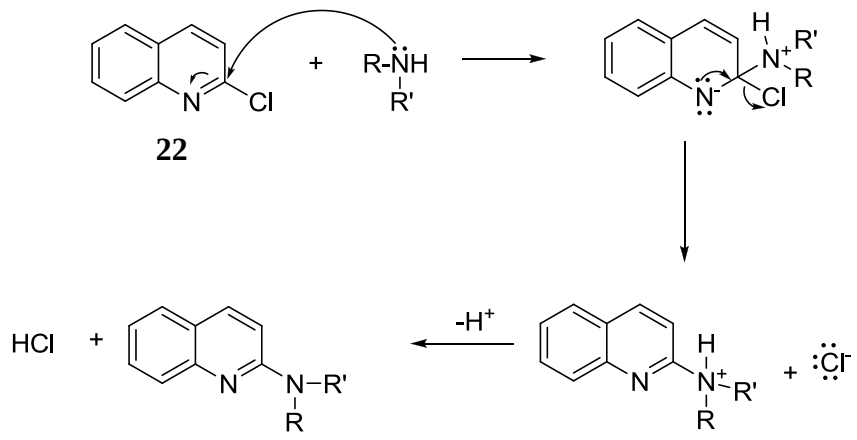
CHAPTER 3: RESULTS AND DISCUSSION

3.1 Synthesis of Quinoline Derivatives

In this chapter, the synthesis of 2-substituted quinolines will be discussed. IR, ^{1}H NMR, ^{13}C NMR and GC-mass spectra of the compounds were analyzed for their structural analysis. Melting points of the solid compounds were also determined. All related spectra are provided in appendices.

In general, reactions between 2-chloroquinoline **(22)** and a series of piperidines and anilines were performed by refluxing in ethanol for 5-8 hours.The mixtures were cooled down to room temperature and the solvent was removed under vacuum. The crudes were dissolved in 10 ml of diethyl ether and washed with 10 ml of distilled water. The organic layers were dried over sodium sulphate anhydrous and filtered. The solvent was evaporated off by using rotary evaporator. The products were further purified by recrystallization from ethanol.

The analysis of spectra has suggested that reaction underwent at position-2 of quinoline which is activated towards nucleophilic attack due to the presence of the adjacent electron withdrawing nitrogen atom. In this S_N2 reaction, the incoming nucleophile attacks the C with halide. A transition state is occurred in which the new nucleophile-carbon bond is partially forming and old C-Cl bond is partially breaking leading to the formation of the product as shown in Scheme 3.1.



Scheme 3.1: Proposed reaction of nucleophilic substitution between 2-chloroquinoline and amines at position-2 of quinoline system

3.1.1 2-*N*-(3-methyl)piperidinoquinoline (25) and 2-*N*-(4-methyl)piperidinoquinoline (26)

Reaction between 2-chloroquinoline **(22)** with 3-methylpiperidine **(23)** and 4-methylpiperidine **(24)** was successfully gave **25** and **26** respectively as shown in Figure 3.1.

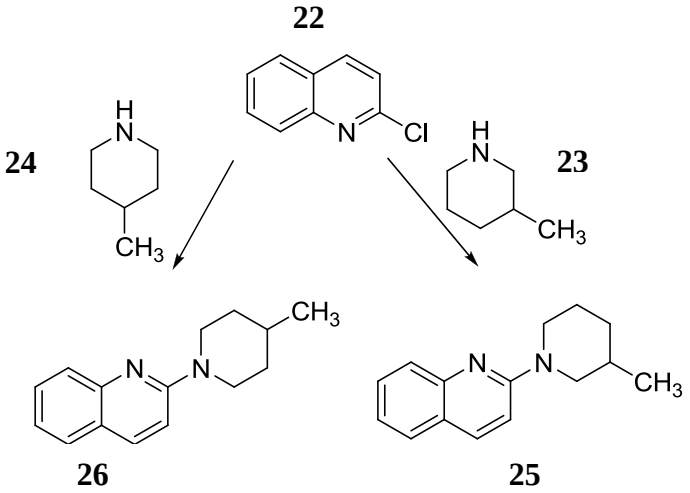
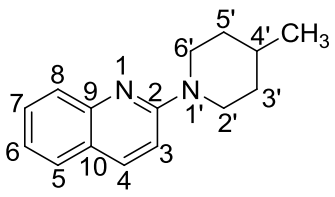


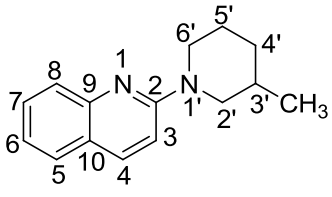
Figure 3.1: Reactions of 2-chloroquinoline with various piperidine

The infrared spectra of **25** and **26** show the similar frequencies, where frequency of -C-H stretching for alkane has been observed at 2944 cm^{-1} while aromatic stretching at 1617 cm^{-1} and 1507 cm^{-1}.

The ^{1}H NMR spectra of **25** and **26** show a doublet signal at δ 7.85 (*J* = 9.04 Hz) due to H-4. A doublet peak at δ 7.68 (*J* = 8.08 Hz) was assigned to H-5. A doublet peak at δ 7.57 (*J* = 7.80 Hz) was due to H-8. Two signals of triplet of doublet at δ 7.50(*J* = 8.32 Hz) and δ 7.18 (*J* = 8.08 Hz) were assigned for H-7 and H-6 respectively. A doublet peak at δ 7.00 (*J* = 9.28 Hz) was due to H-3. For compound **25**, a multiplet peak at δ 4.43 was observed which was due to H-6'. H-2' signal was appeared at δ 2.93 (*J* = 3.16 Hz) as a triplet of doublet peak. A triplet of doublet peak at δ 2.59 (*J* = 10.71 Hz, *J* = 10.47 Hz) was assigned to H-2'.Multiplet peak was observed at δ 1.80 due to H-4' and H-5'. A multiplet peak was observed at δ 1.94 due to H-3'. A doublet signal at δ 0.99 (*J*=6.6 Hz) was assigned to -CH_3. While for compound **26**, a doublet peak was observed at δ 4.52 (*J*= 13.2 Hz) due to H-2'. A triplet of doublet peak at δ 2.58 was assigned to H-6'. A doublet peak was observed at δ 1.76 (*J*=12.92 Hz) due to H-3'. Two multiplet peaks at δ 1.68 and δ 1.28 were assigned to H-4' and H-5' respectively. Signal of -CH_3 was observed at δ 0.97 (*J* = 6.60 Hz) as doublet peak.



26



25

The ^{13}C NMR spectra have a total number of 15 carbons which was in agreement with the molecular formula for compounds **25** and **26**. The signals between δ 157.4 and δ

109.8 in the downfield region were assigned for quinoline ring. Meanwhile, absorption peak observed in the upfield region between δ 52.9 and δ 25.2 for **25** and between δ 45.5 and δ 31.2 for **26** were assigned for the 3-methylpiperidine **(23)** and 4-methylpiperidine **(24)** ring respectively. Signals for methyl were observed at δ 19.3 and δ 21.8 for compounds **25** and **26** respectively.

The GC-mass spectra showed a molecular ion peak at m/z 226 [M^+], which was consistent with the calculated mass from the molecular formula $C_{15}H_{18}N_2$. Signal at m/z 211 probably due the loss of methyl moiety at piperidine group. Loss of quinoline moeity was presented by signal at m/z 129.

3.1.2 Reactions of 22 with Various Amines

Reaction between **22** and aniline **(27)**, *m*-toluidine **(29)**, *p*-toluidine **(31)**, *m*-ethylaniline **(33)**, *p*-ethylaniline **(35)**, *N*-methylaniline **(37)**, *N*-ethylaniline **(39)**, *m*-anisidine **(41)**, *p*-anisidine **(43)**, *m*-chloroaniline **(45)** and *p*-chloroaniline **(47)** produces 2-*N*-anilinoquinoline **(28)**, 2-*N*-(*m*-methyl)anilinoquinoline **(30)**, 2-*N*-(*p*-methyl)anilinoquinoline **(32)**, 2-*N*-(*m*-ethyl)anilinoquinoline **(34)**, 2-*N*-(*p*-ethyl)anilinoquinoline **(36)**, 2-*N*-methylanilinoquinoline **(38),** 2-*N*-ethylanilinoquinoline **(40)**, 2-*N*-(*m*-methoxy)anilinoquinoline **(42)**, 2-*N*-(*p*-methoxy)anilinoquinoline **(44**), 2-*N*-(*m*-chloro)anilinoquinoline **(46)**, and 2-*N*-(*p*-chloro)anilinoquinoline **(48)** respectively. Figure 3.2 show a diagrammatic representation of the starting materials and their respective products.

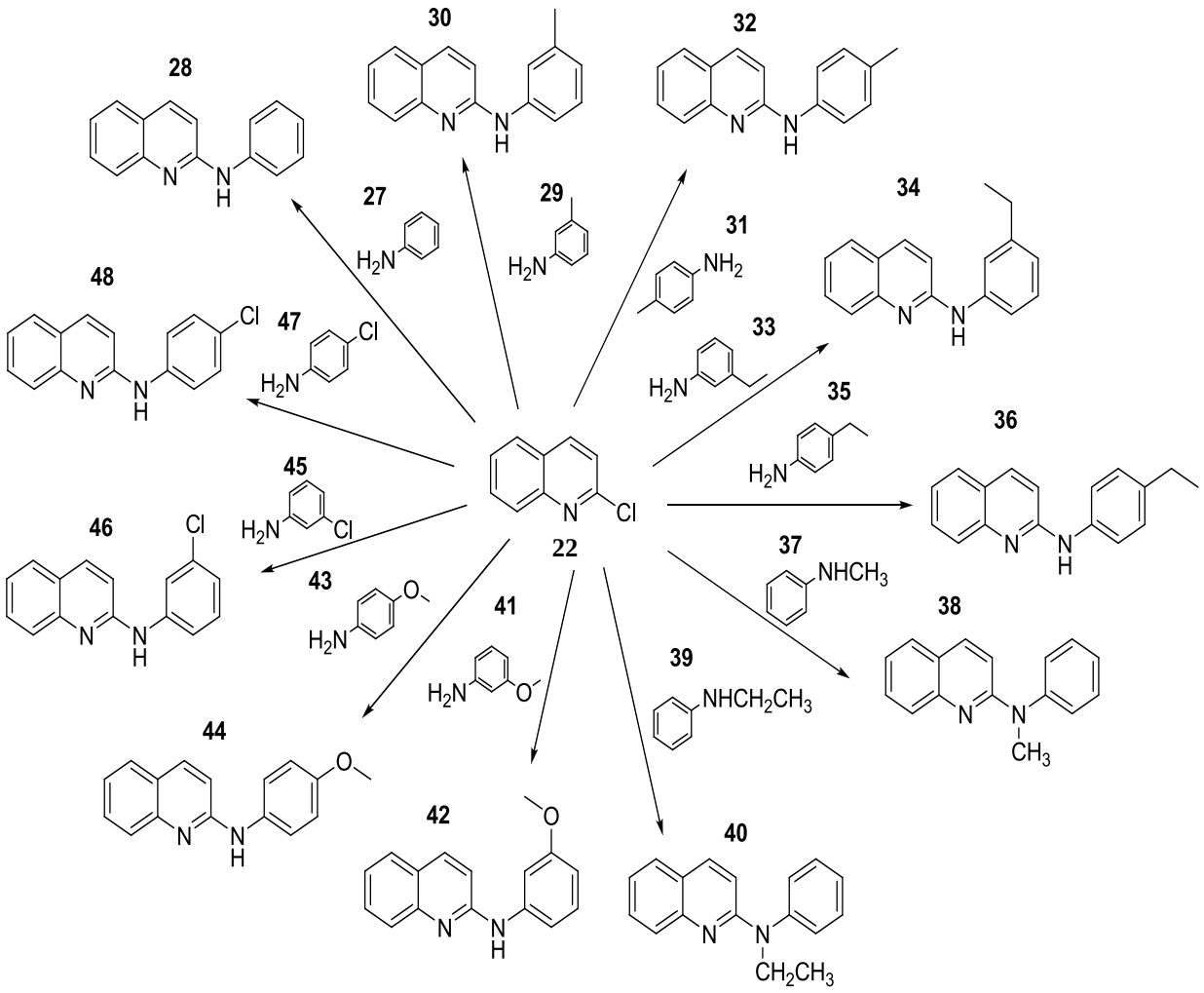
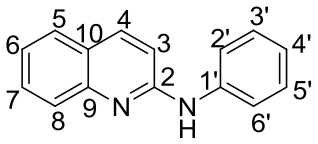


Figure 3.2: Reactions of 2-chloroquinoline with anilines derivatives

Compound **22** reacted with **27** to produce **28** after 5 hour refluxing in ethanol with 60 % yield after recrystallization from ethanol. R_f of the product was determined at 2:1 ratio of hexane and ethyl acetate. The infrared spectra showed the presence of 2° amine due to the N-H stretching at 3405 cm^{-1}. C=N stretch appeared at 1621 cm^{-1}, while aromatic C=C frequencies at 1596 cm^{-1} and 1496 cm^{-1}.

The ^{1}H NMR spectra gave a doublet peak at δ 7.93 (*J* = 8.8 Hz) assigned to H-4. A doublet signal at δ 7.78 (*J* = 8.3 Hz) was due to H-5. A multiplet peak at δ 7.59 was assigned to H-8, H-7, H-2’ and H-6’. H-3’ and H-5’ appeared as a triplet peak at δ 7.37 (*J* = 7.6 Hz). Two signals of triplet were observed at δ 7.30 (*J* = 7.1 Hz) and δ 7.10 (*J* = 7.30 Hz) due to H-4’ and H-6 respectively. A doublet peak appeared at δ 7.0 (*J* = 8.8 Hz) due to H-3.



28

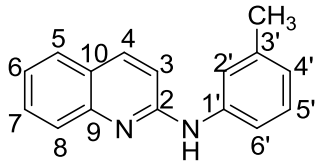
The ^{13}C NMR of **28** indicates the presence of 15 carbon atoms. Carbon resonance of quinoline ring were recorded at δ154.2, 147.2, 137.9, 129.2, 127.4, 126.4, 124.0, 123.3 and 111.6 for C-2, C-9, C-4, C-7, C-5, C-8, C-10, C-6 and C-3 respectively. On the other hand, carbon resonance of aniline ring were observed at δ 139.9, 129.9, 123.3 and120.6 for C-1’, C-3’, C-5’, C-4’, C-2’ and C-6’.

The mass spectra of **28** showed molecular ion peak at m/z 219 [M^{+}], which corresponded to the calculated mass from the molecular formula $C_{15}H_{11}N_2$ with losing a proton. These fragment produce daughter nuclei at m/z 128 by loss of quinoline moiety.

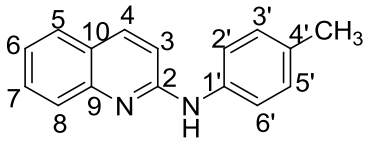
Compound **22** was reacted with **29** and **31** to produce **30** and **32** respectively. The infrared spectra of **30** and **32** showed almost similar frequencies which corresponded to C=N, aromatic C=C and N-H stretching. Compound **30** showed a medium and strong absorption peaks at 692 cm^{-1} and 751cm^{-1}, corresponding to *meta* disubstituted aromatic

ring. Compound **32** on the other hand showed a strong absorption peak at 815 cm^{-1} corresponding to *para* disubstituted aromatic ring.

The ^{1}H NMR spectra showed similar peaks within the range of δ 7.93 and 7.65 for **30** and **32** which were assigned to H-5, H-4, H-8 and H-7. For compound **30**, a triplet of doublet peaks was observed at δ 7.59 due to H-7. H-6, H-2', H-5' and H-6' were assigned as a multiplet at δ 7.29. Two doublet peaks were observed at δ 7.01 (J = 8.8 Hz) and δ 6.93 (J= 7.08 Hz) was assigned to H-3 and H-4' respectively. While for compound **32**, two doublet peaks were observed at δ 7.40 (J = 8.3 Hz) corresponded to H-2' and H-6' and at δ 7.28 Hz (J = 7.10 Hz) due to H-6. H-3' and H-5' was assigned as doublet peaks at δ 7.19 (J = 8.5 Hz). A doublet peak was observed at δ 6.98 with a coupling constant of 9.0 Hz which was due to H-3. For compounds **30** and **32**, N-H peaks were assigned as broad singlet peak within range δ 6.76 and δ 6.72 and a singlet peak observed at δ 2.38-2.35 which was due to $–CH_3$.



30



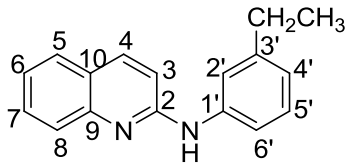
32

The ^{13}C NMR of **30** and **32** indicated the presence of 16 carbon atoms which is in agreement with calculated molecular formula of **30** and **32**. For both compounds, resonance of C-2, C-9 and C-1' were observed between δ 154 and δ 137. Another carbon peaks were observed between δ 139 and δ 111. The carbon resonance of methyl group was observed between δ 21.54 and δ 20.86 for both compounds. The detailed carbon resonances of **30** and **32** were summarized in experimental section.

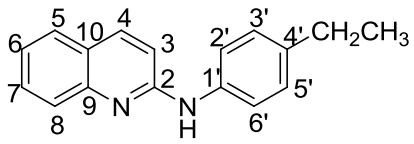
The GC-Mass spectra of **30** and **32** gave molecular ion peaks at m/z 233 [M^+] which corresponded with the calculated mass of molecular formula $C_{16}H_{13}N_2$ with losing a proton. Signal at m/z 218 is probably due to the loss of methyl moiety at methyaniline group. Loss of quinoline moeity was presented by signal at m/z 128.

Compound **22** was treated with **33** and **35** to produce **34** and **36** respectively. The infrared spectra of both compounds show similar absorption peaks as **30** and **32**.

The ^{1}H NMR spectra of **34** and **36** showed similar aromatic signals within the range of δ 7.93 and δ 7.58 which were due to H-5, H-4, H-8 and H-7. For compound **34**, a doublet peak at δ 7.38 (*J* = 8.08 Hz) was due to H-2' and H-4'. A multiplet peak at δ 7.28 was due to H-6 and H-5'. Two doublet peaks at δ 7.01 (*J* = 8.8 Hz) and δ 6.96 (*J* = 7.04 Hz) were assigned to H-6' and H-3. For compound **36**, a doublet peak was observed at δ 7.45 (*J* = 8.56 Hz) due to H-2' and H-6'. A doublet signal was also observed at δ 7.30 (*J* = 7.80 Hz) due to H-6. H-3' and H-5' was observed as doublet peak at δ 7.22 (*J* = 8.32 Hz). A doublet peak was also observed at δ 6.99 (*J* = 8.76 Hz) due to H-3. For both compounds, N-H peak was assigned as a broad singlet peak between δ 6.79 and 6.74. A quartet peak was observed at 2.68-2.67 which was due to -CH_2- and a triplet peak was observed at δ 1.27-1.26 was assigned to -CH_3.



34



36

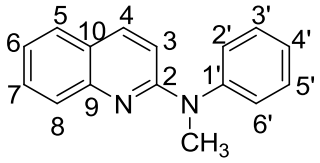
The ^{13}C NMR spectra of **34** and **36** showed the presence of 17 carbon atoms which is in agreement with the molecular formula of both compounds. Carbon resonances of **34**

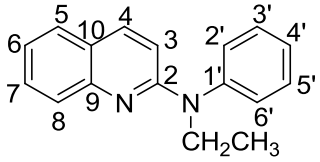
and **36** showed almost similar peak as **28**. For both compounds, carbon resonance of -CH_2- and -CH_3 were observed within range δ 28.88 and δ 28.32 and δ 15.48 and δ 15.73 respectively.

GC-mass spectrum gave a molecular ion at m/z 247 [M^+], which agree with the calculated mass of molecular formula of $C_{17}H_{15}N_2$ with losing a proton. Signal at m/z 233 probably due to the loss of methyl moiety from ethylaniline group. Fragment for the compound with loss of ethyl group moeity ion was assigned at m/z 218. Further loss of quinoline group moiety produced daughter ion peak at m/z 128.

Reaction between **22** with **37** and **39** gave **38** and **40** respectively. The infrared spectra showed similar absorptions to that of compounds **34** and **36**.

The ^{1}H NMR spectra of **38** and **40** show a doublet signal within δ 7.80 and δ 7.66 which were due to H-4 and H-5. For compound **38**, a multiplet peak was observed at δ 7.55 due to H-8 and H-7. Another multiplet peak was observed at δ 7.43 due to H-6 and H-4'. A multiplet peak was also observed at δ 7.29 due to H-2' and H-6'. H-3' and H-5' was observed as a multiplet peak at δ 7.23. A doublet peak was observed at δ 6.75 (J = 9.28 Hz) due to H-3. A broad singlet peak was observed at δ 3.63 which was assigned to -CH_3. However, compound **40** showed a triplet peak at δ 7.55 (J = 7.80 Hz) which was due to H-2' and H-6'. A triplet peak was observed at δ 7.43 (J = 7.84 Hz) which was assigned to H-3' and H-5'. A triplet peak observed at δ 7.28 (J = 9.00 Hz) which was due to H-6, H-7 and H-8. A triplet peak was also observed at δ 7.20 (J = 7.56 Hz) which was due to H-4'. H-3 peak was observed as a doublet at δ 6.60 (J = 9.04 Hz). A -CH_2- group was observed as a quartet at δ 4.19 (J = 7.08 Hz and J = 6.84 Hz). A triplet peak was observed at δ 1.27 (J = 7.08 Hz) due to -CH_3.





38 **40**

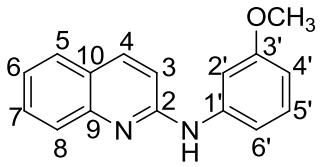
The ^{13}C NMR spectra of compound **38** showed the presence of 16 carbon atoms whereas 17 carbon atoms were recorded for compound **40**. The carbon resonances of compound **38** are almost similar as compound **28** except for the presence of upfield signal at δ 38.59 indicating the presence of -CH_3. Meanwhile, compound **40** showed two absorption peaks in upfield region at δ 44.95 and δ 13.10 which were due to -CH_2- and -CH_3 respectively.

GC-mass spectra of **38** showed a molecular ion at m/z 233 [M^+] which agree with molecular formula $C_{16}H_{13}N_2$ by losing a proton. Signal at m/z 218 was probably due to the compound losing a methyl moiety. M/z 129 indicated the mass of the compound by losing *N*-methylaniline group. Compound **40** gave a molecular ion peak at m/z 247 which was agree with molecular formula $C_{17}H_{16}N_2$.

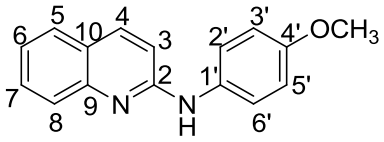
Reaction of **22** and **41** and **43** produced **42** and **44** respectively. The infrared spectra of both compounds showed similar frequency absorption as **30** and **32**.

The ^1H NMR spectra of **42** and **44** showed similar peaks within range δ 7.93 and δ 7.57 due to H-5, H-4, H-8 and H-7. For compound **42**, a triplet peak was assigned at δ 7.38 (J = 2.2 Hz) which was due to H-6. A multiplet peak at δ 7.28 were assigned to H-2' and H-5'. A doublet-doublet peak at δ 7.04 (J = 9.04 Hz) was assigned to H-4'. A doublet peak

was observed at δ 7.00 (J = 9.04 Hz) which was due to H-6'. Another doublet-doublet peak was observed at δ 6.65 (J = 8.04 Hz) due to H-3. For compound **44**, two doublet signals were observed at δ 7.43 (J = 9.0 Hz) assigned to H-2' and H-6' and at δ 7.28 (J = 7.1 Hz) due to H-6. H-3' and H-5' was shown as a doublet peak at δ 6.94 (J = 8.8 Hz). H-3 observed as a doublet peak at δ 6.88 Hz (J = 9.0 Hz). For both compounds, a singlet peak was observed at δ 6.66 which was due to NH. $-OCH_3$ signal was observed as a singlet peak at δ 3.84.



42



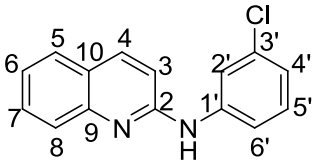
44

The ^{13}C NMR spectra of **42** and **44** indicated the presence of 16 carbon atoms which is in agreement with the calculated molecular formula of both compounds. Carbon resonance was observed between δ 160.46 and δ 106.09 for **42** and resonance at δ 55.29 was due to -OCH_3. For compound **44**, carbon resonance signals appeared in the range of δ 156.43 and δ 110.87 and -OCH_3 resonance was observed at δ 55.57.

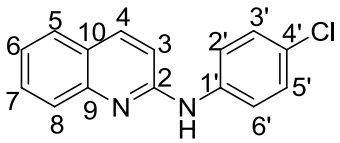
GC-mass spectra showed molecular ion at m/z 249 [M^+] which agree with the calculated mass of molecular formula $C_{16}H_{13}N_2O$ by losing a proton. Signal at m/z 234 is probably methyl moiety of methoxyaniline group and signal at m/z 128 is due to quinoline moiety.

Treatment of **22** with **45** and **47** gave **46** and **48** respectively. The infrared spectra have shown similar absorption characteristic as compound **28**. C-Cl stretching frequency was observed around 828.58 cm^{-1} and 819.86 cm^{-1} for both compounds.

The ^{1}H NMR spectra of **46** and **48** showed similar peaks within the range of δ 7.95 and δ 7.80 due to H-5 and H-4. Compound **46** showed two doublet signals at δ 7.66 (*J* = 8.04 Hz) and δ 7.60 (*J* = 8.52 Hz) which were due to H-8 and H-7 respectively. A doublet of doublet peak was observed at δ 7.55 (*J* = 9.52 Hz) which was assigned to H-3 and H-6'. H-2' and H-4' were observed as a triplet peak at δ 7.38 (J = 7.56 Hz). Two triplet peaks were observed at δ 7.31 (*J* = 8.04 Hz) and at δ 7.12 (*J* = 7.36) due to H-6 and H-5' respectively. A doublet peak was observed at δ 7.00 (*J* = 9.04Hz) due to H-3. For compound **48**, a multiplet observed at δ 7.62 which was due to H-7, H-3'and H-5'. A multiplet peak was also observed at δ 7.33 which was due to H-6, H-2' and H-6'. A doublet signal was observed at δ 6.91 (*J* = 8.8 Hz) which was due to H-3. A singlet peak at δ 6.75 was assigned to N-H.



46



48

The ^{13}C NMR of both compounds indicated the present of 15 carbon atoms. Carbon resonance of **46** and **48** was observed in the downfield region between δ 153 and δ 112. The assignments were similar to that of compound **28**.

GC-mass spectra of **46** and **48** gave a molecular ion peaks at m/z 254 which in agreement with molecular formula of $C_{15}H_{11}ClN_2$. A signal at m/z 218 was probably due to

the loss of chlorine moiety at chloroaniline group. Loss of quinoline moeity was presented by fragment at m/z 128.

Recrystallisation of **48** in ethanol gave a prism, colourless crystals which was analyzed by X-ray diffraction method. The crystals system and refinement data are shown in Table 3.1. The crystal of **48** is having a monoclinic system and space group is P21/c. Figure 3.3 shows the thermal ellipsoid of title compound at 50% probability level, hydrogen atoms were drawn as spheres of arbitrary radius.

Table 3.1: Crystal data and structure refinement of 48

Chemical formula	$C_{15}H_{11}ClN_2$
Formula Weight	254.71
Crystal system	Monoclinic
Space group	P21/c
a(Å)	5.9565 (4)
b(Å)	7.9936 (6)
c(Å)	25.0603 (18)
β(°)	92.7440 (10)
V(Å^3)	1191.85 (15)
Z	4
Absorption coefficient μ (mm^{-1})	0.30
F (000)	528
Crystal size (mm)	0.2 x 0.2 x 0.2
θ range for data collection (°)	1.6-27.5
Index ranges	(-7,-9,-32) to (7,10,31)
Reflections collected	10754
Independent reflections	2726
Data/parameters	2726/167
Goodness-of-fit on F^2	0.134
Final R indices [I>2σ (I)]	0.052

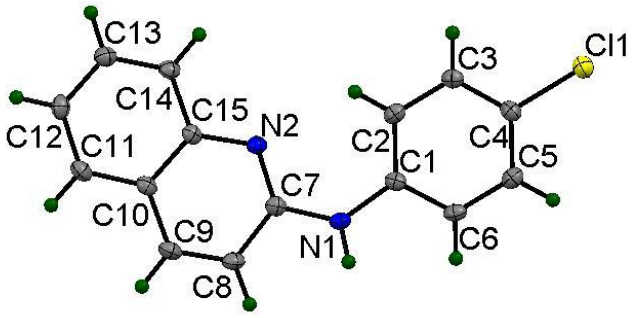


Figure 3.3: Ortep diagram of 2-*N*-(*p*-chloro)anilinoquinoline (48)

3.3 Fluorescence Characteristics

The effects of structure on the emission process are important to effectively utilize fluorescence properties as an analytical tool. Under structural effects, we shall briefly consider on what types of compounds fluoresce and how we might increase or decrease the total emission by making changes in structure of the compounds studied. On environmental effects, we studied how solvents, oxygen, substituents, pH and other variables affect the fluorescence characteristic of compounds.

In this work, various quinoline derivatives were studied and most of them showed fluorescence characteristic at room temperature in ethyl acetate, tetrahydrofuran, chloroform and isopropanol with different concentrations, pH and other variable as mentioned earlier.

2-*N*-anilinoquinoline **(28)**, 2-*N*-(*p*-ethyl)anilinoquinoline **(36)** and 2-*N*-(*p*-chloro)anilinoquinoline **(48)** were choose to study the effect of electron donating and electron withdrawing effect on emission in different solvents. **28**, **36** and **48** showed

fluorescence characteristic with various solvent as shown in Table 3.2, while Figure 3.4 showed the fluorescence intensity of **28**, **36** and **48** in different solvents.

Table 3.2: **Fluorescence characteristic of 28, 36 and 48 in different solvents**

Compounds	Solvents	Excitation Wavelength/nm	Emission Wavelength/nm	Intensity
28 (4.54×10^{-5} M)	Ethyl acetate	316 384	412 413	284.13 223.30
	Tetrahydrofuran	383 326	412 408	246.35 218.88
	Chloroform	348	413	116.79
	Isopropanol	323 389	449 438	36.15 32.71
36 (4.03×10^{-5} M)	Ethyl acetate	305 384	443 436	288.43 220.55
	Tetrahydrofuran	384 325	440 442	239.61 226.56
	Chloroform	320 378	443 439	87.36 79.00
	Isopropanol	324	485	9.48
48 (3.93×10^{-5} M)	Ethyl acetate	322 369	407 401	267.44 236.86
	Tetrahydrofuran	387 328	409 410	255.93 234.75
	Chloroform	324	413	183.76
	Isopropanol	325 384	444 443	57.02 54.37

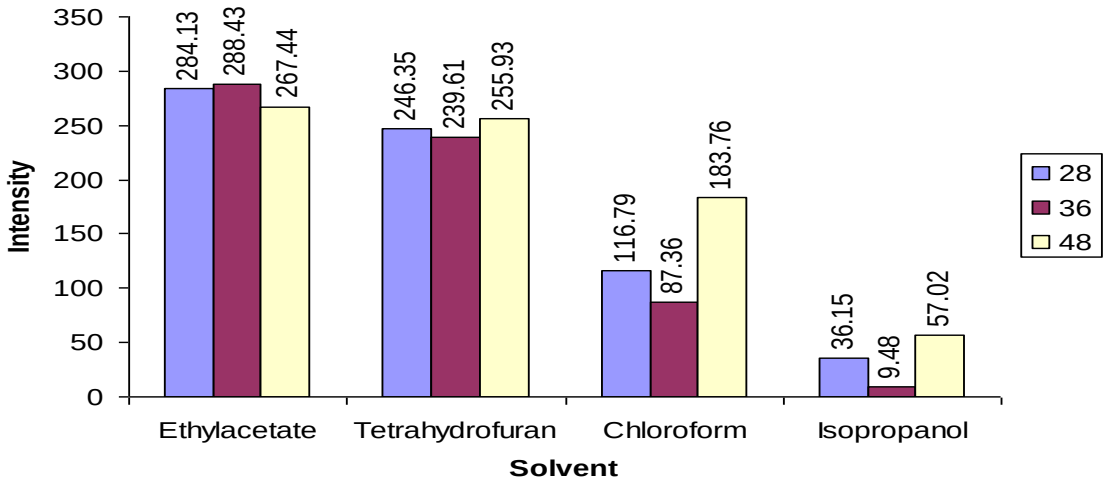


Figure 3.4: Fluorescence intensity of 28, 36 and 48 in different solvent

It can be seen from Table 3.2 that compound **28** showed fluorescence peak at 412 nm in ethyl acetate, 412 nm in THF, 413 nm in chloroform, 449 nm in isopropanol when excited at 316 nm, 383 nm, 348 nm and 323 nm respectively. Figure 3.4 shows compound **28** have the highest fluorescence intensity in ethyl acetate, followed by tetrahydrofuran, chloroform and isopropanol. The same phenomenon was observed for compound **36** and **48**.

The high fluorescence intensity recorded in ethyl acetate maybe due to the formation of a complex with the solvent through hydrogen bonding as suggested in Figure 3.5. Same phenomenon was observed in earlier study [39]. The high fluorescence intensity in ethyl acetate is also believed due to the dielectric properties as well as the polarity of the solvent.[40] In a polar aprotic solvent, the polarity of the solvent tends to give a greater stabilization to π to π^* excited state rather than the ground state, and as a result high fluorescence intensity was observed.[41]

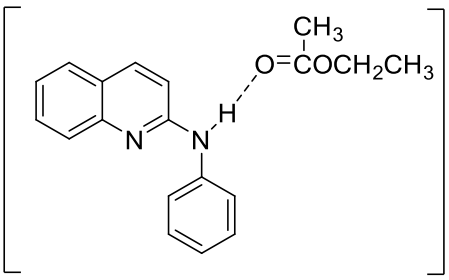


Figure 3.5: The formation of a complex with the solvent through hydrogen bonding

Figure 3.4 also shows that all of the compounds showed second higher fluorescence intensity in tetrahydrofuran. As in ethyl acetate, this observation is also believed due to the formation of a complex with the solvent through hydrogen bonding as suggested in Figure 3.6. This complex enhanced the $\pi \rightarrow \pi^*$ transition in the excited state, resulting in high fluorescence intensity [39].

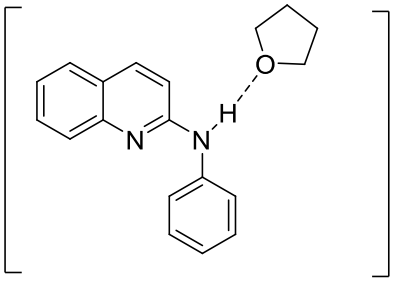


Figure 3.6: **The formation of a complex with the solvent through hydrogen bonding**

From Figure 3.3, all compounds showed low fluorescence intensity in chloroform. There is no clear explanation for this observation because typically, when establishing a solvent-fluorescence relationship, hydrogen bonding, the dielectric constant of the solvent and its viscosity are frequently invoked to explain these relationships [42-43].However, sometimes these effects may cancel each other out and as a result the solvent-fluorescence relationship is largely unpredictable [44].

The lowest fluorescence intensity of all compound were observed in isopropanol. The low fluorescence intensity is probably due to the hydrogen bonding capability of isopropanol whereby in this solvent, the proton transfer to the ring nitrogen is complete as shown in Figure 3.7 , and therefore the fluorescence is completely quenched [45]. The corresponding electron transfer phenomena results in a non-conjugated system in the quinolinyl ring which results in non-fluorescent compounds. As the result, electron is not available to move around the system, thus low fluorescence intensity was observed.

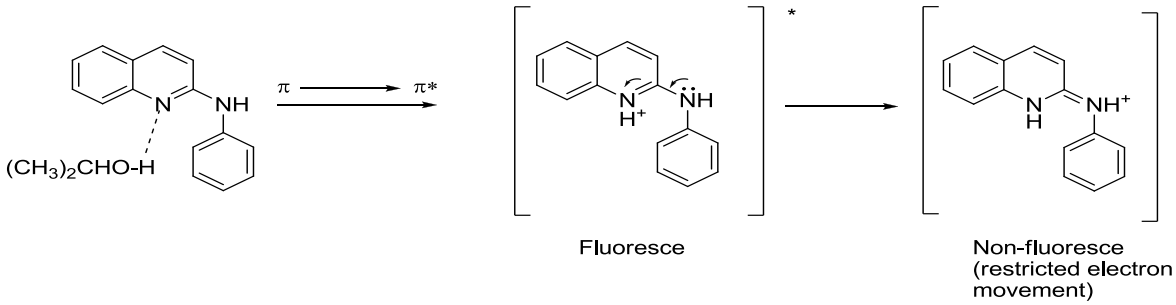


Figure 3.7: Proton transfer to the ring nitrogen

It is also believed that these compounds formed a complex with the solvent as shown in Figure 3.8. It shows the formation of intramolecular charge transfer transitions via hydrogen bonding of the compounds.

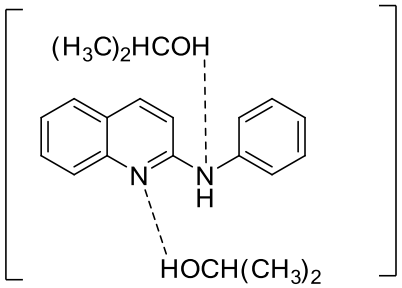
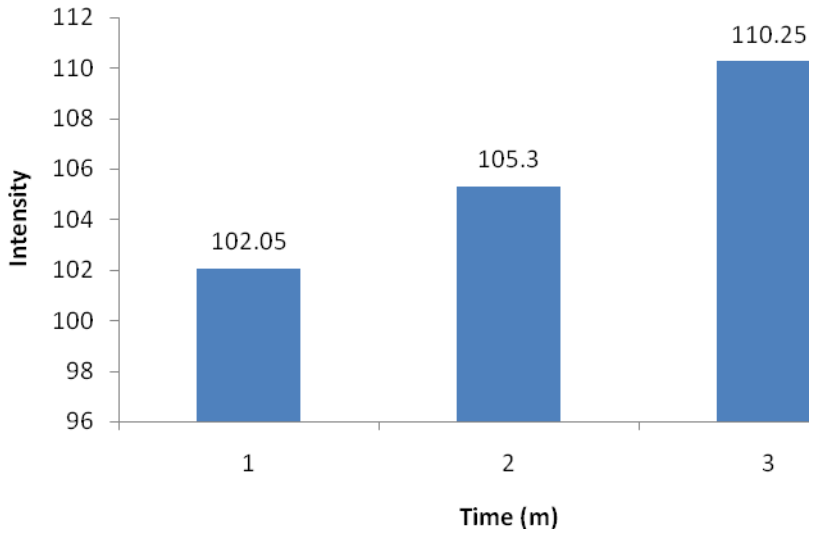


Figure 3.8: Intramolecular charge transfer transitions via hydrogen bonding

This phenomenon is also explained by Weisstuch and Testa [46] which they had reported that in some aromatic heterocyclic compounds with hydrogen bonding formation would quenched the fluorescence intensity. The formation of hydrogen bond which is capable of conjugating with π-electron system of the heterocyclic ring, results in the mobility of π-electron being disturbed and caused the fluorescence intensity to be reduced. This phenomenon favours the low lying n→ π* transitions which refer to the excitation of a nonbonding electron to an antibonding orbital [47]. It was reported that n→ π* were usually not observed in fluorescence spectra and its presence were weak [48]. As a result, a decrease in fluorescence intensity was observed.

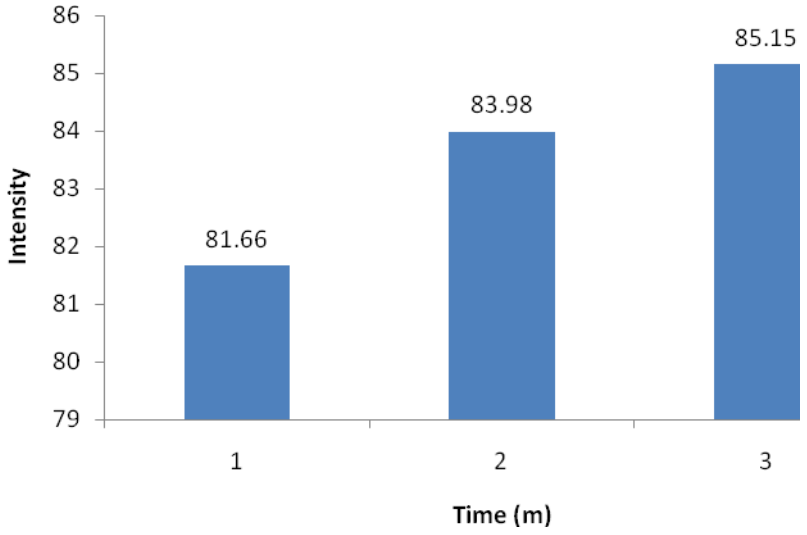
The study on possible delayed fluorescence was carried out with 2-*N*-anilinoquinoline **(28)**, 2-*N*-(*p*-methyl)anilinoquinoline **(32)** and 2-*N*-(*p*-chloro)anilinoquinoline **(48)** by measuring the fluorescence of respective compounds with time.

Figure 3.9, 3.10 and 3.11 shows the fluorescence intensity of **28**, **32** and **48** with time in chloroform. The measurements were taken immediately, after 30 minutes and 60 minutes.



Where 1= 0 min
2= 30 min
3= 60 min

Figure 3.9: Fluorescence intensity of 2-*N*-anilinoquinoline (28) at different times in chloroform (4.5399 X 10^{-4} M)



Where 1= 0 min
2= 30 min
3= 60 min

Figure 3.10: Fluorescence intensity of 2-*N*-(*p*-methyl)anilinoquinoline (32) at different times in chloroform (4.2680 X 10^{-4} M)

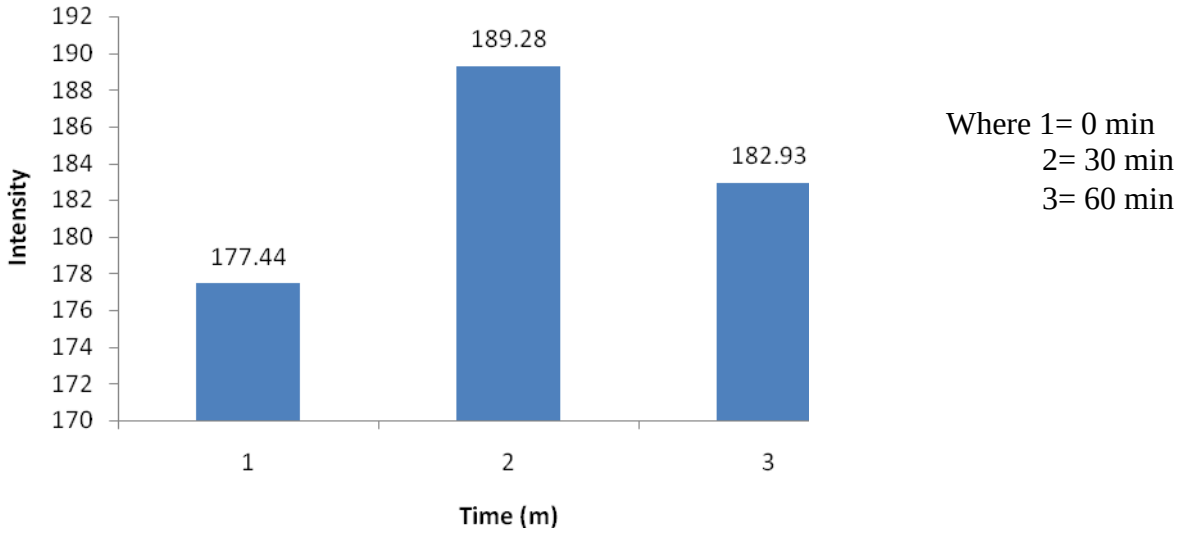


Figure 3.11: Fluorescence intensity of 2-*N*-(*p*-chloro)anilinoquinoline (48) at different times in chloroform (3.9260 X 10^{-4} M)

The fluorescence of **28** and **32** showed an increase in fluorescence intensity with time. The increase in fluorescence intensity observed may be due to the delayed fluorescence that occurs. Delayed fluorescence is spectrally similar to the ordinary fluorescence but has a considerably longer lifetime. It is a result of thermal excitation of molecule in the lowest excited triplet state back to the lowest excited singlet state or reverse intersystem crossing followed by fluorescence. The delayed fluorescence intensity varies as the square of the intensity of the exciting light. This type of fluorescence has been found for many molecules including phenantherene, anthracene and pyrene [49], napthalene, hexahelicene and triphenylene [50].

It can be seen from Figure 3.11 that the fluorescence intensity of compound 48 decreases with time from 30 minute to 60 minute. Reduced fluorescence intensity observed with time is believed to be due to the quenching effect of oxygen. Oxygen, which has an unusually large diffusion coefficient, and on prolongs exposure of the solution to the atmosphere, could result in large quantity of oxygen diffusing into solution [41] and therefore quenched the fluorescence intensity of the compounds [51].

Table 3.3 shows the fluorescence characteristic of 2-*N*-anilinoquinoline **(28)**, 2-*N*-(*p*-ethyl)anilinoquinoline **(36)** and 2-*N*-(*p*-chloro)anilinoquinoline **(48)** in ethyl acetate with respect to different concentration at relatively low concentration. Figure 3.12, 3.13 and 3.14 show their fluorescence intensity in different concentration.

Table 3.3: Fluorescence characteristic of 28, 36 and 48 in different concentrations in ethyl acetate

Compounds	Concentration/M	Excitation Wavelength/nm	Emission Wavelength/nm	Intensity
28	4.54×10^{-5}	294	410	277.60
	4.54×10^{-6}	296	407	84.72
	4.54×10^{-7}	305	429	8.84
36	4.03×10^{-5}	320	437	207.13
	4.03×10^{-6}	309	441	95.45
	4.03×10^{-7}	311	438	16.83
48	3.93×10^{-5}	314	410	282.38
	3.93×10^{-6}	302	415	117.06
	3.93×10^{-7}	302	405	17.15

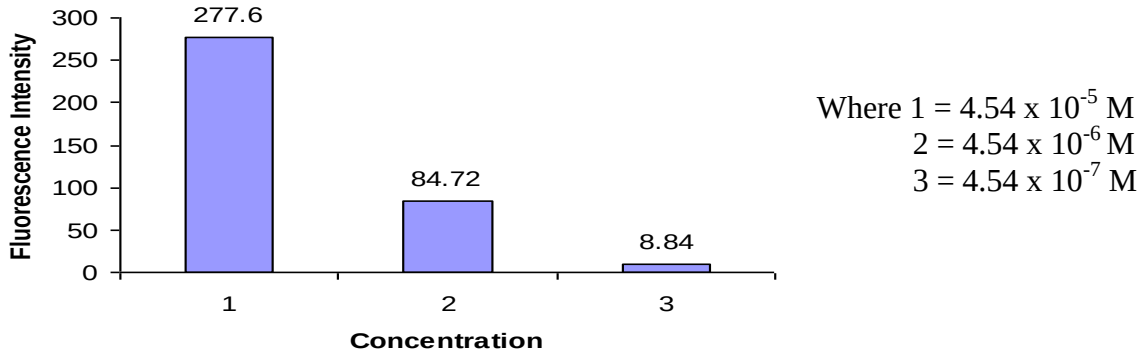
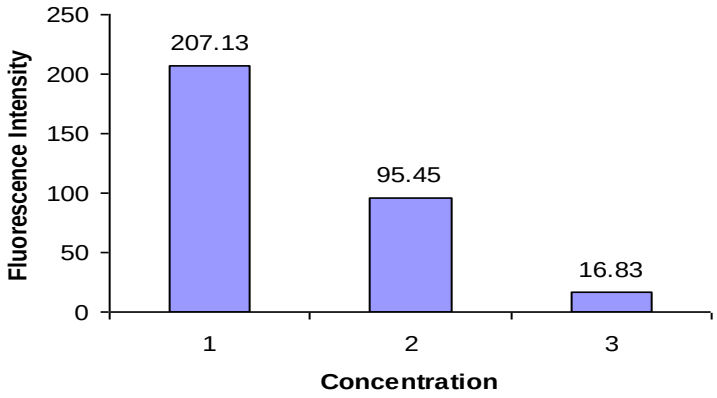
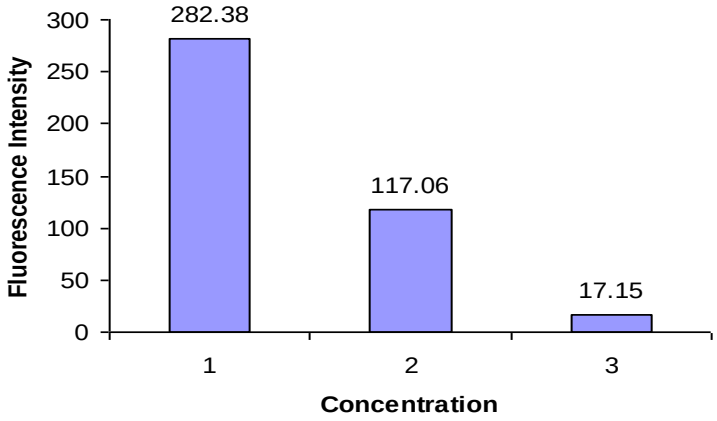


Figure 3.12: Fluorescence intensity of 2-*N*-anilinoquinoline (28) at different concentration in ethyl acetate



Where 1 = 4.03 x 10^{-5} M
2 = 4.03 x10^{-6} M
3 = 4.03 x 10^{-7} M

Figure 3.13: Fluorescence intensity of 2-*N*-(*p*-ethyl)anilinoquinoline (36) at different concentration in ethyl acetate



Where 1 = 3.93 x 10^{-5} M
2 = 3.93x10^{-6} M
3 = 3.93 x 10^{-7} M

Figure 3.14: Fluorescence intensity of 2-*N*-(*p*-chloro)anilinoquinoline (48) at different concentration in ethyl acetate

It was found that fluorescence intensity increases linearly withy increasing concentration at relatively low concentration. It can be seen from Figure 3.12 to 3.14 that higher concentrations tend to increase the fluorescence intensity for compound **28**, **36** and **48**. It has been reported that at higher concentration, the fluorescence intensity may reach a limiting value and usually results in concentration quenching which decrease with further increase in concentration and is often accompanied by wavelength shifts [52].

It was also known that in the limit of high absorber concentration, the linearity between absorbance and concentration breaks down. In very concentrated solutions, the absorbance may become infinite because all of the exciting light will be absorbed before it can completely penetrate the sample cell. On the other hand, the high concentration of sample results in a variety of molecular interactions, such as collisional quenching and energy transfer, which can distort the fluorescence spectrum [52]. In this study, those observations were not seen because the concentrations used did not reach the limit value.

Lavorel [53] has demonstrated that at high concentrations of fluorescein, thionin and chlorophyll dimerisation occurs. The absorption spectra of these dimmers are different from the parent compounds and in these instance, the dimmers have different spectral properties. It is apparent that when more than one molecular absorbing species is present in a solution, fluorescence efficiency will not be constant over the entire spectrum.

Besides concentration effect, pH also influences the fluorescence intensity of the compounds studied. Five different pH values were chosen to study the effect of pH in the fluorescence characteristic of selected 2-*N*-substituted quinoline. Table 3.4 shows the fluorescence characteristic of 2-*N*- (*m*-methyl)anilinoquinoline **(30),** 2-*N*-(*m*-ethyl)anilinoquinoline **(34)** and 2-*N*-(*p*-chloro)anilinquinoline **(48)** in acetonitrile with different pH.

Table 3.4 shows the fluorescence characteristic of **30**, **34** and **48** in acetonitrile under neutral, acidic and basic conditions. The fluorescence intensity of **30**, **34** and **48** in different pH are as shown in Figure 3.15 to Figure 3.17.

Table 3.4: Fluorescence characteristic of 30, 34 and 48 in acetonitrile with variation of pH.

Compounds	Condition	pH	Excitation wavelength (nm)	Fluorescence wavelength (nm)	Intensity
30	acid	4	337	-	-
		5	337	-	-
	neutral	7	337	442	72.51
	base	9	337	452	7.66
		10	337	-	-
34	acid	4	337	-	-
		5	337	446	3.93
	neutral	7	337	444	64.91
	base	9	337	450	5.75
		10	337	459	5.51
48	acid	4	337	-	-
		5	338	449	1.33
	neutral	7	338	436	76.02
	base	9	338	439	7.29
		10	338	434	2.78

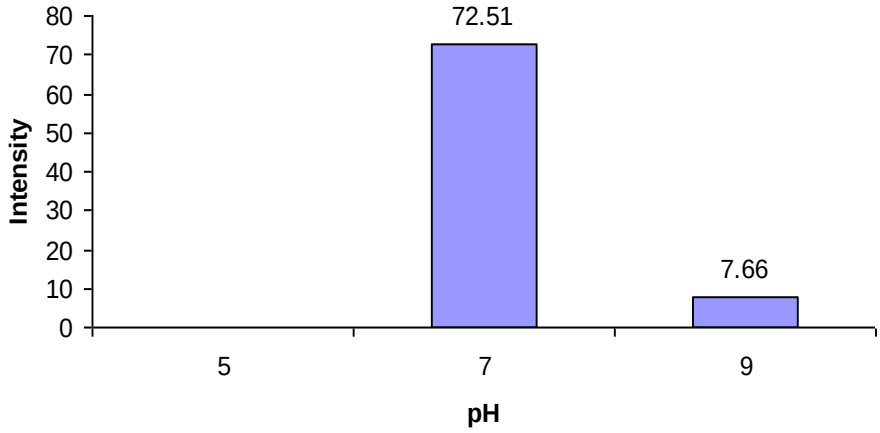


Figure 3.15: Fluorescence intensity of 2-*N*- (*m*-methyl)anilinoquinoline (30) in pH 5, 7 and 9

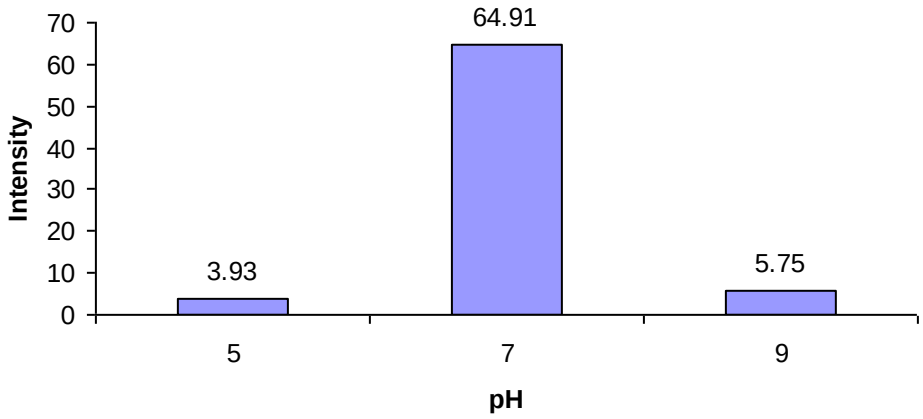


Figure 3.16: Fluorescence intensity of 2-*N*-(*m*-ethyl)anilinoquinoline (34) in pH 5, 7 and 9

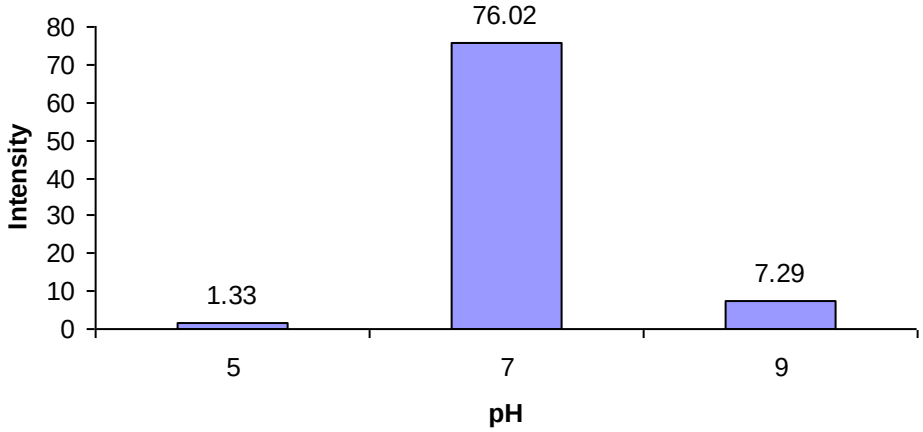


Figure 3.17: Fluorescence intensity of 2-*N*-(*p*-chloro)anilinoquinoline (48) in pH 5, 7 and 9

It can be seen from Figure 3.15 to Figure 3.17 that all of these compounds showed highest fluorescence intensity in neutral conditions. On the other hand, under acidic

and basic conditions, the intensity of fluorescence of these compounds was reduced. This observation is believed to be due to the fluorescence solvatochromism, which is strong under neutral conditions and relatively weak in acid or base which is agreement with the work previously done [41].

Lower fluorescence intensity under acidic medium is probably due to protonation of the compound. The hydrogen atom abstraction from protonated form yielded the lowest intensity which involves the transferring of the proton to the ring nitrogen as shown in Figures 3.18 and Figure 3.19 and as a result the fluorescence is quenched. Previous work [54] shows that in cyclohexane and in the presence of trichloroacetic acid, the fluorescence intensity of indole is reduced to one-tenth its value in cyclohexane and similarly with tryptophane, tryamine and related compounds, all of which fluorescence in neutral pH range, lose fluorescence in acid [55-57].

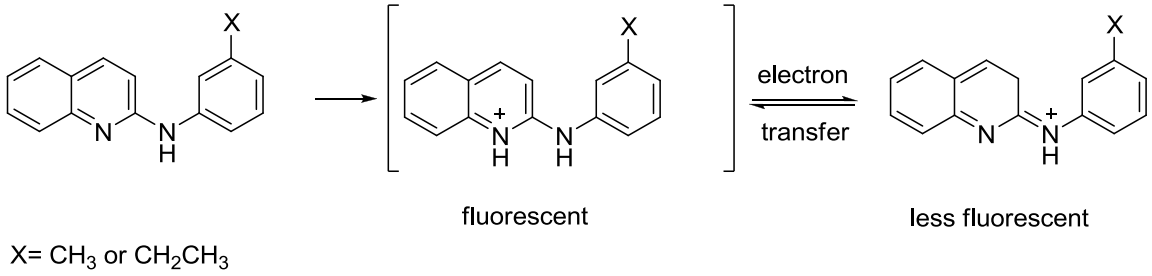


Figure 3.18: The proton transfer to the ring nitrogen of 2-*N*- (*m*-methyl)anilinoquinoline (30) and 2-*N*-(*m*-ethyl)anilinoquinoline (34)

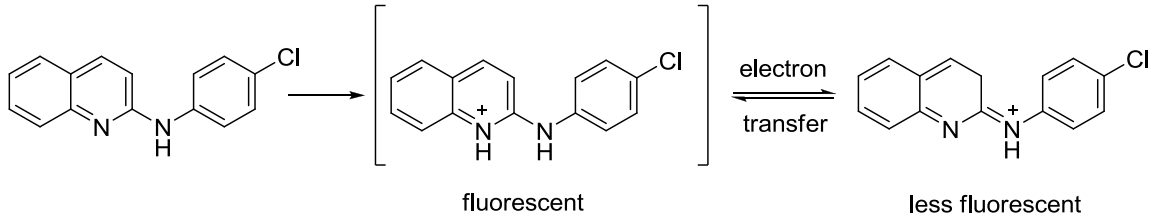


Figure 3.19: The proton transfer to the ring nitrogen of 2-*N*-(*p*-chloro)anilinoquinoline (48)

Studies show that compound **30**, **34** and **48** fluoresced at higher intensities in basic compared to in acidic medium. Upon acidification (pH 5), these compounds undergo reductions in its maximum intensity due to the reasons explained earlier. A further increase in acidity, (pH 4) resulted in non fluorescence intensity of characteristic as shown in Table 3.4.