Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Direct *α*-C–H amination with various amino agents by selective oxidative copper catalyis: a divergent access to functional quinolines

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1. 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 effected at 254 nm; High performance liquid chromatography (HPLC) analyses were performed on a Agilent Technologies 1260 Infinity Ⅱ instrument equipped with a quaternary pump, using Daicel Chiralcel IA Columns (250 mmL × 4.6 mm ϕ). UV absorption was monitored at 254 nm. Unless otherwise stated, all the reagents were purchased from commercial sources (Energy Chemic, J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification; Cyclic voltammetry (CV) analysis was performed on Ingsens IGS-1030 electrochemical workstation (Ingsens Instruments (Guangzhou) Co., Ltd., China) with a conventional three-electrode cell, using a platinum electrode (d = 2 mm) as working electrode, a Pt wire as counter electrode and saturated calomel electrode (SCE) as a reference electrode. Cyclic voltammograms were recorded at 50 mV/s scan rate.

2. Substrates preparation

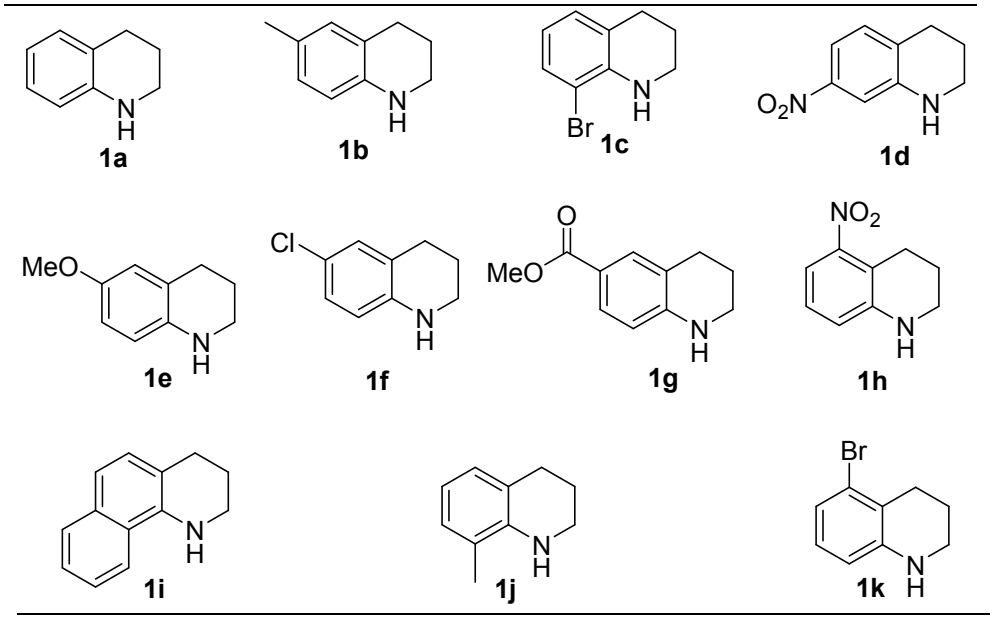
1,2,3,4-tetrahydroquinolines were known compounds and could be commercial or prepared via the literature procedures.[1, 2] Anilines, alkylamines, amides and sulfamides are all purchased form Energy Chemic, J&K Chemic, TCI, Fluka, Acros, SCRC.

References

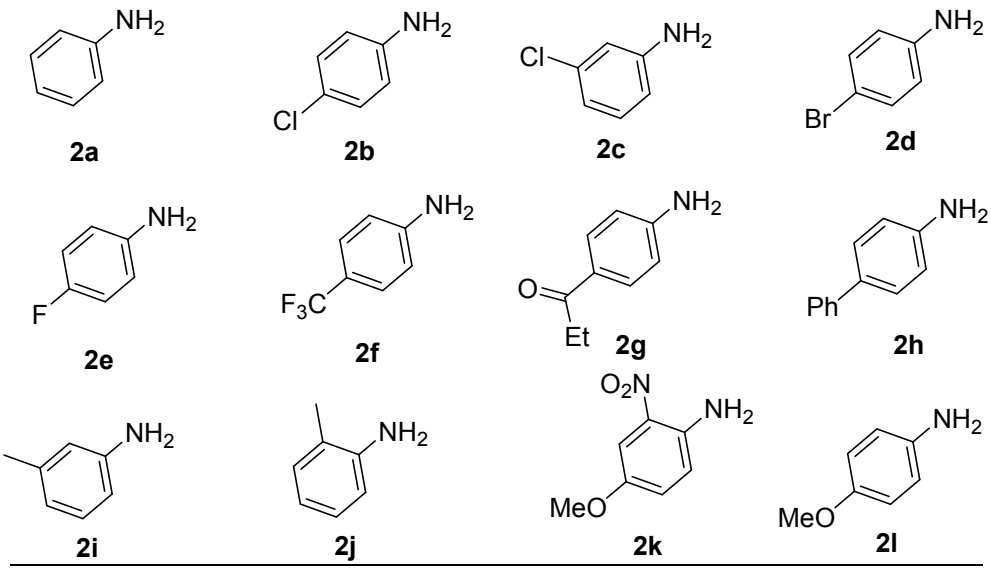
[1] M. Rueping, T. Theissmann, A. P. Antonchick. S*YNLETT.* 2006, **7**, 1071.

[2] S.J. Chen, G.P. Lu. T, C. Chai. S*ynthesis.* 2015**, 47,** 976.

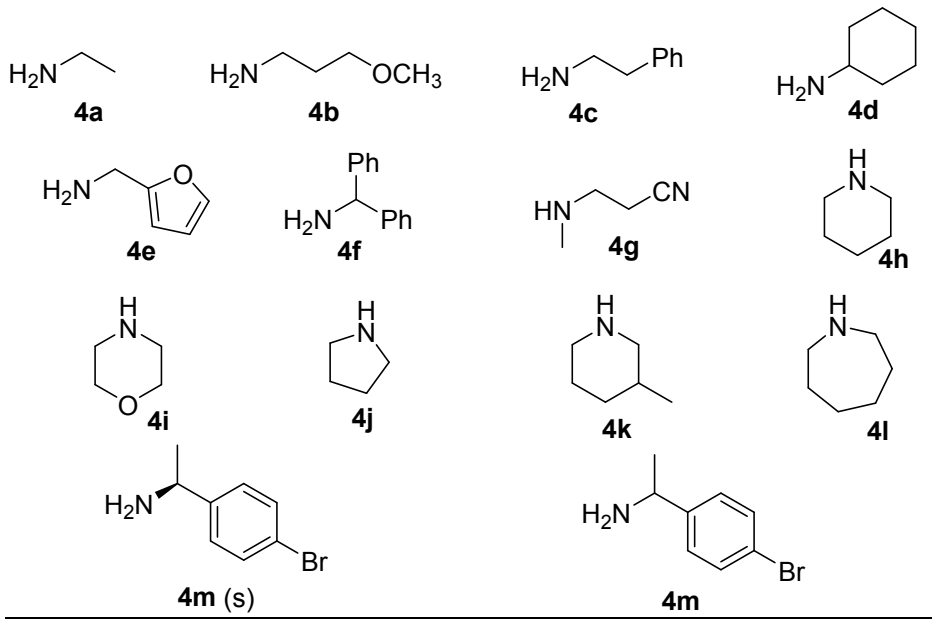
3. Substrates employed for the reaction



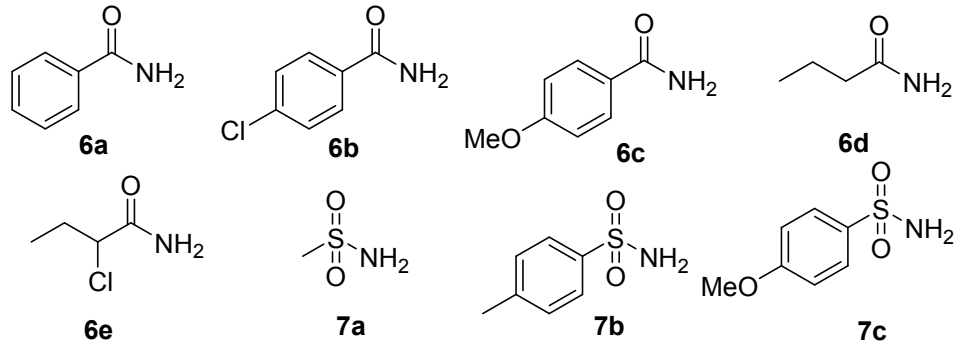
Scheme S1. Tetrahydroquinolines (THQs) employed for the α-C–H Amination.



Scheme S2. Primary arylamines employed for the α-C–H Amination.



Scheme S3. Alkylamines employed for the α-C–H Amination.



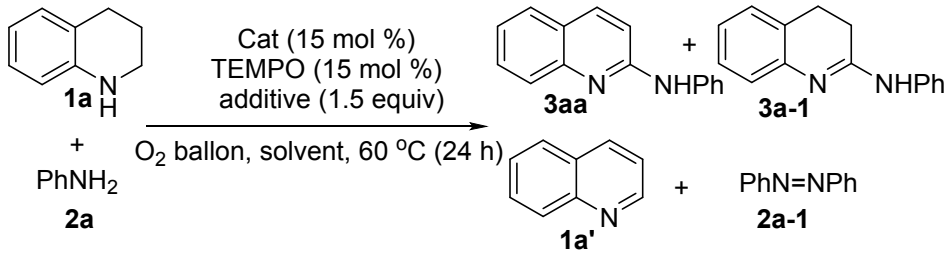
Scheme S4. Primary amides and sulfamides employed for the α-C–H functionalization.

3. Optimization of the reaction conditions

To examine the feasibiliy of the above idea, we initiated our study by choosing the reaction of tetrahydroquinoline **1a** and aniline **2a** as a model system to evaluate different reaction parameters. First, the reaction charged with O_2 balloon in toluene was performed at 60 ^oC for 24 h in the presence of 15 mol % CuCl and 1.5 equivalents of pyridine. However, it failed to give any desired product **3aa**, and only quinoline **1a'** and azo compound **2a-1** were observed (Table 1, entry 1). Interestingly, addition of 15 mol % of TEMPO[16] into the reaction led to generate **3aa** in 32% GC yield along with a certain amount of 2-aminodihydroquinoline **3a-1** (entry 2). Then, upon addition of TEMPO, a series of copper salts (entries 2-8) and solvents (entries 9-12) were screened, and the combination of CuCl and apolar *p*-xylene showed to be the best choice (entry 9). Further,

an increase of reaction temperature to 80 °C or the absence of copper salt failed to afford product **3aa** (entry 13), indicating that the copper catalyst and a low temperature are two key factors for product formation. Similarly, the change of pyridine to other basic additives resulted in no product formation or poor yield (entry 14). Gratifyingly, a gradient change on temperature significantly improved the yield (entry 15, 81%). Thus, the optimal conditions are as indicated in entry 15.

Table S1: Optimization of the reaction conditions[a]



Entry	Cat. (15 mol %)	Additive	Solvent	**3a** yield %[b]
1	CuCl	pyridine	toluene	tarce[c]
2	CuCl	pyridine	toluene	32
3	CuBr	pyridine	toluene	16
4	CuCN	pyridine	toluene	NR
5	CuI	pyridine	toluene	NR
6	$CuCl_2$	pyridine	toluene	NR
7	$Cu(OAC)_2$	pyridine	toluene	NR
8	$Cu(OTf)_2$	pyridine	toluene	NR
9	CuCl	pyridine	*p*-xylene	62
10	CuCl	pyridine	THF	10
11	CuCl	pyridine	DMSO	8
12	CuCl	pyridine	MeCN	21
13	CuCl	pyridine	*p*-xylene	(trace, -)[d]
14	CuCl	base	*p*-xylene	(-, 13, 38, -)[e]
15	CuCl	pyridine	*p*-xylene	(81)[f]

[a] Reaction conditions: unless otherwise stated, the reaction in solvent (1.5 mL) was performed with **1a** (0.3 mmol), **2a** (0.3 mmol), cat. (15 mol %), TEMPO (15 mol %), additive (1.5 equiv) at 60 °C for 24 h charged with a O_2 balloon. [b] GC yield. [c] Without addition of TEMPO. [d] 80 °C or the absence of CuCl. [e] Yield are with respect to use of $(Et)_3N$, DBU, K_2CO_3 and *t*-BuOk as the additives, respectively. [f] 45 °C for 10 h then at 95 °C for 12 h.

4. Typical procedure for synthesis of 2- aminoquinolines

The mixture of 1,2,3,4-tetrahydroquinolines(0.3 mmol), amine (0.3 mmol), pyridine (0.45 mmol), TEMPO (0.045 mmol) and CuCl (0.045 mmol) in *p*-xylene (1.5 mL) was stirred at 45 °C for 10 hours under 1 atm of O_2 atmosphere (using O_2 balloon) and then heat to 95°C for 12 hours. After cooling down to room temperature, the resulting mixture was extracting with ethyl acetate, washed with purified water, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 °C) : ethyl acetate (15:1~1:2) to give 2-aminoquinolines.

5. Representative time course for the model reaction

The model reactions with (a) or without (b) TEMPO were performed at 45 ^{o}C for 10 h, respectively. The reactions were carried out at different reaction times and the reaction mixture was analyzed by GC using hexadecane as the internal standard.

As shown in Figure S1a, THQ **1a** was rapidly consumed to give the dihydroquinolines (imne **1a-1** and enamine **1a-2**) within 1.5 h. Then, the concentrations of aniline **2a** and dihydroquinilines gradually decreased, and 2-aminodihydroquinoline **3a-1** accumulated to a constant yield around 10 h. Then, **3a-1** could be fully transformed into product 2-phenylaminoquinoline (**3aa**) by prolonging the reaction for another 20 h at elevated temperature (95 ^{o}C, see SI, eq 2). The results indicate that dihydroquinolines and **3a-1** are the successive intermediates for the formation of **3aa**. In comparison, the reaction without TEMPO (Figure S1b) leads to slow generation of dihydroquinilines, only small portion of aniline **2a** was slowly converted into **3a-1** and **3aa**, and quinoline **1a'** was produced as a major product. Clearly, the addition of TEMPO makes the first dehydrogenation of THQ a kinetically favorable process, the high concentration of dihydroquinilines favors the addition of amino nucleophiles, even including weak amide and sulfamide nucleophiles, and the conversion of **3a-1** to **3aa** is a thermodynamically driven step.

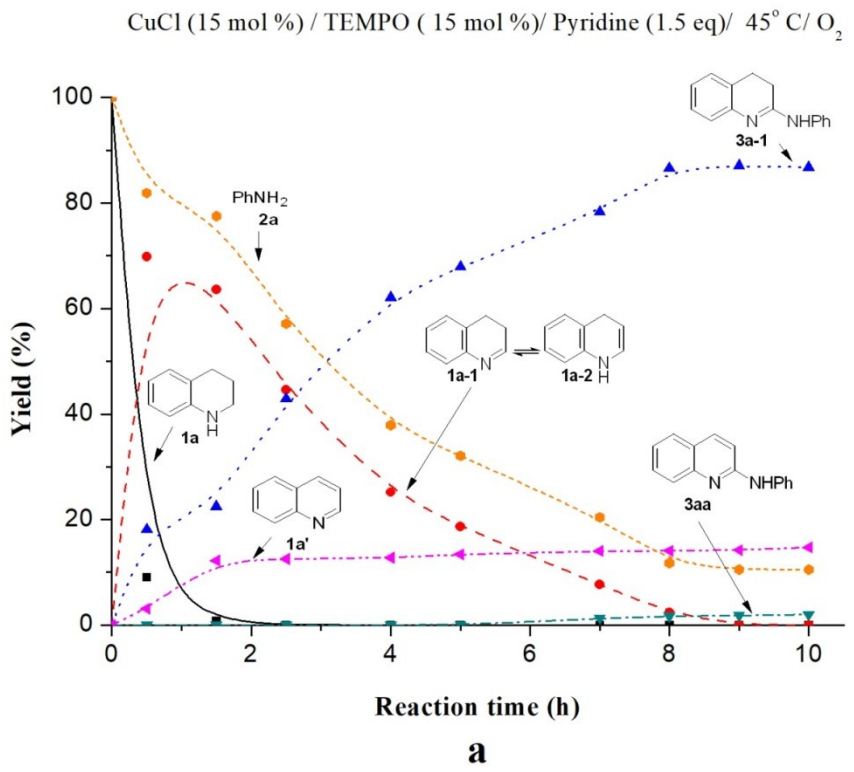


Figure S1a. Representative time course in the presence of TEMPO

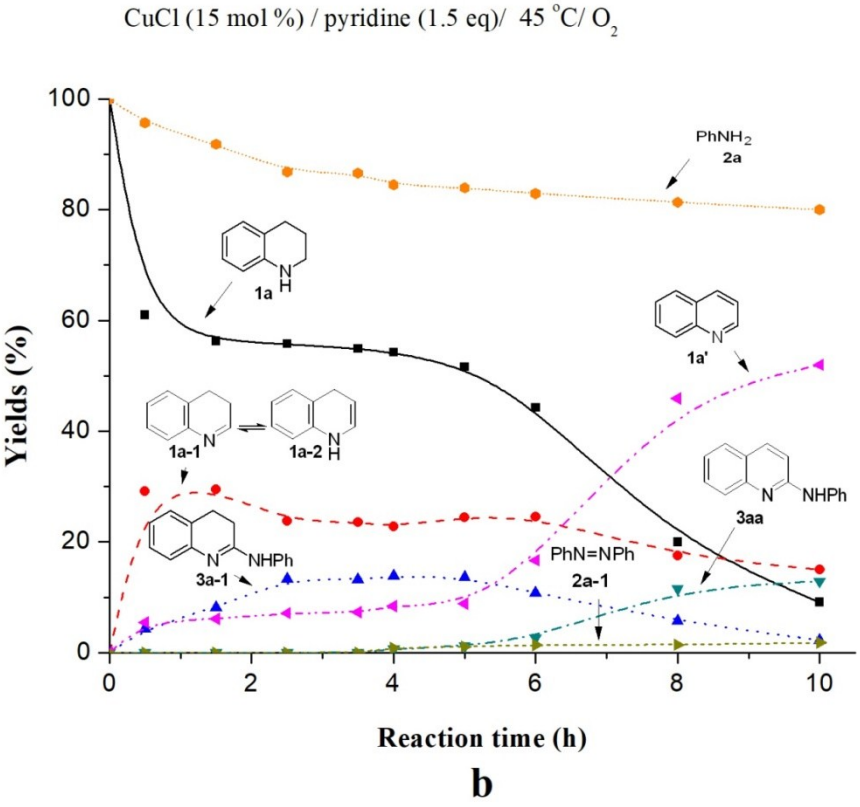
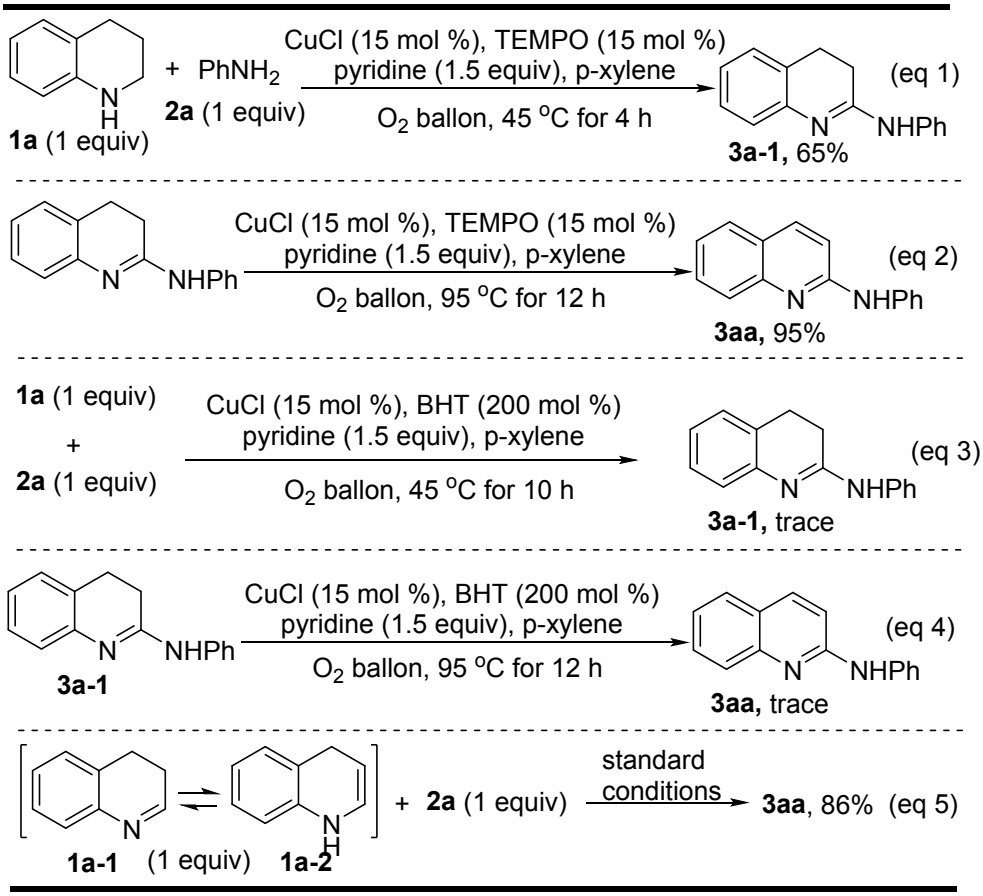


Figure S1b. Representative time course in the absence of TEMPO

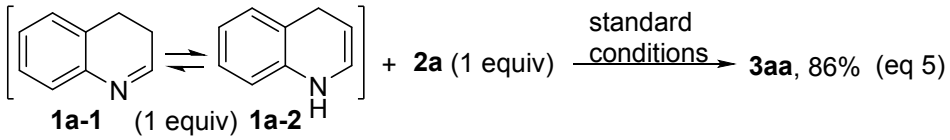
6.The control experiments

To gain insight into the reaction mechanism, several verification experiments were performed. First, the model reaction was performed under the standard conditions but at 45 °C for 4 h and 2-Aminoimine intermediate **3a-1** was isolated and confirmed by GC−MS and NMR analyses (eq 1), and then, **3a-1** could be fully transformed into product 2-phenylaminoquinoline (**3aa**) by prolonging the reaction for another 12 h at elevated temperature (95 °C, eq 2), which indicated that 2-Aminoimine intermediate **3a-1** was the successive intermediate for the formation of **3aa**. Noteworthy, the model reaction or 2-aminodihydroquinoline **3a-1** under the standard conditions by treating with excess BHT (butylated hydroxytoluene) suppressed the formation of product **3aa**, showing that the reaction involves radical pathways (See eq 3 and eq 4). Further, the reaction of **2a** with imine **1a-1** or its tautomer (enamine **1a-2**) under the standard conditions succeed to yield product **3aa** (eq 5), showing that imine **1a-1** or its tautomer (enamine **1a-2**) which generated from the the first dehydrogenation of **1a** are the crucial intermediate.



Scheme S5. The control experiments.

6.1 The Procedure of the Verification experiments （Equation 5）



The mixture of 1,2,3,4-tetrahydroquinolines (0.3 mmol), pyridine (0.6 mmol), 15 mol % TEMPO and 15 mol % CuCl in *p*-xylene (1.5 mL) was stirred at 40 °C for 1.5 hours under 1 atm of O_2 atmosphere (using O_2 balloon). After cooling down to room temperature, the reaction mixture contained the mixture of enamine (**B**) and imine (**C**). Upon GC–MS analysis, the ratio of **1a-1** to **1a-2** is 6:1. Then, we continued adding aniline (0.3 mmol) to the reaction mixture at 45 °C for 10 hours then 95 °C for 12 hours. After cooling down to room temperature, the resulting mixture was extracting with ethyl acetate, washed with purified water, and then concentrated by removing the solvent under vacuum. Finally the residue was purified by preparative TLC on silica.

7.Cyclic voltammograms

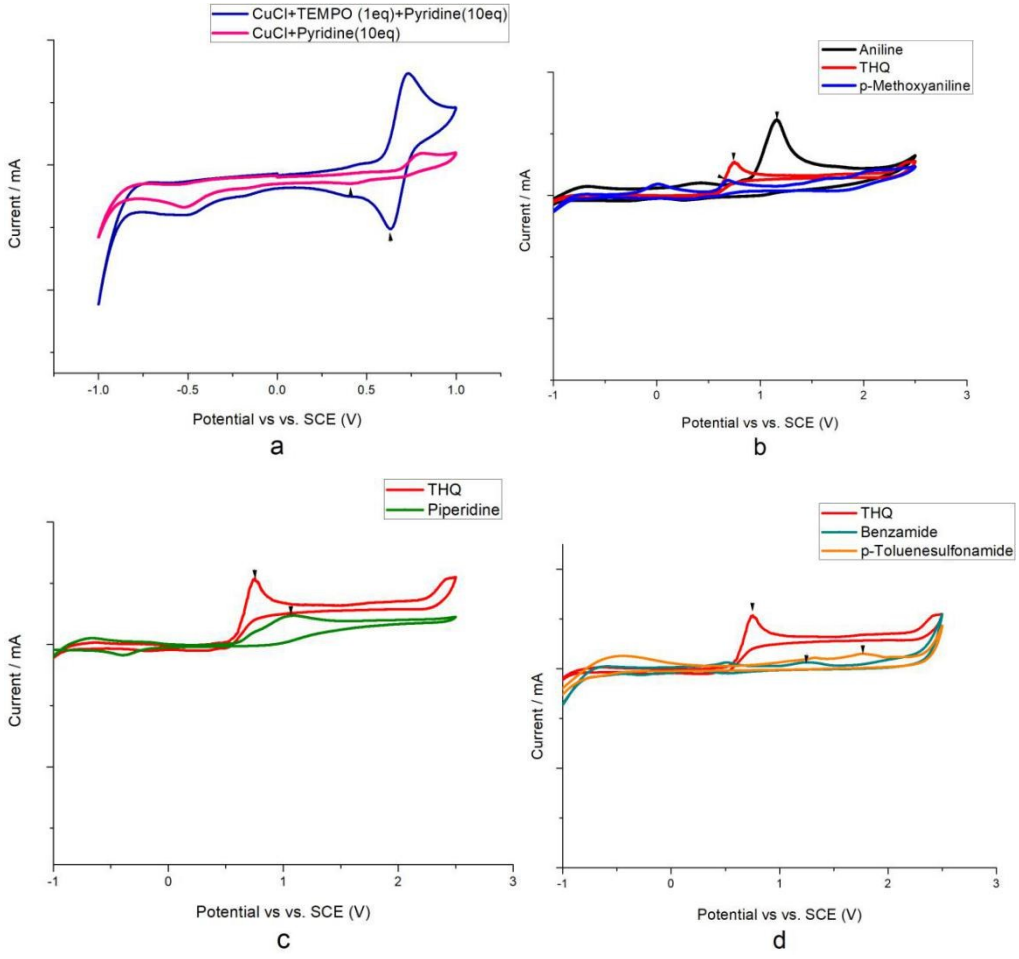
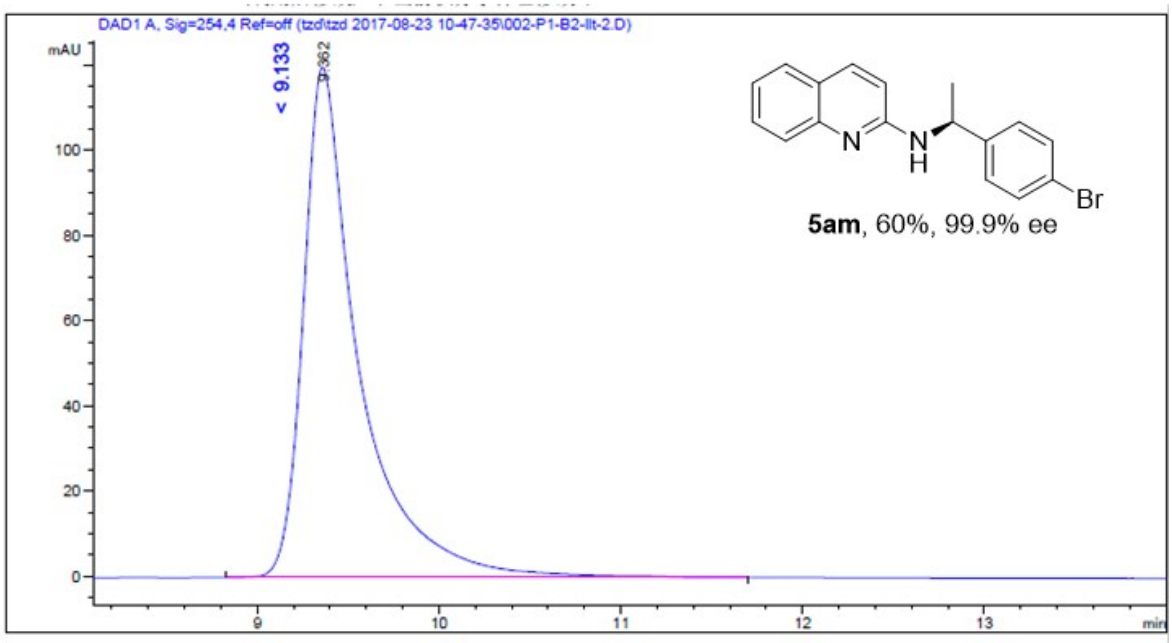


Figure S2. Cyclic voltammograms of 0.1 M $TBAClO_4$ solution in Acetonitrile at room temperature. Conditions: (a) CuCl (0.0045 M) + TEMPO (0.0045 M) + Pyridine (0.045 M) and CuCl (0.0045 M) + Pyridine (0.045 M); (b) THQ (0.03 M), p-methoxyaniline (0.03 M) and Aniline (0.03 M); (c) THQ (0.03 M), Piperidine (0.03 M); (d) THQ (0.03 M), Benzamide (0.03 M) and *p*-Toluenesulfonamide (0.03 M).The voltammogram was obtained with Pt wire as auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The scan rate was 0.05 V/s on a platinum disk electrode (*d* = 2 mm).

8. HPLC Spectra of compound 5am

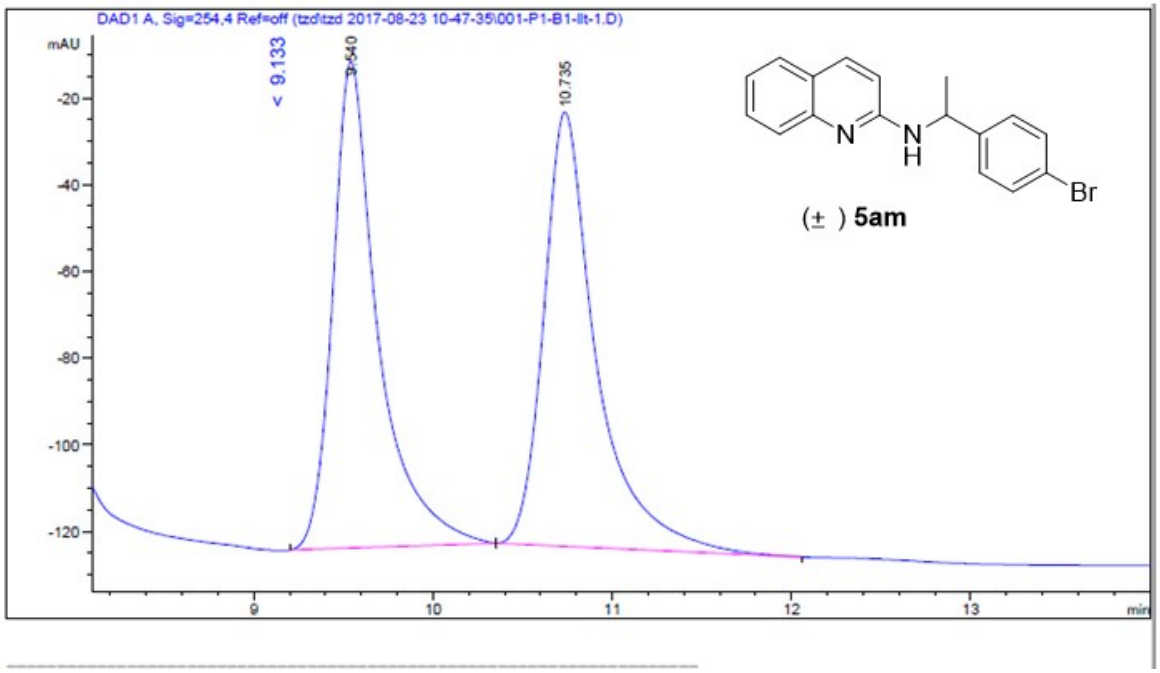
Column: Chiralpak IA, Daicel Corporation;
Eluent: Hexanes/Ethanol (99/1);
Flow rate: 0.5 mL/min;
Detection: UV 254 nm.

HPLC Spectra of Chiral **5am**



Peak #	Retention time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.362	BH	0.3018	2561.55176	119.61930	100.0000

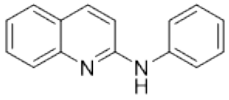
HPLC Spectra of Racemic **5am**



Peak #	Retention time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.540	HH	0.2527	1967.78418	112.15722	49.0716
2	10.735	HB	0.2959	2042.24512	100.15334	50.9284

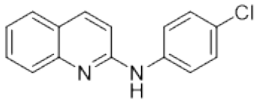
9. Analytic data of the obtained compound

(1) N-phenylquinolin-2-amine(3aa)



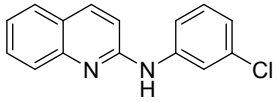
Known compound[1], black solid (40.9 mg, 62 % yield), m.p: 97-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 9.2 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3): δ 154.49, 147.62, 140.24, 137.99, 130.00, 129.40, 127.57, 126.71, 124.26, 123.24, 123.21, 120.77, 111.75. IR (KBr): 3404, 3050, 1620, 1597, 1533, 1401, 823, 752 cm^{-1}. MS (EI, m/z): 220.1 $[M]^+$.

(2) N-(4-chlorophenyl)quinolin-2-amine(3ab)



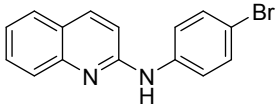
Known compound[1], white solid (36.5 mg, 48 % yield), m.p: 136-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 9.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.6 Hz, 3H), 7.31 (t, *J* = 7.8 Hz, 3H), 6.88 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3): δ 153.94, 147.52, 139.02, 137.96, 130.01, 129.21, 127.57, 127.48, 126.91, 124.28, 123.52, 121.34, 112.13. IR (KBr): 3405, 1596, 1536, 750 cm^{-1}. MS (EI, m/z): 254.1 $[M]^+$.

(3) N-(3-chlorophenyl)quinolin-2-amine(3ac)



Known compound[2], yellow solid (61.7 mg, 81 % yield), m.p: 86-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.64, 147.42, 141.66, 138.06, 134.83, 130.18, 130.06, 127.56, 127.03, 124.35, 123.70, 122.68, 119.72, 117.82, 112.28. IR (KBr): 3413, 1590, 1526, 1479, 1429, 1395, 1345 815, 753, 678 cm^{-1}. MS (EI, m/z): 254.1 $[M]^{+\cdot}$

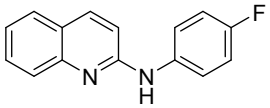
(4) N-(4-bromophenyl)quinolin-2-amine(3ad)



Known compound[1], black solid (38.4 mg, 43 % yield), m.p: 146-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.8

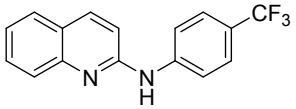
Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.82, 147.46, 139.51, 137.98, 132.13, 130.03, 127.56, 126.91, 124.28, 123.57, 121.60, 115.07, 112.20. IR (KBr): 3402, 1535, 1488, 1239, 818, 750, 542, 497 cm^{-1}. MS (EI, m/z): 298.0 $[M]^+$.

(5) N-(4-fluorophenyl)quinolin-2-amine(3ae)



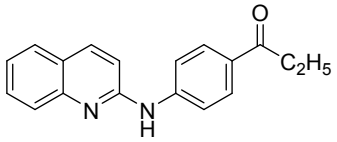
Known compound[1], white solid (46.1 mg, 65 % yield), m.p: 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 9.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.30 (t, J = 7.4 Hz, 1H), 7.07 (t, J = 8.6 Hz, 2H), 6.87 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.34 (d, $^1J_{C\text{-}F}$ = 240 Hz), 157.93, 154.60, 147.62, 138.03, 136.28, 130.02, 127.59, 126.74, 124.22, 123.32, 122.77 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 116.10, 115.87 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 111.58. IR (KBr): 3223, 1618, 1506, 1428, 1216, 1094, 821, 781, 752, 591, 509, 475 cm^{-1}. MS (EI, m/z): 238.1 $[M]^+$.

(6) N-(4-(trifluoromethyl)phenyl)quinolin-2-amine(3af)



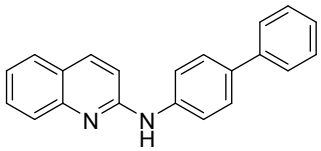
Known compound[2], white solid (59.6 mg, 69 % yield), m.p: 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.62 (dd, J = 17.8, 9.6 Hz, 3H), 7.36 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.28, 147.32, 143.67, 138.05, 130.10, 127.58, 127.14, 126.40 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.94, 124.47 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 123.93, 123.62, 120.24 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 118.57, 112.70. IR (KBr): 3300, 1603, 1529, 1396, 1324, 1253, 1161, 1109, 1066, 818, 816, 756 cm^{-1}. MS (EI, m/z): 288.1 $[M]^+$.

(7) 1-(4-(quinolin-2-ylamino)phenyl)propan-1-one(3ag)



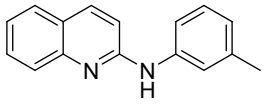
White solid (47.1 mg, 57 % yield), m.p: 171-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.62, 153.17, 147.37, 144.88, 138.00, 131.11, 130.07, 127.53, 127.24, 124.47, 123.94, 123.72, 117.93, 112.92, 60.77, 14.51. IR (KBr): 3348, 1680, 1595, 1535, 1478, 1421, 1278, 1249, 1170, 964, 815, 767, 696 cm^{-1}. HRMS (ESI): Calcd. for $C_{18}H_{17}N_2O$ $[M+H]^+$: 293.1285; found: 293.1290.

(8) N-([1,1'-biphenyl]-4-yl)quinolin-2-amine(3ah)



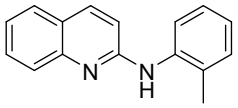
Black solid (50.6 mg, 57 % yield), m.p: 157-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 8.4 Hz, 3H), 7.60 (m, 5H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.33 (dd, *J* = 14.4, 7.2 Hz, 2H), 7.01 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.25, 147.71, 140.87, 139.66, 137.94, 135.94, 130.00, 128.91, 127.97, 127.57, 127.02, 126.87, 124.32, 123.39, 120.63, 112.06. IR (KBr): 3989, 1601, 1524, 1484, 1395, 1346, 816, 759, 696 cm^{-1}. HRMS (ESI): Calcd. for $C_{21}H_{17}N_2$ $[M+H]^+$: 297.1386; found: 297.1390.

(9) N-(*m*-tolyl)quinolin-2-amine(3ai)



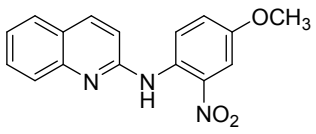
Known compound[1], yellow solid (36.5 mg, 52 % yield), m.p: 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 7.18 (dt, *J* = 15.2, 7.2 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.69, 147.83, 140.18, 139.26, 137.84, 129.89, 129.20, 127.54, 126.75, 124.26, 124.21, 123.18, 121.52, 117.95, 111.70, 21.66. IR (KBr): 3400, 3050, 1605, 1535, 1486, 1430, 1396, 1346 1235, 818, 777, 753, 690 cm^{-1}. MS (EI, m/z): 234.1 $[M]^+$.

(10) N-(o-tolyl)quinolin-2-amine(3aj)



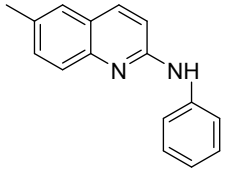
Known compound[1], yellow solid (44.9 mg, 64 % yield), m.p: 97-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 14.0, 7.6 Hz, 2H), 7.23 – 7.12 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.52, 147.80, 138.10, 137.97, 131.82, 131.09, 129.91, 127.54, 126.93, 126.26, 124.94, 124.11, 123.70, 122.94, 110.68, 18.16. IR (KBr): 3410, 3010, 2962, 1619, 1504, 1422, 1346, 819, 750 cm^{-1}. MS (EI, m/z): 234.1 $[M]^+$.

(11) N-(4-methoxy-2-nitrophenyl)quinolin-2-amine(3ak)



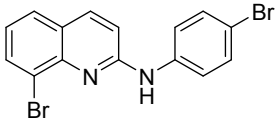
Orange solid (32.5 mg, 41 % yield), m.p: 128-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (brs, 1H), 9.34 (d, *J* = 9.6 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.29 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.03, 152.48, 146.96, 138.02, 135.28, 133.00, 130.03, 127.53, 127.52, 124.89, 124.79, 124.40, 122.63, 114.84, 107.74, 55.94. IR (KBr): 3433, 1594, 1507, 1336, 1275, 1220, 937, 818, 740, 658 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{14}N_3O_3$ $[M+H]^+$: 296.1030; found: 296.1031.

(12) 6-methyl-N-phenylquinolin-2-amine(3ba)



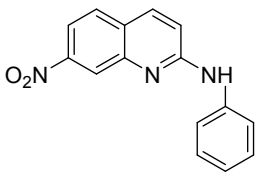
Black solid (57.0mg, 82 % yield), m.p: 93-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.98, 145.96, 140.49, 137.34, 132.80, 131.94, 129.31, 126.68, 126.49, 124.21, 122.99, 120.45, 111.76, 21.32. IR (KBr): 3440, 2919, 1596, 1531, 1498, 1442, 1402, 1350, 1320, 1247, 1126, 824, 749, 692 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{15}N_2$ $[M+H]^+$: 235.1230; found: 235.1227.

(13) 8-bromo-N-(4-bromophenyl)quinolin-2-amine(3cd)



Black solid (99.8 mg, 88 % yield), m.p: 157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.85 (t, *J* = 8.8 Hz, 3H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.88, 144.75, 139.25, 138.15, 133.43, 132.06, 127.21, 125.28, 123.87, 122.28, 121.07, 114.92, 113.44. IR (KBr): 3419, 1604, 1527, 1486, 1421, 1387, 1334, 937, 825 cm^{-1}. HRMS (ESI): Calcd. for $C_{15}H_{11}Br_2N_2$ $[M+H]^+$: 376.9283; found: 376.9282.

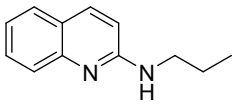
(14) 7-nitro-N-phenylquinolin-2-amine(3da)



Orange solid (71.5mg, 90 % yield), m.p: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.05 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (101 MHz,

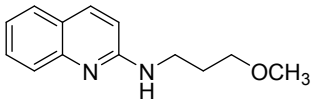
$CDCl_3$): δ 155.66, 148.76, 147.16, 139.33, 137.30, 129.50, 128.75, 127.68, 124.17, 122.65, 121.07, 116.79, 115.36. IR (KBr): 3368, 1596, 1545, 1495, 1463, 1442, 1395, 1343, 973, 890, 840, 734, 686 cm^{-1}. HRMS (ESI): Calcd. for $C_{15}H_{12}N_3O_2$ $[M+H]^+$: 266.0924; found: 266.0920.

(15) N-ethylquinolin-2-amine(5aa)



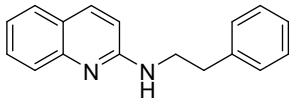
Known compound[1], yellow oil (33.4 mg, 60 % yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 4.80 (s, 1H), 3.44 (dd, *J* = 12.8, 6.8 Hz, 2H), 1.74 -1.64 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.16, 148.11, 137.35, 129.54, 127.43, 126.02, 123.36, 121.90, 110.98, 43.68, 23.00, 11.57. IR (KBr): 3389, 3050, 2961, 2901, 1618, 1525, 1400, 1264, 817, 746 cm^{-1}. MS (EI, m/z): 186.1 $[M]^+$.

(16) N-(3-methoxypropyl)quinolin-2-amine(5ab)



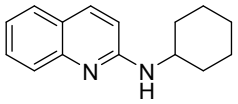
Brown oil (27.2 mg, 42 % yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 5.19 (s, 1H), 3.60 (dd, *J* = 12.0, 6.4 Hz, 2H), 3.53 (t, *J* = 6.0 Hz, 2H), 3.36 (s, 3H), 1.93 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.09, 148.07, 137.32, 129.58, 127.50, 126.04, 123.40, 121.97, 111.52, 71.40, 58.84, 39.87, 29.56. IR (KBr): 3402, 2960, 2852, 1618, 1527, 1118, 818, 753 cm^{-1}. HRMS (ESI): Calcd. for $C_{13}H_{17}N_2O$ $[M+H]^+$: 217.1335; found: 217.1336.

(17) N-phenethylquinolin-2-amine(5ac)



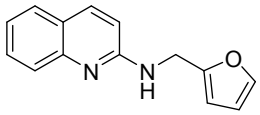
Yellow oil (56.5 mg, 76 % yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 6.63 (d, *J* = 8.8 Hz, 1H), 4.86 (s, 1H), 3.85 (dd, *J* = 12.8, 6.4 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.83, 148.15, 139.47, 137.36, 129.63, 128.98, 128.70, 127.53, 126.50, 126.29, 123.53, 122.15, 111.59, 42.94, 35.83. IR (KBr): 3408, 3030, 3026, 2802, 1617, 1524, 1398, 1346, 816, 751, 699 cm^{-1}. HRMS (ESI): Calcd. for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386; found: 249.1388.

(18) N-cyclohexylquinolin-2-amine(5ad)



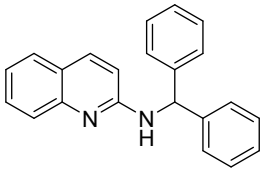
Known compound[2], white solid (29.1 mg, 43 % yield), m.p: 124-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 4.74 (s, 1H), 3.84 (dd, *J* = 11.2, 7.2 Hz, 1H), 2.16 – 2.04 (m, 2H), 1.85 – 1.72 (m, 2H), 1.71 – 1.59 (m, 1H), 1.45 (tt, *J* = 11.6, 3.6 Hz, 2H), 1.30 – 1.20 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.48, 148.06, 137.53, 129.66, 127.52, 126.02, 123.40, 121.93, 111.11, 50.06, 33.66, 25.92, 25.05. IR (KBr): 3401, 2927, 2851, 1617, 1524, 1399, 1346, 1146, 816, 753 cm^{-1}. MS (EI, m/z): 226.1 $[M]^+$.

(19) N-(furan-2-ylmethyl)quinolin-2-amine(5ae)



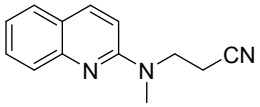
Known compound[3], yellow solid (31.5 mg, 47 % yield), m.p: 93-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 7.25 -7.18 (m, 1H), 6.66 (dd, *J* = 8.8, 1.2 Hz, 1H), 6.39 - 6.25 (m, 2H), 5.02 (s, 1H), 4.74 (d, *J* = 4.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.38, 152.74, 147.98, 142.10, 137.52, 129.70, 127.56, 126.49, 123.77, 122.47, 111.69, 110.56, 107.34, 38.99. IR (KBr): 3255, 1619, 1535, 1400, 1180, 1141, 1011, 913, 810, 758, 738 cm^{-1}. MS (EI, m/z): 224.1 $[M]^+$.

(20) N-benzhydrylquinolin-2-amine(5af)



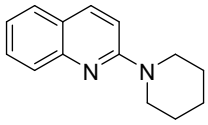
White solid (38.1 mg, 41 % yield), m.p: 184-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 4H), 7.24 (t, *J* = 7.2 Hz, 4H), 7.17 (dd, *J* = 8.4, 6.0 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 6.16 (d, *J* = 6.0 Hz, 1H), 5.36 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.16, 147.96, 142.68, 137.81, 129.74, 128.80, 127.66, 127.54, 127.49, 126.37, 123.75, 122.42, 110.83, 60.05. IR (KBr): 3401, 3031, 3029, 1609, 1569, 1518, 1482, 1397, 1234, 943, 818, 756, 735, 697, 569 cm^{-1}. HRMS (ESI): Calcd. for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543; found: 311.1545.

(21) 3-(methyl(quinolin-2-yl)amino)propanenitrile(5ag)



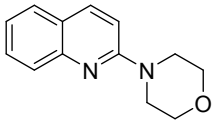
White solid (31.1 mg, 65 % yield), m.p: 99-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 9.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 9.2 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.17 (s, 3H), 2.75 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.94, 147.85, 137.83, 129.73, 127.46, 126.68, 122.86, 122.38, 119.26, 108.83, 47.15, 37.80, 16.07. IR (KBr): 3096, 2916, 2243, 1606, 1555, 1509, 1426, 1388, 986, 810, 752 cm^{-1}. HRMS (ESI): Calcd. for $C_{13}H_{14}N_3$ $[M+H]^+$: 212.1182; found: 212.1183.

(22) 2-(piperidin-1-yl)quinoline(5ah)



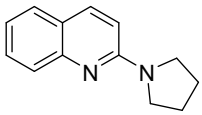
Known compound[4], yellow oil (57.8 mg, 91 % yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 9.2 Hz, 1H), 3.74 (d, *J* = 4.8 Hz, 4H), 1.69 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.71, 148.16, 137.28, 129.42, 127.20, 126.55, 122.87, 122.03, 109.94, 46.36, 25.87, 24.95. IR (KBr): 2930, 2849, 1610, 1505, 1431, 1349, 1228, 1121, 1019, 808, 752 cm^{-1}. MS (EI, m/z): 212.1 $[M]^+$.

(23) 4-(quinolin-2-yl)morpholine(5ai)



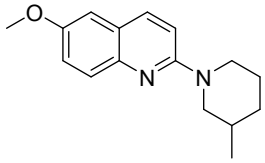
Known compound[4], yellow solid (55.8 mg, 87 % yield), m.p: 86-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 9.2 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.29 -7.21 (m, 1H), 6.93 (dd, *J* = 9.2, 0.8 Hz, 1H), 3.89 - 3.81 (m, 4H), 3.74 – 3.67 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.55, 147.78, 137.58, 129.64, 127.28, 126.79, 123.35, 122.69, 109.31, 66.90, 45.62. IR (KBr): 3051, 2957, 2922, 2851, 1609, 1556, 1428, 1390, 1260, 1229, 1058, 926, 808, 753 cm^{-1}. MS (EI, m/z): 214.1 $[M]^+$.

(24) 2-(pyrrolidin-1-yl)quinoline(5aj)



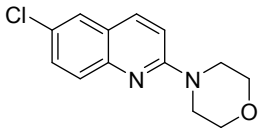
Known compound[4], white solid (31.4 mg, 53 % yield), m.p: 85-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.22 – 7.11 (m, 1H), 6.72 (d, *J* = 9.2 Hz, 1H), 3.62 (t, *J* = 6.4 Hz, 4H), 2.10 – 1.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.79, 148.54, 136.99, 129.41, 127.40, 126.09, 122.60, 121.28, 110.28, 46.85, 25.56. IR (KBr): 3053, 2957, 2924, 2857, 1606, 1553, 1511, 1482, 1430, 1401, 1157, 1118, 869, 807, 752 cm^{-1}. MS (EI, m/z): 198.1 $[M]^+$.

(25) 6-methoxy-2-(3-methylpiperidin-1-yl)-1,2,3,4-tetrahydroquinoline(5ek)



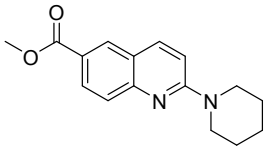
Brown solid (45.0mg, 58 % yield), m.p: 100-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 9.2 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.20 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.98 (d, *J* = 9.2 Hz, 1H), 6.94 (d, *J* = 2.8 Hz, 1H), 4.43 – 4.28 (m, 2H), 3.87 (s, 3H), 2.89 (td, *J* = 12.4, 2.8 Hz, 1H), 2.56 (dd, *J* = 12.8, 10.8 Hz, 1H), 1.91 – 1.81 (m, 1H), 1.81 -1.69 (m, 2H), 1.67 – 1.57 (m, 1H), 1.22 – 1.07 (m, 1H), 0.98 (d, *J* =6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.86, 154.95, 143.70, 136.39, 128.09, 123.22, 120.96, 110.49, 106.19, 55.58, 53.46, 46.10, 33.57, 31.03, 25.37, 19.51. IR (KBr): 2928, 1606, 1556, 1507, 1460, 1402, 1320, 1240, 1147, 1114, 847, 827, 802, 740, 624 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{21}N_2O$ $[M+H]^+$: 257.1648; found: 257.1645.

(26) 4-(6-chloroquinolin-2-yl)morpholine(5fi)



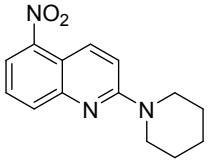
Yellow solid (53.9mg, 72 % yield), m.p: 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 9.2 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.46 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.93 (d, *J* = 9.2 Hz, 1H), 3.83 (t, *J* = 4.0Hz, 4H), 3.69 (t, *J* = 4.0Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.56, 146.29, 136.68, 130.28, 128.32, 127.77, 126.05, 123.86, 110.16, 66.89, 45.54. IR (KBr): 3091, 2958, 2854, 1602, 1548, 1495, 1447, 1395, 1312, 1262, 1230, 1193, 1074, 934, 875, 829, 805, 619 cm^{-1}. HRMS (ESI): Calcd. for $C_{13}H_{14}ClN_2O$ $[M+H]^+$: 249.0789; found: 249.0785.

(27) Methyl 2-(piperidin-1-yl)quinoline-6-carboxylate(5gh)



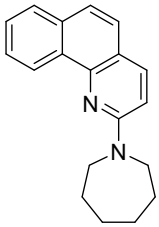
Red solid(38.9 mg, 48 % yield), m.p: 109-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.6 Hz, 1H), 8.09 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 9.2 Hz, 1H), 3.93 (s, 3H), 3.78 (d, *J* = 5.2 Hz, 4H), 1.69 -1.58 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$): δ 167.07, 158.00, 150.91, 138.08, 130.13, 129.25, 125.93, 122.93, 121.39, 109.96, 51.73, 45.88, 25.63, 24.59. IR (KBr): 3342, 2933, 2852, 1712, 1618, 1499, 1406, 1280, 1229, 1196, 1095, 962, 847, 805, 757 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{19}N_2O_2$ $[M+H]^+$: 271.1441; found: 271.1434.

(28) 5-nitro-2-(piperidin-1-yl)quinoline(5hh)



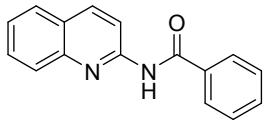
Orange solid (53.9 mg, 70 % yield), m.p: 75-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 9.6 Hz, 1H), 7.84 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 9.6 Hz, 1H), 3.77 – 3.62 (m, 4H), 1.69 – 1.58 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.15, 149.11, 145.84, 133.18, 132.83, 127.48, 119.40, 115.26, 112.57, 46.00, 25.85, 24.85. IR (KBr): 2933, 2853, 1604, 1508, 1422, 1338, 1253, 1225, 1127, 1022, 807, 736 cm^{-1}. HRMS (ESI): Calcd. for $C_{14}H_{16}N_3O_2$ $[M+H]^+$: 258.1237; found: 258.123.

(29) 2-(azepan-1-yl)-1,2,3,4-tetrahydrobenzo[h]quinoline(5il)



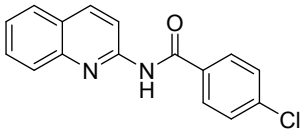
Brown oil (43.8mg, 53 % yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.55 – 7.46 (m, 2H), 7.42 (dd, *J* = 20.0, 8.8 Hz, 2H), 6.80 (d, *J* = 9.2 Hz, 1H), 3.80 (t, *J* = 6.0 Hz, 4H), 1.84 (s, 4H), 1.50 (dd, *J* = 8.4, 5.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.33, 144.94, 136.15, 133.26, 129.81, 126.45, 126.18, 124.52, 124.32, 123.49, 120.71, 117.44, 106.46, 47.06, 26.80, 26.02. IR (KBr): 3433, 2922, 1637 1599, 1514, 1454, 1396, 1263, 1155, 1016, 824, 798, 749 cm^{-1}. HRMS (ESI): Calcd. for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699; found: 277.1696.

(30) N-(quinolin-2-yl)benzamide(8aa)



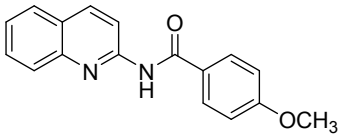
Known compound[5], white solid (46.1 mg, 62 % yield), m.p: 124-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (brs, 1H), 8.43 (d, *J* = 9.2 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 9.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.24, 151.28, 146.62, 138.76, 134.23, 132.43, 130.10, 128.87, 127.67, 127.45, 127.34, 126.47, 125.31, 114.57. IR (KBr): 3059, 1681, 1599, 1497, 1423, 1319, 1283, 1263, 1247, 1123, 921, 829, 705 cm^{-1}. MS (EI, m/z): 248.1 $[M]^+$.

(31) 4-chloro-N-(quinolin-2-yl)benzamide(8ab)



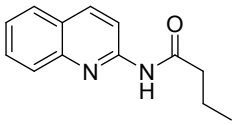
Yellow solid (56.6 mg, 67 % yield), m.p: 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (brs,1H), 8.53 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.79 (dd, *J* = 8.4, 4.0 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.50 – 7.39 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.17, 150.06, 145.36, 137.78, 137.69, 131.52, 129.11, 128.03, 127.79, 126.60, 126.13, 125.40, 124.36, 113.48. IR (KBr): 3331, 1667, 1598, 1500, 1425, 1320, 1260, 849, 821, 745 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{12}N_2ClO$ $[M+H]^+$: 283.0633; found: 283.0632.

(32) 4-methoxy-N-(quinolin-2-yl)benzamide(8ac)



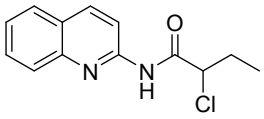
Known compound[5], white solid (50.0 mg, 60 % yield), m.p: 79-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (brs, 1H), 8.57 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.81 (dd, *J* = 14.4, 7.6 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 6.98 (dd, *J* = 9.2, 3.2 Hz, 2H), 3.87 (m, 6.99 – 6.96, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.68, 163.09, 151.50, 146.58, 138.81, 130.17, 129.49, 127.74, 127.25, 126.44, 126.38, 125.27, 114.62, 114.18, 55.61. IR (KBr): 3340, 2728, 1677, 1600, 1495, 1424, 1320, 1247, 1175, 830, 755, 614 cm^{-1}. MS (EI, m/z): 278.0 $[M]^+$.

(33) N-(quinolin-2-yl)butyramide(8ad)



Yellow solid (29.5 mg, 46 % yield), m.p: 89-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (brs, 1H), 8.44 (d, *J* = 8.8 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.79 (dd, *J* = 14.4, 8.8 Hz, 2H), 7.69 – 7.60 (m, 1H), 7.48 – 7.40 (m, 1H), 2.40 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.71 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.17, 151.11, 146.49, 138.66, 130.02, 127.62, 127.20, 126.33, 125.13, 114.38, 39.78, 18.80, 13.69. IR (KBr): 2913, 1697, 1599, 1498, 1425, 1319, 831, 753 cm^{-1}. HRMS (ESI): Calcd. for $C_{13}H_{15}N_2O$ $[M+H]^+$: 215.1179; found: 215.1174.

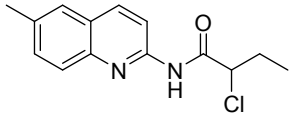
(34) 2-chloro-N-(quinolin-2-yl)butanamide(8ae)



Yellow solid (42.4 mg, 57 % yield), m.p: 97-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (brs, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.61 (m, 1H), 7.53 – 7.42 (m, 1H), 4.46 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.24 (dqd, *J* = 14.4, 7.2, 4.8

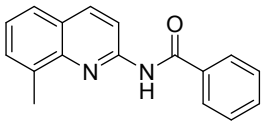
Hz, 1H), 2.17 – 2.04 (m, 1H), 1.13 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.97, 150.08, 146.60, 138.76, 130.18, 127.59, 126.61, 125.56, 113.87, 62.53, 29.03, 10.49. IR (KBr): 3830, 2917, 1702, 1599, 1500, 1427, 1320, 828, 754 cm^{-1}. HRMS (ESI): Calcd. for $C_{13}H_{14}ClN_2O$ $[M+H]^+$: 249.0789; found: 249.0787.

(35) 2-chloro-N-(6-methylquinolin-2-yl)butanamide(8be)



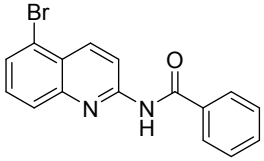
Yellow oil (51.0mg, 65 % yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.34 (d, *J* = 9.2 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.54 (s, 1H), 7.50 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.45 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.51 (s, 3H), 2.24 (dqd, *J* = 14.4, 7.2, 4.8 Hz, 1H), 2.17 – 2.04 (m, 1H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.98, 149.55, 145.12, 138.15, 135.50, 132.51, 127.37, 126.72, 126.61, 113.96, 62.59, 29.11, 21.55, 10.58. IR (KBr): 2971, 1687, 1600, 1492, 1383, 1319, 1282, 826 cm^{-1}. HRMS (ESI): Calcd. for $C_{14}H_{16}ClN_2O$ $[M+H]^+$: 263.0946; found: 263.0942.

(36) N-(8-methylquinolin-2-yl)benzamide(8ja)



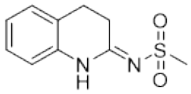
Yellow solid (37.7 mg, 48 % yield), m.p: 97-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 3H), 7.26 (t, *J* = 7.6 Hz, 1H), 2.63 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 165.02, 149.1 , 144.77, 137.87, 133.37, 131.29, 129.15, 127.82, 126.36, 125.21, 124.54, 123.94, 113.03, 16.80. IR (KBr): 3419, 1673, 1599, 1525, 1495, 1432, 1315, 1245, 926, 836, 794, 760, 705 cm^{-1}. HRMS (ESI): Calcd. for $C_{15}H_{11}Br_2N_2$ $[M+H]^+$: 263.1179; found: 263.1173.

(37) N-(5-bromoquinolin-2-yl)benzamide(8ka)



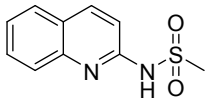
White solid (63.4mg, 65 % yield), m.p: 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.66 (d, *J* = 9.2 Hz, 1H), 8.55 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.49 (dt, *J* = 14.8, 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.14, 151.88, 147.50, 138.33, 134.07, 132.67, 130.34, 129.07, 129.02, 127.49, 127.39, 125.91, 121.95, 115.57. IR (KBr): 1681, 1593, 1487, 1439, 1393, 1318, 935, 804, 704 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{12}BrN_2O$ $[M+H]^+$: 327.0128; found: 327.0123.

(38) N-(3,4-dihydroquinolin-2(1H)-ylidene)methanesulfonamide(9aa')



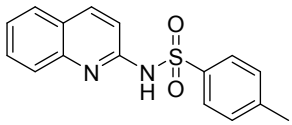
Black solid (38.9 mg, 58 % yield), m.p: 118-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (brs, H), 3.07 (s, 3H), 2.96 -2.86 (m, 2H), 2.73 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.85, 134.87, 128.25, 127.93, 124.80, 124.22, 116.81, 42.48, 30.54, 23.89. IR (KBr): 3288, 2926, 1621, 1580, 1498, 1396, 1276, 1201, 968, 825, 757, 565, 509 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{12}N_2NaO_2S$ $[M+H]^+$: 247.0512; found: 247.0508.

(39) N-(quinolin-2-yl)methanesulfonamide(9aa)



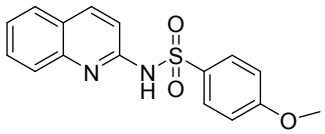
Known compound[6], white solid (38.6 mg, 58 % yield), m.p: 200-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 9.2 Hz, 1H), 7.61 (dd, *J* = 14.8, 7.6 Hz, 2H), 7.37 (dd, *J* = 17.6, 9.2 Hz, 2H), 6.88 (d, *J* = 9.2 Hz, 1H), 3.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.32, 140.74, 136.47, 131.70, 128.15, 124.70, 121.25, 120.90, 117.27, 42.65. IR (KBr): 3397, 3021, 1637, 1392, 1215 cm^{-1}. MS (EI, m/z): 222.1 $[M]^+$.

(40) 4-methyl-N-(quinolin-2-yl)benzenesulfonamide(9ab)



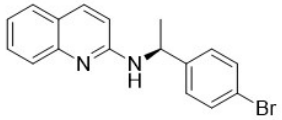
Known compound[6], white solid (47.5 mg, 42 % yield), m.p: 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.61 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 9.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.35, 142.74, 140.77, 139.96, 136.63, 131.75, 129.41, 128.10, 126.32, 124.72, 121.43, 120.63, 117.47, 21.48. IR (KBr): 3176, 2922, 1634, 1597, 1388, 1140, 1086, 836, 756, 554 cm^{-1}. MS (EI, m/z): 298.1 $[M]^+$.

(41) 4-methoxy-N-(quinolin-2-yl)benzenesulfonamide(9ac)



Yellow solid (44.3 mg, 47 % yield), m.p: 108-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.84 (brs, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.59, 154.32, 140.80, 136.82, 134.89, 131.80, 128.45, 128.18, 124.77, 121.52, 120.70, 117.62, 55.64. IR (KBr): 3442, 1634, 1596, 1530, 1499, 1388, 1257, 1138, 1087, 935, 831, 600, 563 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{14}N_2NaO_3S$ $[M+H]^+$: 337.0617; found: 337.0613.

(42) (S)-N-(1-(4-bromophenyl)ethyl)quinolin-2-amine (5am)



Brown oil (58.7 mg, 60 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 17.2, 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 8.8 Hz, 1H), 5.17 (brs, 1H), 5.13 – 5.06 (m, 1H), 1.57 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.07, 147.98, 144.02, 137.63, 131.75, 129.71, 127.98, 127.53, 126.27, 123.61, 122.36, 120.80, 110.92, 50.73, 23.61.IR (KBr):3417, 2967, 1617, 1570, 1517, 1485, 1398, 1247, 1147, 1073, 1009, 817, 755 cm^{-1}. HRMS (ESI): Calcd. for $C_{17}H_{16}BrN_2$ $[M+H]^+$: 327.0491; found: 327.0488.

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[2] R. Saari, J-C. Törmä, T. Nevalainen, *Bioorg. Med. Chem*. 2011, **19**, 939–950.
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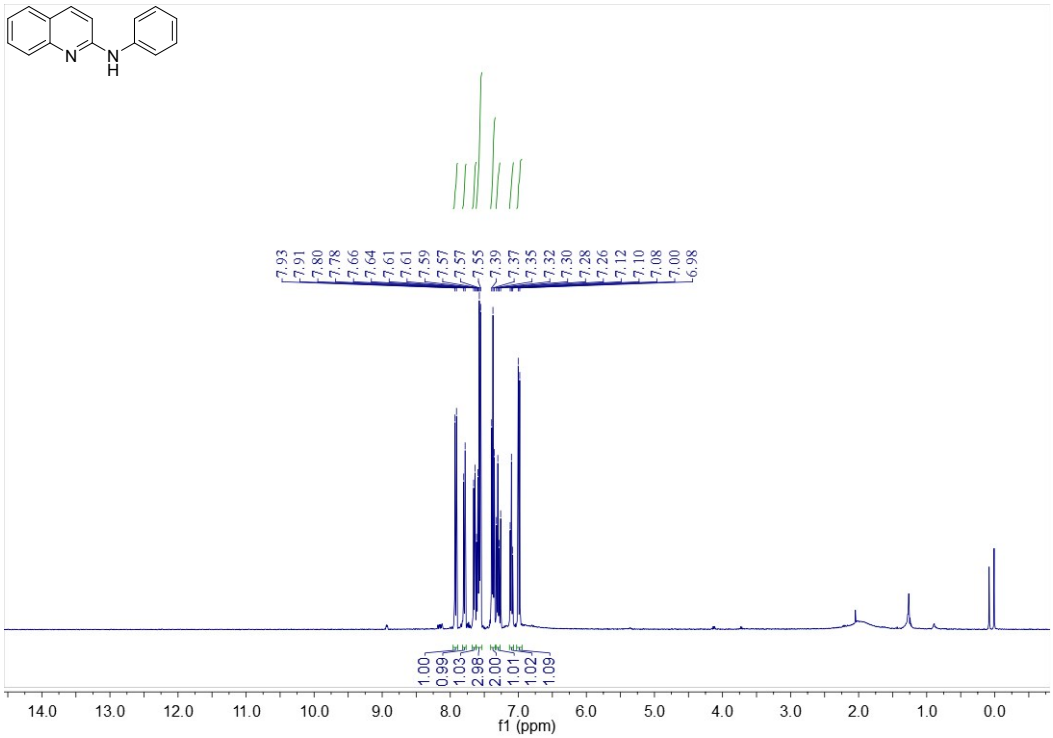
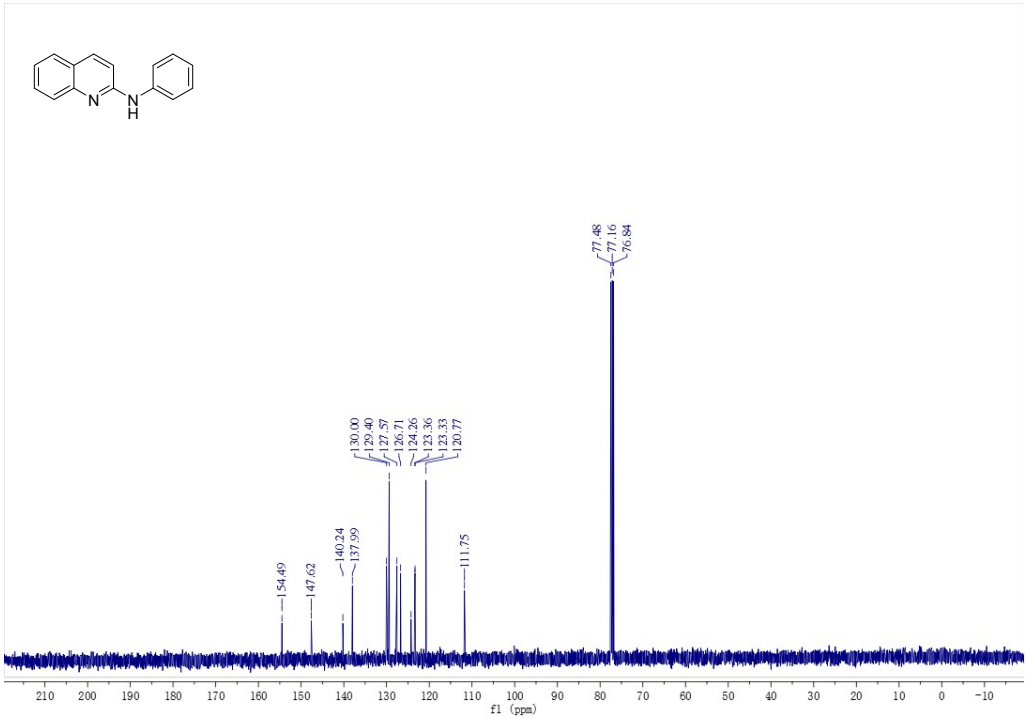
10.NMR spectra of the obtained compounds

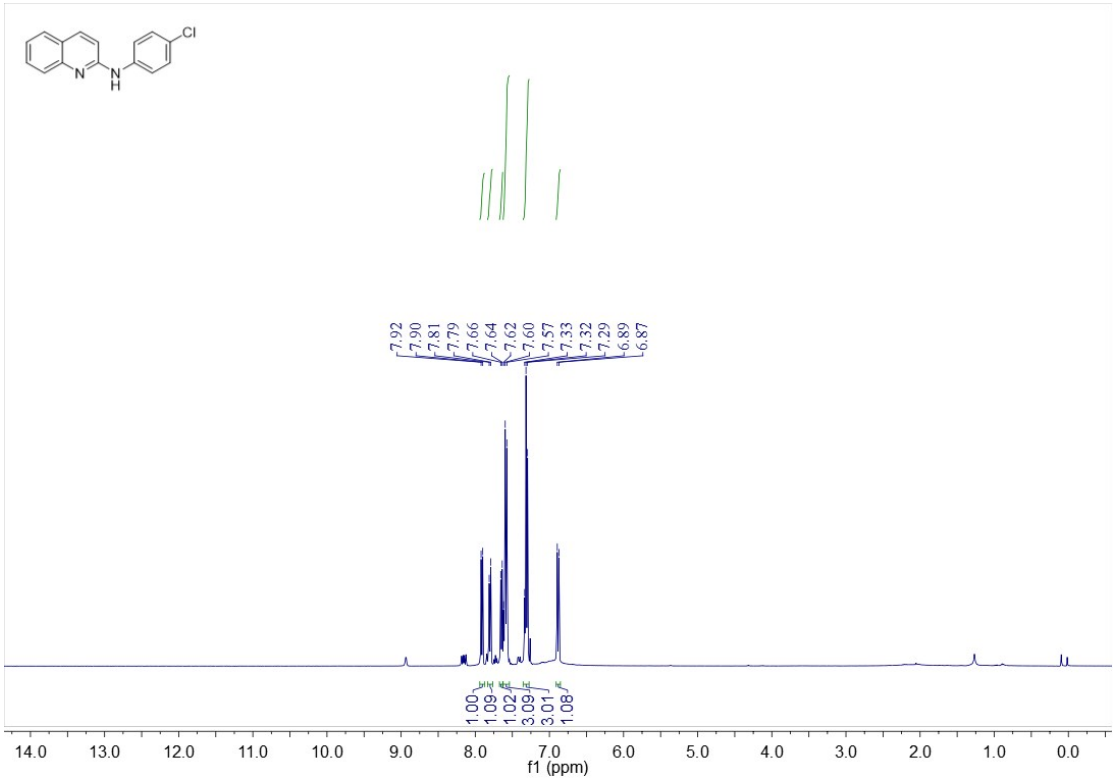
^{1}H-NMR spectrum of 3aa



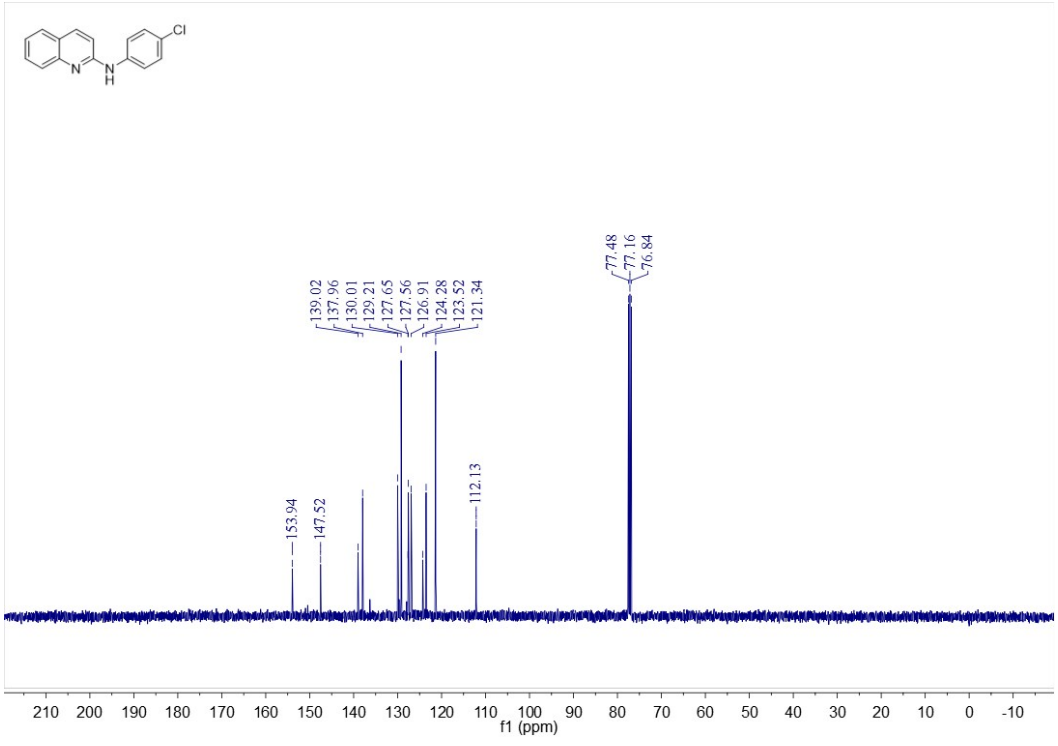
^{13}C-NMR spectrum of 3aa



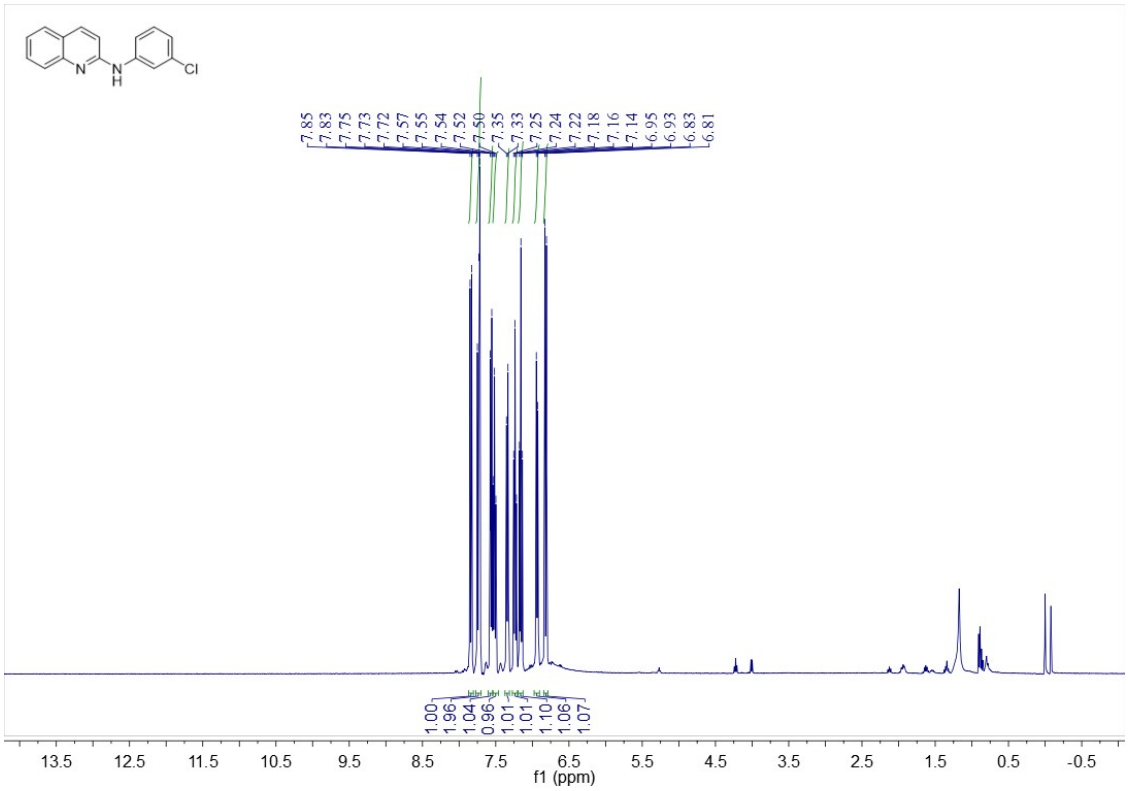
^{1}H-NMR spectrum of 3ab



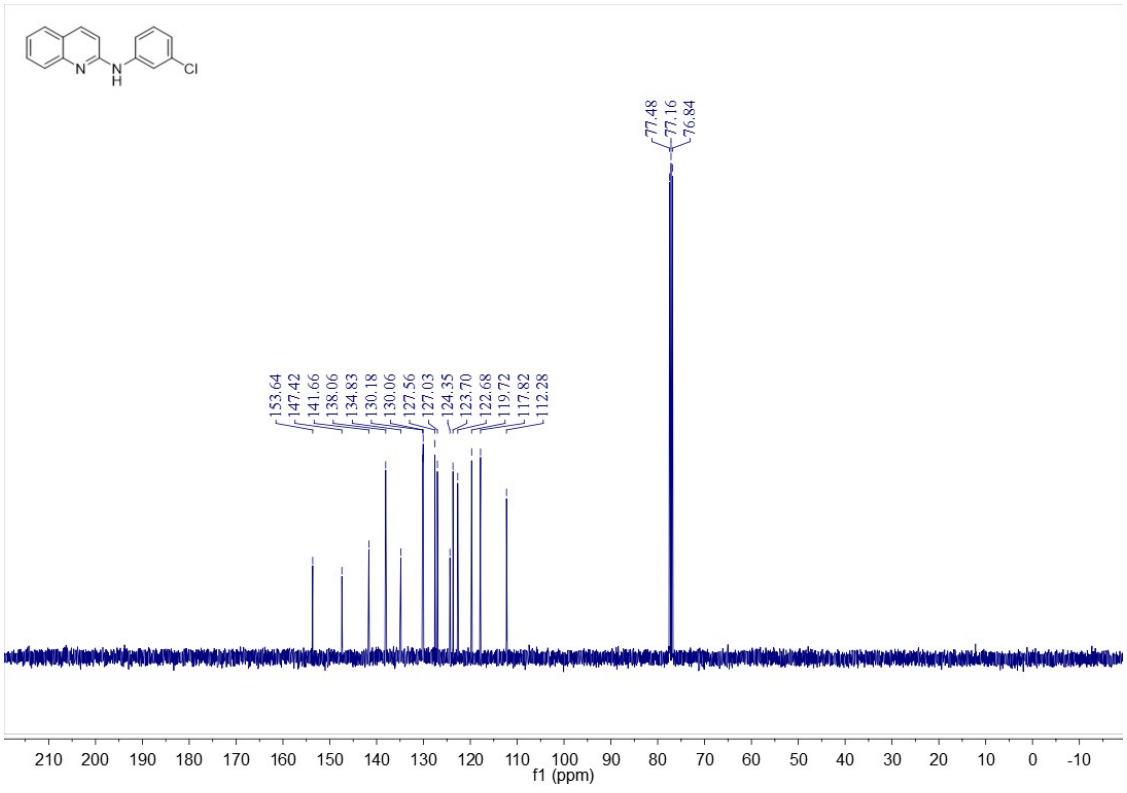
^{13}C-NMR spectrum of 3ab



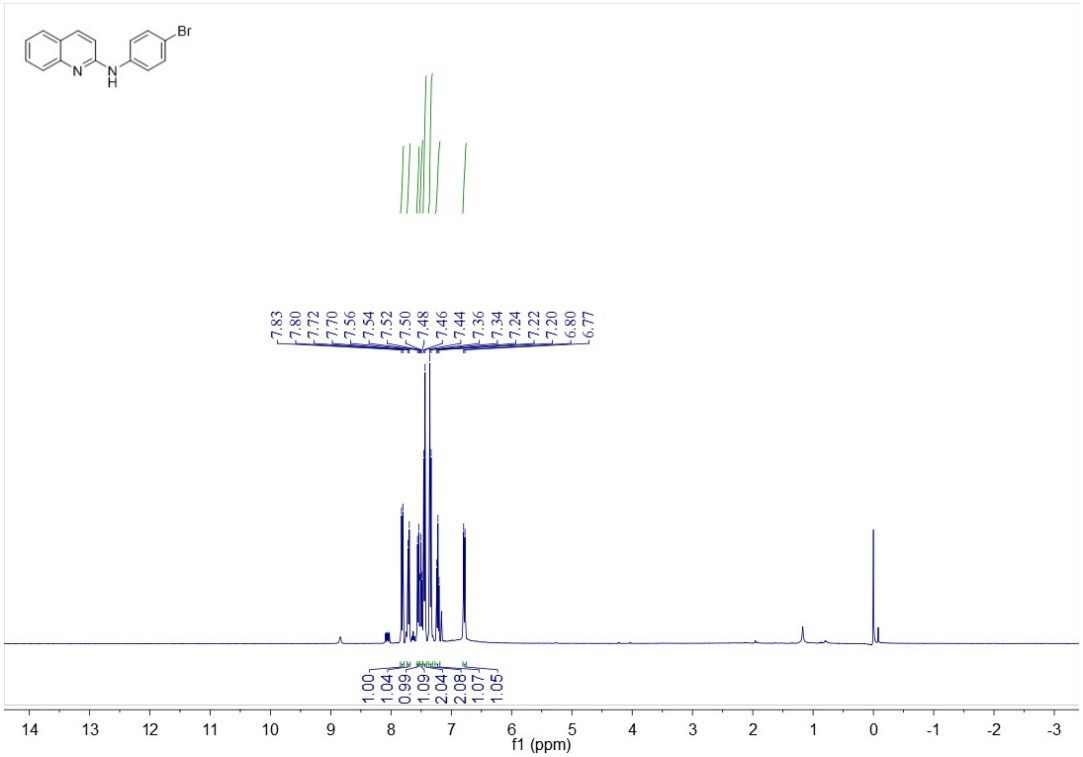
^{1}H-NMR spectrum of 3ac



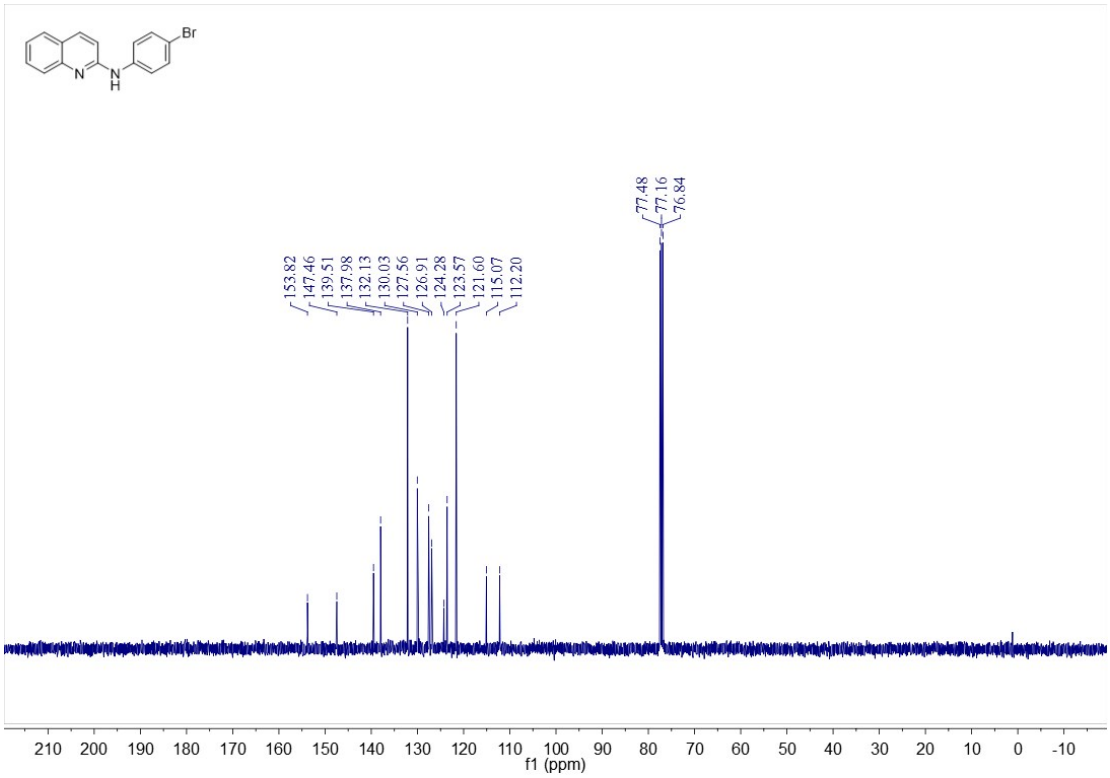
^{13}C-NMR spectrum of 3ac



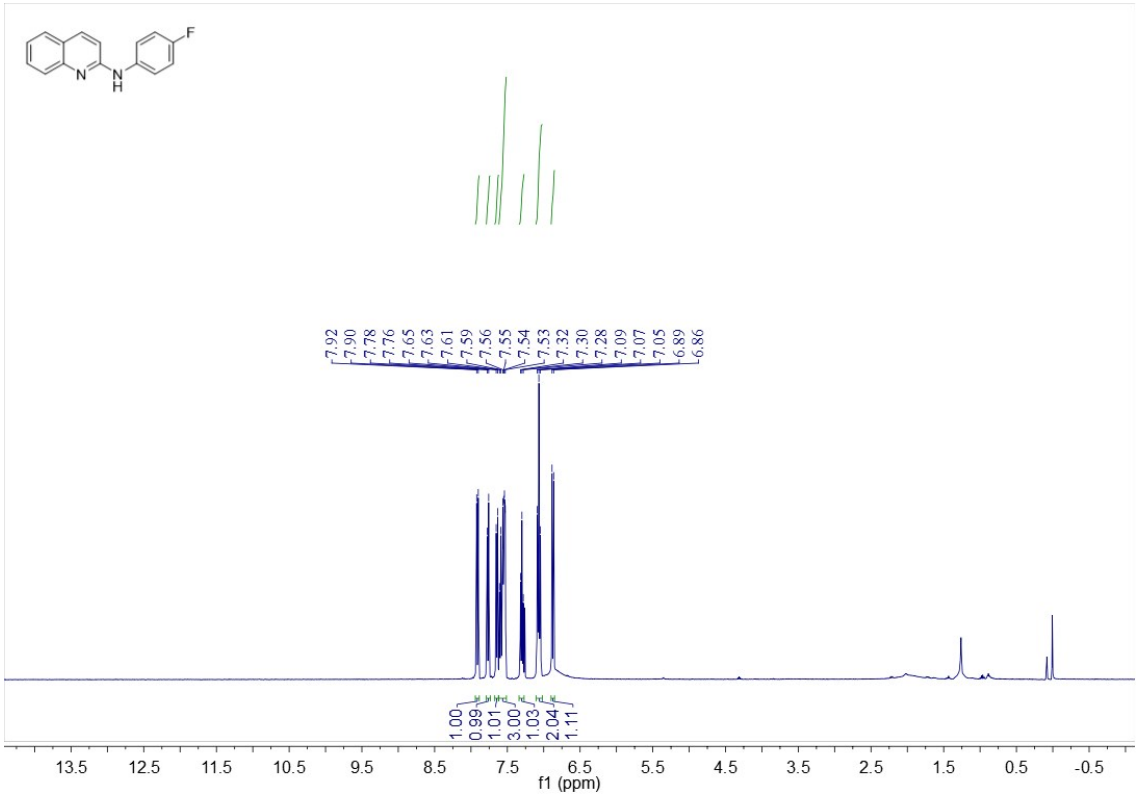
^{1}H-NMR spectrum of 3ad



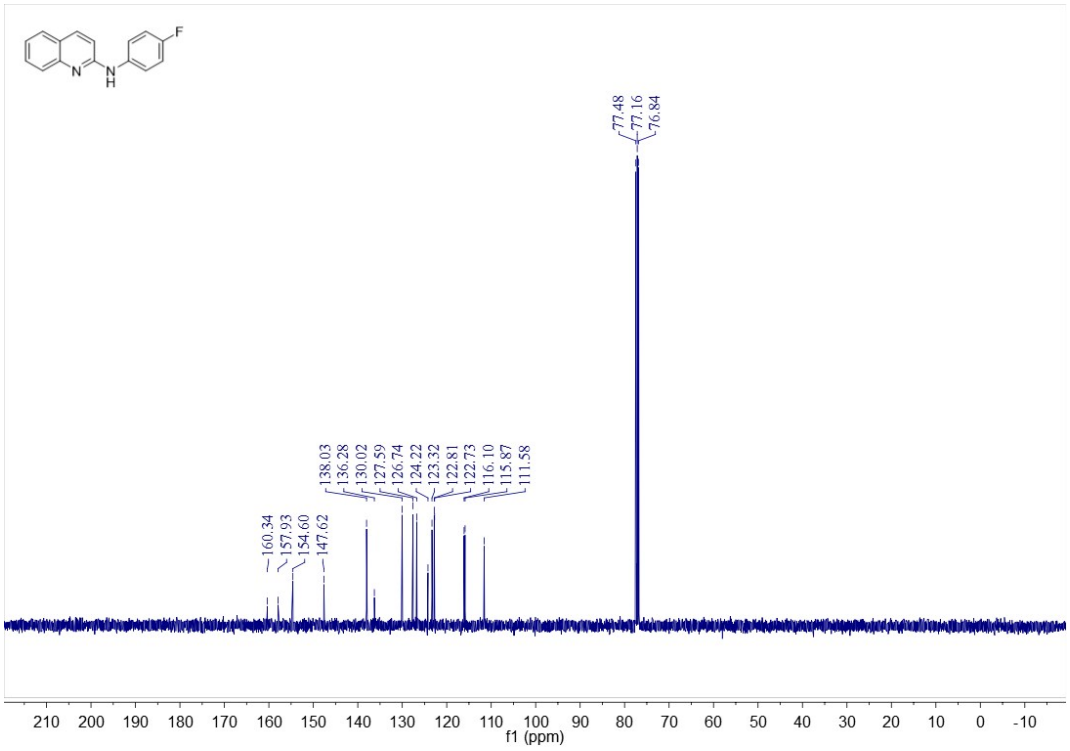
^{13}C-NMR spectrum of 3ad



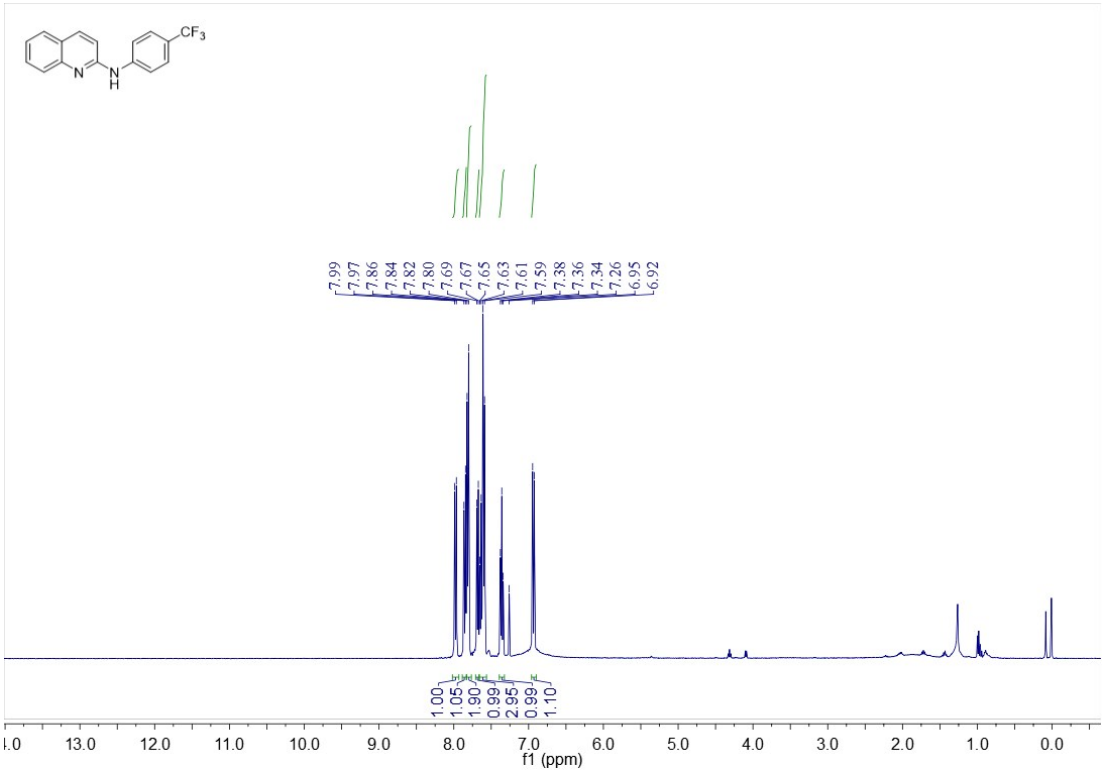
^{1}H-NMR spectrum of 3ae



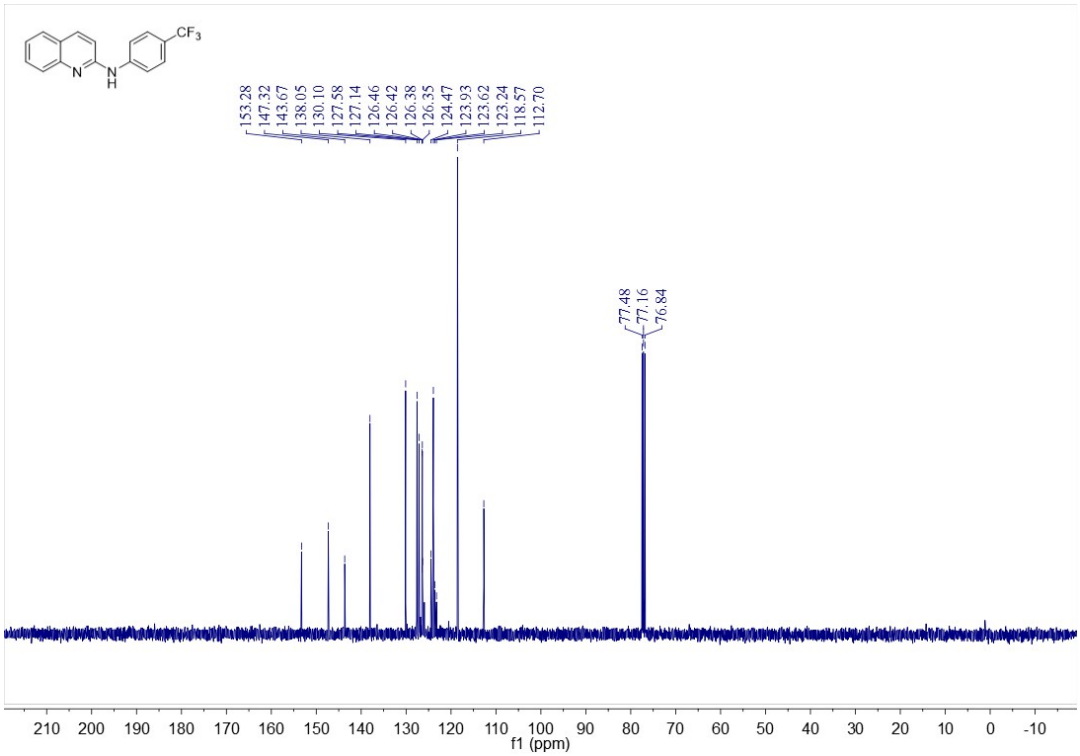
^{13}C-NMR spectrum of 3ae



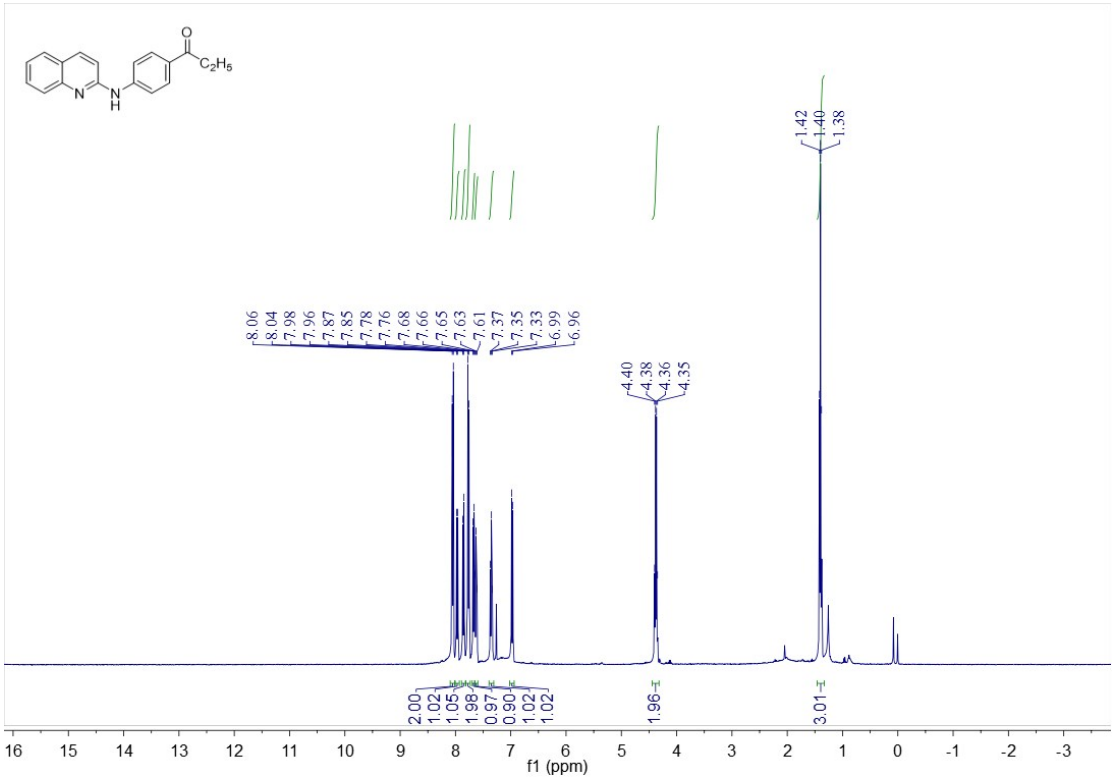
^{1}H-NMR spectrum of 3af



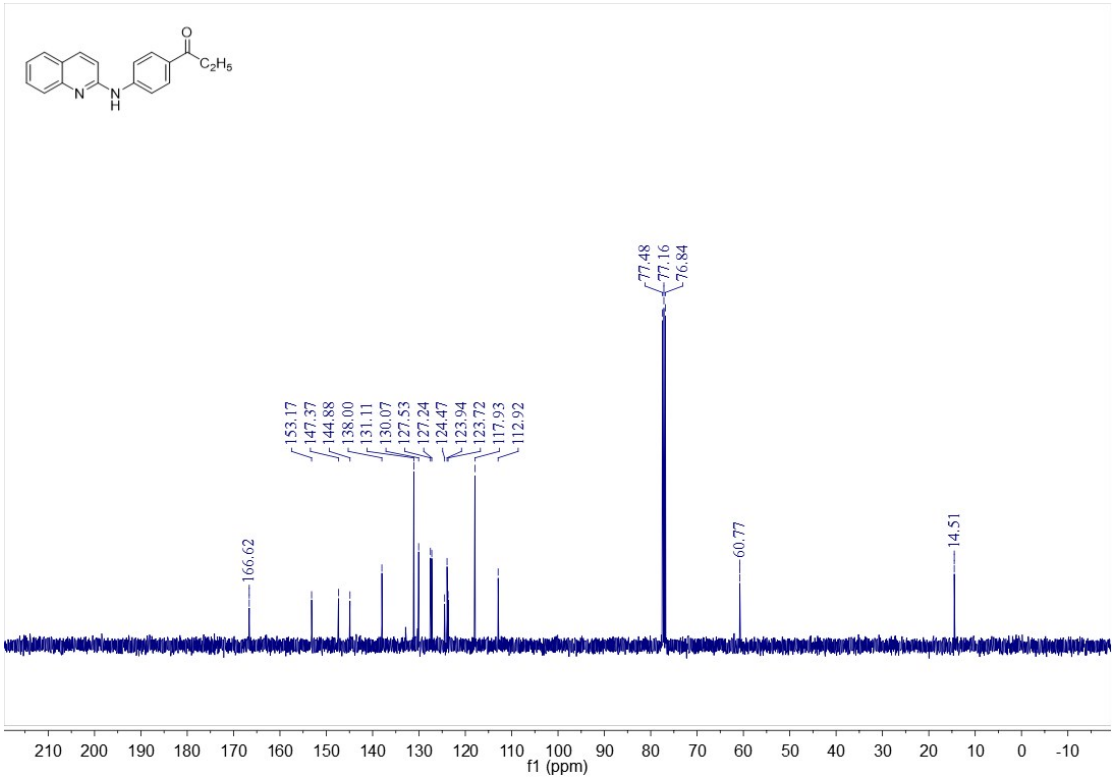
^{13}C-NMR spectrum of 3af



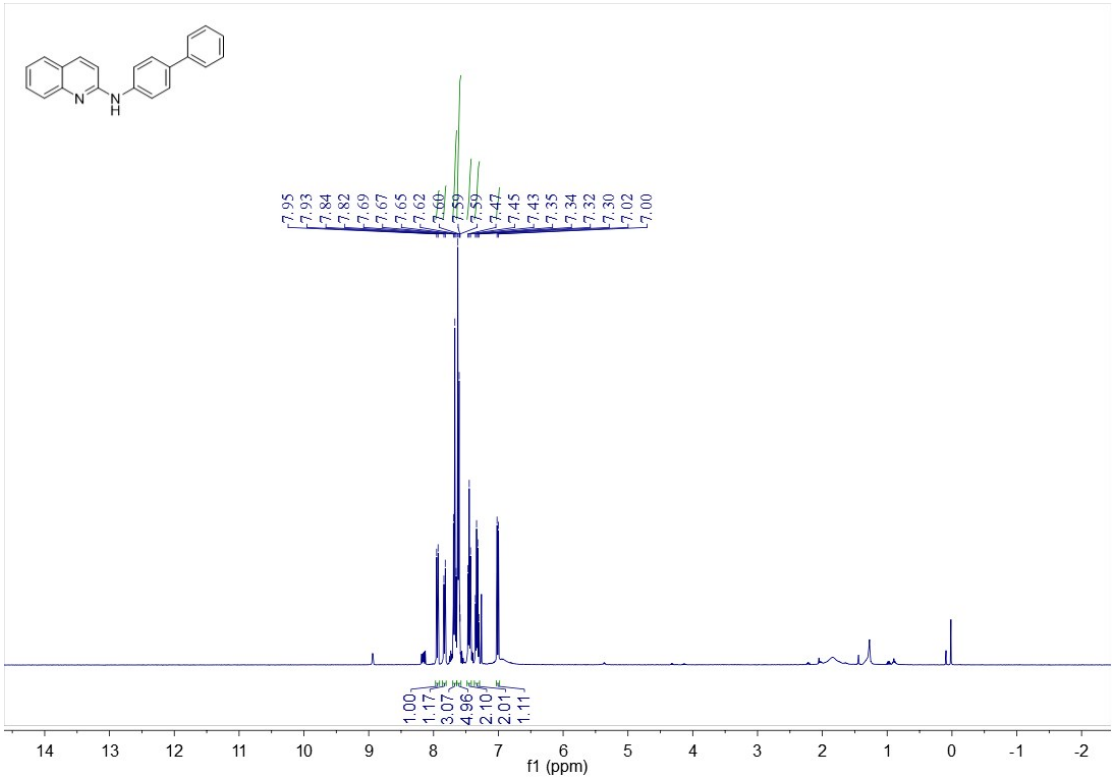
^{1}H-NMR spectrum of 3ag



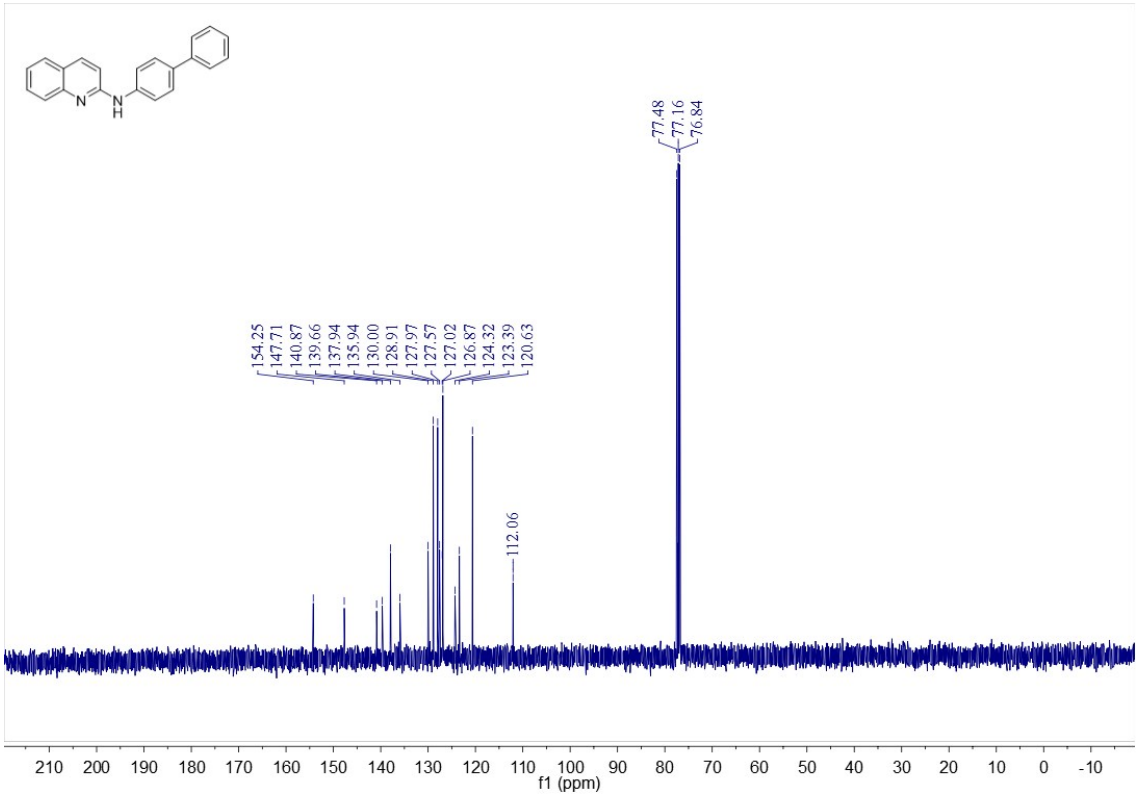
^{13}C-NMR spectrum of 3ag



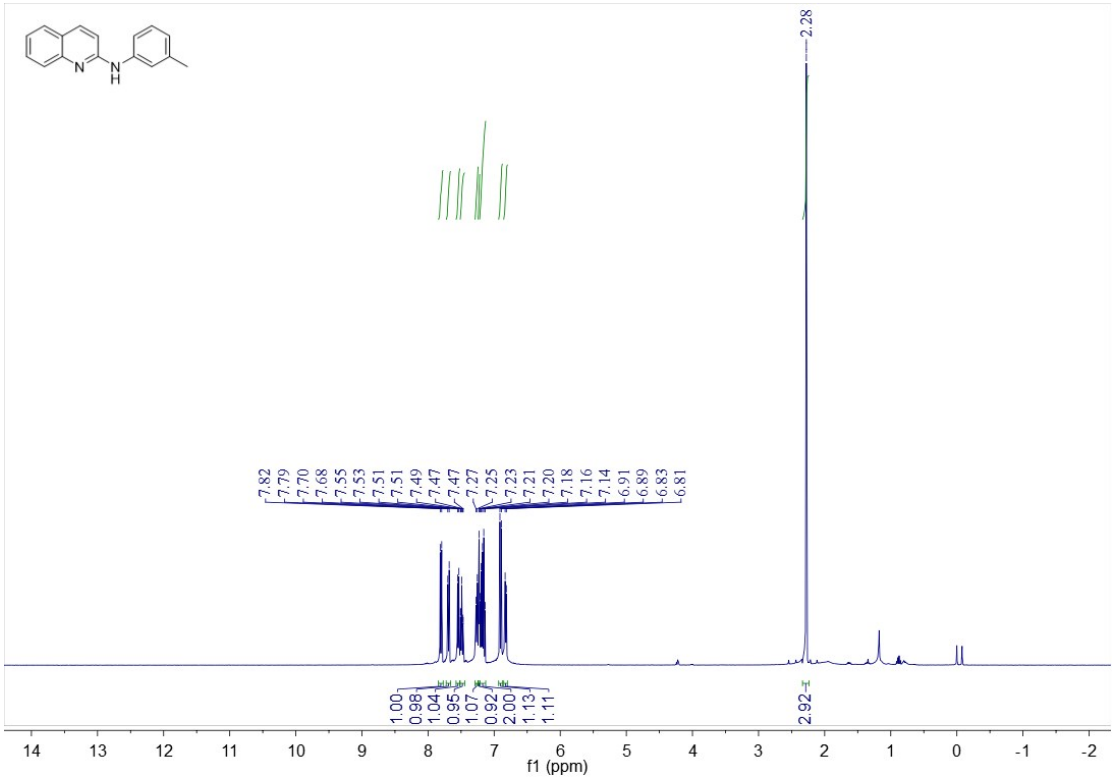
^{1}H-NMR spectrum of 3ah



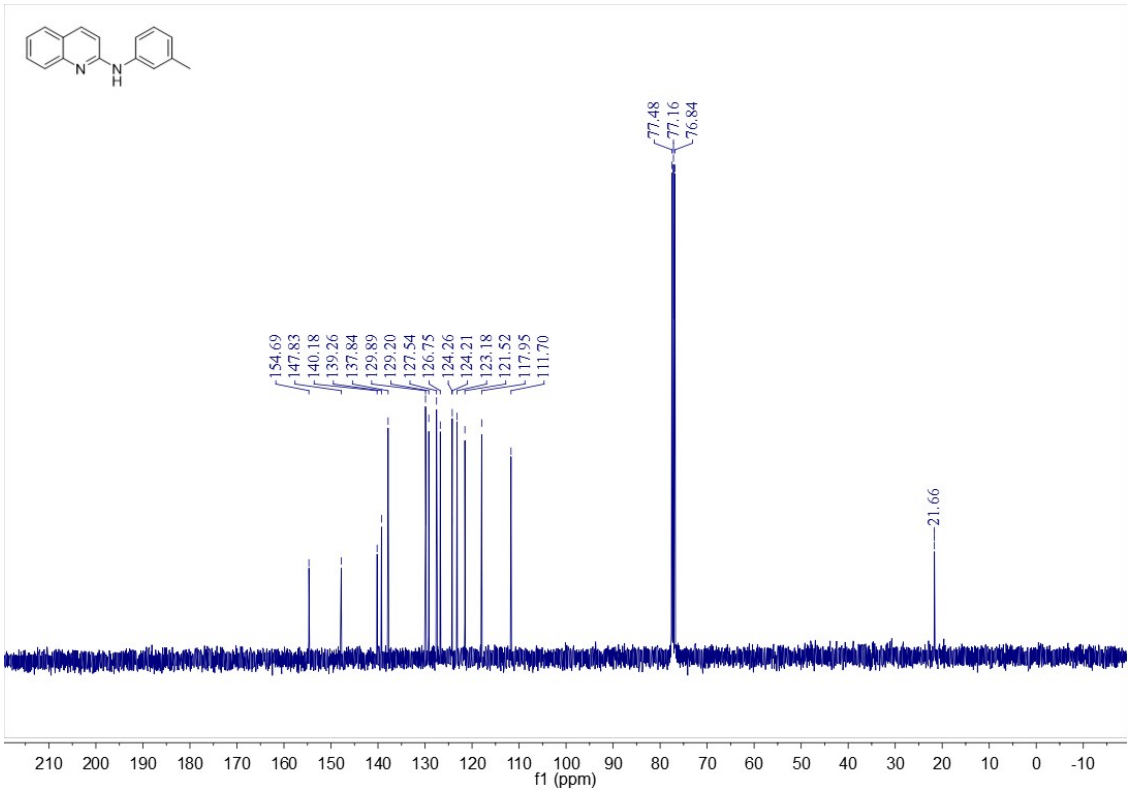
^{13}C-NMR spectrum of 3ah



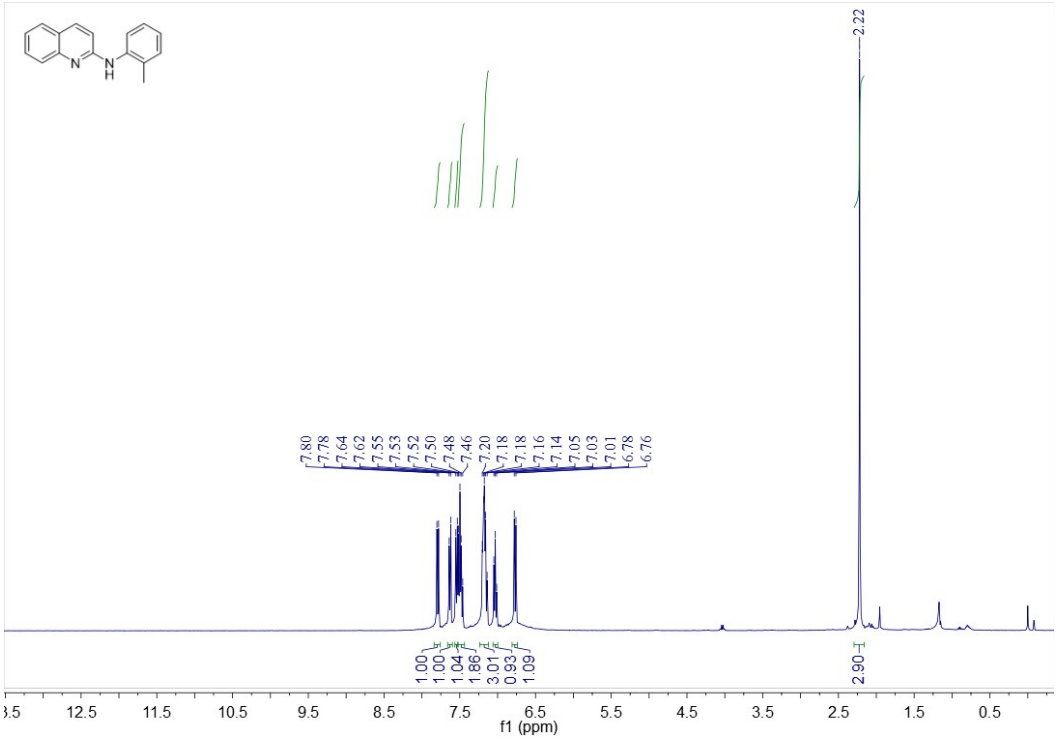
^{1}H-NMR spectrum of 3ai



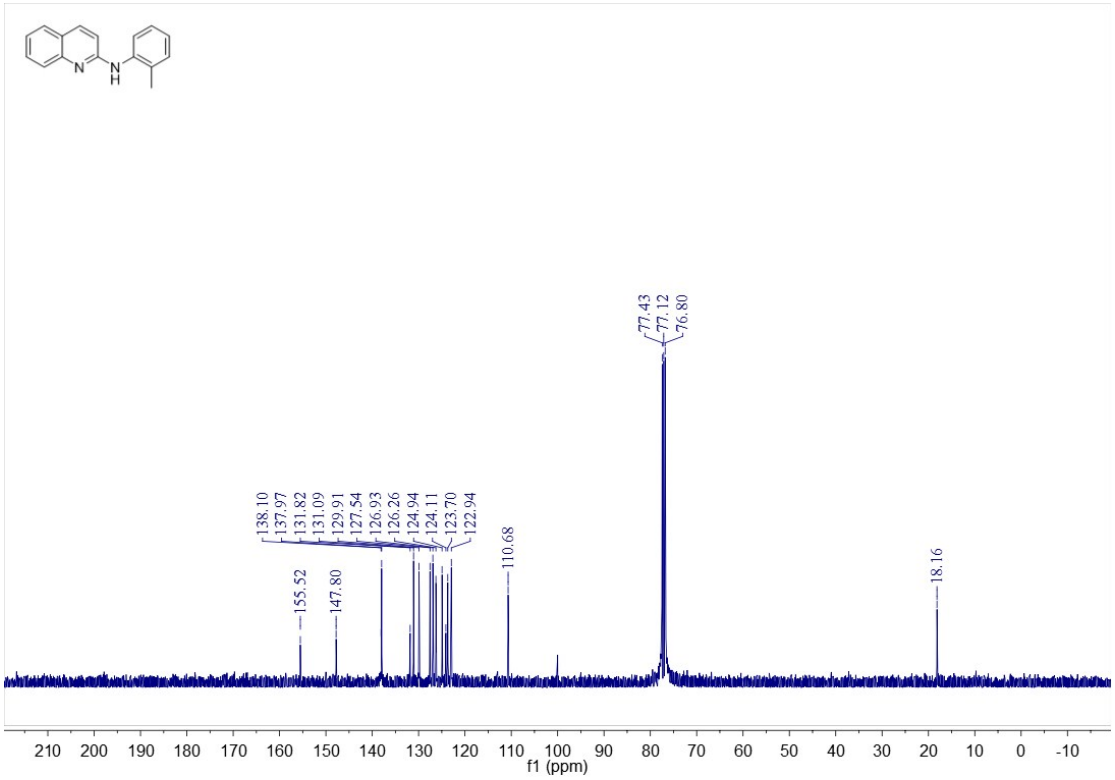
^{13}C-NMR spectrum of 3ai



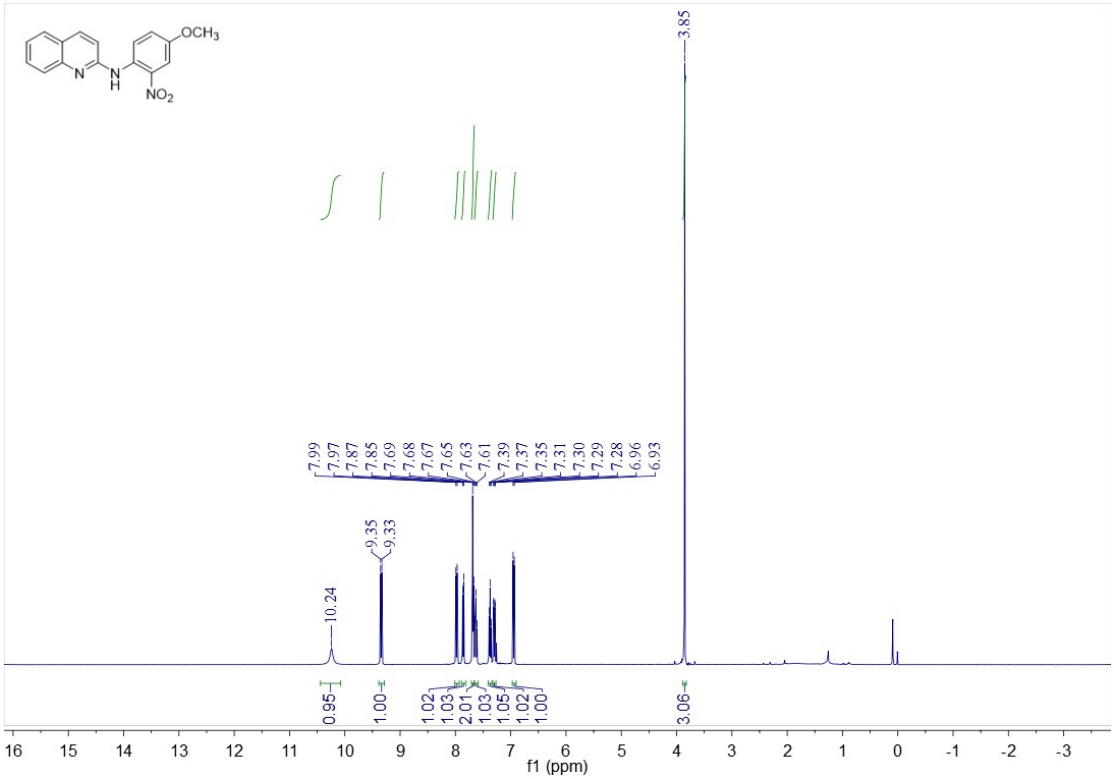
^{1}H-NMR spectrum of 3aj



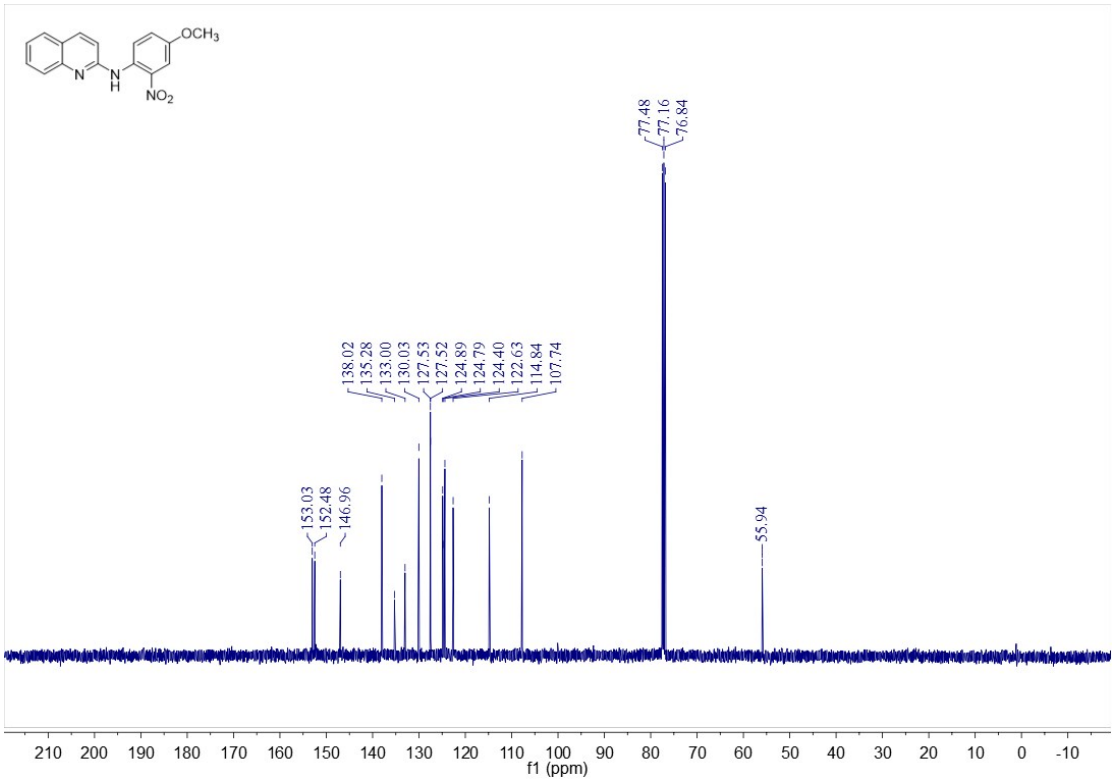
^{13}C-NMR spectrum of 3aj



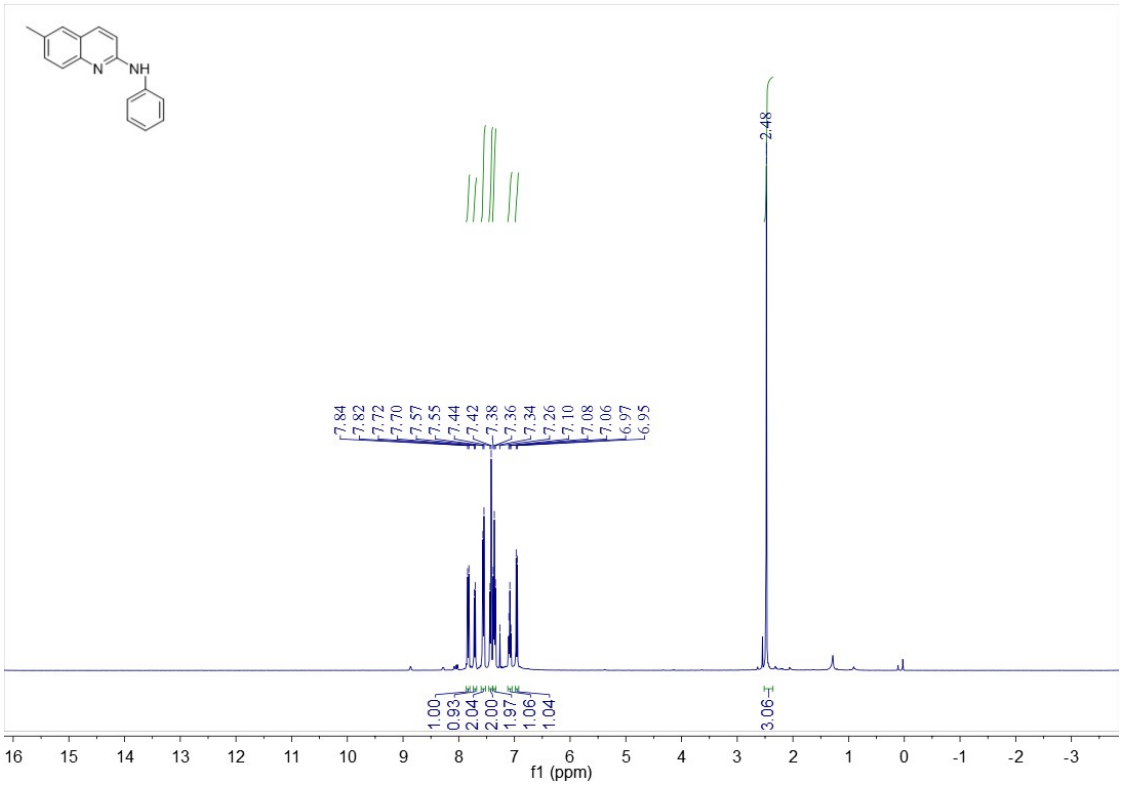
^{1}H-NMR spectrum of 3ak



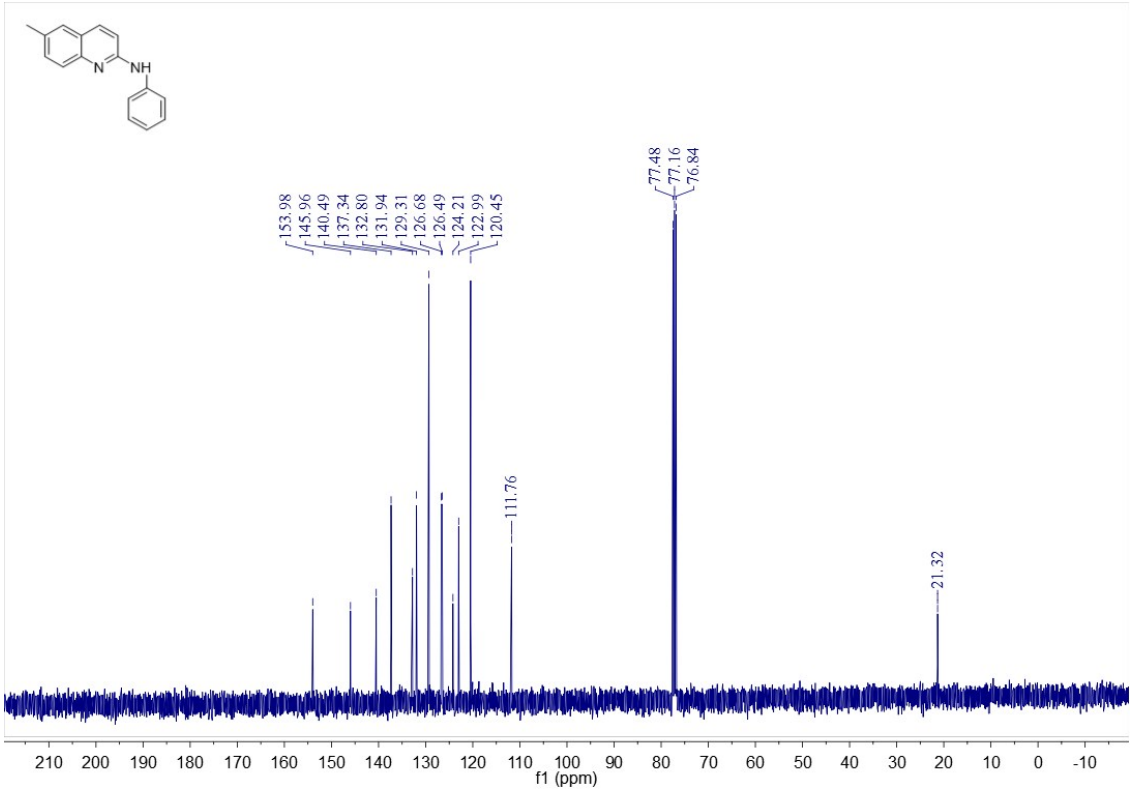
^{13}C-NMR spectrum of 3ak



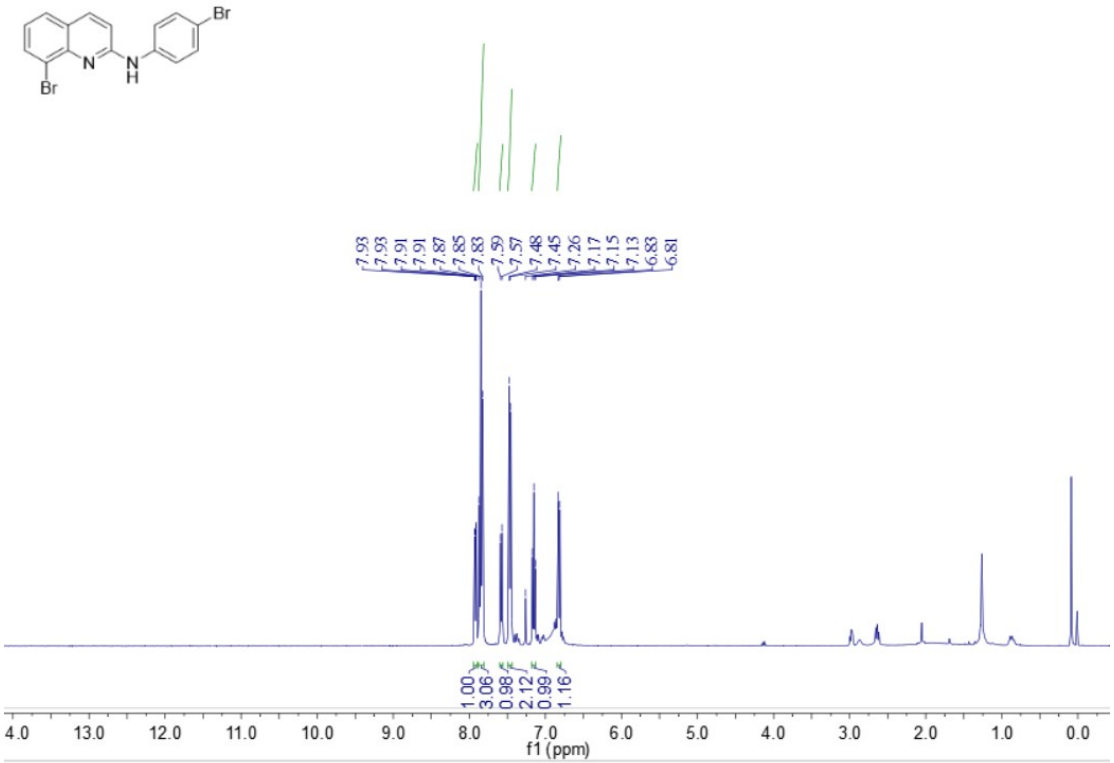
^{1}H-NMR spectrum of 3ba



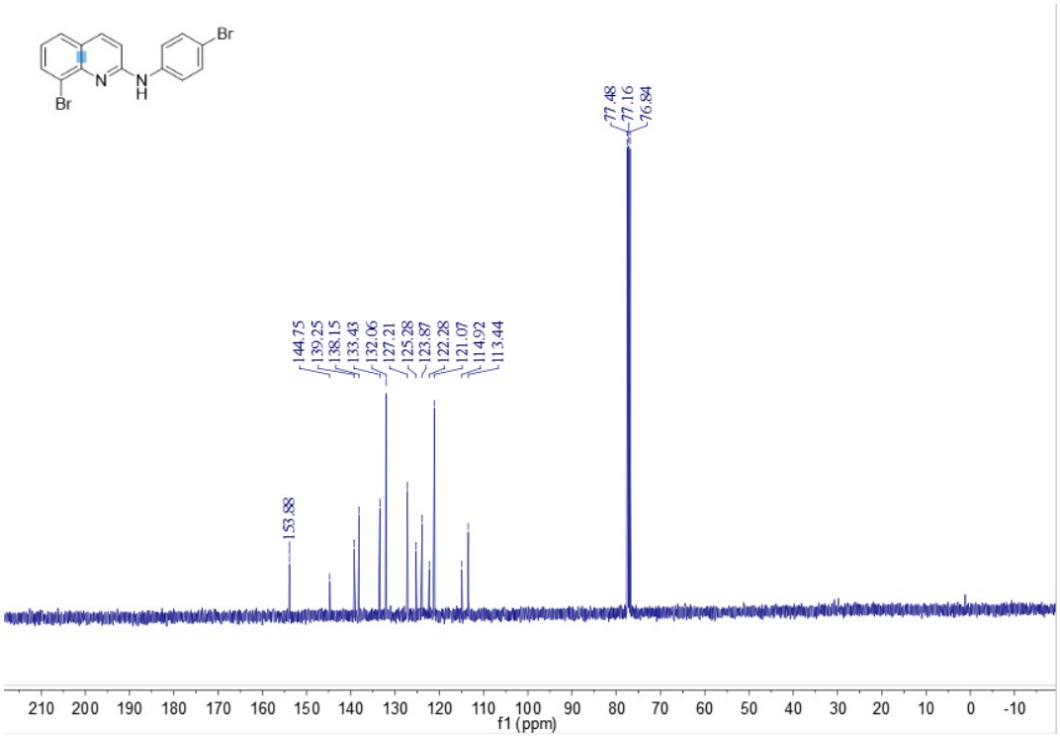
^{13}C-NMR spectrum of 3ba



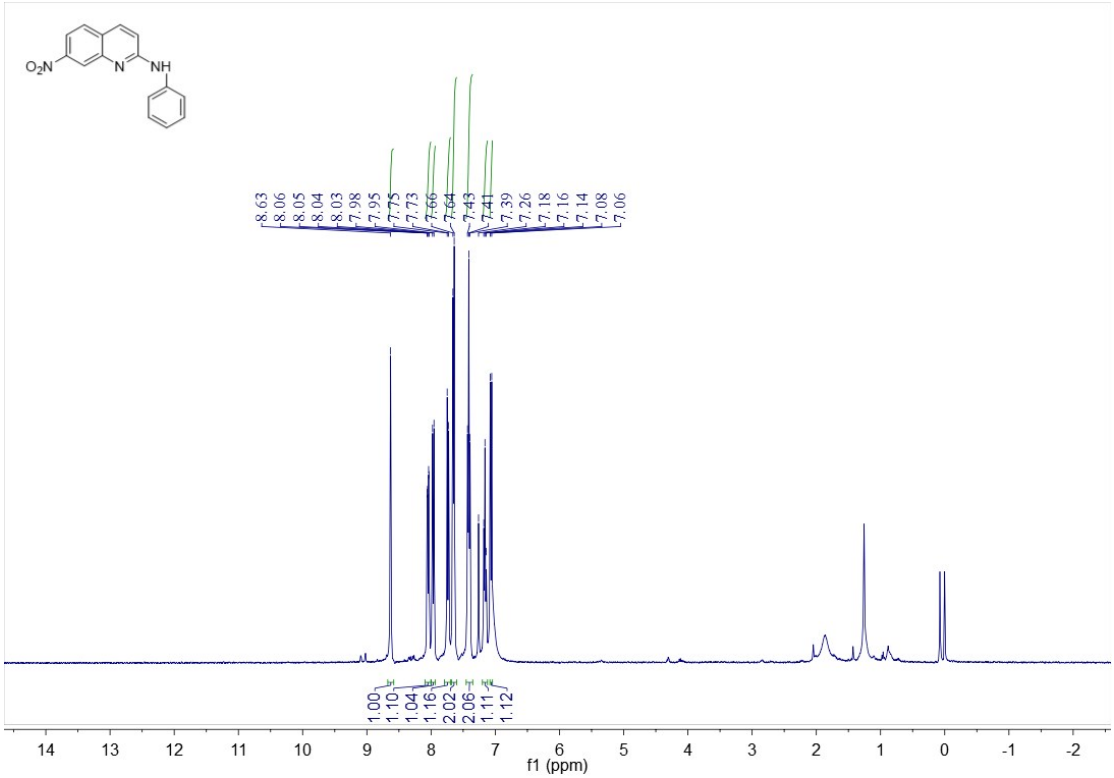
^{1}H-NMR spectrum of 3cd



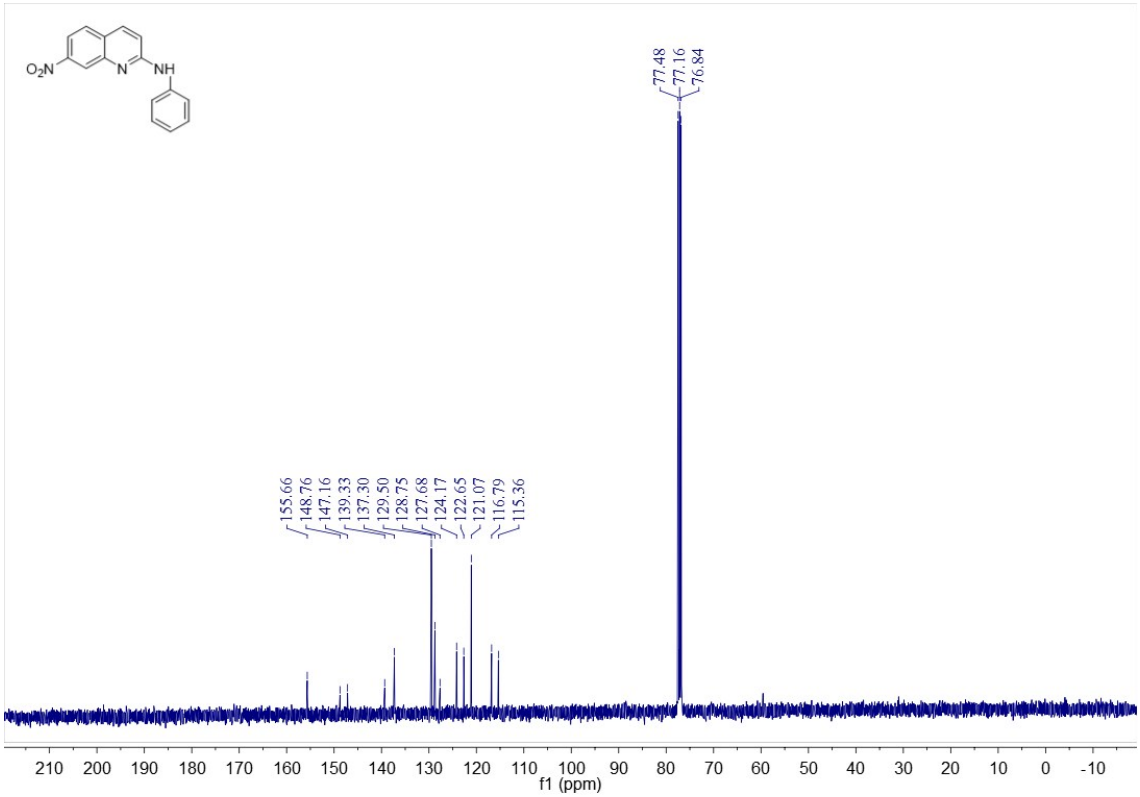
^{13}C-NMR spectrum of 3cd



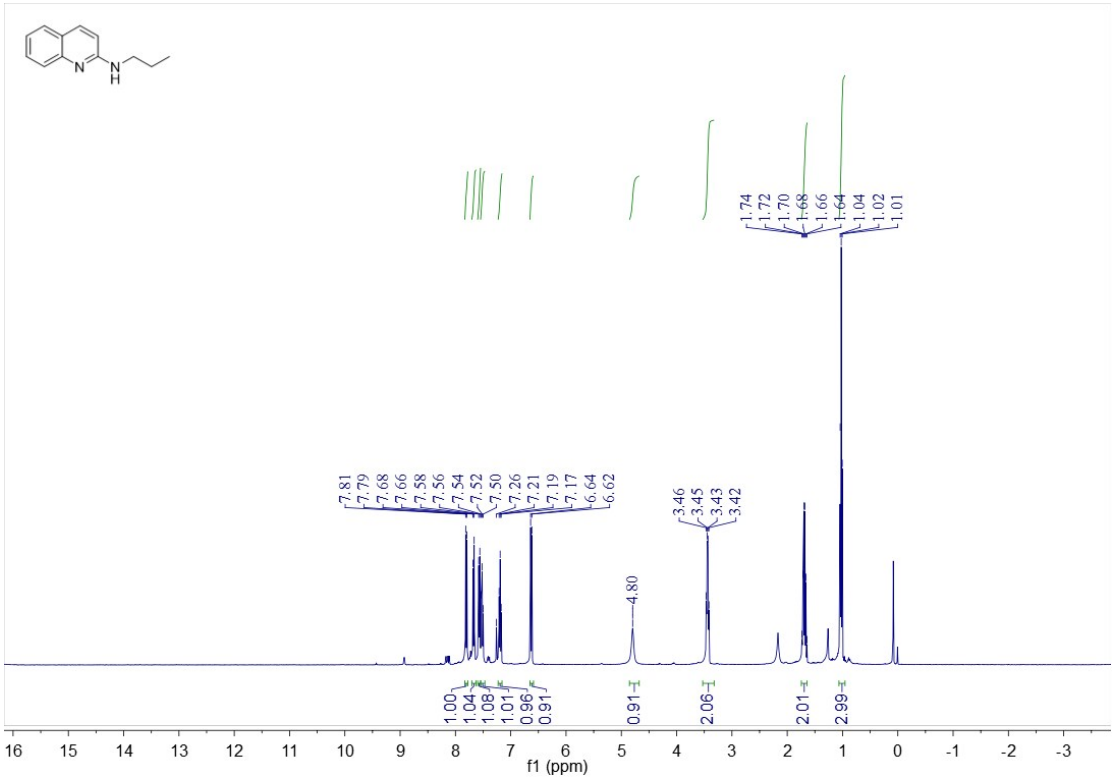
^{1}H-NMR spectrum of 3da



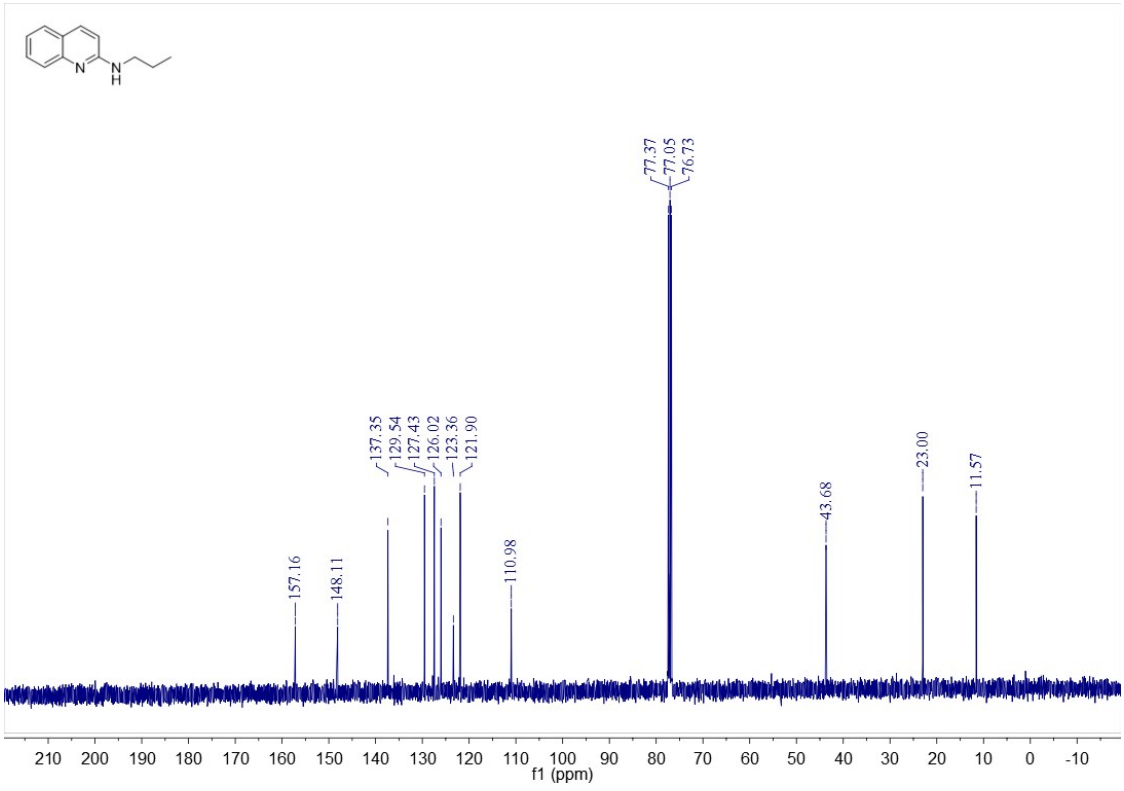
^{13}C-NMR spectrum of 3da



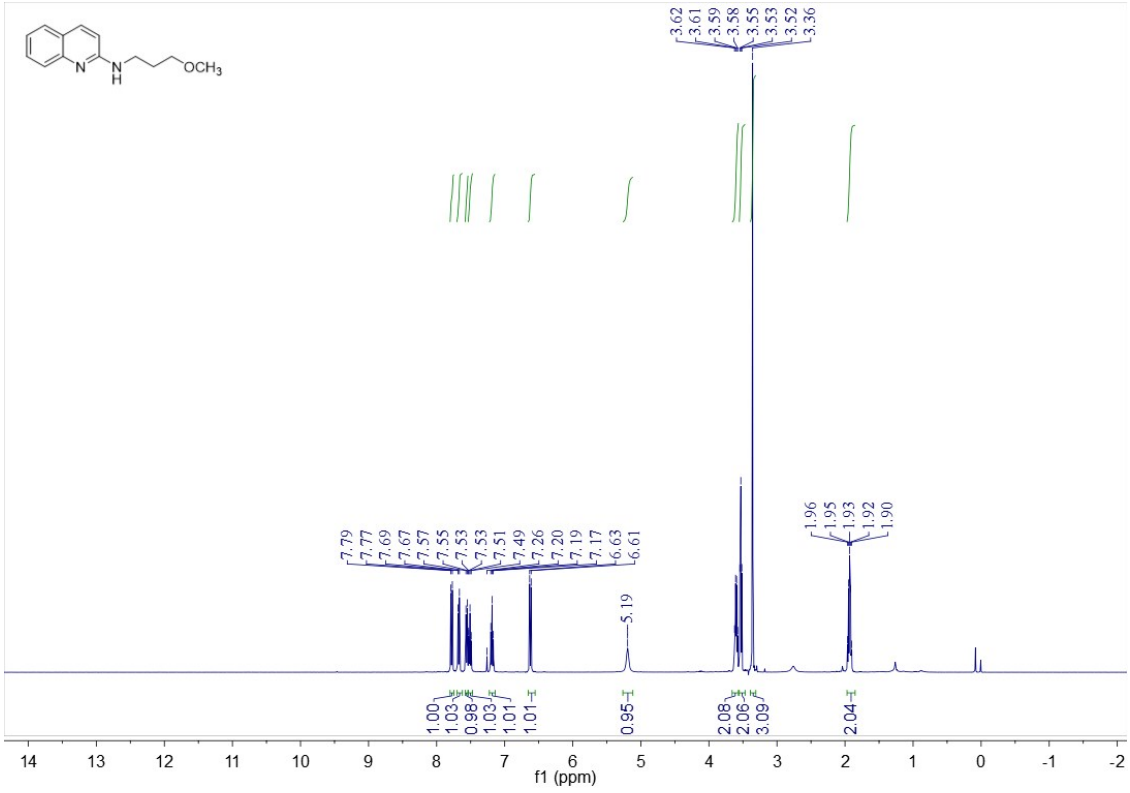
^{1}H-NMR spectrum of 5aa



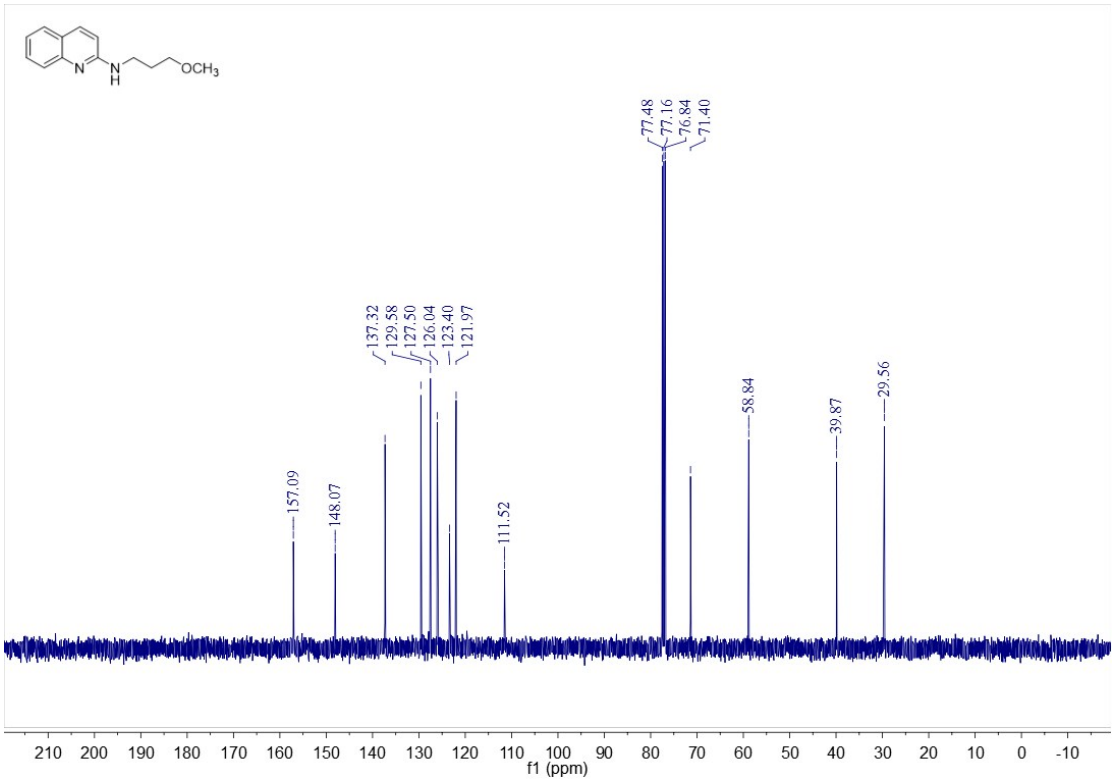
^{13}C-NMR spectrum of 5aa



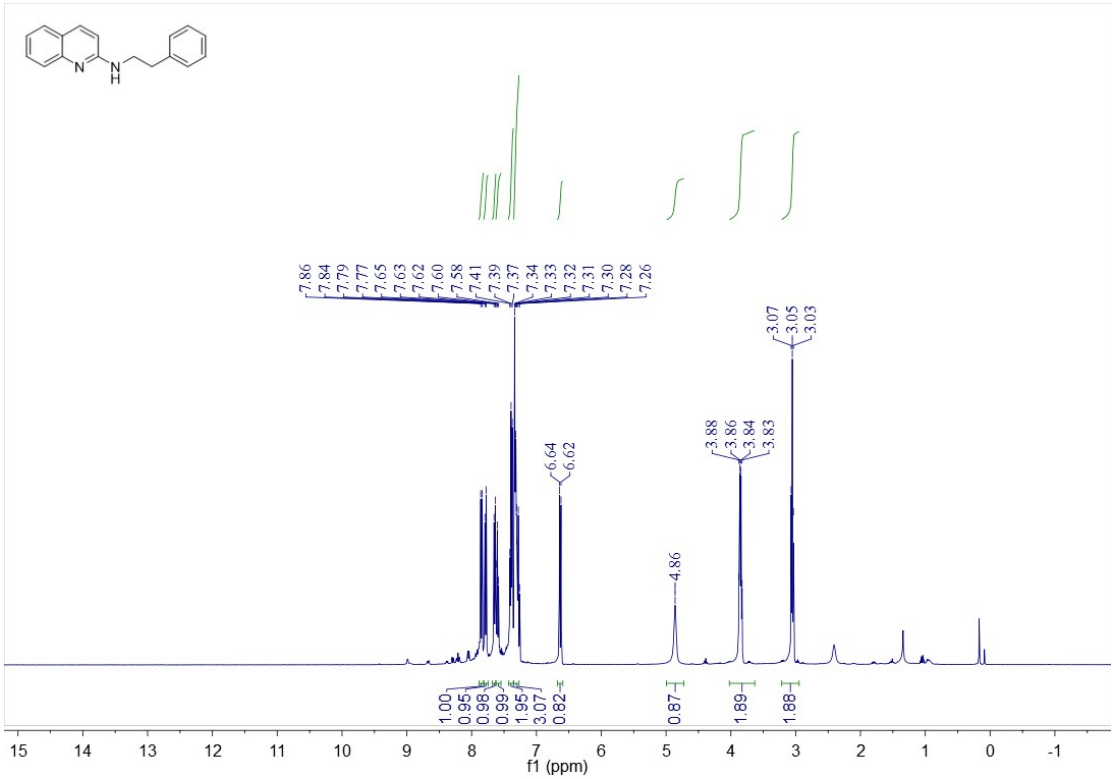
^{1}H-NMR spectrum of 5ab



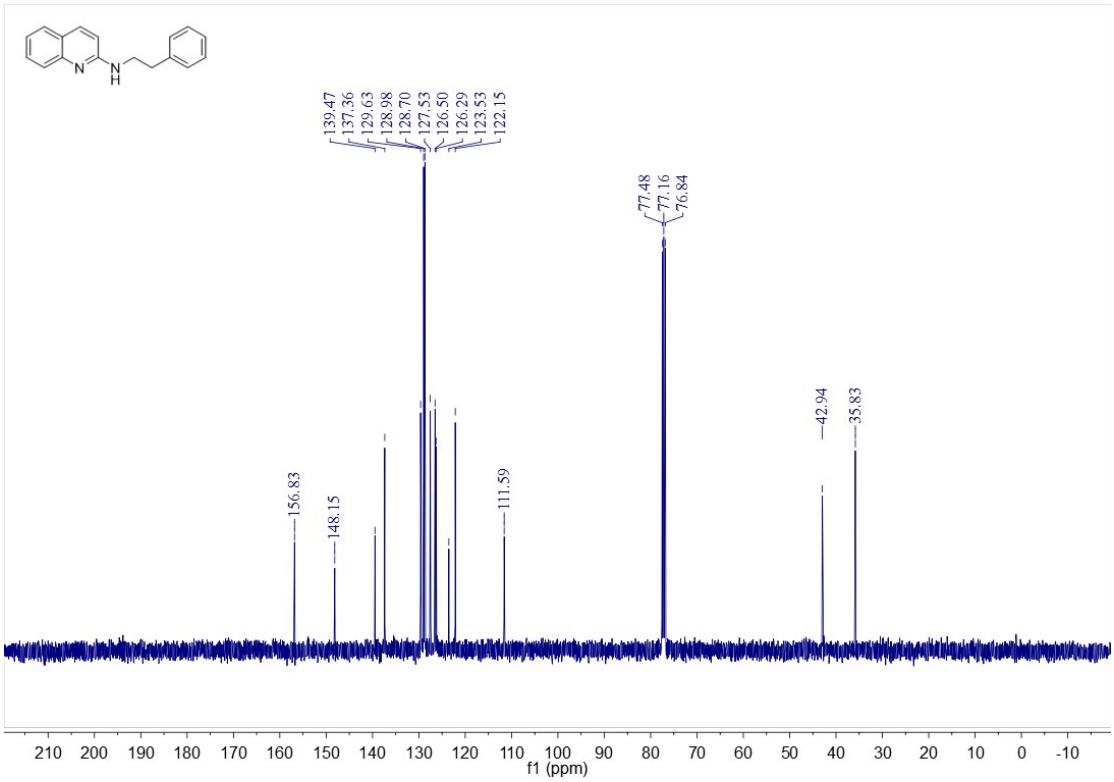
^{13}C-NMR spectrum of 5ab



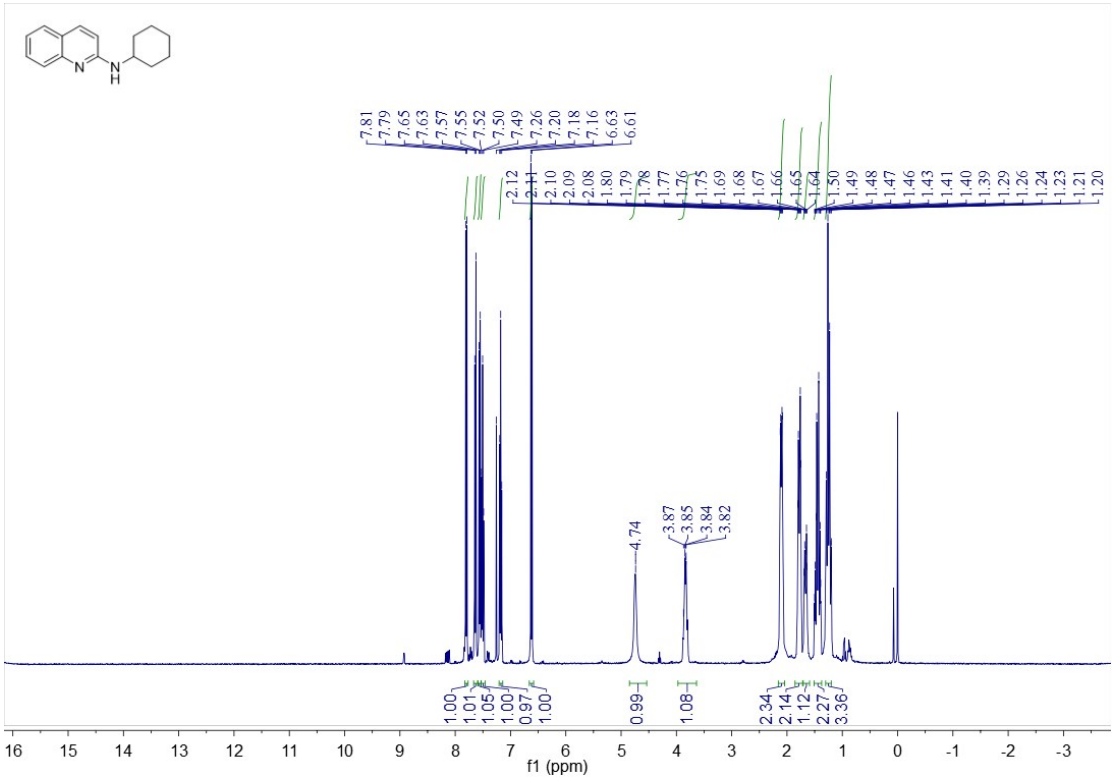
^{1}H-NMR spectrum of 3ac



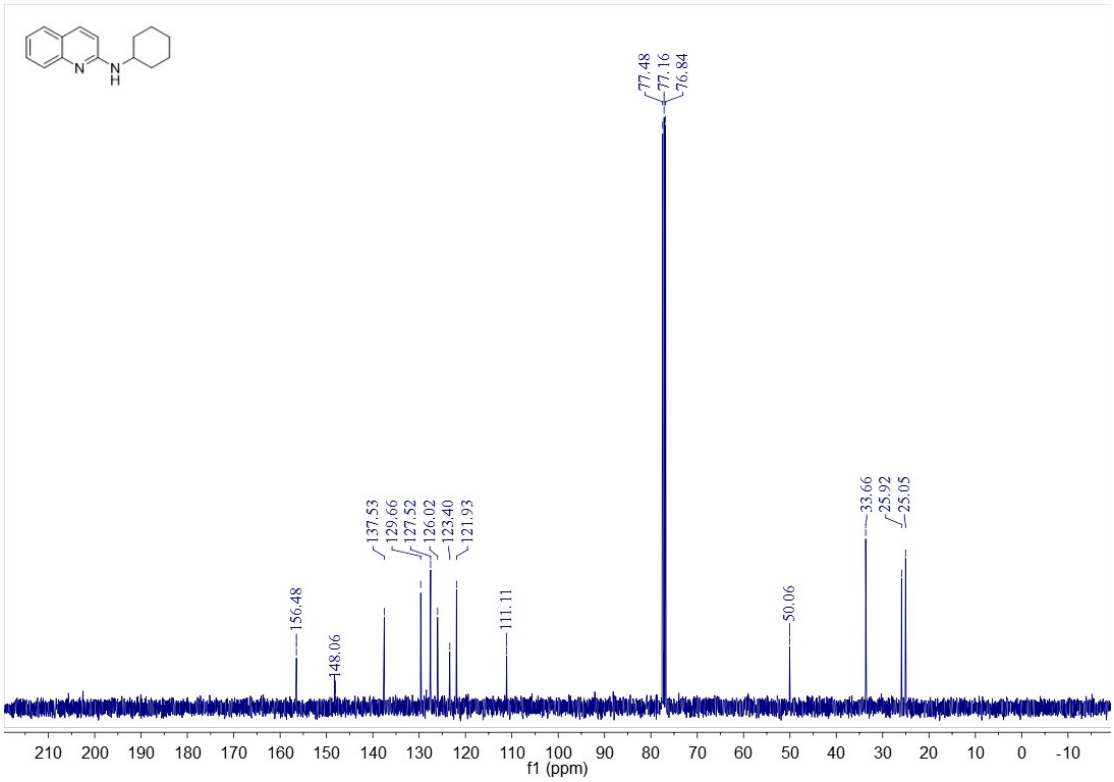
^{13}C-NMR spectrum of 3ac



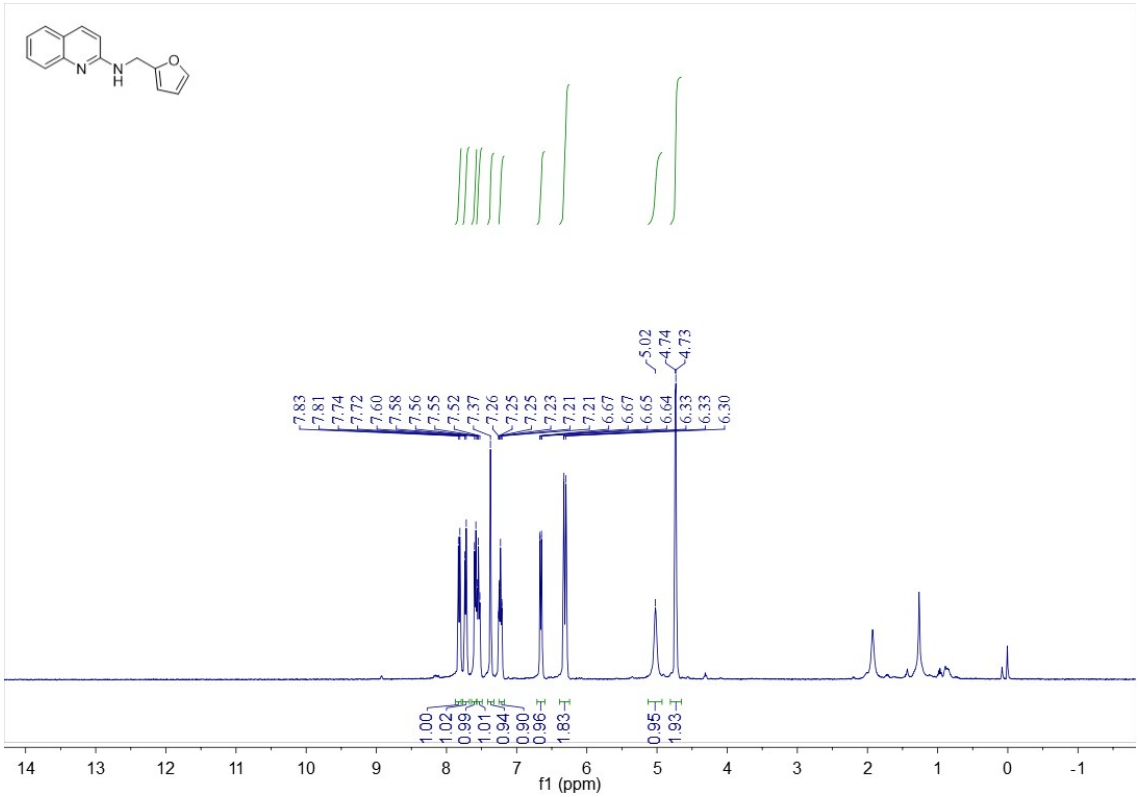
^{1}H-NMR spectrum of 5ad



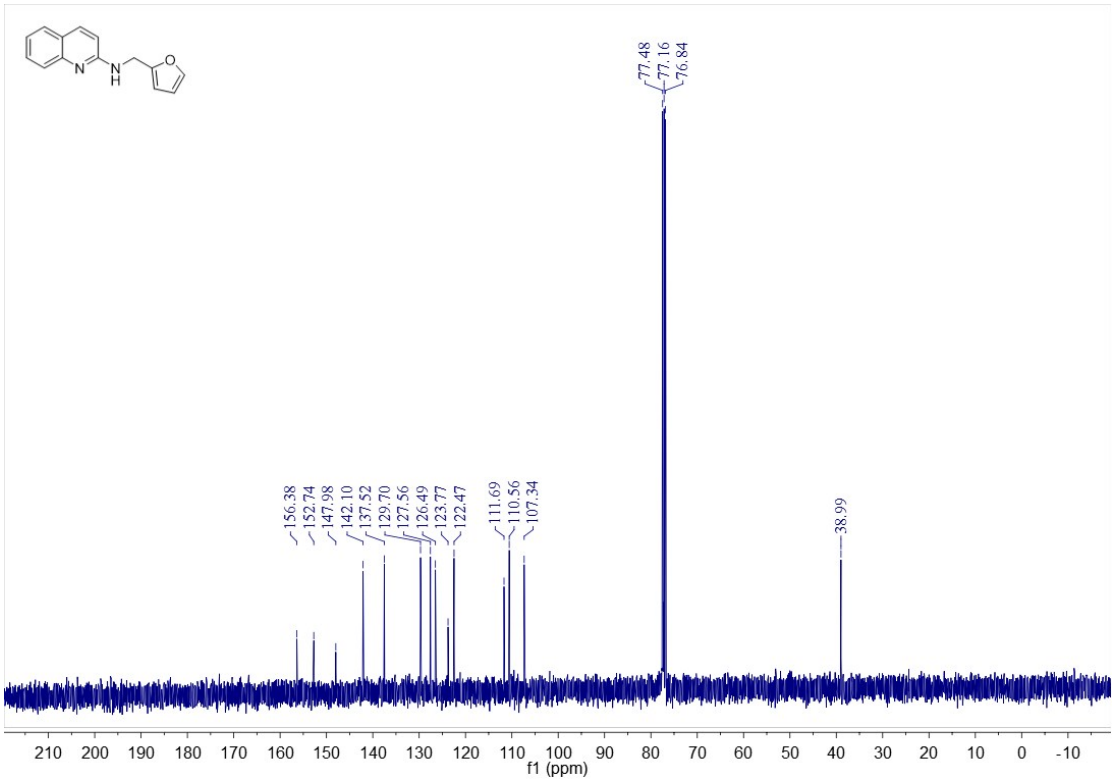
^{13}C-NMR spectrum of 5ad



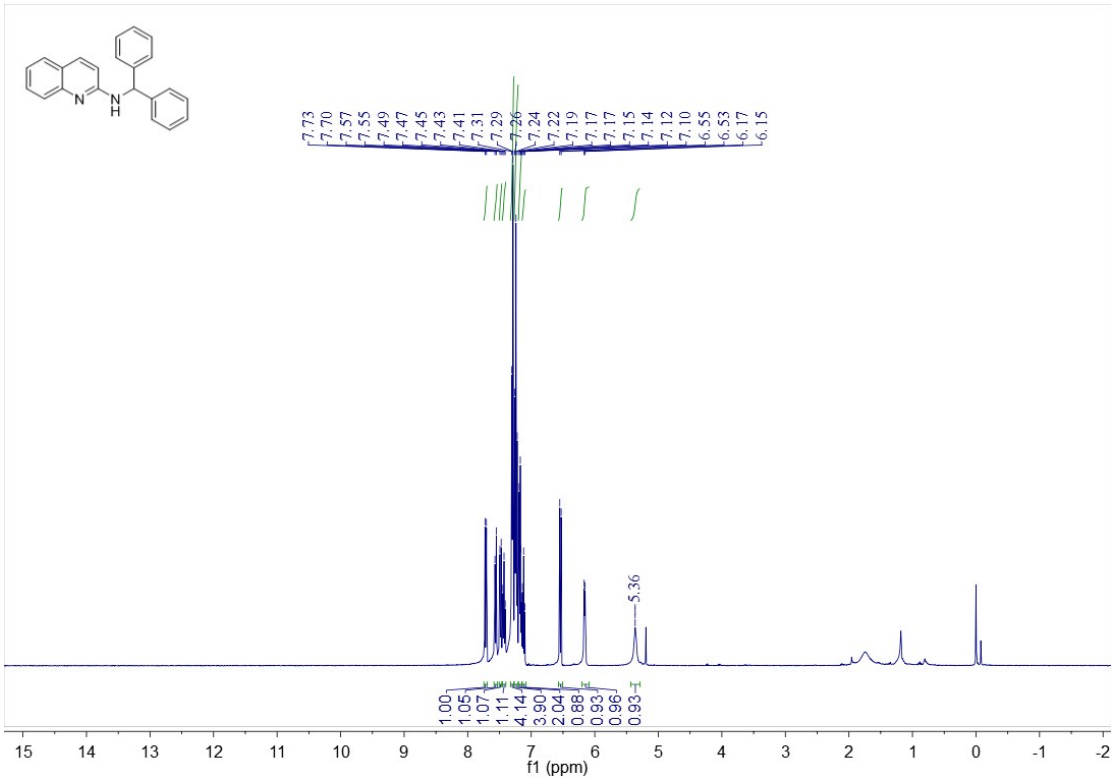
^{1}H-NMR spectrum of 5ae



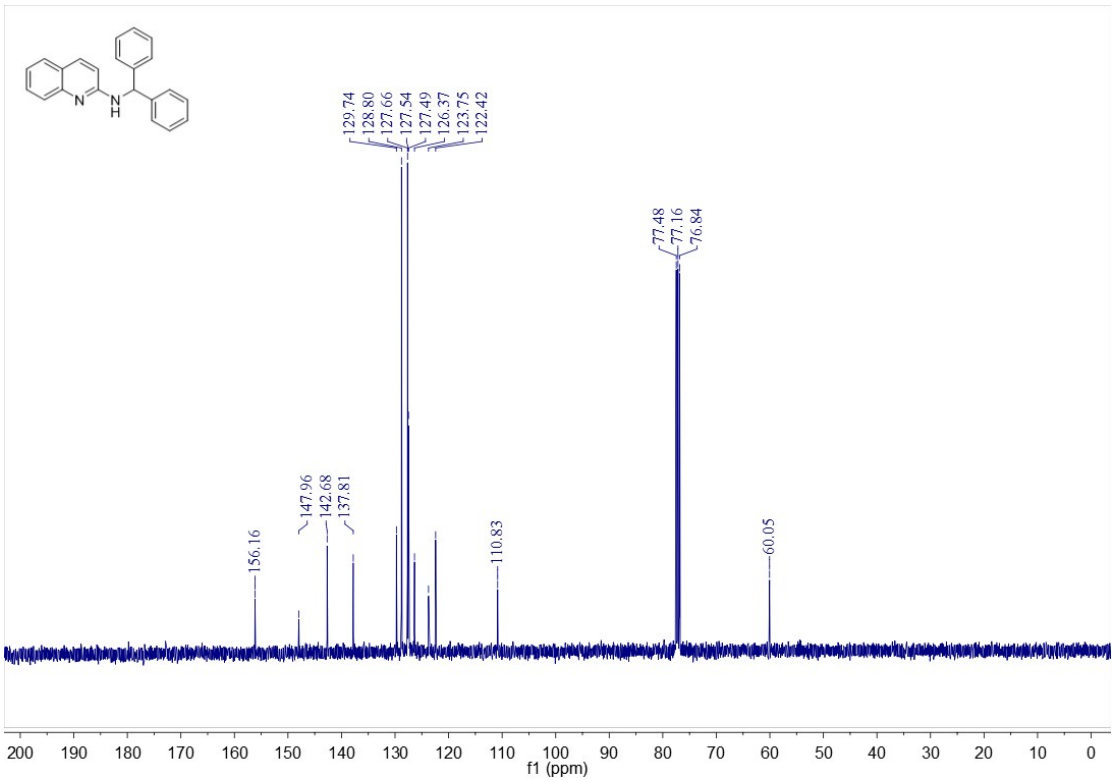
^{13}C-NMR spectrum of 5ae



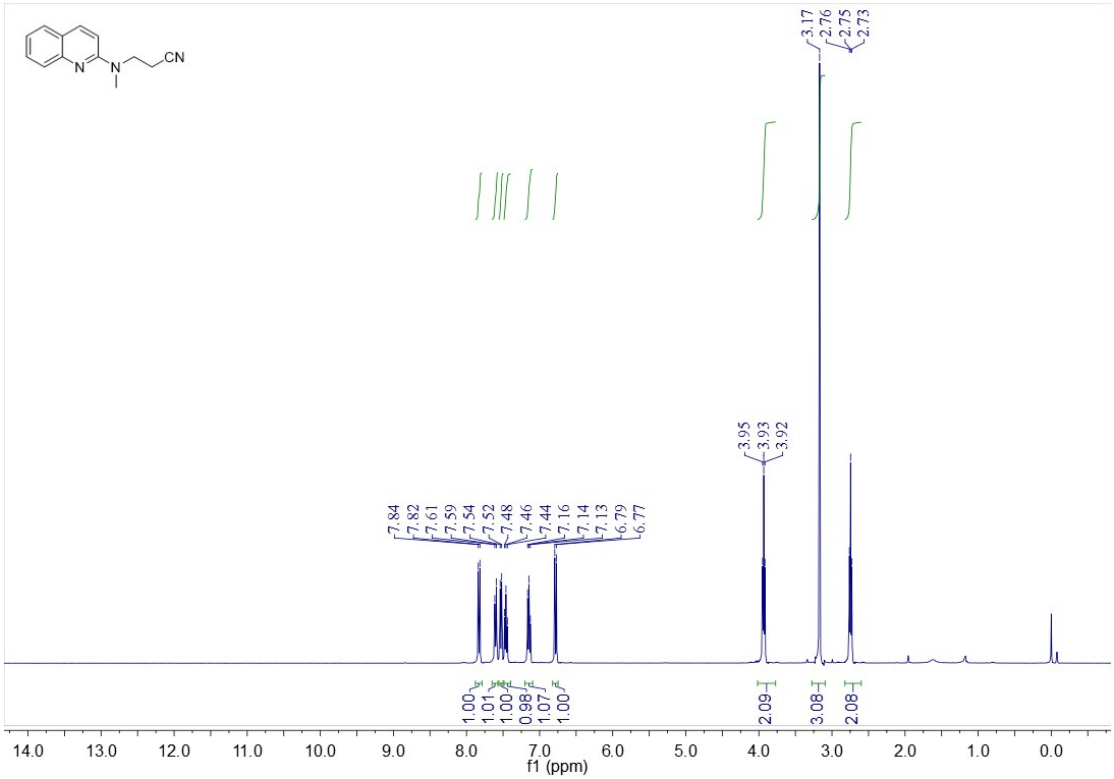
^{1}H-NMR spectrum of 5af



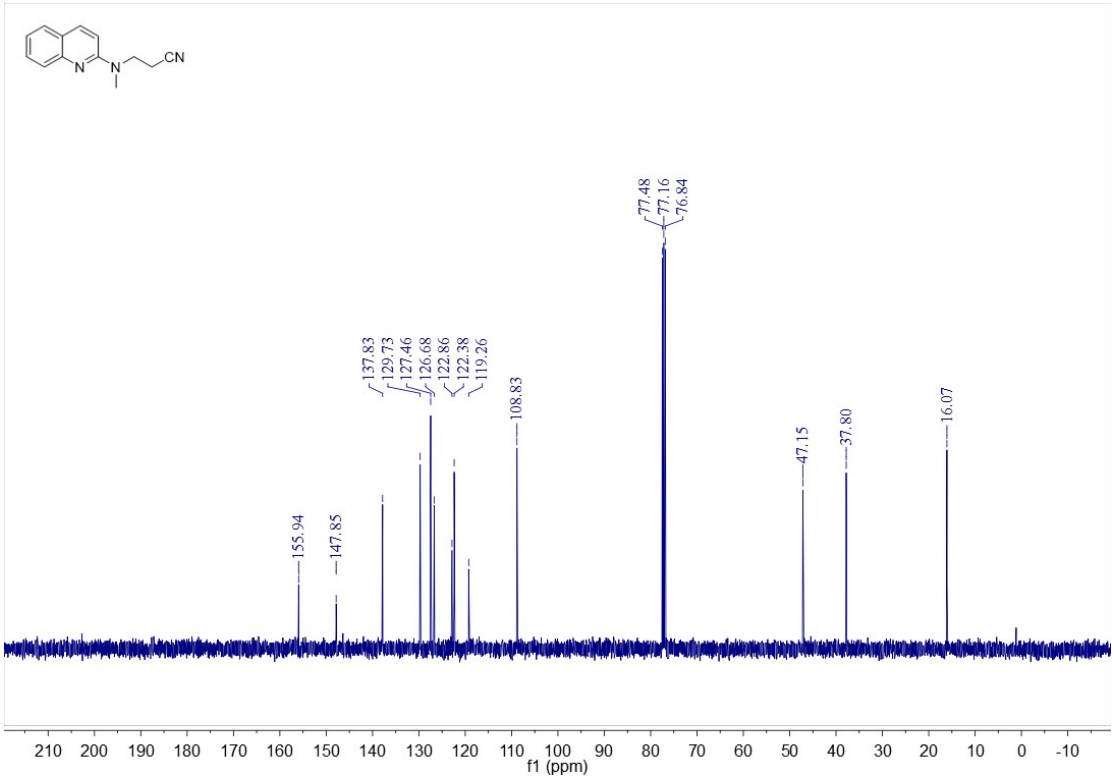
^{13}C-NMR spectrum of 5af



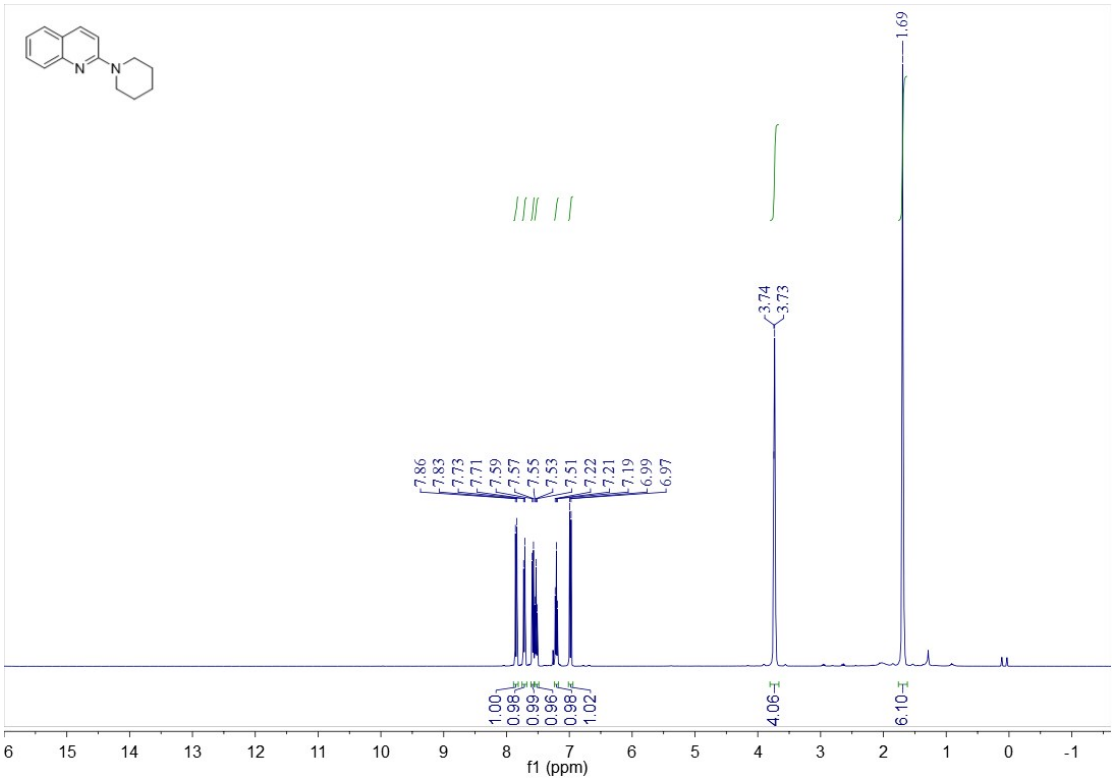
^{1}H-NMR spectrum of 5ag



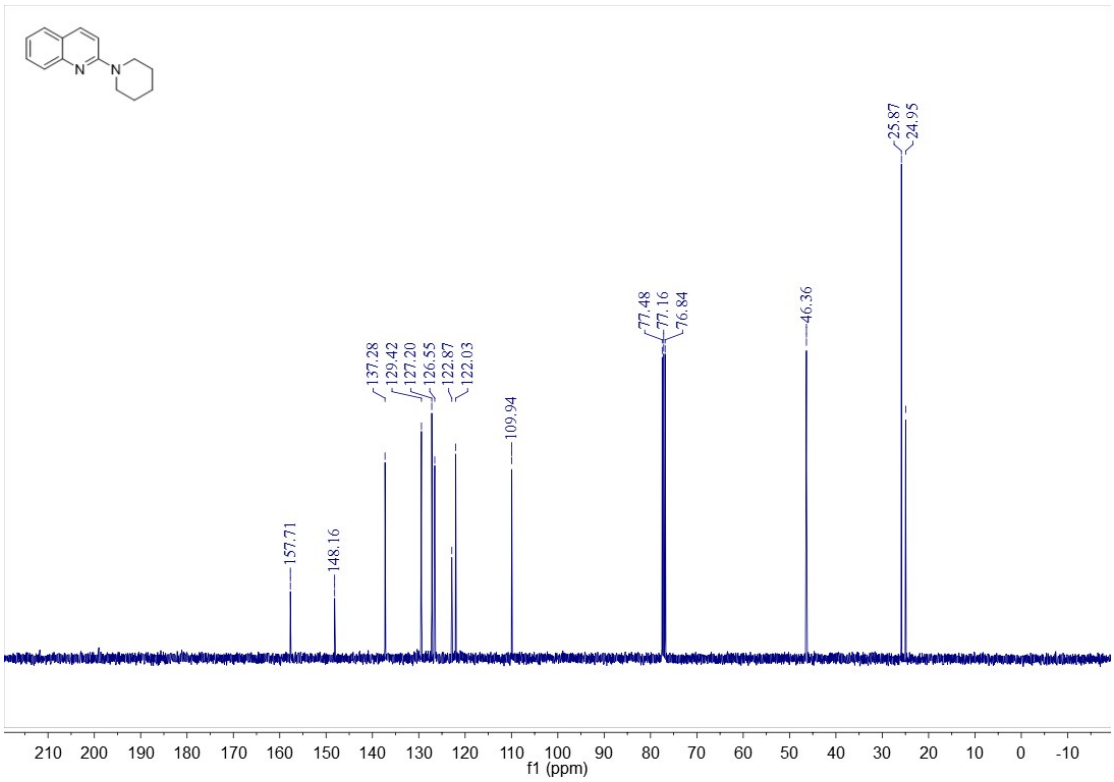
^{13}C-NMR spectrum of 5ag



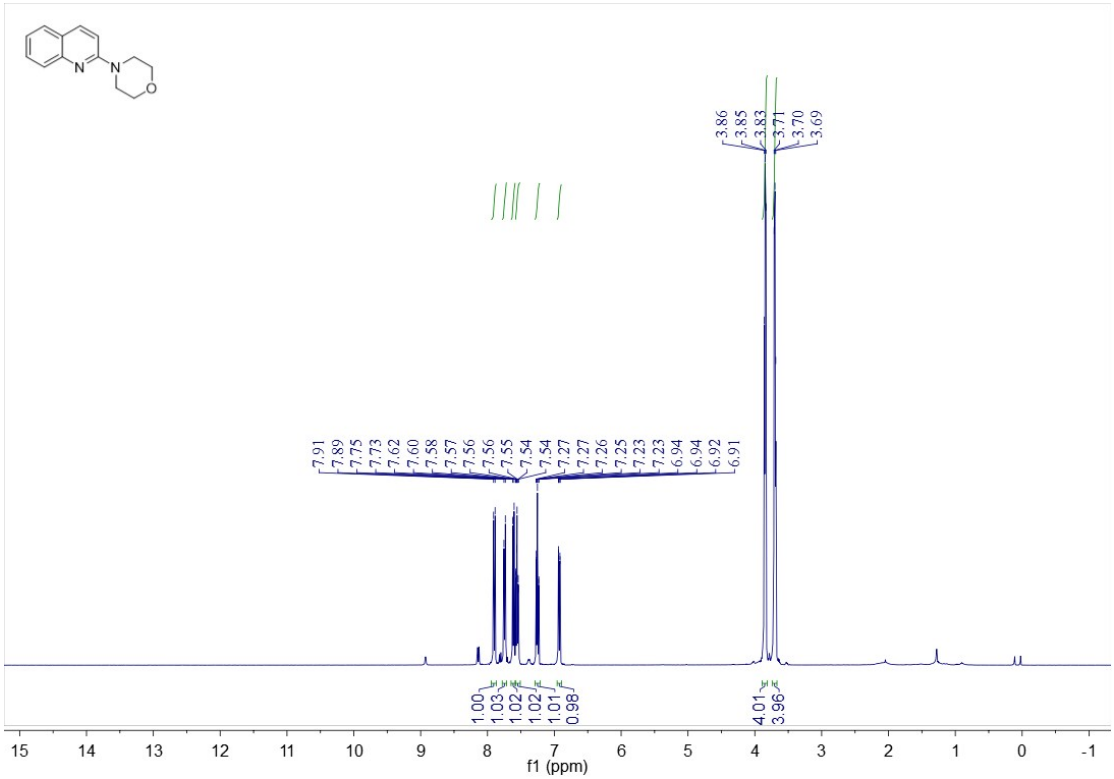
^{1}H-NMR spectrum of 5ah



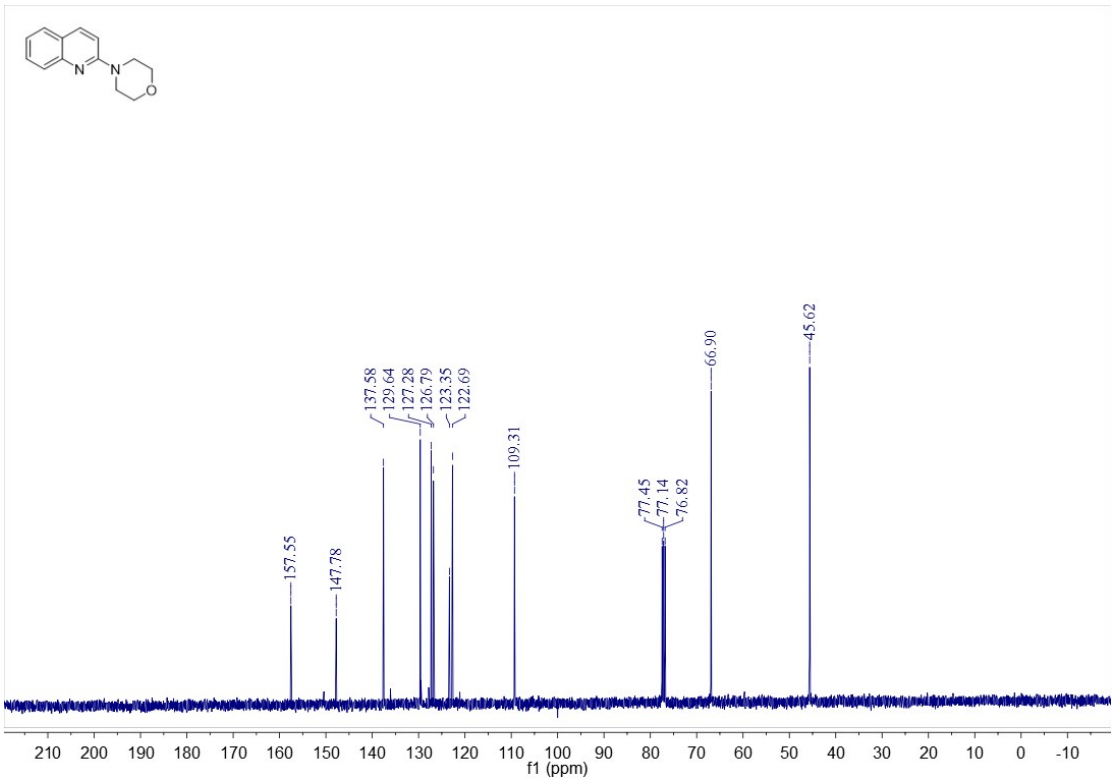
^{13}C-NMR spectrum of 5ah



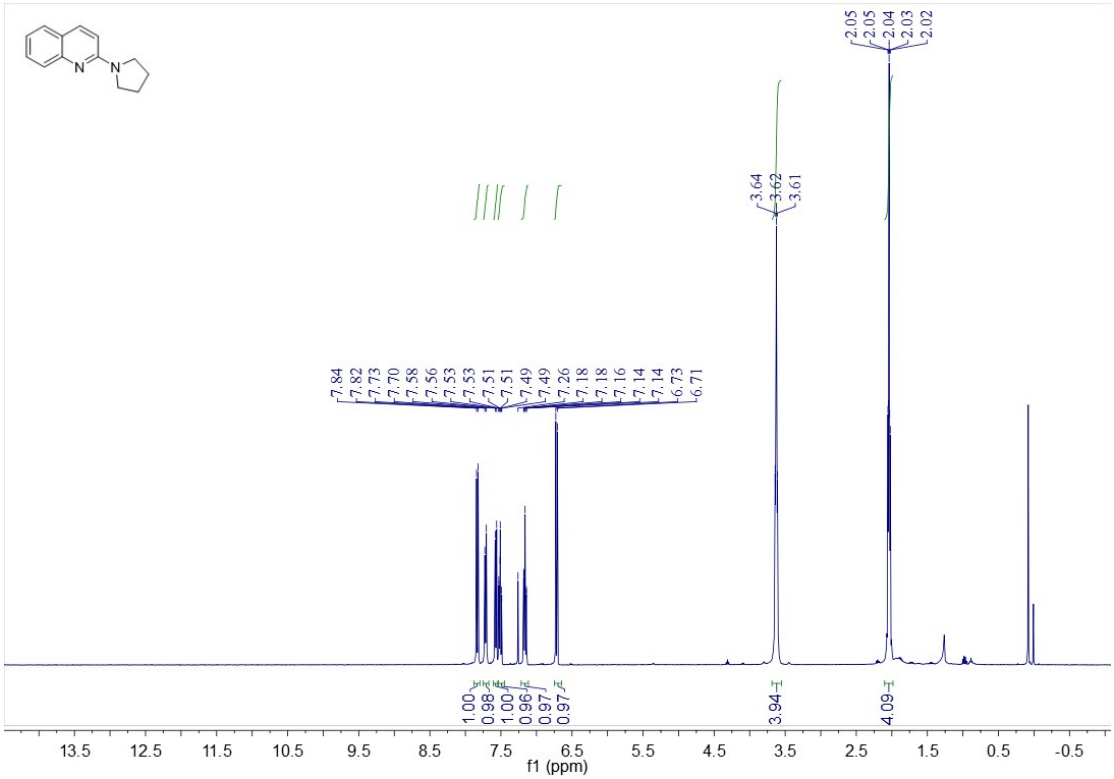
^{1}H-NMR spectrum of 5ai



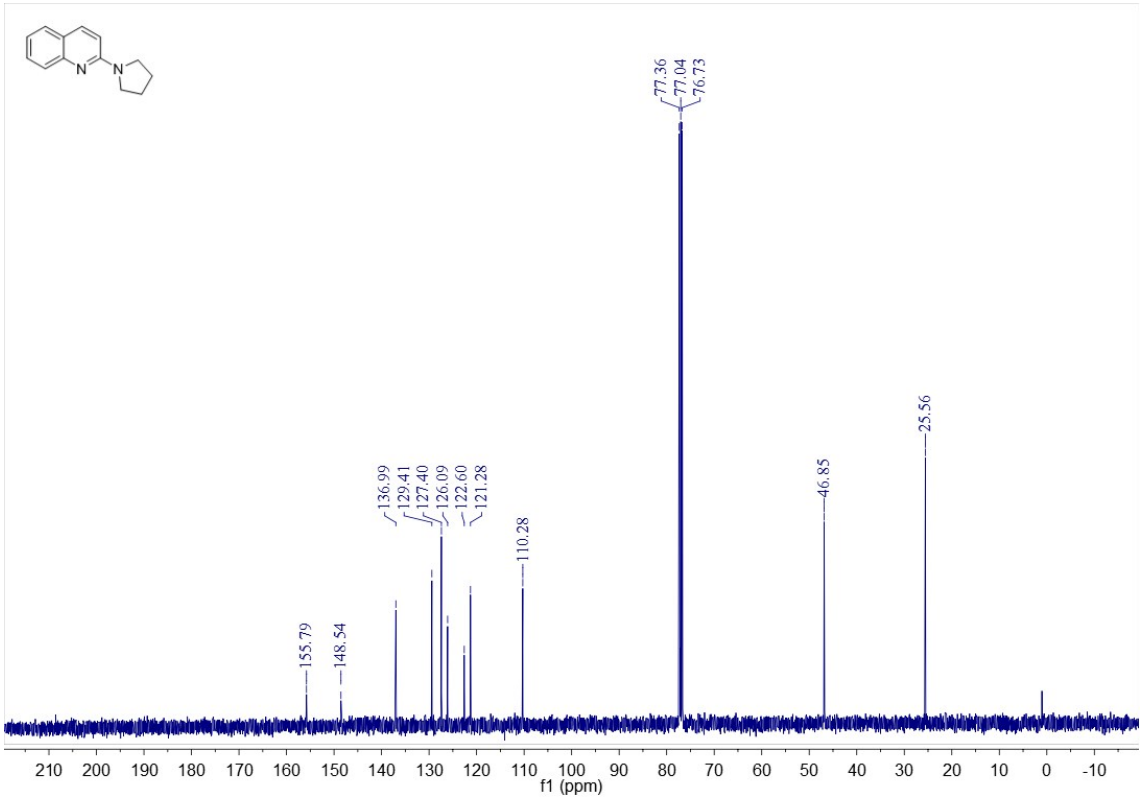
^{13}C-NMR spectrum of 5ai



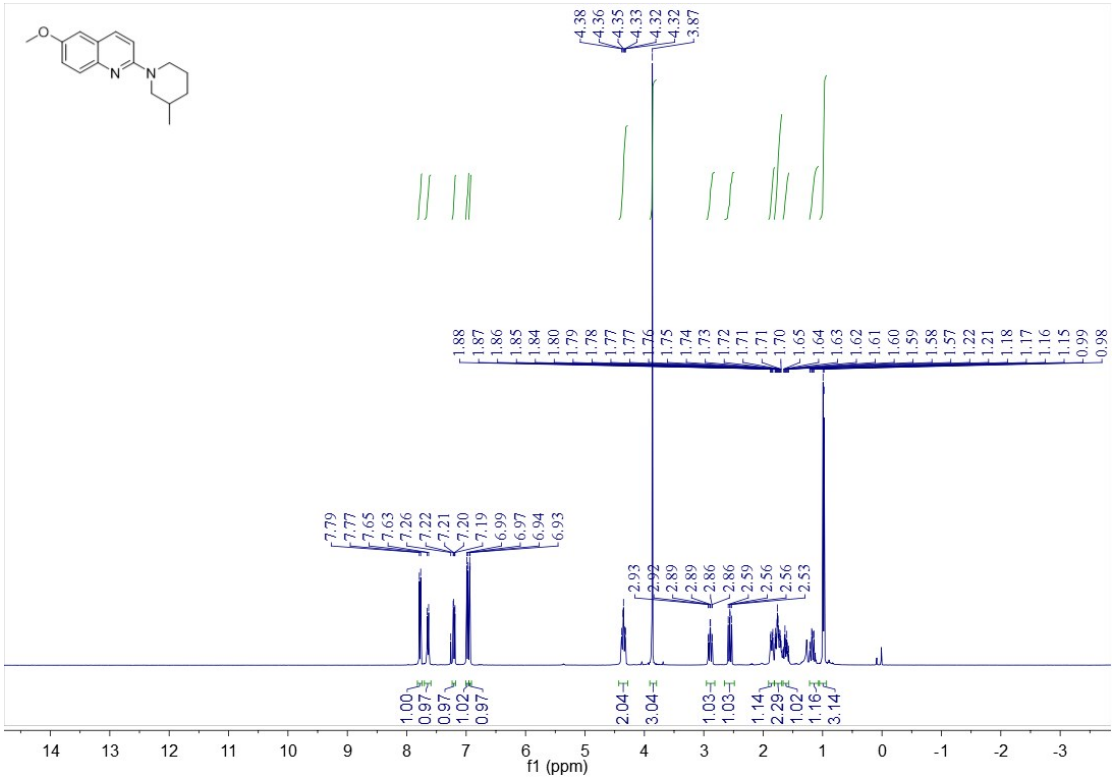
^{1}H-NMR spectrum of 5aj



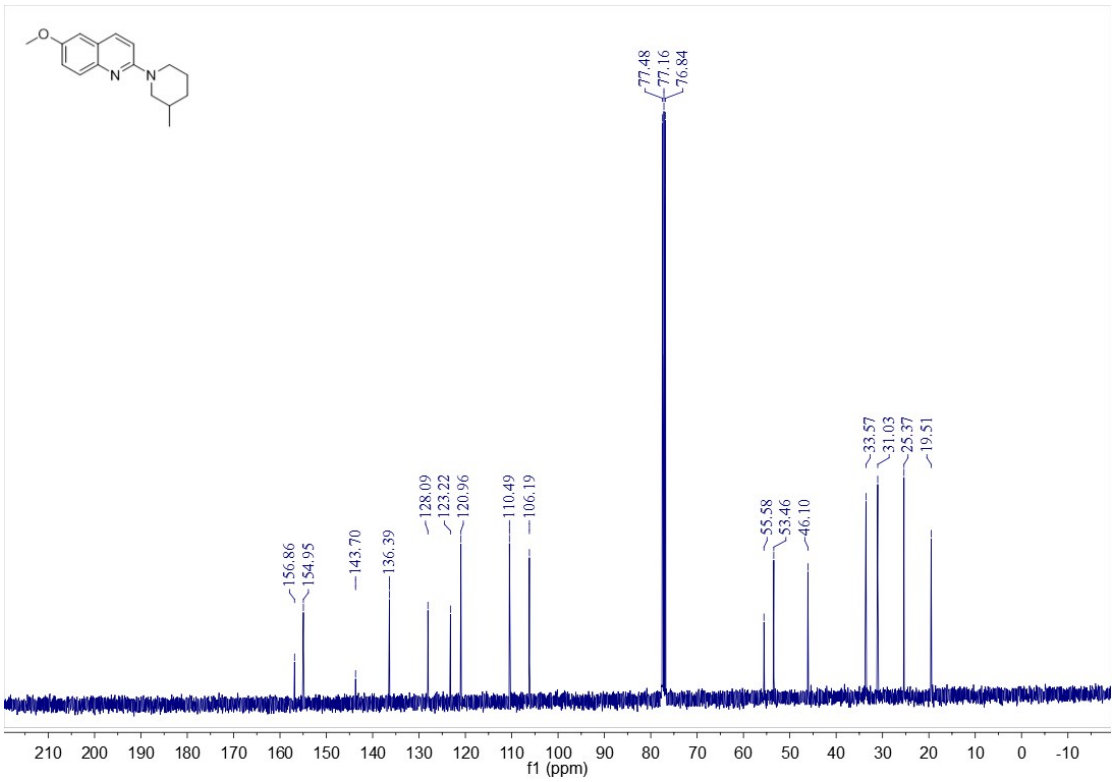
^{13}C-NMR spectrum of 5aj



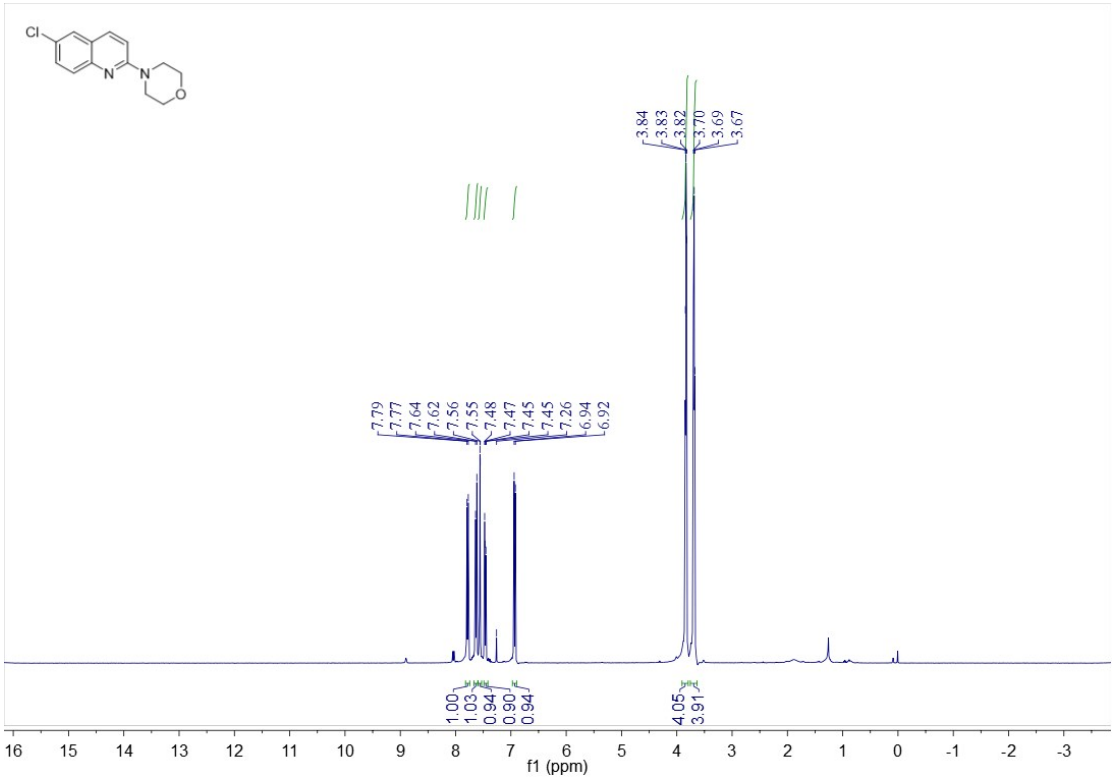
^{1}H-NMR spectrum of 5ek



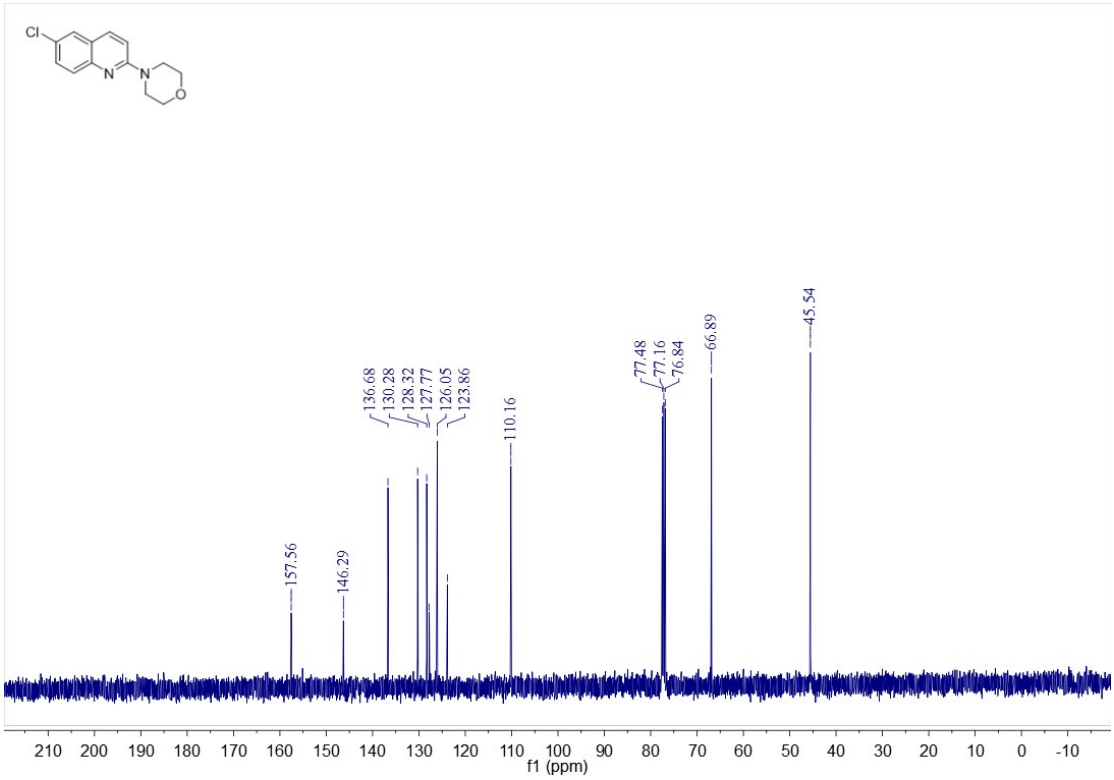
^{13}C-NMR spectrum of 5ek



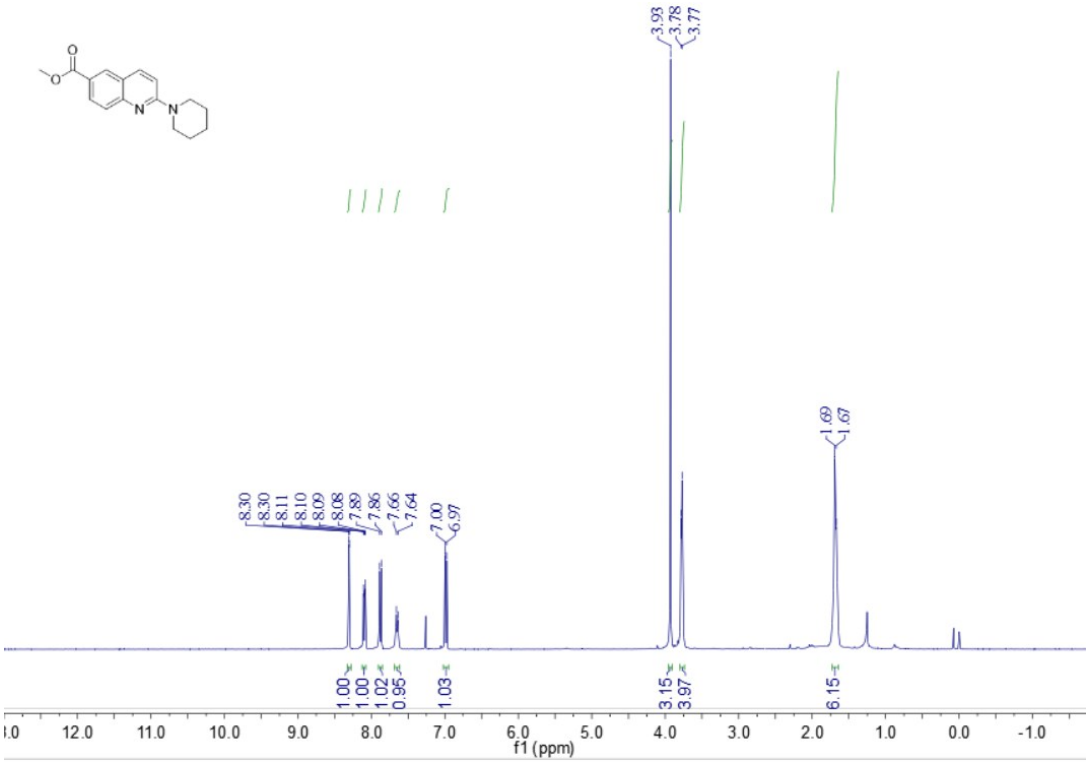
^{1}H-NMR spectrum of 5fi



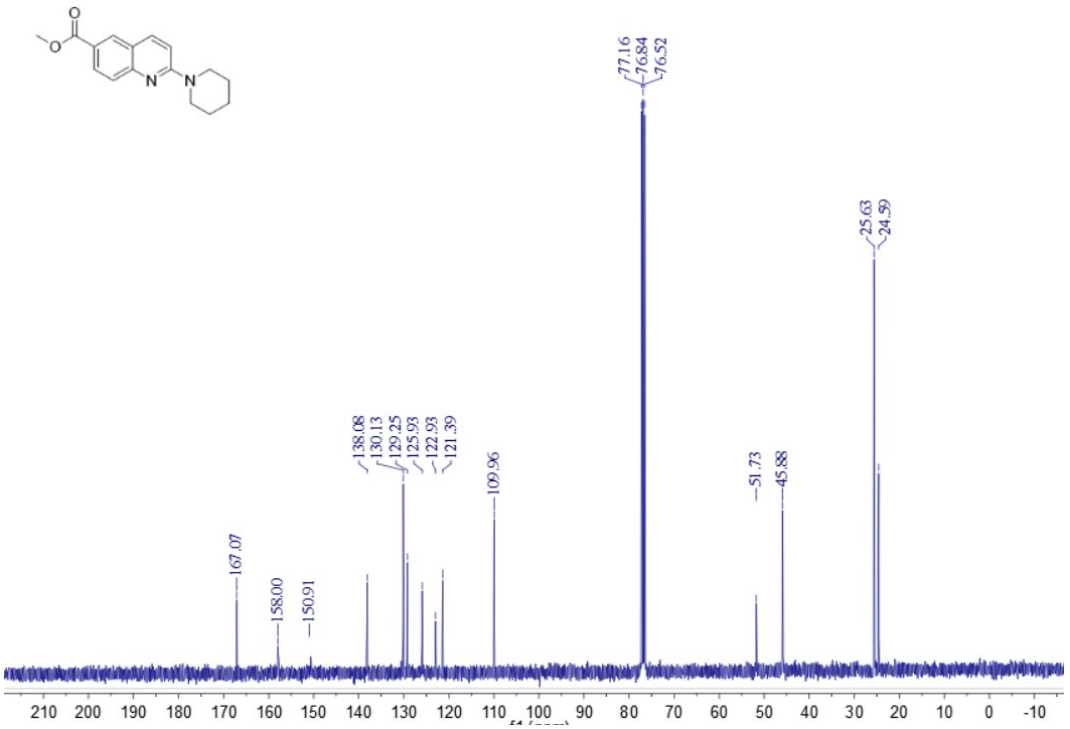
^{13}C-NMR spectrum of 5fi



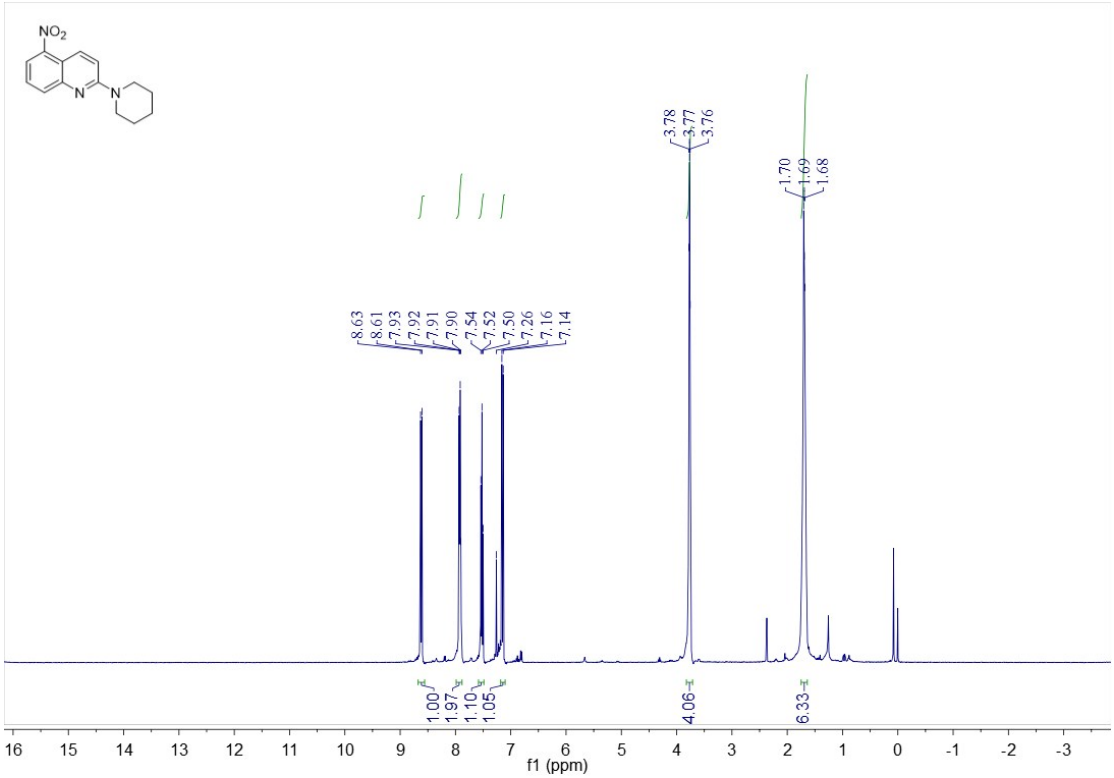
^{1}H-NMR spectrum of 5gh



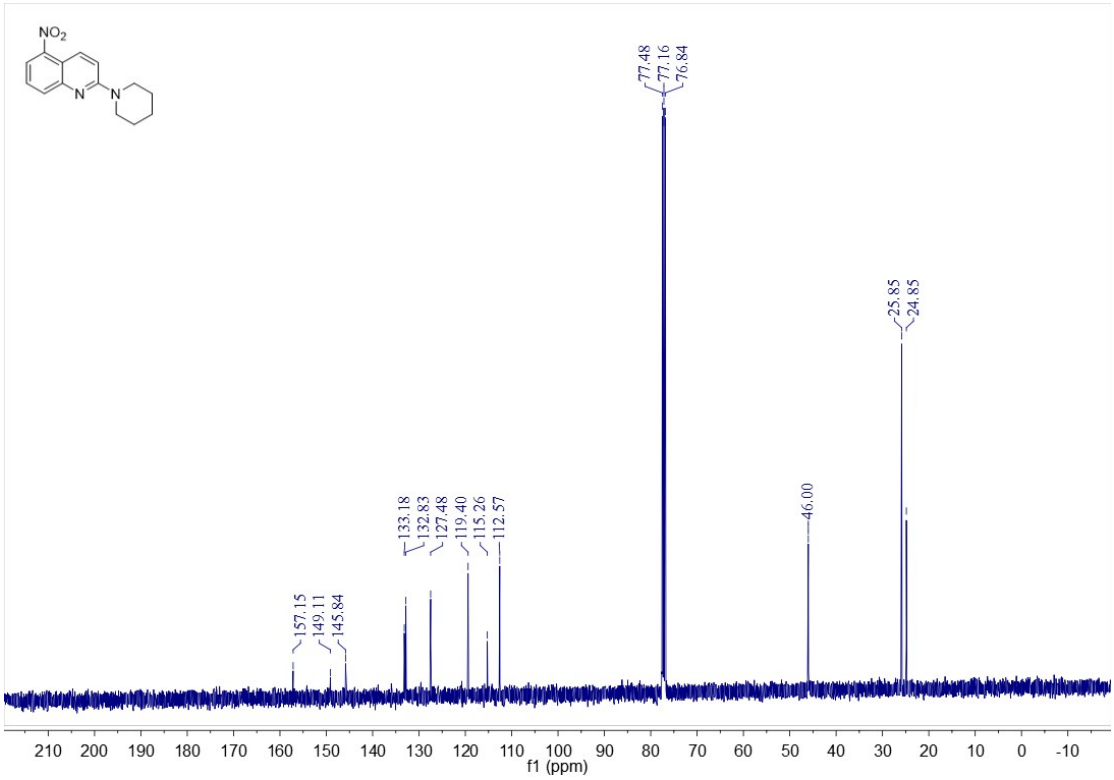
^{13}C-NMR spectrum of 5gh



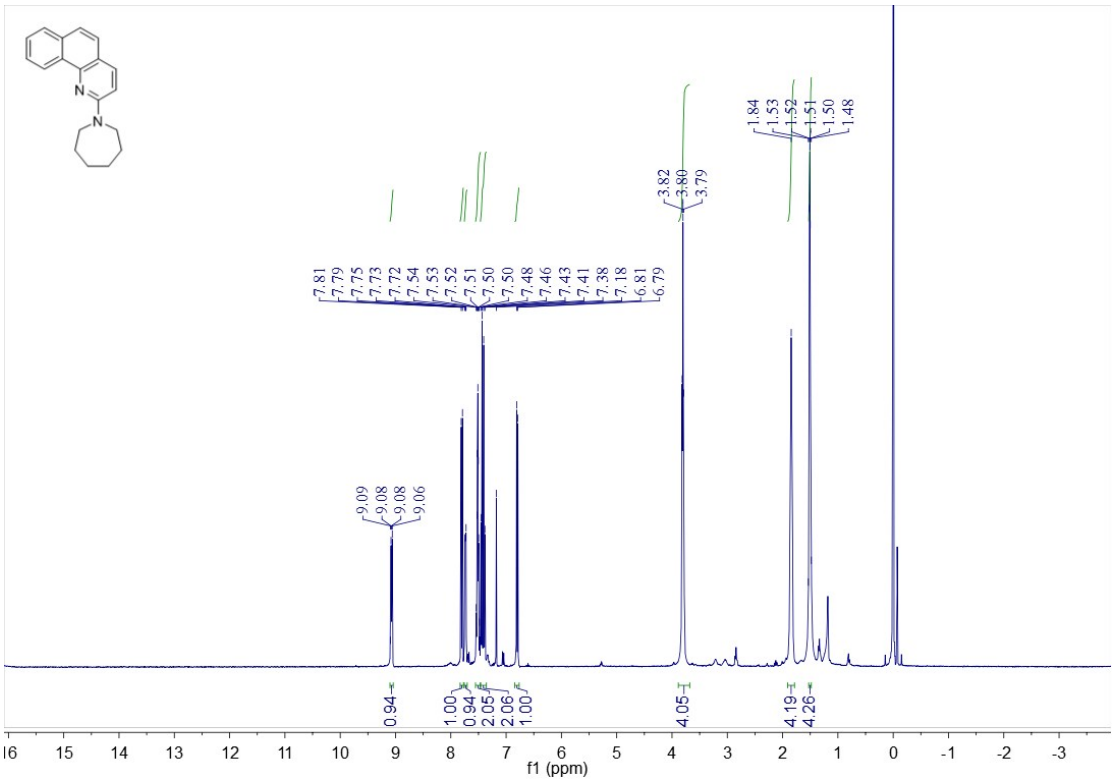
^{1}H-NMR spectrum of 5hh



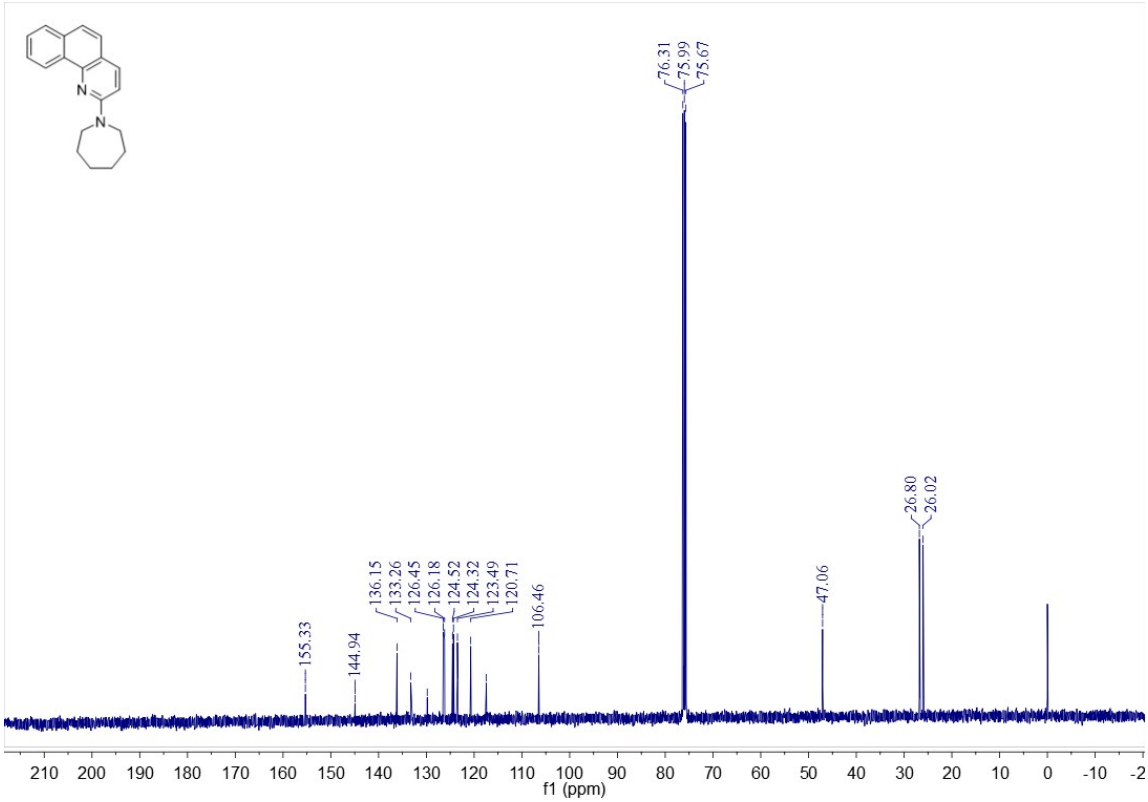
^{13}C-NMR spectrum of 5hh



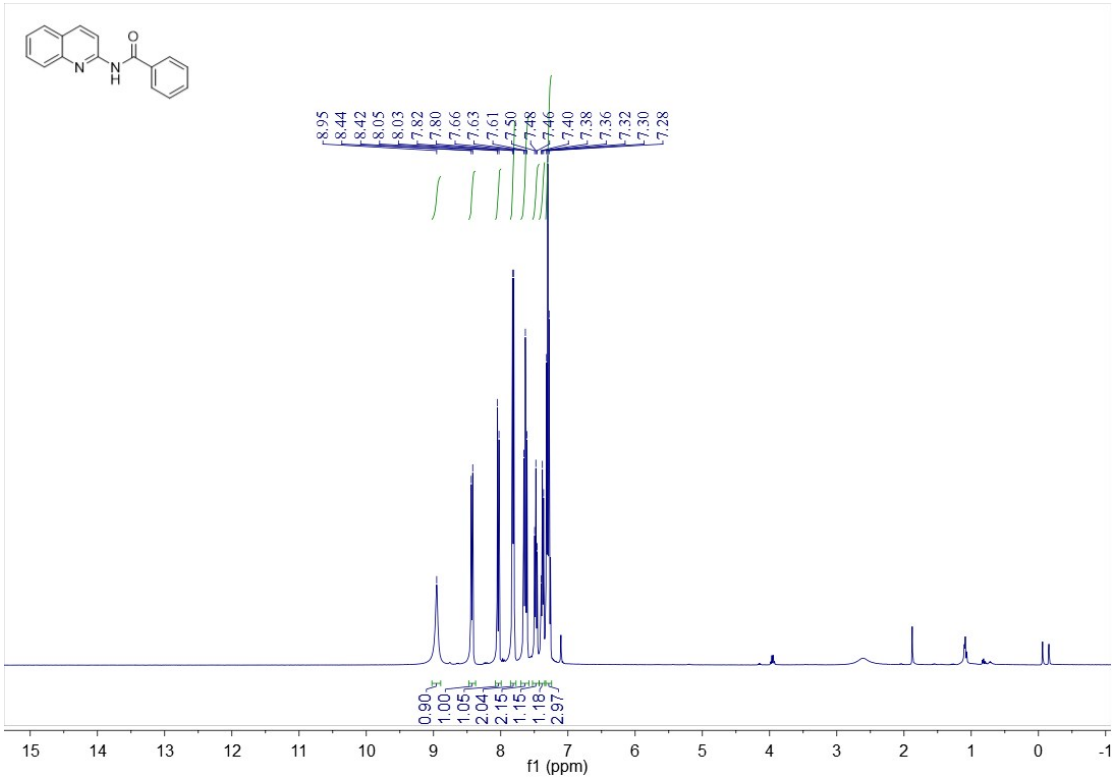
^{1}H-NMR spectrum of 5il



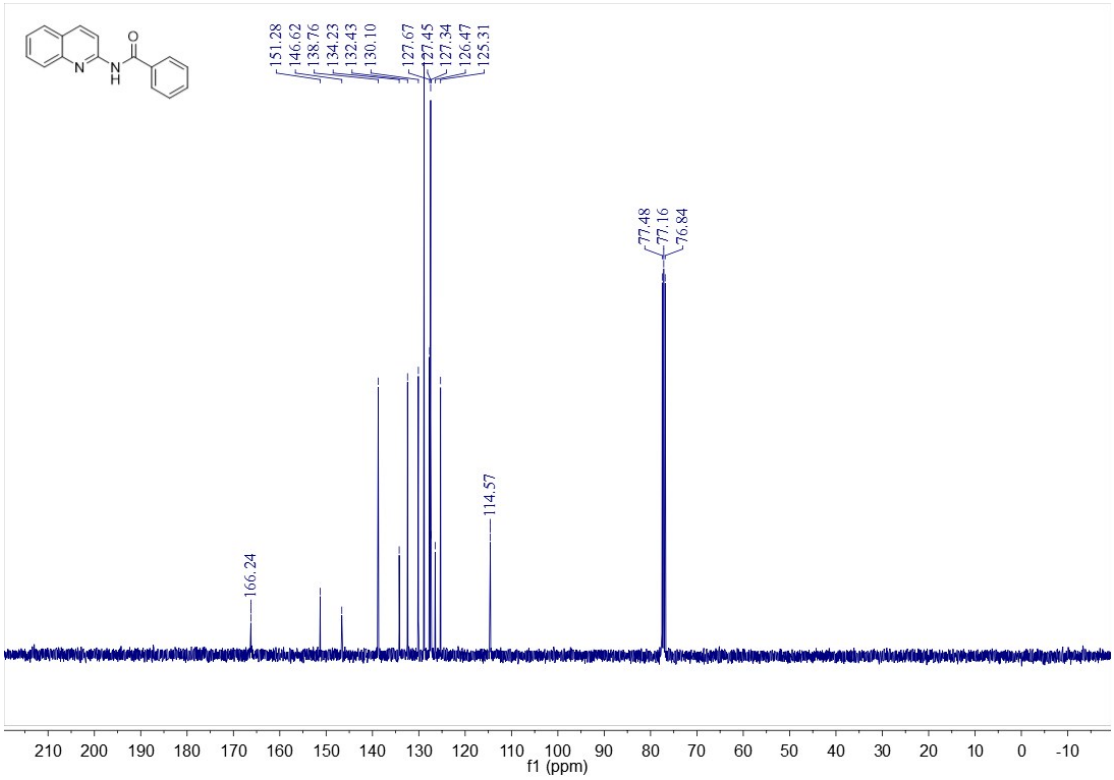
^{13}C-NMR spectrum of 5il



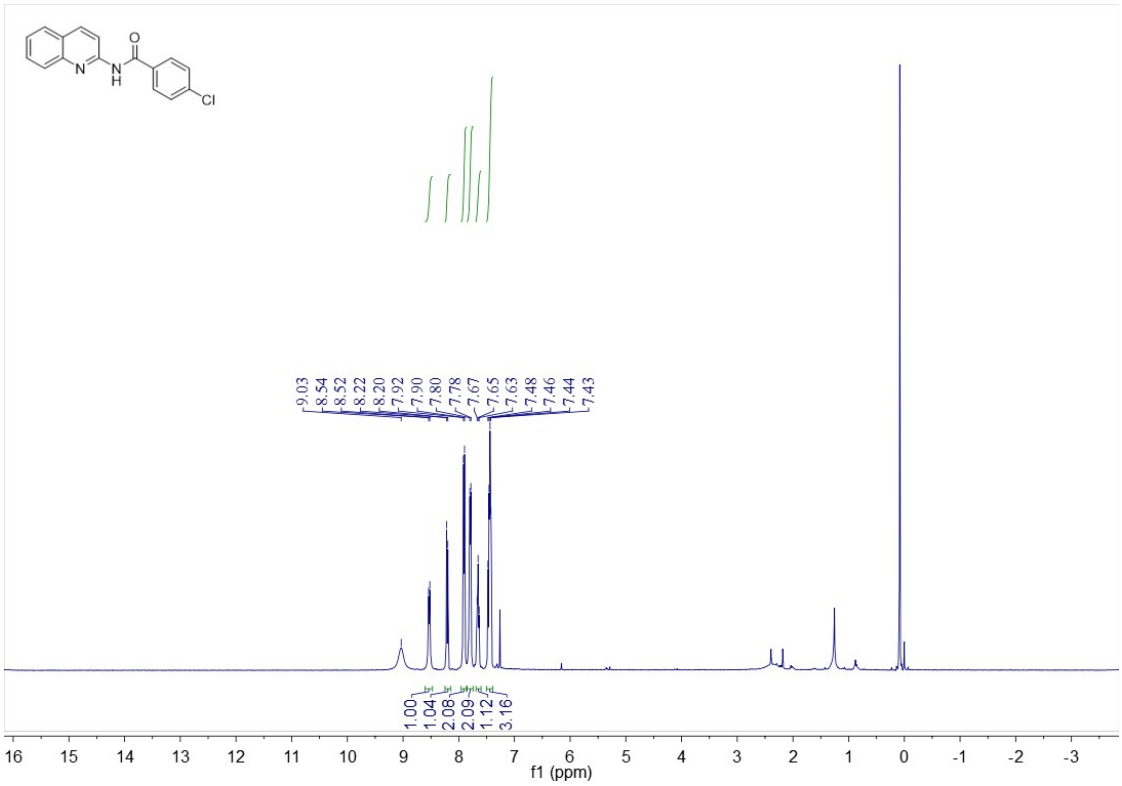
^{1}H-NMR spectrum of 8aa



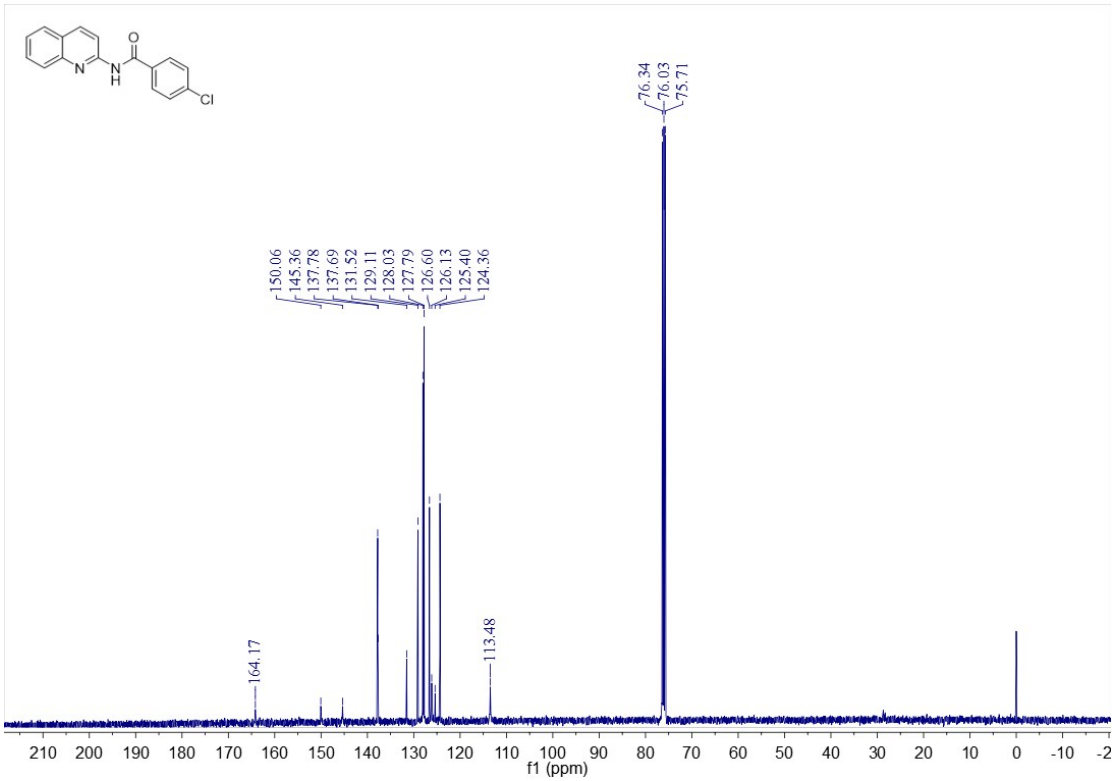
^{13}C-NMR spectrum of 8aa



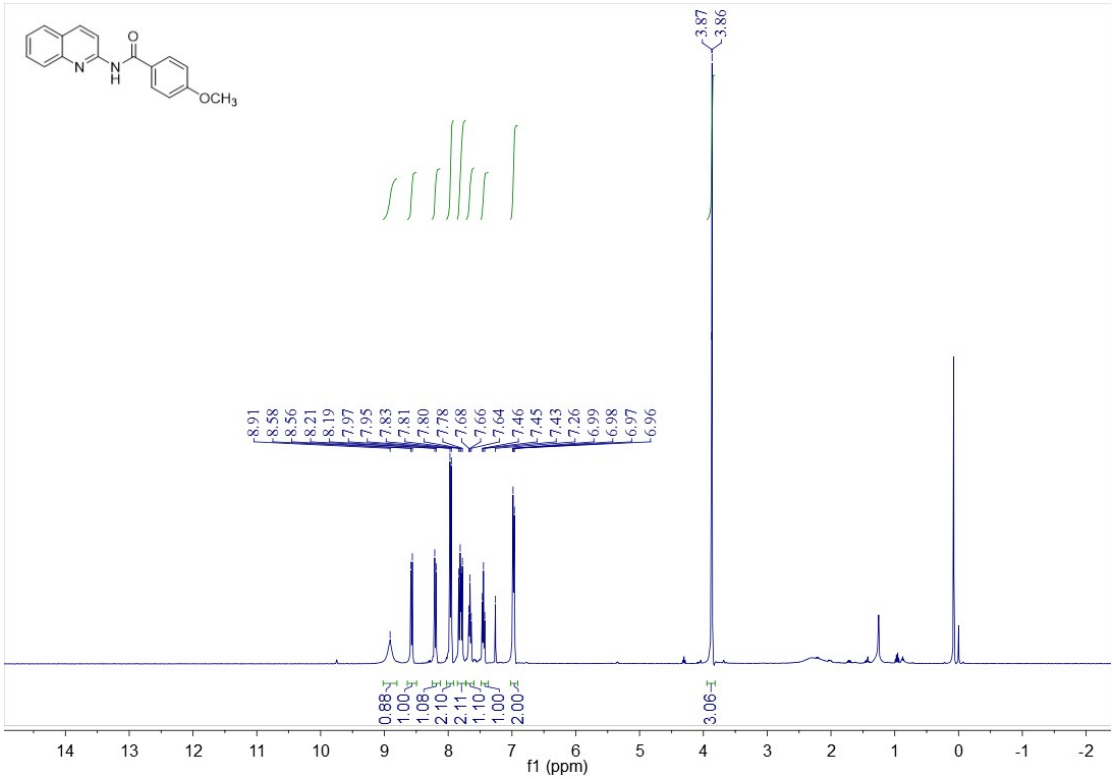
^{1}H-NMR spectrum of 8ab



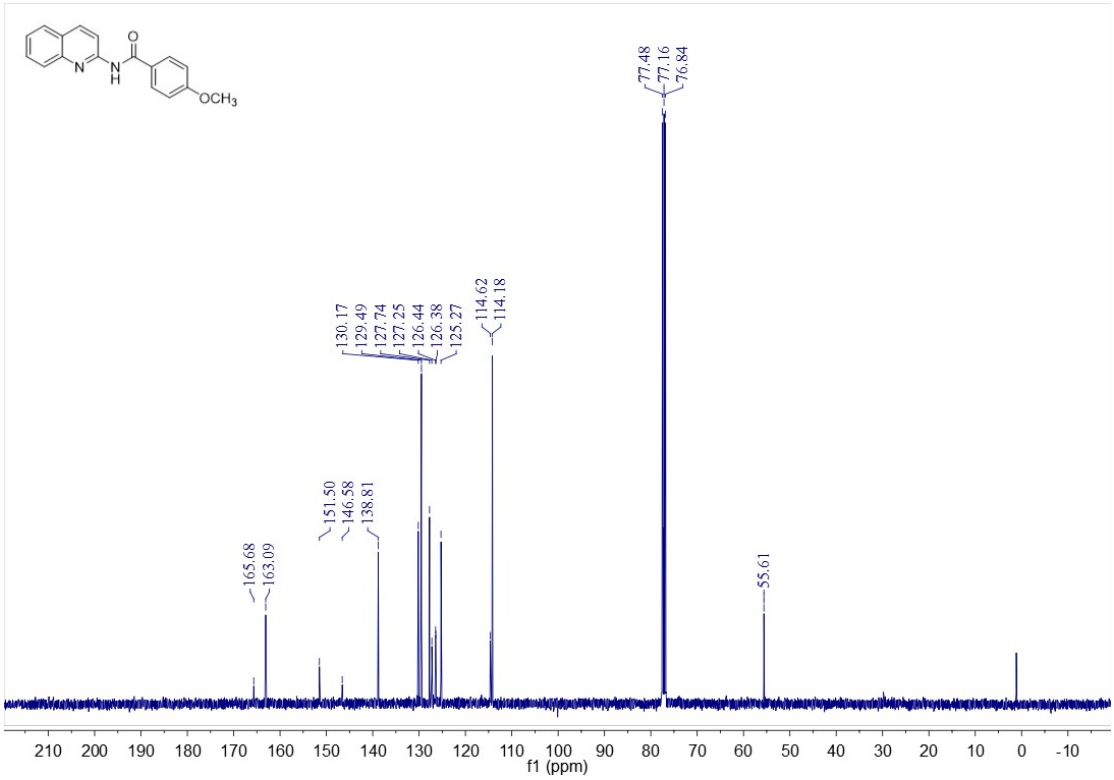
^{13}C-NMR spectrum of 8ab



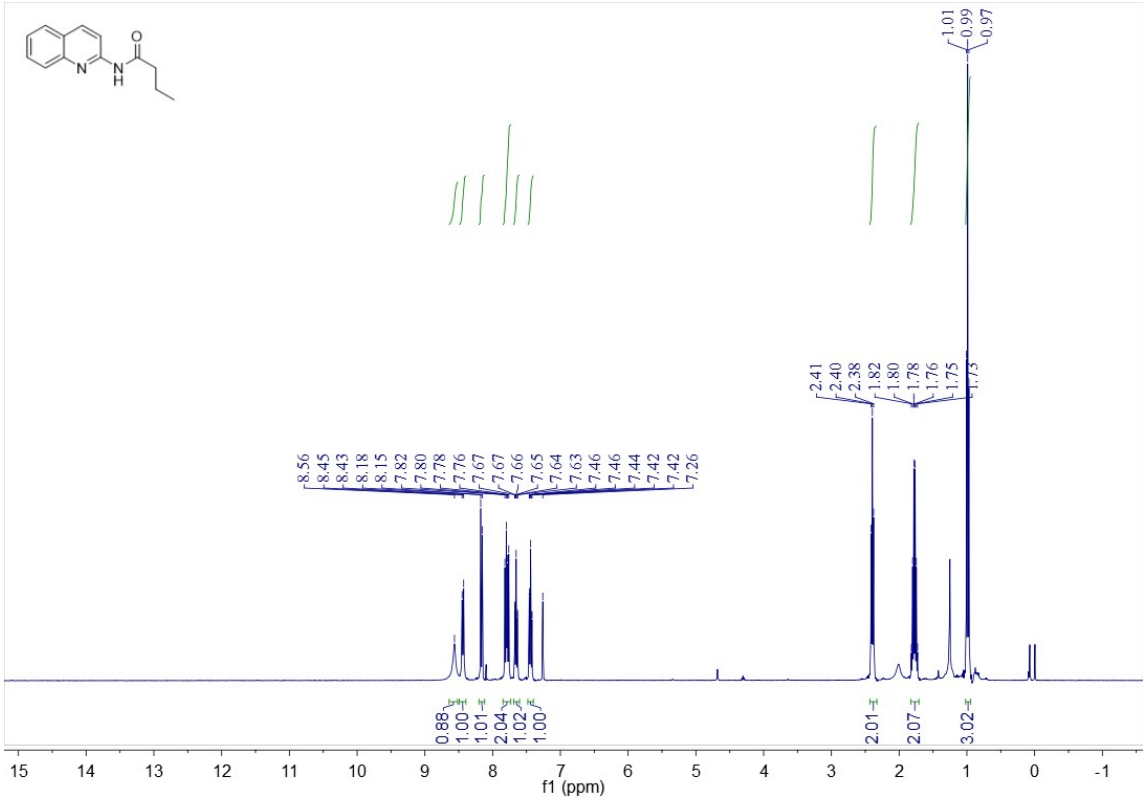
^{1}H-NMR spectrum of 8ac



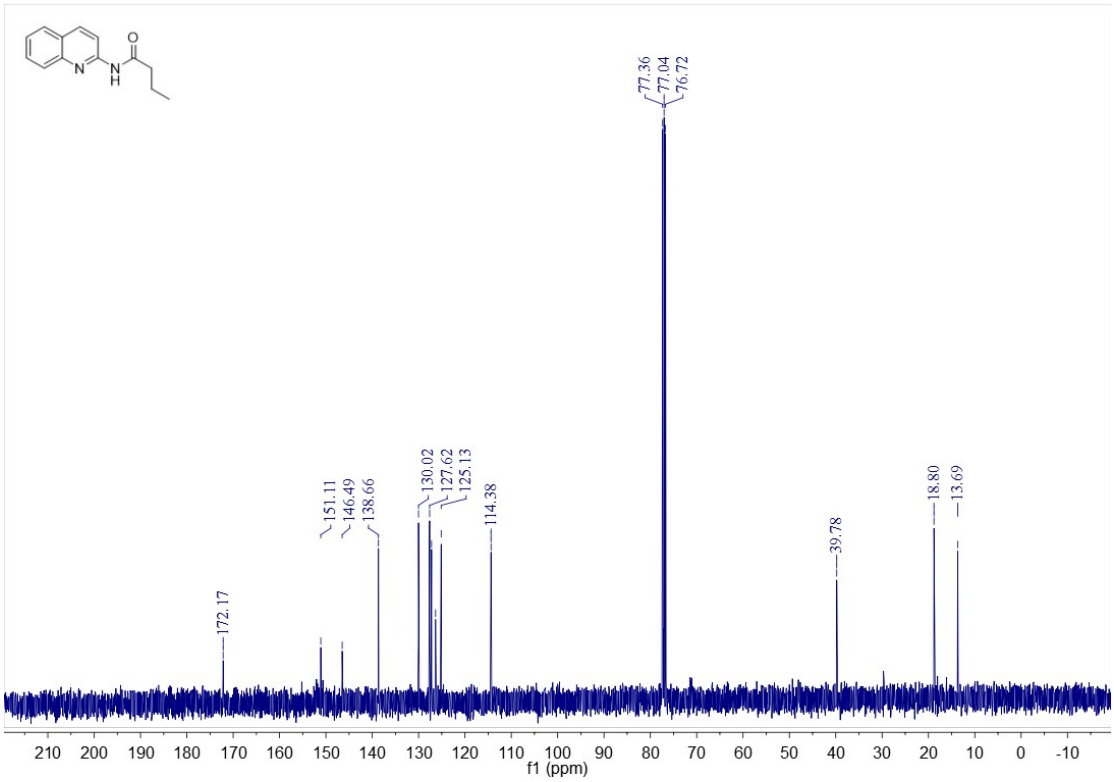
^{13}C-NMR spectrum of 8ac



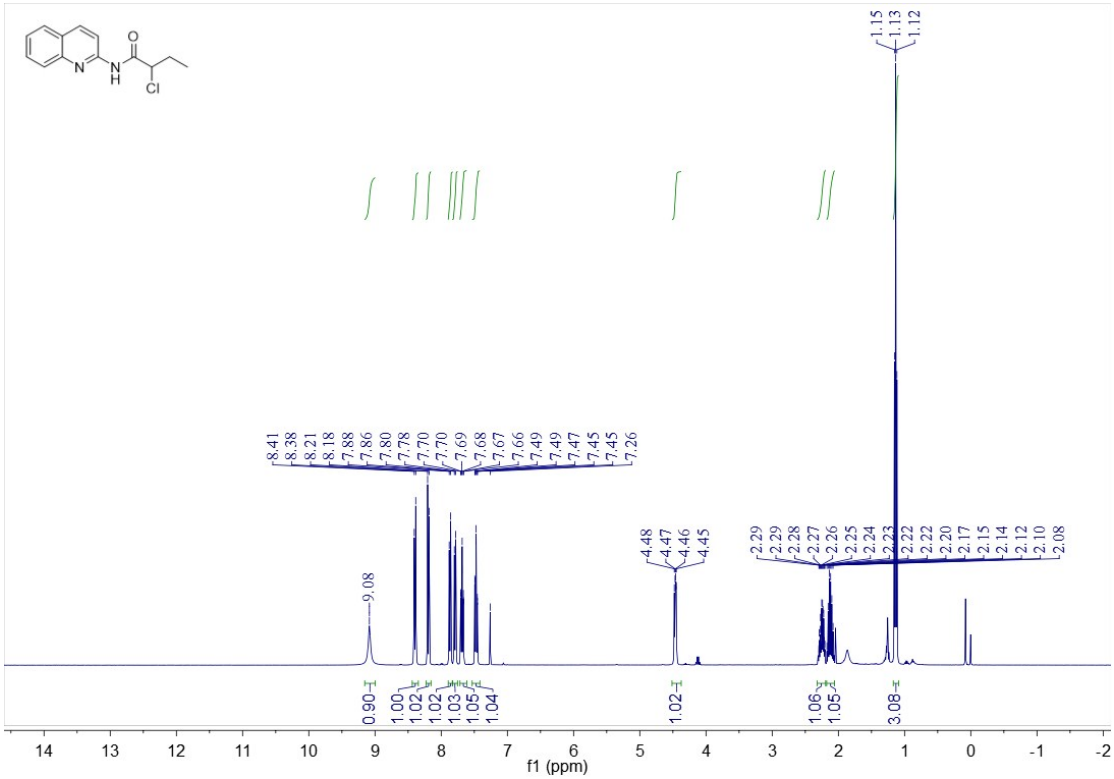
^{1}H-NMR spectrum of 8ad



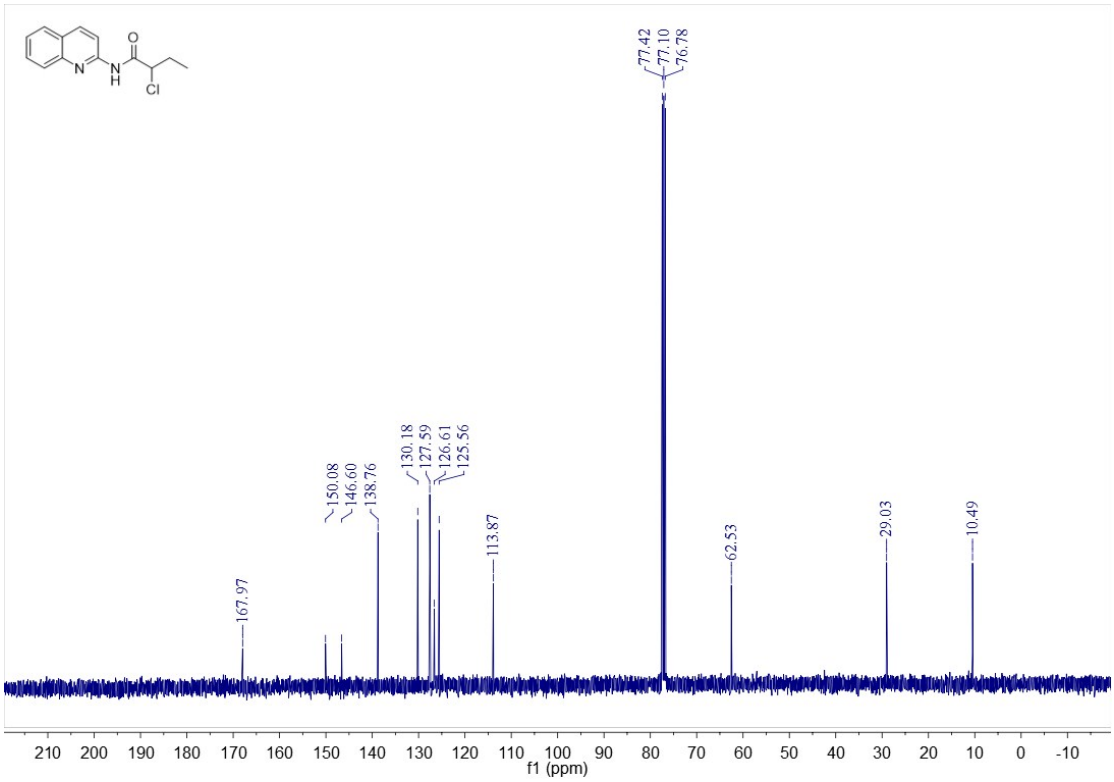
^{13}C-NMR spectrum of 8ad



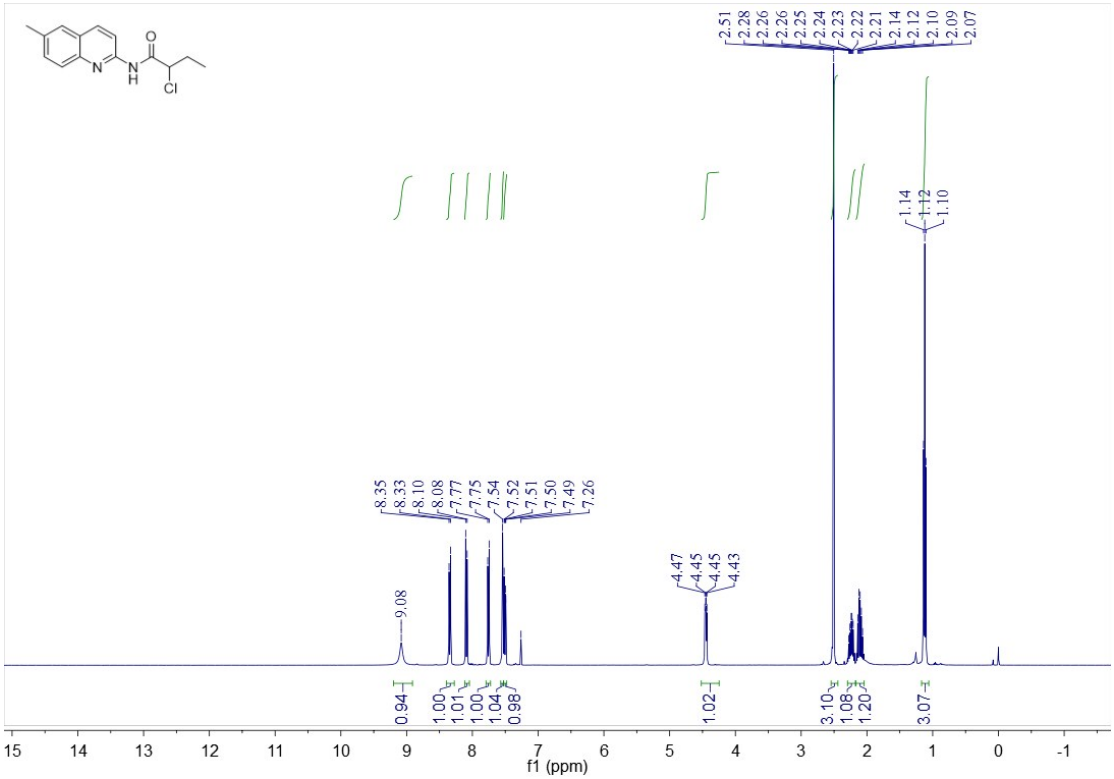
^{1}H-NMR spectrum of 8ae



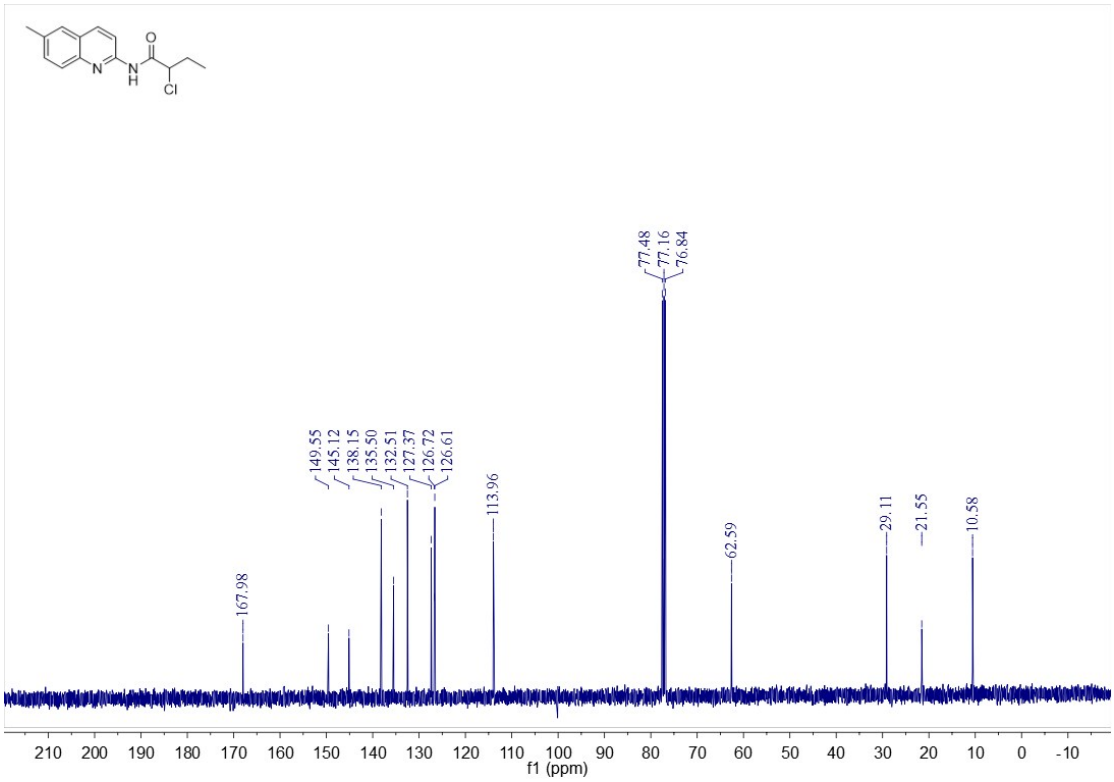
^{13}C-NMR spectrum of 8ae



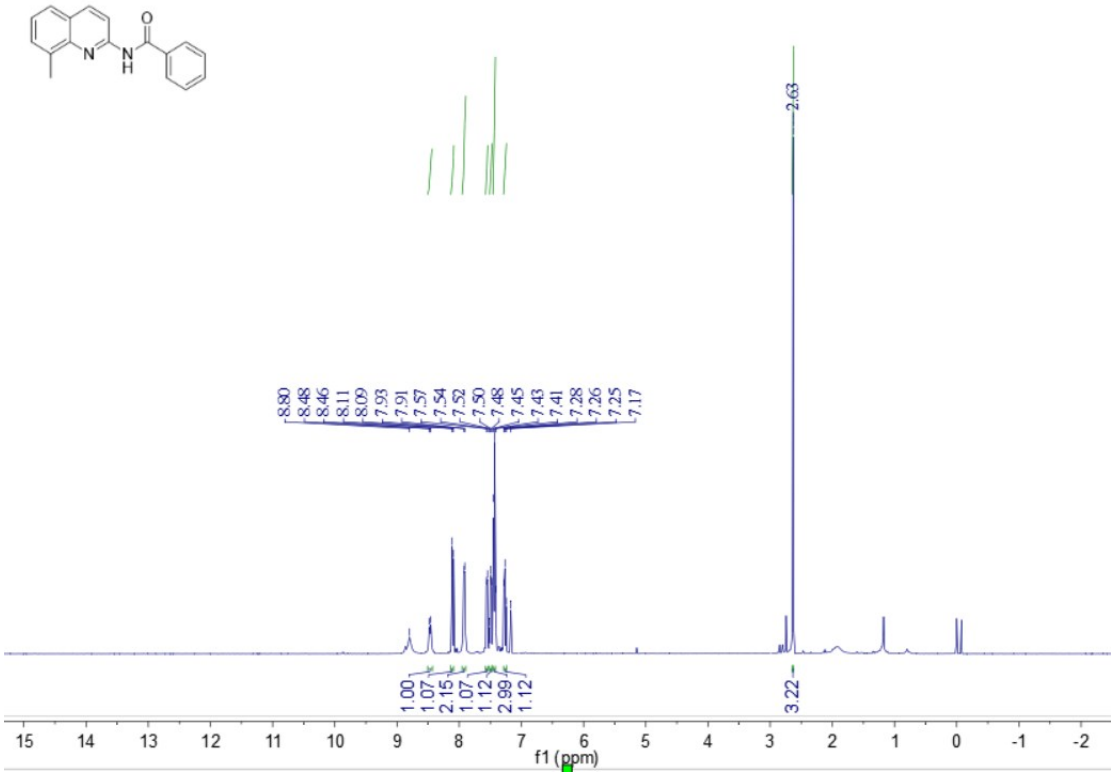
^{1}H-NMR spectrum of 3be



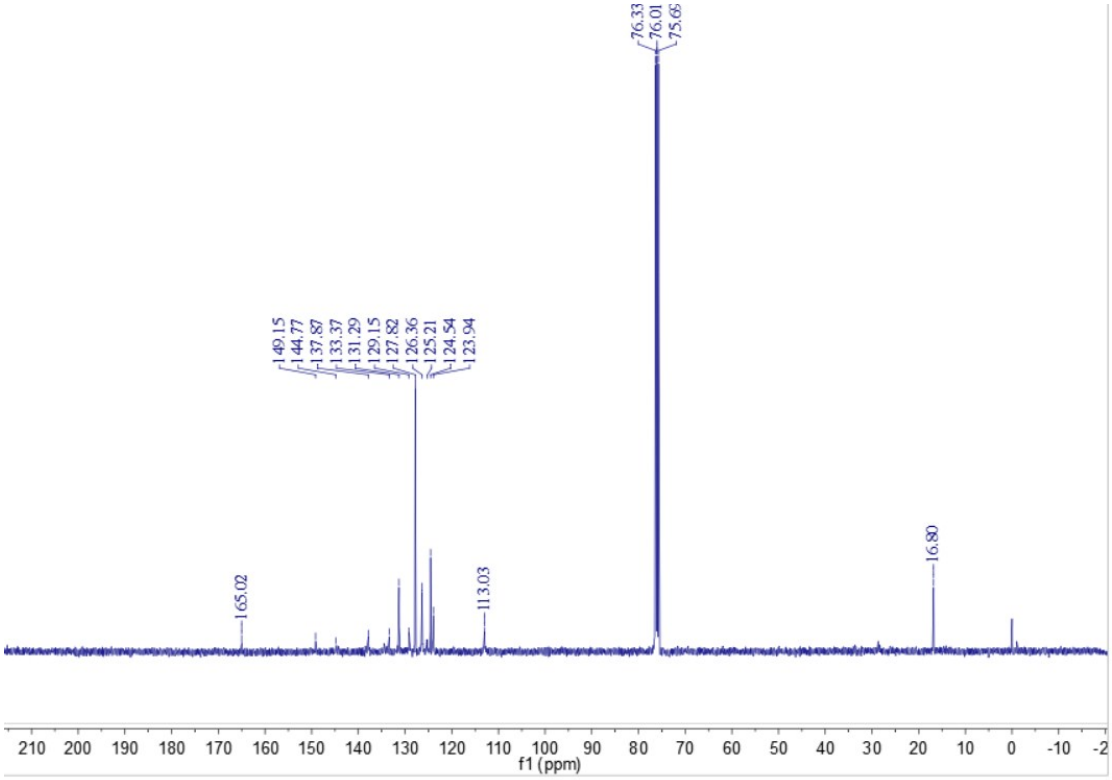
^{13}C-NMR spectrum of 3be



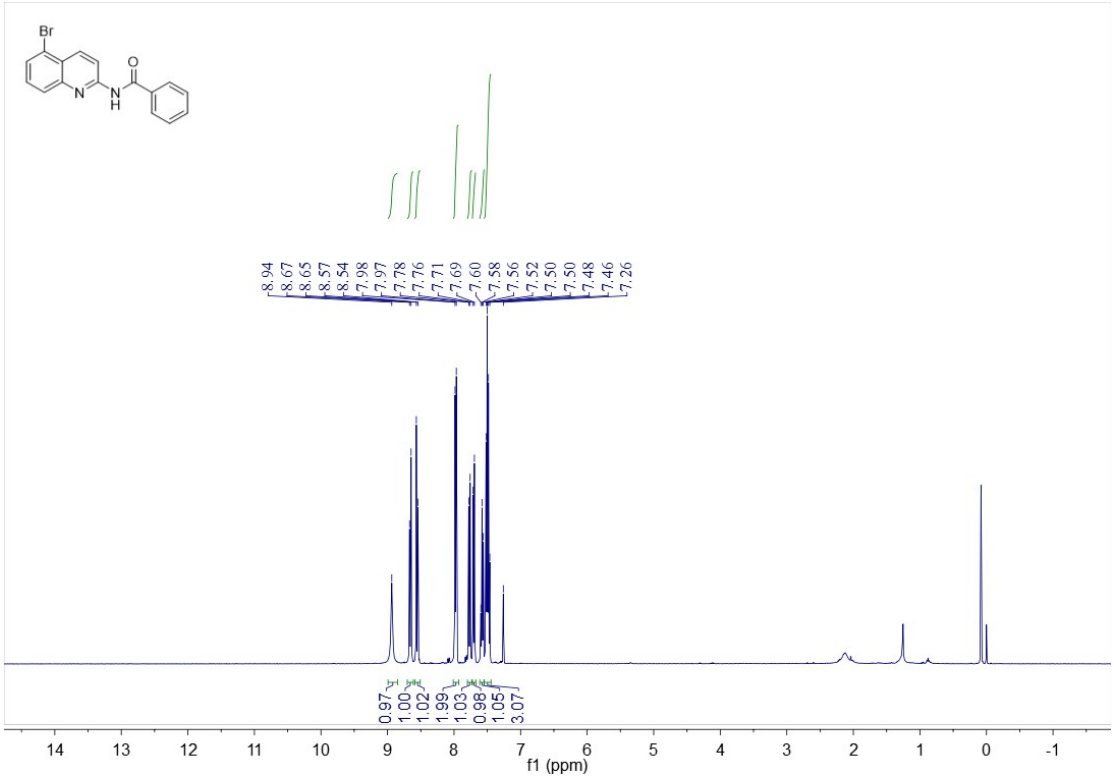
^{1}H-NMR spectrum of 8ja



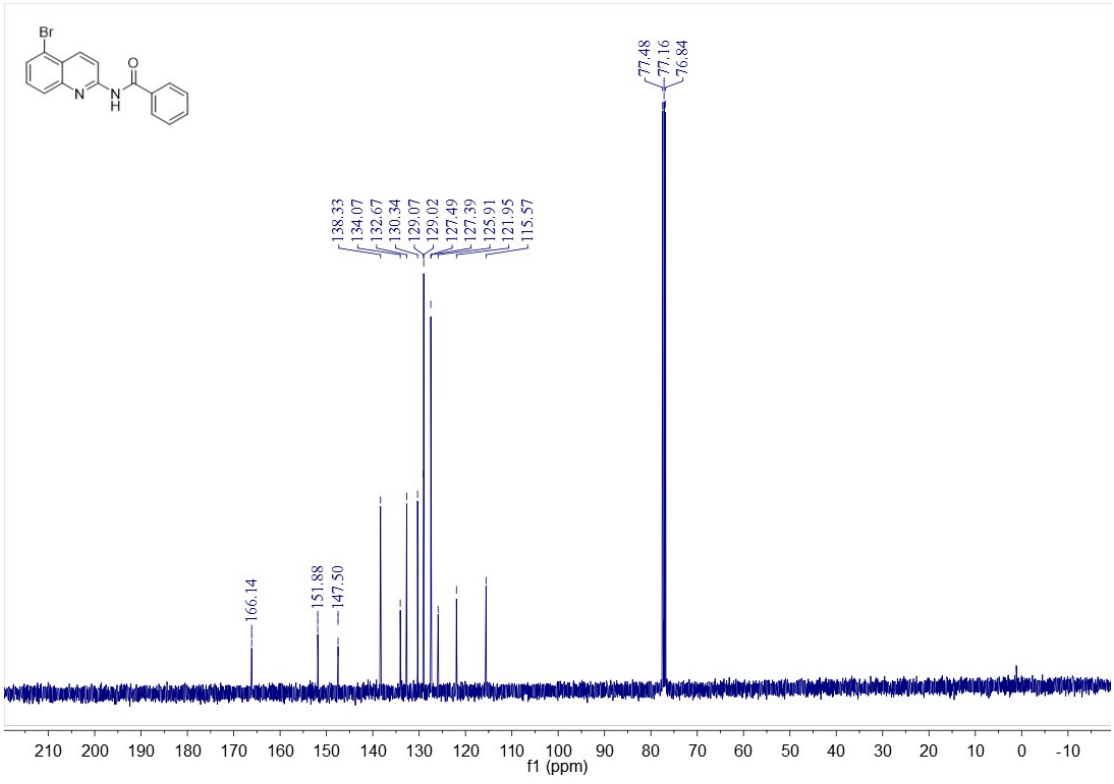
^{13}C-NMR spectrum of 8ja



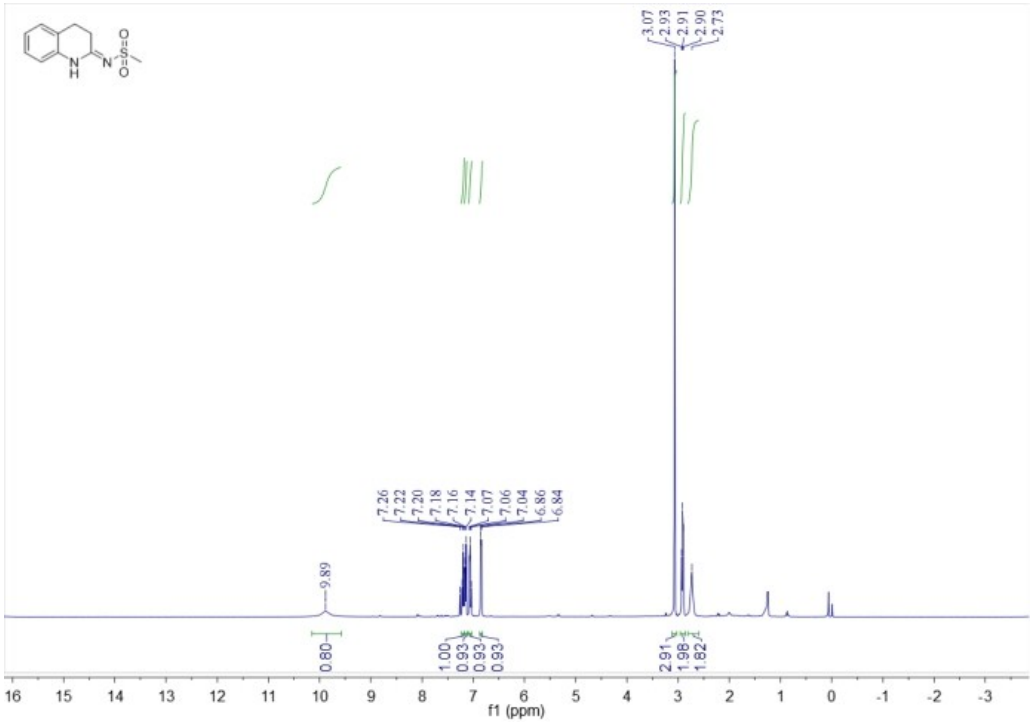
^{1}H-NMR spectrum of 8ka



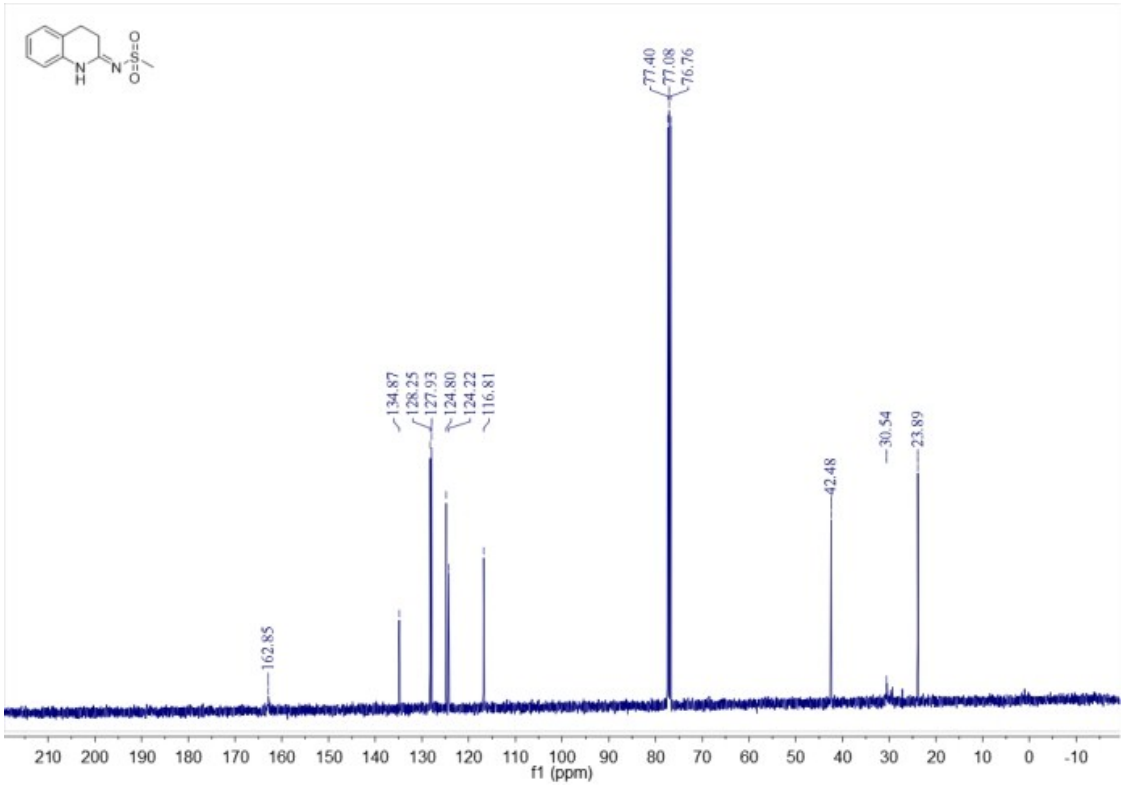
^{13}C-NMR spectrum of 8ka



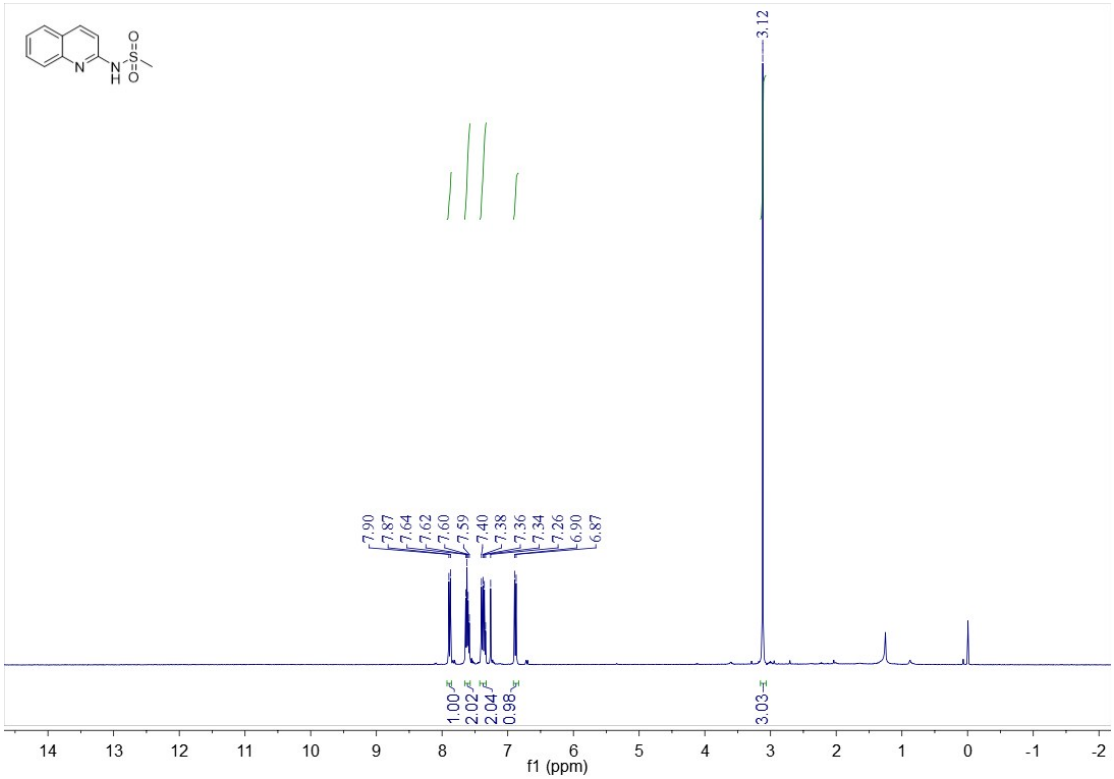
^{1}H-NMR spectrum of 3aa'



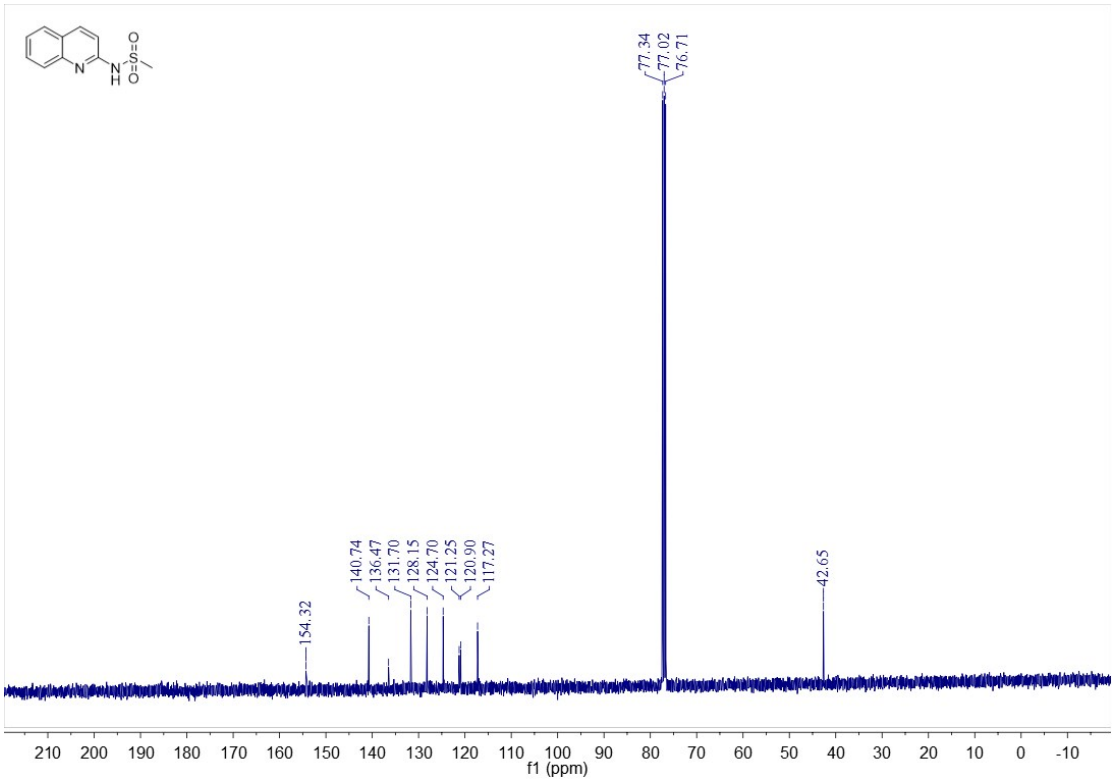
^{13}C-NMR spectrum of 3aa'



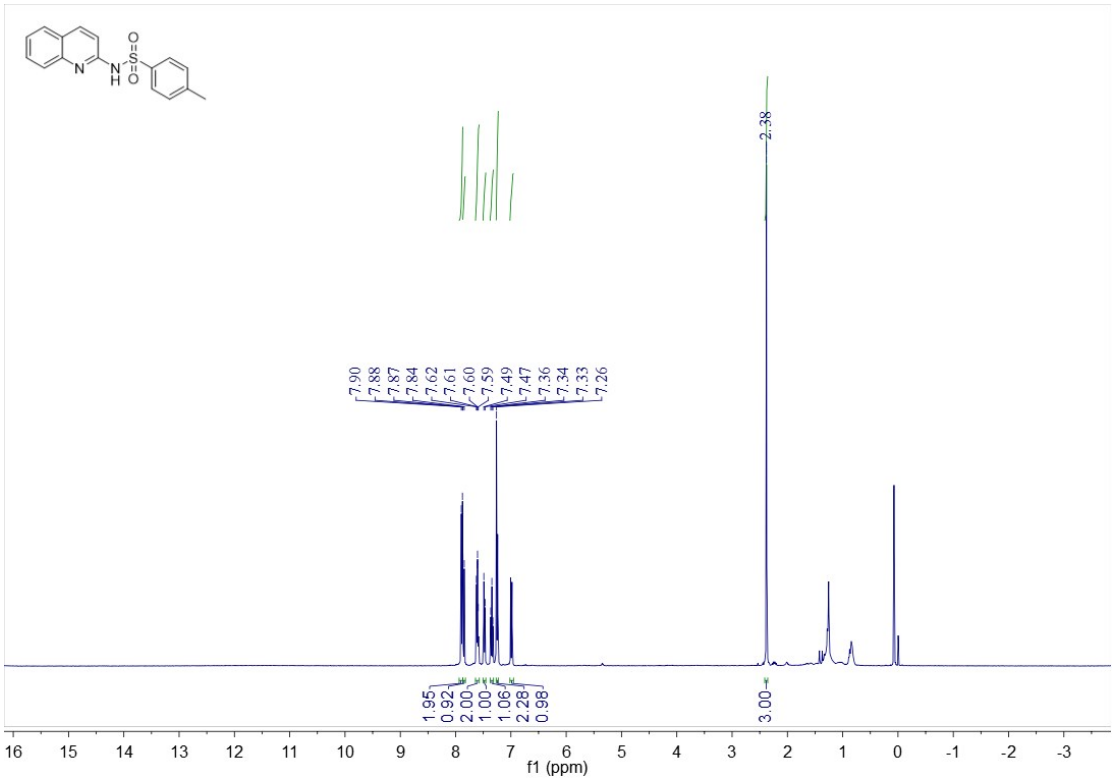
^{1}H-NMR spectrum of 9aa



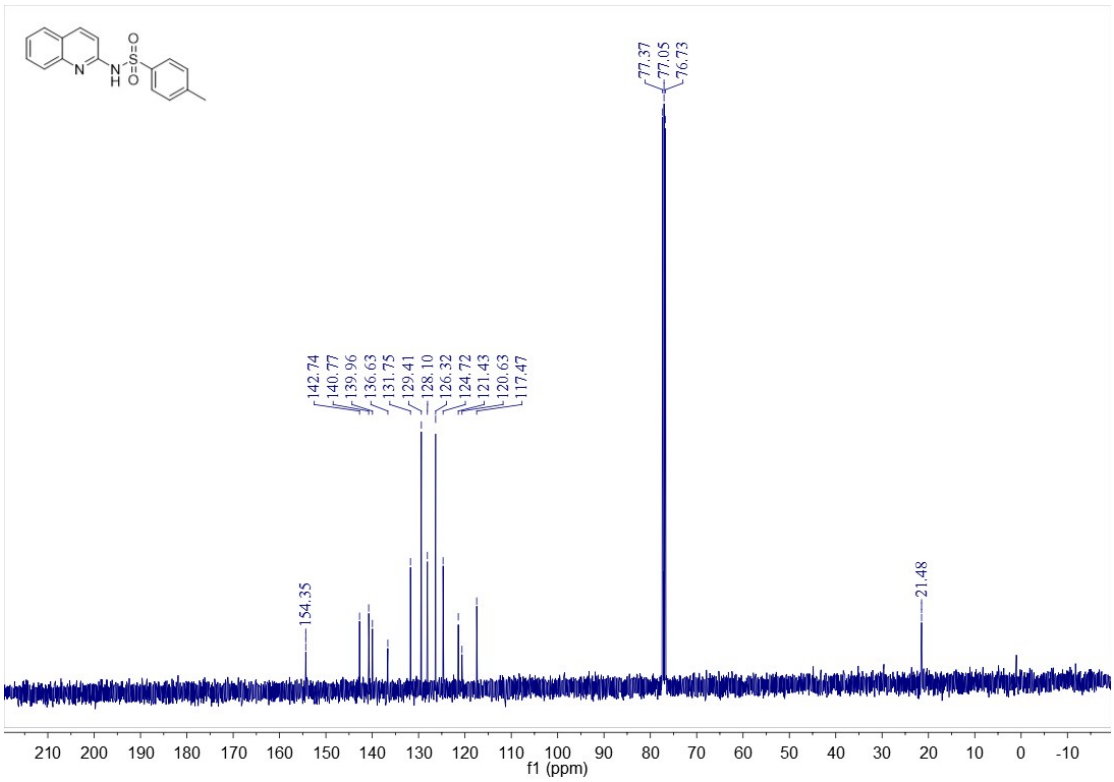
^{13}C-NMR spectrum of 9aa



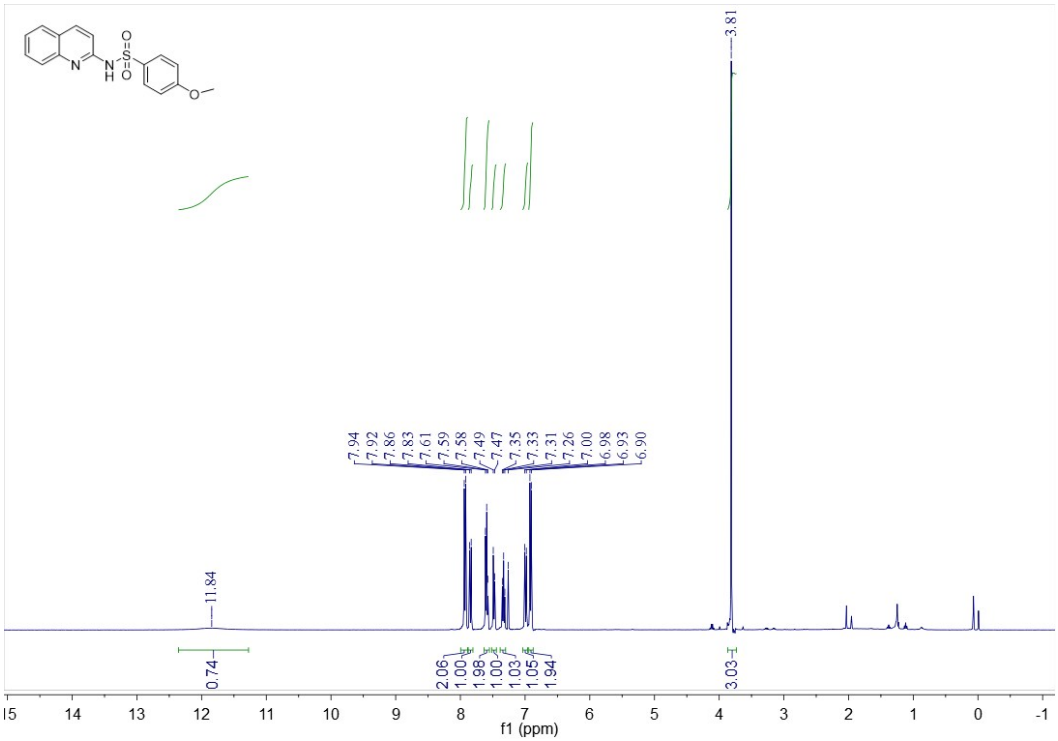
^{1}H-NMR spectrum of 9ab



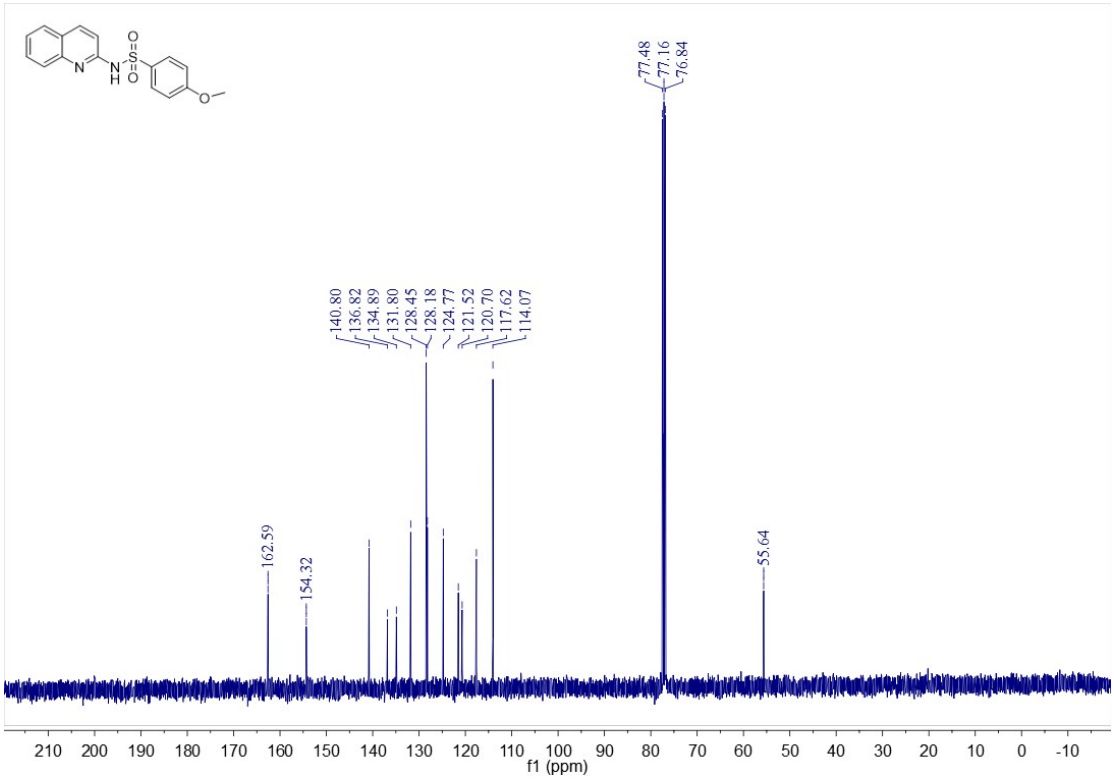
^{13}C-NMR spectrum of 9ab



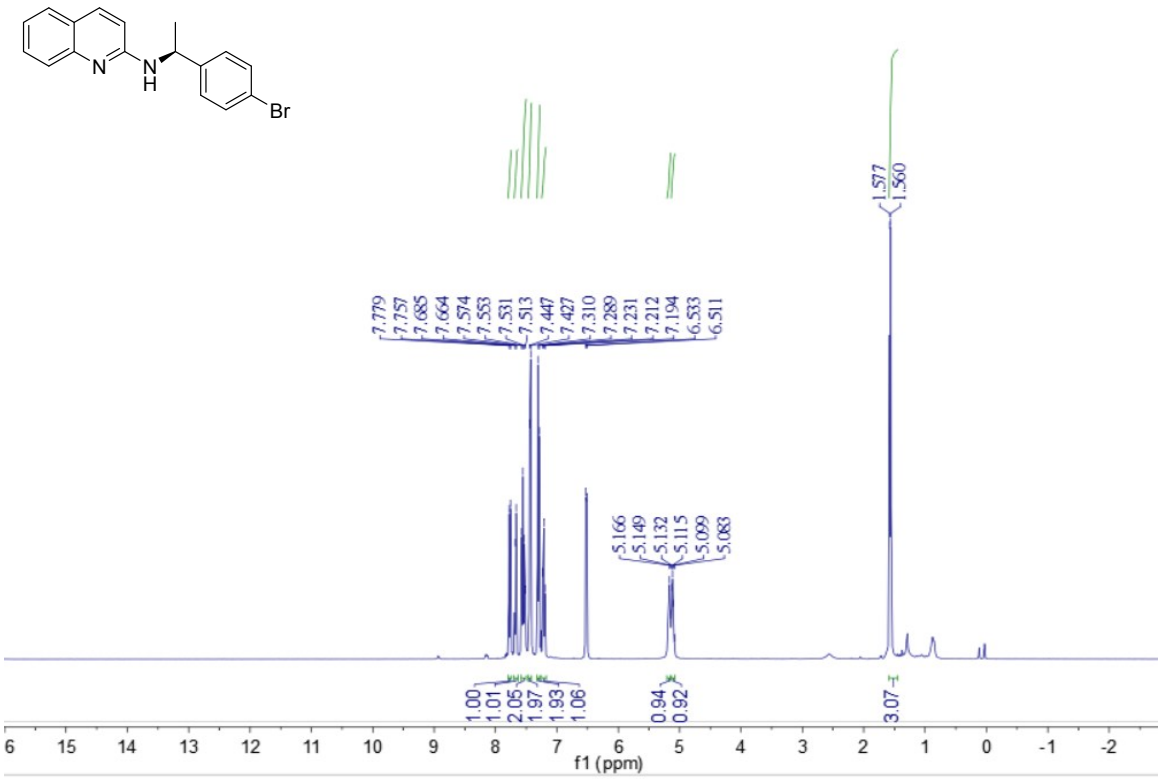
^{1}H-NMR spectrum of 9ac



^{13}C-NMR spectrum of 9ac



^{1}H-NMR spectrum of 5am



^{13}C-NMR spectrum of 5am