Supporting Information

Direct Reductive Quinolyl *β*-C-H Alkylation by Multi-Spherical Cavity Carbon-Supported Cobalt Oxide Nanocatalysts

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Table of Contents

1. General Information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, infrared spectra (IR), and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). 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, ^{13}C-NMR spectra were obtained on Bruker-400; Mass spectra were recorded on Trace DSQ GC/MS，High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. 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; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

XRD was conducted on a TD-3500 powder diffractometer (Tongda, China) operated at 30 kV and 20 mA, using Cu Kα radiation sources in a Bragg angle range of 10−80°. Transmission electron microscopy (TEM) images, and selected area electron diffraction (SAED) were acquired from a JEM-2100HR microscope (JEOL, Japan). The Brunauer-Emmett-Teller (BET) surface area was measured by nitrogen adsorption-desorption on a TriStar II 3020 gas adsorption analyzer.

High-angle annular dark field (HAADF) images and energy dispersive spectrometer (EDS) elemental mapping analysis were performed at 200 kV using scanning transmission electron microscopy (STEM) mode on an aberration-corrected JEM-2100F field emission transmission electron microscope.

X-ray photoelectron spectroscopy (XPS) measurement was performed with an ESCALAB 250Xi imaging photoelectron spectrometer (Thermo Fisher Scientific, USA) using a monochromatic Al Ka X-ray at a power of 150 W.

2. General Procedure for the Preparation of CoO_x/MSCC

The CoO_x/MSCC nanoparticles were prepared by an in-situ hard templates method. Firstly, synthesizing spherical SiO_2 template, then the synthesis of PVP bridged Co-PA (PA: polyaniline) co-coated SiO_2 nanospheres. Finally, pyrolyzing the precursors and reasonably removing the SiO_2 template.

The synthesis of SiO_2 nanospheres

The SiO_2 nanospheres were synthesized according to the reported work.[1] In brief, 82 mg *L*-arginine was dissolved into the mixture of 62 mL deionized water, then added 4 mL cyclohexane. After the solution was heated to 60 °C, 4.9 mL TEOS was dropwise added to the above mixture and kept stirring at 60 °C for 20 h to make the SiO_2 seeds grew into spherical particle. To control the different cavity size of SiO_2 nanospheres, the secondary growth was necessary. Specifically, 216 ml deionized water and 30ml cyclohexane were added to the mother liquor, 21mL TEOS was dropwise added to the above mixture and kept stirring at 60 °C for 30 h, finally SiO_2 nanospheres were obtained.

The synthesis of PVP bridged Co-PA/SiO_2

Furthermore, 1.12g PVP-k30 (polyvinylpyrrolidone) was dissolved into 40 mL SiO_2 nanosphere solution and stirred for 2 hours to coat on SiO_2. Moreover, $Co(OAc)_2 \cdot 4H_2O$ (352.0 mg, 1.4 mmol) was stirred in ethanol (100 mL) for approximately 20 min at room temperature until dissolved. Then the 40ml SiO_2 nanosphere solution was dropwise added to the above mixture, the whole reaction mixture was stirred at 80 °C for 4 h, then kept stirring at room temperature overnight. After that, 2.62 mL concentrated HCl solution (12 M) and 2.05 mL aniline were poured into the above mixture and kept stirring. Subsequently, 21 mL diluted HCl solution (0.75 M) which had dissolved 5.13 g ammonium persulfate, was dropwise added to the above solution, and then kept stirring under ice bath for 24 hours. After vaporing the solvent at 90 °C and grinding the remained bottle-green bulk, the PVP bridged Co-PA/SiO_2 ((PA: polyaniline)) composite powder was obtained.

Pyrolyzing the precursors and removing the SiO_2 template

Subsequently, the Co-PA/SiO_2 composite was pyrolyzed under argon at 800 °C for 2 hour. Finally, the SiO_2 templates were reasonally removing by 2 M NaOH solution for 12 hours at 120 ^{o}C, and after filtering, washing and drying, the CoO_x/MSCC was obtained.

3. Characterization of CoO_x/MSCC

3.1. XRD Measurements and Data of CoO_x/MSCC

The XRD pattern of the CoO_x/MSCC just presents weak (less obvious) peaks ascribed to metal cobalt or its related compounds, indicating that the cobalt species in the catalyst are highly dispersed or amorphous. The presence of metallic cobalt is confirmed by the characteristic peaks at 2θ = 44.21°, 51.52°. Moreover, XRD spectrum of catalyst reused for five runs does not show much difference compared to the fresh catalyst. It means that structure of cobalt catalyst maintains very well after five consecutive runs.

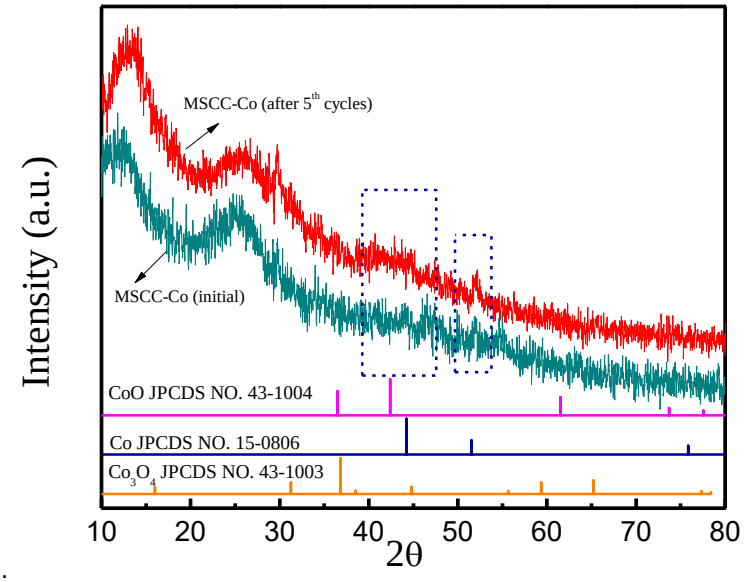


Figure S1. XRD Spectrum of CoO_x/MSCC Catalyst.

3.2 BET and Pore Diameter Measurements of CoO_x/MSCC

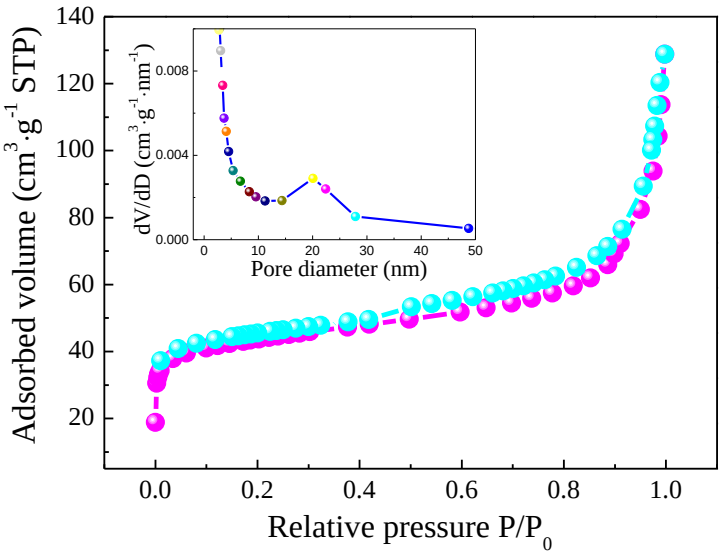


Figure S2. The adsorption-desorption curves and pore diameter distribution of CoO_x/MSCC

3.3 TEM and EDXS Maps of Image of CoO_x/MSCC

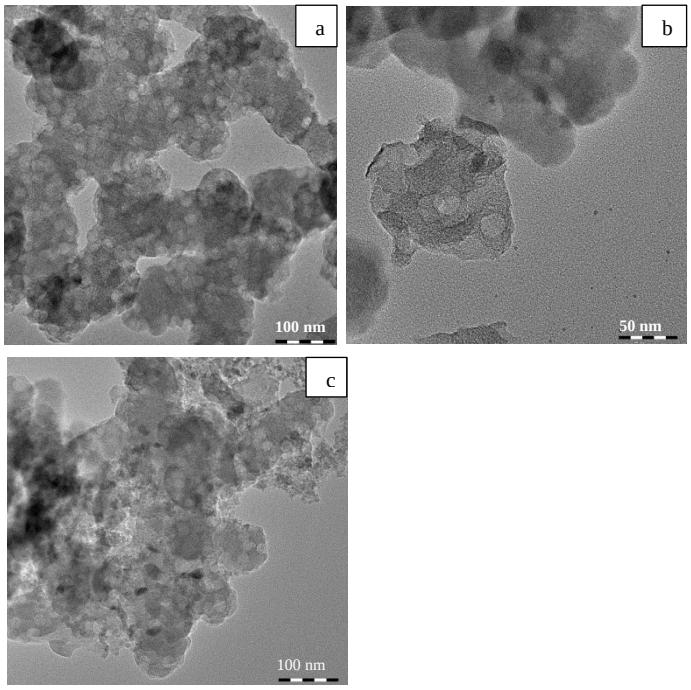


Figure S3. (a-b) TEM images of fresh CoO_x/MSCC, (c) TEM images of reused for five runs.

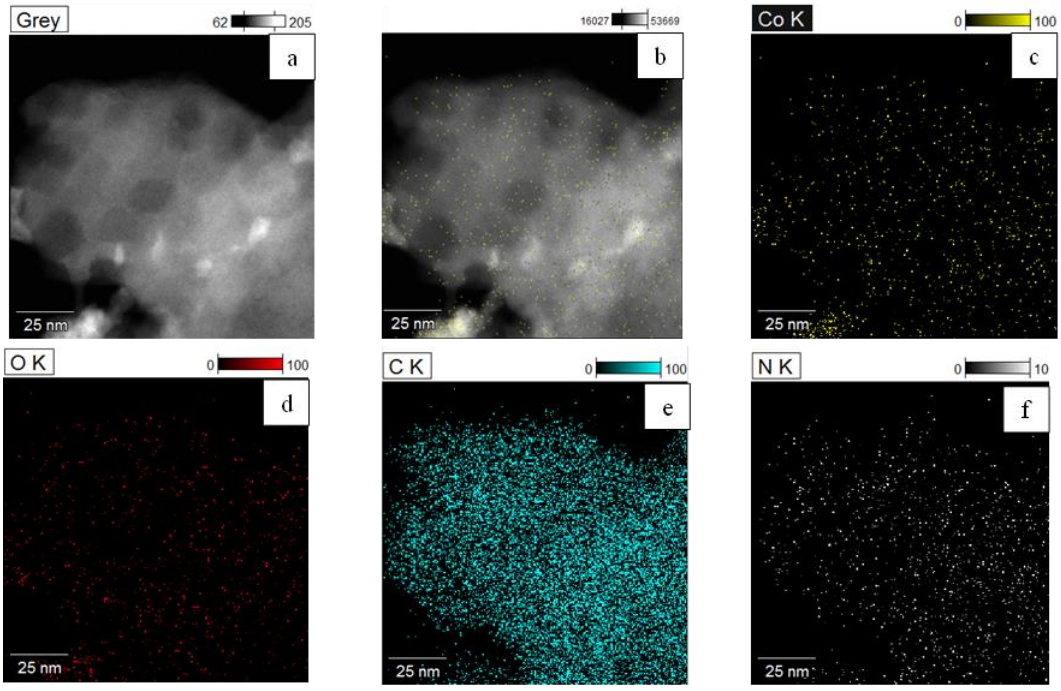


Figure S4. (a) HAADF-STEM image of CoOx/MSCC. EDS elemental maps for combined image (b), Co (c), O (d), C (e), N (f).

3.4. XPS Spectra of CoO_x/MSCC

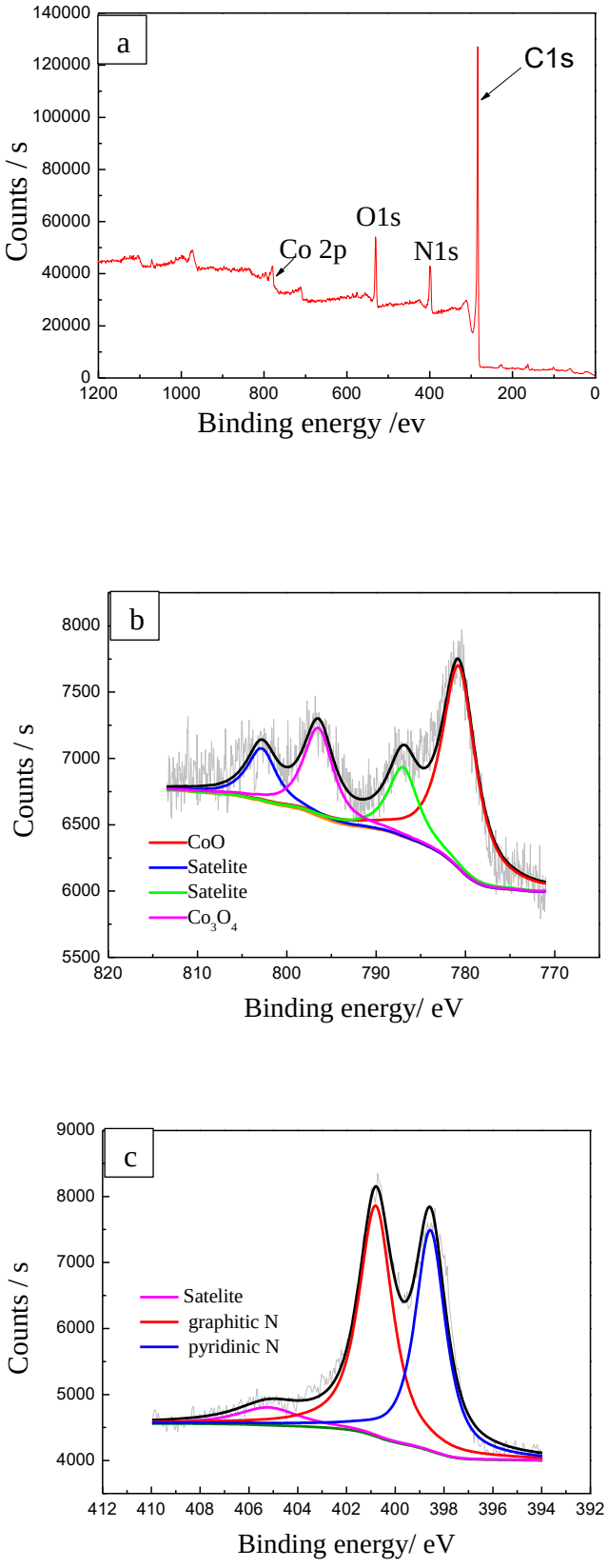
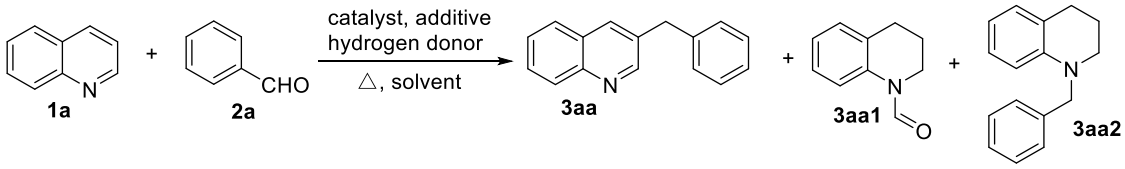


Figure S5. (a) XPS spectra for CoO_x/MSCC, (b) Co 2p and (c) N 1s XPS spectra.

4. Experimental Procedure

4.1 Table S1. Optimization of Reaction Conditions for the Benzylation of Quinoline[a]



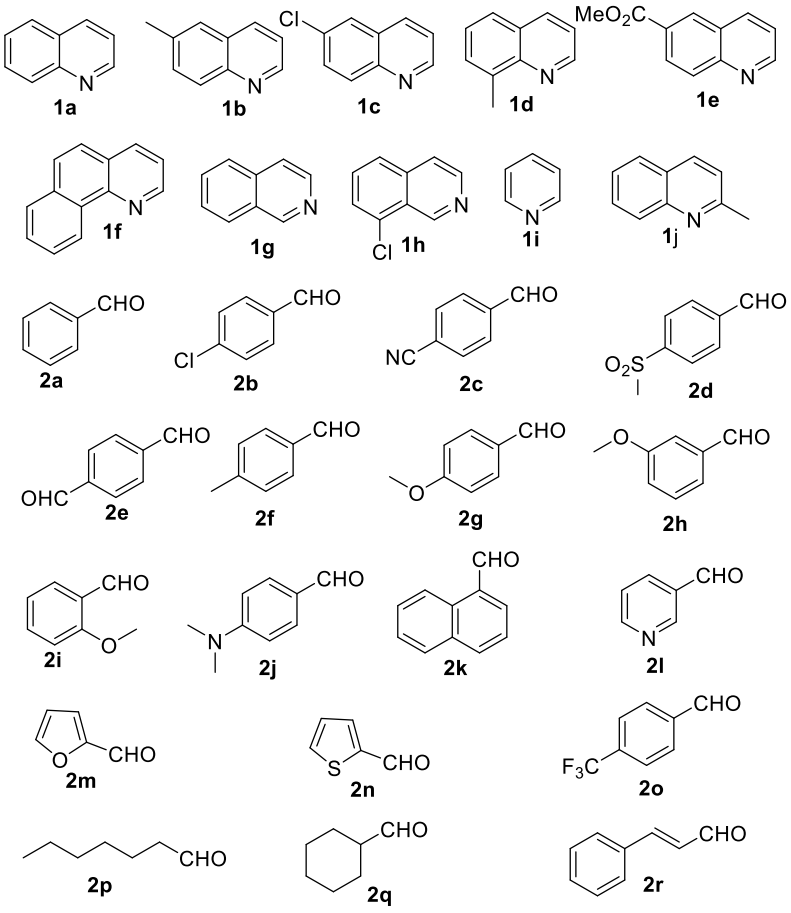
Entry	Catalyst	Additive	**3aa** Yield %[b]	**3aa1** Yield %[b]	**3aa2** Yield %[b]
1	CoO_x/MSCC	-	14	2	0
2	CoO_x/MSCC	benzoic acid	25	2	0
3	-	benzoic acid	0	0	0
4	CoO_x/MSCC	benzoic acid	0[c]	0[c]	0[c]
5	MSCC	benzoic acid	0	0	0
6	CoO_x/MSCC	benzoic acid	0[d]	0[d]	0[d]
7	$Co(OAc)_2$	benzoic acid	0	0	0
8	CoO_x/MSCC	PivOH	33	3	0
9	CoO_x/MSCC	*P*-TSA	27	2	0
10	CoO_x/MSCC	$Yb(OTf)_3$	38	2	0
11	CoO_x/MSCC	CF_3COOH	53	3	0
12	CoO_x/MSCC	CF_3COOH	(42, 0, 21)[e]	(4,0,1)[e]	(0,0,0)[e]
13	CoO_x/MSCC	CF_3COOH	(18,7,16,25)[f]	(0,0,0,0)[f]	(0,0,0,0)[f]
14	CoO_x/MSCC	CF_3COOH	(58,60,60)[g]	(3,4,3)[g]	(0,0,0)[g]
15	CoO_x/MSCC	CF_3COOH	(68,73,72)[h]	(5,6,4)[h]	(0,0,1)[h]
16	CoO_x/MSCC	CF_3COOH	78[i]	4[i]	0[i]
17	CoO_x/MSCC	CF_3COOH	82[j]	5[j]	0[j]
18	CoO_x/MSCC	CF_3COOH	(21, 76, 81)[k]	(0, 3, 7)[k]	(0, 0, 0)[k]
19	CoO_x/MSCC	CF_3COOH	(67, 79)[l]	(2, 4)[l]	(0, 0)[l]
20	CoO_x/MSCC	CF_3COOH	(79, 68)[m]	(4, 2)[m]	(0, 0)[m]
21	CoO_x/MSCC	CF_3COOH	0[n]	85[n]	0[n]

[a] Unless otherwise stated, all reactions were performed at 120 °C for 16 h under N_2 protection by using **1a** (0.75 mmol), **2a** (1.5 eq, 1.13 mmol), catalyst (5 mol %，55 mg), *p*-xylene (1.5 mL), HCO_2H (3.5 eq, 2.63 mmol), additive (0.4 eq, 0.3 mmol), temperature (120 °C), CoO_x/MSCC pyrolyzed at 800 °C. [b] GC yield using hexadecane as an internal standard. [c] Without HCO_2H. [d] Non-pyrolyzed CoO_x/MSCC. [e] Yields with respect to chlorobenzene, DMSO and *t*-amyl alcohol as the solvents, respectively. [f] the hydrogen sources are respect to borane-tetrahydrofuran complex (BF_3-THF), HCOONa, $HCOONH_4$ and hydrogen balloon (1atm). [g] Yields with respect to use of 0.45, 0.6 and 0.75 mmol of CF_3CO_2H, respectively. [h] Yields with respect to use of 3.38, 3.75 and 4.13 mmol of HCO_2H along with additive CF_3COOH (0.6 mmol), respectively. [i] Temperature: 130 °C, additive CF_3COOH (0.6 mmol), HCO_2H (3.75 mmol). [j] Temperature: 130 °C, time: 20 h, additive CF_3COOH (0.6 mmol), HCO_2H (3.75 mmol). [k] Reaction temperature: 130 °C, time: 20 h, additive CF_3COOH (0.6 mmol), HCO_2H (3.75 mmol), the amount of catalyst are with respect to 1 mol % (11 mg), 4 mol % (45 mg), 6 mol % (65 mg). [l] Reaction temperature: 130 °C, time: 20 h, additive CF_3COOH (0.6 mmol), HCO_2H (3.75 mmol), the Co content of catalyst are with respect to 2.8 wt %, 6.2 wt %. [m] CoO_x/MSCC pyrolyzed at 700 °C, 900 °C, respectively, reaction temperature: 130 °C, time: 20 h, additive CF_3COOH (0.6 mmol), HCO_2H (3.75 mmol) . [n] Without **2a**, reaction temperature: 130 °C, time: 20 h, additive CF_3COOH (0.6 mmol), HCO_2H (3.75 mmol).

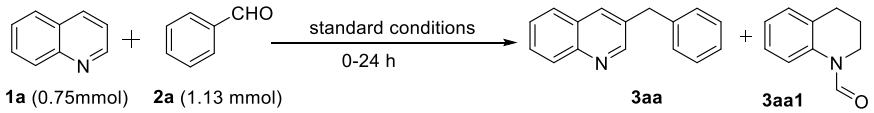
To test the catalytic performance of the prepared CoO_x/MSCC material, we chose the coupling of quinoline **1a** and benzaldehyde **2a** as a model reaction to evaluate different reaction parameters. Initially, the reaction in *p*-xylene was performed at 120 ^oC for 16 h in the presence of 5 mol% of catalyst and 3.5 equivalents of formic acid as the hydrogen donor. To our delight, the desired 3-alkyl quinoline **3aa** was detected in 14 % yield along with 2% of N-formylated tetrahydronquinoline (Table S1, entry 1). And the addition of benzoic acid significantly improved the product yield to 25% (entry 2). However, the absence of catalyst or HCO_2H (entries 3-4) failed to

give any product, indicating that both of which are crucial in affording the products. The use of MSCC material or non-pyrolyzed CoO_x/MSCC or catalyst precursor $Co(OAc)_2$ showed no activity (entries 5-7). Then, a series of acidic additives (entries 8-11), solvents (entry 12) and hydrogen donors (entry 13) were screened, the results indicated that CF_3CO_2H (TFA), *p*-xylene and formic acid constitute the best combination. Further, both increases of additive (entry 14) and hydrogen donor (entry 15) loadings resulted in incremental product yields, and 0.8 equiv of CF_3CO_2H (0.6 mmol) along with 5 equiv of HCO_2H (3.75 mmol) showed to be the best choice. The temperature and time screenings (entries 16-17) indicated that 130 ^oC and 20 h are the preferred parameters to give a highest product yield (82%) with high chemo-selectivity, while both change of catalyst loadings or contents (entries 18-19) were not fruitful since no increase of product yields was obtained. Noteworthy, the catalysts pyrolyzed at 700 °C and 900 °C afforded lower yields as compared with the one pyrolyzed at 800 °C (entry 20), and the absence of aldehyde **2a** only gave the N-formylated product **3aa1** (entry 21). Hence, the optimal conditions are as described in entry 17.

Scheme S1. Substrates Employed for Synthesizing 3-Aryl Quinoline Derivatives



4.2. The Time-Concentration Profile of Benzylation of Quinoline



1a (0.75mmol) **2a** (1.13 mmol) **3aa** **3aa1**

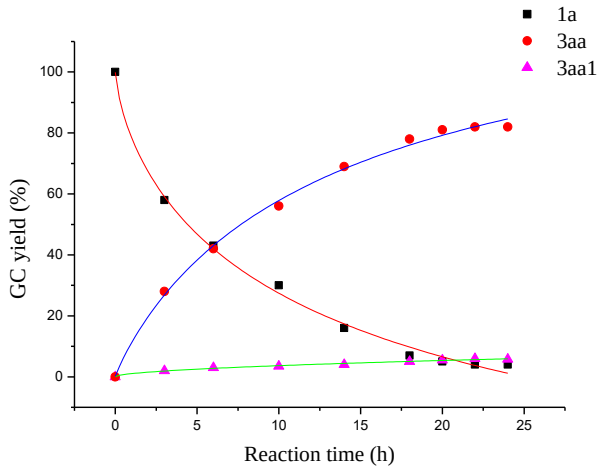
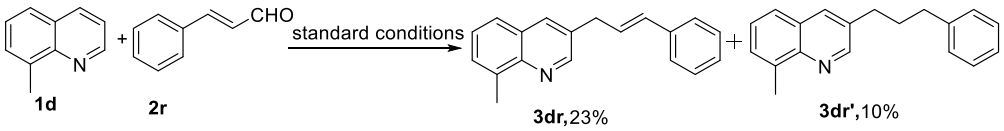


Figure S6. Representative time course of the model reaction

4.3. The Typical Experimental Procedure for the Benzylation of Quinoline

Under nitrogen atmosphere, CoO_x/MSCC (55 mg, 5 mol%), CF_3COOH (68 mg, 0.6 mmol), HCOOH (172 mg, 3.75 mmol), quinoline (**1a**; 97 mg, 0.75 mmol), benzaldehyde (**2a**; 119 mg, 1.13 mmol) and *p*-xylene (1.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 130 °C for 20 h. After cooling to room temperature, the resulting mixture was washed with 10% Na_2CO_3 solution, and then extracted with ethyl acetate, the combined organic layers were dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90°C): ethyl acetate (15 : 1) to give 3-benzylquinoline (**3aa**) as a yellow liquid (108 mg, 70%).

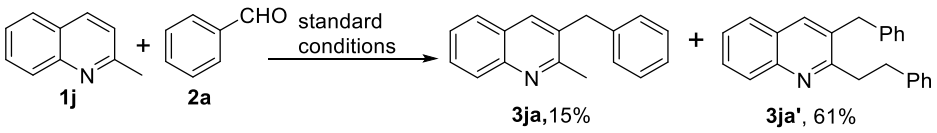
4.4. The Quinolyl β-C-H Alkylation with α,β-Unsaturated Aldehyde



1d **2r** **3dr,**23% **3dr',**10%

The coupling of 8-methylquinoline **1d** with cinnamyl aldehyde **2r** was conducted to evaluate if the α,β-unsaturated aldehyde is also applicable for the catalyst system. Upon GC-MS analysis, we observed product **3dr** and the corresponding reduced product (**3dr'**) in 23%, 10% yields, respectively. Similarly, when replacing **2r** with citral and citronellal as the substrates, only trace of the target products and the corresponding reduced products were observed.

4.5. The Alkylation of 2-Methylquinoline with Aldehyde



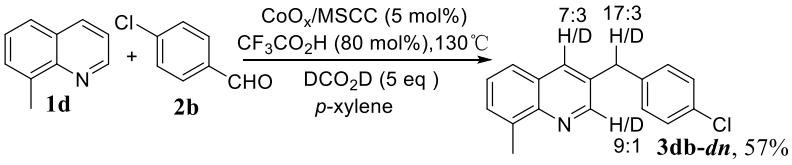
The coupling reaction of 2-methylquinoline **1j** with benzaldehyde **2a** was performed under standard conditions. The mono-alkylated product **3ja** and 2,3-dialkylated product **3ja'** were acquired in 15%, 61% yields, respectively, indicating that the mono-hydrogen transfer is able to generate two enamine intermediates with two reactive beta-sites.

4.6. The Procedure for Synthesis Mixture of Enamine (B1a) and Imine (C1a)

The mixture of 1,2,3,4-tetrahydroquinolines (0.75 mmol), pyridine (1.5 mmol), 20 mol%TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl) and 20 mol% CuCl in *p*-xylene (1.5 ml) was stirred at 40 °C for 2 hours under 1 atm of O_2 atmosphere (using O_2 balloon). After cooling down to room temperature, the reaction mixture was filtrated to afford the clear liquid, which contained the mixture of enamine (**B1a**) and imine (**C1a**). Upon GC–MS analysis, the ratio of **B1a** to **C1a** is 6:1.

4.7 Deuterium-Labelling Experiment

By replacing HCO_2H with DCO_2D in the standard conditions, the reaction of 8-methylquinoline (**1d**) with 4-chlorobenzaldehyde (**2b**) gave product **3db-*dn*** in 57% yield with different deuterium ratios at position -2, -4 and the benzylic site, showing that that the hydrogen from formic acid is transferred to the pyridyl nucleus of quinoline, which is in good agreement with the reaction pathway proposed in **Scheme 2** of the text.



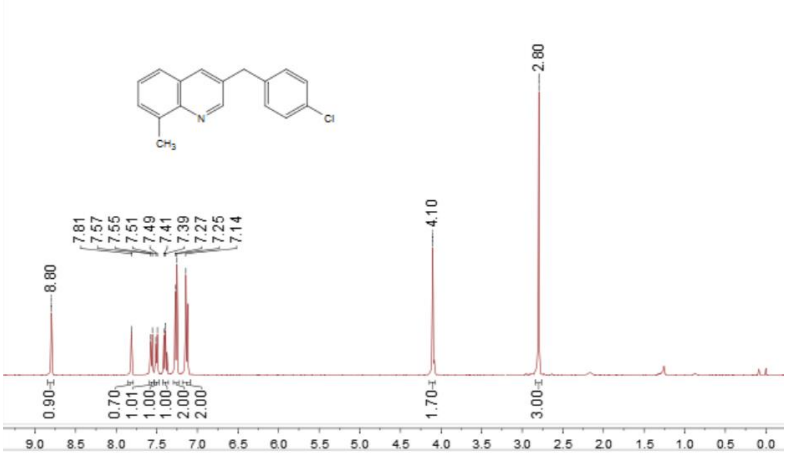


Figure S7. ^{1}H-NMR spectrum of 3db-dn

4.8. Procedure for Catalyst Recycling

Under N_2 atmosphere，CoO_x/MSCC (55 mg), CF_3COOH (0.6 mmol), HCOOH (3.75 mmol), quinoline (0.75 mmol), benzaldehyde (1.13 mmol) and *p*-xylene (1.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 130 °C for 20 h. After cooling down to room temperature, 50 mg *n*-hexadecane was added to the solution and the yield was determined by GC-MS analysis. The catalyst was isolated by centrifugation, washed with ethyl acetate for three times, then dried under vacuum at 60 °C for 4 h. After that, the catalyst was reused for the next circular reaction.

4.9. ICP-AES Analysis

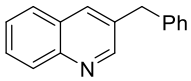
Table S2. Leaching Experiments

Run	Cobalt concentration (ICP-AES)
0	3.57 ppm
1	1.54 ppm
2	0.78 ppm
3	0.64 ppm
4	0.51 ppm
5	0.44 ppm

The ICP-AES analyses for each recycles are summarized in **Table S2** and slight leaching was detected for the reaction media, which is accounted for exfliation resulted from the mechanical abrasion of the catalytic material during the reaction.

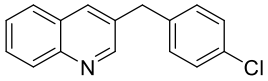
5. Analytical Data of the Obtained Compounds

3-benzylquinoline (**3aa**)



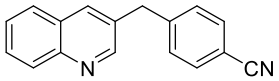
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.87 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.68-7.62 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 6.9 Hz, 3H), 4.15 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.11, 146.92, 139.70, 134.87, 133.87, 129.20, 128.98, 128.87, 128.77, 128.16, 127.47, 126.70, 126.59, 39.27; IR (KBr): 3061, 3027, 1623, 1570, 1378, 786, 715; MS (EI, m/z): 219.10 $[M]^+$.

3-(4-chlorobenzyl)quinoline (**3ab**)



Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (t, *J* = 6.9 Hz, 1H), 8.10 (t, *J* = 11.2 Hz, 1H), 7.84 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 4.12 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.87, 146.96, 138.14, 134.90, 133.30, 132.48, 130.31, 129.20, 129.06, 128.90, 128.08, 127.46, 126.85, 38.56; IR (KBr): 3061, 2925, 1673, 1570, 1089, 1016, 787; MS (EI, m/z): 253.16 $[M]^+$.

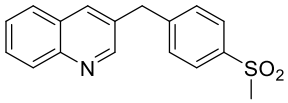
4-(quinolin-3-ylmethyl)benzonitrile (**3ac**)



Yellow solid, m.p.: 132-133°C；^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 1.7 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H),

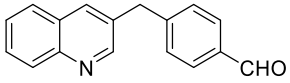
7.88 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.21 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.63, 147.06, 145.26, 135.18, 132.55, 132.16, 129.71, 129.31, 129.22, 127.99, 127.50, 127.04, 118.78, 110.59, 39.22; IR (KBr): 3062, 2927, 1672, 1605, 1497, 1416, 912, 789; HRMS (ESI): Calcd. for $C_{17}H_{13}N_2$ $[M+1]^+$: 245.1073; found: 245.1077.

3-(4-(methylsulfonyl)benzyl)quinoline (**3ad**)



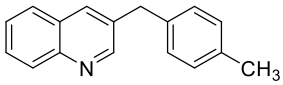
Yellow solid, m.p.: 125-127°C；^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 2.0 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.81-7.75 (m, 3H), 7.67 (s, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.14 (s, 2H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.63, 147.02, 146.22, 138.91, 135.19, 132.27, 129.88, 129.30, 129.16, 128.00, 127.87, 127.52, 127.03, 44.53, 39.05; IR (KBr): 3060, 2926, 1669, 1496, 1306, 1146, 740; HRMS (ESI): Calcd. for $C_{17}H_{16}NO_2S$ $[M+1]^+$: 298.0896; found: 298.0898.

4-(quinolin-3-ylmethyl)benzaldehyde (**3ae**)



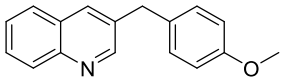
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 8.71 (d, *J* = 2.2 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.44 (t, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.15 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.78, 151.74, 147.01, 146.81, 135.14, 135.06, 132.57, 130.25, 129.62, 129.22, 128.05, 127.48, 126.96, 39.37; IR (KBr): 2828, 1698, 1604, 1497, 1211, 834; HRMS (ESI): Calcd. for $C_{17}H_{14}NO$ $[M+1]^+$: 248.1070; found: 248.1067.

3-(4-methylbenzyl)quinoline (**3af**)



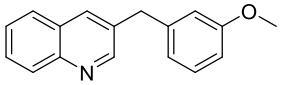
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 1.9 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.89 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.20-7.12 (m, 4H), 4.14 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.17, 146.92, 136.66, 136.13, 134.77, 134.16, 129.46, 129.21, 128.87, 128.80, 128.19, 127.47, 126.65, 38.86, 21.05; IR (KBr): 3051, 2996, 1720, 1597, 1377, 786, 738; MS (EI, m/z): 233.19 $[M]^+$.

3-(4-methoxybenzyl)quinoline (**3ag**)



Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.09 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.33, 152.13, 146.87, 134.70, 134.32, 131.76, 129.96, 129.18, 128.81, 128.17, 127.46, 126.67, 114.18, 55.30, 38.38; IR (KBr): 2998, 2835, 1610, 1510, 1246, 1177, 1035, 788, 747; HRMS (ESI): Calcd. for $C_{17}H_{16}NO$ $[M+1]^+$: 250.1226; found: 250.1229.

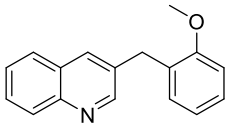
3-(3-methoxybenzyl)quinoline (**3ah**)



Light green liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.72 (d, *J*

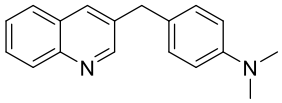
= 8.1 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.79 (dd, *J* = 14.8, 7.8 Hz, 3H), 4.12 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.95, 152.08, 146.94, 141.28, 134.86, 133.70, 129.77, 129.21, 128.87, 128.15, 127.49, 126.69 , 121.38, 114.88, 111.79, 55.20, 39.28; IR (KBr): 2999, 2835, 1599, 1492, 1261, 1048, 787; MS (EI, m/z): 249.21 $[M]^+$.

3-(2-methoxybenzyl)quinoline (**3ai**)



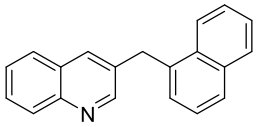
Light green solid, m.p.:78-79°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84-8.70 (m, 1H), 7.99 (t, *J* = 10.5 Hz, 1H), 7.77 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.83-6.74 (m, 2H), 4.03 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.32, 152.44, 146.76, 134.68, 133.95, 130.36, 129.12, 128.61, 128.34, 128.23, 128.06, 127.46, 126.46, 120.66, 110.56, 55.31, 33.73; IR (KBr): 3001, 2937, 2835, 1674, 1494, 1245, 750; MS (EI, m/z): 249.18 $[M]^+$.

N,N-dimethyl-4-(quinolin-3-ylmethyl)aniline (**3aj**)



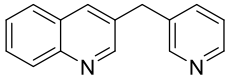
Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 2.1 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 4.05 (s, 2H), 2.90 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.31, 149.44, 146.86, 134.84, 134.60, 129.64, 129.18, 128.64, 128.24, 127.62, 127.48, 126.54, 113.04, 40.75, 38.30; IR (KBr): 2890, 2800, 1672, 1614, 1568, 1348, 806, 787; MS (EI, m/z): 262.23 $[M]^+$.

3-(naphthalen-1-ylmethyl)quinoline (**3ak**)



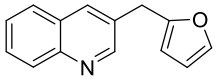
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.90-7.84 (m, 1H), 7.83-7.75 (m, 2H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.49-7.41 (m, 4H), 7.33 (d, *J* = 7.0 Hz, 1H), 4.61 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.91, 146.93, 135.22, 134.79, 134.07, 133.47, 131.88, 129.15, 128.88, 128.15, 127.73, 127.57, 127.51, 126.67, 126.34, 125.84, 125.63, 123.98, 36.46; IR (KBr): 3060, 1596, 1493, 1228, 782, 752; MS (EI, m/z): 269.21 $[M]^+$

3-(pyridin-3-ylmethyl)quinoline (**3al**)



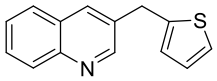
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 2.2 Hz, 1H), 8.49 (d, *J* = 1.6 Hz, 1H), 8.45 – 8.39 (m, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 1.1 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.62-7.56 (m, 1H), 7.43 (dd, *J* = 14.0, 7.1 Hz, 2H), 7.15 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.07 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.63, 150.13, 148.13, 147.01, 136.39, 135.20, 135.00, 132.57, 129.20, 128.00, 127.45, 126.95, 123.67, 36.38; IR (KBr): 3029, 2923, 1674, 1515, 1423, 1124, 753, 787; HRMS (ESI): Calcd. for $C_{15}H_{13}N_2$ $[M+1]^+$: 221.1073; found: 221.1074.

3-(furan-2-ylmethyl)quinoline (**3am**)



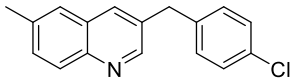
Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.95 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.35 (s, 1H), 6.31 (s, 1H), 6.07 (d, *J* = 2.9 Hz, 1H), 4.14 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.10, 151.68, 147.08, 141.96, 134.96, 130.93, 129.21, 129.05, 128.06, 127.52, 126.76, 110.45, 106.84, 31.96; IR (KBr): 3115, 3063, 1497, 1421, 1011, 788, 731; MS (EI, m/z): 209.15 $[M]^+$.

3-(thiophen-2-ylmethyl)quinoline (**3an**)



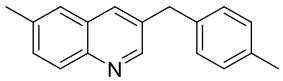
Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 1.6 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 5.1 Hz, 1H), 6.89-6.83 (m, 1H), 6.75 (d, *J* = 3.3 Hz, 1H), 4.23 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.66, 147.09, 142.39, 134.70, 133.14, 129.24, 129.08, 128.07, 127.57, 127.10, 126.80, 125.74, 124.54, 33.43; IR (KBr): 3065, 2920, 1608, 1570, 1252, 849, 753; MS (EI, m/z): 225.14 $[M]^+$.

3-(4-chlorobenzyl)-6-methylquinoline (**3bb**)



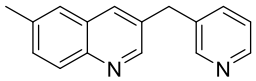
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 9.2 Hz, 1H), 7.74 (d, *J* = 1.2 Hz, 1H), 7.53-7.45 (m, 2H), 7.29-7.23 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.09 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.94, 145.57, 138.28, 136.72, 134.28, 133.24, 132.41, 131.33, 130.28, 128.85, 128.12, 126.30, 38.56, 21.59; IR (KBr): 3061, 2925, 1673, 1570, 1089, 1016, 787; MS (EI, m/z): 267.15 $[M]^+$.

6-methyl-3-(4-methylbenzyl)quinoline (**3bf**)



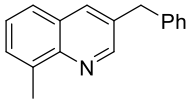
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.65 (s, 1H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.00 (s, 4H), 3.98 (s, 2H), 2.38 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.22, 145.48, 136.77, 136.49, 136.06, 134.20,134.10, 131.09, 129.42, 128.85, 128.81, 128.22, 126.32, 38.85, 21.59, 21.04; IR (KBr): 3015, 2919, 1603, 1570, 1432, 1129, 825; MS (EI, m/z): 247.22 $[M]^+$.

6-methyl-3-(pyridin-3-ylmethyl)quinoline (**3bl**)



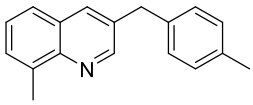
Yellow solid, m.p.: 53-54°C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 2.2 Hz, 1H), 8.57 (d, *J* = 1.8 Hz, 1H), 8.50 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 1.2 Hz, 1H), 7.53 -7.46 (m, 3H), 7.22 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.14 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.74, 150.16, 148.10, 136.84, 136.33, 135.30, 134.34, 132.51, 131.46, 128.87, 128.05, 126.27, 123.61, 36.39, 21.57; IR (KBr): 3028, 2920, 1573, 1423, 1027, 831, 717; HRMS (ESI): Calcd. for $C_{16}H_{15}N_2$ $[M+1]^+$: 235.1230; found: 235.1231.

3-benzyl-8-methylquinoline (**3da**)



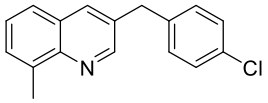
Yellow solid, m.p.: 58-59°C(Lit[2], 61-62°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 2.2 Hz, 1H), 7.71 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 6.9 Hz, 1H), 7.28 -7.22 (m, 1H), 7.21 – 7.13 (m, 2H), 7.10 (dd, *J* = 7.0, 4.8 Hz, 3H), 4.01 (s, 2H), 2.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.95, 146.06, 139.90, 136.95, 135.15, 133.57, 129.10, 129.00, 128.77, 128.17, 126.55, 126.51, 125.59, 39.24, 18.15; IR (KBr): 3127, 2920, 1602, 1492, 1073, 769, 714; MS (EI, m/z): 233.19[M]$^+$.

8-methyl-3-(4-methylbenzyl)quinoline (**3df**)



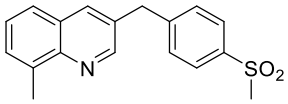
Green liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 2.2 Hz, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.39-7.33 (m, 1H), 7.09 (s, 4H), 4.09 (d, *J* = 7.9 Hz, 2H), 2.79 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.98, 146.01, 136.91, 136.84, 136.06, 135.06, 133.84, 129.43, 129.02, 128.86, 128.18, 126.44, 125.58, 38.81, 21.04, 18.14; IR (KBr): 2920, 1603, 1512, 1402, 1114, 771, 738; HRMS (ESI): Calcd. for $C_{18}H_{18}N$ [M+1]$^+$: 248.1434; found: 248.1433.

3-(4-chlorobenzyl)-8-methylquinoline (**3db**)



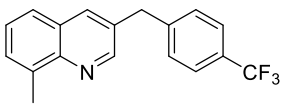
Yellow solid, m.p.: 51-52°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 2.3 Hz, 1H), 7.70-7.66 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.29-7.24 (m, 1H), 7.16-7.12 (m, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.96 (s, 2H), 2.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.70, 146.12, 138.35, 136.99, 135.13, 132.97, 132.41, 130.29, 129.24, 128.86, 128.08, 126.63, 125.56, 38.51, 18.11; IR (KBr): 3030, 2920, 1577, 1405, 1091, 836, 770; MS (EI, m/z): 267.15[M]$^+$.

8-methyl-3-(4-(methylsulfonyl)benzyl)quinoline (**3dd**)



Gray solid, m.p.: 103-104°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 2.3 Hz, 1H), 7.87 (dd, *J* = 5.5, 2.8 Hz, 3H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 6.9 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 3H), 4.23 (s, 2H), 3.03 (s, 3H), 2.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.44, 146.40, 146.15, 138.89, 136.98, 135.43, 131.94, 129.87, 129.48, 128.00, 127.84, 126.82, 125.57, 44.54, 39.02, 18.05; IR (KBr): 2925, 1597, 1492, 1407, 1305, 1148, 774; HRMS (ESI): Calcd. for $C_{18}H_{18}NO_2S$ [M+1]$^+$: 312.1053; found: 312.1051.

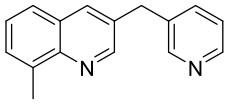
8-methyl-3-(4-(trifluoromethyl)benzyl)quinoline (**3do**)



Yellow solid, m.p.:77-78°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 2.2 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.64-7.54 (m, 4H), 7.47-7.42 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.25 (s, 2H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.59, 146.17, 143.93, 137.03, 135.29, 132.40, 129.34, 129.36, 128.98 (d, *J* = 33.0 Hz), 128.05, 126.71, 125.68 (q, *J* = 4.0 Hz), 38.98, 18.04; IR (KBr): 2925, 1620, 1492, 1418, 1165, 1124, 1067, 773; HRMS

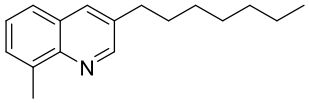
(ESI): Calcd. for $C_{18}H_{15}F_3N$ [M+1]$^+$: 302.1151; found: 302.1152.

8-methyl-3-(pyridin-3-ylmethyl)quinoline (**3dl**)



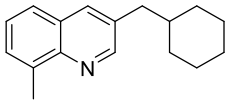
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 2.3 Hz, 1H), 8.47 (d, *J* = 1.8 Hz, 1H), 8.39 (dd, *J* = 4.8, 1.3 Hz, 1H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.43-7.36 (m, 2H), 7.33-7.27 (m, 1H), 7.10 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.04 (s, 2H), 2.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.46, 150.15, 148.08, 146.15, 136.99, 136.32, 135.34, 135.21, 132.23, 129.34, 127.99, 126.72, 125.51, 123.60, 36.32, 18.05; IR (KBr): 3030, 2921, 1576, 1515, 1491, 1424, 1264, 770, 732; HRMS (ESI): Calcd. for $C_{16}H_{15}N_2$ [M+1]$^+$: 235.1230; found: 235.1232.

3-heptyl-8-methylquinoline (3**dp**)



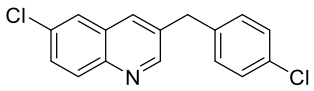
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.0 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.38-7.29 (m, 1H), 2.76-2.69 (m, 5H), 1.64 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.34-1.20 (m, 8H), 0.81 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.92, 145.80, 136.78, 135.08, 134.51, 128.75, 128.21, 126.31, 125.41, 33.13, 31.78, 31.15, 29.14, 29.12, 22.64, 18.13, 14.07; IR (KBr): 2957, 2800, 1639, 1547, 1427, 1173, 1068, 885, 771; HRMS (ESI): Calcd. for $C_{17}H_{24}N$ [M+1]$^+$: 242.1903; found: 242.1899.

3-(cyclohexylmethyl)-8-methylquinoline (**3dq**)



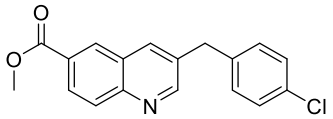
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.1 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 2.84 (s, 3H), 2.68 (d, *J* = 7.0 Hz, 2H), 1.77-1.61 (m, 6H), 1.19 (d, *J* = 8.5 Hz, 3H), 1.03 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.37, 145.91, 136.82, 135.28, 133.53, 128.71, 128.09, 126.27, 125.43, 41.15, 39.66, 33.03, 26.45, 26.21, 18.12; IR (KBr): 2927, 2810, 1629, 1566, 1519, 1481,1173, 1048, 875, 778; MS (EI, m/z): 239.17[M]$^+$

6-chloro-3-(4-chlorobenzyl)quinoline (3**cb**)



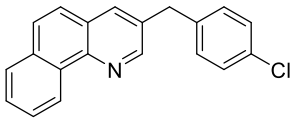
Light yellow solid, m.p.: 130-132°C； ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 2.1 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.61 (s, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.47 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.99 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.08, 145.32, 137.72, 134.34, 133.82, 132.63, 132.55, 130.83, 130.29, 129.91, 128.97, 128.67, 126.11, 38.50; IR (KBr): 3118, 2987, 1597, 1425, 1348, 1072, 798; MS (EI, m/z): 287.11[M]$^+$.

methyl 3-(4-chlorobenzyl)quinoline-6-carboxylate (**3eb**)



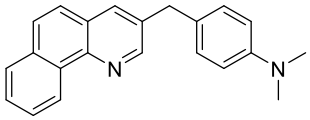
Brown solid, m.p.:97-98°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.51 (d, *J* = 1.6 Hz, 1H), 8.26 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.94 (s, 1H), 7.32 – 7.29 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.15 (s, 2H), 3.99 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$): δ 166.56, 153.94, 148.69, 137.64, 135.97, 134.28, 132.69, 130.63, 130.31, 129.49, 129.00, 128.55, 128.37, 52.41, 38.48; IR (KBr): 2951, 1598, 1493, 1278, 1097, 790, 748; MS (EI, m/z): 311.01[M]$^+$.

3-(4-chlorobenzyl)benzo[h]quinoline (**3fb**)



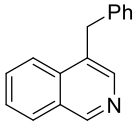
Yellow solid, m.p.:99-100°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, *J* = 8.2 Hz, 1H), 8.69 (d, *J* = 2.2 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 11.4, 8.4 Hz, 2H), 7.52 (dd, *J* = 11.4, 4.8 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 3.94 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.91, 145.13, 138.45, 135.11, 134.09, 133.46, 132.43, 131.46, 130.33, 128.88, 127.18, 126.25, 127.18, 126.25, 125.19, 124.28, 38.46; IR (KBr): 3052, 2839, 1627, 1566, 1446, 1092, 885, 771; HRMS (ESI): Calcd. for $C_{20}H_{15}ClN$ [M+1]$^+$: 304.0888; found: 304.0892.

4-(benzo[h]quinolin-3-ylmethyl)-N,N-dimethylaniline (**3fj**)



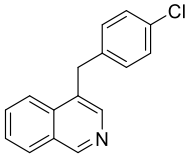
Yellow solid, m.p.:93-94°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (d, *J* = 8.1 Hz, 1H), 8.80 (d, *J* = 2.1 Hz, 1H), 7.81-7.75 (m, 2H), 7.67-7.53 (m, 3H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 4.01 (s, 2H), 2.81 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.22, 149.42, 144.84, 135.66, 135.04, 133.35, 131.53, 129.65, 127.97, 127.81, 127.72, 127.02, 126.33, 125.38, 124.20, 113.09, 40.79, 38.22; IR (KBr): 2907, 2844, 1615, 1446, 1347, 1163, 803; HRMS (ESI): Calcd. for $C_{22}H_{21}N_2$ [M+1]$^+$: 313.1699; found: 313.1694.

4-benzylisoquinoline (**3ga**)



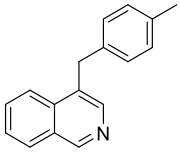
Yellow solid, m.p.:116-117°C(Lit[3], 116-117°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 1H), 8.33 (s, 1H), 7.84 (dd, *J* = 23.7, 8.2 Hz, 2H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.19-7.14 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 3H), 4.28 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.96, 143.79, 139.75, 134.88, 130.41, 129.68, 128.61, 128.56, 128.26, 126.96, 126.38, 123.51, 36.28; IR (KBr): 3022, 2921, 1622, 1492, 1348, 939, 754; MS (EI, m/z): 219.11[M]$^+$.

4-(4-chlorobenzyl)isoquinoline (**3gb**)



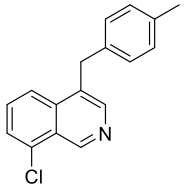
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.30 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 4.23 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.17, 143.71, 138.22, 134.70, 132.20, 130.56, 129.85, 129.17, 128.74, 128.64, 128.36, 127.09, 123.30, 35.64; IR (KBr): 3054, 2926, 1624, 1492, 1390, 1091, 799, 698; MS (EI, m/z): 253.05[M]$^+$.

4-(4-methylbenzyl)isoquinoline (**3gf**)



Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.46 (s, 1H), 7.97 (dd, *J* = 14.1, 8.3 Hz, 2H), 7.68 – 7.63 (m, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.14-7.08 (m, 4H), 4.36 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.88, 143.71, 136.69, 135.88, 134.89, 130.37, 129.95, 129.31, 128.64, 128.44, 128.24, 126.92, 123.54, 35.88, 21.02; IR (KBr): 3019, 2920, 1623, 1512, 1389, 1262, 785, 750; MS (EI, m/z): 233.15$[M]^+$.

8-chloro-4-(4-methylbenzyl)isoquinoline (**3hf**)



Light yellow solid, m.p.:118-119°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 8.53 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.55-7.49 (m, 1H), 7.09 (d, *J* = 2.1 Hz, 4H), 4.36 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.76, 144.65, 136.32 , 136.06, 133.13, 130.22, 129.70, 129.38, 128.37, 127.34, 125.76, 122.77, 35.97, 21.01; IR (KBr): 3019, 1644, 1613, 1511, 1390, 1120, 1078, 896, 745; HRMS (ESI): Calcd. for $C_{17}H_{15}ClN$ $[M+1]^+$: 268.0888; found: 268.0883.

References

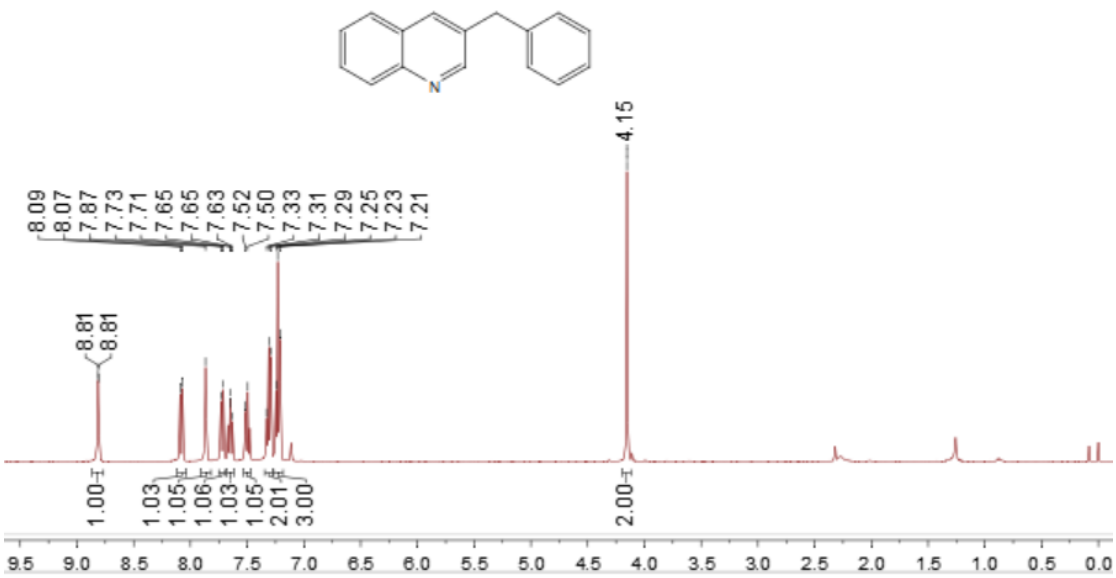
1 Hartlen, K. D.; Athanasopoulos, A. P. T.; Kitaev, V. *Langmuir* **2008**, *24*, 1714-1720.

2 Avramoff, M.; Sprinzak, Y. *J. Org. Chem.* **1957**, *22*, 571-574.

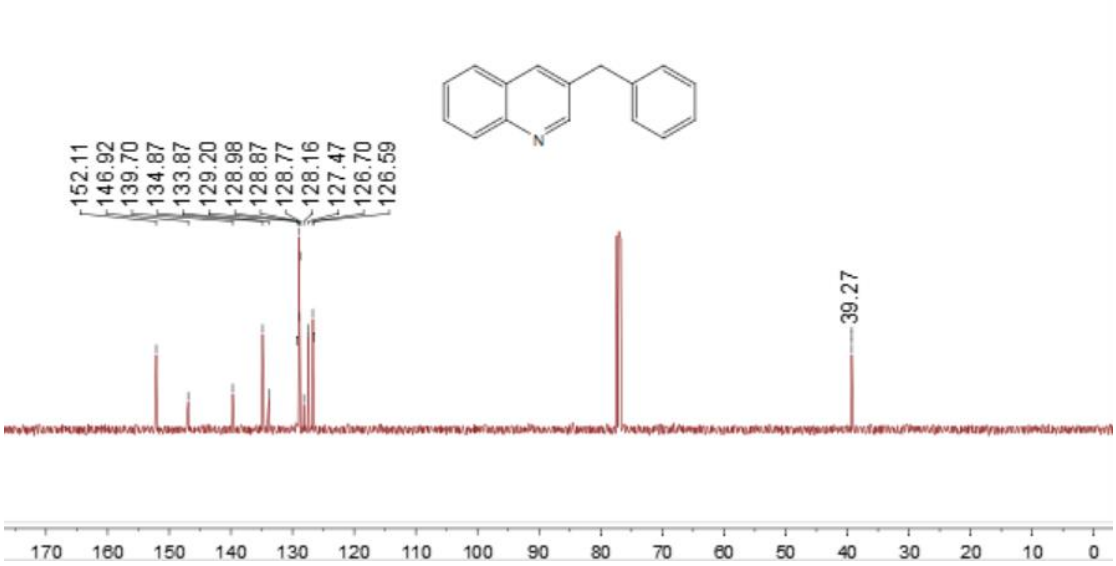
3 Clark, R. D. *Heterocycles* **1987**, *26*, 2945-2948.

6. NMR Spectra of the Obtained Compounds

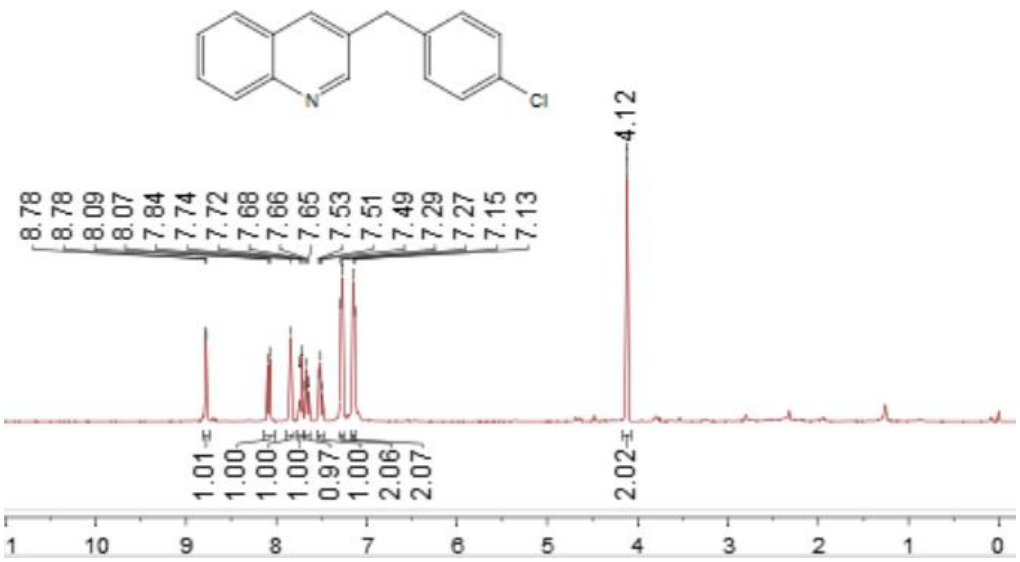
^{1}H- NMR spectrum of 3-benzylquinoline (3aa)



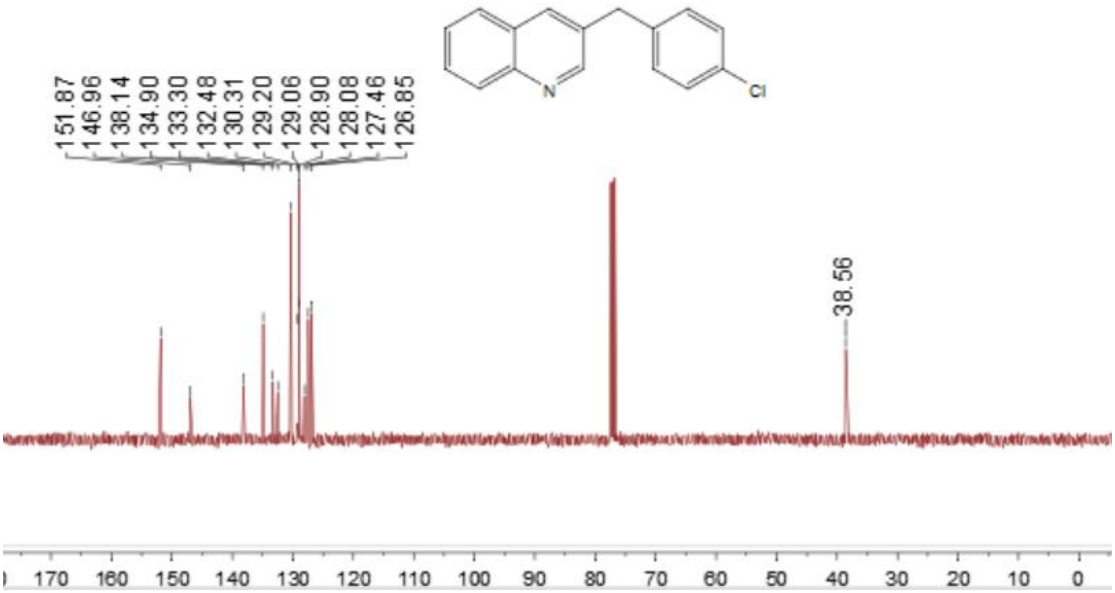
^{13}C-NMR spectrum of 3-benzylquinoline (3aa)



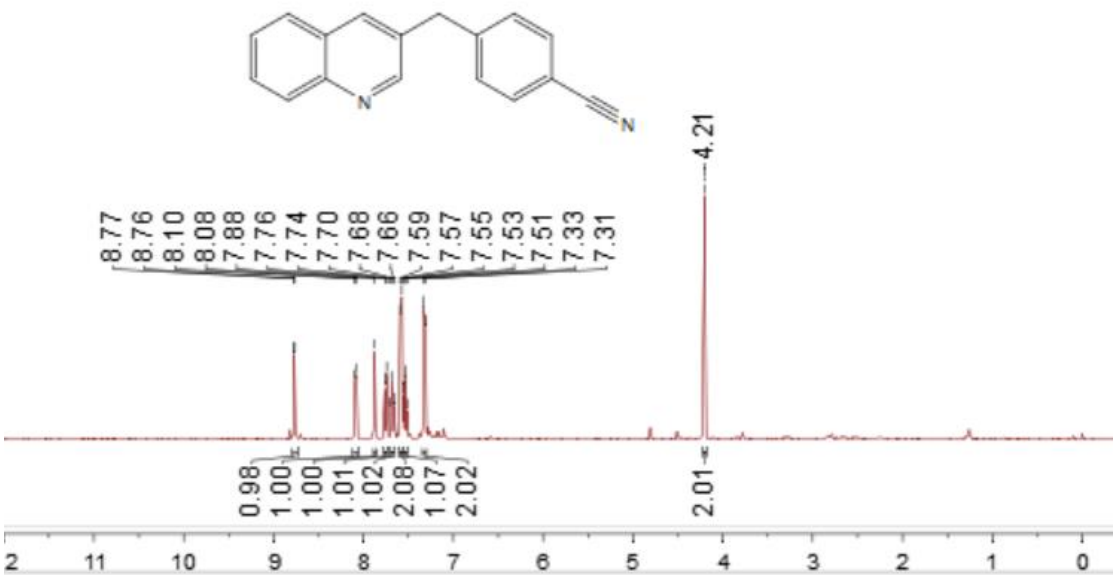
^{1}H- NMR spectrum of 3-(4-chlorobenzyl)quinoline (3ab)



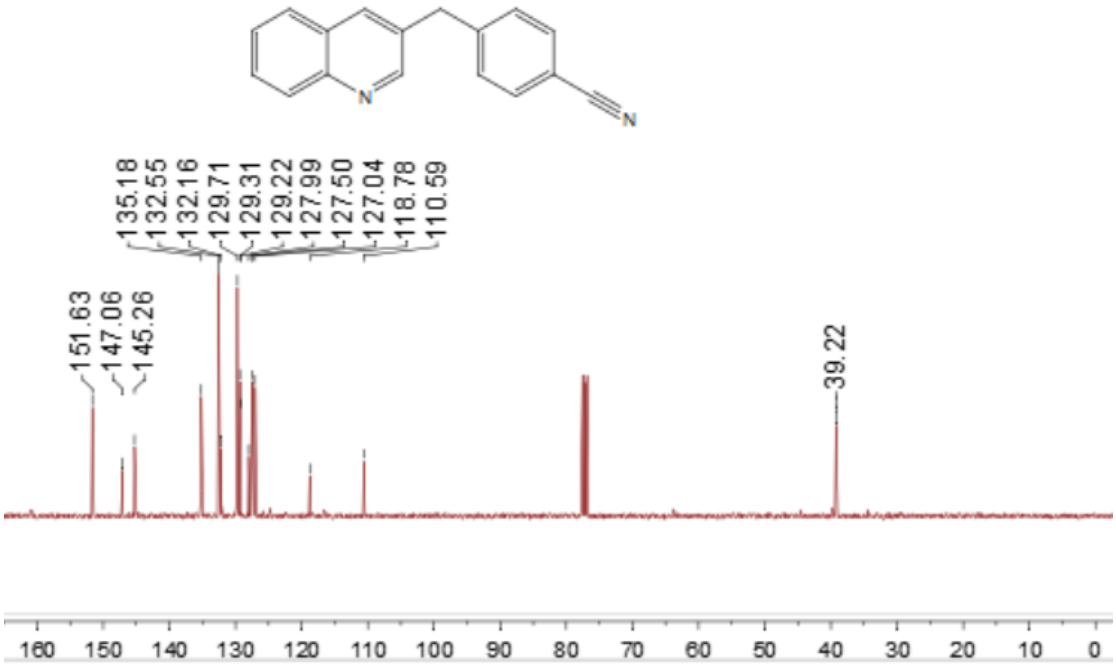
^{13}C-NMR spectrum of 3-(4-chlorobenzyl)quinoline (3ab)



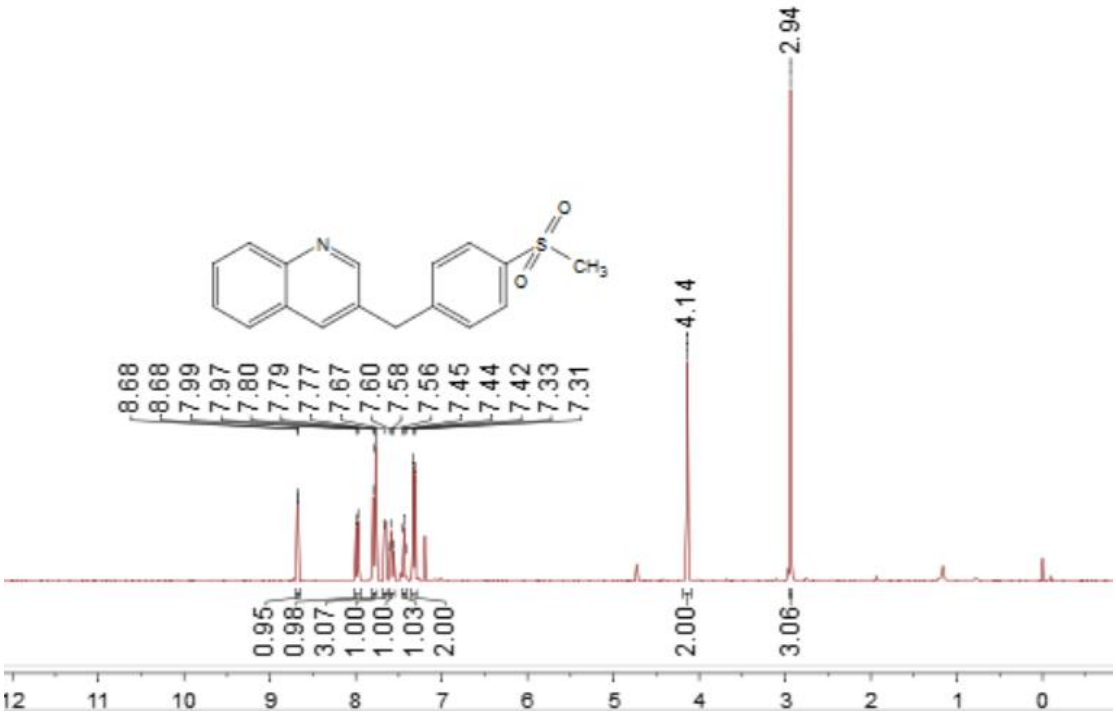
^{1}H- NMR spectrum of 4-(quinolin-3-ylmethyl)benzonitrile (3ac)



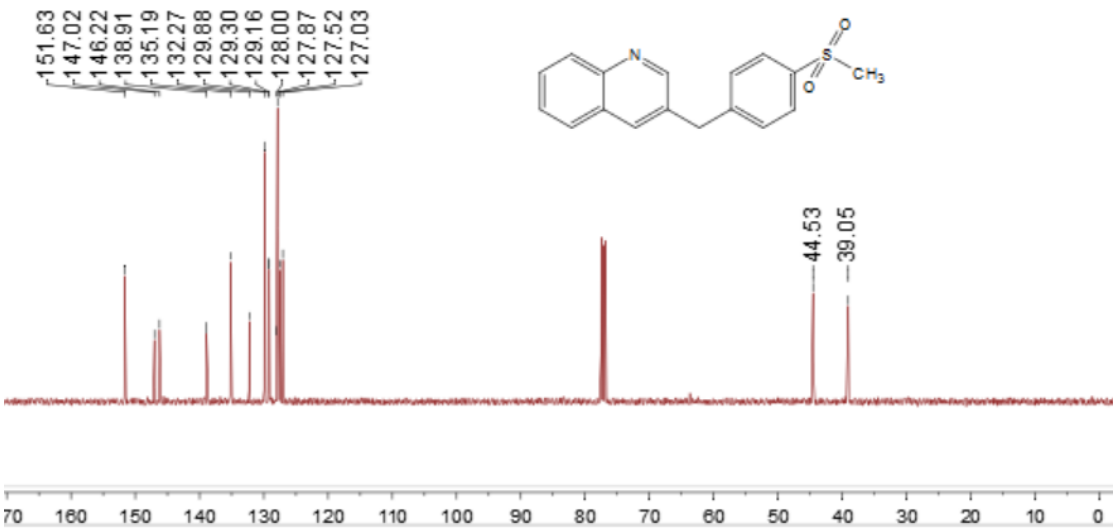
^{13}C-NMR spectrum of 4-(quinolin-3-ylmethyl)benzonitrile (3ac)



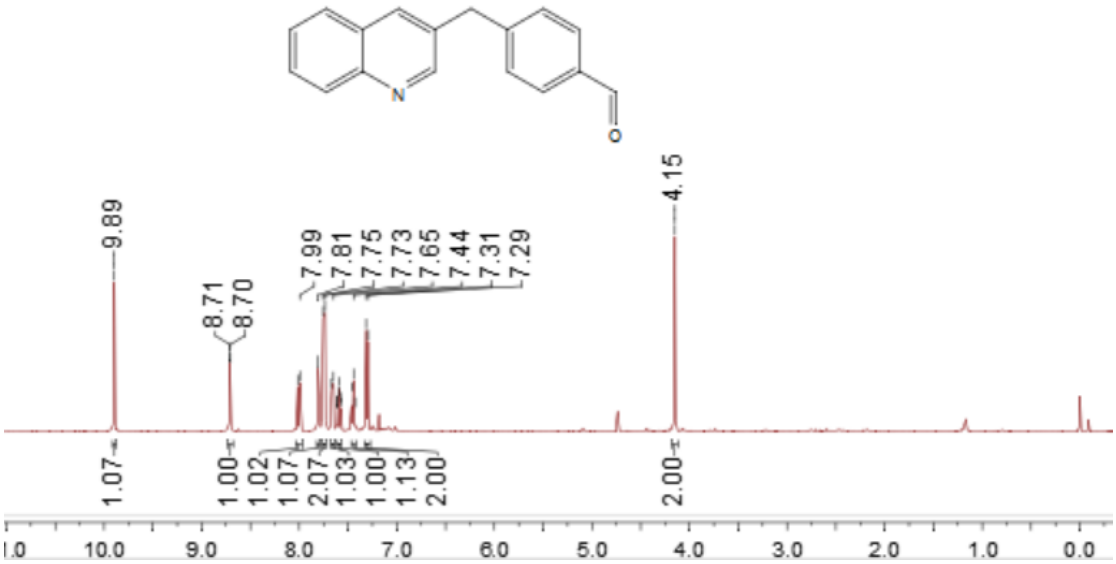
^{1}H- NMR spectrum of 3-(4-(methylsulfonyl)benzyl)quinoline (3ad)



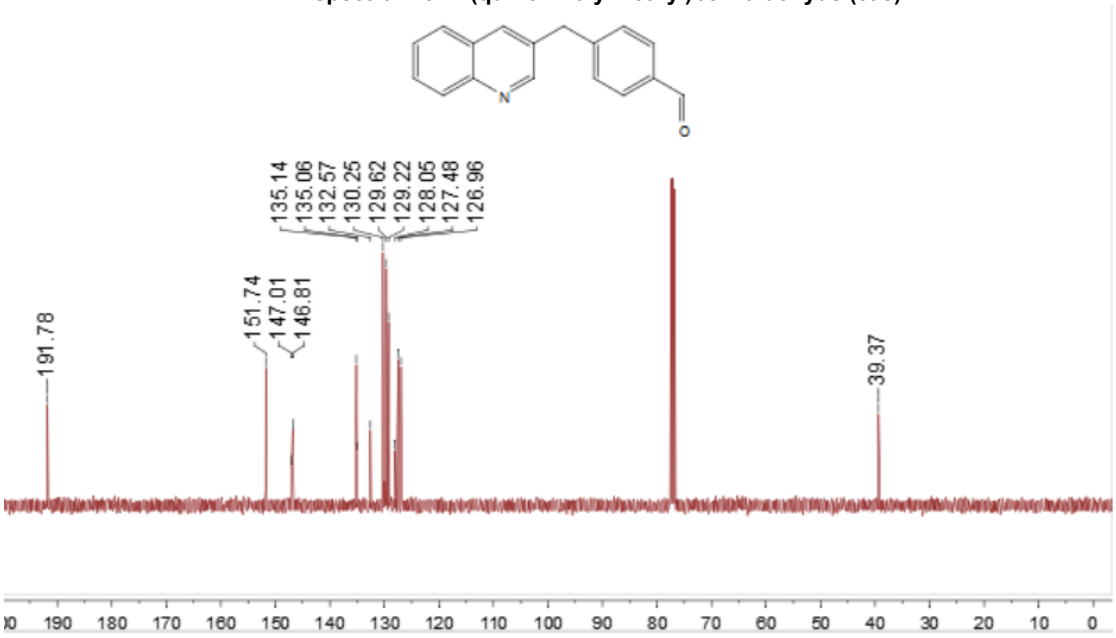
^{13}C-NMR spectrum of 3-(4-(methylsulfonyl)benzyl)quinoline (3ad)



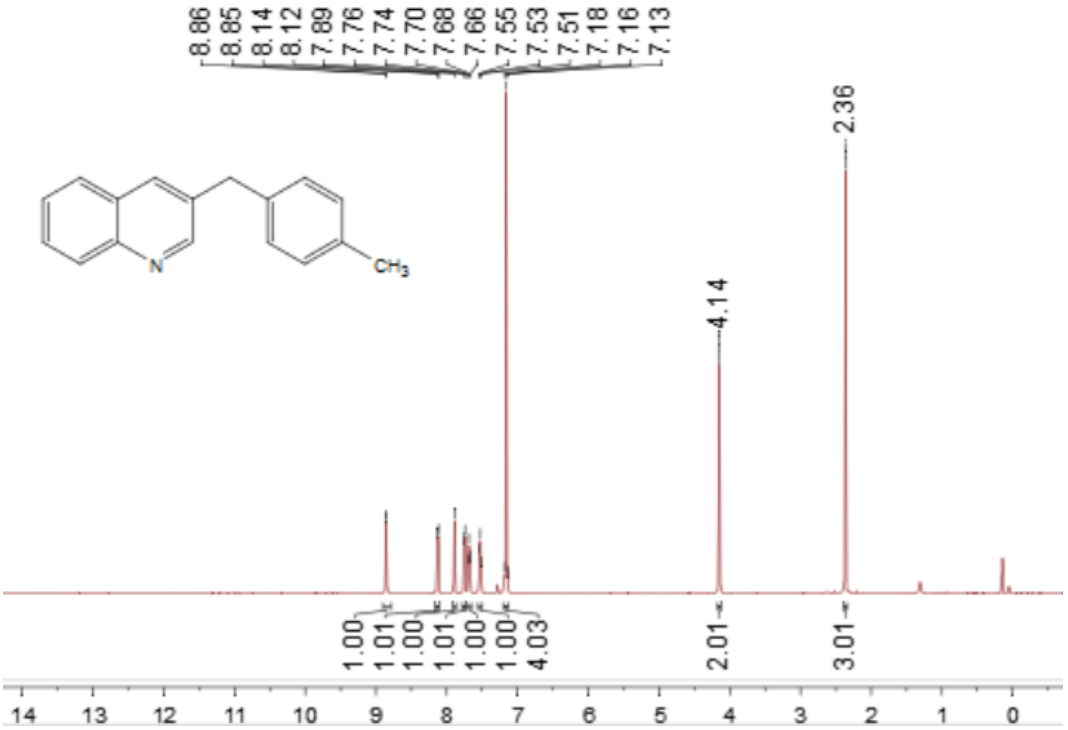
^{1}H- NMR spectrum of 4-(quinolin-3-ylmethyl)benzaldehyde (3ae)



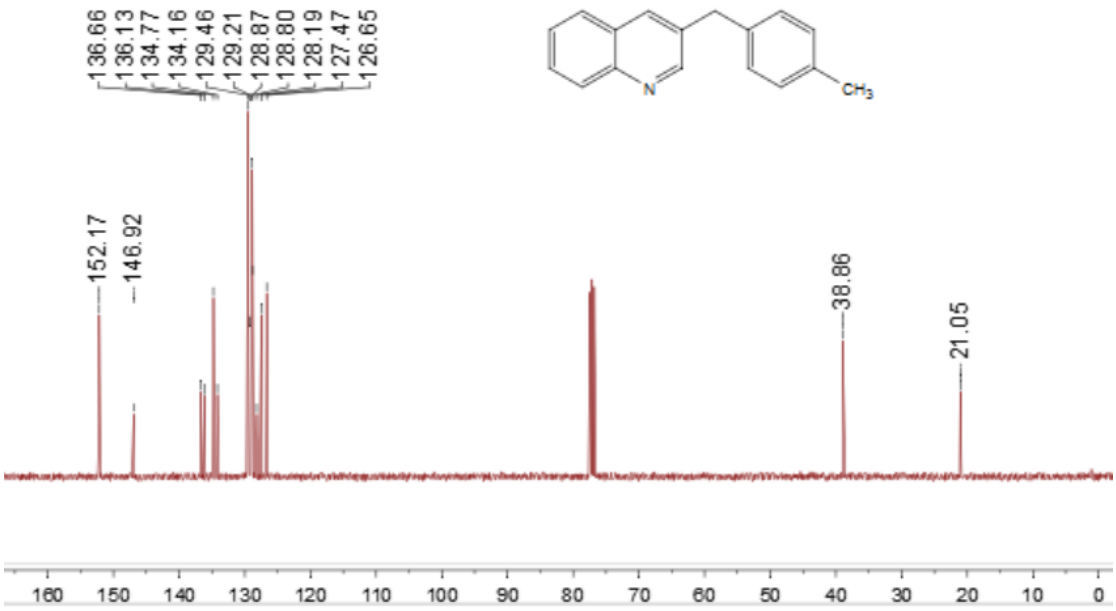
^{13}C-NMR spectrum of 4-(quinolin-3-ylmethyl)benzaldehyde (3ae)



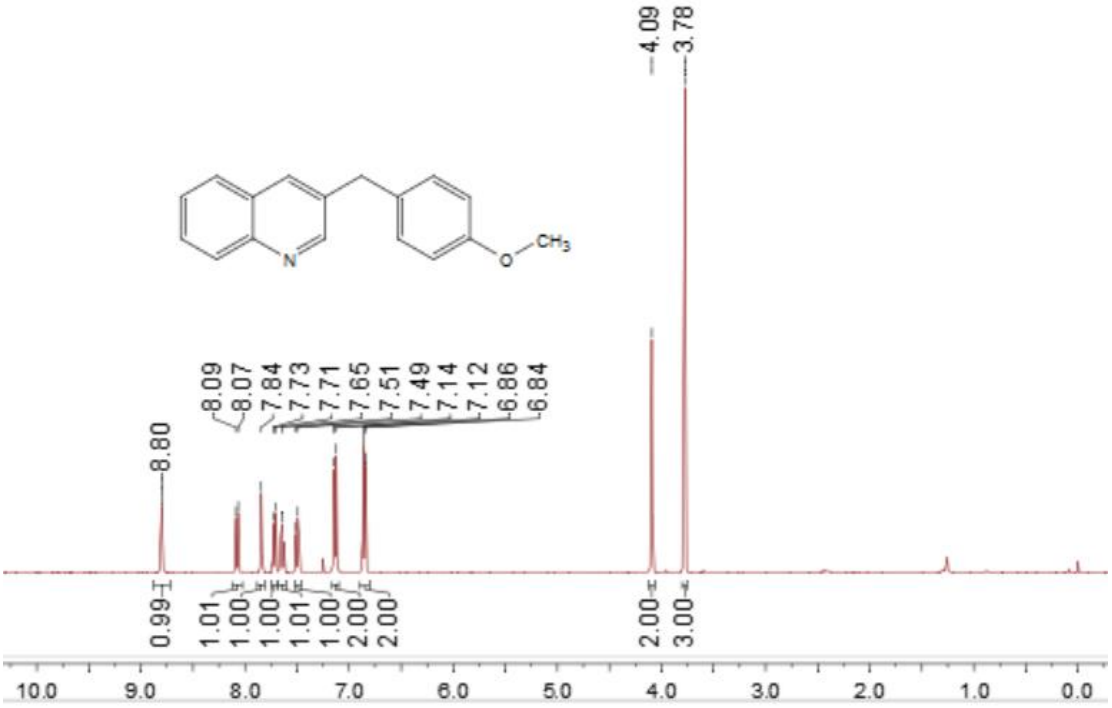
^{1}H- NMR spectrum of 3-(4-methylbenzyl)quinoline (3af)



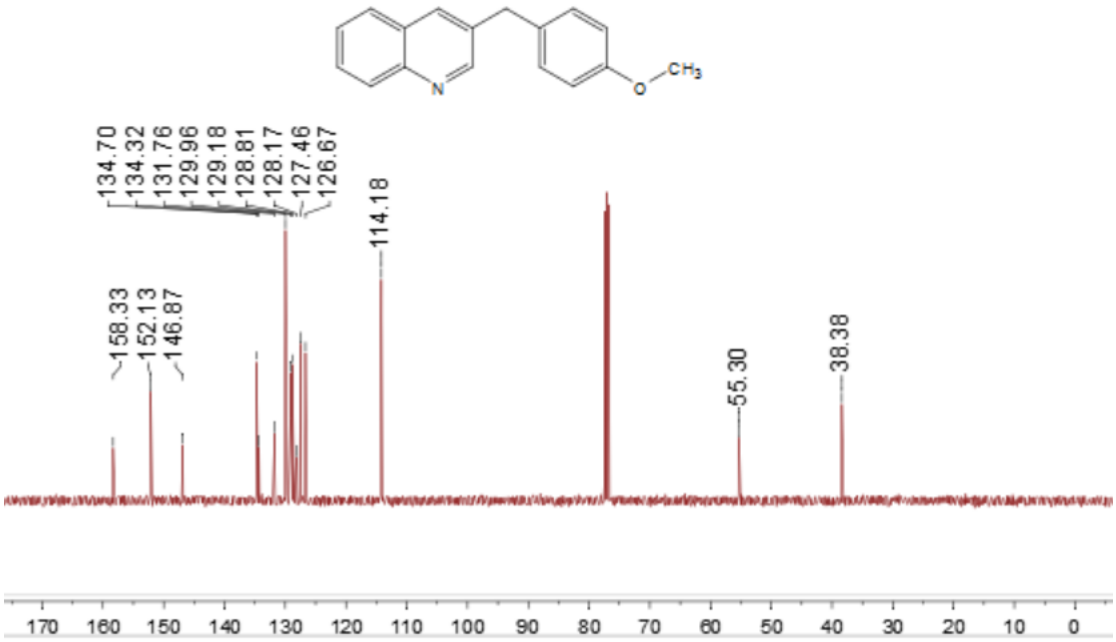
^{13}C-NMR spectrum of 3-(4-methylbenzyl)quinoline (3af)



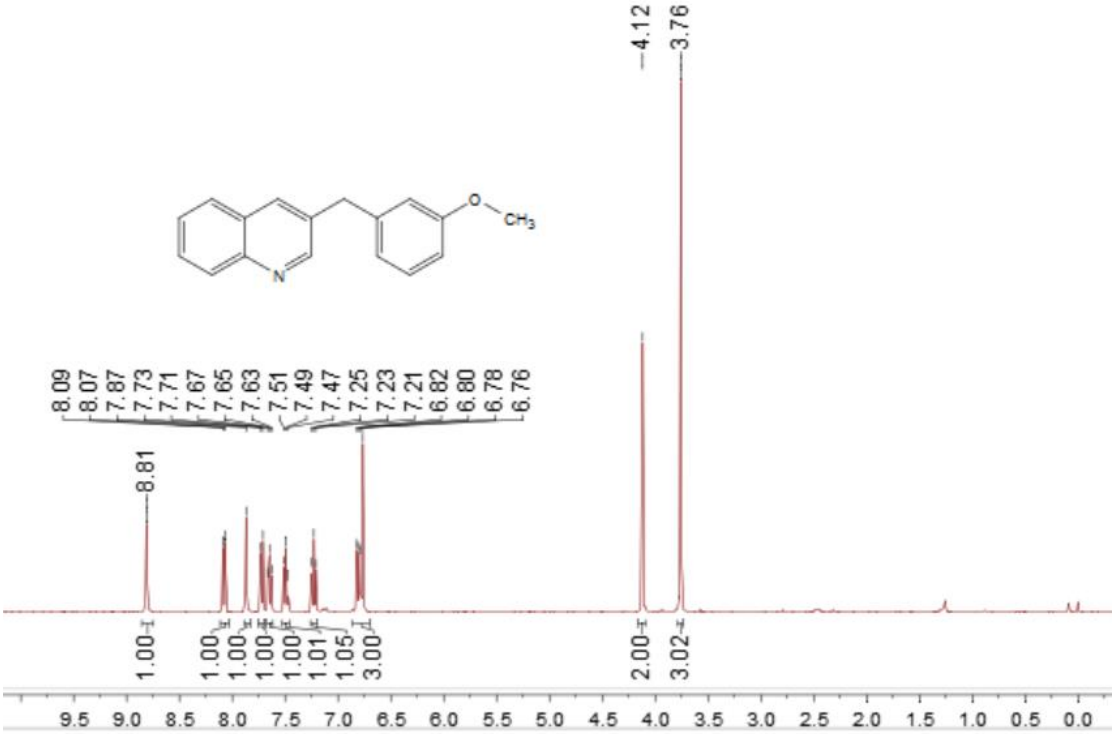
^{1}H- NMR spectrum of 3-(4-methoxybenzyl)quinoline (3ag)



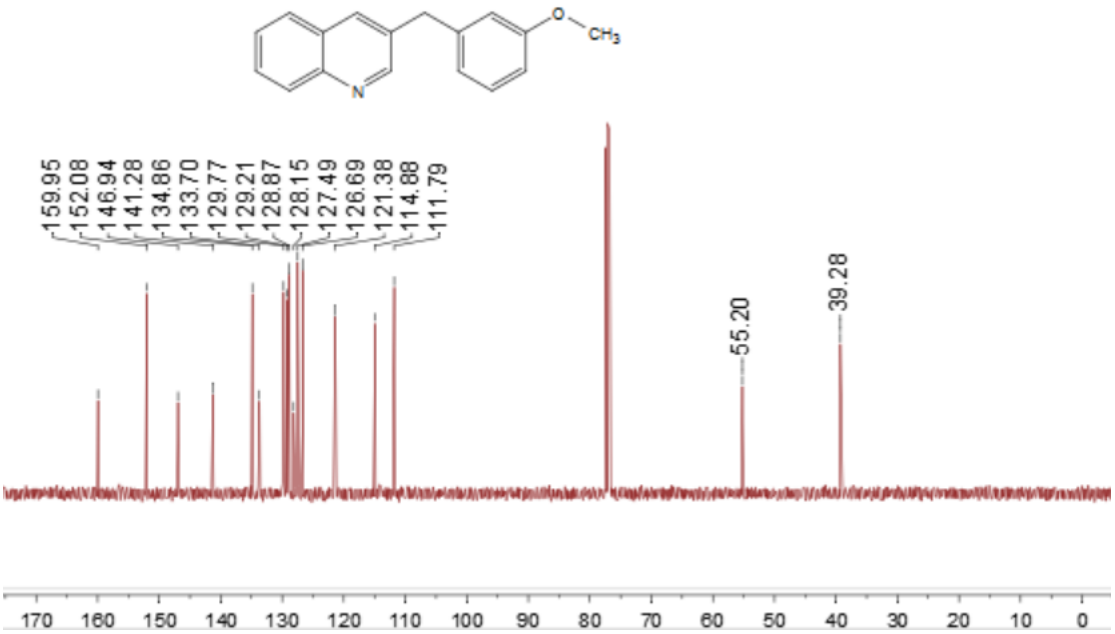
^{13}C-NMR spectrum of 3-(4-methoxybenzyl)quinoline (3ag)



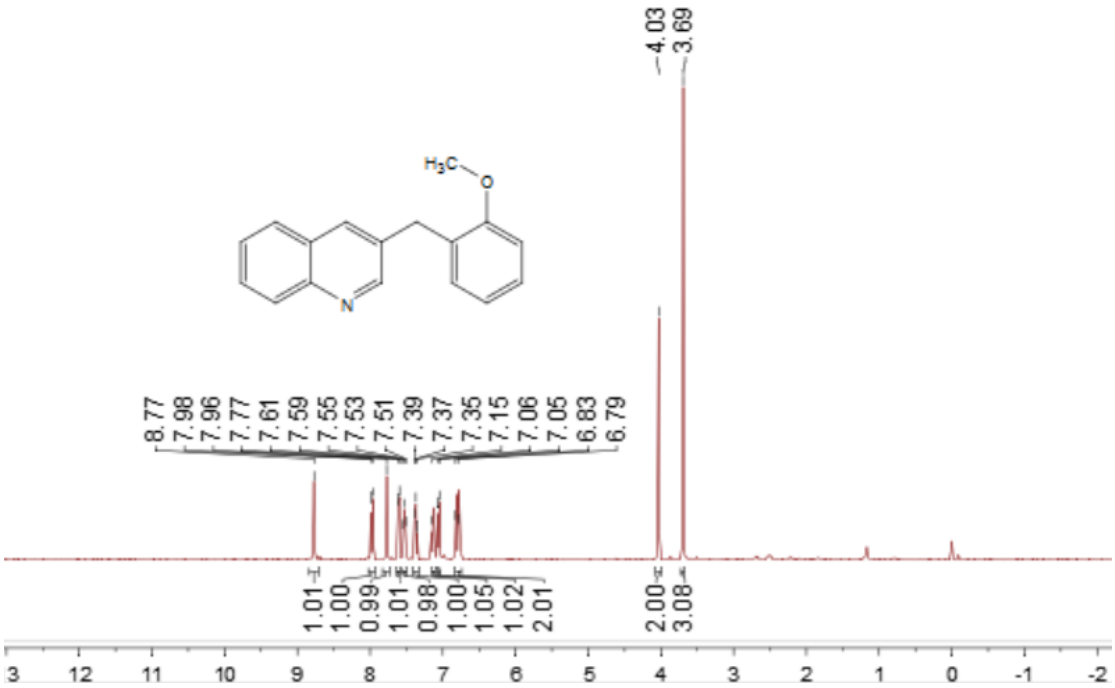
^{1}H-NMR spectrum of 3-(3-methoxybenzyl)quinoline (3ah)



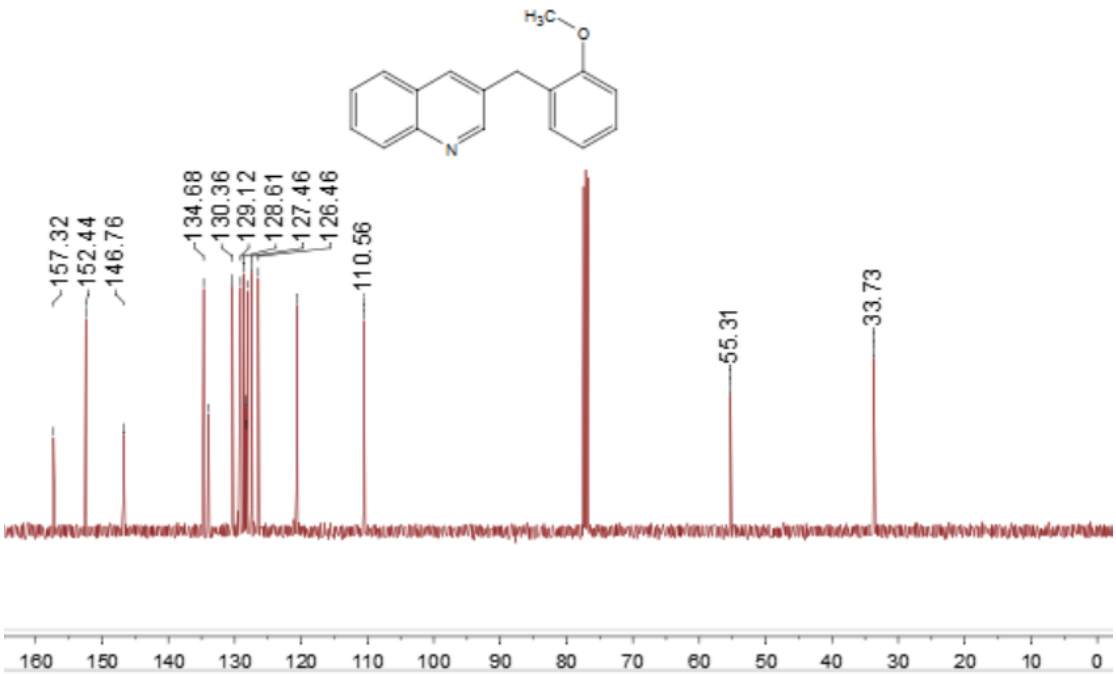
^{13}C-NMR spectrum of 3-(3-methoxybenzyl)quinoline (3ah)



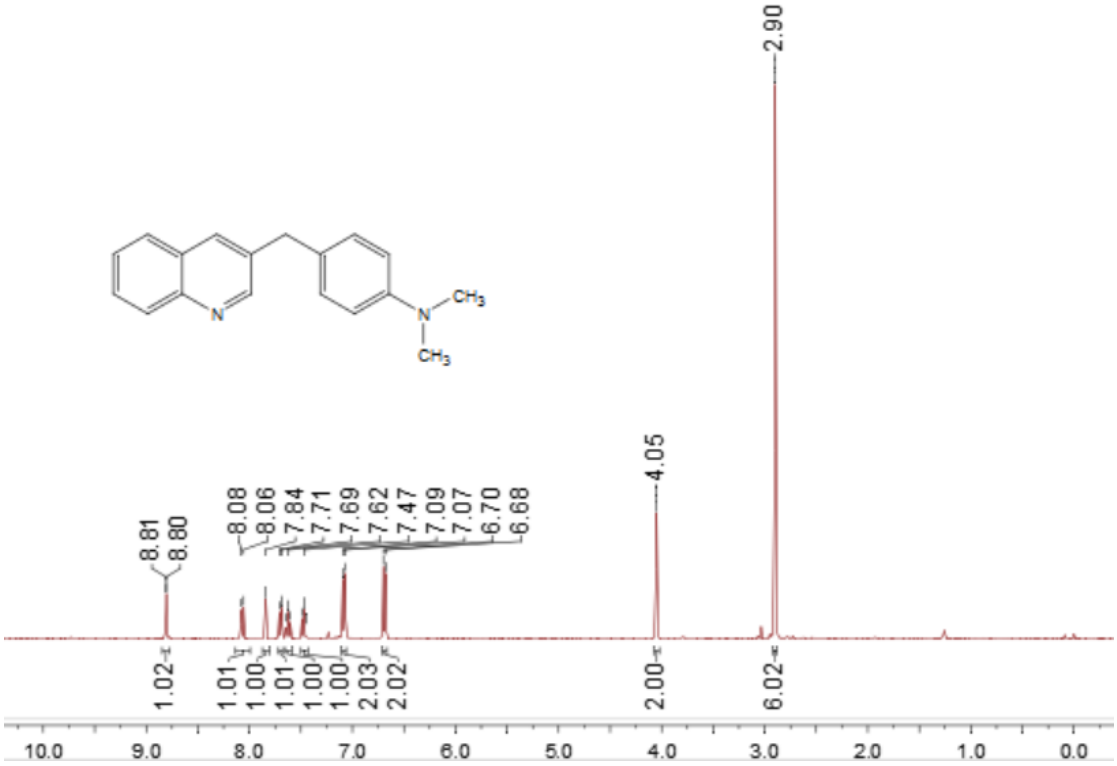
^{1}H-NMR spectrum of 3-(2-methoxybenzyl)quinoline (3ai)



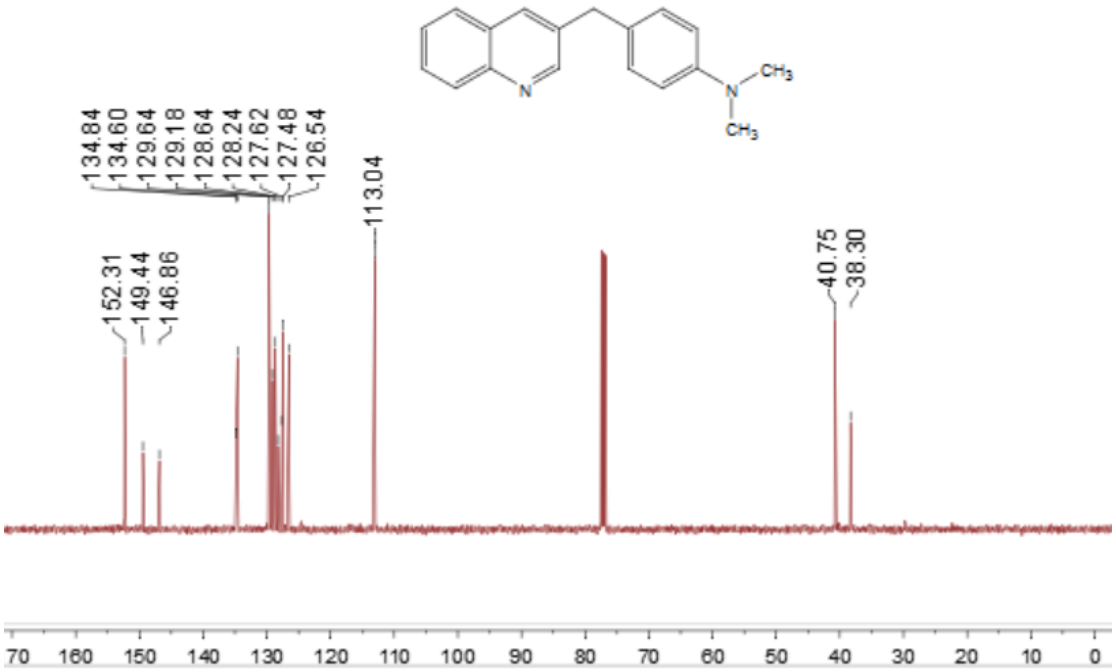
^{13}C-NMR spectrum of 3-(2-methoxybenzyl)quinoline (3ai)



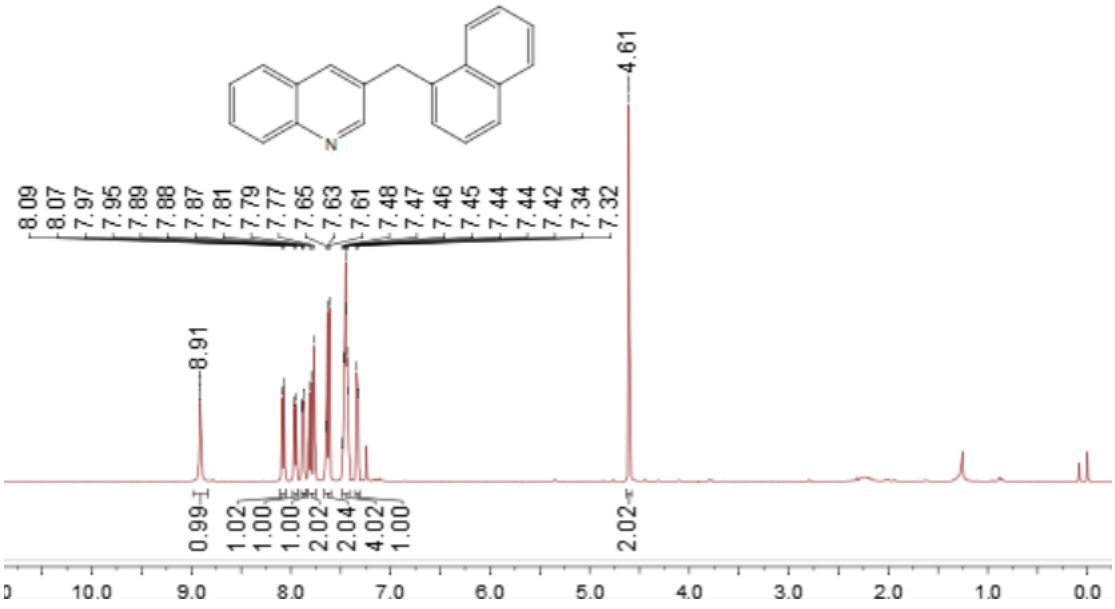
^{1}H-NMR spectrum of N,N-dimethyl-4-(quinolin-3-ylmethyl)aniline (3aj)



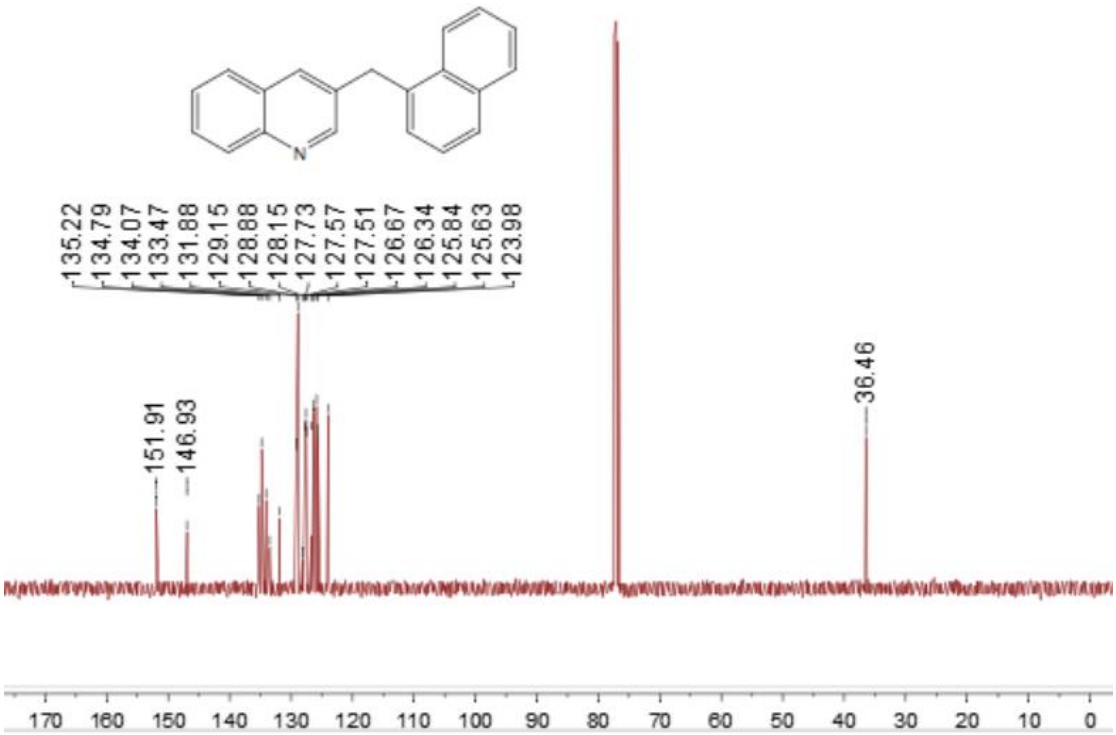
^{13}C-NMR spectrum of N,N-dimethyl-4-(quinolin-3-ylmethyl)aniline (3aj)



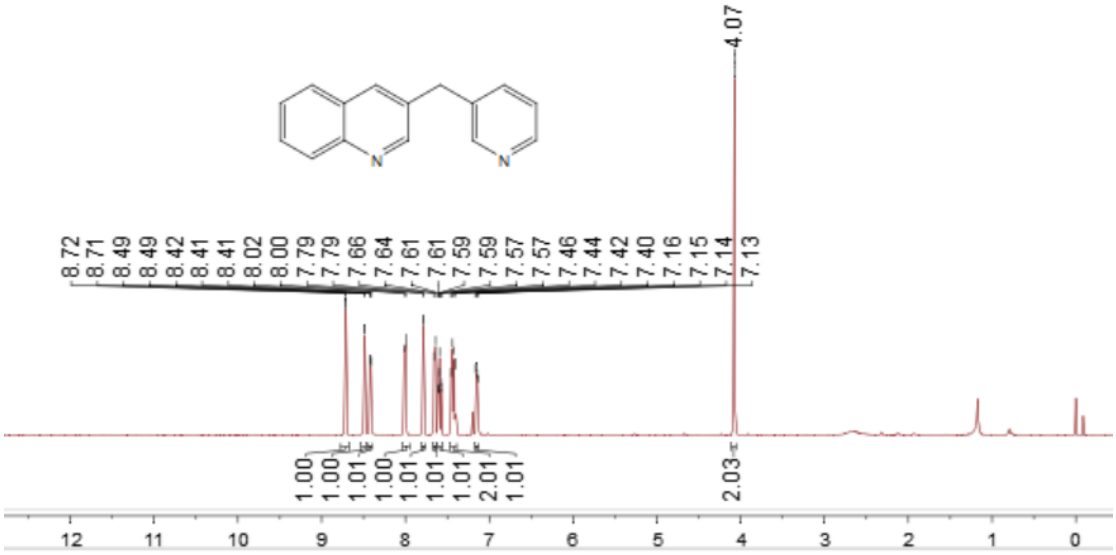
^{1}H-NMR spectrum of 3-(naphthalen-1-ylmethyl)quinoline (3ak)



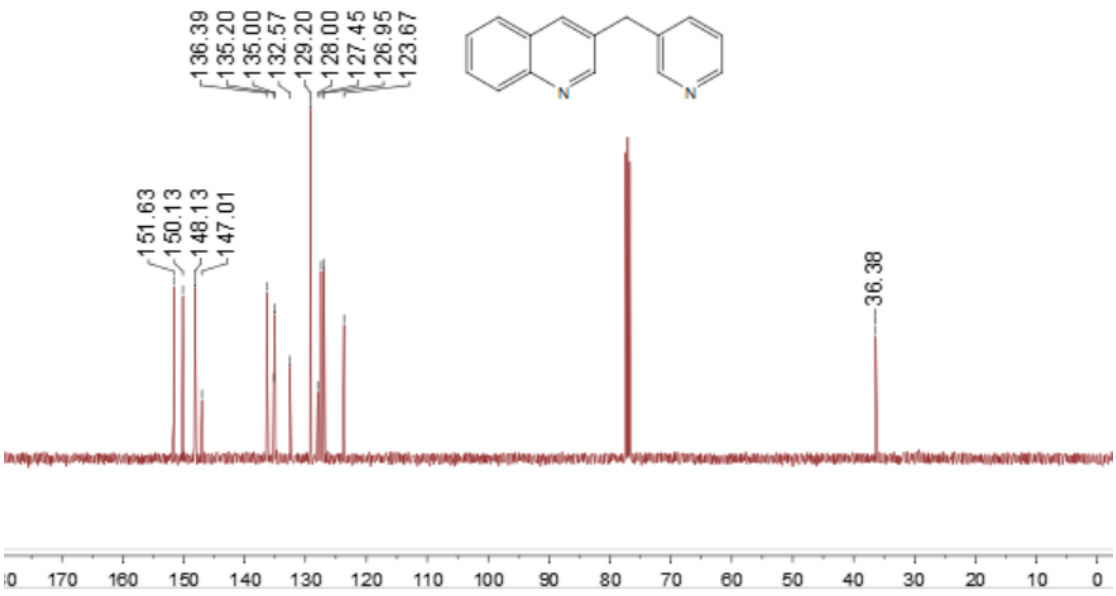
^{13}C-NMR spectrum of 3-(naphthalen-1-ylmethyl)quinoline (3ak)



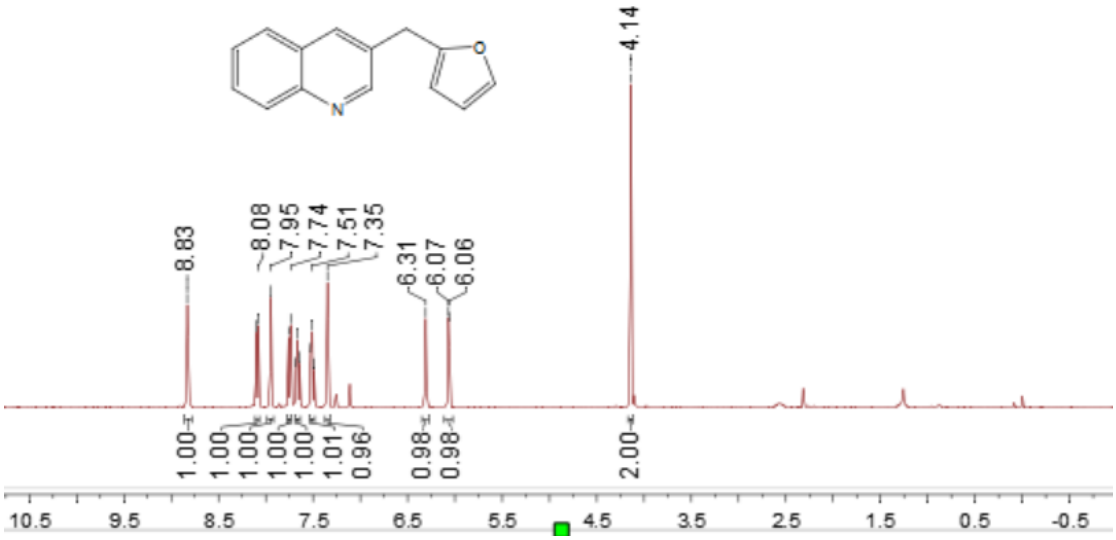
^{1}H-NMR spectrum of 3-(pyridin-3-ylmethyl)quinoline (3al)



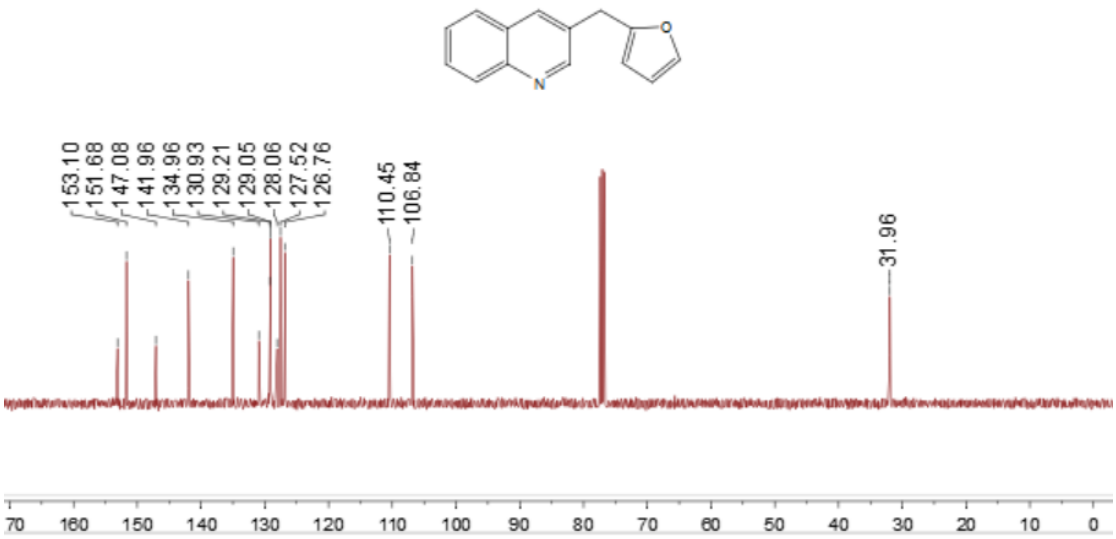
^{13}C-NMR spectrum of 3-(pyridin-3-ylmethyl)quinoline (3al)



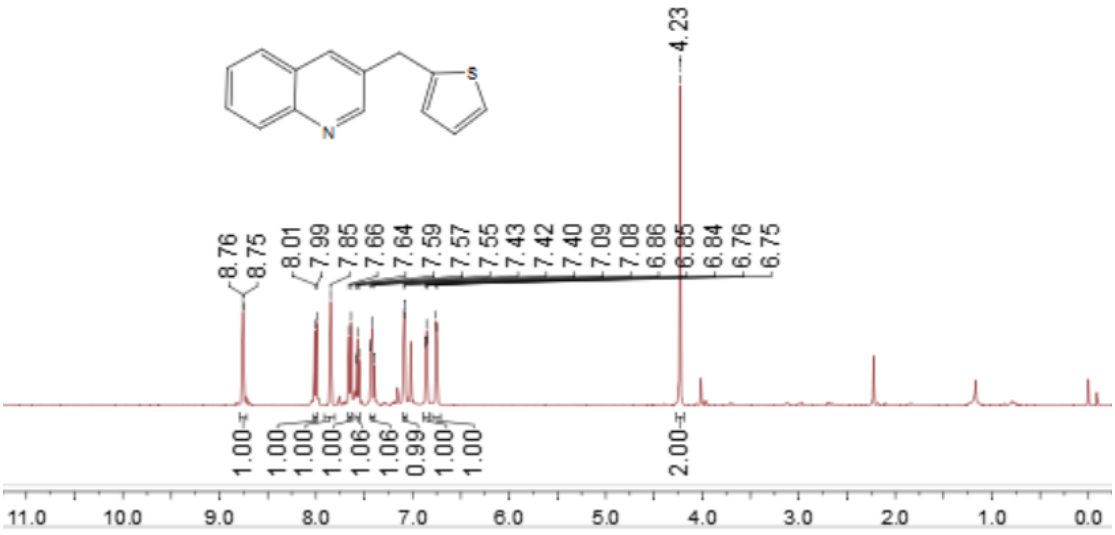
^{1}H-NMR spectrum of 3-(furan-2-ylmethyl)quinoline (3am)



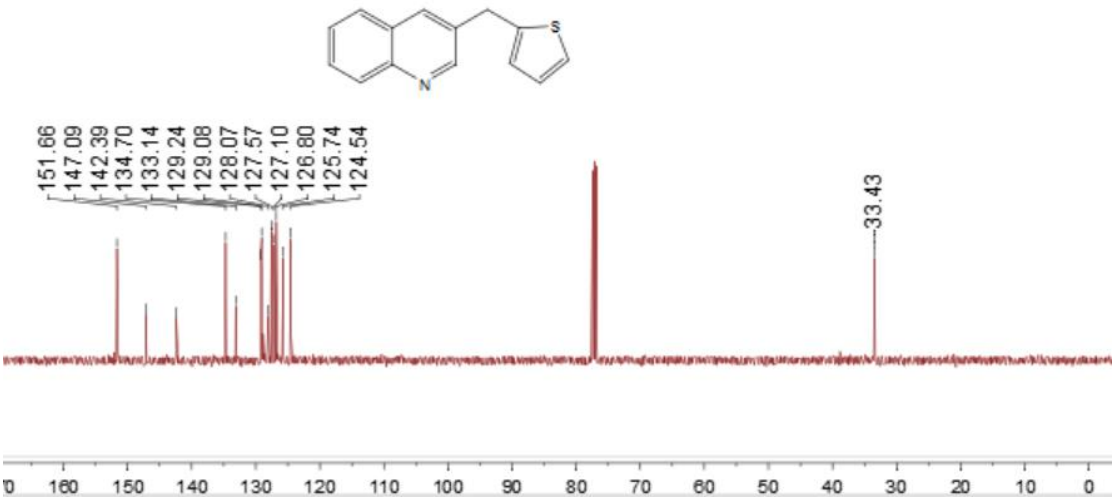
^{13}C-NMR spectrum of 3-(furan-2-ylmethyl)quinoline (3am)



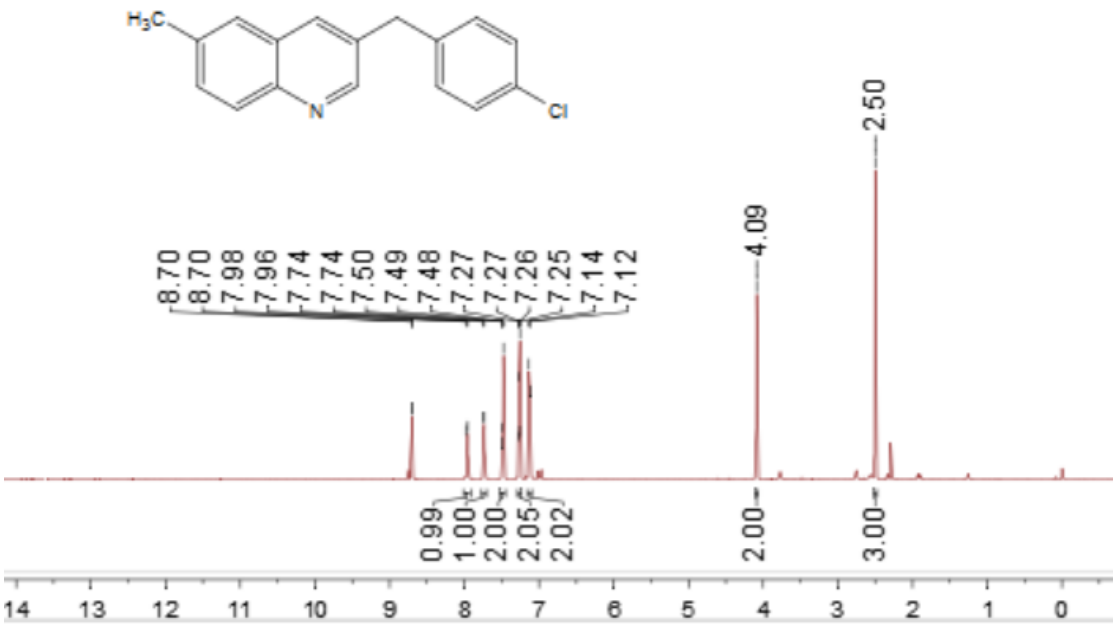
^{1}H-NMR spectrum of 3-(thiophen-2-ylmethyl)quinoline (3an)



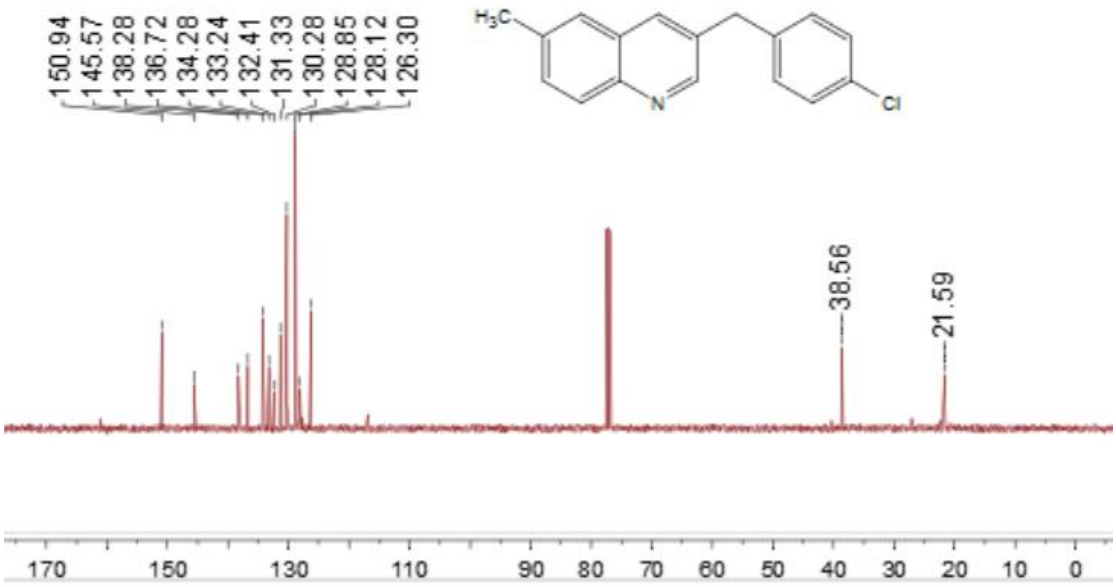
^{13}C-NMR spectrum of 3-(thiophen-2-ylmethyl)quinoline (3an)



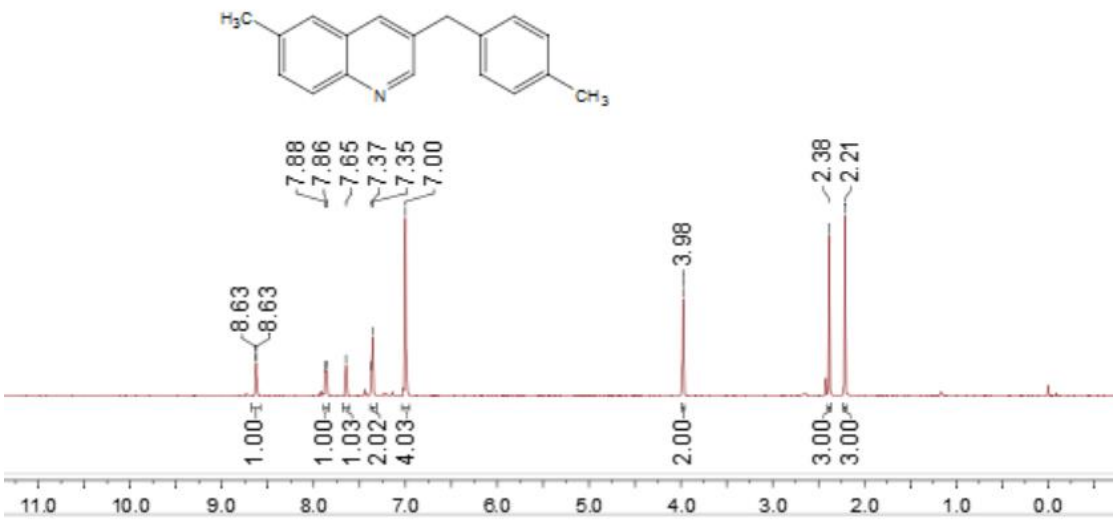
^{1}H-NMR spectrum of 3-(4-chlorobenzyl)-6-methylquinoline (3bb)



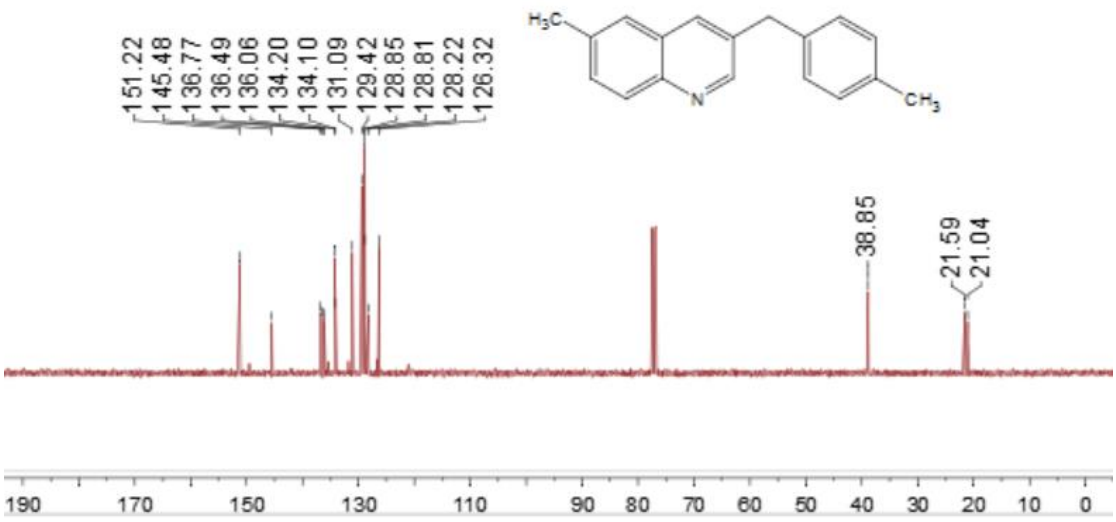
^{13}C-NMR spectrum of 3-(4-chlorobenzyl)-6-methylquinoline (3bb)



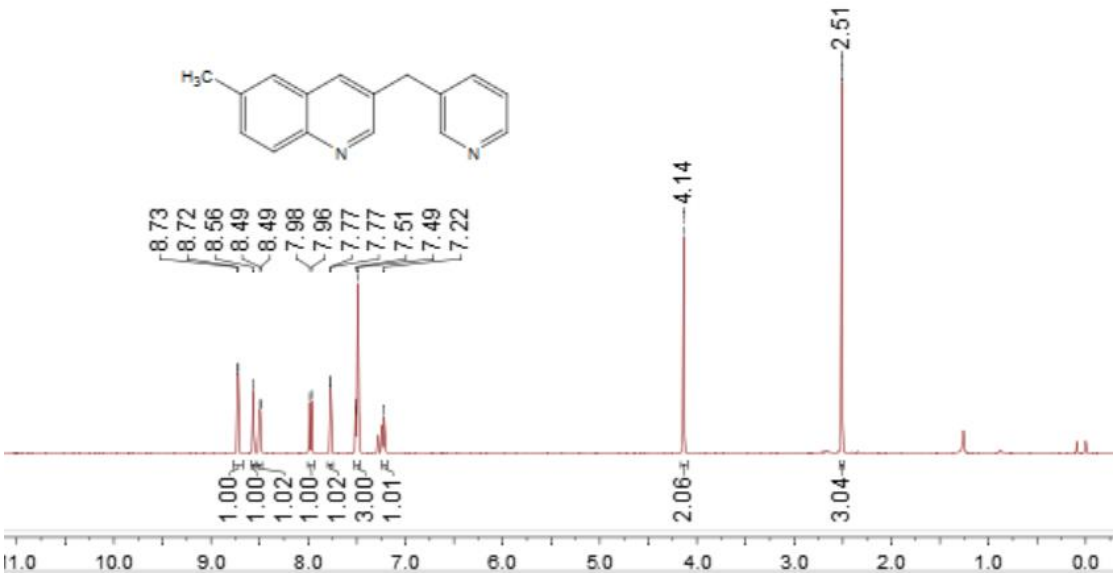
^{1}H-NMR spectrum of 6-methyl-3-(4-methylbenzyl)quinoline (3bf)



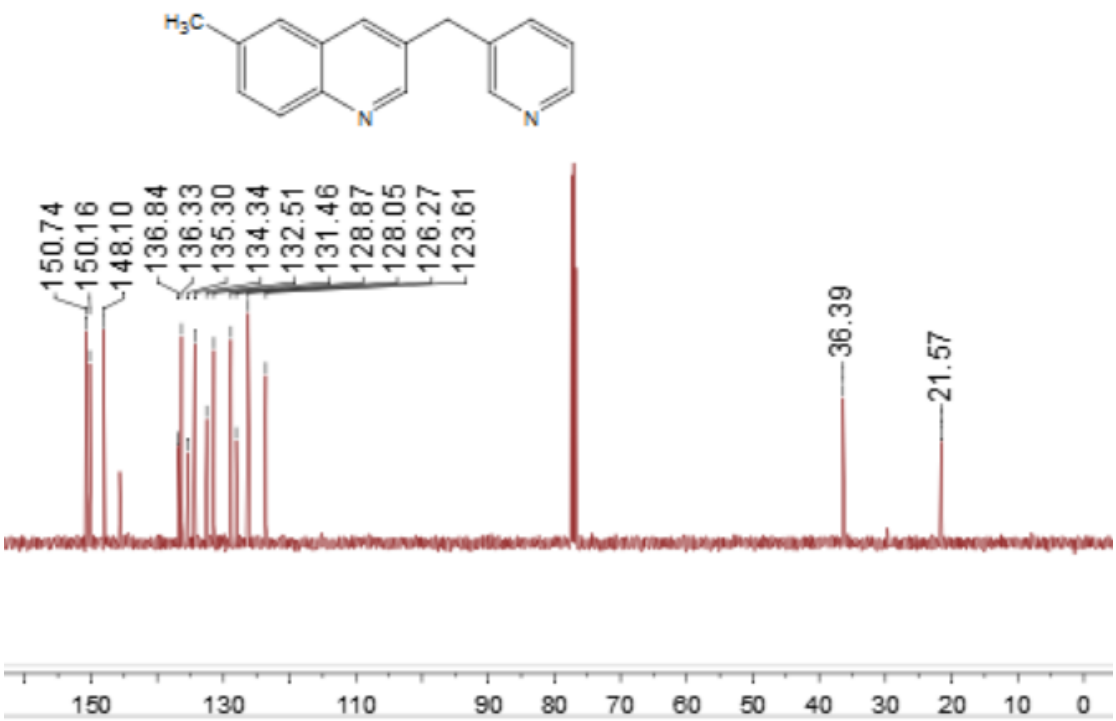
^{13}C-NMR spectrum of 6-methyl-3-(4-methylbenzyl)quinoline (3bf)



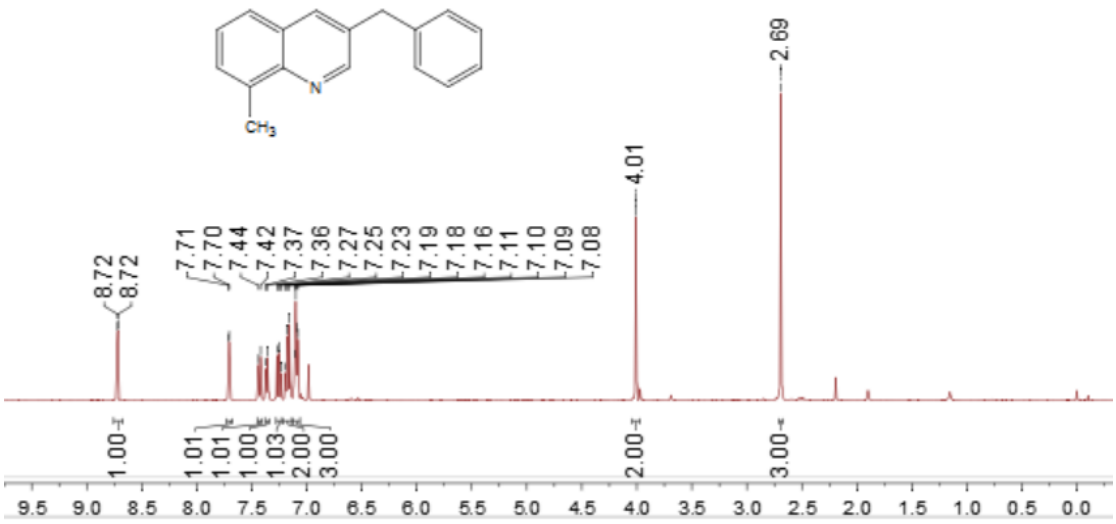
^{1}H-NMR spectrum of 6-methyl-3-(pyridin-3-ylmethyl)quinoline (3bl)



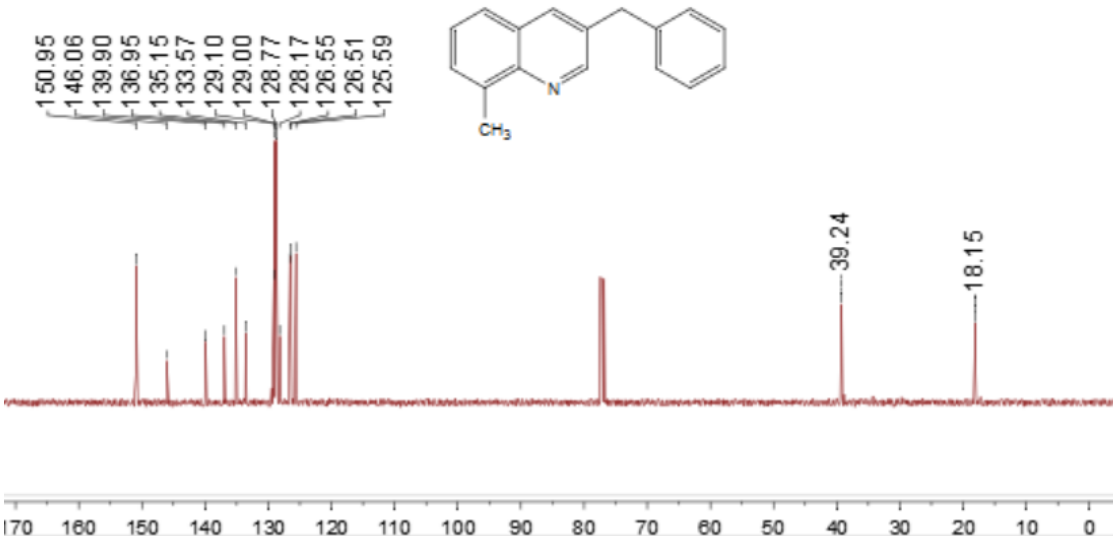
^{13}C-NMR spectrum of 6-methyl-3-(pyridin-3-ylmethyl)quinoline (3bl)



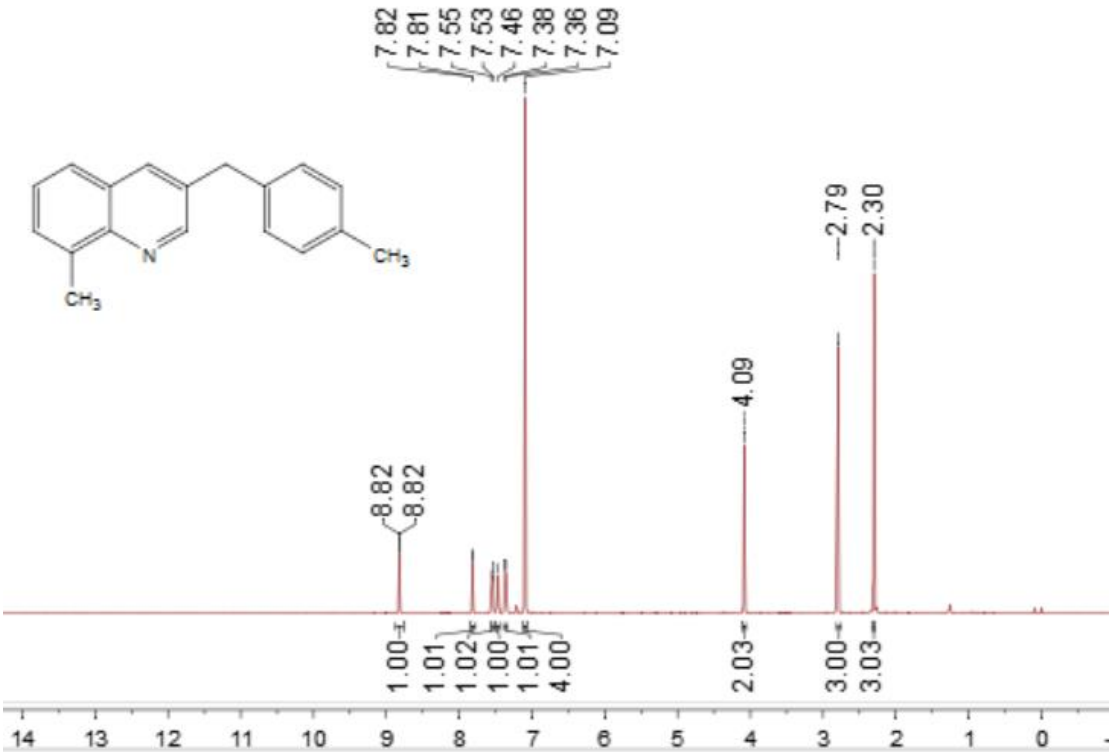
^{1}H-NMR spectrum of 3-benzyl-8-methylquinoline (3da)



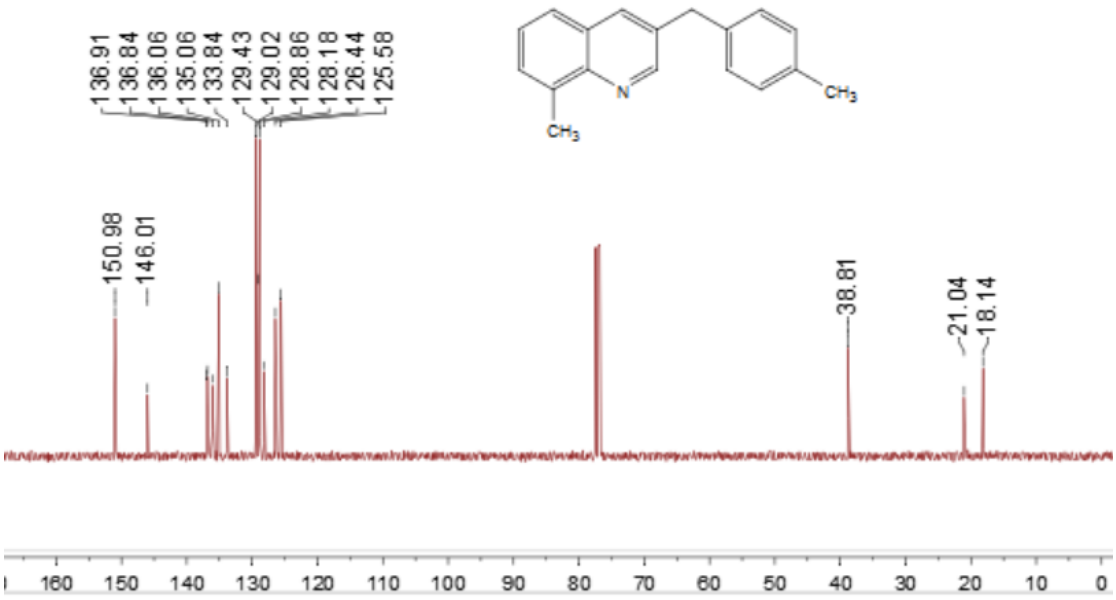
^{13}C-NMR spectrum of 3-benzyl-8-methylquinoline (3da)



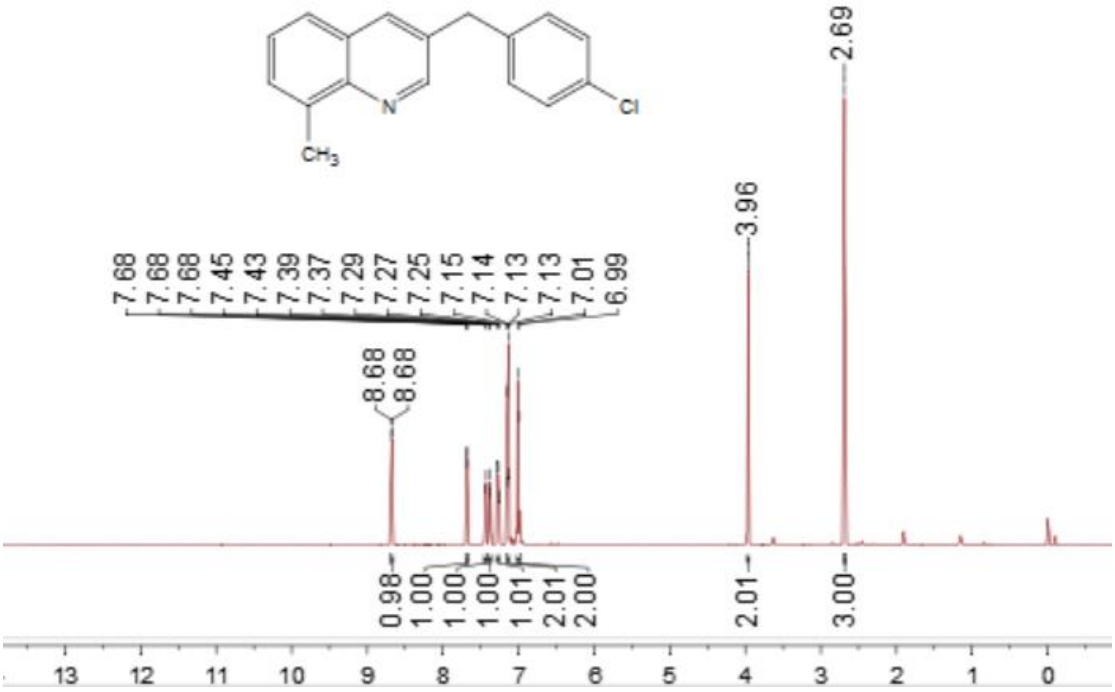
^{1}H-NMR spectrum of 8-methyl-3-(4-methylbenzyl)quinoline (3df)



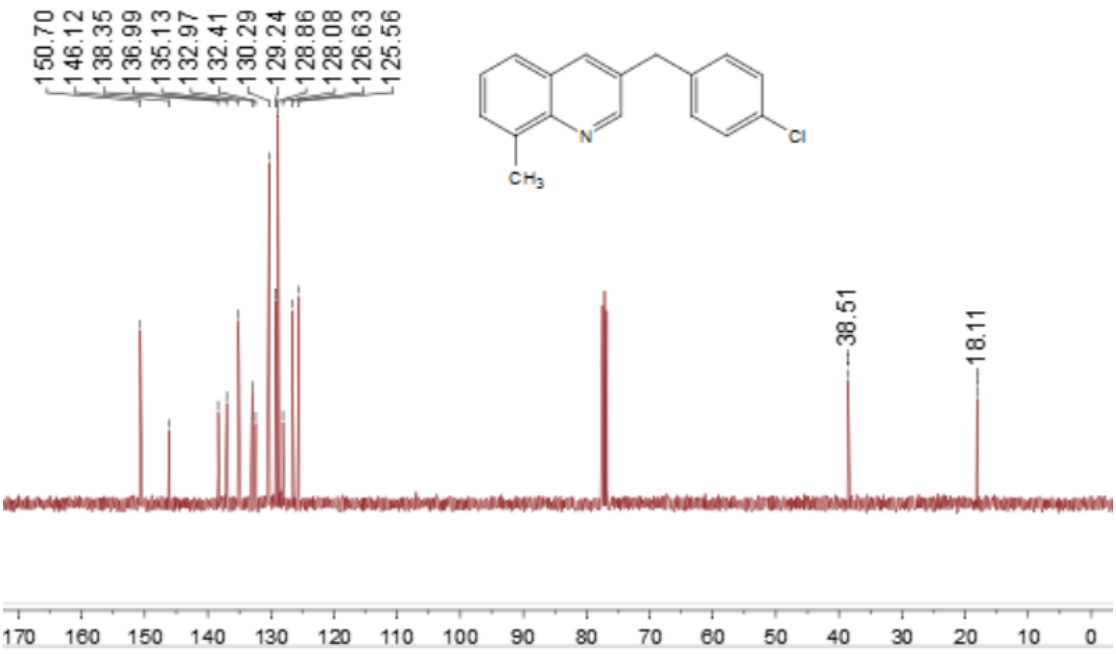
^{13}C-NMR spectrum of 8-methyl-3-(4-methylbenzyl)quinoline (3df)



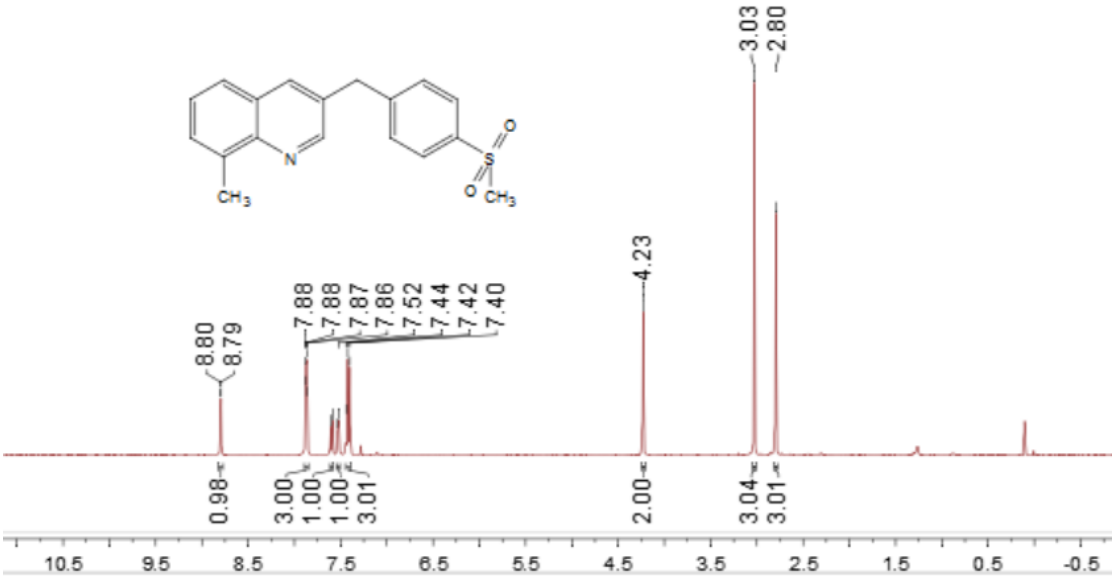
^{1}H-NMR spectrum of 3-(4-chlorobenzyl)-8-methylquinoline (3db)



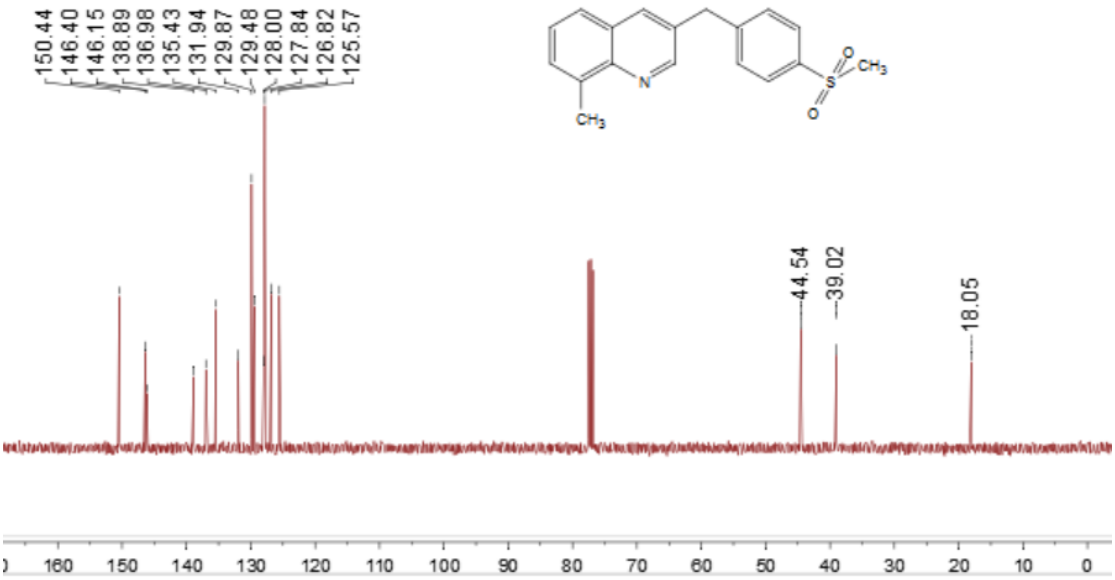
^{13}C-NMR spectrum of 3-(4-chlorobenzyl)-8-methylquinoline (3db)



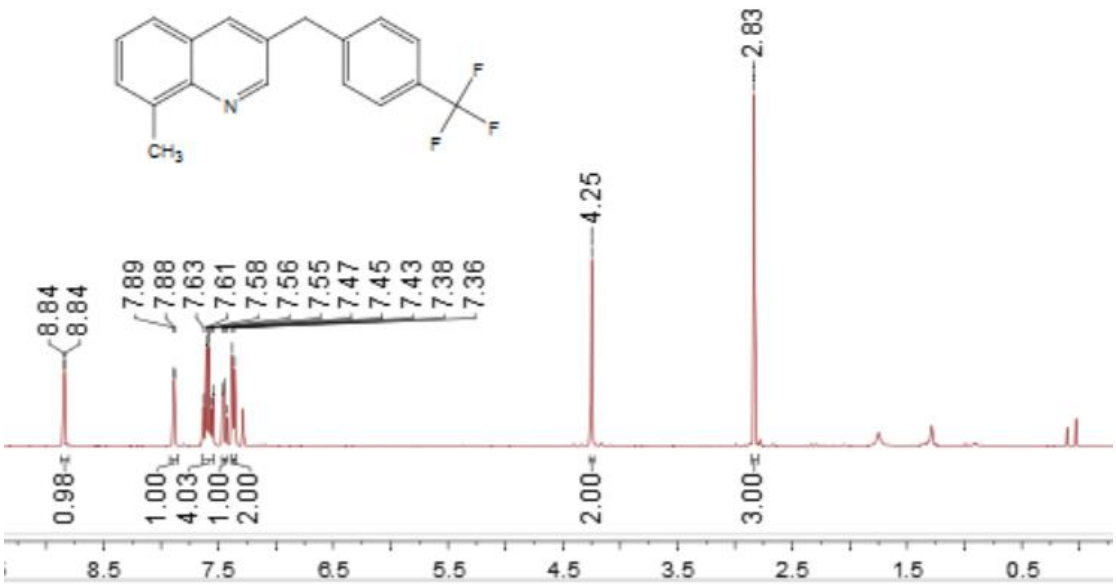
^{1}H-NMR spectrum of 8-methyl-3-(4-(methylsulfonyl)benzyl)quinoline (3dd)



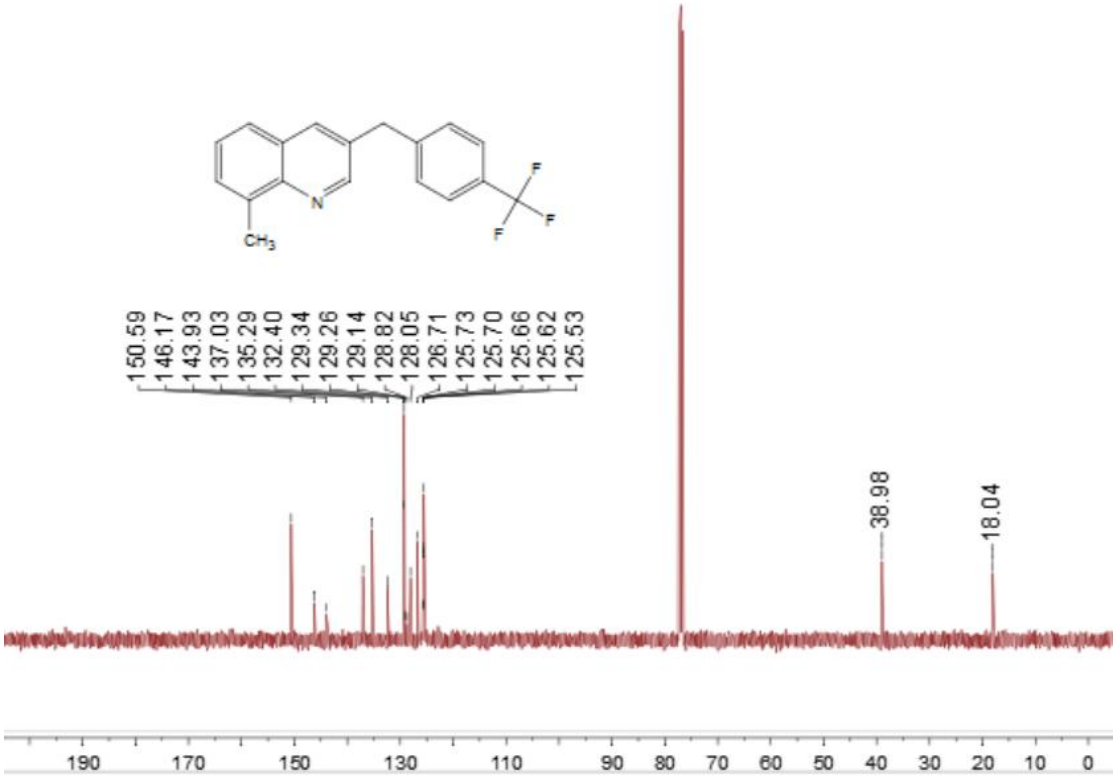
^{13}C-NMR spectrum of 8-methyl-3-(4-(methylsulfonyl)benzyl)quinoline (3dd)



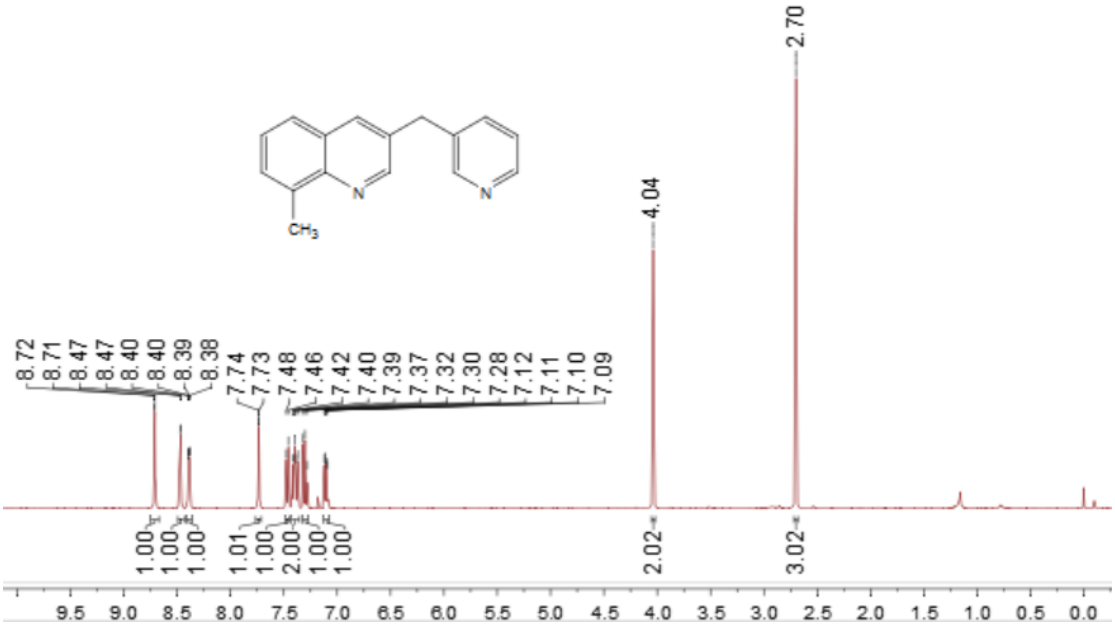
^{1}H-NMR spectrum of 8-methyl-3-(4-(trifluoromethyl)benzyl)quinoline (3do)



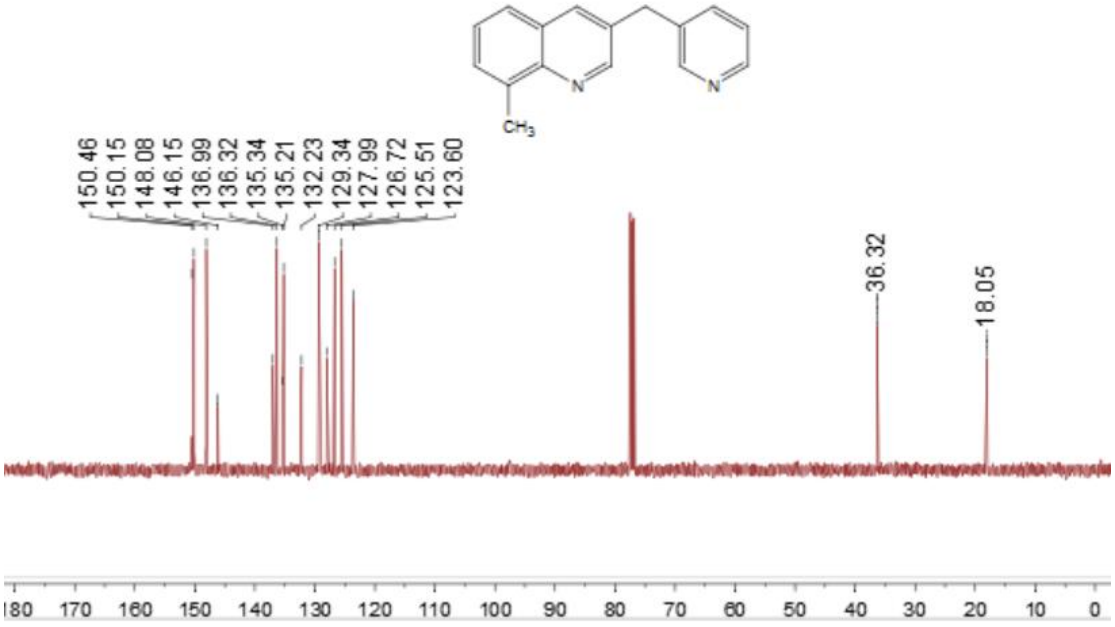
^{13}C-NMR spectrum of 8-methyl-3-(4-(trifluoromethyl)benzyl)quinoline (3do)



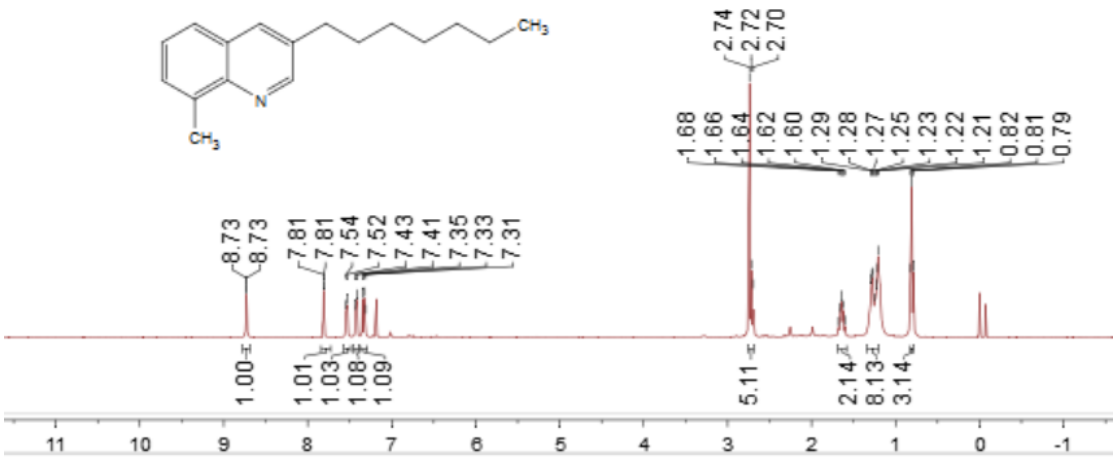
^{1}H-NMR spectrum of 8-methyl-3-(pyridin-3-ylmethyl)quinoline (3dl)



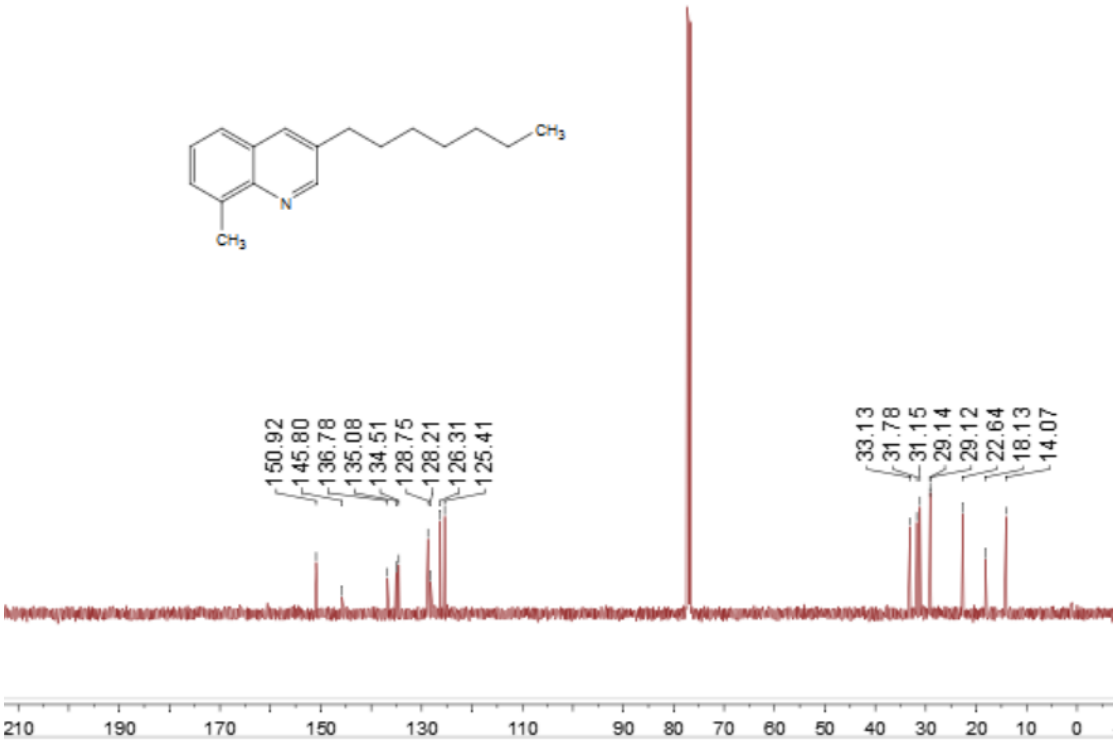
^{13}C-NMR spectrum of 8-methyl-3-(pyridin-3-ylmethyl)quinoline (3dl)



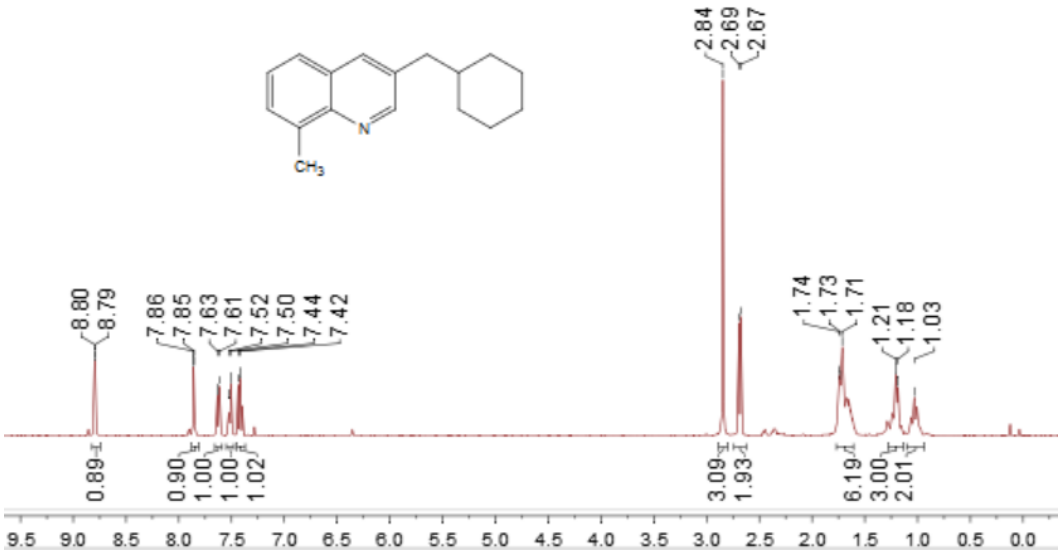
^{1}H-NMR spectrum of 3-heptyl-8-methylquinoline (3dp)



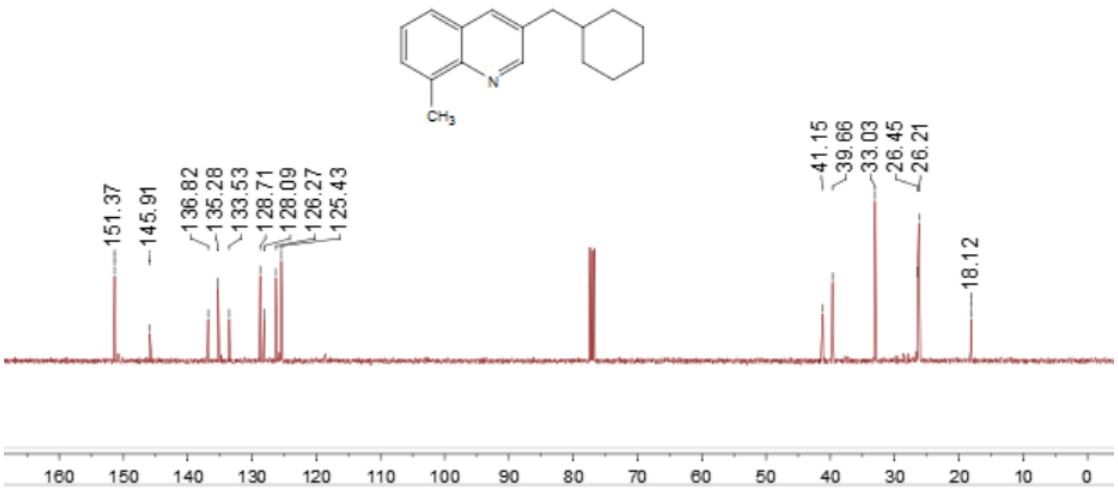
^{13}C-NMR spectrum of 3-heptyl-8-methylquinoline (3dp)



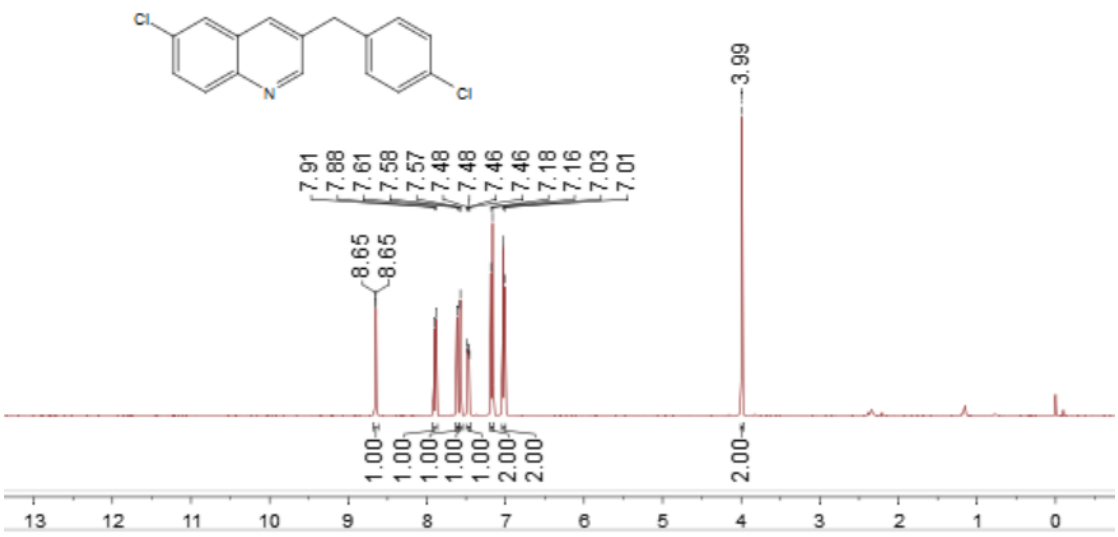
^{1}H-NMR spectrum of 3-(cyclohexylmethyl)-8-methylquinoline (3dq)



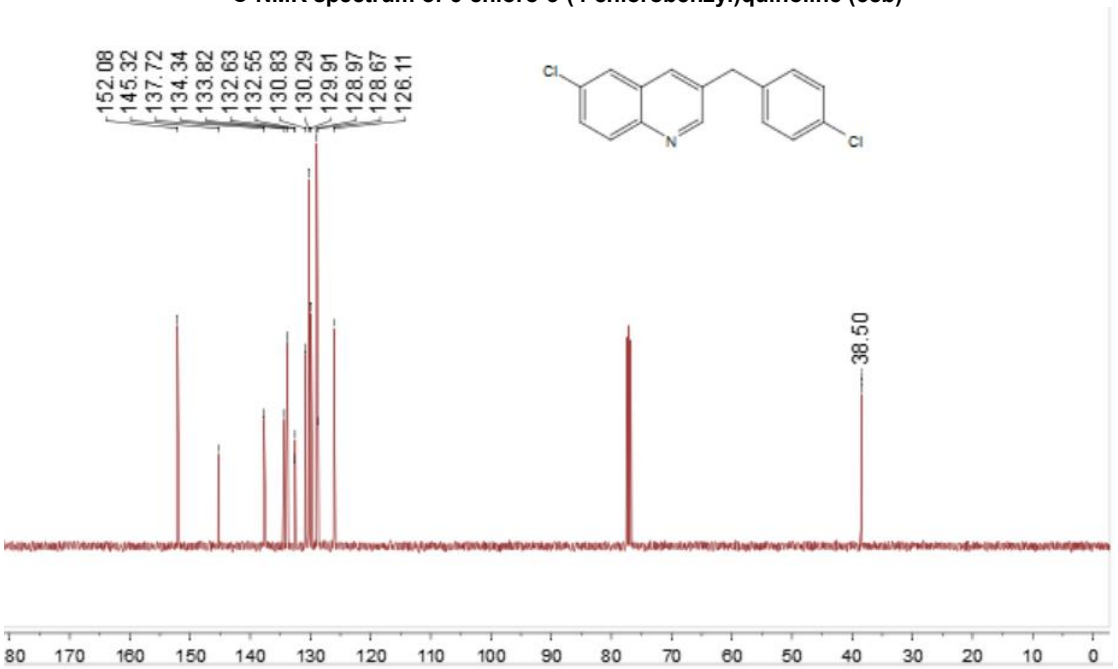
^{13}C-NMR spectrum of 3-(cyclohexylmethyl)-8-methylquinoline (3dq)



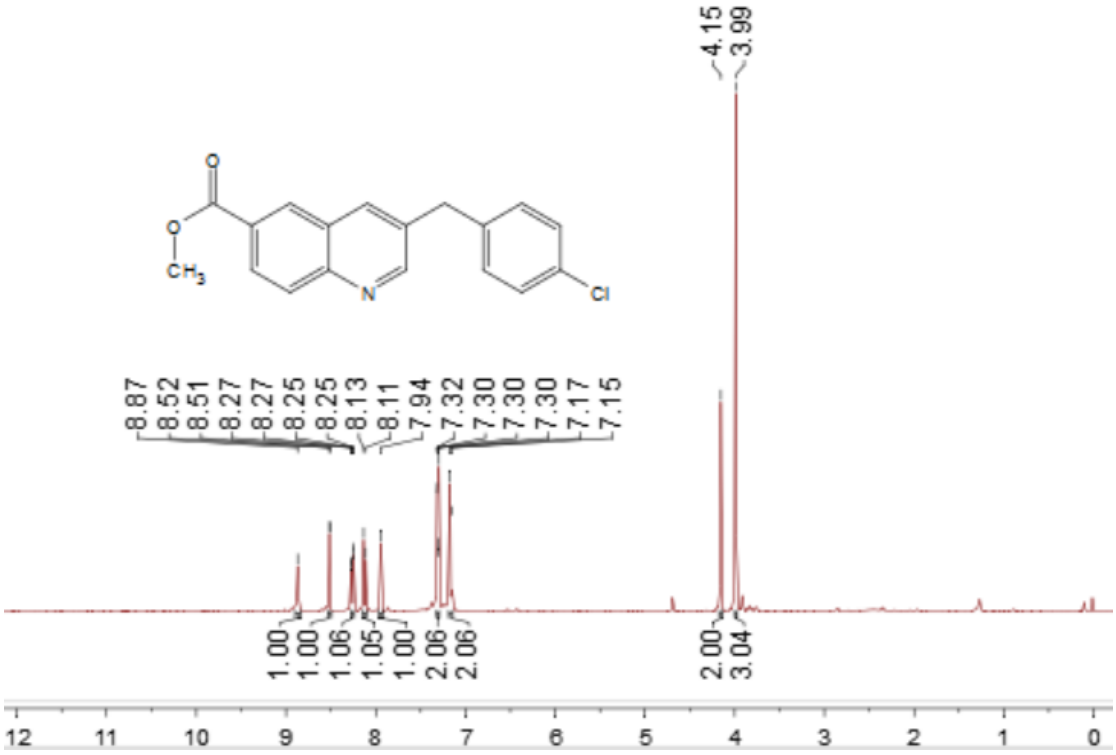
^{1}H-NMR spectrum of 6-chloro-3-(4-chlorobenzyl)quinoline (3cb)



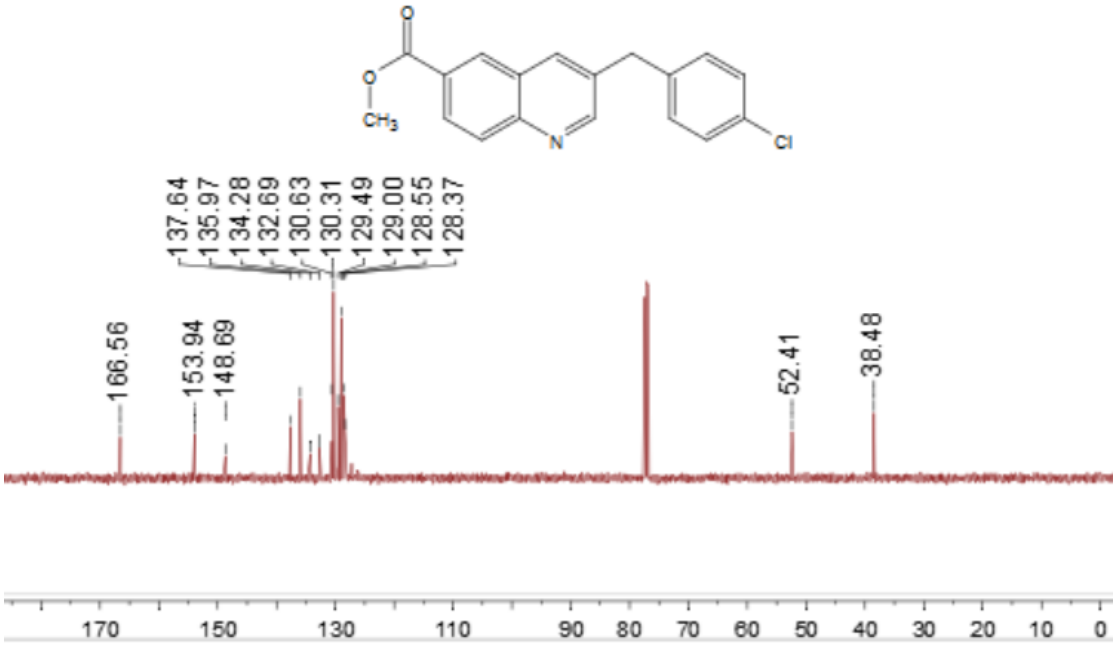
^{13}C-NMR spectrum of 6-chloro-3-(4-chlorobenzyl)quinoline (3cb)



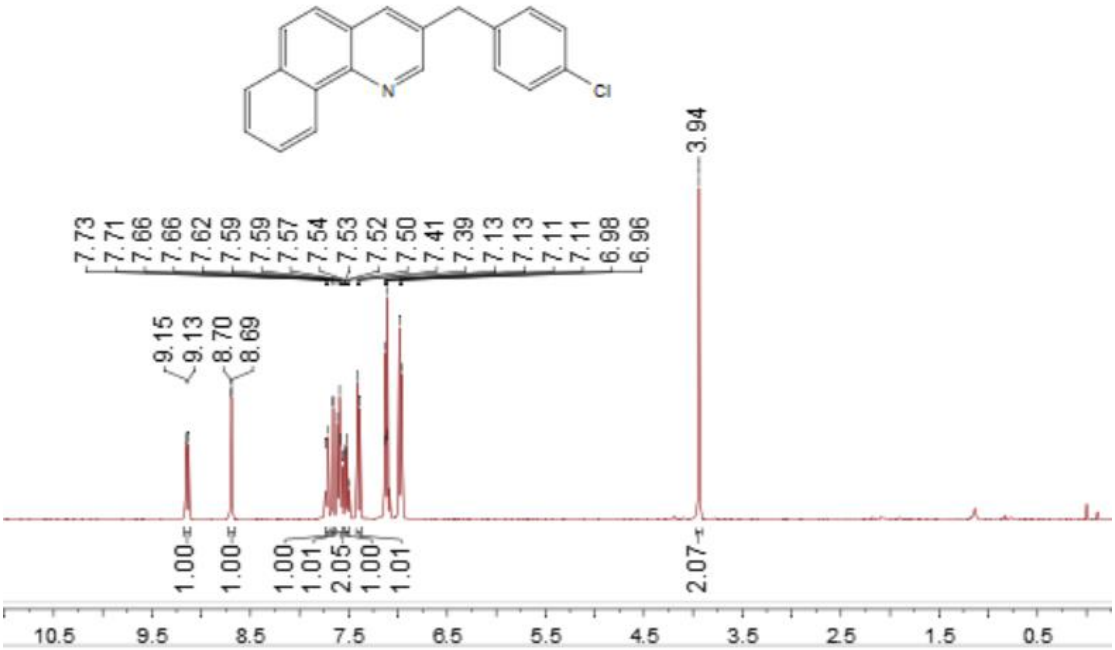
^{1}H-NMR spectrum of methyl 3-(4-chlorobenzyl)quinoline-6-carboxylate (3eb)



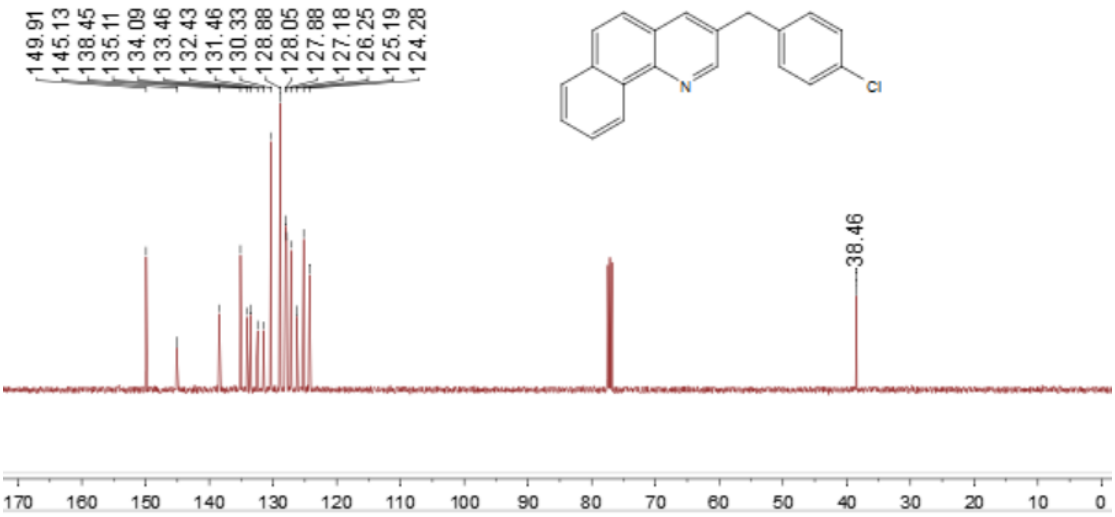
^{13}C-NMR spectrum of methyl 3-(4-chlorobenzyl)quinoline-6-carboxylate (3eb)



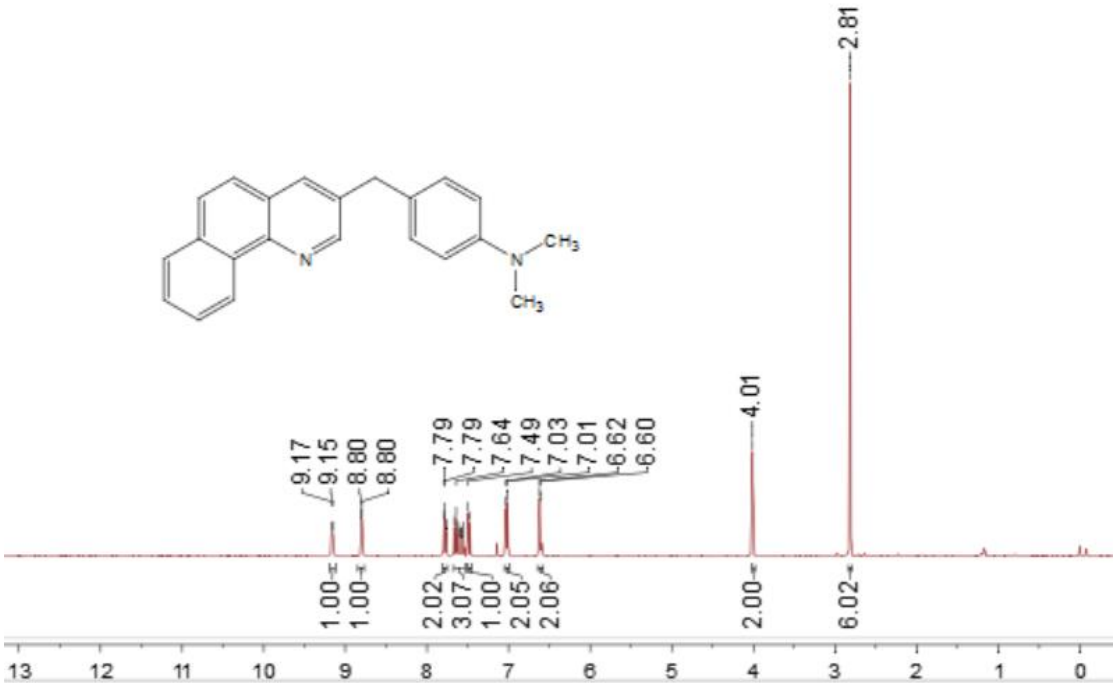
^{1}H-NMR spectrum of 3-(4-chlorobenzyl)benzo[h]quinoline (3fb)



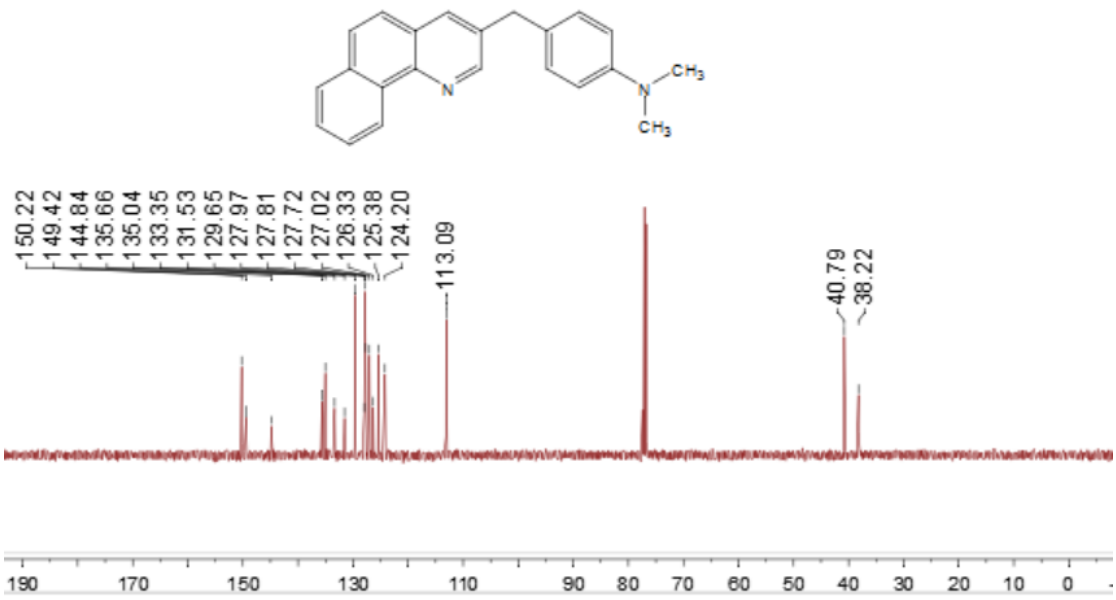
^{13}C-NMR spectrum of 3-(4-chlorobenzyl)benzo[h]quinoline (3fb)



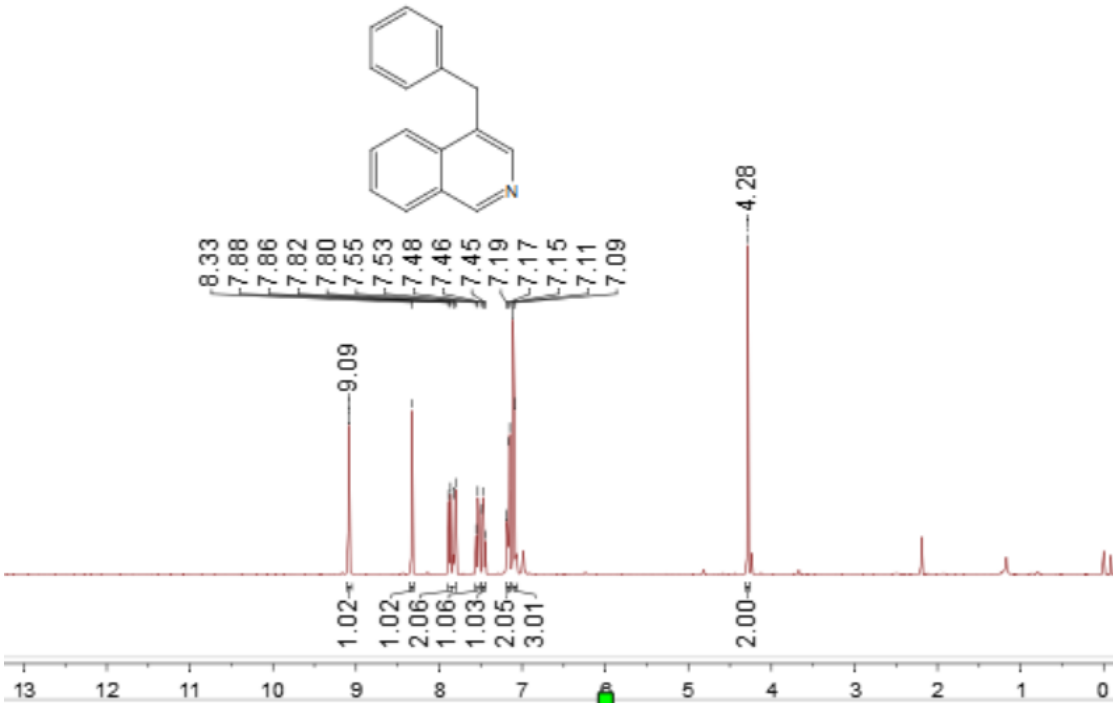
^{1}H-NMR spectrum of 4-(benzo[h]quinolin-3-ylmethyl)-N,N-dimethylaniline (3fj)



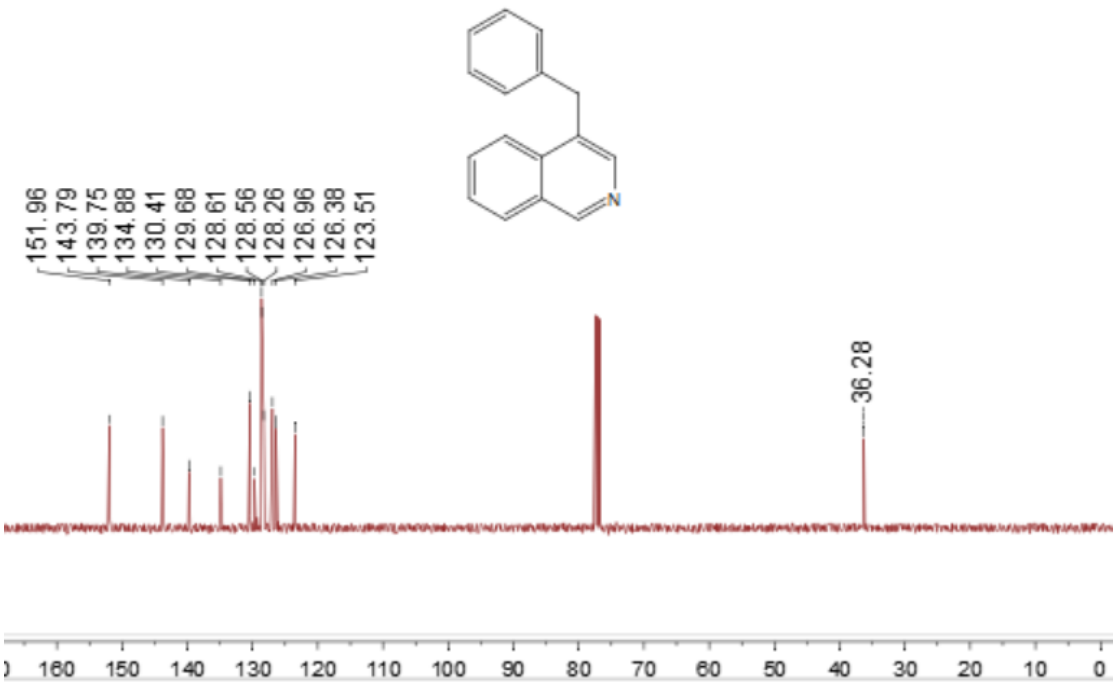
^{13}C-NMR spectrum of 4-(benzo[h]quinolin-3-ylmethyl)-N,N-dimethylaniline (3fj)



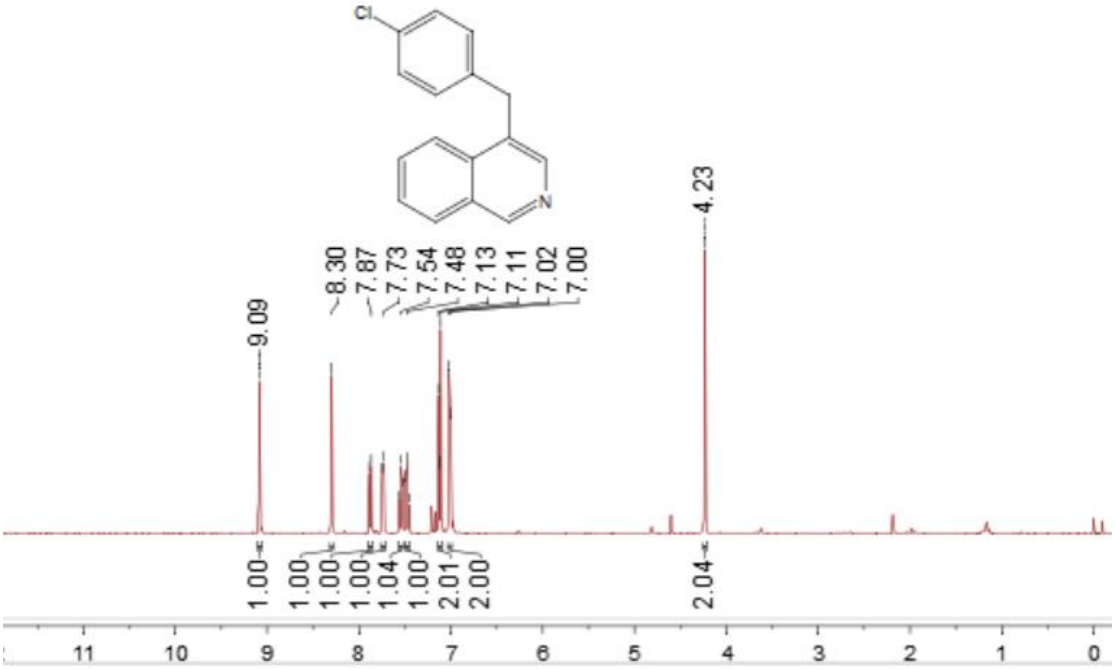
^{1}H-NMR spectrum of 4-benzylisoquinoline (3ga)



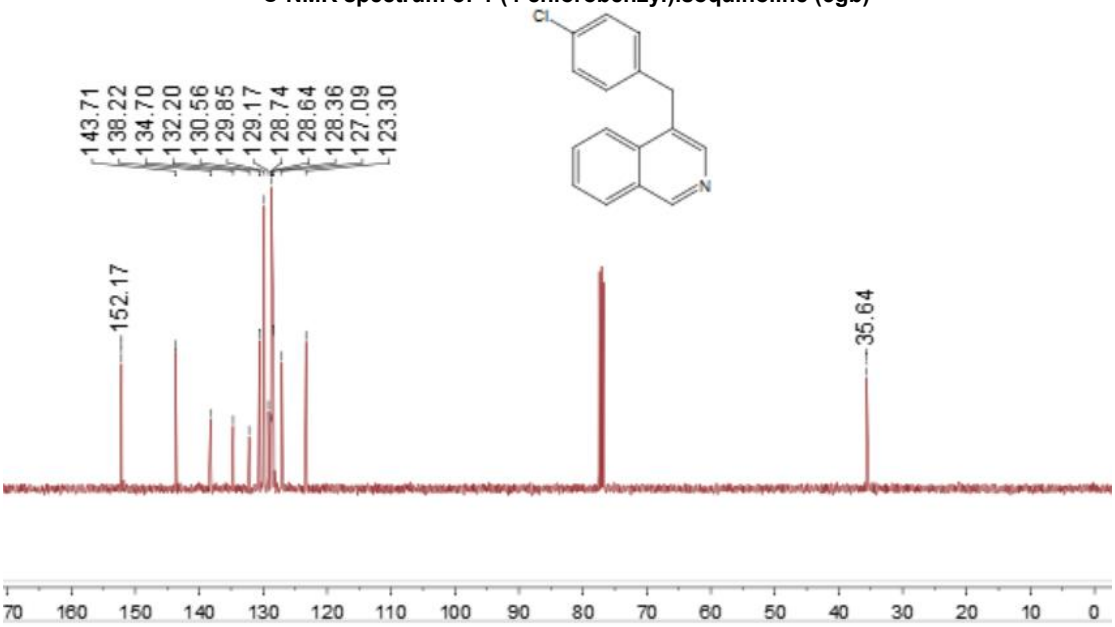
^{13}C-NMR spectrum of 4-benzylisoquinoline (3ga)



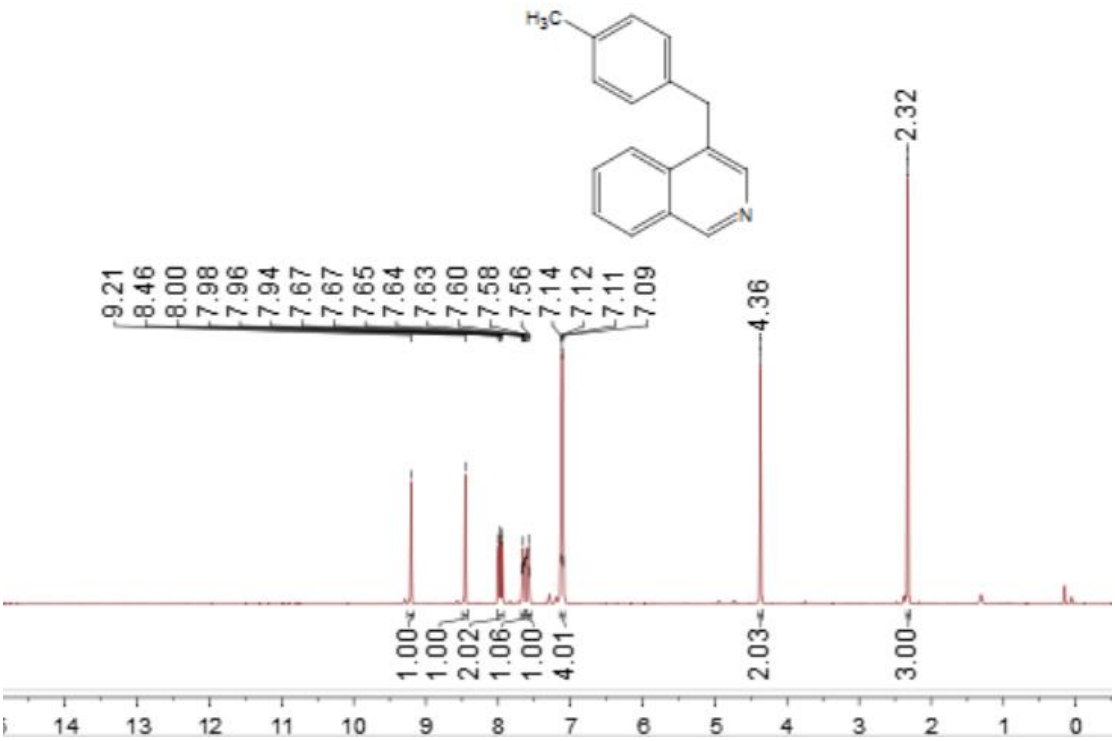
^{1}H-NMR spectrum of 4-(4-chlorobenzyl)isoquinoline (3gb)



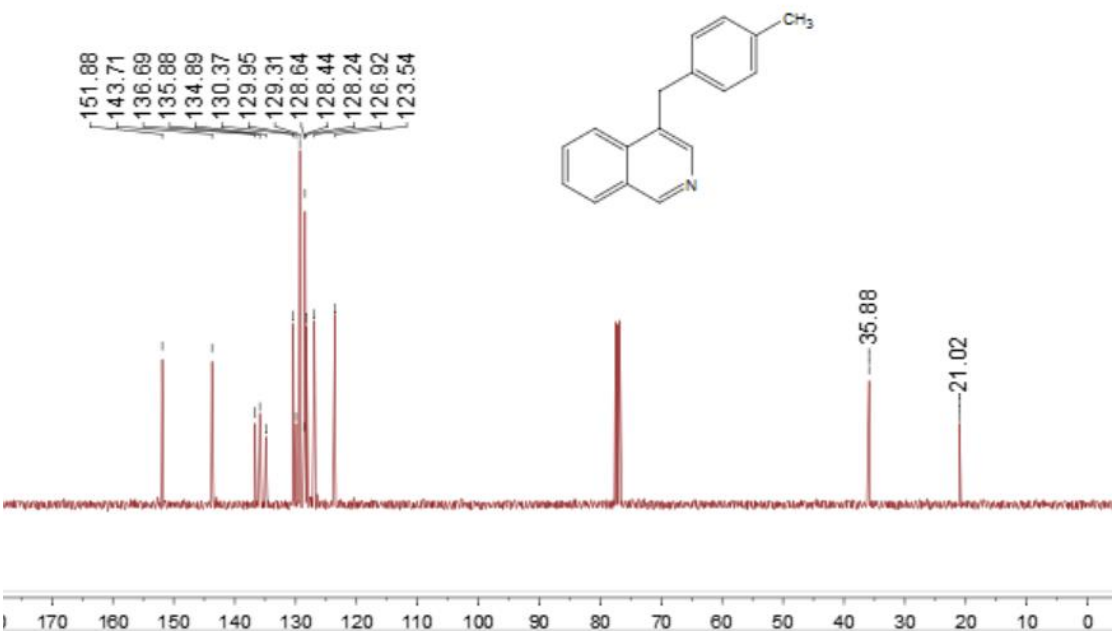
^{13}C-NMR spectrum of 4-(4-chlorobenzyl)isoquinoline (3gb)



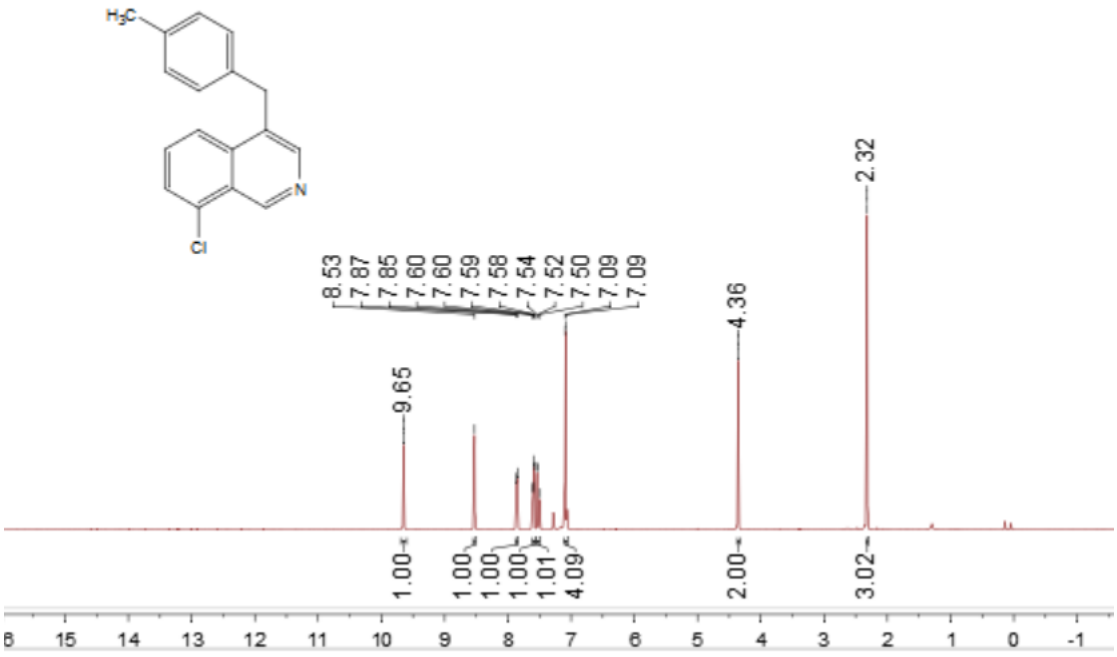
^{1}H-NMR spectrum of 4-(4-methylbenzyl)isoquinoline (3gf)



^{13}C-NMR spectrum of 4-(4-methylbenzyl)isoquinoline (3gf)



^{1}H-NMR spectrum of 8-chloro-4-(4-methylbenzyl)isoquinoline (3hf)



^{13}C-NMR spectrum of 8-chloro-4-(4-methylbenzyl)isoquinoline (3hf)