o-Aminobenzophenones as Starting Material for New Dyes

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Referent: Prof. Dr. Gerhard Müller

To my mother

The present work was done during the time of October 2003 to July 2007, at the Department of Chemistry of the University of Konstanz, under the supervision of Prof.Dr.Ewald Daltrozzo.

My thanks go to:

Prof. Dr. Ewald Daltrozzo for his entire support.

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Mr. W. Sulger for scientific discussions and for the special time we had in our laboratory.

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Abbreviations

AIBN	Azobisisobutyronitrile (2,2′-Azobis(2-methylpropionitrile)
$CHCl_3$	Chloroform
c	Concentration [*mol/L*]
DMF	Dimethylformamide
d	Doublet (NMR)
dd	Double doublet (NMR)
EtOH	Ethanol
E	Extinction
ε	Molar extinction coefficient [$L\ mol^{-1}\ cm^{-1}$]
ESIPT	Excited State Intramolecular Proton Transfer
f	Oscillator strength
λ	Wavelength [*nm*]
m	Multiplet (NMR)
MeCN	Acetonitrile
NEt_3	Triethylamine
NMP	*N*-Methyl-2-pyrrolidone
$\tilde{\upsilon}$	Wavenumber [cm^{-1}]
r.t	Room temperature

s	Singlet
s br.	Singlet broad (NMR)
S_0	Electronic ground state
S_1	First excited electronic state
t	Triplet (NMR)
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TMS	Tetramethylsilane (internal standard used for ^{1}H-NMR spectra)
Φ_f	Fluorescence quantum yield (Φ_f = # photons emitted / # photons absorbed)

1 Introduction

1.1 Background

Fluorescent effects have been observed for thousands of years but it was not until recently that they were analyzed, controlled, and put into use. Chinese books were written about fluorescence and phosphorescence as far back as 1500 B.C., but many consider Athanasius Kircher as the founder of fluorescent science. He wrote a book called 'Ars Magna Lucis et Umbrae' which described the effect of a wood extract in water and discussed the application of fireflies to illuminate houses [7].

In 1852 the true science of fluorescence was brought to light by the British scientist Sir George G. Stokes who observed that fluorite gave off visible light (fluoresce) when exposed to electromagnetic radiation in the ultraviolet wavelength. Fluorite (also called *fluorspar*) is a mineral composed of calcium fluoride. The word *fluorite* is derived from the Latin root *fluo*, meaning "to flow" because the mineral has relatively low melting point and was used as an important flux in smelting [6].

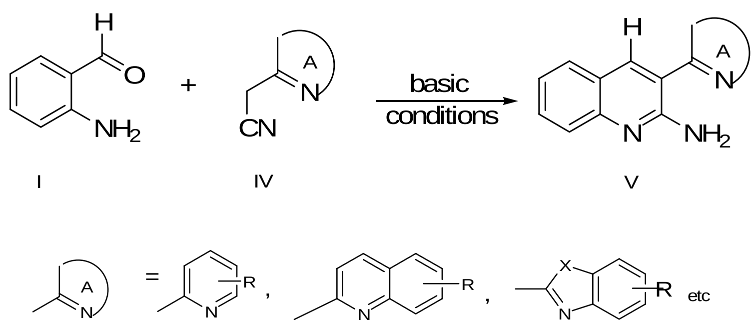
Stokes' studies of fluorescent substances led to the formulation of Stokes' Law, which states that the wavelength of fluorescent light is always greater than that of the exciting radiation [6]. Thus, for any fluorescent molecule the wavelength of emission is always longer than the wavelength of absorption.
Early investigations in the 19th century showed that many specimens (including minerals, crystals, resins, crude drugs, chlorophyll, vitamins, and inorganic compounds) fluoresce when irradiated with ultraviolet light. However, it was not until the 1930s that the use of fluorochromes was initiated in biological investigations to stain tissue components, bacteria, and other pathogens. Several of these stains were highly specific and stimulated the development of the fluorescence microscope. The technique of fluorescence microscopy has become an essential tool in biology and the biomedical sciences. In fact, the fluorescence microscope is capable of revealing the presence of a single molecule [8].

Fluorescence is important in molecular biology, is used in DNA sequencing, in labeling and visualizing DNA, in DNA chip technology and fluorescence microscopy.

1 Introduction

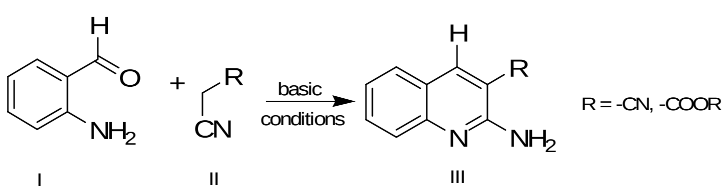
Fluorescent substances are used in paints and coatings; many products today have invisible fluorescent markings for one reason or another. It is this unique effect that makes this technology so vital to our everyday life.
Fluorescent substances usually have highly rigid molecular structures with electrons that are delocalized over the entire framework of the molecule.
The fluorescence quantum yield gives the efficiency of the fluorescence process [6]. It is defined as the ratio of the number of photons emitted to the number of photons absorbed (Φ_f = # photons emitted / # photons absorbed).
The maximum fluorescence quantum yield is 1.0 (100%): every photon absorbed results in a photon emitted. Compounds with quantum yields of 0.10 are still considered as fluorescent dyes.

Synthesis of fluorescent substances represented the main point of interest in our group for decades [14,15,16,58,59,60]. The present work brings a contribution to this aspect. In our group a new series of dyes, that show dual fluorescence, were synthesized by Kammerer [12] according to Scheme 1.1:



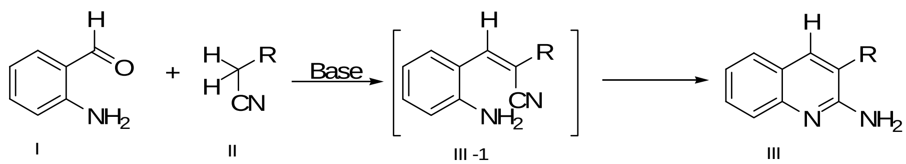
Scheme 1.1 *Synthesis of **V**;*
R= OAlk, ᵗButyl etc.; X= O, S etc.

Basis of these syntheses was the reaction of malononitrile and cyanacetic esters described by Taylor [5] (Scheme 1.2).



Scheme 1.2 *Synthesis of the substituted 2-aminoquinoline **III** from **I** and **II** according to [5].*

The condensation goes through the intermediate **III-1**, sometimes possible to be isolated, which by intramolecular addition of the amino group to the nitrile group leads to products **III** [12] (Scheme 1.3).



Scheme 1.3 *The mechanism of the condensation reaction*

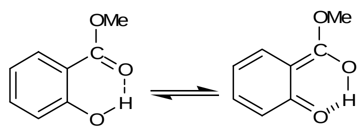
1.2 ESIPT

Ground-state proton transfer reactions are one of the simplest and most important processes found in chemistry. Excited- state proton transfers (ESPT) are much less popular despite their unquestionable importance in fundamental and applied photochemistry. Intermolecular ESPT have been employed as mechanistic tools and in technological applications in pH [18] and pOH [19] jump experiments aimed at the study of proton hydration dynamics [20, 21], photolithography [22], and as probes of the environment around proteins [23-25], micelles [26,27] and films [28]. Analogous intramolecular reactions have been applied in chemical lasers [29], high-energy radiation detectors [30], and polymer stabilizers [31,32].

In 1931, Weber [1] reported for the first time that the shift of an acid-base equilibrium of some organic molecules, occurred at a different pH depending on whether it was observed by absorption or fluorescence spectroscopy. In 1949 Förster [2] provided the correct explanation for this observation and initiated the field of excited state intermolecular proton transfers (*$ESI_{er}PT$).* Soon thereafter, Förster proposed a valuable method to estimate the pK of a molecule in an excited state (pK*) based on its ground state pK and the absorption and/or emission spectra of the molecule [2], which became known as the Förster cycle.

In 1955 Weller [3] found that methyl salicylate presented an unusually large Stokes-shifted fluorescence emission (Scheme 1.4).

He proposed that the red-shifted fluorescence corresponded to an excited state isomer Xb, formed via a proton transfer (PT) in the excited state. Since Weller's initial work, **e**xcited-**s**tate **i**ntramolecular **p**roton **t**ransfers (*$ESI_{ra}PT$*) have been intensively studied.

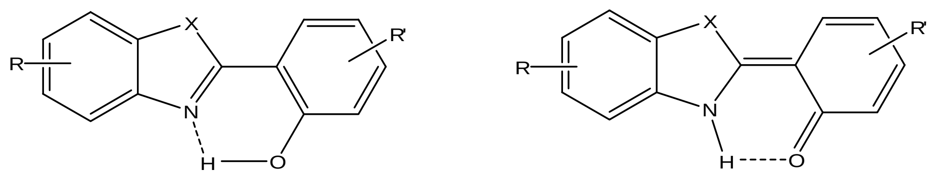


Scheme 1.4

Another effort to rationalize intramolecular PTs was made by Kasha in 1986 [4]. Kasha distinguished four mechanistic classes of reactions: (i) those in which there is an **H** bond between the **H** atom of the donor group and the acceptor (intrinsic intramolecular transfers); (ii) those in which the proton is far away from the acceptor and requires a mediator (concerted biprotonic transfers); (iii) static and dynamic catalysis of PT; and (iv) proton relay transfers. Strictly speaking, only the intrinsic process is a real *$ESI_{ra}PT$*; all the others are varieties of excited-state intermolecular proton transfers (*$ESI_{er}PT$)* within microsolvent clusters.
L.G Arnaut and J. Formosinho reviewed in 1993 interesting aspects about both *$ESI_{ra}PT$* and *$ESI_{er}PT$* [33] [34].

It is now well established that upon photoexcitation the functional groups *R-OH*, *R-NH_2*, *R-NH_3^+* become stronger acids (weaker bases), while the groups *R-CO_2H*, *R-$CO_2H_2^+$*, *R-$SO_3H_2^+$* become stronger bases (weaker acids). It is a general rule in aromatic molecules that electron donating molecules become stronger donors in the excited state, while acceptors will attract the electrons more strongly. In general, *$ESI_{ra}PTs$* are conveniently followed by the rise and decay of the strongly Stokes-shifted fluorescence of the tautomers. The transfer of a proton between two groups of an aromatic molecule causes large electronic and structural rearrangements, which are associated with changes in molecular geometry and quite large fluorescence shifts. In consequence, the dynamics of such processes can be strongly dependent on the nature of the solvent, namely with respect to the formation of hydrogen bonds.

In most examples of molecules which undergo ESIPT the acidic proton donor is a hydroxyl group and the basic acceptor is a nitrogen atom.
N-H…O chelates displaying ESIPT have long been known for their uses as UV-stabilizers [35], laser dyes [36-40] and, more recently, biological probes [41]. Examples for such systems are types **VII** (Scheme 1.5).



VII a

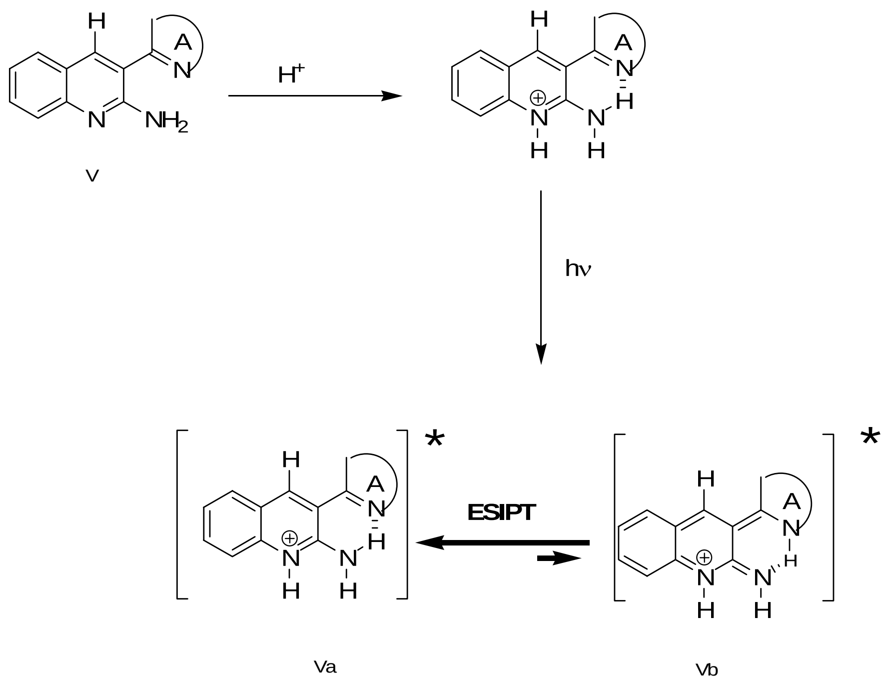
VII b

Scheme 1.5

In these systems, in the electronic ground state (S_0) only the O-H…N tautomer VIIa exists, and in the first excited electronic state (S_1) an intramolecular proton transfer (ESIPT) to the tautomer VIIb occurs. If both tautomers show r.t. fluorescence and the ESIPT only partially proceeds, i.e. if in the S_1, an equilibrium VIIa $\rightleftharpoons$ VIIb exists, r.t dual fluorescence can be observed.

In the case of the derivatives **V**, only after protonation, in the first electronically excited state, tautomer **Vb,** in equilibrium with **Va,** can be detected by fluorescence, i.e only in the excited state, the proton is partially transferred from the acid donor group to the basic acceptor group (ESIPT) [13] (Scheme 1.6).

These are the seldom types of N-H…N chelates showing ESIPT.



Scheme 1.6 *Tautomeric S_1 equilibria after protonation*

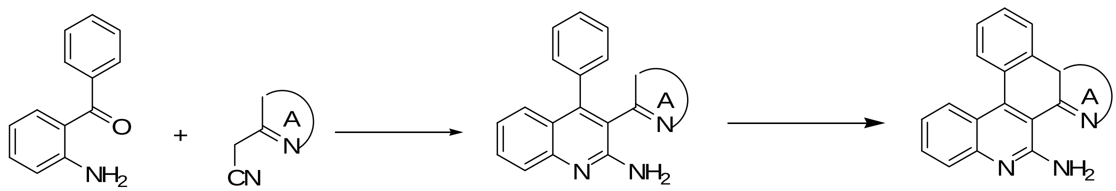
Due to the fact, that both tautomers **Va, Vb** show room temperature fluorescence, depending on the excited state equilibrium **Va**$\rightleftharpoons$**Vb,** emission of **Va** (generally 'blue' fluorescence), of **Vb** (generally long wavelength shifted 'red' fluorescence) or of both fluorescences (i.e. dual fluorescence) can be observed.

By using 2-amino-3-formylpyridine and a variety of π-donor- or π-acceptor- substituted 2-amino benzaldehydes, a great number of chelates of types **V** were synthesized [42].

From the quantitative fluorescence determinations, correlations between fluorescence quantum yields, ESIPT process and molecular structure could be drawn.

1.3 Aim of the Work

An interesting point comes in discussion: The synthesis of types **VIII.**
In this case, the condensation reactions would take place between 2-aminobenzophenones **VI** and heteroarylacetonitrile derivatives **IV** (Scheme 1.7).



VI IV VIII VIII-1

Scheme 1.7 *Condensation reaction using **VI***

Attempts to use the ketones **VI** instead of the aldehydes **I** have been made in our group by Kammerer [12], but without success. **VI** obviously was not reacting at all under the basic conditions used and this was explained by the much lower reactivity of ketones compared with aldehydes.

Finding successful reaction conditions was declared as one of my first tasks.

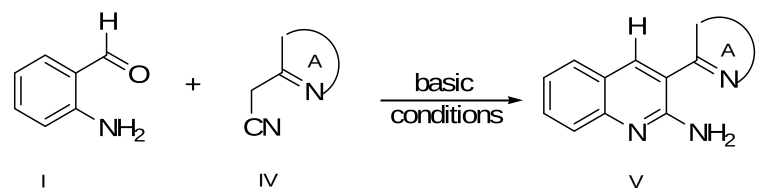
Compounds **VIII** were of interest regarding the influence of the phenyl group on both the fluorescence quantum yields and the extent of ESIPT.

Other goals and tasks were arising during the work (synthesis of new *H-chelates* or of new *polymethines*). But, the main interest of derivatives **VIII** concerned the principal possibility to transform **VIII** into the ring closed derivatives **VIII-1.** From all experiences, derivatives **VIII-1** due to their rigidity should show much higher r.t. fluorescence than **VIII.**

2 Theoretical Part : Syntheses

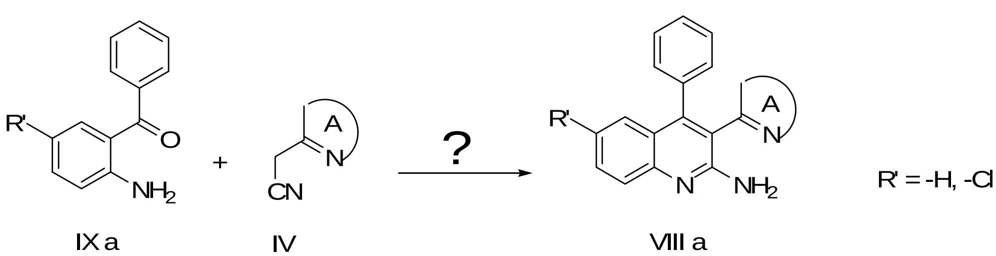
2.1 General Aspects

As mentioned before, the condensation reaction of **I** with **IV** works under basic conditions. A medium which gave good results was EtOH/10% aq NaOH [12] (Scheme 2.1).



__Scheme 2.1__ The condensation reaction of __I__ and __IV__ under basic conditions

Taking in consideration that we use a ketone instead of an aldehyde, one has to expect that, for a successful condensation, the reaction conditions must be more drastic.
What are the best reaction conditions in the case of the condensation between **IXa** and **IV**?



__Scheme 2.2__ Condensation reaction between __IXa__ and __IV__

To get an answer to this question, the first task became clear: Looking for the successful reaction conditions (Scheme 2.2).

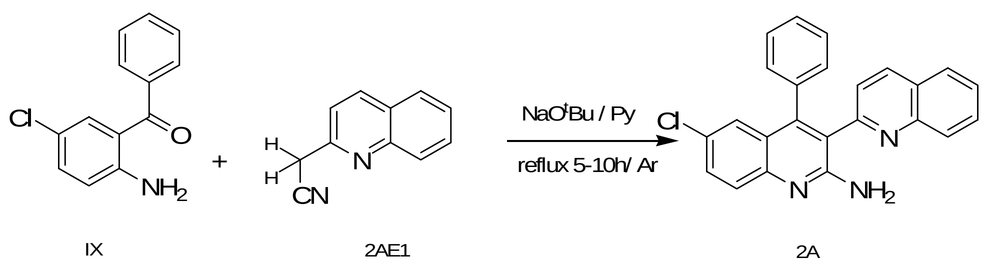
From literature, we have found the following possibilities:
"2-Aminobenzophenone and malononitrile were mixed in pyridine and heated for 24 hours"….[9], "2-Amino-5-chlorobenzophenone, malononitrile and pyridine were heated at reflux for 15 hours"…[10] or "5-substituted-2-aminobenzophenones with equiv. amounts of α-substituted acetonitriles in the

presence of NaH as a basic catalyst in pyridine under reflux for 30 hr…" [11] All these hints were in good agreement with the drastic basic conditions expected for ketones.

2.2 Main Project: Systems with Dual Fluorescence.

2.2.1 6-Chloro-4-phenyl-3-(quinolin-2-yl)-quinolin-2-amine (2A)

The first condensation reaction of interest had as reaction "partners" 2-amino-5-chlorobenzophenone **IX** and 2-(quinolin-2-yl) acetonitrile **2AE1** (Scheme 2.3)
At the beginning, we used both 2-aminobenzophenone and 2-amino-5-chlorobenzophenone, but because of financial and spectroscopic reasons, commercially available **IX** was then mainly used.

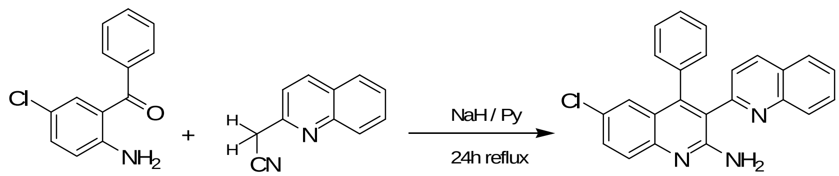


Scheme 2.3** The condensation between 2-amino-5-chlorobenzophenone **IX** and 2-(quinolin-2-yl) acetonitrile **2AE1

Let's go back to the hints found in literature [9, 10, 11]. As we have seen, drastic conditions were used: Long reaction times (15 to 24h), reflux, pyridine as solvent and bases such as NaH.

We have examined different mixtures, based on the literature sources.
Finding the optimal reaction conditions represented a time consuming task.

Based on the literature, the first attempt was the reaction (under reflux for 24hr) between **IX, 2AE1,** NaH as base and pyridine as solvent (Scheme 2.4)



IX 2AE1 2A

Scheme 2.4 *The condensation reaction using NaH as base*

The first problem which occurred, during the work up, was due to the use of NaH from a paraffin oil suspension (it was hard to remove the paraffin oil). Thus, the NaH/paraffin oil suspension was washed under argon with n-hexane prior to use. Still no satisfactory results were obtained.
In other attempts, neither piperidine nor a mixture of piperidine/pyridine (as solvents) were a successful choice.

Instead of NaH, we then decided to use NaO^tBu. Better results have been obtained, but there were still problems with the yields, because of incomplete reaction and a lot of side reactions.

In the following table, a summary of all used mixtures is given (Table 2.5).

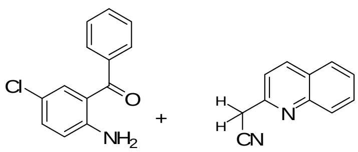
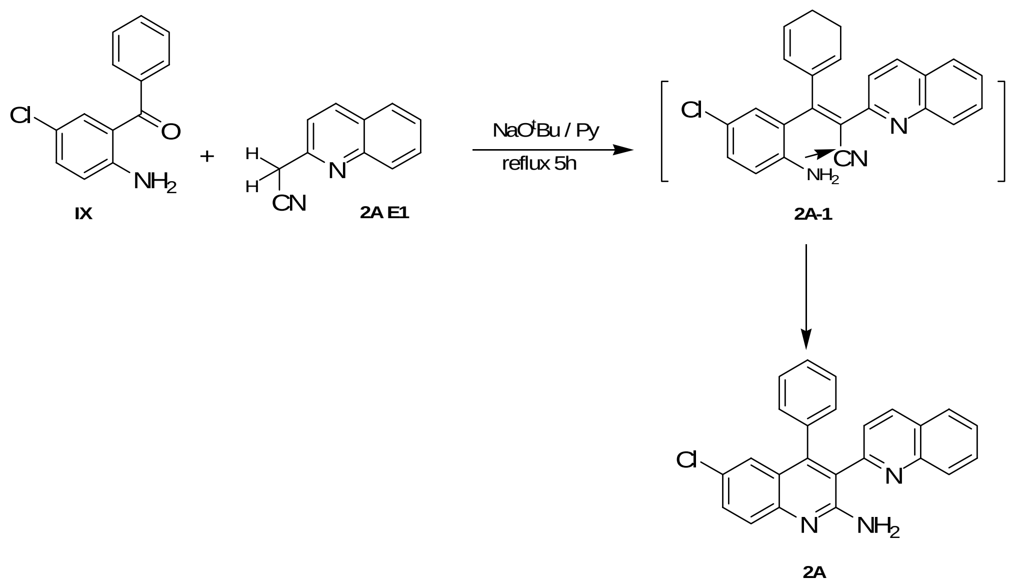
Educts	***Reaction conditions***	***Observations***
 IX 2AE1	NaH / Py / reflux 24h NaH / Py / reflux 30h NaH / Py / reflux 7h	*Difficulties due to NaH/paraffin oil*
	NaH / Py / reflux 7h	*Even with "washed" NaH there are still isolation problems*
	NaH / Pip / reflux 10h NaH / Pip-Py / reflux 10h NaO^{t}Bu / Pip / reflux 6h	*Piperidine as solvent: bad results/isolation problems*
	NaO^{t}Bu / Py / reflux 5h	***Best results***

Table 2.5 *Reaction conditions used for the reaction between* ***IX*** *and* ***2AE1***

We have found:

- Using NaO^{t}Bu as base was the best choice
- The main problem still remains: The reaction is not complete (apart from the desired product, we always isolate the educt **IX**)
- To solve the latter problem, we used an excess of **2AE1**
- Under drastic conditions the reaction works (we can isolate the desired product), but partial decomposition of **2AE1** occurs.
- Using long reaction times is not helpful (side reactions occur and again the educts are decomposed during the reaction). 5-10h seemed to be a reasonable reaction time.

After the formation of the anion of 2AE1 by NaO^tBu, the condensation between the keto-group of **IX** and the anion takes place, followed by an intramolecular addition reaction of the amino- with the nitrile-group ,which (after the ring closure reaction) leads to the desired product **2A** (Scheme 2.6).
The intermediate **2A-1** was not isolated.



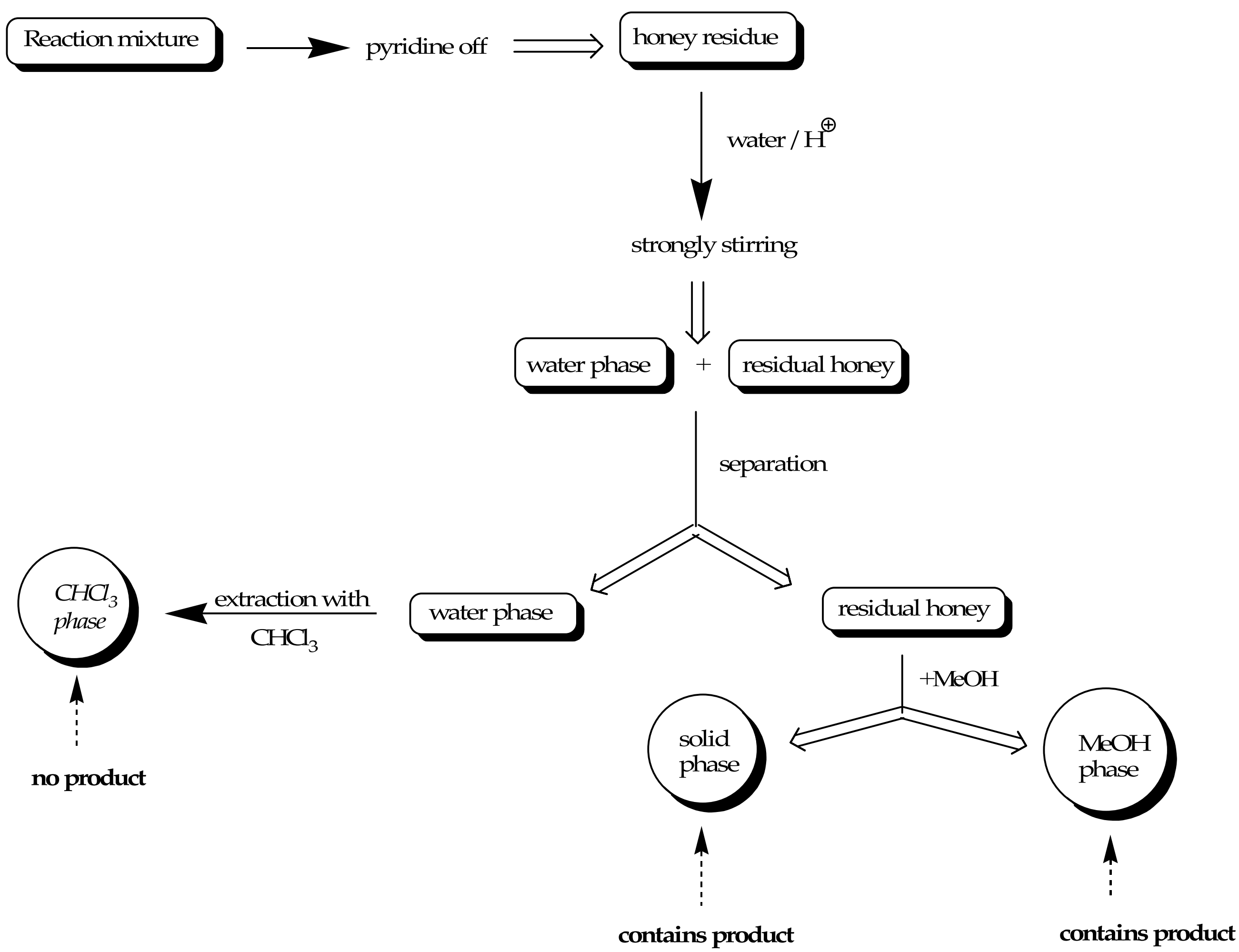
Scheme 2.6 *Schematic representation of the reaction mechanism between 2-amino-5-chlorobenzophenone* ***IX*** *and 2-(quinolin-2-yl) acetonitrile* ***2AE1***

Taking in consideration that the reaction works under drastic conditions (strong base, high temperature and long reaction time) the anion of**2AE1** (formed after the attack of the base) becomes sensitive in the presence of oxygen and this is why an inert medium is required (argon or nitrogen).
As mentioned before, the main problem was that 2-amino-5-chlorobenzophenone **IX** was still to detect.
Thus, finding the "optimized method" became necessary.
The "optimized method" is presented below and then it was used for all the reactions of **IX** with different heteroarylacetonitriles derivatives of the type **IV.**

- *"The optimized method"*

A mixture of 2-(quinolin-2-yl) acetonitrile ***2AE*** *(20mmole), sodium tert-butoxide (20mmole) in 30ml pyridine was stirred at room temperature for 15 min and slowly heated for another 15 min under inert atmosphere(argon).*
Then a solution of 2-amino-5-chlorobenzophenone ***IX*** *(20mmole) dissolved in 20ml pyridine was added dropwise to the hot mixture.*
Heating under reflux for 5h was the next step.

Scheme 2.7 shows the work-up procedure:



Scheme 2.7

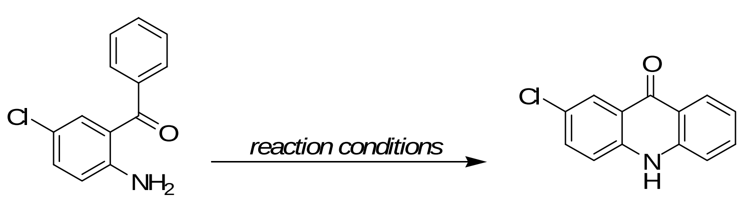
With the "optimized method" much better results were obtained, but the reaction was still not complete and the yields were not excellent.

As a summary we found:

- After using several reaction conditions, with different solvents and bases, the best results were obtained using ***NaO^{t}Bu / Py / 5h / inert atmosphere.***
- We have successfully shown (contrary to Kammerer' results) that the reaction between **IX** and an heteroarylacetonitrile derivative of the type **IV** can be realized.
- Problems occurred due to the drastic reaction conditions (**2AE1** is being partially decomposed, **IX** gives side reactions).
- All these factors, and also problems occurring during the purification of the desired product, are often leading to low yields.
- As a purification method, fractionated vacuum sublimation has been mostly used.
  Recrystallzation or purification by chromatography proved to be unsatisfactory. Sublimation mostly resulted in substances with a high degree of purity. Side reactions during the sublimation and unsatisfactory substance separation, however, could not be avoided in any case.

2.2.1.1 Side Reactions / New Products

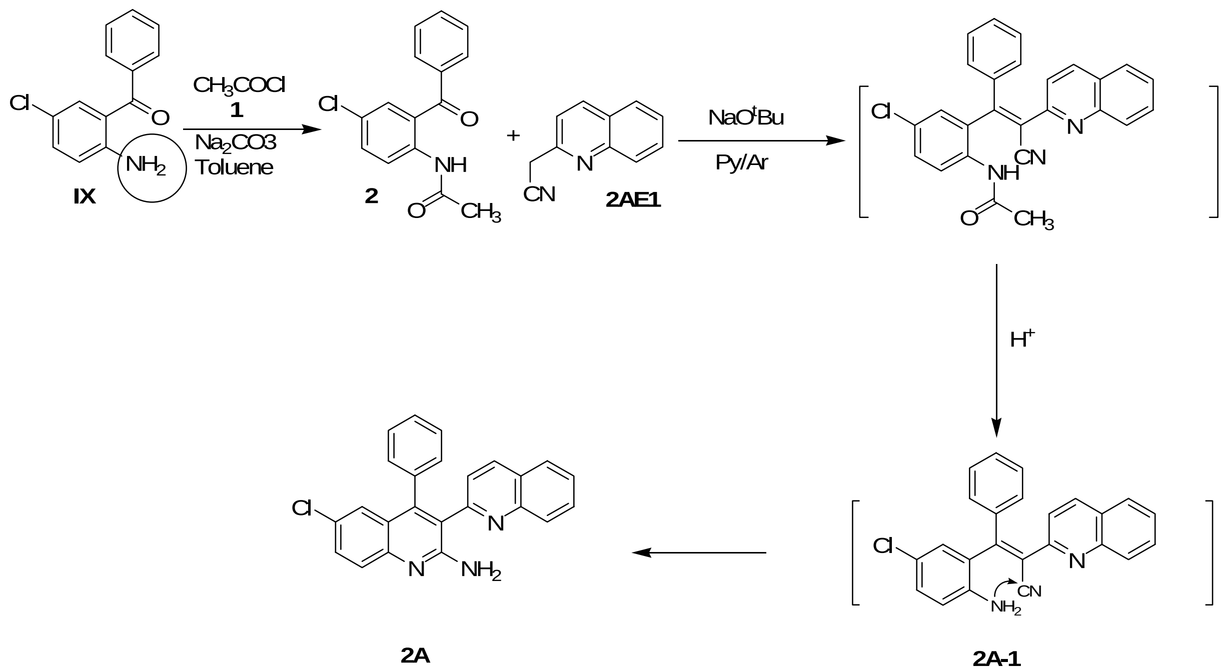
From the analysis of the products, it has been shown that the main side product is given by the intramolecular reaction of **IX,** resulting in 2-chloroacridin-9(10H)-one **IX-2** (Scheme 2.8).



IX IX-2

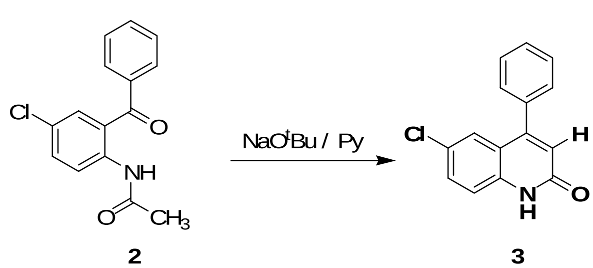
Scheme 2.8 *The side product* ***IX-2***

In order to avoid this side reaction, protection of the amino group was planned. As a first attempt, the reaction between **IX** and the acetylchloride **1** has been carried out, in order to get **2** according to Scheme 2.9.



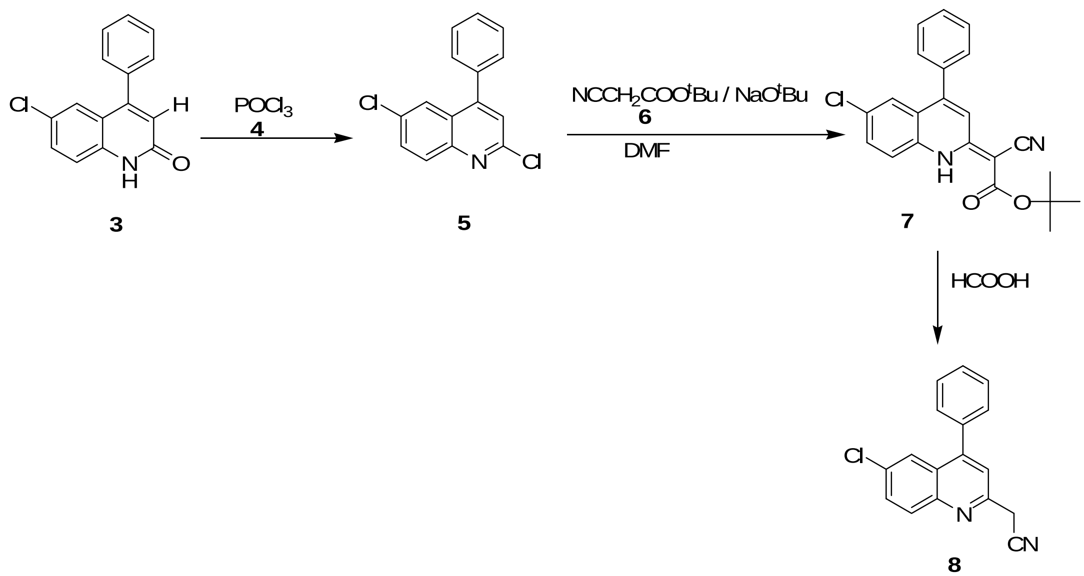
Scheme 2.9 Another way of synthesizing ***2A***

The only change now is that instead of **IX** we use the acetylated system **2.** In the end we should arrive to the same desired ring closed product **2A**, with the only difference that, this time, **IX** shouldn't give any side reactions and side products anymore. The reaction with the acetylchloride **1** works very good, the acetylated system **2** can be isolated in 90% yield.After the successful isolation of the compound **2,** its reaction with 2-(quinolin-2-yl) acetonitrile **2AE1** was examined. But, under basic conditions, **2** led I high yields to 6-chloro-4-phenylquinolin-2(1H)-one **3** (Scheme 2.10).



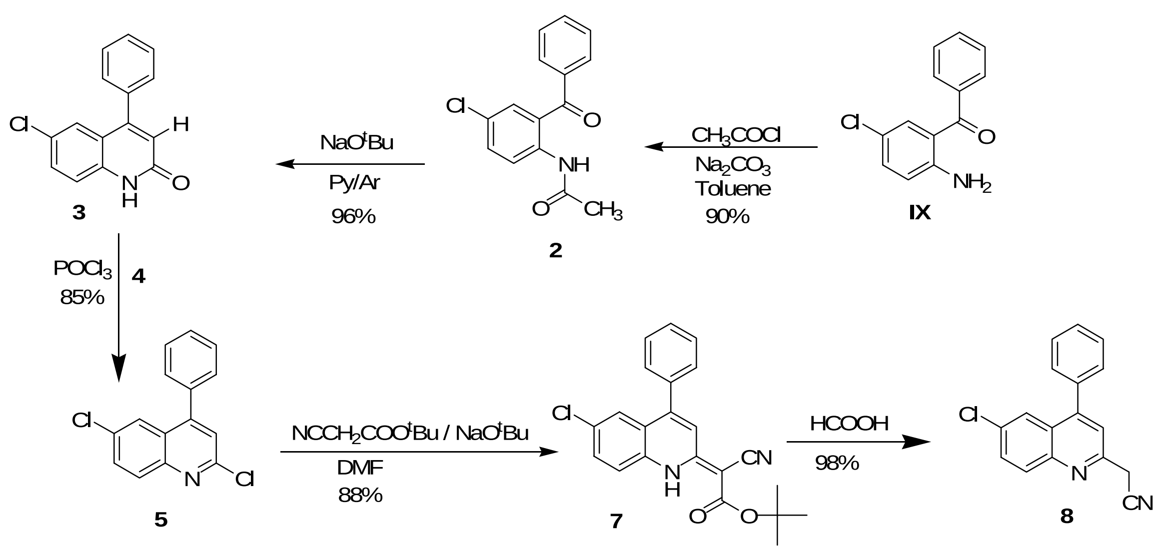
Scheme 2.10

This very result was the starting point for the synthesis of the new heteroarylacetonitrile derivative **8** according to Scheme 2.11.



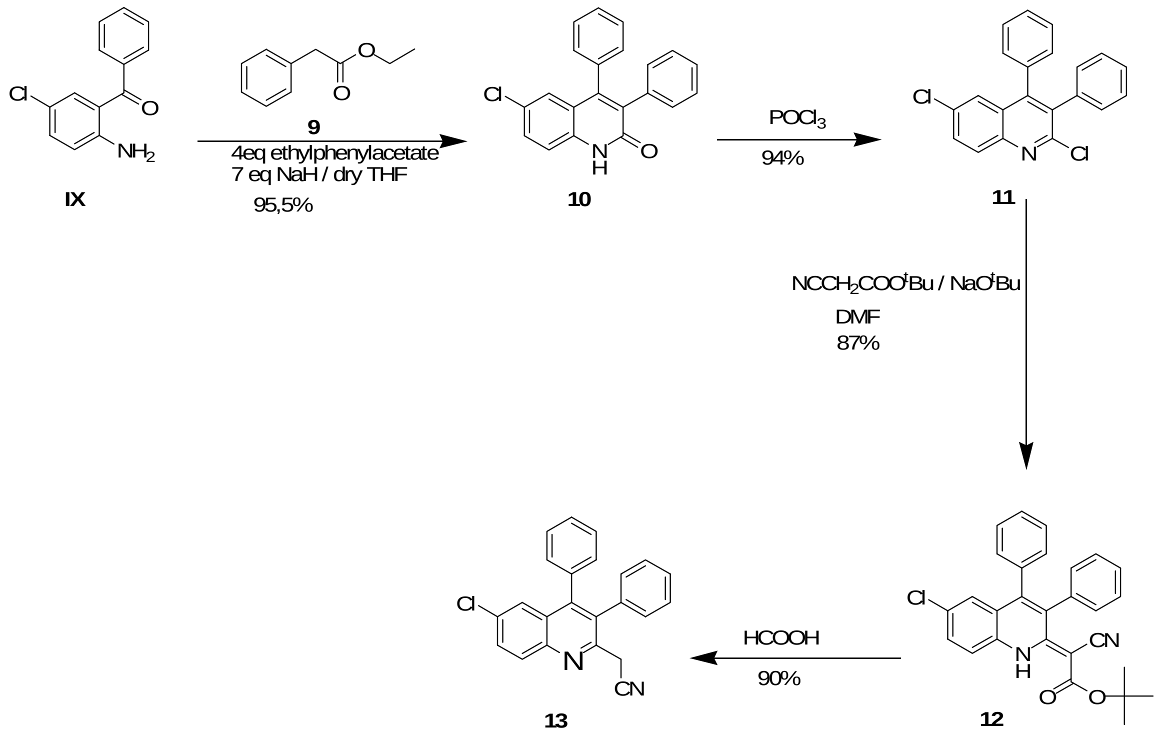
Scheme 2.11 *Synthesis of* **8**

The chlorination reaction with phosphorus oxychloride **4** (in order to obtain 2, 6-dichloro-4-phenylquinoline **5**) is followed by the reaction between **5** and *tert*-butylcyanoacetate **6**.The saponification with formic acid afforded, in high yields, the desired product **8.** Scheme 2.12 summarizes the synthesis of **8** starting from **IX.**



Scheme 2.12 *The reaction steps for the synthesis of* **8**

According to equivalent reaction steps, the heteroarylacetonitrile derivative **13** was synthesized, using again, as starting material, 2-amino-5-chlorobenzophenone **IX** (Scheme 2.13).



Scheme 2.13 *Synthesis of* **13** *from* **IX**

An excess of NaH is important for the successful synthesis of **10.**
A positive conclusion can be extracted: Even if we didn't get the desired results in the case of the reaction between 2-amino-5-chlorobenzophenone **IX** and 2-(quinolin-2-yl) acetonitrile **2AE1**, other interesting results and new substances have been synthesized (**8** and **13**) using as starting material 2-amino-5-chlorobenzophenone **IX** (Fig. 2.14).

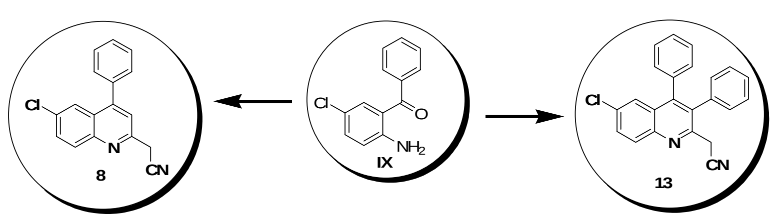
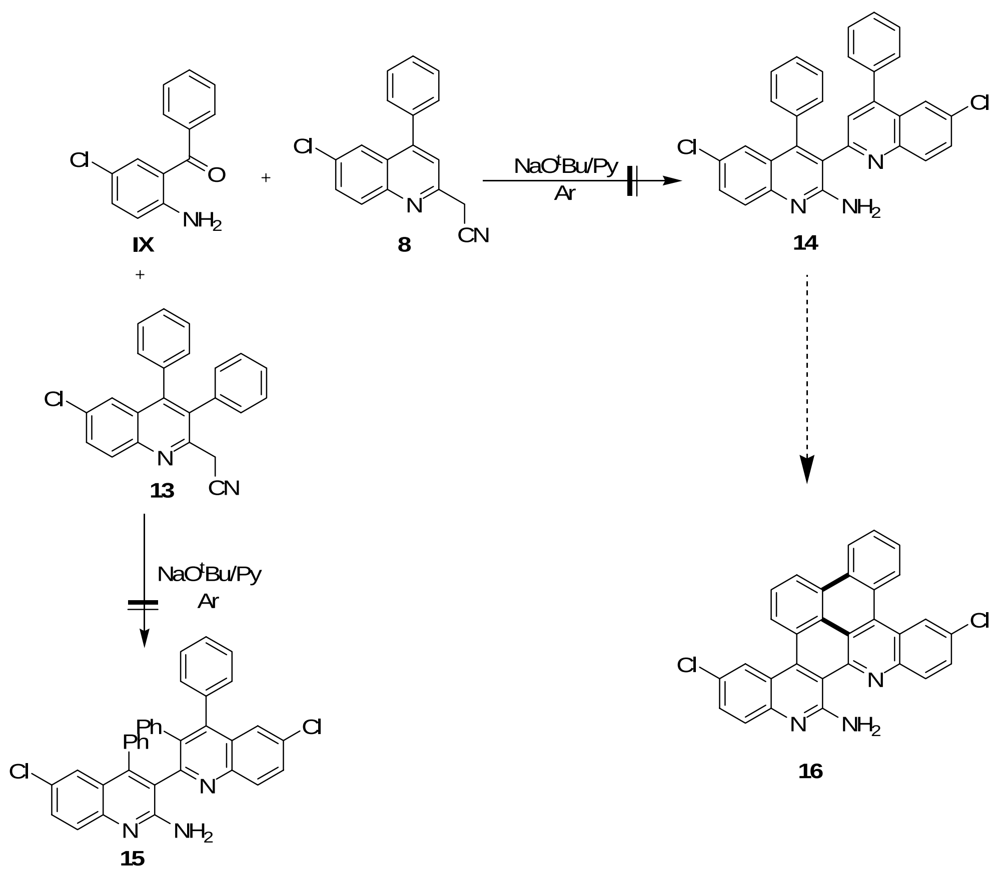


Figure 2.14 *Two new synthesized heteroarylcetonitrile derivatives* ***8*** *and* ***13,*** *having* ***IX*** *as starting material*

Having synthesized the new substances **8** and **13** another question arises: Will the reaction between 2-amino-5-chlorobenzophenone **IX** and the new synthesized substances **8** and **13,** work better than in case of **2AE1**?
The reactions were also carried out under the well- known conditions (basic conditions, inert gas and reflux): **14** exhibits also the possibility of ring closure to **16**, which would significantly increase the fluorescence quantum yield.

The reaction scheme is presented below (Scheme 2.15).

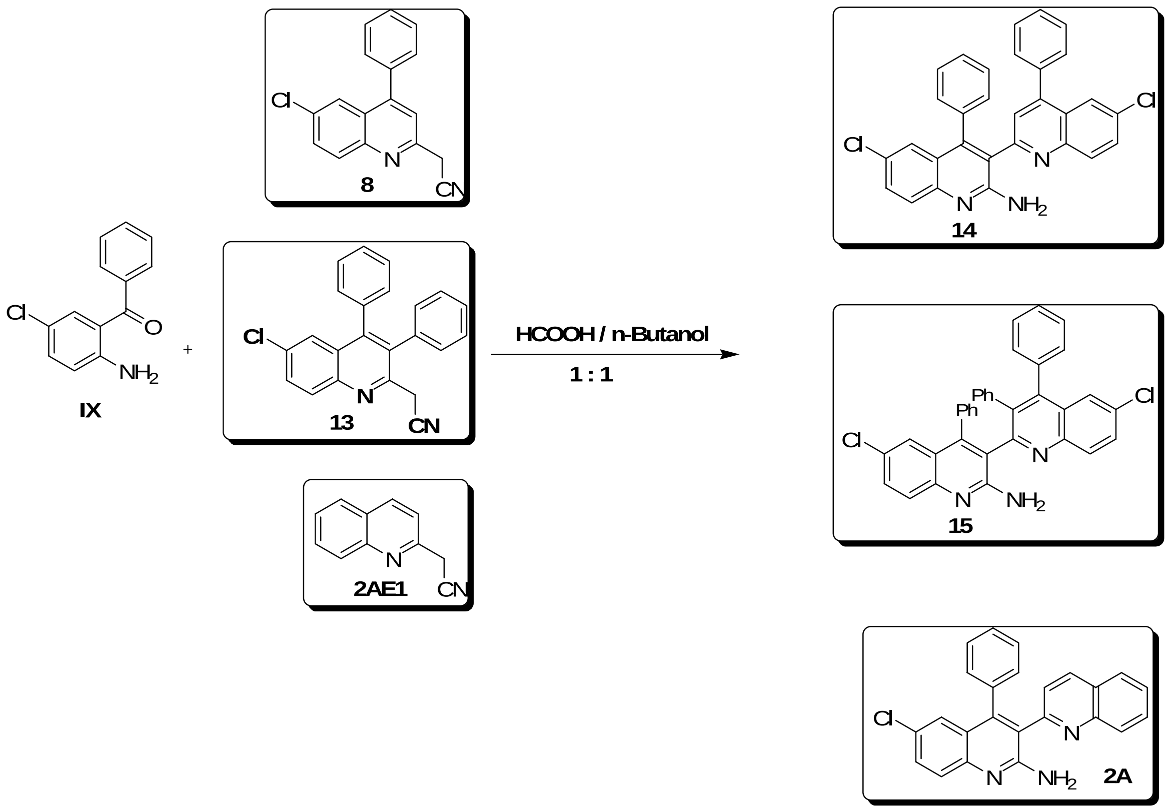


Scheme 2.15** Tried synthesis of **14** and **15

The reactions, however, were not successful; we believe this is due to strong steric hindrances.
What about changing the reaction conditions?

Taking in consideration that for the reactions of **2AE1**, **8** and **13** with **IX,** under basic conditions, the results were not satisfactory, changing the basic conditions arises as a new task.

Using acid conditions, more precisely, the reactions have been carried out using a mixture 1:1 of formic acid and n-butanol (Scheme 2.16).

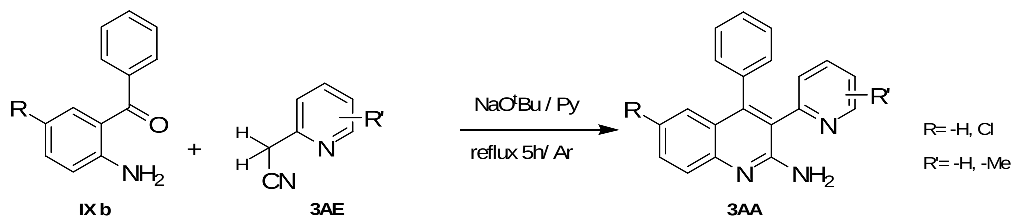


Scheme 2.16 *Synthesis of **3.1**, **14** and **15** under acid conditions*

The reactions worked, but the results were not satisfactory.

2.2.2 6-Chloro-4-phenyl-3-(pyridine-2-yl)-quinolin-2-amine (3A)

In the case of substituted 2-(pyridine-2-yl)acetonitrile derivatives **3AE**, the condensation reactions worked much better.(Scheme 2.17).
The reactions also took place under basic conditions and gave higher yields comparing to **2A.**



Scheme 2.17 *Condensation of **3AE** with **IXb***

Three new condensation products have been synthesized (**3A, 3C, 3D**), as given in Table 2.18.

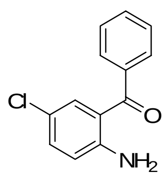
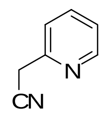
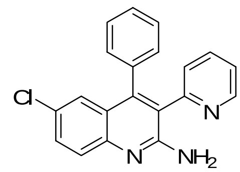
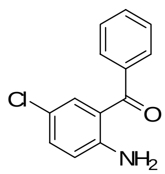
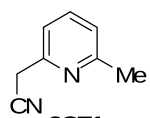
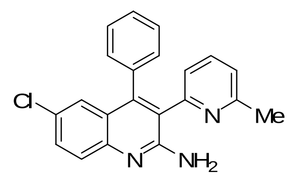
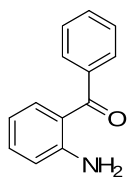
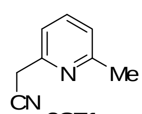
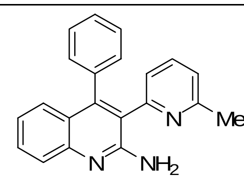
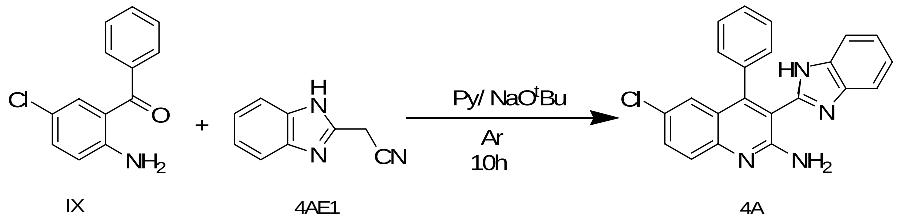
Nr	*Educt1*	*Educt2*	*Product*	*Raw yields*
1		 3AE1	 3A	47%
2		 3CE1	 3C	29%
3	 **IX''**	 3CE1	 3D	32%

Table 2.18 *Three new condensation products:* ***3A, 3C*** *and* ***3D***

2.2.3 3-(1H-Benzo[d]imidazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4A)

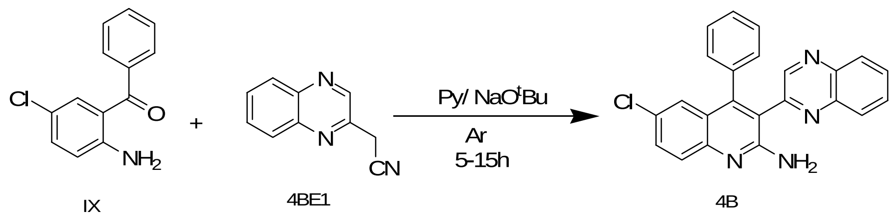
The condensation reaction between **IX** and **4AE1** was carried out under the reaction conditions given under *"the optimized method"* (Chapter 2.2.1, p 13) Heating under reflux for 10h and using a ratio of 1:1.5:1 for the educts IX: NaO^{t}Bu: 4AE1 gave the desired product **4A** in 55% raw yield. (Scheme 2.19).



Scheme 2.19** Synthesis of **4A

2.2.4 6-Chloro-4-phenyl-3-(quinoxalin-2-yl)quinolin-2-amine (4B)

One of the "trouble reactions" is the condensation between **IX** and **4AE1** (Scheme 2.20).



Scheme 2.20** Condensation between **IX** and **4BE1

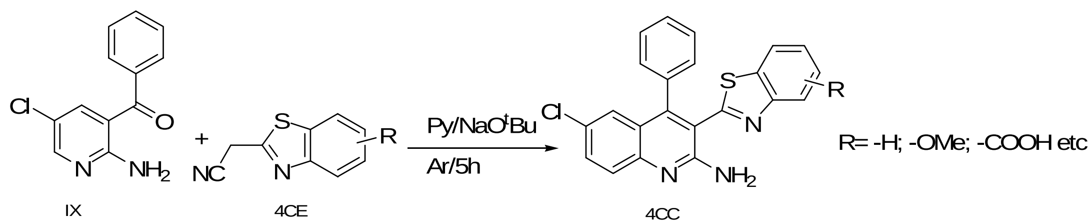
In a first attempt, the reaction of an equimolar mixture of **IX** and **4BE1** was carried out under basic conditions, and a reaction time of 5h. No trace of the desired product **4B** could be isolated.

Increasing the quantity of **IX** (1.5 mole **IX** to 1 mole of **4BE1**) and using the *"optimized method"* (Chapter 2.2.1, p 13) also gave no satisfactory results; only traces of the desired product (5%) could be isolated by purifying the educt **4BE1.**

With a ratio **IX**: NaO^{t}Bu: **4BE1** of 1: 1.5: 1, using "*the optimized method*" and increasing the reaction time up to 9h again resulted in the isolation of traces of the desired product **4B** (still impure according to both ^{1}H-NMR and UV/vis spectra).

2.2.5 3-(Benzo[d]thiazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4C)

Condensation of **IX** with substituted 2-(benzo[*d*]thiazol-2-yl)acetonitrile derivatives **4CE** is shown in Scheme 2.21.



Scheme 2.21 *Condensation reaction of* ***IX*** *with* ***4CE***

Table 2.22 summarizes the condensations which have been performed with different benzothiazolacetonitriles **4CE.**

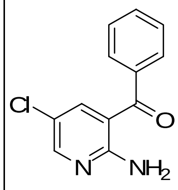
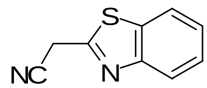
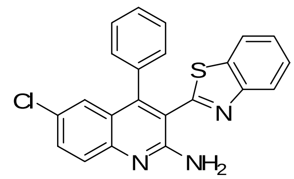
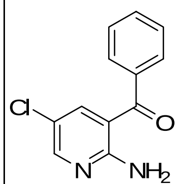
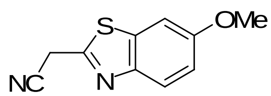
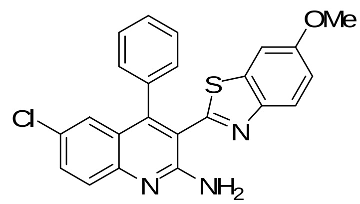
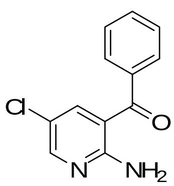
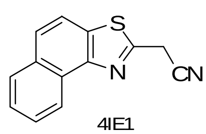
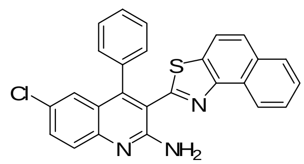
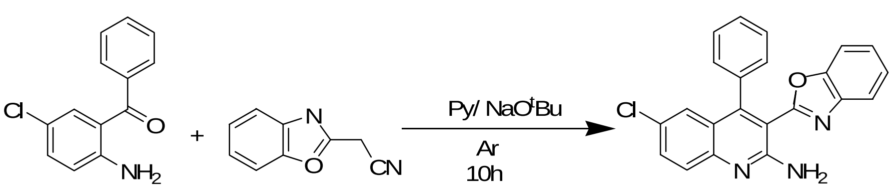
Nr	Educt1	Educt2	Pruduct	Raw yields
1	 IX	 4CE1	 4C	43%
2	 IX	 4EE1	 4 E	15%
3	 IX	 4IE1	 4I	10%

Table 2.21 *New condensation reactions of* ***IX***

2.2.6 3-(Benzo[d]oxazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4D)

The coupling of **IX** with **4DE1** under the "*optimized method*" reaction conditions for 10h led to the desired product **4D,** in good yields (raw yield: 52%) (Scheme 2.22).



IX 4DE1 4D

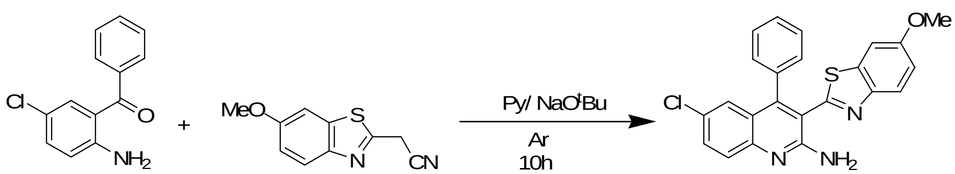
Scheme 2.22 *Condensation between* ***IX*** *and* ***4DE1***

2.2.7 6-Chloro-3-(6-methoxybenzo[d]thiazol-2-yl)-4-phenylquinolin-2- amine(4E)

The condensation reaction between **IX** and **4EE1** has been carried out using a reaction time of 5h, basic conditions and the desired product has been successfully isolated.

Despite of the low raw yield (only 15%) **4E** is the one which revealed the highest fluorescence quantum yield after protonation (Φ_f = 44%).

The reaction scheme is shown below (Scheme 2.23).

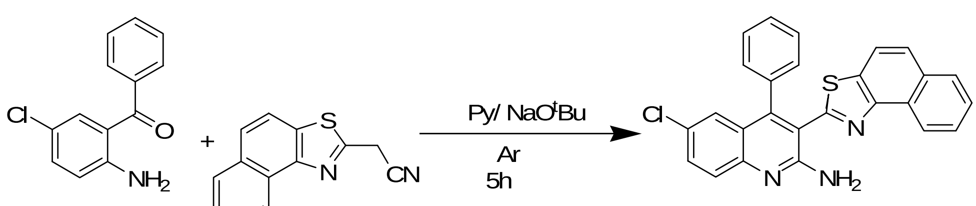


IX 4EE1 4E

Scheme 2.23 *Condensation between* ***IX*** *and* ***4EE1***

2.2.8 6-Chloro-3-(naphtha [1, 2-d] thiazol-2-yl)-4-phenylquinolin-2-amine (4I)

The condensation of **IX** with **4IE1** is shown in Scheme 2.24. Using the *"optimized method"*, the desired product **4I** was successfully isolated.

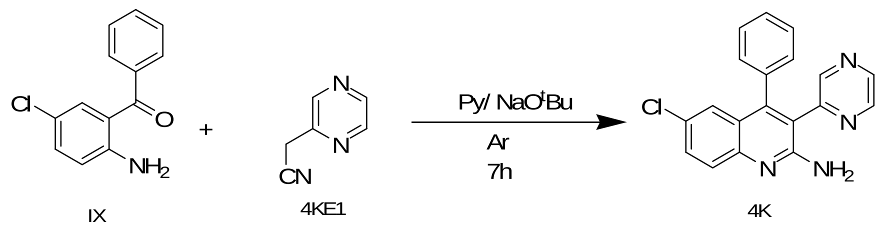


IX **4I E1** **4 I**

Scheme 2.24 *Synthesis of* ***4I***

2.2.9 6-Chloro-4-phenyl-3-(pyrazin-2-yl) quinolin-2-amine (4K)

The reaction was carried out under basic conditions, argon atmosphere and a reaction time of 7h (Scheme 2.25).

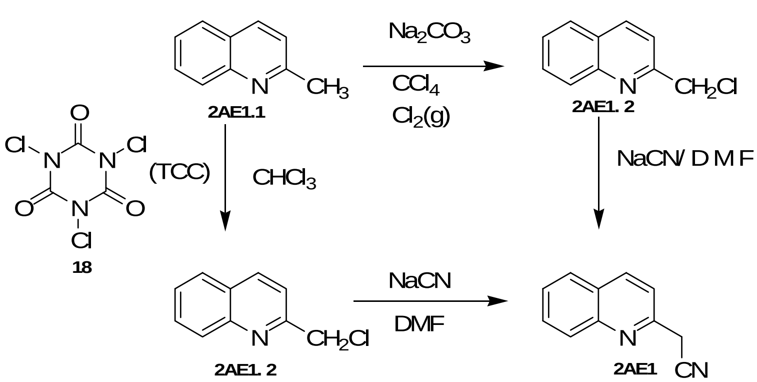


Scheme 2.25 *The condensation between* ***IX*** *and* ***4K***

Due to the small available amounts of **4KE1**, however, sufficient studies of the reaction were not done.

2.2.10 Syntheses of Educts

<u>2.2.10.1 Synthesis of 2-(Quinolin-2-yl) acetonitrile (2AE1)</u>

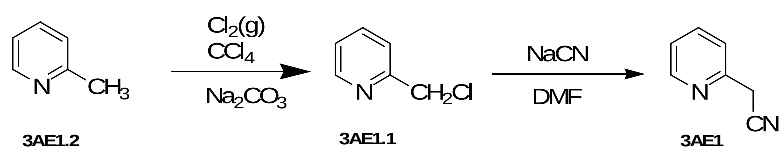


Scheme 2.26 *Synthesis of 2-(quinolin-2-yl) acetonitrile* ***2AE1***

Two ways of synthesis have been carried out [43,44]. In both cases, the chlorination of 2-methylquinoline **2AE1.1** was followed by the reaction with sodium cyanide and DMF in order to afford the desired product **2AE1** (Scheme 2.26).

Two different chlorination paths were used: In the fist case, trichloroisocyanuric acid **18** and chloroform were part of the reaction mixture and in the second case, the use of sodium carbonate, tetrachloromethane and blowing chlorine gas, was the key to afford **2AE1.2.** Good yields and pure substances were obtained using (for the chlorination of **2AE1.1**) the route with TCC and $CHCl_3$.

2.2.10.2 Synthesis of 2-(Pyridin-2-yl) acetonitrile (3AE1)

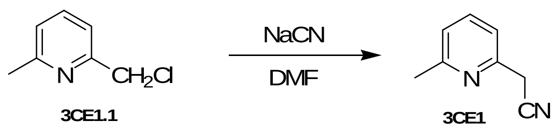


Scheme 2.27** Synthesis of 2-(pyridin-2-yl) acetonitrile **3AE1

For the synthesis of **3AE1**, the chlorination of **3AE1.2** was achieved using tetrachlormethane, sodium carbonate and blowing chlorine gas [44] (Scheme 2.27).
2-(chloromethyl) pyridine **3AE1.1** in reaction with sodium cyanide and DMF led to the formation of the desired product **3AE1** in good yields [14].

2.2.10.3 Synthesis of 2-(6-Methylpyridin-2-yl)acetonitrile (3CE1)

For the synthesis of **3CE1**, 2-(chloromethyl)-6-methylpyridine **3CE1.1,** sodium cyanide and DMF were used [14] (Scheme 2.28).
3CE1.1 was available in the group.



Scheme 2.28 *Synthesis of 2-(6-methylpyridin-2-yl)acetonitrile* ***3CE1***

2.2.10.4 2-(1H-Benzo[d]imidazol-2-yl)acetonitrile (4AE1)

This substance was available in the group.

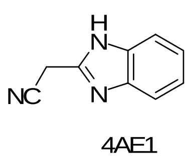
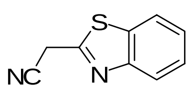


Fig. 2.29 *2-(1H-Benzo[d]imidazol-2-yl)acetonitrile*

2.2.10.5 2-(Benzo[d] thiazol-2-yl)acetonitrile (4CE1)

This substance was available in the group and has been synthesized by W. Sulger.

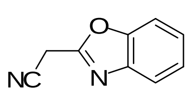


4CE1

Fig. 2.30 *2-(Benzo[d] thiazol-2-yl)acetonitrile*

2.2.10.6 2-(Benzo[d]oxazol-2-yl)acetonitrile (4DE1)

This substance was available in the group and has been synthesized by W. Sulger.

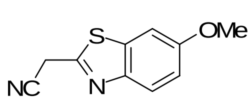


4DE1

Fig. 2.31 *2-(Benzo[d]oxazol-2-yl)acetonitrile*

2.2.10.7 2-(6-Methoxybenzo[d]thiazol-2-yl)acetonitrile (4EE1)

This substance was available in the group and has been synthesized by W. Sulger.

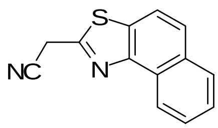


4EE1

Fig. 2.32 *2-(6-Methoxybenzo[d]thiazol-2-yl)acetonitrile*

2.2.10.8 2-(Naphtho[1, 2-d]thiazol-2-yl)acetonitrile (4IE1)

This substance was available in the group and has been synthesized by Chen.



4IE1

Fig. 2.33 *2-(Naphtho[1, 2-d]thiazol-2-yl)acetonitrile*

2.2.11 Other Condensation Reactions of IX

With **4FE1, 4GE1, 4GGE1, 4HE1, 4JE1 4LE1**, **4LE2**, **4LE3**, and **4LE4** under the same basic conditions and inert atmosphere, the reactions with **IX** didn't lead to the desired products.
The unsuccessful reactions are summarized in Table 2.34.

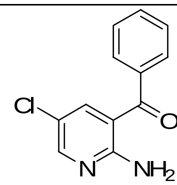
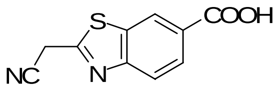
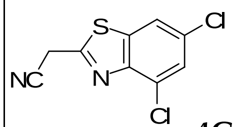
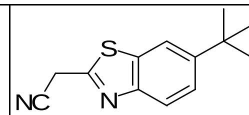
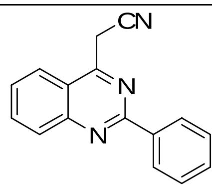
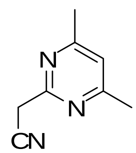
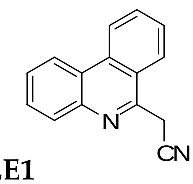
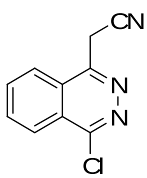
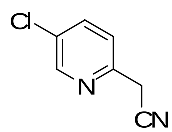
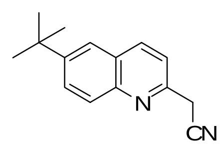
 IX ***in reaction with***		
 **4FE1**	 **4GE1**	 **4GGE1**
 **4HE1**	 **4JE1**	 **4LE1**
 **4LE2**	 **4LE3**	 **4LE4**

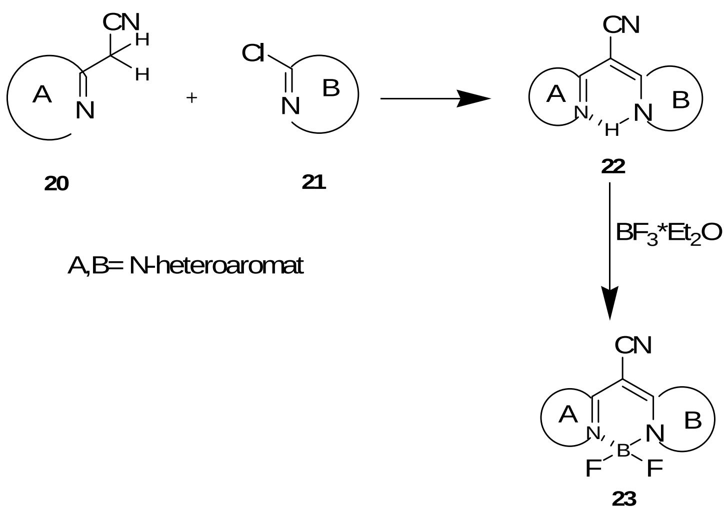
Table 2.34 *Unsuccessful condensations of* ***IX***

2.3 H-Chelates

Heteroarylacetonitrile derivatives **20,** reacting with substituted α-chloroheterocycle derivatives **21,** lead to the formation of H-Chelates **22** [15].

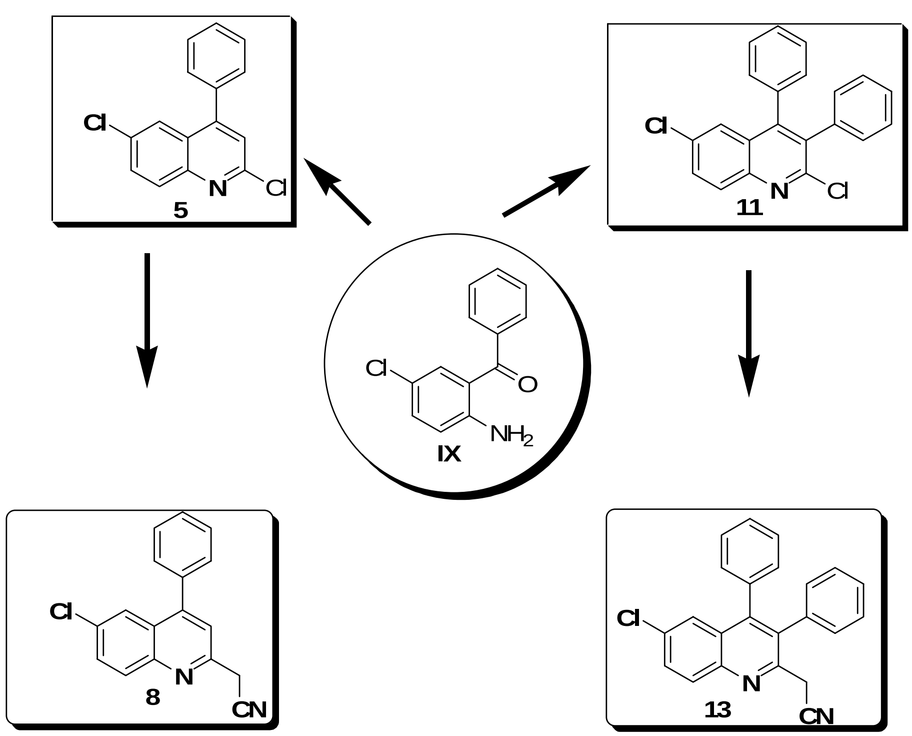
Substitution of the chelate proton by any element or group of the first to the fourth main group of the periodic system gives a great variety of new systems with excellent spectroscopic properties. Thereby, complexation with boron derivatives play a special role due to high reaction yields, easy and cheap syntheses, and generally the highest room temperature fluorescence quantum yields [59].

As an example the general reaction of types **22** with $BF_3 \cdot OR_2$ to **23** is shown (Scheme 2.35).



Scheme 2.35 *Synthesis of* ***23***

The derivatives **8** and **13** described in the Chapter 2.2.1.1 and **5, 11** are reasonable educts for reactions according to Scheme 2.35.



Having this set of educts, synthesizing the corresponding H-chelates came as the next task.
The reactions have been carried out under basic conditions, inert atmosphere and using NMP as solvent. The reaction times varied between 3 and 5 h and the temperature between 80 and 110 ^{0}C. Depending on the used educts, symmetrical or asymmetrical H-chelates should result.
In the case of the reaction between **13** and **11,** the resulting product is colorless. Due to the strong steric hindrance this very compound exists in the "colorless" tautomer, as shown in Table 2.36.

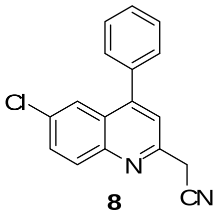
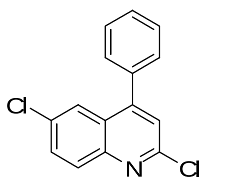
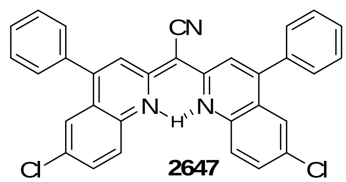
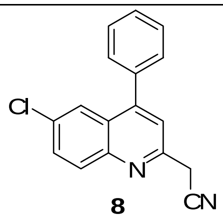
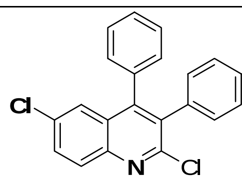
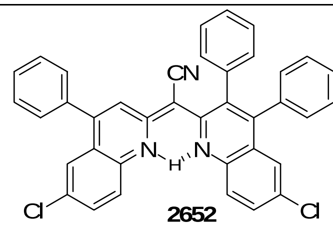
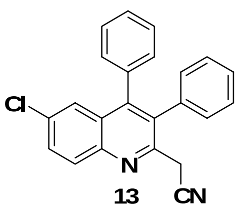
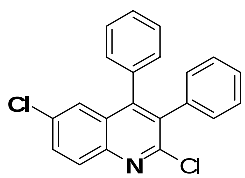
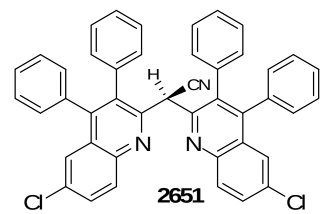
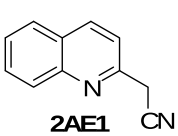
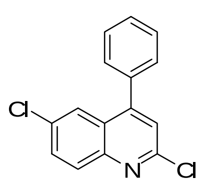
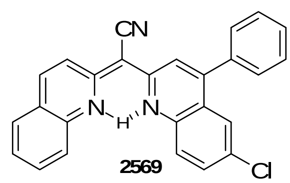
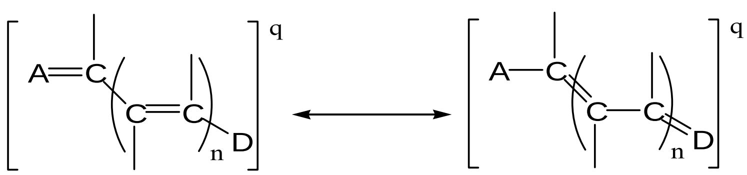
Educt 1	***Educt 2***	***H-chelate***	***Raw yield***
 **8**	 **5**	 **2647**	92%
 **8**	 **11**	 **2652**	95%
 **13**	 **11**	 **2651**	
 **2AE1**	 **5**	 **2569**	98%

Table 2.36 *New H-chelates **2647, 2652, 2651, 2569** and their starting materials.*

2.4 Polymethines

Polymethine dyes are characterized by a chain of uneven methine groups, i.e., by a system of conjugated double bonds [46]. The carbon atoms of the methine groups may be substituted by groups other than hydrogen, or they may be parts of carbocyclic or heterocyclic ring systems. Formal, in polymethine dyes, an electron donor D and an electron acceptor A terminate the chain of methine groups. The structural backbone of polymethine dyes is depicted in Fig. 2.37.



$n = 0, 1, 2, 3...$
$q = -1, 0, +1$

Fig. 2.37 *Structural backbone of polymethine dyes.*

Polymethines can be classified by the number of methine groups in which n= 0, 1, 2, etc. corresponding to mono-, tri-, penta-(etc)-methines. In addition, polymethines can be further subdivided with respect to the structure of the electron donor-acceptors. For instance, in the largest group of cationic polymethine dyes (i.e., q= +1) the donor and acceptor moieties contain nitrogen [47].

Depending on whether or not both or one of the nitrogens are components of a ring moiety, they are named cyanine, hemicyanine, or streptocyanine (‘open chain cyanines’). In the case of the cyanines, both nitrogens are each independently part of a heteroaromatic moiety, such as pyrrole, imidazole, thiazole, pyridine, quinoline, indole, benzothiazole, etc.

The classification of polymethines is illustrated in Table 2.38 [46].

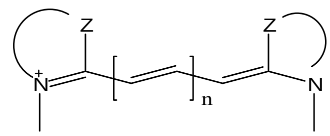
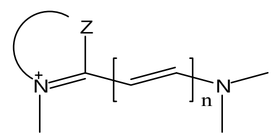
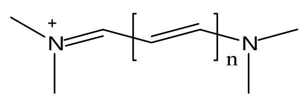
Group Name	*General formula*
Cyanine	
Hemicyanine	
Streptocyanine	

Table 2.38

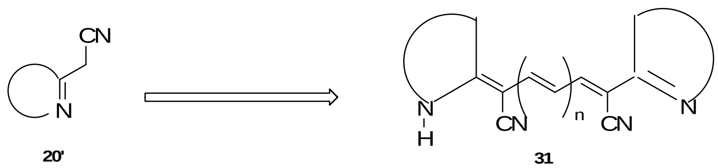
Cationic polymethine dyes (CPDs), best known as cyanine dyes (gr. *cyanos, blue*), with their bright absorption and fluorescence properties, are a powerful tool for fluorescence detection [48]. Historically studied for infrared photography and as laser dyes, in the last ten years have become widely used in biochemical applications for multitasking analysis because they show:

- High structure versatility
- Tunable absorption and emission maxima (UV-Vis-NIR)
- High molar extinction coefficient (ε)
- Competitive quantum yield (Φ_f)

By virtue of their water solubility, cyanine dyes are excellent fluorescent labels for biological assays. The dyes are extremely useful for labeling nucleic acids, nucleotides and proteins [49-51].

According to a patent of our group [52, 61] types **31** can be synthesized (Scheme 2.39).

In the protonated form, these types correspond to the classical heteroaromatic polymethines, well-known as cyanine dyes.



n=0 C_1-synthon $CHCl_3$; DMF/$POCl_3$
n=1 C_3-synthon TMP
n=2 C_5-synthon König's salt

Scheme 2.39 *General reaction scheme for the synthesis of* ***31***

For this type of reaction, the heteroarylacetonitrile derivatives **2AE1**, **8** and **13** have been used (Fig. 2.40)

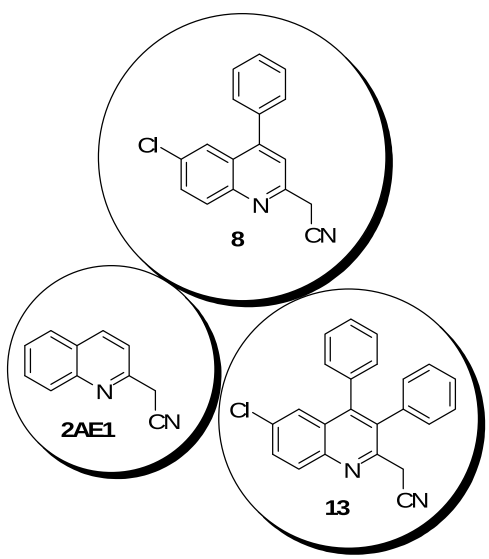
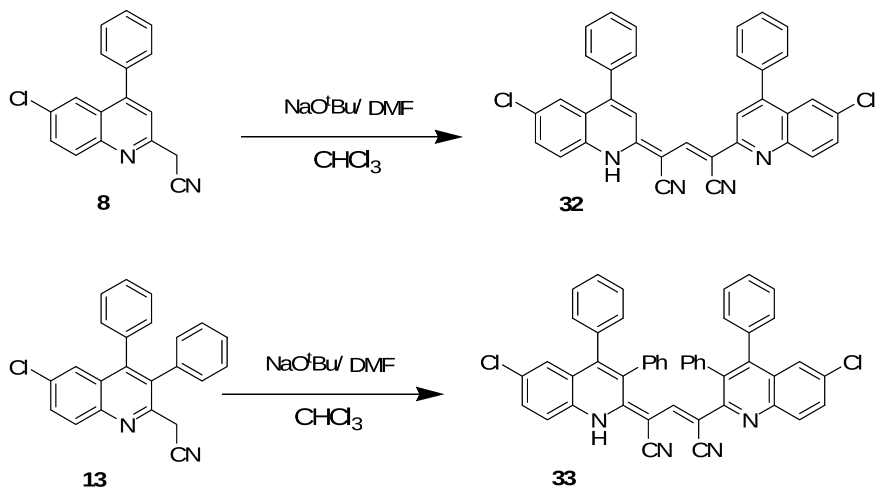


Figure 2.40 *The educts* ***2AE1, 8*** *and* ***13***

2.4.1 Reaction with a C_1-Synthon

2.4.1.1 Reactions with $CHCl_3$ as a C_1-Synthon

In the case of the C_1-Synthon, the following reactions have been carried out (Scheme 2.41).



Scheme 2.41 *Reactions with the C_1-Synthon*

In order to get the desired products **32** and **33,** the ratio **8**(**13**): **base**: **$CHCl_3$** (as C_1-synthon) had to be 1: 1: 0.5.

Reaction conditions: DMF as solvent
3 h and 65^0 for **32** and up to 90^0 for **33**

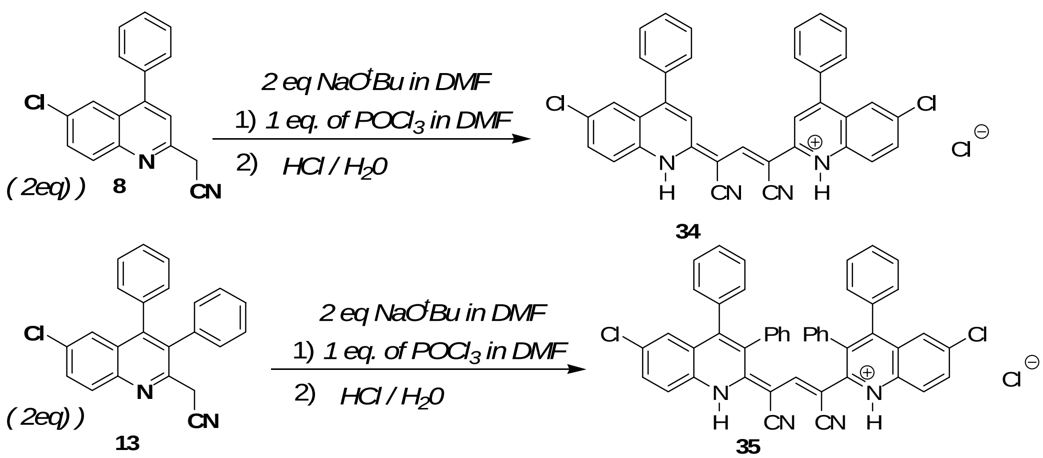
32 and **33** were isolated as crude materials as shown by the UV-vis spectra.

Purification proved to be very complicated.

2.4.1.2 Reactions with the Vilsmeier Complex as a C_1-Synthon

The *Vilsmeier reagent* was used as a C_1-synthon for the reaction of **8** and **13**.

The corresponding reaction schemes are presented below (Scheme 2.42).



Scheme 2.42 *Reactions with the* ***Vilsmeier reagent***

The reaction to **34** was successful, compound **35**, however, could not be isolated. The steric hindrance seems to be too strong. We believe the isolated product has structure **36** (Fig 2.43).

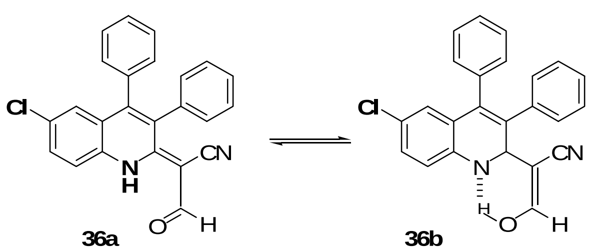
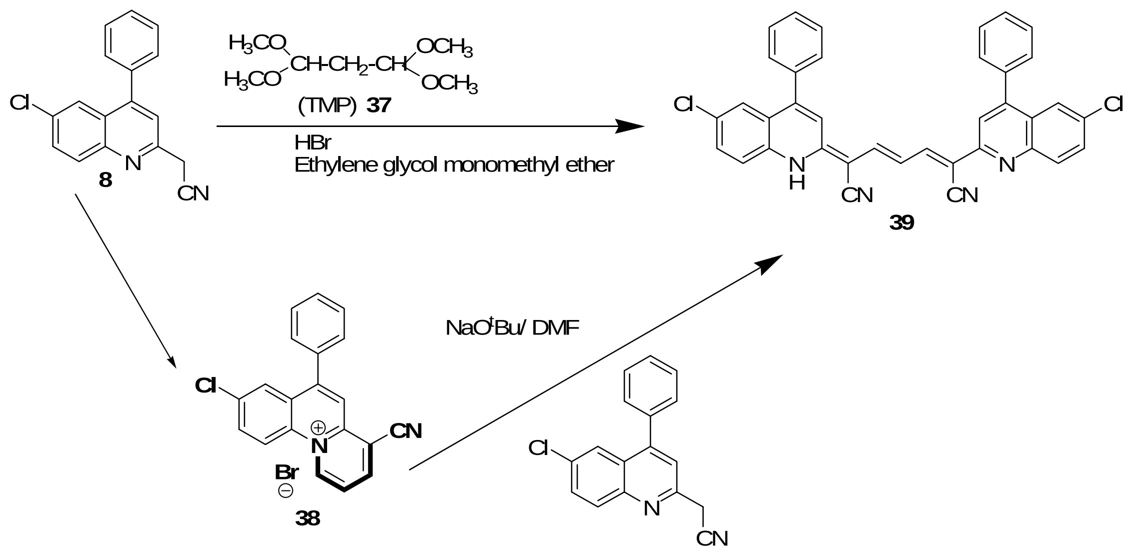


Figure 2.43 *Structure of* ***36***

2.4.2 Reaction with a C_3-Synthon

As precursor of the C_3-synthon malone dialdehyde 1, 1, 3, 3-tetramethoxypropane (TMP) was used (Scheme 2.44).



Scheme 2.44 Reaction with the C_3-Synthon

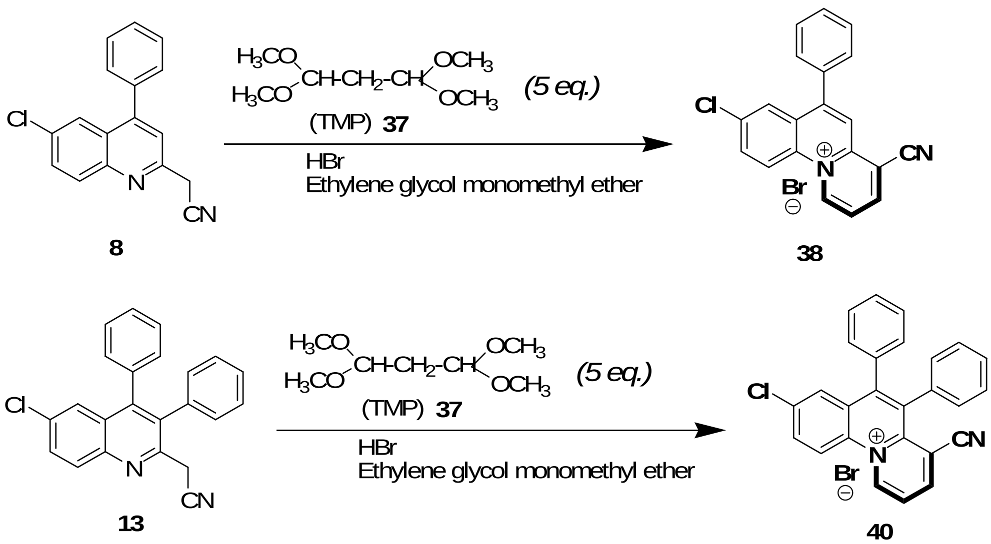
If the ratio **8** : **37** is 1:1, the quinolizinium cation **38** has to be expected. **39** needs a ratio 1:0.5.

38 is part of the reaction path because the intramolecular reaction (which leads to the formation of **38**) is faster than the intermolecular to **39**.

Substances of the type **38** are very reactive; under basic conditions they react very fast with any heteroarylacetonitrile derivative, leading to products of type **39.**

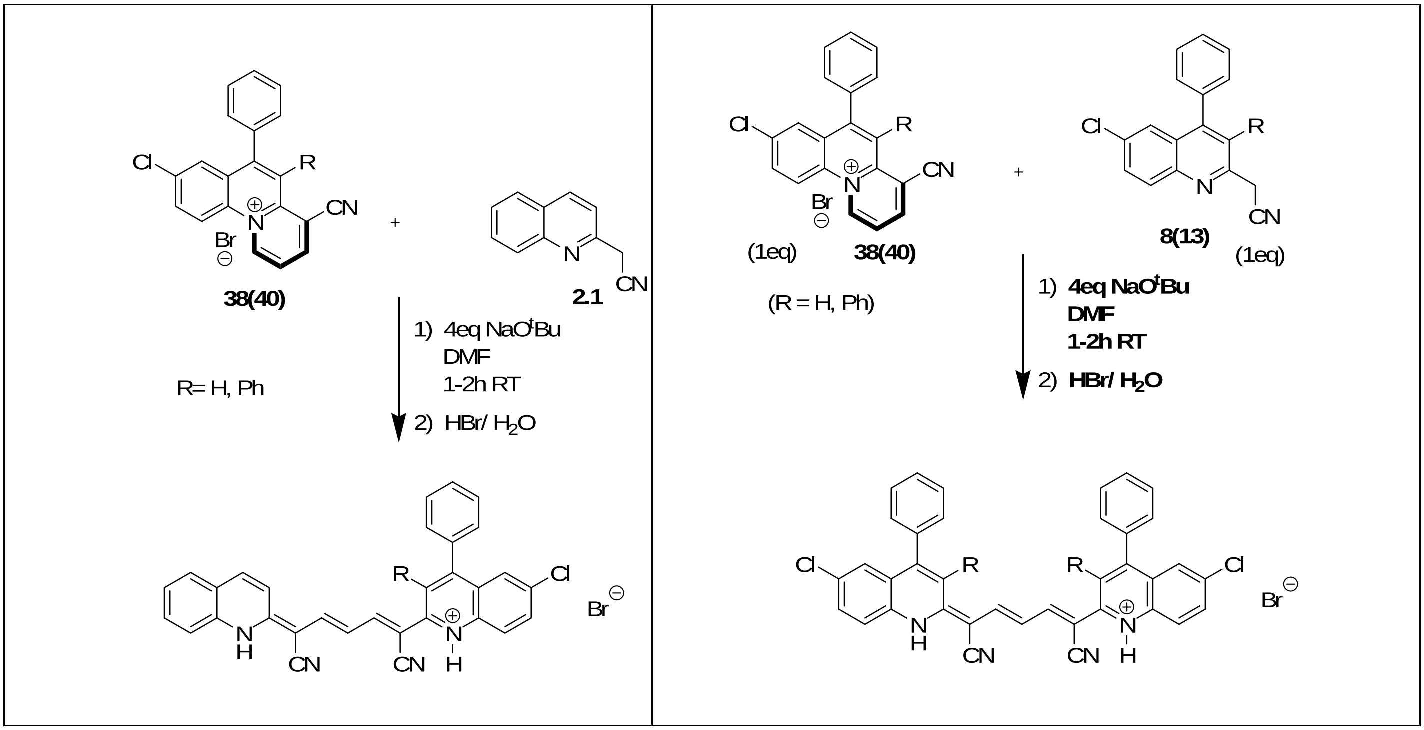
38 under acid conditions is stable against the second attack of **8**, this is why basic conditions are used.
Excess of the solvent (ethylene glycol monomethyl ether) and of TMP **37** are conditions which favour the ring closure reaction.

The expected reactions are according to Scheme 2.45:



Scheme 2.45** Synthesis of **38, 40

The reactions of **38, 40** with heteroarylacetonitrile derivatives **2AE1, 8** and **13,** under basic conditions, lead to new polymethine systems (Scheme 2.46):



Scheme 2.46 *New polymethine systems*

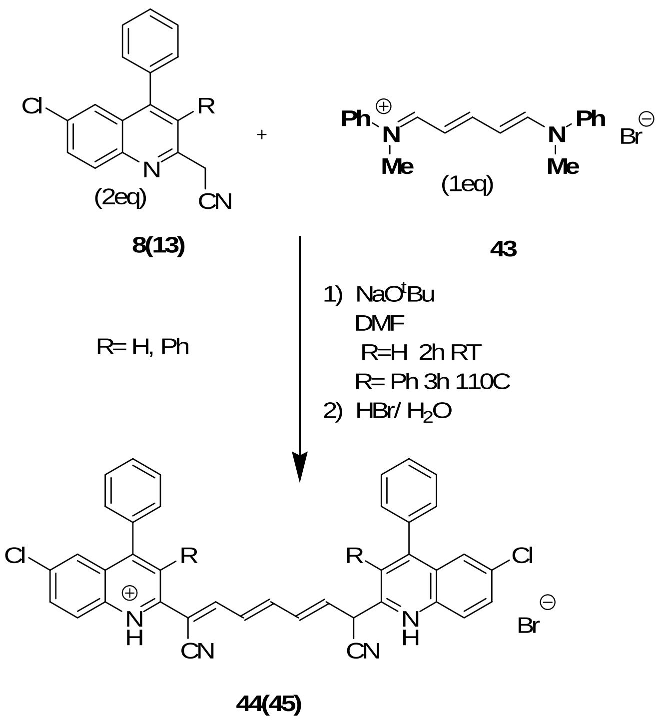
2.4.3 Reaction with a C_5-Synthon

As C_5-Synthon, the König's salt (**43**) has been used.

Reaction conditions:

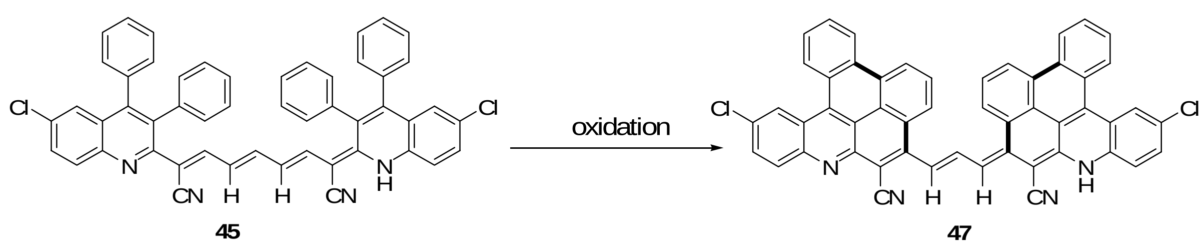
Ratio **8(13)** : **42** has to be 2:1 and in the case of **13** (due to the steric hindrance) heating up to 110 ^{0} is necessary.

The reaction paths are presented below (Scheme 2.47).



Scheme 2.47 *Reactions with **43***

The synthesis of **45** was particularly interesting, as it could be the starting material for **47** (Scheme 2.48).



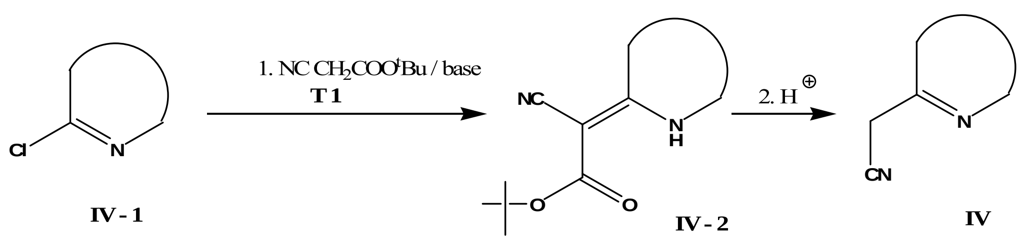
Scheme 2.48 *Ring closure reaction.*

In any case (reactions with C_3 and C_5 synthons) according to the UV/vis spectra, the desired compounds are found, but the isolation of the pure substances could not be achieved.

2.5 Side Projects

2.5.1 Synthesis of 4K and 4LE3

In order to get other heteroarylacetonitrile derivatives **IV**, following synthesis method has been tried.
The general reaction scheme is given below (Scheme 2.49).



Scheme 2.49

In the first step, basic conditions and *tert*-butyl 2-cyanoacetate are necessary to get types **IV-2**, which after saponification lead to the formation of **IV** [15].

Types **IV-1** used are summarized in the Table 2.50:

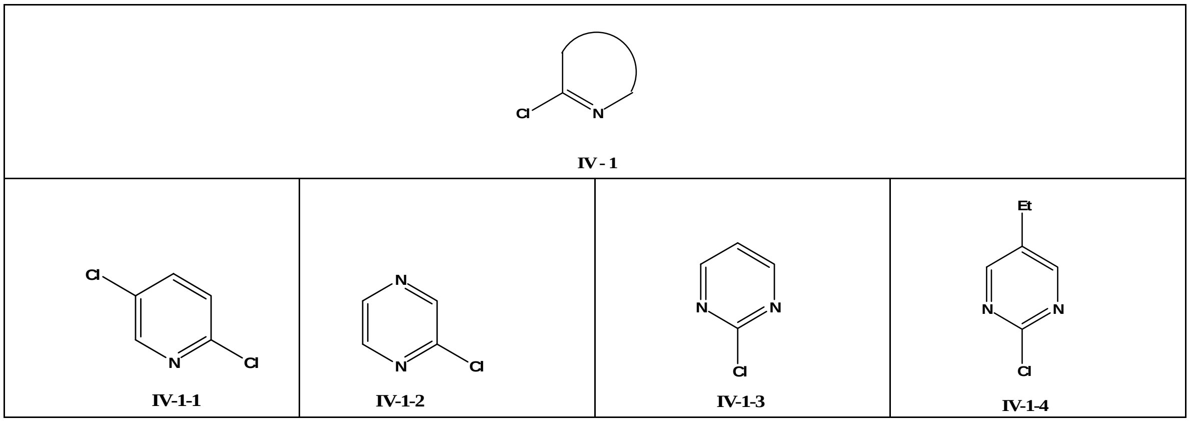
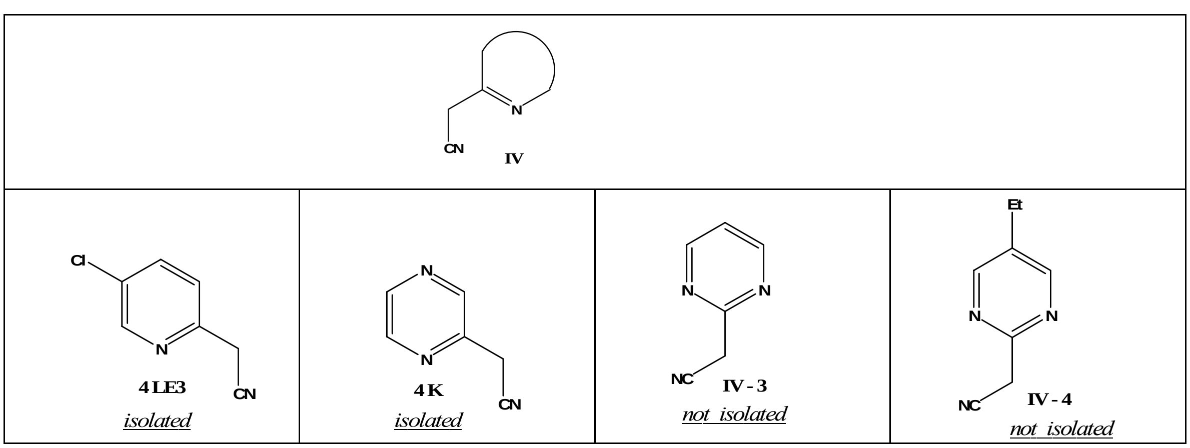


Table 2.50

In order to get types **IV-2**, using NaH (as base), *tert*-butyl 2-cyanoacetate and refluxing for 2 to 4h in dioxane did not lead to satisfactory results. [15]
The best choice proved to be a mixture of NaO^tBu / $NCCH_2COO^tBu$ / NMP and a heating time of 3-4 h at 130 ^{0}C.
Under these reaction conditions, the corresponding **IV-2** derivatives were successfully isolated.
In the second step, saponification with fuming HCl was leading to the desired products **4K** and **4LE3** (Scheme 2.49).

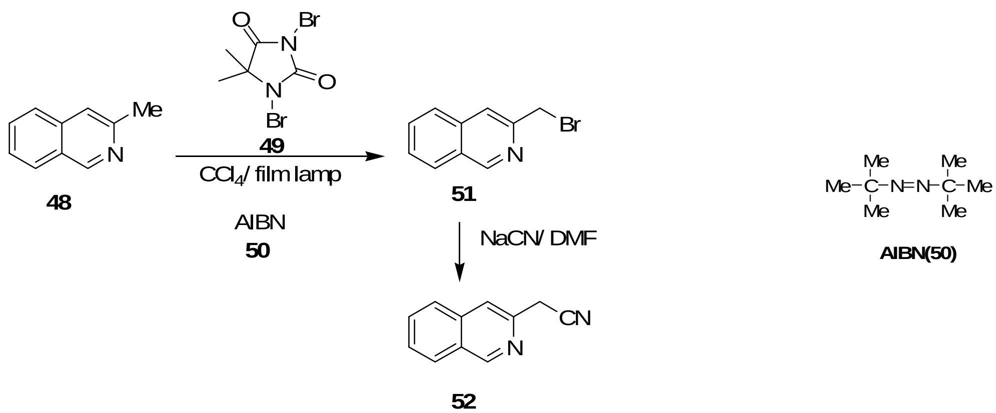
In the case of **IV-3 and IV-4** isolation problems occurred.



2.5.2 Synthesis of 2-(Isoquinolin-3-yl)acetonitrile 52

A substance with interesting spectroscopic properties is 2-(isoquinolin-3-yl)acetonitrile **52.**

Its synthesis follows is given below (Scheme 2.51).



Scheme 2.51 *Synthesis of* **52**

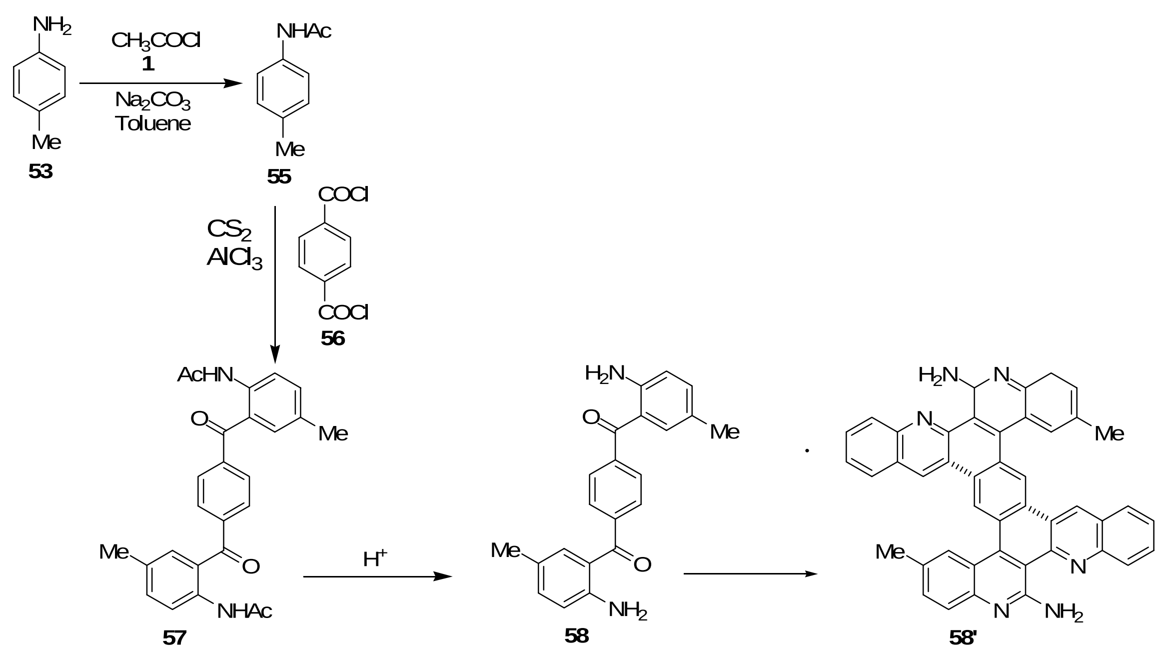
For the synthesis of **51,** 1,3-dibromo-5-5-dimethylimidazoline-2,4-dione **49** and a free radical initiator AIBN **50** have been used.

With a ratio 2:1 of **48** to **49**, one spatula of fresh AIBN, the use of the film lamp and 1h reaction time, **51** has been isolated in very good yields.

NMR analysis shows that both **51** and **52** were clean, but no satisfactory yields were obtained in the second step, the synthesis of **52**.
Thus the project has been abandoned.

2.5.3 Synthesis of 58 as Starting Material for Bichromophor 58'

Taking in consideration that problems were occurring during the synthesis of **2A** due to the occurrence of side reactions of **IX**, the idea of synthesizing a bichromophor according to Scheme 2.52 came up.



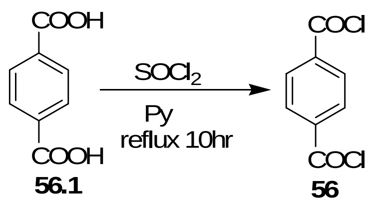
Scheme 2.52** Projected synthesis of the bichromophor **58'

The literature describes the successful reaction between **55** and **56** [56,57], so we have decided to try it.

Synthesis steps:

- Synthesis of **55** (we are familiar with the procedure of the acetylation using acetylchoride **1** sodium carbonate and toluene as solvent. The reaction works with very good yields, up to 80%).

- Synthesis of **56** (literature gives hints of using $SOCl_2$ and pyridine, having as starting material the terephthalic acid **56.1** [54]) (Scheme 2.53).

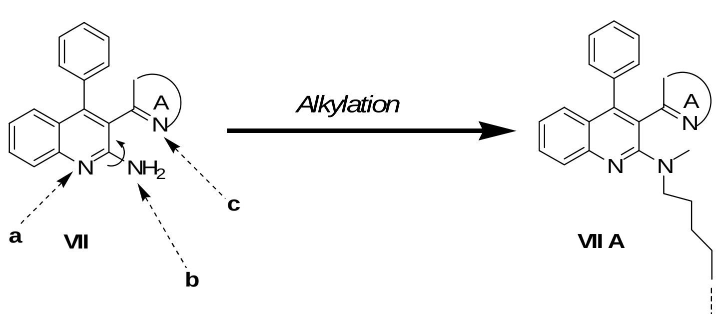


Scheme 2.53 *Synthesis of* ***56***

- Synthesis of **57** (the reaction did not lead to the desired results). We thought that the quality of **56** had an influence, so we have carried out the reaction with freshly bought **56**. We have also used different samples of $AlCl_3$ and of solvents but, purity problems and low yields were the main reasons for giving up the project.

2.5.4 Alkylation

A possibility to restrict the rotation of the amine-group in compounds of the type **VII,** is its alkylation, leading to substances of the type **VII A** (Scheme 2.54).
The alkylation should take place in the **b** position in order to get the desired results.



Scheme 2.54 *Alkylation of* ***VI***

The compound chosen for this type of reaction was **3A** and the reaction partner was 1-brom-hexadecane **59.** (Fig. 2.55)

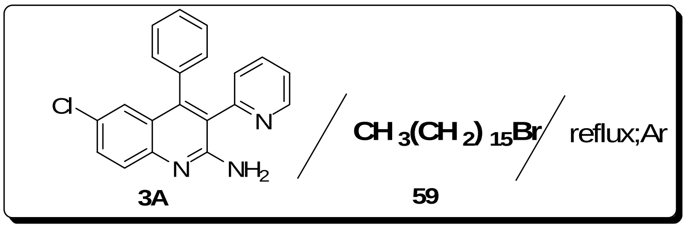


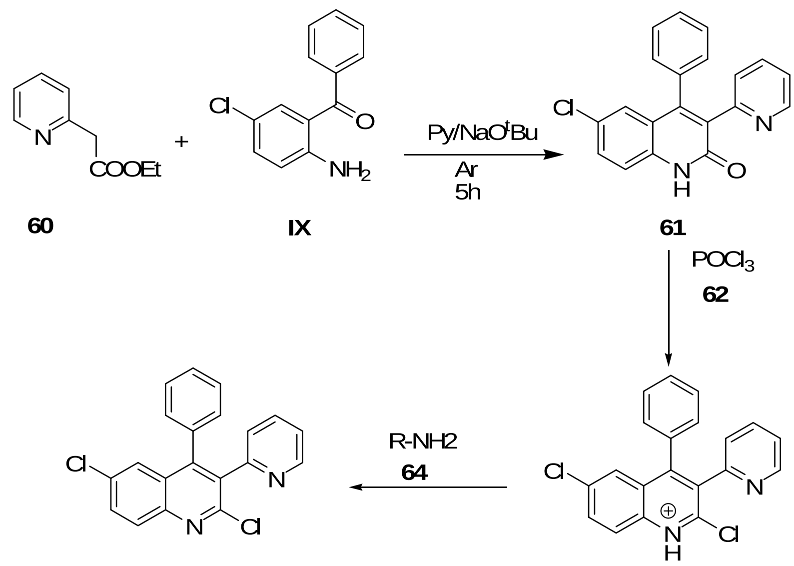
Figure 2.55 Alkylation of 3A

The reaction was carried out by mixing the two educts and heating under reflux and inert gas for 2 h.
Purification by chromatography, gave only small amounts of the desired product.

2.5.5 Synthesis of 3A

As another route for the synthesis of **3A,** we reacted **IX** and ethyl 2-(pyridine-2-yl) acetate **60,** under basic conditions.
For the synthesis of 2, 6-dichloro-4-phenyl-3-(pyridin-2-yl)quinoline **63** from 6-chloro-4-phenyl-3-(pyridin-2-yl)quinolin-2(1*H*)-one **61**, $POCl_3$ **62** has been used and then, in order to isolate the desired product **3A,** a primary amine **64** has been used.

The reaction scheme is presented below (Scheme 2.56).



Scheme 2.56 Another synthesis way for 3A

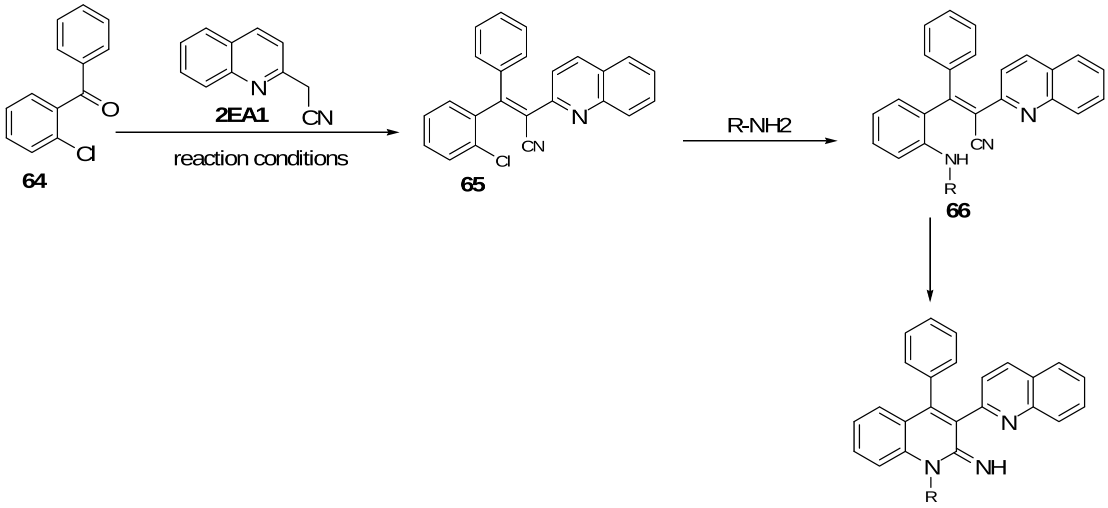
But, isolation problems in the case of **61** occurred, and thus the project has been abandoned.

2.5.6 4-Phenyl-3-(quinolin-2-yl)quinolin-2-amine (67)

In order to improve the yields, to avoid the occurrence of side products and side reactions observed in the case of **2A,** a new method has been tested :The use of 2-chlorobenzophenone **64** instead of 2-amino-5-chlorobenzophenone **IX** [53,56].

After the reaction of **65** with the primary amine, the compound **66** (after ring closure reaction) should lead to the formation of the desired N-alkylated product **67.**

The reaction scheme is given below (Scheme 2.57).



64

65

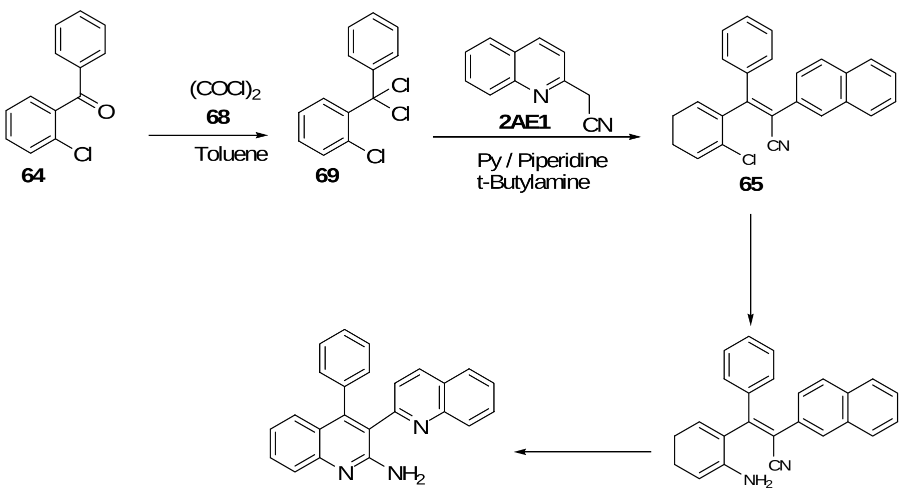
66

67

*Scheme 2.57 Projected synthesis of **67***

All synthetic strategies (methods A-G) used, are subsequently summarized:

Method A



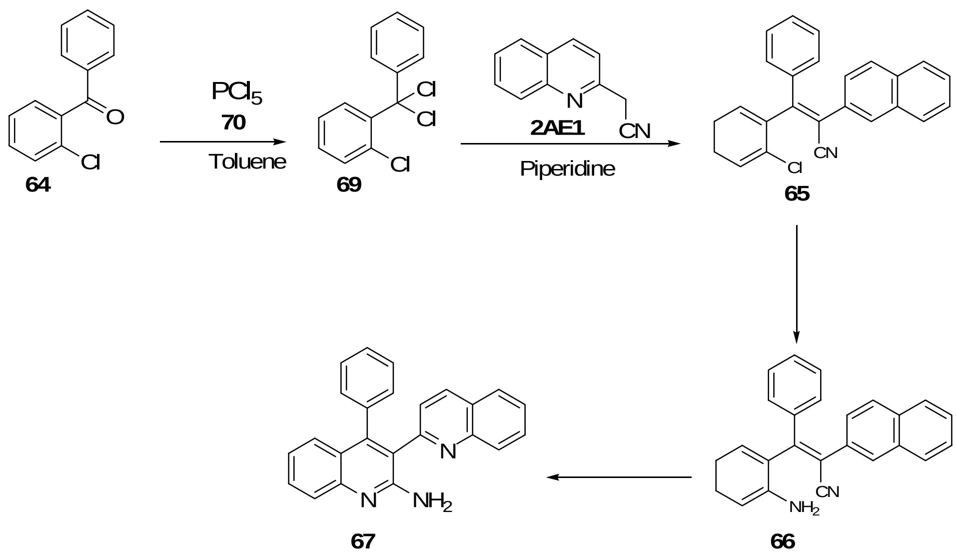
64 69 65

67 66

In the case of *Method A*, for the reaction between **69** and **2AE1** we used a mixture of pyridine/piperidine and instead of the strong sodium-*tert*-butoxide, we used *tert*-butylamine.
Taking in consideration that after the reaction between **64** and **68** in toluene we had problems in isolating both **69** and **65,** we tried another method (see *Method B*).

Method B

In this case, in the first step, we used instead of **68,** phosphorus pentachloride **70** and for the reaction with **2AE1,** we used only piperidine.



Again crystallization problems occurred in the case of **69**, so we decided to use another method (see *Method C*).

Method C

Using a hint found in literature [54], we slowly added **64** to **68** and heated under reflux.
This time no crystallization problems for **69** occurred anymore.

After this, we mixed **69**, **2AE1** and the primary amine **71,** and heated under reflux (Scheme 1.58). But, **72** could not be isolated.

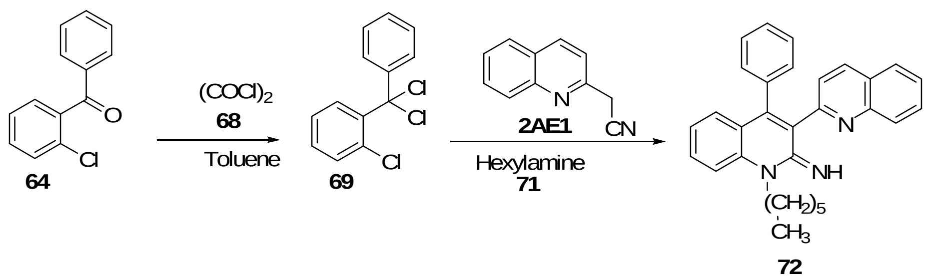
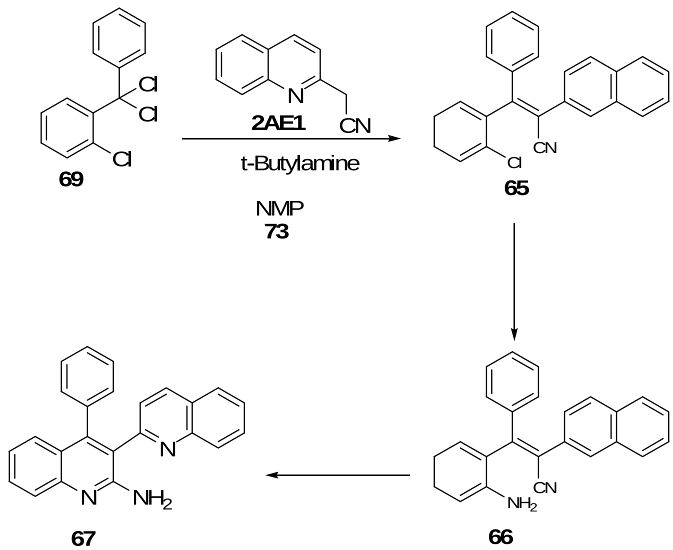


***Figure** 2.58 Projected synthesis of* **72**

Method D

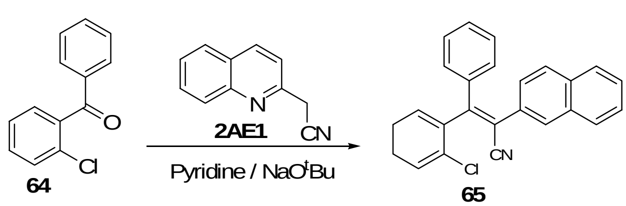
In this method we mixed **2AE1**, *tert*-Butylamine in **73** and then slowly dropping **69.** NMP as a solvent has the advantage of higher applicable reaction temperatures (up to 140 ^{0}C).
The reaction scheme is given below (Scheme 2.59).



Scheme 2.59 *Method D*

Method E

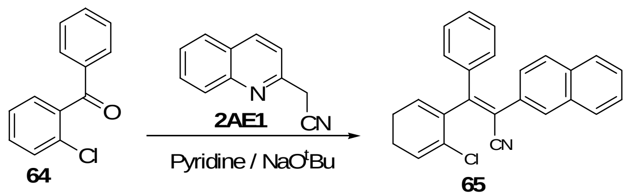
Here we tried the direct reaction between **64** and **2AE1** under the well known basic conditions (sodium *tert*-butoxide) and refluxing in pyridine.
MS analysis gives a mixture of the wanted substance **65** and another substance. Isolation/purification was not successful.



Method E

Method F

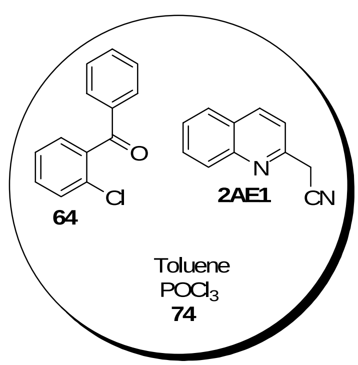
Here, we simply heated to 150^0, a mixture of **64** and **2AE1** in hexylamine **71.** Isolation problems of the desired product **65** occurred.



Method F

Method G

Here we tried the reaction between **64** and **2AE1** using $POCl_3$ and toluene, as solvent.



Method G

The reaction took place, but isolation problems occurred.

3 Spectroscopic Part

In this chapter, the spectra of all synthesized substances are given. Measurements of the absorption and fluorescence spectra were made in different solvents. $CHCl_3$, EtOH, DMF, NMP, and MeCN were used.

Protonation has been achieved with TFA or H_2SO_4.
For deprotonation, solutions of aqueous NaOH, pure NEt_3 or NaO^tBu in EtOH were used.

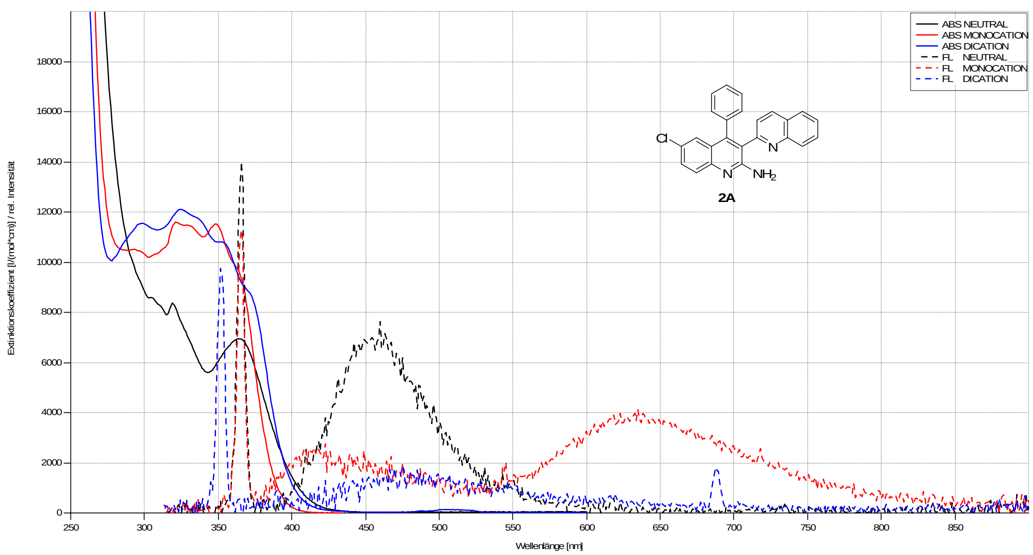
The fluorescence quantum yields $\boldsymbol{\Phi_f}$, and the oscillator strengths $\boldsymbol{f}$ **(s_o-s_1)** are given in tables. $\boldsymbol{\Phi_f}$ values are determined for solutions with $E_{S_0\text{-}S_1} \leq 0,65$ corresponding to $c \leq 9,86 \cdot 10^{-5}$ M.
The spectra abscissa are given both in wavelengths and wavenumbers. In the case of the wavenumbers representation, the fluorescence spectra are $1/ I_f \cdot \lambda^2$.

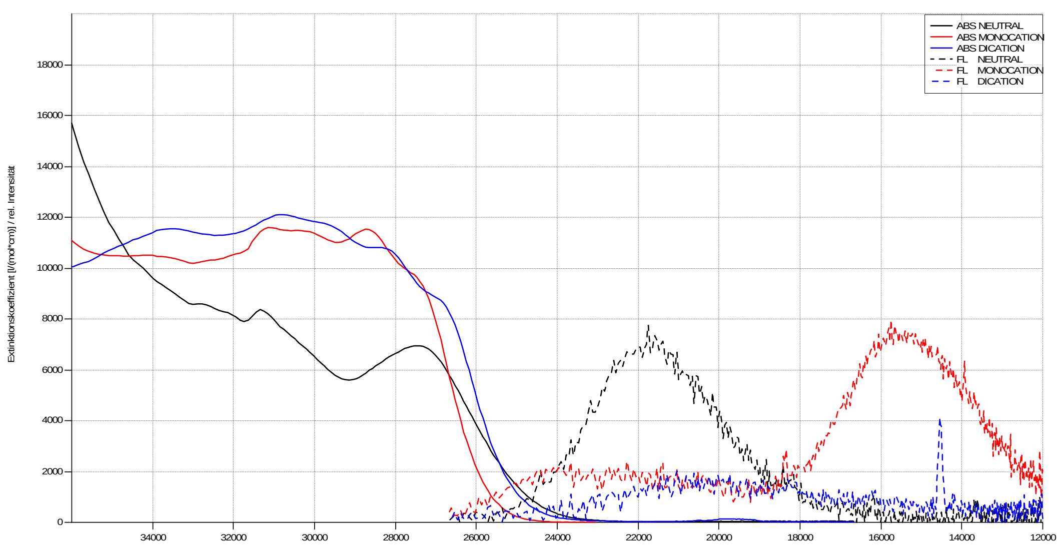
3.1 Systems with Dual Fluorescence

In the case of the systems with dual fluorescence following observations are important:

- The monocations of the systems **2A, 3A, 3C, 3D, 4C** and **4D** show dual fluorescence.
- The fluorescence quantum yields of the systems have values between 1% and 40%.
- The cationic form of the system **4C** possesses the highest value for the fluorescence quantum yield (44 %)
- The cationic form of the system **4C** possesses also the highest value for the oscillator strength ($f_{s_o\text{-}s_1} = 0,43$)

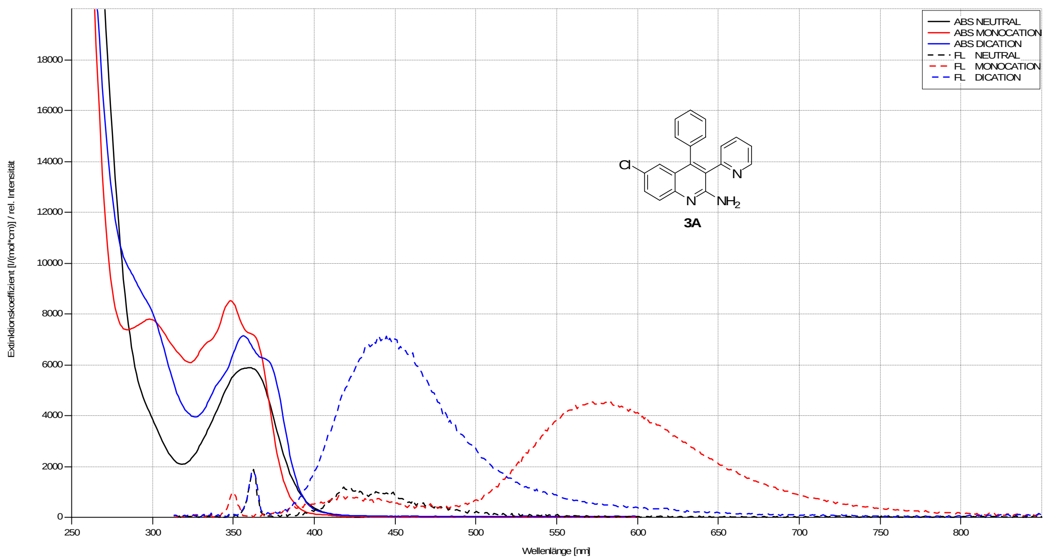
3.1.1 6-Chloro-4-phenyl-3-(quinolin-2-yl)quinolin-2-amine (2A)

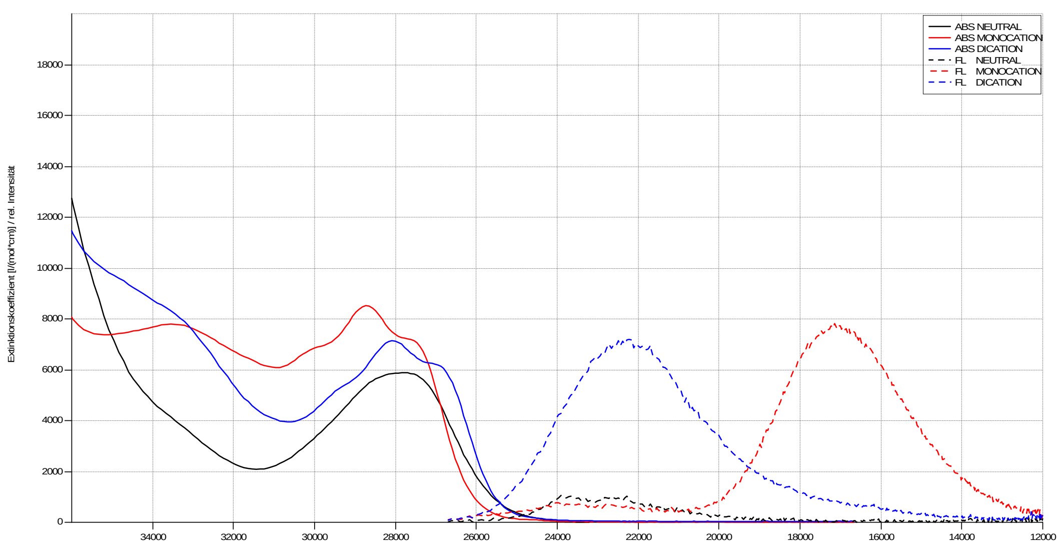




	Neutral	*Monocation*	*Dication*
Φ_f	1,49 % E_{364} = 0,18 (c = $2{,}62 \cdot 10^{-5}$ M)	1,58 % 0,41 (“blue”) 1,17 (“red”)	0,56 %
f	0,09 (EtOH) 22000-29200cm^{-1}	0,13 (EtOH) 22000-29440 cm^{-1}	0,12 (EtOH) 22000-28700 cm^{-1}

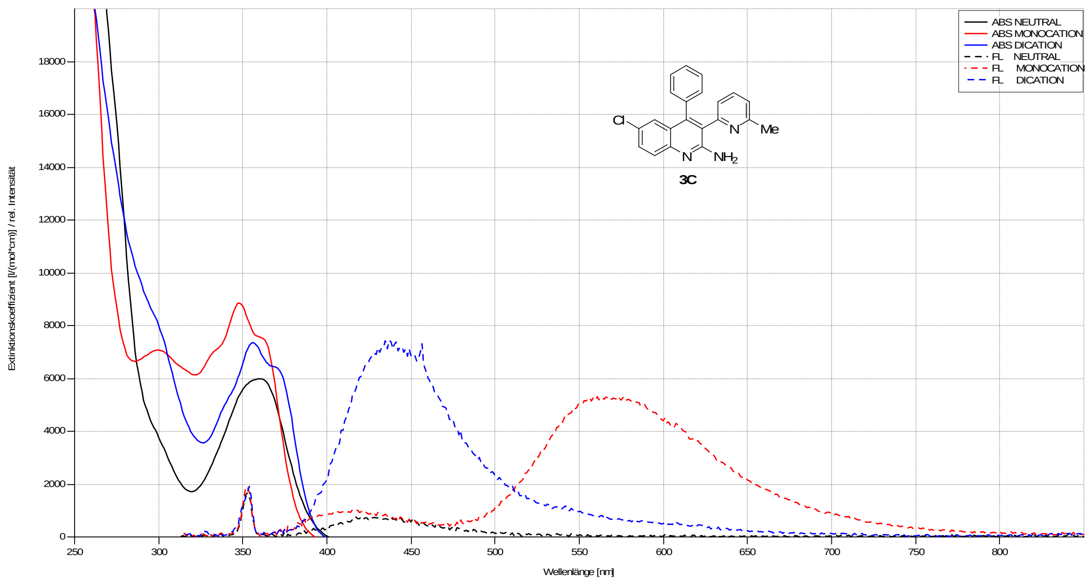
3.1.2 6-Chloro-4-phenyl-3-(pyridine-2-yl)-quinolin-2-amine (3A)

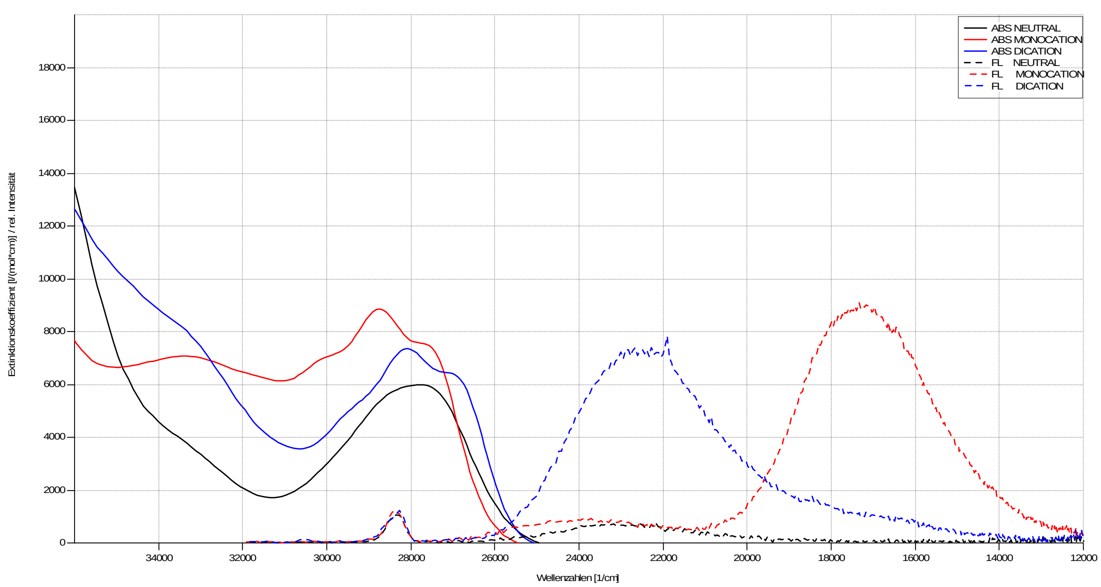




	Neutral	*Monocation*	*Dication*
$\boldsymbol{\Phi_f}$	0,78 % E_{359}= 0,28 (c = 4,88·10^{-5} M)	6,25 % 0,45 (“blue”) 4,09 (“red”)	5,75 %
$\boldsymbol{f}$	0,10 (EtOH) 22000-31500cm^{-1}	0,13 (EtOH) 22000-31000 cm^{-1}	0,12 (EtOH) 22000-30800 cm^{-1}

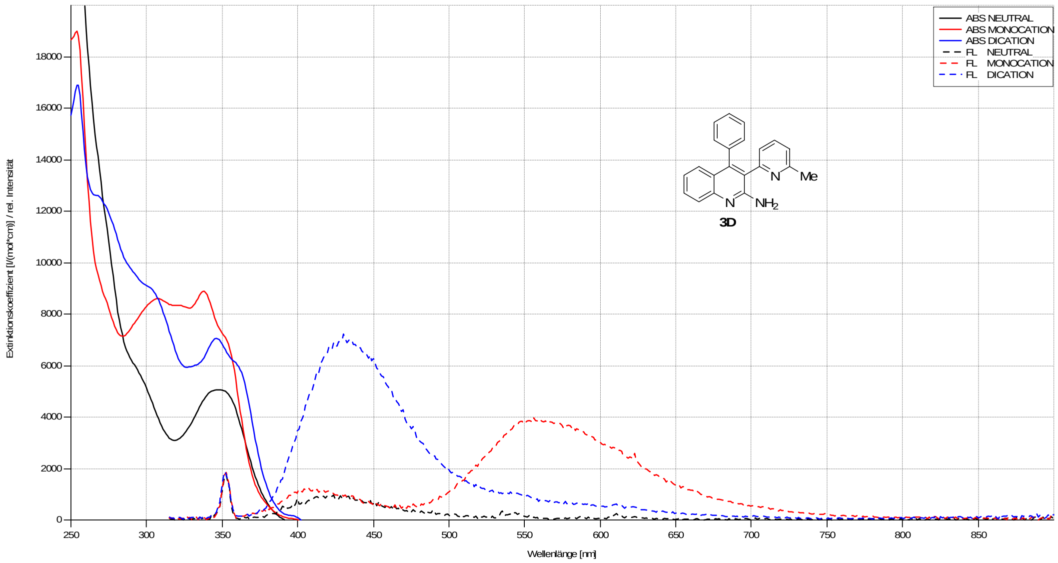
3.1.3 6-Chloro-3-(6-methylpyridin-2-yl)-4-phenylquinolin-2-amine (3C)

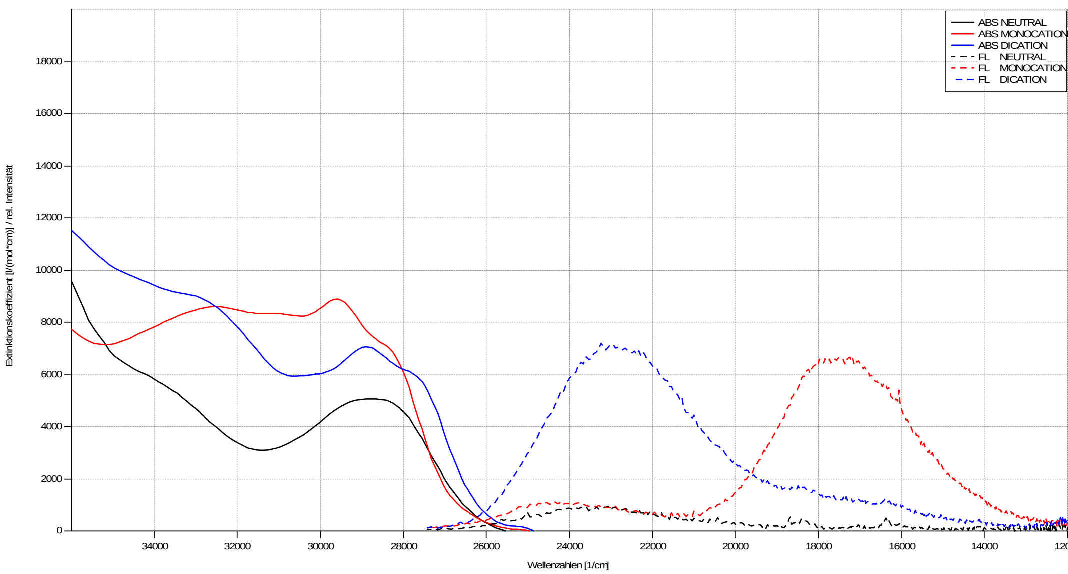




	Neutral	*Monocation*	*Dication*
$\boldsymbol{\Phi_f}$	0,74 % $E_{360} = 0{,}28$ ($c = 4{,}72 \cdot 10^{-5}$ M)	6,40 % 0,57 (“blue”) 5,83 (“red”)	7,31 %
$\boldsymbol{f}$	0,09 (EtOH) 22000-31400cm^{-1}	0,14 (EtOH) 22000-31150 cm^{-1}	0,11 (EtOH) 22000-30660 cm^{-1}

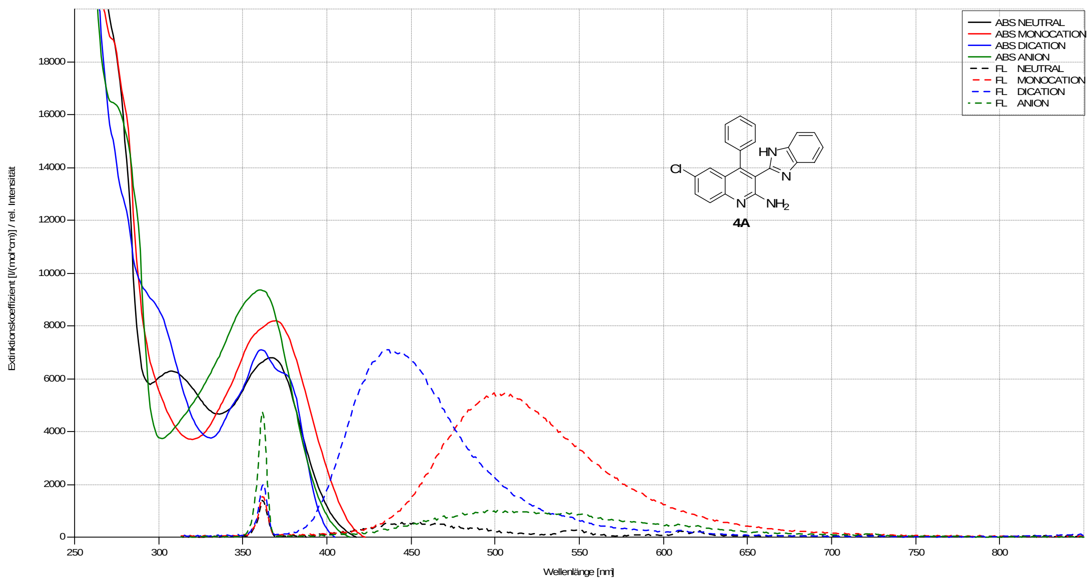
3.1.4 3-(6-Chloropyridin-2-yl)-4-phenylquinolin-2-amine (3D)

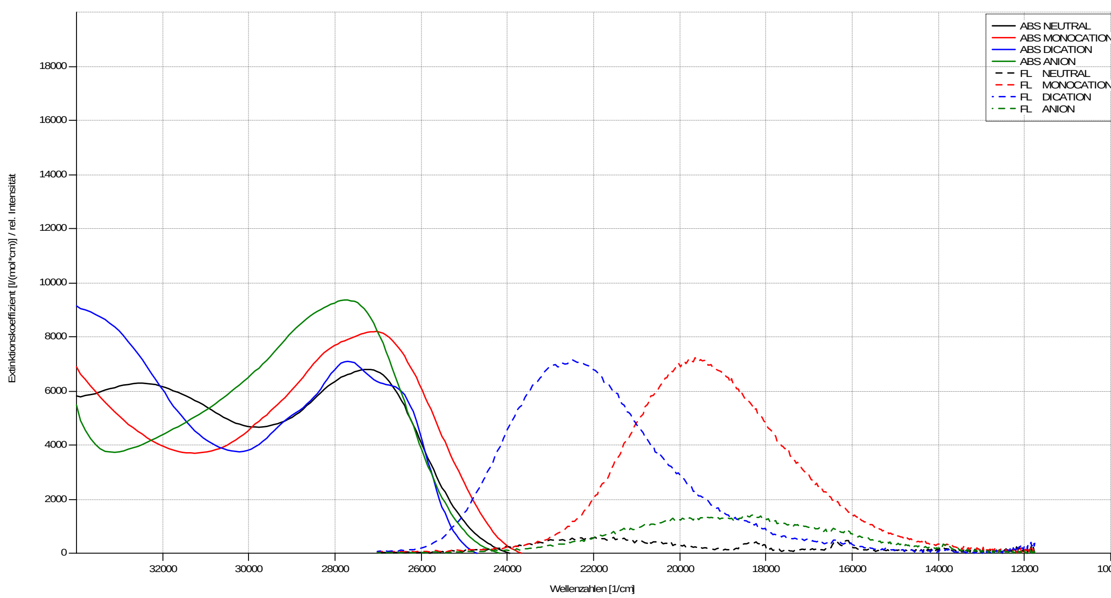




	Neutral	*Monocation*	*Dication*
Φ_f	1,22 % E_{347} = 0,24 (c = $4{,}90 \cdot 10^{-5}$ M)	6,24 % 0,84 (“blue”) 5,40 (“red”)	7,57 %
f	0,08 (EtOH) 22000-31500cm^{-1}	0,10 (EtOH) 22000-30620 cm^{-1}	0,09(EtOH) 22000-30250 cm^{-1}

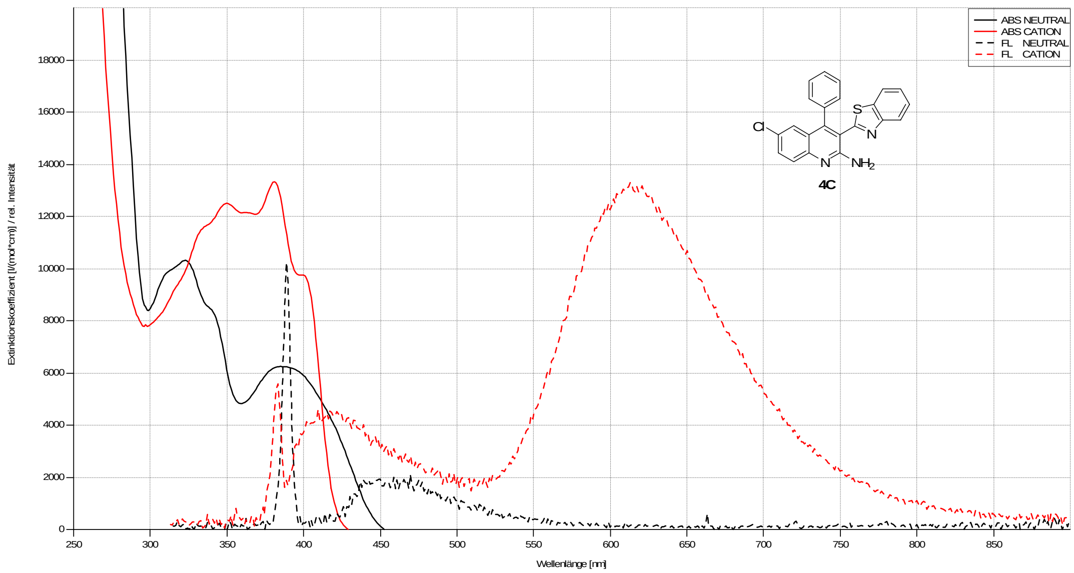
3.1.5 3-(1H-Benzo[d]imidazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4A)

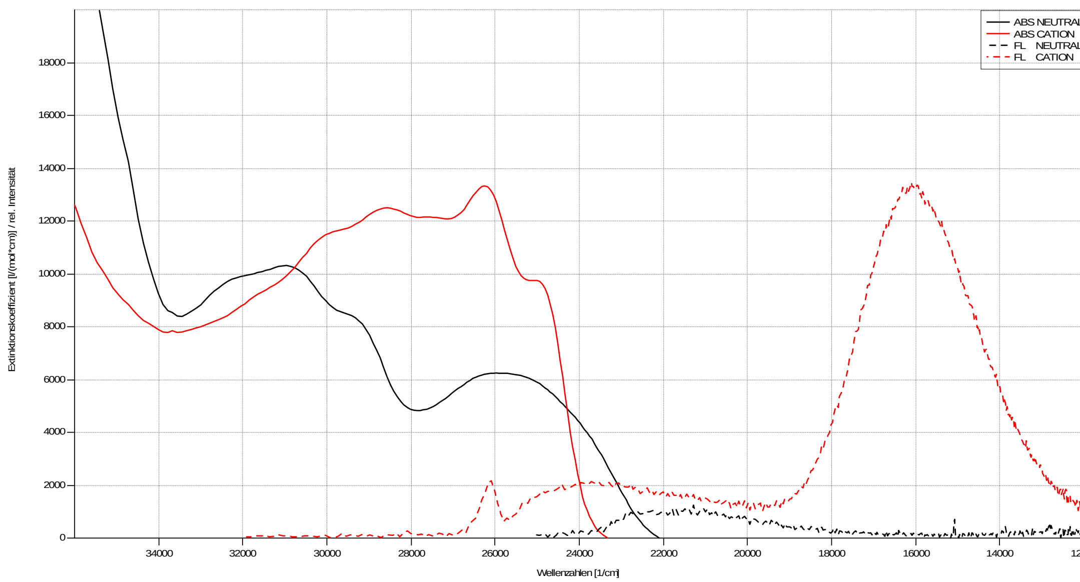




	Neutral	*Monocation*	*Dication*	*Anion*
$\boldsymbol{\Phi_f}$	1,28 % $E_{368} = 0,25$ ($c = 3,77 \cdot 10^{-5}$ M)	11,28 %	12,16 %	2,46 %
$\boldsymbol{f}$	0,10 (EtOH) 22000-30000cm^{-1}	0,16 (EtOH) 22000-31400 cm^{-1}	0,109 (EtOH) 22000-30260 cm^{-1}	0,21 (EtOH) 22000-33250 cm^{-1}

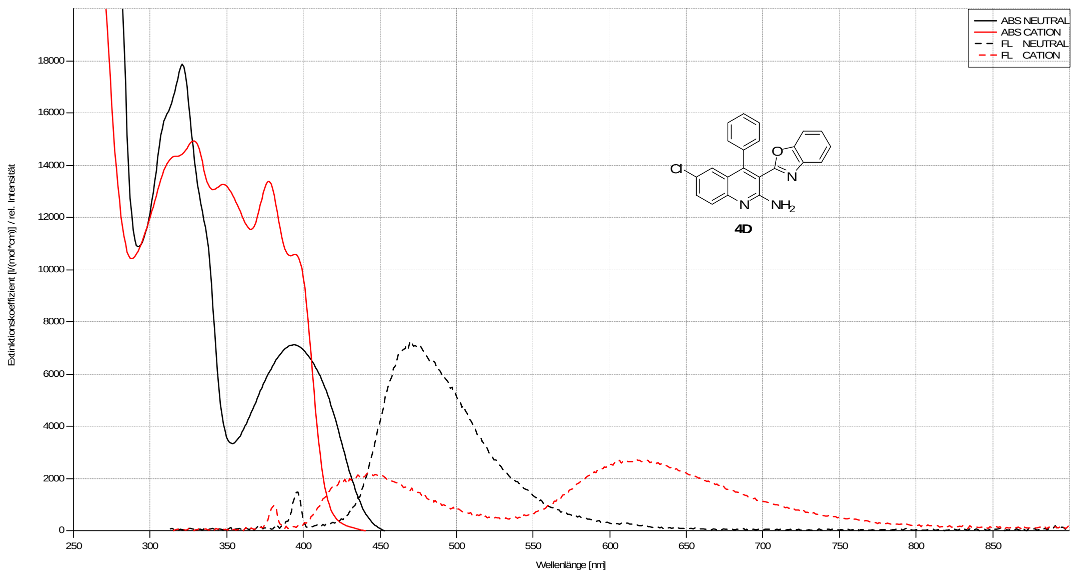
3.1.6 3-(Benzo[d]thiazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4C)

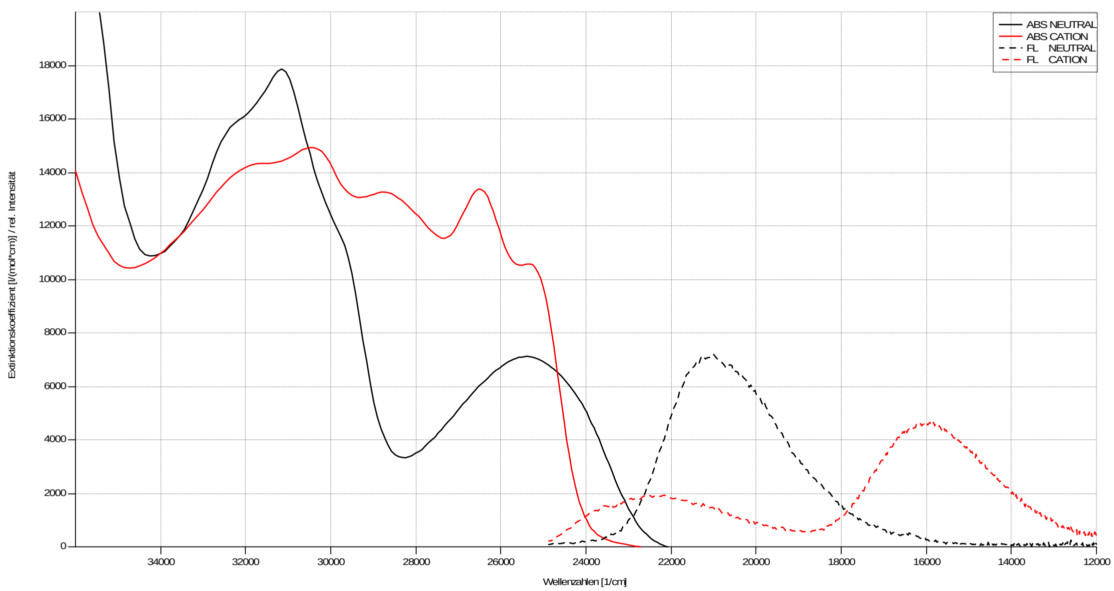




	Neutral	*Cation*
$\boldsymbol{\Phi_f}$	0,64 % E_{384} = 0,21 (c = $3{,}38 \cdot 10^{-5}$ M)	4,30 % 0,69 ("blue") 3,61 ("red")
$\boldsymbol{f}$	0,10 (EtOH) 20000-28000cm^{-1}	0,16 (EtOH) 20000-27600cm^{-1}

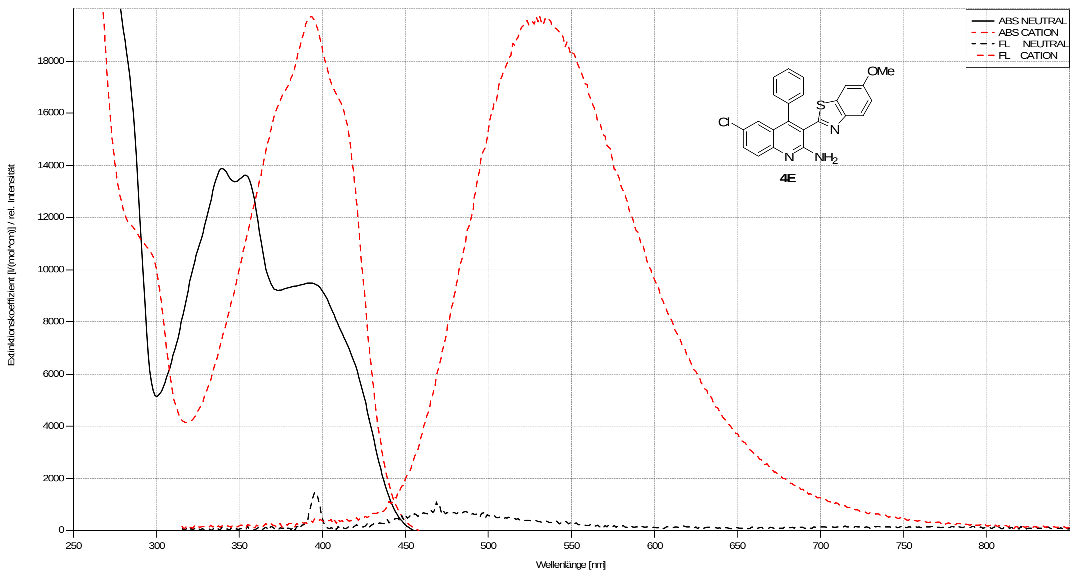
3.1.7 3-(Benzo[d]oxazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4D)

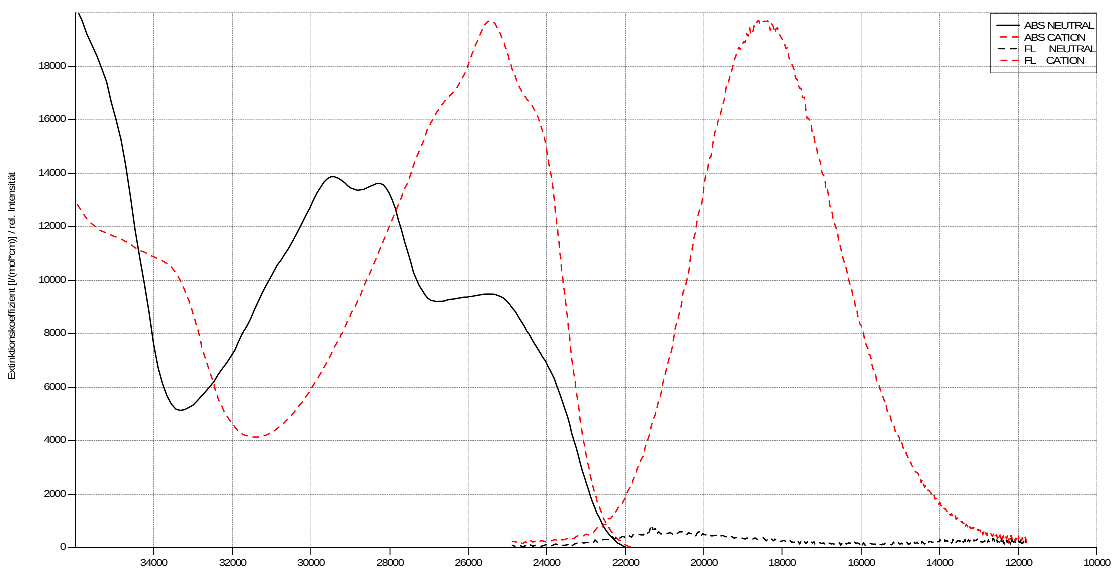




	Neutral	*Cation*
***Φ**f*	3,62 % $E_{394} = 0,35$ ($c = 4,94 \cdot 10^{-5}$ M)	2,59 % 0,83 ("blue") 1,76 ("red")
f	0,12 (EtOH) 20000-28400cm^{-1}	0,17 (EtOH) 20000-27970cm^{-1}

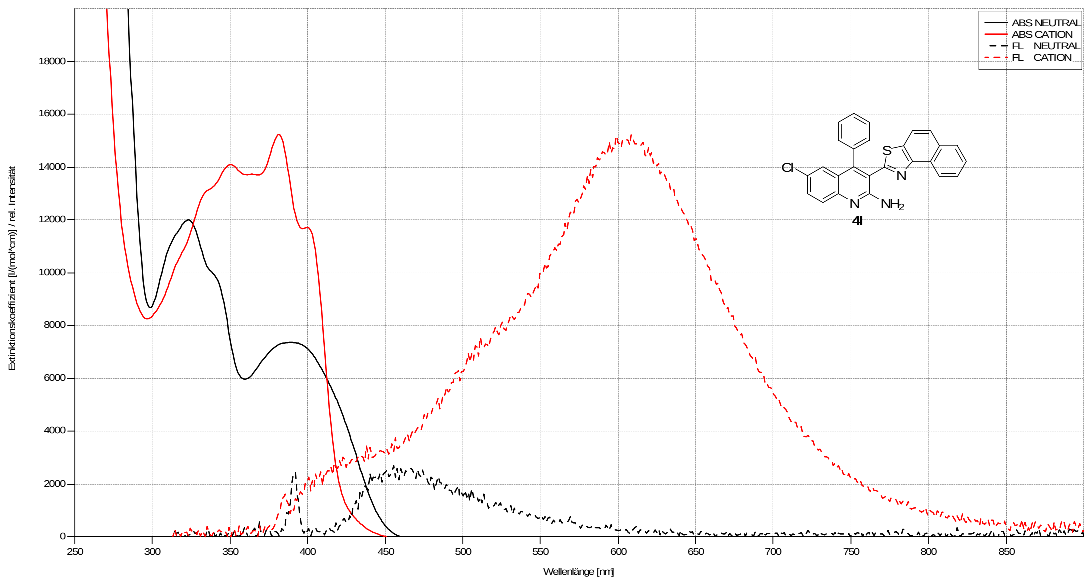
3.1.8 6-Chloro- 3-(6-methoxybenzo[d]thiazol-2-yl)-4-phenylquinolin-2-amine (4E)

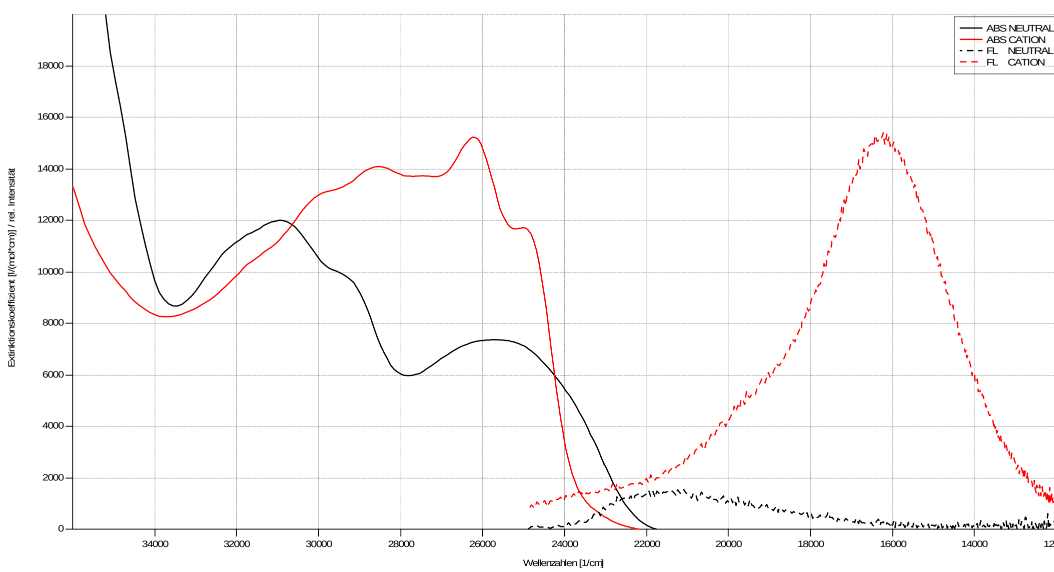




	Neutral	*Cation*
$\boldsymbol{\Phi_f}$	0,25 % E_{393} = 958 (c = 6,13·10^{-5} M)	**43,70 %**
$\boldsymbol{f}$	0,13 (EtOH) 20000-26880cm^{-1}	0,43 (EtOH) 20000-31450cm^{-1}

3.1.9 6-Chloro- 3-(naphto[1,2-d]thiazol-2-yl)-4-phenylquinolin-2-amine (4l)





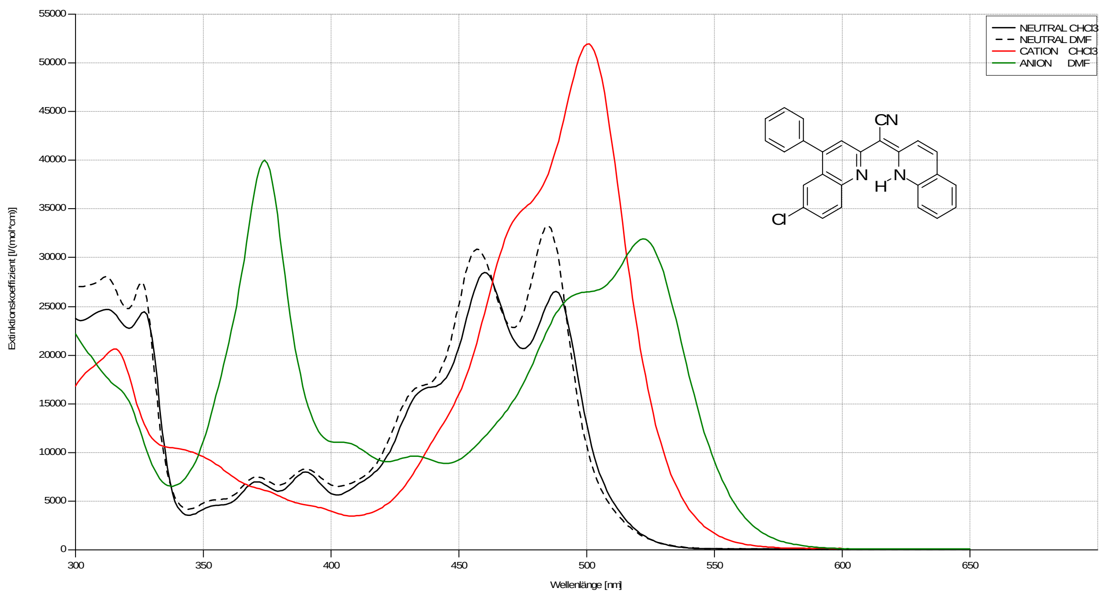
	Neutral	*Cation*
$\boldsymbol{\Phi_f}$	0,76 % E_{389} = 0,43 (c = $5{,}89 \cdot 10^{-5}$ M)	5,02 %
$\boldsymbol{f}$	0,13 (EtOH) 20000-27970cm^{-1}	0,20 (EtOH) 20000-27760cm^{-1}

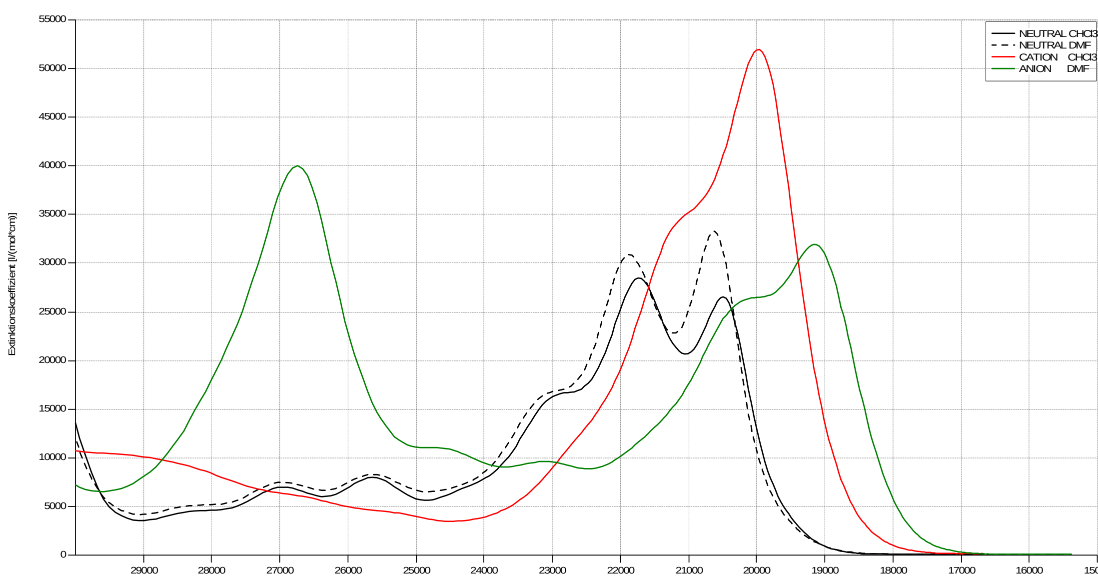
3.2 H-Chelates

3.2.1 Protonation/Deprotonation

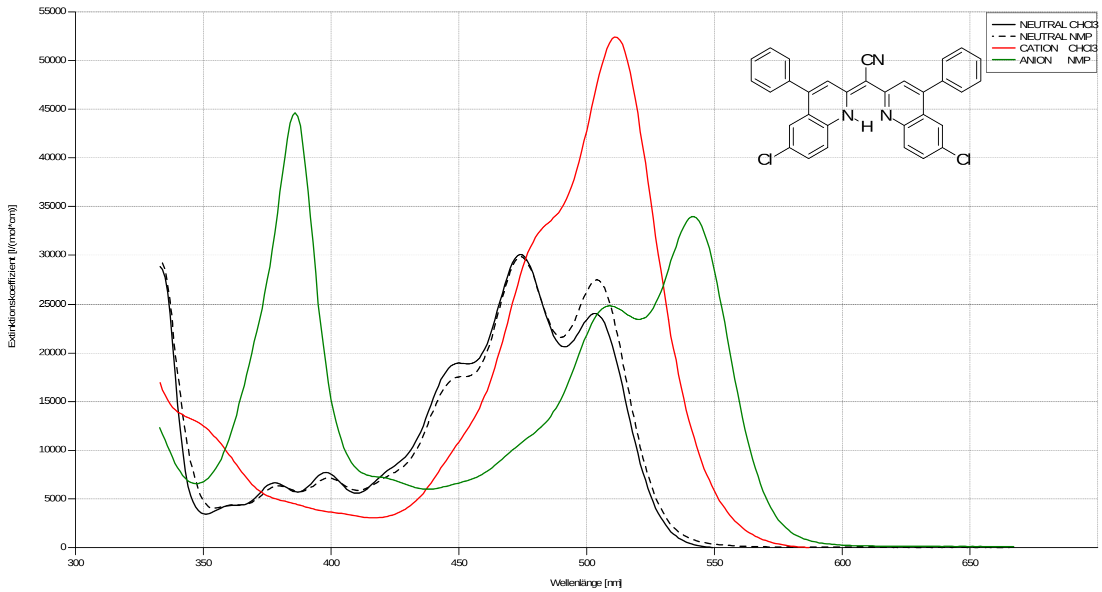
The structures given on the spectra, in all cases, correspond to the neutral forms.

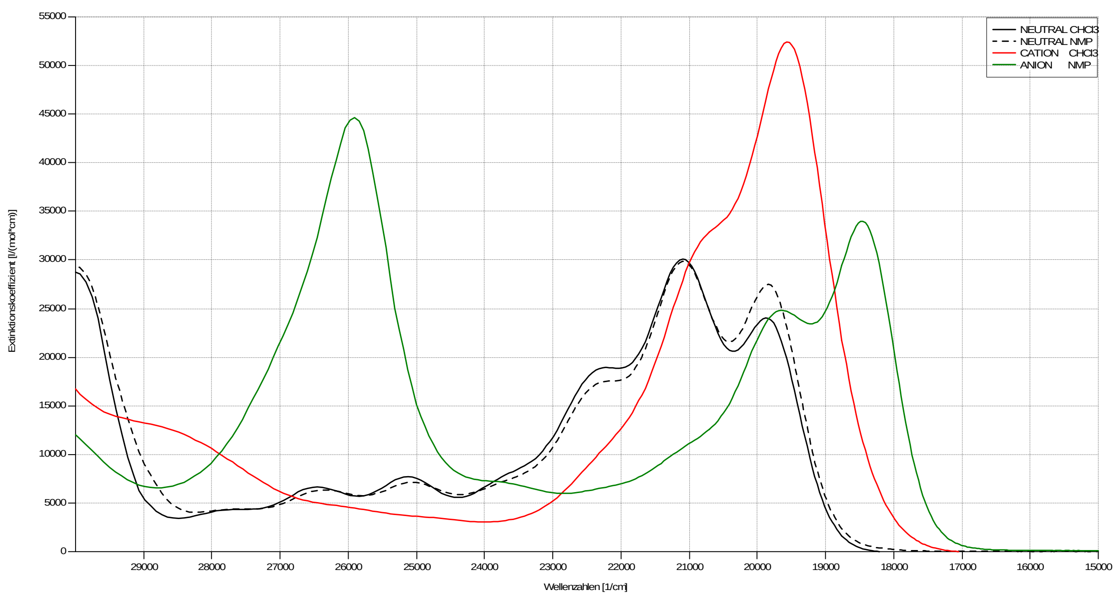
(2*E*)-2-(6-Chloro-4-phenylquinolin-2-yl)-2-(quinolin-2(1*H*)-ylidene)acetonitrile (2569)



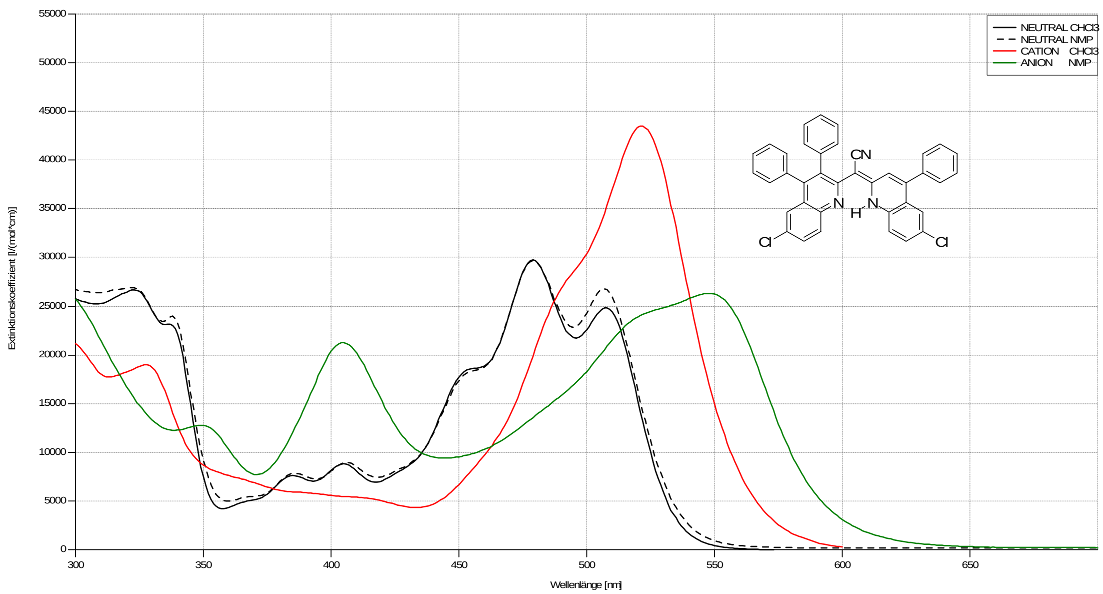


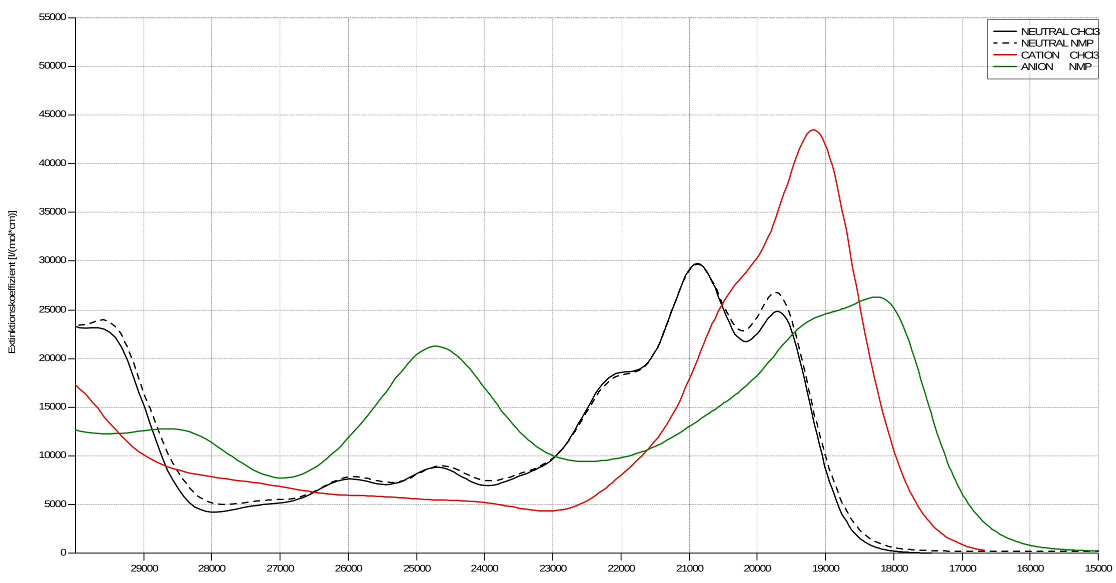
(2*E*)-2-(6-Chloro-4-phenylquinolin-2(1*H*)-ylidene)-2-(6-chloro-4-phenylquinolin-2-yl)acetonitrile (2647)



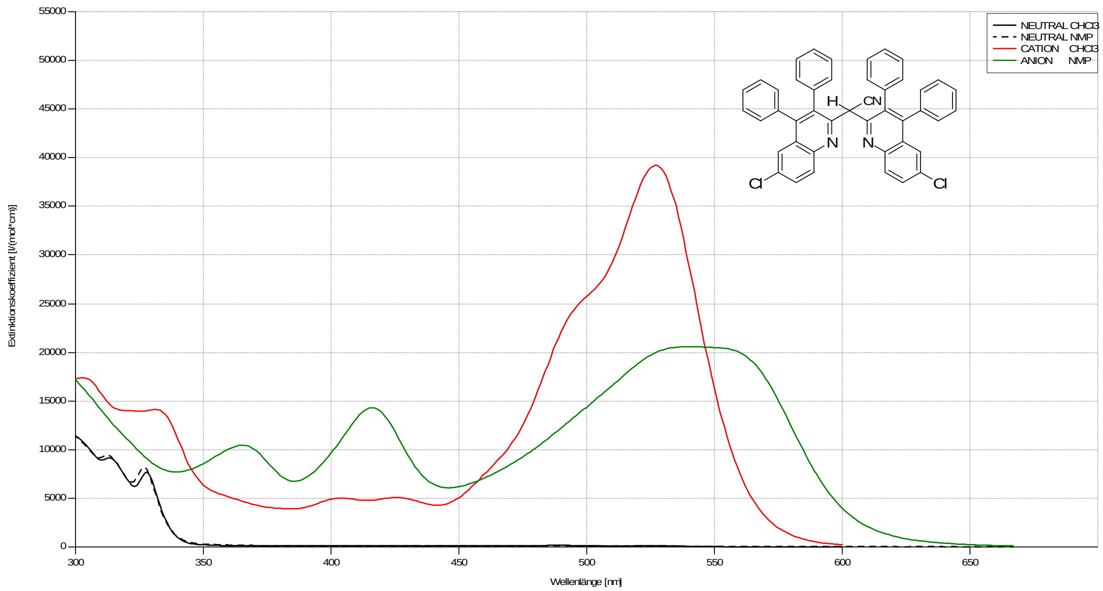


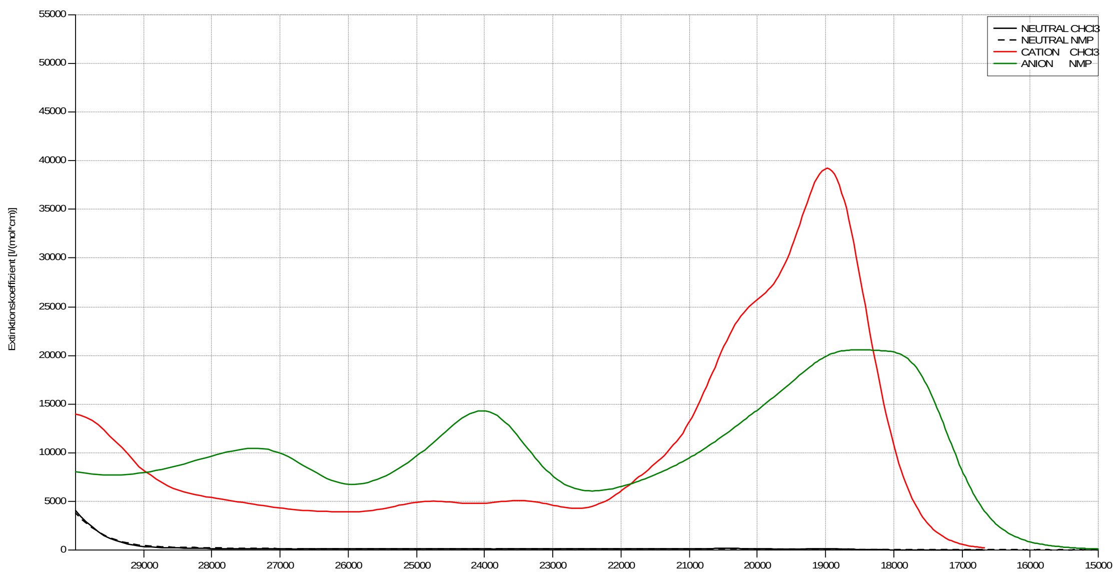
(2*E*)-2-(6-Chloro-3, 4-diphenylquinolin-2-yl)-2-(6-chloro-4-phenylquinolin – -2(1*H*)-ylidene)acetonitrile (2652)





2, 2-Bis (6-chloro-3, 4-diphenylquinolin-2-yl)acetonitrile (2651)



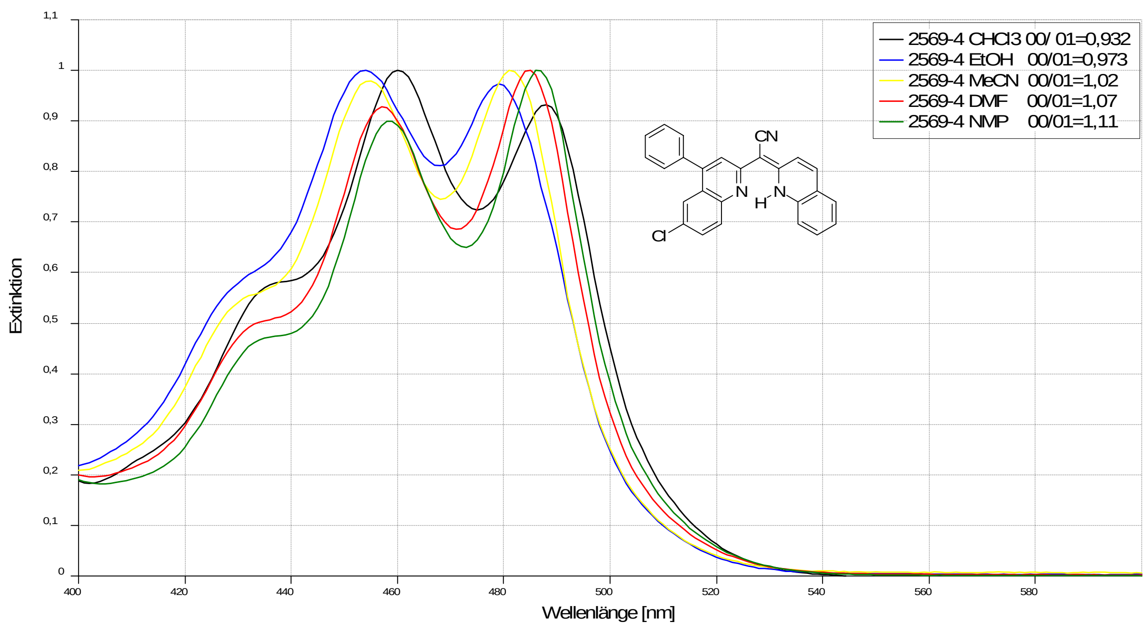


3.2.2 The solvent effect

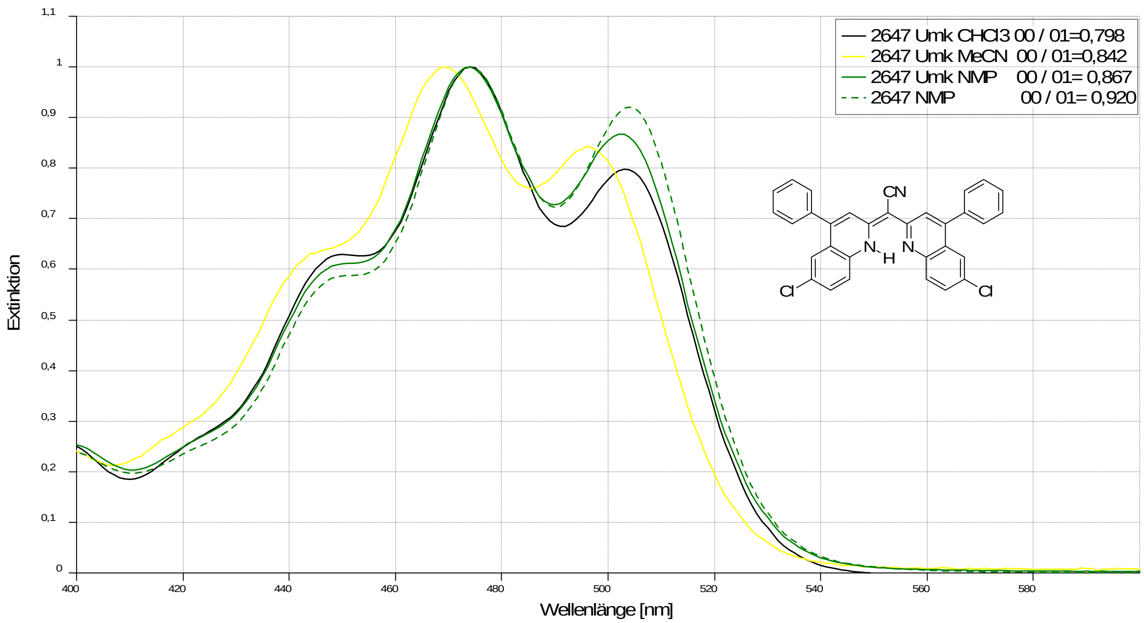
Due to the low solubility of the H-chelates, no measurements were made in EtOH. Thus, protonation was done in $CHCl_3$ with pure TFA; for deprotonation 10%-NaOH in NMP (as solvent) was used.

The dependences of Franck- Condon factors on the solvent were calculated for the neutral forms. The spectra are presented below.

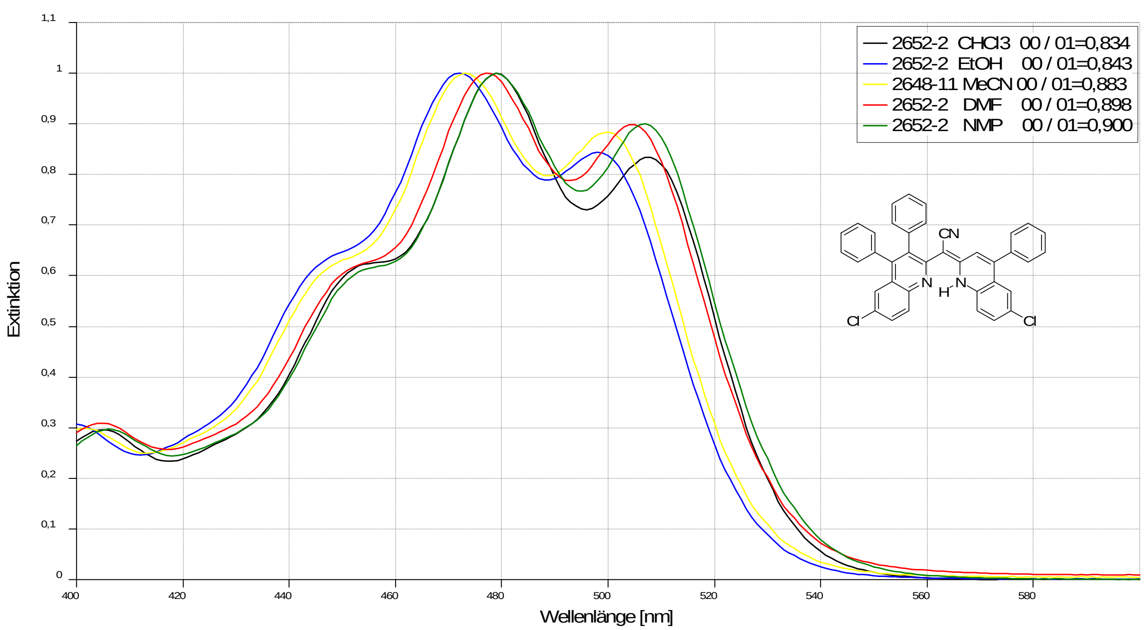
(2*E*)-2-(6-Chloro-4-phenylquinolin-2-yl)-2-(quinolin-2(1*H*)-ylidene)acetonitrile (2569)



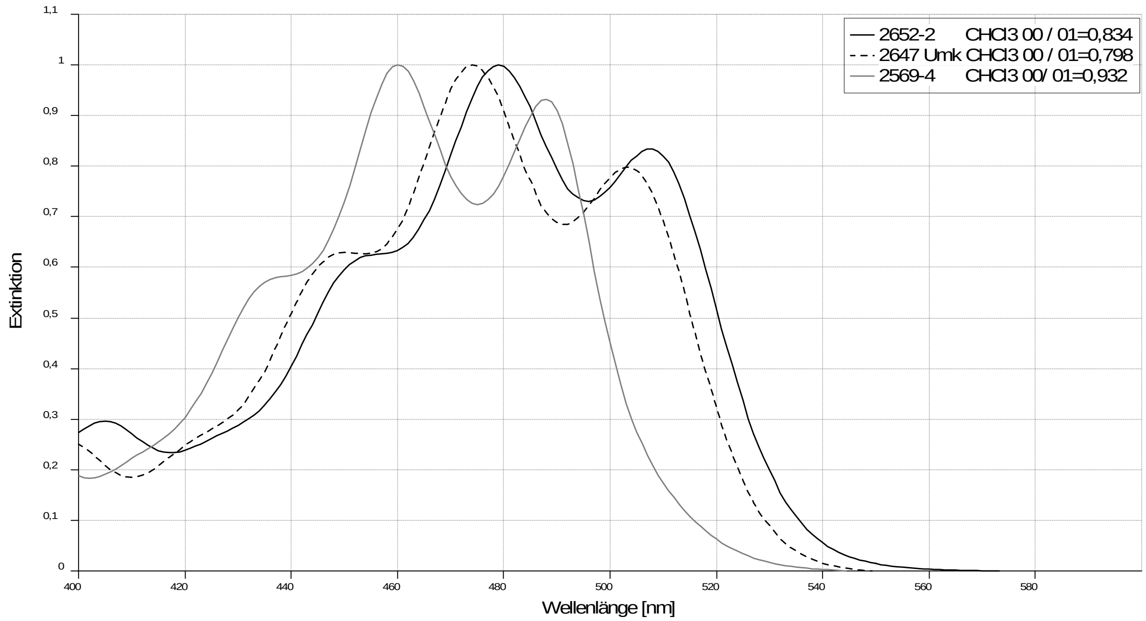
(2*E*)-2-(6-Chloro-4-phenylquinolin-2(1*H*)-ylidene)-2-(6-chloro-4-phenylquinolin-2-yl)acetonitrile (2647)



(2*E*)-2-(6-Chloro-3, 4-diphenylquinolin-2-yl)-2-(6-chloro-4-phenylquinolin -2(1*H*)-ylidene)acetonitrile (2652)



- *Comparison of **2569, 2647,** and **2652** in CHCl3*

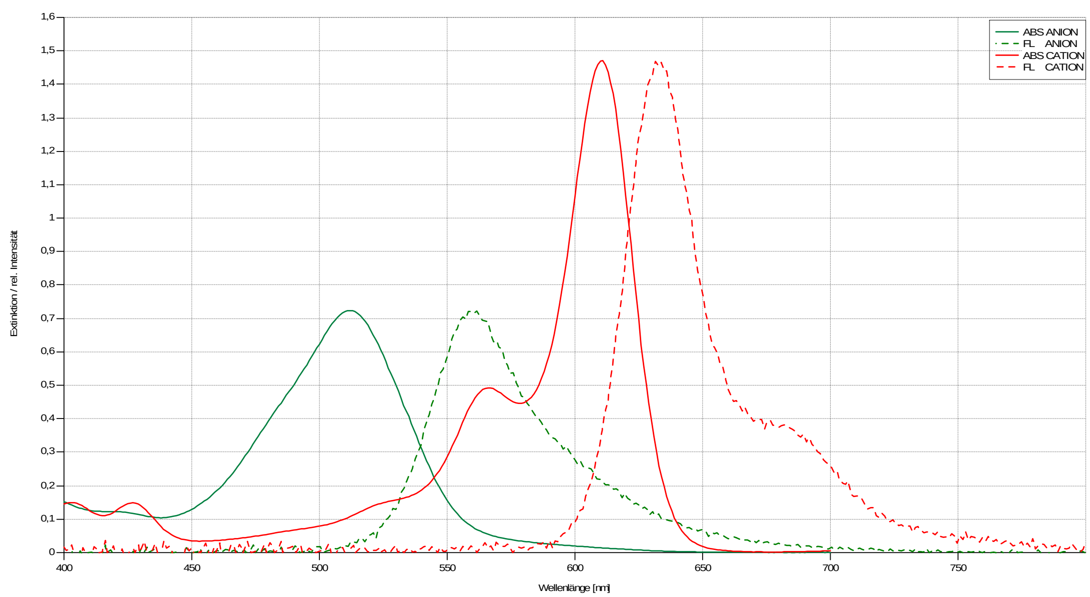


3.3 Polymethines

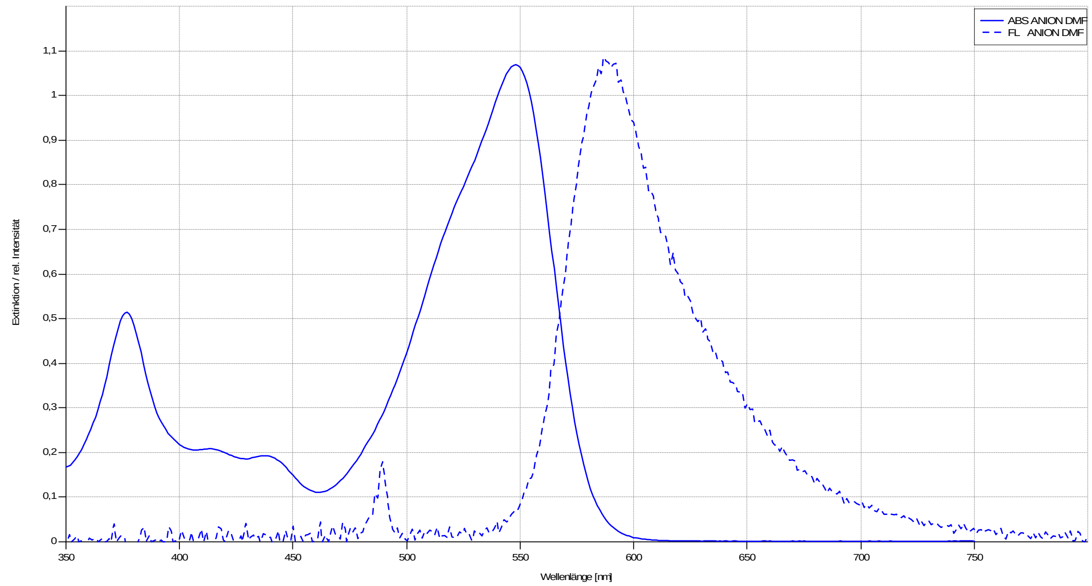
Only for **2654** isolation/purification was successful. Measurements in $CHCl_3$, DMF and MeCN have been made.
In $CHCl_3$, protonation was done by adding pure TFA and deprotonation with pure NEt_3.
In DMF only the anionic form was obtained. In MeCN the cation was obtained by adding a solution of 1% H_2SO_4 in MeCN and the anion using 1% aqueous NaOH.

The spectra are shown below:

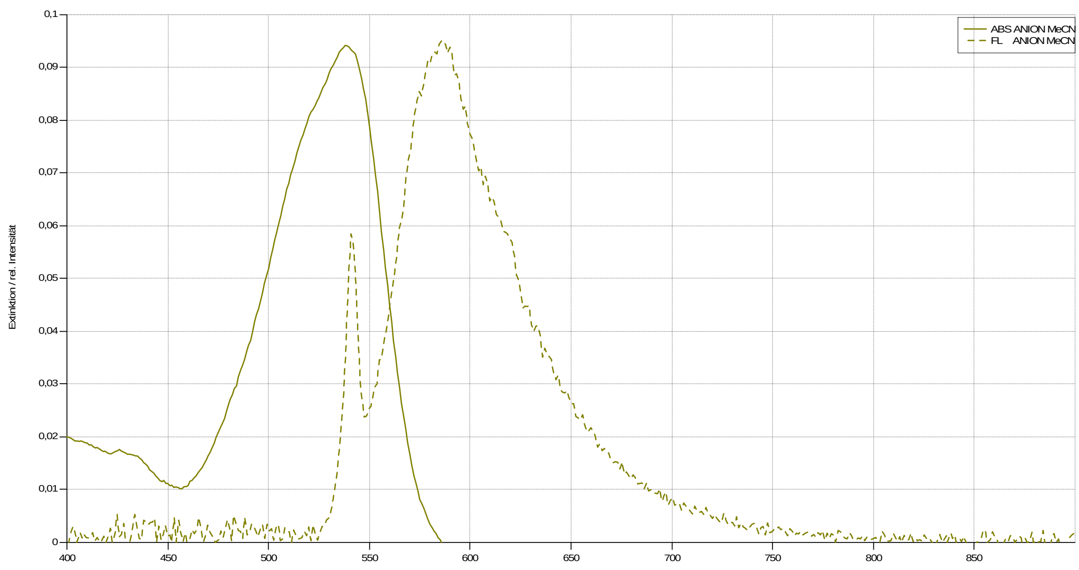
(a) Spectrum in $CHCl_3$



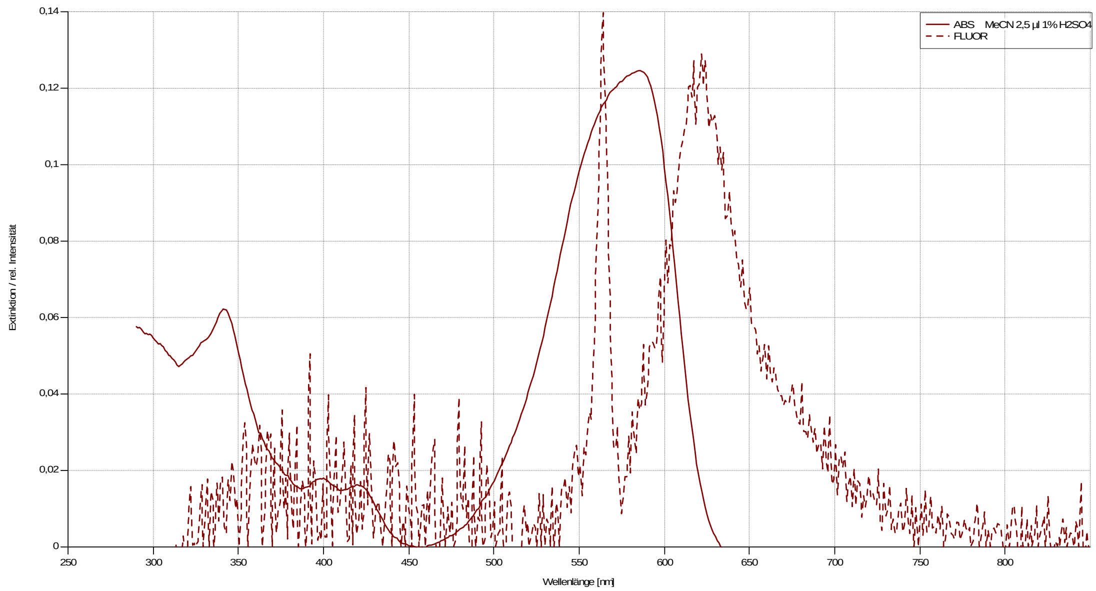
(b) Spectrum in DMF



(c) Spectrum in MeCN (anion)



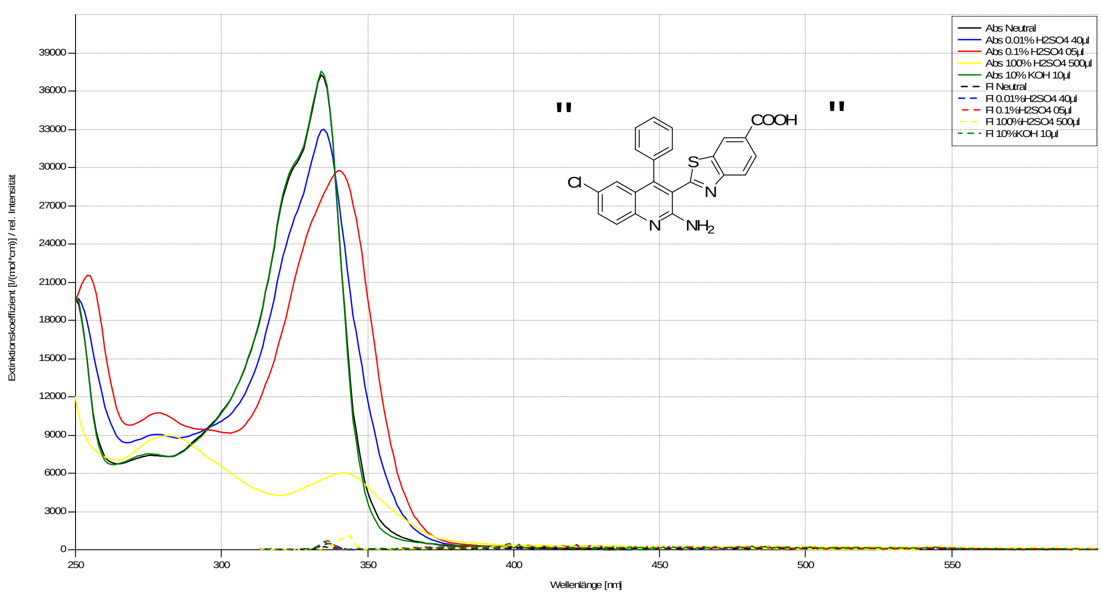
(d) Spectrum in MeCN (cation)



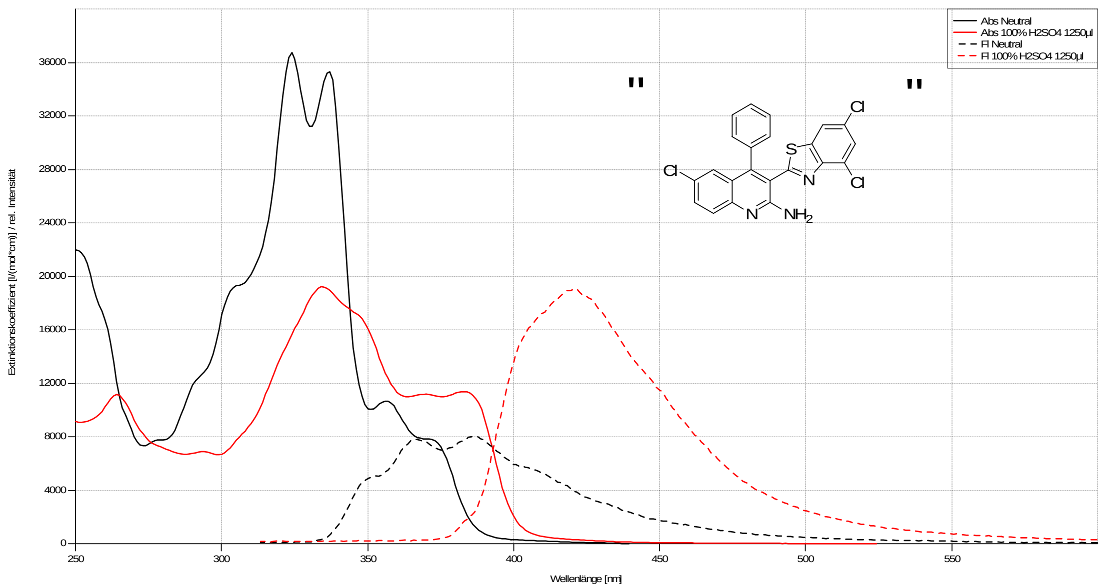
3.4 Unexpected Results

The next figures belong to substances whose spectra do not match with the expected structure.
As both [1]H MNR and EI-Mass spectra show that we have complicated mixtures of substances and purifications were unsuccessful, no reasonable structural assignments could be done.

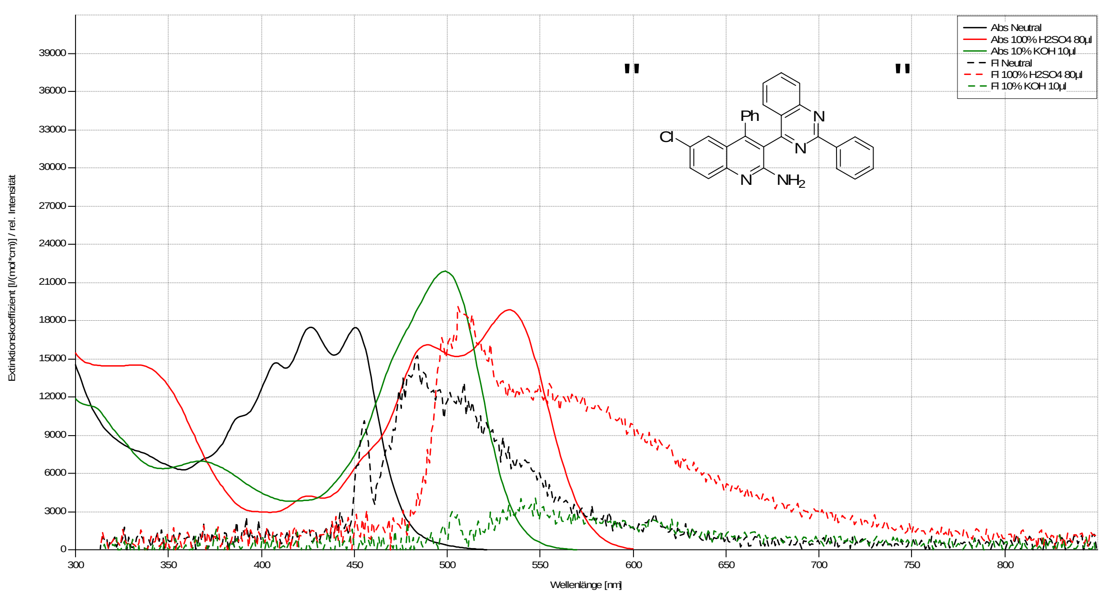
3.4.1 *Tried synthesis of 2-(2-Amino-6-chloro-4-phenylquinolin-3- yl)benzo[d]thiazole-6-carboxylic acid(4F)*



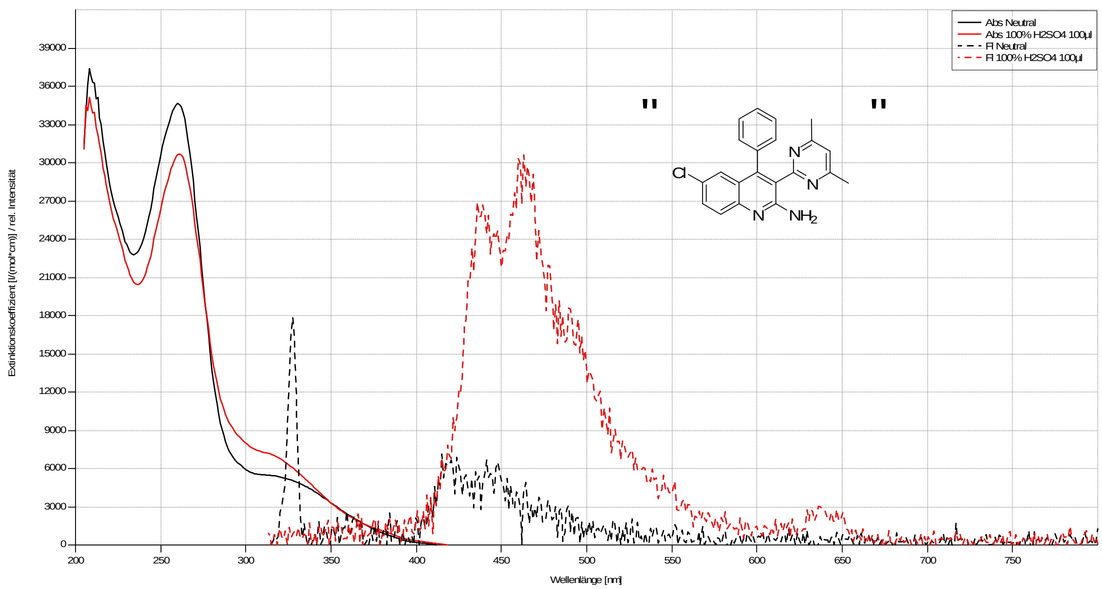
3.4.2 Tried synthesis of 6-Chloro-3-(4, 6-dichlorobenzo[d]thiazol-2-yl)-4-phenylquinolin-2-amine (4G)



3.4.3 Tried synthesis of 6-Chloro-4-phenyl-3-(2-phenylquinazolin-4-yl) quinolin-2-amine (4H)

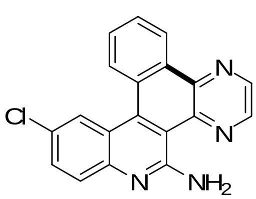


3.4.4 Tried synthesis of 6-Chloro-3-(4, 6-dimethylpyrimidin-2-yl)-4-phenylquinolin-2-amine (4J)

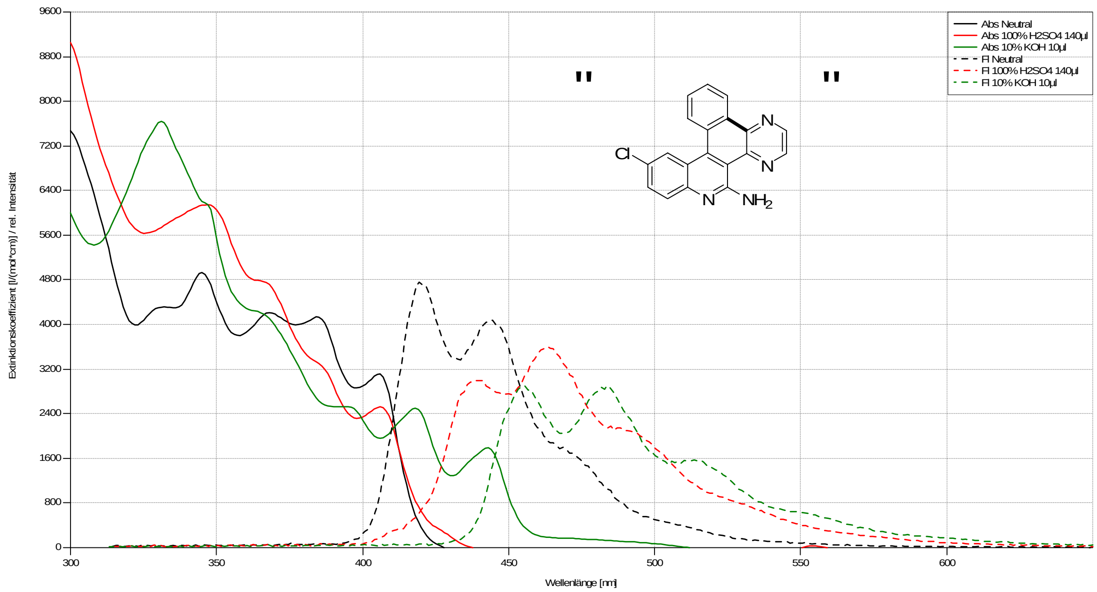


3.4.5 Tried synthesis of 6-Chloro-4-phenyl-3-(pyrazin-2-yl) quinolin-2-amine (4K)

Interesting results have been obtained in the case of the fluorescence spectra of **4K.**We believe these spectra could be assigned to the desired ring closure product **4K'.**



4K'



Unfortunately, the pyrazine acetonitrile **4KE1** was no more available to repeat the synthesis in order to get sufficient amounts of **4K** for detailed studies.

4 Discussion

4.1 Systems with Dual Fluorescence

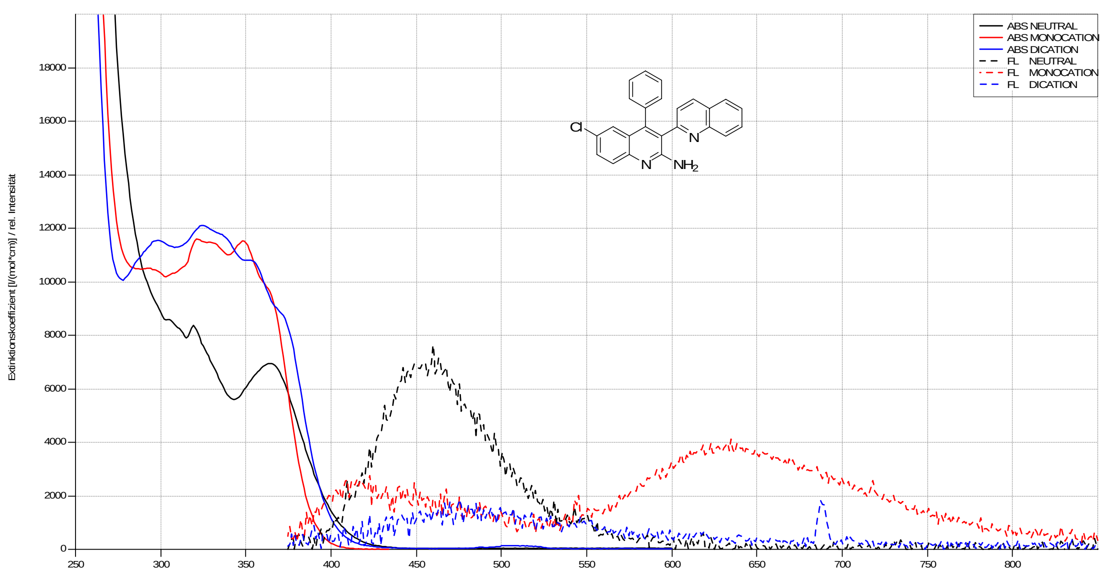
4.1.1 The Solvent Effect

Preferentially EtOH was used as solvent, but also measurements in $CHCl_3$ have been made.

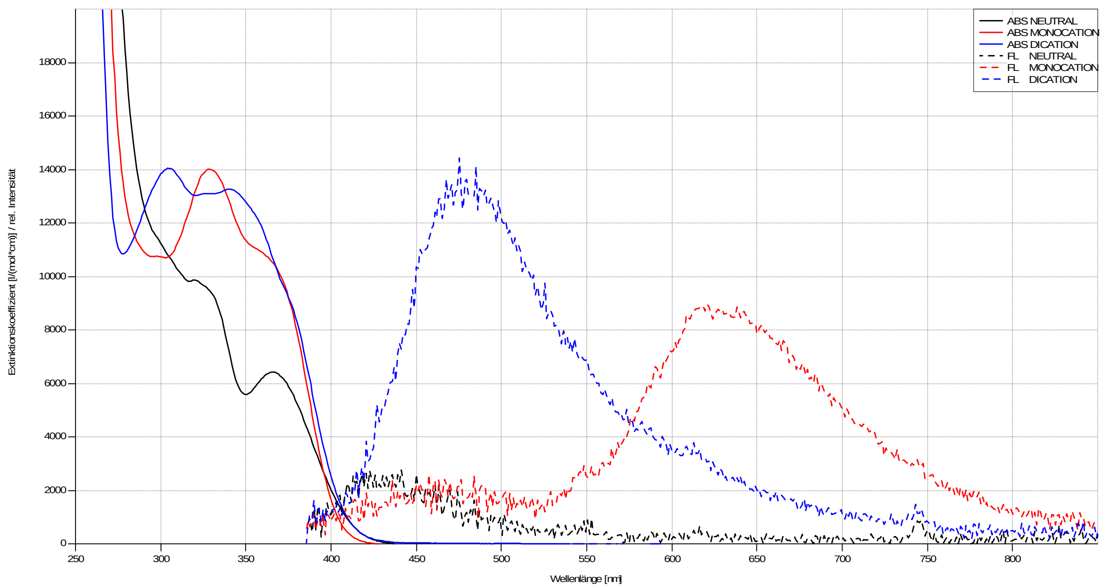
The tables contain the values of the fluorescence quantum yields for the neutral form, monocation and dication.

A) 6-Chloro-4-phenyl-3-(quinolin-2-yl) quinolin-2-amine (2A)

(a) Spectrum in EtOH



(b) Spectrum in $CHCl_3$

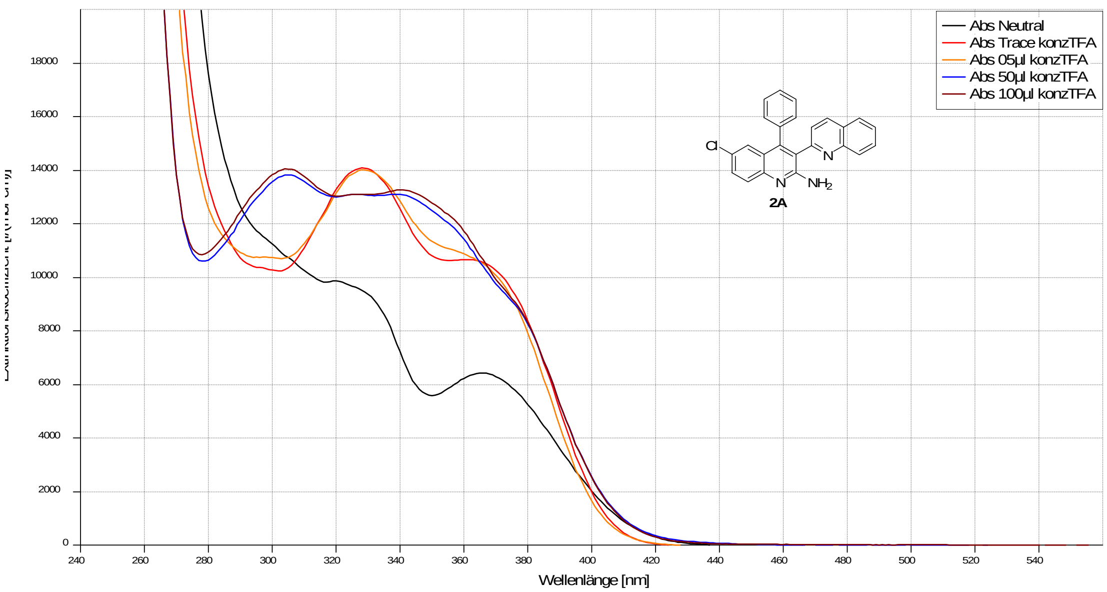


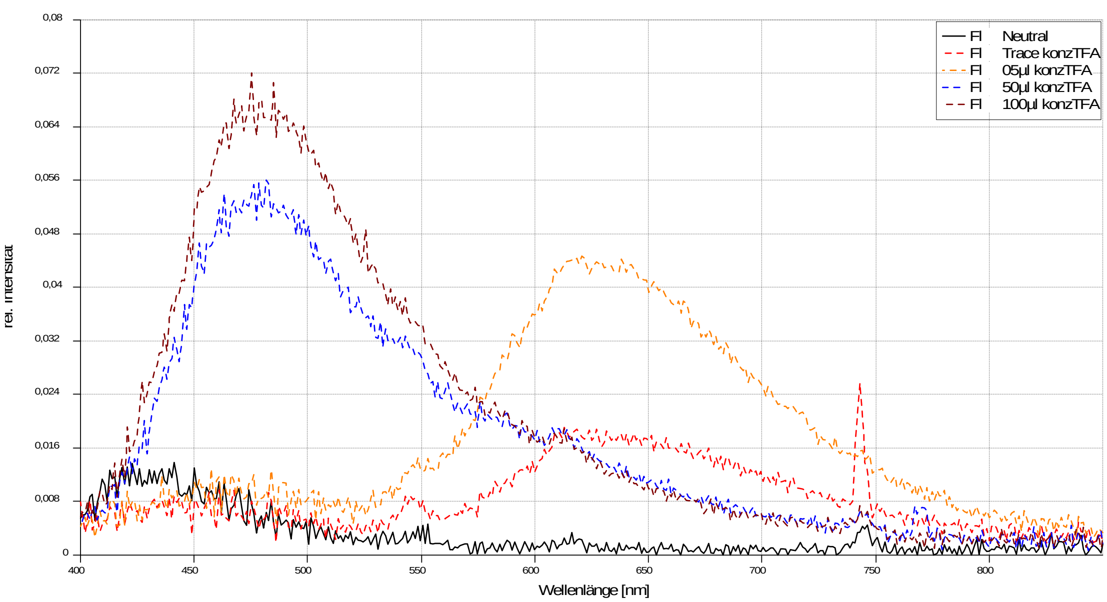
Φ_f (%)		
	EtOH	**$CHCl_3$**
Neutral	1,49 E_{364} = 0,18	0, 55 E_{366} = 0,22
Monocation	1,58 0,41(„blue“) 1,17(„red“) E_{348} = 0,30	2, 10 0, 27(„blue“) 1, 83(„red“) E_{328} = 0,49
Dication	0,57 E_{324}= 0,32	2, 48 E_{341} = 0,46

Table 4.1 *A comparison of the quantum yields in EtOH and $CHCl_3$, respectively.*

The pK_a values, for the S_0 and S_1 are not strongly different. As we do not have the pK_a values, we tested how small amounts of acid added are changing the absorption and fluorescence spectra.

In the case of **2A**, the measurements were made in $CHCl_3$ and protonation has been achieved with conc. TFA.
From the spectra given below, we observe that already with traces of concentrated TFA added to the $CHCl_3$ solution, we get the monocation with dual fluorescence (low amounts of acid show efficient proton transfer).
By adding more acid, the dication is being formed and the substance shows no more dual fluorescence.





- *The Dilution Effect*

The effect of dilution on the fluorescence quantum yields is given in Table 4.2

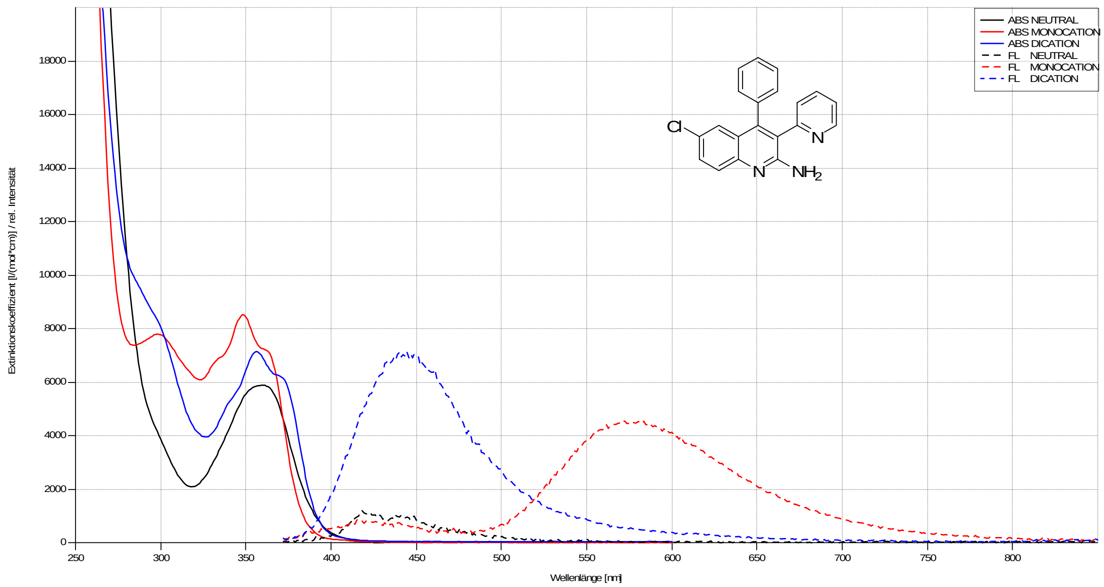
2A				
$CHCl_3$ solution	**E**	**Φ_f (%)**	**E**	**Φ_f (%)**
Neutral	E_{366} = 0,43	0,35	E_{365} = 0,04	1,61
Monocation	E_{329} = 0,94	2,00 (0, 25 "blue" 1, 75 "red")	E_{330} = 0,09	2,69 (0,58 "blue" 2,11 "red)
Dication	**E_{340} = 0,09**	**3,2**	**E_{341} = 0,090**	**3,0**

Table 4.2 *The effect of dilution on* $\boldsymbol{\Phi_f}$

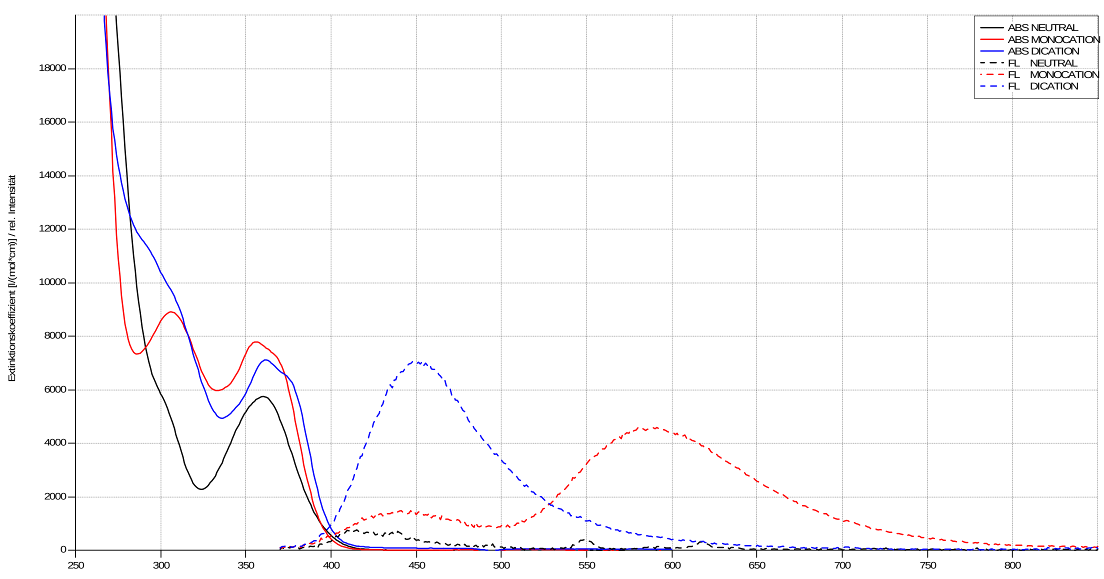
As the table shows, with the dilution of the $CHCl_3$ solution, an increase of the fluorescence quantum yields is observed.

B) 6-Chloro-4-phenyl-3-(pyridin-2-yl)quinolin-2-amine (3A)

(a) Spectrum in EtOH



(b) Spectrum in $CHCl_3$

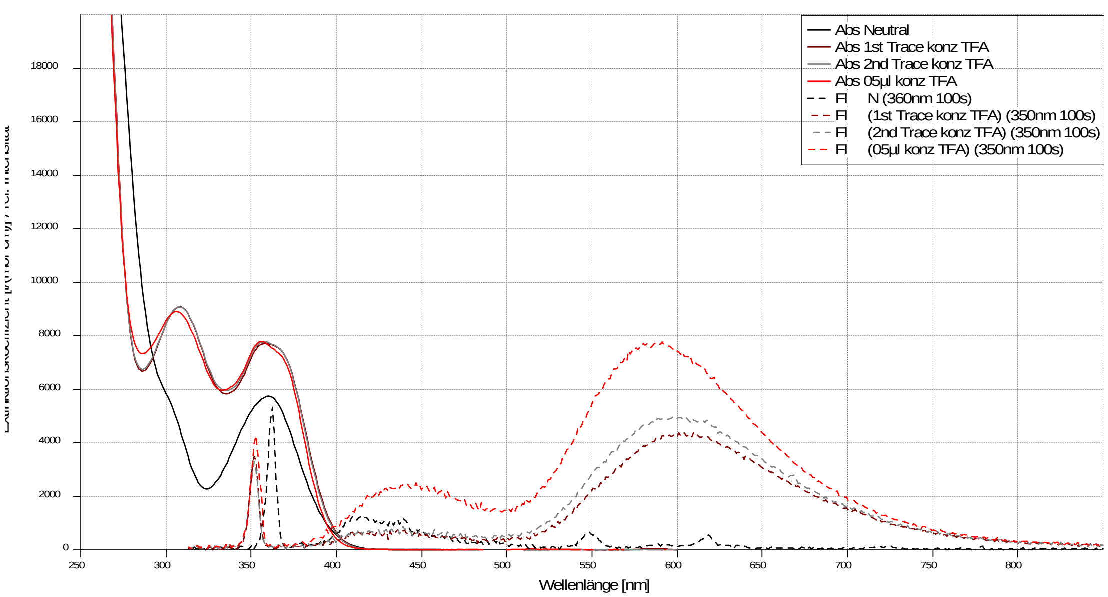


Φ_f (%)		
	EtOH	*$CHCl_3$*
Neutral	0,78 E_{359}=0,28	0,66 E_{360}=0,38
Monocation	6,25 0,51(„blue“) 5,74(„red“) E_{348}=0,41	7, 96 1,27(„blue“) 6,69(„red“) E_{356}=0,52
Dication	5,75 E_{3356}=0,34	9,18 E_{362}=0,47

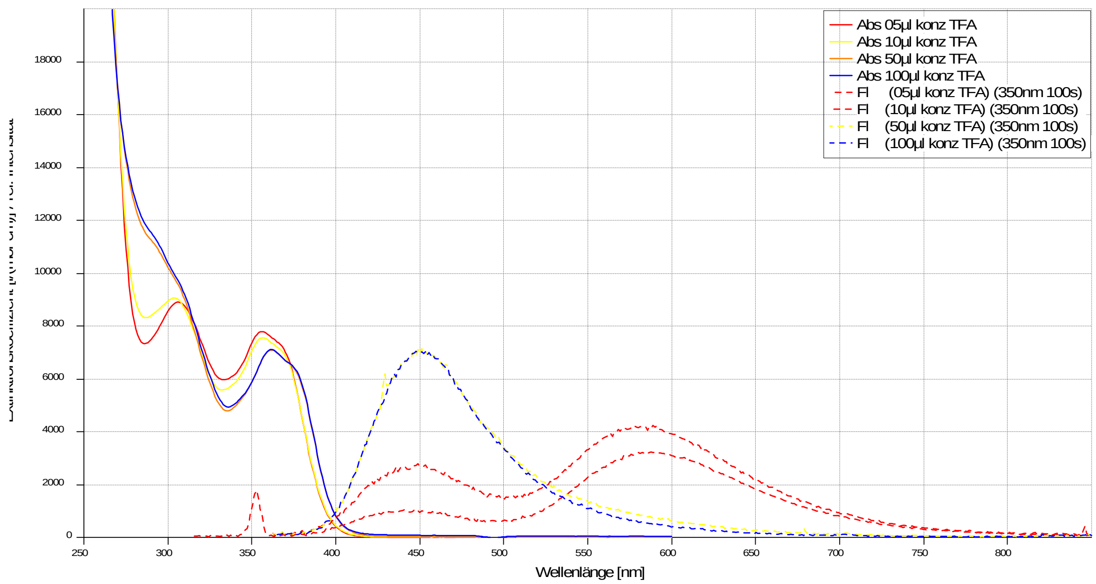
Table 4.3 *Comparison of the quantum yields in $CHCl_3$ and EtOH for* ***3A***

The effect of adding TFA to the $CHCl_3$ solution of **3A** is shown below:

- *Neutral→Monocation*



- *Monocation→Dication*



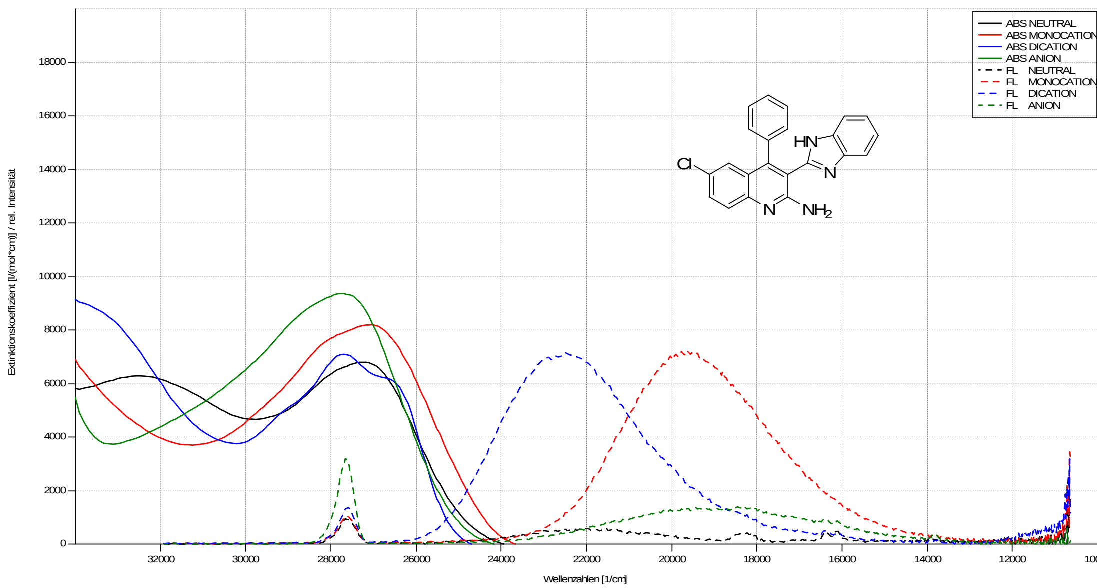
Already traces of TFA lead to full monoprotonation and with 50µl TFA we have full S_0 diprotonation. With 50µl and 100µl we get the diprotonated system. As shown in Table 1.54, the quantum yield of the dication is higher than in the case of the monoprotonated system.
The neutral form shows practically no fluorescence.

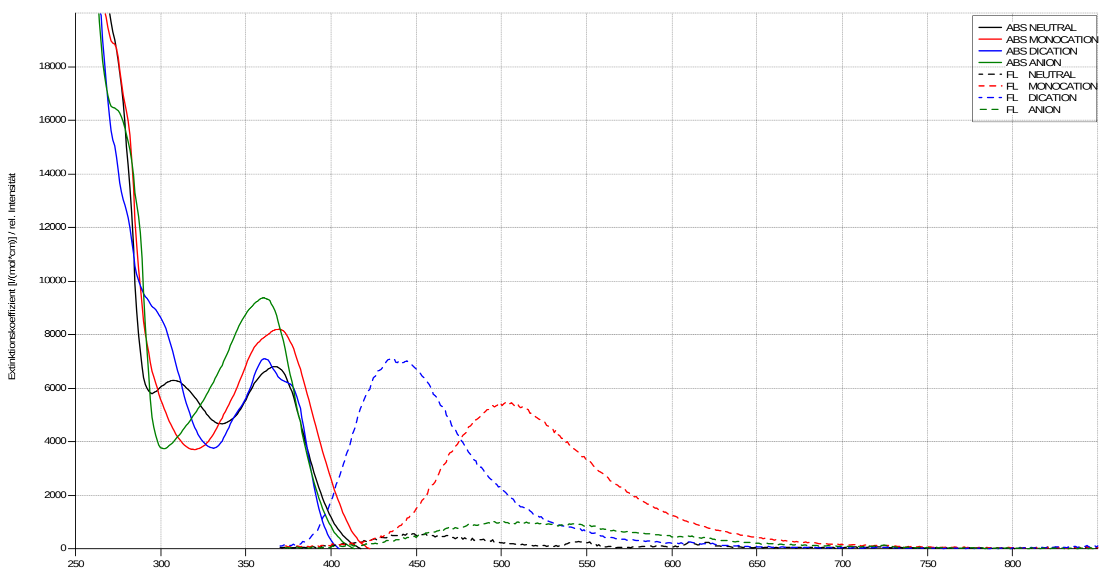
- *Comparison of* ***2A*** *with* ***3A***

Comparing **2A** and **3A,** it's interesting that in the quinoline's case **2A**, the fluorescence intensity of the neutral form is higher than in the case of the protonated system.

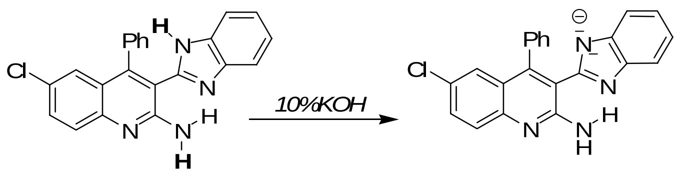
In the pyridine derivatives the situation is exactly reverse: The fluorescence intensity of the protonated form is higher than in the case of the neutral form. This is the general behavior met in the aldehyde's case [12,58].

C) 3-(1*H*-Benzo[*d*]imidazol-2-yl)-6-chloro-4-phenylquinolin-2-amine(4A)



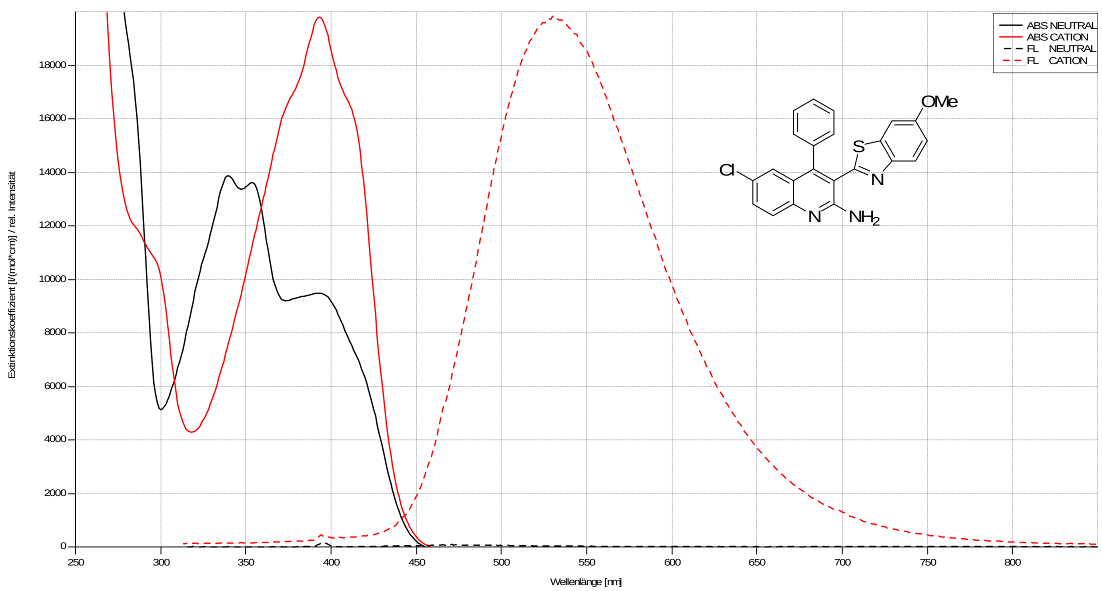


In the case of **4A**, apart from the protonated forms, deprotonation is possible. The anion has the structure shown in Scheme 4.4



Scheme 4.4

D) 6-Chloro-3-(6-methoxybenzo[*d*]thiazol-2-yl)-4-phenylquinolin-2-amine (4E)

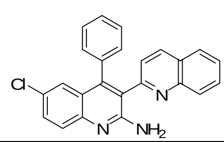
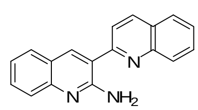
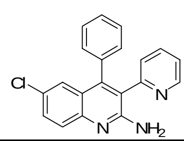
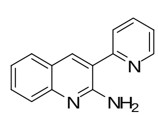
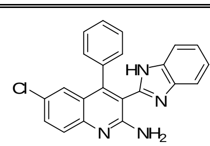
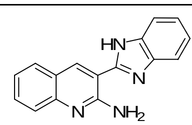


In this case, the monocation shows no dual fluorescence, but high Φ_f values; this is due to the methoxy group.
Having an electron donor group, by a strong π-donation effect of the methoxy group, the structure becomes more rigid in the excited state.

Thus, the fluorescence quantum yield increases. From the spectral distribution of the fluorescence can be derived that no ESIPT occurs; the rather large Stokes effect is indicative for a pronounced change of molecular geometry under electronic excitation.

4.1.2 *The Effect of the Phenyl Group*

As mentioned, we wanted to study the effect of the phenyl group on the spectroscopic properties of the systems with dual fluorescence. For comparison, data from Kammerer's theses are taken [12] Table 4.4.

Nr	***Structure***	***λ*** *(after protonation)*	
		EtOH	***$CHCl_3$***
2A		422nm 634nm (*ESIPT*)	457nm 629nm *(ESIPT)*
22			615nm *(ESIPT)*
3A		420nm 580nm *(ESIPT)*	441nm 591nm *(ESIPT)*
8			575nm *(ESIPT)*
4A		503nm *(ESIPT)*	
13			430nm 560nm *(ESIPT)*

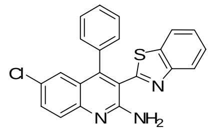
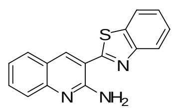
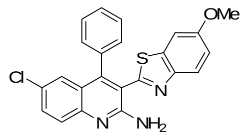
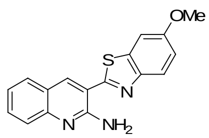
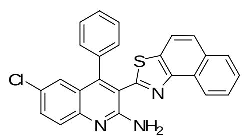
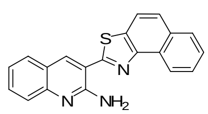
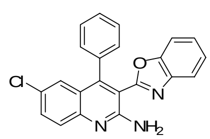
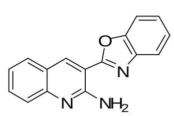
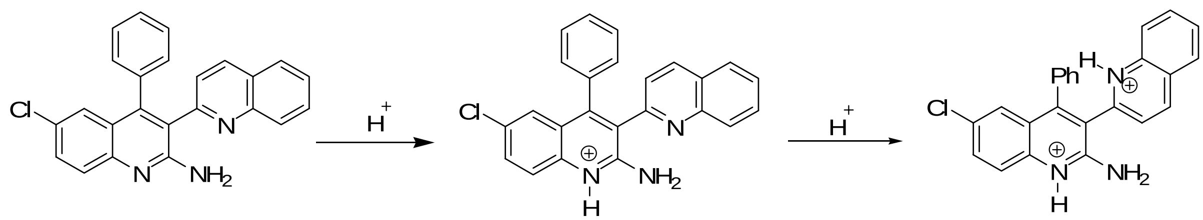
4C		417nm 615nm *(ESIPT)*	
17 ***4E***	 	530nm (*ESIPT*)	436nm 624nm *(ESIPT)* 530nm (*ESIPT*)
19			462nm 600nm *(ESIPT)*
4I		605nm *(ESIPT)*	
21			475nm
4D		442nm 617nm *(ESIPT)*	
27			430nm 620nm *(ESIPT)*

Table 4.4 *The influence of the phenyl-group on the fluorescences*

4.1.3 Monoprotonation / Diprotonation

In the case of **2A** and **3A** apart from monoprotonation, by adding more acid diprotonation can be achieved. The monocation shows dual fluorescence, the dication not.
For example, the monocation ***2AH***$^{+}$ and the dication ***2AH***$_{2}^{2+}$ have the following structures (Scheme 4.5)

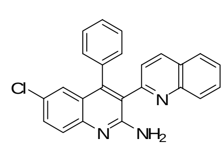


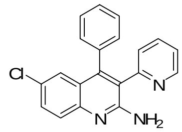
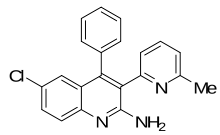
2A | 2AH^{+} | 2AH$_2^{2+}$

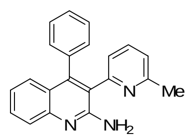
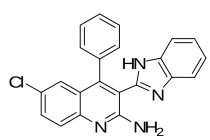
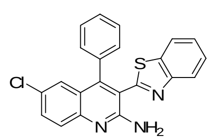
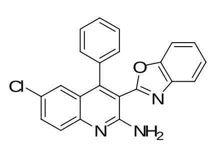
Schem 4.5 *Monoprotonation/Diprotonation of* ***2A***

4.1.4 Dual vs Red Fluorosceence

An overview of the synthesized substances, regarding the type of fluorescence they exhibit, is given in Table 4.6

Nr	***Structure***	**λ** ***(after protonation)*** *EtOH/H_2SO_4*	***Type of fluorescence***
2A		422nm 634nm (*ESIPT*)	*Dual fluorescence*

3A		420nm 580nm *(ESIPT)*	*Dual fluorescence*
3C		415nm 567nm *(ESIPT)*	*Dual fluorescence*

3D		406nm 557nm *(ESIPT)*	*Dual fluorescence*
4A		503nm	*Only one fluorescence*
4C		417nm 615nm *(ESIPT)*	*Dual fluorescence*
4D		442nm 617nm *(ESIPT)*	*Dual fluorescence*

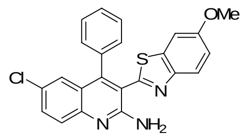
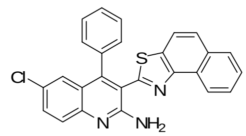
4E		530nm	*Only one fluorescence*
4I		605nm-*(ESIPT)*	*Only one fluorescence*

Table 4.6 *Dual vs red fluorescence*

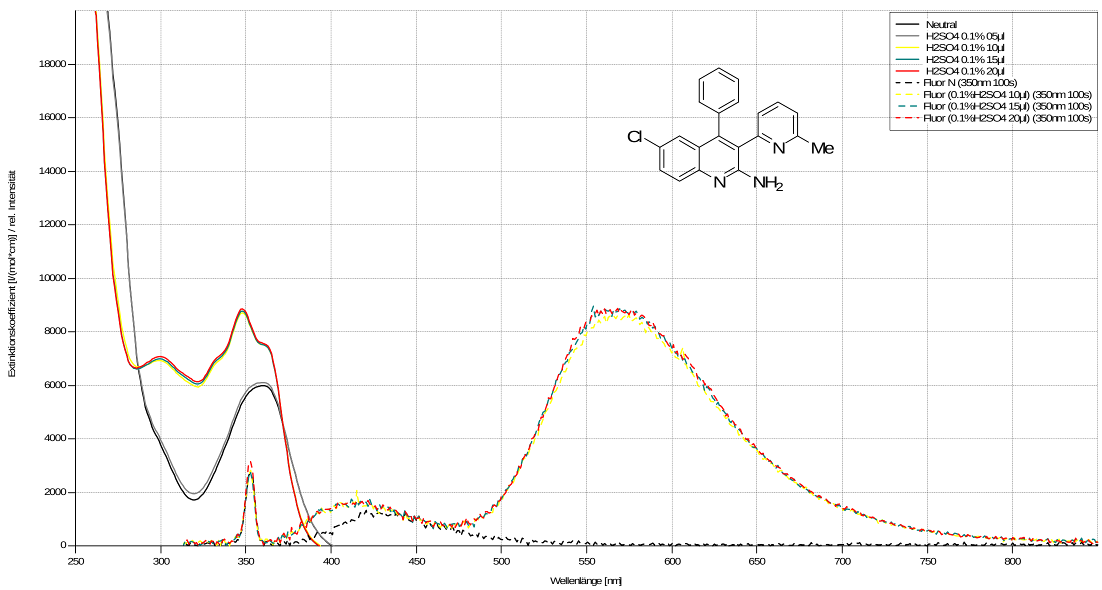
4A, **4E** and **4I** show only one type of fluorescence. Assuming that both tautomers show detectable room temperature fluorescence, in the cases of **4A, 4E** only one fluorescence occurs, whereas for **4I** complete proton transfer could be derived. Final decisions, however, need low temperature investigations.

4.1.5 Monoprotonation / Diprotonation – The Effect on the Fluorescence Quantum Yields

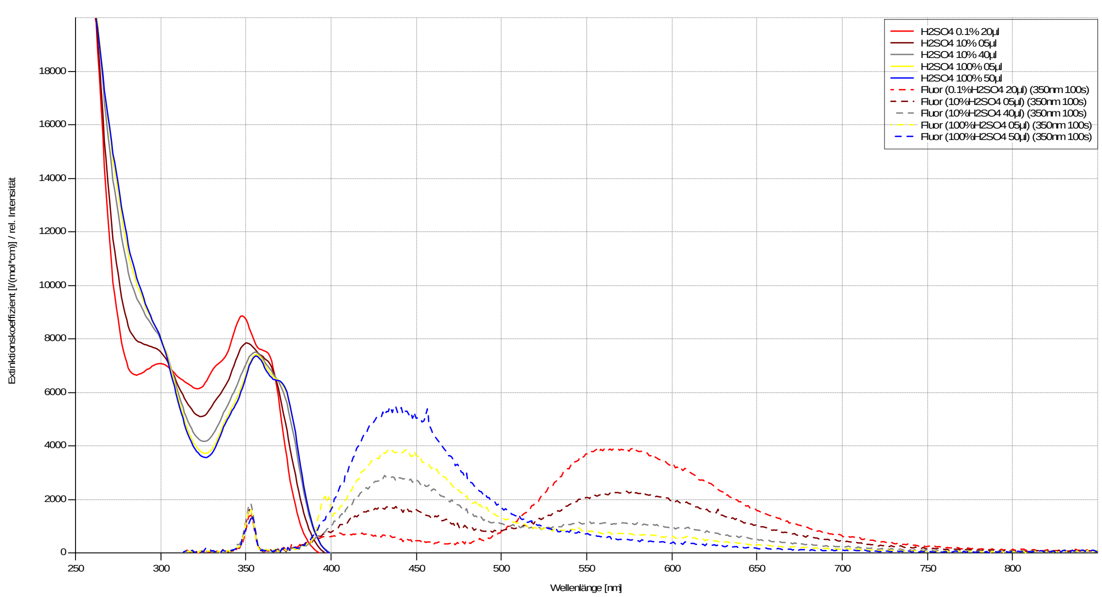
In the following, the effect of adding acid (slow addition of H_2SO_4 to the EtOH solutions or of pure TFA to the $CHCl_3$ solutions) on both the absorption and fluorescence spectra is shown.
From the results follows that the pK_a values of S_0 and S_1 states are not strongly different.
The effect on the fluorescence quantum yields is summarized in Table 4.7; Table 4.8 (p.99)

- **6-Chloro-3-(6-methylpyridin-2-yl) 4-phenylquinolin-2-amine (3C)**

- *Neutral→Monocation*

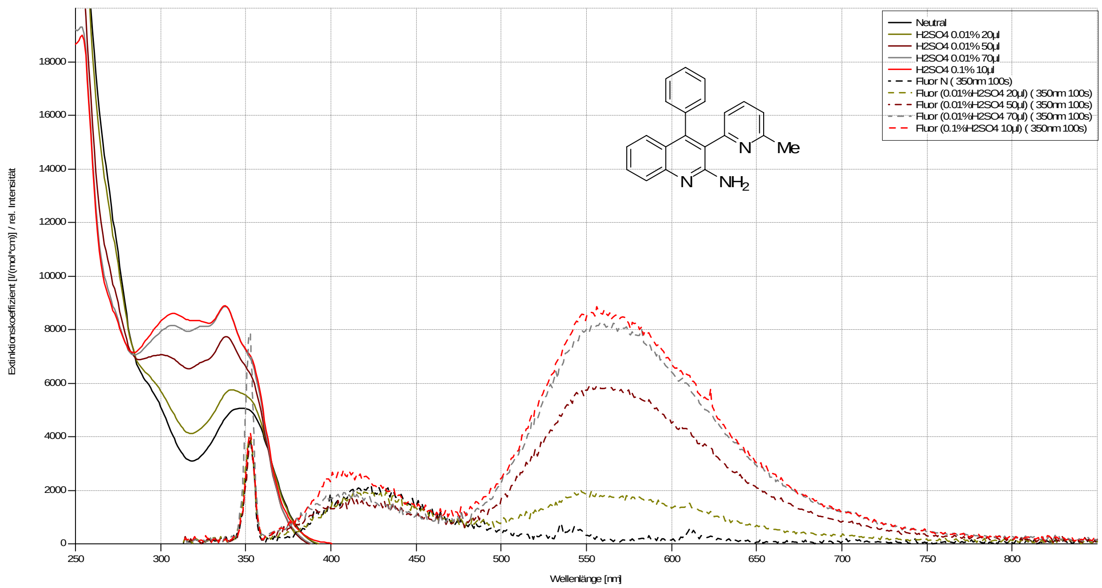


- *Monocation→Dication*

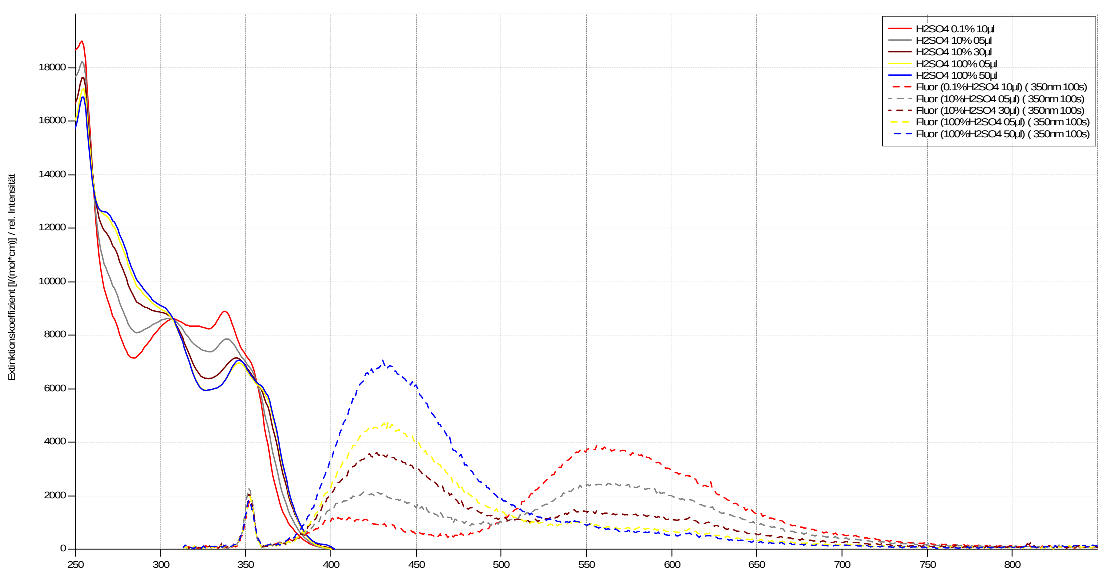


- **3-(6-Methylpyridin-2-yl)-4-phenylquinolin-2-amine (3D)**

- *Neutral→Monocation*

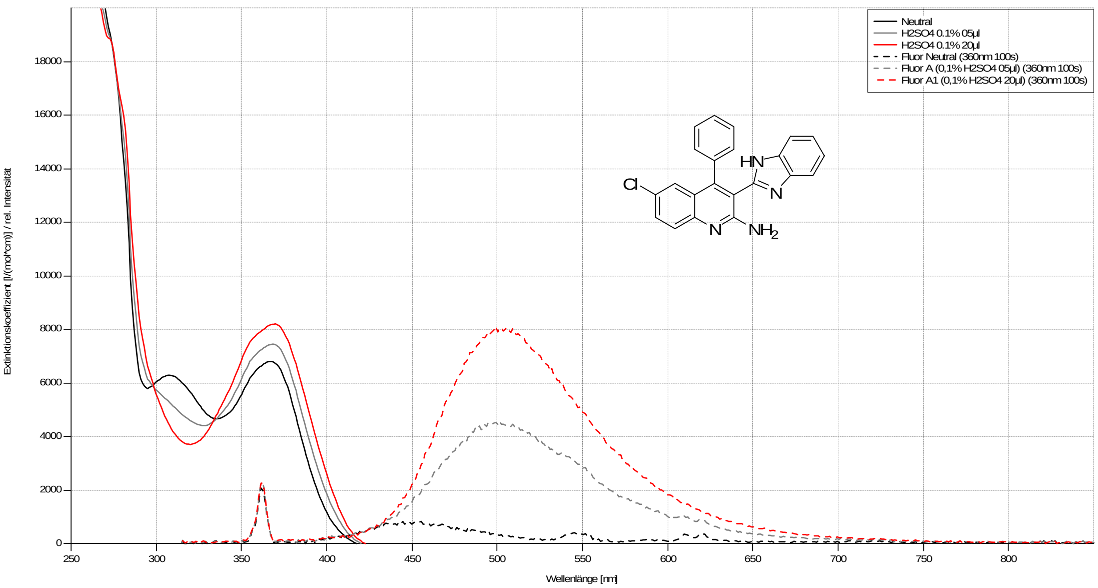


- *Monocation→Dication*

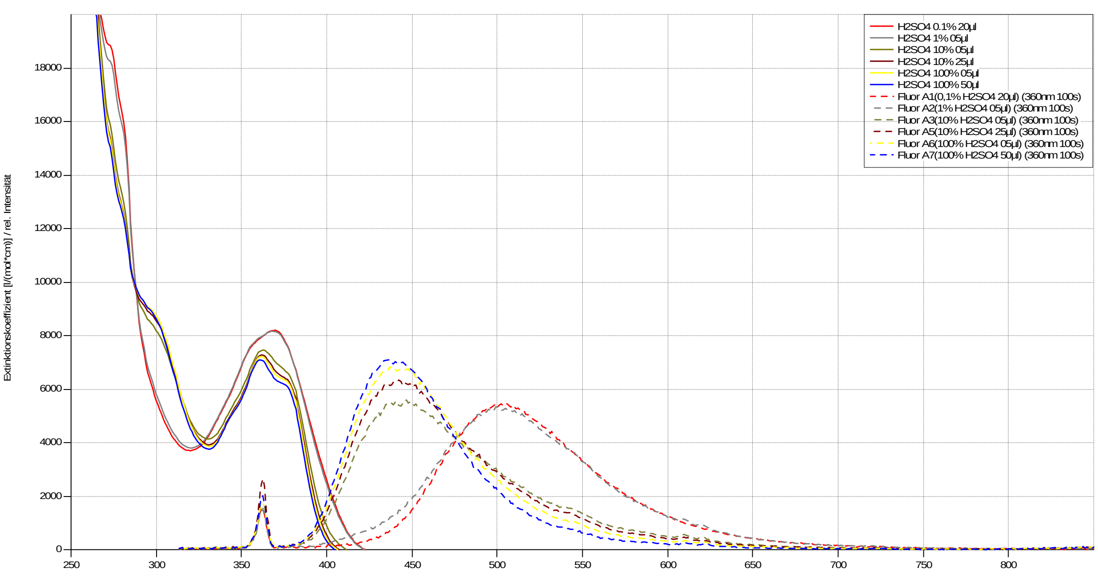


- **3-(1*H*-Benzo[*d*]imidazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4A)**

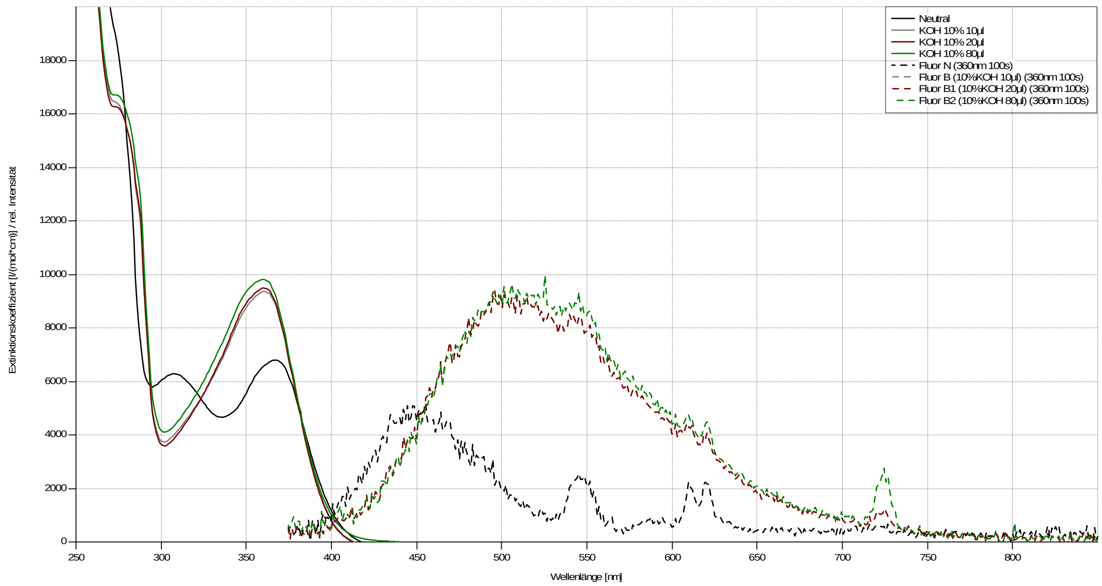
- *Neutral→Monocation*



- *Monocation→Dication*

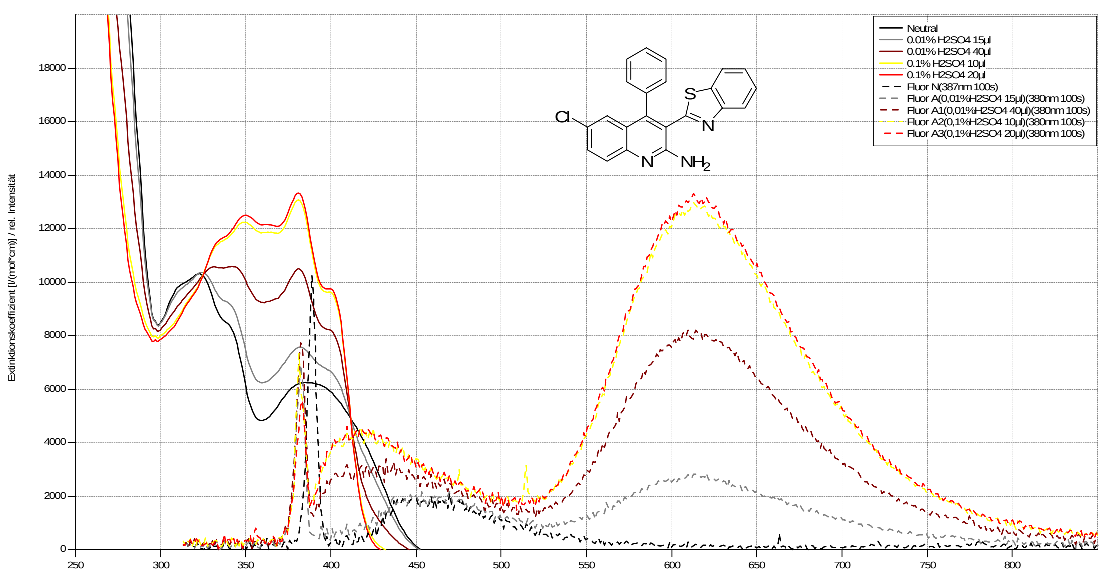


- *Neutral→Anion*



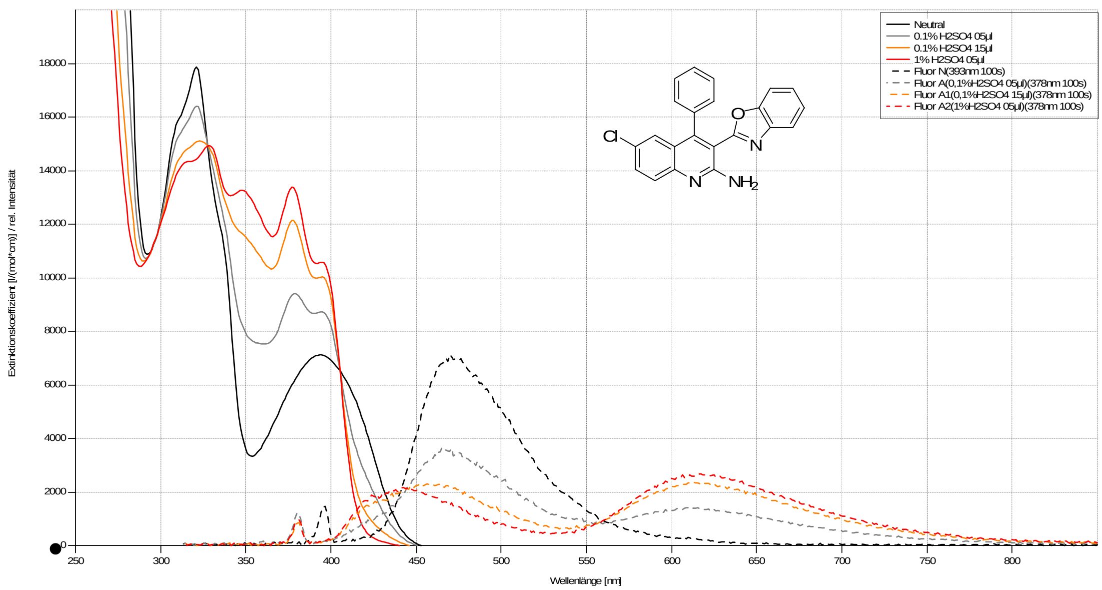
- **3-(Benzo[*d*]thiazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4C)**

- *Neutral→Cation*



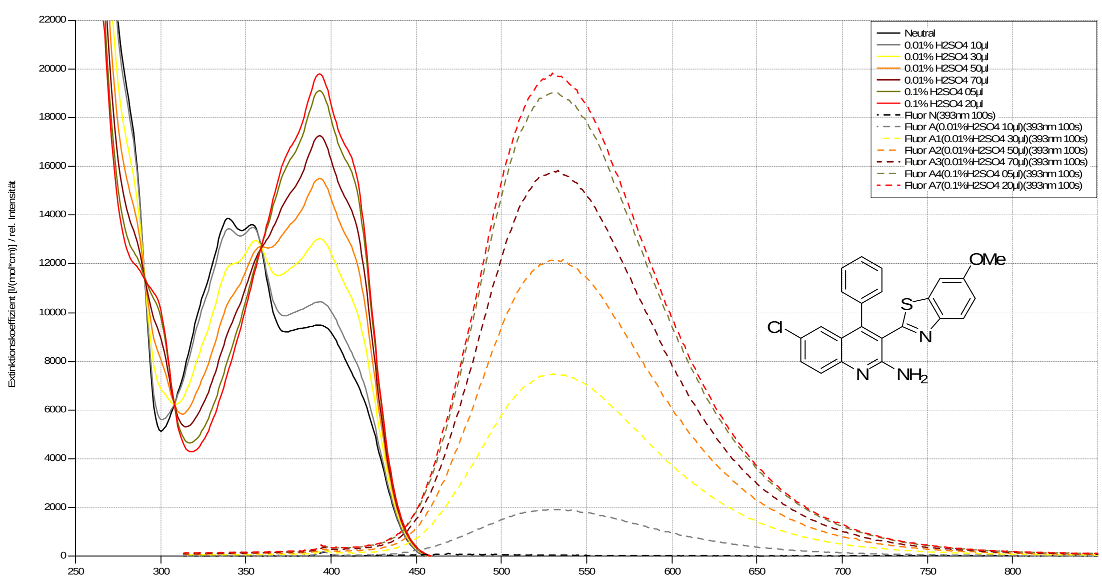
- **3-(Benzo[*d*]oxazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4D)**

- *Neutral→Cation*



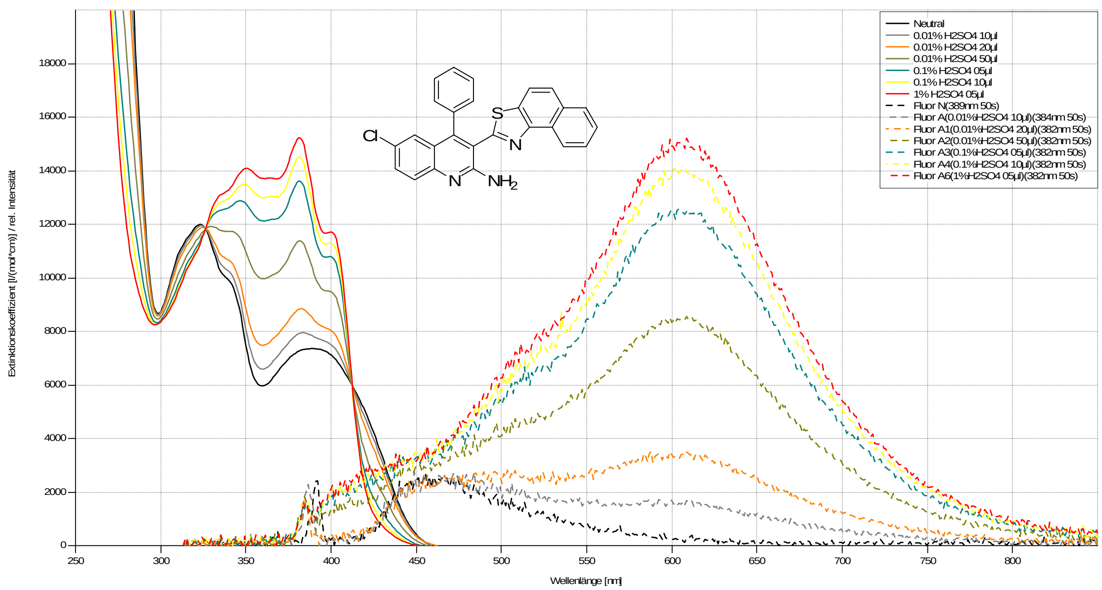
- **6-Chloro-3-(6-methoxybenzo[*d*]thiazol-2-yl)-4-phenylquinolin-2- amine (4E)**

- *Neutral→Cation*



- **6-Chloro-3-(naphtho[1,2-*d*]thiazol-2-yl)-4-phenylquinolin-2-amine (4I)**

- *Neutral→Cation*



The effect of slowly adding acid on the fluorescence quantum yields is summarized in the following tables:
Measurements in both EtOH and $CHCl_3$ have been made. *Fluorescein* was used as standard.

#	*EtOH*	$\Sigma\Phi_f$	$\Phi_{"blue"}$	$\Phi_{"red"}$
2A	*Neutral*	1, 49%	1, 49%	-
	05μl 1% H_2SO_4	1,58%	0,41%	1,17%
	10μl 1% H_2SO_4	1,44%	0,38%	1,06%
	05μl 10% H_2SO_4	1,13%	0,39%	0,74%
	50μl 100% H_2SO_4	0,57%	0,57%	-
	100μl 100% H_2SO_4	0,56%	0,56%	-
3A	*Neutral*	0,78%	0,78%	-
	05μl 1% H_2SO_4	6,25%	0,51%	5,74%
	10μl 1% H_2SO_4	5,97%	0,5%	5,47%
	100μl 100% H_2SO_4	5,75%	5,75%	-
3C	*Neutral*	0,74%	0,74%	-
	10μl 0.1% H_2SO_4	6,27%	0,56%	5,71%
	20μl 0.1% H_2SO_4	6,40%	0,57%	5,83%
	05μl 10% H_2SO_4	5,53%	1,61%	3,92%
	40μl 10% H_2SO_4	5,29%	3,16%	2,13%
	20μl 100% H_2SO_4	6,58%	6,58%	-
	50μl 100% H_2SO_4	7,31%	7,31%	-
3D	*Neutral*	1,22%	1,22%	-
	20μl 0.01% H_2SO_4	2,43%	0,93%	1,50%
	50μl 0.01% H_2SO_4	4,61%	0,61%	4,00%
	70μl 0.01% H_2SO_4	5,77%	0,63%	5,14%
	05μl 0. 1% H_2SO_4	5,95%	0,78%	5,17%
	10μl 0.1% H_2SO_4	6,24%	0,84%	5,4%
	05μl 10% H_2SO_4	5,62%	1,74%	3,88%
	30μl 10% H_2SO_4	5,50%	3,19%	2,31%
	05μl 100% H_2SO_4	5,76%	5,76%	-
	50μl 100% H_2SO_4	7,57%	7,57%	-
4A	*Neutral*	1,28%	1,28%	-
	05μl 0.1% H_2SO_4	7,29%		
	20μl 0.1% H_2SO_4	11,28%		
	05μl 1% H_2SO_4	11,57%		
	05μl 10% H_2SO_4	11,61%		
	15μl 10% H_2SO_4	12,18%		
	25μl 10% H_2SO_4	12,45%		
	05μl 100% H_2SO_4	12,50%		

	50μl 100% H_2SO_4	12,16%		
	10μl 10% KOH	2,46%		
	80μl 10% KOH	2,49%		
4C	*Neutral*	0,64%	0,64%	-
	15μl 0.01% H_2SO_4	1,89%	0,55%	1,34%
	40μl 0.01% H_2SO_4	3,49%	0,71%	2,78%
	10μl 0.1% H_2SO_4	4,29%	0,72%	3,57%
	20μl 0.1% H_2SO_4	4,30%	0,69%	3,61%
	10μl 1% H_2SO_4	4,20%	0,70%	3,50%
	10μl 10% H_2SO_4	3,27%	0,70%	2,57%
	05μl 100% H_2SO_4	2,95%	0,69%	2,26%
	20μl 100% H_2SO_4	2,77%	0,66%	2,11%
4D	*Neutral*	3,62%	3,62%	-
	05μl 0.1% H_2SO_4	3,20%	1,93%	1,27%
	15μl 0.1% H_2SO_4	2,78%	1,06%	1,72%
	05μl 1% H_2SO_4	2,59%	0,83%	1,76%
4E	*Neutral*	0,25%	0,25%	-
	10μl 0.01% H_2SO_4	7,04%	-	7,04%
	30μl 0.01% H_2SO_4	22,55%	-	22,55%
	50μl 0.01% H_2SO_4	31,82%	-	31,82%
	70μl 0.01% H_2SO_4	38,02%	-	38,02%
	05μl 0.1% H_2SO_4	42,37%	-	42,37%
	20μl 0.1% H_2SO_4	42,91%	-	42,91%
	50μl 0.1% H_2SO_4	**43,70%**	-	**43,70%**
	10μl 1% H_2SO_4	42,80%	-	42,80%
	10μl 10% H_2SO_4	40,18%	-	40,18%
	10μl 100% H_2SO_4	39,51%	-	39,51%
4I	*Neutral*	0,76%	0,76%	-
	10μl 0.01% H_2SO_4	1,50%		
	20μl 0.01% H_2SO_4	2,16%		
	50μl 0.01% H_2SO_4	3,82%		
	05μl 0.1% H_2SO_4	4,63%		
	10μl 0.1% H_2SO_4	4,89%		
	20μl 0.1% H_2SO_4	4,96%		
	05μl 1% H_2SO_4	5,02%		
	15μl 1% H_2SO_4	4,99%		

Table 4.7

#	$CHCl_3$	$\Sigma\Phi_f$	$\Phi_{''blue''}$	$\Phi_{''red''}$
2A	*Neutral*	0, 55%	0, 55%	-
	Trace TFA	1, 03%	0, 21%	0, 82%
	05 µl TFA	2, 10%	0, 27%	1, 83%
	50 µl TFA	2, 15%	2, 15%	-
	100 µl TFA	2, 48%	2, 48%	-
3A	*Neutral*	0, 66%	0, 66%	-
	1st trace TFA	4, 33%	0, 36%	3, 97%
	2nd trace TFA	4, 9%	0, 42%	4, 48%
	05 µl TFA	7, 96%	1, 27%	6, 69%
	10 µl TFA	8, 87%	2, 38%	6, 50%
	50 µl TFA	9, 18%	9,18%	-
	100 µl TFA	8, 67%	8, 67%	-

Table 4.8

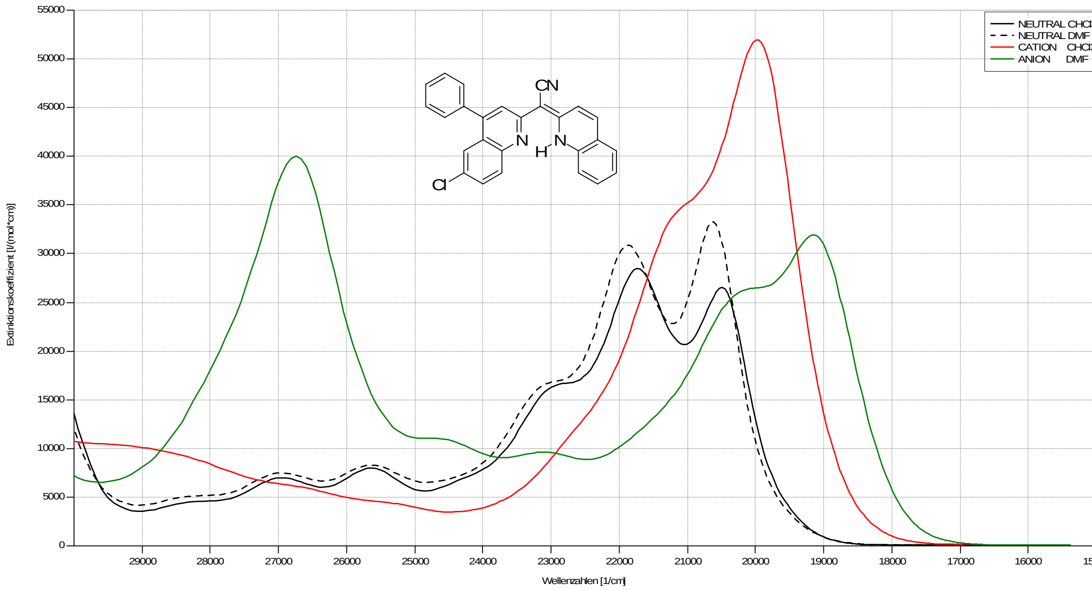
4.2 H-Chelates

4.2.1 Protonation / Deprotonation

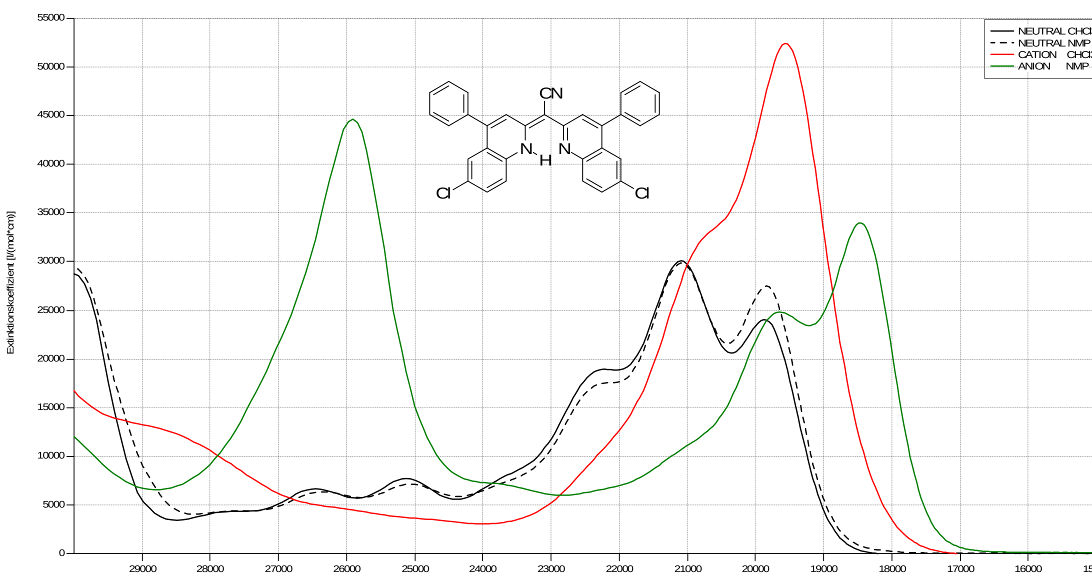
As mentioned before, no measurements in EtOH were made because of the low solubility of the substances.
In this case, we got the protonated systems in $CHCl_3$ by addition of pure TFA and the deprotonated ones in NMP (by addition of 10%-NaOH).

The oscillator strengths were calculated for all chelates and are summarized in Table 4.9.

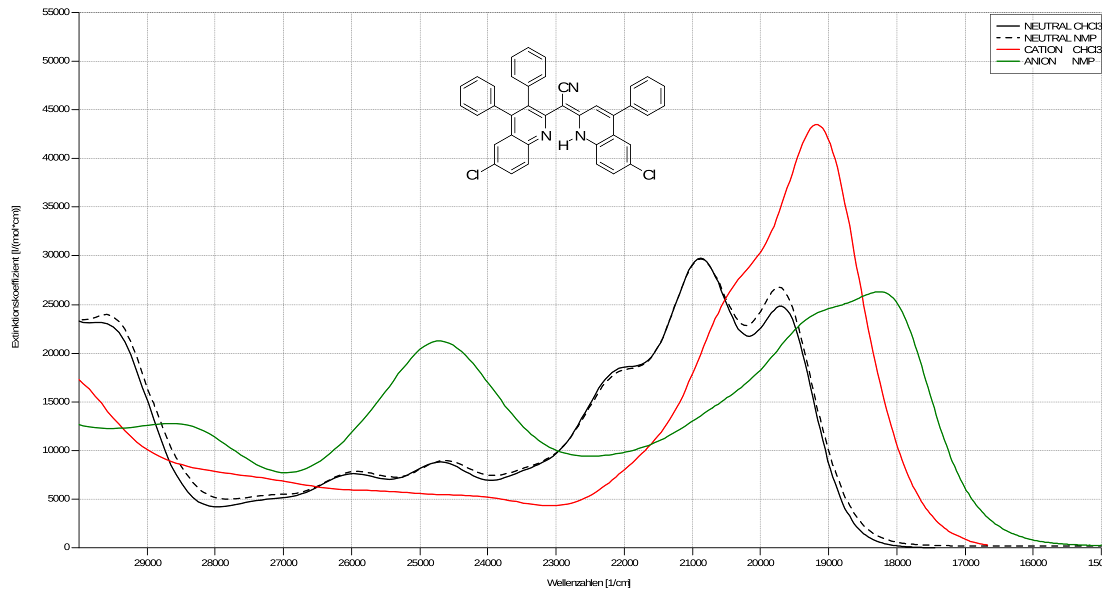
(2E)-2-(6-Chloro-4-phenylquinolin-2-yl)-2-(quinolin-2(1H)-ylidene)acetonitrile (2569)



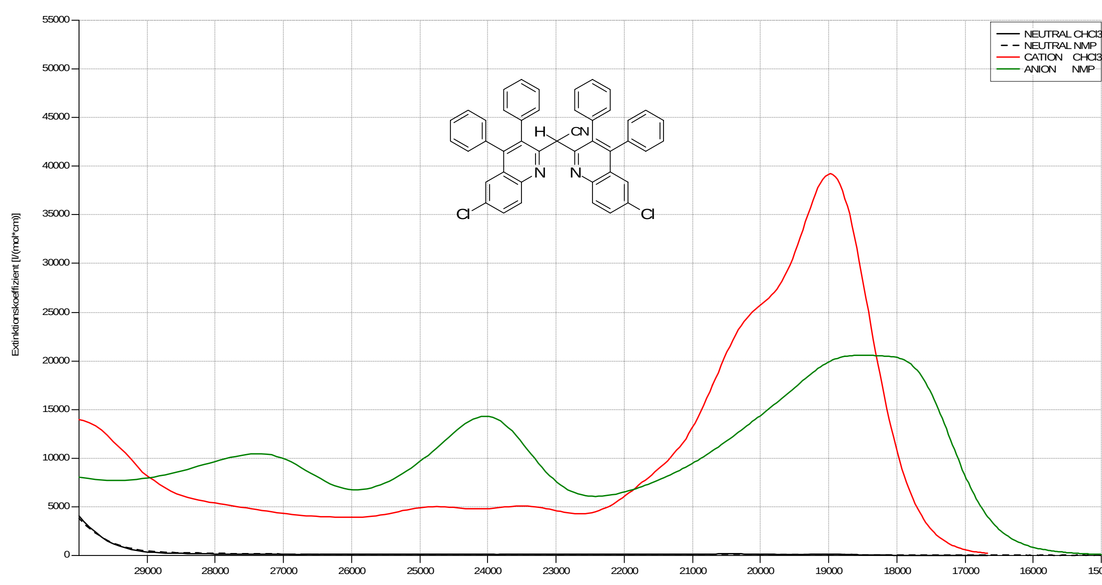
(2E)-2-(6-Chloro-4-phenylquinolin-2(1H)-ylidene)-2-(6-chloro-4-phenylquinolin-2-yl)acetonitrile (2647)



(2E)-2-(6-Chloro-3 , 4-diphenylquinolin-2-yl)-2-(6-chloro-4-phenylquinolin - 2(1H)-ylidene)acetonitrile (2652)



2, 2-Bis (6-chloro-3, 4-diphenylquinolin-2-yl)acetonitrile (2651)



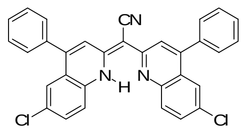
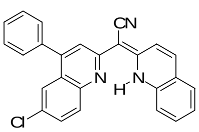
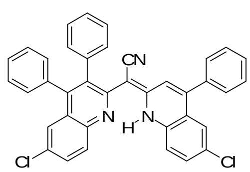
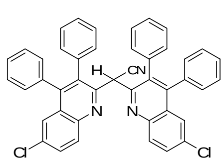
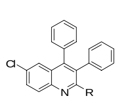
Substance	$f_{S_0\text{-}S_1}$		
	Neutral	***Cation***	***Anion***
2647 	0,40 ($CHCl_3$) 0,408(NMP) *17000-24300cm-1*	0,55($CHCl_3$) *17000-23800 cm-1*	0,37(NMP) *16000-22500 cm-1*
2569 	0,38 ($CHCl_3$) 0,41 (NMP) *17000-24900 cm-1*	0,56($CHCl_3$) *17000-23900 cm-1*	0,386NMP) *16000-22400 cm-1*
2652 	0,384($CHCl_3$) 0,39(NMP) *17000-23500 cm-1*	0,47($CHCl_3$) *16000-22800 cm-1*	0,39(NMP) *15000-21800 cm-1*
2651 	[0,08($CHCl_3$) 0,09(NMP)]* *28000-32500 cm-1*	0,4($CHCl_3$) *16000-22500 cm-1*	0,34(NMP) *15000-22500 cm-1*

Table 4.9 *TheS_0-S_1 oscillator strengths of the H-chelates*

[1] ***f*** is calculated for the

 moiety

In the case of **2647,** the neutral form has the H-chelate structure (the π-conjugated form) **2647N** (Scheme 4.10)

Through protonation or deprotonation a change of configuration occurs. Independent of the number and the positions of the phenyl groups, more or less efficient steric hindrances should influence the configurations of the cationic and anionic forms.
For **2647** and **2569**, both the cation and the anion have the trans-configuration. The spectral changes (**Δλ, Δε**) are in agreement with the theoretical expectation. From the spectra, likewise follows, that no significant steric hindrance comes from the 4, 4'-phenyl substitution. Obviously, the phenyls are more or less perpendicular to the twisted trans-configuration of the chromophoric system.

Interestingly, **2652** shows that the effect of a 3-phenyl substituent is much smaller than expected. This result supports the given interpretation that also in **2647** and **2569** the trans-configuration is strongly twisted (≥ 60^0 deviation from the coplanar configuration).

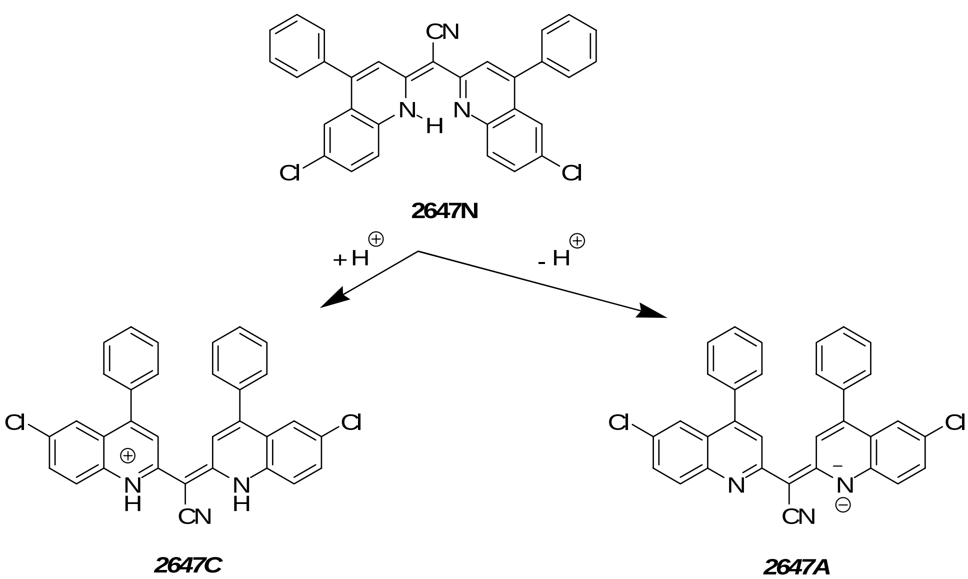


Fig 4.10 *Protonation and deprotonation in the case of* ***2647***

In the case of **2651**, the presence of the phenyl groups in 3, 3' position induces much stronger steric hindrance.
From the UV/vis spectra follows:

1. The neutral form (contrary to **2647, 2569** and **2652**) has the non-conjugated form **2651N** (to 100%).
2. Both, protonation and deprotonation give conjugated systems, as evidenced by the longwavelength absorptions. From the first electronic transitions (spectral positions, oscillatory strengths, half widths, Franck-Condon factors) follows:

(a) The mono-cation has a strongly twisted trans - configuration (twist angle between the quinoline moieties of more than 70^0). The phenyl substituents – having a very small effect on the chromophoric system in all cases **2569, 2652, 2647** and **2651**- are in any case twisted up to perpendicularity.
(b) In the mono-anion an equilibrium between the strongly twisted trans- and the twisted mono cis-configuration exists. (Scheme 4.11)

The value of the oscillator strength of the first electronic transition of the quinoline moiety is 0, 08/2 resp. 0, 009/2 (Table 4.9)

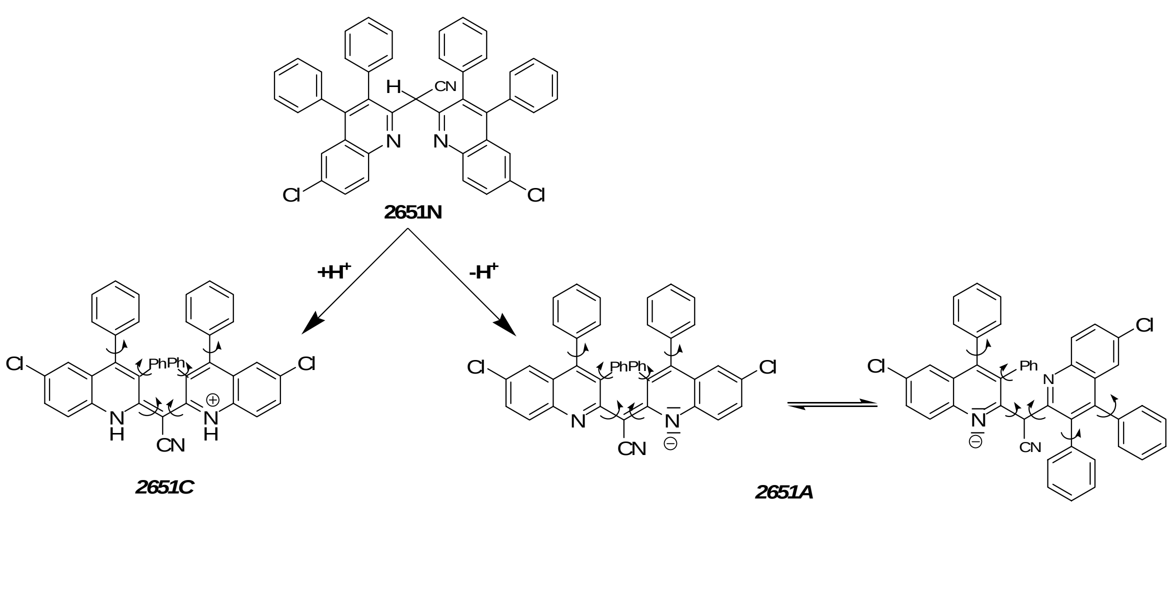
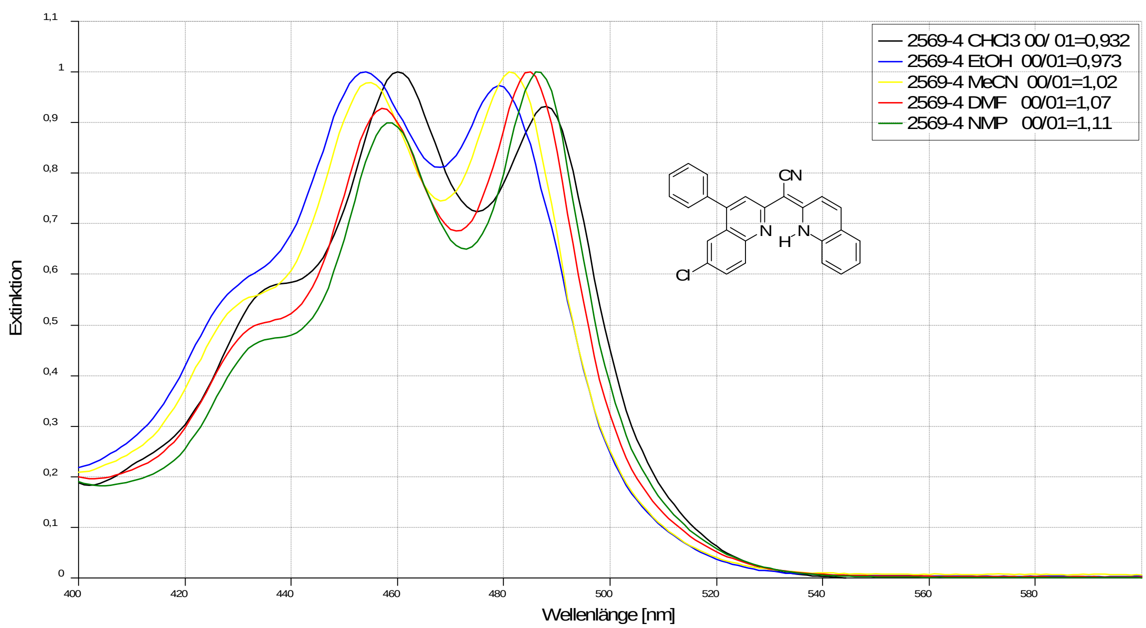


Fig 4.11 Monoprotonation/deprotonation for ***2651***

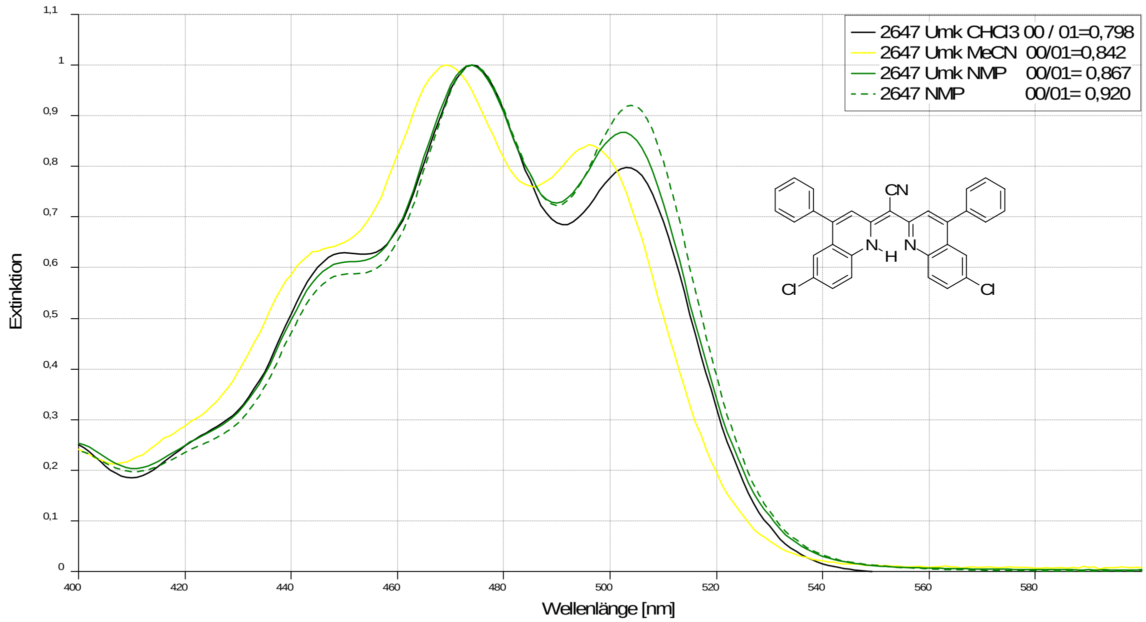
4.2.2 The Solvent Effect

Interestingly, a distinct difference of the Franck-Condon factors of the first electronic transition of the neutral form on the solvent is observed, the Franck-Condon factors varying between 0, 79 and 1, 11.
From this result, a differently strong change of the molecular geometry under electronic excitation can be derived.
The effect corresponds to the solvatochromism, well-known from typical merocyanine dyes.

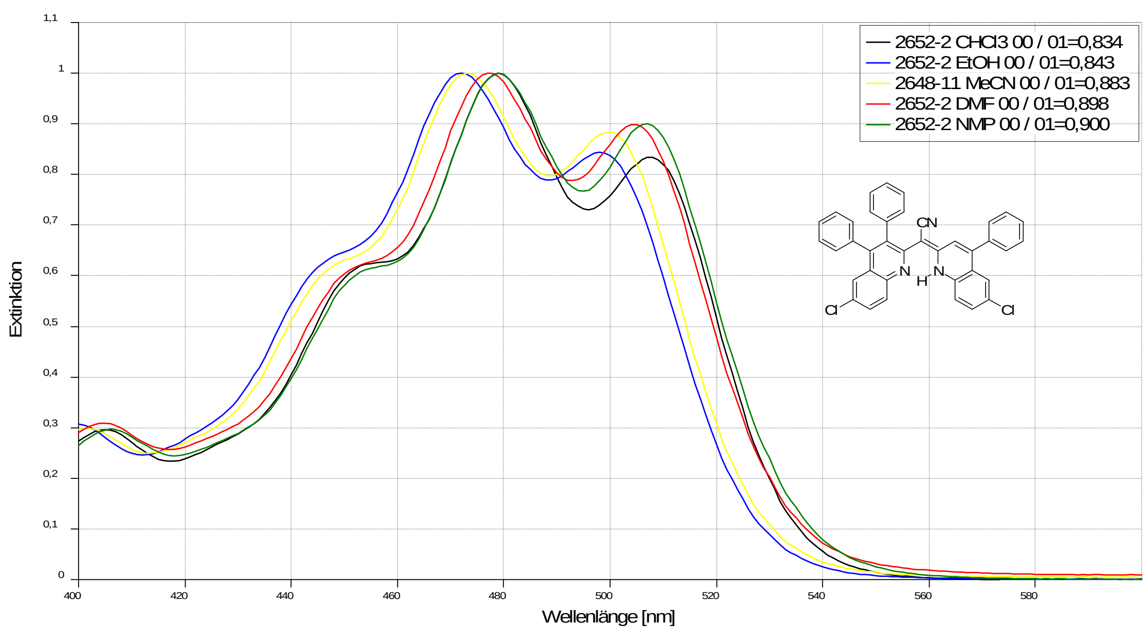
(2E)-2-(6-Chloro-4-phenylquinolin-2-yl)-2-(quinolin-2(1H)-ylidene)acetonitrile (2569)



(2E)-2-(6-Chloro-4-phenylquinolin-2(1H)-ylidene)-2-(6-chloro-4-phenylquinolin-2-yl)acetonitrile (2647)



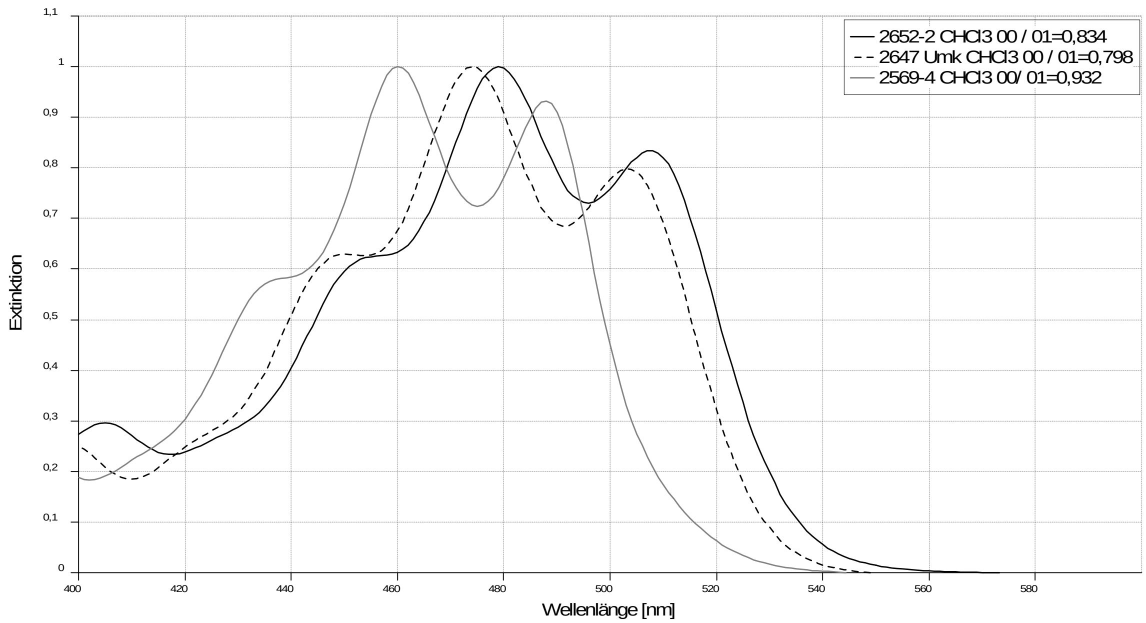
(2E)-2-(6-Chloro-3, 4-diphenylquinolin-2-yl)-2-(6-chloro-4-phenylquinolin -2(1H)-ylidene)acetonitrile (2652)



We clearly observe an increase of the Franck-Condon factor from $CHCl_3$ to NMP in all cases. **2647** has the lowest values.

4.2.3 *The Phenyl Effect*

The spectra of **2647, 2569** and **2652** in $CHCl_3$ are compared in the following figure



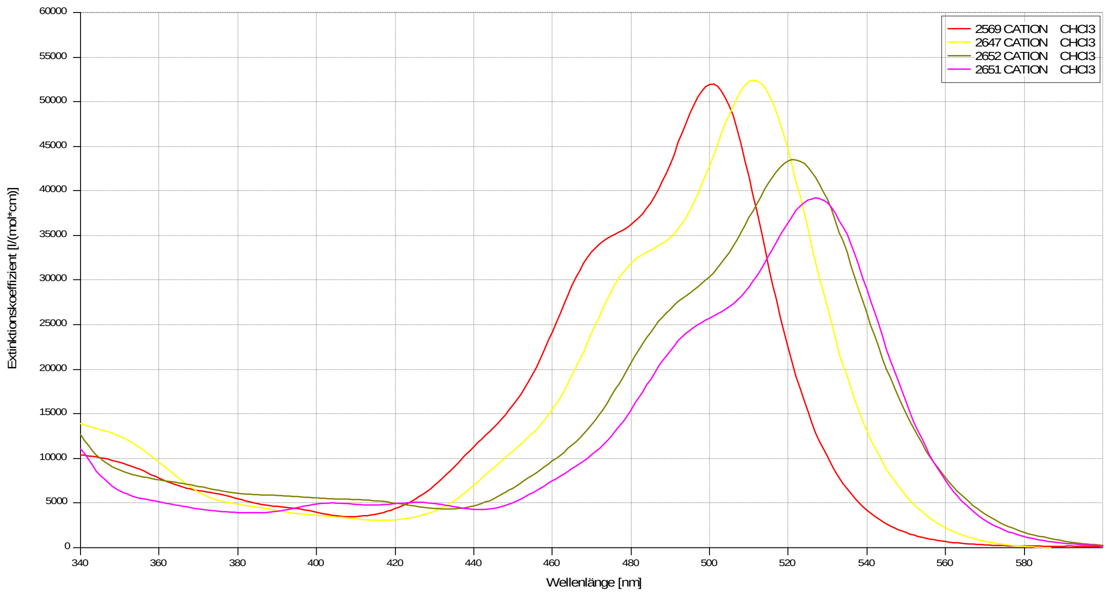
In the order **2569< 2647< 2652** a long-wavelength shift is observed**.**
This fits with the fact that more phenyl groups are introduced in this order. **2652** exhibits the highest bathochromical shift, due to the presence of three phenyl groups.

In the same order the vibronic fine structure decreases. The small extent of this effect, however, demonstrates that the steric hindrances are not strongly enhanced by the number of phenyls.

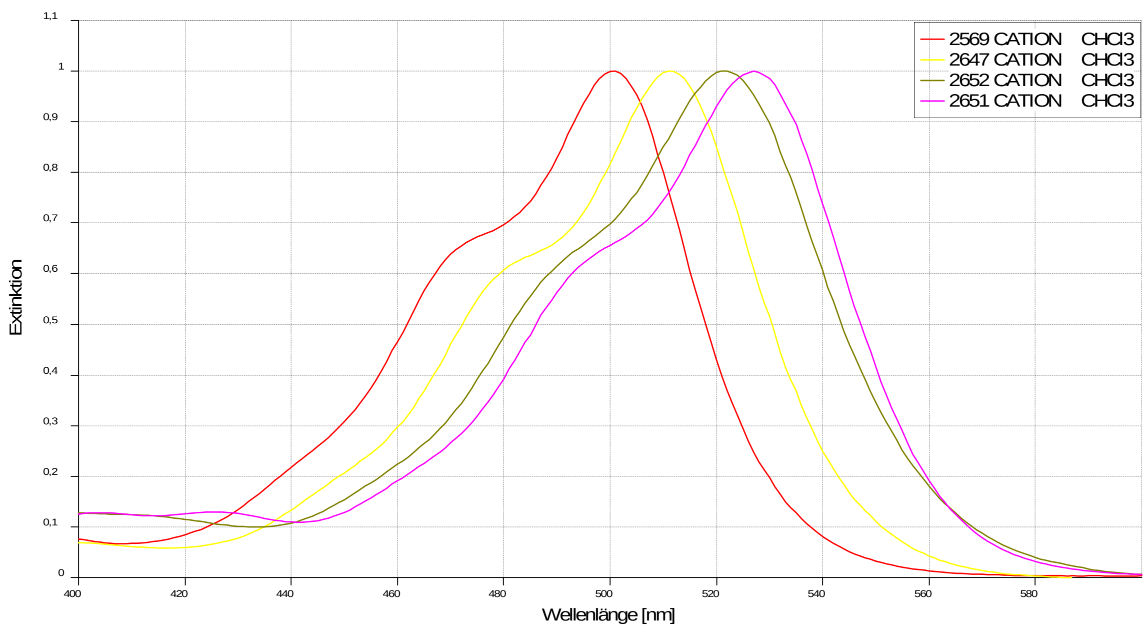
A very strong steric hindrance in **2651**, however, is the reason that in this case no trace of an H-chelate structure is detectable. The compound has the non-conjugated, "open form" **2651N.** The first electronic transition of the monoprotonated forms of **2569, 2647, 2651,** and **2652** are shown below.

(A) Spectra with the correct ε –values
(B) Spectra in the "normalized" form, i.e. the maxima of the 00-transitions are arbitrarily put on the same E value.

(A)

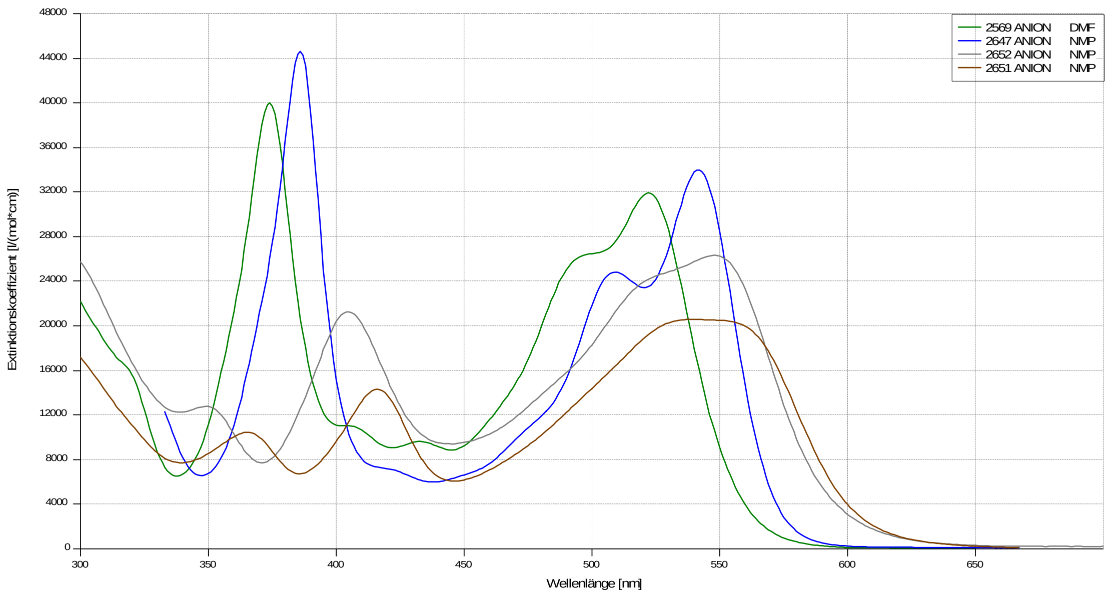


(B)

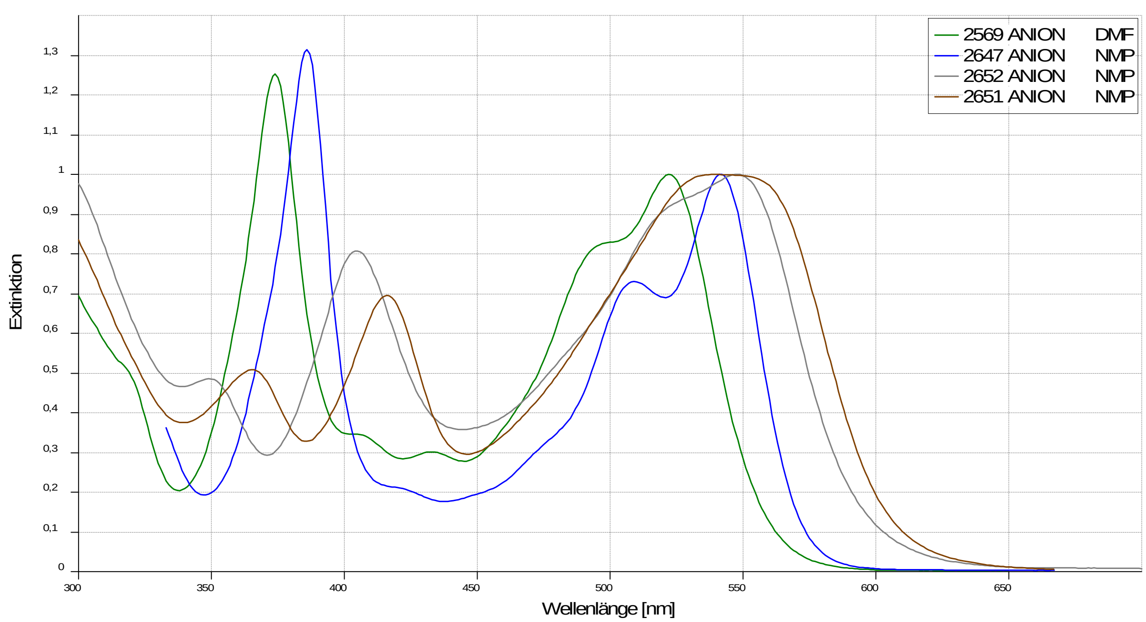


For comparison, the same representations of the anion spectra of **2569, 2647, 2651,** and **2652** are given.

(A)



(B)



4.3 Polymethines

As already mentioned, only for **2654** isolation/purification was successful. Measurements in $CHCl_3$, DMF and MeCN were done.
When we used $CHCl_3$ as solvent, protonation was made with TFA and deprotonation with pure NEt_3.

In DMF we got only the anionic form (without adding any base) and in MeCN the anion was obtained with 1% aq- NaOH and the cation with a solution of 1%H_2SO_4. The structures of the cationic and anionic forms are shown in Fig. 4.12.

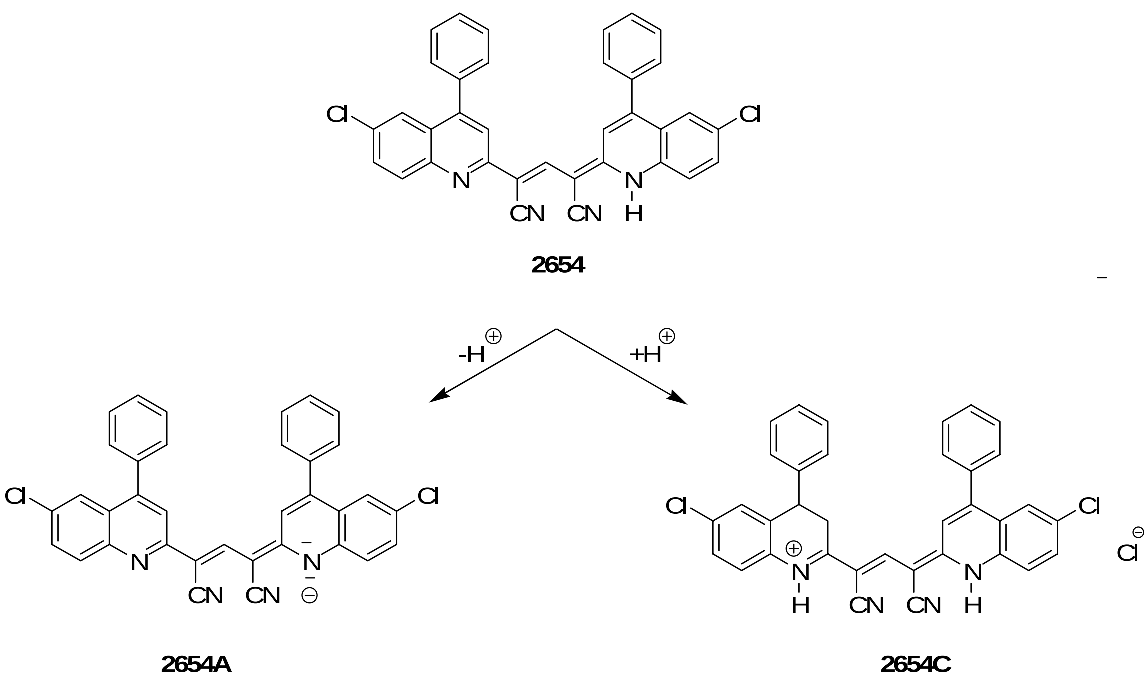
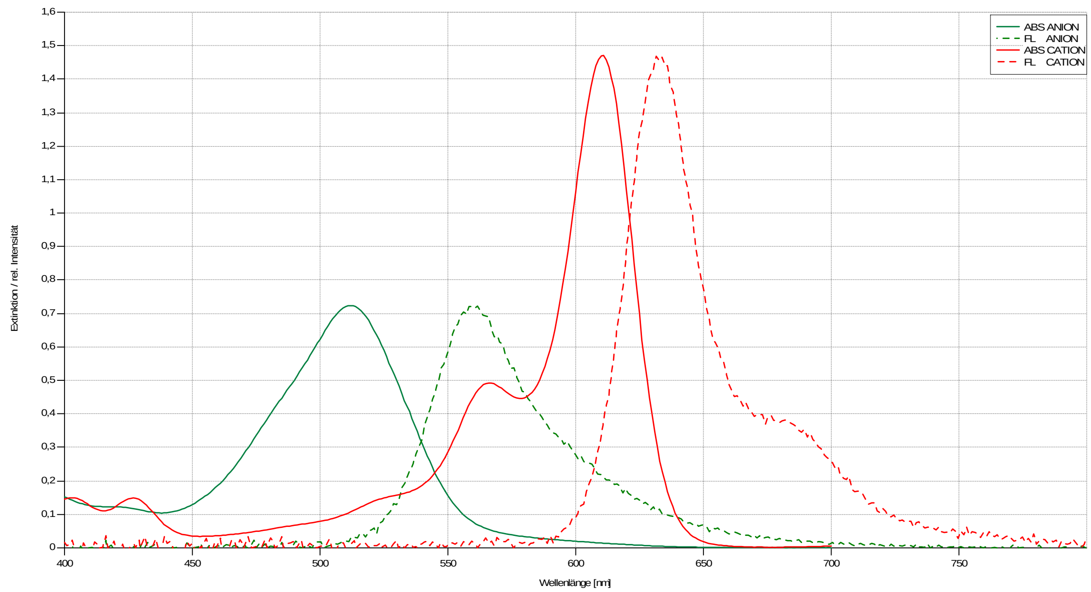
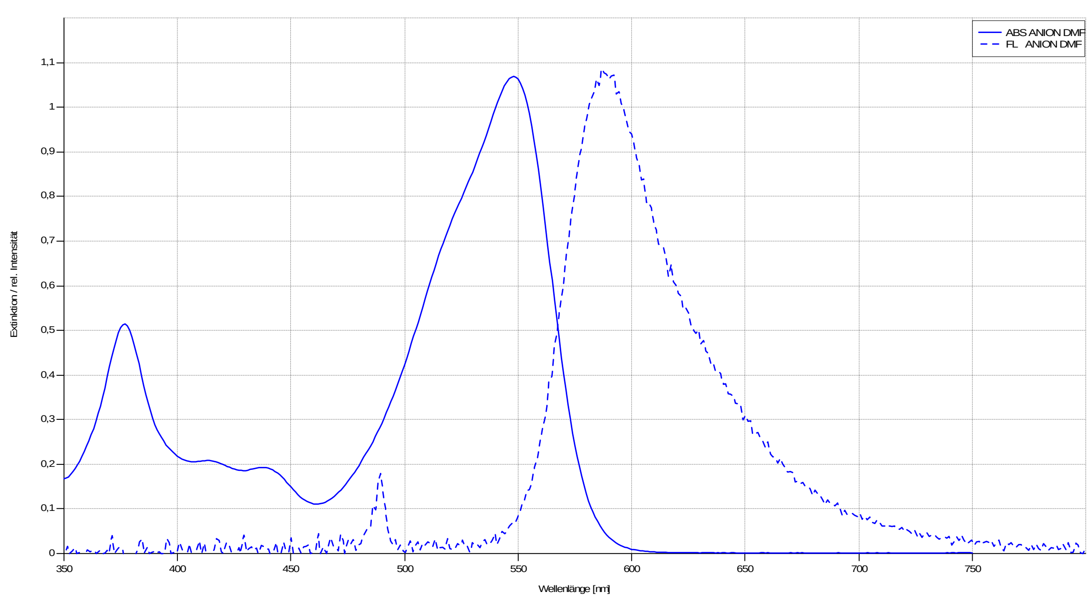


Fig. 4.12

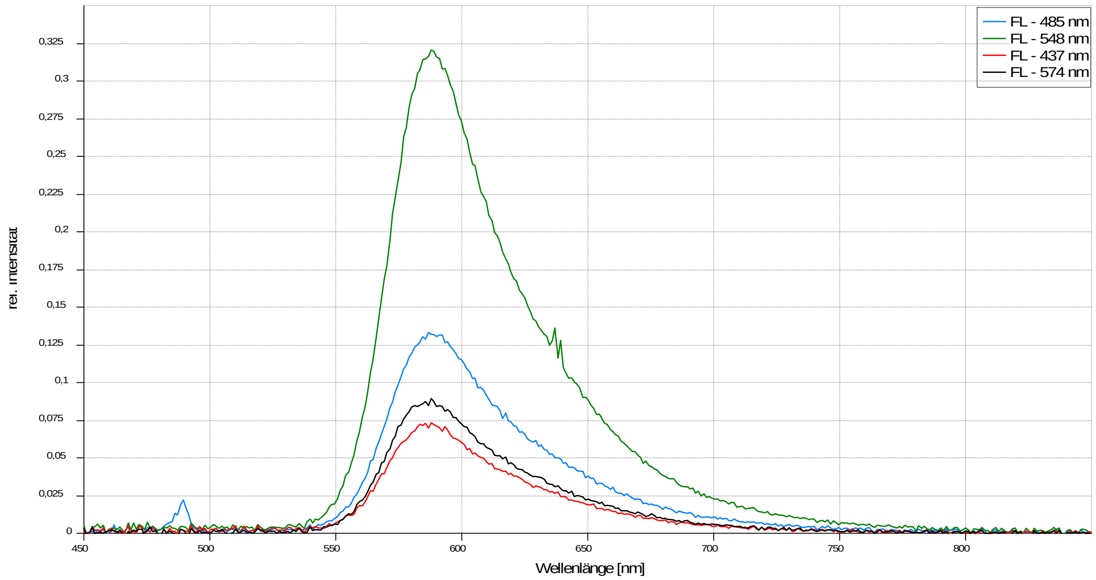
a) **2654-** spectrum in $CHCl_3$



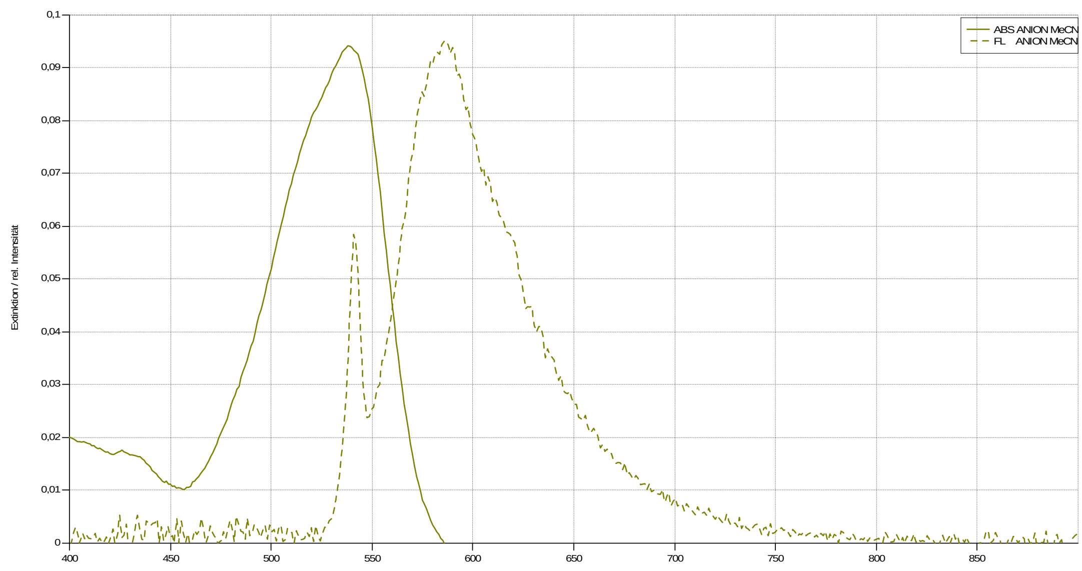
b) **2654** – spectrum in DMF



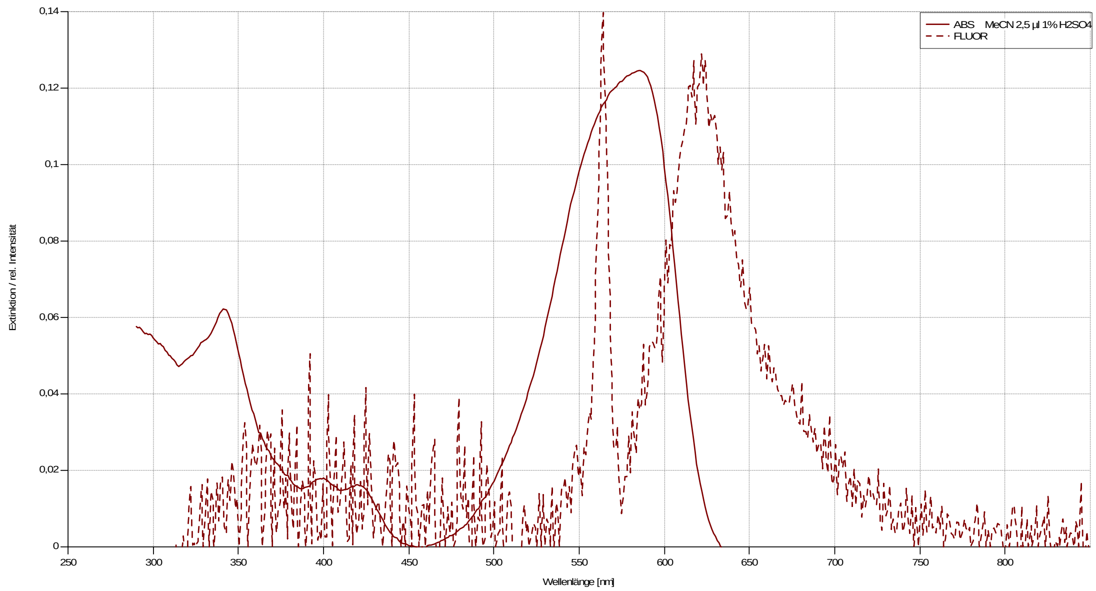
In DMF, different excitation wavelengths were used. The fluorescence spectra are shown below:



c) **2654** – spectrum in MeCN (Anion)



d) **2654**- spectrum in MeCN (Cation)



For the calculation of the fluorescence quantum yields, *Rhodamine 6G and Cz 144,* were used as standards. Spectroscopic data are summarized in Table 4.13.

	2654									
	CHCl$_3$				***DMF***		***MeCN***			
	Anion		*Cation*		*Anion*		*Anion*		*Cation*	
Standard	Φ_f (%)	λ_{exc} (nm)	Φ_f (%)	λ_{exc} (nm)	Φ_f (%)	λ_{exc} (nm)	Φ_f (%)	λ_{exc} (nm)	Φ_f (%)	λ_{exc} (nm)
Rh6G	*9 ,97*	512	*16,59*	565	*19 ,53*	548	*5, 54*	538	*1,16*	560
					19,96	574				
					13,84	437				
					12,19	485				
Cz 144	-	-	*17, 23*	565	*18, 13*	548	*3 ,94*	538	*1,20*	560
					22,02	574				

Table 4.13

In CHCl$_3$ both anionic **2654A** and cationic forms **2654C** were obtained. For the anion, highest quantum yields were obtained in DMF. In DMF only the anionic form was obtained.

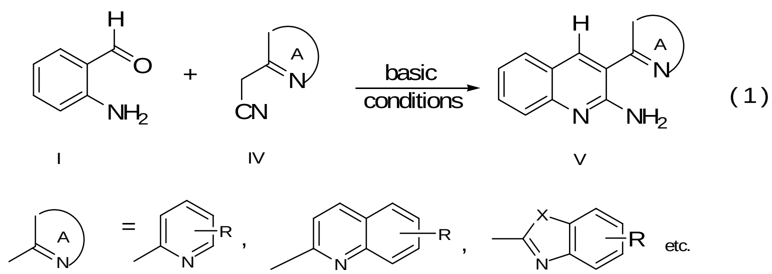
In MeCN, according to the absorption spectra, the anion is obtainable; the Φ_f value in this solvent is significantly lower than in CHCl$_3$ and DMF. With H_2SO_4 in MeCN obviously not the cation obtained in CHCl$_3$ with TFA is formed. The absorption shows a spectrum that is completely different from the absorption expected for the monocation. Thus, the low Φ_f value measured for the acid acetonitrile solution is not surprising. The reason for the different absorption could be an aggregation process.

The neutral form could not be obtained. But, independent on this fact, no r.t fluorescence of the neutral form can be expected as the chromophoric system has C_S symmetry contrary to the C_{2V} symmetry of both the cationic and anionic forms.

5 Summary

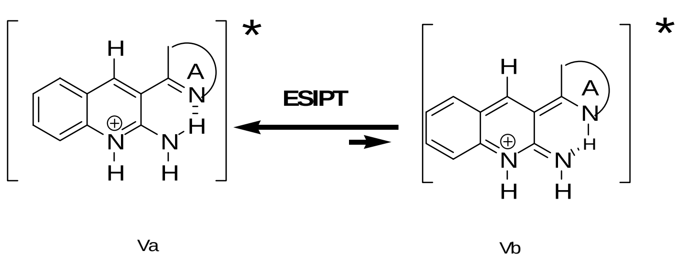
5.1 General aspects

It was known from literature that 2-aminobenzaldehyde and malononitrile or cyanacetic esters, under basic conditions, led to the formation of substituted 2-aminoquinolines [5]. In our group, this reaction type was extended to 2-heteroarylacetonitriles **IV,** yielding a series of new derivatives of type **V** [12] (Eq.1, Scheme 5.1).



Scheme 5.1 *- Synthesis of **V**;*
R= OAlk, ^{t}Butyl etc.; X= O, S etc.

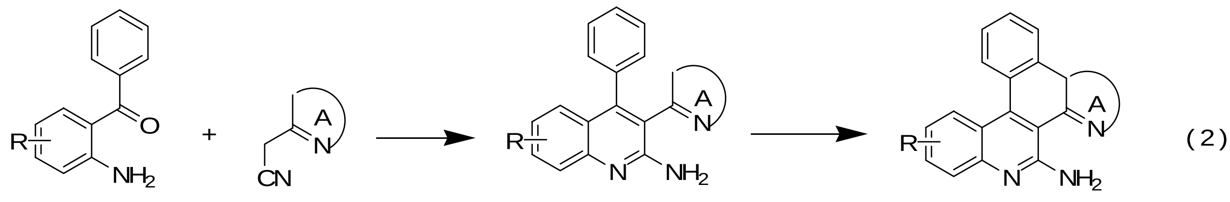
Derivatives **V** are new types of N-H…N chelates whose protonated forms show partial ESIPT (**E**xcited **S**tate **I**ntramolecular **P**roton **T**ransfer) as evidenced by r.t. fluorescence measurements [12, 13] (Scheme 5.2).



***Scheme 5.2** Tautomeric S_1 equilibria after protonation of chelates V*

Due to the fact, that both tautomers **Va**, **Vb** show room temperature fluorescence, depending on the excited state equilibrium **Va**$\rightleftharpoons$**Vb,** emission of **Va** (generally 'blue' fluorescence), of **Vb** (generally long wavelength shifted 'red' fluorescence) or of both fluorescences (i.e. dual fluorescence) can be observed.

Based on these results, a new point comes in discussion: Synthesis of types **VIII.** This was the main task of this work. Here, as starting material, 2-aminobenzophenones **VI** are reasonable (Eq.2, Scheme 5.3).



VI IV VIII VIII-1

Scheme 5.3 *Condensation reaction using* ***VI***

Such attempts to use the ketones **VI** instead of the aldehydes **I** were unsuccessful up-to-date [12]. Compounds **VIII** were of interest regarding the influence of the phenyl group on both the fluorescence quantum yields and the extent of ESIPT. Moreover, the principal possibility to transform **VIII** into the ring closed derivatives **VIII-1** is of particular importance. From all experiences, derivatives **VIII-1,** due to their rigidity, should show much higher r.t. fluorescences than **VIII.**

5.2 Results

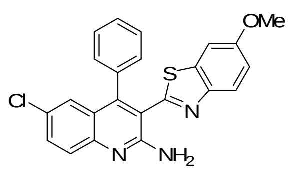
The strongly reduced reactivity of ketones compared with aldehydes afforded significantly more drastic reaction conditions. After intense search of satisfying synthetic methods, a series of the desired chelates **VIII** could be synthesized:

- It could be demonstrated, that contrary to Kammerer' results the reaction between **VI** and **IV** can be realized.
- Due to the drastic reaction conditions (**IV** was partially decomposed, **VI** gave side reactions) problems could not be avoided.

In detail, the derivatives **VIII** with the cyanomethylheterocycles

2-quinolinylacetonitrile (→ **2A**), 2-pyridinylacetonitrile (→ **3A**), substituted 2-pyridinylacetonitrile (**3C, 3D**), 2-benzimidazolylacetonitrile (→ **4A**), 2-benzthiazolylacetonitrile (→ **4C**), substituted 2-benzothiazolylacetonitrile (→**4E**), 2-benzoxazolylacetonitrile (→ **4D**), 2-naphthothiazolylacetonitrile (→ **4I**) were synthesized and characterized by elemental analyses, ^{1}H-NMR and EI-mass spectra.

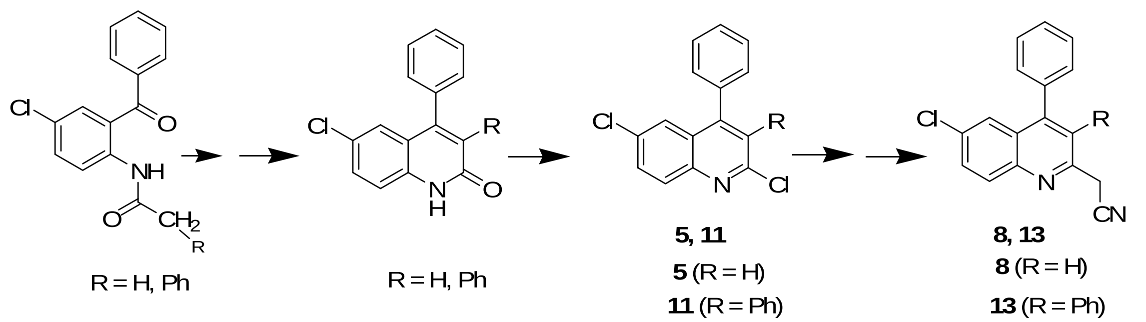
For a more detailed characterization, both UV/vis and fluorescence spectra of the neutral and the protonated compounds have been measured. Fluorescence quantum yields determinations showed generally dual fluorescence with low Φ_f values and low extend of ESIPT. The highest r.t. Φ_f was obtained for the protonated form of **4E** (Φ_f = 44%). This result is not surprising, as by a strong π-donation effect of the methoxy group, the structure becomes more rigid in the excited state. Thus, the fluorescence quantum yield increases.



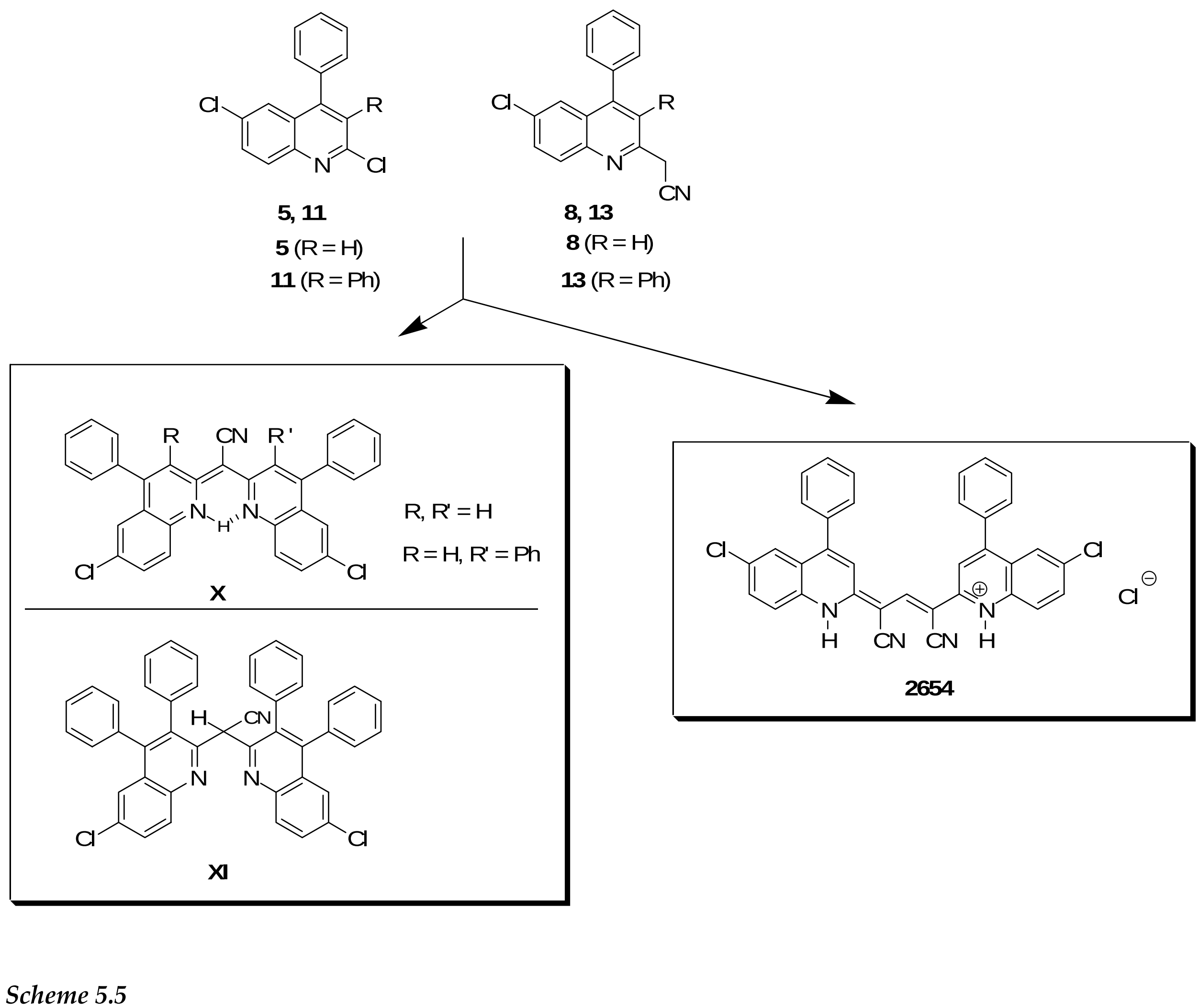
4E

The analysis of the condensation products (Scheme 5.3) showed that the 2-aminobenzophenones are ring closed to the corresponding acridone derivatives. In order to avoid this ring closure reaction, we made the N-acetyl derivatives of the starting 2-aminobenzophenone, but these compounds gave ring closure to the corresponding quinoline derivatives (Scheme 5.4).
By this method, the new quinoline derivatives **5**, **8** (**11, 13**) were obtained. These compounds are starting materials for the new compounds **X** (**XI**) and the *polymethine* **2654** (Scheme 5.5).

The compound with R=R’=Ph, because of steric effects, has the structure **XI**.



Scheme 5.4 *Starting materials* ***5, 8, 11, 13.***



Scheme 5.5

6 Zusammenfassung

2-Aminobenzaldehyd und Malodinitril bzw. Cyanessigester reagieren unter basischen Reaktionsbedienungen zu 2-Aminochinolinen [5]. Diese Reaktion läßt sich auf die verschiedensten 2-Heteroarylacetonitrile **V** übertragen [12] (Abbildung 6.1).

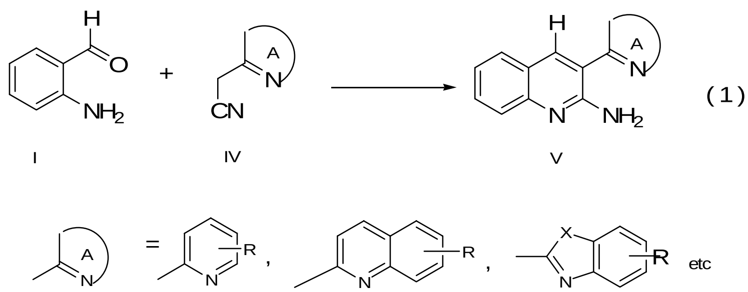
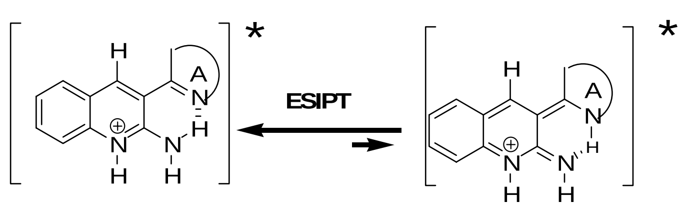


***Abbildung 6.1** – Synthese von **V**;*
R= OAlk, ᵗButyl etc.; X= O, S etc

Die so erhältlichen Verbindungen **V** sind neue Typen unsymmetrisch gebauter N-H...N Chelate. Die protonierte Form dieser Chelate zeigt partiellen ESIPT (**E**xcited **S**tate **I**ntramolecular **P**roton **T**ransfer), wie RT- Fluoreszenzmessungen zeigten [12,13]. Da Lösungen der beiden Tautomeren **Va, Vb** bereits bei RT fluoreszieren, kann abhängig von dem im ersten angeregten Elektronenzustand vorliegenden Gleichgewicht **Va** $\rightleftharpoons$ **Vb**, Fluoreszenz von **Va** (i.a. “blaue“ Fluoreszenz), von **Vb** (langwellig verschobene, i.a. “rote“ Fluoreszenz) oder von beiden Tautomeren **Va, Vb**, d.h. Dualfluoreszenz, beobachtet werden (Abbildung 6.2).



Va Vb

Abbildung 6.2

Aufgabe dieser Arbeit war die Übertragung der Reaktion (1) auf 2-Aminobenzophenone **VI** (Gl. 2) (Abbildung 6.3).

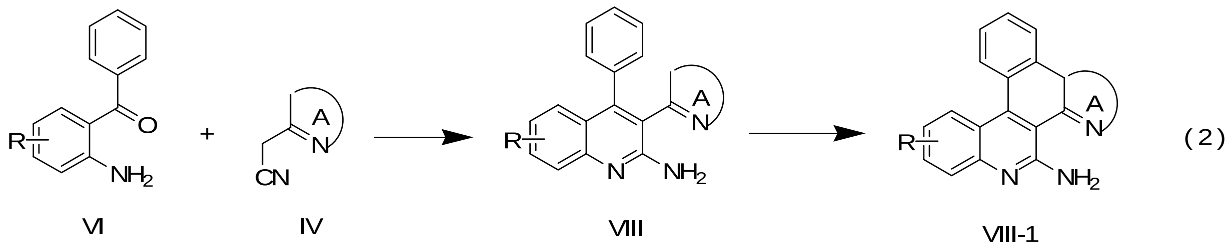


Abbildung 6.3

Bislang unternommene Versuche die Ketone anstelle der Aldehyde **I** einzusetzen verliefen allesamt negativ [12]. Verbindungen von Typ **VIII** sind von Interesse für das Studium des Effektes einer Phenylsubstitution auf die Fluoreszenzquantenausbeuten Φ_f und die Lage des Tautomerengleichgewichtes im S_0- und S_1-Zustand.
Außerdem sollte der Ringschluß zu **VIII-1** - starre Verbindungen mit entsprechend signifikant höheren RT-Fluoreszenzquantenausbeuten ergeben.

Es war von vornherein klar, daß die stark reduzierte Aktivität von Ketonen (verglichen mit Aldehyden) wesentlich drastischere Reaktionsbedingungen erfordern würde. Nach vielen Versuchen konnten schließlich geeignete Reaktionsbedingungen für die Synthese der gewünschten Chelate **VIII** (siedendes Pyridin, Natrium *tert*-Butylat, Ar) gefunden werden.
Im einzelnen wurden die Derivate **VIII** mit den Heterozyklen Chinolin (**2A**), Pyridin (**3A, 3C, 3D**), Benzimidazol (**4A**), Benzthiazol (**4C, 4E**) und Naphthothiazol (**4I**) dargestellt. Die Struktur der Verbindungen wurde durch Elementaranalysen, 400 MHz ^{1}H-NMR Spektren sowie EI-Massenspektren bewiesen. Somit gelang – entgegen der früheren Ergebnisse von Kammerer [12] – die Umsetzung von **VI** mit den heteroaromatischen Acetonitrilen **IV.**
Unbefriedigende Reaktionsausbeuten sind auf die notwendigen drastischen Reaktionsbedienungen zurückzuführen, die zu Zersetzung der eingesetzten 2-Heteroarylacetonitrile führten. Außerdem gelang es nicht, Nebenreaktionen des Aminobenzophenons (u.a. Ringschluß zum Acridon) völlig zu unterdrücken.

Detaillierte Untersuchungen der UV/vis- und Fluoreszenzspektren zeigen, daß mit Außnahme von **4E** alle synthetisierten Verbindungen **VIII** im protonierten Zustand Dualfluoreszenz zeigen. Aus dem Vergleich mit den entsprechenden phenylfreien Verbindungen [12] geht hervor, daß 4-Phenylsubstitution keinen signifikanten Einfluß auf die Fluoreszenzquantenausbeuten und den ESIPT - Prozess hat.
Die Verbindungen **2A, 3A, 3C, 3D, 4A, 4B, 4C, 4D** und **4I** zeigen, wie die 4-phenylfreien Verbindungen, Dualfluoreszenz mit niedrigen Φ_f Werten und nur geringen ESIPT - Prozess.
Das 4-Methoxy-substituierte Benzthiazolderivat **4E** zeigt keinen ESIPT, dafür aber die mit Abstand höchste RT-Fluoreszenzquantenausbeute (Φ_f = 44% in EtOH). Die wesentlich höhere Φ_f ist als Folge der wesentlich höheren S_1-Rotationsbarriere (π-Donator-Effekt der Methoxygruppe) leicht verständlich.

Um die Ringschlußreaktion des Aminoketones zum Acridon zu vermeiden, wurden die N-Acylverbindungen hergestellt und in die Kondensationsreaktion (2) eingesetzt. Dabei zeigte sich, daß Chinolinringschluß erfolgt. Dieses Ergebnis wurde dann verwendet, um aus dem N-Acetyl- bzw N-Phenylacetyl-aminobenzophenon gezielt die 4-Phenyl- bzw. 3,4-Diphenylchinolinderivate **5**, **11** bzw. **8,13** darzustellen (Abbildung 6.4).

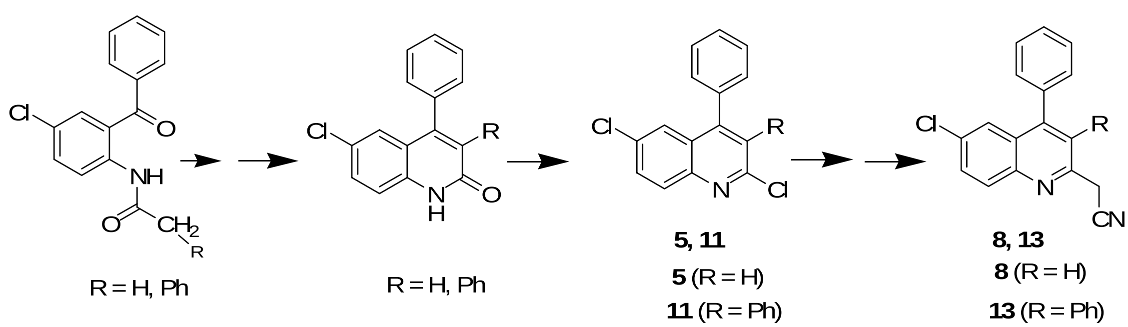


Abbildung 6.4

Umsetzung von **5** bzw. **11** mit **8** bzw. **13** ergibt die H-Chelate **X**.
Für R = R′ = Ph liegt **X** aus sterischen Gründen in der nicht-konjugierten CH-Struktur **XI** vor (Abbildung 6.5). Durch Umsetzung von **8** mit dem *Vilsmeier-Reagenz* konnte **2654** erhalten werden.

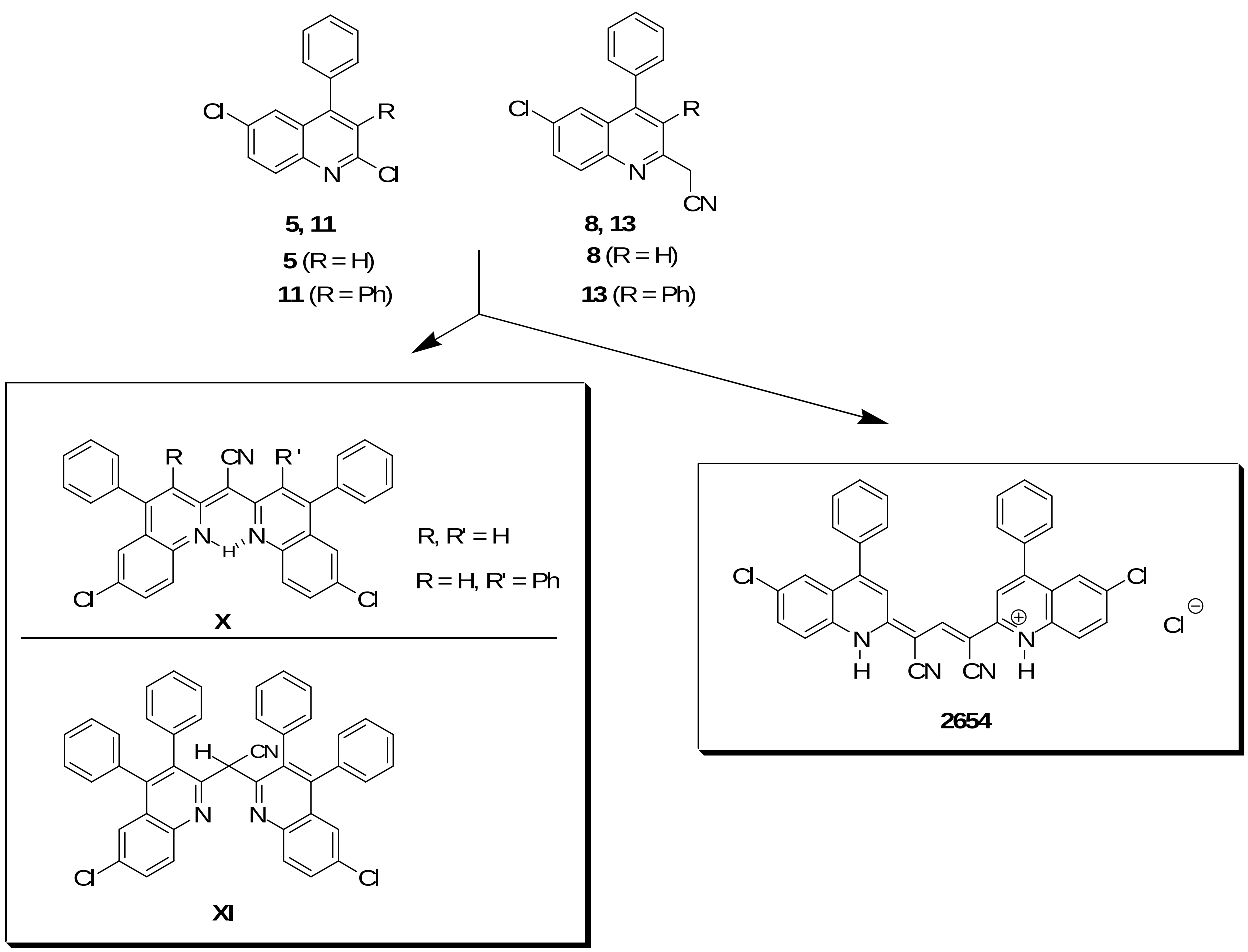


Abbildung 6.5

7 Experimental Part

7.1 General aspects

* Preparative chromatography was carried out on *Silica Gel 60* and analytical thin layer chromatography (TLC) on *Silicagel 60 F_{254}* , both products of **Merck**.

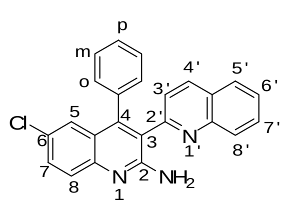
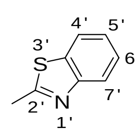
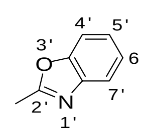
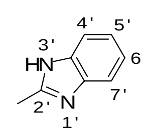
* UV/vis absorption spectra were recorded using a *Cary 50 Bio* **Varian**. Fluorescence spectra were measured on a spectrometer designed in our group by F. Menges [55].

* Elementary analyses (CHN) were carried out on a *vario EL* **Elementar.** The experimental values are given in brackets.

* EI-MS spectra were performed with a *vario EL* **Elementar**.

* ^{1}H-NMR-spectra were obtained on a *JEOL JNM-GX 400* (400MHz). Tetramethylsilane (TMS) was used as internal standard.

For simplification and regarding the importance of the nitrogen atom N1′ in ESIPT, for the systems *benzoxazole* and *benzimidazole* the numbering is given (despite the priority *ONS* and *HN* before *N*) as in the case of *benzthiazole* system:

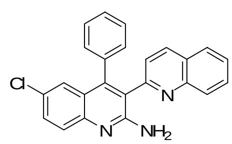
7.2 Systems with Dual Fluorescence

7.2.1 The General Synthesis Method

All systems were synthesized according to the following method ("*the optimized method* Chapter 2 p13) and worked up according to Scheme 2.7 p13.

*A mixture of 2-(quinolin-2-yl) acetonitrile **2AE** (20mmole), sodium tert-butoxide (20mmole) in 30ml pyridine was stirred at room temperature for 15 min and slowly heated for another 15 min under inert atmosphere(argon).*
*Then a solution of 2-Amino-5-chlorobenzophenone **IX** (20mmole) dissolved in20ml pyridine was added dropwise to the hot mixture.*
Heating under reflux for 5h is the next step.

7.2.2 6-Chloro-4-phenyl-3-(quinolin-2-yl)quinolin-2-amine (2A)

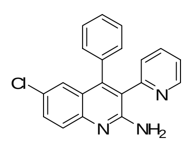


6, 7 g (40 mmol) **2AE1**, 3, 84 g (40 mmol) NaO^tBu and 9, 26 g (40 mmol) **IX** were reacted according to the general synthesis method.

Raw yield: 5, 73 g (15mmol) ≅ 37.5%
Formula: $C_{24}H_{16}ClN_3$
Mol.Wt.: 381,8
Elem. Anal. found (calculated): C 75.51 (75.49); H 4.30 (4.22); N 11.00 (11.00)
UV/Vis Absorption (EtOH): λ_{max} =364nm; $\lambda_{max}(H^+)$ = 348nm; $\lambda_{max}(2H^+)$ = 324nm
Molar extinction coefficient (EtOH): ε_{max} = 6946 $M^{-1}cm^{-1}$;
ε_{max} (H^+) =11530$M^{-1}cm^{-1}$; ε_{max} $(2H^+)$ = 12110 $M^{-1}cm^{-1}$
Fluorescence (EtOH): λ_{max} = 454nm; $\lambda_{1,max}$ (H^+)= 422nm; $\lambda_{2,max}(H^+)$ = 634nm; $\lambda_{max}(2H^+)$=475nm

UV/Vis Absorption ($CHCl_3$): λ_{max}=366nm; $\lambda_{max}(H^+)$ = 328nm; $\lambda_{max}(2H^+)$ = 341nm
Molar extinction coefficient ($CHCl_3$): ε_{max} = 6423 $M^{-1}cm^{-1}$;
ε_{max} (H^+)=14010$M^{-1}cm^{-1}$, ε_{max} $(2H^+)$ = 13260 $M^{-1}cm^{-1}$
Fluorescence ($CHCl_3$): λ_{max} = 422nm; $\lambda_{1,max}$ (H^+)= 458nm; $\lambda_{2,max}(H^+)$ = 627nm; $\lambda_{max}(2H^+)$=475nm
EI-MS: m/z 384.1 (10.95%), 383.2 (38.58%), 382.2 (61.48%), 381.1 (100%), 380.1 (98.48%)
^{1}H-NMR ($CDCl_3$ r.t.), δ **[ppm]**: 5.70 (s, br. 2H, NH_2), 6.91 (d, J=8.54 Hz, 1H, H3′), 7.21 (m, 2H, m-H), 7.28 (m, 3H, o,p-H), 7.45 (d, J=2.44 Hz, 1H, H5), 7.53 (dd, ^{4}J=2.44 Hz, ^{3}J=8.79 Hz, 1H, H7), 7.56 (m, J=7.55 Hz, 1H, H6′), 7.69(d, J=8.79 Hz, 1H, H8), 7.74 (d, J=7.55 Hz, 1H, H5′), 7.74 (m, J=8.30 Hz, 1H, H7′), 7.83 (d, J=8.54 Hz, 1H, H4′), 8.10 (d, J=8.30 Hz, 1H, H8′)

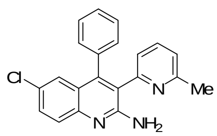
7.2.3 6-Chloro-4-phenyl-3-(pyridin-2-yl)quinolin-2-amine(3A)



2, 36 g (20 mmol) **3AE1**, 1, 92 g(20 mmol) NaO^{t}Bu and 4,63 g(20 mmol) **IX** were reacted according to the general synthesis method.
Raw yield: 3, 16 g (9, 52 mmol) ≅ 47.6%
Formula: $C_{20}H_{14}ClN_3$
Mol.Wt.: 331,8 g/mol
UV/Vis Absorption (EtOH): λ_{max}=359nm; $\lambda_{max}(H^+)$ = 348nm; $\lambda_{max}(2H^+)$ = 356nm
Molar extinction coefficient (EtOH): ε_{max} = 5885 $M^{-1}cm^{-1}$; ε_{max} (H^+)=8529$M^{-1}cm^{-1}$
ε_{max} $(2H^+)$ = 7143 $M^{-1}cm^{-1}$
Fluorescence (EtOH): λ_{max} = 420nm; $\lambda_{1,max}$ (H^+)= 420nm; $\lambda_{2,max}(H^+)$ = 580nm; $\lambda_{max}(2H^+)$=443nm
UV/Vis Absorption ($CHCl_3$): λ_{max}=360nm; $\lambda_{max}(H^+)$ = 356nm; $\lambda_{max}(2H^+)$ = 362nm

Molar extinction coefficient ($CHCl_3$): ε_{max} = 5740 $M^{-1}cm^{-1}$;
ε_{max} (H^+) =7786$M^{-1}cm^{-1}$ ε_{max} ($2H^+$) = 7107 $M^{-1}cm^{-1}$
Fluorescence ($CHCl_3$): λ_{max} = 415nm; $\lambda_{1, max}$ (H^+) = 439nm; $\lambda_{2, max}$ (H^+) = 588nm; λ_{max}($2H^+$)=453nm
EI-MS: m/z 334.3 (89%), 333.3 (35.02%), 332.3 (40.23%), 331.3 (100%), 330.3 (51%)
^{1}H-NMR (DMSO, 100 ^{0}C), δ **[ppm]**: 5.91 (s br., 2H, NH_2), 7.00 (d, J=7.34 Hz, 1H, H3'), 7.14 (d, J=2.44 Hz, 1H, H5), 7.14 (m, 2H, m-H), 7.19 (m, ^{3}J=4.4 Hz, ^{3}J=6.84 Hz, 1H, H5') 7.31 (m, 3H, o,p-H), 7.51 (dd, ^{3}J=9.04 Hz, ^{4}J=2.44 Hz, 1H, H7), 7.55 (t, ^{3}J=6.84 Hz, ^{3}J=7.34 Hz, 1H, H4'), 7.62 (d, J=9.04 Hz, 1H, H8), 8.57 (d, J=4.4 Hz, 1H, H6').

7.2.4 6-Chloro-3-(6-methylpyridin-2-yl) 4-phenylquinolin-2-amine (3C)

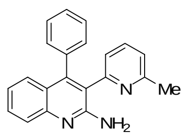


8, 00 g (60 mmol) **3CE1**, 6, 00 g(60 mmol) NaO^{t}Bu and 11 g(60 mmol) **IX** were reacted according to the general synthesis method.

Raw yield: 6, 06 g (17, 52 mmol) ≅ 29%
Formula: $C_{21}H_{16}ClN_3$
Mol.Wt.: 345,8 g/mol
Elem. Anal. found (calculated): C 73.00 (72.93); H 4.86 (4.66); N 12.20 (12.15)
UV/Vis Absorption (EtOH): λ_{max}=360nm; λ_{max}(H^+) = 348nm; λ_{max}($2H^+$) = 356nm
Molar extinction coefficient (EtOH): ε_{max} = 5991 $M^{-1}cm^{-1}$; ε_{max} (H^+) =8853$M^{-1}cm^{-1}$ ε_{max} ($2H^+$) = 7429 $M^{-1}cm^{-1}$
Fluorescence (EtOH): λ_{max} = 428nm; $\lambda_{1,max}$ (H^+)= 415nm; $\lambda_{2,max}$(H^+) = 567nm; λ_{max}($2H^+$)=438nm
EI-MS: m/z 348.3 (7.87%), 347.3 (32.65%), 346.3 (41.59%), 345.3 (100%), 344.3 (59.09%), 330.3 (1.21%)
^{1}H-NMR ($CDCl_3$), δ **[ppm]**: 2.58 (s, 3H, CH_3), 5.51 (s br., 2H, NH_2), 6.65 (d, J=7.81 Hz, 1H, H5'), 6.97 (d, J=7.81 Hz, 1H, H3'), 7.16 (m, 2H, m-H), 7.29 (t, J= 7.81 Hz,

J=7.81 Hz, 1H, H4'), 7.31 (m, 3H, o,p-H), 7.38 (d, J= 2.2 – 2.4 Hz, 1H, H5), 7.50 (dd, ^{4}J=2.2 – 2.4 Hz, ^{3}J=8.8 – 8.9 Hz, 1H, H7), 7.67 (d, J=8.8 – 8.9 Hz, 1H, H8).

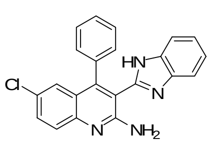
7.2.5 3-(6-Methylpyridin-2-yl)-4-phenylquinolin-2-amine (3D)



2, 00 g (15 mmol) **3DE1**, 0, 92 g(10 mmol) NaO^{t}Bu and 2 g(10 mmol) **IX** were reacted according to the general synthesis method.

Raw yield: 1, 5 g (4, 8 mmol) ≅ 32%
Formula: $C_{21}H_{17}N_3$
Mol.Wt.: 311,38 g/mol
Elem. Anal. found (calculated): C 81.04 (81.00); H 5.66 (5.50); N 13.20 (13.49)
UV/Vis Absorption (EtOH): λ_{max}=347nm; $\lambda_{max}(H^+)$ = 338nm; $\lambda_{max}(2H^+)$ = 346nm
Molar extinction coefficient (EtOH): ε_{max} = 5066 $M^{-1}cm^{-1}$; ε_{max} (H^+) =8913$M^{-1}cm^{-1}$
ε_{max} $(2H^+)$ = 7055 $M^{-1}cm^{-1}$
Fluorescence (EtOH): λ_{max} = 425nm; $\lambda_{1,max}$ (H^+)= 406nm; $\lambda_{2,max}(H^+)$ = 557nm; $\lambda_{max}(2H^+)$=430nm
EI-MS: m/z 312.3 (37.04%), 311.3 (100%), 310.3 (80.8%).

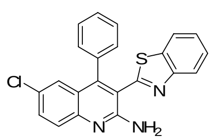
7.2.6 3-(1H-Benzo[d]imidazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4A)



3, 14 g (20 mmol) **4AE1**, 2, 88 g(30 mmol) NaO^{t}Bu and 4,6 g(20 mmol) **IX** were reacted according to the general synthesis method.
Reaction time: 10hr

Raw yield: 4, 08 g (11 mmol) ≅ 55%
Formula: $C_{22}H_{15}ClN_4$
Mol.Wt.: 370,8 g/mol
Elem. Anal. found (calculated): C 71.36 (71.25); H 4.06 (4.08); N 15.05 (15.11)
UV/Vis Absorption (EtOH): λ_{max}=367nm; $\lambda_{max}(H^+)$ = 369nm;
$\lambda_{max}(OH^-)$ = 359nm
Molar extinction coefficient (EtOH): ε_{max} = 6795 $M^{-1}cm^{-1}$; ε_{max} (H^+)=8196$M^{-1}cm^{-1}$
ε_{max} (OH^-) = 9814 $M^{-1}cm^{-1}$
Fluorescence (EtOH): λ_{max} = 449nm; λ_{max} (H^+)= 503nm; $\lambda_{max}(OH^-)$ = 359nm
EI-MS: m/z 373.2 (34.91%), 372.2 (43.04%), 370.2 (100%), 369.2 (54.39%)
^{1}H-NMR (DMSO-D$_6$ 80 ^{0}C), δ **[ppm]**: 6.47 (s br., 2H, NH_2), 7.1 – 7.15 (m, 2H, H5'/H6'), 7.18 (d, 1H, H5), 7.29 (m, 2H, m-H), 7.35 (m, 3H, o,p-H), 7.45 (m br, 1H, H7'), 7.45 (m br., 1H, H4') 7.58 (dd, 1H, H7), 7.63 (d, 1H, H8), 11.67 (s br., 1H, N3').

7.2.7 3-(Benzo[d]thiazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4C)

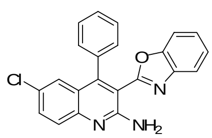


3, 4 g (20 mmol) **4CE1**, 2, 00 g(20 mmol) NaO^{t}Bu and 4,6 g(20 mmol) **IX** were reacted according to the general synthesis method.

Raw yield: 3, 35 g (8, 65 mmol) ≅ 43%
Formula: $C_{22}H_{14}ClN_3S$
Mol.Wt.: 387,0 g/mol
Elem. Anal. found (calculated): C 68.11 (68.12); H 3.79 (3.64); N 10.59 (10.83);
UV/Vis Absorption (EtOH): λ_{max}=384nm; $\lambda_{max}(H^+)$ = 380nm; $\lambda_{max}(2H^+)$ = 380nm
Molar extinction coefficient (EtOH): ε_{max} = 6245 $M^{-1}cm^{-1}$;
ε_{max} (H^+)=13340$M^{-1}cm^{-1}$, ε_{max} $(2H^+)$ = 12 790 $M^{-1}cm^{-1}$
Fluorescence(EtOH): λ_{max} = 453nm; $\lambda_{1,max}$ (H^+)= 417nm; $\lambda_{2,max}(H^+)$ = 615nm;
$\lambda_{1,max}(2H^+)$=417nm , $\lambda_{2,max}(2H^+)$=622nm

EI-MS: m/z: 390.1 (10.85%), 389.1 (38.90%), 388.1 (40.41%), 387.2 (100%), 386.1 (40.83%), 355.2 (7.77%), 354.2 (25.60%)
^{1}H-NMR (DMSO-D$_6$ 100 ^{0}C), δ **[ppm]**: 6.99 (s br., 2H, NH_2), 7.10 (d, 1H, H5), 7.35 (m, 2H, m-H), 7.47 (m, 3H, o,p-H), 7.39 (t, 1H, H5'), 7.48 (t, 1H, H6'), 7.50 (dd, 1H, H7), 7.62 (d, 1H, H8), 7.9 (d, 1H, H4'), 8.05 (d, 1H, H7').

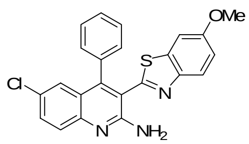
7.2.8 3-(Benzo[d]oxazol-2-yl)-6-chloro-4-phenylquinolin-2-amine (4D)



3, 0 g (20 mmol) **4DE1**, 2, 0 g (20 mmol) NaO^{t}Bu and 4,6 g(20 mmol) **IX** were reacted according to the general synthesis method.

Raw yield: 3, 88 g (10, 43 mmol) ≅ 52%
Formula: $C_{22}H_{14}ClN_3O$
Mol.Wt.: 371,8 g/mol
Elem. Anal. found (calculated): C 70.86 (71.07); H 3.90 (3.80); N 11.20 (11.30);
UV/Vis Absorption (EtOH): λ_{max} =393nm; $\lambda_{max}(H^+)$ = 376nm;
Molar extinction coefficient (EtOH): ε_{max} = 7120 $M^{-1}cm^{-1}$;
ε_{max} (H^+) = 13550$M^{-1}cm^{-1}$
Fluorescence (EtOH): λ_{max} = 470nm; $\lambda_{1,max}$ (H^+)= 442nm; $\lambda_{2,max}(H^+)$ = 617nm;
EI-MS: m/z 374.2 (9.87%), 373.2 (40.03%), 372.2 (29.54), 371.2 (100%), 370.2 (3.85%), 357.2 (8.22%) 350.2 (33.50%), 355.2 (24.65%), 354.3 (91.41%)
^{1}H-NMR ($CDCl_3$), δ **[ppm]**: 6.86 (s br., 2H, NH_2), 7.06 (d, 1H, H4'), 7.25 (t, 1H, H5'), 7.31 (t, 1H, H6'), 7.31 (m, 2H, m-H), 7.47 (m, 3H, o,p-H), 7.34 (d, J=2.44 Hz, 1H, H5), 7.54 (dd, ^{4}J=2.44 Hz, ^{3}J=9.04 Hz, 1H, H7), 7.64 (d, J=9.04 Hz, 1H, H8), 7.72 (d, 1H, H7').

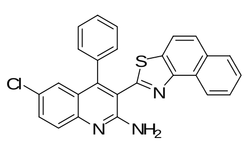
7.2.9 6-Chloro-3-(6-methoxybenzo[d]thiazol-2-yl)-4-phenylquinolin-2-amine (4E)



4, 0 g (20 mmol) **4EE1**, 2,0 g(20 mmol) NaO^{t}Bu and 4,6 g(20 mmol) **IX** were reacted according to the general synthesis method.

Raw yield: 1, 3 g (3, 11 mmol) ≅ 15%
Formula: $C_{23}H_{16}ClN_3OS$
Mol.Wt.: 417,9 g/mol
Elem. Anal. found (calculated): C 66.19 (66.10); H 4.00 (3.86); N 9.83 (10.05);
UV/Vis Absorption (EtOH): $\boldsymbol{\lambda}_{max}$=393nm; $\boldsymbol{\lambda}_{max}$($H^+$) = 393nm;
Molar extinction coefficient (EtOH): ε_{max} = 9487 $M^{-1}cm^{-1}$;
ε_{max} (H^+)=19800$M^{-1}cm^{-1}$
Fluorescence (EtOH): $\boldsymbol{\lambda}_{max}$ = 475nm; $\boldsymbol{\lambda}_{max}$ (H^+)= 530nm;
EI-MS: m/z 420.1 (12.32%), 419.2 (43.12%), 418.2 (41.79%), 417.2 (100%), 416.2 (31.84%), 380.3 (7.34%), 385.3 (5.14%), 384.3 (17.51%)
^{1}H-NMR ($CDCl_3$ r.t), δ [ppm]: 3.82 (s, 3H, OCH_3), 6.85 (s br., 2H, NH_2), 7.06 (dd, ^{4}J=2.44 Hz, ^{3}J=9.04 Hz, 1H, H6'), 7.12 (d, J=2.44 Hz, 1H, H4'), 7.23 (m, 2H, m-H), 7.24 (d, J=2.44 Hz, 1H, H5), 7.50 (m, 3H, o,p-H), 7.51 (dd, ^{4}J=2.44 Hz, ^{3}J=8.30 Hz, 1H H7), 7.62 (d, J=8.30 Hz, 1H, H8), 7.90 (d, J=9.04 Hz, 1H, H7').

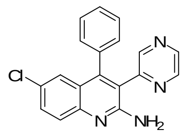
7.2.10 6-Chloro-3-(naphtho[1,2-d]thiazol-2-yl)-4-phenylquinolin-2-amine (4I)



2,76 g (12,3 mmol) **4IE1**, 1,18 g(12,3 mmol) NaO^{t}Bu and 2,8 g(12,3 mmol) **IX** were reacting according to the general synthesis method.

Raw yield: 0, 55 g (3, 11 mmol) ≅ 10%
Formula: $C_{26}H_{16}ClN_3S$
Mol.Wt.: 437,9 g/mol
Elem. Anal. found (calculated): C 66.45 (71.31); H 3.66 (3.68); N 10.36 (9.59);
UV/Vis Absorption (EtOH): λ_{max}=389nm; $\lambda_{max}(H^+)$ = 381nm;
Molar extinction coefficient (EtOH): ε_{max} =7537 $M^{-1}cm^{-1}$; ε_{max} (H^+)=15220$M^{-1}cm^{-1}$
Fluorescence (EtOH): λ_{max} = 457nm; λ_{max} (H^+)= 605nm;
EI-MS: m/z 439.1 (13.97%), 438.1 (11.49%), 437.1 (44.60%), 404 (12.17%).

7.2.11 6-Chloro-4-phenyl-3-(pyrazin-2-yl)quinolin-2-amine (4K)

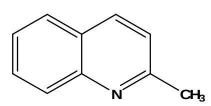


1, 0 g (8, 32 mmol) **4KE1**, 0, 96 g(10 mmol) NaO^tBu and 2,78 g(12 mmol) **IX** were reacted according to the general synthesis method.

Raw yield: 1, 08 g (3, 26 mmol) ≅ 40%
Formula: $C_{19}H_{13}ClN_4$
Mol.Wt.: 332,79 g/mol
EI-MS: m/z 335.3 (8.57%), 334.3 (33.60%) 333.3 (36.03%), 332.3 (100%), 331.3 (43.18%), 330.3 (11.22%)
^{1}H-NMR ($CDCl_3$), δ **[ppm]**: 5.82 (s br., 2H, NH_2), 7.15 (m, 2H, m-H), 7.35 (m, 3H, o,p-H), 7.57 (dd, ^4J=2.2-2.44 Hz, ^3J=8.54-8.90 Hz, 1H, H7), 7.44 (d, J=2.2-2.44 Hz, 1H, H5), 7.72 (d, J=8.54-8.90 Hz, 1H, H8), 8.08 (d, J=1.46 Hz, 1H, H3'), 8.37 (d, J=2.44 -2.69 Hz, 1H, H6'), 8.60 (d, ^4J=1.46 Hz, ^3J=2.44 -2.69 Hz, 1H, H5').

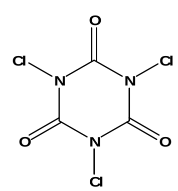
7.2.12 *Educts*

7.2.12.1 2-Methyl quinoline (2AE1.1)



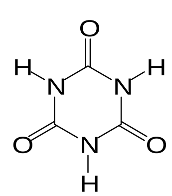
For the synthesis of **2AE1.2,** commercially available **Quinaldine** has been used.

7.2.12.2 Trichloroisocyanuric acid TCC (18)



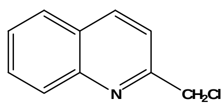
Commercially available **18** has been used (**Acros Organics**).

7.2.12.3 Isocyanuric acid (17)



17 was formed during the synthesis of **2AE1.1**

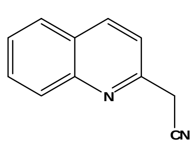
7.2.12.4 2-(Chloromethyl)quinoline (2AE1.2) [43]



In a three necked flask we add to 350 ml $CHCl_3$, 143.2 g (1, 0 mole) **2AE1.1.** Keeping the temperature between 55 and 60^0 C we add, for 2h, small quantities from 83 g (0, 36 mole) **49.**
We keep the reaction mixture by night in the deep freezer.
Then, we isolate by filtration the precipitate which is lying at the bottom of the flask (**50**) and we add a solution of 10% HCl to the filtrate.
We separate the acid phase from the $CHCl_3$ phase and then we filtrate the first phase using charcoal.
During neutralization with Na_2CO_3, the desired product comes at pH=5. We filtrate the precipitate and we dry it. In this way, 84, 36 g (0, 47 mole) of the desired product **2AE1.2** have been obtained.

Yield: 85 g (0, 5 mole) ≅ 53% (Lit 53%)
Formula: $C_{10}H_8ClN$ (177, 63 g/mol)

7.2.12.5 2-(Quinolin-2-yl)acetonitrile (2AE1) [14]

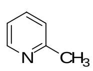


We add carefully an excess of natrium cyanide to 85 g (0, 5 mole) **2AE1.2** dissolved in 300ml DMF. While adding 49 g (1 mole) of NaCN, the reaction mixture is cooled using an ice bath.After adding the last spatula of NaCN, we

start slowly heating up to 60 ^{0}C for 6h and then we leave the reaction mixture stirring by night at room temperature. For the work-up procedure, we remove the solvent under reduced pressure, we wash several times with diethyl ether and then we use a distillation installation, in order to get the pure desired product.
Between 63 ^{0}C and 112 ^{0}C, **2AE1** is coming through the distillation bridge.

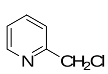
Yield: 35 g (0, 21 mole) ≅ 55, 2 % (Lit 66%)
Formula: $C_{11}H_8N_2$ (168, 19 g/mol)

7.2.12.6 2-Methylpyridine (2-Picoline) (3AE1.2)



Commercially available **2-Picoline** was used.

7.2.12.7 2-(Chloromethyl) pyridine (3AE1.1) [44]

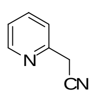


279 g (3 mole) 2-Methylpyridine, 600 g sodium carbonate and 1500 ml CCl_4 were stirred and heated up to 30 ^{0} C. Then, chlorine has been constantly flowed (in1h 88 g=1, 24 mole) to the reaction mixture. The temperature in the reaction flask was kept constant (50 ^{0}C) usin a water bath. 6h proved to be the optimal time for a successful chlorination (528 g Cl_2 = 7, 5 mole).
For the work-up, the reaction mixture has been cooled down to room temperature and 3000 ml water were added (under strong stirring). The pH of the water phase was brought between 8 and 9, by adding 50-100ml of a 2N NaOH solution. After good stirring, we separated the CCl_4 phase from the water phase. The latter one was extracted two times with 100 ml CCl_4. We collected all the CCl_4 phases and we extracted them one time with 400ml 5N HCl and two times with 200ml HCl 2N.

The resulting HCl phases were neutralized with a solution of 200g Na_2CO_3 in 500 ml water (pH = 6-7). The resulting yellow-brownish oil was separated from the water phase, which was first neutralized with the Na_2CO_3 solution and then three times extracted with diethyleher. The yellow-brownish oil and the ether phases were collected and dried with Na_2SO_4. The ether was removed under reduced pressure. Through distillation at 2 Torr, the desired product **3AE1.1** was collected between 45 and 47 ^{0}C.

Yield: 186, 97 g (1, 46 mole) ≅ 48, 85 % (Lit 65%)
Formula: C_6H_6ClN (127, 57 g/mol)

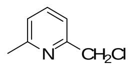
7.2.12.8 2-(Pyridin-2-yl) acetonitrile (3AE1) [14]



We add carefully an excess of natrium cyanide to 186, 97 g (1, 46 mole) **3AE1.1** dissolved in 600ml DMF. While adding 98 g (2 mole) of NaCN, the reaction mixture is cooled using an ice bath.
After adding the last spatula of NaCN, we start slowly heating up to 60 ^{0}C for 4h and then we leave the reaction mixture stirring by night at room temperature.
For the work-up procedure, we remove the solvent under reduced pressure, we wash several times with diethyl ether and then we use a distillation installation, in order to get the pure desired product.
Between 80 ^{0}C and 90 ^{0}C, we collect the desired product **3AE1.**

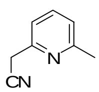
Yield: 110, 39 g (0, 93 mole) ≅ 63, 69 % (Lit 66%)
Formula: $C_7H_6N_2$ (118, 14 g/mol)

7.2.12.9 2-(Chloromethyl)-6-methylpyridine (3CE1.1)



3CE1.1 was available in our group.

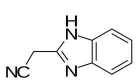
7.2.12.10 2-(6-Methylpyridin-2-yl)acetonitrile (3CE1) [14]



We add carefully an excess of natrium cyanide to a mixture of 101 g (0, 71 mole) **3CE1.1** dissolved in 800ml DMF.
49 g (1mole) of NaCN are added to the reaction mixture under a cool atmosphere (using an ice bath).
After adding the last spatula of NaCN, we start slowly heating up to 60 ^{0}C for 4h and then we leave the reaction mixture stirring by night at room temperature.
For the work-up procedure, we remove the solvent under reduced pressure, we wash several times with diethyl ether and then we use a distillation installation, in order to get the pure desired product.
Between 80 ^{0}C and 90 ^{0}C, **3CE1** has been collected.

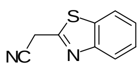
Yield: 60, 12 g (0, 45 mole) ≅ 64, 15 % (Lit 66%)
Formula: $C_8H_8N_2$ (132, 16 g/mol)

7.2.12.11 2-(1*H*-Benzo[*d*]imidazol-2-yl)acetonitrile (4AE1)



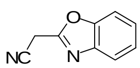
4AE1 was available in the group.

7.2.12.12 2-(Benzo[*d*] thiazol-2-yl)acetonitrile (4CE1)



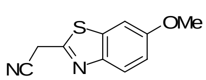
4CE1 was available in the group and was synthesized by W. Sulger.

7.2.12.13 2-(Benzo[*d*]oxazol-2-yl)acetonitrile (4DE1)



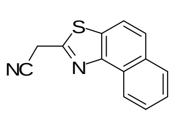
4DE1 was available in the group.

7.2.12.14 2-(6-Methoxybenzo[*d*]thiazol-2-yl)acetonitrile (4EE1)



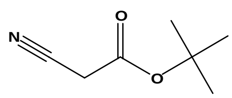
4EE1 was available in the group.

7.2.12.15 2-(Naphtho[1, 2-*d*]thiazol-2-yl)acetonitrile (4IE1)



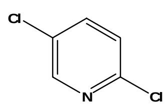
4IE1 was available in the group and has been synthesized by Cheng.

7.2.12.16 *tert*-Butyl 2-cyanoacetate (6)



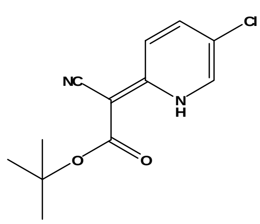
Commercially available **6** was used.

7.2.12.17 2, 5-Dichloropyridine (IV-1-1)



Commercially available **IV-1-1** was used.

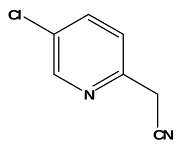
7.2.12.18 (2*Z*)-*tert*-Butyl 2-(5-chloropyridin-2(1*H*)-ylidene)-2-cyanoacetate (IV-2-1) [15]



4, 32 g (0, 045mole) NaO^t^Bu, 6, 33g (0, 045mole) *tert*-Butyl 2-cyanoacetate and 4, 5 g (0, 03 g) **IV-1-1** were dissolved in NMP and heated for 4h at 125 ^{0}C. The solution was then poured in a mixture of ice water-CH_3COOH. The bright yellow solid was then filtrated and dried.

Yield: 3, 82 g (0, 015mole) ≅ 50 %
Formula: $C_{12}N_{13}ClN_2O_2$ (252,7g/mol)

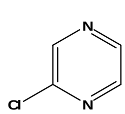
7.2.12.19 2-(5-Chloropyridin-2-yl)acetonitrile (4LE3) [15]



2, 52 g (0,01mole) **IV-2-1** were dissolved in 15ml fuming HCl and the reaction mixture was stirred for 2h at room temperature. Then, we neutralized the solution by adding a mixture of ammoniac–ice water. The desired product **4LE3** was slowly falling and was isolated by filtration by suction.

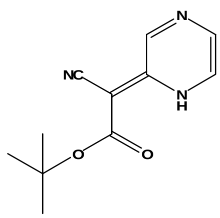
Yield: 1, 06 g (0, 007 mole) ≅ 70 %
Formula: $C_7H_5ClN_2$ (152, 58 g/mol)

7.2.12.20 2-Chloropyrazine (IV-1-2)



Commercially available **IV-1-2** was used.

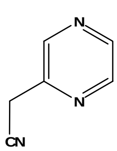
7.2.12.21 (2*Z)*-*tert*-Butyl 2-cyano-2(pyrazin-2(1*H*)-ylidene)acetate (IV-2-2) [15]



7,2g (0, 075mole) NaO^tBu, 10, 55g (0, 075mole) *tert*-Butyl 2-cyanoacetate and 5, 7 g (0, 05 g) **IV-1-2** were dissolved in NMP and heated for 4h at 130 ^0C. The solution was then poured in a mixture of ice water-CH_3COOH. The bright yellow solid was then filtrated and dried.

Yield: 6, 51 g (0, 03mole) ≅ 60 %
Formula: $C_{11}N_{13}N_3O_2$ (219,24g/mol)

7.2.12.22 2-(Pyrazin-2-yl)acetonitrile (4K) [14]

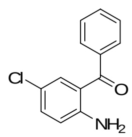


3 g (0,013mole) **IV-2-2** were dissolved in 15ml fuming HCl and the reaction mixture was stirred for 2h at room temperature. Then, the solution was neutralized by adding a mixture of ammoniac–ice water. The desired product **4K** was isolated by filtration by suction.

Yield: 0, 85 g (0, 007 mole) ≅ 54 %
Formula: $C_6H_5N_3$ (119, 12 g/mol)

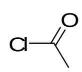
7.3 H-Chelates

7.3.1 2-Amino-5-chlorobenzophenone (IX)



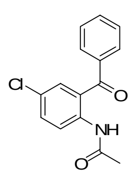
Commercially available **IX** was used.

7.3.2 Acetyl Chloride (1)



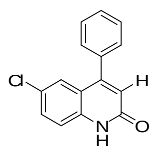
Commercially available **1** was used.

7.3.3 5-Chloro-2-acetamino-benzophenone (2) [56]



9, 26 g (40 mmole) **IX,** and10, 6 g (100 mmole) sodium carbonate, were dissolved in 150 ml toluene. 10, 5 g (135 mmole) acetyl chloride were added dropwise to the reaction mixture (an increase of the inside temperature up to 30 ^{0}C was observed).The solution was then stirred under reflux for 1h. The solvent was removed under reduced pressure and the remained white solid was washed several times with water, filtered and dried.
Yield: 10 g (36, 5 mmole) ≅ 91 %
Formula: $C_{15}H_{12}NO_2$ (273, 7 g/mol)

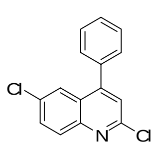
7.3.4 6-Chloro-4-phenylquinolin-2(1*H*)-one (3)



A solution of 13, 6 g (50mmole) **2** and 4, 8 g (50mmole) NaO^tBu in 25ml pyridine was refluxed for 2h. The reaction mixture was cooled down to room temperature, pyridine was removed under reduced pressure and a mixture of water-acetic acid was then added. Under strong stirring, a bright yellow precipiate was isolated by filtration.

Yield: 12, 3 g (48, 10 mmole) ≅ 96 %
Formula: $C_{15}H_{10}ClNO$ (255, 7 g/mol)

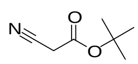
7.3.5 2, 6-Dichloro-4-phenylquinoline (5) [14]



A solution of 24, 57 g (96, 16mmole) **3** in phosphorus oxychloride (100 ml) was heated with stirring at 90 ^{0}C for 2h. The mixture was cooled to room temperature and phosphorus oxychloride was removed by distillation. Dichloromethane was then added (causing dissolution of the "honey" residue), the resulting solution was poured in ice water and neutralized with sodium carbonate. Extraction with dichloromethane (3x100ml) followed. The organic layer was then dried over sodium sulfate. Evaporation under reduced pressure gave the desired product **5.**

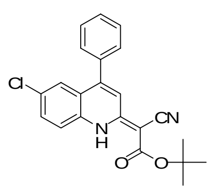
Yield: 22, 38 g (81, 48 mmole) ≅ 85 %
Formula: $C_{15}H_9Cl_2N$ (274, 14 g/mol)

7.3.6 *tert*-Butyl 2-cyanoacetate (6)



Commercially available **6,** was used.

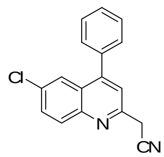
7.3.7 (2Z)-*tert*-Butyl 2-(6-chloro-4-phenylquinolin-2(1*H*)-ylidene)-2-cyanoacetate (7) [15]



To a solution of 141, 17 g (150 mmole) **6** and 96, 1 g (150 mmole) NaO^{t}Bu in 60 ml DMF, 13, 7 g (50 mmole) **5** were added. After stirring for 3h at 105 ^{0}C, the solution was cooled down, DMF was removed under reduced pressure, a mixture of water-acetic acid was added and the resulting solid was filtrated and washed two times with MeOH. After further filtration, the desired product **7** was isolated.

Yield: 16, 66 g (43, 97 mmole) ≅ 88 %
Formula: $C_{22}H_{19}ClN_2O_2$ (378, 85 g/mol)

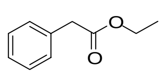
7.3.8 2-(6-Chloro-4-phenylquinolin-2-yl)acetonitrile (8) [14]



5, 00 g (13, 19 mmole) **7** in 140 ml formic acid, were stirred for 1, 5h at 45 ^{0}C. The mixture was poured in an ice-ammonia solution and the resulting yellow solid was filtrated and dried.

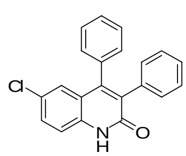
Yield: 3, 6 g (12, 9 mmole) ≅ 98 %
Formula: $C_{17}H_{11}ClN_2$ (278, 74 g/mol)

7.3.9 Ethyl 2-phenylacetate (9)



Commercially available **9,** was used.

7.3.10 6-Chloro-3, 4-diphenylquinolin-2(1*H*)-one (10) [14]

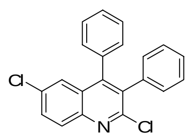


64 ml (7 eq) **9** were added dropwise to a solution of 16, 8 g (4 eq) NaH and 23, 17 g (0, 1 mole) **IX** in 150 ml dry THF. By slowly dropping **9** to the reaction mixture,

an increase of temperature up to 60 ^{0}C was observed. The mixture was stirred by night.
For the work-up, first 200ml ethylacetate were added and second, 150 ml water. The solution became thick and was stirred for 2h at room temperature. The resulting solid was filtrated, washed with ethylacetate and dried.

Yield: 31, 72 g (0, 095 mole) ≅ 95, 5 %
Formula: $C_{21}H_{14}ClNO$ (331, 79 g/mol)

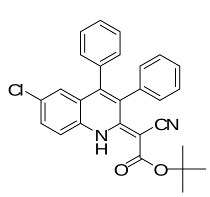
7.3.11 2, 6-Dichloro-3, 4-diphenylquinoline (11) [14]



A solution of 18, 37 g (55, 41 mmole) **10** in 200 ml phosphorus oxychloride was stirred for 1h at 120 ^{0}C. For the work-up procedure, the same steps, like in the case of **5,** were followed (See **7.3.5**).

Yield: 18, 44 g (52, 68 mole) ≅ 94 %
Formula: $C_{21}H_{13}Cl_2N$ (331, 79 g/mol)

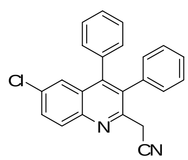
7.3.12 (2*Z*)-*tert*-Butyl 2-(6-chloro-3, 4-diphenylquinolin-2(1*H*)-ylidene)-2-cyanoacetate (12) [15]



To a solution of 37, 8 g (263, 4 mmole) **6** and 25, 3 g (263, 4 mmole) NaO^tBu in 70 ml DMF, 18, 44 g (52, 68 mmole) **11** were added. After stirring for 4h at 130 ^{0}C, the solution was cooled down, DMF was removed under reduced pressure, a mixture of water-acetic acid was added and the resulting solid was filtrated and washed two times with MeOH. After further filtration, the desired product **12** was isolated.

Yield: 20, 78 g (45, 67 mmole) ≅ 87 %
Formula: $C_{28}H_{23}ClN_2O_2$ (454, 95 g/mol)

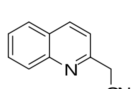
7.3.13 2-(6-Chloro-3, 4 diphenylquinolin-2-yl)acetonitrile (13) [14]



10, 67 g (23, 47 mmole) **12** in 240 ml formic acid, were stirred for 1, 5h at 50 ^{0}C. The mixture was poured in an ice-ammonia solution and the resulting yellow solid was filtrated and dried.

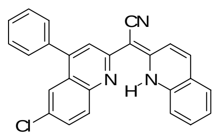
Yield: 8, 21 g (32, 15 mmole) ≅ 98 %
Formula: $C_{23}H_{15}ClN_2$ (354, 83 g/mol)

7.3.14 2-(Quinolin-2-yl)acetonitrile (2AE1) [14]



For the synthesis of **2AE1,** see **7.2.12.5.**

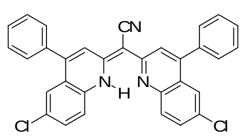
7.3.15 (2E)-2-(6-chloro-4-phenylquinolin-2-yl)-2-(quinolin-2(1H)-ylidene)acetonitrile (2569) [15]



A solution of 3, 36 g (20 mmole) **2AE1,** 3, 84 g (40 mmole) NaO^{t}Bu and 5, 48 g (20 mmole) **5** in 40 ml NMP was stirred for 2h at 80 ^{0}C. The reaction mixture was poured in ice water-acetic acid, the precipitate was filtrated and then washed two times with methanol. The desired product **2569** was recrystallized from acetonitrile.

Yield: 6, 5 g (16, 01 mmole) ≅ 80 %
Formula: $C_{26}H_{16}ClN_3$ (405, 88 g/mol)

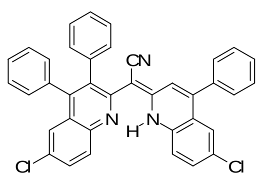
7.3.16 *(2E)*-2-(6-Chloro-4-phenylquinolin-2(1*H*)-ylidene)-2-(6-chloro-4-phenylquinolin-2-yl)acetonitrile (2647)



A solution of 2, 78 g (10 mmole) **8,** 1, 15 g (12 mmole) NaO^{t}Bu and 2, 74 g (10 mmole) **5** in 40 ml NMP was stirred for 2h at 100 ^{0}C. The reaction mixture was poured in ice water-acetic acid, the precipitate was filtrated and then washed four times with distilled water. Fractioned vacuum sublimation was used as purification method.

Raw yield: 4, 75 g (9, 2 mmole) ≅ 92 %
Formula: $C_{32}H_{19}Cl_2N_3$ (516, 42 g/mol)

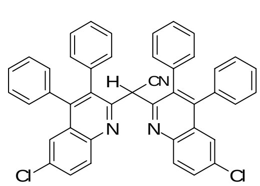
7.3.17 (2*E*)-2-(6-Chloro-3, 4-diphenylquinolin-2-yl)-2-(6-chloro-4-phenylquinolin -2(1*H)*-ylidene)acetonitrile (2652)



A solution of 2, 78 g (10 mmole) **8,** 1, 15 g (12 mmole) NaO^{t}Bu and 3, 5g (10 mmole) **11** in 50 ml NMP was stirred for 3h at 105 ^{0}C. The reaction mixture was poured in ice water-acetic acid, the precipitate was filtrated and then washed four times with distilled water. Fractioned vacuum sublimation was used as purification method.

Raw yield: 5, 62 g (9, 5 mmole) ≅ 95 %
Formula: $C_{38}H_{23}Cl_2N_3$ (592, 5 g/mol)

7.3.18 2, 2-bis (6-Chloro-3, 4-diphenylquinolin-2-yl)acetonitrile

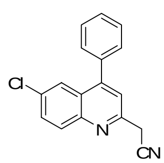


A solution of 0, 88 g (2, 5 mmole) **13,** 0, 48 g (5 mmole) NaO^{t}Bu and 0, 87g (2, 5 mmole) **11** in 30 ml NMP was stirred for 4h at 140 ^{0}C. The reaction mixture was poured in ice water - acetic acid, the precipitate was filtrated and then washed four times with distillated water. Separation on a silica gel column was used as purification method.

Yield:
Formula: $C_{44}H_{27}Cl_2N_3$ (668, 61 g/mol)

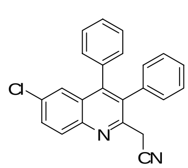
7.4 Polymethines

7.4.1 2-(6-Chloro-4-phenylquinolin-2-yl)acetonitrile (8) [14,15]



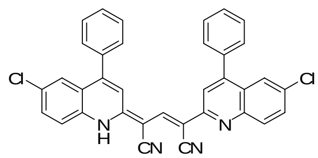
For the synthesis of **8**, see **7.3.8**

7.4.2 2-(6-Chloro-3, 4-diphenylquinolin-2-yl)acetonitrile (13) [14,15]



For the synthesis of **13**, see **7.3.13**

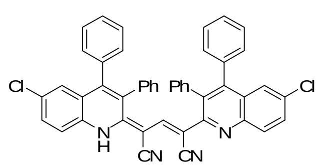
7.4.3 (2*Z*, 4*Z*)-4(6-Chloro-4-phenylquinolin-2(1*H*)-ylidene)-2-(6-chloro-4-phenylquinolin-2-yl)pent-2-enedinitrile (32) [52]



A solution of 1, 19 g (10mmole) $CHCl_3$ in 5 ml DMF was added to a mixture of 5, 56 g (20 mmole) **8** and 1, 92 g (20 mmole) NaO^tBu dissolved in 30 ml DMF. The mixture was stirred for 3h at 65 ^{0} C and then poured in ice water-acetic acid. The precipitate was filtrated and dried.

Raw yield: 5, 56 g (9, 8 mmole) ≅ 49 %
Formula: $C_{35}H_{20}Cl_2N_4$ (567, 47 g/mol)

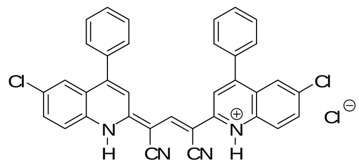
7.4.4 (2*Z*, 4*Z*)-4(6-Chloro-3, 4-diphenylquinolin-2(1*H*)-ylidene)-2-(6-chloro-3, 4-diphenylquinolin-2-yl)pent-2-enedinitrile (33) [52]



A solution of 0, 6 g (5 mmole) $CHCl_3$ in 3 ml DMF was added to a mixture of 3, 54 g (10 mmole) **13** and 0, 96 g (10 mmole) NaO^tBu dissolved in 20 ml DMF. The mixture was stirred for 3h at 90 ^{0} C and then poured in ice water-acetic acid. The precipitate was filtrated and dried.

Raw yield: 3, 00 g (4, 16 mmole) ≅ 42 %
Formula: $C_{47}H_{28}Cl_2N_4$ (567, 47 g/mol)

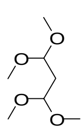
7.4.5 Synthesis of 34 [52]



A solution of 1, 53 g (10 mmole) phosphorus oxychloride in 20 ml DMF was added dropwise to a mixture of 5, 56 g (20 mmole) **8** and 1, 92 g (20 mmole) NaO^tBu dissolved in 20 ml DMF. After stirring for 2h at room temperature, the mixture was then poured in ice water-acetic acid, the precipitate was filtrated, dried and successfully purified by fractioned vacuum sublimation.

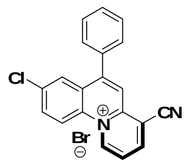
Raw yield: 5, 79 g (9, 61 mmole) ≅ 48 %
Formula: $C_{35}H_{21}Cl_3N_4$ (602, 08 g/mol)

7.4.6 1, 1, 3, 3-Tetramethoxypropane (37)



Commercially available **37,** was used.

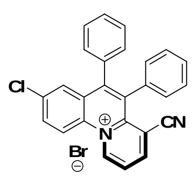
7.4.7 Synthesis of 38 [52]



A solution of 2, 78 g (10 mmole) **8,** 4, 92 g (30 mmole) **37** and 5 ml HBr in 70 ml ethylene glycol monomethyl ether was stirred for 2h at 75 ^{0} C. The solvent was removed under reduced pressure, diethyl ether was added and the precipitate was filtrated and dried. After fractioned vacuum sublimation, 3, 86 g of **38** were isolated.

Yield: 3, 86 g (9, 75 mmole) ≅ 97, 5 %
Formula: $C_{20}H_{12}BrClN_2$ (395, 68 g/mol)

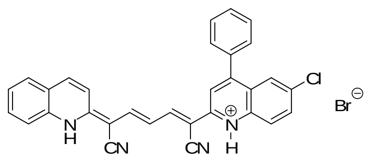
7.4.8 Synthesis of 40



A solution of 3, 54 g (10 mmole) **13,** 8, 21 g (50 mmole) **37** and 7 ml HBr in 70 ml ethylene glycol monomethyl ether was stirred for 2h at 80 ^{0} C. The solvent was removed under reduced pressure, diethyl ether was added and the precipitate was filtrated and dried. After fractioned vacuum sublimation, 3, 52 g of **40** were isolated.

Yield: 3, 25 g (6, 88 mmole) ≅ 69 %
Formula: $C_{26}H_{16}BrClN_2$ (471, 78 g/mol)

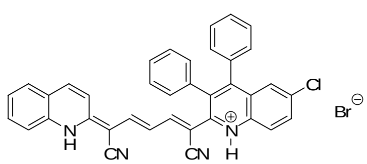
7.4.9 Synthesis of 38-1 [52]



A solution of 0, 59 g (1, 5 mmole) **38**, 0, 3 g (1, 8 mmole) **2AE1** and 0, 57 g (6 mmole) NaO^{t}Bu in 30 ml DMF was stirred for 2h at room temperature. The mixture was then poured in ice water-HBr. The solution was brought to pH acid, by adding more HBr.
The precipitate was filtrated and dried. Isolation of the wanted product **38-1,** by fractioned vacuum sublimation, proved to be difficult.

Raw yield: 0, 31 g (0, 54 mmole) ≅ 37 %
Formula: $C_{31}H_{20}BrClN_4$ (563, 87 g/mol)

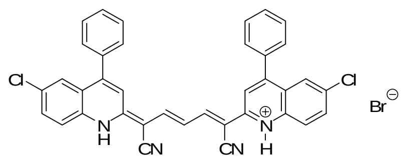
7.4.10 Synthesis of 40-1



A solution of 0, 70 g (1, 5 mmole) **40**, 0, 3 g (1, 8 mmole) **2AE1** and 0, 57 g (6 mmole) NaO^{t}Bu in 30 ml DMF was stirred for 2h at room temperature. The mixture was then poured in ice water-HBr. The solution was brought to pH acid, by adding more HBr.
The precipitate was filtrated and dried. Isolation of the wanted product **40-1,** by fractioned vacuum sublimation, proved to be difficult.

Raw yield: 0, 45 g (0, 7 mmole) ≅ 47 %
Formula: $C_{37}H_{24}BrClN_4$ (639, 97 g/mol)

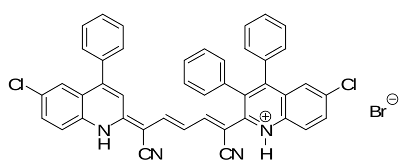
7.4.11 Synthesis of 38-2 [52]



A solution of 0, 70 g (1, 5 mmole) **40**, 0, 3 g (1, 8 mmole) **2AE1** and 0, 57 g (6 mmole) NaO^tBu in 30 ml DMF was stirred for 2h at room temperature. The mixture was then poured in ice water-HBr. The solution was brought to pH acid, by adding more HBr.
The precipitate was filtrated, washed with MeOH and dried. Isolation of the desired product **38-2** by fractioned vacuum sublimation, proved to be difficult.

Raw yield: 0, 99 g (1, 46 mmole) ≅ 49 %
Formula: $C_{37}H_{23}BrCl_2N_4$ (674, 42 g/mol)

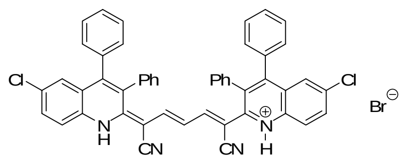
7.4.12 Synthesis of 40-2 [52]



A solution of 0, 70 g (1, 5 mmole) **40**, 0, 8 g (1, 8 mmole) **8** and 0, 57 g (6 mmole) NaO^tBu in 30 ml DMF was stirred for 3h at room temperature. The mixture was then poured in ice water-HBr. The solution was brought to pH acid, by adding more HBr.
The precipitate was filtrated and dried. Isolation of the desired product **40-2,** by fractioned vacuum sublimation, proved to be difficult.

Raw yield: 0, 52 g (0, 69 mmole) ≅ 46 %
Formula: $C_{43}H_{27}BrCl_2N_4$ (750, 51 g/mol)

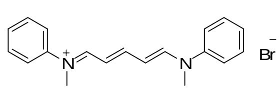
7.4.13 Synthesis of 40-3 [52]



A solution of 0, 70 g (1, 5 mmole) **40**, 0, 63 g (1, 8 mmole) **13** and 0, 57 g (6 mmole) NaO^{t}Bu in 30 ml DMF was stirred for 3h at room temperature. The mixture was then poured in ice water-HBr. The solution was brought to pH acid, by adding more HBr.
The precipitate was filtrated, washed with distillated water, methanol and then dried. Isolation of the desired product **40-3,** by fractioned vacuum sublimation, proved to be difficult.

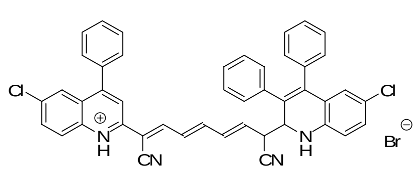
Raw yield: 0, 51 g (0, 61 mmole) ≅ 41 %
Formula: $C_{49}H_{31}BrCl_2N_4$ (826, 61 g/mol)

7.4.14 König's salt (43)



43, was available in our group.

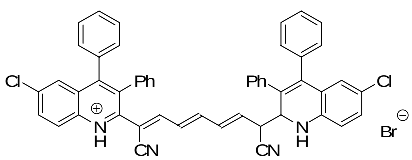
7.4.15 Synthesis of 44 [52]



A solution of 2, 78 g (10 mmole) **8**, 0, 96 g (20 mmole) NaO^tBu, 1, 78g (5 mmole) **43** in 40 ml DMF was stirred for 3h at room temperature. The mixture was then poured in ice water-HCl. The precipitate was filtrated, washed with distillated water, methanol and then dried. Isolation of the desired product **40-3,** by fractioned vacuum sublimation, proved to be difficult.

Raw yield: 2, 02 g (2, 59 mmole) ≅ 51 %
Formula: $C_{45}H_{31}BrCl_2N_4$ (778, 56 g/mol)

7.4.16 Synthesis of 45 [52]



A solution of 3, 54 g (10 mmole) **13**, 0, 96 g (20 mmole) NaO^tBu, 1, 78g (5 mmole) **43** in 40 ml DMF was stirred for 3h at 110 ^{0}C. The mixture was then poured in ice water-HCl. The precipitate was filtrated, washed with distillated water, methanol and then dried. Isolation of the desired product **40-3,** by fractioned vacuum sublimation, proved to be difficult.

Raw yield: 3, 16 g (3, 69 mmole) ≅ 37 %
Formula: $C_{51}H_{35}BrCl_2N_4$ (854, 66 g/mol)

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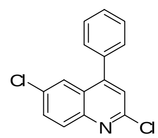
List of the Synthesized Substances



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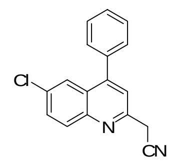

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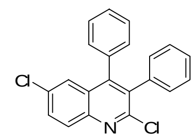

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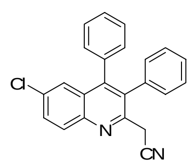

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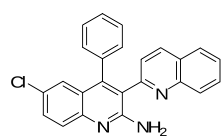

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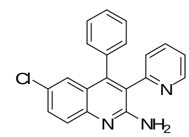

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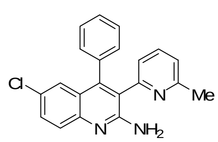

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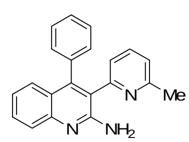

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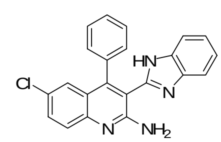

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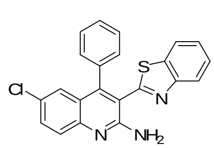

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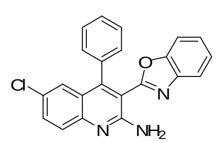

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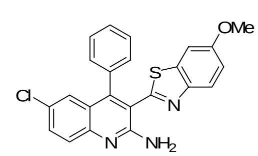

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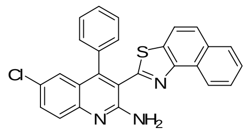

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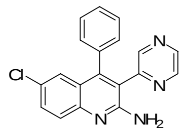

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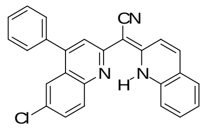

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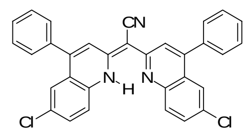

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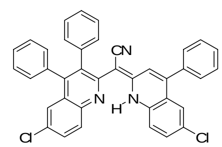

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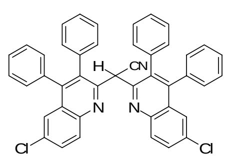

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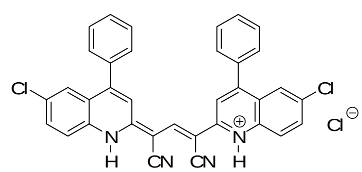

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