Palladium-catalyzed synthesis of pyrrole-, indole- and phenanthridine-fused polycyclic aromatic compounds from *ortho*-dihaloarenes

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Autorship statement

Hereby I declare that this PhD thesis was composed based on my own work unless stated otherwise.

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Ngo Nghia Pham

Abstract

In this PhD research, different palladium-catalyzed syntheses of polycyclic nitrogen heterocycles starting from *ortho*-dihaloarenes were developed. First, convenient syntheses of pyrrole-fused derivatives *via* palladium-catalyzed domino C-C/C-N coupling of *ortho*-dihaloarenes with imines were accomplished. In another context of the study, the employment of *ortho*-dihaloarenes for palladium-catalyzed sequential regioselective Suzuki reaction with *ortho*-bromophenyl boronic acid/double C-N coupling with primary amines afforded corresponding indole-fused structures. Finally, protocols for the synthesis of previously unexplored phenanthridine-fused aromatic compounds were described, which feature a palladium-catalyzed regioselective Sonogashira reaction of *ortho*-dihaloarenes followed by domino or one-pot C-N coupling/hydroamination/C-H arylation.

In dieser Promotionsarbeit wurden verschiedene palladium-katalysierte Synthesen von kondensierten Pyrrolen, Indolen und Phenanthridinen aus *ortho*-Dihaloarenen untersucht. Zuerst wurde eine praktische Synthese von kondensierten Pyrrolen durch palladium-katalysierte C-C/C-N Dominokupplungen erstellt. Außerdem wurden *ortho*-Dihaloarenen durch sequentielle regioselektive Suzuki Reaktion/zweifache C-N Kupplung zur Synthese von kondensierten Indolen eingesetzt. Des Weiteren wurden *ortho*-Dihaloarenen eingesetzt um kondensierte Phenanthridine durch regioselektive Sonogashira Reaktion und anschließende Domino-C-N Kupplung/Hydroaminierung/ C-H Arylierung zu synthetisieren.

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Abbreviations

Ac	Acetyl
Ar	Aryl
Bn	Benzyl
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
BQ	1,4-Benzoquinone
Bz	Benzoyl
CataCXium A	Di(1-adamantyl)-*n*-butylphosphine
Cy	Cyclohexyl
DYRK	Dual specificity tyrosine-phosphorylation-regulated kinase
DavePhos	2-Dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl
dba	Dibenzylideneacetone
DG	Directing group
DMF	*N*,*N*-Dimethylformamide
DNA	Deoxyribonucleic acid
dppe	1,2-Bis(diphenylphosphino)ethane
dppf	1,1'- Bis(diphenylphosphanyl)ferrocene
DPEPhos	(Oxydi-2,1-phenylene)bis(diphenylphosphine)
DTBPF	1,1′-Bis(di-*tert*-butylphosphino)ferrocene
EI	Electron ionization
equiv.	Equivalent
ESI	Electron spray ionization
Et	Ethyl

h	Hour
HIV	Human immunodeficiency virus
JohnPhos	(2-Biphenyl)di-*tert*-butylphosphine
m/z	Mass-to-charge ratio
Me	Methyl
MeCN	Acetonitrile
mp.	Melting point
OLED	Organic light-emitting diode
OTf	Trifluoromethanesulfonate
Ph	Phenyl
pin	Pinacolato
PMP	*para*-Methoxyphenyl
R	Organic fragment
SPhos	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl
THF	Tetrahydrofuran
Tol	Tolyl
TLC	Thin layer chromatography
*t*Bu	*tert*-Butyl
TM	Transition metal
TsOH	*para*-Toluenesulfonic acid
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene
XPhos	2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl

1. General introduction

Nitrogen heterocycles are undoubtedly involved in a plethora of important processes in living creatures on earth. For instance, the genetic codes DNAs are comprised of two base pairs cytosine/guanine and thymine/adenine, which incorporate heterocycles purine and pyrimidine (Figure 1).[1] Moreover, heme, which is a porphyrin complex, has diverse biological functions in living organisms including electron transfer, transportation of diatomic gases and chemical analysis (Figure 1).[2] Another porphyrin complex named chlorophyll is an extremely important biomolecule for the photocatalytic process in plants (Figure 1).[3]

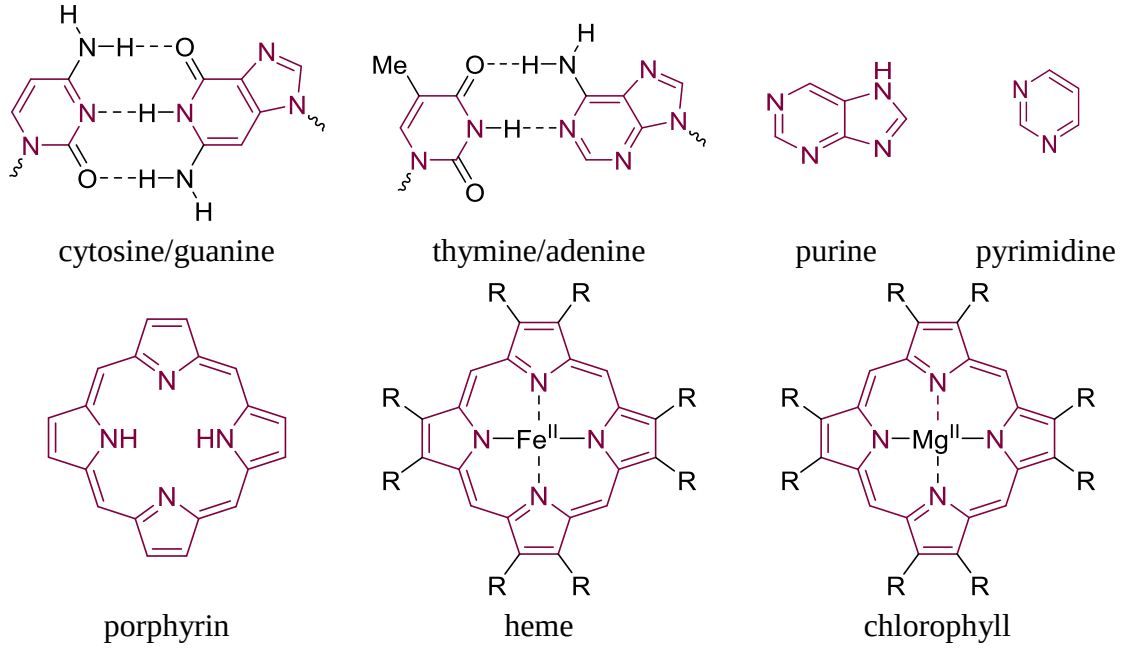


Figure 1: Examples of biologically important nitrogen heterocycles

Owing to their immense importance, nitrogen heterocycles are center of research in many fields, in which a great number of nitrogen heterocycles were explored with important applications. In pharmaceutical research, biochemists have discovered and developed important drugs, for example emtricitabin being employed for the treatment of HIV (Figure 2).[4] Furthermore, chemists have developed powerful catalysts for innovative reactions, for example NHC1 has been applied in C-C and C-N couplings with esters and amines (Figure 2).[5] In material science, physicists have explored materials with enhanced physical properties, for instance CPB has been used in OLED-layers (Figure 2).[6]

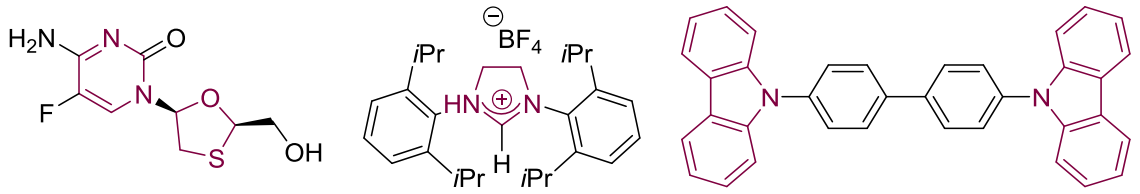
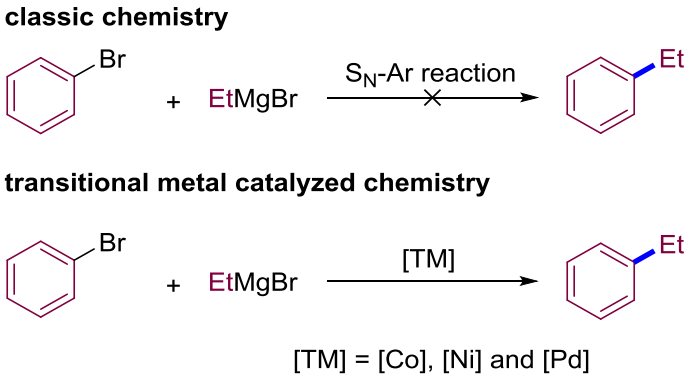


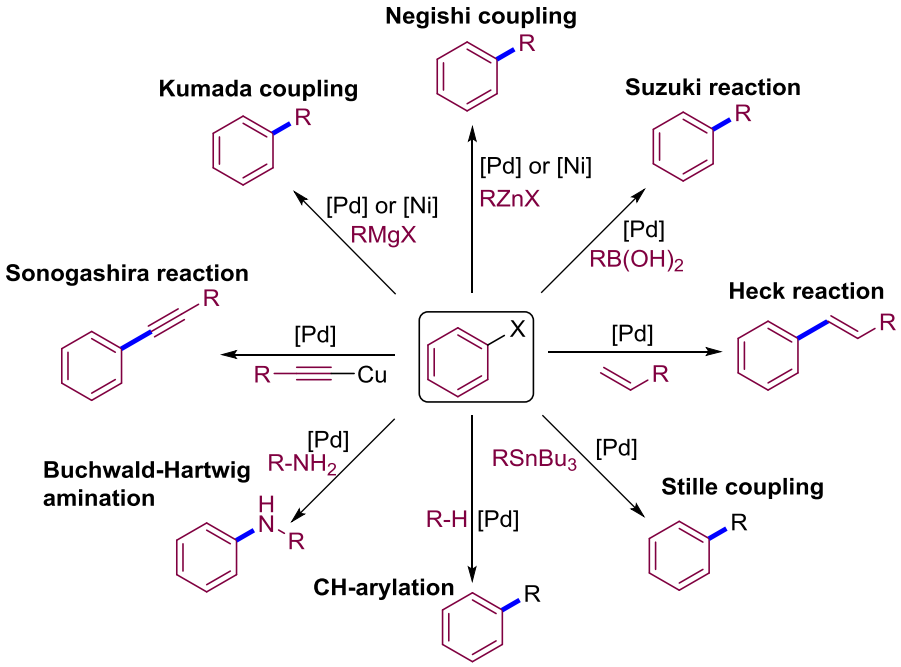
Figure 2: Several relevant nitrogen compounds with applications

In order to provide scientists in the field of pharmaceutical and material science with product libraries for their research, synthetic chemists were devoted since more than a century to develop convenient syntheses of nitrogen heterocycles. Examples for these are Hantzsch pyridine synthesis,[7] Biginelli synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones,[8] Paal-Knorr furan and pyrrole synthesis,[9] Fischer indole synthesis[10] and Friedländer quinoline synthesis,[11] to name but a few. Nevertheless, given the sheer number and the enormous diversity of nitrogen heterocycles in nature and in research, even more powerful, modular and convenient syntheses still remain highly desired.



Scheme 1: Transition metal catalyzed cross-coupling reaction

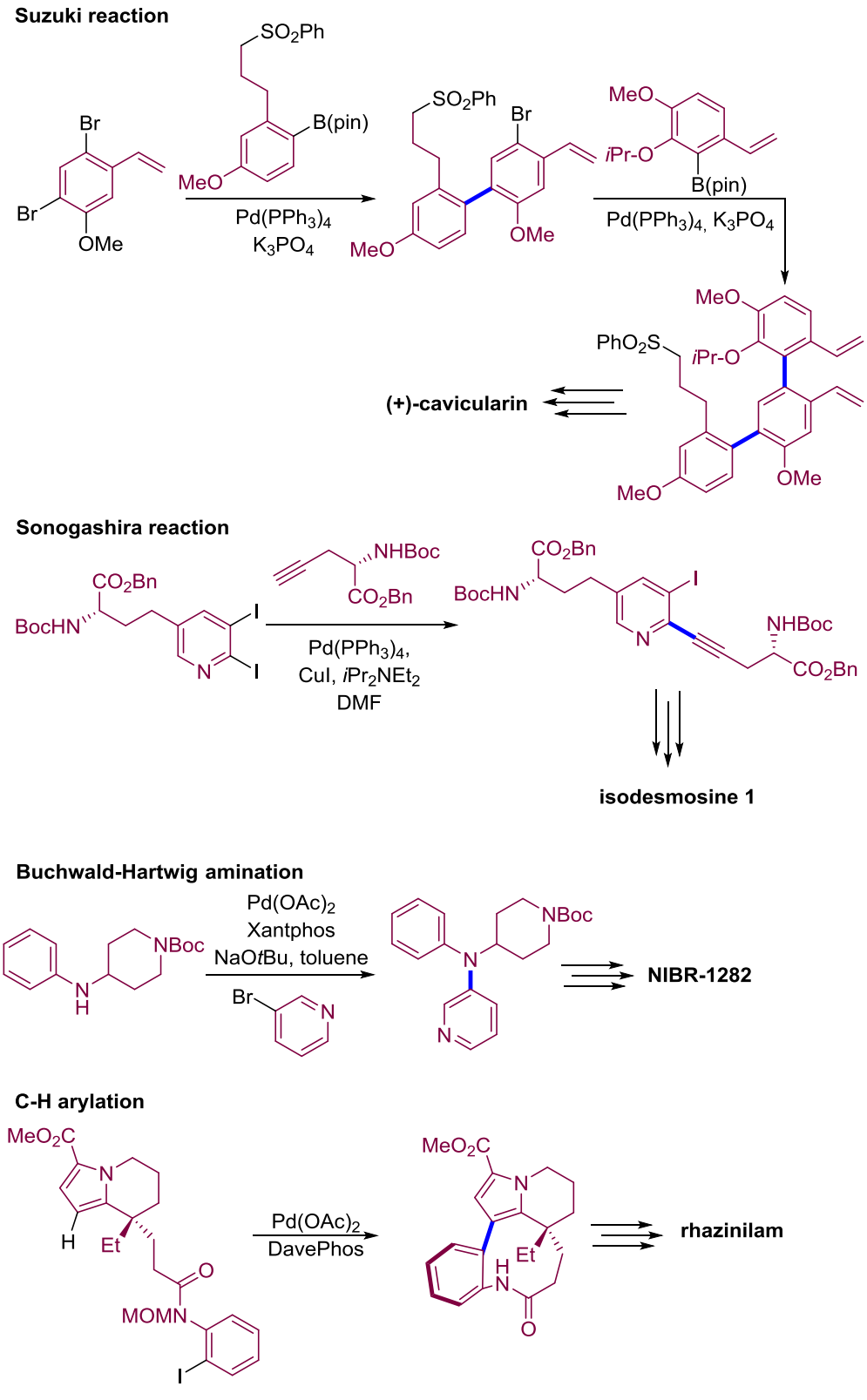
Fortunately, the last four decades have witnessed a boom in the development of cross-coupling reactions catalyzed by transition metals. These catalysts possess great potential for furnishing new C-C, C-N and C-O bonds. As a result, a number of new reaction concepts have been realized. For example, in a Kumada reaction, a Grignard reagent couples with a haloarene in the presence of transition metal catalysts, forming corresponding C-C cross-coupling product (Scheme 1).[12]



Scheme 2: Several important transition metal-catalyzed cross-coupling reactions

Consequently, their potential for creating new bonds has been extensively studied, ultimately leading to the establishment of a number of distinct chemical transformations. These reactions differ in coupling partners, and were named after their discoverers including Kumada, Negishi, Suzuki, Stille, Buchwald-Hartwig and Sonogashira (Scheme 2). For example, in a Suzuki cross-coupling reaction an organoborane is accomodated with an aryl halide as coupling partner, while a Stille cross-coupling reaction takes advantages of an organohalide and an organostanne.[13]

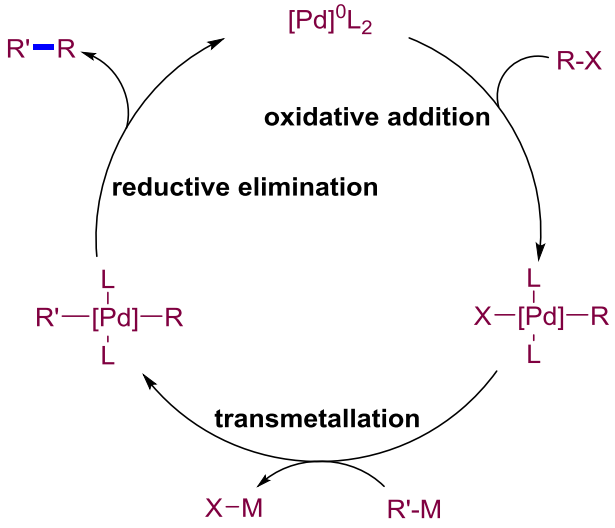
Among the transition metal catalysts, the chemistry of palladium-catalyzed cross-coupling has witnessed a striking development, becoming broadly useful in organic synthesis.[14] Using palladium-catalysts, a large number of structurally complicated compounds with biological and physical relevance have been synthesized (Scheme 3).[15] Overall, palladium-catalyzed cross-coupling reactions have brought enormous enhancements and revolutionized the reaction concepts in organic synthesis. Hence, the pioneers in this field Richard F. Heck, Ei-ichi Negishi and Akira Suzuki were awarded the Nobel Prize in chemistry in 2010.[16]



Scheme 3: Example of palladium-catalyzed reaction in organic synthesis[17], [18], [19], [20]

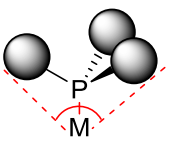
1.1. General mechanism of palladium-catalyzed cross-coupling reactions

In general, the mechanism of palladium-catalyzed cross-coupling reactions features a catalytic cycle, in which the three essential steps are the oxidative addition, the transmetallation and the reductive elimination (Scheme 4). The catalytic cycle is initiated by a catalytically active Pd^0-species. This can be introduced as a pre-catalyst, for example $Pd(PPh_3)_4$ and $Pd(PtBu_3)_2$, or can be generated *in situ* from a palladium source including Pd_2dba_3 and $Pd(OAc)_2$ with corresponding phosphine ligands. The catalytically active Pd^0-species reacts with an organohalide RX in an oxidative addition, forming organopalladium species $RPd^{II}[L_2]X$. This process is commonly considered to be the rate determining step of the catalytic cycle. In the following transmetallation, the organic group of the coupling partner is transferred to the Pd^{II}-species. Finally, the Pd^{II}-species forms the corresponding cross-coupling product in a reductive elimination step, while catalytically active Pd^0-species is regenerated (Scheme 4).



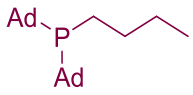
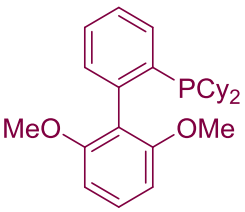
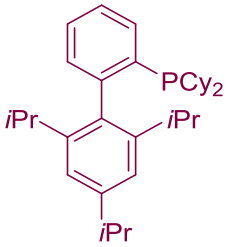
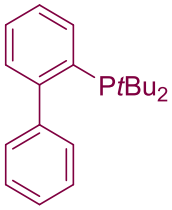
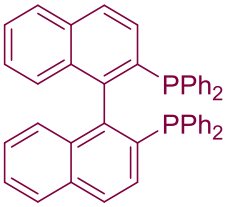
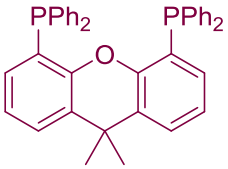
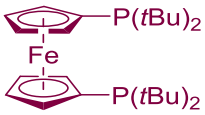
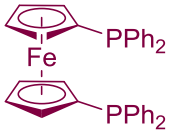
Scheme 4: General catalytic cycle of palladium-catalyzed cross-coupling reactions

The electronic and steric natures of the phosphine ligands can influence certain steps of the catalytic cycle including the oxidative addition and the reductive elimination. Strong σ-donating ligands facilitate the oxidative addition by increasing electron density around the palladium. On the other hand, the reductive elimination is accelerated by bulky ligands, especially those exhibiting large Tolman cone angles.[21] The chemical structures of several important phosphine ligands are shown in Table **1**.



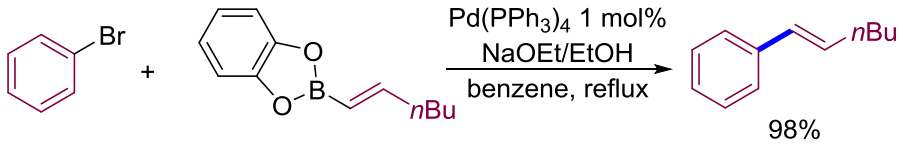
Tolman cone angle

Table 1: Chemical structures of several phosphine ligands

		
CataCXium A	SPhos	XPhos
		
JohnPhos	BINAP	Xantphos
		
dppe	DTBPF	dppf

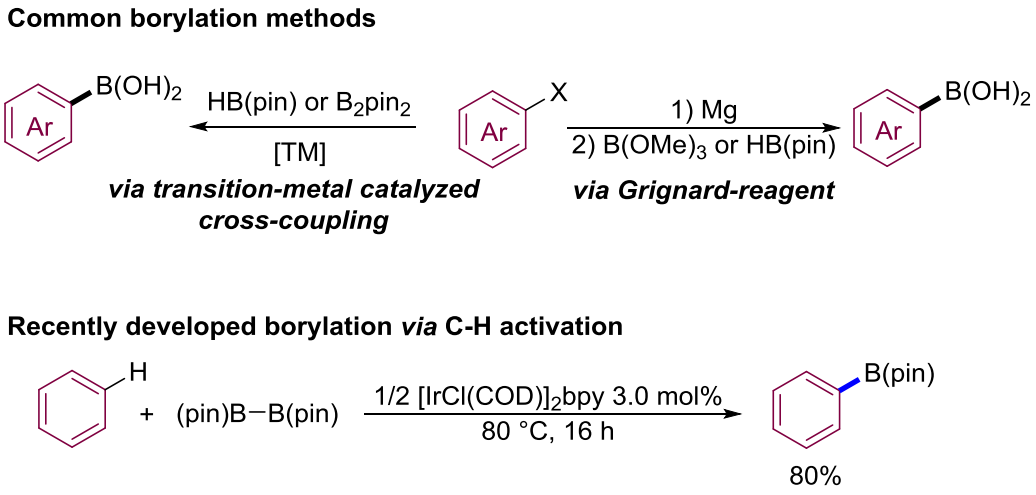
1.2. Palladium-catalyzed Suzuki cross-coupling reaction

In seek of suitable coupling partners for palladium-catalyzed cross-coupling reactions, initial observation of the potential of organoboranes as coupling partners with aryl/alkenyl halides was documented by Heck *et al.* in 1975. In this report, it was determined that the cross-coupling process occurred in the presence of stoichiometric palladium. In 1979, Suzuki *et al.* successfully elevated the level of this chemistry by reporting a catalytic approach for the cross-coupling of organoboranes and aryl/alkenyl halides (Scheme 5).[22] The key to this success is the use of bases in order to activate the organoboranes to organoboronates that are finally capable of engaging in a transmetallation during the catalytic cycle.



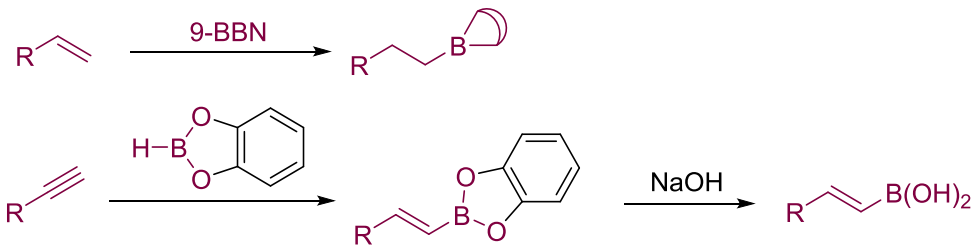
Scheme 5: First example of palladium-catalyzed Suzuki cross-coupling reaction[22]

In general, aryl boronic acids are accessible from aryl halides with boron sources *via* two common pathways (Scheme 6).[23] In the first route, aryl halides are converted to Grignard or lithium reagents which react with boron sources to form corresponding aryl boron compounds. Alternatively, aryl halides and boron sources are treated on cross-coupling reaction to generate aryl boron products (Scheme 6). Frequently employed boron sources for these transformations are pinacol borane (HBpin), bis(pinacolato)diboron (B_2pin_2), and trimethyl borates ($B(OMe)_3$). Recently, an iridium-catalyzed aromatic borylation *via* C-H activation approach has been developed by Hartwig *et al.*, representing a promising borylation method for the future (Scheme 6).[24]



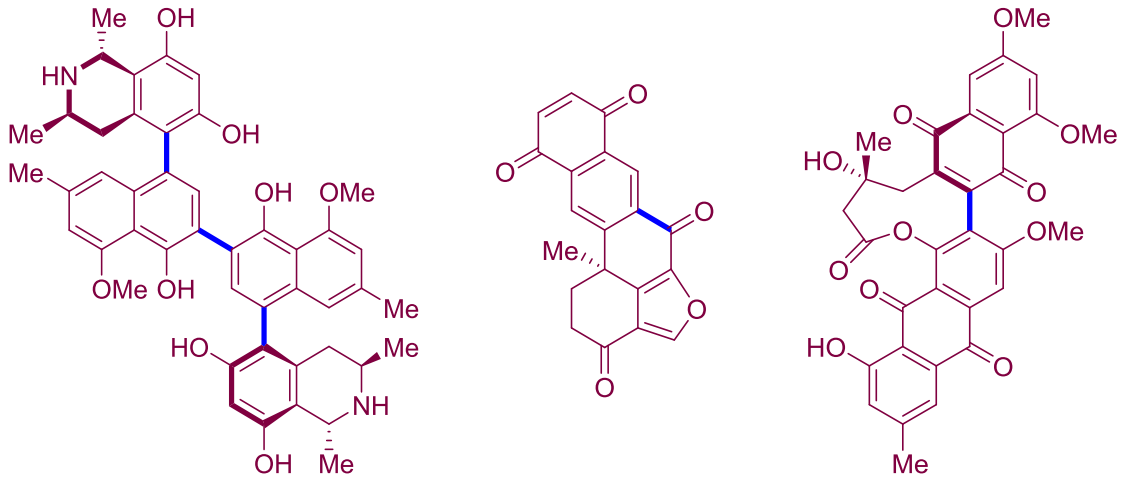
Scheme 6: Synthesis of aryl boronic acids

In comparison, alkyl and alkenyl boron compounds can be synthesized *via* chemo- and regioselective addition of boron sources to alkenes and alkynes, respectively (Scheme 7). In this reaction, alkynyl is more active than alkenyl group and the formation of *trans*- is preferred over the formation of *cis*-configured isomers.



Scheme 7: Stereo- and regioselective synthesis of organoboranes

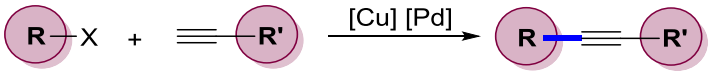
In total, the Suzuki cross-coupling reaction exhibits significant advantages including air-/moisture-stable and less-toxic organoboron substrates, high functional group tolerance with wide diversity of starting materials and reaction media. Nowadays, this reaction is known as a powerful and prevalently employed tool for making new C_{sp2}-C_{sp2} and C_{sp2}-C_{sp3} bonds from organoboranes and aryl/alkenyl halides.[25] A large number of biologically important structures have been synthesized using Suzuki cross-coupling reactions (Figure 3).[26]



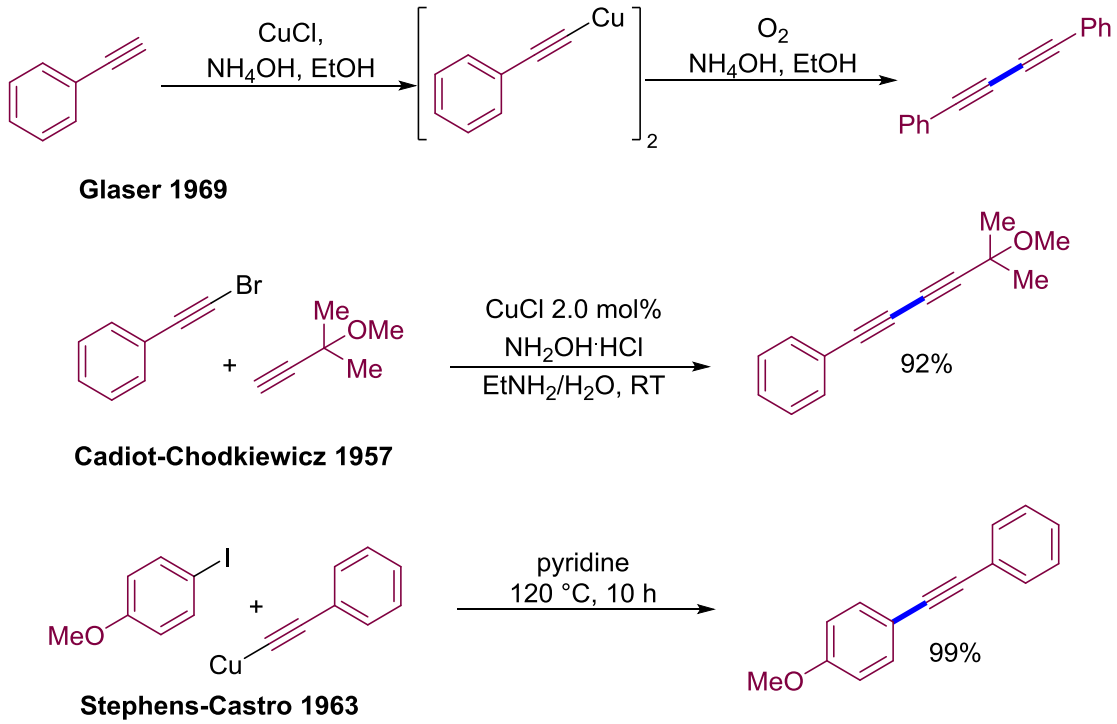
Michellamine B[27] Helenaquinone[28] Dermocanarin 2[29]

Figure 3: Examples of biologically important structures synthesized by Suzuki cross-coupling reaction

1.3. Palladium-catalyzed Sonogashira cross-coupling reaction

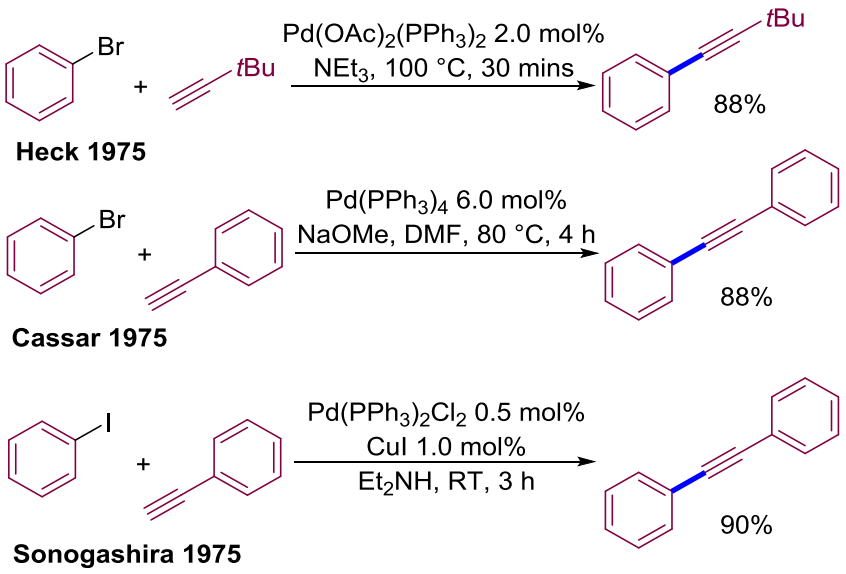


The history of cross-coupling reactions with alkynes was initiated in 1869 when Glaser *et al.* discovered that copper acetylides dimerized under air forming diphenyl diacetylenes (Scheme 8).[30] In 1957, it was further explored that alkynes are capable of participating in copper-catalyzed cross-coupling reactions with haloalkynes (Scheme 8).[31]



Scheme 8: Copper-catalyzed cross-coupling reaction of alkynes and alkynyl salts

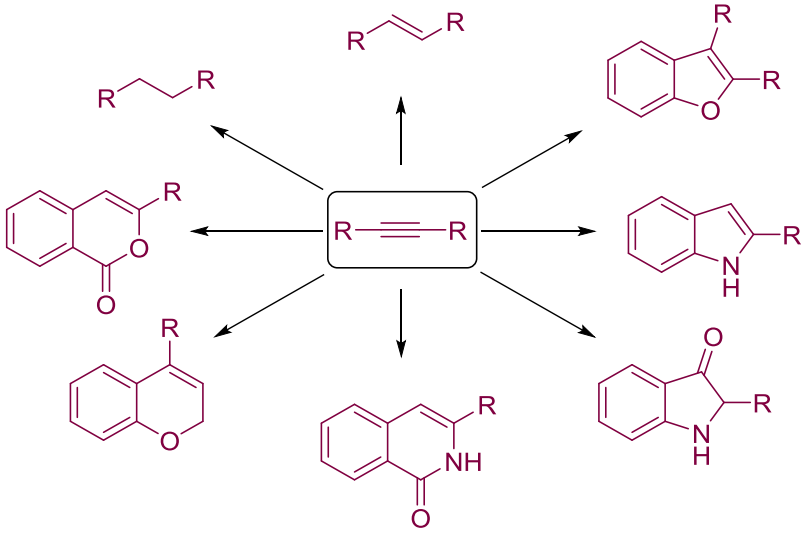
In 1963, Stephens and Castro disclosed that alkynyl copper salts underwent a reaction with haloarenes in organic bases as media to form corresponding cross-coupling products (Scheme 8).[32] However, these methods are limited by several remarkable shortcomings including the stoichiometric use of copper, the need of high reaction temperature, the poor solubility of the alkynyl copper salts and the problem of the formation of homo-coupling products.



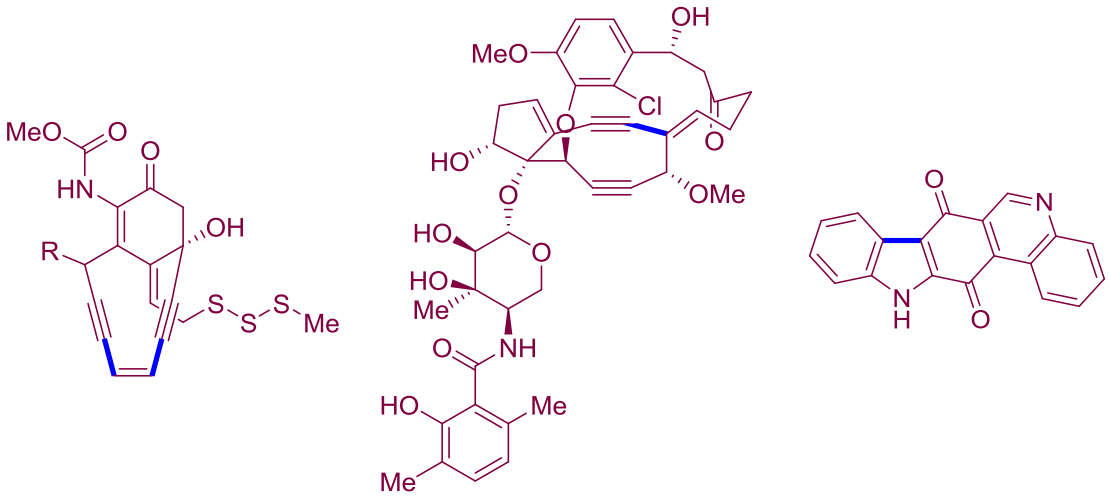
Scheme 9: Palladium-catalyzed cross-coupling of aryl halides with alkynes

In 1975, palladium-catalyzed cross-coupling reactions of aryl halides with alkynes were concurrently documented by Heck *et al.*,[33] Cassar *et al.*[34] and Sonogashira *et al.*[35] (Scheme 9). In the reports of Heck *et al.* and Cassar *et al.*, the reactions employ palladium as a sole catalyst, requiring elevated reaction temperatures. In comparison, Sonogashira *et al.* used copper as a co-catalyst that allows the conduction of the reaction at room temperature. Overall, this reaction displays high tolerance against functional groups and proves especially effective for making new C_{sp}-C_{sp} and C_{sp2}-C_{sp} bonds in conjugated enynes and enediynes of structurally complex molecules.

It is worth mentioning that the products of the Sonogashira reaction can often be accommodated as precursors in further chemical transformations.[36] For example, they can be reduced to alkanes or alkenes (Scheme 10). Alternatively, they can participate in different types of cyclization reactions to construct complex structures, for example indole, benzofuran, isoquinolinone, oxyindole and isochromenone (Scheme 10). These above distinct advantages have rendered Sonogashira reaction an important platform for the synthesis of a great number of natural products nowadays (Figure 4).[37]



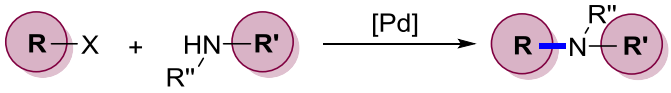
Scheme 10: Possible following transformations of the products of Sonogashira cross-coupling reaction



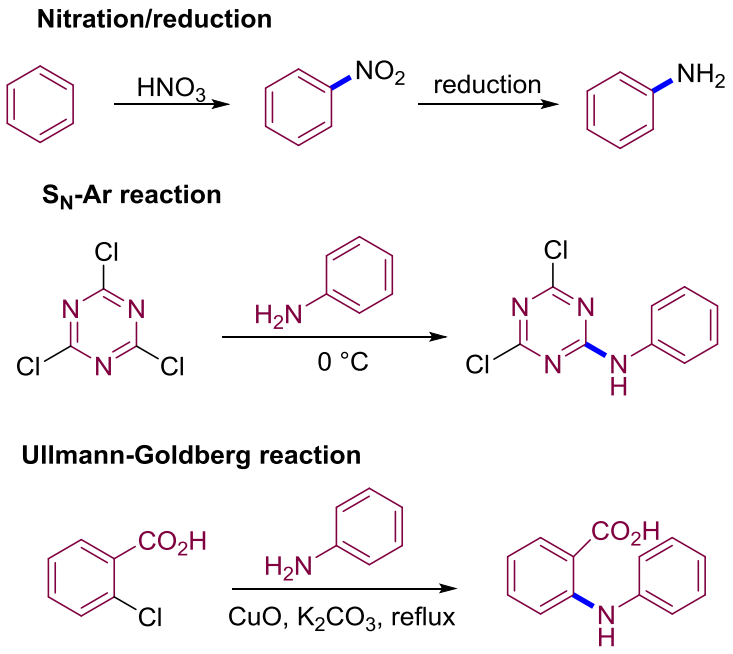
calicheamicin γ1[38] maduropeptin[39] calothrixin B[40]

Figure 4: Natural products obtained by Sonogashira cross-coupling reaction

1.4. Palladium-catalyzed Buchwald-Hartwig C-N cross-coupling reaction

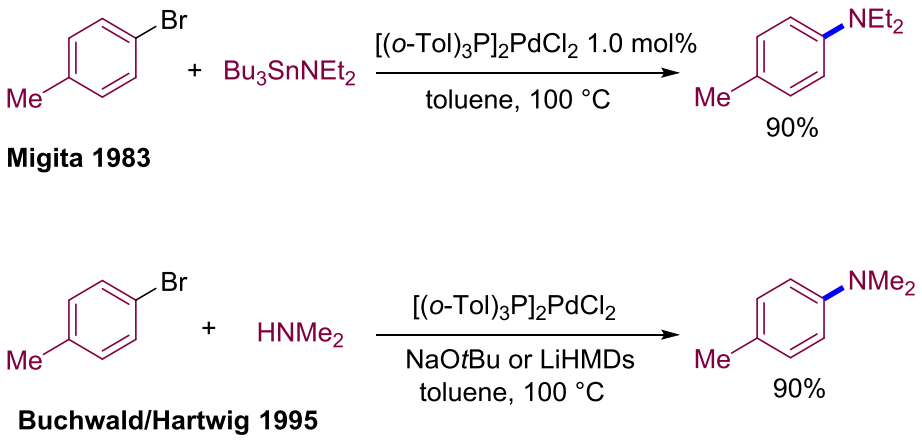


As C_{Ar}-N bonds are abundant in natural products, synthetic chemists have devoted great efforts to developing new methodologies to construct them. In classic chemistry, these bonds were created by several pathways including nitration/reduction of aromatic compound, S_N-Ar reaction and Ullmann-Goldberg reaction (Scheme 11).[41] Unfortunately, these methods were suffered from low regioselectivity and limited substrate scope. For example, the S_N-Ar reaction and Ullmann-Goldberg reaction failed with electronically neutral and electronically rich aromatic systems.



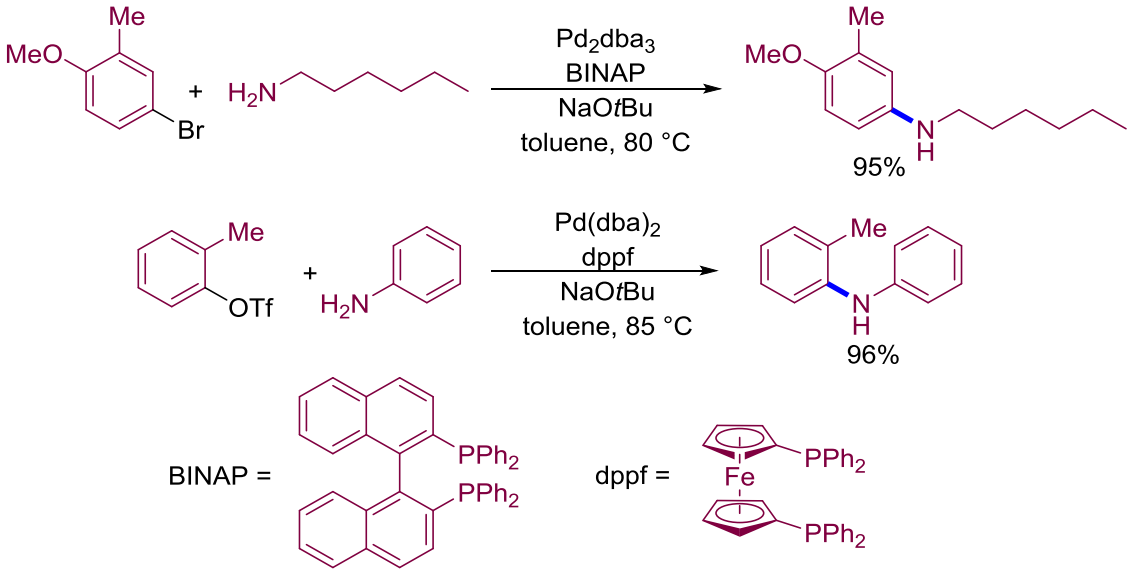
Scheme 11: Formations of C_{Ar}-N bonds in classic chemistry

These shortcomings in substrate scope have been gradually solved by the development of transition metal catalysts. In 1983, Migita *et al.* reported the first palladium-catalyzed C-N cross-coupling reaction (Scheme 12).[42] The reaction worked compatibly with electronically neutral and sterically hindered amines, but necessarily employed toxic tin-reagents.



Scheme 12: Examples of palladium-catalyzed C-N cross-coupling reaction

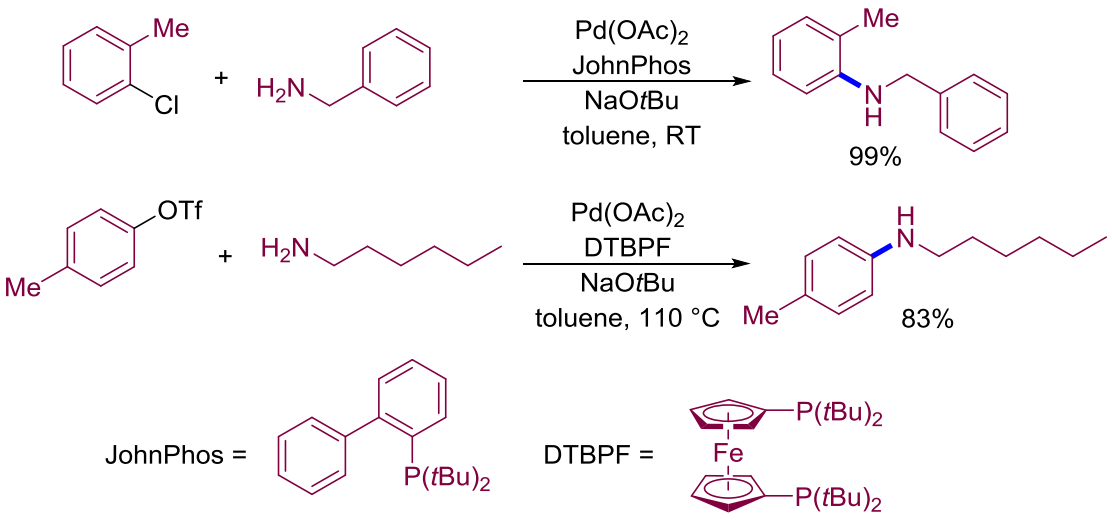
In 1994, Hartwig *et al.* elucidated the formation of the active catalyst Pd[P(*o*-Tol)$_3$]$_2$ during this C-N cross-coupling reaction.[43] Later in this year, Buchwald *et al.* published an improved procedure for this reaction by using an argon purge in the reaction setup.[44] Through this system, diethylamine was removed during the *in situ* generation of aminostannanes, thus allowing a broader amine scope with higher resulting yields. In 1995, Buchwald and Hartwig independently found that the employment of the bulky bases NaO*t*Bu and LiHMDS enables a C-N cross-coupling without the use of toxic tin-reagents (Scheme 12).[45] However, the scope of the reaction was still limited to secondary amines due to the uncontrollable overreaction of primary amines and the hydrodehalogenation of haloarenes.



Scheme 13: Buchwald-Hartwig C-N cross-coupling using bidentate phosphine ligands

To address these limitations, further ligands for the Buchwald-Hartwig C-N cross-coupling reaction were developed. In 1996, Buchwald *et al.* and Hartwig *et al.* independently reported that the bidentate ligands BINAP and dppf gave resulting C-N cross-coupling products in good yields with diverse types of primary amines using lower catalyst loading (Scheme 13).[46] Moreover, these conditions allowed the utility of aryl iodides and aryl triflates. It is assumed that the bidentate nature of these ligands fixes the active catalysts during the catalytic cycle. As a result, the liberation of the coordination sites of the active catalysts during the catalytic cycle is suppressed, thus the undesired β-hydride elimination is prevented.

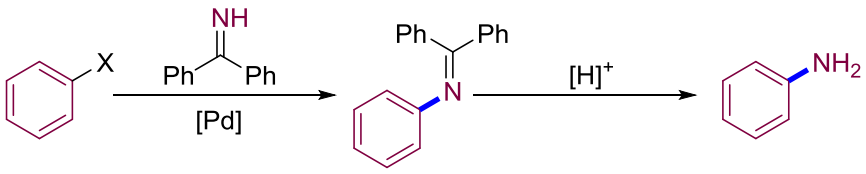
In search of more powerful ligands for the Buchwald-Hartwig C-N cross-coupling reaction, it was discovered that the steric property of ligands was crucial during the reaction in some instances.[47] Voluminous phosphine ligands allow C-N cross-coupling reactions with a broader range of amines including electronically poor and heterocyclic derivatives, and with different types of aryl halides including chloride and triflate (Scheme 14).



Scheme 14: Buchwald-Hartwig C-N cross-coupling reactions using bulky phosphine ligands

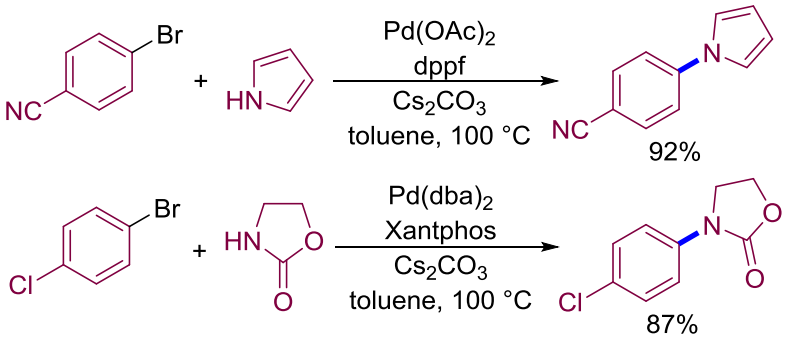
Later development of the Buchwald-Hartwig C-N cross-coupling reaction also unlocked a remaining limitation in the reaction between amines and aryl halides, namely the use of ammonia to construct primary aryl amines. The problem for this lays in the formation of tight bonds between ammonia with the active catalyst that finally inhibits the catalytic activity. To circumvent this, benzophenone imine or silyl amide were accommodated as ammonia equivalence (Scheme 15).[48] These reagents undergo C-N

cross-coupling reactions with aryl halides before being subjected to hydrolysis to assemble the corresponding primary amines.

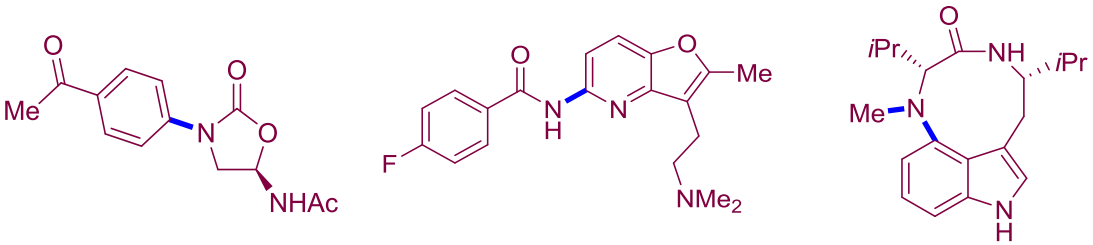


Scheme 15: Strategy of Buchwald-Hartwig C-N cross-coupling reaction for the generation of primary amines

At present, the scope of substrates for the Buchwald-Hartwig C-N cross-coupling reaction has been successfully extended beyond amines. Further competent nitrogen-containing reagents can be engaged in the reaction including amides,[49] carbamates,[49c, 49d] sulfonamides,[49c] sulfoximes,[50] hydrazones[51] and pyrrole-derivatives[49d, 52] (Scheme 16). The Buchwald-Hartwig C-N cross-coupling reaction has become a convenient tool for making new C-N bonds, thereby being broadly applied in organic synthesis to prepare a large number of important compounds (Figure 5).[53]



Scheme 16: Examples of Buchwald-Hartwig C-N coupling with further nitrogen-containing reagents

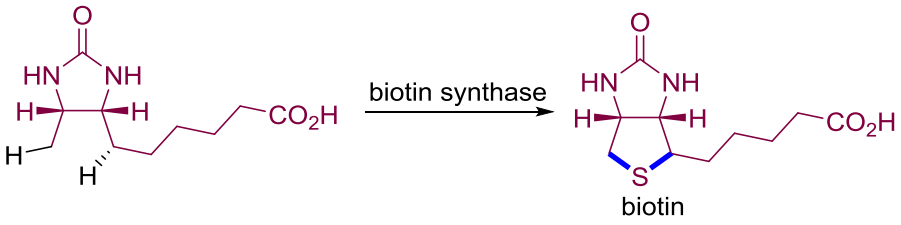


DUP-721[54] FN-325[55] (+)-epi-indolactam V[56]

Figure 5: Biologically important structures synthesized by Buchwald-Hartwig C-N cross-coupling reaction

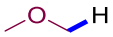
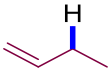
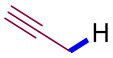
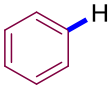
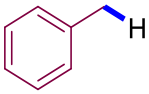
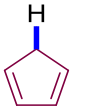
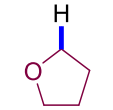
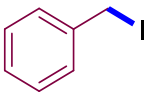
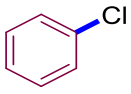
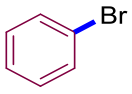
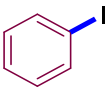
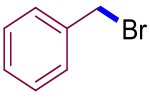
1.5. Palladium-catalyzed C-H arylation

In nature, C-H functionalization is observed in several enzymatic biosynthesis. For example, biotin is synthesized by double C-H functionalization catalyzed by biotin synthase, forming two new C-S bonds in an extremely atom-economic manner (Scheme 17).[57]



Scheme 17: Example of C-H functionalization reaction in nature

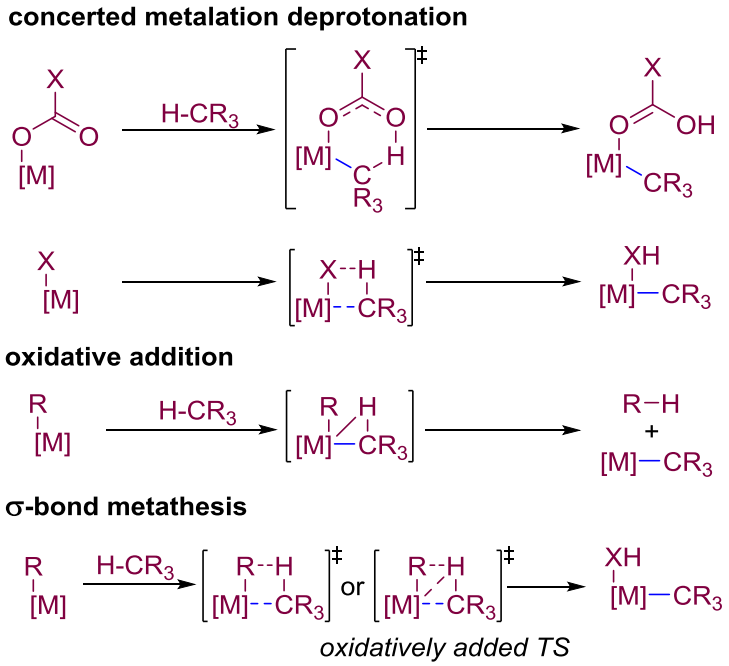
Table 2: Bond dissociation energy of several C-H and C-Hal bonds (kcal·mol^{-1})[58]

Me–H	Et–H	*i*Pr–H	
105	101	99	94
			
111	89	79	94
			
113	90	70	70
Me–Cl	Me–Br	*i*Pr–Br	Et–Br
84	72	74	72
			
91	80	59	51
			
97	84	67	63

Intrigued by these natural enzymatic processes, endeavor was devoted to bringing this reaction concept into practical organic chemistry. In order to achieve this target, many challenges have to be overcome. For instance, the bond dissociation energies of the C-H bonds are generally higher than those of C-Hal bonds (Table 2), and C-H bonds possess no electron lone pairs for coordinating with active catalysts. Thus, they cannot engage

in an oxidative addition during the catalytic cycle like C-Hal bonds. Moreover, unlike several C-M bonds, they are not capable of undergoing a transmetallation. Finally, ideal catalysts for the C-H functionalization have to meet further criteria including being selective to discriminate different C-H bonds, slow in catalyzing over-functionalization, and stable against possible oxidants and functional groups.

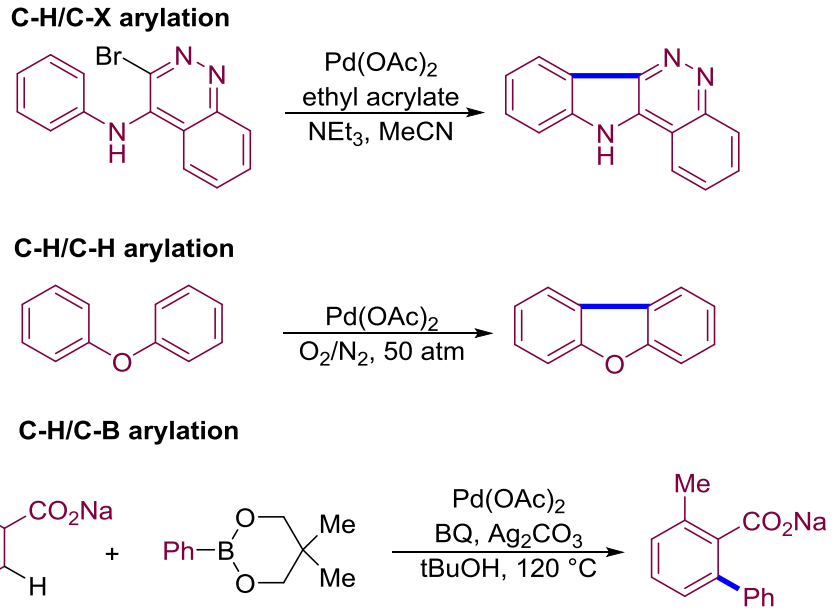
Scheme 18: Example of palladium-catalyzed C-H activation[59]



Scheme 19: General proposed mechanisms of the C-H activation step

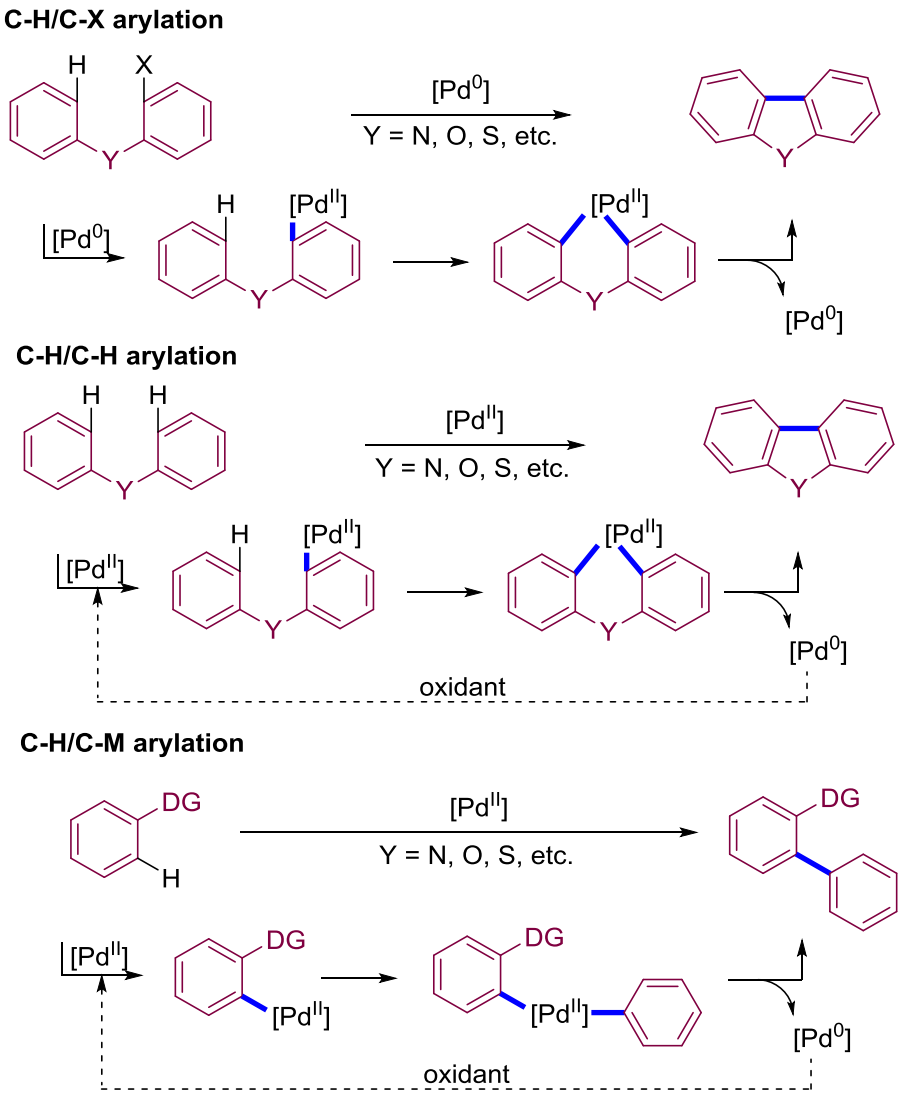
For these reasons, these C-H bonds require particular "activation" during the catalytic cycle. For example, the incorporation of appropriate neighboring groups and organic acids was documented to streamline the C-H activation process. In the exemplified C-H activation reaction shown in Scheme **18**,[59] the catalysts are directed to the neighborhood of the C-H bonds at the *ortho*-position by the carbonyl group. Subsequently, palladium catalysts and *p*-toluenesulfonic acid synergistically activate this C-H bond, forming corresponding final product. In the absence of any of them, the

reaction turns intact. However, the detailed mechanism of these activation processes still remains elusive. General C-H activation steps have been proposed to follow several mechanistic modalities including concerted metalation deprotonation, σ-bond metathesis and oxidative addition (Scheme 19).[60]

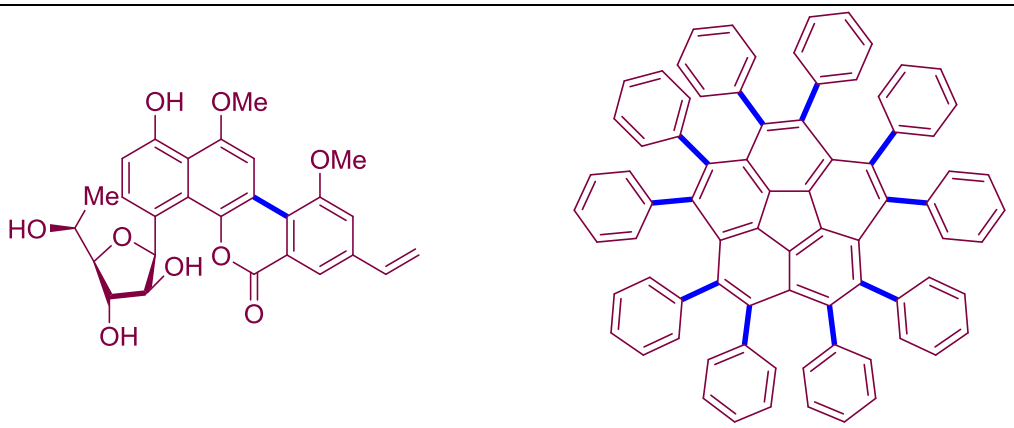


Scheme 20: Examples of palladium-catalyzed C-H functionalization[61]

Among different C-H functionalization methods, of practical importance in organic synthesis are the three forms of C-H arylation between C-H/C-X, C-H/C-H and C-H/C-M bonds (Scheme 20).[62] These arylation reactions differ in the active catalyst during the catalytic cycle, namely Pd^0 for the reaction between C-H/C-X bonds and Pd^{II} for the reaction between C-H/C-H and between C-H/C-M bonds. Alike other C-H activation reactions, the exact mechanisms of these reactions have not yet been fully explained. They have been conjectured to depend on the substrates, catalysts and reaction conditions (Scheme 21). Despite this fact, tremendous developments were achieved in relation to the practical application of C-H arylation in organic synthesis. More recently, C-H arylation has become an increasingly powerful platform for making structurally complex compounds (Figure 6).



Scheme 21: Examples of general mechanism of palladium-catalyzed C-H arylation



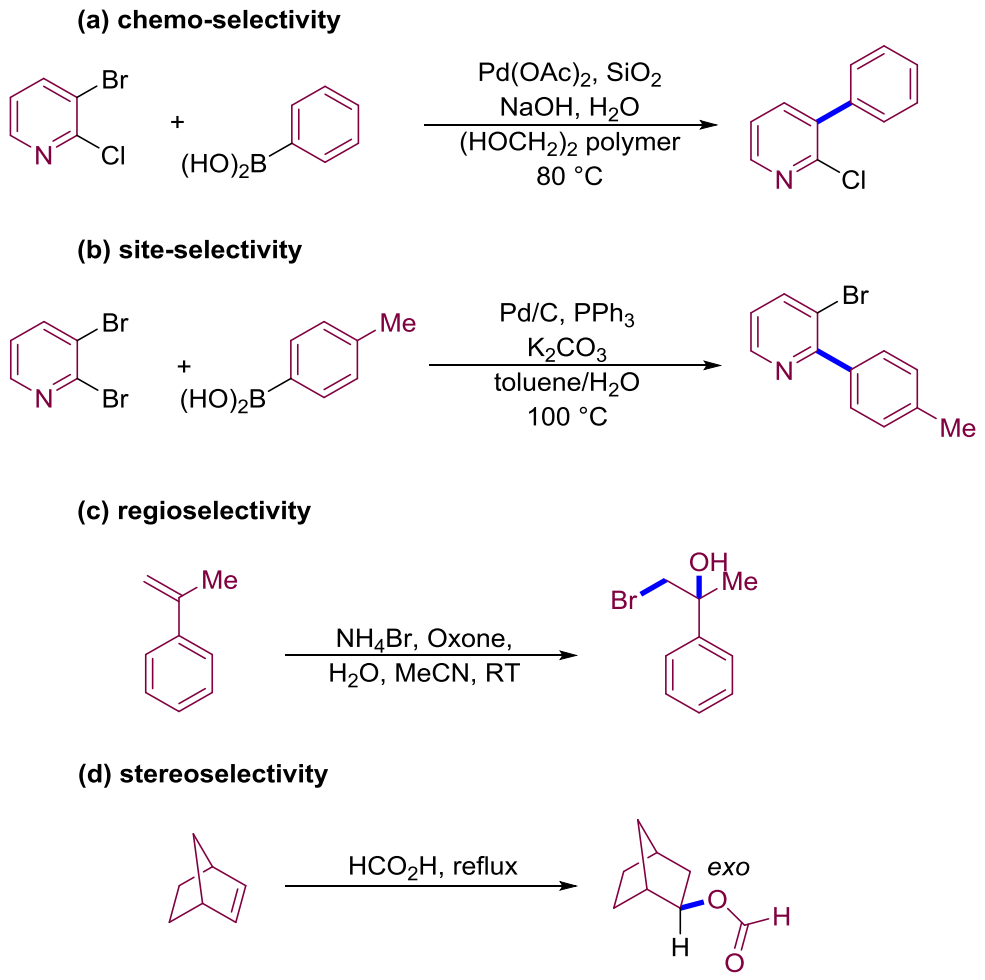
(+)-gilvocarcin M[63]

decaphenylcorannulene[64]

Figure 6: Example of structurally complex compounds synthesized by C-H arylation

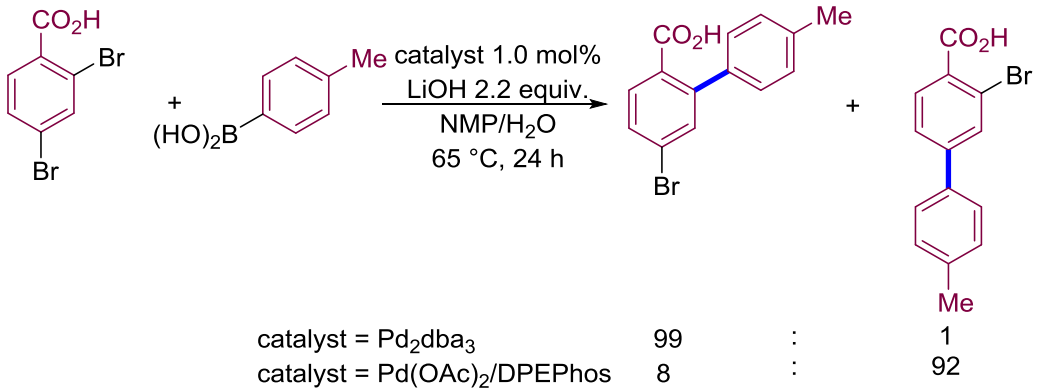
1.6. Selectivity in palladium-catalyzed cross-coupling reactions

Selectivity is an important issue in organic chemistry. It is understood as the preference of one functional group over others during the reaction. There are several types of selectivity. For example, the term chemo-selectivity describes the reaction selection between two chemically different groups, and the site-selectivity is for identical chemical groups at different positions. On the other hand, the term regioselectivity is used for the predominant formation of one isomer over others, while stereoselectivity is related to the selective formation of one stereoisomer over others during the reaction.[65] In practice, the term regioselective can be used for both site- and chemo-selective issues. Representative examples for different types of selectivity in organic synthesis are demonstrated in Scheme **22**.



Scheme 22: Examples of selectivity in organic synthesis[66]

With this regard, palladium-catalyzed cross-coupling reactions can proceed in chemo-selective and site-selective fashion. In chemo-selective palladium-catalyzed cross-coupling reactions, the general reactivity order of the halogen atoms is F < Cl < OTf ≈ Br < I. Taken example **a** in Scheme **22**, position 3 of the pyridine ring is more reactive in a Suzuki cross-coupling reaction, as Br is more reactive than Cl. On the other hand, the attack of general palladium-catalyzed cross-coupling reactions prefers electron-deficient over electron-rich carbon atoms. Therefore, the Suzuki cross-coupling reaction in example **b** in Scheme **22** proceeds site-selectively at position 2 since it is more electron-deficient than position 3.[66a]



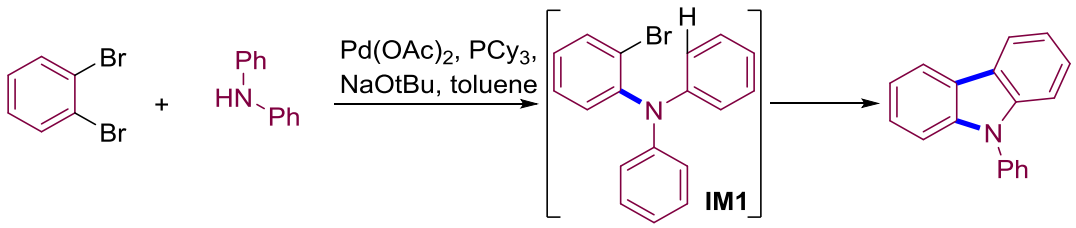
Scheme 23: Example of catalyst-controlled selectivity in palladium-catalyzed cross-coupling reaction[67]

Other factors which can have remarkable influence on the selectivity of palladium-catalyzed cross-coupling reactions are the palladium-source and the ligand.[68] For instance, the Suzuki cross-coupling reaction of 2,4-dibromobenzoic acid with 4-tolylboronic acid (Scheme 23) takes part preferentially at the position 2 of 2,4-dibromobenzoic acid under the presence of phosphine ligand-free catalyst Pd_2dba_3, while the selectivity is reversed by using catalyst system $Pd(OAc)_2$/DPEPhos.[67] The reason for the *ortho*-selectivity by the use of catalyst Pd_2dba_3 is possibly attributed to a coordination of the carboxyl group with the active catalyst during the catalytic cycle. This interaction enhances the proximity of the bromine atom at *ortho*-position with the active catalyst during the catalytic cycle. In contrast, the use of the sterically encumbering bidentate ligand DPEPhos is believed to block the coordination between the carboxyl group and the catalyst $Pd(OAc)_2$. As a result, the bromine atom at *para*-position becomes sterically favored during the reaction.

2. Motivation, objectives and methodologies of this PhD research

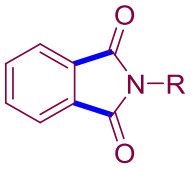
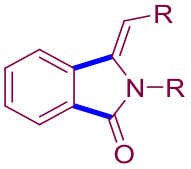
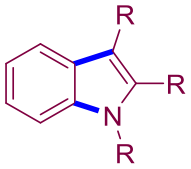
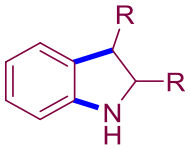
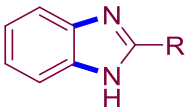
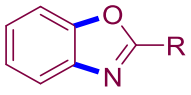
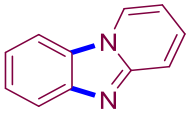
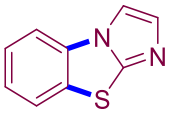
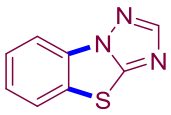
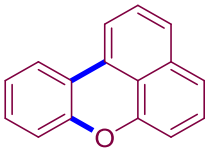
2.1. Motivation

Ortho-dihaloarenes are aromatic compounds with two halogen atoms next to each other. With two electrophilic reaction centers, these compounds have considerable potential to undergo a reaction with a bi-nucleophilic partner, in which a five- or six-membered ring is formed. For example, *ortho*-dibromobenzene reacts with diphenylamine in a palladium-catalyzed domino C-N/C-C cross-coupling (Scheme 24).[69]



Scheme 24: Example of synthesis of heterocycle from *ortho*-dihaloarenes[69]

Table 3: Further examples of heterocycles synthesized from *ortho*-dihaloarenes

 isoindoline-1,3-dione [70]	 3-alkylidene-isoindolin-1-one[71]	 1,2,3-trialkyl-1*H*-indole[72]
 indoline[73]	 1*H*-benzo[d]imidazole[74]	 benzo[*d*]oxazole[75]
 benzo[4,5]imidazo [1,2-*a*]pyridine[76]	 benzo[*d*]imidazo[2,1-*b*]thiazole[77]	 benzo[4,5]-thiazolo[3,2-*b*] [1,2,4]triazole[77]
 benzofurane[78]	 benzo[*kl*]-xanthene[78b]	

First, in the presence of the catalyst system $Pd(OAc)_2/PCy_3$, a C-N coupling between *ortho*-dibromobenzene and diphenylamine takes place wherein **IM1** is formed. Next, an intramolecular C-H arylation of **IM1** is triggered by the same catalyst system to afford the corresponding carbazole (Scheme 24). With this reference, *ortho*-dihaloarenes were applied in a number of other syntheses with amines, carbon monoxides, amides, ketones and phenols delivering different fused nitrogen heterocycles (Table 3).

2.2. Objectives

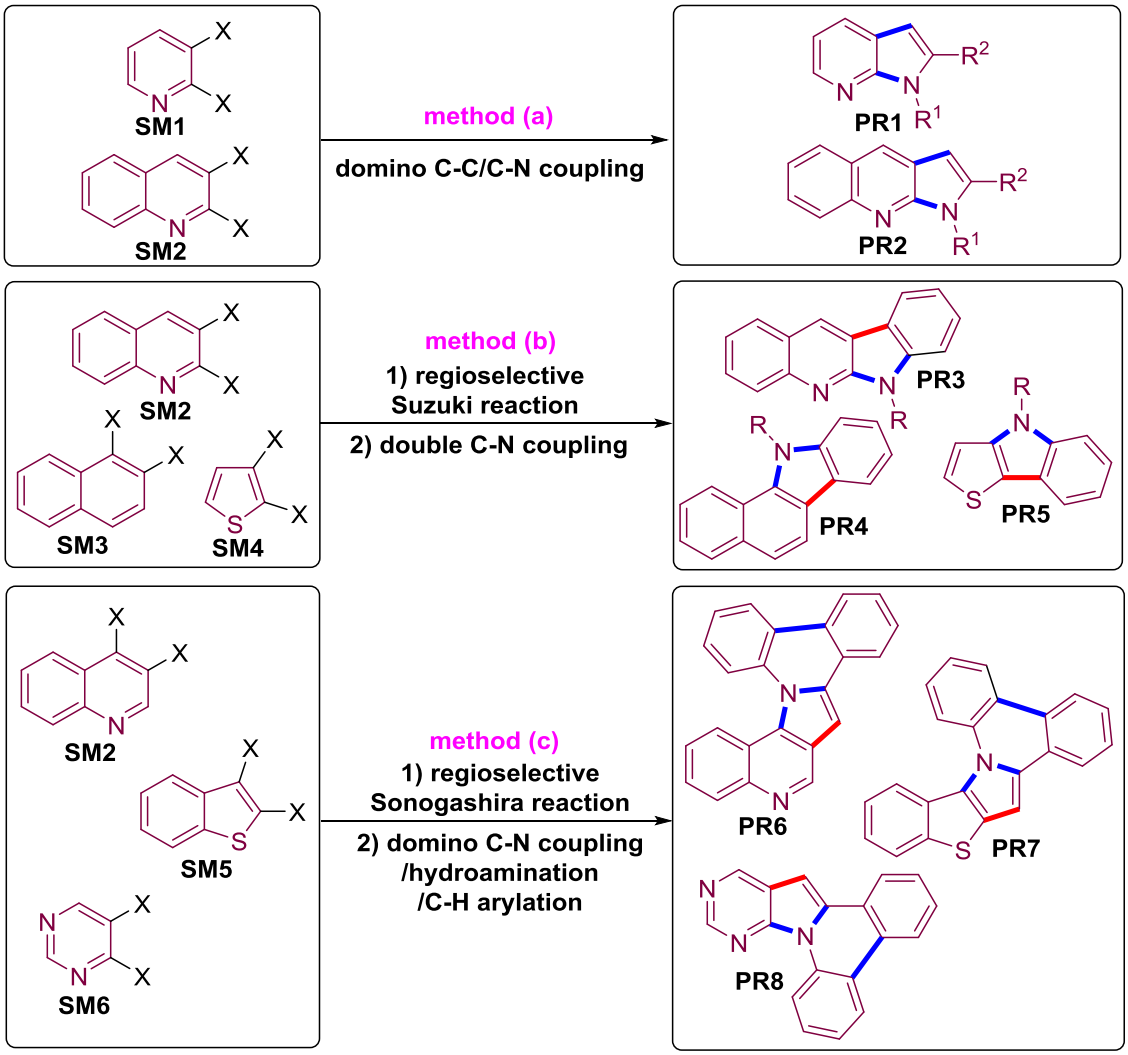
The main target of this study is the development of new convenient, atom-economic and effective methodologies to prepare nitrogen-containing polycyclic aromatic compounds. Starting materials for these syntheses are *ortho*-dihaloarenes of pyridine, quinoline, naphthalene, thiophene, benzothiophene and pyrimidine, since various derivatives of these heterocycles were frequently documented with biological and physical properties.[79]

2.3. Methodologies

In the first part of the PhD research, the domino C-C/C-N coupling reaction of *ortho*-dihaloarenes **SM1-2** with imines is investigated. From these chemical transformations, azaindole-fused compounds **PR1-2** are obtained (Scheme 25 - method a, Chapter 3.1).

The following part focuses on the reaction model sequential regioselective Suzuki reaction/double C-N coupling. *Ortho*-dihaloarenes **SM2-4** are applied as starting materials for these reactions, ultimately furnishing corresponding carbazole-fused derivatives **PR3-5** (Scheme 25 - method b, Chapter 3.2).

Finally, regioselective Sonogashira reaction followed by domino/one-pot C-N coupling/ hydroamination/C-H arylation is studied across *ortho*-dihaloarenes **SM2**, **SM5** and **SM6**, affording hitherto unexplored phenanthridine-fused compounds **PR6-8** (Scheme 25 - method c, Chapter 3.3).

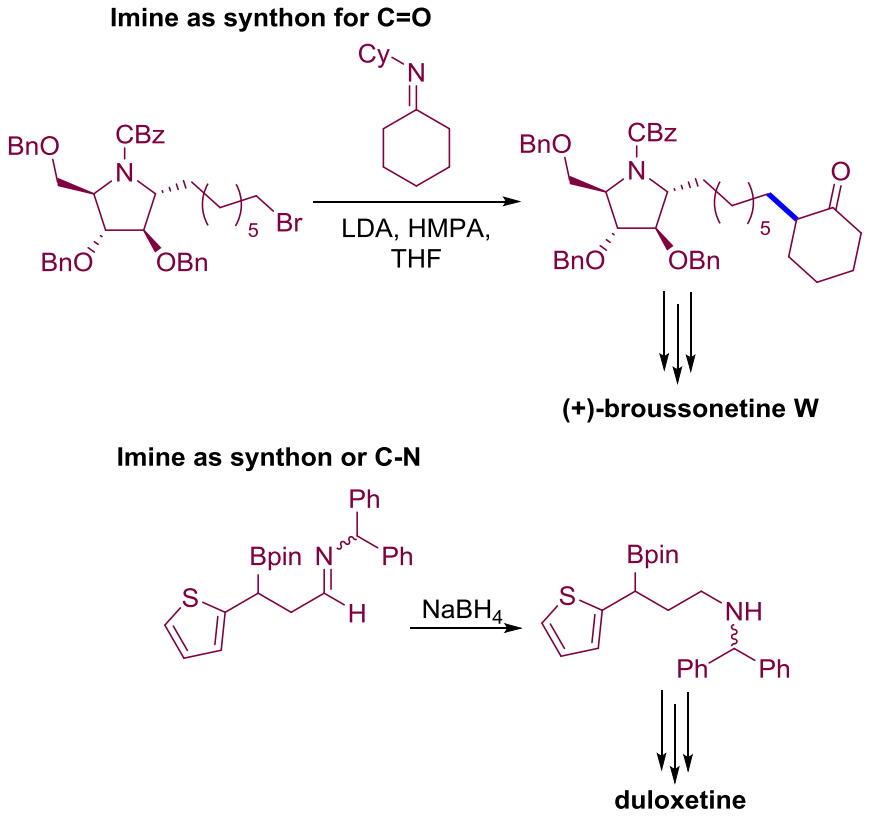


Scheme 25: Synthesis of different nitrogen-containing aromatic compounds in this study

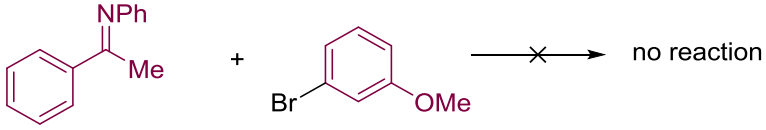
3. Results and discussion

3.1. Synthesis of pyrrole-fused heterocycles by domino C-C/C-N coupling of imines with *ortho*-dihaloarenes

Imines are considered as ambident bi-nucleophilic anions and alternatives to enolates.[80] Their applications in organic synthesis were introduced in the early 1960s.[80] In these publications, imines were utilized in alkylation and aldol condensation reactions. The employment of imines displayed less by-products compared to the uses of ketones and enolates.[80-81] Henceforth, they were frequently applied as synthons for C=O[82] and C-N[83] bonds in organic synthesis (Scheme 26). Nevertheless, the application of imines in classic synthesis was limited by being unable to form new C-C or C-N bonds directly from imines and haloarenes (Scheme 27).

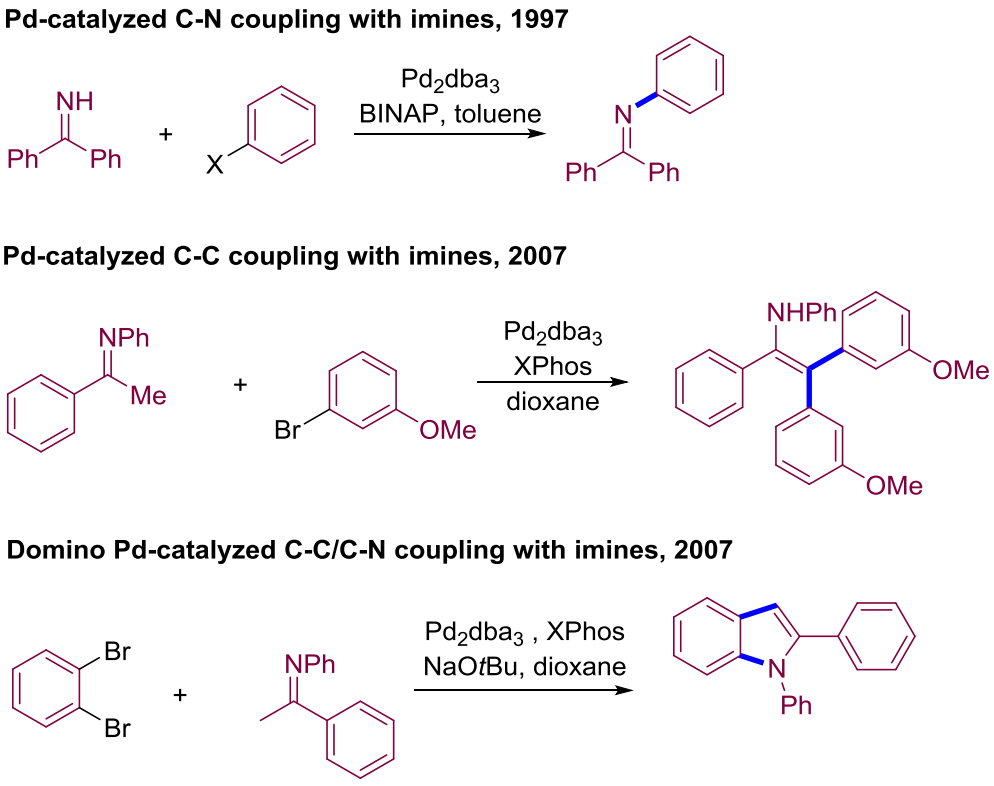


Scheme 26: Applications of imines in the classic synthesis



Scheme 27: Limitations in the application of imines in classic synthesis

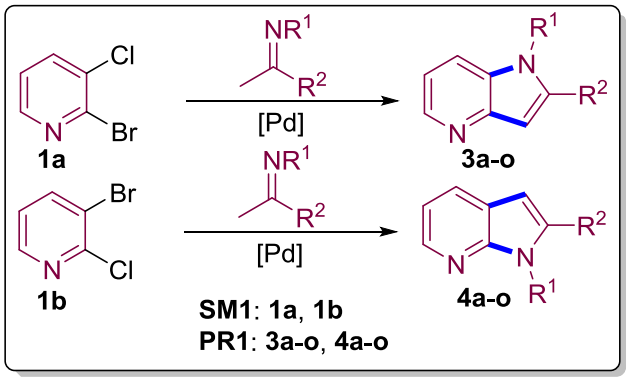
Fortunately, the development of palladium chemistry has gradually enabled both C-C and C-N cross-coupling reactions between imines and haloarenes. The first C-N coupling of imines with haloarenes was published in 1997 (Scheme 28).[48c, 84] However, the use of imine in these C-N couplings with haloarenes was limited by the sole application as ammonia equivalence (Chapter 1.4). In 2007, the first C-C cross-coupling of haloarenes with imines was disclosed by Barluenga *et al.* (Scheme 28).[72b] More importantly, the study took advantage of the ambident property of the imine, triggering both C-C and C-N bond formation reactions by the same catalysts to construct indole structure (Scheme 28).



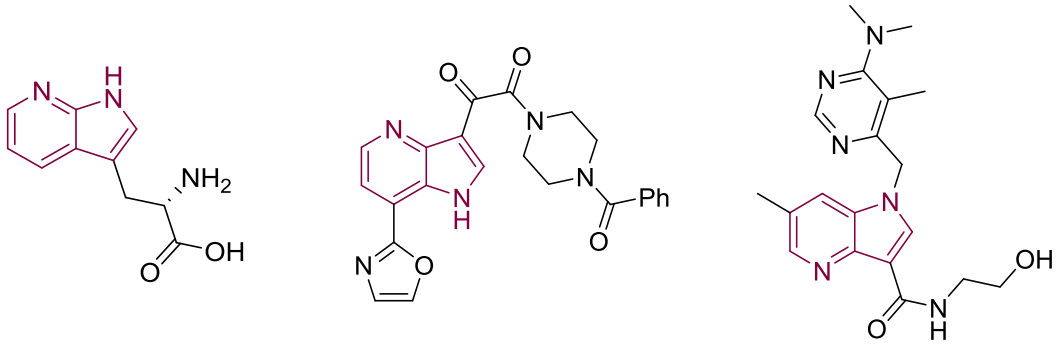
Scheme 28: Palladium-catalyzed cross-coupling with imines[48c] [72b, 72c]

In this regard, it was envisaged that this reaction concept can be adapted to the accommodation of nitrogen-containing *ortho*-dihaloarenes for the syntheses of azaindoles (**PR1**, Chapter 3.1.1) and pyrroloquinolines (**PR2**, Chapter 3.1.2).

3.1.1. Synthesis of azaindoles from *ortho*-dihalopyridines



In nature, azaindoles are considered as bioisosteres of the ubiquitous indole moiety.[85] A large number of azaindole derivatives represent potential candidates for application in medicine. For instance, 7-azatryptophan has been applied as fluorescent marker for visualizing protein-protein interactions in bioligcal systems (Figure 7).[86] In addition, BMS-378806 is an inhibitor against HIV-attachments,[87] while Aza3 can be utilized as an anti-tubercular agent (Figure 7).[88] Taking this biological importance into account, an increasing number of drugs derived from azaindoles have been developed and released in the pharmaceutical industry.[89]

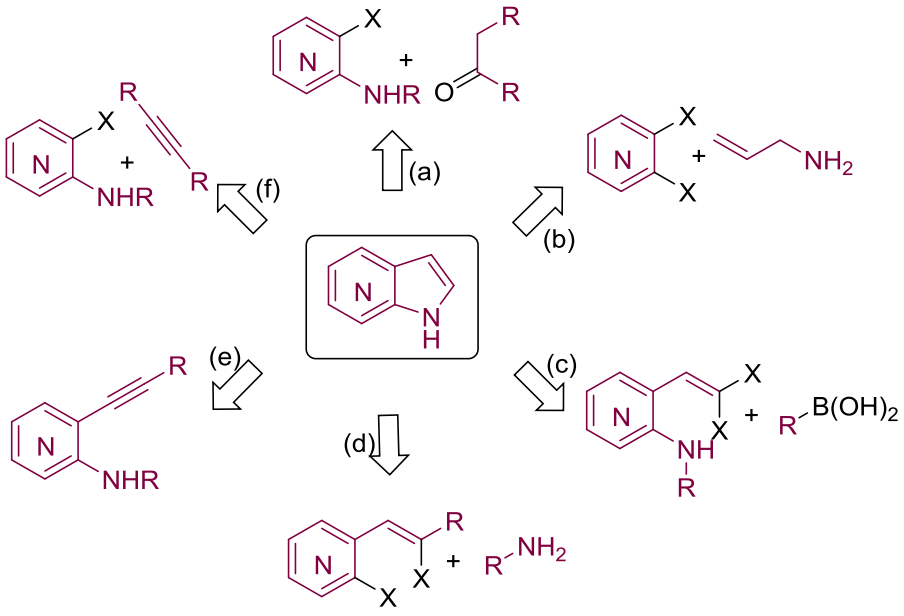


7-azatryptophan BMS-378806 Aza3

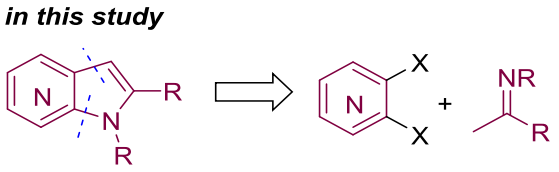
Figure 7: Biologically important azaindole derivatives

Generally, the synthesis of azaindoles begins with a pyridine ring, followed by an annulation to form the corresponding azaindole skeleton.[90] In classic chemistry, the annulation proceeded *via* different syntheses including Fischer,[91] Madelung,[92] Reissert,[93] Bartoli,[94] and Chichibabin.[95] Nonetheless, many of them are suffered from reliance on harsh conditions, low yields or low tolerance against functional groups. Fortunately, these limitations have been gradually solved owed to the striking development of palladium-catalyzed cross-coupling reactions. To date, the annulation

can be accomplished *via* (a, b) C-N/Heck couplings,[96] (c) Suzuki/C-N couplings,[97] (d) C-N/C-N couplings,[72a] (e) hydroamination[98] and (f) Larock synthesis (Scheme 29).[99] Herein, a facile and effective synthetic elaboration of 4- and 7-azaindoles (product series **PR1**) *via* palladium-catalyzed domino C-C/C-N coupling of *ortho*-dihalopyridines and imines is demonstrated (Scheme 30).



Scheme 29: Previous palladium-catalyzed synthesis of azaindoles

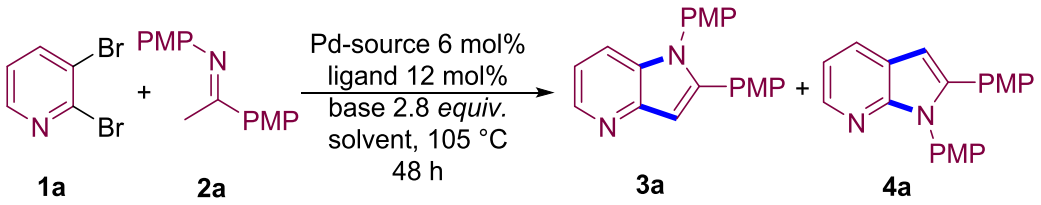


Scheme 30: Synthesis of azaindoles in this study

At first, 2,3-dibromopyridine (**1a**) and 1-bis(4-methoxyphenyl)ethan-1-imine (**2a**) were chosen as model substrates for the optimization experiments (Table 4). Starting from these substrates, the conditions for the indole synthesis documented by Barluenga *et al.* were adopted.[72c] Unfortunately, these conditions resulted in the formation of product mixture of 4- and 7-azaindoles in 12% yield (entry 1, Table 4). Next, bidentate ligands including BINAP, Xantphos and DavePhos were tested, but proved unsuccessful. Conversely, the monodentate ligands PPh_3, CataCXium A and PCy_3 gave rise to the formation of the corresponding 4- and 7-azaindoles **3a** and **4a**. Based on these results, the robustness of these catalyst systems was checked by surveying the influences of palladium sources, bases and temperatures. Suitable conditions for selective generation

of 4- and 7-azaindoles were found, but the yields were moderate (entries 4 and 9, Table 4). In comparison, remarkable improvement was observed in the presence of the catalytic system $Pd(OAc)_2/PCy_3$ with the base NaO*t*Bu in dioxane (entry 8, Table 4). Under these conditions, the resulting azaindoles **3a** and **4a** were furnished in 91% yield, despite an insufficient regioselectivity (**3a**:**4a** were formed in 2:3 ratio).

Table 4: Optimization study for the synthesis of 4- and 7-azaindoles **3a** and **4a**



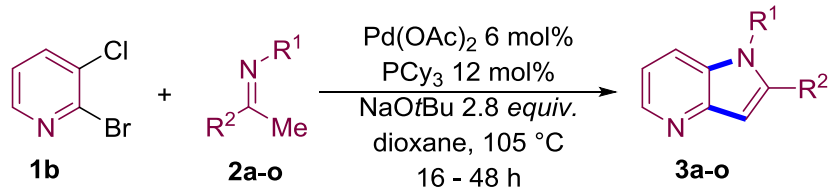
1a **2a** **3a** **4a**

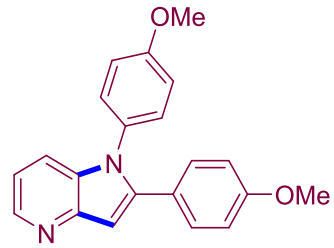
Entry	[Pd]-Source	Ligand	Base	Solvent	Yield (3a:4a)
1	Pd_2dba_3	XPhos	NaO*t*Bu	Dioxane	12%[a] (1:1)[a]
2	Pd_2dba_3	DavePhos	NaO*t*Bu	Dioxane	7%[b] (0:1)[b]
3	Pd_2dba_3	P*t*Bu$_3$	NaO*t*Bu	Dioxane	-
4	Pd_2dba_3	PPh_3	NaO*t*Bu	Dioxane	39%[b] (1:0)[b]
5	Pd_2dba_3	P(*o*-Tol)$_3$	NaO*t*Bu	Dioxane	-
6	Pd_2dba_3	CataCXium A	NaO*t*Bu	Dioxane	53%[b] (1:2)[b]
7	Pd_2dba_3	PCy_3	NaO*t*Bu	Dioxane	73%[b] (2:1)[b]
8	**$Pd(OAc)_2$**	**PCy_3**	**NaO*t*Bu**	**Dioxane**	**91%[a] (2:3)[a]**
9	$Pd(OAc)_2$	PCy_3	K_2CO_3	Dioxane	39%[b] (0:1)[b]

Reaction conditions: **1a** (0.10 mmol), **2a** (0.11 mmol), [Pd]-source (0.06 mmol), ligand (0.012 mmol), base (0.28 mmol), dioxane (2 ml), 105 °C, 48 h
[a] isolated yield; [b] determined by NMR-spectroscopy

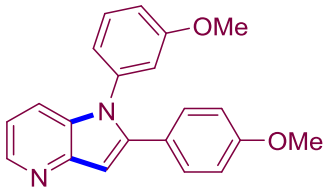
Subsequently, efforts were conducted in order to enhance the regioselectivity from the conditions **8** in Table **5**. To this end, 2-bromo-3-chloropyridine (**1b**) was utilized as starting material for the reaction. With respect to electronic effect, the chemical transformation prefers position 2 over position 3, since it is more electron-deficient. More importantly, the presence of an additional chemo-selective effect occurring in the same direction (position 2 > position 3, Br > Cl) synergistically raises the discrimination in the reactivity between position 2 and position 3. Accordingly, it was expected to obtain higher regioselectivity by using 2-bromo-3-chloropyridine (**1b**) compared to the utility of 2,3-dibromopyridine (**1a**).

Table 5: Synthesis of 4-azaindoles **3a-o**

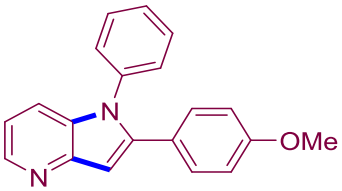




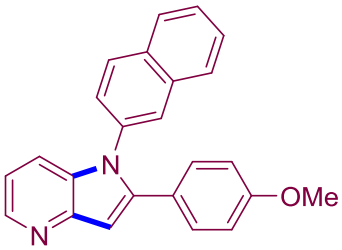
3a (80%)



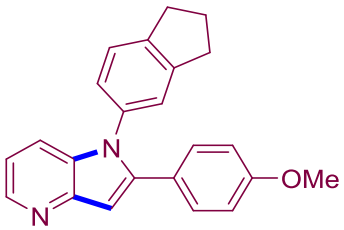
3b (95%)



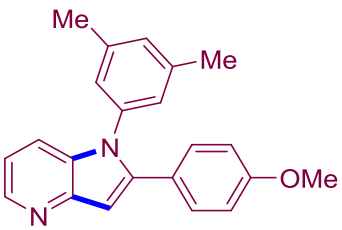
3c (72%)



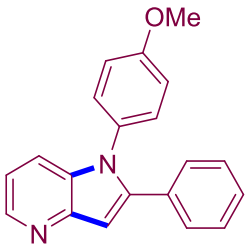
3d (51%)



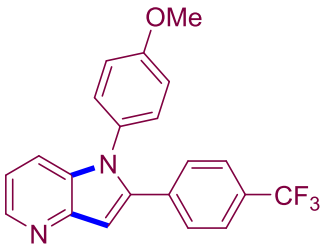
3e (48%)



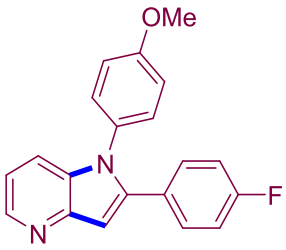
3f (59%)



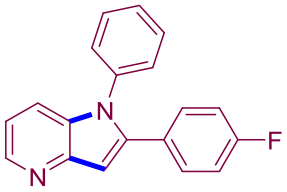
3g (63%)



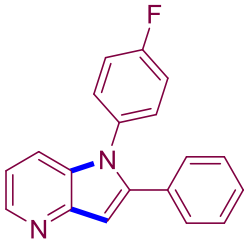
3h (67%)



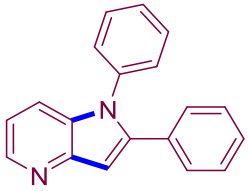
3i (58%)



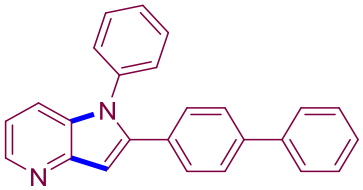
3j (52%)



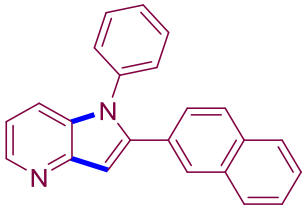
3k (79%)



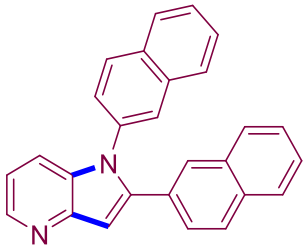
3l (53%)



3m (59%)



3n (89%)



3o (84%)

Reaction conditions: **1a** (0.30 mmol), **2a-o** (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol), NaO*t*Bu (0.84 mmol), dioxane (6 ml), 105 °C, 16 - 48 h. The yields were referred to as isolated yields.

Gratifyingly, by applying 2-bromo-3-chloropyridine (**1b**) in the reaction with imine **2a** using the conditions **8** in Table **4**, the resulting 4-azaindole **3a** was assembled as single regioisomer in very good yield with an excellent level of regioselectivity (Table 5). Motivated by this result, the preparative scope of the reaction was explored. Different electron-rich and electron-poor imines were engaged, giving 4-azaindoles **3b**-**o** (Table 5). The yields varied from moderate to excellent. In general, the yields were good for electron-rich systems, for example 4-azaindoles **3n** and **3o** in Table **6**. The best yield was found with electron-rich 4-azaindole **3b** in 95%, while the lowest occurred with 4-azaindole **3e** in 48%. However, no further detailed information with reference to the correlation between the synthetic efficiency and the chemical structure was revealed from the data.

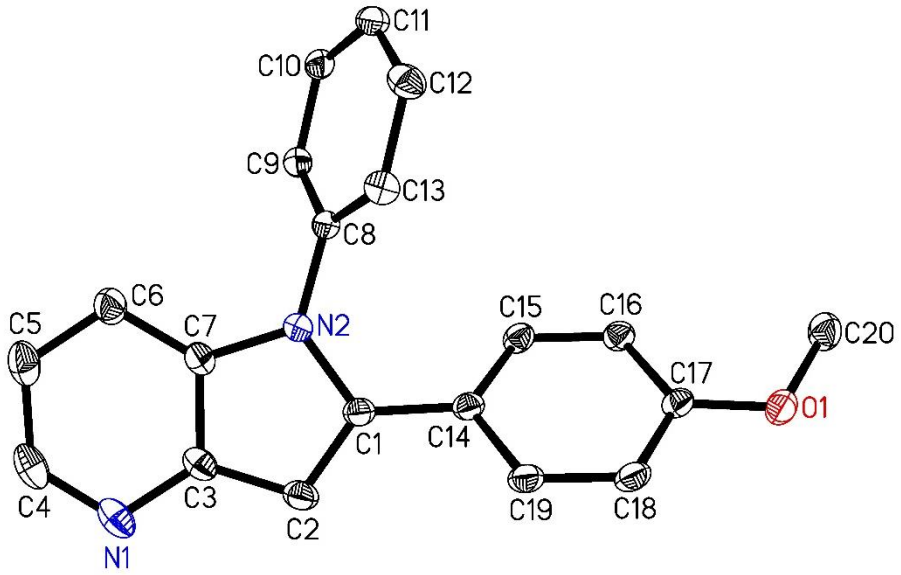
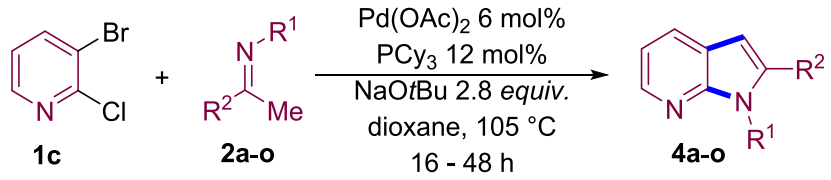


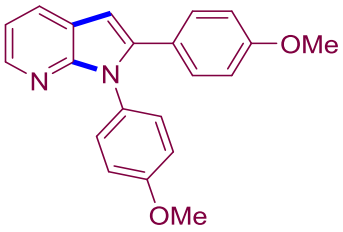
Figure 8: Molecular structure of **3c** in the crystal

The molecular structure of 4-azaindole **3c** was independently confirmed by X-ray crystal structure analysis (Figure 8). As can be seen, the atoms in the azaindole ring are bounded in a planar configuration. The phenyl rings at position 1 and position 2 twist out of the azaindole plane by 35.2 and 69.3 °, respectively. With this conformation, the steric repulsion between the phenyl rings at position 1 and 2 was diminished.

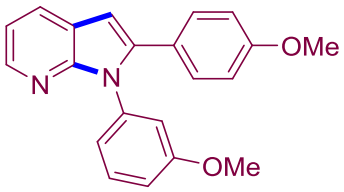
Table 6: Synthesis of 7-azaindoles **4a-o**



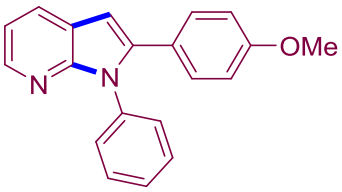
1c **2a-o** **4a-o**



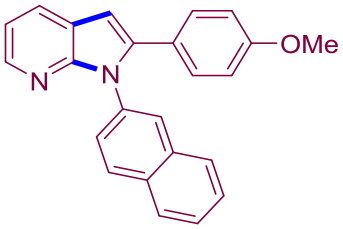
4a (81%)



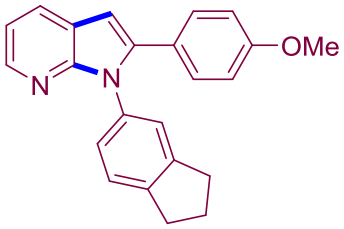
4b (75%)



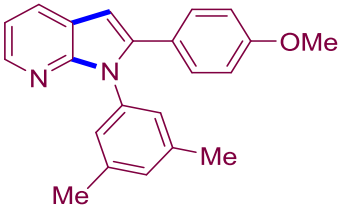
4c (70%)



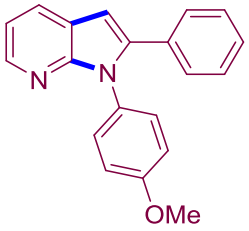
4d (68%)



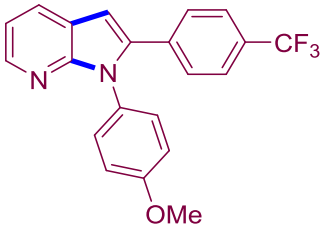
4e (47%)



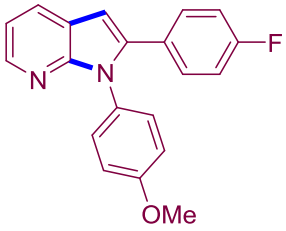
4f (47%)



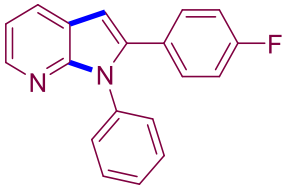
4g (72%)



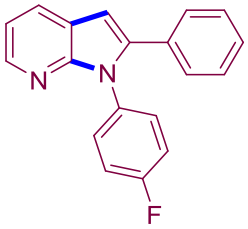
4h (63%)



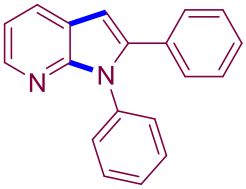
4i (59%)



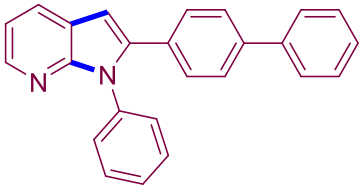
4j (57%)



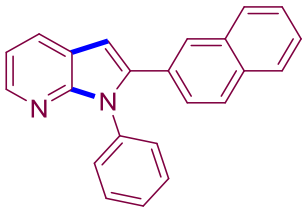
4k (61%)



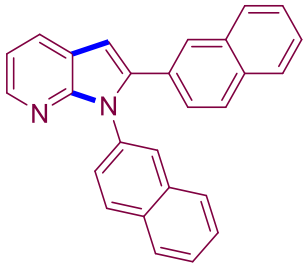
4l (56%)



4m (76%)



4n (67%)



4o (86%)

Reaction conditions: **1c** (0.30 mmol), **2a-o** (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol), NaO*t*Bu (0.84 mmol), dioxane (6 ml), 105 °C, 16 - 48 h. The yields were referred to as isolated yields.

Following the successful synthesis of 4-azaindoles, further investigation of the reaction of 2-chloro-3-bromopyridine (**1c**) with different imines was undertaken (Table 6). In the structure of 2-chloro-3-bromopyridine (**1c**), the chemo-selectivity is reversed, because the positions of Br and Cl are switched. Therefore, position 3 of the pyridine ring turns to be more reactive than position 2, since the chemo-selective effect (Br > Cl) generally overwhelms the electronic effect (position 3 > position 2) in palladium-catalyzed cross-coupling reactions. As expected, by employing 3-bromo-2-chloropyridine (**1c**) in the reactions with different imines, the resulting 7-azaindoles **4a**-**o** were afforded in moderate to very good yields (Table 6). The highest yield was observed for the largely aromatic 7-azaindole **4o** in 86%. In contrast, both 7-azaindoles **4n** and **4o** were furnished in lowest yields (47%), presumably as a result of steric effect.

Additional X-ray structure determination confirmed the molecular structures of 7-azaindoles **4g** and **4n** (Figure 9-10). In similarity with the structure of 4-azaindole **3c**, the azaindole rings of 7-azaindoles **4g** and **4n** are regarded as planar. Additionally, the phenyl rings at position 1 of the azaindole rings of both 7-azaindoles **4g** and **4n** twist out of the aromatic plane by 45.25(5) and 60.20(4) °, respectively, due to steric repulsion. In comparison, the deviations from the azaindole plane observed at position 2 of these compounds are 57.94(4) °(**4g**) and 42.00(3) °(**4n**).

In summary, 4- and 7-azaindoles were successfully prepared using palladium-catalyzed domino C-C/C-N coupling of *ortho*-dihalopyridines with imines. The regiochemistry of these chemical transformations was dictated by the chemo-selectivity present in the *ortho*-dihalopyridine starting materials (Br *versus* Cl).

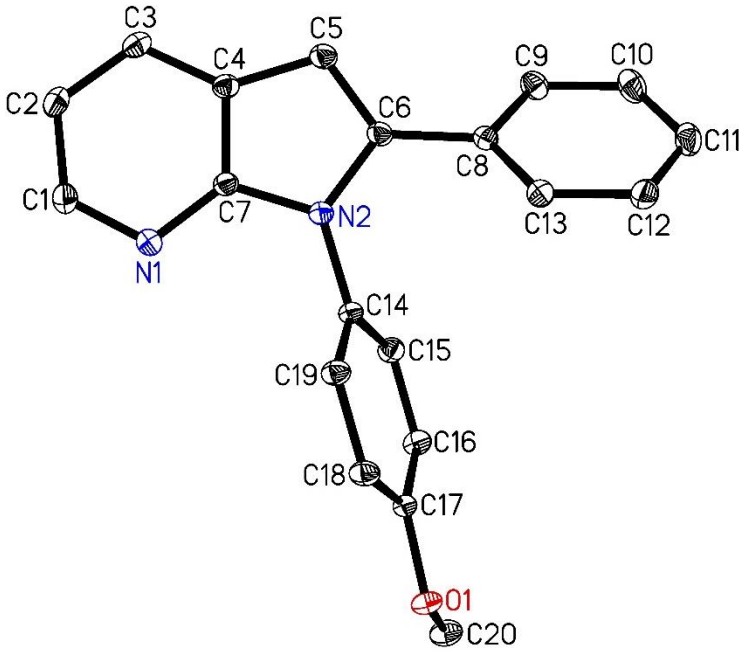


Figure 9: Molecular structure of **4g** in the crystal

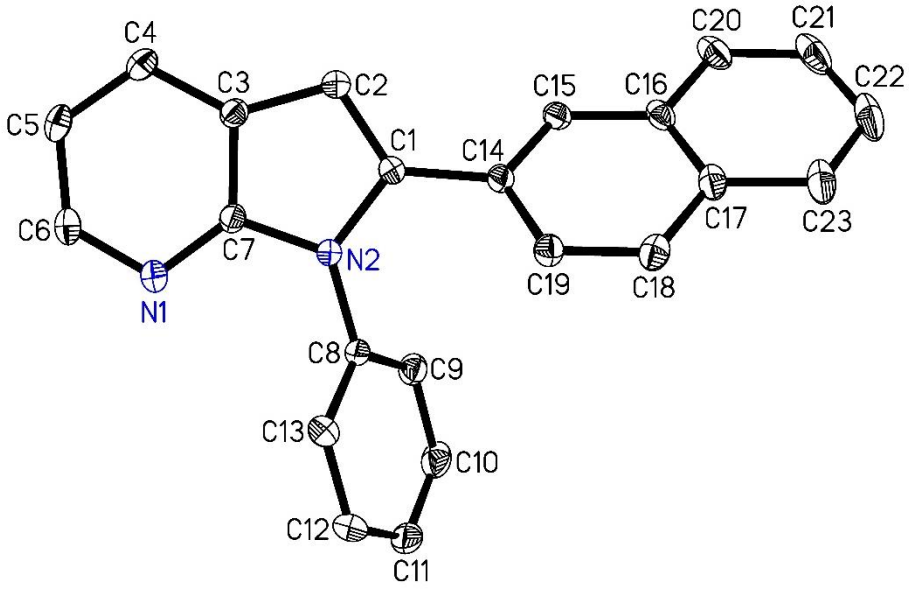
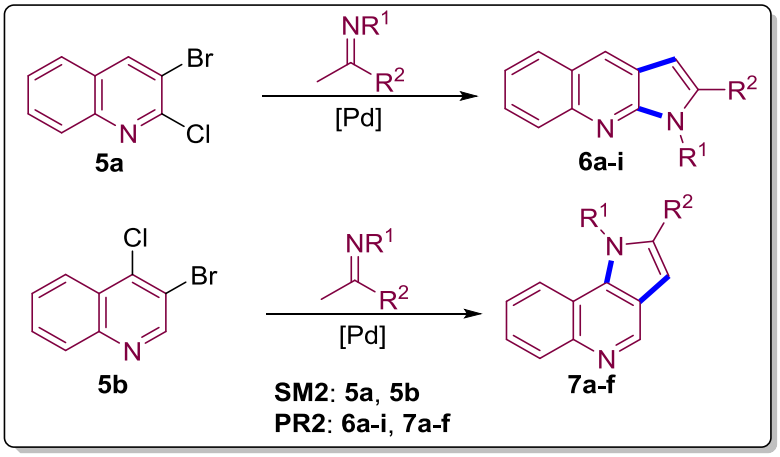


Figure 10: Molecular structure of **4n** in the crystal

3.1.2. Synthesis of pyrroloquinolines from *ortho*-dihaloquinolines



With a wide scope of the synthesis of 4- and 7-azaindoles demonstrated in Chapter **3.1.1**, further investigation of the reaction of *ortho*-dihaloquinoline with imines to assemble pyrroloquinolines (product series **PR2**) was undertaken. Pyrroloquinolines were reported with antineoplastic,[100] antitubercular[101] and cytotoxic activities.[102] For example, SB-742457 is a potential 5-HT_6 receptor antagonist drug for the treatment of cognitive disorder diseases (Figure 11).[103]

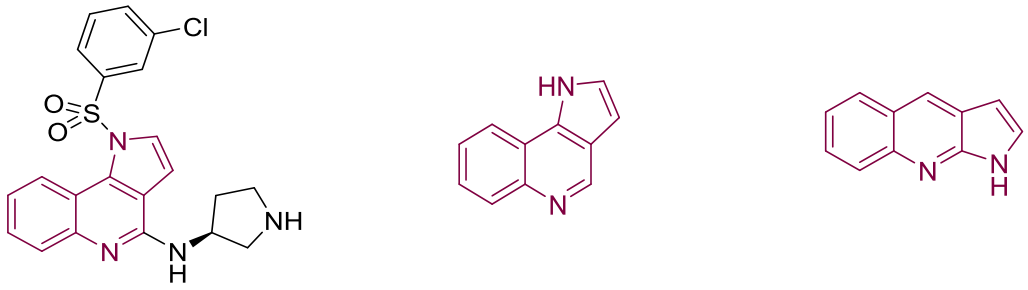
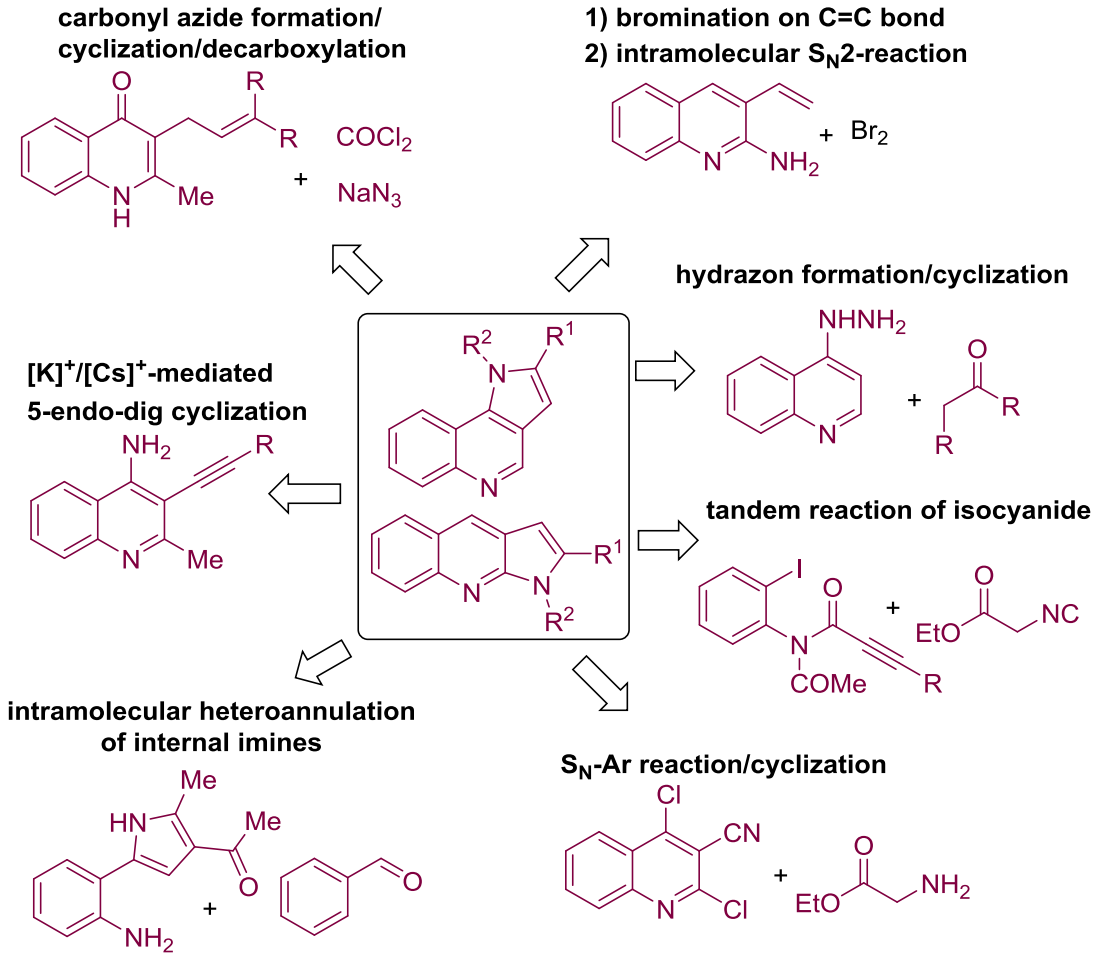


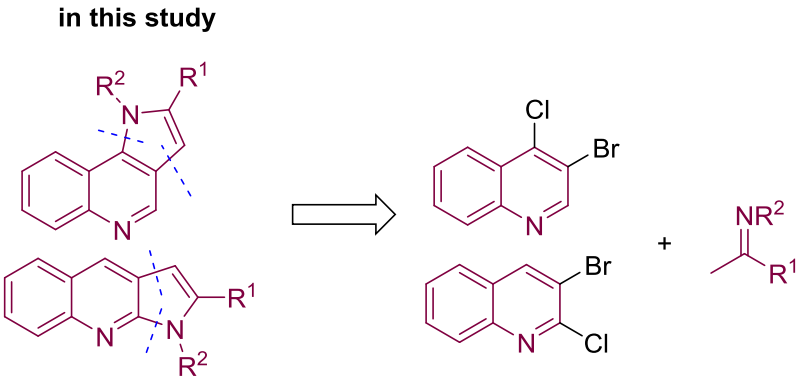
Figure 11: Examples of pyrroloquinolines with biological relevance

Among different pyrroloquinoline architectures, 1*H*-pyrrolo[2,3-*b*]quinolines and 1*H*-pyrrolo[3,2-*c*]quinolines are of interest in this study (Figure 11). Until recently, several approaches for the synthesis of these pyrroloquinolines have been known, namely K^+/Cs^+-mediated 5-endo-dig cyclization,[104] carbonyl azide formation/cyclization/ decarboxylation,[105] bromination/intramolecular S_N2 reaction,[106] hydrazine formation/ thermal cyclization,[107] intramolecular heteroannulation of internal imines,[108] S_N-Ar reaction/cyclization[109] and tandem reaction of isocyanide[110] (Scheme 31). Unfortunately, to a certain extent these

syntheses are considered tedious and not modular. Therefore, the palladium-catalyzed domino C-C/C-N coupling of *ortho*-dihaloquinolines with imines would offer a new convenient and modular access to these structures (Scheme 32).



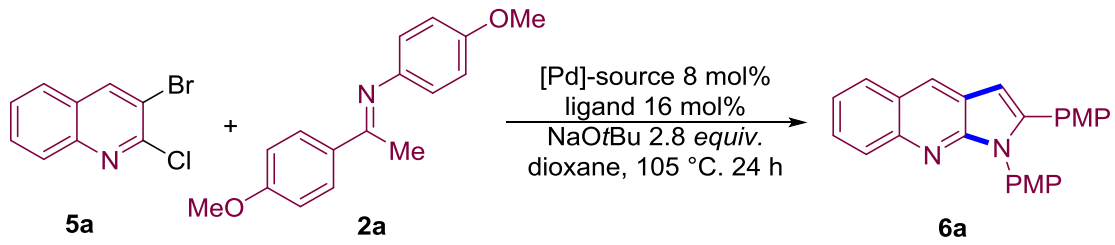
Scheme 31: Previously documented synthesis of 1*H*-pyrrolo[2,3-*b*]quinolines and 1*H*-pyrrolo[3,2-*c*]quinolines



Scheme 32: Synthesis of 1*H*-pyrrolo[2,3-*b*]quinolines and 1*H*-pyrrolo[3,2-*c*]quinolines in this study

The synthetic efforts began with the optimization of the model reaction of 3-bromo-2-chloroquinoline (**5a**) and 1-bis(4-methoxyphenyl)ethan-1-imine (**2a**) affording pyrroloquinoline **6a** (Table 7). The choice of the phosphine ligands for this screening was based on the previous optimization results of the azaindole synthesis described in Table **4**.

Table 7: Optimization study of the synthesis of 1*H*-pyrrolo[2,3-*b*]quinoline **6a**



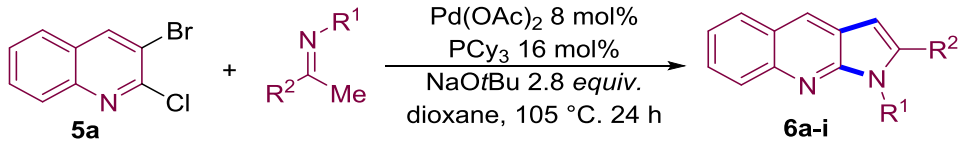
Entry	Pd-source	Ligand	Yield
1	$Pd(OAc)_2$	CataCXium A	61%
2	**$Pd(OAc)_2$**	**PCy_3**	**85%**
3	$Pd(OAc)_2$	PPh_3	45%
4	$Pd(OAc)_2$	XPhos	21%

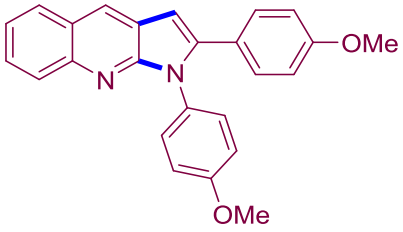
Reaction conditions: **5a** (0.10 mmol), **imines** (0.11 mmol), $Pd(OAc)_2$ (0.008 mmol), PCy_3 (0.016 mmol), NaO*t*Bu (0.28 mmol), dioxane (2 ml), 105 °C, 24 h. The yields were referred to as isolated yields.

From the screening data, the catalyst system $Pd(OAc)_2/PCy_3$ was found to be the best conditions, assembling pyrroloquinoline **6a** in good yield (85%). It is noteworthy that these conditions are identical to those used the synthesis of azaindoles described in Chapter **3.1.1**.

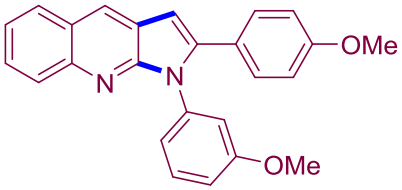
Pyrroloquinolines **6b-i** were prepared on treatment with 3-bromo-2-chloroquinoline (**5a**) under these conditions in up to 85% yields (Table 8). It seems likely that the incorporation of electron-withdrawing groups (-F and $-CF_3$) hampers the formation of the products, since the yields obtained with pyrroloquinoline **6d** and **6i** were lower. Pyrroloquinoline **6i** gave the lowest yield in 56%. Conversely, good yields were obtained with electron-rich 1*H*-pyrrolo[2,3-*b*]quinolines **6a**, **6b**, **6g** and **6h**, all being greater than 75%, with the highest observed for **6g** in 90% yield.

Table 8: Synthesis of 1*H*-pyrrolo[2,3-*b*]quinolines **6a-i**

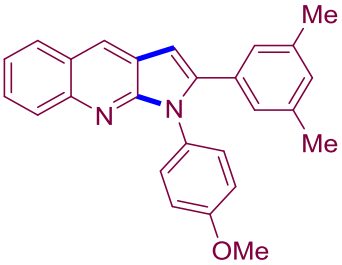




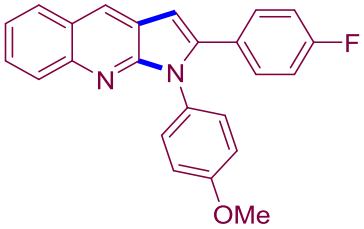
6a (85%)



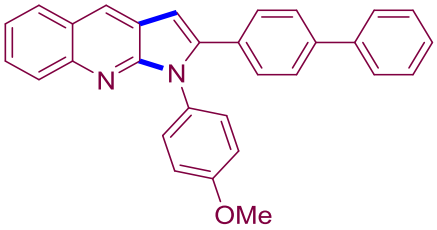
6b (75%)



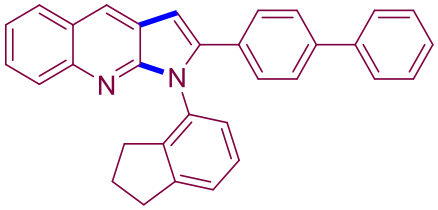
6c (78%)



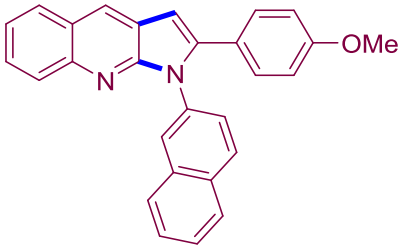
6d (60%)



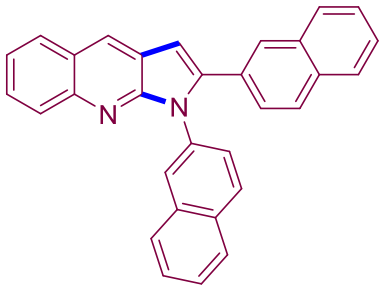
6e (80%)



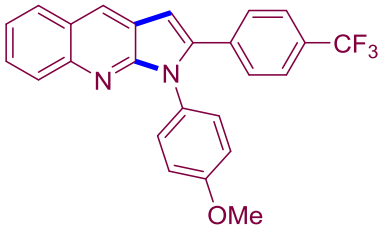
6f (88%)



6g (90%)



6h (87%)

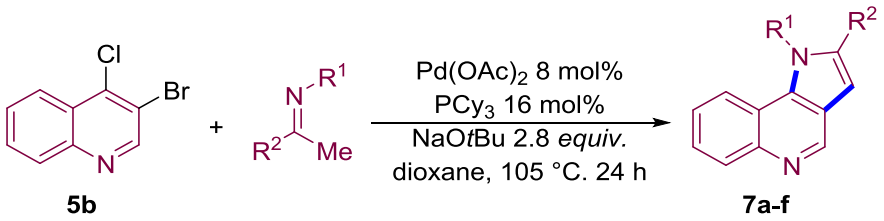


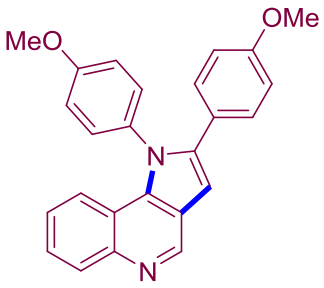
6i (56%)

Reaction conditions: **5a** (0.30 mmol), **imines** (0.33 mmol), $Pd(OAc)_2$ (0.024 mmol), PCy_3 (0.048 mmol), NaO*t*Bu (0.84 mmol), dioxane (6 ml), 105 °C, 24 h. The yields were referred to as isolated yields.

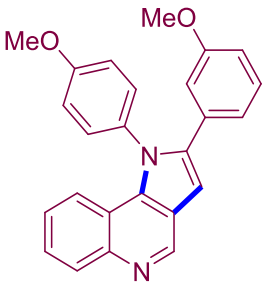
Encouraged by these results, further investigations were accomplished for the reaction of imines with 3-bromo-4-chloroquinoline (**5b**) (Table 9). Applying the same conditions, pyrroloquinolines **7a-f** were assembled in between 46% and 82% yield (Table 9). Compared to the prior series, the yields obtained with these derivatives are slightly lower in general. It is possibly interpreted as a result of the electronic compulsion between the substituents at position 1 with the benzene ring of the quinoline structure that potentially lowers the stability of the entire system. From Table **11**, it is observed in agreement with prior series that products bearing electron-withdrawing groups -F and -CF_3 **7e-f** gave lower yields (46% and 58%, respectively). In comparison, the highest yield was achieved with electronically rich pyrroloquinoline **7a** in 82% yield.

Table 9: Synthesis of pyrrolo[3,2-*c*]quinolines **7a-f**

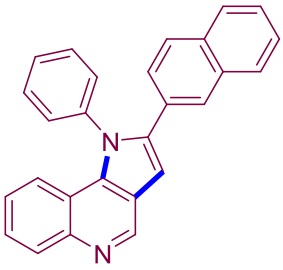




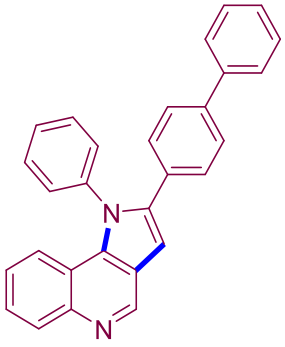
7a (82%)



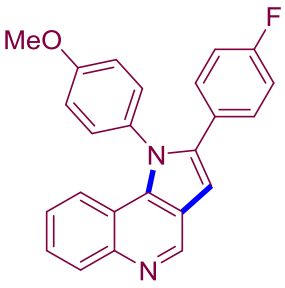
7b (61%)



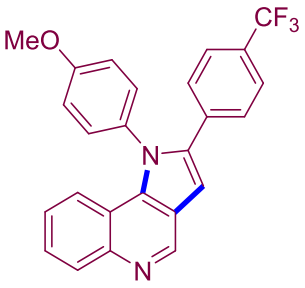
7c (72%)



7d (67%)



7e (46%)



7f (58%)

Reaction conditions: **5b** (0.30 mmol), **imines** (0.33 mmol), $Pd(OAc)_2$ (0.024 mmol), PCy_3 (0.048 mmol), NaO*t*Bu (0.84 mmol), dioxane (6 ml), 105 °C, 24 h. The yields were referred to as isolated yields.

The molecular structure of 1*H*-pyrrolo[3,2-*c*]quinoline **7f** was additionally confirmed by X-ray structure determination (Figure 12). The structure exhibits a planar pyrroloquinoline ring. The phenyl rings at position 1 and 2 twist out of the plane by 83.4(3) and 31.7(5) °, respectively, owing to steric repulsion.

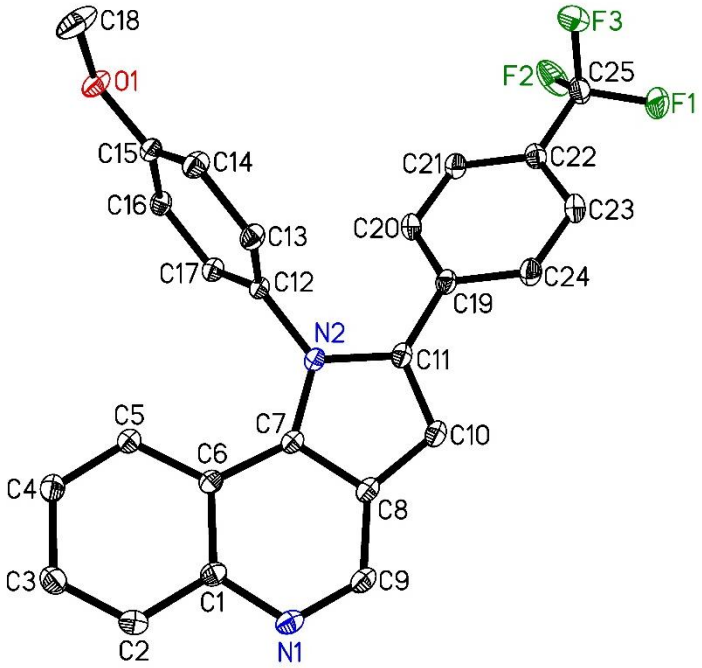
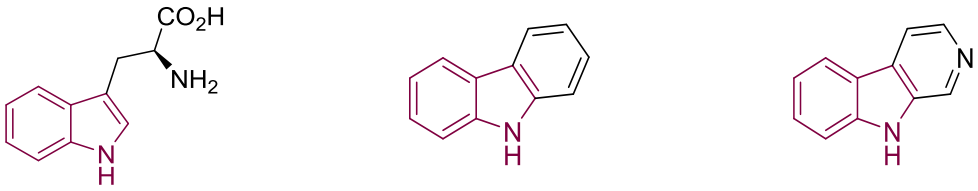


Figure 12: Molecular structure of 1*H*-pyrrolo[3,2-*c*]quinoline **7f** in the crystal

Taken together, two isomeric pyrroloquinolines were prepared by palladium-catalyzed domino C-C/C-N coupling of imines with *ortho*-dihaloquinolines in moderate to good yields. The synthetic utility and versatility of the method are manifested and can be adapted to other *ortho*-dihaloarenes to enable access to more pyrrole-fused aromatic systems.

3.2. Synthesis of indole-fused heterocycles from *ortho*-dihaloarenes by regioselective Suzuki reaction followed by double C-N coupling

Indole is a biologically important heterocycle which is prevalently distributed in nature. In bacterial culture, it is an intercellular molecule which regulates biological functions including plasmid stability and spore formation.[111] Furthermore, indole is incorporated in the chemical structure of the amino acid tryptophan, which participates in the synthesis of proteins and serves as a precursor to the neurotransmitters melatonin and serotonin in human (Figure 13).[112]

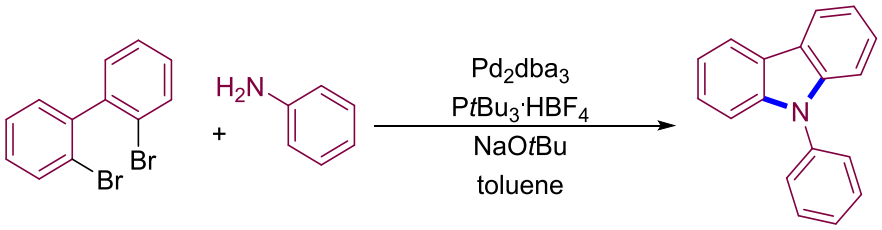


tryptophan carbazole β-carboline

Figure 13: Several biologically and physically important indole-derived structures

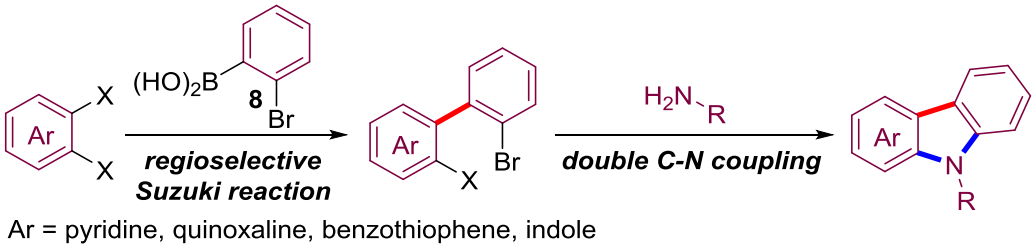
The development of different indole derivatives has attracted attention from the scientific community. Among these, fused indole heterocycles have gained increasing importance, particularly in the field of medicinal and material science. Taken carbazole as an example of an indole-fused scaffold, a handful of carbazole derivatives were found with antitumor activities,[113] or possess low bandgap suitable for the applications in high-performance solar cell techniques.[79c, 114] Another example of indole-fused heterocycles, namely β-carboline, is incorporated in alkaloids with benzodiazepine inverse agonisting properties (Figure 13).[115]

The preparation of fused-indole heterocycles can be achieved by classic syntheses, such as Fischer-indole synthesis, Diels-Alder addition and Cadogan cyclization.[116] Besides, the synthesis can also utilize transition metal catalysts, proceeding through different types of transformations including C-N cross-coupling, hydroamination and domino C-C/C-N coupling.[116] Among them, a development relevant to this PhD research is the practical preparation of carbazoles reported by Nozaki *et al.* in 2003 (Scheme 33).[117] The synthesis capitalizes the potential of the Buchwald-Hartwig amination and the entropic privilege of the intramolecular reaction. 2,2'-Dibromo-1,1'-biphenyl and amines are accommodated in a double C-N cross-coupling reaction Noteworthy, the couplings occur uneventfully even with sterically congested amines.



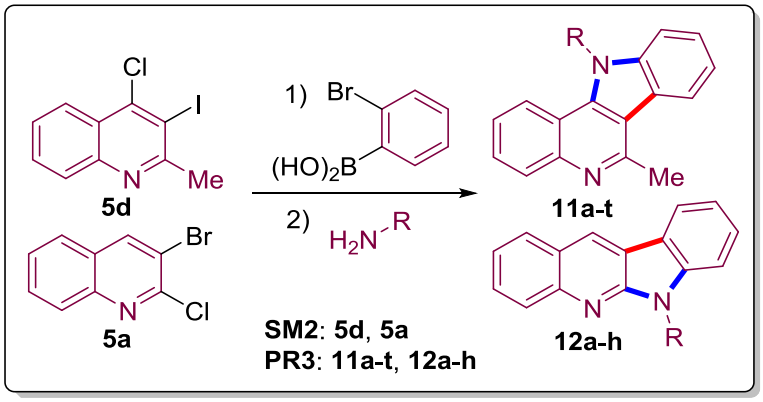
Scheme 33: Synthesis of carbazoles by double C-N cross-coupling reaction[117]

To date, several modifications of this method have been developed by Langer *et al*.[118] In these studies, one phenyl ring in the structure of the substrates 1,1'-dihalobiaryls was exchanged by a heterocycle. The corresponding substrates were synthesized by applying regioselective Suzuki reactions of *ortho*-dihaloarenes with (2-bromophenyl)boronic acid (**8**) (Scheme 34). These strategies are compatible with a broader range of starting materials, which couple with primary amines to give different indole-fused structures (Scheme 34). Along with this development, further modifications of the Nozaki carbazole synthesis have been developed for the preparation of indoloquinolines (**PR3**, Chapter 3.2.1), benzo[*a*]carbazoles (**PR4**, Chapter 3.2.2) and thienoindoles (**PR5**, Chapter 3.2.3) in this contribution.

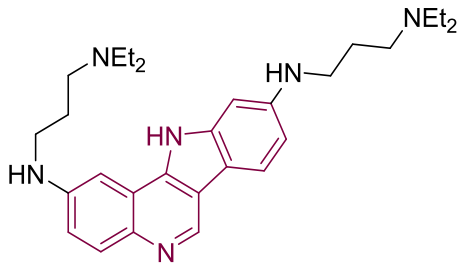


Scheme 34: Examples of previously reported syntheses of indole-fused heterocycles by sequential regioselective Suzuki reaction/double C-N coupling

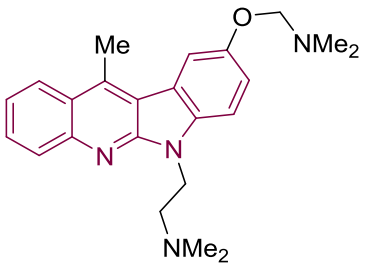
3.2.1. Synthesis of indoloquinolines from *ortho*-dihaloquinolines



Indoloquinolines are biologically active scaffolds which were documented with antimalarial [119] and antitumor properties.[120] Moreover, they can interact with DNA[121] or can be employed as inhibitor for DYRK1A[122] and NQ01,[123] to name but a few. For example, IDQ3D was discovered as G-quadruplex stabilizer in human cells,[124] while MDIQ2 represents a cytotoxic DNA topoisomerase II inhibitor[125] (Figure 14).



IDQ3D

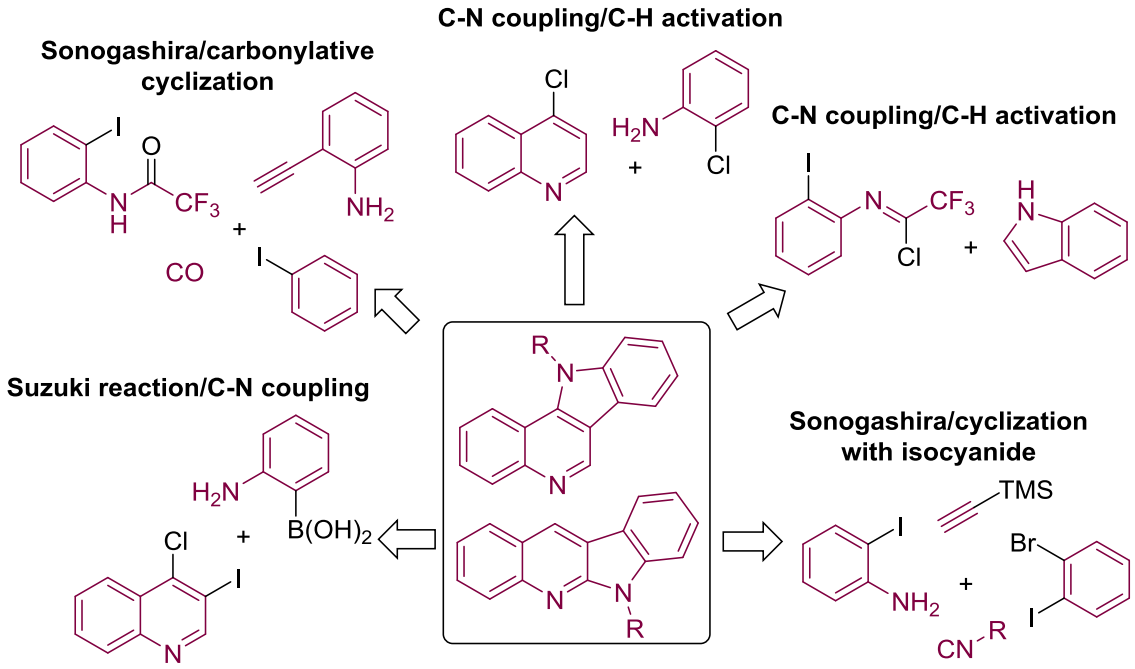


MDIQ2

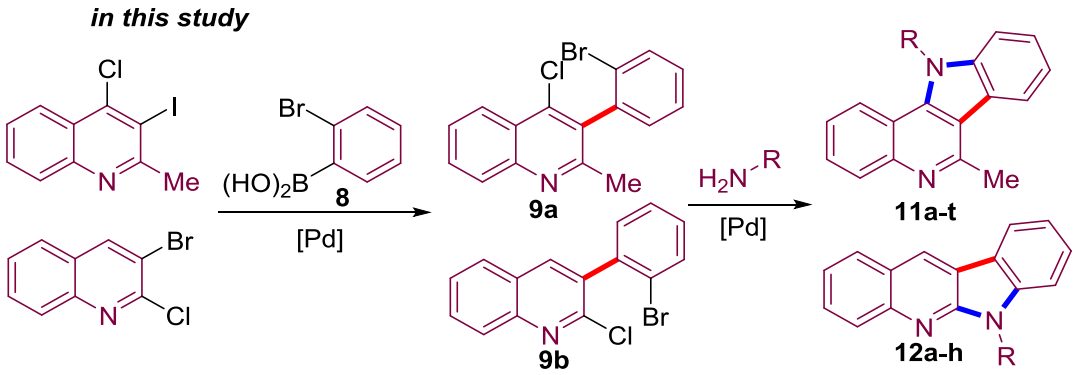
Figure 14: Examples of indoloquinoline related compounds with biological importance

The chemistry of two indoloquinoline derivatives namely 11*H*-indolo[3,2-*c*]quinoline and 6*H*-indolo[2,3-*b*]quinoline is focused in this study. Their preparations can be carried out using classic syntheses including Fischer indolization,[126] Pictet-Sprengler cyclization[127] and Curtius rearragement.[128] Moreover, the synthesis can be accomplished by exploiting the potential of transition metal catalysts[129], for example Suzuki,[130] Sonogashira,[131] C-N coupling/C-H activation,[132] isocyanide insertion,[133] and carbonylative cyclization[134] (Scheme 35).

In this relation, the application of sequential regioselective Suzuki reaction of *ortho*-dihaloquinolines with (2-bromophenyl)boronic acid (**8**) followed by double C-N coupling offers a new convenient pathway to 11-substituted 11*H*-indolo[3,2-*c*]quinolines and 6-substituted 6*H*-indolo[2,3-*b*]quinolines (Scheme 36).



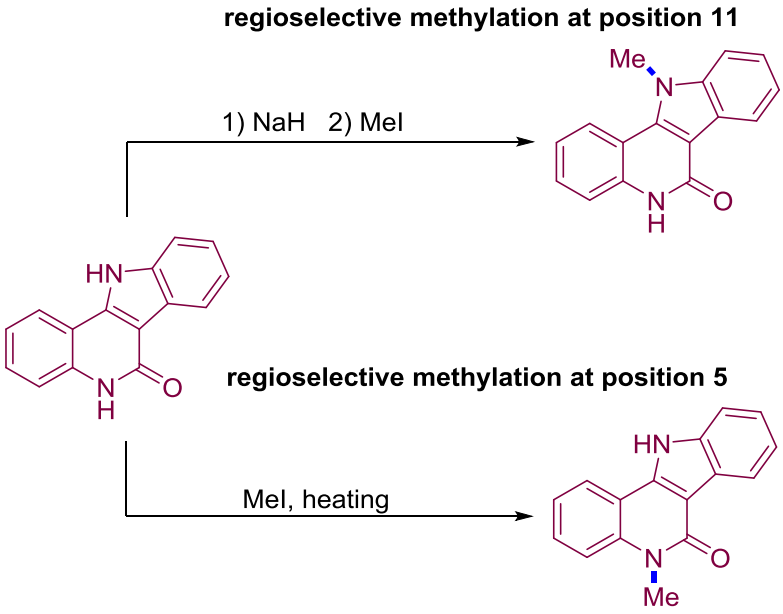
Scheme 35: Examples of palladium-catalyzed synthesis of indoloquinolines [130a, 132a-f, 133c, 134]



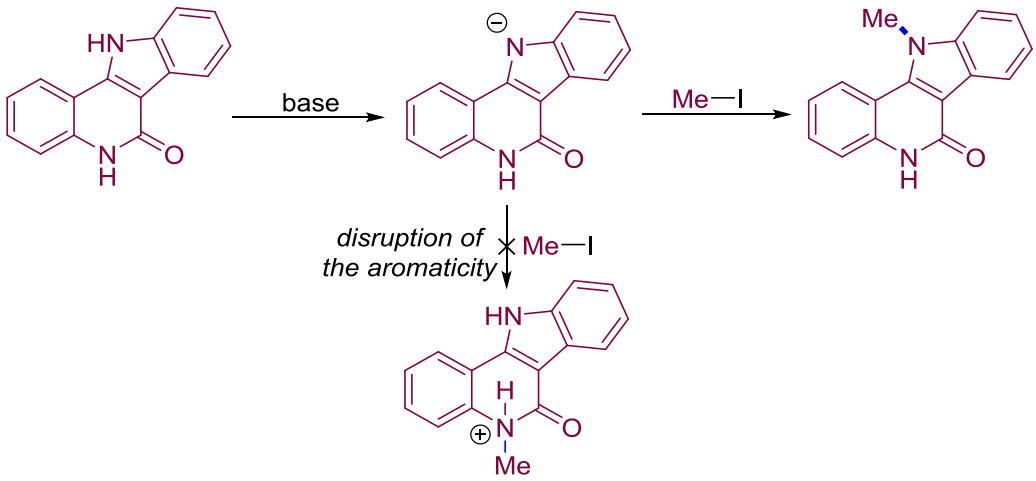
Scheme 36: Synthesis of 11-substitued 11*H*-indolo[3,2-*c*]quinolines and 6-substitued 6*H*-indolo[2,3-b]quinolines in this study

Noticeably, the preparation of 11*H*-indolo[3,2-*c*]quinolines bearing substituents at position 11 using current synthetic platforms still remains a synthetic challenge. Thus far, it has been enabled to synthesize 11*H*-indolo-[3,2-*c*]quinolines with no substituents at position 11, followed by a regioselective successive alkylation (Scheme 37).[135] The

regioselectivity of the reaction relies on the low pK_a value of the N-H group at position 11 and the higher basicity of the nitrogen atom at position 5. In basic medium, the N-H group at position 11 is preferentially deprotonated. The following nucleophilic attack with an alkyl halide proceeds at this position, as the aromaticity of the system is retained until the formation of final product (Scheme 38). On the other hand, in a neutral medium, the higher basicity of the nitrogen atom at position 5 takes over, resulting in a higher nucleophilic character at this position in the *N*-alkylation reaction. However, this regioselective successive alkylation was thus far solely documented for the methylation,[135] possibly due to its incompatibility with other substituents.

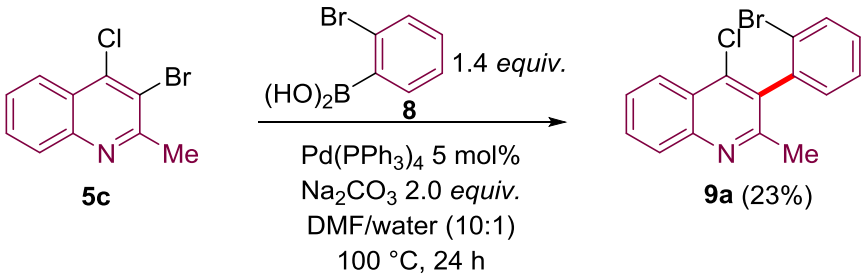


Scheme 37: Regioselective methylation of 11*H*-indolo[3,2-*c*]quinoline

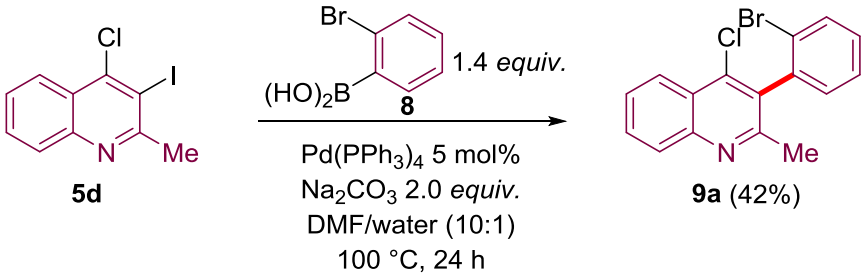


Scheme 38: Mechanism of the regioselective methylation of 11*H*-indolo[3,2-*c*]quinolines at position 11

The initial studies focused on the reaction of 2,3-dihalo-2-methylquinolines **5c-d** with (2-bromophenyl)boronic acid (**8**). Among these 2,3-dihalo-2-methylquinolines, 3-bromo-4-chloro-2-methylquinoline (**5c**) failed to give the desired product 3-(2-bromophenyl)-4-chloro-2-methylquinoline (**9a**) with satisfying yield (23%, Scheme 39). It is presumably ascribed to the lack of reactivity of the bromine atom. For this reason, 4-chloro-3-iodo-2-methylquinoline (**5d**) was utilized instead. In palladium-catalyzed reactions, iodine is considered to be more reactive than bromine. Hence 4-chloro-3-iodo-2-methylquinoline (**5d**) was expected to deliver better result. Pleasingly, the yield increased to 42% (Scheme 40), which was followed by the study of the double C-N coupling of 3-(2-bromophenyl)-4-chloro-2-methylquinoline (**9a**) with different primary amines.



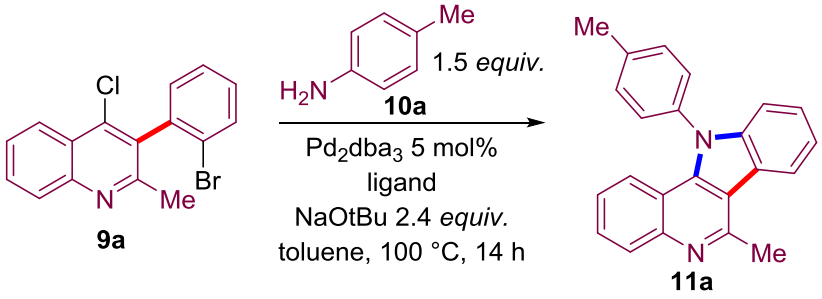
Scheme 39: Regioselective Suzuki reaction of 3-bromo-4-chloro-2-methylquinoline (**5c**) with boronic acid **8**



Scheme 40: Regioselective Suzuki reaction of 4-chloro-3-iodo-2-methylquinoline (**5d**) with boronic acid **8**

Next, an optimization study was carried out for the reaction of 3-(2-bromophenyl)-4-chloro-2-methylquinoline (**9a**) with *p*-toluidine (**10a**), in which indoloquinoline **11a** was formed (Table 10). From the screening results, P*t*Bu$_3$·HBF$_4$ proved superior to other phosphorous ligands, furnishing indoloquinoline **11a** in virtually quantitative yield (95%, entry 2, Table 10).

Table 10: Optimization study for the synthesis of indoloquinoline **11a**

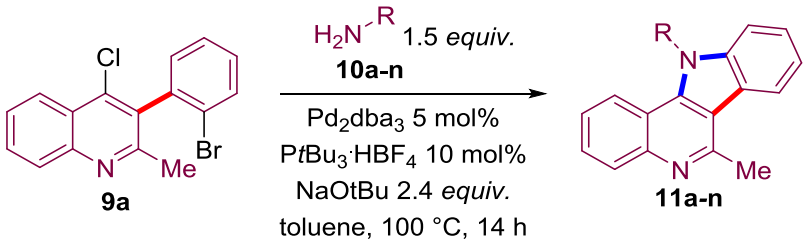


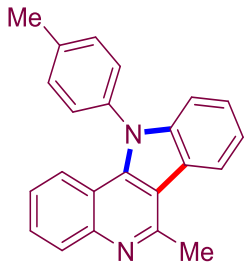
Entry	Ligand	Yield
1	SPhos	56%
2	**P*t*Bu$_3$·HBF$_4$**	**95%**
3	dppf	63%
4	(*S*)-BINAP	78%

Reaction conditions: **9a** (0.10 mmol), **10a** (0.15 mmol), Pd_2dba_3 (0.005 mmol), ligands (0.005 mmol for monodentate or 0.010 mmol for bidentate ligands), NaO*t*Bu (0.24 mmol), toluene (2 ml), 100 °C, 14 h; The yields were referred to as isolated yields

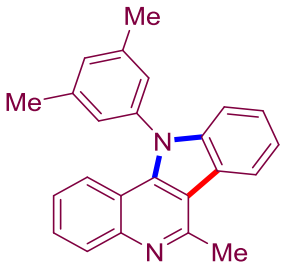
Subsequently, the preparative scope of the reaction was assessed. The reaction of 3-(2-bromophenyl)-4-chloro-2-methylquinoline (**9a**) with different electron-rich aromatic primary amines **10a-n** assembled corresponding indoloquinolines **11a-n** in good to excellent yields (Table 11).

Table 11: Synthesis of 11*H*-indolo[3,2-*c*]quinolines **11a-n** from electronically rich and electronically neutral aromatic amines

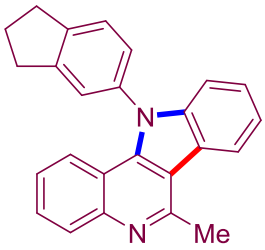




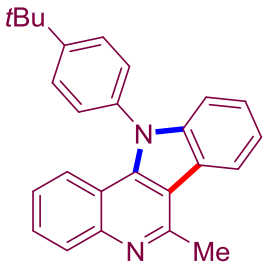
11a (93%)



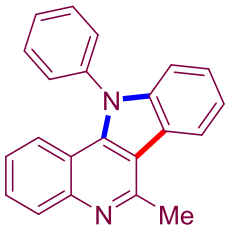
11b (89%)



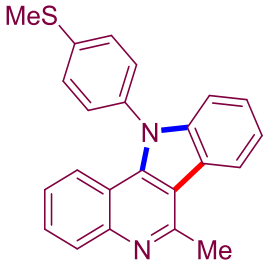
11c (93%)



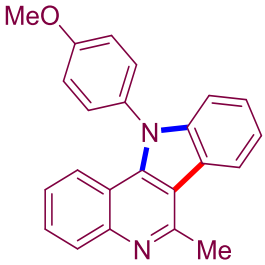
11d (92%)



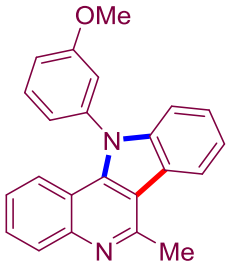
11e (93%)



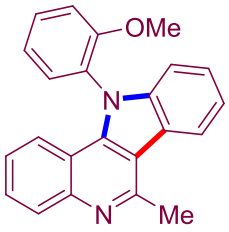
11f (90%)



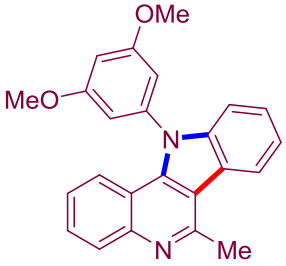
11g (95%)



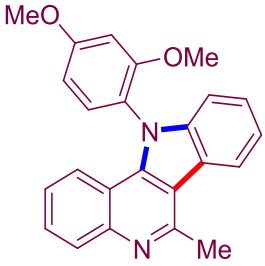
11h (91%)



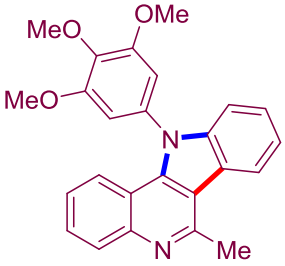
11i (89%)



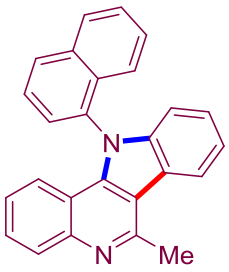
11j (97%)



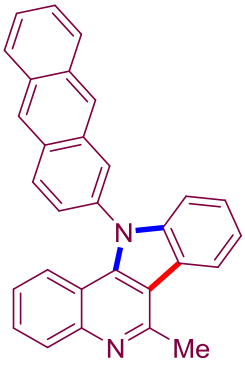
11k (85%)



11l (89%)



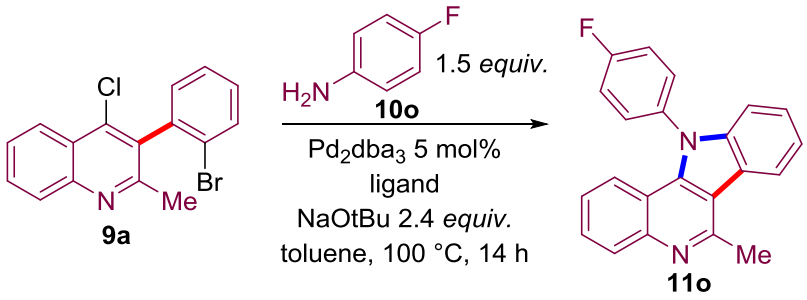
11m (83%)



11n (91%)

Reaction conditions: **9a** (0.150 mmol), **10a-n** (0.225 mmol), Pd_2dba_3 (0.0075 mmol), P*t*Bu_3·HBF_4 (0.015 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 24 h. The yields were referred to as isolated yields.

Table 12: Optimization study for the synthesis of indolo[3,2-*c*]quinoline **11o**



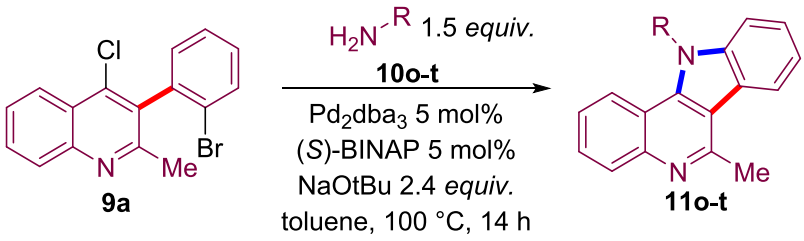
Entry	Ligand	Yield
1	SPhos	73%
2	P*t*Bu$_3$·HBF$_4$	67%
3	dppf	59%
4	**(*S*)-BINAP**	**95%**

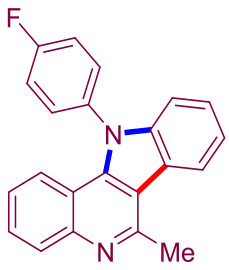
Reaction conditions: **9a** (0.10 mmol), **10o** (0.15 mmol), Pd_2dba_3 (0.005 mmol), ligand (0.005 mmol for monodentate or 0.010 mmol for bidentate ligands, NaO*t*Bu (0.24 mmol), toluene (2 ml), 100 °C, 14 h. The yields were referred to as isolated yields.

For the employment of electronically poor aryl amines, P*t*Bu$_3$·HBF$_4$ did not perform effectively. Thus, another ligand screening was accomplished for the reaction of 3-(2-bromophenyl)-4-chloro-2-methylquinoline (**9a**) and 4-fluoroaniline (**10o**) (Table 12). (*S*)-BINAP was identified as the preferred ligand for this reaction. When using the catalyst system Pd_2dba_3/(*S*)-BINAP and the base NaO*t*Bu in toluene, the resulting indoloquinoline **11o** was afforded in 95% (entry 4, Table 12).

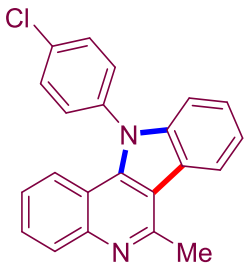
Applying these optimum conditions, the scope of the double C-N coupling with electron-poor aromatic amines **11o-q** was probed (Table 13). The yields were obtained in the range between 77% and 95% (Table 13). The conditions were also found to be applicable for the treatment of 3-(2-bromophenyl)-4-chloro-2-methylquinoline (**9a**) with benzylic and aliphatic amines, in which the resulting indoloquinolines **11r-t** were afforded in good to excellent yield (Table 13).

Table 13: Synthesis of indolo[3,2-*c*]quinolines **11o-t** from electron-poor aromatic, benzylic and aliphatic amines

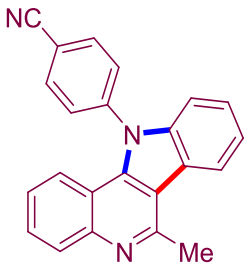




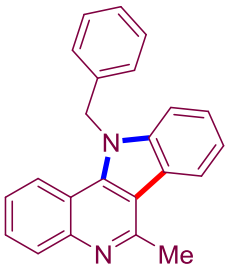
11o (95%)



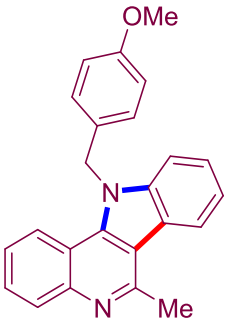
11p (77%)



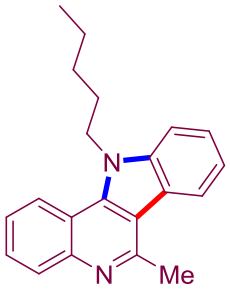
11q (93%)



11r (96%)



11s (83%)



11t (78%)

Reaction conditions: **9a** (0.150 mmol), **10o-t** (0.225 mmol), Pd_2dba_3 (0.0075 mmol), (*S*)-BINAP (0.0075 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 24 h. The yields were referred to as isolated yields.

The molecular structure of indoloquinoline **11g** was independently confirmed by X-ray crystal analysis. The asymmetric unit of indoloquinoline **11g** comprises three molecular units, of which a representative is illustrated in Figure **15**. The core indoloquinoline ring adopts a planar configuration. The methoxylphenyl groups in these molecules deviate from the aromatic plane with angles of 63.53(3) °, 87.13(4) ° and 78.84(3) °. Further observation of these structures reveals π-π-stacking interactions in the molecular network (Figure 16). The shortest distance between two adjacent indoloquinoline planes is 3.639 Å.

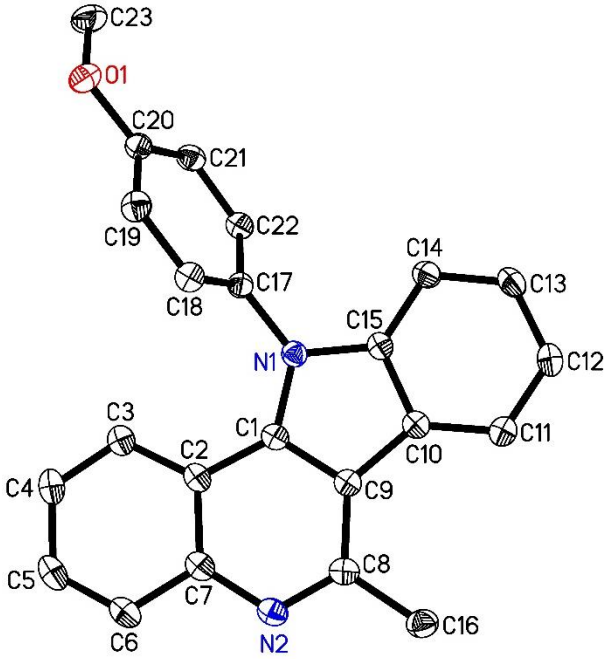


Figure 15: Molecular structure of 11*H*-indolo[3,2-*c*]quinoline **11g** in the crystal

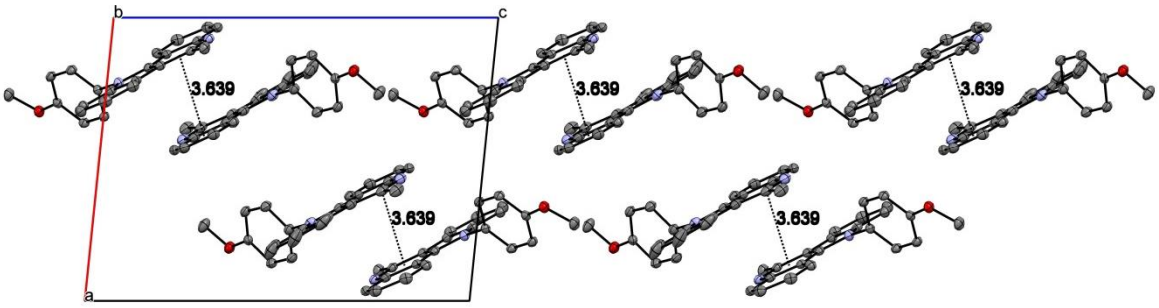
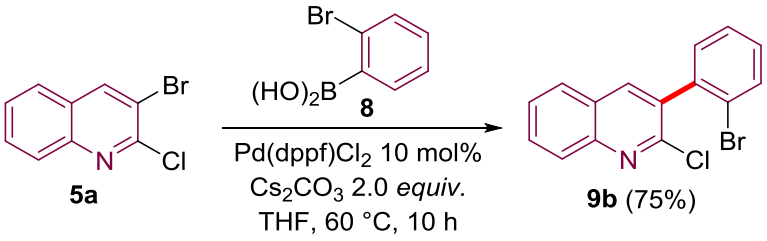


Figure 16: π-π-Stacking interactions in the crystal of 11*H*-indolo[3,2-*c*]quinoline **11g**

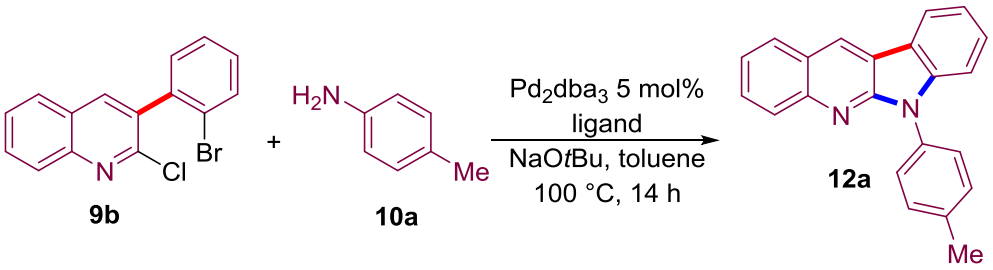
With a series of 11*H*-indolo[3,2-*c*]quinolines **11a-t** successfully prepared, the synthesis of 6*H*-indolo[2,3-*b*]quinolines from 2,3-dihaloquinolines was ascertained. First, the reaction of 3-bromo-2-chloroquinoline (**5a**) with (2-bromophenyl)boronic acid (**8**) occurred predominantly at position 3 of the quinoline ring, since the chemo-selective effect dominates in this instance. The resulting 3-(2-bromophenyl)-2-chloroquinoline (**9b**) was generated in good yield (Scheme 41).



Scheme 41: Regioselective Suzuki reaction of 3-bromo-2-chloroquinoline (**5a**)

Next, the reaction of 3-(2-bromophenyl)-2-chloroquinoline (**9b**) with *p*-toluidine (**10a**) was optimized (Table 15). During the optimization, different ligands were applied using the palladium source Pd_2dba_3 and the base NaO*t*Bu in toluene (Table 15). Among these ligands, P*t*Bu$_3$·HBF$_4$ worked most effectively, yielding indoloquinoline **12a** in 95% (entry 2, Table 14). It is worth noting that these conditions are identical to those applied for the assembly of indoloquinolines **11a-n**.

Table 14: Optimization study of the synthesis of 6*H*-indolo[2,3-*b*]quinoline **12a**

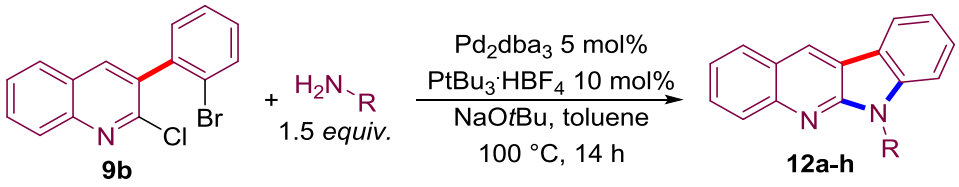


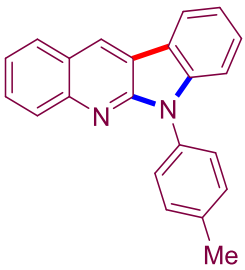
Entry	Ligand	Yield
1	Xantphos	59%
2	**P*t*Bu$_3$·HBF$_4$**	**95%**
3	SPhos	68%
4	dppf	55%
5	(*S*)-BINAP	68%

Reaction conditions: **9b** (0.10 mmol), **10a** (0.15 mmol), Pd_2dba_3 (0.005 mmol), ligand (0.005 mmol for monodentate or 0.010 mmol for bidentate ligands), NaO*t*Bu (0.24 mmol), toluene (2 ml), 100 °C, 14 h.
The yields were referred to as isolated yields.

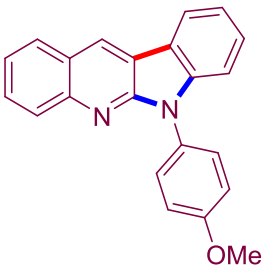
The reaction under the optimized conditions proved effective across different primary amines (Table 15). Corresponding indoloquinolines **12a-h** were afforded in up to 95% yield (Table 15). In general, the yields obtained with electronically neutral and electronically rich aromatic amines were similarly high (**12a-d**, Table 15). The highest yield gave indoloquinoline **12a** in 95%. In comparison, lower yields were afforded with aliphatic and electronically poor aromatic amines, with the lowest observed for indoloquinoline **12g** (Table 15).

Table 15: Synthesis of 6*H*-indolo[2,3-*b*]quinolines **12a-h**

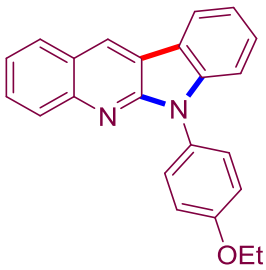




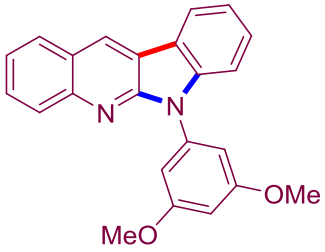
12a (95%)



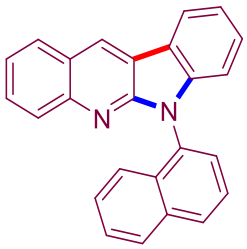
12b (91%)



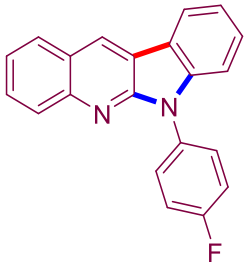
12c (89%)



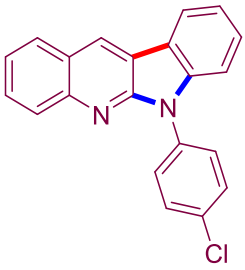
12d (92%)



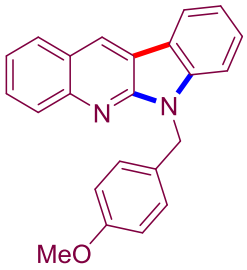
12e (83%)



12f (75%)



12g (68%)

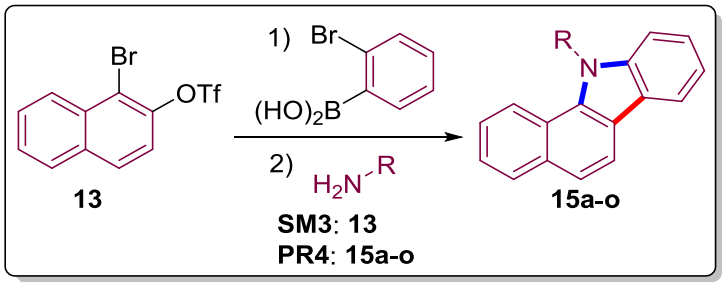


12h (80%)

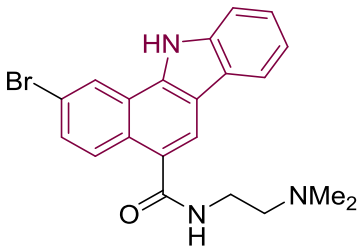
Reaction conditions: **9b** (0.150 mmol), amines (0.225 mmol), Pd_2dba_3 (0.0075 mmol), $PtBu_3 \cdot HBF_4$ (0.015 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 24 h. The yields were referred to as isolated yields.

To summarize, the preparation of 6*H*-indolo[3,2-*c*]quinolines and 6*H*-indolo[2,3-*b*]quinolines by regioselective Suzuki reaction followed by double C-N coupling was established, demonstrating a wide scope with electron-rich, electron-poor aromatic and aliphatic amines being compatible. Noticeably, the syntheses of these two derivatives employed the same reaction conditions for the incorporation of electronically rich and electronically neutral aromatic amines.

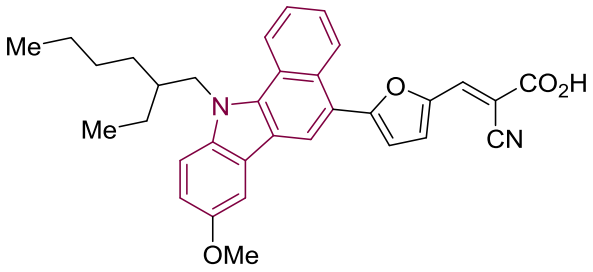
3.2.2. Synthesis of benzo[*a*]carbazoles from *ortho*-dihalonaphthalene



Benzo[*a*]carbazole is a fused form of carbazole with larger structure and greater aromaticity.[136] With these largely fused aromatic systems, they are considered as potential candidates for medicinal and material application. In the medicinal field, a handful of derivatives of benzo[*a*]carbazole are capable of interacting with DNA,[137] binding on estrogen receptor[138] or selectively inhibiting on cyclin dependent Kinase 4.[139] Additionally, other benzo[*a*]carbazole derivatives have been applied in the field of OLED and solar cell.[79c, 114] Representative examples of benzo[*a*]carbazoles with potential applications as antitumor agent (R16-8)[113] and BTB-sensitizers for high efficient solar cell (JY22)[79c] are illustrated in Figure **17**. Given this remarkable potential for applications in both biological and physical field, a large number of patents have emerged with reference to benzo[*a*]carbazole structures lately.



R16-8

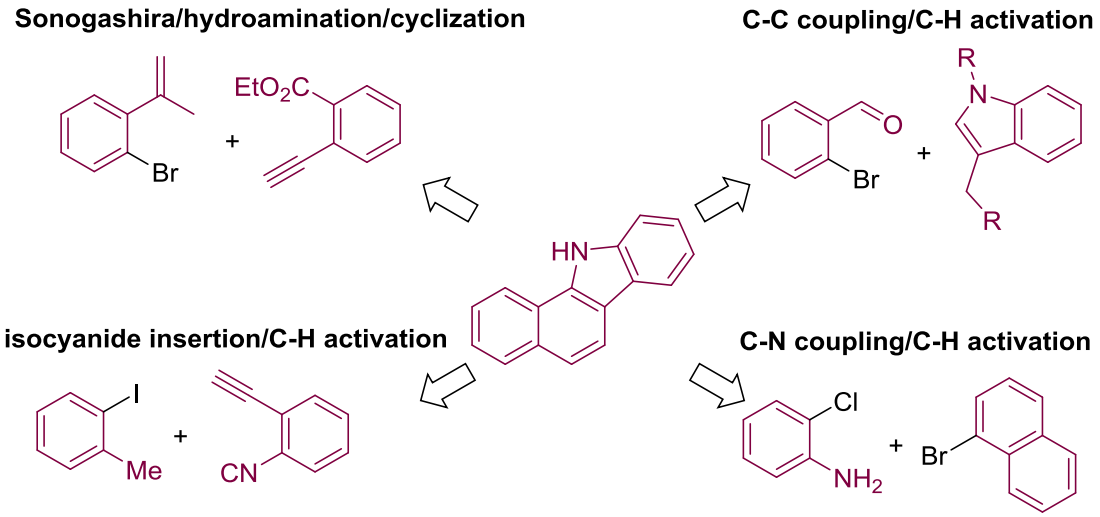


JY22

Figure 17: Examples of benzo[*a*]carbazole derivatives with biological and physical importance

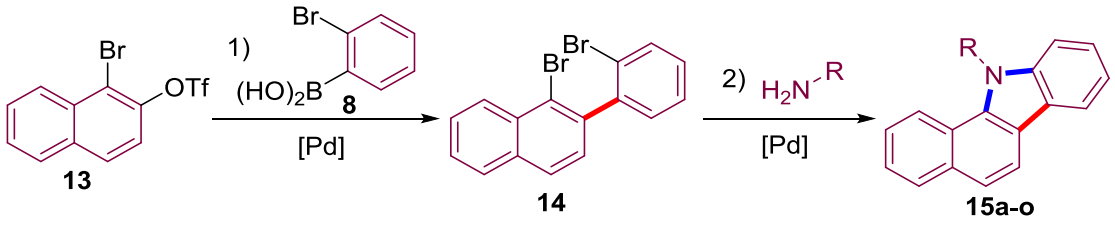
In classic chemistry, the installation of benzo[*a*]carbazole scaffolds can be accomplished *via* different approaches including Diels-Alder reaction,[140] Fischer synthesis/selective oxidation,[113, 141] Fischer-Borsche indole synthesis,[142] Cadogan cyclization,[143] Scholl-type oxidative cyclization,[144] or by exploiting the dual character of benzoquinone.[145] The development of palladium-catalyzed chemistry have ultimately offered additional possibilities for their synthesis, for example

by C-C coupling/C-H activation,[146] C-N coupling/C-H activation,[147] Sonogashira/ hydroamination/cyclization[148] and isocyanide insertion/C-H activation[149] (Scheme 42). Despite these significant progresses, convenient and atom-efficient methods using facilely attainable starting materials for the preparation of these biologically and physically important scaffolds are still needed.



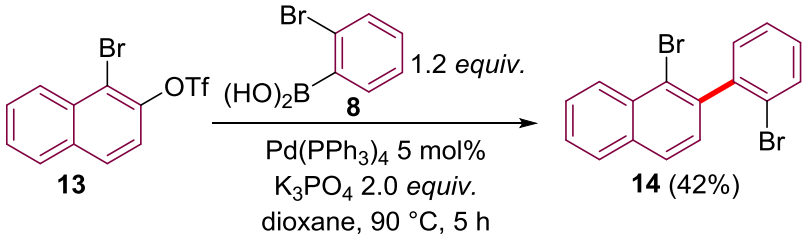
Scheme 42: Examples of palladium-catalyzed synthesis of benzo[*a*]carbazole[146-149]

Following the synthesis of indoloquinolines in Chapter 3.2.1, another study for the assembly of benzo[*a*]carbazoles (**PR4**) from 1,2-dihalonaphthalene was undertaken in this contribution (Scheme 43).



Scheme 43: Synthesis of benzo[*a*]carbazoles in this study

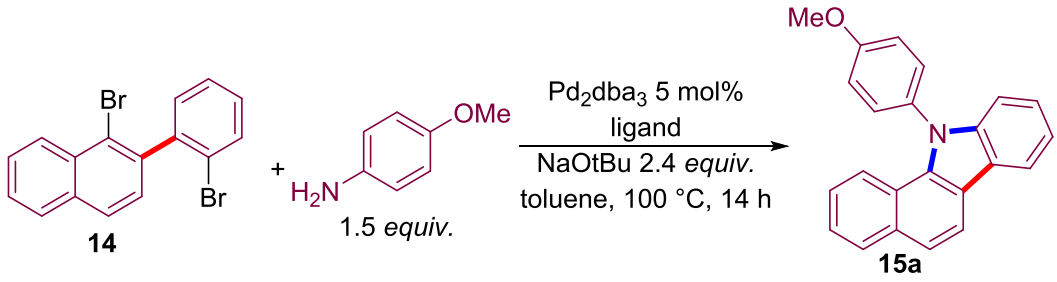
At the beginning of the study, 1-bromo-2-(2-bromophenyl)naphthalene (**14**) was obtained from the regioselective Suzuki reaction of 1-bromonaphthalen-2-yl trifluoromethanesulfonate (**13**) with (2-bromophenyl)boronic acid (**8**) under the previously reported conditions (Scheme 44).[150] Remarkably, the regioselectivity of this reaction was reversed compared to that given in the original report. This is possibly ascribed to the presence of the electron-withdrawing and voluminous bromine atom at the *ortho*-position of the boronic acid **8**.



Scheme 44: Regioselective Suzuki reaction of *ortho*-dihalonaphthalene **13**

The resulting 1-bromo-2-(2-bromophenyl)naphthalene (**14**) and 4-methoxyaniline were selected as model substrates for the optimization study of the double C-N coupling. Different ligands were applied in the presence of the catalyst Pd_2dba_3 and the base NaO*t*Bu in toluene (Table 16). From the optimization results, the monodentate ligand P*t*Bu$_3$·HBF$_4$ afforded benzo[*a*]carbaole **15a** in good yield (89%), but Xantphos outperformed giving benzo[*a*]carbazole **15a** in nearly quantitative yield (95%).

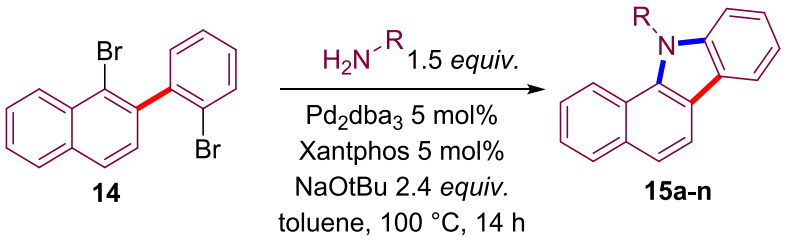
Table 16: Optimization for the synthesis of benzo[*a*]carbazole **15a**

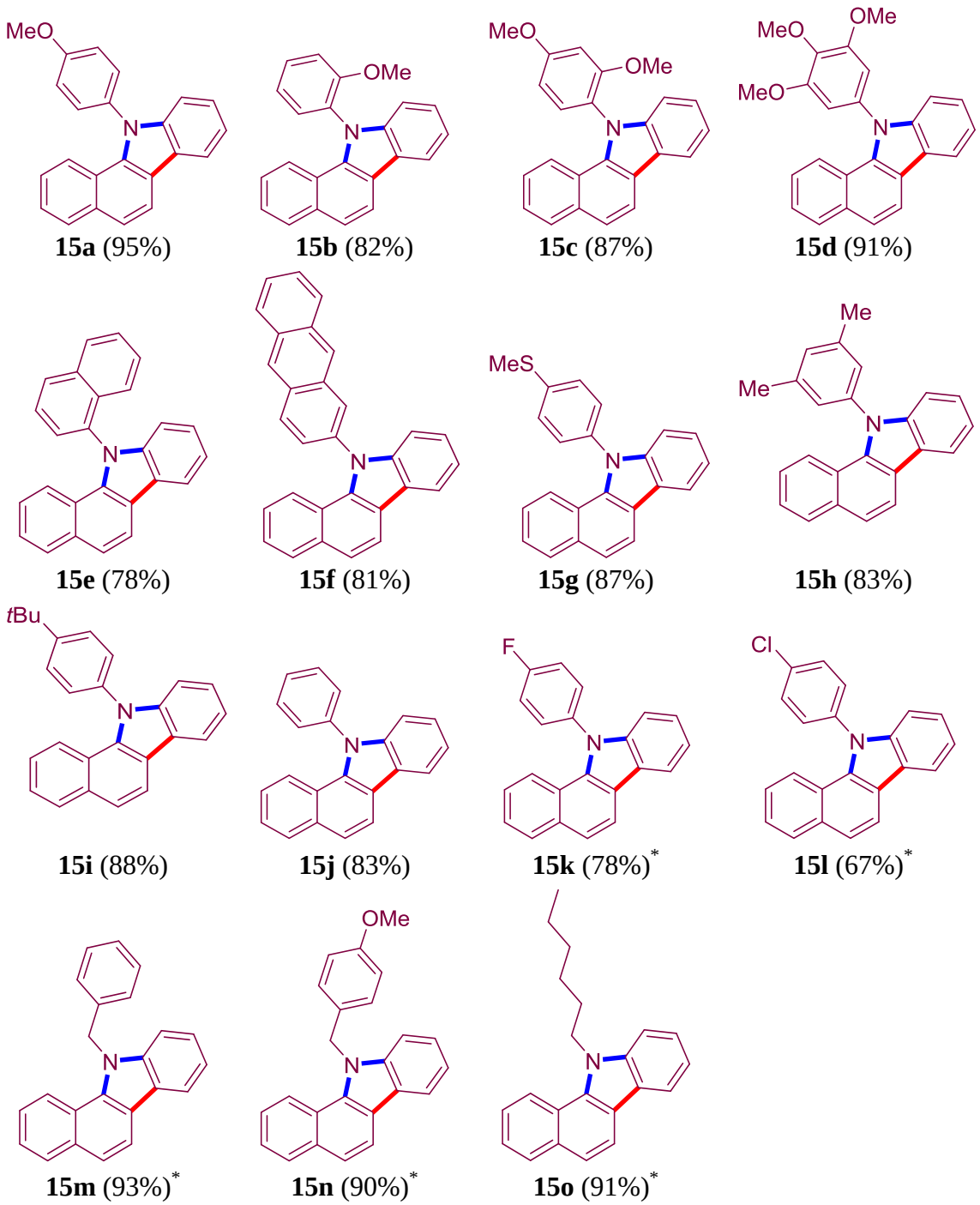


Entry	Ligand	Yield
1	P*t*Bu$_3$·HBF$_4$	89%
2	(*S*)-BINAP	90%
3	SPhos	92%
4	dppf	65%
5	**Xantphos**	**95%**

Reaction conditions: **14** (0.10 mmol), amine (0.15 mmol), Pd_2dba_3 (0.005 mmol), ligands (0.01 mmol for monodentate or 0.005 mmol for bidentate ligands), NaO*t*Bu (0.24 mmol), toluene (2 ml), 100 °C, 14 h.
The yields were referred to as isolated yields.

Table 17: Synthesis of benzo[*a*]carbazoles **15a-n**





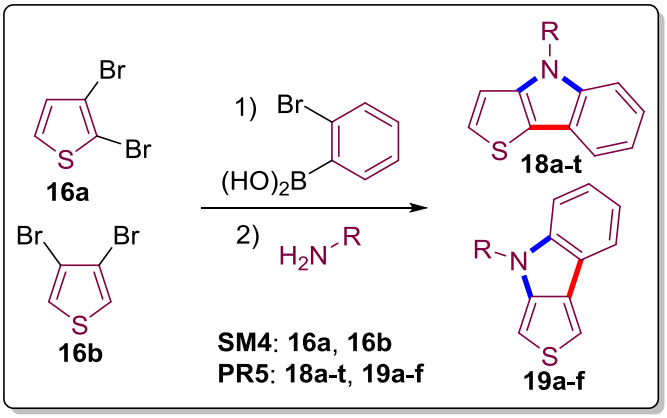
Reaction conditions: **14** (0.150 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), XantPhos (0.0075 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 24 h. The yields were referred to as isolated yields.

* **14** (0.150 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), (*S*)-BINAP (0.0075 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 14 h. The yields were referred to as isolated yields.

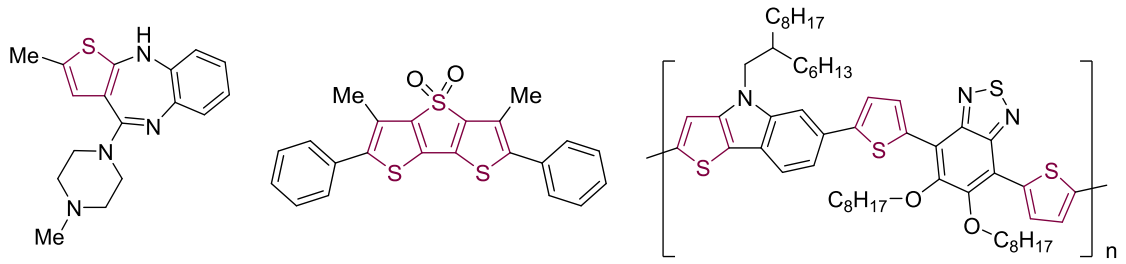
With the optimized conditions in hand, the preparative scope of the reaction was evaluated. Different primary aryl amines were applied (Table 17). For electron-poor and nonaryl amines, Xantphos delivered products in low yields, thus (*S*)-BINAP was used instead. Noticeably, (*S*)-BINAP proved to be the most suited ligand for the double C-N coupling with electron-deficient aromatic amines in Chapter **2.2.1**. Among the synthesized benzo[*a*]carbazoles, the highest yield was obtained with **15a** (95%), while the lowest was observed for the electronically poor system **15l** (67%). In comparison, the yields afforded with benzylic and aliphatic amines were very good, all being higher than 90% (**15m-o**, Table 17). However, no clear correlation between chemical structures and obtained yields was observed.

In conclusion, benzo[*a*]carbazoles were efficiently synthesized by iterative reaction sequence involving a regioselective Suzuki reaction and a double C-N coupling. The reactions proceeded in good to excellent yields.

3.2.3. Synthesis of thienoindoles from *ortho*-dihalothiophenes



Thiophene naturally exists as minority in petroleum. Notwithstanding this minority, thiophene-fused heterocycles have great potential for applications in medicine and material science. For example, Olanzapine has been employed for the treatment of schizophrenia,[151] and DTTO can be used as fluorescent markers for visualizing biological cells[152] (Figure 18).



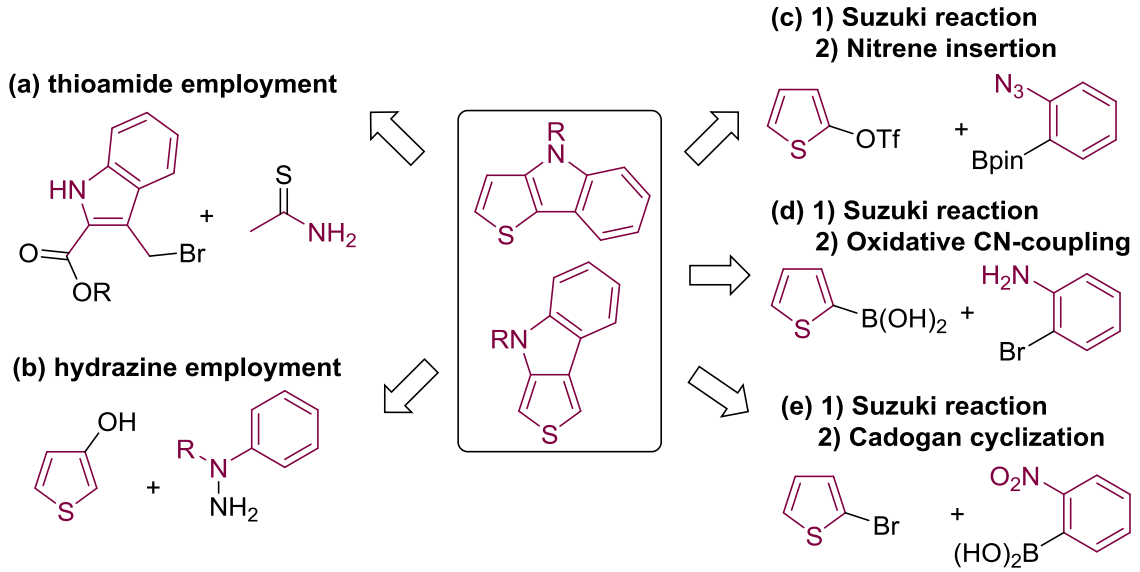
Olanzapine DTTO TI-DTBT3

Figure 18: Relevant thiophene-derived compounds

This study focuses on the chemistry of thienoindoles. These compounds were reported with antiviral properties.[153] Furthermore, thienoindoles can be incorporated in the structures of polymers for solar cell applications. For example, TI-DTBT3 is a donor-acceptor conjugated polymer with high charge carrier mobility (Figure 18).[154]

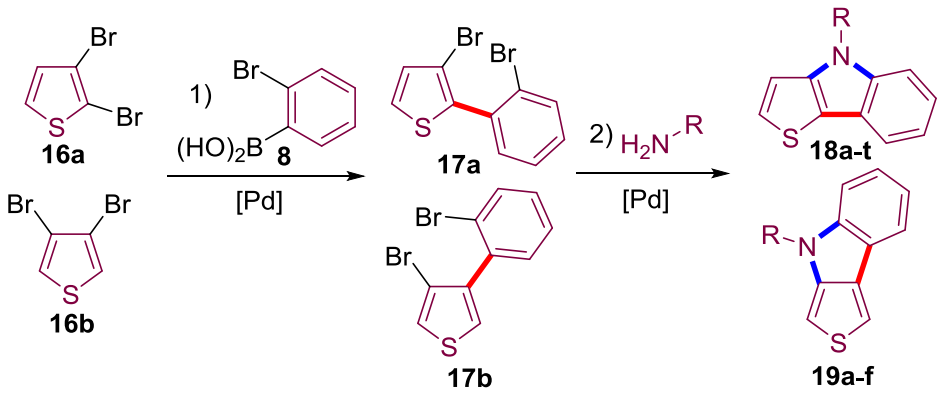
The first syntheses of these thienoindoles were accomplished in 1982 by the reaction of (a) substituted indole with thioamide[155] and (b) 3-hydroxythiophene with hydrazine[153] (Scheme 45). Although these syntheses were considered tedious and not modular, no improvement was documented until 2000. Fortunately, modern palladium-catalyzed cross-coupling reactions have allowed the synthesis of thienoindoles through more convenient routes. These syntheses start with a Suzuki reaction to furnish a new C-C

bond from the thiophene or benzene backbone, followed by a ring-closure. The ring-closing process can be accomplished in different manners including (c) nitrene insertion,[156] (d) oxidative C-N coupling[157] or (e) Cadogan cyclization[158] (Scheme 45).



Scheme 45: Previously reported synthesis of thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles

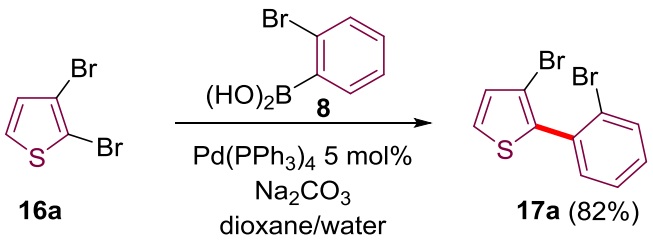
Here, a convenient and efficient approach for the synthesis of thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles (product series **PR5**) is presented. The protocol features a site-selective Suzuki reaction of *ortho*-dihalothiophenes with (2-bromophenyl)boronic acid (**8**), followed by a double C-N coupling with primary amines (Scheme 46).



Scheme 46: Synthesis of thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles in this study

At first, 2,3-dibromothiophene (**16a**) was converted into the desired 3-bromo-2-(2-bromophenyl)thiophene (**17a**) after the treatment with (2-bromophenyl)boronic

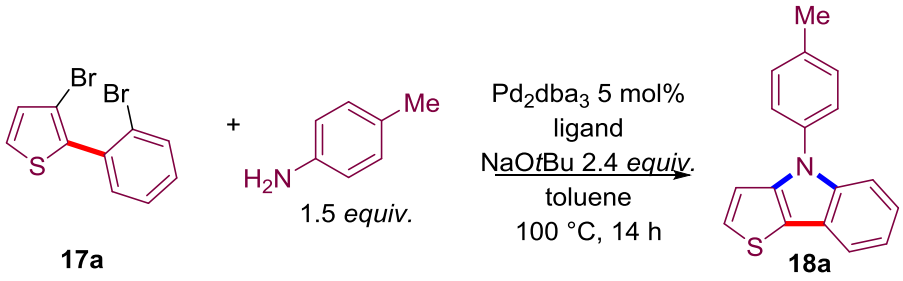
acid (**8**) under palladium-catalyzed conditions (Scheme 47). The reaction proceeded smoothly, with site-selectivity favoring position 2 over position 3 of the thiophene ring. The resulting 3-bromo-2-(2-bromophenyl) thiophene (**17a**) was accessed in 82% yield (Scheme 47).



Scheme 47: Site-selective Suzuki reaction of 2,3-dibromothiophene

Thereafter, 3-bromo-2-(2-bromophenyl) thiophene (**17a**) and 4-toluidine were chosen as model substrates for the optimization of the double C-N coupling. In the presence of the palladium source Pd_2dba_3 and the base NaO*t*Bu in toluene, the ligand screening was conducted (Table 18). From the optimization experiments, dppf proved to be the best ligand while giving thieno[3,2-*b*]indole **18a** in 97% yield (entry 2, Table 18).

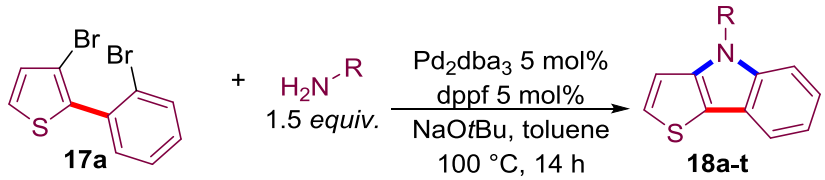
Table 18: Optimization study for synthesis of thieno[3,2-*b*]indole **18a**

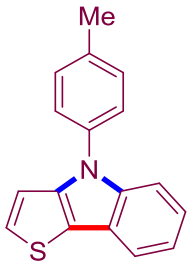


Entry	Ligand	Yield
1	P*t*Bu$_3$·HBF$_4$	86%
2	**dppf**	**97%**
3	SPhos	65%
4	(*S*)-BINAP	67%

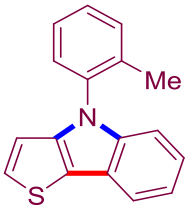
Reaction conditions: **17a** (0.10 mmol), amine (0.15 mmol), Pd_2dba_3 (0.005 mmol), ligands (0.005 mmol for monodentate or 0.010 mmol for bidentate ligands), NaO*t*Bu (0.24 mmol), toluene (2 ml), 100 °C, 14 h. The yields were referred to as isolated yields.

Table 19: Synthesis of thieno[3,2-*b*]indoles **18a-t**

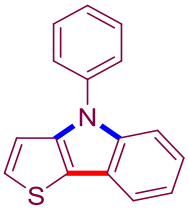




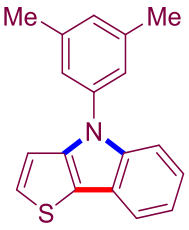
18a (97%)



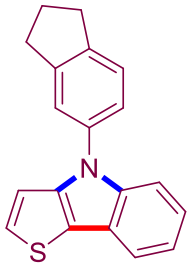
18b (77%)



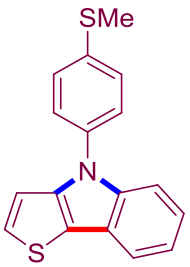
18c (83%)



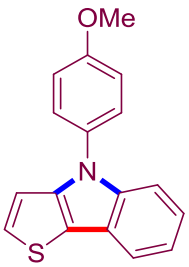
18d (90%)



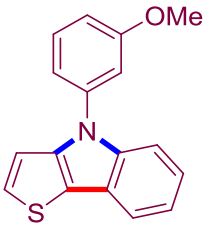
18e (90%)



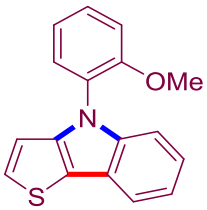
18f (98%)



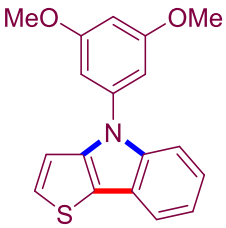
18g (91%)



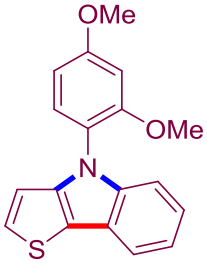
18h (92%)



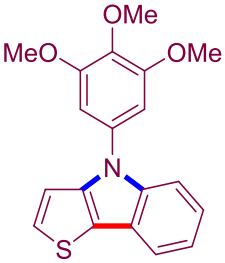
18i (87%)



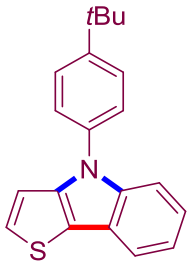
18j (92%)



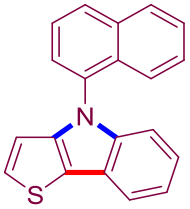
18k (89%)



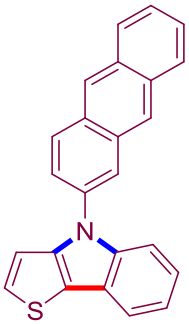
18l (92%)



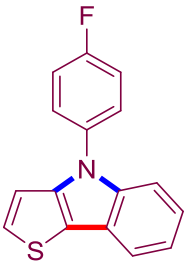
18m (92%)



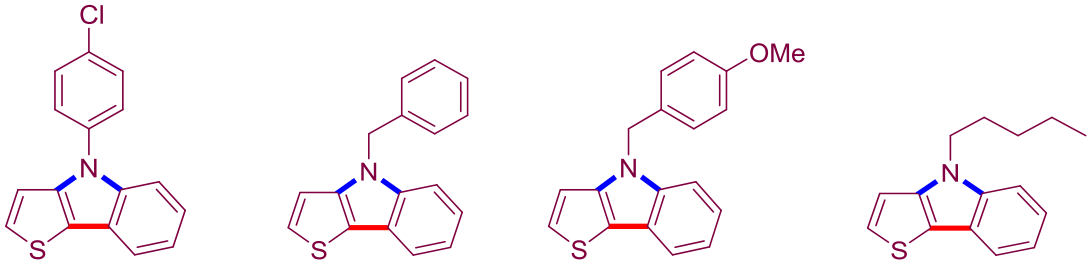
18n (78%)



18o (72%)



18p (91%)[b]



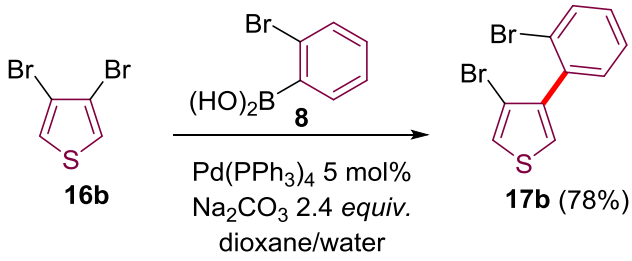
18q (86%)[b] **18r** (81%)[b] **18s** (95%)[b] **18t** (75%)[b]

Reaction conditions: **17a** (0.150 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), dppf (0.0075 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 24 h. The yields were referred to as isolated yields.

[b] **17a** (0.150 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), (*S*)-BINAP (0.0075 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 14 h.

The yields were referred to as isolated yields.

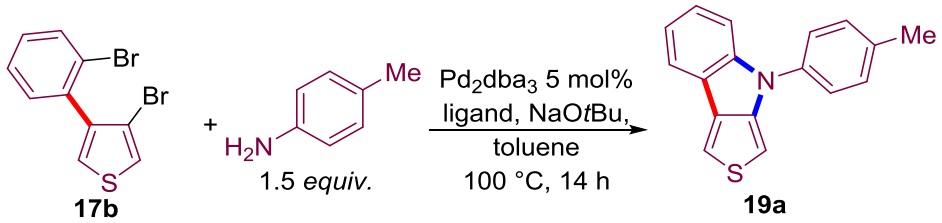
The reaction of 3-bromo-2-(2-bromophenyl) thiophene (**17a**) with different primary amines under these optimized conditions proceeded with good to excellent yields of corresponding thieno[3,2-*b*]indoles **18a-t** (Table 19). For electron-poor and aliphatic amines, the ligand dppf gave low yields, and (*S*)-BINAP was used instead. The highest yield was obtained with the electron-rich thieno[3,2-*b*]indole **18f** (98%) in contrasting to the lowest yield observed for the large π-system **18o** (72%). Moreover, the synthesis also allowed the incorporation of sterically hindered amines in the case of **18b** (77%) and **18k** (89%).



Scheme 48: Site-selective Suzuki reaction of 3,4-dibromothiophene

In another context, the preparation of thieno[3,4-*b*]indoles following the same strategy was studied. 3-Bromo-4-(2-bromophenyl)thiophene (**17b**) was attained from the site-selective Suzuki reaction of 3,4-dibromothiophene (**16b**) with (2-bromophenyl)boronic acid (**8**) (Scheme 48).

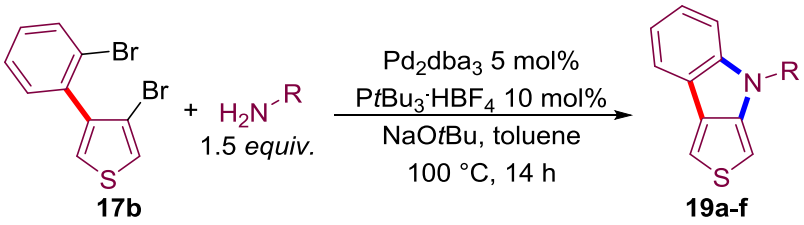
Table 20: Optimization for the synthesis of thieno[3,4-*b*]indole **19a**

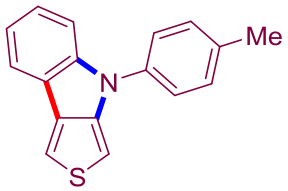


Entry	Ligand	Yield
1	**P*t*Bu$_3$·HBF$_4$**	**95%**
2	dppf	43%
3	SPhos	65%
4	(*S*)-BINAP	36%

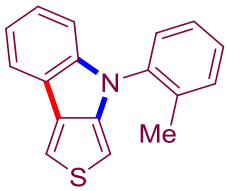
Reaction conditions: **17b** (0.10 mmol), amine (0.15 mmol), Pd_2dba_3 (0.005 mmol), ligands (0.005 mmol for monodentate or 0.010 mmol for bidentate ligands), NaO*t*Bu (0.24 mmol), toluene (2 ml), 100 °C, 14 h. The yields were referred to as isolated yields.

Table 21: Synthesis of thieno[3,4-*b*]indoles **19a-f**

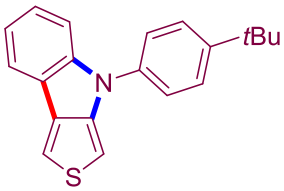




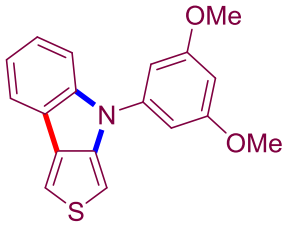
19a (95%)



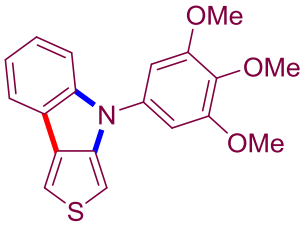
19b (65%)



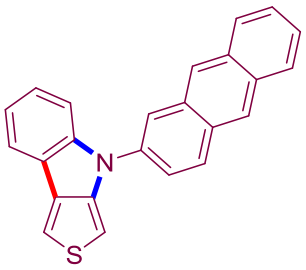
19c (83%)



19d (85%)



19e (81%)



19f (78%)

Reaction conditions: **17b** (0.150 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), P*t*Bu$_3$·HBF$_4$ (0.015 mmol), NaO*t*Bu (0.36 mmol), toluene (3 ml), 100 °C, 24 h. The yields were referred to as isolated yields.

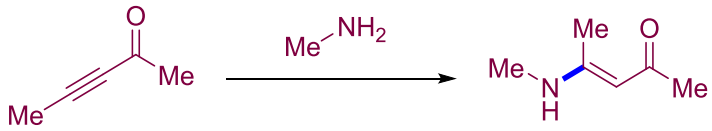
The influence of the ligands on the reaction of 3-bromo-4-(2-bromophenyl)thiophene (**17b**) and 4-toluidine was surveyed (Table 20). The screening data revealed that P*t*Bu$_3$·HBF$_4$ was the preferred ligand for this reaction, furnishing corresponding thienoindole **19a** in almost quantitative yield (entry 1, Table 20).

These conditions were applied for the reaction of 3-bromo-4-(2-bromophenyl)thiophene (**17b**) with different primary aryl amines, delivering corresponding thienoindoles **19a**-**f** in good to excellent yields (65% - 95%, Table 21). In general, the involvement of electron donating groups on the amines resulted in high yield of desired thieno[3,4-*b*]indoles. The highest yield of 95% was observed for the product **19a** which was selected as model substrate for the above optimization. In comparison, thieno[3,4-*b*]indole **19b** was created in moderate yield (65%), possibly as a result of steric hindrance.

To conclude, the preparation of thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles from *ortho*-dibromothiophenes following sequential site-selective Suzuki reaction/double C-N coupling was successfully conducted. The double C-N coupling reaction proceeded with good to excellent yields. The key for the success of the reaction was the ligand choice.

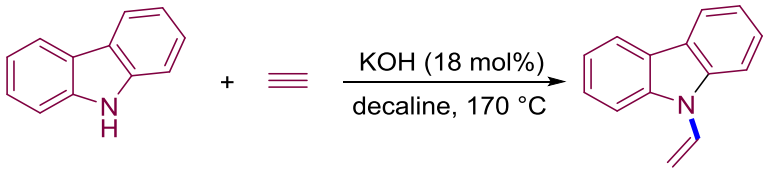
3.3. Synthesis of phenanthridine-fused heterocycles from *ortho*-dihaloarenes by regioselective Sonogashira reaction followed by domino C-N coupling/hydroamination/C-H arylation

The concept hydroamination describes the direct formation of new C-N bond through the addition of an N-H group to a multiple C-C bond. The atom-economic property of this concept makes it appealing to synthetic chemists. However, classic chemistry only allowed such a C-N formation *via* conjugate addition of electron-rich amines to electron-poor alkynyl groups (Scheme 49).

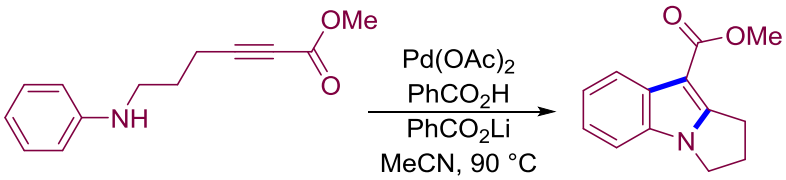


Scheme 49: Conjugate addition on alkynyl group in classic chemistry[159]

For other systems, an activation of the amine or the alkynyl group is required. In 1935, an early effort was made to activate the amines using alkali metal, albeit in harsh conditions (Scheme 50). Later studies discovered milder conditions by using bases, metal catalysts of rare earth group, group IV, and late transition metals.[160]



Scheme 50: Early example of hydroamination

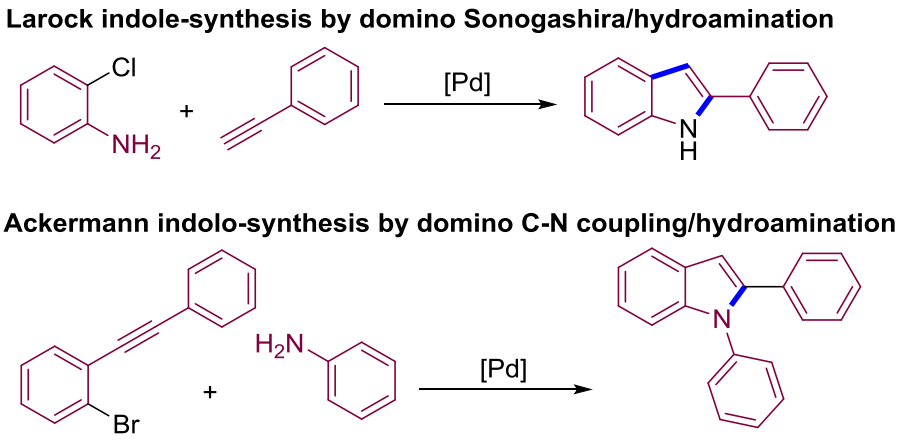


Scheme 51: Example of palladium-catalyzed domino reaction involving intramolecular hydroamination[161]

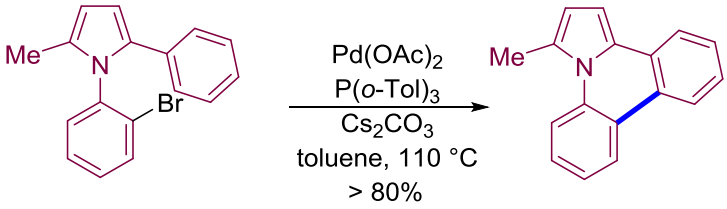
Of practical importance among different types of hydroamination are the palladium-catalyzed intramolecular hydroamination reactions *via* 5-endo-dig cyclization which form pyrrole structures.[162] These reactions were frequently applied in a domino

fashion with other transformations including alkylation,[163] Michael,[164] Heck,[165] Sonogashira,[166] reductive elimination[167] and carbonylation[134] to form different fused heterocycles. These reaction concepts were considered as atom-economic and gained therefore increasing attention in organic chemistry recently (Scheme 51).

One of the interests in this study is the development of new convenient and atom-economic syntheses of nitrogen-containing polycyclic aromatic compounds, which involve Sonogashira-, C-N coupling, hydroamination and C-H arylation in one-pot or domino manner. Regarding this, an indole synthesis from *ortho*-haloanilines and aryl acetylenes *via* domino Sonogashira reaction/hydroamination was disclosed by Larock *et al.* in 1991 (Scheme 52).[168] In 2005, Ackermann *et al.* reported a construction of indole by domino C-N coupling/hydroamination using *ortho*-halo(arylethynyl)-benzenes and aryl amines as starting materials (Scheme 52).[169] Later, this reaction model was optimized for the *ortho*-halo(arylethynyl) heterocyclic systems of benzothiophene,[170] coumarin[171] and quinolone.[172]

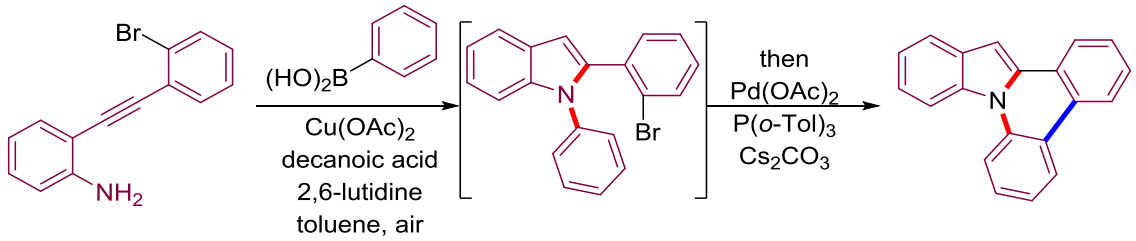


Scheme 52: Synthesis of indole by intramolecular hydroamination

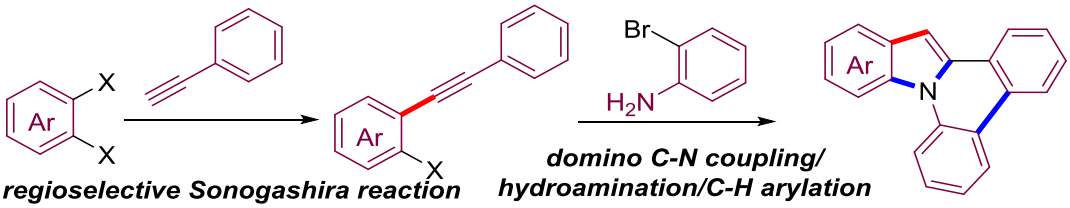


Scheme 53: Synthesis of phenanthridine-fused heterocycles by C-H arylation

Further atom-economic syntheses of nitrogen heterocycles incorporating Sonogashira reaction, C-N coupling and hydroamination emerged in 2006. They were reports with reference to the construction of phenanthridines (Scheme 53).[173] In these syntheses, a six-membered ring arises from a C-X/C-H typed C-H arylation.



Scheme 54: Synthesis of indolo[1,2-*f*]phenanthridines by one-pot hydroamination/C-H arylation[174]

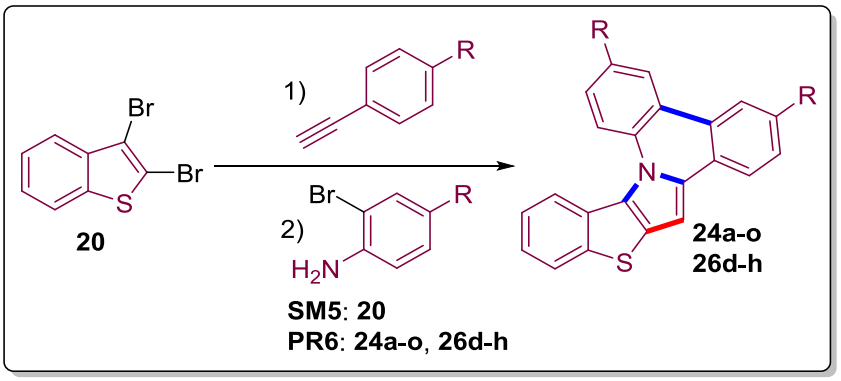


Scheme 55: Synthesis of phenanthridine-fused heterocycles by regioselective Sonogashira reaction followed by a domino C-N coupling/hydroamination/C-H arylation[175]

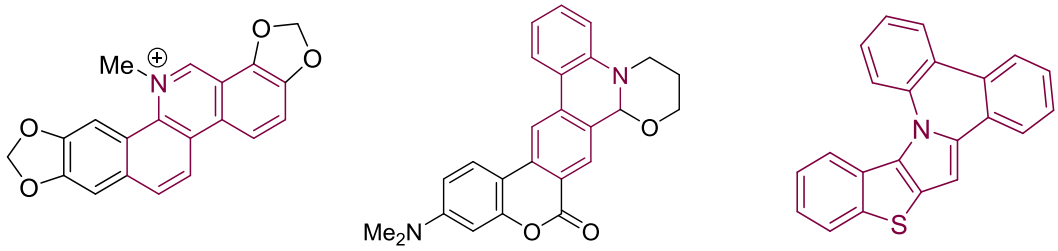
In 2014, this C-H arylation was exploited in a one-pot process involving a domino Chan-Lam C-N coupling followed by a hydroamination (Scheme 54).[174] In 2015, the preparations of phenanthridine-fused compounds which involved domino C-N coupling/hydroamination/C-H arylation have been finally devised by Langer *et al.* (Scheme 55).[175] The syntheses started with an *ortho*-dihaloarene which underwent a regioselective Sonogashira reaction to form an *ortho*-halo-(arylalkynyl)arene. Next, the reactions of the *ortho*-halo-(arylalkynyl)arenes with different *ortho*-haloaryl amines proceeded *via* domino C-N coupling/intramolecular hydroamination/C-H arylation to assemble corresponding phenanthridine-fused heterocycles (Scheme 55).

In this contribution, the reaction model domino C-N coupling/hydroamination/C-H arylation was further exploited representing a gateway to phenanthridine-fused compounds (**PR6-8**, Chapter 3.3.1-3) with no synthetic precedent.

3.3.1. Synthesis of benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines from 2,3-dibromobenzothiophenes



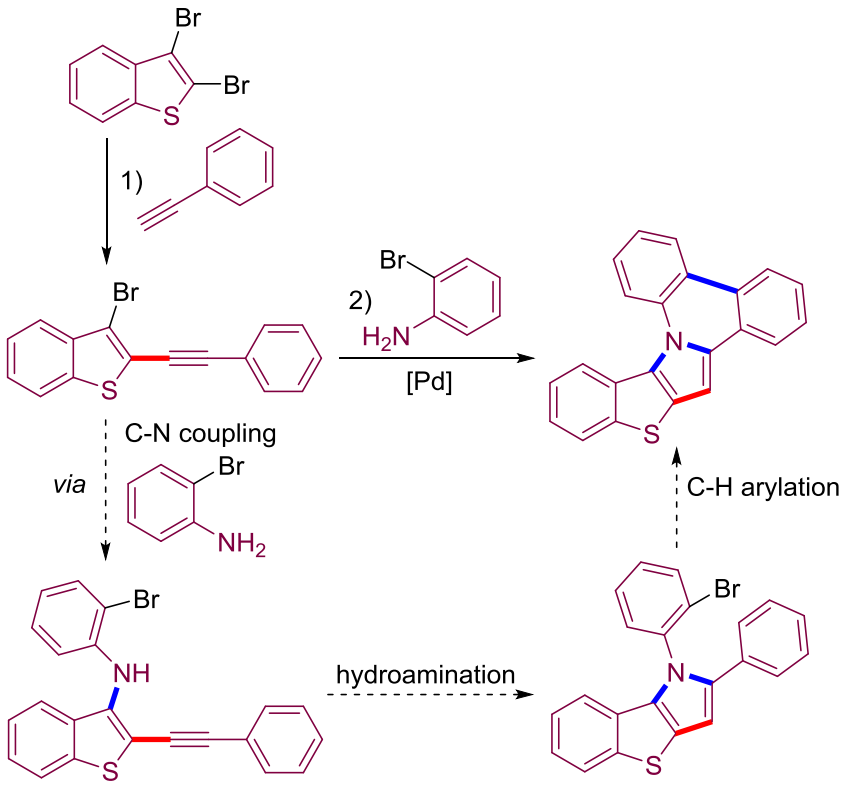
Phenanthridine is a tricyclic heterocycle, of which fused derivatives have found applications in medicine and material science. For example, sanguinarine is a potential candidate for the treatment of cancer, [176] while BT2 exhibits interesting photochemical properties[177] (Figure 19). Henceforth, great efforts were devoted to synthesize fused derivatives of phenanthridine with coumarin, pyrrole, purine, indole, imidazole, benzimidazole and quinazoline.[177-178]



sanguinarine BT2 benzo[4',5']thieno[2',3':4,5]-pyrrolo[1,2-*f*]phenanthridine

Figure 19: Relevant phenanthridine-fused compounds

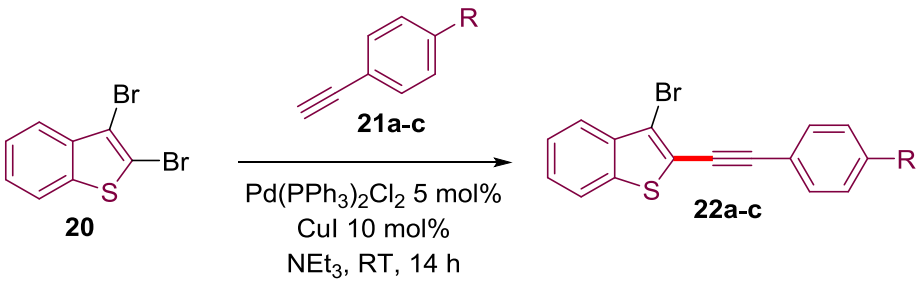
Herein, a synthetic procedure towards a series of phenanthridine-fused benzothiophenes (**PR6**) was developed. The protocol begins with a site-selective Sonogashira reaction of 2,3-dibromobenzothiophene with aryl acetylenes, followed by a domino C-N coupling/hydroamination/C-H arylation with *ortho*-bromoaryl amines to afford corresponding benzo[4',5']thieno[2',3':4,5]-pyrrolo[1,2-*f*]phenanthridines (Scheme 56).

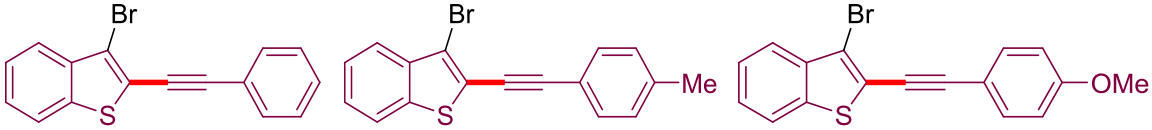


Scheme 56: Synthesis of phenanthridine-fused heterocycles in this study

Initial efforts were conducted to carry out the site-selective Sonogashira reaction of 2,3-dibromothiophene (**20**) with different aryl acetylenes (Table 22). The reactions proceed exclusively at position 2 of 2,3-dibromothiophene, furnishing 3-bromo-2-(arylethynyl)benzo[*b*]thiophenes **22a-c** in good yields (Table 22).

Table 22: Synthesis of 3-bromo-2-(arylethynyl)benzo[*b*]thiophenes **22a-c**

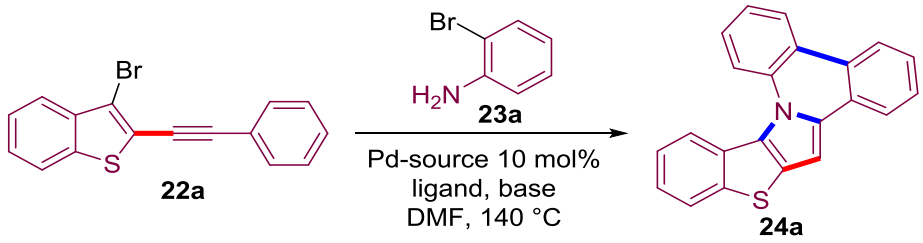




22a (80%) **22b** (85%) **22c** (87%)

Reaction conditions: 2,3-Dibromothiophene (**20**) (3.0 mmol), aryl acetylene (4.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol), CuI (0.3 mmol), NEt_3 (2.0 ml), 80 °C, 14 h. The yields were referred to as isolated yields.

Table 23: Optimization study for the synthesis of benzo[4',5']thieno[2',3':4,5]pyrrolo-[1,2-*f*]phenanthridine (**24a**)



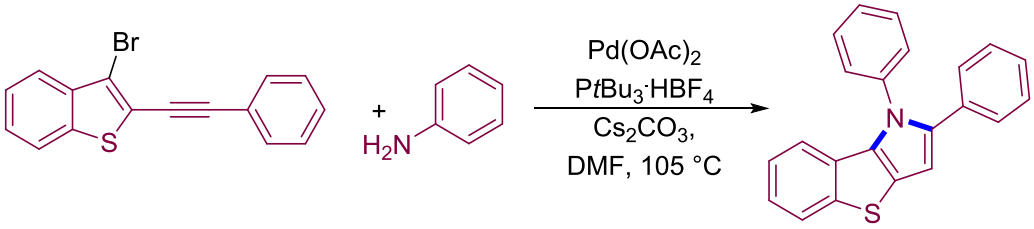
Entry	Pd-source	Ligand	Base	Yield
1	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	30%
2	$Pd(PPh_3)_4$	Xantphos	Cs_2CO_3	-
3	$Pd(OAc)_2$	dppf	Cs_2CO_3	35%
4	$Pd(OAc)_2$	dppe	Cs_2CO_3	42%
5	$Pd(OAc)_2$	XPhos	Cs_2CO_3	38%
6	$Pd(OAc)_2$	DavePhos	Cs_2CO_3	40%
7	$Pd(OAc)_2$	(*S*)-BINAP	Cs_2CO_3	34%
8	$Pd(OAc)_2$	SPhos	Cs_2CO_3	30%
9	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	30%
10	**$Pd(OAc)_2$**	**P*t*Bu$_3$·HBF$_4$**	**Cs_2CO_3**	**65%**
11	$Pd(PPh_3)_4$	P*t*Bu$_3$·HBF$_4$	Cs_2CO_3	-
12	Pd_2dba_3	P*t*Bu$_3$·HBF$_4$	Cs_2CO_3	55%
13	$Pd(OAc)_2$	P*t*Bu$_3$·HBF$_4$	K_2CO_3	-
14	$Pd(OAc)_2$	P*t*Bu$_3$·HBF$_4$	KO*t*Bu	-
15[a]	$Pd(OAc)_2$	P*t*Bu$_3$·HBF$_4$	Cs_2CO_3	60%
16[b]	$Pd(OAc)_2$	P*t*Bu$_3$·HBF$_4$	Cs_2CO_3	-

Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), [Pd]-source (0.01 mmol), ligand (0.02 mmol for monodentate and 0.01 mmol for bidentate ligands), base (0.3 mmol), DMF (3 ml), 140 °C, 24 h. The yields were referred to as isolated yields.
[a] reaction was carried out at 160 °C; [b] reaction was carried out at 120 °C

Next, the domino C-N coupling/hydroamination/C-H arylation of 3-bromo-2-(arylethynyl)benzo[*b*]thiophenes **22a-c** with different *ortho*-bromoaryl amines was studied, in which corresponding benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]-phenanthridines were obtained (Table 23). For the optimization experiments, 3-bromo-2-(arylethynyl)benzo[*b*]thiophene **22a** and 2-bromoaniline (**23a**) were chosen as model substrates. The optimization study was initiated by adopting previously documented conditions for analogous procedures, in which indolo[1,2-*f*]phenanthridines and

azaindolo[1,2-*f*]phenanthridines were assembled by taking advantage of domino C-N coupling/hydroamination/C-H arylation reaction (entries 1-2, Table 23). Unfortunately, these conditions were unsuccessful.

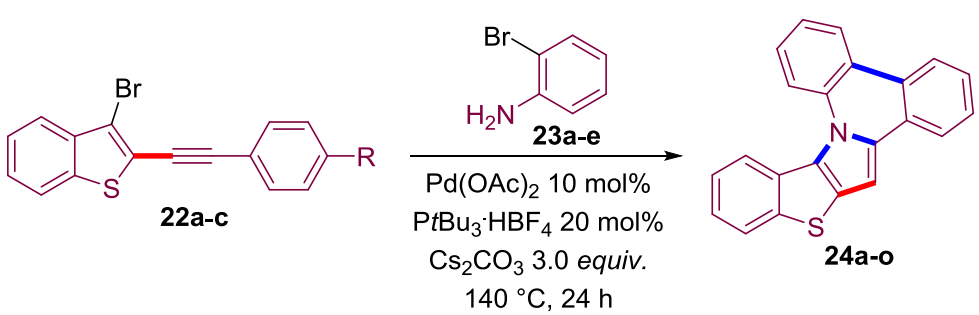
After evaluating other ligands in the presence of $Pd(OAc)_2$ with the base Cs_2CO_3 in DMF (entries 3 - 10, Table 23), the highest yield was observed by using P*t*Bu$_3$·HBF$_4$ (65%, entry 10, Table 23). Subsequently, different options of ligand sources, bases, solvents and reaction temperatures were exhausted (entries 11 - 16, Table 23), but proved to be futile in improving the yields. Therefore, the conditions **10** in Table **24** were chosen for further preparative studies. Interestingly, the parameters of these conditions including catalysts, base and solvent were identical to those applied for the previously documented synthesis of 1*H*-benzo[4,5]thieno-[3,2-*b*]pyrroles by domino C-N coupling/hydroamination (Scheme 57).[170]

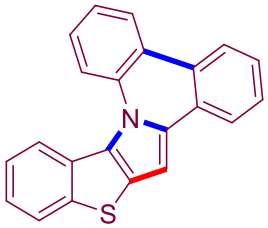


Scheme 57: Previously documented synthesis of 1*H*-benzo[4,5]thieno[3,2-*b*]pyrrole by domino C-N coupling/hydroamination[170]

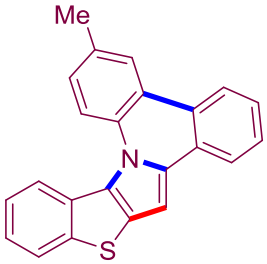
Applying the above optimized conditions, the reaction of 3-bromo-2-(arylethynyl)benzo[*b*]thiophene **22a-c** with 2-bromoaryl amines **23a-c** delivered corresponding benzothieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines **24a-o** in 55% - 80% yield (Table 24). The highest yield gave the electron-rich system **24l**.

Table 24: Synthesis of benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines **24a-o**

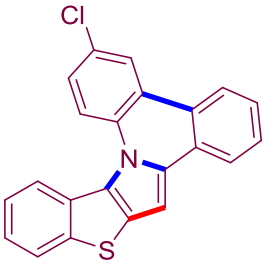




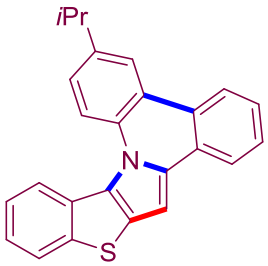
24a (65%)



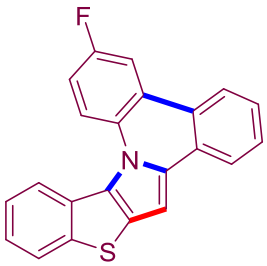
24b (68%)



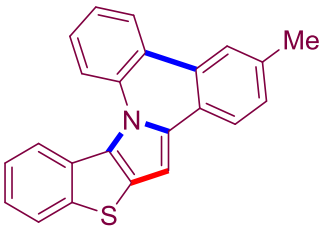
24c (58%)



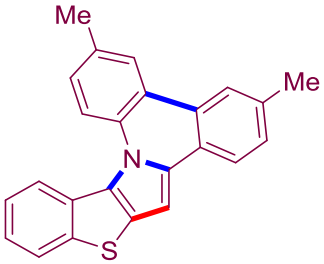
24d (70%)



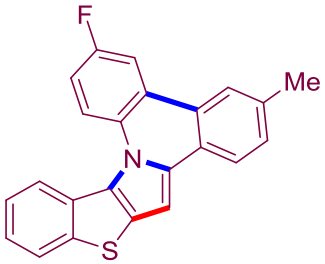
24e (60%)



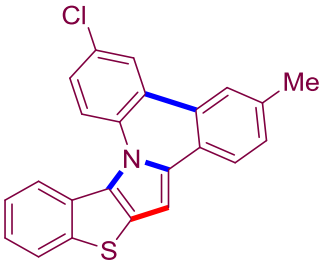
24f (55%)



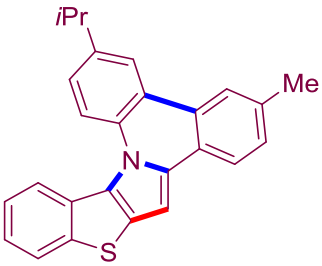
24g (62%)



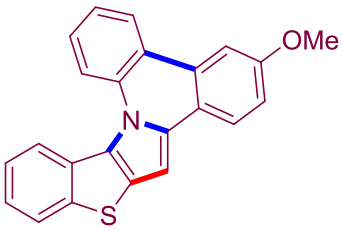
24h (57%)



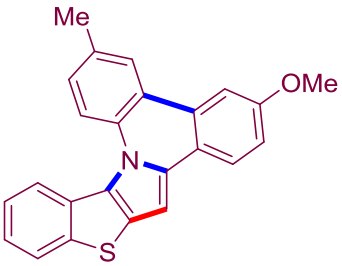
24i (58%)



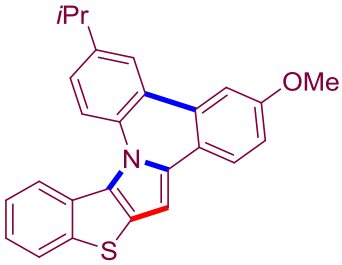
24j (75%)



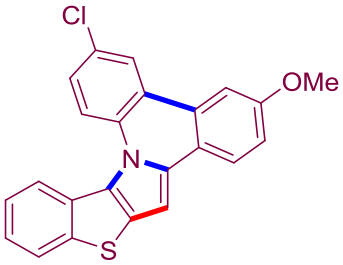
24k (58%)



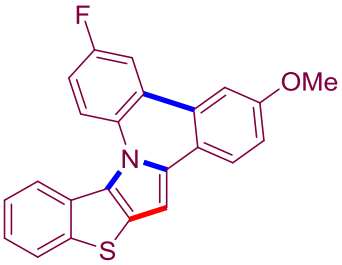
24l (77%)



24m (80%)

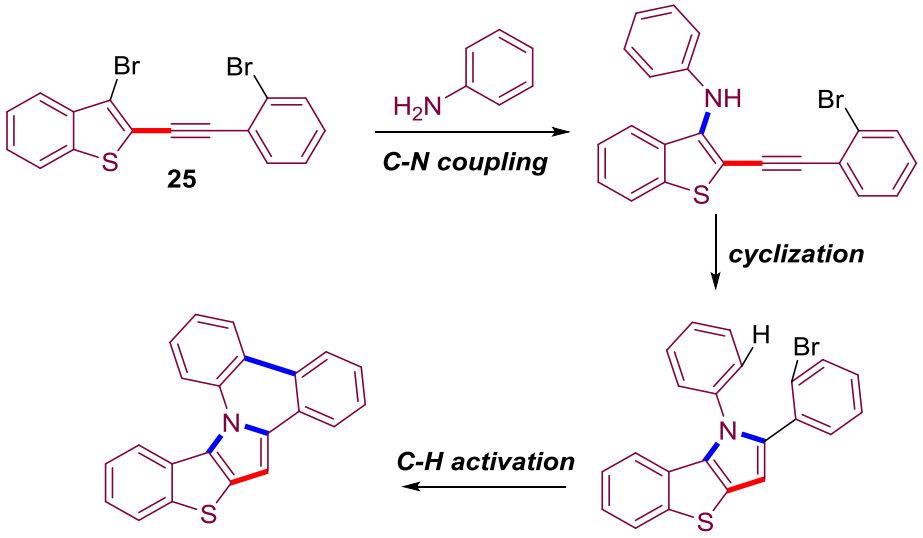


24n (66%)



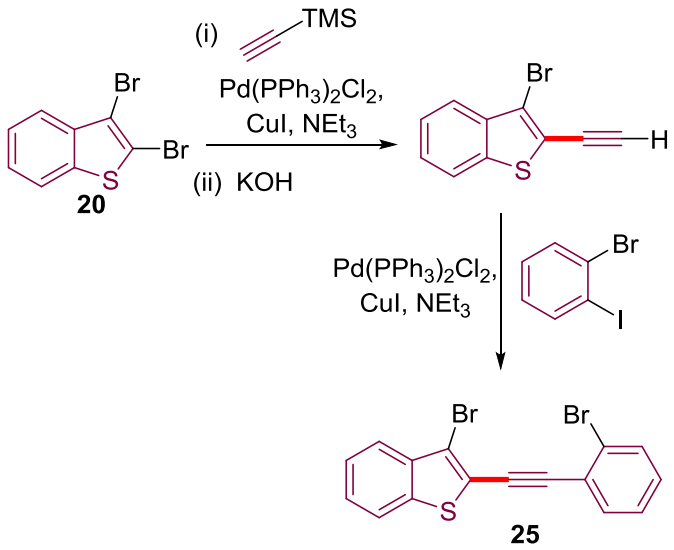
24o (60%)

Reaction conditions: **22a-c** (0.32 mmol), amine (0.38 mmol), $Pd(OAc)_2$ (0.032 mmol), $PtBu_3 \cdot HBF_4$ (0.064 mmol), base (0.96 mmol), DMF (4 ml), 140 °C, 24 h. The yields were referred to as isolated yields.



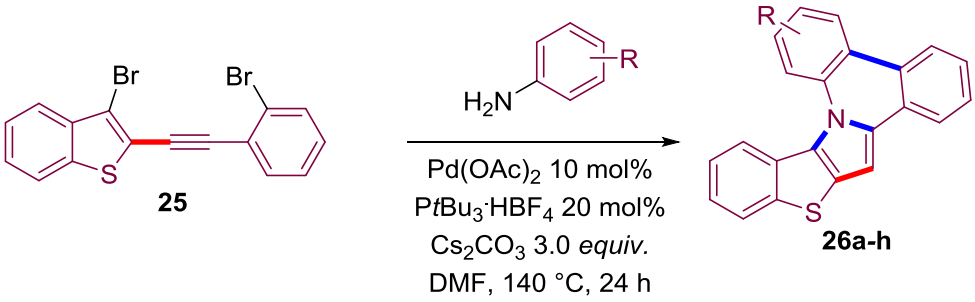
Scheme 58: Alternative route to benzothieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines

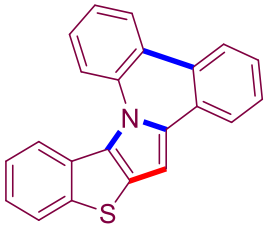
In the next place, an alternative route to benzothieno[2',3':4,5]pyrrolo-[1,2-*f*]phenanthridine was ascertained (Scheme 58). In this route, both bromine atoms are incorporated in the starting material 3-bromo-2-((2-bromophenyl)ethynyl)benzo[*b*]-thiophene (**25**). Therefore, the second reaction partner is simply aryl amine instead of *ortho*-bromoaryl amine (Scheme 59). It is assumed that Pd catalyst would likely attack the C-Br bond at the benzothiophene first (Scheme 58). After the hydroamination, the C-H arylation would occur with the second C-Br bond to form the corresponding product (Scheme 58).



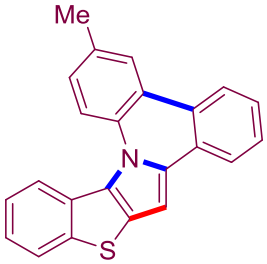
Scheme 59: Synthesis of 3-bromo-2-((2-bromophenyl)ethynyl)benzo[*b*]thiophene (**25**)

Table 25: Synthesis of benzothieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines **26a-h**

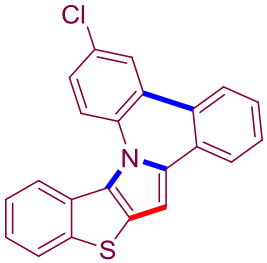




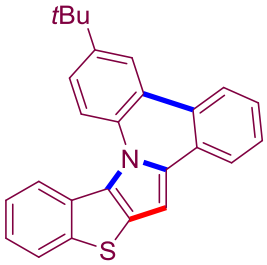
26a (60%) vs. **24a** (65%)



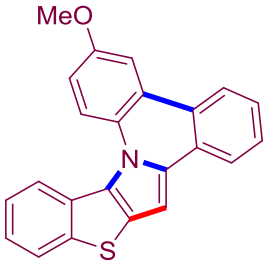
26b (65%) vs. **24b** (58%)



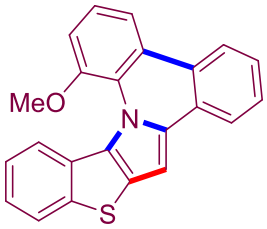
26c (50%) vs. **24c** (58%)



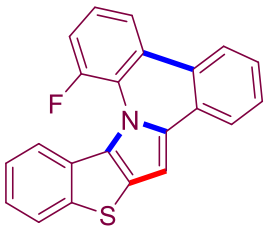
26d (65%)



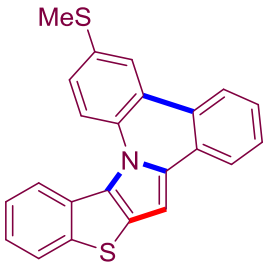
26e (60%)



26f (52%)



26g (55%)



26h (48%)

Reaction conditions: **22a-c** (0.32 mmol), amine (0.38 mmol), $Pd(OAc)_2$ (0.032 mmol), $PtBu_3 \cdot HBF_4$ (0.064 mmol), Cs_2CO_3(0.96 mmol), DMF (4 ml), 140 °C, 24 h. The yields were referred to as isolated yields.

Pleasingly, under the best conditions described in Table **24**, the reaction of 3-bromo-2-((2-bromophenyl)ethynyl)benzo[*b*]thiophene (**25**) with different aryl amines proved to be similarly effective compared to the prior procedure (**26a-c**, Table 25). The yield observed for benzothieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine **26b** was even slightly higher by applying this procedure. Further application of these conditions for the reactions with other amines afforded benzothieno[2',3':4,5]pyrrolo-

[1,2-*f*]phenanthridines **26d-h** in moderate to good yields (48% - 65%, Table 25). Electronically rich, electronically poor and even sterically encumbering amines proved to be compatible reaction partners for this chemical transformation.

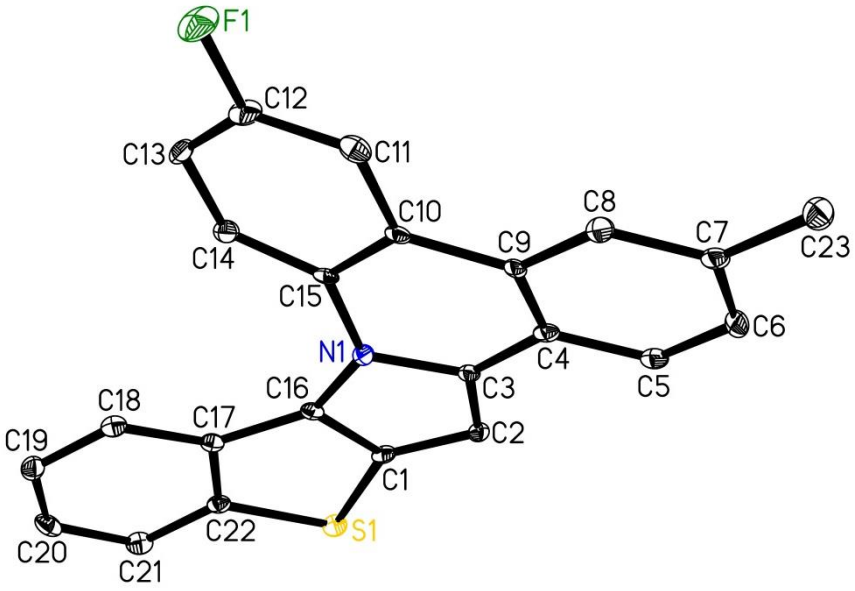
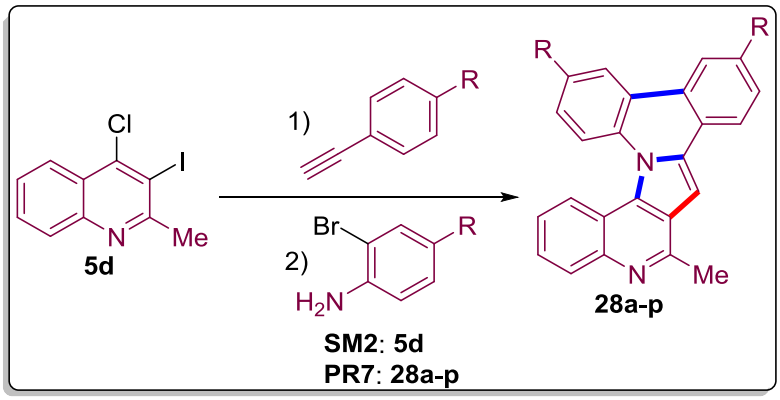


Figure 20: Molecular structure of benzothieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine **24h**

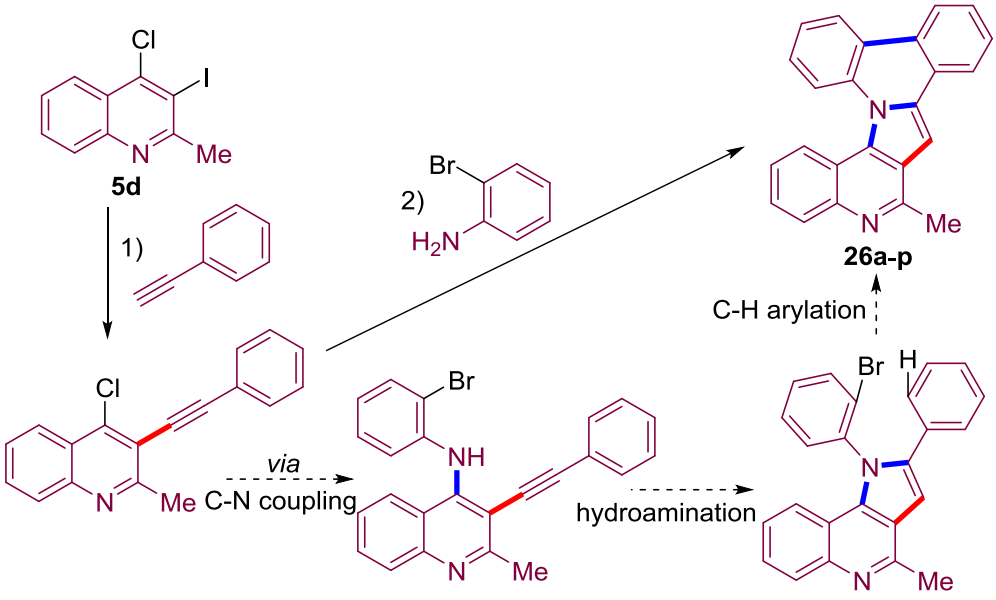
The molecular structure of benzothieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine **24h** was independently confirmed by X-ray structure determination (Figure 20). The aromatic backbone exhibits a noticeable distortion from planarity due to the electronic repulsion between the rings (C17 - C22) and (C10 - C15).

To summarize, by applying regioselective Sonogashira reaction of 2,3-dibromothiophene and aryl acetylene followed by domino C-N coupling/ hydroamination/C-H arylation, the previously unknown fused systems of phenanthridine with benzothiophene were attained in moderate to good yields. For the domino C-N coupling/hydroamination/C-H arylation reaction, two alternative sets of starting materials were applied with the first set involving two bromine atoms at two individual reaction partners and the second set consisting of two bromine atoms at the sole substrate.

3.3.2. Synthesis of quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines from *ortho*-dihaloquinoline



On the basis of the synthesis of benzothieno[2',3':4,5]pyrrolo-[1,2-*f*]phenanthridines, further effort was devoted to prepare quinolino[3',4':4,5]pyrrolo-[1,2-*f*]phenanthridines **28a-p** (product series **PR7**) by an analogous route (Scheme 60).

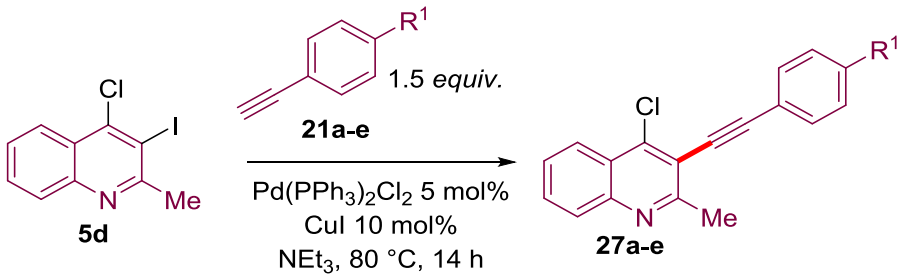


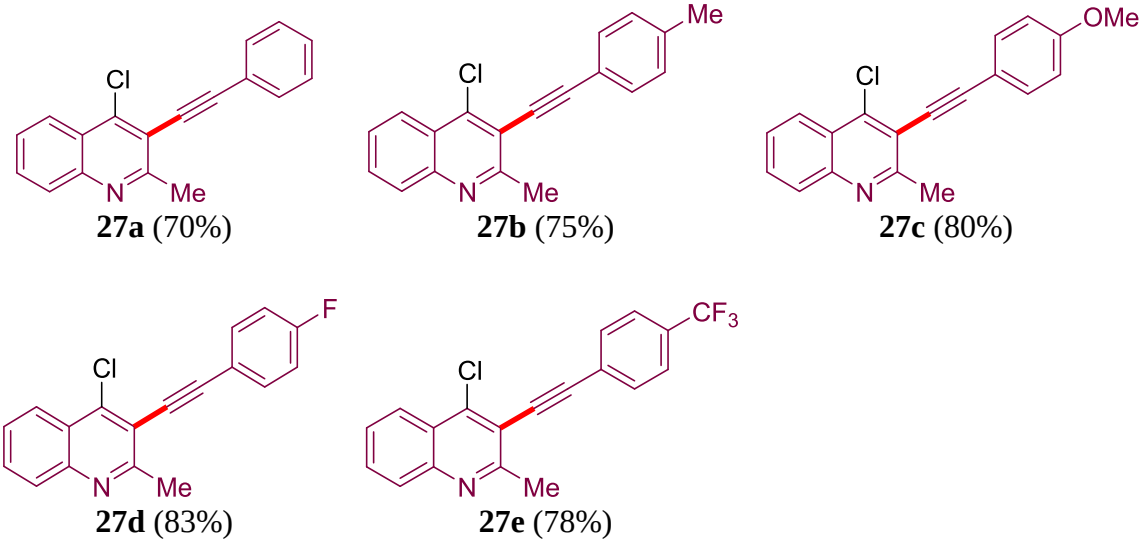
Scheme 60: Synthesis of quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines in this study

Initially, the regioselective Sonogashira reaction of 4-chloro-3-iodo-2-methylquinoline (**5d**) with electronically rich, -neutral and -poor aryl acetylenes (**21a-e**) was carried out. Although position 4 of the quinoline ring is more electron-deficient than position 3, the reaction prefers the latter over the former. The reason for this was the higher reactivity of the iodine compared to chlorine atom. Furthermore the chemo-selectivity factor would take over electronic effect in general palladium-catalyzed reaction. For this

reason, the reactions afforded regioselectively 4-chloro-2-methyl-3-(arylethynyl)quinolines **27a-e** (Table 26).

Table 26: Synthesis of 4-chloro-2-methyl-3-(arylethynyl)quinolines **27a-e** by regioselective Sonogashira reaction



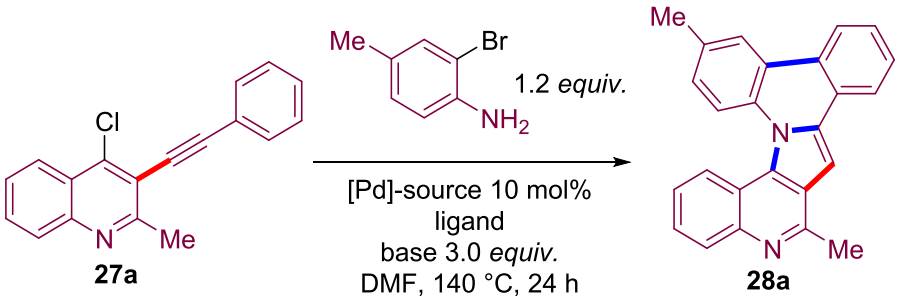


Reaction conditions: 4-Chloro-3-iodo-2-methylquinoline (**5d**) (3.0 mmol), aryl acetylene (4.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol), CuI (0.3 mmol), NEt_3 (2.0 ml), 80 °C, 14 h. The yields were referred to as isolated yields.

Next, 4-chloro-2-methyl-3-(arylethynyl)quinoline (**27a**) and 2-bromo-4-methylaniline (**23a**) were selected as model substrates for the optimization study of the domino C-N coupling/hydroamination/C-H arylation. In the presence of $Pd(OAc)_2$ and the base Cs_2CO_3 in DMF, different ligands were probed. It was found that both monodentate and bidentate ligands yielded the desired product **28a**, but SPhos emerged as preferred ligand giving 6-methylquinolino[3',4':4,5]-pyrrolo[1,2-*f*]phenanthridine **28a** in 65% yield (entry 9, Table 28). Next, the robustness of these reaction conditions was checked. By changing the base, the reaction failed to deliver the expected results. Besides, the palladium source Pd_2dba_3 proved inferior, while $Pd(PPh_3)_4$ yielded virtually no

corresponding product (entry 10-11, Table 27). Therefore, the best conditions **9** in Table **27** were applied for the study of the preparative reaction scope of the reaction.

Table 27: Optimization study for the synthesis of 6-methylquinolino-[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (**28a**)

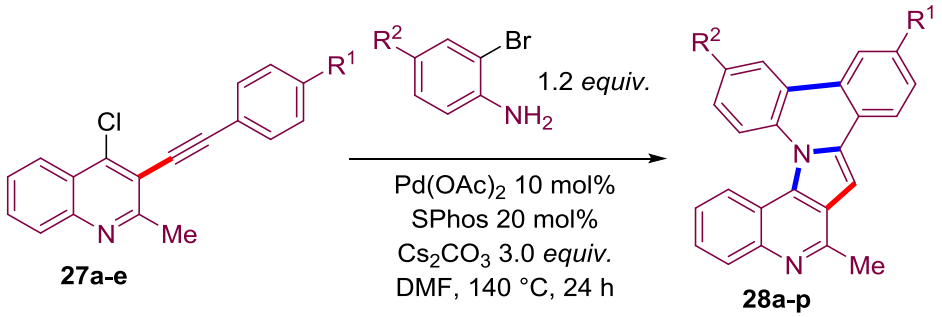


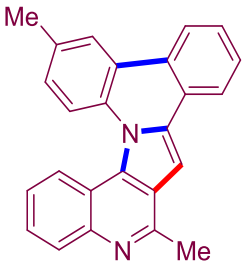
Entry	[Pd]-Source	Ligand	Base	Yield
1	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	25%
2	$Pd(OAc)_2$	dppe	Cs_2CO_3	42%
3	$Pd(OAc)_2$	dppf	Cs_2CO_3	30%
4	$Pd(OAc)_2$	DavePhos	Cs_2CO_3	45%
5	$Pd(OAc)_2$	(*S*)-BINAP	Cs_2CO_3	38%
6	$Pd(OAc)_2$	Xphos	Cs_2CO_3	40%
7	$Pd(OAc)_2$	P*t*Bu$_3$·HBF$_4$	Cs_2CO_3	50%
8	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	30%
9	**$Pd(OAc)_2$**	**Sphos**	**Cs_2CO_3**	**65%**
10	$Pd(PPh_3)_4$	Sphos	Cs_2CO_3	-
11	Pd_2dba_3	Sphos	Cs_2CO_3	55%
12	$Pd(OAc)_2$	Sphos	K_2CO_3	-
13	$Pd(OAc)_2$	Sphos	KO*t*Bu	-

Reaction conditions: **27a** (0.1 mmol), amine (0.12 mmol), [Pd]-source (0.01 mmol), ligand (0.02 mmol for monodentate or 0.01 mmol for bidentate ligands), base (0.3 mmol), DMF (3 ml), 140 °C, 24 h. The yields were referred to as isolated yields.

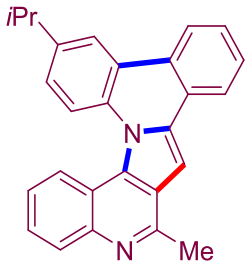
Under these conditions, the reaction of 4-chloro-2-methyl-3-(arylethynyl)quinolines **27a-e** with different 2-bromo-aryl amines produced corresponding quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines **28a-p** in moderate to good yields (42% - 81%, Table 28). Aryl amines with different electronic structures were tolerated, but there is no correlation between the structure and the reaction yield revealed from the data.

Table 28: Synthesis of quinolino[3',4':4,5]pyrrolo[1,2-*f*] phenanthridines **28a-p**

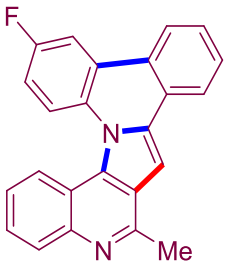




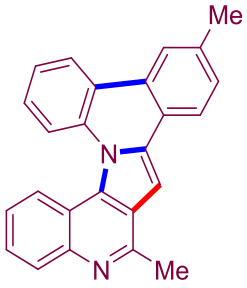
28a (65%)



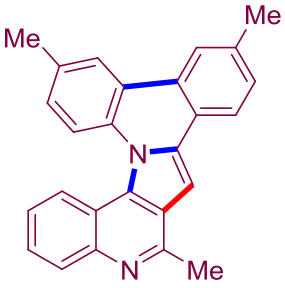
28b (60%)



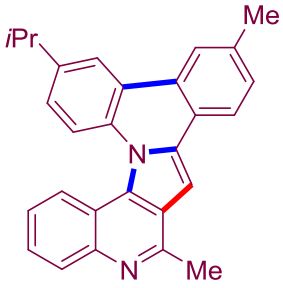
28c (58%)



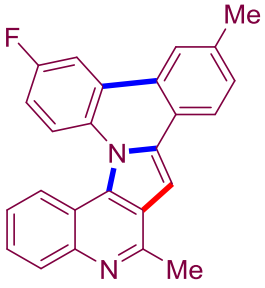
28d (67%)



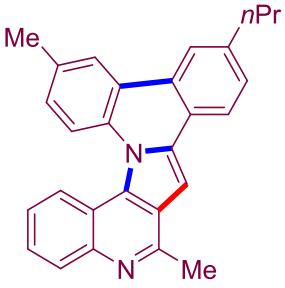
28e (70%)



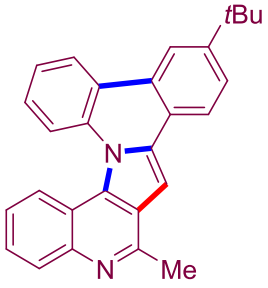
28f (63%)



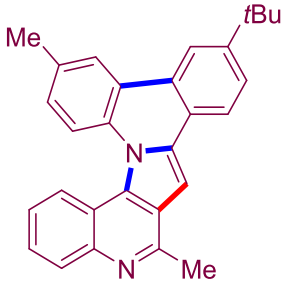
28g (62%)



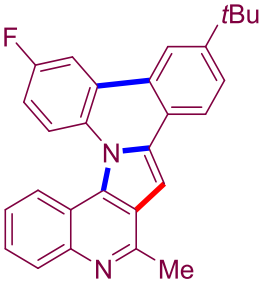
28h (67%)



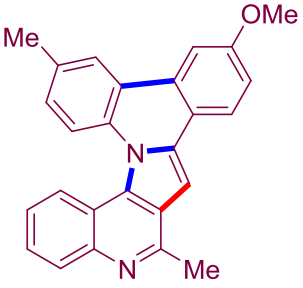
28i (58%)



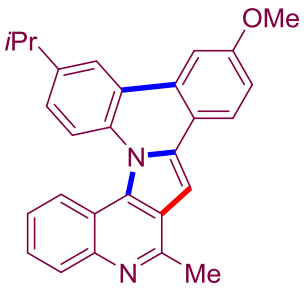
28j (81%)



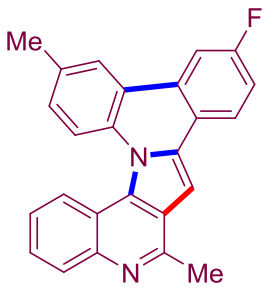
28k (65%)



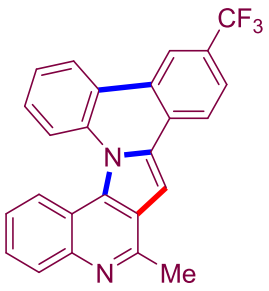
28l (42%)



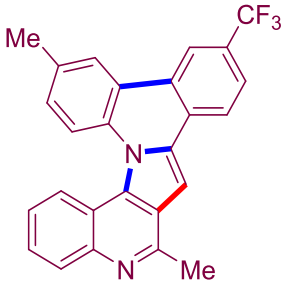
28m (47%)



28n (64%)



28o (67%)



28p (53%)

Reaction conditions: **27a-e** (0.32 mmol), amine (0.38 mmol), $Pd(OAc)_2$ (0.032 mmol), SPhos (0.064 mmol), base (0.96 mmol), DMF (4 ml), 140 °C, 24 h. The yields were referred to as isolated yields.

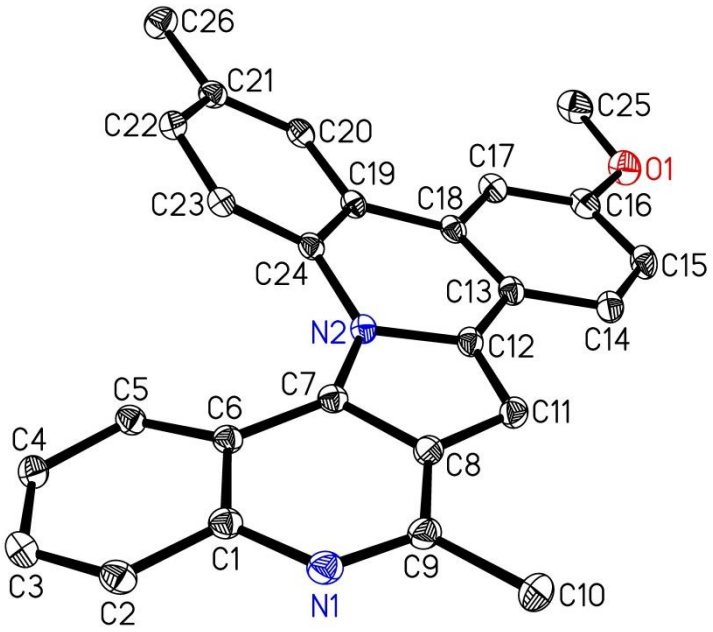
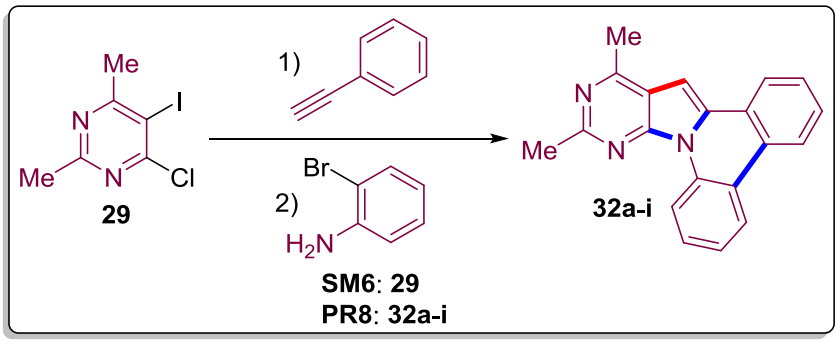


Figure 21: Molecular structure of **28l** in crystal

The molecular structure of quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine **28l** was independently confirmed by means of X-ray crystallographic analysis (Figure 21). The structure proof reveals a helical distortion structure of the core aromatic ring. The distortion from the planarity is interpreted as the result of the electronic repulsion between the hydrogen atoms of the rings (C1-C6) and (C19-C24).

In summary, a series of quinolino[3’,4’:4,5]pyrrolo[1,2-*f*]phenanthridines was synthesized by regioselective Sonogashira reaction followed by domino C-N coupling/hydroamination/C-H arylation in moderate to good yields. Compared to the synthesis of benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines in Chapter **3.3.1**, the monodentate ligand SPhos demonstrated higher effectiveness for the preparation of quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines in this study.

3.3.3. Synthesis of 11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]-phenanthridines from 5,6-dihalopyrimidine



Pyrimidine-fused heterocycles were first known in 1776 during the isolation of uric acid by Scheele *et al.*[179] However, their chemistry progressed only since the second half of the 1800s, while several syntheses were established.[180] Later, pyrimidines were identified to be the core structures of the nucleobases cytosine/guanine and thymine/adenine that constitute the DNAs.[181] This finding has motivated scientists to carry out further research into fused-pyrimidines, from which a sheer number of potential candidates for the application as drugs have been disclosed. For example, NQPPs displays enhanced anti-proliferative activity (Figure 22).

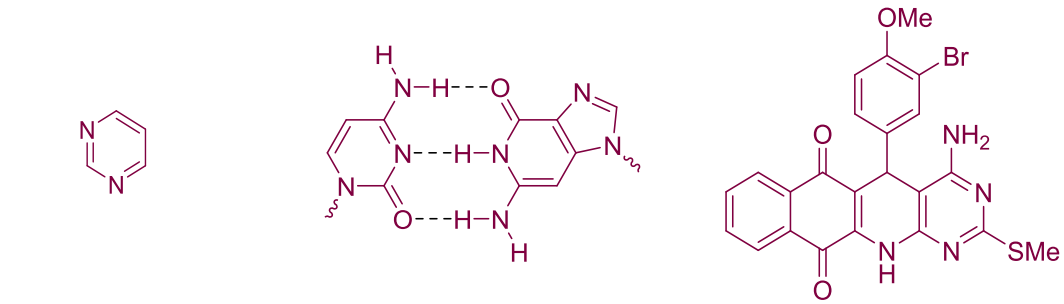
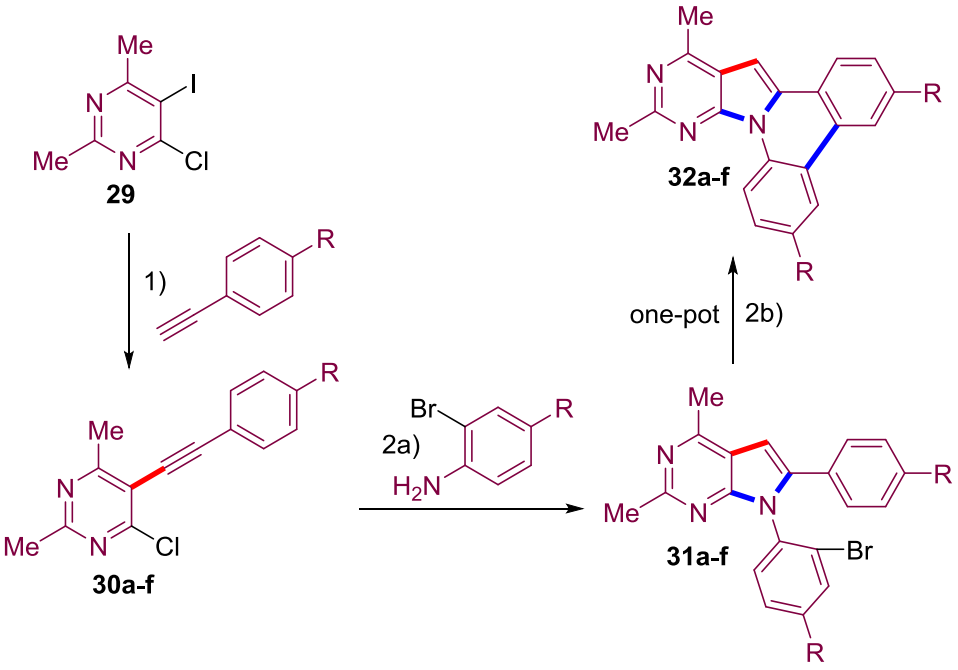


Figure 22: Examples of several pyrimidine-related compounds

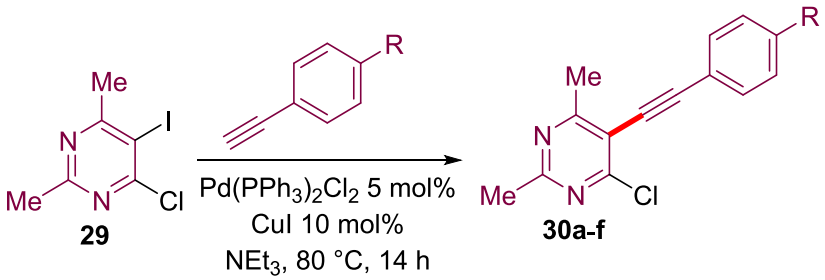
The successes in the syntheses of benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]-phenanthridines (Chapter 3.3.1) and quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines (Chapter 3.3.2) underpins a further investigation into the synthesis of 11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines (**PR8**) in this contribution (Scheme 61). Similarly, the synthesis starts with a regioselective Sonogashira reaction of 4-chloro-5-iodo-2,6-dimethylpyrimidine (**29**) with different aryl acetylene (step 1, Scheme 61). Subsequently, the corresponding products 4-chloro-2,6-dimethyl-5-(arylethynyl)-pyrimidines **30a-f** are coupled with different 2-haloaryl amine *via* a domino C-N coupling/hydroamination to afford corresponding products **31a-f** (step 2a, Scheme 61), which undergo further C-H arylation, furnishing final 11,13-dimethylpyrimido-[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines **32a-f** (step 2b, Scheme 61). For this synthesis, a subjection of additional catalysts and a change of reaction solvents between step **2a** and step **2b** following a one-pot procedure are required (Scheme 61).

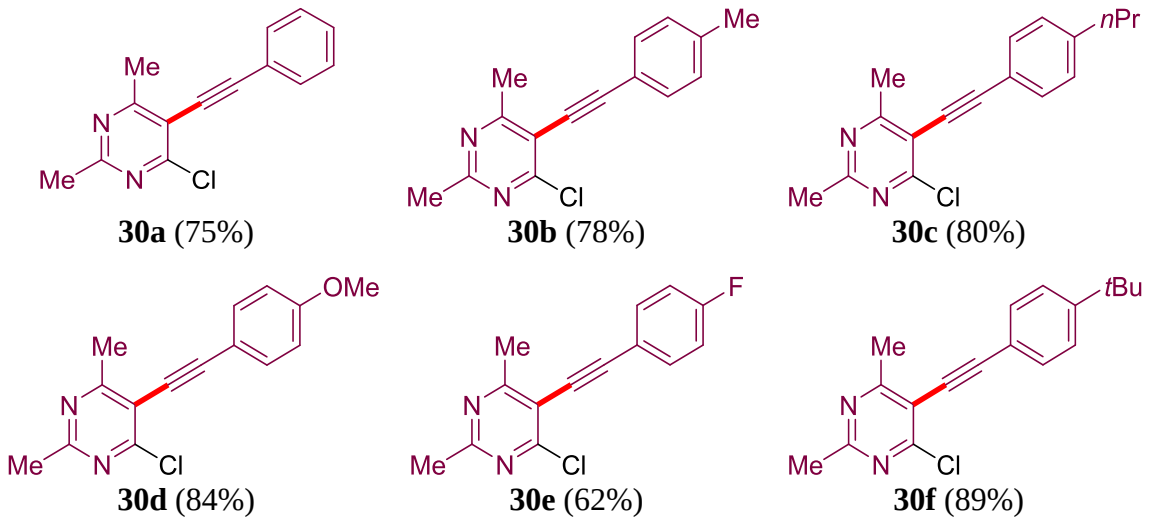


Scheme 61: Synthesis of 11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines in this study

At the outset of the study, the Sonogashira reaction of 4-chloro-5-iodo-2,6-dimethylpyrimidine (**29**) with aryl acetylenes delivered predominantly corresponding 4-chloro-2,6-dimethyl-5-(phenylethynyl)pyrimidines **30a-f** in moderate to good yields (Table 29). The selectivity in this reaction was imparted by the preference in the reactivity of iodine against chlorine.

Table 29: Synthesis of 4-chloro-2,6-dimethyl-5-(phenylethynyl)pyrimidines **30a-f** by regioselective Sonogashira reaction



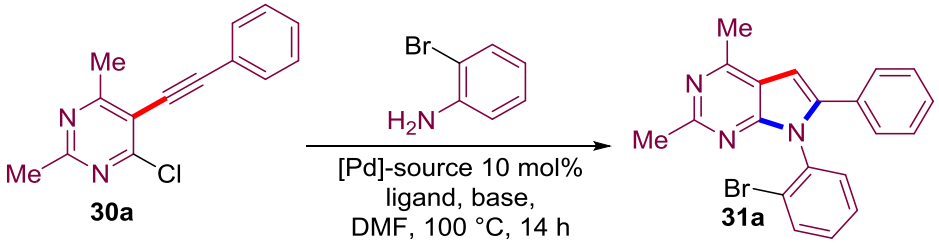


Reaction conditions: 4-Chloro-5-iodo-2,6-dimethylpyrimidine (**29**) (3.0 mmol), aryl acetylene (4.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol), CuI (0.3 mmol), NEt_3 (2.0 ml), 80 °C, 14 h. The yields were referred to as isolated yields.

To study the following domino C-N coupling/hydroamination, 4-chloro-2,6-dimethyl-5-(phenylethynyl)pyrimidine **30a** and 2-bromoaniline were chosen as model substrates for the optimization. In the presence of the palladium source $Pd(OAc)_2$, the base Cs_2CO_3 and the solvent DMF, the influence of different ligands was monitored. Among these ligands, Xantphos was identified as the best ligand, giving corresponding product **31a** in 60% yield (entry 1, Table 30). Next, the palladium sources and bases were tuned. This revealed that the palladium source $Pd(PPh_3)_4$ resulted in an increase of yield compared to $Pd(OAc)_2$. Conducting the reaction in the presence of the catalyst system $Pd(PPh_3)_4$/Xantphos with the base Cs_2CO_3 in DMF led to the formation of product **31a**

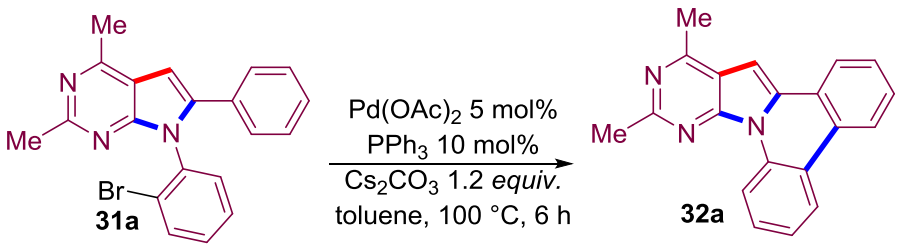
in 72% yield (entry 10, Table 30). In contrast, by changing the palladium source to Pd_2dba_3, the yield dropped to 50% (entry 11, Table 30). Besides, the presence of the base Cs_2CO_3 proved crucial for this chemical transformation. The reaction failed to furnish the desired products when other bases were applied.

Table 30: Optimization study for the synthesis of 7-(2-bromophenyl)-2,4-dimethyl-6-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (**31a**)



Entry	[Pd]-source	Ligand	Base	Yield
1	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	60%
2	$Pd(OAc)_2$	XPhos	Cs_2CO_3	45%
3	$Pd(OAc)_2$	SPhos	Cs_2CO_3	40%
4	$Pd(OAc)_2$	P*t*Bu$_3$·HBF$_4$	Cs_2CO_3	55%
5	$Pd(OAc)_2$	dppe	Cs_2CO_3	42
6	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	37
7	$Pd(OAc)_2$	dppf	Cs_2CO_3	30
8	$Pd(OAc)_2$	Davephos	Cs_2CO_3	34
9	$Pd(OAc)_2$	(*S*)-BINAP	Cs_2CO_3	25
10	**$Pd(Ph_3P)_4$**	**Xantphos**	**Cs_2CO_3**	**72%**
11	Pd_2dba_3	Xantphos	Cs_2CO_3	50
12	$Pd(Ph_3P)_4$	Xantphos	K_2CO_3	-
13	$Pd(Ph_3P)_4$	Xantphos	KO*t*Bu	-

Reaction conditions: **30a** (0.1 mmol), amine (0.12 mmol), [Pd]-source (0.01 mmol), ligand (0.02 mmol for monodentate or 0.01 mmol for bidentate ligands), base (0.3 mmol), DMF (3 ml), 100 °C, 14 h. The yields were referred to as isolated yields.



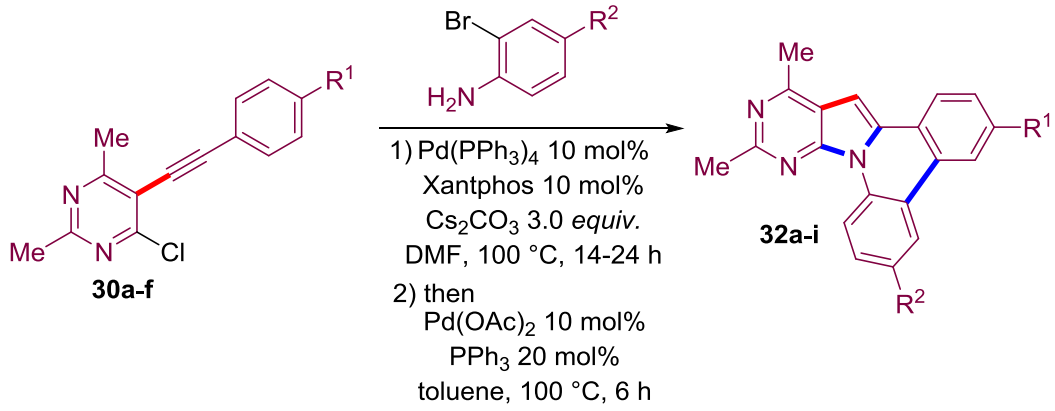
Scheme 62: Synthesis of 11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine by C-H arylation

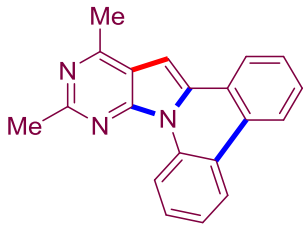
Subsequently, the C-H arylation of 7-(2-bromophenyl)-2,4-dimethyl-6-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (**31a**) was examined. On treatment with catalyst system $Pd(OAc)_2/PPh_3$ in toluene at 100 °C, 11,13-dimethylpyrimido[5',4':4,5]pyrrolo-[1,2-*f*]phenanthridine **32a** was furnished in 87% yield (Scheme 62).

Following this result, a further investigation into the feasibility of conducting the domino C-N coupling/hydroamination and the C-H arylation in an one-pot procedure was carried out. After the domino C-N coupling/hydroamination was finished, the solvent was removed *in vacuo* followed by the addition of new catalysts and solvent. The mixture was heated at 100 °C for additional 6 hours. Gratifyingly, the corresponding 11,13-dimethylpyrimido-[5',4':4,5]pyrrolo[1,2-*f*]-phenanthridine **32a** was afforded *via* this one-pot process in 65% yield. This result indicates that the yield was not remarkably suffered following a one-pot procedure. Therefore, this model was chosen for the following study of the preparative scope of the method.

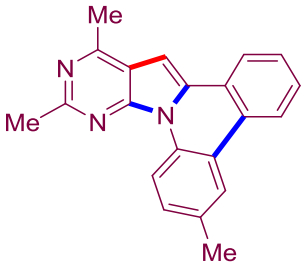
Applying this procedure for the reaction of 4-chloro-2,6-dimethyl-5-(phenylethynyl)pyrimidines **30a-f** and different 2-bromoaryl amines, corresponding pyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines **32a-p** were isolated in moderate to good yields (Table 31). There was no clear trend between chemical structure and reaction yield. The highest yield gave the system **32g** (75%), whereas the lowest reaction efficiency was observed for **32n** (42%).

Table 31: Synthesis of pyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines **32a-i**

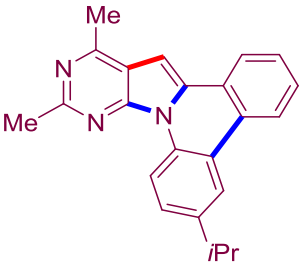




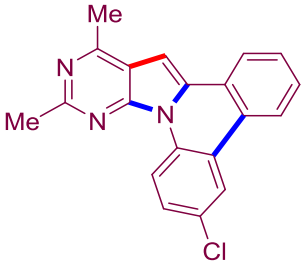
32a (65%)



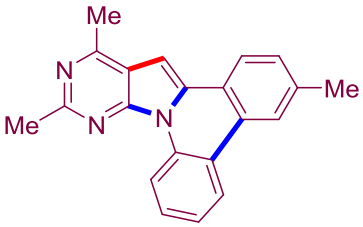
32b (60%)



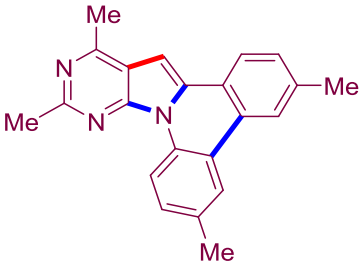
32c (70%)



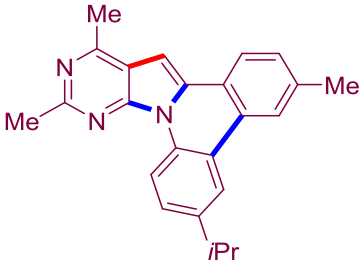
32d (63%)



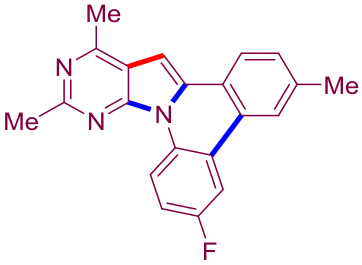
32e (72%)



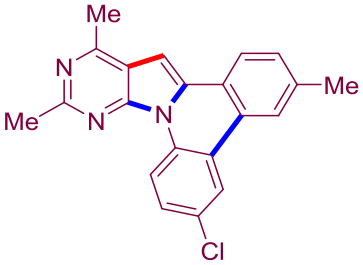
32f (70%)



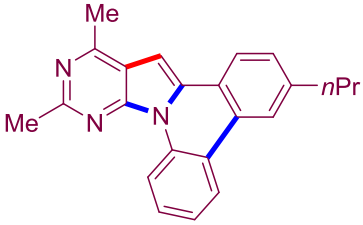
32g (75%)



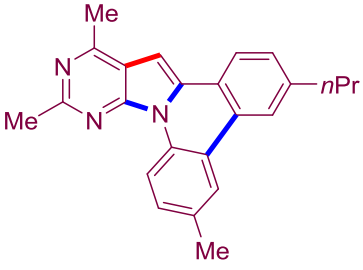
32h (55%)



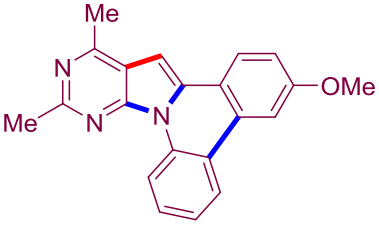
32i (65%)



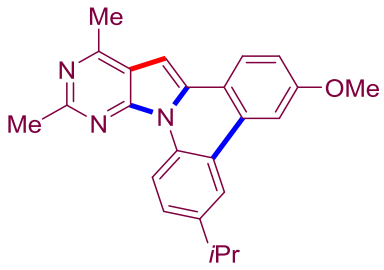
32j (51%)



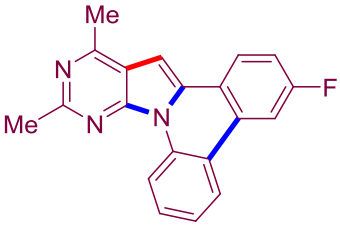
32k (57%)



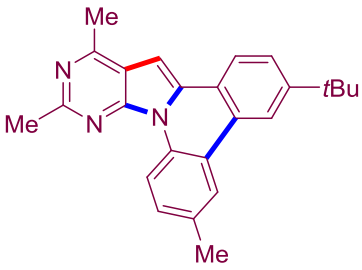
32l (65%)



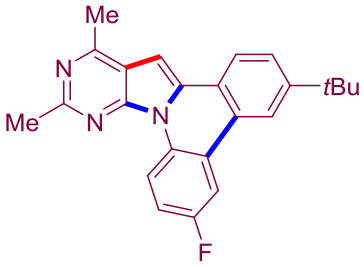
32m (72%)



32n (42%)



32o (45%)



32p (67%)

Reaction conditions: **30a-f** (0.32 mmol), amine (0.38 mmol), $Pd(PPh_3)_4$ (0.032 mmol), XantPhos (0.032 mmol), base (0.96 mmol), DMF (4 ml), 100 °C, 14 - 24 h; then $Pd(OAc)_2$ (0.032 mmol), PPh_3 (0.064 mmol), toluene (2 ml), 100 °C, 6 h.
The yields were referred to as isolated yields.

To sum up, a synthesis of pyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines was developed by regioselective Sonogashira reaction, followed by one-pot domino C-N coupling/hydroamination and C-H arylation. In difference to the synthesis of benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines (Chapter 3.3.1) and quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines (Chapter 3.3.2), an one-pot procedure was applied, in which an addition of further catalysts and a change of solvent between the domino C-N coupling/hydroamination and the C-H arylation were key to the success of the method.

4. Conclusion

In this PhD research, eight different series **PR1**-**8** of 169 nitrogen-containing heterocycles were isolated from *ortho*-dihaloarenes by three different strategies.

First, the palladium-catalyzed domino C-C/C-N coupling of imines with *ortho*-dihalopyridines and *ortho*-dihaloquinolines employed identical reaction conditions, furnishing corresponding azaindoles (**PR1**) and pyrroloquinolines (**PR2**) in moderate to good yields.

Next, indoloquinolines (**PR3**), benzo[*a*]carbazoles (**PR4**) and thienoindoles (**PR5**) were obtained by regioselective Suzuki reaction/double C-N coupling. The resulting yields were from good to excellent. It came obvious that the choice of ligand was essential for the performance of the double C-N coupling.

Finally, product series **PR6**-**8** were synthesized by regioselective Sonogashira reaction followed by domino/one-pot C-N coupling/hydroamination/C-H arylation in moderate to good yields. Noticeably, the synthesis of the product series **PR9** required a switch of solvent and an addition of further catalysts between the C-N coupling/hydroamination and the C-H arylation.

5. Experimental section

Solvents used for the work-up and column chromatography were distilled using standard procedures. Molecular sieves were dried at 300 °C for more than 10 hours. If not otherwise noted, other chemicals and solvents were obtained from commercial sources without further purification. Column chromatography was performed using normal silica gel with particle sizes 0.006 - 0.043 nm.

NMR measurements were performed with Bruker AVANCE 250 II (built 2006), Bruker AVANCE 300 III (built 2007) and Bruker AVANCE 500 (built 2001). NMR peaks were calibrated using standard signals of chloroform (7.260 ppm for ^{1}H-NMR, 77.160 ppm for ^{13}C-NMR), acetone (2.050 ppm for ^{1}H-NMR, 29.840 ppm for ^{13}C-NMR) and DMSO (2.500 ppm for ^{1}H-NMR, 39.520 ppm for ^{13}C-NMR). For peak description, abbreviations s (singlet), d (duplet), t (triplett), q (quartet), sept (septet) and *p*t (*pseudo* triplet) were used.

IR measurements were recorded on a Nicolet 380 FT-IR spectrometer using ATR sampling technique. For peak description, abbreviations w (weak), m (medium) and s (strong) were used.

GC/MS measurements were carried out with Finnigan MAT 95-XP device using HP-5 capillary column with helium carrier gas and electron ionization (EI) scan technique at 70 eV. HRMS was measured with a Finnigan MAT 95 XP device.

The calculations of the yields *via* NMR-spectroscopy were performed using dimethylsulfone as internal standard.

Crystallographic data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods[182] and refined by full-matrix least-squares procedures.[183] XP (Bruker AXS) and Mercury[184] were used for molecular graphics.

5.1. General synthetic procedures

3-Bromo-2-chloroquinoline[132c] (**5a**), 3-bromo-4-chloroquinoline[132c] (**5b**), 3-bromo-4-chloro-2-methylquinoline[185] (**5c**), 4-chloro-3-iodo-2-methylquinoline[186] (**5d**), 1-bromonaphthalen-2-yl trifluoromethanesulfonate[150] (**13**) and 4-chloro-5-iodo-2,6-dimethylpyrimidine[187] (**29**) were synthesized according previously documented procedures.

5.1.1. Synthesis of imines 2a-o

To a dried flask, ketone (10.0 mmol), amine (10.0 mmol), $NaHCO_3$ (4.20 g) and molecular sieve 4Å (8.00 g) in 10.0 ml toluene were added. Subsequently, the reaction mixture was heated to 80 °C or refluxed overnight. After the reaction was finished (monitored by TLC), the mixture was taken up in dichloromethane and filtered. The solvents were removed under reduced pressure. The products were purified by recrystallization in heptane/ethyl acetate or by Kugelrohr distillation under reduced pressure.

5.1.2. Synthesis of 4-azaindoles 3a-o and 7-azaindoles 4a-o

2-Bromo-3-chloropyridine (**1b**) or 3-bromo-2-chloropyridine (**1c**) (0.3 mmol), imine **2a-o** (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol) and NaO*t*Bu (0.84 mmol) were put into a dried glass pressure tube. The tube was then evacuated and backfilled three times with argon. Dried 1,4-dioxane (6.0 ml) was added to the tube under argon atmosphere. The reaction mixture was sealed by a Teflon cap, stirred for 10 minutes at room temperature, and subsequently heated to 105 °C for 16 - 48 hours. The reaction was controlled by TLC until completion. Thereafter, it was cooled down to room temperature, taken up in dichloromethane and filtered. The solvent was removed by evaporation *in vacuo*. The residue was purified by column chromatography (heptane/ethyl acetate).

5.1.3. Synthesis of pyrroloquinolines 6a-i and pyrroloquinolines 7a-f

3-Bromo-2-chloroquinoline (**5a**) or 3-bromo-4-chloroquinoline (**5b**) (0.3 mmol), imine (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol) and NaO*t*Bu (0.84 mmol) were put into a dried glass pressure tube. The tube was then evacuated and backfilled three times with argon. Dried 1,4-dioxane (6.0 ml) was added to the tube under argon atmosphere. The reaction mixture was sealed by a Teflon cap, stirred for 10 minutes at room temperature, and subsequently heated to 105 °C for 24 hours. The reaction was controlled by TLC until completion. Thereafter, it was cooled down to room temperature, taken up in dichloromethane and filtered. The solvent was removed by evaporation *in vacuo*. The residue purified by column chromatography (heptane/ethyl acetate).

5.1.4. Synthesis of 3-(2-bromophenyl)-4-chloro-2-methylquinoline (9a)

3,4-Dihalo-2-methylquinoline **5c-d** (3.0 mmol), (2-bromophenyl)boronic acid (**8**) (4.2 mmol), $Pd(PPh_3)_4$ (0.15 mmol) and Na_2CO_3 (6.0 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon. The solids were solved in 10.0 ml of DMF and 1.0 ml of distilled water. The tube was sealed with a Teflon cap and heated to 100 °C for 24 hours. After the reaction completed (monitored by TLC), it was allowed to cool to room temperature. To the reaction mixture, Na_2SO_4 was added, diluted with ethyl acetate and filtered. The solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane/ethyl acetate).

5.1.5. Synthesis of 3-(2-bromophenyl)-2-chloroquinoline (9b)

3-Bromo-2-chloroquinoline (**5a**) (3.0 mmol), (2-bromophenyl)boronic acid (**8**) (3.6 mmol), $Pd(dppf)Cl_2$ (0.3 mmol) and Cs_2CO_3 (6.0 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon. The solids were solved in 5.0 ml of dried THF. The tube was sealed with a Teflon cap and heated to 60 °C for 10 hours. After the reaction completed (monitored by TLC), it was allowed to cool to room temperature. The solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane).

5.1.6. Synthesis of 1-bromo-2-(2-bromophenyl)naphthalene (14)

1-Bromonaphthalen-2-yl trifluoromethanesulfonate (**13**) (3.0 mmol), (2-bromophenyl)boronic acid (**8**) (3.3 mmol), $Pd(PPh_3)_4$ (0.15 mmol) and K_3PO_4 (6.0 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 5.0 ml of dried 1,4-dioxane was added. The tube was sealed with a Teflon cap and heated to 90 °C for 5 hours. After the reaction completed (monitored by TLC), it was allowed to cool to room temperature. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane).

5.1.7. Synthesis of 3-bromo-2-(2-bromophenyl)-thiophene (17a) and 3-bromo-4-(2-bromophenyl)thiophene (17b)

To a dried glass pressure tube were added 2,3- or 3,4-dibromothiophene **16a-b** (3.0 mmol), (2-bromophenyl)boronic acid (**8**) (3.3 mmol), $Pd(PPh_3)_4$ (0.15 mmol), Na_2CO_3 (6.0 mmol). The tube was evacuated and backfilled three times with argon.

Subsequently, the solids were solved in 8.0 ml of 1,4-dioxane and 2.0 ml of distilled water. The tube was sealed by a Teflon cap and heated to 100 °C for 14 hours. After the reaction was finished (monitored by TLC), it was allowed to cool to room temperature and Na_2SO_4 was added to the mixture, diluted with ethyl acetate and filtered. The solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane).

5.1.8. Synthesis of indoloquinolines 11a-t and indoloquinolines 12a-h

3-(2-Bromophenyl)-4-chloro-2-methylquinoline (**9a**) or 3-(2-bromophenyl)-2-chloroquinoline (**9b**) (0.15 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), P*t*Bu_3·HBF_4 (0.015 mmol) or (*S*)-BINAP (0.0075 mmol) and NaOtBu (0.36 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon. To this tube, 3.0 ml of dried toluene was added. The mixture was heated to 100 °C for 14 hours. After the reaction completed (monitored by TLC), it was allowed to cool to room temperature. The solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane/ethyl acetate).

5.1.9. Synthesis of benzo[*a*]carbazoles 15a-o

1-Bromo-2-(2-bromophenyl)naphthalene (**14**) (0.15 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), Xantphos (0.0075 mmol) or (*S*)-BINAP (0.0075 mmol) and NaO*t*Bu (0.36 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 3.0 ml of dried toluene was added. The mixture was heated to 100 °C for 14 hours until completion (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane/ethyl acetate).

5.1.10. Synthesis of thienoindoles 18a-t and thienoindoles 19a-f

3-Bromo-2-(2-bromophenyl)thiophene (**17a**) (0.15 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), dppf or (*S*)-BINAP (0.0075 mmol) or P*t*Bu·HBF_4 (0.015 mmol) and NaO*t*Bu (0.36 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 3.0 ml of dried toluene was added. The mixture was heated to 100 °C for 14 hours until completion (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane/ethyl acetate).

5.1.11. Synthesis of 3-bromo-2-(arylethynyl)-benzo[*b*]thiophenes 22a-c

2,3-Dibromobenzothiophene (**20**) (3.0 mmol), aryl acetylene (3.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol) and CuI (0.3 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 2.0 ml of triethylamine was added. The tube was sealed with a Teflon cap and stirred at room temperature for 14 hours until completion (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane/ethyl acetate).

5.1.12. Synthesis of 4-chloro-2-methyl-3-(arylethynyl)quinolines 27a-e

4-Chloro-3-iodo-2-methylquinoline (**5d**) (3.0 mmol), aryl acetylene (4.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol) and CuI (0.3 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 4.0 ml of triethylamine was added. The tube was sealed with a Teflon cap and heated to 80 °C for 14 hours until completion (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane/ethyl acetate).

5.1.13. Synthesis of 4-chloro-2,6-dimethyl-5-(phenylethynyl)pyrimidines 30a-f

4-Chloro-5-iodo-2,6-dimethylpyrimidine (**29**) (3.0 mmol), aryl acetylene (4.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol) and CuI (0.3 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 2.0 ml of triethylamine was added. The tube was sealed with a Teflon cap and heated to 80 °C for 14 hours until completion (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was purified by column chromatography (heptane/ethyl acetate).

5.1.14. Synthesis of benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines 24a-o and benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines 26a-h

3-Bromo-2-(phenylethynyl)benzo[*b*]thiophenes (**22a-c**) or 3-bromo-2-((2-bromophenyl)ethynyl)benzo[*b*]-thiophene (**25**) (0.32 mmol), aryl amine (0.38 mmol), $Pd(OAc)_2$ (0.032 mmol), P*t*Bu_3·HBF_4 (0.064 mmol) and Cs_2CO_3 (0.96 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 4.0 ml of dried DMF was added. The tube was

sealed with a Teflon cap and heated to 140 °C for 24 hours. After cooling to room temperature, H_2O was poured to the reaction mixture and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (heptane/ethyl acetate).

5.1.15. Synthesis of quinolino[3',4':4,5]pyrrolo-[1,2-*f*]phenanthridines 28a-p

4-Chloro-3-(arylethynyl)quinoline (**27a-e**) (0.3 mmol), *ortho*-bromoaryl amine (0.36 mmol), $Pd(OAc)_2$ (0.03 mmol), SPhos (0.06 mmol) and Cs_2CO_3 (0.9 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon, then 4.0 ml of dried DMF was added. The tube was sealed with a Teflon cap and heated to 140 °C for 24 hours. After cooling to room temperature, H_2O was poured to the reaction mixture and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (heptane/ethyl acetate).

5.1.18. Synthesis of 11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]-phenanthridines 32a-i

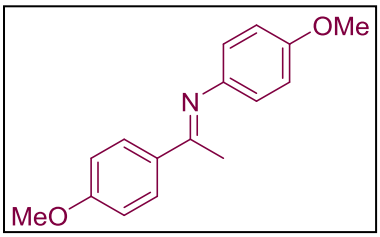
To a dried flask, 4-chloro-2,6-dimethyl-5-(phenylethynyl)pyrimidine (**30a-b**) (0.3 mmol), *ortho*-bromoaryl amine (0.36 mmol), $Pd(PPh_3)_3$ (0.03 mmol), Xantphos (0.03 mmol), Cs_2CO_3 (0.9 mmol) and dried DMF (4.0 ml) were added. The flask was heated to 100 °C for 14 - 24 hours under argon atmosphere. The reaction profile was checked by TLC until completion of the first step. After cooling to room temperature, the solvent was removed under reduced pressure. To the reaction mixture, $Pd(OAc)_2$ (0.03 mmol), PPh_3 (0.06 mmol) and 4.0 ml of dried toluene were added. The reaction mixture was heated for further 6 hours under argon atmosphere. After the reaction was completed, the solvent was removed under reduced pressure. The residue was purified by column chromatography (heptane/ethyl acetate).

5.2. Spectral data

5.2.1. Synthesis of azaindoles from imines by domino C-C/C-N coupling

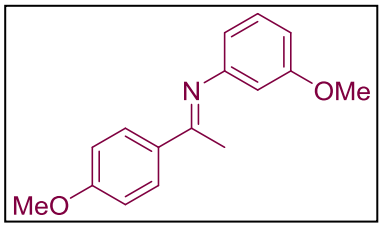
5.2.1.1.Imines

N,1-bis(4-Methoxyphenyl)ethan-1-imine (2a): ^{1}H NMR (250 MHz, Chloroform-*d*)



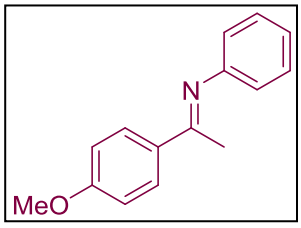
δ = 8.03 - 7.85 (m, 2H, CH_{Ar}), 7.00 - 6.84 (m, 4H, CH_{Ar}), 6.80 - 6.71 (m, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 2.23 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 165.1 (C_{Ar}), 161.7 (C_{Ar}), 156.1 (C_{Ar}), 145.5 (C_{Ar}), 132.7 (C_{Ar}), 129.0 ($2CH_{Ar}$), 121.2 ($2CH_{Ar}$), 114.4 ($2CH_{Ar}$), 113.8 ($2CH_{Ar}$), 55.6 (OCH_3), 55.5 (OCH_3), 17.3 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 256 (10), 255 $[M]^+$ (54), 241 (17), 240 (100), 197 (11). 92 (15), 77 (12), 64 (13), 63 (14). HRMS (EI): Calculated for $C_{16}H_{17}O_2N$ $[M]^+$ 255.12538 found 255.12542. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[188]

N-(3-Methoxyphenyl)-1-(4-methoxyphenyl)ethan-1-imine (2b): ^{1}H NMR (250 MHz,



Chloroform-*d*) δ = 7.88 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.34 - 7.17 (m, 1H, CH_{Ar}), 6.88 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 6.56 (ddd, ^{3}J = 8.3 Hz, ^{4}J = 2.3 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 6.48 - 6.33 (m, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 2.22 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 165.1 (C_{Ar}), 161.8 (C_{Ar}), 160.4 (C_{Ar}), 153.1 (C_{Ar}), 130.7 (C_{Ar}), 129.9 (CH_{Ar}), 129.1 ($2CH_{Ar}$), 113.8 ($2CH_{Ar}$), 112.2 (CH_{Ar}), 109.0 (CH_{Ar}), 105.5 (CH_{Ar}), 55.6 (OCH_3), 55.4 (OCH_3), 17.4 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 255 $[M]^+$ (47), 241 (19), 240 (100), 92 (25), 77 (27). HRMS (EI): Calculated for $C_{16}H_{17}O_2N$ $[M]^+$ 255.12538 found 255.12520. ^{1}H-NMR spectral data is in accordance with the literature.[189]

1-(4-Methoxyphenyl)-N-phenylethan-1-imine (2c): ^{1}H NMR (250 MHz,



Chloroform-*d*) δ = 7.95 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.42 - 7.29 (m, 2H, CH_{Ar}), 7.12 - 7.02 (m, 1H, CH_{Ar}), 6.96 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 6.80 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.2 Hz, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 2.21 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 164.7 (C_{Ar}), 161.7 (C_{Ar}), 152.0 (C_{Ar}), 132.3 (C_{Ar}), 129.0 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 123.2 (CH_{Ar}), 119.7 ($2CH_{Ar}$), 113.7 ($2CH_{Ar}$), 55.5 (OCH_3), 17.3 ($CH_{3\text{-imine}}$).

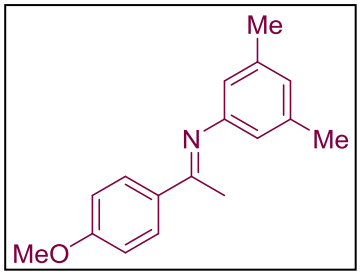
MS (EI, 70 eV): *m/z* (%) = 225 $[M]^+$ (36), 211 (14), 210 (100), 167 (11), 118 (12), 92 (10), 78 (12), 77 (86), 63 (13), 51 (21). HRMS (EI): Calculated for $C_{15}H_{15}NO$ $[M]^+$ 225.11482 found 225.11471. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[190]

1-(4-Methoxyphenyl)-N-(naphthalen-2-yl)ethan-1-imine (2d): Pale yellow crystal, mp. 107 - 108 °C, purified by recrystallization, 61% yield. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.10 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.86 (d, ^3J = 8.9 Hz, 1H, CH_{Ar}), 7.79 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.60 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.53 - 7.35 (m, 3H, CH_{Ar}), 7.02 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.80 (dd, ^3J = 7.2 , ^4J = 1.2 Hz, 1H, CH_{Ar}), 3.90 (s, 3H, OCH_3), 2.18 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 166.0 (C_{Ar}), 162.1 (C_{Ar}), 148.3 (C_{Ar}), 134.5 (C_{Ar}), 132.2 (C_{Ar}), 129.4 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 126.5 (C_{Ar}), 126.4 (CH_{Ar}), 126.2 (CH_{Ar}), 125.7 (CH_{Ar}), 124.0 (CH_{Ar}), 123.4 (CH_{Ar}), 114.1 (CH_{Ar}), 114.0 ($2CH_{Ar}$), 55.8 (OCH_3), 17.8 ($CH_{3\text{-imine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3060 (w), 3012 (w), 2975 (w), 2954 (w), 2840 (w), 2050 (w=, 1962 (w), 1913 (w), 1849 (w), 1821 (w), 1788 (w), 1632 (m), 1596 (m), 1504 (m), 1437 (m), 1360 (m), 1307 (m), 1251 (s), 1173 (m), 1024 (m), 960 (m), 838 (s), 777 (s), 572 (m). MS (EI, 70 eV): *m/z* (%) = 276 (16), 275 $[M]^+$ (80), 261 (20), 260 (100), 217 (20), 127 (64), 77 (15). HRMS (EI): Calculated for $C_{19}H_{17}NO$ $[M]^+$ 275.13047 found 275.13030.

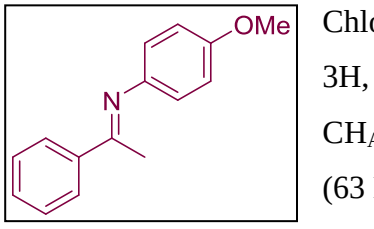
N-(2,3-Dihydro-1H-inden-5-yl)-1-(4-methoxyphenyl)ethan-1-imine (2e): Yellow solid, mp. 61 - 62 °C, purified by Kugelrohr distillation, 54% yield. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.94 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.17 (d, ^3J = 7.9 Hz, 1H, CH_{Ar}), 6.95 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.67 (d, ^4J = 1.2 Hz, 1H, CH_{Ar}), 6.56 (dd, ^3J = 7.8 Hz, ^4J = 2.0 Hz, 1H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 2.90 (t, ^3J = 7.4 Hz, 4H, $CH_{2\text{-aliphatic}}$), 2.22 (s, 3H, $CH_{3\text{-imine}}$), 2.17 - 2.02 (m, 2H, $CH_{2\text{-aliphatic}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 161.6 (C_{Ar}), 145.2 (C_{Ar}), 138.9 (C_{Ar}), 132.5 (C_{Ar}), 130.7 (C_{Ar}), 129.0 ($2CH_{Ar}$), 124.6 (CH_{Ar}), 117.7 (CH_{Ar}), 115.9 (CH_{Ar}), 113.9 (C_{Ar}), 113.7 ($2CH_{Ar}$), 55.5 (OCH_3), 33.2 ($CH_{2\text{-aliphatic}}$), 32.5 ($CH_{2\text{-aliphatic}}$), 25.77 ($CH_{2\text{-aliphatic}}$), 17.3 ($CH_{3\text{-imine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3093 (w), 3015 (w), 2967 (w), 2931 (m), 2841 (m), 2062 (w), 2051 (w), 1983 (w), 1923 (w), 1671 (w), 1628 (m), 1598 (s), 1507 (m), 1483 (m), 1444 (m), 1364 (m), 1304 (m), 1255 (s), 1234 (m), 1173 (s), 1118 (m), 1027 (s), 839 (s), 832 (s), 573 (s). MS (EI, 70 eV): *m/z* (%) = 266 (9), 265 $[M]^+$

(47), 250 (100), 115 (30), 91 (13). HRMS (EI): Calculated for $C_{18}H_{19}ON$ $[M]^+$ 265.14612 found 265.14612.

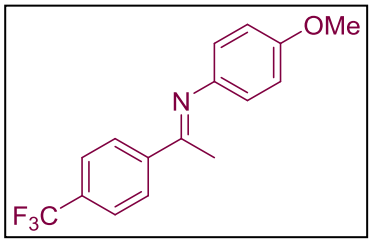
N-(3,5-Dimethylphenyl)-1-(4-methoxyphenyl)ethan-1-imine (2f): Yellow solid, mp. 74 - 75 °C, purified by Kugelrohr distillation, 54% yield. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.92 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.94 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.72 (s, 1H, CH_{Ar}), 6.42 (s, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 2.31 (s, 6H, CH_3), 2.26 - 2.17 (m, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, CDCl3) δ = 164.4 (C_{Ar}), 161.6 (C_{Ar}), 151.9 (C_{Ar}), 138.6 ($2C_{Ar}$), 132.4 (C_{Ar}), 130.7 (C_{Ar}), 128.9 ($2CH_{Ar}$), 124.8 (CH_{Ar}), 117.4 ($2CH_{Ar}$), 113.7 ($2CH_{Ar}$), 55.5 (OCH_3), 21.5 (CH_3), 17.3 ($CH_{3\text{-imine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3005 (w), 2959 (w), 2913 (m), 2838 (w), 2732 (w), 2052 (w), 1910 (w), 1626 (m), 1590 (s), 1509 (m), 1454 (m), 1366 (m), 1308 (m), 1251 (s), 1171 (m), 1028 (s), 829 (s), 689 (m), 571 (s). MS (EI, 70 eV): *m/z* (%) = 254 (10), 253 $[M]^+$ (51), 239 (21), 238 (100), 105 (13), 77 (17). HRMS (EI): Calculated for $C_{17}H_{19}ON$ $[M]^+$ 253.14612 found 253.14642.



N-(4-Methoxyphenyl)-1-phenylethan-1-imine (2g): ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.02 - 7.91 (m, 2H, CH_{Ar}), 7.49 - 7.37 (m, 3H, CH_{Ar}), 6.97 - 6.85 (m, 2H, CH_{Ar}), 6.81 - 6.71 (m, 2H, CH_{Ar}), 3.82 (s, 3H, OCH_3), 2.26 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 166.0 (C_{Ar}), 156.1 (C_{Ar}), 144.9 (C_{Ar}), 139.9 (C_{Ar}), 130.5 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 127.3 ($2CH_{Ar}$), 120.9 ($2CH_{Ar}$), 114.4 ($2CH_{Ar}$), 55.9 (OCH_3), 17.5 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 226 (13), 225 $[M]^+$ (58), 211 (20), 210 (100), 195 (15), 167 (18), 64 (17), 63 (15), 51 (16). HRMS (EI): Calculated for $C_{15}H_{15}NO$ $[M]^+$ 225.11482 found 225.11486. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[191]

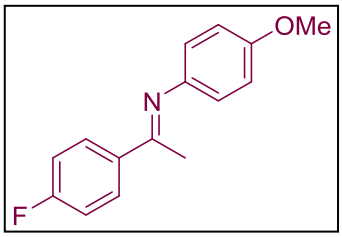


N-(4-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (2h): ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.07 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.69 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 6.93 (dd, ^3J = 9.3 Hz, ^4J = 2.7 Hz, 2H, CH_{Ar}), 6.83 - 6.66 (m, 2H, CH_{Ar}), 3.83 (s, 3H, OCH_3), 2.28 (s, 3H, $CH_{3\text{-imine}}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -62.7 (F_3C). ^{13}C NMR (63 MHz, CDCl3): δ = 164.4 (C_{Ar}), 156.3 (C_{Ar}), 144.1 (C_{Ar}), 142.9 (C_{Ar}), 131.9 (q,

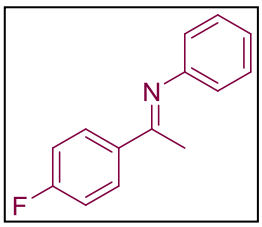


$^{2}J_{CF}$ = 32.4 Hz, C_{Ar}), 127.5 ($2CH_{Ar}$), 125.4 (q, $^{3}J_{CF}$ = 3.8 Hz, $2CH_{Ar}$), 124.1 (q, $^{1}J_{CF}$ = 269.9 Hz, CF_3), 120.7 ($2CH_{Ar}$), 114.3 ($2CH_{Ar}$), 55.5 (OCH_3), 17.4 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 294 (10), 293 $[M]^+$ (56), 279 (16), 278 (100), 148 (12), 92 (15), 77 (21), 64 (12). HRMS (EI): Calculated for $C_{16}H_{14}ONF_3$ $[M]^+$ 293.10220 found 293.10235. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[192]

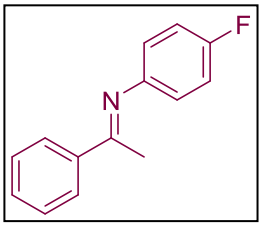
1-(4-Fluorophenyl)-N-(4-methoxyphenyl)ethan-1-imine (2i): ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.01 - 7.92 (m, 2H, CH_{Ar}), 7.17 - 7.05 (m, 2H, CH_{Ar}), 6.96 - 6.86 (m, 2H, CH_{Ar}), 6.79 - 6.69 (m, 2H, CH_{Ar}), 3.82 (s, 3H, OCH_3), 2.24 (s, 3H, $CH_{3\text{-imine}}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.7 (FC_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.5 (C_{Ar}), 164.4 (d, $^{1}J_{CF}$ = 250.4 Hz, C_{Ar}), 156.2 (C_{Ar}), 144.8 (C_{Ar}), 136.1 (d, $^{4}J_{CF}$ = 3.1 Hz, C_{Ar}), 129.3 (d, $^{3}J_{CF}$ = 8.6 Hz, $2CH_{Ar}$), 120.9 ($2CH_{Ar}$), 115.4 (d, $^{2}J_{CF}$ = 21.6 Hz, $2CH_{Ar}$), 114.4 ($2CH_{Ar}$), 55.7 (OCH_3), 17.4 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 243 $[M]^+$ (55), 229 (16), 228 (100), 185 (11), 92 (12), 77 (16). HRMS (EI): Calculated for $C_{15}H_{14}ONF$ $[M]^+$ 243.10539 found 243.10547. ^{1}H- and ^{19}F-NMR spectral data are in accordance with the literature.[193]



1-(4-Fluorophenyl)-N-phenylethan-1-imine (2j): ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.04 - 7.94 (m, 2H, CH_{Ar}), 7.35 (t, ^{3}J = 7.8 Hz, 2H, CH_{Ar}), 7.21 - 7.05 (m, 3H, CH_{Ar}), 6.84 - 6.76 (m, 2H, CH_{Ar}), 2.22 (s, 3H, $CH_{3\text{-imine}}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -105.3 (FC_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.6 (d, $^{1}J_{CF}$ = 252 Hz, CF_{Ar}), 164.5 (C_{Ar}), 152.8 (C_{Ar}), 136.1 (C_{Ar}), 130.2 (d, $^{3}J_{CF}$ = 8.6 Hz, $2CH_{Ar}$), 130.2 ($2CH_{Ar}$), 124.6 (CH_{Ar}), 120.2 ($2CH_{Ar}$), 116.7 (d, $^{2}J_{CF}$ = 21.5 Hz, $2CH_{Ar}$), 17.5 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 213 $[M]^+$ (51), 199 (14), 198 (100), 121 (5), 78 (5), 77 (64), 51 (20). HRMS (EI): Calculated for $C_{14}H_{12}NF$ $[M]^+$ 213.09483 found 213.09477. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[194]

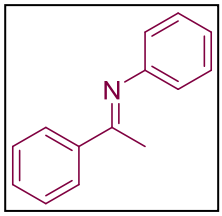


N-(4-Fluorophenyl)-1-phenylethan-1-imine (2k): ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.99 - 7.96 (m, 2H, CH_{Ar}), 7.49 - 7.43 (m, 3H, CH_{Ar}), 7.08 - 7.04 (m, 2H, CH_{Ar}), 6.78 - 6.74 (m, 2H, CH_{Ar}), 2.24 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.5 (C_{Ar}), 159.5 (d, $^{1}J_{CF}$ = 241.1 Hz, CF_{Ar}), 147.8 (d, $^{4}J_{CF}$ = 2.4 Hz, C_{Ar}), 139.5 (C_{Ar}), 130.7 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 127.3 ($2CH_{Ar}$), 120.8 (d, $^{3}J_{CF}$ = 8.2 Hz, $2CH_{Ar}$), 115.7 (d,



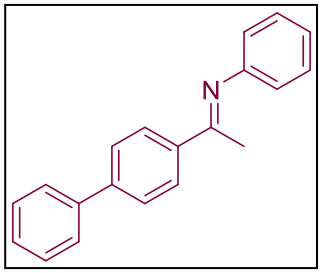
$^{2}J_{CF}$ = 22.0 Hz, 2CH_{Ar}), 17.4 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 213 $[M]^+$ (48), 199 (14), 198 (100), 136 (14), 95 (35), 77 (15), 75 (18). HRMS (EI): Calculated for $C_{14}H_{12}NF$ $[M]^+$ 213.09483 found 213.09496. ^{1}H- and ^{13}C-NMR spectral data is in accordance with the literature.[195]

N,1-Diphenylethan-1-imine (2l): ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.02 - 7.94



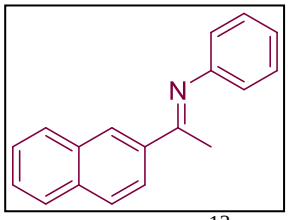
(m, 2H, CH_{Ar}), 7.50 - 7.42 (m, 3H, CH_{Ar}), 7.39 - 7.31 (m, 2H, CH_{Ar}), 7.12 - 7.05 (m, 1H, CH_{Ar}), 6.83 - 6.77 (m, 2H, CH_{Ar}), 2.24 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, Acetone-d^6) δ = 165.5 (C_{Ar}), 152.9 (C_{Ar}), 140.3 (C_{Ar}), 131.1 (CH_{Ar}), 129.7 (2CH_{Ar}), 129.0 (2CH_{Ar}), 128.0 (2CH_{Ar}), 123.8 (CH_{Ar}), 120.0 (2CH_{Ar}), 17.2 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 195 $[M]^+$ (41), 181 (13), 180 (100), 118 (16), 103 (11), 77 (87), 76 (12), 51 (39), 50 (12). HRMS (EI): Calculated for $C_{14}H_{13}N$ $[M]^+$ 195.10425 found 195.10362. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[196]

1-([1,1'-Biphenyl]-4-yl)-N-phenylethan-1-imine (2m): ^{1}H NMR (250 MHz,



Chloroform-*d*): δ = 8.05 (d, ^{3}J = 8.4 Hz, 2H, CH_{Ar}), 7.68 (d, ^{3}J = 8.4 Hz, 2H, CH_{Ar}), 7.65 (d, ^{3}J = 8.0 Hz, 2H, CH_{Ar}), 7.51 - 7.42 (m, 2H, CH_{Ar}), 7.40 - 7.33 (m, 3H, CH_{Ar}), 7.09 (t, ^{3}J = 7.2 Hz, 1H, CH_{Ar}), 6.81 (d, ^{3}J = 7.6 Hz, 2H, CH_{Ar}), 2.26 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 165.2 (C_{Ar}), 151.9 (C_{Ar}), 143.3 (C_{Ar}), 140.6 (C_{Ar}), 138.5 (C_{Ar}), 129.1 (2CH_{Ar}), 129.0 (2CH_{Ar}), 127.9 (CH_{Ar}), 127.8 (2CH_{Ar}), 127.3 (2CH_{Ar}), 127.2 (2CH_{Ar}), 123.4 (CH_{Ar}), 119.6 (2CH_{Ar}), 17.5 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 272 (11), 271 $[M]^+$ (45), 257 (21), 256 (100), 179 (15), 152 (22), 151 (14), 77 (60), 51 (22). HRMS (EI): Calculated for $C_{20}H_{17}N$ $[M]^+$ 271.13555 found 271.13552. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[197]

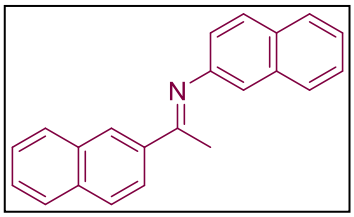
1-(Naphthalen-2-yl)-N-phenylethan-1-imine (2n): ^{1}H NMR (300 MHz,



Chloroform-*d*): δ = 8.35 (s, 1H, CH_{Ar}), 8.23 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 7.96 - 7.85 (m, 3H, CH_{Ar}), 7.59 - 7.48 (m, 2H, CH_{Ar}), 7.38 (dd, ^{3}J = 7.6 Hz, ^{3}J = 7.6 Hz, 2H, CH_{Ar}), 7.12 (t, ^{3}J = 7.6 Hz, 1H, CH_{Ar}), 6.84 (d, ^{3}J = 7.6 Hz, 2H, CH_{Ar}), 2.36 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 165.5 (C_{Ar}), 151.8 (C_{Ar}), 137.0 (C_{Ar}),

134.6 (C_{Ar}), 133.1 (C_{Ar}), 129.1 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 128.2 (CH_{Ar}), 127.8 ($2CH_{Ar}$), 127.3 (CH_{Ar}), 126.5 (CH_{Ar}), 124.4 (CH_{Ar}), 123.5 (CH_{Ar}), 119.6 ($2CH_{Ar}$), 17.5 ($CH_{3\text{-imine}}$). MS (EI, 70 eV): *m/z* (%) = 245 $[M]^+$ (45), 231 (19), 230 (100), 153 (16), 127 (21), 126 (12), 77 (55), 51 (22). HRMS (EI): Calculated for $C_{18}H_{15}N$ $[M]^+$ 245.11990 found 245.12002. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[196]

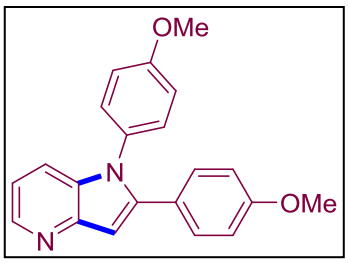
N,1-Di(naphthalen-2-yl)ethan-1-imine (2o): Brown crystal, mp. 136 - 137 °C, purified



by recrystallization, 47% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.47 (s, 1H, CH_{Ar}), 8.41 (dd, ^3J = 8.7 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 8.02 - 7.80 (m, 5H, CH_{Ar}), 7.63 (m, 1H, CH_{Ar}), 7.60 - 7.54 (m, 2H, CH_{Ar}), 7.52 - 7.39 (m, 3H, CH_{Ar}), 6.86 (d, ^3J = 7.2 Hz, 1H, CH_{Ar}), 2.35 (s, 3H, $CH_{3\text{-imine}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.7 (C_{Ar}), 134.8 (C_{Ar}), 134.4 (C_{Ar}), 133.1 (C_{Ar}), 129.7 (C_{Ar}), 129.2 (CH_{Ar}), 128.6 (C_{Ar}), 128.3 (CH_{Ar}), 128.2 (CH_{Ar}), 128.1 (CH_{Ar}), 127.9 (CH_{Ar}), 127.5 (CH_{Ar}), 126.6 (CH_{Ar}), 126.3 (C_{Ar}), 126.2 (CH_{Ar}), 126.1 (CH_{Ar}), 125.6 (CH_{Ar}), 124.5 (CH_{Ar}), 123.8 (CH_{Ar}), 123.6 (CH_{Ar}), 113.8 (CH_{Ar}), 17.9 ($CH_{3\text{-imine}}$). IR (ATR, cm^{-1}): ṽ = 3468 (w), 3397 (w), 3239 (w), 3084 (w), 3050 (m), 3006 (w), 2963 (w), 2852 (w), 2704 (w), 2561 (w), 1938 (w), 1915 (w), 1848 (w), 1690 (w), 1625 (s), 1570 (m), 1504 (m), 1433 (w), 1387 (m), 1366 (m), 1292 (m), 1293 (m), 1223 (m), 1129 (m), 1080 (m), 1014 (m), 858 (m), 802 (m), 777 (s), 747 (m), 868 (m). MS (EI, 70 eV): *m/z* (%) = 296 (17), 295 $[M]^+$ (74), 281 (23), 280 (100), 153 (15), 127 (67), 126 (29). HRMS (EI): Calculated for $C_{22}H_{17}N$ $[M]^+$ 295.13555 found 295.13563.

5.2.1.2.4-Azaindoles

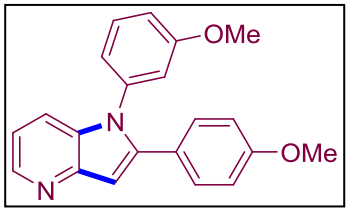
1,2-bis(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*b*]pyridine (3a): Yellow solid,



mp. 188 - 189 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.40 (s, 1H, CH_{Ar}), 7.39 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.16 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.07 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.98 (dd, ^3J = 8.3 Hz, ^3J = 4.5 Hz, 1H, CH_{Ar}), 6.87 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.83 (s, 1H, CH_{Ar}), 6.73 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.75 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.4 (C_{Ar}), 158.8 (C_{Ar}), 146.5 (C_{Ar}), 144.2 (C_{Ar}), 143.8 (C_{Ar}), 132.4 (CH_{Ar}), 130.3 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 124.2 (C_{Ar}), 117.5 (CH_{Ar}), 116.6 (CH_{Ar}), 114.6 ($2CH_{Ar}$), 113.8 (C_{Ar}), 113.8 ($2CH_{Ar}$), 102.9 (CH_{Ar}), 55.5 (OCH_3), 55.2 (OCH_3).

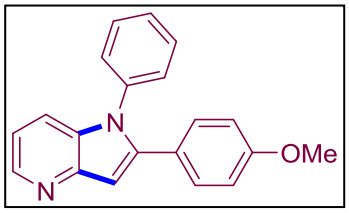
IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3122 (w), 3076 (w), 2918 (m), 2848 (w), 2045 (w), 1923 (w), 1716 (w), 1608 (m), 1510 (s), 1498 (s), 1458 (m), 1414 (s), 1247 (s), 1186 (m), 1104 (m), 1025 (s), 923 (m), 834 (s), 800 (s), 789 (s), 729 (m), 644 (w), 580 (s). MS (EI, 70 eV): *m/z* (%) = 331 (24), 330 $[M]^+$ (100), 315 (28), 243 (17). HRMS (ESI): Calculated for $C_{21}H_{18}N_2O_2$ $[M+H]^+$ 331.14410 found 331.14419.

1-(3-Methoxyphenyl)-2-(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*b*]pyridine (3b): Yellow



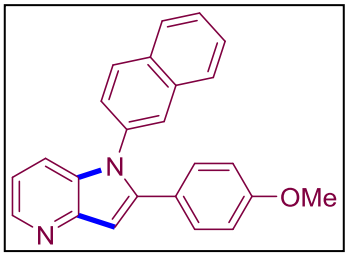
oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.39 (dd, ^3J = 4.7 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.46 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.23 (t, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.16 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 6.97 (dd, ^3J = 8.3 Hz, ^3J = 4.7 Hz, 1H, CH_{Ar}), 6.83 (s, 1H, CH_{Ar}), 6.86 - 6.80 (m, 1H, CH_{Ar}), 6.76 - 6.69 (m, 3H, CH_{Ar}), 6.67 (m, 1H, CH_{Ar}), 3.69 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.4 (C_{Ar}), 159.6 (C_{Ar}), 146.9 (C_{Ar}), 144.3 (CH_{Ar}), 144.0 (C_{Ar}), 138.8 (C_{Ar}), 132.1 (C_{Ar}), 130.4 ($2CH_{Ar}$), 130.2 (CH_{Ar}), 124.3 (C_{Ar}), 120.1 (CH_{Ar}), 117.6 (CH_{Ar}), 116.9 (CH_{Ar}), 113.9 ($2CH_{Ar}$), 113.6 (CH_{Ar}), 113.4 (CH_{Ar}), 103.7 (CH_{Ar}), 55.5 (OCH_3), 55.3 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3036 (w), 2002 (w), 2933 (w), 2834 (w), 2926 (w), 2034 (w), 1891 (w), 1676 (w), 1588 (s), 1491 (s), 1454 (m), 1411 (s), 1281 (m), 1246 (s), 1172 (s), 1027 (s), 833 (m), 778 (s), 725 (m), 694 (m), 552 (m). MS (EI, 70 eV): *m/z* (%) = 331 (25), 330 $[M]^+$ (100), 315 (24), 243 (17). HRMS (EI): Calculated for $C_{21}H_{18}O_2N_2$ $[M]^+$ 330.13628 found 330.13602.

2-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3c): Yellow solid,



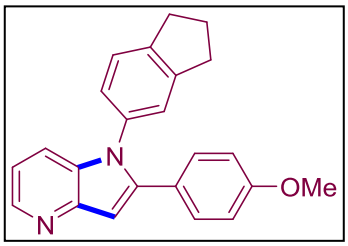
mp. 137 - 138 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.40 (m, 1H, CH_{Ar}), 7.43 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.38 - 7.26 (m, 3H, CH_{Ar}), 7.17 - 7.09 (m, 4H, CH_{Ar}), 6.97 (dd, ^3J = 8.3 Hz, ^3J = 4.6 Hz, 1H, CH_{Ar}), 6.85 (s, 1H, CH_{Ar}), 6.71 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.69 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.6 (C_{Ar}), 146.8 (C_{Ar}), 144.1 (CH_{Ar}) 144.1 (C_{Ar}), 137.8 (C_{Ar}), 132.2 (C_{Ar}), 130.5 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 127.9 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 124.2 (C_{Ar}), 117.6 (CH_{Ar}), 116.9 (CH_{Ar}), 113.9 ($2CH_{Ar}$), 103.6 (CH_{Ar}), 55.3 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3117 (w), 3060 (w), 2960 (w), 2834 (w), 1595 (m), 1500 (s), 1414 (s), 1242 (m), 1179 (m), 1023 (m), 834 (m), 782 (s), 700 (s), 598 (m). MS (EI, 70 eV): *m/z* (%) = 301 (23), 300 $[M]^+$ (100), 285 (39), 255 (27), 128 (10), 77 (10), 51(8). HRMS (EI): Calculated for $C_{20}H_{16}ON_2$ $[M]^+$ 300.12571 found 300.12513

2-(4-Methoxyphenyl)-1-(naphthalen-2-yl)-1*H*-pyrrolo[3,2-*b*]pyridine (3d): Yellow



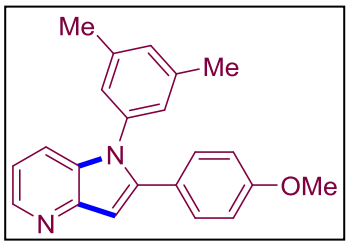
solid, mp. 140 - 141 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.50 (dd, ^{3}J = 4.6 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.94 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.1 Hz, 2H, CH_{Ar}), 7.56 - 7.52 (m, 1H, CH_{Ar}), 7.48 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 7.47 - 7.33 (m, 2H, CH_{Ar}), 7.33 (dd, ^{3}J = 7.3 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.18 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 7.07 (d, ^{3}J = 7.2 Hz, 2H, CH_{Ar}), 6.97 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.5 Hz, 1H, CH_{Ar}), 6.66 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 3.69 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.6 (C_{Ar}), 146.8 (C_{Ar}), 145.5 (C_{Ar}), 144.1 (CH_{Ar}), 134.5 (C_{Ar}), 134.5 (C_{Ar}), 133.4 (C_{Ar}), 131.2 (C_{Ar}), 129.8 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 128.6 (CH_{Ar}), 127.5 (CH_{Ar}), 127.3 (CH_{Ar}), 126.9 (CH_{Ar}), 125.7 (CH_{Ar}), 124.3 (C_{Ar}), 123.2 (CH_{Ar}), 118.2 (CH_{Ar}), 116.9 (CH_{Ar}), 113.9 ($2CH_{Ar}$), 103.1 (CH_{Ar}), 55.3 (OCH_3). IR (ATR, cm^{-1}): ṽ = 3048 (w), 2921 (w), 2850 (w), 1607 (m), 1496 (m), 1417 (m), 1251 (s), 1178 (m), 1024 (m), 842 (m), 806 (s), 797 (s), 773 (s), 590 (m), 539 (m). MS (EI, 70 eV): *m/z* (%) = 351 (22), 350 $[M]^+$ (100), 335 (17), 305 (20), 153 (11). HRMS (ESI): Calculated for $C_{24}H_{18}N_2O$ $[M+H]^+$ 351.14919 found 351.14934

1-(2,3-Dihydro-1*H*-inden-5-yl)-2-(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*b*]pyridine



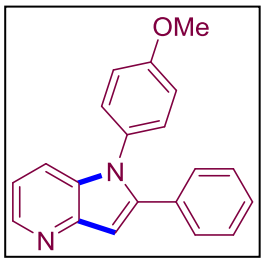
(3e): Yellow solid, mp. 51 - 52 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.39 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.41 (ddd, ^{3}J = 8.3 Hz, ^{4}J = 1.4 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 7.19 (d, ^{4}J = 1.7 Hz, 1H, CH_{Ar}), 7.18 - 7.14 (m, 2H, CH_{Ar}), 7.02 - 6.99 (m, 1H, CH_{Ar}), 6.96 (dd, ^{3}J = 8.3 Hz, ^{4}J = 4.7 Hz, 1H, CH_{Ar}), 6.86 (dd, ^{3}J = 7.9 Hz, ^{4}J = 2.0 Hz, 1H, CH_{Ar}), 6.82 (d, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 6.73 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 3.71 (s, 3H, OCH_3), 2.87 - 2.83 (m, 4H, $CH_{2\text{-aliphatic}}$), 2.13 - 1.99 (m, 2H, $CH_{2\text{-aliphatic}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.5 (C_{Ar}), 146.8 (C_{Ar}), 145.8 (C_{Ar}), 144.2 (C_{Ar}), 144.1 (CH_{Ar}), 144.0 (C_{Ar}), 135.8 (C_{Ar}), 132.5 (C_{Ar}), 130.4 ($2CH_{Ar}$), 125.9 (CH_{Ar}), 125.1 (CH_{Ar}), 124.5 (C_{Ar}), 123.8 (CH_{Ar}), 117.7 (CH_{Ar}), 116.7 (CH_{Ar}), 113.9 ($2CH_{Ar}$), 103.2 (CH_{Ar}), 55.4 (OCH_3), 33.0 ($CH_{2\text{-aliphatic}}$), 32.7 ($CH_{2\text{-aliphatic}}$), 25.7 ($CH_{2\text{-aliphatic}}$). IR (ATR, cm^{-1}): ṽ = 3038 (w), 3005 (w), 2924 (m), 2844 (m), 2197 (w), 2058 (w), 2035 (w), 1889 (w), 1722 (w), 1674 (w), 1068 (m), 1596 (w), 1496 (s), 1412 (s), 1281 (m), 1246 (s), 1174 (s), 1028 (m), 832 (m), 780 (s), 726 (m). MS (EI, 70 eV): *m/z* (%) = 341 (25), 340 $[M]^+$ (100), 325 (18), 156 (12), 115 (6). HRMS (EI): Calculated for $C_{23}H_{20}ON_2$ $[M]^+$ 340.15701 found 340.15685.

1-(3,5-Dimethylphenyl)-2-(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*b*]pyridine (3f):



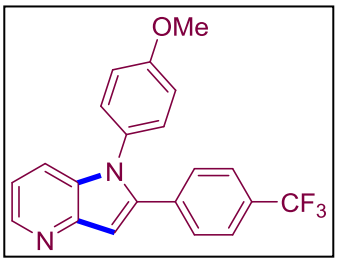
Yellow solid, mp. 143 - 144 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.38 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.41 (dd, ^{3}J = 8.2 Hz, ^{4}J = 2.1 Hz, 1H, CH_{Ar}), 7.17 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 6.96 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.7 Hz, 1H, CH_{Ar}), 6.92 (s, 1H, CH_{Ar}), 6.82 (d, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 6.78 - 6.69 (m, 4H, CH_{Ar}), 3.70 (s, 3H, OCH_3), 2.22 (s, 6H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.5 (C_{Ar}), 146.9 (C_{Ar}), 144.1 (C_{Ar}), 144.0 (CH_{Ar}), 139.3 ($2C_{Ar}$), 137.62 (C_{Ar}), 132.3 (C_{Ar}), 130.4 ($2CH_{Ar}$), 129.5 (CH_{Ar}), 125.6 ($2CH_{Ar}$), 124.5 (C_{Ar}), 117.7 (CH_{Ar}), 116.7 (CH_{Ar}), 113.9 ($2CH_{Ar}$), 103.3 (CH_{Ar}), 55.4 (OCH_3), 21.4 ($2CH_3$). IR (ATR, cm^{-1}): ṽ = 3038 (w), 3008 (w), 2920 (w), 2837 (w), 1610 (m), 1594 (m), 1497 (s), 1413 (s), 1377 (m), 1250 (s), 1177 (m), 1037 (m), 837 (m), 783 (m). MS (EI, 70 eV): *m/z* (%) = 329 (25), 328 $[M]^+$ (100), 313 (21), 269 (13), 157 (12). HRMS (EI): Calculated for $C_{22}H_{20}ON_2$ $[M]^+$ 328.15701 found 328.15685.

1-(4-Methoxyphenyl)-2-phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3g):



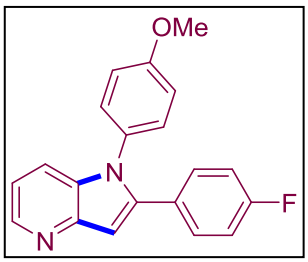
Yellow solid, mp. 146 - 147 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.50 (d, ^{3}J = 4.1 Hz, 1H, CH_{Ar}), 7.50 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 7.35 - 7.25 (m, 5H, CH_{Ar}), 7.14 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.08 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.6 Hz, 1H, CH_{Ar}), 6.99 (s, 1H, CH_{Ar}), 6.94 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 3.84 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.9 (C_{Ar}), 146.3 (C_{Ar}), 144.2 (C_{Ar}), 143.9 (CH_{Ar}), 132.6 (C_{Ar}), 131.7 (C_{Ar}), 130.2 (C_{Ar}), 129.1 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 117.8 (CH_{Ar}), 116.9 (CH_{Ar}), 114.7 ($2CH_{Ar}$), 103.8 (CH_{Ar}), 55.5 (OCH_3). IR (ATR, cm^{-1}): ṽ = 3128 (w), 3012 (w), 2921 (w), 2850 (w), 2044 (w), 1891 (w), 1852 (w), 1597 (m), 1510 (s), 1414 (s), 1245 (s), 1176 (m), 1022 (m), 843 (m), 769 (s), 696 (s), 583 (m). MS (EI, 70 eV): *m/z* (%) = 301 (22), 300 $[M]^+$ (100), 209 (19), 285 (18), 255 (22), 128 (11). HRMS (EI): Calculated for $C_{20}H_{16}ON_2$ $[M]^+$ 300.12571 found 300.12562.

1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[3,2-*b*]pyridine (3h): Yellow solid, mp. 143 - 144 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.52 (dd, ^{3}J = 4.6 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.56 - 7.47 (m, 3H, CH_{Ar}), 7.41 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 7.14 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.10 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.6 Hz, 1H, CH_{Ar}), 7.04 (d, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 6.96 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 3.85 (s, 3H, OCH_3).

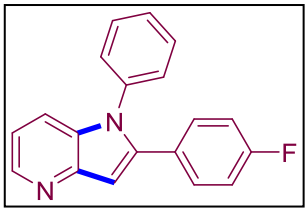


^{19}F NMR (282 MHz, $CDCl_3$) δ = -62.7 (F_3C). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 146.4 (C_{Ar}), 144.7 (CH_{Ar}), 142.2 (C_{Ar}), 135.4 (C_{Ar}), 133.0 (C_{Ar}), 130.0 (C_{Ar}), 129.8 (q, $^2J_{CF}$ = 32.6 Hz, C_{Ar}), 129.2 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 125.4 (q, $^3J_{CF}$ = 3.7 Hz, $2CH_{Ar}$), 124.1 (q, $^1J_{CF}$ = 272.1 Hz, CF_3), 118.0 (CH_{Ar}), 117.7 (CH_{Ar}), 115.0 ($2CH_{Ar}$), 105.2 (CH_{Ar}), 55.6 (OCH_3). IR (ATR, cm^{-1}): ṽ = 3044 (w), 3014 (w), 2959 (w), 2932 (w), 2840 (w), 1726 (w), 1616 (w), 1514 (s), 1416 (m), 1322 (s), 1317 (s), 1245 (m), 1167 (s), 1109 (s), 1061 (m), 856 (m), 804 (s), 758 (m), 623 (m). MS (EI, 70 eV): *m/z* (%) = 369 (23), 368 (100), 367 (19), 255 (11), 182 (11), 128 (11). HRMS (EI): Calculated for $C_{21}H_{15}ON_2F_3$ $[M]^+$ 368.11310 found 368.11256.

2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*b*]pyridine (3i): Yellow solid, mp. 143 - 144 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.42 (dd, ^3J = 4.6 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.40 (ddd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, ^4J = 0.7 Hz, 1H, CH_{Ar}), 7.20 (dd, ^3J = 8.9 Hz, ^3J = 5.3 Hz, 2H, CH_{Ar}), 7.05 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.99 (dd, ^3J = 8.3 Hz, ^3J = 4.6 Hz, 1H, CH_{Ar}), 6.92 (m, 1H, CH_{Ar}), 6.90 - 6.83 (m, 4H, CH_{Ar}), 3.76 (s, 3H, OCH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -113.3 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 162.6 (d, $^1J_{CF}$ = 248.6 Hz, C_{Ar}), 159.1 (C_{Ar}), 146.5 (C_{Ar}), 144.4 (CH_{Ar}), 143.1 (C_{Ar}), 132.6 (C_{Ar}), 131.0 (d, $^3J_{CF}$ = 8.2 Hz, $2CH_{Ar}$), 130.1 (C_{Ar}), 129.0 ($2CH_{Ar}$), 128.1 (d, $^4J_{CF}$ = 3.4 Hz, C_{Ar}), 117.8 (CH_{Ar}), 117.2 (CH_{Ar}), 115.6 (d, $^2J_{CF}$ = 21.7 Hz, $2CH_{Ar}$), 114.8 ($2CH_{Ar}$), 103.9 (CH_{Ar}), 55.6 (OCH_3). IR (ATR, cm^{-1}): ṽ = 3117 (w), 3050 (w=, 3014 (w), 2916 (w), 2835 (w), 1600 (m), 1558 (w), 1515 (s), 1496 (s), 1419 (m), 1359 (m), 1248 (s), 1221 (m), 1158 (m), 1108 (m), 1024 (s), 840 (s), 681 (s), 577 (s). MS (EI, 70 eV): *m/z* (%) = 319 (23), 318 $[M]^+$ (100), 317 (17), 275 (18), 137 (9). HRMS (EI): Calculated for $C_{20}H_{15}ON_2F$ $[M]^+$ 318.11629 found 318.11615.

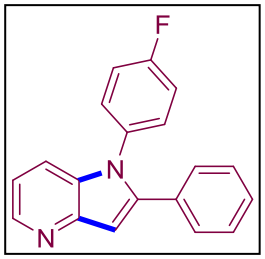


2-(4-Fluorophenyl)-1-phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3j): Yellow solid, mp. 128 - 129 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.44 (s, 1H, CH_{Ar}), 7.48 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.42 - 7.28 (m, 3H, CH_{Ar}), 7.26 - 7.08 (m, 4H, CH_{Ar}), 7.04 (dd, ^3J = 8.3 Hz, ^3J = 4.6 Hz, 1H, CH_{Ar}), 6.95 - 6.82 (m, 3H, CH_{Ar}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.9 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 162.7

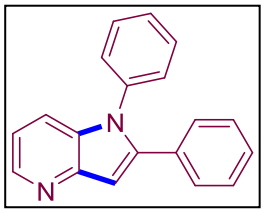


(d, $^{1}J_{CF}$ = 249.0 Hz, CF_{Ar}), 146.1 (C_{Ar}), 143.8 (CH_{Ar}), 143.4 (C_{Ar}), 137.3 (CH_{Ar}), 132.3 (C_{Ar}), 131.0 (d, $^{3}J_{CF}$ = 8.2 Hz, $2CH_{Ar}$), 129.8 ($2CH_{Ar}$), 128.1 (C_{Ar}), 127.9 ($2CH_{Ar}$), 127.8 (d, $^{4}J_{CF}$ = 3.4 Hz, C_{Ar}), 118.3 (CH_{Ar}), 117.3 (CH_{Ar}), 115.6 (d, $^{2}J_{CF}$ = 21.7 Hz, $2CH_{Ar}$), 104.1 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3046 (w), 2920 (w), 2851 (w), 1893 (w), 1596 (m), 1495 (s), 1412 (s), 1359 (m), 1219 (m), 1156 (m), 1013 (m), 835 (s), 798 (s), 782 (s), 696 (s), 594 (s). MS (EI, 70 eV): *m/z* (%) = 289 (20), 288 $[M]^{+}$ (100), 287 (47), 286 (15), 120 (7), 77 (12), 51 (12). HRMS (EI): Calculated for $C_{19}H_{13}FN_2$ $[M]^{+}$ 288.10573 found 288.10600.

1-(4-Fluorophenyl)-2-phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3k): Yellow solid, mp. 120 - 121 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.51 (dd, ^{3}J = 4.6 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.49 (ddd, ^{3}J = 8.3 Hz, ^{4}J = 1.4 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 7.28 -7.23 (m, 5H, CH_{Ar}), 7.22 - 7.17 (m, 2H, CH_{Ar}), 7.15 - 7.07 (m, 3H, CH_{Ar}), 6.99 (s, 1H, CH_{Ar}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -113.2 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 161.8 (d, $^{1}J_{CF}$ = 248.2 Hz, CF_{Ar}), 146.8 (C_{Ar}), 144.6 (CH_{Ar}), 144.1 (C_{Ar}), 133.7 (d, $^{4}J_{CF}$ = 3.0 Hz, C_{Ar}), 133.6 (C_{Ar}), 131.6 (C_{Ar}), 129.5 (d, $^{3}J_{CF}$ = 8.5 Hz, $2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 117.6 (CH_{Ar}), 117.3 (CH_{Ar}), 116.6 (d, $^{2}J_{CF}$ = 22.8 Hz, $2CH_{Ar}$), 104.7 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 2924 (w), 2853 (w), 1888 (w), 1599 (w), 1560 (w), 1507 (s), 1415 (s), 1221 (s), 1153 (m), 965 (m), 850 (m), 763 (s), 693 (s), 581 (s). MS (EI, 70 eV): *m/z* (%) = 289 (21), 288 $[M]^{+}$ (100), 287 (45), 286 (14), 143 (8), 75 (7). HRMS (EI): Calculated for $C_{19}H_{13}NF$ $[M]^{+}$ 288.10573 found 288.10531.

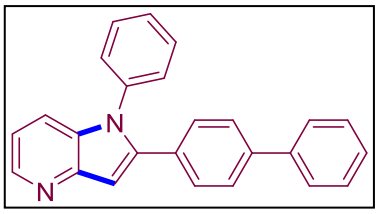


1,2-Diphenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3l): Yellow solid, mp. 117 - 118 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.49 (d, ^{3}J = 4.3 Hz, 1H, CH_{Ar}), 7.54 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 7.46 - 7.34 (m, 3H, CH_{Ar}), 7.28 - 7.25 (m, 4H, CH_{Ar}), 7.24 - 7.20 (m, 2H, CH_{Ar}), 7.20 - 7.17 (m, 1H, CH_{Ar}), 7.07 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.6 Hz, 1H, CH_{Ar}), 6.99 (d, ^{5}J = 0.5 Hz, 1H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 146.7 (C_{Ar}), 144.3 (C_{Ar}), 144.1 (CH_{Ar}), 137.8 (C_{Ar}), 132.4 (C_{Ar}), 131.8 (C_{Ar}), 129.6 ($2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 128.2 (CH_{Ar}), 127.9 ($2CH_{Ar}$), 127.8 (CH_{Ar}), 117.9 (CH_{Ar}), 117.2 (CH_{Ar}), 104.5 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3046 (w), 2920 (w), 2850 (w), 1595 (m), 1558 (w), 1598 (m), 1454 (w), 1412 (s), 1382 (m), 1327 (m), 1290 (m), 1178 (m), 1113 (m), 963 (m), 769 (s), 690 (s), 604 (s). MS (EI, 70 eV): *m/z* (%) = 271 (21), 270 $[M]^{+}$ (100), 269

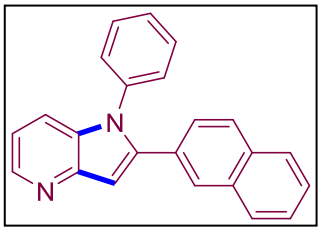


(52), 268 (18), 77 (12), 51 (14). HRMS (ESI): Calculated for $C_{19}H_{14}N_2$ $[M+H]^+$ 271.12297 found 271.12302. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[169j]

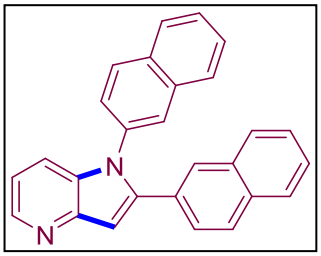
2-([1,1'-Biphenyl]-4-yl)-1-phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3m): Yellow solid, mp. 169 - 170 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.45 (d, ^3J = 4.5 Hz, 1H, CH_{Ar}), 7.55 - 7.25 (m, 13H, CH_{Ar}), 7.24 - 7.15 (m, 2H, CH_{Ar}), 7.07 - 6.97 (m, 2H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 146.7 (C_{Ar}), 144.4 (C_{Ar}), 143.7 (CH_{Ar}), 140.8 (C_{Ar}), 140.3 (C_{Ar}), 137.7 (C_{Ar}), 132.5 (C_{Ar}), 130.7 (C_{Ar}), 129.7 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 127.9 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.7 (CH_{Ar}), 127.1 ($2CH_{Ar}$), 127.1 ($2CH_{Ar}$), 117.8 (CH_{Ar}), 117.2 (CH_{Ar}), 104.6 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3113 (w), 3061 (w), 2921 (w), 2851 (w), 1920 (w), 1681 (w), 1596 (m), 1494 (m), 1411 (s), 1353 (m), 844 (m), 805 (m), 785 (m), 769 (s), 698 (s), 605 (m). MS (EI, 70 eV): *m/z* (%) = 346 $[M]^+$ (100), 347 (27), 345 (32), 269 (8), 77 (11), 51 (7). HRMS (EI): Calculated for $C_{25}H_{18}N_2$ $[M]^+$ 346.14645 found 346.14578.



2-(Naphthalen-2-yl)-1-phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3n): Brownish solid, mp. 130 - 131 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.46 (s, 1H, CH_{Ar}), 7.80 - 7.57 (m, 4H, CH_{Ar}), 7.51 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.44 - 7.13 (m, 8H, CH_{Ar}), 7.11 - 6.97 (m, 2H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 146.6 (C_{Ar}), 144.2 (CH_{Ar}), 144.1 (C_{Ar}), 137.7 (C_{Ar}), 133.2 (C_{Ar}), 132.8 (C_{Ar}), 129.7 ($2CH_{Ar}$), 129.7 (C_{Ar}), 129.2 (C_{Ar}), 128.6 (CH_{Ar}), 128.4 (CH_{Ar}), 128.0 (CH_{Ar}), 127.9 ($2CH_{Ar}$), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.6 (CH_{Ar}), 118.0 (CH_{Ar}), 117.3 (CH_{Ar}), 104.8 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053 (w), 2923 (w), 2851 (w), 1592 (m), 1497 (s), 1414 (s), 1288 (m), 865 (m), 827 (m), 781 (s), 759 (m), 693 (s). MS (EI, 70 eV): *m/z* (%) = 321 (26), 320 $[M]^+$ (100), 319 (49), 318 (16), 159 (7). HRMS (ESI): Calculated for $C_{23}H_{16}N_2$ $[M+H]^+$ 320.13080 found 320.13045.



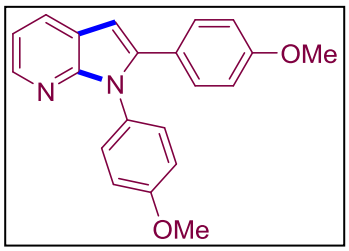
1,2-Di(naphthalen-2-yl)-1*H*-pyrrolo[3,2-*b*]pyridine (3o): yellow solid, mp. 157 - 158 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.46 (dd, ^3J = 4.6 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.85 (dd, ^3J = 8.3 Hz, ^3J = 3.4 Hz, 1H, CH_{Ar}), 7.69 (d, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.63 - 7.55 (m, 1H, CH_{Ar}), 7.52 - 7.26 (m, 10H, CH_{Ar}), 7.23 (dd, ^3J = 8.6 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.18 - 7.15 (m, 1H, CH_{Ar}), 7.04 (ddd, ^3J = 8.3 Hz,



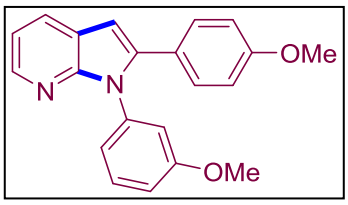
^{4}J = 1.4 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 6.92 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.6 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.7 (C_{Ar}), 145.3 (C_{Ar}), 144.4 (C_{Ar}), 134.4 (CH_{Ar}), 134.3 (C_{Ar}), 133.6 (C_{Ar}), 133.0 (C_{Ar}), 132.7 (C_{Ar}), 131.1 (C_{Ar}), 129.2 (C_{Ar}), 129.1 (CH_{Ar}), 128.5 (CH_{Ar}), 128.2 (CH_{Ar}), 127.9 (CH_{Ar}), 127.8 (CH_{Ar}), 127.5 (CH_{Ar}), 127.5 (CH_{Ar}), 127.2 (CH_{Ar}), 126.8 (CH_{Ar}), 126.4 (CH_{Ar}), 126.3 (CH_{Ar}), 125.9 (CH_{Ar}), 125.5 (CH_{Ar}), 123.1 (CH_{Ar}), 118.2 (CH_{Ar}), 117.2 (CH_{Ar}), 104.4 (CH_{Ar}). IR (ATR, cm^{-1}): ṽ = 3050 (w), 2923 (w), 2850 (w), 1595 (m), 1505 (m), 1465 (m), 1415 (m), 1399 (m), 1284 (m), 1016 (m), 863 (m), 798 (m), 770 (s), 755 (m), 663 (m), 589 (m). MS (EI, 70 eV): *m/z* (%) = 371 (31), 370 $[M]^+$ (100), 369 (36), 368 (13), 367 (15), 184 (13). HRMS (EI): Calculated for $C_{27}H_{18}N_2$ $[M]^+$ 370.14645 found 370.14572.

5.2.1.3.7-Azaindoles

1,2-Bis(4-Methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (4a): White solid, mp. 145 - 146 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.22 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.85 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.22 - 7.09 (m, 4H, CH_{Ar}), 7.02 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.8 Hz, 1H, CH_{Ar}), 6.92 - 6.82 (m, 2H, CH_{Ar}), 6.78 - 6.69 (m, 2H, CH_{Ar}), 6.56 (s, 1H, CH_{Ar}), 3.75 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 158.6 (C_{Ar}), 150.0 (C_{Ar}), 143.2 (CH_{Ar}), 141.2 (C_{Ar}), 130.2 ($2CH_{Ar}$), 129.9 (C_{Ar}), 129.5 ($2CH_{Ar}$), 128.0 (CH_{Ar}), 124.6 (C_{Ar}), 120.9 (C_{Ar}), 116.8 (CH_{Ar}), 114.4 ($2CH_{Ar}$), 113.8 ($2CH_{Ar}$), 99.9 ($CH_{pyrrole}$), 55.4 (OCH_3), 55.2 (OCH_3). IR (ATR, cm^{-1}): ṽ = 3114 (w), 3049 (w), 3018 (w), 2929 (w), 2835 (w), 2037 (w), 1905 (w), 1833 (w), 1610 (m), 1567 (w), 1515 (s), 1500 (s), 1454 (m), 1371 (m), 1301 (m), 1242 (s), 1184 (m), 1024 (m), 833 (s), 798 (s), 766 (s), 584 (m). MS (EI, 70 eV): *m/z* (%) = 331 (18), 330 $[M]^+$ (83), 329 (100), 286 (11), 243 (17), 121 (7). HRMS (ESI): Calculated for $C_{21}H_{18}N_2O_2$ $[M+H]^+$ 331.14410 found 331.14454.

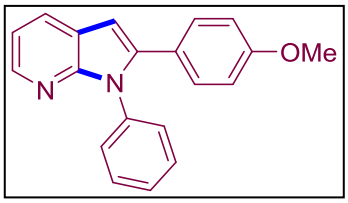


1-(3-Methoxyphenyl)-2-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (4b): Yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.30 - 8.04 (m, 1H, CH_{Ar}), 7.83 (t, ^{3}J = 8.0 Hz, 1H, CH_{Ar}), 7.32 - 7.06 (m, 3H, CH_{Ar}), 7.06 - 6.93 (m, 1H, CH_{Ar}), 6.92 - 6.62 (m, 5H, CH_{Ar}), 6.55 (d, ^{3}J = 9.6 Hz, 1H, CH_{Ar}), 3.69 (s, OCH_3), 3.63 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.1 (C_{Ar}), 159.5 (C_{Ar}), 150.0 (C_{Ar}), 143.4



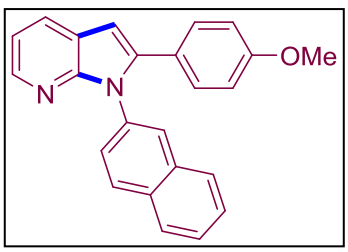
(CH_{Ar}), 141.2 (C_{Ar}), 138.3 (C_{Ar}), 130.2 ($2CH_{Ar}$), 129.8 (CH_{Ar}), 128.1 (CH_{Ar}), 124.8 (C_{Ar}), 121.1 (CH_{Ar}), 121.0 (C_{Ar}), 117.1 (CH_{Ar}), 114.3 (CH_{Ar}), 113.9 ($2CH_{Ar}$), 113.5 (CH_{Ar}), 100.6 (CH_{Ar}), 55.5 (OCH_3), 55.4 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3041 (w), 3001 (w), 2933 (w), 2834 (w), 2222 (w), 2032 (w), 1920 (w), 1731 (w), 1604 (m), 1588 (m), 1498 (s), 1455 (m), 1406 (s), 1368 (m), 1283 (m), 1247 (s), 1173 (m), 1028 (m), 833 (m), 802 (m), 767 (m), 692 (m), 612 (m). MS (EI, 70 eV): *m/z* (%) = 331 (20), 330 $[M]^+$ (98), 329 (100), 243 (16), 121 (13). HRMS (EI): Calculated for $C_{21}H_{18}O_2N_2$ $[M]^+$ 330.13628 found 330.13539.

2-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4c): Yellow solid,



mp. 138 - 139 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.21 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.83 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.37 - 7.28 (m, 2H, CH_{Ar}), 7.28 - 7.19 (m, 3H, CH_{Ar}), 7.11 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.02 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Ar}), 6.70 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 6.56 (s, 1H, $CH_{pyrrole}$), 3.68 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 149.9 (C_{Ar}), 143.3 (CH_{Ar}), 141.1 (CH_{Ar}), 137.2 (C_{Ar}), 130.2 ($2CH_{Ar}$), 129.1 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 127.3 (CH_{Ar}), 124.6 (C_{Ar}), 121.0 (C_{Ar}), 117.0 (CH_{Ar}), 113.8 ($2CH_{Ar}$), 100.5 ($CH_{pyrrole}$), 55.2 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3044 (w), 3008 (w), 2953 (m), 2833 (m), 1674 (w), 1608 (m), 1500 (s), 1408 (s), 1368 (m), 1242 (s), 1182 (m), 1024 (s), 836 (m), 799 (s), 766 (s), 696 (s), 597 (s). MS (EI, 70 eV): *m/z* (%) = 301 (18), 300 $[M]^+$ (91), 299 (100), 285 (8), 255 (31), 128 (18), 51 (9). HRMS (EI): Calculated for $C_{20}H_{16}ON_2$ $[M]^+$ 300.12571 found 300.12482.

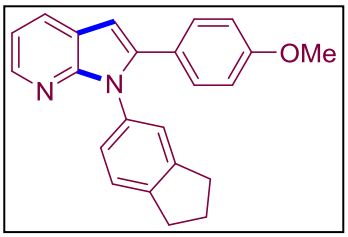
2-(4-Methoxyphenyl)-1-(naphthalen-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (4d): Yellow



solid, mp. 123 - 124 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.13 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.91 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.87 - 7.77 (m, 2H, CH_{Ar}), 7.48 - 7.30 (m, 3H, CH_{Ar}), 7.29 - 7.18 (m, 2H, CH_{Ar}), 7.05 (d, ^3J = 8.8 Hz, 1H, CH_{Ar}), 7.04 - 6.97 (m, 1H, CH_{Ar}), 6.69 (s, 1H, $CH_{pyrrole}$), 6.55 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.58 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 150.9 (C_{Ar}), 143.4 (C_{Ar}), 142.5 (C_{Ar}), 134.4 (CH_{Ar}), 134.2 (C_{Ar}), 131.7 (C_{Ar}), 129.5 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 128.3 (CH_{Ar}), 128.1 (CH_{Ar}), 127.6 (CH_{Ar}), 127.0 (CH_{Ar}), 126.4 (CH_{Ar}), 125.5 (CH_{Ar}), 124.6

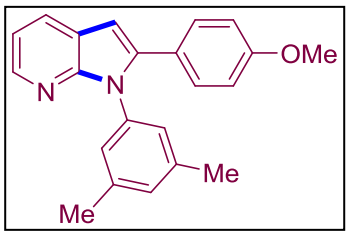
(C_{Ar}), 123.5 (CH_{Ar}), 120.9 (C_{Ar}), 116.9 (CH_{Ar}), 113.7 ($2CH_{Ar}$), 100.0 ($CH_{pyrrole}$), 55.1 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3604 (w), 3388 (w), 3044 (w), 2961 (w), 2835 (w), 1609 (m), 1497 (s), 1469 (m), 1425 (m), 1298 (m), 1245 (s), 1176 (m), 1024 (m), 833 (m), 798 (s), 761 (s). MS (EI, 70 eV): *m/z* (%) = 351 (23), 350 $[M]^+$ (100), 349 (87), 305 (29), 243 (25), 153 (13). HRMS (EI): Calculated for $C_{24}H_{18}N_2O$ $[M+H]^+$ 351.14919 found 351.14934.

1-(2,3-Dihydro-1*H*-inden-5-yl)-2-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine



(4e): Yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.21 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, CH_{Ar}), 7.83 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Ar}), 7.19 - 7.12 (m, 3H, CH_{Ar}), 7.11 (s, 1H, CH_{Ar}), 7.00 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Ar}), 6.94 (dd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, 1H, CH_{Ar}), 6.73 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 6.55 (s, 1H, $CH_{pyrrole}$), 3.70 (s, 1H, OCH_3), 2.84 (t, ^3J = 7.0 Hz, 4H, $CH_{2\text{-aliphatic}}$), 2.09 - 1.93 (m, 2H, $CH_{2\text{-aliphatic}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 150.3 (C_{Ar}), 145.3 (C_{Ar}), 143.8 (C_{Ar}), 143.3 (CH_{Ar}), 141.4 (C_{Ar}), 135.3 (C_{Ar}), 130.3 ($2CH_{Ar}$), 128.0 (CH_{Ar}), 126.5 (CH_{Ar}), 125.0 (C_{Ar}), 124.8 (CH_{Ar}), 124.6 (CH_{Ar}), 121.0 (C_{Ar}), 116.8 (CH_{Ar}), 113.9 ($2CH_{Ar}$), 100.0 ($CH_{pyrrole}$), 55.4 (OCH_3), 33.1 ($CH_{2\text{-aliphatic}}$), 32.8 ($CH_{2\text{-aliphatic}}$), 25.7 ($CH_{2\text{-aliphatic}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3042 (w), 2944 (m), 2839 (w), 1675 (w), 1609 (m), 1499 (s), 1407 (m), 1248 (s), 1176 (m), 1030 (m), 834 (m), 803 (m), 769 (m). MS (EI, 70 eV): *m/z* (%) = 341 (17), 340 (79), 339 $[M]^+$ (100), 296 (10), 115 (12). HRMS (EI): Calculated for $C_{23}H_{19}ON_2$ $[M]^+$ 339.14919 found 339.14923.

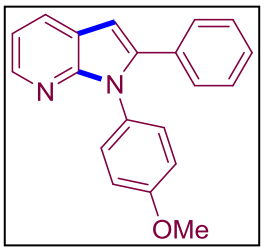
1-(3,5-Dimethylphenyl)-2-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (4f):



Yellow solid, mp. 95 - 96 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.21 (dd, ^3J = 4.8 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.83 (dd, ^3J = 7.8 Hz, ^3J = 1.5 Hz, 1H, CH_{Ar}), 7.15 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.01 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Ar}), 6.90 (s, 1H, CH_{Ar}), 6.85 (s, 2H, CH_{Ar}), 6.72 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 6.55 (s, 1H, $CH_{pyrrole}$), 3.71 (s, 3H, OCH_3), 2.22 (s, 6H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 150.2 (C_{Ar}), 143.3 (CH_{Ar}), 141.3 (C_{Ar}), 138.7 ($2C_{Ar}$), 137.1 (C_{Ar}), 130.2 ($2CH_{Ar}$), 129.6 (CH_{Ar}), 128.0 (CH_{Ar}), 126.5 ($2CH_{Ar}$), 124.9 (C_{Ar}), 121.0 (C_{Ar}), 116.8 (CH_{Ar}), 113.8 ($2CH_{Ar}$), 100.1 ($CH_{pyrrole}$), 55.3 (OCH_3), 21.5 ($2CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3040 (w), 3006 (w), 2917 (w), 2836

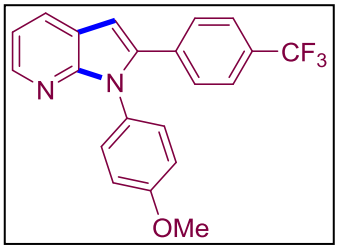
(w), 1609 (m), 1546 (w), 1498 (s), 1473 (m), 1405 (s), 1369 (m), 1247 (s), 1175 (m), 1026 (m), 836 (m), 801 (m), 767 (m), 696 (m). MS (EI, 70 eV): *m/z* (%) = 329 (21), 328 $[M]^+$ (99), 327 (100), 313 (12), 312 (14), 269 (17), 157 (12), 135 (10). HRMS (ESI): Calculated for $C_{22}H_{19}ON_2$ $[M-H]^+$ 327.14919 found 327.14906.

1-(4-Methoxyphenyl)-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4g): Yellow solid,



mp. 188 - 189 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.24 (dd, ^3J = 4.7 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.87 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.28 - 7.11 (m, 7H, CH_{Ar}), 7.03 (dd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, 1H, CH_{Ar}), 6.85 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.63 (s, 1H, $CH_{pyrrole}$), 3.74 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.7 (C_{Ar}), 150.1 (C_{Ar}), 143.5 (CH_{Ar}), 141.2 (C_{Ar}), 132.2 (C_{Ar}), 129.8 (C_{Ar}), 129.4 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 128.3 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 120.8 (C_{Ar}), 116.9 (CH_{Ar}), 114.4 ($2CH_{Ar}$), 100.9 ($CH_{pyrrole}$), 55.4 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3067 (w), 3043 (w), 3010 (w), 2840 (w), 1901 (w), 1856 (w), 1604 (w), 1510 (m), 1419 (m), 1236 (s), 1025 (s), 842 (m), 806 (m), 752 (s), 693 (s), 556 (s). MS (EI, 70 eV): *m/z* (%) = 301 (13), 300 $[M]^+$ (68), 299 (100), 256 (27), 255 (20), 128 (9). HRMS (ESI): Calculated for $C_{20}H_{15}ON_2$ $[M-H]^+$ 299.11789 found 299.11775.

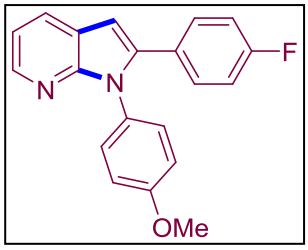
1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[2,3-*b*]pyridine



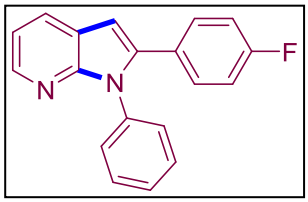
(4h): Yellow solid, mp. 158 - 159 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.27 (dd, ^3J = 4.7 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.89 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.45 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 7.33 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.15 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.05 (dd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, 1H, CH_{Ar}), 6.88 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.70 (s, 1H, $CH_{pyrrole}$), 3.75 (s, 3H, OCH_3). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -62.6 (F_3C).^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.0 (C_{Ar}), 150.5 (C_{Ar}), 144.5 (CH_{Ar}), 139.5 (C_{Ar}), 135.8 (C_{Ar}), 129.7 (q, $^2J_{CF}$ = 32.6 Hz, C_{Ar}), 129.6 (C_{Ar}), 129.5 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 128.9 (CH_{Ar}), 125.4 (q, $^3J_{CF}$ = 3.8 Hz, $2CH_{Ar}$), 124.2 (q, $^1J_{CF}$ = 272.1 Hz, CF_3), 120.6 (C_{Ar}), 117.3 (CH_{Ar}), 114.7 ($2CH_{Ar}$), 102.3 ($CH_{pyrrole}$), 55.6 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3020 (w), 2971 (w), 2843 (w), 2549 (w), 2315 (w), 2051 (w), 1934 (w), 1869 (w), 1613 (m), 1567 (w), 1515 (s), 1468 (m), 1442 (m), 1323 (s), 1300 (m), 1250 (s), 1162 (s), 1115 (s), 1028 (m), 918 (m), 844 (s), 800 (s), 764 (s), 591 (m), 561 (m). MS (EI, 70 eV): *m/z* (%) = 369 (13),

368 $[M]^+$ (69), 367 (100), 324 (22), 323 (10), 255 (7). HRMS (ESI): Calculated for $C_{21}H_{14}ON_2F_3$ $[M-H]^+$ 367.10527 found 367.10514.

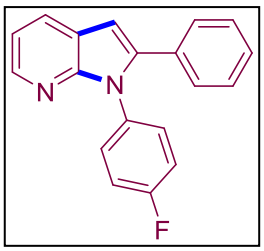
2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (4i): Yellow solid, mp. 173 - 174 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.24 (dd, ^3J = 4.7 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.86 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.23 - 7.10 (m, 4H, CH_{Ar}), 7.04 (dd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, 1H, CH_{Ar}), 6.94 - 6.83 (m, 4H, CH_{Ar}), 6.59 (s, 1H, $CH_{pyrrole}$), 3.75 (s, 3H, OCH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -113.6 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 162.5 (d, $^1J_{CF}$ = 248.2 Hz, C_{Ar}), 158.9 (C_{Ar}), 150.2 (C_{Ar}), 143.9 (CH_{Ar}), 140.3 (C_{Ar}), 130.8 (d, $^3J_{CF}$ = 8.1 Hz, $2CH_{Ar}$), 129.8 (C_{Ar}), 129.6 ($2CH_{Ar}$), 128.5 (C_{Ar}), 128.4 (CH_{Ar}), 120.8 (C_{Ar}), 117.1 (CH_{Ar}), 115.5 (d, $^2J_{CF}$ = 21.7 Hz, $2CH_{Ar}$), 114.6 ($2CH_{Ar}$), 100.9 ($CH_{pyrrole}$), 55.6 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3103 (w), 3014 (w), 2969 (w), 2841 (w), 2050 (w), 1893 (w), 1602 (w), 1511 (s), 1496 (s), 1297 (m), 1245 (s), 1152 (m), 1106 (m), 1029 (m), 834 (s), 813 (s), 773 (s), 581 (s). MS (EI, 70 eV): *m/z* (%) = 319 (12), 318 $[M]^+$ (67), 317 (100), 274 (29), 273 (21), 137 (7), 63 (8). HRMS (ESI): Calculated for $C_{20}H_{14}ON_2F$ $[M-H]^+$ 317.10847 found 317.10836.



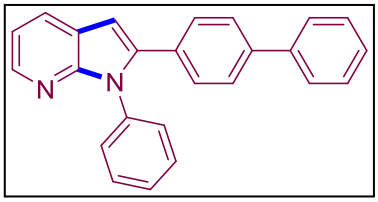
2-(4-Fluorophenyl)-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4j): White solid, mp. 141 - 142 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.34 (d, ^3J = 4.7 Hz, 1H, CH_{Ar}), 7.90 (d, ^3J = 7.8 Hz, 1H, CH_{Ar}), 7.35 (d, ^3J = 7.7 Hz, 2H, CH_{Ar}), 7.29 (d, ^3J = 7.1 Hz, 1H, CH_{Ar}), 7.23 (d, ^3J = 7.1 Hz, 2H, CH_{Ar}), 7.17 (dd, ^3J = 7.1 Hz, ^3J = 5.3 Hz, 2H, CH_{Ar}), 7.15 (dd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, 1H, CH_{Ar}), 6.89 (t, ^3J = 8.7 Hz, 2H, CH_{Ar}), 6.70 (s, 1H, $CH_{pyrrole}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -113.4 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 162.6 (d, $^1J_{CF}$ = 248.4 Hz, CF_{Ar}), 149.8 (C_{Ar}), 143.8 (CH_{Ar}), 140.3 (C_{Ar}), 136.9 (C_{Ar}), 130.8 (d, $^3J_{CF}$ = 8.2 Hz, $2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 128.4 (d, $^4J_{CF}$ = 3.4 Hz, C_{Ar}), 127.7 (CH_{Ar}), 121.0 (C_{Ar}), 117.3 (CH_{Ar}), 115.5 (d, $^2J_{CF}$ = 21.7 Hz, $2CH_{Ar}$), 101.5 ($CH_{pyrrole}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3064 (w), 3043 (w), 2921 (w), 1589 (m), 1543 (m), 1496 (s), 1424 (m), 1402 (m), 1220 (s), 1157 (m), 840 (s), 802 (s), 768 (s), 691 (s), 592 (s), 539 (m). MS (EI, 70 eV): *m/z* (%) = 289 (10), 288 $[M]^+$ (62), 287 (100), 286 (21), 143 (6), 51 (7). HRMS (ESI): Calculated for $C_{19}H_{13}FN_2$ $[M+H]^+$ 289.11355 found 289.11359.



1-(4-Fluorophenyl)-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4k): Yellow solid, mp. 164 - 165 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.31 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 7.95 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 7.35 - 7.20 (m, 7H, CH_{Ar}), 7.16 - 7.04 (m, 3H, CH_{Ar}), 6.64 (s, 1H, $CH_{pyrrole}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.4 (FC_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.7 (d, $^{1}J_{CF}$ = 247.1 Hz, CF_{Ar}), 150.1 (C_{Ar}), 143.8 (CH_{Ar}), 141.2 (C_{Ar}), 133.1 (d, $^{4}J_{CF}$ = 3.2 Hz, C_{Ar}), 132.0 (C_{Ar}), 130.1 (d, $^{3}J_{CF}$ = 8.6 Hz, $2CH_{Ar}$), 129.1 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 121.0 (C_{Ar}), 117.3 (CH_{Ar}), 116.1 (d, $^{2}J_{CF}$ = 22.8 Hz, $2CH_{Ar}$), 101.6 ($CH_{pyrrole}$). IR (ATR, cm^{-1}): ṽ = 3110 (w), 3059 (w), 3008 (w), 2924 (w), 1907 (w), 1858 (w), 1675 (w), 1568 (w), 1508 (m), 1420 (m), 1208 (m), 1096 (w), 852 (m), 804 (s), 747 (s). 698 (s), 552 (m). MS (EI, 70 eV): *m/z* (%) = 289 (10), 288 $[M]^+$ (60), 287 (100), 286 (21), 75 (11). HRMS (ESI): Calculated for $C_{19}H_{12}FN_2$ $[M-H]^+$ 287.09790 found 287.09747.



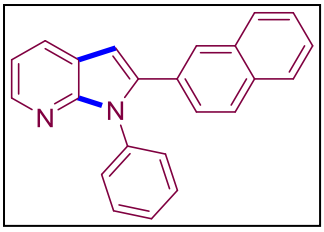
1,2-Diphenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4l): White solid, mp. 130 - 132 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.33 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 7.97 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 7.48 - 7.26 (m, 10H, CH_{Ar}), 7.14 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.7 Hz, 1H, CH_{Ar}), 6.74 (s, 1H, $CH_{pyrrole}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 150.1 (C_{Ar}), 143.8 (CH_{Ar}), 141.3 (C_{Ar}), 137.2 (C_{Ar}), 132.3 (C_{Ar}), 129.2 ($2CH_{Ar}$), 129.1 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.5 (CH_{Ar}), 121.0 (C_{Ar}), 117.2 (CH_{Ar}), 101.6 ($CH_{pyrrole}$). IR (ATR, cm^{-1}): ṽ = 3116 (w), 3064 (w), 2925 (w), 1852 (w), 1594 (m), 1540 (m), 1496 (s), 1474 (m), 1425 (m), 1401 (m), 1370 (m), 1224 (s), 1158 (m), 841 (m), 799 (s), 767 (s), 692 (s), 593 (s). MS (EI, 70 eV): *m/z* (%) = 271 (11),270 $[M]^+$ (59), 269 (100), 268 (21), 135 (8). HRMS (ESI): Calculated for $C_{19}H_{14}N_2$ $[M+H]^+$ 271.12297 found 271.12322. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[198]



2-([1,1'-Biphenyl]-4-yl)-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4m): White solid, mp. 182 - 183 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.36 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.99 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.48 (d, ^{3}J = 7.0 Hz, 2H, CH_{Ar}), 7.42 (d, ^{3}J = 8.3 Hz, 2H, CH_{Ar}), 7.39 - 7.31 (m, 4H, CH_{Ar}), 7.28 (m, 4H, CH_{Ar}), 7.26 - 7.21 (m, 2H, CH_{Ar}), 7.15 (dd,

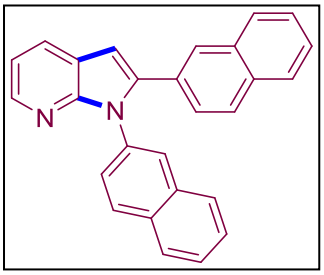
^{3}J = 7.8 Hz, ^{3}J = 4.7 Hz, 1H, CH_{Ar}), 6.80 (s, 1H, $CH_{pyrrole}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 150.2 (C_{Ar}), 143.8 (CH_{Ar}), 140.9 (C_{Ar}), 140.5 (C_{Ar}), 140.4 (C_{Ar}), 137.2 (C_{Ar}), 131.1 (C_{Ar}), 129.3 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 128.6 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 ($2CH_{Ar}$), 127.1 ($2CH_{Ar}$), 127.0 (CH_{Ar}), 121.0 (C_{Ar}), 117.2 (CH_{Ar}), 101.6 ($CH_{pyrrole}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3110 (w), 3050 (w), 3034 (w), 3001 (w), 1591 (w), 1500 (m), 1421 (m), 1293 (w), 1247 (w), 997 (w), 842 (m), 807 (m), 760 (s), 694 (s), 610 (w). MS (EI, 70 eV): *m/z* (%) = 347 (19), 346 $[M]^+$ (84), 345 (100), 268 (8), 173 (6), 77 (9). HRMS (ESI): Calculated for $C_{25}H_{18}N_2$ $[M+H]^+$ 347.15419 found 347.15428.

2-(Naphthalen-2-yl)-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4n): Yellow solid, mp. 180 - 181 °C.



^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.37 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 8.01 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.83 (d, ^{4}J = 1.1 Hz, 1H, $CH_{naphthalene}$), 7.81 - 7.77 (m, 1H, CH_{Ar}), 7.71 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.54 - 7.43 (m, 2H, CH_{Ar}), 7.43 - 7.30 (m, 6H, CH_{Ar}), 7.17 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.7 Hz, 1H, CH_{Ar}), 6.87 (s, 1H, $CH_{pyrrole}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 150.1 (C_{Ar}), 143.8 (CH_{Ar}), 141.2 (C_{Ar}), 137.2 (C_{Ar}), 133.3 (C_{Ar}), 132.8 (C_{Ar}), 129.7 (C_{Ar}), 129.3 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 128.3 (CH_{Ar}), 127.9 (CH_{Ar}), 127.8 (CH_{Ar}), 127.5 (CH_{Ar}), 126.6 (CH_{Ar}), 126.6 (CH_{Ar}), 126.5 (CH_{Ar}), 121.1 (C_{Ar}), 117.3 (CH_{Ar}), 102.0 ($CH_{pyrrole}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053 (w), 2923 (w), 2851 (w), 1957 (w), 1930 (w), 1879 (w), 1865 (w), 1674 (w), 1592 (m), 1499 (m), 1416 (s), 1293 (m), 827 (m), 802 (s), 772 (s), 755 (s), 596 (s), 578 (m). MS (EI, 70 eV): *m/z* (%) = 321 (15),320 $[M]^+$ (68), 319 (100), 318 (22), 317 (10), 159 (13). HRMS (ESI): Calculated for $C_{23}H_{16}N_2$ $[M+H]^+$ 321.13862 found 321.13885.

1,2-Di(naphthalen-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (4o): Yellow solid, mp. 168 - 169 °C.

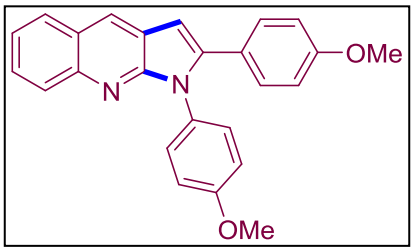


^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.29 (dd, ^{3}J = 4.7 Hz, ^{3}J = 1.6 Hz, 1H, CH_{Ar}), 8.07 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 7.96 - 7.87 (m, 2H, CH_{Ar}), 7.75 (d, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.71 - 7.64 (m, 1H, CH_{Ar}), 7.60 - 7.51 (m, 2H, CH_{Ar}), 7.51 - 7.45 (m, 2H, CH_{Ar}), 7.45 - 7.42 (m, 1H, CH_{Ar}), 7.42 - 7.34 (m, 4H, CH_{Ar}), 7.31 (dd, ^{3}J = 8.6 Hz, ^{4}J = 1.8 Hz, 1H, CH_{Ar}), 7.17 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.7 Hz, 1H, CH_{Ar}), 7.00 (s, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.2 (C_{Ar}), 144.0 (CH_{Ar}), 142.5 (C_{Ar}), 134.4 (C_{Ar}), 134.2 (C_{Ar}),

133.0 (C_{Ar}), 132.6 (C_{Ar}), 131.7 (C_{Ar}), 129.5 (C_{Ar}), 129.1 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.2 (CH_{Ar}), 127.7 (CH_{Ar}), 127.7 (CH_{Ar}), 127.5 (CH_{Ar}), 127.5 (CH_{Ar}), 127.1 (CH_{Ar}), 126.5 (CH_{Ar}), 126.3 (CH_{Ar}), 126.2 (CH_{Ar}), 125.8 (CH_{Ar}), 125.5 (CH_{Ar}), 123.4 (CH_{Ar}), 120.8 (C_{Ar}), 117.1 (CH_{Ar}), 101.4 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 2922 (w), 2851 (w), 1929 (w), 1595 (m), 1415 (m), 1297 (m), 958 (w), 786 (m), 768 (s), 758 (s). MS (EI, 70 eV): *m/z* (%) = 371 (28), 370 $[M]^+$ (99), 369 (100), 367 (16), 243 (25), 184 (10), 127 (11), 77 (6). HRMS (EI): Calculated for $C_{27}H_{18}N_2$ $[M]^+$ 370.14645 found 370.14531.

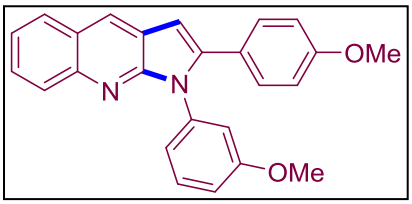
5.2.2. Synthesis of pyrroloquinolines from imines by domino C-C/C-N coupling

5.2.2.1. Pyrrolo[2,3-*b*]quinolines

1,2-Bis(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]quinoline (6a): Pale yellow solid, mp. 201 - 203 °C. 

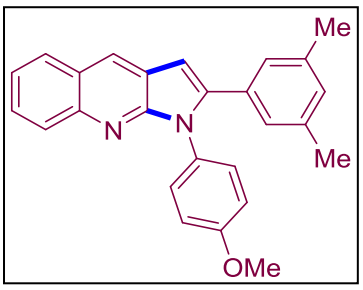
^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.36 (s, 1H, $CH_{pyridine}$), 8.05 (d, ^3J = 8.9 Hz, 1H, CH_{Ar}), 7.92 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.57 (ddd, ^3J = 8.5 Hz, ^3J = 6.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.40 (ddd, ^3J = 8.1 Hz, ^3J = 6.7 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.33 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.28 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.98 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.84 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 6.75 (s, 1H, $CH_{pyrrole}$), 3.87 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.8 (C_{Ar}), 158.7 (C_{Ar}), 145.3 (CH_{Ar}), 145.1 (C_{Ar}), 130.4 ($2CH_{Ar}$), 130.1 (C_{Ar}), 129.8 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.0 (CH_{Ar}), 127.5 (CH_{Ar}), 126.7 (C_{Ar}), 125.6 (C_{Ar}), 125.1 (C_{Ar}), 124.6 (C_{Ar}), 123.3 (CH_{Ar}), 122.5 (C_{Ar}), 114.4 ($2CH_{Ar}$), 114.0 ($2CH_{Ar}$), 99.8 (CH_{Ar}), 55.6 (OCH_3), 55.4 (OCH_3). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3112 (w), 3049 (w), 3013 (w), 2930 (w), 2831 (w), 2546 (w), 2050 (w), 1891 (w), 1793 (w), 1605 (m), 1570 (m), 1514 (m), 1496 (m), 1397 (m), 1293 (m), 1247 (s), 1177 (m), 1027 (m), 894 (m), 829 (s), 768 (m), 745 (m), 628 (m), 590 (m). MS (EI, 70 eV): *m/z* = 381 (23), 380 $[M]^+$ (98), 379 (100), 336 (15), 294 (10), 293 (23), 292 (12). HRMS (ESI): Calculated for $C_{25}H_{20}N_2O$ $[M+H]^+$ 381.15975 found 381.16007.

1-(3-Methoxyphenyl)-2-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]quinoline (6b): Pale yellow solid, mp. 180 - 181 °C.^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.37 (s, 1H, $CH_{pyridine}$), 8.08 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.93 (dd, ^3J = 8.2 Hz, ^3J = 1.6 Hz, 1H, CH_{Ar}), 7.59 (ddd, ^3J = 8.5 Hz, ^3J = 6.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.42 (ddd,



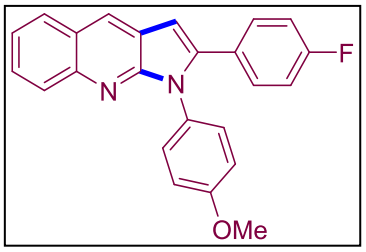
^{3}J = 8.1 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.35 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.30 (d, ^{3}J = 8.7 Hz, 2H, CH_{Ar}), 7.04 (t, ^{4}J = 2.2 Hz, 1H, CH_{Ar}), 6.98 (ddd, ^{3}J = 7.9 Hz, ^{4}J = 1.9 Hz, ^{5}J = 0.9 Hz, 1H, CH_{Ar}), 6.92 (ddd, ^{3}J = 8.3 Hz, ^{4}J = 2.6 Hz, ^{5}J = 1.0 Hz, 1H, CH_{Ar}), 6.85 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 6.76 (s, 1H, $CH_{pyrrole}$), 3.81 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.0 (C_{Ar}), 159.8 (C_{Ar}), 151.4 (C_{Ar}), 145.2 (C_{Ar}), 145.0 (C_{Ar}), 138.3 (C_{Ar}), 130.3 ($2CH_{Ar}$), 129.6 (CH_{Ar}), 128.6 (CH_{Ar}), 128.0 (CH_{Ar}), 127.5 (CH_{Ar}), 126.6 (CH_{Ar}), 125.7 (C_{Ar}), 124.6 (C_{Ar}), 123.4 (CH_{Ar}), 122.5 (C_{Ar}), 121.1 (CH_{Ar}), 114.4 (CH_{Ar}), 114.0 ($2CH_{Ar}$), 113.3 (CH_{Ar}), 100.4 (CH_{Ar}), 55.5 (OCH_3), 55.4 (OCH_3). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3066 (w), 3053 (w), 2950 (w), 2930 (w), 2907 (w), 2834 (w), 1594 (m), 1493 (m), 1453 (m), 1393 (m), 1376 (m), 1284 (m), 1246 (m), 1181 (m), 1171 (m), 1123 (m), 1027 (m), 991 (m), 892 (m), 839 (s), 785 (m), 773 (m), 754 (m), 695 (m), 615 (m). MS (EI, 70 eV): *m/z* = 381 (25), 380 $[M]^+$ (100), 379 (91), 321 (10), 293 (14), 146 (10). HRMS (ESI): Calculated for $C_{25}H_{20}N_2O_2$ $[M+H]^+$ 381.15975 found 381.15979.

2-(3,5-Dimethylphenyl)-1-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]quinoline (6c): Pale



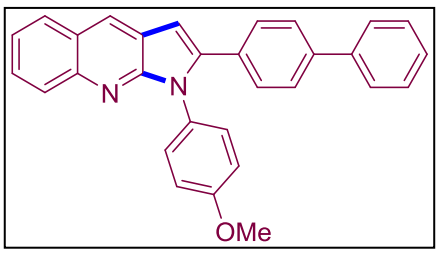
yellow solid, mp. 210 - 212 °C .^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.36 (s, 1H, $CH_{pyridine}$), 8.08 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 7.92 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.58 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.40 (ddd, ^{3}J = 8.1 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.29 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 7.02 (d, ^{3}J = 0.8 Hz, 2H, CH_{Ar}), 7.01 (s, 1H, CH_{Ar}), 6.84 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 6.75 (s, 1H, $CH_{pyrrole}$), 3.81 (s, 3H, OCH_3), 2.33 (s, 6H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.7 (C_{Ar}), 145.2 (C_{Ar}), 138.6 (CH_{Ar}), 137.0 ($2C_{Ar}$), 136.2 (C_{Ar}), 135.2 (C_{Ar}), 130.3 ($2CH_{Ar}$), 129.3 (CH_{Ar}), 128.6 (CH_{Ar}), 128.0 (CH_{Ar}), 127.4 (CH_{Ar}), 126.5 ($2CH_{Ar}$), 125.6 (C_{Ar}), 124.7 (C_{Ar}), 123.3 (CH_{Ar}), 122.6 (C_{Ar}), 114.4 (C_{Ar}), 113.9 ($2CH_{Ar}$), 99.9 (CH_{Ar}), 55.4 (OCH_3), 21.5 ($2CH_3$). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3114 (w), 3062 (w), 3041 (w), 3016 (w), 2918 (w), 2839 (w), 2042 (w), 1980 (w), 1946 (w), 1898 (w), 1604 (m), 1498 (m), 1397 (m), 1331 (m), 1250 (s), 1182 (m), 1118 (m), 1022 (m), 904 (m), 836 (m), 753 (m), 613 (m). MS (EI, 70 eV): *m/z* = 379 (24), 378 $[M]^+$ (100), 377 (90), 363 (13), 362 (15), 320 (12), 319 (22), 159 (14). HRMS (ESI): Calculated for $C_{26}H_{22}N_2O$ $[M+H]^+$ 379.18049 found 379.18053.

2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]quinoline (6d): Pale



yellow solid, mp. 240 - 242 °C. ^{1}H NMR (250 MHz, DMSO-d_6) δ = 8.55 (s, 1H, $CH_{pyridine}$), 8.02 (dd, ^{3}J = 8.3 Hz, ^{3}J = 1.6 Hz, 1H, CH_{Ar}), 7.86 (d, ^{3}J = 8.9 Hz, 1H, CH_{Ar}), 7.59 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 7.49 - 7.35 (m, 3H, CH_{Ar}), 7.27 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.14 (t, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.02 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 6.95 (s, 1H, $CH_{pyrrole}$), 3.83 (s, 3H, OCH_3). ^{19}F NMR (235 MHz, DMSO) δ = -113.1 (FC_{Ar}). ^{13}C NMR (63 MHz, DMSO) δ = 161.7 (d, $^{1}J_{CF}$ = 247.1 Hz, CF_{Ar}), 158.1 (C_{Ar}), 151.1 (C_{Ar}), 144.4 (C_{Ar}), 143.6 (C_{Ar}), 130.37 (d, $^{3}J_{CF}$ = 8.3 Hz, $2CH_{Ar}$), 129.4 (C_{Ar}), 129.3 ($2CH_{Ar}$), 127.71 (d, $^{4}J_{CF}$ = 3.2 Hz, C_{Ar}), 127.6 (CH_{Ar}), 127.2 (CH_{Ar}), 127.0 (CH_{Ar}), 126.2 (CH_{Ar}), 124.8 (C_{Ar}), 122.6 (CH_{Ar}), 121.3 (C_{Ar}), 114.8 (d, $^{2}J_{CF}$ = 21.8 Hz, $2CH_{Ar}$), 114.0 ($2CH_{Ar}$), 100.2 (CH_{Ar}), 55.0 (OCH_3). IR (ATR, cm^{-1}) ṽ = 3110 (w), 3072 (w), 3052 (w), 3022 (w), 2937 (w), 2964 (w), 2922 (w), 2850 (w), 2828 (w), 1570 (m), 1513 (s), 1496 (s), 1401 (m), 1298 (m), 1242 (m), 1226 (m), 1164 (m), 1026 (m), 886 (m), 844 (s), 823 (m), 775 (m), 732 (s), 629 (m), 588 (m). MS (EI, 70 eV): *m/z* = 369 (17), 368 $[M]^+$ (77), 367 (100), 324 (25), 323 (17), 162 (10). HRMS (ESI): Calculated for $C_{24}H_{17}FN_2O$ $[M+H]^+$ 369.13977 found 369.13985.

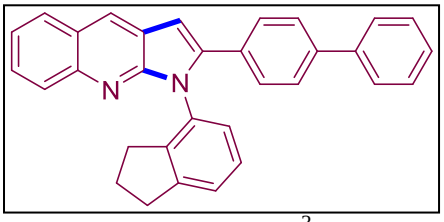
2-([1,1'-Biphenyl]-4-yl)-1-(4-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]quinoline (6e): Pale



yellow solid, mp. 230 - 231 °C. ^{1}H NMR (250 MHz, DMSO-d_6) δ = 8.56 (s, 1H, $CH_{pyridine}$), 8.04 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.7 Hz, 1H, CH_{Ar}), 7.87 (dd, ^{3}J = 8.6 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.69 - 7.67 (m, 1H, CH_{Ar}), 7.70 - 7.59 (m, 3H, CH_{Ar}), 7.61 - 7.55 (m, 1H, CH_{Ar}), 7.53 - 7.39 (m, 5H, CH_{Ar}), 7.39 - 7.29 (m, 3H, CH_{Ar}), 7.09 - 7.01 (m, 3H, CH_{Ar}), 3.84 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, DMSO) δ = 158.1 (C_{Ar}), 151.2 (C_{Ar}), 144.4 (C_{Ar}), 144.1 (C_{Ar}), 139.5 (C_{Ar}), 138.8 (C_{Ar}), 130.2 (C_{Ar}), 129.6 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 128.6 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 127.5 (CH_{Ar}), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 126.9 ($2CH_{Ar}$), 126.1 ($2CH_{Ar}$), 126.0 (CH_{Ar}), 125.9 (CH_{Ar}), 124.8 (C_{Ar}), 122.5 (C_{Ar}), 121.3 (C_{Ar}), 113.9 ($2CH_{Ar}$), 100.2 (CH_{Ar}), 55.0 (OCH_3). IR (ATR, cm^{-1}) ṽ = 3049 (w), 3026 (w), 3010 (w), 2950 (w), 2933 (w), 2906 (w), 2854 (w), 2833 (w), 1610 (w), 1567 (w), 1514 (m)k, 1483 (m), 1424 (m), 1330 (m), 1299 (m), 1244 (m), 1173 (m),

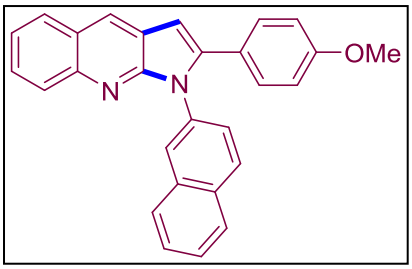
1035 (m), 891 (m), 842 (m), 820 (m), 756 (s), 732 (s), 697 (m), 593 (m). MS (EI, 70 eV): *m/z* = 427 (28), 426 $[M]^+$ (100), 425 (99), 382 (26), 381 (17), 77 (12). HRMS (ESI): Calculated for $C_{30}H_{22}N_2O$ $[M+H]^+$ 427.18049 found 427.18019.

2-([1,1'-Biphenyl]-4-yl)-1-(2,3-dihydro-1*H*-inden-4-yl)-1H-pyrrolo[2,3-*b*]quinoline



(6f): Pale yellow solid, mp. 218 - 220 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.33 (s, 1H, $CH_{pyridine}$), 8.03 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.86 (dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.56 - 7.50 (m, 3H, CH_{Ar}), 7.47 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.40 - 7.35 (m, 3H, CH_{Ar}), 7.34 (d, ^4J = 3.1 Hz, 2H, CH_{Ar}), 7.32 - 7.27 (m, 1H, CH_{Ar}), 7.26 - 7.24 (m, 1H, CH_{Ar}), 7.20 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.07 (dd, ^3J = 7.9 Hz, ^4J = 2.0 Hz, 1H, CH_{Ar}), 6.81 (s, 1H, $CH_{pyrrole}$), 2.88 (td, ^3J = 7.4 Hz, ^3J = 4.8 Hz, 4H, $CH_{2\text{-aliphatic}}$), 2.06 (p, ^3J = 7.5 Hz, 2H, $CH_{2\text{-aliphatic}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 151.8 (C_{Ar}), 145.3 (C_{Ar}), 145.0 (CH_{Ar}), 143.7 (C_{Ar}), 140.8 (C_{Ar}), 140.4 (C_{Ar}), 135.1 (C_{Ar}), 131.1 (C_{Ar}), 129.4 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.1 (CH_{Ar}), 127.7 (CH_{Ar}), 127.1 ($2CH_{Ar}$), 127.0 ($2CH_{Ar}$), 126.8 (CH_{Ar}), 126.6 (CH_{Ar}), 125.6 (C_{Ar}), 124.8 (CH_{Ar}), 124.7 (CH_{Ar}), 123.4 (CH_{Ar}), 122.5 (C_{Ar}), 114.0 (C_{Ar}), 112.2 (C_{Ar}), 100.9 (CH_{Ar}), 33.1 ($CH_{2\ aliphatic}$), 32.8 ($CH_{2\ aliphatic}$), 25.7 ($CH_{2\ aliphatic}$). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3062 (w), 3048 (w), 3027 (w), 2936 (w), 2891 (w), 2840 (w), 2245 (w), 1562 (w), 1492 (m), 1482 (m), 1396 (m), 1330 (m), 1252 (m), 1122 (w), 905 (m), 842 (m), 754 (m), 729 (s), 694 (m), 601 (m). MS (EI, 70 eV): *m/z* = 437 (27), 436 $[M]^+$ (94), 435 (100), 407 (14), 115 (11). HRMS (ESI): Calculated for $C_{32}H_{24}N_2$ $[M+H]^+$ 437.20123 found 437.20101.

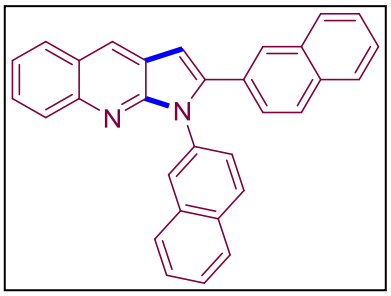
2-(4-Methoxyphenyl)-1-(naphthalen-1-yl)-1*H*-pyrrolo[2,3-*b*]quinoline (6g): Pale



yellow solid, mp. 163 - 164 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.45 (s, 1H, CH_{Ar}), 8.01 - 7.88 (m, 4H, CH_{Ar}), 7.56 (dd, ^3J = 8.1 Hz, ^3J = 7.3 Hz, 1H, CH_{Ar}), 7.52 - 7.46 (m, 3H, CH_{Ar}), 7.48 - 7.36 (m, 1H, CH_{Ar}), 7.37 (d, ^3J = 1.3 Hz, 1H, CH_{Ar}), 7.31 (ddd, ^3J = 8.5 Hz, ^3J = 6.6 Hz, ^3J = 1.2 Hz, 1H, CH_{Ar}), 7.20 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 6.90 (s, 1H, CH_{Ar}), 6.66 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.70 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.7 (C_{Ar}), 147.8 (C_{Ar}), 146.5 (C_{Ar}), 139.8 (C_{Ar}), 134.6 (C_{Ar}), 134.5 (C_{Ar}), 132.0 (CH_{Ar}), 129.7 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 128.7 (C_{Ar}), 128.5 (C_{Ar}), 128.4 (CH_{Ar}), 128.1 (CH_{Ar}), 128.0 (CH_{Ar}), 127.7 (CH_{Ar}), 127.5 (CH_{Ar}), 126.9 (CH_{Ar}), 126.5 (CH_{Ar}),

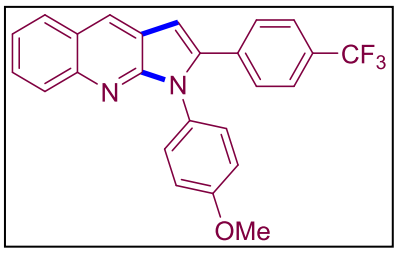
125.7 (CH_{Ar}), 124.5 (C_{Ar}), 123.9 (CH_{Ar}), 123.4 (CH_{Ar}), 122.5 (C_{Ar}), 113.9 ($2CH_{Ar}$), 99.7 (CH_{Ar}), 55.3 (OCH_3).IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3060 (w), 2997 (w), 2921 (m), 2850 (w), 1599 (m), 1575 (m), 1496 (m), 1465 (m), 1393 (m), 1330 (m), 1250 (m), 1181 (m), 1025 (m), 866 (m), 834 (m), 792 (m), 767 (s), 750 (s), 731 (s), 623 (m). MS (EI, 70 eV): *m/z* = 401 (30), 400 $[M]^+$ (100), 399 (48), 356 (15), 355 (27), 354 (10), 293 (42), 292 (12). HRMS (ESI): Calculated for $C_{28}H_{20}N_2O$ $[M+H]^+$ 401.16484 found 401.16472.

1-(Naphthalen-1-yl)-2-(naphthalen-2-yl)-1*H*-pyrrolo[2,3-*b*]quinoline (6h): Pale



yellow solid, mp. 208 - 210 °C.^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.52 (s, 1H, $CH_{pyridine}$), 8.03 - 7.88 (m, 4H, CH_{Ar}), 7.80 (s, 1H, CH_{Ar}), 7.74 - 7.65 (m, 1H, CH_{Ar}), 7.61 - 7.50 (m, 5H, CH_{Ar}), 7.50 - 7.37 (m, 5H, CH_{Ar}), 7.37 - 7.29 (m, 2H, CH_{Ar}), 7.11 (s, 1H, $CH_{pyrrole}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 146.6 (C_{Ar}), 134.6 (C_{Ar}), 134.3 (C_{Ar}), 133.1 (C_{Ar}), 133.0 (C_{Ar}), 132.0 (C_{Ar}), 131.6 (C_{Ar}), 129.4 (C_{Ar}), 129.2 (CH_{Ar}), 128.4 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 128.2 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 127.9 (C_{Ar}), 127.9 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 127.0 (CH_{Ar}), 126.7 (CH_{Ar}), 126.5 (CH_{Ar}), 126.4 (CH_{Ar}), 125.8 (CH_{Ar}), 125.7 (CH_{Ar}), 125.7 (CH_{Ar}), 125.7 (C_{Ar}), 123.8 (CH_{Ar}), 123.6 (CH_{Ar}), 122.4 (C_{Ar}), 101.3 (CH_{Ar}). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3050 (w), 2957 (w), 2921 (w), 2851 (w), 1945 (w), 1921 (w), 1592 (m), 1497 (m), 1467 (m), 1418 (m), 1391 (m), 1324 (m), 1290 (m), 1259 (m), 1014 (m), 894 (m), 826 (m), 793 (m), 766 (m), 745 (s), 726 (s), 598 (m). MS (EI, 70 eV): *m/z* = 421 (31), 420 $[M]^+$ (100), 419 (66), 418 (12), 417 (15), 294 (11), 293 (50), 292 (19), 209 (11), 127 (15). HRMS (ESI): Calculated for $C_{31}H_{20}N_2$ $[M+H]^+$ 421.16993 found 421.16957.

1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[2,3-*b*]quinoline

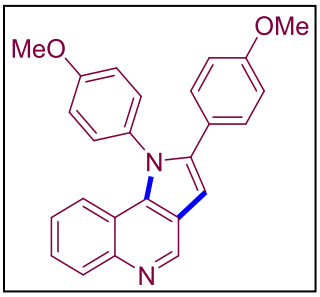


(6i): Pale yellow solid, mp. 214 - 215 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.37 (s, 1H, $CH_{pyridine}$), 8.05 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.87 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.59 - 7.45 (m, 3H, CH_{Ar}), 7.41 - 7.30 (m, 3H, CH_{Ar}), 7.23 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.91 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.82 (s, 1H, $CH_{pyrrole}$), 3.79 (s, 3H, OCH_3). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -62.7 (F_3C). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.0 (CH_{Ar}), 151.3 (C_{Ar}), 145.3 (C_{Ar}), 143.5 (C_{Ar}), 135.6 (C_{Ar}), 130.14 (q, $^2J_{CF}$ = 32.7 Hz, C_{Ar}), 129.7 ($2CH_{Ar}$), 129.5 (C_{Ar}), 129.2 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 128.2 (CH_{Ar}), 125.6 (C_{Ar}), 125.5 (C_{Ar}), 125.3

(q, $^{3}J_{CF}$ = 3.7 Hz, 2CH_{Ar}), 125.2 (C_{Ar}), 124.13 (q, $^{1}J_{CF}$ = 272.2 Hz, CF_3), 123.7 (CH_{Ar}), 122.1 (CH_{Ar}), 114.7 (2CH_{Ar}), 102.1 (CH_{Ar}), 55.6 (OCH_3). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 2924 (w), 2836 (w), 1513 (m), 1442 (m), 1321 (m), 1165 (m), 1122 (s), 1012 (m), 719 (s), 592 (m). MS (EI, 70 eV): *m/z* = 419 (17), 418 $[M]^+$ (75), 417 (100), 374 (21), 373 (12). HRMS (ESI): Calculated for $C_{25}H_{17}F_3N_2O$ $[M+H]^+$ 419.13657 found 419.13670.

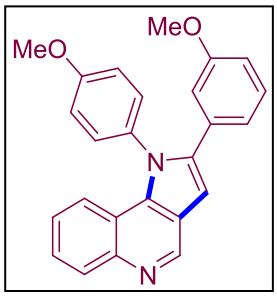
5.2.2.2.Pyrrolo[2,3-c]quinolines

1,2-Bis(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*c*]quinoline (7a): Pale yellow solid, mp. 198 - 200 °C.



^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.11 (s, 1H, $CH_{pyridine}$), 8.09 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.40 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 6.0 Hz, ^{4}J = 2.3 Hz, 1H, CH_{Ar}), 7.19 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 7.13 - 7.04 (m, 4H, CH_{Ar}), 6.90 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 6.78 (s, 1H, $CH_{pyrrole}$), 6.68 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 3.80 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.0 (C_{Ar}), 159.3 (C_{Ar}), 146.0 (CH_{Ar}), 144.8 (C_{Ar}), 141.7 (C_{Ar}), 135.9 (C_{Ar}), 132.2 (C_{Ar}), 130.8 (2CH_{Ar}), 130.5 (2CH_{Ar}), 130.4 (CH_{Ar}), 126.1 (CH_{Ar}), 125.3 (CH_{Ar}), 124.5 (C_{Ar}), 121.2 (C_{Ar}), 120.7 (CH_{Ar}), 118.5 (C_{Ar}), 114.9 (2CH_{Ar}), 113.7 (2CH_{Ar}), 102.8 (CH_{Ar}), 55.6 (OCH_3), 55.3 (OCH_3). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3102 (w), 3055 (w), 3009 (w), 2934 (w), 2910 (w), 2834 (w), 2547 (w), 1608 (m), 1508 (m), 1491 (m), 1441 (m), 1366 (m), 1242 (s), 1175 (m), 1028 (m), 836 (m), 803 (m), 755 (s), 585 (m), 431 (m). MS (EI, 70 eV): *m/z* = 381 (27), 380 $[M]^+$ (100), 365 (28), 293 (11). HRMS (ESI): Calculated for $C_{25}H_{20}N_2O_2$ $[M+H]^+$ 381.15975 found 381.15965.

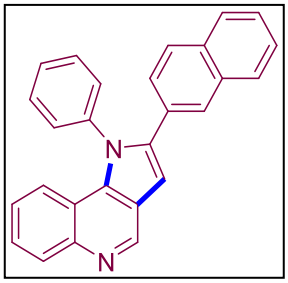
2-(3-Methoxyphenyl)-1-(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*c*]quinoline (7b): Yellow solid, mp. 168 - 170 °C.



^{1}H NMR (250 MHz, Chloroform-*d*) δ = 9.21 (s, 1H, $CH_{pyridine}$), 8.21 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 7.51 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 5.5 Hz, ^{4}J = 2.8 Hz, 1H, CH_{Ar}), 7.49 - 7.35 (m, 1H, CH_{Ar}), 7.23 - 7.17 (m, 4H, CH_{Ar}), 7.08 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 2.5 Hz, ^{5}J = 1.0 Hz, 1H, CH_{Ar}), 7.02 (ddd, ^{3}J = 7.7 Hz, ^{4}J = 1.9 Hz, ^{5}J = 1.0 Hz, 1H, CH_{Ar}), 6.90 (s, 1H, $CH_{pyrrole}$), 6.89 (d, ^{4}J = 1.9 Hz, 1H, CH_{Ar}), 6.78 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 3.77 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.7 (C_{Ar}), 159.4 (C_{Ar}), 145.8 (CH_{Ar}), 144.5 (C_{Ar}), 141.6 (C_{Ar}), 140.6 (C_{Ar}), 135.7 (C_{Ar}), 130.7 (2CH_{Ar}), 130.5 (CH_{Ar}), 130.1 (CH_{Ar}), 126.3 (CH_{Ar}), 125.5 (CH_{Ar}), 124.3 (C_{Ar}), 121.9 (CH_{Ar}),

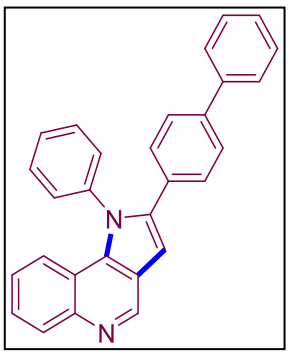
121.2 (C_{Ar}), 120.8 (CH_{Ar}), 118.4 (C_{Ar}), 115.4 (CH_{Ar}), 115.0 (CH_{Ar}), 113.8 ($2CH_{Ar}$), 103.1 (CH_{Ar}), 55.7 (CH_3), 55.3 (CH_3). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3059 (w), 2996 (w), 2964 (w), 2936 (m), 2835 (m), 1604 (m), 1489 (s), 1367 (m), 1288 (m), 1248 (m), 1175 (m), 1023 (m), 843 (m), 762 (s), 690 (m), 558 (m). MS (EI, 70 eV): *m/z* (%) = 381 (26), 380 $[M]^+$ (100), 365 (26). HRMS (EI): Calculated for $C_{25}H_{20}O_2N_2$ $[M]^+$ 380.15193 found 380.15172.

2-(Naphthalen-2-yl)-1-phenyl-1*H*-pyrrolo[3,2-*c*]quinoline (7c): Yellow solid,



mp. 177 - 178 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.27 (s, 1H, $CH_{pyridine}$), 8.25 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.81 - 7.73 (m, 2H, CH_{Ar}), 7.69 (dd, ^3J = 9.2 Hz, ^4J = 2.9 Hz, 2H, CH_{Ar}), 7.58 - 7.48 (m, 4H, CH_{Ar}), 7.48 - 7.43 (m, 4H, CH_{Ar}), 7.33 (dd, ^3J = 8.5 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.25 - 7.19 (m, 1H, CH_{Ar}), 7.19 - 7.14 (m, 1H, CH_{Ar}), 7.10 (s, 1H, $CH_{pyrrole}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.9 (CH_{Ar}), 144.6 (C_{Ar}), 141.7 (C_{Ar}), 139.6 (C_{Ar}), 136.2 (C_{Ar}), 133.1 (C_{Ar}), 132.6 (C_{Ar}), 130.2 (CH_{Ar}), 130.0 ($2CH_{Ar}$), 129.7 ($2CH_{Ar}$), 129.6 (CH_{Ar}), 129.3 (C_{Ar}), 128.9 (CH_{Ar}), 128.3 (CH_{Ar}), 127.8 (CH_{Ar}), 127.7 (CH_{Ar}), 127.0 (CH_{Ar}), 126.6 (CH_{Ar}), 126.5 ($2CH_{Ar}$), 125.6 (CH_{Ar}), 121.3 (C_{Ar}), 120.8 (CH_{Ar}), 118.4 (C_{Ar}), 104.3 (CH_{Ar}). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3059 (w), 2923 (w), 2169 (w), 1497 (m), 1366 (m), 1169 (w), 932 (m), 862 (m), 752 (m), 723 (s), 693 (m), 638 (m), 475 (m). MS (EI, 70 eV): *m/z* = 371 (27), 370 $[M]^+$ (100), 369 (24), 184 (11). HRMS (EI): Calculated for $C_{27}H_{18}N_2$ $[M]^+$ 370.14645 found 370.14589.

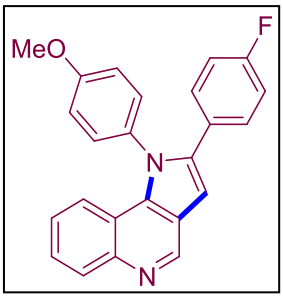
2-([1,1'-Biphenyl]-4-yl)-1-phenyl-1*H*-pyrrolo[3,2-*c*]quinoline (7d): Yellow solid,



mp. 203 - 204 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.26 (s, 1H, $CH_{pyridine}$), 8.24 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.59 - 7.52 (m, 6H, CH_{Ar}), 7.54 - 7.46 (m, 1H, CH_{Ar}), 7.48 - 7.39 (m, 5H, CH_{Ar}), 7.35 (d, ^3J = 7.3 Hz, 1H, CH_{Ar}), 7.31 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.21 (ddd, ^3J = 8.1 Hz, ^3J = 6.2 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.14 (ddd, ^3J = 8.5 Hz, ^4J = 1.6 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.04 (s, 1H, $CH_{pyrrole}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.9 (CH_{Ar}), 144.6 (C_{Ar}), 141.4 (C_{Ar}), 140.5 (C_{Ar}), 140.3 (C_{Ar}), 139.6 (C_{Ar}), 136.1 (C_{Ar}), 130.8 (C_{Ar}), 130.2 (CH_{Ar}), 130.0 ($2CH_{Ar}$), 129.8 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 129.6 (CH_{Ar}), 128.9 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 127.0 ($2CH_{Ar}$), 126.9 ($2CH_{Ar}$), 126.5 (CH_{Ar}), 125.6 (CH_{Ar}), 121.3 (C_{Ar}), 120.7 (CH_{Ar}), 118.4 (C_{Ar}), 103.9 (CH_{Ar}).

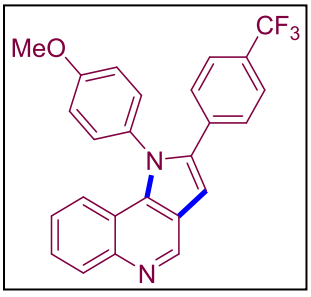
IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3369 (w), 3031 (w), 2957 (w), 2855 (w), 1497 (m), 1481 (m), 1367 (m), 1332 (m), 1005 (m), 840 (m), 755 (s), 691 (m), 605 (m), 508 (m). MS (EI, 70 eV): *m/z* = 397 (31), 396 $[M]^+$ (100), 395 (17). HRMS (EI): Calculated for $C_{29}H_{20}N_2$ $[M]^+$ 396.16210 found 396.16215.

2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrolo[3,2-*c*]quinoline (7e): Yellow



solid, mp. 174 - 175 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 9.12 (s, 1H), 8.13 (dd, ^3J = 7.9 Hz, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.43 (ddd, ^3J = 8.4 Hz, ^3J = 6.2 Hz, ^4J = 2.1 Hz, 1H, CH_{Ar}), 7.24 - 7.08 (m, 6H, CH_{Ar}), 6.97 - 6.82 (m, 5H, CH_{Ar}), 3.82 (s, 3H, OCH_3). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -113.6 (FC_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.5 (d, $^1J_{CF}$ = 248.4 Hz, CF_{Ar}), 160.2 (C_{Ar}), 145.9 (CH_{Ar}), 144.7 (C_{Ar}), 140.9 (C_{Ar}), 136.2 (C_{Ar}), 131.8 (C_{Ar}), 131.3 (d, $^3J_{CF}$ = 8.1 Hz, $2CH_{Ar}$), 130.5 ($2CH_{Ar}$), 130.2 (CH_{Ar}), 128.2 (d, $^4J_{CF}$ = 3.4 Hz, C_{Ar}), 126.4 (CH_{Ar}), 125.6 (CH_{Ar}), 121.0 (C_{Ar}), 120.7 (CH_{Ar}), 118.5 (C_{Ar}), 115.4 (d, $^2J_{CF}$ = 21.6 Hz, $2CH_{Ar}$), 115.0 ($2CH_{Ar}$), 103.6 (CH_{Ar}), 55.7 (OCH_3). IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3102 (w), 3059 (m), 2995 (m), 2962 (m), 2931 (m), 2833 (m), 1510 (s), 1489 (m), 1440 (m), 1369 (m), 1335 (m), 1294 (m), 1239 (m), 1217 (m), 1182 (m), 1028 (m), 838 (m), 811 (m), 760 (s), 699 (m), 578 (m), 422 (m). MS (EI, 70 eV): *m/z* = 369 (26), 368 $[M]^+$ (100), 353 (17). HRMS (EI): Calculated for $C_{24}H_{17}ON_2F$ $[M]^+$ 368.13194 found 368.13161.

1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[3,2-*c*]quinoline



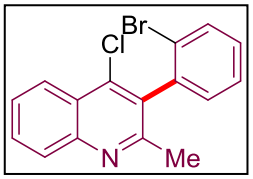
(7f): Yellow solid, mp. 146 - 147 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.22 (s, 1H, $CH_{pyridine}$), 8.22 (ddd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 7.57 - 7.54 (m, 1H, CH_{Ar}), 7.54 - 7.48 (m, 2H, CH_{Ar}), 7.41 - 7.35 (m, 2H, CH_{Ar}), 7.31 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.23 (dd, ^3J = 6.6 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.19 (ddd, ^3J = 8.5 Hz, ^4J = 1.8 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 7.07 - 7.01 (m, 3H, CH_{Ar}), 3.92 (s, 3H, OCH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -62.6 (F_3C). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.4 (C_{Ar}), 145.9 (CH_{Ar}), 144.7 (C_{Ar}), 140.1 (C_{Ar}), 136.7 (C_{Ar}), 135.6 (C_{Ar}), 131.6 (C_{Ar}), 130.5 ($2CH_{Ar}$), 130.2 (CH_{Ar}), 129.7 (q, $^2J_{CF}$ = 32.6 Hz, C_{Ar}), 129.5 ($2CH_{Ar}$), 126.8 (CH_{Ar}), 125.8 (CH_{Ar}), 125.2 (q, $^3J_{CF}$ = 3.8 Hz, $2CH_{Ar}$), 124.13 (q, $^1J_{CF}$ = 272.1 Hz, CF_3), 121.0 (C_{Ar}), 120.8 (CH_{Ar}), 118.4 (C_{Ar}), 115.2 ($2CH_{Ar}$), 104.8 (CH_{Ar}), 55.7 (OCH_3).

IR (ATR, cm^{-1}) $\tilde{\nu}$ = 3065 (w), 2999 (w), 2963 (w), 2935 (w), 2837 (w), 2185 (w), 1511 (m), 1322 (m), 1250 (m), 1160 (m), 1111 (m), 1066 (m), 838 (m), 764 (m), 725 (s), 701 (m), 637 (m), 429 (m). MS (EI, 70 eV): *m/z* = 419 (26), 418 $[M]^+$ (100), 403 (17). HRMS (EI): Calculated for $C_{25}H_{17}ON_2F_3$ $[M]^+$ 418.12875 found 418.12870.

5.2.3. Synthesis of indoloquinolines by sequential regioselective Suzuki reaction/double C-N coupling

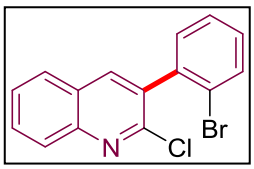
5.2.3.1. Starting materials for double C-N coupling

3-(2-Bromophenyl)-4-chloro-2-methylquinoline (9a): Colorless oil. ^1H NMR



(250 MHz, Chloroform-*d*) δ = 8.26 (ddd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 8.15 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.85 - 7.73 (m, 2H, CH_{Ar}), 7.64 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.48 (td, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.43 - 7.28 (m, 1H, CH_{Ar}), 7.26 (dd, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 1H, CH_{Ar}), 2.48 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.0 (C_{Ar}), 147.4 (C_{Ar}), 142.1 (C_{Ar}), 138.3 (C_{Ar}), 133.4 (C_{Ar}), 133.2 (CH_{Ar}), 130.9 (CH_{Ar}), 130.8 (CH_{Ar}), 130.2 (CH_{Ar}), 128.8 (CH_{Ar}), 128.1 (CH_{Ar}), 127.3 (CH_{Ar}), 125.1 (C_{Ar}), 124.8 (CH_{Ar}), 123.8 (C_{Ar}), 24.7 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3660 (w), 3399 (w), 3060 (m), 2998 (w), 2954 (w), 2919 (w), 2848 (w), 1613 (m), 1581 (m), 1555 (m), 1475 (m), 1433 (m), 1394 (m), 1345 (s), 1253 (w), 1057 (m), 1026 (m), 924 (m), 840 (m), 751 (s), 638 (m), 592 (m). MS (EI, 70 eV): *m/z* (%) = 335 (29), 334 (18), 333 $[M]^+$ (100), 331 (71), 298 (12), 296 (11), 254 (16), 253 (12), 252 (43), 251 (10), 176 (45), 175 (14), 174 (10), 150 (15), 126 (13), 109 (10), 88 (14), 87 (14), 75 (15). HRMS (EI): Calculated for $C_{16}H_{11}NBrCl$ $[M]^+$ 330.97579 found 330.97625, calculated for $C_{16}H_{11}N^{81}BrCl$ $[M]^+$ 332.97374 found 332.97349, calculated for $C_{16}H_{11}NBr^{37}Cl$ $[M]^+$ 332.97284 found 332.97349, calculated for $C_{16}H_{11}N^{81}Br^{37}Cl$ $[M]^+$ 334.97079 found 334.97103.

3-(2-Bromophenyl)-2-chloroquinoline (9b-71): Yellow solid, mp. 124 - 125 °C.

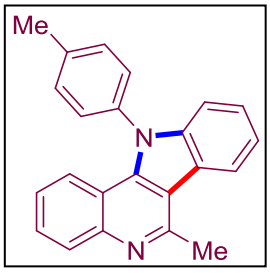


^1H NMR (300 MHz, Chloroform-*d*) δ = 8.10 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.07 (s, 1H, $CH_{pyridine}$), 7.85 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.78 (ddd, ^3J = 8.5 Hz, ^3J = 7.0 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.72 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.60 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.47 - 7.40 (m, 1H, CH_{Ar}), 7.38 - 7.29 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.0 (C_{Ar}), 147.4 (C_{Ar}), 139.2 (CH_{Ar}),

138.7 (C_{Ar}), 134.3 (C_{Ar}), 132.9 (CH_{Ar}), 131.4 (CH_{Ar}), 130.9 (CH_{Ar}), 130.2 (CH_{Ar}), 128.6 (CH_{Ar}), 127.8 (CH_{Ar}), 127.5 (CH_{Ar}), 127.5 (CH_{Ar}), 127.0 (C_{Ar}), 124.1 (C_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2921 (w), 1560 (m), 1477 (m), 1362 (m), 1134 (m), 1095 (m), 1023 (m), 922 (m), 747 (s), 653 (m), 596 (m). MS (EI, 70 eV): *m/z* (%) = 321 (17), 320 (10), 319 (63), 318 (12), 317 (49), 240 (34), 239 (19), 238 (100), 204 (16), 203 (96), 202 (28), 201 (27), 150 (11), 119 (13), 101 (18). HRMS (EI): Calculated for $C_{15}H_9N^{81}BrCl$ $[M]^+$ 318.95809 found 318.95836, calculated for $C_{15}H_9N^{81}Br^{37}Cl$ 320.95514 found 320.05587.

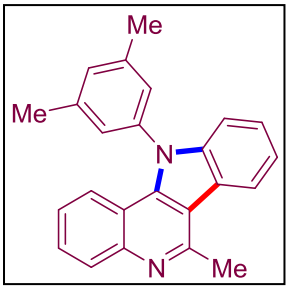
5.2.3.2.Indolo[3,2-c]quinolines

6-Methyl-11-(*p*-tolyl)-11*H*-indolo[3,2-*c*]quinoline (11a): Yellow oil. ^{1}H NMR



(300 MHz, Chloroform-*d*) δ = 8.32 - 8.27 (m, 1H, CH_{Ar}), 8.21 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.60 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.48 (d, ^3J = 7.7 Hz, 2H, CH_{Ar}), 7.44 (dd, ^3J = 6.1 Hz, ^4J = 3.2 Hz, 2H, CH_{Ar}), 7.40 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.36 (ddd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.25 - 7.18 (m, 2H, CH_{Ar}), 3.28 (s, 3H, CH_3), 2.58 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.9 (C_{Ar}), 146.1 (C_{Ar}), 142.1 (C_{Ar}), 140.2 (C_{Ar}), 139.7 (C_{Ar}), 135.9 (C_{Ar}), 131.0 ($2CH_{Ar}$), 129.2 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 125.3 (CH_{Ar}), 124.5 (CH_{Ar}), 122.4 (C_{Ar}), 121.9 (CH_{Ar}), 121.7 (CH_{Ar}), 121.6 (CH_{Ar}), 116.7 (C_{Ar}), 114.3 (C_{Ar}), 110.8 (CH_{Ar}), 25.0 ($CH_{3\text{-quinoline}}$), 21.5 ($CH_{3\text{-Ar}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 3035 (w), 2951 (w), 2918 (w), 2852 (w), 1560 (w), 1509 (m), 1428 (m), 1365 (m), 1197 (w), 1118 (w), 740 (s), 507 (m). MS (EI, 70 eV): *m/z* (%) = 323 (27), 322 $[M]^+$ (100), 321 (24), 306 (8), 153 (10). HRMS (ESI): Calculated for $C_{23}H_{18}N_2$ $[M+H]^+$ 323.15428 found 323.15462.

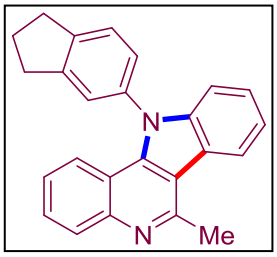
11-(3,5-Dimethylphenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11b): Yellow solid,



mp. 182 - 183 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.34 - 8.30 (m, 1H, CH_{Ar}), 8.23 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.63 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.49 - 7.44 (m, 2H, CH_{Ar}), 7.40 (dd, ^3J = 8.4 Hz, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.32 (s, 1H, CH_{Ar}), 7.29 - 7.22 (m, 2H, CH_{Ar}), 7.16 (s, 2H, CH_{Ar}), 3.30 (s, 3H, $CH_{3\text{-quinoline}}$), 2.47 (s, 6H, $CH_{3\text{-Ar}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.9 (C_{Ar}), 146.1 (C_{Ar}), 142.0 ($2C_{Ar}$), 140.2 (C_{Ar}), 140.1 (C_{Ar}), 138.4 (C_{Ar}), 131.2 (CH_{Ar}), 129.2 (CH_{Ar}), 127.8 (CH_{Ar}), 126.4 ($2CH_{Ar}$),

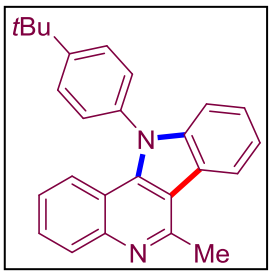
125.2 (CH_{Ar}), 124.5 (CH_{Ar}), 122.3 (C_{Ar}), 122.1 (CH_{Ar}), 121.7 (CH_{Ar}), 121.5 (CH_{Ar}), 116.7 (C_{Ar}), 114.2 (C_{Ar}), 110.9 (CH_{Ar}), 25.0 ($CH_{3\text{-quinoline}}$), 21.4 ($2CH_{3\text{-Ar}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3038 (w), 2995 (w), 2960 (w), 2916 (w), 2855 (w), 1595 (w), 1560 (m), 1506 (m), 1470 (m), 1363 (m), 1244 (m), 1181 (w), 1023 (w), 858 (m), 744 (s), 726 (m). MS (EI, 70 eV): *m/z* (%) = 337 (28), 336 $[M]^+$ (100), 160 (8). HRMS (ESI): Calculated for $C_{24}H_{20}N_2$ $[M+H]^+$ 337.16993 found 337.1701.

11-(2,3-Dihydro-1*H*-inden-5-yl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11c): White



solid, mp. 185 - 186 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.33 - 8.27 (m, 1H, CH_{Ar}), 8.22 (dd, ^3J = 8.6 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.61 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.50 (d, ^3J = 8.0 Hz, 1H, CH_{Ar}), 7.47 - 7.42 (m, 2H, CH_{Ar}), 7.39 (d, ^3J = 7.5 Hz, 1H, CH_{Ar}), 7.34 (s, 1H, CH_{Ar}), 7.30 - 7.19 (m, 3H, CH_{Ar}), 3.29 (s, 3H, $CH_{3\text{-quinoline}}$), 3.19 - 2.99 (m, $4H_{aliphatic}$, CH_2), 2.34 - 2.19 (m, $2H_{aliphatic}$, CH_2). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.9 (C_{Ar}), 146.9 (C_{Ar}), 146.1 (C_{Ar}), 146.0 (C_{Ar}), 142.2 (C_{Ar}), 140.3 (C_{Ar}), 136.4 (C_{Ar}), 129.0 (CH_{Ar}), 128.0 (CH_{Ar}), 126.7 (CH_{Ar}), 125.9 (CH_{Ar}), 125.2 (CH_{Ar}), 124.7 (CH_{Ar}), 124.5 (CH_{Ar}), 122.3 (C_{Ar}), 122.0 (CH_{Ar}), 121.6 (CH_{Ar}), 121.6 (CH_{Ar}), 116.7 (C_{Ar}), 114.2 (C_{Ar}), 110.9 (CH_{Ar}), 33.0 (CH_2), 32.8 (CH_2), 25.6 (CH_2), 24.9 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3039 (w), 3004 (w), 2946 (m), 2841 (m), 1561 (m), 1493 (m), 1428 (m), 1361 (m), 1238 (m), 1154 (m), 838 (w), 734 (s), 627 (w), 429 (m). MS (EI, 70 eV): *m/z* (%) = 349 (30), 348 $[M]^+$ (100), 347 (25), 160 (7). HRMS (EI): Calculated for $C_{25}H_{20}N_2$ $[M]^+$ 348.16210 found 348.16164.

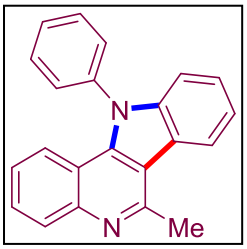
11-(4-(*tert*-Butyl)phenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11d): Yellow solid,



mp. 137 - 138 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.33 - 8.28 (m, 1H, CH_{Ar}), 8.23 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.69 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.60 (ddd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.48 - 7.40 (m, 4H, CH_{Ar}), 7.32 (ddd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.25 - 7.17 (m, 2H, CH_{Ar}), 3.29 (s, 3H, $CH_{3\text{-quinoline}}$), 1.49 (s, 9H, $CH_{3\text{-}t\text{Bu}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.8 (C_{Ar}), 152.9 (C_{Ar}), 145.9 (C_{Ar}), 142.1 (C_{Ar}), 140.2 (C_{Ar}), 135.7 (C_{Ar}), 129.0 (CH_{Ar}), 128.3 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.2 ($2CH_{Ar}$), 125.3 (CH_{Ar}), 124.6 (CH_{Ar}), 122.3 (CH_{Ar}), 121.9 (CH_{Ar}), 121.6 (CH_{Ar}), 116.7 (C_{Ar}), 114.2 (C_{Ar}), 112.9 (C_{Ar}), 110.9 (CH_{Ar}), 35.0 ($C_{t\text{Bu}}$), 31.5 ($3CH_{3\text{-}t\text{Bu}}$), 25.0 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}):

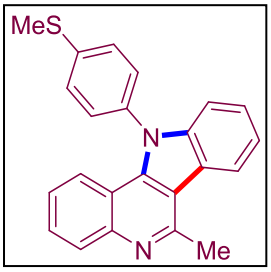
$\tilde{\nu}$ = 3393 (w), 3064 (w), 3045 (w), 2956 (m), 2903 (w), 2866 (w), 1561 (m), 1506 (m), 1458 (m), 1429 (m), 1323 (m), 1239 (m), 1199 (m), 1116 (m), 740 (s), 629 (m). MS (EI, 70 eV): *m/z* (%) = 364 $[M]^+$ (100), 349 (52), 307 (8), 160 (11). HRMS (ESI): Calculated for $C_{26}H_{24}N_2$ $[M+H]^+$ 365.20123 found 365.20144.

6-Methyl-11-phenyl-11*H*-indolo[3,2-*c*]quinoline (11e): Yellow solid,



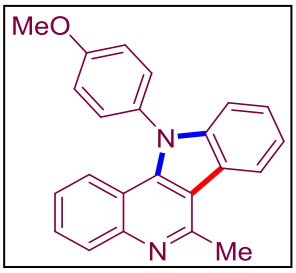
mp. 195 - 196 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.30 (ddd, ^3J = 6.2 Hz, ^4J = 3.1 Hz, ^5J = 0.8 Hz, 1H, CH_{Ar}), 8.22 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.73 - 7.66 (m, 3H, CH_{Ar}), 7.60 (ddd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.56 - 7.51 (m, 2H, CH_{Ar}), 7.45 (dd, ^3J = 6.2 Hz, ^4J = 3.1 Hz, 2H, CH_{Ar}), 7.29 (dd, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.23 - 7.17 (m, 2H, CH_{Ar}), 3.28 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.0 (C_{Ar}), 146.2 (C_{Ar}), 142.1 (C_{Ar}), 140.2 (C_{Ar}), 138.7 (C_{Ar}), 130.5 ($2CH_{Ph}$), 129.8 (CH_{Ar}), 129.4 (CH_{Ar}), 129.1 ($2CH_{Ph}$), 128.0 (CH_{Ar}), 125.5 (CH_{Ar}), 124.7 (CH_{Ar}), 122.5 (C_{Ar}), 121.9 (CH_{Ar}), 121.9 (CH_{Ar}), 121.8 (CH_{Ar}), 116.7 (C_{Ar}), 114.5 (C_{Ar}), 110.8 (CH_{Ar}), 25.1 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2992 (w), 2947 (w), 2912 (w), 2848 (w), 1591 (w), 1559 (m), 1502 (m), 1455 (m), 1435 (m), 1368 (m), 1235 (m), 1197 (m), 1917 (m), 736 (s), 701 (m), 625 (m). MS (EI, 70 eV): *m/z* (%) = 309 (22), 308 $[M]^+$ (100), 307 (30), 153 (5). HRMS (ESI): Calculated for $C_{22}H_{16}N_2$ $[M+H]^+$ 309.13862 found 309.13876.

6-Methyl-11-(4-(methylthio)phenyl)-11*H*-indolo[3,2-*c*]quinoline (11f): Yellow



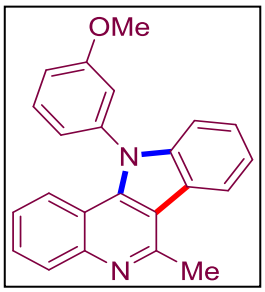
solid, mp. 170 - 171 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.32 - 8.26 (m, 1H, CH_{Ar}), 8.21 (d, ^3J = 8.0 Hz, 1H, CH_{Ar}), 7.61 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.51 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.47 - 7.37 (m, 5H, CH_{Ar}), 7.28 - 7.23 (m, 1H, CH_{Ar}), 7.23 - 7.17 (m, 1H, CH_{Ar}), 3.26 (s, 3H, $CH_{3\text{-quinoline}}$), 2.64 (s, 3H, SCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.8 (C_{Ar}), 146.0 (C_{Ar}), 142.0 (C_{Ar}), 140.9 (C_{Ar}), 140.1 (C_{Ar}), 135.1 (C_{Ar}), 129.2 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.3 ($2CH_{Ar}$), 125.4 (CH_{Ar}), 124.7 (CH_{Ar}), 122.4 (C_{Ar}), 121.8 ($2CH_{Ar}$), 121.7 ($2CH_{Ar}$), 116.6 (C_{Ar}), 114.3 (C_{Ar}), 110.7 (CH_{Ar}), 25.0 ($CH_{3\text{-quinoline}}$), 15.4 (SCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 2948 (w), 2918 (w), 1560 (w), 1496 (m), 1432 (m), 1363 (m), 1198 (m), 1087 (m), 737 (s), 626 (m), 511 (m). MS (EI, 70 eV): *m/z* (%) = 355 (27), 354 $[M]^+$ (100), 306 (10), 153 (6). HRMS (EI): Calculated for $C_{23}H_{18}N_2S$ $[M]^+$ 354.11852 found 354.11843.

11-(4-Methoxyphenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11g): Yellow solid,



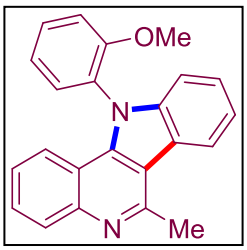
mp. 234 - 236 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.54 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 8.32 - 8.28 (m, 1H, CH_{Ar}), 7.68 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.6 Hz, ^{4}J = 1.7 Hz, 1H, CH_{Ar}), 7.51 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.45 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.38 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 1.7 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 7.32 (dd, ^{3}J = 6.7 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.25 - 7.17 (m, 3H, CH_{Ar}), 4.00 (s, 3H, OCH_3), 3.42 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.4 ($C_{Ar}OCH_3$), 154.5 ($C_{quinoline\text{-}Me}$), 144.9 (C_{Ar}), 142.4 (C_{Ar}), 140.5 (C_{Ar}), 130.7 (C_{Ar}), 129.9 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 125.6 (CH_{Ar}), 124.9 (CH_{Ar}), 122.2 (CH_{Ar}), 121.9 (CH_{Ar}), 121.9 (C_{Ar}), 121.7 (CH_{Ar}), 116.5 (C_{Ar}), 115.6 ($2CH_{Ar}$), 114.1 (CH_{Ar}), 113.9 (C_{Ar}), 110.9 (CH_{Ar}), 55.7 (OCH_3), 24.2 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3398 (w), 3056 (m), 3004 (w), 2958 (w), 2933 (m), 2837 (m), 2546 (m), 2198 (m), 2056 (w), 1891 (w), 1635 (m), 1606 (m), 1508 (s), 1435 (s), 1368 (m), 1296 (m), 1248 (s), 1198 (m), 1026 (m), 908 (m), 842 (m), 723 (s), 526 (m). MS (EI, 70 eV): *m/z* (%) = 338 $[M]^+$ (100), 323 (10), 294 (21), 147 (14). HRMS (EI): Calculated for $C_{23}H_{18}ON_2$ $[M]^+$ 338.14136 found 338.14096.

11-(3-Methoxyphenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11h): Yellow solid,



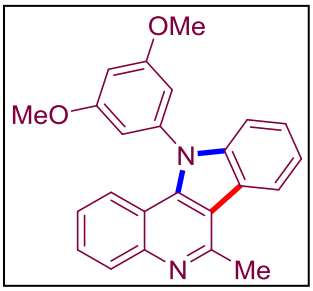
mp. 206 – 207 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.32 - 8.28 (m, 1H, CH_{Ar}), 8.22 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 7.64 - 7.60 (m, 1H, CH_{Ar}), 7.60 - 7.56 (m, 1H, CH_{Ar}), 7.50 - 7.41 (m, 2H, CH_{Ar}), 7.38 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 1.5 Hz, ^{5}J = 0.6 Hz, 1H, CH_{Ar}), 7.28 - 7.20 (m, 3H, CH_{Ar}), 7.13 (ddd, ^{3}J = 7.7 Hz, ^{4}J = 1.9 Hz, ^{5}J = 1.0 Hz, 1H, CH_{Ar}), 7.05 (t, ^{4}J = 2.2 Hz, 1H, CH_{Ar}), 3.85 (s, 3H, OCH_3), 3.28 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.1 ($C_{Ar}OCH_3$), 154.8 (C_{Ar}), 146.0 (C_{Ar}), 141.9 (C_{Ar}), 140.0 (C_{Ar}), 139.6 (C_{Ar}), 131.1 (CH_{Ar}), 129.2 (CH_{Ar}), 128.0 (CH_{Ar}), 125.4 (CH_{Ar}), 124.7 (CH_{Ar}), 122.4 (CH_{Ar}), 122.0 (C_{Ar}), 121.7 ($2CH_{Ar}$), 121.1 (CH_{Ar}), 116.6 (C_{Ar}), 115.7 (CH_{Ar}), 114.3 (C_{Ar}), 114.2 (CH_{Ar}), 110.8 (CH_{Ar}), 55.6 (OCH_3), 25.0 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3037 (w), 3008 (w), 2967 (w), 2837 (w), 1594 (m), 1494 (m), 1427 (m), 1364 (m), 1243 (m), 1029 (m), 860 (m), 793 (m), 737 (s), 709 (m), 635 (m). MS (EI, 70 eV): *m/z* (%) = 339 (25), 338 $[M]^+$ (100), 323 (6), 294 (12). HRMS (ESI): Calculated for $C_{23}H_{18}N_2O$ $[M+H]^+$ 339.14919 found 339.14961.

11-(2-Methoxyphenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11i): Brown oil.



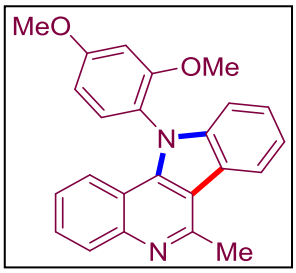
^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.36 - 8.25 (m, 2H, CH_{Ar}), 7.73 - 7.59 (m, 2H, CH_{Ar}), 7.52 (dd, ^{3}J = 7.7 Hz, ^{4}J = 1.7 Hz, 1H, CH_{Ar}), 7.49 - 7.45 (m, 2H, CH_{Ar}), 7.39 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 1.5 Hz, ^{5}J = 0.6 Hz, 1H, CH_{Ar}), 7.31 - 7.15 (m, 4H, CH_{Ar}), 3.60 (s, 3H, OCH_3), 3.33 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 156.5 ($C_{Ar}OCH_3$), 154.6 (C_{Ar}), 145.2 (C_{Ar}), 141.6 (C_{Ar}), 140.6 (C_{Ar}), 131.3 (CH_{Ar}), 130.4 (CH_{Ar}), 128.6 (CH_{Ar}), 128.1 (CH_{Ar}), 126.8 (C_{Ar}), 125.4 (CH_{Ar}), 124.8 (CH_{Ar}), 122.5 (C_{Ar}), 121.7 (CH_{Ar}), 121.7 (CH_{Ar}), 121.6 (CH_{Ar}), 121.2 (CH_{Ar}), 117.0 (C_{Ar}), 114.3 (C_{Ar}), 112.8 (CH_{Ar}), 110.7 (CH_{Ar}), 55.8 (OCH_3), 24.5 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3358 (m), 3056 (m), 3011 (m), 2939 (m), 2839 (m), 2563 (w), 1596 (m), 1559 (m), 1502 (s), 1455 (m), 1432 (m), 1366 (m), 1244 (m), 1118 (m), 1019 (m), 741 (s), 626 (m). MS (EI, 70 eV): *m/z* (%) = 338 $[M]^+$ (100), 323 (12), 293 (10). HRMS (EI): Calculated for $C_{23}H_{18}ON_2$ $[M]^+$ 338.14136 found 338.14102.

11-(3,5-Dimethoxyphenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11j): Yellow solid, mp. 203 - 204 °C.



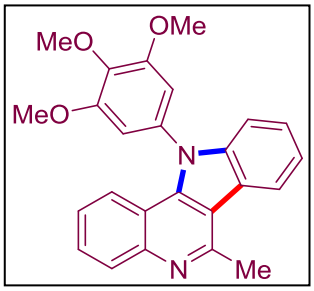
^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.33 - 8.27 (m, 1H, CH_{Ar}), 8.22 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 7.63 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.53 - 7.43 (m, 3H, CH_{Ar}), 7.34 - 7.24 (m, 2H, CH_{Ar}), 6.77 (t, ^{4}J = 2.3 Hz, 1H, CH_{Ar}), 6.68 (d, ^{4}J = 2.3 Hz, 2H, CH_{Ar}), 3.83 (s, 6H, OCH_3), 3.28 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 162.0 ($2C_{Ar}OCH_3$), 154.8 (C_{Ar}), 146.1 (C_{Ar}), 141.7 (C_{Ar}), 140.1 (C_{Ar}), 139.9 (C_{Ar}), 129.2 (CH_{Ar}), 127.9 (CH_{Ar}), 125.4 (CH_{Ar}), 124.7 (CH_{Ar}), 122.4 (C_{Ar}), 122.1 (CH_{Ar}), 121.7 ($2CH_{Ar}$), 116.5 (C_{Ar}), 114.3 (C_{Ar}), 110.8 (CH_{Ar}), 106.9 ($2CH_{Ar}$), 101.9 (CH_{Ar}), 55.7 ($2OCH_3$), 25.0 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3004 (m), 2966 (m), 2939 (m), 2858 (m), 1607 (m), 1582 (m), 1422 (m), 1192 (m), 1151 (s), 1060 (m), 989 (m), 854 (m), 745 (s), 724 (m), 633 (m). MS (EI, 70 eV): *m/z* (%) = 369 (27), 368 $[M]^+$ (100), 309 (7). HRMS (EI): Calculated for $C_{24}H_{20}O_2N_2$ $[M]^+$ 368.15193 found 368.15148.

11-(2,4-Dimethoxyphenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11k): White solid, mp. 137 - 138 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.33 - 8.26 (m, 1H, CH_{Ar}), 8.22 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 7.60 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.49 - 7.41 (m, 3H, CH_{Ar}), 7.39 (dd, ^{3}J = 8.0 Hz, ^{5}J = 0.9 Hz, 1H, CH_{Ar}), 7.24



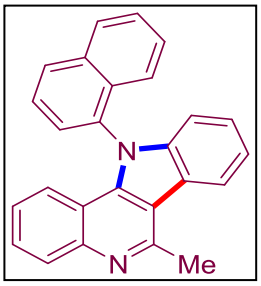
(ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.19 - 7.13 (m, 1H, CH_{Ar}), 6.74 (d, ^{3}J = 8.0 Hz, 2H, CH_{Ar}), 3.98 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.28 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 161.8 ($C_{Ar}OCH_3$), 157.4 ($C_{Ar}OCH_3$), 154.8 (C_{Ar}), 145.7 (C_{Ar}), 141.9 (C_{Ar}), 140.6 (C_{Ar}), 130.8 (CH_{Ar}), 128.9 (CH_{Ar}), 127.8 (CH_{Ar}), 125.2 (CH_{Ar}), 124.6 (C_{Ar}), 122.4 (C_{Ar}), 121.6 (C_{Ar}), 121.5 (CH_{Ar}), 121.2 (C_{Ar}), 119.8 (C_{Ar}), 117.2 (CH_{Ar}), 114.2 (CH_{Ar}), 110.6 (CH_{Ar}), 105.1 (CH_{Ar}), 100.2 (CH_{Ar}), 55.8 (OCH_3), 55.7 (OCH_3), 24.8 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): ṽ = 3369 (w), 3057 (w), 3011 (w), 2930 (w), 2838 (w), 2573 (w), 1605 (w), 1587 (m), 1510 (m), 1368 (m), 1285 (m), 1208 (m), 1159 (m), 1021 (m), 835 (m), 744 (s), 547 (m). MS (EI, 70 eV): *m/z* (%) = 369 (26), 368 $[M]^+$ (100), 293 (5), 281 (9), 147 (5). HRMS (EI): Calculated for $C_{24}H_{20}O_2N_2$ $[M]^+$ 368.15193 found 368.15197.

6-Methyl-11-(3,4,5-trimethoxyphenyl)-11*H*-indolo[3,2-*c*]quinoline (11l): White



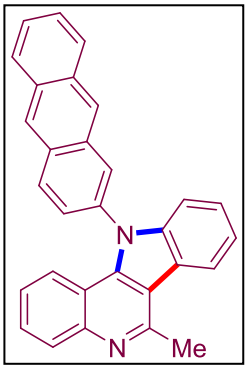
solid, mp. 201 - 202 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.33 - 8.28 (m, 1H, CH_{Ar}), 8.24 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 7.63 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.51 - 7.45 (m, 2H, CH_{Ar}), 7.43 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 1.5 Hz, ^{5}J = 0.6 Hz, 1H, CH_{Ar}), 7.34 - 7.28 (m, 2H, CH_{Ar}), 6.76 (s, 2H, CH_{Ar}), 4.06 (s, 3H, OCH_3), 3.84 (s, 6H, OCH_3), 3.29 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.8 (C_{Ar}), 154.6 ($2C_{Ar}OCH_3$), 145.8 (C_{Ar}), 142.0 (C_{Ar}), 140.1 (C_{Ar}), 138.8 (C_{Ar}), 133.8 (C_{Ar}), 129.0 (CH_{Ar}), 128.1 (CH_{Ar}), 125.5 (CH_{Ar}), 124.9 (CH_{Ar}), 122.3 (C_{Ar}), 121.9 (CH_{Ar}), 121.8 (CH_{Ar}), 121.7 (CH_{Ar}), 116.5 (C_{Ar}), 114.1 (C_{Ar}), 110.8 (CH_{Ar}), 106.0 ($2CH_{Ar}$), 61.2 (OCH_3), 56.4 ($2OCH_3$), 24.8 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): ṽ = 3049 (w), 2993 (w), 2939 (w), 2827 (w), 2454 (w), 1591 (m), 1503 (m), 1346 (w), 1227 (m), 1118 (s), 1000 (m), 747 (s). MS (EI, 70 eV): *m/z* (%) = 398 $[M]^+$ (100), 383 (22), 297 (8). HRMS (EI): Calculated for $C_{25}H_{22}O_3N_2$ $[M]^+$ 398.16249 found 398.16215.

6-Methyl-11-(naphthalen-1-yl)-11*H*-indolo[3,2-*c*]quinoline (11m): Red solid, mp. 197 - 198 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.38 (ddd, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 8.20 (d, ^{3}J = 8.4 Hz, 2H, CH_{Ar}), 8.07 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 7.82 - 7.66 (m, 2H, CH_{Ar}), 7.58 - 7.54 (m, 1H, CH_{Ar}), 7.53 - 7.49 (m, 1H, CH_{Ar}), 7.49 - 7.43 (m, 1H, CH_{Ar}), 7.38 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.2 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.27 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.2 Hz,



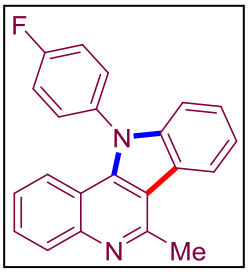
1H, CH_{Ar}), 7.10 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 7.02 - 6.99 (m, 1H, CH_{Ar}), 6.99 - 6.94 (m, 2H, CH_{Ar}), 3.35 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 155.0 (C_{Ar}), 146.1 (C_{Ar}), 142.2 (C_{Ar}), 140.8 (C_{Ar}), 135.0 (C_{Ar}), 134.7 (C_{Ar}), 131.1 (C_{Ar}), 130.2 (CH_{Ar}), 129.1 (CH_{Ar}), 128.5 (CH_{Ar}), 127.9 (CH_{Ar}), 127.8 (CH_{Ar}), 127.2 (CH_{Ar}), 127.2 (CH_{Ar}), 126.0 (CH_{Ar}), 125.5 (CH_{Ar}), 124.7 (CH_{Ar}), 122.8 (CH_{Ar}), 122.5 (CH_{Ar}), 121.8 (CH_{Ar}), 121.5 (CH_{Ar}), 116.6 (C_{Ar}), 114.4 (C_{Ar}), 111.0 (CH_{Ar}), 100.0 (C_{Ar}), 25.1 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3047 (m), 2889 (w), 2915 (w), 2849 (w), 1595 (w), 1560 (m), 1508 (m), 1433 (m), 1364 (m), 1240 (m), 1117 (m), 776 (m), 738 (s), 638 (m). MS (EI, 70 eV): *m/z* (%) = 359 (30), 358 $[M]^+$ (100), 357 (20), 178 (5). HRMS (ESI): Calculated for $C_{26}H_{18}N_2$ $[M+H]^+$ 359.15428 found 359.15493.

11-(Anthracen-2-yl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11n): Yellow solid,



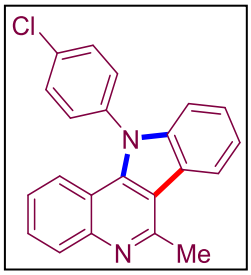
mp. 290 - 291 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.66 (d, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 8.54 (d, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 8.39 - 8.26 (m, 4H, CH_{Ar}), 8.17 - 8.02 (m, 2H, CH_{Ar}), 7.64 - 7.55 (m, 3H, CH_{Ar}), 7.53 - 7.40 (m, 4H, CH_{Ar}), 7.36 - 7.28 (m, 1H, CH_{Ar}), 7.11 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 3.35 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.7 (C_{Ar}), 142.1 (C_{Ar}), 140.3 (C_{Ar}), 135.1 (C_{Ar}), 132.6 (C_{Ar}), 132.4 (C_{Ar}), 131.3 (C_{Ar}), 131.2 (CH_{Ar}), 131.0 (C_{Ar}), 128.3 (CH_{Ar}), 128.2 ($2CH_{Ar}$), 127.9 ($2CH_{Ar}$), 127.2 (CH_{Ar}), 126.9 ($2CH_{Ar}$), 126.4 ($2CH_{Ar}$), 125.7 (C_{Ar}), 125.6 (CH_{Ar}), 124.9 (CH_{Ar}), 122.5 (C_{Ar}), 122.0 ($2CH_{Ar}$), 121.8 (CH_{Ar}), 116.6 (C_{Ar}), 114.5 (C_{Ar}), 110.9 (CH_{Ar}), 24.6 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3046 (w), 2911 (w), 1672 (m), 1582 (m), 1558 (m), 1430 (m), 1364 (m), 1289 (m), 736 (s), 636 (m), 468 (s). MS (EI, 70 eV): *m/z* (%) = 409 (32), 408 $[M]^+$ (100), 407 (54), 204 (11). HRMS (EI): Calculated for $C_{30}H_{20}N_2$ $[M]^+$ 408.16210 found 408.16132.

11-(4-Fluorophenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11o): Orange solid, mp. 226 - 227 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.38 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 8.32 - 8.24 (m, 1H, CH_{Ar}), 7.64 (dt, ^{3}J = 8.4 Hz, ^{4}J = 4.3 Hz, 1H, CH_{Ar}), 7.57 - 7.46 (m, 4H, CH_{Ar}), 7.45 - 7.36 (m, 2H, CH_{Ar}), 7.27 (m, 2H, CH_{Ar}), 7.22 - 7.15 (m, 1H, CH_{Ar}), 3.32 (s, 3H, $CH_{3\text{-quinoline}}$). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -110.0 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 163.1 (d, $^{1}J_{CF}$ = 250.8 Hz, $C_{Ar}F$), 154.3 (C_{Ar}),

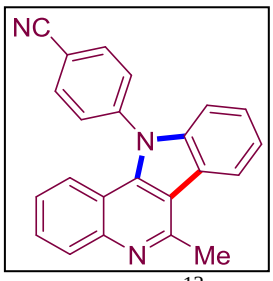


144.2 (C_{Ar}), 142.2 (C_{Ar}), 140.5 (C_{Ar}), 134.1 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 130.7 (d, $^3J_{CF}$ = 8.8 Hz, 2CH_{Ar}), 128.7 (CH_{Ar}), 128.0 (CH_{Ar}), 126.0 (CH_{Ar}), 125.3 (CH_{Ar}), 122.4 (CH_{Ar}), 122.3 (C_{Ar}), 121.8 (CH_{Ar}), 121.6 (CH_{Ar}), 117.7 (d, $^2J_{CF}$ = 22.8 Hz, 2CH_{Ar}), 116.2 (C_{Ar}), 114.2 (C_{Ar}), 110.8 (CH_{Ar}), 23.8 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3060 (w), 2465 (w), 2426 (w), 1886 (w), 1636 (w), 1585 (w), 1506 (m), 1436 (m), 1370 (m), 1220 (m), 1198 (m), 845 (m), 756 (m), 738 (m), 521 (m). MS (EI, 70 eV): *m/z* (%) = 327 (23), 326 $[M]^+$ (100), 325 (28). HRMS (EI): Calculated for $C_{22}H_{15}N_2F$ $[M]^+$ 326.12138 found 326.12098.

11-(4-Chlorophenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11p): Yellow solid, mp. 261 - 262 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.59 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.34 - 8.24 (m, 1H, CH_{Ar}), 7.76 - 7.66 (m, 3H, CH_{Ar}), 7.58 - 7.47 (m, 4H, CH_{Ar}), 7.38 - 7.32 (m, 2H, CH_{Ar}), 7.24 - 7.17 (m, 1H, CH_{Ar}), 3.43 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 153.8 (C_{Ar}), 149.7 (C_{Ar}), 146.0 (C_{Ar}), 142.2 (CH_{Ar}), 140.7 (C_{Ar}), 136.3 (C_{Ar}), 136.2 (C_{Ar}), 131.0 (2CH_{Ar}), 130.1 (2CH_{Ar}), 129.5 (CH_{Ar}), 126.6 (CH_{Ar}), 126.1 (CH_{Ar}), 123.0 (CH_{Ar}), 122.2 (C_{Ar}), 121.9 (CH_{Ar}), 121.7 (CH_{Ar}), 115.8 (C_{Ar}), 114.2 (C_{Ar}), 111.0 (CH_{Ar}), 22.8 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3050 (w), 2453 (m), 1876 (w), 1584 (w), 1493 (m), 1433 (m), 1368 (m), 1198 (m), 1085 (m), 1013 (m), 843 (m), 740 (s), 626 (m), 508 (m). MS (EI, 70 eV): *m/z* (%) = 342 $[M]^+$ (100), 306 (8), 153 (14). HRMS (EI): Calculated for $C_{22}H_{15}N_2Cl$ $[M]^+$ 342.09183 found 342.09087, calculated for $C_{22}H_{15}N_2{}^{37}Cl$ $[M]^+$ 344.08888 found 344.08934.

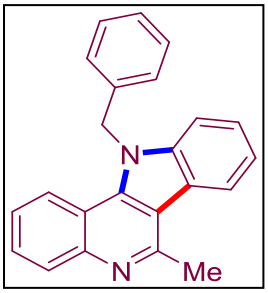


4-(6-Methyl-11*H*-indolo[3,2-*c*]quinolin-11-yl)benzonitrile (11q): White solid, mp. 221 - 222 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.35 - 8.26 (m, 1H, CH_{Ar}), 8.22 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.01 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.70 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.62 (ddd, ^3J = 8.4 Hz, ^3J = 6.6 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.53 - 7.44 (m, 2H, CH_{Ar}), 7.30 - 7.13 (m, 3H, CH_{Ar}), 3.25 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.9 (C_{Ar}), 146.0 (C_{Ar}), 142.8 (C_{Ar}), 141.3 (C_{Ar}), 139.7 (C_{Ar}), 134.3 (2CH_{Ar}), 130.0 (2CH_{Ar}), 129.5 (CH_{Ar}), 128.3 (CH_{Ar}), 125.9 (CH_{Ar}), 125.0 (CH_{Ar}), 122.8 (C_{Ar}), 122.4 (CH_{Ar}), 122.1 (CH_{Ar}), 121.3 (CH_{Ar}), 117.8 (C_{Ar}), 116.1 (C_{Ar}), 115.0 (C_{Ar}), 113.6 (C_{Ar}), 110.2 (CH_{Ar}), 24.9 ($CH_{3\text{-quinoline}}$).



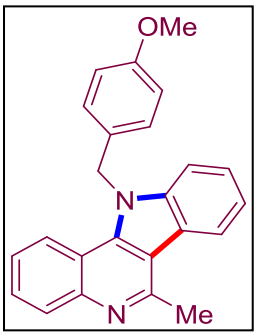
IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3033 (w), 2992 (w), 2919 (w), 2654 (w), 2475 (w), 2226 (w), 1602 (w), 1561 (m), 1431 (m), 1363 (m), 1228 (m), 1198 (m), 1117 (w), 733 (s), 626 (m), 547 (m). MS (EI, 70 eV): *m/z* (%) = 334 (23), 333 $[M]^+$ (100), 331 (23). HRMS (EI): Calculated for $C_{23}H_{15}N_3$ $[M]^+$ 333.12605 found 333.12566.

11-Benzyl-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11r): Yellow oil. ^{1}H NMR



(250 MHz, Chloroform-*d*) δ = 8.32 - 8.23 (m, 2H, CH_{Ar}), 8.15 (ddd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.64 (ddd, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.55 - 7.52 (m, 1H, CH_{Ar}), 7.52 - 7.51 (m, 1H, CH_{Ar}), 7.50 - 7.44 (m, 1H, CH_{Ar}), 7.39 (ddd, ^3J = 8.6 Hz, ^3J = 7.1 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.33 - 7.28 (m, 3H, CH_{Ar}), 7.19 - 7.14 (m, 2H, CH_{Ar}), 5.95 (s, 2H, $CH_{2\text{-aliphatic}}$), 3.23 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.7 (C_{Ar}), 145.9 (C_{Ar}), 140.8 (C_{Ar}), 140.0 (C_{Ar}), 136.2 (CH_{Ar}), 129.3 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 128.0 (CH_{Ar}), 127.8 (CH_{Ar}), 125.8 ($2CH_{Ar}$), 125.6 (CH_{Ar}), 125.1 (CH_{Ar}), 122.5 (CH_{Ar}), 122.0 (CH_{Ar}), 121.7 (CH_{Ar}), 121.7 (CH_{Ar}), 116.6 (C_{Ar}), 114.3 (C_{Ar}), 109.7 (CH_{Ar}), 49.4 (CH_2), 24.8 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3031 (m), 2921 (m), 2852 (m), 1561 (m), 1513 (m), 1441 (m), 1350 (m), 1239 (m), 1122 (m), 738 (s), 724 (s), 689 (m), 470 (m). MS (EI, 70 eV): *m/z* (%) = 323 (16), 322 $[M]^+$ (63), 231 (15), 204 (7), 91 (100), 65 (12). HRMS (EI): Calculated for $C_{23}H_{18}N_2$ $[M]^+$ 322.14645 found 322.14659.

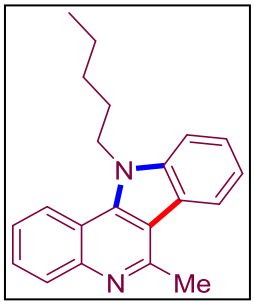
11-(4-Methoxybenzyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11s): Yellow solid,



mp. 168 - 169 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.29 (dt, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 2H, CH_{Ar}), 8.20 (ddd, ^3J = 8.5 Hz, ^4J = 1.4 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.66 (ddd, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.57 - 7.52 (m, 2H, CH_{Ar}), 7.50 - 7.38 (m, 2H, CH_{Ar}), 7.09 (m, 2H, CH_{Ar}), 6.84 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 5.93 (s, 2H, $CH_{2\text{-aliphatic}}$), 3.74 (s, 3H, OCH_3), 3.26 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.2 ($C_{Ar}OCH_3$), 154.5 (C_{Ar}), 145.5 (C_{Ar}), 140.8 (C_{Ar}), 140.0 (C_{Ar}), 129.0 (CH_{Ar}), 128.1 (CH_{Ar}), 128.0 (C_{Ar}), 127.0 ($2CH_{Ar}$), 125.6 (CH_{Ar}), 125.3 (CH_{Ar}), 122.4 (C_{Ar}), 122.0 (CH_{Ar}), 121.8 (CH_{Ar}), 121.7 (CH_{Ar}), 116.6 (C_{Ar}), 114.6 ($2CH_{Ar}$), 114.2 (C_{Ar}), 109.8 (CH_{Ar}), 55.3 (OCH_3), 48.9 (CH_2), 24.6 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3059 (w), 3002 (w), 2962 (w), 2936 (w), 2907 (w), 2830 (w), 2641 (w), 1613 (w), 1560 (w), 1511 (m), 1439 (m), 1242 (m), 1164 (w), 1024 (m), 808 (m), 741 (s), 506 (m). MS (EI, 70 eV):

m/z (%) = 352 $[M]^+$ (25), 122 (12), 121 (100), 95 (5), 78 (8). HRMS (EI): Calculated for $C_{24}H_{20}ON_2$ $[M]^+$ 352.15701 found 352.15643.

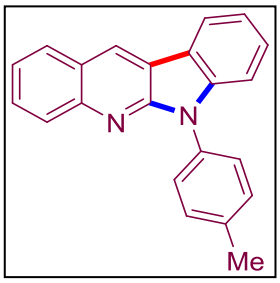
6-Methyl-11-pentyl-11*H*-indolo[3,2-*c*]quinoline (11t): Yellow oil. ^{1}H NMR



(250 MHz, Chloroform-*d*) δ = 8.35 (dd, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 8.28 (dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.23 (dt, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.71 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.63 - 7.51 (m, 3H, CH_{Ar}), 7.42 (ddd, ^3J = 8.0 Hz, ^3J = 6.0 Hz, ^4J = 2.2 Hz, 1H, CH_{Ar}), 4.74 - 4.60 (m, 2H, $CH_{2\text{-aliphatic}}$), 3.18 (s, 3H, $CH_{3\text{-quinoline}}$), 2.03 (p, ^3J = 7.7 Hz, 2H, $CH_{2\text{-aliphatic}}$), 1.60 - 1.34 (m, 4H, $CH_{2\text{-aliphatic}}$), 0.94 (t, ^3J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.7 (C_{Ar}), 145.9 (C_{Ar}), 140.1 (C_{Ar}), 139.1 (C_{Ar}), 129.6 (CH_{Ar}), 127.7 (CH_{Ar}), 125.1 (CH_{Ar}), 125.0 (CH_{Ar}), 122.2 (CH_{Ar}), 121.9 (C_{Ar}), 121.5 (CH_{Ar}), 121.1 (CH_{Ar}), 116.9 (C_{Ar}), 114.1 (C_{Ar}), 109.4 (CH_{Ar}), 45.7 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 24.8 ($CH_{3\text{-quinoline}}$), 22.4 (CH_2), 14.0 (CH_3). IR (ATR, cm^{-1}): ṽ =3054 (w), 2950 (m), 2923 (m), 2853 (w), 1560 (m), 1439 (m), 1364 (m), 1251 (m), 1161 (m), 1111 (m), 1029 (w), 736 (s), 621 (m). MS (EI, 70 eV): *m/z* (%) = 303 (13), 302 $[M]^+$ (52), 246 (19), 245 (100), 204 (10). HRMS (EI): Calculated for $C_{21}H_{22}N_2$ $[M]^+$ 302.17775 found 302.17686.

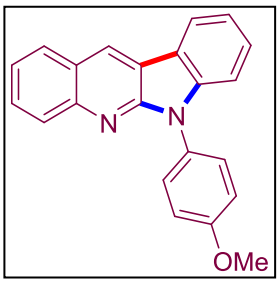
5.2.3.3.Indolo[2,3-b]quinolines

6-(*p*-Tolyl)-6*H*-indolo[2,3-*b*]quinoline (12a): White solid, mp. 135 - 137 °C. ^{1}H NMR

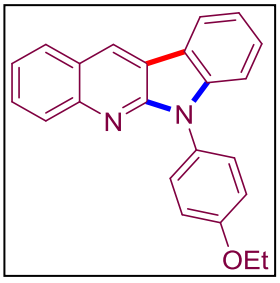


(300 MHz, Chloroform-*d*) δ = 8.79 (s, 1H, $CH_{pyridine}$), 8.21 (dd, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 8.09 (dd, ^3J = 8.4 Hz, ^3J = 1.2 Hz, 1H, CH_{Ar}), 8.02 (dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.72 - 7.61 (m, 3H, CH_{Ar}), 7.53 - 7.42 (m, 5H, CH_{Ar}), 7.38 - 7.34 (m, 1H, CH_{Ar}), 2.51 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.9 (C_{Ar}), 147.0 (C_{Ar}), 142.9 (C_{Ar}), 137.5 (C_{Ar}), 133.8 (C_{Ar}), 130.4 (2CH_{Ar}), 128.8 (CH_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 128.2 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (2CH_{Ar}), 124.7 (C_{Ar}), 123.4 (CH_{Ar}), 121.5 (CH_{Ar}), 120.9 (C_{Ar}), 120.8 (CH_{Ar}), 118.5 (C_{Ar}), 110.3 (CH_{Ar}), 21.5 (CH_3). IR (ATR, cm^{-1}): ṽ = 3064 (w), 3033 (w), 2958 (w), 2918 (w), 2851 (w), 1602 (m), 1516 (m), 1460 (m), 1407 (m), 1226 (m), 897 (m), 740 (s), 596 (m), 475 (m). MS (EI, 70 eV): *m/z* (%) = 309 (22), 308 $[M]^+$ (100), 307 (86), 292 (13). HRMS (ESI): Calculated for $C_{22}H_{16}N_2$ $[M+H]^+$ 309.13862 found 309.13878.

6-(4-Methoxyphenyl)-6*H*-indolo[2,3-*b*]quinoline (12b): Pale yellow solid, mp. 182 - 184 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.80 (s, 1H, $CH_{pyridine}$), 8.21 (d, ^{3}J = 7.3 Hz, 1H, CH_{Ar}), 8.10 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 8.03 (dd, ^{3}J = 8.0 Hz, ^{3}J = 1.6 Hz, 1H, CH_{Ar}), 7.73 - 7.60 (m, 3H, CH_{Ar}), 7.55 - 7.49 (m, 1H, CH_{Ar}), 7.49 - 7.43 (m, 1H, CH_{Ar}), 7.40 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 7.36 - 7.31 (m, 1H, CH_{Ar}), 7.16 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 3.94 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.1 (C_{Ar}), 143.2 (C_{Ar}), 129.1 (C_{Ar}), 129.0 ($2C_{Ar}$), 129.0 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.3 (CH_{Ar}), 128.1 (CH_{Ar}), 127.8 (CH_{Ar}), 124.7 (C_{Ar}), 124.7 (C_{Ar}), 123.5 (CH_{Ar}), 121.5 (CH_{Ar}), 120.9 (CH_{Ar}), 120.8 (CH_{Ar}), 118.6 (C_{Ar}), 115.1 ($2CH_{Ar}$), 110.3 (CH_{Ar}), 55.7 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ =3050 (w), 3033 (w), 3015 (w), 2955 (w), 2918 (w), 1602 (m), 1516 (m), 1461 (m), 1408 (m), 1227 (m), 1176 (m), 1024 (m), 742 (s), 598 (m), 476 (m). MS (EI, 70 eV): *m/z* (%) = 325 (24), 324 $[M]^+$ (100), 323 (29), 309 (33), 281 (16), 280 (13), 279 (13), 218 (10), 140 (12). HRMS (ESI): Calculated for $C_{22}H_{16}N_2O$ $[M+H]^+$ 325.13354 found 325.13339.



6-(4-Ethoxyphenyl)-6*H*-indolo[2,3-*b*]quinoline (12c): White solid, mp. 165 - 166 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.78 (s, 1H, $CH_{pyridine}$), 8.20 (dt, ^{3}J = 7.6 Hz, ^{4}J = 1.0 Hz, 1H, CH_{Ar}), 8.10 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 8.02 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.68 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.62 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.55 - 7.49 (m, 1H, CH_{Ar}), 7.49 - 7.44 (m, 1H, CH_{Ar}), 7.46 - 7.38 (m, 1H, CH_{Ar}), 7.34 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.15 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 4.16 (q, ^{3}J = 7.0 Hz, 2H, OCH_2), 1.51 (t, ^{3}J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.4 (C_{Ar}), 153.1 (C_{Ar}), 147.0 (C_{Ar}), 143.2 (C_{Ar}), 128.9 (C_{Ar}), 128.9 ($2CH_{Ar}$), 128.8 (CH_{Ar}), 128.8 (C_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 128.2 (CH_{Ar}), 127.5 (CH_{Ar}), 124.7 (C_{Ar}), 123.4 (CH_{Ar}), 121.5 (CH_{Ar}), 120.8 (CH_{Ar}), 118.4 (C_{Ar}), 115.5 ($2CH_{Ar}$), 110.2 (CH_{Ar}), 63.9 (OCH_2), 15.0 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3044 (w), 2981 (w), 2934 (w), 2876 (w), 2738 (w), 1603 (m), 1514 (m), 1473 (m), 1407 (m), 1224 (m), 1112 (m), 1041 (m), 742 (s), 587 (m). MS (EI, 70 eV): *m/z* (%) = 339 (24), 338 $[M]^+$ (100), 310 (29), 309 (94), 281 (31), 280 (24), 279 (26), 218 (19), 29 (24). HRMS (ESI): Calculated for $C_{23}H_{18}N_2O$ $[M+H]^+$ 339.14919 found 339.14919.

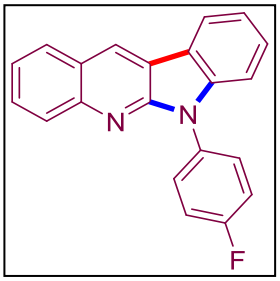


6-(3,5-Dimethoxyphenyl)-6*H*-indolo[2,3-*b*]quinoline (12d): White solid, mp. 143 - 145 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.79 (s, 1H, CH_{Ar}), 8.20 (ddd, ^{3}J = 7.7 Hz, ^{4}J = 1.3 Hz, ^{4}J = 0.8 Hz, 1H, CH_{Ar}), 8.12 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 8.02 (ddd, ^{3}J = 8.7 Hz, ^{4}J = 1.5 Hz, ^{5}J = 0.6 Hz, 1H, CH_{Ar}), 7.69 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.57 (ddd, ^{3}J = 8.2 Hz, ^{4}J = 1.5 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 7.55 - 7.50 (m, 1H, CH_{Ar}), 7.50 - 7.45 (m, 1H, CH_{Ar}), 7.35 (ddd, ^{3}J = 7.6 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 6.95 (d, ^{4}J = 2.3 Hz, 2H, CH_{Ar}), 6.61 (t, ^{4}J = 2.3 Hz, 1H, CH_{Ar}), 3.88 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.5 ($2C_{Ar}OCH_3$), 152.7 (C_{Ar}), 147.0 (C_{Ar}), 142.6 (C_{Ar}), 138.0 (C_{Ar}), 128.9 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 127.6 (CH_{Ar}), 124.8 (C_{Ar}), 123.6 (CH_{Ar}), 121.5 (CH_{Ar}), 121.0 (C_{Ar}), 121.0 (CH_{Ar}), 118.5 (C_{Ar}), 110.6 (CH_{Ar}), 105.8 ($2CH_{Ar}$), 100.2 (CH_{Ar}), 55.7 ($2OCH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2998 (w), 2931 (w), 2833 (w), 1593 (m), 1460 (m), 1405 (m), 1221 (m), 1193 (m), 1148 (m), 1063 (m), 1016 (m), 782 (m), 731 (s), 685 (m), 574 (m), 473 (m). MS (EI, 70 eV): *m/z* (%) = 355 (24), 354 $[M]^+$ (100), 353 (83), 325 (14), 324 (31), 281 (14), 280 (10), 279 (12), 267 (22), 218 (23), 190 (10). HRMS (ESI): Calculated for $C_{23}H_{18}N_2O_2$ $[M+H]^+$ 355.14410 found 355.14436.

6-(Naphthalen-1-yl)-6*H*-indolo[2,3-*b*]quinoline (12e): Pale yellow solid, mp. 155 - 157 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.89 (d, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 8.28 (dd, ^{3}J = 7.3 , ^{5}J = 0.9 Hz, 1H, CH_{Ar}), 8.12 - 8.07 (m, 1H, CH_{Ar}), 8.07 - 8.01 (m, 2H, CH_{Ar}), 7.99 (d, ^{3}J = 8.7 Hz, 1H, CH_{Ar}), 7.79 - 7.69 (m, 2H, CH_{Ar}), 7.64 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.57 - 7.49 (m, 1H, CH_{Ar}), 7.46 (dt, ^{3}J = 6.8 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.46 - 7.25 (m, 4H, CH_{Ar}), 6.96 (dt, ^{3}J = 8.1 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 153.8 (C_{Ar}), 146.9 (C_{Ar}), 144.0 (C_{Ar}), 135.1 (C_{Ar}), 133.0 (C_{Ar}), 131.1 (C_{Ar}), 129.5 (CH_{Ar}), 129.0 (CH_{Ar}), 128.7 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.2 (CH_{Ar}), 127.9 (CH_{Ar}), 127.6 (CH_{Ar}), 127.0 (CH_{Ar}), 126.7 (CH_{Ar}), 126.2 (CH_{Ar}), 124.7 (C_{Ar}), 123.7 (CH_{Ar}), 123.6 (CH_{Ar}), 122.2 (C_{Ar}), 121.5 (CH_{Ar}), 121.0, 120.8 (CH_{Ar}), 118.6 (C_{Ar}), 110.8 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3050 (w), 2957 (w), 2922 (m), 2851 (w), 1600 (m), 1468 (m), 1409 (m), 1224 (m), 1015 (m), 741 (s), 587 (m), 478 (m). MS (EI, 70 eV):

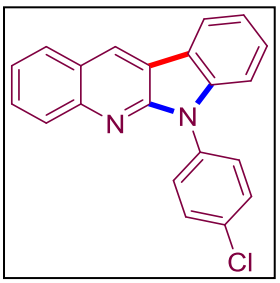
m/z (%) = 345 (13), 344 $[M]^+$ (61), 343 (100), 342 (31), 172 (11). HRMS (ESI): Calculated for $C_{25}H_{16}N_2$ $[M+H]^+$ 345.13862 found 345.13882.

6-(4-Fluorophenyl)-6*H*-indolo[2,3-*b*]quinoline (12f): Pale yellow solid,



mp. 166 - 167 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.79 (s, 1H, CH_{Ar}), 8.21 (dt, ^3J = 7.6 Hz, ^4J = 0.9 Hz, 1H, CH_{Ar}), 8.08 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.03 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.77 - 7.65 (m, 3H, CH_{Ar}), 7.51 (m, 2H, CH_{Ar}), 7.42 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.40 - 7.30 (m, 3H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.8 (d, $^1J_{CF}$ = 246.9 Hz, CF_{Ar}), 152.8 (C_{Ar}), 146.9 (C_{Ar}), 142.7 (C_{Ar}), 132.4 (d, $^4J_{CF}$ = 3.1 Hz, C_{Ar}), 129.4 (CH_{Ar}), 129.3 (d, $^3J_{CF}$ = 8.5 Hz, $2CH_{Ar}$), 128.5 (CH_{Ar}), 128.3 (CH_{Ar}), 128.2 (CH_{Ar}), 127.7 (CH_{Ar}), 124.8 (C_{Ar}), 123.7 (CH_{Ar}), 121.6 (CH_{Ar}), 121.1 (CH_{Ar}), 121.0 (C_{Ar}), 118.4 (C_{Ar}), 116.7 (d, $^2J_{CF}$ = 22.8 Hz, $2CH_{Ar}$), 110.1 (CH_{Ar}). IR (ATR, cm^{-1}): ṽ = 3053 (w), 1604 (m), 1510 (m), 1461 (m), 1403 (m), 1220 (m), 1159 (m), 839 (m), 783 (m), 732 (s), 595 (m), 509 (m), 446 (m). MS (EI, 70 eV): *m/z* (%) = 313 (21), 312 $[M]^+$ (99), 311 (100), 310 (19; 156 (12), 75 (16). HRMS (ESI): Calculated for $C_{21}H_{13}FN_2$ $[M+H]^+$ 313.11355 found 313.11384.

6-(4-Chlorophenyl)-6*H*-indolo[2,3-*b*]quinoline (12g): Pale yellow solid,



mp. 193 - 195 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.77 (s, 1H, CH_{Ar}), 8.20 (dd, ^3J = 7.7 Hz, ^4J = 0.9 Hz, 1H, CH_{Ar}), 8.08 (dd, ^3J = 8.7 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.02 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.76 - 7.66 (m, 3H, CH_{Ar}), 7.65 - 7.57 (m, 2H, CH_{Ar}), 7.59 - 7.48 (m, 1H, CH_{Ar}), 7.51 - 7.43 (m, 2H, CH_{Ar}), 7.43 - 7.31 (m, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.5 (C_{Ar}), 146.9 (C_{Ar}), 142.3 (C_{Ar}), 135.0 (C_{Ar}), 133.1 (C_{Ar}), 129.9 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.2 (CH_{Ar}), 127.7 (CH_{Ar}), 124.9 (C_{Ar}), 123.7 (CH_{Ar}), 121.7 (CH_{Ar}), 121.3 (CH_{Ar}), 121.1 (C_{Ar}), 118.5 (C_{Ar}), 110.1 (CH_{Ar}). IR (ATR, cm^{-1}): ṽ = 3421 (w). 3044 (w), 2959 (w), 2923 (w), 2852 (w), 1601 (m), 1496 (m), 1405 (m), 1223 (m), 1088 (m), 1014 (m), 740 (s), 586 (m). MS (EI, 70 eV): *m/z* (%) = 330 (33), 329 (45), 328 $[M]^+$ (100), 327 (74), 293 (19), 292 (37), 291 (13), 146 (30), 75 (16). HRMS (ESI): Calculated for $C_{21}H_{13}ClN_2$ $[M+H]^+$ 329.0840 found 329.08391, calculated for $C_{21}H_{13}N_2Cl$ $[M]^+$ 328.07618 found 328.07527, calculated for $C_{21}H_{13}N_2{}^{37}Cl$ $[M]^+$ 330.07323 found 330.07376.

6-(4-Methoxybenzyl)-6*H*-indolo[2,3-*b*]quinoline (12h): Pale yellow solid, mp. 157 - 159 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.76 (s, 1H), 8.17 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 8.16 (ddd, ^{3}J = 7.7 Hz, ^{4}J = 1.2 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 8.03 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.53 - 7.48 (m, 1H, CH_{Ar}), 7.48 - 7.44 (m, 1H, CH_{Ar}), 7.34 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 7.35 - 7.27 (m, 2H, CH_{Ar}), 7.30 - 7.27 (m, 1H, CH_{Ar}), 6.80 (d, ^{3}J = 8.6 Hz, 2H, CH_{Ar}), 5.72 (s, 2H, $CH_{2\text{-benzyl}}$), 3.74 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.1 (C_{Ar}), 142.2 (C_{Ar}), 129.5 (C_{Ar}), 129.0 (CH_{Ar}), 128.8 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 128.2 (CH_{Ar}), 127.8 (C_{Ar}), 127.7 (CH_{Ar}), 124.5 (C_{Ar}), 123.2 (CH_{Ar}), 121.6 (CH_{Ar}), 121.1 (CH_{Ar}), 120.8 (C_{Ar}), 120.3 (CH_{Ar}), 120.2 (C_{Ar}), 118.4 (C_{Ar}), 114.2 ($2CH_{Ar}$), 109.9 (CH_{Ar}), 55.4 (OCH_3), 44.7 ($CH_{2\text{-aliphatic}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053 (w), 3033 (w), 3002 (w), 2957 (w), 2929 (w), 2838 (w), 2552 (w), 1605 (m), 1514 (m), 1467 (m), 1403 (m), 1244 (m), 1203 (m), 1116 (m), 1031 (m), 742 (s), 475 (m). MS (EI, 70 eV): *m/z* (%) = 339 (16), 338 $[M]^+$ (67), 337 (14), 323 (10), 190 (11), 121 (100), 78 (10). HRMS (ESI): Calculated for $C_{23}H_{18}N_2O$ $[M+H]^+$ 339.14919 found 339.14898.

5.2.4. Synthesis of benzo[*a*]carbazoles by sequential regioselective Suzuki reaction/double C-N coupling

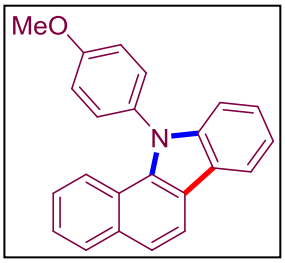
5.2.4.1. Starting material for double C-N coupling

1-Bromo-2-(2-bromophenyl)naphthalene (14): Colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.29 (dd, ^{3}J = 8.4 Hz, ^{4}J = 0.7 Hz, 1H, CH_{Ar}), 7.81 - 7.69 (m, 1H, CH_{Ar}), 7.60 (dd, ^{3}J = 7.9 Hz, ^{4}J = 0.9 Hz, 1H, CH_{Ar}), 7.52 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.45 (ddd, ^{3}J = 8.1 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.33 - 7.26 (m, 1H, CH_{Ar}), 7.24 - 7.19 (m, 3H, CH_{Ar}), 7.19 - 7.10 (m, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.1 (C_{Ar}), 140.2 (C_{Ar}), 134.0 (C_{Ar}), 132.7 (CH_{Ar}), 132.4 (C_{Ar}), 131.2 (CH_{Ar}), 129.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.0 (CH_{Ar}), 127.9 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 127.3 (CH_{Ar}), 127.0 (CH_{Ar}), 123.6 (C_{Ar}), 123.5 (C_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 2924 (w), 1425 (m), 1321 (m), 1021 (m), 954 (m), 817 (m), 750 (s), 654 (m), 527 (m), 455 (m). MS (EI, 70 eV): *m/z* (%) = 364 (21), 362 (42), 360 (21), 293 (25), 281 (24), 203 (16), 202 (100), 201 (25), 200 (36), 101 (22), 100 (13). HRMS (EI): Calculated for $C_{16}H_{10}Br_2$ $[M]^+$ 359.91438 found 359.91420, calculated for $C_{16}H_{10}Br^{81}Br$ $[M]^+$

361.91233 found 361.91190, calculated for $C_{16}H_{10}{}^{81}Br_2$ $[M]^+$ 363.91028 found 363.91017.

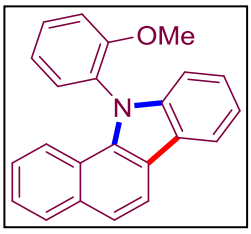
5.2.4.2.Benzo[*a*]carbazoles

11-(4-Methoxyphenyl)-11*H*-benzo[*a*]carbazole (15a): Colorless solid,



mp. 198 - 200 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.13 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.11 - 8.07 (m, 1H, CH_{Ar}), 7.89 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.61 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.40 (dd, ^3J = 8.5 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.38 - 7.30 (m, 3H, CH_{Ar}), 7.30 - 7.21 (m, 2H, CH_{Ar}), 7.18 - 7.11 (m, 1H, CH_{Ar}), 7.10 - 7.03 (m, 3H, CH_{Ar}), 3.87 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.9 (C_{Ar}), 142.5 (C_{Ar}), 135.8 (C_{Ar}), 133.6 (C_{Ar}), 132.7 (C_{Ar}), 130.3 ($2CH_{Ar}$), 129.2 (CH_{Ar}), 125.1 (CH_{Ar}), 125.0 (CH_{Ar}), 124.8 (CH_{Ar}), 123.3 (C_{Ar}), 122.3 (CH_{Ar}), 122.2 (C_{Ar}), 121.1 (CH_{Ar}), 120.3 (CH_{Ar}), 119.6 (CH_{Ar}), 119.34 (C_{Ar}), 119.2 (CH_{Ar}), 115.4 ($2CH_{Ar}$), 110.5 (CH_{Ar}), 55.8 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 3008 (w), 2956 (w), 2928 (w), 2834 (w), 1509 (m), 1439 (m), 1248 (m), 1224 (m), 1024 (m), 812 (m), 747 (s), 621 (m), 553 (m). MS (EI, 70 eV): *m/z* (%) = 324 (24), 323 $[M]^+$ (100), 308 (11), 279 (17), 278 (23), 139 (10). HRMS (EI): Calculated for $C_{23}H_{17}ON$ $[M]^+$ 323.13047 found 323.13082.

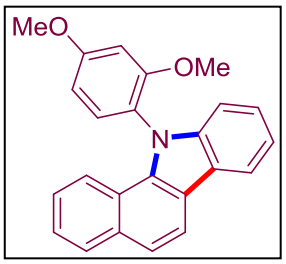
11-(2-Methoxyphenyl)-11*H*-benzo[*a*]carbazole (15b): Yellow oil. ^{1}H NMR



(250 MHz, Chloroform-*d*) δ = 8.24 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.22 - 8.17 (m, 1H, CH_{Ar}), 7.98 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.70 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.62 (ddd, ^3J = 8.4 Hz, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.50 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.51 - 7.46 (m, 1H, CH_{Ar}), 7.45 - 7.40 (m, 1H, CH_{Ar}), 7.39 - 7.32 (m, 2H, CH_{Ar}), 7.26 - 7.18 (m, 3H, CH_{Ar}), 7.13 - 7.07 (m, 1H, CH_{Ar}), 3.60 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 157.0 (C_{Ar}), 141.7 (C_{Ar}), 135.7 (C_{Ar}), 133.4 (C_{Ar}), 131.0 (CH_{Ar}), 130.6 (CH_{Ar}), 129.1 (CH_{Ar}), 128.6 (C_{Ar}), 125.1 (CH_{Ar}), 124.9 (CH_{Ar}), 124.7 (CH_{Ar}), 123.5 (C_{Ar}), 122.6 (C_{Ar}), 121.68 (CH_{Ar}), 121.5 (CH_{Ar}), 120.9 (CH_{Ar}), 120.2 (CH_{Ar}), 119.6 (CH_{Ar}), 119.4 (C_{Ar}), 119.3 (CH_{Ar}), 112.9 (CH_{Ar}), 110.4 (CH_{Ar}), 56.0 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3078 (w), 3016 (w), 2959 (w), 2930 (w), 2836 (w), 1594 (w), 1503 (m), 1460 (m), 1404 (m), 1274 (m), 1224 (m), 1120 (m), 1023 (m), 811 (m), 742 (s), 439 (m). MS (EI, 70 eV): *m/z* (%) = 324 (26), 323 $[M]^+$

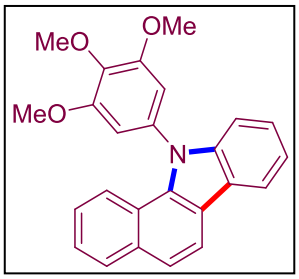
(100), 308 (20), 307 (20), 279 (12), 278 (25). HRMS (ESI): Calculated for $C_{23}H_{17}ON$ $[M+H]^+$ 324.13829 found 324.13865.

11-(2,4-Dimethoxyphenyl)-11*H*-benzo[*a*]carbazole (15c): White solid,



mp. 156 - 158 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.23 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.19 (ddd, ^3J = 7.4 Hz, ^4J = 1.6 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 7.98 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.69 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.58 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.46 - 7.42 (m, 1H, CH_{Ar}), 7.40 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.36 - 7.34 (m, 1H, CH_{Ar}), 7.33 - 7.27 (m, 1H, CH_{Ar}), 7.14 - 7.09 (m, 1H, CH_{Ar}), 3.98 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.4 (C_{Ar}), 157.9 (C_{Ar}), 142.0 (C_{Ar}), 135.9 (C_{Ar}), 133.4 (C_{Ar}), 131.3 (CH_{Ar}), 129.1 (CH_{Ar}), 125.1 (CH_{Ar}), 124.8 (CH_{Ar}), 124.7 (CH_{Ar}), 123.4 (C_{Ar}), 122.6 (C_{Ar}), 121.7 (CH_{Ar}), 121.5 (C_{Ar}), 120.7 (CH_{Ar}), 120.1 (CH_{Ar}), 119.5 (CH_{Ar}), 119.3 (CH_{Ar}), 119.2 (C_{Ar}), 110.4 (CH_{Ar}), 105.1 (CH_{Ar}), 100.3 (CH_{Ar}), 56.0 (OCH_3), 55.8 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3378 (w), 3026 (w), 2858 (w), 2767 (w), 2664 (w), 1505 (w), 1119 (m), 1083 (m), 973 (m), 949 (m), 901 (m), 800 (m), 719 (s), 639 (m), 547 (m), 438 (m). MS (EI, 70 eV): *m/z* (%) = 354 (27), 353 $[M]^+$ (100), 278 (12), 265 (10), 177 (10), 139 (14), 133 (15). HRMS (EI): Calculated for $C_{24}H_{19}O_2N$ $[M]^+$ 353.14103 found 353.14075.

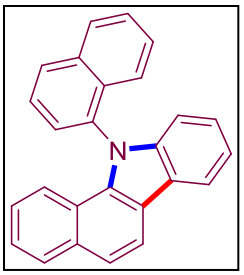
11-(3,4,5-Trimethoxyphenyl)-11*H*-benzo[*a*]carbazole (15d): White solid,



mp. 157 - 159 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.23 (d, ^3J = 8.6 Hz, 1H), 8.22 - 8.18 (m, 1H), 8.00 (ddd, ^3J = 8.7 Hz, ^4J = 1.2 Hz, ^5J = 0.6 Hz, 1H), 7.73 (d, ^3J = 8.3 Hz, 1H), 7.54 (d, ^3J = 8.6 Hz, 1H), 7.49 - 7.45 (m, 1H), 7.44 - 7.40 (m, 1H), 7.39 - 7.35 (m, 1H), 7.32 (dt, ^3J = 8.6 Hz, ^4J = 1.5 Hz, 1H), 7.29 - 7.26 (m, 1H), 6.78 (s, 2H, CH_{Ar}), 4.05 (s, 3H, OCH_3), 3.83 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.4 ($2C_{Ar}OCH_3$), 142.1 (C_{Ar}), 138.4 (C_{Ar}), 135.6 (C_{Ar}), 135.5 (C_{Ar}), 133.6 (C_{Ar}), 129.2 (CH_{Ar}), 125.3 (CH_{Ar}), 125.1 (CH_{Ar}), 125.0 (CH_{Ar}), 123.4 (C_{Ar}), 122.4 (CH_{Ar}), 122.0 (C_{Ar}), 121.3 (CH_{Ar}), 120.4 (CH_{Ar}), 119.7 (CH_{Ar}), 119.4 (C_{Ar}), 119.2 ($2CH_{Ar}$), 110.5 (CH_{Ar}), 106.4 (CH_{Ar}), 61.4 (OCH_3), 56.5 ($2OCH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053 (w), 2998 (w), 2961 (w), 2936 (m), 2828 (w), 2592 (w), 1589 (m), 1500 (m), 1460 (m), 1412 (m), 1361 (m), 1300 (m), 1223 (m), 1122 (s), 1004 (m), 809 (m), 732 (s), 654 (m), 441 (m). MS (EI, 70 eV): *m/z* (%) = 384 (23), 383 $[M]^+$

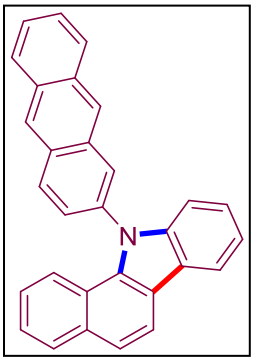
(100), 281 (12), 216 (11). HRMS (EI): Calculated for $C_{25}H_{21}O_3N$ $[M]^+$ 383.15160 found 383.15163.

11-(Naphthalen-1-yl)-11*H*-benzo[*a*]carbazole (15e): White solid, mp. 189 - 191 °C.



^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.37 - 8.26 (m, 1H, CH_{Ar}), 8.30 - 8.25 (m, 1H, CH_{Ar}), 8.17 (dd, ^3J = 7.2 Hz, ^4J = 2.3 Hz, 1H, CH_{Ar}), 8.06 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.97 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.76 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.73 (d, ^3J = 5.7 Hz, 1H, CH_{Ar}), 7.71 (m, 1H, CH_{Ar}), 7.54 (ddd, ^3J = 8.2 Hz, ^3J = 6.4 Hz, ^4J = 1.7 Hz, 1H, CH_{Ar}), 7.41 - 7.36 (m, 1H, CH_{Ar}), 7.36 - 7.33 (m, 1H, CH_{Ar}), 7.32 - 7.29 (m, 1H, CH_{Ar}), 7.29 - 7.26 (m, 1H, CH_{Ar}), 7.25 - 7.18 (m, 1H, CH_{Ar}), 7.15 - 7.04 (m, 1H, CH_{Ar}), 7.02 (dd, ^3J = 6.8 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 6.96 - 6.91 (m, 1H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 142.44 (C_{Ar}), 136.67 (C_{Ar}), 136.32 (C_{Ar}), 134.87 (C_{Ar}), 133.53 (C_{Ar}), 131.81 (C_{Ar}), 129.70 (CH_{Ar}), 129.12 (CH_{Ar}), 128.52 (CH_{Ar}), 127.64 (CH_{Ar}), 127.46 (CH_{Ar}), 127.12 (CH_{Ar}), 126.17 (CH_{Ar}), 125.25 (CH_{Ar}), 125.15 (CH_{Ar}), 124.82 (CH_{Ar}), 123.54 (C_{Ar}), 123.51 (CH_{Ar}), 122.11 (C_{Ar}), 121.98 (CH_{Ar}), 121.32 (CH_{Ar}), 120.45 (CH_{Ar}), 119.65 (CH_{Ar}), 119.48 (C_{Ar}), 119.30 (CH_{Ar}), 110.75 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 1594 (w), 1460 (m), 1432 (m), 1409 (m), 1377 (m), 1228 (m), 1112 (m), 781 (m), 748 (s), 682 (m), 544 (m), 418 (m). MS (EI, 70 eV): *m/z* (%) = 344 (28), 343 $[M]^+$ (100), 342 (16), 341 (22), 170 (28), 158 (14). HRMS (EI): Calculated for $C_{26}H_{17}N$ $[M]^+$ 343.13555 found 343.13524.

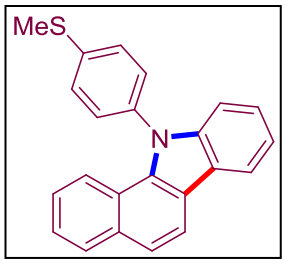
11-(Anthracen-2-yl)-11*H*-benzo[*a*]carbazole (15f): Pale yellow solid,



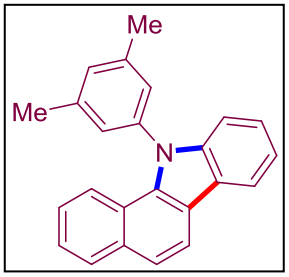
mp. 218 - 220 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.63 (d, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.53 (d, ^4J = 1.1 Hz, 1H, CH_{Ar}), 8.31 - 8.27 (m, 2H, CH_{Ar}), 8.27 - 8.25 (m, 1H, CH_{Ar}), 8.25 - 8.22 (m, 1H, CH_{Ar}), 8.16 - 8.09 (m, 1H, CH_{Ar}), 8.09 - 8.03 (m, 1H, CH_{Ar}), 8.01 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.77 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.62 - 7.54 (m, 3H, CH_{Ar}), 7.51 (dd, ^3J = 8.9 Hz, ^4J = 2.1 Hz, 1H, CH_{Ar}), 7.45 - 7.35 (m, 3H, CH_{Ar}), 7.35 - 7.27 (m, 1H, CH_{Ar}), 7.12 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 142.2 (C_{Ar}), 137.0 (C_{Ar}), 135.7 (C_{Ar}), 133.6 (C_{Ar}), 132.5 (C_{Ar}), 132.4 (C_{Ar}), 131.7 (C_{Ar}), 131.1 (C_{Ar}), 130.8 (CH_{Ar}), 129.3 (CH_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 127.6 (CH_{Ar}), 127.0 (CH_{Ar}), 126.8 (CH_{Ar}), 126.6 (CH_{Ar}), 126.3 (CH_{Ar}), 126.2 (CH_{Ar}), 125.2 (2CH_{Ar}), 124.9 (CH_{Ar}), 123.7 (C_{Ar}), 122.5 (CH_{Ar}), 122.3 (C_{Ar}), 121.5 (CH_{Ar}), 120.6

(CH_{Ar}), 119.9 (C_{Ar}), 119.7 (CH_{Ar}), 119.3 (CH_{Ar}), 110.6 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3047 (w), 1616 (w), 1461 (m), 1433 (m), 1381 (m), 1324 (m), 1219 (m), 1155 (m), 893 (m), 809 (m), 741 (s), 650 (m), 468 (m). MS (EI, 70 eV): *m/z* (%) = 394 (29), 393 $[M]^+$ (100), 392 (36), 391 (29), 390 (11), 197 (23), 196 (27), 195 (20), 189 (11), 176 (11). HRMS (EI): Calculated for $C_{30}H_{19}N$ $[M]^+$ 393.15120 found 393.15099.

11-(4-(Methylthio)phenyl)-11*H*-benzo[*a*]carbazole (15g): Pale yellow solid, mp. 147 - 149 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.23 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.21 - 8.16 (m, 1H, CH_{Ar}), 7.99 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.72 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.55 - 7.52 (m, 1H, CH_{Ar}), 7.52 - 7.50 (m, 1H, CH_{Ar}), 7.50 - 7.46 (m, 3H, CH_{Ar}), 7.44 (q, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.42 - 7.38 (m, 1H, CH_{Ar}), 7.38 - 7.33 (m, 1H, CH_{Ar}), 7.30 - 7.23 (m, 1H, CH_{Ar}), 7.21 - 7.16 (m, 1H, CH_{Ar}), 2.64 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142.2 (C_{Ar}), 139.8 (C_{Ar}), 136.9 (C_{Ar}), 135.6 (C_{Ar}), 133.6 (C_{Ar}), 129.6 ($2CH_{Ar}$), 129.3 (CH_{Ar}), 127.5 ($2CH_{Ar}$), 125.2 (CH_{Ar}), 125.1 (CH_{Ar}), 124.9 (CH_{Ar}), 123.5 (C_{Ar}), 122.3 (CH_{Ar}), 122.1 (C_{Ar}), 121.3 (CH_{Ar}), 120.5 (CH_{Ar}), 119.6 (C_{Ar}), 119.6 (CH_{Ar}), 119.2 (CH_{Ar}), 110.5 (CH_{Ar}), 15.8 (SCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3076 (w), 3043 (w), 2982 (w), 2917 (w), 2818 (w), 1495 (m), 1560 (m), 1403 (m), 1224 (m), 1094(m), 809 (m), 738 (s), 617 (m), 552 (m). MS (EI, 70 eV): *m/z* (%) = 340 (26), 339 $[M]^+$ (100), 325 (18), 291 (26), 146 (32). HRMS (EI): Calculated for $C_{23}H_{17}NS$ 339.10762 found 339.10776.

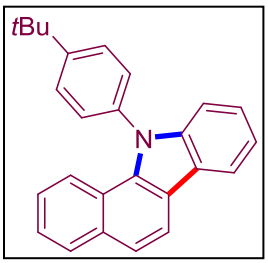


11-(3,5-Dimethylphenyl)-11*H*-benzo[*a*]carbazole (15h): Yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.23 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.21 - 8.17 (m, 1H, CH_{Ar}), 7.99 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.72 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.51 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.44 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.40 - 7.36 (m, 1H, CH_{Ar}), 7.36 - 7.30 (m, 1H, CH_{Ar}), 7.28 - 7.24 (m, 2H, CH_{Ar}), 7.23 - 7.18 (m, 1H, CH_{Ar}), 7.16 (s, 2H, CH_{Ar}), 2.44 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142.2 (C_{Ar}), 140.0 (C_{Ar}), 139.9 ($2C_{Ar}$), 135.6 (C_{Ar}), 133.6 (C_{Ar}), 130.6 (CH_{Ar}), 129.2 (CH_{Ar}), 126.7 ($2CH_{Ar}$), 125.0 (CH_{Ar}), 124.9 (CH_{Ar}), 124.8 (CH_{Ar}), 123.4 (C_{Ar}), 122.6 (CH_{Ar}), 122.2 (C_{Ar}), 121.1 (CH_{Ar}), 120.2 (CH_{Ar}), 119.6 (CH_{Ar}), 119.4 (C_{Ar}), 119.2 (CH_{Ar}), 110.6 (CH_{Ar}), 21.5 ($2CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3006 (w), 2930 (w), 2837 (w), 2820 (w), 1591 (m), 1504 (m), 1460 (m), 1204 (m), 1120 (m), 1026 (m), 809 (m), 740 (s), 702 (m), 437 (m). MS (EI, 70 eV):



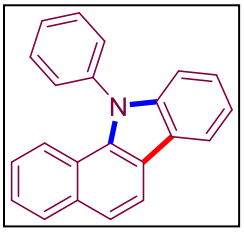
m/z (%) = 322 (26), 321 $[M]^+$ (100), 305 (12), 146 (19). HRMS (EI): Calculated for $C_{24}H_{19}N$ $[M]^+$ 321.15120 found 321.15109.

11-(4-(*tert*-Butyl)phenyl)-11*H*-benzo[*a*]carbazole (15i): Yellow solid,



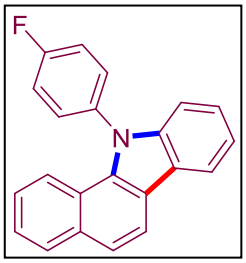
mp. 258 - 259 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.24 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.22 - 8.17 (m, 1H, CH_{Ar}), 7.99 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.72 (dd, ^3J = 8.5 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.66 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.49 - 7.41 (m, 4H, CH_{Ar}), 7.41 - 7.30 (m, 2H, CH_{Ar}), 7.26 - 7.18 (m, 2H, CH_{Ar}), 1.49 (s, 9H, $CH_{3\text{-}t\text{Bu}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.1 (C_{Ar}), 142.3 (C_{Ar}), 137.4 (C_{Ar}), 135.7 (C_{Ar}), 133.6 (C_{Ar}), 129.2 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 127.1 ($2CH_{Ar}$), 125.0 (CH_{Ar}), 125.0 (CH_{Ar}), 124.8 (CH_{Ar}), 123.4 (C_{Ar}), 122.4 (CH_{Ar}), 122.2 (C_{Ar}), 121.1 (CH_{Ar}), 120.3 (CH_{Ar}), 119.6 (CH_{Ar}), 119.5 (C_{Ar}), 119.2 (CH_{Ar}), 110.6 (CH_{Ar}), 35.1 ($C_{t\text{Bu}}$), 31.7 ($3CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 2960 (w), 2902 (w), 2866 (w), 1516 (m), 1462 (m), 1405 (m), 1306 (m), 1226 (s), 1190 (m), 1119 (m), 981 (m), 810 (m), 741 (m), 625 (m), 557 (m). MS (EI, 70 eV): *m/z* (%) = 350 (29), 349 (100), 334 (26), 319 (13), 291 (13), 216 (14), 153 (11), 146 (30). HRMS (EI): Calculated for $C_{30}H_{19}N$ $[M]^+$ 393.15120 found 3903.15099.

11-Phenyl-11*H*-benzo[*a*]carbazole (15j): Colorless oil. ^{1}H NMR (300 MHz,



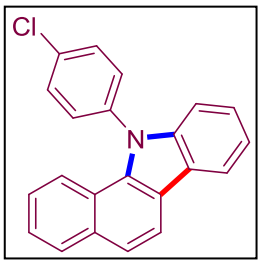
Chloroform-*d*) δ = 8.13 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 8.11 - 8.08 (m, 1H, CH_{Ar}), 7.89 (dd, ^3J = 8.5 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.62 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.58 - 7.50 (m, 3H, CH_{Ar}), 7.44 (dd, ^3J = 7.7 Hz, ^4J = 2.0 Hz, 2H, CH_{Ar}), 7.37 - 7.23 (m, 4H, CH_{Ar}), 7.15 - 7.06 (m, 2H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 142.2 (C_{Ar}), 140.2 (C_{Ar}), 135.6 (C_{Ar}), 133.6 (C_{Ar}), 130.2 ($2CH_{Ar}$), 129.3 ($3CH_{Ar}$), 128.9 (CH_{Ar}), 125.1 (CH_{Ar}), 125.0 (CH_{Ar}), 124.8 (CH_{Ar}), 123.5 (C_{Ar}), 122.4 (CH_{Ar}), 122.1 (C_{Ar}), 121.3 (CH_{Ar}), 120.4 (CH_{Ar}), 119.6 (CH_{Ar}), 119.2 (CH_{Ar}), 118.4 (C_{Ar}), 110.5 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3397 (w), 3053 (m), 2957 (w), 2867 (w), 1594 (m), 1496 (m), 1461 (m), 1401 (m), 1224 (m), 1157 (m), 1025 (m), 906 (m), 807 (m), 740 (s), 695 (m), 622 (m), 554 (m). MS (EI, 70 eV): *m/z* (%) = 294 (23), 293 $[M]^+$ (100), 292 (30), 291 (36), 214 (12), 146 (14), 77 (15), 51 (13). HRMS (EI): Calculated for $C_{22}H_{15}N$ $[M]^+$ 293.11990 found 293.11970.

11-(4-Fluorophenyl)-11*H*-benzo[*a*]carbazole (15k): Colorless oil. ^{1}H NMR



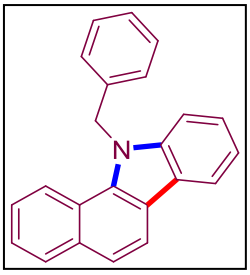
(300 MHz, Chloroform-*d*) δ = 8.11 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 8.10 - 8.06 (m, 1H, CH_{Ar}), 7.89 (dd, ^{3}J = 8.1 Hz, ^{4}J = 0.9 Hz, 1H, CH_{Ar}), 7.65 - 7.59 (m, 1H, CH_{Ar}), 7.40 (dd, ^{3}J = 8.9 Hz, ^{3}J = 4.9 Hz, 2H, CH_{Ar}), 7.36 - 7.20 (m, 6H, CH_{Ar}), 7.16 (dd, ^{3}J = 6.8 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.09 - 6.99 (m, 1H, CH_{Ar}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.0 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 162. 7 (d, $^{1}J_{CF}$ = 248.8 Hz, CF_{Ar}), 142.2 (C_{Ar}), 136.2 (d, $^{4}J_{CF}$ = 3.3 Hz, C_{Ar}), 135.6 (C_{Ar}), 133.6 (C_{Ar}), 130.99 (d, $^{3}J_{CF}$ = 8.6 Hz, $2CH_{Ar}$), 129.4 (CH_{Ar}), 125.2 (CH_{Ar}), 125.2 (CH_{Ar}), 124.9 (CH_{Ar}), 123.5 (C_{Ar}), 122.1 (CH_{Ar}), 122.0 (C_{Ar}), 121.5 (CH_{Ar}), 120.6 (CH_{Ar}), 119.7 (CH_{Ar}), 119.7 (C_{Ar}), 119.2 (CH_{Ar}), 117.25 (d, $^{2}J_{CF}$ = 22.7 Hz, $2CH_{Ar}$), 110.3 (CH_{Ar}). IR (ATR, cm^{-1}): ṽ = 3399 (w), 3052 (w), 2956 (w), 2925 (w), 2867 (w), 2688 (w), 2565 (w), 2245 (w), 1891 (w), 1506 (s), 1462 (m), 1402 (m), 1219 (m), 1151 (m), 1089 (m), 907 (m), 807 (m), 740 (s), 618 (m), 515 (m). MS (EI, 70 eV): *m/z* (%) = 312 (25), 311 $[M]^+$ (100), 310 (29), 309 (32), 214 (11), 75 (16). HRMS (EI): Calculated for $C_{22}H_{14}NF$ $[M]^+$ 311.11048 found 311.11027.

11-(4-Chlorophenyl)-11*H*-benzo[*a*]carbazole (15l): Colorless oil. ^{1}H NMR



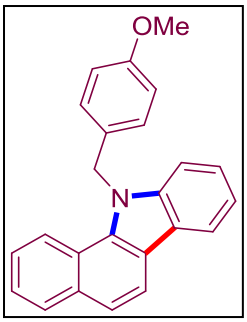
(250 MHz, Chloroform-*d*) δ = 8.23 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 8.21 - 8.17 (m, 1H, CH_{Ar}), 8.01 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.4 Hz, 2H, CH_{Ar}), 7.74 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 7.64 (d, ^{3}J = 8.7 Hz, 1H, CH_{Ar}), 7.49 (d, ^{3}J = 8.7 Hz, 2H, CH_{Ar}), 7.46 - 7.34 (m, 4H, CH_{Ar}), 7.32 - 7.27 (m, 1H, CH_{Ar}), 7.21 - 7.14 (m, 1H, CH_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.1 (C_{Ar}), 138.9 (C_{Ar}), 135.4 (C_{Ar}), 134.8 (C_{Ar}), 133.6 (CH_{Ar}), 130.6 (CH_{Ar}), 130.5 ($2CH_{Ar}$), 129.4 (C_{Ar}), 129.4 (CH_{Ar}), 125.3 ($2CH_{Ar}$), 125.0 (CH_{Ar}), 123.7 (C_{Ar}), 122.2 (C_{Ar}), 122.0 (CH_{Ar}), 121.6 (CH_{Ar}), 120.7 (CH_{Ar}), 119.9 (C_{Ar}), 119.8 (CH_{Ar}), 119.2 (CH_{Ar}), 110.3 (CH_{Ar}). IR (ATR, cm^{-1}): ṽ = 3392 (w), 3054 (w), 2959 (w), 2932 (w), 2867 (w), 1492 (m), 1461 (m), 1224 (m), 1086 (m), 807 (m), 741 (s), 501 (m). MS (EI, 70 eV): *m/z* (%) = 329 (36), 328 (29), 327 $[M]^+$ (100), 325 (10), 291 (27), 146 (21). HRMS (EI): Calculated for $C_{22}H_{14}NCl$ $[M]^+$ 327.08093.

11-Benzyl-11*H*-benzo[*a*]carbazole (15m): White solid, mp. 146 - 148 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.32 - 8.21 (m, 3H, CH_{Ar}), 8.04 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.73 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 7.55 - 7.20 (m, 10H, CH_{Ar}), 6.02 (d, ^{4}J = 1.0 Hz, 2H, $CH_{2\text{-benzyl}}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.2 (C_{Ar}),



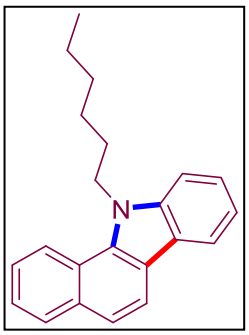
137.7 (C_{Ar}), 135.4 (C_{Ar}), 133.8 (C_{Ar}), 129.5 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 127.6 (CH_{Ar}), 126.1 ($2CH_{Ar}$), 125.6 (CH_{Ar}), 125.2 (CH_{Ar}), 124.8 (CH_{Ar}), 123.5 (C_{Ar}), 122.2 (C_{Ar}), 122.1 (CH_{Ar}), 121.1 (C_{Ar}), 120.2 (CH_{Ar}), 119.8 (CH_{Ar}), 119.5 (CH_{Ar}), 119.3 (CH_{Ar}), 109.4 (CH_{Ar}), 49.9 ($CH_{2\text{-aliphatic}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 3022 (w), 2935 (w), 1467 (m), 1407 (m), 1326 (m), 1189 (m), 808 (m), 739 (s), 739 (s), 693 (m), 436 (m). MS (EI, 70 eV): *m/z* (%) = 308 (25), 307 $[M]^+$ (99), 217 (17), 216 (100), 215 (23), 214 (20), 190 (11), 189 (13), 91 (66), 65 (12). HRMS (EI): Calculated for $C_{23}H_{17}N$ $[M]^+$ 307.13555 found 307.13537.

11-(4-Methoxybenzyl)-11*H*-benzo[*a*]carbazole (15n): White solid, mp. 139 - 140 °C.



^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.31 (d, ^3J = 7.9 Hz, 1H, CH_{Ar}), 8.24 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 8.03 (dd, ^3J = 8.0 , ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.71 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.52 - 7.41 (m, 4H, CH_{Ar}), 7.40 - 7.32 (m, 1H, CH_{Ar}), 7.18 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 6.86 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 5.96 (t, ^5J = 0.8 Hz, 2H, $CH_{2\text{-benzyl}}$), 3.76 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.1 (C_{Ar}), 141.2 (C_{Ar}), 135.4 (C_{Ar}), 133.8 (C_{Ar}), 129.6 (C_{Ar}), 129.5 (CH_{Ar}), 127.3 ($2CH_{Ar}$), 125.6 (CH_{Ar}), 125.2 (CH_{Ar}), 124.8 (CH_{Ar}), 123.4 (C_{Ar}), 122.2 (C_{Ar}), 122.2 (CH_{Ar}), 121.0 (CH_{Ar}), 120.1 (CH_{Ar}), 119.8 (CH_{Ar}), 119.5 (C_{Ar}), 119.3 (CH_{Ar}), 114.6 ($2CH_{Ar}$), 109.5 (CH_{Ar}), 55.4 (OCH_3), 49.3 ($CH_{2\text{-benzyl}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3142 (w), 3116 (w), 3074 (w), 3032 (w), 2989 (w), 2917 (w), 1612 (m), 1509 (m), 1472 (m), 1385 (m), 1330 (m), 1289 (m), 1241 (s), 1171 (m), 1032 (m), 902 (m), 840 (m), 791 (m), 705 (m), 626 (m), 536 (m). MS (EI, 70 eV): *m/z* (%) = 337 $[M]^+$ (28), 216 (18), 121 (100). HRMS (EI): Calculated for $C_{24}H_{19}NO$ $[M]^+$ 337.14612 found 337.14594.

11-Hexyl-11*H*-benzo[*a*]carbazole (15o): Colorless oil.



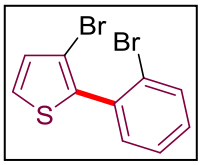
^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.52 (dd, ^3J = 8.5 Hz, ^3J = 1.2 Hz, 1H), 8.21 (d, ^3J = 8.4 Hz, 1H), 8.19 (d, ^3J = 7.7 Hz, 1H), 8.07 (dd, ^3J = 8.0 Hz, ^3J = 1.5 Hz, 1H), 7.69 (d, ^3J = 8.5 Hz, 1H), 7.64 (ddd, ^3J = 8.5 Hz, ^3J = 6.9 Hz, ^4J = 1.6 Hz, 1H), 7.60 - 7.57 (m, 1H), 7.58 - 7.54 (m, 1H), 7.54 - 7.49 (m, 1H), 7.34 (ddd, ^3J = 7.9 Hz, ^3J = 6.8 Hz, ^3J = 1.2 Hz, 1H), 4.88 - 4.72 (m, 2H), 2.09 (p, ^3J = 7.6 Hz, 2H), 1.57 (p, ^3J = 7.6 Hz, ^3J = 7.1 Hz, 2H), 1.48 - 1.35 (m, 4H), 0.94 (t, ^3J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.5 (C_{Ar}), 134.6 (C_{Ar}), 133.8 (C_{Ar}), 129.8 (CH_{Ar}),

125.5 (CH_{Ar}), 124.8 (CH_{Ar}), 124.6 (CH_{Ar}), 123.1 (C_{Ar}), 122.4 (C_{Ar}), 122.0 (CH_{Ar}), 120.6 (CH_{Ar}), 119.7 (C_{Ar}), 119.6 (CH_{Ar}), 119.4 (CH_{Ar}), 119.3 (CH_{Ar}), 109.2 (CH_{Ar}), 46.1 ($CH_{2\text{-aliphatic}}$), 31.7 ($CH_{2\text{-aliphatic}}$), 30.1 ($CH_{2\text{-aliphatic}}$), 26.9 ($CH_{2\text{-aliphatic}}$), 22.7 ($CH_{2\text{-aliphatic}}$), 14.2 ($CH_{3\text{-aliphatic}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 2953 (m), 2925 (m), 2854 (m), 1466 (m), 1407 (m), 1383 (m), 1333 (m), 1186 (m), 1125 (m), 804 (m), 737 (s), 553 (m), 438 (m). MS (EI, 70 eV): *m/z* (%) = 302 (14), 301 $[M]^+$ (57), 231 (19), 230 (100), 217 (11), 216 (20), 202 (17). HRMS (EI): Calculated for $C_{22}H_{23}N$ 301.18250 $[M]^+$ found 301.18213.

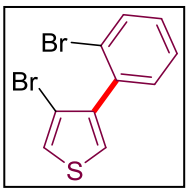
5.2.5. Synthesis of thienoindoles by sequential site-selective Suzuki reaction/double C-N coupling

5.2.5.1. Starting materials for double C-N coupling

3-Bromo-2-(2-bromophenyl)thiophene (17a): White solid, mp. 63 - 64 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.69 (d, ^3J = 8.0 Hz, 1H, CH_{Ar}), 7.42 - 7.34 (m, 3H, CH_{Ar}), 7.28 (ddd, ^3J = 8.0 Hz, ^3J = 6.7 Hz, ^4J = 2.5 Hz, 1H, CH_{Ar}), 7.07 (d, ^3J = 5.3 Hz, 1H, $CH_{thiophene}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 137.3 (C_{Ar}), 134.0 (C_{Ar}), 133.1 (CH_{Ar}), 132.9 (CH_{Ar}), 130.6 (CH_{Ar}), 130.3 (CH_{Ar}), 127.3 (CH_{Ar}), 126.2 (CH_{Ar}), 125.2 (C_{Ar}), 111.2 (C_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3110 (w), 3085 (w), 3059 (w), 1528 (w), 1463 (m), 1419 (m), 1340 (m), 1148 (w), 1024 (m), 857 (m), 756 (s), 712 (s), 654 (m), 620 (m), 522 (m), 446 (m). MS (EI, 70 eV): *m/z* (%) = 318 $[M]^+$ (45), 239 (22), 158 (100), 114 (30), 79 (21). HRMS (EI): Calculated for $C_{10}H_6Br_2S$ $[M]^+$ 315.85515 found 315.85464, calculated for $C_{10}H_6Br^{81}BrS$ $[M]^+$ 317.85310 found 317.85281, calculated for $C_{10}H_6{}^{81}Br_2S$ $[M]^+$ 319.85105 found 319.85069.



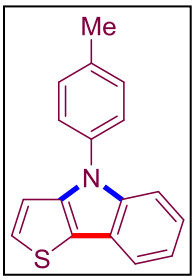
3-Bromo-4-(2-bromophenyl)thiophene (17b): Colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.67 (d, ^3J = 8.1 Hz, $1H_{Ar}$), 7.39 - 7.34 (m, 2H, CH_{Ar}), 7.31 - 7.24 (m, 3H, CH_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.5 (C_{Ar}), 136.6 (C_{Ar}), 132.9 (CH_{Ar}), 132.0 (CH_{Ar}), 129.8 (CH_{Ar}), 127.2 (CH_{Ar}), 124.9 (CH_{Ar}), 124.5 (C_{Ar}), 123.3 (CH_{Ar}), 112.4 (C_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3107 (w), 3057 (w), 1560 (w), 1525 (w), 1464 (m), 1425 (m), 1339 (m), 1257 (w), 1081 (w), 1026 (m), 921 (m), 852 (m), 792 (m), 751 (s), 710 (m), 653 (m), 451 (m). MS (EI, 70 eV): *m/z* (%) = 320 (23), 318 $[M]^+$ (43), 239 (31), 158 (100),



114 (26), 113 (20), 79 (24). HRMS (EI): Calculated for $C_{10}H_6Br_2S$ $[M]^+$ 315.85515 found 315.85490, calculated for $C_{10}H_6Br^{81}BrS$ $[M]^+$ 317.85310 found 317.85301, calculated for $C_{10}H_6{}^{81}Br_2S$ $[M]^+$ 319.85105 found 319.85073.

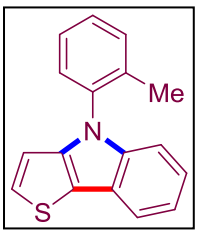
5.2.5.2.Indolo[3,2-*b*]thiophene

4-(*p*-Tolyl)-4*H*-thieno[3,2-*b*]indole (18a): Yellow solid, mp. 92 - 93 °C. ^{1}H NMR



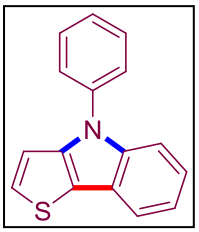
(300 MHz, Chloroform-*d*) δ = 7.82 - 7.77 (m, 1H, CH_{Ar}), 7.55 - 7.50 (m, 1H, CH_{Ar}), 7.47 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 7.40 - 7.33 (m, 3H, CH_{Ar}), 7.30 - 7.19 (m, 2H, CH_{Ar}), 7.08 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 2.47 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.3 (C_{Ar}), 141.6 (C_{Ar}), 136.8 (C_{Ar}), 136.4 (C_{Ar}), 130.5 ($2CH_{Ar}$), 126.9 (CH_{Ar}), 125.2 ($2CH_{Ar}$), 123.0 (CH_{Ar}), 122.4 (C_{Ar}), 120.2 (CH_{Ar}), 119.1 (CH_{Ar}), 117.8 (C_{Ar}), 111.6 (CH_{Ar}), 111.2 (CH_{Ar}), 21.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3393 (w), 3109 (w), 3080 (w), 3056 (w), 3030 (w), 2917 (w), 2857 (w), 1600 (m), 1510 (s), 1450 (s), 1392 (m), 1337 (m), 1200 (m), 1085 (m), 1044 (m), 847 (m), 812 (m), 709 (s), 663 (m), 650 (m), 568 (m), 506 (m), 433 (m). MS (EI, 70 eV): *m/z* (%) = 264 (20), 263 $[M]^+$ (100), 262 (15), 248 (7), 247 (6), 128 (5). HRMS (EI): Calculated for $C_{17}H_{13}NS$ $[M]^+$ 263.07632 found 263.07598.

4-(*o*-Tolyl)-4*H*-thieno[3,2-*b*]indole (18b): Yellow oil. ^{1}H NMR (250 MHz,



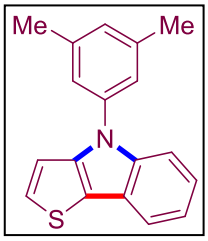
Chloroform-*d*) δ = 7.74 - 7.68 (m, 1H, CH_{Ar}), 7.34 - 7.29 (m, 2H, CH_{Ar}), 7.28 - 7.24 (m, 2H, CH_{Ar}), 7.23 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.15 - 7.10 (m, 2H, CH_{Ar}), 7.01 - 6.95 (m, 1H, CH_{Ar}), 6.70 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 1.94 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.8 (C_{Ar}), 142.3 (C_{Ar}), 137.2 (C_{Ar}), 136.5 (C_{Ar}), 131.6 (CH_{Ar}), 128.6 (CH_{Ar}), 128.6 (CH_{Ar}), 127.2 (CH_{Ar}), 127.0 (CH_{Ar}), 122.9 (CH_{Ar}), 122.0 (C_{Ar}), 119.9 (CH_{Ar}), 119.0 (CH_{Ar}), 117.1 (C_{Ar}), 111.3 (CH_{Ar}), 111.2 (CH_{Ar}), 17.9 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 2917 (w), 1601 (w), 1505 (m), 1486 (m), 1451 (m), 1486 (m), 1450 (s), 1332 (m), 1082 (m), 820 (m), 734 (s), 649 (s), 431 (m). MS (EI, 70 eV): *m/z* (%) = 264 (21), 263 $[M]^+$ (100), 262 (47), 230 (16), 218 (11), 217 (13), HRMS (EI): Calculated for $C_{17}H_{13}NS$ $[M]^+$ 263.07632 found 263.07591.

4-Phenyl-4*H*-thieno[3,2-*b*]indole (18c): Yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.86 - 7.79 (m, 1H, CH_{Ar}), 7.66 - 7.54 (m, 5H, CH_{Ar}), 7.45 - 7.39 (m,



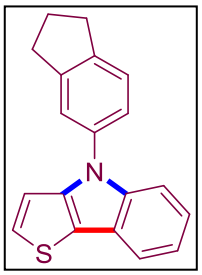
1H, CH_{Ar}), 7.38 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.34 - 7.21 (m, 2H, CH_{Ar}), 7.12 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.1 (C_{Ar}), 141.4 (C_{Ar}), 139.0 (C_{Ar}), 129.9 ($2CH_{Ph}$), 127.0 (CH_{Ar}), 126.9 (CH_{Ar}), 125.2 ($2CH_{Ph}$), 123.2 (CH_{Ar}), 122.5 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.1 (C_{Ar}), 111.6 (CH_{Ar}), 111.2 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3083 (w), 3050 (w), 1594 (m), 1505 (s), 1449 (s), 1392 (m), 1337 (m), 1201 (m), 1086 (m), 839 (m), 779 (m), 737 (s), 696 (s), 653 (s), 430 (m). MS (EI, 70 eV): *m/z* (%) = 249 $[M]^+$ (100), 217 (6), 204 (9), 172 (5), 128 (8), 77 (9), 51 (13). HRMS (EI): Calculated for $C_{16}H_{11}NS$ $[M]^+$ 249.06067 found 249.06073.

4-(3,5-Dimethylphenyl)-4*H*-thieno[3,2-*b*]indole (18d): Yellow solid,



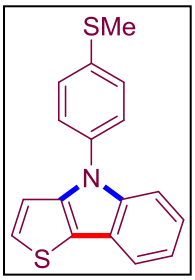
mp. 112 - 113 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.73 - 7.67 (m, 1H, CH_{Ar}), 7.51 - 7.44 (m, 1H, CH_{Ar}), 7.27 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.22 - 7.09 (m, 4H, CH_{Ar}), 7.01 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 6.95 (s, 1H, CH_{Ar}), 2.33 (s, 6H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.2 (C_{Ar}), 141.4 (C_{Ar}), 139.7 ($2C_{Ar}$), 138.8 (C_{Ar}), 128.6 (CH_{Ar}), 126.8 (CH_{Ar}), 123.0 (CH_{Ar}), 122.9 ($2CH_{Ar}$), 122.4 (C_{Ar}), 120.2 (CH_{Ar}), 119.1 (CH_{Ar}), 117.8 (C_{Ar}), 111.8 (CH_{Ar}), 111.3 (CH_{Ar}), 21.5 ($2CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 3006 (w), 2956 (m), 2915 (m), 2851 (w), 1731 (m), 1594 (m), 1504 (m), 1449 (m), 1343 (m), 1173 (m), 1090 (m), 839 (m), 815 (m), 738 (s), 701 (m), 568 (s). MS (EI, 70 eV): *m/z* (%) = 278 (21), 277 $[M]^+$ (100), 276 (7), 262 (8), 260 (7), 228 (5), 77 (5). HRMS (EI): Calculated for $C_{18}H_{15}NS$ $[M]^+$ 277.09197 found 277.09166.

4-(2,3-Dihydro-1*H*-inden-5-yl)-4*H*-thieno[3,2-*b*]indole (18e): Yellow solid,



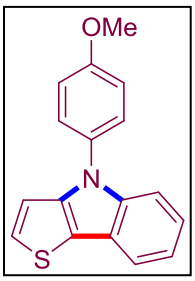
mp. 81 - 82 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.74 - 7.68 (m, 1H, CH_{Ar}), 7.49 - 7.42 (m, 1H, CH_{Ar}), 7.37 - 7.20 (m, 4H, CH_{Ar}), 7.15 (m, 2H, CH_{Ar}), 7.00 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 2.92 (t, ^{3}J = 7.4 Hz, 4H, CH_2), 2.10 (p, ^{3}J = 7.5 Hz, 2H, CH_2). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 146.2 (C_{Ar}), 145.4 (C_{Ar}), 143.1 (C_{Ar}), 141.7 (C_{Ar}), 137.1 (C_{Ar}), 126.8 (CH_{Ar}), 125.4 (CH_{Ar}), 123.3 (CH_{Ar}), 123.0 (CH_{Ar}), 122.3 (C_{Ar}), 121.4 (CH_{Ar}), 120.1 (CH_{Ar}), 119.0 (CH_{Ar}), 117.6 (C_{Ar}), 111.7 (CH_{Ar}), 111.3 (CH_{Ar}), 33.2 (CH_2), 32.7 (CH_2), 25.8 (CH_2). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2933 (w), 2837 (w), 1606 (w), 1505 (m), 1486 (m), 1451 (m), 1344 (m), 1099 (m), 820 (m), 736 (s), 648 (s), 426 (m). MS (EI, 70 eV): *m/z* (%) = 289 $[M]^+$ (100), 255 (5), 172 (12), 115 (10). HRMS (EI): Calculated for $C_{19}H_{15}NS$ $[M]^+$ 289.09197 found 289.09201.

4-(4-(Methylthio)phenyl)-4*H*-thieno[3,2-*b*]indole (18f): White solid, mp. 91 - 92 °C.



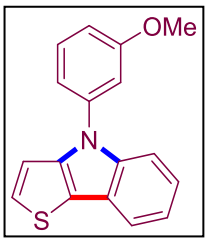
^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.69 - 7.63 (m, 1H, CH_{Ar}), 7.41 - 7.27 (m, 5H, CH_{Ar}), 7.21 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.15 - 7.08 (m, 2H, CH_{Ar}), 6.92 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 2.41 (s, 3H, SCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.0 (C_{Ar}), 141.3 (C_{Ar}), 137.1 (C_{Ar}), 136.1 (C_{Ar}), 127.9 ($2CH_{Ar}$), 127.1 (CH_{Ar}), 125.6 ($2CH_{Ar}$), 123.1 (CH_{Ar}), 122.5 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.0 (C_{Ar}), 111.4 (CH_{Ar}), 111.0 (CH_{Ar}), 16.2 (SCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3381 (w), 3095 (w), 3082 (w), 3046 (w), 2917 (w), 1591 (w), 1505 (s), 1491 (s), 1450 (s), 1393 (m), 1339 (m), 1294 (m), 1094 (m), 1044 (m), 1012 (m), 814 (s), 750 (s), 709 (m), 662 (s), 506 (m). MS (EI, 70 eV): *m/z* (%) = 295 $[M]^+$ (100), 280 (68), 247 (22), 148 (10). HRMS (EI): Calculated for $C_{17}H_{13}NS_2$ 295.04839 found 295.04844.

4-(4-Methoxyphenyl)-4*H*-thieno[3,2-*b*]indole (18g): White solid, mp. 124 - 125 °C.



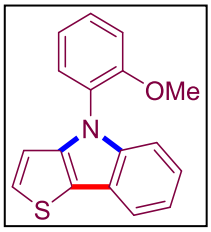
^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.77 - 7.65 (m, 1H, CH_{Ar}), 7.46 - 7.34 (m, 3H, CH_{Ar}), 7.27 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.22 - 7.08 (m, 2H, CH_{Ar}), 6.99 (m, 2H, CH_{Ar}), 6.95 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 3.82 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.5 (C_{Ar}), 145.6 (C_{Ar}), 141.9 (C_{Ar}), 131.8 (C_{Ar}), 126.9 (CH_{Ar}), 126.8 ($2CH_{Ar}$), 123.0 (CH_{Ar}), 122.2 (C_{Ar}), 120.1 (CH_{Ar}), 119.1 (CH_{Ar}), 117.5 (C_{Ar}), 115.1 ($2CH_{Ar}$), 111.4 (CH_{Ar}), 111.0 (CH_{Ar}), 55.7 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3140 (w), 3097 (w), 3082 (w), 2838 (w), 1510 (m), 1243 (m), 1024 (m), 824 (m), 754 (s), 713 (m). MS (EI, 70 eV): *m/z* (%) = 279 $[M]^+$ (100), 264 (45), 236 (15), 191 (9), 140 (8). HRMS (EI): Calculated for $C_{17}H_{13}ONS$ $[M]^+$ 279.07124 found 279.07129.

4-(3-Methoxyphenyl)-4*H*-thieno[3,2-*b*]indole (18h): Yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.73 - 7.67 (m, 1H, CH_{Ar}), 7.54 - 7.48 (m, 1H, CH_{Ar}), 7.36 (t, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.26 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.22 - 7.12 (m, 2H, CH_{Ar}), 7.12 - 7.06 (m, 1H, CH_{Ar}), 7.06 - 7.00 (m, 2H, CH_{Ar}), 6.84 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 2.5 Hz, ^{5}J = 0.9 Hz, 1H, CH_{Ar}), 3.76 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.8 (C_{Ar}), 145.0 (C_{Ar}), 141.3 (C_{Ar}), 140.1 (C_{Ar}), 130.6 (CH_{Ar}), 127.0 (CH_{Ar}), 123.2 (CH_{Ar}), 122.6 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.2 (C_{Ar}), 117.4 (CH_{Ar}), 112.5 (CH_{Ar}), 111.7 (CH_{Ar}), 111.3 (CH_{Ar}), 111.0 (CH_{Ar}), 55.6 (OCH_3).

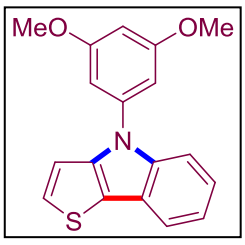


IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3392 (w), 3084 (w), 3051 (w), 3000 (w), 2956 (w), 2833 (w), 1589 (s), 1505 (s), 1489 (s), 1450 (s), 1391 (m), 1340 (m), 1313 (m), 1278 (m), 1252 (m), 1233 (m), 1193 (m), 1160 (m), 1086 (m), 1036 (m), 821 (m), 777 (m), 738 (s), 695 (s), 656 (s), 431 (m). MS (EI, 70 eV): *m/z* (%) = 279 $[M]^+$ (100), 236 (23), 204 (5), 191 (8), 139 (9). HRMS (EI): Calculated for $C_{17}H_{13}ONS$ $[M]^+$ 279.07124 found 279.07131.

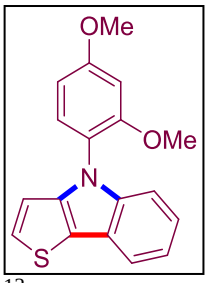
4-(2-Methoxyphenyl)-4*H*-thieno[3,2-*b*]indole (18i): Yellow oil. ^1H NMR (300 MHz, Chloroform-*d*) δ = 7.81 - 7.76 (m, 1H, CH_{Ar}), 7.50 - 7.41 (m, 2H, CH_{Ar}), 7.32 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.25 - 7.18 (m, 3H, CH_{Ar}), 7.18 - 7.08 (m, 2H, CH_{Ar}), 6.88 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 3.77 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.1 (C_{Ar}), 145.8 (C_{Ar}), 142.2 (C_{Ar}), 129.1 (CH_{Ar}), 128.7 (CH_{Ar}), 127.2 (C_{Ar}), 126.5 (CH_{Ar}), 122.8 (CH_{Ar}), 122.3 (C_{Ar}), 121.2 (CH_{Ar}), 119.9 (CH_{Ar}), 118.9 (CH_{Ar}), 117.4 (C_{Ar}), 112.8 (CH_{Ar}), 112.1 (CH_{Ar}), 111.7 (CH_{Ar}), 55.8 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3396 (w), 3048 (w), 3006 (w), 2958 (w), 2930 (w), 2835 (w), 1594 (m), 1509 (s), 1449 (s), 1393 (m), 1337 (m), 1273 (m), 1243 (m), 1118 (m), 1083 (m), 1021 (m), 702 (m), 654 (m), 430 (m). MS (EI, 70 eV): *m/z* (%) = 279 $[M]^+$ (100), 263 (20), 236 (11), 204 (5), 191 (7), 139 (8). HRMS (EI): Calculated for $C_{17}H_{13}ONS$ $[M]^+$ 279.07124 found 279.07092.



4-(3,5-Dimethoxyphenyl)-4*H*-thieno[3,2-*b*]indole (18j): Yellow oil. ^1H NMR (300 MHz, Chloroform-*d*) δ = 7.74 - 7.66 (m, 1H, CH_{Ar}), 7.59 - 7.52 (m, 1H, CH_{Ar}), 7.28 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.24 - 7.11 (m, 2H, CH_{Ar}), 7.07 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 6.67 (d, ^4J = 2.3 Hz, 2H, CH_{Ar}), 6.42 (t, ^4J = 2.3 Hz, 1H, CH_{Ar}), 3.76 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.8 ($2C_{Ar}OCH_3$), 143.9 (C_{Ar}), 140.3 (C_{Ar}), 139.6 (C_{Ar}), 126.0 (CH_{Ar}), 122.2 (CH_{Ar}), 121.6 (C_{Ar}), 119.5 (CH_{Ar}), 118.1 (CH_{Ar}), 117.2 (C_{Ar}), 110.9 (CH_{Ar}), 110.5 (CH_{Ar}), 102.5 ($2CH_{Ar}$), 98.0 (CH_{Ar}), 54.7 ($2OCH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3050 (w), 2959 (w), 2930 (w), 2837 (w), 1590 (s), 1505 (m), 1477 (m), 1449 (s), 1362 (m), 1285 (m), 1267 (m), 1202 (m), 1150 (s), 1062 (m), 1037 (m), 813 (m), 737 (s). MS (EI, 70 eV): *m/z* (%) = 310 (20), 309 $[M]^+$ (100), 266 (12), 251 (13), 234 (5). HRMS (EI): Calculated for $C_{18}H_{15}O_2NS$ $[M]^+$ 309.08180 found 309.08198.

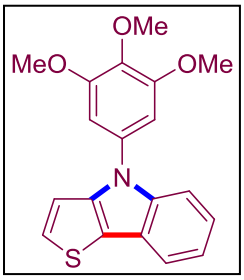


4-(2,4-Dimethoxyphenyl)-4*H*-thieno[3,2-*b*]indole (18k): Colorless solid,



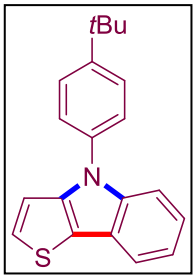
mp. 165 - 166 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.83 - 7.76 (m, 1H, CH_{Ar}), 7.36 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 7.32 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.25 - 7.16 (m, 3H, CH_{Ar}), 6.87 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 6.71 (d, ^{4}J = 2.6 Hz, 1H, CH_{Ar}), 6.63 (dd, ^{3}J = 8.6 Hz, ^{4}J = 2.6 Hz, 1H, CH_{Ar}), 3.91 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.5 (C_{Ar}), 156.3 (C_{Ar}), 146.2 (C_{Ar}), 142.5 (C_{Ar}), 129.4 (CH_{Ar}), 126.4 (CH_{Ar}), 122.7 (CH_{Ar}), 122.1 (C_{Ar}), 120.2 (C_{Ar}), 119.7 (CH_{Ar}), 118.9 (CH_{Ar}), 116.9 (C_{Ar}), 111.9 (CH_{Ar}), 111.5 (CH_{Ar}), 104.8 (CH_{Ar}), 100.2 (CH_{Ar}), 55.8 (OCH_3), 55.8 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3087 (w), 3045 (w), 3005 (w), 2965 (w), 2931 (w), 2835 (w), 1611 (m), 1584 (m), 1518 (s), 1451 (s), 1305 (m), 1204 (s), 1158 (s), 1050 (m), 1022 (m), 928 (w), 827 (m), 740 (s), 651 (m), 581 (m). MS (EI, 70 eV): *m/z* (%) = 309 $[M]^+$ (100), 294 (19), 251 (12), 223 (8). HRMS (EI): Calculated for $C_{18}H_{15}O_2NS$ $[M]^+$ 309.08180 found 309.08151.

4-(3,4,5-Trimethoxyphenyl)-4*H*-thieno[3,2-*b*]indole (18l): White solid,



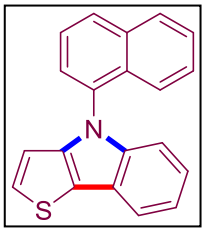
mp. 94 - 95 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.75 - 7.67 (m, 1H, CH_{Ar}), 7.52 - 7.46 (m, 1H, CH_{Ar}), 7.30 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.26 - 7.10 (m, 2H, CH_{Ar}), 7.02 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 6.72 (s, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 3.80 (s, 6H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.1 ($2C_{Ar}OCH_3$), 145.2 (C_{Ar}), 141.6 (C_{Ar}), 137.0 (C_{Ar}), 134.7 (C_{Ar}), 127.1 (CH_{Ar}), 123.2 (CH_{Ar}), 122.4 (C_{Ar}), 120.4 (CH_{Ar}), 119.2 (CH_{Ar}), 117.9 (C_{Ar}), 111.6 (CH_{Ar}), 111.2 (CH_{Ar}), 103.0 ($2CH_{Ar}$), 61.2 (OCH_3), 56.5 ($2OCH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3082 (w), 3051 (w), 2926 (m), 2824 (w), 1593 (m), 1505 (m), 1450 (m), 1415 (m), 1289 (m), 1226 (m), 1124 (s), 1007 (m), 818 (m), 740 (m), 655 (m). MS (EI, 70 eV): *m/z* (%) = 339 $[M]^+$ (100), 324 (75), 296 (10), 266 (9), 210 (9), 172 (13), 154 (8). HRMS (EI): Calculated for $C_{19}H_{17}O_3NS$ $[M]^+$ 339.09237 found 339.09217.

4-(4-(*tert*-Butyl)phenyl)-4*H*-thieno[3,2-*b*]indole (18m): Yellow oil. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.75 - 7.67 (m, 1H, CH_{Ar}), 7.52 - 7.39 (m, 5H, CH_{Ar}), 7.26 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.20 - 7.12 (m, 2H, CH_{Ar}), 7.02 (d, ^{3}J = 5.2 Hz, 1H, $CH_{thiophene}$), 1.32 (s, 9H, *t*Bu). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 149.9 (C_{Ar}), 145.2 (C_{Ar}), 141.5 (C_{Ar}), 136.3 (C_{Ar}), 126.9 (CH_{Ar}), 126.7 ($2CH_{Ar}$), 124.7 ($2CH_{Ar}$), 123.0 (CH_{Ar}), 122.4 (C_{Ar}), 120.2 (CH_{Ar}), 119.1 (CH_{Ar}), 117.8 (C_{Ar}), 111.7 (CH_{Ar}), 111.3



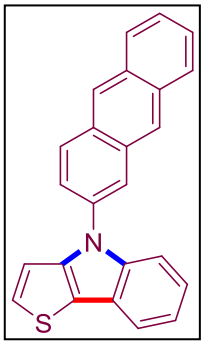
(CH_{Ar}), 34.9 (C_{tBu}), 31.6 ($3CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3049 (w), 2959 (m), 2901 (w), 2865 (w), 1602 (w), 1519 (s), 1451 (s), 1394 (m), 1337 (m), 1267 (m), 1205 (m), 1112 (m), 1086 (m), 1046 (m), 1016 (m), 922 (w), 825 (m), 705 (m), 648 (m), 552 (m). MS (EI, 70 eV): *m/z* (%) = 305 $[M]^+$ (100), 290 (95), 275 (16), 262 (11), 172 (17), 131 (11). HRMS (EI): Calculated for $C_{20}H_{19}NS$ $[M]^+$ 305.12327 found 305.12374.

4-(Naphthalen-1-yl)-4*H*-thieno[3,2-*b*]indole (18n): Colorless solid, mp. 141 - 142 °C.



^{1}H NMR (300 MHz, Acetone-d_6) δ = 8.19 - 8.09 (m, 2H, CH_{Ar}), 7.92 - 7.87 (m, 1H, CH_{Ar}), 7.79 - 7.70 (m, 2H, CH_{Ar}), 7.61 (ddd, ^3J = 8.2 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.54 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.45 (ddd, ^3J = 8.2 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.32 - 7.27 (m, 1H, CH_{Ar}), 7.27 - 7.16 (m, 2H, CH_{Ar}), 7.06 - 6.99 (m, 1H, CH_{Ar}), 6.79 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$). ^{13}C NMR (75 MHz, Acetone-d_6) δ = 147.6 (C_{Ar}), 144.0 (C_{Ar}), 135.8 (C_{Ar}), 135.6 (C_{Ar}), 131.2 (C_{Ar}), 129.8 (CH_{Ar}), 129.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.0 (CH_{Ar}), 127.7 (CH_{Ar}), 126.9 (CH_{Ar}), 126.7 (CH_{Ar}), 123.9 (CH_{Ar}), 123.8 (CH_{Ar}), 123.0 (C_{Ar}), 121.1 (CH_{Ar}), 119.7 (CH_{Ar}), 117.9 (C_{Ar}), 112.3 (CH_{Ar}), 112.1 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3047 (m), 1592 (w), 1575 (w), 1504 (m), 1448 (m), 1401 (m), 1327 (m), 1211 (m), 1110 (m), 1076 (m), 1914 (m), 800 (m), 773 (m), 735 (s), 657 (m). MS (EI, 70 eV): *m/z* (%) = 299 $[M]^+$ (100), 265 (18), 149 (8), 127 (7). HRMS (EI): Calculated for $C_{20}H_{13}NS$ $[M]^+$ 299.07632 found 299.07610.

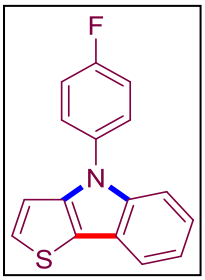
4-(Anthracen-2-yl)-4*H*-thieno[3,2-*b*]indole (18o): Yellow solid, mp. 176 - 177 °C.



^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.53 (s, 1H, CH_{Ar}), 8.47 (s, 1H, CH_{Ar}), 8.25 - 8.14 (m, 2H, CH_{Ar}), 8.05 (m, 2H, CH_{Ar}), 7.90 - 7.78 (m, 1H, CH_{Ar}), 7.78 - 7.65 (m, 2H, CH_{Ar}), 7.59 - 7.47 (m, 2H, CH_{Ar}), 7.42 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.37 - 7.18 (m, 3H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.2 (C_{Ar}), 141.5 (C_{Ar}), 135.7 (C_{Ar}), 132.3 (C_{Ar}), 131.9 (C_{Ar}), 131.7 (C_{Ar}), 130.2 (CH_{Ar}), 130.1 (C_{Ar}), 128.3 (CH_{Ar}), 128.0 (CH_{Ar}), 127.0 (CH_{Ar}), 126.5 (CH_{Ar}), 126.1 (CH_{Ar}), 126.0 (CH_{Ar}), 125.7 (CH_{Ar}), 123.7 (CH_{Ar}), 123.1 (CH_{Ar}), 122.6 (C_{Ar}), 122.3 (CH_{Ar}), 120.5 (CH_{Ar}), 119.1 (CH_{Ar}), 118.3 (C_{Ar}), 111.8 (CH_{Ar}), 111.4 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3049 (w), 2954 (w), 1670 (w), 1592 (w), 1504 (m), 1450 (m), 1321 (m), 887 (m), 738 (s), 652 (m), 603 (m), 469 (m), 429 (m). MS (EI, 70 eV): *m/z* (%) = 349 $[M]^+$ (100),

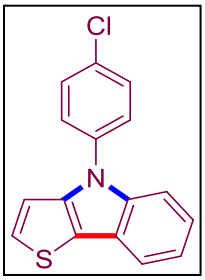
315 (4), 176 (7). HRMS (EI): Calculated for $C_{24}H_{15}NS$ $[M]^+$ 349.09197 found 349.09165.

4-(4-Fluorophenyl)-4*H*-thieno[3,2-*b*]indole (18p): White solid, mp. 117 - 118 °C.



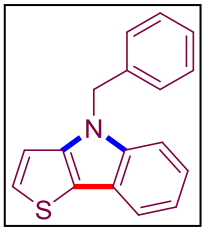
^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.75 - 7.68 (m, 1H, CH_{Ar}), 7.50 - 7.41 (m, 2H, CH_{Ar}), 7.40 - 7.36 (m, 1H, CH_{Ar}), 7.28 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.23 - 7.11 (m, 4H, CH_{Ar}), 6.95 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.6 (FC_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.2 (d, $^1J_{CF}$ = 246.7 Hz, CF_{Ar}), 145.2 (C_{Ar}), 141.6 (C_{Ar}), 134.6 (d, $^4J_{CF}$ = 3.1 Hz, C_{Ar}), 127.1 (CH_{Ar}), 127.0 (d, $^3J_{CF}$ = 8.5 Hz, $2CH_{Ar}$), 123.2 (CH_{Ar}), 122.3 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.0 (C_{Ar}), 116.7 (d, $^2J_{CF}$ = 22.8 Hz, $2CH_{Ar}$), 111.2 (CH_{Ar}), 110.9 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3106 (w), 3093 (w), 3050 (w), 1600 (w), 1510 (s), 1451 (m), 1340 (m), 1218 (m), 1090 (m), 826 (m), 740 (s), 708 (m), 571 (m), 515 (m). MS (EI, 70 eV): *m/z* (%) = 267 $[M]^+$ (100), 235 (9), 222 (9), 128 (5), 75 (10). HRMS (EI): Calculated for $C_{16}H_{10}NFS$ $[M]^+$ 267.05125 found 267.05098.

4-(4-Chlorophenyl)-4*H*-thieno[3,2-*b*]indole (18q): Colorless solid, mp. 114 - 115 °C.



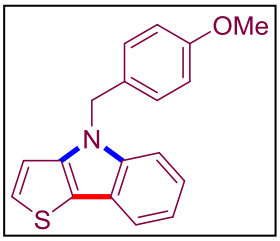
^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.76 - 7.69 (m, 1H, CH_{Ar}), 7.46 (m, 5H, CH_{Ar}), 7.31 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.25 - 7.13 (m, 2H, CH_{Ar}), 6.99 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 144.8 (C_{Ar}), 141.2 (C_{Ar}), 137.6 (C_{Ar}), 132.4 (C_{Ar}), 130.1 ($2CH_{Ar}$), 127.3 (CH_{Ar}), 126.4 ($2CH_{Ar}$), 123.4 (CH_{Ar}), 122.6 (C_{Ar}), 120.7 (CH_{Ar}), 119.3 (CH_{Ar}), 118.5 (C_{Ar}), 111.3 (CH_{Ar}), 110.9 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3099 (w), 3084 (w), 3050 (w), 2959 (w), 2920 (w), 2848 (w), 1592 (w), 1505 (s), 1488 (m), 1452 (m), 1390 (m), 1356 (w), 1338 (m), 1204 (m), 1088 (s), 1012 (m), 823 (s), 748 (s), 708 (s), 661 (m), 646 (m), 509 (m), 479 (m), 431 (w). MS (EI, 70 eV): *m/z* (%) = 285 (32), 283 $[M]^+$ (100), 247 (12), 128 (10), 75 (18). HRMS (EI): Calculated for $C_{16}H_{10}NClS$ 283.02170 found 283.02225, calculated for $C_{16}H_{10}N^{37}ClS$ $[M]^+$ 285.01875 found 285.01936.

4-Benzyl-4*H*-thieno[3,2-*b*]indole (18r): Yellow oil. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.69 (ddd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 7.25 (dd, ^4J = 1.4 Hz, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.23 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.21 - 7.11 (m, 5H, CH_{Ar}), 7.11 - 7.03 (m, 2H, CH_{Ar}), 6.84 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 5.36 (s,



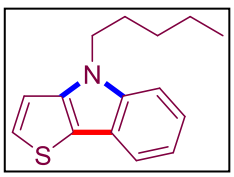
2$H_{aliphatic}$, CH_2). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.6 (C_{Ar}), 141.7 (C_{Ar}), 137.3 (C_{Ar}), 128.9 (2CH_{Ar}), 127.7 (CH_{Ar}), 127.0 (CH_{Ar}), 126.8 (2CH_{Ar}), 122.7 (CH_{Ar}), 122.1 (C_{Ar}), 119.5 (CH_{Ar}), 119.1 (CH_{Ar}), 116.7 (C_{Ar}), 110.7 (CH_{Ar}), 110.3 (CH_{Ar}), 48.9 (CH_2). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3422 (w), 3081 (w), 3054 (w), 3025 (w), 2921 (w), 2852 (w), 1733 (w), 1583 (w), 1507 (m), 1463 (m), 1349 (m), 1161 (m), 736 (s), 695 (m), 654 (s), 430 (m). MS (EI, 70 eV): *m/z* (%) = 264 (15), 263 $[M]^+$ (71), 172 (27), 128 (13), 91 (100), 65 (17). HRMS (EI): Calculated for $C_{17}H_{13}NS$ $[M]^+$ 263.07632 found 263.07642.

4-(4-methoxybenzyl)-4*H*-thieno[3,2-*b*]indole (18s): Colorless oil. ^{1}H NMR



(250 MHz, Chloroform-*d*) δ = 7.68 (m, 1H, CH_{Ar}), 7.28 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.22 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 7.20 - 7.12 (m, 1H, CH_{Ar}), 7.12 - 7.04 (m, 1H, CH_{Ar}), 7.00 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 6.82 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 6.70 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 5.28 (s, 2$H_{aliphatic}$, CH_2), 3.65 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.2 (C_{Ar}), 145.5 (C_{Ar}), 141.7 (C_{Ar}), 129.4 (C_{Ar}), 128.2 (2CH_{Ar}), 126.9 (CH_{Ar}), 122.7 (CH_{Ar}), 122.1 (C_{Ar}), 119.4 (CH_{Ar}), 119.1 (CH_{Ar}), 116.6 (C_{Ar}), 114.3 (2CH_{Ar}), 110.7 (CH_{Ar}), 110.3 (CH_{Ar}), 55.4 (OCH_3), 48.4 (CH_2). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3105 (w), 3051 (w), 3024 (w), 2997 (m), 2955 (m), 2915 (w), 2832 (m), 1613 (m), 1584 (m), 1508 (s), 1457 (s), 1439 (m), 1348 (m), 1245 (s), 1161 (s), 1025 (m), 807 (s), 735 (s), 653 (s), 430 (m). MS (EI, 70 eV): *m/z* (%) = 294 (6), 293 $[M]^+$ (28), 121 (100), 78 (10). HRMS (EI): Calculated for $C_{18}H_{15}ONS$ $[M]^+$ 293.08689 found 293.08643.

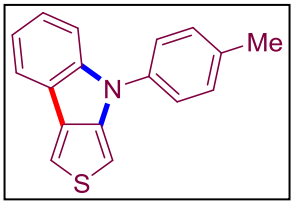
4-Pentyl-4*H*-thieno[3,2-*b*]indole (18t): Yellow oil. ^{1}H NMR (250 MHz,



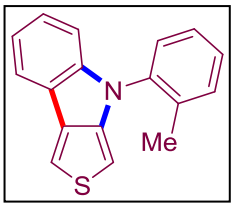
Chloroform-*d*) δ = 7.76 (ddd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 7.43 - 7.35 (m, 2H, CH_{Ar}), 7.34 - 7.26 (m, 1H, CH_{Ar}), 7.17 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.08 (d, ^3J = 5.2 Hz, 1H, $CH_{thiophene}$), 4.27 (t, ^3J = 7.1 Hz, 2$H_{aliphatic}$, CH_2), 2.00 - 1.74 (m, 2$H_{aliphatic}$, CH_2), 1.34 (m, 4$H_{aliphatic}$, 2CH_2), 0.98 - 0.80 (m, 3$H_{aliphatic}$, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 145.5 (C_{Ar}), 141.4 (C_{Ar}), 126.8 (CH_{Ar}), 122.4 (CH_{Ar}), 121.9 (C_{Ar}), 119.1 (CH_{Ar}), 119.0 (CH_{Ar}), 116.0 (C_{Ar}), 110.5 (CH_{Ar}), 110.0 (CH_{Ar}), 45.4 (CH_2, pentyl), 29.6 (CH_2, pentyl), 29.4 (CH_2, pentyl), 22.5 (CH_2, pentyl), 14.1 (CH_3, pentyl). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3081 (w), 3052 (w), 2954 (m), 2927 (m), 2856 (m), 1610 (w), 1509 (m), 1123 (m), 1348 (m), 1317 (m), 1162 (m), 1079 (m), 1017 (w),

815 (w), 735 (s), 653 (m), 431 (m). MS (EI, 70 eV): *m/z* (%) = 243 $[M]^+$ (30), 186 (100), 115 (12). HRMS (EI): Calculated for $C_{15}H_{17}NS$ $[M]^+$ 243.10762 found 243.10811.

5.2.5.3.Indolo[3,4-b]thiophene

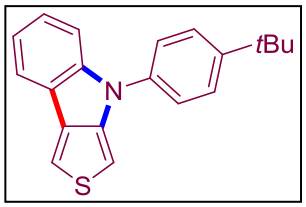
4-(*p*-Tolyl)-4*H*-thieno[3,4-*b*]indole (19a): Yellow oil. ^{1}H NMR (250 MHz, 

Chloroform-*d*) δ = 7.86 (dt, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.54 (m, 1H, CH_{Ar}), 7.50 (s, 1H, CH_{Ar}), 7.49 (s, 1H, CH_{Ar}), 7.31 - 7.21 (m, 4H, CH_{Ar}), 7.14 (ddd, ^3J = 7.6 Hz, ^3J = 6.6 Hz, ^4J = 1.7 Hz, 1H, CH_{Ar}), 6.59 (m, 1H, CH_{Ar}), 2.36 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 148.1 (C_{Ar}), 146.3 (C_{Ar}), 136.8 (C_{Ar}), 136.1 (C_{Ar}), 133.5 (C_{Ar}), 130.5 ($2CH_{Ar}$), 126.5 (CH_{Ar}), 124.4 ($2CH_{Ar}$), 121.5 (CH_{Ar}), 120.3 (C_{Ar}), 119.8 (CH_{Ar}), 110.6 (CH_{Ar}), 109.9 (CH_{Ar}), 92.6 (CH_{Ar}), 21.3 (CH_3). IR (ATR, cm^{-1}): ṽ = 3399 (w), 3101 (w), 3030 (w), 2917 (w), 2859 (w), 1608 (w), 1576 (m), 1512 (s), 1449 (m), 1397 (m), 1321 (m), 1223 (m), 1152 (m), 1108 (w), 1020 (w), 928 (w), 816 (m), 740 (s), 619 (m), 499 (m). MS (EI, 70 eV): *m/z* (%) = 263 $[M]^+$ (100), 247 (8), 218 (12), 128 (7). HRMS (EI): Calculated for $C_{17}H_{13}NS$ $[M]^+$ 263.07632 found 263.07634.

4-(*o*-Tolyl)-4*H*-thieno[3,4-*b*]indole (19b): Yellow oil. ^{1}H NMR (300 MHz, 

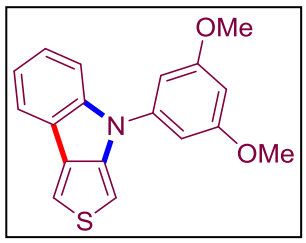
Acetone-d_6) δ = 8.02 - 7.92 (m, 2H, CH_{Ar}), 7.89 - 7.79 (m, 1H, CH_{Ar}), 7.79 (d, ^4J = 2.5 Hz, 1H, $CH_{thiophene}$), 7.58 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.48 - 7.32 (m, 2H, CH_{Ar}), 7.16 (m, 1H, CH_{Ar}), 6.93 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 6.51 (d, ^4J = 2.5 Hz, 1H, $CH_{thiophene}$), 2.22 (s, 3H, CH_3). ^{13}C NMR (75 MHz, Acetone-d_6) δ = 149.9 (C_{Ar}), 147.5 (C_{Ar}), 141.0 (C_{Ar}), 137.8 (C_{Ar}), 134.1 (C_{Ar}), 131.2 (CH_{Ar}), 129.5 (CH_{Ar}), 127.5 (CH_{Ar}), 126.9 (CH_{Ar}), 122.3 (CH_{Ar}), 121.3 (CH_{Ar}), 120.8 (C_{Ar}), 120.4 (CH_{Ar}), 112.0 (CH_{Ar}), 110.5 (CH_{Ar}), 93.2 (CH_{Ar}), 18.2 (CH_3). IR (ATR, cm^{-1}): ṽ = 3412 (w), 3103 (w), 3052 (w), 2919 (w), 2853 (w), 1577 (m), 1499 (m), 1450 (m), 1395 (m), 1316 (m), 1227 (m), 1151 (m), 824 (m), 741 (s), 622 (m), 445 (m). MS (EI, 70 eV): *m/z* (%) = 264 (21), 263 $[M]^+$ (100), 262 (41), 260 (11), 231 (16), 228 (11), 218 (20), 217 (32), 216 (11), 204 (15), 128 (17). HRMS (EI): Calculated for $C_{17}H_{13}NS$ $[M]^+$ 263.07632 found 263.07567.

4-(4-(*tert*-Butyl)phenyl)-4*H*-thieno[3,4-*b*]indole (19c): Yellow oil. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.78 (m, 1H, CH_{Ar}), 7.48 (m, 4H, CH_{Ar}), 7.41 (s, $1H_{Ar}$),



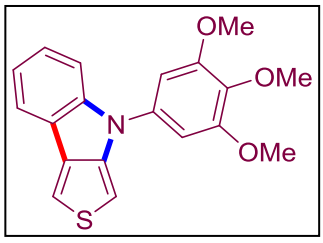
7.33 (ddd, ^{3}J = 8.3 Hz, ^{4}J = 1.2 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 7.25 (dd, ^{3}J = 7.1 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.18 (s, 1H, CH_{Ar}), 7.09 - 7.02 (m, 1H, CH_{Ar}), 1.33 (s, 9H, *t*Bu). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 149.2 (C_{Ar}), 148.1 (C_{Ar}), 146.2 (C_{Ar}), 136.8 (C_{Ar}), 133.5 (C_{Ar}), 126.8 ($2CH_{Ar}$), 126.5 (CH_{Ar}), 123.9 ($2CH_{Ar}$), 121.5 (CH_{Ar}), 120.4 (C_{Ar}), 119.8 (CH_{Ar}), 110.5 (CH_{Ar}), 110.0 (CH_{Ar}), 92.7 (CH_{Ar}), 34.8 (C_{tBu}), 31.6 ($3CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3401 (w), 3053 (w), 2958 (m), 2865 (w), 1605 (w), 1578 (m), 1517 (s), 1451 (m), 1399 (m), 1323 (m), 1224 (m), 1190 (m), 1152 (m), 1017 (w), 827 (m), 742 (s), 622 (m), 552 (m). MS (EI, 70 eV): *m/z* (%) = 305 $[M]^+$ (97), 290 (100), 275 (18), 262 (8), 172 (20), 131 (40), 109 (9). HRMS (EI): Calculated for $C_{20}H_{19}NS$ $[M]^+$ 305.12327 found 305.12400.

4-(3,5-Dimethoxyphenyl)-4*H*-thieno[3,4-*b*]indole (19d): Yellow oil. ^{1}H NMR



(300 MHz, Chloroform-*d*) δ = 7.85 (m, 1H, CH_{Ar}), 7.52 - 7.45 (m, 2H, CH_{Ar}), 7.33 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 7.3 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.15 (td, ^{3}J = 7.3 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 6.81 (d, ^{4}J = 2.3 Hz, 2H, CH_{Ar}), 6.68 (d, ^{4}J = 2.5 Hz, 1H, $CH_{thiophene}$), 6.45 (t, ^{4}J = 2.3 Hz, 1H, CH_{Ar}), 3.85 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.9 ($2C_{Ar}$), 147.7 (C_{Ar}), 145.8 (C_{Ar}), 141.2 (C_{Ar}), 133.5 (C_{Ar}), 126.6 (CH_{Ar}), 121.5 (CH_{Ar}), 120.6 (C_{Ar}), 120.1 (CH_{Ar}), 110.8 (CH_{Ar}), 110.4 (CH_{Ar}), 102.6 ($2CH_{Ar}$), 98.4 (CH_{Ar}), 93.3 (CH_{Ar}), 55.7 ($2OCH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3388 (w), 3102 (w), 3056 (w), 2998 (w), 2929 (w), 2837 (w), 1591 (s), 1498 (m), 1451 (s), 1293 (m), 1258 (s), 1202 (s), 1149 (s), 1056 (m), 929 (m), 823 (m), 742 (s), 689 (m), 627 (m). MS (EI, 70 eV): *m/z* (%) = 310 (21), 309 $[M]^+$ (100), 294 (22), 264 (8), 251 (19), 250 (18), 234 (10), 191 (6), 178 (11), 128 (9). HRMS (EI): Calculated for $C_{18}H_{15}O_2NS$ $[M]^+$ 309.08180 found 309.08182.

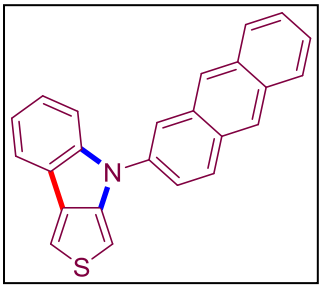
4-(3,4,5-Trimethoxyphenyl)-4*H*-thieno[3,4-*b*]indole (19e): Colorless solid,



mp. 96 - 97 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.87 (ddd, ^{3}J = 7.7 Hz, ^{4}J = 1.3 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 7.50 (d, ^{4}J = 1.8 Hz, 1H, $CH_{thiophene}$), 7.40 (ddd, ^{3}J = 8.2 Hz, ^{4}J = 1.3 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 7.33 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.16 (ddd, ^{3}J = 7.7 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 6.85 (s, 2H, CH_{Ar}), 6.61 (d, ^{4}J = 2.5 Hz, 1H, $CH_{thiophene}$), 3.94 (s, 3H, CH_3), 3.89 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.2

($2C_{Ar}OCH_3$), 148.1 (C_{Ar}), 146.3 (C_{Ar}), 136.5 (C_{Ar}), 135.1 (C_{Ar}), 133.4 (C_{Ar}), 126.6 (CH_{Ar}), 121.6 (CH_{Ar}), 120.4 (C_{Ar}), 120.0 (CH_{Ar}), 110.9 (CH_{Ar}), 110.0 (CH_{Ar}), 102.2 ($2CH_{Ar}$), 92.7 (CH_{Ar}), 61.2 (OCH_3), 56.5 ($2OCH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3101 (m), 3056 (w), 2999 (m), 2929 (m), 2829 (w), 1592 (m), 1502 (m), 1450 (m), 1416 (m), 1354 (m), 1262 (m), 1226 (m), 1123 (s), 998 (m), 823 (m), 736 (s). MS (EI, 70 eV): *m/z* (%) = 339 $[M]^+$ (100), 324 (78), 296 (6), 280 (8), 238 (10), 210 (8), 172 (14). HRMS (EI): Calculated for $C_{19}H_{17}O_3NS$ $[M]^+$ 339.09237 found 339.09241.

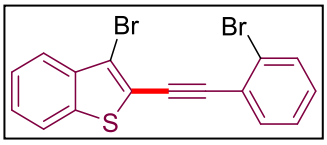
4-(Anthracen-2-yl)-4*H*-thieno[3,4-*b*]indole (19f): Light yellow solid, mp. 171 - 172 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.50 (s, 1H, CH_{Ar}), 8.44 (s, 1H, CH_{Ar}), 8.24 - 8.13 (m, 2H, CH_{Ar}), 8.11 - 7.96 (m, 2H, CH_{Ar}), 7.91 (ddd, ^3J = 7.5 Hz, ^4J = 1.3 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 7.79 (dd, ^3J = 9.0 Hz, ^4J = 2.1 Hz, 1H, CH_{Ar}), 7.59 - 7.44 (m, 4H, CH_{Ar}), 7.36 (ddd, ^3J = 8.3 Hz, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.20 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 6.76 (d, ^4J = 2.5 Hz, 1H, $CH_{thiophene}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 147.9 (C_{Ar}), 146.0 (C_{Ar}), 136.4 (C_{Ar}), 133.5 (C_{Ar}), 132.4 (C_{Ar}), 132.0 (C_{Ar}), 131.9 (C_{Ar}), 130.4 (CH_{Ar}), 130.1 (C_{Ar}), 128.4 (CH_{Ar}), 128.1 (CH_{Ar}), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.1 (CH_{Ar}), 125.9 (CH_{Ar}), 125.7 (CH_{Ar}), 123.2 (CH_{Ar}), 121.6 (CH_{Ar}), 121.3 (CH_{Ar}), 120.7 (C_{Ar}), 120.3 (CH_{Ar}), 110.9 (CH_{Ar}), 110.2 (CH_{Ar}), 93.2 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3093 (w), 3050 (w), 2956 (w), 1628 (w), 1573 (m), 1451 (m), 1389 (w), 1216 (w), 891 (m), 742 (s), 472 (m). MS (EI, 70 eV): *m/z* (%) = 349 $[M]^+$ (100), 304 (48), 174 (24), 152 (20), 128 (6). HRMS (EI): Calculated for $C_{24}H_{15}NS$ $[M]^+$ 349.09197 found 349.09161.



5.2.6. Synthesis of benzothieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridines by site-selective Sonogashira reaction followed by domino C-N coupling/hydroamination/C-H arylation.

5.2.6.1. Starting materials

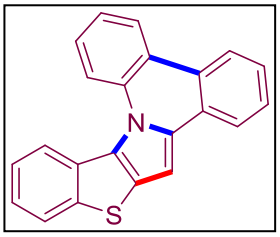
3-Bromo-2-((2-bromophenyl)ethynyl)benzo[*b*]thiophene (25): White solid, mp. 190 - 191 °C. ^{1}H NMR (300 MHz, Chloroform-*d*): δ = 7.70 - 7.62 (m, 2H, CH_{Ar}), 7.53 - 7.49 (m, 2H, CH_{Ar}), 7.37 - 7.29 (m, 2H, CH_{Ar}), 7.22 - 7.17 (m, 1H, CH_{Ar}), 7.13 - 7.07 (m, 1H, CH_{Ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.5 (C_{Ar}), 137.5 (C_{Ar}),



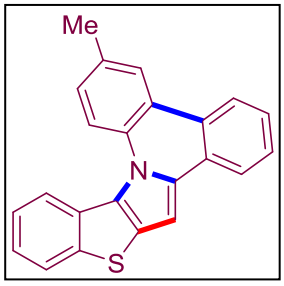
133.5 (CH_{Ar}), 132.6 (CH_{Ar}), 130.2 (CH_{Ar}), 127.1 (CH_{Ar}), 126.7 (CH_{Ar}), 125.6 (CH_{Ar}), 125.5 (C_{Ar}), 124.6 (C_{Ar}), 123.8 (CH_{Ar}), 122.3 (CH_{Ar}), 120.0 (C_{Ar}), 114.5 (C_{Ar}), 97.4 (C_{sp}), 86.1 (C_{sp}).IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3111, 3056, 3026, 2747, 2324, 2286, 2211 (w), 1942, 1907, 1879, 1820, 1782, 1688 (m), 1659, 1603 (w), 1587, 1555, 1522 (m), 1504, 1480 (w), 1463, 1451, 1432 (s), 1320, 1311, 1287 (m), 1271 (w), 1240 (s), 1210, 1201 (w), 1160, 1124 (m), 1105, 1079 (w), 1063 (m), 1038, 1025, 1017 (s), 974, 939 (w), 924 (s), 855 (m), 820 (s), 762 (m), 740, 717, 662 (s), 634, 599, 546 (m). MS (EI, 70 eV): *m/z* (%) = 394 (54) 392 $[M]^+$ (100), 390 (50), 232 (84), 196 (15), 187 (62), 161 (10), 116 (42). HRMS (EI): Calculated for $C_{16}H_8Br^{81}BrS$ $[M]^+$ 391.86875 found: 391.8684; calculated for $C_{16}H_8{}^{81}Br_2S_1$ $[M]^+$ 393.86670 found 393.86649.

5.2.6.2.Benzothieno[2',3':4,5]pyrrolo[1,2-f]phenanthridines

Benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24a/26a): Pale yellow solid, mp. 188 - 189 °C. ^{1}H NMR (250 MHz, DMSO): δ = 8.51 (d, 1H, ^3J = 8.1 Hz, CH_{Ar}), 8.46 - 8.41 (m, 2H, CH_{Ar}), 8.33 (d, 1H, ^3J = 8.2 Hz, CH_{Ar}), 8.21 - 8.17 (m, 1H, CH_{Ar}), 7.98 (d, 1H, ^3J = 7.9 Hz, CH_{Ar}), 7.75 - 7.69 (m, 1H, CH_{Ar}), 7.60 - 7.46 (m, 5H, CH_{Ar}), 7.36 - 7.30 (m, 1H, CH_{Ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 141.4 (C_{Ar}), 135.9 (C_{Ar}), 133.2 (C_{Ar}), 129.6 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (CH_{Ar}), 128.0 (CH_{Ar}), 127.7 (C_{Ar}), 127.2 (CH_{Ar}), 125.7 (C_{Ar}), 125.6 (C_{Ar}), 124.6 (CH_{Ar}), 124.5 (CH_{Ar}), 124.4 (CH_{Ar}), 124.2 (CH_{Ar}), 123.2 (CH_{Ar}), 123.0 (CH_{Ar}), 122.8 (CH_{Ar}), 121.8 (C_{Ar}), 120.6 (CH_{Ar}), 117.7 (CH_{Ar}), 96.4 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3116 (w), 3052 (w), 3029 (w), 2918 (m), 2849 (m), 1892 (w), 1807 (w), 1682 (w), 1605 (m), 1585 (m), 1532 (m), 1471 (m), 1455, 1436 (s), 1376 (m), 1354 (s), 1293 (w), 1233 (w), 1160 (m), 1010 (w), 975 (w), 962 (w), 948, 922 (m), 863 (w), 847 (w), 796 (w), 750, 735, 710, 694 (s), 666 (m), 652 (m), 614 (m), 563, 532 (m). MS (EI, 70 eV): *m/z* (%) = 324 (26), 323 $[M]^+$ (100), 322 (22), 321 (07), 221 (07), 162 (06), 146 (06). HRMS (EI): Calculated for $C_{22}H_{13}NS$ $[M]^+$ 323.07632 found 323.07692.

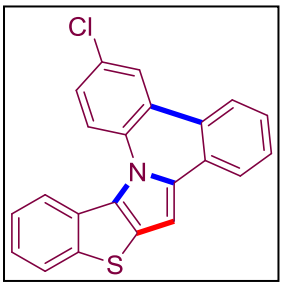


6-Methylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24b/26b): Pale yellow solid, mp. 159 - 160 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.31 (d, 1H, ^3J = 8.4 Hz, CH_{Ar}), 8.27 (d, 1H, ^3J = 8.4 Hz, CH_{Ar}), 8.24 - 8.21 (m, 1H, CH_{Ar}), 8.09 (s, 1H, CH_{Ar}), 7.96 - 8.01 (m, 1H, CH_{Ar}), 7.80 (dd, 1H, ^3J = 7.9 Hz, ^5J = 0.6 Hz, CH_{Ar}), 7.47 - 7.32 (m, 4H, CH_{Ar}), 7.25 - 7.20 (m, 1H, CH_{Ar}), 7.19 (s, 1H, CH_{Ar}), 2.50 (s, 3H,



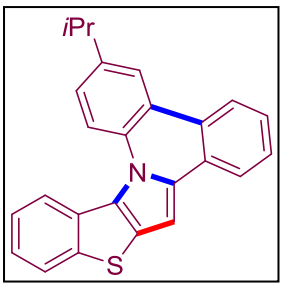
CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 142.0 (C_{Ar}), 136.2 (C_{Ar}), 133.6 (C_{Ar}), 131.9 (C_{Ar}), 130.1 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (CH_{Ar}), 128.4 (C_{Ar}), 128.2 (CH_{Ar}), 126.7 (CH_{Ar}), 126.4 (C_{Ar}), 126.2 (C_{Ar}), 124.4 (CH_{Ar}), 124.3 (CH_{Ar}), 123.8 (CH_{Ar}), 123.2 (CH_{Ar}), 122.7 (CH_{Ar}), 122.5 (CH_{Ar}), 122.2 (C_{Ar}), 120.8 (CH_{Ar}), 118.2 (CH_{Ar}), 95.4 (CH_{Ar}), 21.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3037 (w), 2913 (w), 2851 (w), 1606 (w), 1532 (m), 1498 (m), 1482 (m), 1447 (s), 1409, 1372 (m), 1352 (s), 1292 (w), 1196 (w), 1181 (w), 1117 (w), 874, 843 (w), 817 (s), 811 (s), 767 (s), 750 (s), 738 (s), 721 (s), 681 (w), 665 (m), 578 (s). MS (EI, 70 eV): *m/z* (%) = 338 (27), 337 $[M]^+$ (100), 336 (18), 322 (08), 161 (16). HRMS (EI): Calculated for $C_{23}H_{15}NS$ $[M]^+$ 337.09199 found 337.09137.

6-Chlorobenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24c/26c): Pale



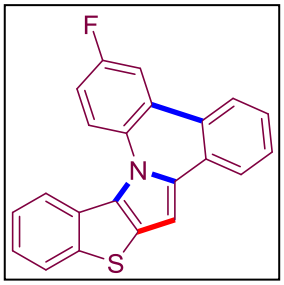
yellow solid, mp. 227 - 228 °C. ^1H NMR (250 MHz, DMSO): δ = 8.53 (d, ^4J = 2.4 Hz, 1H, CH_{Ar}), 8.47 - 8.43 (m, 2H, CH_{Ar}), 8.31 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.22 - 8.19 (m, 1H, CH_{Ar}), 8.01 - 7.97 (m, 1H, CH_{Ar}), 7.75 (d, ^3J = 8.8 Hz, 1H, CH_{Ar}), 7.62 - 7.58 (m, 1H, CH_{Ar}), 7.58 - 7.46 (m, 3H, CH_{Ar}), 7.36 (ddd, ^3J = 8.2 Hz, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 141.6 (C_{Ar}), 135.8 (C_{Ar}), 132.0 (C_{Ar}), 129.7 (C_{Ar}), 129.6 (C_{Ar}), 129.2 (CH_{Ar}), 129.1 (C_{Ar}), 127.8 (CH_{Ar}), 127.6 (C_{Ar}), 127.3 (CH_{Ar}), 126.0 (C_{Ar}), 124.7 (C_{Ar}), 124.5 (CH_{Ar}), 124.3 (CH_{Ar}), 124.0 (CH_{Ar}), 123.7 (C_{Ar}), 123.3 (CH_{Ar}), 123.2 (CH_{Ar}), 123.1 (CH_{Ar}), 120.5 (CH_{Ar}), 119.4 (CH_{Ar}), 96.8 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (w), 3056 (w), 2925 (w), 2850 (w), 1942 (w), 1897 (w), 1606 (m), 1585 (m), 1557 (m), 1529 (s), 1491 (w), 1605, 1476 (m), 1444, 1408 (s), 1371 (w), 1352 (m), 1293 (m), 1253 (m), 1188 (m), 1158 (m), 1102 (s), 950 (m), 923 (m), 861 (m), 835 (m), 811 (s), 767 (m), 758 (m), 739 (s), 722 (s), 710 (s), 652 (m), 578 (s), 529 (s). MS (EI, 70 eV): *m/z* (%) = 359 (40), 357 $[M]^+$ (100), 322 (21), 321 (10), 255 (08), 178 (08), 161 (33). HRMS (EI): Calculated for $C_{22}H_{12}N^{35}ClS$ $[M]^+$ 357.03735 found 357.03685, calculated for $C_{22}H_{12}N^{37}ClS$ $[M]^+$ 359.03440 found 359.03457.

6-Isopropylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24d): Pale yellow solid, mp. 111 - 112 °C. ^1H NMR (300 MHz, Chloroform-*d*): δ = 8.31 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.26 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.21 (dd, ^3J = 6.8 Hz, ^4J = 2.5 Hz, 1H, CH_{Ar}), 8.01 (d, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.92 - 7.96 (m, 1H, CH_{Ar}), 7.78



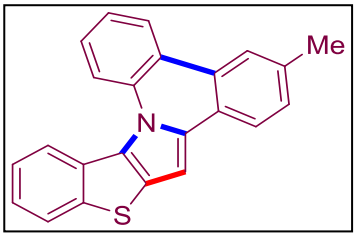
(d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.30 - 7.42 (m, 4H, CH_{Ar}), 2.17 - 7.22 (m, 1H, CH_{Ar}), 7.13 (s, 1H, CH_{Ar}), 2.97 - 3.09 (m, 1H, CH_{iPr}), 1.32 (d, ^{3}J = 6.9 Hz, 6H, $CH_{3\text{-}iPr}$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.6 (C_{Ar}), 142.0 (C_{Ar}), 136.2 (C_{Ar}), 132.2 (C_{Ar}), 130.1 (C_{Ar}), 129.2 (C_{Ar}), 128.4 (C_{Ar}), 128.1 (CH_{Ar}), 126.7 (CH_{Ar}), 126.4 (C_{Ar}), 126.3 (C_{Ar}), 125.9 (CH_{Ar}), 124.4 (CH_{Ar}), 123.8 (CH_{Ar}), 123.2 (CH_{Ar}), 122.7 (CH_{Ar}), 122.4 (CH_{Ar}), 122.1 (C_{Ar}), 121.8 (CH_{Ar}), 120.9 (CH_{Ar}), 118.3 (CH_{Ar}), 95.4 (CH_{Ar}), 34.1 (CH_{iPr}), 24.2 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3125 (w), 3065 (w), 2949, 2920 (m), 2863 (m), 1608 (m), 1584 (s), 1562 (w), 1532 (s), 1497, 1483, 1471 (w), 1446 (s), 1410 (m), 1374 (m), 1353 (m), 1291 (m), 949 (m), 873 (m), 858 (m), 822 (s), 787 (m), 772 (m), 761 (m), 559 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 366 (27), 365 $[M]^+$ (100), 350 (29), 349 (14), 348 (10), 323 (7), 322 (8), 175 (5). HRMS (EI): Calculated for $C_{25}H_{19}NS$ $[M]^+$ 365.12327 found 365.12286.

6-Fluorobenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24e): Pale yellow solid, mp. 184 - 185 °C.

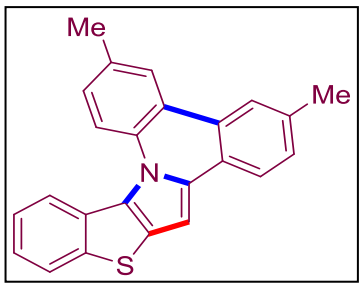


^{1}H NMR (500 MHz, DMSO): δ = 8.49 - 8.44 (m, 2H, CH_{Ar}), 8.38 (dd, ^{3}J = 10.4 Hz, ^{4}J = 2.9 Hz, 1H, CH_{Ar}), 8.31 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 8.23 (d, ^{3}J = 8.0 Hz, 1H, CH_{Ar}), 8.02 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.65 - 7.62 (m, 1H, CH_{Ar}), 7.61 (s, 1H, CH_{Ar}), 7.60 - 7.57 (m, 1H, CH_{Ar}), 7.55 - 7.49 (m, 2H, CH_{Ar}), 7.40 - 7.36 (m, 1H, CH_{Ar}). ^{19}F NMR (235.4 MHz, $CDCl_3$): δ = -118.5 (FC_{Ar}). ^{13}C NMR (125.8 MHz, DMSO): δ = 159.5 (d, $^{1}J_{CF}$ = 242.8 Hz, CF_{Ar}), 141.4 (C_{Ar}), 135.5 (C_{Ar}), 131.9 (C_{Ar}), 129.8 (d, $^{4}J_{CF}$ = 3.3 Hz, C_{Ar}), 129.5 (C_{Ar}), 129.3 (CH_{Ar}), 129.0 (d, $^{3}J_{CF}$ = 8.7 Hz, C_{Ar}), 127.4 (C_{Ar}), 127.3 (CH_{Ar}), 125.8 (C_{Ar}), 125.0 (d, $^{4}J_{CF}$ = 3.3 Hz, C_{Ar}), 124.6 (CH_{Ar}), 124.3 (CH_{Ar}), 123.5 (CH_{Ar}), 123.3 (CH_{Ar}), 123.2 (CH_{Ar}), 120.4 (CH_{Ar}), 119.5 (d, $^{3}J_{CF}$ = 8.5 Hz, CH_{Ar}), 115.3 (d, $^{2}J_{CF}$ = 23.7 Hz, CH_{Ar}), 110.6 (d, $^{2}J_{CF}$ = 23.4 Hz, CH_{Ar}), 95.6 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (w), 3062 (w), 2920 (w), 2850 (w), 1621 (m), 1591 (m), 1563 (m), 1535 (m), 1496 (m), 1484 (m), 1446 (m), 1425 (s), 1375, 1354 (m), 1269 (m), 1252 (s), 1175 (s), 950 (m), 922 (m), 896 (s), 852 (s), 810 (s), 617 (m), 595 (m), 554 (s). MS (EI, 70 eV): *m/z* (%) = 342 (25), 341 $[M]^+$ (100), 239 (08), 169 (05), 154 (06). HRMS (EI): Calculated for $C_{22}H_{12}NFS$ $[M]^+$ 341.06690 found 341.06633.

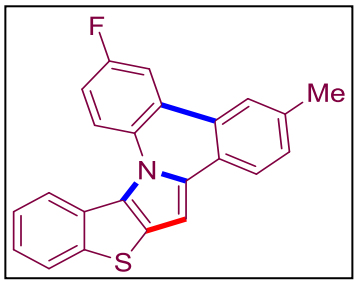
3-Methylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24f): Pale yellow solid, mp. 152 - 153 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.38 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 8.28 - 8.23 (m, 2H, CH_{Ar}), 7.99 (s, 1H, CH_{Ar}), 7.85 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.79 (dd, ^{3}J = 7.9 Hz, ^{5}J = 0.7 Hz, 1H, CH_{Ar}), 7.52 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 7.3 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.38 - 7.26 (m, 3H, CH_{Ar}), 7.24 - 7.20 (m, 1H, CH_{Ar}), 7.11 (s, 1H, CH_{Ar}), 2.44 (s, 3H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 140.9 (C_{Ar}), 135.6 (C_{Ar}), 135.5 (C_{Ar}), 133.0 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (CH_{Ar}), 128.5 (C_{Ar}), 127.4 (C_{Ar}), 126.4 (CH_{Ar}), 125.1 (C_{Ar}), 123.3 (CH_{Ar}), 123.1 (CH_{Ar}), 123.0 (CH_{Ar}), 122.9 (C_{Ar}), 122.8 (CH_{Ar}), 122.1 (CH_{Ar}), 121.6 (CH_{Ar}), 121.5 (CH_{Ar}), 121.2 (C_{Ar}), 119.7 (CH_{Ar}), 117.3 (CH_{Ar}), 94.0 (CH_{Ar}), 20.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 1606 (w), 1584 (w), 1563 (w), 1532 (m), 1498 (m), 1482 (m), 1447 (s), 1411 (m), 1362 (m), 1353 (s), 815 (m), 813 (m), 766 (m), 751 (m), 739 (m), 722 (s), 665 (m), 578 (s). MS (EI, 70 eV): *m/z* (%) = 338 (26), 337 $[M]^+$ (100), 336 (19), 322 (07), 169 (06), 161 (06). HRMS (EI): Calculated for $C_{23}H_{15}NS$ $[M]^+$ 337.09197 found 337.09137.



3,6-Dimethylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24g): Pale yellow solid, mp. 154 - 155 °C. ^{1}H NMR (300 MHz, Chloroform-*d*): δ = 8.25 (d, ^{3}J = 8.7 Hz, 1H, CH_{Ar}), 8.20 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 8.00 (s, 1H, CH_{Ar}), 7.94 (s, 1H, CH_{Ar}), 7.81 - 7.76 (m, 2H, CH_{Ar}), 7.34 - 7.27 (m, 2H, CH_{Ar}), 7.22 - 7.17 (m, 2H, CH_{Ar}), 7.06 (s, 1H, CH_{Ar}), 2.44 (s, 3H, CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 141.9 (C_{Ar}), 136.5 (C_{Ar}), 136.4 (C_{Ar}), 133.4 (C_{Ar}), 132.0 (C_{Ar}), 129.7 (C_{Ar}), 129.4 (CH_{Ar}), 129.2 (C_{Ar}), 128.4 (C_{Ar}), 128.3 (CH_{Ar}), 126.1 (C_{Ar}), 124.3 (CH_{Ar}), 124.2 (CH_{Ar}), 123.9 (C_{Ar}), 123.7 (CH_{Ar}), 123.1 (CH_{Ar}), 122.5 (CH_{Ar}), 122.4 (CH_{Ar}), 122.0 (C_{Ar}), 120.7 (CH_{Ar}), 118.1 (CH_{Ar}), 94.7 (CH_{Ar}), 21.8 (CH_3), 21.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3049 (w), 2914 (w), 2851 (w), 2729 (w), 1896 (w), 1810 (w), 1765 (w), 1585 (m), 1563 (m), 1537 (m), 1453 (s), 1374 (m), 1351 (s), 1153 (m), 1030 (m), 877 (m), 870 (m), 845 (m), 814 (m), 767 (m), 736 (m), 720 (s), 667 (m), 646 (m), 538 (s). MS (EI, 70 eV): *m/z* (%) = 352 (27), 351 $[M]^+$ (100), 350 (14), 334 (06), 176 (11), 168 (10), 167 (11), 161 (12), 145 (06). HRMS (EI): Calculated for $C_{24}H_{17}NS$ $[M]^+$ 351.10762 found 351.10722.

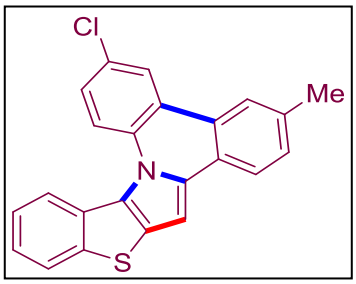


6-Fluoro-3-methylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24h):



Pale yellow solid, mp. 142 - 143 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.20 (dd, ^{3}J = 9.0 Hz, ^{3}J = 5.0 Hz, 1H, CH_{Ar}), 8.08 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 7.78 (d, ^{4}J = 2.8 Hz, 1H, CH_{Ar}), 7.74 - 7.69 (m, 3H, CH_{Ar}), 7.30 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.5 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.22 - 7.09 (m, 3H, CH_{Ar}), 6.96 (s, 1H, CH_{Ar}), 2.37 (s, 3H, CH_3). ^{19}F NMR (235.4 MHz, $CDCl_3$): δ = -118.3 (FC_{Ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 159.3 (d, $^{1}J_{CF}$ = 242.6 Hz, CF_{Ar}), 141.9 (C_{Ar}), 136.6 (C_{Ar}), 136.0 (C_{Ar}), 130.3 (d, $^{4}J_{CF}$ = 3.5 Hz, C_{Ar}), 130.1 (CH_{Ar}), 129.6 (C_{Ar}), 129.4 (C_{Ar}), 128.1 (C_{Ar}), 125.2 (d, $^{4}J_{CF}$ = 3.3 Hz, C_{Ar}), 124.4 (CH_{Ar}), 124.0 (C_{Ar}), 123.9 (C_{Ar}), 123.8 (CH_{Ar}), 123.1 (CH_{Ar}), 122.7 (CH_{Ar}), 122.6 (CH_{Ar}), 120.3 (CH_{Ar}), 119.3 (d, $^{3}J_{CF}$ = 8.3 Hz, CH_{Ar}), 114.4 (d, $^{2}J_{CF}$ = 23.9 Hz, CH_{Ar}), 109.8 (d, $^{2}J_{CF}$ = 23.6 Hz, CH_{Ar}), 95.1 (CH_{Ar}), 21.7 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3117 (w), 3056 (w), 2919 (w), 2852 (w), 1898 (w), 1689 (w), 1620 (m), 1587 (m), 1562 (m), 1537 (m), 1494 (m), 1432 (s), 1374 (m), 1353 (m), 1293 (m), 1256 (m), 1196 (m), 1170 (s), 939 (m), 871 (m), 857 (m), 809 (s), 734 (m), 718 (m), 709 (s), 668 (m), 651 (m), 620 (m), 607 (m), 541 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 356 (25), 355 $[M]^+$ (100), 340 (07), 253 (05), 177 (14), 170 (07). HRMS (EI): Calculated for $C_{23}H_{14}NFS$ $[M]^+$ 355.08255 found 355.08186.

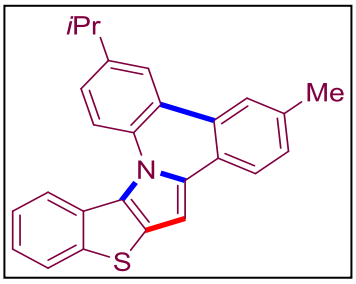
6-Chloro-3-methylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24i):



Pale yellow solid, mp. 182 - 183 °C. ^{1}H NMR (300 MHz, Chloroform-*d*): δ = 8.19 (d, ^{3}J = 8.9 Hz, 1H, CH_{Ar}), 8.12 - 7.09 (m, 2H, CH_{Ar}), 7.81 (s, 1H, CH_{Ar}), 7.77 (dd, ^{3}J = 8.7 Hz, 2H, ^{3}J = 8.0 Hz, CH_{Ar}), 7.40 (dd, ^{3}J = 8.8 Hz, ^{4}J = 2.3 Hz, 1H, CH_{Ar}), 7.29 - 7.34 (m, 1H, CH_{Ar}), 7.22 (d, ^{3}J = 7.4 Hz, 2H,CH_{Ar}), 7.02 (s, 1H, CH_{Ar}), 2.41 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 142.0 (C_{Ar}), 136.8 (C_{Ar}), 136.2 (C_{Ar}), 132.4 (C_{Ar}), 130.2 (CH_{Ar}), 129.6 (C_{Ar}), 129.3 (C_{Ar}), 128.5 (C_{Ar}), 128.1 (C_{Ar}), 127.2 (CH_{Ar}), 125.0 (C_{Ar}), 124.4 (CH_{Ar}), 124.0 (C_{Ar}), 123.9 (CH_{Ar}), 123.8 (CH_{Ar}), 123.7 (C_{Ar}), 123.1 (CH_{Ar}), 122.8 (CH_{Ar}), 122.6 (CH_{Ar}), 120.4 (CH_{Ar}), 119.3 (CH_{Ar}), 95.4 (CH_{Ar}), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3110 (w), 3045 (w), 2917 (w), 2849 (w), 1905 (w), 1673 (w), 1603 (w), 1586 (m), 1554 (m), 1529 (m), 1487 (m), 1453 (m), 1416 (s), 1350 (m), 1294 (m), 1254 (m), 1102 (m), 900 (m), 859 (m), 845 (m), 812 (m), 762 (m), 738 (m),

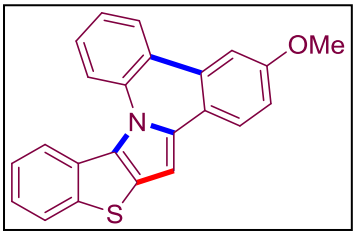
721 (s), 666 (m), 649 (m), 537 (m). MS (EI, 70 eV): *m/z* (%) = 373 (40), 371 $[M]^+$ (100), 336 (09), 334 (10), 186 (13), 167 (14), 161 (14), 151 (08). HRMS (EI): Calculated for $C_{23}H_{14}N^{35}ClS$ $[M]^+$ 371.05300 found 371.05213, calculated for $C_{23}H_{14}N^{37}ClS$ $[M]^+$ 373.05005 found 373.05078.

6-Isopropyl-3-methylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine



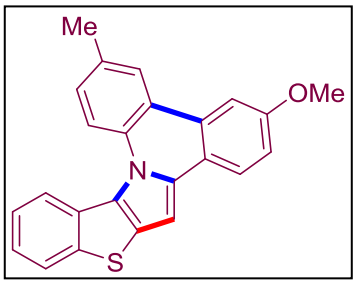
(24j): Pale yellow solid, mp. 94 - 95 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.28 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 8.24 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.07 (d, ^4J = 1.9 Hz, 1H, CH_{Ar}), 7.98 (s, 1H, CH_{Ar}), 7.82 - 7.74 (m, 2H, CH_{Ar}), 7.40 - 7.28 (m, 2H, CH_{Ar}), 7.21 - 7.15 (m, 2H, CH_{Ar}), 7.05 (s, 1H, CH_{Ar}), 3.09 - 2.88 (m, 1H, CH_{iPr}), 2.43 (s, 3H, CH_3), 1.33 (d, 6H, ^3J = 6.9 Hz, $CH_{3\text{-}iPr}$). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 144.5 (C_{Ar}), 141.9 (C_{Ar}), 136.5 (C_{Ar}), 136.4 (C_{Ar}), 132.3 (C_{Ar}), 129.7 (C_{Ar}), 129.4 (CH_{Ar}), 129.2 (C_{Ar}), 128.4 (C_{Ar}), 126.3 (C_{Ar}), 125.7 (CH_{Ar}), 124.3 (CH_{Ar}), 123.9 (C_{Ar}), 123.7 (CH_{Ar}), 123.2 (CH_{Ar}), 122.5 (CH_{Ar}), 122.4 (CH_{Ar}), 122.0 (C_{Ar}), 121.7 (CH_{Ar}), 120.7 (CH_{Ar}), 118.3 (CH_{Ar}), 94.8 (CH_{Ar}), 34.1 (CH_{iPr}), 24.3 ($2CH_{3\text{-}iPr}$), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3043 (w), 3010 (w), 2952 (m), 2926 (m), 1617 (m), 1583 (m), 1563 (m), 1540 (m), 1488 (m), 1444 (m), 1427 (s), 1353 (m), 1309 (m), 1287 (m), 1220 (s), 1173 (m), 1093 (m), 1066 (m), 1049 (m), 1038 (s), 873 (m), 854 (m), 810 (m), 772 (m), 739 (m), 720 (s), 578 (m), 568 (s). MS (EI, 70 eV): *m/z* (%) = 380 (29), 379 $[M]^+$ (100), 364 (18), 349 (10), 348 (06), 182 (05). HRMS (EI): Calculated for $C_{26}H_{21}NS$ $[M]^+$ 379.13384 found 379.13367.

3-Methoxybenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24k): Pale yellow solid, mp. 133 - 134 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.30 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.17 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.10 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.78 - 7.74 (m, 2H, CH_{Ar}), 7.52 (d, ^4J = 2.5 Hz, 1H, CH_{Ar}), 7.47 (ddd, ^3J = 8.4 Hz, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.33 - 7.27 (m, 2H, CH_{Ar}), 7.20 - 7.14 (m, 1H, CH_{Ar}), 6.95 (dd, ^3J = 8.8 Hz, ^4J = 2.5 Hz, 2H, CH_{Ar}), 3.82 (s, 3H, OCH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 158.7 (C_{Ar}), 141.7 (C_{Ar}), 136.5 (C_{Ar}), 134.1 (C_{Ar}), 129.7 (C_{Ar}), 129.3 (C_{Ar}), 128.4 (C_{Ar}), 127.6 (CH_{Ar}), 127.5 (C_{Ar}), 124.7 (CH_{Ar}), 124.3 (CH_{Ar}), 124.1 (CH_{Ar}), 123.8 (CH_{Ar}), 123.7 (CH_{Ar}), 122.4 (CH_{Ar}), 121.9 (C_{Ar}), 120.5 (CH_{Ar}), 120.0



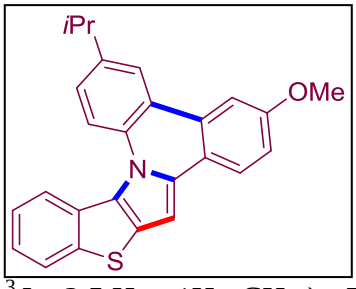
(C_{Ar}), 118.3 (CH_{Ar}), 116.4 (CH_{Ar}), 105.6 (CH_{Ar}), 94.2 (CH_{Ar}), 55.4 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3120 (w), 3050 (w), 3006 (w), 2955 (w), 2918 (w), 2849 (w), 2830 (w), 1616 (m), 1584 (m), 1560 (m), 1540 (m), 1487 (m), 1467 (m), 1446 (m), 1428 (s), 1354 (s), 1214 (s), 1071 (m), 1034 (m), 1017 (m), 860 (m), 812 (m), 752 (m), 735 (m), 713 (s), 695 (m), 662 (m), 610 (m), 573 (m), 542 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 354 (26), 353 $[M]^+$ (100), 339 (11), 338 (45), 310 (31), 309 (22), 177 (21), 155 (16), 154 (19), 133 (09). HRMS (EI): Calculated for $C_{23}H_{15}ONS$ $[M]^+$ 353.08689 found 353.08653.

3-Methoxy-6-methylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24l):



Pale yellow solid, mp. 129 - 130 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.27 - 8.19 (m, 2H, CH_{Ar}), 7.95 (s, 1H, CH_{Ar}), 7.85 (d, ^3J = 8.8 Hz, 1H, CH_{Ar}), 7.77 (dd, ^4J = 0.7 Hz, ^3J = 8.0 Hz, 1H, CH_{Ar}), 7.59 (d, ^4J = 2.5 Hz, 1H, CH_{Ar}), 7.36 - 7.29 (m, 2H, CH_{Ar}), 7.22 - 7.15 (m, 1H, CH_{Ar}), 7.01 (dd, ^3J = 8.8 Hz, ^4J = 2.5 Hz, 2H, CH_{Ar}), 3.89 (s, 3H, OCH_3), 2.46 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 158.7 (C_{Ar}), 141.7 (C_{Ar}), 136.4 (C_{Ar}), 133.3 (C_{Ar}), 132.2 (C_{Ar}), 129.4 (C_{Ar}), 129.3 (C_{Ar}), 128.6 (CH_{Ar}), 128.4 (C_{Ar}), 127.6 (C_{Ar}), 124.8 (CH_{Ar}), 124.3 (CH_{Ar}), 124.2 (CH_{Ar}), 123.7 (CH_{Ar}), 122.3 (CH_{Ar}), 121.8 (C_{Ar}), 120.4 (CH_{Ar}), 120.2 (C_{Ar}), 118.2 (CH_{Ar}), 116.3 (CH_{Ar}), 105.4 (CH_{Ar}), 94.0 (CH_{Ar}), 55.5 (OCH_3), 21.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2917 (m), 2848 (m), 1614 (m), 1586 (m), 1564 (m), 1541 (m), 1488 (m), 1448 (m), 1431 (m), 1417 (s), 1374 (w), 1355 (m), 1308, 1300 (w), 1283 (m), 1221 (s), 1066 (m), 1053 (m), 1032 (s), 859 (m), 851 (m), 842 (m), 805 (m), 759 (m), 732 (m), 717 (m), 710 (s), 567 (m), 549 (s). MS (EI, 70 eV): *m/z* (%) = 368 (27), 367 $[M]^+$ (100), 352 (42), 324 (19), 309 (06), 183 (08), 160 (06). HRMS (EI): Calculated for $C_{24}H_{17}ONS$ $[M]^+$ 367.10254 found 367.10298.

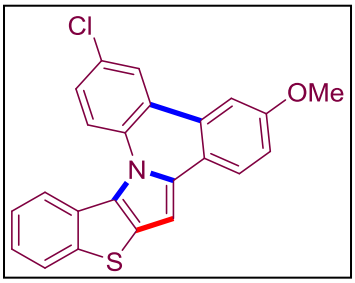
6-Isopropyl-3-methoxybenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine



(24m): Pale yellow solid, mp. 136 - 137 °C. ^{1}H NMR (300 MHz, Chloroform-*d*): δ = 8.34 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.26 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.04 (d, ^4J = 1.9 Hz, 1H, CH_{Ar}), 7.91 (d, ^3J = 7.9 Hz, 1H, CH_{Ar}), 7.79 (dd, ^4J = 0.6 Hz, ^3J = 8.0 Hz, 1H, CH_{Ar}), 7.67 (d, ^3J = 2.5 Hz, 1H, CH_{Ar}), 7.43 (dd, ^4J = 1.9 Hz, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.34 (ddd,

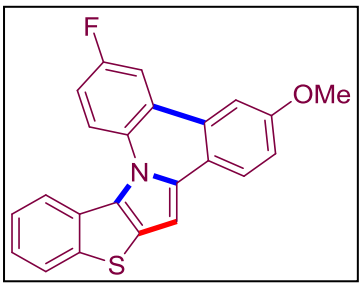
^4J = 1.2 Hz, ^3J = 7.2 Hz, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.22 - 7.17 (m, 1H, CH_{Ar}), 7.05 (dd, ^4J = 2.5 Hz, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.92 (s, 3H, OCH_3), 3.04 - 3.09 (m, 1H, CH_{iPr}), 1.34 (d, ^3J = 6.9 Hz, 6H, $CH_{3\text{-}iPr}$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 157.7 (C_{Ar}), 144.3 (C_{Ar}), 143.5 (C_{Ar}), 142.4 (C_{Ar}), 140.7 (C_{Ar}), 135.4 (C_{Ar}), 131.5 (C_{Ar}), 128.4 (C_{Ar}), 127.5 (C_{Ar}), 126.8 (C_{Ar}), 125.0 (CH_{Ar}), 123.8 (CH_{Ar}), 123.3 (CH_{Ar}), 122.7 (CH_{Ar}), 121.3 (CH_{Ar}), 120.8 (C_{Ar}), 119.5 (CH_{Ar}), 119.2 (CH_{Ar}), 117.4 (CH_{Ar}), 114.9 (CH_{Ar}), 104.9 (CH_{Ar}), 93.0 (CH_{Ar}), 55.6 (OCH_3), 33.1 (CH_{iPr}), 23.2 ($2CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (w), 3046 (w), 3008 (w), 2957 (m), 2922 (m), 1614 (m), 1585 (m), 1561 (m), 1539 (m), 1484 (m), 1446, 1423 (s), 1351 (m), 1307 (m), 1282 (m), 1218 (s), 1170 (m), 1093 (m), 1065 (m), 1049 (m), 1036 (s), 873 (m), 854 (m), 810 (m), 772 (m), 739 (m), 720 (s), 578 (m), 568 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 396 (30), 395 $[M]^+$ (100), 380 (30), 364 (06), 336 (15), 308 (06), 190 (10), 173 (08). HRMS (EI): Calculated for $C_{26}H_{21}ONS$ $[M]^+$ 395.13384 found 395.13367.

6-Chloro-3-methoxybenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine



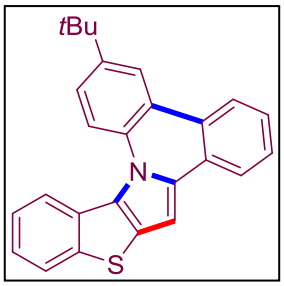
(24n): Pale yellow solid, mp. 202 - 203 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.27 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 8.14 - 8.08 (m, 2H, CH_{Ar}), 7.81 (dd, ^3J = 10.7 Hz, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.48 - 7.43 (m, 2H, CH_{Ar}), 7.36 - 7.29 (m, 1H, CH_{Ar}), 7.24 - 7.21 (m, 1H, CH_{Ar}), 7.04 (dd, ^3J = 8.8 Hz, ^4J = 2.5 Hz, 1H, CH_{Ar}), 6.99 (s, 1H, CH_{Ar}), 3.87 (s, 3H, OCH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 158.8 (C_{Ar}), 141.8 (C_{Ar}), 136.2 (C_{Ar}), 132.6 (C_{Ar}), 129.9 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C_{Ar}), 128.1 (C_{Ar}), 127.5 (CH_{Ar}), 126.4 (C_{Ar}), 124.9 (CH_{Ar}), 124.4 (CH_{Ar}), 123.9 (CH_{Ar}), 123.8 (CH_{Ar}), 123.5 (C_{Ar}), 122.6 (CH_{Ar}), 120.3 (C_{Ar}), 120.2 (CH_{Ar}), 119.4 (CH_{Ar}), 117.3 (CH_{Ar}), 105.4 (CH_{Ar}), 94.6 (CH_{Ar}), 55.7 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3131 (w), 3047 (w), 2924 (w), 2835 (w), 1614 (m), 1586 (m), 1557 (m), 1537 (m), 1485 (m), 1466 (m), 1453 (m), 1441 (m), 1431 (m), 1416 (s), 1291 (m), 1284 (m), 1228 (m), 1216 (s), 1107 (m), 1097 (m), 1065 (m), 1053 (m), 1029 (s), 909 (m), 868 (m), 837 (m), 761 (m), 719 (s), 548 (s). MS (EI, 70 eV): *m/z* (%) = 389 (39), 387 $[M]^+$ (100), 374 (15), 372 (46), 344 (20), 309 (14), 194 (09), 154 (10). HRMS (EI): Calculated for $C_{23}H_{14}NClS$ $[M]^+$ 387.04791 found 387.04692, calculated for $C_{23}H_{14}N^{37}ClS$ $[M]^+$ 389.04496 found 389.04425.

6-Fluoro-3-methoxybenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24o): Pale yellow solid, mp. 172 - 173 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.29 (dd,



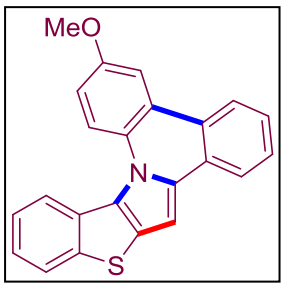
^{3}J = 9.0 Hz, ^{3}J = 5.0 Hz, 1H, CH_{Ar}), 8.12 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 7.84 - 7.76 (m, 3H, CH_{Ar}), 7.43 (d, ^{4}J = 2.8 Hz, 1H, CH_{Ar}), 7.36 - 7.29 (m, 1H, CH_{Ar}), 7.25 - 7.18 (m, 2H, CH_{Ar}), 7.03 (dd, ^{3}J = 8.8 Hz, ^{4}J = 2.5 Hz, 1H, CH_{Ar}), 6.96 (s, 1H, CH_{Ar}), 3.86 (s, 3H, OCH_3). ^{19}F NMR (235.4 MHz, $CDCl_3$): δ = -118.2 (FC_{Ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 159.0 (d, $^{1}J_{CF}$ = 242.8 Hz, CF_{Ar}), 158.7 (C_{Ar}), 141.8 (C_{Ar}), 136.1 (C_{Ar}), 130.6 (d, $^{4}J_{CF}$ = 3.3 Hz, C_{Ar}), 129.6 (C_{Ar}), 129.3 (C_{Ar}), 128.1 (C_{Ar}), 126.8 (d, $^{4}J_{CF}$ = 3.2 Hz, C_{Ar}), 124.8 (CH_{Ar}), 124.4 (CH_{Ar}), 123.8 (CH_{Ar}), 123.8 (d, $^{3}J_{CF}$ = 8.5 Hz, C_{Ar}), 122.6 (CH_{Ar}), 120.3 (C_{Ar}), 120.1 (CH_{Ar}), 119.6 (d, $^{3}J_{CF}$ = 8.3 Hz, CH_{Ar}), 117.2 (CH_{Ar}), 114.8 (d, $^{2}J_{CF}$ = 23.4 Hz, CH_{Ar}), 110.1 (d, $^{2}J_{CF}$ = 23.9 Hz, CH_{Ar}), 105.6 (CH_{Ar}), 94.4 (CH_{Ar}), 55.5 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3116 (w), 3045 (w), 3001 (w), 2922 (w), 2846 (w), 2254 (w), 2054 (w), 1903 (w), 1731 (w), 1614 (m), 1564 (m), 1538 (m), 1490 (m), 1464 (m), 1446 (m), 1426 (s), 1336 (m), 1282 (m), 1259 (m), 1228 (m), 1191 (m), 1171 (s), 1065 (m), 1031 (s), 964 (m), 916 (m), 834 (m), 758 (m), 732, 715 (s). MS (EI, 70 eV): *m/z* (%) = 372 (25), 371 $[M]^+$ (100), 356 (40), 328 (27), 281 (08), 253 (06), 207 (06), 185 (26), 163 (20), 141 (15). HRMS (EI): Calculated for $C_{23}H_{14}O_1NFS$ $[M]^+$ 371.07746 found 371.07755.

6-(tert-Butyl)benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (26d): Pale yellow solid, mp. 75 - 76 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.35 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 8.28 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 8.24 - 8.19 (m, 2H, CH_{Ar}), 7.86 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 7.76 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.52 - 7.46 (m, 2H, CH_{Ar}), 7.34 - 7.29 (m, 2H, CH_{Ar}), 2.18 - 7.14 (m, 1H, CH_{Ar}), 7.08 (s, 1H, CH_{Ar}), 1.37 (s, 9H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 149.8 (C_{Ar}), 141.9 (C_{Ar}), 136.4 (C_{Ar}), 134.0 (C_{Ar}), 129.9 (C_{Ar}), 129.6 (C_{Ar}), 128.4 (C_{Ar}), 127.3 (CH_{Ar}), 126.2 (CH_{Ar}), 125.7 (C_{Ar}), 124.4 (CH_{Ar}), 124.0 (CH_{Ar}), 123.9 (CH_{Ar}), 123.8 (CH_{Ar}), 123.0 (CH_{Ar}), 122.6 (CH_{Ar}), 120.7 (CH_{Ar}), 120.6 (C_{Ar}), 118.6 (CH_{Ar}), 118.5 (C_{Ar}), 118.3 (CH_{Ar}), 95.1 (CH_{Ar}), 35.1 (C_{tBu}), 31.4 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (w), 3055 (w), 2951, 2862 (m), 1607 (w), 1585 (m), 1554 (m), 1538 (m), 1474 (m), 1441 (m), 1427 (s), 1347 (s), 1191 (m), 1121 (m), 1054 (m), 1026 (m), 877 (m), 821 (m), 736 (m), 623 (m), 542 (s). MS (EI, 70 eV): *m/z* (%) = 380



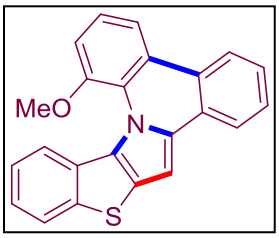
(29), 379 $[M]^+$ (100), 365 (17), 364 (60), 350 (08), 349 (31), 348 (09), 323 (09), 168 (15). HRMS (EI): Calculated for $C_{26}H_{21}NS$ $[M]^+$ 379.13892 found 379.13866.

6-Methoxybenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (26e): Pale



yellow solid, mp. 152 - 153 °C. ^{1}H NMR (250 MHz, DMSO): δ = 8.60 (d, ^3J = 7.2 Hz, 1H, CH_{Ar}), 8.38 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.27 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.11 (d, ^3J = 8.8 Hz, 1H, CH_{Ar}), 7.99 (d, ^3J = 7.3 Hz, 1H, CH_{Ar}), 7.92 (d, ^4J = 2.4 Hz, 1H, CH_{Ar}), 7.75 - 7.63 (m, 1H, CH_{Ar}), 7.50 (d, ^3J = 7.9 Hz, 1H, CH_{Ar}), 7.45 - 7.42 (m, 2H, CH_{Ar}), 7.30 (t, ^3J = 7.2 Hz, 1H, CH_{Ar}), 7.18 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H, CH_{Ar}), 3.94 (s, 3H, OCH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 158.7 (C_{Ar}), 140.7 (C_{Ar}), 136.0 (C_{Ar}), 133.1 (C_{Ar}), 129.2 (C_{Ar}), 128.4 (C_{Ar}), 128.3 (CH_{Ar}), 127.7 (C_{Ar}), 127.1 (C_{Ar}), 125.0 ($2CH_{Ar}$), 124.6 (CH_{Ar}), 124.3 ($2CH_{Ar}$), 122.7 (CH_{Ar}), 121.4 (C_{Ar}), 120.3 (CH_{Ar}), 119.1 (C_{Ar}), 117.7 (CH_{Ar}), 117.2 (CH_{Ar}), 105.8 (CH_{Ar}), 94.9 (CH_{Ar}), 55.5 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (w), 3005 (w), 2955 (w), 2830 (w), 1681 (m), 1615 (m), 1590 (m), 1560 (m), 1487 (m), 1467 (w), 1446 (m), 1428 (s), 1376 (w), 1353 (m), 1285 (m), 1214 (s), 1019 (m), 994 (s), 860 (m), 812 (m), 752 (m), 712 (s). MS (EI, 70 eV): *m/z* (%) = 354 (26), 353 $[M]^+$ (100), 339 (11), 338 (45), 311 (08), 310 (32), 309 (22), 308 (14), 177 (22), 155 (22), 154 (20), 133 (10). HRMS (EI): Calculated for $C_{23}H_{15}ONS$ $[M]^+$ 353.08685 found 353.08676.

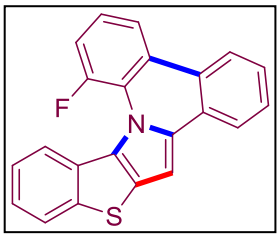
7-Methoxybenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (26f): Pale



yellow solid, mp. 108 - 109 °C. ^{1}H NMR (250 MHz, Chloroform-*d*): δ = 8.59 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 8.37 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.26 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.11 (d, ^3J = 8.8 Hz, 1H, CH_{Ar}), 7.99 (d, ^3J = 8.0 Hz, 1H, CH_{Ar}), 7.92 (d, ^4J = 2.4 Hz, 1H, CH_{Ar}), 7.73 - 7.68 (m, 1H, CH_{Ar}), 7.42 - 7.52 (m, 3H, CH_{Ar}), 7.29 (m, 1H, CH_{Ar}), 7.17 (dd, 1H, ^3J = 8.8 Hz, ^4J = 2.4 Hz, CH_{Ar}), 3.93 (s, 3H, OCH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 158.7 (C_{Ar}), 141.8 (C_{Ar}), 136.5 (C_{Ar}), 134.2 (C_{Ar}), 129.7 (C_{Ar}), 129.5 (C_{Ar}), 128.5 (C_{Ar}), 127.7 (CH_{Ar}), 127.6 (C_{Ar}), 124.8 (CH_{Ar}), 124.4 (CH_{Ar}), 124.2 (CH_{Ar}), 123.9 (CH_{Ar}), 123.8 (CH_{Ar}), 122.4 (CH_{Ar}), 122.0 (C_{Ar}), 120.5 (CH_{Ar}), 120.1 (C_{Ar}), 118.4 (CH_{Ar}), 116.5 (CH_{Ar}), 105.7 (CH_{Ar}), 94.3 (CH_{Ar}), 55.5 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (w), 3005 (w), 2955 (w), 2830 (w), 1681 (m), 1615 (m), 1590 (m), 1560 (m), 1487 (m), 1467 (w), 1446 (m), 1428 (s), 1376 (w), 1353 (m), 1285 (m), 1214 (s), 1019 (m), 994 (s), 860 (m), 812 (m), 752 (m), 735

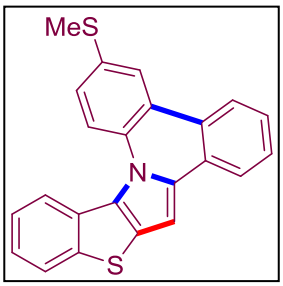
(m), 712 (s). MS (EI, 70 eV): *m/z* (%) = 354 (26), 353 $[M]^+$ (100), 339 (12), 338 (47), 310 (34), 309 (23), 308 (15), 177 (18), 155 (14), 154 (19). HRMS (EI): Calculated for $C_{23}H_{15}ONS$ $[M]^+$ 353.08689 found 353.08628.

8-Fluorobenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (26g): Pale



yellow solid, mp. 194 - 195 °C. ^{1}H NMR (300 MHz, DMSO): δ = 8.49 (d, J = 8.5 Hz, 1H, CH_{Ar}), 8.44 - 8.38 (m, 2H, CH_{Ar}), 8.27 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.22 (d, ^3J = 8.0 Hz, 1H, CH_{Ar}), 8.04 (d, ^3J = 7.8 Hz, 1H, CH_{Ar}), 7.62 - 7.56 (m, 3H, CH_{Ar}), 7.53 - 7.46 (m, 2H, CHAr), 7.38 - 7.34 (m, 1H, CH_{Ar}). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -117.3. ^{13}C NMR (75.5 MHz, DMSO): δ = 159.2 (d, $^1J_{CF}$ = 242.8 Hz, CF_{Ar}), 141.2 (C_{Ar}), 135.5 (C_{Ar}), 129.6 (d, $^4J_{CF}$ = 3.3 Hz, C_{Ar}), 129.3 (CH_{Ar}), 129.2 (C_{Ar}), 128.9 (C_{Ar}), 128.1 (C_{Ar}), 127.2 (CH_{Ar}), 125.6 (C_{Ar}), 124.8 (d, $^4J_{CF}$ = 3.3 Hz, C_{Ar}), 124.6 (CH_{Ar}), 124.3 (CH_{Ar}), 123.7 (C_{Ar}), 123.5 (CH_{Ar}), 123.3 (CH_{Ar}), 123.2 (CH_{Ar}), 120.4 (CH_{Ar}), 119.5 (d, $^3J_{CF}$ = 8.7 Hz, CH_{Ar}), 115.4 (d, $^2J_{CF}$ = 23.5 Hz, CH_{Ar}), 110.7 (d, $^2J_{CF}$ = 23.6 Hz, CH_{Ar}), 96.6 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 2920 (w), 2850 (w), 1623 (m), 1589 (m), 1559 (m), 1537 (m), 1497 (m), 1479 (m), 1443 (m), 1421 (s), 1374 (m), 1351 (m), 1309 (w), 1295 (m), 1270 (m), 953 (m), 926 (m), 893 (m), 849 (m), 811 (s), 786 (m), 767 (m), 755 (m), 617 (m), 595 (m), 560 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 342 (30), 341 $[M]^+$ (100), 239 (16), 239 (18), 171 (16), 155 (15). HRMS (EI): Calculated for $C_{22}H_{12}NFS$ $[M]^+$ 341.06690 found 341.06653.

6-(Methylthio)benzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (26h): Dark



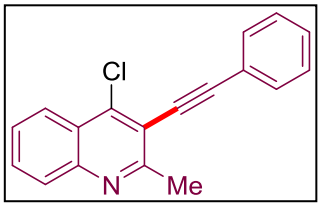
brown solid, mp. 182 - 183 °C. ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.54 (d, ^4J = 2.1 Hz, 1H, CH_{Ar}), 8.52 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.46 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.32 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.87 (d, ^3J = 7.9 Hz, 1H, CH_{Ar}), 7.78 (d, ^3J = 7.5 Hz, 1H, CH_{Ar}), 7.49 - 7.46 (m, 2H, CH_{Ar}), 7.39 - 7.30 (m, 3H, CH_{Ar}), 6.93 (s, 1H, CH_{Ar}), 2.59 (s, 3H, SCH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 139.8 (C_{Ar}), 136.3 (C_{Ar}), 133.5 (C_{Ar}), 132.6 (C_{Ar}), 132.1 (C_{Ar}), 131.8 (C_{Ar}), 130.6 (C_{Ar}), 126.7 (CH_{Ar}), 125.5 (CH_{Ar}), 125.3 (CH_{Ar}), 125.2 (C_{Ar}), 124.1 (C_{Ar}), 123.8 (CH_{Ar}), 123.4 (CH_{Ar}), 123.3 (CH_{Ar}), 122.7 (C_{Ar}), 122.5 (CH_{Ar}), 122.3 (CH_{Ar}), 121.4 (CH_{Ar}), 116.9 (CH_{Ar}), 114.3 (CH_{Ar}), 96.4 (CH_{Ar}), 17.3 (SCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (w), 3005 (w), 2955 (w), 2830 (w), 1681 (m), 1615 (m), 1590

(m), 1560 (m), 1540 (m), 1487 (m), 1467 (w), 1446 (m), 1428 (s), 1376 (w), 1353 (m), 1285 (m), 1214 (s), 1019 (m), 994 (s), 860 (m), 812 (m), 752 (m), 735 (m), 712 (s). MS (EI, 70 eV): *m/z* (%) = 370 (26), 369 $[M]^+$ (100), 354 (25), 321 (13), 310 (38), 184 (19), 160 (26), 155 (16). HRMS (EI): Calculated for $C_{23}H_{15}N_1S_2$ $[M]^+$ 369.06404 found 369.06379.

5.2.7. Synthesis of quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines by regioselective Sonogashira reaction followed by domino C-N coupling/hydroamination/C-H arylation

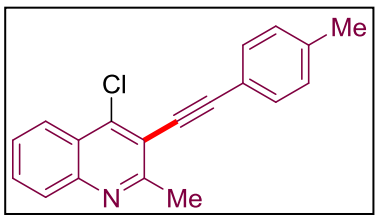
5.2.7.1. Starting materials

4-Chloro-2-methyl-3-(phenylethynyl)quinoline (27a): Yellow solid, mp. 95 - 96 °C.



^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.14 (ddd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.99 (ddd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.68 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.64 - 7.59 (m, 2H, CH_{Ar}), 7.54 (ddd, ^3J = 8.3 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.41 - 7.35 (m, 3H, CH_{Ar}), 2.92 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.7 (C_{Ar}), 146.6 (C_{Ar}), 143.9 (C_{Ar}), 131.8 ($2CH_{Ar}$), 130.6 (CH_{Ar}), 129.1 (CH_{Ar}), 129.0 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 127.2 (CH_{Ar}), 124.6 (C_{Ar}), 124.3 (CH_{Ar}), 122.7 (C_{Ar}), 117.5 (C_{Ar}), 100.8 (C_{sp}), 84.5 (C_{sp}), 25.2 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3058 (w), 3030 (w), 2997 (w), 2913 (w), 2207 (w), 1553 (w), 1477 (m), 1442 (m), 1405 (m), 1354 (m), 941 (m), 833 (m), 752 (s), 683 (m), 638 (m), 599 (m), 524 (m), 468 (m). MS (EI, 70 eV): *m/z* (%) = 279 (37), 278 (23), 277 (100), 276 (12), 243 (11), 242 (66), 241 (55), 240 (18), 201 (11), 200 (25), 174 (12), 150 (12), 121 (16), 100 (13), 51 (12). HRMS (ESI): Calculated for $C_{18}H_{12}ClN$ $[M+H]^+$ 278.07310 found 278.07296, calculated for $C_{18}H_{12}{}^{37}ClN$ $[M+H]^+$ 280.07068 found 280.07087.

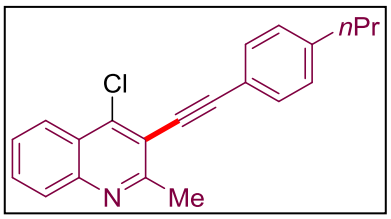
4-Chloro-2-methyl-3-(*p*-tolylethynyl)quinoline (27b): Yellow solid, mp. 94 - 95 °C.



^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.18 (ddd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 8.02 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.71 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.58 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.52 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.20 (d, ^3J = 7.8 Hz, 2H, CH_{Ar}), 2.93 (s, 3H, $CH_{3\text{-quinoline}}$), 2.40 (s, 3H, CH_3). ^{13}C NMR

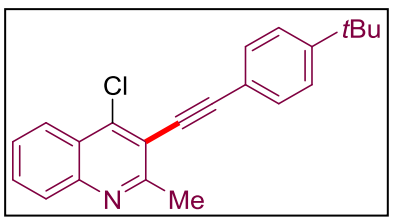
(75 MHz, $CDCl_3$) δ = 159.9 (C_{Ar}), 146.5 (C_{Ar}), 143.8 (C_{Ar}), 139.6 (C_{Ar}), 131.8 ($2CH_{Ar}$), 130.6 (CH_{Ar}), 129.4 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 127.3 (CH_{Ar}), 124.7 (C_{Ar}), 124.4 (CH_{Ar}), 119.7 (C_{Ar}), 117.8 (C_{Ar}), 101.2 (C_{sp}), 83.9 (C_{sp}), 25.3 (CH_3), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3079 (w), 3059 (m), 2983 (m), 2945 (w), 2912 (m), 2847 (w), 2728 (w), 2206 (m), 1960 (w), 1933 (w), 1880 (w), 1819 (w), 1584 (m), 1510 (m), 1478 (m), 1406 (m), 1372 (m), 1354 (m), 1342 (m), 1267 (m), 1088 (m), 941 (m), 834 (m), 811 (s), 753 (s), 639 (m), 598 (m). MS (EI, 70 eV): *m/z* (%) = 293 (34), 292 (26), 291 $[M]^+$ (100), 290 (20), 256 (35), 255 (14), 254 (16), 241 (26), 240 (11), 213 (19), 128 (11). HRMS (EI): Calculated for $C_{19}H_{14}NCl$ $[M]^+$ 291.08093 found 291.09085.

4-Chloro-2-methyl-3-((4-propylphenyl)ethynyl)quinoline (27c): Yellow solid,



mp. 95 - 96 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.21 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 8.12 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.75 (ddd, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.63 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.55 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.22 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 2.98 (s, 3H, $CH_{3\text{-quinoline}}$), 2.76 - 2.50 (m, 2H, $CH_{2\text{-aliphatic}}$), 1.67 (m, 2H, $CH_{2\text{-aliphatic}}$), 0.96 (t, ^3J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.8 (C_{Ar}), 146.3 (C_{Ar}), 144.4 (C_{Ar}), 144.0 (C_{Ar}), 131.8 ($2CH_{Ar}$), 130.7 (CH_{Ar}), 128.9 (CH_{Ar}), 128.8 ($2CH_{Ar}$), 127.4 (CH_{Ar}), 124.8 (C_{Ar}), 124.4 (CH_{Ar}), 119.9 (C_{Ar}), 117.9 (C_{Ar}), 101.4 (C_{sp}), 83.8 (C_{sp}), 38.2 (CH_2), 25.2 (CH_3), 24.5 (CH_2), 13.9 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3065 (w), 3048 (w), 3030 (w), 2957 (m), 2918 (w), 2859 (w), 2208 (w), 1898 (w), 1552 (w), 1510 (m), 1479 (m), 1406 (m), 1355 (m), 1089 (w), 942 (w), 831 (m), 810 (m), 758 (s), 640 (m), 540 (m). MS (EI, 70 eV): *m/z* (%) = 321 (23), 320 (17), 319 $[M]^+$ (68), 292 (35), 291 (21), 290 (100), 255 (10), 254 (33), 253 (11), 213 (15), 127 (12). HRMS (EI): Calculated for $C_{21}H_{18}NCl$ $[M]^+$ 319.11223 found 319.11219, calculated for $C_{21}H_{18}N^{37}Cl$ $[M]^+$ 321.10928 found 321.10997.

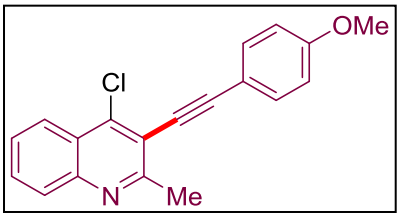
3-((4-(*tert*-Butyl)phenyl)ethynyl)-4-chloro-2-methylquinoline (27d): Yellow oil.



^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.19 (ddd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 8.04 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.72 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.63 - 7.53 (m, 3H, CH_{Ar}), 7.47 - 7.39 (m, 2H, CH_{Ar}), 2.94 (s, 3H, $CH_{3\text{-quinoline}}$), 1.35 (s, 9H, $CH_{3\text{-}t\text{Bu}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.9 (C_{Ar}), 152.7 (C_{Ar}), 146.4 (C_{Ar}), 144.0 (C_{Ar}), 131.6

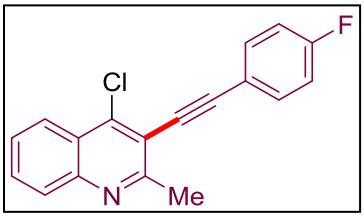
($2CH_{Ar}$), 130.7 (CH_{Ar}), 128.9 (CH_{Ar}), 127.4 (CH_{Ar}), 125.7 ($2CH_{Ar}$), 124.8 (C_{Ar}), 124.4 (CH_{Ar}), 119.7 (C_{Ar}), 117.9 (C_{Ar}), 101.3 (C_{sp}), 83.8 (C_{sp}), 35.1 (C_{tBu}), 31.3 ($3CH_3$), 25.2 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3063 (w), 2958 (m), 2904 (w), 2867 (w), 2208 (w), 1554 (m), 1504 (m), 1477 (m), 1403 (m), 1353 (m), 1267 (m), 1087 (m), 1015 (m), 942 (m), 831 (s), 755 (s), 638 (m), 560 (m). MS (EI, 70 eV): *m/z* (%) = 335 (18), 334 (13), 333 $[M]^+$ (52), 320 (34), 319 (23), 318 (100), 128 (12). HRMS (EI): Calculated for $C_{22}H_{20}N^{35}Cl$ $[M]^+$ 333.12788 found 333.12789, calculated for $C_{22}H_{20}N^{37}Cl$ $[M]^+$ 335.12493 found 335.12556.

4-Chloro-3-((4-methoxyphenyl)ethynyl)-2-methylquinoline (27e): Yellow solid,



mp. 111 - 113 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.15 (ddd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 8.00 (dd, ^3J = 8.4 Hz, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.68 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.60 - 7.50 (m, 3H, CH_{Ar}), 6.90 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.83 (s, 3H, OCH_3), 2.92 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 160.4 (C_{Ar}), 159.7 (C_{Ar}), 146.4 (C_{Ar}), 143.5 (C_{Ar}), 133.4 ($2CH_{Ar}$), 130.5 (CH_{Ar}), 129.0 (CH_{Ar}), 127.2 (CH_{Ar}), 124.7 (C_{Ar}), 124.3 (CH_{Ar}), 117.9 (C_{Ar}), 114.8 (C_{Ar}), 114.3 ($2CH_{Ar}$), 101.2 (C_{sp}), 83.4 (C_{sp}), 55.5 (OCH_3), 25.2 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3362 (w), 3228 (w), 3100 (w), 3033 (w), 2964 (w), 2930 (w), 2913 (w), 2835 (w), 2539 (w), 2205 (w), 2164 (w), 2050 (w), 1602 (w), 1509 (w), 1480 (w), 1291 (w), 1247 (s), 1170 (m), 1104 (m), 1024 (m), 942 (m), 827 (s), 753 (s), 640 (m), 531 (m). MS (EI, 70 eV): *m/z* (%) = 309 (34), 308 (21), 307 $[M]^+$ (100), 294 (14), 293 (10), 292 (43), 272 (14), 264 (16), 229 (23), 228 (23), 227 (11), 187 (19), 136 (11). HRMS (ESI): Calculated for $C_{19}H_{14}{}^{35}ClNO$ $[M+H]^+$ 308.08367 found 308.08381, calculated for $C_{19}H_{14}{}^{37}ClNO$ $[M+H]^+$ 310.08135 found 310.08124.

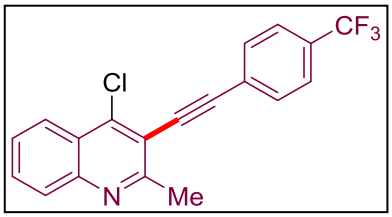
4-chloro-3-((4-fluorophenyl)ethynyl)-2-methylquinoline (27f): Yellow solid,



mp. 147 - 148 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.10 (ddd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.96 (ddd, ^3J = 8.4 Hz, ^3J = 1.2 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.66 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.59 - 7.46 (m, 3H, CH_{Ar}), 7.05 (*pt*, ^3J = 8.7 Hz, 2H, CH_{Ar}), 2.88 (s, 3H, $CH_{3\text{-quinoline}}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -109.3 (FC_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.0 (d, $^1J_{CF}$ = 251.0 Hz, CF_{Ar}), 159.5 (C_{Ar}), 146.5 (C_{Ar}), 143.9

(C_{Ar}), 133.63 (d, $^{3}J_{CF}$ = 8.5 Hz, $2CH_{Ar}$), 130.7 (CH_{Ar}), 129.0 (CH_{Ar}), 127.2 (CH_{Ar}), 124.5 (C_{Ar}), 124.3 (CH_{Ar}), 118.8 (d, $^{4}J_{CF}$ = 3.5 Hz, C_{Ar}), 117.3 (C_{Ar}), 115.8 (d, $^{2}J_{CF}$ = 22.2 Hz, $2CH_{Ar}$), 99.6 (C_{sp}), 84.2 (C_{sp}), 25.2 ($CH_{3\text{-quinoline}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3060 (w), 3000 (w), 2958 (w), 2922 (w), 2845 (w), 2208 (w), 2165 (w), 1931 (w), 1889 (w), 1599 (m), 1506 (m), 1478 (m), 1406 (m), 1355 (m); 1215 (m), 1159 (m), 1091 (m), 940 (m), 828 (s), 749 (s), 639 (m), 524 (m). MS (EI, 70 eV): *m/z* (%) = 297 (34), 296 (24), 295 (100), 261 (13), 260 (69), 259 (45), 258 (13), 218 (29), 130 (11). HRMS (ESI): Calculated for $C_{18}H_{11}{}^{35}ClFN$ $[M+H]^{+}$ 296.06368 found 296.06375, calculated for $C_{18}H_{11}{}^{37}ClFN$ $[M+H]^{+}$ 298.06126 found 298.06147.

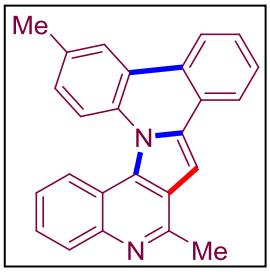
4-Chloro-2-methyl-3-((4-(trifluoromethyl)phenyl)ethynyl)quinoline (27g): White



solid, mp. 138 – 139 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.22 (dd, ^{3}J = 8.5 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 8.07 (d, ^{3}J = 7.9 Hz, 1H, CH_{Ar}), 7.81 - 7.58 (m, 6H, CH_{Ar}), 2.96 (s, 3H, $CH_{3\text{-quinoline}}$). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -62.9 (F_3C). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.6 (C_{Ar}), 146.8 (C_{Ar}), 144.7 (C_{Ar}), 132.0 ($2CH_{Ar}$), 132.0 (CH_{Ar}), 130.8 (d, $^{2}J_{CF}$ = 32.8 Hz, C_{Ar}), 129.1 (C_{Ar}), 128.9 (CH_{Ar}), 127.5 (CH_{Ar}), 125.6 (q, $^{3}J_{CF}$ = 3.8 Hz, $2CH_{Ar}$), 125.2 (q, $^{1}J_{CF}$ = 262.3 Hz, CF_3), 124.6 (C_{Ar}), 124.5 (CH_{Ar}), 116.9 (C_{Ar}), 99.0 (C_{sp}), 86.6 (C_{sp}), 25.2 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 3052 (w), 2921 (w), 1614 (m), 1581 (m), 1555 (m), 1478 (m), 1403 (m), 1356 (m), 1315 (s), 1167 (m), 1114 (m). MS (EI, 70 eV): *m/z* (%) = 347 (34), 346 (22), 345 (100), 310 (47), 241 (16). HRMS (ESI): Calculated for $C_{19}H_{11}{}^{35}ClF_3N$ $[M+H]^{+}$ 346.06049 found 346.06062, calculated for $C_{19}H_{11}{}^{37}ClF_3N$ $[M+H]^{+}$ 348.05812 found 348.05842.

5.2.7.2.Quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridines

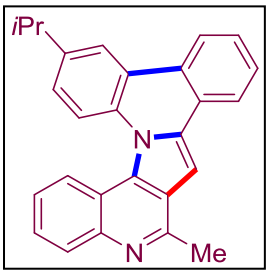
6,13-Dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28a): Pale yellow



solid, m.p. 177 - 178 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.36 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.0 Hz, 1H, CH_{Ar}), 8.22 (m, 2H, CH_{Ar}), 8.09 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 8.10 - 8.02 (m, 1H, CH_{Ar}), 8.04 - 8.02 (m, 1H, CH_{Ar}), 7.59 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.52 - 7.47 (m, 2H, CH_{Ar}), 7.41 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.30 (s, 1H, CH_{Ar}), 7.21 (dd, ^{3}J = 8.5 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 3.00 (s, 3H, $CH_{3\text{-quinoline}}$), 2.51 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.5 (C_{Ar}), 144.5 (C_{Ar}), 136.3 (C_{Ar}), 134.7 (C_{Ar}), 132.3

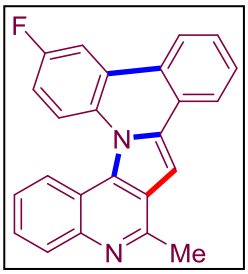
(C_{Ar}), 132.0 (C_{Ar}), 129.7 (CH_{Ar}), 128.4 (CH_{Ar}), 128.1 (CH_{Ar}), 127.9 (CH_{Ar}), 127.6 (C_{Ar}), 126.6 (C_{Ar}), 126.4 (CH_{Ar}), 124.8 (CH_{Ar}), 124.1 (CH_{Ar}), 124.0 (C_{Ar}), 123.8 (CH_{Ar}), 123.6 (C_{Ar}), 122.7 (CH_{Ar}), 122.4 (CH_{Ar}), 119.5 (CH_{Ar}), 118.5 (C_{Ar}), 96.5 (CH_{Ar}), 22.8 (CH_3), 21.4 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3042 (m), 2987 (m), 2915 (m), 2850 (m), 1567 (m), 1511 (m), 1496 (m), 1453 (m), 1371 (m), 1294 (m), 827 (m), 758 (s), 744 (s), 713 (m), 585 (m). MS (EI, 70 eV): *m/z* (%) = 347 (26), 346 $[M]^+$ (100), 345 (28), 330 (12), 165 (11). HRMS (EI): Calculated for $C_{25}H_{18}N_2$ $[M]^+$ 346.14645 found 346.14601.

13-Isopropyl-6-methylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28b): Pale



yellow solid, m.p. 118 - 120 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.43 (dd, ^3J = 8.6 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 8.36 - 8.27 (m, 1H, CH_{Ar}), 8.25 - 8.20 (m, 1H, CH_{Ar}), 8.19 (d, ^3J = 8.7 Hz, 1H, CH_{Ar}), 8.15 - 8.10 (m, 2H, CH_{Ar}), 7.61 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.56 - 7.51 (m, 2H, CH_{Ar}), 7.45 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.36 (s, 1H, CH_{Ar}), 7.33 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1H, CH_{Ar}), 3.11 (sept, ^3J = 6.9 Hz, 1H, CH_{iPr}), 3.02 (s, 3H, $CH_{3\text{-quinoline}}$), 1.40 (d, ^3J = 6.9 Hz, 6H, $CH_{3\text{-}iPr}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.5 (C_{Ar}), 145.8 (C_{Ar}), 144.5 (C_{Ar}), 136.5 (C_{Ar}), 132.7 (C_{Ar}), 132.2 (C_{Ar}), 129.7 (CH_{Ar}), 128.5 (CH_{Ar}), 128.0 (CH_{Ar}), 127.8 (C_{Ar}), 126.6 (C_{Ar}), 126.5 (CH_{Ar}), 125.6 (CH_{Ar}), 124.2 (CH_{Ar}), 124.1 (C_{Ar}), 123.9 (CH_{Ar}), 123.62(C_{Ar}), 122.7 (CH_{Ar}), 122.5 (CH_{Ar}), 122.3 (CH_{Ar}), 119.7 (CH_{Ar}), 118.5 (C_{Ar}), 96.6 (CH_{Ar}), 34.2 (CH_3), 24.3 ($2CH_3$), 22.8 (CH_{iPr}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3058 (m), 2956 (m), 2921 (m), 2866 (m), 1567 (m), 1512 (m), 1453 (m), 1416 (m), 1370 (m), 1256 (m), 866 (m), 758 (s), 744 (s), 705 (m), 629 (m). MS (EI, 70 eV): *m/z* (%) = 375 (30), 374 $[M]^+$ (100), 360 (10), 359 (36), 331 (13). HRMS (EI): Calculated for $C_{27}H_{22}N_2$ $[M]^+$ 374.17775 found 374.17728.

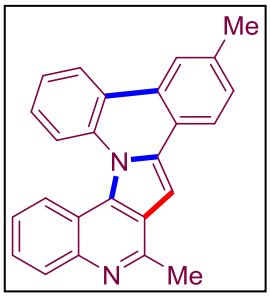
13-Fluoro-6-methylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28c): Pale



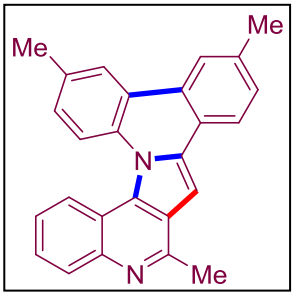
yellow solid, m.p. 168 - 169 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.25 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.20 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.14 (dd, ^3J = 9.1 Hz, ^3J = 5.0 Hz, 1H, CH_{Ar}), 8.10 - 8.02 (m, 2H, CH_{Ar}), 7.84 (dd, ^3J = 9.8 Hz, ^4J = 2.8 Hz, 1H, CH_{Ar}), 7.59 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.54 - 7.47 (m, 2H, CH_{Ar}), 7.39 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.27 (s, 1H, CH_{Ar}), 7.10 (ddd, ^3J = 9.2 Hz, ^3J = 7.5 Hz, ^4J = 2.8 Hz, 1H, CH_{Ar}), 2.97 (s, 3H, $CH_{3\text{-quinoline}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.9

(d, $^{1}J_{CF}$ = 244.6 Hz, CF_{Ar}), 154.5 (C_{Ar}), 144.5 (C_{Ar}), 136.0 (C_{Ar}), 132.1 (C_{Ar}), 130.8 (d, $^{4}J_{CF}$ = 2.4 Hz, C_{Ar}), 129.8 (CH_{Ar}), 129.2 (CH_{Ar}), 128.1 (CH_{Ar}), 126.8 (C_{Ar}), 126.7 (C_{Ar}), 126.7 (CH_{Ar}), 125.6 (d, $^{3}J_{CF}$ = 7.9 Hz, C_{Ar}), 124.1 (CH_{Ar}), 124.0 (CH_{Ar}), 122.9 (CH_{Ar}), 121.9 (CH_{Ar}), 121.0 (d, $^{3}J_{CF}$ = 8.3 Hz, CH_{Ar}), 118.1 (C_{Ar}), 116.8 (C_{Ar}), 114.4 (d, $^{2}J_{CF}$ = 23.4 Hz, CH_{Ar}), 110.7 (d, $^{2}J_{CF}$ = 24.0 Hz, CH_{Ar}), 96.9 (CH_{Ar}), 22.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3059 (w), 2954 (w), 2918 (m), 2849 (m), 1616 (m), 1576 (m), 1511 (m), 1494 (m), 1451 (m), 1416 (m), 1372 (m), 1278 (m), 1177 (m), 863 (m), 820 (m), 758 (s), 744 (s), 708 (m), 626 (m). MS (EI, 70 eV): *m/z* (%) = 351 (25), 350 $[M]^+$ (100). 349 (42), 348 (20), 347 (10), 175 (9). HRMS (EI): Calculated for $C_{24}H_{15}N_2F$ $[M]^+$ 350.12138 found 350.12067.

6,10-Dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28d): Pale yellow solid, m.p. 221 - 222 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.39 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 8.31 - 8.21 (m, 3H, CH_{Ar}), 8.07 (s, 1H, $CH_{Pyrrole}$), 8.01 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.60 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.47 - 7.40 (m, 3H, CH_{Ar}), 7.36 (ddd, ^{3}J = 8.2 Hz, ^{4}J = 1.7 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 7.32 (s, 1H, CH_{Ar}), 3.02 (s, 3H, $CH_{3\text{-quinoline}}$), 2.55 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.4 (C_{Ar}), 138.1 (C_{Ar}), 136.9 (C_{Ar}), 134.6 (C_{Ar}), 132.1 (C_{Ar}), 130.0 (CH_{Ar}), 129.6 (CH_{Ar}), 129.6 (C_{Ar}), 127.6 (C_{Ar}), 127.2 (CH_{Ar}), 126.5 (CH_{Ar}), 125.1 (CH_{Ar}), 126.0 (C_{Ar}), 124.7 (CH_{Ar}), 124.3 (C_{Ar}), 124.2 (CH_{Ar}), 123.9 (CH_{Ar}), 123.8 (C_{Ar}), 122.9 (CH_{Ar}), 122.4 (CH_{Ar}), 119.8 (CH_{Ar}), 118.5 (C_{Ar}), 96.1 (CH_{Ar}), 22.7 (CH_3), 22.0 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3058 (m), 2919 (m), 2851 (w), 1567 (w), 1512 (m), 1489 (m), 1446 (m), 1435 (m), 1370 (m), 1297 (w), 1175 (w), 1032 (w), 814 (m), 756 (s), 747 (s), 695 (m). MS (EI, 70 eV): *m/z* (%) = 347 (26), 346 $[M]^+$ (100), 345 (31), 330 (10), 165 (10). HRMS (EI): Calculated for $C_{25}H_{18}N_2$ $[M]^+$ 346.14645 found 346.14570.

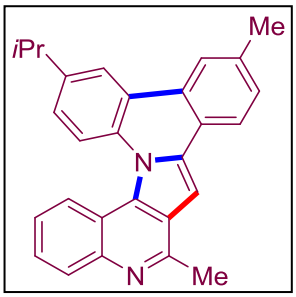


6,10,13-Trimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28e): Pale yellow solid, m.p. 217 - 218 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.37 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 8.20 (d, ^{3}J = 8.0 Hz, 1H, CH_{Ar}), 8.11 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 8.06 - 8.01 (m, 2H, CH_{Ar}), 7.97 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.57 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.4 Hz, 1H,



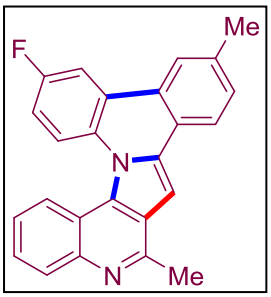
CH_{Ar}), 7.40 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.31 (ddd, ^{3}J = 8.2 Hz, ^{4}J = 1.6 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 7.24 (s, 1H, CH_{Ar}), 7.26 - 7.17 (m, 1H, CH_{Ar}), 2.98 (s, 3H, $CH_{3\text{-quinoline}}$), 2.52 (s, 3H, CH_3), 2.51 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.4 (C_{Ar}), 138.0 (C_{Ar}), 136.7 (C_{Ar}), 134.7 (C_{Ar}), 132.5 (C_{Ar}), 131.9 (C_{Ar}), 129.8 (CH_{Ar}), 129.6 (CH_{Ar}), 129.5 (C_{Ar}), 128.0 (CH_{Ar}), 127.6 (C_{Ar}), 126.4 (CH_{Ar}), 124.7 (CH_{Ar}), 124.2 (C_{Ar}), 124.1 (C_{Ar}), 124.1 (CH_{Ar}), 123.8 (CH_{Ar}), 123.6 (C_{Ar}), 122.9 (CH_{Ar}), 122.4 (CH_{Ar}), 119.6 (CH_{Ar}), 118.5 (C_{Ar}), 95.8 (CH_{Ar}), 22.7 (CH_3), 22.0 (CH_3), 21.4 (CH_3). IR (ATR, cm^{-1}): ṽ = 3026 (w), 2914 (m), 2855 (m), 1566 (w), 1512 (m), 1454 (m), 1369 (m), 1274 (m), 1254 (m), 1032 (m), 949 (m), 863 (m), 811 (m), 760 (s), 694 (m), 538 (m). MS (EI, 70 eV): *m/z* (%) = 361 (27), 360 $[M]^+$ (100), 359 (21), 344 (11), 172 (9). HRMS (EI): Calculated for $C_{26}H_{20}N_2$ $[M]^+$ 360.16210 found 360.16150.

13-Isopropyl-6,10-dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28f):



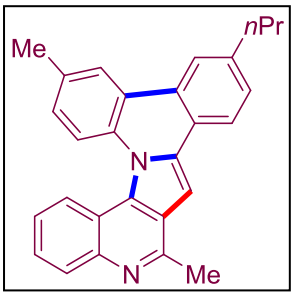
Yellow solid, m.p. 126 – 127 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.44 (dd, ^{3}J = 8.5 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 8.22 (d, ^{3}J = 7.9 Hz, 1H, CH_{Ar}), 8.21 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 8.13 (d, ^{4}J = 2.0 Hz, 1H, CH_{Ar}), 8.11 (s, 1H, CH_{Ar}), 8.03 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.60 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.45 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.39 - 7.30 (m, 3H, CH_{Ar}), 3.12 (sept, ^{3}J = 6.9 Hz, 1H, $CH_{i\text{Pr}}$), 3.02 (s, 3H, $CH_{3\text{-quinoline}}$), 2.57 (s, 3H, CH_3), 1.41 (d, ^{3}J = 6.9 Hz, 6H, $CH_{3\text{-}i\text{Pr}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.4 (C_{Ar}), 145.8 (C_{Ar}), 138.0 (C_{Ar}), 136.8 (C_{Ar}), 132.8 (C_{Ar}), 132.0 (C_{Ar}), 129.8 (CH_{Ar}), 129.6 (CH_{Ar}), 127.8 (C_{Ar}), 126.4 (CH_{Ar}), 125.5 (CH_{Ar}), 124.2 (C_{Ar}), 124.2 (C_{Ar}), 124.2 (CH_{Ar}), 123.8 (CH_{Ar}), 123.6 (C_{Ar}), 122.9 (CH_{Ar}), 122.5 (CH_{Ar}), 122.3 (CH_{Ar}), 120.7 (C_{Ar}), 119.8 (CH_{Ar}), 118.5 (C_{Ar}), 95.9 (CH_{Ar}), 34.2 (CH_3), 24.3 ($2CH_3$), 22.6 ($CH_{aliphatic}$), 22.1 (CH_3). IR (ATR, cm^{-1}): ṽ = 3053 (w), 2956 (m), 2920 (m), 2865 (m), 1615 (w), 1566 (m), 1513 (m), 1482 (w), 1456 (m), 1424 (m), 1370 (m), 1304 (m), 1256 (m), 814 (m), 777 (m), 757 (s), 700 (m), 554 (m). MS (EI, 70 eV): *m/z* (%) = 389 (30), 388 $[M]^+$ (100), 373 (26), 345 (9). HRMS (EI): Calculated for $C_{28}H_{24}N_2$ $[M]^+$ 388.19340 found 388.19309.

13-Fluoro-6,10-dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28g): Yellow solid, m.p. 185 - 186 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.25 (d, ^{3}J = 8.4 Hz, 1H, CH_{Ar}), 8.19 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 8.14 (dd, ^{3}J = 9.1 Hz,



^{4}J = 5.0 Hz, 1H, CH_{Ar}), 7.91 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.88 - 7.79 (m, 2H, CH_{Ar}), 7.58 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.39 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.33 (d, ^{3}J = 7.6 Hz, 1H, CH_{Ar}), 7.20 (s, 1H, CH_{Ar}), 7.09 (ddd, ^{3}J = 9.0 Hz, ^{3}J = 7.4 Hz, ^{4}J = 2.7 Hz, 1H, CH_{Ar}), 2.96 (s, 3H, $CH_{3\text{-quinoline}}$), 2.51 (s, 3H, CH_3). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -116.8 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.9 (d, $^{1}J_{CF}$ = 244.5 Hz, CF_{Ar}), 154.4 (C_{Ar}), 144.4 (C_{Ar}), 138.2 (C_{Ar}), 136.3 (C_{Ar}), 131.9 (C_{Ar}), 130.8 (d, $^{4}J_{CF}$ = 2.5 Hz, C_{Ar}), 130.5 (CH_{Ar}), 129.8 (CH_{Ar}), 129.5 (C_{Ar}), 129.1 (C_{Ar}), 126.5 (CH_{Ar}), 125.6 (d, $^{3}J_{CF}$ = 7.9 Hz, C_{Ar}), 124.3 (C_{Ar}), 124.1 (CH_{Ar}), 123.9 (CH_{Ar}), 123.0 (CH_{Ar}), 121.9 (CH_{Ar}), 121.0 (d, $^{3}J_{CF}$ = 8.3 Hz, CH_{Ar}), 118.2 (C_{Ar}), 114.2 (d, $^{2}J_{CF}$ = 23.5 Hz, CH_{Ar}), 110.6 (d, $^{2}J_{CF}$ = 23.9 Hz, CH_{Ar}), 96.1 (CH_{Ar}), 22.7 (CH_3), 21.9 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3050 (w), 2918 (w), 2851 (w), 1567 (w), 1549 (w), 1512 (w), 1494 (m), 1484 (m), 1429 (m), 1371 (m), 1282 (m), 1259 (m), 1201 (m), 1173 (m), 871 (m), 864 (m), 812 (m), 774 (m), 759 (s), 695 (m). MS (EI, 70 eV): *m/z* (%) = 355 (27), 364 $[M]^+$ (100), 363 (29), 348 (9), 174 (9). HRMS (EI): Calculated for $C_{25}H_{17}N_2F$ $[M]^+$ 364.13703 found 364.13645.

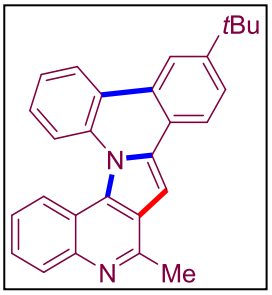
6,13-Dimethyl-10-propylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28h):



Brown solid, mp. 153 - 154 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.37 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 8.29 - 8.20 (m, 1H, CH_{Ar}), 8.09 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 8.06 - 8.03 (m, 2H, CH_{Ar}), 7.98 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.58 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.41 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.34 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 7.26 (s, 1H, CH_{Ar}), 7.21 (ddd, ^{3}J = 8.5 Hz, ^{4}J = 2.1 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 3.00 (s, 3H, CH_3), 2.81 - 2.73 (m, 2H, $CH_{2\text{-}n\text{Pr}}$), 2.52 (s, 3H, CH_3), 1.77 (m, 2H, $CH_{2\text{-}n\text{Pr}}$), 1.03 (t, ^{3}J = 7.3 Hz, 3H, $CH_{3\text{-}n\text{Pr}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.3 (C_{Ar}), 144.0 (C_{Ar}), 142.9 (C_{Ar}), 136.7 (C_{Ar}), 134.7 (C_{Ar}), 132.4 (C_{Ar}), 131.9 (C_{Ar}), 129.4 (CH_{Ar}), 129.2 (CH_{Ar}), 128.0 (CH_{Ar}), 127.5 (C_{Ar}), 126.4 (CH_{Ar}), 124.7 (CH_{Ar}), 124.3 (C_{Ar}), 124.1 (C_{Ar}), 124.0 (CH_{Ar}), 123.8 (CH_{Ar}), 123.7 (CH_{Ar}), 123.7 (C_{Ar}), 122.3 (CH_{Ar}), 119.6 (CH_{Ar}), 118.4 (C_{Ar}), 95.9 (CH_{Ar}), 38.5 ($CH_{2\text{-}n\text{Pr}}$), 24.8 ($CH_{2\text{-}n\text{Pr}}$), 22.6 (CH_3), 21.4 (CH_3), 14.0 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3366 (w), 3053 (w), 2955 (m), 2921 (m), 2867 (m), 2184 (w), 1916 (w), 1565 (m), 1511 (m),

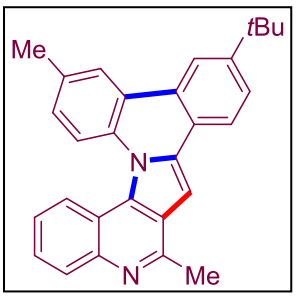
1434 (m), 1369 (m), 1925 (m), 1254 (m), 1157 (m), 1033 (m), 906 (m), 863 (m), 820 (m), 777 (m), 758 (s), 726 (s), 642 (m), 550 (m), 439 (m). MS (EI, 70 eV): *m/z* (%) = 389 (30), 388 $[M]^+$ (100), 360 (17), 359 (58), 343 (11), 171 (12). HRMS (EI): Calculated for $C_{28}H_{24}N_2$ $[M]^+$ 388.19340 found 388.19296.

10-(*tert*-Butyl)-6-methylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28i): Pale



yellow solid, mp. 180 - 181 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.66 - 8.56 (m, 1H, CH_{Ar}), 8.43 (s, 1H, CH_{Ar}), 8.31 (d, ^3J = 8.0 Hz, 1H, CH_{Ar}), 8.27 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 8.18 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.09 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.76 (d, ^4J = 1.7 Hz, 1H, CH_{Ar}), 7.72 - 7.66 (m, 1H, CH_{Ar}), 7.62 (ddd, ^3J = 8.3 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.59 - 7.47 (m, 3H, CH_{Ar}), 2.93 (s, 3H, $CH_{3\text{-quinoline}}$), 1.44 (s, 9H, $CH_{3\text{-}t\text{Bu}}$). ^{13}C NMR (75 MHz, DMSO) δ = 154.0 (C_{Ar}), 151.2 (C_{Ar}), 144.0 (C_{Ar}), 135.9 (C_{Ar}), 133.6 (C_{Ar}), 129.4 (CH_{Ar}), 128.1 (C_{Ar}), 127.5 (CH_{Ar}), 126.6 (CH_{Ar}), 126.5 (CH_{Ar}), 125.9 (C_{Ar}), 125.4 (CH_{Ar}), 124.2 (CH_{Ar}), 124.0 (CH_{Ar}), 123.9 (C_{Ar}), 123.5 (C_{Ar}), 123.3 (C_{Ar}), 121.8 (CH_{Ar}), 119.2 (CH_{Ar}), 119.0 (CH_{Ar}), 117.8 (C_{Ar}), 97.0 (CH_{Ar}), 35.0 (CH_3), 31.1 ($3CH_3$), 22.4 ($C_{t\text{Bu}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 2954 (m), 2922 (m), 2866 (w), 1563 (w), 1491 (m), 1435 (m), 1368 (m), 1297 (m), 1255 (m), 824 (m), 756 (s), 703 (m), 638 (m). MS (EI, 70 eV): *m/z* (%) = 389 (33), 388 $[M]^+$ (100), 374 (19), 373 (60), 358 (21), 357 (14), 172 (16). HRMS (EI): Calculated for $C_{28}H_{24}N_2$ $[M]^+$ 388.19340 found 388.19318.

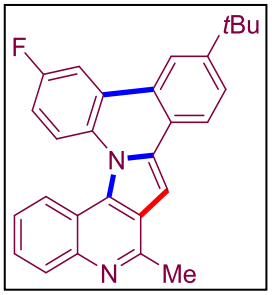
10-(*tert*-Butyl)-6,13-dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28j):



Pale yellow solid, mp. 198 - 200 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.40 (dd, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 8.29 (d, ^4J = 1.9 Hz, 1H, CH_{Ar}), 8.25 (d, ^3J = 7.8 Hz, 1H, CH_{Ar}), 8.13 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.10 (s, 1H, CH_{Ar}), 8.05 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.59 (ddd, ^3J = 8.2 Hz, ^3J = 6.4 Hz, ^4J = 1.7 Hz, 2H, CH_{Ar}), 7.43 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.31 (s, 1H, CH_{Ar}), 7.29 - 7.19 (m, 1H, CH_{Ar}), 3.03 (s, 3H, $CH_{3\text{-quinoline}}$), 2.56 (s, 3H, CH_3), 1.49 (s, 9H, $CH_{3\text{-}t\text{Bu}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.3 (C_{Ar}), 151.3 (C_{Ar}), 144.0 (C_{Ar}), 136.7 (C_{Ar}), 134.8 (C_{Ar}), 132.4 (C_{Ar}), 132.0 (C_{Ar}), 129.4 (CH_{Ar}), 128.0 (CH_{Ar}), 127.2 (C_{Ar}), 126.5 (CH_{Ar}), 126.4 (CH_{Ar}), 124.7 (CH_{Ar}), 124.2 (C_{Ar}), 124.1 (C_{Ar}), 124.0 (C_{Ar}), 124.0 (CH_{Ar}), 123.9 (CH_{Ar}), 122.3 (CH_{Ar}),

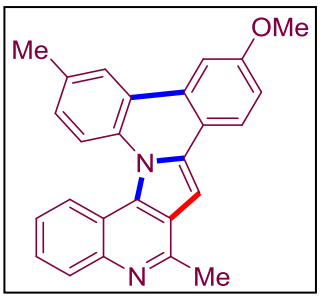
119.7 (CH_{Ar}), 118.9 (CH_{Ar}), 118.4 (C_{Ar}), 96.0 (CH_{Ar}), 35.3 (CH_3), 31.5 ($3CH_3$), 22.6 (CH_3), 21.5 (C_{tBu}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3398 (w), 3055 (w), 2953 (m), 2921 (m), 2861 (w), 1562 (m), 1509 (m), 1479 (m), 1422 (m), 1373 (m), 1295 (m); 1254 (m), 1032 (m), 820 (m), 788 (m), 758 (s), 711 (m), 555 (m). MS (EI, 70 eV): *m/z* (%) = 403 (34), 402 $[M]^+$ (100), 388 (16), 387 (50), 382 (19), 371 (11), 172 (11). HRMS (EI): Calculated for $C_{29}H_{26}N_2$ $[M]^+$ 402.20905 found 402.20888.

10-(*tert*-Butyl)-13-fluoro-6-methylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine



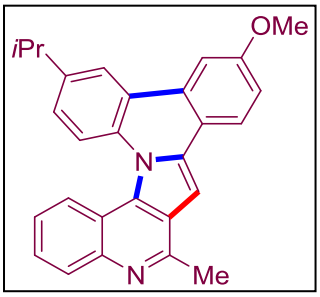
(28k): Pale yellow solid, mp. 242 - 244 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.32 - 8.25 (m, 2H, CH_{Ar}), 8.15 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.09 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.02 (t, ^3J = 9.2 Hz, 1H, CH_{Ar}), 7.69 - 7.57 (m, 2H, CH_{Ar}), 7.50 (dd, ^3J = 8.1 Hz, ^3J = 5.0 Hz, 1H, CH_{Ar}), 7.49 - 7.37 (m, 2H, CH_{Ar}), 7.28 (ddd, ^3J = 11.2 Hz, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 3.09 (s, 3H, $CH_{3\text{-quinoline}}$), 1.47 (s, 9H, $CH_{3\text{-}tBu}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -108.2 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 153.8 (d, $^1J_{CF}$ = 254.2 Hz, CF_{Ar}), 153.8 (CH_{Ar}), 151.8 (C_{Ar}), 136.0 (C_{Ar}), 135.3 (C_{Ar}), 135.3 (C_{Ar}), 128.0 (CH_{Ar}), 127.2 (d, $^2J_{CF}$ = 25.1 Hz, CH_{Ar}), 126.1 (d, $^4J_{CF}$ = 2.5 Hz, C_{Ar}), 125.7 (d, $^3J_{CF}$ = 8.2 Hz, C_{Ar}), 125.8 (C_{Ar}), 125.67 (CH_{Ar}), 124.3 (C_{Ar}), 124.2 (CH_{Ar}), 123.8 (CH_{Ar}), 123.1 (C_{Ar}), 121.5 (d, $^3J_{CF}$ = 10.3 Hz, CH_{Ar}), 120.0 (CH_{Ar}), 119.7 (C_{Ar}), 119.6 (C_{Ar}), 119.5 (CH_{Ar}), 115.2 (d, $^2J_{CF}$ = 20.3 Hz, CH_{Ar}), 97.0 (CH_{Ar}), 35.4 (CH_3), 31.5 ($3CH_3$), 22.2 (C_{tBu}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3361 (w), 3055 (w), 2954 (m), 2865 (w), 2212 (w), 1911 (w), 1563 (m), 1511 (m), 1456 (m), 1365 (m), 1247 (m), 1187 (m), 1077 (m), 826 (m), 760 (s), 712 (s), 642 (m), 557 (m). MS (EI, 70 eV): *m/z* (%) = 407 (30), 406 $[M]^+$ (100), 392 (18), 391 (61), 376 (18), 356 (10), 196 (10), 181 (24), 172 (16), 171 (12). HRMS (EI): Calculated for $C_{28}H_{23}N_2F$ $[M]^+$ 406.18398 found 406.18345.

10-Methoxy-6,13-dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28l): Pale yellow solid, mp. 197 – 199 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.35 (dd, ^3J = 8.7 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.31 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 8.07 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.98 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.97 (s, 1H, CH_{Ar}), 7.65 (d, ^4J = 2.5 Hz, 1H, CH_{Ar}), 7.59 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.42 (ddd, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^3J = 1.4 Hz, 1H, CH_{Ar}), 7.22 (ddd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.17 (s, 1H, CH_{Ar}), 7.10 (dd, ^3J = 8.8 Hz, ^4J = 2.5 Hz, 1H, CH_{Ar}), 3.99 (s, 3H, OCH_3), 3.03 (s, 3H, $CH_{3\text{-quinoline}}$), 2.52 (s, 3H, CH_3).

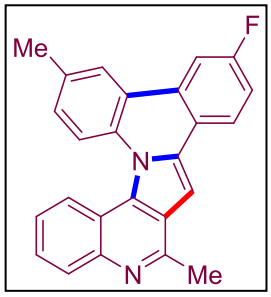


^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.8 (C_{Ar}), 154.0 (C_{Ar}), 137.0 (C_{Ar}), 134.9 (C_{Ar}), 132.4 (C_{Ar}), 131.8 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (CH_{Ar}), 128.3 (CH_{Ar}), 126.6 (CH_{Ar}), 126.2 (C_{Ar}), 125.8 (CH_{Ar}), 124.8 (CH_{Ar}), 124.1 (C_{Ar}), 124.0 (CH_{Ar}), 123.5 (C_{Ar}), 122.2 (CH_{Ar}), 120.0 (C_{Ar}), 119.6 (CH_{Ar}), 118.3 (C_{Ar}), 116.4 (CH_{Ar}), 106.2 (CH_{Ar}), 95.1 (CH_{Ar}), 55.7 (OCH_3), 22.2 (CH_3), 21.4 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2920 (w), 2831 (w), 1611 (m), 1558 (m), 1482 (m), 1408 (m), 1368 (m), 1282 (m), 1222 (m), 1170 (m), 1030 (m), 862 (m), 817 (m), 759 (m), 729 (m), 697 (m), 583 (m). MS (EI, 70 eV): *m/z* (%) = 377 (25), 376 $[M]^+$ (100), 361 (25), 333 (11), 332 (16), 331 (13), 317 (13), 359 (11). HRMS (EI): Calculated for $C_{26}H_{20}ON_2$ $[M]^+$ 376.15071 found 376.15721.

13-Isopropyl-10-methoxy-6-methylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28m): White solid, mp. 178 – 180 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.35 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 8.21 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 8.10 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 8.00 (d, ^4J = 2.0 Hz, 1H, CH_{Ar}), 7.92 (d, ^3J = 8.7 Hz, 1H, CH_{Ar}), 7.27 (dd, ^3J = 8.7 Hz, ^4J = 2.4 Hz, 1H, CH_{Ar}), 7.57 (ddd, ^3J = 8.3 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.41 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.29 (d, ^4J = 1.9 Hz, 1H, CH_{Ar}), 7.11 (s, 1H, CH_{Ar}), 7.05 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H, CH_{Ar}), 3.96 (s, 3H, OCH_3), 3.08 (p, ^3J = 6.9 Hz, 1H, CH_{iPr}), 2.97 (s, 3H, $CH_{3\text{-quinoline}}$), 1.38 (d, ^3J = 6.9 Hz, 6H, $CH_{3\text{-}iPr}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.6 (C_{Ar}), 154.1 (C_{Ar}), 145.6 (C_{Ar}), 144.0 (C_{Ar}), 136.6 (C_{Ar}), 132.8 (C_{Ar}), 131.6 (C_{Ar}), 129.5 (CH_{Ar}), 129.3 (C_{Ar}), 126.2 (CH_{Ar}), 125.7 (CH_{Ar}), 125.6 (CH_{Ar}), 124.1 (C_{Ar}), 123.7 (CH_{Ar}), 123.3 (C_{Ar}), 122.3 (CH_{Ar}), 122.2 (CH_{Ar}), 120.1 (C_{Ar}), 119.7 (CH_{Ar}), 118.4 (C_{Ar}), 115.8 (CH_{Ar}), 106.5 (CH_{Ar}), 94.9 (CH_{Ar}), 55.7 (OCH_3), 34.1 (CH_{iPr}), 24.2 ($2CH_3$), 22.7 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3528 (w). 3160 (w), 3077 (w), 2958 (m), 2868 (w), 2838 (w), 2398 (w), 2084 (w), 2008 (w), 1613 (m), 1568 (m), 1485 (m), 1417 (m), 1369 (m), 1278 (m), 1225 (s), 1030 (m), 864 (m), 814 (m), 760 (s), 699 (m). MS (EI, 70 eV): *m/z* (%) = 405 (30), 404 $[M]^+$ (100), 389 (24), 345 (11). HRMS (EI): Calculated for $C_{28}H_{24}ON_2$ $[M]^+$ 404.18831 found 404.18819.

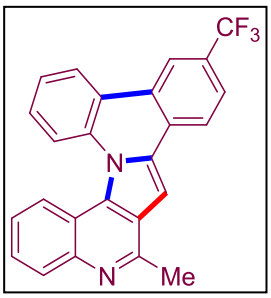


10-Fluoro-6,13-dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28n):



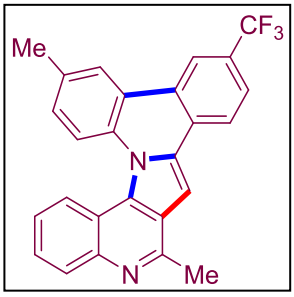
Brown solid, mp. 198 - 200 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.30 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.5 Hz, 2H, CH_{Ar}), 8.04 (d, ^{3}J = 8.5 Hz, 2H, CH_{Ar}), 8.02 - 7.98 (m, 1H, CH_{Ar}), 7.89 (s, 1H, CH_{Ar}), 7.84 (dd, ^{3}J = 10.3 Hz, ^{4}J = 2.5 Hz, 1H, CH_{Ar}), 7.60 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.41 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.28 - 7.15 (m, 2H, CH_{Ar}), 3.01 (s, 3H, $CH_{3\text{-quinoline}}$), 2.50 (s, 3H, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -111.7 (FC_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.6 (d, $^{1}J_{CF}$ = 247.6 Hz, CF_{Ar}), 154.1 (C_{Ar}), 150.5 (C_{Ar}), 143.3 (C_{Ar}), 136.0 (C_{Ar}), 135.2 (CH_{Ar}), 132.4 (C_{Ar}), 132.0 (C_{Ar}), 129.6 (d, $^{3}J_{CF}$ = 8.2 Hz, C_{Ar}), 129.0 (C_{Ar}), 128.9 (CH_{Ar}), 126.9 (CH_{Ar}), 126.3 (d, $^{3}J_{CF}$ = 8.8 Hz, CH_{Ar}), 124.9 (CH_{Ar}), 124.2 (CH_{Ar}), 123.8 (C_{Ar}), 122.8 (d, $^{4}J_{CF}$ = 2.8 Hz, C_{Ar}), 122.2 (CH_{Ar}), 119.6 (CH_{Ar}), 118.1 (C_{Ar}), 116.5 (d, $^{2}J_{CF}$ = 23.2 Hz, CH_{Ar}), 108.9 (d, $^{2}J_{CF}$ = 23.2 Hz, CH_{Ar}), 96.2 (CH_{Ar}), 22.2 (CH_3), 21.4 (CH_3). IR (ATR, cm^{-1}): ṽ = 3063 (w), 3034 (w), 2983 (w), 2904 (w), 1614 (w), 1568 (m), 1481 (m), 1440 (m), 1371 (m), 1273 (m), 1180 (m), 941 (m), 856 (m), 809 (m), 764 (m), 748 (s), 735 (m), 541 (m). MS (EI, 70 eV): *m/z* (%) = 365 (27), 364 (100), 363 (29), 348 (12), 174 (14). HRMS (EI): Calculated for $C_{25}H_{17}N_2F$ $[M]^+$ 364.13703 found 364.13640.

6-Methyl-10-(trifluoromethyl)quinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine



(28o): White solid, mp. 169 - 171 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 8.44 (s, 1H, CH_{Ar}), 8.27 (d, ^{3}J = 8.6 Hz, 2H, CH_{Ar}), 8.21 (d, ^{3}J = 9.5 Hz, 1H, CH_{Ar}), 8.15 (d, ^{3}J = 9.5 Hz, 1H, CH_{Ar}), 8.08 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 7.70 (d, ^{3}J = 8.3 Hz, 1H, CH_{Ar}), 7.63 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.48 - 7.39 (m, 3H, CH_{Ar}), 7.34 (s, 1H, CH_{Ar}), 3.00 (s, 3H, $CH_{3\text{-quinoline}}$). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -62.4 ($FC_{aliphatic}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 154.4 (C_{Ar}), 144.0 (C_{Ar}), 135.2 (C_{Ar}), 134.4 (C_{Ar}), 132.7 (C_{Ar}), 130.0 (C_{Ar}), 129.8 (q, $^{2}J_{CF}$ = 32.7 Hz, C_{Ar}), 129.3 (CH_{Ar}), 129.0 (C_{Ar}), 128.2 (CH_{Ar}), 127.6 (C_{Ar}), 127.3 (CH_{Ar}), 125.6 (CH_{Ar}), 124.9 (q, $^{3}J_{CF}$ = 3.6 Hz, CH_{Ar}), 124.8 (CH_{Ar}), 124.6 (CH_{Ar}), 124.3 (CH_{Ar}), 124.2 (q, $^{1}J_{CF}$ = 272 Hz, CF_3), 123.8 (C_{Ar}), 122.7 (C_{Ar}), 122.4 (CH_{Ar}), 120.0 (q, $^{3}J_{CF}$ = 4.0 Hz, CH_{Ar}), 119.7 (CH_{Ar}), 118.0 (C_{Ar}), 98.5 (CH_{Ar}), 22.2 (CH_3). IR (ATR, cm^{-1}): ṽ = 3362 (w), 3062 (w), 2917 (w), 1621 (m), 1514 (m),k 1441 (m),

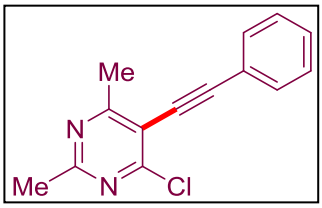
1370 (m), 1341 (m), 1315 (m), 1264 (m), 1169 (m), 1113 (s), 1080 (m); 1022 (m), 827 (m), 758 (s), 644 (m). MS (EI, 70 eV): *m/z* (%) = 401 (25), 400 (100), 399 (47), 398 (13), 166 (9). HRMS (EI): Calculated for $C_{25}H_{15}N_2F_3$ $[M]^+$ 400.11818 found 400.11760.

6,13-Dimethyl-10-(trifluoromethyl)quinolino[3',4':4,5]pyrrolo[1,2-*f*]-phenanthridine (28p): 

White solid, mp. 190 - 192 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.34 (s, 1H, CH_{Ar}), 8.26 - 8.18 (m, 2H, CH_{Ar}), 7.93 (t, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.88 (s, 1H, CH_{Ar}), 7.60 (ddd, ^3J = 7.6 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 2H, CH_{Ar}), 7.37 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.18 - 7.11 (m, 2H, CH_{Ar}), 2.92 (s, 3H, $CH_{3\text{-quinoline}}$), 2.45 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -62.3 ($FC_{aliphatic}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.4 (C_{Ar}), 144.2 (C_{Ar}), 135.2 (C_{Ar}), 134.7 (C_{Ar}), 132.3 (C_{Ar}), 132.2 (C_{Ar}), 129.5 (CH_{Ar}), 129.4 (d, $^2J_{CF}$ = 32.6 Hz, C_{Ar}), 128.9 (q, $^4J_{CF}$ = 1.1 Hz, CH_{Ar}), 127.4 (C_{Ar}), 127.0 (CH_{Ar}), 126.1 (C_{Ar}), 124.8 (C_{Ar}), 124.6 (CH_{Ar}), 124.5 (q, $^3J_{CF}$ = 4.0 Hz, CH_{Ar}), 124.5 (CH_{Ar}), 124.2 (q, $^1J_{CF}$ = 274 Hz, CF_3), 124.0 (CH_{Ar}), 123.6 (C_{Ar}), 122.3 (CH_{Ar}), 119.7 (q, $^3J_{CF}$ = 4.4 Hz, CH_{Ar}), 119.4 (CH_{Ar}), 118.0 (C_{Ar}), 98.1 (CH_{Ar}), 22.4 (CH_3), 21.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3376 (w), 3067 (w), 2919 (w), 2856 (w), 2641 (w), 1618 (w), 1515 (w), 1501 (w), 1435 (m), 1372 (m), 1339 (m), 1316 (s), 1262 (m), 1168 (m), 1106 (s), 1079 (m), 824 (m), 758 (s), 566 (m). MS (EI, 70 eV): *m/z* (%) = 415 (28), 414 (100), 413 (30), 398 (10), 199 (8). HRMS (EI): Calculated for $C_{26}H_{17}F_3N_2$ $[M]^+$ 415.14166 found 415.14181.

5.2.8. Synthesis of pyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines by regioselective Sonogashira reaction followed by one-pot C-N coupling/hydroamination/C-H arylation

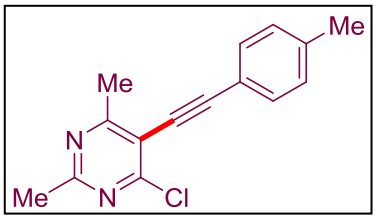
5.2.8.1. Starting materials

4-Chloro-2,6-dimethyl-5-(phenylethynyl)pyrimidine (30a): 

Yellow solid, mp. 125 - 126 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.59 - 7.53 (m, 2H, CH_{Ph}), 7.40 - 7.36 (m, 3H, CH_{Ph}), 2.70 (s, 3H, CH_3), 2.68 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 170.1 (C_{Ar}), 165.7 (C_{Ar}), 161.2 (C_{Ar}), 131.7 ($2CH_{Ph}$), 129.4 (CH_{Ar}), 128.6 ($2CH_{Ph}$), 122.3 (C_{Ar}), 115.3 (C_{Ar}), 102.0 (C_{sp}), 81.5 (C_{sp}), 25.9 ($CH_{3\text{-pyrimidine}}$), 23.8 ($CH_{3\text{-pyrimidine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 2993 (w), 2960

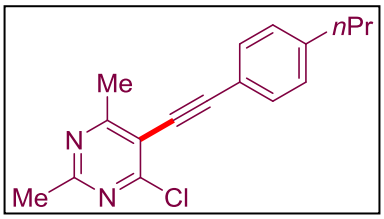
(w), 2923 (w), 2852 (w), 1560 (m), 1503 (m), 1488 (m), 1418 (s), 1351 (m), 1308 (m), 1245 (m), 1073 (m), 863 (m), 766 (s), 695 (m), 565 (m). MS (EI, 70 eV): *m/z* (%) = 244 (33), 243 (17), 242 $[M]^+$ (100), 207 (10), 167 (11), 166 (85), 160 (26), 140 (18), 139 (26), 125 (11). HRMS (EI): Calculated for $C_{14}H_{11}N_2Cl$ $[M]^+$ 242.06053 found 242.06022, calculated for $C_{14}H_{11}N_2{}^{37}Cl$ $[M]^+$ 244.05758 found 244.05770.

4-Chloro-2,6-dimethyl-5-(*p*-tolylethynyl)pyrimidine (30b): Yellow solid,



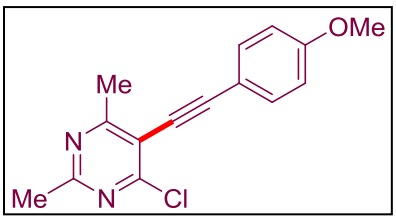
mp. 67 - 68 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.45 (d, ^3J = 8.1 Hz, 2H), 7.18 (d, ^3J = 8.1 Hz, 2H), 2.69 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 2.38 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 170.0 (C_{Ar}), 165.5 (C_{Ar}), 161.1 (C_{Ar}), 139.8 (C_{Ar}), 131.6 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 119.2 (C_{Ar}), 115.5 (C_{Ar}), 102.4 (C_{sp}), 80.9 (C_{sp}), 25.9 ($CH_{3\text{-pyrimidine}}$), 23.8 ($CH_{3\text{-pyrimidine}}$), 21.7 (CH_3). IR (ATR, cm^{-1}): ṽ = 2957 (w), 2919 (w), 2859 (w), 2214 (w), 1897 (w), 1506 (m), 1419 (m), 1249 (m), 1031 (m), 812 (s), 526 (m). MS (EI, 70 eV): *m/z* (%) = 258 (40), 257 (23), 256 (100), 255 (12), 200 (16), 181 (12), 180 (80), 178 (12), 175 (10), 174 (13), 173 (25), 164 (18), 153 (19), 152 (24), 151 (13), 139 (31), 138 (16), 127 (10), 42 (37). HRMS (EI): Calculated for $C_{15}H_{13}N_2Cl$ 256.07618 $[M]^+$ found 256.07597, calculated for $C_{15}H_{13}N_2{}^{37}Cl$ 258.07323 $[M]^+$ found 258.07349.

4-Chloro-2,6-dimethyl-5-((4-propylphenyl)ethynyl)pyrimidine (30c): Yellow solid,

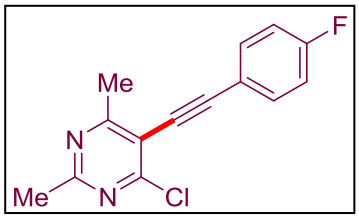


mp. 51 - 52 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.44 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.21 - 7.12 (m, 2H, CH_{Ar}), 2.66 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.65 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.65 - 2.51 (m, 2H, $CH_{2\text{-aliphatic}}$), 1.62 (h, ^3J = 7.3 Hz, 2H, $CH_{2\text{-aliphatic}}$), 0.91 (t, ^3J = 7.3 Hz, 3H, $CH_{3\text{-}n\text{Pr}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 169.9 (C_{Ar}), 165.4 (C_{Ar}), 161.0 (C_{Ar}), 144.4 (C_{Ar}), 131.6 ($2CH_{Ar}$), 128.7 ($2CH_{Ar}$), 119.4 (C_{Ar}), 115.4 (C_{Ar}), 102.4 ($C_{alkynyl}$), 80.9 ($C_{alkynyl}$), 38.1 (CH_2), 25.8 (CH_3), 24.4 (CH_2), 23.8 (CH_3), 13.8 (CH_3). IR (ATR, cm^{-1}): ṽ = 3032 (w), 2961 (m), 2932 (m), 2868 (w), 2216 (w), 1903 (w), 1503 (m), 1418 (s), 1366 (m), 1309 (m), 1245 (m), 1112 (m), 842 (m), 824 (s), 740 (m), 563 (m), 544 (m). MS (EI, 70 eV): *m/z* (%) = 286 (16), 285 (11), 284 $[M]^+$ (49), 257 (32), 256 (17), 255 (100), 179 (11), 173 (16), 164 (14), 152 (10), 151 (11), 138 (14), 42 (11), 29 (12). HRMS (EI): Calculated for $C_{17}H_{17}N_2Cl$ $[M]^+$ 284.10748 found 284.10761, calculated for $C_{17}H_{17}N_2{}^{37}Cl$ $[M]^+$ 286.10453 found 286.10539.

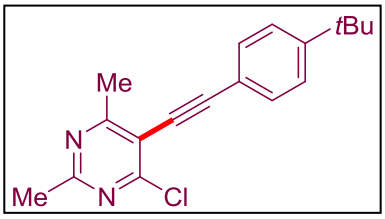
4-Chloro-5-((4-methoxyphenyl)ethynyl)-2,6-dimethylpyrimidine (30d): Yellow solid, mp. 104 - 105 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.42 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 6.83 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 3.76 (s, 3H, OCH_3), 2.62 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.61 (s, 3H, $CH_{3\text{-pyrimidine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 169.8 (C_{Ar}), 165.3 (C_{Ar}), 161.0 (C_{Ar}), 160.6 (C_{Ar}), 133.3 ($2CH_{Ar}$), 115.7 (C_{Ar}), 114.3 ($2CH_{Ar}$), 102.4 (C_{sp}), 80.4 (C_{sp}), 55.5 (OCH_3), 25.8 ($CH_{3\text{-pyrimidine}}$), 23.8 ($CH_{3\text{-pyrimidine}}$). (One C_{Ar} is overlapped by other peaks). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3003 (w), 2914 (w), 2838 (w), 2535 (w), 2215 (w), 1904 (w), 1604 (m), 1504 (s), 1443 (m), 1287 (m), 1248 (s), 1172 (m), 1107 (m), 1024 (m), 866 (m), 836 (s), 635 (m), 592 (m), 537 (m). MS (EI, 70 eV): *m/z* (%) = 274 (38), 273 $[M]^+$ (20), 272 (100), 259 (14), 257 (39), 196 (26), 175 (10), 153 (19), 149 (19). HRMS (EI): Calculated for $C_{15}H_{13}ClN_2O$ $[M]^+$ 273.07892 found 273.07924, calculated for $C_{15}H_{13}{}^{37}ClN_2O$ $[M]^+$ 275.07639 found 275.07620.



4-Chloro-5-((4-fluorophenyl)ethynyl)-2,6-dimethylpyrimidine (30e): Yellow soild, mp. 90 - 91 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.53 (dd, ^{3}J = 8.9 Hz, ^{3}J = 5.4 Hz, 2H, CH_{Ar}), 7.07 (dd, ^{3}J = 8.9 Hz, ^{3}J = 8.5 Hz, 2H, CH_{Ar}), 2.68 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.68 (s, 3H, $CH_{3\text{-pyrimidine}}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -109.0 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 170.1 (C_{Ar}), 165.8 (C_{Ar}), 165.2 (C_{Ar}), 163.22 (d, $^{1}J_{CF}$ = 251.4 Hz, CF_{Ar}), 161.2 (C_{Ar}), 133.7 (d, $^{3}J_{CF}$ = 8.6 Hz, $2CH_{Ar}$), 118.4 (d, $^{4}J_{CF}$ = 3.6 Hz, C_{Ar}), 116.1 (d, $^{2}J_{CF}$ = 22.2 Hz, $2CH_{Ar}$), 115.2 (C_{Ar}), 100.9 (C_{sp}), 81.2 (d, $^{5}J_{CF}$ = 1.5 Hz, C_{sp}), 25.9 ($CH_{3\text{-pyridine}}$), 23.8 ($CH_{3\text{-pyridine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3106 (w), 3080 (w), 3055 (w), 2919 (w), 2220 (w), 1888 (w), 1602 (m), 1505 (m), 1419 (m), 1227 (m), 1155 (m), 861 (m), 833 (s), 759 (m), 639 (m), 557 (m), 528 (m). MS (EI, 70 eV): *m/z* (%) = 262 (28), $[M]^+$ 261 (12), 260 (78), 225 (12), 184 (100), 180 (11), 178 (27), 169 (13), 158 (11), 157 (29), 143 (14), 133 (17), 89 (17), 42 (16). HRMS (EI): Calculated for $C_{14}H_{10}ClFN_2$ 261.05893 found 261.05941, calculated for $C_{14}H_{10}{}^{37}ClFN_2$ 263.05631 found 263.05655.



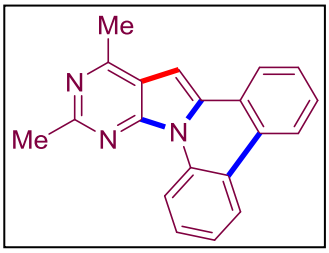
5-((4-(*tert*-Butyl)phenyl)ethynyl)-4-chloro-2,6-dimethylpyrimidine (30f): Brown solid, mp. 67 - 68 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 7.42 (d, ^{3}J = 8.4 Hz, 2H, CH_{Ar}), 7.31 (d, ^{3}J = 8.4 Hz, 2H, CH_{Ar}), 2.61 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.60 (s, 3H, $CH_{3\text{-pyrimidine}}$), 1.24 (s, 9H, $CH_{3\text{-}t\text{Bu}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 170.0 (C_{Ar}), 165.5



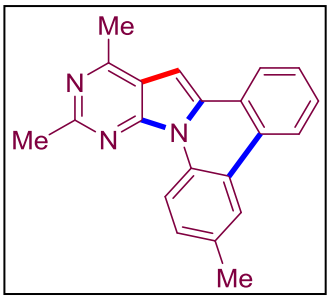
(C_{Ar}), 161.0 (C_{Ar}), 152.9 (C_{Ar}), 131.5 (2CH), 125.6 (2CH), 119.2 (C_{Ar}), 115.5 (C_{Ar}), 102.3 (C_{sp}), 80.9 (C_{sp}), 35.0 (C_{tBu}), 31.2 ($3CH_{3\text{-}tBu}$), 25.9 ($CH_{3\text{-pyrimidine}}$), 23.8 ($CH_{3\text{-pyrimidine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3040 (w), 2959 (m), 2907 (w), 2869 (w), 2832 (w), 2214 (m), 1556 (m), 1502 (m), 1418 (m), 1364 (m), 1251 (m), 1101 (m), 1022 (m), 864 (m), 837 (s), 761 (m), 714 (m), 562 (m). MS (EI, 70 eV): *m/z* (%) = 300 (12). 298 (36), 285 (30), 284 (19), 283 (100), 255 (13), 165 (12), 42 (15), 31 (15). HRMS (EI): Calculated for $C_{18}H_{19}ClN_2$ 299.13095 found 299.13092, calculated for $C_{18}H_{19}{}^{37}ClN_2$ 301.12854 found 301.12879.

5.2.8.2.Pyrimido[5',4':4,5]pyrrolo[1,2-f]phenanthridines

11,13-Dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32a): Pale yellow solid, mp. 210 - 211 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 10.03 (dd, ^3J = 8.5 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.22 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 8.18 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 8.05 - 7.99 (m, 1H, CH_{Ar}), 7.60 (ddd, ^3J = 8.6 Hz, ^3J = 7.2 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.52 - 7.45 (m, 2H, CH_{Ar}), 7.38 (ddd, ^3J = 8.3 Hz, ^3J = 7.2 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.00 (s, 1H, $CH_{pyrrole}$), 2.90 (s, 3H, CH_3), 2.79 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.4 (C_{Ar}), 159.0 (C_{Ar}), 150.3 (C_{Ar}), 135.0 (C_{Ar}), 134.1 (C_{Ar}), 129.3 (CH_{Ar}), 128.8 (CH_{Ar}), 128.4 (CH_{Ar}), 127.5 (C_{Ar}), 125.2 (C_{Ar}), 124.5 (CH_{Ar}), 124.1 (CH_{Ar}), 123.2 (CH_{Ar}), 122.8 (CH_{Ar}), 121.7 (C_{Ar}), 119.7 (CH_{Ar}), 116.5 (C_{Ar}), 91.4 (CH_{Ar}), 26.4 (CH_3), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3033 (w), 2959 (w), 2917 (m), 2850 (m), 1955 (w), 1927 (w), 1895 (w), 1722 (w), 1586 (m), 1550 (m), 1465 (m), 1440 (m), 1360 (m), 1290 (m), 1257 (m), 1021 (m), 743 (s), 715 (m). MS (EI, 70 eV): *m/z* (%) = 298 (22), 297 $[M]^+$ (100), 255 (26), 253 (11). HRMS (EI): Calculated for $C_{20}H_{15}N_3$ $[M]^+$ 297.12605 found 297.12588.

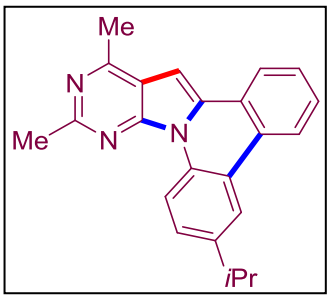


6,11,13-Trimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32b): Pale yellow solid, mp. 226 - 227 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.79 (d, ^3J = 8.5 Hz, 1H, $CH_{Ar\text{-}22}$), 8.10 (dd, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 1H), 7.99 - 7.86 (m, 2H), 7.42 (pd, ^3J = 7.1 Hz, ^4J = 1.5 Hz, 2H), 7.32 (dd, ^3J = 8.6 Hz, ^4J = 1.4 Hz, 1H), 6.88 (s, 1H, $CH_{pyrrole}$), 2.86 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 2.47 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.0 (C_{Ar}), 157.6 (C_{Ar}), 148.7 (C_{Ar}), 132.6 (C_{Ar}), 132.5 (C_{Ar}), 131.5 (C_{Ar}), 128.8 (CH_{Ar}), 127.3 (CH_{Ar}), 126.9 (CH_{Ar}), 126.2 (C_{Ar}), 124.0 (C_{Ar}), 122.8 (CH_{Ar}), 122.1



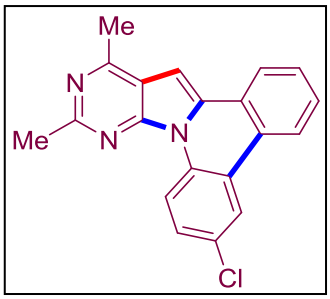
(CH_{Ar}), 121.4 (CH_{Ar}), 120.2 (C_{Ar}), 118.2 (CH_{Ar}), 115.1 (C_{Ar}), 89.8 (CH_{Ar}), 25.2 (CH_3), 20.6 (CH_3), 20.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3090 (w), 2958 (m), 2917 (m), 2851 (m), 1923 (w), 1721 (m), 1659 (m), 1583 (m), 1546 (m), 1499 (m), 1460 (m), 1414 (m), 1387 (m), 1358 (m), 1286 (m), 1252 (m), 1178 (m), 1155 (m), 1024 (m), 944 (m), 819 (m), 773 (m), 761 (m), 725 (s), 577 (m). MS (EI, 70 eV): *m/z* (%) = 312 (24), 311 $[M]^+$ (100), 269 (18), 253 (10), 156 (4). HRMS (EI): Calculated for $C_{21}H_{17}N_3$ $[M]^+$ 311.14170 found 311.14147.

6-Isopropyl-11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32c):



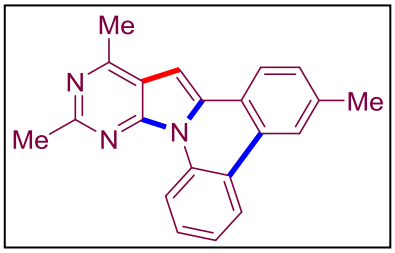
Pale yellow solid, mp. 180 - 181 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.93 (d, ^3J = 8.7 Hz, 1H, CH_{Ar}), 8.20 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H, CH_{Ar}), 8.06 (d, ^4J = 2.0 Hz, 1H, CH_{Ar}), 7.99 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.54 - 7.40 (m, 3H, CH_{Ar}), 6.95 (s, 1H), 3.09 (sept, ^3J = 6.9 Hz, 1H, CH_{iPr}), 2.88 (s, 3H, CH_3), 2.77 (s, 3H, CH_3), 1.39 (d, ^3J = 6.9 Hz, 6H, $CH_{3\text{-}iPr}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.33 (C_{Ar}), 158.91 (C_{Ar}), 149.97 (C_{Ar}), 144.72 (C_{Ar}), 133.86 (C_{Ar}), 133.02 (C_{Ar}), 128.56 (CH_{Ar}), 128.12 (CH_{Ar}), 127.60 (C_{Ar}), 127.52 (CH_{Ar}), 125.23 (C_{Ar}), 124.09 (CH_{Ar}), 122.66 (CH_{Ar}), 121.47 (C_{Ar}), 120.82 (CH_{Ar}), 119.58 (CH_{Ar}), 116.31 (C_{Ar}), 91.01 (CH_{Ar}), 34.2 (CH_{iPr}), 26.4 (CH_3), 24.3 ($2CH_{3\text{-}iPr}$), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3090 (w), 2957 (s), 2923 (m), 2865 (m), 1725 (w), 1661 (w), 1583 (m), 1548 (m), 1461 (m), 1419 (m), 1388 (m), 1360 (m), 1259 (m), 1080 (m), 1016 (m), 944 (m), 824 (m), 797 (m), 755 (s), 726 (s), 719 (m), 621 (m). MS (EI, 70 eV): *m/z* (%) = 340 (17), 339 $[M]^+$ (100), 337 (12), 325 (19), 324 (50), 281 (13), 268 (14), 267 (11). HRMS (EI): Calculated for $C_{21}H_{21}N_3$ $[M]^+$ 339.17300 found 339.17298.

6-Chloro-11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-f]phenanthridine (32d): Pale yellow solid, mp. 284 - 285 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ = 9.95 (d, ^3J = 9.0 Hz, 1H, CH_{Ar}), 8.42 (d, ^4J = 2.4 Hz, 1H, CH_{Ar}), 8.40 - 8.37 (m, 1H, CH_{Ar}), 8.28 (dd, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 1H, CH_{Ar}), 7.65 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1H, CH_{Ar}), 7.63 - 7.59 (m, 2H, CH_{Ar}), 7.46 (s, 1H, $CH_{pyrrole}$), 2.79 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.78 (s, 3H, $CH_{3\text{-pyrimidine}}$). ^{13}C NMR (126 MHz, DMSO) δ = 158.9 (C_{Ar}), 158.7 (C_{Ar}), 149.2 (C_{Ar}), 132.4 (C_{Ar}), 128.7 (CH_{Ar}), 128.7 (CH_{Ar}), 128.3 (CH_{Ar}), 128.0 (C_{Ar}), 125.1 (C_{Ar}), 124.5



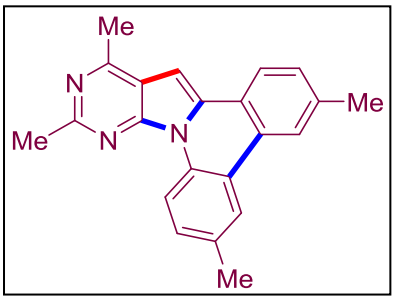
(CH_{Ar}), 123.6 (C_{Ar}), 122.9 (C_{Ar}), 122.7 (CH_{Ar}), 122.6 (CH_{Ar}), 119.8 (CH_{Ar}), 115.6 (C_{Ar}), 98.8 (C_{Ar}), 91.9 (CH_{Ar}), 25.1 (CH_3), 20.6 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3379 (m), 3288 (m), 3111 (m), 2962 (w), 2922 (m), 2851 (w), 1651 (m), 1585 (m), 1548 (m), 1462 (m), 1414 (m), 1387 (m), 1279 (m), 1022 (m), 993 (m), 822 (m), 761 (s), 732 (s), 579 (s), 540 (s). MS (EI, 70 eV): *m/z* (%) = 333 (34), 332 (23), 331 $[M]^+$ (100), 289 (22), 254 (11), 253 (24), 166 (14). HRMS (EI): Calculated for $C_{20}H_{14}N_3Cl$ $[M]^+$ 331.08708 found 331.08702, calculated for $C_{20}H_{14}N_3{}^{37}Cl$ $[M]^+$ 333.08413 found 333.08511.

3,11,13-Trimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32e): Pale



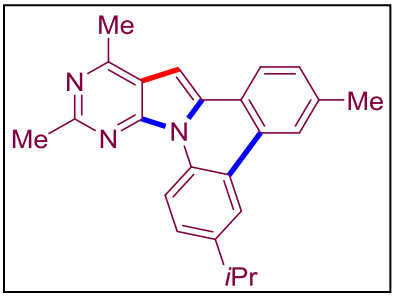
yellow solid, mp. 190 - 191 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.95 (dd, ^3J = 8.5 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.14 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.87 (s, 1H, CH_{Ar}), 7.78 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.54 (ddd, ^3J = 8.6 Hz, ^3J = 7.2 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.32 (ddd, ^3J = 8.3 Hz, ^3J = 7.2 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.19 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 6.80 (s, 1H, $CH_{pyrrole}$), 2.87 (s, 3H $CH_{3\text{-pyrimidine}}$), 2.73 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.47 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.1 (C_{Ar}), 158.6 (C_{Ar}), 150.1 (C_{Ar}), 138.6 (C_{Ar}), 135.0 (C_{Ar}), 134.1 (C_{Ar}), 129.5 (CH_{Ar}), 129.0 (CH_{Ar}), 127.2 (C_{Ar}), 124.2 (CH_{Ar}), 124.0 (CH_{Ar}), 123.0 (CH_{Ar}), 122.8 (CH_{Ar}), 122.6 (C_{Ar}), 121.6 (C_{Ar}), 119.6 (CH_{Ar}), 116.5 (C_{Ar}), 90.5 (CH_{Ar}), 26.4 (CH_3), 22.0 (CH_3), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3116 (w), 3087 (w), 2919 (m), 2851 (m), 1715 (w), 1699 (w), 1661 (w), 1583 (m), 1563 (m), 1549 (m), 1496 (m), 1445 (s), 1416 (m), 1386 (m), 1359 (m), 1292 (m), 1023 (m), 943 (m), 813 (m), 749 (s), 633 (m). MS (EI, 70 eV): *m/z* (%) = 312 (25), 311 $[M]^+$ (100), 269 (22), 253 (11), 155 (12). HRMS (EI): Calculated for $C_{21}H_{17}N_3$ $[M]^+$ 311.14170 found 311.14129.

3,6,11,13-Tetramethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32f): Yellow solid, mp. 203 - 204 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.76 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.88 (s, 1H, CH_{Ar}), 7.84 (s, 1H, CH_{Ar}), 7.76 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.30 (ddd, ^3J = 8.5 Hz, ^4J = 1.9 Hz, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.17 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 6.78 (s, 1H, CH_{Ar}), 2.86 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.73 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.49 - 2.42 (m, 6H, $2CH_3$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.9 (C_{Ar}), 158.4 (C_{Ar}), 149.8 (C_{Ar}), 138.4 (C_{Ar}), 134.0 (C_{Ar}), 133.5 (C_{Ar}), 132.7 (C_{Ar}), 129.8



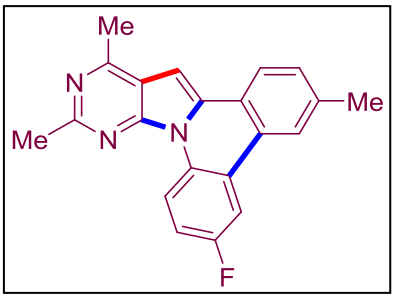
(CH_{Ar}), 129.3 (CH_{Ar}), 127.2 (C_{Ar}), 123.9 (CH_{Ar}), 123.1 (CH_{Ar}), 122.7 (CH_{Ar}), 122.6 (C_{Ar}), 121.4 (C_{Ar}), 119.3 (CH_{Ar}), 116.3 (C_{Ar}), 90.1 (CH_{Ar}), 26.4 (CH_3), 22.0 (CH_3), 21.7 (CH_3), 21.5 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3090 (w), 2918 (m), 2853 (m), 2166 (m), 1723 (w), 1616 (w), 1583 (m), 1552 (m), 1501 (m), 1423 (m), 1388 (m), 1359 (m), 1306 (m), 1289 (m), 1249 (m), 1190 (m), 944 (m), 816 (m), 768 (m), 732 (s), 724 (s), 714 (m), 641 (m), 536 (m). MS (EI, 70 eV): *m/z* (%) = 326 (24), 325 $[M]^+$ (100); 283 (15), 163 (12), 141 (5), 121 (5). HRMS (EI): Calculated for $C_{22}H_{19}N_3$ $[M]^+$ 325.15735 found 325.15688.

6-Isopropyl-3,11,13-trimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine



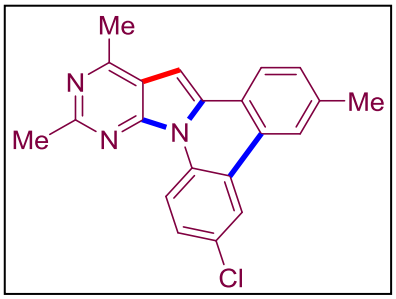
(32g): Yellow solid, mp. 191 - 192 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.90 (d, ^3J = 8.7 Hz, 1H, CH_{Ar}), 8.02 (d, ^4J = 2.0 Hz, 1H, CH_{Ar}), 7.93 (d, ^4J = 1.7 Hz, 1H, CH_{Ar}), 7.82 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.47 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1H, CH_{Ar}), 7.21 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 6.84 (s, 1H, $CH_{pyrrole}$), 3.09 (sept, ^3J = 6.9 Hz, 1H, CH_{iPr}), 2.87 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 1.40 (d, ^3J = 6.9 Hz, 6H, $3CH_{3\text{-}iPr}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.0 (C_{Ar}), 158.5 (C_{Ar}), 149.9 (C_{Ar}), 144.6 (C_{Ar}), 138.5 (C_{Ar}), 134.1 (C_{Ar}), 133.1 (C_{Ar}), 129.5 (CH_{Ar}), 127.5 (C_{Ar}), 127.3 (CH_{Ar}), 124.0 (CH_{Ar}), 122.7 (C_{Ar}), 122.7 (CH_{Ar}), 121.5 (C_{Ar}), 120.7 (CH_{Ar}), 119.6 (CH_{Ar}), 116.4 (C_{Ar}), 90.2 (CH_{Ar}), 34.2 (CH_{iPr}), 26.4 (CH_3), 24.3 ($2CH_{3\text{-}iPr}$), 22.1 (CH_3), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3087 (w), 3062 (w), 3021 (w), 2958 (m), 2920 (m), 2870 (m), 1699 (w), 1584 (m), 1551 (m), 1496 (m), 1432 (m), 1388 (m), 1359 (m), 1193 (m), 1177 (m), 1045 (m), 944 (m), 830 (m), 808 (m), 768 (m), 737 (m), 720 (s), 551 (m). MS (EI, 70 eV): *m/z* (%) = 354 (28). 353 $[M]^+$ (100), 339 (16), 338 (58), 282 (13), 169 (12). HRMS (EI): Calculated for $C_{24}H_{23}N_3$ $[M]^+$ 353.18865 found 353.18798.

6-Fluoro-3,11,13-trimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32h): Yellow solid, mp. 235 - 236 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.83 (dd, ^3J = 9.2 Hz, ^3J = 5.4 Hz, $1H_{Ar}$), 7.69 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.67 - 7.59 (m, 2H, CH_{Ar}), 7.19 - 7.15 (m, 1H, CH_{Ar}), 7.13 (ddd, ^3J = 9.2 Hz, ^3J = 7.5 Hz, ^4J = 2.8 Hz, 1H, CH_{Ar}), 6.70 (s, 1H, $CH_{pyrrole}$), 2.83 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.71 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.44



(s, 3H, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -117.7 (FC_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.5 (d, $^1J_{CF}$ = 243.2 Hz, CF_{Ar}), 159.4 (C_{Ar}), 158.8 (C_{Ar}), 149.8 (C_{Ar}), 138.7 (C_{Ar}), 133.6 (C_{Ar}), 131.3 (d, $^4J_{CF}$ = 2.3 Hz, C_{Ar}), 130.1 (CH_{Ar}), 126.4 (d, $^4J_{CF}$ = 2.5 Hz, C_{Ar}), 123.9 (CH_{Ar}), 123.64 (d, $^3J_{CF}$ = 7.6 Hz, C_{Ar}), 122.9 (C_{Ar}), 122.9 (CH_{Ar}), 121.4 (d, $^3J_{CF}$ = 7.8 Hz, CH_{Ar}), 116.3 (C_{Ar}), 115.7 (d, $^2J_{CF}$ = 22.5 Hz, CH_{Ar}), 109.0 (d, $^2J_{CF}$ = 24.1 Hz, CH_{Ar}), 90.5 (CH_{Ar}), 26.3 (CH_3), 21.9 (CH_3), 21.7 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3089 (w), 3039 (w), 2961 (m), 2919 (m), 2851 (m), 1582 (m), 1566 (m), 1551 (m), 1497 (m), 1438 (m), 1258 (m), 1201 (m), 1191 (m), 1169 (m), 1156 (m), 1014 (m), 937 (m), 795 (s), 766 (m), 726 (m), 584 (m). MS (EI, 70 eV): *m/z* (%) = 330 (24), 329 $[M]^+$ (100), 287 (25), 165 (10), 143 (5), 130 (4). HRMS (EI): Calculated for $C_{21}H_{16}N_3F$ $[M]^+$ 329.13228 found 329.13204.

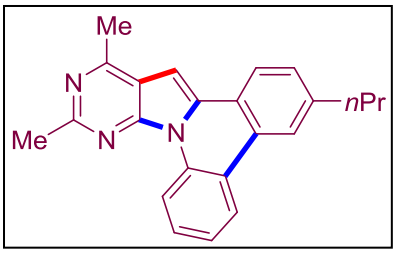
6-Chloro-3,11,13-trimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32i):



Yellow solid, mp. 265 - 266 °C. ^1H NMR (300 MHz, Chloroform-*d*) δ = 9.87 (d, ^3J = 9.0 Hz, 1H, CH_{Ar}), 8.03 (d, ^4J = 2.4 Hz, 1H, CH_{Ar}), 7.81 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.77 (s, 1H, CH_{Ar}), 7.43 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1H, CH_{Ar}), 7.29 - 7.22 (m, 1H, CH_{Ar}), 6.85 (s, 1H, CH_{Ar}), 2.87 (s, 3H, CH_3), 2.77 (s, 3H, CH_3), 2.49 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 158.9 (C_{Ar}), 150.0 (C_{Ar}), 138.9 (C_{Ar}), 133.8 (C_{Ar}), 133.3 (C_{Ar}), 130.2 (CH_{Ar}), 129.9 (C_{Ar}), 128.7 (CH_{Ar}), 128.1 (C_{Ar}), 126.1 (C_{Ar}), 124.0 (CH_{Ar}), 123.3 (C_{Ar}), 122.9 (CH_{Ar}), 122.8 (CH_{Ar}), 121.0 (CH_{Ar}), 116.5 (C_{Ar}), 90.9 (CH_{Ar}), 26.3 (CH_3), 22.0 (CH_3), 21.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3375 (m), 3112 (m), 3046 (m), 3030 (m), 2917 (m), 2850 (m), 1584 (m), 1549 (m), 1488 (m), 1419 (m), 1384 (m), 1305 (m), 1279 (m), 1176 (m), 1161 (m), 1108 (m), 1023 (m), 994 (m), 943 (m), 827 (m), 810 (m), 766 (s), 728 (s), 534 (m). MS (EI, 70 eV): *m/z* (%) = 347 (35), 346 (26), 345 $[M]^+$ (100), 303 (18), 267 (13), 172 (12), 120 (10). HRMS (EI): Calculated for $C_{21}H_{16}N_3Cl$ $[M]^+$ 345.10273 found 345.10249.

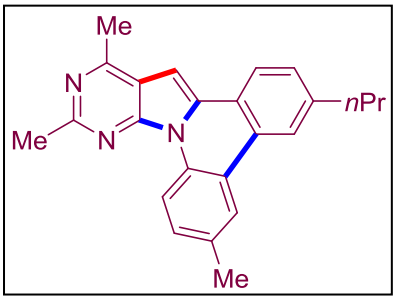
11,13-Dimethyl-3-propylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32j):

Yellow solid, mp. 106 - 108 °C. ^1H NMR (300 MHz, Chloroform-*d*) δ = 9.89 (dd, ^3J = 8.5 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.12 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.86 (s, 1H, CH_{Ar}), 7.76 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.50 (ddd, ^3J = 8.6 Hz, ^3J = 7.2 Hz,



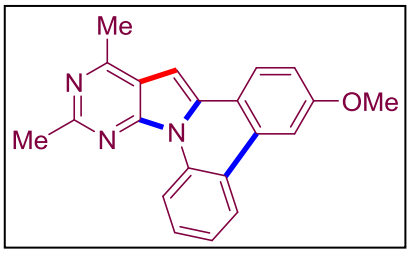
^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.30 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.2 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.20 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 6.75 (s, 1H, CH_{Ar}), 2.84 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.76 - 2.64 (m, 5H, $CH_{2\text{-aliphatic}}$ and $CH_{3\text{-pyrimidine}}$), 1.74 (h, ^{3}J = 7.3 Hz, 2H, $CH_{2\text{-aliphatic}}$), 1.02 (t, ^{3}J = 7.3 Hz, 3H, $CH_{3\text{-}n\text{Pr}}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.0 (C_{Ar}), 158.5 (C_{Ar}), 150.0 (C_{Ar}), 143.3 (C_{Ar}), 134.8 (C_{Ar}), 134.1 (C_{Ar}), 128.9 (CH_{Ar}), 128.8 (CH_{Ar}), 127.2 (C_{Ar}), 124.2 (CH_{Ar}), 123.9 (CH_{Ar}), 122.9 (CH_{Ar}), 122.8 (C_{Ar}), 122.2 (CH_{Ar}), 121.6 (C_{Ar}), 119.5 (CH_{Ar}), 116.4 (C_{Ar}), 90.4 (CH_{Ar}), 38.5 ($CH_{2\text{-aliphatic}}$), 26.3 (CH_3), 24.6 ($CH_{2\text{-aliphatic}}$), 21.7 (CH_3), 14.0 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2956 (w), 2926 (m), 2869 (w), 1586 (m), 1444 (m), 1385 (m), 1289 (m), 944 (m), 816 (m), 752 (s), 504 (m). MS (EI, 70 eV): *m/z* (%) = 340 (25), 339 $[M]^+$ (100), 311 (16), 310 (69), 267 (10), 253 (6). HRMS (ESI): Calculated for $C_{23}H_{21}N_3$ $[M+H]^+$ 340.18082 found 34018071.

6,11,13-Trimethyl-3-propylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32k):



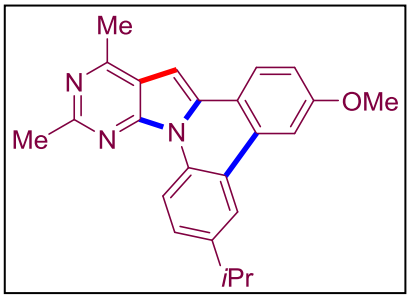
White solid, mp. 163 - 164 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.70 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 7.87 (s, 1H, CH_{Ar}), 7.83 (s, 1H, CH_{Ar}), 7.75 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.26 (ddd, ^{3}J = 8.6 Hz, ^{4}J = 2.0 Hz, ^{5}J = 0.8 Hz, 1H, CH_{Ar}), 7.18 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.6 Hz, 1H, CH_{Ar}), 6.73 (s, 1H, $CH_{pyrrole}$), 2.84 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.72 - 2.67 (m, 5H, $CH_{2\text{-aliphatic}}$ and $CH_{3\text{-pyrimidine}}$), 2.45 (s, 3H, CH_3), 1.74 (h, ^{3}J = 7.3 Hz, 2H, $CH_{2\text{-aliphatic}}$), 1.03 (t, ^{3}J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.7 (C_{Ar}), 158.4 (C_{Ar}), 149.7 (C_{Ar}), 143.2 (C_{Ar}), 134.0 (C_{Ar}), 133.5 (C_{Ar}), 132.6 (C_{Ar}), 129.7 (CH_{Ar}), 128.6 (CH_{Ar}), 127.2 (C_{Ar}), 123.9 (CH_{Ar}), 123.1 (CH_{Ar}), 122.9 (C_{Ar}), 122.1 (CH_{Ar}), 121.4 (C_{Ar}), 119.3 (CH_{Ar}), 116.3 (C_{Ar}), 90.1 (CH_{Ar}), 38.5 ($CH_{2\text{-aliphatic}}$), 26.3 (CH_3), 24.7 ($CH_{2\text{-aliphatic}}$), 21.6 (CH_3), 21.5 (CH_3), 14.0 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3086 (w), 3028 (w), 2954 (m), 2920 (m), 2864 (m), 1582 (m), 1552 (m), 1440 (m), 1360 (m), 1287 (m), 1251 (m), 943 (m), 818 (s), 770 (m), 734 (s), 722 (m), 548 (m). MS (EI, 70 eV): *m/z* (%) = 354 (26), 353 $[M]^+$ (100), 325 (14), 324 (56), 267 (8), 133 (5). HRMS (EI): Calculated for $C_{24}H_{23}N_3$ $[M+H]^+$ 354.19647 found 354.19654.

3-Methoxy-11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-f]phenanthridine (32l):



Yellow solid, mp. 192 - 193 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 9.80 (dd, ^{3}J = 8.5 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.93 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.60 (d, ^{3}J = 8.8 Hz, 1H, CH_{Ar}), 7.46 (ddd, ^{3}J = 8.6 Hz, ^{3}J = 7.2 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.33 (d, ^{4}J = 2.4 Hz, 1H, CH_{Ar}), 7.24 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.2 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 6.85 (dd, ^{3}J = 8.8 Hz, ^{4}J = 2.4 Hz, 1H, CH_{Ar}), 6.49 (s, 1H, $CH_{pyrrole}$), 3.88 (s, 3H, OCH_3), 2.82 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.65 (s, 3H, $CH_{3\text{-pyrimidine}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.9 (C_{Ar}), 158.5 (C_{Ar}), 157.9 (C_{Ar}), 149.8 (C_{Ar}), 134.9 (C_{Ar}), 133.9 (C_{Ar}), 129.1 (CH_{Ar}), 128.6 (C_{Ar}), 125.5 (CH_{Ar}), 124.0 (CH_{Ar}), 122.9 (CH_{Ar}), 121.2 (C_{Ar}), 119.5 (CH_{Ar}), 118.3 (C_{Ar}), 116.4 (C_{Ar}), 115.9 (CH_{Ar}), 105.7 (CH_{Ar}), 89.3 (CH_{Ar}), 55.4 (OCH_3), 26.2 ($CH_{3\text{-pyrimidine}}$), 21.6 ($CH_{3\text{-pyrimidine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3398 (w), 3121 (w), 3073 (w), 3031 (w), 3005 (w), 2917 (w), 2837 (w), 2173 (w), 1614 (m), 1489 (m), 1451 (m), 1386 (m), 1280 (m), 1219 (m), 1148 (m), 1033 (m), 940 (m), 837 (m), 749 (m), 719 (s), 637 (m), 501 (m). MS (EI, 70 eV): *m/z* (%) = 328 (24), 327 $[M]^+$ (100), 312 (14), 284 (22), 242 (10). HRMS (ESI): Calculated for $C_{21}H_{17}N_3O$ 328.14444 found 328.14425.

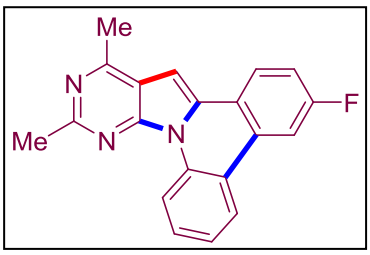
6-Isopropyl-3-methoxy-11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]-phenanthridine (32m):



Pale yellow solid, mp. 207 - 208 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 9.69 (d, ^{3}J = 8.8 Hz, 1H, CH_{Ar}), 7.75 (s, 1H, CH_{Ar}), 7.57 (dd, ^{3}J = 9.5 Hz, ^{3}J = 3.9 Hz, 1H, CH_{Ar}), 7.33 (dd, ^{3}J = 7.0 Hz, ^{4}J = 2.0 Hz, 2H, CH_{Ar}), 6.86 - 6.73 (m, 1H, CH_{Ar}), 6.45 (d, ^{4}J = 2.0 Hz, 1H, CH_{Ar}), 3.82 (s, 3H, OCH_3), 2.96 (p, ^{3}J = 6.9 Hz, 1H, CH_{iPr}), 2.75 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.57 (s, 3H, $CH_{3\text{-pyrimidine}}$), 1.29 (d, ^{3}J = 6.9 Hz, 6H, $CH_{3\text{-}iPr}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.8 (C_{Ar}), 158.5 (C_{Ar}), 157.9 (C_{Ar}), 149.7 (C_{Ar}), 144.3 (C_{Ar}), 133.9 (C_{Ar}), 133.1 (C_{Ar}), 128.9 (C_{Ar}), 127.4 (CH_{Ar}), 125.5 (CH_{Ar}), 121.1 (C_{Ar}), 120.6 (CH_{Ar}), 119.5 (CH_{Ar}), 118.5 (C_{Ar}), 116.3 (C_{Ar}), 115.4 (CH_{Ar}), 105.9 (CH_{Ar}), 89.1 (CH_{Ar}), 55.5 (OCH_3), 34.1 ($CH_{i\text{-Pr}}$), 26.3($CH_{3\text{-pyrimidine}}$), 24.2 ($2CH_{3\text{-}iPr}$), 21.6 ($CH_{3\text{-pyrimidine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3004 (w), 2960 (m), 2924 (w), 2834 (w), 2182 (w), 1614 (m), 1586 (m), 1556 (m), 1492 (m), 1429 (m), 1390 (m), 1278 (m), 1224 (s), 1035 (m),

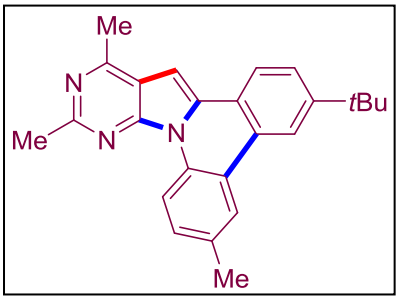
936 (m), 835 (m), 736 (m), 718 (s), 638 (m), 578 (m). MS (EI, 70 eV): *m/z* (%) = 370 (27), 369 $[M]^+$ (100), 354 (37), 311 (11), 177 (7). HRMS (ESI): Calculated for $C_{24}H_{23}N_3O$ $[M+H]^+$ 370.19139 found 370.19112.

3-Fluoro-11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine (32n):



Yellow solid, mp. 233 - 234 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 9.90 (dd, ^3J = 8.6 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.97 (dd, ^3J = 8.1 Hz, ^3J = 1.5 Hz, 1H, CH_{Ar}), 7.83 (dd, ^3J = 8.8 Hz, ^3J = 5.6 Hz, 1H, CH_{Ar}), 7.68 (dd, ^3J = 10.6 Hz, ^4J = 2.5 Hz, 1H, CH_{Ar}), 7.55 (ddd, ^3J = 8.6 Hz, ^3J = 7.2 Hz, ^3J = 1.5 Hz, 1H, CH_{Ar}), 7.32 (ddd, ^3J = 8.3 Hz, ^3J = 7.2 Hz, ^3J = 1.2 Hz, 1H, CH_{Ar}), 7.10 (ddd, ^3J = 8.8 Hz, ^3J = 7.9 Hz, ^4J = 2.5 Hz, 1H, CH_{Ar}), 6.75 (s, 1H, $CH_{pyrrole}$), 2.88 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.75 (s, 3H, $CH_{3\text{-pyrimidine}}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -111.0. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.1 (d, $^1J_{CF}$ = 248.1 Hz, CF_{Ar}), 159.2 (C_{Ar}), 158.7 (C_{Ar}), 150.0 (C_{Ar}), 134.9 (C_{Ar}), 133.3 (C_{Ar}), 129.9 (CH_{Ar}), 129.6 (d, $^3J_{CF}$ = 8.3 Hz, C_{Ar}), 126.2 (d, $^3J_{CF}$ = 8.8 Hz, CH_{Ar}), 124.5 (CH_{Ar}), 123.3 (CH_{Ar}), 121.4 (d, $^4J_{CF}$ = 2.5 Hz, C_{Ar}), 120.7 (d, $^4J_{CF}$ = 3.0 Hz, C_{Ar}), 119.6 (CH_{Ar}), 116.3 (C_{Ar}), 116.3 (d, $^2J_{CF}$ = 23.3 Hz, CH_{Ar}), 108.82 (d, $^2J_{CF}$ = 23.4 Hz, CH_{Ar}), 90.9 (d, $^5J_{CF}$ = 1.8 Hz, CH_{Ar}), 26.2 ($CH_{3\text{-pyrimidine}}$), 21.6 ($CH_{3\text{-pyrimidine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3063 (w), 2992 (w), 2918 (w), 1555 (m), 1452 (m), 1276 (m), 1197 (m), 898 (m), 822 (m), 751 (s), 603 (m), 507 (m). MS (EI, 70 eV): *m/z* (%) = 316 (23), 315 (100), 274 (14), 273 (37), 271 (11), 42 (15). HRMS (ESI): Calculated for $C_{20}H_{14}FN_3$ $[M+H]^+$ 316.12445 found 316.12459.

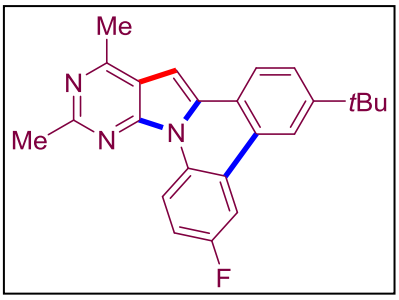
3-(*tert*-Butyl)-6,11,13-trimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]phenanthridine



(32o): Pale yellow solid, mp. 255 – 256 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 9.87 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 8.21 (d, ^4J = 1.8 Hz, 1H, CH_{Ar}), 8.03 (d, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.97 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.55 (dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.37 (ddd, ^3J = 8.6 Hz, ^4J = 2.0 Hz, ^5J = 0.7 Hz, 1H, CH_{Ar}), 6.96 (s, 1H, $CH_{pyrrole}$), 2.89 (s, 3H, $CH_{3\text{-aliphatic}}$), 2.80 (s, 3H, $CH_{3\text{-aliphatic}}$), 2.53 (s, 3H, $CH_{3\text{-aliphatic}}$), 1.48 (s, 9H, $CH_{3\text{-}t\text{Bu}}$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.8 (C_{Ar}), 158.5 (C_{Ar}), 151.9 (C_{Ar}), 149.9 (C_{Ar}), 134.3 (C_{Ar}), 133.8 (C_{Ar}), 132.8 (C_{Ar}), 130.0 (CH_{Ar}), 127.1 (C_{Ar}), 126.1 (CH_{Ar}), 124.1 (CH_{Ar}), 123.2 (CH_{Ar}), 122.8 (C_{Ar}), 121.9 (C_{Ar}), 119.5

(CH_{Ar}), 119.0 (CH_{Ar}), 116.5 (C_{Ar}), 90.5 (CH_{Ar}), 35.4 ($C_{t\text{Bu}}$), 31.5 ($3CH_{3\text{-}t\text{Bu}}$), 26.3 ($CH_{3\text{-aliphatic}}$), 21.7 ($CH_{3\text{-aliphatic}}$), 21.6 ($CH_{3\text{-aliphatic}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2951 (m), 2915 (m), 2862 (m), 2166 (m), 1583 (m), 1489 (m), 1429 (m), 1357 (m), 1182 (m), 945 (m), 820 (m), 722 (s), 638 (m), 551 (m). MS (EI, 70 eV): *m/z* (%) = 368 (27), 367 (100), 353 (16), 352 (59), 337 (18), 162 (11). HRMS (ESI): Calculated for $C_{25}H_{25}N_3$ $[M+H]^+$ 368.21212 found 368.21201.

3-(*tert*-Butyl)-6-fluoro-11,13-dimethylpyrimido[5',4':4,5]pyrrolo[1,2-*f*]-phenanthridine (32p):



Pale yellow solid, mp. 226 - 228 °C. ^{1}H NMR (250 MHz, Chloroform-*d*) δ = 9.92 (dd, ^3J = 9.3 Hz, ^3J = 5.5 Hz, 1H, CH_{Ar}), 8.03 (d, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.91 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.82 (dd, ^3J = 10.4 Hz, ^4J = 2.9 Hz, 1H, CH_{Ar}), 7.57 (dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.20 (ddd, ^3J = 9.3 Hz, ^3J = 7.5 Hz, ^4J = 2.8 Hz, 1H, CH_{Ar}), 6.88 (s, 1H, $CH_{pyrrole}$), 2.86 (s, 3H, $CH_{3\text{-pyrimidine}}$), 2.78 (s, 3H, $CH_{3\text{-pyrimidine}}$), 1.47 (s, 9H, $3CH_{3\text{-}t\text{Bu}}$). ^{19}F NMR (235 MHz, $CDCl_3$) δ = -117.3 (FC_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.5 (d, $^1J_{CF}$ = 243.0 Hz, CF_{Ar}), 159.1 (C_{Ar}), 158.7 (C_{Ar}), 152.1 (C_{Ar}), 149.7 (C_{Ar}), 133.9 (C_{Ar}), 131.20 (d, $^4J_{CF}$ = 2.2 Hz, C_{Ar}), 126.9 (CH_{Ar}), 126.14 (d, $^4J_{CF}$ = 2.4 Hz, C_{Ar}), 124.1 (d, $^3J_{CF}$ = 7.6 Hz, C_{Ar}), 124.0 (CH_{Ar}), 122.9 (C_{Ar}), 121.4 (d, $^3J_{CF}$ = 7.8 Hz, C_{Ar}), 119.2 (CH_{Ar}), 116.3 (C_{Ar}), 115.9 (d, $^2J_{CF}$ = 22.7 Hz, CH_{Ar}), 109.1 (d, $^2J_{CF}$ = 24.0 Hz, CH_{Ar}), 90.7 (CH_{Ar}), 35.4 ($C_{t\text{Bu}}$), 31.4 ($3CH_{3\text{-}t\text{Bu}}$), 26.2 ($CH_{3\text{-pyrimidine}}$), 21.7 ($CH_{3\text{-pyrimidine}}$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3096 (w), 2965 (m), 2868 (m), 2184 (m), 1582 (m), 1562 (m), 1496 (m), 1437 (m), 1389 (m), 1278 (m), 1177 (m), 931 (m), 850 (m), 871 (s), 772 (m), 733 (m), 574 (m). MS (EI, 70 eV): *m/z* (%) = 372 (30), 371 (100), 357 (21), 356 (72), 341 (21), 328 (10), 164 (16). HRMS (ESI): Calculated for $C_{24}H_{22}FN_3$ $[M+H]^+$ 372.18705 found 372.18693.

5.3. Crystallographic data

5.3.1. 2-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (3c)

Chemical formular	$C_{20}H_{16}N_2O$
M_r	320.35
Crystal system, space group	Triclinic, P^1
Temperature (K)	173
a, *b*, *c* (Å)	8.5374 (2), 10.3276 (2), 18.5918 (3)
α, β, γ (°)	74.951 (1), 77.508 (1), 84.490 (1)
V (Å^3)	1544.18 (5)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.08
Crystal size (mm)	0.29 × 0.28 × 0.25
Data collection	
Diffractometer	Bruker-Nonius Apex X8-CCD-diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2004)
T_{min}, T_{max}	0.718, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	53379, 11167, 8411
R_{int}	0.031
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.756
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.053, 0.128, 1.05
No. of reflections	11167
No. of parameters	417
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, -0.25

* Computer programs: Bruker Apex V7.51A, Bruker *SAINT*, *SHELXS2013* (Sheldrick, 2013), *SHELXL2013* (Sheldrick, 2013), *ORTEP-3.2*.01 (Farrugia, 1997), *SHELXL2013*.

5.3.2. 1-(4-Methoxyphenyl)-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4g)

Chemical formular	$C_{20}H_{16}N_2O$
M_r	300.35
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	173
a, *b*, *c* (Å)	5.9896 (1), 11.3423 (2), 11.1347 (2)
α, β, γ (°)	96.311 (1)
V (Å^3)	751.86 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.08
Crystal size (mm)	0.43 × 0.29 × 0.07
Data collection	
Diffractometer	Bruker-Nonius Apex X8-CCD-diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2004)
T_{min}, T_{max}	0.723, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	14227, 5379, 4806
R_{int}	0.023
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.756
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.110, 1.06
No. of reflections	5379
No. of parameters	209
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, -0.28

* Computer programs: Bruker Apex V7.51A, Bruker *SAINT*, *SHELXS2013* (Sheldrick, 2013), *SHELXL2013* (Sheldrick, 2013), *ORTEP-3.2*.01 (Farrugia, 1997), *SHELXL2013*.

5.3.3. 2-(Naphthalen-2-yl)-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4n)

Chemical formular	$C_{23}H_{16}N_2$
M_r	320.38
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, *b*, *c* (Å)	8.9404 (3), 19.2009 (5), 9.6620 (3)
α, β, γ (°)	92.373 (1)
V (Å^3)	1657.19 (9)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.08
Crystal size (mm)	0.53 × 0.22 × 0.11
Data collection	
Diffractometer	Bruker-Nonius Apex X8-CCD-diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2004)
T_{min}, T_{max}	0.713, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	26989, 4828, 3789
R_{int}	0.031
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.133, 1.07
No. of reflections	4828
No. of parameters	226
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, -0.24

* Computer programs: Bruker Apex V7.51A, Bruker *SAINT*, *SHELXS2013* (Sheldrick, 2013), *SHELXL2013* (Sheldrick, 2013), *ORTEP-3.2*.01 (Farrugia, 1997), *SHELXL2013*.

5.3.4. 1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1H-pyrrolo[3,2-*c*]quinoline (7f)

Chemical formular	$C_{25}H_{17}F_3N_2O$
M_r	418.13
Crystal system, space group	Triclinic, *P*
Temperature (K)	150
a, *b*, *c* (Å)	10.5714 (2), 11.3891 (2), 12.0542 (2)
α, β, γ (°)	62.4386 (5), 82.6061 (6), 68.6034 (5)
V (Å^3)	1196.52 (4)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.43
Crystal size (mm)	0.43 × 0.30 × 0.26
Data collection	
Diffractometer	Bruker *APEX-II CCD* diffractometer
Absorption correction	Multi-scan *SADABS* (Bruker, 2014)
T_{min}, T_{max}	0.85, 0.90
No. of measured, independent and observed [I > 2σ(I)] reflections	35088, 6370, 5619
R_{int}	0.018
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.682
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.035, 0.096, 1.06
No. of reflections	6370
No. of parameters	317
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, -0.34

* Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2015).

5.3.5. 11-(4-Methoxyphenyl)-6-methyl-11*H*-indolo[3,2-*c*]quinoline (11g)

Chemical formular	$C_{23}H_{18}N_2O$
M_r	338.39
Crystal system, space group	Triclinic, *P*
Temperature (K)	150
a, *b*, *c* (Å)	11.9183 (2), 14.2302 (3), 16.0093 (3)
α, β, γ (°)	99.1242 (8), 93.7878 (8), 101.7422 (8)
V (Å^3)	2611.10 (9)
Z	6
Radiation type	Mo *K*α
μ (mm^{-1})	0.08
Crystal size (mm)	0.42 × 0.37 × 0.30
Data collection	
Diffractometer	Bruker APEX-II CCD diffractometer
Absorption correction	Multi-scan SADABS (Bruker, 2014)
T_{min}, T_{max}	0.93, 0.98
No. of measured, independent and observed [I > 2σ(I)] reflections	70195, 10264, 8228
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.133, 1.02
No. of reflections	10264
No. of parameters	709
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.74, -0.29

[*] Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2015)..

5.3.6. 6-Fluoro-3-methylbenzo[4',5']thieno[2',3':4,5]pyrrolo[1,2-*f*]phenanthridine (24h)

Chemical formular	$C_{23}H_{14}FNS$
M_r	355.41
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	123
a, *b*, *c* (Å)	3.8697 (3), 13.8753 (13), 29.542 (3)
V (Å^3)	1586.2 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.22
Crystal size (mm)	0.49 × 0.03 × 0.02
Data collection	
Diffractometer	Bruker-Nonius Apex X8-CCD-diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2004)
T_{min}, T_{max}	0.625, 0.745
No. of measured, independent and observed [I > 2σ(I)] reflections	8022, 2778, 2160
R_{int}	0.086
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.098, 1.03
No. of reflections	2278
No. of parameters	237
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, -0.28

* Computer programs: Bruker Apex V7.51A, Bruker *SAINT*, *SHELXS2013* (Sheldrick, 2013), *SHELXL2013* (Sheldrick, 2013), *ORTEP-3.2*.01 (Farrugia, 1997), *SHELXL2013*.

5.3.7. 10-Methoxy-6,13-dimethylquinolino[3',4':4,5]pyrrolo[1,2-*f*]phenanthridine (28l)

Chemical formular	$C_{26}H_{20}N_2O$
M_r	376.15
Crystal system, space group	Triclinic, P^1
Temperature (K)	150
a, *b*, *c* (Å)	7.2427 (2), 10.3539 (2), 15.8131 (3)
α, β, γ (°)	90.3390 (7), 102.6184 (7), 96.4918 (7)
V (Å^3)	1149.19 (4)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.42
Crystal size (mm)	0.43 × 0.17 × 0.16
Data collection	
Diffractometer	Bruker APEX-II CCD diffractometer
Absorption correction	Multi-scan SADABS (Bruker, 2014)
T_{min}, T_{max}	0.94, 0.99
No. of measured, independent and observed [I > 2σ(I)] reflections	24568, 5298, 4567
R_{int}	0.018
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.123, 1.05
No. of reflections	5298
No. of parameters	301
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.87, -0.53

[*] Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2015)..

6. References

[1] J. D. Watson, F. H. C. Crick, *Nature* **1953**, *171*, 737-738.

[2] (a) A. Pamplona, A. Ferreira, J. Balla, V. Jeney, G. Balla, S. Epiphanio, A. Chora, C. D. Rodrigues, I. P. Gregoire, M. Cunha-Rodrigues, S. Portugal, M. P. Soares, M. M. Mota, *Nat. Med.* **2007**, *13*, 703-710; (b) R. Larsen, R. Gozzelino, V. Jeney, L. Tokaji, F. A. Bozza, A. M. Japiassú, D. Bonaparte, M. M. Cavalcante, Â. Chora, A. Ferreira, I. Marguti, S. Cardoso, N. Sepúlveda, A. Smith, M. P. Soares, *Sci. Transl. Med.* **2010**, *2*, 51ra71-51ra71.

[3] I. A. N. Fleming, *Nature* **1967**, *216*, 151-152.

[4] J. K. Rockstroh, U. Spengler, *Dtsch. med. Wochenschr.* **2004**, *129*, 1921-1924.

[5] W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1290-1309.

[6] D. Chen, S.-J. Su, Y. Cao, *J. Mater. Chem. C* **2014**, *2*, 9565-9578.

[7] A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 1637-1638.

[8] P. Biginelli, *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 1317-1319.

[9] C. Paal, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 367-371.

[10] E. Fischer, O. Hess, *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 559-568.

[11] P. Friedlaender, *Ber. Dtsch. Chem. Ges.* **1882**, *15*, 2572-2575.

[12] (a) K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374-4376; (b) M. S. Kharasch, C. F. Fuchs, *J. Am. Chem. Soc.* **1943**, *65*, 504-507; (c) M. Kumada, in *Pure Appl. Chem., Vol. 52*, **1980**, p. 669.

[13] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504-519.

[14] C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 5062-5085.

[15] K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 4442-4489.

[16] X.-F. Wu, P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem., Int. Ed. Engl.* **2010**, *49*, 9047-9050.

[17] P. Zhao, C. M. Beaudry, *Angew. Chem., Int. Ed. Engl.* **2014**, *53*, 10500-10503.

[18] Y. Koseki, T. Sugimura, K. Ogawa, R. Suzuki, H. Yamada, N. Suzuki, Y. Masuyama, Y. Y. Lin, T. Usuki, *Eur. J. Org. Chem.* **2015**, *2015*, 4024-4032.

[19] Y. Liu, M. Prashad, W.-C. Shieh, *Org. Process Res. Dev.* **2014**, *18*, 239-245.

[20] A. L. Bowie, C. C. Hughes, D. Trauner, *Org. Lett.* **2005**, *7*, 5207-5209.

[21] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348.

[22] N. Miyaura, A. Suzuki, *J. Chem. Soc., Chem. Commun.* **1979**, 866-867.

[23] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457-2483.

[24] T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 390-391.

[25] S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633-9695.

[26] I. Maluenda, O. Navarro, *Molecules* **2015**, *20*, 7528.

[27] P. D. Hobbs, V. Upender, J. Liu, D. J. Pollart, D. W. Thomas, M. I. Dawson, *Chem. Commun.* **1996**, 923-924.

[28] A. Kojima, T. Takemoto, M. Sodeoka, M. Shibasaki, *J. Org. Chem.* **1996**, *61*, 4876-4877.

[29] S. Yamaguchi, N. Takahashi, D. Yuyama, K. Sakamoto, K. Suzuki, T. Matsumoto, *Synlett* **2016**, *27*, 1262-1268.

[30] (a) C. Glaser, *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422-424; (b) C. Glaser, *Liebigs Ann.* **1870**, *154*, 137-171.

[31] W. Chodkiewicz, *Ann. Chim. Paris* **1957**, *2*, 819-969.

[32] R. D. Stephens, C. E. Castro, *J. Org. Chem.* **1963**, *28*, 3313-3315.

[33] H. A. Dieck, F. R. Heck, *J. Organomet. Chem.* **1975**, *93*, 259-263.

[34] L. Cassar, *J. Organomet. Chem.* **1975**, *93*, 253-257.

[35] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467-4470.

[36] D. Wang, S. Gao, *Org. Chem. Front.* **2014**, *1*, 556-566.

[37] P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2632-2657.

[38] (a) K. C. Nicolaou, C. W. Hummel, E. N. Pitsinos, M. Nakada, A. L. Smith, K. Shibayama, H. Saimoto, *J. Am. Chem. Soc.* **1992**, *114*, 10082-10084; (b) S. Avidan-Shlomovich, H. Ghosh, A. M. Szpilman, *ACS Catal.* **2015**, *5*, 336-342.

[39] (a) K. Komano, S. Shimamura, Y. Norizuki, D. Zhao, C. Kabuto, I. Sato, M. Hirama, *J. Am. Chem. Soc.* **2009**, *131*, 12072-12073; (b) K. Komano, S. Shimamura, M. Inoue, M. Hirama, *J. Am. Chem. Soc.* **2007**, *129*, 14184-14186.

[40] N. Ramkumar, R. Nagarajan, *Org. Biomol. Chem.* **2015**, *13*, 11046-11051.

[41] (a) B. Bitter, H. Zollinger, *Helv. Chim. Acta* **1961**, *44*, 812-823; (b) A. A. Goldberg, *J. Chem. Soc.* **1952**, 4368-4373.

[42] K. Masanori, K. Masayuki, M. Toshihiko, *Chem. Lett.* **1983**, *12*, 927-928.

[43] F. Paul, J. Patt, J. F. Hartwig, *J. Am. Chem. Soc.* **1994**, *116*, 5969-5970.

[44] A. S. Guram, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 7901-7902.

[45] (a) A. S. Guram, R. A. Rennels, S. L. Buchwald, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348-1350; (b) J. Louie, J. F. Hartwig, *Tetrahedron Lett.* **1995**, *36*, 3609-3612.

[46] (a) M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc.* **1996**, *118*, 7217-7218; (b) J. P. Wolfe, S. Wagaw, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 7215-7216; (c) J. Louie, M. S. Driver, B. C. Hamann, J. F. Hartwig, *J. Org. Chem.* **1997**, *62*, 1268-1273.

[47] (a) J. P. Wolfe, S. L. Buchwald, *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2413-2416; (b) B. C. Hamann, J. F. Hartwig, *J. Am. Chem. Soc.* **1998**, *120*, 7369-7370; (c) J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1158-1174; (d) J. P. Stambuli, R. Kuwano, J. F. Hartwig, *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 4746-4748; (e) X. Huang, K. W. Anderson, D. Zim, L. Jiang, A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 6653-6655; (f) D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722-9723.

[48] (a) S. Lee, M. Jørgensen, J. F. Hartwig, *Org. Lett.* **2001**, *3*, 2729-2732; (b) X. Huang, S. L. Buchwald, *Org. Lett.* **2001**, *3*, 3417-3419; (c) J. P. Wolfe, J. Åhman, J. P. Sadighi, R. A. Singer, S. L. Buchwald, *Tetrahedron Lett.* **1997**, *38*, 6367-6370.

[49] (a) J. Yin, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 6043-6048; (b) W. C. Shakespeare, *Tetrahedron Lett.* **1999**, *40*, 2035-2038; (c) J. Yin, S. L. Buchwald, *Org. Lett.* **2000**, *2*, 1101-1104; (d) J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcazar-Roman, *J. Org. Chem.* **1999**, *64*, 5575-5580.

[50] (a) C. Bolm, J. P. Hildebrand, *Tetrahedron Lett.* **1998**, *39*, 5731-5734; (b) C. Bolm, J. P. Hildebrand, J. Rudolph, *Synthesis* **2000**, *2000*, 911-913; (c) C. Bolm, J. P. Hildebrand, *J. Org. Chem.* **2000**, *65*, 169-175.

[51] (a) S. Wagaw, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 6621-6622; (b) S. Wagaw, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 10251-10263; (c) J. F. Hartwig, *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2090-2093.

[52] (a) G. Mann, J. F. Hartwig, M. S. Driver, C. Fernández-Rivas, *J. Am. Chem. Soc.* **1998**, *120*, 827-828; (b) M. Watanabe, M. Nishiyama, T. Yamamoto, Y.

Koie, *Tetrahedron Lett.* **2000**, *41*, 481-483; (c) D. W. Old, M. C. Harris, S. L. Buchwald, *Org. Lett.* **2000**, *2*, 1403-1406.

[53] P. Ruiz-Castillo, S. L. Buchwald, *Chem. Rev.* **2016,** *116*, 12564-12649.

[54] D. J. Madar, H. Kopecka, D. Pireh, J. Pease, M. Pliushchev, R. J. Sciotti, P. E. Wiedeman, S. W. Djuric, *Tetrahedron Lett.* **2001**, *42*, 3681-3684.

[55] B. M. Mathes, S. A. Filla, *Tetrahedron Lett.* **2003**, *44*, 725-728.

[56] M. Mari, F. Bartoccini, G. Piersanti, *J. Org. Chem.* **2013**, *78*, 7727-7734.

[57] M. Lotierzo, B. Tse Sum Bui, D. Florentin, F. Escalettes, A. Marquet, *Biochem. Soc. Trans.* **2005**, *33*, 820-823.

[58] (a) S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255-263; (b) in *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Ltd, **2006**.

[59] M. D. K. Boele, G. P. F. van Strijdonck, A. H. M. de Vries, P. C. J. Kamer, J. G. de Vries, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2002**, *124*, 1586-1587.

[60] (a) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507-514; (b) L. David, F. Keith, *Chem. Lett.* **2010**, *39*, 1118-1126; (c) R. Waterman, *Organometallics* **2013**, *32*, 7249-7263.

[61] (a) D. E. Ames, D. Bull, *Tetrahedron* **1982**, *38*, 383-387; (b) A. Shiotani, H. Itatani, *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 471-472; (c) R. Giri, N. Maugel, J.-J. Li, D.-H. Wang, S. P. Breazzano, L. B. Saunders, J.-Q. Yu, *J. Am. Chem. Soc.* **2007**, *129*, 3510-3511.

[62] (a) T.-S. Mei, L. Kou, S. Ma, K. M. Engle, J.-Q. Yu, *Synthesis* **2012**, *44*, 1778-1791; (b) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196-5217.

[63] T. Hosoya, E. Takashiro, T. Matsumoto, K. Suzuki, *J. Am. Chem. Soc.* **1994**, *116*, 1004-1015.

[64] Q. Zhang, K. Kawasumi, Y. Segawa, K. Itami, L. T. Scott, *J. Am. Chem. Soc.* **2012**, *134*, 15664-15667.

[65] A. Ault, *J. Chem. Educ.* **1977**, *54*, 614.

[66] (a) C.-G. Dong, T.-P. Liu, Q.-S. Hu, *Synlett* **2009**, *2009*, 1081-1086; (b) A. K. Macharla, R. Chozhiyath Nappunni, N. Nama, *Tetrahedron Lett.* **2012**, *53*, 1401-1405; (c) F. Bergmann, H. Japhe, *J. Am. Chem. Soc.* **1947**, *69*, 1826-1827.

[67] I. N. Houpis, C. Huang, U. Nettekoven, J. G. Chen, R. Liu, M. Canters, *Org. Lett.* **2008**, *10*, 5601-5604.

[68] K. Manabe, M. Yamaguchi, *Catalysts* **2014**, *4*, 307.

[69] (a) M. Uchiyama, Y. Matsumoto, S. Nakamura, T. Ohwada, N. Kobayashi, N. Yamashita, A. Matsumiya, T. Sakamoto, *J. Am. Chem. Soc.* **2004**, *126*, 8755-8759; (b) L. Ackermann, A. Althammer, *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 1627-1629; (c) L. Ackermann, A. Althammer, P. Mayer, *Synthesis* **2009**, *2009*, 3493-3503.

[70] (a) H. Cao, H. Alper, *Org. Lett.* **2010**, *12*, 4126-4129; (b) M. V. Khedkar, S. R. Khan, D. N. Sawant, D. B. Bagal, B. M. Bhanage, *Adv. Synth. Catal.* **2011**, *353*, 3415-3422; (c) D. N. Sawant, Y. S. Wagh, K. D. Bhatte, B. M. Bhanage, *Eur. J. Org. Chem.* **2011**, *2011*, 6719-6724; (d) J. Chen, K. Natte, A. Spannenberg, H. Neumann, M. Beller, X.-F. Wu, *Org. Biomol. Chem.* **2014**, *12*, 5578-5581; (e) M. V. Khedkar, A. R. Shinde, T. Sasaki, B. M. Bhanage, *J. Mol. Catal. A Chem.* **2014**, *385*, 91-97; (f) P. K. Prasad, A. Sudalai, *Adv. Synth. Catal.* **2014**, *356*, 2231-2238; (g) N. Sharma, G. Sekar, *Adv. Synth. Catal.* **2016**, *358*, 314-320.

[71] H. Cao, L. McNamee, H. Alper, *Org. Lett.* **2008**, *10*, 5281-5284.

[72] (a) M. C. Willis, G. N. Brace, I. P. Holmes, *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 403-406; (b) J. Barluenga, A. Jiménez-Aquino, C. Valdés, F. Aznar, *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 1529-1532; (c) J. Barluenga, A. Jiménez-Aquino, F. Aznar, C. Valdés, *J. Am. Chem. Soc.* **2009**, *131*, 4031-4041; (d) W. Hao, W. Geng, W.-X. Zhang, Z. Xi, *Chem. - Eur. J.* **2014**, *20*, 2605-2612.

[73] D. Katayev, M. Nakanishi, T. Burgi, E. P. Kundig, *Chem. Sci.* **2012**, *3*, 1422-1425.

[74] X. Deng, H. McAllister, N. S. Mani, *J. Org. Chem.* **2009**, *74*, 5742-5745.

[75] (a) G. Altenhoff, F. Glorius, *Adv. Synth. Catal.* **2004**, *346*, 1661-1664; (b) H. C. Ma, X. Z. Jiang, *Synlett* **2008**, *2008*, 1335-1340; (c) R. D. Viirre, G. Evindar, R. A. Batey, *J. Org. Chem.* **2008**, *73*, 3452-3459; (d) M. A. Ali, M. Suri, T. Punniyamurthy, *Synthesis* **2013**, *45*, 501-506; (e) X.-F. Wu, H. Neumann, S. Neumann, M. Beller, *Tetrahedron Lett.* **2013**, *54*, 3040-3042; (f) S.-K. Xiang, D.-X. Zhang, H. Hu, J.-L. Shi, L.-G. Liao, C. Feng, B.-Q. Wang, K.-Q. Zhao, P. Hu, H. Yang, W.-H. Yu, *Adv. Synth. Catal.* **2013**, *355*, 1495-1499; (g) D.-X. Zhang, S.-K. Xiang, H. Hu, W. Tan, C. Feng, B.-Q. Wang, K.-Q. Zhao, P. Hu, H. Yang, *Tetrahedron* **2013**, *69*, 10022-10029;

(h) C. S. Demmer, J. C. Hansen, J. Kehler, L. Bunch, *Adv. Synth. Catal.* **2014**, *356*, 1047-1055; (i) F. Wu, J. Zhang, Q. Wei, P. Liu, J. Xie, H. Jiang, B. Dai, *Org. Biomol. Chem.* **2014**, *12*, 9696-9701.

[76] (a) D. Zhao, J. Hu, N. Wu, X. Huang, X. Qin, J. Lan, J. You, *Org. Lett.* **2011**, *13*, 6516-6519; (b) K. Liubchak, K. Nazarenko, A. Tolmachev, *Tetrahedron* **2012**, *68*, 2993-3000.

[77] T. Beresneva, J. Popelis, E. Abele, *Heterocycl. Comp.* **2013**, *49*, 345-347.

[78] (a) J. P. Bachelet, P. Caubere, *J. Org. Chem.* **1982**, *47*, 234-238; (b) T. Yoshito, S. Tetsuya, M. Masahiro, N. Masakatsu, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2345-2350; (c) V. R. Veeramaneni, M. Pal, K. R. Yeleswarapu, *Tetrahedron* **2003**, *59*, 3283-3290; (d) M. C. Willis, D. Taylor, A. T. Gillmore, *Org. Lett.* **2004**, *6*, 4755-4757; (e) M. C. Willis, D. Taylor, A. T. Gillmore, *Tetrahedron* **2006**, *62*, 11513-11520; (f) B. Lu, B. Wang, Y. Zhang, D. Ma, *J. Org. Chem.* **2007**, *72*, 5337-5341; (g) J. Bonnamour, M. Piedrafita, C. Bolm, *Adv. Synth. Catal.* **2010**, *352*, 1577-1581; (h) N. Aljaar, C. C. Malakar, J. Conrad, S. Strobel, T. Schleid, U. Beifuss, *J. Org. Chem.* **2012**, *77*, 7793-7803.

[79] (a) E. Abele, R. Abele, E. Lukevics, *Chem. Heterocycl. Compd.* **2003**, *39*, 825-865; (b) S. Kumar, S. Bawa, H. Gupta, *Mini Rev. Med. Chem.* **2009**, *9*, 1648-1654; (c) X. Qian, Y.-Z. Zhu, W.-Y. Chang, J. Song, B. Pan, L. Lu, H.-H. Gao, J.-Y. Zheng, *ACS Appl. Mater. Interfaces* **2015**, *7*, 9015-9022; (d) E. Abele, E. Lukevics, *Chem. Heterocycl. Compd.* **2001**, *37*, 141-169; (e) C. Seo, J. M. Choi, S.-S. Hong, J. Y. Lee, S. Seo, *Dyes Pigm.* **2017**, *136*, 145-149; (f) M. Suzuki, H. Iwasaki, Y. Fujikawa, M. Sakashita, M. Kitahara, R. Sakoda, *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1285-1288.

[80] G. Wittig, H. Reiff, *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 7-14.

[81] (a) G. Stork, S. R. Dowd, *J. Am. Chem. Soc.* **1963**, *85*, 2178-2180; (b) G. Wittig, H. D. Frommeld, P. Suchanek, *Angew. Chem.* **1963**, *75*, 978-979.

[82] (a) Y. Yamaoka, M. Taniguchi, K.-i. Yamada, K. Takasu, *Synthesis* **2015**, *47*, 2819-2825; (b) J. Pérard-Viret, F. Souquet, M.-L. Manisse, J. Royer, *Tetrahedron Lett.* **2010**, *51*, 96-98; (c) A. D. J. Calow, E. Fernandez, A. Whiting, *Org. Biomol. Chem.* **2014**, *12*, 6121-6127.

[83] Y.-Y. Song, K. Kinami, A. Kato, Y.-M. Jia, Y.-X. Li, G. W. J. Fleet, C.-Y. Yu, *Org. Biomol. Chem.* **2016**, *14*, 5157-5174.

[84] (a) S. R. Stauffer, S. Lee, J. P. Stambuli, S. I. Hauck, J. F. Hartwig, *Org. Lett.* **2000**, *2*, 1423-1426; (b) G. A. Grasa, M. S. Viciu, J. Huang, S. P. Nolan, *J. Org. Chem.* **2001**, *66*, 7729-7737; (c) I. C. F. R. Ferreira, M.-J. R. P. Queiroz, G. Kirsch, *Tetrahedron* **2003**, *59*, 975-981; (d) A. S. Gajare, K. Toyota, M. Yoshifuji, F. Ozawa, *J. Org. Chem.* **2004**, *69*, 6504-6506; (e) O. Grossman, K. Rueck-Braun, D. Gelman, *Synthesis* **2008**, *2008*, 537-542; (f) R. J. Lundgren, A. Sappong-Kumankumah, M. Stradiotto, *Chem. - Eur. J.* **2010**, *16*, 1983-1991.

[85] (a) M. Layek, Y. Syam Kumar, A. Islam, R. Karavarapu, A. Sengupta, D. Halder, K. Mukkanti, M. Pal, *Med. Chem. Comm.* **2011**, *2*, 478-485; (b) J.-Y. Mérour, F. Buron, K. Plé, P. Bonnet, S. Routier, *Molecules* **2014**, *19*, 19935.

[86] (a) R. L. Rich, F. Gai, J. W. Lane, J. W. Petrich, A. W. Schwabacher, *J. Am. Chem. Soc.* **1995**, *117*, 733-739; (b) K. L. Rich, M. Négrerie, J. Li, S. Elliott, R. W. Thornburg, J. W. Petrich, *Photochem. Photobiol. Sci.* **1993**, *58*, 28-30; (c) S. Lepthien, M. G. Hoesl, L. Merkel, N. Budisa, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 16095-16100.

[87] T. Wang, Z. Yang, Z. Zhang, Y.-F. Gong, K. A. Riccardi, P.-F. Lin, D. D. Parker, S. Rahematpura, M. Mathew, M. Zheng, N. A. Meanwell, J. F. Kadow, J. A. Bender, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 213-217.

[88] M. Chatterji, R. Shandil, M. R. Manjunatha, S. Solapure, V. Ramachandran, N. Kumar, R. Saralaya, V. Panduga, J. Reddy, P. KR, S. Sharma, C. Sadler, C. B. Cooper, K. Mdluli, P. S. Iyer, S. Narayanan, P. S. Shirude, *Antimicrob. Agents Chemother.* **2014**, *58*, 5325-5331.

[89] (a) G. Bollag, J. Tsai, J. Zhang, C. Zhang, P. Ibrahim, K. Nolop, P. Hirth, *Nat. Rev. Drug Discov.* **2012**, *11*, 873-886; (b) E. Krambovitis, F. Porichis, D. A. Spandidos, *Acta Pharmacol. Sin.* **2005**, *26*, 1165-1173; (c) C. Teixeira, J. R. B. Gomes, P. Gomes, F. Maurel, *Eur. J. Med. Chem.* **2011**, *46*, 979-992.

[90] J.-Y. Mérour, S. Routier, F. Suzenet, B. Joseph, *Tetrahedron* **2013**, *69*, 4767-4834.

[91] (a) D. Thomae, M. Jeanty, J. Coste, G. Guillaumet, F. Suzenet, *Eur. J. Org. Chem.* **2013**, *2013*, 3328-3336; (b) R. S. Alekseyev, S. R. Amirova, E. V. Kabanova, V. I. Terenin, *Heterocycl. Comp.* **2014**, *50*, 1305-1315; (c) M. Jeanty, J. Blu, F. Suzenet, G. Guillaumet, *Org. Lett.* **2009**, *11*, 5142-5145; (d) F. Pin, F.

Buron, F. Saab, L. Colliandre, S. Bourg, F. Schoentgen, R. Le Guevel, C. Guillouzo, S. Routier, *Med. Chem. Comm.* **2011**, *2*, 899-903.

[92] (a) M. M. Robinson, B. L. Robison, *J. Am. Chem. Soc.* **1955**, *77*, 457-460; (b) J. Jadhav, S. Khanapaure, R. Kurane, R. Salunkhe, G. Rashinkar, *Tetrahedron Lett.* **2013**, *54*, 6858-6863.

[93] T. Storz, M. D. Bartberger, S. Sukits, C. Wilde, T. Soukup, *Synthesis* **2008**, *2008*, 201-214.

[94] Z. Zhang, Z. Yang, N. A. Meanwell, J. F. Kadow, T. Wang, *J. Org. Chem.* **2002**, *67*, 2345-2347.

[95] (a) Y. Ma, S. Breslin, I. Keresztes, E. Lobkovsky, D. B. Collum, *J. Org. Chem.* **2008**, *73*, 9610-9618; (b) R. Buchan, M. Fraser, P. V. S. K. T. Lin, *J. Org. Chem.* **1985**, *50*, 1324-1325; (c) R. Buchan, M. Fraser, C. Shand, *J. Org. Chem.* **1977**, *42*, 2448-2454; (d) R. Buchan, M. Fraser, C. Shand, *J. Org. Chem.* **1976**, *41*, 351-355.

[96] (a) S. D. Debenham, A. Chan, K. Liu, K. Price, H. B. Wood, *Tetrahedron Lett.* **2005**, *46*, 2283-2285; (b) N. Lachance, M. April, M.-A. Joly, *Synthesis* **2005**, *2005*, 2571-2577; (c) S. H. Spergel, D. R. Okoro, W. Pitts, *J. Org. Chem.* **2010**, *75*, 5316-5319; (d) K. C. Majumdar, S. Ganai, B. Chattopadhyay, K. Ray, *Synlett* **2011**, *2011*, 2369-2373; (e) T. Jensen, H. Pedersen, B. Bang-Andersen, R. Madsen, M. Jørgensen, *Angew. Chem., Int. Ed. Engl.* **2008**, *47*, 888-890.

[97] (a) D. K. Whelligan, D. W. Thomson, D. Taylor, S. Hoelder, *J. Org. Chem.* **2010**, *75*, 11-15; (b) Y.-Q. Fang, J. Yuen, M. Lautens, *J. Org. Chem.* **2007**, *72*, 5152-5160.

[98] S. Cacchi, G. Fabrizi, L. M. Parisi, *J. Com. Chem.* **2005**, *7*, 510-512.

[99] X. Li, W. Yin, P. V. V. S. Sarma, H. Zhou, M. Jun, J. M. Cook, *Tetrahedron Lett.* **2004**, *45*, 8569-8573.

[100] M. G. Ferlin, B. Gatto, G. Chiarelotto, M. Palumbo, *Bioorg. Med. Chem.* **2000**, *8*, 1415-1422.

[101] M. Akula, J. P. Sridevi, P. Yogeeswari, D. Sriram, A. Bhattacharya, *Monatsh. Chem.* **2014**, *145*, 811-819.

[102] N. Varvarigou, G. Megariotis, G. Leonis, E. Vrontaki, A.-M. Maniati, M. Vlachou, A. Eikosipentaki, R. Kompogennitaki, M. G. Papadopoulos, S. G. Grdadolnik, D. Komiotis, T. Mavromoustakos, A. Tsotinis, *Bioorg. Med. Chem.* **2012**, *20*, 6276-6284.

[103] (a) K. Grychowska, G. Satała, T. Kos, A. Partyka, E. Colacino, S. Chaumont-Dubel, X. Bantreil, A. Wesołowska, M. Pawłowski, J. Martinez, P. Marin, G. Subra, A. J. Bojarski, F. Lamaty, P. Popik, P. Zajdel, *ACS Chem. Neurosci.* **2016**, *7*, 972-983; (b) G. Maher-Edwards, C. Watson, J. Ascher, C. Barnett, D. Boswell, J. Davies, M. Fernandez, A. Kurz, O. Zanetti, B. Safirstein, J. P. Schronen, M. Zvartau-Hind, M. Gold, *Alzheimers Dement (N. Y.)* **2015**, *1*, 23-36.

[104] (a) A. L. Rodriguez, C. Koradin, W. Dohle, P. Knochel, *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2488-2490; (b) C. Koradin, W. Dohle, A. L. Rodriguez, B. Schmid, P. Knochel, *Tetrahedron* **2003**, *59*, 1571-1587.

[105] G. Höfle, B. Böhlendorf, T. Fecker, F. Sasse, B. Kunze, *J. Nat. Prod.* **2008**, *71*, 1967-1969.

[106] M. Murugesan, K. Ramasamy, P. Shanmugam, *Z. Naturforsch. B* **1979**, *35*, 746-748.

[107] (a) M. A. Khan, J. F. da Rocha, *J. Heterocycl. Chem.* **1978**, *15*, 913-921; (b) A. A. Avetisyan, I. L. Aleksanyan, L. P. Ambartsumyan, *Russ. J. Org. Chem.* **2010**, *46*, 427-431; (c) K. K. Park, H. Rapoport, *J. Heterocycl. Chem.* **1992**, *29*, 1031-1032; (d) P. Helissey, H. Parrot-Lopez, J. Renault, S. Cros, *Eur. J. Med. Chem.* **1987**, *22*, 366-368; (e) P. Helissey, H. Parrot-Lopez, Eacute, Egrave, Ne, J. Renault, S. Cros, *Chem. Pharm. Bull.* **1987**, *35*, 3547-3557; (f) P. Helissey, H. Parrot-Lopez, J. Renault, S. Cros, C. Paoletti, *Eur. J. Med. Chem.* **1987**, *22*, 277-282; (g) F. Dudouit, R. Houssin, J.-P. Hénichart, *J. Heterocycl. Chem.* **2001**, *38*, 755-758.

[108] M. L. Testa, L. Lamartina, F. Mingoia, *Tetrahedron* **2004**, *60*, 5873-5880.

[109] R. A. Mekheimer, *Synthesis* **2000**, *2000*, 2078-2084.

[110] F. Zhou, J. Liu, K. Ding, J. Liu, Q. Cai, *J. Org. Chem.* **2011**, *76*, 5346-5353.

[111] (a) J.-H. Lee, J. Lee, *FEMS Microbiol. Rev.* **2010**, *34*, 426-444; (b) S. Piñero-Fernandez, C. Chimerel, U. F. Keyser, D. K. Summers, *J. Bacteriol.* **2011**, *193*, 1793-1798; (c) H. Gaimster, J. Cama, S. Hernández-Ainsa, U. F. Keyser, D. K. Summers, *PLoS ONE* **2014**, *9*, e93168; (d) Y.-G. Kim, J.-H. Lee, M. H. Cho, J. Lee, *BMC Microbiol.* **2011**, *11*, 119; (e) J.-H. Lee, T. K. Wood, J. Lee, *Trends Microbiol.*, *23*, 707-718.

[112] A. Slominski, I. Semak, A. Pisarchik, T. Sweatman, A. Szczesniewski, J. Wortsman, *FEBS Lett.* **2002**, *511*, 102-106.

[113] Y.-Q. Wang, X.-H. Li, Q. He, Y. Chen, Y.-Y. Xie, J. Ding, Z.-H. Miao, C.-H. Yang, *Eur. J. Med. Chem.* **2011**, *46*, 5878-5884.

[114] M. C. Suh, S.-R. Park, Y. R. Cho, D. H. Shin, P.-G. Kang, D. A. Ahn, H. S. Kim, C.-B. Kim, *ACS Appl. Mater. Interfaces* **2016**, *8*, 18256-18265.

[115] P. Venault, G. Chapouthier, *Scientific World J.* **2007**, *7*.

[116] (a) R. Vicente, *Org. Biomol. Chem.* **2011**, *9*, 6469-6480; (b) R. S. Hosmane, S. P. Hiremath, S. W. Schneller, *J. Chem. Soc., Perkin Trans. 1* **1973**, 2450-2453.

[117] K. Nozaki, K. Takahashi, K. Nakano, T. Hiyama, H.-Z. Tang, M. Fujiki, S. Yamaguchi, K. Tamao, *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 2051-2053.

[118] (a) T. Q. Hung, T. T. Dang, A. Villinger, T. V. Sung, P. Langer, *Org. Biomol. Chem.* **2012**, *10*, 9041-9044; (b) T. Q. Hung, D. H. Hoang, N. N. Thang, T. T. Dang, K. Ayub, A. Villinger, A. Friedrich, S. Lochbrunner, G.-U. Flechsig, P. Langer, *Org. Biomol. Chem.* **2014**, *12*, 6151-6166; (c) T. Q. Hung, T. T. Dang, J. Janke, A. Villinger, P. Langer, *Org. Biomol. Chem.* **2015**, *13*, 1375-1386; (d) T. Q. Hung, S. Hancker, A. Villinger, S. Lochbrunner, T. T. Dang, A. Friedrich, W. Breitsprecher, P. Langer, *Org. Biomol. Chem.* **2015**, *13*, 583-591.

[119] (a) N. Wang, K. J. Wicht, E. Shaban, T. A. Ngoc, M.-Q. Wang, I. Hayashi, M. I. Hossain, Y. Takemasa, M. Kaiser, I. El Tantawy El Sayed, T. J. Egan, T. Inokuchi, *Med. Chem. Comm.* **2014**, *5*, 927-931; (b) L. R. Whittell, K. T. Batty, R. P. M. Wong, E. M. Bolitho, S. A. Fox, T. M. E. Davis, P. E. Murray, *Bioorg. Med. Chem.* **2011**, *19*, 7519-7525.

[120] (a) L. Wang, M. Switalska, N. Wang, Z.-J. Du, Y. Fukumoto, N. K. Diep, R. Kiguchi, J. Nokami, J. Wietrzyk, T. Inokuchi, *Molecules* **2014**, *19*, 19021-19035; (b) C.-M. Lu, Y.-L. Chen, H.-L. Chen, C.-A. Chen, P.-J. Lu, C.-N. Yang, C.-C. Tzeng, *Bioorg. Med. Chem.* **2010**, *18*, 1948-1957; (c) A. Beauchard, A. Jaunet, L. Murillo, B. Baldeyrou, A. Lansiaux, J.-R. Cherouvrier, L. Domon, L. Picot, C. Bailly, T. Besson, V. Thiery, *Eur. J. Med. Chem.* **2009**, *44*, 3858-3865.

[121] (a) S. Alcaro, C. Musetti, S. Distinto, M. Casatti, G. Zagotto, A. Artese, L. Parrotta, F. Moraca, G. Costa, F. Ortuso, E. Maccioni, C. Sissi, *J. Med. Chem.* **2013**, *56*, 843-855; (b) E. Ayel, C. Escude, *Nucleic Acids Res.* **2010**, *38*, e31/31-e31/10; (c) M. Mahalingam, P. S. Mohan, K. Gayathri, R. Gomathi, P. Subhapriya, *J. Chem. Sci. (Bangalore, India)* **2013**, *125*, 1015-1027.

[122] H. Falke, A. Chaikuad, A. Becker, N. Loaec, O. Lozach, S. Abu Jhaisha, W. Becker, P. G. Jones, L. Preu, K. Baumann, S. Knapp, L. Meijer, C. Kunick, *J. Med. Chem.* **2015**, *58*, 3131-3143.

[123] K. A. Nolan, D. J. Timson, I. J. Stratford, R. A. Bryce, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 6246-6254.

[124] J. Lavrado, S. A. Ohnmacht, I. Correia, C. Leitao, S. Pisco, M. Gunaratnam, R. Moreira, S. Neidle, D. J. V. A. dos Santos, A. Paulo, *Chem. Med. Chem.* **2015**, *10*, 836-849.

[125] W. Luniewski, J. Wietrzyk, J. Godlewska, M. Switalska, M. Piskozub, W. Peczynska-Czoch, L. Kaczmarek, *Bioorg. Med. Chem.* **2012**, *22*, 6103-6107.

[126] (a) L. M. Werbel, S. J. Kesten, W. R. Turner, *Eur. J. Med. Chem.* **1993**, *28*, 837-852; (b) L. He, H.-X. Chang, T.-C. Chou, N. Savaraj, C. C. Cheng, *Eur. J. Med. Chem.* **2003**, *38*, 101-107.

[127] (a) P. K. Agarwal, D. Sawant, S. Sharma, B. Kundu, *Eur. J. Org. Chem.* **2009**, *2009*, 292-303; (b) G. A. Kraus, H. Guo, G. Kumar, G. Pollock Iii, H. Carruthers, D. Chaudhary, J. Beasley, *Synthesis* **2010**, *2010*, 1386-1393.

[128] K. Hayashi, T. Choshi, K. Chikaraishi, A. Oda, R. Yoshinaga, N. Hatae, M. Ishikura, S. Hibino, *Tetrahedron* **2012**, *68*, 4274-4279.

[129] G. Abbiati, A. Arcadi, M. Chiarini, F. Marinelli, E. Pietropaolo, E. Rossi, *Org. Biomol. Chem.* **2012**, *10*, 7801-7808.

[130] (a) L. N. Tumey, D. H. Boschelli, N. Bhagirath, J. Shim, E. A. Murphy, D. Goodwin, E. M. Bennett, M. Wang, L.-L. Lin, B. Press, M. Shen, R. K. Frisbie, P. Morgan, S. Mohan, J. Shin, V. R. Rao, *Bioorg. Med. Chem. Lett.* **2014**, *24*, 2066-2072; (b) F. Trécourt, F. Mongin, M. Mallet, G. Quéguiner, *Synth. Commun.* **1995**, *25*, 4011-4024; (c) H. Gao, Q.-L. Xu, M. Yousufuddin, D. H. Ess, L. Kürti, *Angew. Chem., Int. Ed. Engl.* **2014**, *53*, 2701-2705.

[131] M. Xu, Q. Hou, S. Wang, H. Wang, Z.-J. Yao, *Synthesis* **2011**, *2011*, 626-634.

[132] (a) T. H. M. Jonckersa, B. U. W. Maes, G. L. F. Lemièrea, G. Romboutsa, L. Pietersb, A. Haemersb, R. A. Dommisse, *Synlett* **2003**, *5*, 0615-0618; (b) T. Dhanabal, R. Sangeetha, P. S. Mohan, *Tetrahedron* **2006**, *62*, 6258-6263; (c) B. Bogányi, J. Kámán, *Tetrahedron* **2013**, *69*, 9512-9519; (d) R. M. Gengan, P. Pandian, C. Kumarsamy, P. S. Mohan, *Molecules* **2010**, *15*, 3171; (e) G. Senthil Kumar, M. A. Ali, T. S. Choon, K. J. Rajendra Prasad, *Monatsh. Chem.* **2015**, *146*, 2127-2134; (f) J. Zhu, H. Xie, Z. Chen, S. Li, Y. Wu, *Chem.*

Commun. **2011**, *47*, 1512-1514; (g) C. Meyers, G. Rombouts, K. T. J. Loones, A. Coelho, B. U. W. Maes, *Adv. Synth. Catal.* **2008**, *350*, 465-470.

[133] (a) T. Nanjo, S. Yamamoto, C. Tsukano, Y. Takemoto, *Org. Lett.* **2013**, *15*, 3754-3757; (b) Y. Wang, Q. Zhu, *Adv. Synth. Catal.* **2012**, *354*, 1902-1908; (c) B. Liu, H. Gao, Y. Yu, W. Wu, H. Jiang, *J. Org. Chem.* **2013**, *78*, 10319-10328.

[134] S. Cacchi, G. Fabrizi, P. Pace, F. Marinelli, *Synlett* **1999**, *1999*, 620-622.

[135] N. Wang, K. Imai, C.-Q. Pang, M.-q. Wang, M. Yonezawa, Y. Zhang, J. Nokami, T. Inokuchi, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 864-869.

[136] S. Radenković, J. Kojić, J. Petronijević, M. Antić, *J. Phys. Chem. A* **2014**, *118*, 11591-11601.

[137] (a) J.-B. Le Pecq, Nguyen-Dat-Xuong, C. Gosse, C. Paoletti, *Proc. Natl. Acad. Sci. USA* **1974**, *71*, 5078-5082; (b) D. Pelaprat, R. Oberlin, I. L. Guen, J. B. Le Pecq, B. P. Roques, *J. Med. Chem.* **1980**, *23*, 1330-1335.

[138] E. Von Angerer, J. Prekajac, *J. Med. Chem.* **1986**, *29*, 380-386.

[139] D. J. Carini, R. F. Kaltenbach Iii, J. Liu, P. A. Benfield, J. Boylan, M. Boisclair, L. Brizuela, C. R. Burton, S. Cox, R. Grafstrom, B. A. Harrison, K. Harrison, E. Akamike, J. A. Markwalder, Y. Nakano, S. P. Seitz, D. M. Sharp, G. L. Trainor, T. M. Sielecki, *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2209-2211.

[140] (a) L. Wu, H. Huang, P. Dang, Y. Liang, S. Pi, *RSC Adv.* **2015**, *5*, 64354-64357; (b) G. W. Gribble, R. A. Silva, M. G. Saulnier, *Synth. Commun.* **1999**, *29*, 729-747; (c) S. Brooks, M. Sainsbury, D. K. Weerasinge, *Tetrahedron* **1982**, *38*, 3019-3022; (d) J. R. Stepherson, C. E. Ayala, T. H. Tugwell, J. L. Henry, F. R. Fronczek, R. Kartika, *Org. Lett.* **2016**, *18*, 3002-3005.

[141] (a) F. Dufour, G. Kirsch, *Synlett* **2006**, *2006*, 1021-1022; (b) A. R. Katritzky, Z. Wang, *J. Heterocyclic Chem.* **1988**, *25*, 671-675; (c) A. R. Katritzky, Z. Wang, G. P. Savage, *J. Heterocycl. Chem.* **1991**, *28*, 321-323.

[142] (a) M. M. Oliveira, M. A. Salvador, P. J. Coelho, L. M. Carvalho, *Tetrahedron* **2005**, *61*, 1681-1691; (b) F. Xiao, Y. Liao, M. Wu, G.-J. Deng, *Green Chem.* **2012**, *14*, 3277-3280; (c) M. V. Niladari Raju, M. E. Mohanty, P. R. Bangal, J. R. Vaidya, *J. Phys. Chem. C* **2015**, *119*, 8563-8575; (d) A. Cordero-Vargas, I. Perez-Martin, B. Quiclet-Sire, S. Z. Zard, *Org. Biomol. Chem.* **2004**, *2*, 3018-3025.

[143] C. Du, J. Chen, Y. Guo, K. Lu, S. Ye, J. Zheng, Y. Liu, Z. Shuai, G. Yu, *J. Org. Chem.* **2009**, *74*, 7322-7327.

[144] N. J. Truax, F. Banales Mejia, D. O. Kwansare, M. M. Lafferty, M. H. Kean, E. T. Pelkey, *J. Org. Chem.* **2016**, *81*, 6808-6815.

[145] (a) C.-W. Kuo, A. Konala, L. Lin, T.-T. Chiang, C.-Y. Huang, T.-H. Yang, V. Kavala, C.-F. Yao, *Chem. Commun.* **2016**, *52*, 7870-7873; (b) E. Conchon, F. Anizon, B. Aboab, M. Prudhomme, *Synthesis* **2008**, *2008*, 2569-2574.

[146] E. Kianmehr, M. Ghanbari, *Eur. J. Org. Chem.* **2012**, *2012*, 256-259.

[147] (a) R. B. Bedford, M. Betham, J. P. H. Charmant, A. L. Weeks, *Tetrahedron* **2008**, *64*, 6038-6050; (b) R. B. Bedford, M. Betham, *J. Org. Chem.* **2006**, *71*, 9403-9410; (c) T. Q. Hung, N. N. Thang, D. H. Hoang, T. T. Dang, A. Villinger, P. Langer, *Org. Biomol. Chem.* **2014**, *12*, 2596-2605.

[148] A. Yasuhara, Y. Takeda, N. Suzuki, T. Sakamoto, *Chem. Pharm. Bull.* **2002**, *50*, 235-238.

[149] T. Nanjo, C. Tsukano, Y. Takemoto, *Org. Lett.* **2012**, *14*, 4270-4273.

[150] Z. Hassan, M. Hussain, A. Villinger, P. Langer, *Tetrahedron* **2012**, *68*, 6305-6313.

[151] (a) I. Bitter, M. R. K. Dossenbach, S. Brook, P. D. Feldman, S. Metcalfe, C. A. Gagiano, J. Füredi, G. Bartko, Z. Janka, C. M. Banki, G. Kovacs, A. Breier, *Prog. Neuropsychopharmacol. Biol. Psychiatry* **2004**, *28*, 173-180; (b) Kimberly H. Littrell, Craig G. Johnson, Nicole M. Hilligoss, Carol D. Peabody, S. H. Littrell, *J. Clin. Psychiatry* **2000**, *61*, 912-915.

[152] I. Palamà, F. Di Maria, I. Viola, E. Fabiano, G. Gigli, C. Bettini, G. Barbarella, *J. Am. Chem. Soc.* **2011**, *133*, 17777-17785.

[153] A. N. Grinev, Y. I. Trofimkin, E. V. Lomanova, G. N. Pershin, L. M. Polukhina, I. S. Nikolaeva, T. V. Pushkina, L. N. Filitis, E. A. Golovanova, O. V. Okinshevich, *Pharm. Chem. J.* **1982**, *16*, 827-830.

[154] (a) H. Huang, Q. Li, M. Qiu, Z. Wang, X. Zhang, S. Liu, N. Fu, B. Zhao, R. Yang, W. Huang, *RSC Adv.* **2016**, *6*, 45873-45883; (b) I. Jeong, J. Kim, J. Kim, J. Lee, D. Y. Lee, I. Kim, S. H. Park, H. Suh, *Synth. Met.* **2016**, *213*, 25-33.

[155] A. Shafiee, S. Sattari, *J. Heterocycl. Chem.* **1982**, *19*, 227-231.

[156] (a) I. T. Alt, B. Plietker, *Angew. Chem., Int. Ed. Engl.* **2016**, *55*, 1519-1522; (b) P. A. S. Smith, J. H. Boyer, *J. Am. Chem. Soc.* **1951**, *73*, 2626-2629; (c) N. Jana, Q. Nguyen, T. G. Driver, *J. Org. Chem.* **2014**, *79*, 2781-2791;

(d) M. Pudlo, D. Csányi, F. Moreau, G. Hajós, Z. Riedl, J. Sapi, *Tetrahedron* **2007**, *63*, 10320-10329.

[157] K. Takamatsu, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2014**, *16*, 2892-2895.

[158] (a) C. Lo, B. I. Doucoure, J.-J. Aaron, J. Svoboda, V. Kozmik, J.-C. Brochon, E. Henry, F. Maurel, M. Capochichi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2014**, *120*, 47-54; (b) P. Appukkuttan, E. Van der Eycken, W. Dehaen, *Synlett* **2005**, *2005*, 127-133; (c) S.-G. Liu, W.-Y. Su, R.-K. Pan, X.-P. Zhou, X.-L. Wen, Y.-Z. Chen, S. Wang, X.-B. Shi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2013**, *103*, 417-422.

[159] P. Margaretha, C. Schroeder, S. Wolff, W. C. Agosta, *J. Org. Chem.* **1983**, *48*, 1925-1926.

[160] (a) E. Haak, I. Bytschkov, S. Doye, *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3389-3391; (b) Y. Li, T. J. Marks, *Organometallics* **1996**, *15*, 3770-3772; (c) W. Reppe, H. Friederich, H. Mueller-Tamm, DE618120, **1956**; (d) K. Utimoto, H. Miwa, H. Nozaki, *Tetrahedron Lett.* **1981**, *22*, 4277-4278.

[161] (a) L. Ren, Z. Shi, N. Jiao, *Tetrahedron* **2013**, *69*, 4408-4414; (b) Y.-Q. Zhang, D.-Y. Zhu, B.-S. Li, Y.-Q. Tu, J.-X. Liu, Y. Lu, S.-H. Wang, *J. Org. Chem.* **2012**, *77*, 4167-4170.

[162] (a) K. Iritani, S. Matsubara, K. Utimoto, *Tetrahedron Lett.* **1988**, *29*, 1799-1802; (b) A. Arcadi, S. Cacchi, F. Marinelli, *Tetrahedron Lett.* **1989**, *30*, 2581-2584; (c) D. E. Rudisill, J. K. Stille, *J. Org. Chem.* **1989**, *54*, 5856-5866; (d) S. Cacchi, V. Carnicelli, F. Marinelli, *J. Organomet. Chem.* **1994**, *475*, 289-296; (e) M. S. Yu, L. Lopez de Leon, M. A. McGuire, G. Botha, *Tetrahedron Lett.* **1998**, *39*, 9347-9350; (f) T. E. Müller, M. Grosche, E. Herdtweck, A.-K. Pleier, E. Walter, Y.-K. Yan, *Organometallics* **2000**, *19*, 170-183; (g) H. Sakai, K. Tsutsumi, T. Morimoto, K. Kakiuchi, *Adv. Synth. Catal.* **2008**, *350*, 2498-2502; (h) L. Chen, M.-H. Xu, *Adv. Synth. Catal.* **2009**, *351*, 2005-2012; (i) K. C. Majumdar, N. De, B. Roy, *Synthesis* **2010**, *2010*, 4207-4212; (j) Z. Wang, X. Xing, L. Xue, F. Gao, L. Fang, *Org. Biomol. Chem.* **2013**, *11*, 7334-7341; (k) S. R. LaPlante, M. Bös, C. Brochu, C. Chabot, R. Coulombe, J. R. Gillard, A. Jakalian, M. Poirier, J. Rancourt, T. Stammers, B. Thavonekham, P. L. Beaulieu, G. Kukolj, Y. S. Tsantrizos, *J. Med. Chem.* **2014**, *57*, 1845-1854; (l) A. Ikeda, M. Omote, K. Kusumoto, M. Komori, A. Tarui, K. Sato, A. Ando,

Org. Biomol. Chem. **2016**, *14*, 2127-2133; (m) R.-Y. Tang, X.-K. Guo, J.-N. Xiang, J.-H. Li, *J. Org. Chem.* **2013**, *78*, 11163-11171.

[163] (a) S. Cacchi, G. Fabrizi, A. Goggiamani, C. Molinaro, R. Verdiglione, *J. Org. Chem.* **2014**, *79*, 401-407; (b) C. Xu, V. K. Murugan, S. A. Pullarkat, *Org. Biomol. Chem.* **2012**, *10*, 3875-3881.

[164] (a) D. Janreddy, V. Kavala, C.-W. Kuo, T.-S. Kuo, C.-H. He, C.-F. Yao, *Tetrahedron* **2013**, *69*, 3323-3330; (b) V. Reddy, R. Vijaya Anand, *Org. Lett.* **2015**, *17*, 3390-3393.

[165] (a) Q. Wang, L. Huang, X. Wu, H. Jiang, *Org. Lett.* **2013**, *15*, 5940-5943; (b) J. G. Denis, G. Franci, L. Altucci, J. M. Aurrecoechea, A. R. de Lera, R. Alvarez, *Org. Biomol. Chem.* **2015**, *13*, 2800-2810.

[166] N. Ahmed, C. Dubuc, J. Rousseau, F. Bénard, J. E. van Lier, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 3212-3216.

[167] S. Cacchi, G. Fabrizi, L. M. Parisi, *Synthesis* **2004**, *2004*, 1889-1894.

[168] R. C. Larock, E. K. Yum, *J. Am. Chem. Soc.* **1991**, *113*, 6689-6690.

[169] (a) L. Ackermann, *Org. Lett.* **2005**, *7*, 439-442; (b) Z.-Y. Tang, Q.-S. Hu, *Adv. Synth. Catal.* **2006**, *348*, 846-850; (c) R. Sanz, M. P. Castroviejo, V. Guilarte, A. Pérez, F. J. Fañanás, *J. Org. Chem.* **2007**, *72*, 5113-5118; (d) L. Ackermann, S. Barfüßer, H. K. Potukuchi, *Adv. Synth. Catal.* **2009**, *351*, 1064-1072; (e) L. Ackermann, W. Song, R. Sandmann, *J. Organomet. Chem.* **2011**, *696*, 195-201; (f) P. G. Alsabeh, R. J. Lundgren, L. E. Longobardi, M. Stradiotto, *Chem. Commun.* **2011**, *47*, 6936-6938; (g) A. Prakash, M. Dibakar, K. Selvakumar, K. Ruckmani, M. Sivakumar, *Tetrahedron Lett.* **2011**, *52*, 5625-5628; (h) H. Wang, Y. Li, L. Jiang, R. Zhang, K. Jin, D. Zhao, C. Duan, *Org. Biomol. Chem.* **2011**, *9*, 4983-4986; (i) C. B. Lavery, R. McDonald, M. Stradiotto, *Chem. Commun.* **2012**, *48*, 7277-7279; (j) S. M. Crawford, C. B. Lavery, M. Stradiotto, *Chem. - Eur. J.* **2013**, *19*, 16760-16771.

[170] G. A. Salman, M. Hussain, V. Iaroshenko, A. Villinger, P. Langer, *Adv. Synth. Catal.* **2011**, *353*, 331-336.

[171] T. N. Ngo, O. A. Akrawi, T. T. Dang, A. Villinger, P. Langer, *Tetrahedron Lett.* **2015**, *56*, 86-88.

[172] Z. Wang, L. Xue, Y. He, L. Weng, L. Fang, *J. Org. Chem.* **2014**, *79*, 9628-9638.

[173] (a) H. Ren, P. Knochel, *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 3462-3465; (b) H. Ren, Z. Li, P. Knochel, *Chem. - Asian J.* **2007**, *2*, 416-433; (c) B. Roy, R.

N. De, S. Hazra, *Monatsh. Chem.* **2012**, *143*, 119-125; (d) W. Hagui, K. Yuan, N. Besbes, E. Srasra, J.-F. Soulé, H. Doucet, *Chem. Cat. Chem.* **2015**, *7*, 3544-3554.

[174] J. Gao, Y. Shao, J. Zhu, J. Zhu, H. Mao, X. Wang, X. Lv, *J. Org. Chem.* **2014**, *79*, 9000-9008.

[175] (a) T. N. Ngo, P. Ehlers, T. T. Dang, A. Villinger, P. Langer, *Org. Biomol. Chem.* **2015**, *13*, 3321-3330; (b) T. N. Ngo, F. Janert, P. Ehlers, D. H. Hoang, T. T. Dang, A. Villinger, S. Lochbrunner, P. Langer, *Org. Biomol. Chem.* **2016**, *14*, 1293-1301.

[176] (a) V. M. Adhami, M. H. Aziz, H. Mukhtar, N. Ahmad, *Clin. Cancer Res.* **2003**, *9*, 3176-3182; (b) B. J. R. Pitts, L. R. Meyerson, *Drug Dev. Res.* **1981**, *1*, 43-49; (c) N. Aburai, M. Yoshida, M. Ohnishi, K.-i. Kimura, *Biosci. Biotechnol. Biochem.* **2010**, *74*, 548-552.

[177] J.-J. Chen, K.-T. Li, D.-Y. Yang, *Org. Lett.* **2011**, *13*, 1658-1661.

[178] (a) B. Banerji, S. Bera, S. Chatterjee, S. K. Killi, S. Adhikary, *Chem. - Eur. J.* **2016**, *22*, 3506-3512; (b) O. E. Alawode, V. K. Naganaboina, T. Liyanage, J. Desper, S. Rayat, *Org. Lett.* **2014**, *16*, 1494-1497; (c) L. Yan, D. Zhao, J. Lan, Y. Cheng, Q. Guo, X. Li, N. Wu, J. You, *Org. Biomol. Chem.* **2013**, *11*, 7966-7977; (d) C. Chen, G. Shang, J. Zhou, Y. Yu, B. Li, J. Peng, *Org. Lett.* **2014**, *16*, 1872-1875.

[179] C. W. Scheele, *Opuscula* **1776**, *2*, 73.

[180] (a) A. Albert, in *Adv. Heterocycl. Chem., Vol. Volume 32* (Ed.: A. R. Katritzky), Academic Press, **1982**, pp. 1-81; (b) S. Gabriel, R. Jansen, *Ber. Dtsch. Chem. Ges.* **1890**; (c) S. Gabriel, R. Jansen, *Ber. Dtsch. Chem. Ges.* **1891**; (d) A. Bischler, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 1891-1903.

[181] (a) *Arch. Anat. Physiol. wiss. Med.* **1889**, 524-536; (b) P. A. Levene, *J. Biol. Chem.* **1919**, *40*, 415-424.

[182] G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112-122.

[183] G. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 3-8.

[184] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Cryst.* **2006**, *39*, 453-457.

[185] H. Wang, K. A. Jurado, X. Wu, M.-C. Shun, X. Li, A. L. Ferris, S. J. Smith, P. A. Patel, J. R. Fuchs, P. Cherepanov, M. Kvaratskhelia, S. H. Hughes, A. Engelman, *Nucleic Acids Res.* **2012**, *40*, 11518-11530.

[186] K. R. Fandrick, W. Li, Y. Zhang, W. Tang, J. Gao, S. Rodriguez, N. D. Patel, D. C. Reeves, J.-P. Wu, S. Sanyal, N. Gonnella, B. Qu, N. Haddad, J. C. Lorenz, K. Sidhu, J. Wang, S. Ma, N. Grinberg, H. Lee, Y. Tsantrizos, M.-A. Poupart, C. A. Busacca, N. K. Yee, B. Z. Lu, C. H. Senanayake, *Angew. Chem., Int. Ed. Engl.* **2015**, *54*, 7144-7148.

[187] (a) T. Sakamoto, Y. Kondo, H. Yamanaka, *Chem. Pharm. Bull.* **1982**, *30*, 2417-2420; (b) T. Sakamoto, Y. Kondo, R. Y. O. Watanabe, H. Yamanaka, *Chem. Pharm. Bull.* **1986**, *34*, 2719-2724.

[188] N. D. Kimpe, C. Stevens, *Tetrahedron* **1991**, *47*, 3407-3416.

[189] A. Luhl, H. Pada Nayek, S. Blechert, P. W. Roesky, *Chem. Commun.* **2011**, *47*, 8280-8282.

[190] G. W. Buchanan, B. A. Dawson, *Org. Magn. Resonance* **1980**, *13*, 293-298.

[191] D. Xiao, X. Zhang, *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3425-3428.

[192] N. Yoshikai, A. Matsumoto, J. Norinder, E. Nakamura, *Angew. Chem., Int. Ed. Engl.* **2009**, *48*, 2925-2928.

[193] K. Gao, N. Yoshikai, *Angew. Chem.* **2011**, *123*, 7020-7024.

[194] J. S. M. Samec, J.-E. Bäckvall, *Chem. - Eur. J.* **2002**, *8*, 2955-2961.

[195] T. Imamoto, N. Iwadate, K. Yoshida, *Org. Lett.* **2006**, *8*, 2289-2292.

[196] K. Kutlescha, G. T. Venkanna, R. Kempe, *Chem. Commun.* **2011**, *47*, 4183-4185.

[197] Y. Liu, H. Du, *J. Am. Chem. Soc.* **2013**, *135*, 6810-6813.

[198] G. Qian, X. Hong, B. Liu, H. Mao, B. Xu, *Org. Lett.* **2014**, *16*, 5294-5297.

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Publikationen

Stefan Berger, Dieter Sicker, "Classics in Spectroscopy: Isolation and Structure Elucidation of Natural Products", Wiley-VCH, **2009**, ISBN: 3527326170, Chapter 2.4: Isolation of Δ9-Tetrahydrocannabinol from Marihuana. (Laboratory work contribution)

Ngo Nghia Pham, Thanh Tuan Dang, Ngoc Thang Ngo, Alexander Villinger, Peter Ehlers, Peter Langer*, *Org. Biomol. Chem.* **2015**, *13*, 6047-6058. "Facile synthesis of 4- and 7-azaindoles from corresponding imines by palladium-catalyzed cascade C-C and C-N coupling".

Ngo Nghia Pham, Ghazwan Ali Salman, Nadjah Belattar, Tuan Thanh Dang, Peter Ehlers, Peter Langer*, *Eur. J. Org. Chem.* **2017**, 989-995. "Synthesis of pyrimido-[5',4':4,5]pyrrolo[1,2-*f*]phenanthridines by one-pot C-N coupling/ hydroamination/ C-H arylation".

Ngo Nghia Pham, Silvio Parpart, Sevak Grigoryan, Thang Ngoc Ngo, Tuan Thanh Dang, Peter Ehlers, Peter Langer*, *Eur. J. Org. Chem.* **2017**, 538–550. "Convenient synthesis of thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles by sequential site-selective Suzuki- and double C-N coupling reaction".

Ghazwan Ali Salman, **Ngo Nghia Pham**, Thang Ngoc Ngo, Peter Ehlers, Alexander Villinger, Peter Langer*, *Adv. Synth. Catal.* **2017**, accepted. "Palladium(0)-catalyzed Domino C-N Coupling/Hydroamination/C-H Arylation: Efficient Synthesis of Benzothieno[2′,3′:4,5]pyrrolo[1,2-*f*]phenanthridines".