Electrochemically Assisted Friedlander Reaction: Highly Efficient and Sustainable Method for Quinoline Synthesis

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1. General information

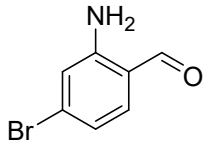
Reagents and Apparatus. All chemicals and reagents were obtained from commercial sources. Cyclic voltammetry, controlled-potential coulometry, constant current electrolysis, and preparative electrolysis were performed using an Ivium model PGSTAT 20 potentiostat/ galvanostat, Atom Lab and Zag Chemie digital coulometer model ZCL-74A. The working electrode used in the voltammetry experiments was a glassy carbon disc, and a platinum wire was used as the counter electrode. The working electrode potentials were measured vs Ag/AgCl (saturated KCl) electrode (all electrodes from AZAR Electrodes). Before each experiment, the GC electrode was polished using alumina slurry (from Iran Alumina Co).

Experimental section

General Procedure for Electrosynthesis of 3a−3YYY. Into the both compartment of a divided H cell equipped with a graphite carbon anode (1 cm diameter and 7 cm length) and a nickel foam cathode (1 × 2 cm), aqueous solution containing 5% H_2SO4 (10.0 mL), were added. In cases where the starting materials did not dissolve, some acetonitrile was added. Cathodic compartment was also charged with aldehyde (1.0 mmol) and beta diketone, ketone or malononitrile (1.0 mmol). For constant potential electrolysis, an Ag/AgCl (saturated KCl) reference electrode was also placed in the cathodic chamber, and electrolysis was performed at 80 ^{o}C, by applying the potential of E^{p}_{C0} (-0.3 V) to the working electrode. The constant current preparative electrolysis with a current density of 5.0 mA/cm^2 was performed at 80 ^{o}C temperature. In both cases (constant current and constant potential), the electrolysis was followed by cyclic voltammetry analysis and when the cathodic peak C_0 disappeared (after application of about 600 C (6.0 F)), the electrolysis was stopped. For the separation of the products, after cooling down the solution, and neutralization with sodium hydroxide solution up to pH 7.0. The neutralized solution was transferred into a separator funnel, where AcOEt (20 mL) and water (20 mL) were added. The aqueous phase was again extracted with AcOEt (20 mL), organic phases were washed with brine (20 ml) and dried

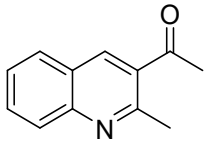
over $MgSO_4$. The solution was concentrated under reduced pressure and the crude was purified by column chromatography to afford the corresponding quinolones.

2-amino-4-bromobenzaldehyde



Colorless solid (yield 85%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.80 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 6.89 – 6.81 (m, 2H), 6.16 (s, 2H).
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 193.28, 150.52, 136.99, 130.55, 119.93, 118.69, 117.79.

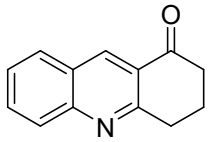
1-(2-methylquinolin-3-yl)ethan-1-one (3a)



Orange solid (yield 84%), mp 60-62°C; ^{1}H NMR (300 MHz, Acetone) δ 8.82 (s, 1H), 7.99 (dd, *J* = 15.3, 8.3 Hz, 2H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 8.1 Hz, 1H), 2.81 (s, 3H), 2.72 (s, 3H).

^{13}C NMR (75 MHz, Acetone) δ 200.73, 158.03, 149.24, 139.24, 132.34, 132.21, 129.68, 129.48, 127.48, 126.90, 25.86.

3,4-dihydroacridin-1(2H)-one (3b)

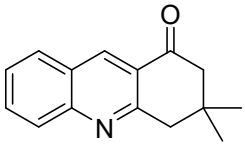


Light yellow solid (yield 86%), mp 108-109°C.

^{1}H NMR (300 MHz, Acetone) δ 8.81 (s, 1H), 8.10 (d, *J* = 6.4 Hz, 1H), 8.00 (d, *J* = 9.6 Hz, 1H), 7.86 (ddd, *J* = 8.6, 6.9, 1.6 Hz, 1H), 7.61 (t, *J* = 8.1 Hz, 1H), 3.30 – 3.25 (m, 2H), 2.81 – 2.75 (m, 2H), 2.26 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (75 MHz, Acetone) δ 197.81, 163.26, 150.70, 137.03, 132.94, 130.76, 129.63, 127.86, 127.52, 127.49, 39.68, 34.21, 22.61.

3,3-dimethyl-3,4-dihydroacridin-1(2H)-one (3c)

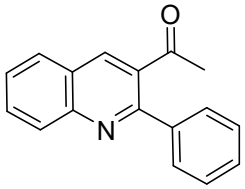


White solid (yield 81%), mp 110-111℃;

^{1}H NMR (300 MHz, Acetone) δ 8.80 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.85 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 3.19 (s, 2H), 2.66 (s, 2H), 1.12 (s, 6H).

^{13}C NMR (75 MHz, Acetone) δ 197.81, 161.92, 151.02, 136.50, 132.88, 130.82, 129.62, 127.78, 127.55, 126.43, 52.90, 47.76, 33.34, 28.59.

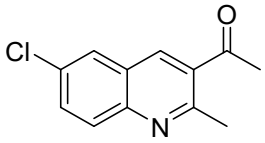
(2-methylquinolin-3-yl)(phenyl)methanone (3d)



Red oil (yield 76%); ^{1}H NMR (300 MHz, Acetone) δ 8.30 (s, 1H), 8.01 (dd, *J* = 14.8, 8.3 Hz, 2H), 7.92 – 7.78 (m, 3H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.66 – 7.49 (m, 3H), 2.67 (s, 3H).

^{13}C NMR (75 MHz, Acetone) δ 197.18, 157.15, 149.02, 138.39, 137.49, 134.55, 133.15, 131.79, 130.95, 129.75, 129.58, 129.38, 127.51, 126.37, 24.44.

1-(6-chloro-2-methylquinolin-3-yl)ethan-1-one (3e)

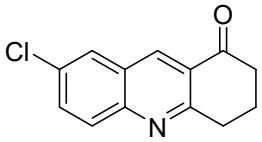


White solid (yield 87%), mp 116℃;

^{1}H NMR (300 MHz, Acetone) δ 8.80 (s, 1H), 8.07 (s, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 2.79 (s, 3H), 2.71 (s, 3H).

13C NMR (75 MHz, Acetone) δ 200.63, 158.59, 147.51, 138.24, 133.03, 132.74, 132.39, 131.43, 128.17, 127.66, 25.71.

7-chloro-3,4-dihydroacridin-1(2H)-one (3f)

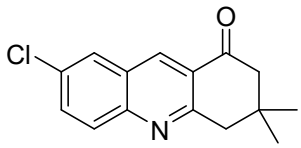


Light yellow needles (yield 84%), mp 150-151°C

^{1}H NMR (600 MHz, CDCl3) δ 8.73 (s, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 2.4 Hz, 1H), 7.71 (dd, J = 9.0, 2.4 Hz, 1H), 3.29 (t, J = 6.3 Hz, 2H), 2.78 (dd, J = 7.3, 5.8 Hz, 2H), 2.26 (p, J = 6.3 Hz, 2H).

^{13}C NMR (151 MHz, CDCl3) δ 197.4, 162.2, 147.8, 136.1, 133.2, 132.4, 130.1, 128, 127.4, 126.8, 39, 33.2, 21.6.

7-chloro-3,3-dimethyl-3,4-dihydroacridin-1(2H)-one (3g)

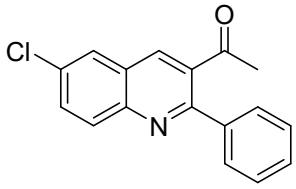


White solid (yield 85%), mp 147-149℃;

^{1}H NMR (300 MHz, Acetone) δ 8.80 (s, 1H), 8.21 (d, *J* = 2.4 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.83 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.20 (s, 2H), 2.68 (s, 2H), 1.14 (s, 6H).

^{13}C NMR (75 MHz, Acetone) δ 197.62, 162.52, 149.33, 135.81, 133.35, 132.53, 131.57, 129.25, 128.52, 127.09, 52.81, 47.65, 33.29, 28.52.

(6-chloro-2-methylquinolin-3-yl)(phenyl)methanone (3h)

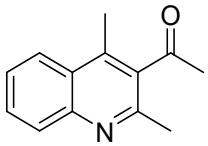


Colorless needles (yield 79%), mp 110-112℃;

^{1}H NMR (300 MHz, Acetone) δ 8.31 (s, 1H), 8.07 (d, *J* = 2.4 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.81 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 2.66 (s, 3H).

^{13}C NMR (75 MHz, Acetone) δ 196.83, 157.71, 147.30, 138.00, 136.54, 134.74, 134.00, 132.44, 132.23, 131.51, 130.97, 129.78, 127.96, 127.15, 24.28.

1-(2,4-dimethylquinolin-3-yl)ethenone (3i)

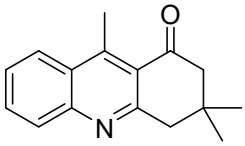


Light yellow oil (yield 71%);

^{1}H NMR (300 MHz, Acetone) δ 8.13 – 8.07 (m, 1H), 7.99 – 7.90 (m, 1H), 7.74 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 2.62 (s, 3H), 2.60 (s, 3H), 2.56 (s, 3H).

^{13}C NMR (75 MHz, Acetone) δ 196.83, 157.71, 147.30, 138.00, 136.54, 134.74, 134.00, 132.44, 132.23, 131.51, 130.97, 129.78, 127.96, 127.15, 24.28.

3,3,9-trimethyl-3,4-dihydroacridin-1(2H)-one (3j)

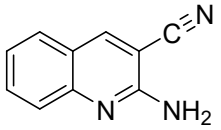


Light yellow solid (yield 86%), mp 100-102℃

^{1}H NMR (600 MHz, CDCl3) δ 8.19 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 3.16 (s, 2H), 3.04 (s, 3H), 2.64 (s, 2H), 1.11 (s, 6H).

^{13}C NMR (151 MHz, CDCl3) δ 200.5, 161, 149.7, 148.1, 131.4, 129.1, 127.6, 126.3, 125.4, 124.1, 54.7, 48.4, 32, 28.2, 16.

2-aminoquinoline-3-carbonitrile (3k)

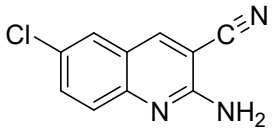


Green solid (yield 74%), mp 208-209℃;

^{1}H NMR (300 MHz, Acetone) δ 8.58 (s, 1H), 7.79 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.29 (m, 1H), 6.32 (s, 2H).

^{13}C NMR (75 MHz, Acetone) δ 155.32, 149.09, 144.18, 144.10, 128.03, 125.80, 122.74, 121.22, 115.62, 98.70.

2-amino-6-chloroquinoline-3-carbonitrile (3l)

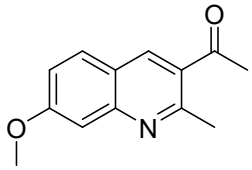


Dark yellow solid (yield 78%), mp 275-277°C;

^{1}H NMR (300 MHz, DMSO) δ 8.65 (s, 1H), 7.85 (s, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.12 (s, 2H).

^{13}C NMR (75 MHz, DMSO) δ 156.02, 147.72, 144.64, 132.95, 127.53, 126.95, 126.54, 121.53, 116.19, 95.60.

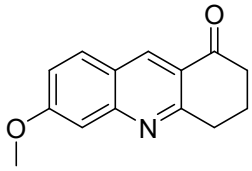
1-(7-methoxy-2-methylquinolin-3-yl)ethan-1-one (3m)



White solid (yield 87%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.42 (s, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.19 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.96 (s, 3H), 2.90 (s, 3H), 2.69 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.57, 162.91, 158.60, 150.48, 138.38, 129.61, 128.91, 120.78, 120.09, 106.90, 55.82, 29.13, 26.02.

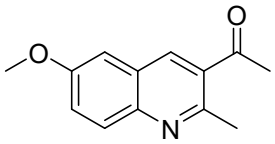
6-methoxy-3,4-dihydroacridin-1(2H)-one (3n)



White solid (yield 84%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.75 (s, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.35 (d, *J* = 2.7 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.27 (t, *J* = 6.3 Hz, 2H), 2.79 – 2.75 (m, 2H), 2.29 – 2.23 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.98, 163.37, 162.71, 151.97, 136.65, 130.98, 124.73, 122.26, 120.43, 106.65, 55.85, 39.10, 33.58, 22.00.

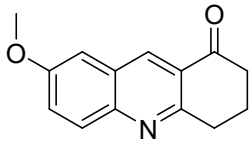
1-(6-methoxy-2-methylquinolin-3-yl)ethan-1-one (3o)



White solid (yield 85%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.36 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.11 (d, *J* = 2.7 Hz, 1H), 3.93 (s, 3H), 2.86 (s, 3H), 2.70 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 200.35, 157.95, 155.02, 144.62, 137.00, 131.53, 130.15, 126.72, 124.46, 105.75, 55.74, 29.43, 25.42.

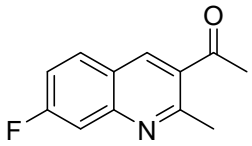
7-methoxy-3,4-dihydroacridin-1(2H)-one (3p)



White solid (yield 83%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.73 (s, 1H), 7.93 (d, *J* = 9.3 Hz, 1H), 7.45 (dd, *J* = 9.3, 2.9 Hz, 1H), 7.15 (d, *J* = 2.9 Hz, 1H), 3.93 (s, 3H), 3.30 – 3.25 (m, 2H), 2.80 – 2.76 (m, 2H), 2.30 – 2.22 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.29, 159.61, 157.87, 146.16, 135.67, 130.08, 127.93, 126.53, 125.63, 106.41, 55.76, 39.25, 33.28, 22.04.

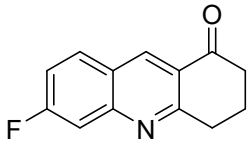
1-(7-fluoro-2-methylquinolin-3-yl)ethan-1-one (3q)



White solid (yield 87%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.47 (s, 1H), 7.86 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.66 (dd, *J* = 10.1, 2.6 Hz, 1H), 7.40 – 7.30 (m, 1H), 2.91 (s, 3H), 2.71 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.66, 165.94, 163.42, 159.11, 149.66, 138.09, 130.58, 122.74, 117.52, 112.85, 29.29, 25.85.

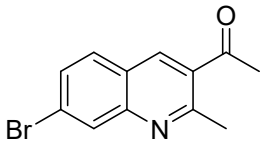
6-fluoro-3,4-dihydroacridin-1(2H)-one (3r)



White solid (yield 85%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.84 (s, 1H), 7.94 (dd, *J* = 9.0, 6.1 Hz, 1H), 7.67 (dd, *J* = 10.1, 2.9 Hz, 1H), 7.40 – 7.32 (m, 1H), 3.33 – 3.28 (m, 2H), 2.82 – 2.78 (m, 2H), 2.31 – 2.24 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.75, 163.31, 151.11, 137.01, 132.18, 132.07, 125.99, 124.04, 117.81, 117.55, 112.74, 112.53, 39.11, 33.56, 21.80.

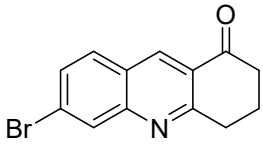
1-(7-bromo-2-methylquinolin-3-yl)ethan-1-one (3s)



White solid (yield 80%), ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.43 (s, 1H), 8.22 (s, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.64 (dd, J = 8.6, 1.9 Hz, 1H), 2.90 (s, 3H), 2.71 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.74, 159.01, 148.89, 137.93, 131.55, 131.33, 130.46, 129.59, 126.24, 124.38, 29.38, 25.82.

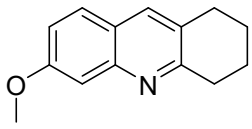
6-bromo-3,4-dihydroacridin-1(2H)-one (3t)



White solid (yield 83%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.81 (s, 1H), 8.25 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.30 (t, *J* = 6.3 Hz, 2H), 2.82 – 2.78 (m, 2H), 2.28 (p, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.67, 163.26, 150.18, 137.02, 131.32, 130.91, 130.54, 127.12, 126.67, 125.56, 39.14, 33.57, 21.76.

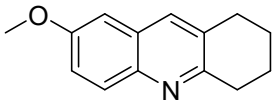
6-methoxy-1,2,3,4-tetrahydroacridine (3u)



White solid (yield 70%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.86 (d, *J* = 9.1 Hz, 1H), 7.69 (s, 1H), 7.27 (d, *J* = 2.9 Hz, 1H), 7.25 (d, *J* = 2.7 Hz, 1H), 6.96 (d, *J* = 2.9 Hz, 1H), 3.90 (d, *J* = 0.7 Hz, 3H), 3.08 (t, *J* = 6.6 Hz, 2H), 2.95 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.95 (m, 2H), 1.91 – 1.84 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 157.20, 156.75, 142.92, 134.05, 131.33, 129.90, 128.14, 121.28, 104.55, 55.58, 33.43, 29.43, 23.48, 23.10.

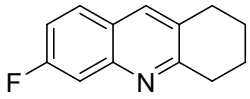
7-methoxy-1,2,3,4-tetrahydroacridine (3v)



White solid (yield 67%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.71 (s, 1H), 8.03 (d, *J* = 9.3 Hz, 1H), 7.83 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H), 3.15 (t, *J* = 6.6 Hz, 2H), 3.00 (t, *J* = 6.5 Hz, 2H), 2.04 – 1.98 (m, 2H), 1.94 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 167.22, 160.75, 145.97, 134.74, 133.40, 131.28, 129.83, 127.25, 125.20, 52.46, 33.71, 29.58, 23.22, 22.87.

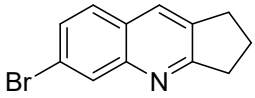
6-fluoro-1,2,3,4-tetrahydroacridine (3w)



White solid (yield 69%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.80 (s, 1H), 7.68 (dd, *J* = 9.0, 6.1 Hz, 1H), 7.60 (dd, *J* = 10.4, 2.9 Hz, 1H), 7.22 (td, *J* = 8.7, 2.6 Hz, 1H), 3.11 (t, *J* = 6.6 Hz, 2H), 2.96 (t, *J* = 6.5 Hz, 2H), 2.03 – 1.95 (m, 2H), 1.92 – 1.85 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 163.94, 161.48, 160.65, 135.17, 130.44, 128.91, 124.34, 116.36, 116.10, 112.03, 111.83, 33.64, 29.25, 23.25, 22.97.

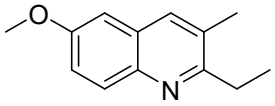
6-bromo-2,3-dihydro-1H-cyclopenta[b]quinolone (3x)



White solid (yield 65%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.18 (s, 1H), 7.85 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 8.6, 2.0 Hz, 1H), 3.15 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 8.2 Hz, 2H), 2.25 – 2.17 (m, 2H).

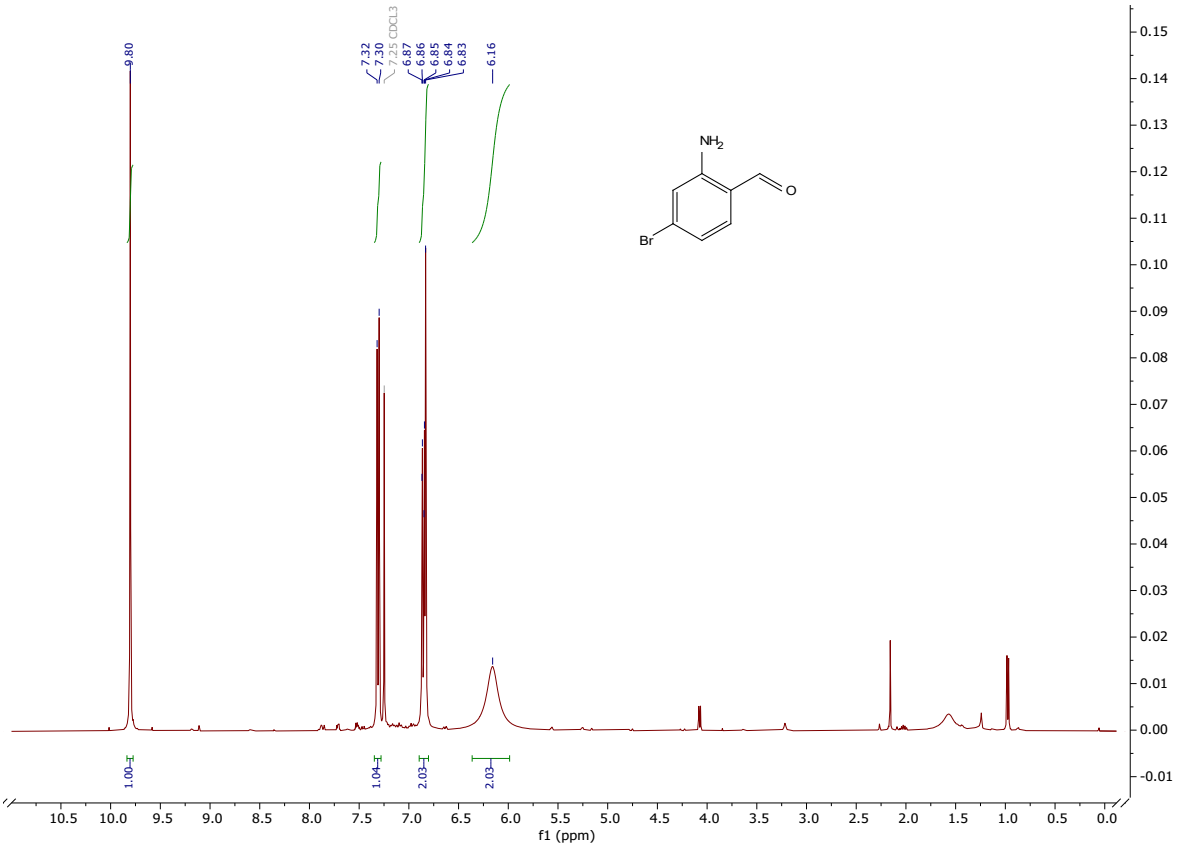
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 169.26, 148.38, 136.31, 131.19, 130.29, 129.12, 128.80, 126.18, 122.28, 34.80, 30.68, 23.70.

2-ethyl-6-methoxy-3-methylquinoline (3y)

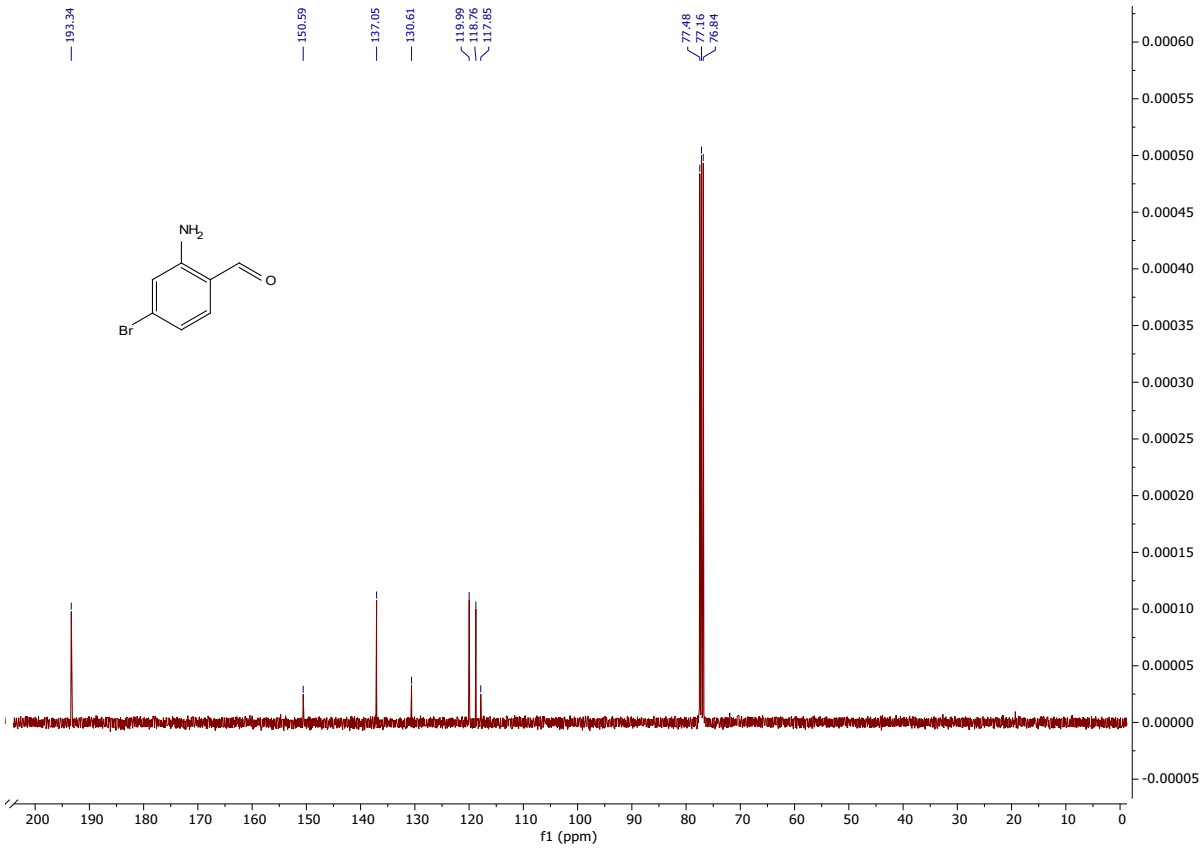


Yellow solid (yield 76%), ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.71 (s, 1H), 7.26 – 7.23 (m, 1H), 6.96 (d, *J* = 2.9 Hz, 1H), 3.88 (s, 3H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.34 (t, *J* = 7.5 Hz, 3H).

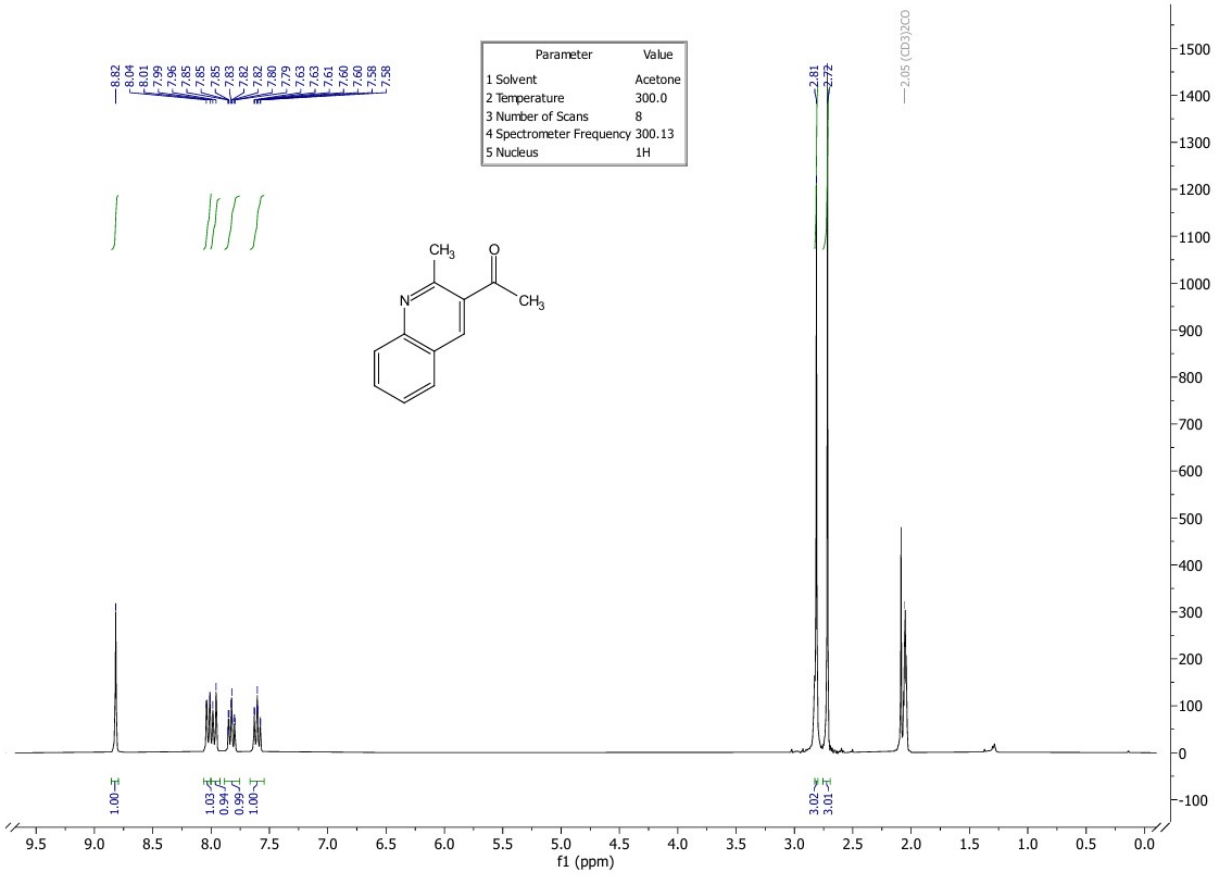
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 160.84, 157.28, 142.82, 134.91, 130.10, 129.79, 128.26, 120.44, 104.64, 55.58, 29.39, 19.25, 13.07.



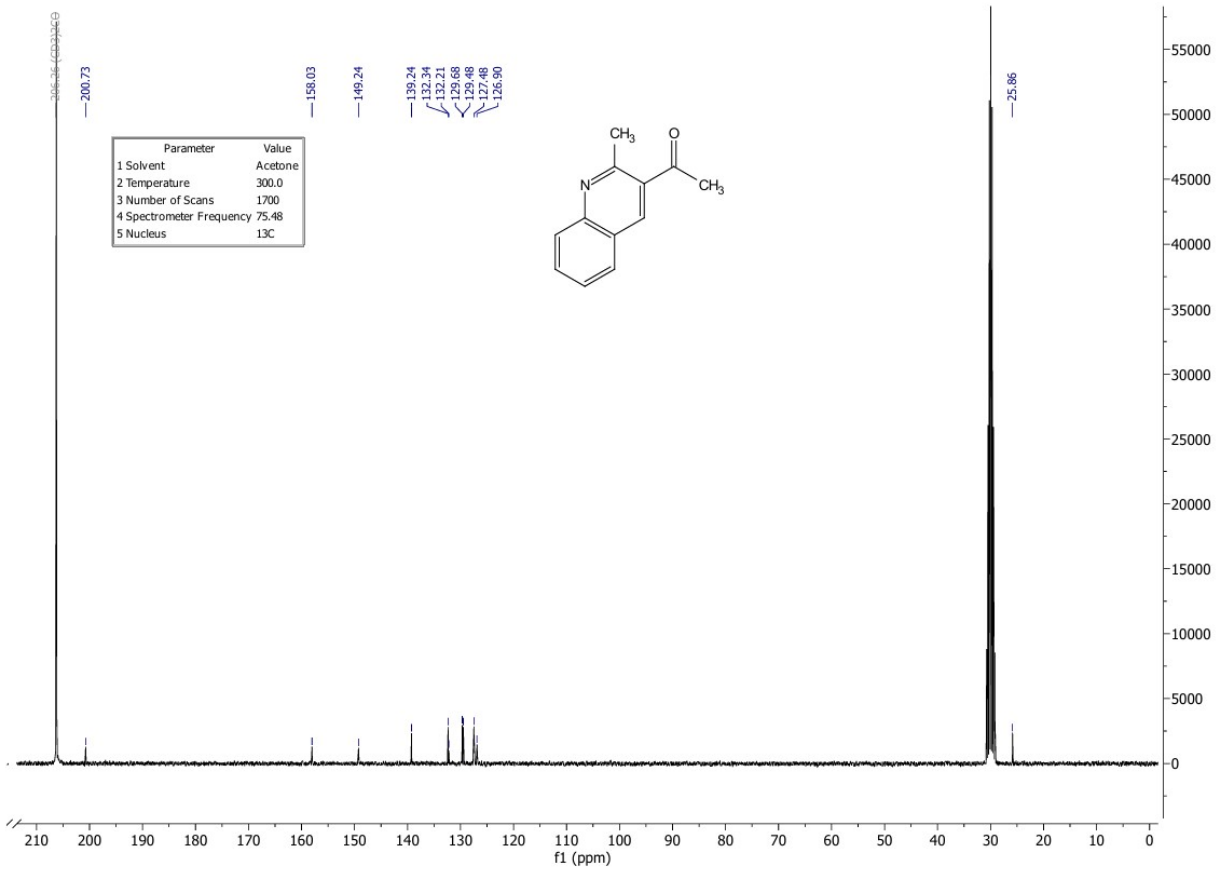
^{1}H NMR spectrum of 2-amino-4-bromobenzaldehyde synthesized from 1g.



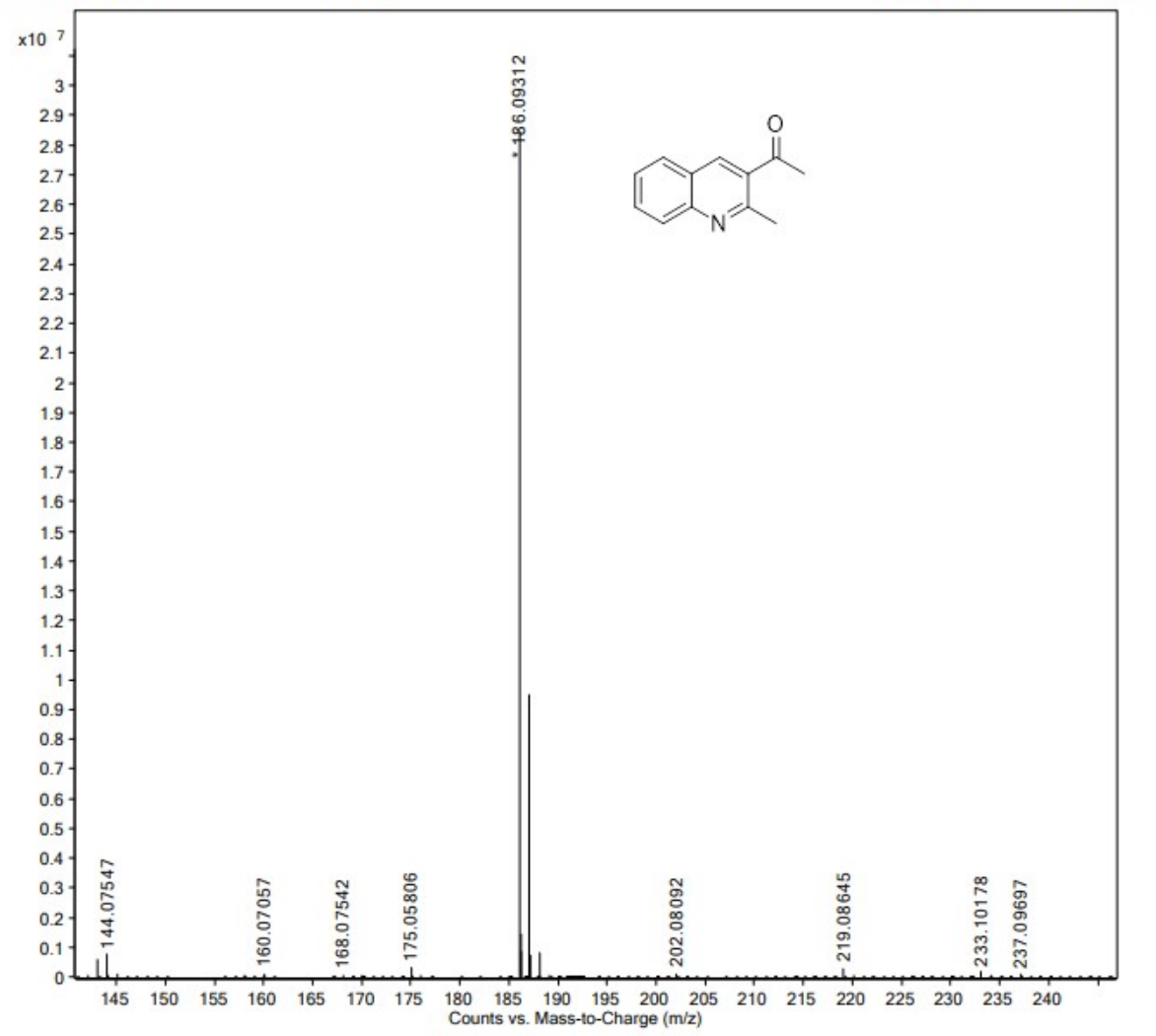
^{13}C NMR spectrum of 2-amino-4-bromobenzaldehyde synthesized from 1g.



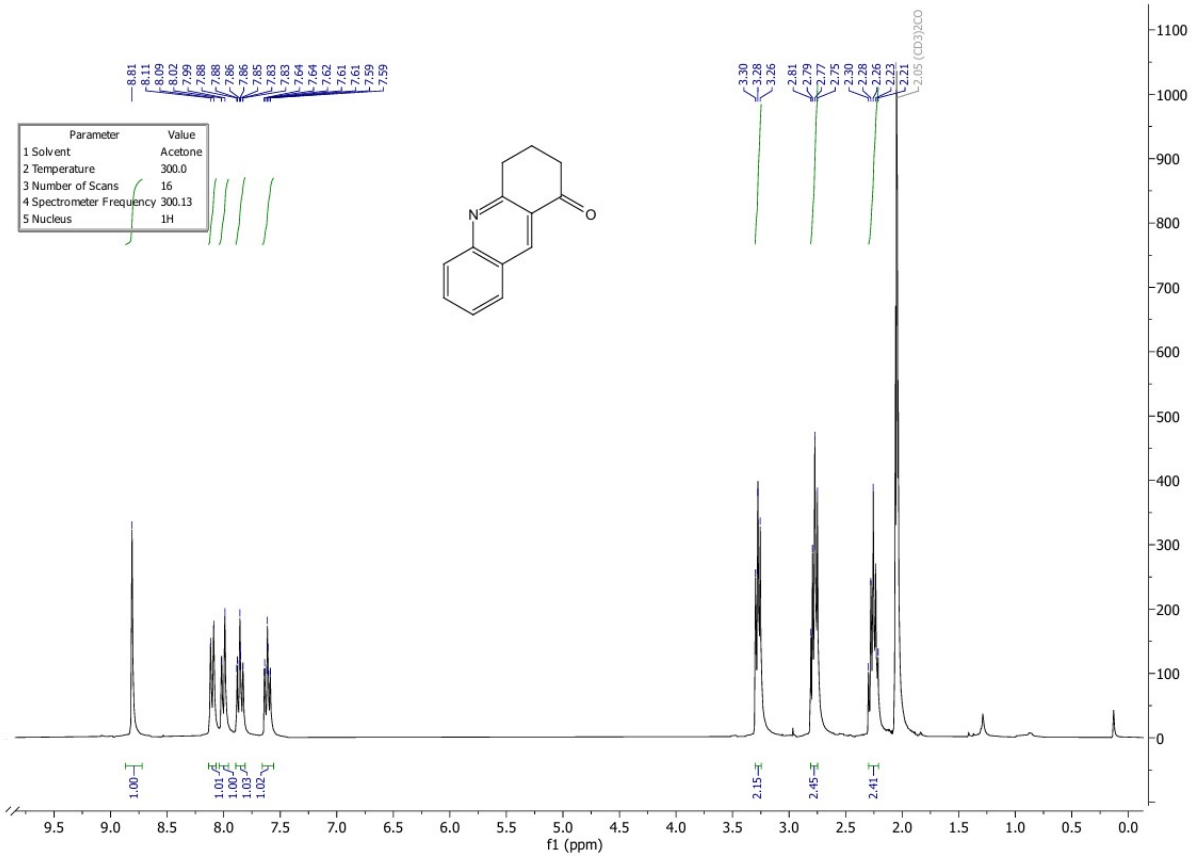
^{1}H NMR spectrum of 3a



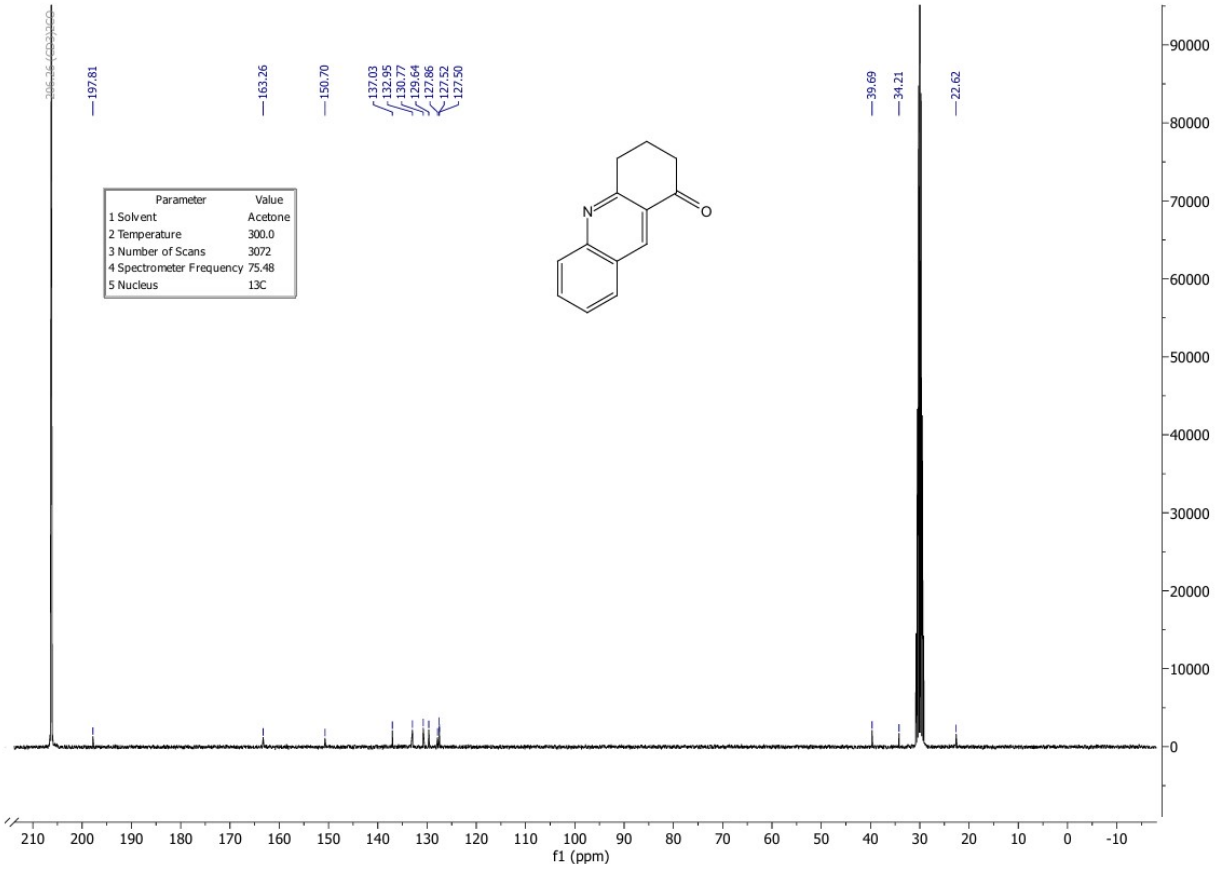
^{13}C NMR spectrum of 3a



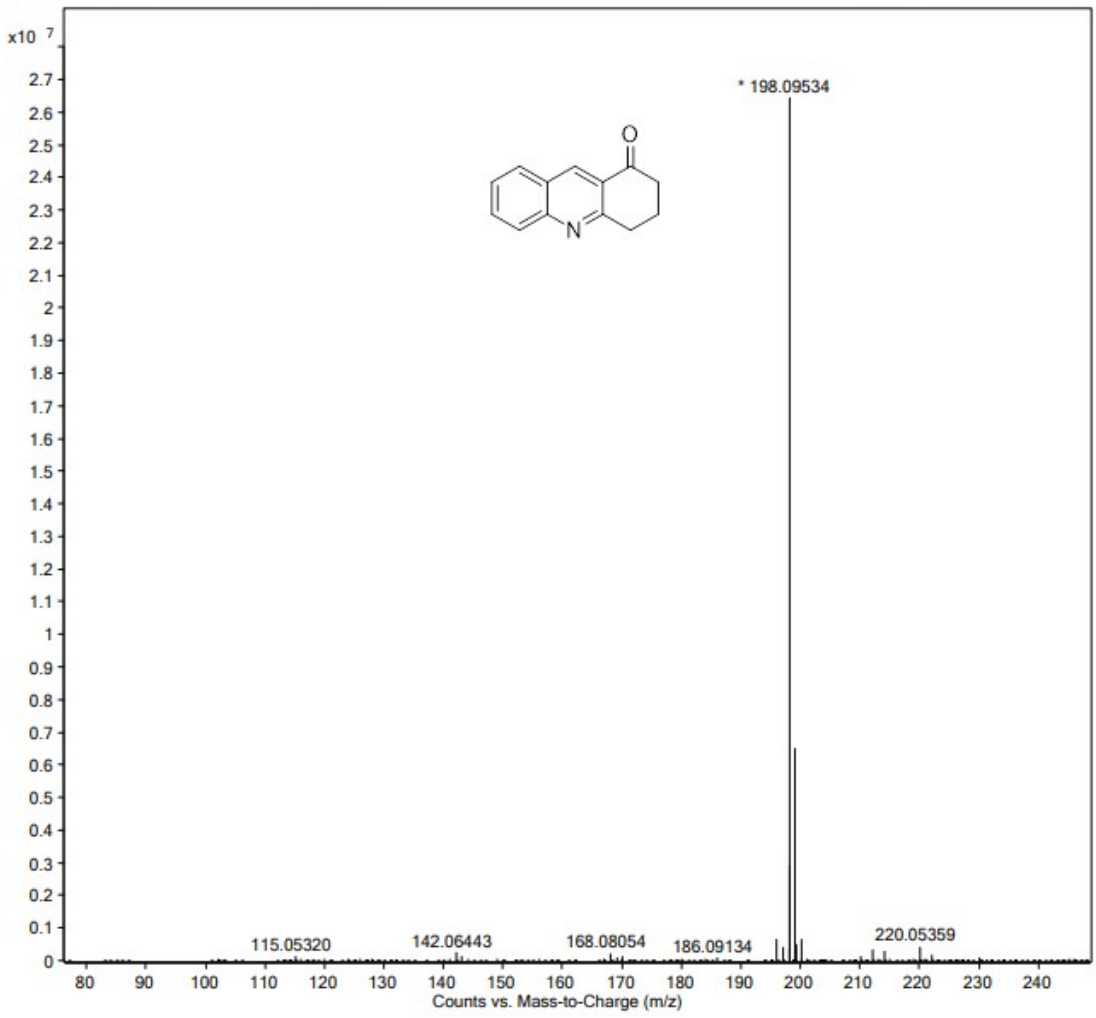
HRMS spectrum of 3a



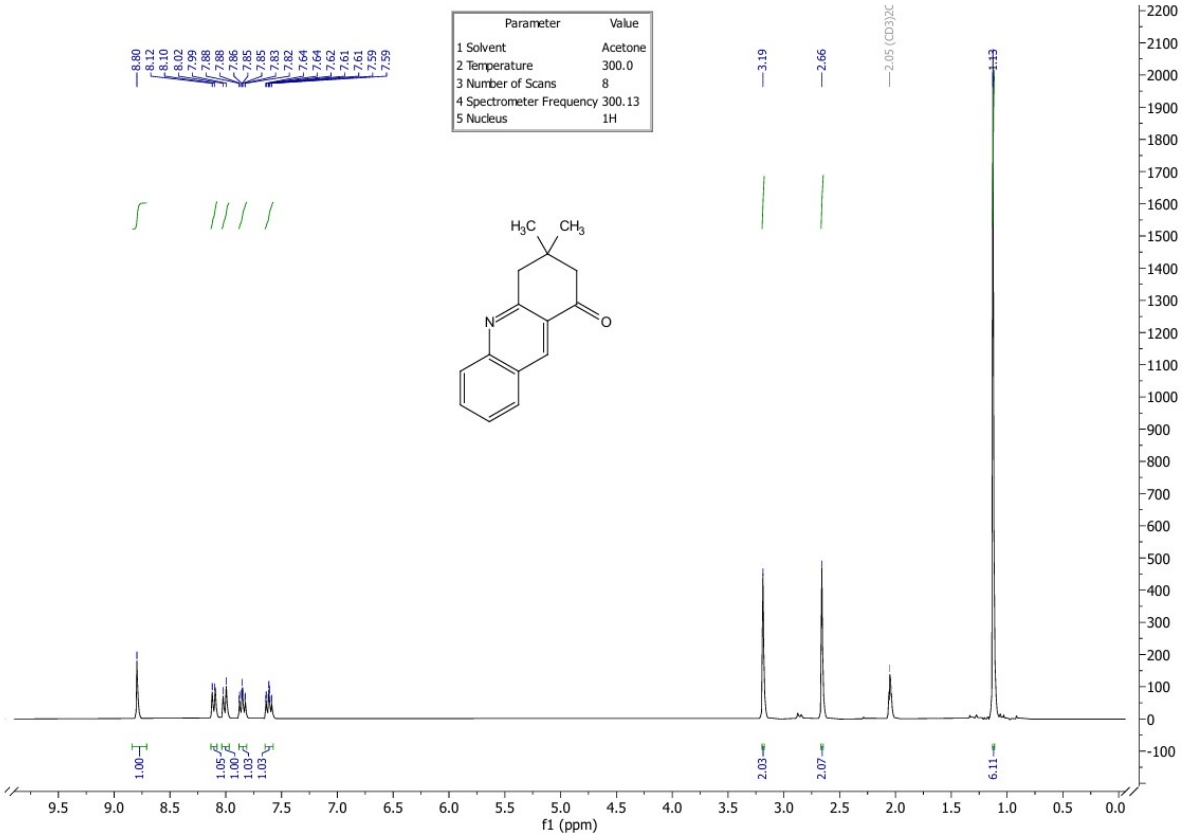
^{1}H NMR spectrum of 3b



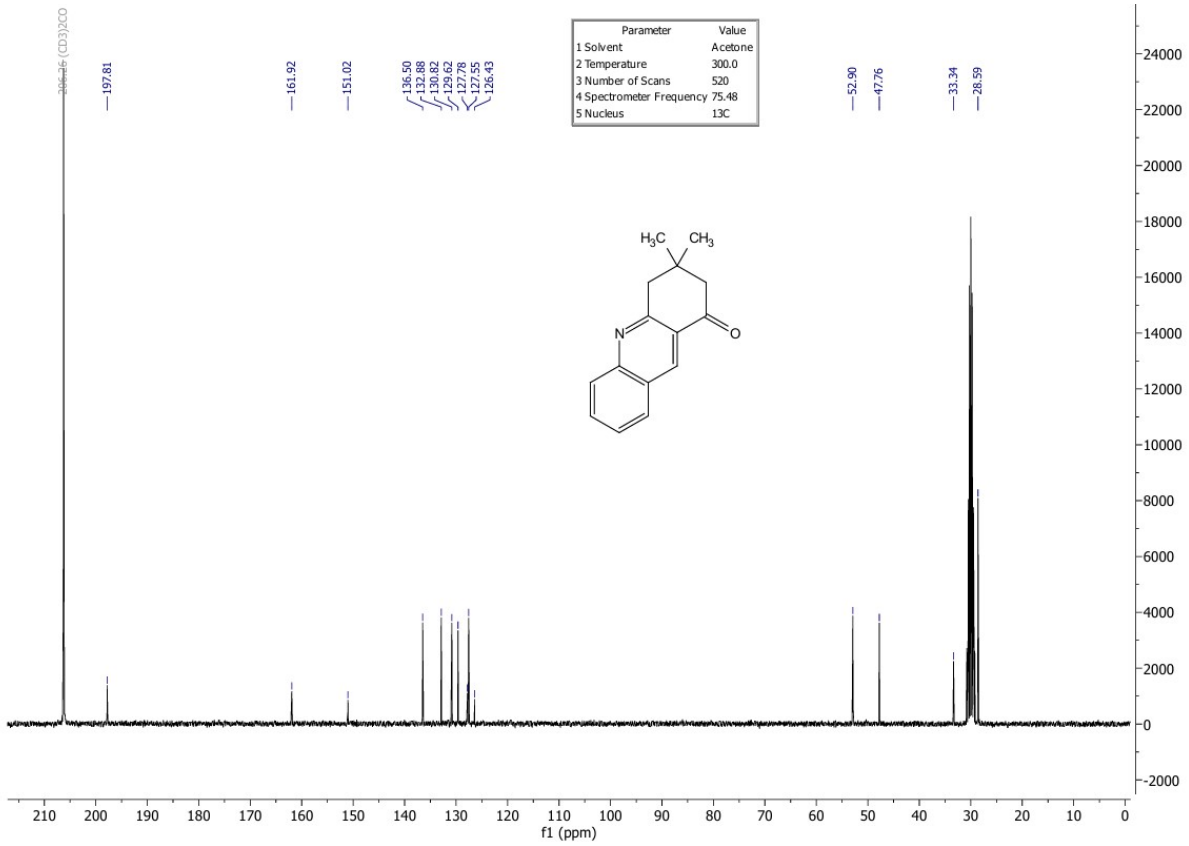
^{13}C NMR spectrum of 3b



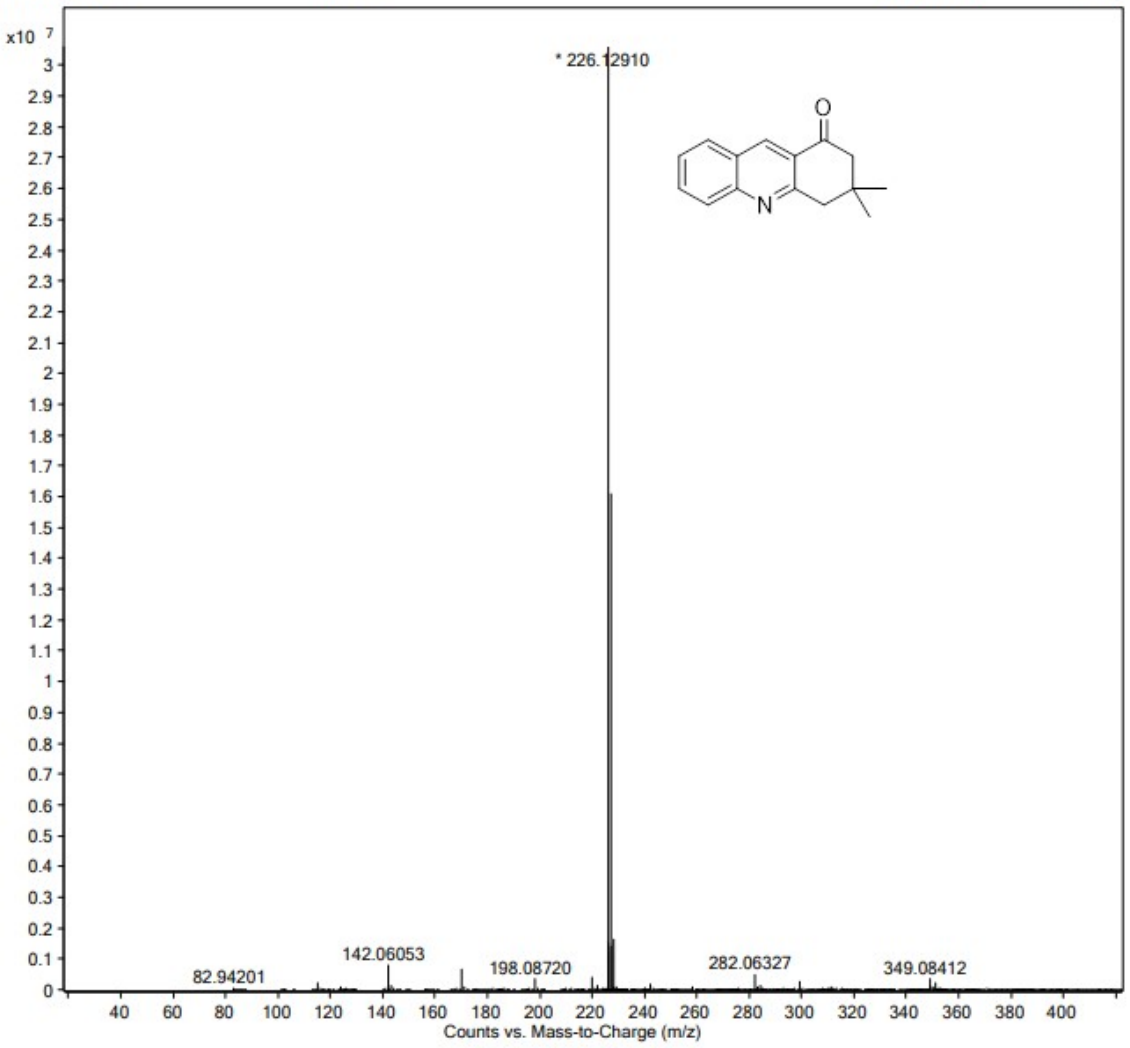
HRMS spectrum of 3b



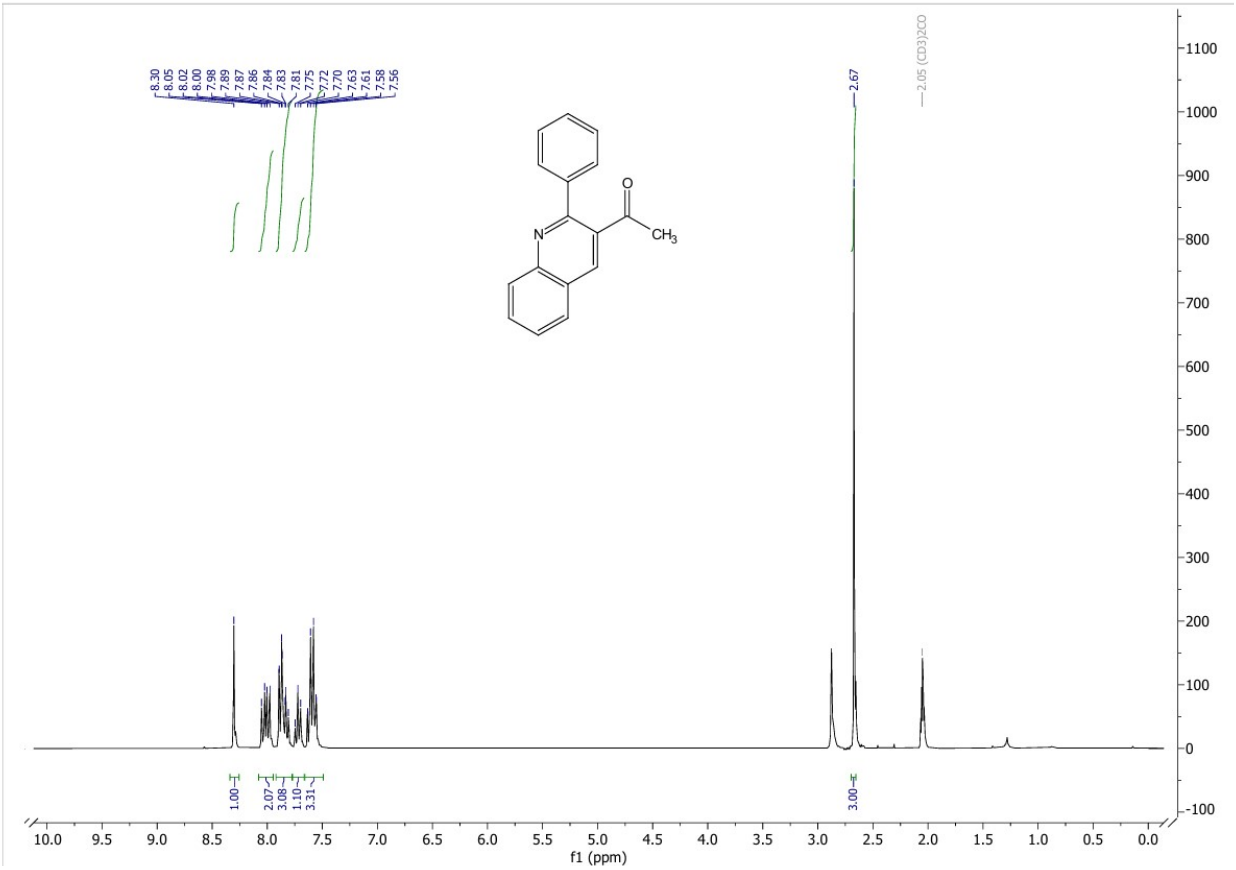
^{1}H NMR spectrum of 3c



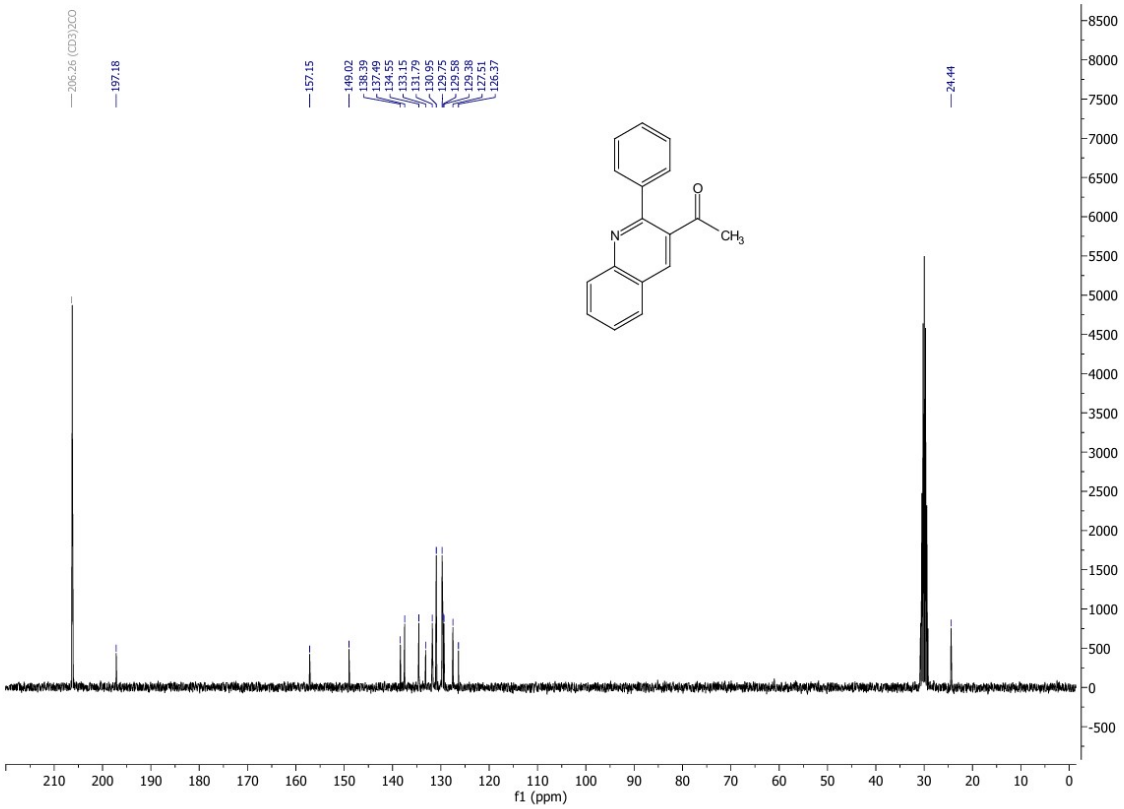
^{13}C NMR spectrum of 3c



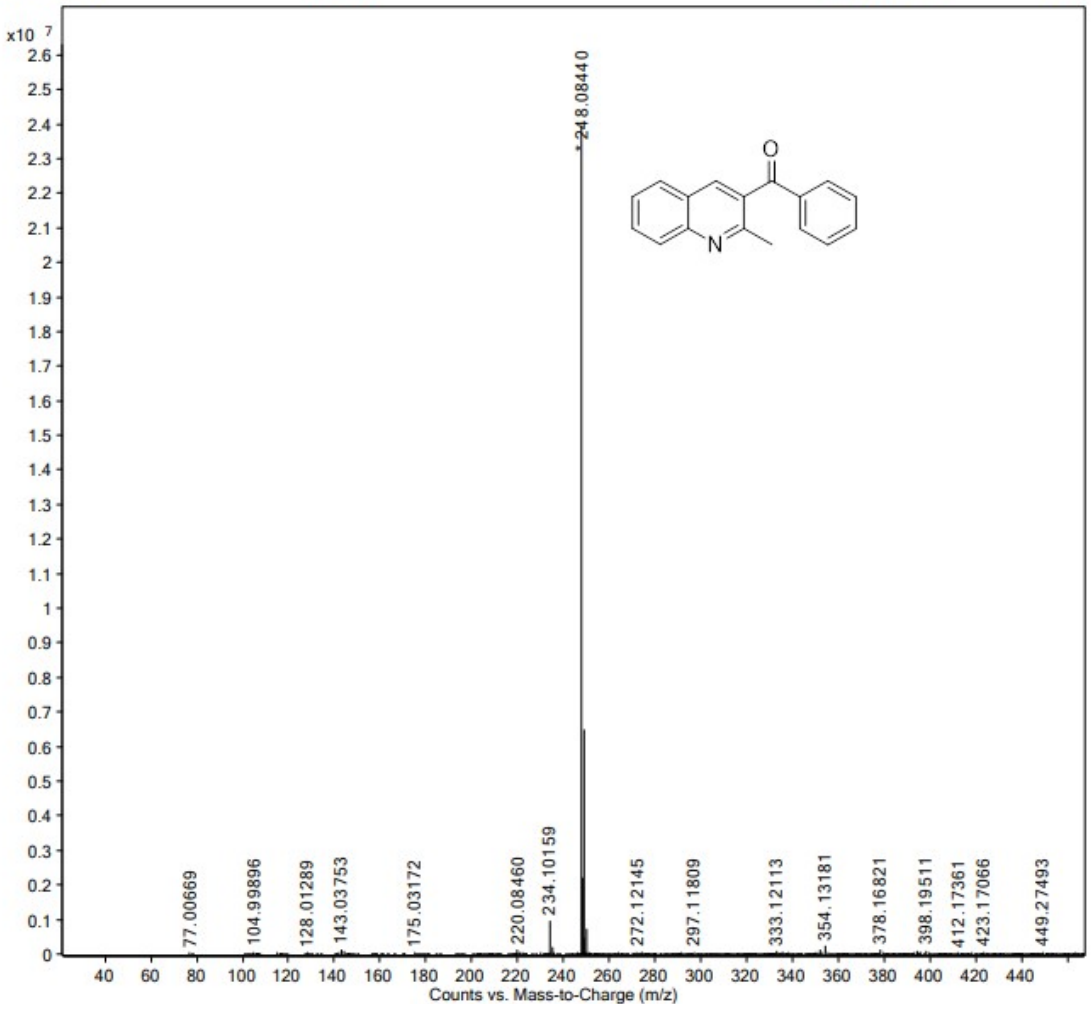
HRMS spectrum of 3c



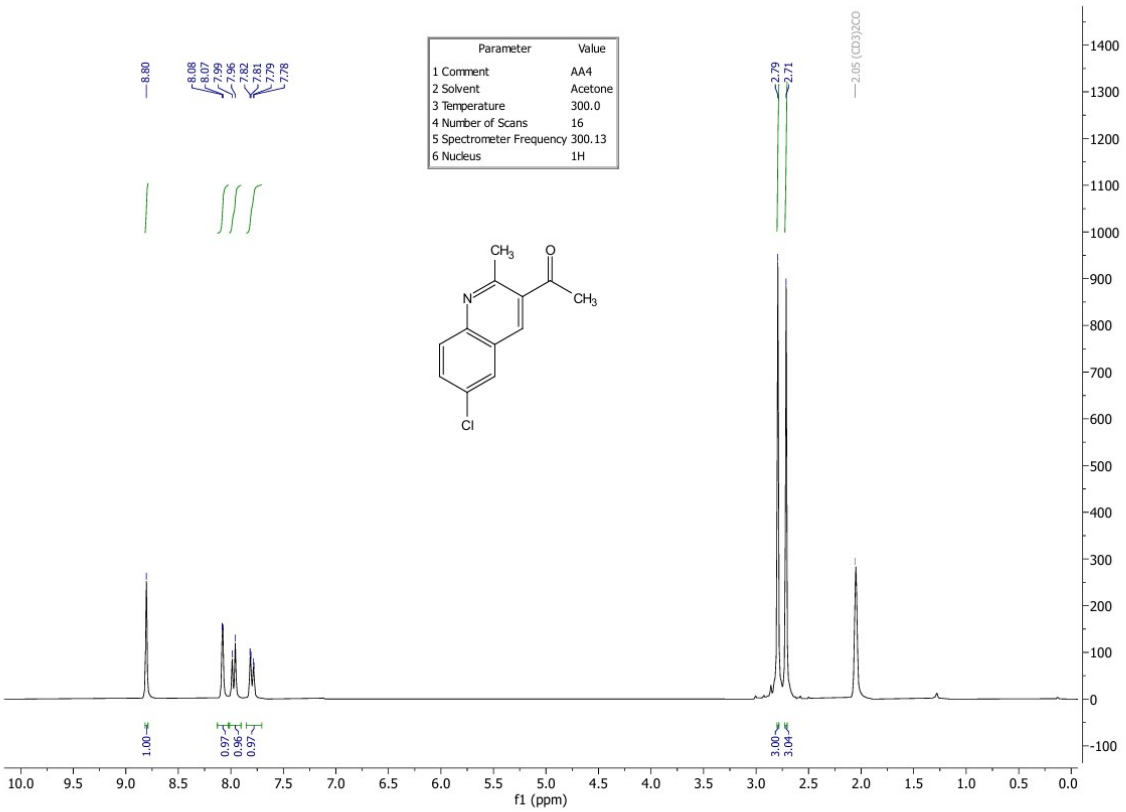
^{1}H NMR spectrum of 3d



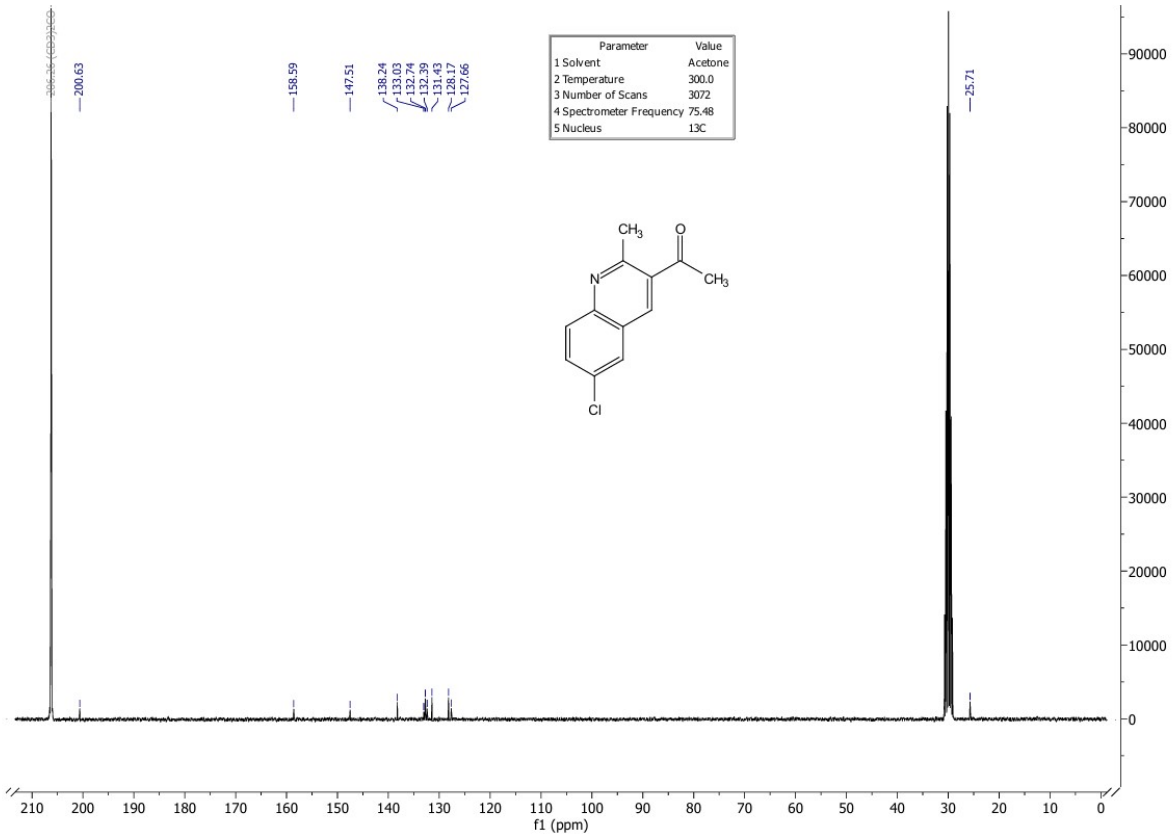
^{13}C NMR spectrum of 3d



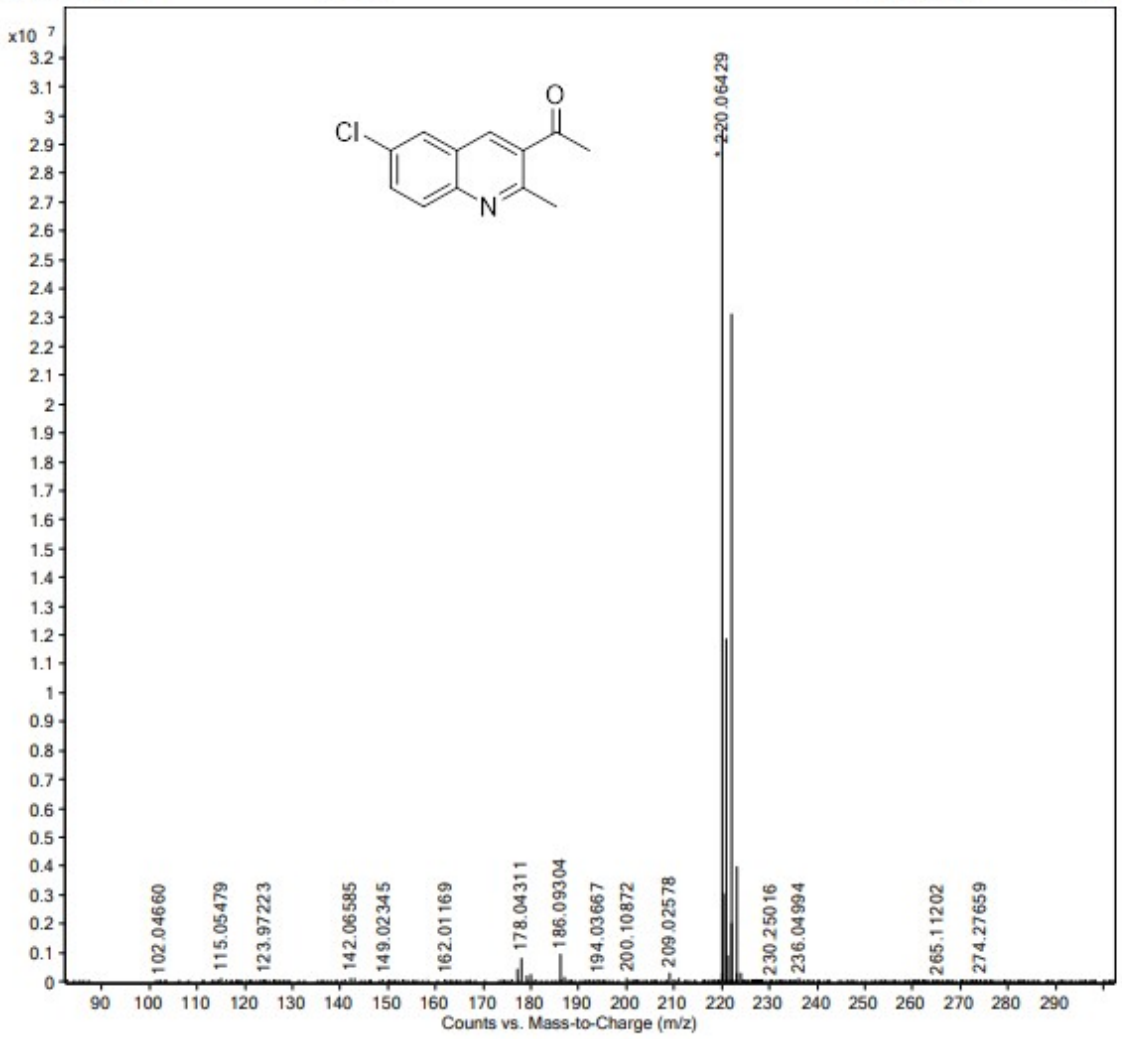
HRMS spectrum of 3d



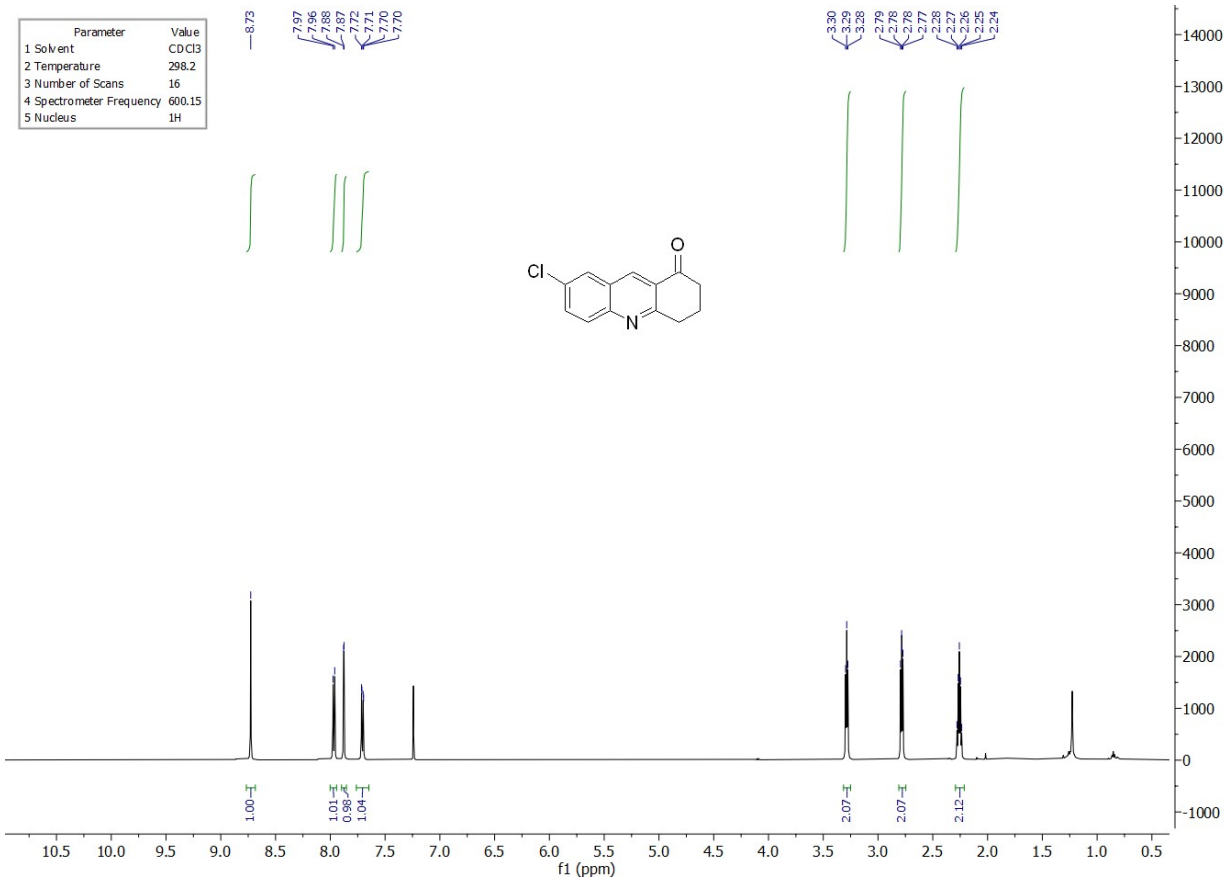
^{1}H NMR spectrum of 3e



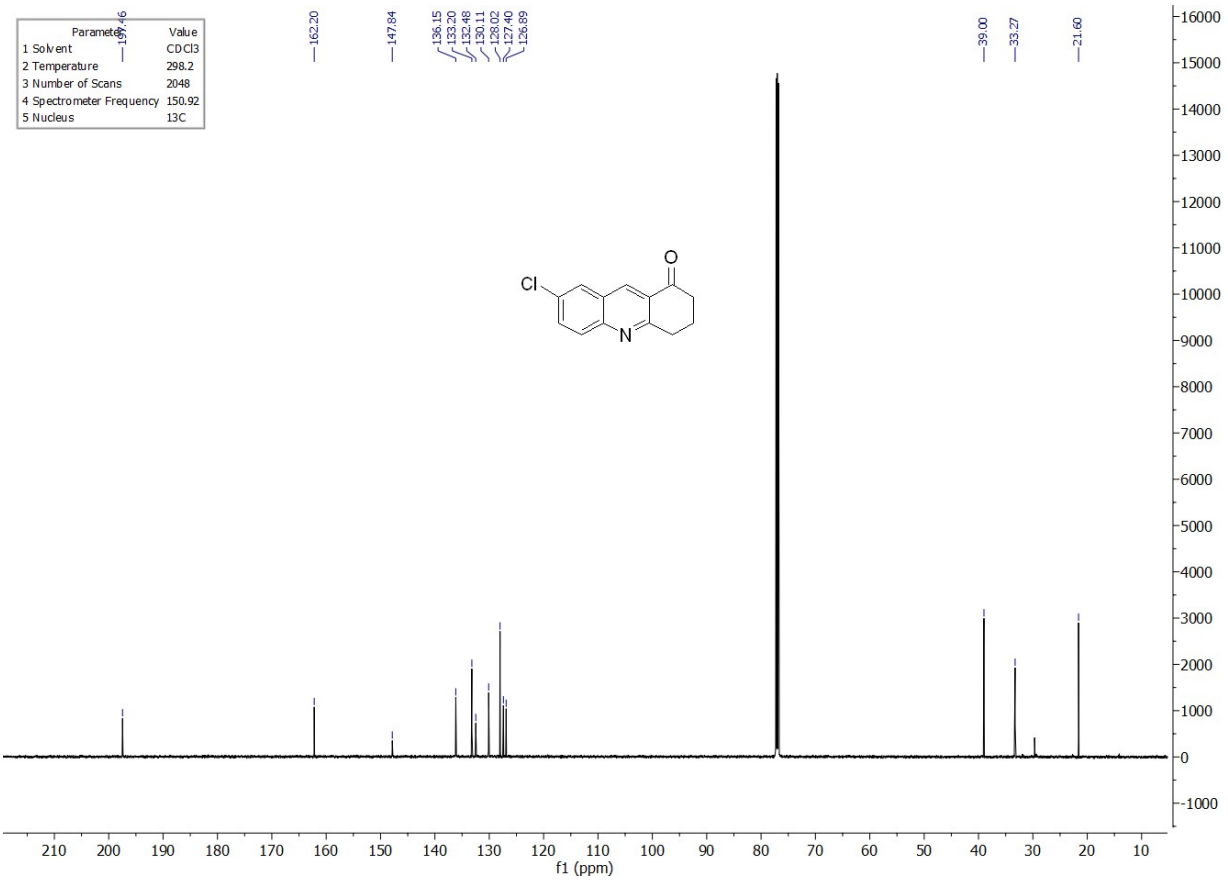
^{13}C NMR spectrum of 3e



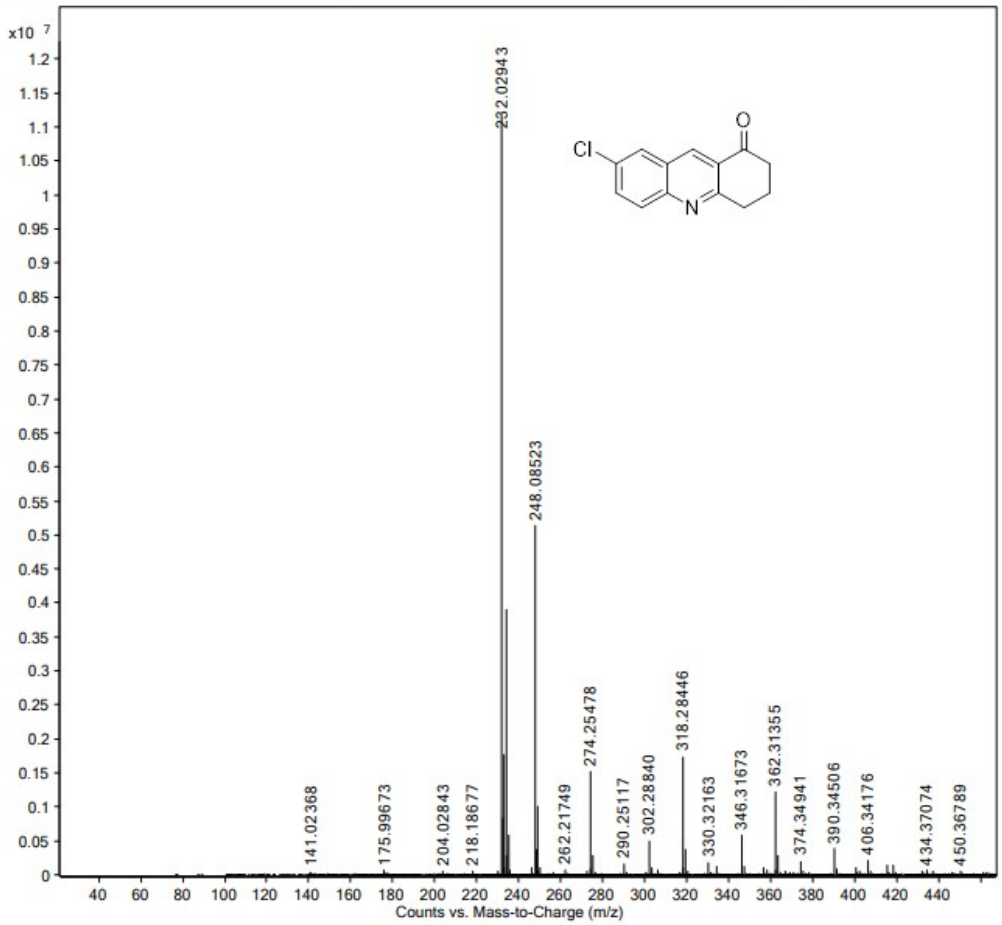
HRMS spectrum of 3e



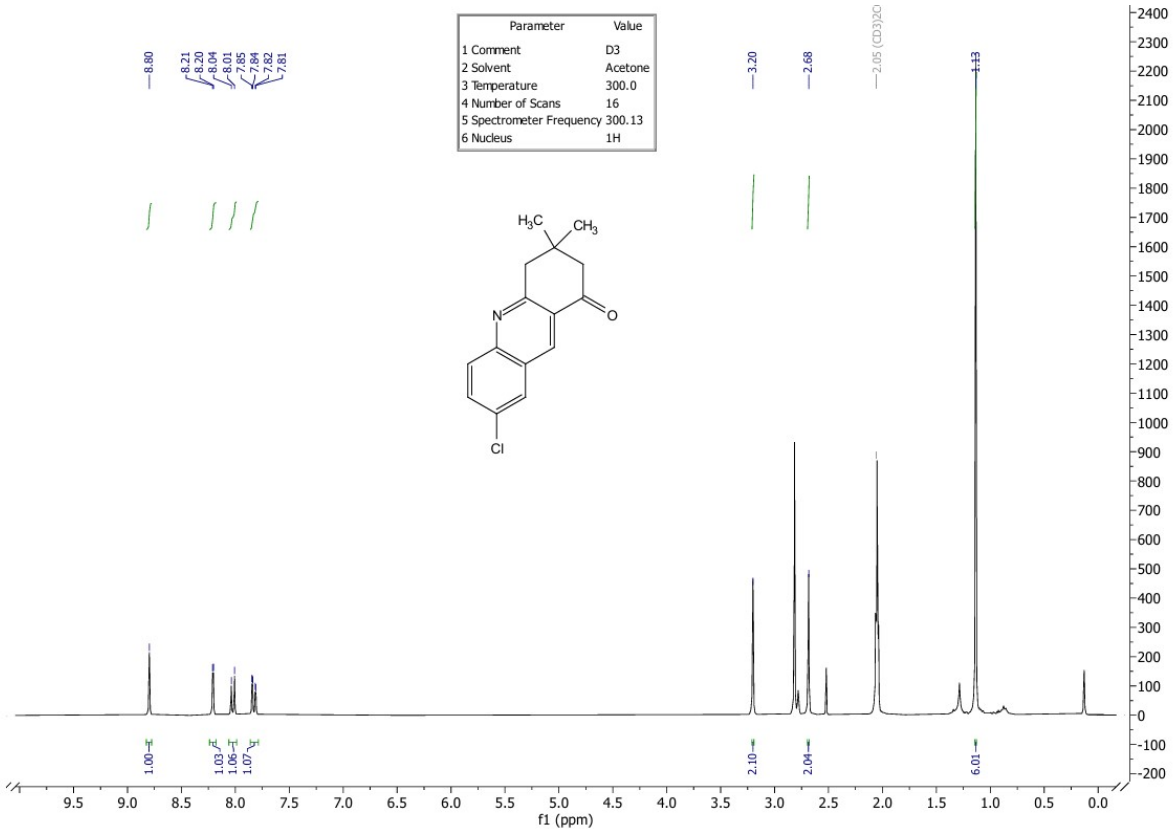
^{1}H NMR spectrum of 3f



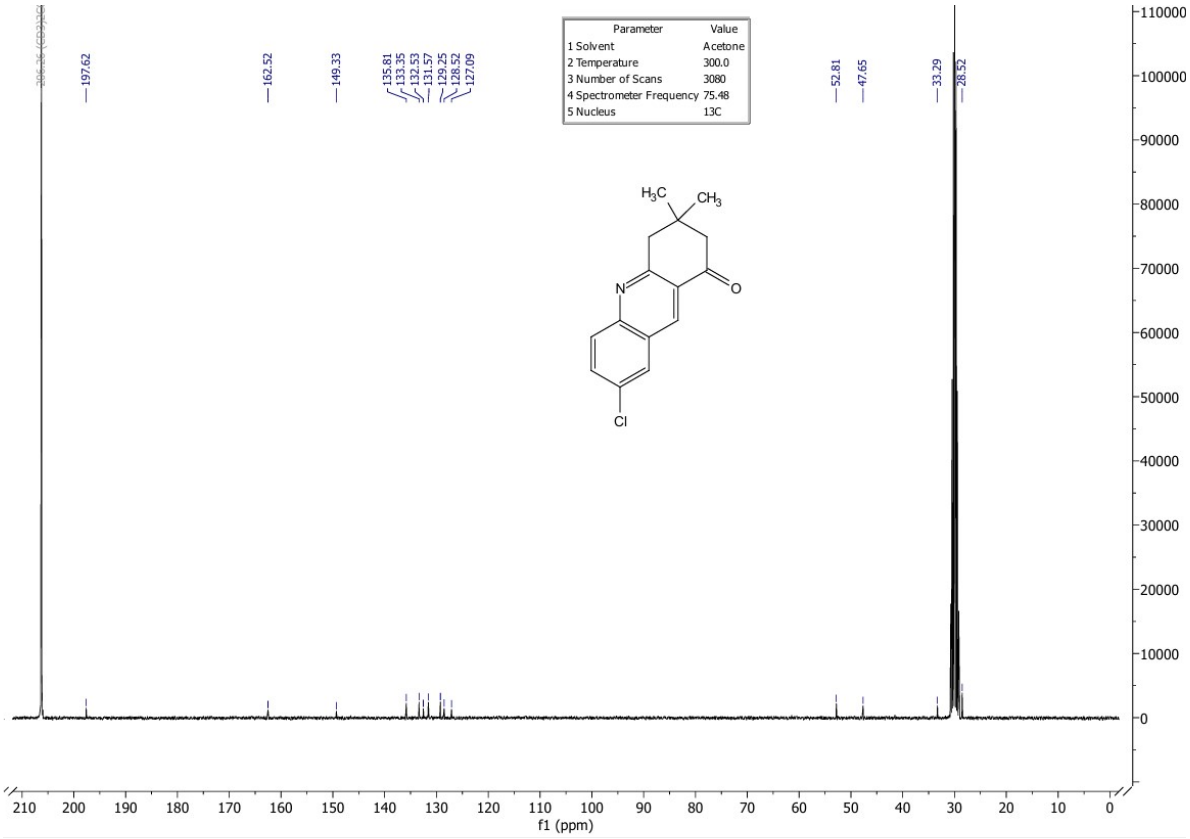
^{13}C NMR spectrum of 3f



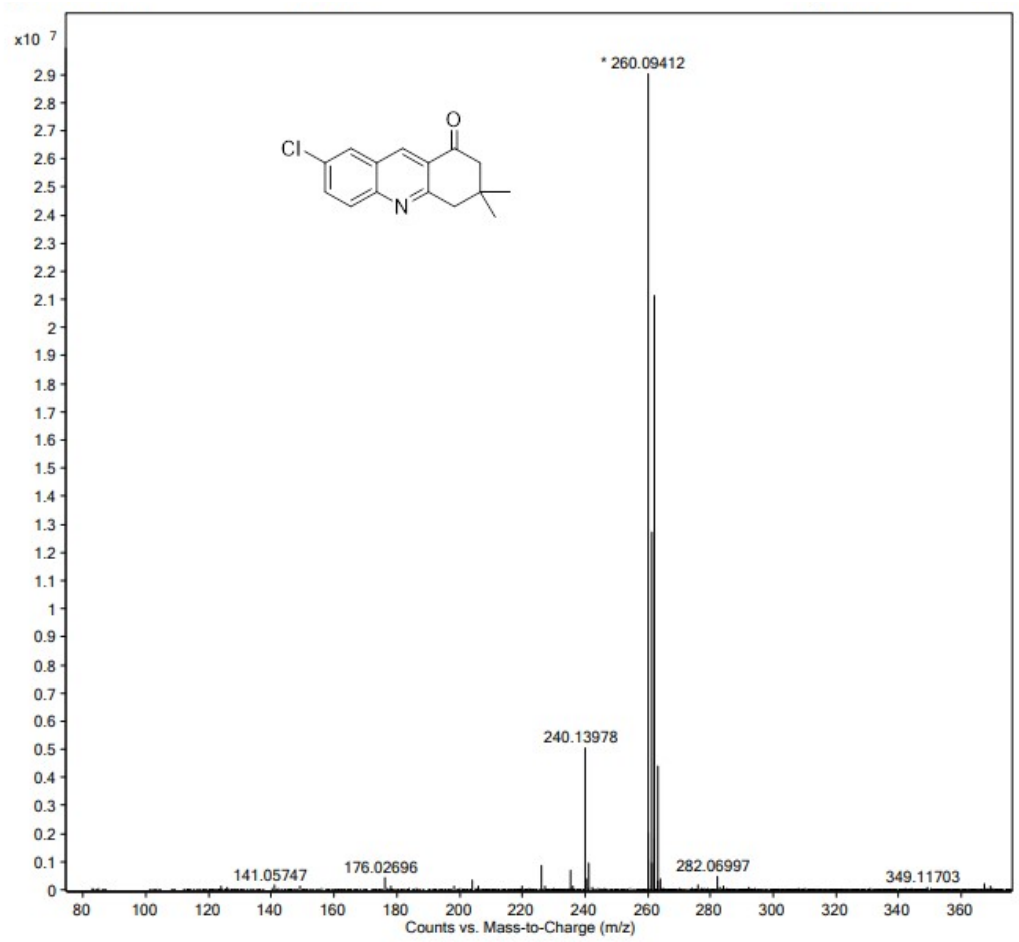
HRMS spectrum of 3f



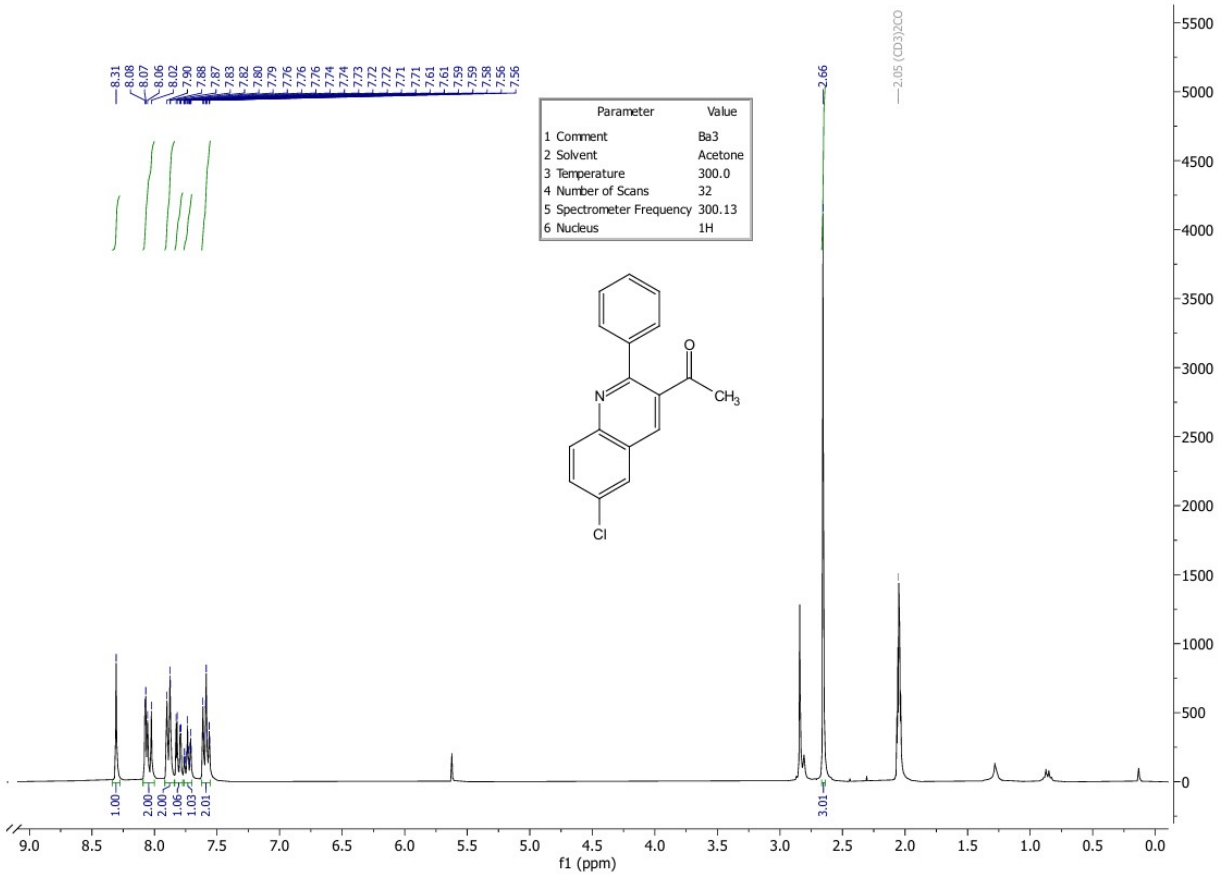
^{1}H NMR spectrum of 3g



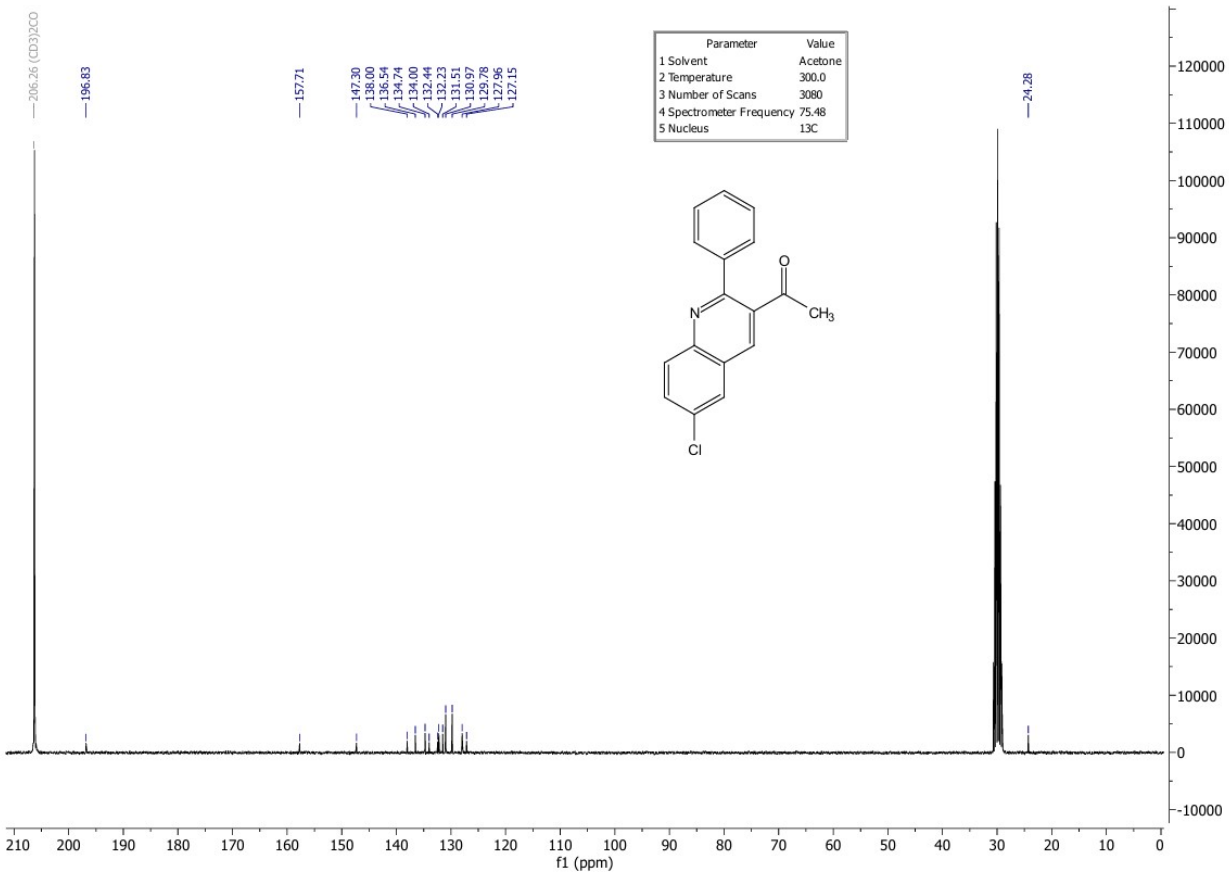
^{13}C NMR spectrum of 3g



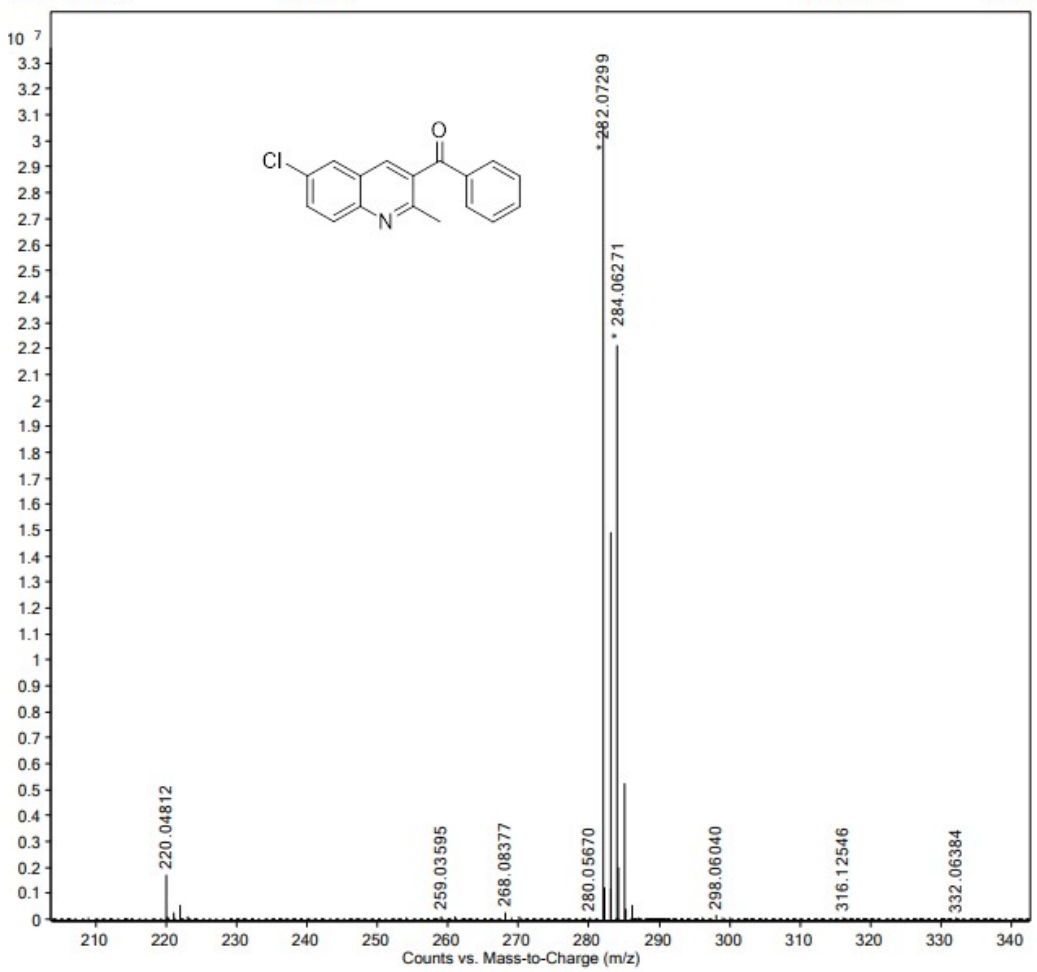
HRMS spectrum of 3g



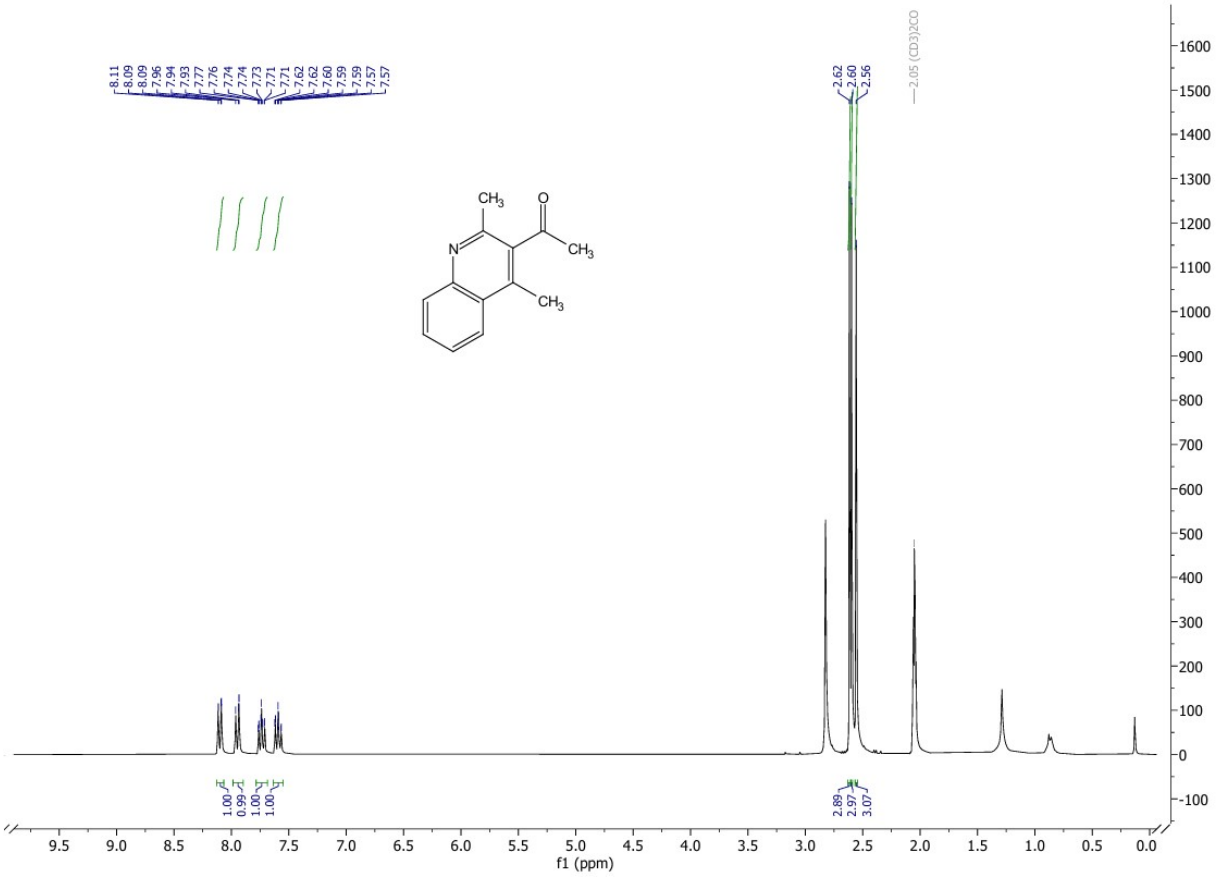
^{1}H NMR spectrum of 3h



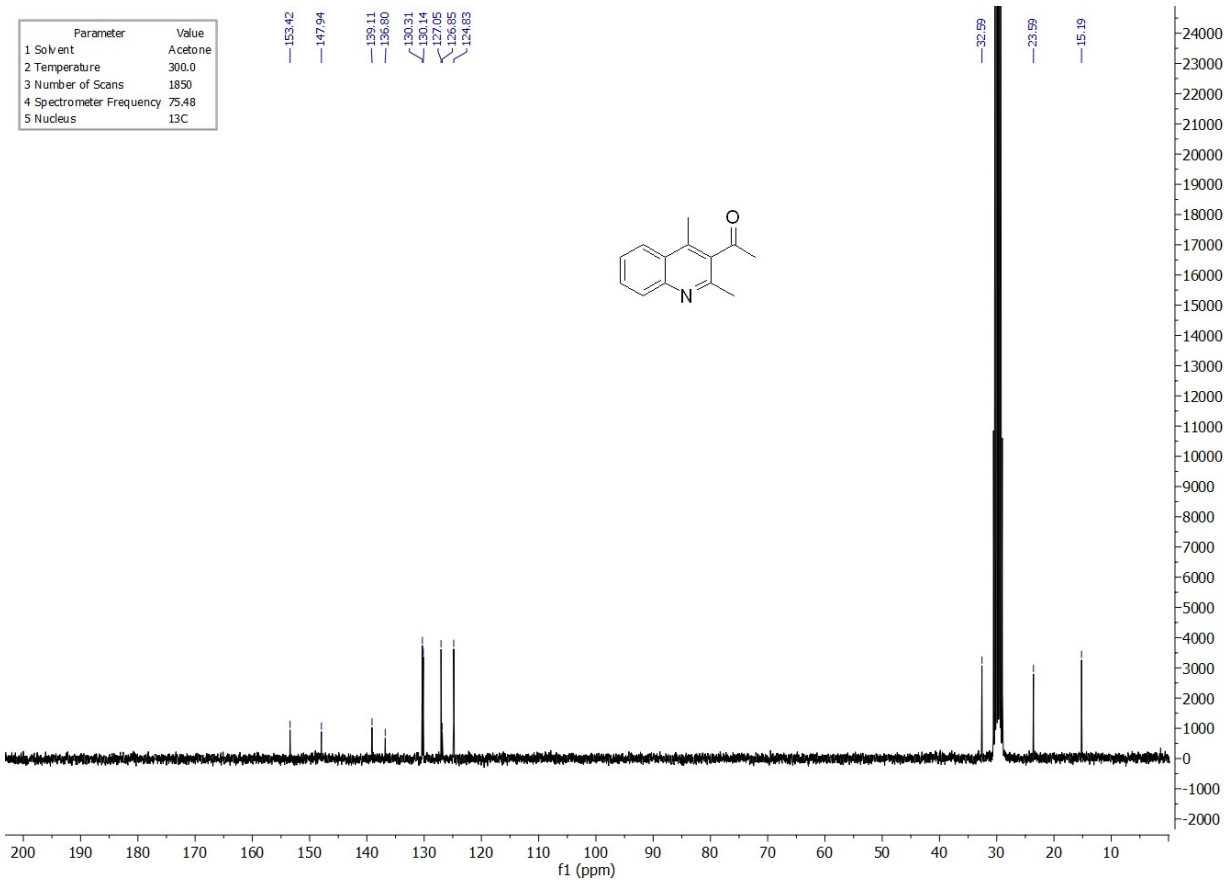
^{13}C NMR spectrum of 3h



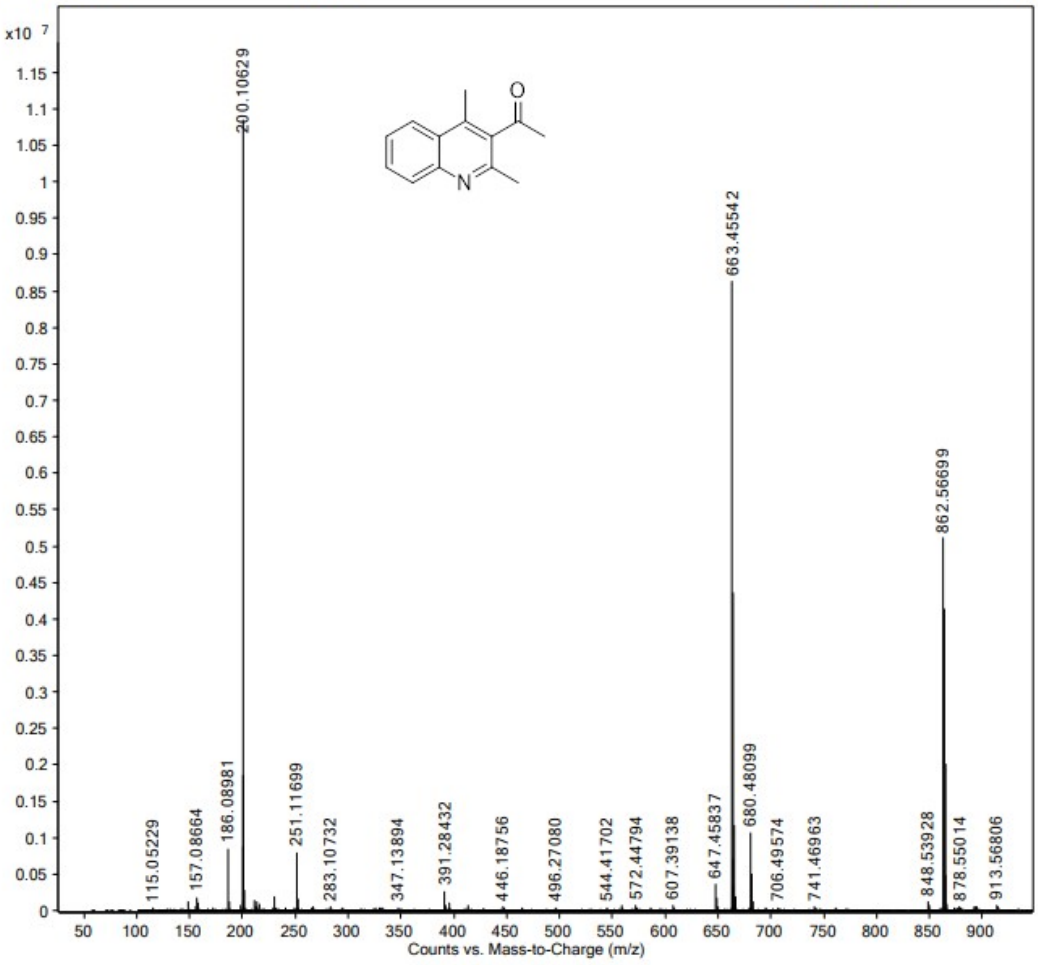
HRMS spectrum of 3h



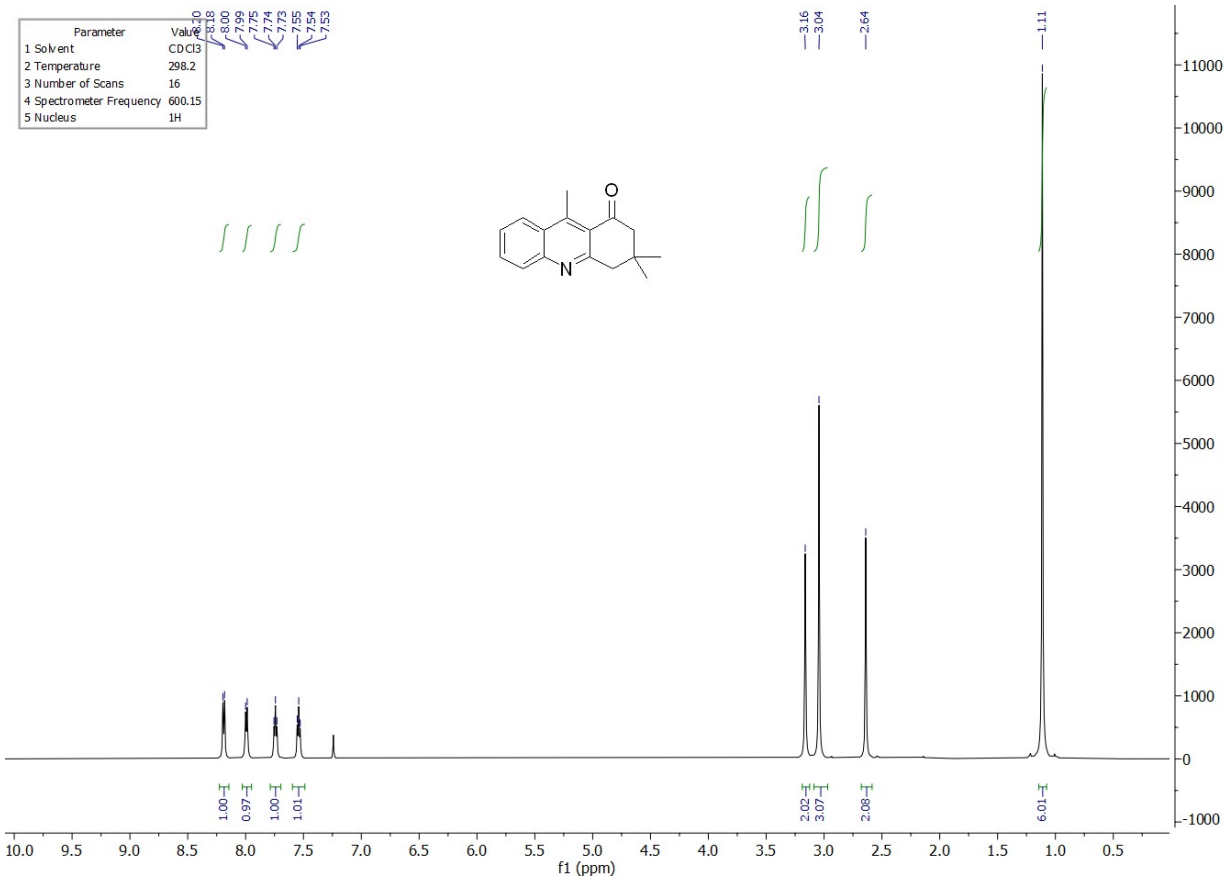
^{1}H NMR spectrum of 3i



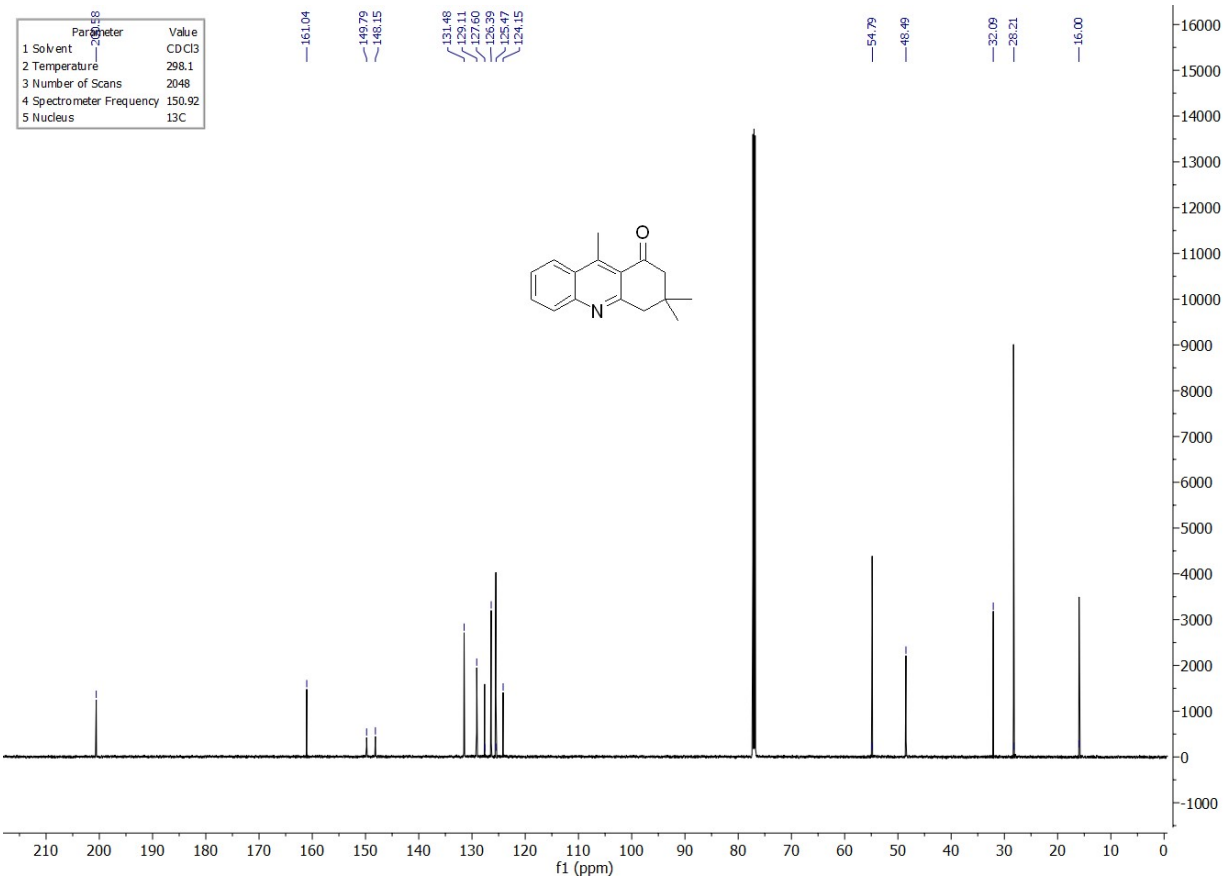
^{13}C NMR spectrum of 3i



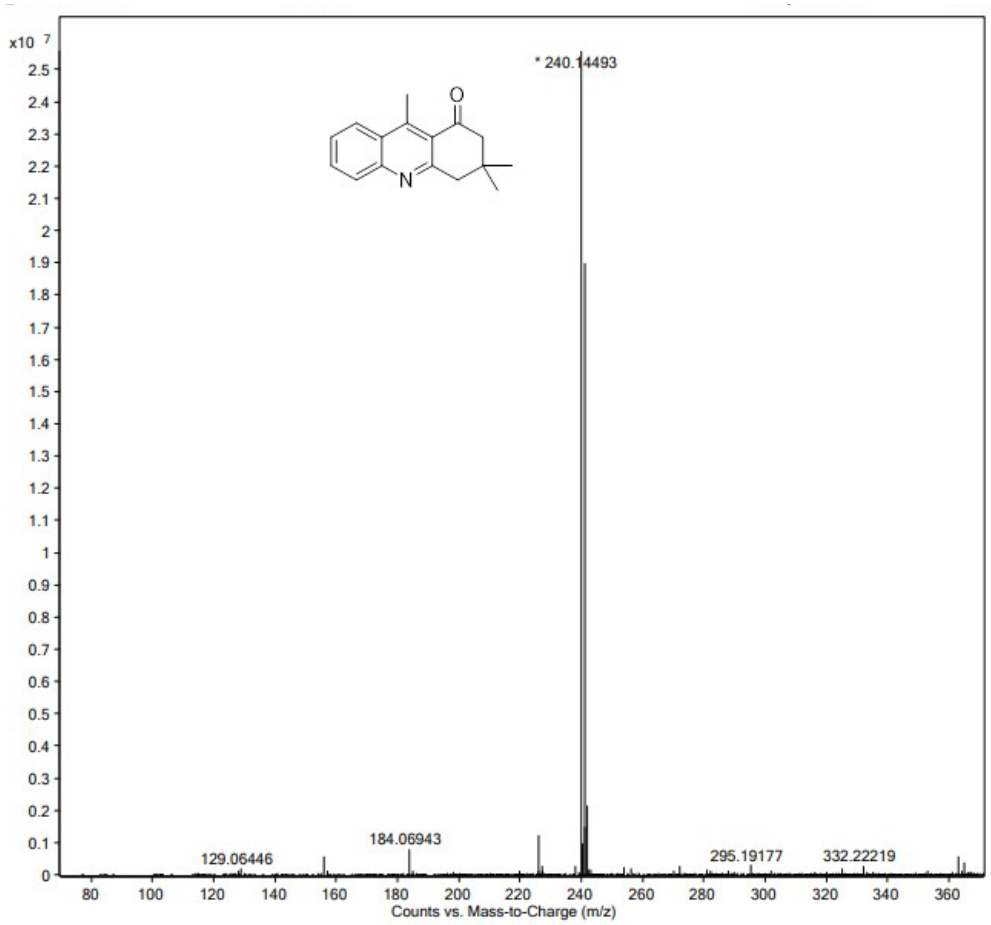
HRMS spectrum of 3i



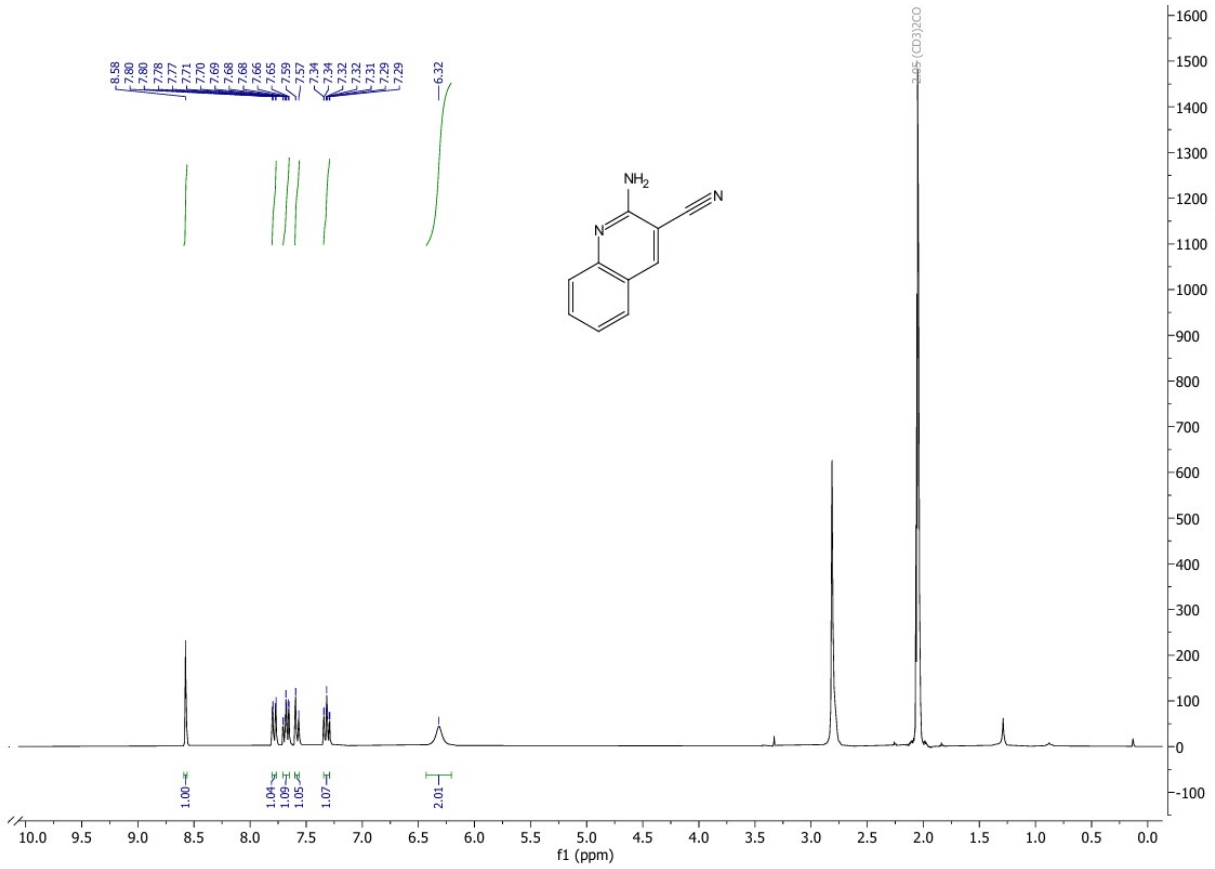
^{1}H NMR spectrum of 3j



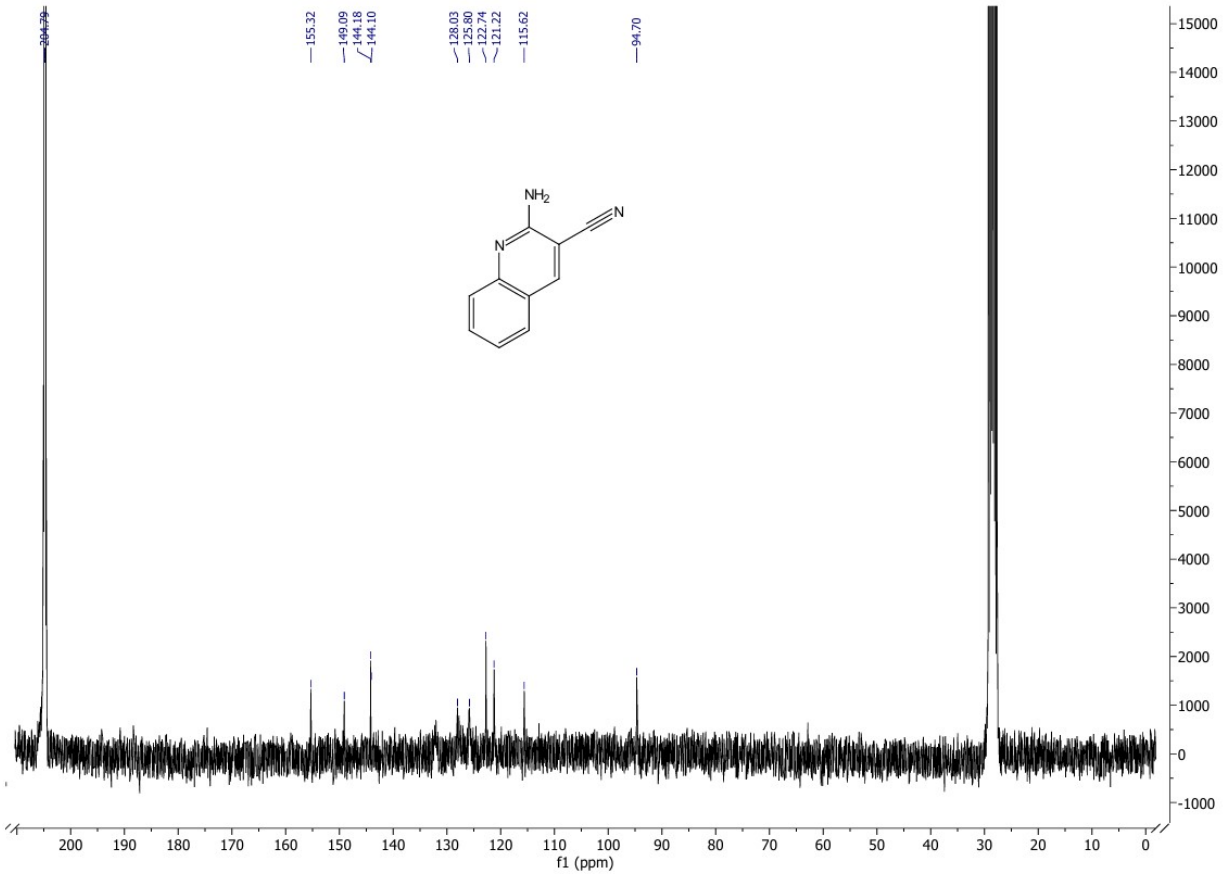
^{13}C NMR spectrum of 3j



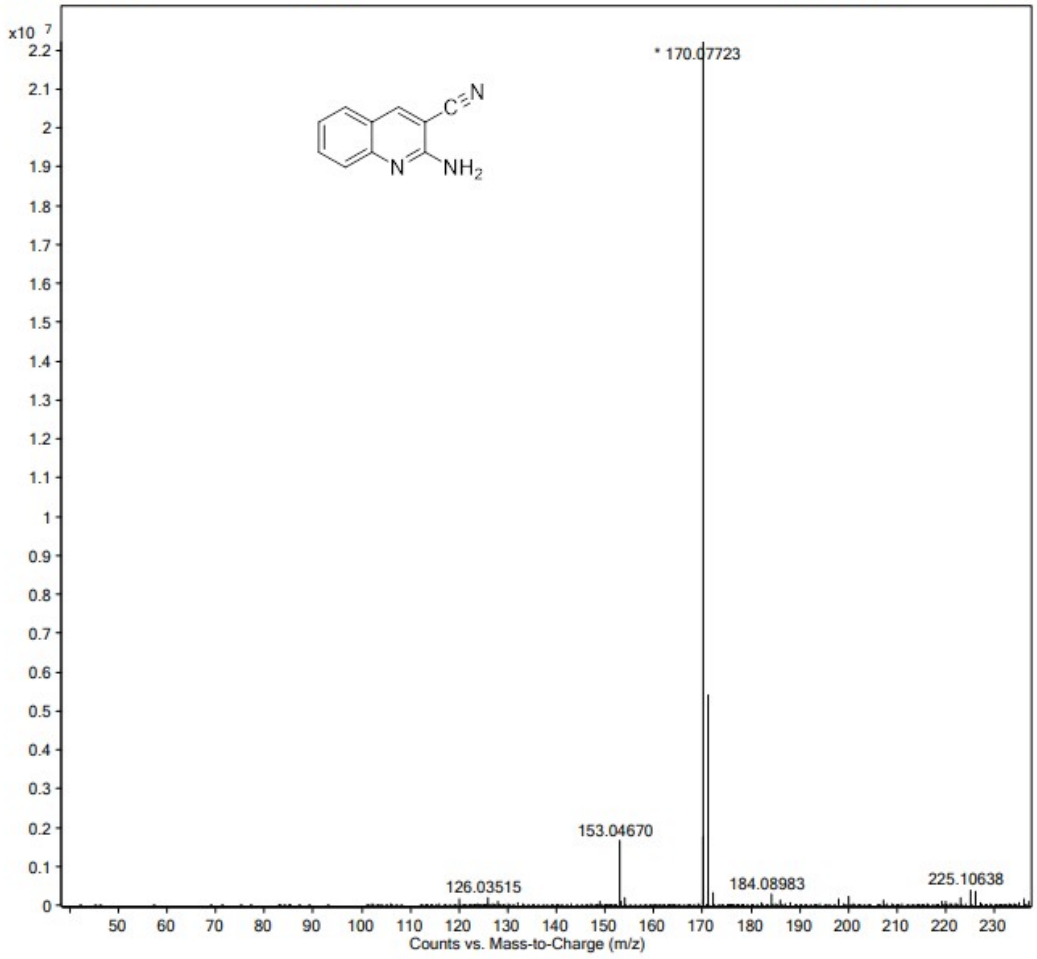
HRMS spectrum of 3j



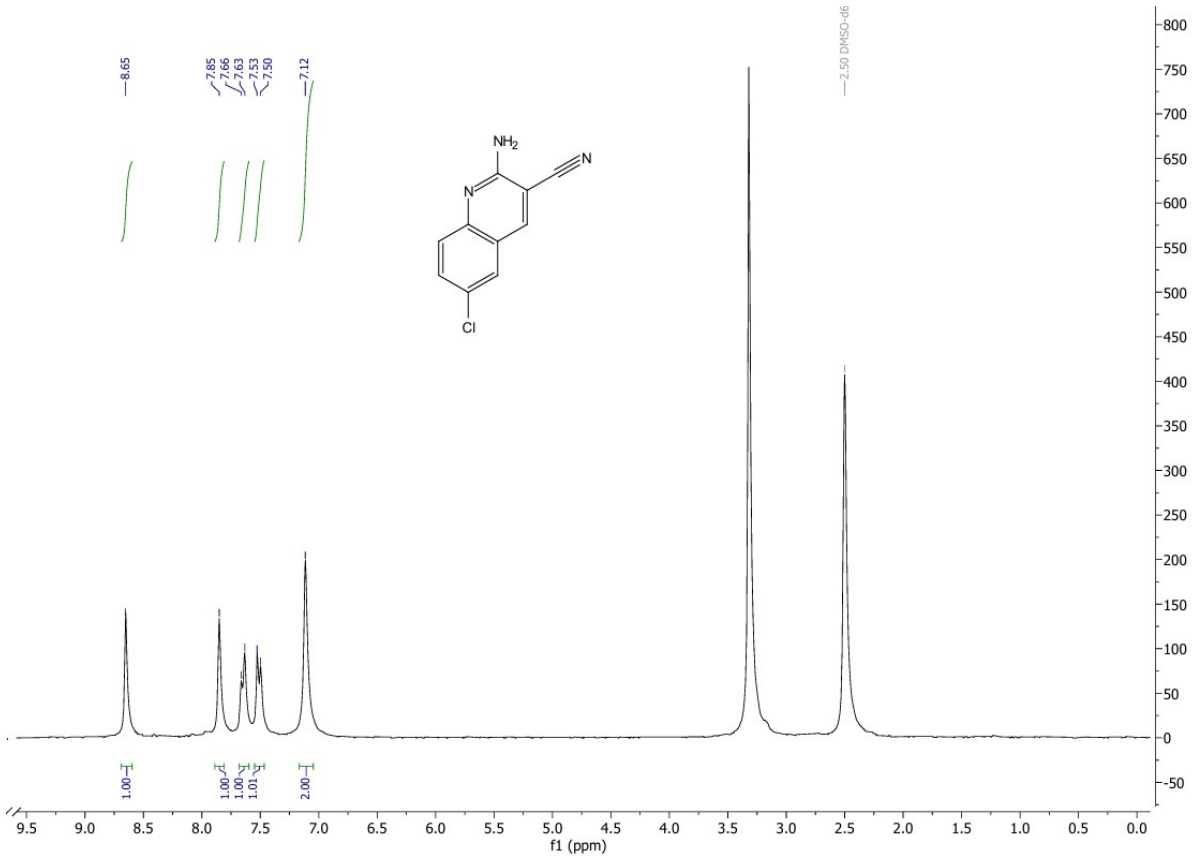
^{1}H NMR spectrum of 3k



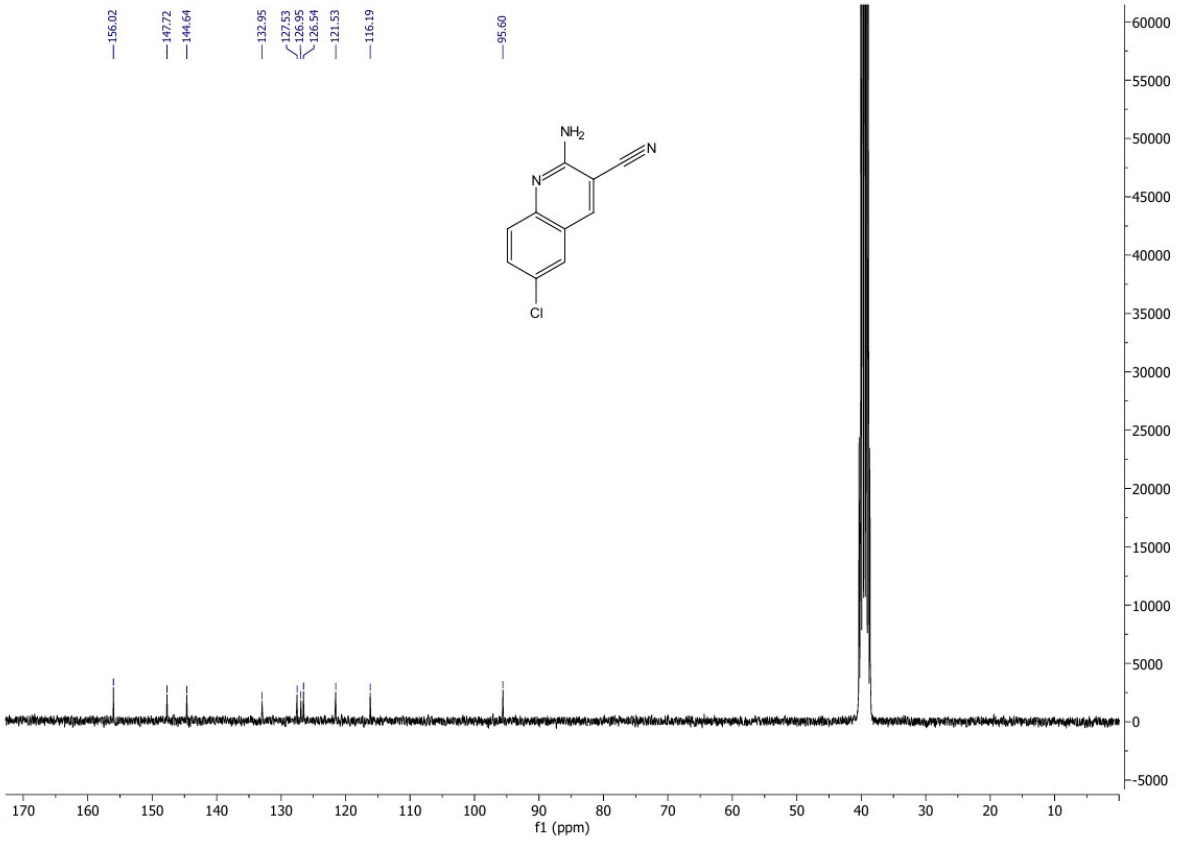
^{13}C NMR spectrum of 3k



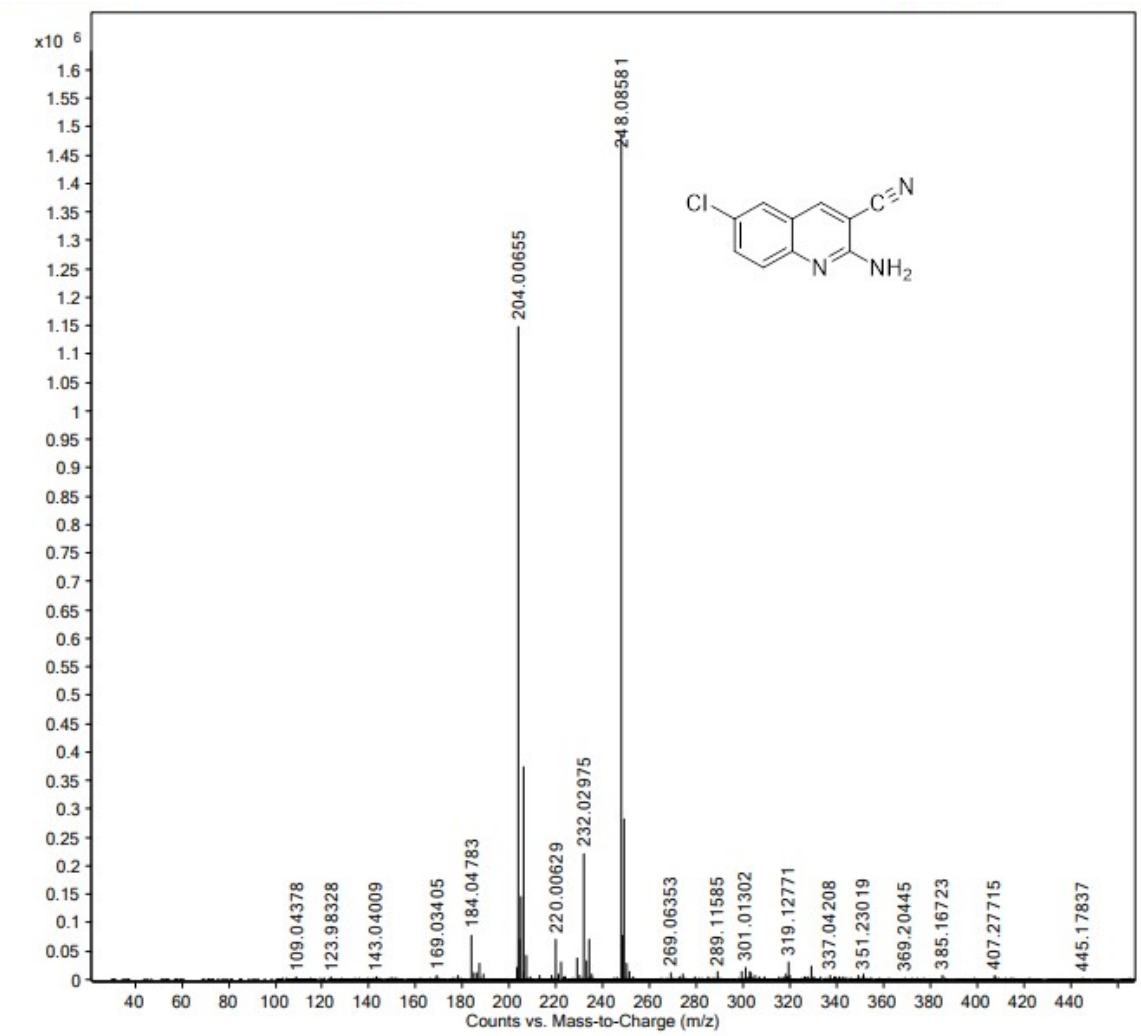
HRMS spectrum of 3k



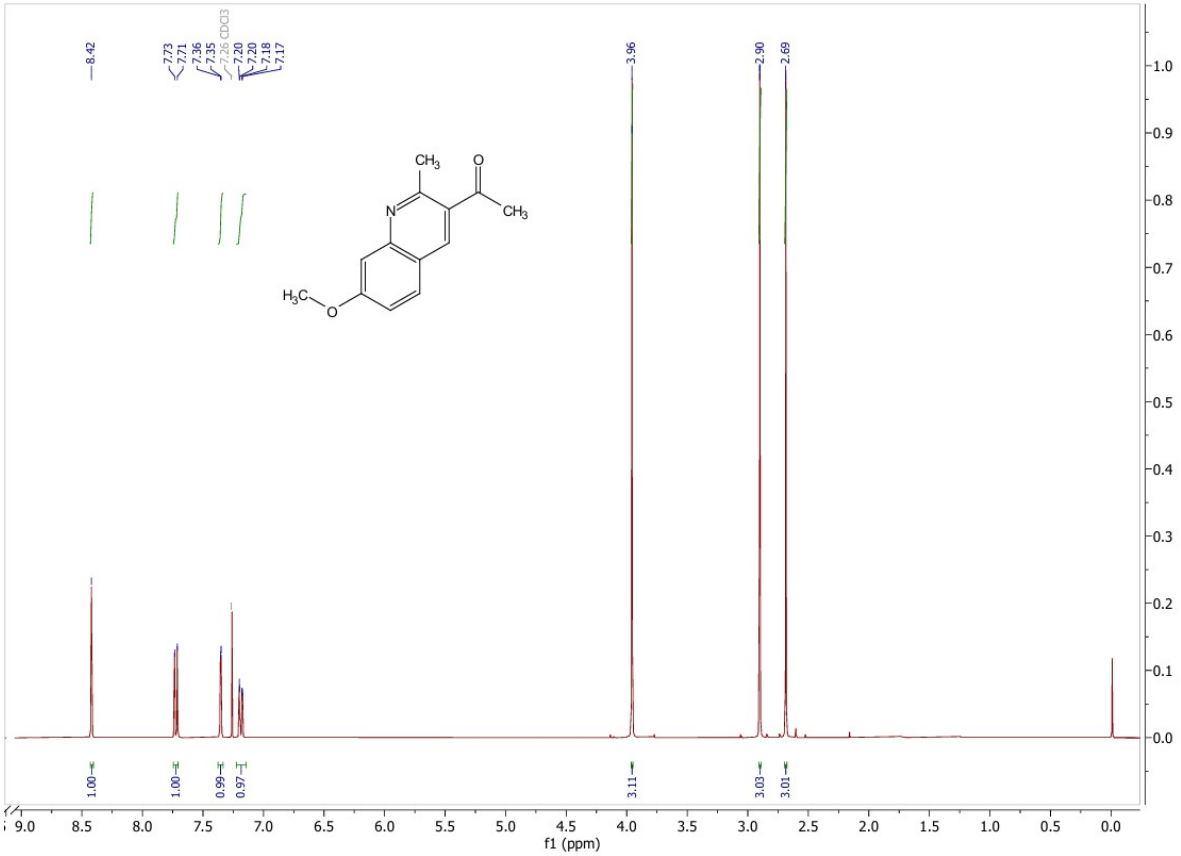
^{1}H NMR spectrum of 3l



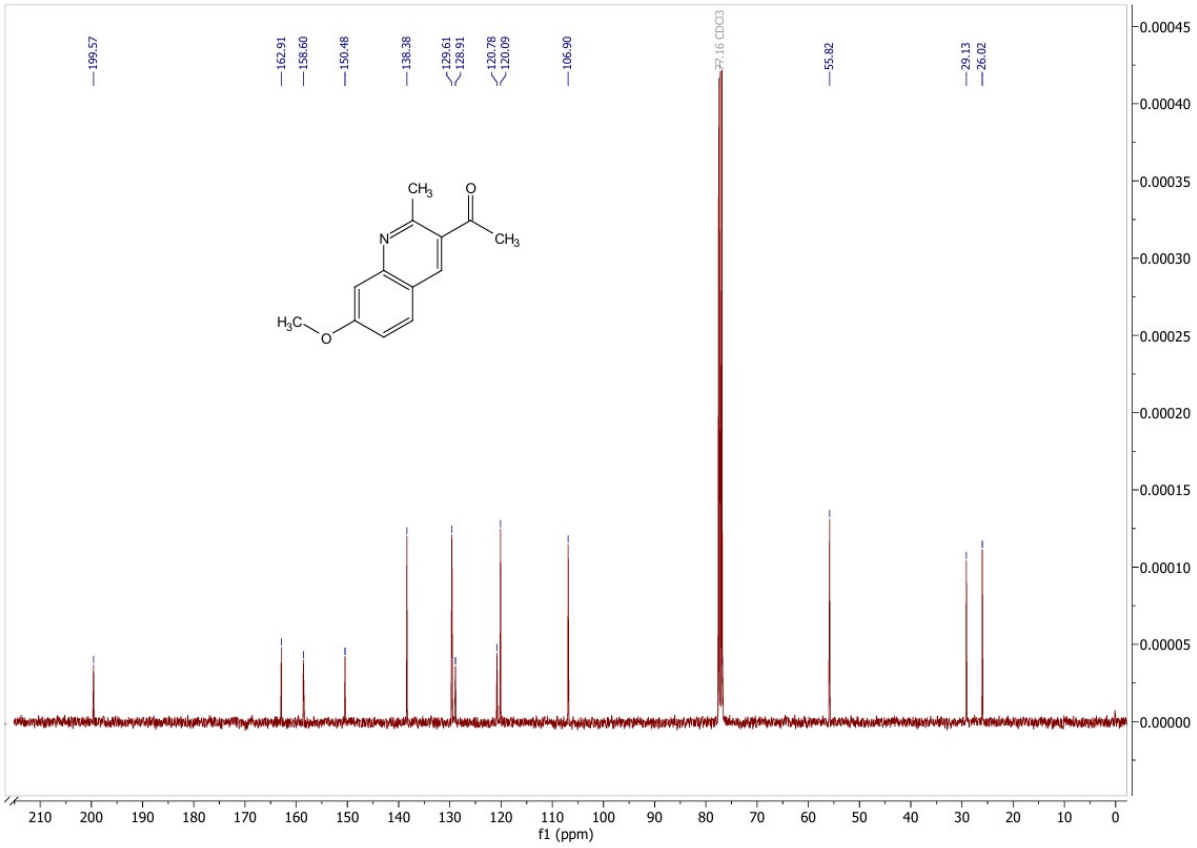
^{13}C NMR spectrum of 3l



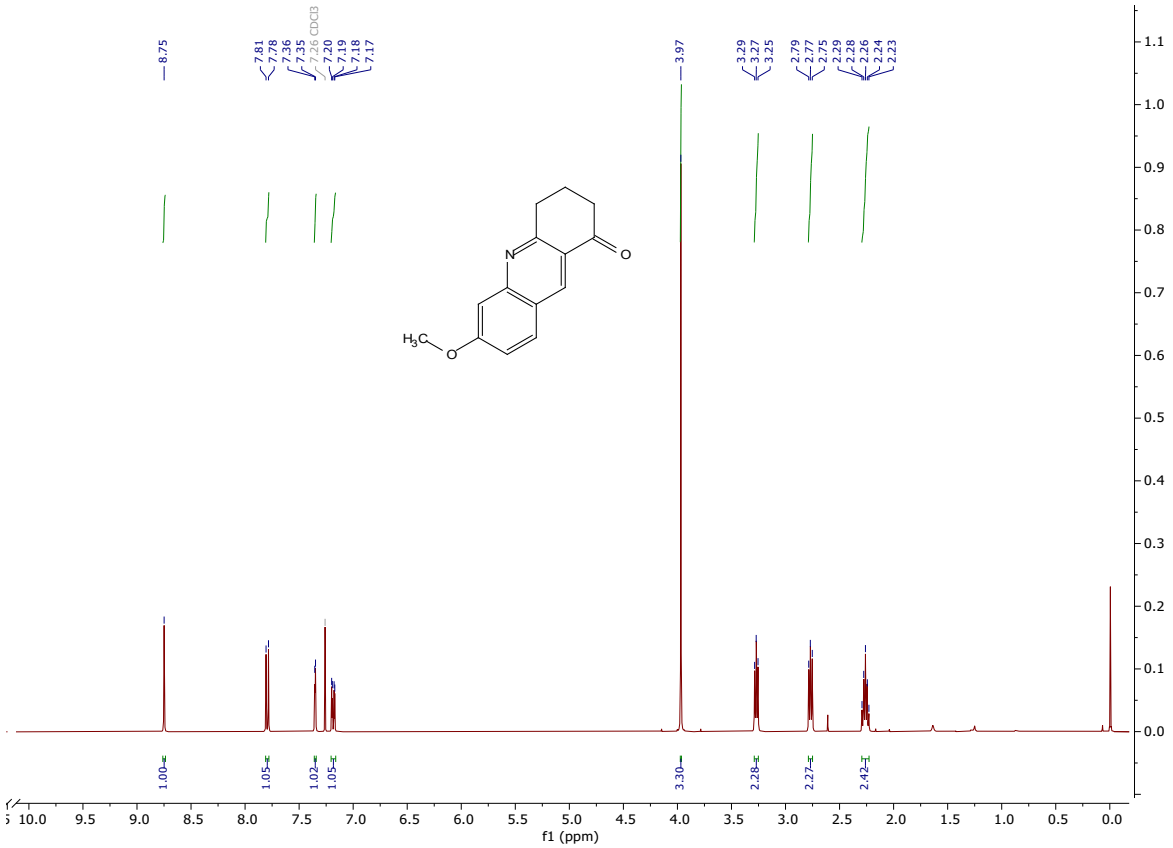
HRMS spectrum of 3l



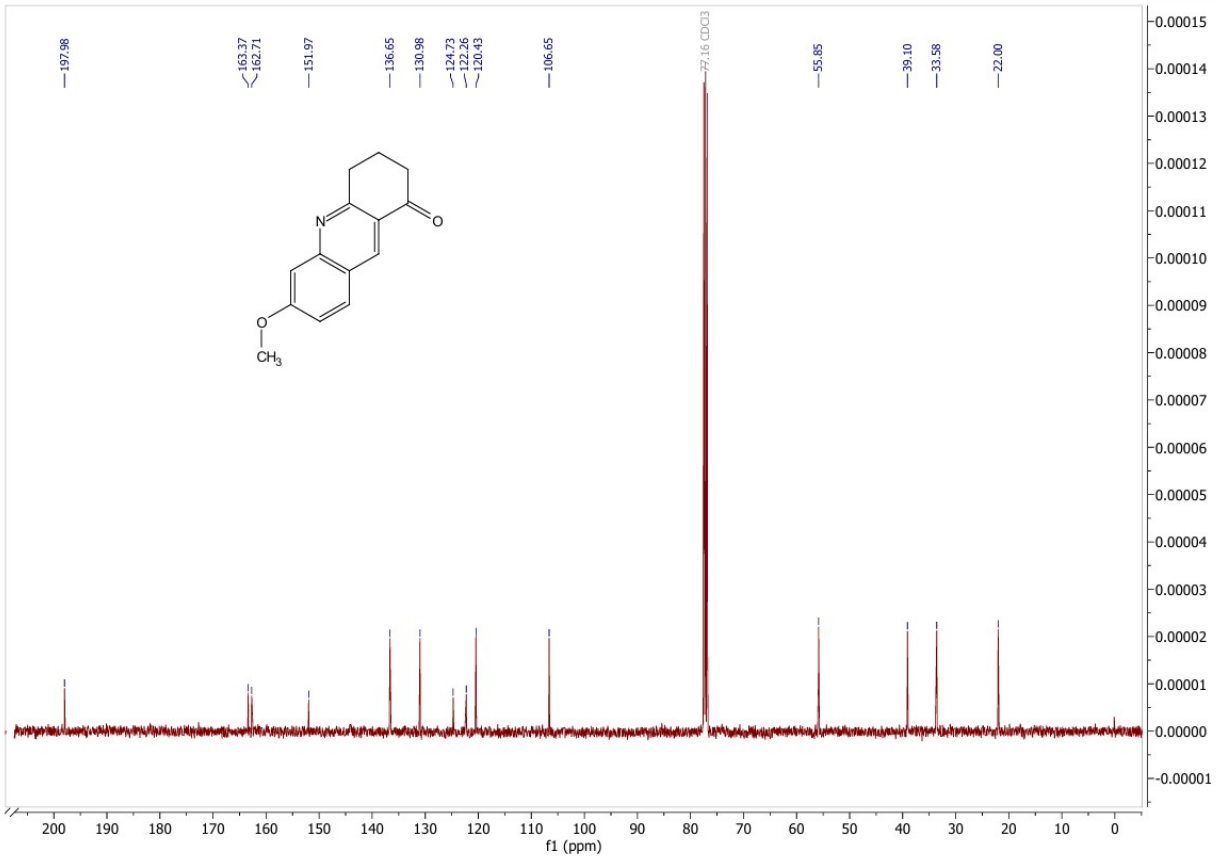
^{1}H NMR spectrum of 3m



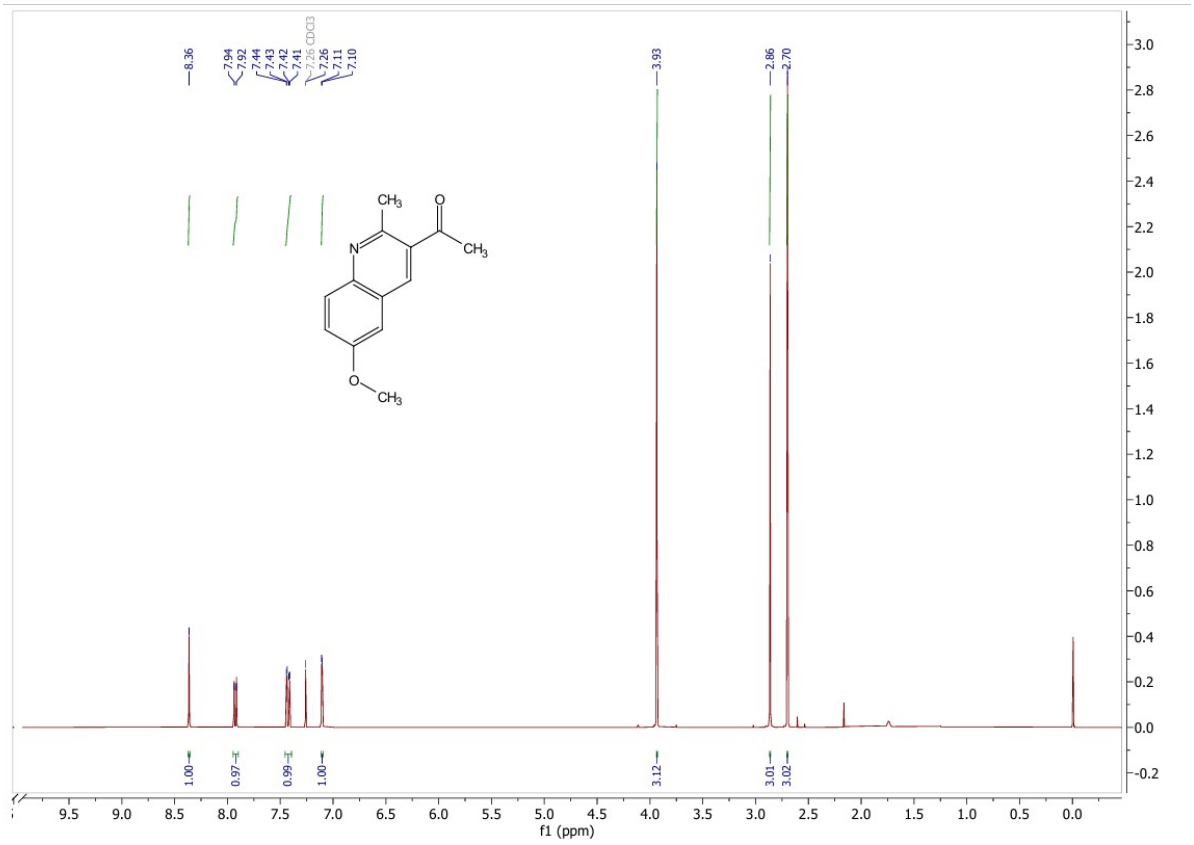
^{13}C NMR spectrum of 3m



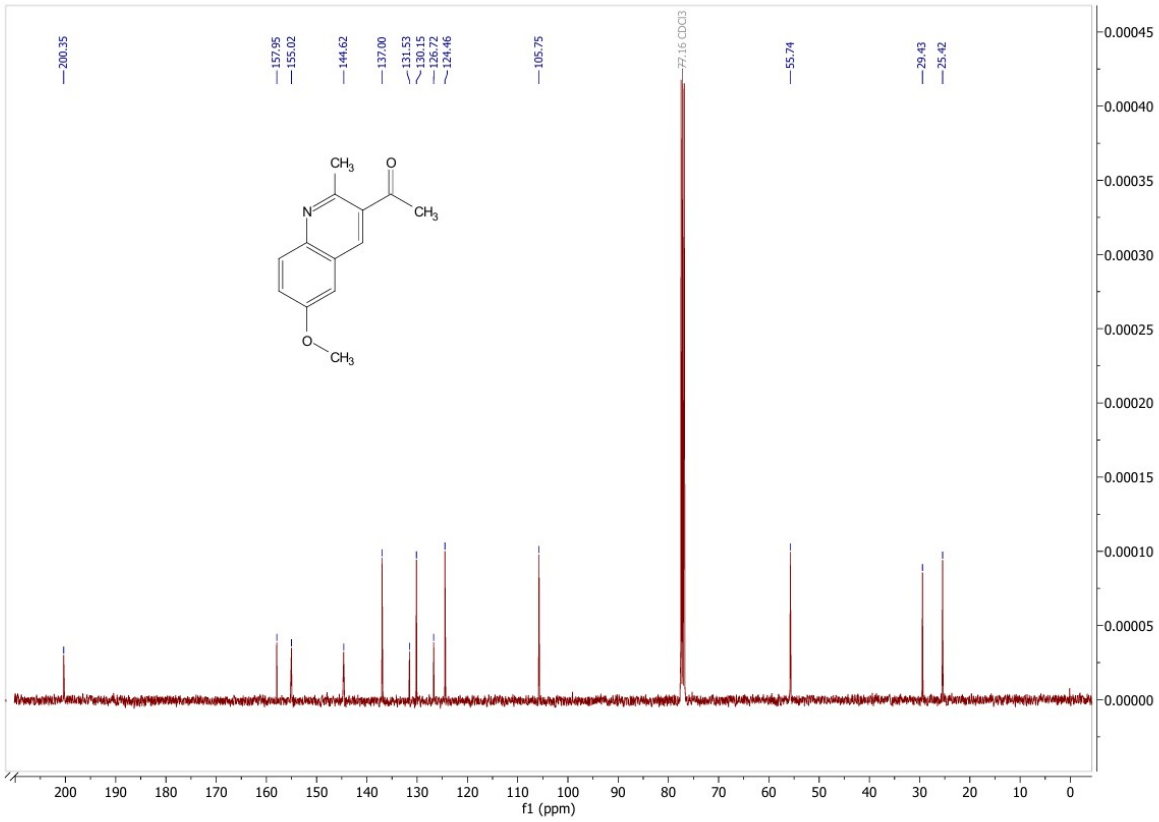
^{1}H NMR spectrum of 3n



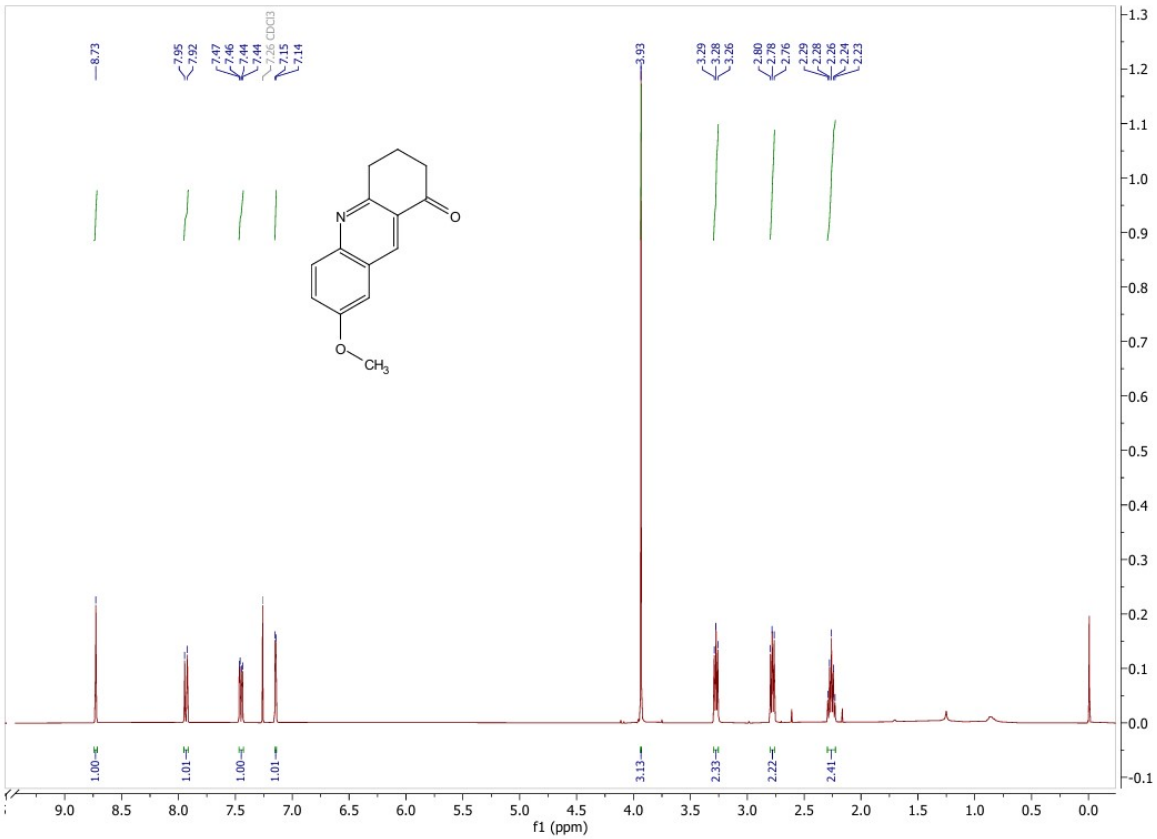
^{13}C NMR spectrum of 3n



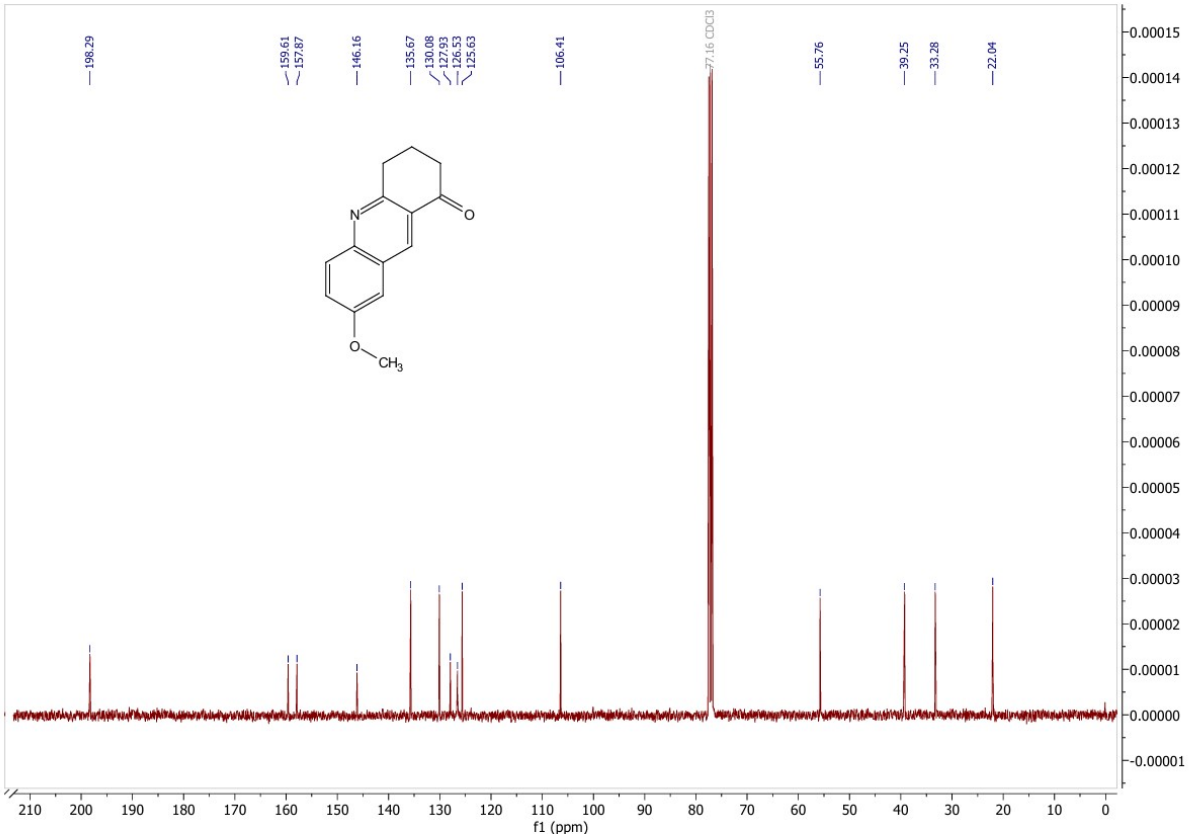
^{1}H NMR spectrum of 3o



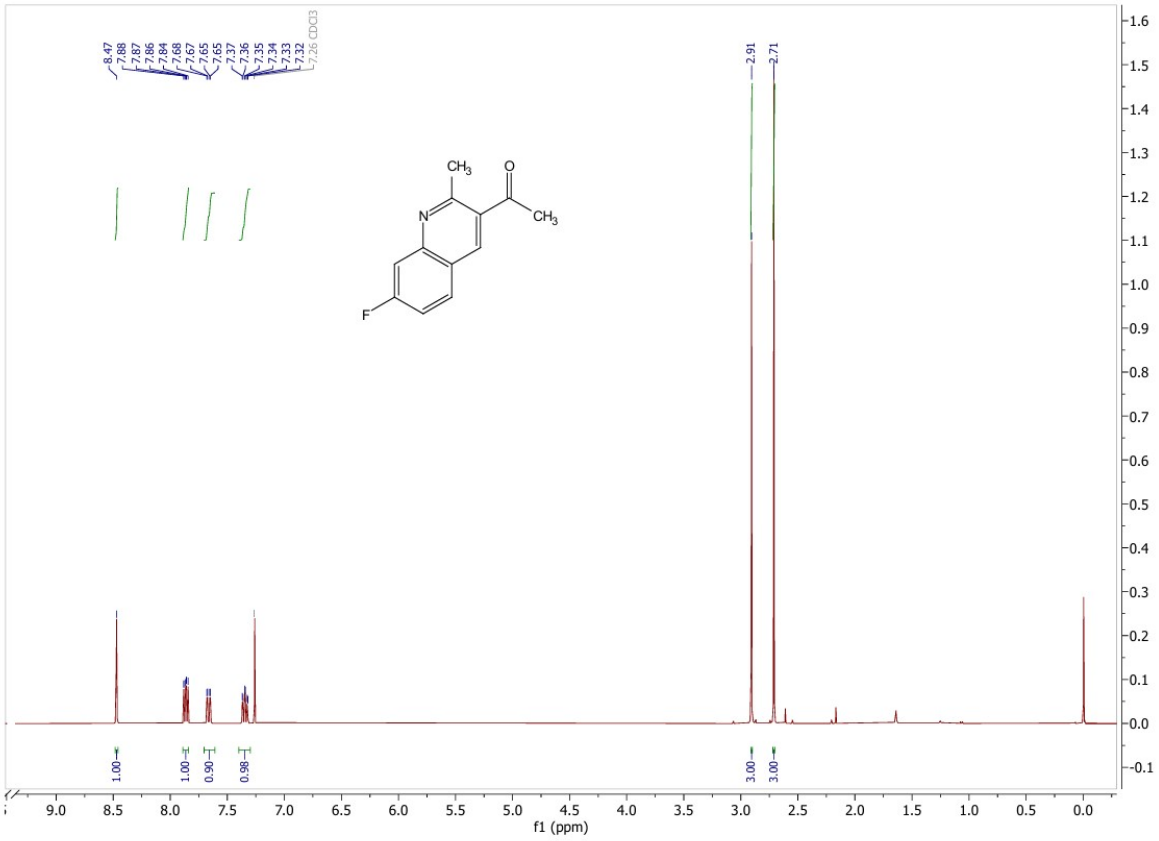
^{13}C NMR spectrum of 3o



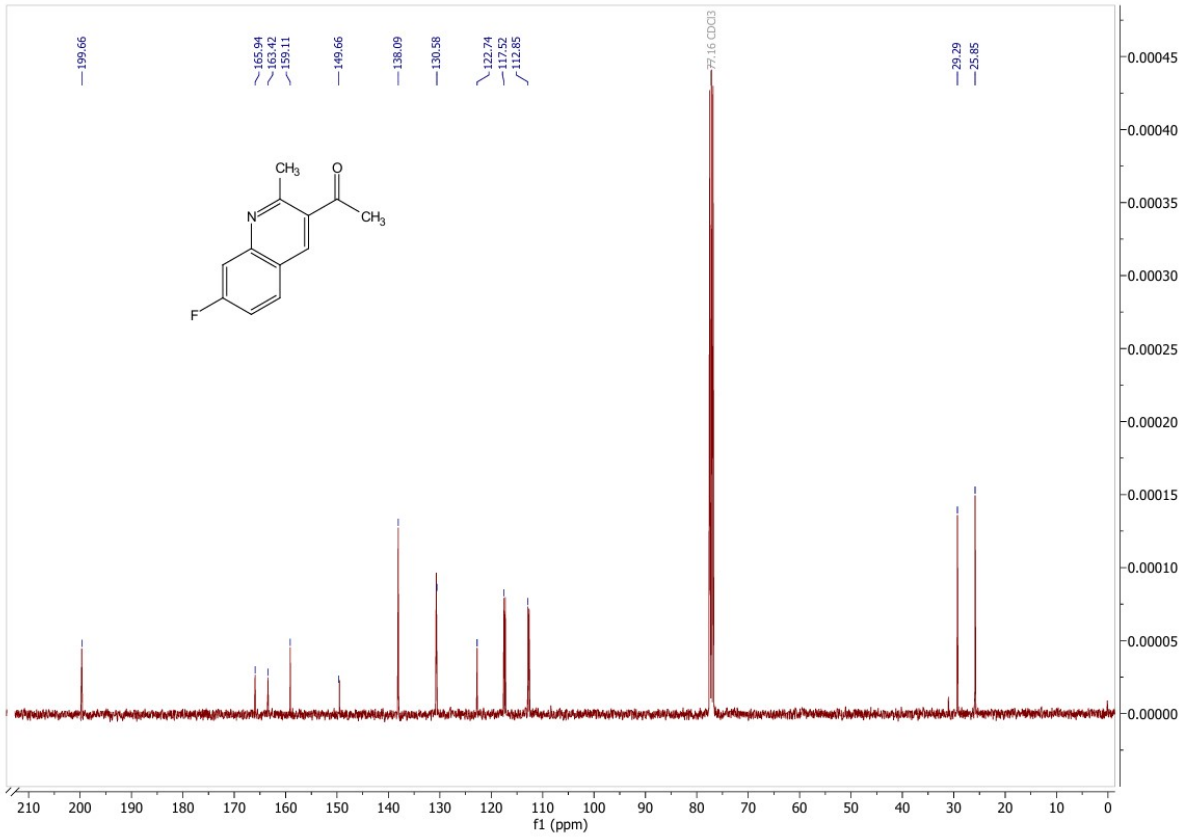
^{1}H NMR spectrum of 3p



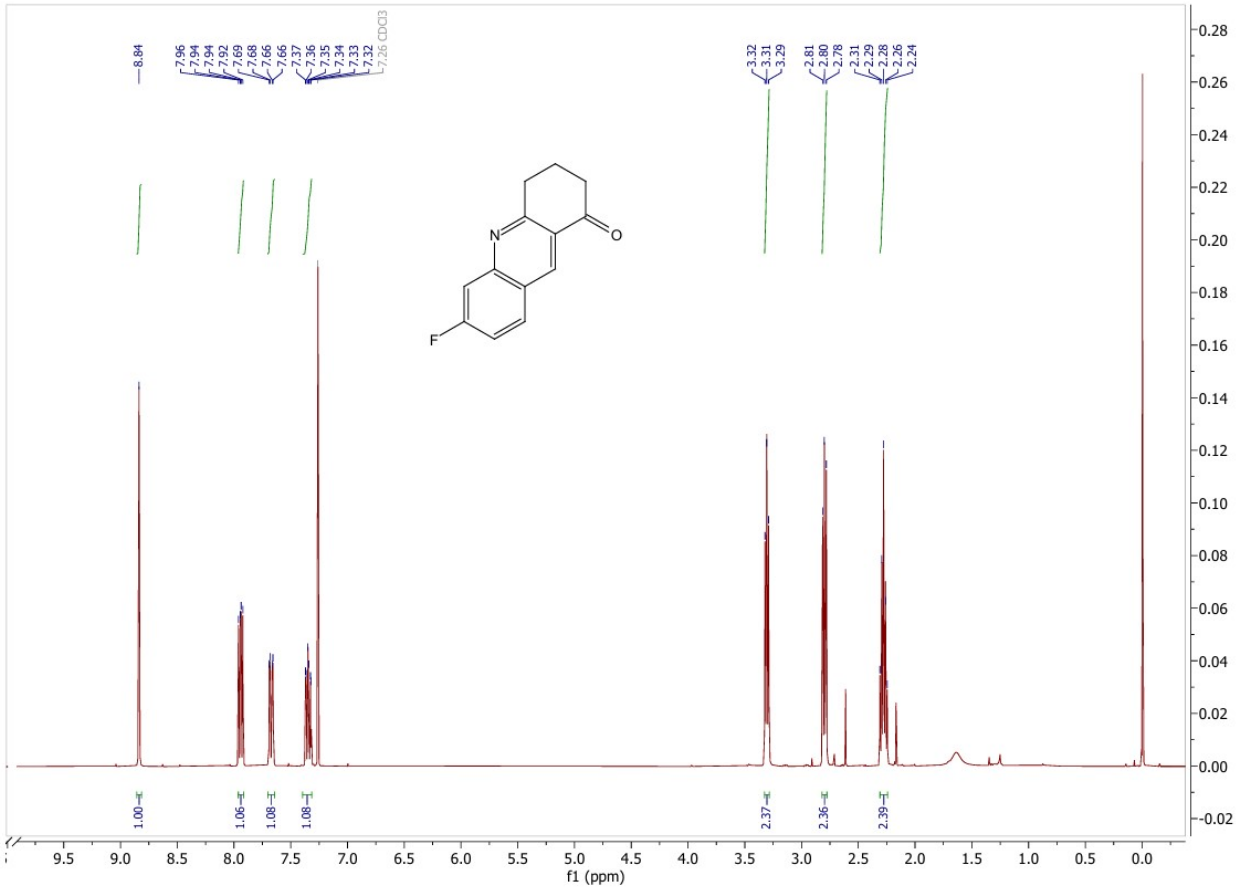
^{13}C NMR spectrum of 3p



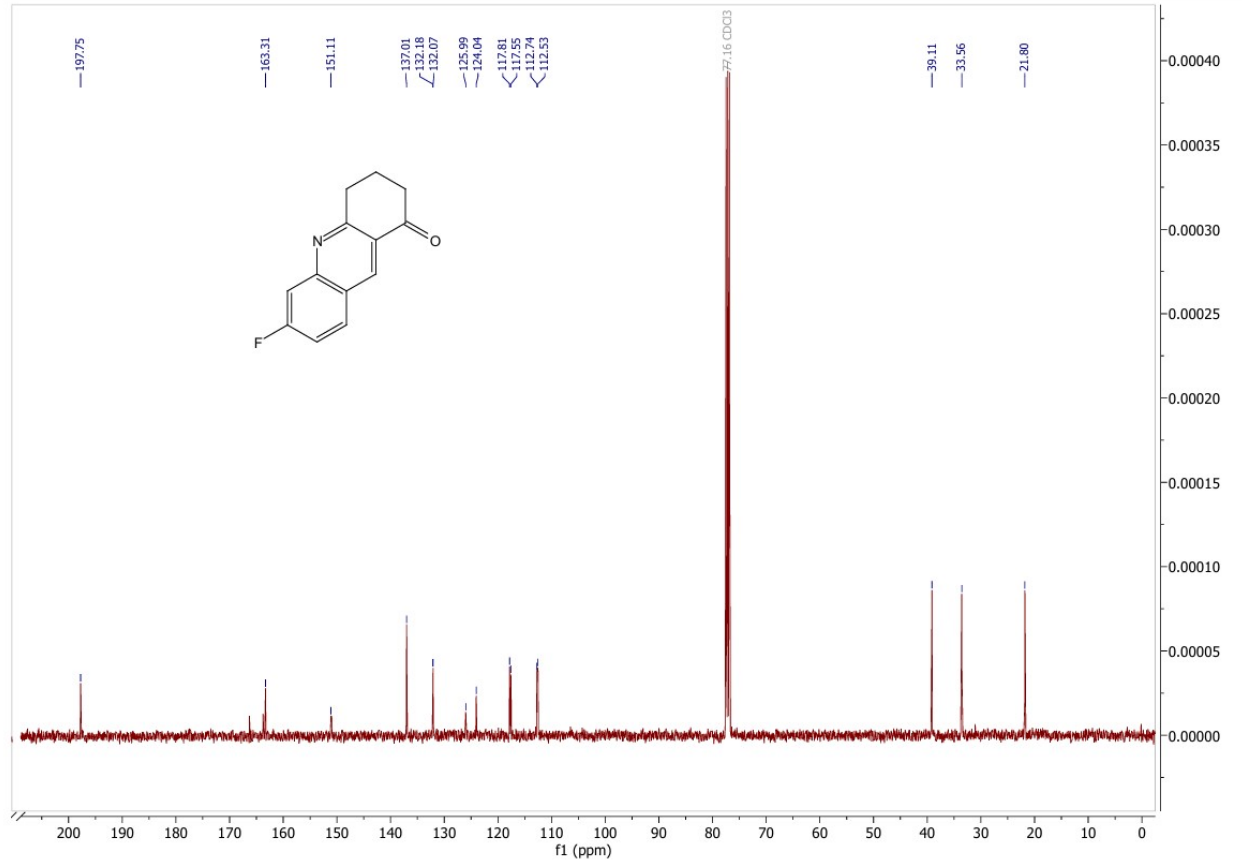
^{1}H NMR spectrum of 3q



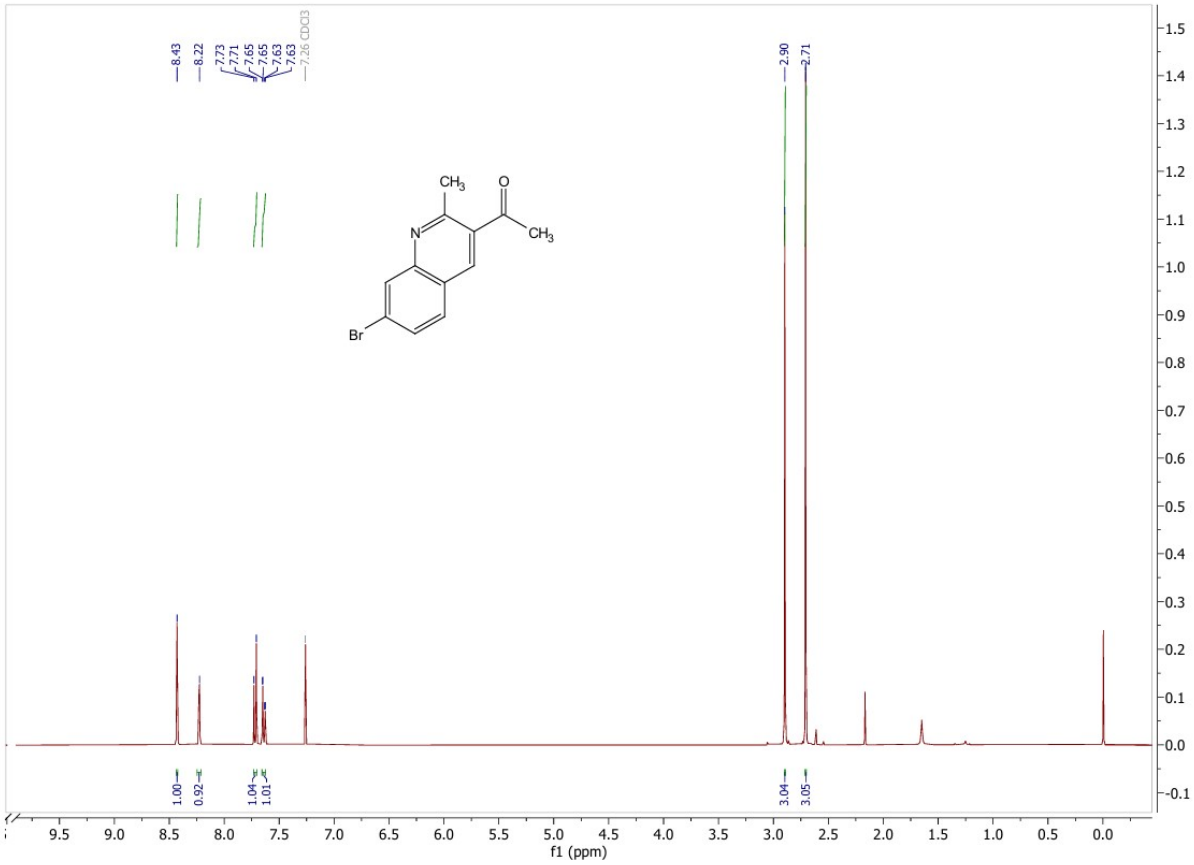
^{13}C NMR spectrum of 3q



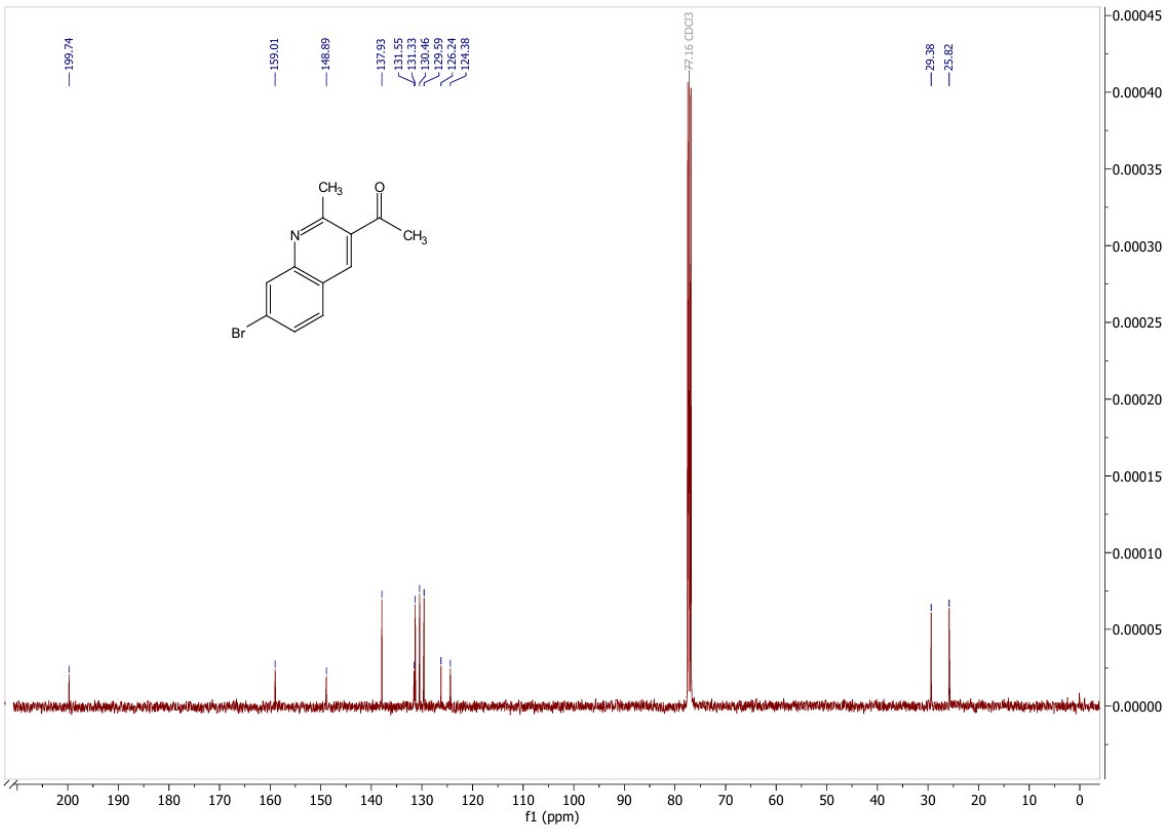
^{1}H NMR spectrum of 3r

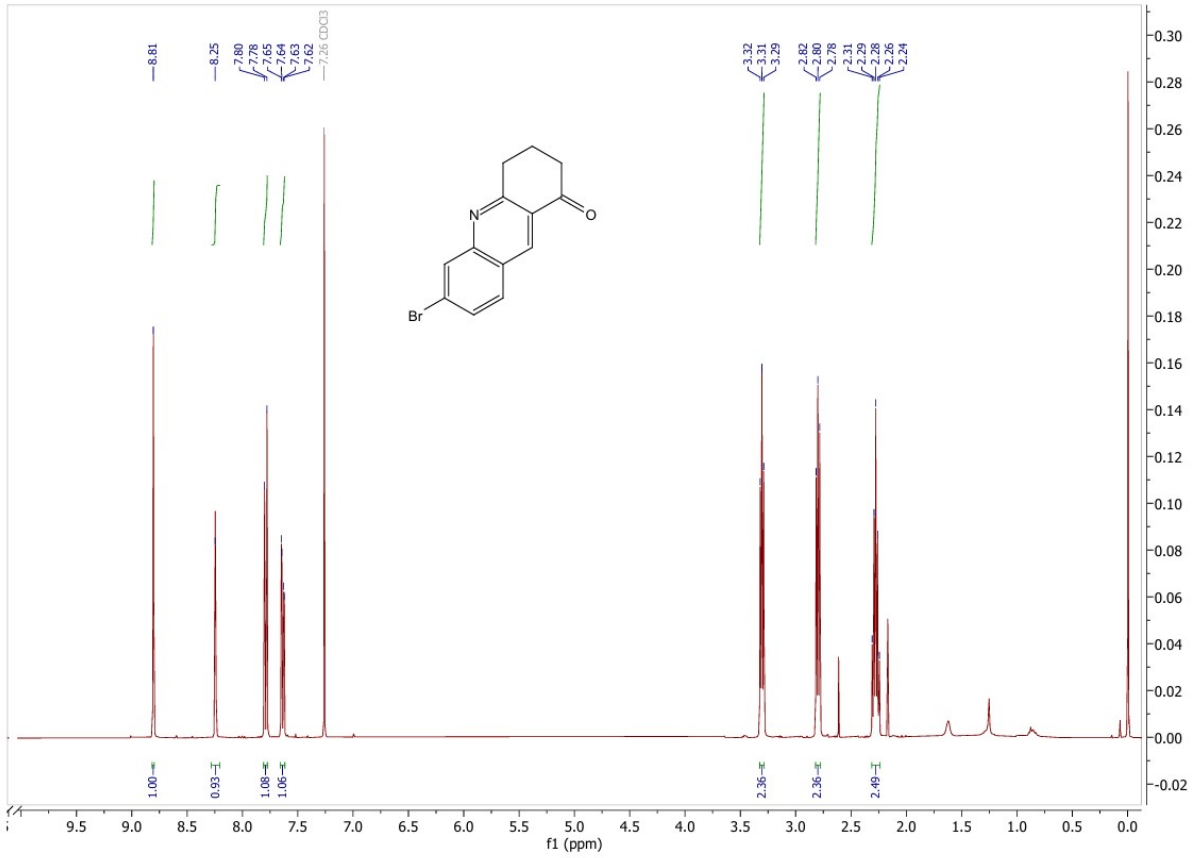


^{13}C NMR spectrum of 3r

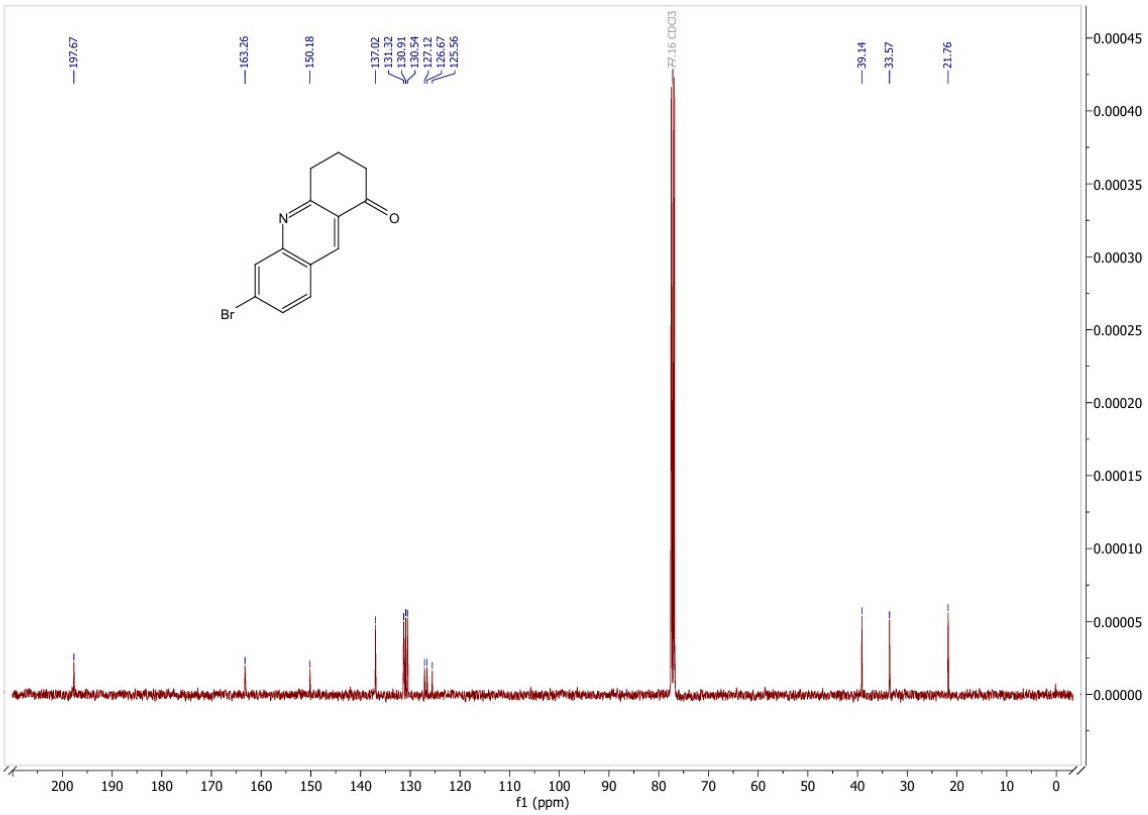


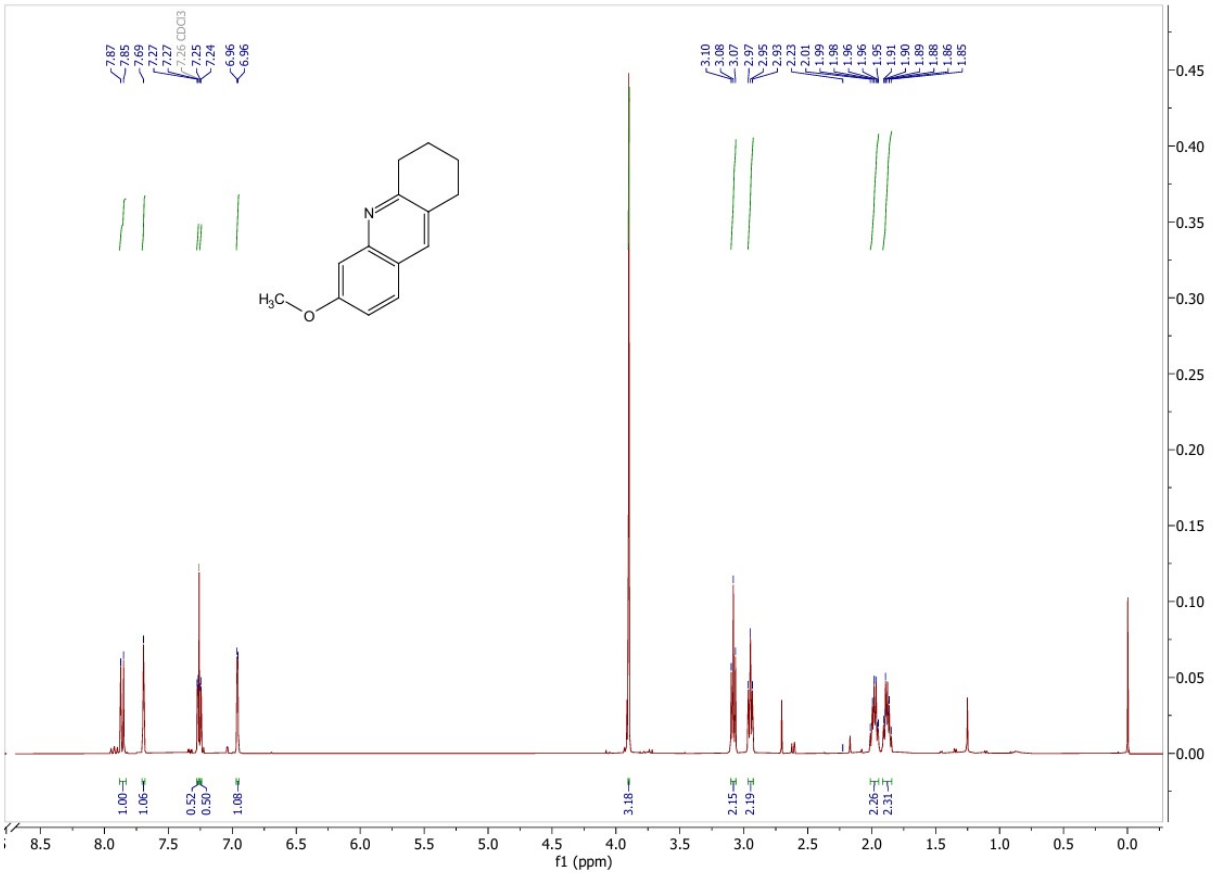
^{1}H NMR spectrum of 3s


199.74
159.01
148.89
137.93
131.55
131.33
130.46
129.59
126.24
124.38
77.16 CDCl3
29.38
25.82
CH3
O
N
CH3
Br
0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

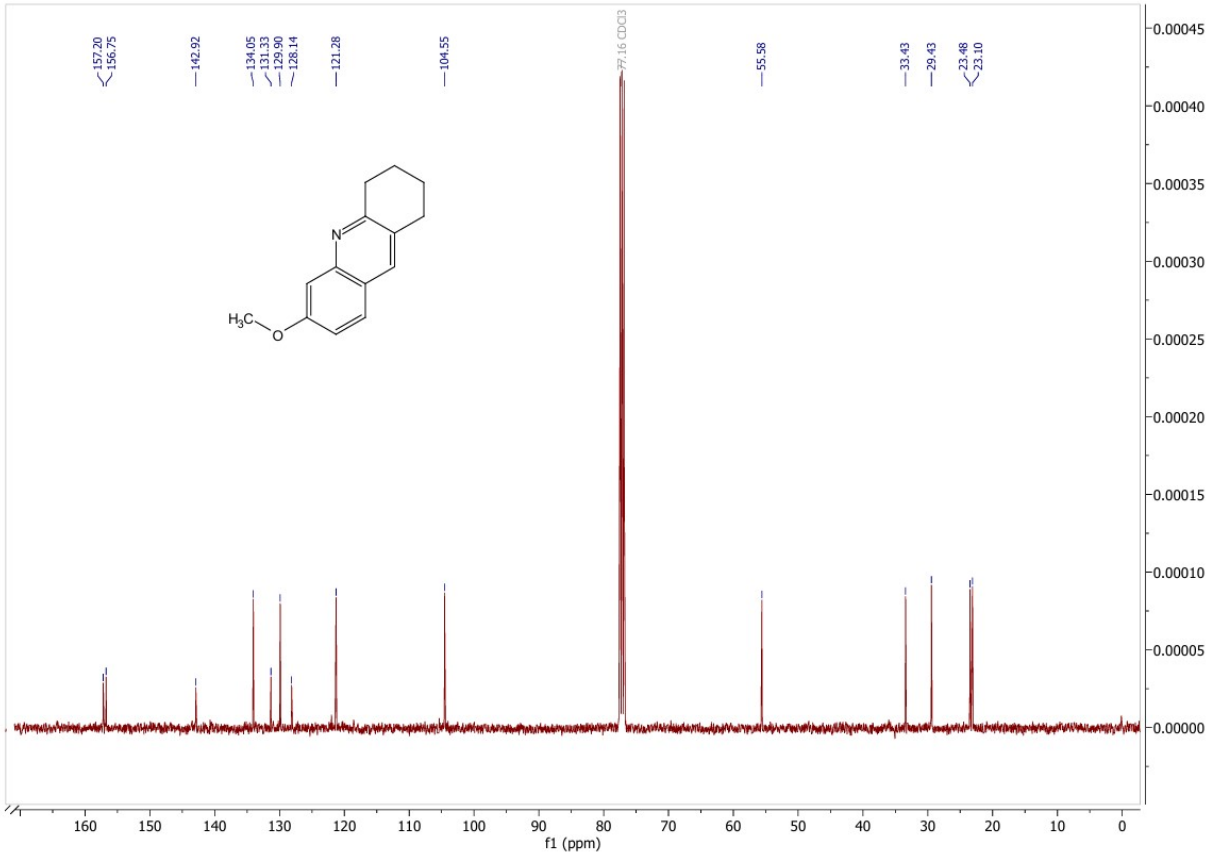


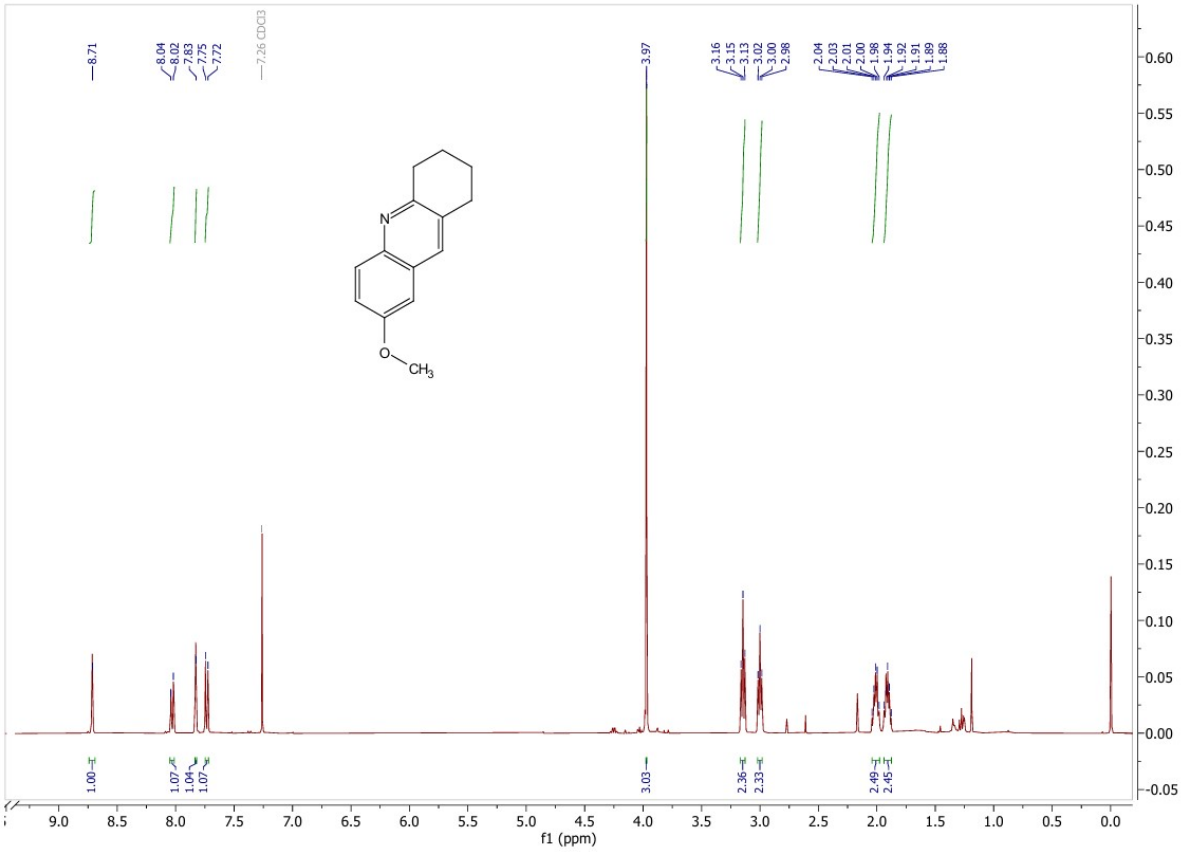
^{1}H NMR spectrum of 3t


197.67
163.26
150.18
137.02
131.32
130.91
130.54
127.12
126.67
125.56
77.16 CDCl3
39.14
33.57
21.76
N
O
Br
0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

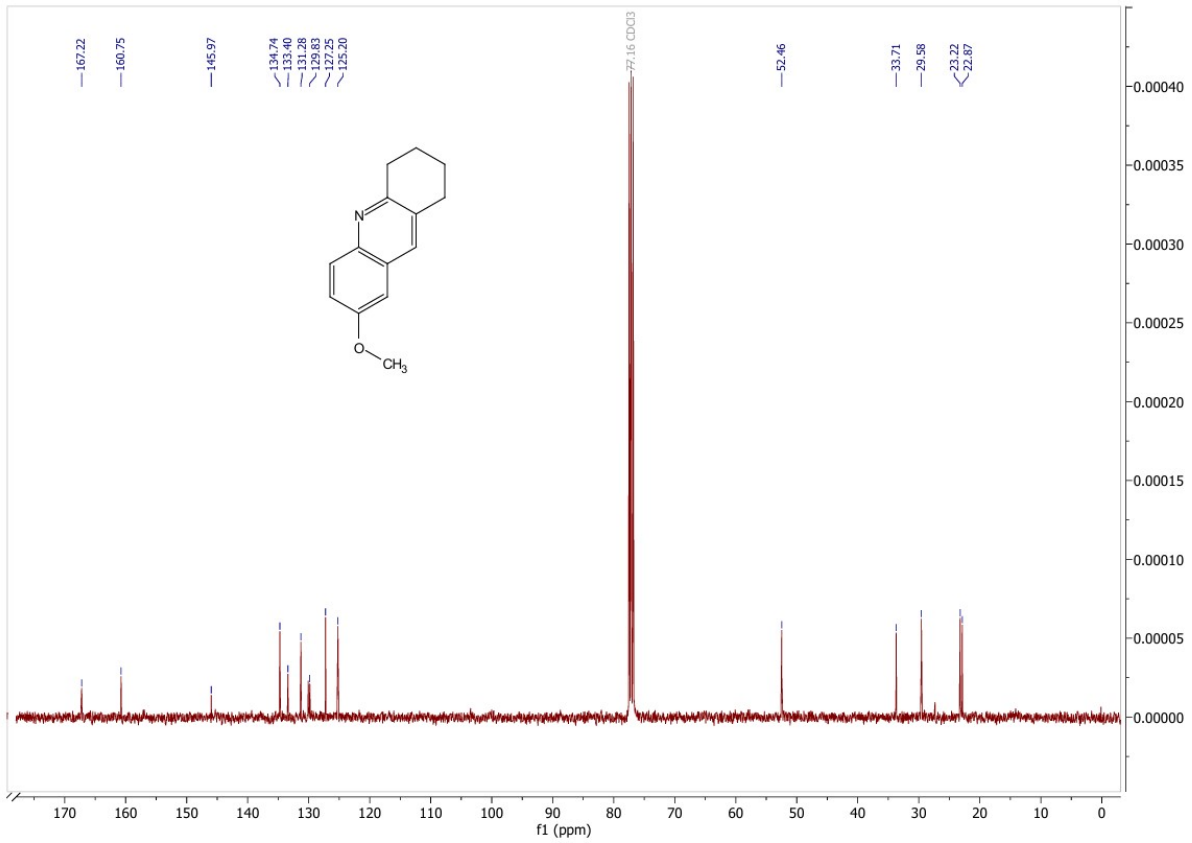


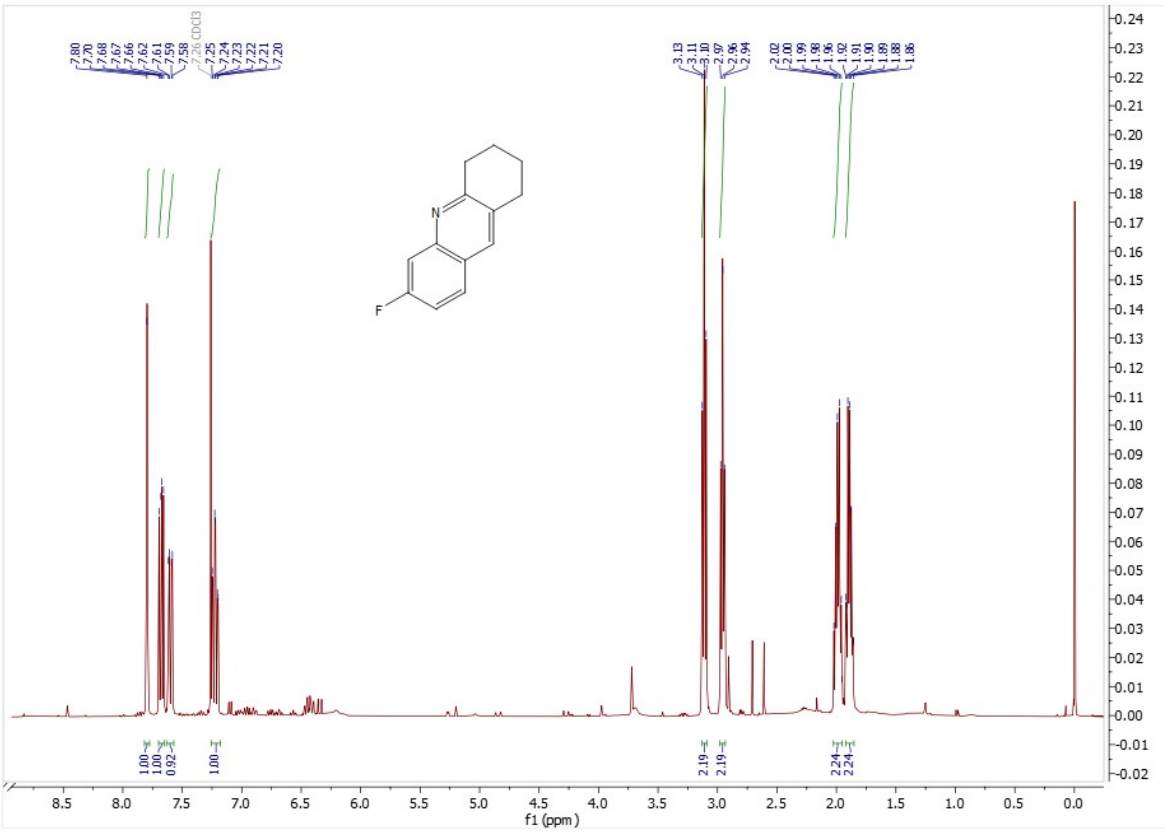
^{1}H NMR spectrum of 3u


157.20
156.75
142.92
134.05
131.33
129.90
128.14
121.28
104.55
77.16 CDCl3
55.58
33.43
29.43
23.48
23.10
N
H3C
O
0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

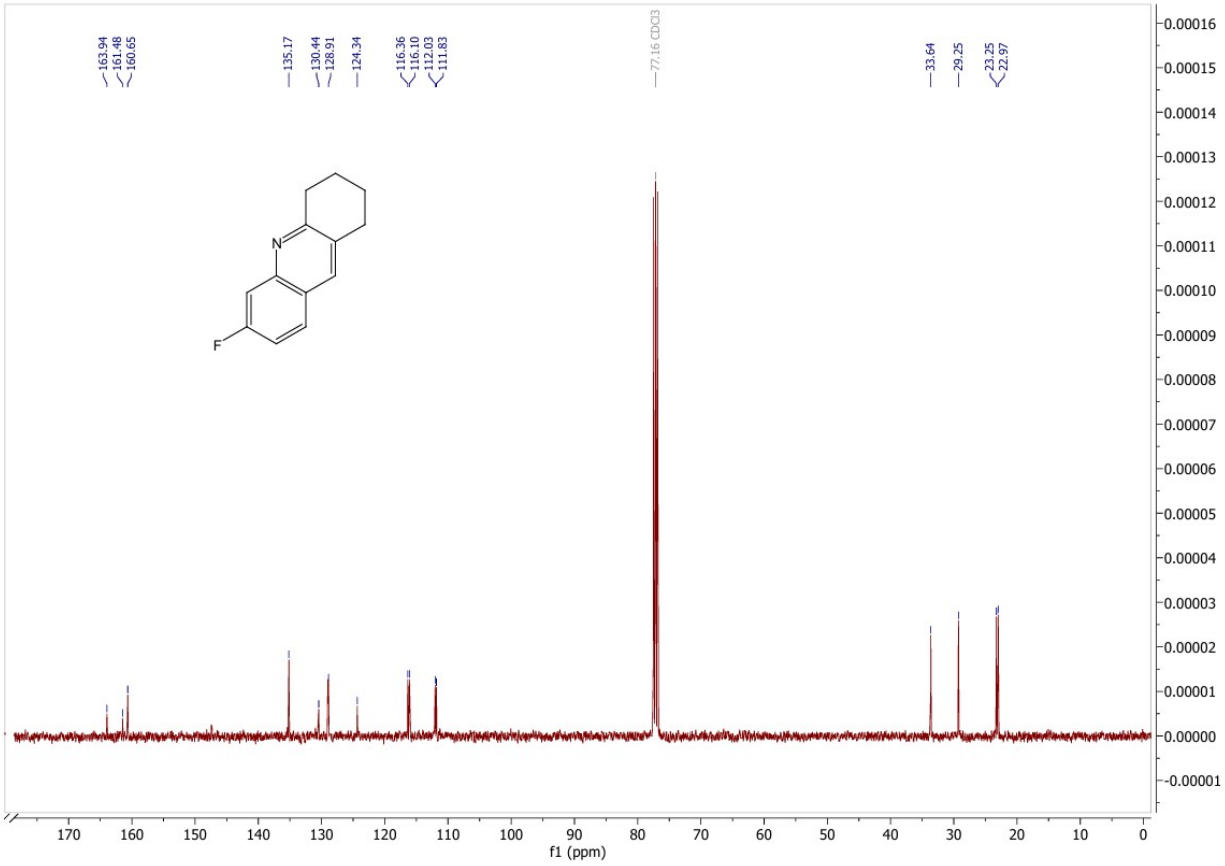


^{1}H NMR spectrum of 3v

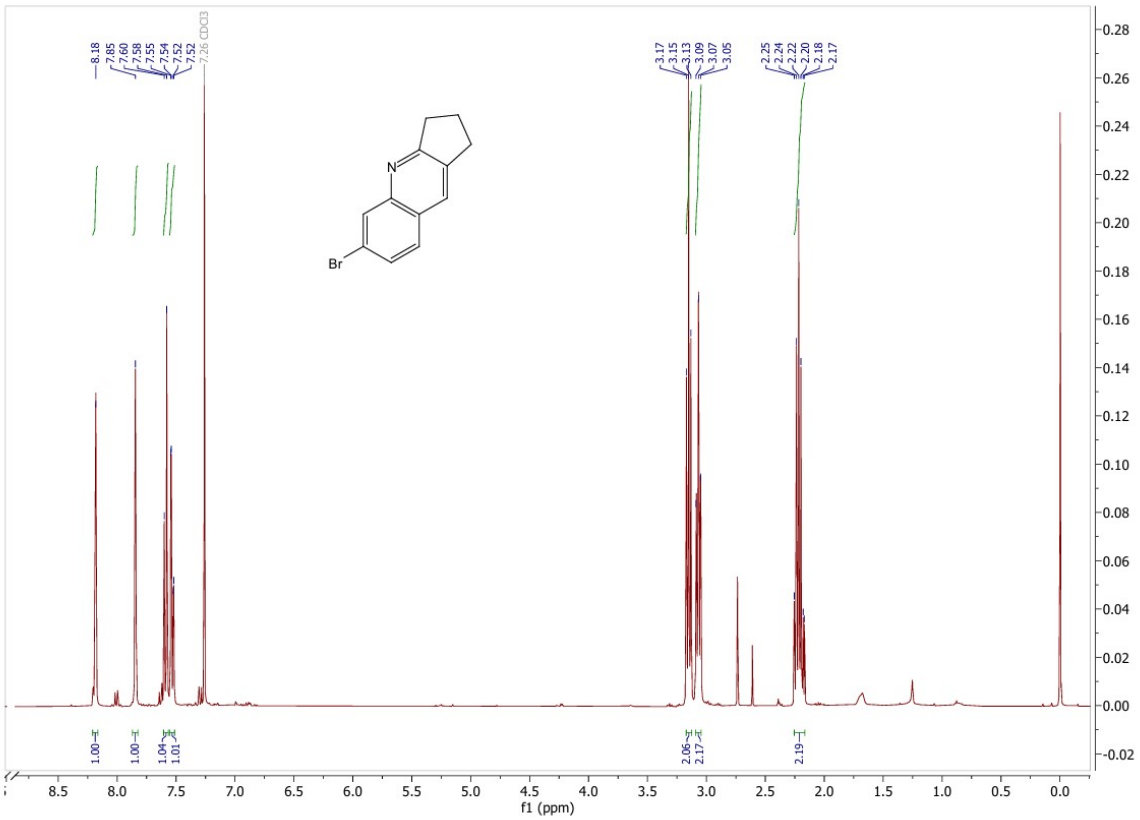

167.22
160.75
145.97
134.74
133.40
131.28
129.83
127.25
125.20
77.16 CDCl3
52.46
33.71
29.58
23.22
22.87
N
O
CH3
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



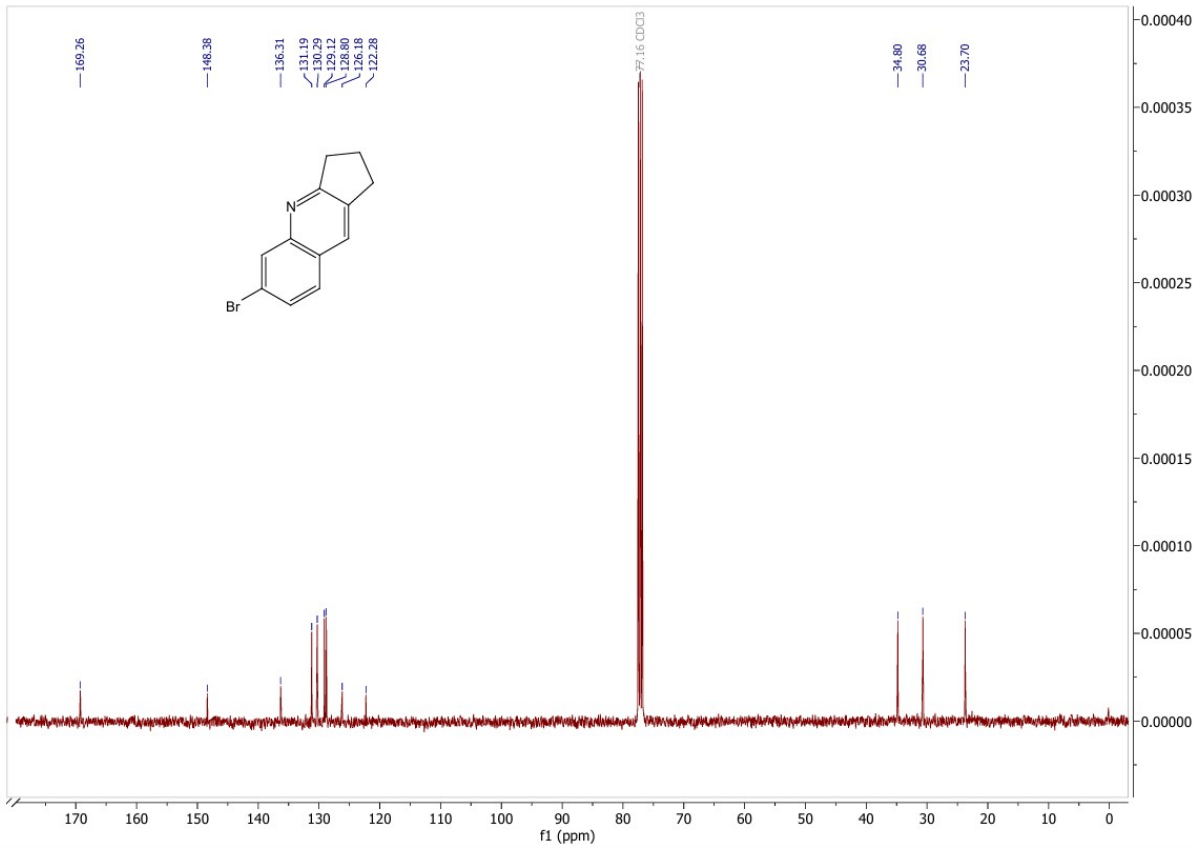
^{1}H NMR spectrum of 3w



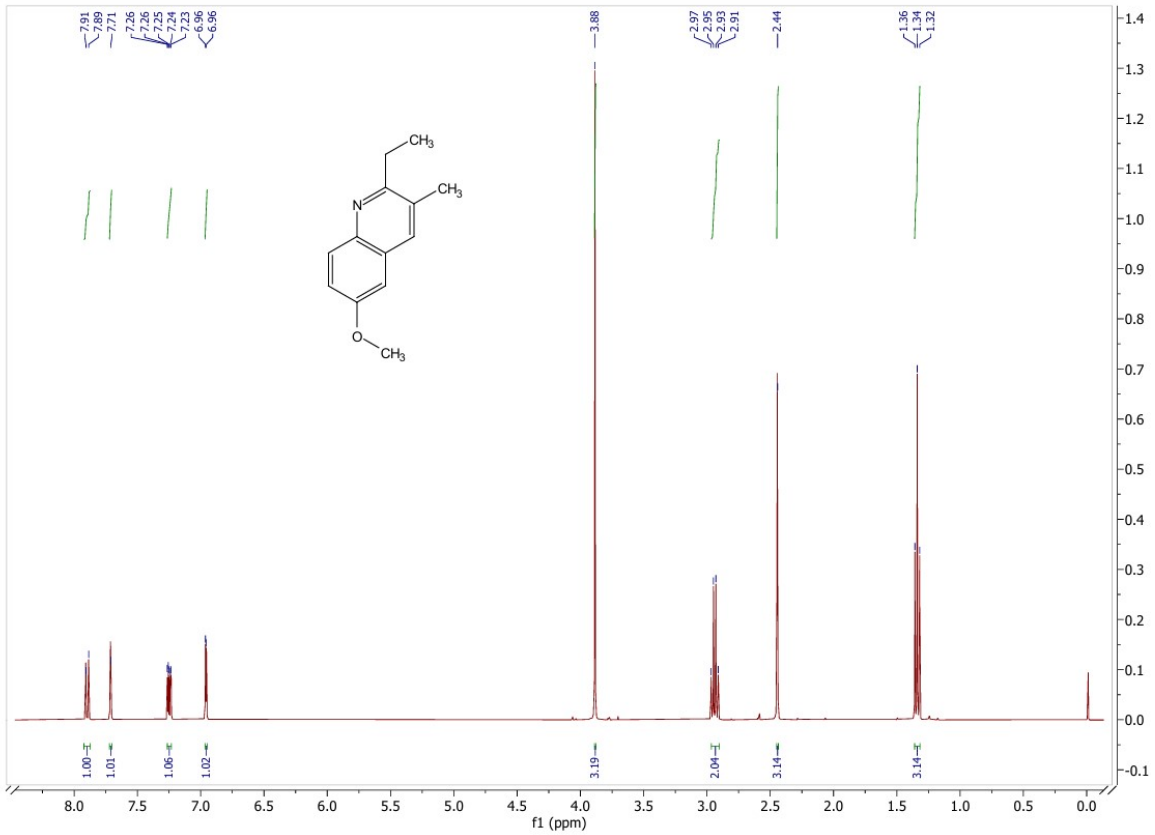
^{13}C NMR spectrum of 3r



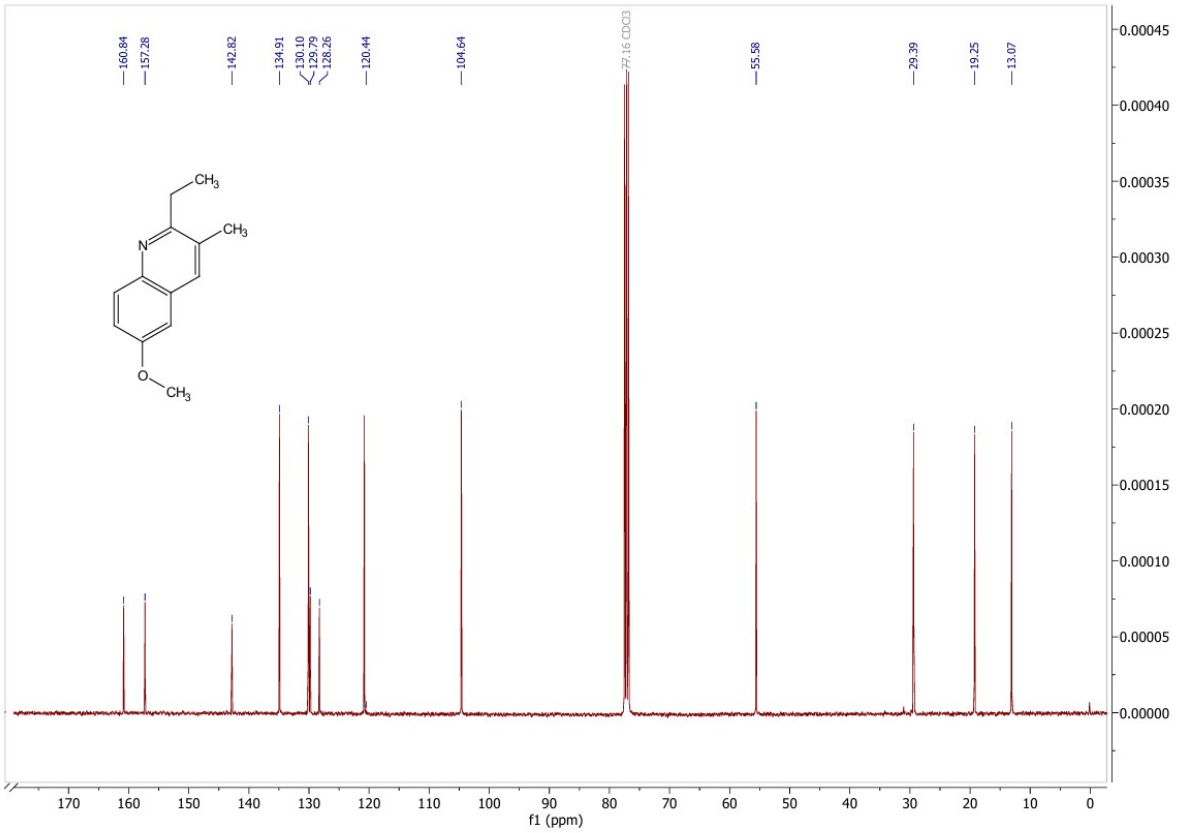
^{1}H NMR spectrum of 3x



^{13}C NMR spectrum of 3x



^{1}H NMR spectrum of 3y



^{13}C NMR spectrum of 3y