UNIVERSITY OF CALIFORNIA
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One-Step Synthesis of Substituted 2-(2'-Pyridyl)Quinolines for the Study of Their Gold(III) Complexes

A Thesis submitted in partial satisfaction
of the requirements for the degree of

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in

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by

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ABSTRACT OF THE THESIS

One-Step Synthesis of Substituted 2-(2'-Pyridyl)Quinolines for the Study of Their Gold(III) Complexes

by

Edward Marcell Laguna

Master of Science, Graduate Program in Chemistry
University of California, Riverside, December 2014
Professor Catharine H. Larsen, Chairperson

The Larsen group focuses on accessing small molecules through one-step multi-component coupling reactions from inexpensive starting materials and a catalyst source. To this end, we have developed a solvent-free catalytic method to access various substituted 2-(2'-pyridyl)quinoline compounds in one step directly from inexpensive and commercially available materials. Purification is simple and is accomplished with the use of a short basic alumina plug and diethyl ether as the eluent. Current published methods to access these targets are plagued with lengthy multi-step reactions, hazardous reagents, and/or the wasteful use of solvents and other materials for purification purposes. *In vitro* studies of two substituted 2-(2'-pyridyl)quinoline compounds revealed cytotoxic activities in the A549 lung cancer cell line.

In addition to the synthesis of various bidentate substituted 2-(2'-pyridyl)quinoline ligands, the neutral 5-coordinate gold(III) complexes of 6-phenyl-2-(2'-pyridyl)quinolines substituted at position 6 of the quinoline ring with fluorine, methyl, methoxy, and phenyl

groups were also achieved. The x-ray crystallographic data revealed that the neutral complexes have distorted square pyramidal geometries. Furthermore, the cationic gold(III) complex of a 6-phenyl-2-(2'-pyridyl)quinoline with a methoxy moiety at position 6 of the quinoline ring was also synthesized with a tetrafluoroborate counter anion. The x-ray structure of this cationic complex revealed its distorted square planar geometry.

Table of Contents

Part II: Synthesis of 2-(2'-pyridyl)quinoline-Gold(III) Complexes

List of Figures

PART I

Figure

PART II

List of Tables

PART I

Table

PART II

Table

Part I: One-step Catalytic Synthesis of Substituted 2-(2'-pyridyl)quinoline Compounds Under Solvent-free Conditions

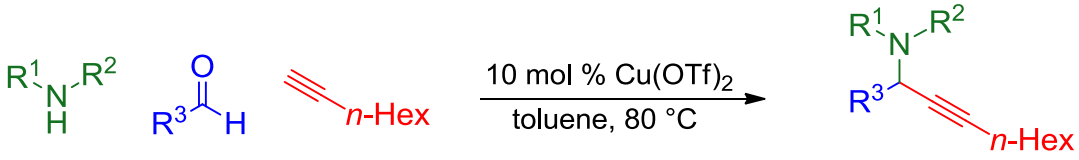
CHAPTER 1

INTRODUCTION

Advancing organic synthetic methods for the facile access of complicated compounds is invaluable, especially when the target molecules possess bioactive utility. A broad example would be any targets which contain a quinoline moiety, as quinolines are known therapies for a range of ailments ranging from malaria[1] to cancer.[2] A second example would be propargylamine targets since they have been shown to be HIV reverse transcriptase inhibitors and antihypertensive compounds.[3,4] Since the origin of the substituted 2-(2'-pyridyl)quinoline research presented herein can be traced to the latter example—specifically a three-component coupling reaction that yields propargylamines—a brief summary regarding past research which led to the investigation of substituted 2-(2'-pyridyl)quinolines will be introduced.

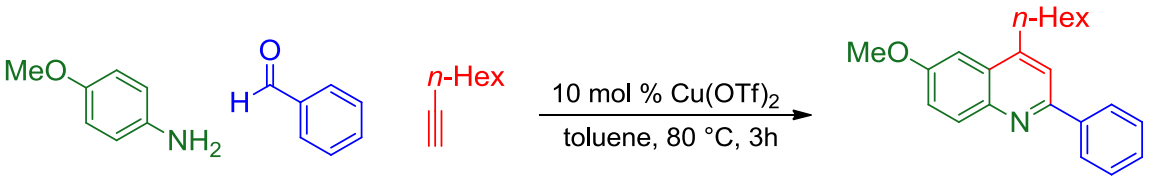
Past research in the Larsen group involved the discovery of the first catalytic alkynylation that formed sulfonated propargylamines using copper(II) triflate ($Cu(OTf)_2$) as the catalyst.[5] It was also found that mixing the coupling substrates—*p*-toluenesulfonamide, cyclohexanecarboxaldehyde, and 1-octyne—and running as a three-component coupling reaction using $Cu(OTf)_2$ increased the rate of propargylamine formation by a multiple of 20 than when preforming and isolating the imine intermediate and alkynylating in a second step.[5] Figure 1 shows the general synthesis for propargylamine formation which was found to be tolerant toward a wide variety of amine

Figure 1. Propargylamines from a range of nitrogen sources with $Cu(OTf)_2$: amines, amides, anilines, and *N*-heterocycles.



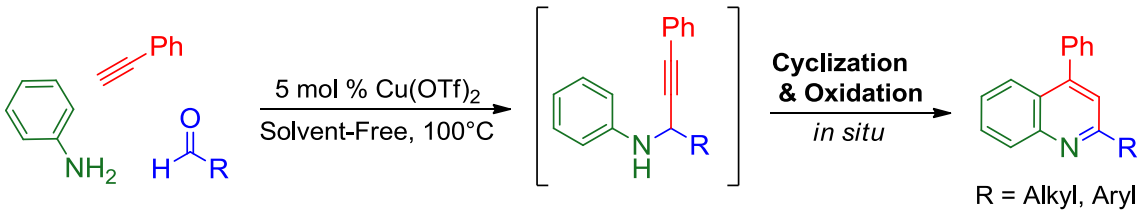
sources such as anilines, alkylamines, benzylamines, *N*-heterocycles (piperidine, morpholine, and pyrrolidine), and sulfonamide. A range of alkyl and aryl aldehydes were also tolerated under these conditions.

Figure 2. Conditions which form propargylamine formed quinoline when using *p*-anisidine, benzaldehyde, 1-octyne, and $Cu(OTf)_2$ as the catalyst.



Under identical conditions, using *p*-anisidine and benzaldehyde as the respective amine and aldehyde sources did not yield the expected propargylamine product with 1-octyne. Instead, the product formed in this case was found to be a quinoline compound (Figure 2).[6] This led to the discovery that $Cu(OTf)_2$ catalyzed the synthesis of 2- and/or 4-alkyl quinoline compounds at 100 °C using 5 mol % catalyst loading and solvent-free conditions (Figure 3).[6] When the propargylamine derived from *p*-anisidine, cyclohexanecarboxaldehyde, and 1-octyne was heated to 100 °C in the presence of $Cu(OTf)_2$, cyclization and oxidation to quinoline was observed.[6]

Figure 3: One-pot synthesis of alkyl-substituted quinolines using $Cu(OTf)_2$.



There are several well-known methods for the synthesis of quinoline compounds. A few of the classic approaches include the Skraup,[7] Doebner-Von Miller,[8] Friedländer,[9] Combes,[10] and Povarov[11] methods. The synthesis of one particular quinoline analog,

however, is limited. Synthetic routes to access substituted 2-(2'-pyridyl)quinoline compounds remain limited in the literature (Figure 4). This is likely due to the difficulty associated with their synthesis. Published syntheses are plagued by lengthy multi-step reactions, low yields, hazardous reagents, and/or the wasteful use of solvents for purification purposes.

Figure 4. 2-(2'-Pyridyl)quinoline.

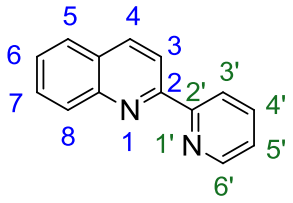
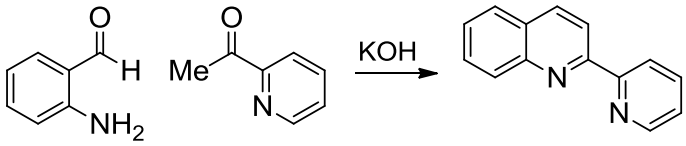
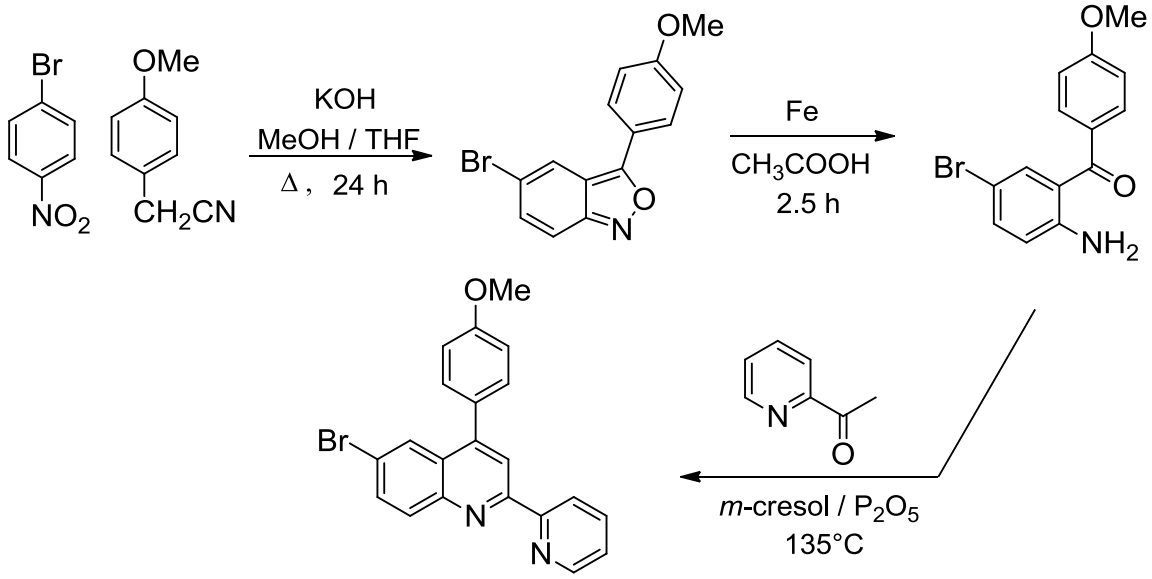


Figure 5. Smirnoff synthesis of 2-(2'-pyridyl)quinoline.



The first reported synthesis of 2-(2'-pyridyl)quinoline was accomplished through what would later become known as the Smirnoff synthesis (Figure 5).[12] Today, this method remains the most common when trying to access unsubstituted 2-(2'-pyridyl)quinoline. However, the downside to this approach is that only simple 2-(2'-pyridyl)quinolines can be attained. Accessing more functionalized targets via the Smirnoff method is limited due to the fact that more substituted 2-aminobenzaldehyde sources, which are needed as starting materials, are not readily available commercially. In order to achieve more functionalized targets, placing functional groups onto the starting material would have to be accomplished prior to running the Smirnoff reaction. An example of a multi-step synthesis that achieved a substituted 2-(2'-pyridyl)quinoline was demonstrated in 2010 with the synthesis of 4-*p*-methoxyphenyl-6-bromo-2-(2'-pyridyl)quinoline.[13] The drawbacks to this 3-step method were that it required a total of 70 hours of reaction time, 3 recrystallizations, and one purification using column chromatography (Figure 6).

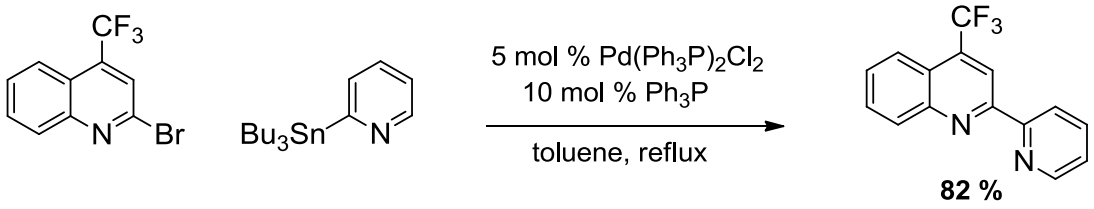
Figure 6. Synthesis of 4-*p*-methoxyphenyl-6-bromo-2-(2'-pyridyl)quinoline (mphbr-pq).



3-step yield: 33%

One other type of common approach for accessing 2-(2'-pyridyl)quinolines is via a cross-coupling reaction which fuses the pyridine moiety to position 2 of the quinoline ring (Figure 7).[14] Although this approach generally results in high yields, it typically requires the use of toxic heavy metals and/or harsh reaction conditions. Furthermore, this route is sensitive to aryl halides which presents a limitation if the target product is expected to contain an aryl halide like the product shown in Figure 3. Cross-coupling would then occur non-selectively at both positions and result in a mixture of products.

Figure 7. Synthesis of a 2-(2'-pyridyl)quinoline compound via a Stille cross-coupling reaction.



82 %

There are previous reports which outline the bioactivities of 2-(2'-pyridyl)quinolines as being antiparasitic[15] and antifungal[16] agents as well as potential therapy candidates against transmissible spongiform encephalopathy, also known as prion disease.[17] The fact that they exhibit any bioactivity at all is not unexpected due to the quinoline core that they possess. It would then follow that a more direct synthesis to access a broader range of substituted 2-(2'-pyridyl)quinolines would be desirable so future investigations of any scientific nature are not limited by a complex multi-step synthesis. Though the focus of this report is primarily on the synthesis and purification of the title compounds, preliminary data regarding the *in vitro* studies of two title compounds against two different cancer cell lines will be briefly discussed.

We herein have investigated a range of reaction conditions as well as a range of acid catalysts for the synthesis of substituted 2-(2'-pyridyl)quinolines. The conditions which allow access to a range of products are via a one-step three-component coupling reaction of an aniline, aldehyde, and alkyne source in air while using trifluoromethanesulfonic (triflic) acid as the catalyst. The reaction is stirred at 110˚C for 4 hours and aniline sources with electron-donating as well as electron-withdrawing substituents can be incorporated. Additionally, the yields are comparable to other published methods in the literature that utilize less direct methods to access the target compounds. Our facile method is convenient from the beginning setup step to the ending purification step since it does not require column chromatography for purification.

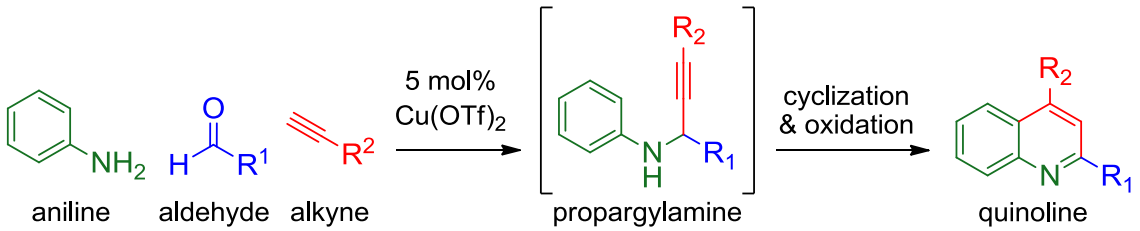
CHAPTER 2

RESULTS AND DISCUSSION

2.1 Rationale

A past graduate student from the Larsen group, Courtney Meyet, found that when she combined an aniline, alkyne, aryl aldehyde, and copper(II) trifluoromethanesulfonate (triflate) as the catalyst, she formed quinoline products as opposed to her expected propargylamine targets (Figure 8). A similar observation had been previously reported which also formed quinoline products via a 3-component coupling reaction using a copper(I) chloride source as the catalyst.[18] The cyclization is held to be driven by the increase in stabilization from the extended conjugated π-system. Following this observation, it was proposed that using a different aryl aldehyde, such as 2-pyridinecarboxaldehyde, may be a facile route to access new bidentate 2-(2'-pyridyl)quinoline products. This prompted a series of optimizations that would ultimately lead to the synthesis reported herein.

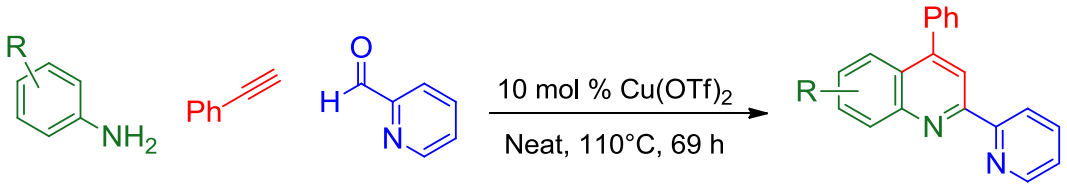
Figure 8. Quinoline formation via a 3-component coupling reaction using a copper(II) catalyst.

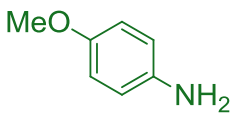
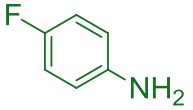


2.2 One-step reaction leading to 2-(2'-pyridyl)quinolines

The first objective was to run an analogous reaction using the new aldehyde with copper(II) triflate as the catalyst. Two separate reactions were prepared using 2-pyridinecarboxaldehyde and copper(II) triflate (Table 1). Although both products were isolated and fully characterized, the yields were low as anticipated. It was reasoned that the bidentate nature of both the imine intermediates and the products inhibit the reaction by sequestering the copper catalyst, rendering the reactions inactive. Despite this shortcoming, using boron trifluoride diethyl etherate as the catalyst gave slightly higher yields for a broader range of substrates than did other Lewis acids that were tried according to gas chromatographic (GC) data. With the exception of boron trifluoride diethyl etherate, using different metal Lewis acids while incorporating organic solvents and changing other variables such as reaction temperature and reaction time also failed to increase yields according to gas chromatographic data.

Table 1. Low isolated yields of 2-(2'-pyridyl)quinolines when using copper(II) triflate catalyst.[a]

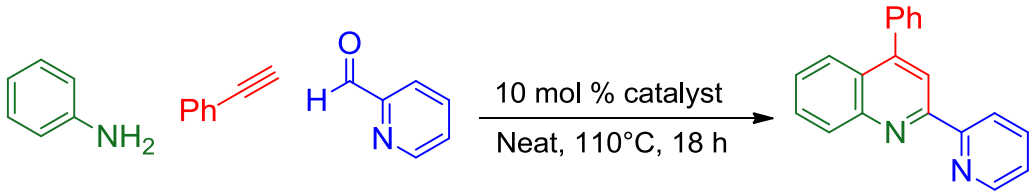


Aniline	Isolated Yield
	15%
	3%

[a] General conditions: 0.5 mmol scale; aniline, 1.0 equiv.; alkyne and aldehyde, 1.2 equiv.

After screening a variety of metal Lewis acids, we then focused our efforts on testing the effectiveness of the available Brønsted-Lowry acids in our laboratory for their ability to catalyze our one-step synthesis. Although this particular study used our poorest-reacting substrate aniline, gas chromatographic data revealed that the alkyne was noticeably more consumed when using trifluoromethanesulfonic acid as the catalyst relative to all other acids. In addition to the alkyne being more consumed, the area percentage of the product peak was also greater than all others in the study (Table 2).

Table 2. GC area percentages (%) of starting materials, intermediate, and product.[a]



Acid Catalyst	Aniline	Alkyne	Aldehyde	Imine	Product
Trifluoroacetic acid	4	65	0	15	2
Fluoroboric acid (48-50%)	3	46	2	32	5
HCl (6M)	3	78	0	2	1
Triflic acid	4	17	0	5	**40**

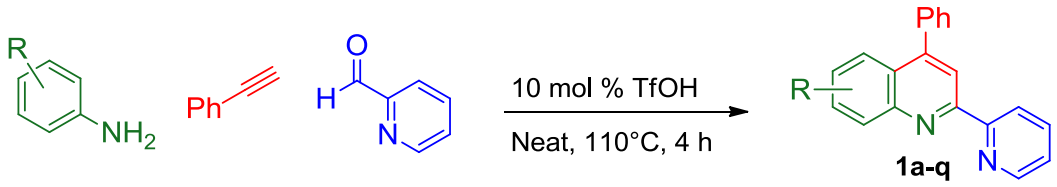
[a] General conditions: 0.5 mmol scale; aniline, 1.0 equiv.; alkyne and aldehyde, 1.2 equiv.

After reviewing the results of the Brønsted-Lowry acid study, we were interested in investigating triflic acid more thoroughly with different substituted aniline reagents known to give higher product yields based on past data. These studies, which used the same conditions as those listed in Table 2, produced the highest product yields according to gas chromatographic data. It was clear that triflic acid up to that point was

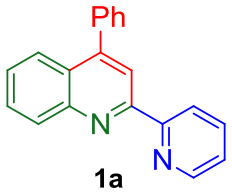
the best catalyst for our one-step synthesis. Therefore, we continued forward with triflic acid as the catalyst and examined several conditions, such as including different reaction solvents and varying reaction times, in attempts to further increase yields. This led to the conclusion that the best conditions to access substituted 2-(2'-pyridyl)quinoline compounds in one-step using triflic acid as the catalyst would be in solvent-free conditions set at 110°C for a total of four hours. These conditions led to the highest yields of the substituted 2-(2'-pyridyl)quinoline products shown in Table 3.

This simple and green procedure[19] proceeds efficiently without the need of an inert atmosphere. All reactions were set up on the benchtop in an air atmosphere in disposable vials sealed with screw caps. Positions 4-8 on the quinoline ring were all possible to substitute by selecting the appropriate aniline and alkyne substrates. Additionally, aniline substrates with both electron-donating to electron-withdrawing substituents converted to products. An added benefit to this method is that column chromatography is not necessary for purification of the crude reaction mixtures which further decreases waste generation. Vacuum filtration of the crude reaction mixtures through basic alumina using 100% diethyl ether and rinsing the eluting solid with cold hexanes affords spectroscopically pure products. Furthermore, reaction yields remain unchanged when running reactions on a 0.5-5.0 mmol scale. One aniline substrate, however, did not convert to product when using triflic acid as the catalyst. Product **1r**, derived from 4-aminobenzonitrile, resulted in a 17% uncorrected GC yield and 5% isolated yield when using boron trifluoride diethyl etherate as the catalyst.

Table 3. Isolated yields of one-step synthesis to subtituted 2-(2'-pyridyl)quinolines.[a]



1a-q



1a
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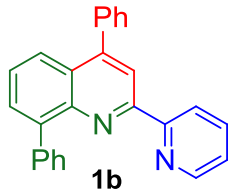

1b
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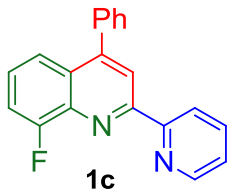

1c
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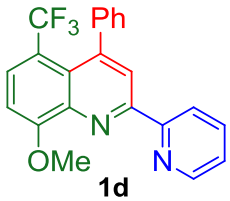
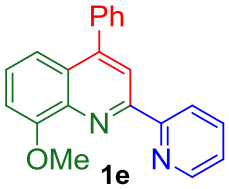


1d
23%



1e
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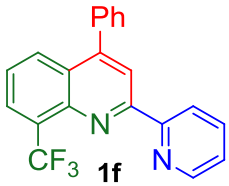

1f
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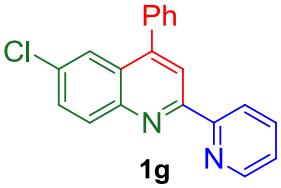

1g
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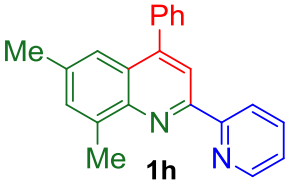

1h
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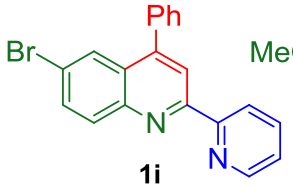

1i
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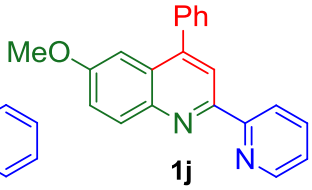

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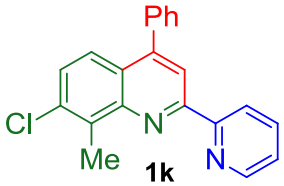

1k
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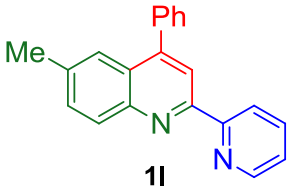

1l
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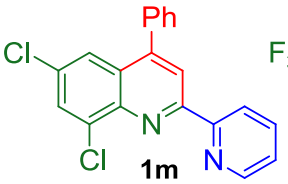

1m
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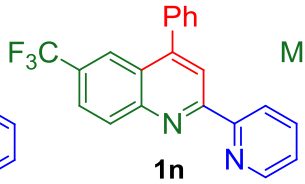

1n
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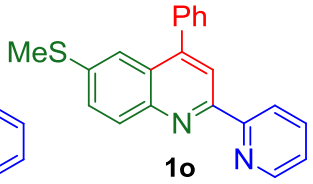

1o
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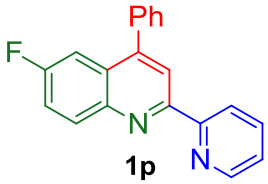

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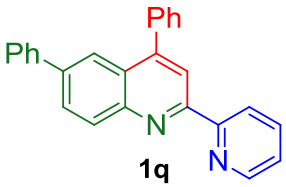

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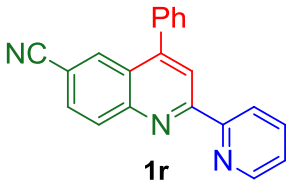


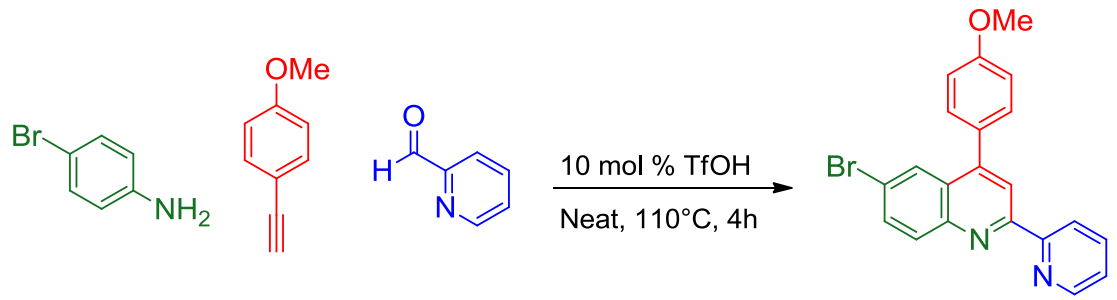
1r
5%[(b)]

[a] General conditions: 2 mmol scale; aniline, 1.0 equiv.; alkyne and aldehyde, 1.2 equiv.

[b] No reaction to product when using triflic acid; used boron trifluoride diethyl etherate as the catalyst.

Next, we were interested in whether or not our method could access 4-p-methoxyphenyl-6-bromo-2-(2'-pyridyl)quinoline, the target molecule in Figure 6. We combined 4-bromoaniline, 2-pyridinecarboxaldehyde, and 4-ethynylanisole under our standard conditions and were able to achieve a 20% isolated yield as shown in Figure 9. Although this yield was 13% lower than the yield achieved using the synthesis shown in Figure 6, our method is significantly more straight forward and produces a fraction of the waste. Additionally, the possibility of trace metal contamination is eliminated. Although the focus of this work has been on using substituted aniline substrates, the example shown in Figure 9 demonstrates how substitution on the aromatic ring is tolerated. Substituted 2-pyridinecarboxaldehydes should also allow for the formation of more functionalized 2-(2'-pyridyl)quinolines.

Figure 9. One-step route to 4-*p*-methoxyphenyl-6-bromo-2-(2'-pyridyl)quinoline (mphbr-pq).[a]

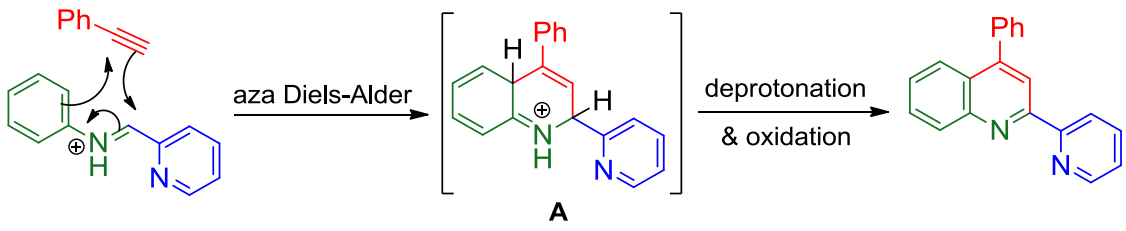


[a] General conditions: 0.5 mmol scale; aniline, 1 equiv.; aldehyde and alkyne, 1.2 equiv.

2.3 Proposed mechanism of one-step 2-(2'-pyridyl)quinoline synthesis

Throughout the investigation of our method, gas chromatogram traces of the crude reaction mixtures were consistently clean and consisted primarily of unreacted alkyne and trace aniline starting materials. The aldehyde was consistently undetected by GC analysis, signifying total consumption. Additionally, when using triflic acid as the catalyst, a small imine peak would occasionally be observed followed by the product peak. Besides these peaks, no other major peaks were observed. Taking this into consideration, we know that the aniline and aldehyde substrates condense together to form an iminium intermediate. It is proposed that the next step is an inverse electron-demand aza Diels-Alder reaction between the iminium and alkyne to form unobserved intermediate **A** shown in Figure 10. Lastly, deprotonation and oxidation of intermediate **A** leads to the final 2-(2'-pyridyl)quinoline target. Brønsted-Lowry acids have been shown to catalyze inverse electron-demand aza Diels-Alder reactions in past reports.[20] There is also a noticeable amount of black solid material that remains atop the alumina after vacuum filtration with 100% diethyl ether. A brief investigation using gas chromatography coupled to a mass spectrometer (GCMS) revealed mass-to-charge ratios above 700 m/z, signifying the possibility of polymerization as a side reaction of the aniline and/or aldehyde substrates.

Figure 10. Proposed inverse-electron demand aza Diels-Alder reaction to 2-(2'-pyridyl)quinolines.



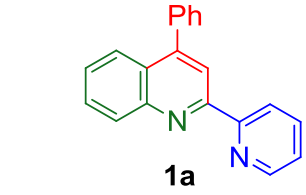
2.4 Tumor cell cytotoxicity of substituted 2-(2'-pyridyl)quinolines

Collaboration with UC Riverside's Dr. Jack Eichler (Chemistry Department) and Prof. Emma Wilson (Biomedical Sciences Department) allowed for the *in vitro* study of two substituted 2-(2'-pyridyl)quinolines in attempts to discover an alternative chemotherapeutic to the current therapy cisplatin. Although cisplatin is effective in treating a variety of cancers, the development of resistant tumor lines[21] as well as interruption of DNA replication in healthy cells during treatment necessitates the search for improved chemotherapies.[22] It has been proposed that polypyridyl compounds induce tumor cell death by sequestering metal ions necessary for the cell's survival.[23] Since previous studies report cytotoxic activities of polypyridyl ligands to be greater than their respective metal complexes,[24] we decided to investigate our new 2-(2'-pyridyl)quinoline ligands.

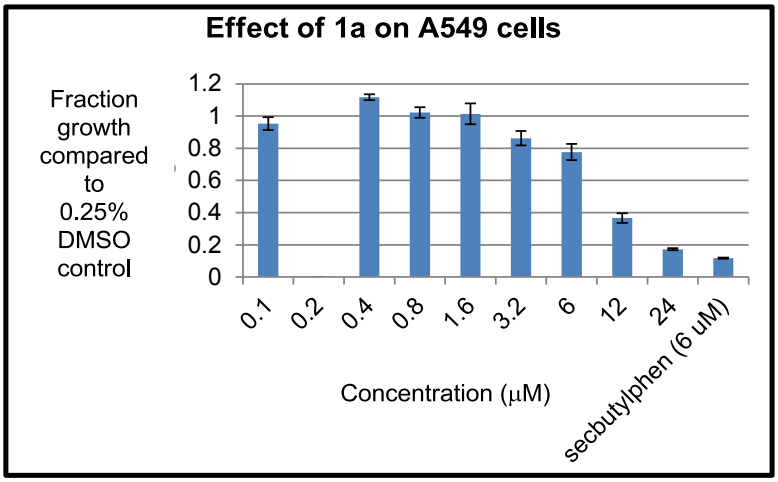
The drug candidates were tested on the GL26 mouse glioma head and neck tumor cell line as well as the A549 human lung tumor cell line. To test the effects of compounds **1a** and **1j**, sulforhodamine B (SRB) cytotoxicity assays were carried out as described in previous reports.[24a,25] The compounds were added in varying concentrations (0-25 μM) and tested alongside 2-9-di-*sec*-butylphenanthroline, a potent inhibitor in both cell lines. Although neither drug candidate reached an IC_{50} for the GL26 cell line, both candidates reached an IC_{50} in the A549 lung cancer cell line (Figure 11).

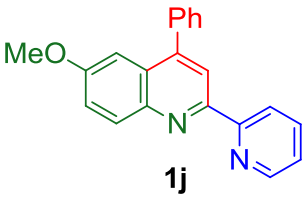
A preliminary study revealed that compound **1a** has an IC_{50} between 6-12 μM (estimated to be 10 μM). Compound **1j**, however, had an IC_{50} at 6 μM. It seems that addition of a methoxy group at position 6 resulted in a more potent drug candidate. It is possible that other substituted 2-(2'-pyridyl)quinoline compounds may also display potent activity *in vitro*, though future studies will reveal if that is the case.

Figure 11. Sulforhodamine B (SRB) assay results of **1a** and **1j** on A549 lung cancer cells.

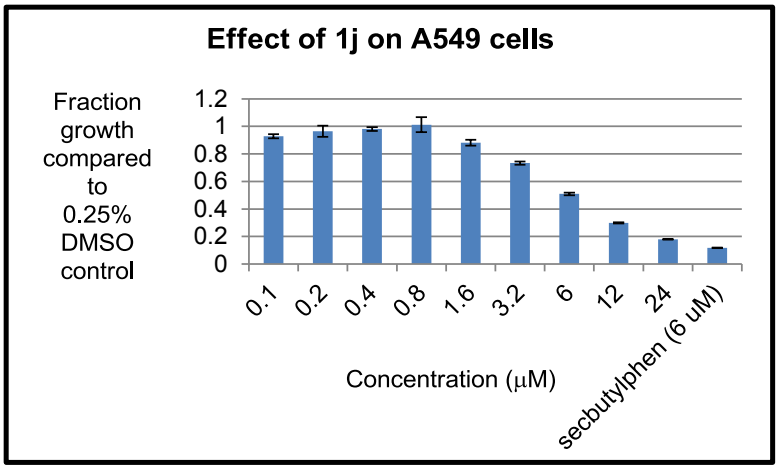


1a





1j



CHAPTER 3

CONCLUSION

The synthesis of substituted 2-(2'-pyridyl)quinolines can be traced back to previous research in the Larsen group which involved the coupling of an aldehyde, terminal alkyne, and a range of amines using $Cu(OTf)_2$ as the catalyst to access various propargylamine products. It was determined that alkynylation of the *in situ* formed iminium intermediate occurred at a faster rate (20 times faster) when running the reaction as a one-pot three-component coupling reaction as opposed to preforming and isolating the imine intermediate then alkynylating in a second step. When *p*-anisidine, benzaldehyde, and 1-octyne produced a quinoline product instead of the expected propargylamine product, research regarding quinoline targets using $Cu(OTf)_2$ began. After a range or alkyl and aryl aldehydes were demonstrated to convert to quinolines when combining with aniline and alkyne sources, using 2-pyridinecarboxaldehyde was the next substrate of choice. Using this aldehyde, however, decreased yields due to possible sequestration of the metal catalyst by the bidentate imine and/or product. Research to optimize yields when using this new aldehyde gave rise to the work presented in this thesis.

A new, green, metal-free, method to access substituted 2-(2'-pyridyl)quinoline compounds in one step under solvent-free conditions and an air environment has, herein, been reported. The reaction uses an aniline source, an alkyne source, 2-pyridinecarboxaldehyde, and triflic acid as the catalyst. The substrates are stirred together at 110°C for 4 hours before vacuum filtration of the crude mixtures through basic alumina for purification. This method is simple and quickly provides an array of

bidentate ligands with electron-withdrawing to electron-donating substituents. The mechanism by which these compounds are achieved is proposed to be via an inverse-electron demand aza Diels-Alder reaction catalyzed by the Brønsted-Lowry acid. Since a metal Lewis acid is not used in this reaction, alkynylation of the iminium intermediate is not considered a mechanistic pathway since an acetylide nucleophile is not produced. Under these conditions, a range of novel 2-(2'-pyridyl)quinoline compounds have been synthesized, isolated, and characterized.

A preliminary *in vitro* study of two 2-(2'-pyridyl)quinoline compounds has also been completed. Unsubstituted 2-(2'-pyridyl)quinoline **1a** and 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline **1j** were tested for their antitumor properties against the GL26 mouse glioma and A549 human lung cancer cell lines. Although neither drug candidate had any cytotoxic activity against the GL26 cell line, both drug candidates reached IC_{50} values for the A549 lung cancer cell line. Compound **1a** was discovered to have an IC_{50} estimated at about 10 μM. Compound **1j** was discovered to be more cytotoxic in the A549 cell line, reaching an IC_{50} of 6 μM.

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Part II: Synthesis of 2-(2'-pyridyl)quinoline-Gold(III) Complexes

CHAPTER 1

INTRODUCTION

Gold compounds have long been valued for their catalytic power and therapeutic effects.[1-7] Gold(III) has been shown to catalyze numerous transformations[1], and complexes of nitrogen-based ligands have had impact in many biomedical areas.[2,3] Gold(III) chloride complexes of 2,9-dialkyl phenanthrolines have been shown to be highly active against cisplatin-resistant cancer cell lines.[3e] The distorted square pyramidal geometry increases stability and allows for different modes of action compared to square planar platinum(II) and gold(III) complexes.[3,6] Steric crowding at gold(III) from 2-(2'-pyridyl)quinoline, 2,9-dimethylphenanthroline, and 2,2'-biquinoline forces halides out of the bidentate ligand plane forming neutral five-coordinate complexes.[4-6] Due to the magnitude of ligand-field splitting in this diamagnetic d^8 third row transition metal, the axial distortion of these complexes reduces the energy of the gold(III) high-spin (triplet) state by minimizing the ligand interaction with d_z^2 without producing a high-spin ground state.[4,5]

Past reports show how bidentate 2-(2'-pyridyl)quinoline ligands have been applied to study various metals.[7-9] Precise ligand tuning requires the ability to install substituents ranging from electron-donating to electron-withdrawing. Classic syntheses of 2-(2'-pyridyl)quinoline continue to be applied but are not readily adapted for additional substituents.[8-10] For the accelerated testing of relationships between ligand structure and catalytic or biomedical activity, a one-step ligand synthesis would ideally employ inexpensive starting materials bearing a range of substituents. Since a new facile green[11] method to access various substituted 2-(2'-pyridyl)quinoline ligands in one step

using inexpensive starting materials and trifluoromethanesulfonic acid as the catalyst has been reported in part I of this thesis, gold(III) metal complexes were easier targets to obtain.

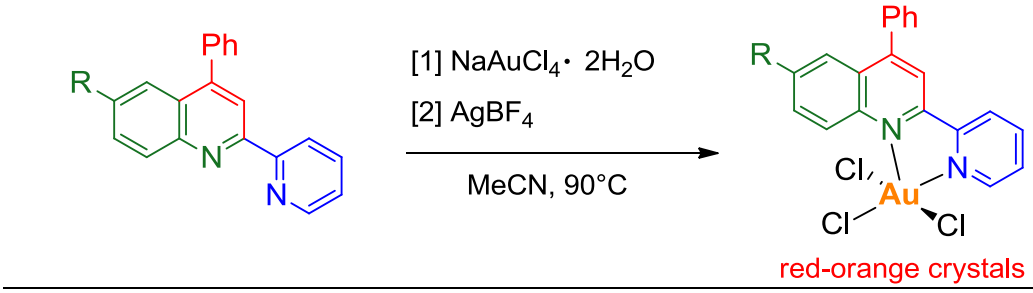
Herein, we report the synthesis and characterization of the following four neutral five-coordinate gold(III) complexes: 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$, 6-methyl-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$, 4,6-diphenyl-2-(2'-pyridyl)quinoline-$AuCl_3$, and 6-fluoro-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$. Additionally, we also report the synthesis and characterization of the gold(III) cationic complex of [6-methyl-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$]BF_4. X-ray crystallographic analysis revealed that the neutral gold(III) complexes have a distorted square pyramidal ligand environment while the cationic gold(III) complex displayed a distorted square planar configuration. Select bond lengths and angles of all complexes will be included. This work was completed in collaboration with Dr. Jack Eichler (Chemistry Department) and Pauline Olsen (chemistry undergraduate).

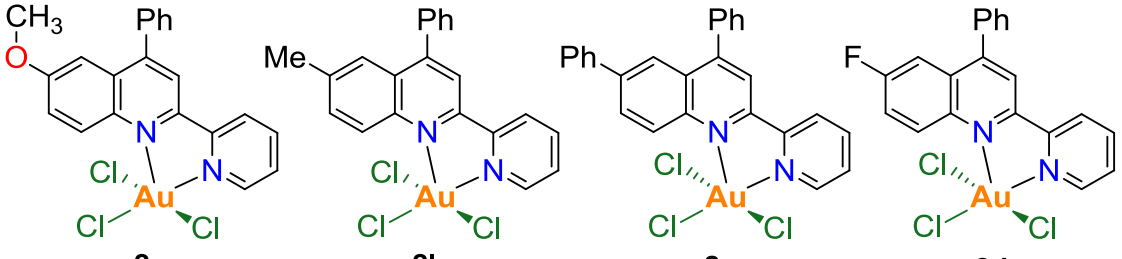
CHAPTER 2

RESULTS AND DISCUSSION

With various bidentate 2-(2'-pyridyl)quinoline ligands in hand, complexation to a gold(III) metal center using procedures reported in the literature[12] was accomplished. Using equimolar amounts of a ligand, sodium tetrachloroaurate(III) dihydrate, and silver tetrafluoroborate in acetonitrile stirred overnight under reflux afforded red-orange mixtures. Red to orange crystals were achieved in good yields upon filtration of the crude mixtures and overnight recrystallization in the appropriate solvent as shown in Table 1. Compounds **2a**-**2c** were recrystallized overnight directly from acetonitrile upon completion of the filtration. However, compound **2d** only recrystallized after switching the solvent to toluene. X-ray analysis revealed the expected distorted square pyramidal geometry about the gold(III) metal centers.

Table 1. Synthesis of Au(III) complexes of substituted 2-(2'-pyridyl)quinolines.[a]

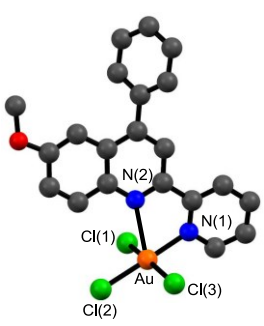
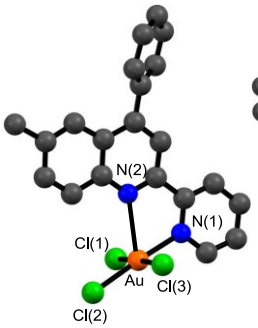
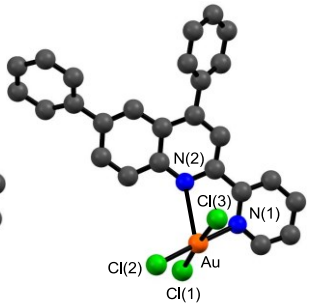
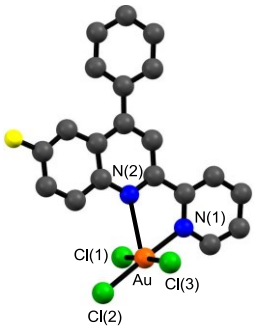




[a] General conditions: 0.3 mmol scale (0.02 M); equimolar amounts of ligand, $NaAuCl_4$, and $AgBF_4$.

Upon comparison of the complexes, all bond lengths and angles are in good agreement with those reported by O'Connor and Sinn for trichloro-[2-(2'-pyrridyl)quinoline]gold(III): Au-N1 = 2.11(2) Å, Au1-N2 = 2.68(2) Å, and N1-Au-N2 = 68.0°.[4b] As shown in Figure 1, substituted 2-(2'-pyridyl)quinoline complexes **2a**-**2d**, Au-N1 is 2.039-2.064 Å, Au-N2 is 2.633-2.736 Å, and the N1-Au-N2 angle is 69.5-72.2°. Although the axial Au-N2 bonds are weaker (covalent Au-N = 1.40 + 0.74 = 2.04 Å), they are markedly shorter than the Van der Waals radii (nonbonded Au-N = 2.2 + 1.5 = 3.7 Å).[4b]

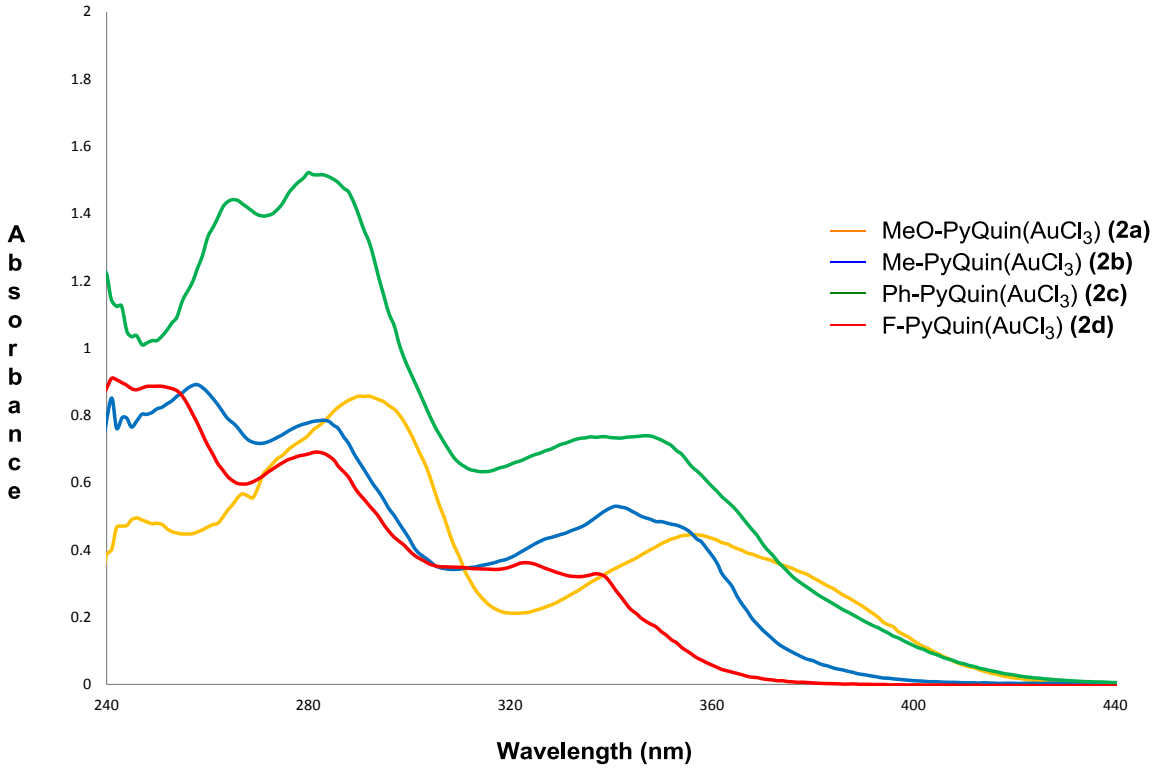
Table 2. Selected bond lengths and angles of Au(III) complexes **2a-2d.**

			
2a	**2b**	**2c**	**2d**
Bond lengths [Å]	Bond lengths [Å]	Bond lengths [Å]	Bond lengths [Å]
Au-N(1) 2.039 Au-N(2) 2.633	Au-N(1) 2.063 Au-N(2) 2.639	Au-N(1) 2.061 Au-N(2) 2.736	Au-N(1) 2.064 Au-N(2) 2.633
Bond angle [°]	Bond angle [°]	Bond angle [°]	Bond angle [°]
N(1)-Au-N(2) 72.15	N(1)-Au-N(2) 70.51	N(1)-Au-N(2) 69.49	N(1)-Au-N(2) 71.02

Uv-vis analyses were initiated by the preparation of 6.00 mM solutions of the complexes in dimethylsulfoxide and diluting to a final concentration of 0.03 mM using acetonitrile. Uv-vis analysis of the neutral gold(III) complexes were characteristic of polypyridyl coordination since they exhibited a strong absorption maximum at approximately 250-295 nm, which results from intraligand 2-(2'-pyridyl)quinoline $\pi \rightarrow \pi^*$

transitions (Figure 2).[6,12] Additionally, an absorption maximum at approximately 350-400 nm assigned as the ligand-to-metal charge transfer (LMCT) was also observed.[6,12] Although all of the samples were prepared to achieve the same final concentrations, complex **2c** in Figure 2 (shown in green) had noticeably greater absorption maxima which is believed to be the result of its extended π-conjugation.

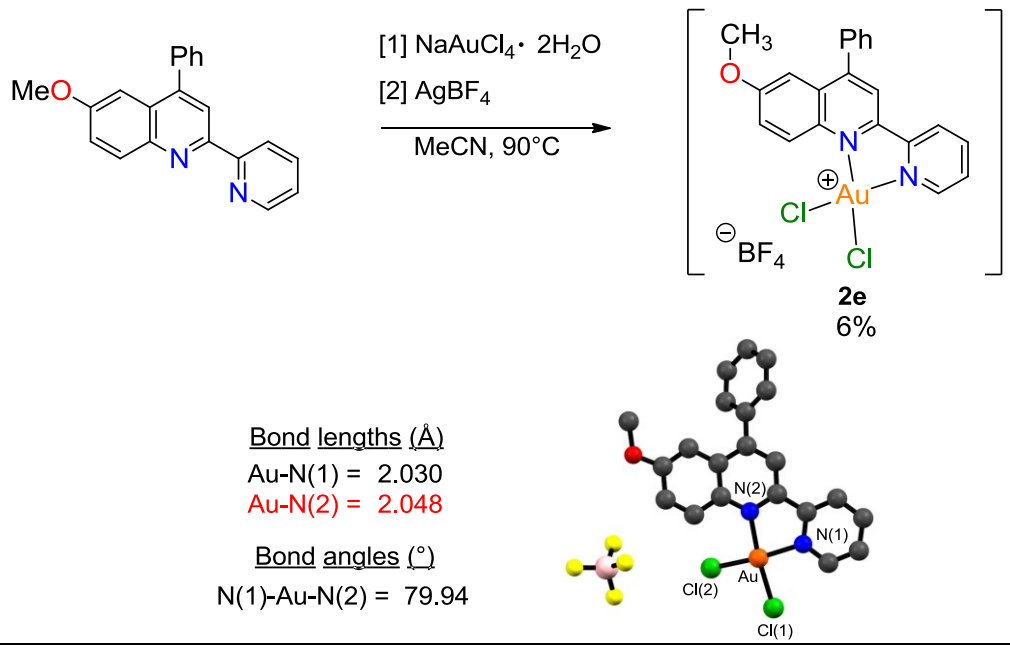
Figure 1. Uv-vis spectra of neutral gold(III) complexes **2a-2d**.



In addition to the neutral gold(III) complexes **2a-2d**, we were also successful in synthesizing the cationic gold(III) tetrafluoroborate salt of 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline (**2e**). This reaction, however, included two equivalents of the silver reagent for the removal of two chlorine atoms. This reaction originally failed to yield crystals in acetonitrile, so switching to dichloromethane and washing with water afforded

the x-ray quality crystals on two separate accounts. When recrystallizing in dichloromethane, only after washing the organic layer with water would recrystallization occur. Although this may seem counter-intuitive when dealing with a salt, this was the only method that consistently afforded the deep reddish-black crystals. Attempts to recrystallize from toluene were unsuccessful. The geometry around the gold(III) center in this case was found to be distorted square planar. Relative to complexes **2a**-**2d**, the Au-N2 bond length in **2e** was significantly closer to that of Au-N1 as could be predicted. Figure 3 outlines the synthesis as well as important bond lengths and angles of the cationic gold(III) complex **2e**.

Figure 2. Synthesis of cationic Au(III) complex **2e** and corresponding bond lengths and angles.[a]

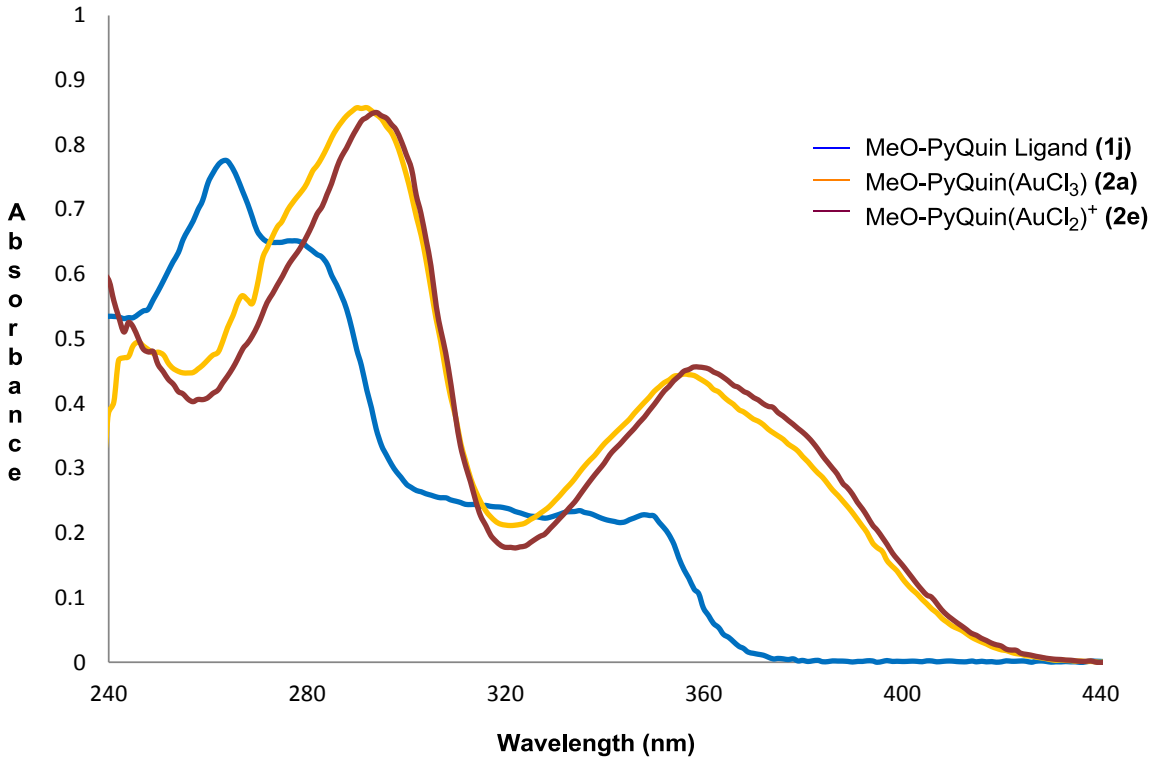


[a] General conditions: 0.3 mmol scale (0.02 M); equimolar amounts of ligand and $NaAuCl_4$; $AgBF_4$ (2 equiv.).

Uv-vis analysis of cationic gold(III) complex **2e** was also characteristic of polypyridyl coordination since it exhibited a strong absorption maximum at approximately

250-295 nm resulting from intraligand 2-(2'-pyridyl)quinoline π → π* transitions (Figure 4).[6,12] Additionally, an absorption maximum at approximately 350-400 nm assigned as the ligand-to-metal charge transfer (LMCT) was also observed.[6,12] Figure 4 also features the uv-vis spectra of the 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline ligand as well as the neutral gold(III) complex **2a** for comparison. Neutral complex **2a** and cationic complex **2e** absorb nearly identically while the free ligand has noticeable differences, such as in the 360-440 nm region. The cationic gold(III) complex was prepared for uv-vis analysis in the same fashion as previously discussed for the neutral gold(III) complexes **2a-2d**.

Figure 3. Uv-vis spectra of 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline ligand **(1j)**, its neutral gold(III) complex **(2a)**, and its cationic gold(III) complex **(2e)**.



Ligand exchange studies were carried out using benzylamine, pyridine, and benzyl alcohol as the ligands. The study introduced incrementally larger concentrations of a given ligand to a fixed concentration of gold(III) complex to investigate at what concentration of ligand (0.001 mM, 0.01 mM, 0.015 mM, etc.) would exchange occur with a chlorine atom. The change in the absorption maxima at 355 nm upon increasing concentrations of ligand was used to determine the binding constant as previously described in the literature.[3e,13] Additionally, the Stern-Volmer equation was used to determine the Stern-Volmer quenching constant (K_{sv}) and the quenching rate constant (K_q) as described in previous reports with the following equation:[3e]

$$F_o / F = 1 + K_{sv}[\text{ligand}] = 1 + K_q \tau_o [\text{ligand}]$$

The following form of the Stern-Volmer equation was used to calculate the binding constant (K_b):[3e]

$$\log(F_o - F) / F = \log K_b + n\log[\text{ligand}]$$

Where F_o and F represent the steady-state absorption intensities in the absence and presence of the ligand under investigation, respectively. The plot of [$\log(F_o - F) / F$] vs. log[ligand] provides the binding constant K_b and the number of binding sites *n*.[3e] Figure 4 shows the uv-vis spectra collected for complex **2a** in varying concentrations of benzylamine—the ligand under investigation. Using the Stern-Volmer equation, the number of binding sites *n* was determined to be 1. Table 3 shows the Stern-Volmer data extrapolated for complexes **2a**-**2e**. Since complexes **2b** and **2d** did not show a significant change at 355 nm after addition of benzyl alcohol, a Stern-Volmer relationship could not be determined.

Figure 4. Ligand exchange study between **2a** and benzylamine monitored by uv-vis and its repective Stern-Volmer relationship.

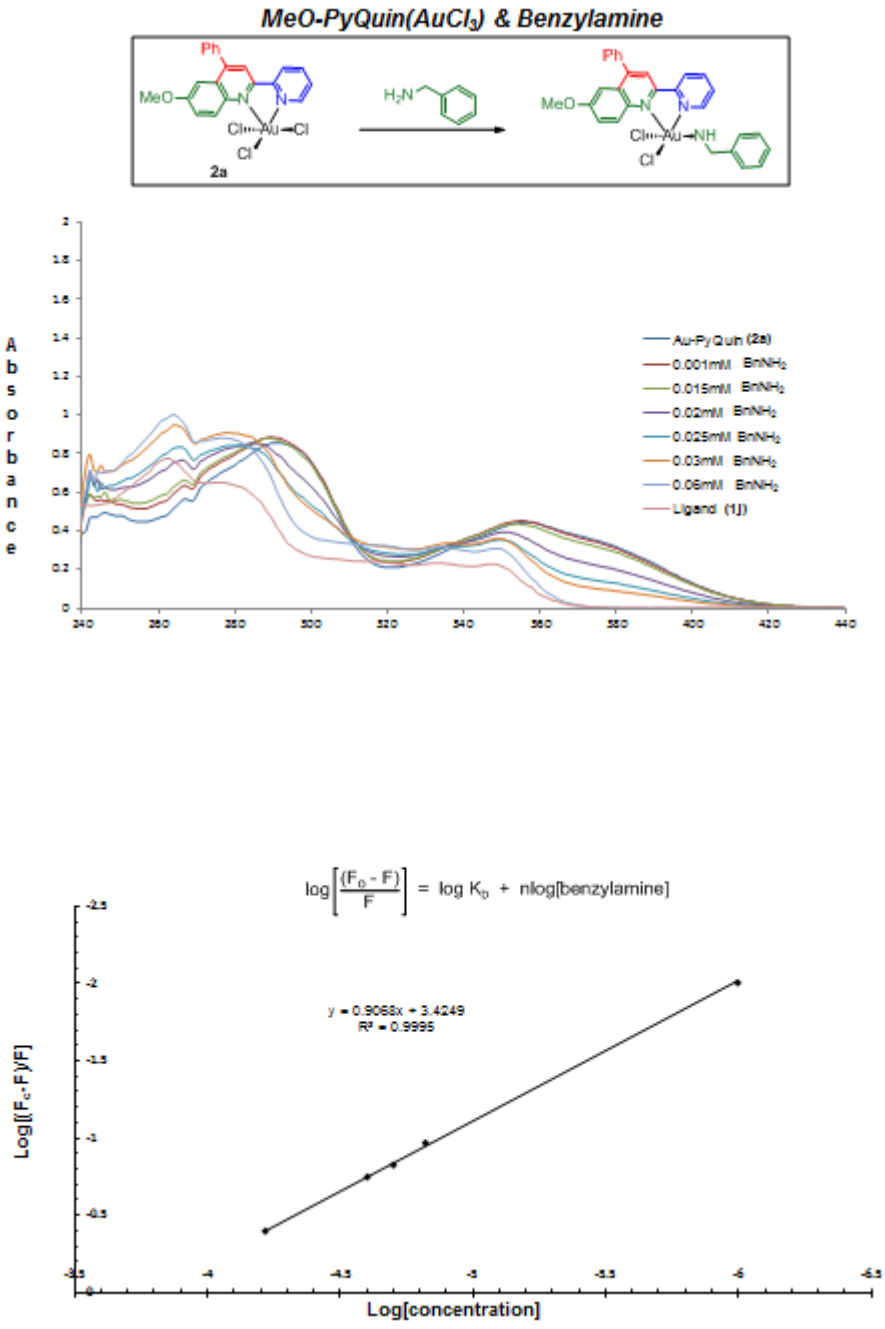
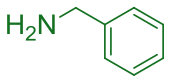
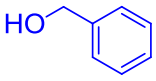


Table 3. Stern-Volmer data for complexes **2a-2e** extrapolated from uv-vis experiments.[a]

			
MeO-PyQuin-$AuCl_3$ **(2a)**	y = 0.9068x + 3.4249 R^2 = 0.9995	y = 0.1226x + 0.7168 R^2 = 0.9728	y = 0.0081x + 0.3842 R^2 = 0.7023
Me-PyQuin-$AuCl_3$ **(2b)**	y = 0.786x + 3.6541 R^2 = 0.9854	y = 0.0663x + 1.349 R^2 = 0.7653	n/a
Ph-PyQuin-$AuCl_3$ **(2c)**	y = -0.0449x - 4.5581 R^2 = 0.0018	y = 1.5873x - 4.0959 R^2 = 0.9594	y = 1.4092x - 3.7457 R^2 = 0.9928
F-PyQuin-$AuCl_3$ **(2d)**	y = 0.366x + 1.1914 R^2 = 0.9609	y = 0.292x - 0.5033 R^2 = 0.8784	n/a
[MeO-PyQuin($AuCl_2$)]BF_4 **(2e)**	y = 1.5834x - 4.4317 R^2 = 0.9924	y = 0.8405x - 4.336 R^2 = 0.9951	y = -0.1755x - 4.364 R^2 = 0.3735

[a] Uv-vis data can be found in part II of the supplementary information.

CHAPTER 3

CONCLUSION

We herein have demonstrated a one-pot synthesis of neutral gold(III) complexes using substituted 2-(2'-pyridyl)quinoline ligands. The reaction is not air sensitive and does not require dry solvents or equipment. Four neutral gold(III) complexes were obtained using substituted 2-(2'-pyridyl)quinolines with substituents ranging from electron-donating to electron-withdrawing at position 6 of the quinoline ring. Complexes **2a-2c** recrystallized from acetonitrile while **2d** only recrystallized when using toluene as the solvent. X-ray crystallographic analysis confirmed that the neutral complexes **2a**-**2d** display a distorted square pyramidal ligand environment and all bond lengths and angles were found to be in good agreement with previous reports in the literature involving trichloro-[2-(2'-pyrridyl)quinoline]gold(III).[4b] In addition, the cationic gold(III) complex of 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline was also synthesized. This complex was found to have a distorted square planar geometry.

Uv-vis studies revealed absorption maxima that is also in good agreement with previous reports regarding polypyridyl gold(III) complexes. Uv-vis analysis of neutral gold(III) complexes **2a-2d** exhibited strong absorption maxima at approximately 250-295 nm which results from intraligand 2-(2'-pyridyl)quinoline $\pi \rightarrow \pi^*$ transitions.[6,12] Absorption maxima at approximately 350-400 nm, assigned as the ligand-to-metal charge transfer (LMCT), were also present.[6,12] Cationic gold(III) complex **2e** also exhibited these absorption maxima and displayed a striking resemblance to the uv-vis spectrum of its respective neutral gold(III) complex **2a**. Ligand exchange studies were carried out using benzylamine, pyridine, or benzyl alcohol as the ligands and followed by

uv-vis. The collected uv-vis data was used to extrapolate Stern-Volmer relationships. Research to isolate the ligand-exchange products is currently ongoing.

In addition to the organometallic chemistry of these complexes, new medicinal results may arise as the five-coordinate geometry is believed to provide both added stability and alternate modes of action in regards to chemotherapies.[3-6] Lastly, a one-step ligand synthesis that does not require column chromatography for purification coupled with a one-pot complexation reaction would serve to streamline the study of electronic effects of ligands on a range of metal centers.

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PART I: EXPERIMENTAL PROCEDURES & PRODUCT CHARACTERIZATIONS

General reagent information

All reactions were set up on the benchtop in oven-dried screw-cap glass vials with dried magnetic stirrers and carried out under an air atmosphere. Crude 2-(2'-pyridyl)quinoline reactions were vacuum filtrated through basic alumina (Brockmann I, 50-200 μm, 60 Å) purchased from Acros Organics. The copper(II) trifluoromethanesulfonate, trifluoroacetic acid, anhydrous hexanes, and trifluoromethanesulfonic acid were purchased from Acros Organics and used as supplied. The boron trifluoride diethyl etherate was purchased from Sigma Aldrich and used as supplied. The fluoroboric acid and anhydrous ethyl ether were purchased from Fisher Scientific and used as supplied. 2-pyridinecarboxaldehyde was purchased from Acros Organics and was distilled and stored under argon prior to use. Phenylacetylene was purchased from Alfa Aesar and was distilled and stored under argon prior to use. Aniline reagents were purchased from Alfa Aesar, Acros Organics, or Chem-Impex International and used as supplied or purified before use as in:

Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*. 6th ed.; Butterworth-Heinemann: Oxford, U.K. 2009.

General analytical information

^{1}H and ^{13}C spectra were measured on a Varian Inova 300 or 400 (MHz) spectrometer using $CDCl_3$ as the solvent at room temperature. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s - singlet, d - doublet, t - triplet, q - quartet, m - multiplet, and br - broad. NMR spectra

were acquired at 300 K. Gas chromatography spectra were obtained on an Agilent Technologies 7890A GC System using dodecane as an internal standard. IR spectra were recorded on a Spectrum One FT-IR Spectrometer with a universal ATR sampling accessory. Attenuated total reflection infrared (ATR-IR) was used for analysis with selected absorption maxima reported in wavenumbers (cm^{-1}). No sample preparation was necessary for ATR analysis. ATR-IR is based on the propagation of the infrared radiation through an internal reflection element (crystal) with a high refractive index and its reflection at the interface between the crystal and the solid material. Mass spectroscopic data was collected on an Agilent LCTOF (2006) which utilizes a high resolution TOF analyzer with Windows XP based OS and APCI/ESI ionization. Samples were prepared in acetonitrile and analyzed using positive ionization.

Cell Culturing: A549 Cells

A549 cells were cultured in RPMI media supplemented with 10% Fetal Bovine Serum and 1% nonessential amino acids. Sub-culturing was carried out every 3-4 days and was completed by removing the supernatant media and treating the adherent cells with 1.0 mL of a 0.25% (w/v) Trypsin/0.5 mM EDTA solution. The cells were then treated for approximately 3 minutes in a 37°C incubator under a 5% CO_2 atmosphere. Trypsinization was stopped by the addition of 7.0 mL of cell culture media, the suspended cells were collected by centrifugation, and the resulting cell pellet was re-suspended in fresh cell culture media. The cells were then diluted 1:4 by volume and incubated in a 37°C incubator with 5% CO_2. Cells were grown to 80-90% confluency prior to being used in the SRB colorimetric assays.

Calorimetric Assay: A549 Cells

Cells were maintained in RPMI media as described above, collected, and diluted so that cells could be seeded in 96-well plates at a density of 4,000 cells/well. The 96-well plate was incubated overnight at 37^0C under a 5% CO_2 atmosphere. Subsequently, sterifiltered DMSO stock solutions of the drug candidates were added to the wells in various concentrations (0–25 μM) and the 96-well plate was incubated at 37^0C under a 5% CO_2 for an additional 72 hours. The supernatant cell culture medium was then removed and the cells were fixed for 1 hour with 10% cold trichloroacetic acid (100 μL per well). The trichloroacetic acid was discarded and the plates were washed 5 times with de-ionized water and air dried. After being stained with 0.4% SRB (50 μL per well) and incubated at room temperature for 10 minutes, the cells were washed 5 times with 1% acetic acid and air dried. The bound SRB was dissolved in 10 mM unbuffered Tris, pH 10.5 (100 μL per well) for 10 minutes at room temperature, and the absorbance at 492 nm was measured using a microplate reader. The percent cell growth was then calculated based upon the absorbance values relative to control samples not containing any drug. Each drug concentration was done in triplicate to yield a percent growth vs. drug concentration curve, and these growth curves were subsequently repeated two additional times. The growth curves from the three experiments were then plotted in GraphPad Prism and best-fit curves were used to generate the IC_{50} values for each curve.

Cell Culturing: GL-26 Cells

The murine (C57BL/6) glioma cell line, GL-26, which is highly tumorigenic in the C57BL/6 mice, was obtained as a generous gift from Dr. Pedro Lowenstein, University of Michigan, Ann Arbor. GL-26 cells were cultured in DMEM/F12 supplemented with 10% FCS, 1% penicillin/ streptomycin, 1% L-glutamine and 1% non-essential amino acids. Human foreskin fibroblasts (HFFs) were cultured in DMEM/F12 supplemented with 10% FCS and 1% penicillin/ streptomycin. Primary murine astrocytes were purified from C57BL/6 neonate brains and cultured in DMEM/F12 supplemented with 10% FCS, 1% non-essential amino acids, 1% L-glutamine, 50IU/ml penicillin, 50mg/ml streptomycin and 10mM Hepes buffer.

SRB Growth Assay: GL-26 Cells

GL-26 cells were plated in 96-well plates at a density of 4,000 cells/well in a volume of 100mL overnight at 37°C and 5% CO_2. DMSO stock solutions of the drug candidates were used at a concentration range of 0.1–25 μM for 48 hr before the supernatant was discarded and the cells were fixed for 1 hr with 10% cold trichloroacetic acid (100 μL per well). Cells used in recovery assay received fresh media for 48hrs following the 48hr drug incubation. The plate was then washed 5 times with de-ionized water, air dried, and stained with 0.4% SRB for 10 min (50 μL per well). After washing 5 times in 1% acetic acid and air-drying, bound SRB was dissolved in 10 mM unbuffered Tris base (pH 10.5; 100 μL per well). Bound SRB was then read by absorbance at 492 nm on a SpectraMax plate reader (Molecular Devices). The percent survival was then calculated based upon the absorbance values relative to control wells (0 mM SBP in 0.1% DMSO).

General procedure for substituted 2-(2'-pyridyl)quinoline synthesis

An aniline source (1.0 equiv.), 2-pyridinecarboxaldehyde (1.2 equiv.), and phenylacetylene (1.2 equiv.) were added to an oven-dried screw-cap glass vial charged with a dried magnetic stir bar. Lastly, trifluoromethanesulfonic acid (0.1 equiv.) was carefully added into the reaction mixture. The reaction was then capped and placed on a heating medium (aluminum block or oil bath) set at 110˚C for 4 hours. Upon completion, 1-mL of methylene chloride was added to the reaction vial followed by magnetic stirring at room temperature until the crude solid dissolved completely. The crude mixture was then run through a basic alumina plug prepared in the following manner: a 60-mL fritted filtration funnel with a vacuum sidearm adapter was charged with a 0.5-cm layer of sand followed by a 3.5-cm layer of basic alumina as the top layer. A 500-mL round-bottom receiving flask was attached to the funnel and clamped. The crude material was then pipetted onto the top of the dry basic alumina. Diethyl ether was used to rinse and transfer any residual crude material. Once the crude material was transferred to the basic alumina plug, 250-mL of diethyl ether was used to flush the plug thoroughly under a light vacuum. The organic solvents were removed under rotary evaporation and then the flask was placed under a high-vacuum for 10 minutes. The solid was then rinsed with cold hexanes (~ 5-mL) which resulted in spectroscopically clean product.

2-(2'-pyridyl)quinoline (**1a**)

Aniline (91 µL, 1 mmol), 2-pyridinecarboxaldehyde (114 µL, 1.2 mmol), phenylacetylene (132 µL, 1.2 mmol), trifluoromethanesulfonic acid (9 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a light beige/white solid in 10% yield (0.029 g, 0.1 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. ^{1}H NMR (300 MHz, $CDCl_3$, 25˚C) δ 8.74 (t, J = 5.1 Hz, 2H), 8.55 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.01-7.85 (m, 2H), 7.76 (t, J = 7.1 Hz, 1H), 7.65-7.45 (m, 6H), 7.37 (dd, J = 7.3, 5.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25˚C) δ 156.04, 155.48, 149.83, 149.28, 148.24, 138.38, 137.21, 130.05, 129.80, 128.63, 128.55, 127.08, 126.92, 125.99, 124.33, 122.27, 119.48.

For full characterization, see:

Campagna, S.; Mamo, A.; Stille, J.K. *J. Chem. Soc. Dalton Trans*. **1991**, 2545.

4,8-diphenyl-2-(2'-pyridyl)quinoline (**1b**)

2-aminobiphenyl (169 mg, 1 mmol), 2-pyridinecarboxaldehyde (114 µL, 1.2 mmol), phenylacetylene (132 µL, 1.2 mmol), trifluoromethanesulfonic acid (9 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a light beige solid in 22% yield (0.157 g, 0.44 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3055, 1587, 1488, 769, 692 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{26}H_{19}N_2$ requires 359.1543, found 359.1559. ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.73-8.67 (m, 1H), 8.65 (s, 1H), 8.52 (d, J = 8.0 Hz, 1H), 7.98 (dd, J = 8.4, 1.2 Hz, 1H), 7.95-7.87 (m, 2H), 7.84-

7.76 (m, 2H), 7.68-7.47 (m, 9H), 7.34-7.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.57, 154.78, 149.60, 148.98, 145.90, 141.28, 140.06, 138.88, 136.97, 131.33, 130.30, 129.83, 128.56, 128.35, 127.76, 127.37, 127.23, 126.62, 125.63, 124.02, 122.16, 118.90.

8-fluoro-4-phenyl-2-(2'-pyridyl)quinoline (**1c**)

2-fluoroaniline (387 µL, 4 mmol), 2-pyridinecarboxaldehyde (457 µL, 4.8 mmol), phenylacetylene (521 µL, 4.8 mmol), trifluoromethanesulfonic acid (35 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a light beige solid in 7% yield (0.079 g, 0.26 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3058, 1588, 1488, 1403, 1245, 1071, 756, 702 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{20}H_{14}N_2F$ requires 300.1057, found 300.1063. ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.77 (dd, J = 8.0, 0.9 Hz, 1H), 8.73-8.68 (m, 1H), 8.61 (s, 1H), 7.93-7.84 (m, 1H), 7.75-7.69 (m, 1H), 7.60-7.48 (m, 5H), 7.44-7.34 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.71 – -124.82 (m). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 159.93, 157.38, 156.03, 155.78, 149.34, 149.21, 138.21, 137.15, 129.71, 128.65, 126.40, 126.32, 124.45, 122.31, 121.66, 120.20, 113.65, 113.46.

8-methoxy-4-phenyl-2-(2'-pyridyl)-5-(trifluoromethyl)quinoline (**1d**)

2-methoxy-5-(trifluoromethyl)aniline (382 mg, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a light beige solid in 23% yield (0.174 g, 0.46 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3050, 2965, 1588, 1553, 1457, 1319, 1230, 1119, 700 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{22}H_{16}N_2OF_3$ requires 381.1209, found 381.1197. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.70 (d, J = 7.9 Hz, 1H), 8.65 (dd, J= 2.8, 2.0 Hz, 1H), 8.50 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.82 (td, J = 7.7, 1.8 Hz, 1H), 7.39 (s, 5H), 7.29 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 4.12 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, 25˚C) δ -52.78 (s). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 158.73, 155.46, 153.92, 149.21, 149.06, 141.34, 136.99, 129.42, 129.03, 128.96, 127.99, 127.82, 127.32, 125.28, 125.00, 124.33, 122.56, 122.20, 105.67, 56.51.

8-methoxy-4-phenyl-2-(2'-pyridyl)quinoline (**1e**)

o-anisidine (1.1 mL, 10 mmol), 2-pyridinecarboxaldehyde (1.3 mL, 12 mmol), phenylacetylene (1.3 mL, 12 mmol), trifluoromethanesulfonic acid (89 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a light beige solid in 2% yield (0.061 g, 0.20 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3067, 3017, 1588, 1452, 1402, 1260, 1094, 739, 697 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{17}N_2O$ requires 313.1336, found 313.1342. ^1H NMR (400 MHz, $CDCl_3$, 25˚C)

δ 8.75 (d, J = 8.0 Hz, 1H), 8.71-8.67 (m, 1H), 8.55 (s, 1H), 7.86 (td, J = 7.7, 1.7 Hz, 1H), 7.58 (dd, J = 8.0, 1.4 Hz, 2H), 7.54-7.43 (m, 4H), 7.40 (t, J = 8.1 Hz, 1H), 7.32 (dd, J = 6.6, 5.2 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 4.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.48, 155.90, 154.55, 149.40, 149.13, 140.51, 138.76, 137.02, 129.75, 128.49, 128.34, 128.06, 126.91, 124.06, 122.30, 119.94, 117.84, 107.93, 56.39.

4-phenyl-2-(2'-pyridyl)-8-(trifluoromethyl)quinoline (**1f**)

2-(trifluoromethyl)aniline (251 µL, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a light beige solid in 19% yield (0.133 g, 0.38 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and recrystallizing from diethyl ether. IR (crystal) 3062, 1588, 1560, 1306, 1121, 768, 698 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{14}N_2F_3$ requires 351.1104, found 351.1122. ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.84 (d, *J* = 8.0 Hz, 1H), 8.73 – 8.69 (m, 1H), 8.68 (s, 1H), 8.12 (dd, *J* = 13.9, 7.8 Hz, 2H), 7.91 (td, *J* = 7.7, 1.7 Hz, 1H), 7.61 – 7.46 (m, 6H), 7.37 (ddd, *J* = 7.4, 4.8, 1.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.23 (s). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 155.90, 155.85, 149.68, 149.13, 144.98, 138.03, 137.27, 130.42, 129.79, 128.74, 128.10, 128.04, 127.38, 125.89, 125.27, 124.62, 123.16, 122.56, 119.75.

6-chloro-4-phenyl-2-(2'-pyridyl)quinoline (**1g**)

4-chloroaniline (255 mg, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 30% yield (0.190 g, 0.60 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3059, 1587, 1485, 699 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{20}H_{14}N_2Cl$ requires 317.0840, found 317.0849. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.70 (d, *J* = 3.9 Hz, 1H), 8.65 (d, *J* = 7.9 Hz, 1H), 8.55 (s, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.91 (s, 1H), 7.84 (t, *J* = 6.9 Hz, 1H), 7.69 – 7.60 (m, 1H), 7.61 – 7.39 (m, 5H), 7.39 – 7.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 155.97, 155.87, 149.25, 148.50, 146.93, 137.79, 136.98, 132.76, 131.86, 130.37, 129.61, 128.76, 128.66, 127.51, 124.70, 124.26, 121.86, 120.04.

6,8-dimethyl-4-phenyl-2-(2'-pyridyl)quinoline (**1h**)

2,4-dimethylaniline (247 µL, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 42% yield (0.261 g, 0.84 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3059, 2910, 1588, 1557, 858, 793, 701 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{22}H_{19}N_2$ requires 311.1543, found 311.1557. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.89 – 8.80 (m, 1H), 8.79 – 8.71 (m, 1H), 8.62 (s, 1H), 7.84 (td, *J* = 7.8, 1.7 Hz, 1H), 7.70 – 7.60 (m, 3H),

7.60 – 7.47 (m, 3H), 7.45 (s, 1H), 7.34 – 7.26 (m, 1H), 3.00 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.81, 153.11, 148.90, 148.55, 145.97, 139.10, 137.52, 136.65, 136.25, 131.80, 129.71, 128.35, 128.01, 126.69, 123.65, 122.51, 121.60, 118.82, 21.87, 18.31.

6-bromo-4-phenyl-2-(2'-pyridyl)quinoline (**1i**)

4-bromoaniline (344 mg, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 25% yield (0.180 g, 0.50 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3053, 1586, 1483, 1360, 780, 704 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{20}H_{14}N_2Br$ requires 361.0335, found 361.0353. ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.71 (d, *J* = 4.0 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.55 (s, 1H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.87 (td, *J* = 7.8, 1.7 Hz, 1H), 7.79 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.60 – 7.47 (m, 5H), 7.39 – 7.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.03, 149.32, 148.50, 147.18, 137.80, 137.06, 132.99, 132.01, 129.66, 128.81, 128.72, 128.06, 124.34, 121.94, 121.10, 120.09.

6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline (**1j**)

p-anisidine (246 mg, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a colorless solid in 42% yield

(0.265 g, 0.85 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3055, 2935, 1622, 1587, 1477, 1223, 1032, 714 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{17}N_2O$ requires 313.1336, found 313.1337. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.69 (d, J = 4.7 Hz, 1H), 8.64 (d, J = 8.0 Hz, 1H), 8.48 (s, 1H), 8.15 (d, J = 9.2 Hz, 1H), 7.82 (td, J = 7.7, 1.7 Hz, 1H), 7.60 (d, J = 6.9 Hz, 2H), 7.49 (dt, J = 22.2, 7.1 Hz, 3H), 7.39 (dd, J = 9.2, 2.8 Hz, 1H), 7.29 (dd, J = 6.9, 5.3 Hz, 1H), 7.23 (d, J = 2.7 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 158.20, 156.56, 153.47, 149.13, 147.84, 144.61, 138.75, 136.87, 131.75, 129.50, 128.61, 128.28, 127.77, 123.71, 121.85, 121.51, 119.60, 103.78, 55.46.

7-chloro-8-methyl-4-phenyl-2-(2'-pyridyl)quinoline (**1k**)

3-chloro-2-methylaniline (478 µL, 4 mmol), 2-pyridinecarboxaldehyde (457 µL, 4.8 mmol), phenylacetylene (527 µL, 4.8 mmol), trifluoromethanesulfonic acid (35 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a colorless solid in 42% yield (0.265 g, 0.85 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3058, 2923, 1592, 1574, 1440, 761, 699 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{16}N_2Cl$ requires 331.0997, found 331.1003. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.75 (d, *J* = 8.0 Hz, 1H), 8.72 – 8.67 (m, 1H), 8.54 (s, 1H), 7.85 (td, *J* = 7.7, 1.8 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.56 – 7.45 (m, 5H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.32 (ddd, *J* = 7.4, 4.8, 1.0 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.36, 154.90, 149.63,

149.10, 147.84, 138.42, 136.90, 135.40, 134.94, 129.74, 128.57, 128.44, 127.88, 125.33, 124.22, 124.18, 121.94, 118.79, 14.96.

6-methyl-4-phenyl-2-(2'-pyridyl)quinoline (**1l**)

p-toluidine (429 mg, 4 mmol), 2-pyridinecarboxaldehyde (457 µL, 4.8 mmol), phenylacetylene (527 µL, 4.8 mmol), trifluoromethanesulfonic acid (35 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 28% yield (0.328 g, 1.12 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3047, 2920, 1587, 1490, 765, 699 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{17}N_2$ requires 297.1386, found 297.1400. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.75 – 8.65 (m, 2H), 8.51 (s, 1H), 8.17 (d, J = 8.6 Hz, 1H), 7.84 (ddd, J = 9.6, 1.7, 0.8 Hz, 1H), 7.71 (s, 1H), 7.63 – 7.45 (m, 6H), 7.34 – 7.27 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.51, 154.79, 149.15, 148.54, 147.11, 138.64, 136.89, 136.84, 131.70, 129.98, 129.69, 128.50, 128.23, 126.75, 124.60, 123.89, 121.74, 119.35, 21.92.

6,8-dichloro-4-phenyl-2-(2'pyridyl)quinoline (**1m**)

2,4-dichloroaniline (324 mg, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 25% yield (0.177 g, 0.50 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal)

3058, 1587, 1477, 1359, 1154, 782, 699 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{20}H_{13}N_2Cl_2$ requires 351.0451, found 351.0455. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.82 (d, *J* = 8.0 Hz, 1H), 8.70 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.63 (s, 1H), 7.90 (td, *J* = 7.7, 1.8 Hz, 1H), 7.83 (dd, *J* = 5.5, 2.2 Hz, 2H), 7.60 – 7.47 (m, 5H), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.03, 155.66, 149.22, 143.33, 137.57, 137.19, 135.67, 131.92, 130.24, 129.66, 128.90, 128.86, 128.51, 124.64, 124.01, 122.43, 120.76.

4-phenyl-2-(2'-pyridyl)-6-(trifluoromethyl)quinoline (**1n**)

4-(trifluoromethyl)aniline (252 µL, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a colorless solid in 20% yield (0.137 g, 0.39 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, rinsing solid with cold hexanes followed by recrystallization in 100% diethyl ether. IR (crystal) 3062, 1459, 1308, 1106, 706 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{14}N_2F_3$ requires 351.1104, found 351.1116. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.75 – 8.66 (m, 2H), 8.64 (s, 1H), 8.33 (d, J = 8.8 Hz, 1H), 8.27 (s, 1H), 7.94 – 7.80 (m, 2H), 7.68 – 7.44 (m, 5H), 7.35 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, 25˚C) δ -62.54 (s). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 157.54, 155.66, 150.19, 149.56, 149.29, 137.50, 137.01, 131.44, 129.65, 128.88, 125.90, 125.09, 124.56, 123.91, 123.87, 122.09, 120.37.

6-(methylthio)-4-phenyl-2-(2'-pyridyl)quinoline (**1o**)

4-(methylthio)aniline (249 µL, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 36% yield (0.236 g, 0.72 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3057, 3003, 1584, 1484, 703 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{17}N_2S$ requires 329.1107, found 329.1123. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.72 – 8.69 (m, 1H), 8.66 (dd, *J* = 8.0, 0.6 Hz, 1H), 8.50 (s, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 7.86 (td, *J* = 7.6, 1.2 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.64 – 7.46 (m, 6H), 7.33 (dd, *J* = 7.4, 4.8 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.40, 154.92, 149.27, 147.99, 146.83, 138.34, 137.86, 137.02, 130.53, 129.67, 128.85, 128.67, 128.50, 127.25, 124.04, 121.80, 121.00, 119.93, 15.76.

6-fluoro-4-phenyl-2-(2'-pyridyl)quinoline (**1p**)

4-fluoroaniline (190 µL, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 35% yield (0.212 g, 0.71 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3060, 1491, 1194, 794, 700 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{20}H_{14}N_2F$ requires 301.1136, found 301.1148. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.77 – 8.68 (m, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.55 (s, 1H), 8.22 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.84 (td, *J* = 7.7, 1.8 Hz,

1H), 7.63 – 7.43 (m, 7H), 7.32 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, 25˚C) δ -112.52 – -112.69 (m). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 160.92 (d, *J* = 247.9 Hz), 156.12, 155.14, 149.21, 148.75 (d, *J* = 5.2 Hz), 145.64, 137.99, 136.96, 132.70 (d, *J* = 9.0 Hz), 129.52, 128.72, 128.60, 127.61 (d, *J* = 9.5 Hz), 124.12, 121.72, 119.82, 119.62 (d, *J* = 26.1 Hz), 109.28 (d, *J* = 23.2 Hz).

4,6-diphenyl-2-(2'-pyridyl)quinoline (**1q**)

4-aminobiphenyl (338 mg, 2 mmol), 2-pyridinecarboxaldehyde (228 µL, 2.4 mmol), phenylacetylene (264 µL, 2.4 mmol), trifluoromethanesulfonic acid (18 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a light beige/white solid in 34% yield (0.245 g, 0.68 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3054, 1588, 1486, 763, 695 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{26}H_{19}N_2$ requires 359.1543, found 359.1545. ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.81 – 8.69 (m, 2H), 8.62 (s, 1H), 8.35 (d, *J* = 8.7 Hz, 1H), 8.20 (d, *J* = 1.9 Hz, 1H), 8.02 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.87 (ddd, *J* = 7.6, 5.6, 1.7 Hz, 1H), 7.73 – 7.61 (m, 4H), 7.61 – 7.48 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 156.31, 155.53, 149.34, 149.17, 147.96, 140.59, 139.48, 138.41, 136.90, 130.73, 129.72, 129.19, 128.92, 128.62, 128.41, 127.65, 127.45, 126.93, 124.04, 123.54, 121.86, 119.72.

6-cyano-4-phenyl-2-(2'-pyridyl)quinoline (**1r**)

4-aminobenzonitrile (473 mg, 4 mmol), 2-pyridinecarboxaldehyde (457 µL, 4.8 mmol), phenylacetylene (527 µL, 4.8 mmol), boron trifluoride diethyl etherate (49 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as clear crystals in 5% yield (0.057 g, 0.19 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. IR (crystal) 3050, 2227, 1586, 1547, 1364, 801, 763, 702 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{14}N_3$ requires 308.1182, found 308.1181. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 8.72 (d, *J* = 4.6 Hz, 1H), 8.69 (d, *J* = 8.1 Hz, 1H), 8.65 (s, 1H), 8.31 (s, 1H), 8.27 (d, *J* = 8.7 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.51 (m, 5H), 7.42 – 7.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 158.27, 155.37, 149.85, 149.55, 149.43, 137.14, 136.99, 132.52, 131.64, 130.09, 129.63, 129.16, 129.00, 126.38, 124.87, 122.26, 120.68, 119.00, 110.22.

4-p-methoxyphenyl-6-bromo-2-(2'-pyridyl)quinoline (Figure 6)

4-bromoaniline (86 mg, 0.5 mmol), 2-pyridinecarboxaldehyde (57 µL, 0.6 mmol), 4-ethynylanisole (78 µL, 0.6 mmol), trifluoromethanesulfonic acid (4 µL, 10 mol%) were stirred at 110˚C for 4h to afford the title compound as a white solid in 20% yield (0.040 g, 0.10 mmol) after flushing through a basic aluminum oxide plug with 100% diethyl ether, removing solvent *in vacuo*, and rinsing solid with cold hexanes. ^1H NMR (300 MHz, $CDCl_3$, 25˚C) δ 8.71 (d, *J* = 4.0 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.51 (s, 1H), 8.12 (d, *J* = 2.1 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.86 (td, *J* = 7.8, 1.7 Hz, 1H), 7.78 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.35 (ddd, *J* = 7.4, 4.8, 1.0 Hz, 1H), 7.11 – 7.03 (m,

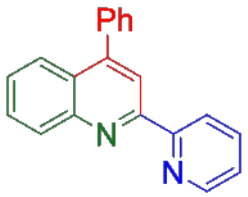
2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C) δ 160.11, 156.12, 156.04, 149.31, 148.25, 147.27, 137.05, 132.89, 132.01, 130.95, 130.08, 128.25, 128.14, 124.29, 121.94, 120.96, 119.96, 114.30, 55.52.

For full characterization, see:

Mamo, A.; Aureliano, A.; Recca, A. *Molecules* **2010**, *15*, 1324.

Table 3 - 1a

^{1}H NMR of 2-(2'-pyridyl)quinoline
300 MHz, 25 °C, $CDCl_3$



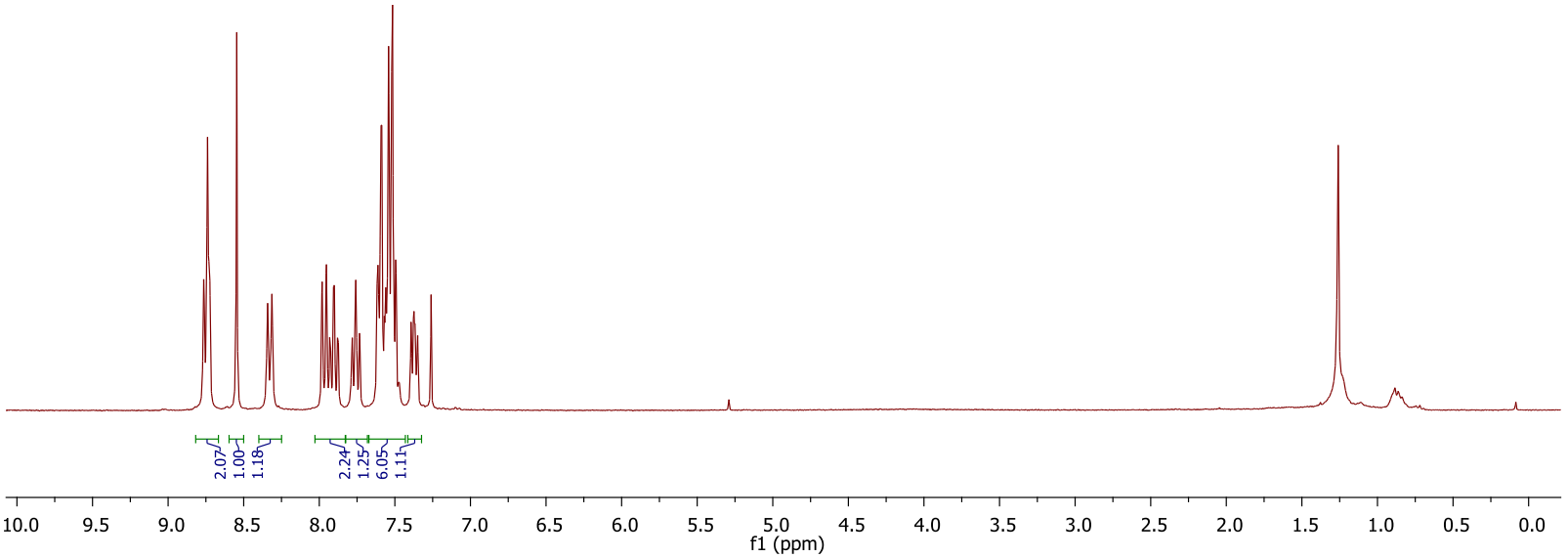
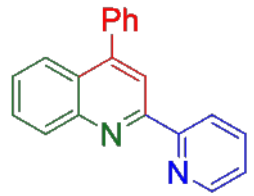


Table 3 - 1a

156.04
155.48
149.83
149.28
148.24
138.38
137.21
130.05
129.80
128.63
128.55
127.08
126.92
125.99
124.33
122.27
119.48

^{13}C NMR of 2-(2'-pyridyl)quinoline
75 MHz, 25 °C, $CDCl_3$



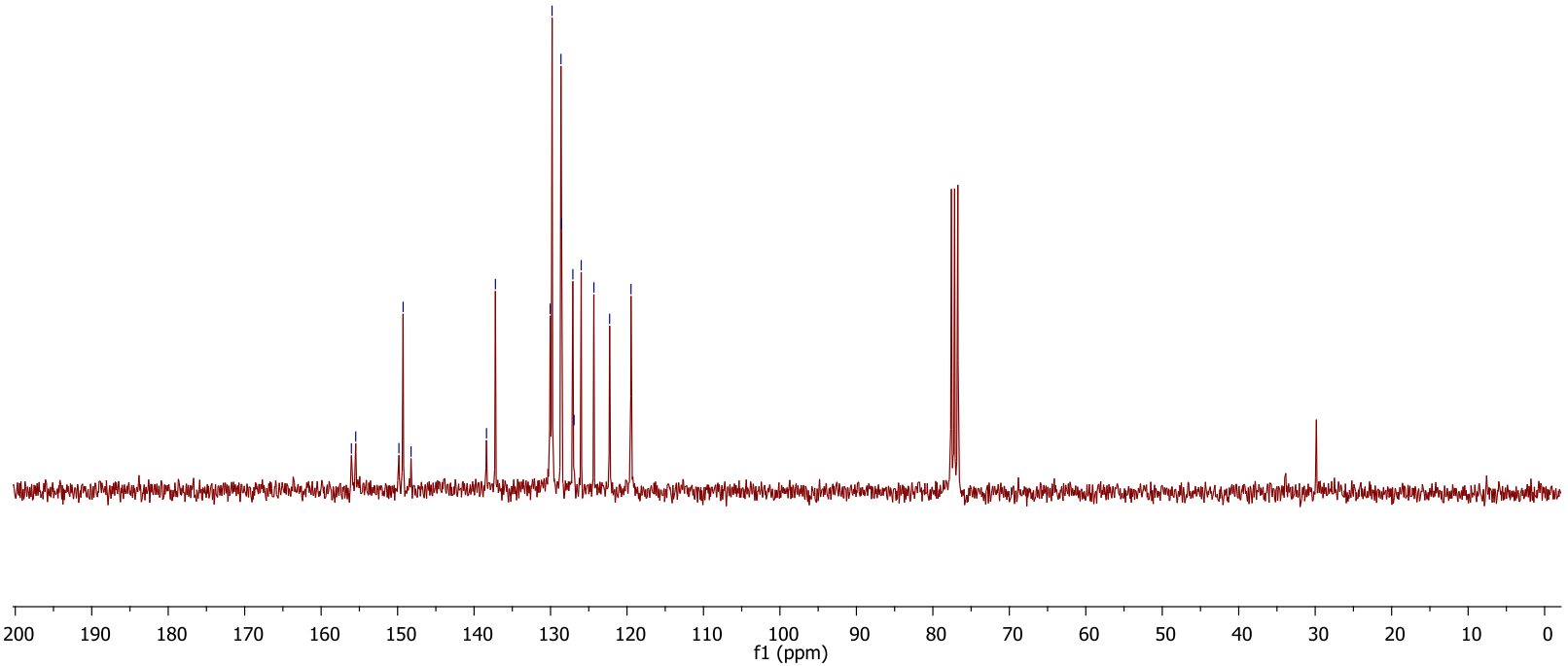


Table 3 - 1b

^{1}H NMR of 4,8-diphenyl-2-(2'-pyridyl)quinoline
400 MHz, 25 °C, $CDCl_3$

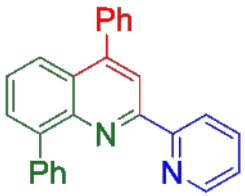
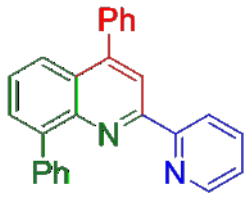


Table 3 - 1b

156.57
154.78
149.60
148.98
145.90
141.28
140.06
138.88
136.97
131.33
130.30
129.83
128.56
128.35
127.76
127.37
127.23
126.62
125.63
124.02
122.16
118.90

^{13}C NMR of 4,8-diphenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



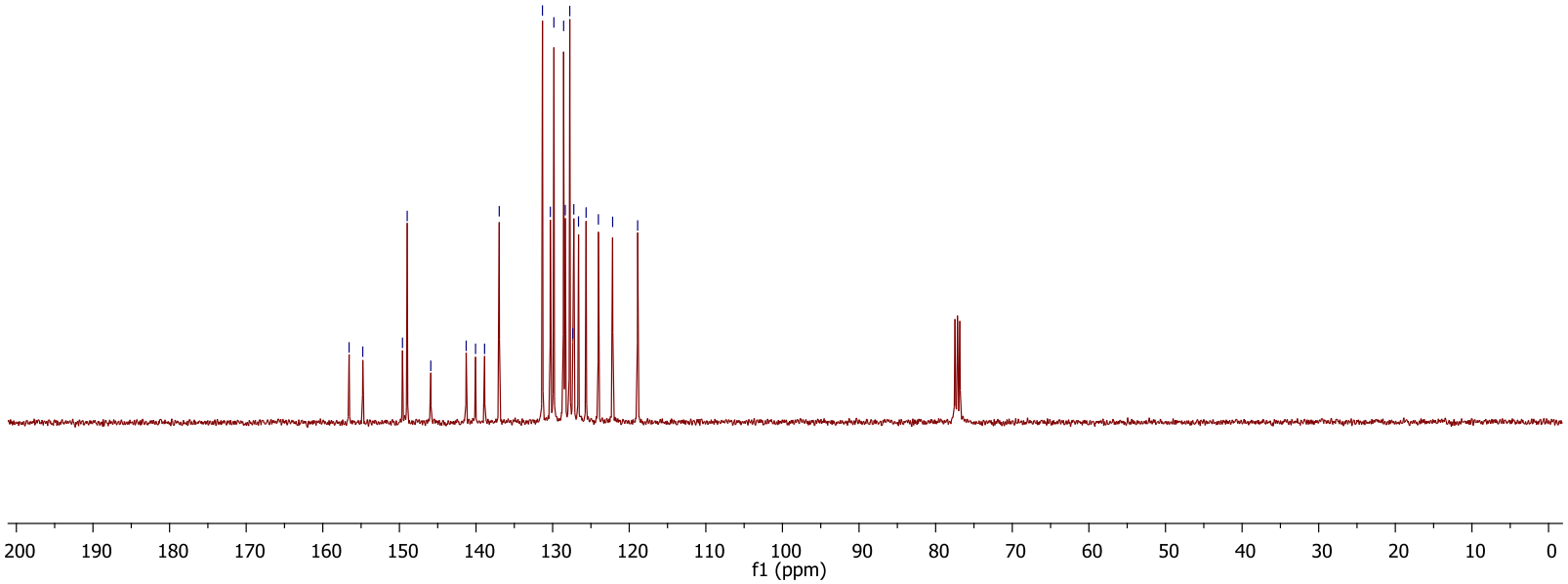


Table 3 - 1c

^{1}H NMR of 8-fluoro-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$

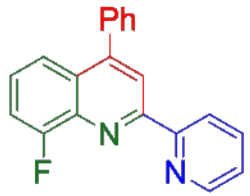
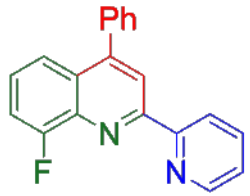


Table 3 - 1c

159.93
157.38
156.03
155.78
149.34
149.21
138.21
137.15
129.71
128.65
126.40
124.45
122.31
121.66
120.20
113.46

^{13}C NMR of 8-fluoro-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



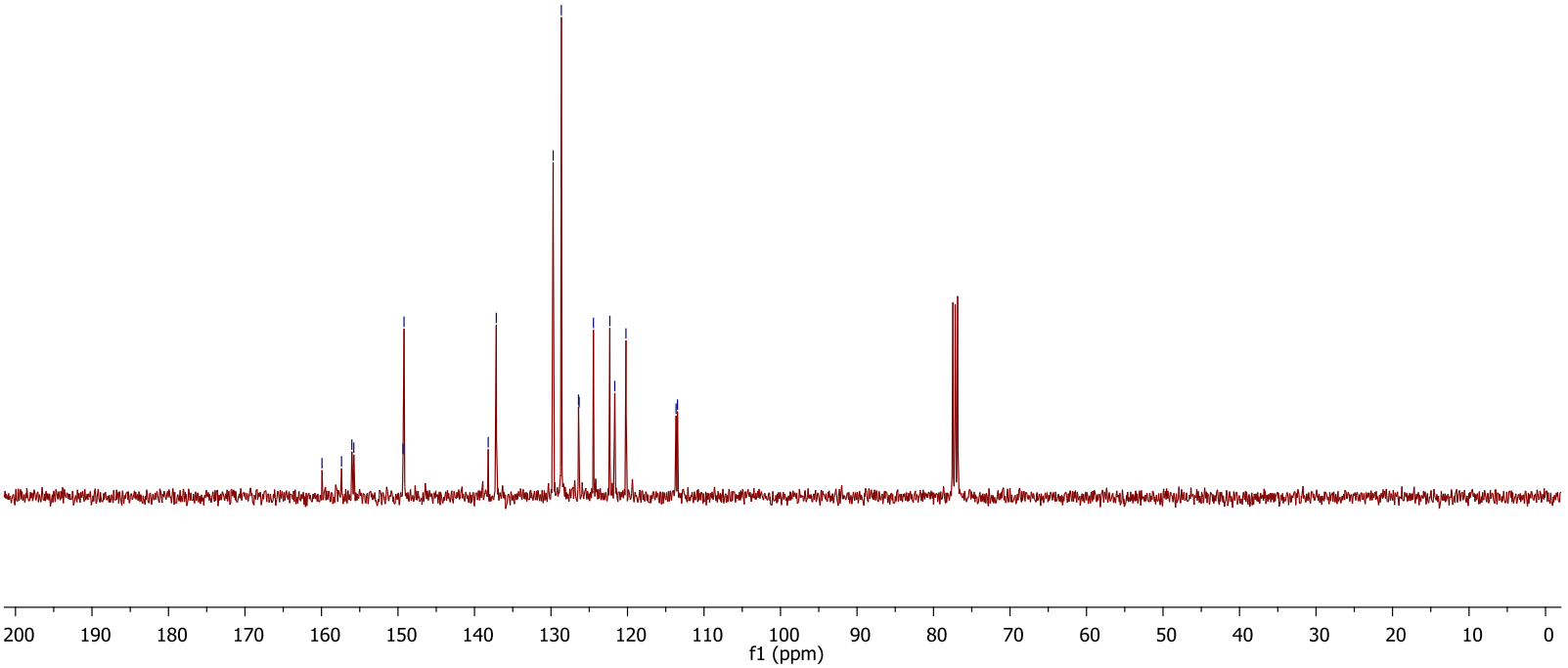
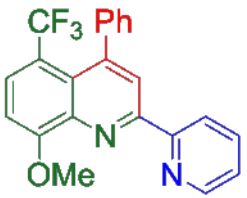


Table 3 - 1d

^{1}H NMR of 8-methoxy-4-phenyl-2-(2'-pyridyl)-5-(trifluoromethyl)quinoline

400 MHz, 25 °C, $CDCl_3$



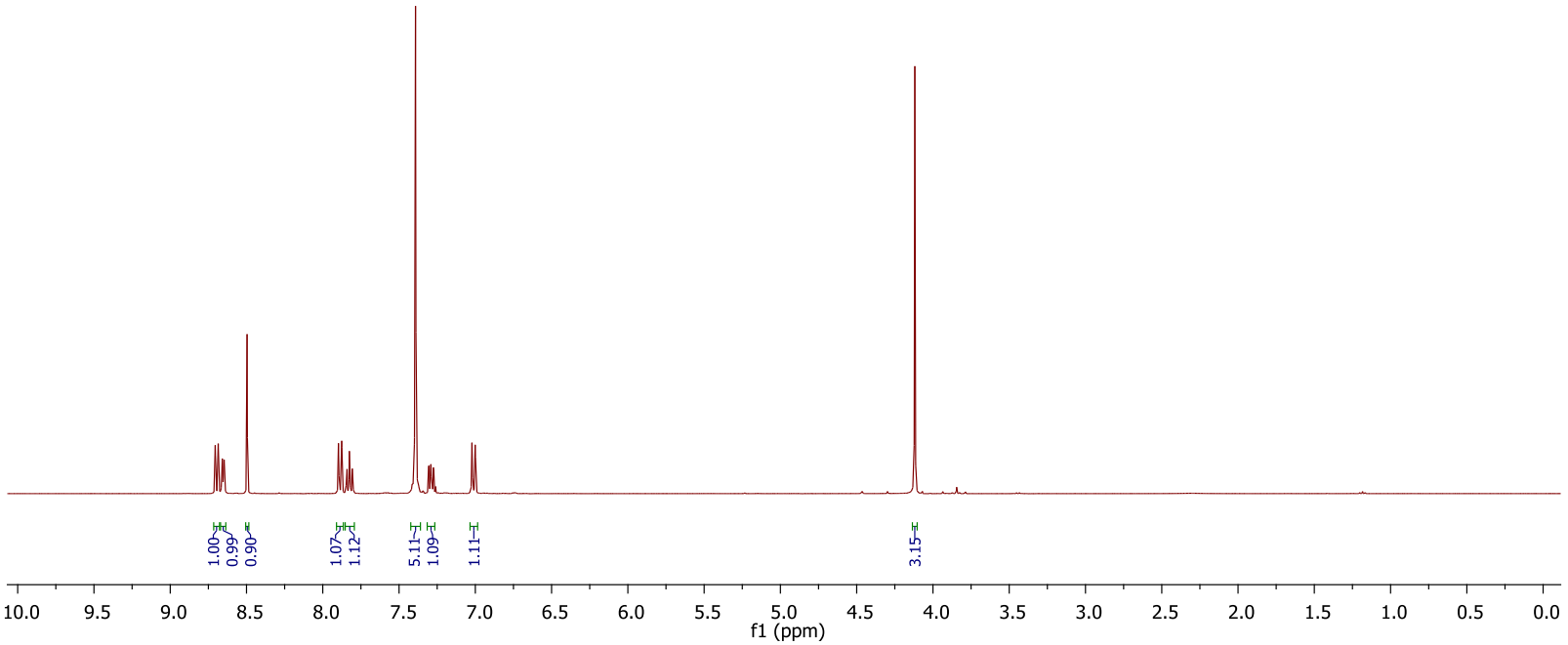
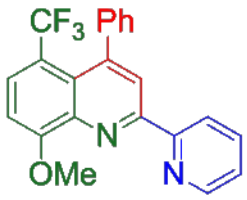


Table 3 - 1d

158.73
155.46
153.92
149.21
149.06
141.34
136.99
135.42
129.03
128.96
127.99
127.82
127.32
125.28
125.00
124.33
122.56
122.20
105.67
56.51

^{13}C NMR of 8-methoxy-4-phenyl-2-(2'-pyridyl)-5-(trifluoromethyl)quinoline

100 MHz, 25 °C, $CDCl_3$



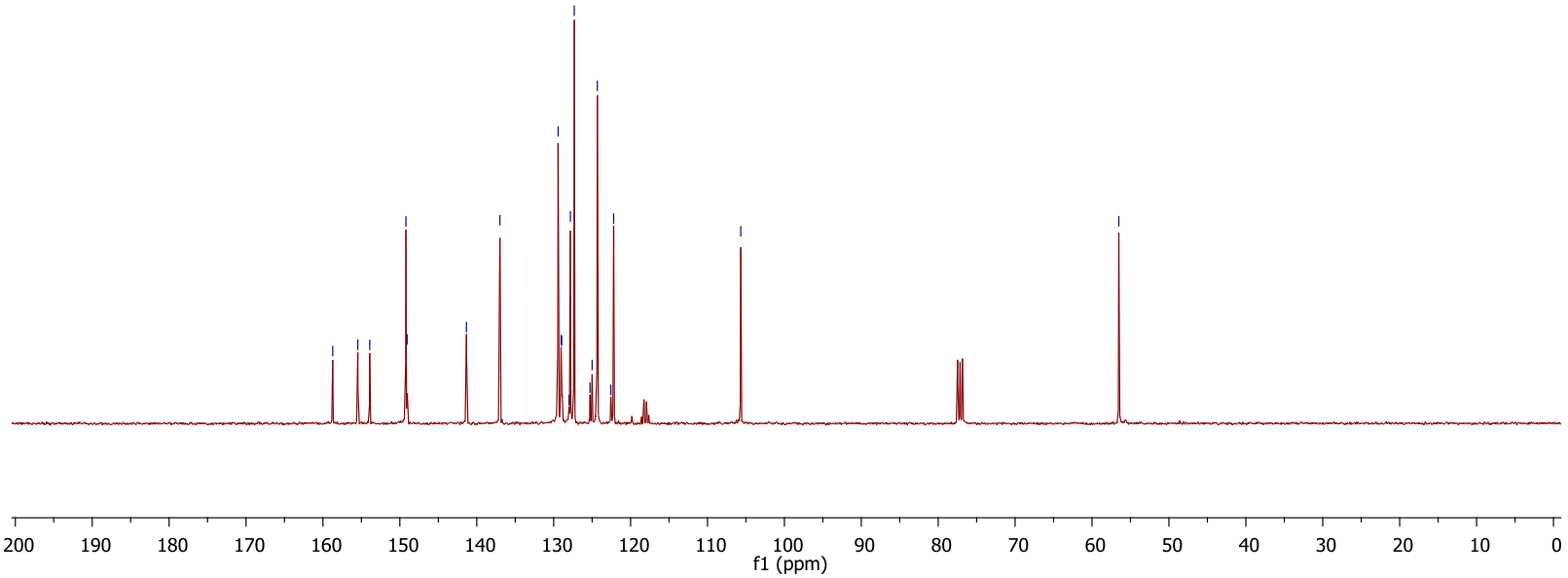


Table 3 - 1e

^{1}H NMR of 8-methoxy-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$

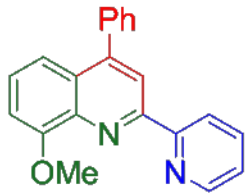


Table 3 - 1e

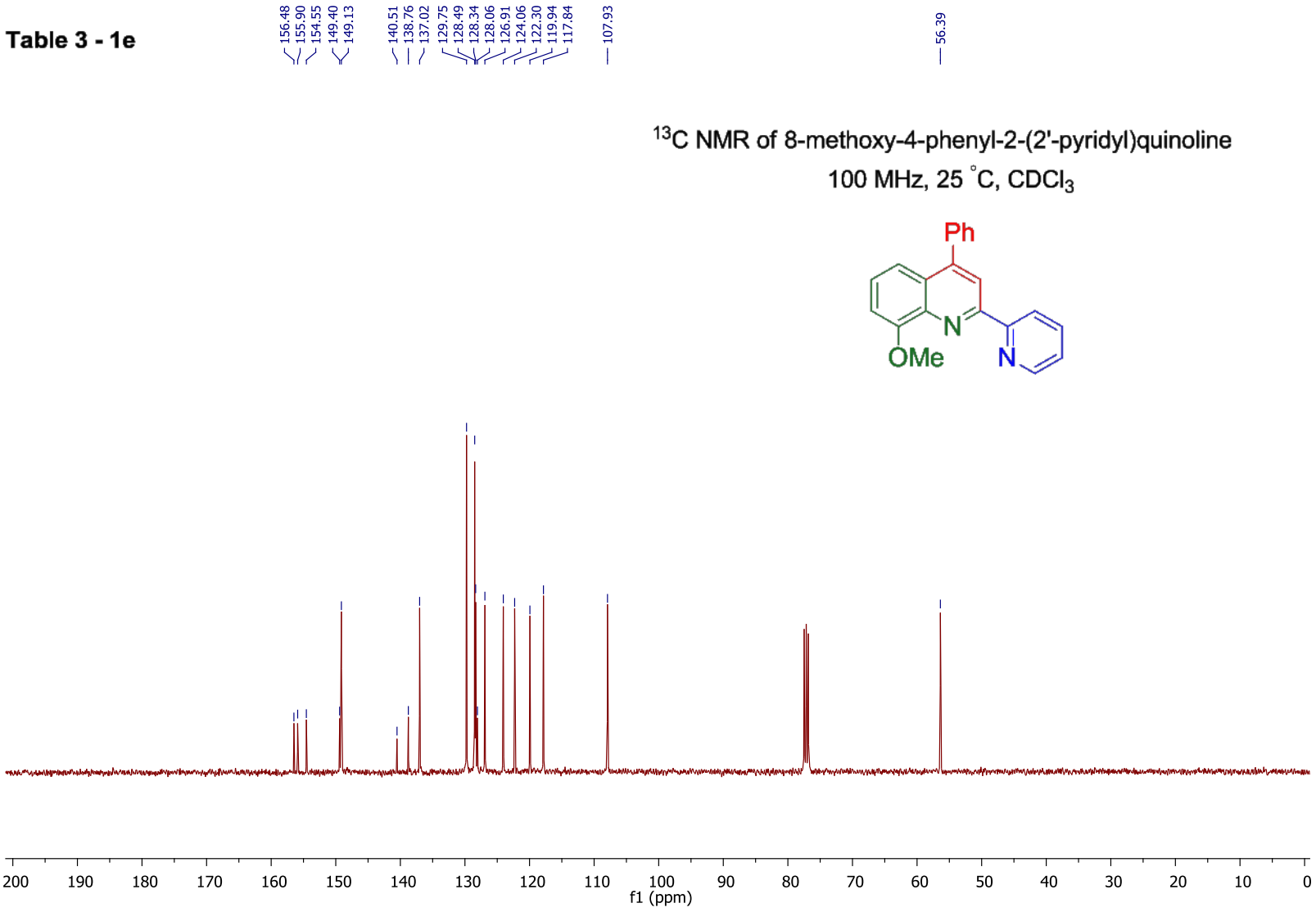

156.48
155.90
154.55
149.40
149.13
140.51
138.76
137.02
129.75
128.49
128.34
128.06
126.91
124.06
122.30
119.94
117.84
107.93
56.39
13C NMR of 8-methoxy-4-phenyl-2-(2'-pyridyl)quinoline
100 MHz, 25 °C, CDCl3
Ph
N
OMe
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 3 - 1f

^{1}H NMR of 4-phenyl-2-(2'-pyridyl)-8-(trifluoromethyl)quinoline

400 MHz, 25 °C, $CDCl_3$

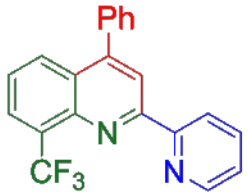
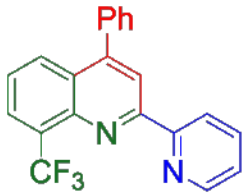


Table 3 - 1f

155.90
155.85
149.68
149.13
144.98
138.03
137.27
130.42
129.79
128.74
128.10
128.04
127.38
125.89
125.27
124.62
123.16
122.56
119.75

^{13}C NMR of 4-phenyl-2-(2'-pyridyl)-8-(trifluoromethyl)quinoline

100 MHz, 25 °C, $CDCl_3$



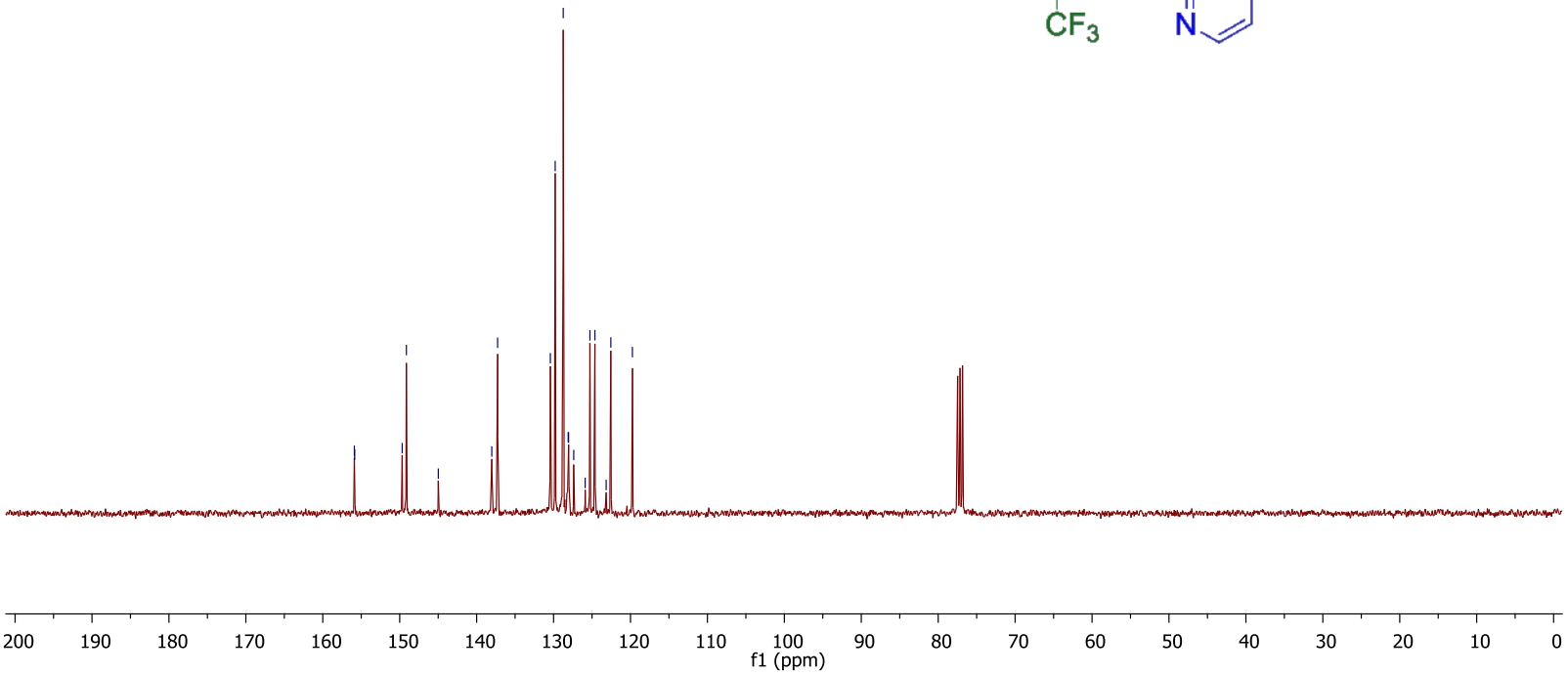


Table 3 - 1g

^{1}H NMR of 6-chloro-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$

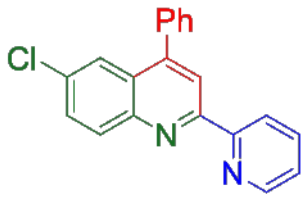
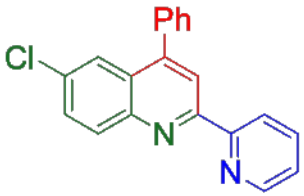


Table 3 - 1g

155.97
155.87
149.25
148.50
146.93
137.79
136.98
132.76
131.86
130.37
129.61
128.76
128.66
127.51
124.70
124.26
121.86
120.04

^{13}C NMR of 6-chloro-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



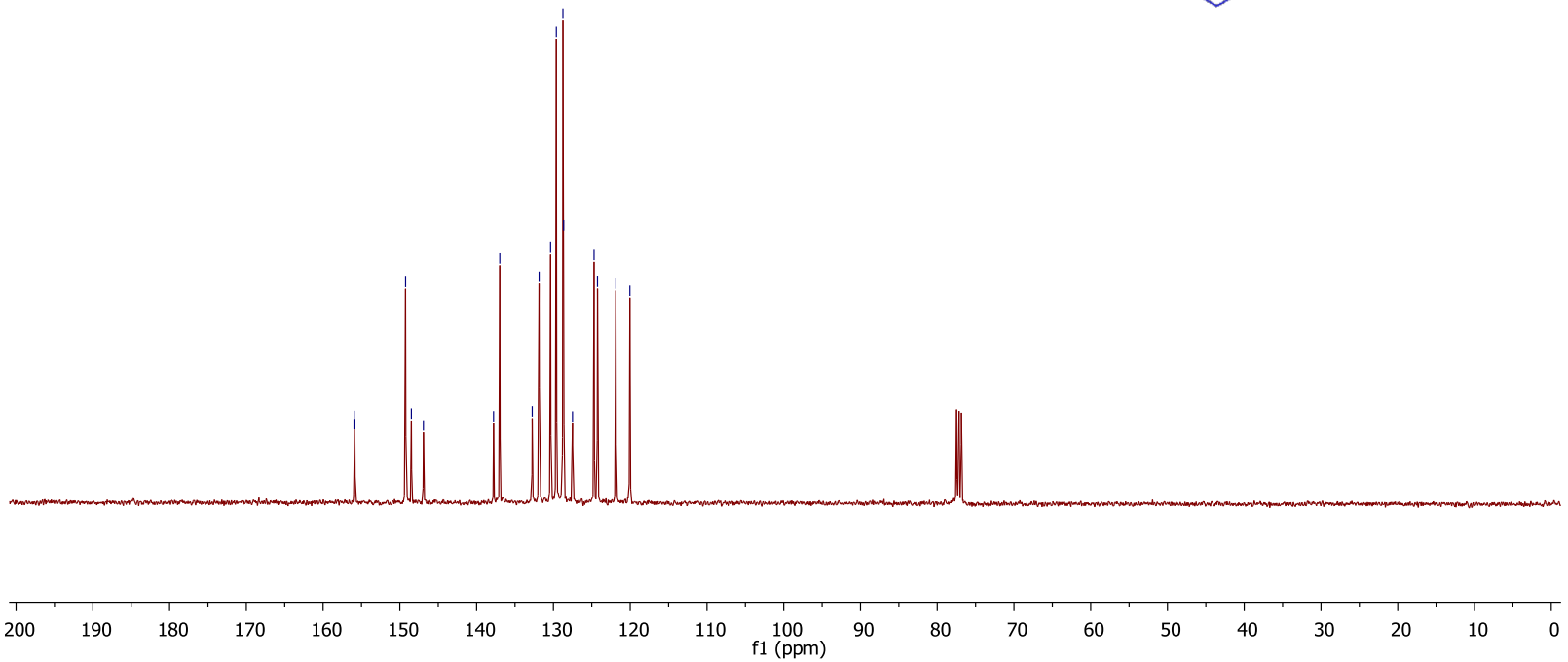
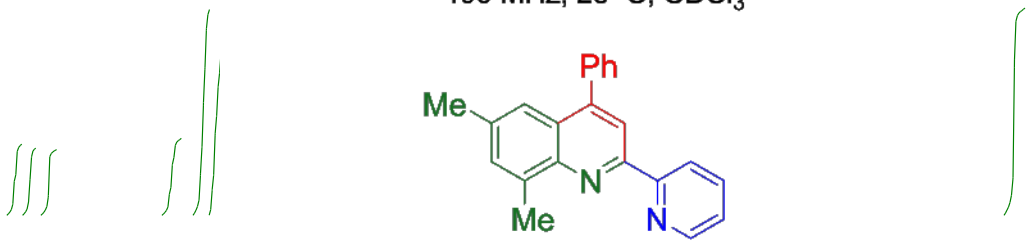


Table 3 - 1h

^{1}H NMR of 6,8-dimethyl-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$



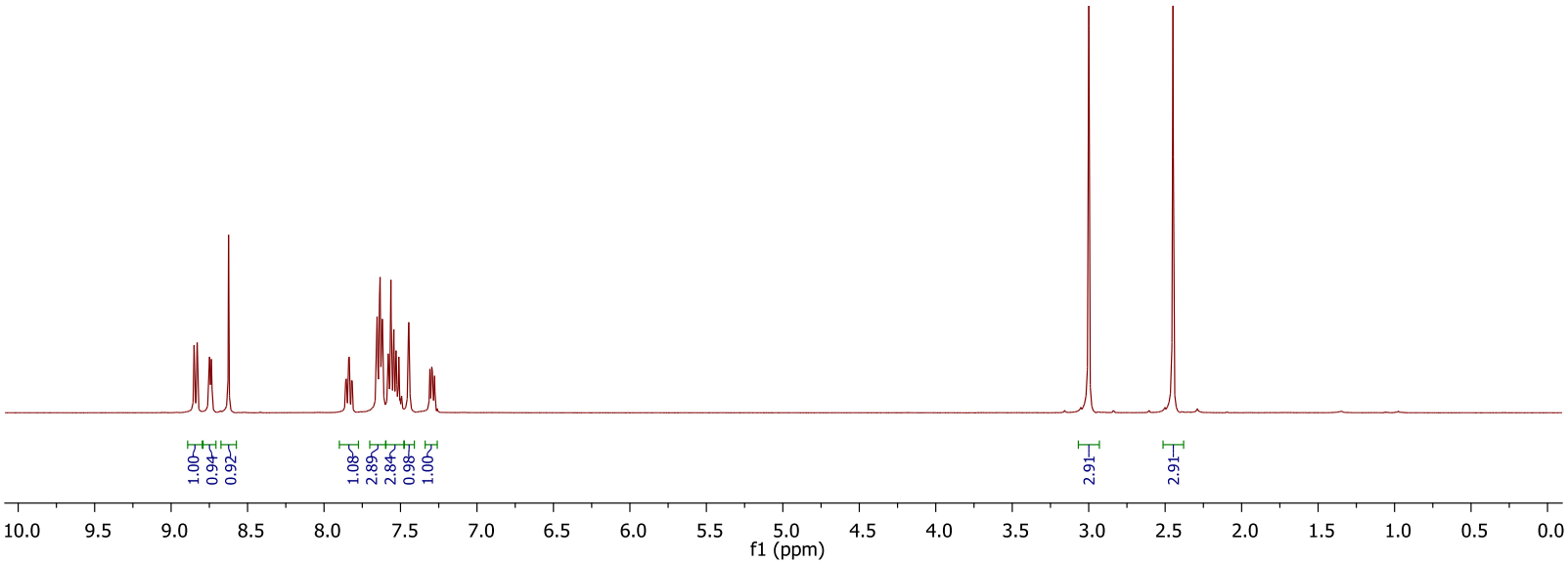


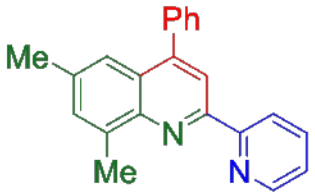
Table 3 - 1h

156.81
153.11
148.90
148.55
145.97
139.10
137.52
136.65
136.25
131.80
129.71
128.35
128.01
126.69
123.65
122.51
121.60
118.82

21.87
18.31

^{13}C NMR of 6,8-dimethyl-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



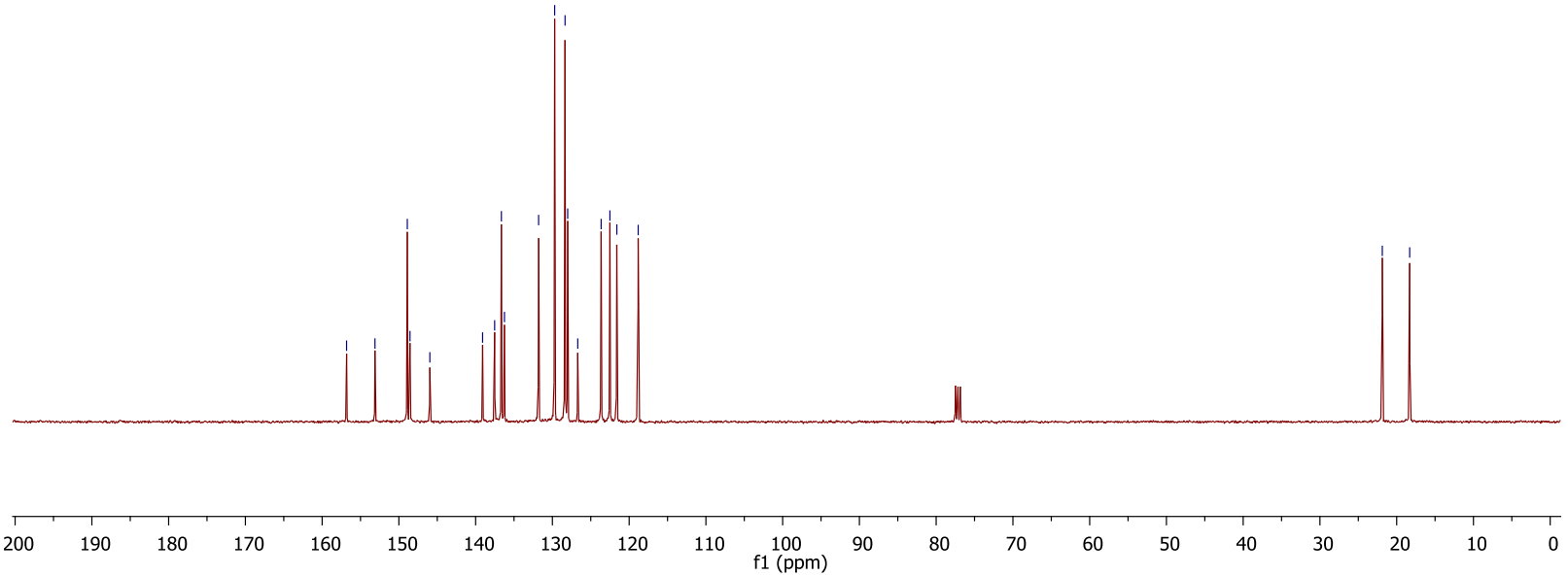


Table 3 - 1i

^{1}H NMR of 6-bromo-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$

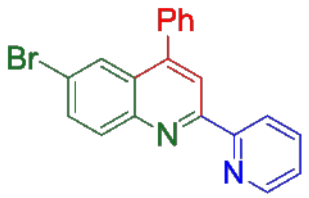
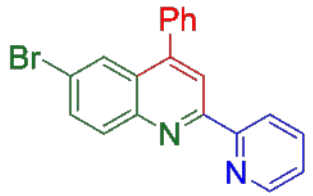


Table 3 - 1i

156.03
149.32
148.50
147.18
137.80
137.06
132.99
132.01
129.66
128.81
128.72
128.06
124.34
121.94
121.10
120.09

^{13}C NMR of 6-bromo-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 $^{\circ}C$, $CDCl_3$



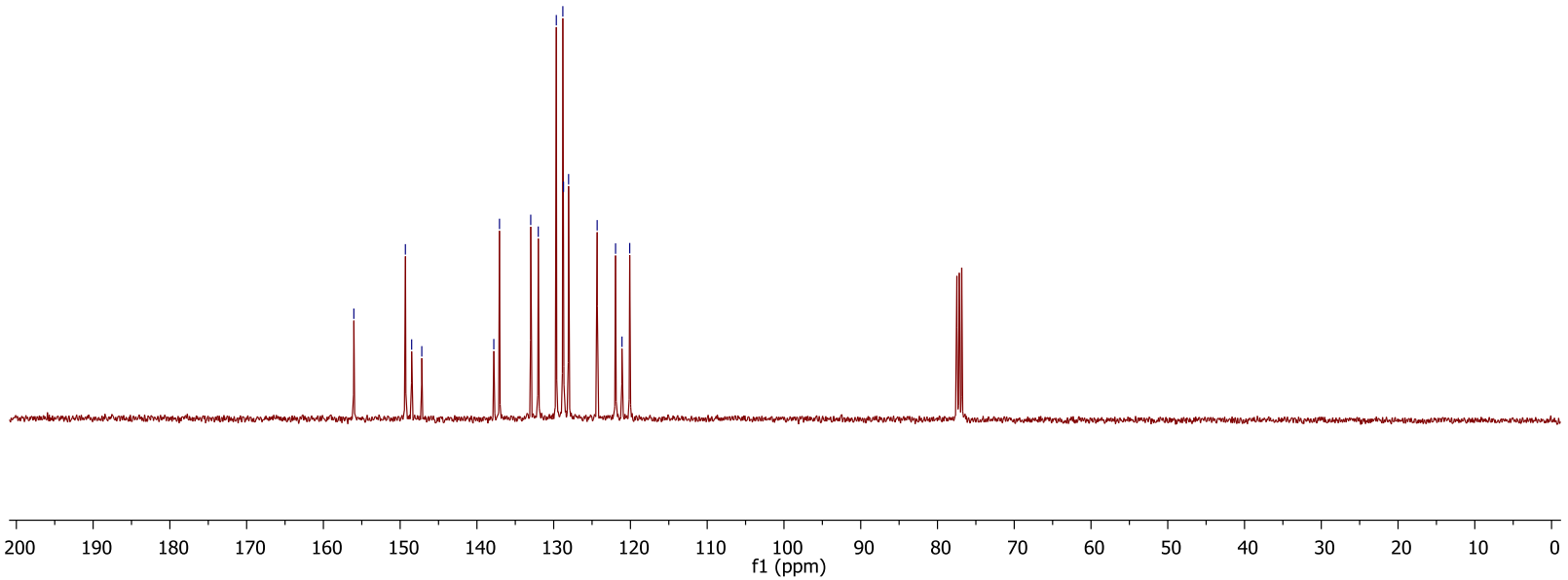
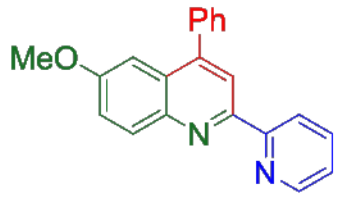


Table 3 - 1j

^{1}H NMR of 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$



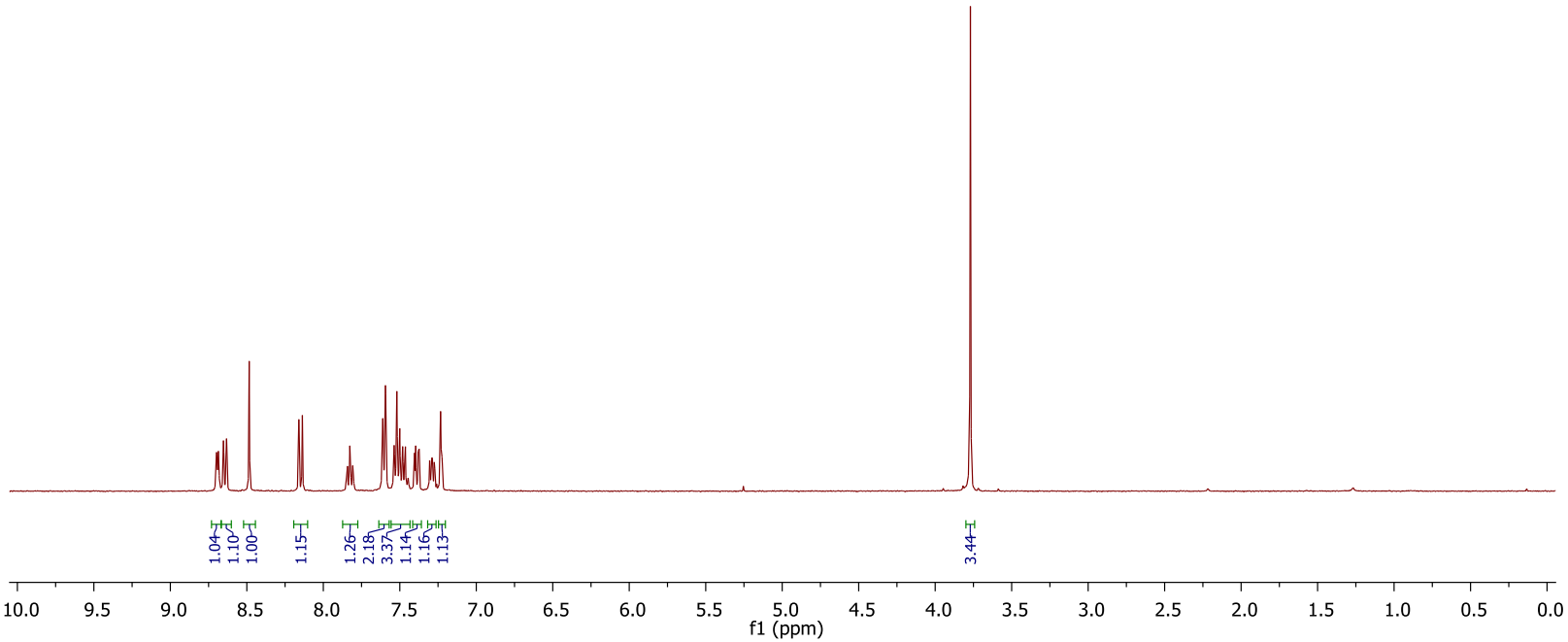
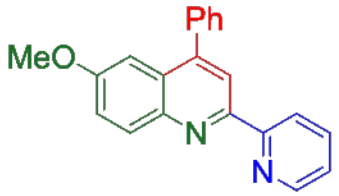


Table 3 - 1j

158.20
156.56
153.47
149.13
147.84
144.61
138.75
136.87
131.75
129.50
128.61
128.28
127.77
123.71
121.85
121.51
119.60
103.78
55.46

^{13}C NMR of 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



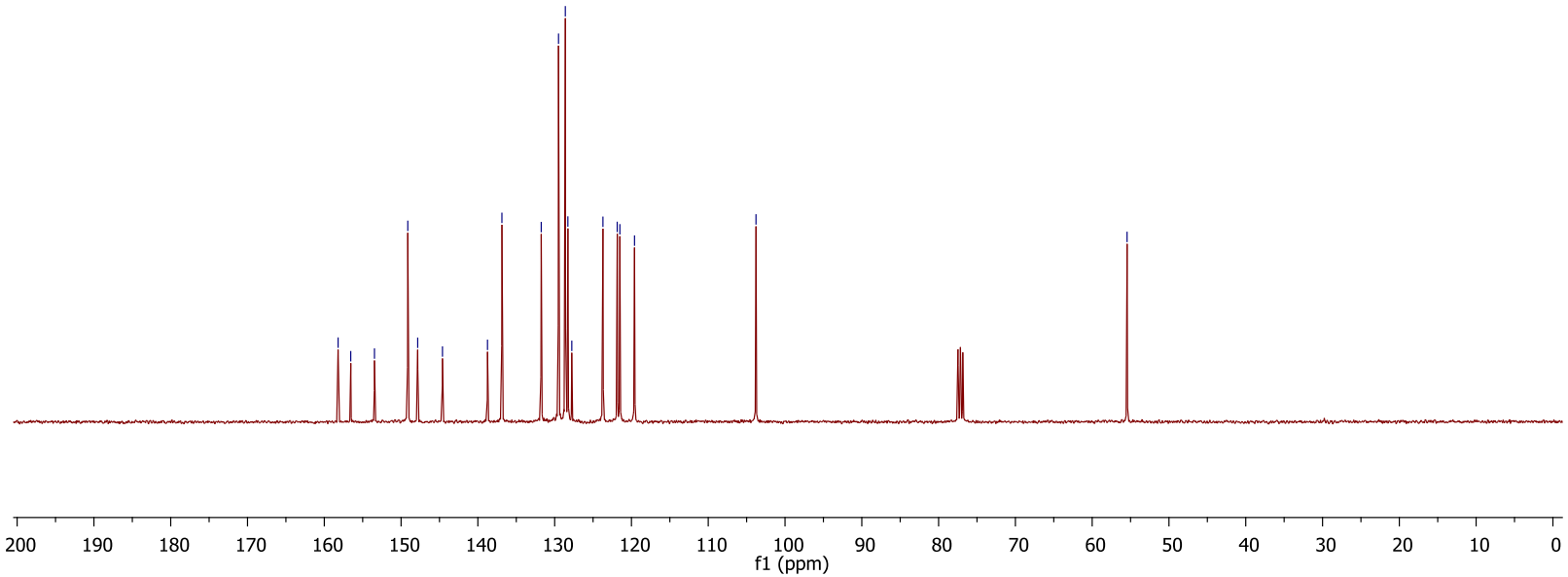
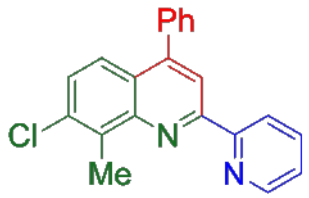


Table 3 - 1k

^{1}H NMR of 7-chloro-8-methyl-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$



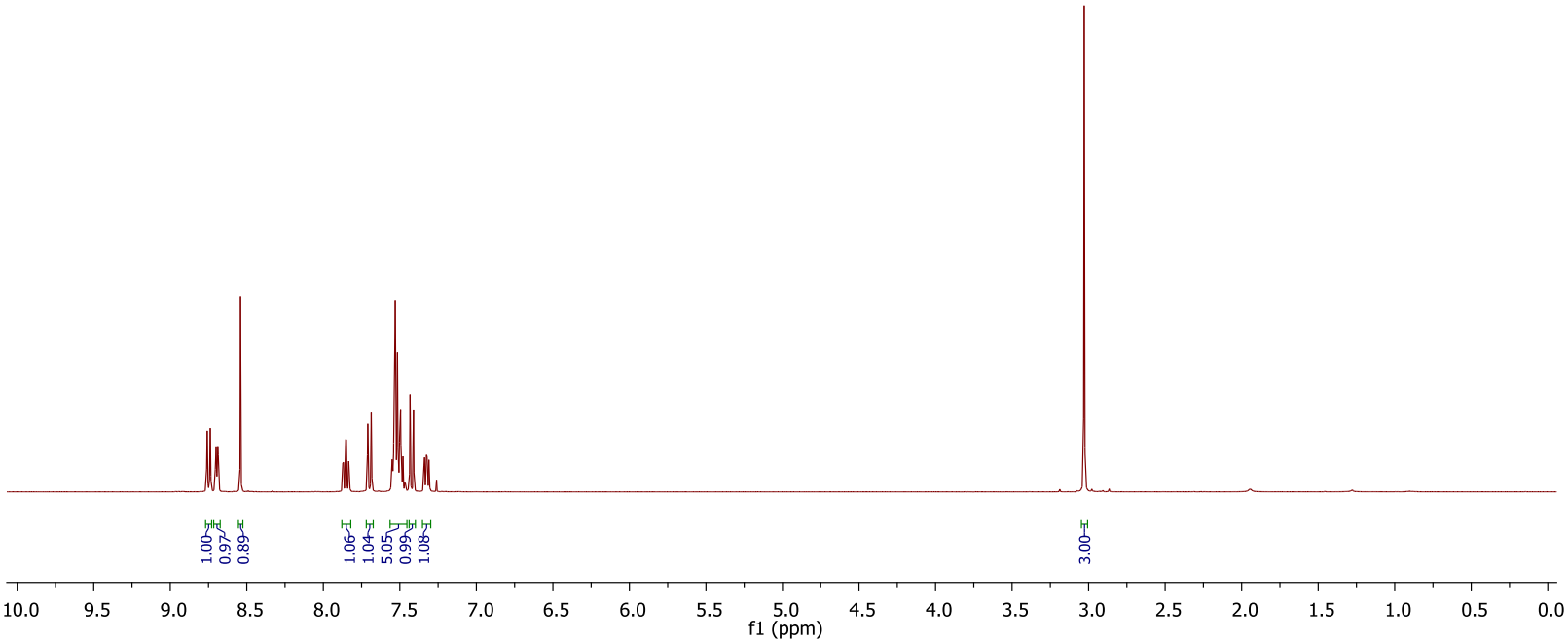
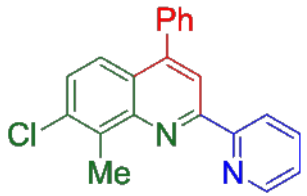


Table 3 - 1k

156.36
154.90
149.63
149.10
147.84
138.42
136.90
135.40
134.94
129.74
128.57
128.44
127.88
125.33
124.22
124.18
121.94
118.79
14.96

^{13}C NMR of 7-chloro-8-methyl-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



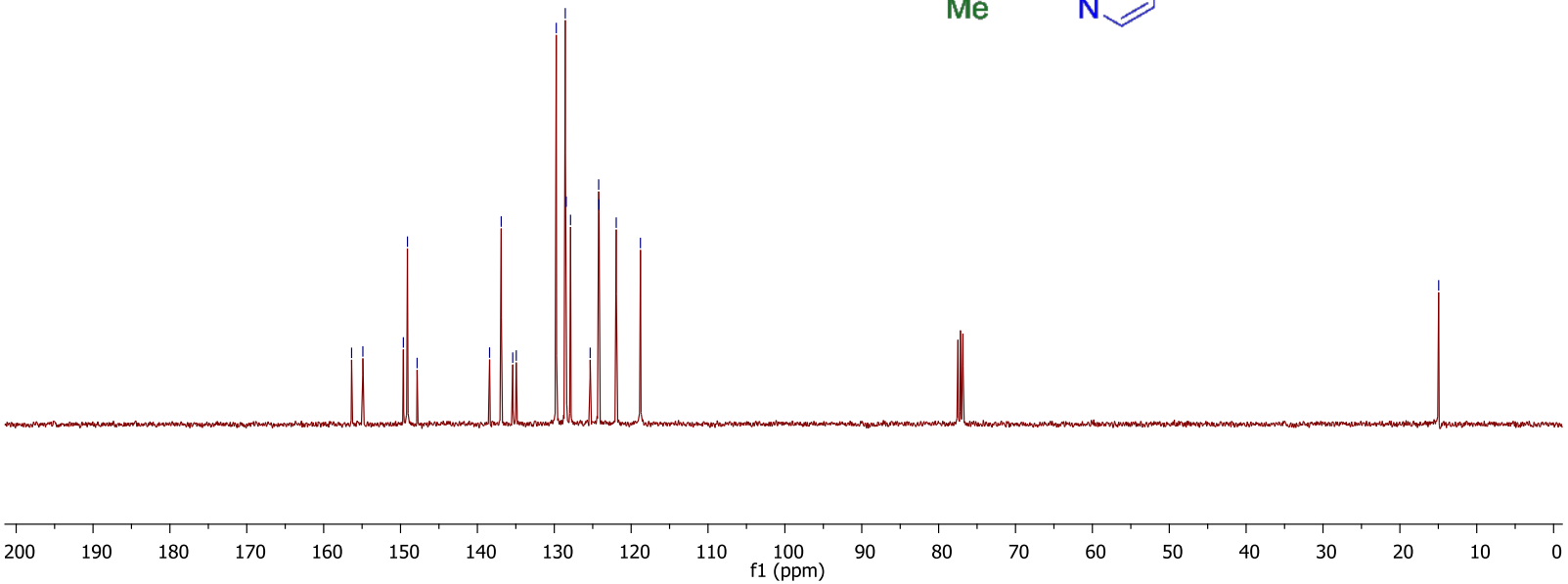


Table 3 - 1l

^{1}H NMR of 6-methyl-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$

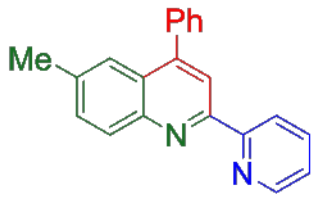
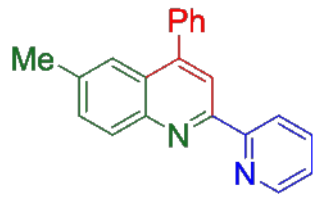


Table 3 - 1l

156.51
154.79
149.15
148.54
147.11
138.64
136.89
136.84
131.70
129.98
129.69
128.50
128.23
126.75
124.60
123.89
121.74
119.35
21.92

^{13}C NMR of 6-methyl-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



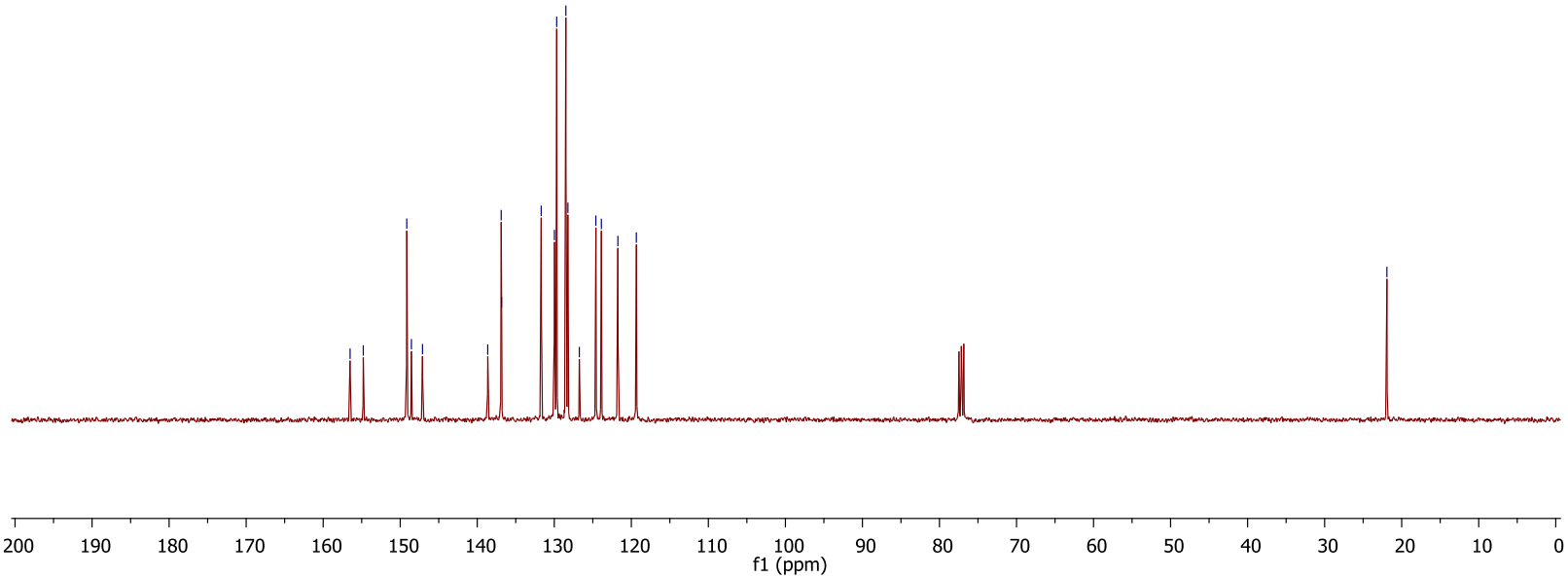


Table 3 - 1m

^{1}H NMR of 6,8-dichloro-4-phenyl-2-(2'pyridyl)quinoline
400 MHz, 25 °C, $CDCl_3$

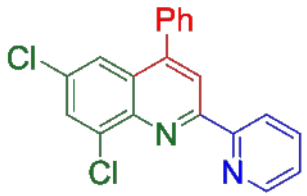
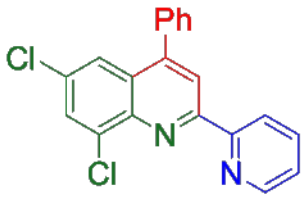


Table 3 - 1m

156.03
155.66
149.22
143.33
137.57
137.19
135.67
131.92
130.24
129.66
128.90
128.86
128.51
124.64
124.01
122.43
120.76

^{13}C NMR of 6,8-dichloro-4-phenyl-2-(2'pyridyl)quinoline
100 MHz, 25 °C, $CDCl_3$



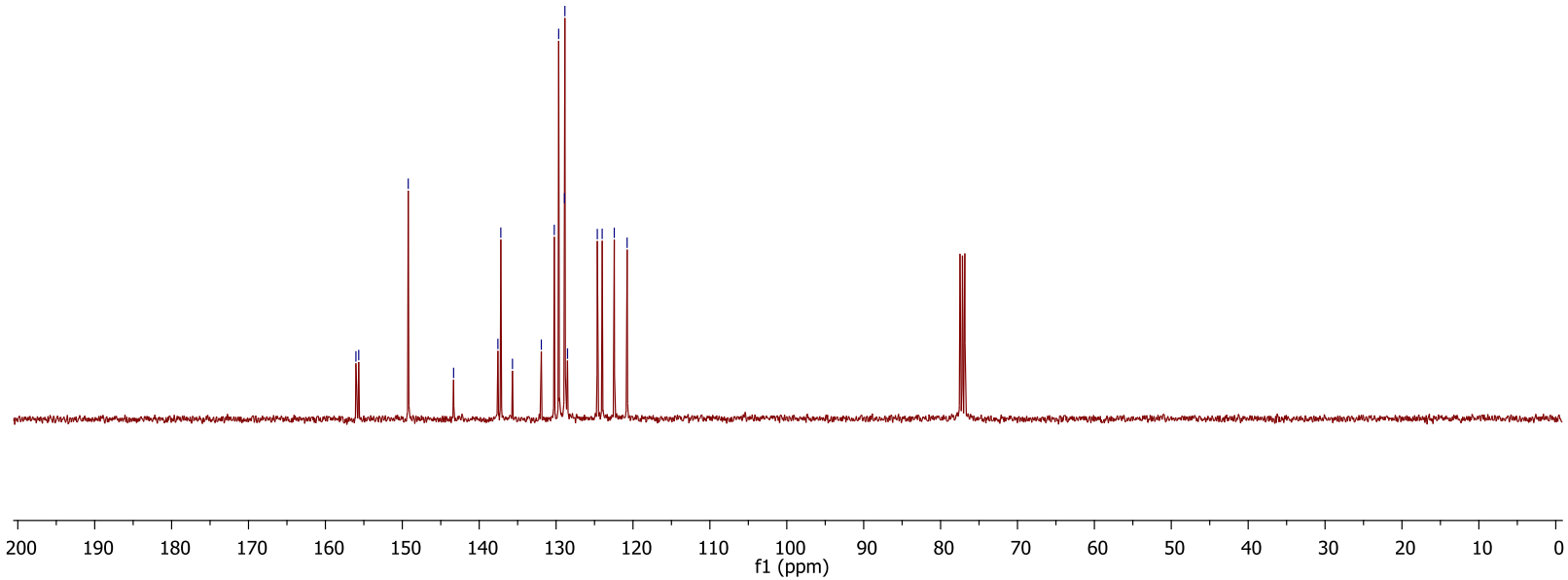


Table 3 - 1n

^{1}H NMR of 4-phenyl-2-(2'-pyridyl)-6-(trifluoromethyl)quinoline
400 MHz, 25 °C, $CDCl_3$

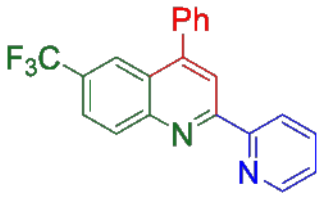
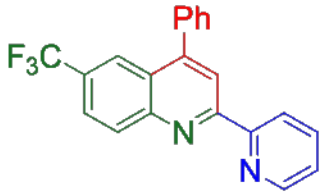


Table 3 - 1n

157.54
155.66
150.19
149.56
149.29
137.48
137.01
131.44
129.65
128.88
125.90
125.09
124.56
123.91
123.87
122.09
120.37

^{13}C NMR of 4-phenyl-2-(2'-pyridyl)-6-(trifluoromethyl)quinoline
100 MHz, 25 °C, $CDCl_3$



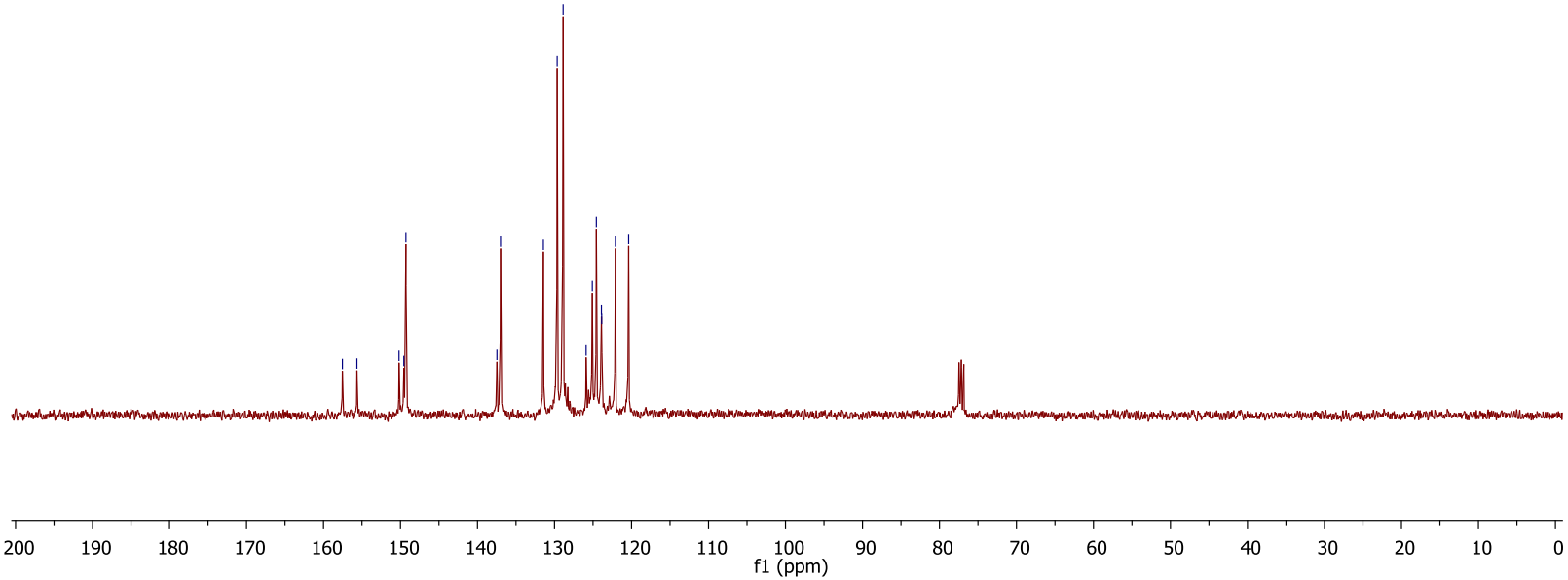


Table 3 - 1o

^{1}H NMR of 6-(methylthio)-4-phenyl-2-(2'-pyridyl)quinoline
400 MHz, 25 °C, $CDCl_3$

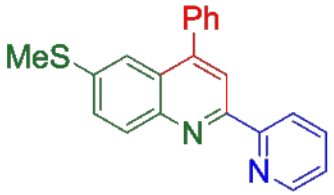
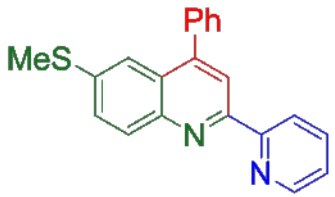


Table 3 - 1o

156.40
154.92
149.27
147.99
146.83
138.34
137.86
137.02
130.53
129.67
128.85
128.67
128.50
127.25
124.04
121.80
121.00
119.93
15.76

^{13}C NMR of 6-(methylthio)-4-phenyl-2-(2'-pyridyl)quinoline
100 MHz, 25 °C, $CDCl_3$



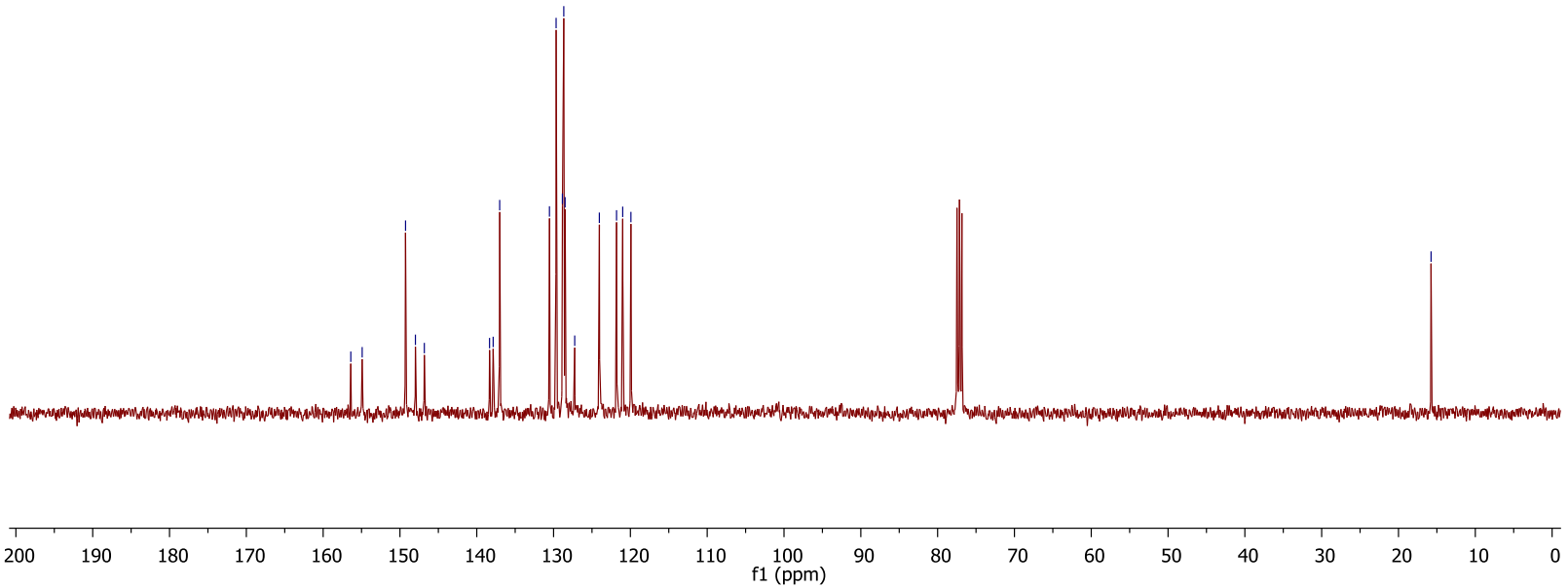


Table 3 - 1p

^{1}H NMR of 6-fluoro-4-phenyl-2-(2'-pyridyl)quinoline
400 MHz, 25 °C, $CDCl_3$

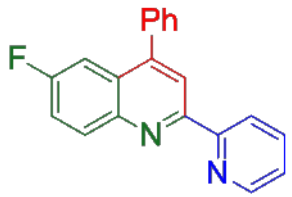
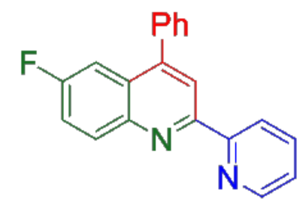


Table 3 - 1p

^{13}C NMR of 6-fluoro-4-phenyl-2-(2'-pyridyl)quinoline
100 MHz, 25 °C, $CDCl_3$



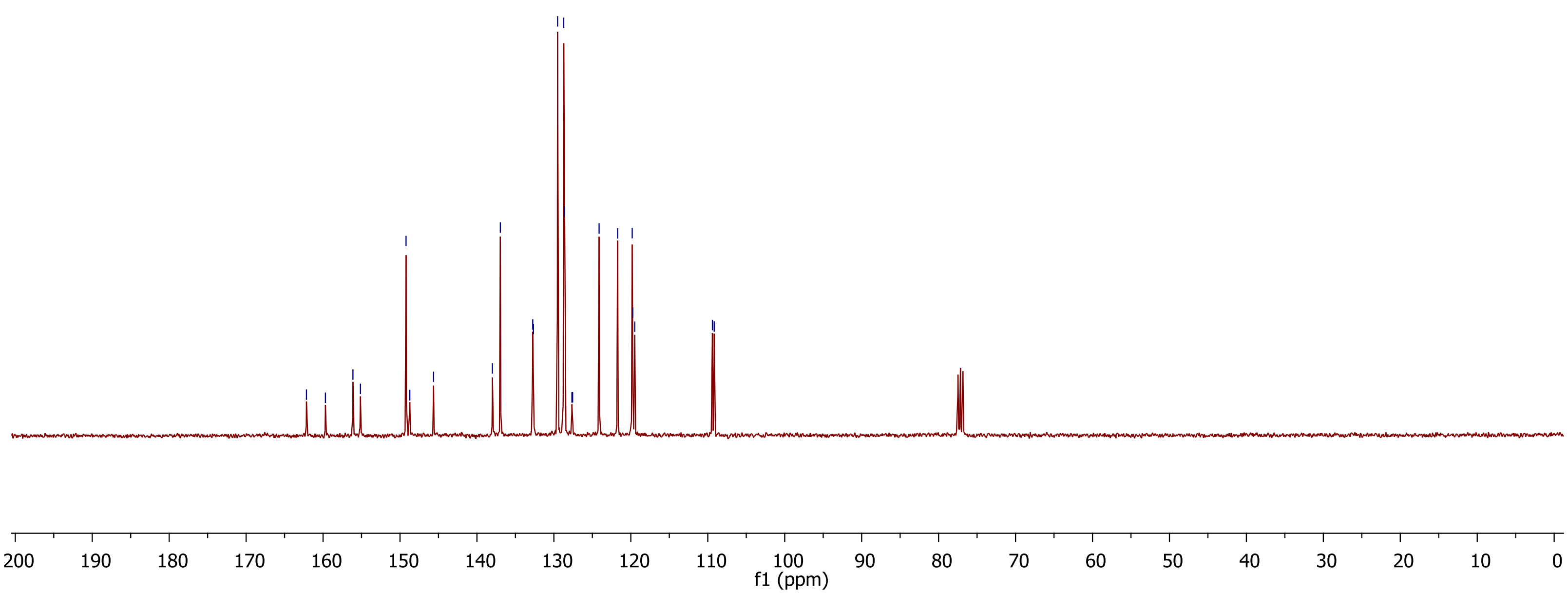


Table 3 - 1q

^{1}H NMR of 4,6-diphenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$

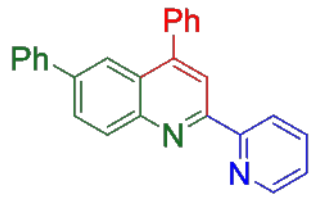
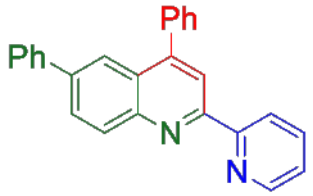


Table 3 - 1q

156.31
155.53
149.34
149.17
147.96
140.59
139.48
138.41
136.90
130.73
129.72
129.10
128.92
128.62
128.41
127.65
127.45
126.93
124.04
123.54
121.86
119.72

^{13}C NMR of 4,6-diphenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



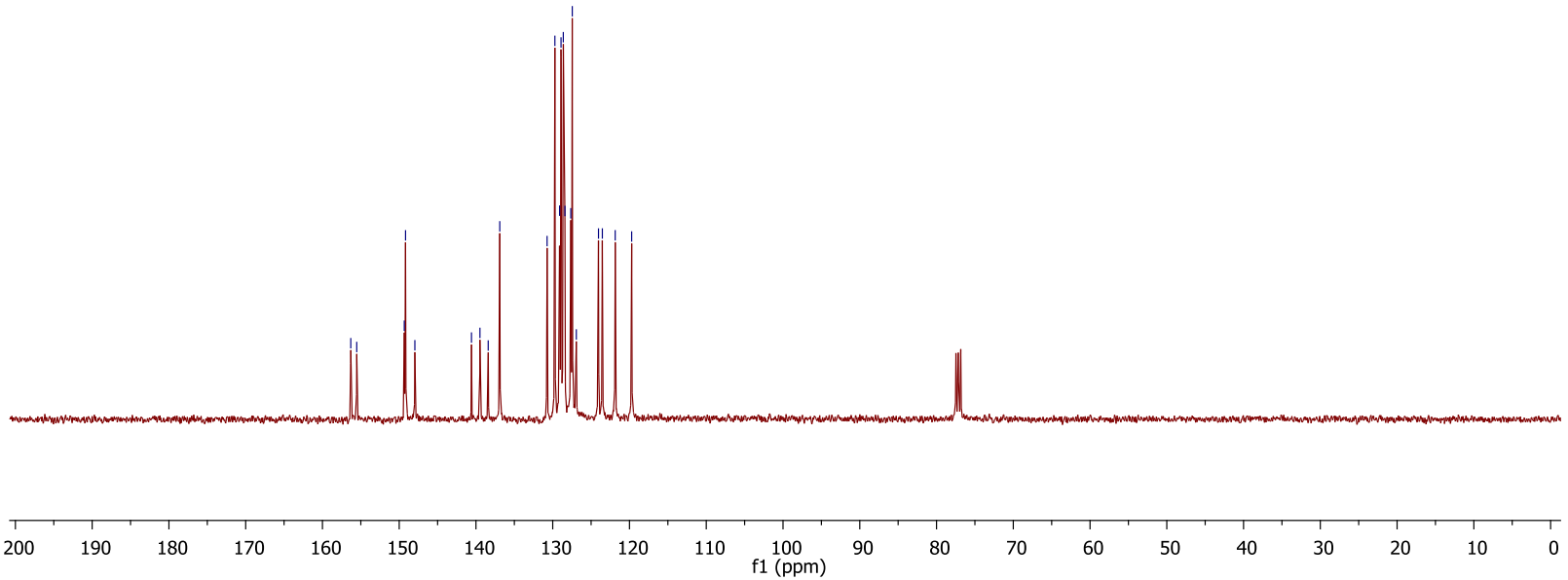


Table 3 - 1r

^{1}H NMR of 6-cyano-4-phenyl-2-(2'-pyridyl)quinoline

400 MHz, 25 °C, $CDCl_3$

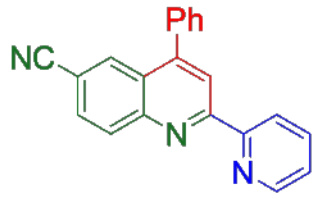
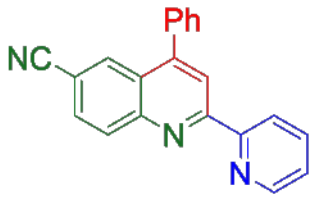


Table 3 - 1r

158.27
155.37
149.85
149.55
149.43
137.14
136.99
132.52
131.64
130.09
129.63
129.16
129.00
126.38
124.87
122.26
120.68
119.00
110.22

^{13}C NMR of 6-cyano-4-phenyl-2-(2'-pyridyl)quinoline

100 MHz, 25 °C, $CDCl_3$



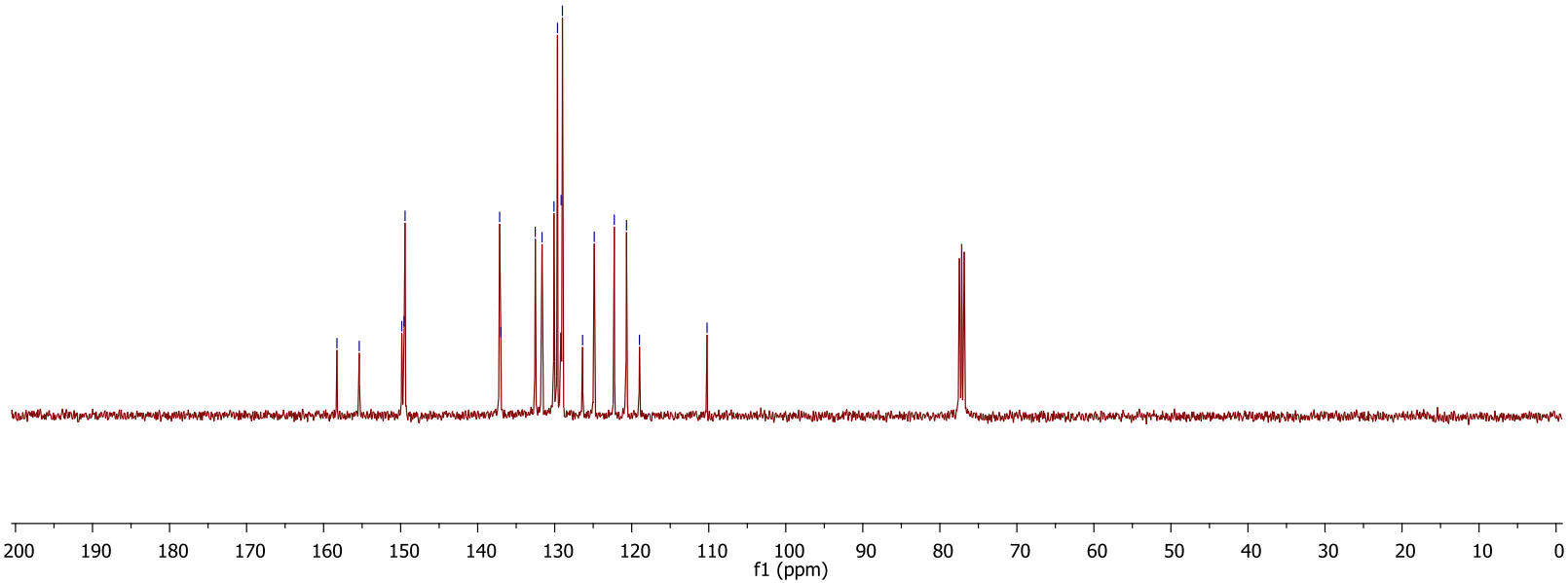
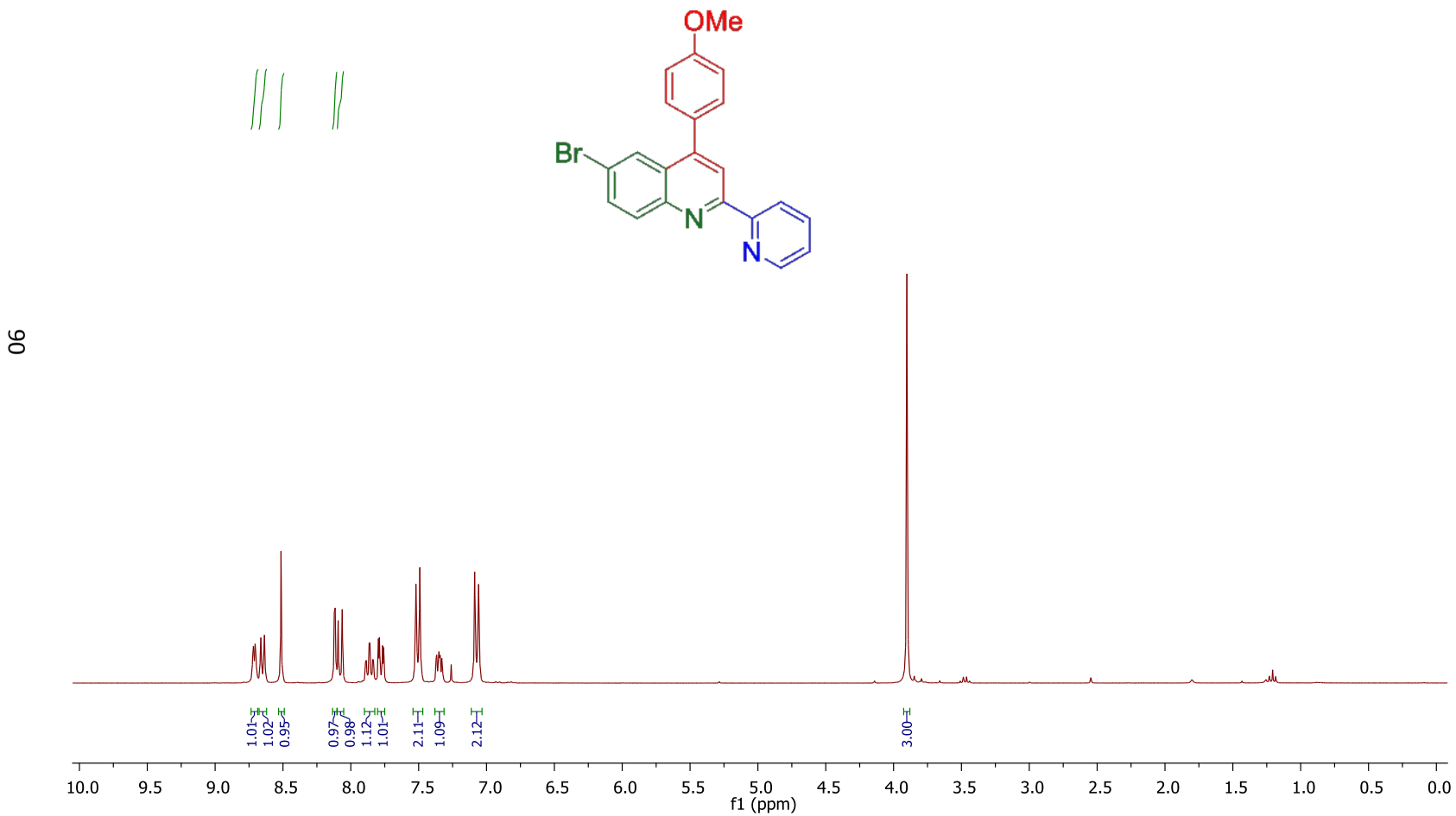


Figure 6

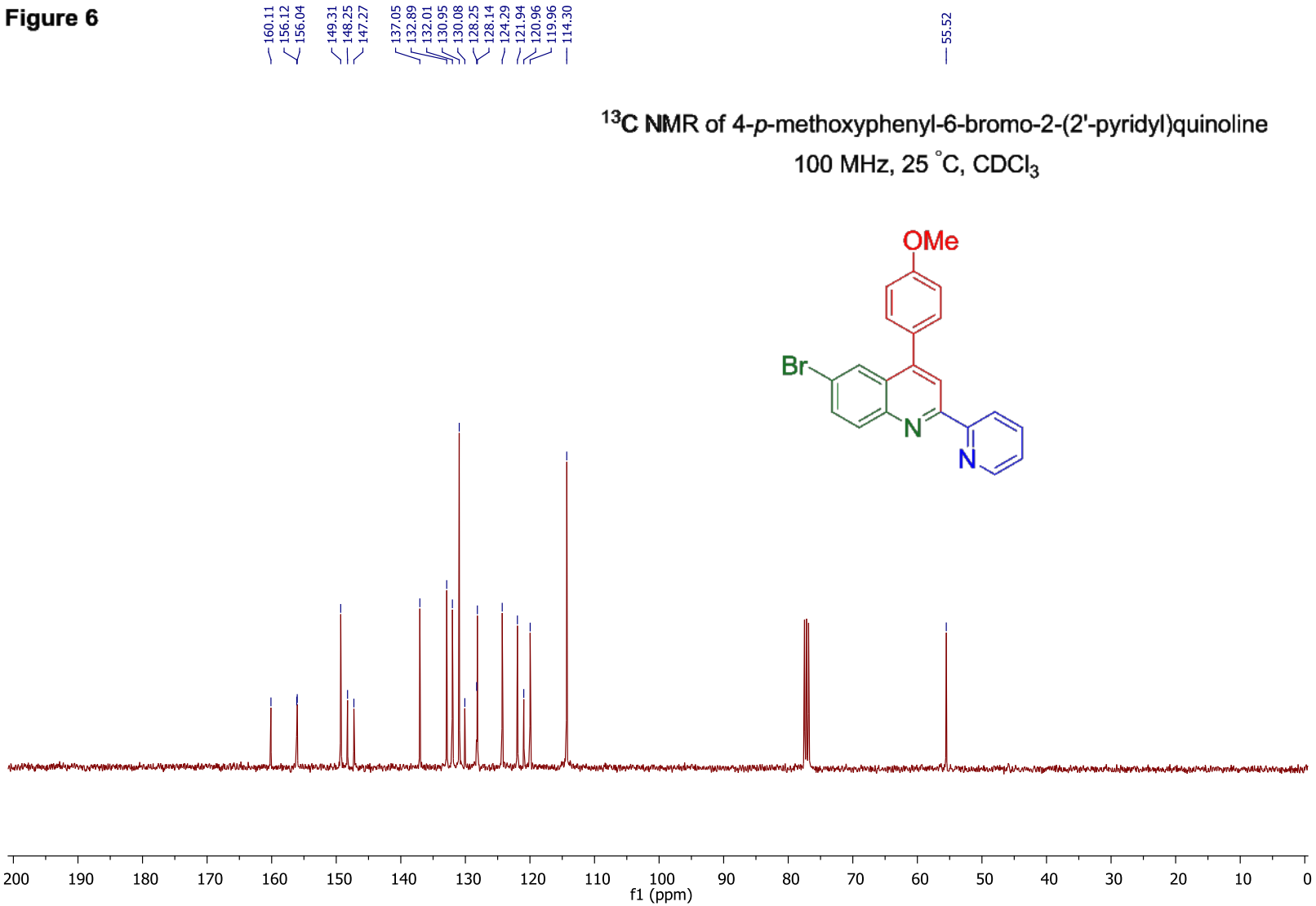
^{1}H NMR of 4-*p*-methoxyphenyl-6-bromo-2-(2'-pyridyl)quinoline

300 MHz, 25 °C, $CDCl_3$



90

Figure 6


160.11
156.12
156.04
149.31
148.25
147.27
137.05
132.89
132.01
130.95
130.08
128.25
128.14
124.29
121.94
120.96
119.96
114.30
55.52
^{13}C NMR of 4-*p*-methoxyphenyl-6-bromo-2-(2'-pyridyl)quinoline
100 MHz, 25 °C, $CDCl_3$
OMe
Br
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

PART II: EXPERIMENTAL PROCEDURES & PRODUCT CHARACTERIZATIONS

General reagent information

All reactions were set up on the benchtop in oven-dried screw-cap glass vials with dried magnetic stirrers and carried out under an air atmosphere. Sodium tetrachloroaurate(III) dihydrate was purchased from Sigma Aldrich, and silver tetrafluoroborate was purchased from Strem Chemicals. Both metal salts were stored in a glovebox under a nitrogen atmosphere and used as supplied. Anhydrous acetonitrile, packaged under argon, was purchased from Alfa Aesar in a Chem-Seal bottle. Celite 545 was purchased from Acros Organics. Submicron-filtered methylene chloride was purchased from Fisher Scientific and used as supplied. The dimethyl sulfoxide and toluene solvents were both purchased from EMD Millipore and used as supplied. The pyridine reagent was purchased from EMD Millipore and freshly distilled before use. Benzyl alcohol was purchased from Alfa Aesar and was freshly distilled before use. The benzylamine reagent was purchased from TCI America and was also freshly distilled before use.

General analytical information

^{1}H NMR spectra were measured on a Varian Inova 400 (400 MHz) spectrometer using either $CDCl_3$ or DMSO-D_6 as a solvent at room temperature. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s - singlet, d - doublet, t - triplet, q - quartet, m - multiplet, and br - broad. NMR spectra were acquired at 300 K. IR spectra were recorded on a Spectrum One FT-IR Spectrometer with a universal ATR sampling accessory. Attenuated total reflection infrared (ATR-IR) was used for analysis with selected absorption maxima reported in

wavenumbers (cm^{-1}). No sample preparation was necessary for ATR analysis. ATR-IR is based on the propagation of the infrared radiation through an internal reflection element (crystal) with a high refractive index and its reflection at the interface between the crystal and the solid material. Mass spectroscopic data was collected on an Agilent LCTOF (2006) which utilizes a high resolution TOF analyzer with Windows XP based OS and APCI/ESI ionization. Samples were prepared in acetonitrile and analyzed using positive ionization. UV-Vis spectra were recorded on a Varian Cary 50 Bio UV-Vis spectrophotometer using 1.0 cm quartz cuvettes and elemental analyses were completed by Atlantic Microlab Inc., Norcross, GA. X-ray analyses were completed at the crystallography facility located at the University of California, San Diego.

General procedure for synthesis of 5-coordinate gold(III) complexes (0.6 mmol scale)

A 2-(2'-pyridyl)quinoline ligand (1 equiv.) is added to a dry 100-mL round-bottom flask charged with a dry magnetic stir bar. Anhydrous acetonitrile (10 mL) is added to the flask and stirred to dissolve the ligand. Sodium tetrachloroaurate(III) dihydrate (1 equiv.) and anhydrous acetonitrile (10 mL) is added, and the mixture is heated to reflux in a 90 °C oil bath under air. After refluxing for 2 hours, a solution of silver tetrafluoroborate in anhydrous acetonitrile (10 mL) is added and rinsed down with a small amount of acetonitrile. The reaction was then left to reflux overnight. The cooled reaction was gravity filtered through celite. Additional filtrations through celite with acetonitrile were usually necessary for removing the silver solids completely. X-ray quality crystals form overnight in its respective selected solvent.

General procedure for synthesis of cationic gold(III) complex (0.35 mmol scale)

The 2-(2'-pyridyl)quinoline ligand (1 equiv.) was added to a dry 100-mL round-bottom flask charged with a dry magnetic stir bar. Anhydrous acetonitrile (10 mL) was then added to the flask and stirred to dissolve the ligand. Sodium tetrachloroaurate(III) dihydrate (1 equiv.) and anhydrous acetonitrile (10 mL) is added, and the mixture is heated to reflux in a 90 °C oil bath under air. After refluxing for 2 hours, a solution of silver tetrafluoroborate (2 equiv.) in anhydrous acetonitrile (10 mL) is added and rinsed down with a small amount of acetonitrile. The reaction was then left to reflux overnight. The cooled reaction was gravity filtered through celite. The solvent was removed *in vacuo*, and the solid washed twice in methylene chloride and water. The organic layer was filtered through celite to remove any remaining solids. The deep red solution was allowed to recrystallize on the benchtop for 48 h.

General procedures for uv-vis and ligand exchange studies

Uv-vis analyses of complexes **2a-2e** were initiated by the preparation of 6.00 mM stock solutions of the complexes in dimethylsulfoxide and diluting to a final concentration of 0.03 mM using acetonitrile (final volume of solution = 3 mL). Ligand exchange studies involved preparing a 6.00 mM stock solution of the ligand being investigated (benzylamine, pyridine, or benzyl alcohol) in acetonitrile. Separate sample solutions were prepared by introducing incrementally larger amounts of the ligand stock solution to a fixed concentration of complex to investigate at what concentration of ligand (0.001 mM, 0.01 mM, 0.015 mM, etc.) would exchange occur. The change in the absorption maxima at 355 nm upon increasing concentrations of ligand was used to determine the

binding constant as previously described in the literature.[3e,13] Additionally, the Stern-Volmer equation was used to determine the quenching constant (K_{sv}), quenching rate constant (K_q), and the number of binding sites (K_b) as described in published reports.[3e]

6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$ (**2a**)

6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline (105 mg**,** 0.34 mmol) and sodium tetrachloroaurate(III) dihydrate (135 mg, 0.34 mmol) were dissolved in acetonitrile (10 mL, 0.034 M) and stirred under reflux at 90˚C for 2h followed by the addition of silver tetrafluoroborate (66 mg, 0.34 mmol). Mixture was stirred overnight under reflux at 90˚C (0.02 M) and then filtered through a celite plug. The filtrate was left on the benchtop overnight at room temperature which allowed for the crystallization of the title complex as orange crystals in 60% yield (0.125 g, 0.20 mmol). Anal. Calcd. for $C_{21}H_{17}N_2OAuCl_3$: C, 40.97; H, 2.62. Found: C, 41.20; H, 2.62. IR (crystal) 3047, 2836, 1601, 1486, 1225, 776, 710 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{17}N_2OCl_3Au$ requires 615.0067, found 615.0084. ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C) δ 9.13 (d, *J* = 5.9 Hz, 1H), 8.81 (d, *J* = 9.2 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 8.21 – 8.15 (m, 1H), 7.96 (s, 1H), 7.74 – 7.70 (m, 1H), 7.67 – 7.50 (m, 6H), 7.24 (d, *J* = 2.7 Hz, 1H), 3.85 (s, 3H).

6-methyl-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$ (**2b**)

6-methyl-4-phenyl-2-(2'-pyridyl)quinoline (202 mg, 0.68 mmol) and sodium tetrachloroaurate(III) dihydrate (271 mg, 0.68 mmol) were dissolved in acetonitrile (20 mL, 0.034 M) and stirred under reflux at 90˚C for 2h followed by the addition of silver

tetrafluoroborate (132 mg, 0.68 mmol). Mixture was stirred overnight under reflux at 90˚C (0.02 M) and then filtered through a celite plug. The filtrate was left on the benchtop overnight at room temperature which allowed for the crystallization of the title complex as reddish-orange crystals in 72% yield (0.294 g, 0.49 mmol). Anal. Calcd. for $C_{21}H_{17}N_2AuCl_3$: C, 42.06%; H, 2.69%. Found: C, 41.90%; H, 2.66%. IR (crystal) 3040, 1571, 1488, 762, 700 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{17}N_2Cl_3Au$ requires 599.0118, found 599.0129. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 9.15 (d, *J* = 5.6 Hz, 1H), 8.85 (d, *J* = 8.7 Hz, 1H), 8.35 (d, *J* = 7.9 Hz, 1H), 8.21 – 8.15 (m, 1H), 7.98 (s, 1H), 7.80 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.74 (t, *J* = 6.6 Hz, 2H), 7.65 – 7.51 (m, 5H), 2.54 (s, 3H).

4,6-diphenyl-2-(2'-pyridyl)quinoline-$AuCl_3$ (**2c**)

4,6-diphenyl-2-(2'-pyridyl)quinoline (240 mg, 0.67 mmol) and sodium tetrachloroaurate(III) dihydrate (267 mg, 0.67 mmol) were dissolved in acetonitrile (20 mL, 0.034 M) and stirred under reflux at 90˚C for 2h followed by the addition of silver tetrafluoroborate (130 mg, 0.67 mmol). Mixture was stirred overnight under reflux at 90˚C (0.02 M) and then filtered through a celite plug. The filtrate was left on the benchtop overnight at room temperature which allowed for the crystallization of the title complex as orange crystals in 43% yield (0.189 g, 0.29 mmol). Anal. Calcd. for $C_{26}H_{19}N_2AuCl_3$: C, 47.19; H, 2.74. Found: C, 47.04; H, 2.74. IR (crystal) 3046, 1482, 1433, 842, 760, 694 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{26}H_{19}N_2Cl_3Au$ requires 661.0274, found 661.0295. ^1H NMR (400 MHz, $CDCl_3$, 25˚C) δ 9.17 (d, *J* = 5.6 Hz, 1H), 8.97 (d, *J* = 8.8 Hz, 1H), 8.40 (d, *J* = 7.9 Hz, 1H), 8.26 – 8.18 (m, 2H), 8.16 (d, *J* = 1.9

Hz, 1H), 8.03 (s, 1H), 7.80 – 7.74 (m, 1H), 7.71 – 7.54 (m, 6H), 7.49 (dd, *J* = 14.7, 7.6 Hz, 2H), 7.45 – 7.37 (m, 2H).

6-fluoro-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$ (**2d**)

6-fluoro-2-(2'-pyridyl)quinoline (100 mg, 0.33 mmol) and sodium tetrachloroaurate(III) dihydrate (131 mg, 0.33 mmol) were dissolved in acetonitrile (20 mL, 0.034 M) and stirred under reflux at 90˚C for 2h followed by the addition of silver tetrafluoroborate (64 mg, 0.33 mmol). Mixture was stirred overnight under reflux at 90˚C (0.02 M) and then filtered through a celite plug. The filtrate was removed *in vacuo* and the resulting solid dissolved in toluene. X-ray quality crystals formed overnight to afford the title complex as red-orange crystals in 57% yield (0.114 g, 0.19 mmol). Anal. Calcd. for $C_{20}H_{13}N_2FAuCl_3$: C, 39.79; H, 2.17. Found: C, 39.77; H, 2.20. IR (crystal) 3037, 1574, 1486, 783, 758, 700 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{20}H_{14}N_2FAuCl_3$ requires 602.9867, found 602.9881. ^1H NMR (400 MHz, $CDCl_3$, 25°C) δ 9.16 (d, *J* = 5.8 Hz, 1H), 8.83 (dd, *J* = 9.3, 5.4 Hz, 1H), 8.41 (d, *J* = 7.2 Hz, 1H), 8.31 – 8.20 (m, 1H), 8.01 (s, 1H), 7.85 – 7.75 (m, 1H), 7.75 – 7.66 (m, 1H), 7.66 – 7.47 (m, 6H).

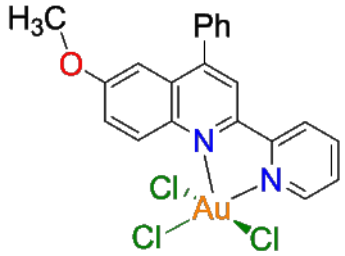
[6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_2$]BF_4 (**2e**)

6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline (110 mg, 0.35 mmol) and sodium tetrachloroaurate(III) dihydrate (139 mg, 0.35 mmol) were dissolved in acetonitrile (20 mL, 0.018 M) and stirred under reflux at 90˚C for 2h followed by the addition of silver tetrafluoroborate (136 mg, 0.7 mmol). Mixture was stirred overnight under reflux at 90˚C

(0.012 M) and then filtered through a celite plug. The filtrate was stripped of its solvent under reduced pressure. The crude material was extracted 2 times using methylene chloride and DI water and the combined organic methylene chloride layers filtered through celite once more. The filtrate was left on the benchtop overnight at room temperature which allowed for the crystallization of the title complex as black crystals (deep red crystals under flashlight) in 6% yield (0.024 g, 0.036 mmol). Anal. Calcd. for $C_{21}H_{17}N_2OAuCl_2BF_4$: C, 35.14; H, 2.41. Found: C, 35.87; H, 2.35. IR (crystal) 3087, 2840, 1600, 1489, 1250, 1234, 1048, 1032, 778, 699 cm^{-1}. HRMS (ESI) *m/z* calcd for $[M+H]^+$ $C_{21}H_{17}N_2OAuCl_2BF_4$ requires 579.0305, found 579.0325. ^1H NMR (400 MHz, DMSO-D_6, 25°C) δ 8.77 (d, *J* = 4.5 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.46 (s, 1H), 8.19 (d, *J* = 9.2 Hz, 1H), 8.17 – 8.12 (m, 1H), 7.73 – 7.52 (m, 7H), 7.25 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 3H).

Table 1 - 2a

^{1}H NMR of 6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline-$AuCl_3$
400 MHz, 25 °C, $CDCl_3$



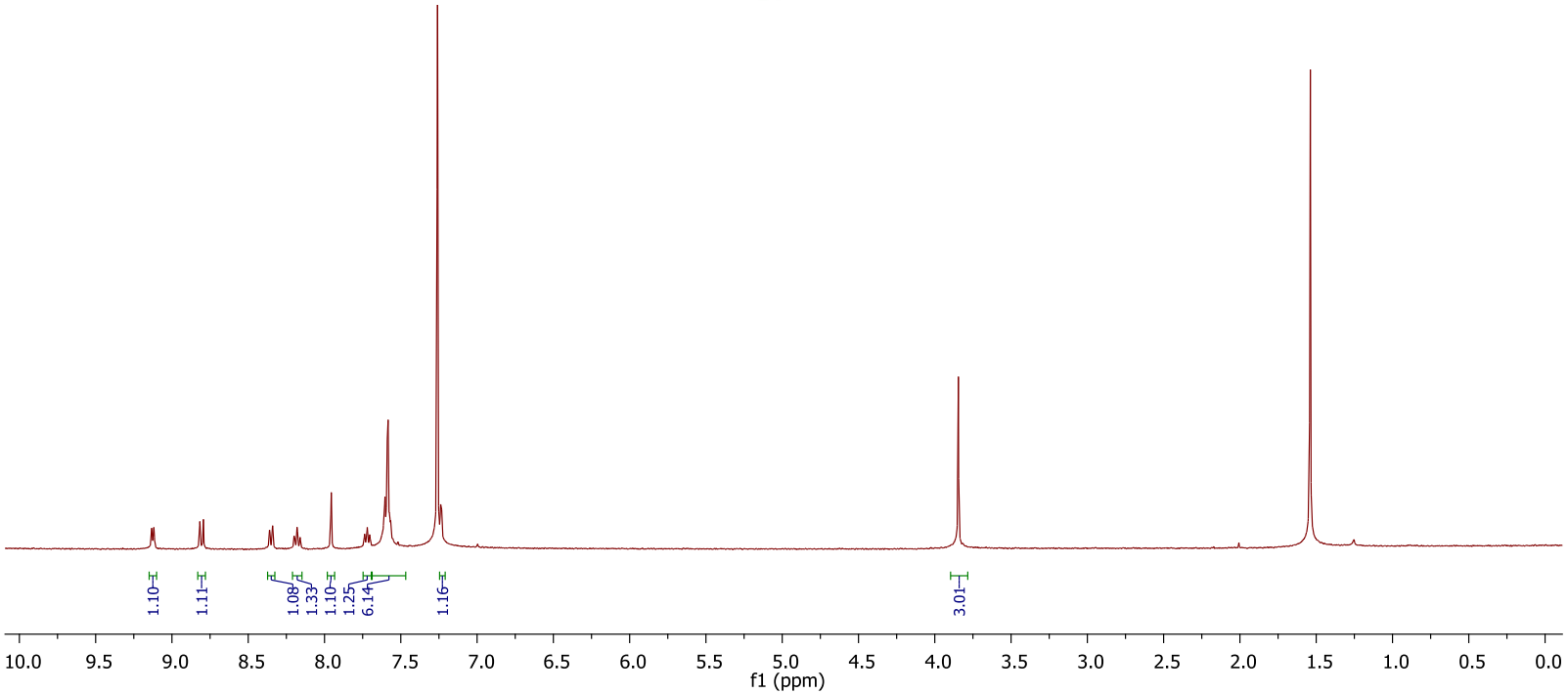


Table 1 - 2b

^{1}H NMR of 6-methyl-4-phenyl-2-(2'-pyridyl)quinoline-AuCl$_3$
400 MHz, 25 °C, CDCl$_3$

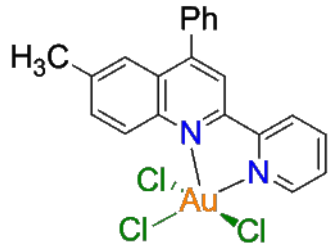


Table 1 - 2c

^{1}H NMR of 4,6-diphenyl-2-(2'-pyridyl)quinoline-$AuCl_3$
400 MHz, 25 °C, $CDCl_3$

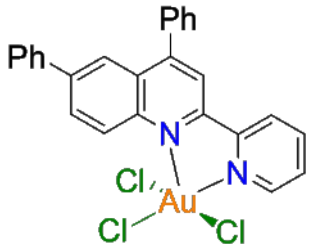


Table 1 - 2d

^{1}H NMR of 6-fluoro-2-(2'-pyridyl)quinoline-$AuCl_3$
400 MHz, 25 °C, $CDCl_3$

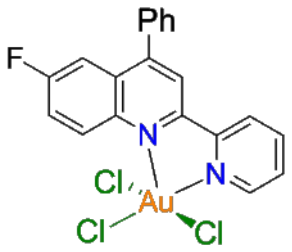


Table 1 - 2e

^{1}H NMR of [6-methoxy-4-phenyl-2-(2'-pyridyl)quinoline-AuCl$_2$]BF$_4$
400 MHz, 25 °C, DMSO-D$_6$

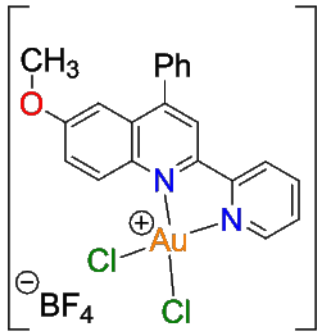
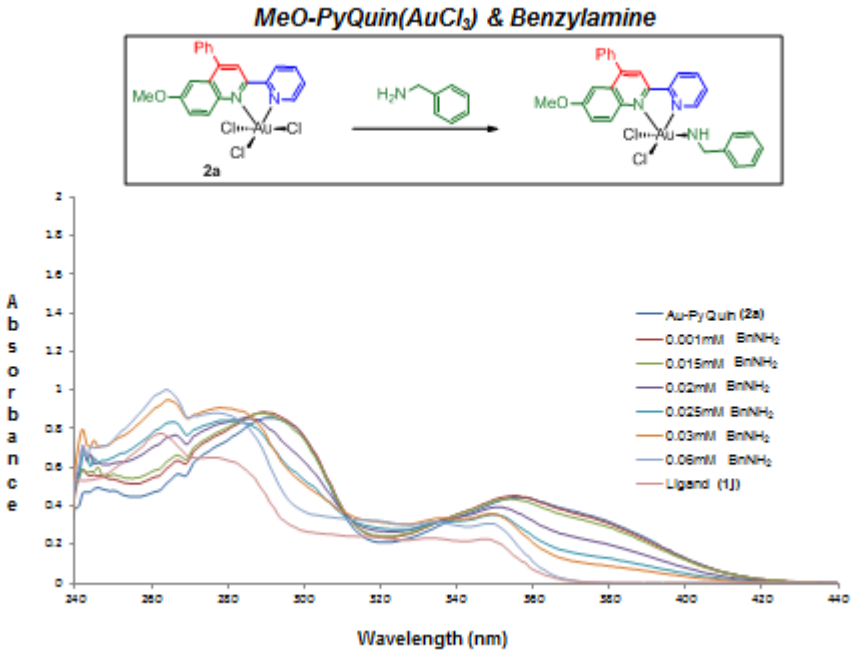


Table 3 - 2a


MeO-PyQuin(AuCl3) & Benzylamine
Ph
MeO
N
N
Cl
Au
Cl
Cl
2a
H2N
Ph
MeO
N
N
Cl
Au
NH
Cl
Absorbance
Au-PyQuin (2a)
0.001mM BnNH2
0.015mM BnNH2
0.02mM BnNH2
0.025mM BnNH2
0.03mM BnNH2
0.06mM BnNH2
Ligand (1j)
Wavelength (nm)

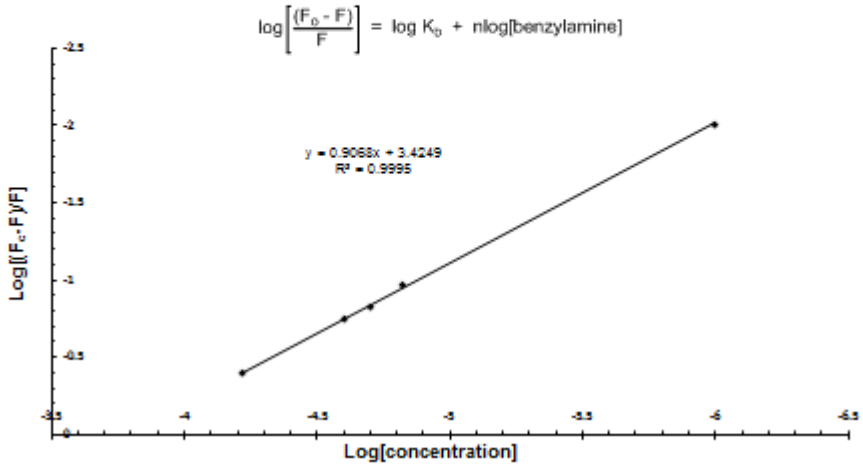
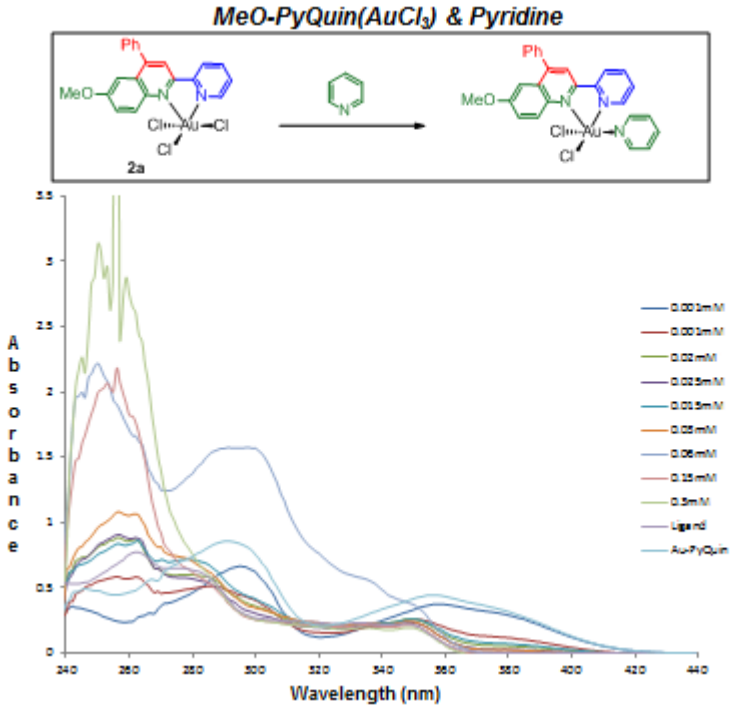

log[(F0 - F)/F] = log K0 + nlog[benzylamine]
y = 0.9068x + 3.4249
R² = 0.9995
Log[(F0-F)/F]
Log[concentration]

Table 3 - 2a


MeO-PyQuin(AuCl3) & Pyridine
Ph
MeO
N
Cl
Au
Cl
Cl
2a
Ph
MeO
N
N
Cl
Au
N
Cl
Absorbance
Wavelength (nm)
0.001mM
0.001mM
0.02mM
0.025mM
0.035mM
0.05mM
0.06mM
0.1mM
0.5mM
Ligand
Au-PyQuin

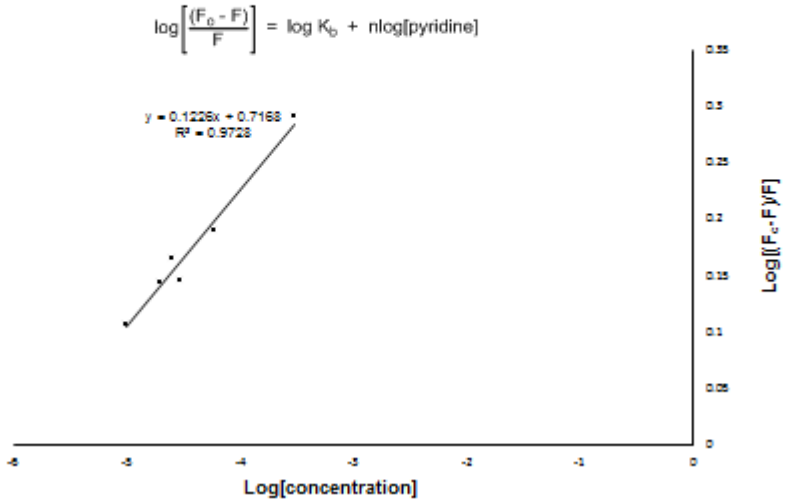
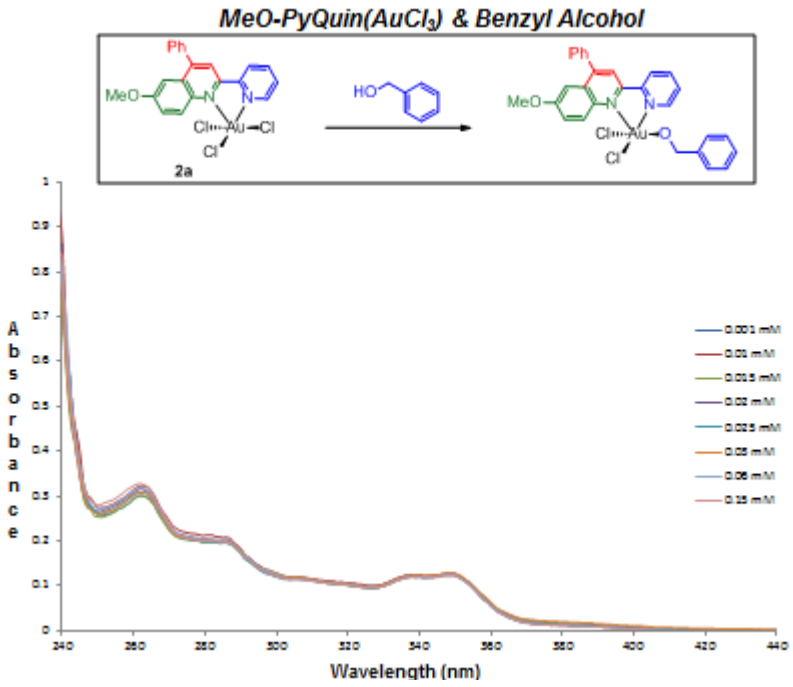

log[(Fo - F)/F] = log Kb + nlog[pyridine]
y = 0.1226x + 0.7168
R² = 0.9728
Log[(Fo-F)/F]
Log[concentration]

Table 3 - 2a



$$\log\left[\frac{(F_0 - F)}{F}\right] = \log K_b + n\log[\text{benzyl alcohol}]$$

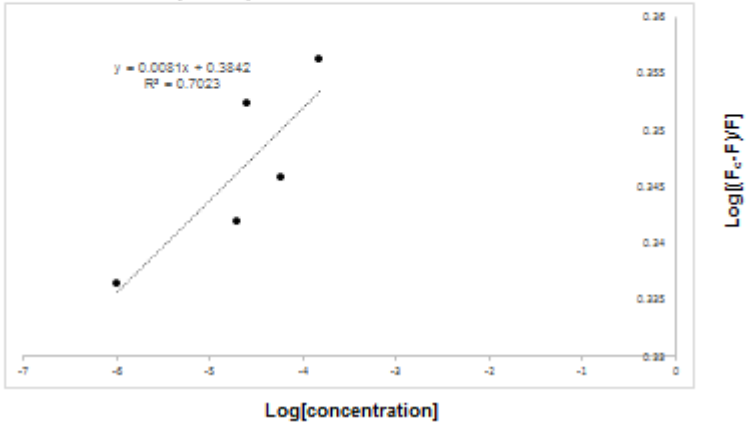
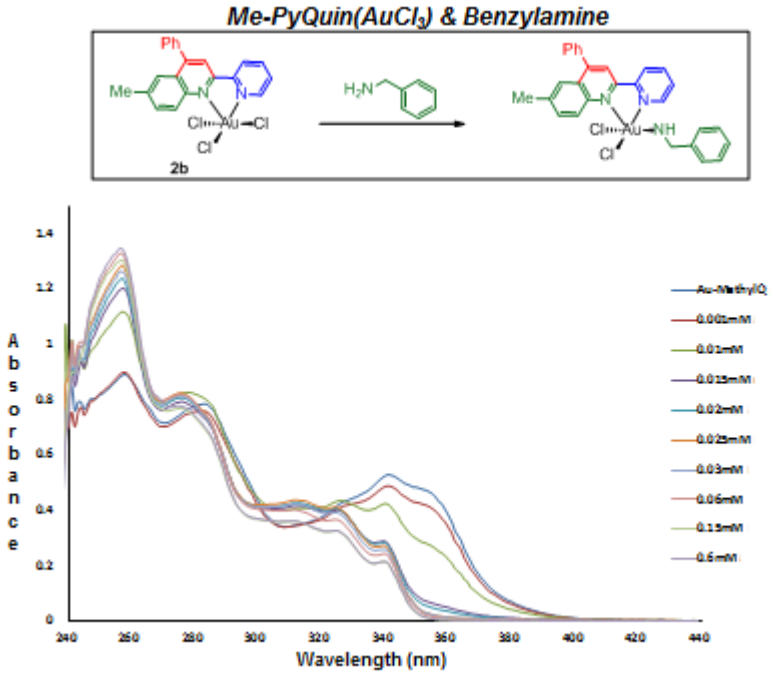


Table 3 - 2b


Me-PyQuin(AuCl3) & Benzylamine
Ph
Me
N
N
Cl
Au
Cl
Cl
2b
H2N
Ph
Me
N
N
Cl
Au
NH
Cl
Absorbance
Wavelength (nm)
Au-MethylQ
0.005mM
0.01mM
0.015mM
0.02mM
0.025mM
0.03mM
0.06mM
0.15mM
0.6mM

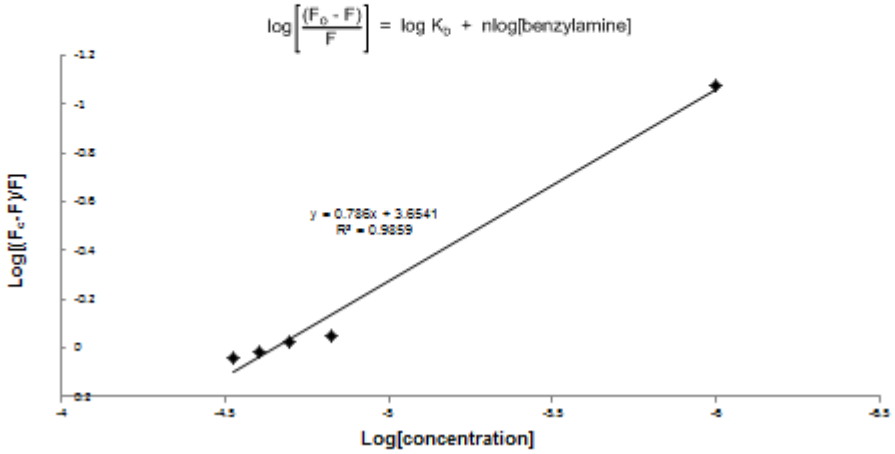
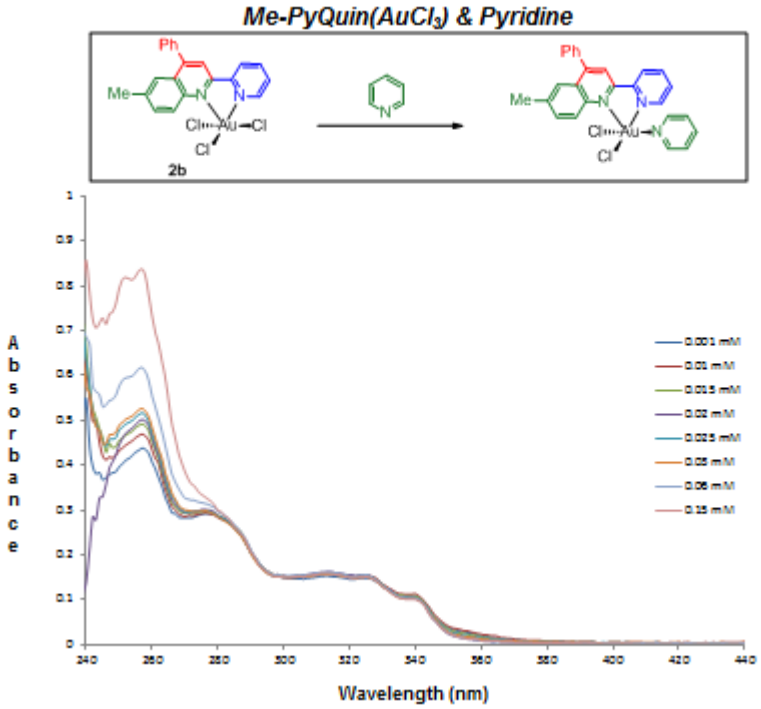

log[(F0 - F)/F] = log K0 + nlog[benzylamine]
y = 0.786x + 3.6541
R² = 0.9859
Log[(F0-F)/F]
Log[concentration]

Table 3 - 2b



$$\log\left[\frac{(F_c - F)}{F}\right] = \log K_b + n\log[\text{pyridine}]$$

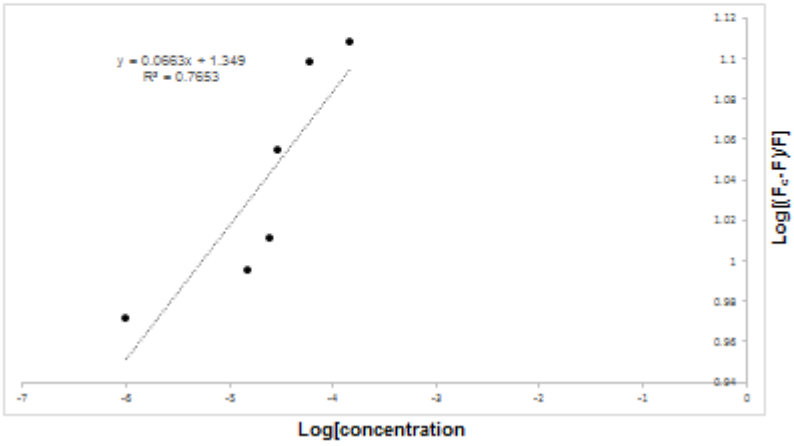


Table 3 - 2b

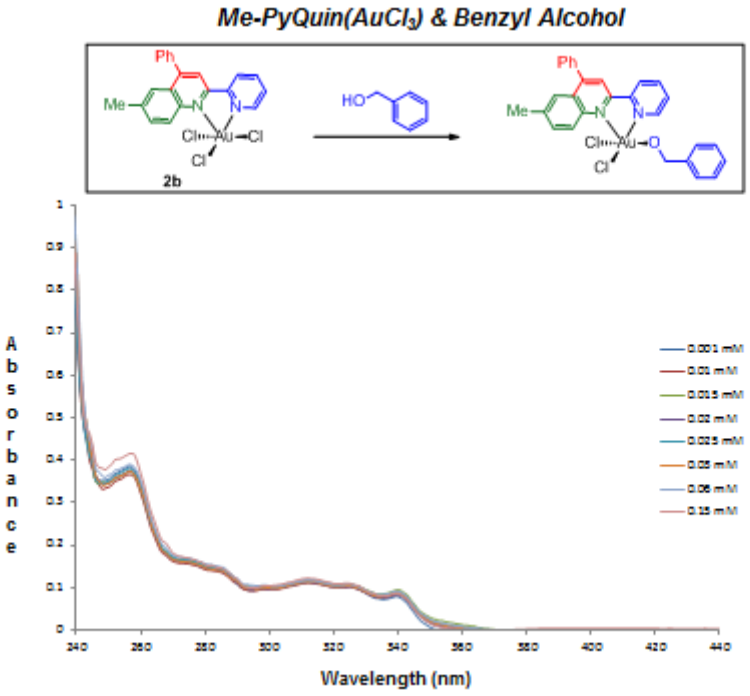
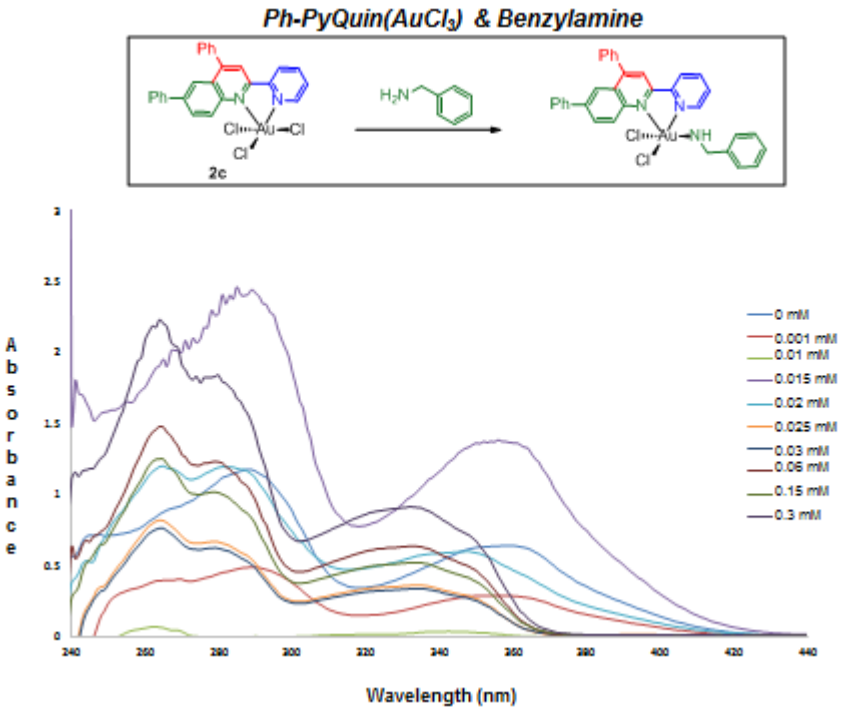

Me-PyQuin(AuCl3) & Benzyl Alcohol
Ph
Me
N
N
Cl
Au
Cl
Cl
2b
HO
Ph
Me
N
N
Cl
Au
O
Cl
Absorbance
Wavelength (nm)
0.001 mM
0.01 mM
0.015 mM
0.02 mM
0.025 mM
0.05 mM
0.06 mM
0.15 mM

Table 3 - 2c


Ph-PyQuin(AuCl3) & Benzylamine
Ph
Ph
Cl
Au
Cl
Cl
2c
H2N
Ph
Ph
N
N
Cl
Au
NH
Cl
Absorbance
Wavelength (nm)
0 mM
0.001 mM
0.01 mM
0.015 mM
0.02 mM
0.025 mM
0.03 mM
0.06 mM
0.15 mM
0.3 mM

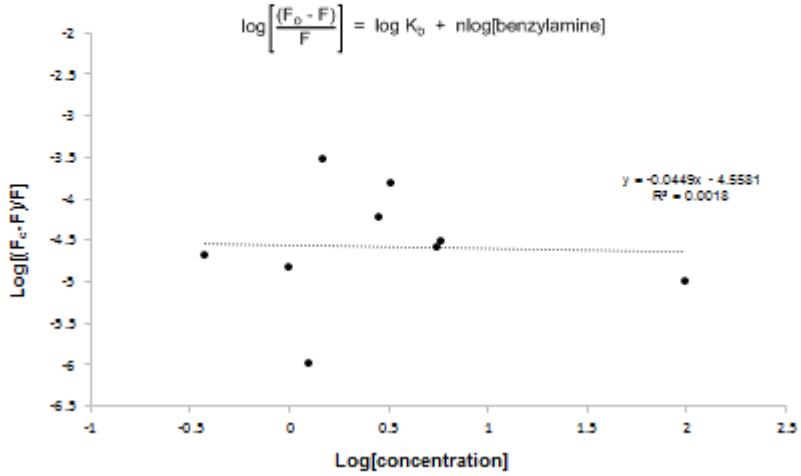
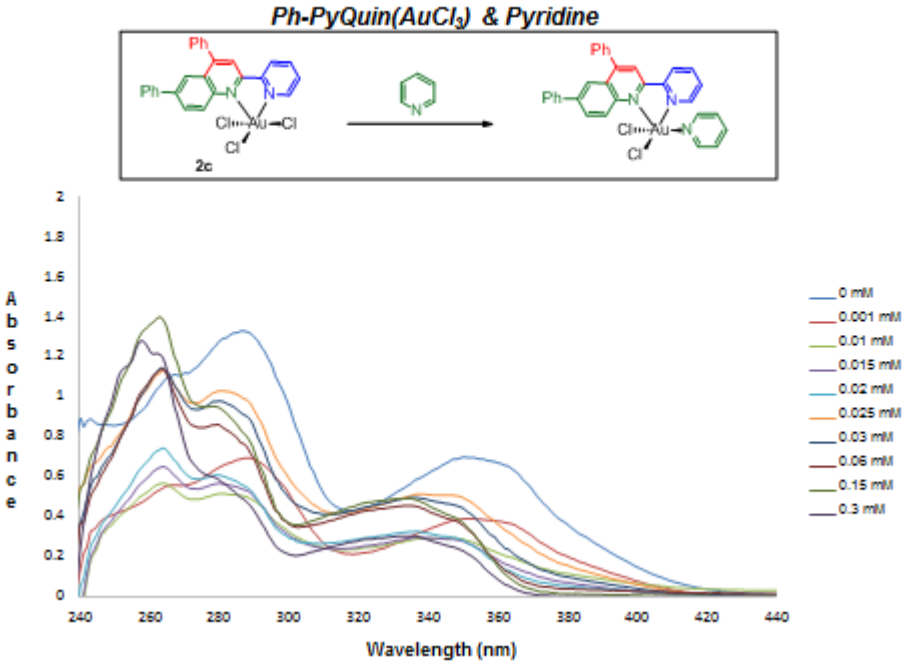

log[(F0 - F)/F] = log K0 + nlog[benzylamine]
y = -0.0449x - 4.5581
R² = 0.0018
Log[(F0-F)/F]
Log[concentration]

Table 3 - 2c


Ph-PyQuin(AuCl3) & Pyridine
Ph
Ph
Cl
Au
Cl
Cl
2c
N
Ph
Ph
N
N
Cl
Au
N
Cl
Absorbance
Wavelength (nm)
0 mM
0.001 mM
0.01 mM
0.015 mM
0.02 mM
0.025 mM
0.03 mM
0.06 mM
0.15 mM
0.3 mM

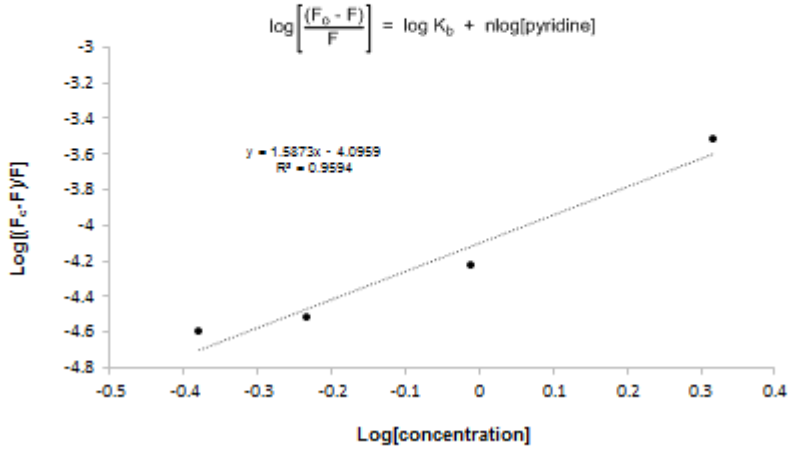
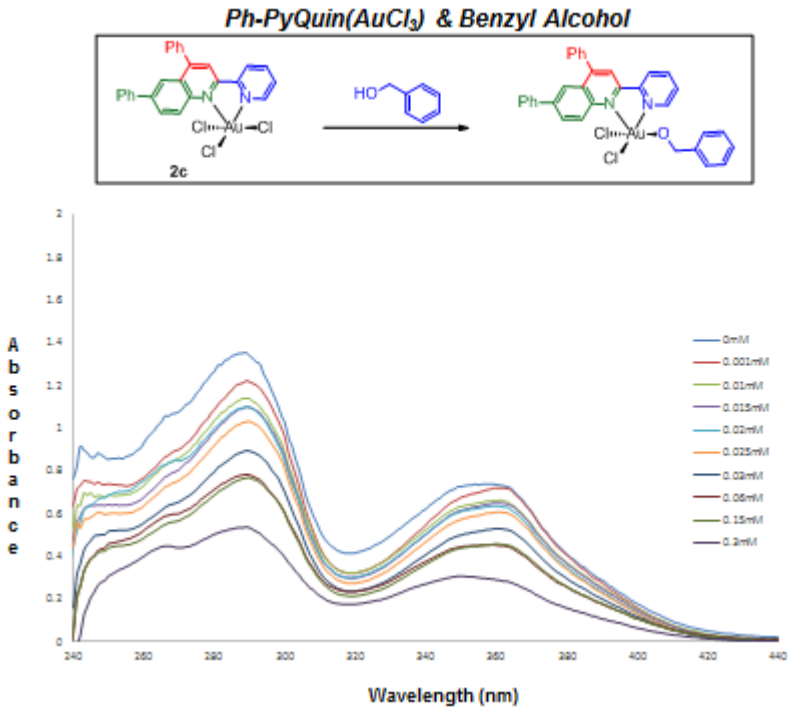

log[(F0 - F)/F] = log Kb + nlog[pyridine]
y = 1.5873x - 4.0959
R² = 0.9594
Log[(F0-F)/F]
Log[concentration]

Table 3 - 2c


Ph-PyQuin(AuCl3) & Benzyl Alcohol
Ph
Ph
N
N
Cl
Au
Cl
Cl
2c
HO
Ph
Ph
N
N
Cl
Au
O
Cl
Absorbance
Wavelength (nm)

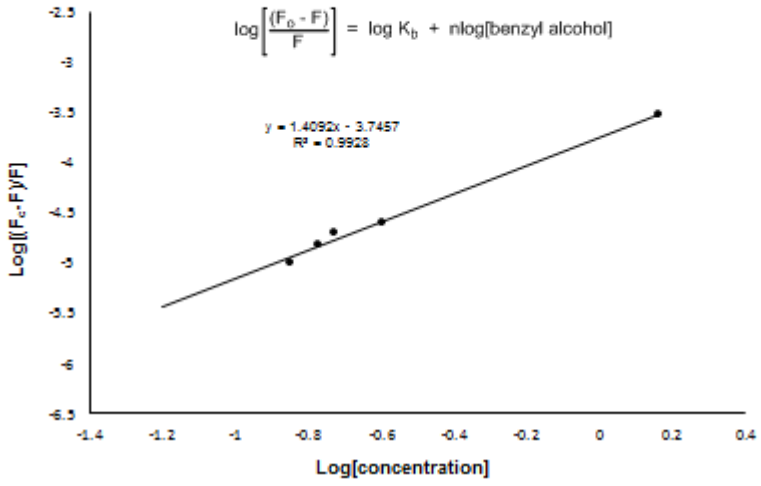
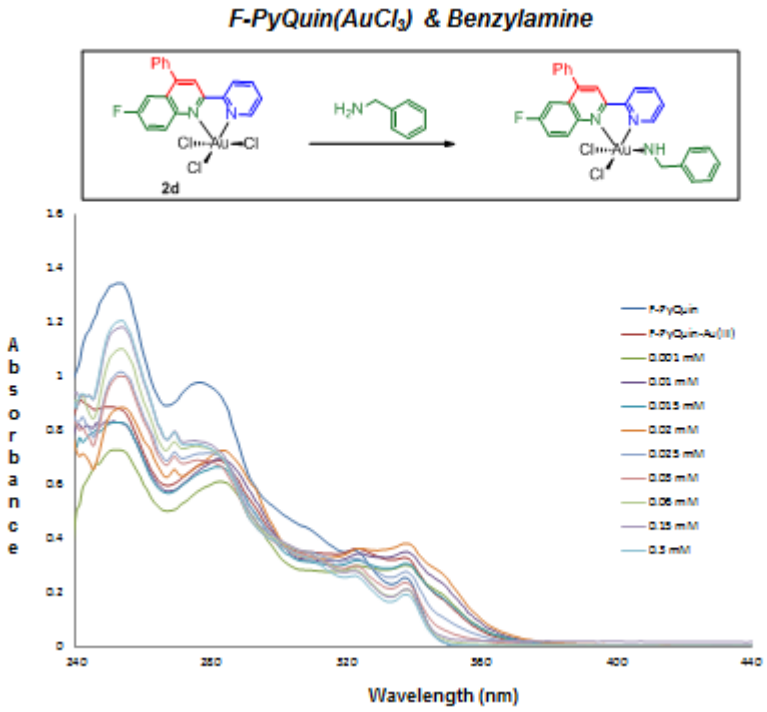

log[(F0 - F)/F] = log Kb + nlog[benzyl alcohol]
y = 1.4092x - 3.7457
R² = 0.9928
Log[(Fc-F)/F]
Log[concentration]

Table 3 - 2d



$$\log\left[\frac{(F_0 - F)}{F}\right] = \log K_b + n\log[\text{benzylamine}]$$

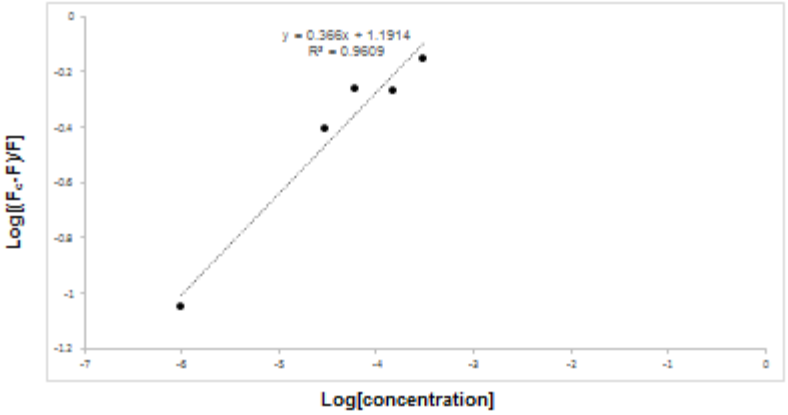
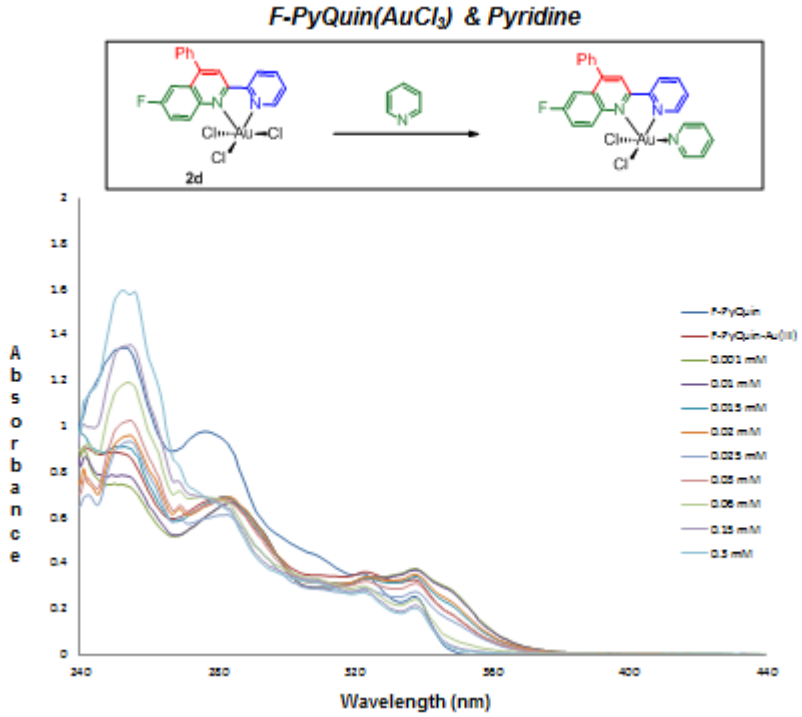


Table 3 - 2d



$$\log\left[\frac{(F_0 - F)}{F}\right] = \log K_b + n\log[\text{pyridine}]$$

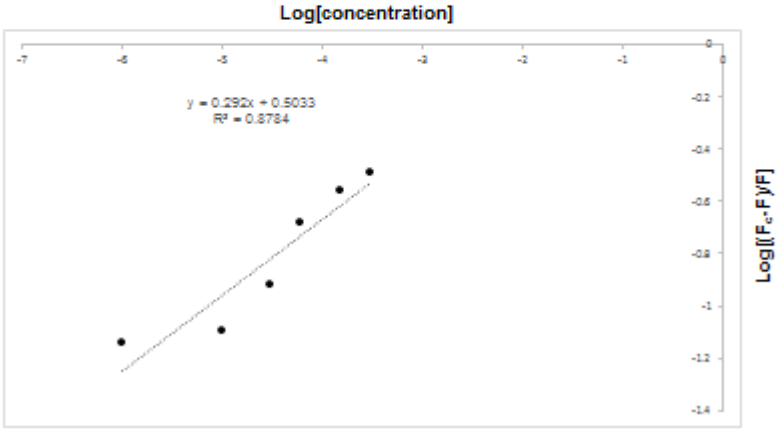


Table 3 - 2d

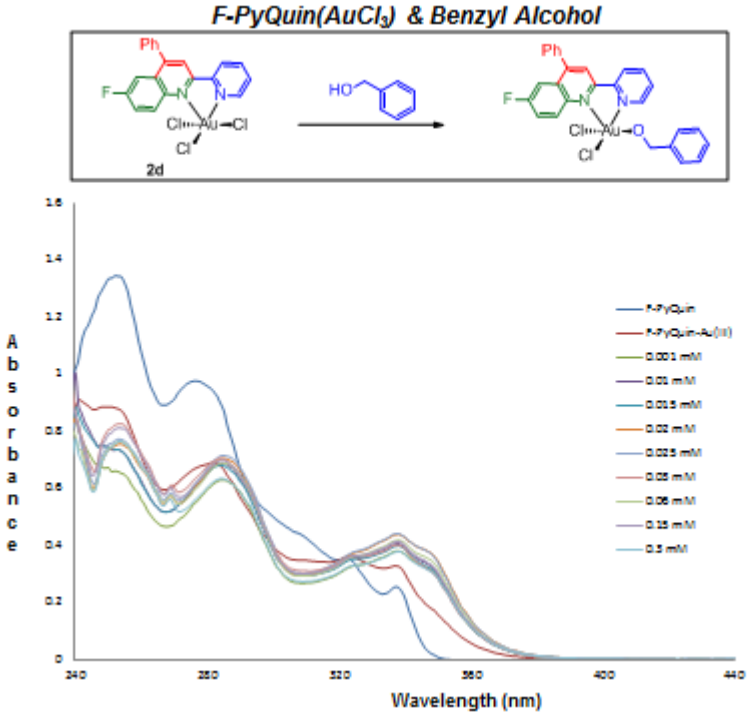
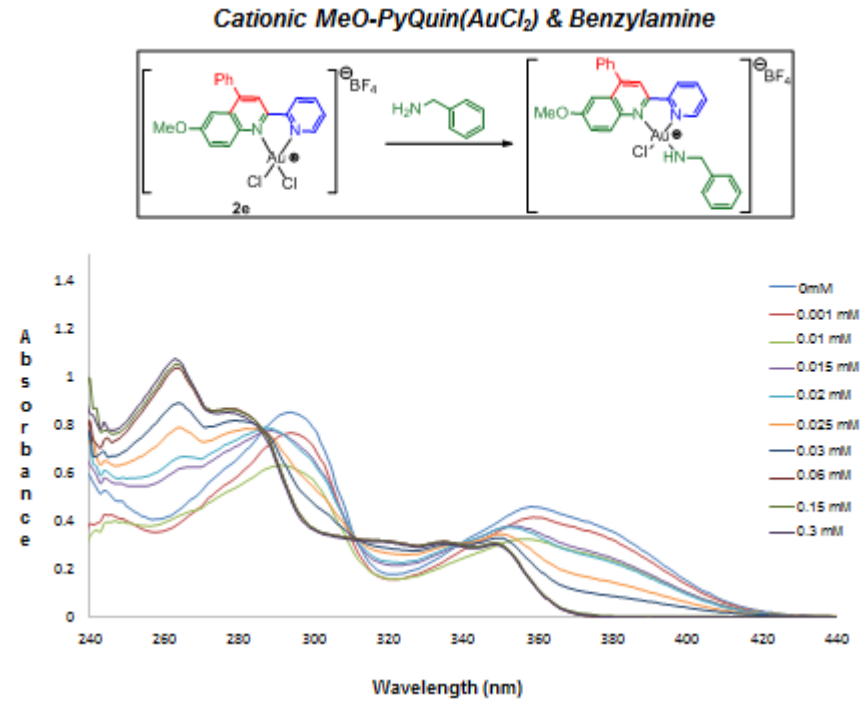

F-PyQuin(AuCl3) & Benzyl Alcohol
Ph
F
N
N
Cl
Au
Cl
Cl
2d
HO
Ph
F
N
N
Cl
Au
O
Cl
Absorbance
Wavelength (nm)
F-PyQuin
0.001 mM
0.01 mM
0.015 mM
0.02 mM
0.025 mM
0.05 mM
0.06 mM
0.15 mM
0.5 mM

Table 3 - 2e


Cationic MeO-PyQuin(AuCl2) & Benzylamine
Ph
MeO
N
N
Au
Cl
Cl
BF4
2e
H2N
Ph
MeO
N
N
Au
Cl
HN
BF4
Absorbance
Wavelength (nm)
0mM
0.001 mM
0.01 mM
0.015 mM
0.02 mM
0.025 mM
0.03 mM
0.06 mM
0.15 mM
0.3 mM

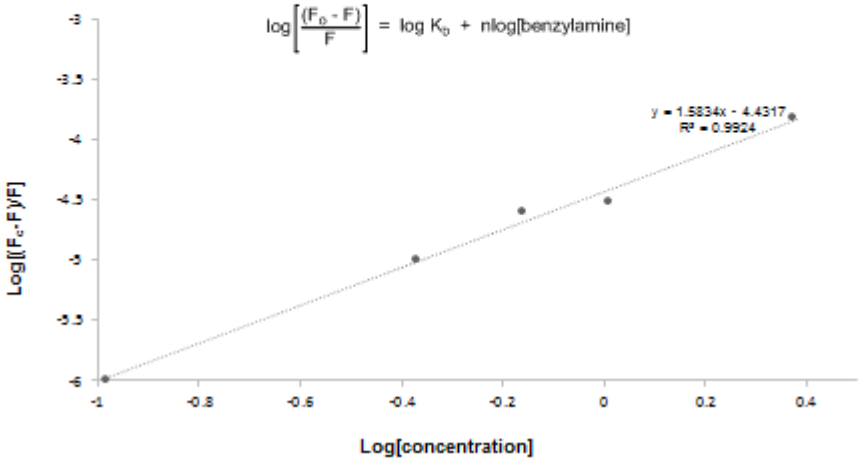
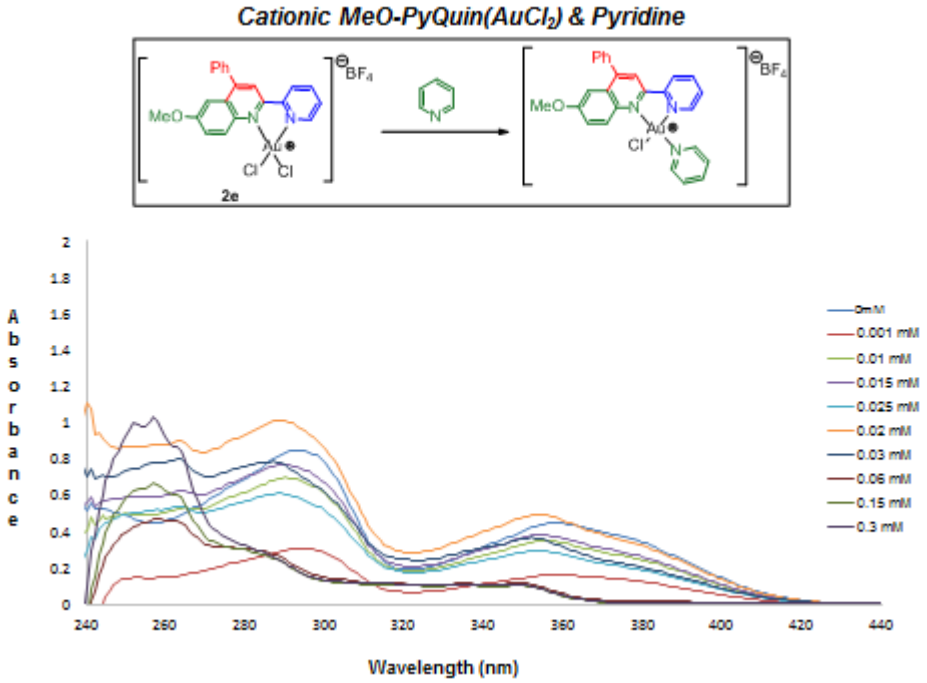

log[(F0 - F)/F] = log K0 + nlog[benzylamine]
y = 1.5834x - 4.4317
R² = 0.9924
Log[(F0-F)/F]
Log[concentration]

Table 3 - 2e


Cationic MeO-PyQuin(AuCl2) & Pyridine
Ph
MeO
N
Au
Cl
Cl
BF4
2e
Absorbance
Wavelength (nm)
0mM
0.001 mM
0.01 mM
0.015 mM
0.025 mM
0.02 mM
0.03 mM
0.06 mM
0.15 mM
0.3 mM

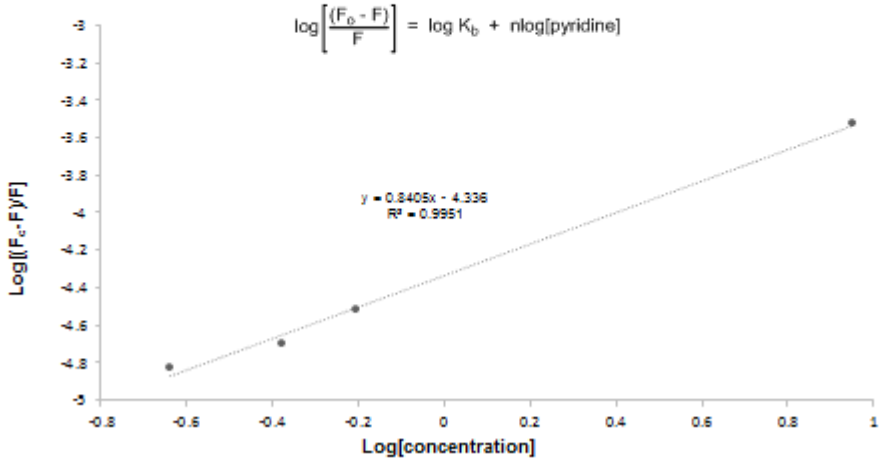
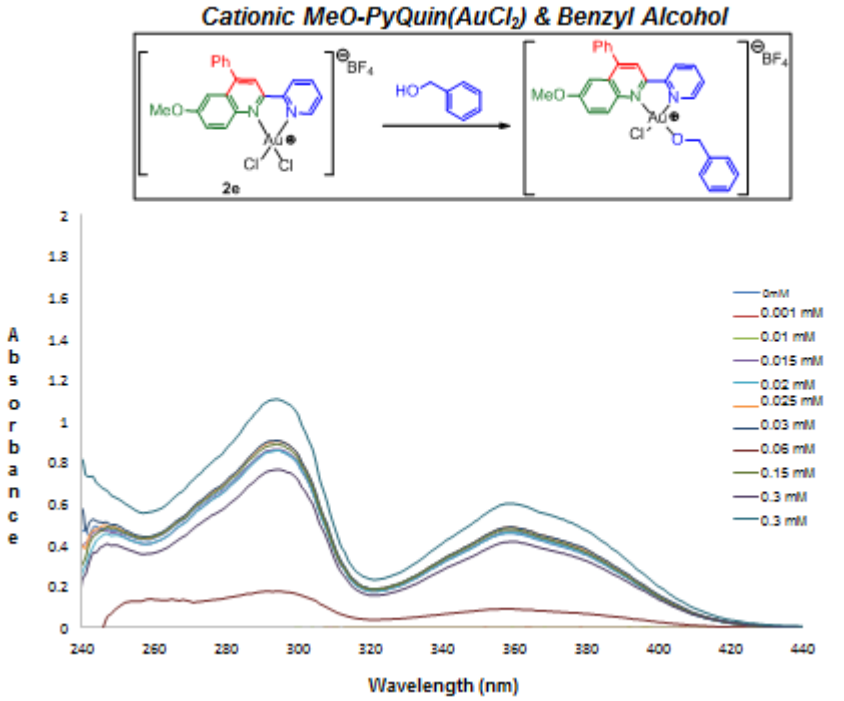
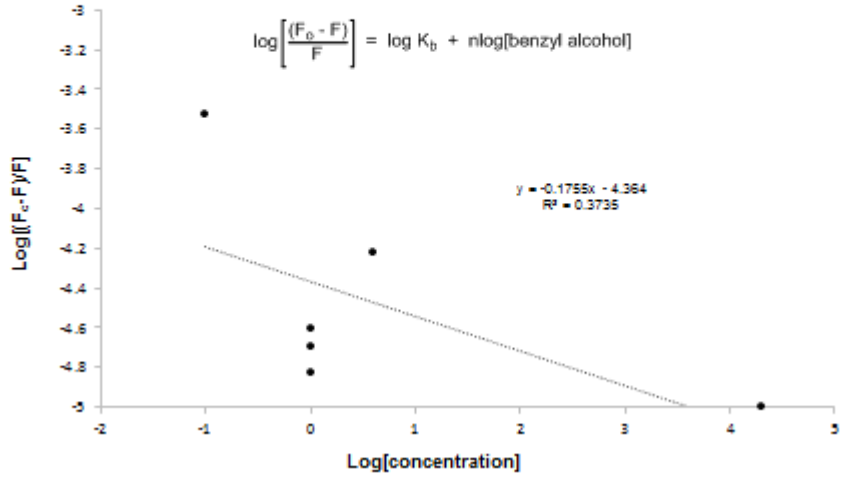
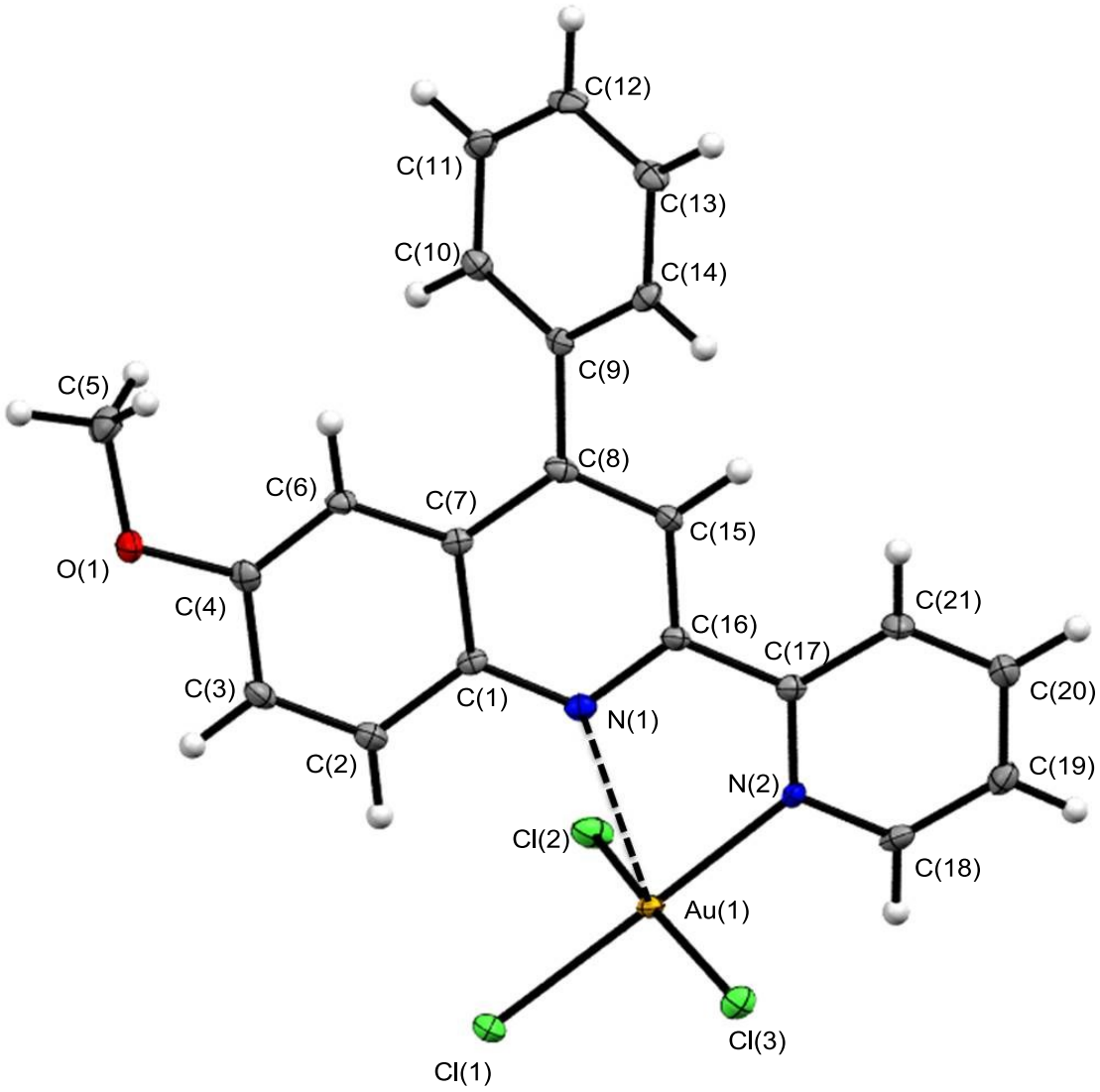

log[(F0 - F)/F] = log Kb + nlog[pyridine]
y = 0.8405x - 4.336
R² = 0.9951
Log[(F0-F)/F]
Log[concentration]

Table 3 - 2e


Cationic MeO-PyQuin(AuCl2) & Benzyl Alcohol
Ph
MeO
N
N
Au
Cl
Cl
BF4
2e
HO
Ph
MeO
N
N
Au
Cl
O
BF4
Absorbance
Wavelength (nm)
0mM
0.001 mM
0.01 mM
0.015 mM
0.02 mM
0.025 mM
0.03 mM
0.06 mM
0.15 mM
0.3 mM
0.3 mM


log[(Fo - F)/F] = log Kb + nlog[benzyl alcohol]
y = -0.1755x - 4.364
R² = 0.3735
Log[(Fo-F)/F]
Log[concentration]



(6-methoxy-PyQuin)$AuCl_3$•CH_3CN **(2a)**

Thermal ellipsoids shown at 50% probability

Solvent omitted for clarity

Table 4. Crystal data & structure refinement for (6-methoxy-PyQuin)$AuCl_3$•CH_3CN **(2a)**.

Formula	$C_{23}H_{19}N_3OAuCl_3$
Formula weight	656.73
Temperature	100(2) K
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a, Å	7.2272(4)
b, Å	12.8348(7)
c, Å	24.2847(13)
α, °	90
β, °	94.064(2)
γ, °	90
Volume	2247.0(2) $Å^3$
Z,	4
Calculated density, g/cm^3	1.941
Absorption coefficient, mm^{-1}	6.925
F(000)	1264
Crystal size, mm^3	0.28 x 0.24 x 0.22
Theta range for data collection, deg	2.89 to 26.46
Index ranges	$-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $-29 \leq l \leq 30$
Reflections collected / unique	13480
Independent reflections	4584 [R(int)=0.0332]
Completeness to θ = 25.00°	99.7 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4584 / 0 / 282
Goodness-of-fit on F^2	1.084
Final *R* indices [I>2σ(I)]	*R*1 = 0.0234, *wR*2 = 0.0584
R indices (all data)	*R*1 = 0.0262, *wR*2 = 0.0598
Extinction coefficient	n/a
Largest diff. peak and hole, $eÅ^3$	1.195 and -1.094

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (6-methoxy-PyQuin)$AuCl_3$•CH_3CN (**2a**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	1242(1)	6073(1)	661(1)	9(1)
Cl(1)	3724(1)	4995(1)	808(1)	15(1)
Cl(2)	281(1)	5738(1)	1521(1)	18(1)
Cl(3)	1705(1)	6172(1)	-261(1)	14(1)
O(1)	8652(3)	9071(2)	2305(1)	15(1)
N(1)	2384(4)	7915(2)	1022(1)	11(1)
N(2)	-883(4)	7102(2)	509(1)	9(1)
N(3)	7120(5)	11265(3)	861(1)	23(1)
C(1)	3900(4)	8260(2)	1337(1)	9(1)
C(2)	5362(4)	7545(3)	1466(1)	12(1)
C(3)	6900(5)	7850(3)	1782(1)	14(1)
C(4)	7050(5)	8881(2)	1986(1)	12(1)
C(5)	8839(5)	10074(3)	2568(2)	19(1)
C(6)	5675(4)	9594(3)	1868(1)	11(1)
C(7)	4046(4)	9301(3)	1546(1)	9(1)
C(8)	2519(5)	9982(3)	1417(1)	11(1)
C(9)	2431(4)	11075(2)	1622(1)	10(1)
C(10)	2844(5)	11316(3)	2177(1)	13(1)
C(11)	2654(4)	12332(3)	2368(1)	14(1)
C(12)	2036(4)	13104(3)	2007(1)	16(1)
C(13)	1614(4)	12884(3)	1452(1)	14(1)
C(14)	1814(4)	11863(3)	1263(1)	12(1)
C(15)	1008(4)	9602(3)	1105(1)	10(1)
C(16)	989(4)	8562(3)	911(1)	10(1)
C(17)	-704(4)	8144(3)	600(1)	10(1)
C(18)	-2459(4)	6703(3)	258(1)	13(1)
C(19)	-3907(5)	7327(3)	72(1)	14(1)
C(20)	-3743(5)	8395(3)	142(1)	16(1)

C(21)	-2146(5)	8799(3)	410(2)	16(1)
C(22)	6947(5)	11951(3)	1146(1)	17(1)
C(23)	6730(5)	12829(3)	1516(2)	25(1)

Bond lengths [Å] and angles [°] for (6-methoxy-PyQuin)$AuCl_3$•CH_3CN (**2a**).

Au(1)-N(2)	**2.039(3)**
Au(1)-Cl(1)	**2.2745(8)**
Au(1)-Cl(2)	**2.2886(8)**
Au(1)-Cl(3)	**2.2910(8)**
Au(1)-N(1)	**2.633(3)**
O(1)-C(4)	1.368(4)
O(1)-C(5)	1.440(4)
N(1)-C(16)	1.320(4)
N(1)-C(1)	1.365(4)
N(2)-C(18)	1.354(4)
N(2)-C(17)	1.360(4)
N(3)-C(22)	1.132(5)
C(1)-C(2)	1.418(5)
C(1)-C(7)	1.431(4)
C(2)-C(3)	1.363(5)
C(3)-C(4)	1.415(5)
C(4)-C(6)	1.366(5)
C(6)-C(7)	1.417(4)
C(7)-C(8)	1.425(5)
C(8)-C(15)	1.374(5)
C(8)-C(9)	1.491(4)
C(9)-C(10)	1.394(5)
C(9)-C(14)	1.389(5)
C(10)-C(11)	1.395(5)
C(11)-C(12)	1.377(5)
C(12)-C(13)	1.389(5)
C(13)-C(14)	1.399(5)

C(15)-C(16)	1.415(5)
C(16)-C(17)	1.491(4)
C(17)-C(21)	1.392(5)
C(18)-C(19)	1.368(5)
C(19)-C(20)	1.386(5)
C(20)-C(21)	1.384(5)
C(22)-C(23)	1.456(5)

N(2)-Au(1)-Cl(1)	**176.67(8)**
N(2)-Au(1)-Cl(2)	**90.73(7)**
Cl(1)-Au(1)-Cl(2)	**91.64(3)**
N(2)-Au(1)-Cl(3)	**87.06(7)**
Cl(1)-Au(1)-Cl(3)	**91.10(3)**
Cl(2)-Au(1)-Cl(3)	**167.78(3)**
N(2)-Au(1)-N(1)	**72.15(9)**
Cl(1)-Au(1)-N(1)	**105.58(6)**
Cl(2)-Au(1)-N(1)	**88.45(6)**
Cl(3)-Au(1)-N(1)	**102.27(6)**
C(4)-O(1)-C(5)	117.4(3)
C(16)-N(1)-C(1)	118.8(3)
C(16)-N(1)-Au(1)	106.2(2)
C(1)-N(1)-Au(1)	134.3(2)
C(18)-N(2)-C(17)	120.8(3)
C(18)-N(2)-Au(1)	115.8(2)
C(17)-N(2)-Au(1)	123.1(2)
N(1)-C(1)-C(2)	118.0(3)
N(1)-C(1)-C(7)	122.6(3)
C(2)-C(1)-C(7)	119.4(3)
C(3)-C(2)-C(1)	120.3(3)
C(2)-C(3)-C(4)	120.3(3)
C(6)-C(4)-O(1)	125.0(3)
C(6)-C(4)-C(3)	121.1(3)
O(1)-C(4)-C(3)	113.9(3)
C(4)-C(6)-C(7)	120.2(3)

C(6)-C(7)-C(8)	124.0(3)
C(6)-C(7)-C(1)	118.7(3)
C(8)-C(7)-C(1)	117.3(3)
C(15)-C(8)-C(7)	118.4(3)
C(15)-C(8)-C(9)	117.9(3)
C(7)-C(8)-C(9)	123.7(3)
C(10)-C(9)-C(14)	118.9(3)
C(10)-C(9)-C(8)	121.3(3)
C(14)-C(9)-C(8)	119.7(3)
C(9)-C(10)-C(11)	120.7(3)
C(12)-C(11)-C(10)	119.7(3)
C(11)-C(12)-C(13)	120.7(3)
C(12)-C(13)-C(14)	119.2(3)
C(9)-C(14)-C(13)	120.8(3)
C(8)-C(15)-C(16)	120.5(3)
N(1)-C(16)-C(15)	122.4(3)
N(1)-C(16)-C(17)	117.7(3)
C(15)-C(16)-C(17)	119.8(3)
N(2)-C(17)-C(21)	118.7(3)
N(2)-C(17)-C(16)	120.1(3)
C(21)-C(17)-C(16)	121.2(3)
N(2)-C(18)-C(19)	121.7(3)
C(18)-C(19)-C(20)	118.8(3)
C(21)-C(20)-C(19)	119.3(3)
C(20)-C(21)-C(17)	120.6(3)
N(3)-C(22)-C(23)	179.6(4)

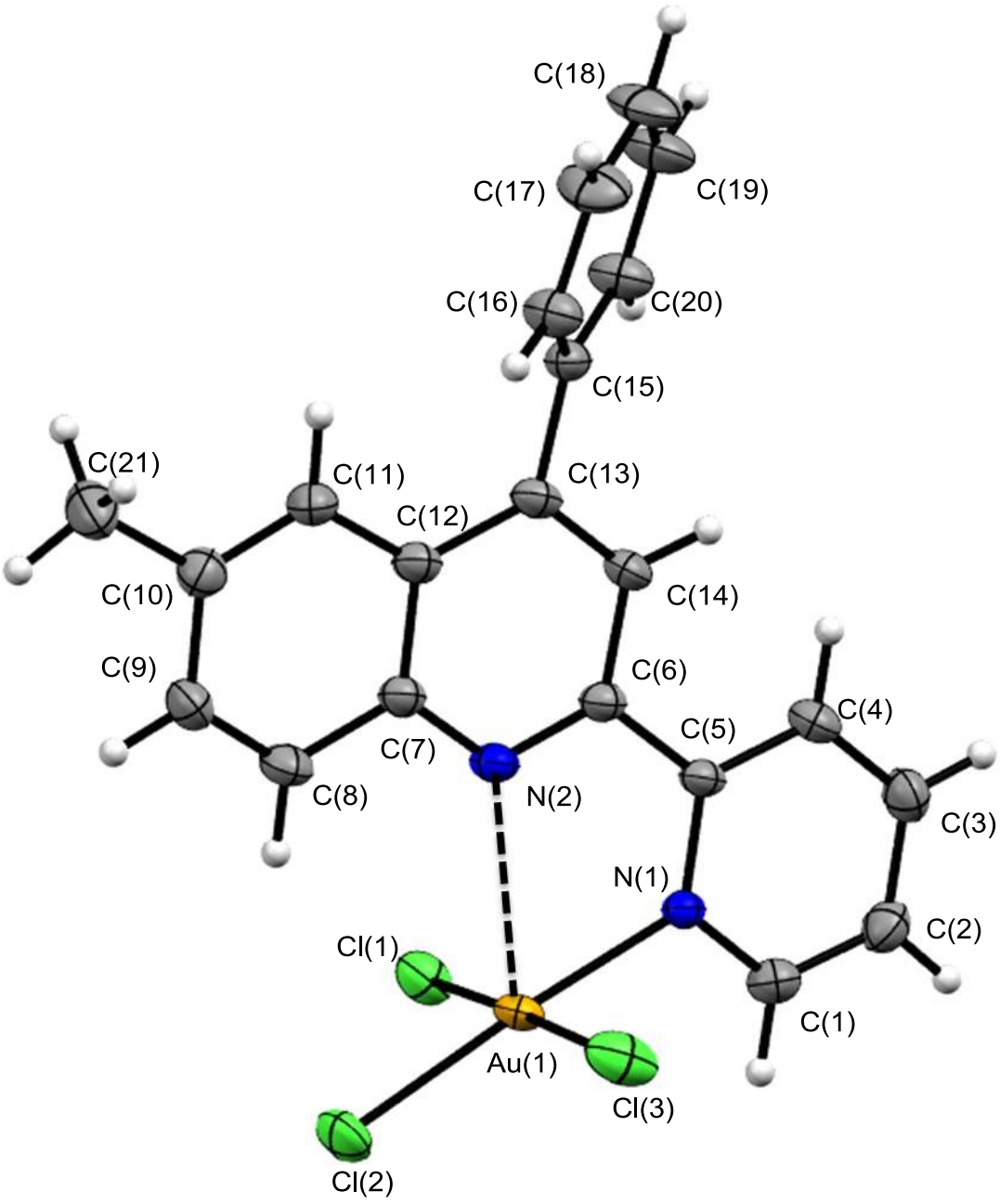
Anisotropic displacement parameters ($Å^2$ x 10^3) for (6-methoxy-PyQuin)$AuCl_3$•CH_3CN (**2a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	12(1)	7(1)	9(1)	-1(1)	0(1)	0(1)
Cl(1)	16(1)	11(1)	18(1)	-2(1)	-2(1)	4(1)
Cl(2)	28(1)	16(1)	11(1)	2(1)	5(1)	7(1)
Cl(3)	15(1)	17(1)	11(1)	0(1)	3(1)	-1(1)
O(1)	10(1)	15(1)	20(1)	-2(1)	-3(1)	1(1)
N(1)	12(1)	11(1)	11(1)	-1(1)	3(1)	0(1)
N(2)	11(1)	10(1)	7(1)	-1(1)	-2(1)	1(1)
N(3)	22(2)	18(2)	30(2)	3(2)	-1(2)	5(1)
C(1)	10(2)	8(2)	9(2)	0(1)	2(1)	-2(1)
C(2)	13(2)	11(2)	13(2)	-1(1)	3(1)	2(1)
C(3)	15(2)	13(2)	13(2)	1(1)	2(1)	6(2)
C(4)	9(2)	15(2)	12(2)	1(1)	4(1)	1(1)
C(5)	14(2)	21(2)	22(2)	-6(2)	-2(1)	-3(2)
C(6)	13(2)	7(2)	12(2)	0(1)	1(1)	0(1)
C(7)	11(2)	8(2)	8(2)	1(1)	3(1)	-2(1)
C(8)	15(2)	8(2)	10(2)	2(1)	3(1)	2(1)
C(9)	6(2)	9(2)	15(2)	-1(1)	2(1)	-2(1)
C(10)	12(2)	13(2)	14(2)	1(1)	1(1)	2(1)
C(11)	12(2)	16(2)	14(2)	-5(1)	2(1)	-1(1)
C(12)	12(2)	8(2)	27(2)	-6(1)	4(1)	-3(1)
C(13)	12(2)	10(2)	21(2)	2(1)	2(1)	-1(1)
C(14)	10(2)	13(2)	12(2)	-1(1)	1(1)	-3(1)
C(15)	10(2)	9(2)	12(2)	-1(1)	1(1)	2(1)
C(16)	12(2)	8(2)	9(2)	-1(1)	2(1)	1(1)
C(17)	14(2)	9(2)	8(2)	1(1)	2(1)	1(1)
C(18)	14(2)	13(2)	12(2)	-5(1)	3(1)	-3(1)
C(19)	12(2)	18(2)	13(2)	-3(1)	-1(1)	-3(2)
C(20)	15(2)	17(2)	16(2)	-2(1)	-2(1)	4(2)

C(21)	17(2)	10(2)	20(2)	-3(1)	-3(2)	2(1)
C(22)	14(2)	18(2)	18(2)	5(2)	-1(1)	-1(2)
C(23)	18(2)	27(2)	31(2)	-7(2)	9(2)	-4(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (6-methoxy-PyQuin)$AuCl_3$•CH_3CN (**2a**).

	x	y	z	U(eq)
H(16)	5269	6851	1332	14
H(15)	7877	7368	1866	16
H(1)	8891	10618	2286	29
H(2)	9982	10089	2811	29
H(3)	7772	10198	2787	29
H(14)	5811	10287	2002	13
H(8)	3258	10782	2427	15
H(7)	2950	12491	2746	17
H(6)	1897	13795	2138	19
H(5)	1194	13420	1204	17
H(4)	1523	11708	884	14
H(13)	-31	10040	1019	12
H(12)	-2562	5970	209	15
H(11)	-5004	7033	-102	17
H(10)	-4716	8846	8	19
H(9)	-2033	9530	464	19
H(19)	7503	12718	1859	37
H(18)	5427	12887	1599	37
H(17)	7116	13471	1338	37



(6-methyl-PyQuin)$AuCl_3$ (**2b**)

(Thermal ellipsoids shown at 50% probability)

Table 5. Crystal data & structure refinement for (6-methyl-PyQuin)$AuCl_3$ (**2b**).

Formula	$C_{21}H_{16}N_2AuCl_3$
Formula weight	599.68
Temperature	245(2) K
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	P-1
a, Å	8.5146(4)
b, Å	11.2882(6)
c, Å	11.2979(6)
α, °	102.905(2)
β, °	101.006(2)
γ, °	104.341(2)
Volume	990.01(9) $Å^3$
Z,	2
Calculated density, g/cm^3	2.012
Absorption coefficient, mm^{-1}	7.843
F(000)	572
Crystal size, mm^3	0.25 x 0.20 x 0.15
Theta range for data collection, deg	2.56 to 26.45
Index ranges	$-10 \leq h \leq 9$, $-14 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected / unique	19138
Independent reflections	4051 [R(int)=0.0599]
Completeness to θ = 25.00°	99.2 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4051 / 0 / 246
Goodness-of-fit on F^2	1.107
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0226, *wR*2 = 0.0514
R indices (all data)	*R*1 = 0.0281, *wR*2 = 0.0663
Extinction coefficient	0.0003(3)
Largest diff. peak and hole, $eÅ^3$	0.875 and -1.582

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (6-methyl-PyQuin)$AuCl_3$ (**2b**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	6649(1)	5291(1)	1887(1)	22(1)
Cl(1)	7091(2)	3601(1)	2566(1)	32(1)
Cl(2)	8744(2)	5290(1)	922(1)	36(1)
Cl(3)	6068(2)	6866(1)	1091(1)	41(1)
N(1)	4642(4)	5217(3)	2671(3)	19(1)
N(2)	7685(4)	6853(3)	4190(3)	24(1)
C(1)	3169(5)	4389(4)	1935(4)	26(1)
C(2)	1730(5)	4169(4)	2337(5)	30(1)
C(3)	1795(6)	4818(4)	3526(5)	30(1)
C(4)	3303(5)	5693(4)	4278(4)	26(1)
C(5)	4741(5)	5898(4)	3854(4)	21(1)
C(6)	6378(5)	6841(4)	4637(4)	22(1)
C(7)	9190(5)	7697(4)	4874(4)	23(1)
C(8)	10572(5)	7683(4)	4367(4)	29(1)
C(9)	12120(6)	8510(4)	4999(5)	31(1)
C(10)	12382(5)	9381(4)	6180(4)	29(1)
C(11)	11060(5)	9394(4)	6693(4)	27(1)
C(12)	9424(5)	8582(4)	6060(4)	23(1)
C(13)	7981(5)	8562(4)	6526(4)	23(1)
C(14)	6470(5)	7685(4)	5798(4)	24(1)
C(15)	8004(5)	9427(4)	7737(4)	24(1)
C(16)	8761(6)	10743(4)	8061(4)	31(1)
C(17)	8622(7)	11516(5)	9152(5)	44(1)
C(18)	7803(7)	11007(5)	9938(5)	47(2)
C(19)	7082(7)	9721(5)	9631(5)	42(1)
C(20)	7172(6)	8938(4)	8546(4)	31(1)
C(21)	14118(6)	10274(5)	6844(5)	44(1)

Bond lengths [Å] and angles [°] for (6-methyl-PyQuin)$AuCl_3$ (**2b**).

Au(1)-N(1)	**2.063(3)**
Au(1)-Cl(2)	**2.2608(12)**
Au(1)-Cl(3)	**2.2790(12)**
Au(1)-Cl(1)	**2.2948(12)**
Au(1)-N(2)	**2.639(3)**
N(1)-C(1)	1.346(5)
N(1)-C(5)	1.360(5)
N(2)-C(6)	1.305(6)
N(2)-C(7)	1.355(5)
C(1)-C(2)	1.372(7)
C(2)-C(3)	1.362(6)
C(3)-C(4)	1.388(6)
C(4)-C(5)	1.385(6)
C(5)-C(6)	1.494(6)
C(6)-C(14)	1.414(6)
C(7)-C(8)	1.406(6)
C(7)-C(12)	1.426(6)
C(8)-C(9)	1.361(6)
C(9)-C(10)	1.411(6)
C(10)-C(11)	1.362(6)
C(10)-C(21)	1.505(6)
C(11)-C(12)	1.409(6)
C(12)-C(13)	1.423(6)
C(13)-C(14)	1.383(6)
C(13)-C(15)	1.486(6)
C(15)-C(20)	1.386(6)
C(15)-C(16)	1.397(6)
C(16)-C(17)	1.386(7)
C(17)-C(18)	1.368(8)
C(18)-C(19)	1.363(8)
C(19)-C(20)	1.369(6)
N(1)-Au(1)-Cl(2)	**176.64(9)**

N(1)-Au(1)-Cl(3)	**89.17(10)**
Cl(2)-Au(1)-Cl(3)	**90.60(5)**
N(1)-Au(1)-Cl(1)	**90.33(10)**
Cl(2)-Au(1)-Cl(1)	**89.66(4)**
Cl(3)-Au(1)-Cl(1)	**175.90(4)**
N(1)-Au(1)-N(2)	**70.51(12)**
Cl(2)-Au(1)-N(2)	**112.85(8)**
Cl(3)-Au(1)-N(2)	**90.89(9)**
Cl(1)-Au(1)-N(2)	**92.77(9)**
C(1)-N(1)-C(5)	120.3(4)
C(1)-N(1)-Au(1)	115.0(3)
C(5)-N(1)-Au(1)	124.7(3)
C(6)-N(2)-C(7)	118.6(4)
C(6)-N(2)-Au(1)	108.2(3)
C(7)-N(2)-Au(1)	132.8(3)
N(1)-C(1)-C(2)	122.5(4)
C(3)-C(2)-C(1)	118.7(4)
C(2)-C(3)-C(4)	119.0(4)
C(5)-C(4)-C(3)	121.4(4)
N(1)-C(5)-C(4)	118.1(4)
N(1)-C(5)-C(6)	119.2(4)
C(4)-C(5)-C(6)	122.6(4)
N(2)-C(6)-C(14)	122.5(4)
N(2)-C(6)-C(5)	117.0(4)
C(14)-C(6)-C(5)	120.5(4)
N(2)-C(7)-C(8)	117.1(4)
N(2)-C(7)-C(12)	123.4(4)
C(8)-C(7)-C(12)	119.5(4)
C(9)-C(8)-C(7)	120.3(4)
C(8)-C(9)-C(10)	121.1(4)
C(11)-C(10)-C(9)	119.3(4)
C(11)-C(10)-C(21)	121.6(4)
C(9)-C(10)-C(21)	119.1(4)
C(10)-C(11)-C(12)	121.8(4)

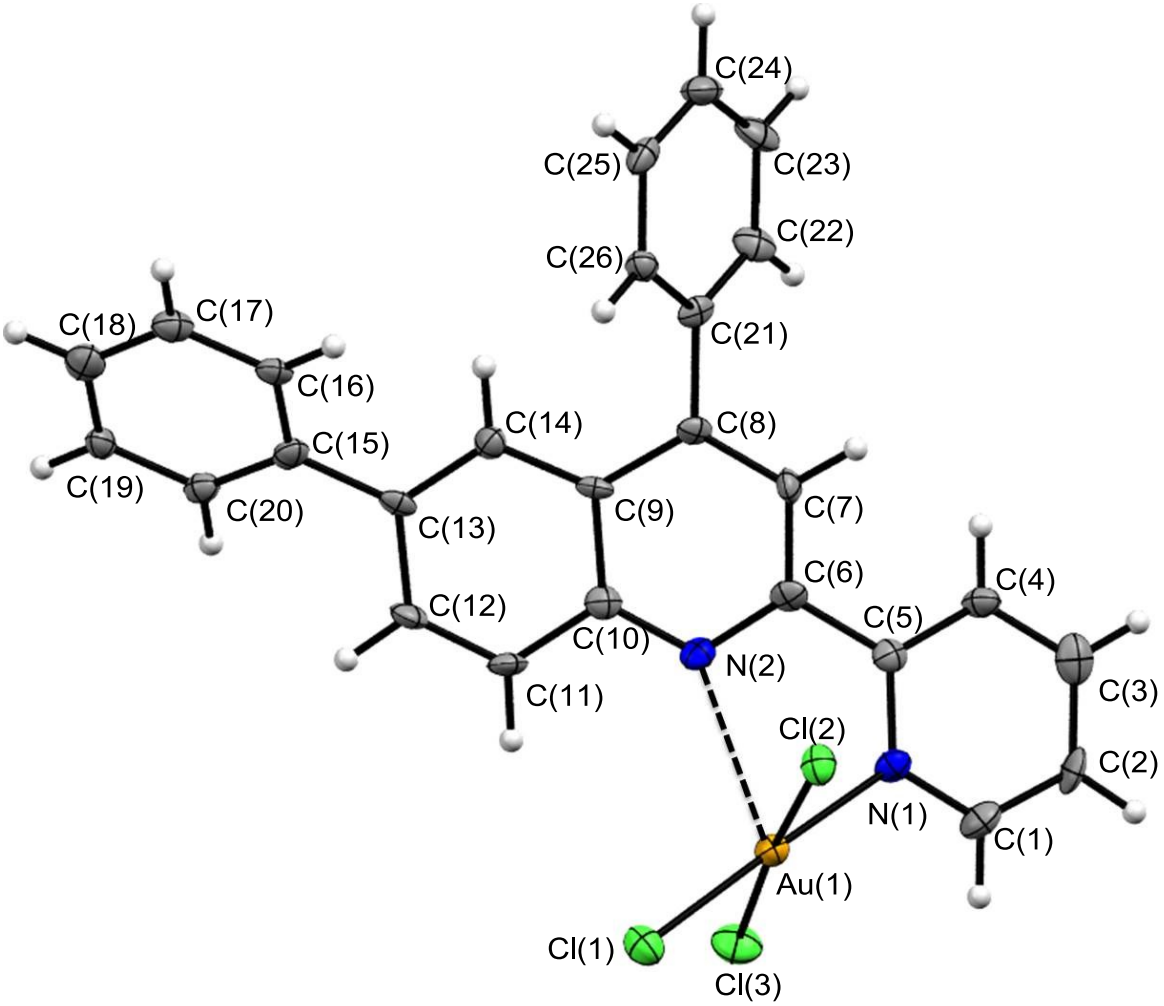
C(11)-C(12)-C(13)	124.8(4)
C(11)-C(12)-C(7)	118.0(4)
C(13)-C(12)-C(7)	117.2(4)
C(14)-C(13)-C(12)	117.5(4)
C(14)-C(13)-C(15)	118.5(4)
C(12)-C(13)-C(15)	124.0(4)
C(13)-C(14)-C(6)	120.8(4)
C(20)-C(15)-C(16)	118.2(4)
C(20)-C(15)-C(13)	119.8(4)
C(16)-C(15)-C(13)	122.0(4)
C(17)-C(16)-C(15)	119.5(5)
C(18)-C(17)-C(16)	121.1(5)
C(19)-C(18)-C(17)	119.4(5)
C(18)-C(19)-C(20)	120.6(5)
C(19)-C(20)-C(15)	121.2(4)

Anisotropic displacement parameters ($Å^2$ x 10^3) for (6-methyl-PyQuin)$AuCl_3$ (**2b**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	27(1)	24(1)	15(1)	3(1)	9(1)	8(1)
Cl(1)	41(1)	32(1)	33(1)	14(1)	19(1)	18(1)
Cl(2)	36(1)	49(1)	32(1)	16(1)	21(1)	17(1)
Cl(3)	68(1)	34(1)	34(1)	15(1)	23(1)	27(1)
N(1)	23(2)	21(2)	15(2)	5(1)	5(1)	9(1)
N(2)	29(2)	27(2)	17(2)	4(2)	7(2)	10(2)
C(1)	30(2)	26(2)	21(2)	5(2)	5(2)	7(2)
C(2)	25(2)	29(2)	29(3)	4(2)	0(2)	6(2)
C(3)	25(2)	34(3)	33(3)	11(2)	12(2)	10(2)
C(4)	31(2)	27(2)	22(2)	4(2)	12(2)	11(2)
C(5)	28(2)	23(2)	15(2)	5(2)	7(2)	13(2)
C(6)	27(2)	22(2)	17(2)	4(2)	6(2)	10(2)
C(7)	27(2)	24(2)	18(2)	6(2)	6(2)	10(2)
C(8)	33(2)	29(2)	23(2)	1(2)	10(2)	11(2)
C(9)	27(2)	36(3)	30(3)	7(2)	13(2)	11(2)
C(10)	29(2)	27(2)	29(3)	5(2)	6(2)	10(2)
C(11)	28(2)	30(2)	21(2)	2(2)	5(2)	9(2)
C(12)	29(2)	24(2)	18(2)	6(2)	7(2)	10(2)
C(13)	32(2)	24(2)	17(2)	6(2)	9(2)	12(2)
C(14)	27(2)	28(2)	19(2)	4(2)	10(2)	11(2)
C(15)	26(2)	26(2)	18(2)	3(2)	5(2)	10(2)
C(16)	36(2)	27(2)	26(3)	5(2)	12(2)	6(2)
C(17)	53(3)	27(3)	37(3)	-7(2)	12(3)	3(2)
C(18)	61(4)	43(3)	28(3)	-9(2)	20(3)	9(3)
C(19)	56(3)	44(3)	26(3)	5(2)	22(2)	14(3)
C(20)	43(3)	27(2)	24(3)	5(2)	14(2)	8(2)
C(21)	30(2)	45(3)	45(3)	-6(3)	9(2)	9(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (6-methyl-PyQuin)$AuCl_3$ (**2b**).

	x	y	z	U(eq)
H(1)	3124	3945	1113	32
H(2)	720	3581	1804	36
H(3)	833	4675	3832	36
H(16)	3348	6156	5093	31
H(15)	10426	7100	3587	34
H(14)	13029	8500	4642	37
H(10)	11244	9960	7490	33
H(4)	5493	7650	6078	29
H(9)	9359	11103	7543	37
H(8)	9098	12404	9355	52
H(7)	7738	11540	10684	57
H(6)	6518	9368	10169	50
H(5)	6661	8054	8346	38
H(12)	14126	11144	6896	66
H(11)	14906	10061	6380	66
H(13)	14443	10191	7686	66



(6-phenyl-PyQuin)$AuCl_3$ (**2c**)

(Thermal ellipsoids shown at 50% probability)

Table 6. Crystal data & structure refinement for (6-phenyl-PyQuin)$AuCl_3$ (**2c**).

Formula	$C_{26}H_{18}N_2AuCl_3$
Formula weight	661.74
Temperature	100(2) K
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
a, Å	9.2431(16)
b, Å	17.093(3)
c, Å	14.727(3)
α, °	90
β, °	99.481(5)
γ, °	90
Volume	2294.9(7) $Å^3$
Z,	4
Calculated density, Mg/m^3	1.915
Absorption coefficient, mm^{-1}	6.777
F(000)	1272
Crystal size, mm^3	0.18 x 0.07 x 0.07
Theta range for data collection, deg	1.84 to 26.43
Index ranges	$-11 \leq h \leq 11$, $-21 \leq k \leq 21$, $-18 \leq l \leq 18$
Reflections collected / unique	22596
Independent reflections	4722 [R(int)=0.0900]
Completeness to θ = 25.00°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4722 / 0 / 289
Goodness-of-fit on F^2	1.004
Final *R* indices [I>2σ(I)]	*R*1 = 0.0379, *wR*2 = 0.0610
R indices (all data)	*R*1 = 0.0720, *wR*2 = 0.0693
Extinction coefficient	n/a
Largest diff. peak and hole, $eÅ^3$	1.263 and -1.159

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (6-phenyl-PyQuin)$AuCl_3$ (**2c**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	5485(1)	685(1)	2644(1)	18(1)
Cl(1)	6028(2)	-153(1)	3850(1)	27(1)
Cl(2)	6902(2)	1624(1)	3462(1)	22(1)
Cl(3)	4213(2)	-272(1)	1763(1)	30(1)
N(1)	5092(5)	1456(3)	1555(4)	19(1)
N(2)	3142(5)	1624(3)	2801(3)	18(1)
C(1)	5728(7)	1315(4)	825(4)	25(2)
C(2)	5749(7)	1844(4)	133(4)	24(2)
C(3)	5055(7)	2555(4)	184(5)	26(2)
C(4)	4328(7)	2692(4)	922(4)	20(2)
C(5)	4337(6)	2141(4)	1612(4)	18(2)
C(6)	3526(6)	2272(4)	2388(4)	17(2)
C(7)	3138(6)	3020(4)	2642(4)	16(1)
C(8)	2289(6)	3122(3)	3312(4)	15(1)
C(9)	1817(6)	2451(3)	3761(4)	13(1)
C(10)	2339(6)	1705(4)	3481(4)	18(2)
C(11)	1948(6)	1018(4)	3920(4)	19(2)
C(12)	1095(6)	1065(4)	4593(4)	20(2)
C(13)	534(6)	1784(3)	4867(4)	14(1)
C(14)	891(6)	2449(4)	4433(4)	17(2)
C(15)	-387(6)	1809(4)	5588(4)	19(2)
C(16)	-213(6)	2415(3)	6240(4)	17(2)
C(17)	-1059(7)	2433(4)	6939(5)	22(2)
C(18)	-2083(7)	1847(4)	7009(5)	25(2)
C(19)	-2268(6)	1253(4)	6362(4)	18(2)
C(20)	-1435(6)	1233(4)	5667(4)	18(2)
C(21)	1839(6)	3929(4)	3553(4)	16(2)
C(22)	1180(7)	4420(3)	2850(5)	22(2)

C(23)	743(7)	5167(4)	3050(5)	27(2)
C(24)	955(7)	5423(4)	3941(5)	26(2)
C(25)	1610(6)	4944(4)	4654(5)	21(2)
C(26)	2062(6)	4204(3)	4449(4)	17(1)

Bond lengths [Å] and angles [°] for (6-phenyl-PyQuin)$AuCl_3$ (**2c**).

Au(1)-N(1)	**2.061(5)**
Au(1)-Cl(1)	**2.2727(17)**
Au(1)-Cl(2)	**2.2850(15)**
Au(1)-Cl(3)	**2.2884(16)**
Au(1)-N(2)	**2.736(5)**
N(1)-C(1)	1.330(8)
N(1)-C(5)	1.372(7)
N(2)-C(6)	1.338(7)
N(2)-C(10)	1.349(8)
C(1)-C(2)	1.365(8)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.383(9)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.389(9)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.385(8)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.484(9)
C(6)-C(7)	1.396(8)
C(7)-C(8)	1.369(8)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.427(8)
C(8)-C(21)	1.500(8)

C(9)-C(14)	1.411(8)
C(9)-C(10)	1.447(8)
C(10)-C(11)	1.416(8)
C(11)-C(12)	1.366(9)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.419(8)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.370(8)
C(13)-C(15)	1.467(9)
C(14)-H(14A)	0.9500
C(15)-C(20)	1.399(8)
C(15)-C(16)	1.402(8)
C(16)-C(17)	1.393(9)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.394(8)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.384(8)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.379(8)
C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9500
C(21)-C(26)	1.384(8)
C(21)-C(22)	1.393(8)
C(22)-C(23)	1.386(8)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.367(9)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.389(9)
C(24)-H(24A)	0.9500
C(25)-C(26)	1.381(8)
C(25)-H(25A)	0.9500
C(26)-H(26A)	0.9500

N(1)-Au(1)-Cl(1)	**177.43(14)**
N(1)-Au(1)-Cl(2)	**88.46(14)**
Cl(1)-Au(1)-Cl(2)	**89.82(6)**
N(1)-Au(1)-Cl(3)	**90.46(14)**
Cl(1)-Au(1)-Cl(3)	**91.10(6)**
Cl(2)-Au(1)-Cl(3)	**175.57(7)**
N(1)-Au(1)-N(2)	**69.49(18)**
Cl(1)-Au(1)-N(2)	**112.31(12)**
Cl(2)-Au(1)-N(2)	**86.33(11)**
Cl(3)-Au(1)-N(2)	**97.32(11)**
C(1)-N(1)-C(5)	120.0(6)
C(1)-N(1)-Au(1)	117.9(4)
C(5)-N(1)-Au(1)	121.6(4)
C(6)-N(2)-C(10)	118.2(5)
C(6)-N(2)-Au(1)	100.0(4)
C(10)-N(2)-Au(1)	131.5(4)
N(1)-C(1)-C(2)	123.2(6)
N(1)-C(1)-H(1A)	118.4
C(2)-C(1)-H(1A)	118.4
C(1)-C(2)-C(3)	118.5(7)
C(1)-C(2)-H(2A)	120.8
C(3)-C(2)-H(2A)	120.8
C(2)-C(3)-C(4)	118.7(6)
C(2)-C(3)-H(3A)	120.7
C(4)-C(3)-H(3A)	120.7
C(5)-C(4)-C(3)	120.9(6)
C(5)-C(4)-H(4A)	119.5
C(3)-C(4)-H(4A)	119.5
N(1)-C(5)-C(4)	118.5(6)
N(1)-C(5)-C(6)	120.2(6)
C(4)-C(5)-C(6)	121.3(6)
N(2)-C(6)-C(7)	122.4(6)
N(2)-C(6)-C(5)	115.5(6)
C(7)-C(6)-C(5)	122.0(6)

C(8)-C(7)-C(6)	120.9(6)
C(8)-C(7)-H(7A)	119.6
C(6)-C(7)-H(7A)	119.6
C(7)-C(8)-C(9)	119.1(6)
C(7)-C(8)-C(21)	120.1(6)
C(9)-C(8)-C(21)	120.8(6)
C(14)-C(9)-C(8)	126.5(6)
C(14)-C(9)-C(10)	117.8(6)
C(8)-C(9)-C(10)	115.8(6)
N(2)-C(10)-C(11)	117.9(6)
N(2)-C(10)-C(9)	123.5(6)
C(11)-C(10)-C(9)	118.6(6)
C(12)-C(11)-C(10)	120.2(6)
C(12)-C(11)-H(11A)	119.9
C(10)-C(11)-H(11A)	119.9
C(11)-C(12)-C(13)	122.6(6)
C(11)-C(12)-H(12A)	118.7
C(13)-C(12)-H(12A)	118.7
C(14)-C(13)-C(12)	117.2(6)
C(14)-C(13)-C(15)	121.8(6)
C(12)-C(13)-C(15)	120.9(6)
C(13)-C(14)-C(9)	123.4(6)
C(13)-C(14)-H(14A)	118.3
C(9)-C(14)-H(14A)	118.3
C(20)-C(15)-C(16)	117.8(6)
C(20)-C(15)-C(13)	122.1(6)
C(16)-C(15)-C(13)	120.1(6)
C(17)-C(16)-C(15)	120.5(6)
C(17)-C(16)-H(16A)	119.7
C(15)-C(16)-H(16A)	119.7
C(16)-C(17)-C(18)	120.6(6)
C(16)-C(17)-H(17A)	119.7
C(18)-C(17)-H(17A)	119.7
C(19)-C(18)-C(17)	119.0(7)

C(19)-C(18)-H(18A)	120.5
C(17)-C(18)-H(18A)	120.5
C(20)-C(19)-C(18)	120.6(6)
C(20)-C(19)-H(19A)	119.7
C(18)-C(19)-H(19A)	119.7
C(19)-C(20)-C(15)	121.5(6)
C(19)-C(20)-H(20A)	119.2
C(15)-C(20)-H(20A)	119.2
C(26)-C(21)-C(22)	118.8(6)
C(26)-C(21)-C(8)	122.3(6)
C(22)-C(21)-C(8)	118.8(6)
C(23)-C(22)-C(21)	120.3(6)
C(23)-C(22)-H(22A)	119.8
C(21)-C(22)-H(22A)	119.8
C(24)-C(23)-C(22)	119.9(6)
C(24)-C(23)-H(23A)	120.1
C(22)-C(23)-H(23A)	120.1
C(23)-C(24)-C(25)	120.8(6)
C(23)-C(24)-H(24A)	119.6
C(25)-C(24)-H(24A)	119.6
C(26)-C(25)-C(24)	119.0(6)
C(26)-C(25)-H(25A)	120.5
C(24)-C(25)-H(25A)	120.5
C(25)-C(26)-C(21)	121.1(6)
C(25)-C(26)-H(26A)	119.5
C(21)-C(26)-H(26A)	119.5

Anisotropic displacement parameters ($Å^2$ x 10^3) for (6-phenyl-PyQuin)$AuCl_3$ (**2c**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	18(1)	18(1)	19(1)	0(1)	4(1)	2(1)
Cl(1)	31(1)	24(1)	26(1)	4(1)	4(1)	-1(1)
Cl(2)	24(1)	24(1)	20(1)	0(1)	4(1)	-4(1)
Cl(3)	34(1)	23(1)	32(1)	-6(1)	-2(1)	-2(1)
N(1)	12(3)	22(3)	21(3)	0(3)	1(2)	3(2)
N(2)	17(3)	18(3)	18(3)	-5(2)	3(2)	-2(2)
C(1)	25(4)	29(4)	22(4)	-7(3)	7(3)	3(3)
C(2)	23(4)	38(5)	11(4)	-1(3)	9(3)	-2(3)
C(3)	19(4)	36(4)	22(4)	1(3)	-2(3)	-10(3)
C(4)	21(4)	18(4)	20(4)	0(3)	2(3)	6(3)
C(5)	15(3)	16(4)	22(4)	-4(3)	2(3)	-4(3)
C(6)	13(3)	20(4)	15(3)	2(3)	-3(3)	5(3)
C(7)	18(3)	15(3)	18(4)	2(3)	7(3)	-5(3)
C(8)	7(3)	14(4)	22(4)	0(3)	-1(3)	1(3)
C(9)	14(3)	8(3)	15(3)	-2(3)	-4(3)	3(3)
C(10)	14(3)	17(4)	22(4)	-3(3)	0(3)	-2(3)
C(11)	16(3)	12(3)	30(4)	-4(3)	4(3)	5(3)
C(12)	21(4)	8(3)	30(4)	1(3)	3(3)	0(3)
C(13)	12(3)	11(3)	17(3)	2(3)	-5(3)	2(3)
C(14)	17(3)	19(4)	16(4)	2(3)	3(3)	2(3)
C(15)	16(3)	21(4)	21(4)	2(3)	4(3)	7(3)
C(16)	16(3)	13(3)	22(4)	0(3)	1(3)	4(3)
C(17)	18(4)	18(4)	29(4)	-2(3)	1(3)	2(3)
C(18)	23(4)	27(4)	24(4)	6(3)	2(3)	7(3)
C(19)	14(3)	15(4)	25(4)	3(3)	5(3)	0(3)
C(20)	18(3)	18(4)	17(4)	0(3)	2(3)	4(3)
C(21)	6(3)	17(3)	24(4)	-7(3)	1(3)	-3(3)
C(22)	20(3)	16(4)	28(4)	-3(3)	-2(3)	-4(3)

C(23)	23(4)	13(4)	43(5)	4(3)	0(3)	-4(3)
C(24)	23(4)	16(4)	40(5)	-2(3)	10(3)	4(3)
C(25)	18(3)	24(4)	23(4)	-8(3)	10(3)	-6(3)
C(26)	15(3)	16(4)	20(3)	2(3)	3(3)	1(3)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (6-phenyl-PyQuin)$AuCl_3$ (**2c**).

	x	y	z	U(eq)
H(1A)	6190	823	783	30
H(2A)	6230	1726	-373	28
H(3A)	5075	2943	-276	31
H(4A)	3817	3171	954	24
H(7A)	3466	3464	2346	20
H(11A)	2280	522	3747	23
H(12A)	868	597	4888	24
H(14A)	494	2933	4592	21
H(16A)	487	2815	6203	21
H(17A)	-936	2849	7373	26
H(18A)	-2647	1855	7493	30
H(19A)	-2974	855	6397	22
H(20A)	-1576	819	5231	21
H(22A)	1031	4242	2231	26
H(23A)	296	5501	2568	32
H(24A)	651	5935	4075	31
H(25A)	1745	5123	5273	25
H(26A)	2534	3879	4932	21

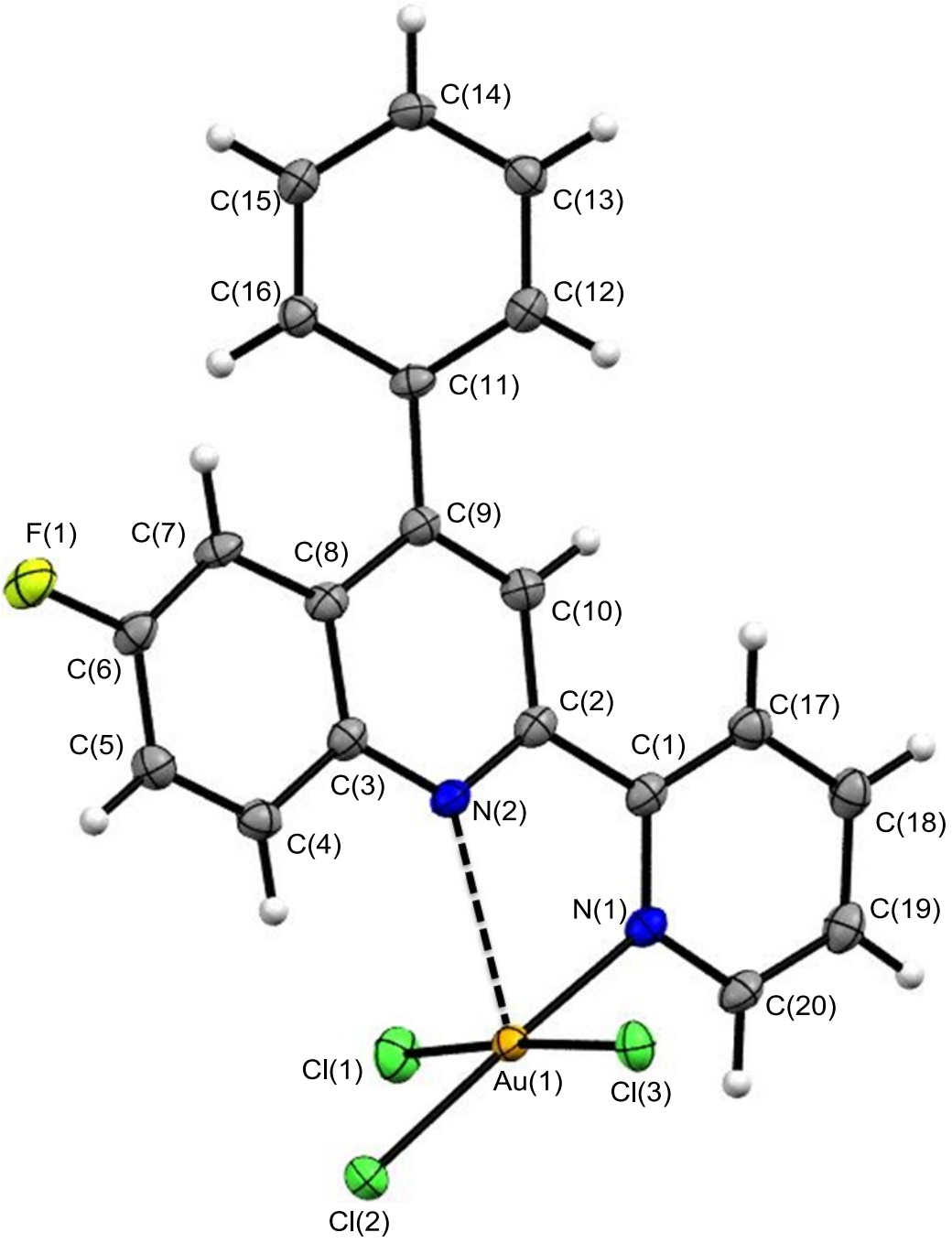
Torsion angles [°] for (6-phenyl-PyQuin)$AuCl_3$ (**2c**).

Cl(1)-Au(1)-N(1)-C(1)	60(4)
Cl(2)-Au(1)-N(1)-C(1)	108.1(4)
Cl(3)-Au(1)-N(1)-C(1)	-67.6(4)
N(2)-Au(1)-N(1)-C(1)	-165.2(5)
Cl(1)-Au(1)-N(1)-C(5)	-113(3)
Cl(2)-Au(1)-N(1)-C(5)	-64.7(4)
Cl(3)-Au(1)-N(1)-C(5)	119.6(4)
N(2)-Au(1)-N(1)-C(5)	22.0(4)
N(1)-Au(1)-N(2)-C(6)	-30.5(4)
Cl(1)-Au(1)-N(2)-C(6)	147.6(3)
Cl(2)-Au(1)-N(2)-C(6)	59.3(3)
Cl(3)-Au(1)-N(2)-C(6)	-118.2(3)
N(1)-Au(1)-N(2)-C(10)	-173.3(5)
Cl(1)-Au(1)-N(2)-C(10)	4.7(5)
Cl(2)-Au(1)-N(2)-C(10)	-83.6(5)
Cl(3)-Au(1)-N(2)-C(10)	98.9(5)
C(5)-N(1)-C(1)-C(2)	4.0(9)
Au(1)-N(1)-C(1)-C(2)	-168.9(5)
N(1)-C(1)-C(2)-C(3)	-1.2(10)
C(1)-C(2)-C(3)-C(4)	-2.0(9)
C(2)-C(3)-C(4)-C(5)	2.2(9)
C(1)-N(1)-C(5)-C(4)	-3.6(8)
Au(1)-N(1)-C(5)-C(4)	169.0(4)
C(1)-N(1)-C(5)-C(6)	175.1(5)
Au(1)-N(1)-C(5)-C(6)	-12.3(7)
C(3)-C(4)-C(5)-N(1)	0.5(9)
C(3)-C(4)-C(5)-C(6)	-178.1(5)
C(10)-N(2)-C(6)-C(7)	0.6(8)
Au(1)-N(2)-C(6)-C(7)	-148.6(5)
C(10)-N(2)-C(6)-C(5)	-176.7(5)
Au(1)-N(2)-C(6)-C(5)	34.1(5)
N(1)-C(5)-C(6)-N(2)	-23.1(8)

C(4)-C(5)-C(6)-N(2)	155.6(5)
N(1)-C(5)-C(6)-C(7)	159.6(5)
C(4)-C(5)-C(6)-C(7)	-21.7(8)
N(2)-C(6)-C(7)-C(8)	-2.4(9)
C(5)-C(6)-C(7)-C(8)	174.7(5)
C(6)-C(7)-C(8)-C(9)	0.8(8)
C(6)-C(7)-C(8)-C(21)	-177.9(5)
C(7)-C(8)-C(9)-C(14)	-177.0(6)
C(21)-C(8)-C(9)-C(14)	1.7(9)
C(7)-C(8)-C(9)-C(10)	2.2(8)
C(21)-C(8)-C(9)-C(10)	-179.1(5)
C(6)-N(2)-C(10)-C(11)	-179.4(5)
Au(1)-N(2)-C(10)-C(11)	-41.8(8)
C(6)-N(2)-C(10)-C(9)	2.8(8)
Au(1)-N(2)-C(10)-C(9)	140.4(5)
C(14)-C(9)-C(10)-N(2)	175.1(5)
C(8)-C(9)-C(10)-N(2)	-4.2(8)
C(14)-C(9)-C(10)-C(11)	-2.6(8)
C(8)-C(9)-C(10)-C(11)	178.1(5)
N(2)-C(10)-C(11)-C(12)	-177.9(5)
C(9)-C(10)-C(11)-C(12)	0.0(9)
C(10)-C(11)-C(12)-C(13)	1.6(9)
C(11)-C(12)-C(13)-C(14)	-0.5(9)
C(11)-C(12)-C(13)-C(15)	179.6(6)
C(12)-C(13)-C(14)-C(9)	-2.3(9)
C(15)-C(13)-C(14)-C(9)	177.6(5)
C(8)-C(9)-C(14)-C(13)	-176.9(5)
C(10)-C(9)-C(14)-C(13)	3.9(9)
C(14)-C(13)-C(15)-C(20)	141.6(6)
C(12)-C(13)-C(15)-C(20)	-38.4(8)
C(14)-C(13)-C(15)-C(16)	-39.6(8)
C(12)-C(13)-C(15)-C(16)	140.3(6)
C(20)-C(15)-C(16)-C(17)	0.3(8)
C(13)-C(15)-C(16)-C(17)	-178.5(5)

C(15)-C(16)-C(17)-C(18)	0.5(9)
C(16)-C(17)-C(18)-C(19)	-1.1(9)
C(17)-C(18)-C(19)-C(20)	1.0(9)
C(18)-C(19)-C(20)-C(15)	-0.3(9)
C(16)-C(15)-C(20)-C(19)	-0.4(9)
C(13)-C(15)-C(20)-C(19)	178.4(5)
C(7)-C(8)-C(21)-C(26)	-127.9(7)
C(9)-C(8)-C(21)-C(26)	53.4(8)
C(7)-C(8)-C(21)-C(22)	51.7(8)
C(9)-C(8)-C(21)-C(22)	-127.0(6)
C(26)-C(21)-C(22)-C(23)	-0.8(9)
C(8)-C(21)-C(22)-C(23)	179.6(6)
C(21)-C(22)-C(23)-C(24)	-0.1(10)
C(22)-C(23)-C(24)-C(25)	0.2(10)
C(23)-C(24)-C(25)-C(26)	0.7(10)
C(24)-C(25)-C(26)-C(21)	-1.7(9)
C(22)-C(21)-C(26)-C(25)	1.7(9)
C(8)-C(21)-C(26)-C(25)	-178.7(5)

Symmetry transformations used to generate equivalent atoms:



(6-fluoro-PyQuin)$AuCl_3$ (**2d**)

(Thermal ellipsoids shown at 50% probability)

Table 7. Crystal data & structure refinement for (6-fluoro-PyQuin)$AuCl_3$ (**2d**).

Formula	$C_{20}H_{13}N_2FAuCl_3$
Formula weight	603.64
Temperature	100(2) K
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	C 2/c
a, Å	19.3904(8)
b, Å	13.6914(6)
c, Å	15.9497(5)
α, °	90
β, °	116.7360(10)
γ, °	90
Volume	3781.7(3) $Å^3$
Z,	8
Calculated density, Mg/m^3	2.120
Absorption coefficient, mm^{-1}	8.221
F(000)	2288
Crystal size, mm^3	0.240 x 0.200 x 0.120
Theta range for data collection, deg	1.896 to 28.336
Index ranges	$-25 \leq h \leq 25$, $-17 \leq k \leq 18$, $-21 \leq l \leq 16$
Reflections collected / unique	17528
Independent reflections	4710 [R(int)=0.0347]
Completeness to θ = 25.00°	99.9 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4710 / 0 / 244
Goodness-of-fit on F^2	1.037
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0221, *wR*2 = 0.0519
R indices (all data)	*R*1 = 0.0261, *wR*2 = 0.0538
Extinction coefficient	n/a
Largest diff. peak and hole, $eÅ^3$	1.630 and -1.198

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (6-fluoro-PyQuin)$AuCl_3$ (**2d**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	786(1)	1308(1)	5572(1)	17(1)
Cl(1)	-455(1)	1451(1)	4424(1)	27(1)
Cl(2)	361(1)	1172(1)	6677(1)	22(1)
Cl(3)	2026(1)	1022(1)	6705(1)	22(1)
F(1)	824(1)	6467(1)	7082(1)	30(1)
N(1)	1168(2)	1373(2)	4557(2)	19(1)
N(2)	1145(2)	3127(2)	5406(2)	19(1)
C(1)	1430(2)	2201(2)	4321(2)	18(1)
C(2)	1360(2)	3154(2)	4732(2)	18(1)
C(3)	1073(2)	3986(2)	5793(2)	18(1)
C(4)	852(2)	3926(2)	6531(2)	21(1)
C(5)	768(2)	4754(2)	6949(2)	21(1)
C(6)	908(2)	5657(2)	6646(2)	21(1)
C(7)	1141(2)	5763(2)	5959(2)	20(1)
C(8)	1213(2)	4919(2)	5496(2)	18(1)
C(9)	1442(2)	4927(2)	4758(2)	18(1)
C(10)	1511(2)	4045(2)	4390(2)	19(1)
C(11)	1630(2)	5843(2)	4398(2)	18(1)
C(12)	2282(2)	5855(2)	4239(2)	20(1)
C(13)	2477(2)	6682(2)	3888(2)	21(1)
C(14)	2010(2)	7501(2)	3667(2)	21(1)
C(15)	1355(2)	7494(2)	3810(2)	22(1)
C(16)	1160(2)	6673(2)	4169(2)	19(1)
C(17)	1744(2)	2130(2)	3695(2)	21(1)
C(18)	1774(2)	1242(2)	3295(2)	23(1)
C(19)	1479(2)	419(2)	3524(2)	24(1)
C(20)	1183(2)	509(2)	4163(2)	22(1)

Bond lengths [Å] and angles [°] for (6-fluoro-PyQuin)$AuCl_3$ (**2d**).

Au(1)-N(1)	2.064(3)
Au(1)-Cl(2)	2.2647(7)
Au(1)-Cl(1)	2.2834(8)
Au(1)-Cl(3)	2.3011(8)
Au(1)-N(2)	2.633(2)
F(1)-C(6)	1.358(3)
N(1)-C(20)	1.346(4)
N(1)-C(1)	1.363(4)
N(2)-C(2)	1.316(4)
N(2)-C(3)	1.365(4)
C(1)-C(17)	1.388(4)
C(1)-C(2)	1.493(4)
C(2)-C(10)	1.420(4)
C(3)-C(4)	1.423(4)
C(3)-C(8)	1.430(4)
C(4)-C(5)	1.362(4)
C(5)-C(6)	1.398(4)
C(6)-C(7)	1.367(4)
C(7)-C(8)	1.412(4)
C(8)-C(9)	1.432(4)
C(9)-C(10)	1.375(4)
C(9)-C(11)	1.493(4)
C(11)-C(12)	1.397(4)
C(11)-C(16)	1.398(4)
C(12)-C(13)	1.389(4)
C(13)-C(14)	1.383(4)
C(14)-C(15)	1.389(4)
C(15)-C(16)	1.389(4)
C(17)-C(18)	1.385(4)
C(18)-C(19)	1.386(4)
C(19)-C(20)	1.382(4)

N(1)-Au(1)-Cl(2)	177.76(7)
N(1)-Au(1)-Cl(1)	89.30(8)
Cl(2)-Au(1)-Cl(1)	90.62(3)
N(1)-Au(1)-Cl(3)	90.28(8)
Cl(2)-Au(1)-Cl(3)	89.60(3)
Cl(1)-Au(1)-Cl(3)	175.11(3)
N(1)-Au(1)-N(2)	71.02(8)
Cl(2)-Au(1)-N(2)	111.22(5)
Cl(1)-Au(1)-N(2)	93.95(6)
Cl(3)-Au(1)-N(2)	90.52(6)
C(20)-N(1)-C(1)	120.9(3)
C(20)-N(1)-Au(1)	114.8(2)
C(1)-N(1)-Au(1)	124.26(19)
C(2)-N(2)-C(3)	118.8(2)
C(2)-N(2)-Au(1)	107.71(18)
C(3)-N(2)-Au(1)	133.11(19)
N(1)-C(1)-C(17)	118.6(3)
N(1)-C(1)-C(2)	119.1(3)
C(17)-C(1)-C(2)	122.3(3)
N(2)-C(2)-C(10)	122.3(3)
N(2)-C(2)-C(1)	117.3(3)
C(10)-C(2)-C(1)	120.4(3)
N(2)-C(3)-C(4)	117.1(3)
N(2)-C(3)-C(8)	123.0(2)
C(4)-C(3)-C(8)	119.9(3)
C(5)-C(4)-C(3)	120.2(3)
C(4)-C(5)-C(6)	118.8(3)
F(1)-C(6)-C(7)	118.9(3)
F(1)-C(6)-C(5)	117.2(2)
C(7)-C(6)-C(5)	123.9(3)
C(6)-C(7)-C(8)	118.5(3)
C(7)-C(8)-C(3)	118.6(2)
C(7)-C(8)-C(9)	124.3(3)
C(3)-C(8)-C(9)	117.0(3)

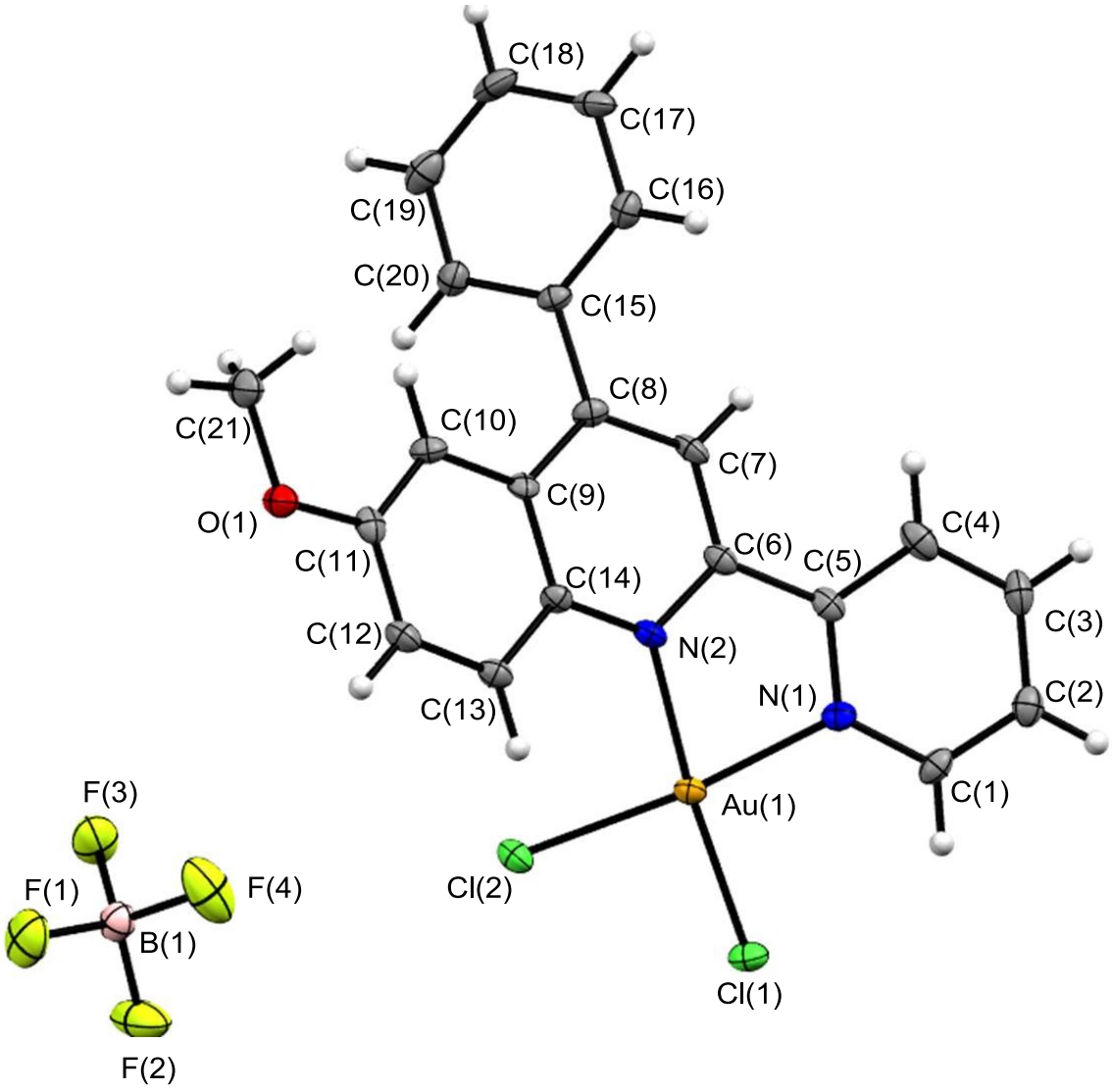
C(10)-C(9)-C(8)	118.1(3)
C(10)-C(9)-C(11)	119.1(2)
C(8)-C(9)-C(11)	122.9(3)
C(9)-C(10)-C(2)	120.9(3)
C(12)-C(11)-C(16)	118.7(3)
C(12)-C(11)-C(9)	118.5(3)
C(16)-C(11)-C(9)	122.7(3)
C(13)-C(12)-C(11)	120.9(3)
C(14)-C(13)-C(12)	119.9(3)
C(13)-C(14)-C(15)	119.7(3)
C(16)-C(15)-C(14)	120.8(3)
C(15)-C(16)-C(11)	119.9(3)
C(18)-C(17)-C(1)	121.0(3)
C(17)-C(18)-C(19)	119.0(3)
C(20)-C(19)-C(18)	118.6(3)
N(1)-C(20)-C(19)	121.8(3)

Anisotropic displacement parameters ($Å^2$ x 10^3) for (6-fluoro-PyQuin)$AuCl_3$ (**2d**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	16(1)	13(1)	21(1)	-1(1)	8(1)	0(1)
Cl(1)	17(1)	31(1)	28(1)	0(1)	5(1)	2(1)
Cl(2)	21(1)	22(1)	27(1)	0(1)	14(1)	-1(1)
Cl(3)	17(1)	26(1)	21(1)	-1(1)	8(1)	3(1)
F(1)	48(1)	20(1)	26(1)	-4(1)	21(1)	2(1)
N(1)	20(1)	15(1)	18(1)	-2(1)	6(1)	-1(1)
N(2)	21(1)	14(1)	21(1)	0(1)	9(1)	0(1)
C(1)	15(2)	17(1)	18(1)	0(1)	3(1)	1(1)
C(2)	17(2)	16(1)	19(1)	-1(1)	4(1)	1(1)
C(3)	16(2)	18(1)	17(1)	0(1)	4(1)	1(1)
C(4)	19(2)	21(1)	22(1)	2(1)	8(1)	-1(1)
C(5)	22(2)	23(2)	19(1)	0(1)	9(1)	0(1)
C(6)	26(2)	17(1)	20(1)	-2(1)	10(1)	2(1)
C(7)	26(2)	12(1)	20(1)	-2(1)	8(1)	-3(1)
C(8)	16(2)	17(1)	18(1)	-2(1)	5(1)	-2(1)
C(9)	18(2)	16(1)	19(1)	1(1)	7(1)	0(1)
C(10)	19(2)	19(1)	18(1)	0(1)	7(1)	-1(1)
C(11)	21(2)	13(1)	17(1)	-2(1)	7(1)	-3(1)
C(12)	20(2)	18(1)	19(1)	-1(1)	7(1)	2(1)
C(13)	19(2)	24(2)	23(1)	2(1)	11(1)	-1(1)
C(14)	24(2)	18(1)	23(1)	4(1)	11(1)	-1(1)
C(15)	23(2)	17(1)	25(1)	0(1)	11(1)	3(1)
C(16)	17(2)	19(1)	21(1)	0(1)	7(1)	0(1)
C(17)	21(2)	21(2)	21(1)	2(1)	9(1)	1(1)
C(18)	26(2)	24(2)	20(1)	-2(1)	11(1)	3(1)
C(19)	26(2)	21(2)	23(1)	-6(1)	9(1)	1(1)
C(20)	23(2)	15(1)	24(1)	-3(1)	8(1)	-2(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (6-fluoro-PyQuin)$AuCl_3$ (**2d**).

	x	y	z	U(eq)
H(9)	764	3306	6733	25
H(8)	616	4719	7438	26
H(7)	1252	6391	5797	24
H(1)	1662	4032	3900	23
H(6)	2597	5289	4373	23
H(5)	2930	6686	3800	26
H(4)	2137	8065	3418	26
H(3)	1036	8058	3660	26
H(2)	707	6674	4258	23
H(10)	1942	2699	3538	26
H(11)	1994	1199	2871	28
H(12)	1479	-195	3246	28
H(13)	985	-54	4329	26



[(6-methoxy-PyQuin)$AuCl_2$]BF_4 (**2e**)

(Thermal ellipsoids shown at 50% probability)

Solvent omitted for clarity

Table 8. Crystal data & structure refinement for [(6-methoxy-PyQuin)$AuCl_2$]BF_4 (**2e**).

Formula	$C_{22}H_{18}N_2OF_4AuCl_4B$
Formula weight	751.96
Temperature	100 K
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P 1 21/c 1
a, Å	9.0040(18)
b, Å	10.2139(19)
c, Å	26.530(6)
α, °	90
β, °	94.410(5)
γ, °	90
Volume	2432.6(8) Å^3
Z,	4
Calculated density, Mg/m^3	2.053
Absorption coefficient, mm^{-1}	6.538
F(000)	1440
Crystal size, mm^3	0.24 x 0.10 x 0.06
Theta range for data collection, deg	2.520 to 26.390
Index ranges	$-11 \leq h \leq 11$, $-6 \leq k \leq 12$, $-33 \leq l \leq 33$
Reflections collected / unique	12890
Independent reflections	4972 [R(int)=0.0324]
Completeness to θ = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4972 / 0 / 317
Goodness-of-fit on F^2	1.035
Final *R* indices [I>2σ(I)]	*R*1 = 0.0287, *wR*2 = 0.0619
R indices (all data)	*R*1 = 0.0380, *wR*2 = 0.0652
Extinction coefficient	n/a
Largest diff. peak and hole, eÅ^3	1.313 and -1.036

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [(6-methoxy-PyQuin)$AuCl_2$]BF_4 (**2e**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	8587(1)	6269(1)	5164(1)	13(1)
Cl(1)	9390(1)	4887(1)	5796(1)	20(1)
Cl(2)	6947(1)	4700(1)	4887(1)	18(1)
O(1)	2772(3)	8123(3)	3439(1)	20(1)
N(1)	10290(4)	7557(3)	5296(2)	15(1)
N(2)	8091(4)	7576(3)	4590(1)	14(1)
C(1)	11254(5)	7600(4)	5708(2)	17(1)
C(2)	12541(5)	8342(4)	5715(2)	19(1)
C(3)	12827(5)	9053(4)	5287(2)	20(1)
C(4)	11817(5)	9034(4)	4868(2)	20(1)
C(5)	10532(5)	8267(4)	4876(2)	15(1)
C(6)	9337(5)	8217(4)	4473(2)	15(1)
C(7)	9409(5)	8805(4)	4001(2)	15(1)
C(8)	8198(5)	8776(4)	3651(2)	14(1)
C(9)	6807(5)	8295(4)	3803(2)	13(1)
C(10)	5451(5)	8449(4)	3500(2)	15(1)
C(11)	4147(5)	8000(4)	3682(2)	16(1)
C(12)	4158(5)	7385(4)	4156(2)	17(1)
C(13)	5442(5)	7242(4)	4460(2)	16(1)
C(14)	6796(4)	7687(4)	4286(2)	13(1)
C(15)	8383(4)	9239(4)	3126(2)	14(1)
C(16)	9049(5)	10451(4)	3052(2)	18(1)
C(17)	9281(5)	10855(5)	2565(2)	22(1)
C(18)	8911(5)	10057(5)	2156(2)	26(1)
C(19)	8272(5)	8848(5)	2227(2)	25(1)
C(20)	7984(5)	8448(4)	2711(2)	18(1)
C(21)	2650(5)	8802(4)	2966(2)	23(1)
Cl(3)	4875(1)	5768(1)	2677(1)	27(1)
Cl(4)	7198(2)	4801(1)	3406(1)	45(1)
C(22)	5279(6)	4804(5)	3222(2)	32(1)
F(1)	1876(3)	1594(3)	3875(1)	40(1)
F(2)	3925(3)	753(3)	4294(2)	47(1)

F(3)	4122(3)	1679(3)	3528(1)	35(1)
F(4)	3714(4)	2939(3)	4202(2)	46(1)
B(1)	3402(6)	1744(6)	3974(2)	22(1)

Bond lengths [Å] and angles [°] for [(6-methoxy-PyQuin)$AuCl_2$]BF_4 (**2e**)

Au(1)-Cl(1)	2.2669(12)
Au(1)-Cl(2)	2.2627(11)
Au(1)-N(1)	2.030(4)
Au(1)-N(2)	2.048(4)
O(1)-C(11)	1.357(5)
O(1)-C(21)	1.433(6)
N(1)-C(1)	1.342(6)
N(1)-C(5)	1.363(6)
N(2)-C(6)	1.355(5)
N(2)-C(14)	1.371(6)
C(1)-H(1)	0.9500
C(1)-C(2)	1.383(6)
C(2)-H(2)	0.9500
C(2)-C(3)	1.389(7)
C(3)-H(3)	0.9500
C(3)-C(4)	1.381(7)
C(4)-H(4)	0.9500
C(4)-C(5)	1.398(6)
C(5)-C(6)	1.458(7)
C(6)-C(7)	1.394(6)
C(7)-H(7)	0.9500
C(7)-C(8)	1.377(7)
C(8)-C(9)	1.430(6)
C(8)-C(15)	1.494(6)
C(9)-C(10)	1.417(6)
C(9)-C(14)	1.425(6)
C(10)-H(10)	0.9500

C(10)-C(11)	1.382(6)
C(11)-C(12)	1.405(6)
C(12)-H(12)	0.9500
C(12)-C(13)	1.365(6)
C(13)-H(13)	0.9500
C(13)-C(14)	1.412(5)
C(15)-C(16)	1.397(6)
C(15)-C(20)	1.390(6)
C(16)-H(16)	0.9500
C(16)-C(17)	1.386(6)
C(17)-H(17)	0.9500
C(17)-C(18)	1.378(7)
C(18)-H(18)	0.9500
C(18)-C(19)	1.381(7)
C(19)-H(19)	0.9500
C(19)-C(20)	1.391(7)
C(20)-H(20)	0.9500
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
Cl(3)-C(22)	1.765(6)
Cl(4)-C(22)	1.758(5)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
F(1)-B(1)	1.388(6)
F(2)-B(1)	1.381(7)
F(3)-B(1)	1.393(6)
F(4)-B(1)	1.381(6)

Cl(2)-Au(1)-Cl(1)	87.80(4)
N(1)-Au(1)-Cl(1)	94.70(11)
N(1)-Au(1)-Cl(2)	168.62(10)
N(1)-Au(1)-N(2)	79.94(14)
N(2)-Au(1)-Cl(1)	173.96(10)
N(2)-Au(1)-Cl(2)	96.93(11)
C(11)-O(1)-C(21)	117.9(3)
C(1)-N(1)-Au(1)	126.5(3)
C(1)-N(1)-C(5)	121.0(4)

C(5)-N(1)-Au(1)	111.7(3)
C(6)-N(2)-Au(1)	110.4(3)
C(6)-N(2)-C(14)	120.4(4)
C(14)-N(2)-Au(1)	128.2(3)
N(1)-C(1)-H(1)	119.4
N(1)-C(1)-C(2)	121.2(4)
C(2)-C(1)-H(1)	119.4
C(1)-C(2)-H(2)	120.6
C(1)-C(2)-C(3)	118.9(5)
C(3)-C(2)-H(2)	120.6
C(2)-C(3)-H(3)	120.0
C(4)-C(3)-C(2)	119.9(4)
C(4)-C(3)-H(3)	120.0
C(3)-C(4)-H(4)	120.3
C(3)-C(4)-C(5)	119.4(5)
C(5)-C(4)-H(4)	120.3
N(1)-C(5)-C(4)	119.6(5)
N(1)-C(5)-C(6)	115.2(4)
C(4)-C(5)-C(6)	125.1(4)
N(2)-C(6)-C(5)	115.3(4)
N(2)-C(6)-C(7)	120.7(4)
C(7)-C(6)-C(5)	124.0(4)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-C(6)	120.4(4)
C(8)-C(7)-H(7)	119.8
C(7)-C(8)-C(9)	118.9(4)
C(7)-C(8)-C(15)	118.9(4)
C(9)-C(8)-C(15)	122.2(4)
C(10)-C(9)-C(8)	122.5(4)
C(10)-C(9)-C(14)	119.4(4)
C(14)-C(9)-C(8)	118.0(4)
C(9)-C(10)-H(10)	120.5
C(11)-C(10)-C(9)	118.9(4)
C(11)-C(10)-H(10)	120.5
O(1)-C(11)-C(10)	124.9(4)
O(1)-C(11)-C(12)	114.2(4)
C(10)-C(11)-C(12)	120.9(4)
C(11)-C(12)-H(12)	119.2

C(13)-C(12)-C(11)	121.6(4)
C(13)-C(12)-H(12)	119.2
C(12)-C(13)-H(13)	120.5
C(12)-C(13)-C(14)	119.0(4)
C(14)-C(13)-H(13)	120.5
N(2)-C(14)-C(9)	120.0(3)
N(2)-C(14)-C(13)	119.8(4)
C(13)-C(14)-C(9)	120.1(4)
C(16)-C(15)-C(8)	119.4(4)
C(20)-C(15)-C(8)	121.0(4)
C(20)-C(15)-C(16)	119.5(4)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-C(15)	119.4(5)
C(17)-C(16)-H(16)	120.3
C(16)-C(17)-H(17)	119.5
C(18)-C(17)-C(16)	120.9(4)
C(18)-C(17)-H(17)	119.5
C(17)-C(18)-H(18)	120.0
C(17)-C(18)-C(19)	119.9(5)
C(19)-C(18)-H(18)	120.0
C(18)-C(19)-H(19)	120.1
C(18)-C(19)-C(20)	119.8(5)
C(20)-C(19)-H(19)	120.1
C(15)-C(20)-C(19)	120.3(4)
C(15)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
O(1)-C(21)-H(21A)	109.5
O(1)-C(21)-H(21B)	109.5
O(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Cl(3)-C(22)-H(22A)	109.4
Cl(3)-C(22)-H(22B)	109.4
Cl(4)-C(22)-Cl(3)	111.4(3)
Cl(4)-C(22)-H(22A)	109.4
Cl(4)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0

F(1)-B(1)-F(3)	110.7(5)
F(2)-B(1)-F(1)	108.7(4)
F(2)-B(1)-F(3)	109.1(4)
F(2)-B(1)-F(4)	109.3(5)
F(4)-B(1)-F(1)	110.3(4)
F(4)-B(1)-F(3)	108

Anisotropic displacement parameters ($Å^2$ x 10^3) for [(6-methoxy-PyQuin)$AuCl_2$]BF_4 (**2e**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	13(1)	13(1)	14(1)	2(1)	3(1)	0(1)
Cl(1)	22(1)	20(1)	17(1)	6(1)	2(1)	2(1)
Cl(2)	17(1)	15(1)	24(1)	2(1)	3(1)	-3(1)
O(1)	12(1)	25(2)	23(2)	8(2)	-1(1)	-1(1)
N(1)	14(2)	15(2)	16(2)	2(2)	2(2)	3(1)
N(2)	14(2)	11(2)	16(2)	1(2)	5(2)	-1(1)
C(1)	17(2)	21(2)	14(3)	-1(2)	-1(2)	6(2)
C(2)	18(2)	18(2)	20(3)	-5(2)	-1(2)	2(2)
C(3)	14(2)	18(2)	27(3)	-7(2)	-3(2)	0(2)
C(4)	15(2)	17(2)	30(3)	-2(2)	7(2)	0(2)
C(5)	15(2)	9(2)	20(3)	-2(2)	4(2)	2(2)
C(6)	13(2)	13(2)	20(3)	1(2)	4(2)	0(2)
C(7)	11(2)	12(2)	24(3)	3(2)	4(2)	-2(2)
C(8)	16(2)	15(2)	13(2)	1(2)	5(2)	3(2)
C(9)	16(2)	8(2)	16(3)	2(2)	0(2)	1(2)
C(10)	17(2)	15(2)	14(2)	4(2)	3(2)	3(2)
C(11)	15(2)	10(2)	22(3)	-3(2)	-1(2)	2(2)
C(12)	15(2)	15(2)	22(3)	2(2)	4(2)	-2(2)
C(13)	15(2)	14(2)	18(3)	1(2)	5(2)	0(2)
C(14)	13(2)	14(2)	13(2)	-1(2)	4(2)	0(2)
C(15)	14(2)	16(2)	13(2)	3(2)	1(2)	3(2)

C(16)	17(2)	21(2)	16(3)	-3(2)	0(2)	1(2)
C(17)	21(2)	24(2)	23(3)	12(2)	5(2)	-1(2)
C(18)	27(2)	39(3)	12(3)	8(2)	1(2)	4(2)
C(19)	23(2)	36(3)	17(3)	-3(2)	1(2)	6(2)
C(20)	16(2)	22(2)	16(3)	-2(2)	0(2)	-1(2)
C(21)	16(2)	27(3)	26(3)	5(2)	-2(2)	-2(2)
Cl(3)	24(1)	25(1)	30(1)	-5(1)	-3(1)	1(1)
Cl(4)	41(1)	40(1)	52(1)	9(1)	-21(1)	-2(1)
C(22)	33(3)	32(3)	31(3)	5(3)	4(3)	1(2)
F(1)	17(1)	63(2)	41(2)	-1(2)	-2(1)	-2(1)
F(2)	27(2)	53(2)	60(3)	36(2)	-3(2)	-4(2)
F(3)	37(2)	43(2)	27(2)	-9(2)	11(2)	-7(1)
F(4)	45(2)	36(2)	62(3)	-26(2)	26(2)	-10(1)
B(1)	18(2)	26(3)	21(3)	-1(3)	1(2)	0(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [(6-methoxy-PyQuin)$AuCl_2$]BF_4 (**2e**).

	x	y	z	U(eq)
H(1)	11049	7112	5999	21
H(2)	13218	8364	6008	23
H(3)	13716	9552	5282	24
H(4)	11994	9537	4578	24
H(7)	10300	9228	3921	18
H(10)	5438	8855	3178	18
H(12)	3251	7059	4268	21
H(13)	5425	6850	4784	19
H(16)	9341	10995	3333	21
H(17)	9700	11693	2513	26
H(18)	9096	10338	1825	31
H(19)	8030	8291	1946	30
H(20)	7512	7630	2758	22

H(21A)	2975	9711	3018	35
H(21B)	1611	8788	2825	35
H(21C)	3280	8372	2730	35
H(22A)	4728	5151	3502	39
H(22B)	4941	3895	3154	39