Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A novel iridium/acid co-catalyzed transfer hydrogenative C(sp^3)-H bond alkylation to access functionalized *N*-heteroaromatics

Table of contents

General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-

NMR and infrared spectra (IR). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 and referenced to 7.26 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated,, all the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), used without further purification.

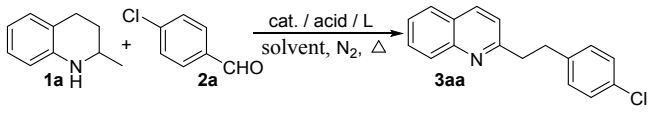
Substrates preparation

9-methyl-1,2,3,4,4a,9,9a,10-octahydroacridine **1h** was unknown compound and prepared via the literature procedures.[1]

Typical procedure for synthesis of 3aa

Under N_2 atmosphere, benzoic acid (50 mol%), $[IrCp^*Cl_2]_2$ (1 mol%), 4-chlorobenzaldehyde **2a** (0.6 mmol), 2-methyl-1,2,3,4-tetrahydroquinoline **1a** (0.5 mmol) and *p*-xylene (1.0 ml) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 150 ^{o}C for 20 h. After cooling down to room temperature, the resulting mixture was extracting with ethyl acetate, washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TCL on silica to give 2-(4-chlorophenethyl)quinoline **3aa**.

Table S1. Optimization of reaction conditions[a]

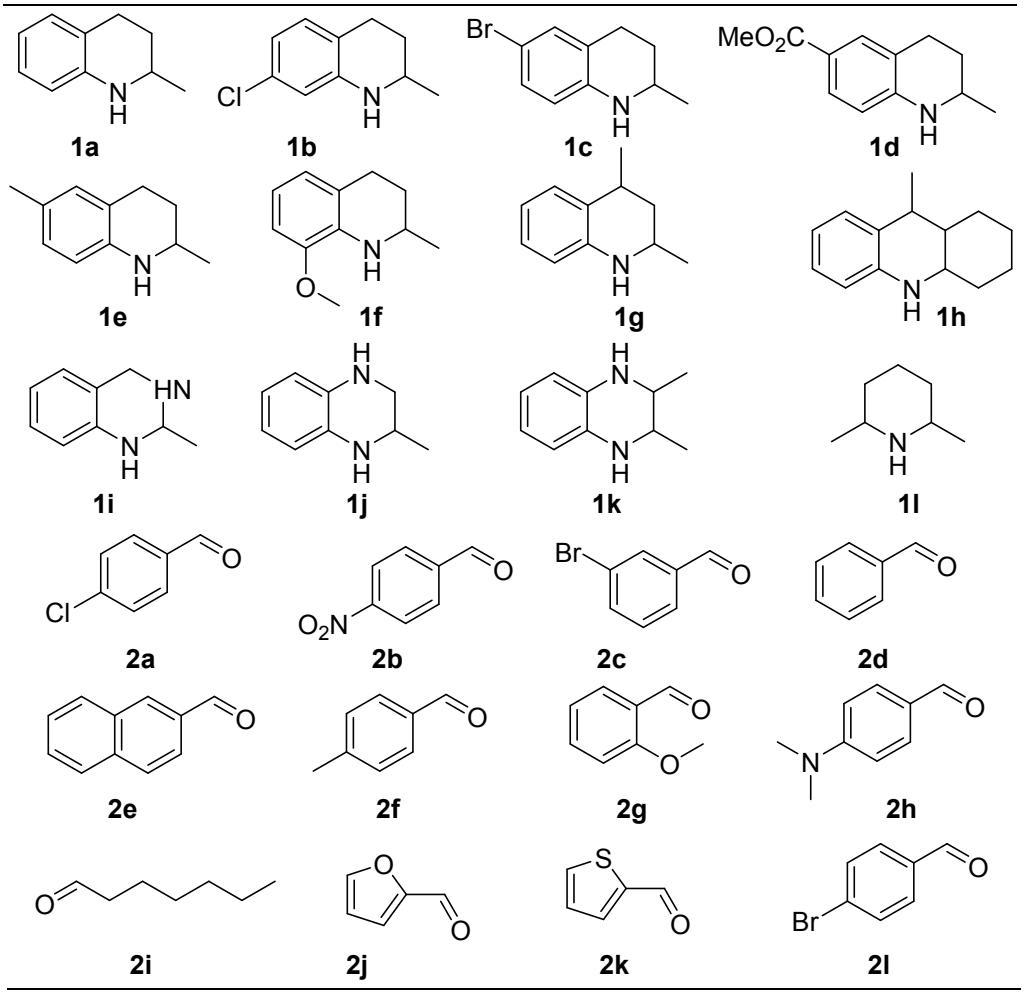


Entry	Catalyst (mol%)	Acid	**3aa** (yield%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$ (1)	-	0
2	$[Cp^*IrCl_2]_2$ (1)	-	39
3	$[Cp^*IrCl_2]_2$ (1)	4-nitrobenzoic acid	75
4	$[IrCl_2COD]_2$ (1)	4-nitrobenzoic acid	53
5	-	4-nitrobenzoic acid	0
6	$[Cp^*IrCl_2]_2$ (1)	CH_3COOH	10
7	$[Cp^*IrCl_2]_2$ (1)	CF_3COOH	13
8	$[Cp^*IrCl_2]_2$ (1)	*p*-TSA[c]	5
9	$[Cp^*IrCl_2]_2$ (1)	DPPA[d]	18
10	$[Cp^*IrCl_2]_2$ (1)	benzoic acid	90
11	$[Cp^*IrCl_2]_2$ (1)	D-CSA [e]	5

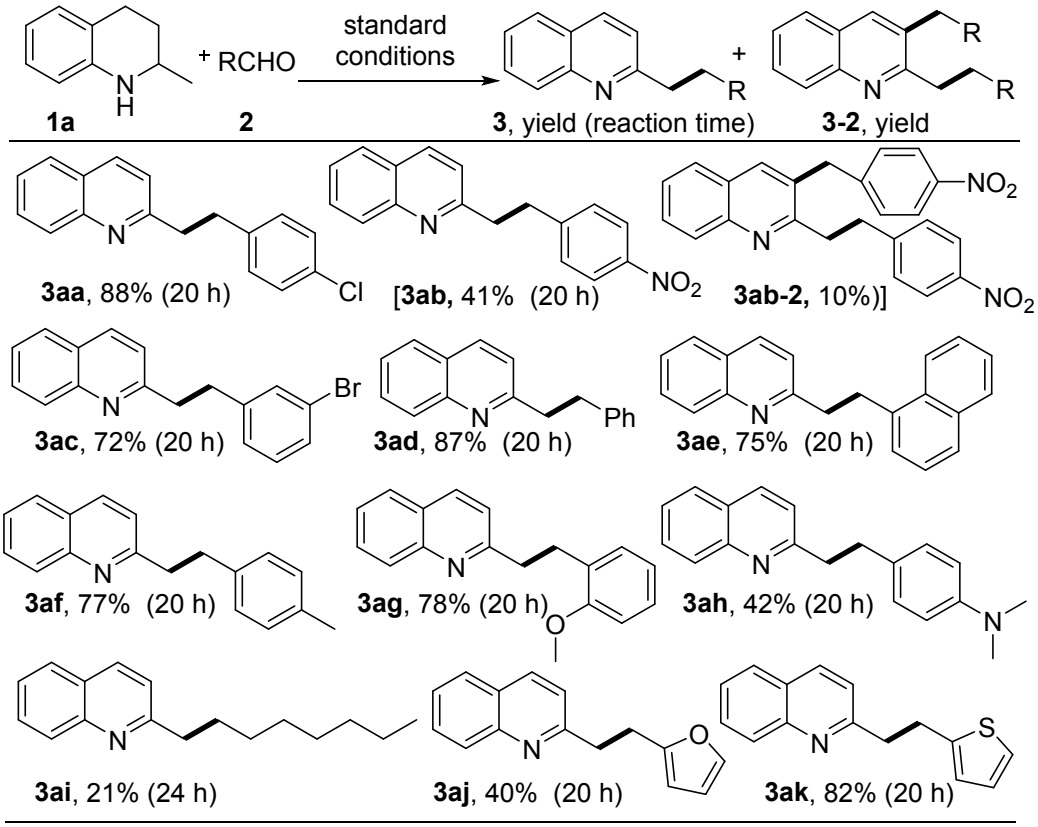
12	$[Cp^*IrCl_2]_2$ (1)	$Sm(OTf)_3$	23
13	$[Cp^*IrCl_2]_2$ (1)	benzoic acid	(trace, 35, 5)[f]
14	$[Cp^*IrCl_2]_2$ (1)	benzoic acid	(65, 88)[g]
15	$[Cp^*IrCl_2]_2$ (1)	benzoic acid	0[h]

[a] Unless otherwise stated, the reaction was performed with **1a** (0.5 mmol), **2a** (0.6 mmol), cat. (as indicated in table S1), acid (50 mol%) in *p*-xylene (1.0 mL) at 150 °C for 20 h under N_2 protection. [b] GC yield by using hexadecane as an internal standard. [c] *p*-TSA: para-toluenesufonic acid. [d] DPPA: diphenylphosphinic acid. [e] D-CSA: D-camphorsulfonic acid. [f] Yields are with respect to DMSO, toluene and t-amyl alcohol used as the solvents, respectively. [g] Yields are with respect to at 140 and 160 °C, respectively. [h] Addition of xantphos or dppf as a ligand(2 mol%).

Scheme S2. Substrates employed for synthesizing 2-alkyl *N*-heteroaromatics (3)

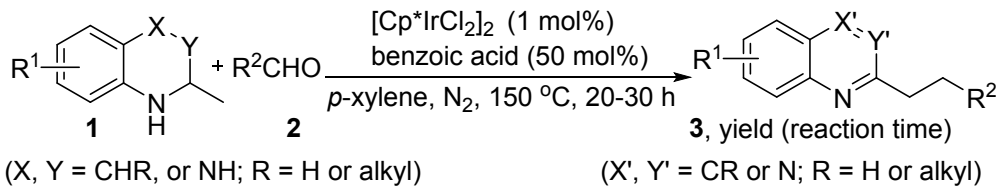


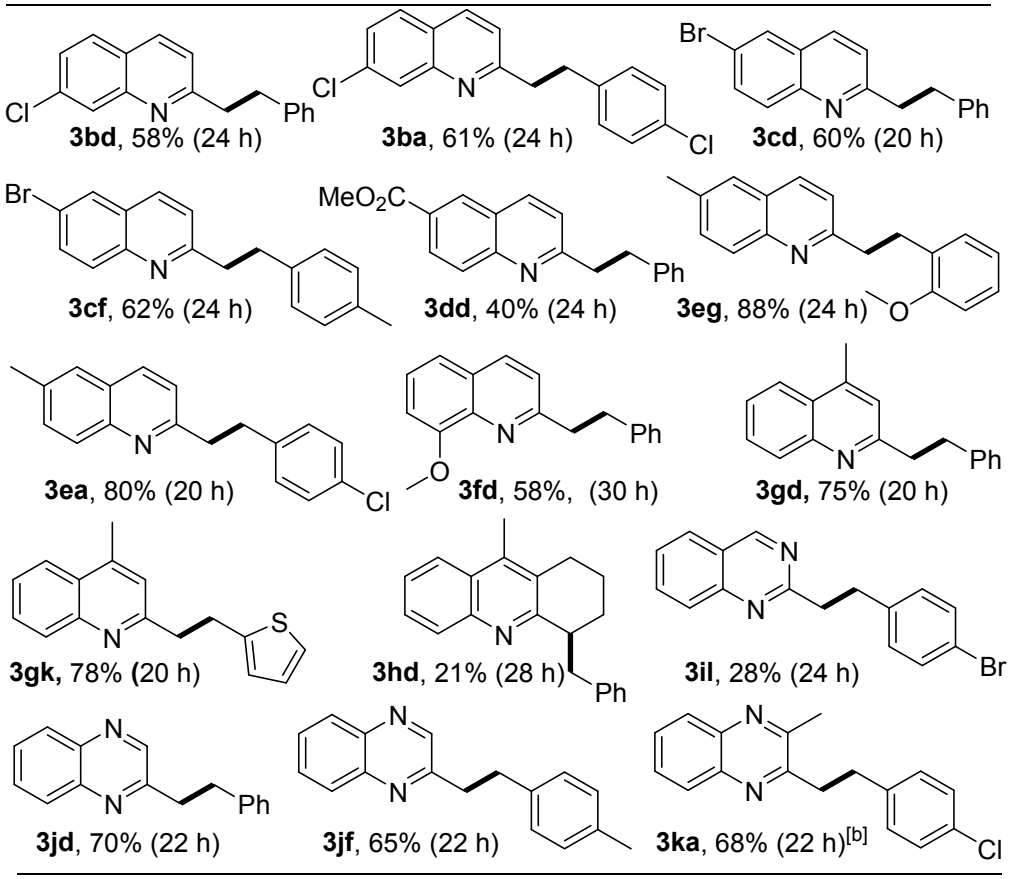
Scheme S2-1. Variation of aldehydes.[a]



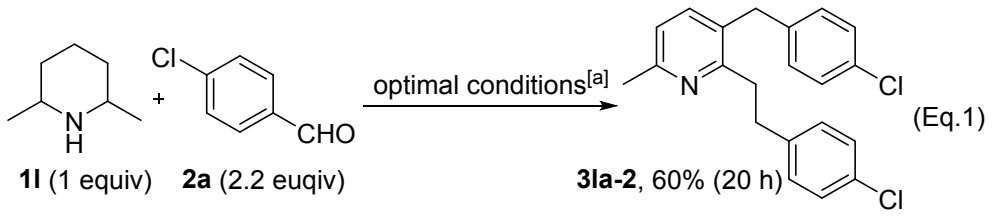
[a] The reaction was performed with **1a** (0.5 mmol), **2** (0.6 mmol), $[IrCp^*Cl_2]_2$ (1 mol%), benzoic acid (50 mol%) in *p*-xylene (1.0 mL) at 150 °C under N_2 protection.

Scheme S2-2. Both variations of cyclic amines and aldehydes.[a]





[a] The reaction was performed with **1** (0.5 mmol), **2** (0.6 mmol), $[IrCp^*Cl_2]_2$ (1 mol%), benzoic acid (50 mol%) in *p*-xylene (1.0 mL) at 150 °C under N_2 protection. [b] The reaction was performed with **1k** (0.6 mmol), **2a** (0.5 mmol), $[IrCp^*Cl_2]_2$ (1 mol%), benzoic acid (50 mol%) in *p*-xylene (1.0 mL) at 150 °C for 22 h under N_2 protection.



[a] The reaction was performed with **1l** (0.5 mmol), **2a** (1.1 mmol), $[IrCp^*Cl_2]_2$ (1 mol%), benzoic acid (50 mol%) in *p*-xylene (1.0 mL) at 150 °C for 20 h under N_2 protection.

Typical time course for the reaction

Under the optimized reaction conditions, the reaction was carried out at different reaction times and the reaction mixture was analyzed by GC using hexadecane as the internal standard.

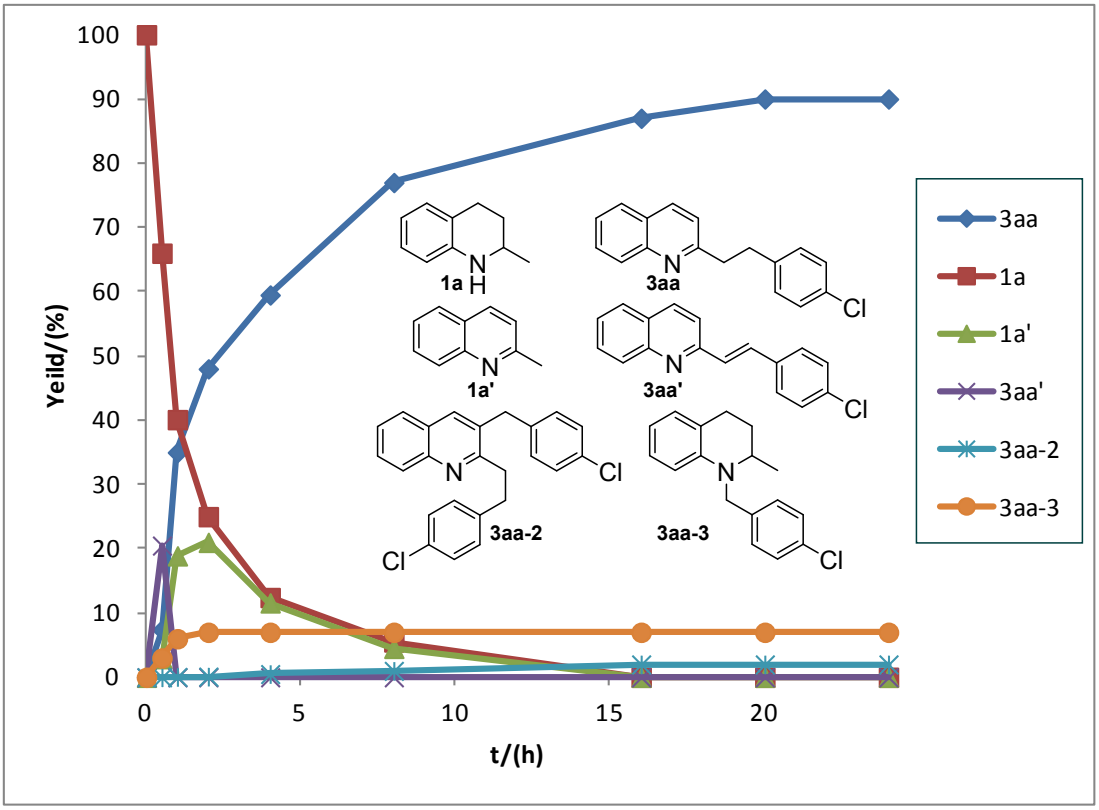
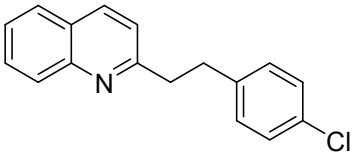


Figure S1, Representative time course of the transfer hydrogenative C(sp3)-H bond alkylation of 2-methyl-1,2,3,4-tetrahydroquinoline(**1a**) with aldehyde to **3aa** under the optimized reaction condition. (♦)**3aa**, (■)**1a**, (▲)**1a'**, (x)**3aa'**, (※)**3aa-2**, (●)**3aa-3**.

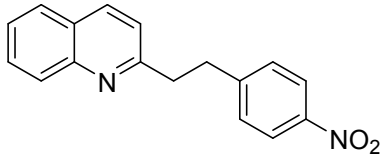
Analytic data of the obtained compounds

(1)2-(4-chlorophenethyl)quinoline **(3aa)**[2]



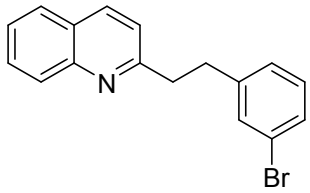
Pale yellow oil liquid, (117.5 mg, 88% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 9.9 Hz, 3H), 3.26-3.19 (m, 2H), 3.14-3.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.30, 148.00, 139.97, 136.31, 131.74, 129.91, 129.51, 128.87, 128.49, 127.59, 126.84, 125.91, 121.52, 40.67, 35.09. IR (KBr): 3050, 2925, 2857, 1603, 1563, 1496, 1429, 1092, 822, 756 cm^{-1}. MS (EI, m/z): 267.07 $[M]^+$.

(2) 2-(4-nitrophenethyl)quinoline **(3ab)**[3]



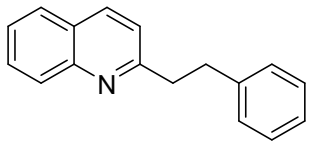
White solid, (57.0 mg, 41% yeild), m.p: 101-102°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 3.28-3.16 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.46, 149.41, 147.94, 146.47, 136.51, 129.64, 129.37, 128.81, 127.60, 126.86, 126.08, 123.64, 121.39, 39.92, 35.30. IR (KBr): 3055, 2923, 2852, 1596, 1510, 1426, 1340, 825, 756 cm^{-1}. MS (EI, m/z): 278.05 $[M]^+$.

(3) 2-(3-bromophenethyl)quinoline **(3ac)**



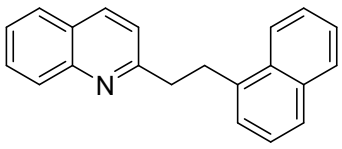
Pale yellow oil liquid, (111.9 mg, 72% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 9.4 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.67-7.58 (m, 1H), 7.46-7.39 (m, 1H), 7.34 (s, 1H), 7.24 (dt, *J* = 7.2, 1.7 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.10-7.01 (m, 2H), 3.23-3.16 (m, 2H), 3.10-3.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.17, 147.98, 143.91, 136.36, 131.62, 129.96, 129.51, 129.16, 128.88, 127.57, 127.22, 126.85, 125.93, 122.46, 121.47, 40.55, 35.36. IR (KBr): 3052, 2924, 2855, 1595, 1564, 1502, 1425, 822, 775, 755 cm^{-1}. MS (EI, m/z): 311.01 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{15}BrN$ $[M+H]^+$: 312.0382; found: 312.0378.

(4) 2-phenethylquinoline **(3ad)** [2]



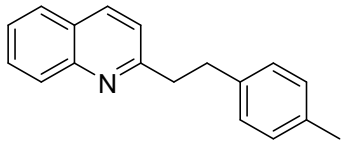
Clear oil liquid, (101.3 mg, 87% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.71-7.64 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31-7.13 (m, 6H), 3.32-3.25 (m, 2H), 3.19-3.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.83, 148.02, 141.56, 136.24, 129.43, 128.90, 128.55, 128.43, 127.56, 126.85, 126.04, 125.83, 121.58, 40.98, 35.94. IR(KBr): 3056, 3030, 2924, 2855, 1600, 1562, 1500, 1427, 820, 749, 698 cm^{-1}. MS (EI, m/z): 233.07 $[M]^+$.

(5) 2-(2-(naphthalen-1-yl)ethyl)quinoline **(3ae)**



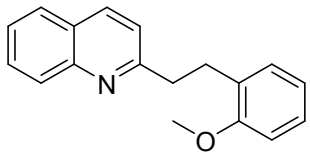
Pale yellow oil liquid, (106.1 mg, 75% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.88-7.80 (m, 1H), 7.77-7.65 (m, 3H), 7.55-7.42 (m, 3H), 7.39-7.30 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 3.67-3.56 (m, 2H), 3.47-3.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.96, 148.11, 137.65, 136.29, 133.99, 131.93, 129.50, 128.98, 128.90, 127.62, 126.92, 126.19, 126.01, 125.89, 125.65, 125.58, 123.84, 121.64, 40.09, 33.00. IR (KBr): 3050, 2928, 2861, 1597, 1563, 1503, 1427, 826, 774 cm^{-1}. MS (EI, m/z): 283.11 $[M]^+$. HRMS (ESI): Calcd. for $C_{21}H_{18}N$ $[M+H]^+$: 284.1434; found: 284.1437.

(6) 2-(4-methylphenethyl)quinoline **(3af)** [2]



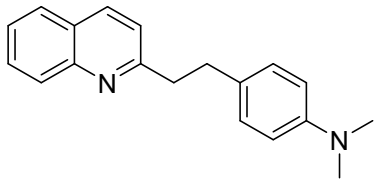
Clear oil liquid, (95.1 mg, 77% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.65-7.57 (m, 1H), 7.43-7.37 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.03 (dd, *J* = 22.9, 8.0 Hz, 4H), 3.24-3.16 (m, 2H), 3.08-3.00 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.94, 147.90, 138.42, 136.31, 135.46, 129.45, 129.10, 128.81, 128.40, 127.54, 126.83, 125.83, 121.59, 41.07, 35.53, 21.03. IR (KBr): 3049, 3013, 2923, 2857, 1602, 1563, 1507, 1427, 819. 749 cm^{-1}. MS (EI, m/z): 247.00 $[M]^+$.

(7) 2-(2-methoxyphenethyl)quinoline **(3ag)**[4]



Pale yellow oil liquid, (102.5 mg, 78% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.56 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.39-7.32 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.11-7.02 (m, 2H), 6.74 (t, *J* = 7.5 Hz, 2H), 3.69 (s, 3H), 3.20-3.13 (m, 2H), 3.08-3.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.56, 157.57, 147.97, 136.06, 130.03, 129.88, 129.31, 128.92, 127.52, 127.34, 126.82, 125.70, 121.67, 120.45, 110.25, 55.25, 39.31, 30.67. IR (KBr): 3053, 3005, 2930, 2838, 1596, 1496, 1460, 1433, 1241, 1110, 1028, 823, 750 cm^{-1}. MS (EI, m/z): 262.96 $[M]^+$.

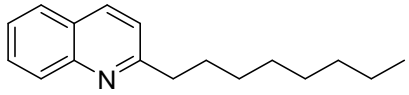
(8) N,N-dimethyl-4-(2-(quinolin-2-yl)ethyl)aniline **(3ah)**



Pale yellow solid, (58.0 mg, 42% yeild), m.p: 66-67°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.73-7.65

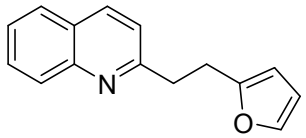
(m, 1H), 7.52-7.43 (m, 1H), 7.24 (d, J = 8.3 Hz, 1H), 7.13 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 3.31-3.21 (m, 2H), 3.11-3.02 (m, 2H), 2.90 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.28, 149.17, 147.89, 136.24, 129.69, 129.40, 129.12, 128.80, 127.53, 126.81, 125.76, 121.67, 113.05, 41.39, 40.90, 35.08. IR (KBr): 3048, 2924, 2853, 2799, 1607, 1560, 1517, 1342, 1219, 1159, 817, 752 cm^{-1}. MS (EI, m/z): 276.15 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699; found: 277.1698.

(9) 2-octylquinoline **(3ai)**[5]



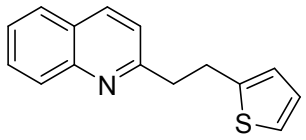
Clear oil liquid, (25.3 mg, 21% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.1 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 2.97(t, J = 8.0 Hz, 2H), 1.81 (dt, J = 15.5, 7.6 Hz, 1H), 1.50-1.19 (m, 6H), 0.87 (t, J = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.13, 147.84, 136.23, 129.34, 128.77, 127.47, 126.72, 125.65, 121.37, 39.35, 31.85, 30.08, 29.58, 29.49, 29.22, 22.65, 14.09. IR (KBr): 3053, 2925, 2856, 1604, 1563, 1503, 1460, 1428, 823, 750 cm^{-1}. MS (EI, m/z): 241.03 $[M]^+$.

(10) 2-(2-(furan-2-yl)ethyl)quinoline **(3aj)**



Pale yellow oil liquid, (44.6 mg, 40% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.93 (m, 2H), 7.71 (d, J = 8.1 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.25 (s, 1H), 7.17 (d, J = 8.8 Hz, 1H), 6.19 (s, 1H), 5.92 (s, 1H), 3.27 (t, J = 7.7 Hz, 2H), 3.12 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.23, 155.12, 147.90, 140.98, 136.34, 129.46, 128.85, 127.52, 126.85, 125.88, 121.34, 110.16, 105.40, 37.39, 27.90. IR (KBr): 3053, 2923, 2854, 1598, 1563, 1503, 1429, 823, 734 cm^{-1}. MS (EI, m/z): 223.10 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{14}NO$ $[M+H]^+$: 224.1070; found: 224.1072.

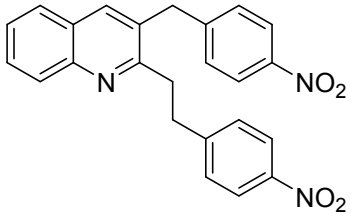
(11) 2-(2-(thiophen-2-yl)ethyl)quinoline **(3ak)**[6]



Pale yellow oil liquid, (98.0 mg, 82% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.72-7.64 (m, 1H), 7.53-7.43 (m, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.09 (dd, J = 5.1, 1.1 Hz, 1H), 6.89 (dd, J = 5.1, 3.4 Hz, 1H), 6.81 (dd, J = 3.4, 0.8 Hz, 1H), 3.43-3.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.07, 147.96, 144.24, 136.34, 129.50, 128.89, 127.57, 126.89, 126.76, 125.92, 124.61, 123.23, 121.54, 41.00, 29.72. IR (KBr): 3054, 2921, 2851,

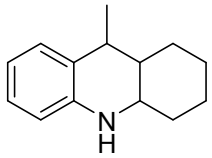
1600, 1562, 1502, 1431, 823, 748, 693 cm^{-1}. MS (EI, m/z): 239.04 $[M]^+$.

(12) 3-(4-nitrobenzyl)-2-(4-nitrophenethyl)quinoline **(3ab-2)**



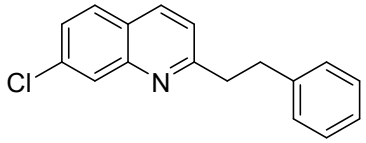
White solid, (20.6 mg, 10% yeild); ^1H NMR (400 MHz, CDCl3) δ 8.21-8.05 (m, 5H), 7.82 (s, 1H), 7.79-7.69 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 7.3 Hz, 2H), 4.20 (s, 2H), 3.34-3.25 (m, 2H), 3.23-3.14 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 159.28, 149.53, 146.93, 146.68, 146.50, 137.24, 133.57, 130.53, 129.73, 129.52, 129.35, 128.46, 127.20, 127.07, 126.69, 124.03, 123.65, 38.52, 36.28, 34.38. MS (EI, m/z): 413.10 $[M]^+$. HRMS (ESI): Calcd. for $C_{24}H_{20}N_3O_4$ $[M+H]^+$: 414.1448; found: 414.1453.

(13) 9-methyl-1,2,3,4,4a,9,9a,10-octahydroacridine **(1h)**



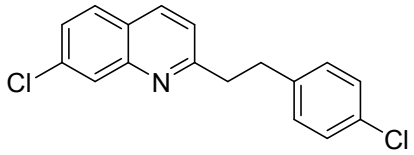
Clear oil liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 6.32 (d, *J* = 7.9 Hz, 1H), 3.59 (s, 1H), 3.38 (brs, 1H), 3.05-2.88 (m, 1H), 1.70-1.45 (m, 5H), 1.43-1.29 (m, 2H), 1.26-1.09 (m, 4H), 1.02-0.86 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.11, 126.73, 126.58, 123.88, 116.33, 112.49, 51.12, 39.71, 35.00, 32.34, 25.69, 20.33, 19.93, 16.15. IR (KBr): 3399, 3051, 3023, 2929, 2853, 1606, 1491, 1451, 1306, 1248, 744 cm^{-1}. MS (EI, m/z): 201.15 $[M]^+$. HRMS (ESI): Calcd. for $C_{14}H_{20}N$ $[M+H]^+$: 202.1590; found: 202.1587.

(14) 7-chloro-2-phenethylquinoline **(3bd)**



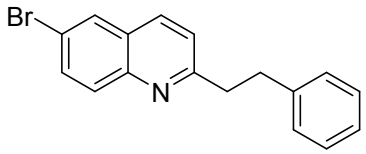
Pale yellow solid, (77.4 mg, 58% yeild), m.p: 94-95°C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.33 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.21-7.05 (m, 6H), 3.21-3.14 (m, 2H), 3.09-3.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.96, 148.36, 141.36, 135.96, 135.22, 128.74, 128.52, 128.45, 128.00, 126.84, 126.09, 125.16, 121.81, 40.85, 35.66. IR (KBr): 3058, 3031, 2923, 2855, 1603, 1557, 1492, 1449, 1412, 863, 846, 698, 672 cm^{-1}. MS (EI, m/z): 267.00 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{15}ClN$ $[M+H]^+$: 268.0888; found: 268.0888.

(15) 7-chloro-2-(4-chlorophenethyl)quinoline **(3ba)**



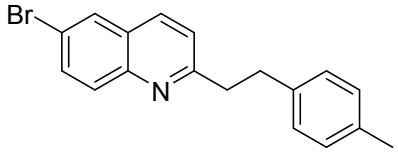
White solid, (91.8 mg, 61% yeild), m.p: 99-100°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.43 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.25-7.08 (m, 5H), 3.27-3.20 (m, 2H), 3.15-3.08 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.44, 148.32, 139.78, 136.04, 135.30, 131.79, 129.87, 128.75, 128.51, 127.97, 126.93, 125.15, 121.76, 40.56, 34.81. IR (KBr): 3054, 2924, 2856, 1607, 1492, 1372, 838, 770 cm^{-1}. MS (EI, m/z): 301.03 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{14}Cl_2N$ $[M+H]^+$: 302.0498; found: 302.0500.

(16) 6-bromo-2-phenethylquinoline **(3cd)**[7]



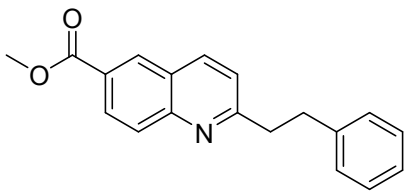
White solid, (93.3 mg, 60% yeild), m.p: 106-107°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.87 (m, 3H), 7.74 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.31-7.14 (m, 6H), 3.31-3.23 (m, 2H), 3.19-3.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.29, 146.53, 141.31, 135.19, 132.83, 130.64, 129.57, 128.51, 128.45, 127.94, 126.09, 122.45, 119.56, 77.39, 77.07, 76.75, 40.87, 35.68. IR (KBr): 3058, 3031, 2923, 2855, 1589, 1486, 1452, 887, 816, 742, 695 cm^{-1}. MS (EI, m/z): 310.95 $[M]^+$.

(17) 6-bromo-2-(4-methylphenethyl)quinoline **(3cf)**



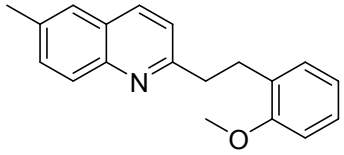
White solid, (100.7 mg, 62% yeild), m.p: 109-110°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.78 (m, 3H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.01 (q, *J* = 7.9 Hz, 4H), 3.21-3.11 (m, 2H), 3.07-2.96 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.43, 146.53, 138.22, 135.53, 135.17, 132.81, 130.64, 129.56, 129.13, 128.38, 127.94, 122.46, 119.53, 41.01, 35.28, 21.04. IR (KBr): 3044, 2921, 2854, 1592, 1551, 1484, 1450, 878, 823 cm^{-1}. MS (EI, m/z): 325.05 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{17}BrN$ $[M+H]^+$: 326.0539; found: 326.0540.

(18) methyl 2-phenethylquinoline-6-carboxylate **(3dd)**



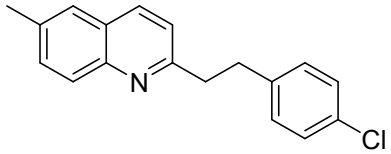
Pale yellow solid, (58.2 mg, 40% yeild), m.p: 104-105°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 1.3 Hz, 1H), 8.19 (dd, *J* = 8.8, 1.7 Hz, 1H), 8.02 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.24-7.07 (m, 6H), 3.89 (s, 3H), 3.28-3.17 (m, 2H), 3.15-3.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 164.31, 149.87, 141.27, 137.37, 130.74, 129.16, 129.00, 128.50, 128.45, 127.41, 126.11, 125.94, 122.41, 52.35, 41.04, 35.62. IR (KBr): 3074, 3028, 2959, 2927, 2857, 1714, 1595, 1450, 1275, 1188, 1090, 803, 755, 700 cm^{-1}. MS (EI, m/z): 291.14 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332; found: 292.1336.

(19) 2-(2-methoxyphenethyl)-6-methylquinoline **(3eg)**



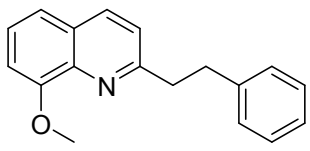
Pale yellow oil liquid, (121.8 mg, 88% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.1 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.11-6.99 (m, 3H), 6.73 (t, *J* = 8.1 Hz, 2H), 3.67 (s, 3H), 3.19-3.09 (m, 2H), 3.08 -2.97 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.58, 157.57, 146.53, 135.44, 135.39, 131.53, 130.03, 129.95, 128.58, 127.30, 126.83, 126.43, 121.62, 120.44, 110.24, 55.25, 39.23, 30.72, 21.50. IR (KBr): 3056, 3024, 2928, 2838, 1598, 1494, 1459, 1243, 1111, 1031, 830, 752 cm^{-1}. MS (EI, m/z): 277.08 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539; found: 278.1537.

(20) 2-(4-chlorophenethyl)-6-methylquinoline **(3ea)**



Pale yellow solid, (112.4 mg, 80% yeild), m.p: 74-75°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.1 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 6.4 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 3H), 3.25-3.17 (m, 2H), 3.14-3.04 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.32, 146.54, 140.02, 135.68, 131.74, 131.69, 129.90, 128.51, 128.46, 126.84, 126.45, 121.48, 40.61, 35.18, 21.50. IR (KBr): 3035, 2955, 2922, 2856, 1632, 1598, 1491, 1446, 1090, 828 cm^{-1}. MS (EI, m/z): 281.05 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{17}ClN$ $[M+H]^+$: 282.1044; found: 282.1042.

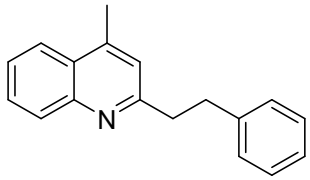
(21) 8-methoxy-2-phenethylquinoline **(3fd)**[8]



Yellow oil liquid, (76.2 mg, 58% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.24-7.15 (m, 5H),

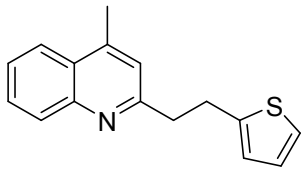
7.14-7.07 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.01 (s, 3H), 3.34-3.24 (m, 2H), 3.12-3.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.97, 155.03, 141.60, 139.78, 136.26, 128.54, 128.40, 127.97, 125.98, 125.91, 122.00, 119.51, 107.86, 56.15, 40.96, 36.09. IR (KBr): 3055, 3026, 2926, 2845, 1602, 1562, 1499, 1462, 1257, 1107, 800, 750, 702 cm^{-1}. MS (EI, m/z): 263.03 $[M]^+$.

(22) 4-methyl-2-phenethylquinoline **(3gd)**[9]



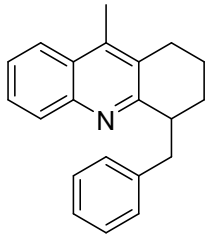
Pale yellow oil liquid, (92.6 mg, 75% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.58-7.48 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.20-7.11 (m, 4H), 7.10-7.02 (m, 1H), 6.93 (s, 1H), 3.153.07 (m, 2H), 3.06-2.98 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.50, 147.85, 144.31, 141.72, 129.43, 129.13, 128.56, 128.44, 126.92, 126.03, 125.60, 123.68, 122.28, 40.95, 35.97, 18.66. IR (KBr): 3061, 3027, 2952, 2923, 2856, 1602, 1561, 1507, 1496, 757, 699 cm^{-1}. MS (EI, m/z): 246.98 $[M]^+$.

(23) 4-methyl-2-(2-(thiophen-2-yl)ethyl)quinoline **(3gk)**



Pale yellow oil liquid, (98.6 mg, 78% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 5.3 Hz, 2H), 6.90 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.83 (d, *J* = 3.3 Hz, 1H), 3.43-3.34 (m, 2H), 3.34-3.25 (m, 2H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.71, 147.72, 144.51, 144.37, 129.36, 129.19, 126.95, 126.73, 125.68, 124.53, 123.66, 123.17, 122.22, 40.91, 29.73, 18.67. IR (KBr): 3064, 2920, 2852, 1602, 1560, 1507, 1442, 757, 694 cm^{-1}. MS (EI, m/z): 253.01 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{16}NS$ $[M+H]^+$: 254.0998; found: 254.1000.

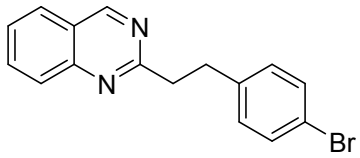
(24) 4-benzyl-9-methyl-1,2,3,4-tetrahydroacridine **(3hd)**



Pale yellow oil liquid, (30.1 mg, 21% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.3 Hz,

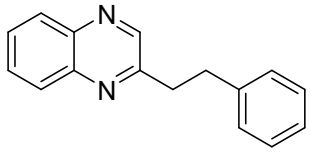
1H), 7.37-7.26 (m, 4H), 7.26-7.16 (m, 1H), 3.72 (dd, *J* = 13.6, 4.0 Hz, 1H), 3.46-3.31 (m, 1H), 3.00-2.71 (m, 3H), 2.57 (s, 3H), 2.08-1.91 (m, 1H), 1.90-1.71 (m, 2H), 1.71-1.56 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.81, 141.13, 129.46, 129.27, 128.67, 128.23, 128.05, 126.86, 125.84, 125.46, 123.29, 43.82, 41.12, 27.40, 26.11, 19.81, 13.74. IR (KBr): 3062, 3025, 2928, 2860, 1575, 1494, 1450, 752, 699 cm^{-1}. MS (EI, m/z): 287.15 $[M]^+$. HRMS (ESI): Calcd. for $C_{21}H_{22}N$ $[M+H]^+$: 288.1747; found: 288.1751.

(25) 2-(4-bromophenethyl)quinazoline **(3il)**



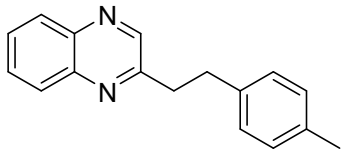
Pale yellow solid, (43.7 mg, 28% yeild), m.p: 97-98°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 3.46-3.39 (m, 2H), 3.27-3.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.30, 160.47, 150.35, 140.49, 134.16, 131.43, 130.29, 127.92, 127.19, 127.14, 123.18, 119.74, 41.23, 34.05. IR (KBr): 3026, 2961, 2925, 2855, 1617, 1578, 1485, 1404, 813, 758 cm^{-1}. MS (EI, m/z): 312.05 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{14}BrN_2$ $[M+H]^+$: 313.0335; found: 313.0335.

(26) 2-phenethylquinoxaline **(3jd)** [2]



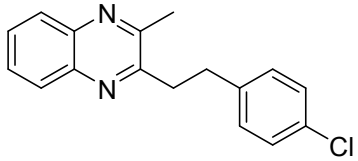
Brownish red oil liquid, (81.9 mg, 70% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.86-7.60 (m, 2H), 7.40-7.11 (m, 5H), 3.39-3.28 (m, 2H), 3.25-3.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.46, 145.82, 142.27, 141.30, 140.77, 130.00, 129.24, 129.10, 128.91, 128.57, 128.49, 126.30, 38.13, 35.29. IR (KBr): 3061, 3025, 2925, 2856, 1605, 1558, 1492, 1451, 758, 698 cm^{-1}. MS (EI, m/z): 233.97 $[M]^+$.

(27) 2-(4-methylphenethyl)quinoxaline **(3jf)**[4]



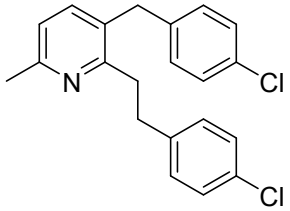
Brownish solid, (80.6 mg, 65% yeild), m.p: 65-66°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.82-7.66 (m, 2H), 7.10 (q, *J* = 8.2 Hz, 4H), 3.38-3.28 (m, 2H), 3.21-3.10 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 145.85, 142.20, 141.29, 137.64, 135.79, 130.01, 129.25, 129.22, 129.09, 128.87, 128.35, 38.25, 34.90, 21.02. IR (KBr): 3052, 3015, 2923, 2857, 2729, 1620, 1561, 1493, 808, 760 cm^{-1}. MS (EI, m/z): 247.99 $[M]^+$.

(28) 2-(4-chlorophenethyl)-3-methylquinoxaline **(3ka)**[10]



Pale yellow solid, (95.8 mg, 68% yeild), m.p: 108-109°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-7.96 (m, 2H), 7.72-7.65 (m, 2H), 7.29-7.23 (m, 2H), 7.23-7.16 (m, 2H), 3.32-3.23 (m, 2H), 3.23-3.15 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.21, 153.00, 141.14, 140.93, 139.88, 131.95, 129.88, 129.06, 128.89, 128.61, 128.55, 128.35, 37.23, 33.10, 22.72. IR (KBr): 3042, 2957, 2853, 1566, 1488, 1398, 1315, 806, 758 cm^{-1}. MS (EI, m/z): 281.94 $[M]^+$.

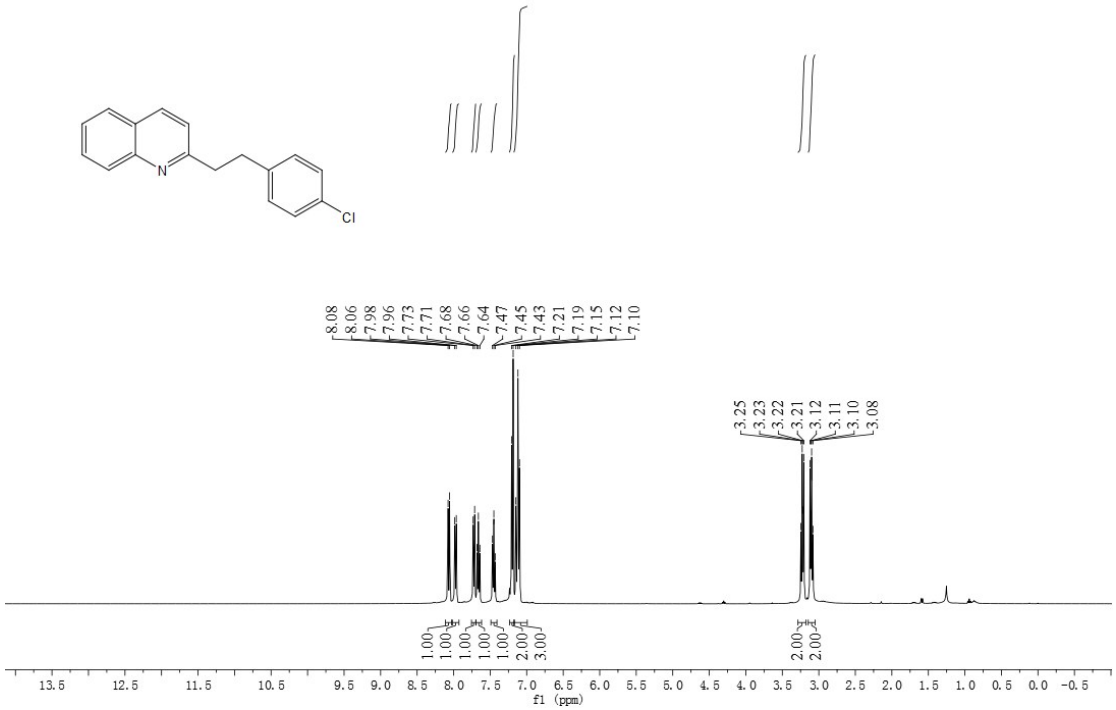
(29) 3-(4-chlorobenzyl)-2-(4-chlorophenethyl)-6-methylpyridine **(3la-2)**



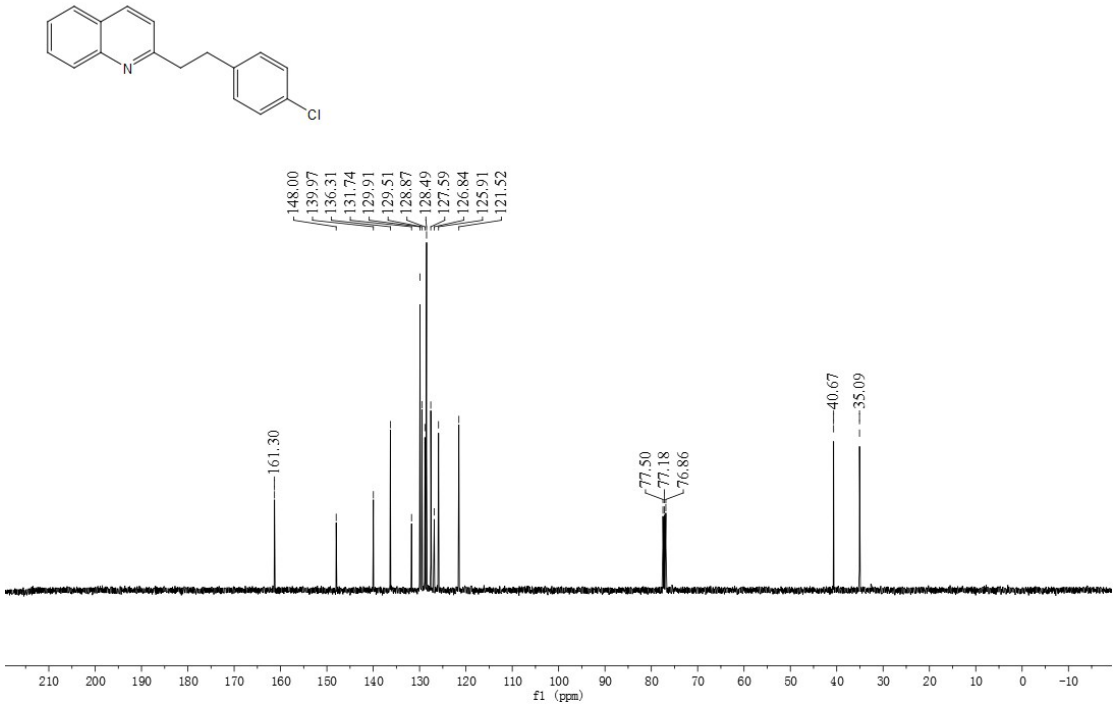
Pale yellow oil liquid, (106.5 mg, 60% yeild); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.15 (m, 5H), 7.04-6.88 (m, 5H), 3.78 (s, 2H), 3.02-2.93 (m, 2H), 2.93-2.84 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.36, 156.13, 140.27, 138.28, 132.19, 131.65, 130.12, 129.95, 129.86, 128.72, 128.37, 121.12, 37.24, 36.65, 34.84, 24.09. IR (KBr): 3029, 2923, 2857, 1584, 1490, 1458, 1404, 1029, 1014, 813 cm^{-1}. MS (EI, m/z): 355.10 $[M]^+$. HRMS (ESI): Calcd. for $C_{21}H_{20}Cl_2N$ $[M+H]^+$: 356.0967; found: 356.0973.

NMR spectra of the obtained compounds

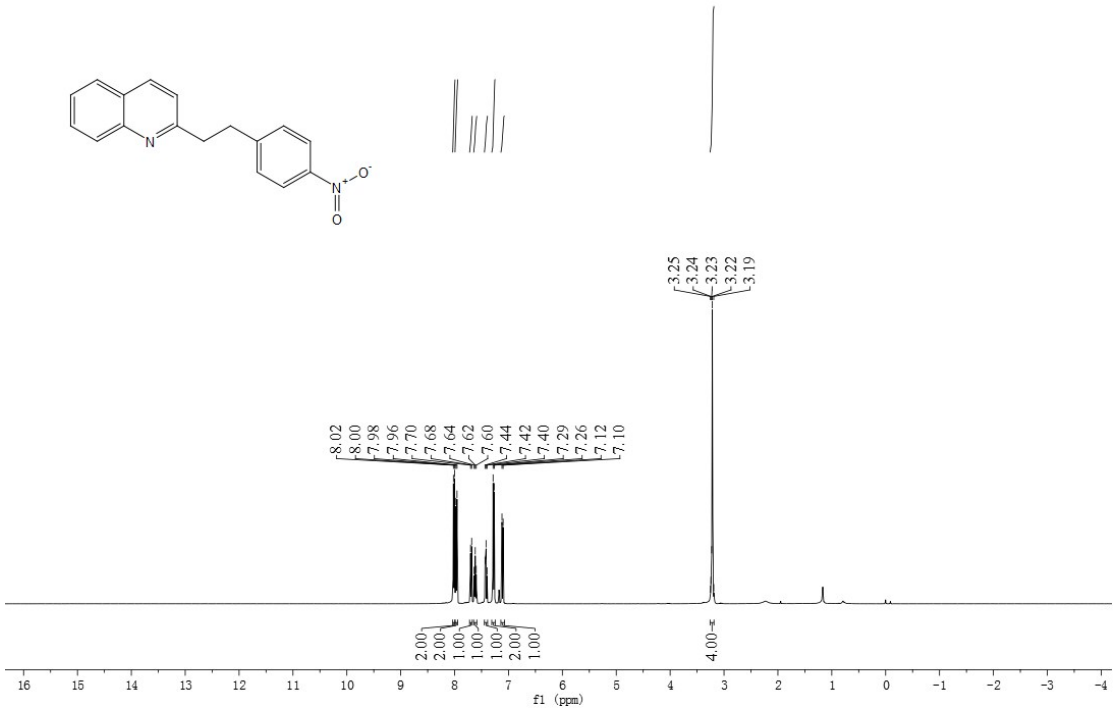
^{1}H-NMR spectrum of 3aa



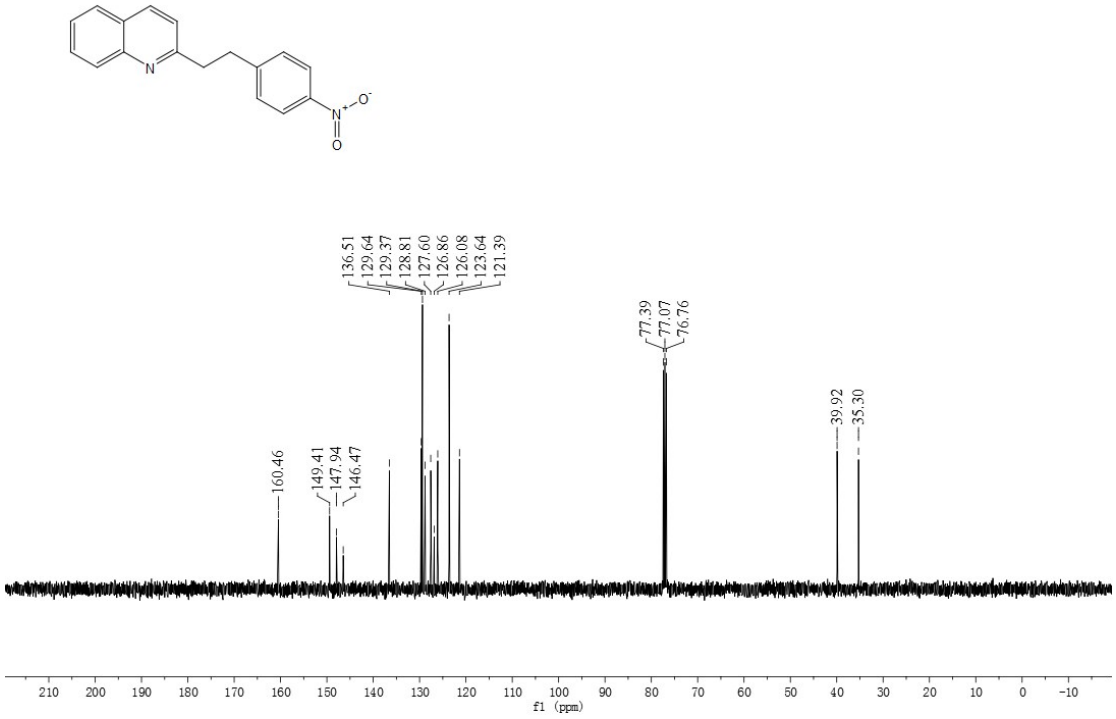
^{13}C-NMR spectrum of 3aa



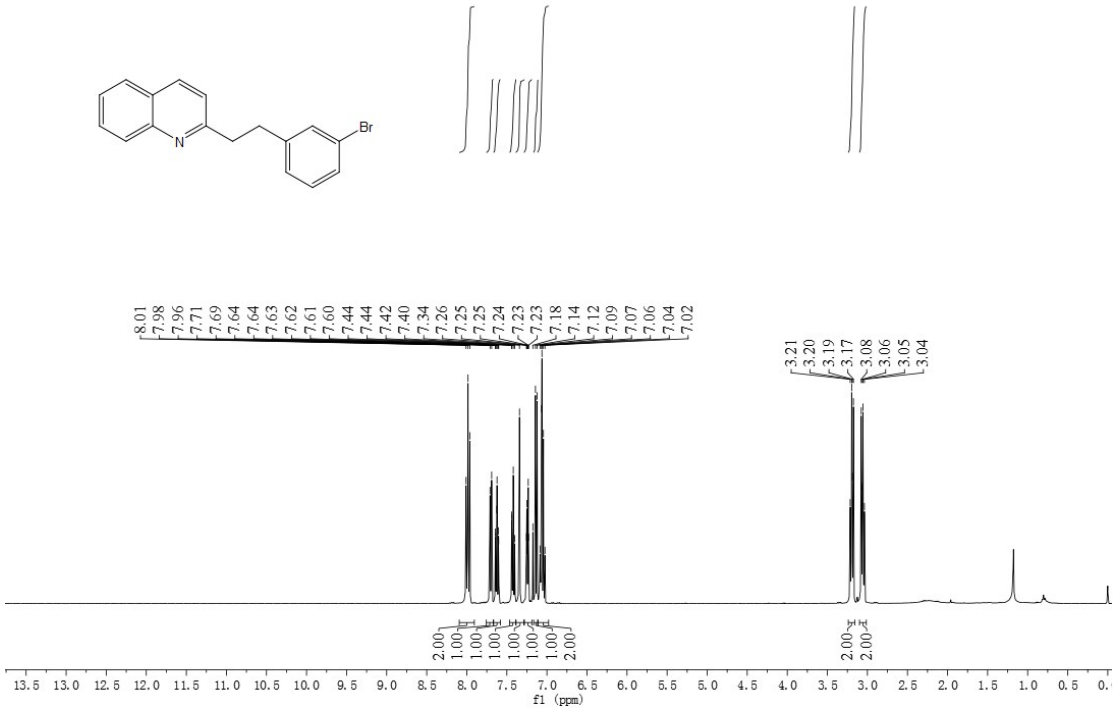
^{1}H-NMR spectrum of 3ab



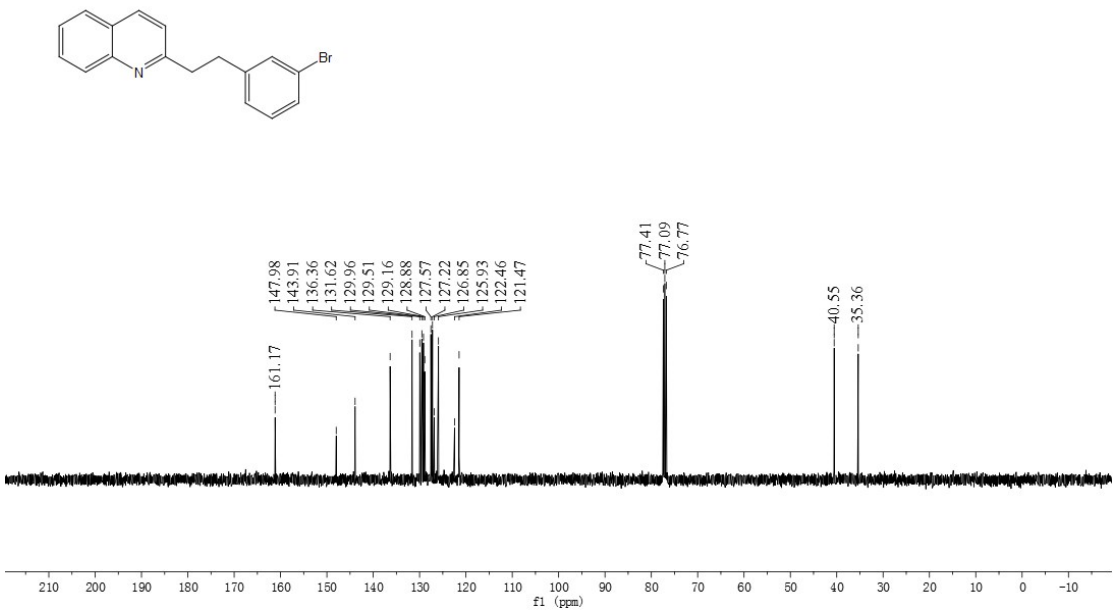
^{13}C-NMR spectrum of 3ab



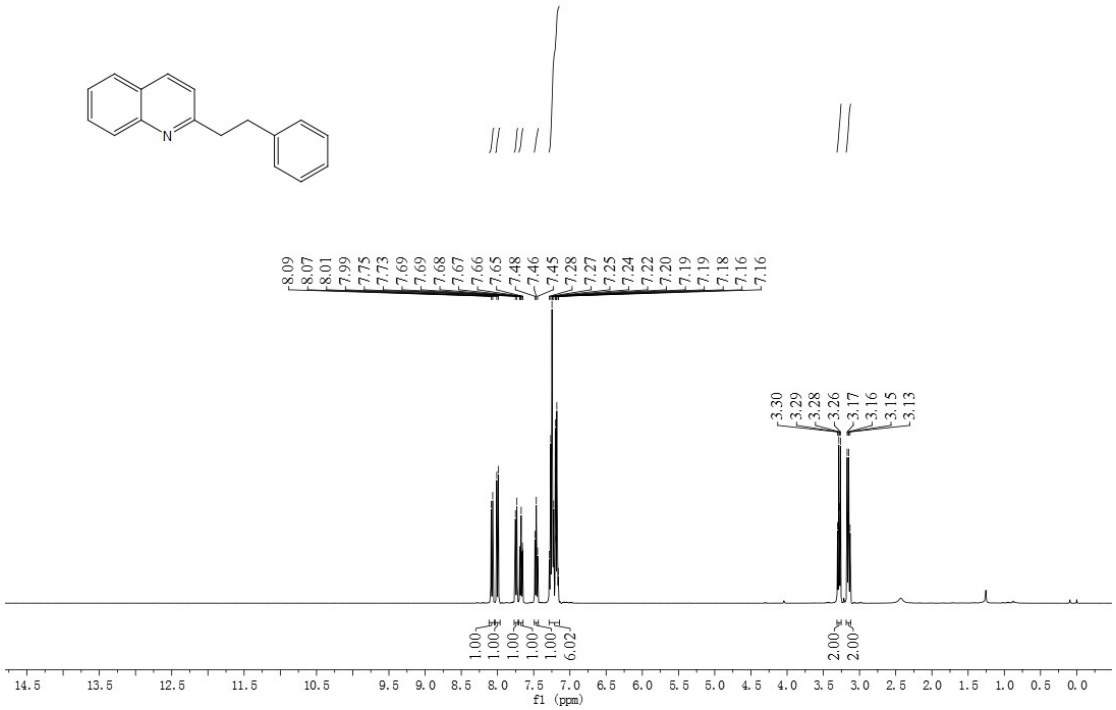
^{1}H-NMR spectrum of 3ac



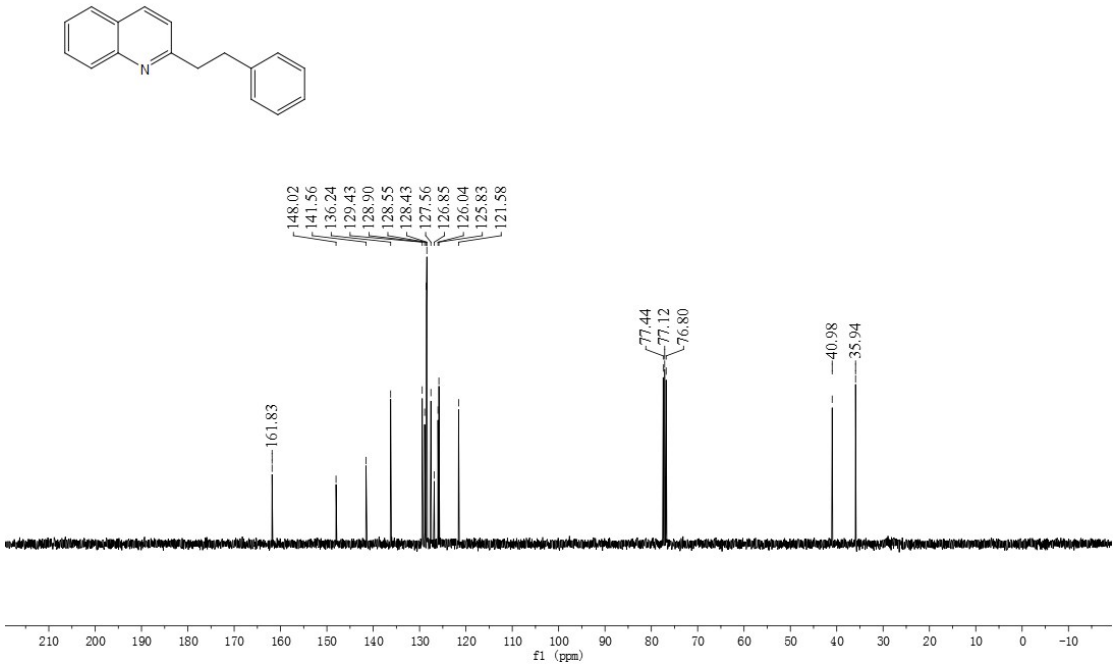
^{13}C-NMR spectrum of 3ac



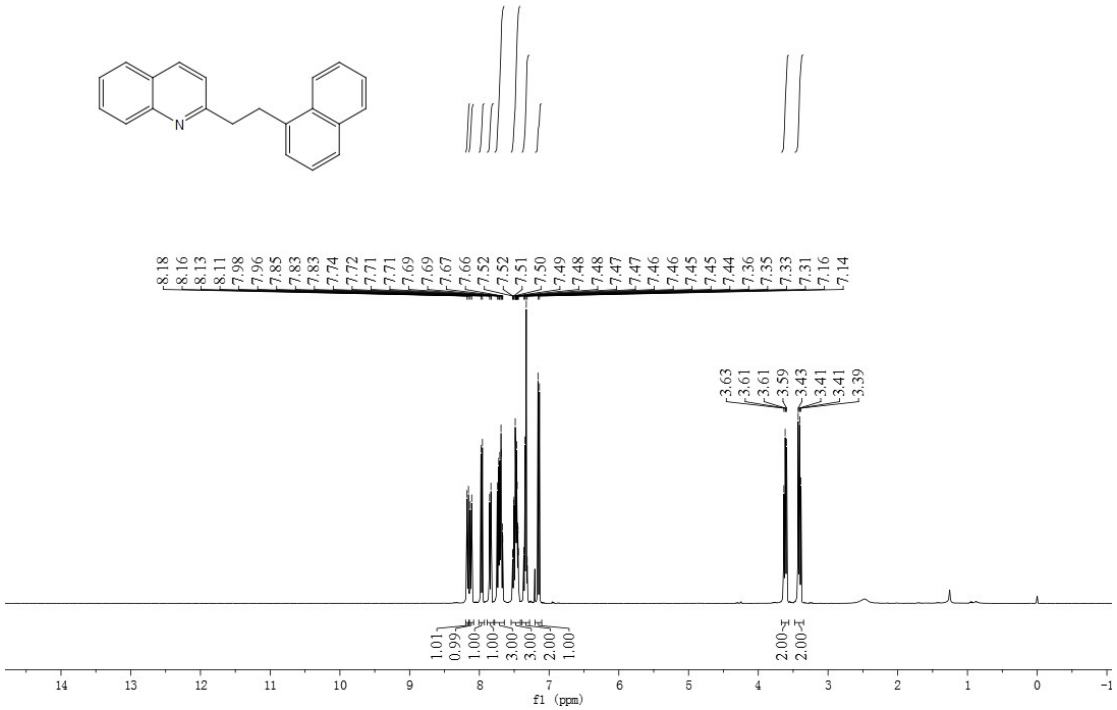
^{1}H-NMR spectrum of 3ad



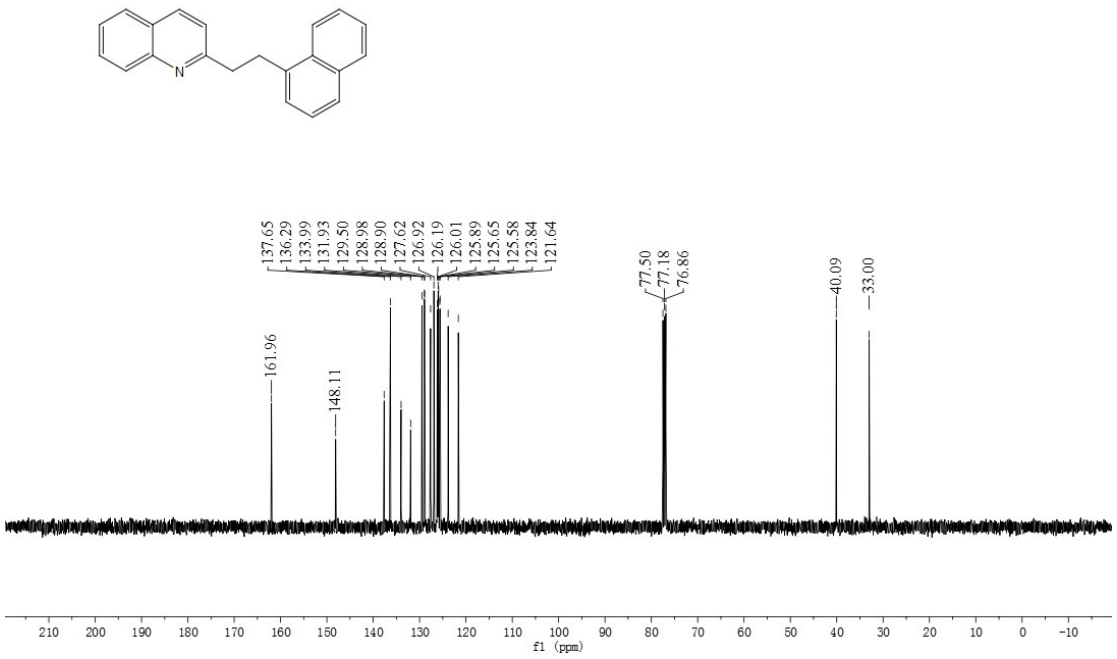
^{13}C-NMR spectrum of 3ad



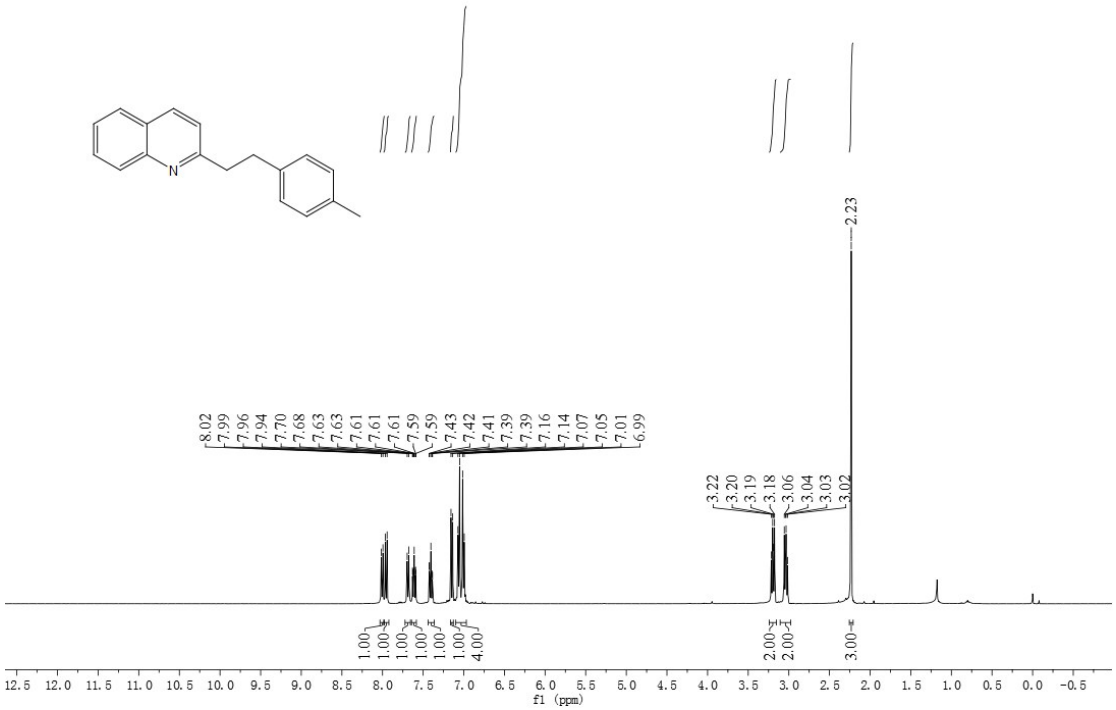
^{1}H-NMR spectrum of 3ae



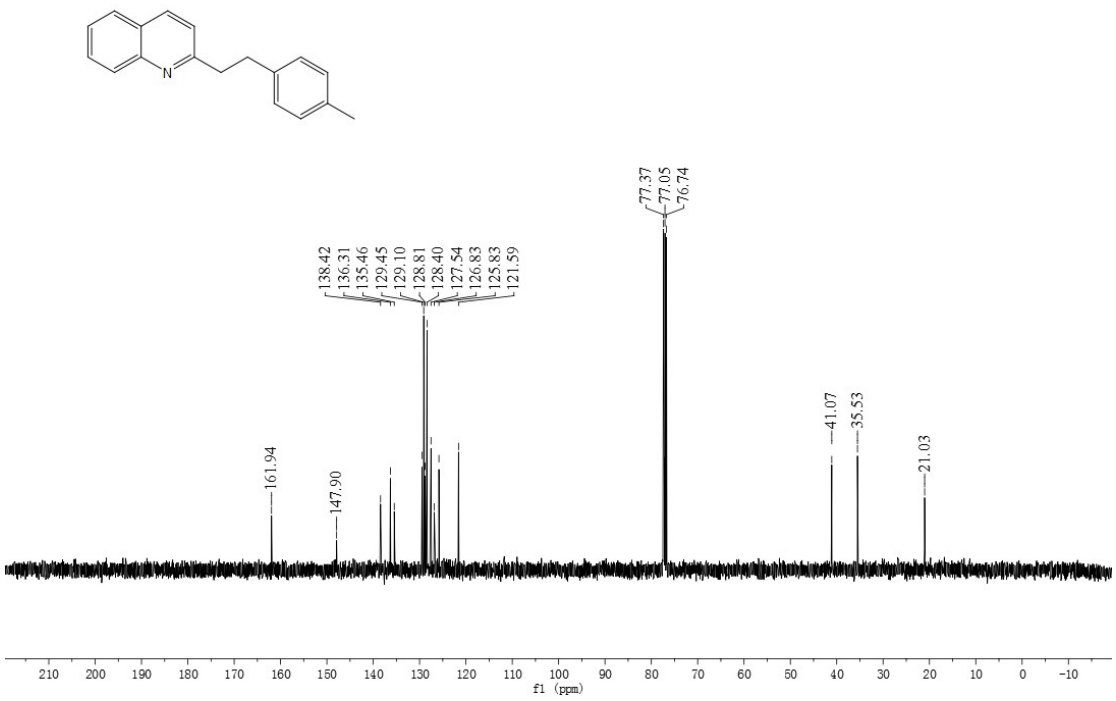
^{13}C-NMR spectrum of 3ae



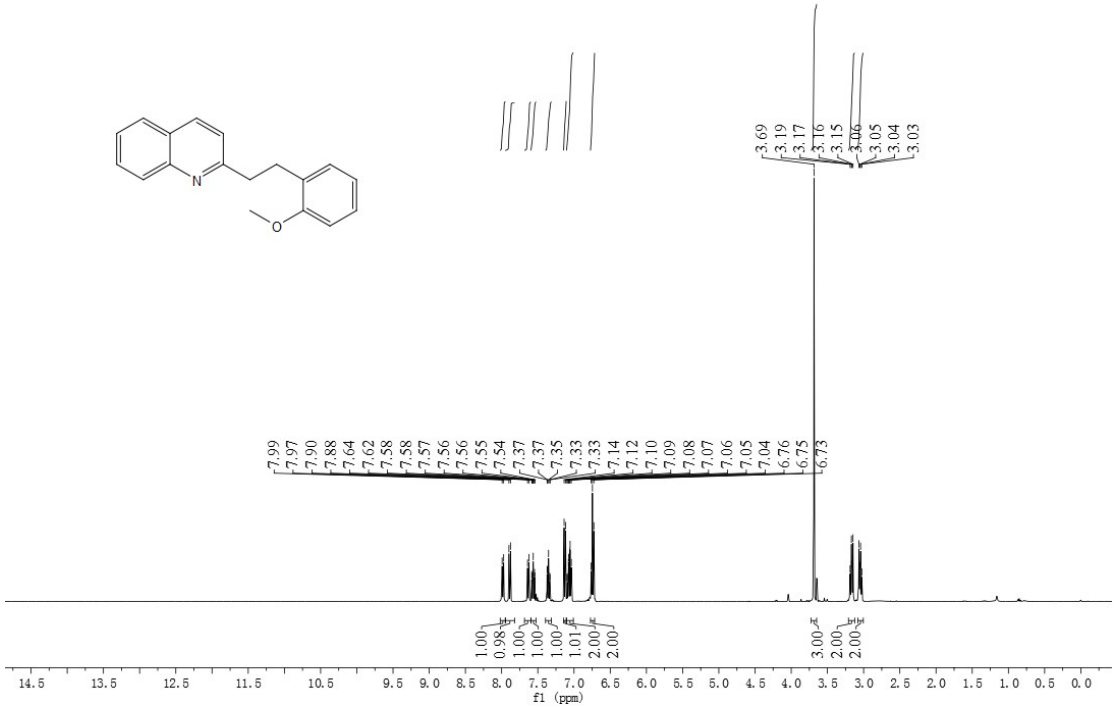
^{1}H-NMR spectrum of 3af



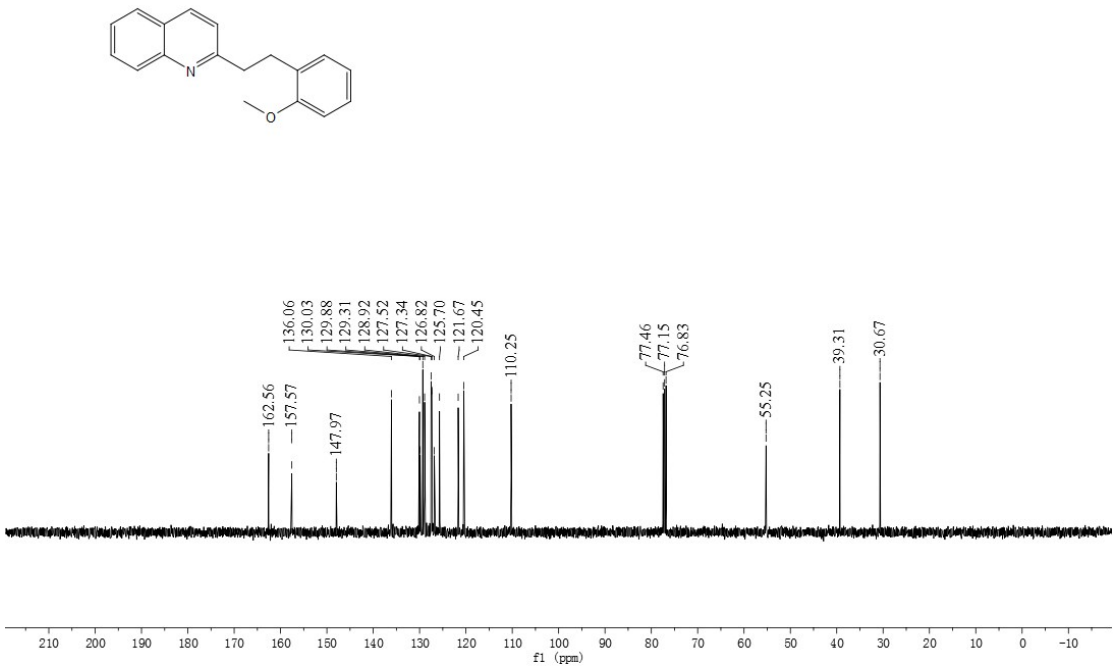
^{13}C-NMR spectrum of 3af



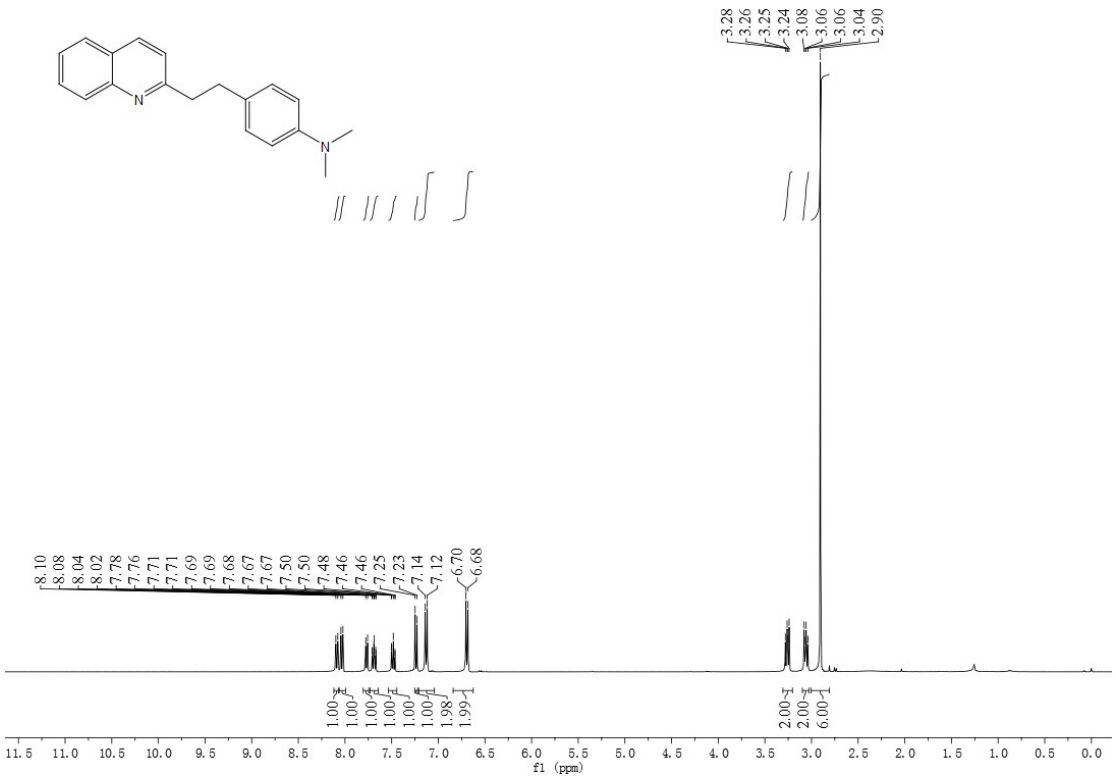
^{1}H-NMR spectrum of 3ag



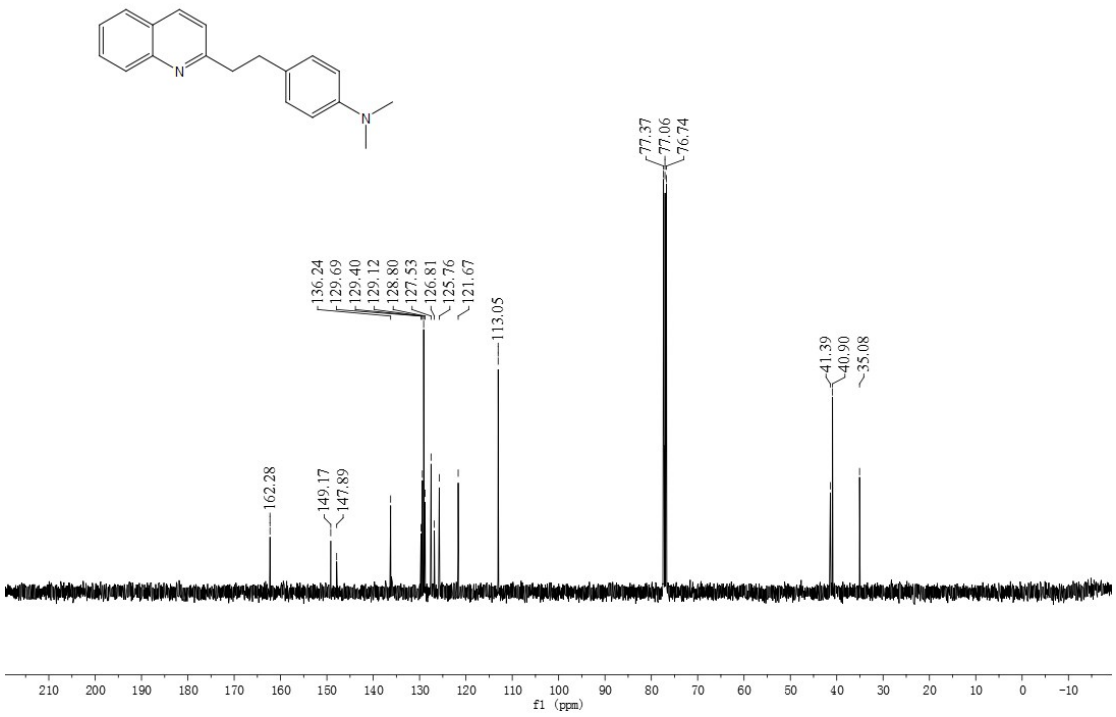
^{13}C-NMR spectrum of 3ag



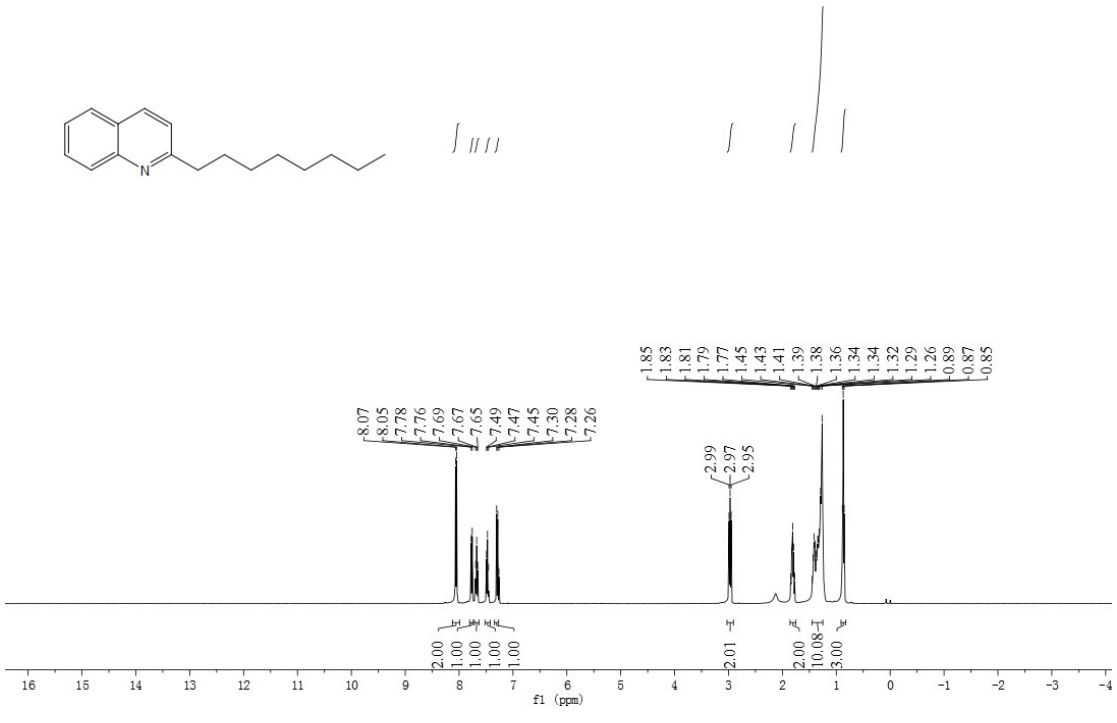
^{1}H-NMR spectrum of 3ah



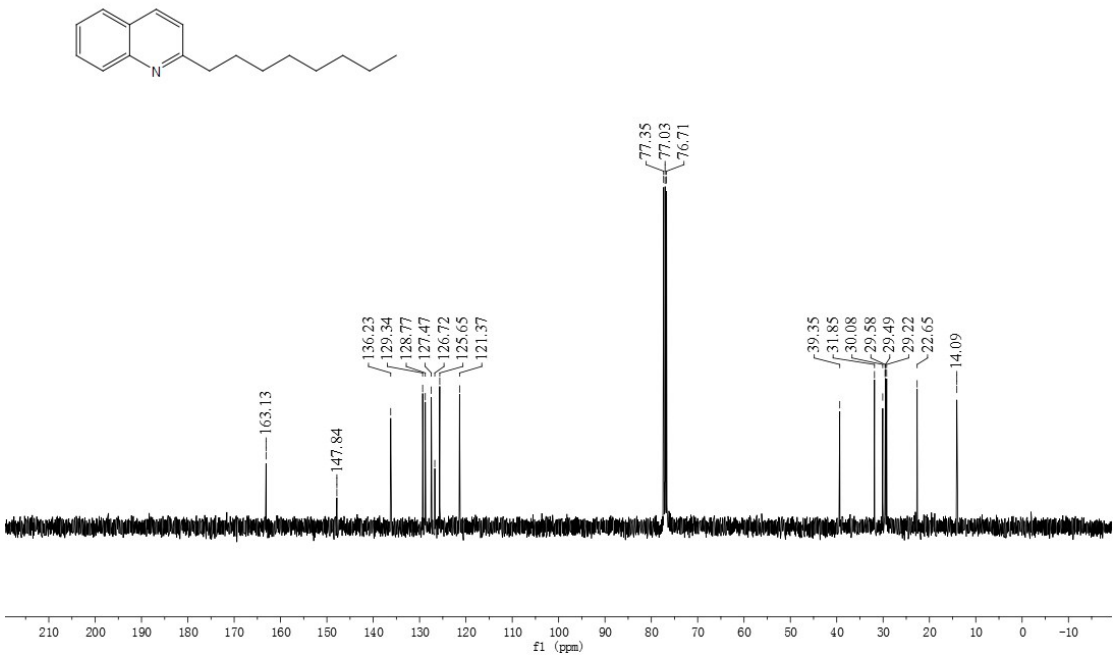
^{13}C-NMR spectrum of 3ah



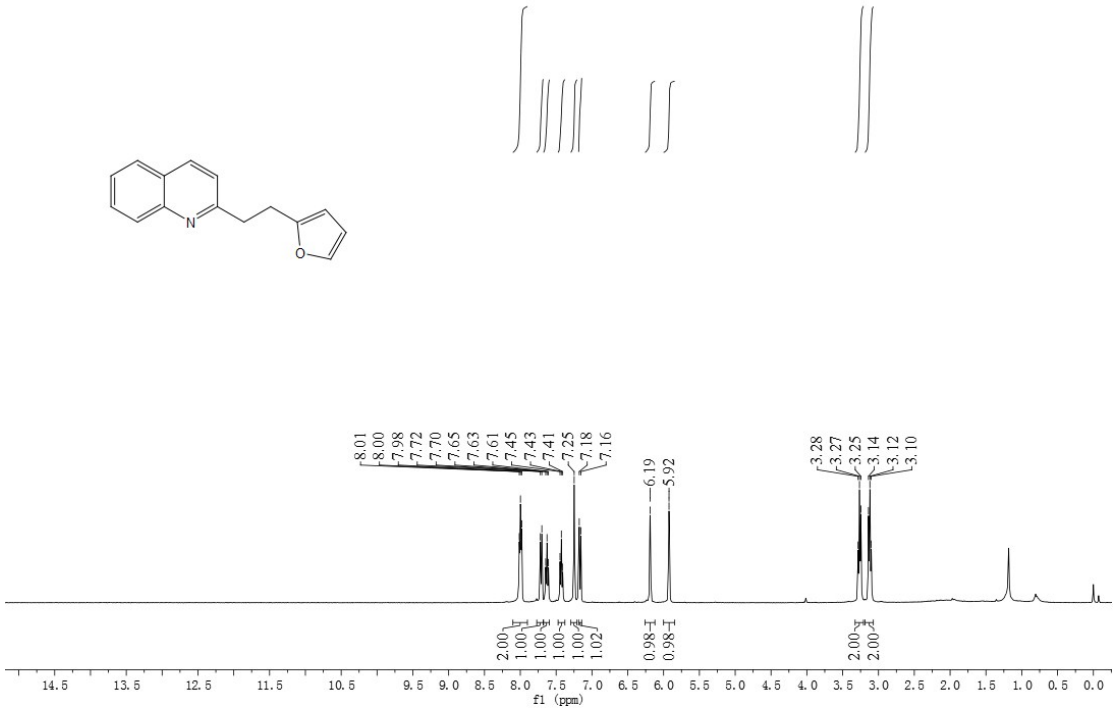
^{1}H-NMR spectrum of 3ai



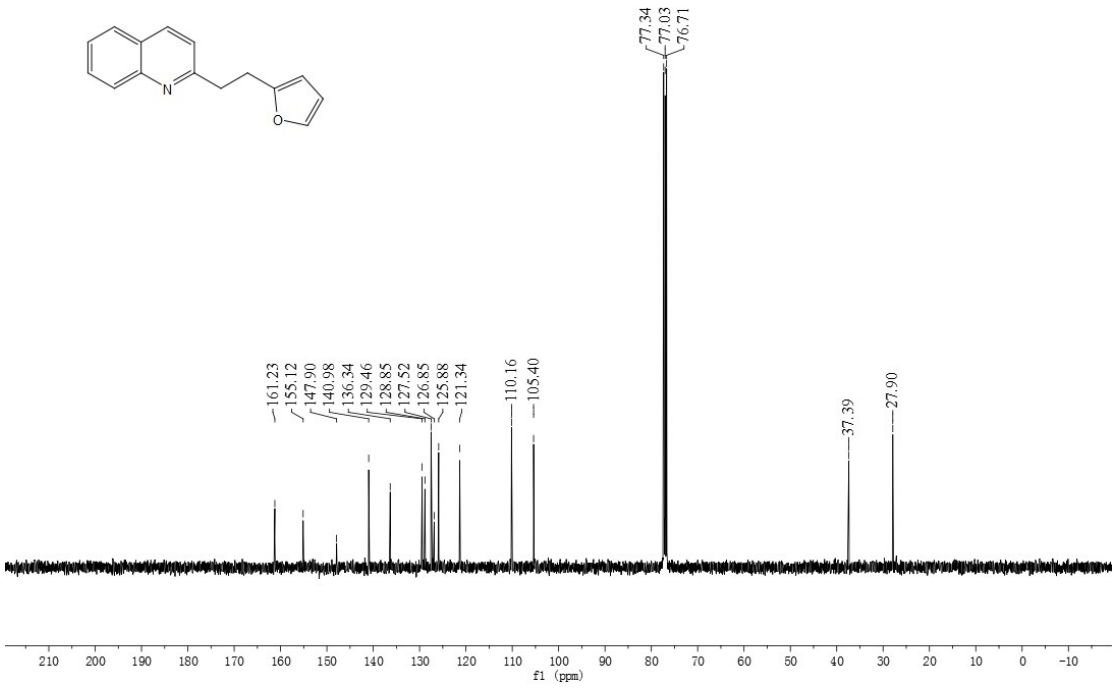
^{13}C-NMR spectrum of 3ai



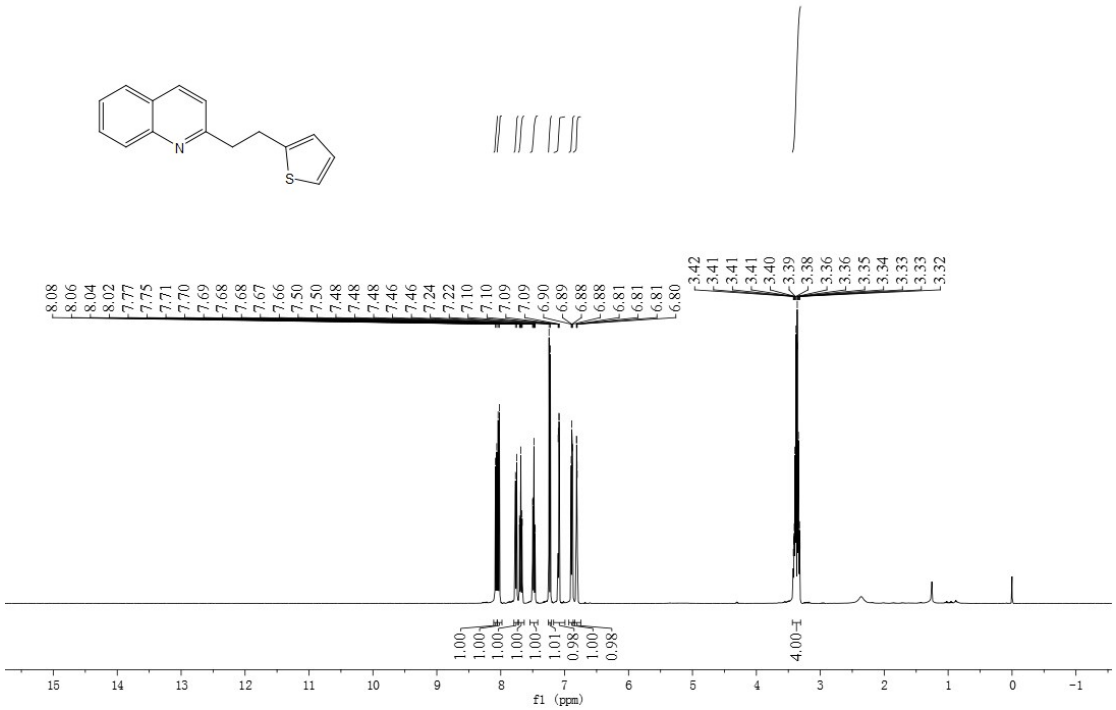
^{1}H-NMR spectrum of 3aj



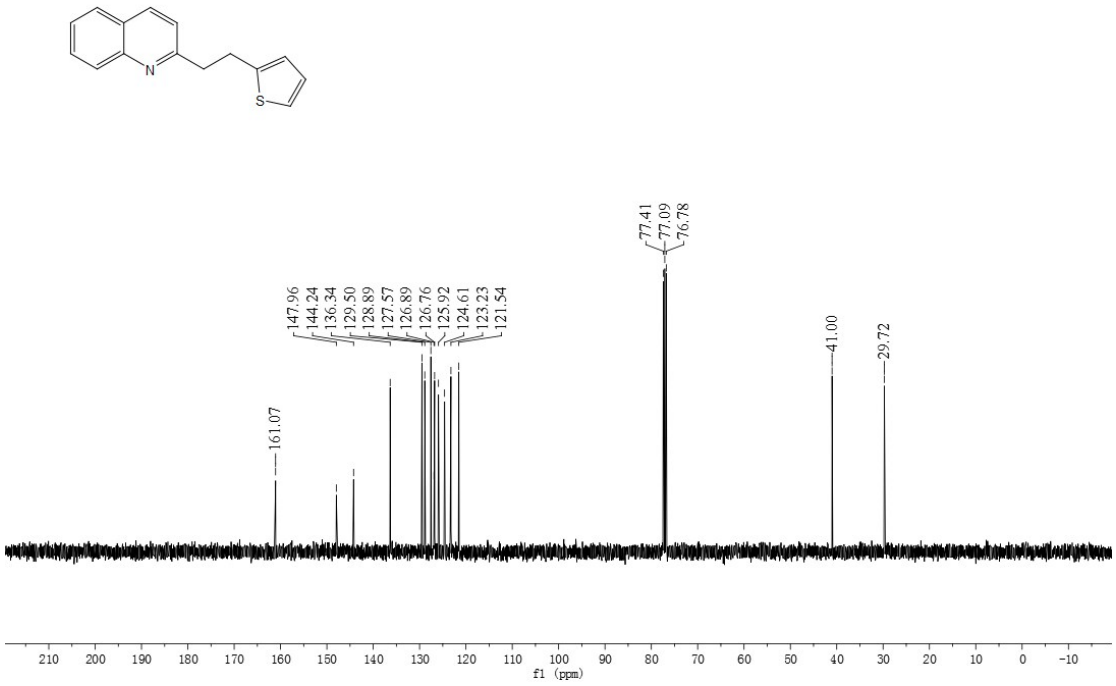
^{13}C-NMR spectrum of 3aj



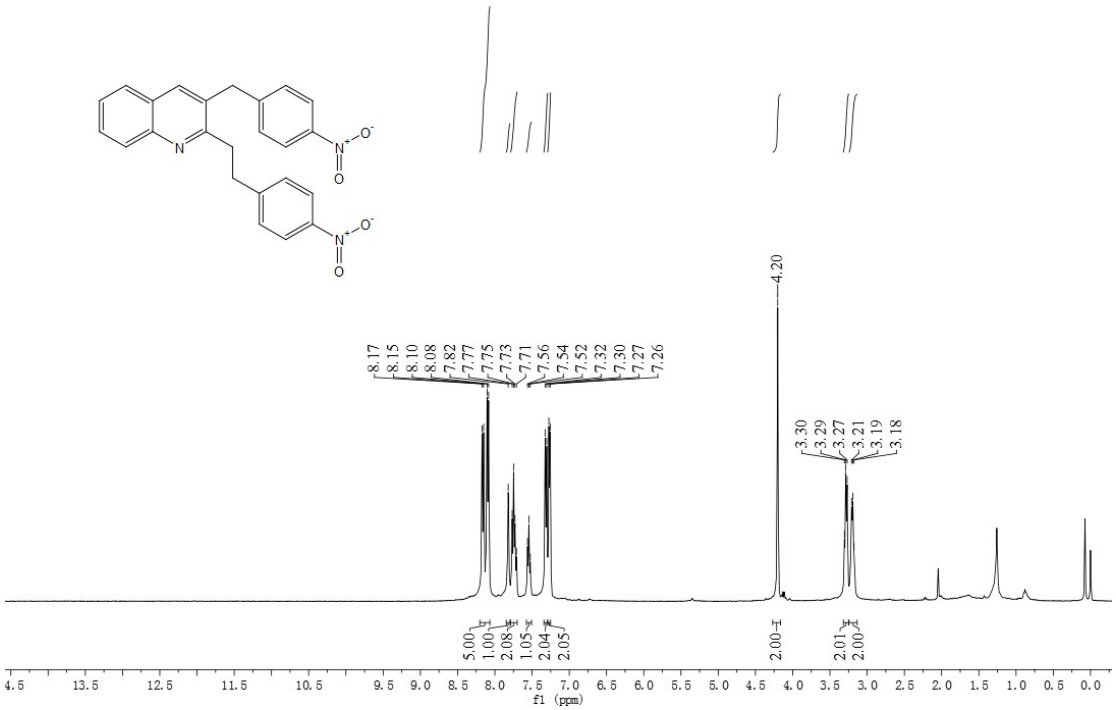
^{1}H-NMR spectrum of 3ak



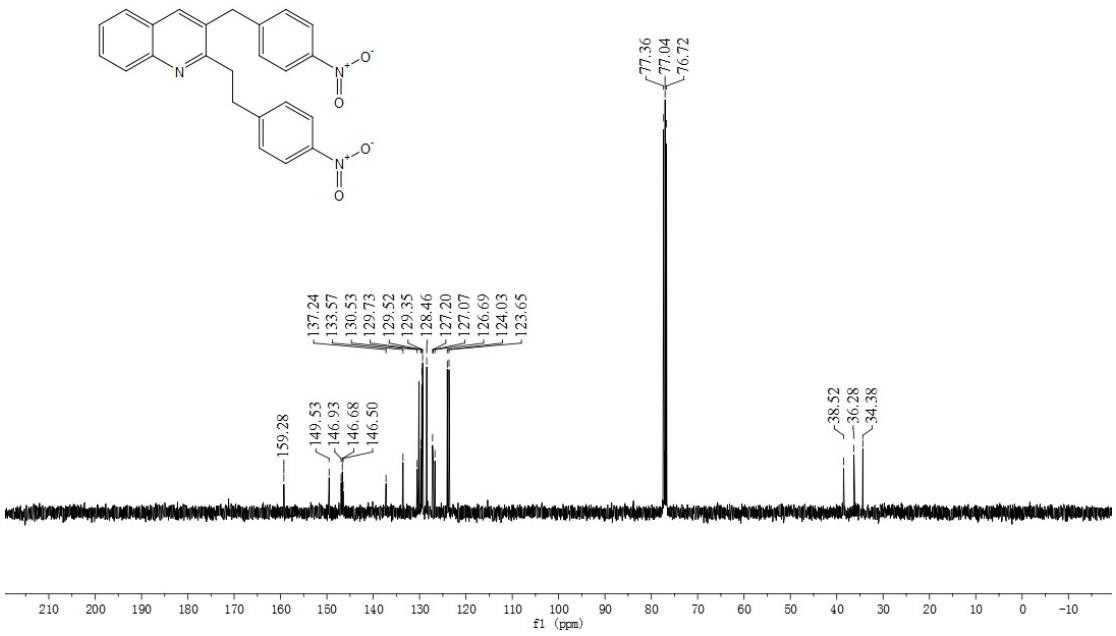
^{13}C-NMR spectrum of 3ak



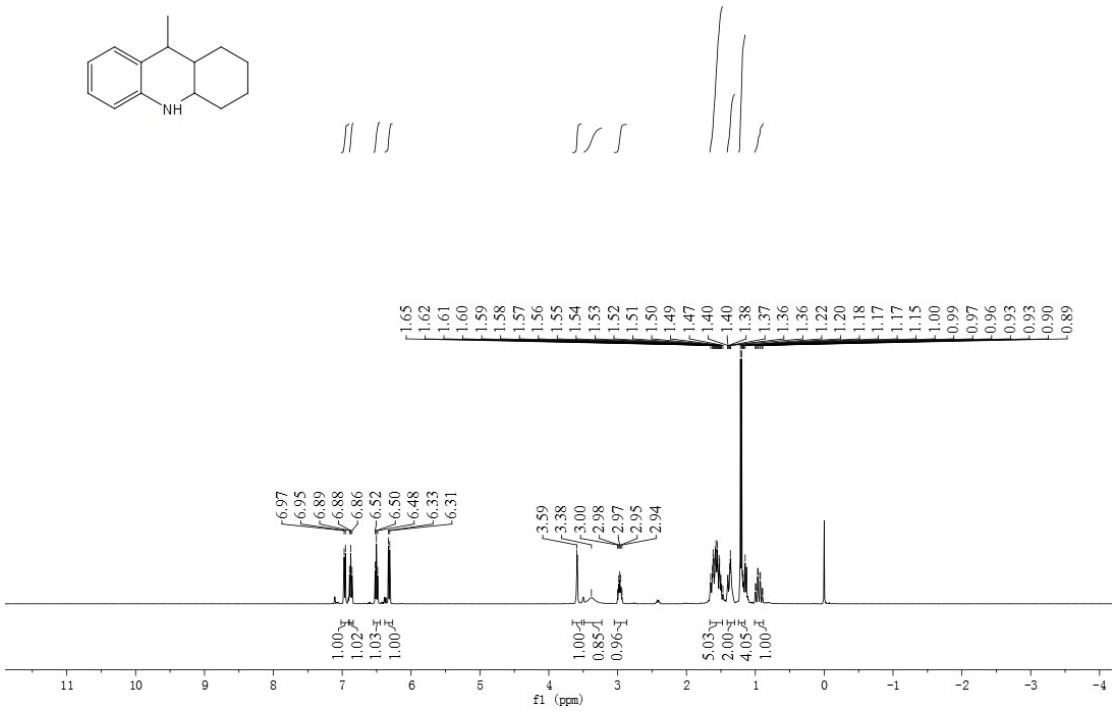
^{1}H-NMR spectrum of 3ab-2



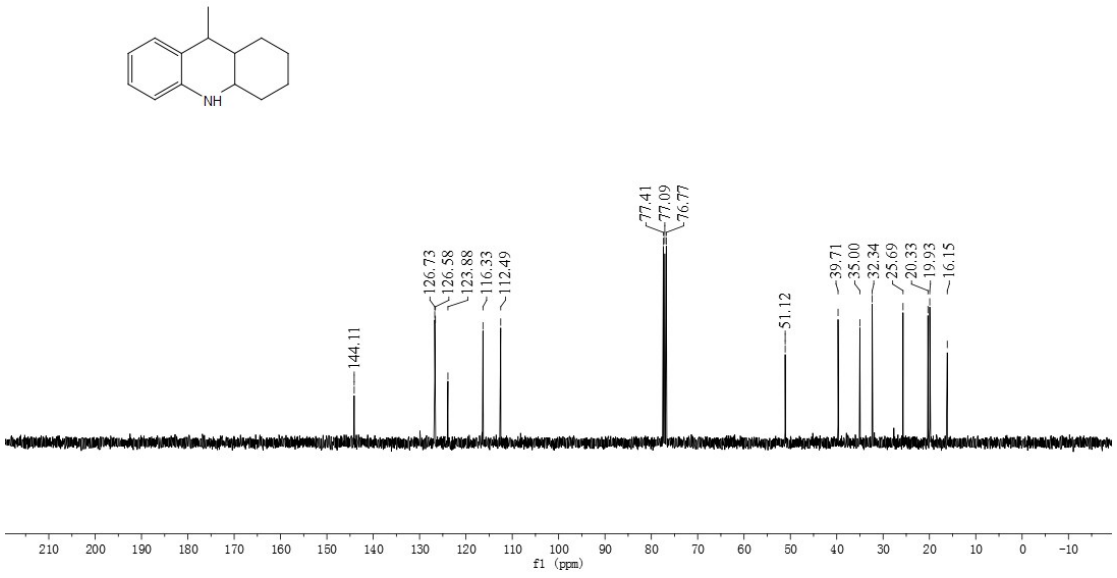
^{13}C-NMR spectrum of 3ab-2



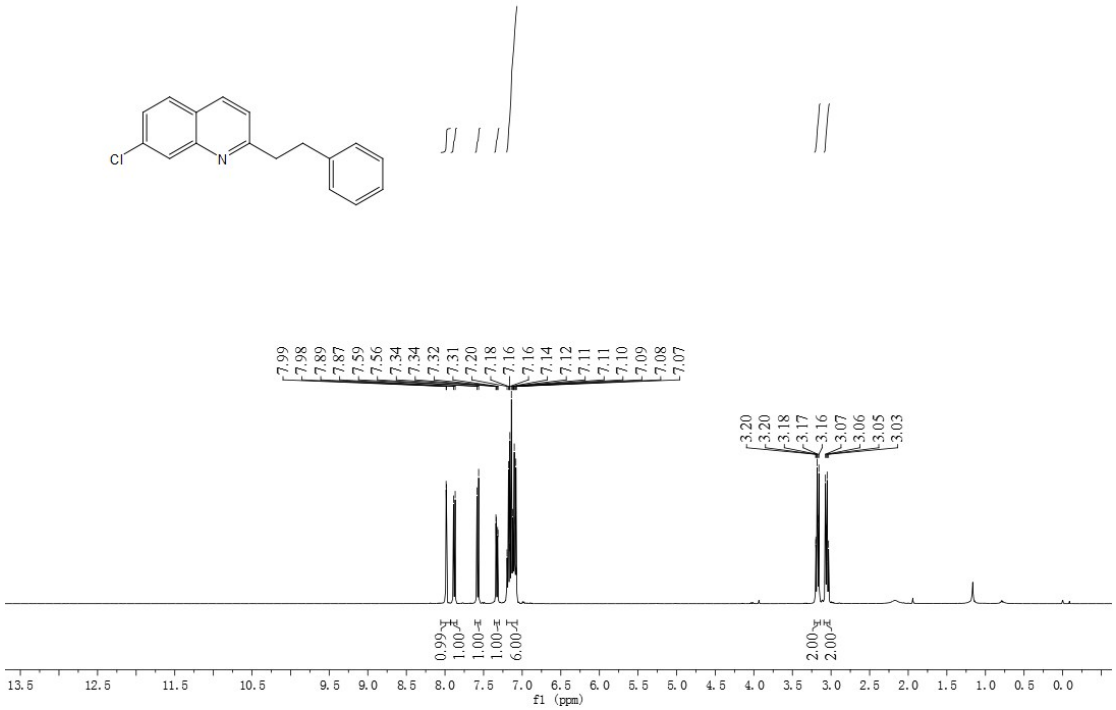
^{1}H-NMR spectrum of 1h



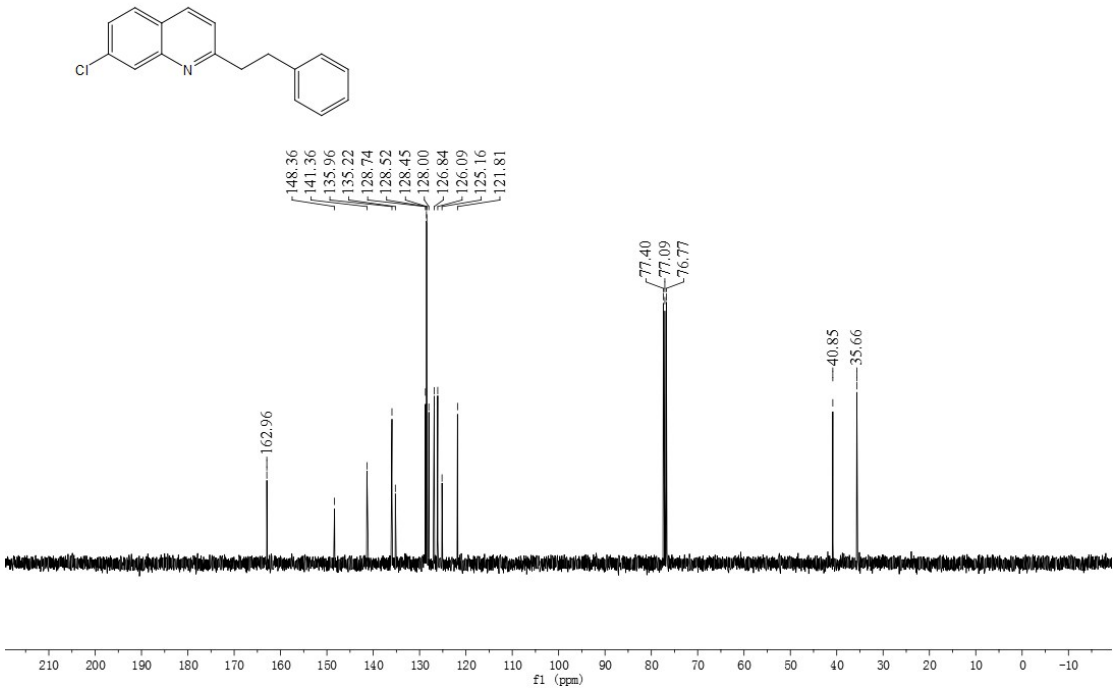
^{13}C-NMR spectrum of 1h



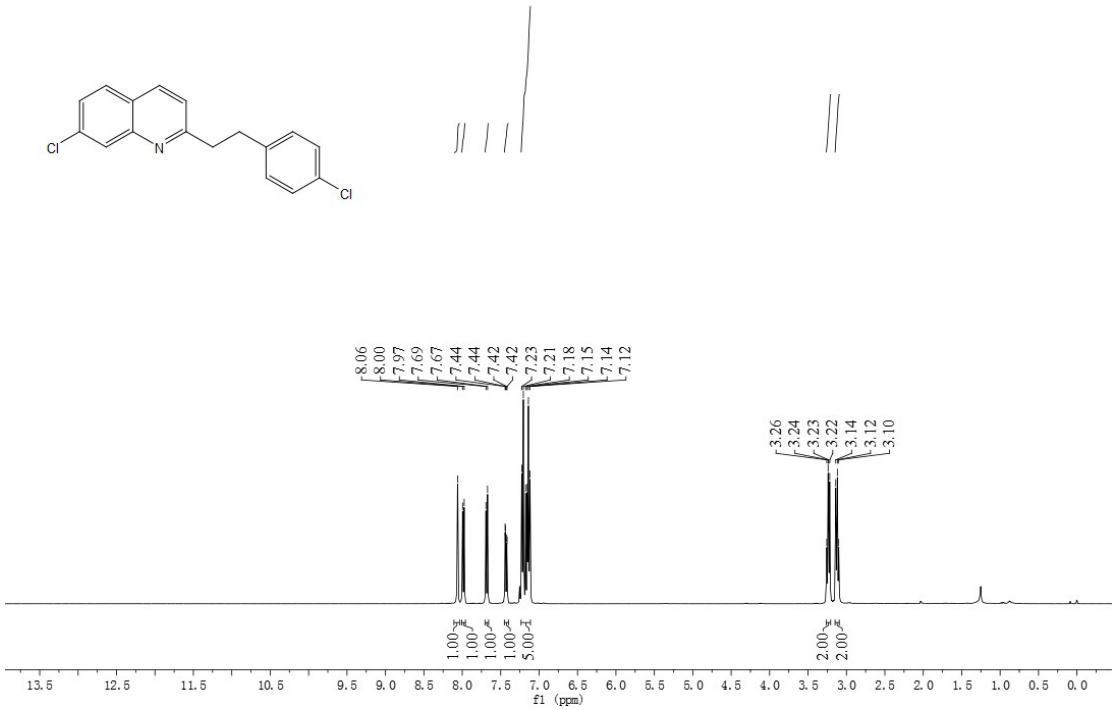
^{1}H-NMR spectrum of 3bd



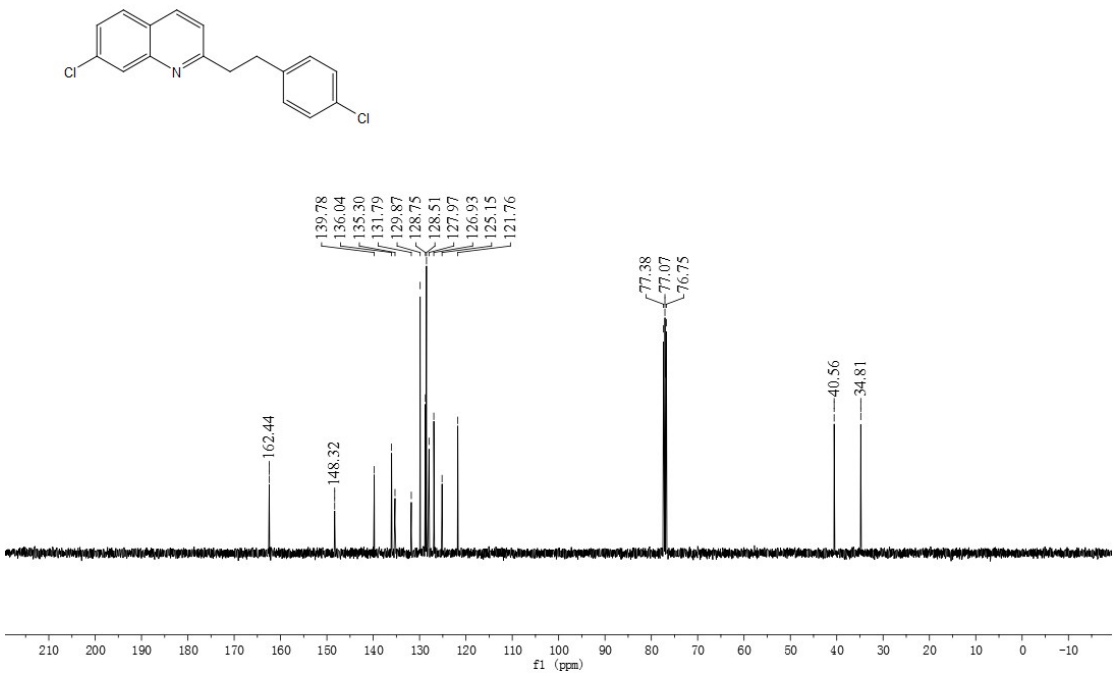
^{13}C-NMR spectrum of 3bd



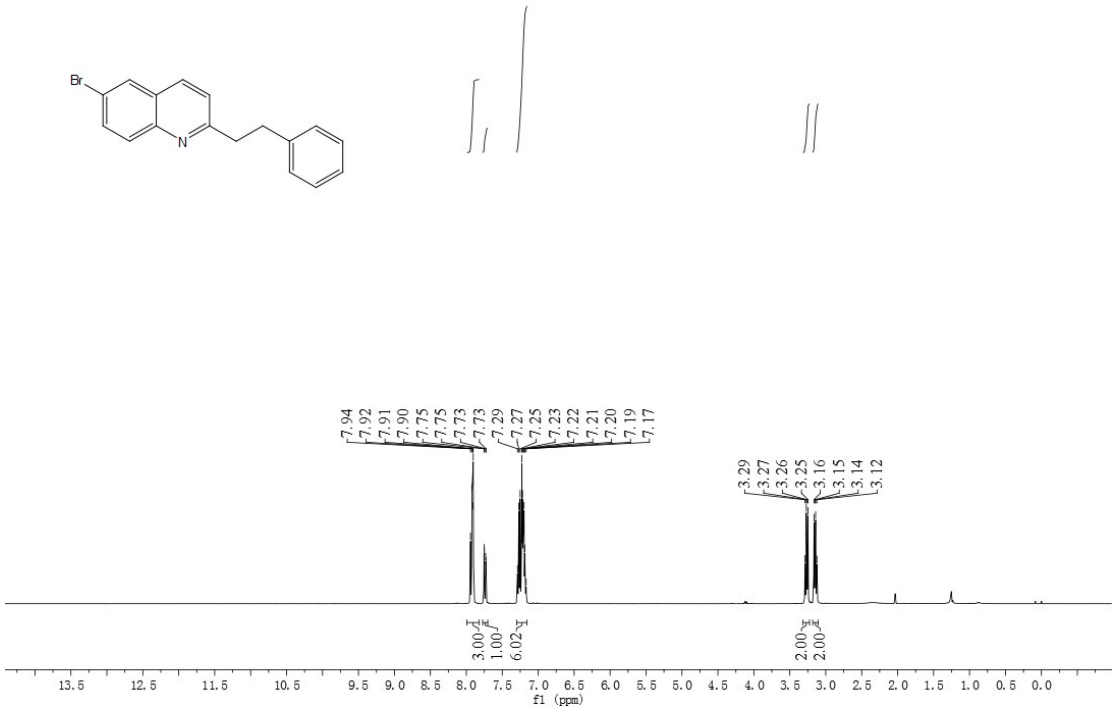
^{1}H-NMR spectrum of 3ba



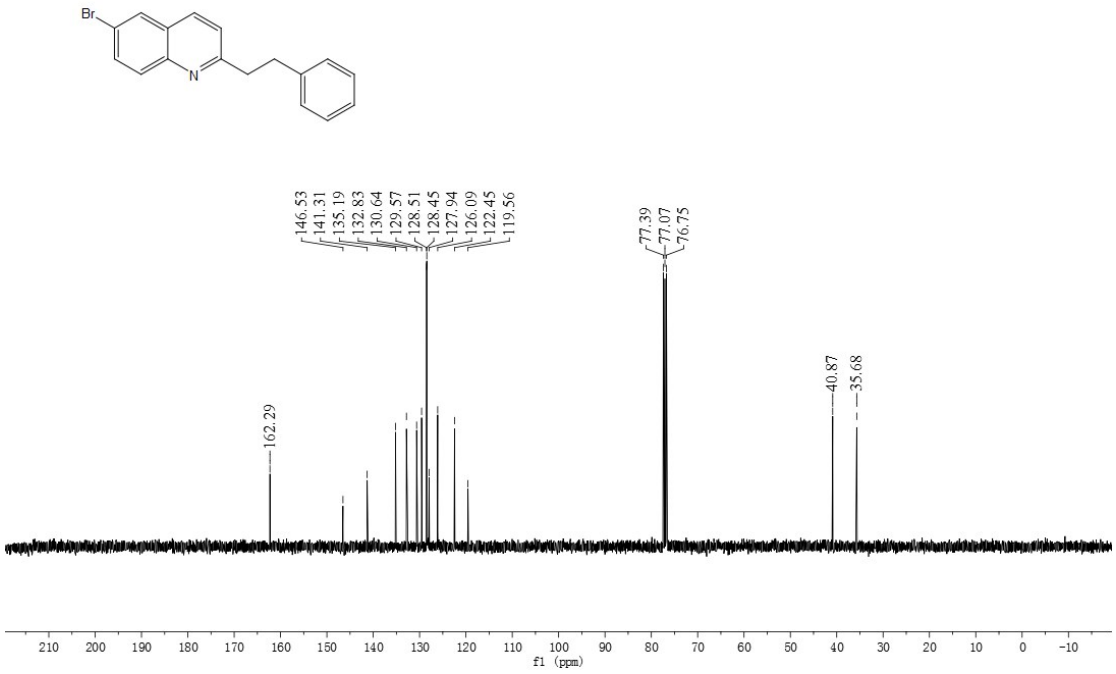
^{13}C-NMR spectrum of 3ba



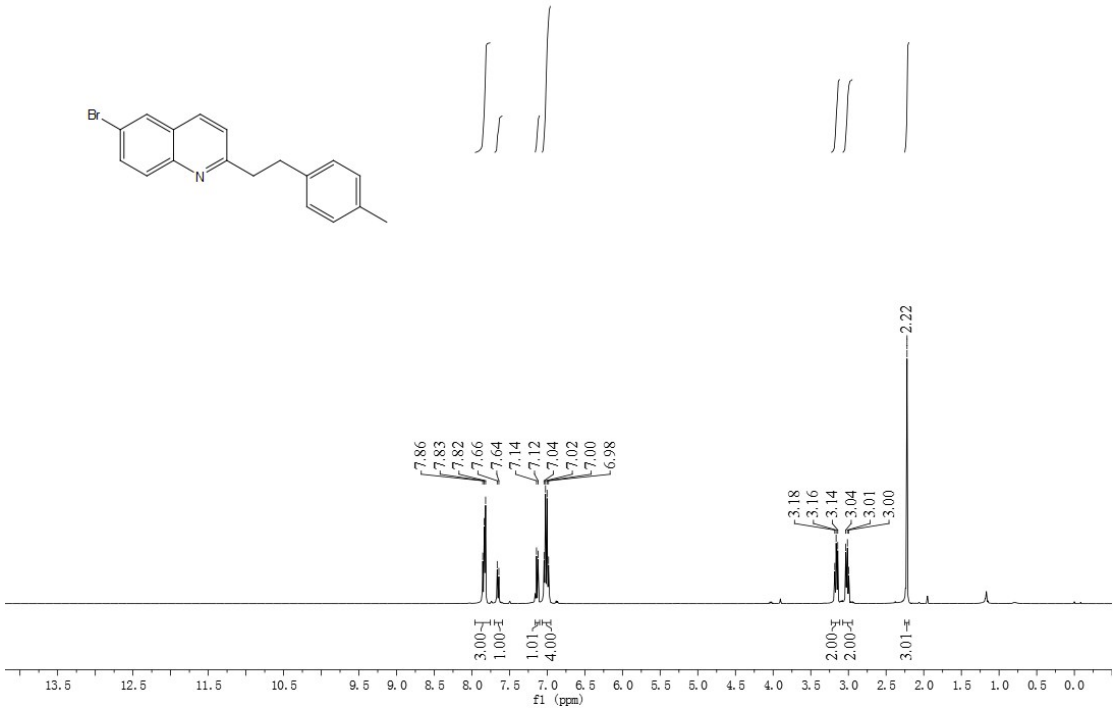
^{1}H-NMR spectrum of 3cd



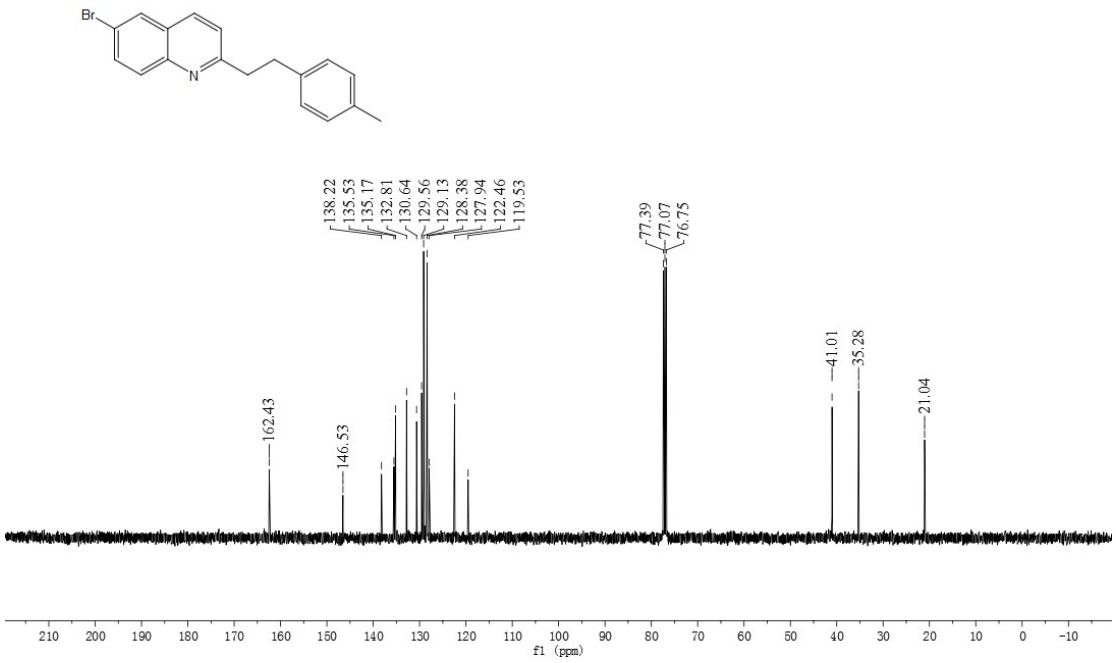
^{13}C-NMR spectrum of 3cd



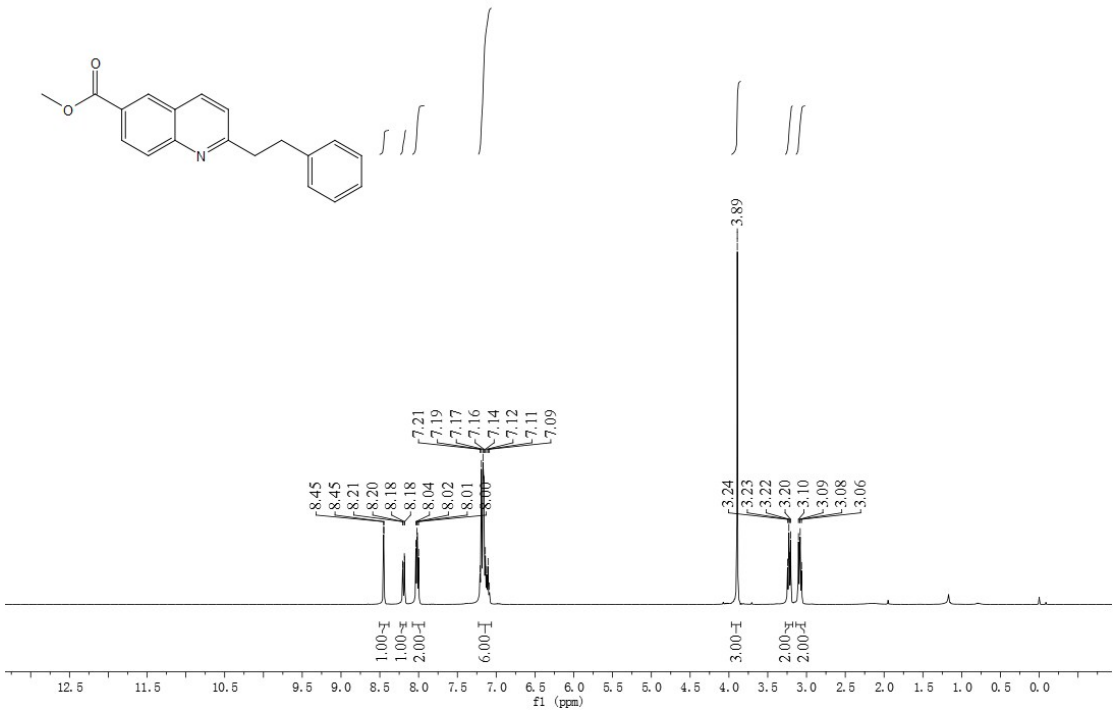
^{1}H-NMR spectrum of 3cf



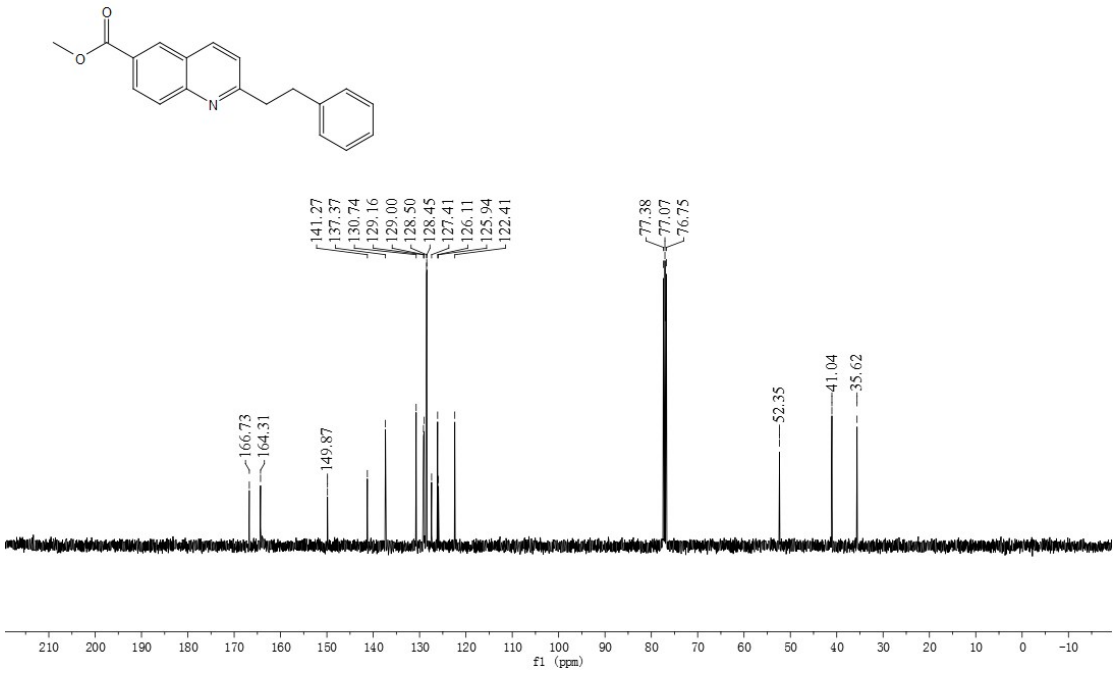
^{13}C-NMR spectrum of 3cf



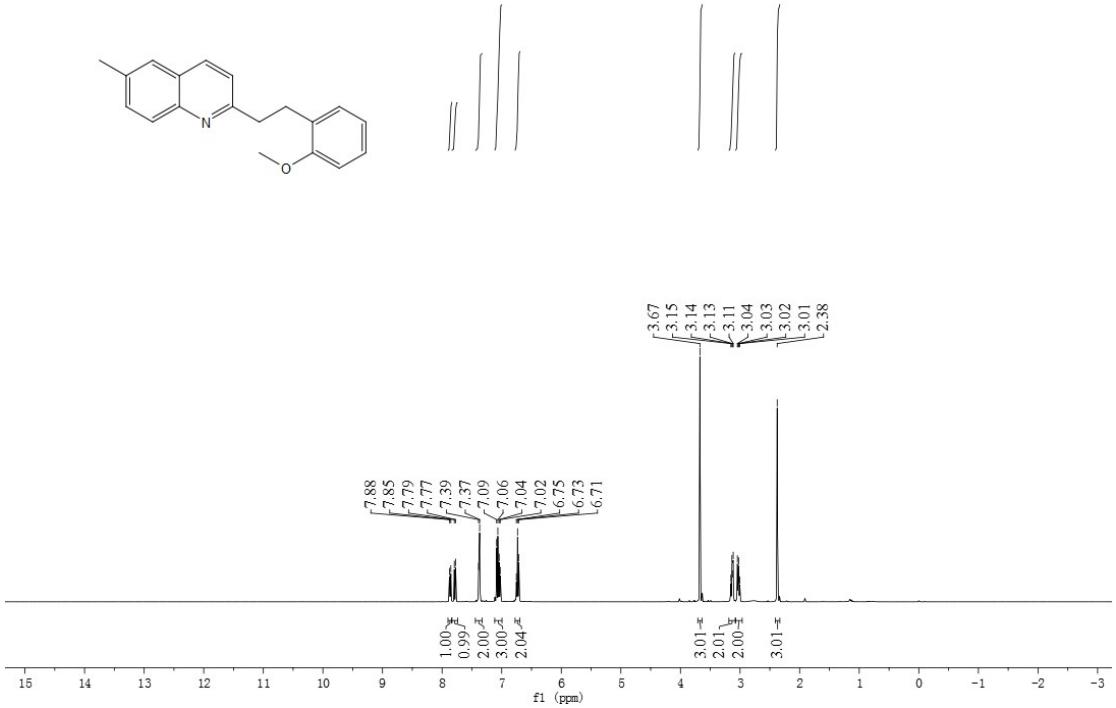
^{1}H-NMR spectrum of 3dd



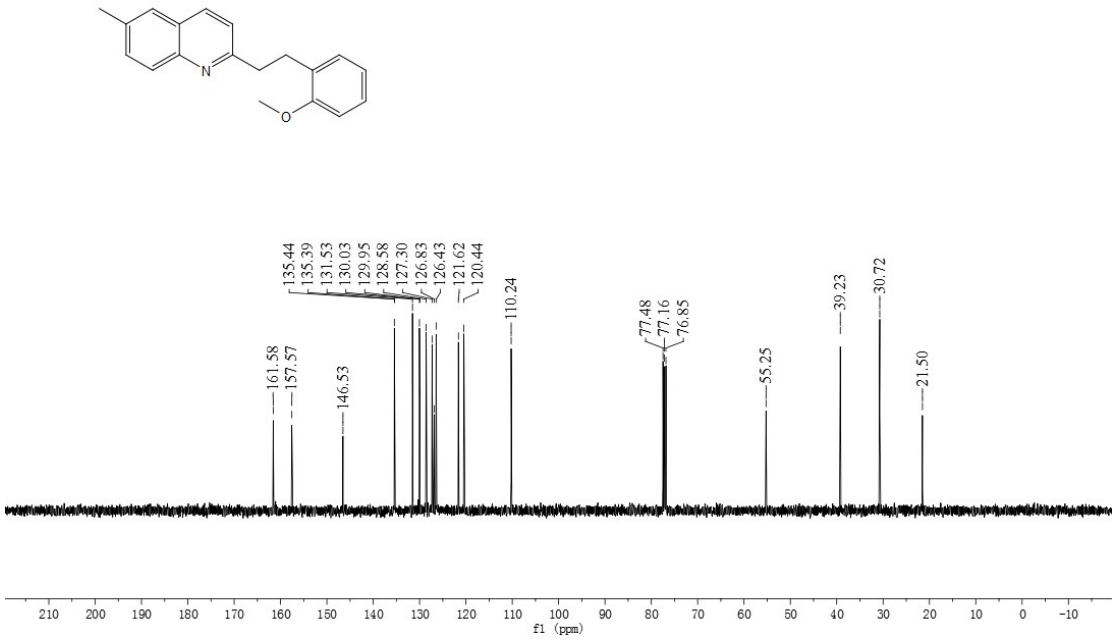
^{13}C-NMR spectrum of 3dd



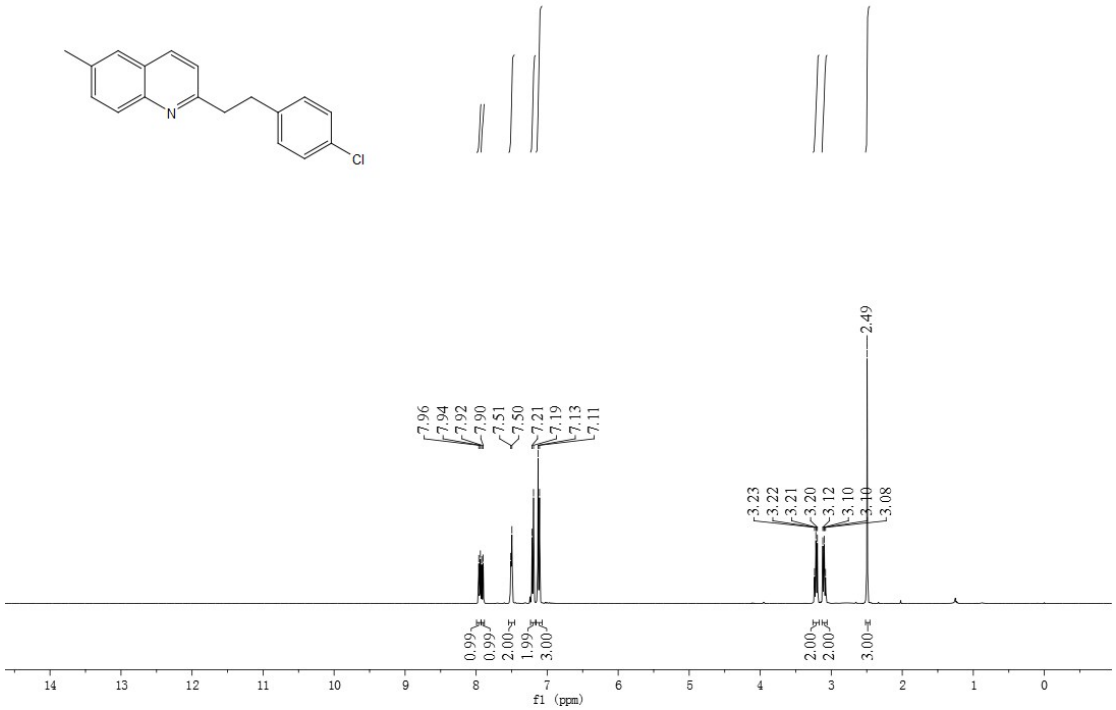
^{1}H-NMR spectrum of 3eg



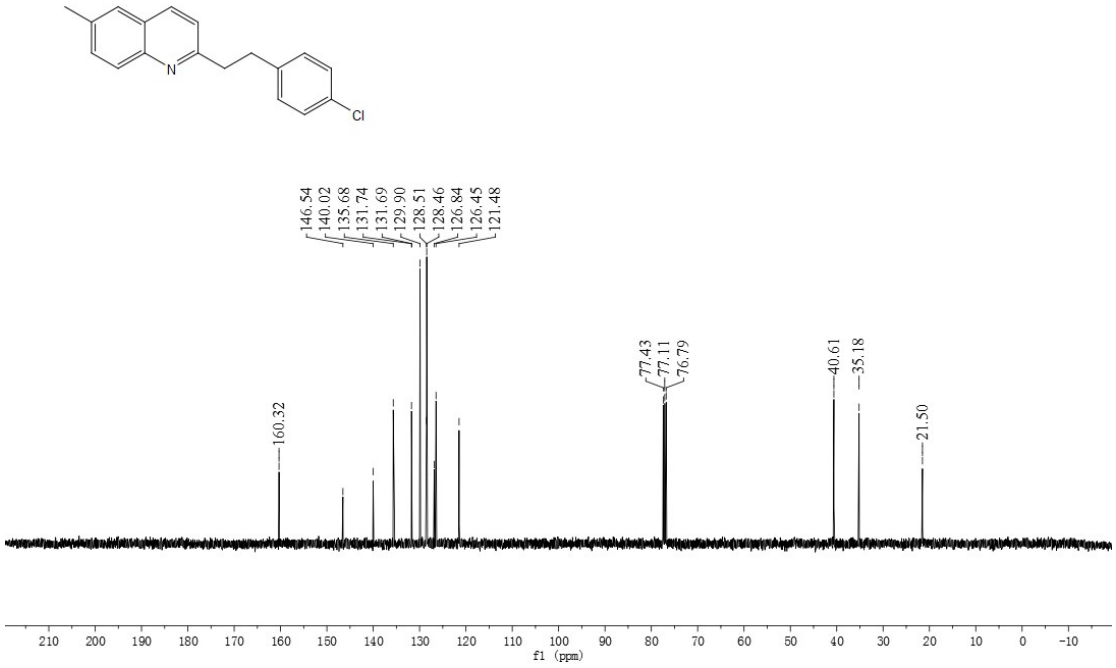
^{13}C-NMR spectrum of 3eg



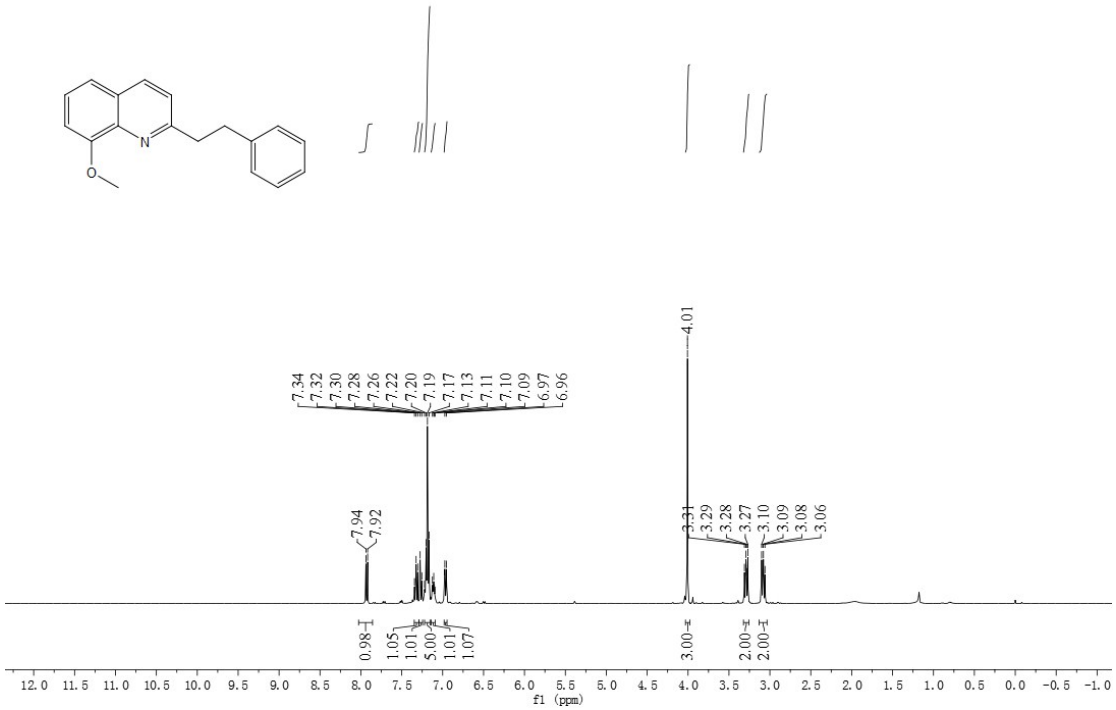
^{1}H-NMR spectrum of 3ea



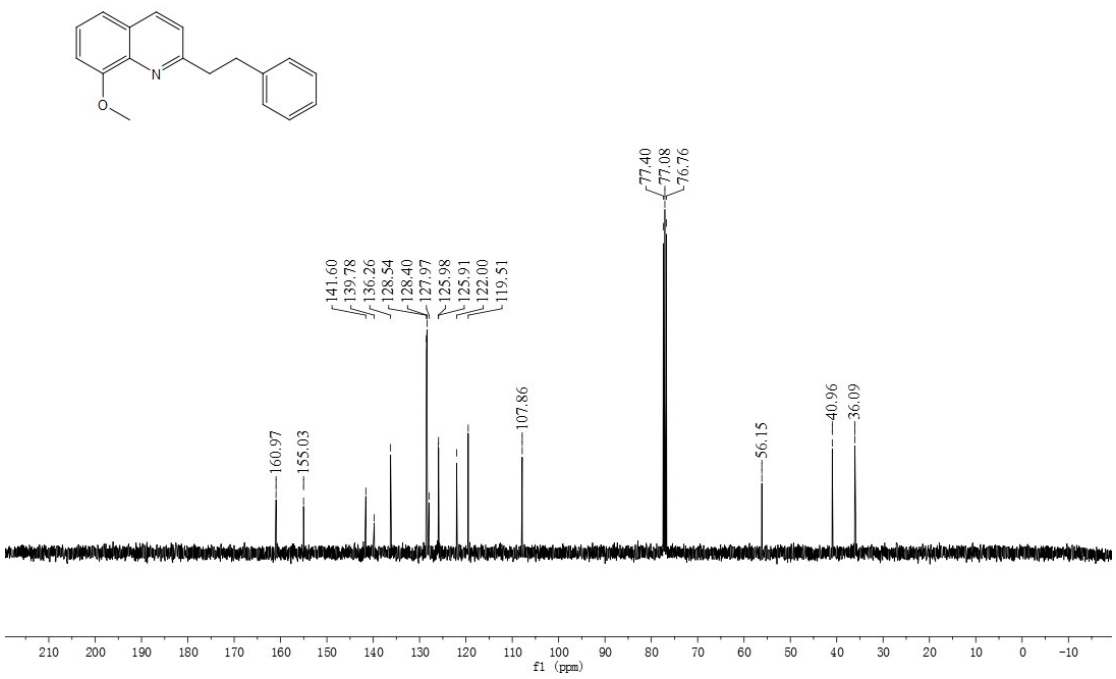
^{13}C-NMR spectrum of 3ea



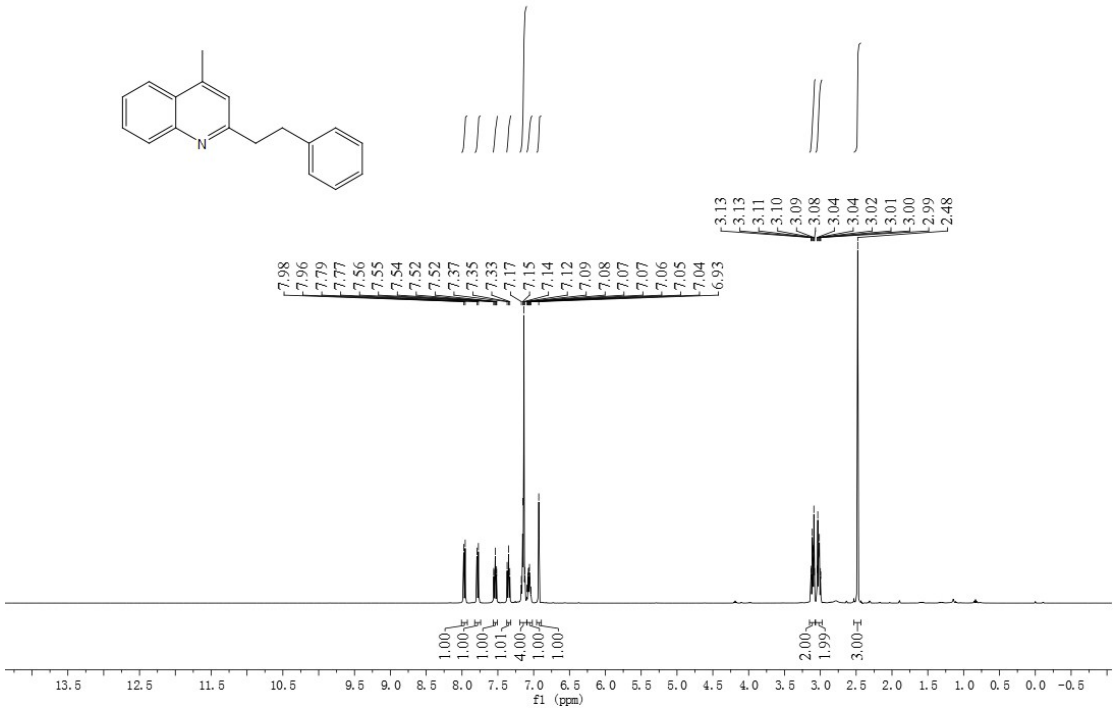
^{1}H-NMR spectrum of 3fd



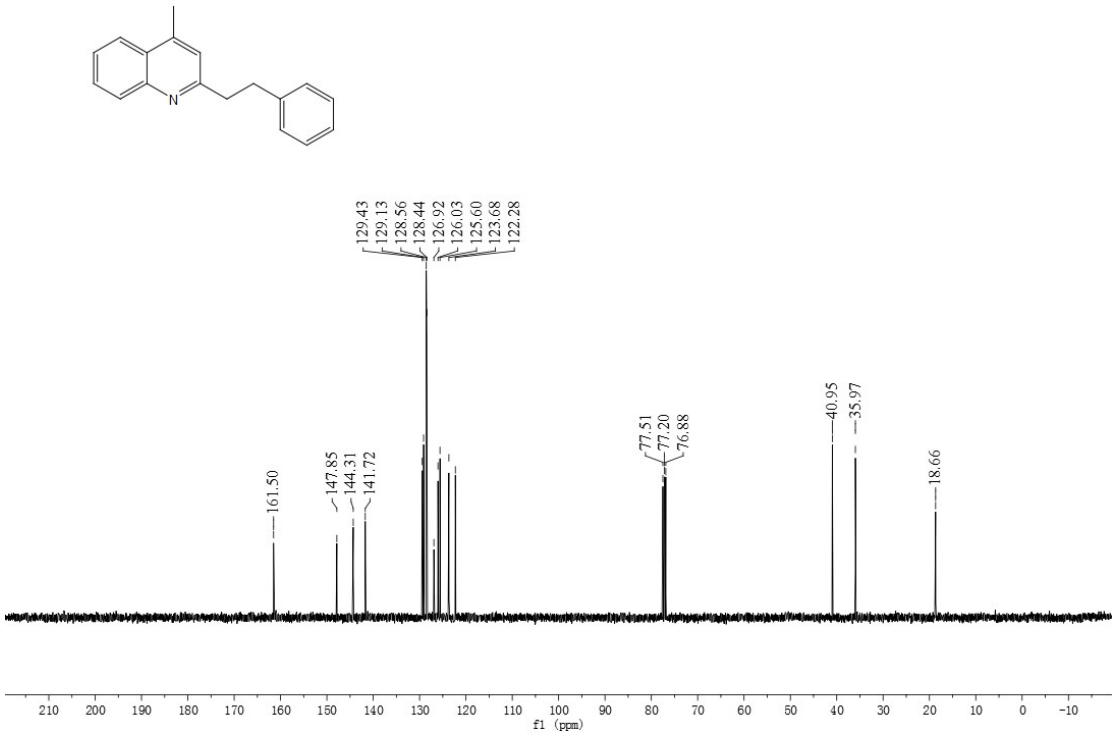
^{13}C-NMR spectrum of 3fd



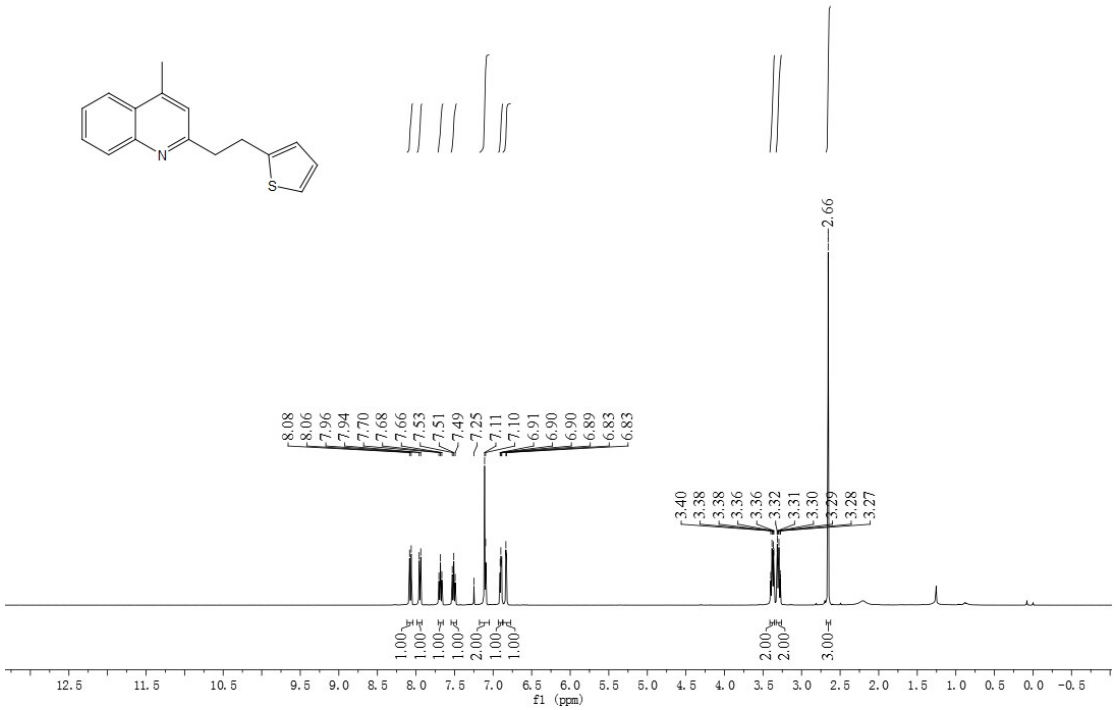
^{1}H-NMR spectrum of 3gd



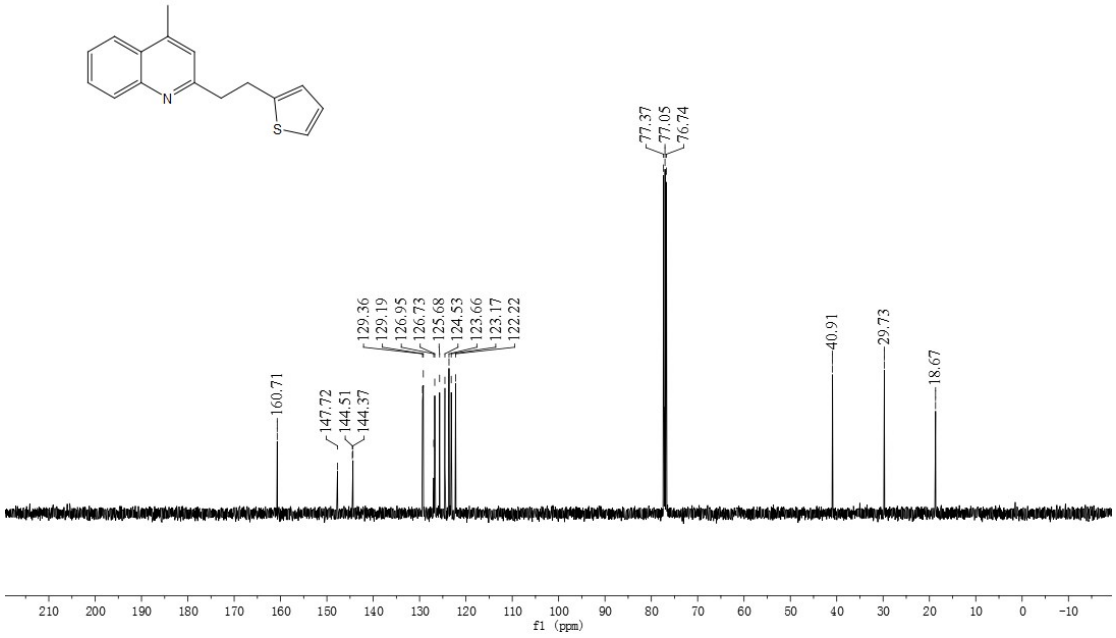
^{13}C-NMR spectrum of 3gd



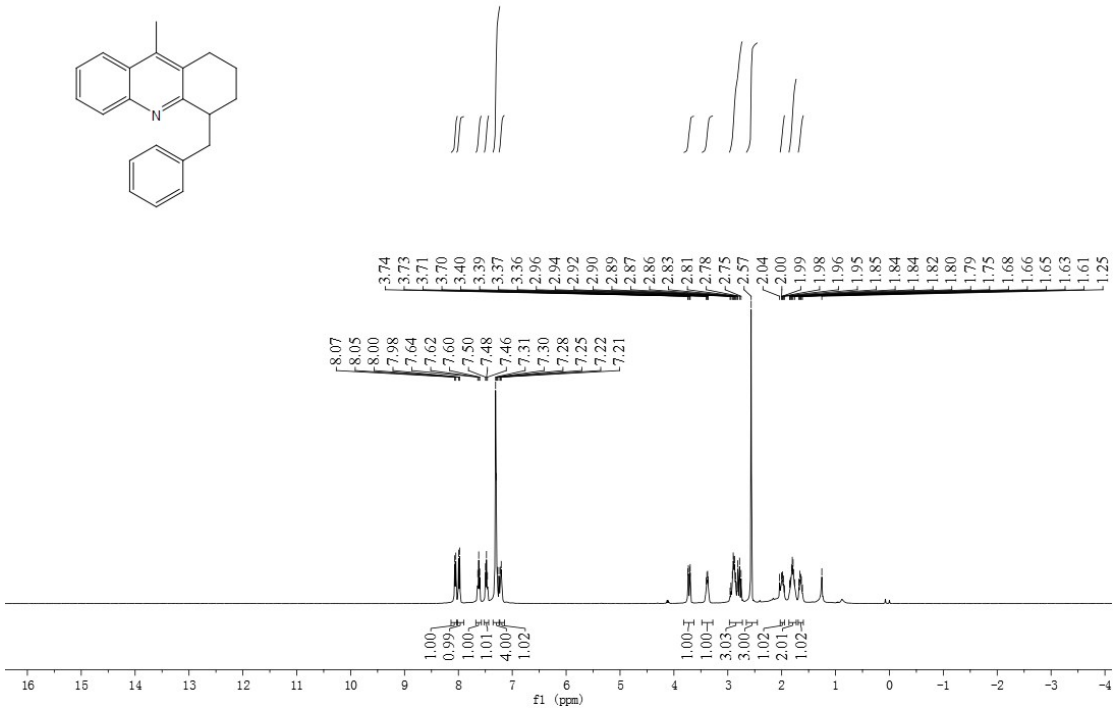
^{1}H-NMR spectrum of 3gk



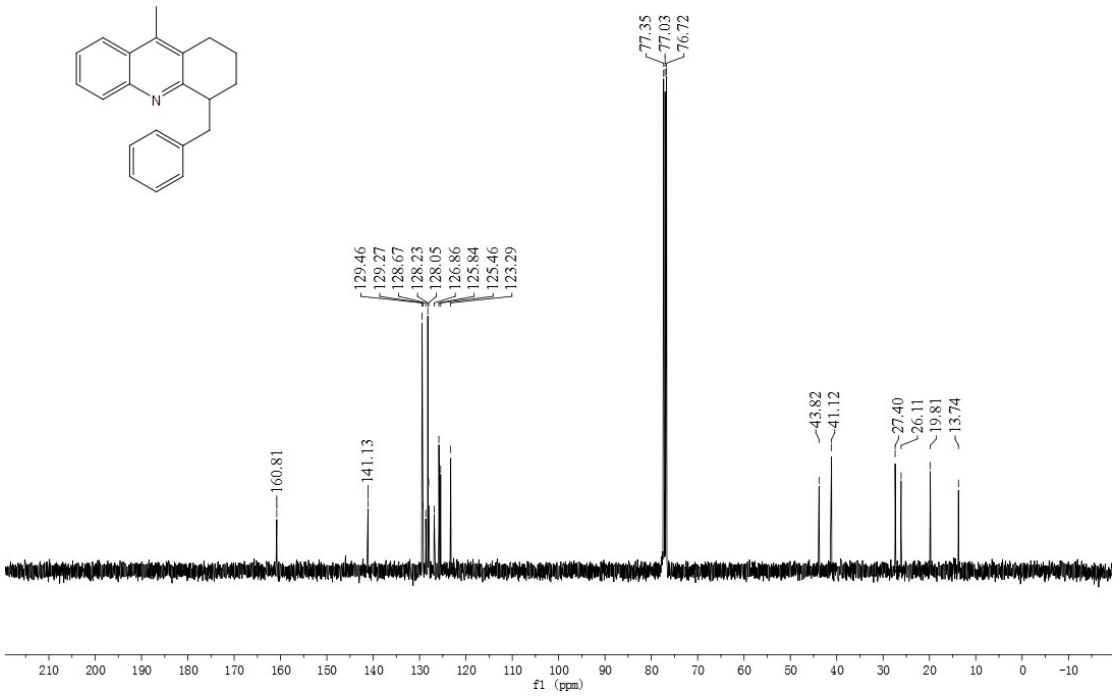
^{13}C-NMR spectrum of 3gk



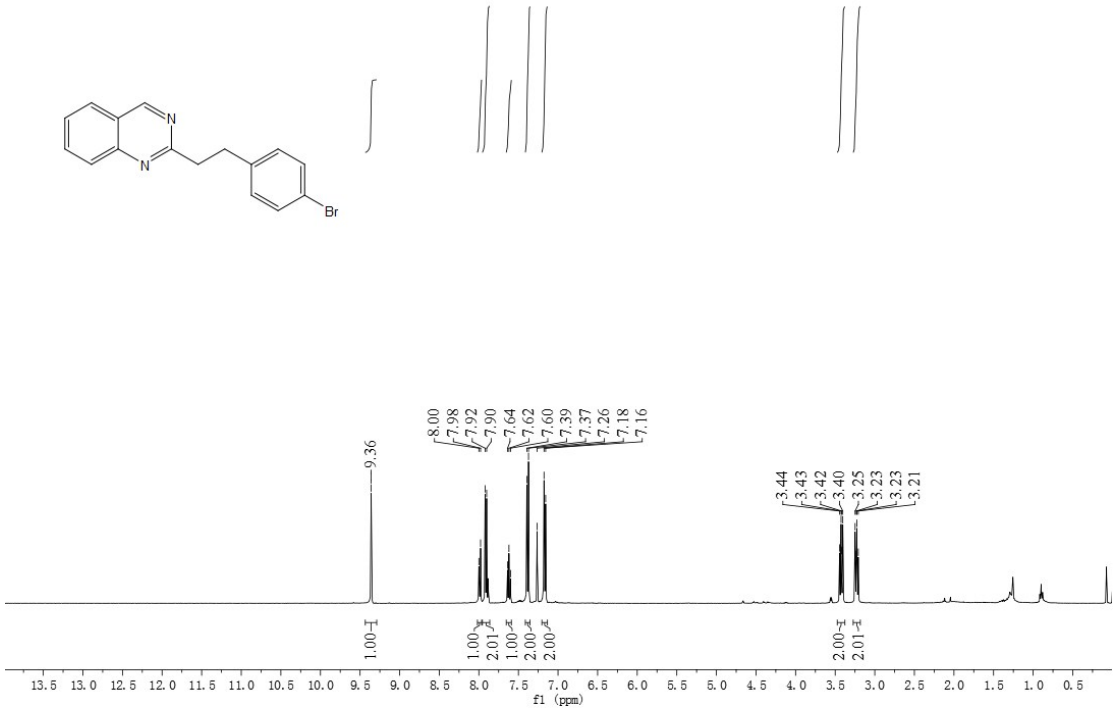
^{1}H-NMR spectrum of 3hd



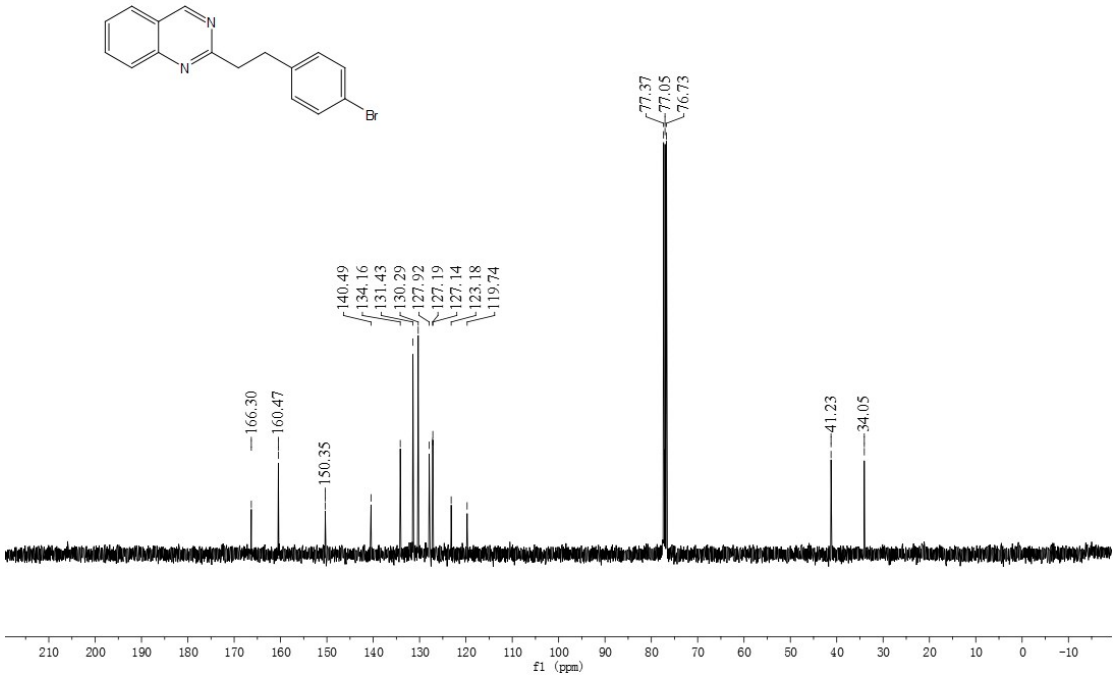
^{13}C-NMR spectrum of 3hd



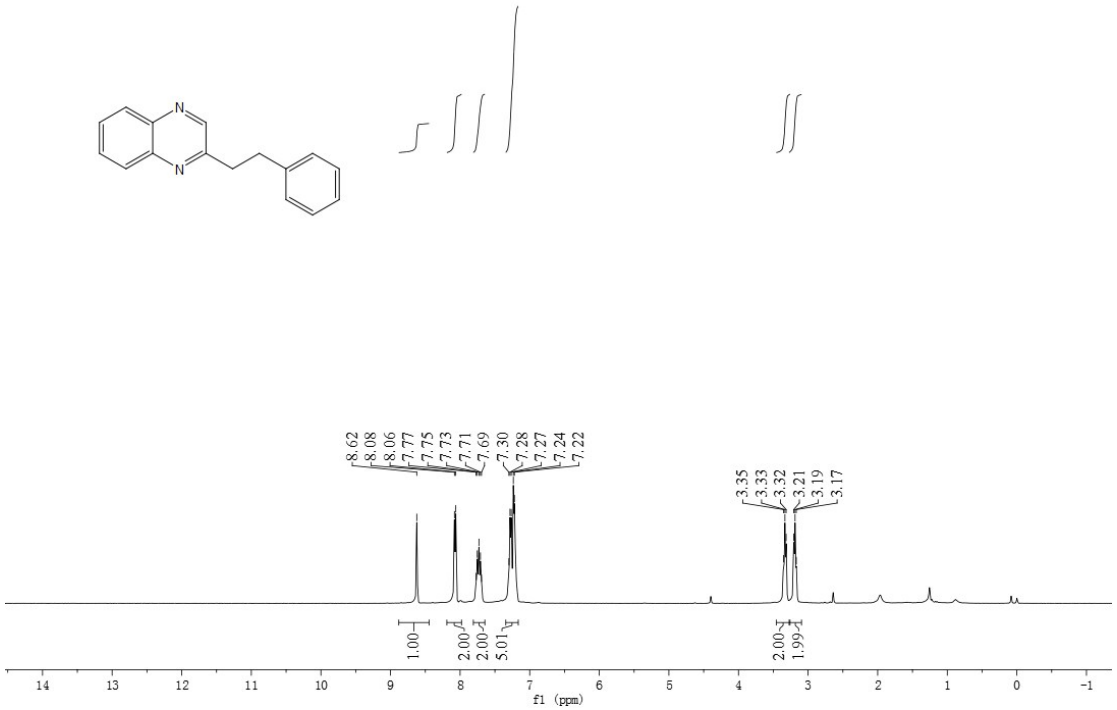
^{1}H-NMR spectrum of 3il



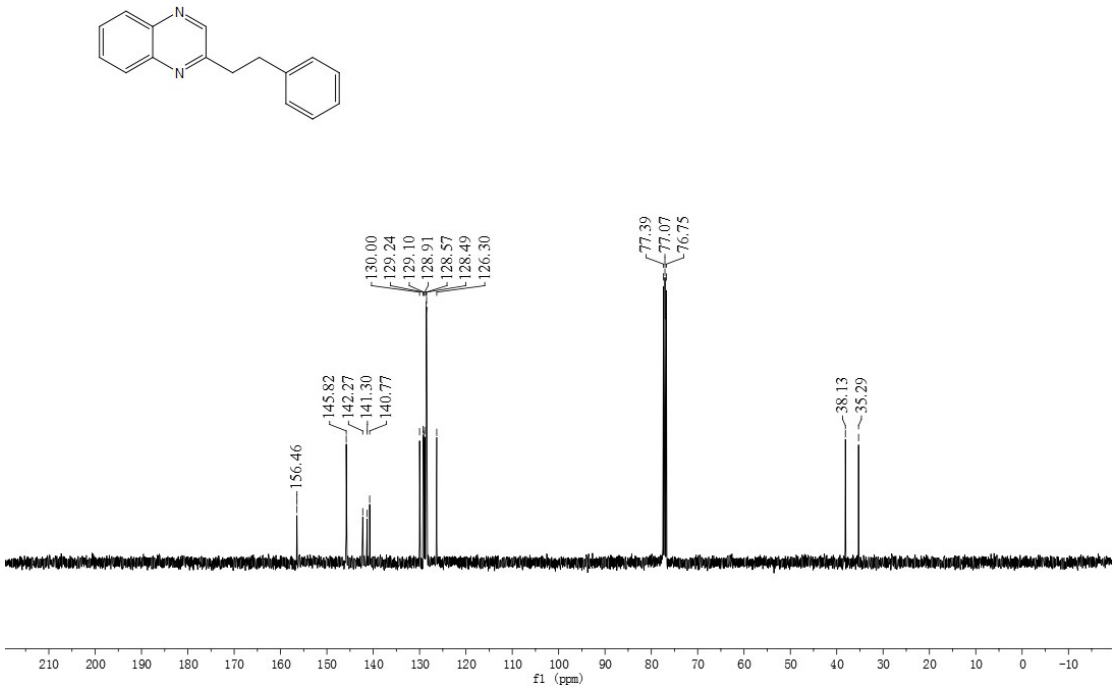
^{13}C-NMR spectrum of 3il



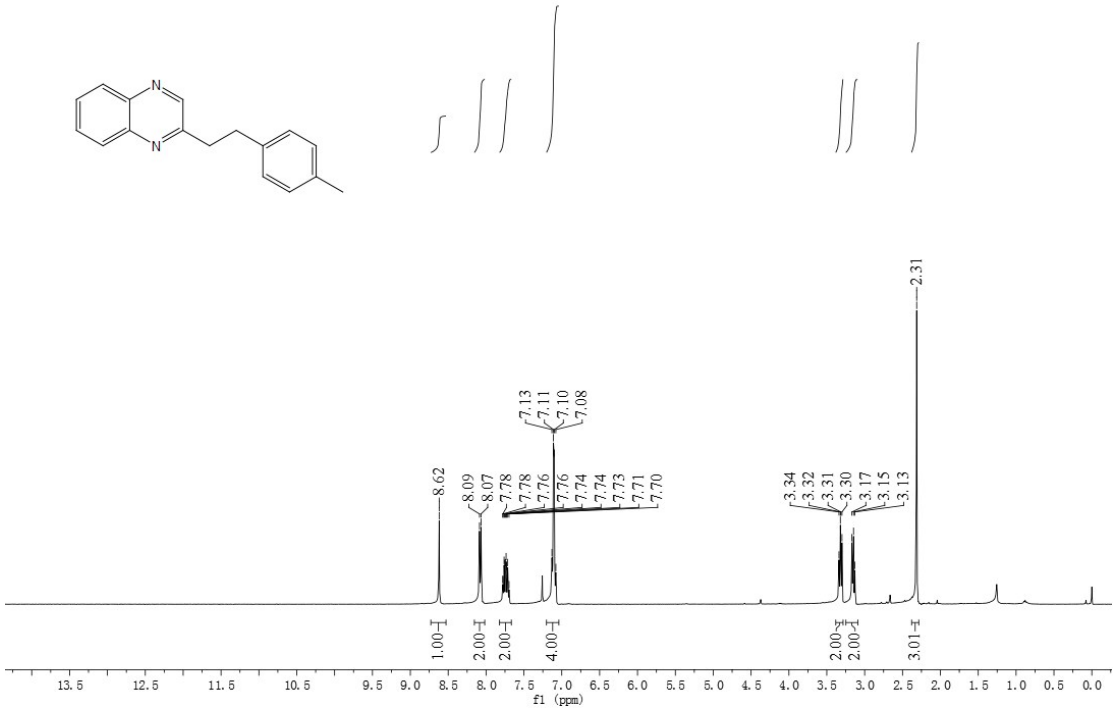
^{1}H-NMR spectrum of 3jd



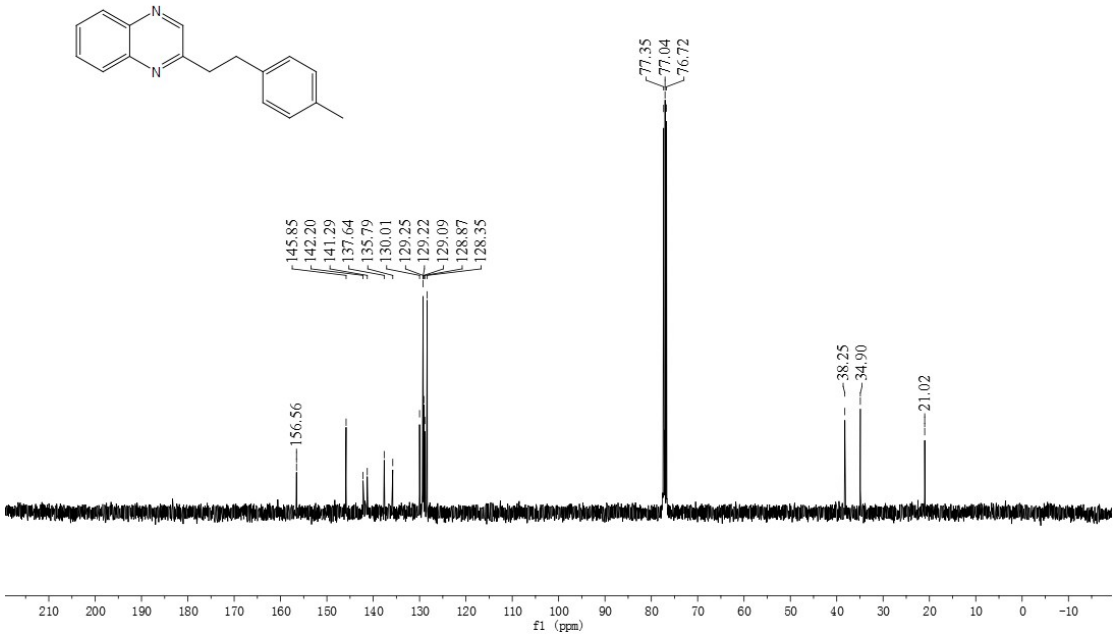
^{13}C-NMR spectrum of 3jd



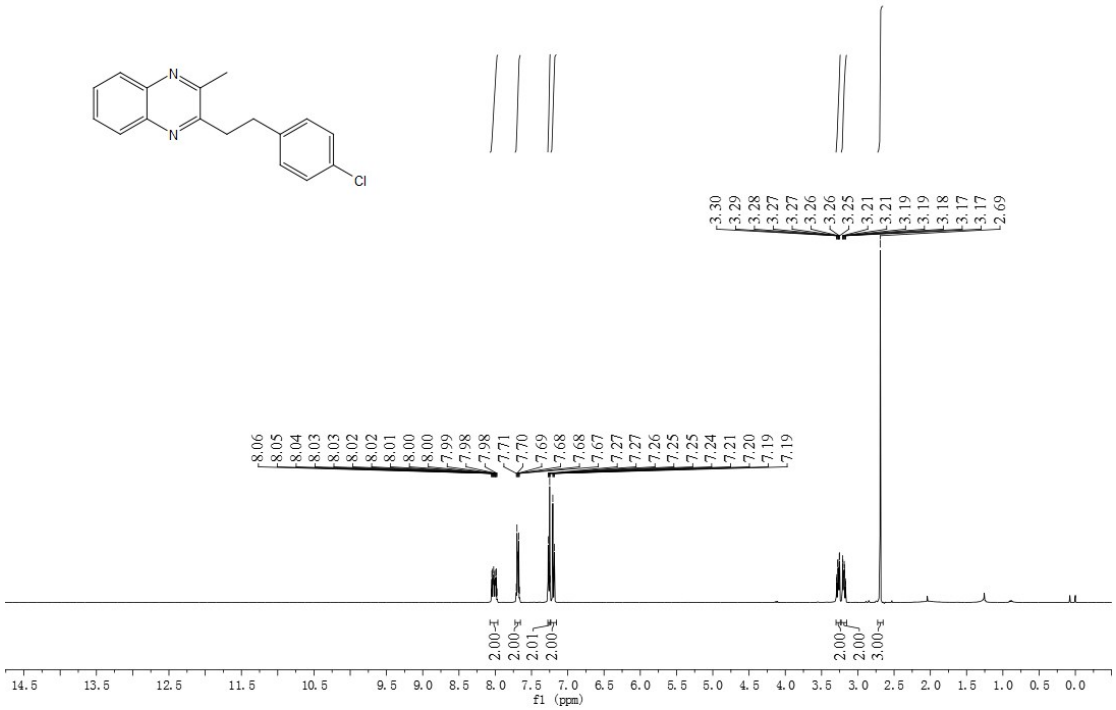
^{1}H-NMR spectrum of 3jf



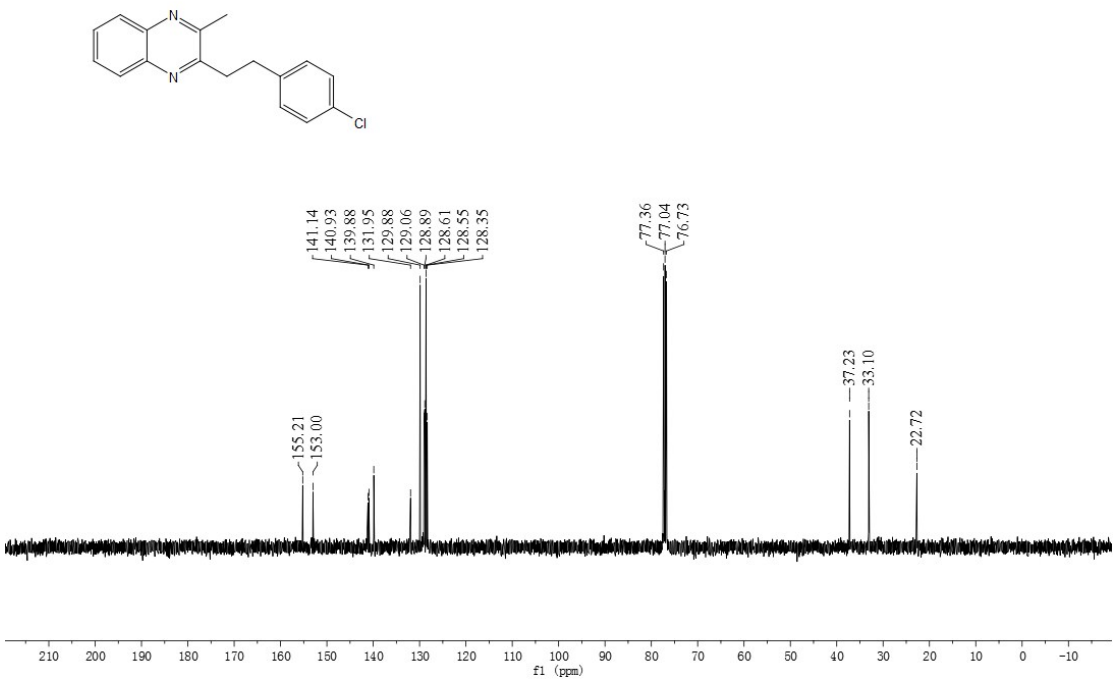
^{13}C-NMR spectrum of 3jf



^{1}H-NMR spectrum of 3ka

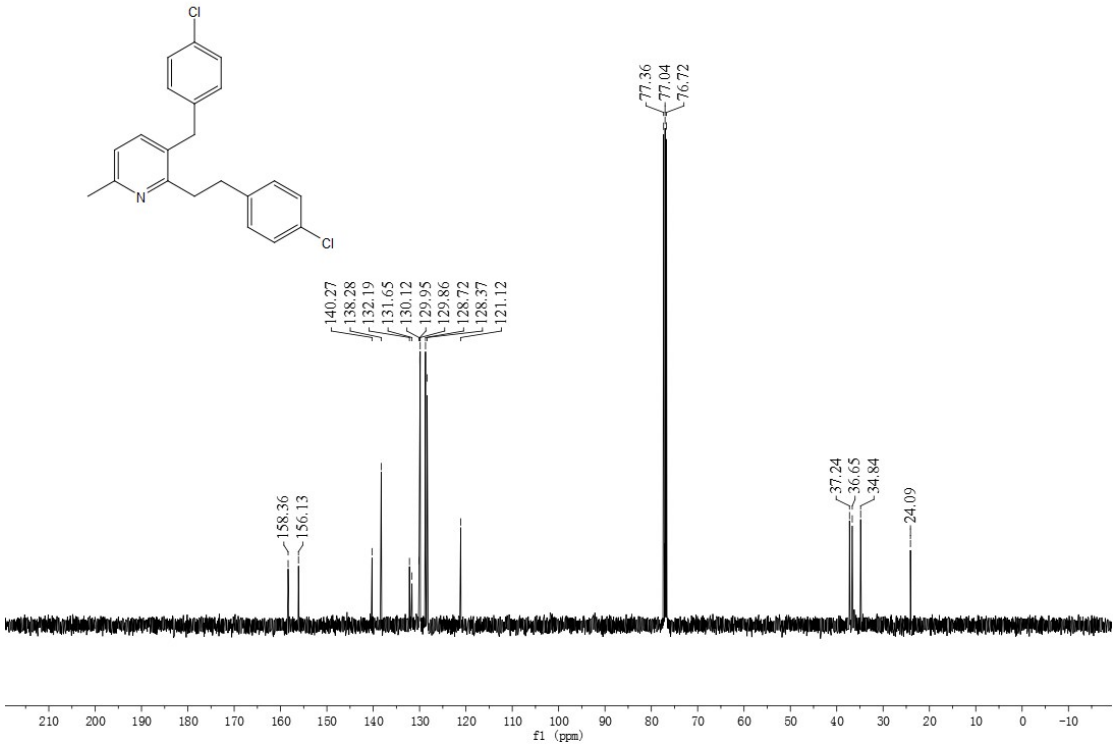


^{13}C-NMR spectrum of 3ka

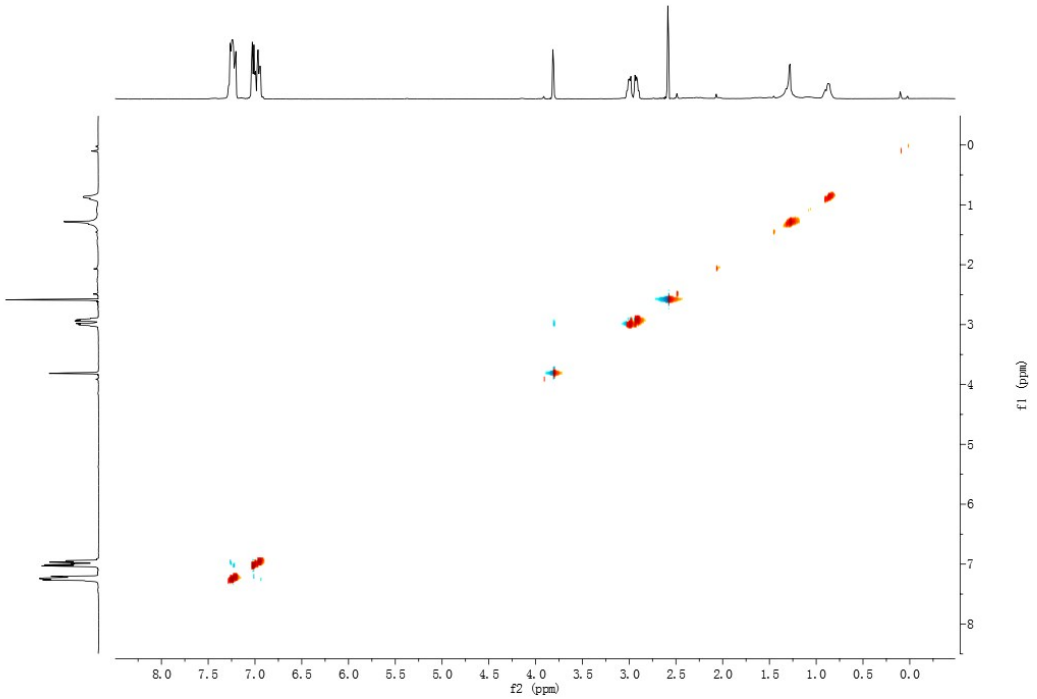


^{1}H-NMR spectrum of 3la-2

^{13}C-NMR spectrum of 3la-2



NOE-NMR spectrum of 3la-2



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