C NMR spectrum of compound **47**



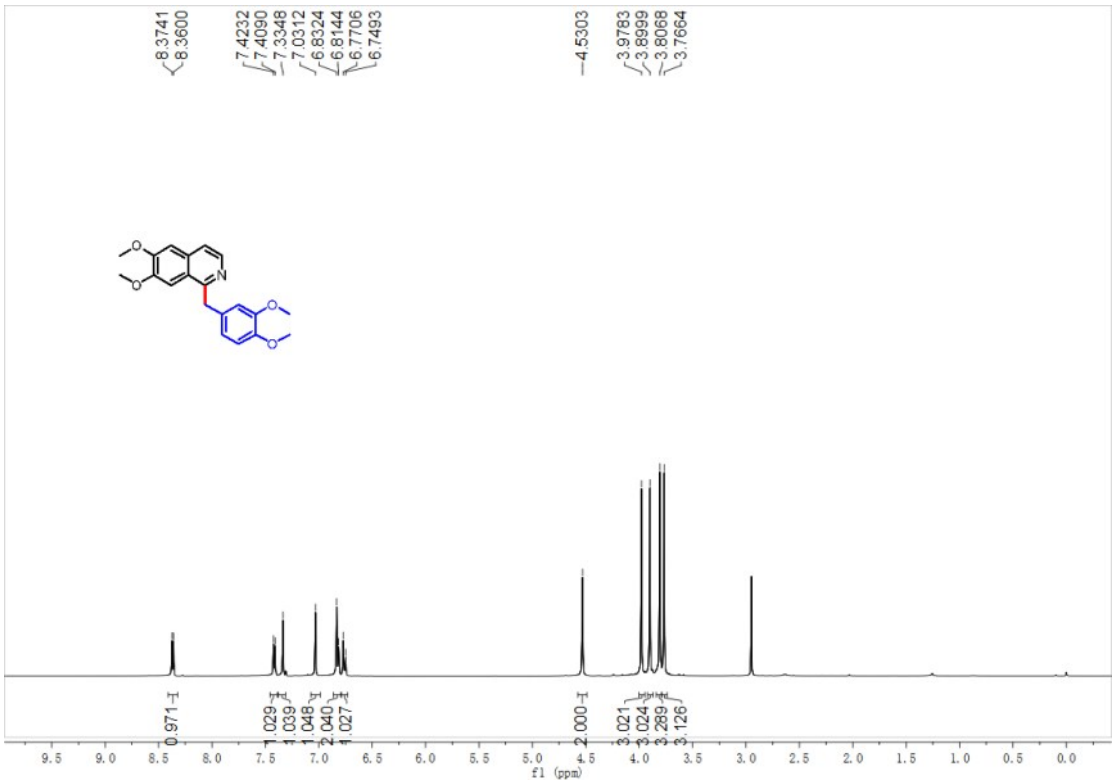
^{1}H NMR spectrum of compound **48**



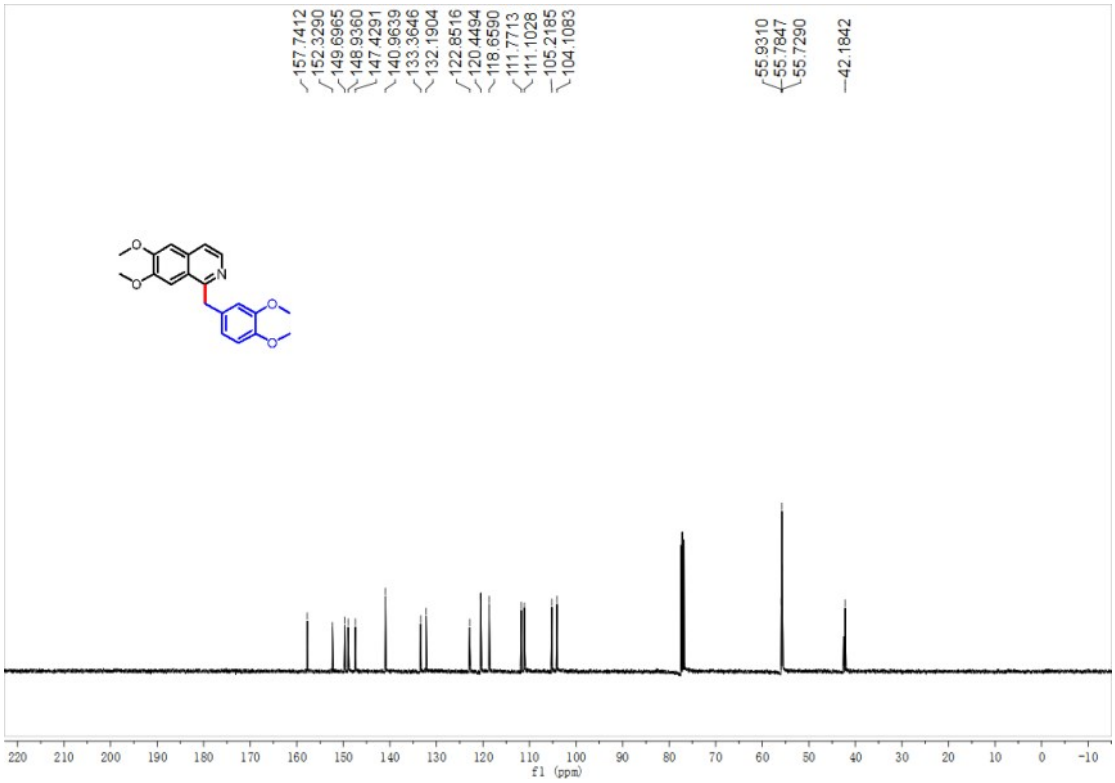
^{13}C NMR spectrum of compound **48**



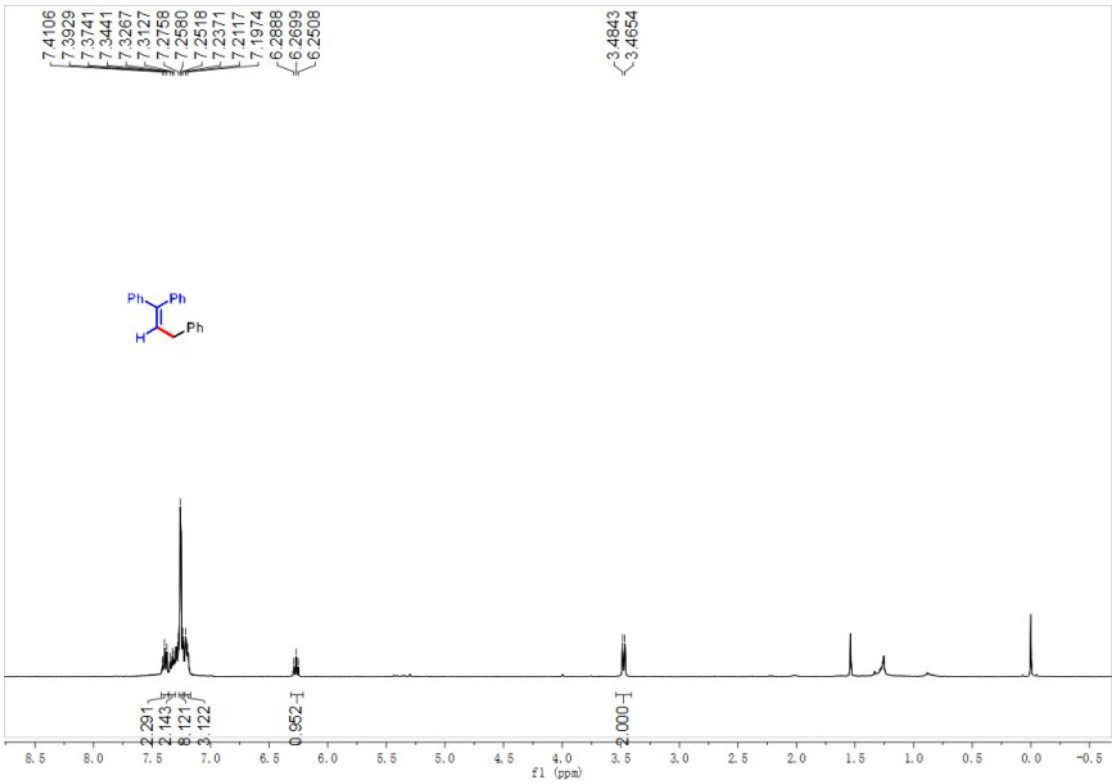
^{1}H NMR spectrum of compound **49**



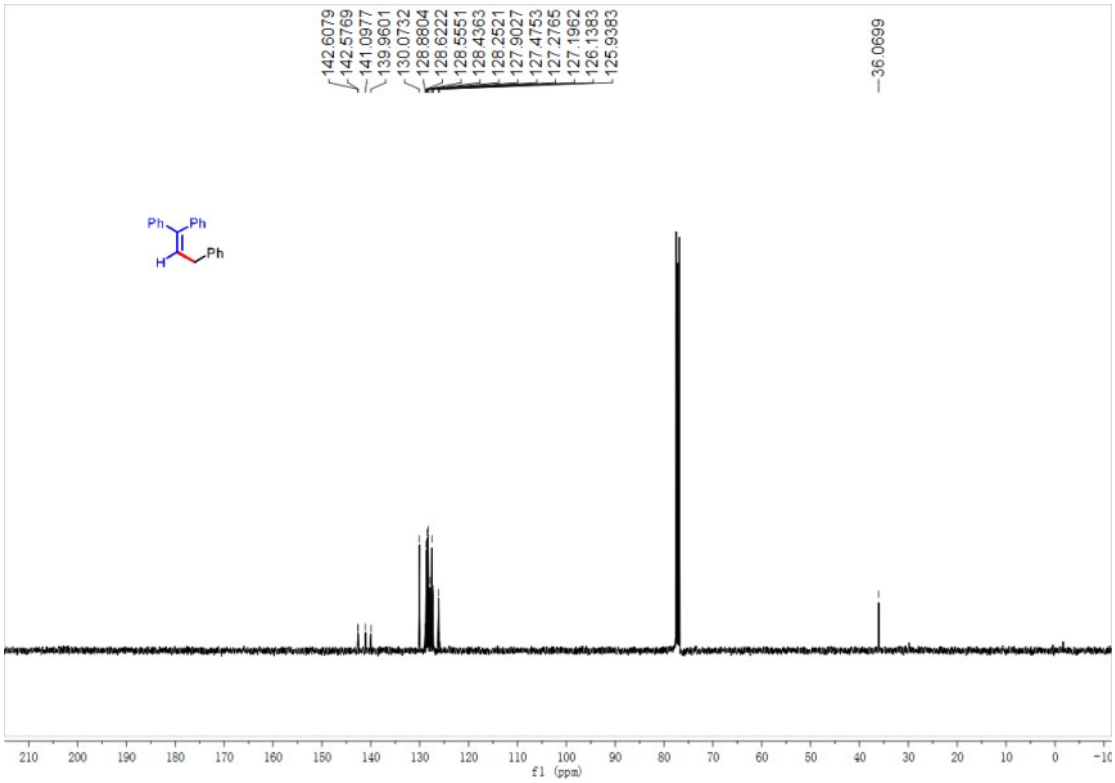
^{13}C NMR spectrum of compound **49**



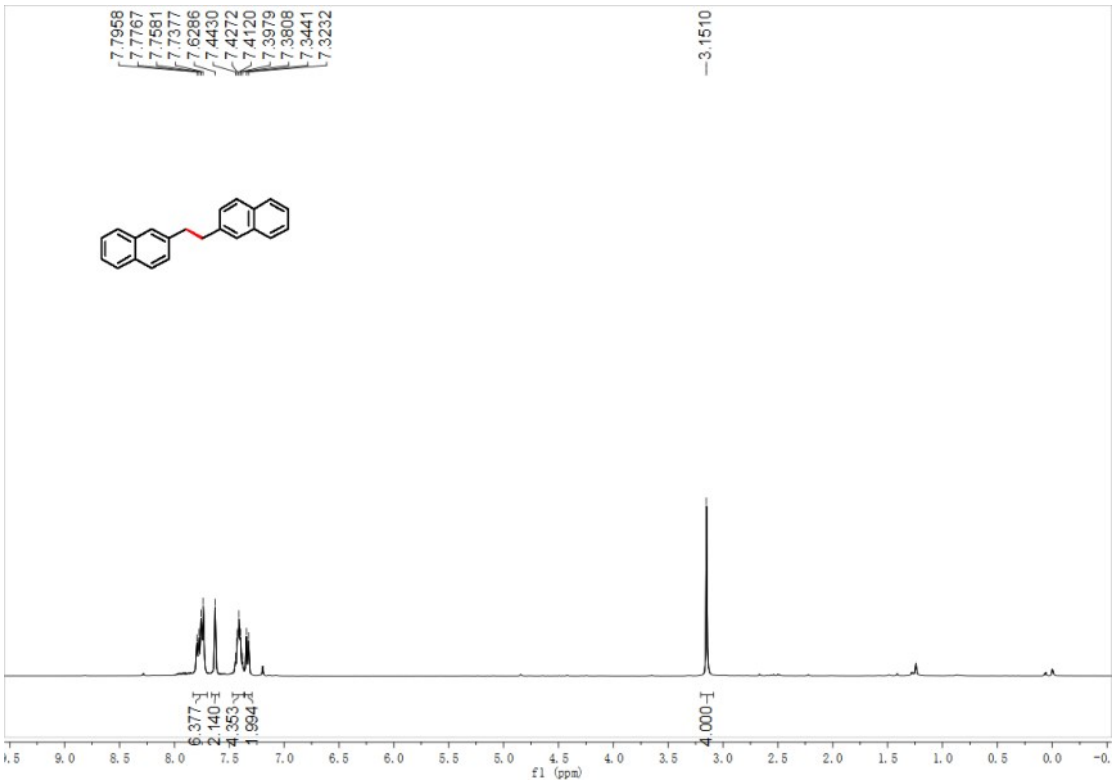
^{1}H NMR spectrum of compound **51**



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



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



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