Supporting Information

Visible-light-mediated photoredox decarbonylative Minisci-type alkylation with aldehydes under ambient air conditions

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1. General information

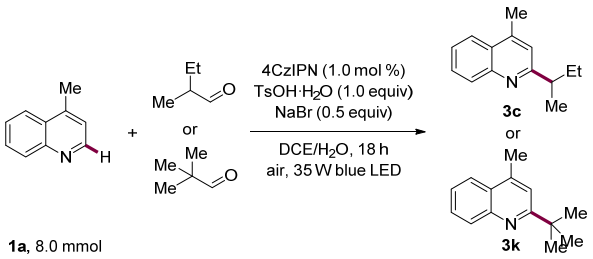
The reactions via general procedure were carried out under an atmosphere of air unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$, acetone-d_6 or dimethyl sulfoxide-d_6 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 potentiostat at room temperature in MeCN. *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 100 $mV \cdot s^{-1}$.

2. General procedure for alkylations

Reaction device diagram: We use a commercially available 35W (HIPAR30) blue LED lamp as the reaction light source.

General procedure for alkylations: A 10 mL reaction vessel was charged with NaBr (10.3 mg, 0.1 mmol), 4CzIPN (1.6 mg, 0.002 mmol), 4-methylquinoline (26.4 μL, 0.2 mmol), TsOH·H_2O (38.0 mg, 0.2 mmol), H_2O (18 μL, 1.0 mmol), DCE (3.0 mL), 2-ethylcapronaldehyde (62 μL, 0.4 mmol). The resulting mixture was stirred under ambient air for 18 h under irradiation with a 35W blue LED. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×10 mL). The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **3a**.

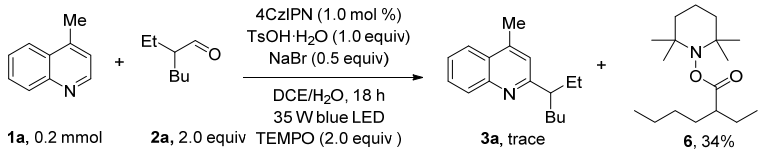
Gram scale reactions: A 250 mL round bottom flask was charged with NaBr (0.42 g, 4.0 mmol), 4CzIPN (63.0 mg, 0.08 mmol), 4-methylquinoline (1.06 mL, 8.0 mmol), TsOH·H_2O (1.52 g, 8.0 mmol), H_2O (0.5 mL), DCE (60 mL), 2-methylbutyraldehyde (1.72 mL, 16 mmol) or trimethylacetaldehyde (1.75 mL, 16 mmol). The resulting mixture was stirred under air for 18 h under irradiation with 3×35w blue LED. The crude reaction mixture was quenched with saturated sodium carbonate the organic layer was separated and extracted with dichloromethane (3×30 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 60:1) to give **3c** (1.21 g, 76% yield) or **3k** (1.30 g, 82% yield), respectively.



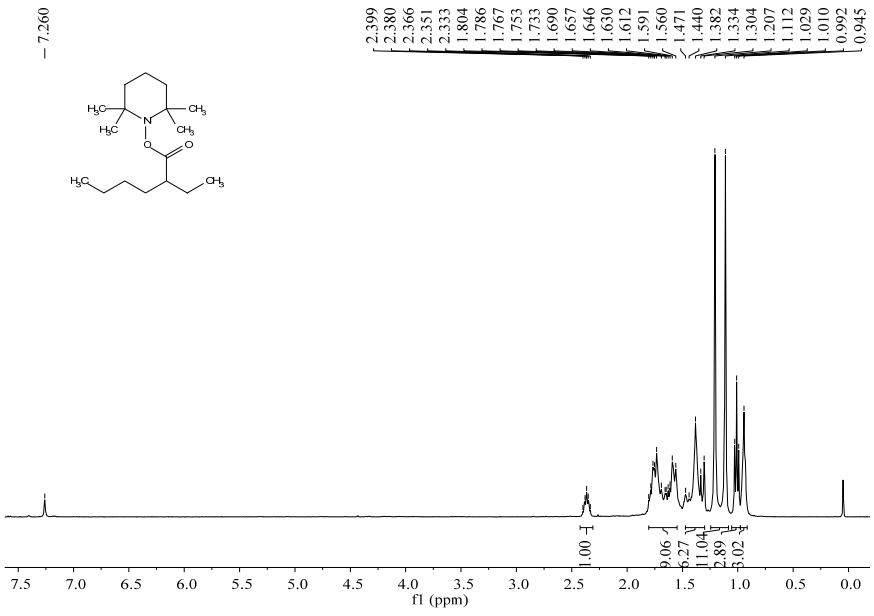
3. Mechanistic studies

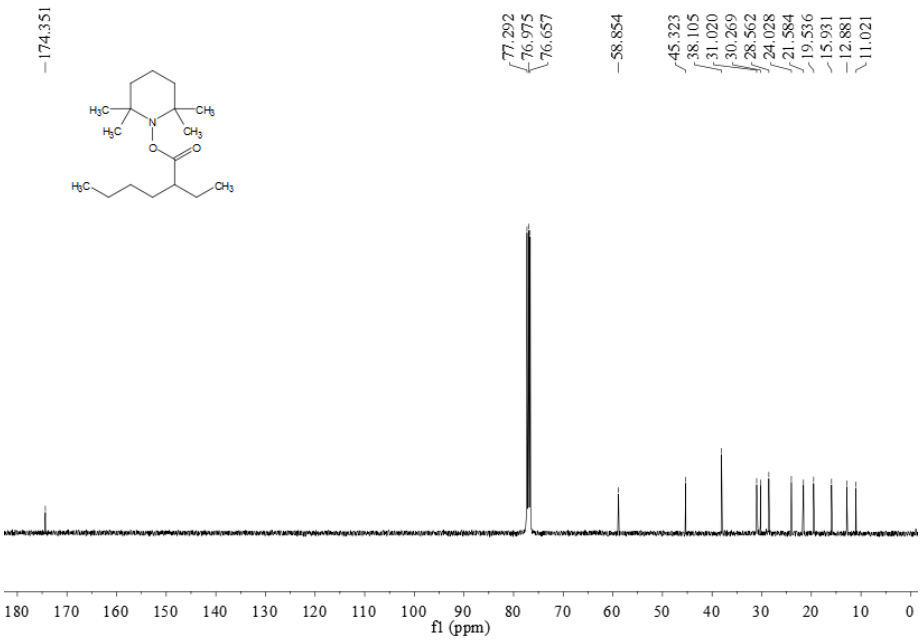
3.1. Radical trapping experiments

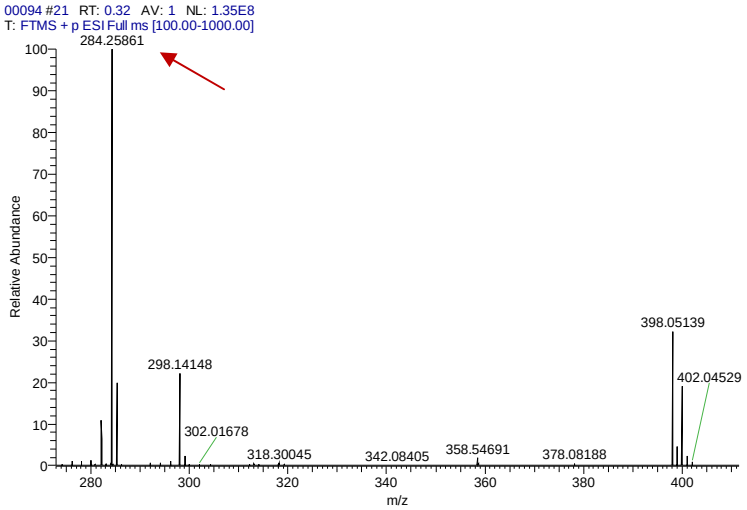
4-Methylquinoline (26.4 μL, 0.2 mmol), 2-ethylhexanal (62 μL, 0.4 mmol, 2.0 equiv), NaBr (10.5 mg, 0.1 mmol), *p*-toluenesulfonic acid (38.2 mg, 0.2 mmol), H_2O (18 μL, 1.0 mmol, 5.0 equiv) 4CzIPN (1.6 mg, 1.0 mol%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.8 mg, 0.4 mmol, 2.0 equiv), and DCE (3.0 mL) were placed in a 10 mL reaction tube. The reaction mixture was stirred under air using a 35 W blue LED for 18 h. The formation of **3a** was suppressed. Meanwhile, the TEMPO-trapped product (**6**) was isolated in 34% yield (PE/EA = 30/1, 38.5 mg).



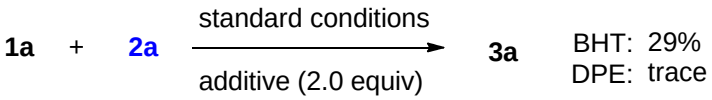
2,2,6,6-Tetramethylpiperidin-1-yl 2-ethylhexanoate (6): Red oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.37 (p, J = 7.4 Hz, 1H), 1.81 – 1.55 (m, 9H), 1.48 – 1.30 (m, 6H), 1.28 – 1.05 (m, 11H), 1.01 (t, J = 7.4 Hz, 3H), 0.95 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.4, 58.9, 45.3, 38.1, 31.0, 30.3, 28.6, 24.0, 21.6, 19.5, 15.9, 12.9, 11.0. HRMS (ESI) m/z calcd for $C_{17}H_{34}NO_2^+$ $(M+H)^+$ 284.2584, found 284.2586.







4-Methylquinoline **(1a**, 26.4 µL, 0.2 mmol), 2-ethylhexanal **(2a**, 62 µL, 0.4 mmol, 2.0 equiv), NaBr (10.5 mg, 0.1 mmol), *p*-toluenesulfonic acid (38.2 mg, 0.2 mmol), H_2O (18 µL, 1.0 mmol, 5.0 equiv) 4CzIPN (1.6 mg, 1.0 mol%), butylated hydroxytoluene (BHT) (88.0 mg, 0.4 mmol, 2.0 equiv) or 1,1-Diphenylethylene (DPE) (71 µL, 0.4 mmol, 2.0 equiv), and DCE (3.0 mL) were placed in a 10 mL reaction tube. The reaction mixture was stirred under air using a 35 W blue LED for 18 h. The formation of **3a** was suppressed.

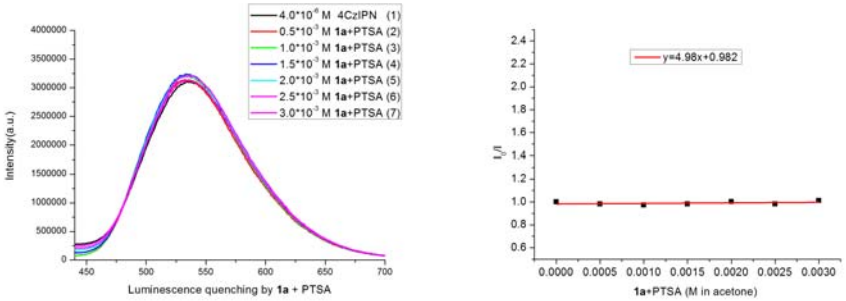


3.2. Stern–Volmer Quenching[1]

Formulation solution: 4-Methylquinoline (357.7 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration is 0.1 M. *p*-$CH_3C_6H_4SO_3H{\cdot}H_2O$ (475.6 mg) was dissolved in deionized water in a 25 mL volumetric flask to set the concentration is 0.1 M. NaBr (129 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration is 0.05 M. 2-Ethylhexanal (780 μL) was dissolved in DCE in a 25 mL volumetric flask to set the concentration is 0.2 M. Photocatalyst 4CzIPN (2.0 mg) was dissolved in DCE or acetone (25 mL) to set the concentration is 0.1 mM.

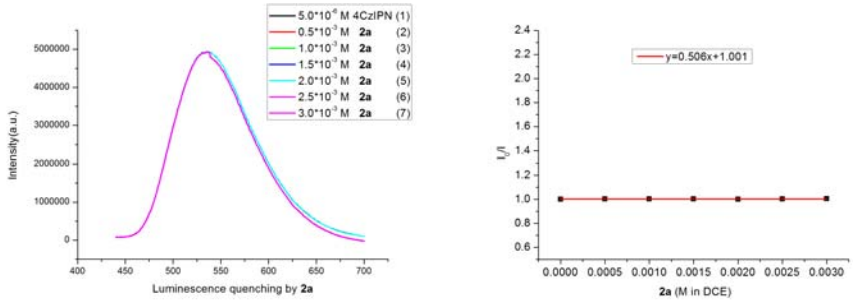
Experimental procedure: The resulting 0.1 mM solution (80 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding further solvent (acetone) to prepare a 4.0 μM solution. The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 375 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 10.0 μL of 4-methylquinoline solution and 10.0 μL of *p*-$CH_3C_6H_4SO_3H{\cdot}H_2O$ was successively added, uniformly stirred and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 375 nm. Fluorescence emission spectra of 0 μL, 10.0 μL, 20.0 μL, 30.0 μL, 40.0 μL, 50.0 μL, 60.0μL (**1a**+PTSA) fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

(a) 4CzIPN quenched by **1a**+PTSA in acetone.



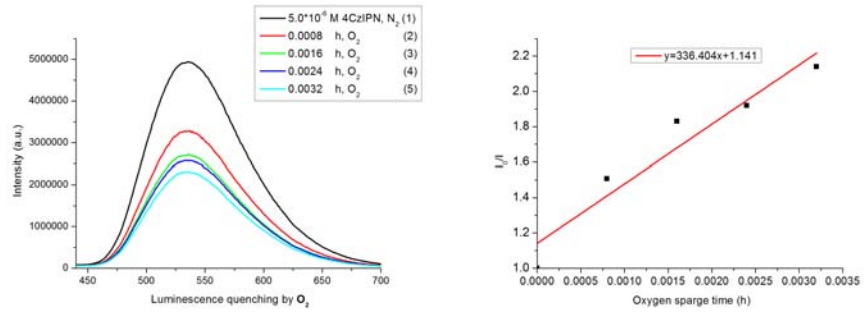
The emission intensity of the 4CzIPN catalyst solution was not affected by the gradual increase of the amount of **1**a+PTSA.

(b) 4CzIPN quenched by **2a** in DCE.



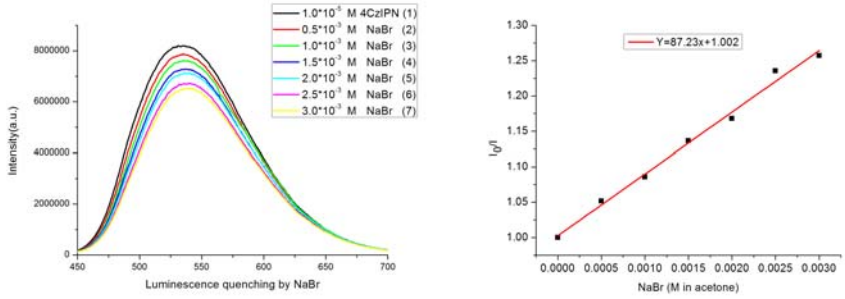
The emission intensity of the 4CzIPN catalyst solution was not affected by the gradual increase of the amount of **2a**.

(c) 4CzIPN quenched by O_2 in DCE.



The emission intensity of the 4CzIPN catalyst solution was strongly affected by the gradual increase of the amount of O_2.

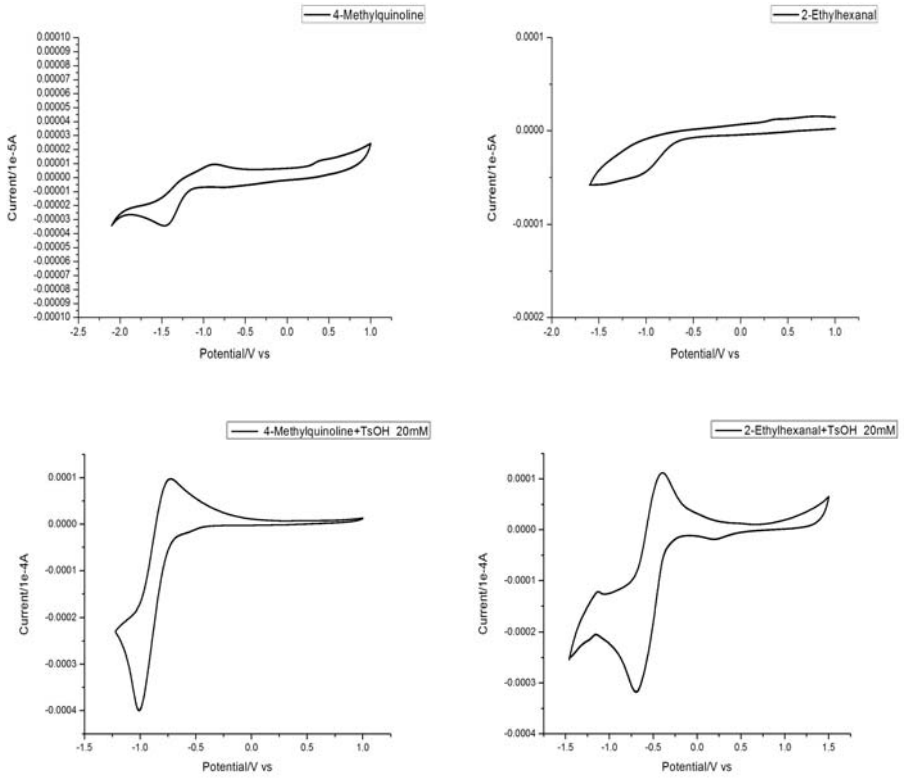
(d) 4CzIPN quenched by NaBr in acetone.



The emission intensity of the 4CzIPN catalyst solution was slightly affected by the gradual increase of the amount of NaBr.

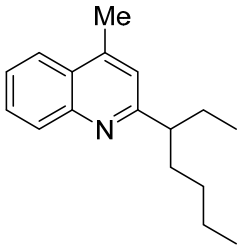
3.3. Cyclic Voltammetry

Cyclic voltammograms were recorded with a CHI604E potentiostat at room temperature in MeCN. *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 100 $mV \cdot s^{-1}$.



4. Characterization data of products

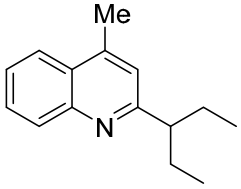
2-(Heptan-3-yl)-4-methylquinoline (3a)[2]



The general procedure was followed using 4-methylquinoline (29.2 mg, 0.2 mmol), 2-ethylcapronaldehyde (65 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3a** (37.9 mg, 78%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.4, 1.4 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.50 (td, J = 7.3, 6.9, 1.3 Hz, 1H), 7.11 (s, 1H), 2.84 – 2.77 (m, 1H), 2.69 (s, 3H), 1.81 – 1.72 (m, 4H), 1.35 – 1.23 (m, 3H), 1.17 – 1.07 (m, 1H), 0.83 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.0, 147.7, 144.1, 129.7, 128.9, 127.2, 125.4, 123.7, 120.8, 50.7, 35.3, 30.0, 28.7, 23.0, 19.0, 14.1, 12.4. HRMS (ESI) m/z calcd for $C_{17}H_{24}N^+$ $(M+H)^+$ 242.1903, found 242.1921.

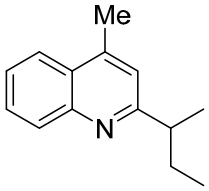
4-Methyl-2-(pentan-3-yl)quinoline (3b)[3]



The general procedure was followed using 4-methylquinoline (29.1 mg, 0.2 mmol), 2-ethylbutyraldehyde (50 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3b** (33 mg, 77%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 8.1 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.11 (s, 1H), 2.80 – 2.71 (m, 1H), 2.69 (s, 3H), 1.83 – 1.73 (m, 4H), 0.83 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.8, 147.8, 144.1, 129.7, 129.0, 127.2, 125.5, 123.7, 120.9, 52.3, 28.4, 19.0, 12.4. HRMS (ESI) m/z calcd for $C_{15}H_{20}N^+$ $(M+H)^+$ 214.1590, found 214.1600.

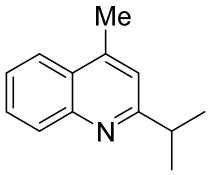
2-(sec-Butyl)-4-methylquinoline (3c)[4]



The general procedure was followed using 4-methylquinoline (29.0 mg, 0.2 mmol), 2-methylbutyraldehyde (43 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3c** (35.5 mg, 89%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.67 (ddd, J = 8.3, 6.8, 1.5 Hz, 1H), 7.50 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.15 (d, J = 17.2 Hz, 1H), 3.25 – 2.91 (m, 1H), 2.68 (s, 3H), 1.98 – 1.54 (m, 2H), 1.37 (dd, J = 12.5, 7.0 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 147.7, 144.3, 129.6, 129.0, 127.1, 125.5, 123.7, 120.3, 44.7, 30.0, 20.5, 18.9, 12.4. HRMS (ESI) m/z calcd for $C_{14}H_{18}N^+$ $(M+H)^+$ 200.1434, found 200.1436.

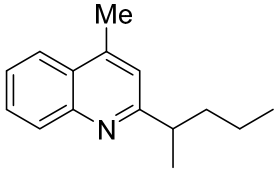
2-Isopropyl-4-methylquinoline (3d)[5]



The general procedure was followed using 4-methylquinoline (29.2 mg, 0.2 mmol), 2-methylpropanal (37 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3d** (33.5 mg, 90%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.50 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.18 (s, 1H), 3.27 – 3.16 (m, 1H), 2.69 (s, 3H), 1.39 (d, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.5, 147.7, 144.5, 129.6, 129.1, 127.1, 125.5, 123.7, 119.9, 37.4, 22.7, 19.0. HRMS (ESI) m/z calcd for $C_{13}H_{16}N^+$ $(M+H)^+$ 186.1277, found 186.1272.

4-Methyl-2-(pentan-2-yl)quinoline (3e)[6]

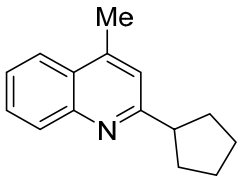


The general procedure was followed using 4-methylquinoline (29.1 mg, 0.2 mmol),

2-methylvaleraldehyde (50 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3e** (42.3 mg, 93%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.49 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.14 (s, 1H), 3.08 – 3.01 (m, 1H), 2.68 (s, 3H), 1.84 – 1.75 (m, 1H), 1.69 – 1.60 (m, 1H), 1.42 – 1.30 (m, 4H), 1.29 – 1.16 (m, 1H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.0, 147.7, 144.3, 129.6, 129.0, 127.1, 125.5, 123.7, 120.3, 42.8, 39.4, 21.0, 20.9, 19.0, 14.3. HRMS (ESI) m/z calcd for $C_{15}H_{20}N^+$ $(M+H)^+$ 214.1590, found 214.1587.

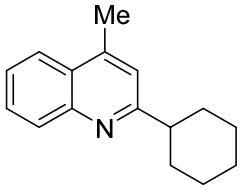
2-Cyclopentyl-4-methylquinoline (3f)[7]



The general procedure was followed using 4-methylquinoline (29.0 mg, 0.2 mmol), cyclopentanecarbaldehyde (42 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3f** (13 mg, 31%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.4 Hz, 1H), 7.93 (dd, J = 8.3, 1.4 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.18 (s, 1H), 3.33 (m, 1H), 2.67 (m, 3H), 2.21 – 2.12 (m, 2H), 1.88 (m, 5H), 1.75 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 147.6, 144.2, 129.6, 129.0, 127.1, 125.5, 123.7, 120.8, 48.9, 33.7, 26.2, 18.9. HRMS (ESI) m/z calcd for $C_{15}H_{18}N^+$ $(M+H)^+$ 212.1434, found 212.1434.

2-Cyclohexyl-4-methylquinoline (3g)[7]

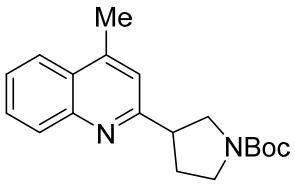


The general procedure was followed using 4-methylquinoline (29.0 mg, 0.2 mmol), cyclohexanecarbaldehyde (50 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3g** (31.1 mg, 69%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.65 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.48 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.16 (s, 1H), 2.87 (tt, J = 12.0, 3.4

Hz, 1H), 2.67 (s, 3H), 2.01 (d, *J* = 11.7 Hz, 2H), 1.89 (d, *J* = 12.9 Hz, 2H), 1.79 (d, *J* = 12.4 Hz, 1H), 1.62 (qd, *J* = 12.4, 2.8 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.35 (tt, *J* = 12.7, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 147.7, 144.3, 129.6, 129.0, 127.1, 125.5, 123.7, 120.4, 47.7, 32.9, 26.7, 26.2, 18.9. HRMS (ESI) m/z calcd for $C_{16}H_{20}N^+$ $(M+H)^+$ 226.1590, found 226.1593.

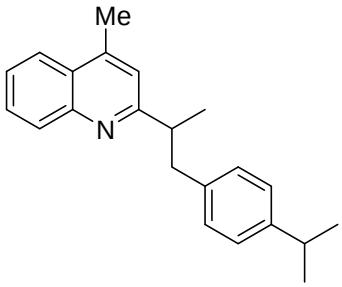
tert-Butyl 3-(4-methylquinolin-2-yl)pyrrolidine-1-carboxylate (3h)



The general procedure was followed using 4-methylquinoline (29.2 mg, 0.2 mmol), 3-formyl-pyrrolidine-1-carboxylicacidtert-butylester (70 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **3h** (32.5 mg, 52%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 3.94 – 3.83 (m, 1H), 3.74 – 3.62 (m, 3H), 3.51 – 3.42 (m, 1H), 2.70 (s, 3H), 2.36-2.31 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.0, 154.8, 147.8, 144.9, 129.8, 129.4, 127.3, 126.0, 123.7, 120.8, 79.3, 51.3, 51.0, 47.1, 46.2, 46.0, 45.9, 32.4, 31.7, 28.7, 18.9. HRMS (ESI) m/z calcd for $C_{19}H_{25}N_2O_2^+$ $(M+H)^+$ 313.1911, found 313.1910.

2-(1-(4-Isopropylphenyl)propan-2-yl)-4-methylquinoline (3i)

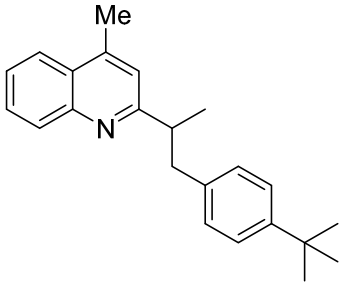


The general procedure was followed using 4-methylquinoline (29.1 mg, 0.2 mmol), cyclamen aldehyder (80 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3i** (37.6 mg, 62%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.12 (s, 5H), 3.39-3.31 (m, 1H), 3.26 – 3.13 (m, 1H), 2.87 (ddd, *J* = 13.7, 8.0, 5.6 Hz, 2H), 2.68 (d, *J* = 9.3 Hz, 3H), 1.40 (d, *J* = 7.0 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 5H). ^{13}C NMR (100 MHz,

Chloroform-*d*) δ 166.2, 147.8, 146.5, 144.3, 138.0, 129.7, 129.3, 129.1, 127.2, 126.3, 125.6, 123.7, 121.0, 44.6, 42.6, 33.8, 24.2, 22.7, 20.1, 18.9. HRMS (ESI) m/z calcd for $C_{22}H_{26}N^+$ $(M+H)^+$ 304.2060, found 304.2061.

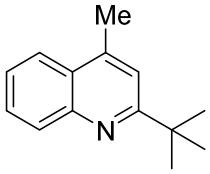
2-(1-(4-(tert-Butyl)phenyl)propan-2-yl)-4-methylquinoline (3j)



The general procedure was followed using 4-methylquinoline (29.2 mg, 0.2 mmol), lily aldehyde (87 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3j** (50.5 mg, 80%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.13 (m, 3H), 3.41 – 3.33 (m, 1H), 3.24 (dd, *J* = 13.5, 6.1 Hz, 1H), 2.89 (dd, *J* = 13.5, 8.9 Hz, 1H), 2.68 (s, 3H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.2, 148.7, 147.8, 144.3, 137.7, 129.7, 129.0, 129.0, 127.2, 125.6, 125.2, 123.7, 120.9, 44.5, 42.5, 34.4, 31.5, 20.1, 18.9. HRMS (ESI) m/z calcd for $C_{23}H_{28}N^+$ $(M+H)^+$ 318.2216, found 318.2222.

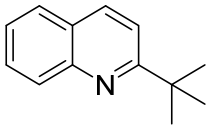
2-(tert-Butyl)-4-methylquinoline (3k)[8]



The general procedure was followed using 4-methylquinoline (29.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **3k** (35.8 mg, 90%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 2.70 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.1, 147.4, 143.7, 130.1, 128.8, 126.7, 125.5, 123.5, 119.0, 38.0, 30.3, 19.1. HRMS (ESI) m/z calcd for $C_{14}H_{18}N^+$ $(M+H)^+$ 200.1434, found 200.1436.

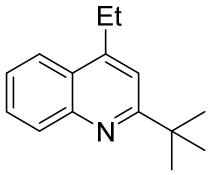
2-(tert-Butyl)quinoline (4a)[9]



The general procedure was followed using quinoline (25.8 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4a** (20.0 mg, 54%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 8.07 (s, 1H), 7.78 (dd, J = 8.0, 1.5 Hz, 1H), 7.68 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.49 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.4, 147.5, 136.0, 129.5, 129.1, 127.4, 126.6, 125.7, 118.4, 38.3, 30.3. HRMS (ESI) m/z calcd for $C_{13}H_{16}N^+$ $(M+H)^+$ 186.1277, found 186.1276.

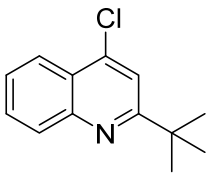
2-(tert-Butyl)-4-ethylquinoline (4b)



The general procedure was followed using 4-ethylquinoline (32.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4b** (30.0 mg, 68%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.49 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.38 (s, 1H), 3.11 (q, J = 7.5 Hz, 2H), 1.49 (s, 9H), 1.41 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.2, 149.4, 147.7, 130.3, 128.7, 125.8, 125.5, 123.2, 116.9, 38.2, 30.3, 25.6, 14.5. HRMS (ESI) m/z calcd for $C_{15}H_{20}N^+$ $(M+H)^+$ 214.1590, found 214.1593.

2-(tert-Butyl)-4-chloroquinoline (4c)

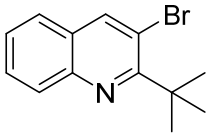


The general procedure was followed using 4-chloroquinoline (33.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was

performed (PE/EA: 60/1) to yield **4c** (33.0 mg, 75%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, J = 8.4 Hz, 1H), 8.09 (dd, J = 8.5, 1.2 Hz, 1H), 7.73 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.62 (s, 1H), 7.58 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.5, 148.5, 142.4, 130.1, 129.9, 126.8, 124.8, 123.8, 118.6, 38.4, 30.1. HRMS (ESI) m/z calcd for $C_{13}H_{15}ClN^+$ $(M+H)^+$ 220.0888, found 220.0886.

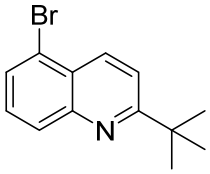
3-Bromo-2-(tert-butyl)quinoline (4d)



The general procedure was followed using 3-bromoquinoline (41.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4d** (22.2 mg, 42%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.50 (t, J = 7.5 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 145.3, 141.5, 129.6, 129.5, 127.8, 127.0, 126.1, 116.6, 40.4, 29.2. HRMS (ESI) m/z calcd for $C_{13}H_{15}BrN^+$ $(M+H)^+$ 264.0382, found 264.0383.

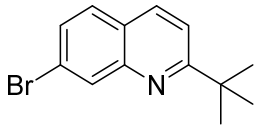
5-Bromo-2-(tert-butyl)quinoline (4e)



The general procedure was followed using 5-bromoquinoline (41.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4e** (36.0 mg, 68%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, J = 8.9 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.74 (dd, J = 7.5, 1.1 Hz, 1H), 7.61 (d, J = 8.9 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 148.3, 135.4, 129.5, 129.5, 129.3, 126.1, 121.7, 119.6, 38.2, 30.2. HRMS (ESI) m/z calcd for $C_{13}H_{15}BrN^+$ $(M+H)^+$ 264.0382, found 264.0383.

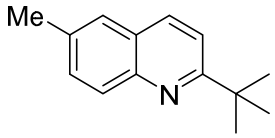
7-Bromo-2-(tert-butyl)quinoline (4f)



The general procedure was followed using 7-bromoquinoline (41.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4f** (44.2 mg, 84%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, J = 1.7 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.57 – 7.50 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 148.2, 135.8, 131.9, 129.2, 128.6, 125.1, 123.10, 118.7, 38.4, 30.2. HRMS (ESI) m/s calcd for $C_{13}H_{15}BrN^+$ $(M+H)^+$ 264.0382, found 264.0383.

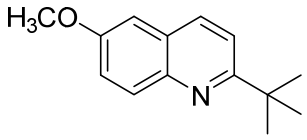
2-(tert-Butyl)-6-methylquinoline (4g)[10]



The general procedure was followed using 6-methylquinoline (29.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4g** (32.5 mg, 81%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, J = 8.5, 4.4 Hz, 2H), 7.54 – 7.48 (m, 3H), 2.53 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.4, 146.1, 135.4, 135.4, 131.3, 129.2, 126.6, 126.2, 118.3, 38.1, 30.3, 21.6. HRMS (ESI) m/z calcd for $C_{14}H_{17}N^+$ $(M+H)^+$ 200.1434; found 200.1435.

2-(tert-Butyl)-6-methoxyquinoline (4h)

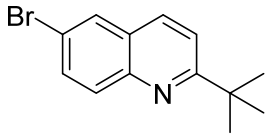


The general procedure was followed using 6-methoxyquinoline (32.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 20/1) to yield **4h** (17.5 mg, 40%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, J = 8.9, 4.0 Hz, 2H), 7.49 (d, J = 8.7 Hz, 1H), 7.33 (dd, J = 9.2, 2.8 Hz, 1H), 7.05 (d, J = 2.8 Hz, 1H), 3.93 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz,

Chloroform-*d*) δ 167.0, 157.3, 143.6, 134.9, 130.9, 127.3, 121.6, 118.6, 105.1, 55.6, 38.0, 30.3. HRMS (ESI) m/z calcd for $C_{14}H_{18}NO^+$ $(M+H)^+$ 216.1383, found 216.1388.

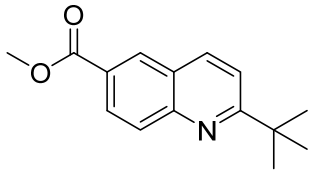
6-Bromo-2-(tert-butyl)quinoline (4i)



The general procedure was followed using 6-bromoquinoline (41.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4i** (36.3 mg, 69%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, J = 8.0 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.72 (dd, J = 8.9, 2.3 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.9, 146.1, 135.0, 132.5, 131.3, 129.4, 127.7, 119.4, 119.2, 38.4, 30.2. HRMS (ESI) m/z calcd for $C_{13}H_{15}BrN^+$ $(M+H)^+$ 264.0382, found 264.0383.

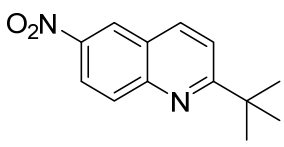
Methyl 2-(tert-butyl)quinoline-6-carboxylate (4j)



The general procedure was followed using quinoline-6-carboxylate (37.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 15/1) to yield **4j** (45.2 mg, 93%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, J = 2.0 Hz, 1H), 8.24 (dd, J = 8.8, 1.9 Hz, 1H), 8.14 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 3.97 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 167.0, 149.5, 137.1, 130.6, 129.8, 128.6, 127.2, 125.6, 119.2, 52.4, 38.5, 30.1. HRMS (ESI) m/z calcd for $C_{15}H_{18}NO_2^+$ $(M+H)^+$ 244.1332, found 244.1334.

2-(tert-Butyl)-6-nitroquinoline (4k)

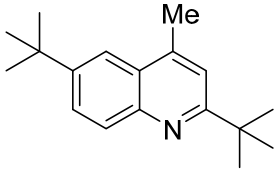


The general procedure was followed using 6-nitroquinoline (35.0 mg, 0.2 mmol),

trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 20/1) to yield **4k** (14.0 mg, 30%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (d, J = 2.6 Hz, 1H), 8.43 (dd, J = 9.3, 2.6 Hz, 1H), 8.24 (d, J = 8.7 Hz, 1H), 8.16 (d, J = 9.2 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 149.8, 145.1, 137.6, 131.2, 125.3, 124.3, 122.6, 120.4, 38.9, 30.0. HRMS (ESI) m/z calcd for $C_{13}H_{15}N_2O_2^+$ $(M+H)^+$ 231.1128, found 231.1134.

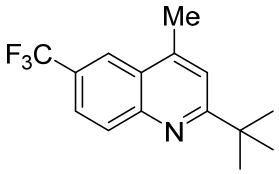
2,6-Di-tert-butyl-4-methylquinoline (4l)



The general procedure was followed using 6-(tert-butyl)-4-methylquinoline (40.1 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4l** (22.0 mg, 55%) as a colorless solid. mp: 112 – 114 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, J = 8.9 Hz, 1H), 7.85 (d, J = 2.2 Hz, 1H), 7.76 (dd, J = 8.9, 2.2 Hz, 1H), 7.33 (d, J = 1.2 Hz, 1H), 2.71 (s, 3H), 1.46 (s, 9H), 1.44(s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.4, 148.2, 145.8, 143.6, 129.6, 127.6, 126.1, 119.0, 118.3, 77.2, 77.2, 76.8, 37.9, 35.1, 31.5, 30.3, 19.2. HRMS(ESI) m/z calcd for $C_{18}H_{26}N^+$ $(M+H)^+$ 256.2060, found 256.2065.

2-(tert-Butyl)-4-methyl-6-(trifluoromethyl)quinoline (4m)

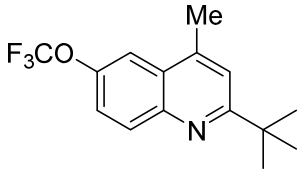


The general procedure was followed using 4-methyl-6-(trifluoromethyl)quinoline (42.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4m** (41.5 mg, 77%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.83 (dd, J = 8.8, 2.0 Hz, 1H), 7.45 (s, 1H), 2.74 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.5, 148.6, 144.7, 131.2, 127.3 (q, J = 32.2 Hz), 125.8, 124.5 (d, J = 270.4 Hz), 124.5 (q, J = 3.1 Hz), 121.6 (q, J = 4.3 Hz), 120.2, 38.3, 30.1, 19.0. HRMS (ESI) m/z calcd for $C_{15}H_{17}F_3N^+$ $(M+H)^+$

268.1308, found 268.1310.

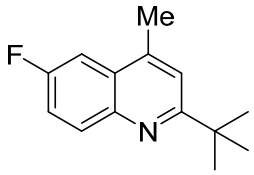
2-(tert-Butyl)-4-methyl-6-(trifluoromethoxy)quinoline (4n)



The general procedure was followed using 4-methyl-6-(trifluoromethoxy)quinoline (46.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 20/1) to yield **4n** (48.2 mg, 85%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 9.1 Hz, 1H), 7.75 (s, 1H), 7.53 (d, *J* = 10.2 Hz, 1H), 7.41 (s, 1H), 2.68 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 169.8, 146.4 (d, *J* = 1.92 Hz), 145.8, 143.7, 132.2, 126.9, 122.8, 122.1 (q, *J* = 258.4 Hz), 119.9, 114.5, 38.2, 30.2, 19.0. HRMS (ESI) m/z calcd for $C_{15}H_{17}F_3NO^+$ $(M+H)^+$ 284.1257, found 284.1260.

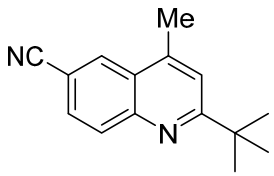
2-(tert-Butyl)-6-fluoro-4-methylquinoline (4o)



The general procedure was followed using 4-methyl-6-(trifluoromethoxy)quinoline (32.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4o** (33.5 mg, 77%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.05 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.53 (dd, *J* = 9.9, 2.8 Hz, 1H), 7.42 (ddd, *J* = 9.2, 8.2, 2.8 Hz, 1H), 7.37 (s, 1H), 2.64 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 168.4 (d, *J* = 2.5 Hz), 158.9 (d, *J* = 246.6 Hz), 144.5, 143.2 (d, *J* = 5.3 Hz), 132.3 (d, *J* = 9.1 Hz), 127.3 (d, *J* = 9.3 Hz), 119.6, 118.5 (d, *J* = 25.4 Hz,), 107.0 (d, *J* = 22.0 Hz,), 38.0, 30.2, 19.1. HRMS (ESI) m/z calcd for $C_{14}H_{17}FN^+$ $(M+H)^+$ 218.1340, found 218.1340.

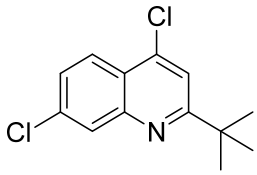
2-(tert-Butyl)-4-methylquinoline-6-carbonitrile (4p)



The general procedure was followed using 4-methylquinoline-6-carbonitrile (34.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 20/1) to yield **4p** (38.1 mg, 85%) as a colorless solid. mp: 97 – 99 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, J = 1.5 Hz, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.78 (dd, J = 8.7, 1.7 Hz, 1H), 7.46 (s, 1H), 2.71 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.5, 148.6, 144.3, 131.4, 130.1, 129.6, 126.2, 120.6, 119.3, 108.9, 38.5, 30.0, 18.9. HRMS (ESI) m/z calcd for $C_{15}H_{17}N_2^+$ $(M+H)^+$ 225.1386, found 225.1384.

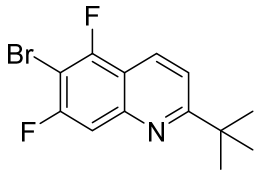
2-(tert-Butyl)-4,7-dichloroquinoline (4q)



The general procedure was followed using 4,7-dichloroquinoline (39.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4q** (44.6 mg, 88%) as a colorless solid. mp: 60 – 62°C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, J = 5.5, 3.4 Hz, 2H), 7.59 (s, 1H), 7.51 (dd, J = 9.0, 2.1 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 148.8, 142.4, 136.1, 128.8, 127.7, 125.2, 123.3, 118.8, 38.5, 30.0. HRMS(ESI) m/s calcd for $C_{13}H_{14}Cl_2N^+$ $(M+H)^+$ 254.0498, found 254.0497.

6-Bromo-2-(tert-butyl)-5,7-difluoroquinoline (4r)

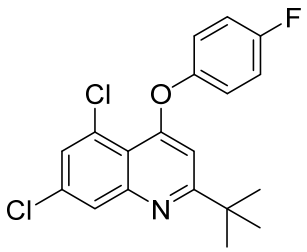


The general procedure was followed using 6-bromo-5,7-difluoroquinoline (49.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **4r** (53.5 mg, 89%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, J = 8.9 Hz, 1H), 7.61 (dd, J = 9.7, 1.9 Hz, 1H), 7.56 (d, J = 8.9 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 159.7 (dd, J = 242.5, 5.3 Hz), 155.6 (dd, J = 247.8, 6.2 Hz), 146.7 (q, J = 9.3, 4.2 Hz), 128.9 (t, J = 2.9 Hz),

118.5 (t, J = 2.9 Hz), 114.5 (q, J = 15.2, 1.6 Hz), 110.0 (q, J = 17.5, 4.6 Hz), 95.4 (q, J = 23.9, 3.7 Hz), 38.6, 30.0. HRMS (ESI) m/z calcd for $C_{13}H_{13}BrF_2N^+$ $(M+H)^+$ 300.0194, found 300.0195.

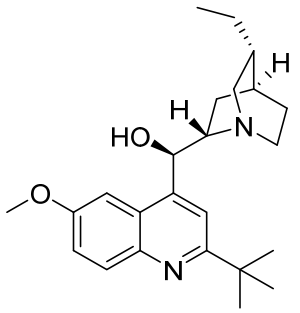
2-(tert-Butyl)-5,7-dichloro-4-(4-fluorophenoxy)quinoline (4s)[8]



The general procedure was followed using 5,7-dichloro-4-(4-fluorophenoxy)quinoline (61.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **4s** (53.1 mg, 73%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, J = 2.1 Hz, 1H), 7.50 (d, J = 2.1 Hz, 1H), 7.18 – 7.08 (m, 4H), 6.77 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.3, 162.1, 159.8 (d, J = 244.7 Hz), 151.1, 150.8 (d, J = 2.7 Hz), 150.8, 134.7, 129.8, 128.8, 128.0, 121.8, 121.7, 117.2, 116.9, 104.8, 38.4, 29.8. HRMS (ESI) m/z calcd for $C_{19}H_{17}Cl_2FNO^+$ $(M+H)^+$ 364.0666, found 364.0668.

(*R*)-(2-(tert-Butyl)-6-methoxyquinolin-4-yl)[(1S,2S,4S,5R)-5-ethylquinuclidin-2-yl]methanol (4t)[11]

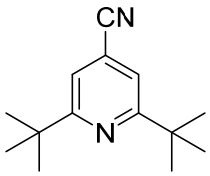


The general procedure was followed using (R)-((1S,2S,4S,5R)-5-ethylquinuclidin-2-yl)(6-methoxyquinolin-4-yl)methanol (65.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (CH_2Cl_2/MeOH: 10:1) to yield **4t** (54.3 mg, 71%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.60 (d, J = 9.2 Hz, 1H), 6.79 (dd, J = 9.1, 2.1 Hz, 1H), 6.71 (s, 1H), 6.31 (s, 1H), 6.12 (s, 1H), 4.53 (t, J = 11.3 Hz, 1H), 3.50 (s, 3H), 3.43 – 3.36 (m, 1H), 3.26 – 3.20 (m, 1H), 3.06 (td, J = 11.8, 5.5 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.25 (t, J =

10.9 Hz, 1H), 2.13 (dd, *J* = 13.1, 7.1 Hz, 1H), 2.00 (s, 1H), 1.83 (s, 1H), 1.74 (t, *J* = 12.2 Hz, 1H), 1.47 (s, 9H), 1.19 (p, *J* = 7.5 Hz, 3H), 0.77 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 165.7, 157.4, 143.5, 143.1, 131.3, 123.2, 121.5, 115.7, 99.1, 66.3, 60.3, 57.1, 56.8, 44.2, 37.9, 35.7, 30.4, 27.0, 24.9, 24.8, 17.8, 11.5. HRMS (ESI) m/z calcd for $C_{24}H_{34}N_2O_2^+$ $(M+H)^+$ 382.2620 , Found 382.2607.

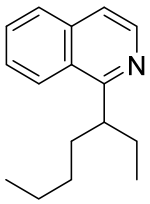
2,6-Di-tert-butylisonicotinonitrile (5a)[12]



The general procedure was followed using isonicotinonitrile (21.0 mg, 0.2 mmol), trimethylacetaldehyde (88 μL, 0.8 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **5a** (22.5 mg, 52%) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.31 (s, 2H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 169.5, 120.4, 118.1, 117.6, 38.2, 30.0. Mass spectrum, m/e (relative intensity) 216 (M^+, 19), 215 (23), 201 (100), 186 (14), 185 (23), 174 (35), 171 (14), 145 (39), 97 (30), 41 (28), 39 (20).

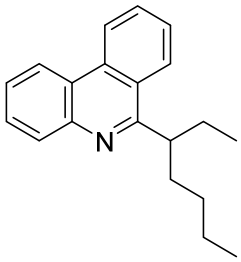
1-(Heptan-3-yl)isoquinoline (5b)



The general procedure was followed using phenanthridine (26.0 mg, 0.2 mmol), 2-ethylcapronaldehyde (65 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **5b** (23.2 mg, 51%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.52 (d, *J* = 5.7 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.58 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.48 (d, *J* = 5.7 Hz, 1H), 3.59 (tt, *J* = 8.4, 5.5 Hz, 1H), 2.02 – 1.90 (m, 2H), 1.88 – 1.75 (m, 2H), 1.29 – 1.18 (m, 3H), 1.11-1.03 (m, 1H), 0.78 (dt, *J* = 9.2, 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 165.5, 142.2, 136.4, 129.7, 128.2, 127.6, 126.9, 125.0, 118.8, 43.3, 35.3, 30.2, 28.7, 23.1, 14.2, 12.5. HRMS (ESI) m/z calcd for $C_{16}H_{22}N^+$ $(M+H)^+$ 228.1747, found 228.1750.

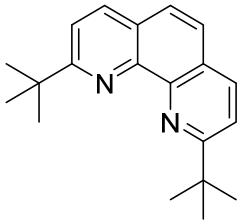
6-(Heptan-3-yl)phenanthridine (5c)



The general procedure was followed using phenanthridine (36.0 mg, 0.2 mmol), 2-ethylcapronaldehyde (65 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 60/1) to yield **5c** (36.2 mg, 65%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 (d, J = 8.2 Hz, 1H), 8.57 (d, J = 8.1 Hz, 1H), 8.37 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 8.1 Hz, 1H), 7.84 (t, J = 7.6 Hz, 1H), 7.72 (q, J = 7.9 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 3.68 (ddd, J = 13.6, 7.9, 5.8 Hz, 1H), 2.18 – 2.07 (m, 2H), 1.92 – 1.81 (m, 2H), 1.34 – 1.19 (m, 4H), 0.89 – 0.81 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.1, 144.1, 133.0, 130.1, 130.0, 128.5, 127.2, 126.3, 126.2, 125.8, 123.3, 122.6, 122.0, 43.7, 34.7, 30.3, 28.2, 23.2, 14.2, 12.6. HRMS (ESI) m/z calcd for $C_{20}H_{24}N^+$ $(M+H)^+$ 278.1903, found 278.1908.

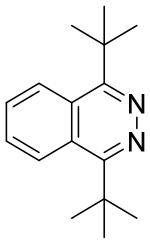
2,9-Di-tert-butyl-1,10-phenanthroline (5d)



The general procedure was followed using 1,10-phenanthroline (21.0 mg, 0.2 mmol), trimethylacetaldehyde (88 μL, 0.8 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **5d** (13.5 mg, 23%) as a colorless solid. mp: 154 – 156 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, J = 8.5 Hz, 2H), 7.72 (s, 1H), 7.70 (s, 3H), 1.60 (s, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.4, 144.9, 136.1, 127.0, 125.5, 119.8, 38.8, 30.4. HRMS (ESI) m/z calcd for $C_{20}H_{25}N_2^+$ $(M+H)^+$ 293.2012, found 293.2017.

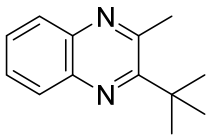
1,4-Di-tert-butylphthalazine (5e)



The general procedure was followed using phthalazine (26.2 mg, 0.2 mmol), trimethylacetaldehyde (88 μL, 0.8 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **5e** (9.8 mg, 20%) as a colorless solid. mp: 134 – 136 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (dd, J = 6.5, 3.4 Hz, 2H), 7.80 (dd, J = 6.6, 3.4 Hz, 2H), 1.71 (s, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 129.7, 127.3, 125.8, 39.0, 31.2. HRMS (ESI) m/z calcd for $C_{16}H_{23}N_2^+$ $(M+H)^+$ 243.1856, found 243.1862.

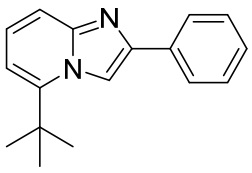
2-(tert-Butyl)-3-methylquinoxaline (5f)



The general procedure was followed using 3-methylquinoxaline (29.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **5f** (8.1 mg, 20%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.98 (m, 1H), 7.98 – 7.92 (m, 1H), 7.69 – 7.62 (m, 2H), 2.94 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1, 152.8, 140.3, 140.1, 129.2, 129.1, 128.7, 127.9, 38.9, 29.6, 26.4. HRMS (ESI) m/z calcd for $C_{13}H_{17}N_2^+$ $(M+H)^+$ 201.1386, found 201.1388.

5-(tert-Butyl)-2-phenylimidazo[1,2-a]pyridine (5g)

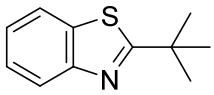


The general procedure was followed using 2-phenylimidazo[1,2-a]pyridine (39.0 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **5g** (11.0 mg, 22%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 8.00 (dd, J = 8.2, 1.3 Hz, 2H), 7.59 (d, J = 8.9 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.18 (dd, J = 8.9, 7.3 Hz, 1H), 6.74 (d, J

= 7.2 Hz, 1H), 1.58 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.5, 146.0, 144.8, 134.0, 129.0, 128.1, 126.3, 125.2, 115.7, 109.0, 108.9, 35.6, 27.8. HRMS (ESI) m/z calcd for $C_{17}H_{19}N_2^+$ $(M+H)^+$ 251.1543, found 251.1546.

2-(tert-Butyl)benzo[d]thiazole (5h)[13]



The general procedure was followed using benzothiazole (27.5 mg, 0.2 mmol), trimethylacetaldehyde (44 μL, 0.4 mmol). Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **5h** (18.0 mg, 47%) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.46 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.35 (ddd, J = 8.2, 7.3, 1.2 Hz, 1H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.0, 153.4, 135.1, 125.9, 124.6, 122.8, 121.6, 38.4, 30.9. HRMS (ESI) m/z calcd for $C_{13}H_{16}NO^+$ $(M+H)^+$ 202.1226, found 202.1229.

5. References

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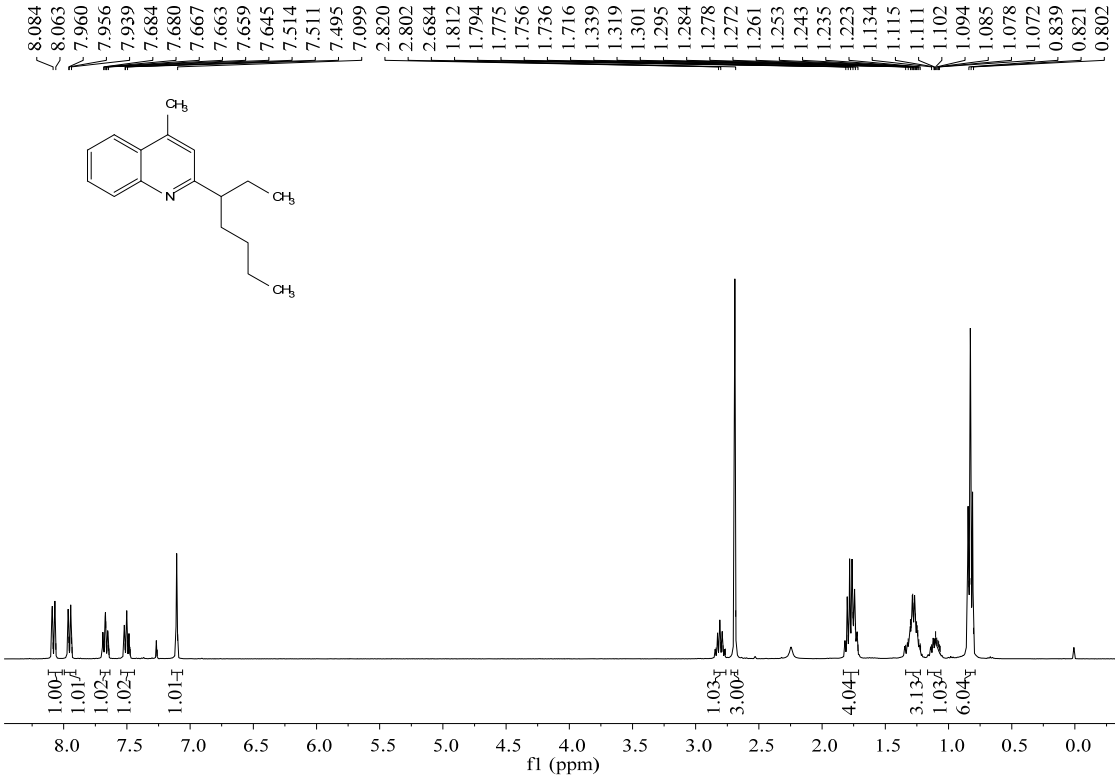
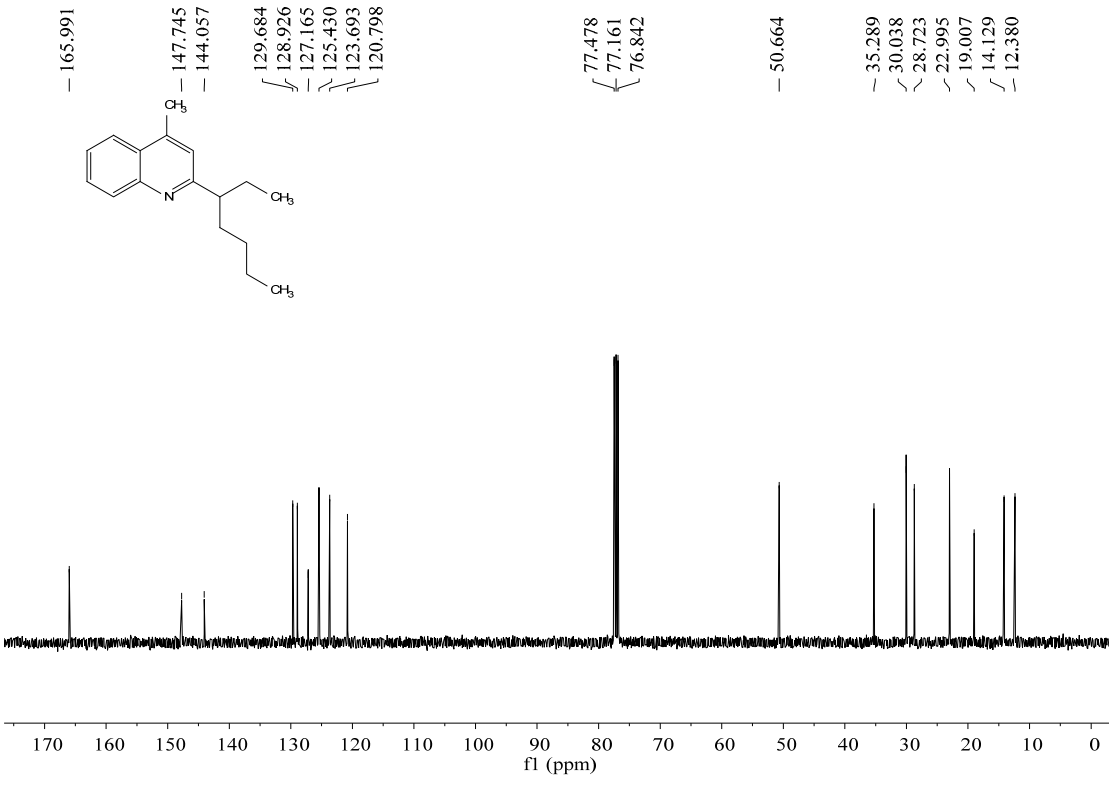
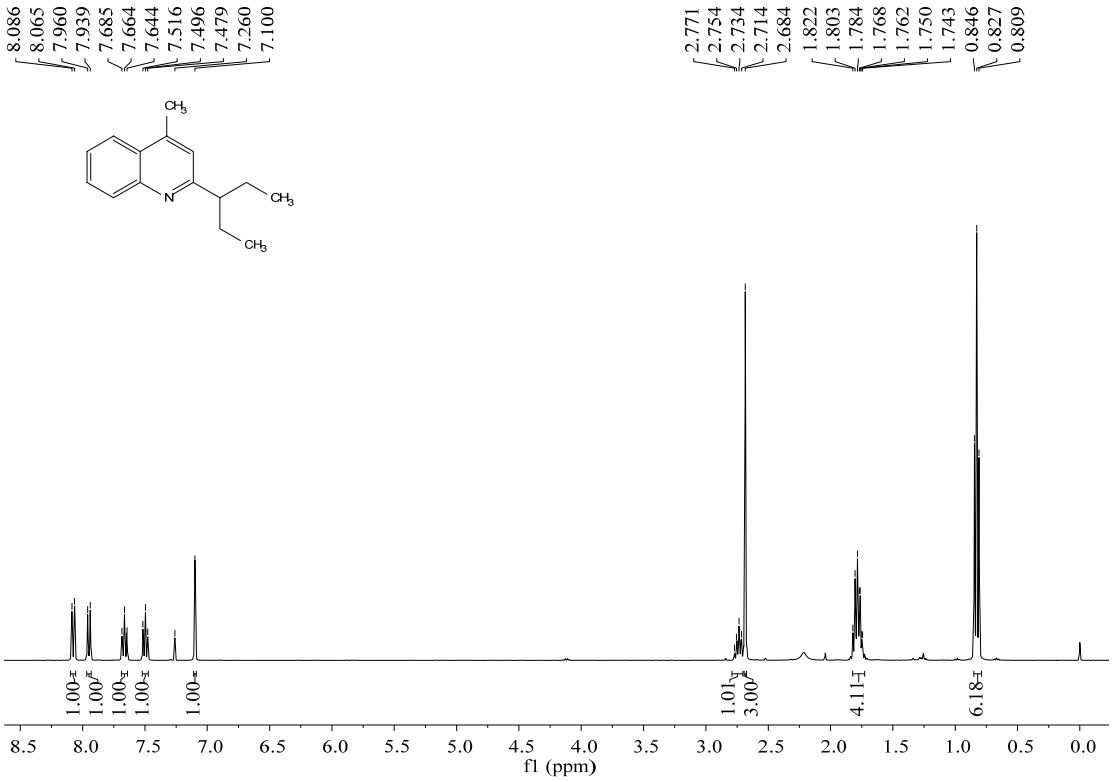
6.Copies of ^{1}H and ^{13}C NMR spectra of all products

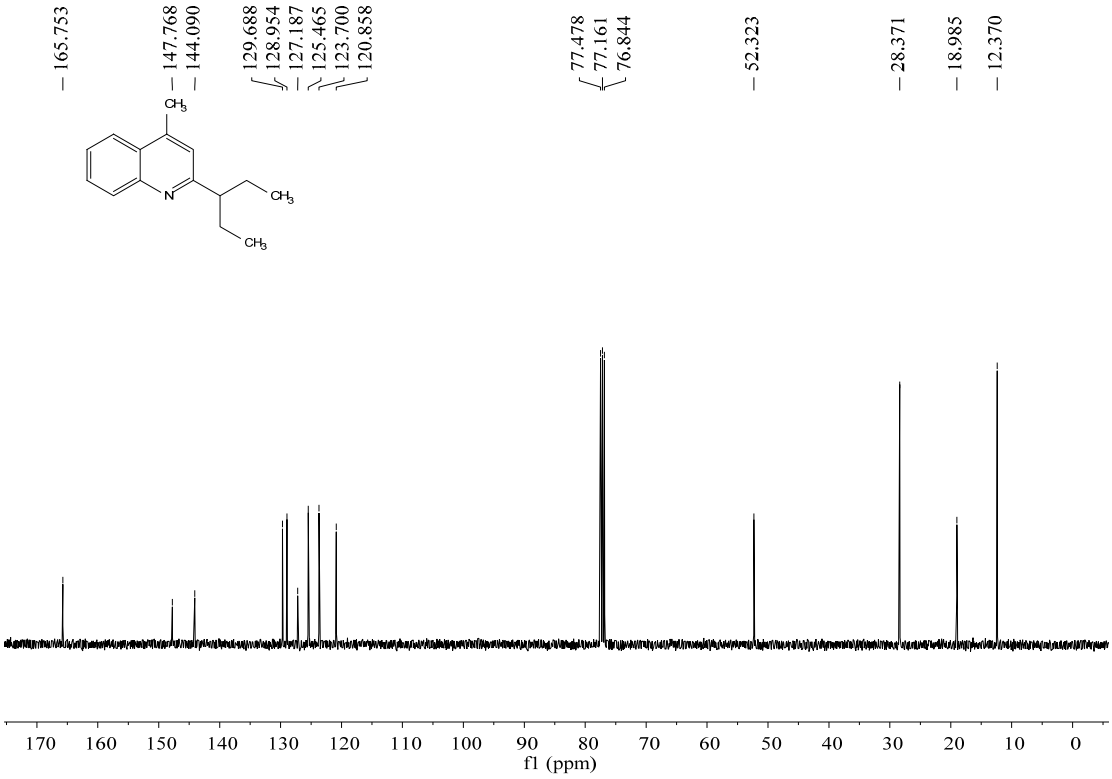
^{1}H and ^{13}C NMR spectra of 3a



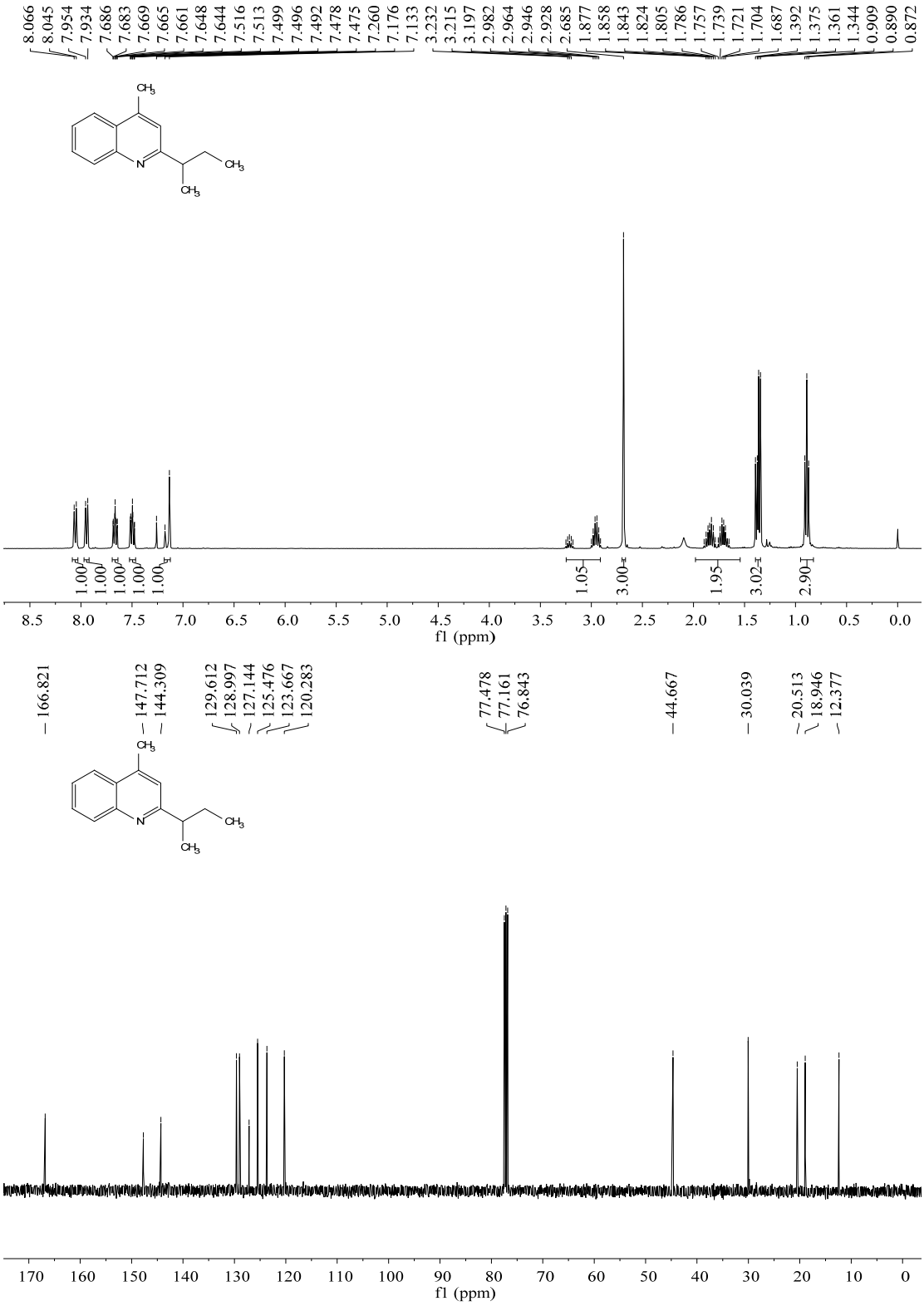


^{1}H and ^{13}C NMR spectra of 3b

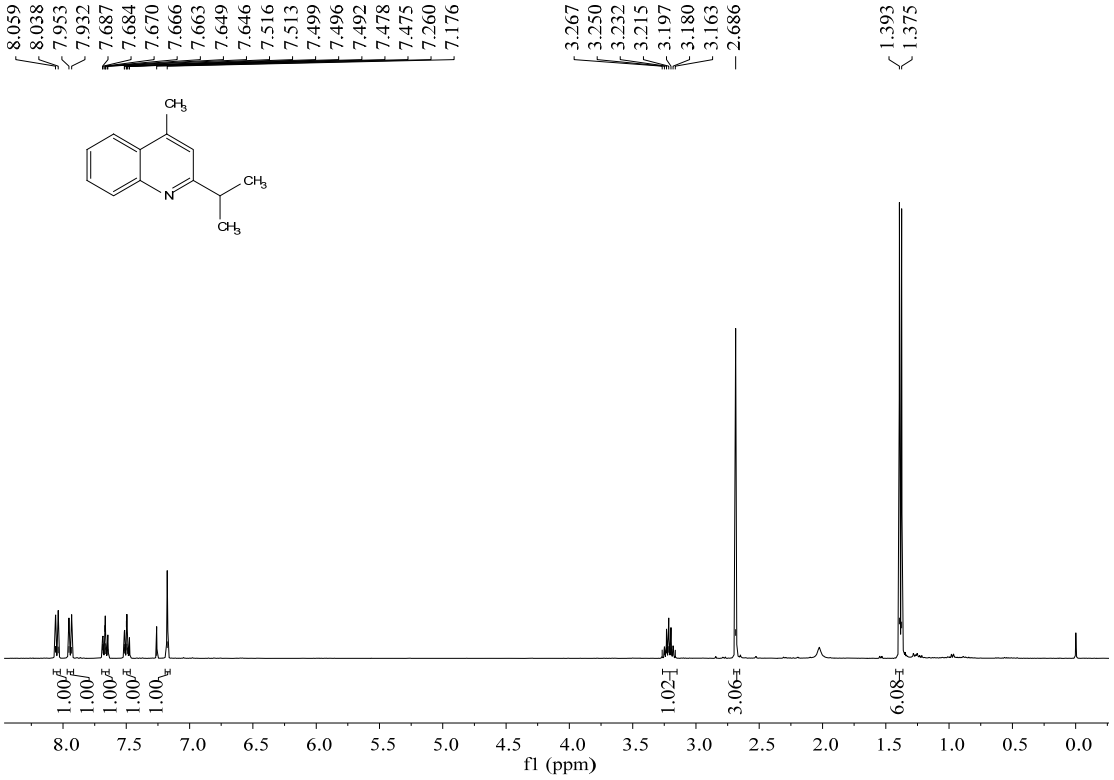


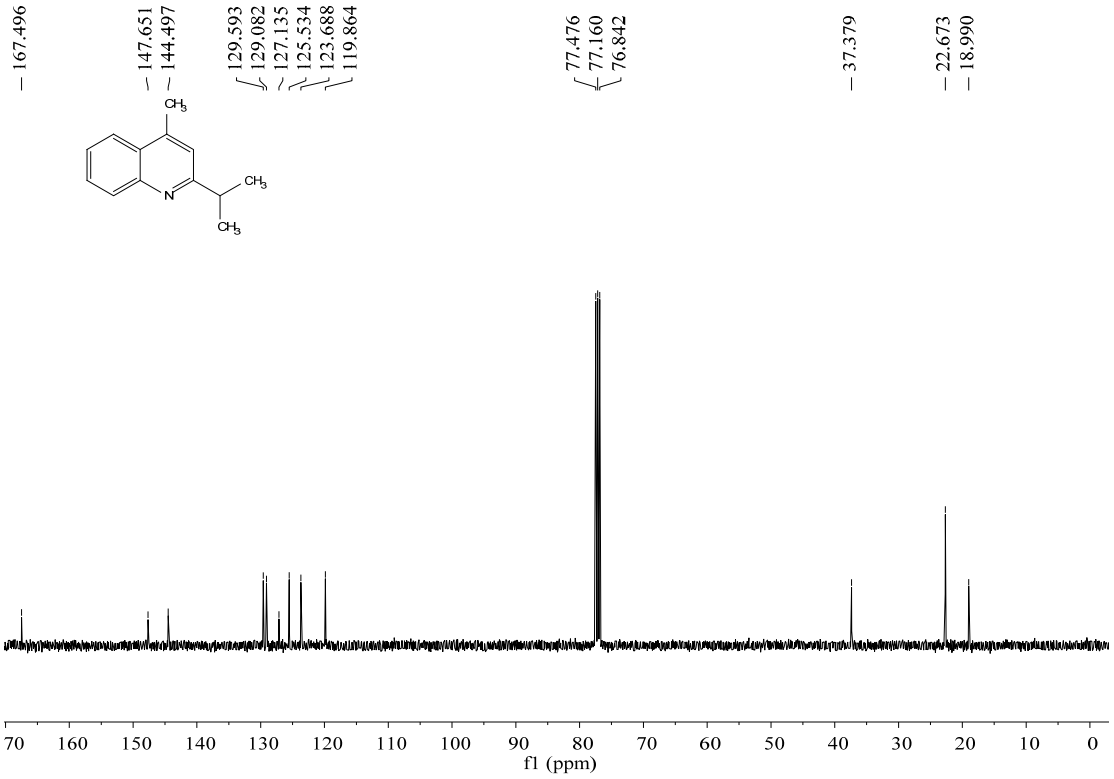


^{1}H and ^{13}C NMR spectra of 3c

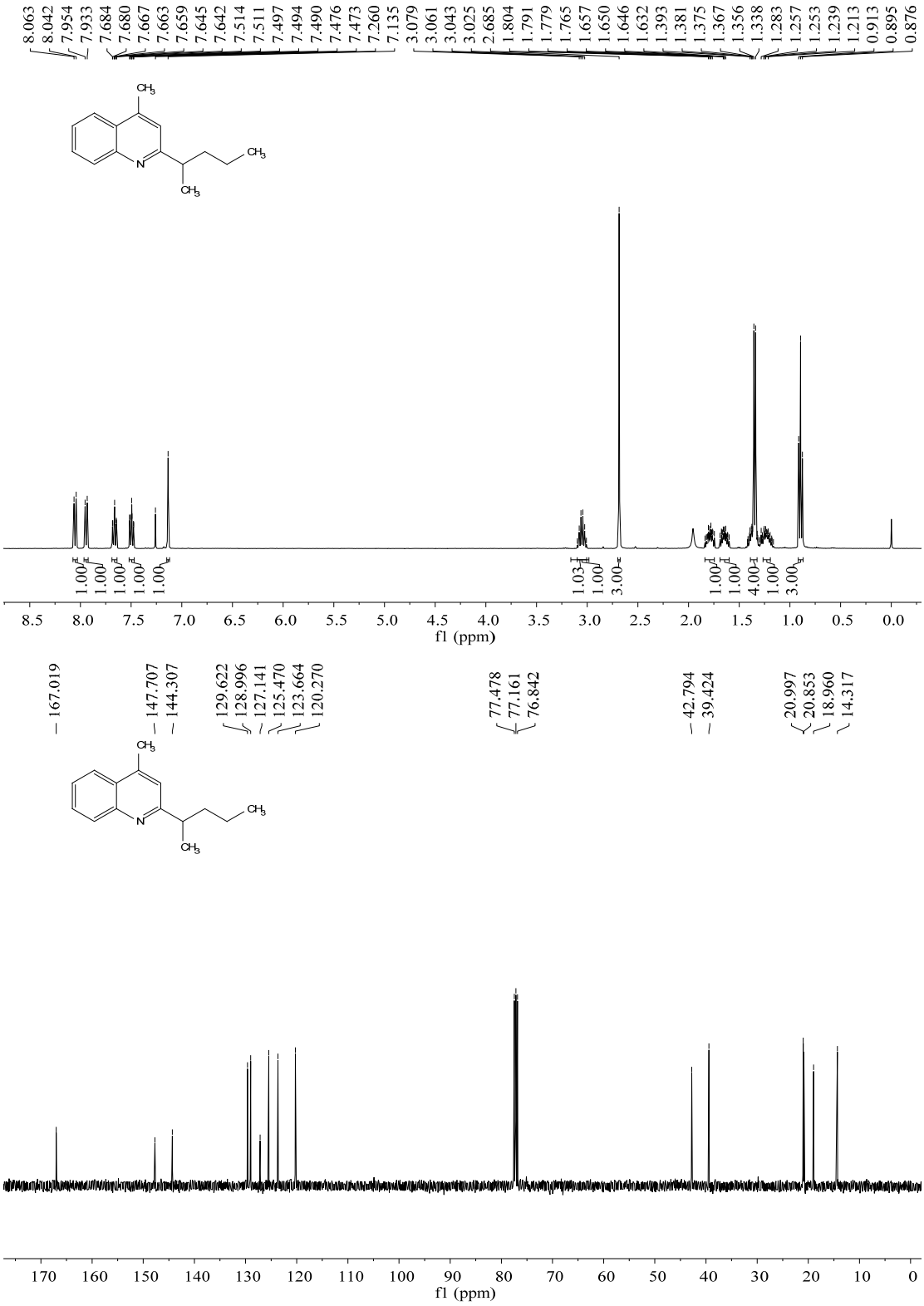


^{1}H and ^{13}C NMR spectra of 3d

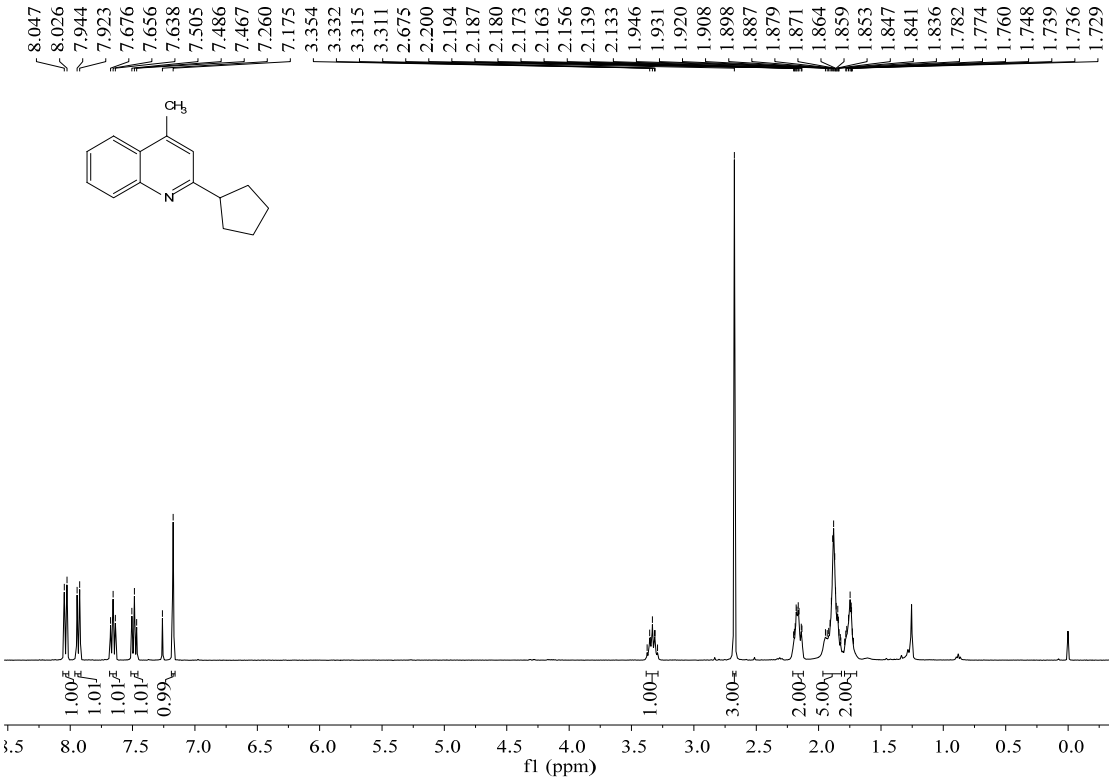


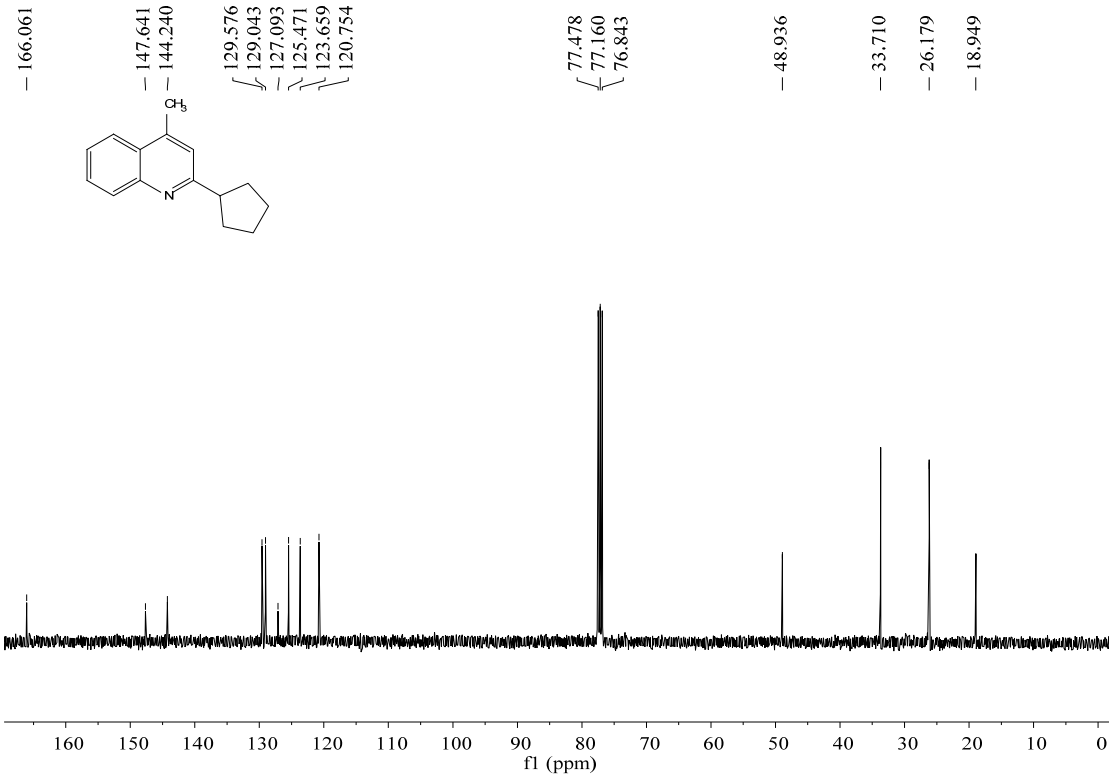


^{1}H and ^{13}C NMR spectra of 3e

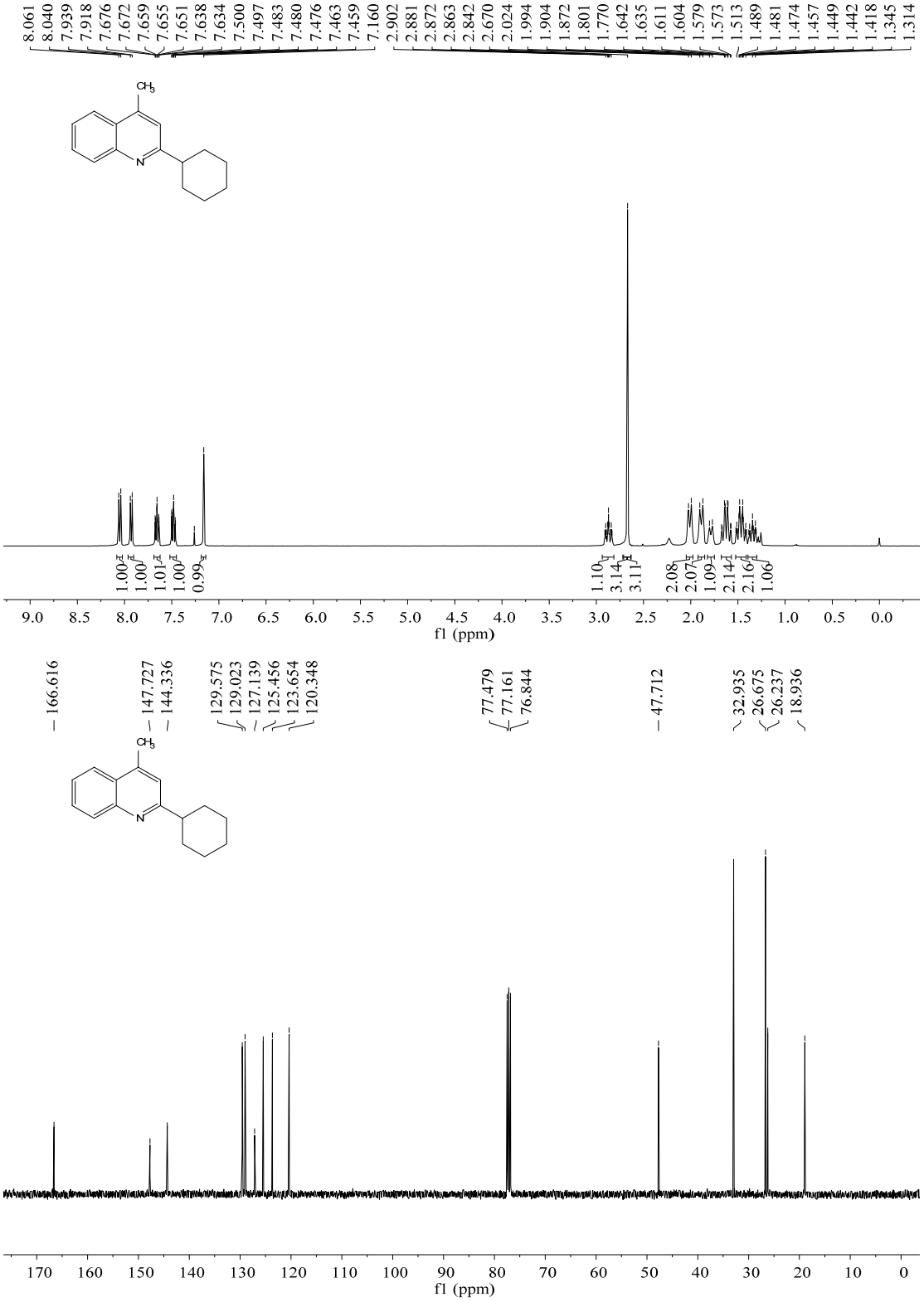


^{1}H and ^{13}C NMR spectra of 3f





^{1}H and ^{13}C NMR spectra of 3g



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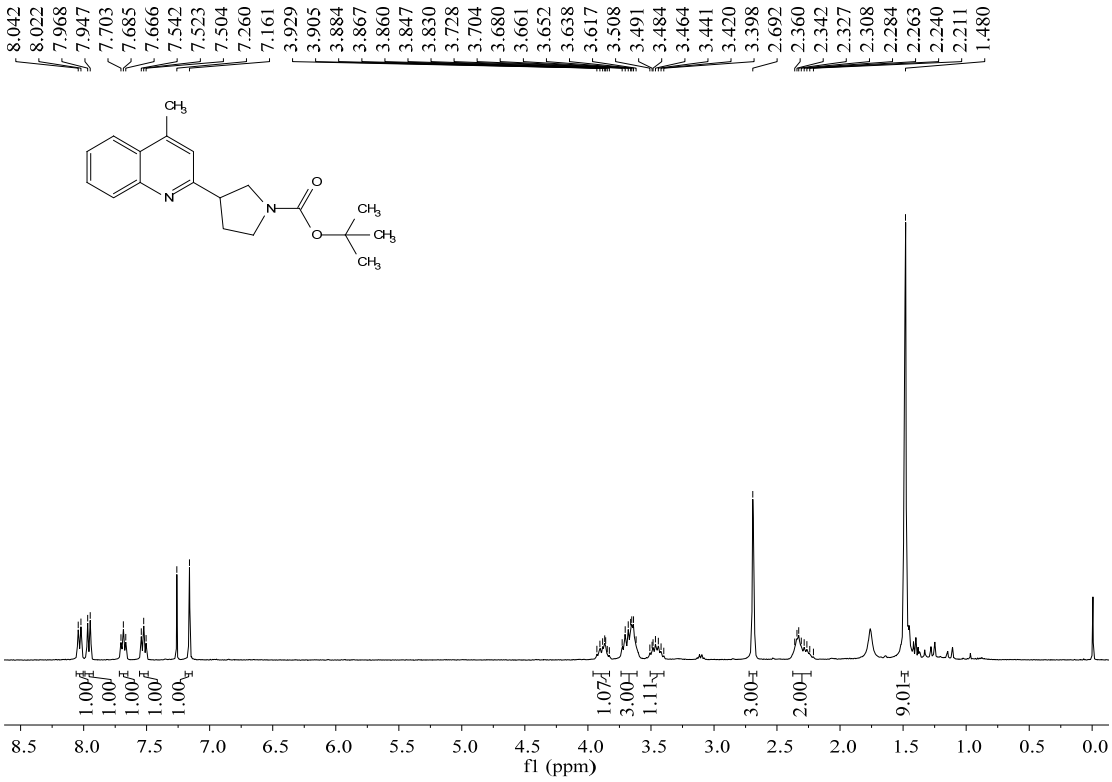
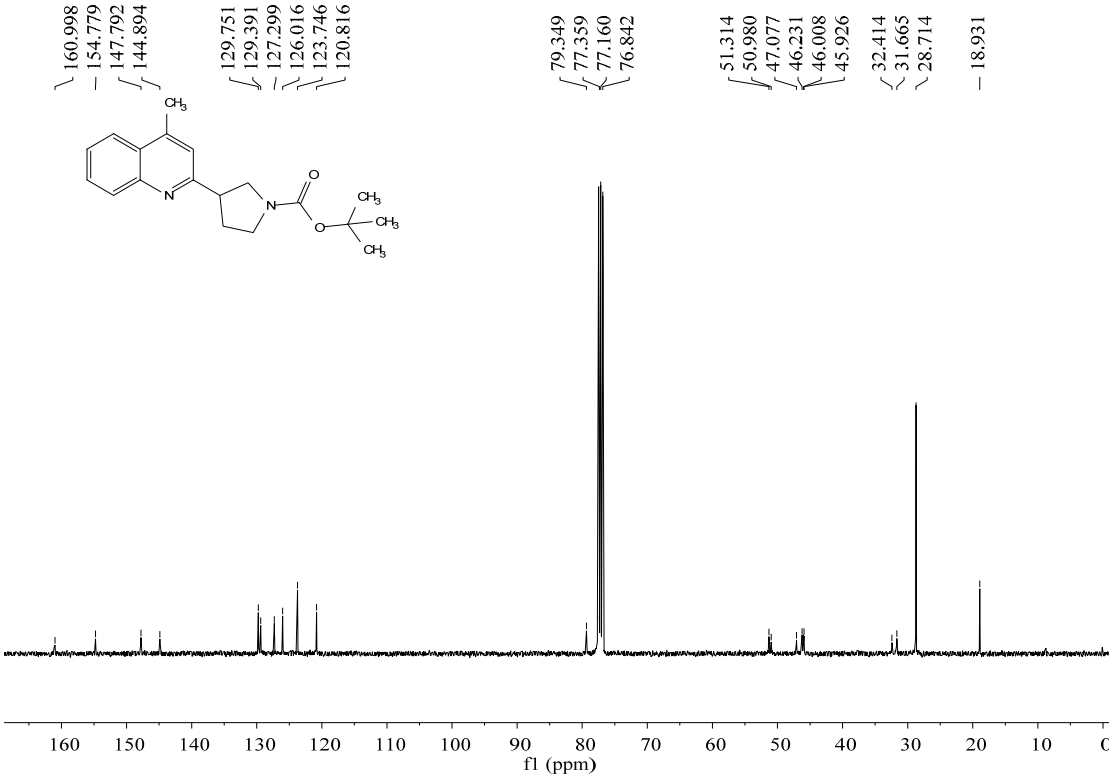
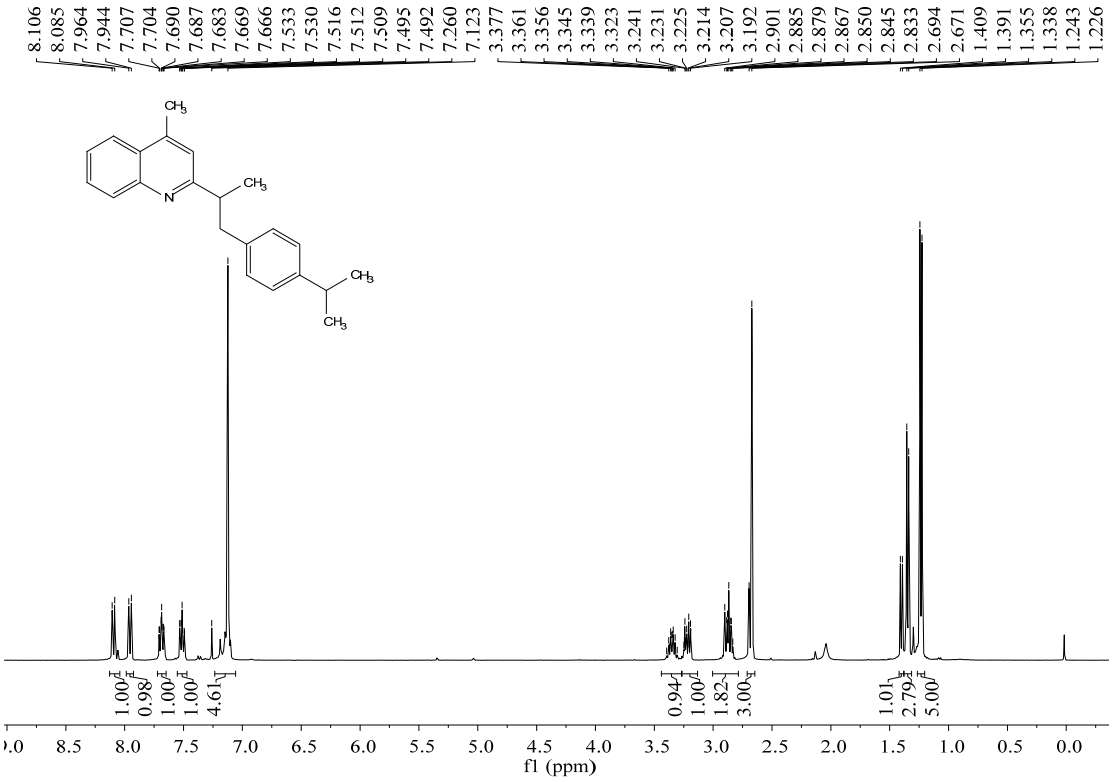
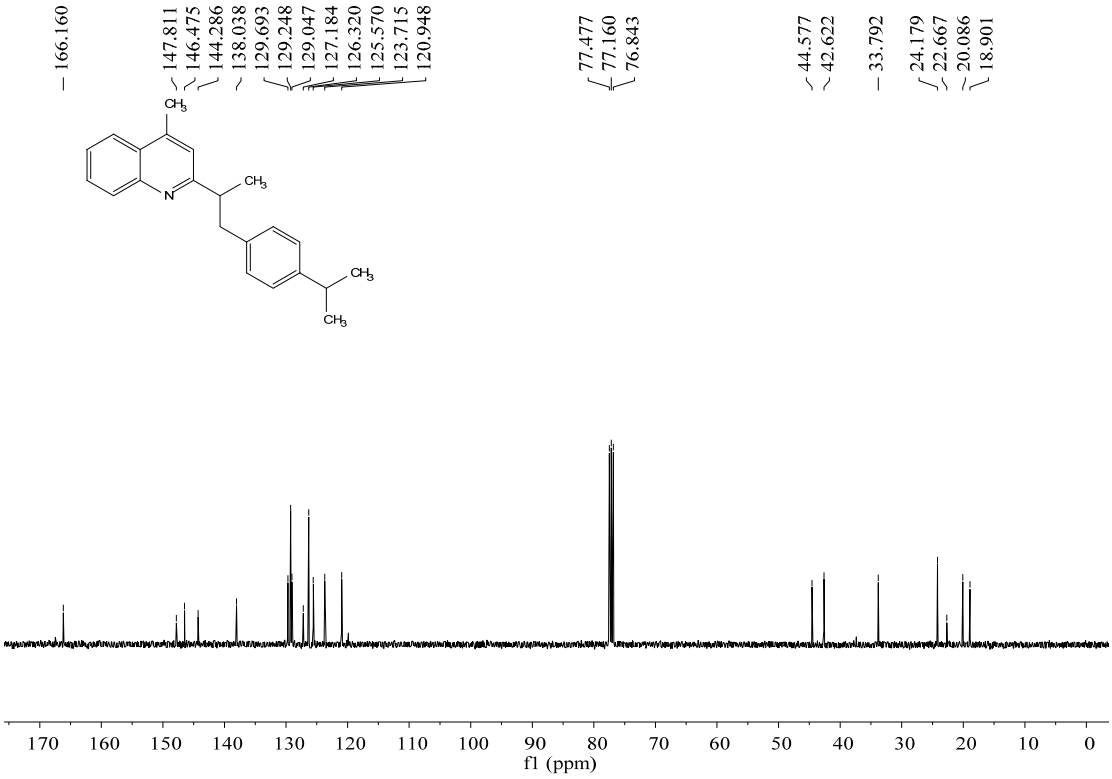


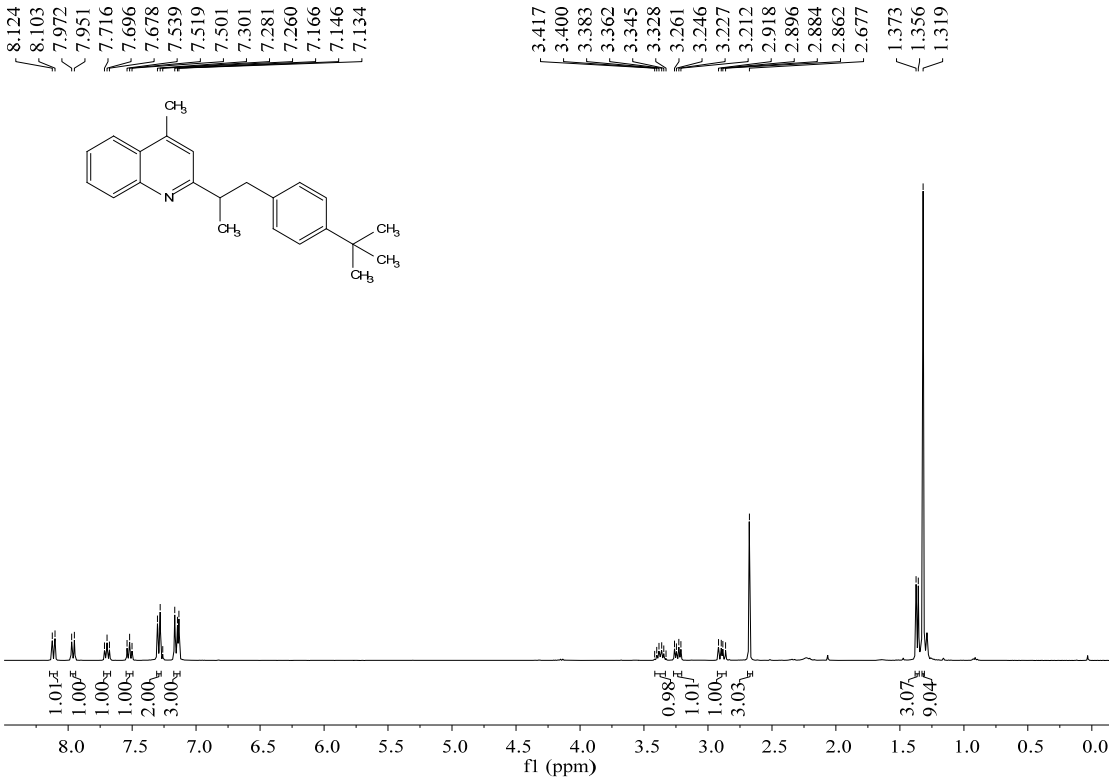


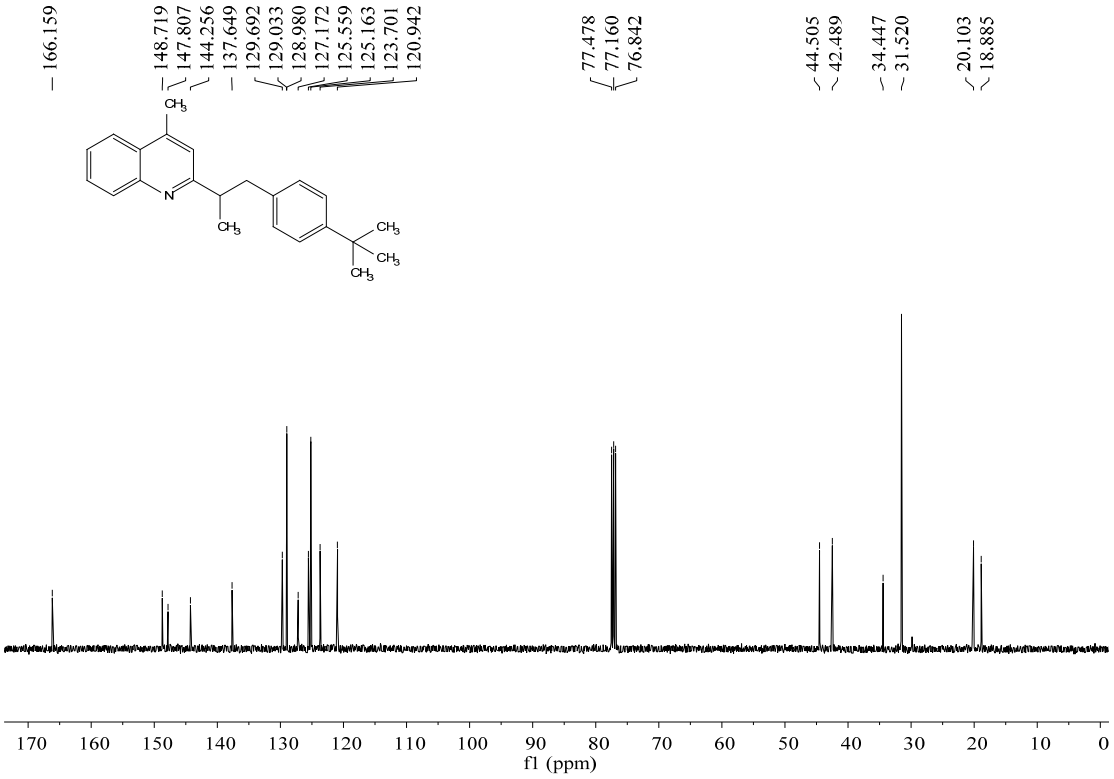
^{1}H and ^{13}C NMR spectra of 3i



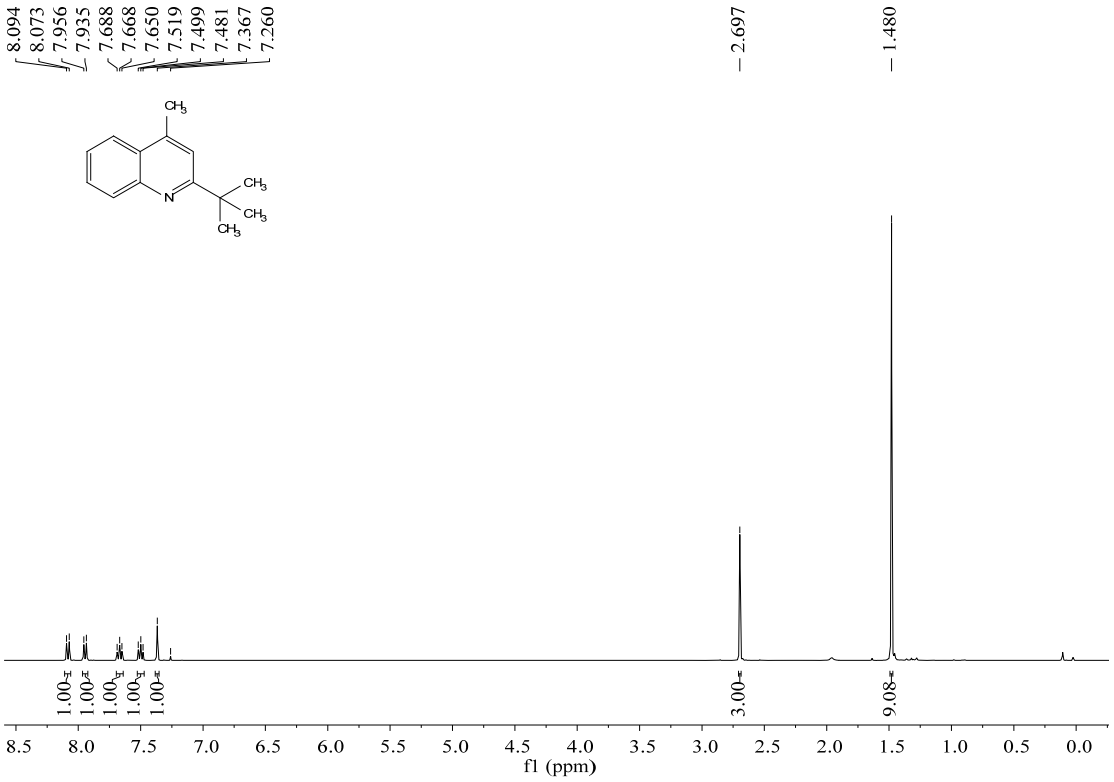


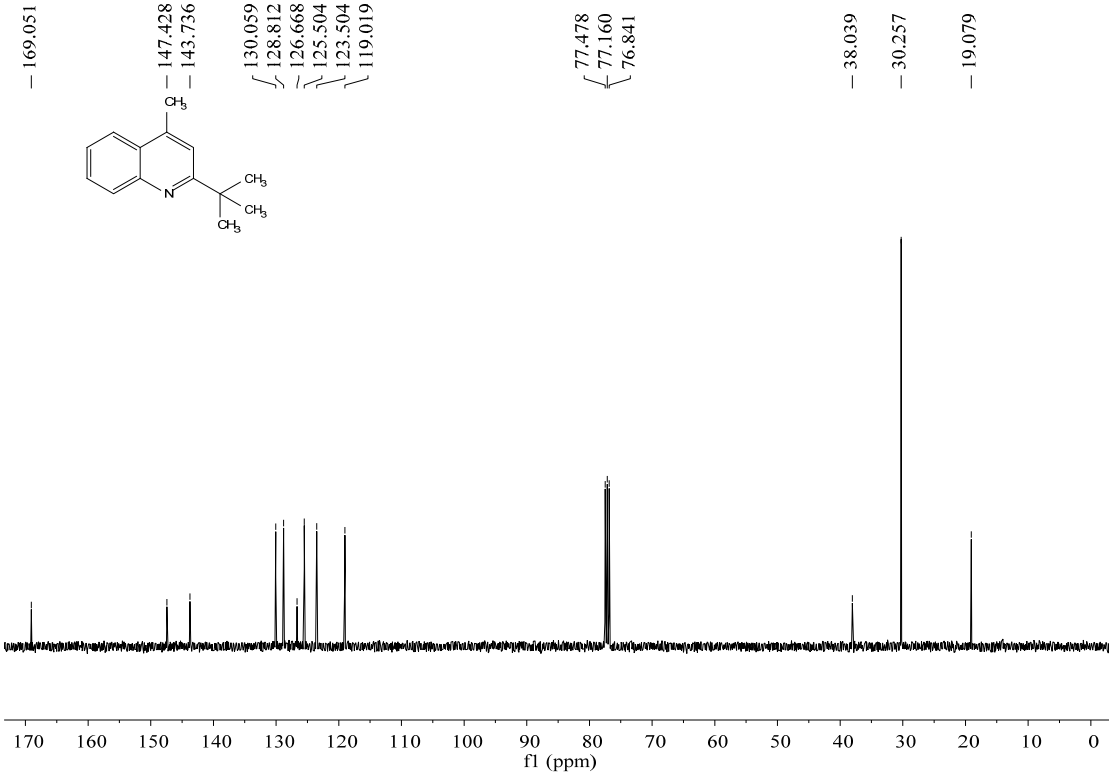
^{1}H and ^{13}C NMR spectra of 3j



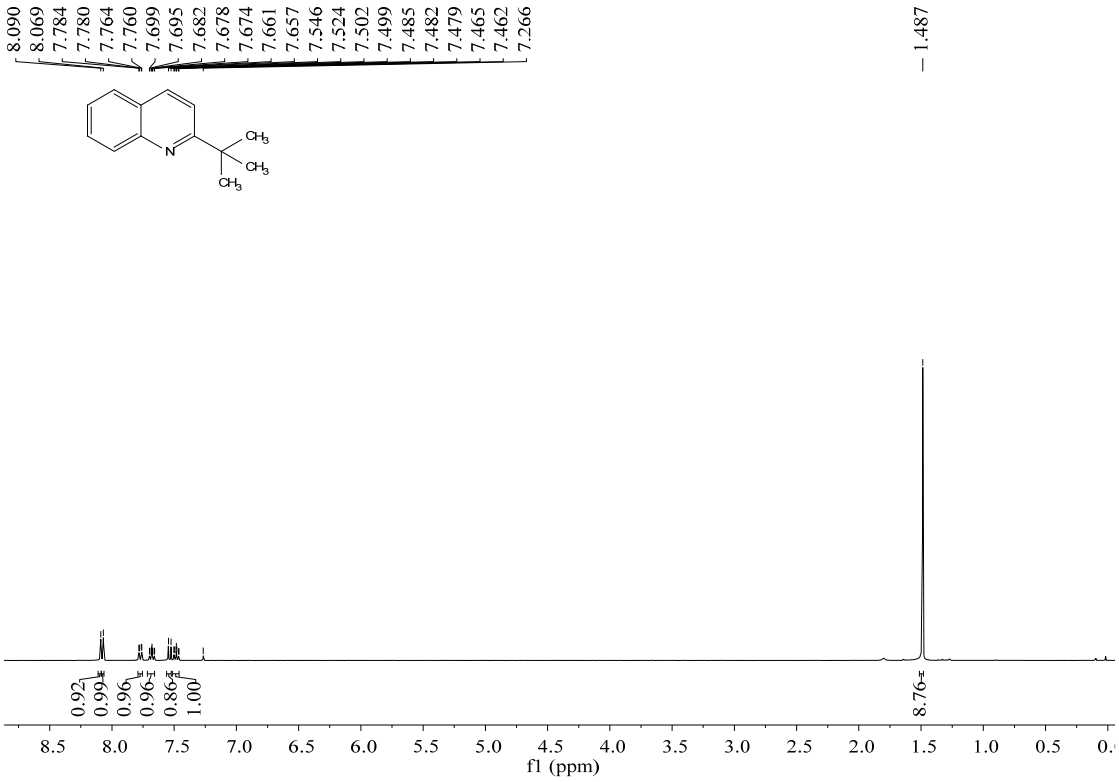


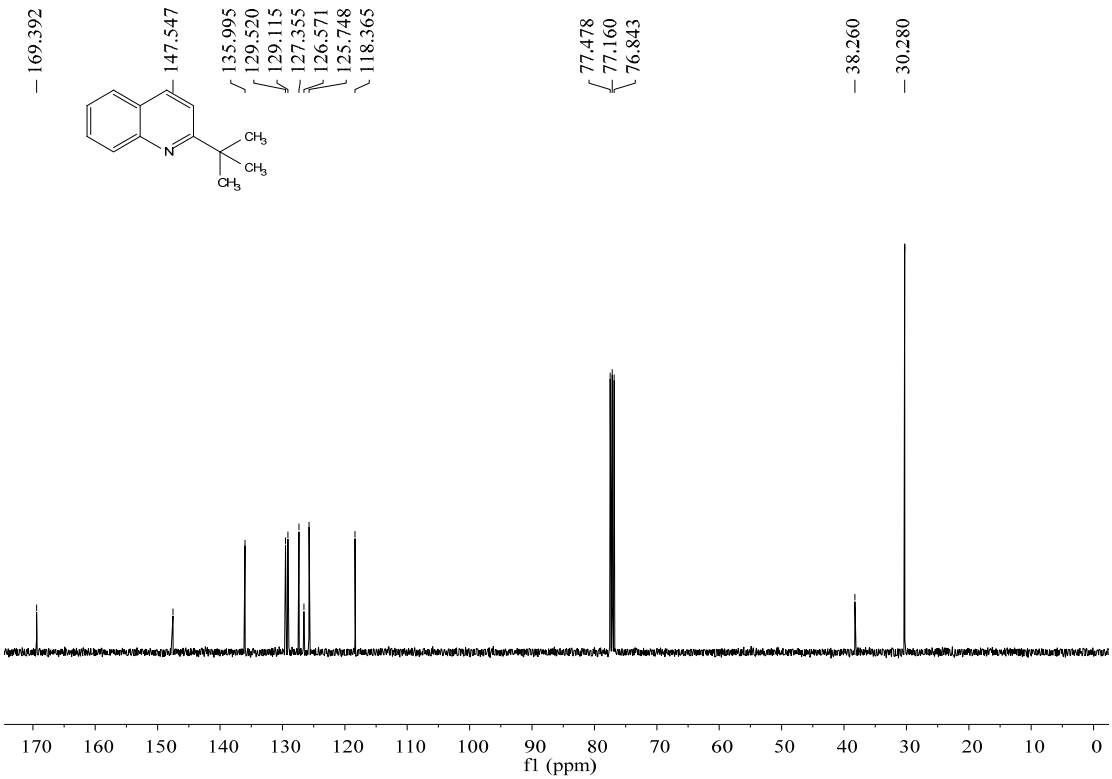
^{1}H and ^{13}C NMR spectra of 3k





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





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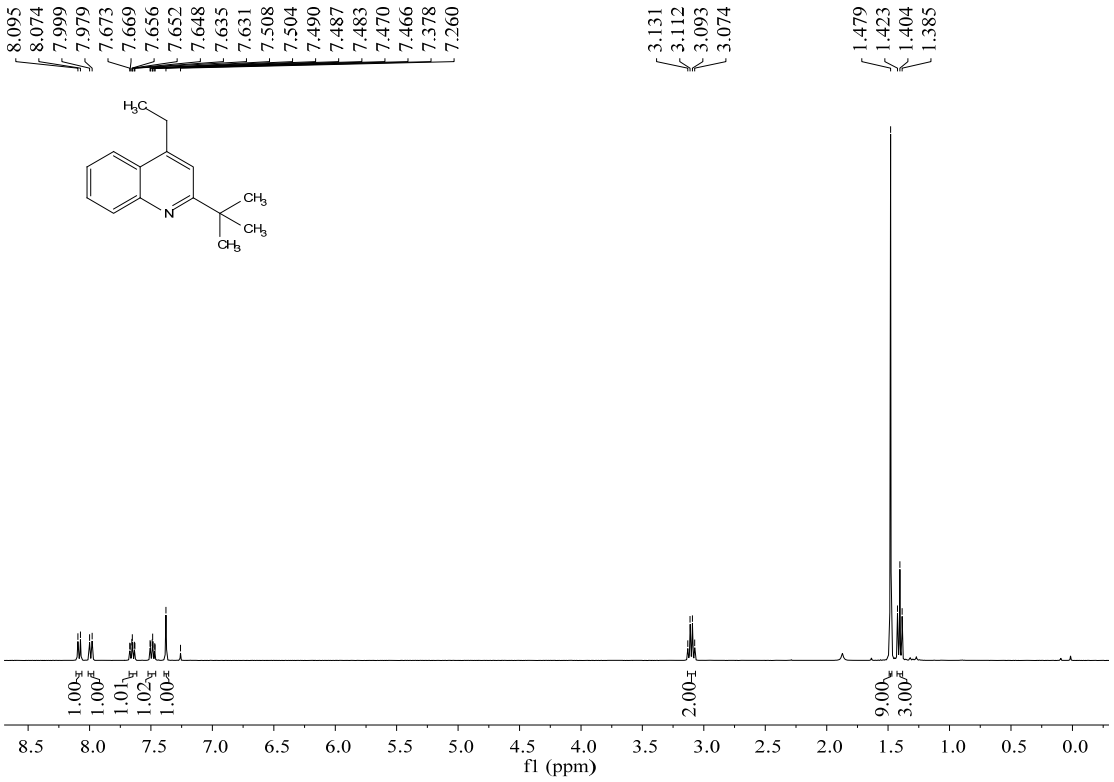
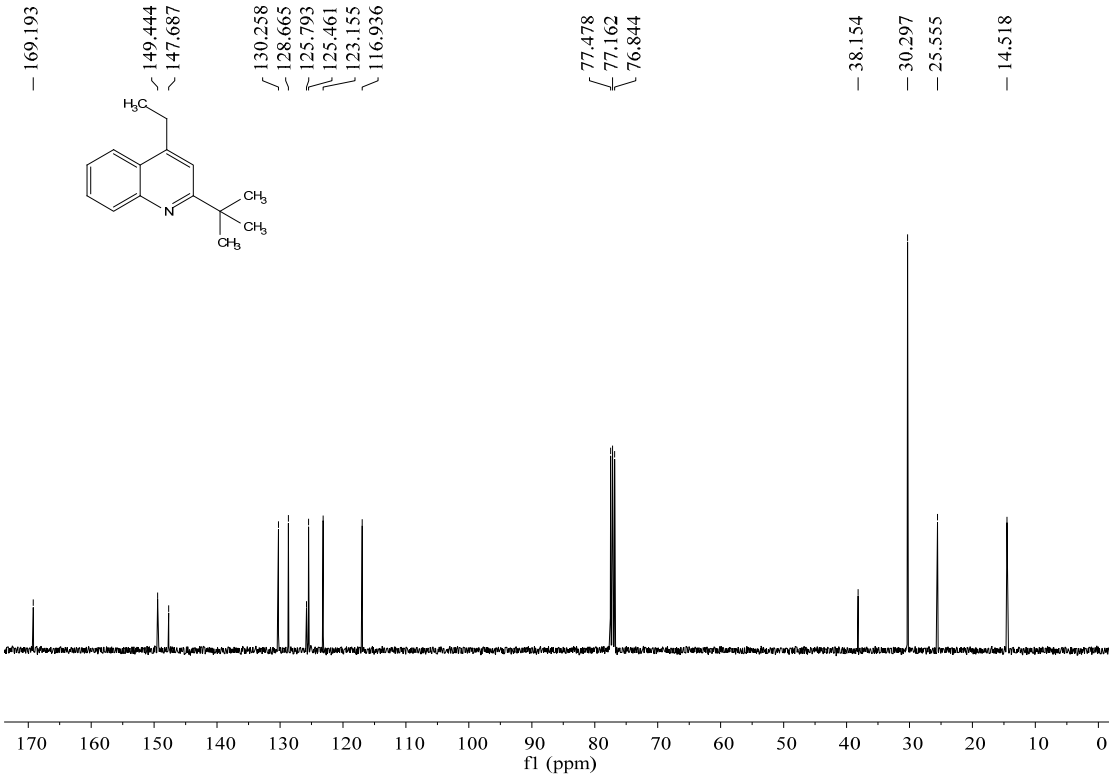
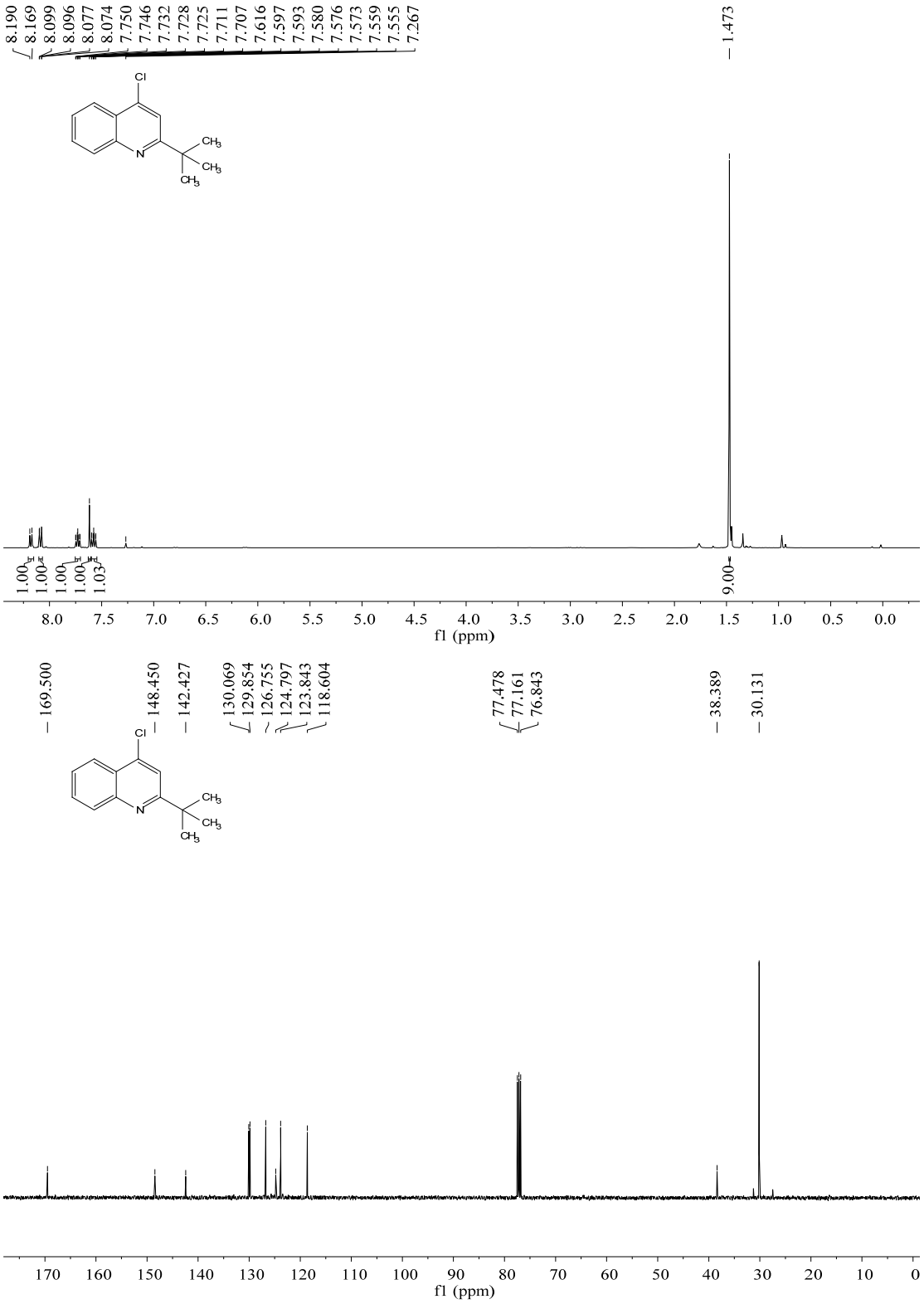
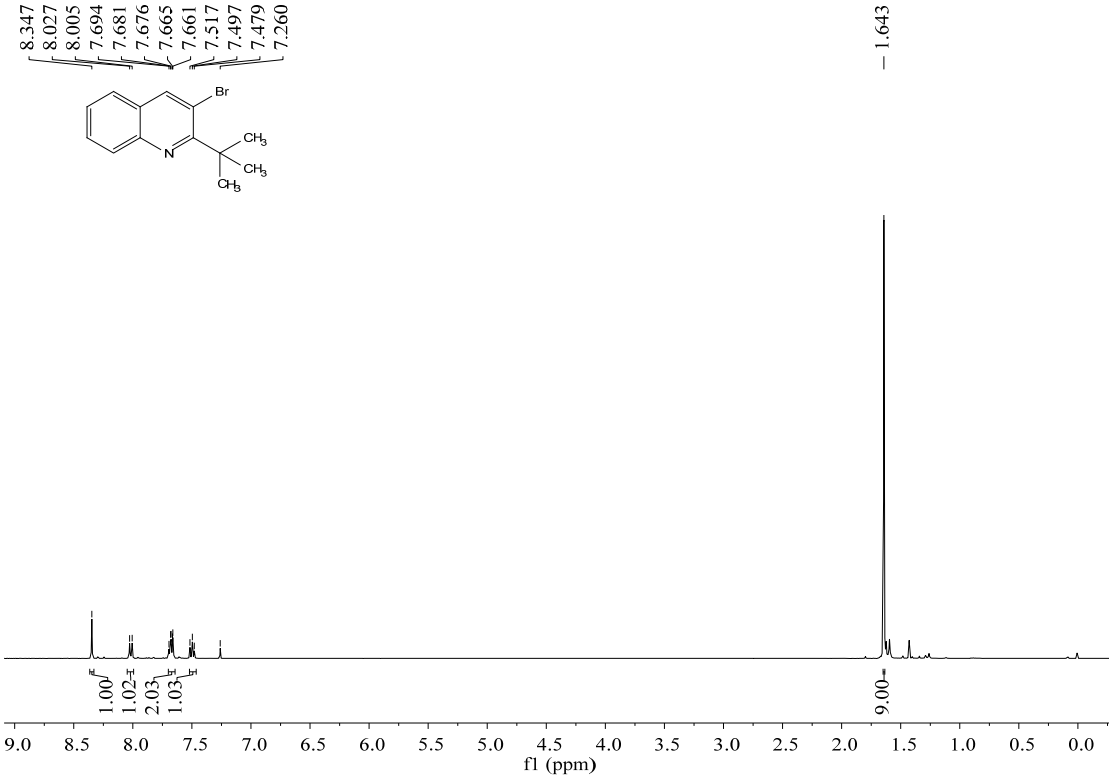


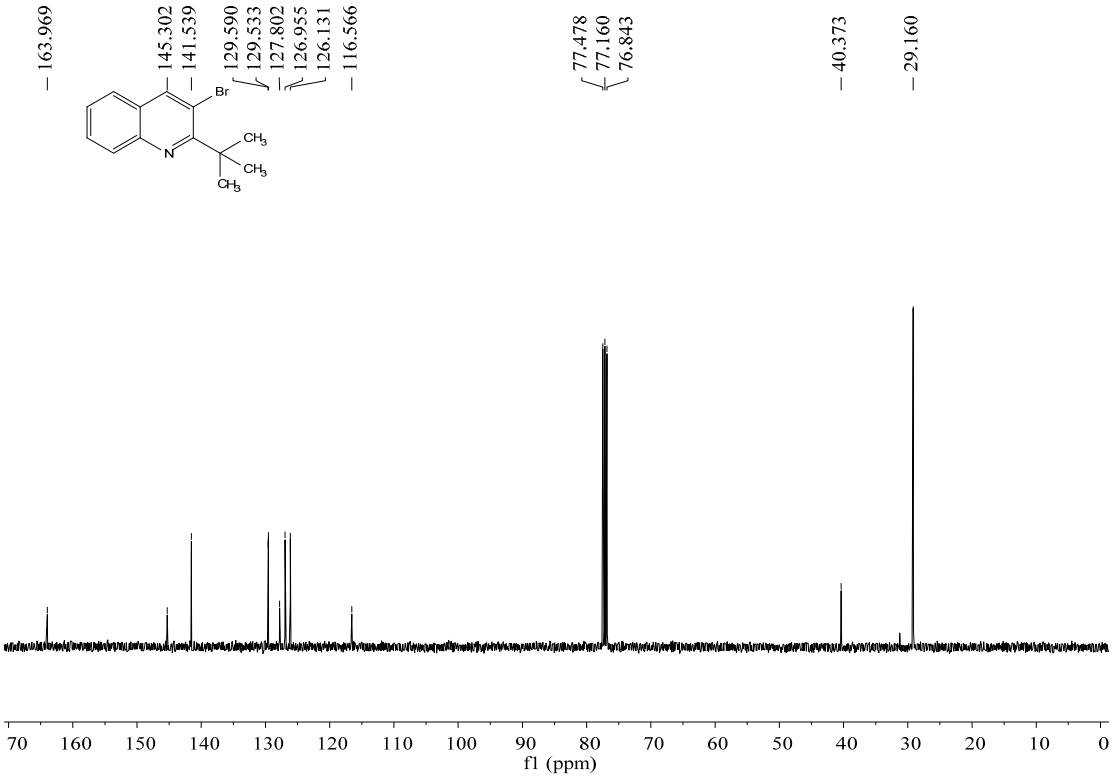


^{1}H and ^{13}C NMR spectra of 4c

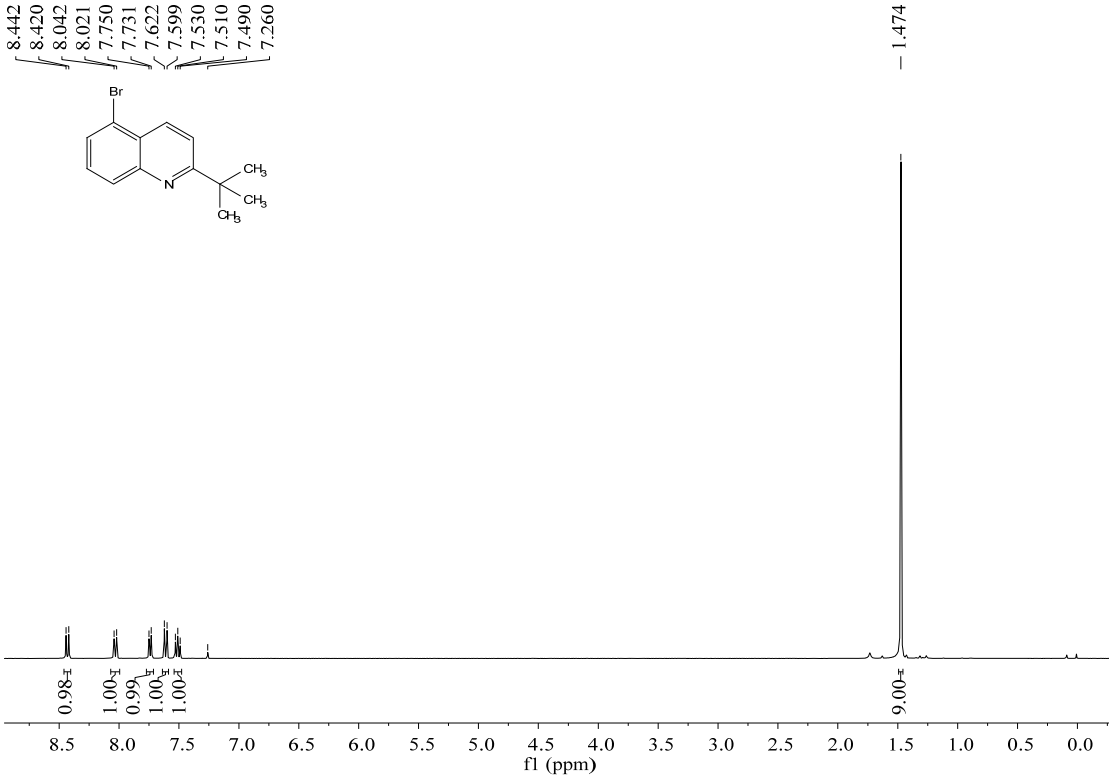


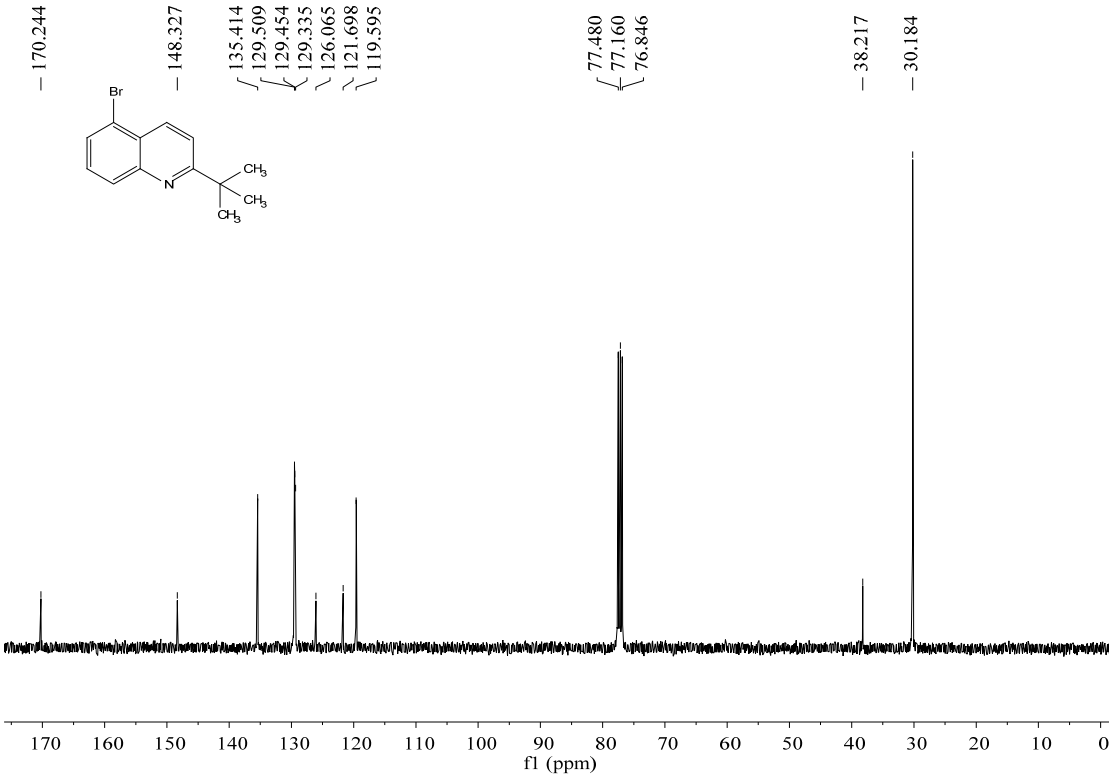
^{1}H and ^{13}C NMR spectra of 4d



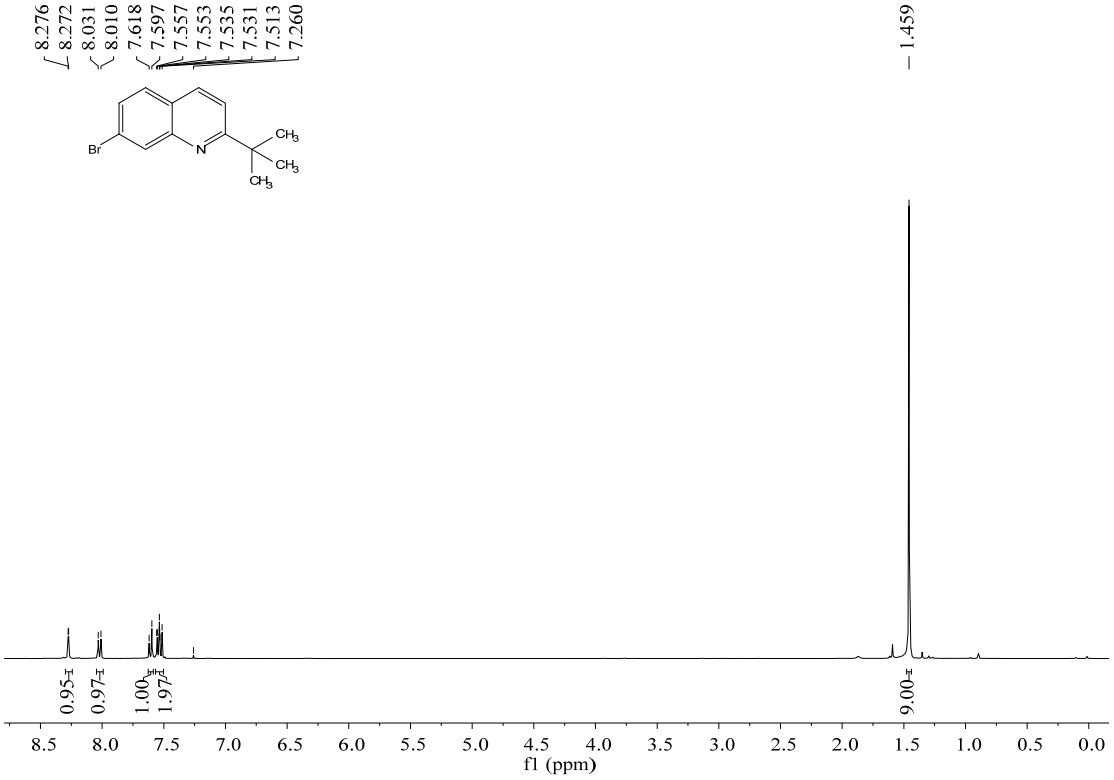


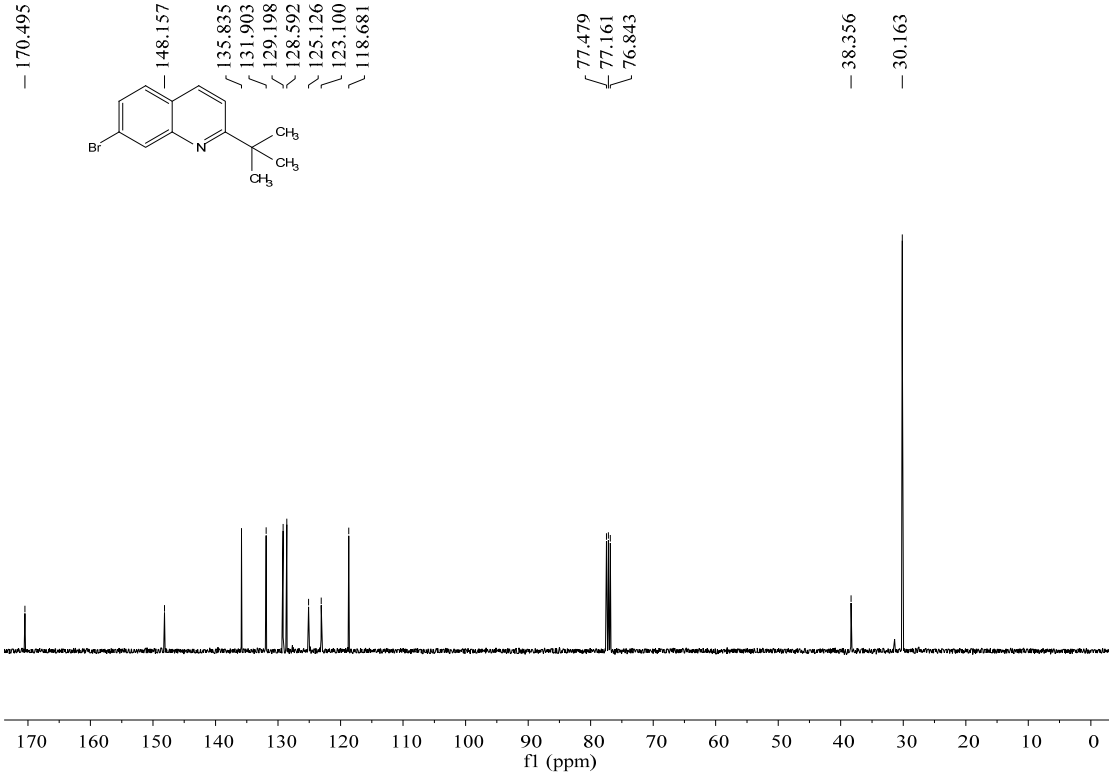
^{1}H and ^{13}C NMR spectra of 4e



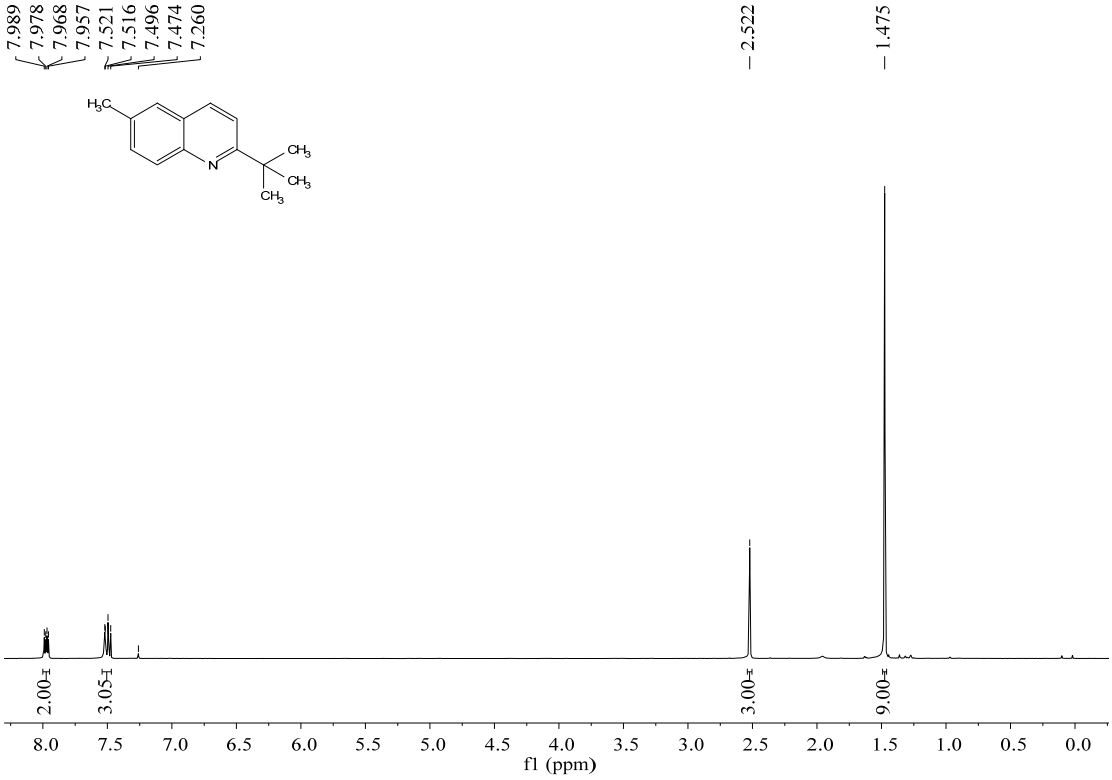


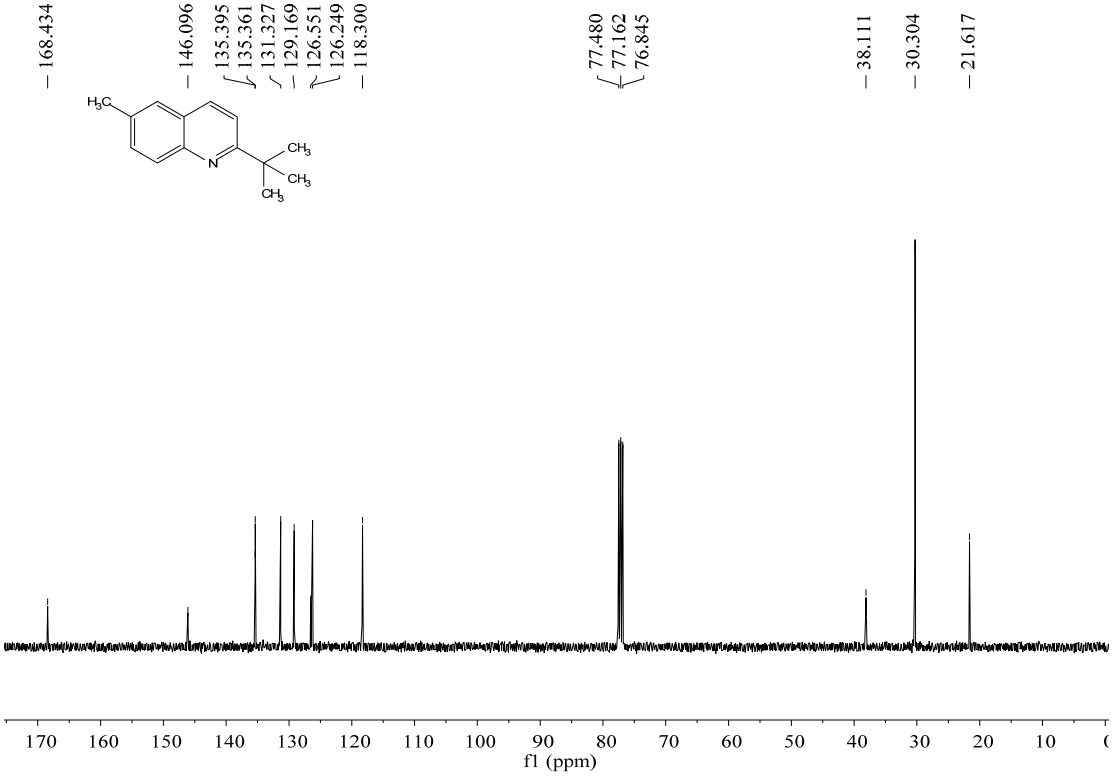
^{1}H and ^{13}C NMR spectra of 4f



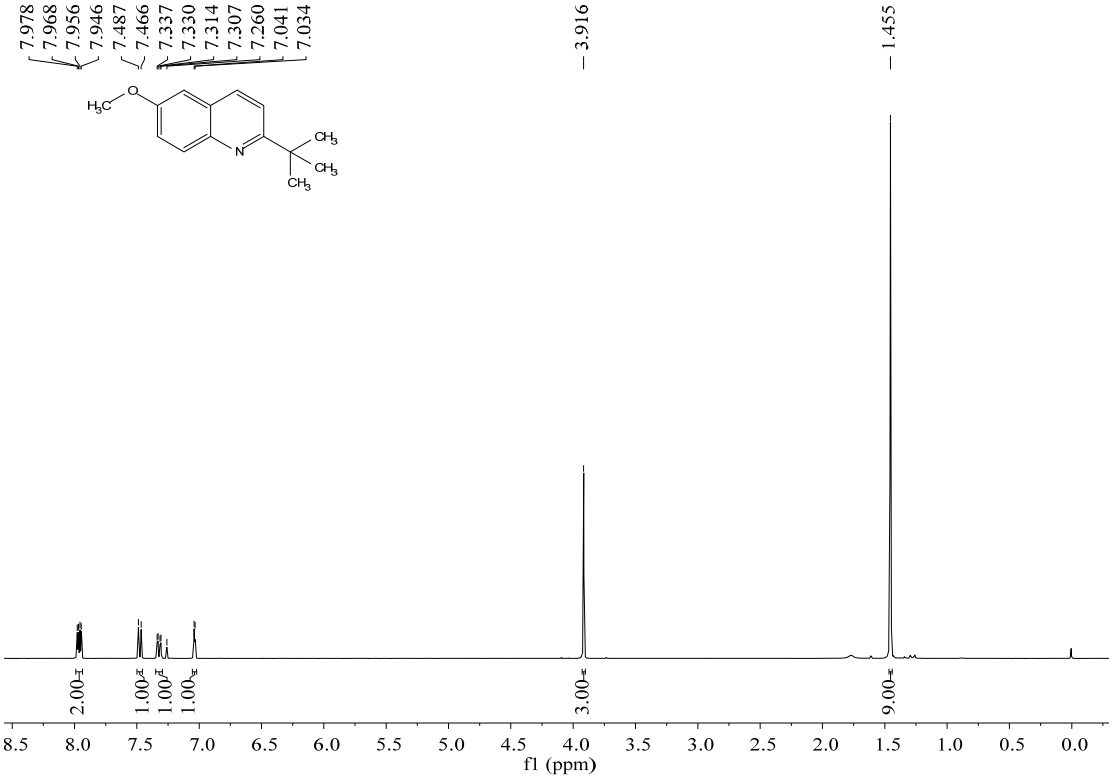


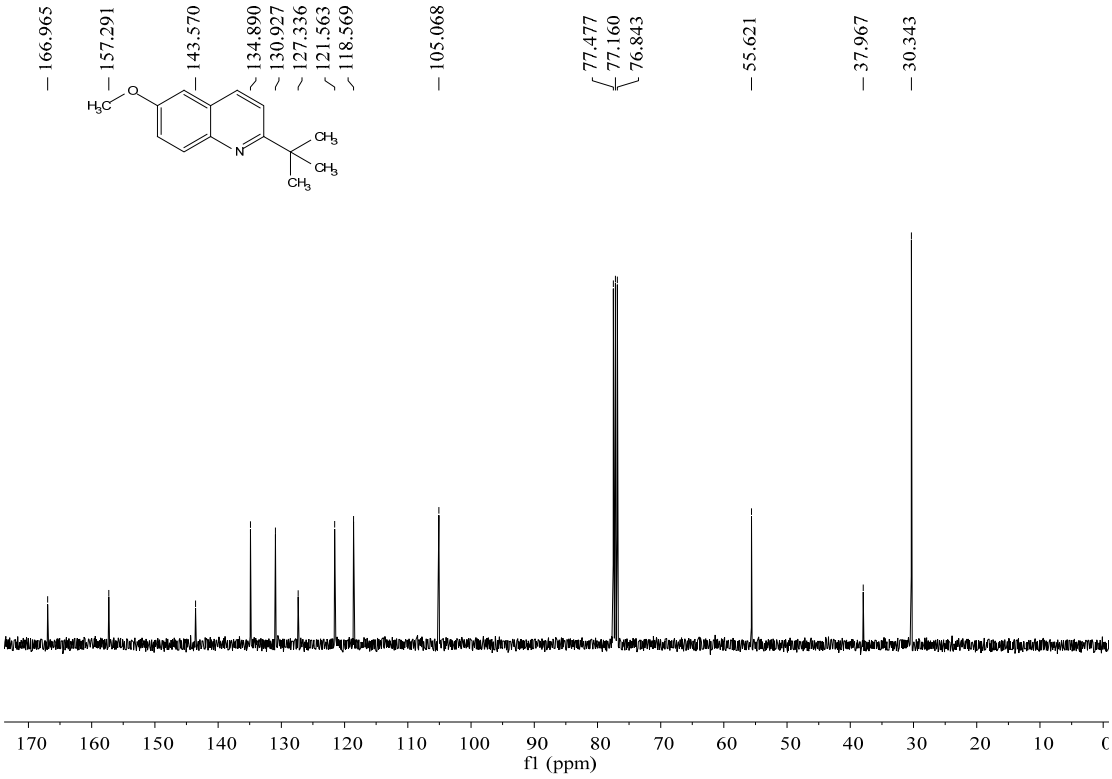
^{1}H and ^{13}C NMR spectra of 4g



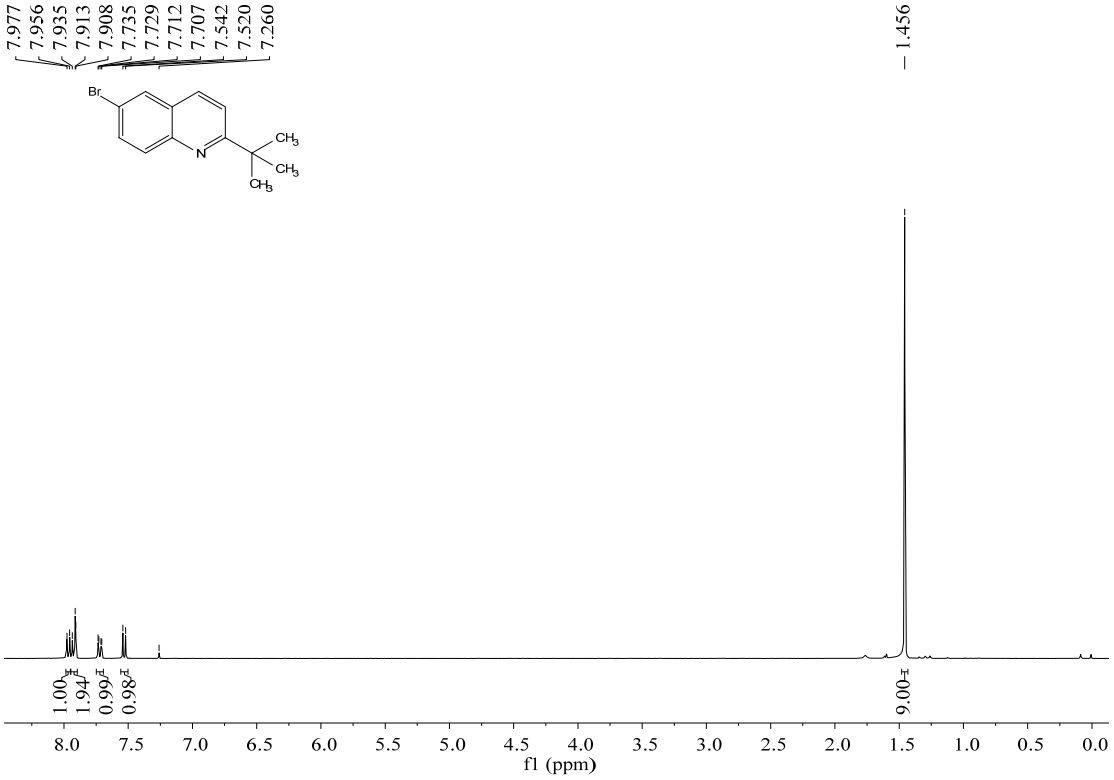


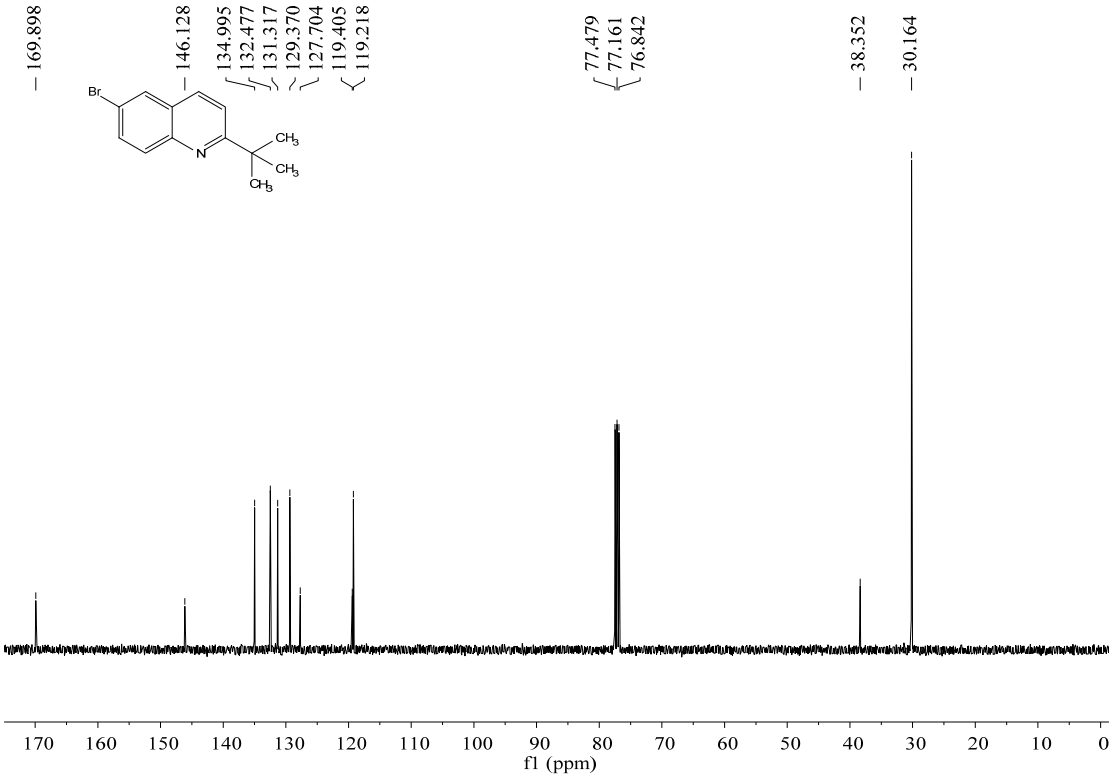
^{1}H and ^{13}C NMR spectra of 4h





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





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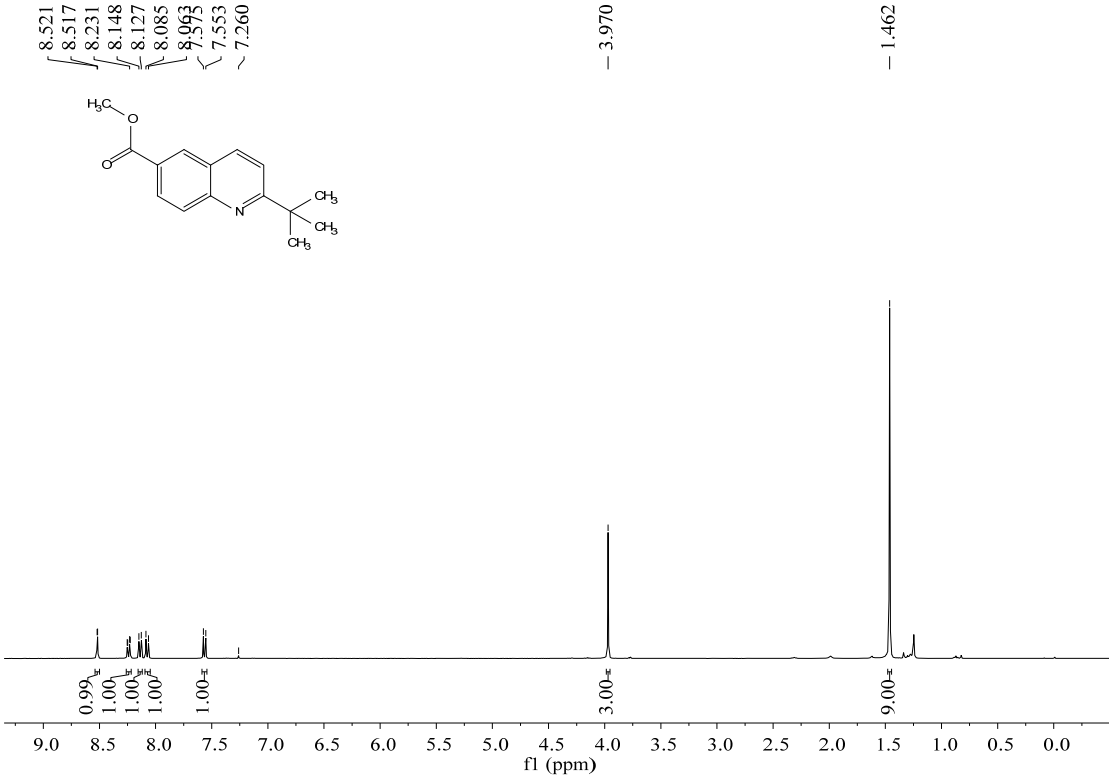
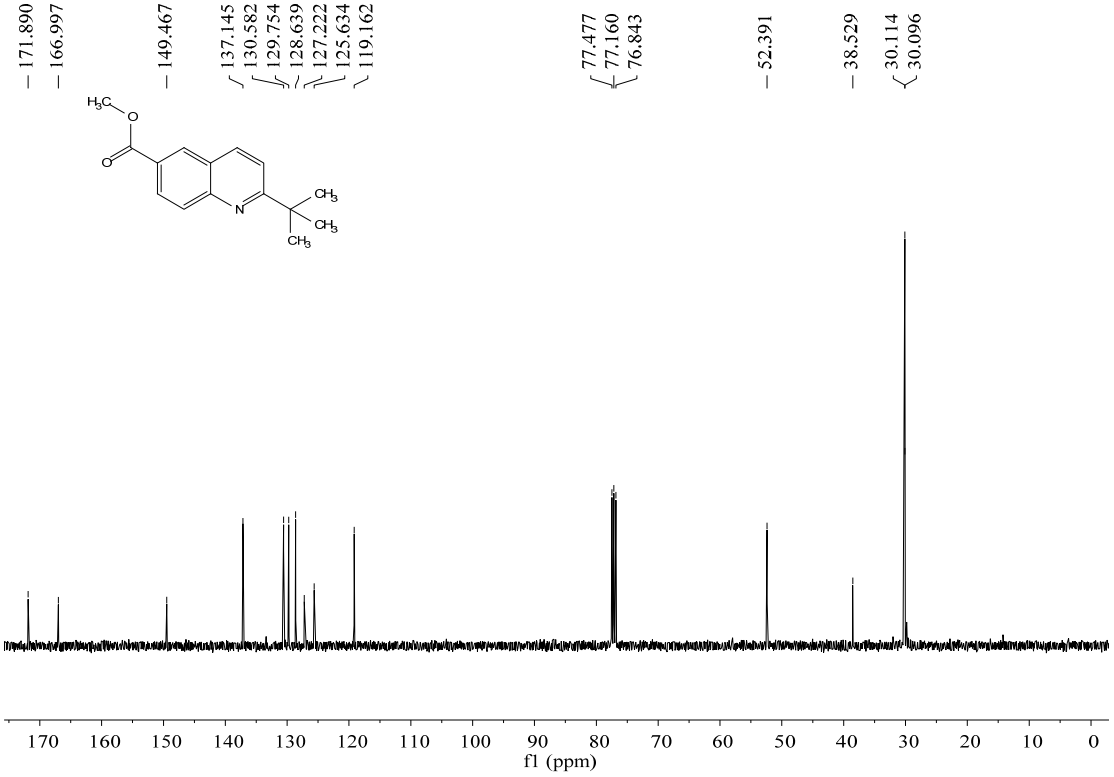
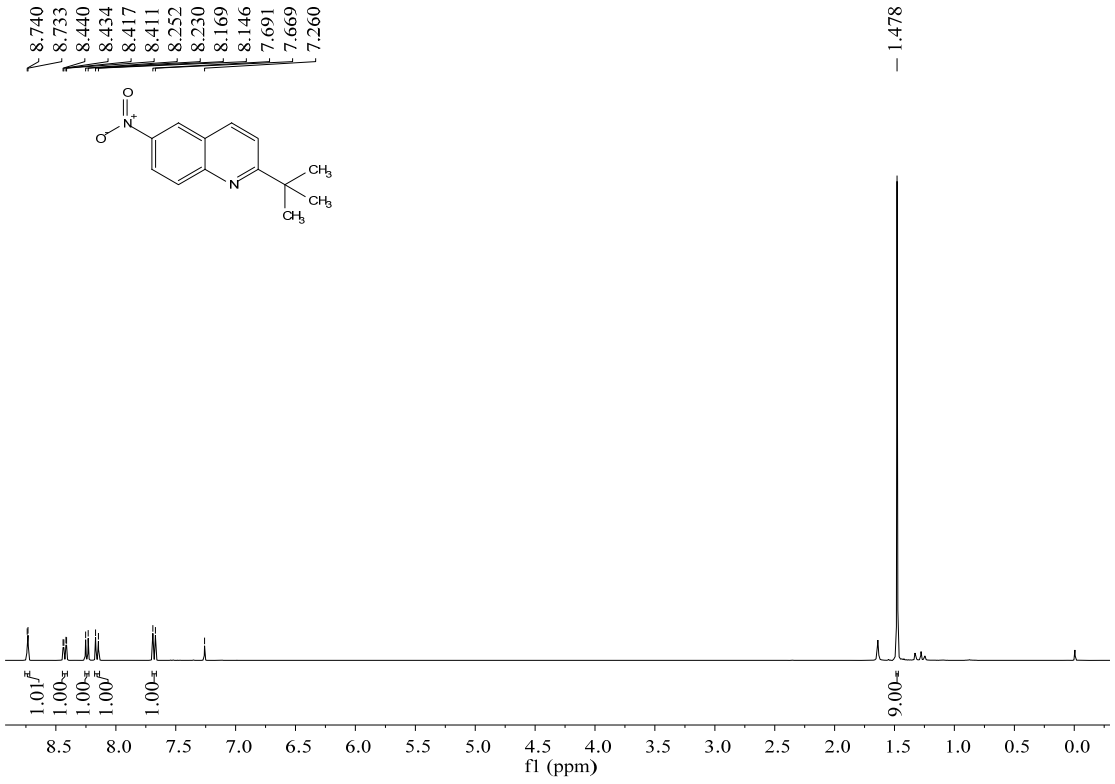
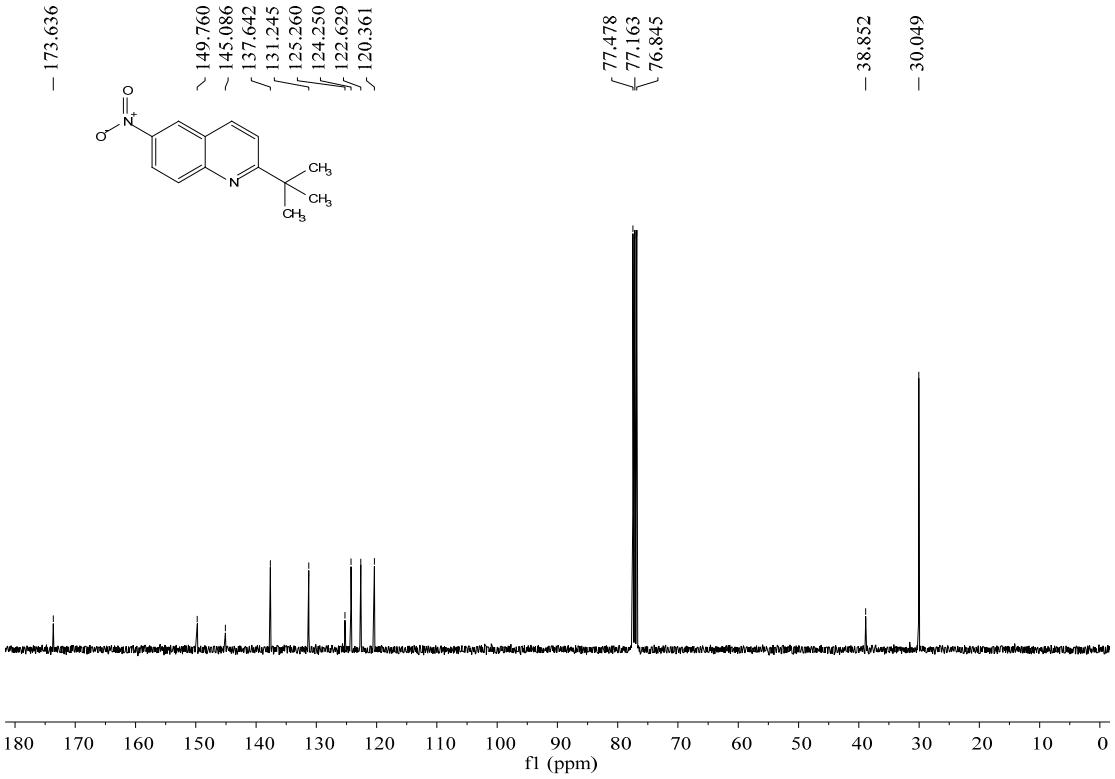


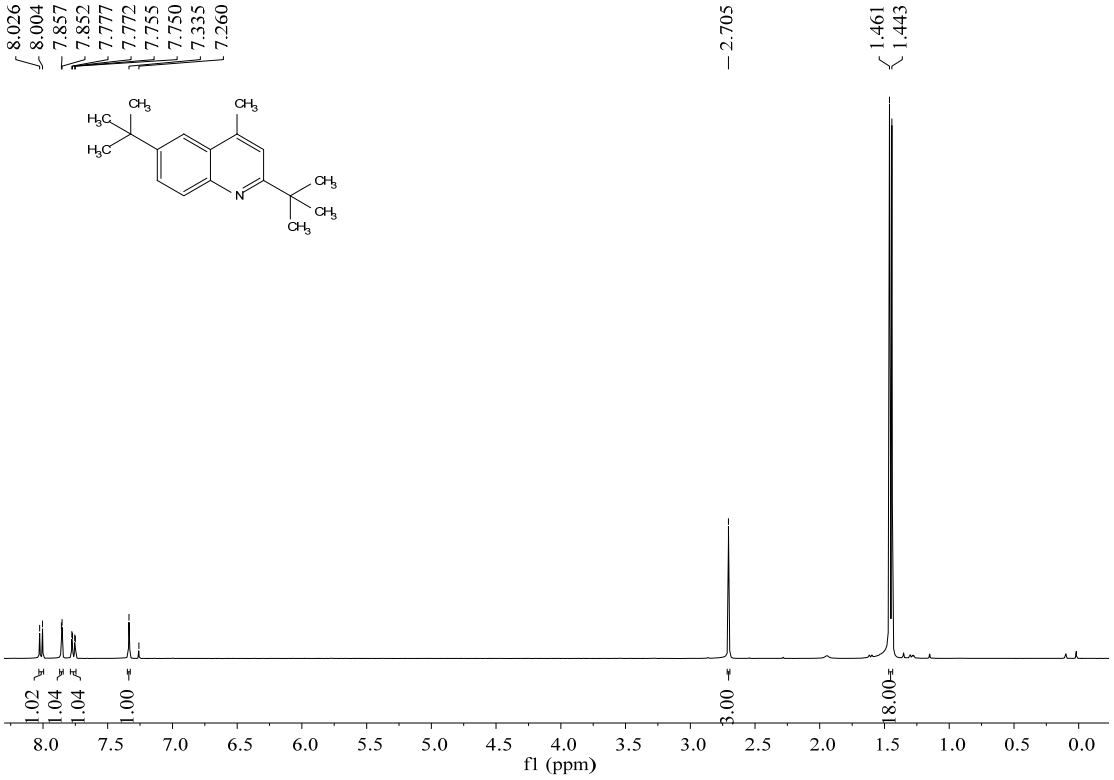


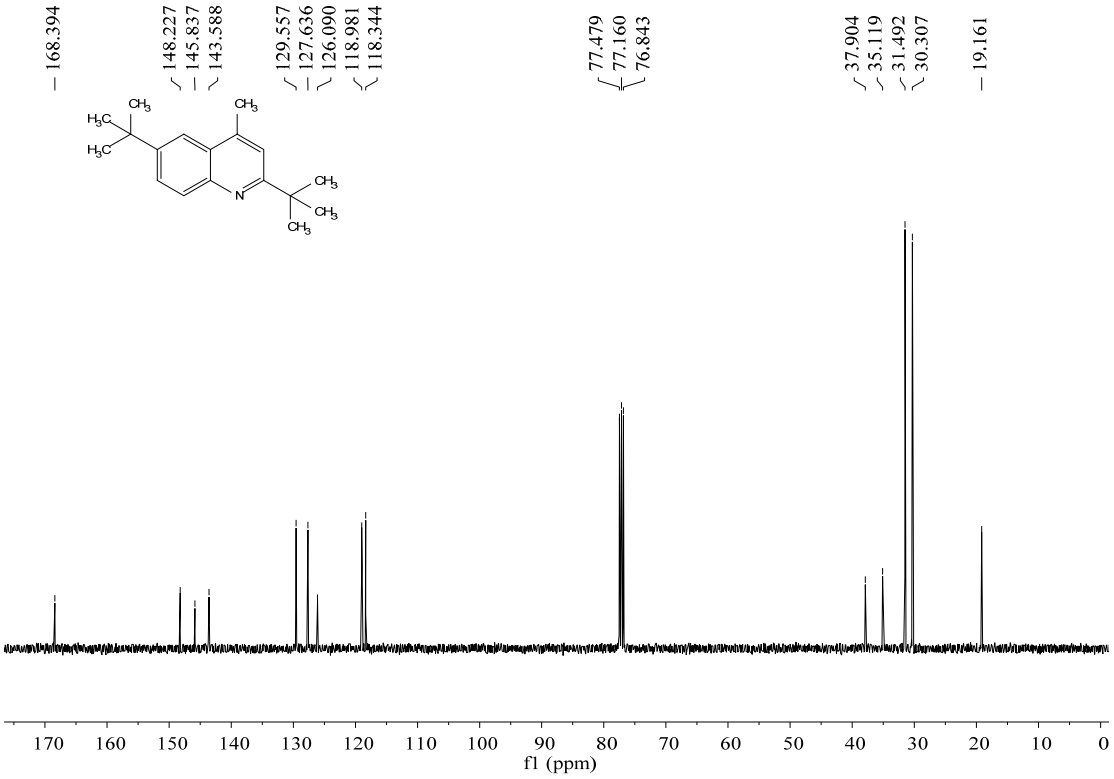
^{1}H and ^{13}C NMR spectra of 4k



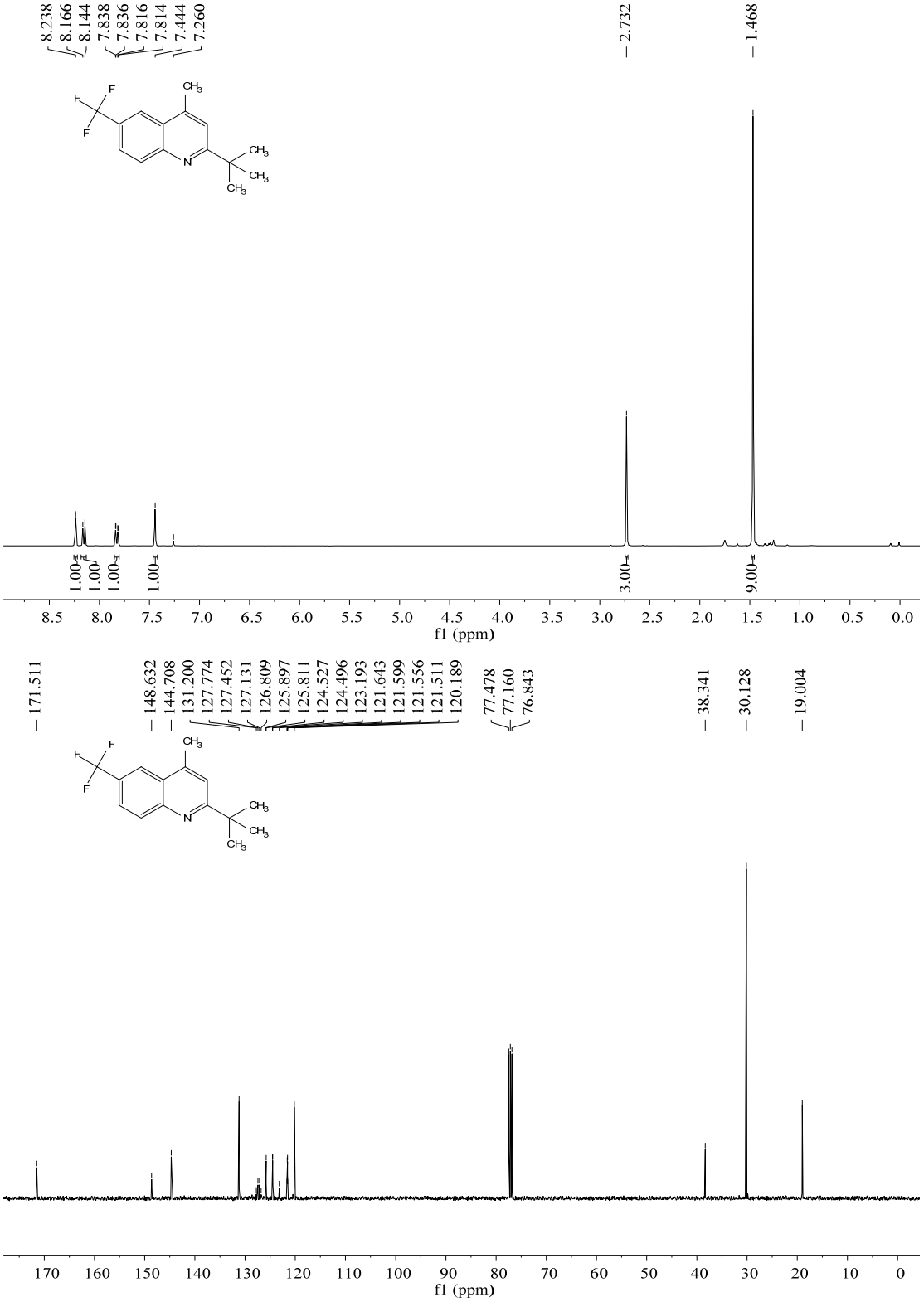


^{1}H and ^{13}C NMR spectra of 4l

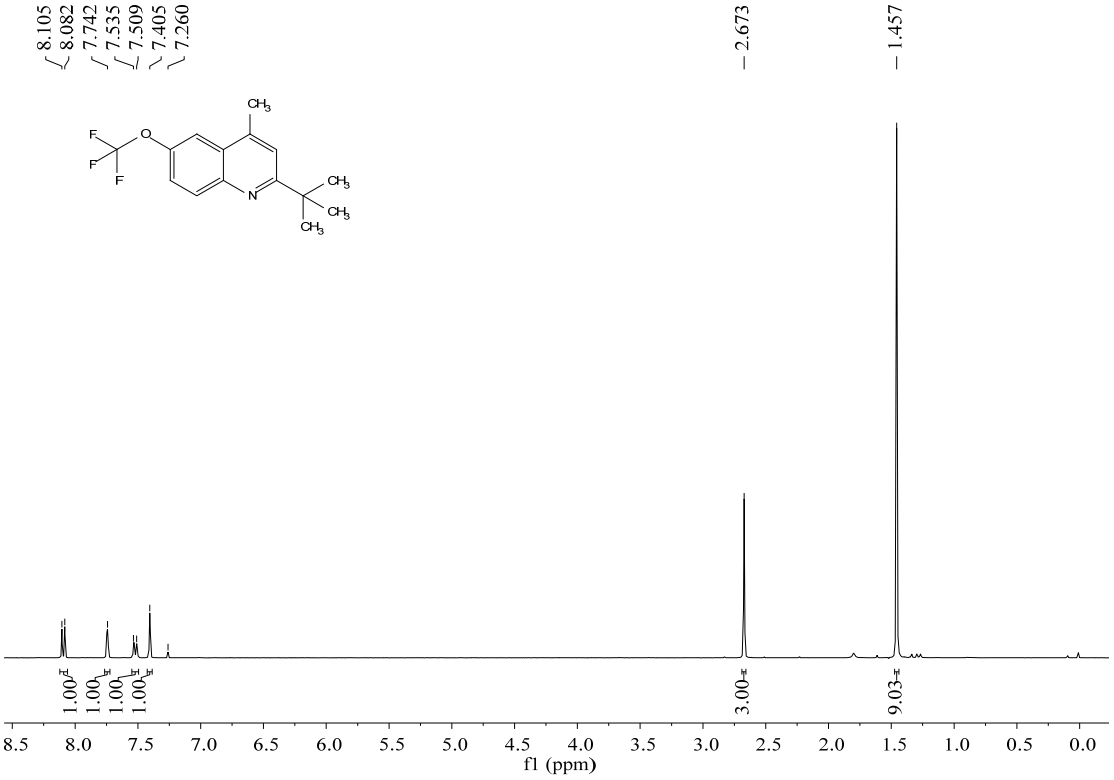


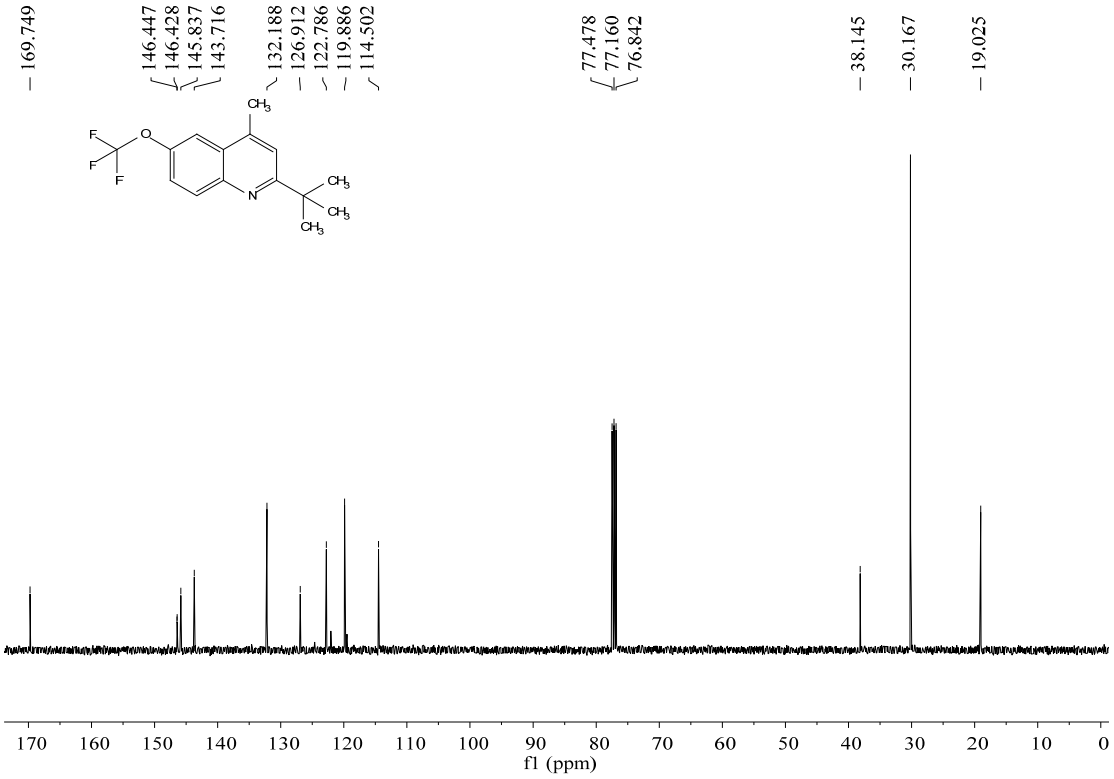


^{1}H and ^{13}C NMR spectra of 4m

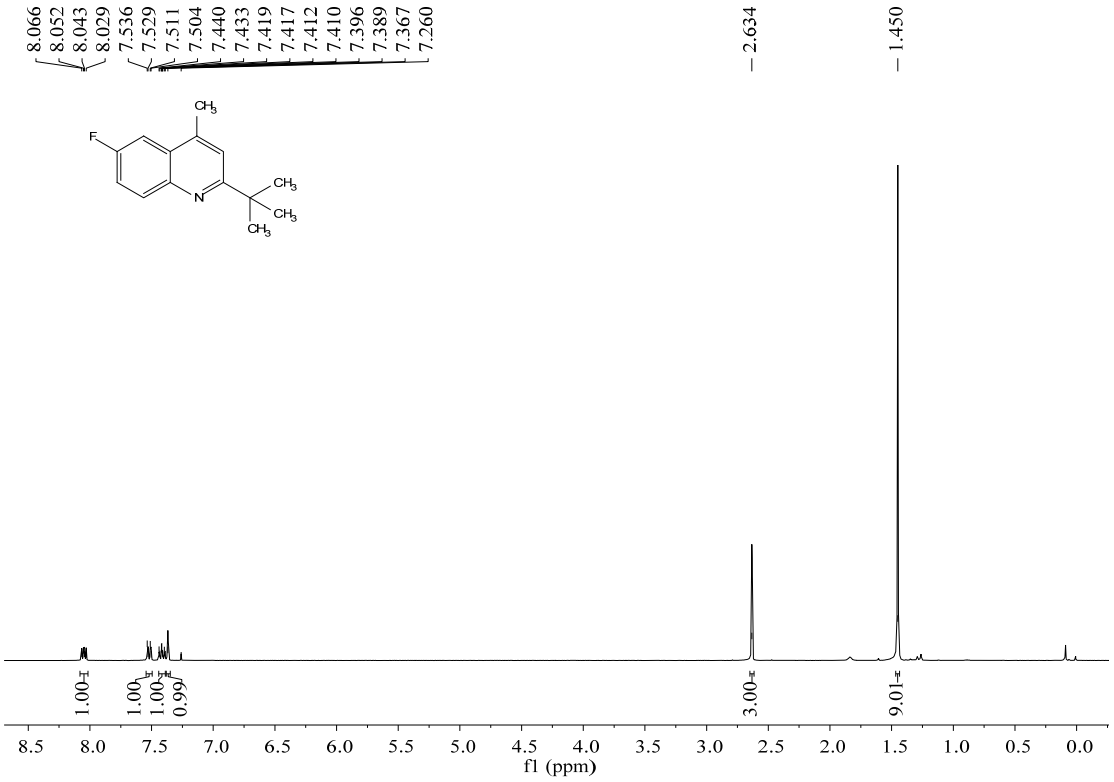


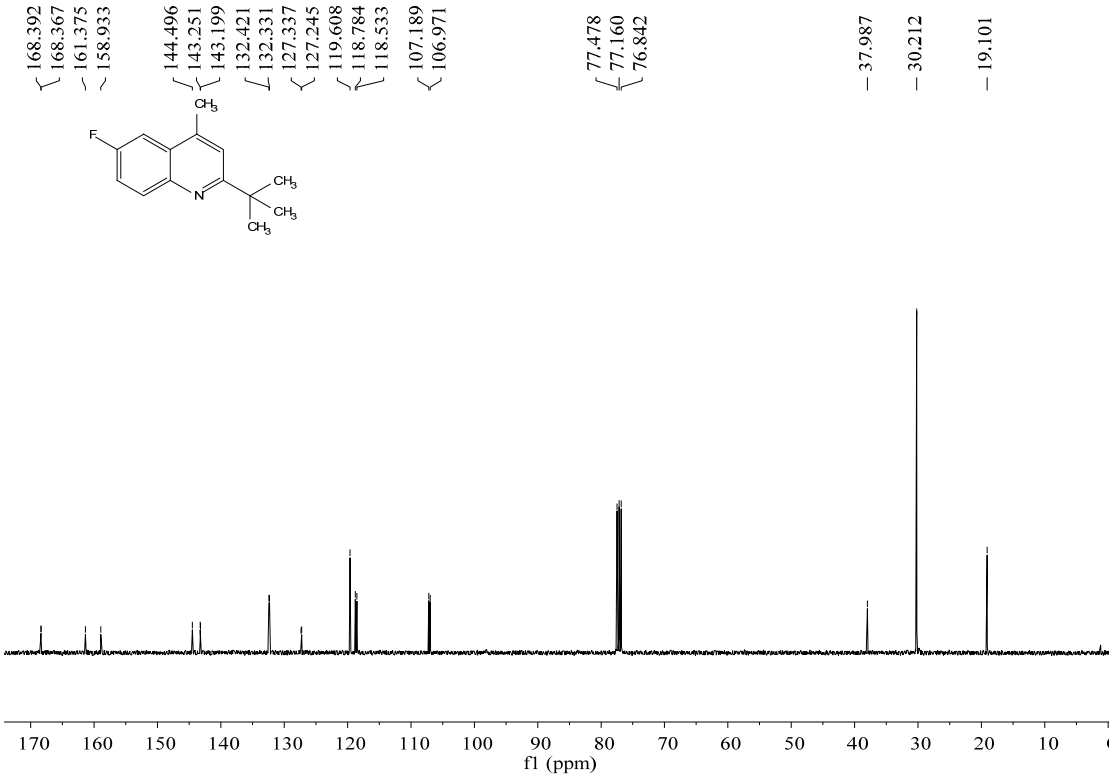
^{1}H and ^{13}C NMR spectra of 4n



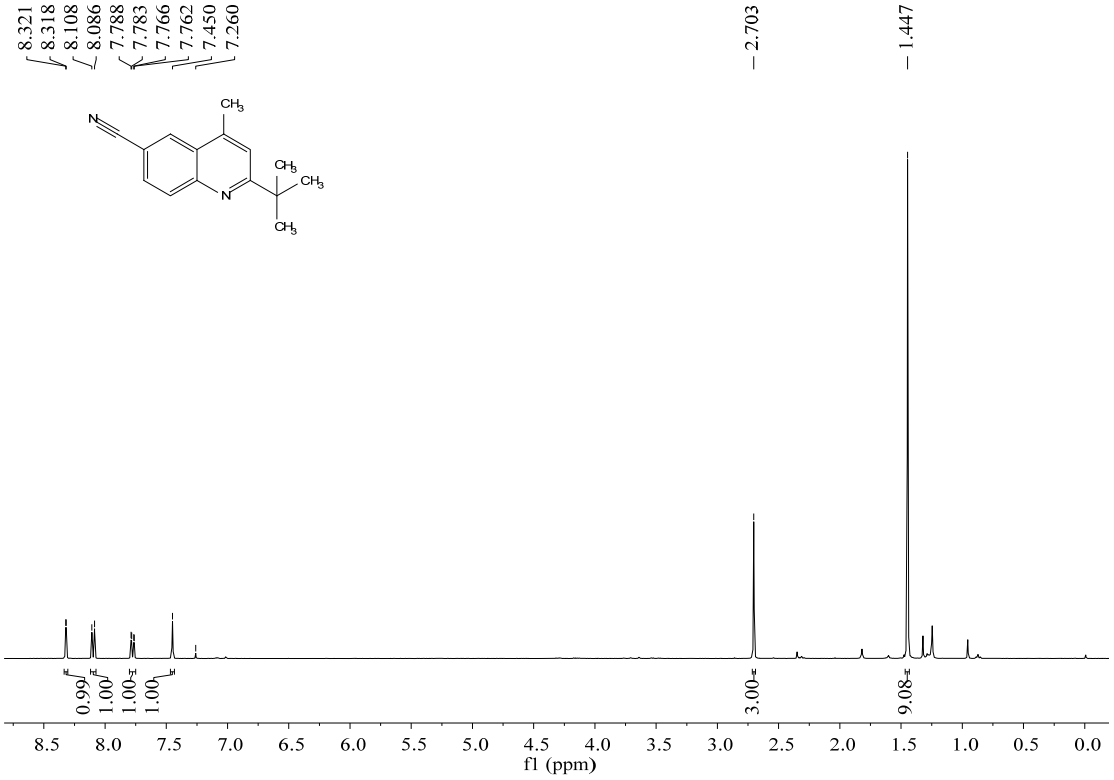


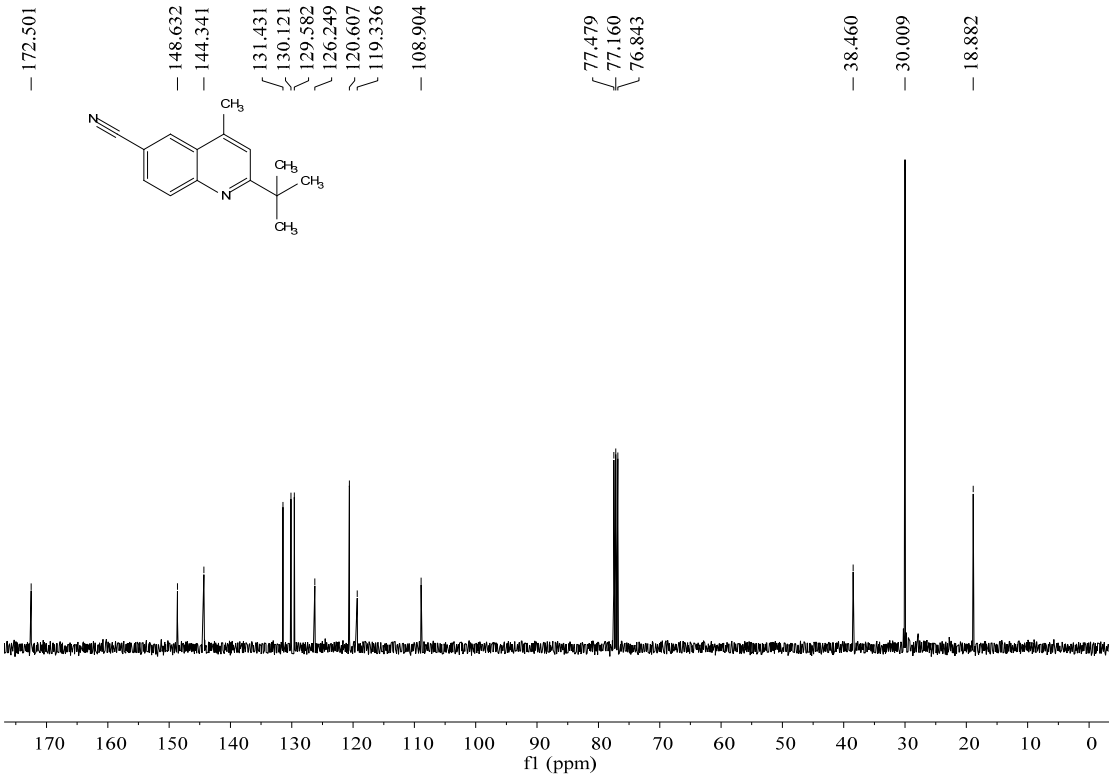
^{1}H and ^{13}C NMR spectra of 4o



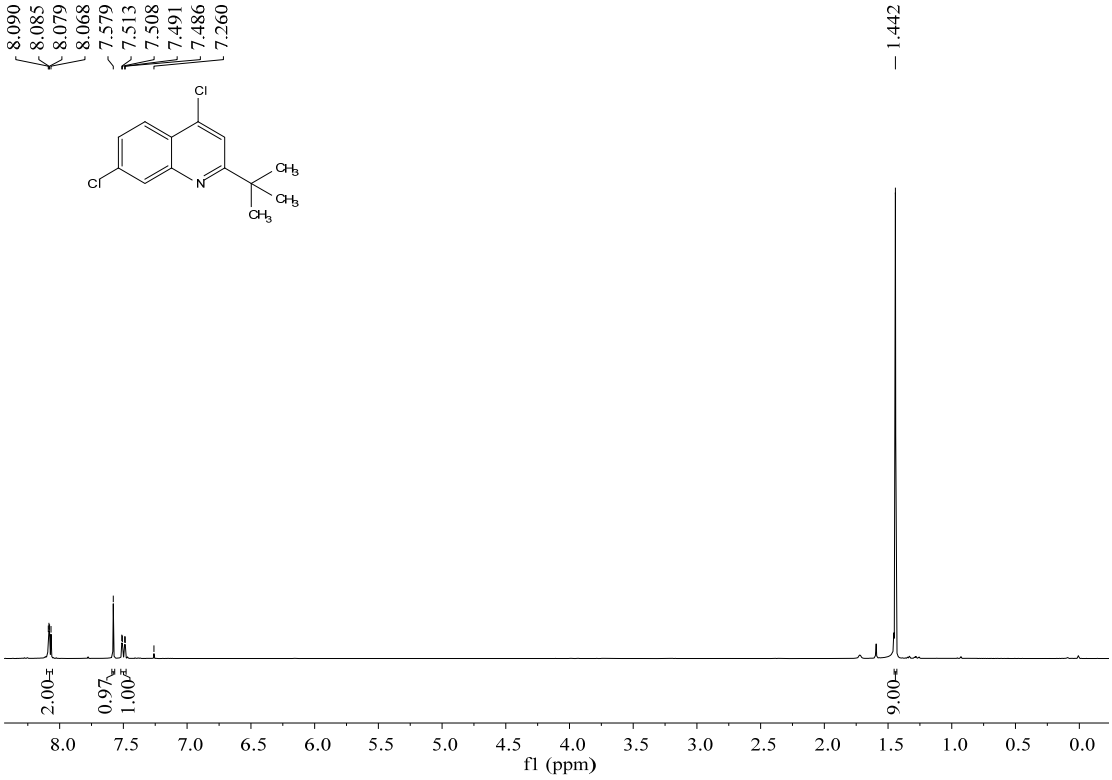


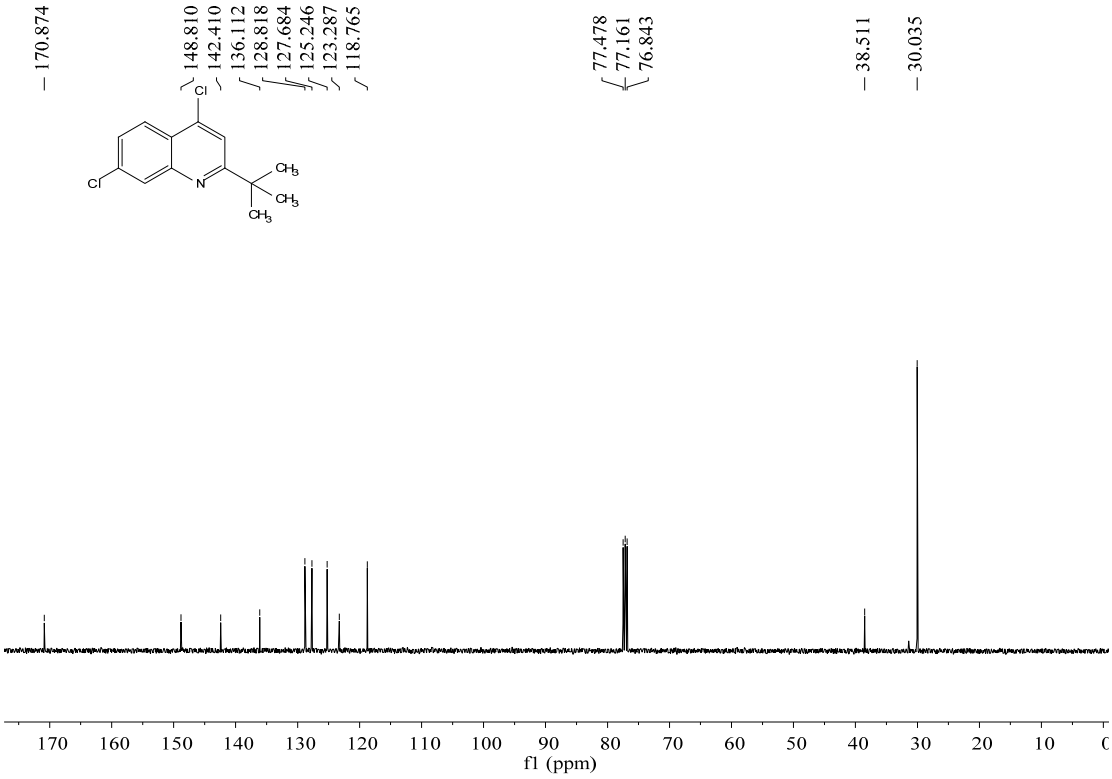
^{1}H and ^{13}C NMR spectra of 4p



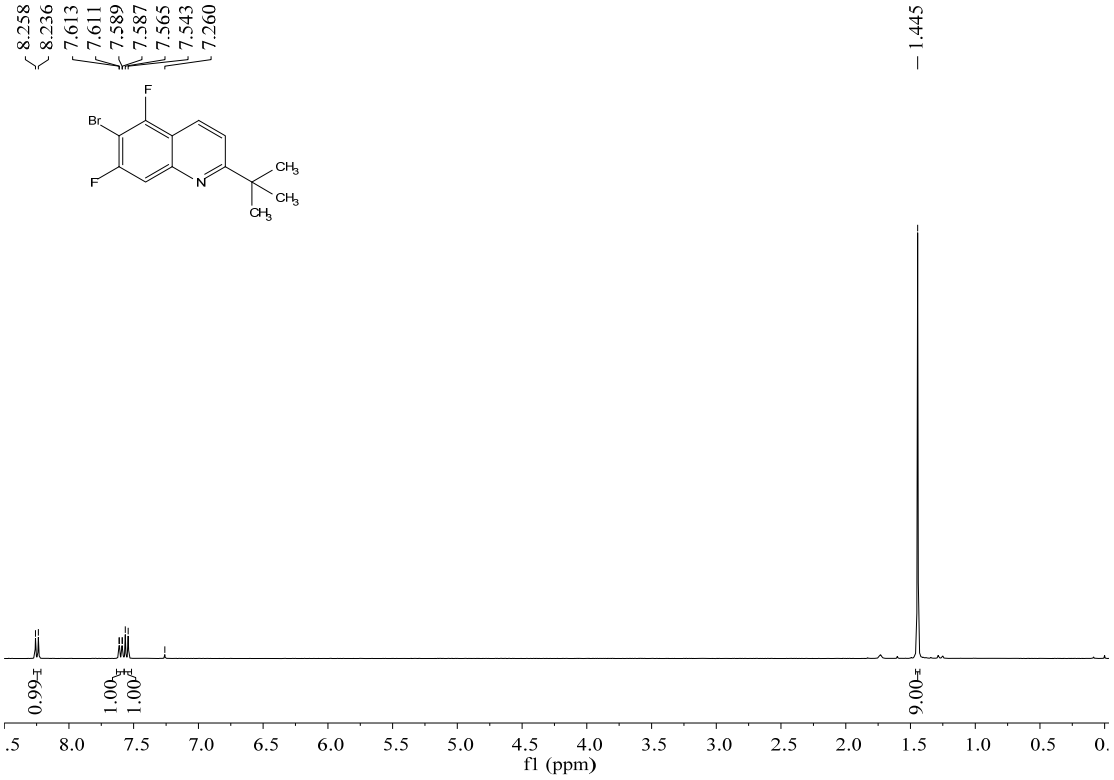


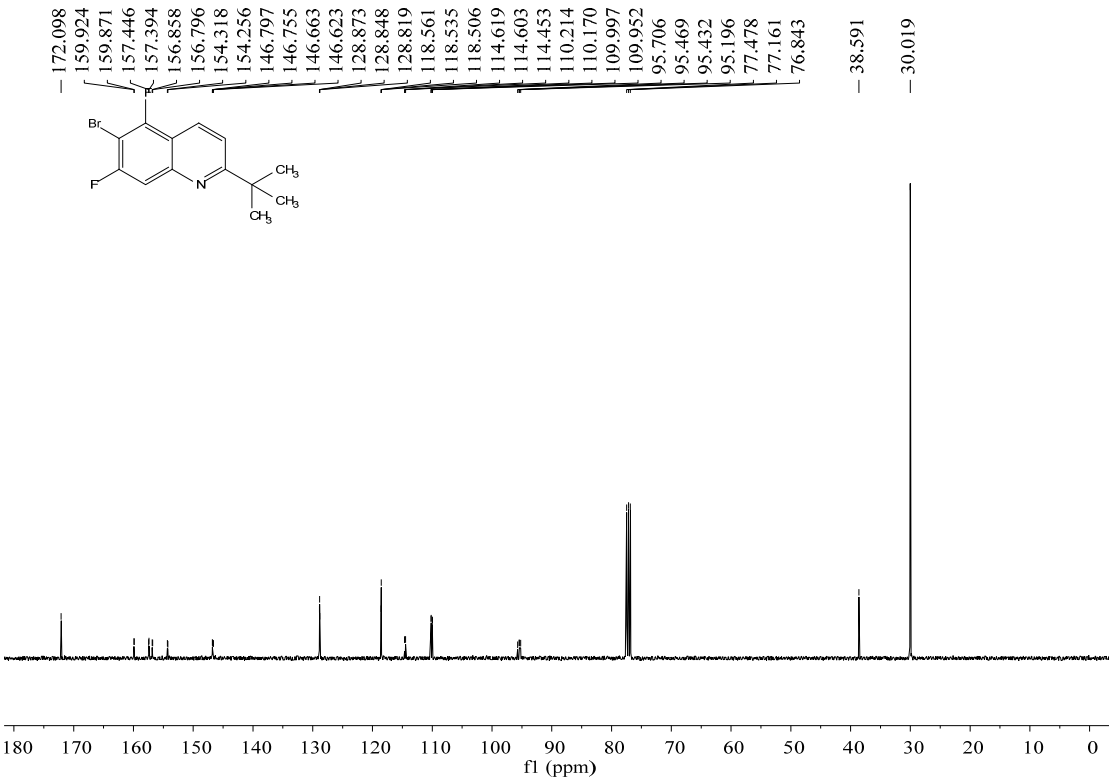
^{1}H and ^{13}C NMR spectra of 4q



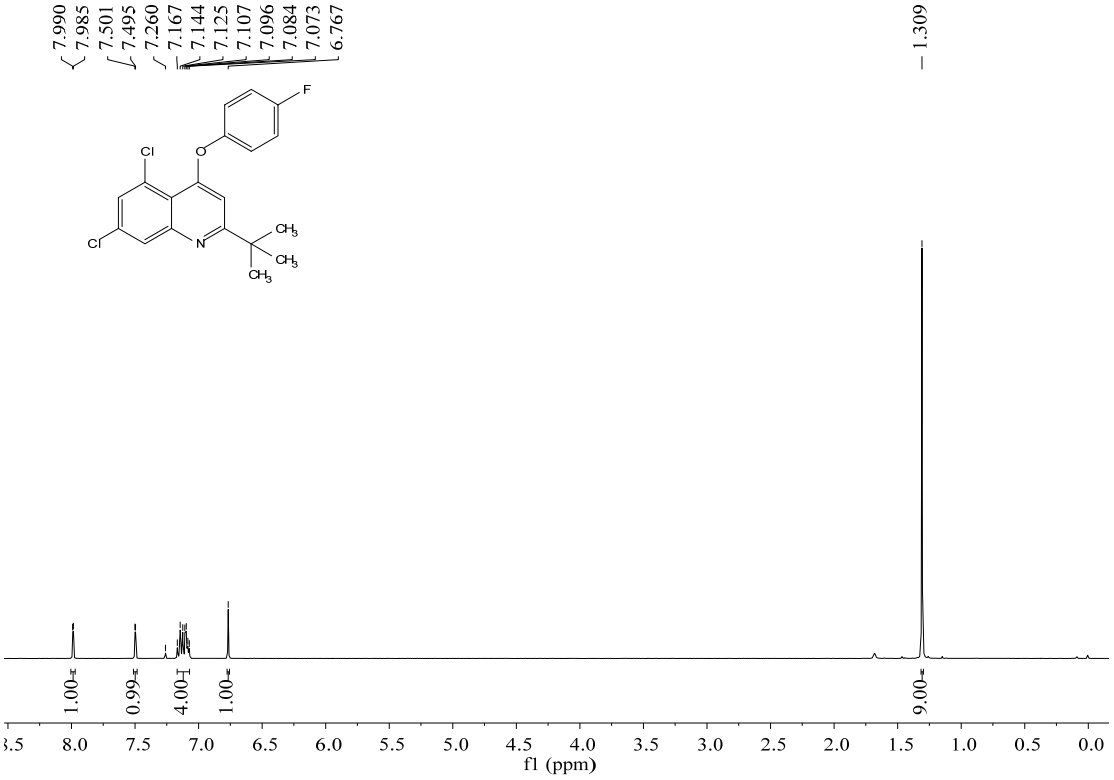


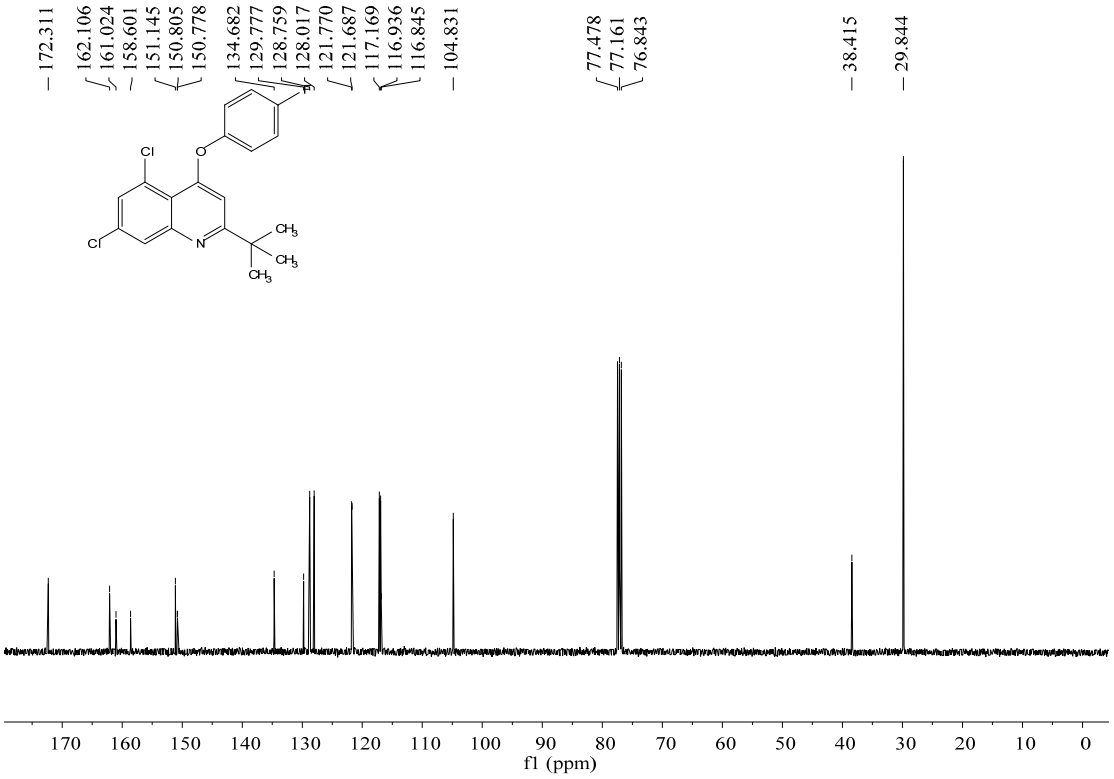
^{1}H and ^{13}C NMR spectra of 4r



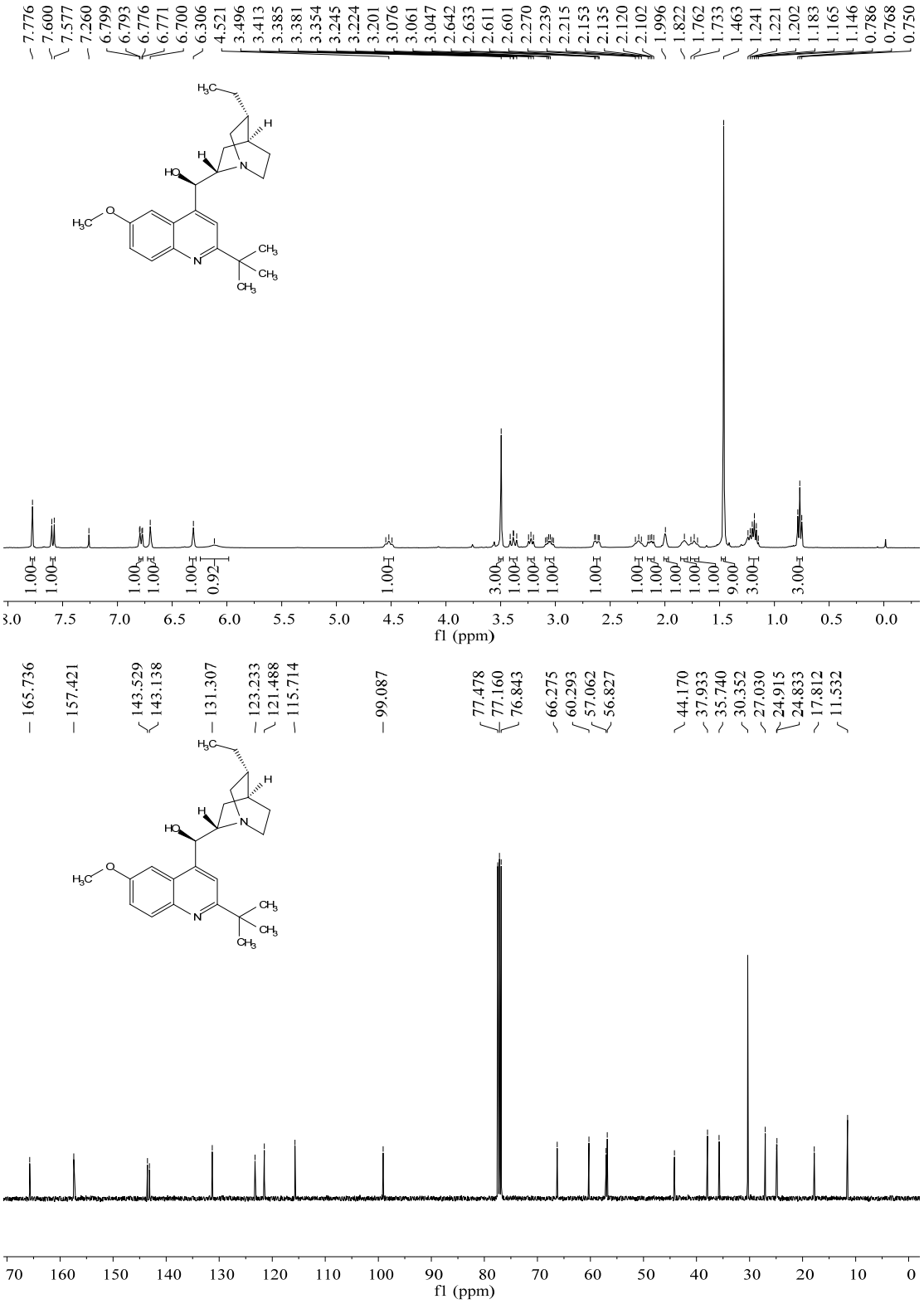


^{1}H and ^{13}C NMR spectra of 4s

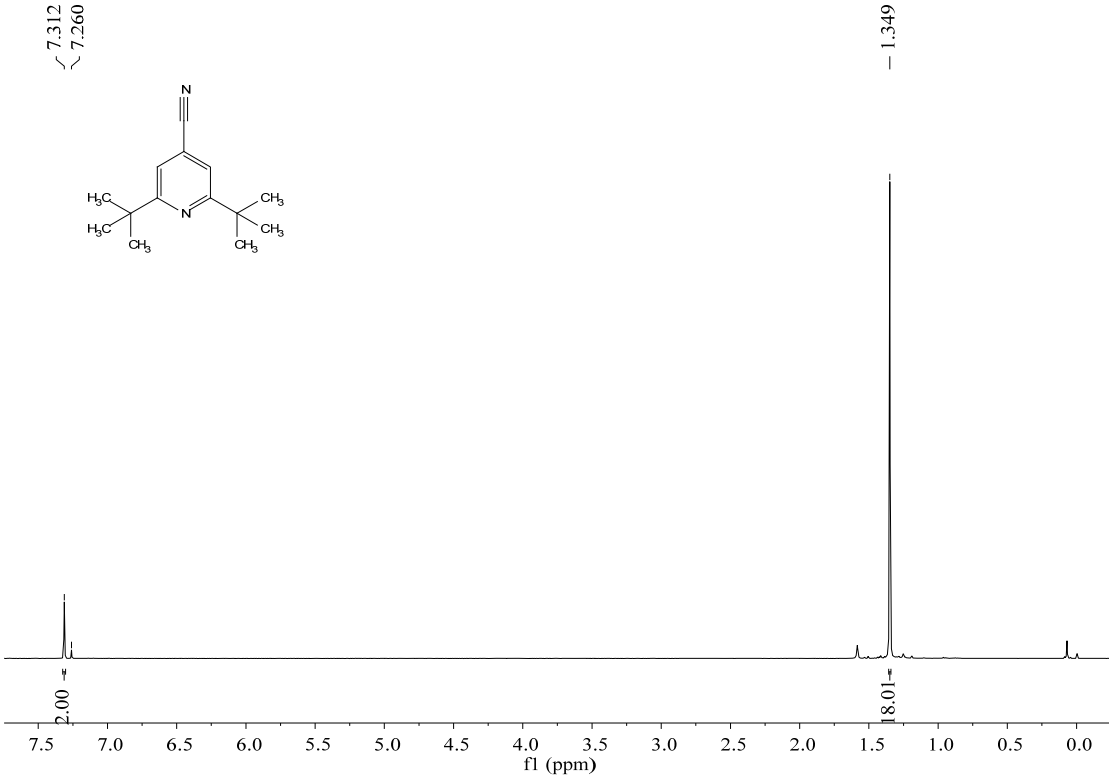


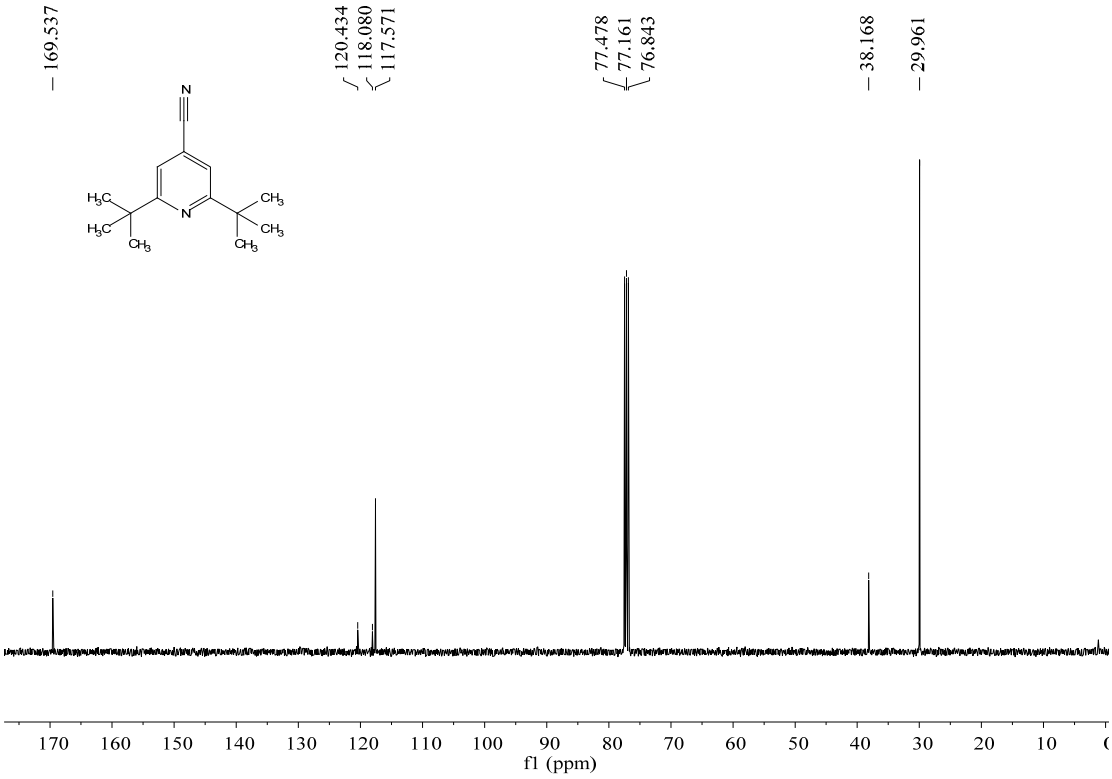


^{1}H and ^{13}C NMR spectra of 4t

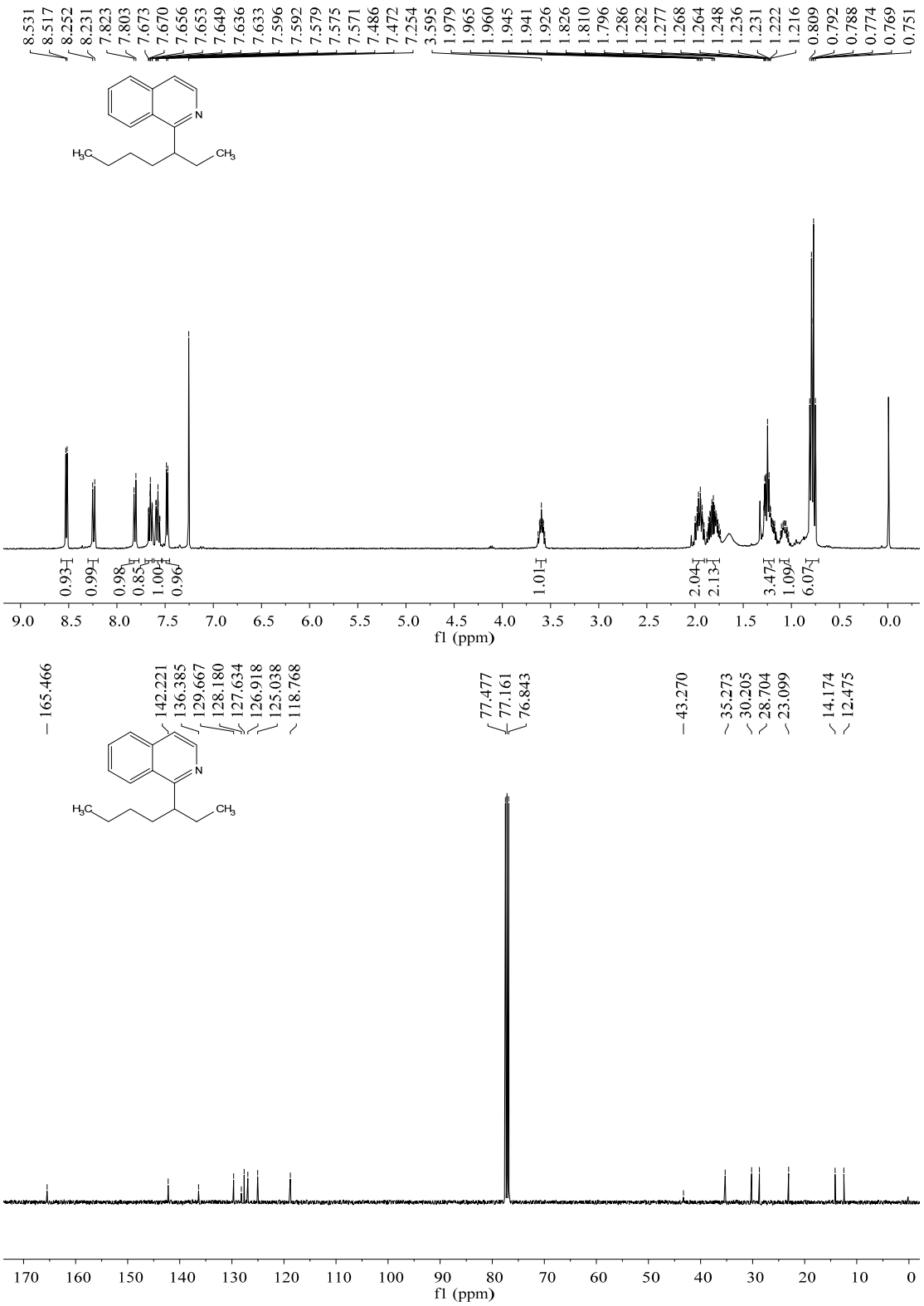


^{1}H and ^{13}C NMR spectra of 5a

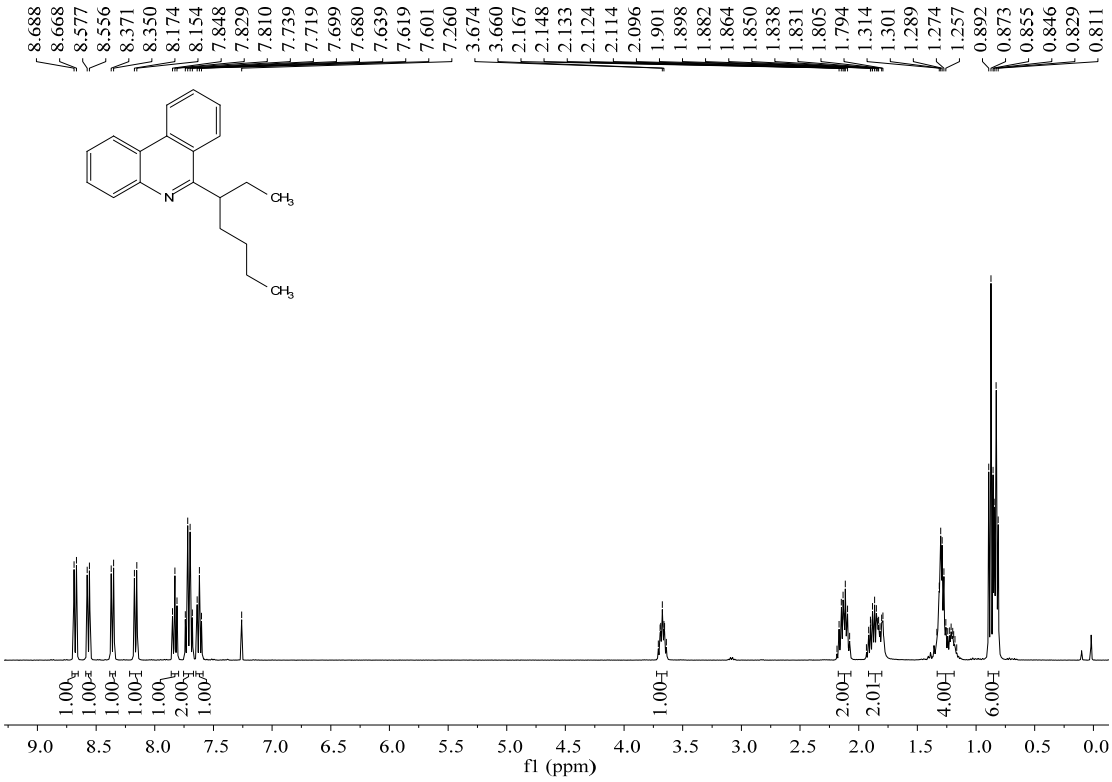


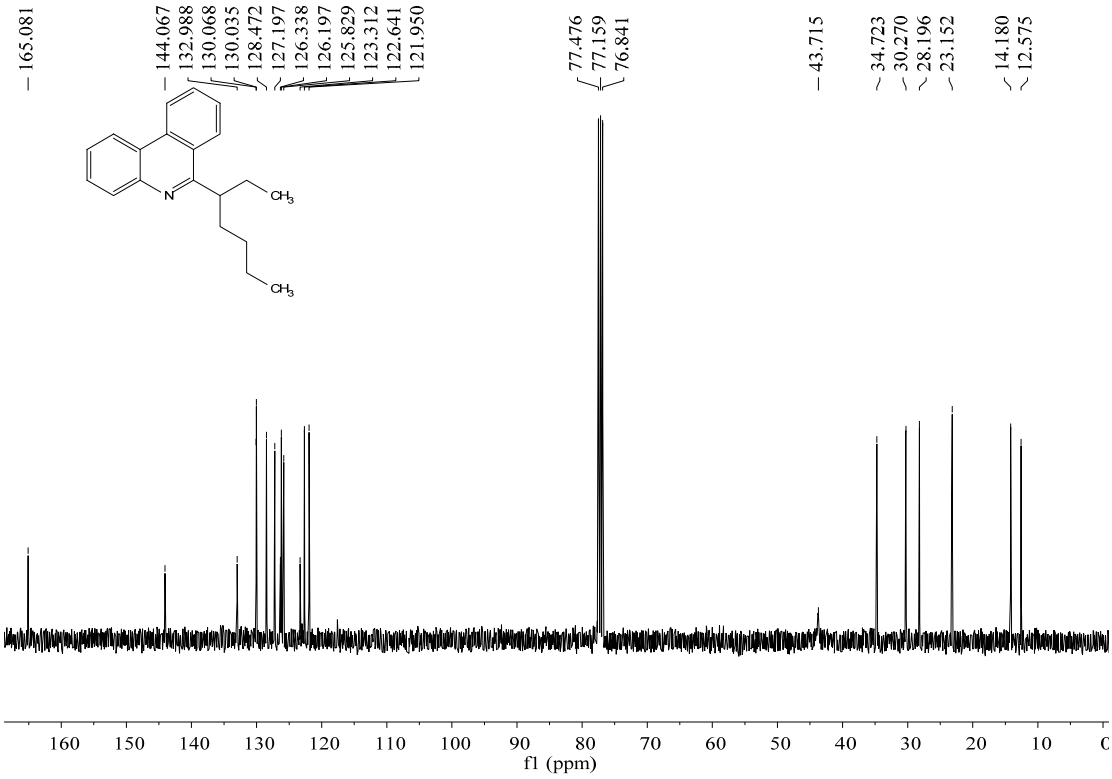


^{1}H and ^{13}C NMR spectra of 5b

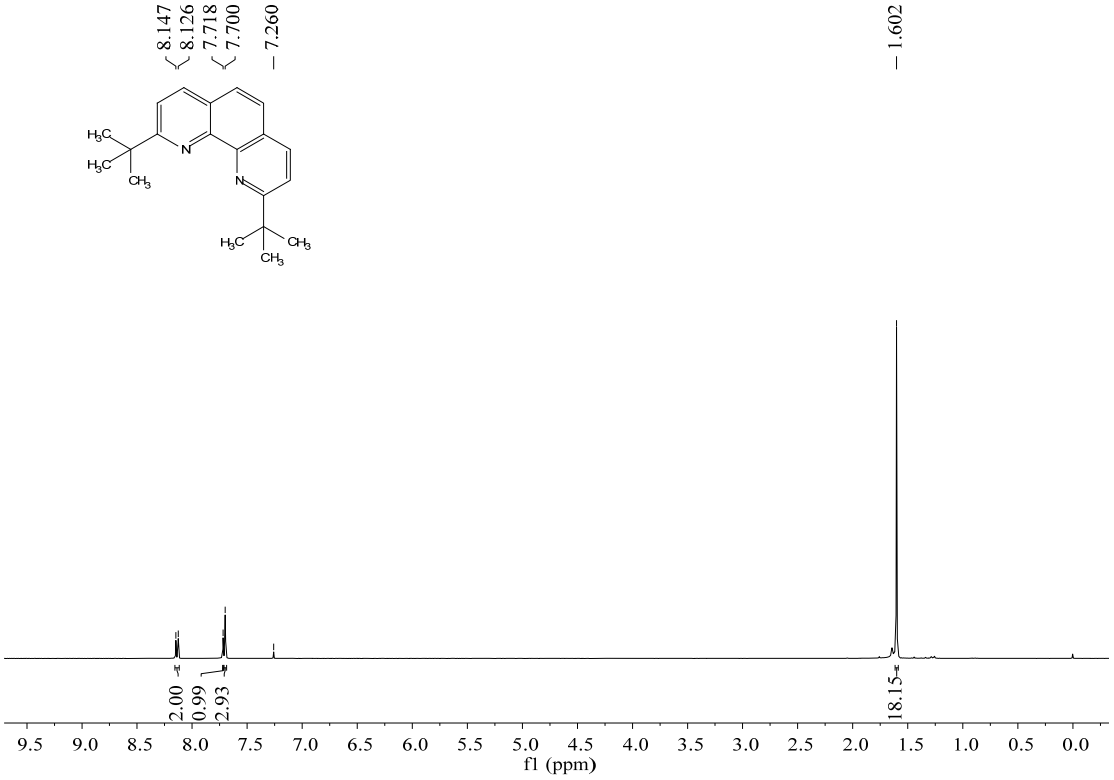


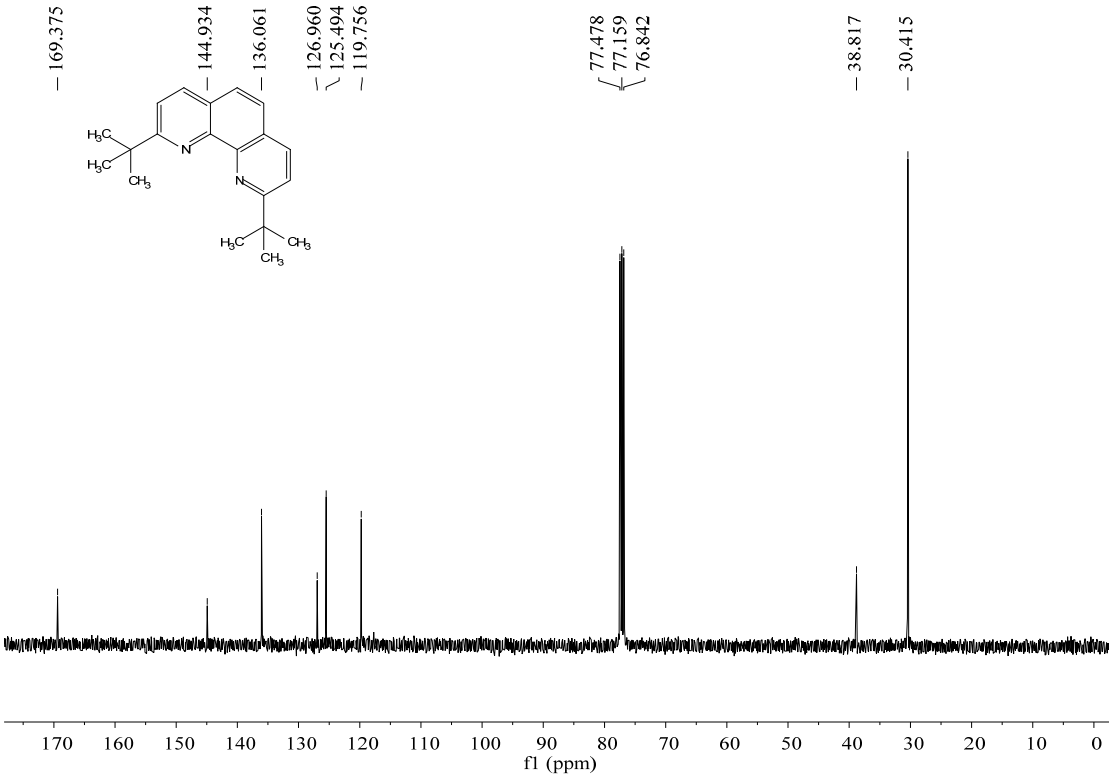
^{1}H and ^{13}C NMR spectra of 5c



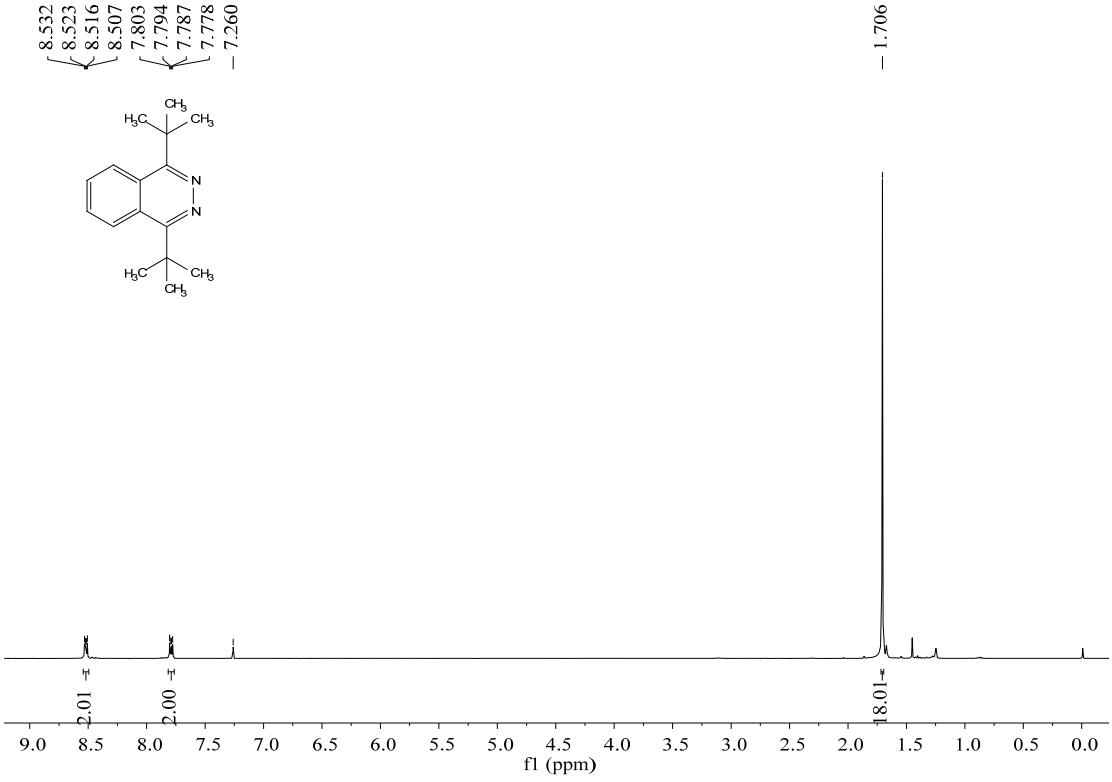


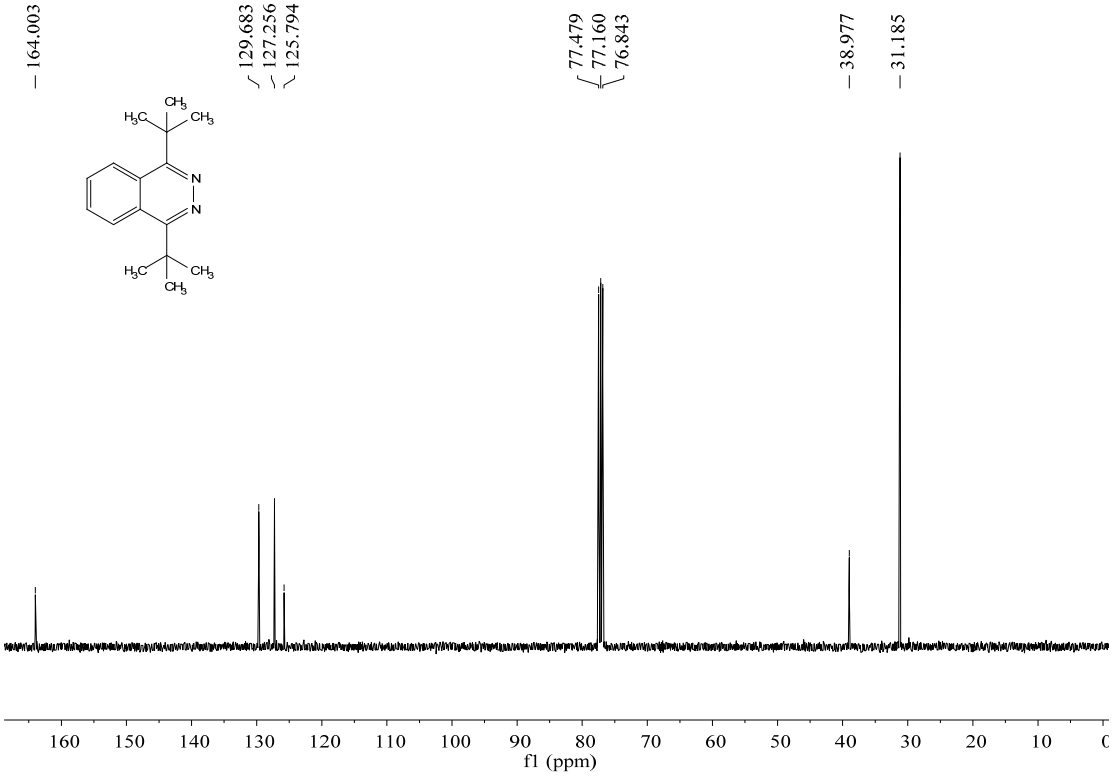
^{1}H and ^{13}C NMR spectra of 5d



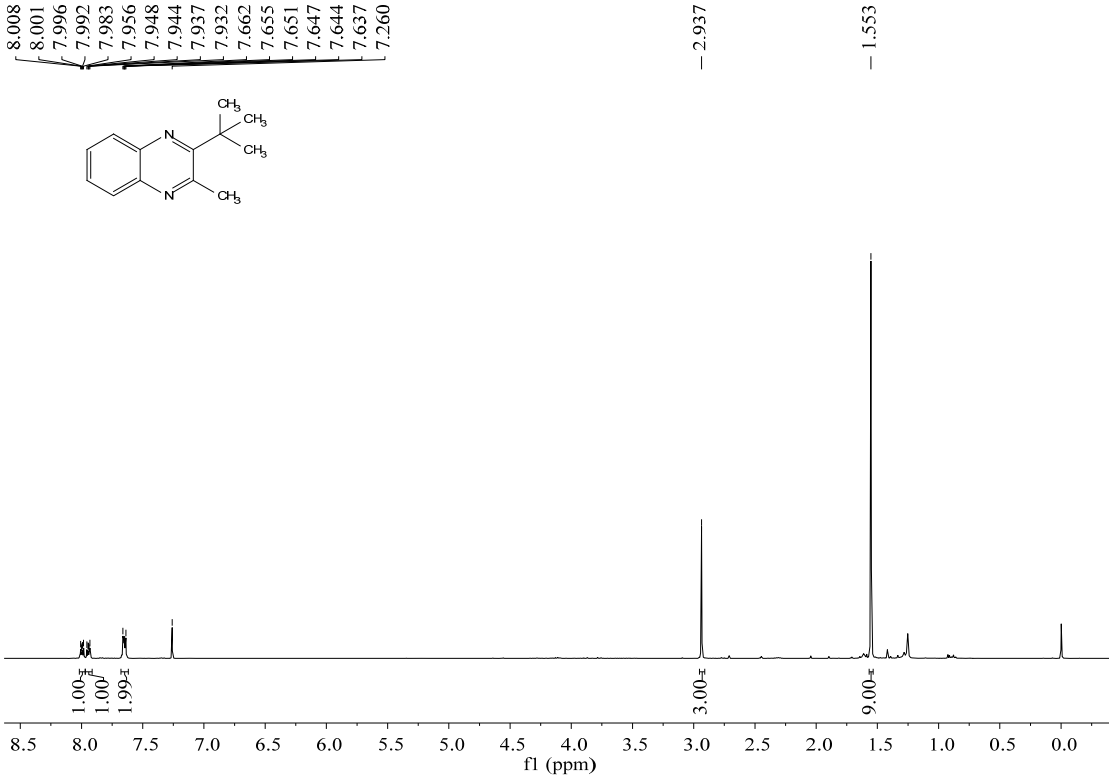


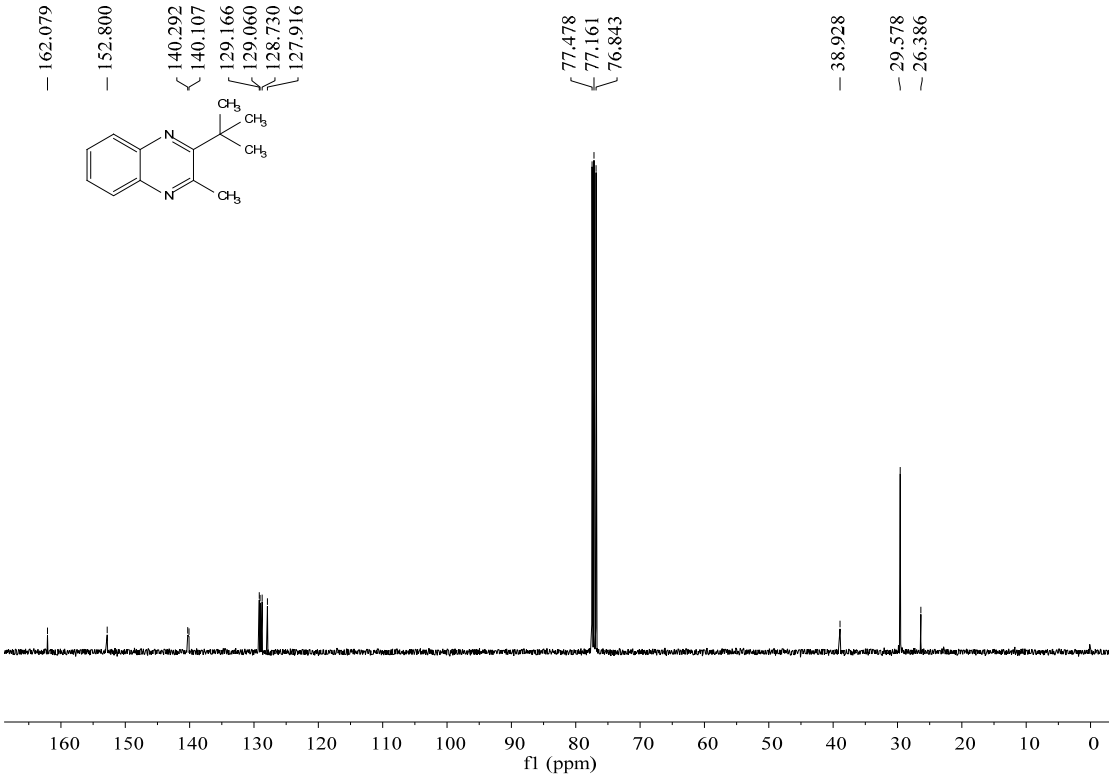
^{1}H and ^{13}C NMR spectra of 5e



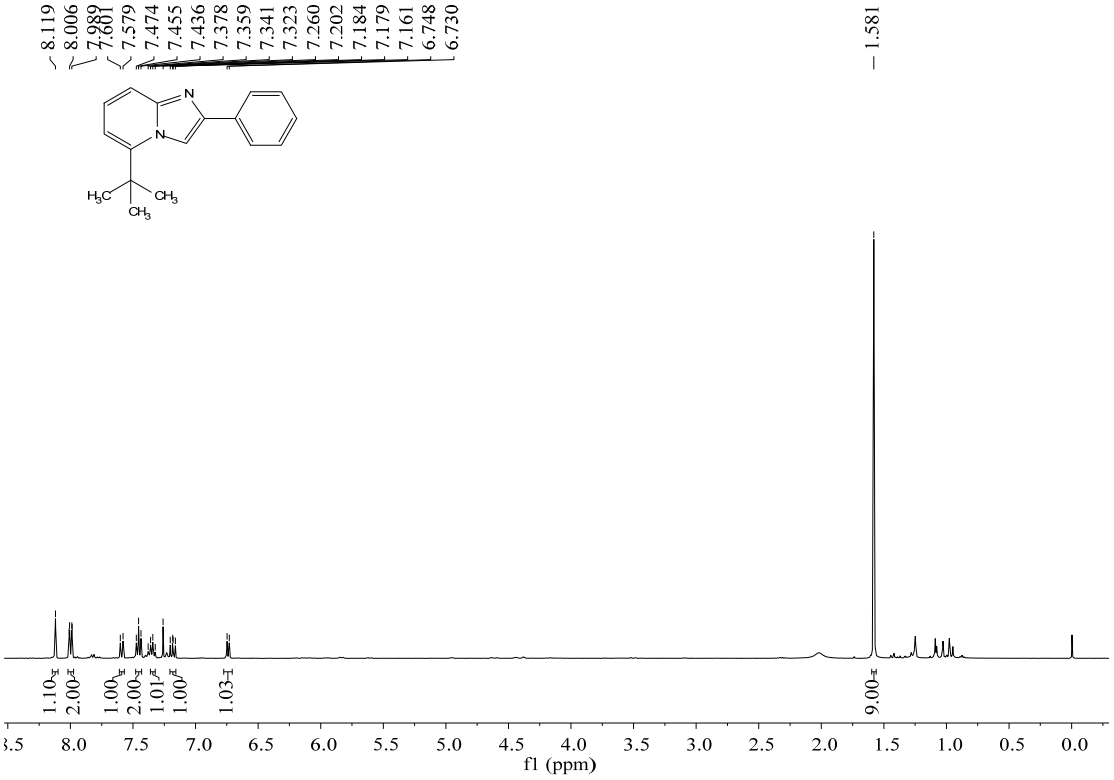


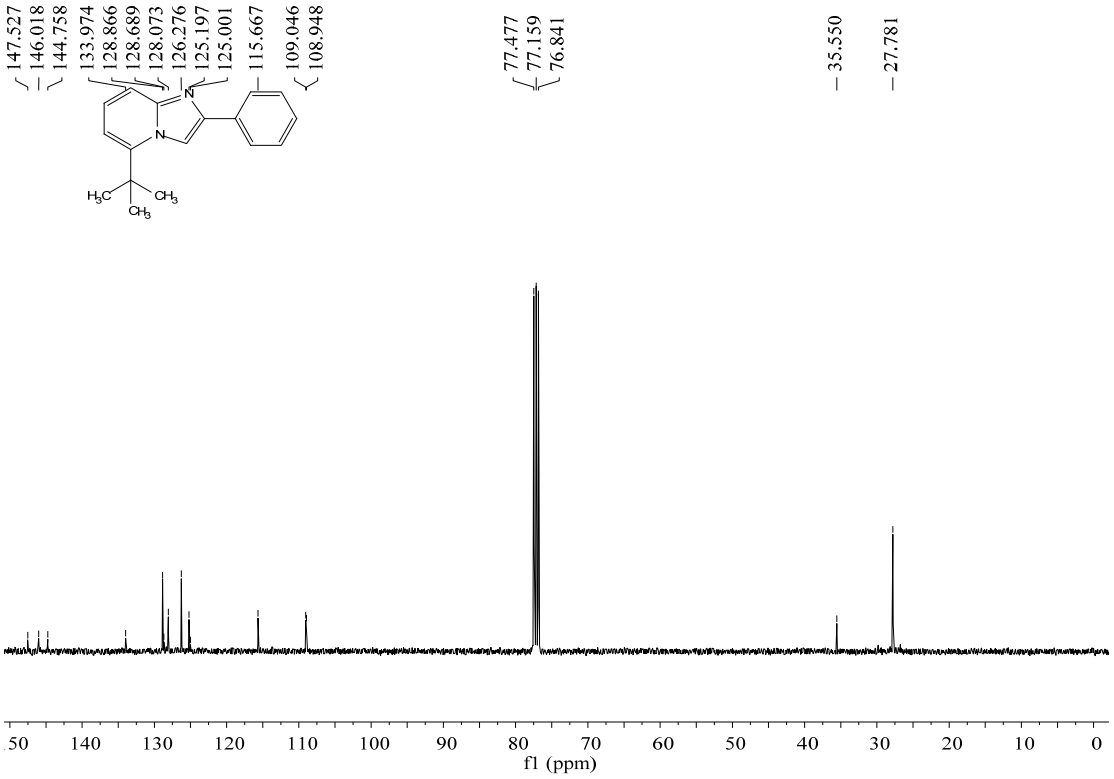
^{1}H and ^{13}C NMR spectra of 5f





^{1}H and ^{13}C NMR spectra of 5g





^{1}H and ^{13}C NMR spectra of 5h