Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-Light-Induced 4CzIPN/LiBr System: A Tireless Electron Shuttle to Enable Reductive Deoxygenation of N-Heteroaryl Carbonyls

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1. General information

The reactions via general procedure was carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$ as solvent. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and HRMS data with those in literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Cyclic voltammograms were recorded with a CHI604E electrochemical analyzer/workstation at room temperature in anhydrous acetonitrile. *n*-Bu_4NBF_4 was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 40 $mV \cdot s^{-1}$.

2. General procedure for the synthesis of substrates.

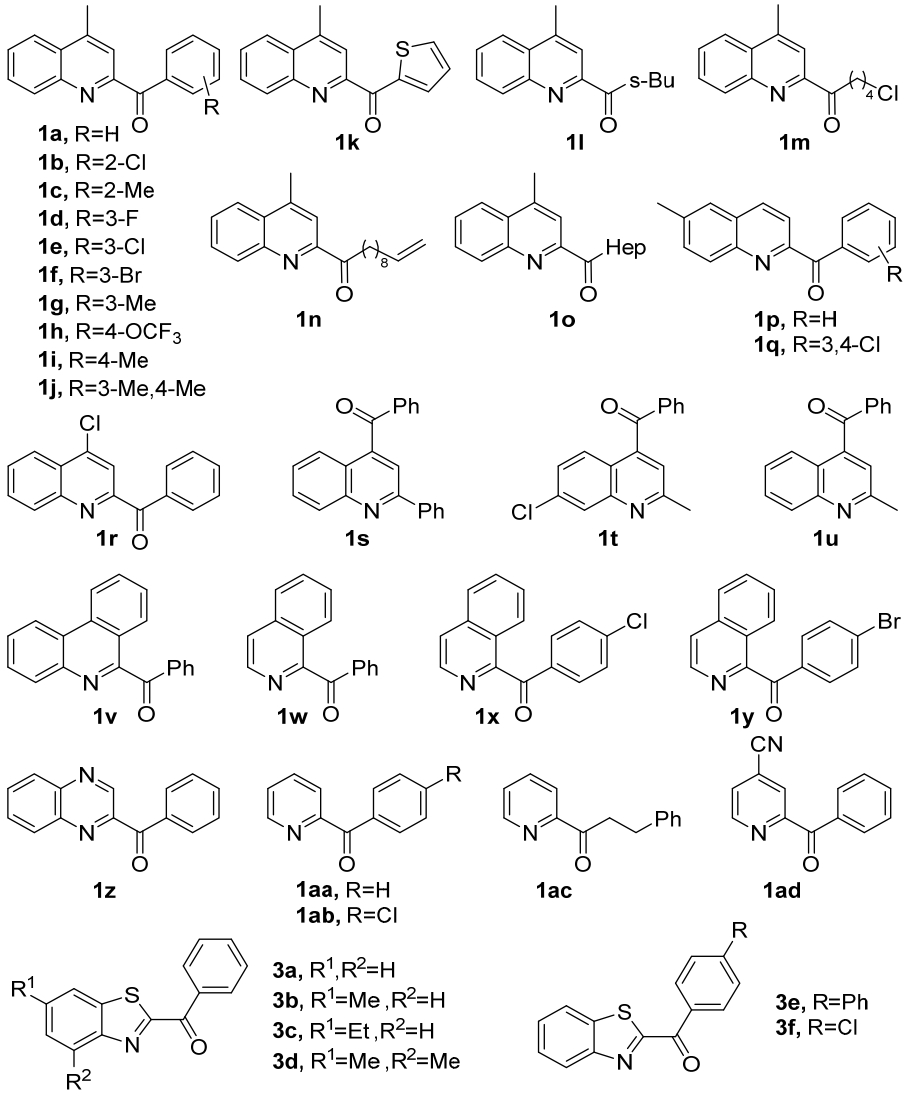
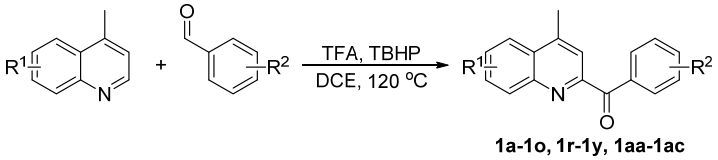


Figure S1. Starting materials.

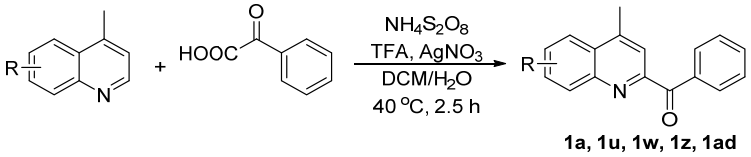
2.1 Synthesis of aryl N-heteroaryl ketones[1-3]

Method A: To the solution of 4-methylquinoline (0.25 mmol) in DCE (1.2 mL) was added benzaldehyde (0.5 mmol), TFA (0.25 mmol), and TBHP (70% solution in water, 0.75 mmol). The resulting solution was heated at 110 °C with vigorous stirring for 12 h. Then the reaction mixture was cooled to room temperature and treated with saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate (3×25 mL), and the combined organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated under vacuum. The residue was purified by flash chromatography using petroleum ether/ethyl acetate (60:1 to 10:1).



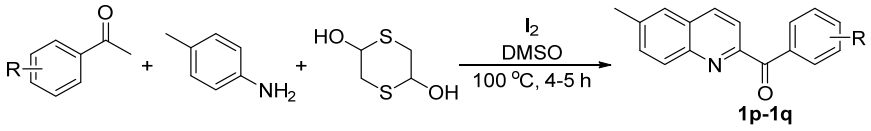
1a-1o, 1r-1y, 1aa-1ac

Method B: A mixture of 4-methylquinoline (2.5 mmol), aryl-keto acid (7.5 mmol), $AgNO_3$ (0.2 mmol), $NH_4S_2O_8$ (0.2 mmol), and CF_3COOH (0.2 mmol) in 25 mL of water and 25 mL of CH_2Cl_2 was stirred for 2 h at 40 °C. The aqueous solution was made basic with NaOH, the organic solvent was separated, and the aqueous solution was further extracted with CH_2Cl_2 (3×25 mL). The reaction products were isolated by flash chromatography using petroleum ether/ethyl acetate (5:1).



1a, 1u, 1w, 1z, 1ad

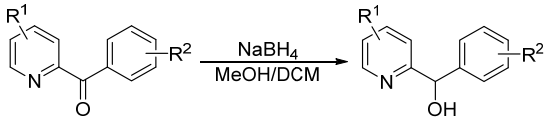
Method C: A mixture of acetophenone (1.0 mmol), iodine (1.6 mmol) in DMSO (3 mL), the mixture was stirred at 100 ℃, till almost completed conversion of the substrates by TLC, then 1,4-dithane-2,5-diol (1.0 mmol), Aniline (1.0 mmol) were added to the reaction vessel. The solution extracted with ethyl acetate (3×25 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (3×50 mL). The extract was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The reaction products were isolated by flash chromatography using petroleum ether/ethyl acetate (10:1).



1p-1q

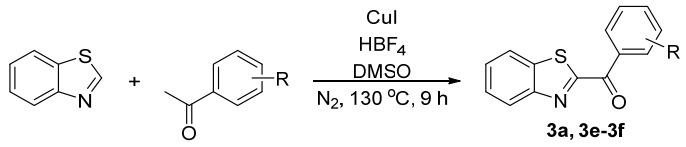
2.2 Synthesis of aryl N-heteroaryl methanols[4]

The corresponding aryl N-heteroaryl ketone (0.4 mmol) was dissolved in 2.0 mL MeOH and 0.5 mL DCM, and $NaBH_4$ (0.8 mmol) was added slowly. The mixture was stirred for 3-6 h. Then 10.0 mL of H_2O was added slowly, and the residue was extracted with ethyl acetate (3×25 mL). The combined organic layer was dried over $MgSO_4$ and evaporated in vacuo. The product was further purified by silica gel column using petroleum ether/ethyl acetate (2:1).



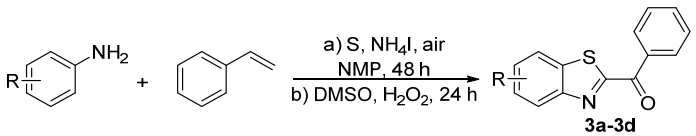
2.3 Synthesis of benzothiazol-2-aryl methanones[5,6]

Method A: A sealed tube was charged with benzothiazole (0.5 mmol), CuI (2 mol%), acetophenone (1.0 mmol), HBF_4 (0.25 mmol, 40% in aq.) and DMSO (0.75 mL). The resulting solution was purged by N_2 and sealed, then stirred at 130 °C under N_2 for 9 hours. After cooling down to room temperature, ethyl acetate (10 mL) was added, and the organic layer was washed with saturate $NaHCO_3$ solution and brine. The combined aqueous layers were extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed via rotary evaporator and the product was purified by silica gel column using petroleum ether/ethyl acetate (30:1).



3a, 3e-3f

Method B: Styrene (0.4 mmol), aniline (1.0 mmol), sulfur (1.6 mmol), NH_4I (0.4 mmol), N-methyl-2-pyrrolidone (1.2 mL) were added to a 10 mL oven-dried reaction vessel. The sealed reaction vessel was stirred at 160 °C for 48 h. And then 30% hydrogen peroxide aqueous solution (1.0 equiv.), dimethyl sulfoxide (1.0 mL) was added to the reaction vessel. The sealed reaction vessel was stirred at 110 °C for 24 h. After cooling to room temperature, the reaction was diluted with ethyl acetate and washed with saturated sodium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×25 mL). The combined organic layer was dried over magnesium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1).



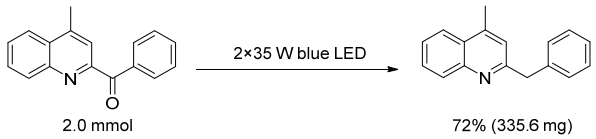
3a-3d

3. General procedure for the reductive deoxygenation of heteroaryl ketones.

Reaction set-up for irradiation of mixture with blue LEDs: A commercially available blue LED (35W, HIPAR30) was purchased from Shenzhen Jing Feng Times Lighting Technology Co., Ltd as the reaction light source, and the homemade insulation attached to the apparatus was used to maintain the reaction temperature at 60 ºC.

A 10 mL reaction vessel was charged with LiBr (4.3 mg, 0.05 mmol), 4CzIPN (2.4 mg, 0.003 mmol), 2-benzoyl-4-methylquinoline (**1a**, 24.7 mg, 0.1 mmol), CH_3SO_3H (20 μL, CH_3SO_3H/H_2O=1/5 aqueous (v/v,), 0.1 mmol), $(PhO)_2PO_2H$ (15.0 mg, 0.06 mmol), H_2O (50 equiv) and PhCl (1.5 mL), The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). Then, benzaldehyde (21 μL, 0.2 mmol, 2.0 equiv) was added by syringe. The resulting mixture was stirred for 60 h under irradiation with a 35 W blue LEDs at 60 ºC. After cooling to room temperature, the crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3×10 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) (petroleum ether/ethyl acetate = 10:1) to give product **2a** as a yellow solid (20.1 mg, 86%), mp: 63 – 65 °C.

Scale-up experiment:



A 100 mL single neck round bottom flask was charged with LiBr (86.0 mg, 0.05 mmol), 4CzIPN (48.0 mg, 0.003 mmol), 2-benzoyl-4-methylquinoline (494.0 mg, 2.0 mmol), CH_3SO_3H (aq., 400 μL, 20.0 mmol), $(PhO)_2PO_2H$ (300.0 mg, 0.06 mmol), H_2O (1.56 mL) and PhCl (25.0 mL), The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). Then, benzaldehyde (410 μL, 4.0 mmol, 2.0 equiv) was added by syringe. The resulting mixture was stirred for 64 h under irradiation with two 35 W blue LEDs at 60 ºC. After cooling to room temperature, the crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3×50 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh, petroleum ether/ethyl acetate = 10:1) to give product **2a** as a yellow solid (335.6 mg, 72%).

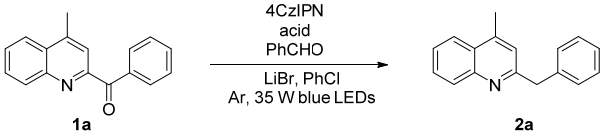
4. Optimization of reaction conditions

Table S1. Screening of solvent[a]

Entry	Solvent	Yield (%)[b]
1	DCM	74
2	CH_3CN	37
3	acetone	32
4	PhCl	89 (86)
5	1,4-dioxane	49
6	DMSO	N.D.
7	NMP	6
8	EtOH	53
9	t-BuOH	60
10[c]	PhCl	63
11[d]	PhCl	60

[a] Reaction conditions: **1a** (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), CF_3SO_3H (aq., 1.0 equiv), $(PhO)_2PO_2H$ (0.6 equiv), H_2O (50 equiv), solvent (1.5 mL), 60 ºC under Ar, 60 h. [b] Yields were determined by crude ^1H NMR with CH_2Br_2 as internal standard and isolated yield was given in parentheses. [c] PhCl (1.0 mL). [d] LiBr (1.0 equiv). N.D.= Not Detected.

Table S2. Screening of acids[a]

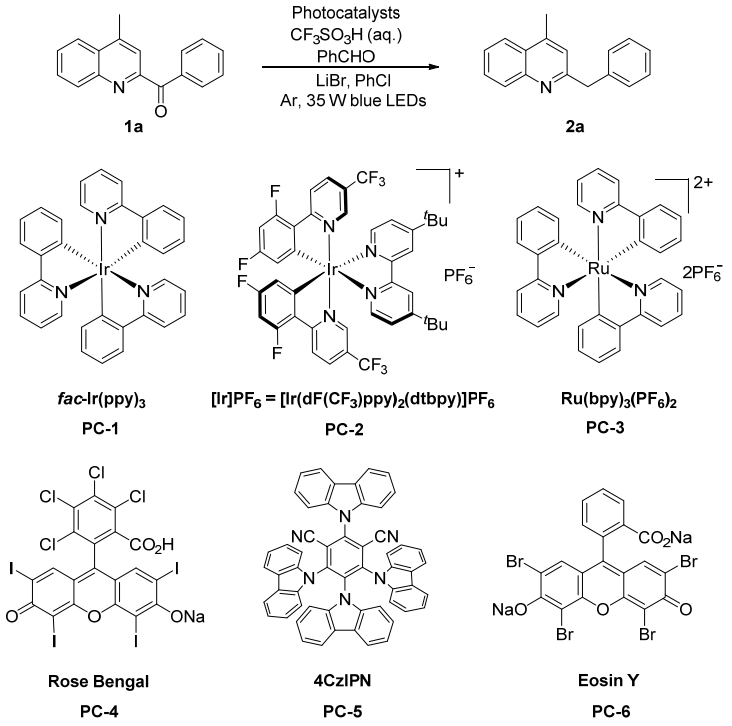


Entry	Acid	Yield (%)[b]
1	-	37
2	CF_3SO_3H	59
3	p-TsOH·H_2O	80
4	TFA	54
5	p-TsOH·$5H_2O$	68
6	AcOH·$5H_2O$	20
7	CF_3SO_3H·$5H_2O$	89 (86)
8	TFA·$5H_2O$	61
9	MSA·$5H_2O$	43
10[c]	CF_3SO_3H·$5H_2O$	76
11[d]	CF_3SO_3H·$5H_2O$	62

12[e]	$CF_3SO_3H{\cdot}5H_2O$	61
13[f]	$CF_3SO_3H{\cdot}5H_2O$	61

[a] Reaction conditions: **1a** (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), acid (aq., 1.0 equiv), $(PhO)_2PO_2H$ (0.6 equiv), H_2O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. [b] Yields were determined by crude ^1H NMR with CH_2Br_2 as internal standard and isolated yield was given in parentheses. [c] $(PhO)_2PO_2H$ (1.0 equiv). [d] No $(PhO)_2PO_2H$. [e] CF_3SO_3H (aq., 0.75 equiv). [f] CF_3SO_3H (aq., 0.5 equiv).

Table S3. Screening of photocatalyst[a]



Entry	Photocatalyst	Yield (%)[b]
1	-	N.D.
2	**PC-1**	trace
3	**PC-2**	42
4	**PC-3**	trace
5	**PC-4**	trace
6	**PC-5**	89(86)
7	**PC-6**	9
8[c]	**PC-5**	59
9[d]	**PC-5**	N.D.

[a] Reaction conditions: **1a** (0.1 mmol), PhCHO (2.0 equiv), Photocatalyst (3 mol %), LiBr (0.5 equiv), CF_3SO_3H (aq., 1.0 equiv), $(PhO)_2PO_2H$ (0.6 equiv), H_2O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. [b] Yields were determined by crude ^1H NMR with CH_2Br_2 as internal standard and isolated yield was given in parentheses. [c] PC-5 (2.0 mol %). [d] No light.

Table S4. Screening of additive[a]

Entry	additive	Yield (%)[b]
1	-	12
2	NaBr	71
3	LiBr	89 (86)
4	LiCl	24
5	KI	N.D.
6	LiBr	69

[a] Reaction conditions: **1a** (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), additive (0.5 equiv), CF_3SO_3H (aq., 1.0 equiv), $(PhO)_2PO_2H$ (0.6 equiv), H_2O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. [b] Yields were determined by crude ^1H NMR with CH_2Br_2 as internal standard and isolated yield was given in parentheses. [c] LiBr (1.0 equiv).

Table S5. Screening of reductant[a]

Entry	Reductant	Yield (%)[b]
1	PhCHO	89 (86)
2[c]	PhCHO	38
3	*p*-Chlorobenzaldehyde	59
4	Biphenyl-4-carboxaldehyde	50
5	*p*-Methyl benzaldehyde	70
6	*p*-Methoxy benzaldehyde	57
7	Ph_3SiH	52
8[d]	Et_3SiH	65
9	$(i\text{-}Pr)_3SiH$	52
10	Benzyl alcohol	67

[a] Reaction conditions: **1a** (0.1 mmol), reductant (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), CF_3SO_3H (aq., 1.0 equiv), $(PhO)_2PO_2H$ (0.6 equiv), H_2O (50 equiv), PhCl (1.5 mL), 60 ºC under Ar, 60 h. [b] Yields were determined by crude ^1H NMR with CH_2Br_2 as internal standard and isolated yield was given in parentheses. [c] Benzaldehyde (1.0 equiv). [d] Et_3SiH (4.0 equiv).

Table S6. Screening of the temperature and time[a]

Entry	Temp./Time	Yield (%)[b]
1	60 ºC, 48 h	58
2	65 ºC, 48 h	58 (56)
3	55 ºC, 60 h	(68)
4	60 ºC, 60 h	89 (86)
5	65 ºC, 60 h	51 (48)

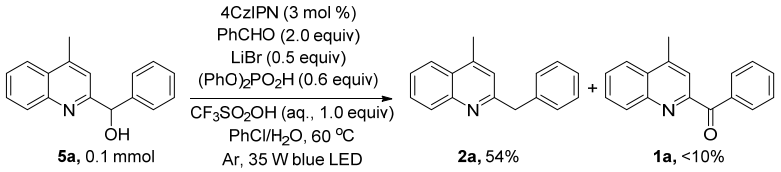
[a] Reaction conditions: **1a** (0.1 mmol), PhCHO (2.0 equiv), 4CzIPN (3 mol %), LiBr (0.5 equiv), CF_3SO_3H (aq., 1.0 equiv), $(PhO)_2PO_2H$ (0.6 equiv), H_2O (50 equiv), PhCl (1.5 mL), under Ar. [b] Yields were determined by crude ^1H NMR with CH_2Br_2 as internal standard and isolated yield was given in parentheses. [c] PhCl (1.0 mL). [d] LiBr (1.0 equiv).

5. Mechanistic studies

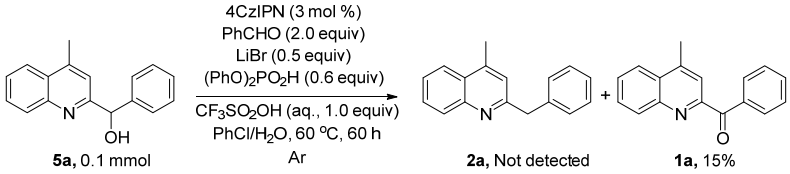
5.1. Radical trapping experiments

5.2. Exploratory experiments

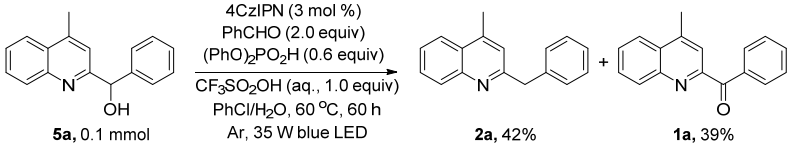
(1) Within 12 h



(2) In dark



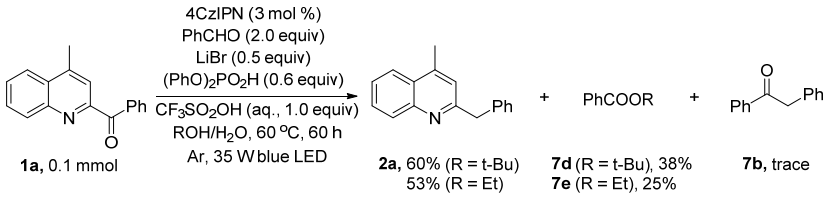
(3) No LiBr



(4) Competitive reactivity of C_2 and C_4 carbonyls

(5) Competitive reactivity of heteroaryl ketone and alcohol

(6) Alcohol as solvent

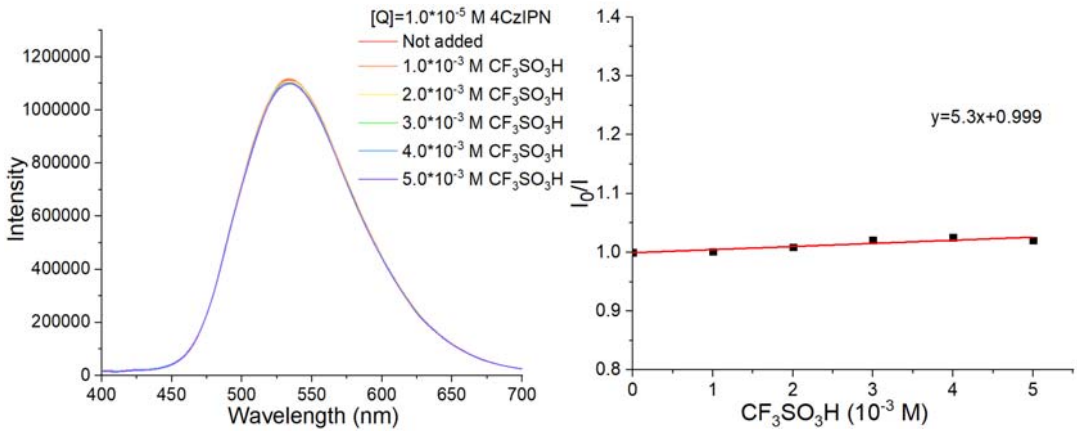


5.3. Stern–Volmer quenching

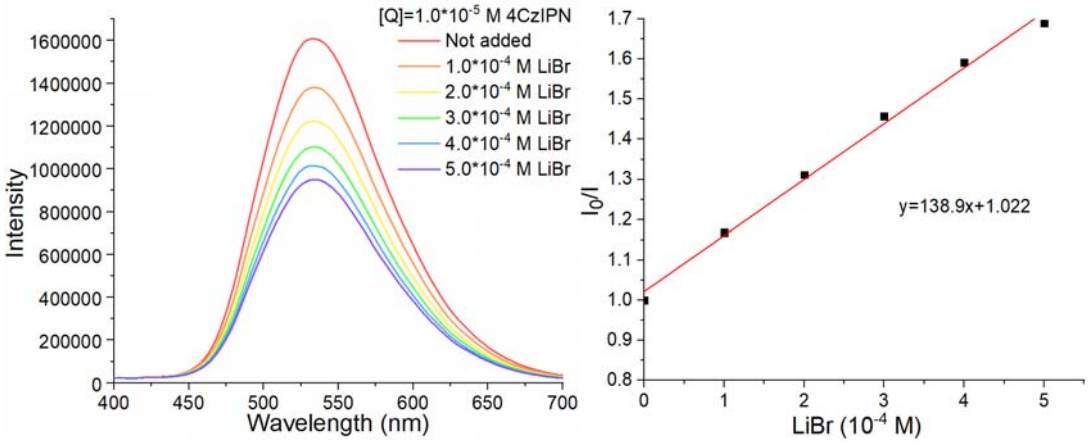
Formulation solution: (4-methylquinolin-2-yl)(phenyl)methanone (**1a**, 618.3 mg) was dissolved in dichloromethane in a 25 mL volumetric flask to set the concentration to be 0.1 M. $CF_3SO_3H{\cdot}5H_2O$ (443 μL) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.1 M. LiBr (108.6 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.05 M. PhCHO (254 μL) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.1 M. $(PhO)_2PO_2H$ (375.3 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.06 M. Photocatalyst 4CzIPN (2.0 mg) was dissolved in dichloromethane (25 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 mM solution (200 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding acetone to prepare a 1.0 μM solution. The resulting mixture was sparged with argon for 1 minutes and then irradiated at 375 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 20.0 μL of a (4-methylquinolin-2-yl)(phenyl)methanone solution was successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 1 minutes and irradiated at 375 nm. Fluorescence emission spectra of 0 μL, 20.0 μL, 40.0 μL, 60.0 μL, 80.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

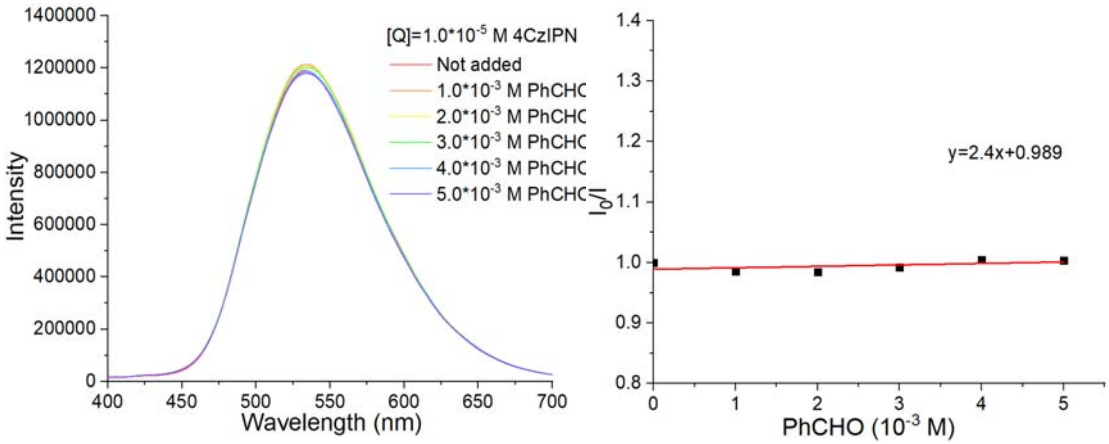
(a) 4CzIPN quenched by CF_3SO_3H in acetone. Linear quenching was not observed.



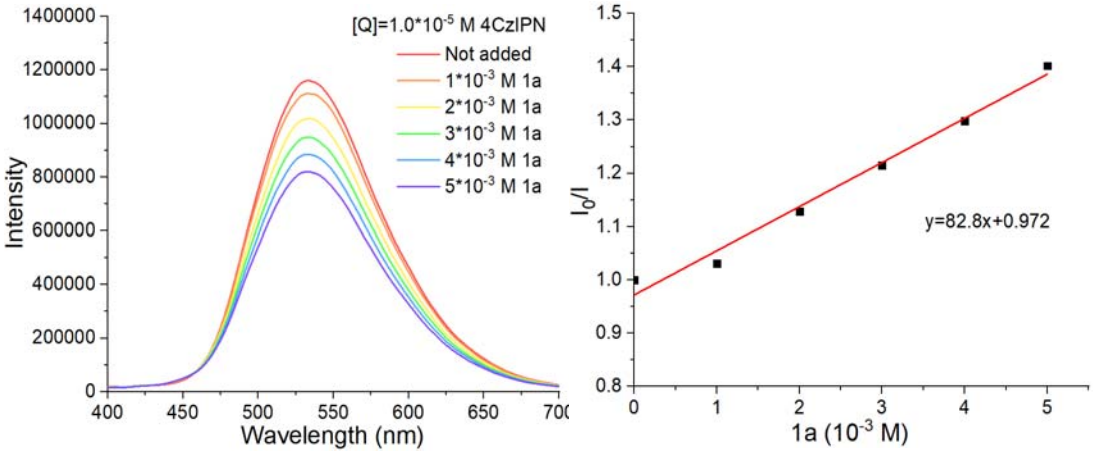
(b) 4CzIPN quenched by LiBr in acetone. The emission intensity of the 4CzIPN catalyst solution was prohibited by the gradual increase of the amount of LiBr.



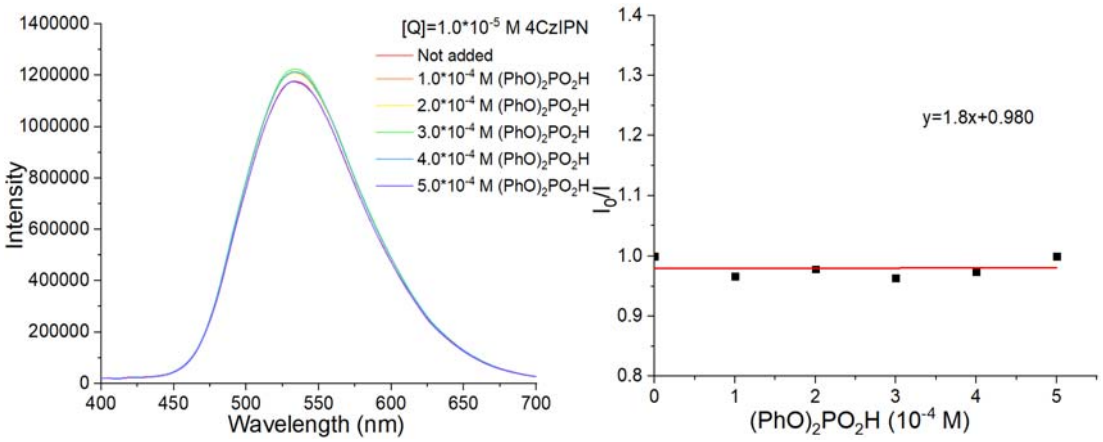
(c) 4CzIPN quenched by PhCHO in acetone. Linear quenching is not observed.



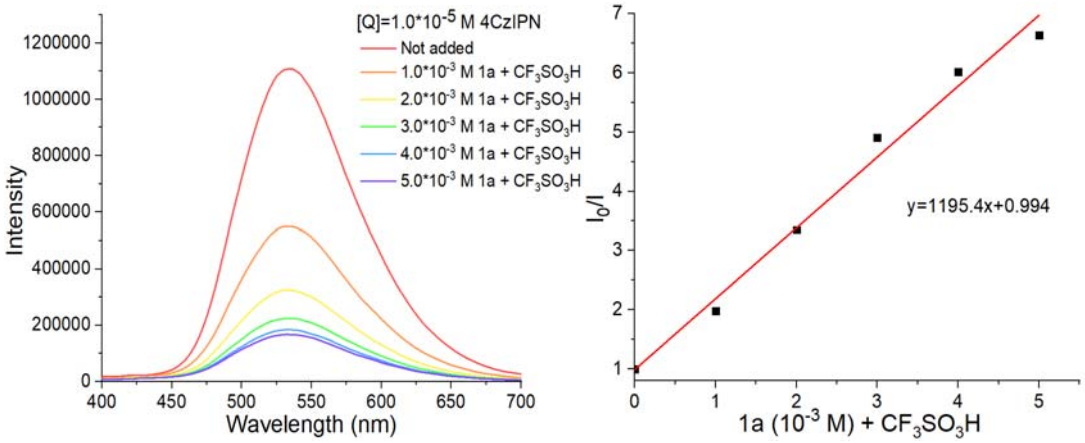
(d) 4CzIPN quenched by 2-benzoyl-4-methylquinoline in acetone. The emission intensity of the 4CzIPN catalyst solution was prohibited by the gradual increase of the amount of 2-benzoyl-4-methylquinoline.



(e) 4CzIPN quenched by $(PhO)_2PO_2H$ in acetone. Linear quenching is not observed.

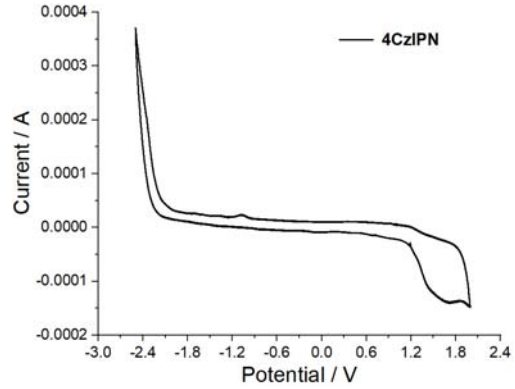


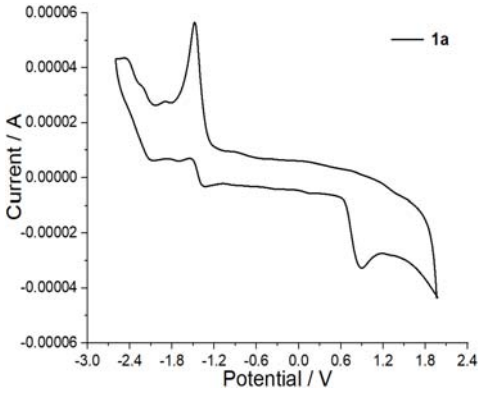
(f) 4CzIPN quenched by 2-benzoyl-4-methylquinoline + CF_3SO_3H in acetone. The emission intensity of the 4CzIPN catalyst solution was prohibited by the gradual increase of the amount of 2-benzoyl-4-methylquinoline + CF_3SO_3H.

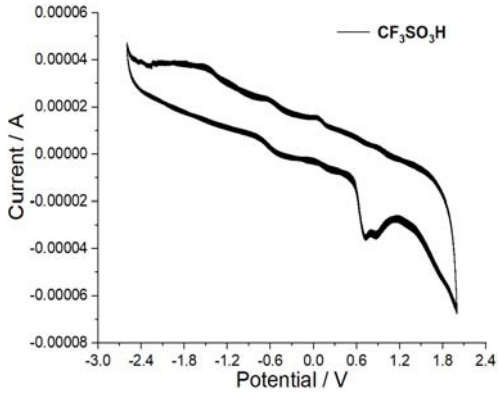


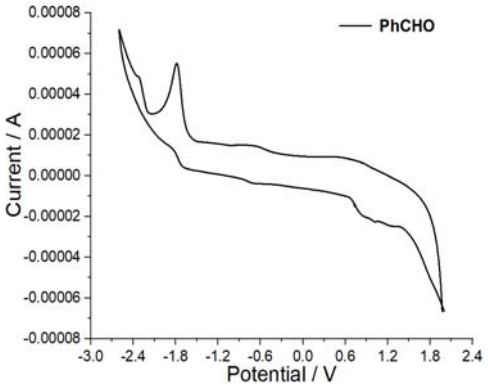
5.4. Cyclic Voltammetry

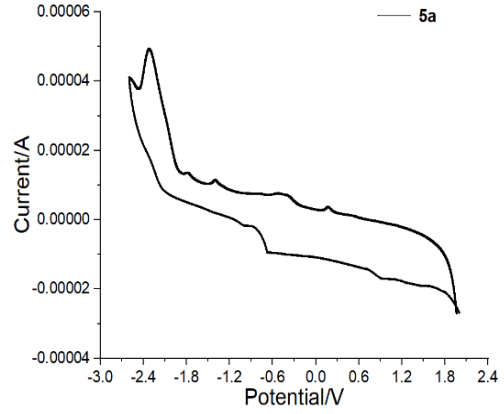
Cyclic voltammograms were recorded with a CHI604E electrochemical analyzer/workstation (Shanghai Chen Hua Instrument Co., Ltd) at room temperature in acetonitrile (Adamas-beta, 99.9%, with molecular sieves, water≤50 ppm (by K.F.)). *n*-Bu_4NBF_4 (0.1 M) was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 40 $mV \cdot s^{-1}$.

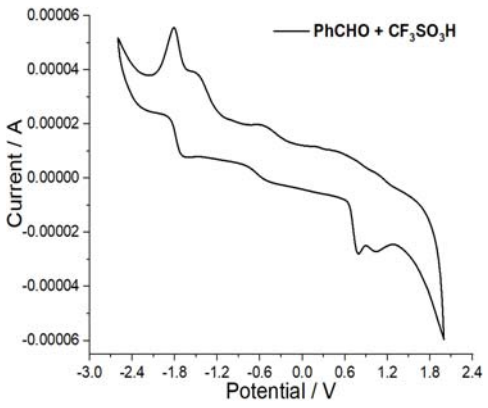

4CzIPN
Current / A
Potential / V

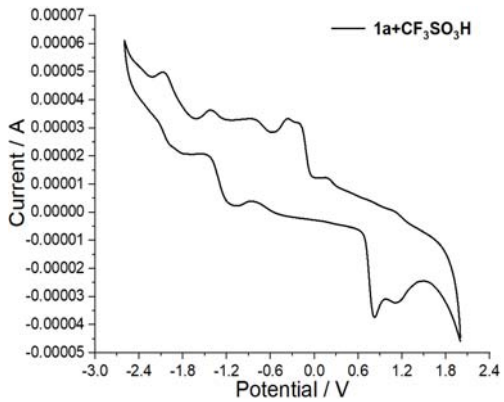

1a
Current / A
Potential / V

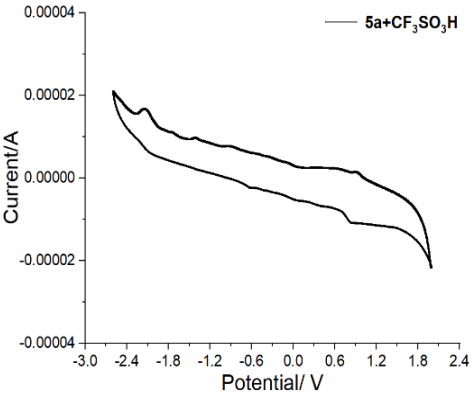

CF3SO3H
Current / A
Potential / V


PhCHO
Current / A
Potential / V

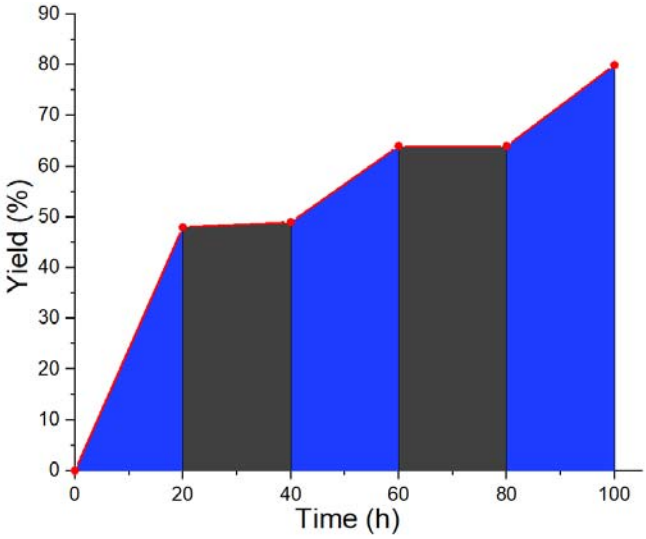

5a
Current/A
Potential/V


PhCHO + CF3SO3H
Current / A
Potential / V


1a+CF3SO3H
Current / A
Potential / V

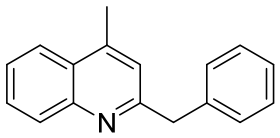

5a+CF3SO3H
Current/A
Potential/ V

5.5. Light on/off experiment



6. Characterization data of products

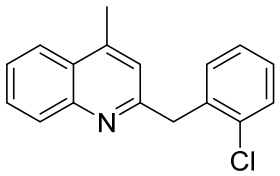
2-Benzyl-4-methylquinoline (2a)[7]



The reaction was conducted with 2-benzoyl-4-methylquinoline (24.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2a** (20.1 mg, 86%) as a light yellow solid, mp: 63 – 65 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.54 – 7.49 (m, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.06 (s, 1H), 4.33 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.8, 147.5, 144.6, 139.3, 129.4, 129.2, 129.1, 128.6, 126.8, 126.4, 125.7, 123.6, 122.1, 45.4, 18.7.

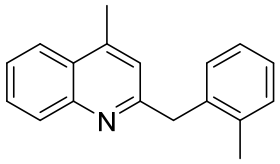
2-(2-Chlorobenzyl)-4-methylquinoline) (2b)[7]



The reaction was conducted with (2-chlorophenyl)(4-methylquinolin-2-yl)methanone (28.2 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2b** (15.3 mg, 57%) as a light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.08 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.54 – 7.50 (m, 1H), 7.43 – 7.39 (m, 1H), 7.28 – 7.24 (m, 1H), 7.21 – 7.17 (m, 2H), 7.04 (s, 1H), 4.44 (s, 2H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 159.6, 147.7, 144.7, 137.0, 134.3, 131.4, 129.5, 129.5, 129.2, 128.0, 126.9, 126.9, 125.8, 123.6, 121.9, 42.4, 18.7.

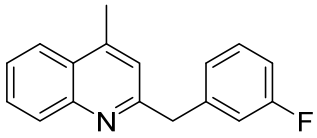
4-Methyl-2-(2-methylbenzyl)quinolone) (2c)[7]



The reaction was conducted with (4-methylquinolin-2-yl)(o-tolyl)methanone (26.1 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2c** (13.8 mg, 56%) as a white solid, mp: 53 – 55 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.69 (t, J = 8.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 2.6 Hz, 4H), 6.94 (s, 1H), 4.31 (s, 2H), 2.59 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.6, 147.6, 144.6, 137.4, 137.1, 130.4, 130.2, 129.4, 129.1, 126.8, 126.8, 126.1, 125.7, 123.6, 121.6, 43.2, 19.9, 18.7.

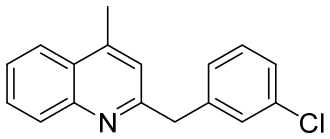
2-(3-Fluorobenzyl)-4-methylquinoline (2d)



The reaction was conducted with (3-fluorophenyl)(4-methylquinolin-2-yl)methanone (26.5 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2d** (15.6 mg, 62%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.54 – 7.50 (m, 1H), 7.28 – 7.23 (m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.06 (s, 1H), 7.03 – 6.99 (m, 1H), 6.93 – 6.89 (m, 1H), 4.28 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.9 (d, J = 244.2 Hz), 160.0, 147.6, 144.9, 141.7 (d, J = 7.3 Hz), 129.9 (d, J = 8.4 Hz), 129.5, 129.3, 126.9, 125.9, 124.8 (d, J = 2.8 Hz), 123.6, 122.1, 116.0 (d, J = 20.9 Hz), 113.3 (d, J = 21.2 Hz), 45.0 (d, J = 1.8 Hz), 18.7. HRMS (ESI) m/z calcd for $C_{17}H_{15}FN^+$ $(M+H)^+$ 252.1183, found 252.1186.

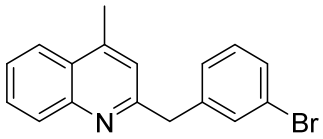
2-(3-Chlorobenzyl)-4-methylquinoline) (2e)[7]



The reaction was conducted with (3-chlorophenyl)(4-methylquinolin-2-yl)methanone (28.2 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2e** (14.2 mg, 53%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.54 – 7.50 (m, 1H), 7.30 (s, 1H), 7.23 - 7.17 (m, 3H), 7.05 (s, 1H), 4.25 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.8, 147.6, 144.9, 141.3, 134.3, 129.8, 129.5, 129.3, 129.2, 127.3, 126.9, 126.6, 125.9, 123.6, 122.1, 45.0, 18.7.

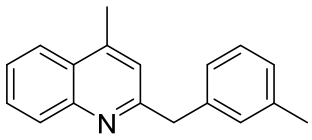
2-(3-Bromobenzyl)-4-methylquinoline) (2f)[7]



The reaction was conducted with (3-bromophenyl)(4-methylquinolin-2-yl)methanone (32.6 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2f** (10.0 mg, 32%) as a white solid, mp: 55 – 57 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 7.47 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 4.25 (s, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.8, 147.6, 144.9, 141.6, 132.1, 130.1, 129.5, 129.5, 129.3, 127.8, 126.9, 125.9, 123.6, 122.6, 122.0, 44.9, 18.7.

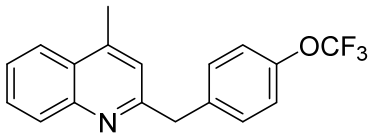
4-Methyl-2-(3-methylbenzyl)quinolone (2g)



The reaction was conducted with (4-methylquinolin-2-yl)(m-tolyl)methanone (26.1 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2g** (14.1 mg, 57%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.53 – 7.49 (m, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 8.2 Hz, 2H), 7.06 – 7.03 (m, 2H), 4.25 (s, 2H), 2.60 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.9, 147.5, 144.5, 139.2, 138.2, 129.9, 129.4, 129.1, 128.4, 127.2, 126.8, 126.2, 125.7, 123.6, 122.2, 45.4, 21.4, 18.7. HRMS (ESI) m/z calcd for $C_{18}H_{18}N^+$ $(M+H)^+$ 248.1434, found 248.1435.

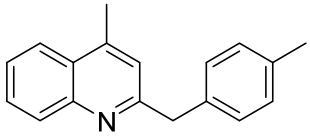
4-Methyl-2-(4-(trifluoromethoxy)benzyl)quinolone (2h)[7]



The reaction was conducted with (4-methylquinolin-2-yl)(4-(trifluoromethoxy)phenyl)methanone (33.1 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2h** (16.2 mg, 51%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.3, Hz, 1H), 7.94 (d, J = 8.2, Hz, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 7.33 (d, J = 8.4, Hz, 2H), 7.14 (d, J = 8.0, Hz, 2H), 7.06 (s, 1H), 4.28 (s, 2H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.0, 147.8, 147.8 (d, J = 4.0 Hz), 147.6, 144.9, 138.0, 130.3, 129.4, 129.3, 126.8, 125.9, 123.6, 122.0, 121.1, 44.6, 18.7.

4-Methyl-2-(4-methylbenzyl)quinolone (2i)

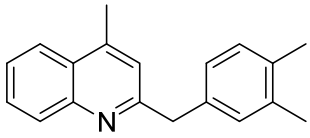


The reaction was conducted with (4-methylquinolin-2-yl)(p-tolyl)methanone (26.1 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2i** (12.3 mg, 54%) as a yellow solid, mp: 63 – 65 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.70 - 7.66 (m, 1H), 7.52 – 7.48 (m, 1H), 7.20 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 7.05 (s, 1H),

4.25 (s, 2H), 2.59 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.1, 147.6, 144.5, 136.3, 135.9, 129.5, 129.2, 129.1, 129.0, 126.8, 125.6, 123.6, 122.1, 45.0, 21.0, 18.6. HRMS (ESI) m/z calcd for $C_{18}H_{18}N^+$ $(M+H)^+$ 248.1434, found 248.1437.

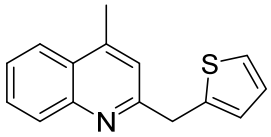
2-(3,4-Dimethylbenzyl)-4-methylquinoline (2j)



The reaction was conducted with (3,4-dimethylphenyl)(4-methylquinolin-2-yl)methanone (27.5 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2j** (12.0 mg, 46%) as a white solid, mp:65 – 67 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.53 – 7.49 (m, 1H), 7.09 – 7.03 (m, 4H), 4.22 (s, 2H), 2.60 (s, 3H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 161.2, 147.5, 144.5, 136.7, 136.7, 134.6, 130.5, 129.8, 129.5, 129.1, 126.9, 126.5, 125.6, 123.6, 122.2, 45.1, 19.7, 19.7, 18.7. HRMS (ESI) m/z calcd for $C_{19}H_{20}N^+$ $(M+H)^+$ 262.1590, found 262.1591.

4-methyl-2-(thiophen-2-ylmethyl)quinoline (2k)

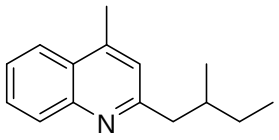


The reaction was conducted with (4-methylquinolin-2-yl)(thiophen-2-yl)methanone (25.3 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2k** (16.7 mg, 70%) as a light yellow solid, mp: 115 – 117 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 7.19 – 7.17 (m, 2H), 6.97 – 6.93 (m, 2H), 4.47 (s, 2H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.7, 147.5, 144.9, 141.5, 129.5, 129.3, 127.0, 126.9,

125.9, 125.9, 124.4, 123.6, 121.7, 39.5, 18.8. HRMS (ESI) m/z calcd for $C_{15}H_{14}NS^+$ $(M+H)^+$ 240.0841, found 240.0852.

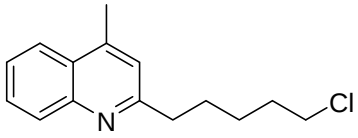
4-Methyl-2-(2-methylbutyl)quinoline (2l)[7]



The reaction was conducted with 2-methyl-1-(4-methylquinolin-2-yl)butan-1-one (22.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield **2l** (10.3 mg, 48%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 8.2, 1H), 7.69 – 7.65 (m, 1H), 7.52 – 7.48 (m, 1H), 7.11 (s, 1H), 2.94 (dd, J = 13.1, 6.3 Hz, 1H), 2.72 – 2.67 (m, 4H), 2.02 – 1.96 (m, 1H), 1.50 – 1.43(m, 1H), 1.31 – 1.23 (m, 1H), 0.95 – 0.90 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.0, 147.7, 143.8, 129.3, 128.9, 126.7, 125.3, 123.5, 122.7, 46.4, 35.6, 29.5, 19.0, 18.7, 11.4.

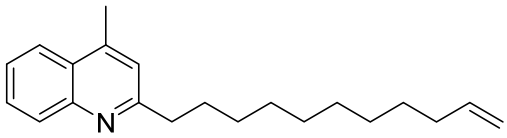
2-(5-Chloropentyl)-4-methylquinoline (2m)[7]



The reaction was conducted with 5-chloro-1-(4-methylquinolin-2-yl)pentan-1-one (26.2 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield **2m** (13.1 mg, 53%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.52 – 7.47 (m, 1H), 7.13 (s, 1H), 3.53 (t, J = 6.7 Hz, 2H), 2.93 (t, J = 7.6 Hz, 2H), 2.67 (s, 3H), 1.87 – 1.80 (m, 4H), 1.59 – 1.51 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1, 147.6, 144.3, 129.2, 129.0, 126.7, 125.4, 123.5, 121.9, 44.9, 38.9, 32.4, 29.1, 26.7, 18.6.

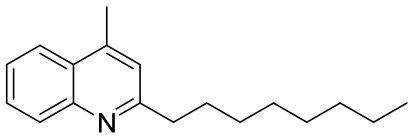
4-Methyl-2-(undec-10-en-1-yl)quinoline (2n)[7]



The reaction was conducted with 1-(4-methylquinolin-2-yl)undec-10-en-1-one (30.9 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield **2n** (19.6 mg, 66%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.3, 1.4 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.51 – 7.47 (m, 1H), 7.14 (s, 1H), 5.86 – 5.75 (m, 1H), 5.01 – 4.91 (m, 2H), 2.91 (J = 7.6 Hz, 2H), 2.67 (s, 3H), 2.03 (q, J = 7.1 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.44 – 1.27 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.7, 147.6, 144.1, 139.2, 129.3, 129.0, 126.7, 125.3, 123.5, 122.0, 114.0, 39.3, 33.8, 30.1, 29.6, 29.5, 29.4, 29.4, 29.1, 28.9, 18.7.

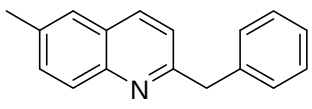
4-Methyl-2-octylquinoline (2o)[7]



The reaction was conducted with 1-(4-methylquinolin-2-yl)octan-1-one (26.9 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield **2o** (18.9 mg, 74%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.14 (s, 1H), 2.91 (t, J = 7.8 Hz, 2H), 2.67 (s, 3H), 1.79 (p, J = 8.0, 7.5 Hz, 2H), 1.45 – 1.26 (m, 10H), 0.89 – 0.86 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.8, 147.6, 144.1, 129.2, 128.9, 126.7, 125.3, 123.5, 122.0, 39.3, 31.8, 30.1, 29.6, 29.5, 29.2, 22.6, 18.6, 14.1.

2-benzyl-6-methylquinoline (2p)[8]

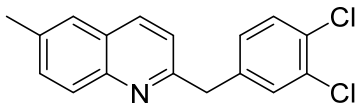


The reaction was conducted with (6-methylquinolin-2-yl)(phenyl)methanone (24.7 mg, 0.1mmol)

and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2p** (18.4 mg, 79%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.30 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.32 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.2, 146.2, 139.3, 135.8, 135.7, 131.7, 129.1, 128.5, 128.5, 126.7, 126.4, 126.3, 121.4, 45.4, 21.4.

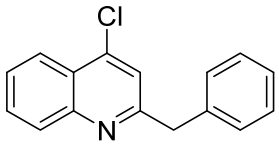
2-(3,4-dichlorobenzyl)-6-methylquinoline (2q)



The reaction was conducted with (3,4-dichlorophenyl)(6-methylquinolin-2-yl)methanone (31.6 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2q** (14.5 mg, 48%) as a light yellow solid, mp: 89 – 91 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.95 (m, 2H), 7.56 – 7.54 (m, 2H), 7.39 – 7.34 (m, 2H), 7.17 – 7.12 (m, 2H), 4.26 (s, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 146.4, 139.5, 136.2, 136.1, 132.4, 132.0, 131.0, 130.5, 130.4, 128.6, 128.5, 126.8, 126.4, 121.3, 44.3, 21.5. HRMS (ESI) m/z calcd for $C_{17}H_{14}Cl_2N^+$ $(M+H)^+$ 302.0498, found 302.0507.

2-Benzyl-4-Chloroquinoline (2r)

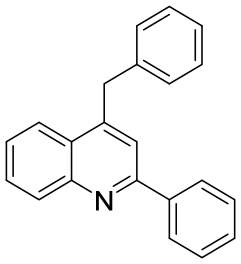


The reaction was conducted with (4-chloroquinolin-2-yl)(phenyl)methanone (26.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2r** (11.4 mg, 45%) as a white solid, mp: 57 – 59 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.08 (m, 2H), 7.74 – 7.70 (m, 1H), 7.57 – 7.53 (m, 1H), 7.31 – 7.29 (m, 5H), 7.25 – 7.21 (m, 1H), 4.29 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.1, 148.5, 142.8, 138.4, 130.3, 129.2, 129.1, 128.7, 126.9, 126.7, 124.9, 123.9, 121.4, 45.2.

HRMS (ESI) m/z calcd for $C_{16}H_{13}ClN^+$ $(M+H)^+$ 254.0731, found 254.0739.

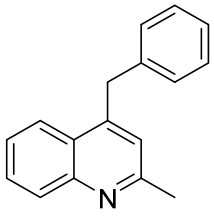
4-Benzyl-2-phenylquinoline (2s)[7]



The reaction was conducted with phenyl(2-phenylquinolin-4-yl)methanone (30.9 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield **2s** (19.2 mg, 65%) as a yellow oil.

H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, J = 8.4 Hz, 1H), 8.11 – 8.09 (m, 2H), 8.01 (d, J = 8.3, 1H), 7.71 - 7.67 (m, 1H), 7.64 (s, 1H), 7.52 – 7.42 (m, 4H), 7.32 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 4.49 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.1, 148.5, 147.0, 139.7, 138.7, 130.4, 129.3, 129.2, 128.8, 128.7, 128.7, 127.5, 126.6, 126.6, 126.2, 123.7, 119.9, 38.5.

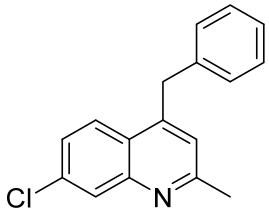
4-Benzyl-2-methylquinoline (2t)[9]



The reaction was conducted with (2-methylquinolin-4-yl)(phenyl)methanone (24.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 5/1) to yield **2t** (12.1 mg, 52%) as a white solid, mp: 52 – 54 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.29 – 7.15 (m, 5H), 6.98 (s, 1H), 4.33 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.6, 147.9, 146.3, 138.5, 129.1, 129.0, 128.7, 128.5, 126.4, 125.7, 125.5, 123.5, 122.5, 37.9, 25.1.

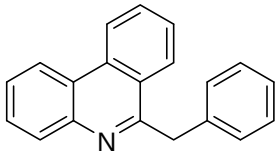
4-Benzyl-7-chloro-2-methylquinoline (2u)[7]



The reaction was conducted with (7-chloro-2-methylquinolin-4-yl)(phenyl)methanone (28.1 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2u** (15.2 mg, 57%) as a yellow solid, mp: 91 – 93 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 2.2 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.40 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.25 – 7.23 (m, 1H), 7.18 – 7.16 (m, 2H), 7.04 (s, 1H), 4.37 (s, 2H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.1, 148.6, 146.4, 138.3, 134.9, 128.7, 128.7, 128.2, 126.7, 126.5, 125.1, 124.3, 122.9, 38.1, 25.3.

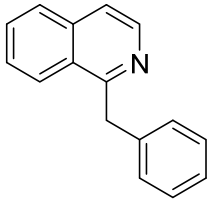
6-Benzylphenanthridine (2v)



The reaction was conducted with phenanthridin-6-yl(phenyl)methanone (28.3 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield **2v** (17.5 mg, 65%) as a white solid, mp: 104 – 106 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 2H), 7.81 – 7.73 (m, 2H), 7.68 – 7.64 (m, 1H), 7.61 – 7.56 (m, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 4.76 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.1, 143.7, 139.1, 133.2, 130.3, 129.8, 128.7, 128.5, 127.3, 127.1, 126.7, 126.3, 125.4, 123.9, 122.4, 121.9, 43.1. HRMS (ESI) m/z calcd for $C_{20}H_{16}N^{+}$ $(M+H)^{+}$ 270.1277, found 270.1288.

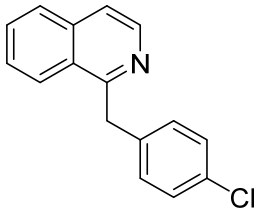
1-Benzylisoquinoline (2w)[8]



The reaction was conducted with isoquinolin-1-yl(phenyl)methanone (23.3 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2w** (5.3 mg, 24%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 5.7 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.56 – 7.49 (m, 2H), 7.29 - 7.22 (m, 4H), 7.18 – 7.16 (m, 1H), 4.67 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.1, 142.0, 139.4, 136.5, 129.8, 128.5, 128.5, 127.3, 127.2, 127.1, 126.2, 125.8, 119.8, 42.0.

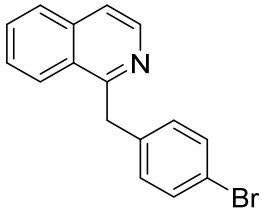
1-(4-Chlorobenzyl)isoquinoline (2x)[10]



The reaction was conducted with (4-chlorophenyl)(isoquinolin-1-yl)methanone (26.8 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield **2x** (15.2 mg, 60%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 5.7 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.22 - 7.20 (m, 4H), 4.63 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.5, 141.9, 137.7, 136.5, 132.0, 129.9, 129.9, 128.5, 127.4, 127.3, 126.9, 125.4, 120.0, 41.1.

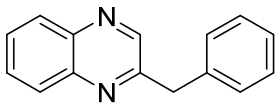
1-(4-Bromobenzyl)isoquinoline (2y)[10]



The reaction was conducted with (4-bromophenyl)(isoquinolin-1-yl)methanone (31.2 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield **2y** (18.2 mg, 61%) as a white solid, mp: 67–69 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 5.7 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.61 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4, 141.9, 138.2, 136.4, 131.4, 130.2, 129.9, 127.3, 127.3, 126.9, 125.4, 120.1, 120.0, 41.2.

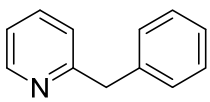
2-Benzylquinoxaline (2z)[11]



The reaction was conducted with phenyl(quinoxalin-2-yl)methanone (23.4 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2z** (13.2 mg, 60%) as a light yellow solid, mp: 81 – 83 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 8.08 – 8.04 (m, 2H), 7.74 – 7.66 (m, 2H), 7.33 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 4.36 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.7, 145.8, 141.9, 141.0, 137.7, 129.9, 129.1, 129.0, 129.0, 128.9, 128.7, 126.8, 42.8.

2-Benzylpyridine (2aa)[12]

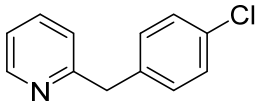


The reaction was conducted with phenyl(pyridin-2-yl)methanone (18.3 mg, 0.1mmol) and

benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 5/1) to yield **2aa** (14.0 mg, 83%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 – 8.53 (m, 1H), 7.57 – 7.52 (m, 1H), 7.32 – 7.25 (m, 4H), 7.23 – 7.19 (m, 1H), 7.08 (dd, *J* = 7.6, 4.5 Hz, 2H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.9, 149.2, 139.4, 136.4, 129.0, 128.5, 126.3, 123.0, 121.1, 44.6.

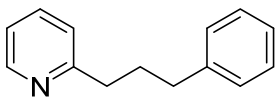
2-(4-Chlorobenzyl)pyridine (2ab)[12]



The reaction was conducted with (4-chlorophenyl)(pyridin-2-yl)methanone (21.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2ab** (16.2 mg, 80%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 5.0 Hz, 1H), 7.55 (td, *J* = 7.7, 1.9 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.18 – 7.16 (m, 2H), 7.10 – 7.06 (m, 2H), 4.10 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.2, 149.3, 137.8, 136.5, 132.0, 130.2, 128.5, 122.9, 121.2, 43.8.

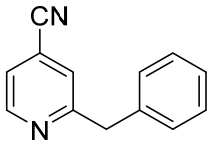
2-(3-Phenylpropyl)pyridine (2ac)[13]



The reaction was conducted with 3-phenyl-1-(pyridin-2-yl)propan-1-one (21.1 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 10/1) to yield **2ac** (6.3 mg, 32%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 – 8.51 (m, 1H), 7.55 (td, *J* = 7.7, 1.9 Hz, 1H), 7.26 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 7.12 – 7.05 (m, 2H), 2.84 – 2.80 (m, 2H), 2.69 – 2.66 (m, 2H), 2.10 – 2.03 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.8, 149.1, 142.0, 136.1, 128.3, 128.2, 125.6, 122.6, 120.9, 37.8, 35.4, 31.4.

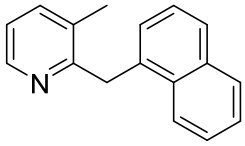
2-Benzyl-4-cyanopyridine (2ad)[14]



The reaction was conducted with 2-benzoylisonicotinonitrile (20.8 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 5/1) to yield **2ad** (3.0 mg, 15%) as a light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 – 8.67 (m, 1H), 7.34 – 7.29 (m, 4H), 7.26 – 7.23 (m, 3H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.5, 150.1, 137.7, 128.9, 128.7, 126.7, 124.4, 122.5, 120.6, 116.4, 44.2.

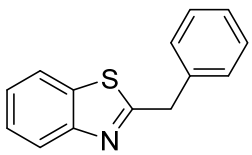
3-methyl-2-(naphthalen-1-ylmethyl)pyridine (2ae)



The reaction was conducted with (3-methylpyridin-2-yl)(naphthalen-1-yl)methanol (25.0 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/acetone = 10/1) to yield **2ae** (9.9 mg, 42%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.3 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.94 (d, *J* = 7.0 Hz, 1H), 4.65 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.4, 146.9, 138.0, 135.0, 133.7, 132.3, 132.2, 128.6, 126.9, 125.9, 125.7, 125.5, 125.4, 123.8, 121.8, 39.3, 19.0. HRMS (ESI) m/z calcd for $C_{17}H_{16}N^+$ $(M+H)^+$ 234.1277, found 234.1306.

2-Benzylbenzo[d]thiazole (4a)[6]

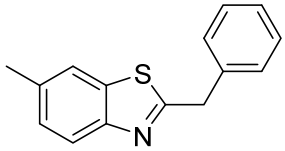


The reaction was conducted with (benzo[d]thiazol-2-yl(phenyl)methanone (23.9 mg, 0.1mmol)

and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield **4a** (16.9 mg, 75%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.39 – 7.26 (m, 6H), 4.44 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 153.2, 137.1, 135.6, 129.1, 128.8, 127.3, 125.9, 124.8, 122.7, 121.5, 40.6.

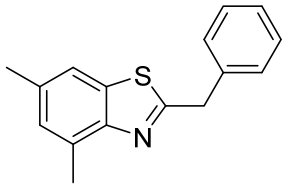
2-Benzyl-6-Methylbenzo[d]thiazole (4b)[6]



The reaction was conducted with (6-methylbenzo[d]thiazol-2-yl)(phenyl)methanone (25.3 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield **4b** (16.0 mg, 67%) as a white solid, mp: 26 – 28 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.37 – 7.24 (m, 6H), 4.41 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.0, 151.3, 137.3, 135.8, 134.9, 129.1, 128.8, 127.5, 127.3, 122.2, 121.2, 40.5, 21.4.

2-Benzyl-4,6-dimethylbenzo[d]thiazole (4c)[6]

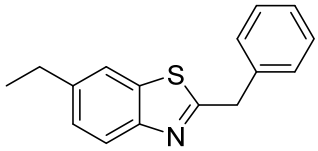


The reaction was conducted with (4,6-dimethylbenzo[d]thiazol-2-yl)(phenyl)methanone (26.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield **4c** (15.9 mg, 63%) as a light yellow solid, mp: 39 – 41 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.28 (m, 6H), 7.06 (s, 1H), 4.43 (s, 2H), 2.72 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 150.6, 137.5, 135.7, 134.6, 132.0,

129.2, 128.7, 128.2, 127.2, 118.6, 40.6, 21.4, 18.4.

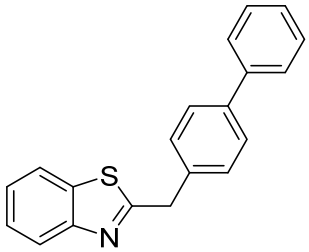
2-Benzyl-6-Ethylbenzo[d]thiazole (4d)[6]



The reaction was conducted with (6-ethylbenzo[d]thiazol-2-yl)(phenyl)methanone (26.7 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 30/1) to yield **4d** (16.5 mg, 65%) as a light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.37 – 7.24 (m, 6H), 4.41 (s, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.1, 151.4, 141.3, 137.3, 135.8, 129.1, 128.8, 127.2, 126.4, 122.3, 120.0, 40.5, 28.8, 15.9.

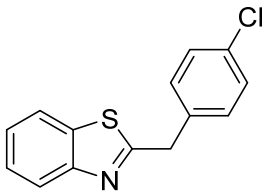
2-([1,1'-biphenyl]-4-ylmethyl)benzo[d]thiazole (4e)



The reaction was conducted with [1,1'-biphenyl]-4-yl(benzo[d]thiazol-2-yl)methanone (31.5 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 50/1) to yield **4e** (19.9 mg, 66%) as a white solid, mp: 103 – 105 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 4H), 7.48 – 7.42 (m, 5H), 7.34 (t, *J* = 7.5 Hz, 2H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.0, 153.2, 140.6, 140.2, 136.1, 135.6, 129.5, 128.7, 127.5, 127.3, 127.0, 126.0, 124.8, 122.8, 121.5, 40.2. HRMS (ESI) m/z calcd for $C_{20}H_{16}NS^+$ $(M+H)^+$ 302.0998, found 302.1011.

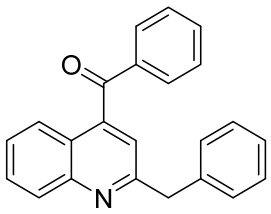
2-(4-Chlorobenzyl)benzo[d]thiazole (4f)[15]



The reaction was conducted with benzo[d]thiazol-2-yl(4-chlorophenyl)methanone (27.3 mg, 0.1mmol) and benzaldehyde (21 μL, 0.2 mmol). Purification by thin layer chromatography was performed (petroleum ether/ethyl acetate = 20/1) to yield **4f** (21.8 mg, 84%) as a light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.36 – 7.28 (m, 5H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.3, 153.2, 135.6, 135.5, 133.2, 130.4, 129.0, 126.1, 124.9, 122.8, 121.5, 39.8.

(2-benzylquinolin-4-yl)(phenyl)methanone (7c)



7c (16.2 mg, 50%) as a light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 7.5 Hz, 1H), 7.80 – 7.72 (m, 4H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.30 – 7.19 (m, 6H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.1, 160.5, 148.2, 144.8, 138.6, 136.5, 134.1, 130.3, 130.1, 129.5, 129.1, 128.7, 127.0, 126.7, 125.2, 123.5, 120.1, 45.5. HRMS (ESI) m/z calcd for $C_{23}H_{18}NO^+$ $(M+H)^+$ 324.1383, found 324.1402.

7. Reference

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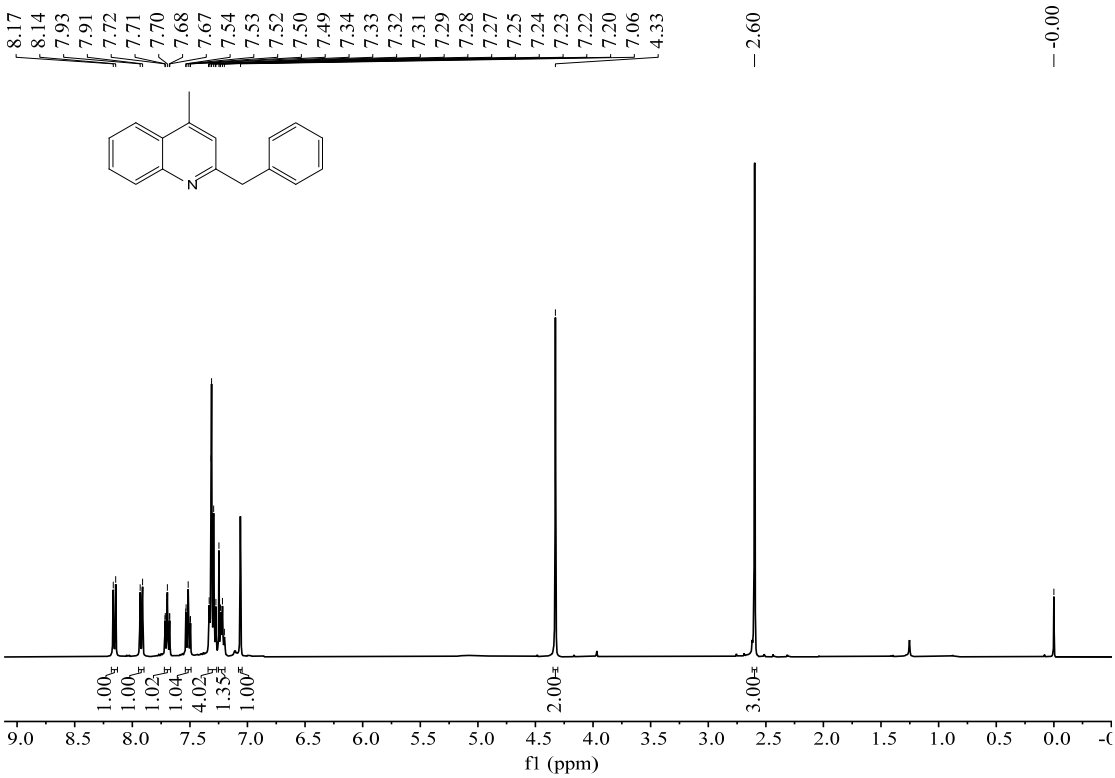
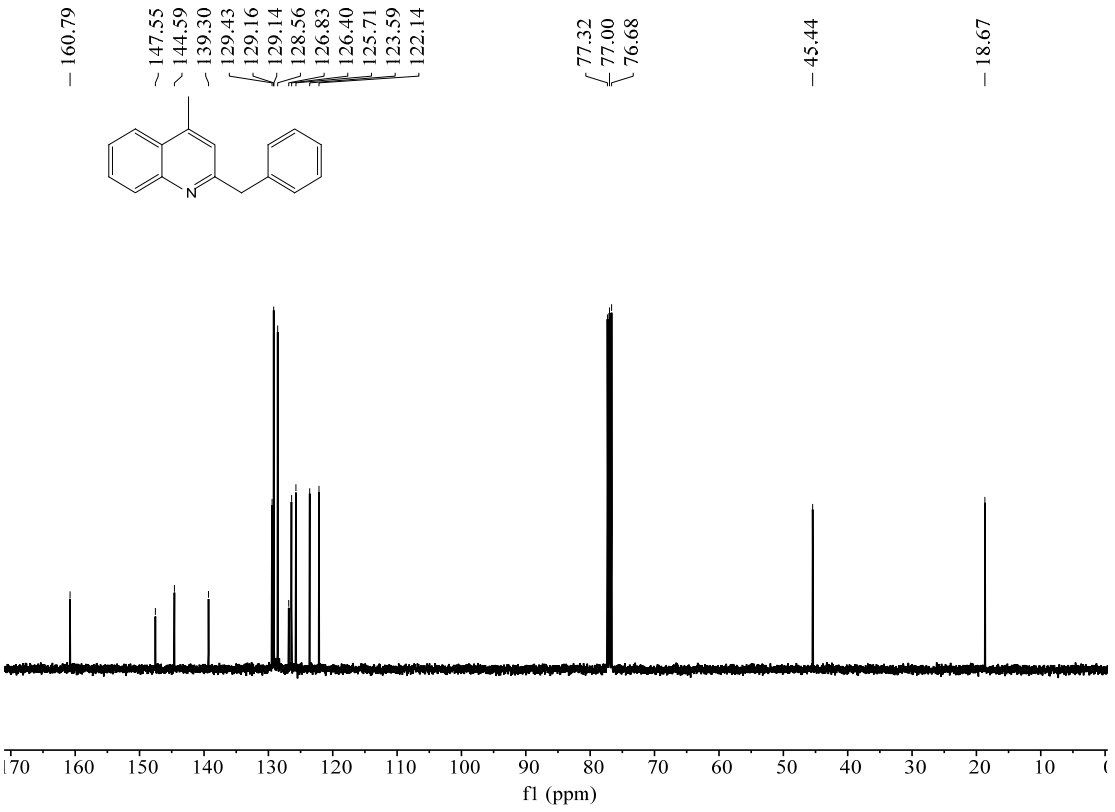
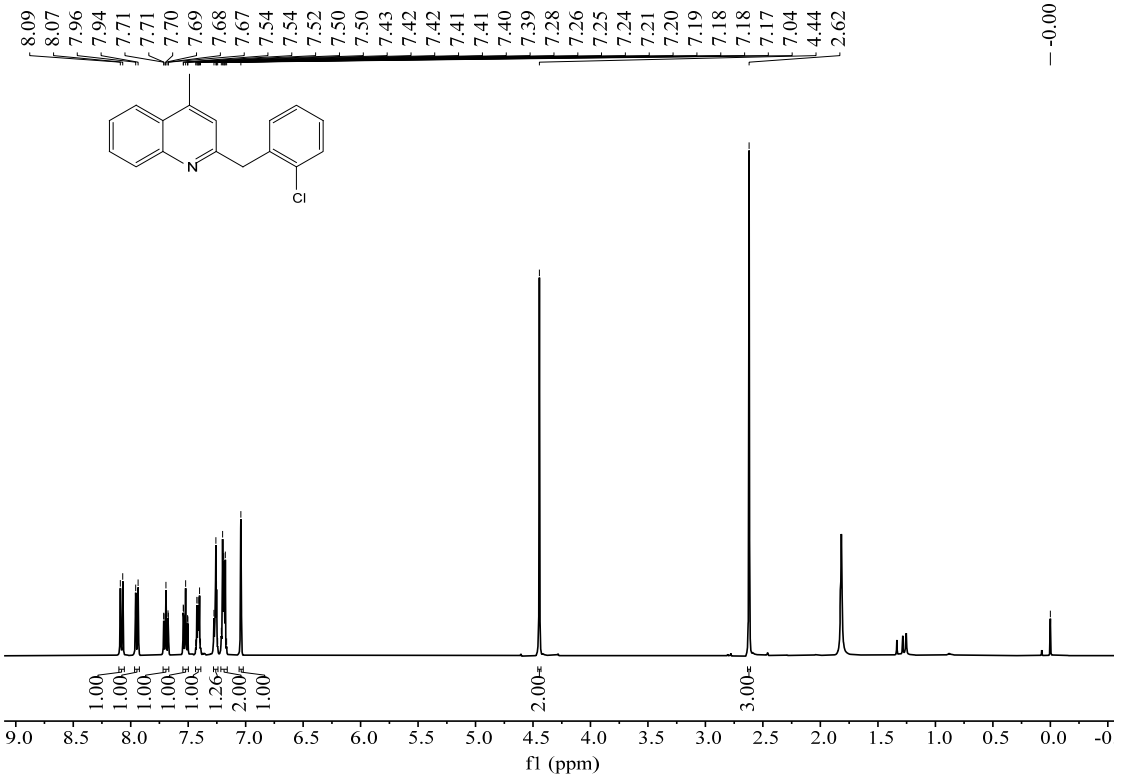
8. Copies of ^{1}H and ^{13}C NMR spectra of all products

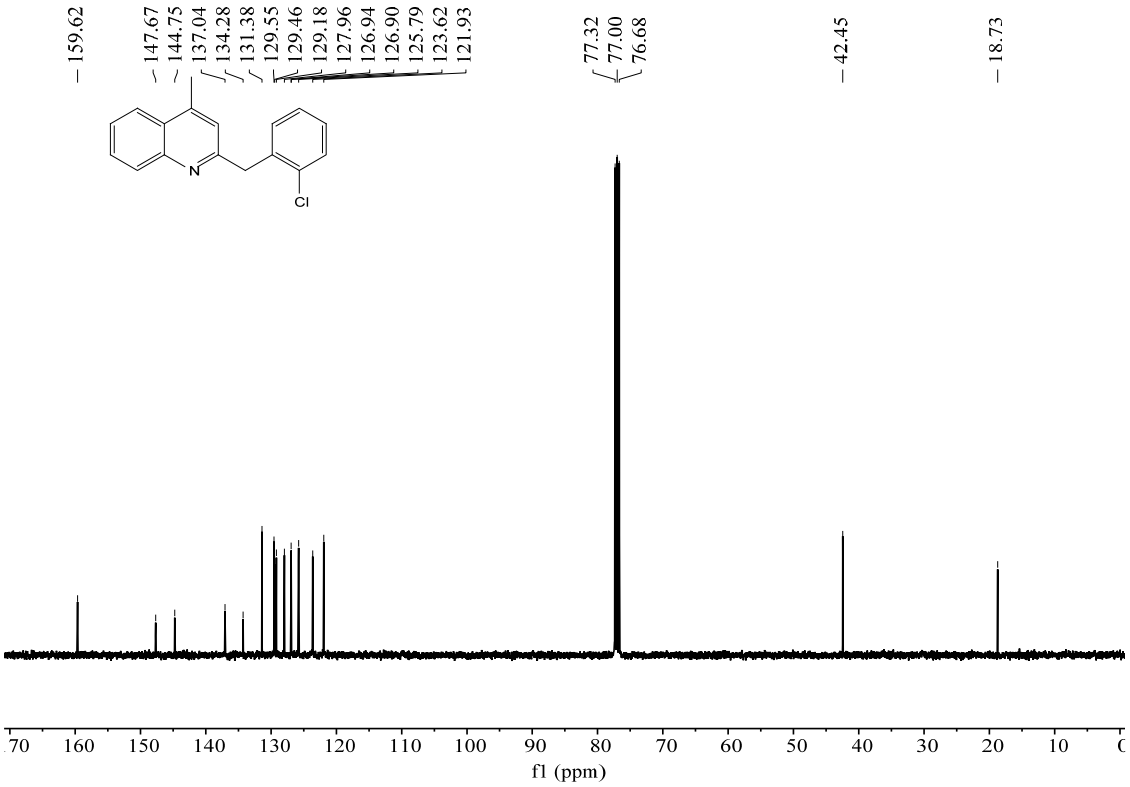
^{1}H and ^{13}C NMR spectra of 2a





^{1}H and ^{13}C NMR spectra of 2b





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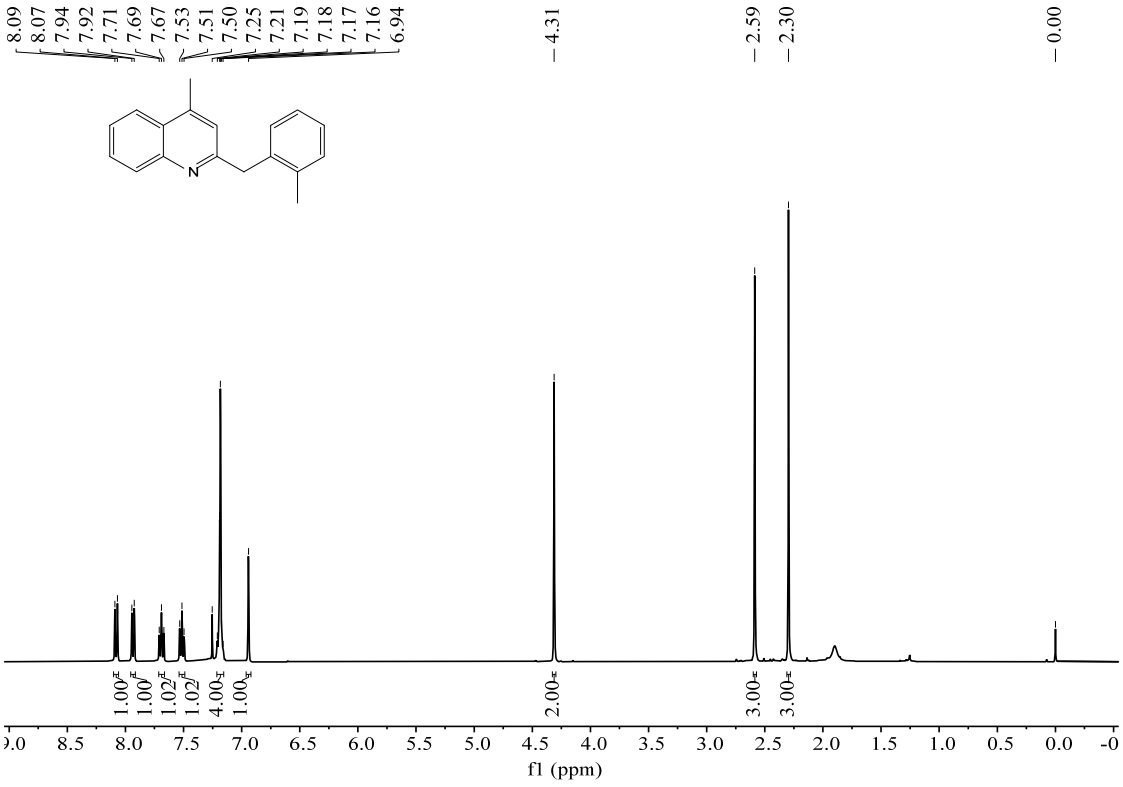

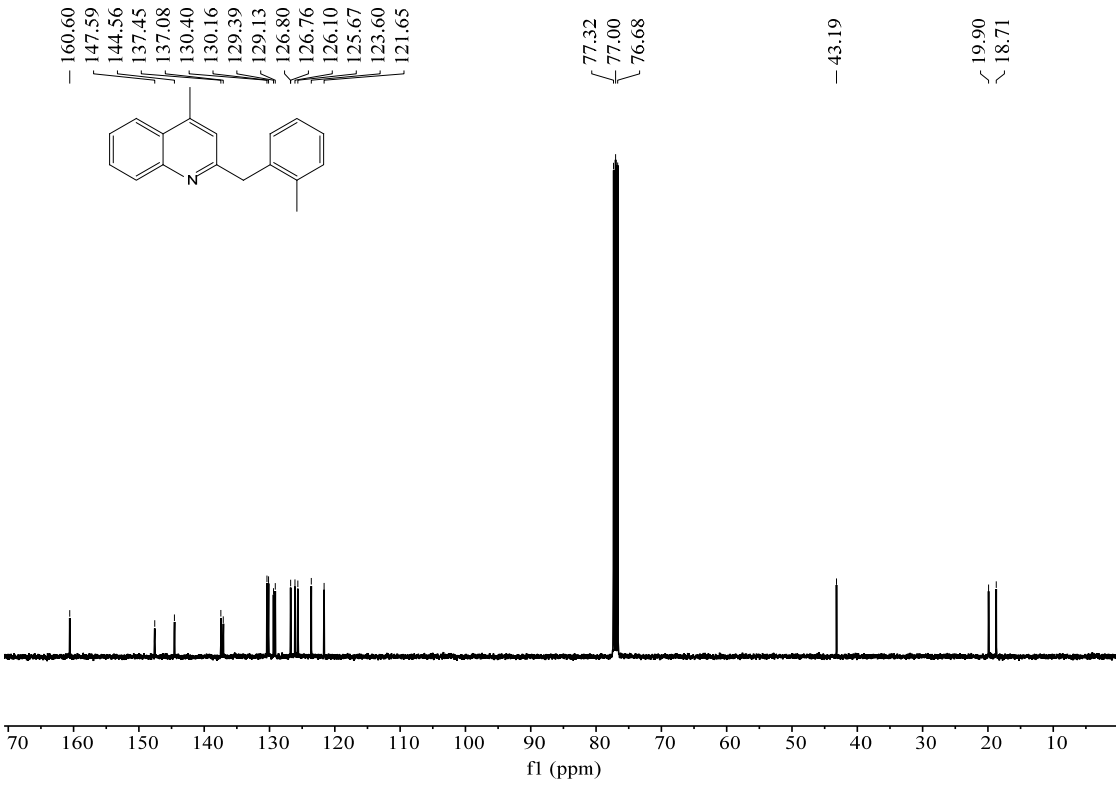

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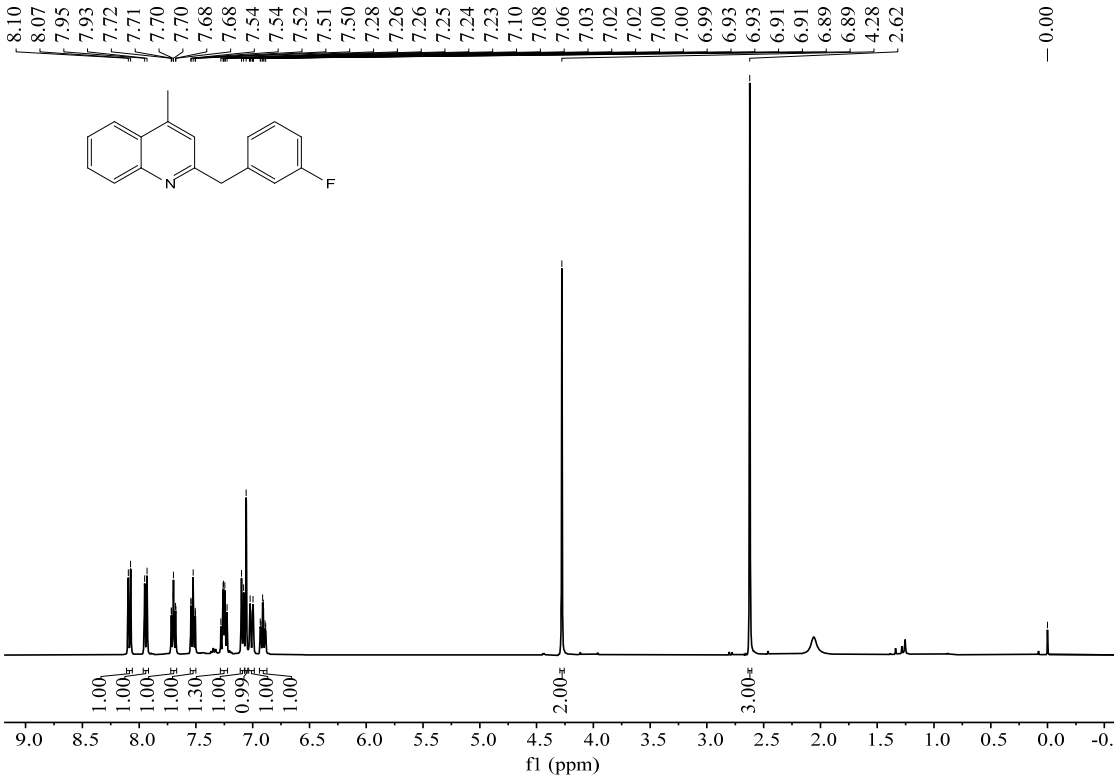

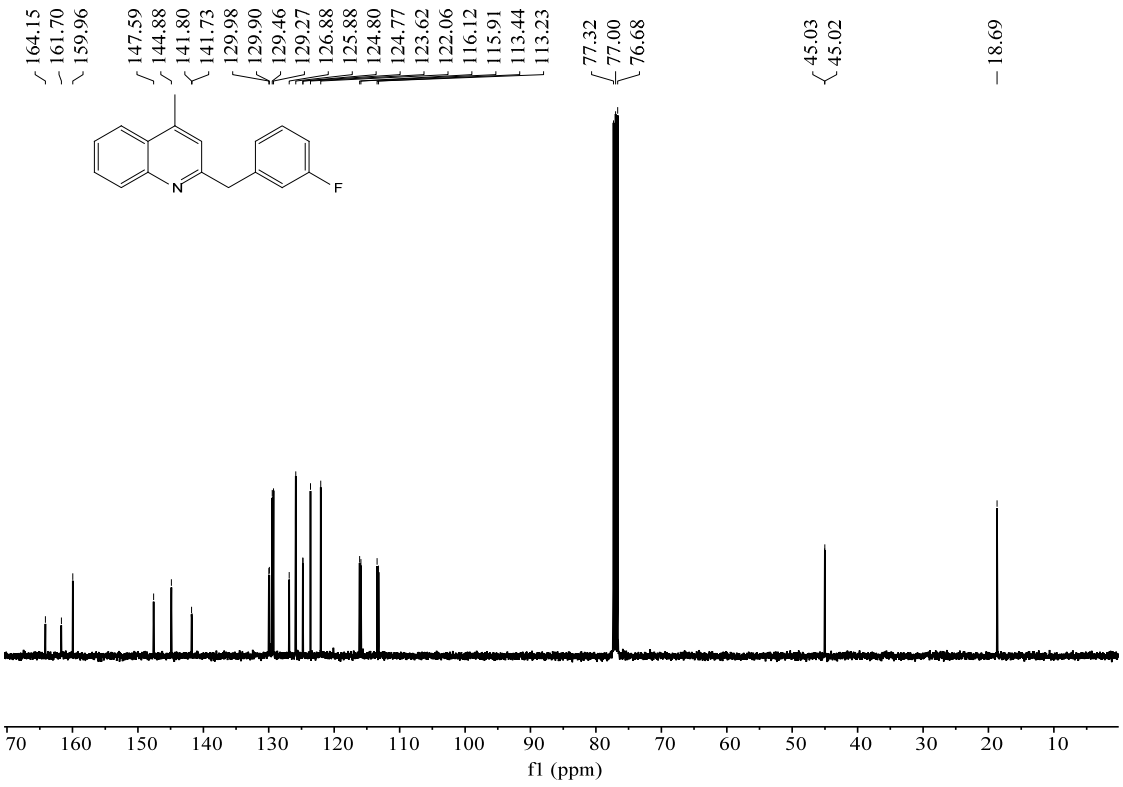

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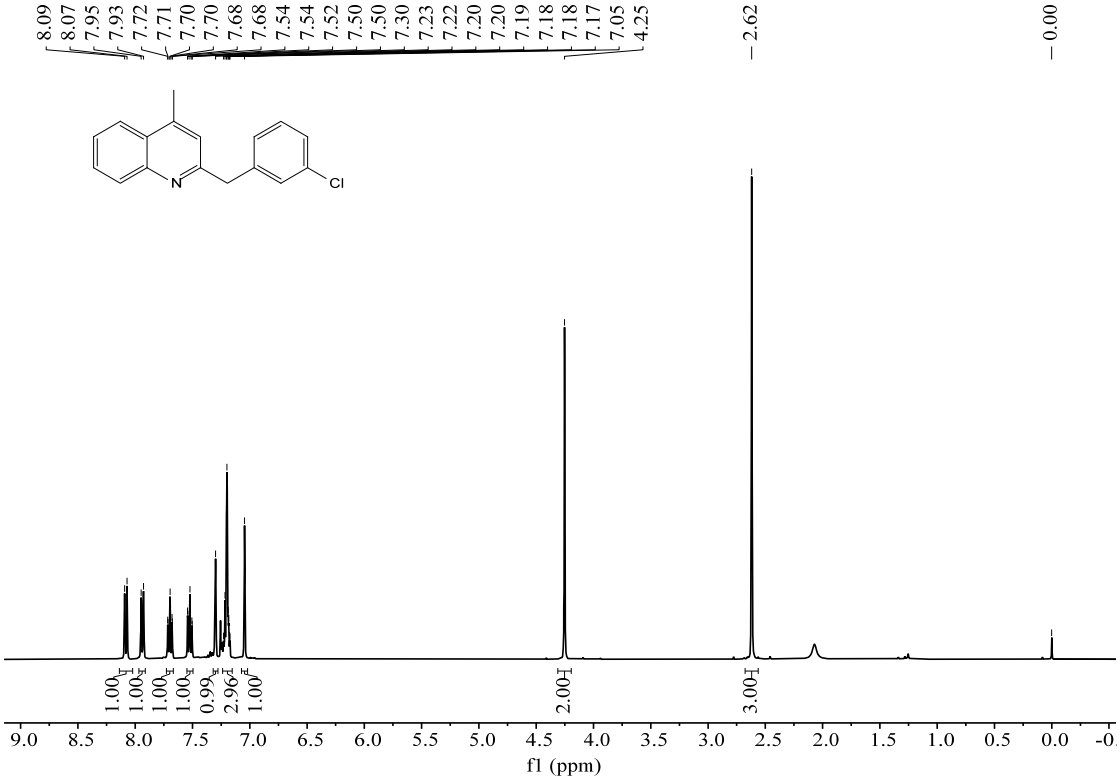
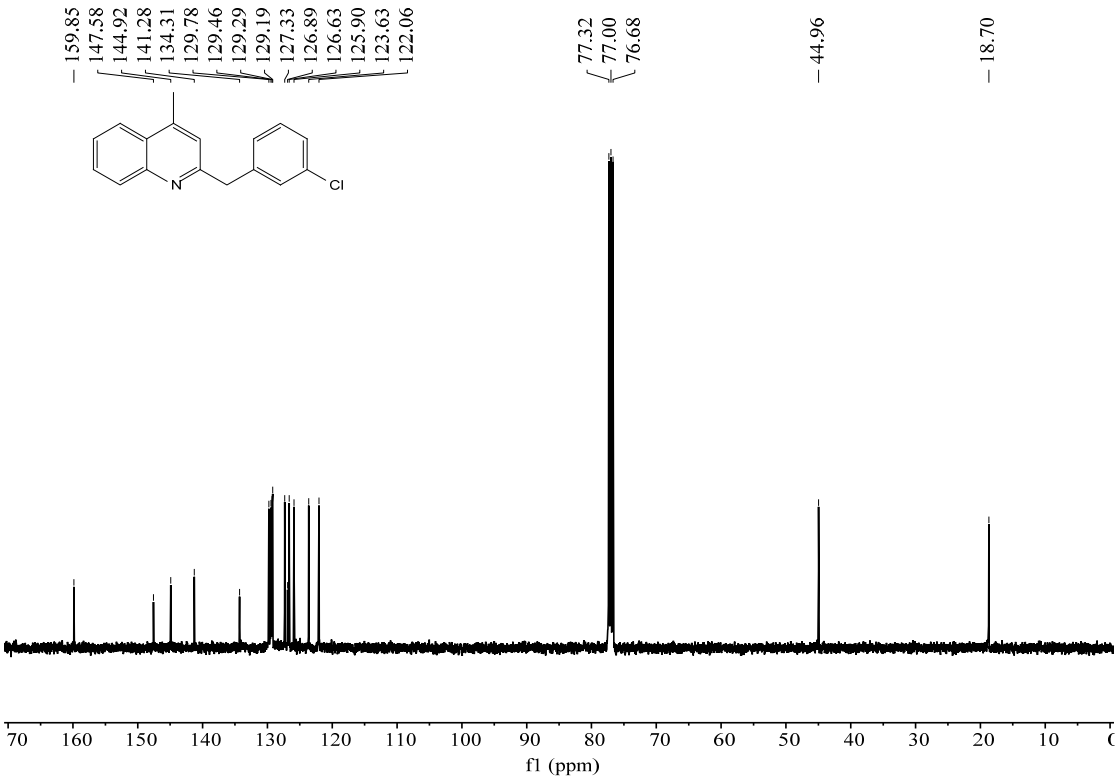
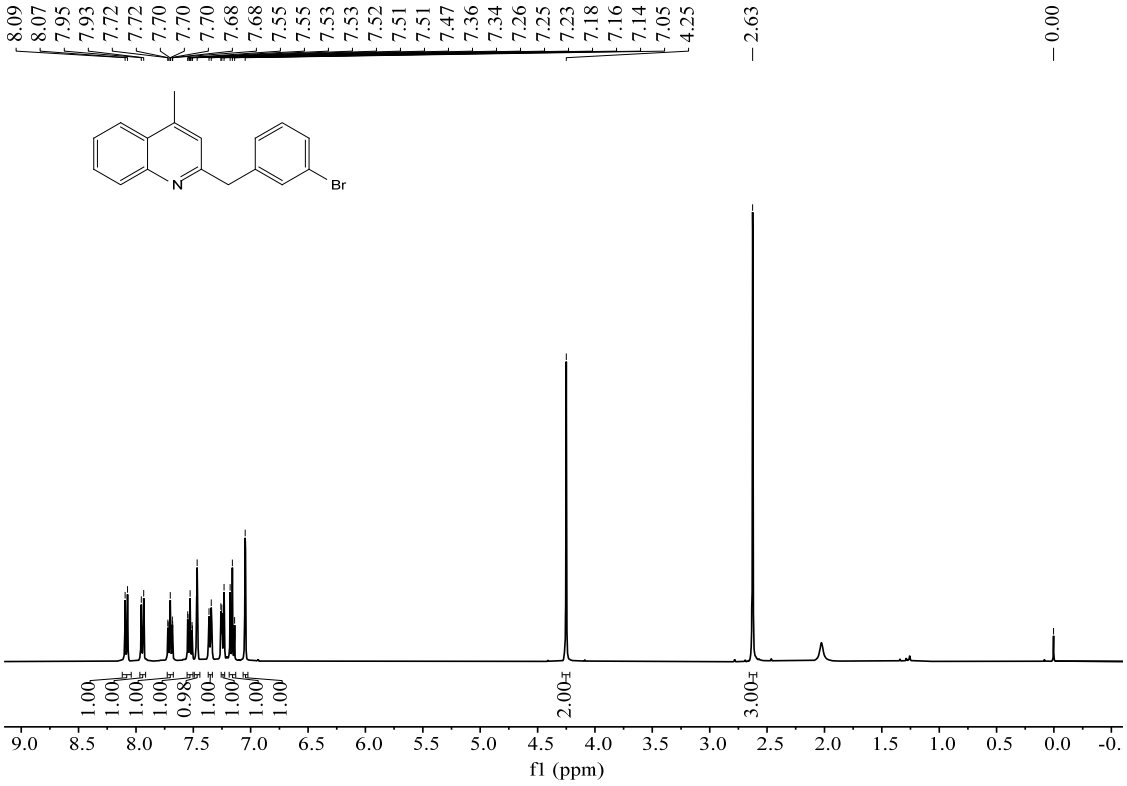
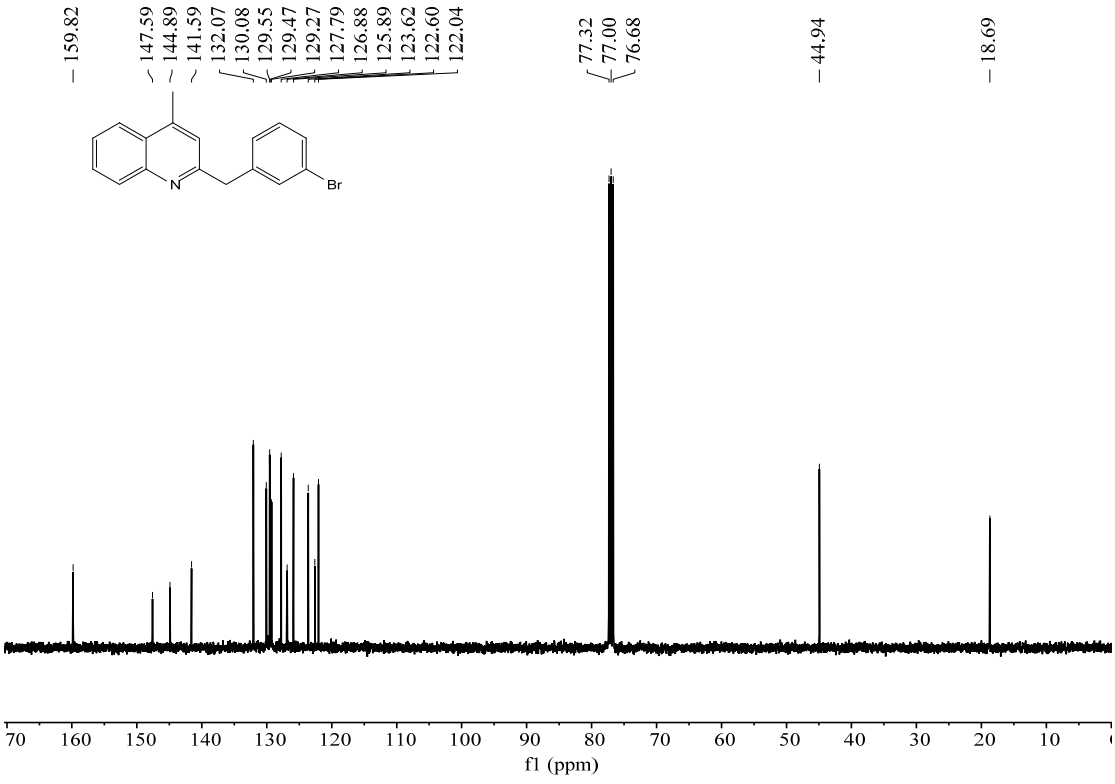


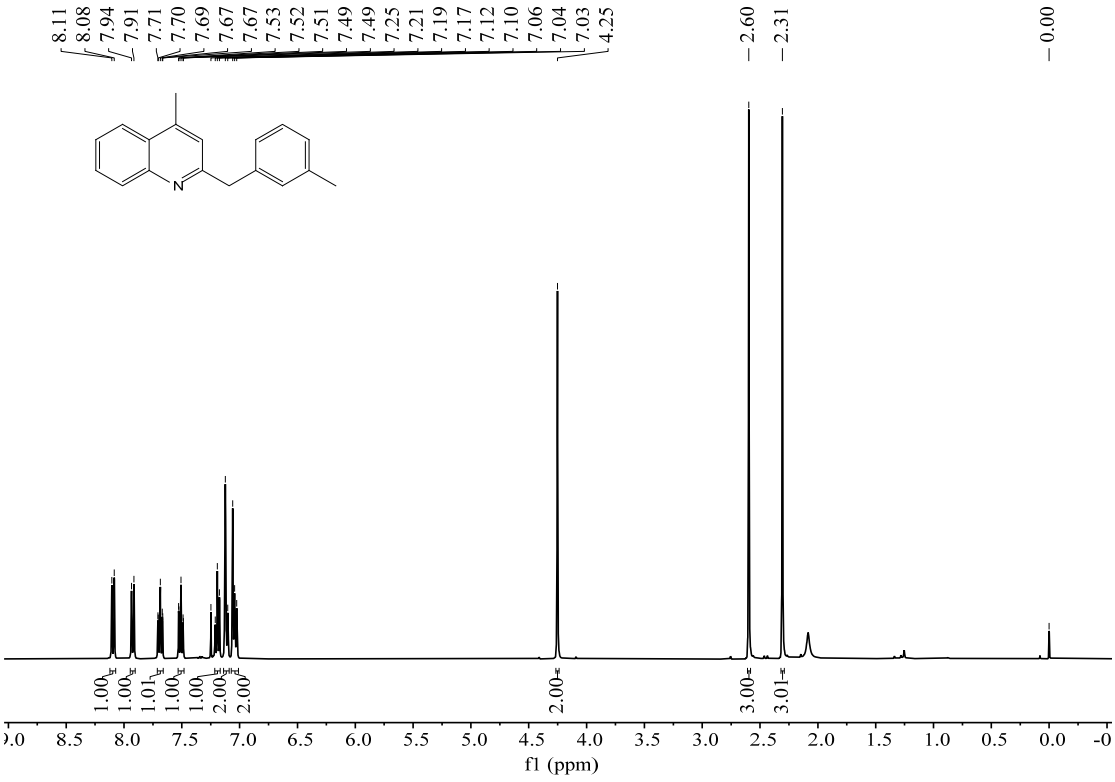


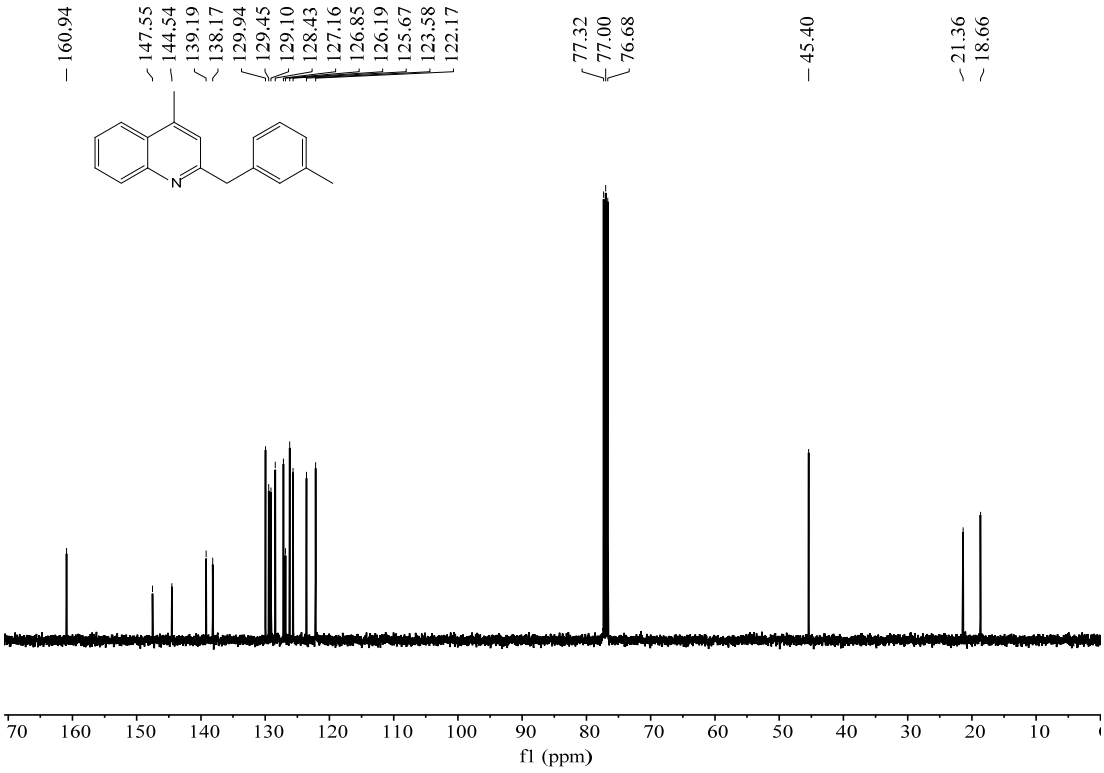
^{1}H and ^{13}C NMR spectra of 2f



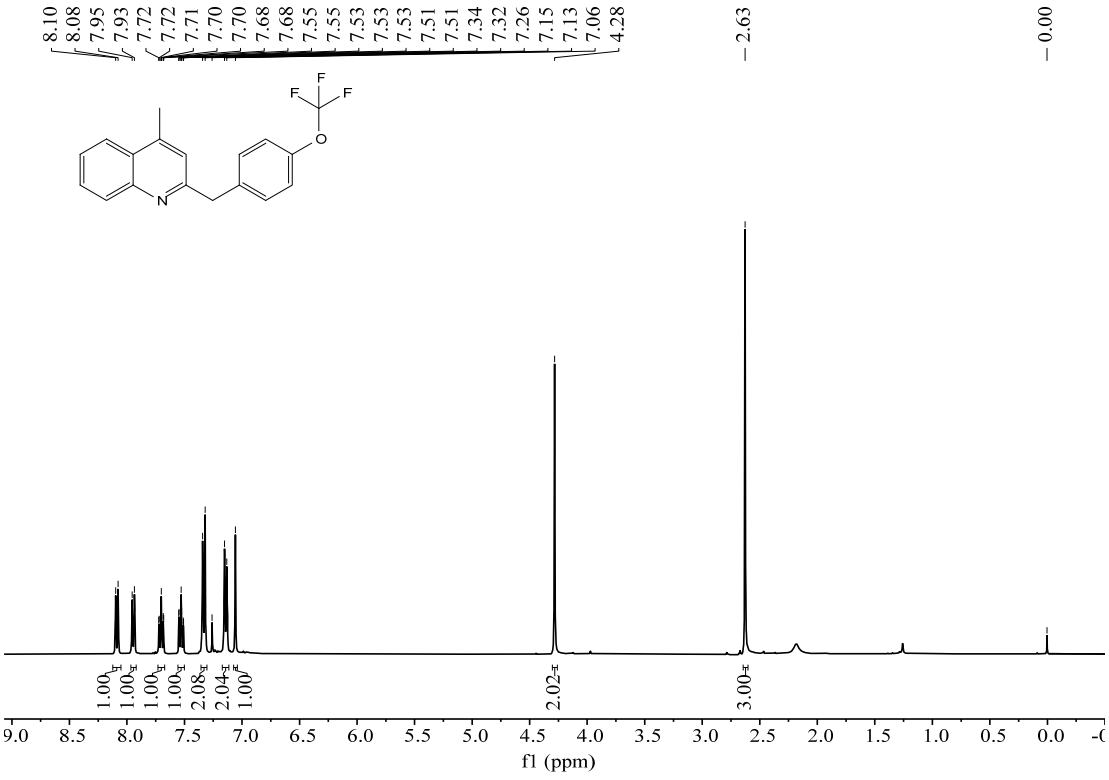


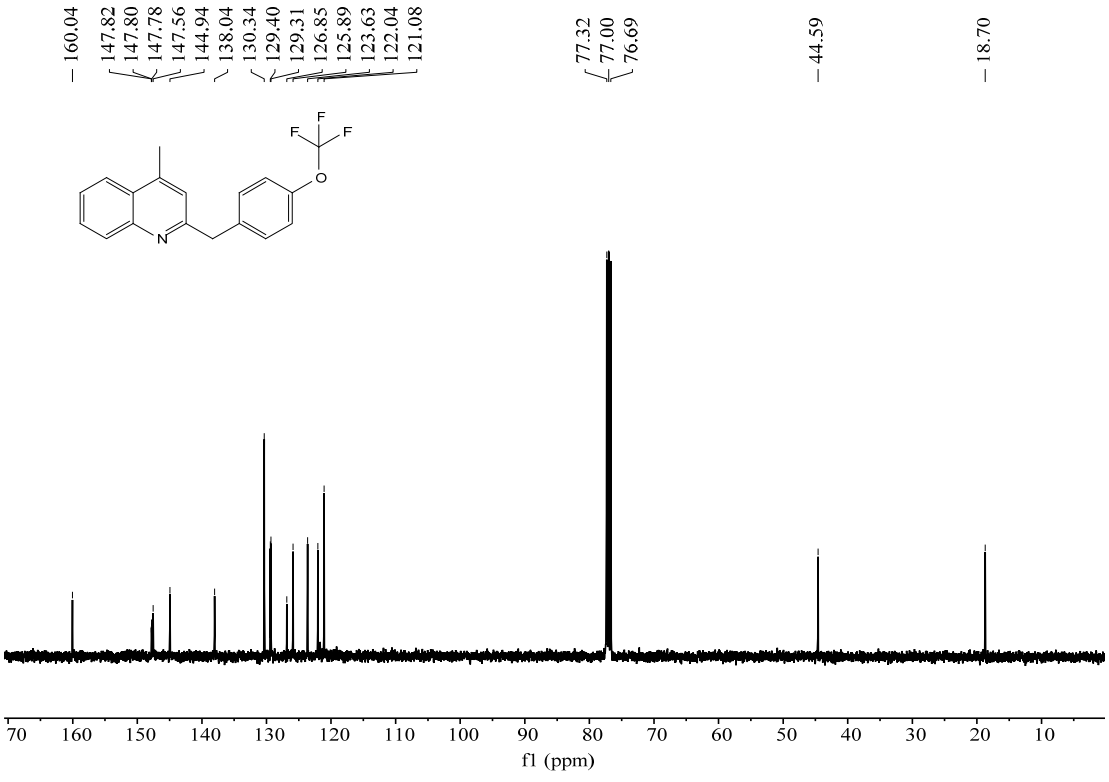
^{1}H and ^{13}C NMR spectra of 2g



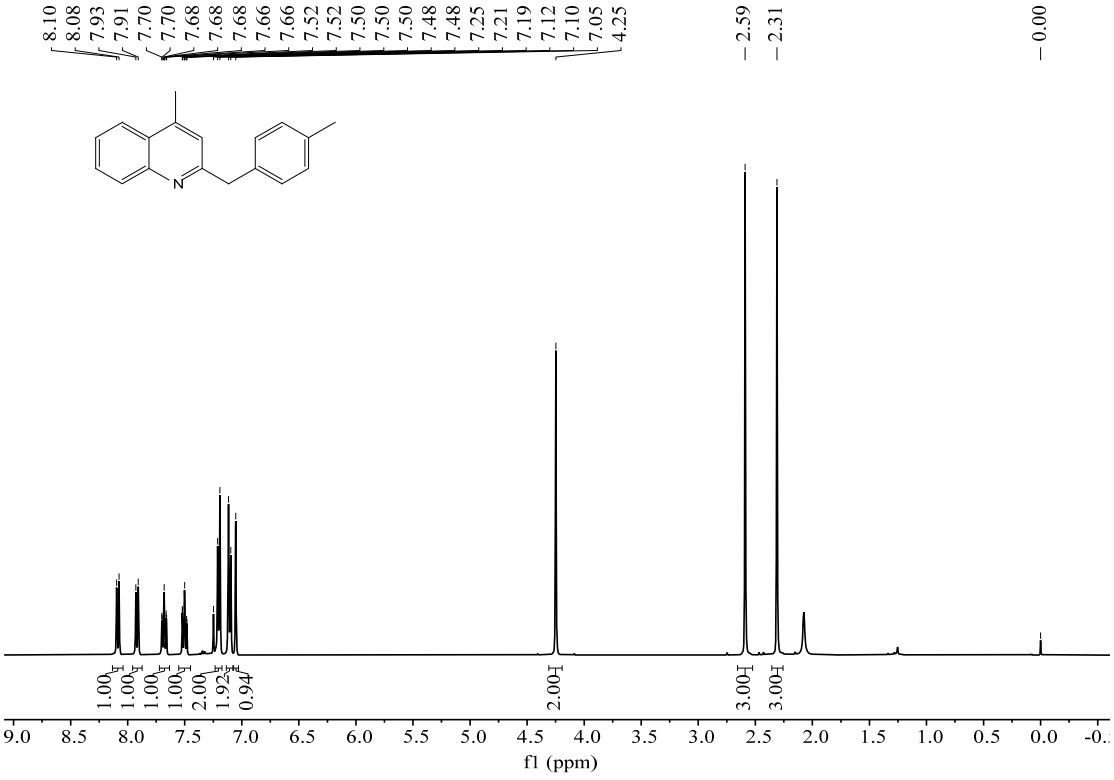


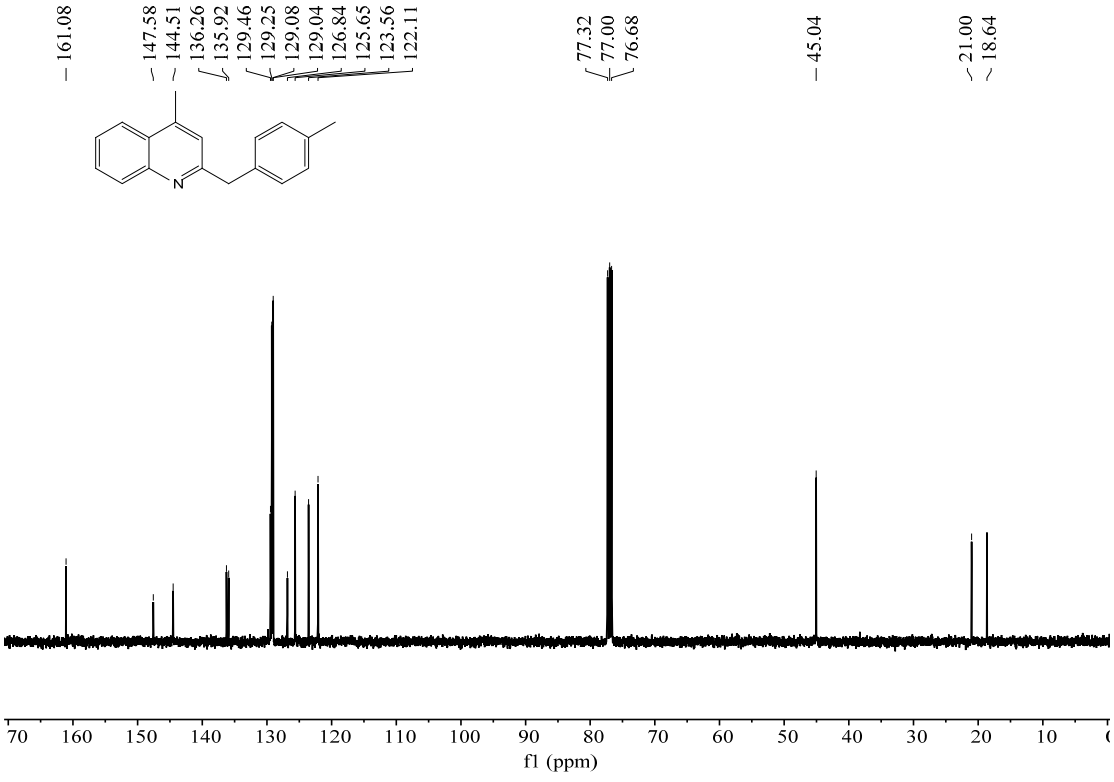
^{1}H and ^{13}C NMR spectra of 2h



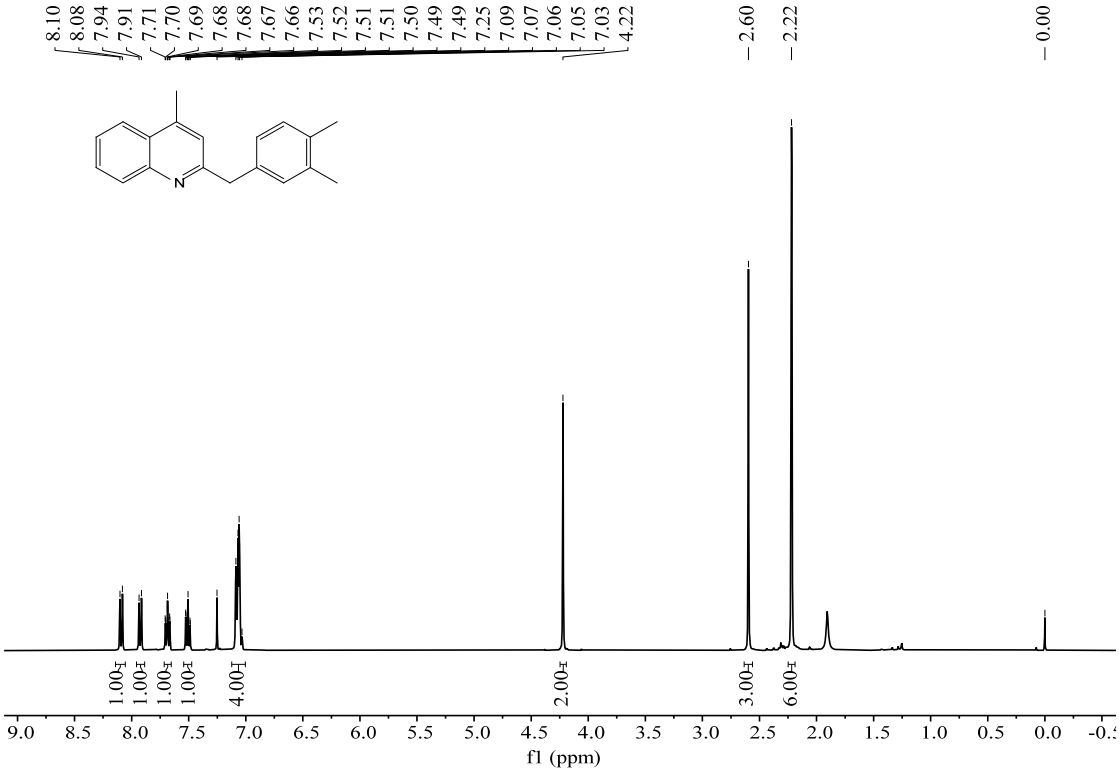


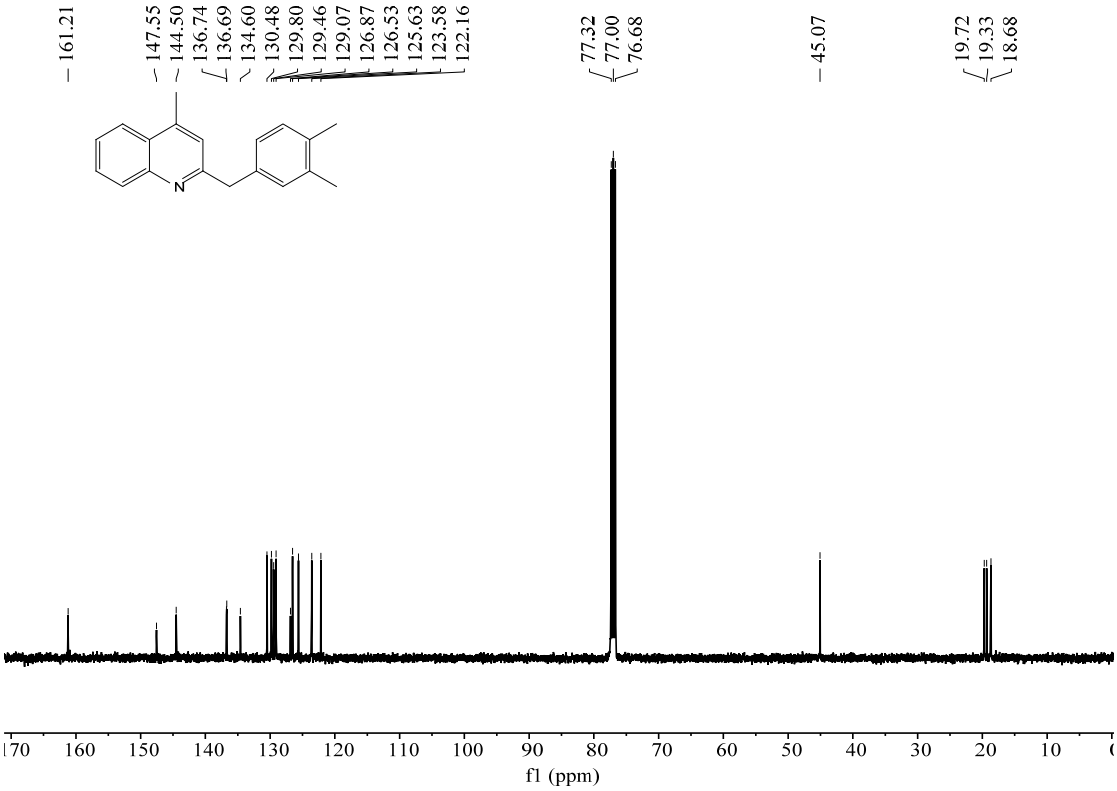
^{1}H and ^{13}C NMR spectra of 2i



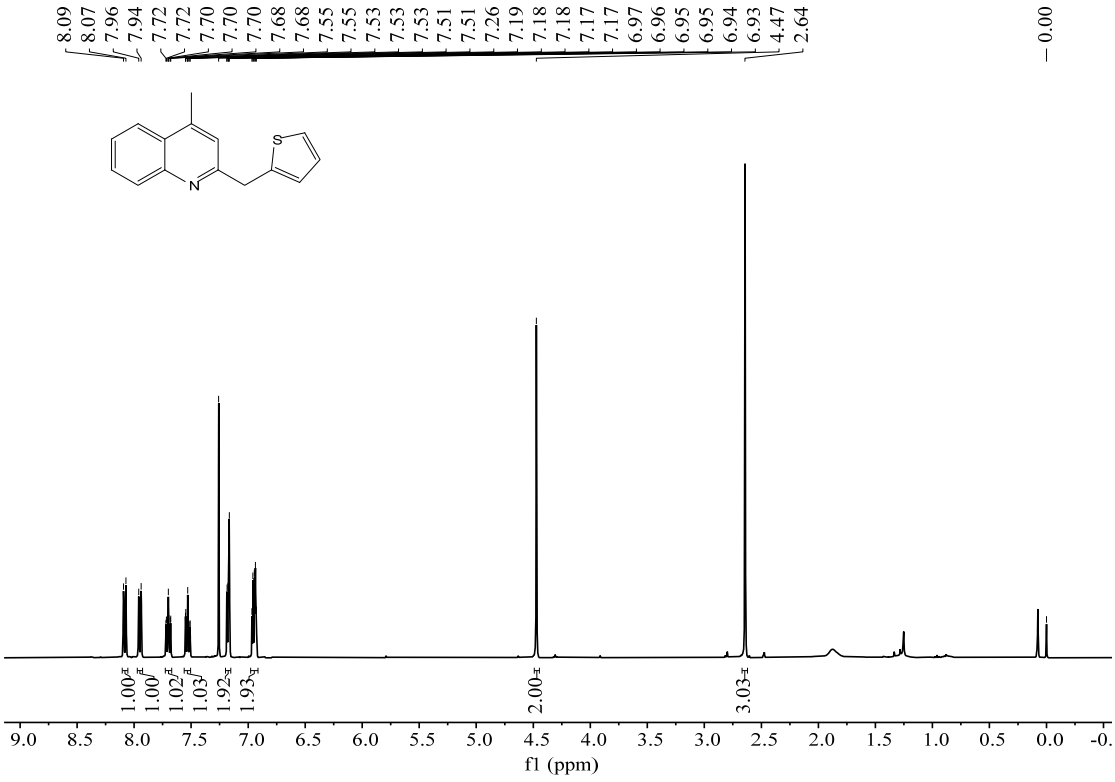


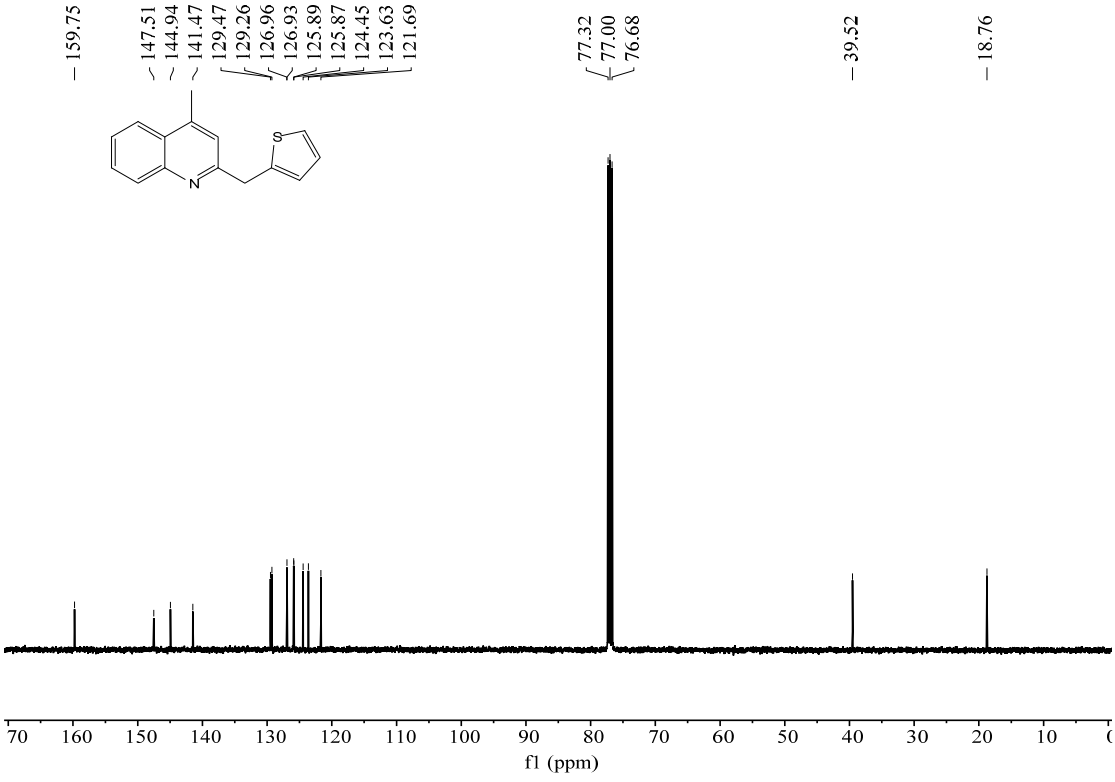
^{1}H and ^{13}C NMR spectra of 2j





^{1}H and ^{13}C NMR spectra of 2k





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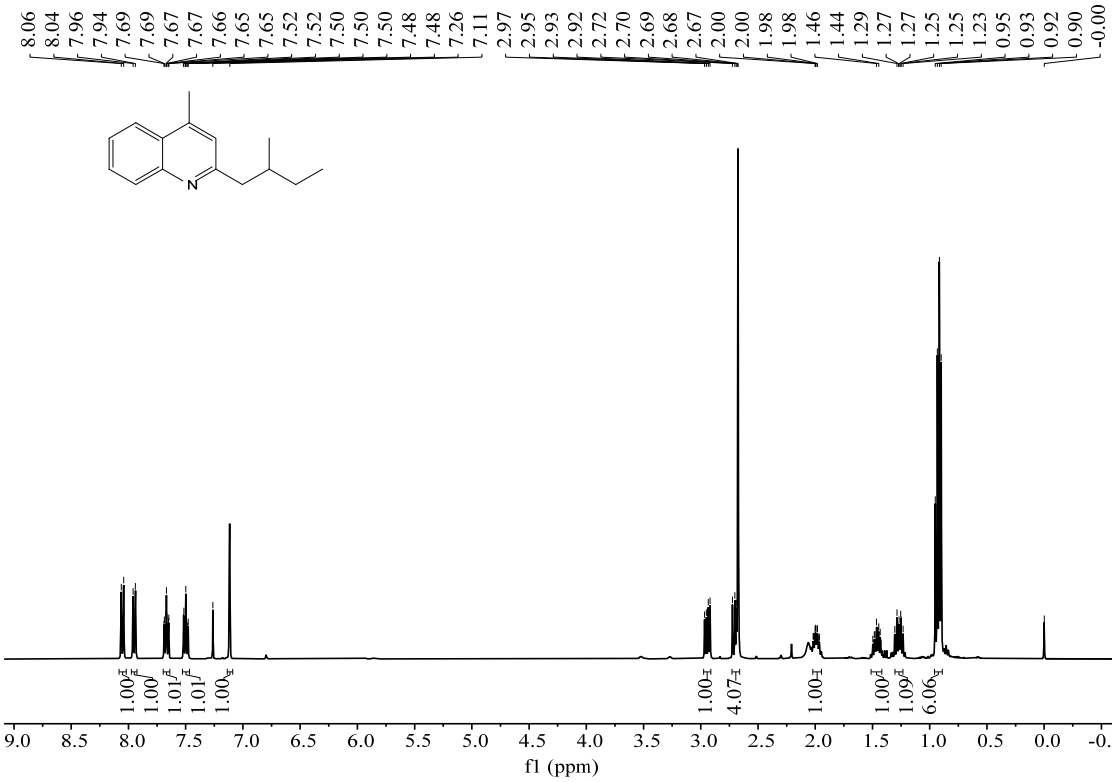
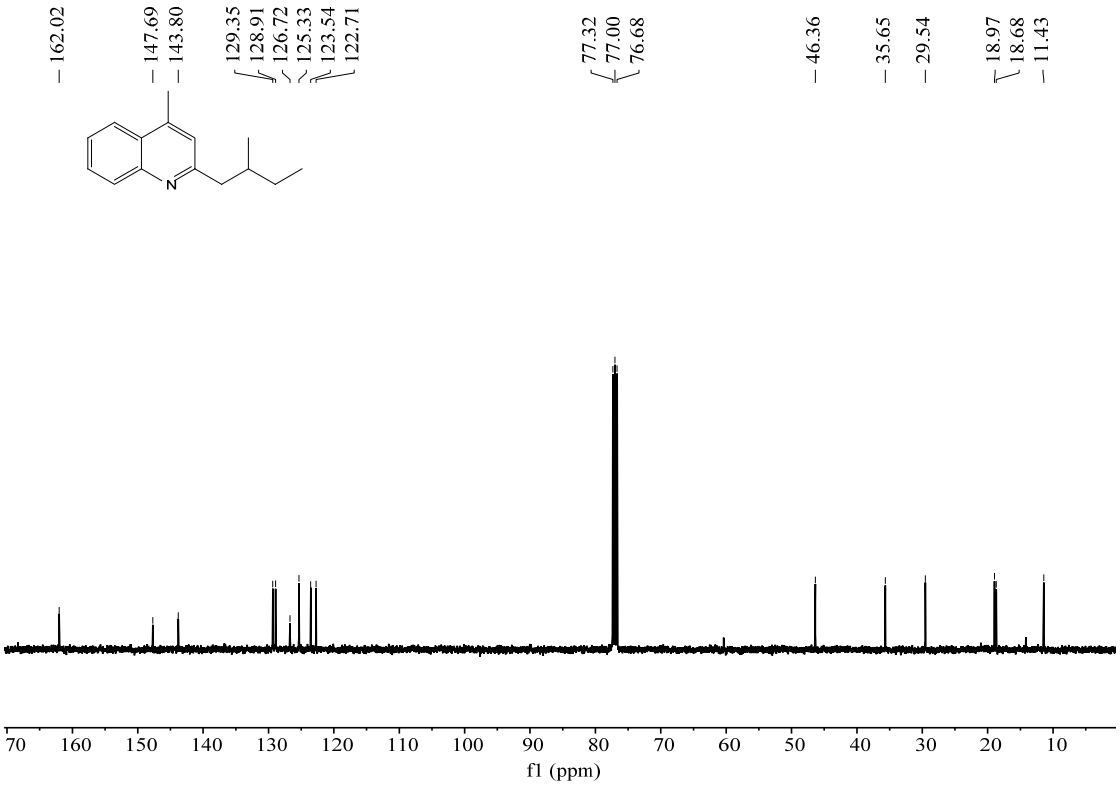
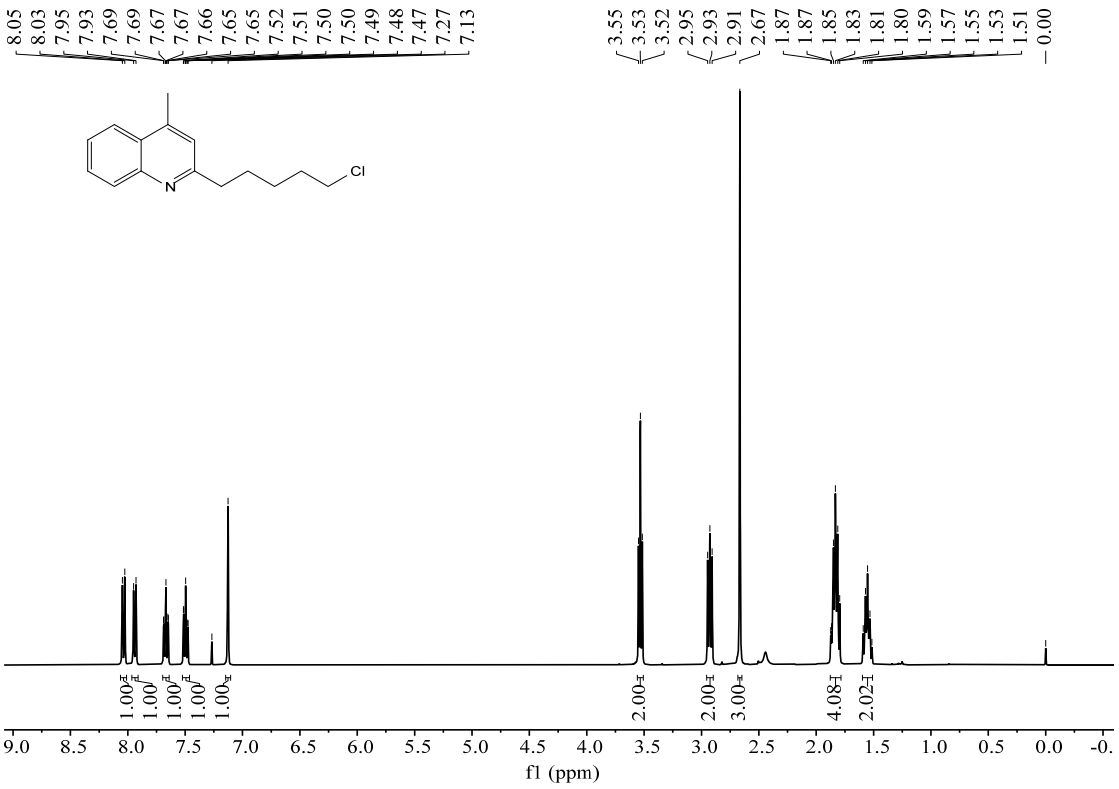
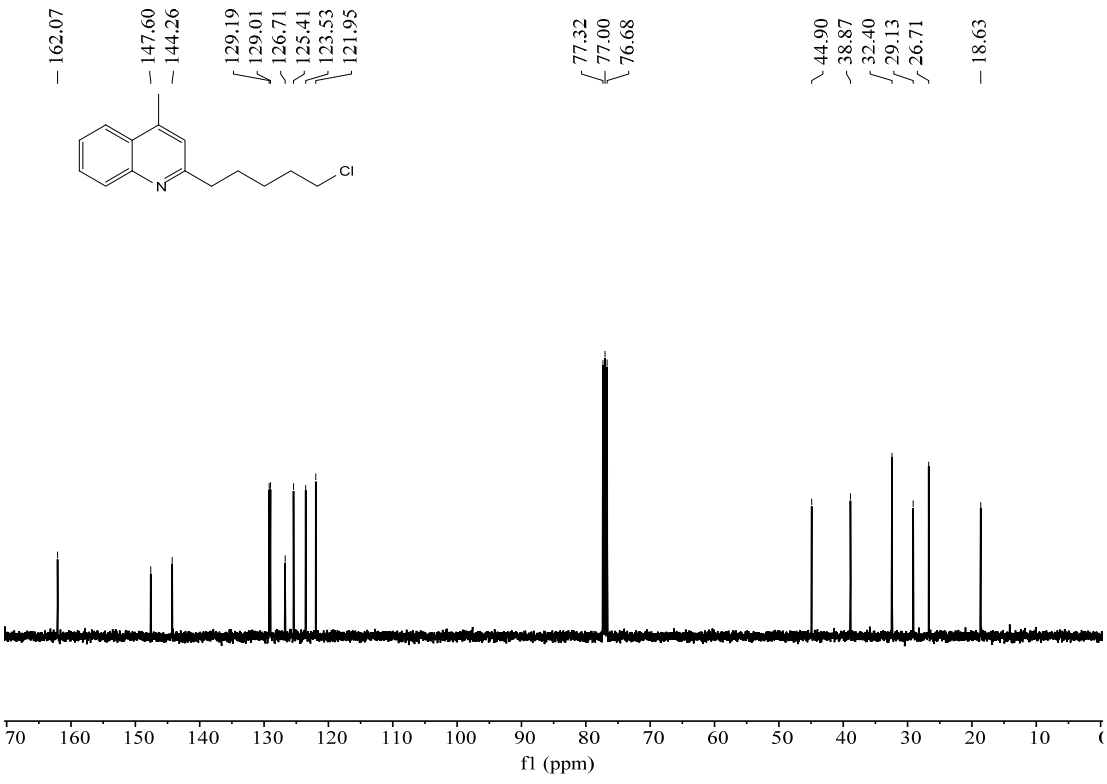


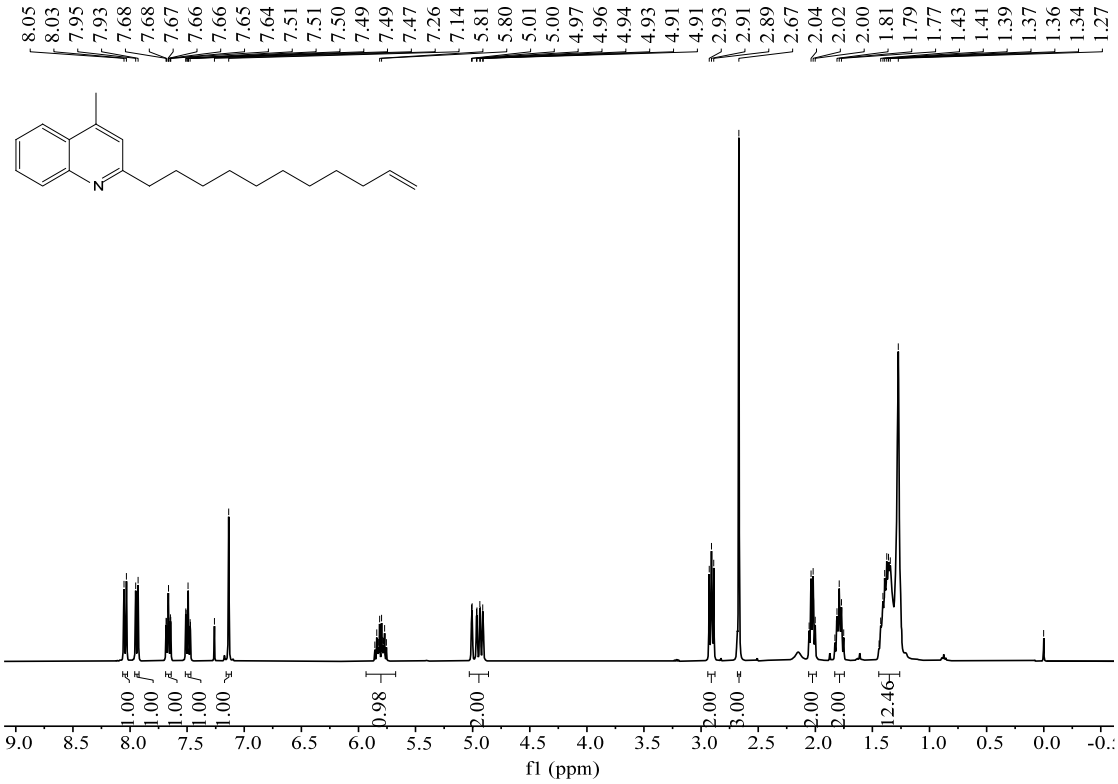


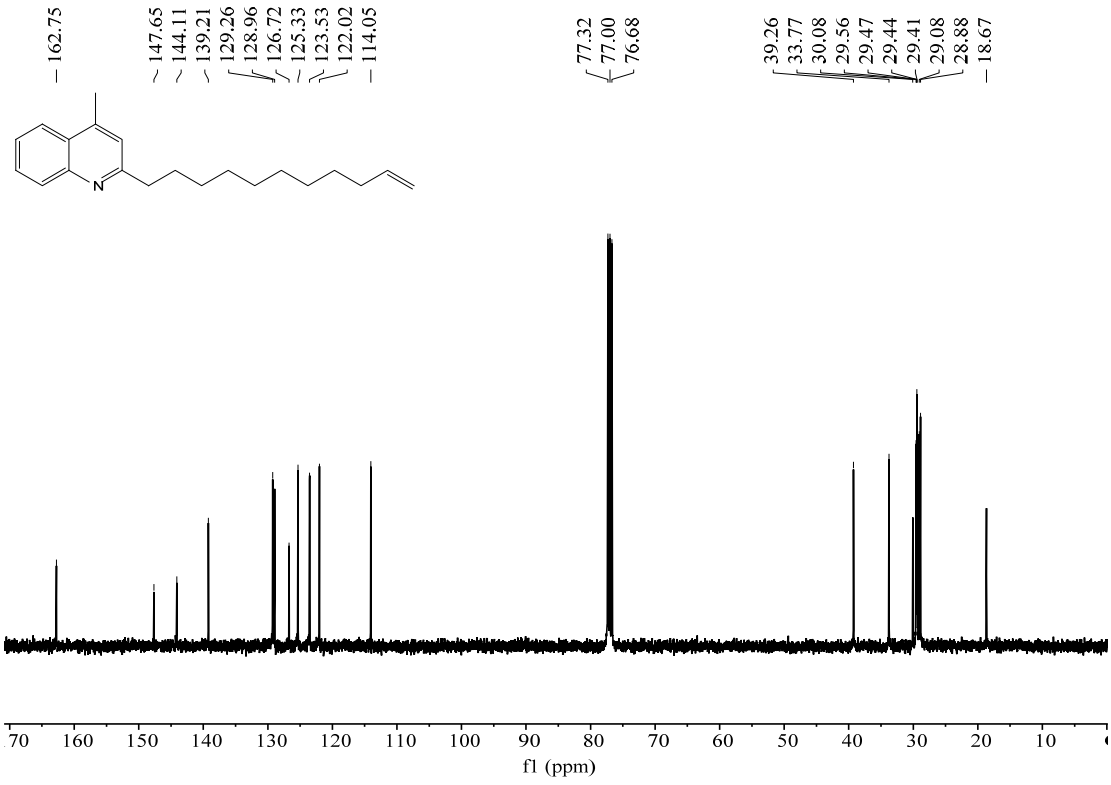
^{1}H and ^{13}C NMR spectra of 2m



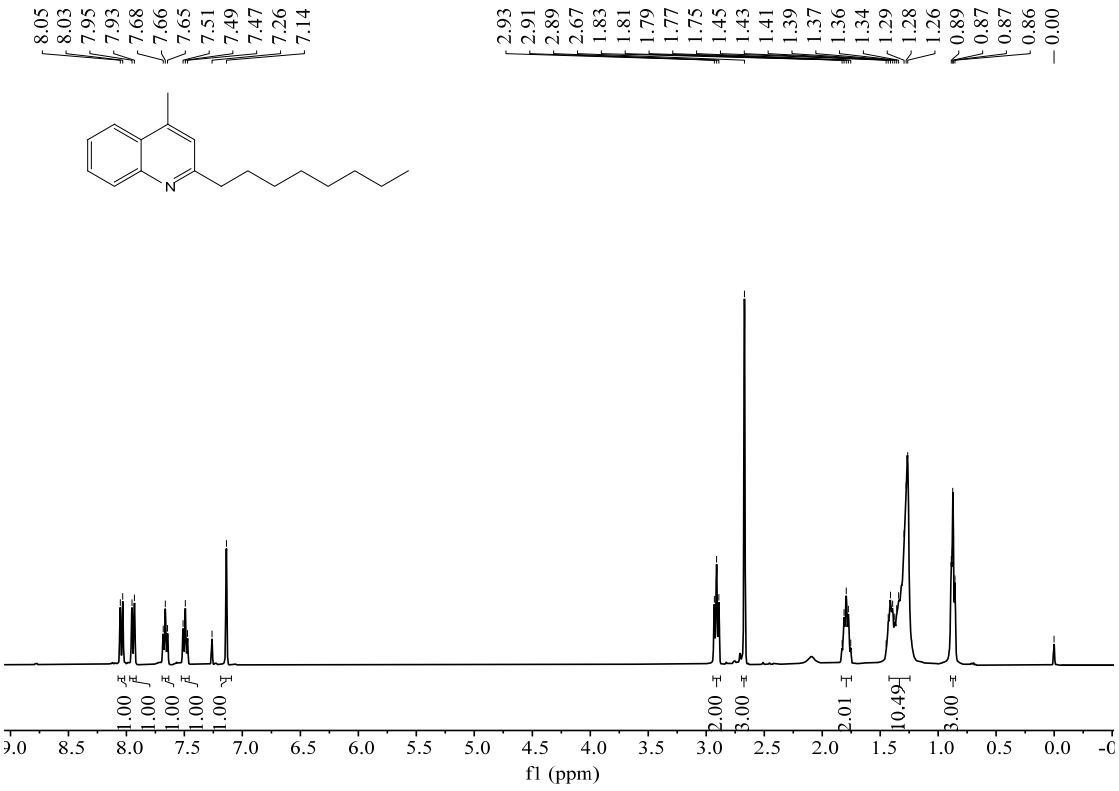


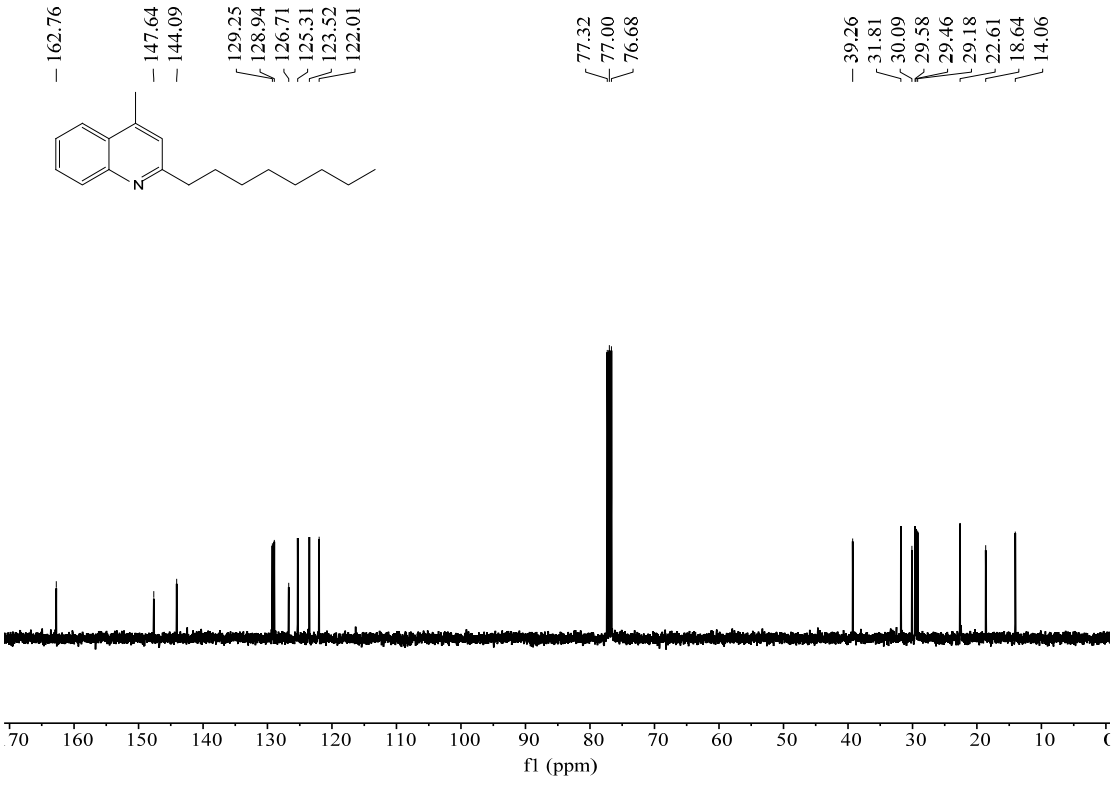
^{1}H and ^{13}C NMR spectra of 2n



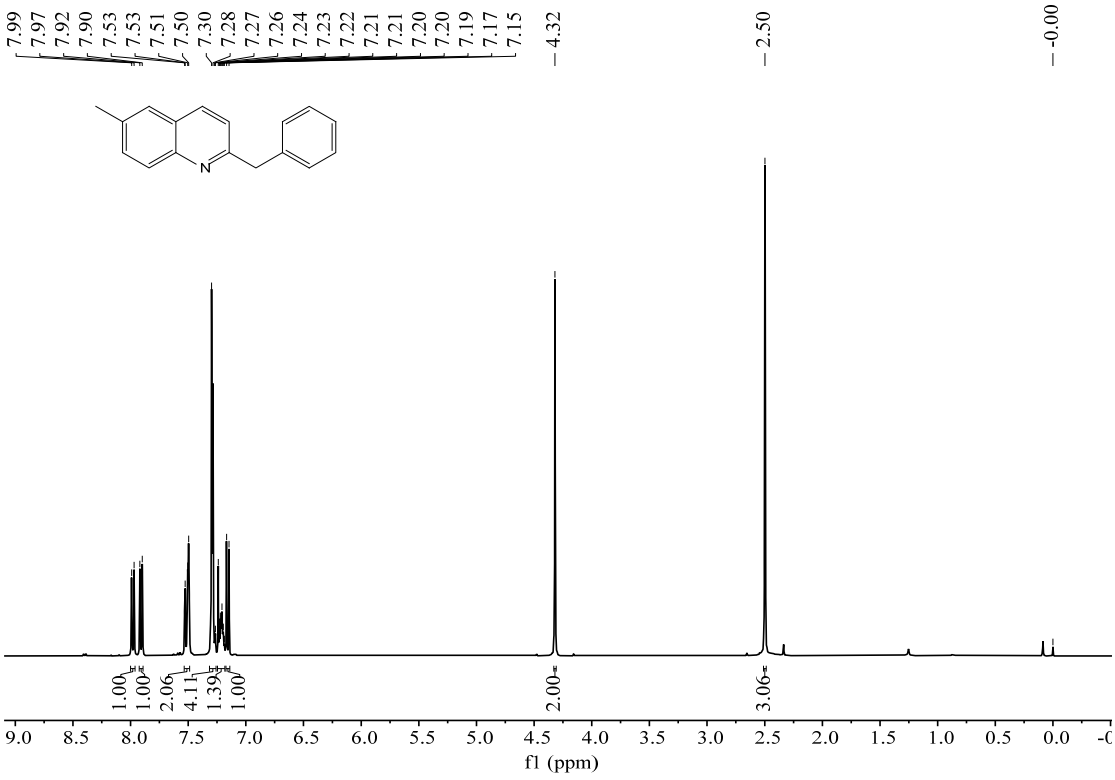


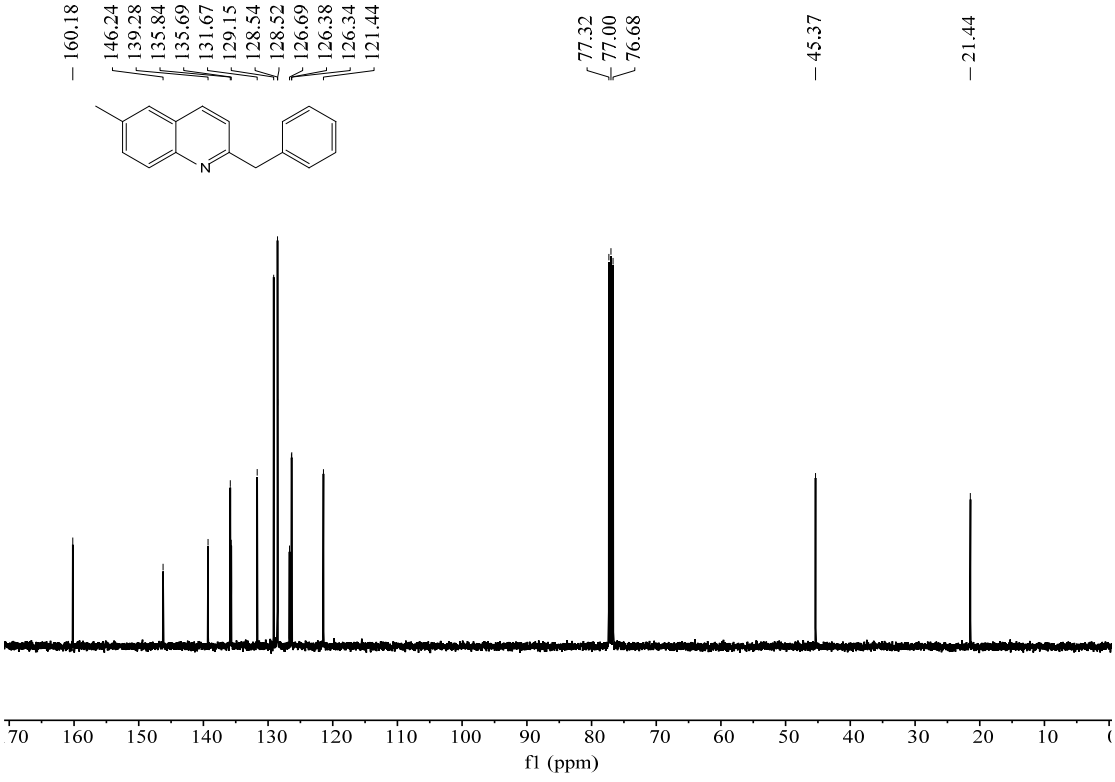
^{1}H and ^{13}C NMR spectra of 2o



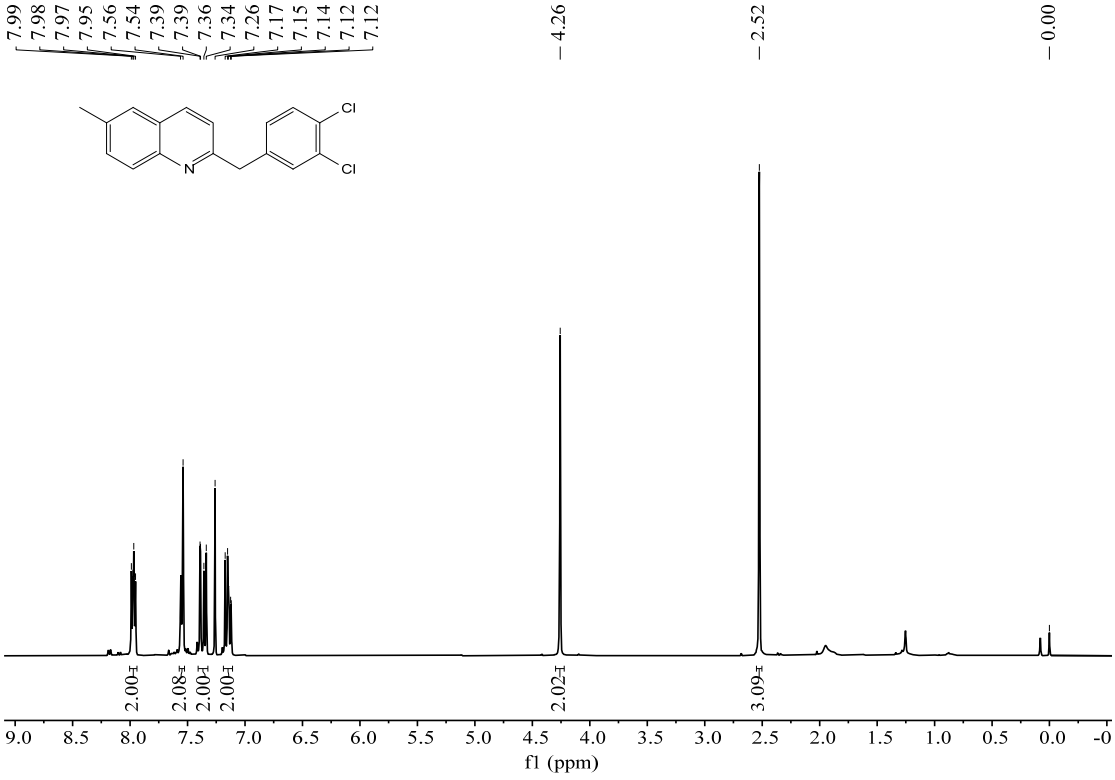


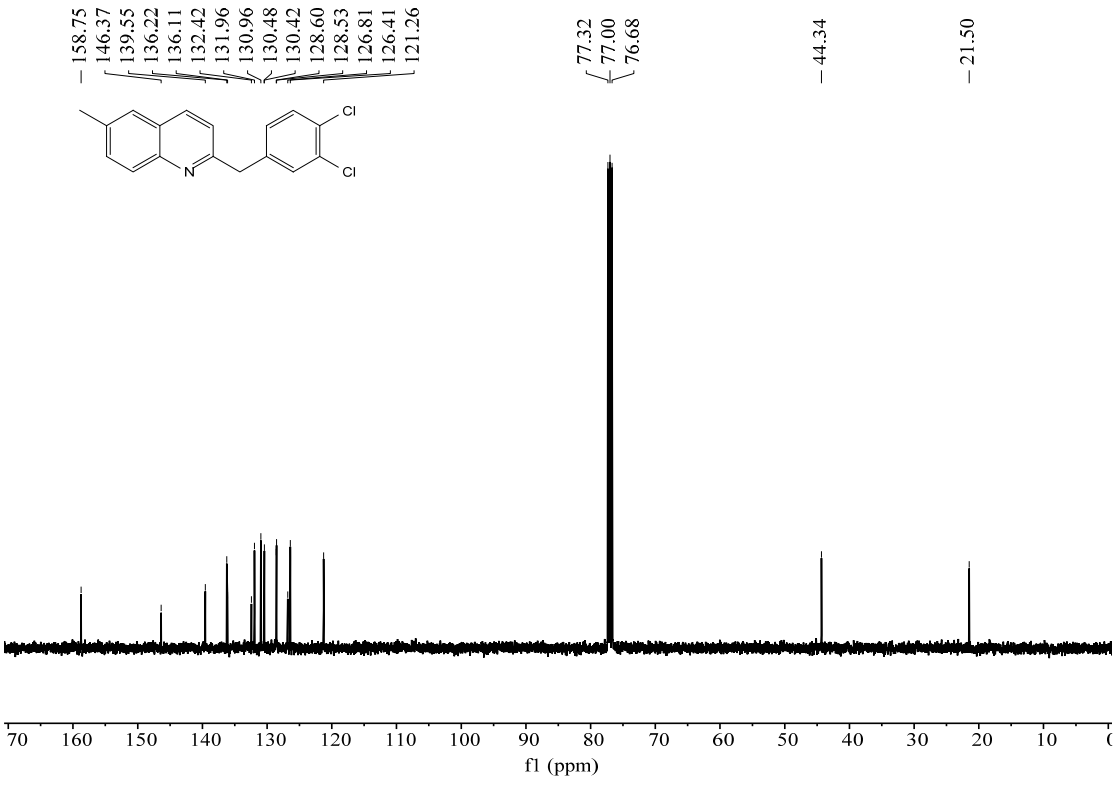
^{1}H and ^{13}C NMR spectra of 2p



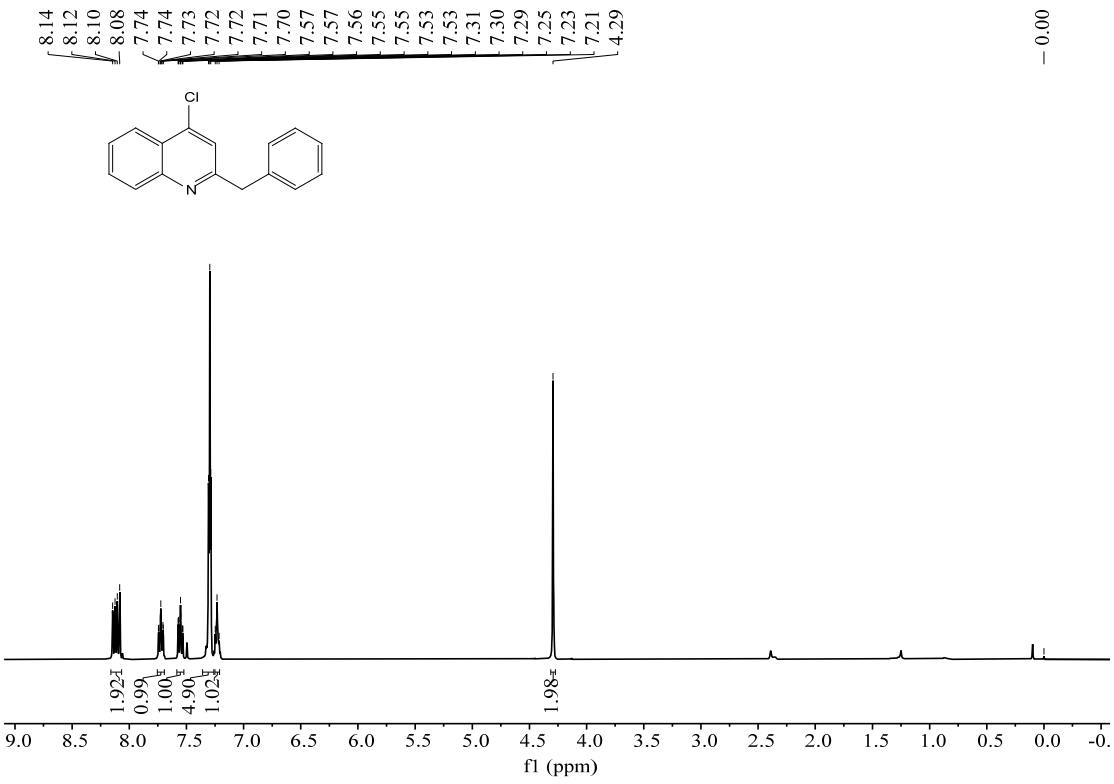


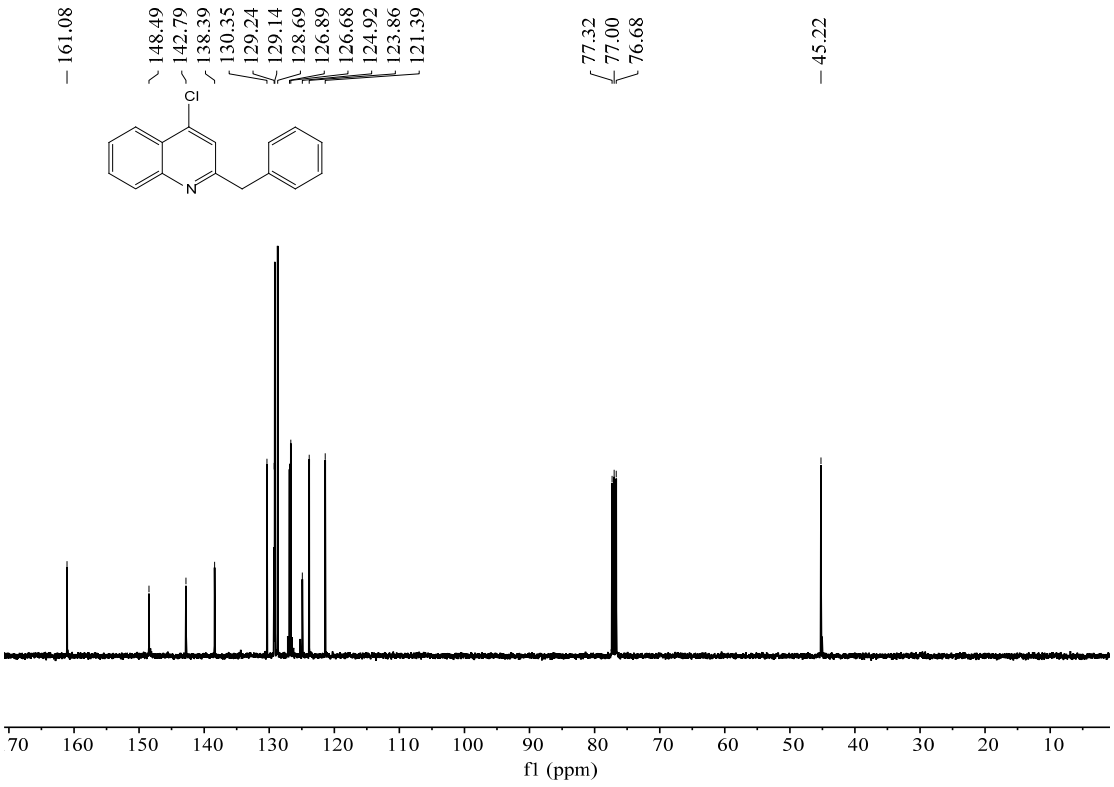
^{1}H and ^{13}C NMR spectra of 2q



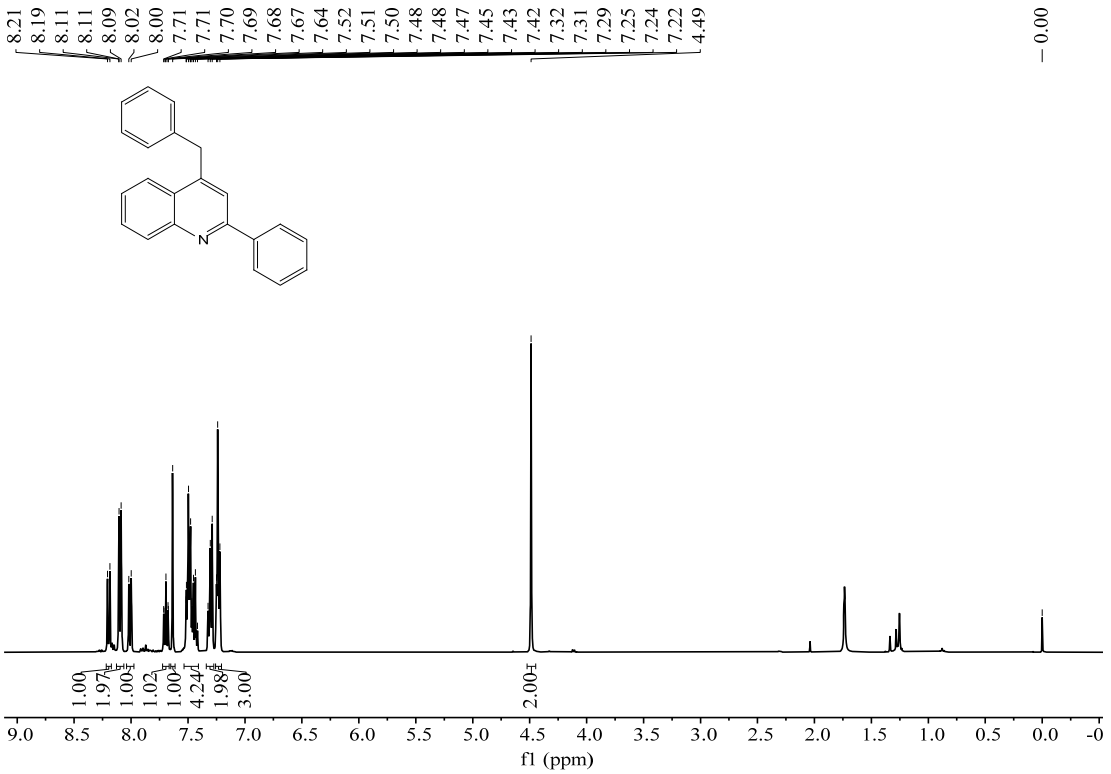


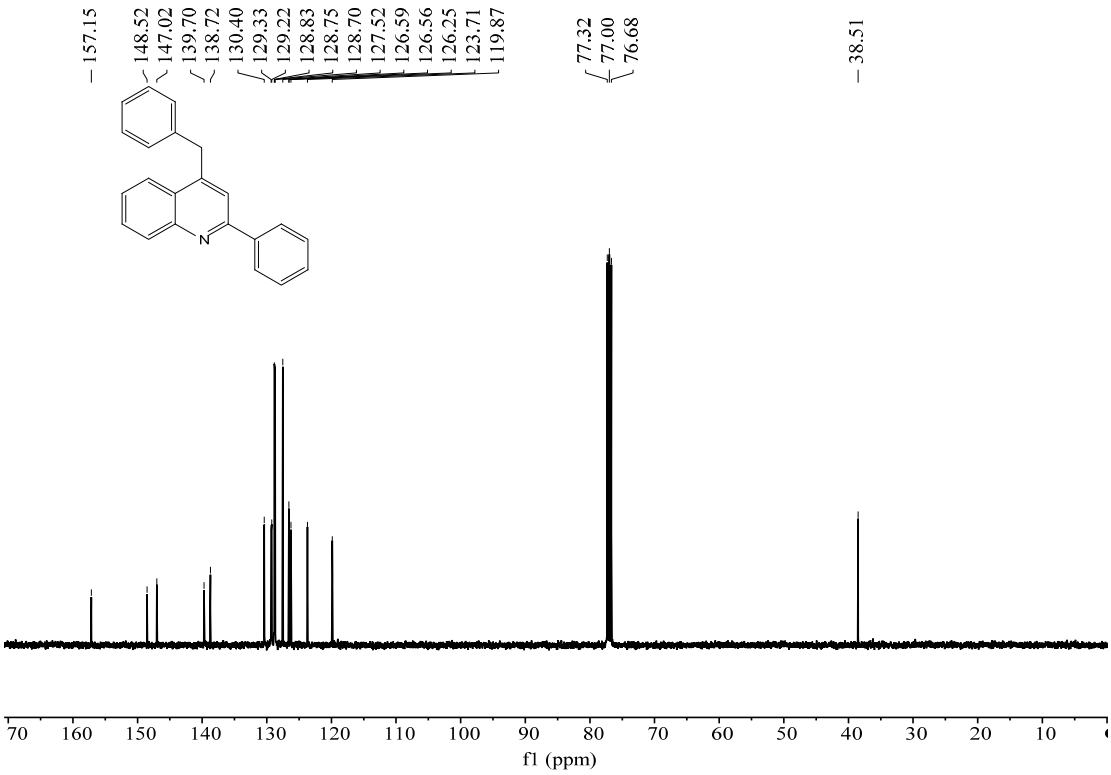
^{1}H and ^{13}C NMR spectra of 2r



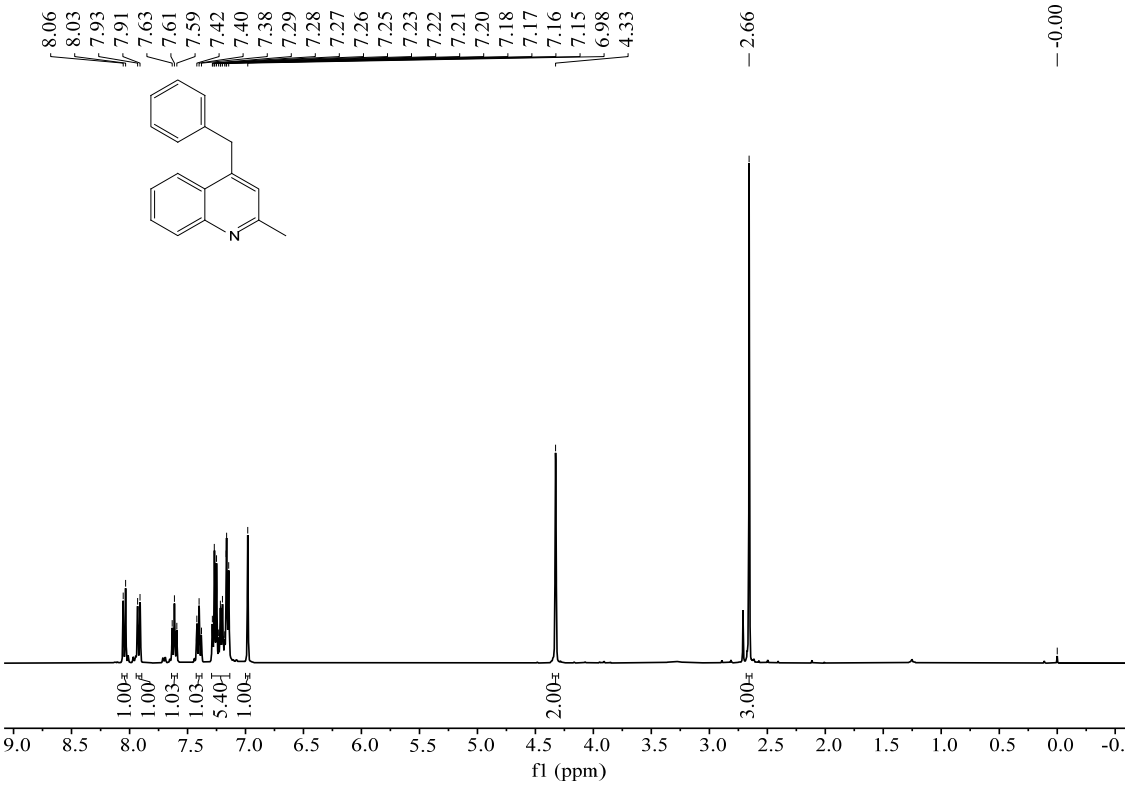


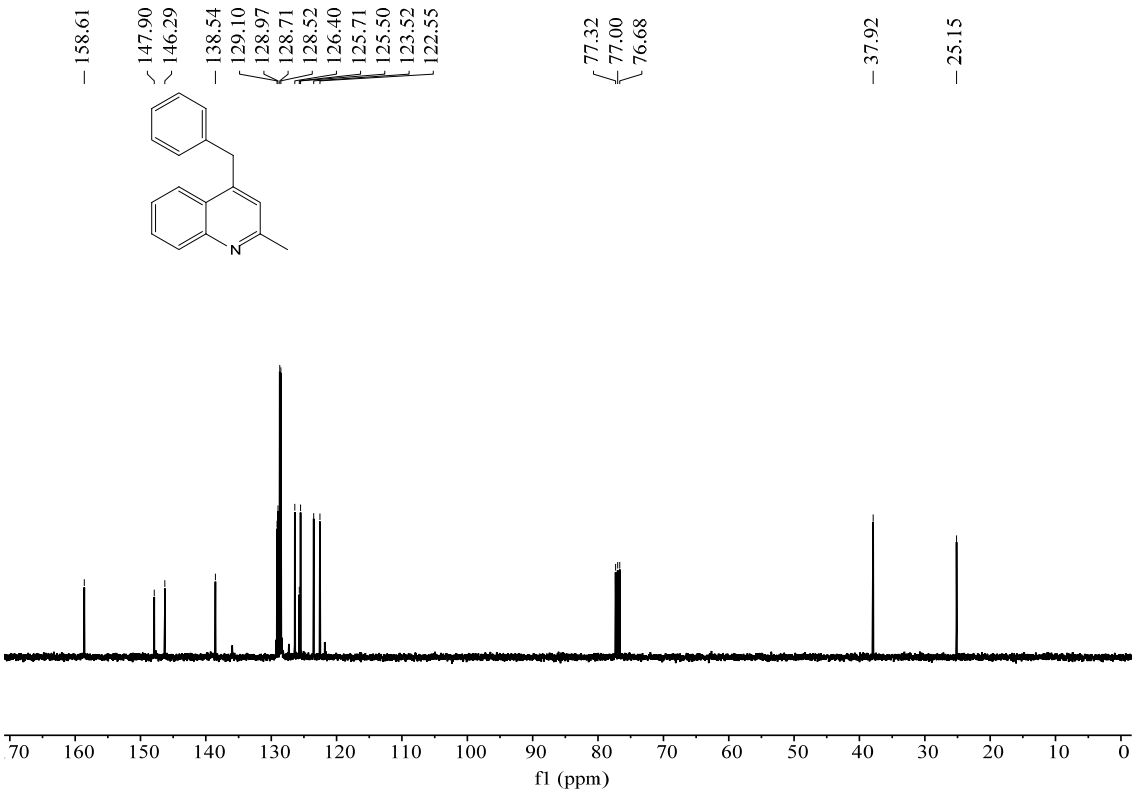
^{1}H and ^{13}C NMR spectra of 2s



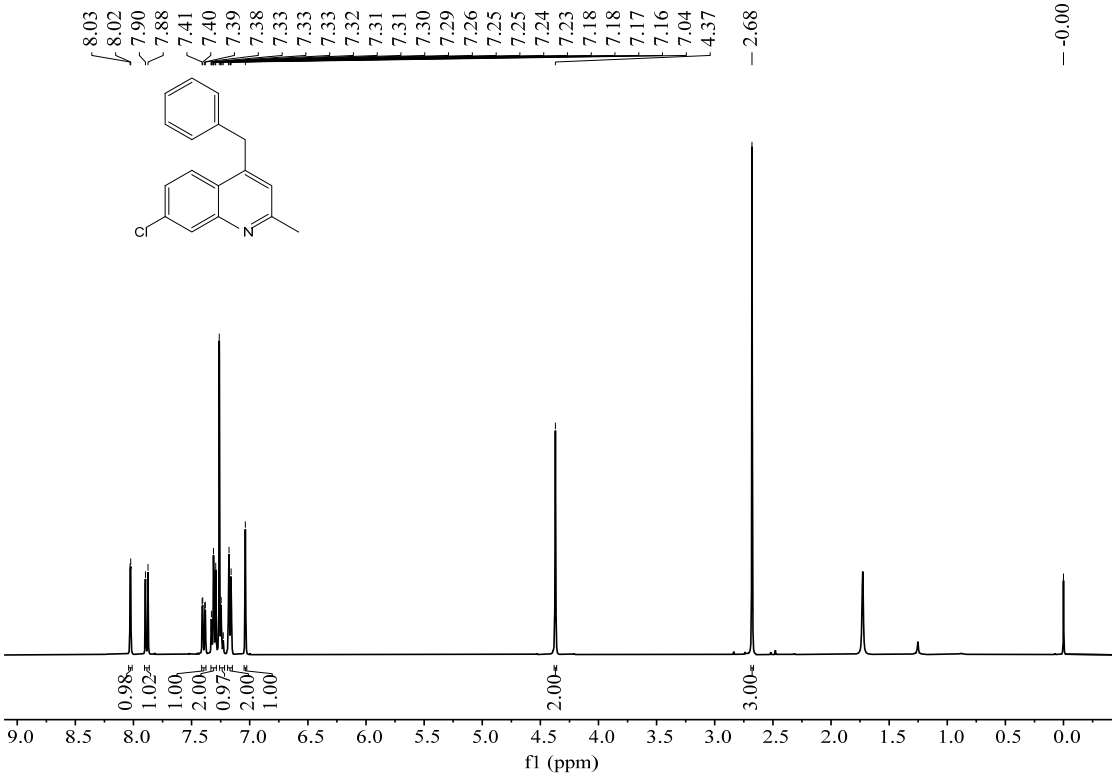


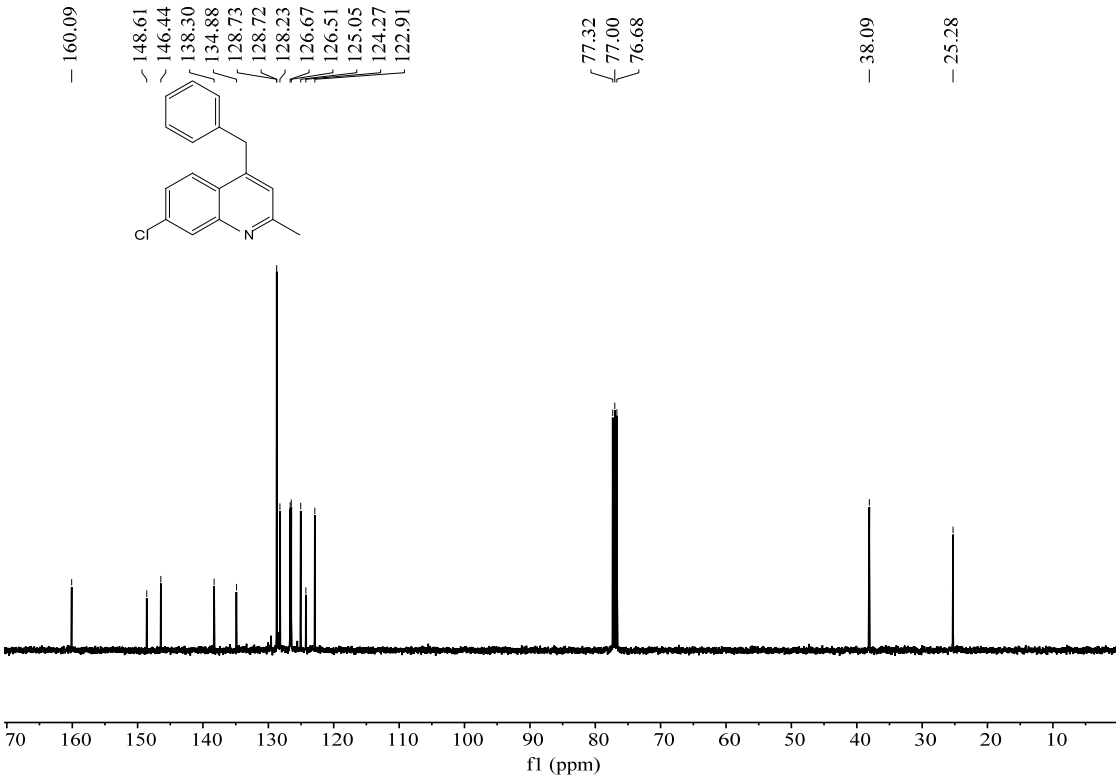
^{1}H and ^{13}C NMR spectra of 2t



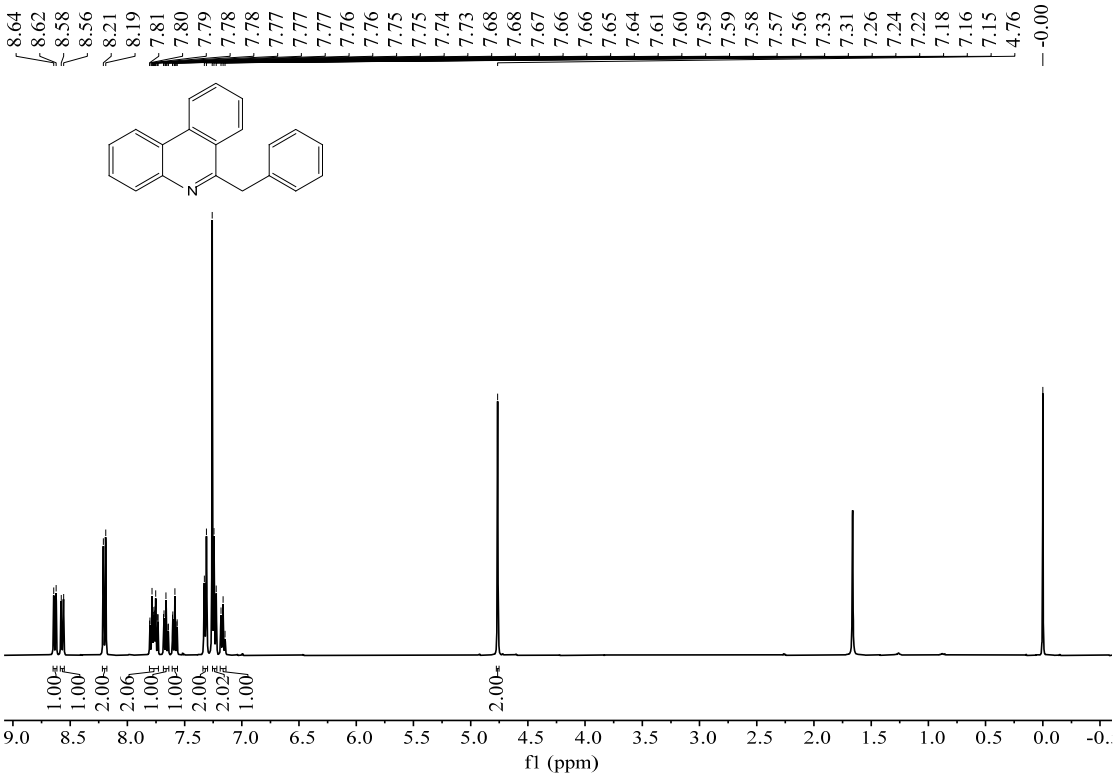


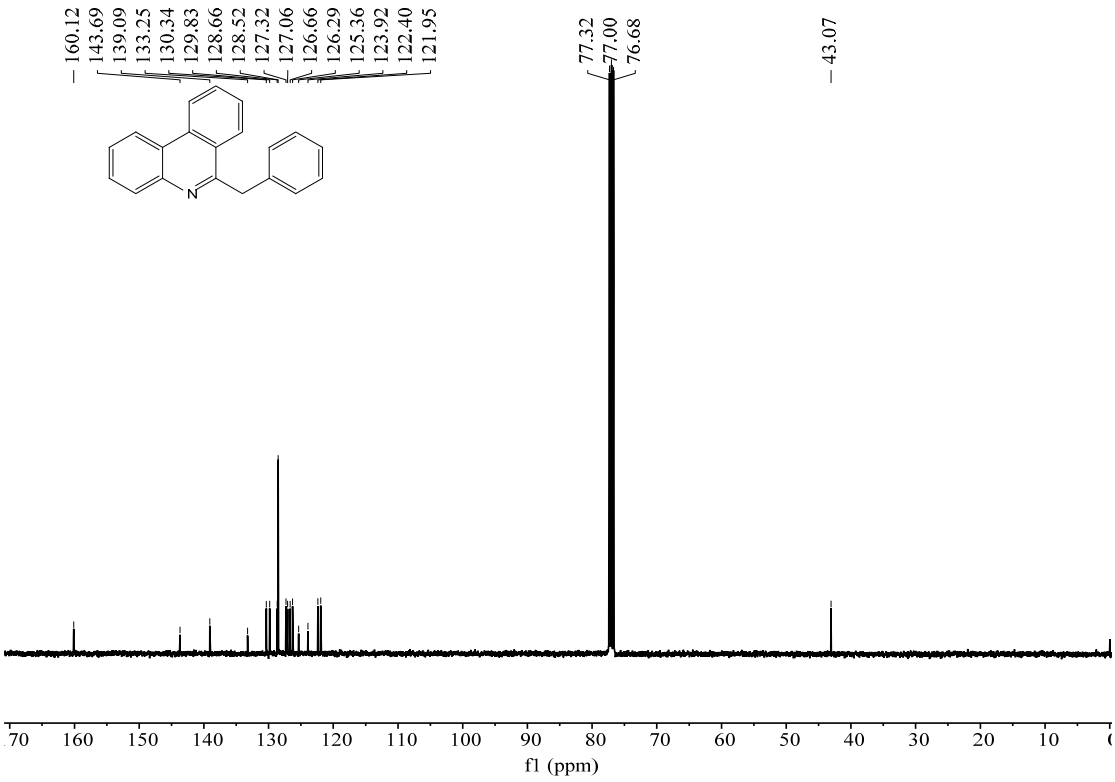
^{1}H and ^{13}C NMR spectra of 2u



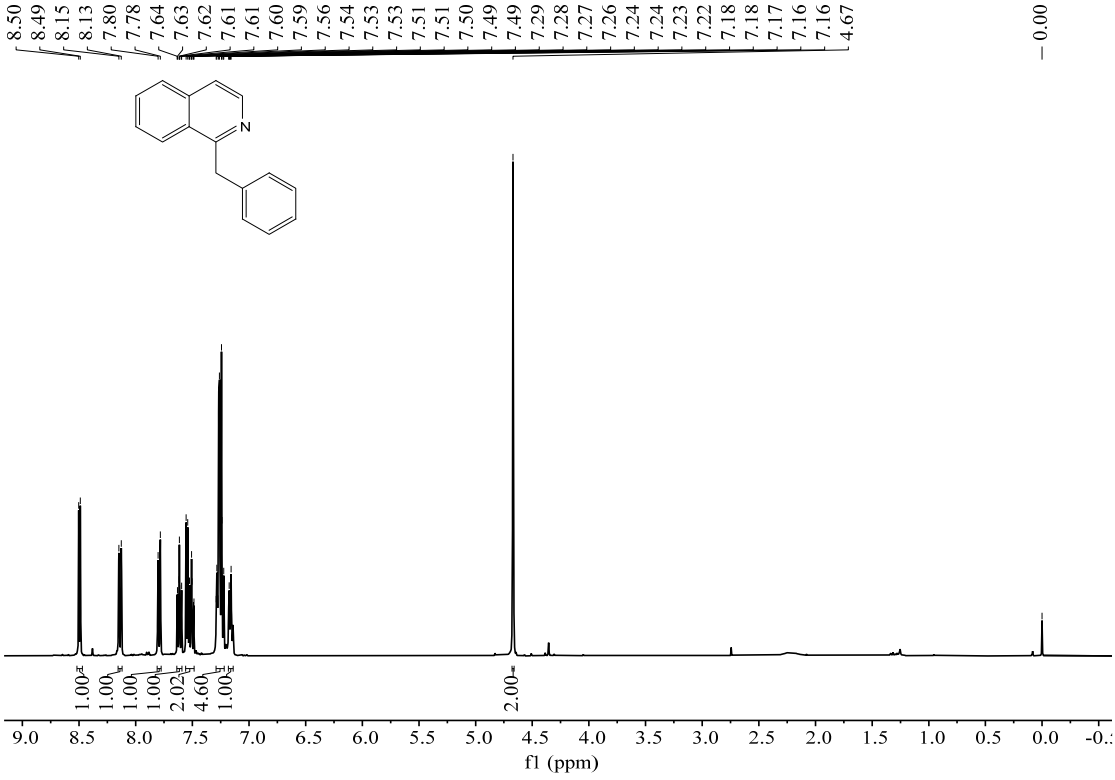


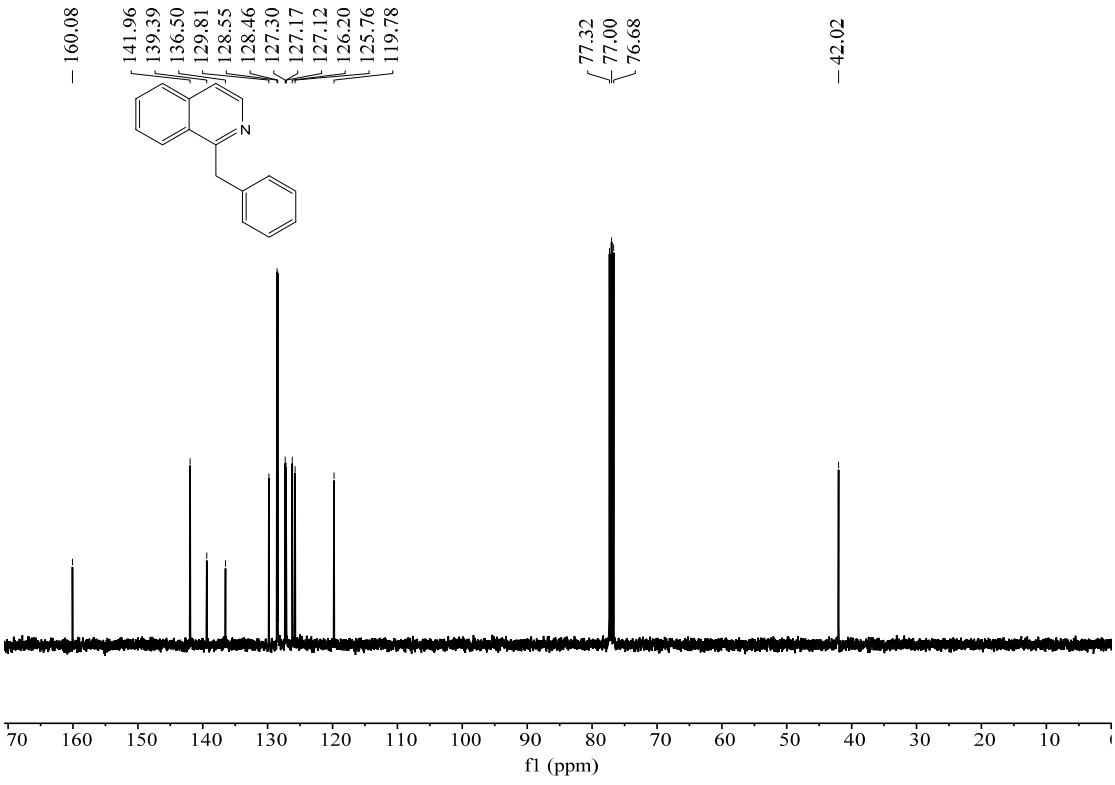
^{1}H and ^{13}C NMR spectra of 2v



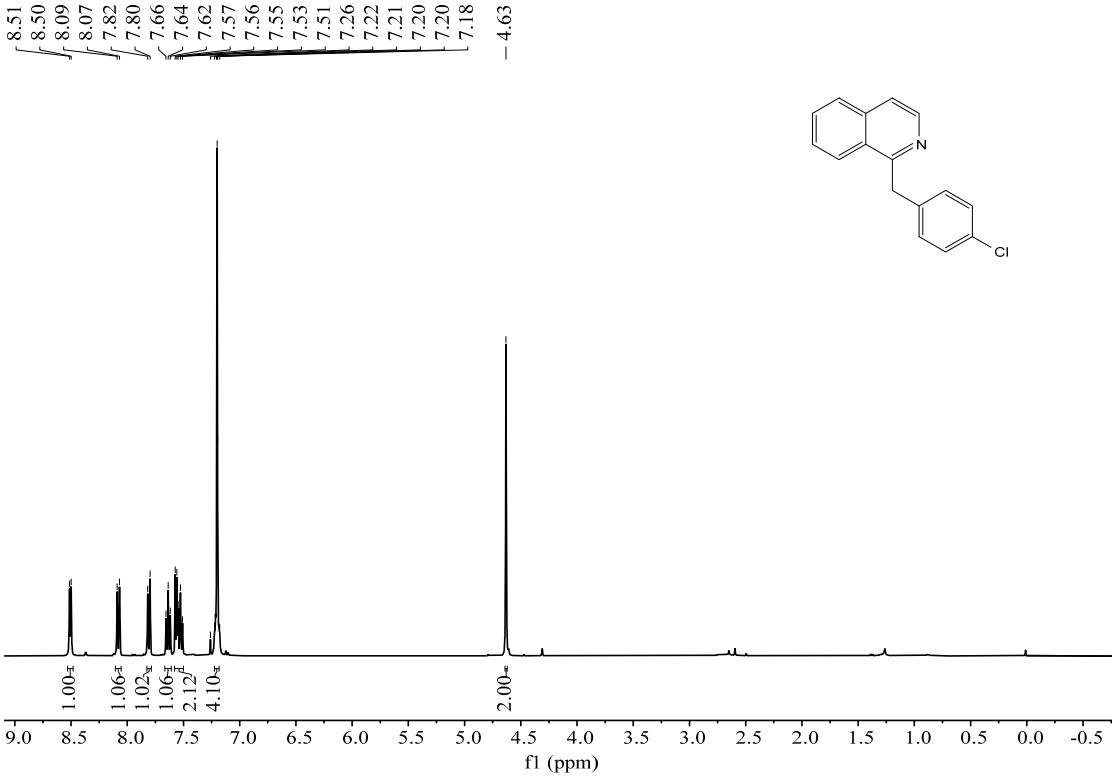


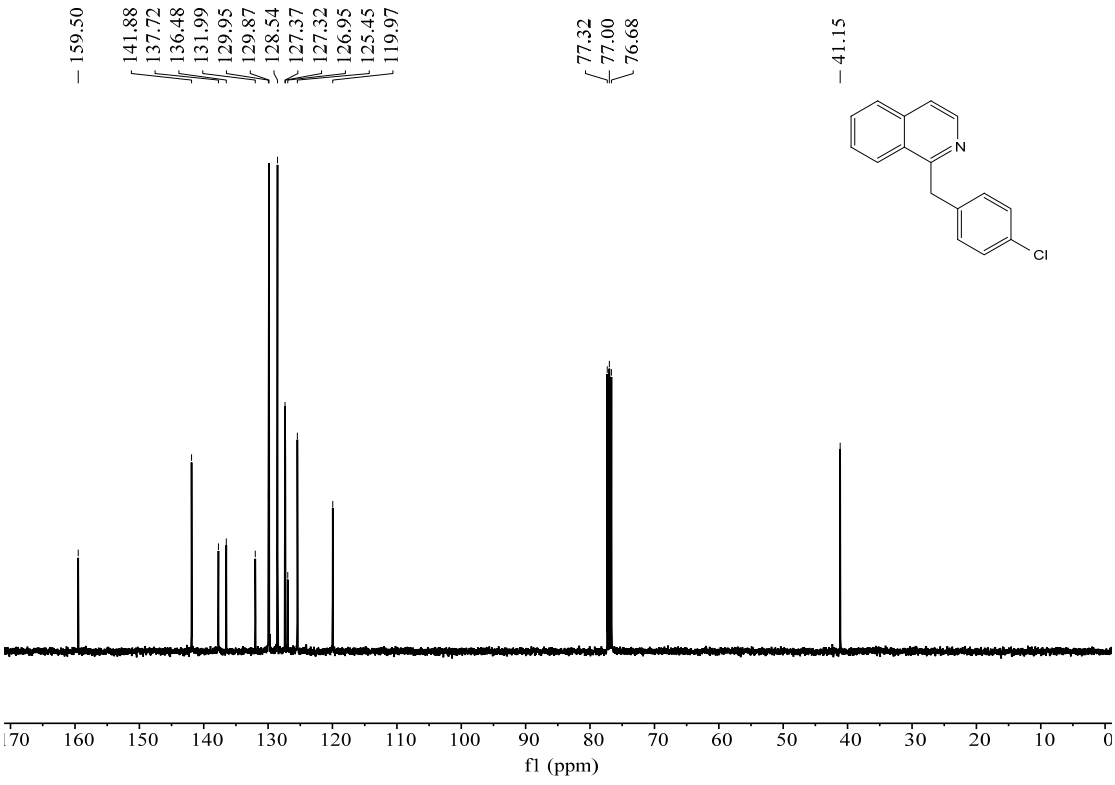
^{1}H and ^{13}C NMR spectra of 2w



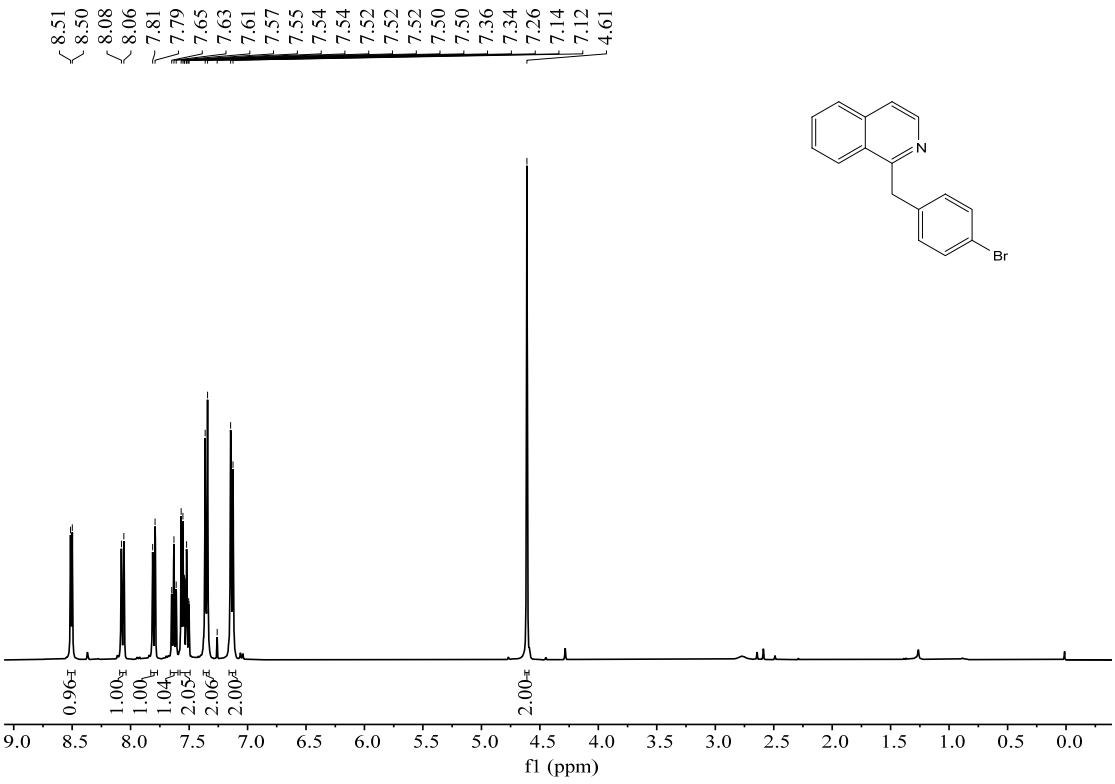


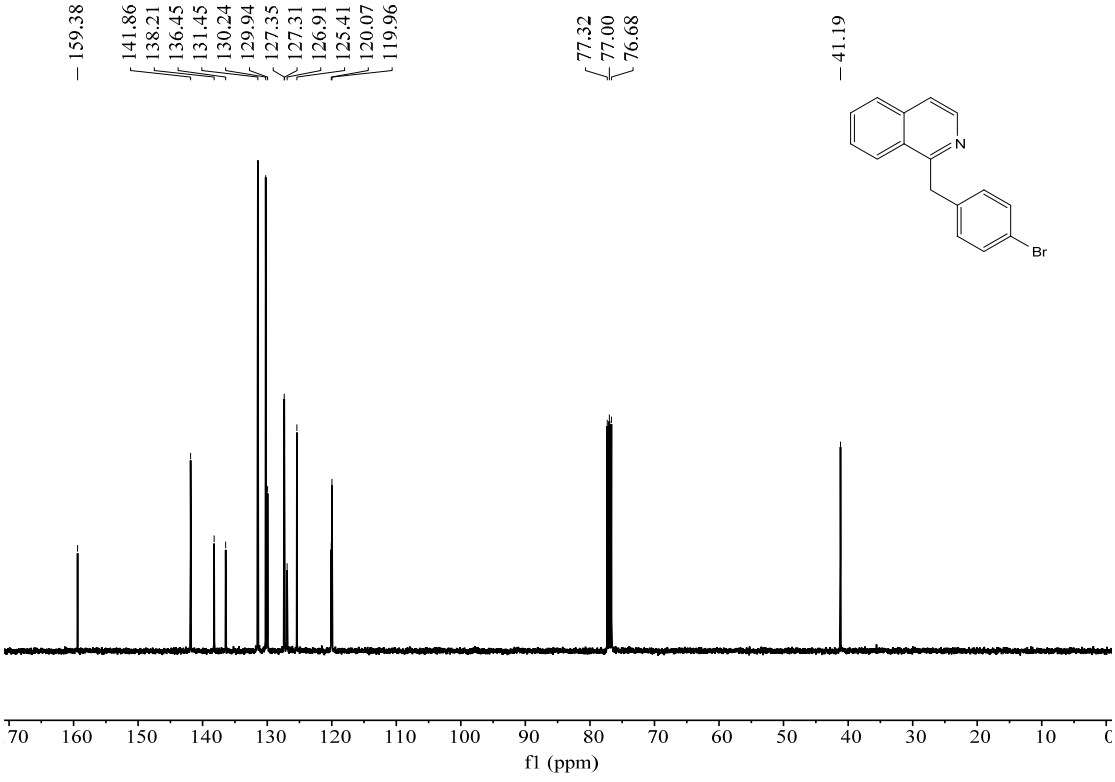
^{1}H and ^{13}C NMR spectra of 2x



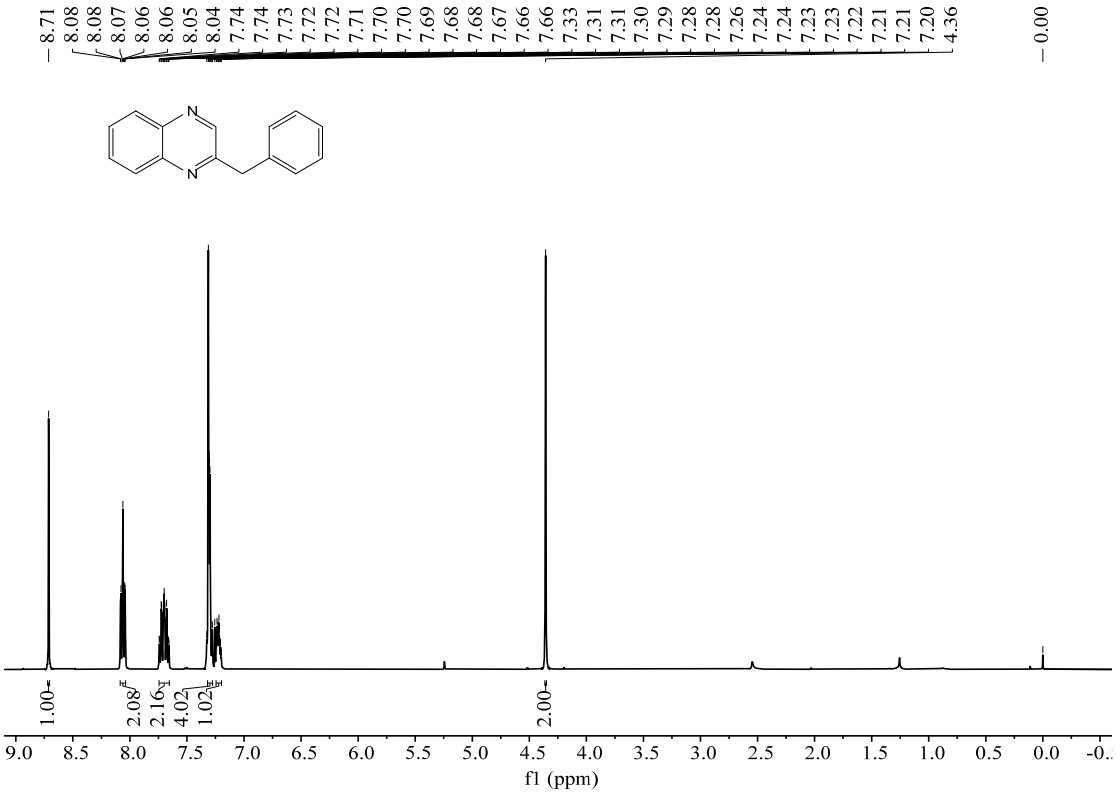


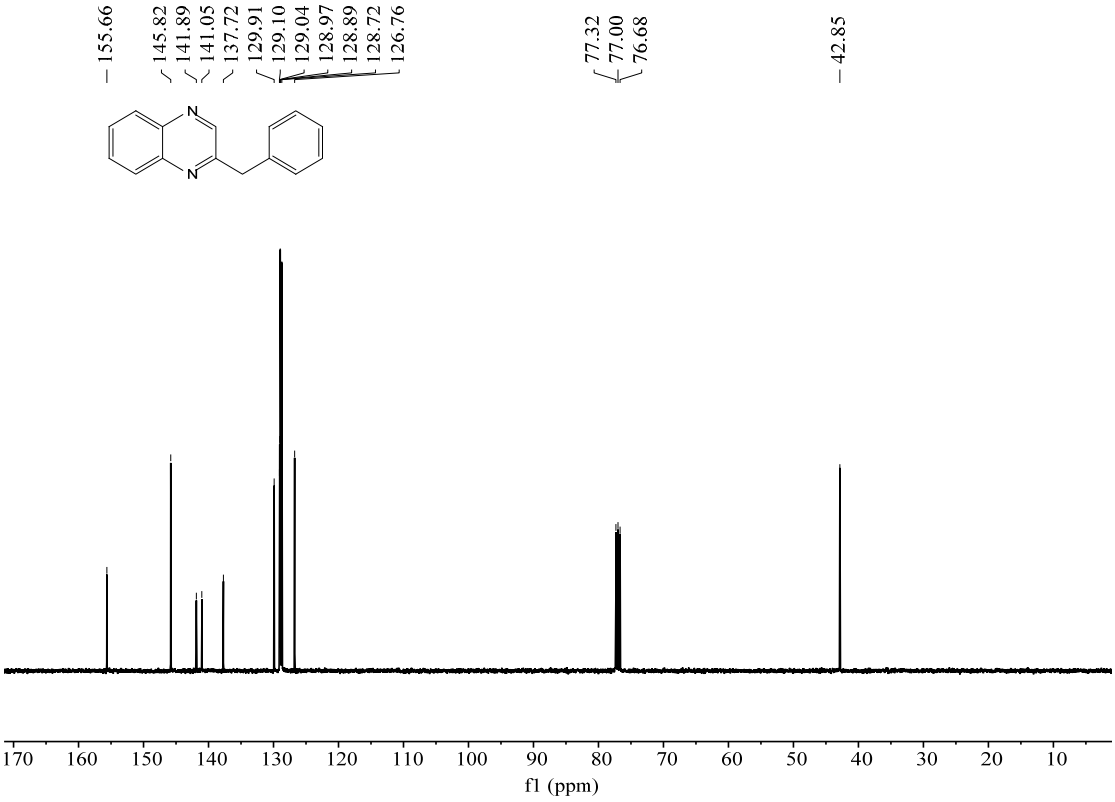
^{1}H and ^{13}C NMR spectra of 2y



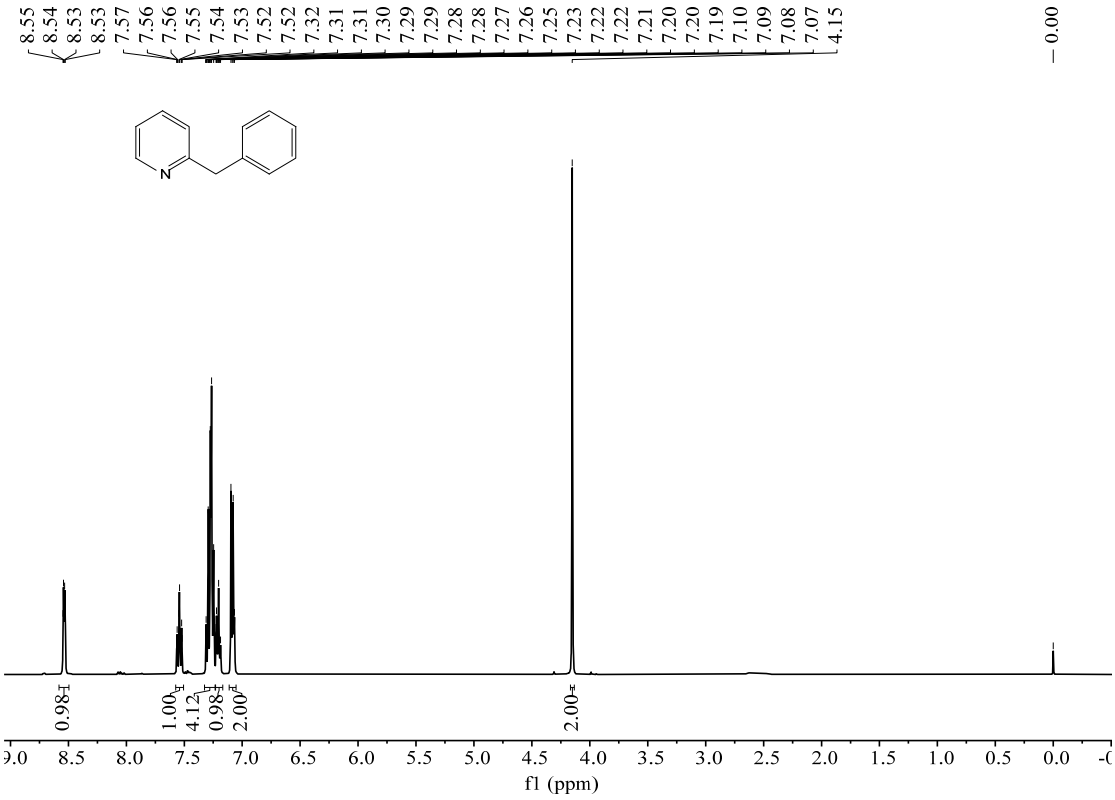


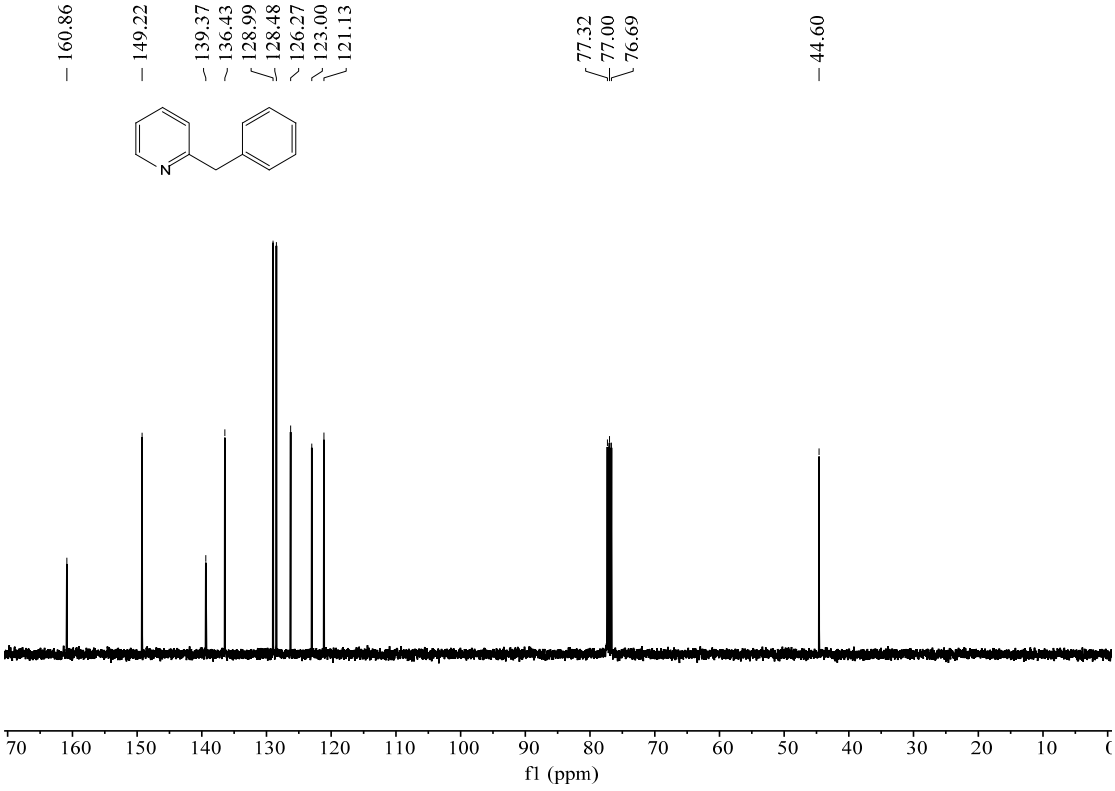
^{1}H and ^{13}C NMR spectra of 2z



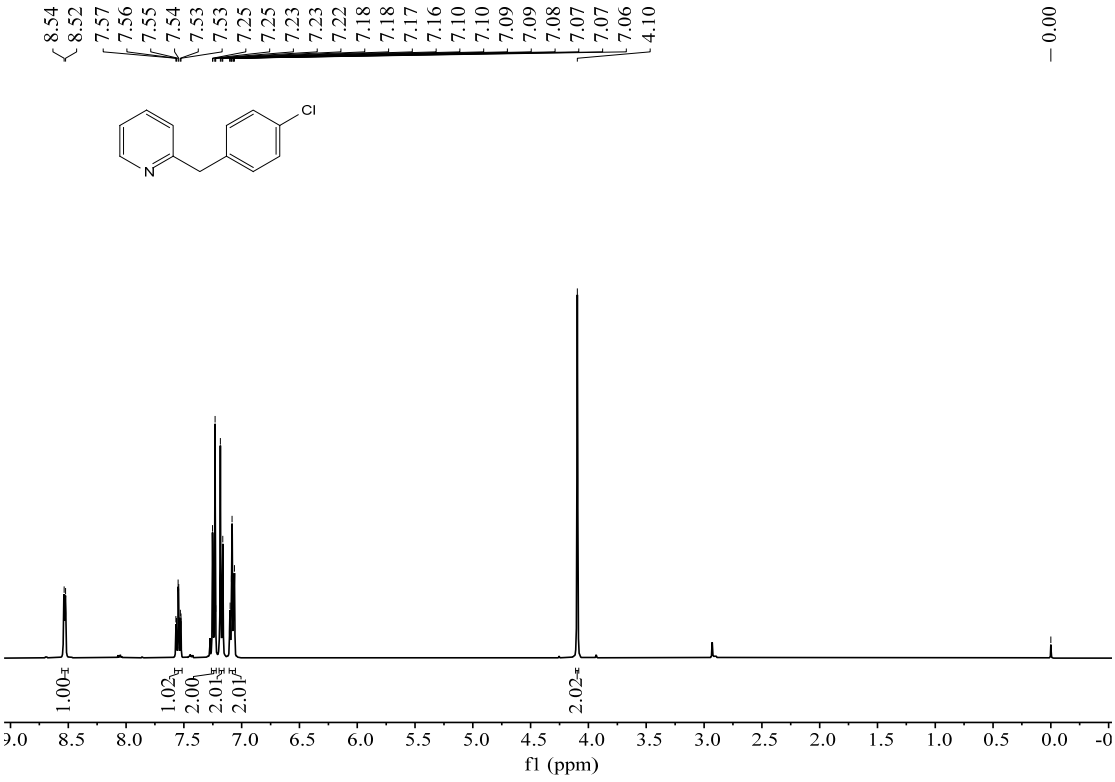


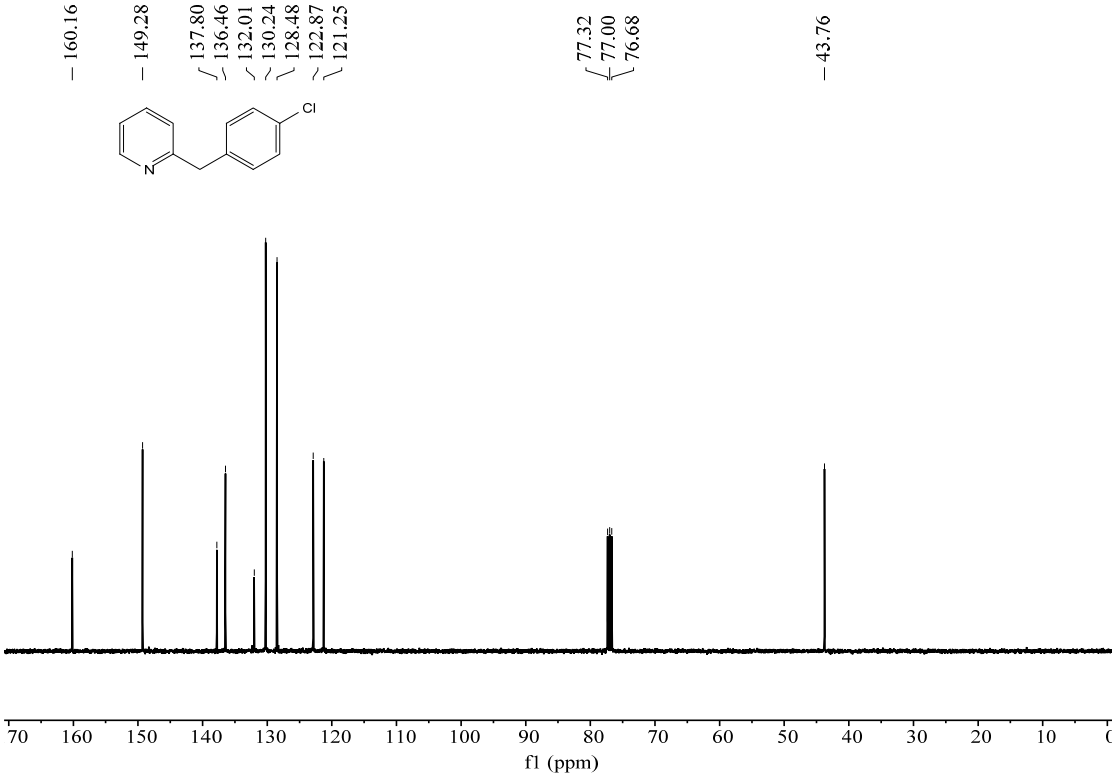
^{1}H and ^{13}C NMR spectra of 2aa



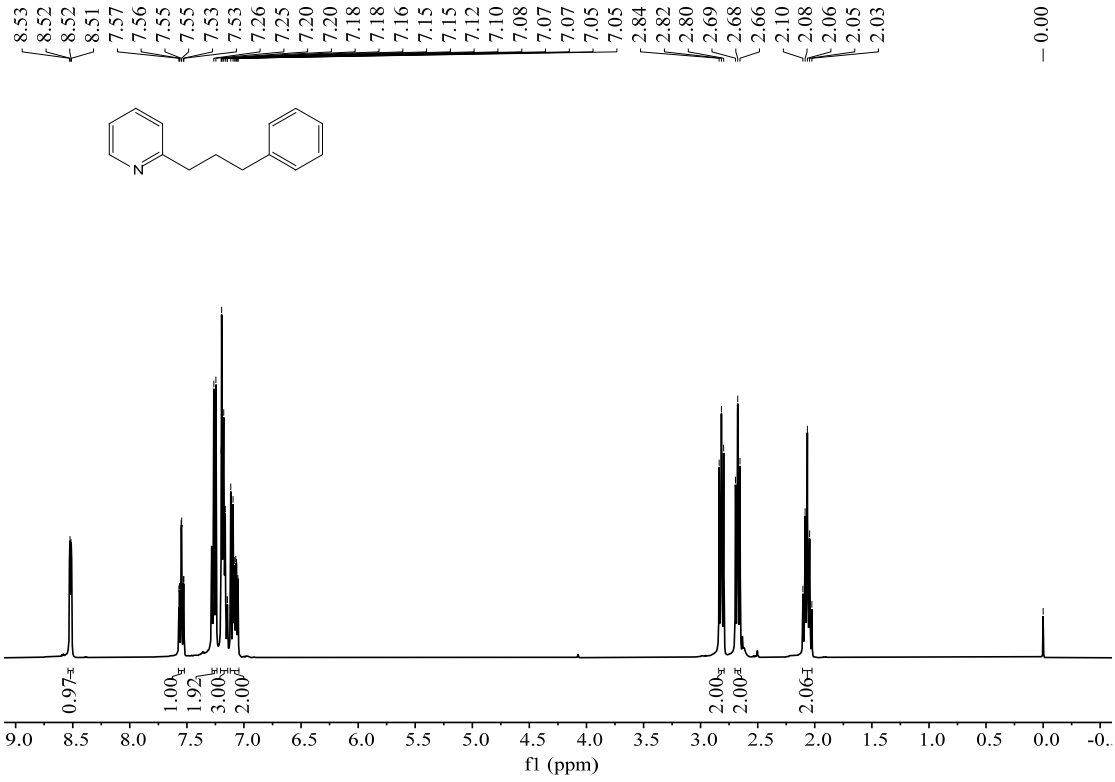


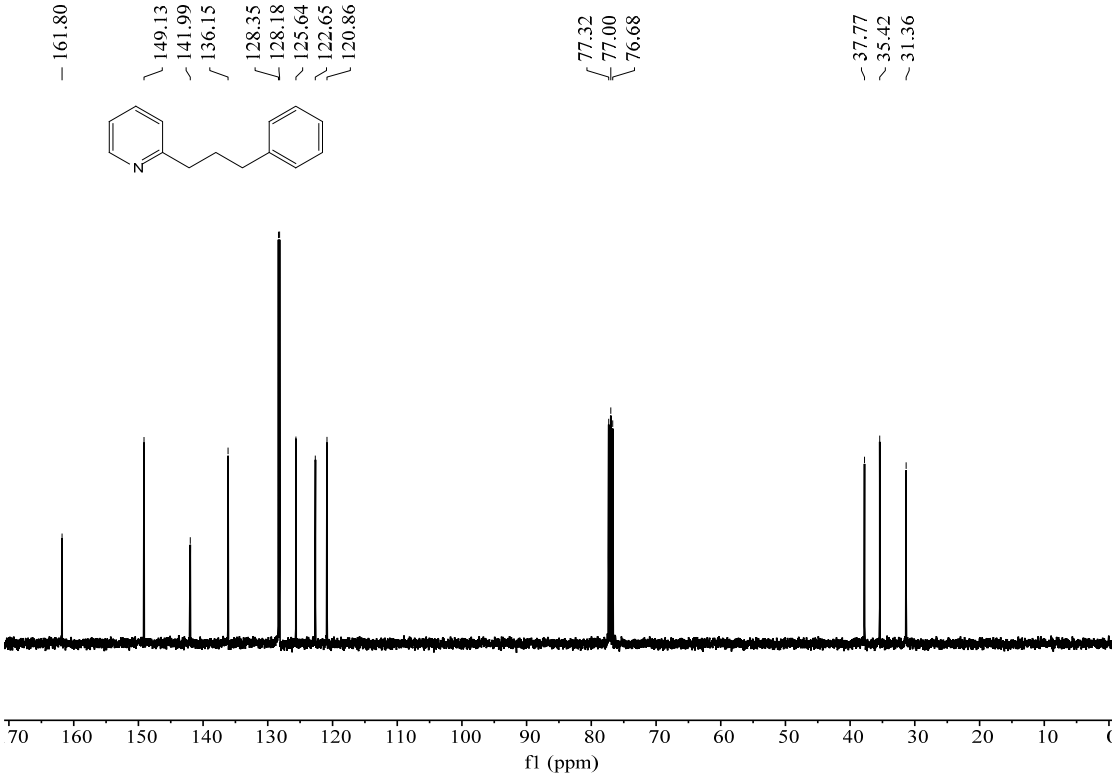
^{1}H and ^{13}C NMR spectra of 2ab



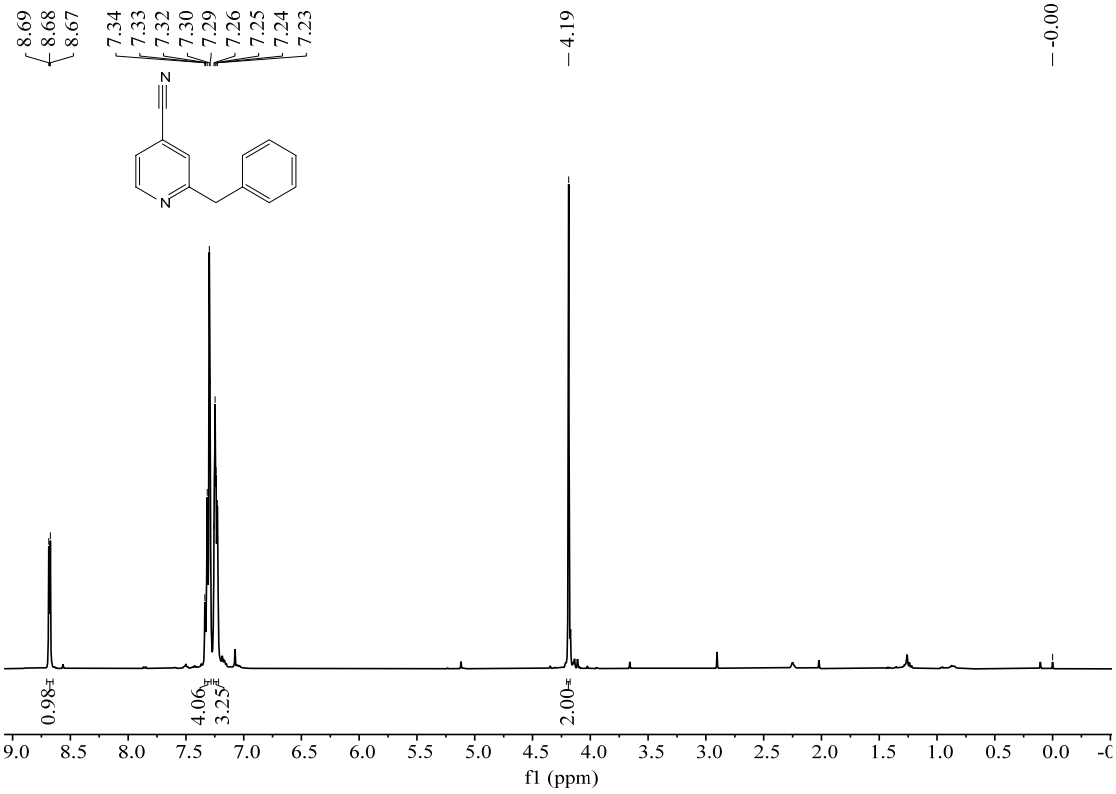


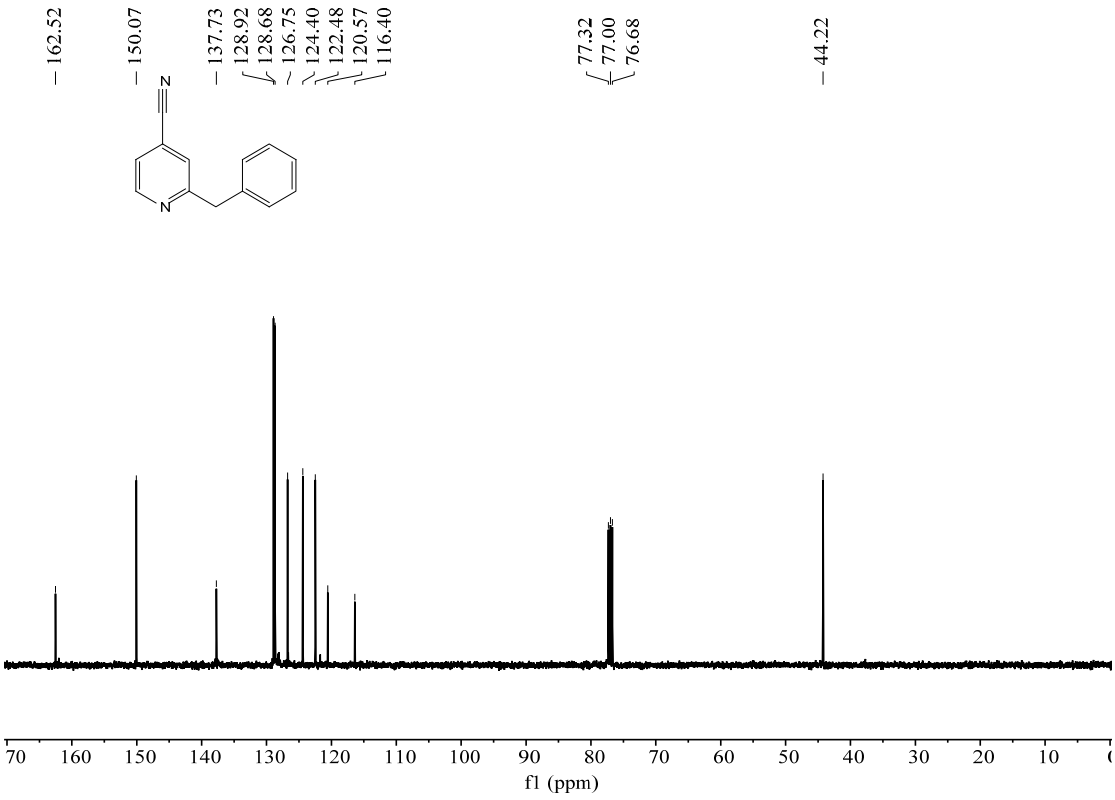
^{1}H and ^{13}C NMR spectra of 2ac



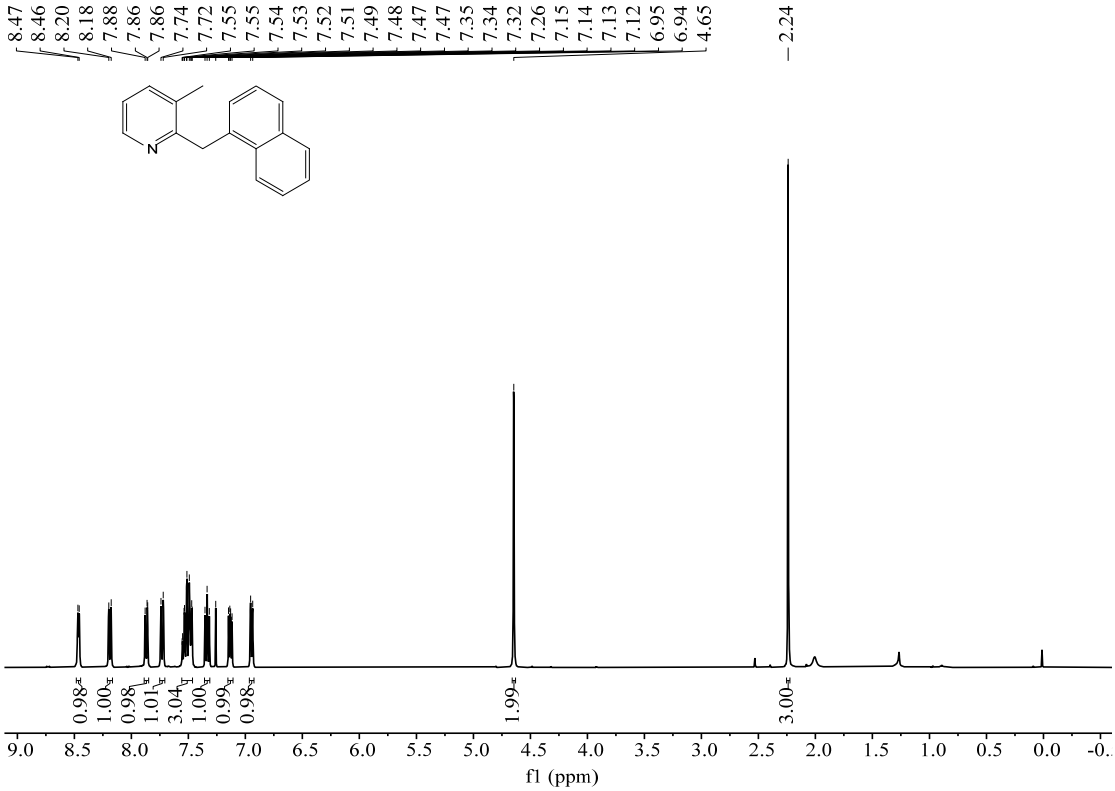


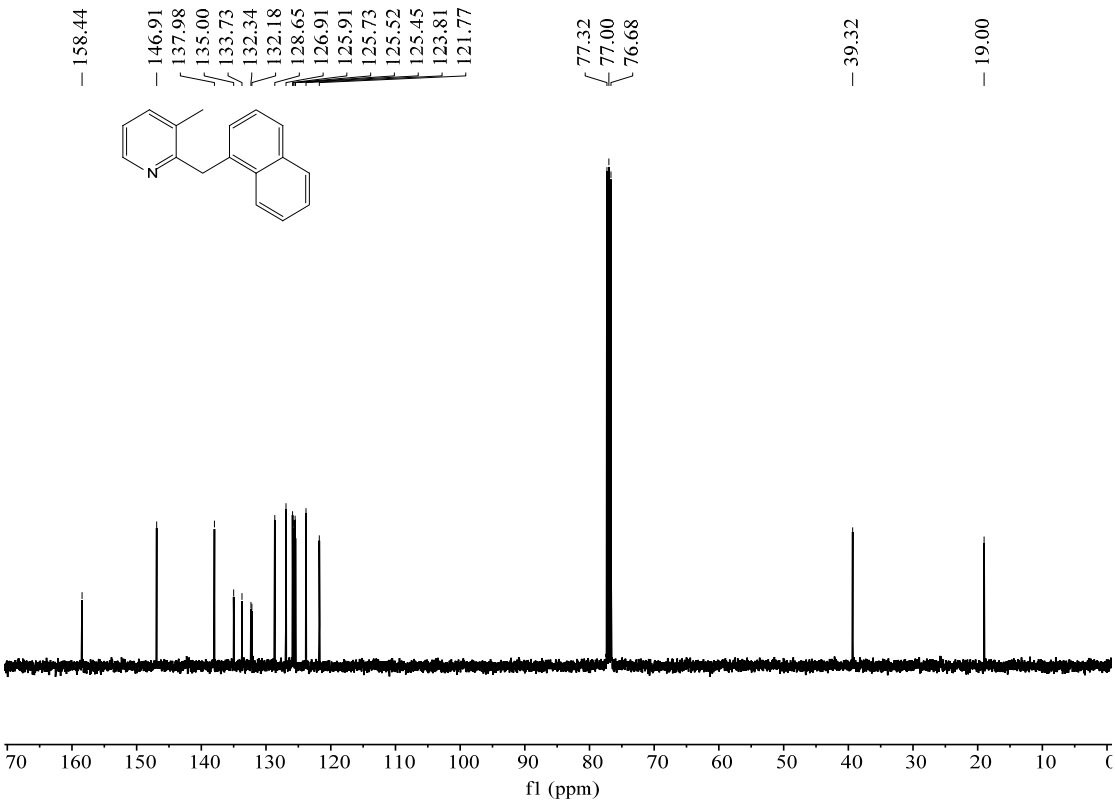
^{1}H and ^{13}C NMR spectra of 2ad



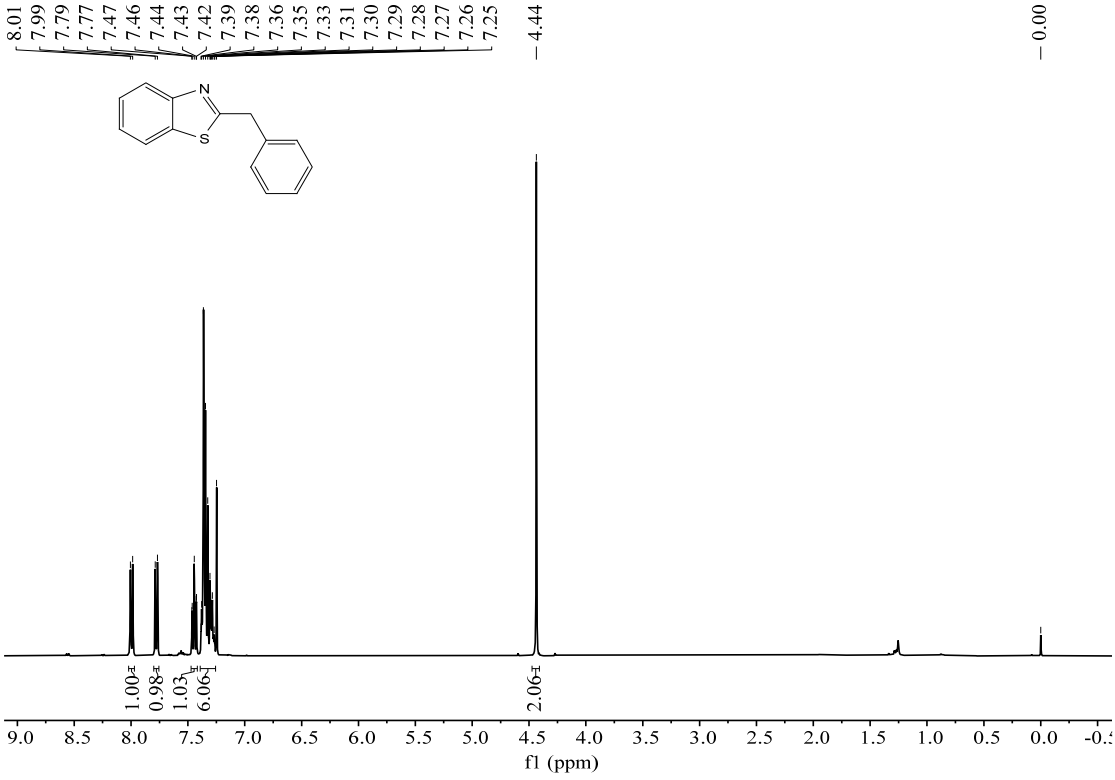


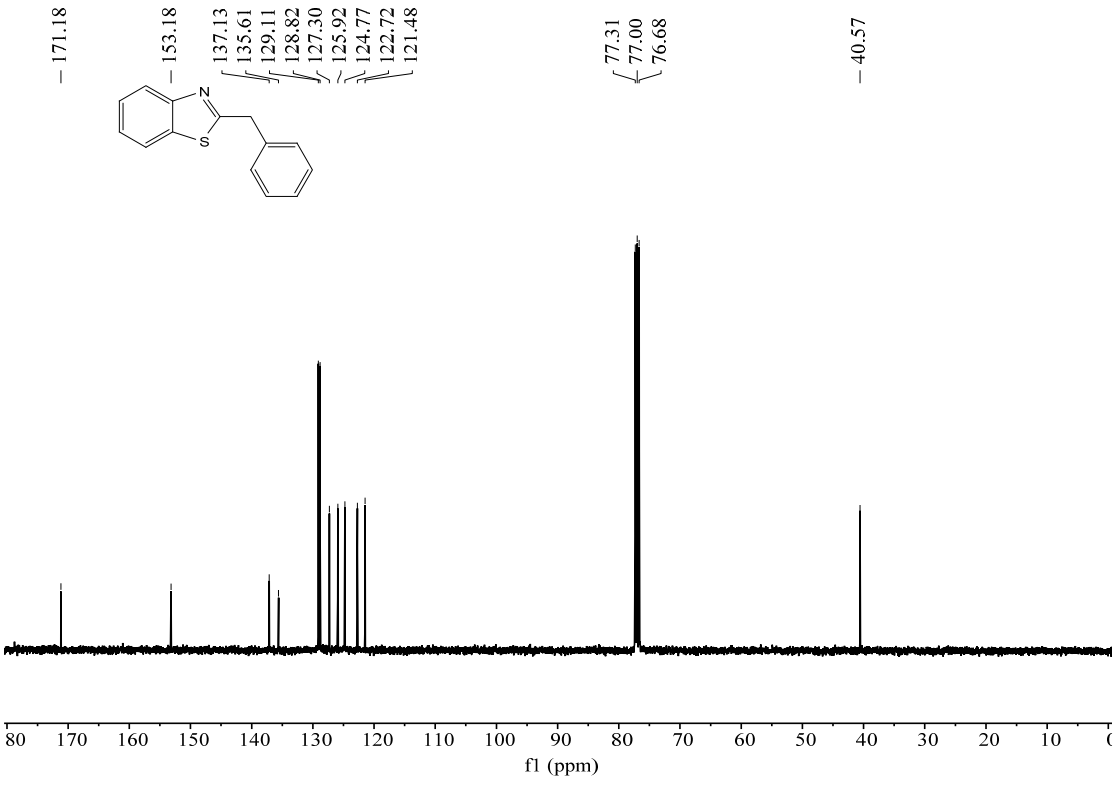
^{1}H and ^{13}C NMR spectra of 2ae



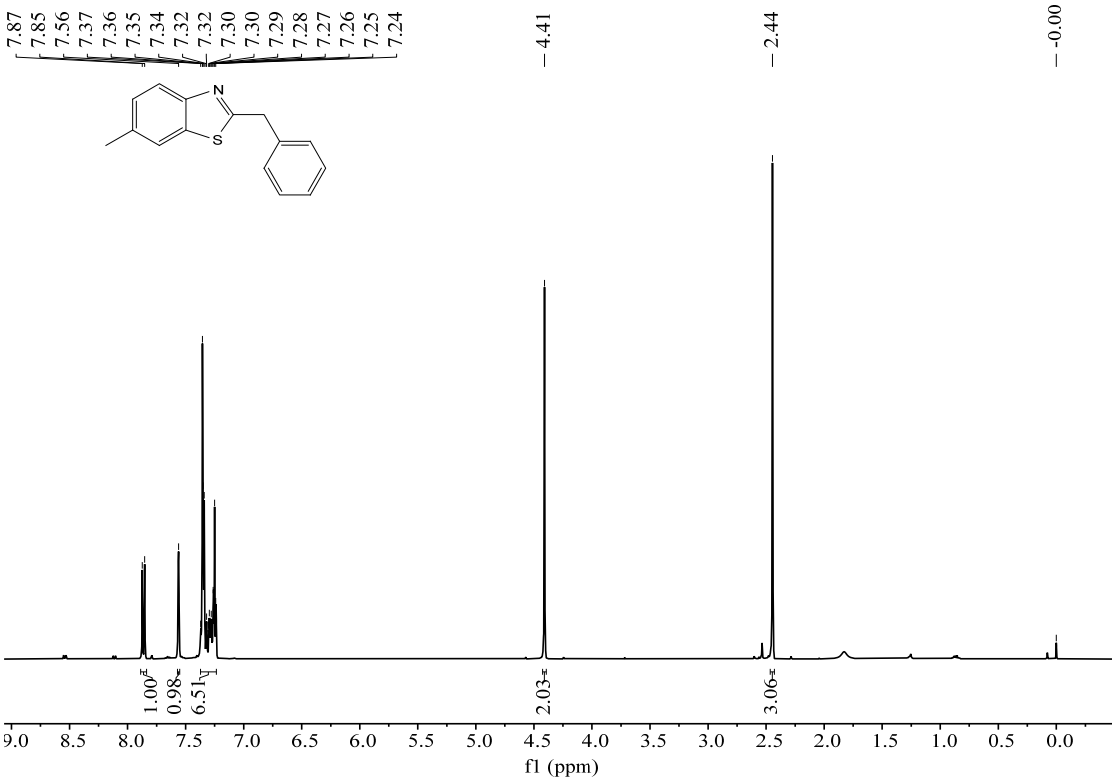


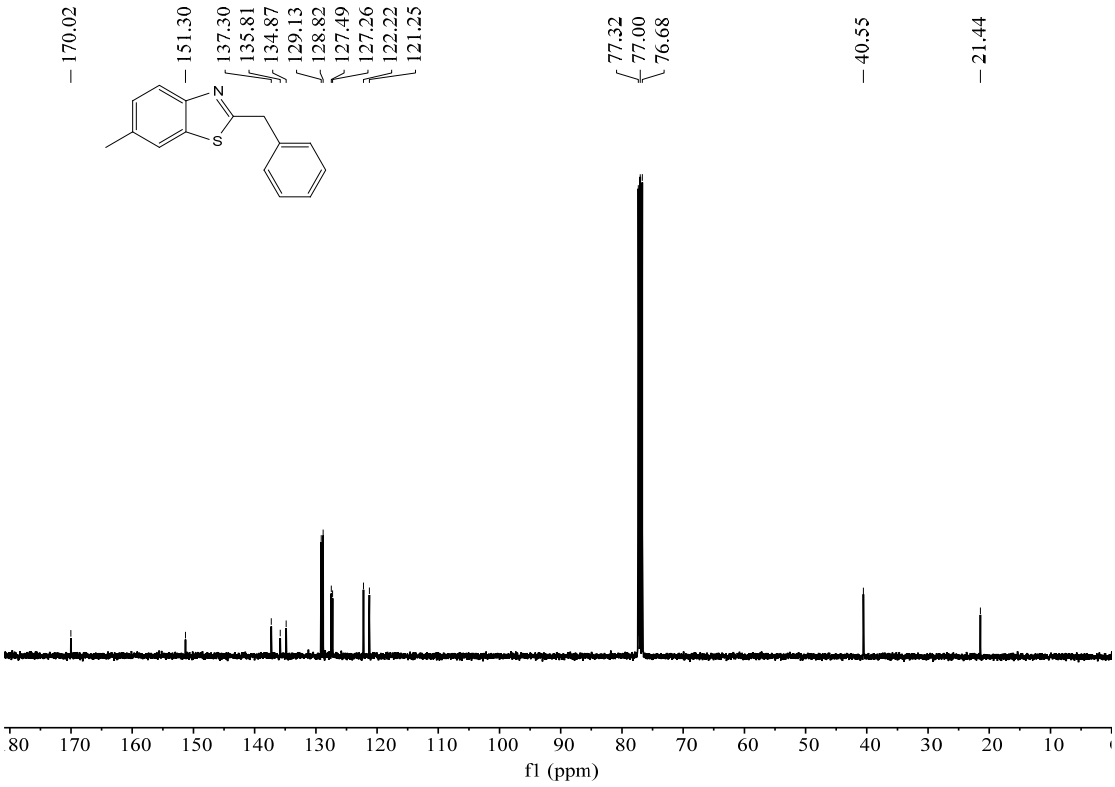
^{1}H and ^{13}C NMR spectra of 4a



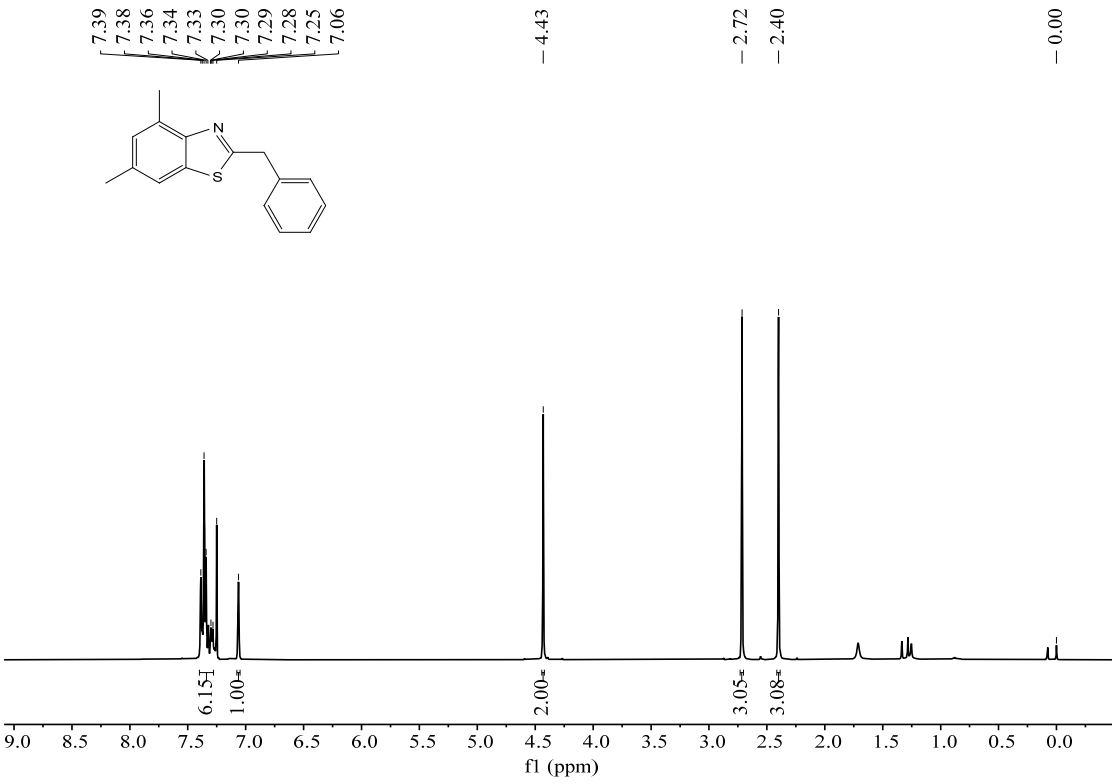


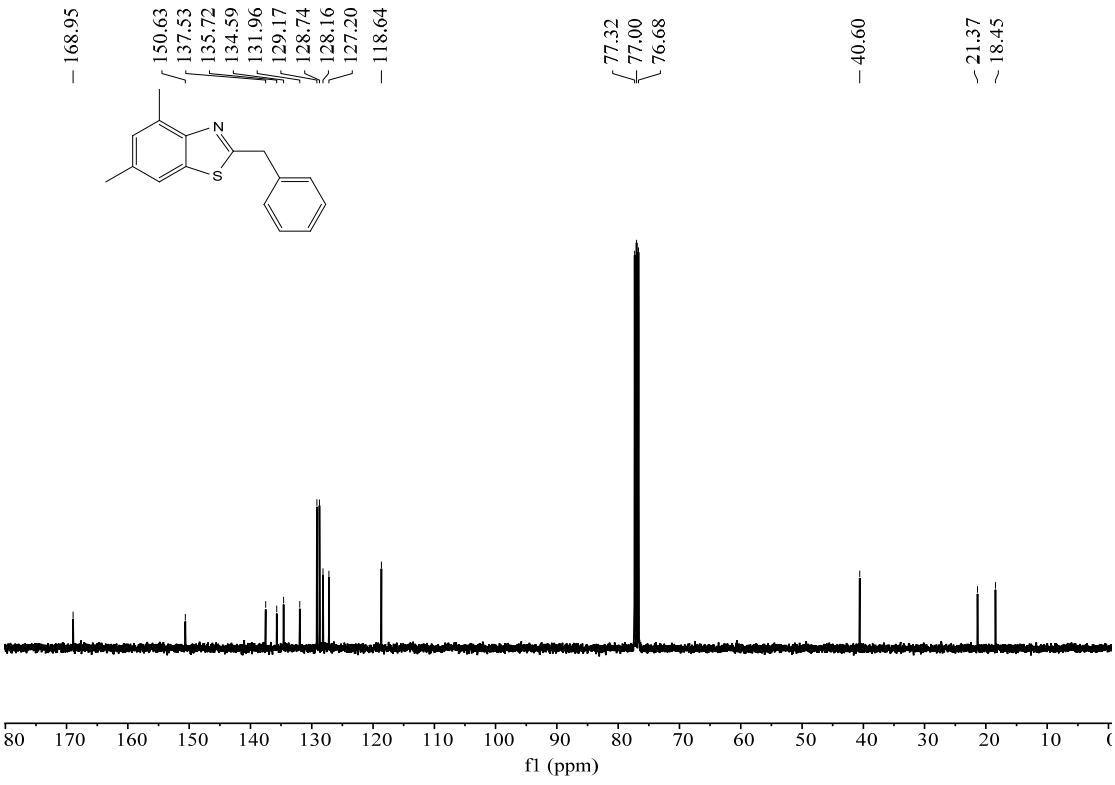
^{1}H and ^{13}C NMR spectra of 4b



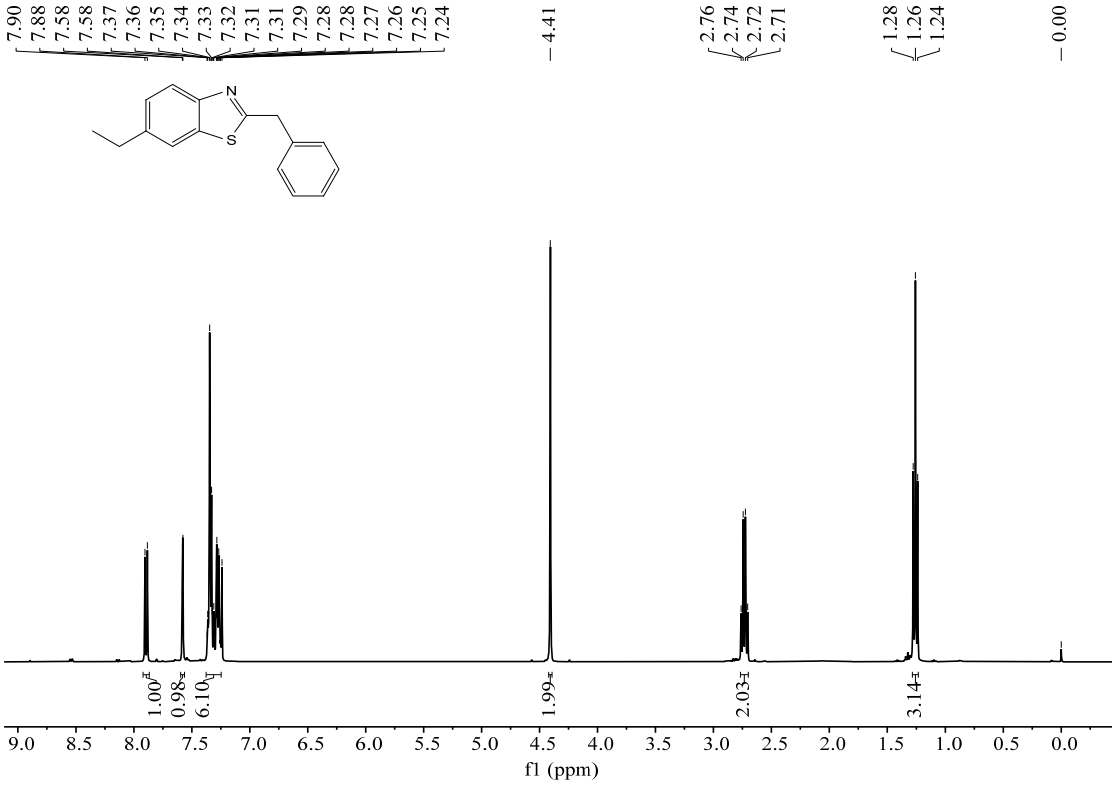


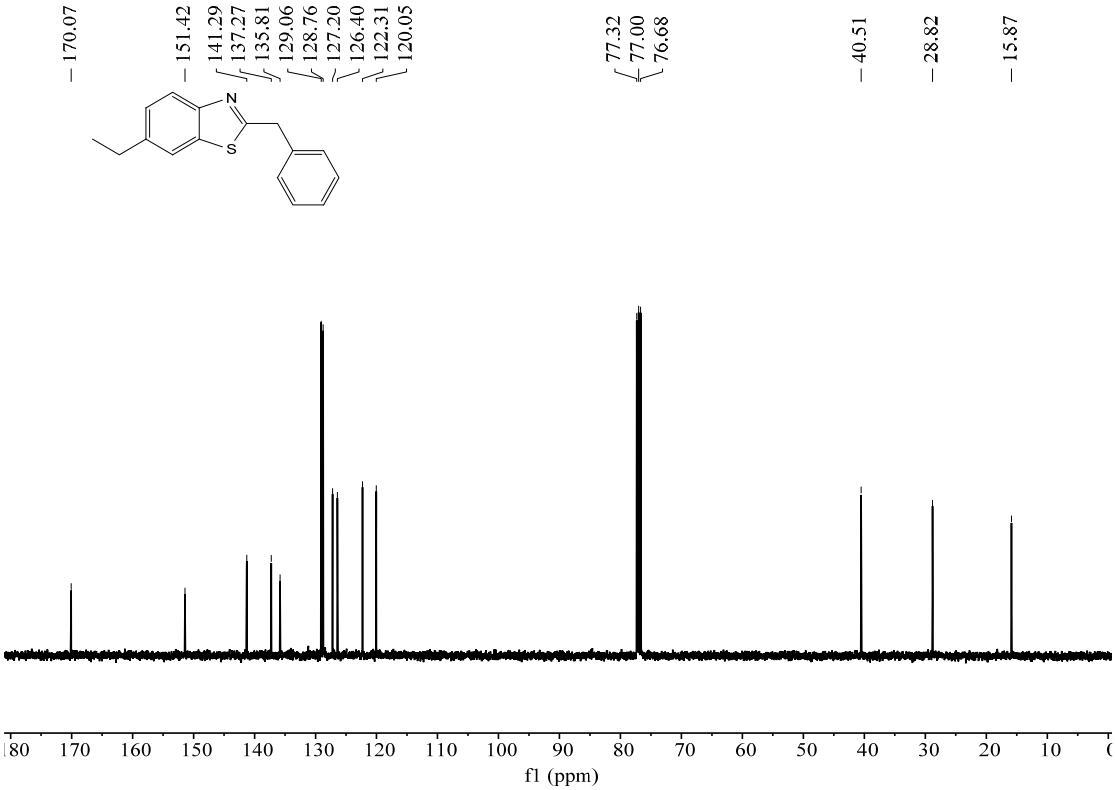
^{1}H and ^{13}C NMR spectra of 4c



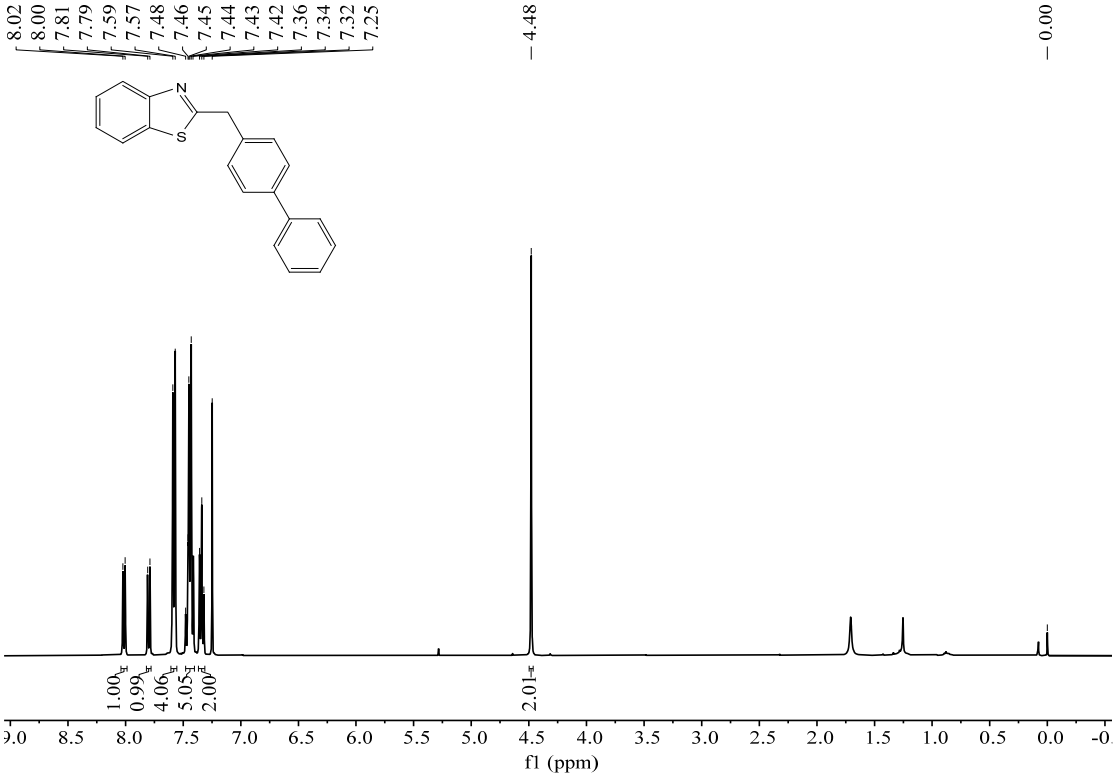


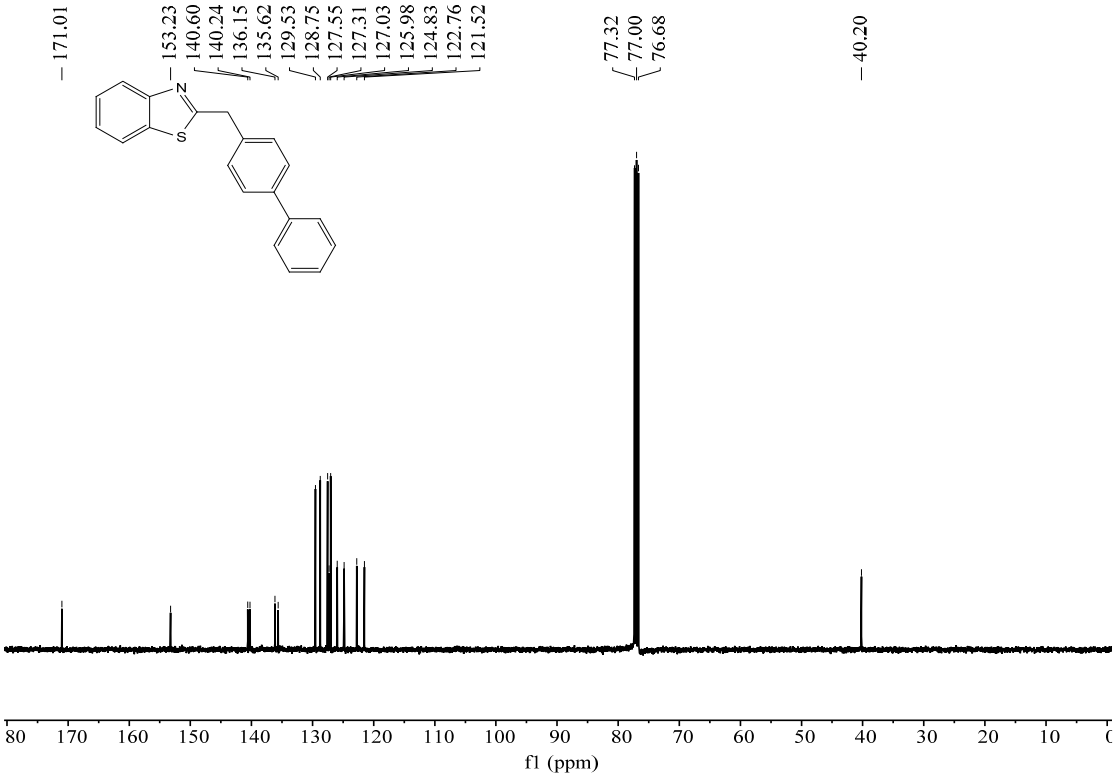
^{1}H and ^{13}C NMR spectra of 4d



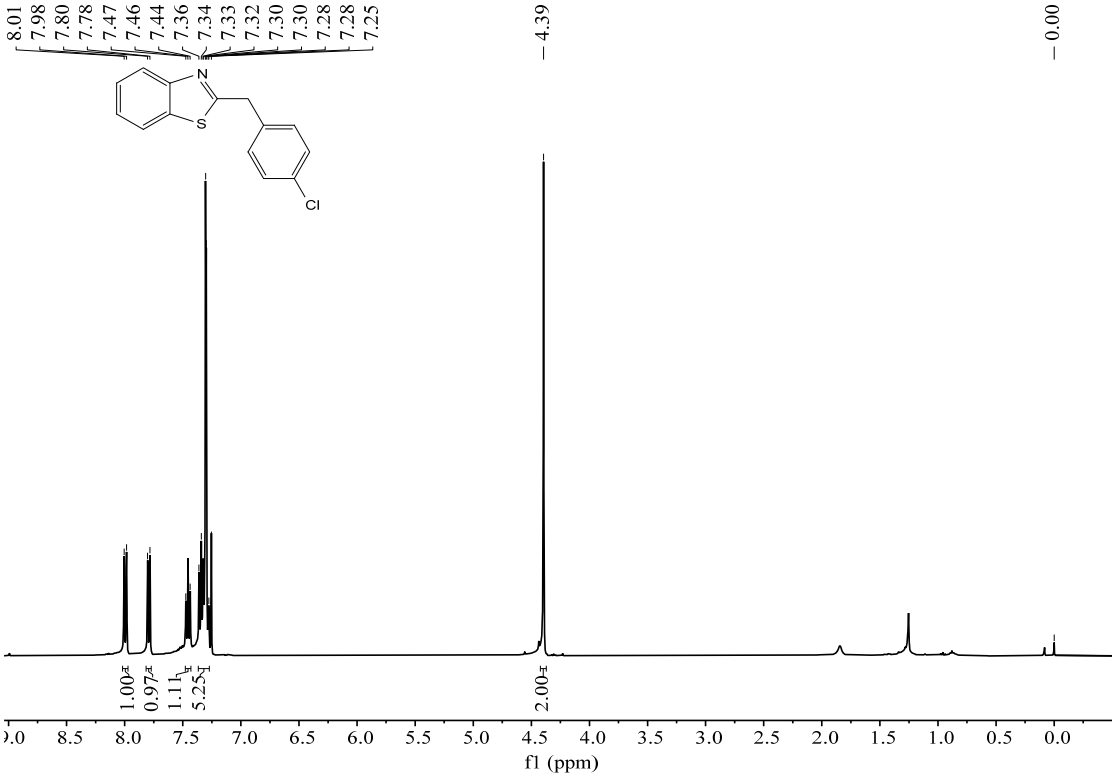


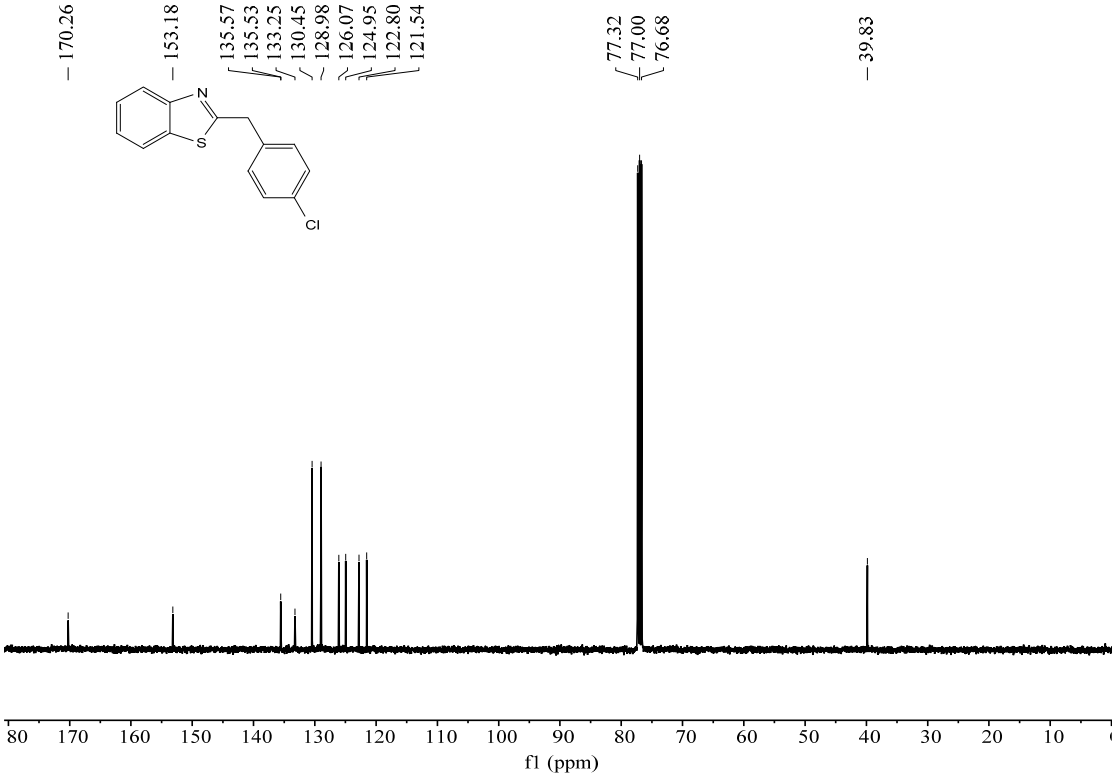
^{1}H and ^{13}C NMR spectra of 4e





^{1}H and ^{13}C NMR spectra of 4f





^{1}H and ^{13}C NMR spectra of 7c