Organic Dye Catalyzed Regioselective C-8 Arylation of 1-(Pyridin-2-yl)quinolin-4(1*H*)-one

M.Sc. Thesis

CH-800

By

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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A THESIS

Submitted in partial fulfillment

Of the requirements for the award of the degree

Of

Master of Science

by

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being reported in this thesis entitled **"Organic dye catalyzed regioselective C-8 arylation of 1-(pyridine-2-yl)quinolin-4(1*H*)-one"** in the partial fulfillment of the requirements for the award of the degree of **Master of Science** and submitted in the **Department of Chemistry**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the period from July 2022 to May 2023 under the supervision of **Dr. Umesh A. Kshirsagar,** Assistant Professor, Department of Chemistry, IIT Indore.

Biswajit Biswas (16/05/23)
(Signature of the student with date)

(Biswajit Biswas)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

16/05/2023
Dr. Umesh A. Kshirsagar

Biswajit Biswas has successfully given his M.Sc. oral examination was held on 16 May 2023.

Signature of Supervisor of MSc thesis

Dr. Umesh A. Kshirsagar

Date 16/05/2023

Convener, DPGC 02/06/2023

Date

2/6/2023.
Signature PSPC member

Prof. Apurba K. Das

Signature of PSPC member

Prof. Sampak Samanta

23/5/2023

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Finally, I'd like to thank IIT Indore for its infrastructure and everyone who has helped and assisted me directly or indirectly over the past two years of my M.Sc.

[Biswajit Biswas]

DEDICATE TO MY FAMILY, FRIENDS

AND TEACHERS.....

ABSTRACT

A regioselective C-8 arylation of **1-(pyridine-2-yl)quinolin-4(1*H*)-one** using diazonium salt as an aryl source in the presence of palladium acetate as transition metal catalyst, eosin Y as the photocatalyst, under mild condition is described The reaction proceeds in good yields using inexpensive, readily available visible-light sources The use of visible light and photoredox catalysis emerged as a powerful and sustainable tool for organic synthesis, showing the high value of distinctly different ways of bond creation.

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ACRONYMS

^{1}H NMR	Proton NMR spectroscopy
^{13}C NMR	^{13}C NMR spectroscopy
CDC	Cross-dehydrogenative coupling
CH_3CN	Acetonitrile
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
ESI	Electron spray ionization
HRMS	High resolution mass spectrometry
LCMS	Liquid chromatography mass spectrometry
ppm	Parts per million
SET	Single electron transfer
TCI	Tokyo chemical industry
XRD	X-ray diffraction

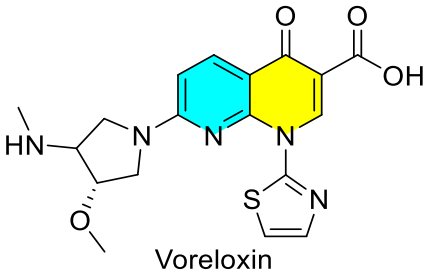
NOMENCLATURE

δ	chemical shift
ºC	degree Celsius
equiv.	equivalent
h	hour
mg	milligram
mL	milliliter
mmol	millimole
min	minutes
rt	room temperature

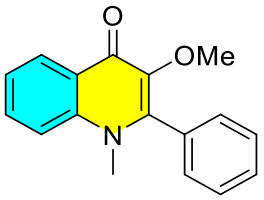
Chapter 1

A: INTRODUCTION:

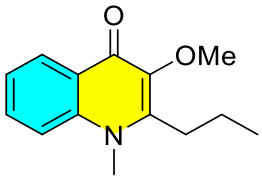
Heterocyclic compounds are an important class of organic compounds because of their biological activity and medicinal application. So, the



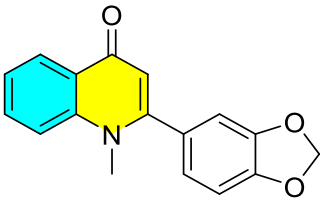
Voreloxin
(anti-cancer drug)



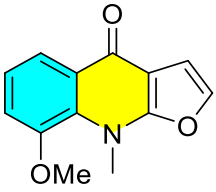
Japonine
(Effect on muscle)



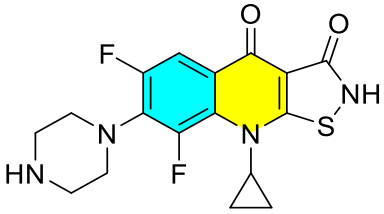
Leiokinine A
(Antifeedant activity)



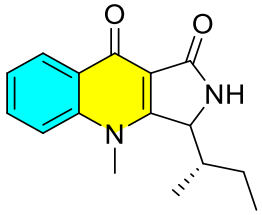
Graveoline
(Anti-tumor & Herbicidal activity)



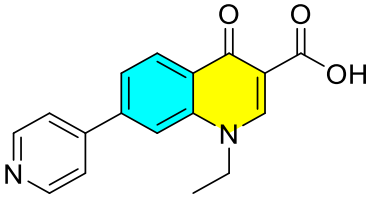
Iso-γ-fagarine
(Anti-tumor activity)



A-65281
(Anti-cancer activity)



Quinolactacin
(Anti-inflammatory activity)



Rosoxacin
(Treating gonococcal infections)

Figure 1: Biologically active compounds of 4-quinolone.

functionalization of some simple heterocyclic precursors leads to the formation of biologically active or drug molecules.

Due to its wide range of chemical and pharmacological characteristics such as anti-bacterial, anti-feedant, anti-tumor, anti-fungal, quinolone, and its derivatives have traditionally been interesting for the biological chemist. [1], [2]

The cutting-edge and quickly developing branch of organic chemistry, C-H activation, focuses on directly manipulating C-H bonds in organic compounds. Moreover, C-H activation offers a more effective and environmentally friendly method by avoiding the requirement for starting materials that have already been functionalized and instead directly converting C-H bonds into desired functional groups, simplifying synthetic pathways and minimizing waste. Due to its ability to simplify synthetic pathways, enhance step and atom economy, and enable the synthesis of complex organic compounds, such as medicines, agrochemicals, and materials, C-H activation has emerged as a valuable tool.

As early as **1912** Ciamician recognized that light had the potential to serve as an inexpensive, abundant, renewable, and non-polluting reagent for chemical synthesis. [3]

In parallel scientists also developed photocatalytic C-H functionalization using transition metal catalysts containing Ru, Ir, Rh, etc., and organic dyes like Eosin-Y, Rhodamine, Methylene blue, etc. Merging these two types of catalysts and two catalytic cycles working together to form a new bond proved to be a potent technique. In dual synergistic catalysis, one catalyst activates one reactant and the other catalyst activates another reactant.

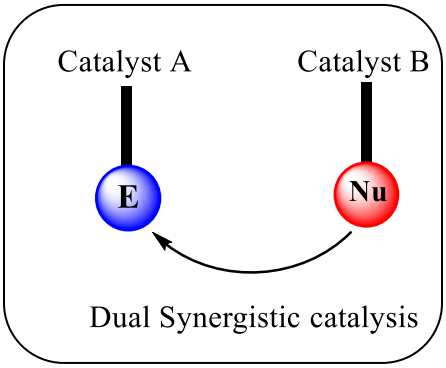


Figure 2: Dual synergistic catalysis merging [4]

The advantage of dual synergistic catalysis is that one catalyst reacts with one substrate and increases the energy of HOMO and another catalyst reacts with another substrate to decrease the energy of LUMO. Thus HOMO-LUMO energy gap decreases which can help to reaction occur in mild conditions.[4]

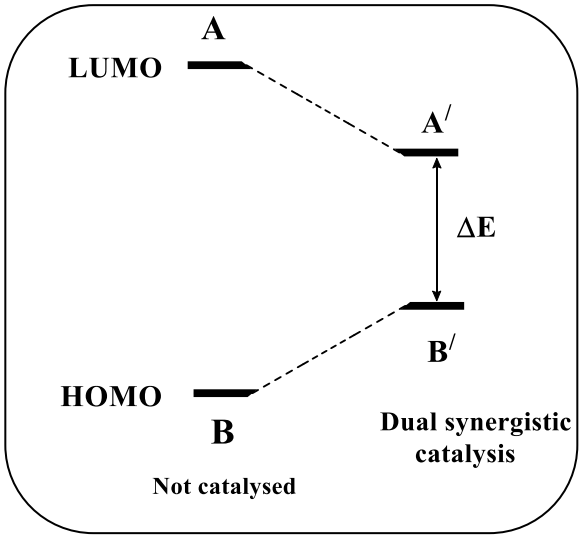
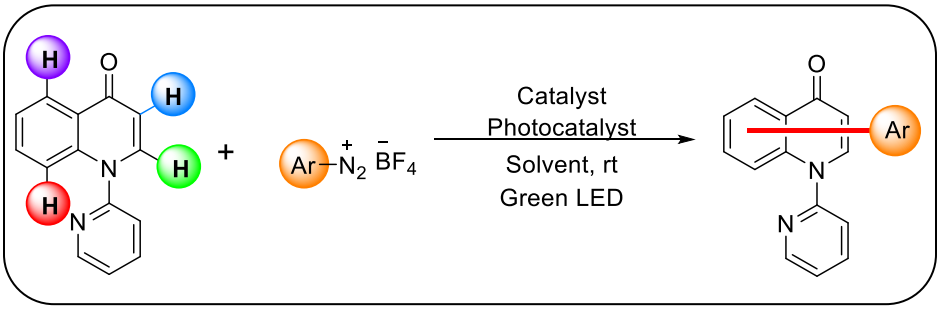


Figure 3: MO energy diagram for synergistic catalysis [4]

B. OBJECTIVE:

So far, there are several reports on the functionalization of heterocyclic compounds. The formation of a new C-C or C-hetero atom bond via C-H

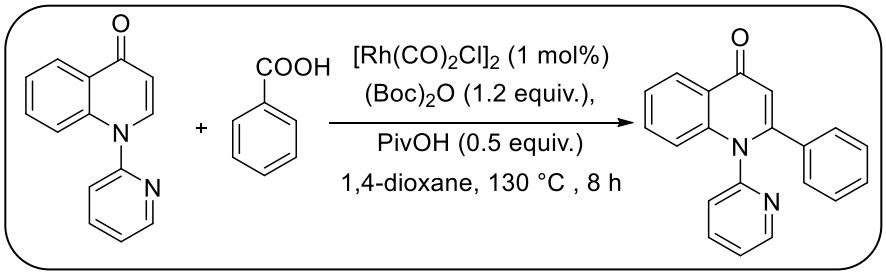
bond functionalization has long been regarded as the holy grail of organic synthesis. C-H functionalization of Quinolone and its derivatives have been widely interested due to its biological or medicinal activity. Thereafter the motive of our work is to synthesize C-H functionalized Quinolone and its derivative via photocatalysis C-H bond activation methodology.



Scheme 1: General objective of our work

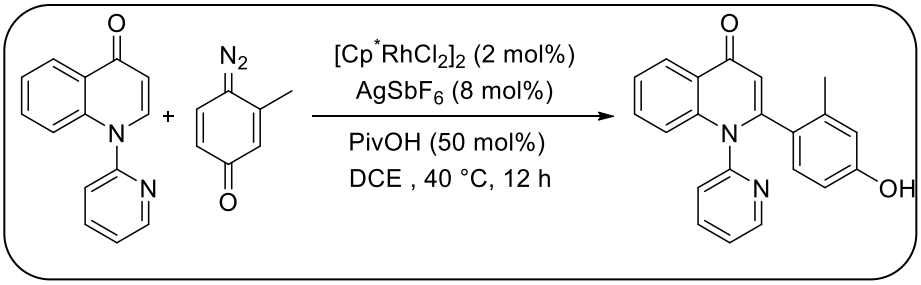
C. Previous Work:

From the literature survey, we have found the following previously reported reactions which involved C-H activation, Photocatalysis, dual catalysis merging, and arylation of Quinolone.



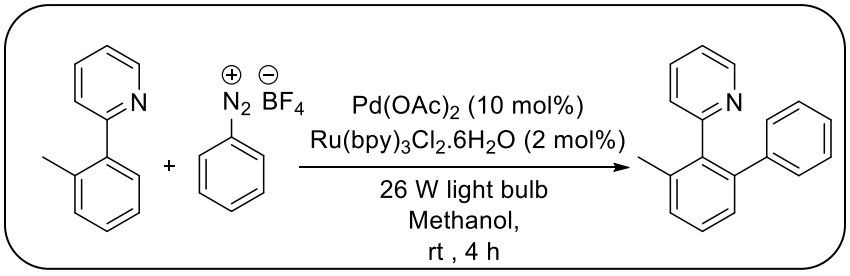
Scheme 2: Arylation of 1-(2-Pyridinyl)-4(1H)-quinolinone using benzoic acid

In 2021, Walsh et al. reported C-2 arylation method of 1-(2-Pyridinyl)-4(1*H*)-quinolinone. Where they used benzoic acid as an arylating agent, $[Rh(CO)_2Cl]_2$ as C-H activating catalyst, pivalic acid as an additive, and 1,4-dioxane as a solvent. The yield of the product is 88%. One of the drawbacks of this reaction is it requires very harsh conditions. [5]



Scheme 3: Arylation using quinone diazide and Rh (III) catalyst

In **2021**, R. Samanta *et.al* also developed C-2 arylation method of 1-(2-Pyridinyl)-4(1*H*)-quinolinone. Where they reacted the starting material with quinone diazide, $[Cp^*RhCl_2]_2$ catalysts, and $AgSbF_6$ in DCE at 40 °C. Pivalic acid was added as an additive to get the product with a 61% yield.[6]



Scheme 4: First reported dual catalyst merging

In **2011,** Sanford *et al.* developed the first example of dual catalyst merging. Here the starting material reacts with phenyl diazonium fluoroborate in the presence of transition metal catalyst $Pd(OAc)_2$ and photo-redox catalyst $[Ru(bpy)_3Cl_2].6H_2O$ using a light bulb as an energy source and methanol as a solvent. The C-2 arylated product was formed in 76% yield. [7]

Chapter 2

A: RESULTS AND DISCUSSION:

Here discussing the synthesis of C-8 arylation of 1-(2-pyridinyl)-4(1*H*)-quinolinone using 1-(2-Pyridinyl)-4(1*H*)-quinolinone as the starting material, aryldiazonium salt is used as a source ayl group and using different photocatalyst, catalyst, and solvent for better yield of the product i.e., 8-(4-chlorophenyl)-1-(Pyridin-2-yl)-quinoline-4 (1*H*)-one.

B: OPTIMIZATION OF REACTION:

In optimization of the reaction, 1-(2-pyridinyl)-4(1*H*)-quinolinone reacts with a diazonium salt in the presence of a photocatalyst, transition metal catalyst, and solvent at room temperature under the green LED light. We choose compound 1-(2-pyridinyl)-4(1*H*)-quinolinone **1a** and 4-chlorobenzene diazonium tetrafluoroborate **2a** as our starting materials to investigate the visible-light-driven arylation reaction. The screening conditions are summarized in Table 1. When $[Ru(bpy)_3Cl_2] . 6H_2O$ is used as a photosensitizer using $Pd(OAc)_2$ as catalyst under green LED we got 32% yield (entry 1). To improve the efficiency of the reaction we screened different photocatalysts (entry 2-4), Eosin-Y was found to be the best photocatalyst for our reaction which gives 46% yield (entry 3). Then we screened different solvents (entries 5-7), and our previously chosen solvent MeOH was found to be the best. To further improve efficiency we changed the catalyst to $Pd(TFA)_2$ we got a slight increase in yield 50% (entry 8). Then we add Trifluoroacetic acid as an additive in the presence of $Pd(OAc)_2$ we got 57% yield (entry 9).

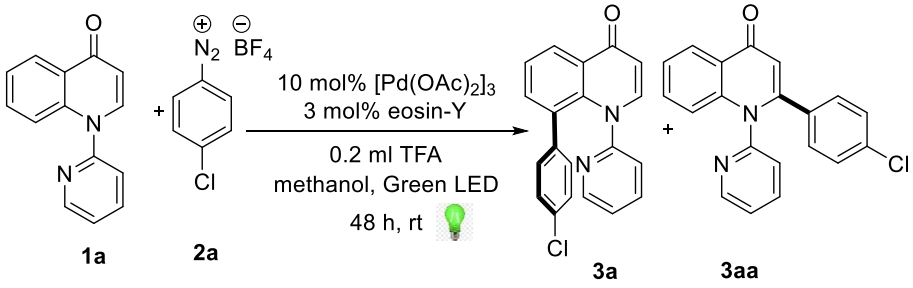


Table 1: Optimization table for reaction

Entry	Catalyst	Photocatalyst	Additive	Solvent	Time	Yield(%)[b]
1	$Pd(OAc)_2$	$Ru(bpy)_3Cl_2.6H2O$	-	MeOH	24 h	32
2	$Pd(OAc)_2$	methylene blue	-	MeOH	24 h	NR
3	$Pd(OAc)_2$	eosin-Y	-	MeOH	24 h	46
4	$Pd(OAc)_2$	Rhodamine B	-	MeOH	24 h	NR
5	$Pd(OAc)_2$	eosin-Y	-	DMF	24 h	30
6	$Pd(OAc)_2$	eosin-Y	-	DMSO	24 h	Trace
7	$Pd(OAc)_2$	eosin-Y	-	MeCN	24 h	12
8	$Pd(TFA)_2$	eosin-Y	-	MeOH	24 h	50
9	$Pd(OAc)_2$	eosin-Y	TFA	MeOH	24 h	57
10	$[Pd(OAc)_2]_3$	eosin-Y	TFA	MeOH	24 h	71
11	$[Pd(OAc)_2]_3$	eosin-Y	TFA	MeOH	36 h	74
12	$[Pd(OAc)_2]_3$	eosin-Y	TFA	MeOH	48 h	81
13	$[Pd(OAc)_2]_3$	-	TFA	MeOH	48 h	32
14	-	eosin-Y	TFA	MeOH	48 h	NR
15[c]	$[Pd(OAc)_2]_3$	eosin-Y	TFA	MeOH	48 h	NR
16[d]	$[Pd(OAc)_2]_3$	eosin-Y	TFA	MeOH	48 h	81
17[e]	$[Pd(OAc)_2]_3$	eosin-Y	TFA	MeOH	48 h	47

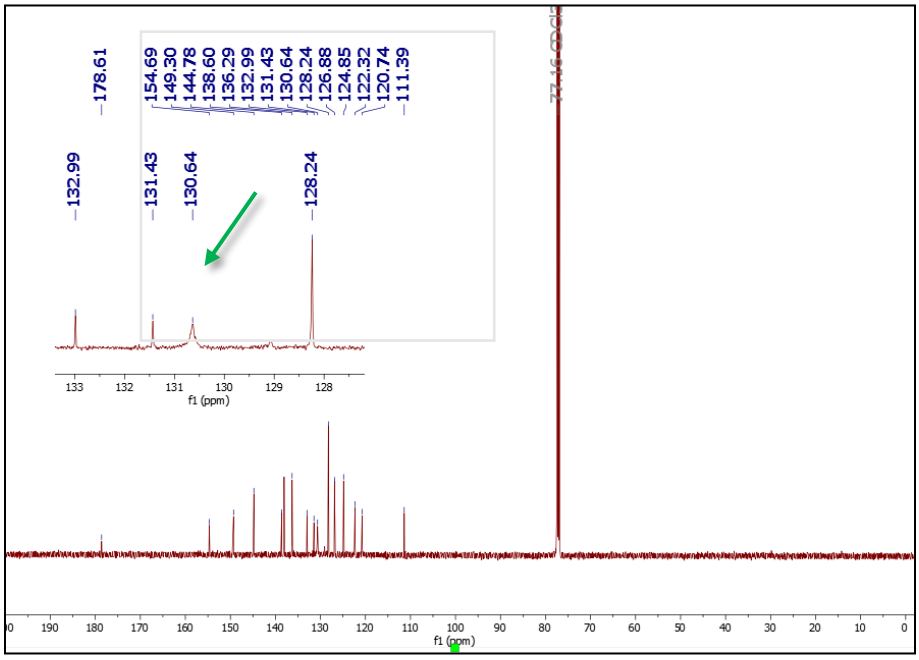
Reaction condition[a]: **1a** (1 equiv. 0.11 mmol), **2a** (3 equiv.), Catalyst (10 mol%), Photocatalyst (3 mol%), Additive (0.2 mL),Solvent (0.5 mL).[b] Isolated yield [c]Without light. [d]Photocatalyst (5 mol%).[e]**2a** (4 equiv.)

Then we changed our catalyst to $[Pd(OAc)_2]_3$ and we got 71% yield. Then we optimize the reaction from 24-48 h and got the highest yield of 81% (entry 12). To know whether the reaction components are necessary or not we have done the reaction in the absence of Eosin-Y, and there is a decrease in yield to 32% (entry 13). Without light and without catalyst there is no

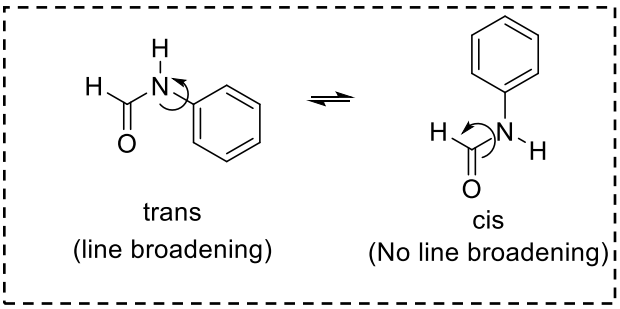
reaction (entry 14-15). Lastly, we increased the amount of **2a** to 4 equiv. but there is a decrease in yield to 68% (entry 17).

Explanation for the ^{13}C NMR peak broadening:

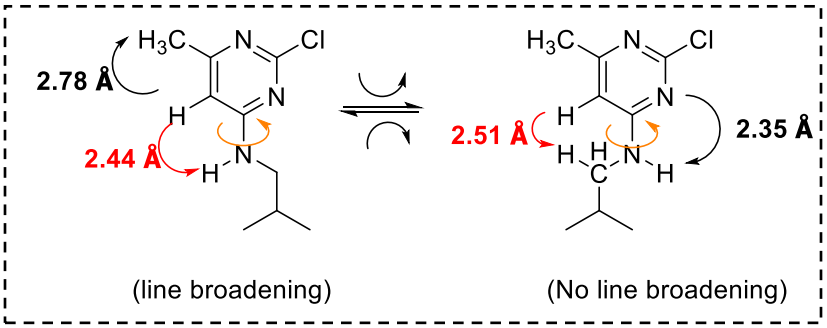
During the characterization of **3a** by NMR spectroscopy we encountered there was broadening of the ^{13}C NMR peak at **δ = 130.64 ppm** which is an absurd phenomenon.



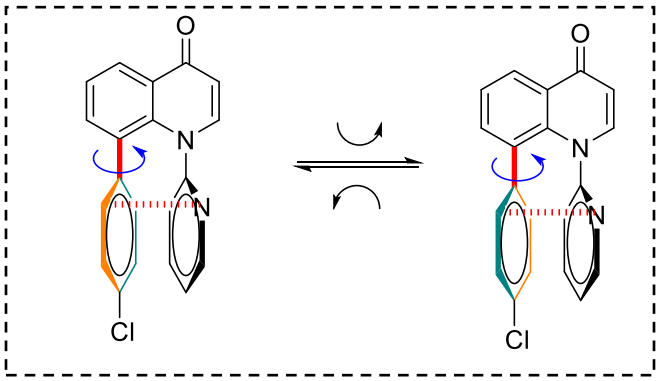
In 1974 Nakanishi and Yamamoto described ^{13}C NMR peak broadening of Formanilide where the cis isomer of formanilide shows a broadening effect due to the interaction of carbonyl oxygen with ortho-hydrogens of the phenyl ring. [8]



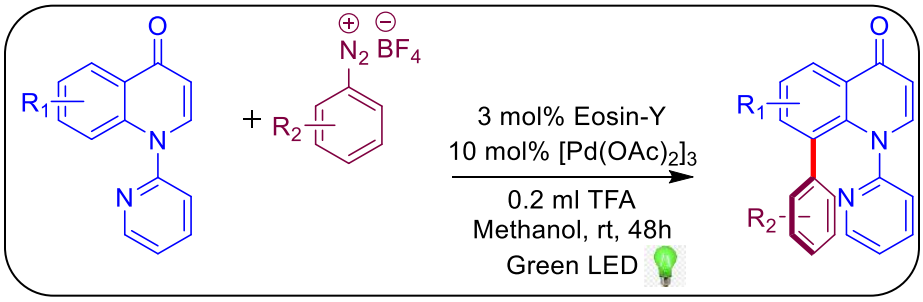
In 2004, Garner et.al described ^{13}C NMR broadening due to the rotamer effect of 2-chloro-N-isobutyl-6-methylpyrimidin-4-amine. [9]

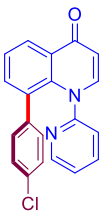


We believed a similar type of effect is answerable for the ^{13}C NMR broadening in our case. Where there occurs an interaction between pyridine N-atom with the Ortho-carbons of the 8-substituted aryl ring.

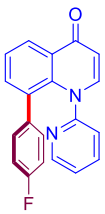


SUBSTRATE SCOPE:

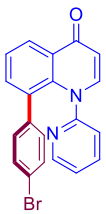




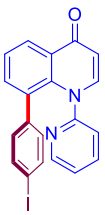
3a(81%)



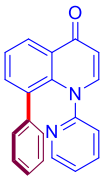
3b(32%)



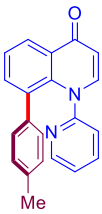
3c(74%)



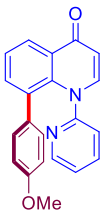
3d(54%)



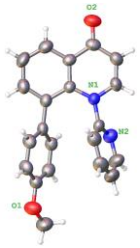
3e(23%)

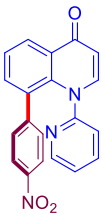


3f(75%)

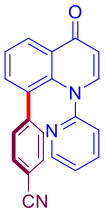


3g(71%)

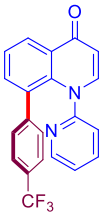




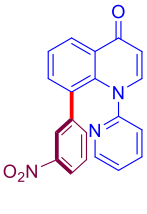
3h(67%)



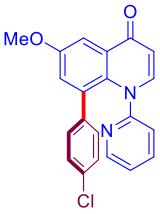
3i(48%)



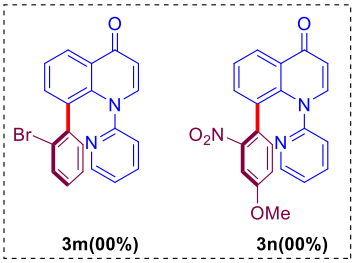
3j(46%)



3k(64%)



3l(27%)



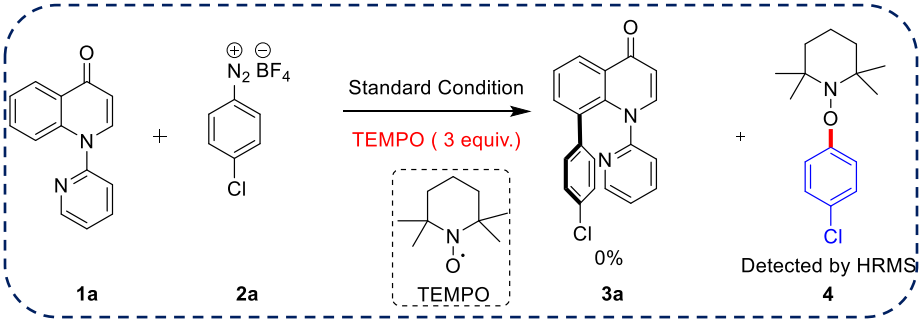
3m(00%) 3n(00%)

With optimized condition in our hands, we next examined the scope of our reaction. At first, we changed different halogen substituents (**3b-3d**) and we got 32-74% yield. When we tried the reaction without any substituent on diazonium salt we got product **3e** in 23% yield. After that, we add different donating groups –Me, -OMe group, and we **3f** and **3g** in 75% and 71% yield respectively. Following we changed different withdrawing groups (**3h-3j**) and we got 46-67% yield. When we changed the substituent position from

para to *meta* got a good yield of 64%. Then we changed our starting material from **1a** to **1b** and reacted it with **2a** to get **3l** with an 27% yield. When changed substituent position to *ortho* the reaction doesn't occur, we believed this is due to steric hindrance created by *ortho* substituents.

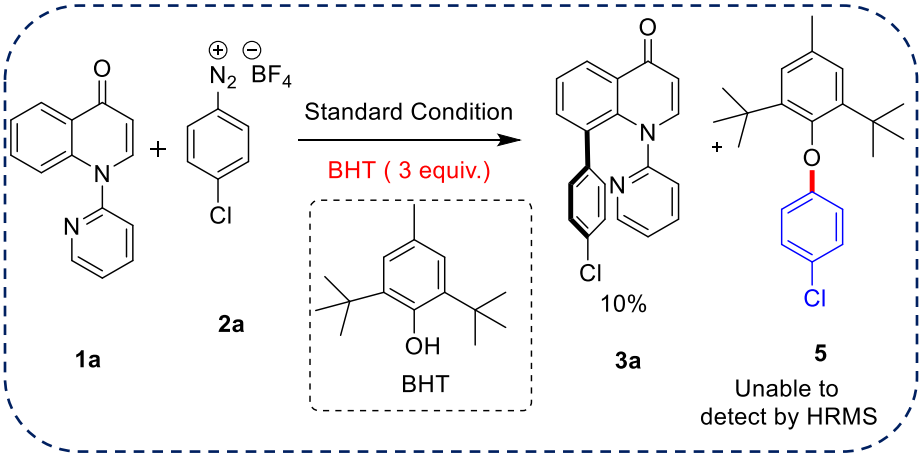
D: CONTROL EXPERIMENTS:

Radical trapping experiments:



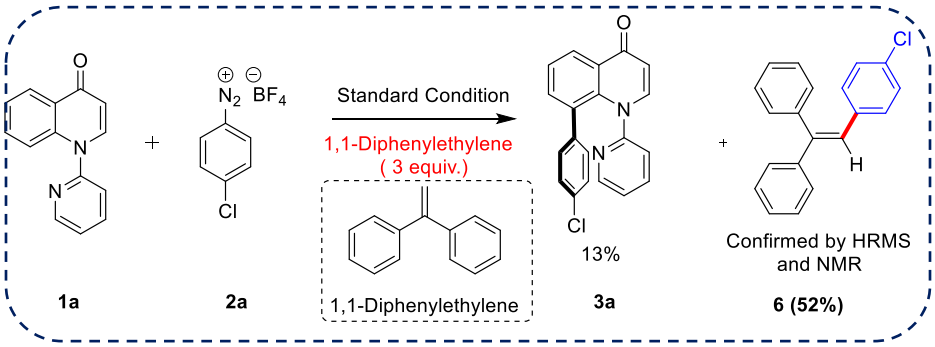
Scheme 5: Radical trapping by TEMPO

Using 2,2,6,6-tetramethy-1-piperdinyloxy (TEMPO) as a radical scavenger the product formation of **3a** was quenched to 00%. And the adduct was detected using mass spectrometry.



Scheme 6: Radical trapping by BHT

When we used butylated hydroxytolune (BHT) as a radical scavenger the reaction was quenched and the product **3a** was obtained in 10% yield.



Scheme 7: Radical scavenged by 1,1-Diphenylethylene

When we used 1,1-diphenylethylene as a radical scavenger the reaction was quenched and the product **3a** was obtained in 13% yield. The adduct **6** was isolated by coloumn chromatography in 52% yield and confirmed by mass spectrometry and NMR spectroscopy.

Stern-Volmer Quenching Experiment:

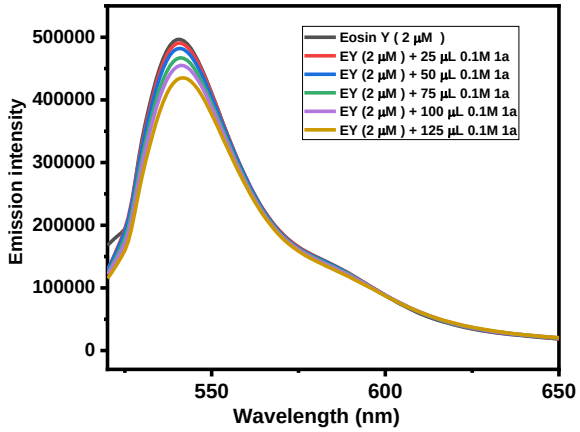


*Figure 4: Fluorescence quenching in presence of **1a***

From fluorescence spectra in presence of **1a** (**Figure 4**) it is observed that there is no significant decrease in emission intensity of eosin Y.

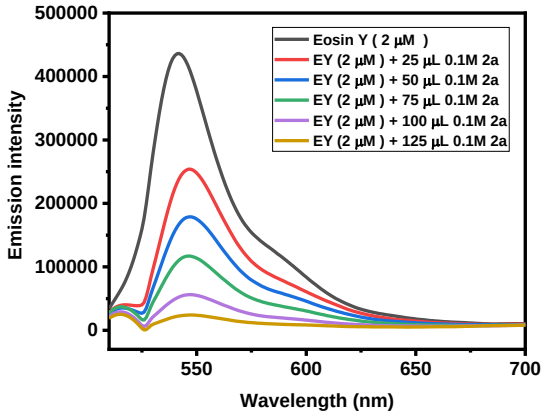


*Figure 5: Fluorescence quenching in presence of **2a***

But in presence of **2a** there is significant decrease in emission intensity as we increase the concentration of **2a.** From this observation we can conclude that there is an electron transfer occur from photocatalyst to diazonium salt (**2a**).

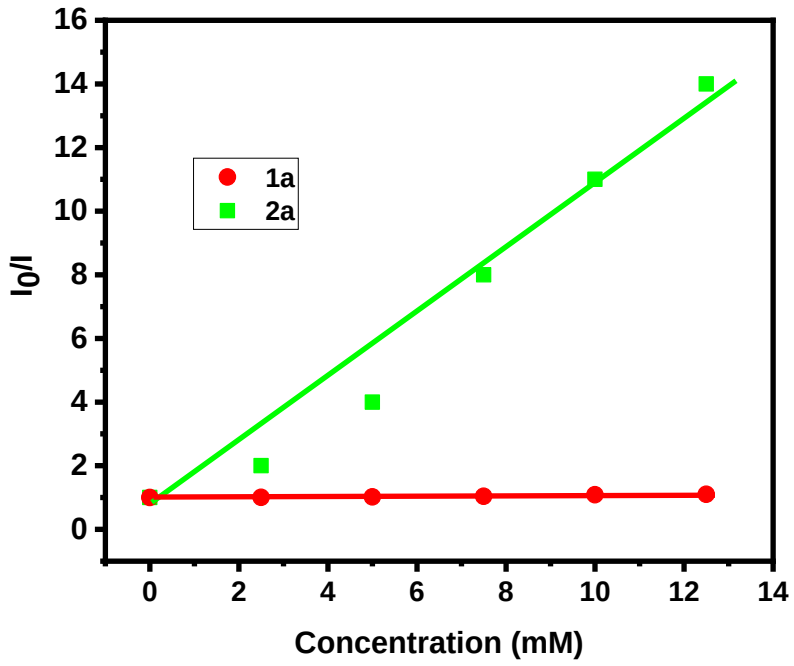


Figure 6: Stern-Volmer plot

Quantum yield calculation:

Determination of the light intensity

The method of Yoon [10] was used to determine the photon flux of the LED (λ_{max} = 515 nm) using conventional ferrioxalate actinometry. Potassium ferrioxalate hydrate (0.737 g) was dissolved in H_2SO4 (10 mL of a 0.05 M solution) to create a ferrioxalate solution of concentration 0.15 M. A buffered solution of 1,10-phenanthroline was made by dissolving Sodium acetate (1.13 g) and 1,10-phenanthroline (5.0 mg) in H_2SO4 (5.0 mL of a 0.5 M solution) Both solutions were kept in a dark location. The ferrioxalate solution (2.0 mL) was put in a dry test tube and exposed to radiation for 120 seconds at λ_{max}= 515 nm in order to measure the photon flux of the LED, the phenanthroline solution (0.35 mL) was then added to the test tube and stir for 1 h in dark. Similarly, a non-irradiated sample was prepared. The

absorbance of both of the solutions was measured at 510 nm. The conversion was calculated using eq 1.

	Non-irradiated	Irradiated
$A_{510\ nm}$	0.7851	2.4422

$$\text{Mol of } Fe^{2+} = \frac{V.\Delta A}{l.\varepsilon} = \frac{(0.00235\ L).(1.6571)}{(1.00\ cm).(11{,}100\ \frac{L}{mol}\ cm)} = 3.5 \times 10^{-7}\ \text{mol} \quad (1)$$

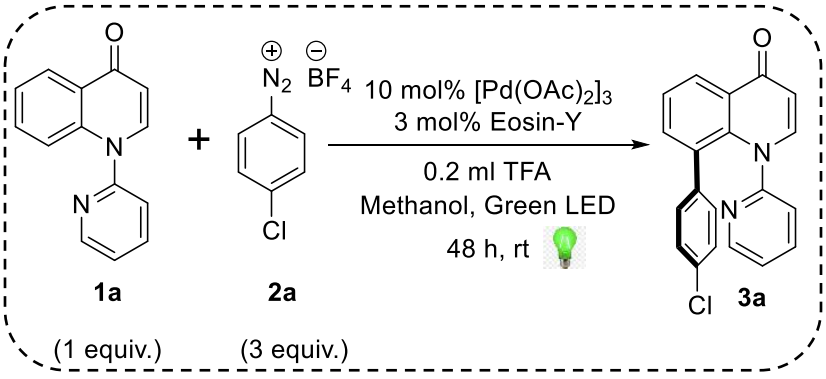
V is the total volume (0.00235 L) of the solution after the addition of phenanthroline, ΔA is the difference in absorbance between irradiated and non-irradiated solutions, l is the path length (1 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L $mol^{-1}cm^{-1}$). The photon flux can be calculated using eq 2.

$$\text{Photon flux} = \frac{mol\ of\ Fe2+}{\varphi.t.f} = \frac{3.50 \times 10{-}7\ \text{mol}}{(0.93)(120\ s)(0.0596)} = 5.26 \times 10^{-8}\ \text{einstein/s} \quad (2)$$

Where f is the percentage of light at 515 nm that is absorbed by the ferrioxalate actinometer, t is the irradiation period, and is the quantum yield for the ferrioxalate actinometer (0.93 at = 515 nm). Equation 3 can be used to determine this value. Where A is the ferrioxalate solution's absorbance at 510 nm, which was determined to be 0.026693.

$$f = 1 - 10^{-A_{515\ nm}} = 1 - 10^{-0.026693} = 0.0596 \quad (3)$$

Determination of reaction quantum yield:



For 48 hours, the reaction mixture was stirred while being exposed to green LED light (max = 515 nm). Utilising cyclohexane as an internal standard, the ^{1}H NMR method was used to calculate the product's yield. Product **3a** had a 90% yield (1.01 $\times 10^{-4}$ mol). Using eq. 4, the reaction quantum yield (φ) was calculated. An absorption spectrum of the catalyst (0.0025 M) gave an absorbance value of 3.4354 at 515 nm (figure 3), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.999.

$$\Phi = \frac{mol\ of\ product}{flux.t.f} = \frac{1.01\times10-4}{(5.26\times10-8).(48\times3600).(0.999)} = 0.03$$

The reaction quantum yield was calculated to be 0.03, which denies possibility of any chain reaction.

C: PLAUSIBLE MECHANISM:

Based on the above mechanistic study and relevant literature reports [11], we proposed a plausible reaction mechanism. The reaction goes via a radical pathway. At first, the photocatalyst Eosin-Y absorbs green light from the light source to generate the activated species $[EY]^{*}$. Then the activated species undergoes oxidative quenching by reaction with Diazonium salt (2a) [13] to obtain oxidized photocatalytic species $[EY]^{\cdot+}$ [12] radical cation and Aryl radical. On the other hand $[Pd(OAc)_2]_3$ reacts with added Trifluoro

acetic acid to form activated catalytic species $Pd(TFA)_2$ which then undergoes C-H activation directed by pyridine nitrogen to give species **[A]**. Then the aryl radical undergoes oxidative addition to species **[B]**, which then transfers a single electron to the radical cation to regenerate the photocatalyst and generate Pd (IV) species **[C]**. The species **[C]** then undergoes reductive elimination to give the final product (3a) and regenerate catalytic activated species $Pd(TFA)_2$.

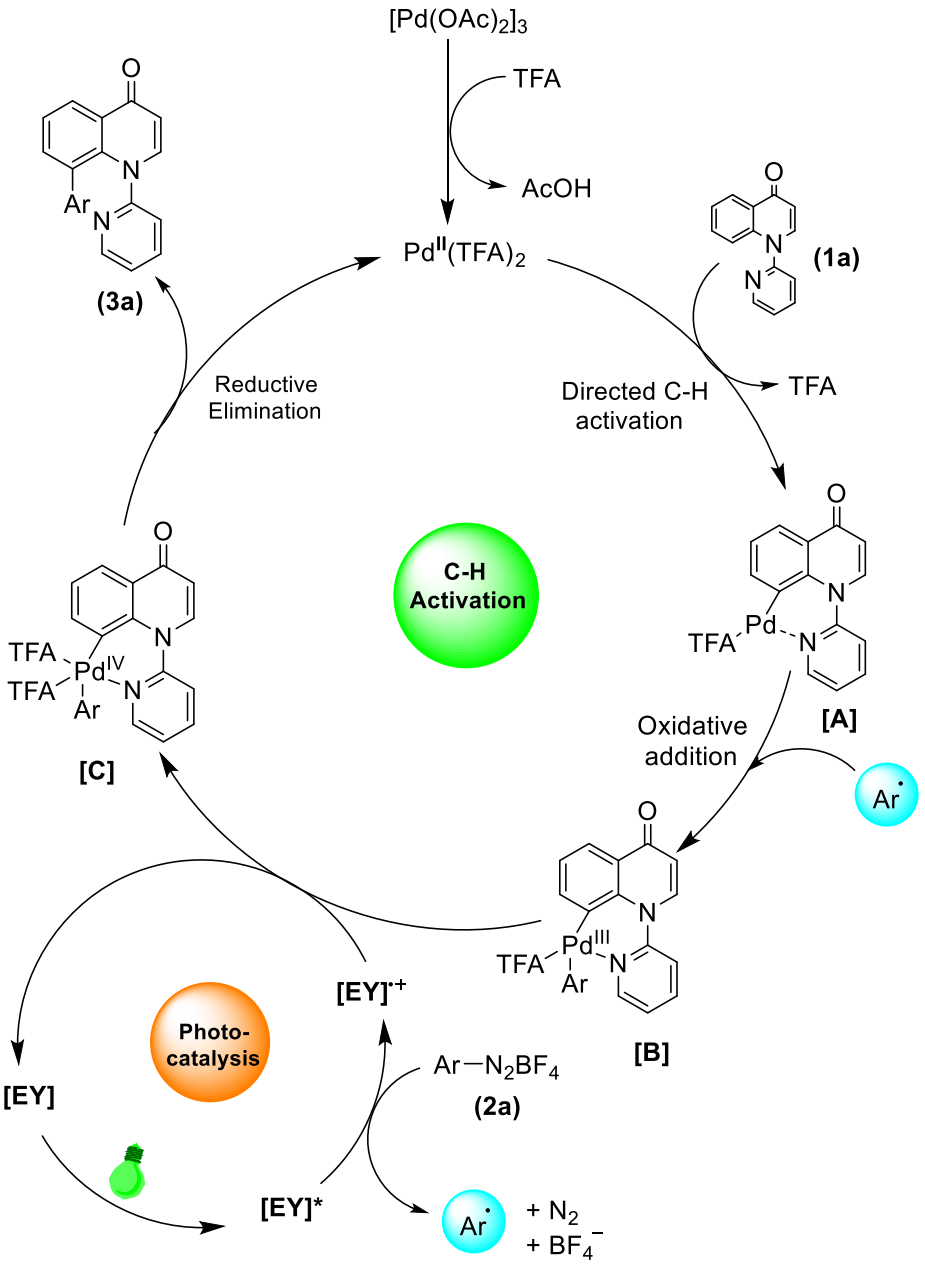


Figure 7: Plausible mechanism of arylation

Chapter 3

EXPERIMENTAL WORK:

A. Material and instrumentation

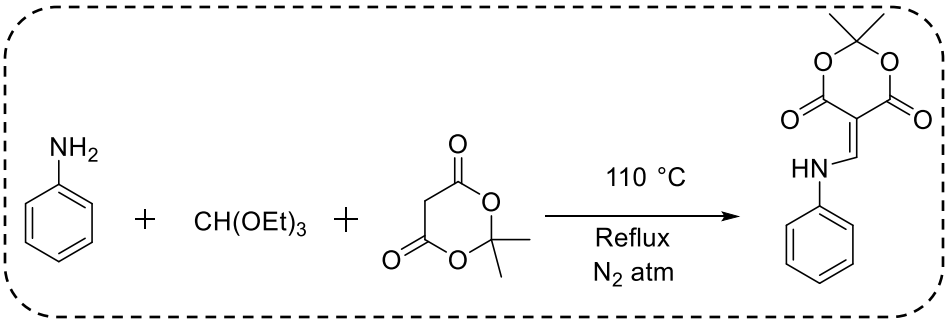
All the chemicals were bought from Sigma Aldrich, TCI, Spectrochem and Avra. The mass spectrometry (ESI-MS) was performed using a Bruker MicrOTOF-Q II that used positive-mode electron spray ionization. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) were recorded in deuterated solvent (D_2O) using Bruker Advance 500.

A. Synthesis of starting material

The starting material 1-(2-pyridyl)-4(1*H*)-quinolinone was synthesized by using the following two previously reported methods. First is the synthesis of Quinoline-4(1*H*)-one then substituting the 1*H* with the 2-pyridyl group [14],[15].

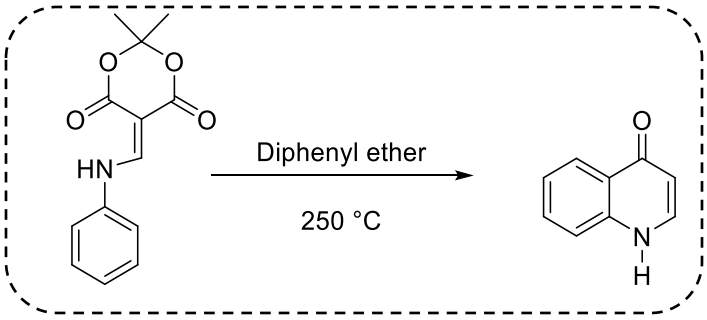
Synthesis of quinoline-4(1*H*)-one:

A solution of Meldrum's acid (1.5 equiv.) in triethyl orthoformate (10 equiv.) was refluxed at 115 ˚C for 2 h under an N_2 atmosphere. Once that reaction mixture had reached room temperature, it was removed. Then 1 equiv. of aniline was added to the mixture and again refluxed at 115 ˚C for 2 h. The precipitate was then filtered, and hexane was used to wash it.



Scheme 8: Synthesis of intermediate

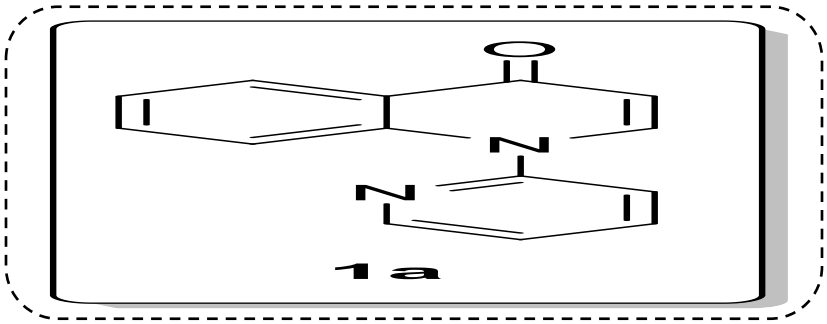
Diphenyl ether was preheated to 250 ˚C and the intermediate portioned addition was made. The reaction was then kept going for 30 minutes before being cooled to room temperature. And hexane was added. The precipitate was filtered and then washed with hexane [14].



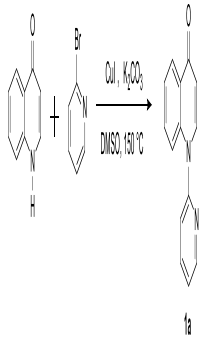
Scheme9: Synthesis of Quinoline-4(1H)-one from intermediate

Synthesis of 1-(2-pyridyl)-4(1*H*)-quinolinone(1a):

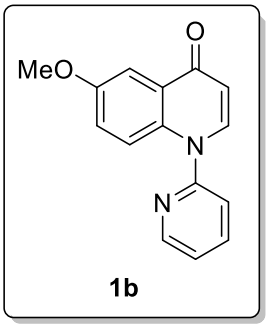
1 equiv. of quinoline-4(1*H*)-one, 2 equiv. of K_2CO_3, and 10 mol% of CuI were added in 10 mL of DMSO, and Heat was applied to the reaction mixture at 150 ˚C while N_2 was present. Next, 2 mmol of 2-bromopyridine was added to the reaction mixture. After 12 hours of stirring, the reaction was cooled to room temperature. After that, the reaction mixture was quenched with water, and the organic layer was extracted with ethyl acetate, concentrating the organic layer under reduced pressure. Crystalize with ethanol to get a pure product [15].



*Scheme10: Synthesis of **1a***

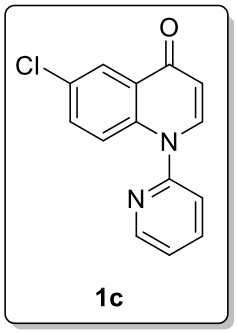


1-(2-Pyridyl)-4(1*H*)-quinolinone (1a): Yellow solid; 44% **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (m, 1H), 8.44 (dd, 1H), 7.97 (dt, 1H), 7.80 (d, 1H), 7.48 (m, 3H), 7.36 (t, 1H), 7.23 (d, 1H), 6.39 (d, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.6, 153.5, 150.5, 141.7, 140.1, 139.4, 132.0, 126.8, 126.6, 124.4, 124.3, 121.6; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{11}N_2O$ $[M+H]^+$:223.0866, found: 223.0863.



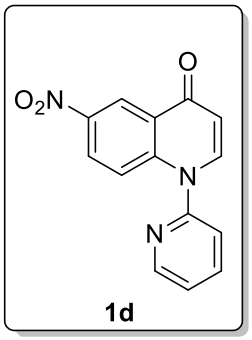
1b

6-Methoxy-1-(pyridin-2-yl)quinolin-4(1*H*)-one (1b): Brown solid; 48% **^{1}H NMR** (500 MHz, DMSO) δ 8.74 – 8.67 (m, 1H), 8.11 (dd, *J* = 41.3, 7.7 Hz, 2H), 7.79 – 7.59 (m, 3H), 7.30 – 7.10 (m, 2H), 6.18 (d, *J* = 7.7 Hz, 1H), 3.86 (s, 3H); **^{13}C NMR** (126 MHz, DMSO) δ 176.1, 155.9, 153.0, 149.8, 142.0, 140.2, 134.4, 127.1, 124.6, 121.9, 121.9, 119.2, 108.5, 105.2, 55.5; **HRMS** (ESI, *m/z*): Calculated for $C_{15}H_{13}N_2O_2$ $[M+H]^+$: 253.0972, found: 253.0966.



1c

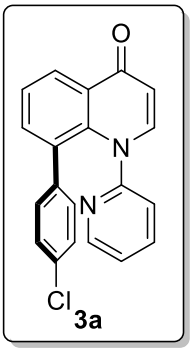
6-Chloro-1-(pyridin-2-yl)quinolin-4(1*H*)-one (1c): Brown solid; 62% **; ^{1}H NMR** (500 MHz, DMSO) δ 8.71 (s, 1H), 8.16 (dd, *J* = 17.2, 9.1 Hz, 3H), 7.70 (dd, *J* = 53.1, 9.0 Hz, 3H), 7.25 (d, *J* = 9.0 Hz, 1H), 6.25 (d, *J* = 7.7 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 175.4, 152.5, 149.8, 143.2, 140.3, 138.5, 132.0, 128.7, 124.8, 124.4, 121.9, 119.9, 109.7; **HRMS** (ESI, *m/*z): Calculated for $C_{14}H_{10}ClN_2O$ $[M+H]^+$: 257.0476, found: 257.0465.



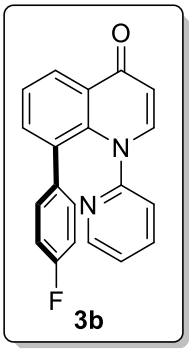
6-Nitro-1-(pyridin-2-yl)quinolin-4(1*H*)-one (1d): Yellow solid; 34%; ^{1}H NMR (500 MHz, DMSO) δ 8.93 (d, *J* = 2.8 Hz, 1H), 8.75 (dd, *J* = 5.0, 1.9 Hz, 1H), 8.37 (dd, *J* = 9.4, 2.9 Hz, 1H), 8.27 – 8.19 (m, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.71 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.40 (d, *J* = 9.4 Hz, 1H), 6.36 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (126 MHz, DMSO) δ 176.0, 152.4, 150.1, 144.3, 143.5, 143.2, 140.6, 126.2, 125.3, 125.2, 122.1, 121.8, 119.5, 110.9; **HRMS** (ESI, *m/z*): Calculated for $C_{14}H_{10}N_3O_3$ $[M+H]^+$: 268.0717, found: 268.0703

C. General Procedure for the reactions:

In 25 mL of a dry test tube, a mixture of 1-(2-pyridyl)-4(1*H*)-quinolinone (1.0 equiv.), diazonium salt (3 equiv.), $[Pd(OAc)_2]_3$ (10 mol%), Eosin-y (3 mol%), and 0.2 mLTFA was taken, and 0.5 mL of Solvent was added. This reaction mixture was stirred under the green LED light for 48 hours at room temperature.

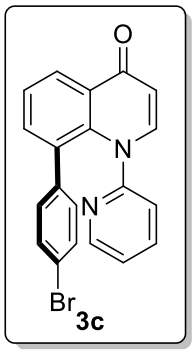


8-(4-Chlorophenyl)-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3a): Dark brown solid; 81% (30.4 mg); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.55 (dd, *J* = 6.2, 3.5 Hz, 1H), 8.39 – 8.25 (m, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.45 (m, 2H), 7.33 (td, *J* = 7.7, 1.9 Hz, 1H), 7.11 – 6.92 (m, 5H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H); **^{13}C{^{1}H }NMR** (126 MHz, $CDCl_3$): δ 178.6, 154.6, 149.3, 144.7, 138.6, 136.2, 132.9, 131.4, 130.6, 128.2, 126.8, 124.8, 122.3, 120.7, 111.3; **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{15}ClN_2O$ $[M+H]^+$: 333.0789, found: 333.0786



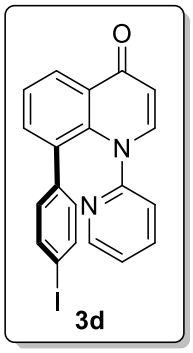
8-(4-Fluorophenyl)-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3b): Brown solid; 32% (11.4 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (t, *J* = 4.9 Hz, 1H), 8.25 (t, *J* = 3.0 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 4.9 Hz, 2H), 7.31 (td, *J* = 7.8, 2.0 Hz, 1H), 7.02 – 6.91 (m, 3H), 6.72 (dd, *J* = 8.8, 5.2 Hz, 3H), 6.43 (d, *J* = 7.9 Hz, 1H); **^{13}C{^{1}H }NMR** (126 MHz, $CDCl_3$) δ 178.6, 162.5, 160.5, 154.5, 149.1, 144.8, 138.0, 136.4, 136.0 (d, *J* = 3.7 Hz),

131.6, 130.9, 128.9, 126.5, 124.7, 122.3, 120.6, 115.0 (d, *J* = 21.6 Hz), 111.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ-114.9; **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{14}FN_2O$ $[M+H]^+$: 317.1085, found-317.1094



3c

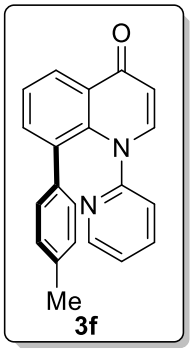
8-(4-Bromophenyl)-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3c): Brown solid; 74% (31.4 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 6.0, 3.7 Hz, 1H), 8.28 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.45 (m, 2H), 7.33 (td, *J* = 7.7, 1.9 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 1H (126 MHz, $CDCl_3$) δ 178.5, 154.6, 149.2, 144.8, 139.0, 138.0, 137.9, 136.2, 131.4, 131.1, 130.9, 128.9, 126.8, 124.8, 122.3, 121.1, 120.7, 111.3; **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{14}BrN_2O$ $[M+H]^+$: 377.0284, found- 377.0267



3d

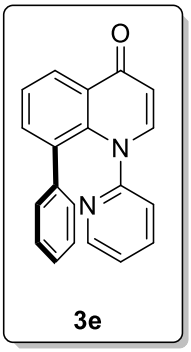
8-(4-Iodophenyl)-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3d): Brown solid; 54% (25.7 mg) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 6.1, 3.6 Hz,

1H), 8.28 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.45 (m, 2H), 7.39 – 7.30 (m, 3H), 6.99 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 7.9 Hz, 1H); **^{13}C NMR{^{1}H}** (126 MHz, $CDCl_3$) δ 178.5, 154.6, 149.2, 144.8, 139.6, 138.0, 137.9, 137.1, 136.1, 131.4, 131.1, 128.9, 126.8, 124.8, 122.2, 120.8, 111.2, 92.6. **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{14}IN_2O$ $[M+H]^+$:425.0145, found- 425.0131.



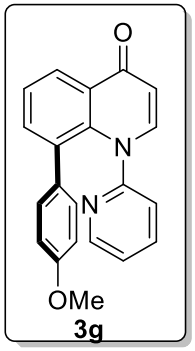
3f

8-Phenyl-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3e): Brown solid; 22% (7 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.7 Hz, 1H), 8.26 (s, 1H), 8.05 (d, *J* = 6.6 Hz, 1H), 7.53 (dt, *J* = 14.7, 7.3 Hz, 2H), 7.26 (s, 2H), 7.02 (dd, *J* = 22.7, 4.7 Hz, 5H), 6.89 (t, *J* = 5.9 Hz, 1H), 6.74 (s, 1H), 6.59 – 6.42 (m, 1H); **^{13}C NMR{^{1}H}** (126 MHz, DMSO) δ 178.9, 154.6, 149.0, 144.9, 140.1, 137.9, 136.5, 132.8, 129.4, 128.2, 126.9, 126.5, 124.9, 122.2, 120.7, 111.2; **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{15}N_2O$ $[M+H]^+$: 299.1179, found- 299.1181



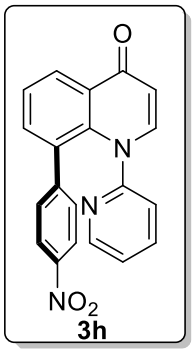
3e

1-(Pyridin-2-yl)-8-(p-tolyl)quinolin-4(1*H*)-one (3f): Brownish orange solid; 75% (26.3 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 7.8, 1.9 Hz, 1H), 8.24 (dd, *J* = 5.0, 1.9 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.45 (m, 2H), 7.27 – 7.23 (m, 1H), 6.95 – 6.79 (m, 5H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 2.19 (s, 3H). **^{13}C NMR {^{1}H}** (126 MHz, $CDCl_3$) δ 178.7, 154.6, 148.9, 144.9, 138.0, 137.7, 137.1, 136.6, 136.4, 132.8, 129.2, 128.9, 128.8, 126.1, 124.8, 122.0, 120.7, 111.0, 21.0.; **HRMS** (ESI, *m/z*): Calculated for $C_{21}H_{17}N_2O$ $[M+H]^+$: 313.1335, found- 313.1337



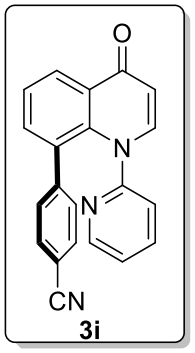
3g

8-(4-Methoxyphenyl)-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3g): Brownish red solid; 71% (26.2 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 7.5, 2.2 Hz, 1H), 8.27 – 8.23 (m, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.31 – 7.26 (m, 1H), 6.98 – 6.89 (m, 3H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 2H), 6.45 (d, *J* = 7.9 Hz, 1H), 3.71 (s, 3H). **^{13}C NMR {^{1}H}** (126 MHz, $CDCl_3$) δ 178.8, 158.5, 154.6, 149.0, 144.8, 138.0, 136.3, 132.6, 132.5, 130.5, 129.0, 126.0, 124.8, 122.0, 120.6, 113.6, 111.1, 55.4. **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{14}BrN_2O$ $[M+H]^+$: 328.1285, found- 328.1278.



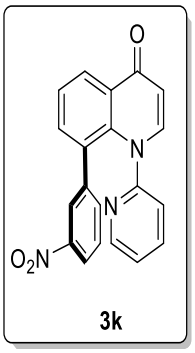
3h

8-(4-Nitrophenyl)-1-(pyridin-2-yl)quinolin-4(1*H*)-one(3h): Brownish yellow solid; 67% (25.8 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 6.9, 2.8 Hz, 1H), 8.26 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.48 (m, 2H), 7.34 (td, *J* = 7.7, 1.9 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.91 (dd, *J* = 7.4, 4.8 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H); **^{13}C{^{1}H }NMR** (126 MHz, $CDCl_3$) δ 178.3, 154.6, 149.6, 146.8, 146.3, 144.8, 138.4, 137.9, 136.2, 130.2, 130.1, 128.9, 127.9, 124.9, 123.1, 122.6, 120.5, 111.7; **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{14}N_3O_3$ $[M+H]^+$:344.1030, found-344.1030



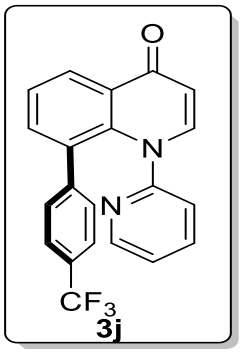
3i

4-(4-Oxo-1-(pyridin-2-yl)-1,4-dihydroquinolin-8-yl)benzonitrile (3i): HRMS (ESI, *m/z*): Black solid; 48%(17.5 mg)Calculated for $C_{21}H_{14}N_3O$ $[M+H]^+$: 324.1131, found- 324.1126



3k

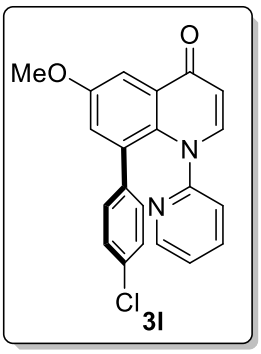
1-(Pyridin-2-yl)-8-(4-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3j): Brown solid; 46% (19 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 7.5, 2.1 Hz, 1H), 8.28 – 8.20 (m, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.31 – 7.24 (m, 1H), 7.00 – 6.84 (m, 3H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 7.9 Hz, 1H), 3.69 (s, 3H).**^{13}C NMR {^{1}H}(**126 MHz, $CDCl_3$) δ 178.76, 158.48, 154.53, 148.94, 144.95, 137.99, 136.40, 132.49, 130.46, 128.90, 125.95, 124.84, 122.11, 120.66, 113.65, 110.96, 55.39. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.90. **HRMS** (ESI, *m/z*): Calculated for $C_{21}H_{14}FN_2O$ $[M+H]^+$: 367.1053, found- 367.1047.



3j

8-(3- Nitrophenyl)-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3k): Brown solid; 64% (24.7 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.63 – 7.49 (m, 2H), 7.42 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.35 (td, *J* = 7.8, 1.9 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.99 – 6.80 (m, 2H), 6.47 (d, *J* = 7.9 Hz, 1H); **^{13}C{^{1}H }NMR** (126

MHz, $CDCl_3$) δ 178.3, 154.8, 149.5, 147.6, 144.8, 141.8, 138.4, 138.1, 136.3, 135.2, 130.0, 129.0, 127.7, 124.9, 124.1, 122.6, 121.7, 120.6, 111.6; **HRMS** (ESI, *m/z*): Calculated for $C_{20}H_{14}N_3O_3$ $[M+H]^+$:344.1030, found-344.1017



3l

8-(4-Chlorophenyl)-6-methoxy-1-(pyridin-2-yl)quinolin-4(1*H*)-one (3l): Brownish red solid; 27% (11 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 5.0, 1.9 Hz, 1H), 8.00 (td, *J* = 7.7, 2.0 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.4, 3.5 Hz, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.24 (m, 2H), 7.19 – 7.10 (m, 3H), 6.17 (d, *J* = 7.8 Hz, 1H), 3.71 (s, 3H); **^{13}C NMR{^{1}H }** (126 MHz, $CDCl_3$) δ 178.7, 154.1, 153.8, 150.5, 140.4, 139.7, 136.8, 136.0, 132.2, 130.7, 130.4, 128.9, 128.6, 127.7, 125.2, 124.3, 121.7, 118.2, 117.0, 111.3, 56.90.**HRMS** (ESI, *m/z*): Calculated for $C_{21}H_{16}ClN_2O_2$ $[M+H]^+$: 363.0895, found- 363.0895

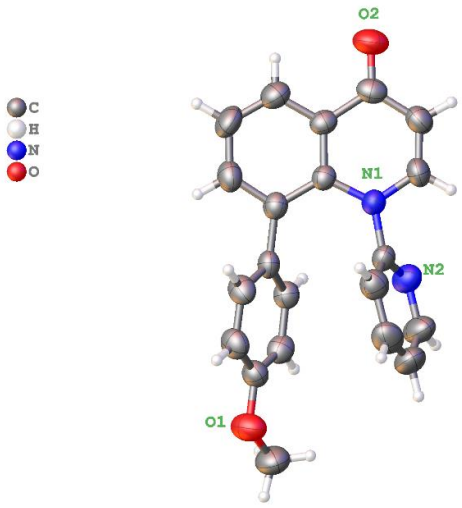


*Figure 8: Single crystal XRD structure of **3g***

Table 2: single crystal data table

Empirical formula	$C_{21}H_{16}N_2O_2$
Formula weight	328.36
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.8272(6)
b/Å	10.3307(12)
c/Å	11.0634(14)
α/°	67.081(12)
β/°	80.978(9)
γ/°	77.360(8)
Volume/ $Å^3$	80.978(9)
Z	2
ρ_{cal} g/cm^3	1.361
μ/mm^{-1}	0.089
F(000)	344.0
Crystal size/mm^3	0.3x0.28x0.2
Radiation	MoKα (λ=0.71073)
2Θ range for data collection/ °	6.268 to 58.314
Index ranges	$-10 \leq h \leq 10$, $-12 \leq k \leq 13$, $-14 \leq 1 \leq 14$
Reflection collected	8218
Independent reflection	3802 [R_{int} = 0.0876, R_{sigma} =0.1133]
Data/restraints/parameters	3802/0/228
Goodness-of-fit on F^2	1.040

Final R indexes [I=2σ (I)]	R_1 = 0.0763, wR_2 = 0.1837
Final R indexes [all data]	R_1 = 0.1697, wR_2 = 0.2358
Largest diff. peak/hole/ e $Å^{-3}$	0.20/-0.17

Chapter 4

CONCLUSION:

In conclusion, we have synthesized regioselective C-8 arylation of 1-(2-pyridyl)-4(1*H*)-quinolinone under mild conditions following the synergistic approach by merging palladium acetate and Eosin-Y. The reaction has broad substrate scope with the only limitation has *ortho* substituents. Try to explain the ^{13}C NMR broadening. Some mechanistic study to construct the plausible mechanism.

APPENDIX-

^{1}H and ^{13}C NMR of 1a-1d, 3a-3l, 6

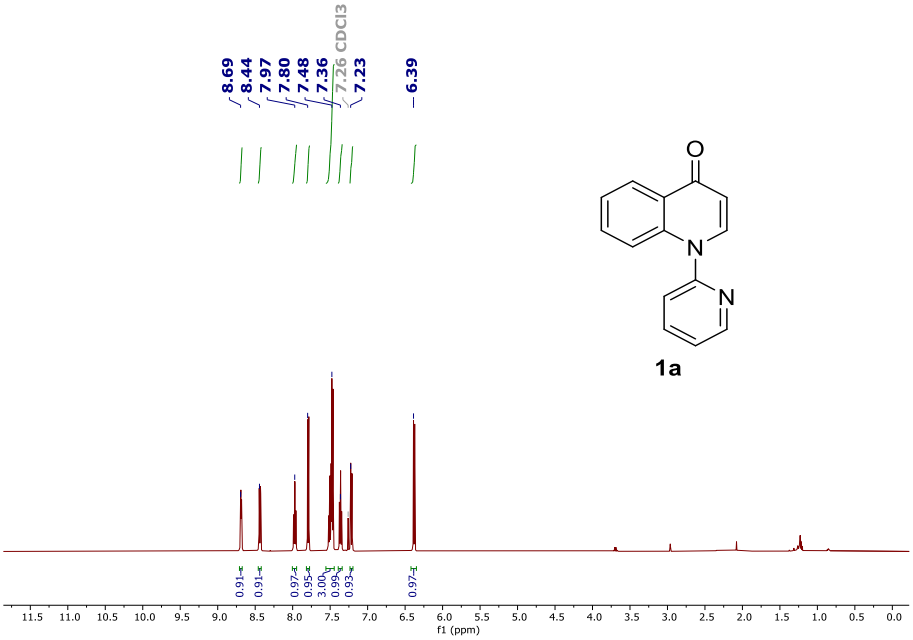


*Figure 6: ^{1}H NMR spectrum of **1a***

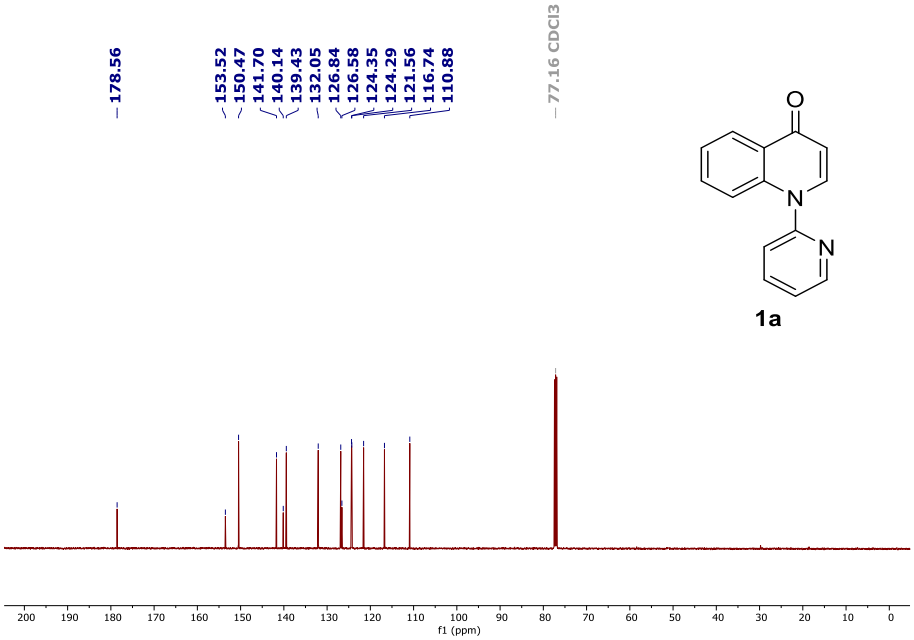


*Figure 7: ^{13}C NMR spectrum of **1a***

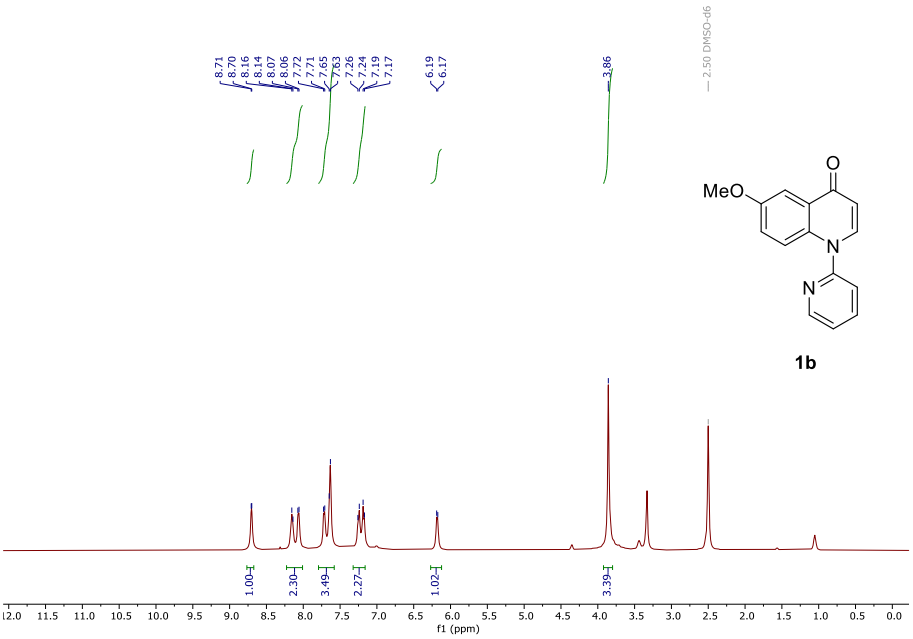


*Figure 8:[1]H NMR spectrum of **1b***

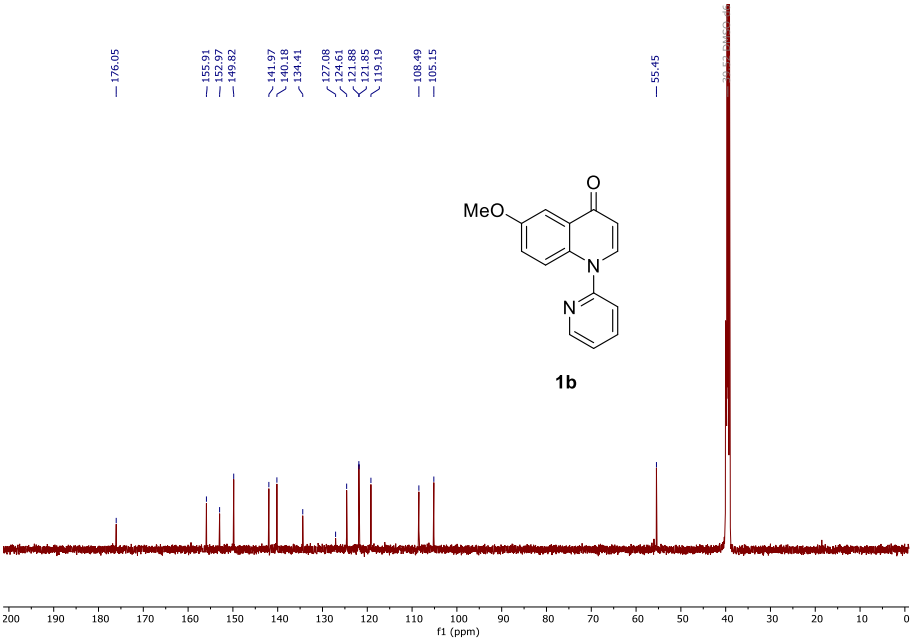


*Figure 9: [13]C NMR spectrum of **1b***

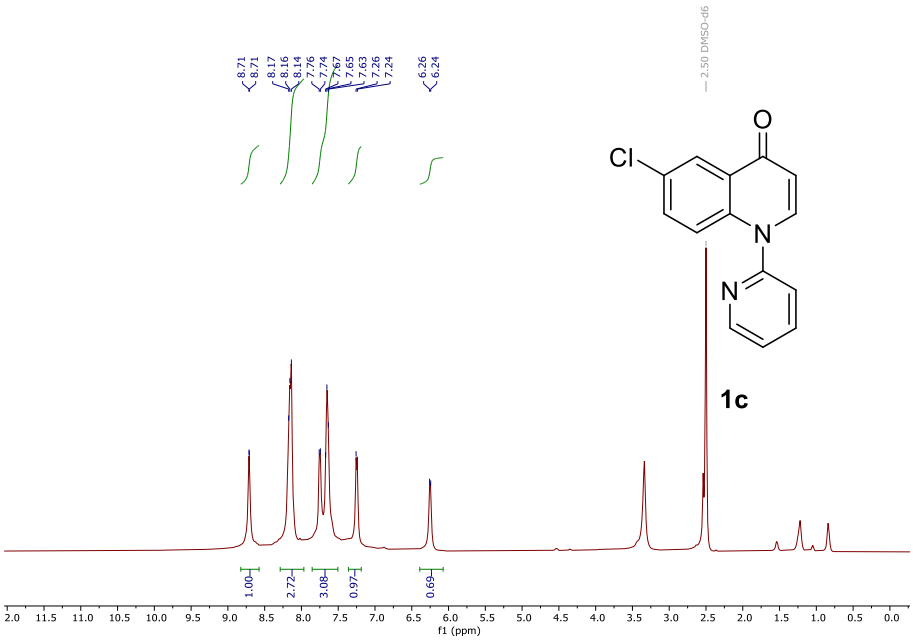


*Figure 10:[1]H NMR spectrum of **1c***

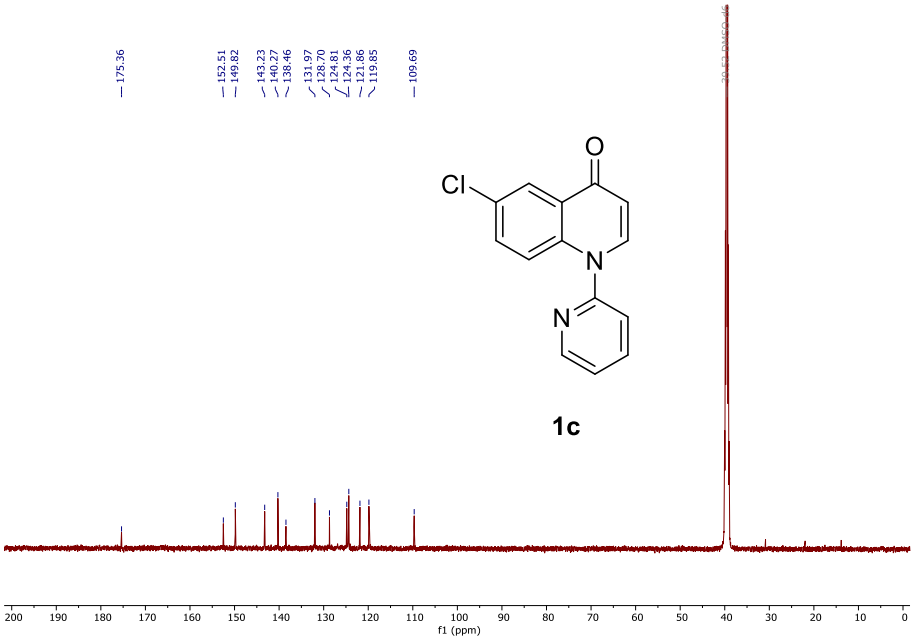


*Figure 11:[13]C NMR spectrum of **1c***

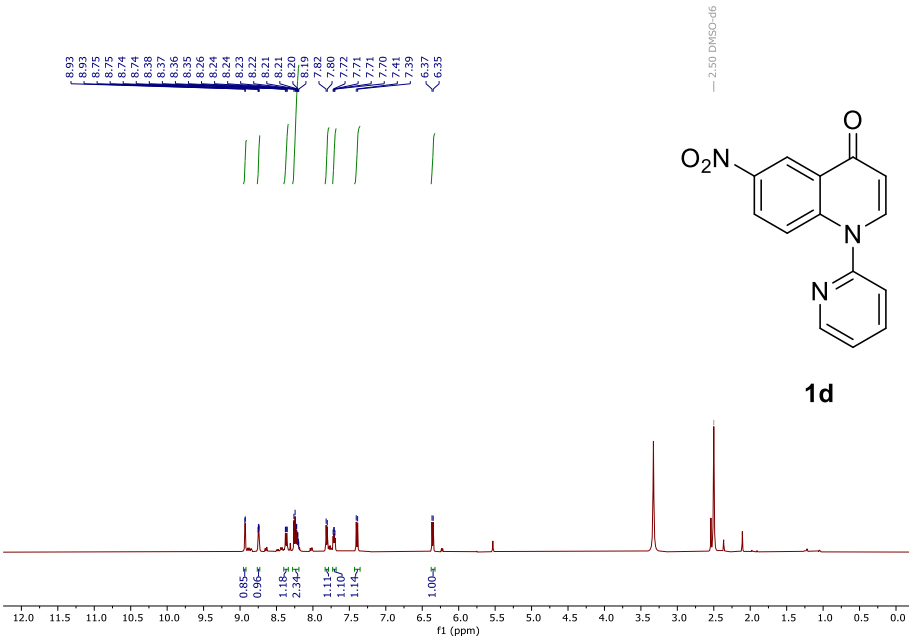


*Figure 12:[1]H NMR spectrum of **1d***

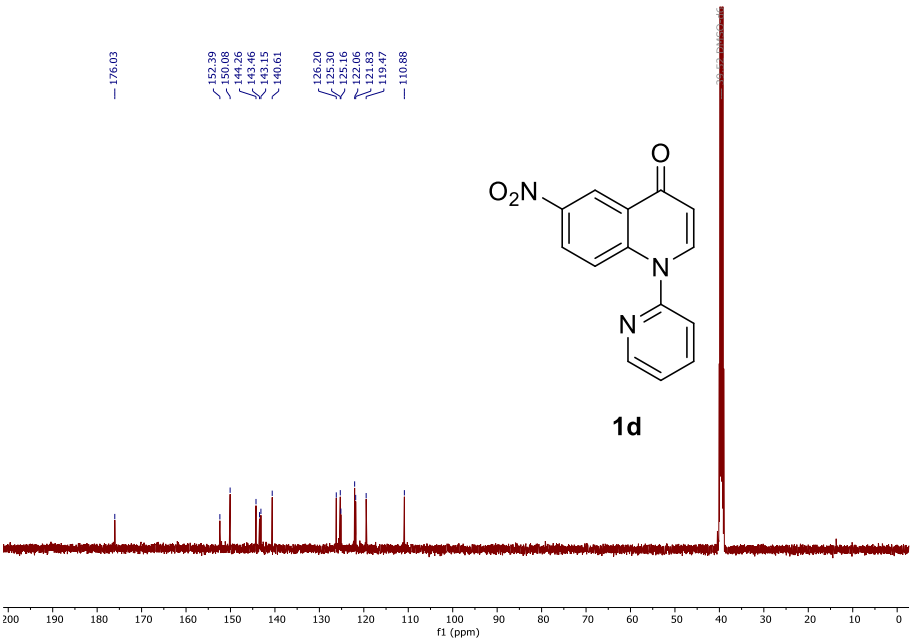


*Figure 13:[13]C NMR spectrum of **1d***

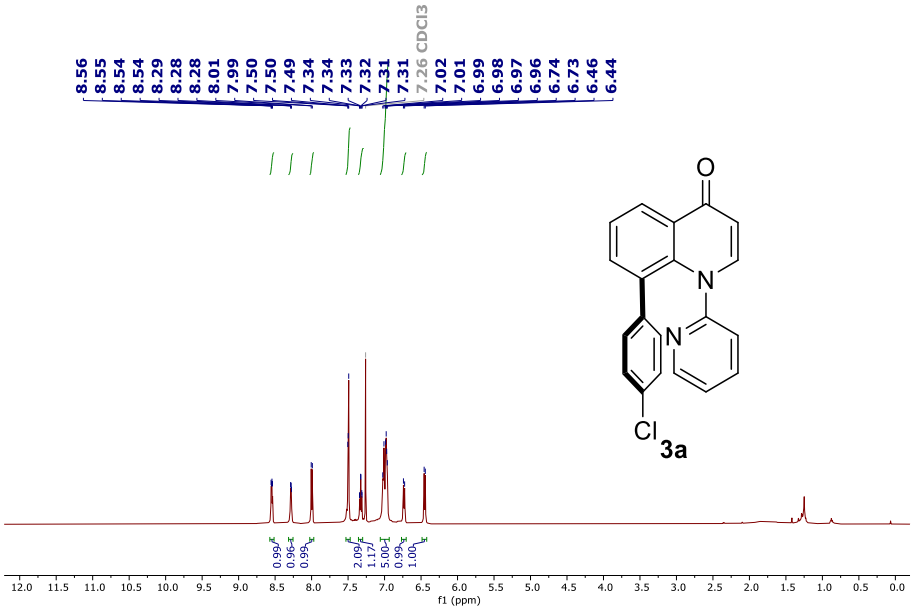


*Figure 14:[1]H NMR spectrum of **3a***

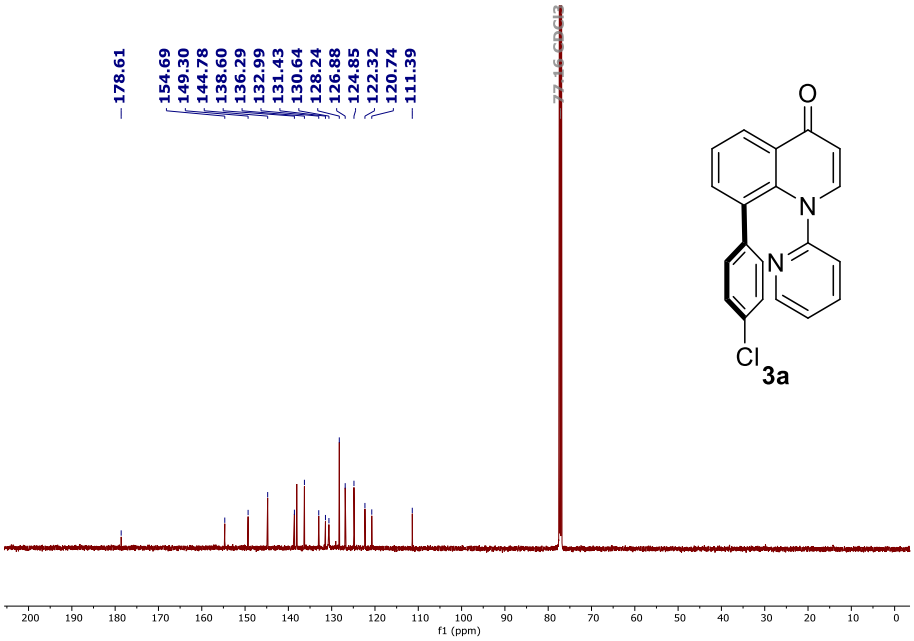


*Figure 15:[13]C NMR spectrum of **3a***

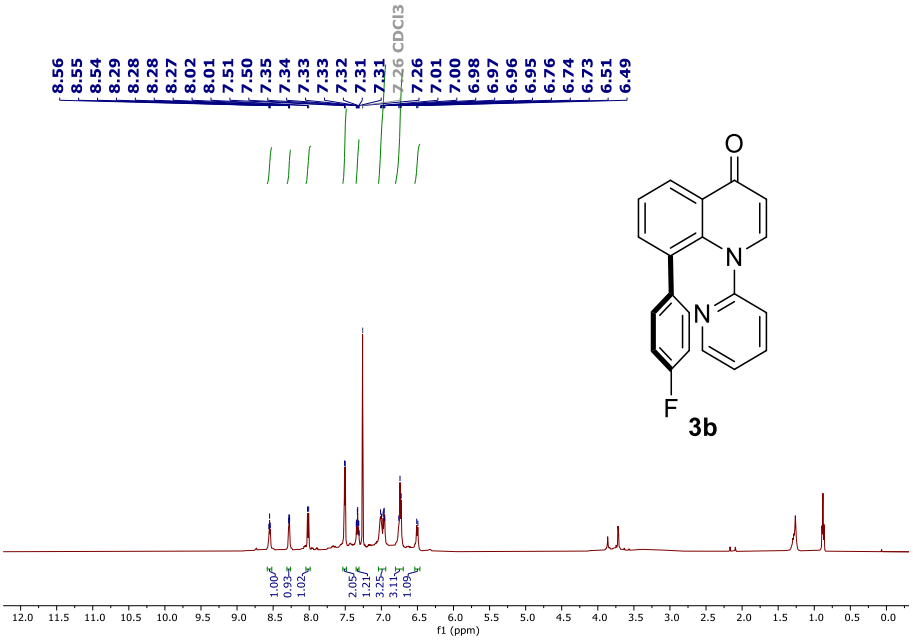


*Figure 16:[1]H NMR spectrum of **3b***

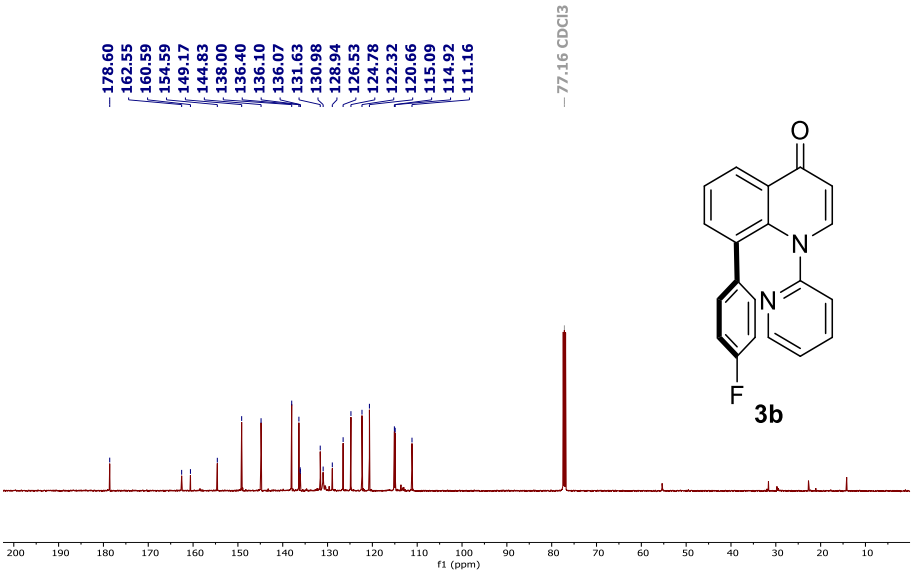


*Figure 17:[13]C NMR spectrum of **3b***

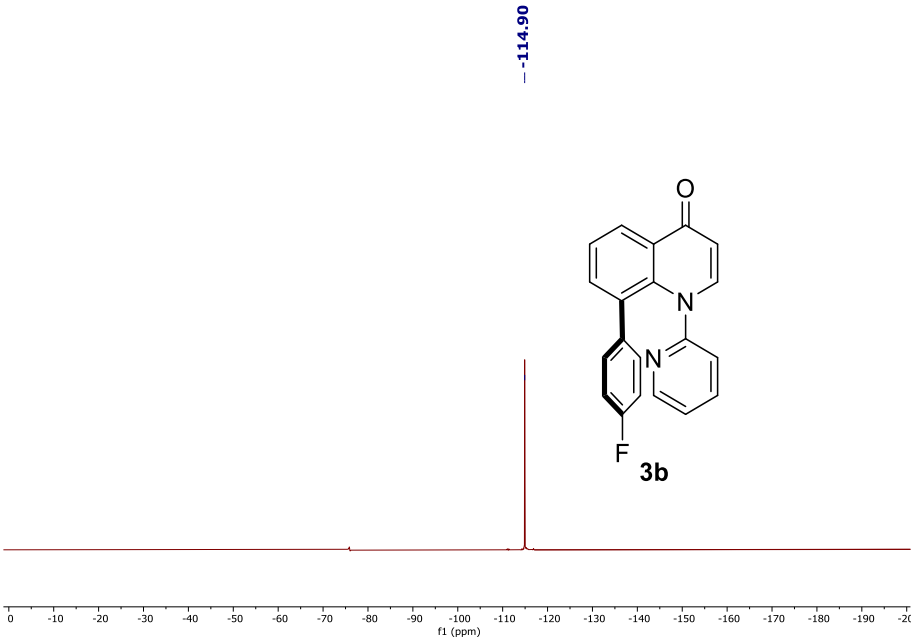


*Figure 18:[19]F NMR spectrum of **3b***

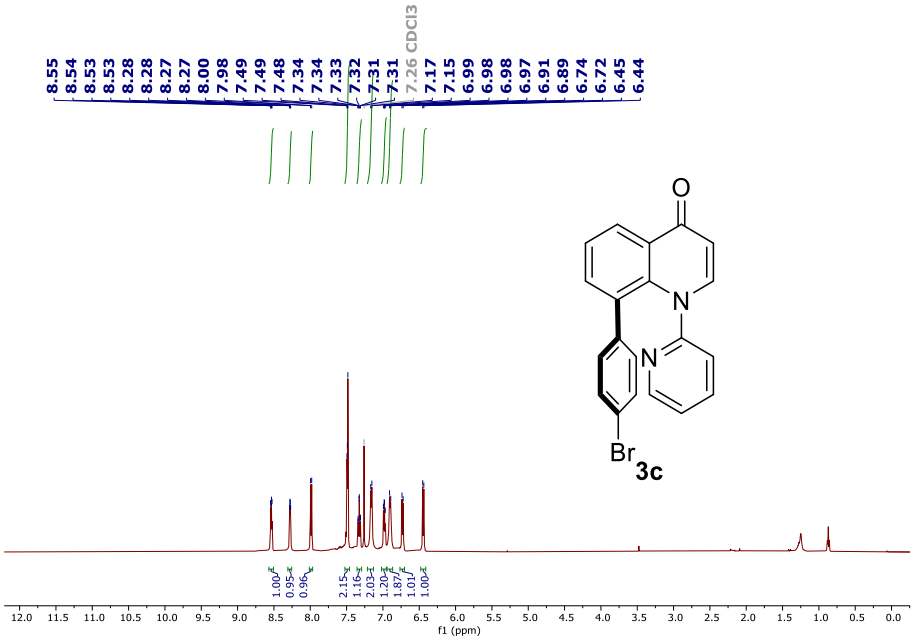


*Figure 19:[1]H NMR spectrum of **3c***

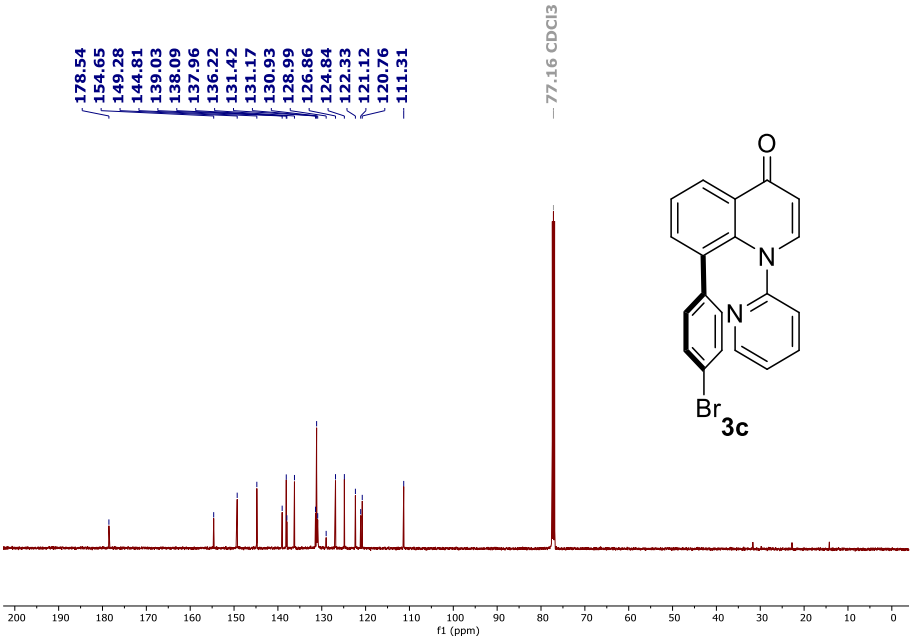


*Figure 20:[13]C NMR spectrum of **3c***

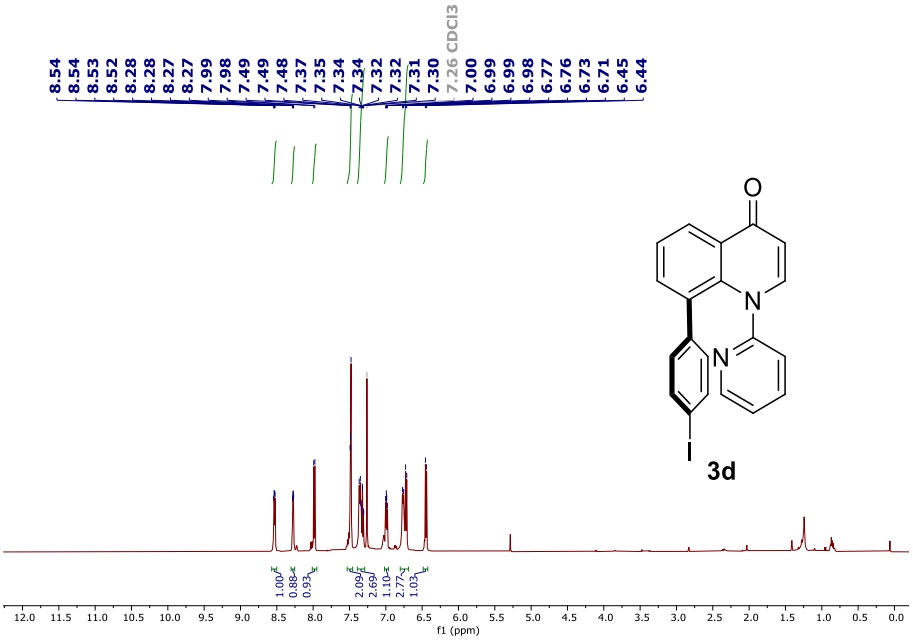


*Figure 21:[1]H NMR spectrum of **3d***

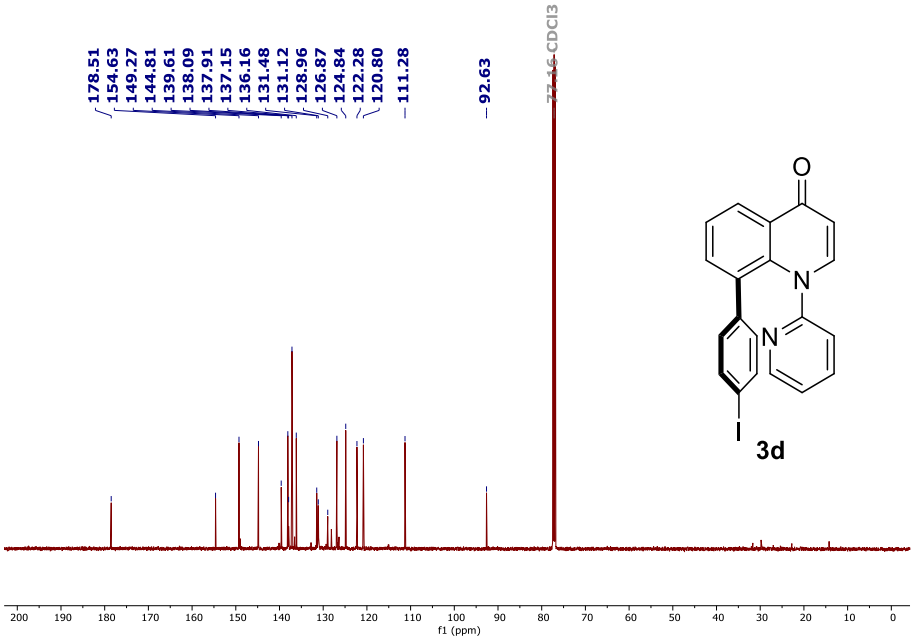


*Figure 22:[13]C NMR spectrum of **3d***

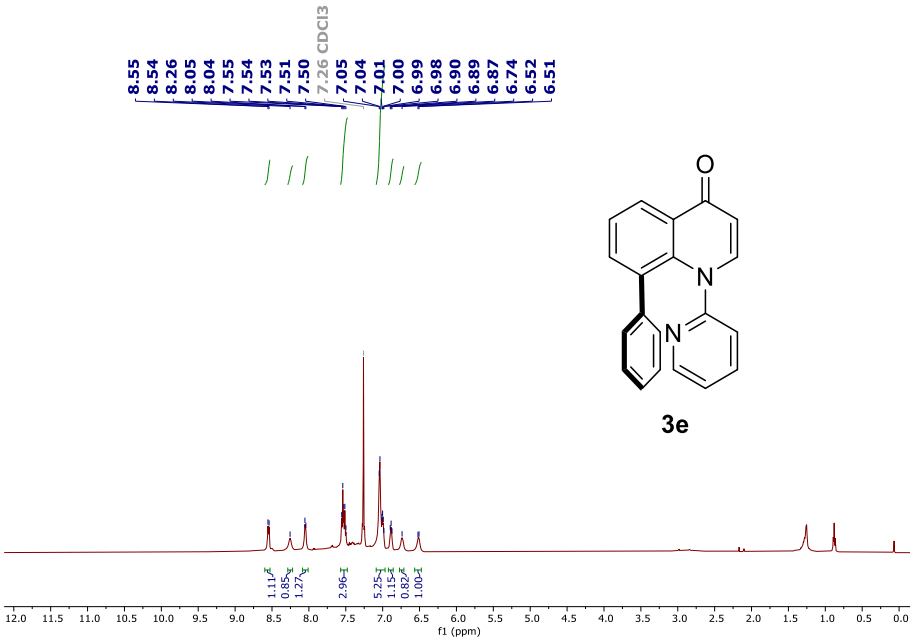


*Figure 23:[1]H NMR spectrum of **3e***

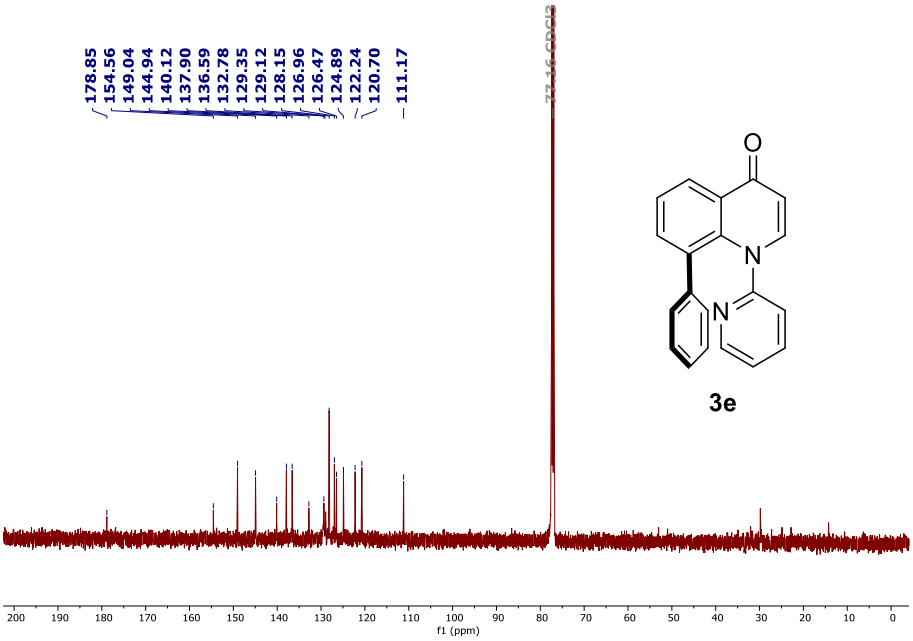


*Figure 24:[13]C NMR spectrum of **3e***

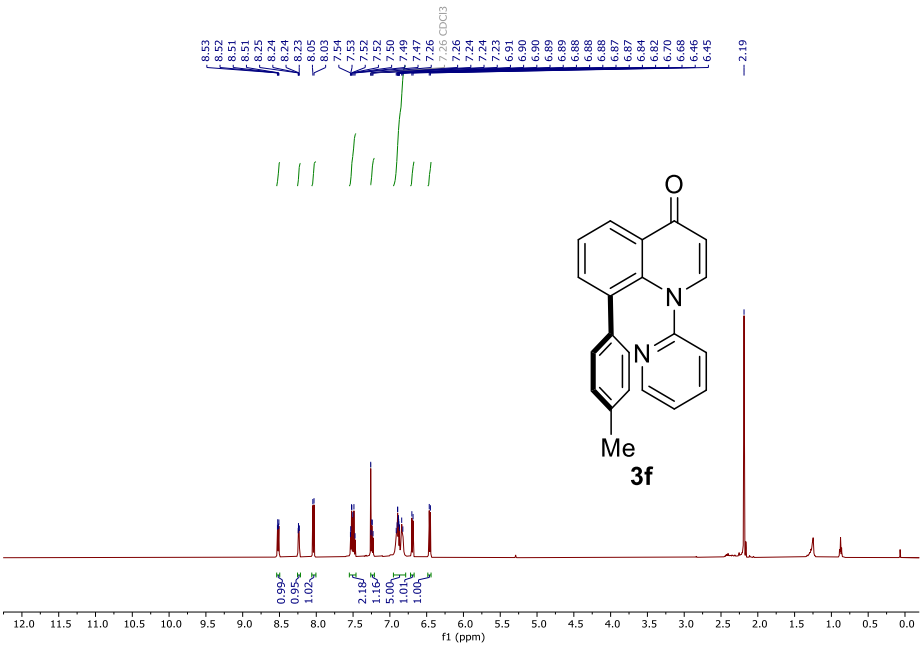


*Figure 25:[1]H NMR spectrum of **3f***

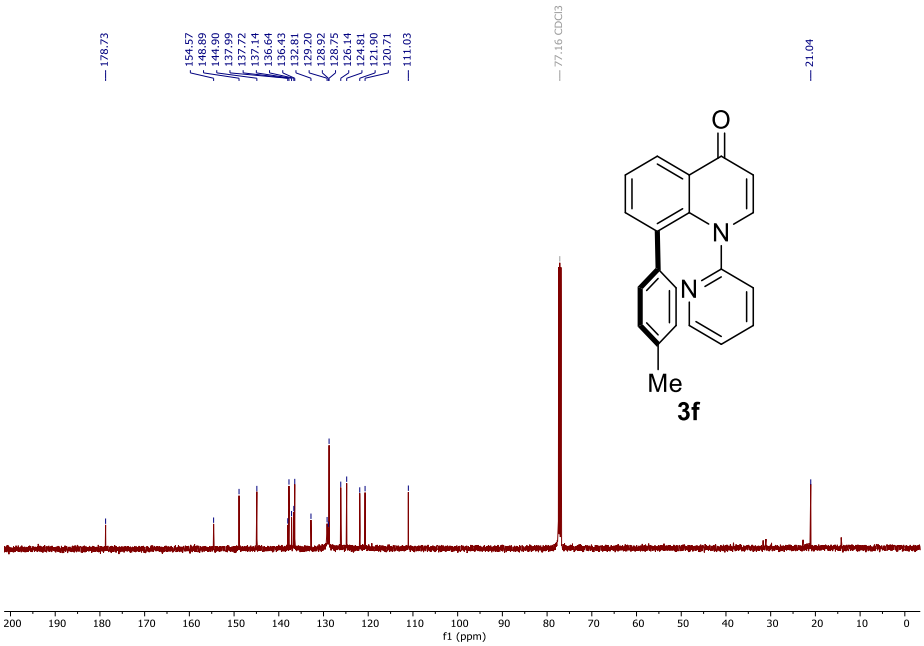


*Figure 26:[13]C NMR spectrum of **3f***

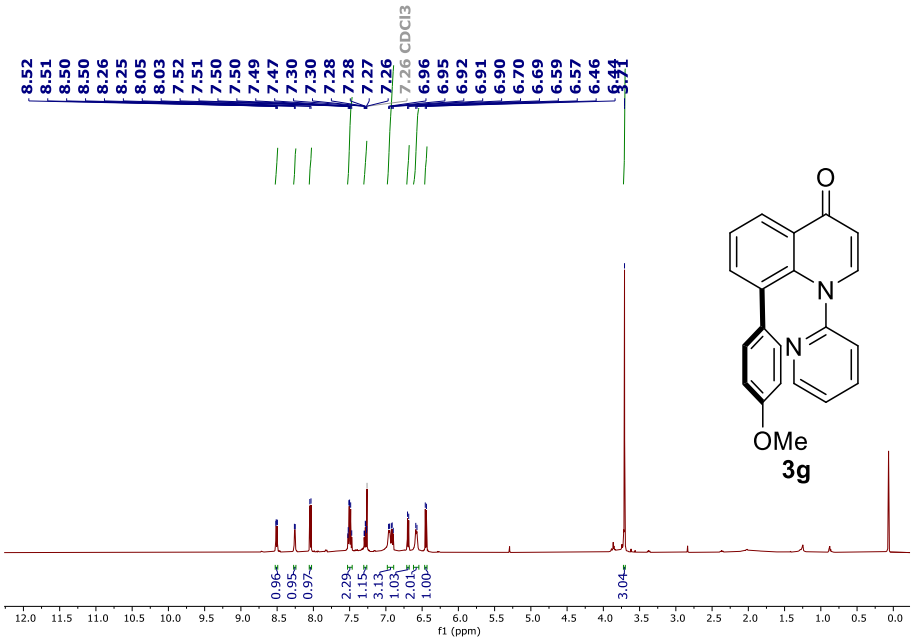


*Figure 27:[1]H NMR spectrum of **3g***

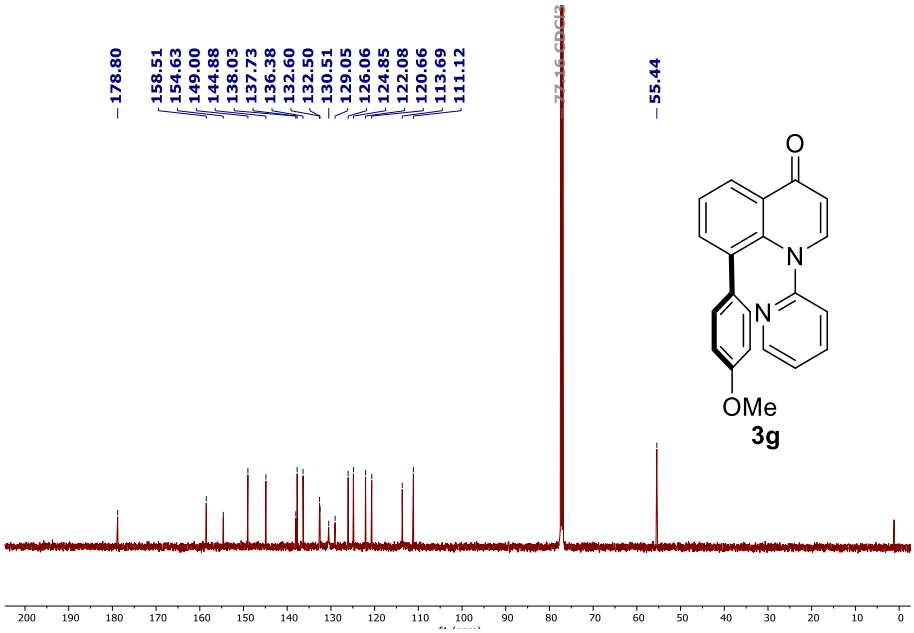


*Figure 28:[13]C NMR spectrum of **3g***

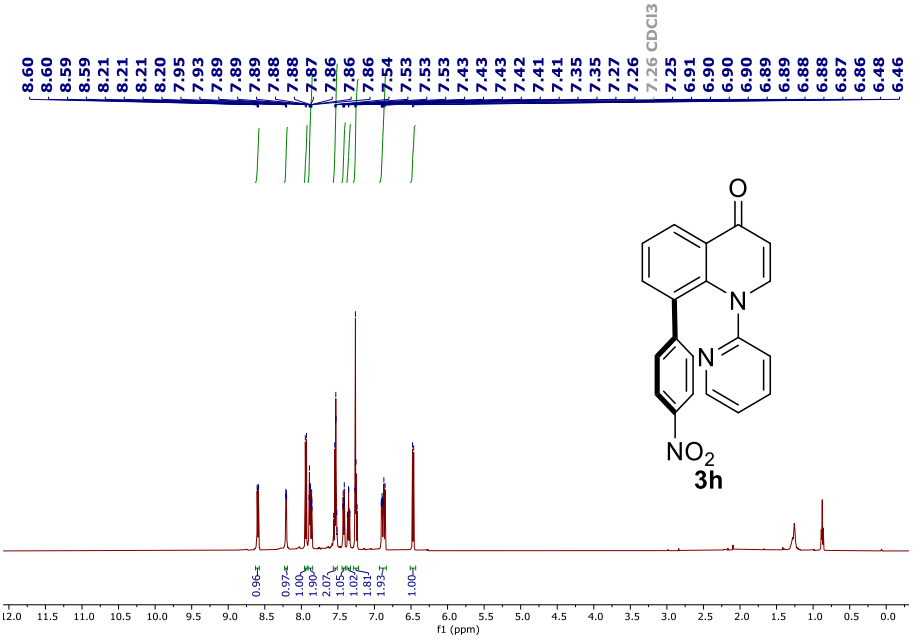


*Figure 29:[1]H NMR spectrum of **3h***

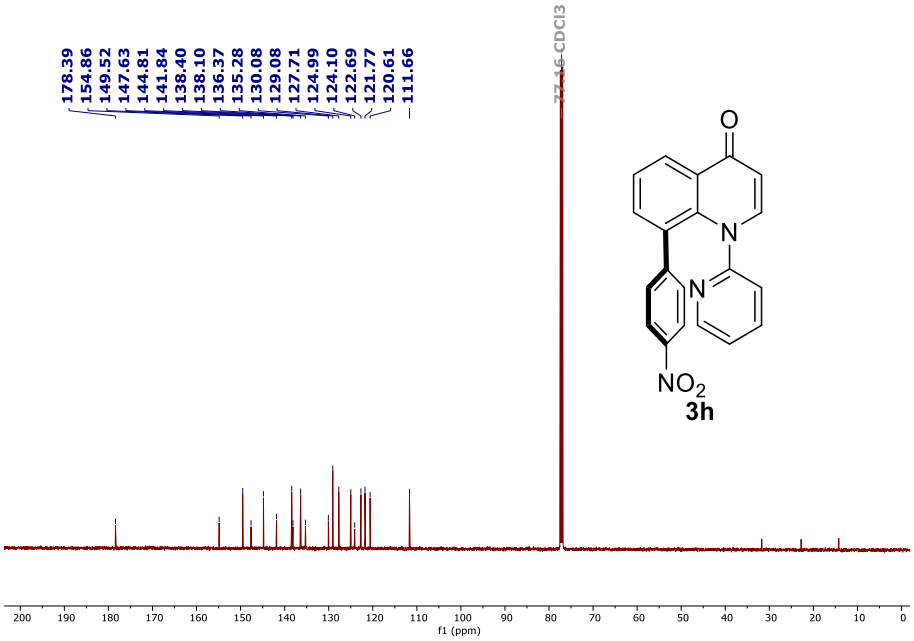


*Figure 30:[13]C NMR spectrum of **3h***

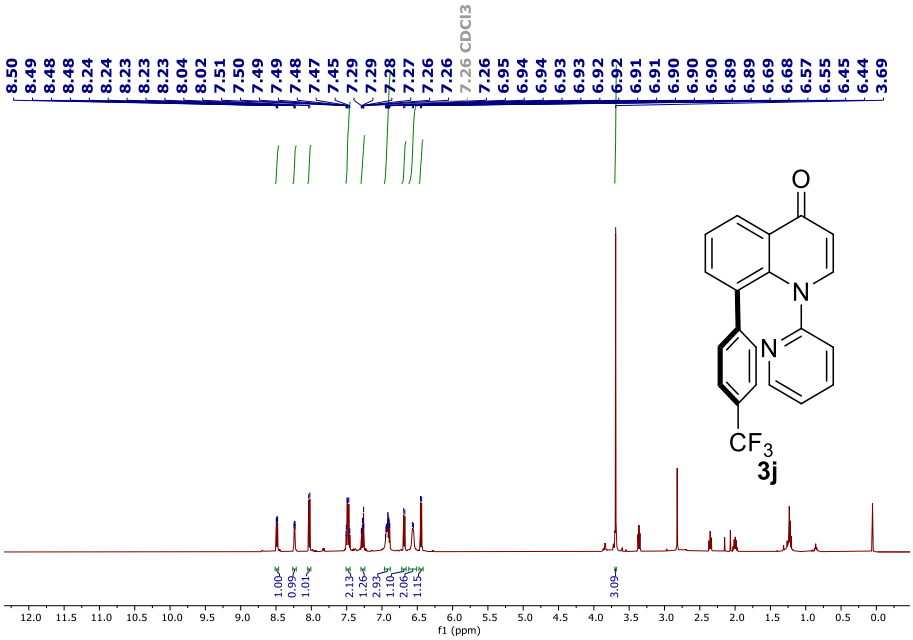


*Figure 31:[1]H NMR spectrum of **3j***

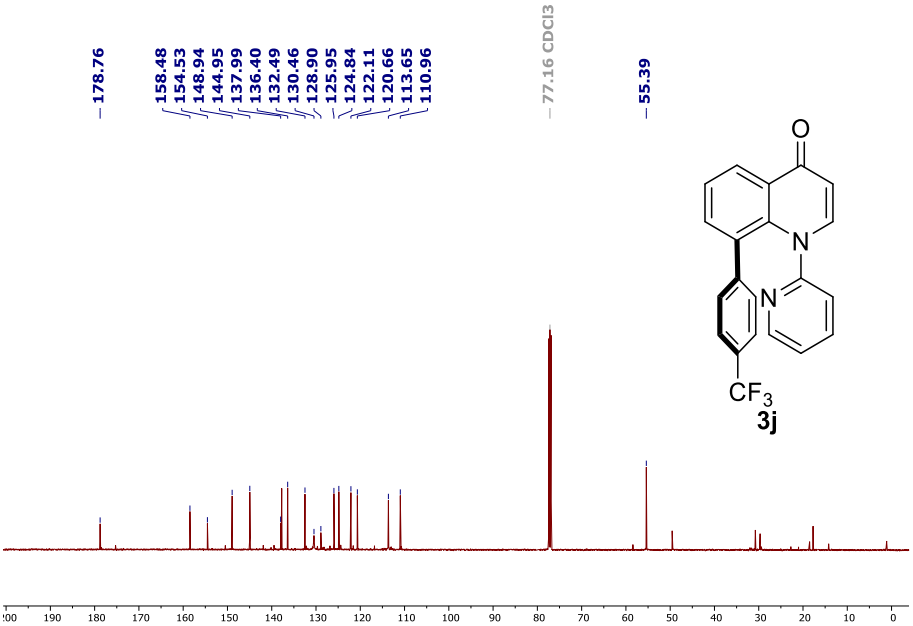


*Figure 32:[13]C NMR spectrum of **3j***

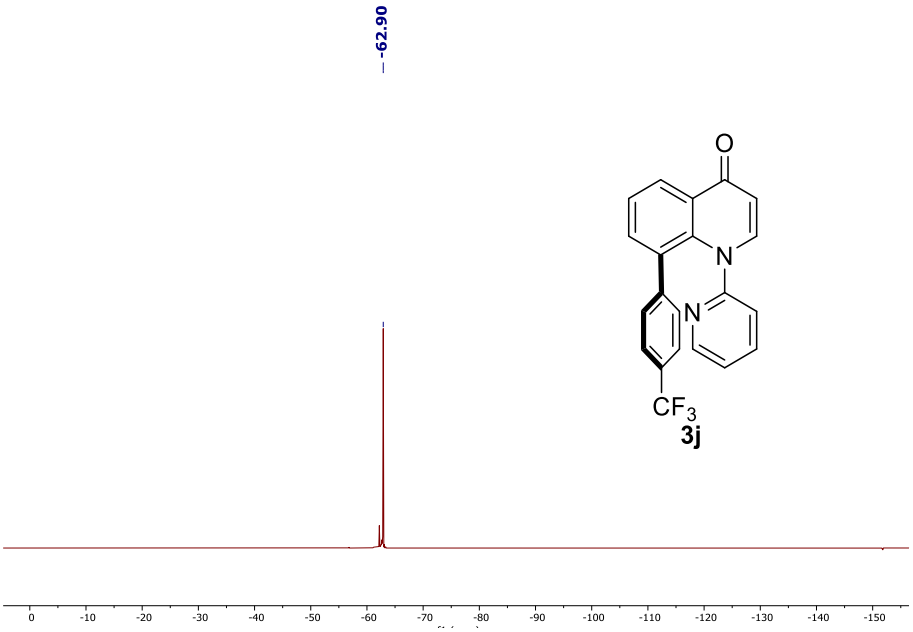


*Figure 33:[19]F NMR spectrum of **3j***

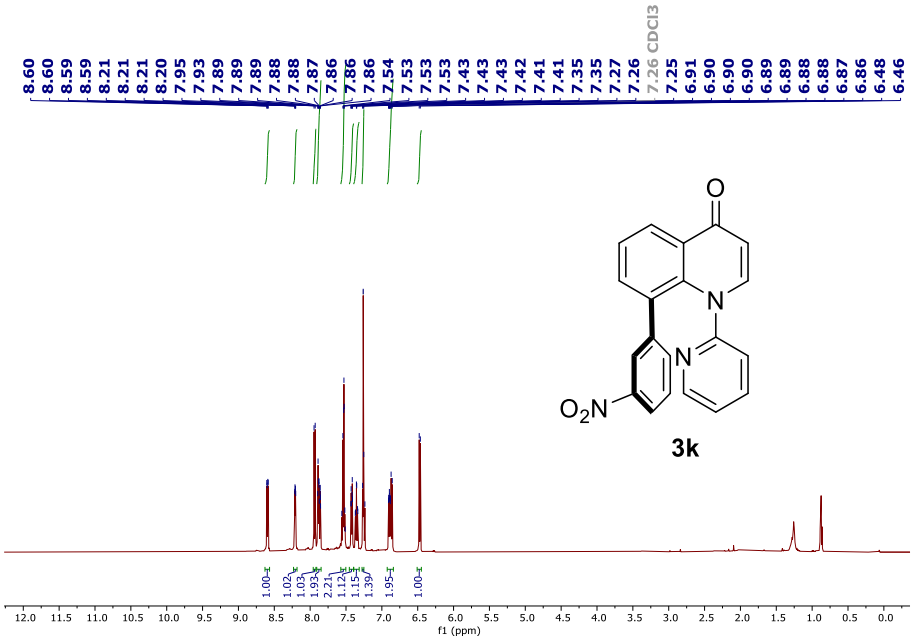


*Figure 34: ^{1}H NMR spectrum of **3k***

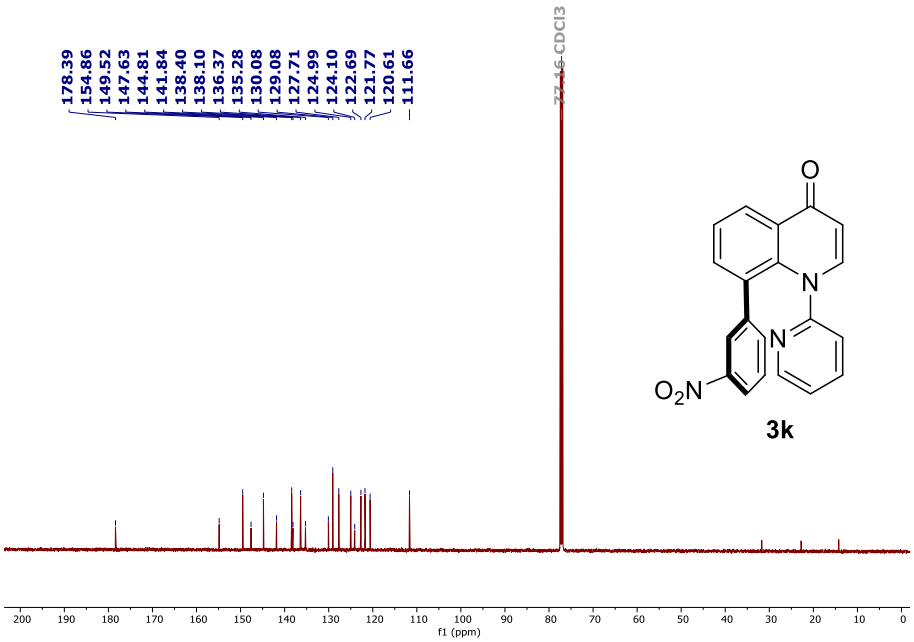


*Figure 35: ^{13}C NMR spectrum of **3k***

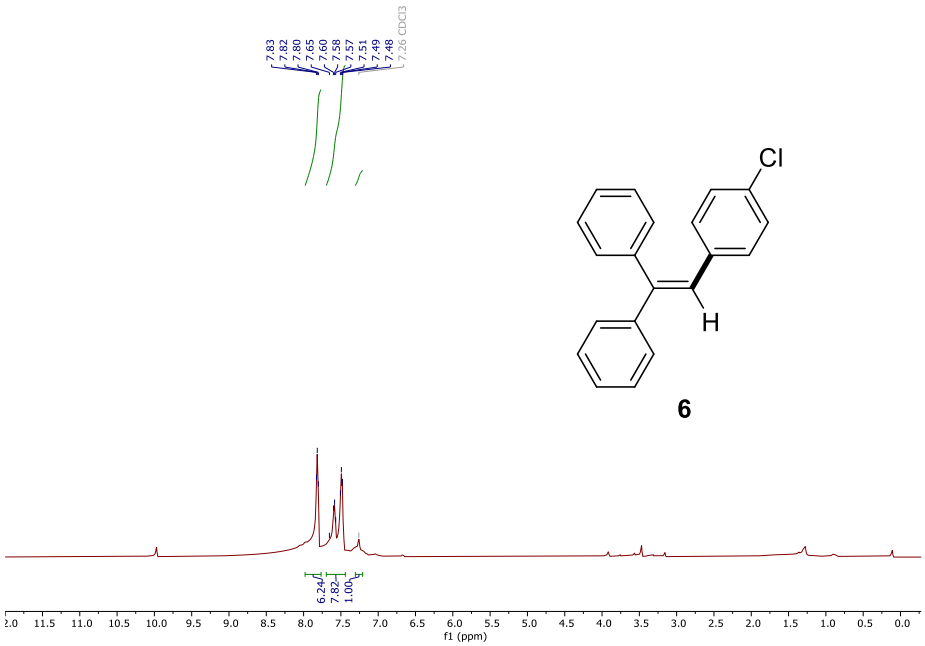


*Figure 36: ^{1}H NMR spectrum of **6***

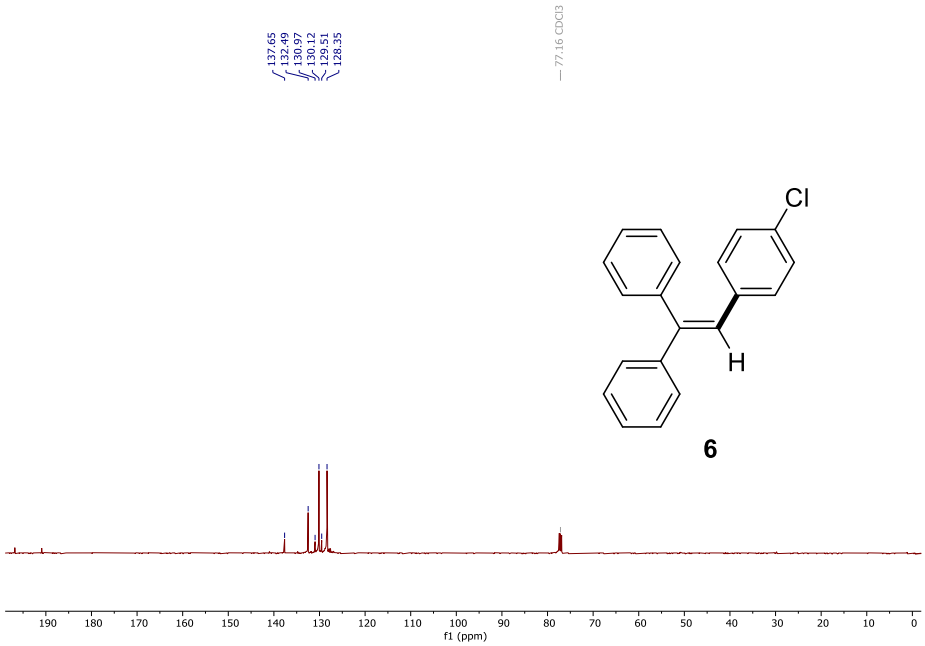


*Figure 37: ^{13}C NMR spectrum of **6***

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