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Synthesis of Quinolines through Copper-Catalyzed Intermolecular Cyclization Reaction from Anilines and Terminal Acetylene Esters

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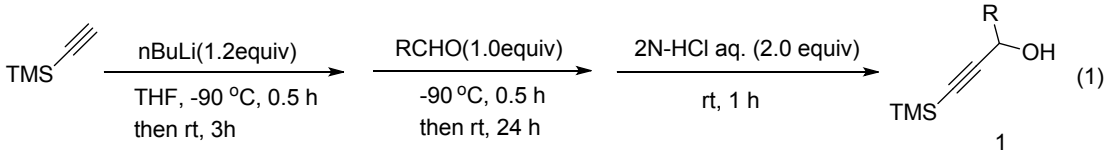
1) General Information

NMR spectra of the **3a-3w, 4a-4f** were recorded using Bruker Avance-500 instruments, calibrated to TMS (^{1}H NMR spectra) and $CDCl_3$ (^{13}C NMR spectra) as the internal reference (0.00 ppm for ^{1}H NMR spectra and 77.00 ppm for ^{13}C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected. Reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel (200-300 mesh).

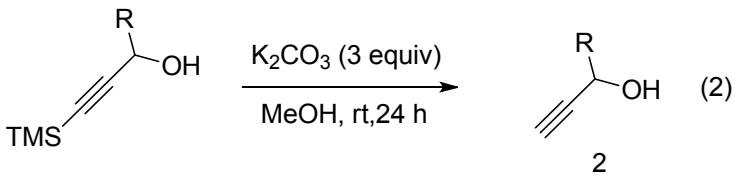
2) Synthesis of Starting Materials[1]

(i) General Procedure for the Synthesis of propargyl alcohol derivatives



(1)

To a freshly distilled THF solution (100 mL) of trimethylsilylacetylene (1.96 g, 20.0 mmol) in a glass flask that contained a magnetic stirring bar, n-BuLi (15 mL, 1.6 M in hexane) was dropwise added under a N_2 atmosphere at -90 °C. The mixture was stirred and slowly warmed to room temperature for 3 h. To the above reaction mixture was added an aldehyde (20.0 mmol) at -90 °C, and the mixture was slowly warmed to room temperature with stirring. After stirring for 16 h, the reaction was quenched with 2M-HCl aq. (20 mL), and then extracted with AcOEt, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified via silica gel column chromatography (petroleum ether : AcOEt = 9 : 1) to give the corresponding propargyl alcohol derivative 1 (eq 1).

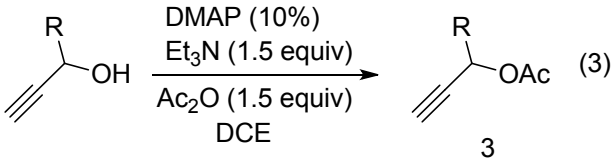


(2)

The propargyl alcohol derivative 1 was dissolved in distilled MeOH (10 mL)

containing K_2CO_3 (2.07g, 15.0 mmol), and the mixture was stirred for 24 h at room temperature. To quench the reaction, AcOEt (10 mL) and H_2O (10 mL) were added. The organic layer was separated, washed with H_2O (10 mL), and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : AcOEt = 9 : 1) to give the corresponding propargyl alcohol derivative 2 (eq 2).

(ii) General Procedure to Synthesis of propargylic ester substrates

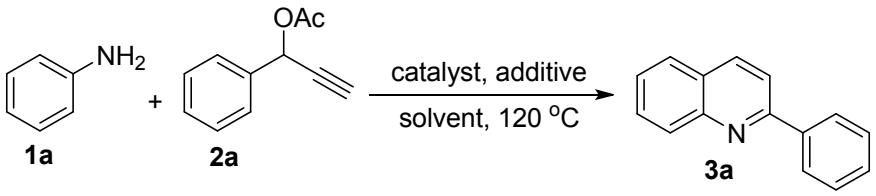


(3)

To a solution of 1-phenylprop-2-yn-1-ol (1.32 g, 10 mmol) in 15 mL CH_2Cl_2 at 0 ^oC was added DMAP (123 mg, 1 mmol), triethylamine (2.1 mL, 15 mmol), Ac_2O (2.0 mL, 15 mmol), and the reaction mixture was stirred for 2 h. After addition of an appropriate volume of aqueous water, the reaction was extracted with CH_2Cl_2. The combined organic layer was washed twice with saturated NaCl aqueous, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) to give the desired propargylic acetate 3 in almost quantitative yield as a yellow oil (eq 3).

3) Typical Procedures

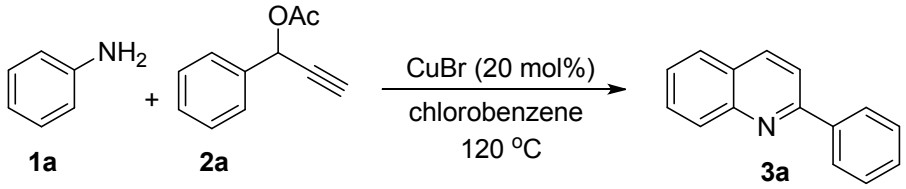
(i) Partial Optimization of the Reaction Conditions for the Synthesis of Quinolines[a]



entry	[Cu]	additive	solvent	yield(%)[b]
1	CuBr	-	PhCl	60
2[c]	CuBr	TEMED	PhCl	trace
3[c]	CuBr	TMEDA	PhCl	trace
4[d]	CuBr	$NaHCO_3$	PhCl	19
5[d]	CuBr	K_2CO_3	PhCl	trace
6[d]	CuBr	t-BuOK	PhCl	trace

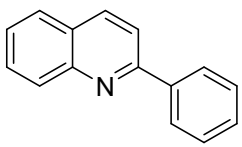
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (20 mol %), PhCl (2 mL) in sealed Schlenk tube, at 120 °C for 12 h. [b]Isolated yields. [c]Ligands (40 mol%). [d]Bases (1 equiv).

(ii) Synthesis of Substituted Quinolines



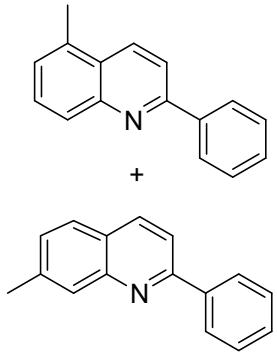
The stirred mixture of aromatic aniline **1a** (0.2 mmol), propargylic acetate **2a** (0.3 mmol, 1.5 equiv) and CuBr (0.04 mmol, 20%) in PhCl (2 mL) at 120 °C for 12 h . After the completion of the reaction (monitored by TLC), the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 100:1) to provide the desired products **3a** as a white solid.

4) Characterization Data

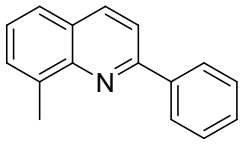


2-phenylquinoline (3a): white solid, isolated yield 60% (24.6 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.23-8.18 (m, 4H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H),

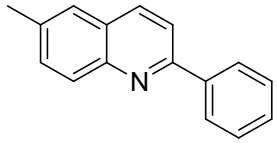
7.56-7.52 (m, 3H), 7.48 (t, J = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 157.3, 148.2, 139.6, 136.8, 129.7, 129.6, 129.3, 128.8, 127.6, 127.4, 127.1, 126.3, 119.0.



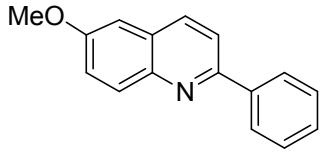
7-methyl-2-phenylquinoline (3b) and 5-methyl-2-phenylquinoline (3b'): pale yellow solid, isolated yield 76% (33.2 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.36 (d, J = 9.0 Hz, 1H), 8.20-8.15 (m, 5H), 8.06 (d, J = 8.5 Hz, 1H), 8.00 (s, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.62 (t, J = 7.0 Hz, 1H), 7.56-7.52 (m, 4H), 7.49-7.46 (m, 2H), 7.36 (t, J = 7.0 Hz, 2H), 2.70 (s, 3H), 2.60 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 157.2, 156.7, 148.5, 148.4, 139.9, 139.7, 139.6, 136.4, 134.3, 133.2, 129.3, 129.2, 129.2, 128.8, 128.7, 128.6, 128.5, 128.0, 127.5, 127.0, 126.7, 126.4, 125.2, 118.4, 118.1, 21.8, 18.5.



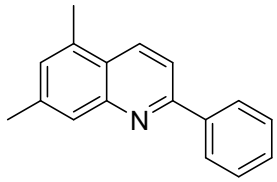
8-methyl-2-phenylquinoline (3c): pale yellow solid, isolated yield 61% (26.7 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.25 (d, J = 7.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 2.90 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 155.5, 147.2, 139.8, 137.7, 136.9, 129.6, 129.2, 128.7, 127.4, 127.1, 126.0, 125.4, 118.2, 17.9.



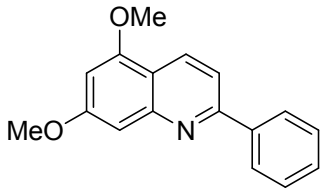
6-methyl-2-phenylquinoline (3d): white solid, isolated yield 53% (23.2 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.16 (d, *J* = 7.5 Hz, 2H), 8.13-8.10 (m, 2H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.58-7.52 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 156.5, 146.8, 139.7, 136.1, 136.1, 131.9, 129.3, 129.1, 128.8, 127.4, 127.2, 126.3, 119.0, 21.6.



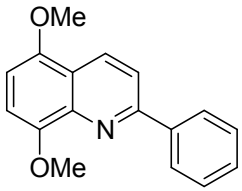
6-methoxy-2-phenylquinoline (3e): pale yellow solid, isolated yield 46% (21.6 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.12 (d, *J* = 7.5 Hz, 2H), 8.07 (t, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 3.93 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 157.6, 155.0, 144.3, 139.8, 135.5, 131.1, 128.9, 128.8, 128.1, 127.3, 122.3, 119.2, 105.0, 55.5.



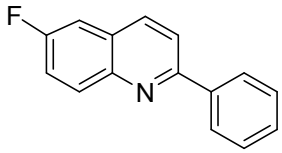
5,7-dimethyl-2-phenylquinoline (3f): white solid, isolated yield 61% (28.4 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.30 (d, *J* = 9.0 Hz, 1H), 8.18 (d, *J* = 7.5 Hz, 2H), 7.87 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.20 (s, 1H), 2.65 (s, 3H), 2.54 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 156.6, 148.7, 139.6, 139.5, 133.9, 133.0, 129.1, 128.7, 127.4, 126.8, 124.5, 117.6, 21.8, 18.4.



5,7-dimethoxy-2-phenylquinoline (3g): pale yellow solid, isolated yield 45% (23.9 mg); mp: 98.0-100.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.48 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.15 (s, 1H), 6.50 (s, 1H), 4.00 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 161.4, 158.0, 155.9, 150.3, 139.7, 131.5, 129.1, 128.7, 127.5, 115.9, 115.6, 99.9, 97.9, 55.7, 55.6; HRMS (ESI) m/z calcd for $C_{17}H_{16}NO_2^+$(M+H)$^+$266.11756, found 266.11755.

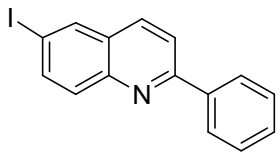


5,8-dimethoxy-2-phenylquinoline (3h): pale yellow solid, isolated yield 67% (35.5 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.60 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.1 (s, 3H), 4.0 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 156.5, 149.5, 148.7, 140.4, 139.5, 131.7, 129.2, 128.6, 127.6, 120.4, 118.4, 107.6, 103.5, 56.3, 55.7.

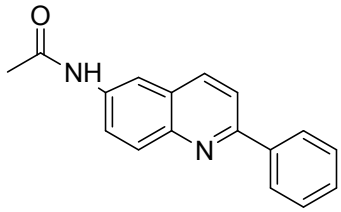


6-fluoro-2-phenylquinoline (3i): white solid, isolated yield 20% (9.0 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.21-8.14 (m, 4H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.55-7.43 (m, 5H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 160.3 (d, *J* = 246.5 Hz), 156.7 (d, J = 2.6 Hz), 145.2, 139.2, 136.2 (d, *J* = 5.3 Hz), 132.1 (d, *J* = 9.0 Hz), 129.4, 128.9, 127.7 (d, *J* = 10.0 Hz), 127.4, 119.9 (d, *J* = 25.5 Hz), 119.7, 110.5

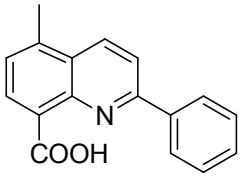
(d, J = 21.6 Hz).



6-iodo-2-phenylquinoline (3j): white solid, isolated yield 18% (12.0 mg); mp: 137.0-139.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.20 (s, 1H), 8.15 (d, J = 7.0 Hz, 2H), 8.09 (d, J = 9.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.87 (d, J = 8.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 157.7, 147.0, 138.9, 138.4, 136.2, 135.7, 131.2, 129.7, 128.9, 128.8, 127.6, 119.6, 91.7; HRMS (ESI) m/z calcd for $C_{15}H_{11}IN^+(M+H)^+$331.99307, found 331.99283.

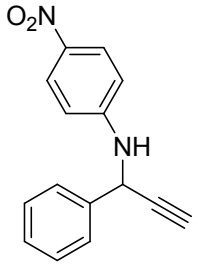


N-(2-phenylquinolin-6-yl)acetamide (3k): yellow solid, isolated yield 40% (21.0 mg); mp: 163.0-165.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.32 (s, 1H), 8.13-8.06 (m, 4H), 8.87 (s, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 168.8, 156.5, 145.4, 139.5, 136.6, 135.6, 130.2, 129.2, 128.8, 127.6, 127.4, 123.3, 119.6, 115.9, 24.6; HRMS (ESI) m/z calcd for C17H15N2O+(M+H)+263.11789, found 263.11789.

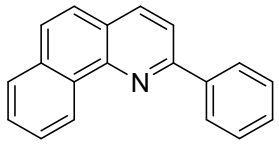


5-methyl-2-phenylquinoline-8-carboxylic acid (3l): yellow solid, isolated yield 40% (21.0 mg); mp: 172.5-174.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.58-8.54 (m, 2H), 7.99-7.97 (m, 3H), 7.56-7.53 (m, 3H), 7.45 (d, J = 7.5 Hz, 1H), 2.74 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 167.5,

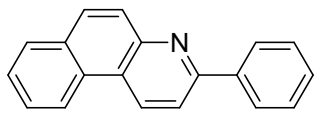
155.8, 145.1, 141.1, 136.5, 136.0, 135.2, 130.8, 129.4, 127.5, 127.4, 126.2, 122.2, 119.2, 19.0; HRMS (ESI) m/z calcd for $C_{17}H_{14}NO_2^+(M+H)^+$264.10191, found 264.10202.



4-nitro-N-(1-phenylprop-2-ynyl)benzenamine (3m): yellow solid, isolated yield 50% (25.2 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.11 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.44-7.37 (m, 3H), 6.69 (d, *J* = 9.0 Hz, 2H), 5.38 (s, 1H), 4.88 (s, 1H), 2.56 (d, *J* = 2.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 151.2, 139.2, 137.3, 129.1, 128.8, 127.1, 126.1, 112.4, 81.1, 74.1, 49.3.

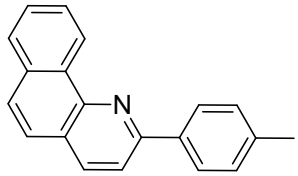


2-phenylbenzo[h]quinoline (3n): white solid, isolated yield 70% (35.7 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.56 (d, *J* = 8.0 Hz, 1H), 8.38 (d, *J* = 7.0 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.81-7.78 (m, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 155.4, 146.2, 139.7, 136.5, 133,8, 131.8, 129.2, 128.8, 128.1, 127.7, 127.4, 126.8, 125.1, 125.0, 124.7, 118.8.

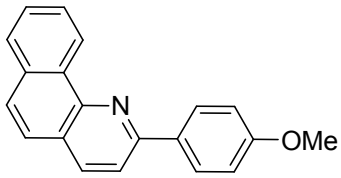


3-phenylbenzo[f]quinoline (3o): white solid, isolated yield 40% (20.4 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.95 (d, *J* = 8.5 Hz, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.99 (t, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.70-7.63 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 156.8, 148.1, 139.4, 131.6,

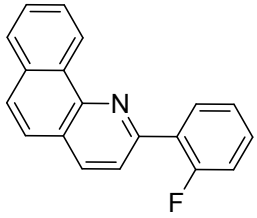
131.4, 130.9, 130.0, 129.2, 128.8, 128.7, 128.6, 127.4, 127.1, 127.0, 124.1, 122.6, 118.7.



2-p-tolylbenzo[h]quinoline (3p): pale yellow solid, isolated yield 61% (32.8 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.55 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.80-7.78 (m, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 2.49 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 155.4, 146.1, 139.2, 136.8, 136.4, 133.8, 131.7, 129.5, 128.0, 127.7, 127.3, 127.2, 126.8, 125.0, 124.9, 124.7, 118.6, 21.3.

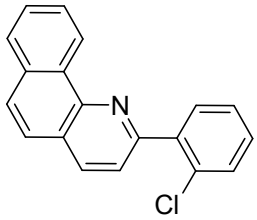


2-(4-methoxyphenyl)benzo[h]quinoline (3q): pale yellow solid, isolated yield 59% (33.6 mg); mp: 110.9-112.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.52 (d, *J* = 8.0 Hz, 1H), δ = 8.32 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.79-7.76 (m, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 160.7, 155.1, 146.0, 136.4, 133.8, 132.3, 131.7, 128.7, 128.0, 127.7, 126.9, 126.7, 125.1, 124.7, 118.2, 114.1, 55.3; HRMS (ESI) m/z calcd for $C_{20}H_{16}NO^+(M+H)^+$286.12264, found 286.12259.

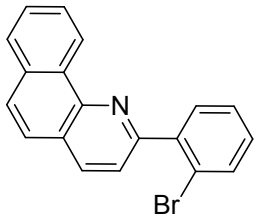


2-(2-fluorophenyl)benzo[h]quinoline (3r): white solid, isolated yield 59% (32.3 mg); mp: 81.0-82.9 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.43 (d, *J* = 8.0 Hz, 1H), 8.40 (t, *J* = 8.0 Hz, 1H), 8.18

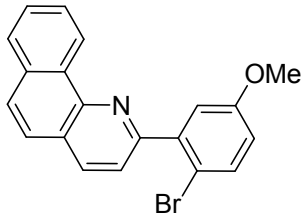
(d, *J* = 8.5 Hz, 1H), 8.04 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.70-7.65 (m, 2H), 7.44-7.40 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.22-7.19 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 161.0 (d, *J* = 248.5 Hz), 151.9 (d, *J* = 1.8 Hz), 146.3, 136.0, 133.7, 131.8 (d, *J* = 2.8 Hz), 131.7, 130.6 (d, *J* = 8.5 Hz), 128.2, 127.9 (d, *J* = 11.3 Hz), 127.8, 126.9, 125.2, 125.0, 124.6, 124.6, 122.8 (d, *J* = 9.9 Hz), 116.3 (d, *J* = 22.9 Hz); HRMS (ESI) m/z calcd for $C_{19}H_{13}FN^+(M+H)^+$274.10265, found 274.10263.



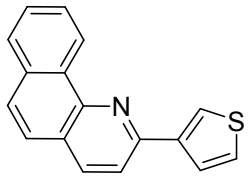
2-(2-chlorophenyl)benzo[h]quinoline (3s): white solid, isolated yield 62% (36.1 mg); mp: 121.6-124.1 ^oC; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.43 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.96-7.90 (m, 3H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.76-7.70 (m, 3H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 155.4, 146.2, 139.6, 135.4, 133.7, 132.5, 132.4, 131.6, 130.3, 129.7, 128.2, 128.0, 127.7, 127.0 (2C), 125.1, 125.0, 124.8, 123.1; HRMS (ESI) m/z calcd for $C_{19}H_{13}ClN^+(M+H)^+$290.07310, found 290.07291.



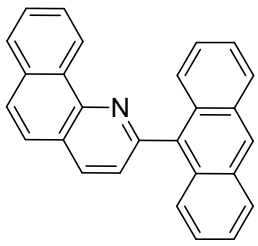
2-(2-bromophenyl)benzo[h]quinoline (3t): pale yellow solid, isolated yield 68% (45.6 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.42 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.77-7.70 (m, 4H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 156.8, 146.1, 141.7, 135.4, 133.7, 133.5, 132.2, 131.6, 129.8, 128.2, 127.9, 127.7, 127.6, 127.0, 125.1, 125.0, 124.8, 123.0, 122.1.



2-(2-bromo-5-methoxyphenyl)benzo[h]quinoline (3u): pale yellow solid, isolated yield 64% (46.6 mg); mp: 91.0-93.2 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.43 (d, *J* = 7.5 Hz, 1H), δ = 8.23 (d, *J* = 8.0 Hz, 1H), 7.94-7.91 (m, 2H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.76-7.70 (m, 3H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.39 (d, *J* = 3.0 Hz, 1H), 6.91 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 159.0, 156.6, 146.0, 142.3, 135.4, 134.2, 133.7, 131.5, 128.2, 128.0, 127.7, 127.0, 125.1, 125.0, 124.8, 123.0, 117.4, 116.0, 112.5, 55.6. HRMS (ESI) m/z calcd for $C_{20}H_{15}BrNO^{+}(M+H)^{+}$364.03315, found 364.03268.



2-(thiophen-3-yl)benzo[h]quinoline (3v): pale yellow solid, isolated yield 64% (33.4 mg); mp: 106.0-108.1 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.47 (d, *J* = 8.5 Hz, 1H), δ = 8.15-8.11 (m, 2H), 8.02 (d, *J* = 5.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.79-7.76 (m, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.49-7.47 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 151.7, 146.1, 142.9, 136.4, 133.8, 131.6, 128.1, 127.7, 127.1, 126.8, 126.7, 126.2, 125.0, 124.9, 124.6, 124.1, 118.9; HRMS (ESI) m/z calcd for $C_{17}H_{12}NS^{+}(M+H)^{+}$261.06850, found 261.06854.



2-(anthracen-10-yl)benzo[h]quinoline (3w): yellow solid, isolated yield 49% (34.8 mg); mp:

206.9-209.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.36 (d, *J* = 8.5 Hz, 1H), 8.62 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.99-7.93 (m, 2H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.77-7.71 (m, 4H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 157.1, 146.6, 135.8, 133.8, 131.7, 131.5, 130.2, 128.5, 128.3, 128.0, 127.7, 127.6, 127.0, 126.4, 125.8, 125.3, 125.2, 125.1 (2C), 125.0; HRMS (ESI) m/z calcd for $C_{27}H_{18}N^+(M+H)^+$356.14338, found 356.14316.

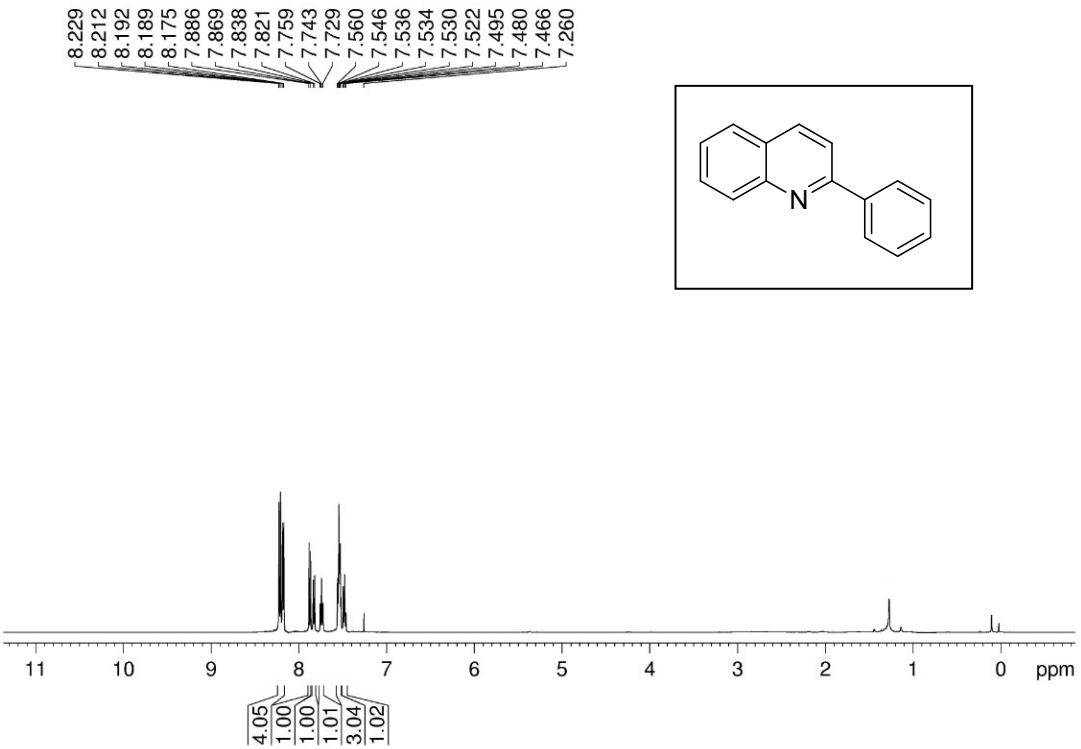
3x: yellow solid, isolated yield 58% (23.8 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.24-8.22 (m, 0.57H), 8.19-8.16 (m, 3H), 7.89 (t, *J* = 4.5 Hz, 0.8H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.75-7.72 (m, 1H), 7.55-7.52 (m, 3H), 7.49-7.45 (m, 1H).

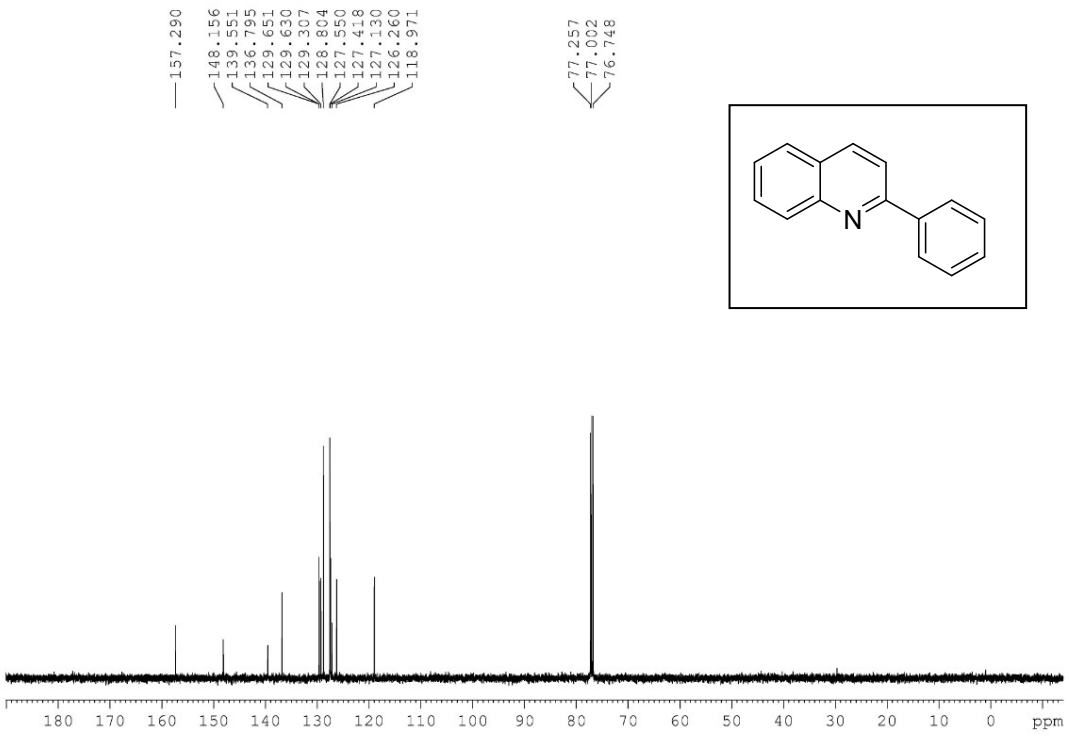
5) References

1. Nielsen, T. E.; Quement, S. L.; David, T. *Synthesis.* **2004**, 9, 1381.

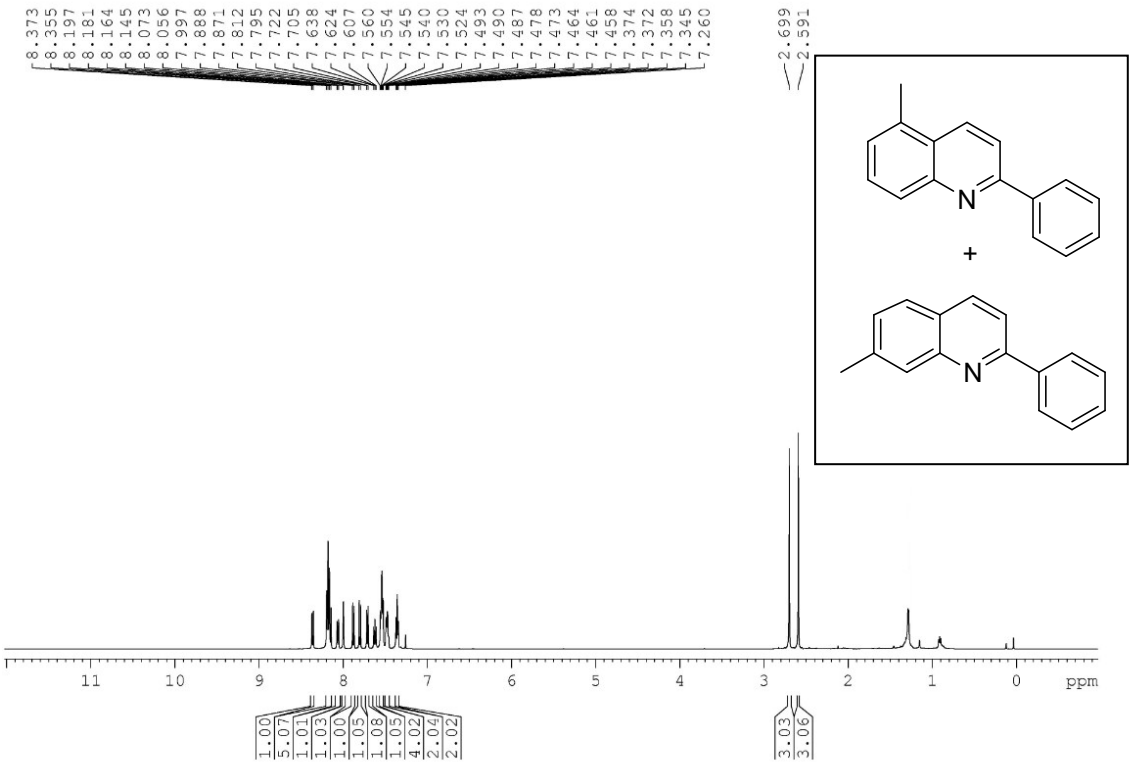
6) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

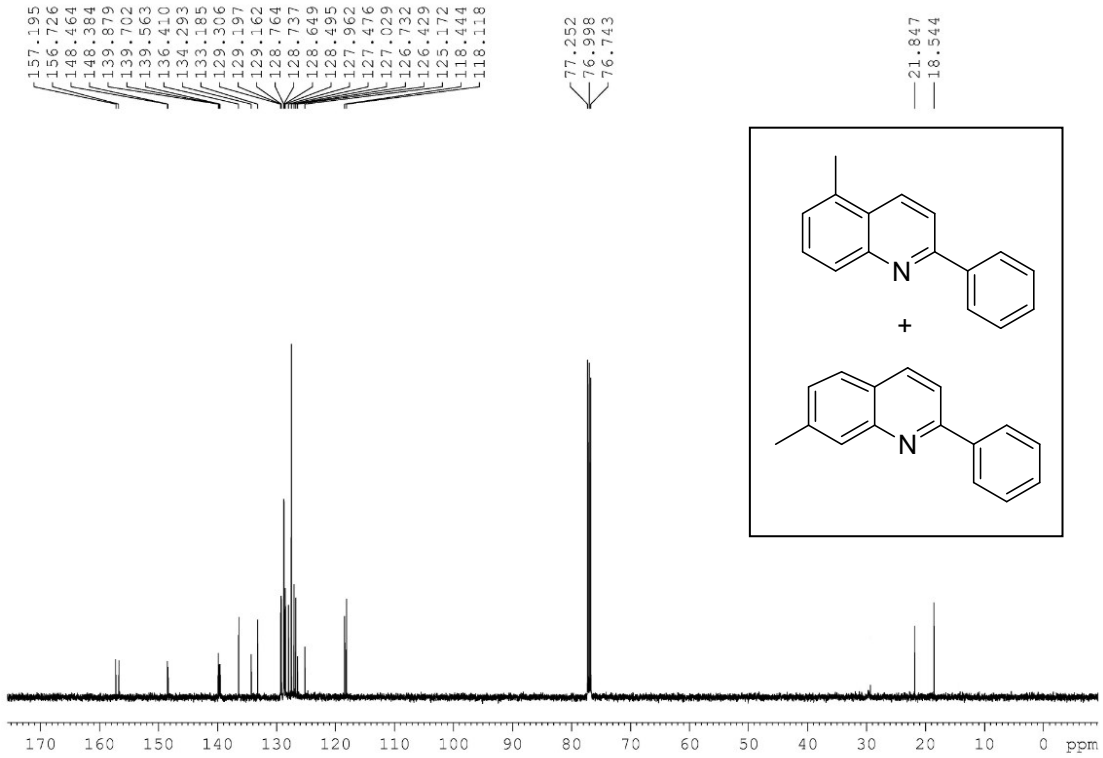
^{1}H and ^{13}C Spectrum of Compound **3a**



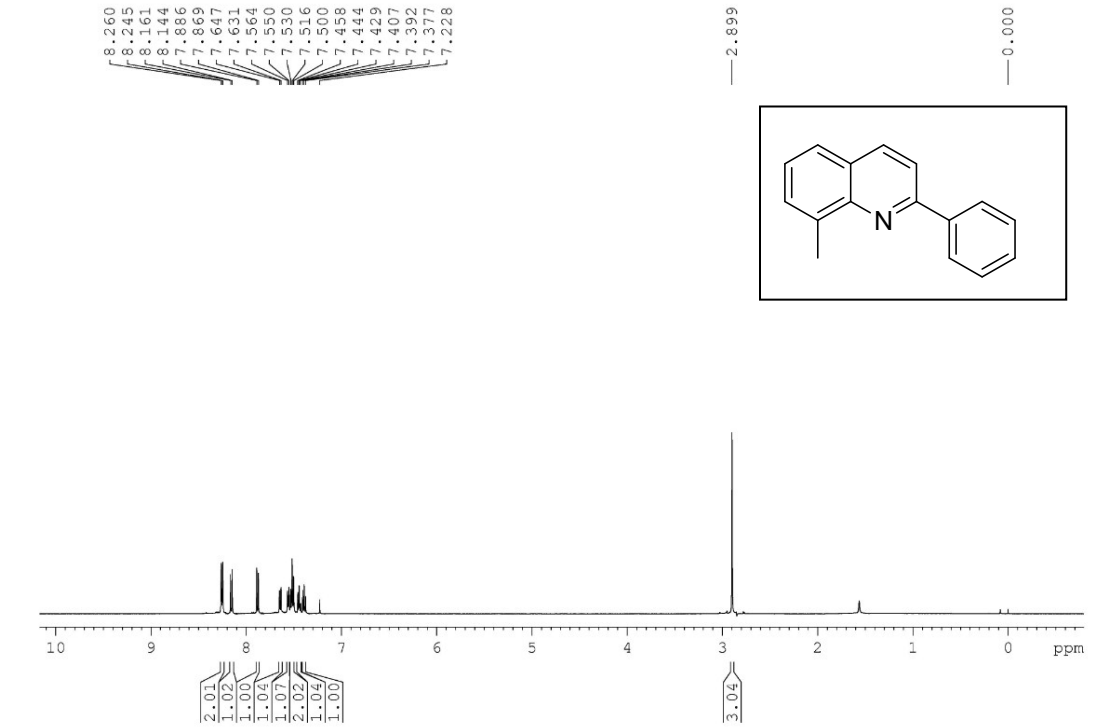


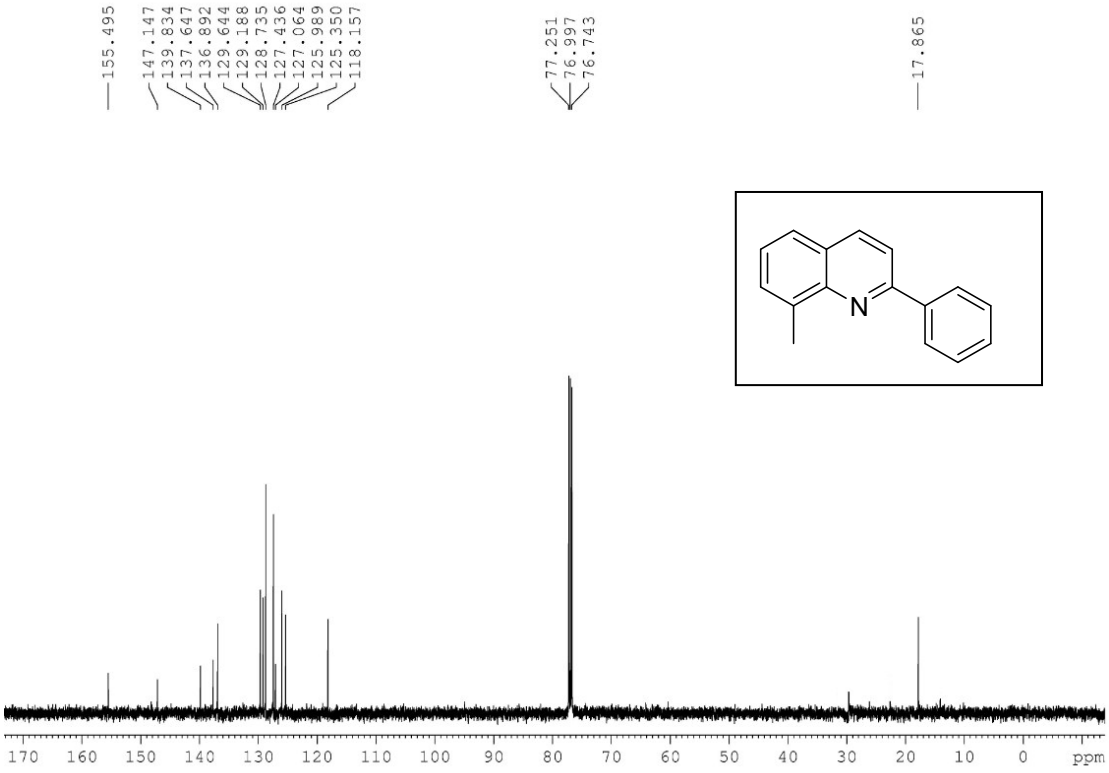
^{1}H and ^{13}C Spectrum of Compound **3b, 3b'**



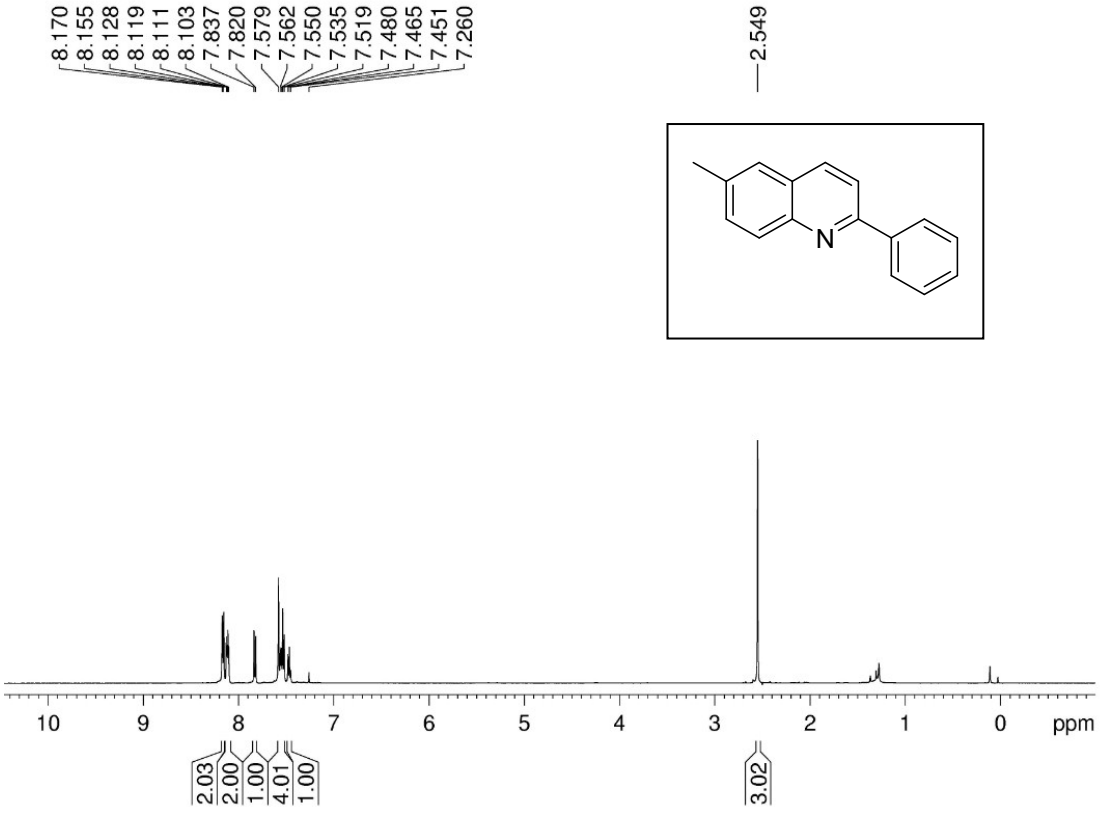


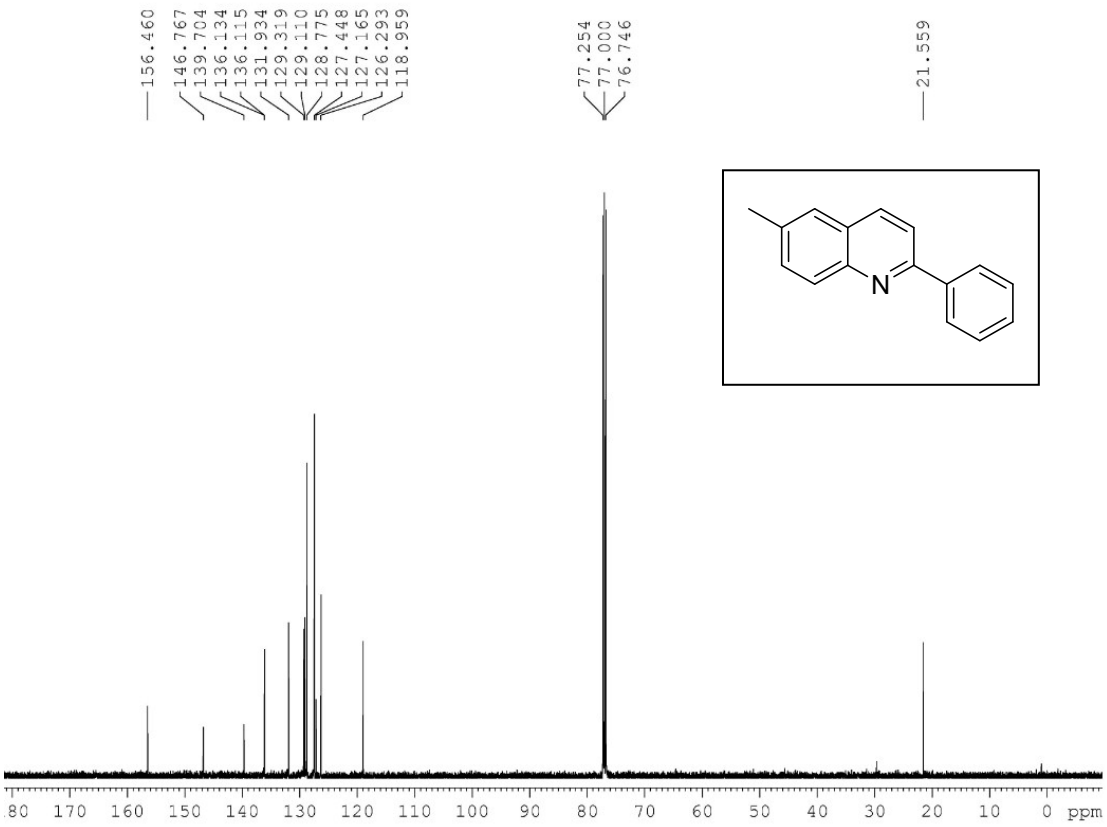
^{1}H and ^{13}C Spectrum of Compound **3c**



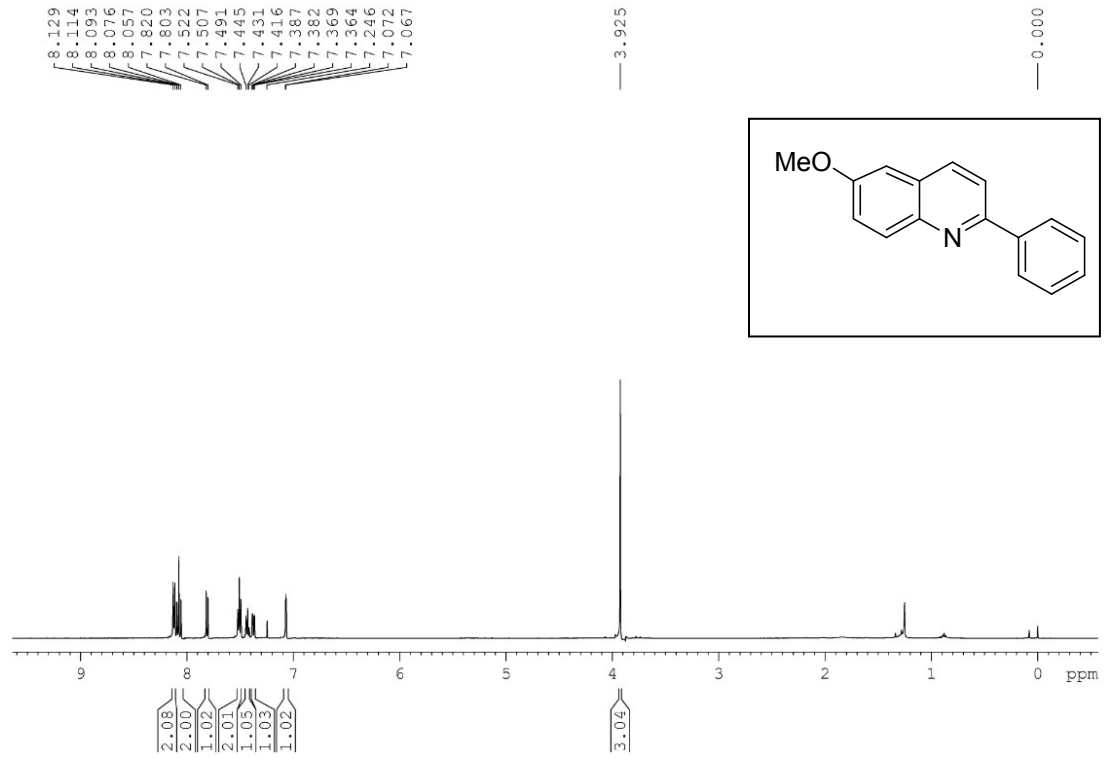


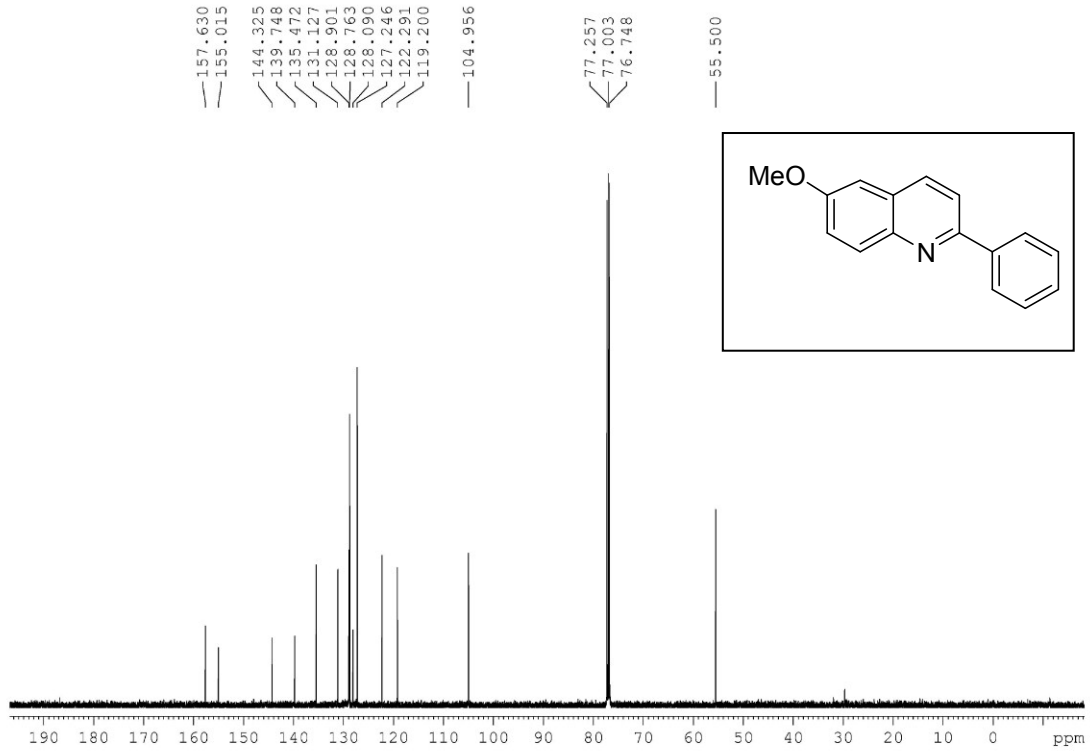
^{1}H and ^{13}C Spectrum of Compound **3d**



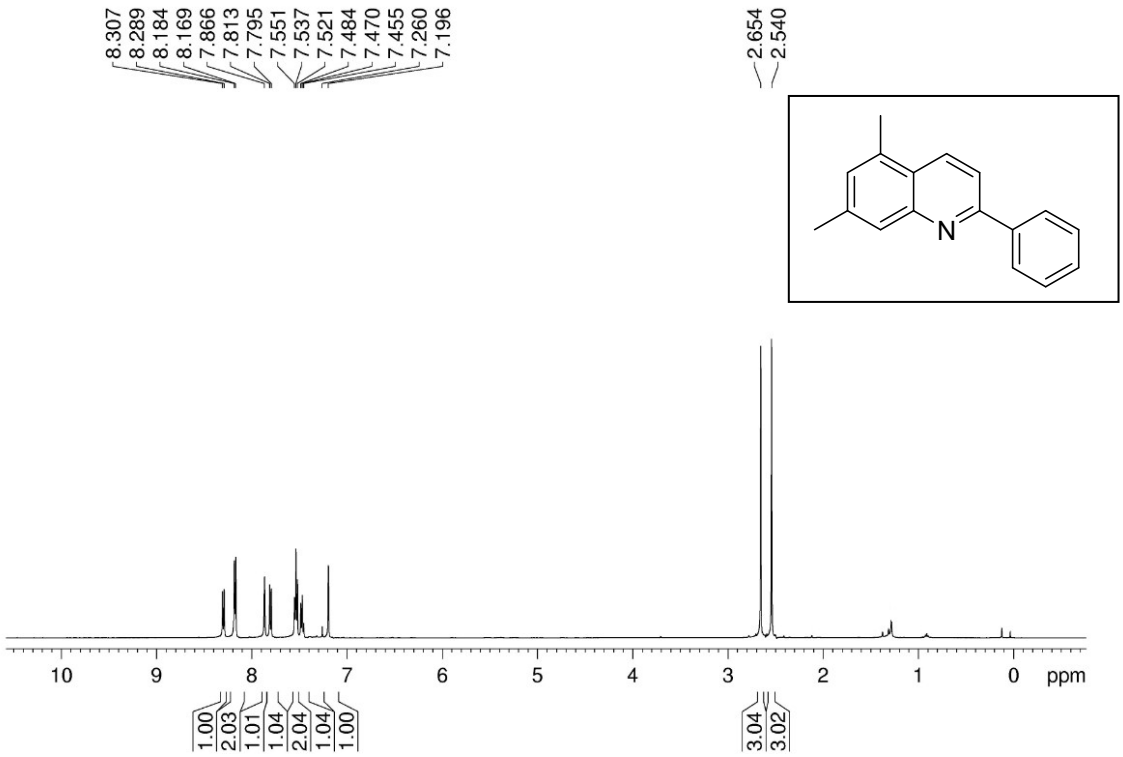


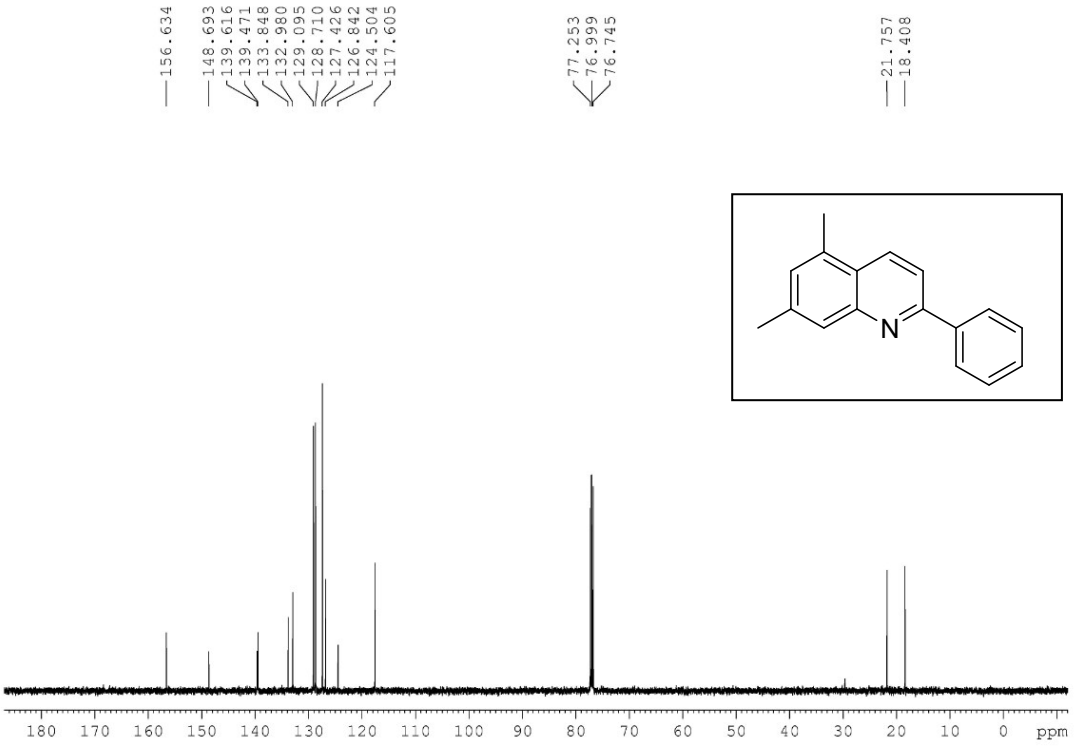
^{1}H and ^{13}C Spectrum of Compound **3e**



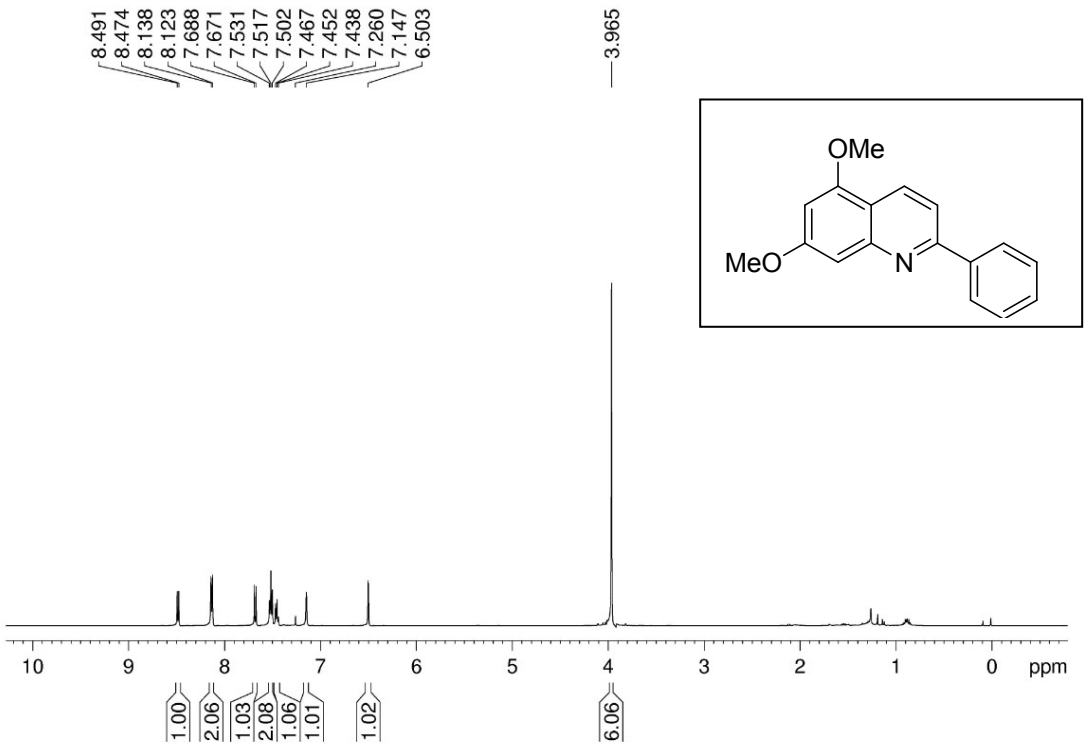


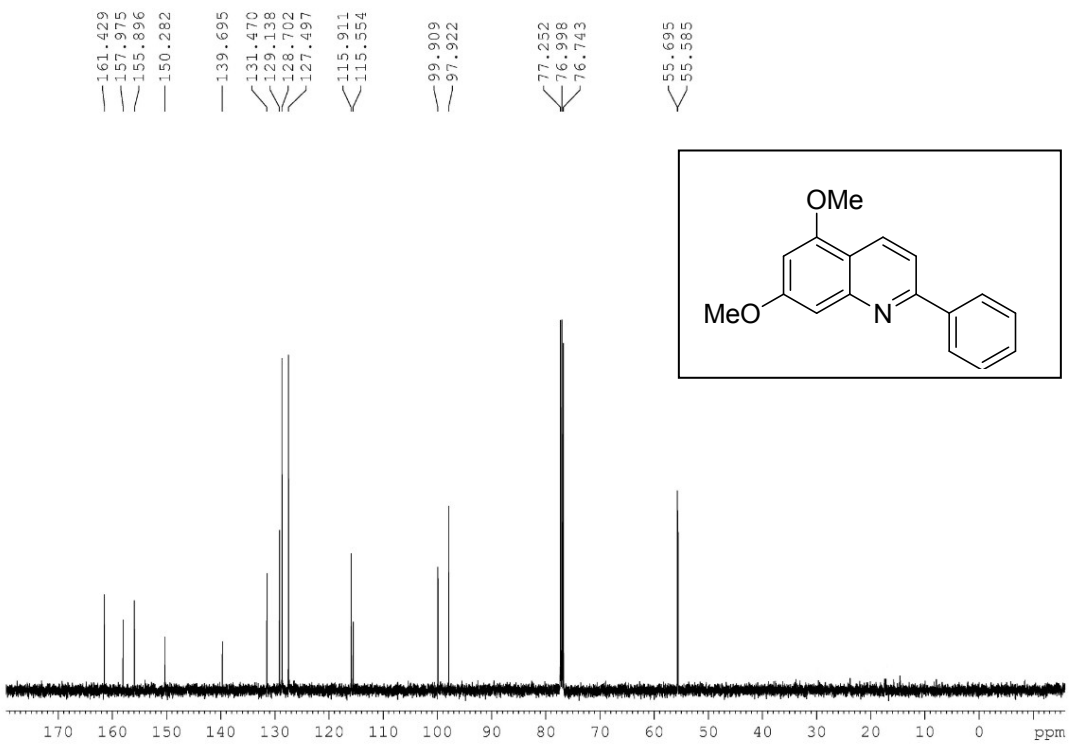
^{1}H and ^{13}C Spectrum of Compound **3f**



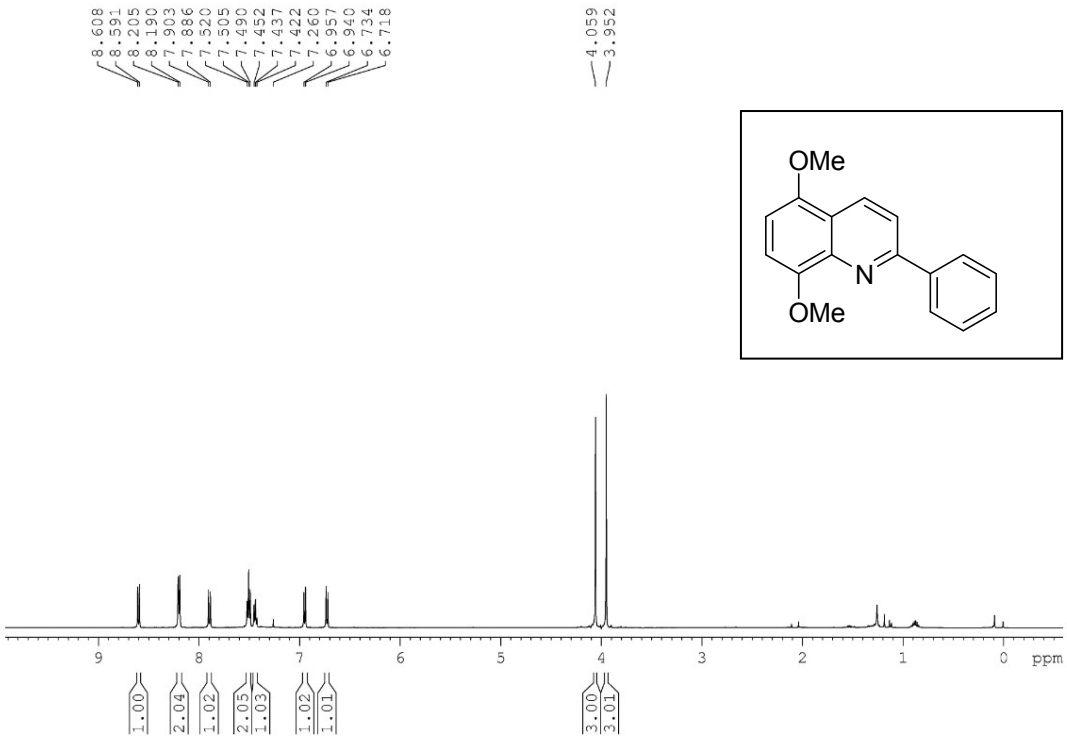


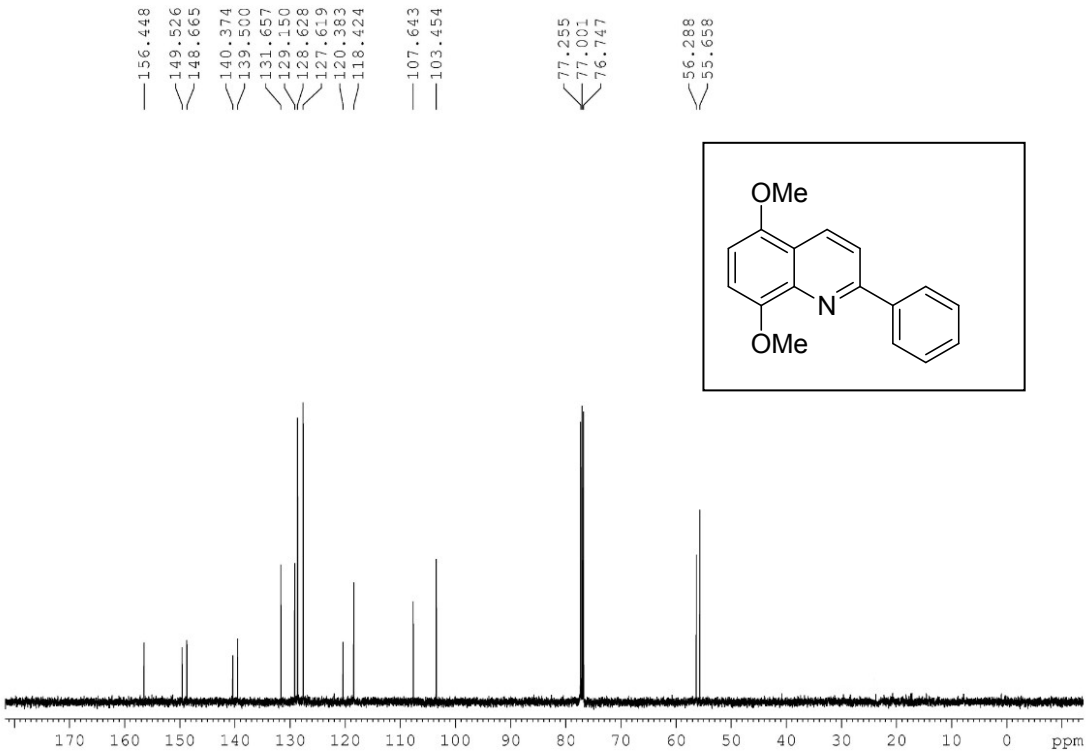
^{1}H and ^{13}C Spectrum of Compound **3g**



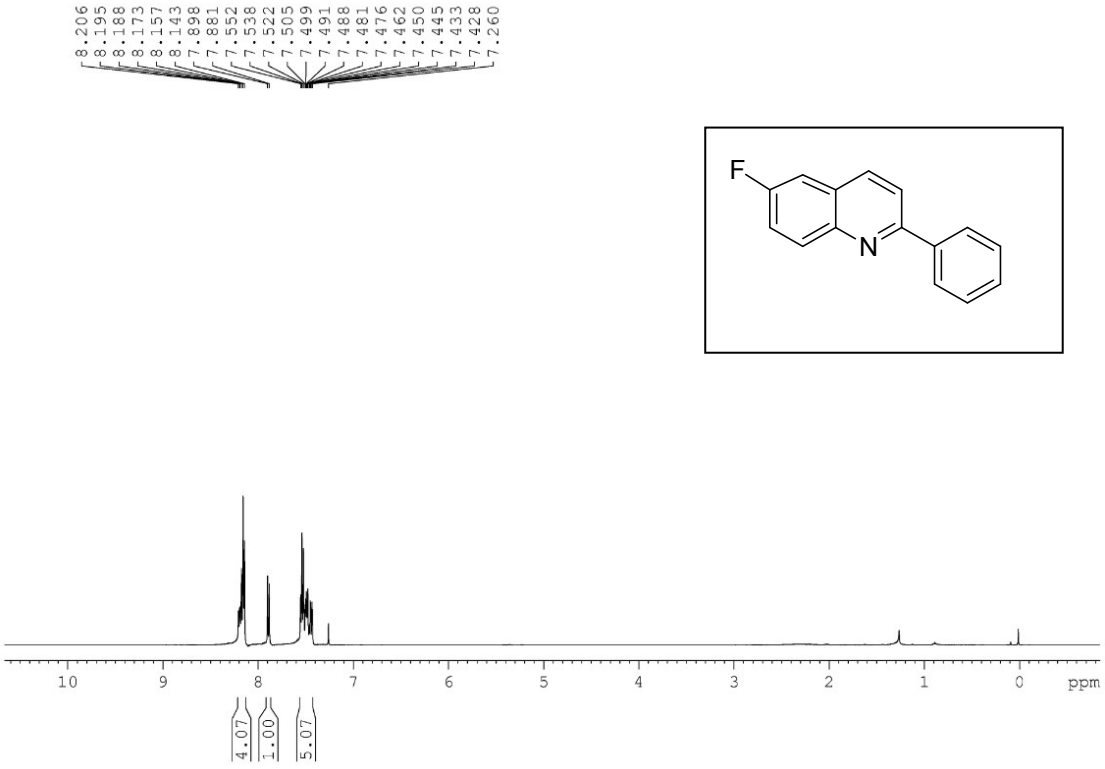


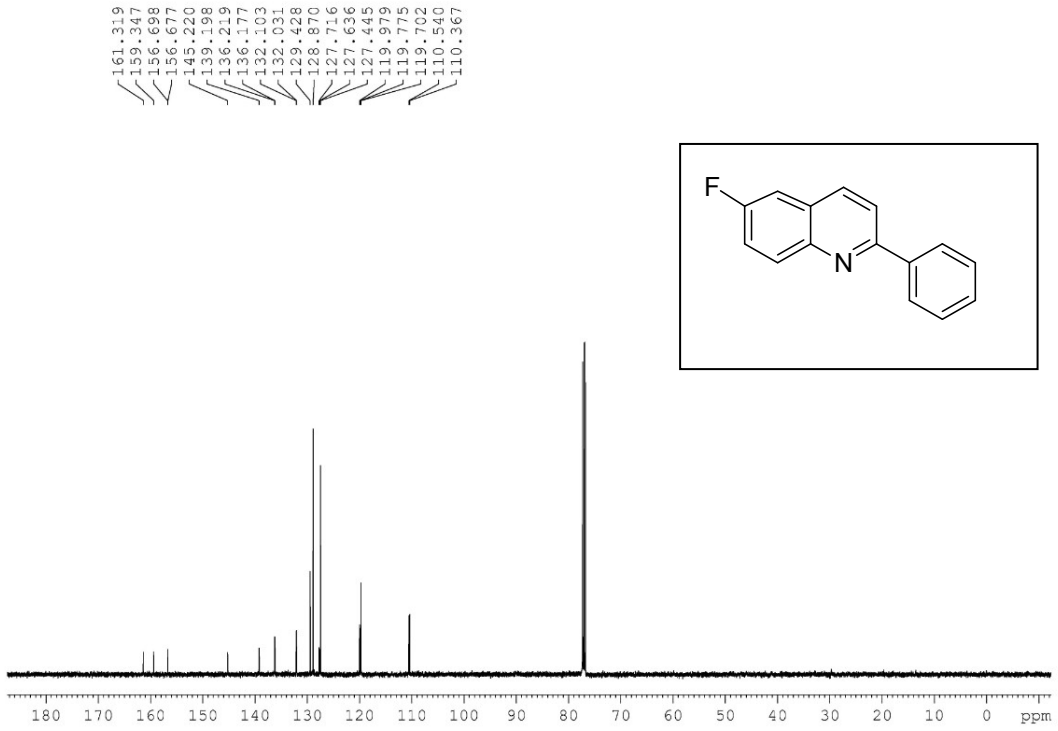
^{1}H and ^{13}C Spectrum of Compound **3h**



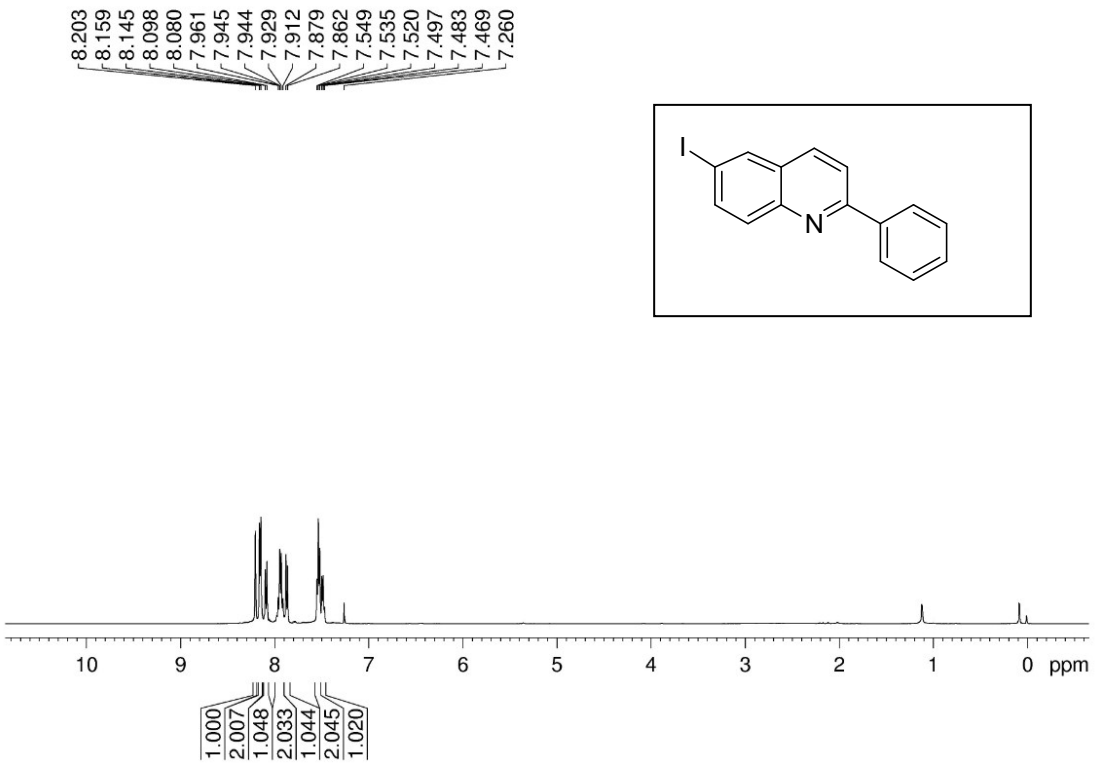


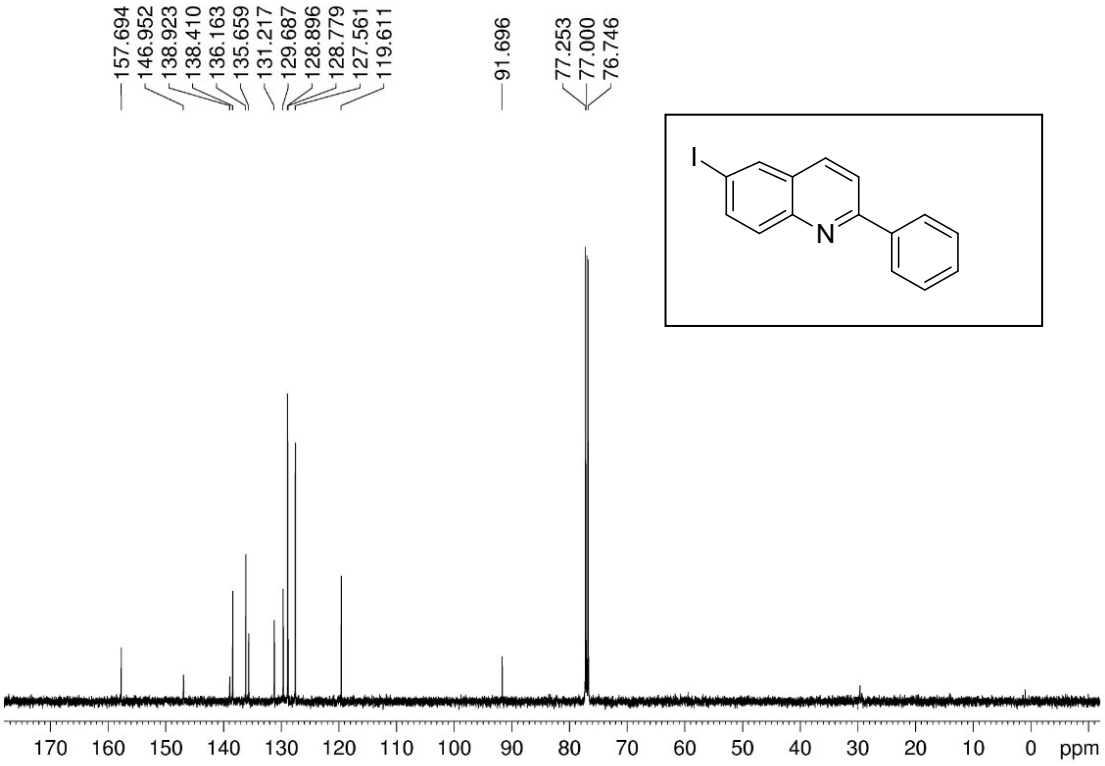
^{1}H and ^{13}C Spectrum of Compound **3i**



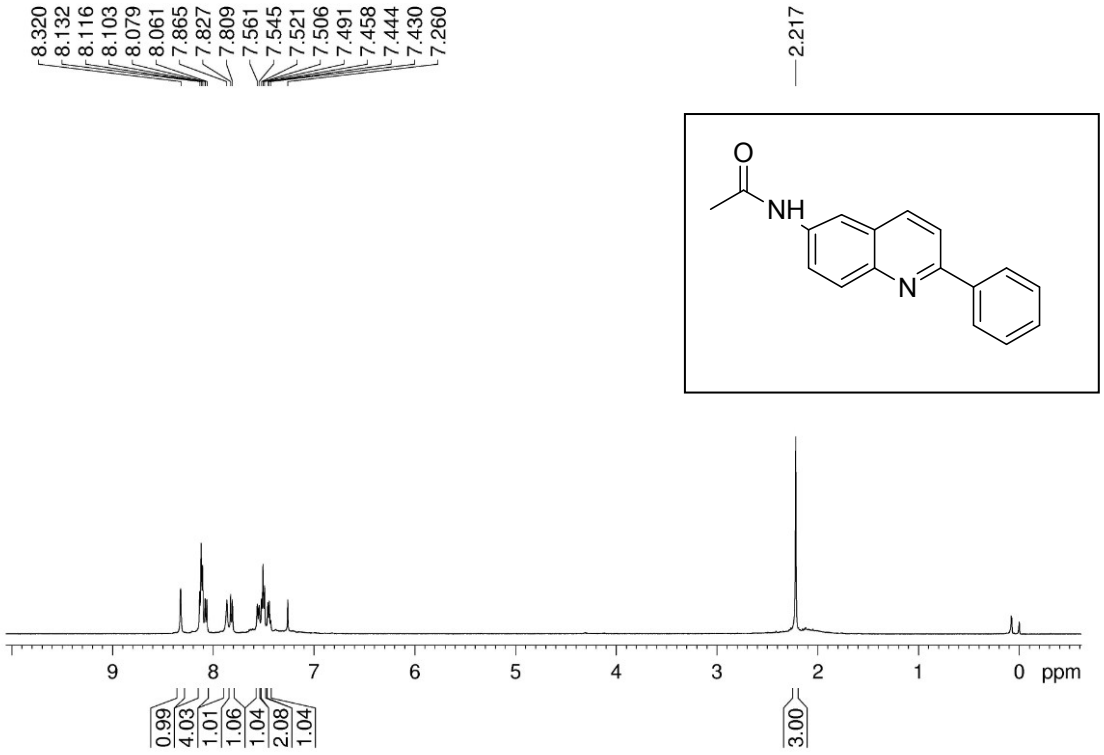


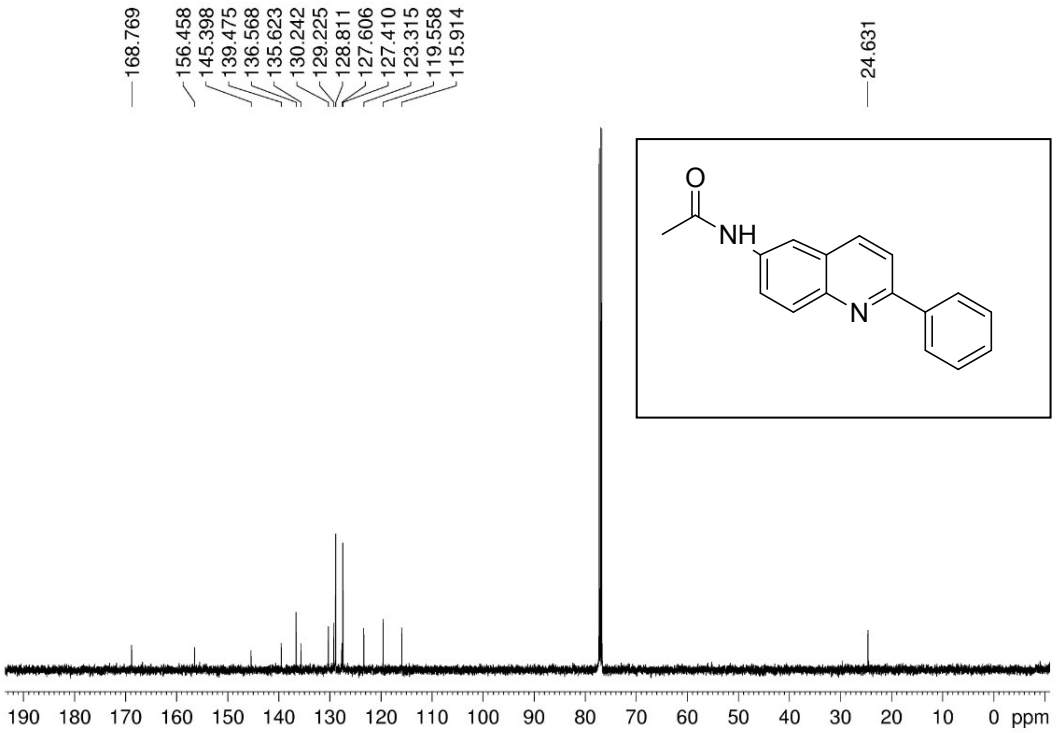
^{1}H and ^{13}C Spectrum of Compound **3j**



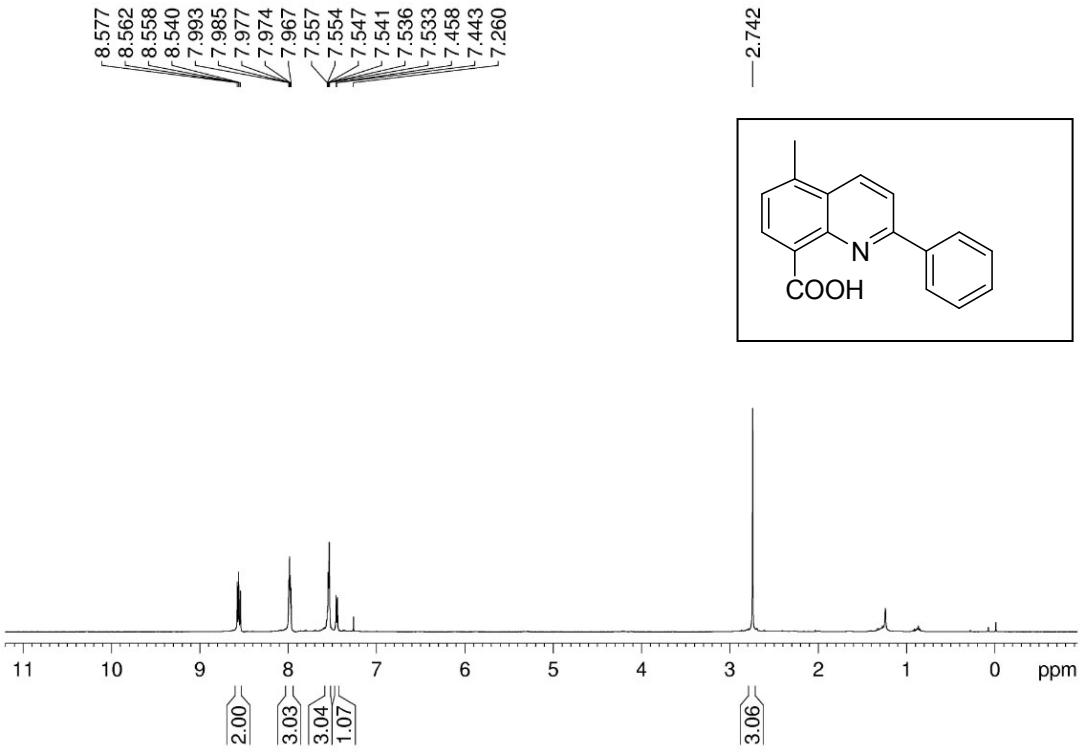


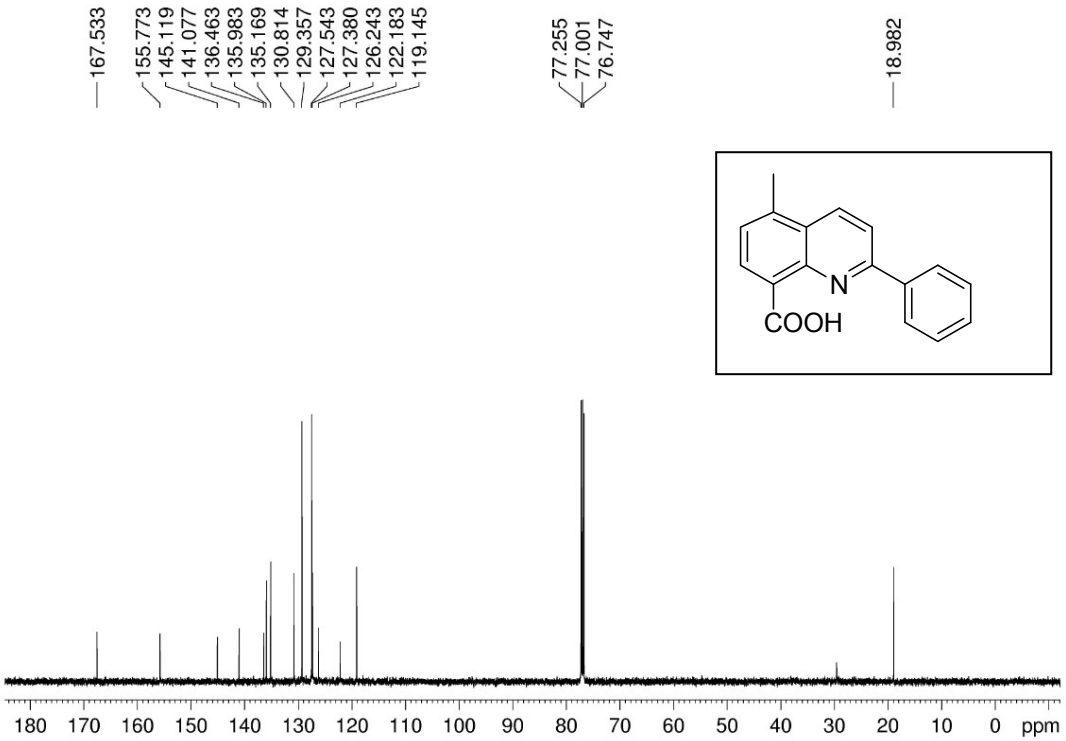
^{1}H and ^{13}C Spectrum of Compound **3k**



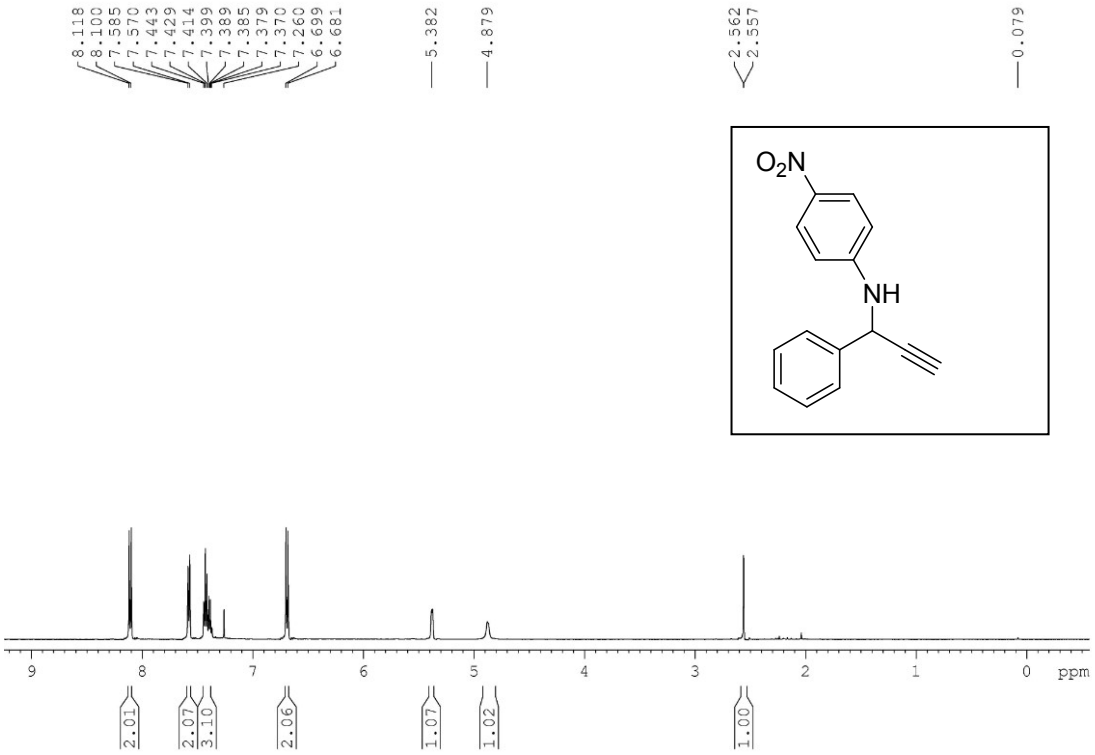


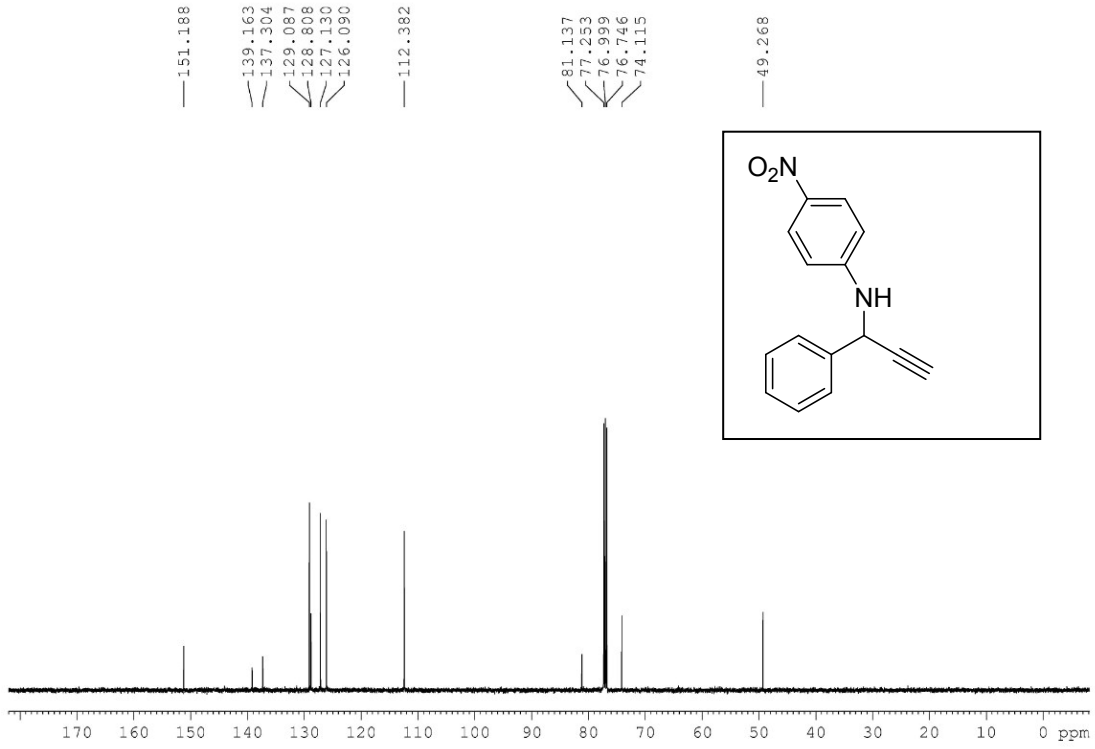
^{1}H and ^{13}C Spectrum of Compound **3l**



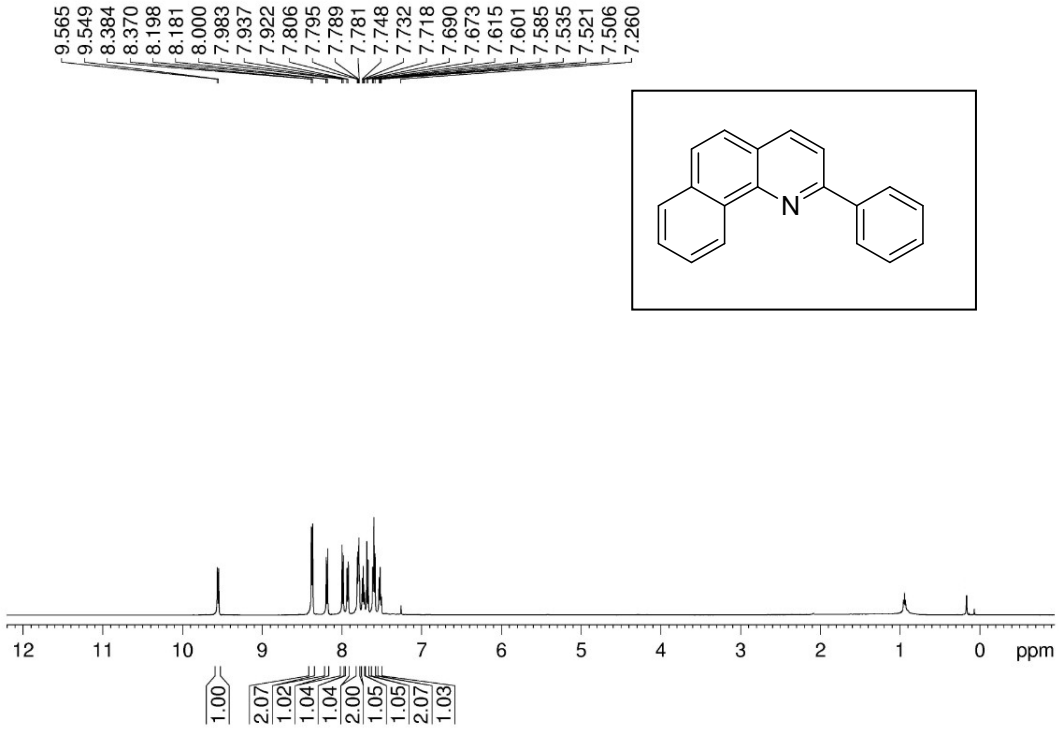


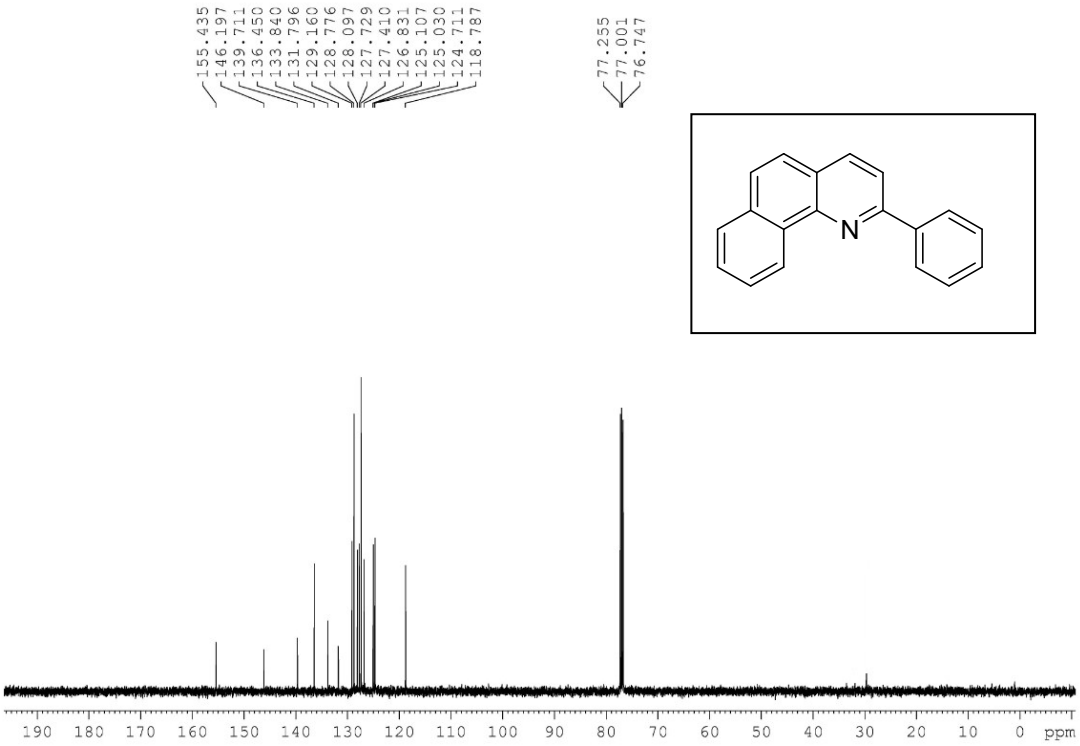
^{1}H and ^{13}C Spectrum of Compound **3m**



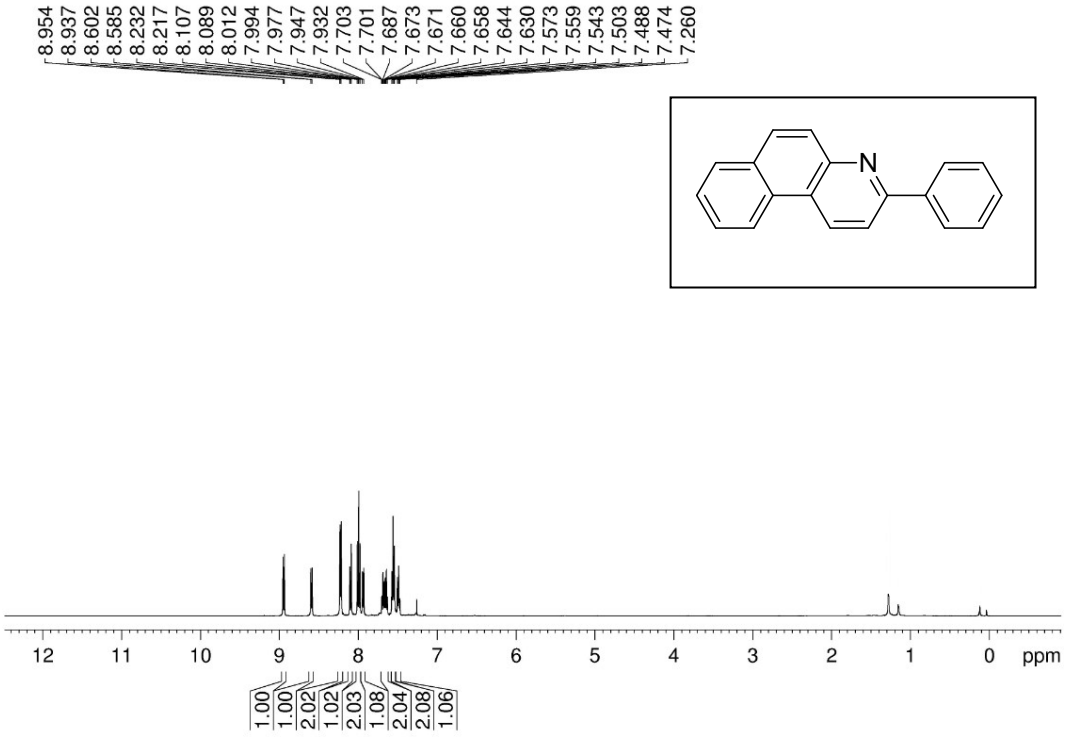


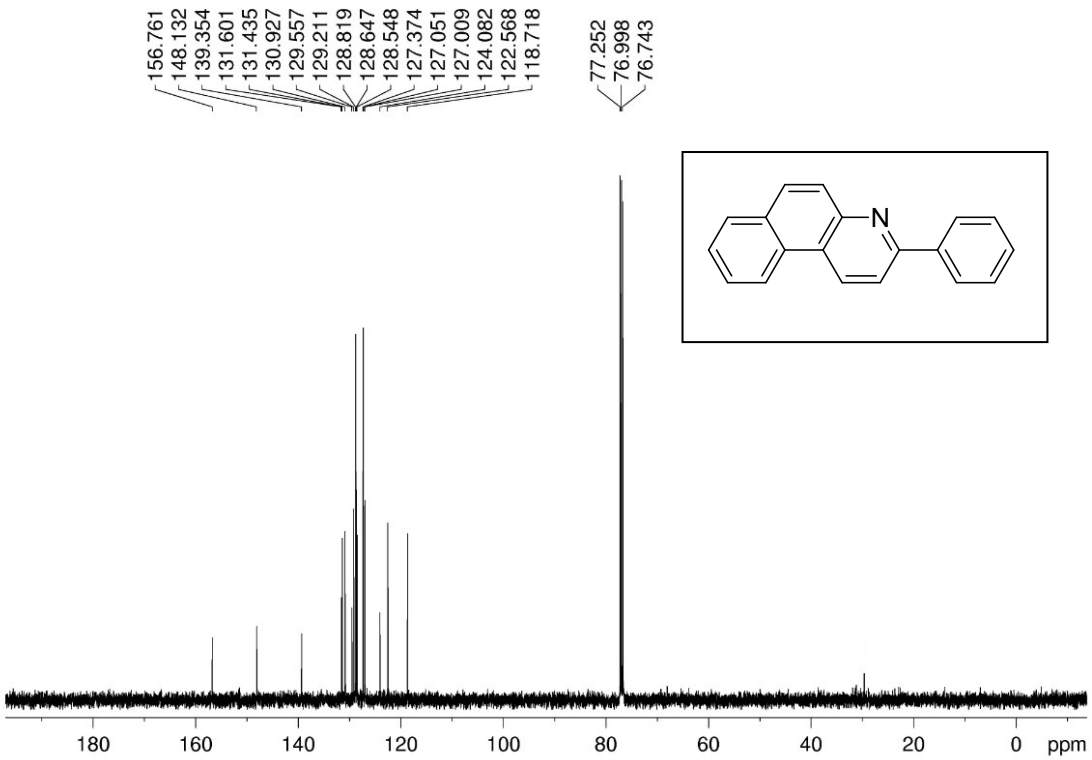
^{1}H and ^{13}C Spectrum of Compound **3n**



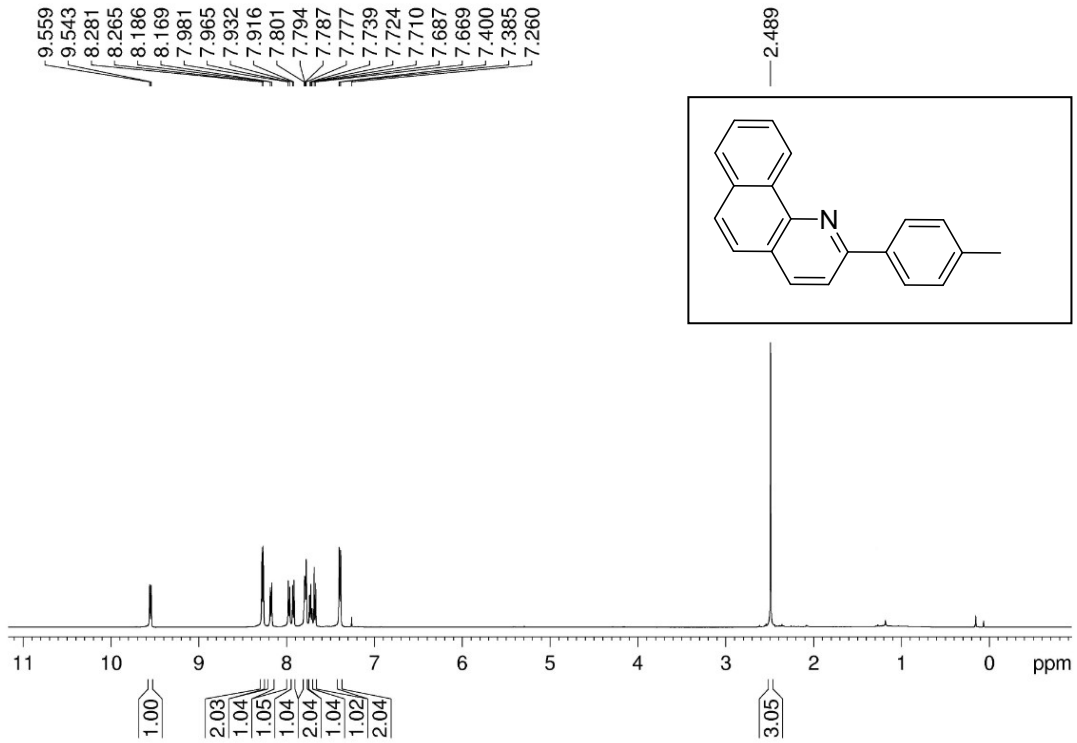


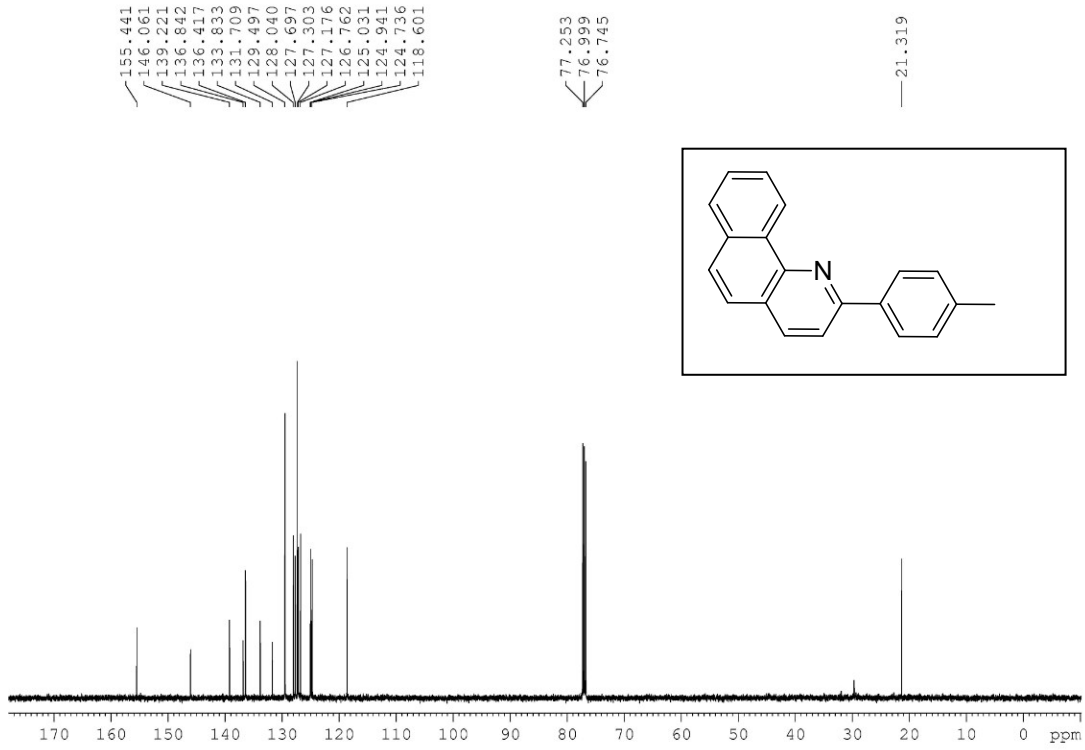
^{1}H and ^{13}C Spectrum of Compound **3o**



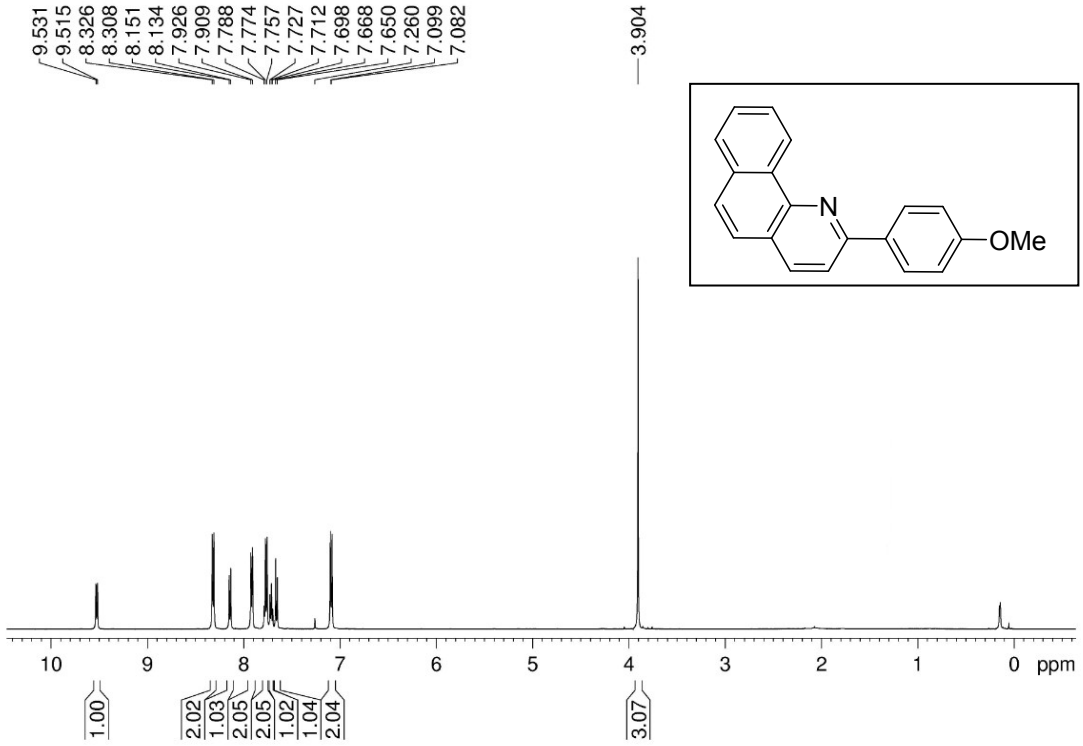


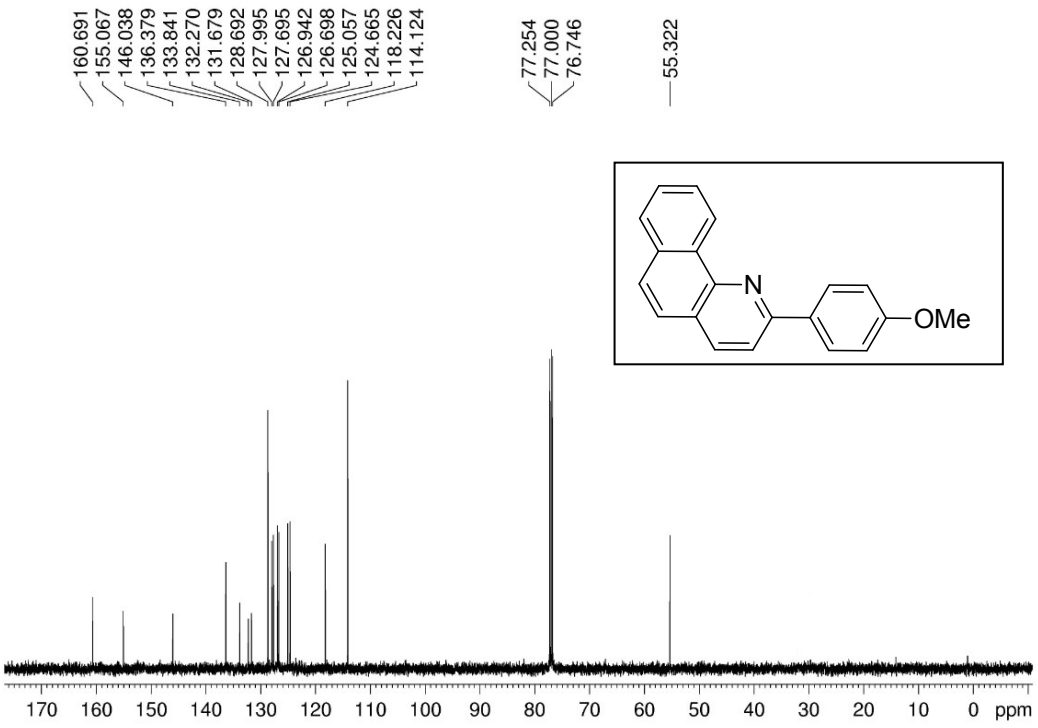
^{1}H and ^{13}C Spectrum of Compound **3p**



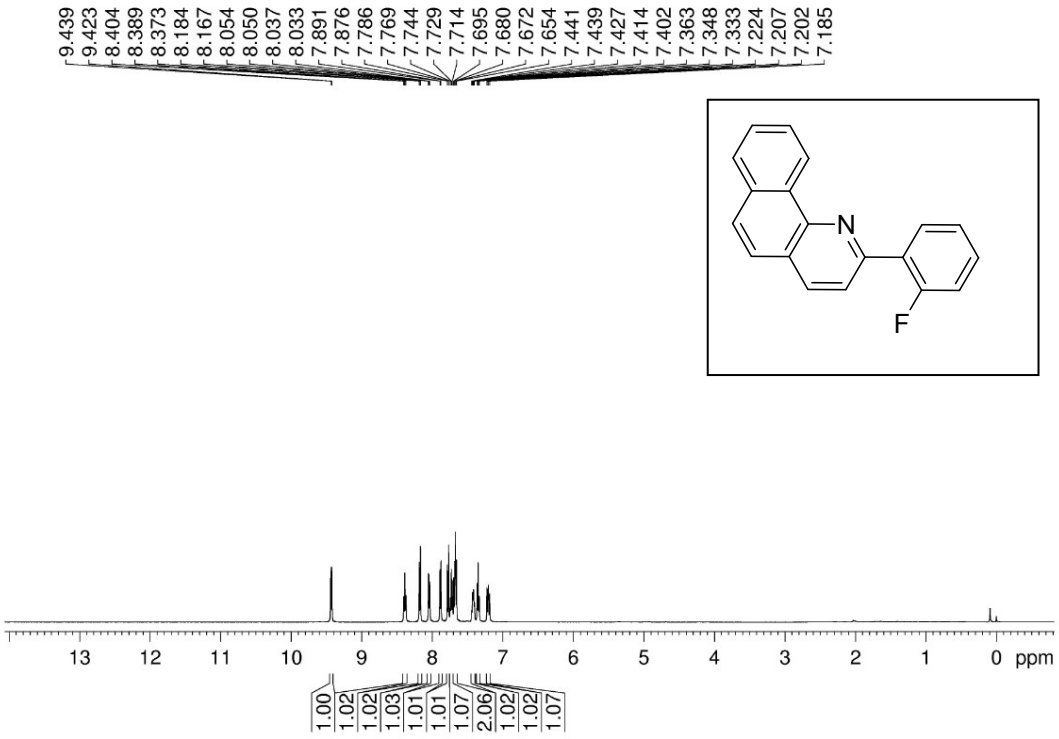


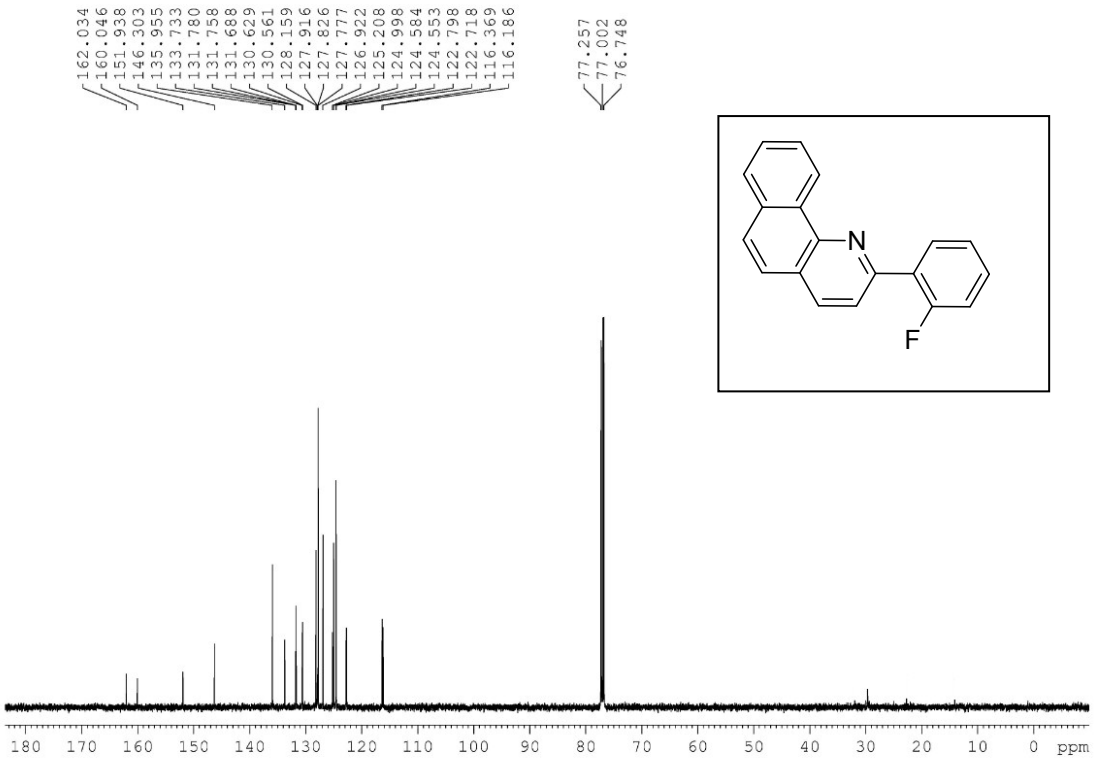
^{1}H and ^{13}C Spectrum of Compound **3q**



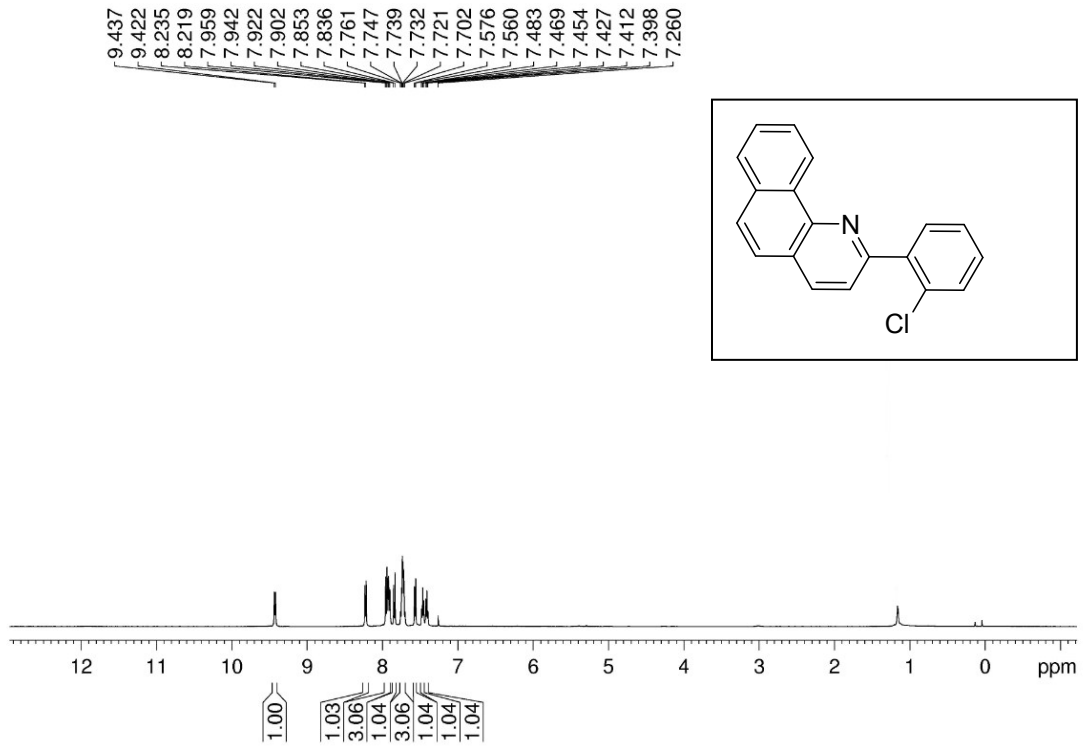


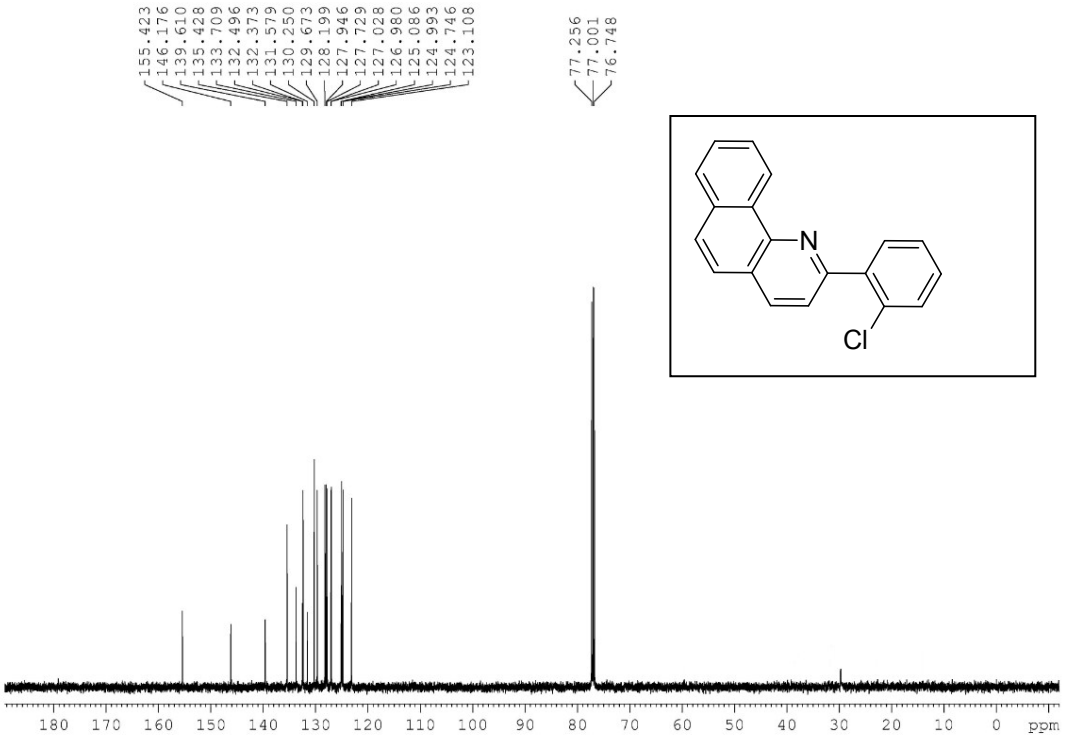
^{1}H and ^{13}C Spectrum of Compound **3r**



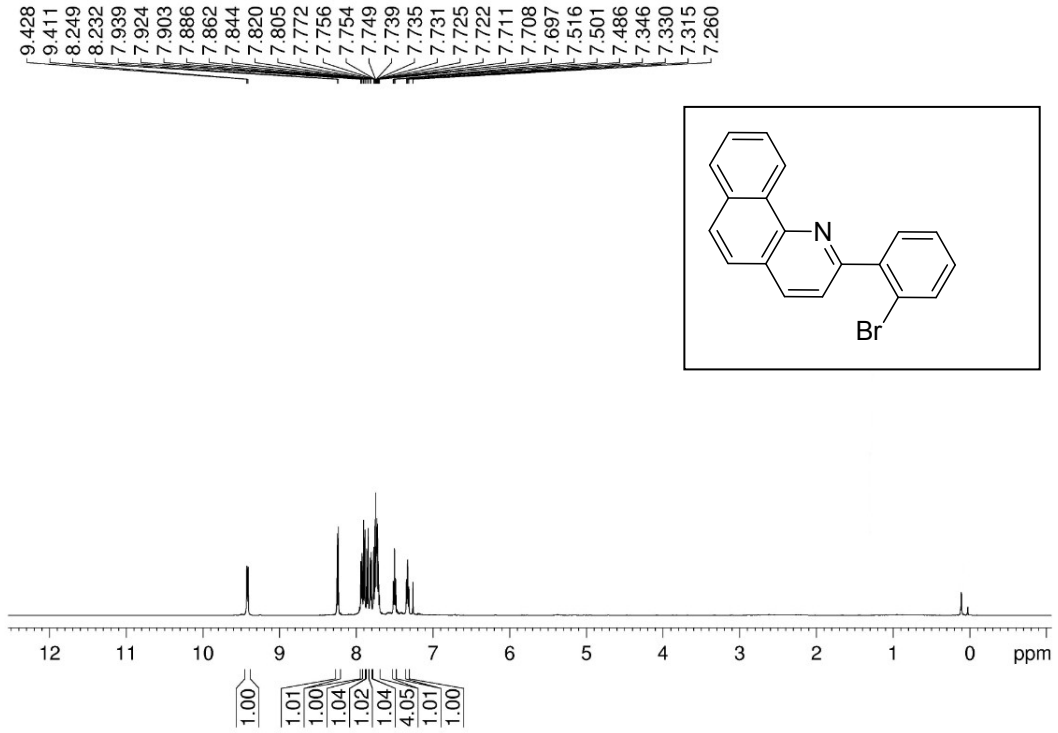


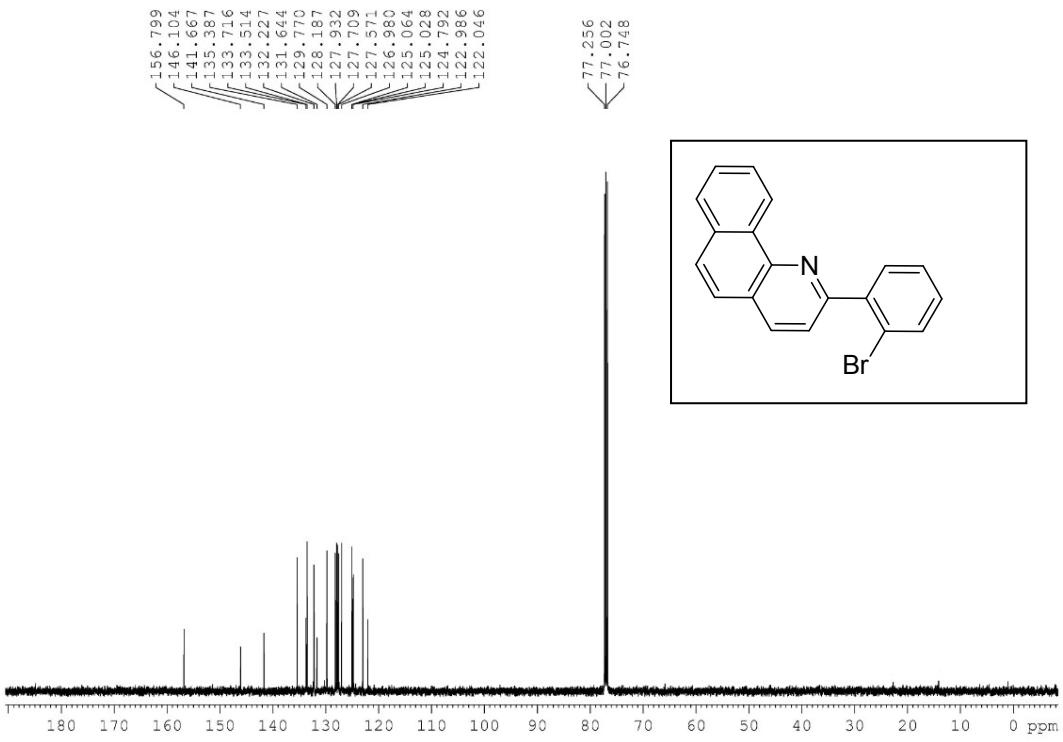
^{1}H and ^{13}C Spectrum of Compound **3s**



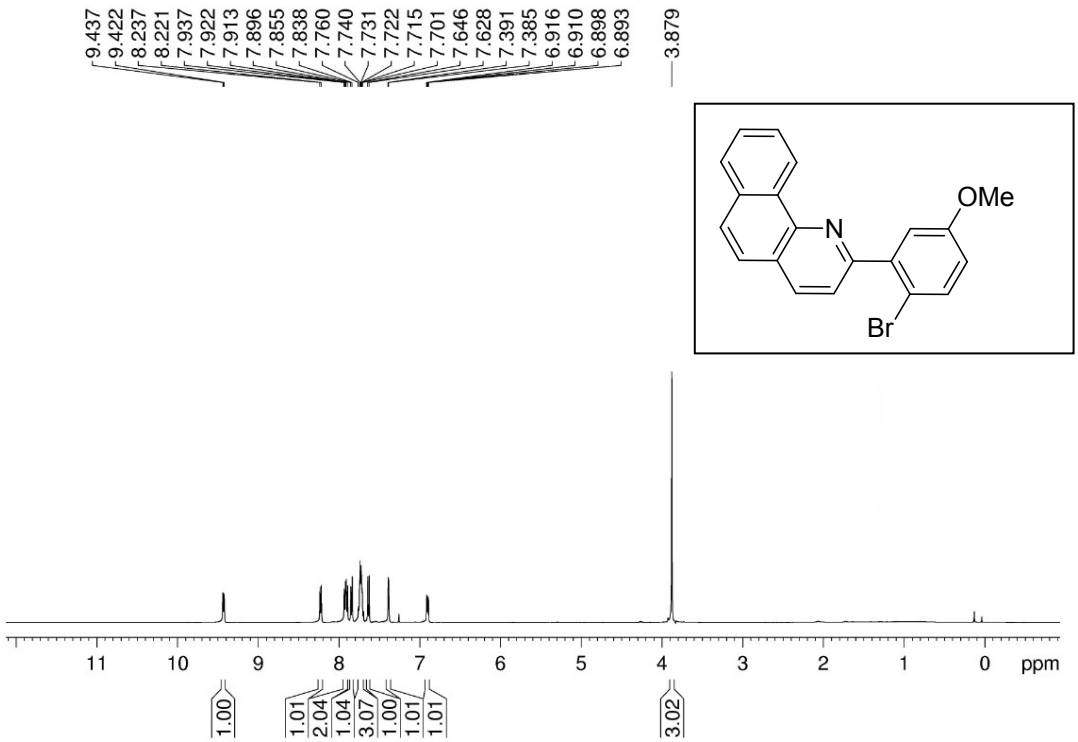


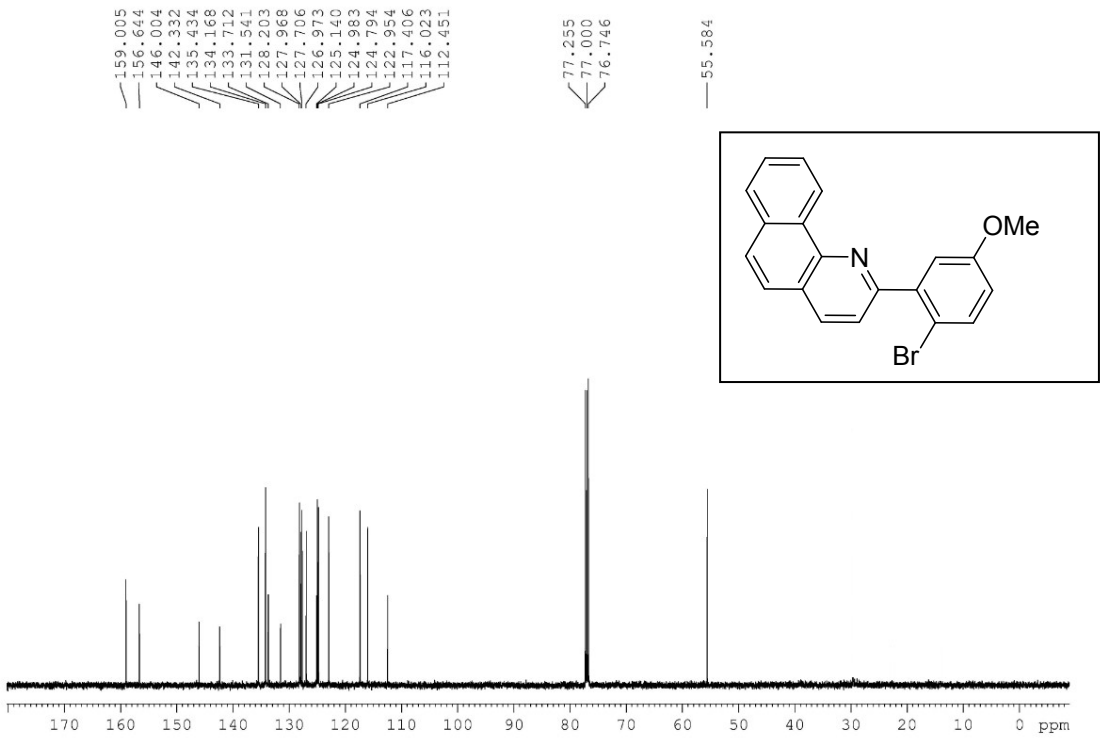
^{1}H and ^{13}C Spectrum of Compound **3t**



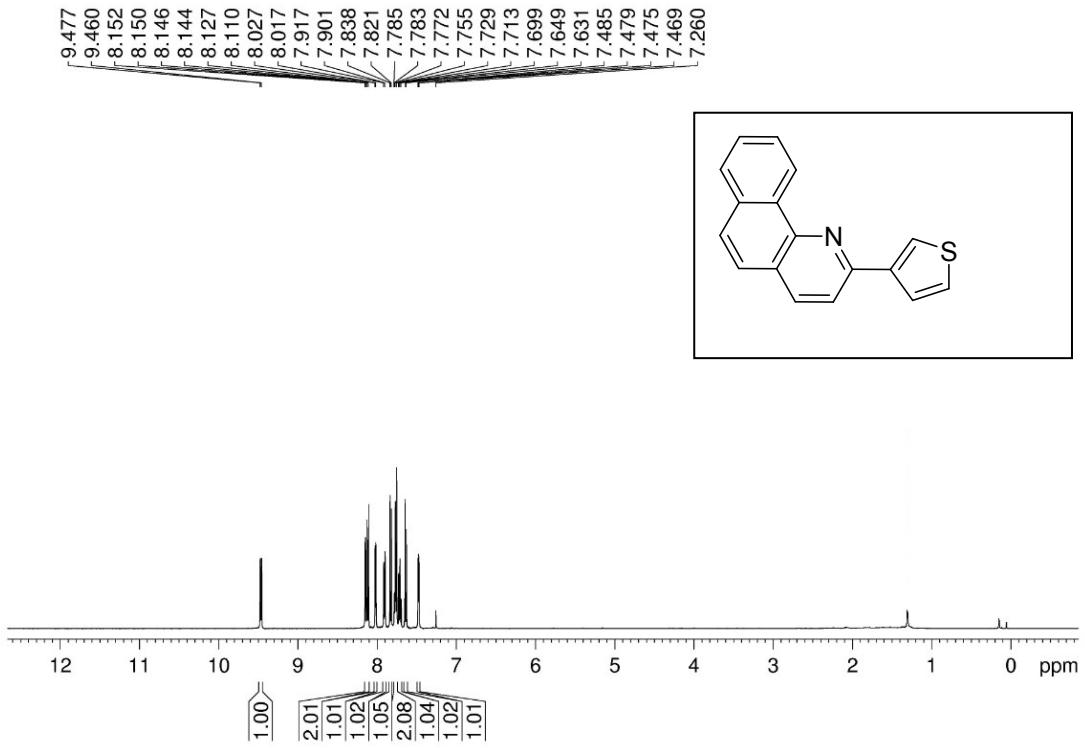


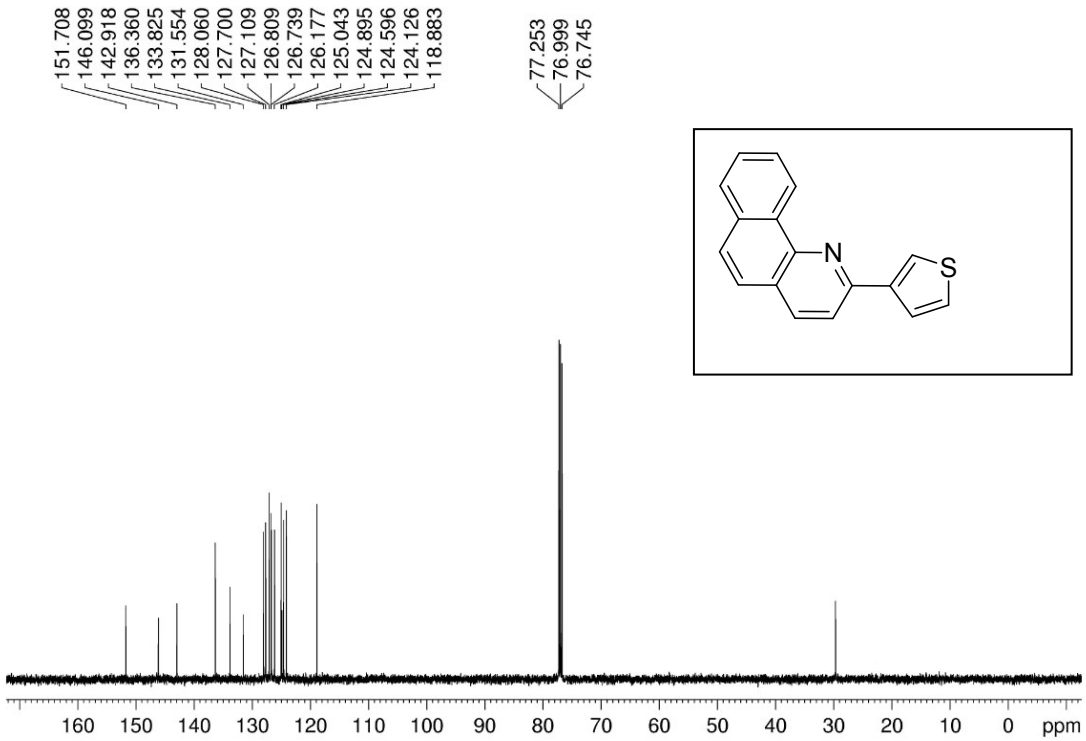
^{1}H and ^{13}C Spectrum of Compound **3u**



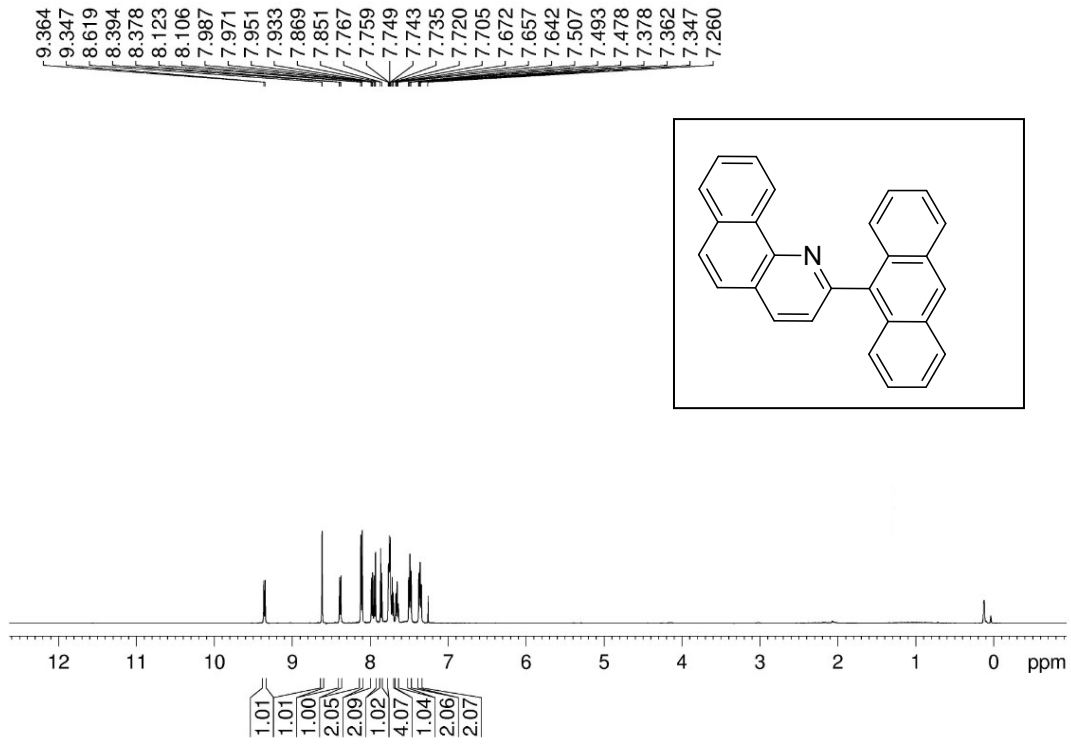


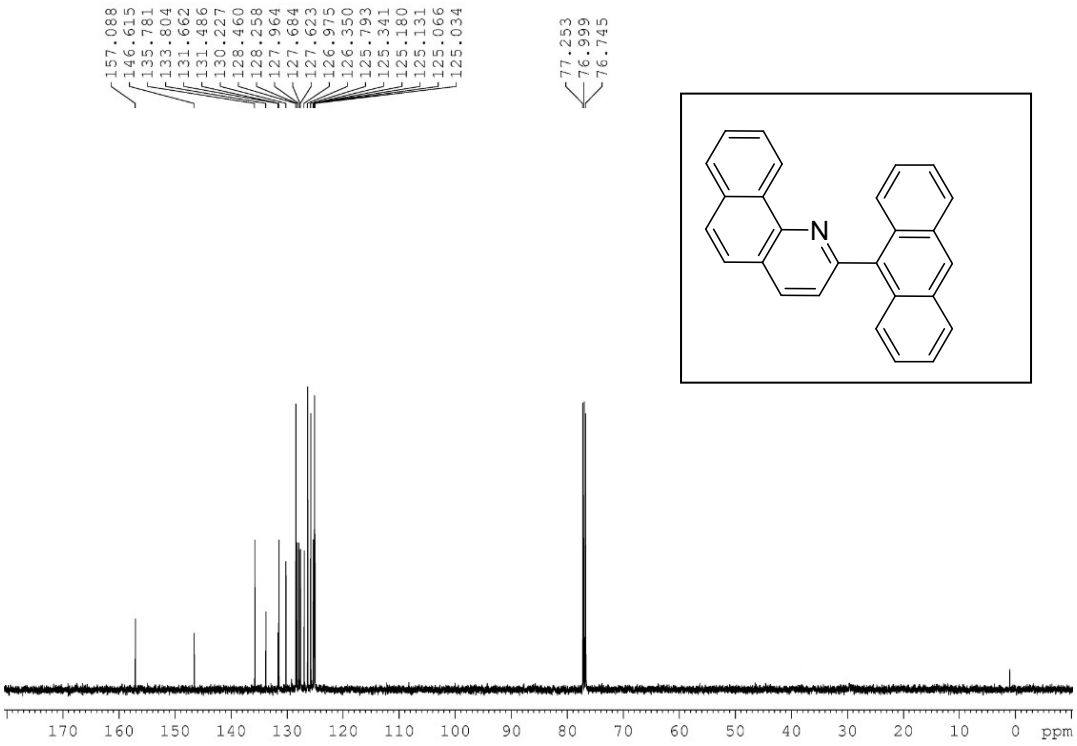
^{1}H and ^{13}C Spectrum of Compound **3v**





^{1}H and ^{13}C Spectrum of Compound **3w**





^{1}H Spectrum of Compound **3a'**