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Synthesis of benzoacridines and benzophenanthridines by regioselective Pd catalyzed cross-couplings followed by acid mediated cycloisomerizations

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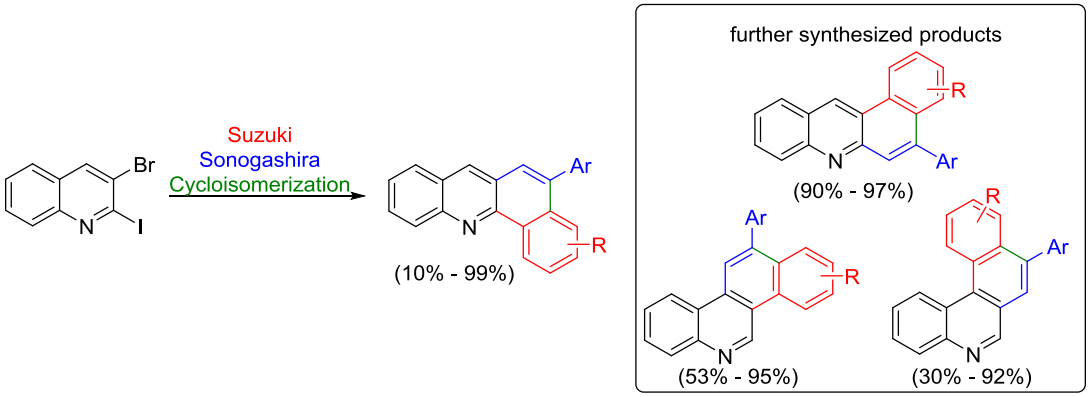
Abstract. A convenient synthesis of various benzoacridines and benzophenanthridines from readily available dihalogenated quinolines is reported. The synthesis is based on regioselective Suzuki- and Sonogashira reactions followed by Brønsted acid mediated cycloisomerization. The developed methodology is highly modular and allows the construction of various ring systems and substitution patterns in high yields. The optical and electrochemical properties of selected derivatives were investigated.

Keywords: cyclization; catalysis; palladium; heterocycles; regioselectivity

Graphical Abstract



Key Topic: Cycloisomerisation

TOC Text:

Various Benzoacridines and Benzophenanthridines have been synthesized by Brønsted acid mediated cycloisomerisation as the key step. The optical and and electrochemical properties have been studied by UV/Vis- and emission spectroscopy as well as CV measurements. Obtained results have been verified by DFT calculations.

Introduction

Polyaromatic *N*-heterocycles, such as acridines, phenanthridines and related compounds, have attracted considerable interest, because of their broad range of properties[1],[2]. They constitute well-known classes of biologically active compounds with pharmacological effects, including antibacterial, antimalarial and anticancer activities.[3] There action is often based on DNA and RNA intercalating.[4] Proflavine (a Rev inhibitor),[5,6] aminacrine (antibacterial activity)[7], and ethacridine (antibacterial activity)[7] as well as NK109 (antitumor activity)[8], Ethidium (antitumor activity)[6] and Fagaronine (antileukemic activity)[9] represent pharmacologically significant acridines or phenanthridines (Figure 1). Furthermore, such substances have been applied in industry as pigments or dyes and are expected to be promising candidates for the development of organic semiconductors.[10–12]

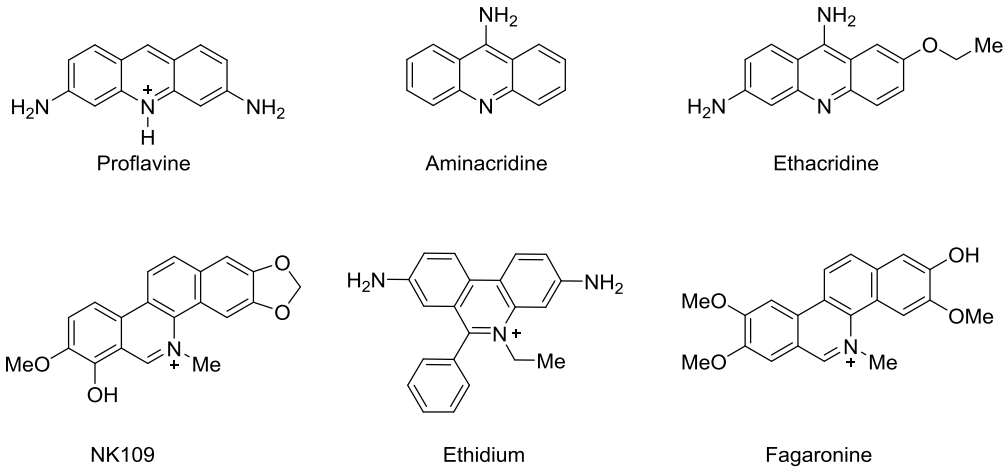
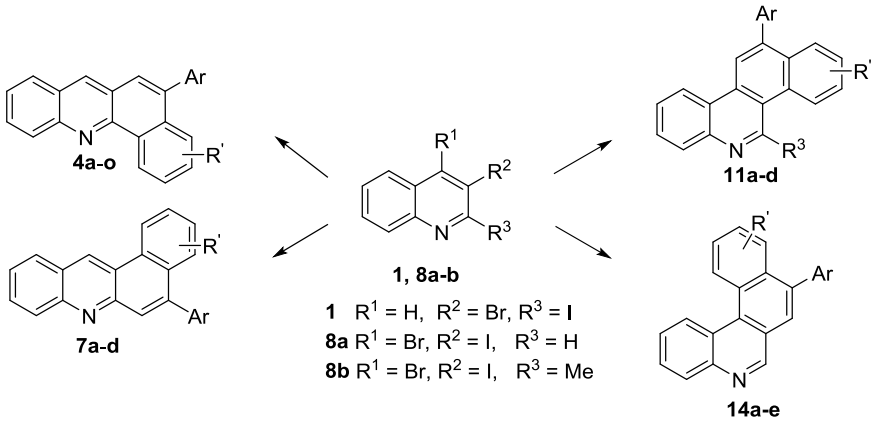


Figure 1. Pharmacologically important acridines and phenanthridines

In this regard, many studies have been focused on the development of efficient synthetic methodologies for the synthesis of such compounds. Reported synthetic strategies mainly rely

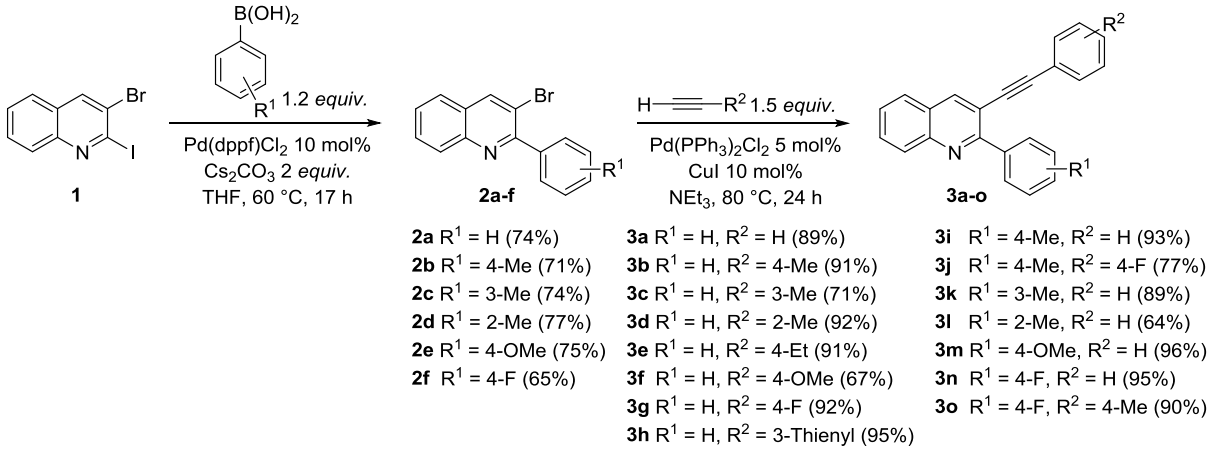
on C–H functionalizations,[13,10–12] reductions,[14] dehydrations,[15] intermolecular annulations,[16] intramolecular cyclizations[17] and other methods[18]. However, the applicability of those methods is often limited with regard to the preparative scope. As part of our ongoing interest in chemoselective Pd-catalyzed reactions of quinolines[19] and cycloisomerization reactions,[20] we herein wish to report a new and convenient synthesis of benzoacridine and benzophenanthridine derivatives starting from dihalogenated quinolines (Scheme 1).



Scheme 1. Synthesis of benzoacridine and benzophenanthridine derivatives

Results and Discussion

The starting materials, 3-bromo-2-iodoquinoline (**1**) and 4-bromo-3-iodoquinolines **8a,b**, were prepared according to previously reported procedures (Scheme 1).[21] Subsequently, chemoselective Suzuki reactions of **1** with various arylboronic acids were carried out, followed by Sonogashira reaction in position 3 (Scheme 2). Due to the better leaving group ability of iodide as compared to bromide, the Suzuki reaction of **1** proceeds chemoselectively at the carbon-iodine bond to give 2-aryl-3-bromoquinolines **2a-f** in 65-77% yield. During the optimization, the use of Pd(dppf)Cl_2 as the catalyst (10 mol%) and Cs_2CO_3 as the base and the temperature (60 °C) proved to be important parameters to avoid double coupling reactions and to get the desired products in good yields. The Sonogashira reaction of **2a-f** with various alkynes afforded 2-aryl-3-alkynylquinolines **3a-o** in 64-96% yields. The highest yield was observed for **3m**, while the lowest occurred with 64% for **3l**.



Scheme 2. Synthesis of coupling products **2a-f** and **3a-o**

The Brønsted acid mediated cycloisomerization of **3a** was studied next using different sulfonic acids (Table 1). *p*-Toluenesulfonic acid (*p*TSA) and methanesulfonic acid (MSA) performed equally well and gave the final product **4a** in quantitative yields. During the optimization it became apparent that "solvent-free" conditions are superior as compared to the employment of xylene as solvent. The use of MSA allowed to decrease the amount of acid to 30 equivalents. Further reduction of the amount of acid resulted in low conversion, due to poor solubility of the employed reagents.

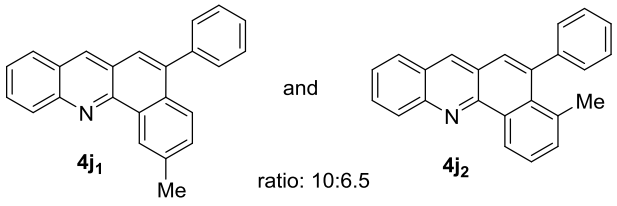
Table 1. Optimization for the cyclization reaction of **3a**

Entry	Sulfonic acid	Solvent	Equivalents	Yield[a]
1	*p*TSA	xylene	60	79%
2	*p*TSA	--	60	98%
3	Triflic acid	--	60	67%
4	MSA	--	60	99%
5	**MSA**	**--**	**30**	**99%**

[a] Isolated yields

With the optimized conditions in hand, the scope was studied and cyclization reactions of compounds **3a-o** were carried out (Table 2). Electron-poor and electron-rich systems gave

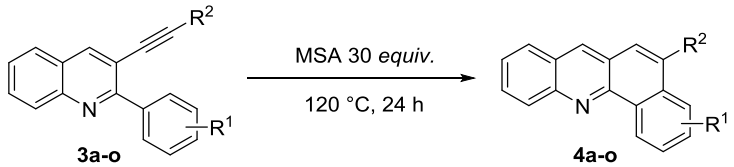
equally good results independently from the substitution pattern of the alkynyl groups (**4b-d**) and aryl groups (**4i-k**). Slightly deviating results were observed for **4m** and **4n**, due to the presence of the electron withdrawing fluorine substituent, deactivating the aryl ring for electrophilic substitution. Heterocyclic product **4h**, containing a thiophene moiety, could also be prepared, albeit, in only 30% yield. The low yield can be explained by purification problems during column chromatography. Methoxy groups were cleaved under the reaction conditions to give the corresponding phenol derivatives in high yields. Benzoacridine **4j** was, as expected, obtained as a mixture of isomers in a ratio of 10:6.5 in favor of the less sterically hindered derivative **4j$_1$** (Figure 2).



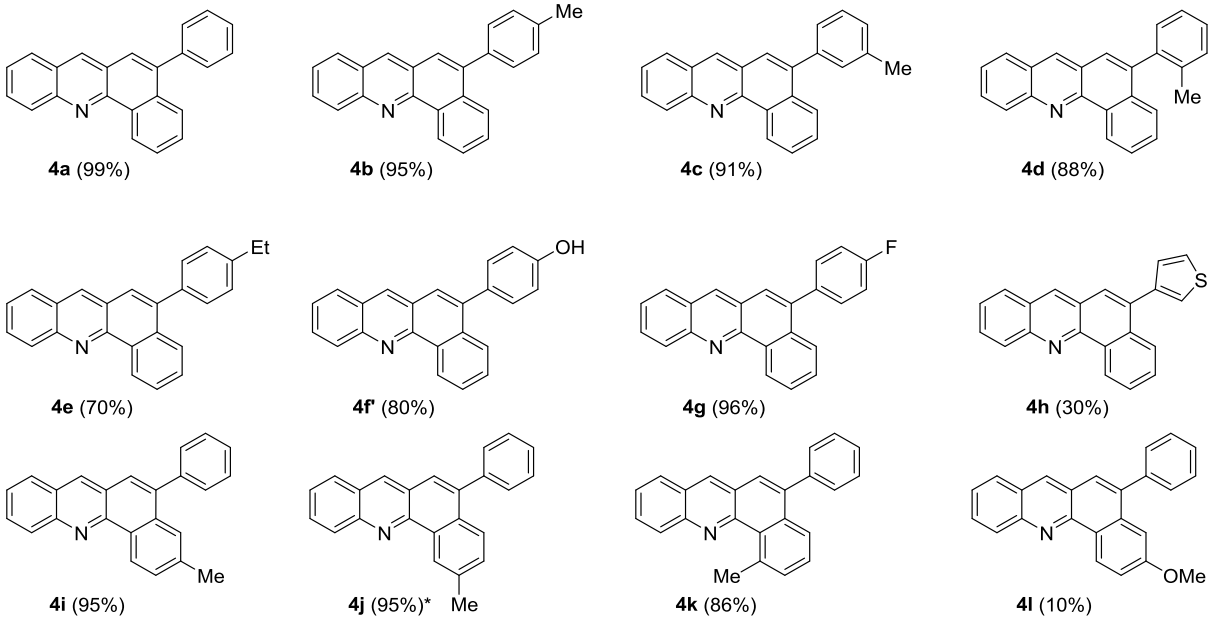
4j$_1$ **4j$_2$**

Figure 2. Isomeric ratio of compound **4j** as determined by ^{1}H-NMR of the isomeric mixture after purification

Table 2. Synthesis of benzo[*c*]acridines **4a-o**[a]



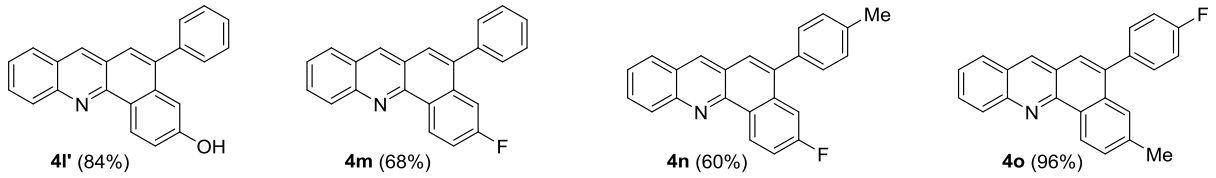
3a-o **4a-o**



4a (99%) **4b** (95%) **4c** (91%) **4d** (88%)

4e (70%) **4f'** (80%) **4g** (96%) **4h** (30%)

4i (95%) **4j** (95%)* **4k** (86%) **4l** (10%)



[a] Isolated yields. * Mixture of regioisomers (10:6.5).

The molecular structure of benzo[*c*]acridine **4n** was independently confirmed by X-ray crystal structure analysis (Figure 3). It forms layers in a triclinic crystal lattice. The aromatic 3-fluorobenzoacridine core is planar with the *p*-tolyl ring twisted out of plane by 54.5°.

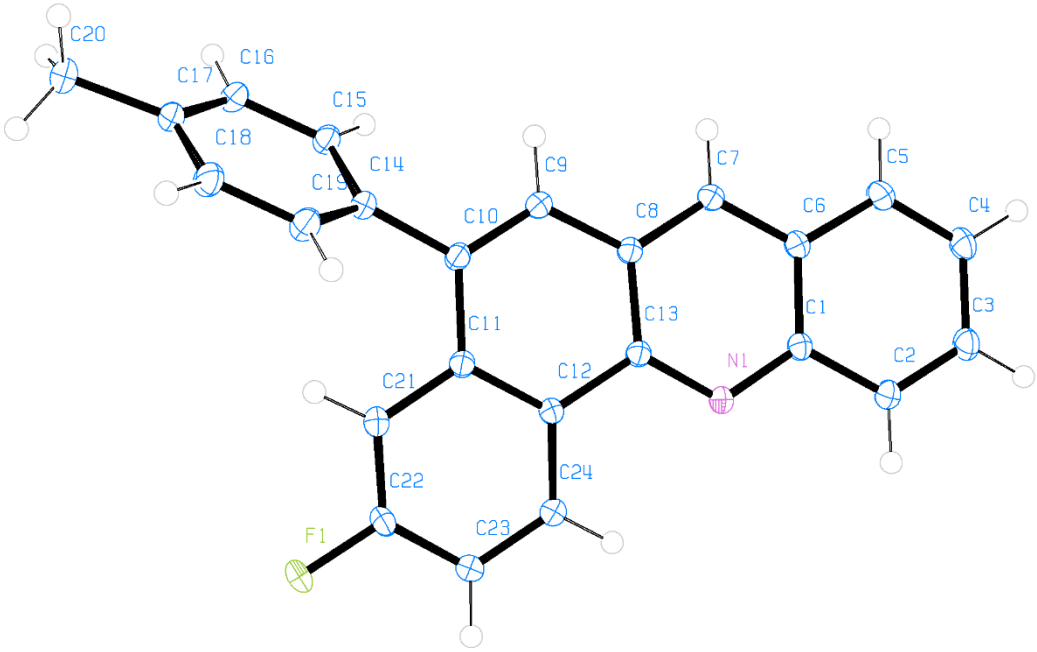


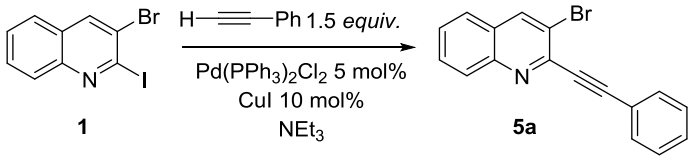
Figure 3. ORTEP of compound **4n** (propability of ellipsoids: 50%)[22]

With a series of benzo[*c*]acridines **4a-o** being prepared, we turned our attention to the synthesis of regioisomeric benzo[*a*]acridines, benzo[*i*]phenanthridines and benzo[*k*]phenanthridines. This required the synthesis of the corresponding alkynylarylquinolines as cyclization precursors. During the optimization of the conditions of the synthesis of these starting materials, the first coupling reaction of the dihalogenated quinoline played a crucial role to avoid double couplings.

The Sonogashira reaction of **1** with phenylacetylene in the presence of $Pd(PPh_3)_4$ (5 mol%) at 20 °C afforded the desired 2-aryl-3-bromoquinoline **5a** in 80% yield (Table 3). 2,3-

Dibromoquinoline could not be used as the starting material, as both bromide atoms reacted rapidly in the Sonogashira reaction. Although position 2 is more electron poor than position 3, this difference is oviously not strong enough to guarantee a high degree of regioselectivity. This can be explained by the fact that the reactivity of the system is increased after the first coupling steps. This effect has been earlier observed for Sonogashira reactions of pentachloropyridine.[23] The temperature also played an important role. At elevated temperature (80 °C) no product could be isolated, because of formation of significant amounts of product derived from double coupling.

Table 3. Optimization for the Sonogashira reaction of **1**

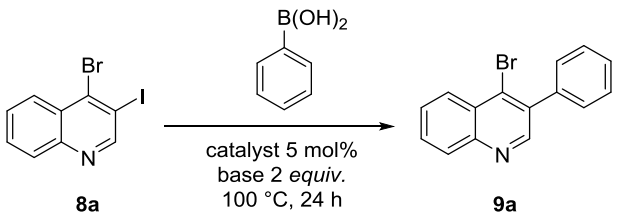


Entry	Temperature	Time	Yield[a]
1	80 °C	24 h	0%
2	**rt**	**2 h**	**94%**

[a] Isolated yields

The Suzuki reaction of **8a** with phenylboronic acid afforded 3-aryl-4-bromoquinoline **9a** in up to 65% yield. During the optimization, the solvent (DMF/water) played an important role (Table 4).

Table 4. Optimization for the Suzuki reaction of **8a**



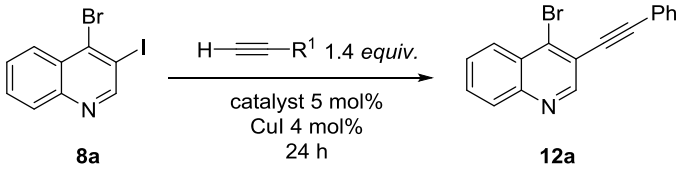
Entry	Catalyst	Base	Solvent	Equivalents (boronic acid)	Yield[a]

1	$Pd(dppf)Cl_2$	Cs_2CO_3	THF	1.2	48%
2	$Pd(PPh_3)_4$	Na_2CO_3	DMF/water (10:1)	1.2	59%
3	**$Pd(PPh_3)_4$**	**Na_2CO_3**	**DMF/water (10:1)**	**1**	**65%**

[a] Isolated yields

The Sonogashira reaction of **8a** with phenylacetylene in the presence of $Pd(PPh_3)_4$ (5 mol%) at 25 °C afforded the desired 3-alkynyl-4-bromoquinoline **12a** in 68% yield (Table 5). Besides the choice of the catalyst, the solvent (NEt_3/MeCN) and the temperature (25 °C) played an important role to avoid Sonogashira reaction at position 4 and also nucleophilic attack at the highly activated position 2.

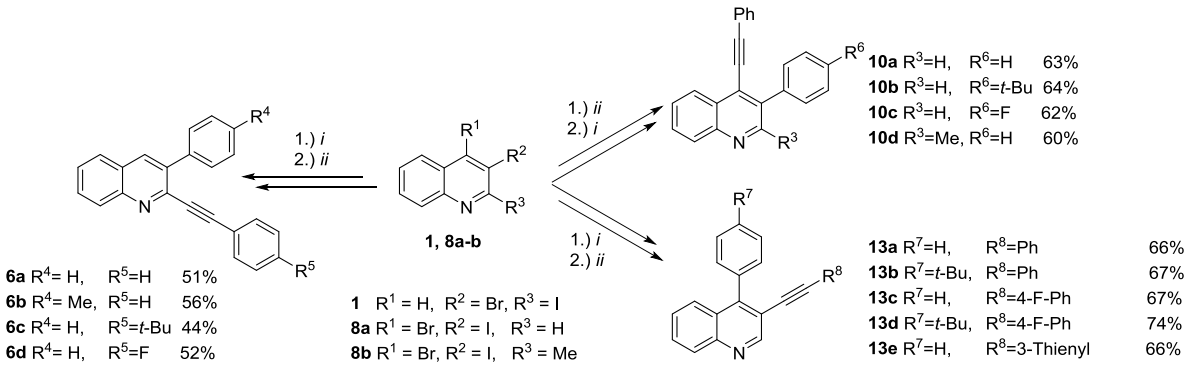
Table 5. Optimization for the Sonogashira reaction of **8a**



Entry	Catalyst	Solvent	Temperature	Yield[a]
1	$Pd(PPh_3)_2Cl_2$	NEt_3	25 °C	46%
2	$Pd(PPh_3)_2Cl_2$	NEt_3	80 °C	56%
3	**$Pd(PPh_3)_4$**	**NEt_3/MeCN**	**25 °C**	**68%**

[a] Isolated yields

The required starting materials were synthesized as shown in Scheme 3 (for synthetic details see SI). The Sonogashira and subsequent Suzuki reaction of 3-bromo-2-iodoquinoline (**1**) afforded 2-alkynyl-3-arylquinolines **6a-d** *via* **5a-d**. The Suzuki and subsequent Sonogashira reaction of 4-bromo-3-iodoquinolines **8a,b** gave 3-aryl-4-alkynylquinolines **10a-d** *via* **9a-d**. The Sonogashira and subsequent Suzuki reaction of 4-bromo-3-iodoquinolines **8a** gave 3-alkynyl-4-arylquinolines **13a-e** *via* **12a-d.**

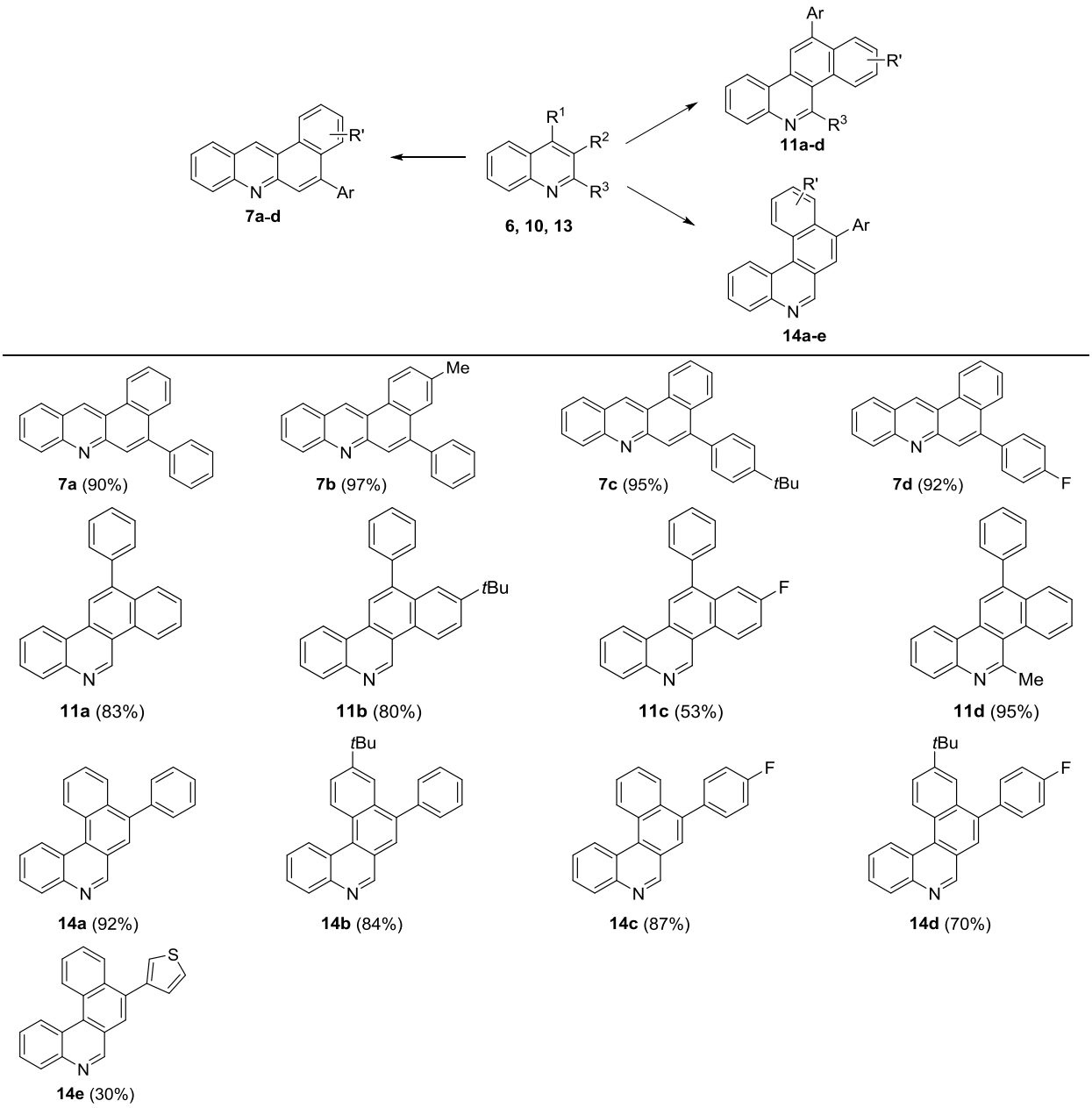


Scheme 3. Synthesis of alkynylarylquinolines **6a-d**, **10a-d** and **13a-e**; *i*, Sonogashira reaction, *ii*, Suzuki reaction (for details, see experimental section)

The MSA mediated cycloisomerization of alkynylarylquinolines was next studied. The cyclosomerization of **6a-d**, **10a-d** and **13a-e** afforded benzo[*a*]acridines **7a-d**, benzo[*i*]phenanthridines **11a-d** and benzo[*k*]phenanthridines **14a-e**, respectively (Table 6). The yields vary from moderate to excellent. The highest, nearly quantitative yields were obtained for alkyl-substituted products **7b**, **7c** and **11d**. Compound **11c**, containing an

electron-withdrawing group, was obtained in a moderate yield of 53% which might be explained by the fact that the acid mediated cycloisomerization via electrophilic aromatic substitution naturally proceeds more slowly in case of electron poor systems. Heterocyclic product **14e**, containing a thiophene moiety, could be isolated in 30% yield. The relatively low yield can be explained by purification problems during column chromatography.

Table 6. Synthesis of cyclization products **7a-d**, **11a-d** and **14a-e**[a]



[a] *Reaction conditions*: MSA (30 *equiv.*), 120 °C, 24 h. Yields of isolated products

The comparison of benzoacridines and benzophenanthridines shows that both derivatives can be synthesized in good to excellent yields by acid mediated cycloisomerization. The reaction

conditions slightly differ but electron-withdrawing and electron-donating groups both proved to be compatible with the reactions and gave equally good yields. The yield of benzoacridine and benzophenanthridine with a thiophene moiety is low but comparable to each other.

Physical properties

Absorption and emission spectra were measured for selected derivatives **4** and compared with their regioisomeric analogues **7a**, **11a** and **14a**. All derivatives of **4** show similar optoelectronic properties. They show a strong absorption in the range of 280 nm to 300 nm, followed by less intensive bands with a certain fine structure up to 390 nm, typical for benzoacridine derivatives.[24] The excitation energy for emission was about 360 nm for compounds **4** and **7** and approximately 340 nm for **11** and **14**. For all studied derivatives of **4** an emission maximum was observed at approximately 400 nm, containing a shoulder at higher wavelengths (Figure 4). Fluorescence quantum yields are in the range of 20−43% (Table 7 and SI). Intersection of the normalized absorption and emission spectra were used to determine the optical band gaps [$E_{(0\text{-}0)}$] ranging from 3.14 eV to 3.20 eV (Table 7 and SI). In comparison to **4a**, acridine **7a**, exhibiting a different annulation system, shows only little differences with regard to the optical properties (Figure 5). In contrast, the absorbtion and emission bands of phenanthridines **11a** and **14a** are hypsochromically shifted with regard to **4a**, with **11a** showing a stronger blue shift than **14a**. The quantum yield decreases to 13% for **11a** and 16% for **14a** (Figure 5, Table 7 and SI). The optical band gap [$E_{(0\text{-}0)}$] ranges from 3.29 eV for **11a** to 3.50 eV for **14a** (Table 7 and SI) and, thus, are slightly increased as compared to acridines **4** and **7**.

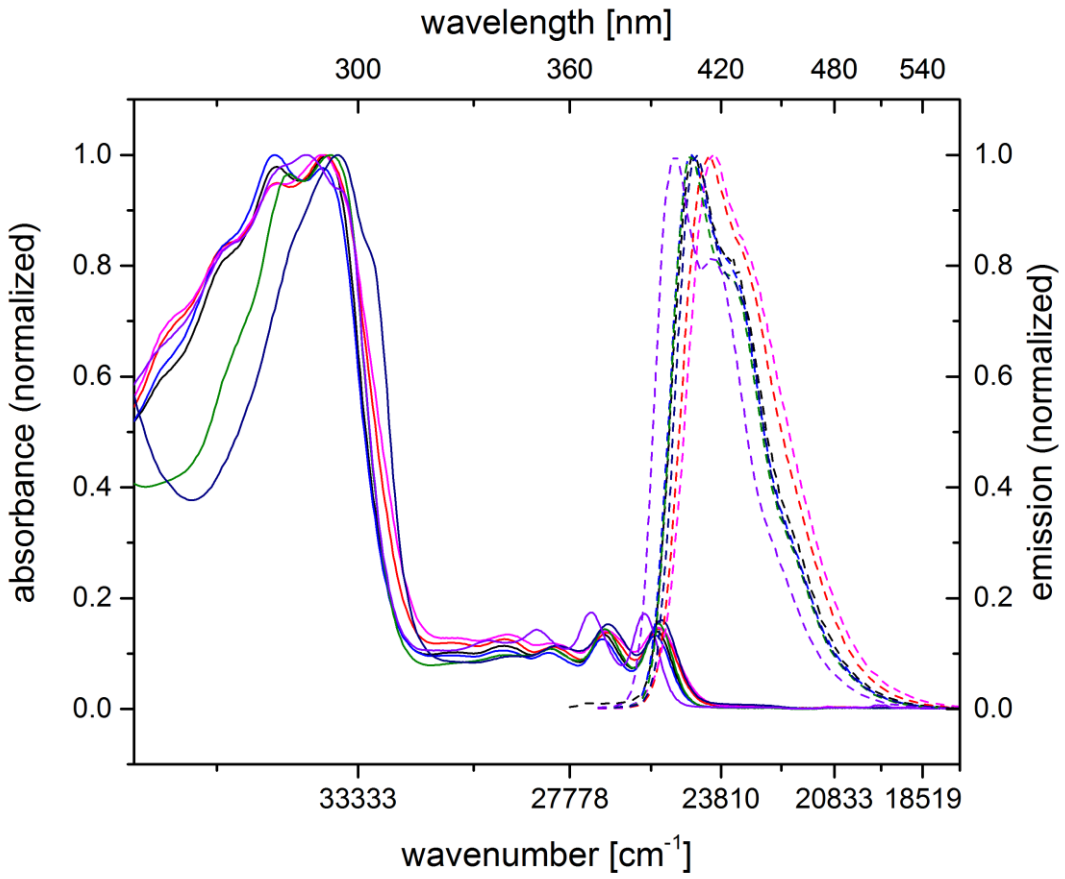


Figure 4. Absorption and emission spectra for **4a** (black), **4b** (red), **4g** (blue), **4h** (magenta), **4i** (green), **4l** (dark blue), **4m** (purple)

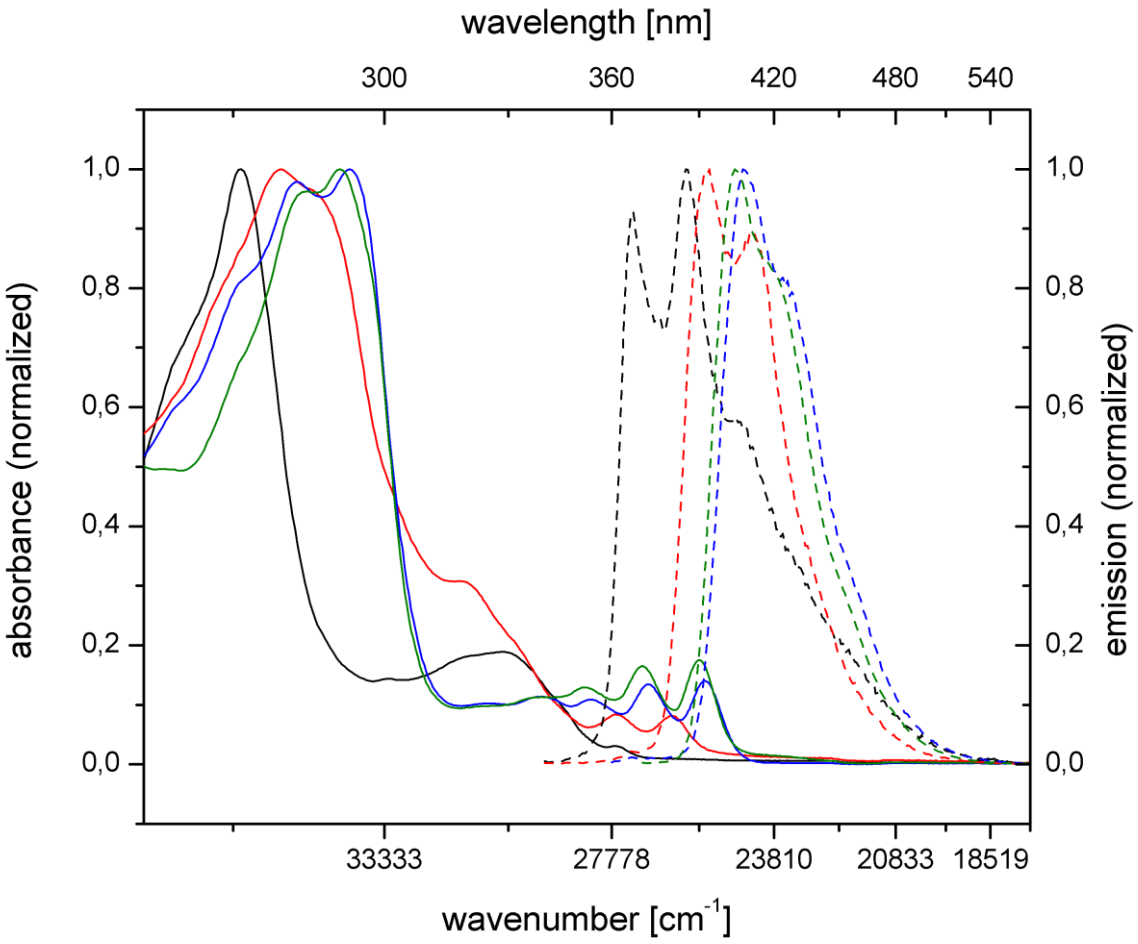


Figure 5. Absorption and emission spectra for **4a** (blue), **7a** (green), **11a** (black), **14a** (red)

Table 7. Optical data

Property	**4a**	**4b**	**4g**	**4h**	**4i**	**4l**	**4m**	**7a**	**11a**	**14a**
λ_{abs1}[nm] (ε_1[a])	282 (5.7)	282 (4.6)	281 (6.4)	282 (4.1)	284 (5.8)	295 (6.0)	283 (4.9)	283 (4.4)	271 (6.2)	279 (3.4)
λ_{abs2} [nm] (ε_2[a])	292 (5.9)	292 (4.9)	292 (6.2)	292 (4.3)	293 (6.0)	340 (0.6)	288 (4.9)	290 (4.6)	329 (1.2)	318 (1.1)
λ_{abs3} [nm] (ε_3[a])	324 (0.6)	324 (0.6)	338 (0.7)	324 (0.5)	339 (0.6)	355 (0.7)	296 (4.6)	338 (0.6)		361 (0.3)
λ_{abs4} [nm] (ε_4[a])	338 (0.7)	339 (0.6)	353 (0.6)	340 (0.6)	353 (0.6)	373 (0.9)	334 (0.6)	352 (0.6)		380 (0.3)
λ_{abs5} [nm] (ε_5[a])	353 (0.6)	354 (0.5)	371 (0.8)	354 (0.5)	372 (0.9)	394 (1.0)	349 (0.7)	370 (0.8)		

λ_{abs6} [nm] (ε_6[a])	372 (0.8)	373 (0.7)	391 (0.8)	372 (0.6)	393 (0.9)		367 (0.9)	390 (0.9)		
λ_{abs7} [nm] (ε_7[a])	392 (0.8)	393 (0.7)		393 (0.6)			387 (0.9)			
λ_{em1} [nm]	407[b]	415[b]	408[b]	418	407[b]	409[b]	400	404[b]	367	394
λ_{em2} [nm]							416		385[b]	410
ϕ [%]	21	26	23	20	28	43	26	37	13	16
$E_{(0\text{-}0)}$ [eV][c]	3.16	3.14	3.17	3.14	3.16	3.15	3.20	3.18	3.29	3.50

[a] [10^{-4} $Lmol^{-1}cm^{-1}$]. [b] contains a shoulder. [c] Measured in dichloromethane and determined via intersection of the normalized absorption and emission spectrum

Cyclic voltammetry measurements were performed for selected derivatives **7a** and **11a** in CH_2Cl_2 using 0.1M Bu_4NPF_6 as the electrolyte, a glassy carbon working electrode, ANE2 as the reference electrode, and a Pt counter-electrode with ferrocene as the standard (Figure 6). The oxidation potentials ($E_{(S^+/S)}$) vary between 0.39 V and 0.40 V as well as 0.87 V and 0.99 V and the reduction potentials $E_{(S/S^-)}$ between -1.31 V and -1.34 V versus NHE (Table 8). In comparison, benzophenanthridine **11a** shows a higher oxidation potential and lower reduction potential than benzoacridine **7a**.

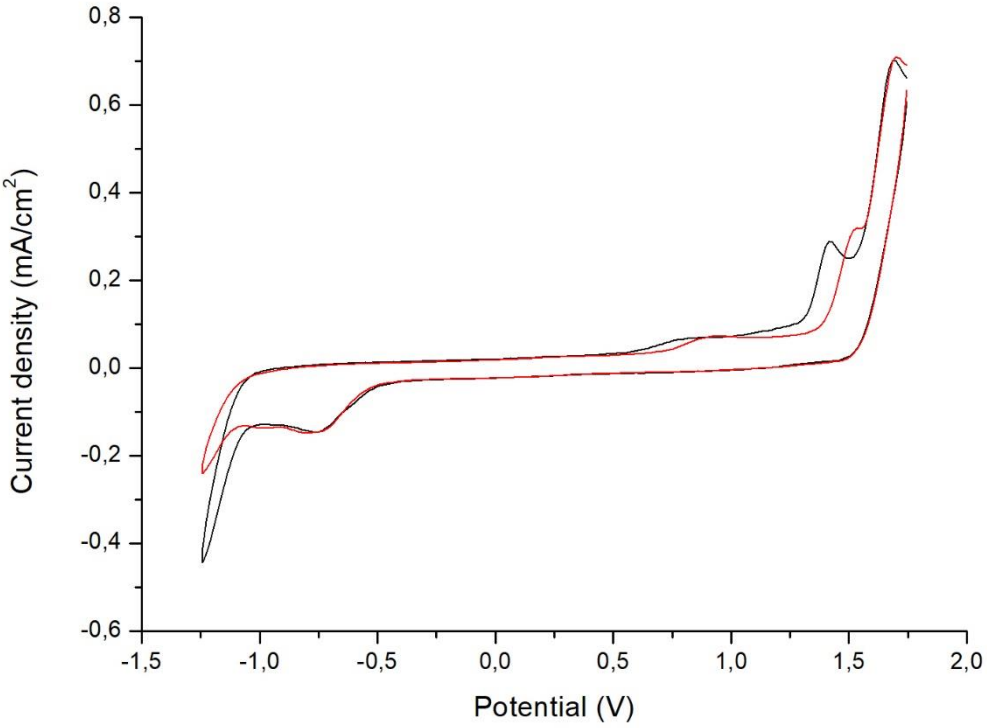


Figure 6: Cyclic Voltammetry measured in CH_2Cl_2, 0.1M Bu_4NPF_6, glassy carbon working electrode, ANE2 as reference electrode, and Pt counter electrode with ferrocene as standard. Red **11a**, black **7a**

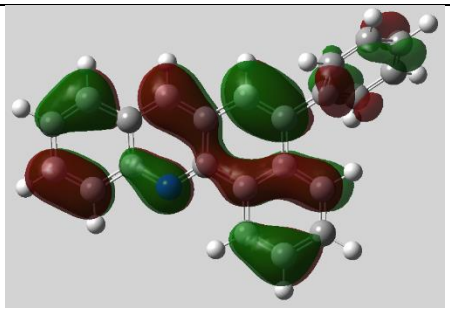
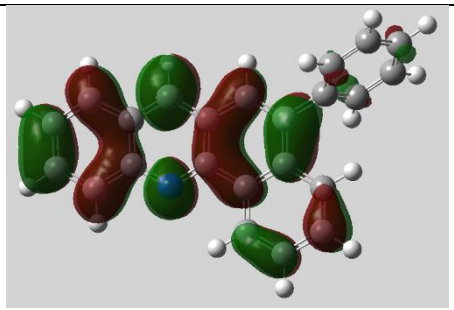
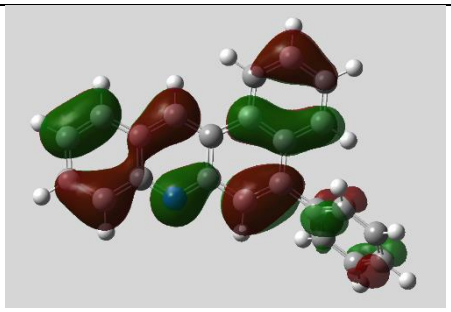
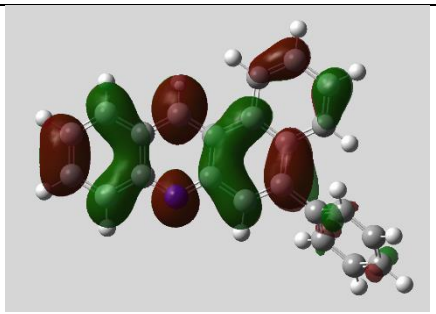
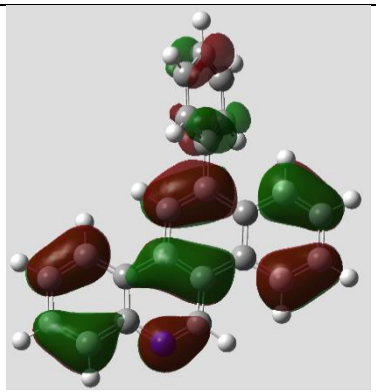
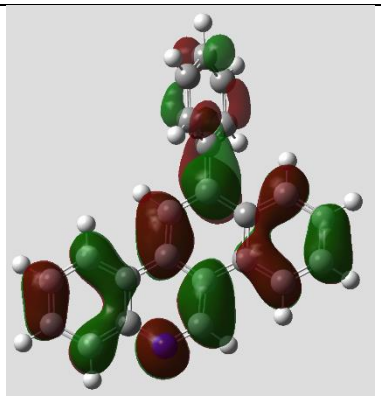
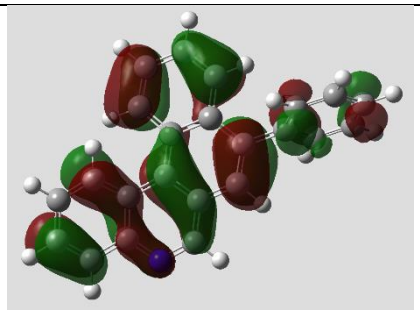
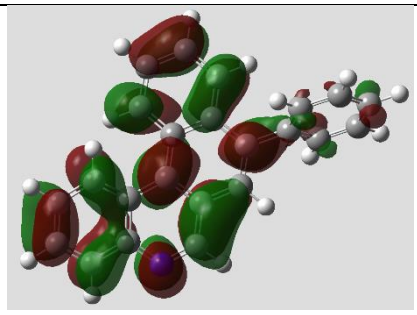
Table 8: Electrochemical data of **4a**, **7a**, **11a** and **14a**

Property	**4a**	**7a**	**11a**	**14a**
$E_{(0\text{-}0)}$ [eV][a]	3.16	3.18	3.29	3.50
$E_{(S^+/S)1}$ [V][b]		0.39	0.40	
$E_{(S^+/S)2}$ [V][b]		0.87	0.99	
$E_{(S/S^-)1}$ [V][b]		-1.31	-1.34	
$E_{HOMO\ CV}$[eV][c]	-	-5.67	-5.79	
$E_{HOMO\ Calc}$[eV][d]	-5.86	-5.93	-6.08	-5.98
$E_{LUMO\ Calc}$[eV][d]	-2.14	-2.15	-1.90	-1.91
$E_{(0\text{-}0)\ Calc}$ [eV][d]	3.72	3.77	4.17	4.07

[a] Measured in dichloromethane and determined via intersection of the normalized absorption and emission spectrum. [b] Determined from the maximal oxidation potential. Measured in CH_2Cl_2, 0.1M Bu_4NPF_6, glassy carbon working electrode, ANE2 as reference electrode and Pt counter-electrode with ferrocene as standard, given versus NHE. [c] Determined from the onset oxidation potential. [d] Computed and optimized with B3LYP at the 6-311G** Level

DFT calculations, using the B3LYP 6-311G(d,p) basis set, have been performed to verify the experimental results.[25] Visualization of the HOMO and LUMO orbitals are shown in Table 9. For all studied compounds, the HOMOs and LUMOs are mainly located at the benzoacridine or phenanthridine core structure, respectively. The aryl substituents are expected not to significantly influence the electronic situation of the central core structure, because they are twisted out of plane. The calculated data of the HOMO energies are slightly lower as compared to the experimental data, whereby the HOMO energy of **7a** decreases from -5.67 eV (experimental value) to -5.93 eV (calculated value) and in case of **11a** from -5.79 eV (experimental value) to -6.08 eV (calculated value) (Table 9 and SI).

Table 9. Visualization of HOMO and LUMO orbitals of **4a**, **7a**, **11a** and **14a** from Y-Axis

HOMO orbitals	LUMO orbitals
 **4a**	 **4a**
 **7a**	 **7a**
 **11a**	 **11a**
 **14a**	 **14a**

In conclusion, we developed a convenient synthetic pathway for the preparation of four different series of benzoacridines and benzophenanthridines via cross-coupling reactions followed by Brønsted acid mediated cycloisomerization. In all reactions, dihalogenated quinolines were used as the starting materials. The different products could be accessed based on location of the leaving groups in the quinoline system and based on the order of Sonogashira and Suzuki reactions during the synthesis. The reactions are broadly applicable and robust, various electron-withdrawing as well as electron-donating groups are tolerated and the products were generally isolated in good to excellent yields. Selected products were investigated by cyclic voltammetry as well as absorption and fluorescence spectroscopy. These compounds show fluorescence with emission maxima around 390 nm and quantum yields up to 43%. A slight difference between benzoacridines and benzophenanthridines was observed regarding the HOMO-LUMO gap and the oxidation potential.

Experimental Section

General

If not otherwise indicated, chemicals used in this study were obtained from commercial sources. No further purifications were done. Solvents, which were employed for work-up and purification processes, were distilled according to standard procedures. Silica gel (particle sizes 0.006 - 0.043 mm) were used for column chromatography.

Micro-Hot-Stage Galen TM III Cambridge Instrument was used for melting point determination. The results were not further corrected.

NMR samples were measured with Bruker AVANCE 250 II (built 2006), Bruker AVANCE 300 III (built 2007) and AVANCE 500 (built

01). NMR-peaks were calibrated using standard peaks of chloroform (7.260 ppm for ^{1}H and at 77.160 ppm for ^{13}C) and dimethylsulfoxide (2.500 ppm for ^{1}H and at 39.520 ppm for ^{13}C). For peak descriptions, following abbreviations were used: s (singlet), d (doublet), t (triplet), dd (doublet doublet), td (triplet doublet), dt (doublet triplet), ddd (double doublet doublet).

IR measurement was performed with Bruker ALPHA-P spectrometer using ATR sampling technique. W (weak), m (medium) and s (strong) were used for peak description.

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

For HRMS, Finnigan MAT 95 XP device was employed. Only signals with deviation of less than ±2 mDa were accounted as correct.

X-Ray single crystal structure analysis was performed on a Bruker-Nonius Apex X8 CCD-diffractometer.

UV−Vis spectra were recorded on an Agilent Cary 60 UV-Vis Spectrophotometer in 1 cm cuvettes. Emission spectra were recorded on an Agilent Cary Eclipse Fluorescence Spectrophotometer. Quantum yields were determined using quinine hemisulfate in 0.05 M H_2SO_4 as fluorescence standard ($\phi = 0.51$[1]). Cyclo voltammetric measurements were performed on a Parstat 4000.

General synthetic procedures

3-Bromo-2-iodoquinoline **1** and 4-bromo-3-iodoquinolines **8a-b** were prepared according to previously reported procedures.[2]

General procedure for the synthesis of 3-bromo-2-phenylquinolines 2a-f and 3-Phenyl-2-(phenylethynyl)quinolines 6a-d by Suzuki reaction

3-Bromo-2-iodoquinoline **1** (0.6 mmol) or 3-bromo-2-(phenylethynyl)quinolines **5a-c** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) were subjected to a dried glass pressure tube. Afterwards, the tube was evacuated and backfilled with argon three times. The solids were solved in 2.0 ml of dry THF, sealed with a Teflon cap before being heated to 60 °C for 17 hours. After the reaction was completed (monitored by TLC), it was allowed to cool to room temperature. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with water (20.0 ml) and dried over Na_2SO_4. The crude oil was purified by column chromatography (heptane/ethyl acetate 40:1).

General procedure for the synthesis of 2-phenyl-3-(phenylethynyl)quinolines 3a-o by Sonogashira reaction

3-Bromo-2-phenylquinolines **2a-f** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) were subjected to a dried glass pressure tube. Afterwards, the tube was evacuated and backfilled with argon three times. The solids were solved in 6.0 ml of triethylamine, sealed with a Teflon cap before being heated to 80 °C for 24 hours. After 24 hours, it was allowed to cool to room temperature. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with water (20.0 ml) and dried over Na_2SO_4. The crude oil was purified by column chromatography (heptane/ethyl acetate 20:1).

General procedure for the synthesis of 3-bromo-2-(phenylethynyl)quinolines 5a-c by Sonogashira reaction

3-Bromo-2-iodoquinoline **1** (0.8 mmol), alkyne (1.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 mmol) and CuI (0.08 mmol) were subjected to a dried glass pressure tube. Afterwards, the tube was evacuated and backfilled with argon three times. The solids were solved in 3.0 ml of triethylamine, sealed with a Teflon cap before being stirred at room temperature for 2 hours. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with water (20.0 ml) and dried over Na_2SO_4. The crude oil was purified by column chromatography (heptane/ethyl acetate 20:1).

General procedure for the synthesis of benzoacridines 4a-o and 7a-d

2-Phenyl-3-(phenylethynyl)quinolines **3a-o** or 3-phenyl-2-(phenylethynyl)quinolines **6a-d** (0.3 mmol), methanesulfonic acid (~0.65 ml) were added to a dried glass pressure tube. The tube was evacuated and backfilled with argon three times. The mixture was heated to 120 °C for 24 hours. After the reaction was completed (monitored by TLC), it was allowed to cool to room temperature. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with saturated $NaHCO_3$ (20.0 ml) and dried over Na_2SO_4. The crude oil was purified by column chromatography (heptane/ethyl acetate 20:1).

General procedure for the synthesis of 4-bromo-3-(phenyl)quinolines 9a-d by Suzuki reaction

4-Bromo-3-iodoquinolines **8a-b** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.03 mmol) and Na_2CO_3 (1.2 mmol) were subjected to a dried glass pressure tube. Afterwards, the tube was evacuated and backfilled with argon three times. The solids were solved in 3.0 ml of DMF and 0.3 ml of water, sealed with a Teflon cap before being stirred at 100 °C for 24 hours. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with water (20.0 ml) and dried over Na_2SO_4. The crude product was purified by column chromatography (heptane/ethyl acetate 10:1).

General procedure for the synthesis of 4-phenylethynyl-3-(phenyl)quinolines 10a-d by Sonogashirareaction

4-Bromo-3-phenylquinoline **9a-d** (0.4 mmol), alkyne (0.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.02 mmol) were subjected to a dried glass pressure tube. Afterwards, the tube was evacuated and backfilled with argon three times. The solids were solved in 3.0 ml of triethylamine, sealed with a Teflon cap before being stirred at 80 °C for 24 hours. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with water (20.0 ml) and dried over Na_2SO_4. The crude product was purified by column chromatography (heptane/ethyl acetate 10:1).

General procedure for the synthesis of 4-bromo-3-(phenylethynyl)quinolines 12a-c by Sonogashira reaction

4-Bromo-3-iodoquinoline **8a** (0.8 mmol), alkyne (1.3 mmol), $Pd(PPh_3)_4$ (0.04 mmol) and CuI (0.04 mmol) were subjected to a dried glass pressure tube. Afterwards, the tube was evacuated and backfilled with argon three times. The solids were solved in 1.0 ml of triethylamine and 2 ml of acetonitrile, sealed with a Teflon cap before being stirred at room temperature for

24 hours. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with water (20.0 ml) and dried over Na_2SO_4. The crude product was purified by column chromatography (heptane/ethyl acetate 10:1).

General procedure for the synthesis of 4-phenyl-3-(phenylethynyl)quinolines 13a-e by Suzuki reaction

4-Bromo-3-phenylethynylquinoline **12** (0.4 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.02 mmol) and Na_2CO_3 (0.8 mmol) were subjected to a dried glass pressure tube. Afterwards, the tube was evacuated and backfilled with argon three times. The solids were solved in 3.0 ml of DMF and 0.3 ml of water, sealed with a Teflon cap before being stirred at 100 °C for 24 hours. The residue was dissolved in CH_2Cl_2 (20.0 ml), washed with water (20.0 ml) and dried over Na_2SO_4. The crude product was purified by column chromatography (heptane/ethyl acetate 10:1).

General procedure for the synthesis of benzophenanthridines 14a-e and 11a-d

3-Phenyl-4-(phenylethynyl)quinolines **13a-e** or 4-phenyl-3-(phenylethynyl)quinolines **10a-d** (~0.3 mmol), methanesulfonic acid (~0.65 ml) were added to a dried glass pressure tube. The tube was evacuated and backfilled with argon three times. The mixture was heated to 120 °C for 24 hours. After the reaction was completed (monitored by TLC), it was allowed to cool to room temperature. The reaction was diluted with CH_2Cl_2 (20.0 ml), washed with saturated $NaHCO_3$ (20.0 ml) and dried over Na_2SO_4. The crude product was purified by column chromatography (heptane/ethyl acetate 5:1).

3-Bromo-2-phenylquinoline 2a

3-Bromo-2-iodoquinoline **1** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **2a** as white solid (125 mg, 74%), mp. 99 - 101 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.50 (s, 1H, CH_{Ar}), 8.14 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.79 – 7.70 (m, 4H, CH_{Ar}), 7.58 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.53 – 7.46 (m, 3H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.8 (C_{Ar}), 146.7 (C_{Ar}), 140.1 (CH_{Ar}), 140.0 (C_{Ar}), 130.2 (CH_{Ar}), 129.7 (CH_{Ar}), 129.5 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 128.3 (C_{Ar}), 128.1 ($2CH_{Ar}$), 127.5 (CH_{Ar}), 126.6 (CH_{Ar}), 117.0 (C_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3049 (w), 2920 (w), 2850 (w), 1577 (m), 1480 (m), 1443 (m), 1396 (m), 950 (m), 897 (m), 761 (m), 742 (s), 708 (m), 687 (s), 590 (m), 474 (m).

MS (EI, 70 eV): *m/z* (%) = 285 ($[M]^+$, 15), 283 ($[M]^+$, 15), 205 (17), 204 (100), 203 (21), 202 (8), 177 (8), 176 (13), 102 (10), 101 (8), 75 (14), 51 (8). HRMS (EI): Calculated for $C_{15}H_{10}{}^{79}BrN$ 282.99911 found 282.9989, calculated for $C_{15}H_{10}{}^{81}BrN$ 284.9971 found 284.99691.

3-Bromo-2-(p-tolyl)quinoline 2b

3-Bromo-2-iodoquinoline **1** (0.6 mmol), arylboronic acid (0.6 mmol), Pd(dppf)Cl_2 (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **2b** as pale yellow solid (127 mg, 71%), mp. 91 - 93 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.48 (s, 1H, CH_{Ar}), 8.14 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.80 – 7.64 (m, 4H, CH_{Ar}), 7.56 (d, ^3J = 7.5 Hz, 1H, CH_{Ar}), 7.32 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 2.45 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.3 (C_{Ar}), 146.7 (C_{Ar}), 140.0 (CH_{Ar}), 139.0 (C_{Ar}), 137.2 (C_{Ar}), 130.1 (CH_{Ar}), 129.6 (CH_{Ar}), 129.5 ($2CH_{Ar}$), 128.8 ($2CH_{Ar}$), 128.2 (C_{Ar}), 127.4 (CH_{Ar}), 126.5 (CH_{Ar}), 117.1 (C_{Ar}), 21.5 (CH_3). IR (ATR, cm^{-1}): ṽ = 3055 (w), 2911 (w), 2852 (w), 1955 (w), 1928 (w), 1905 (w), 1795 (w), 1581 (m), 1542 (m), 1482 (m), 1395 (m), 1067 (m), 950 (m), 893 (m), 881 (m), 819 (m), 779 (m), 748 (s), 724 (m), 587 (m), 513 (m), 465 (m). MS (EI, 70 eV): *m/z* (%) = 300 (4), 299 ($[M]^+$, 23), 297 ($[M]^+$, 23), 219 (18), 218 (100), 217 (25), 216 (13), 203 (9), 109 (13). HRMS (ESI): Calculated for $C_{16}H_{12}{}^{79}BrN$ $[M+H]^+$ 298.0226 found 298.0228, calculated for $C_{16}H_{12}{}^{81}BrN$ $[M+H]^+$ 300.0207 found 300.0208.

3-Bromo-2-(m-tolyl)quinoline 2c

3-Bromo-2-iodoquinoline **1** (0.6 mmol), arylboronic acid (0.6 mmol), Pd(dppf)Cl_2 (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **2c** as pale yellow solid (132 mg, 74%), mp. 61 - 63 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.49 (s, 1H, CH_{Ar}), 8.19 – 8.10 (m, 1H, CH_{Ar}), 7.75 (ddd, ^3J = 8.4 Hz, ^3J = 7.2 Hz, ^4J = 3.8 Hz, 2H, CH_{Ar}), 7.61 – 7.51 (m, 3H, CH_{Ar}), 7.42 – 7.36 (m, 1H, CH_{Ar}), 7.29 (d, ^3J = 7.6 Hz, 1H, CH_{Ar}), 2.46 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.6 (C_{Ar}), 146.7 (C_{Ar}), 140.1 (CH_{Ar}), 139.9 (C_{Ar}), 138.0 (C_{Ar}), 130.2 (CH_{Ar}), 130.1 (CH_{Ar}), 129.8 (CH_{Ar}), 129.7 (CH_{Ar}), 128.4 (C_{Ar}), 128.0 (CH_{Ar}), 127.5 (CH_{Ar}), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 117.2 (C_{Ar}), 21.7 (CH_3). IR (ATR, cm^{-1}): ṽ = 3055 (w), 2919 (w), 1578 (m), 1543 (m), 1483 (m), 1446 (m), 1397 (m), 1385 (m), 1370 (m), 1272 (m), 1197 (m), 1082 (m), 1072 (m), 961 (m), 906 (m), 866 (m), 828 (m), 794 (m), 777 (m), 756 (s), 719 (m), 697 (m), 476 (m). MS (EI, 70 eV): *m/z* (%) = 299 ($[M]^+$, 19), 297 ($[M]^+$, 19),

219 (18), 218 (100), 217 (28), 216 (13), 203 (7), 109 (12). HRMS (ESI): Calculated for $C_{16}H_{12}{}^{79}BrN$ $[M+H]^+$ 298.0226 found 298.0226, calculated for $C_{16}H_{12}{}^{81}BrN$ $[M+H]^+$ 300.0207 found 300.0207.

3-Bromo-2-(o-tolyl)quinoline 2d

3-Bromo-2-iodoquinoline **1** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **2d** as white solid (138 mg, 77%), mp. 101 - 103 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.49 (s, 1H, CH_{Ar}), 8.15 (dd, ^3J = 8.4 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 7.83 – 7.72 (m, 2H, CH_{Ar}), 7.60 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.42 – 7.28 (m, 4H, CH_{Ar}), 2.18 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.7 (C_{Ar}), 146.6 (C_{Ar}), 140.1 (C_{Ar}), 139.2 (CH_{Ar}), 135.9 (C_{Ar}), 130.3 (CH_{Ar}), 130.1 (CH_{Ar}), 129.6 (CH_{Ar}), 128.9 (CH_{Ar}), 128.7 (CH_{Ar}), 128.5 (C_{Ar}), 127.6 (CH_{Ar}), 126.7 (CH_{Ar}), 125.8 (CH_{Ar}), 118.5 (C_{Ar}), 19.6 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 3047 (w), 3018 (w), 2926 (w), 1484 (m), 1398 (m), 1370 (m), 1066 (m), 1038 (m), 954 (m), 906 (m), 870 (m), 784 (m), 760 (s), 728 (m), 595 (m), 472 (m). MS (EI, 70 eV): *m/z* (%) = 299 ($[M]^+$, 7), 297 ($[M]^+$, 7), 219 (17), 218 (100), 217 (46), 216 (21), 109 (16). HRMS (ESI): Calculated for $C_{16}H_{12}{}^{79}BrN$ $[M+H]^+$ 298.0226 found 298.0227, calculated for $C_{16}H_{12}{}^{81}BrN$ $[M+H]^+$ 300.0207 found 300.0207.

3-Bromo-2-(4-methoxyphenyl)quinoline 2e

3-Bromo-2-iodoquinoline **1** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **2e** as yellow solid (141 mg, 75%), mp. 124 - 126 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.48 (s, 1H, CH_{Ar}), 8.12 (dd, ^3J = 8.3 Hz, ^4J = 0.7 Hz, 1H, CH_{Ar}), 7.80 – 7.69 (m, 4H, CH_{Ar}), 7.61 – 7.51 (m, 1H, CH_{Ar}), 7.08 – 6.95 (m, 2H, CH_{Ar}), 3.88 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.2 (C_{Ar}), 157.7 (C_{Ar}), 146.6 (C_{Ar}), 140.0 (CH_{Ar}), 132.3 (C_{Ar}), 131.0 ($2CH_{Ar}$), 130.0 (CH_{Ar}), 129.4 (CH_{Ar}), 128.1 (C_{Ar}), 127.2 (CH_{Ar}), 126.4 (CH_{Ar}), 117.1 (C_{Ar}), 113.4 ($2CH_{Ar}$), 55.4 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3049 (w), 2934 (w), 2838 (w), 2048 (w), 1963 (w), 1607 (m), 1581 (m), 1514 (m), 1481 (m), 1451 (m), 1396 (m), 1371 (m), 1302 (m), 1289 (m), 1248 (m), 1174 (m), 1108 (m), 1070 (m), 1029 (m), 950 (m), 897 (m), 880 (m), 856 (m), 825 (s), 798 (m), 778 (m), 744 (s), 732 (m), 587 (m), 530 (m), 475 (m). MS (EI, 70 eV): *m/z* (%) = 316 (9), 315 ($[M]^+$, 54), 314 (10), 313 ($[M]^+$, 53), 235 (19), 234 (100), 219 (28), 192 (8), 191 (55), 190 (36), 164

(10), 163 (10), 96 (13), 75 (8). HRMS (ESI): Calculated for $C_{16}H_{12}{}^{79}BrNO$ $[M+H]^+$ 314.0175 found 314.0176, calculated for $C_{16}H_{12}{}^{81}BrNO$ $[M+H]^+$ 316.0156 found 316.0156.

3-Bromo-2-(4-fluorophenyl)quinoline 2f

3-Bromo-2-iodoquinoline **1** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **2f** as white solid (117 mg, 65%), mp. 142 - 144 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.50 (s, 1H, CH_{Ar}), 8.12 (dd, ^3J = 8.3 Hz, ^4J = 0.9 Hz, $1H_{Ar}$), 7.89 – 7.65 (m, 4H, CH_{Ar}), 7.65 – 7.47 (m, 1H, CH_{Ar}), 7.32 – 7.06 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.2 (d, $^1J_{CF}$ = 248.6 Hz, C_{FAr}), 157.1 (C_{Ar}), 146.5 (C_{Ar}), 140.1 (C_{Ar}), 135.9 (d, $^4J_{CF}$ = 3.3 Hz, C_{Ar}), 131.5 (d, $^3J_{CF}$ = 8.4 Hz, $2CH_{Ar}$), 130.2 (CH_{Ar}) , 129.5 (CH_{Ar}), 128.2 (CH_{Ar}), 127.6 (CH_{Ar}), 126.5 (CH_{Ar}), 116.7 (C_{Ar}), 115.1 (d, $^2J_{CF}$ = 21.7 Hz, $2CH_{Ar}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.38 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 2923 (w), 1598 (m), 1581 (m), 1510 (m), 1483 (m), 1394 (m), 1218 (m), 1162 (m), 1100 (m), 1069 (m), 953 (m), 900 (m), 881 (m), 835 (s), 780 (m), 747 (s), 729 (m), 587 (m), 151 (m), 479 (m). MS (EI, 70 eV): *m/z* (%) = 303 ($[M]^+$, 24), 301 ($[M]^+$, 24), 223 (17), 222 (100), 221 (17), 194 (7), 111 (10). HRMS (ESI): Calculated for $C_{15}H_9{}^{79}BrFN$ $[M+H]^+$ 301.9975 found 301.9974, calculated for $C_{16}H_{12}{}^{81}BrFN$ $[M+H]^+$ 303.9956 found 303.9956.

2-Phenyl-3-(phenylethynyl)quinoline 3a

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3a** as yellow solid (191 mg, 89%), mp. 136 - 138 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.45 (s, 1H, CH_{Ar}), 8.18 (dd, ^3J = 8.4 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 8.12 – 8.08 (m, 2H, CH_{Ar}), 7.82 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.74 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.61 – 7.49 (m, 4H, CH_{Ar}), 7.46 – 7.38 (m, 2H, CH_{Ar}), 7.37 – 7.30 (m, 3H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.4 (C_{Ar}), 147.0 (C_{Ar}), 140.6 (CH_{Ar}), 139.8 (C_{Ar}), 131.5 ($2CH_{Ar}$), 130.4 (CH_{Ar}), 129.7 ($2CH_{Ar}$), 129.7 (CH_{Ar}), 129.1 (CH_{Ar}), 128.7 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 128.0 ($2CH_{Ar}$), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 126.4 (C_{Ar}), 123.0 (C_{Ar}), 116.3 (C_{Ar}), 94.7 (C_{Alkyne}), 88.1 (C_{Alkyne}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3030 (w), 2923 (w), 2212 (w), 1596 (w), 1570 (w), 1479 (m), 1442 (m), 1413 (m), 1368 (m), 911 (m), 769 (m), 750 (s), 718 (m), 695 (m), 686 (s), 533 (m), 477 (m). MS (EI, 70 eV): *m/z* (%) = 306 (11), 305 ($[M]^+$, 58), 304 (100), 303 (21), 302 (13), 301 (7), 200 (7), 152 (9), 151 (8). HRMS (ESI): Calculated for $C_{23}H_{15}N$ $[M+H]^+$ 306.1277 found 306.1273.

2-Phenyl-3-(p-tolylethynyl)quinoline 3b

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3b** as yellow solid (204 mg, 91%), mp. 143 - 145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.43 (s, 1H, CH_{Ar}), 8.16 (d, ^3J = 9.1 Hz, 1H, CH_{Ar}), 8.11 – 8.06 (m, 2H, CH_{Ar}), 7.82 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.59 – 7.48 (m, 4H, CH_{Ar}), 7.33 – 7.28 (m, 2H, CH_{Ar}), 7.14 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 2.36 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.9 (C_{Ar}), 147.4 (C_{Ar}), 140.9 (CH_{Ar}), 140.3 (C_{Ar}), 139.4 (C_{Ar}), 131.9 ($2CH_{Ar}$), 130.8 (CH_{Ar}), 130.2 ($2CH_{Ar}$), 130.1 (CH_{Ar}), 129.7 ($2CH_{Ar}$), 129.5 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 126.9 (C_{Ar}), 120.4 (C_{Ar}), 117.0 (C_{Ar}), 95.4 (C_{Alkyne}), 87.9 (C_{Alkyne}), 22.1 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3039 (w), 3024 (w), 2912 (w), 2851 (w), 2211 (w), 1585 (w), 1554 (w), 1509 (m), 1479 (m), 1411 (m), 1367 (m), 1182 (m), 953 (m), 913 (m), 816 (m), 768 (m), 750 (s), 719 (m), 696 (s), 534 (m). MS (EI, 70 eV): *m/z* (%) = 320 (19), 319 ($[M]^+$, 88), 318 (100), 317 (12), 316 (16), 315 (9), 305 (9), 304 (39), 303 (25), 302 (11), 301 (6), 213 (7), 158 (14), 152 (11), 151 (7). HRMS (ESI): Calculated for $C_{24}H_{17}N$ $[M+H]^+$ 320.1434 found 320.1428.

2-Phenyl-3-(m-tolylethynyl)quinoline 3c

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3c** as yellow solid (161 mg, 71%), mp. 83 - 85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.31 (s, 1H, CH_{Ar}), 8.06 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.98 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 2H, CH_{Ar}), 7.68 (d, ^3J = 8.0 Hz, 1H, CH_{Ar}), 7.65 – 7.57 (m, 1H, CH_{Ar}), 7.48 – 7.37 (m, 4H, CH_{Ar}), 7.11 (d, ^3J = 5.3 Hz, 3H, CH_{Ar}), 7.06 – 6.99 (m, 1H, CH_{Ar}), 2.22 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.9 (C_{Ar}), 146.4 (C_{Ar}), 140.2 (CH_{Ar}), 139.3 (C_{Ar}), 137.7 (C_{Ar}), 131.6 (CH_{Ar}), 129.9 (CH_{Ar}), 129.3 ($2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 128.1 (CH_{Ar}), 127.9 (CH_{Ar}), 127.6 ($2CH_{Ar}$), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.0 (C_{Ar}), 122.4 (C_{Ar}), 115.9 (C_{Ar}), 94.5 (C_{Alkyne}), 87.3 (C_{Alkyne}), 20.9 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3041 (w), 2965 (w), 2914 (w), 2852 (w), 2728 (w), 2345 (w), 2213 (w), 1956 (w), 1814 (w), 1597 (m), 1579 (m), 1480 (m), 1441 (m), 1407 (m), 906 (m), 863 (m), 785 (m), 767 (m), 752 (s), 718 (m), 688 (s), 611 (m), 603 (m), 515 (m), 475 (m). MS (EI, 70 eV): *m/z* (%) = 320 (19), 319 ($[M]^+$, 85), 318 (100), 317 (12), 316 (17), 315 (9), 305

(12), 304 (50), 303 (27), 302 (13), 301 (7), 213 (8), 152 (10),151 (7). HRMS (ESI): Calculated for $C_{24}H_{17}N$ $[M+H]^+$ 320.1434 found 320.1435.

2-Phenyl-3-(o-tolylethynyl)quinoline 3d

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3d** as pale yellow solid (207 mg, 92%), mp. 123 - 125 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.47 (s, 1H, CH_{Ar}), 8.21 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.09 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 2H, CH_{Ar}), 7.84 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.76 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.62 – 7.50 (m, 4H, CH_{Ar}), 7.44 (d, ^3J = 7.6 Hz, 1H, CH_{Ar}), 7.27 – 7.15 (m, 3H, CH_{Ar}), 2.36 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.9 (C_{Ar}), 146.4 (C_{Ar}), 140.3 (CH_{Ar}), 139.9 (C_{Ar}), 139.5 (C_{Ar}), 131.6 (CH_{Ar}), 129.9 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 129.2 (CH_{Ar}), 129.1 (CH_{Ar}), 128.6 (CH_{Ar}), 128.3 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.0 (C_{Ar}), 125.2 (CH_{Ar}), 122.3 (C_{Ar}), 116.2 (C_{Ar}), 93.4 (C_{Alkyne}), 91.1 (C_{Alkyne}), 20.2 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 3035 (w), 2921 (w), 2852 (w), 2209 (w), 1599 (w), 1575 (w), 1480 (m), 1455 (m), 1441 (m), 1410 (m), 1366 (m), 907 (m), 766 (m), 756 (m), 748 (s), 718 (m), 695 (s), 452 (m). MS (EI, 70 eV): *m/z* (%) = 320 (15), 319 ($[M]^+$, 71), 318 (100), 317 (47), 316 (34), 315 (9), 304 (9), 213 (9), 159 (11), 152 (6), 139 (5), 77 (7), 76 (6), 51 (6). HRMS (ESI): Calculated for $C_{24}H_{17}N$ $[M+H]^+$ 320.1434 found 320.1435.

3-((4-Ethylphenyl)ethynyl)-2-phenylquinoline 3e

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3e** as yellow solid (214 mg, 91%), mp. 88 - 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.43 (s, 1H, CH_{Ar}), 8.19 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.15 – 8.09 (m, 2H, CH_{Ar}), 7.80 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.60 – 7.49 (m, 4H, CH_{Ar}), 7.35 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.18 (d, ^{3}J = 8.3 Hz, 2H, CH_{Ar}), 2.67 (q, ^3J = 7.6 Hz, 2H, CH_2-CH_3), 1.25 (t, ^3J = 7.6 Hz, 3H, CH_2-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.9 (C_{Ar}), 146.4 (C_{Ar}), 144.7 (C_{Ar}), 140.0 (CH_{Ar}), 139.3 (C_{Ar}), 131.0 ($2CH_{Ar}$), 129.8 (CH_{Ar}), 129.3 ($2CH_{Ar}$), 129.2 (CH_{Ar}), 128.6 (CH_{Ar}), 127.6 ($2CH_{Ar}$), 127.5 ($2CH_{Ar}$), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.0 (C_{Ar}), 119.7 (C_{Ar}), 116.1 (C_{Ar}), 94.6 (C_{Alkyne}), 87.0 (C_{Alkyne}), 28.5 (CH_2-CH_3), 14.9 (CH_2-CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3041 (w), 3023 (w), 2967 (w), 2930 (m), 2872 (w), 2213 (w),

1510 (m), 1480 (m), 1413 (m), 1368 (m), 914 (m), 832 (m), 768 (m), 750 (m), 718 (m), 695 (s), 538 (m), 478 (m). MS (EI, 70 eV): *m/z* (%) = 334 (25), 333 ($[M]^+$, 100), 332 (64), 319 (14), 318 (59), 317 (38), 316 (36), 315 (20), 314 (10), 305 (12), 304 (50), 303 (16), 302 (10), 159 (13), 157 (9). HRMS (ESI): Calculated for $C_{25}H_{19}N$ $[M+H]^+$ 334.1590 found 334.1593.

3-((4-Methoxyphenyl)ethynyl)-2-phenylquinoline 3f

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3f** as yellow solid (169 mg, 67%), mp. 81 - 83 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.27 (s, 1H, CH_{Ar}), 8.05 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.98 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H, CH_{Ar}), 7.66 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.59 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.46 – 7.36 (m, 4H, CH_{Ar}), 7.27 – 7.19 (m, 2H, CH_{Ar}), 6.77 – 6.70 (m, 2H, CH_{Ar}), 3.68 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.9 (C_{Ar}), 159.3 (C_{Ar}), 146.7 (C_{Ar}), 140.1 (CH_{Ar}), 139.8 (C_{Ar}), 132.9 ($2CH_{Ar}$), 130.2 (CH_{Ar}), 129.7 ($2CH_{Ar}$), 129,5 (CH_{Ar}) 129.0 (CH_{Ar}), 127.9 ($2CH_{Ar}$), 127.1 (CH_{Ar}), 127.0 (CH_{Ar}), 126.4 (C_{Ar}), 116.6 (C_{Ar}), 115.1 (C_{Ar}), 114.1 ($2CH_{Ar}$), 94.9 (C_{Alkyne}), 86.8 (C_{Alkyne}), 55.3 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 3010 (w), 2974 (w), 2934 (w), 2837 (w), 2540 (w), 2209 (w), 1604 (m), 1508 (m), 1480 (m), 1293 (m), 1248 (m), 1171 (m), 1106 (m), 1026 (m), 1006 (m), 909 (m), 828 (s), 767 (m), 747 (m), 720 (m), 698 (s), 535 (m), 477 (m). MS (EI, 70 eV): *m/z* (%) = 336 (24), 335 ($[M]^+$, 100), 334 (26), 321 (23), 320 (91), 292 (25), 291 (75), 290 (47), 289 (10), 265 (10), 264 (10), 187 (11), 146 (22). HRMS (ESI): Calculated for $C_{24}H_{17}NO$ $[M+H]^+$ 336.1383 found 336.1384.

3-((4-Fluorophenyl)ethynyl)-2-phenylquinoline 3g

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3g** as white solid (208 mg, 92%), mp. 128 - 130 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.43 (s, 1H, CH_{Ar}), 8.16 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.09 – 8.02 (m, 2H, CH_{Ar}), 7.82 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.74 (ddd, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.60 – 7.48 (m, 4H, CH_{Ar}), 7.41 – 7.33 (m, 2H, CH_{Ar}), 7.08 – 6.98 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.7 (d, $^1J_{CF}$ = 250.3 Hz, C_{FAr}), 159.3 (C_{Ar}), 146.9 (C_{Ar}), 140.5 (CH_{Ar}), 139.7 (C_{Ar}), 133.3 (d, $^3J_{CF}$ = 8.4 Hz, $2CH_{Ar}$), 130.4 (CH_{Ar}) , 129.6 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 127.9 ($2CH_{Ar}$), 127.1 ($2CH_{Ar}$), 126.3 (C_{Ar}), 119.1 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 116.1 (C_{Ar}), 115.1 (d, $^2J_{CF}$ = 22.2 Hz, $2CH_{Ar}$), 93.5 (C_{Alkyne}), 87.7

(C_{Alkyne}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.10 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 3051 (w), 3038 (w), 2922 (w), 2852 (w), 2216 (w), 1899 (w), 1584 (w), 1505 (m), 1480 (m), 1234 (m), 1223 (m), 1155 (m), 915 (m), 836 (m), 768 (m), 750 (m), 719 (m), 696 (s), 534 (m). MS (EI, 70 eV): *m/z* (%) = 324 (12), 323 (61), 322 ([M]$^+$, 100), 321 (19), 320 (11), 218 (6), 161 (7). HRMS (EI): Calculated for $C_{23}H_{13}FN$ 322.1027 found 322.1025.

2-Phenyl-3-(thiophen-3-ylethynyl)quinoline 3h

3-Bromo-2-phenylquinoline **2a** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3h** as white solid (207 mg, 95%), mp. 117 - 119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.34 (s, 1H, CH_{Ar}), 8.09 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.02 – 7.94 (m, 2H, CH_{Ar}), 7.72 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.64 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.51 – 7.38 (m, 4H, CH_{Ar}), 7.34 (dd, ^3J = 3.0 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.22 – 7.16 (m, 1H, CH_{Ar}), 7.00 (dd, ^3J = 5.0 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.2 (C_{Ar}), 146.7 (C_{Ar}), 140.4 (CH_{Ar}), 139.5 (C_{Ar}), 130.3 (CH_{Ar}), 129.6 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 129.0 (CH_{Ar}), 127.9 ($2CH_{Ar}$), 127.1 (CH_{Ar}), 127.0 (CH_{Ar}), 126.3 (C_{Ar}), 125.5 (CH_{Ar}), 122.0 (C_{Ar}), 116.2 (C_{Ar}), 90.0 (C_{Alkyne}), 87.4 (C_{Alkyne}). IR (ATR, cm^{-1}): ṽ = 3105 (w), 3083 (w), 3057 (w), 3037 (w), 2922 (w), 2853 (w), 2209 (w), 1820 (w), 1586 (w), 1554 (w), 1480 (m), 1422 (m), 1400 (m), 1367 (m), 1355 (m), 912 (m), 865 (m), 769 (s), 750 (m), 696 (s), 622 (m), 477 (m). MS (EI, 70 eV): *m/z* (%) = 313 (4), 312 (17), 311 ([M]$^+$, 66), 310 (100), 309 (19), 308 (5), 264 (6), 163 (7), 155 (6). HRMS (ESI): Calculated for $C_{21}H_{13}NS$ [M+H]$^+$ 312.0842 found 312.0842.

3-(Phenylethynyl)-2-(p-tolyl)quinoline 3i

3-Bromo-2-phenylquinoline **2b** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3i** as white solid (199 mg, 93%), mp. 133 – 135 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.44 (s, 1H, CH_{Ar}), 8.17 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.06 – 8.00 (m, 2H, CH_{Ar}), 7.81 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.55 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.48 – 7.41 (m, 2H, CH_{Ar}), 7.37 – 7.32 (m, 5H, CH_{Ar}), 2.47 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 159.3 (C_{Ar}), 147.0 (C_{Ar}), 140.9 (CH_{Ar}), 139.2 (C_{Ar}), 136.9 (C_{Ar}), 131.5 ($2CH_{Ar}$), 130.4 (CH_{Ar}), 129.7 ($2CH_{Ar}$), 129.6 (CH_{Ar}), 128.8 ($2CH_{Ar}$), 128.7 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 127.2 (CH_{Ar}), 127.0 (CH_{Ar}), 126.4 (C_{Ar}), 123.2 (C_{Ar}), 116.3 (C_{Ar}), 94.6 (C_{Alkyne}),

88.3 (C_{Alkyne}), 21.6 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 3031 (w), 2927 (w), 2213 (w), 1608 (m), 1581 (m), 1570 (m), 1489 (m), 1479 (m), 1443 (m), 1411 (m), 1367 (m), 1185 (m), 1006 (m), 952 (m), 909 (m), 859 (m), 845 (m), 816 (m), 784 (m), 754 (s), 736 (m), 688 (m), 534 (m). MS (EI, 70 eV): *m/z* (%) = 320 (17), 319 ($[M]^+$, 78), 318 (100), 317 (12), 316 (16), 315 (9), 305 (7),304 (30), 303 (21), 302 (10), 159 (10), 158 (7), 152 (12), 151 (7). HRMS (ESI): Calculated for $C_{24}H_{17}N$ $[M+H]^+$ 320.1434 found 320.1436.

3-((4-Fluorophenyl)ethynyl)-2-(p-tolyl)quinoline 3j

3-Bromo-2-phenylquinoline **2b** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3j** as white solid (174 mg, 77%), mp. 108 - 110 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.42 (s, 1H, CH_{Ar}), 8.16 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.00 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.80 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.54 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.46 – 7.37 (m, 2H, CH_{Ar}), 7.34 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.10 – 6.98 (m, 2H, CH_{Ar}), 2.46 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 162.8 (d, $^1J_{CF}$ = 250.3 Hz, C_{FAr}), 159.2 (C_{Ar}), 147.0 (C_{Ar}), 140.8 (CH_{Ar}), 139.2 (C_{Ar}), 136.9 (C_{Ar}), 133.4 (d, $^3J_{CF}$ = 8.4 Hz, $2CH_{Ar}$), 130.5 (CH_{Ar}) , 129.7 ($2CH_{Ar}$), 129.6 (CH_{Ar}), 128.8 ($2CH_{Ar}$), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 126.3 (C_{Ar}), 119.3 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 116.1 (C_{Ar}), 115.9 (d, $^2J_{CF}$ = 22.1 Hz, $2CH_{Ar}$), 93.5 (C_{Alkyne}), 87.9 (C_{Alkyne}), 21.6 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.19 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3063 (w), 3016 (w), 3001 (w), 2924 (w), 2863 (w), 1880 (w), 1600 (m), 1586 (m), 1505 (m), 1415 (m), 1370 (m), 1230 (m), 1153 (m), 1006 (m), 913 (m), 844 (m), 826 (s), 786 (m), 750 (s), 734 (m), 529 (m), 463 (m). MS (EI, 70 eV): *m/z* (%) = 338 (18), 337 ($[M]^+$, 84), 336 (100), 335 (13), 334 (15), 333 (8), 322 (28), 321 (20), 320 (9), 168 (9), 161 (11), 160 (7), 158 (7). HRMS (ESI): Calculated for $C_{24}H_{16}FN$ $[M+H]^+$ 338.1340 found 338.1342.

3-(Phenylethynyl)-2-(m-tolyl)quinoline 3k

3-Bromo-2-phenylquinoline **2c** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3k** as white solid (192 mg, 89%), mp. 113 - 115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.45 (s, 1H, CH_{Ar}), 8.18 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.90 (dd, ^3J = 7.8 Hz, ^4J = 0.5 Hz, 2H, CH_{Ar}), 7.82 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.56 (ddd, ^3J = 8.1 Hz,

^{3}J = 7.0 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.46 – 7.39 (m, 3H, CH_{Ar}), 7.37 – 7.28 (m, 4H, CH_{Ar}), 2.48 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.6 (C_{Ar}), 147.0 (C_{Ar}), 140.7 (CH_{Ar}), 139.7 (C_{Ar}), 137.7 (C_{Ar}), 131.5 ($2CH_{Ar}$), 130.4 (CH_{Ar}), 130.4 (CH_{Ar}), 129.9 (CH_{Ar}), 129.7 (CH_{Ar}), 128.7 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 126.9 (CH_{Ar}), 126.4 (C_{Ar}), 123.1 (C_{Ar}), 116.4 (C_{Ar}), 94.7 (C_{Alkyne}), 88.2 (C_{Alkyne}), 21.7 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3030 (w), 2972 (w), 2915 (w), 2851 (w), 1614 (w), 1578 (w), 1557 (w), 1545 (w), 1491 (m), 1478 (m), 1442 (m), 1412 (m), 1369 (m), 913 (m), 781 (m), 754 (s), 730 (m), 687 (m), 471 (m). MS (EI, 70 eV): *m/z* (%) = 320 (13), 319 (60), 318 ($[M]^+$, 100), 317 (23), 316 (23), 315 (9), 304 (28), 303 (14), 241 (7), 200 (11), 158 (16), 152 (10), 151 (7). HRMS (EI): Calculated for $C_{24}H_{16}N$ 318.1277 found 318.1277.

3-(Phenylethynyl)-2-(o-tolyl)quinoline 3l

3-Bromo-2-phenylquinoline **2d** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3l** as yellow oil (138 mg, 64%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.33 (s, $1H_{Ar}$), 8.09 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 7.76 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.66 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.50 (ddd, ^{3}J = 8.1 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.41 – 7.35 (m, 1H, CH_{Ar}), 7.31 – 7.22 (m, 3H, CH_{Ar}), 7.20 – 7.15 (m, 3H, CH_{Ar}), 7.11 – 7.06 (m, 2H, CH_{Ar}), 2.20 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 161.8 (C_{Ar}), 146.6 (C_{Ar}), 139.9 (C_{Ar}), 139.1 (CH_{Ar}), 136.4 (C_{Ar}), 131.6 ($2CH_{Ar}$), 130.4 (CH_{Ar}), 130.2 (CH_{Ar}), 129.6 (CH_{Ar}), 129.4 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 126.6 (C_{Ar}), 125.6 (CH_{Ar}), 122.9 (C_{Ar}), 117.9 (C_{Ar}), 94.7 (C_{Alkyne}), 87.3 (C_{Alkyne}), 19.9 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3031 (w), 3020 (w), 2957 (w), 2922 (w), 2859 (w), 2212 (w), 1806 (w), 1614 (w), 1585 (w), 1490 (m), 1481 (m), 1410 (m), 908 (m), 751 (s), 729 (s), 687 (m),. MS (EI, 70 eV): *m/z* (%) = 320 (23), 319 ($[M]^+$, 100), 318 (86), 317 (51), 316 (30), 315 (13), 241 (12), 217 (36), 216 (10), 200 (11), 158 (24), 157 (10), 152 (11), 145 (10), 89 (12), 63 (10), 51 (10). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1346.

2-(4-Methoxyphenyl)-3-(phenylethynyl)quinoline 3m

3-Bromo-2-phenylquinoline **2e** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3m** as yellow solid (205 mg, 96%), mp. 112 - 114 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.43 (s, 1H, CH_{Ar}), 8.18 – 8.07 (m, 3H,

CH_{Ar}), 7.80 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.72 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.53 (ddd, ^{3}J = 8.1 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.49 – 7.43 (m, 2H, CH_{Ar}), 7.39 – 7.32 (m, 3H, CH_{Ar}), 7.11 – 7.02 (m, 2H, CH_{Ar}), 3.90 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 160.6 (C_{Ar}), 158.8 (C_{Ar}), 147.0 (C_{Ar}), 141.0 (CH_{Ar}), 132.3 (C_{Ar}), 131.5 ($2CH_{Ar}$), 131.3 ($2CH_{Ar}$), 130.4 (CH_{Ar}), 129.5 (CH_{Ar}), 128.7 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 127.2 (CH_{Ar}), 126.9 (CH_{Ar}), 126.3 (C_{Ar}), 123.1 (C_{Ar}), 116.1 (C_{Ar}), 113.5 ($2CH_{Ar}$), 94.6 (C_{Alkyne}), 88.3 (C_{Alkyne}), 55.5 (OCH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 3001 (w), 2950 (w), 2931 (w), 2836 (w), 1602 (m), 1572 (m), 1512 (m), 1480 (m), 1440 (m), 1413 (m), 1294 (m), 1243 (m), 1174 (m), 1023 (m), 1014 (m), 842 (m), 788 (m), 752 (s), 741 (m), 686 (m), 536 (m). MS (EI, 70 eV): *m/z* (%) = 336 (24), 335 ($[M]^+$, 100), 334 (54), 320 (12), 319 (18), 304 (19), 292 (19), 291 (60), 290 (24), 289 (9), 145 (37), 132 (8). HRMS (ESI): Calculated for $C_{24}H_{17}NO$ $[M+H]^+$ 336.1383 found 336.1384.

2-(4-Fluorophenyl)-3-(phenylethynyl)quinoline 3n

3-Bromo-2-phenylquinoline **2f** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3n** as yellow solid (203 mg, 95%), mp. 159 - 161 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.45 (s, 1H, CH_{Ar}), 8.15 (d, ^{3}J = 7.8 Hz, 1H, CH_{Ar}), 8.13 – 8.06 (m, 2H, CH_{Ar}), 7.82 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.74 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.56 (ddd, ^{3}J = 8.1 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.45 – 7.39 (m, 2H, CH_{Ar}), 7.38 – 7.33 (m, 3H, CH_{Ar}), 7.25 – 7.18 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.6 (d, $^{1}J_{CF}$ = 248.5 Hz, C_{FAr}), 158.3 (C_{Ar}), 147.0 (C_{Ar}), 140.9 (CH_{Ar}), 135.9 (d, $^{4}J_{CF}$ = 3.2 Hz, C_{Ar}), 131.8 (d, $^{3}J_{CF}$ = 8.4 Hz, $2CH_{Ar}$), 131.5 ($2CH_{Ar}$), 130.6 (CH_{Ar}), 129.7 (CH_{Ar}), 128.9 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 127.3 (CH_{Ar}), 127.2 (CH_{Ar}), 126.5 (C_{Ar}), 122.9 (C_{Ar}), 116.2 (C_{Ar}), 115.0 (d, $^{2}J_{CF}$ = 21.6 Hz, $2CH_{Ar}$), 94.9 (C_{Alkyne}), 87.9 (C_{Alkyne}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.52 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3059 (w), 3046 (w), 2921 (w), 2851 (w), 2213 (w), 1595 (m), 1579 (m), 1510 (m), 1480 (m), 1416 (m), 1367 (m), 1221 (m), 1158 (m), 1101 (m), 914 (m), 849 (m), 786 (m), 755 (s), 737 (s), 686 (s), 534 (m), 514 (m), 479 (m). MS (EI, 70 eV): *m/z* (%) = 324 (16), 323 (68), 322 ($[M]^+$, 100), 321 (19), 320 (8), 200 (10), 161 (10), 121 (8). HRMS (EI): Calculated for $C_{23}H_{13}FN$ 322.1027 found 322.1025.

2-(4-Fluorophenyl)-3-(p-tolylethynyl)quinoline 3o

3-Bromo-2-phenylquinoline **2f** (0.7 mmol), alkyne (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 mmol) and CuI (0.07 mmol) in 6.0 ml of triethylamine gave **3o** as white solid (200 mg, 90%), mp. 134 - 136 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.43 (s, 1H, CH_{Ar}), 8.17 – 8.06 (m, 3H, CH_{Ar}), 7.81 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.56 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.35 – 7.29 (m, 2H, CH_{Ar}), 7.26 – 7.18 (m, 2H, CH_{Ar}), 7.18 – 7.14 (m, 2H, CH_{Ar}), 2.38 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.6 (d, $^1J_{CF}$ = 248.4 Hz, C_{FAr}), 158.2 (C_{Ar}), 146.9 (C_{Ar}), 140.7 (CH_{Ar}), 139.2 (C_{Ar}), 135.9 (d, $^4J_{CF}$ = 3.2 Hz, C_{Ar}), 131.8 (d, $^3J_{CF}$ = 8.4 Hz, $2CH_{Ar}$), 131.4 ($2CH_{Ar}$), 130.5 (CH_{Ar}), 129.6 (CH_{Ar}), 129.4 ($2CH_{Ar}$), 127.2 (CH_{Ar}), 127.2 (CH_{Ar}), 126.5 (C_{Ar}),119.8 (C_{Ar}), 116.4 (C_{Ar}), 115.0 (d, $^2J_{CF}$ = 21.6 Hz, $2CH_{Ar}$), 95.2 (C_{Alkyne}), 87.3 (C_{Alkyne}), 21.7 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.62 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3065 (w), 3047 (w), 3025 (w), 2956 (w), 2918 (w), 2866 (w), 2206 (w), 1884 (w), 1751 (w), 1597 (m), 1509 (m), 1484 (m), 1417 (m), 1225 (m), 1155 (m), 826 (m), 808 (s), 789 (s), 750 (s), 738 (m), 530 (m), 518 (m). MS (EI, 70 eV): *m/z* (%) = 338 (21), 337 ([M]$^+$, 100), 336 (78), 335 (11), 334 (13), 323 (9), 322 (40), 321 (19), 320 (8), 213 (9), 168 (12), 161 (10), 139 (9), 121 (8), 75 (8), 39 (9). HRMS (EI): Calculated for $C_{24}H_{16}FN$ 337.1261 found 337.1251.

5-Phenylbenzo[c]acridine 4a

2-Phenyl-3-(phenylethynyl)quinoline **3a** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4a** as yellow solid (99 mg, 99%), mp. 101 - 103 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 9.67 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 8.59 (d, ^4J = 0.9 Hz, 1H, CH_{Ar}), 8.42 (dd, ^3J = 8.7 Hz, ^4J = 0.7 Hz, 1H, CH_{Ar}), 8.00 (dd, ^3J = 8.6 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.89 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.86 – 7.76 (m, 2H, CH_{Ar}), 7.72 – 7.64 (m, 2H, CH_{Ar}), 7.63 – 7.49 (m, 6H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 147.8 (C_{Ar}), 147.6 (C_{Ar}), 140.3 (C_{Ar}), 139.6 (C_{Ar}), 135.0 (CH_{Ar}), 133.4 (C_{Ar}), 132.0 (C_{Ar}), 130.0 ($2CH_{Ar}$), 129.9 (CH_{Ar}), 129.7 (CH_{Ar}), 129.0 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.8 (CH_{Ar}), 127.4 (C_{Ar}), 127.2 (CH_{Ar}), 126.6 (CH_{Ar}), 126.1 (CH_{Ar}), 126.0 (CH_{Ar}), 125.7 (CH_{Ar}), 124.9 (C_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3047 (w), 2927 (w), 1486 (m), 1376 (m), 909 (m), 759 (s), 738 (m), 696 (s), 595 (m), 534 (m). MS (EI, 70 eV): *m/z* (%) = 306 (23), 305 ([M]$^+$, 100), 304 (57), 303 (15), 302 (13), 301 (6), 152 (10), 151 (11). HRMS (EI): Calculated for $C_{23}H_{15}N$ 305.1199 found 305.1197.

5-(p-Tolyl)benzo[c]acridine 4b

2-Phenyl-3-(phenylethynyl)quinoline **3b** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4b** as yellow solid (95 mg, 95%), mp. 167 - 169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.67 (dd, ^{3}J = 8.1 Hz, , ^{3}J = 1.0 Hz, 1H, CH_{Ar}), 8.58 (s, 1H, CH_{Ar}), 8.42 (dd, ^{3}J = 8.6 Hz, , ^{4}J = 0.7 Hz, 1H, CH_{Ar}), 7.99 (dd, ^{3}J = 8.3 Hz, , ^{4}J = 0.6 Hz, 1H, CH_{Ar}), 7.93 (dd, ^{3}J = 8.1 Hz, , ^{4}J = 0.8 Hz, 1H, CH_{Ar}), 7.88 – 7.77 (m, 2H, CH_{Ar}), 7.71 – 7.64 (m, 2H, CH_{Ar}), 7.58 (ddd, ^{3}J = 8.0 Hz, , ^{3}J = 6.7 Hz, , ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.52 – 7.47 (m, 2H, CH_{Ar}), 7.37 (d, ^{3}J = 7.8 Hz, 2H, CH_{Ar}), 2.51 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.7 (C_{Ar}), 147.5 (C_{Ar}), 139.5 (C_{Ar}), 137.4 (C_{Ar}), 137.3 (C_{Ar}), 134.8 (CH_{Ar}), 133.5 (C_{Ar}), 131.9 (C_{Ar}), 129.8 (CH_{Ar}), 129.8 ($2CH_{Ar}$), 129.6 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 128.9 (CH_{Ar}), 127.8 (CH_{Ar}), 127.3 (C_{Ar}), 127.1 (CH_{Ar}), 126.6 (CH_{Ar}), 125.9 ($2CH_{Ar}$), 125.6 (CH_{Ar}), 124.9 (C_{Ar}), 21.4 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 3035 (w), 3021 (w), 2957 (w), 2916 (w), 2853 (w), 1903 (w), 1823 (w), 1713 (w), 1563 (w), 1512 (w), 1486 (m), 1372 (m), 913 (m), 816 (m), 764 (s), 744 (m), 709 (m), 517 (m), 472 (m). MS (EI, 70 eV): *m/z* (%) = 320 (25), 319 ($[M]^+$, 100), 318 (36), 317 (8), 316 (11), 304 (17), 303 (14), 159 (13), 152 (11), 41 (15), 39 (11). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1355.

5-(m-Tolyl)benzo[c]acridine 4c

2-Phenyl-3-(phenylethynyl)quinoline **3c** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4c** as yellow oil (91 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.53 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.0 Hz, 1H, CH_{Ar}), 8.43 (s, 1H, CH_{Ar}), 8.29 (d, ^{3}J = 8.7 Hz, 1H, CH_{Ar}), 7.84 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.76 (dd, ^{3}J = 8.1 Hz, ^{4}J = 0.8 Hz, 1H, CH_{Ar}), 7.72 – 7.62 (m, 2H, CH_{Ar}), 7.57 – 7.51 (m, 1H, CH_{Ar}), 7.50 (s, 1H, CH_{Ar}), 7.43 (ddd, ^{3}J = 8.0 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.35 – 7.22 (m, 3H, CH_{Ar}), 7.21 – 7.16 (m, 1H, CH_{Ar}), 2.35 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.6 (C_{Ar}), 147.4 (C_{Ar}), 140.1 (C_{Ar}), 139.6 (C_{Ar}), 138.0 (C_{Ar}), 134.9 (CH_{Ar}), 133.4 (C_{Ar}), 131.7 (C_{Ar}), 130.6 (CH_{Ar}), 129.7 (CH_{Ar}), 129.6 (CH_{Ar}), 128.9 (CH_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 127.7 (CH_{Ar}), 127.2 (C_{Ar}), 127.1 (CH_{Ar}), 127.0 (CH_{Ar}), 126.6 (CH_{Ar}), 125.9 (CH_{Ar}), 125.8 (CH_{Ar}), 125.6 (CH_{Ar}), 124.8 (C_{Ar}), 21.5 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 3035 (w), 2953 (w), 2918 (w), 2855 (w), 2731 (w), 1944 (w), 1711 (m), 1578 (w), 1487 (m), 1371 (m), 1359 (m), 912 (m), 790 (m), 765 (s), 745 (s), 709 (s), 474 (m). MS (EI, 70 eV): *m/z* (%) = 320 (24), 319 ($[M]^+$, 100), 318 (34), 317 (6), 316 (10), 304 (21), 303 (14), 158 (6), 152 (8). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1351.

5-(o-Tolyl)benzo[c]acridine 4d

2-Phenyl-3-(phenylethynyl)quinoline **3d** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4d** as yellow oil (88 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.53 (dd, ^{3}J = 8.1 Hz, ^{4}J = 0.9 Hz, 1H, CH_{Ar}), 8.43 (s, 1H, CH_{Ar}), 8.29 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 7.84 (dd, ^{3}J = 8.3 Hz, ^{4}J = 0.5 Hz, 1H, CH_{Ar}), 7.73 – 7.59 (m, 2H, CH_{Ar}), 7.54 – 7.38 (m, 3H, CH_{Ar}), 7.34 (dd, ^{3}J = 8.1 Hz, ^{4}J = 0.7 Hz, 1H, CH_{Ar}), 7.29 – 7.19 (m, 4H, CH_{Ar}), 1.98 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.7 (C_{Ar}), 147.5 (C_{Ar}), 139.6 (C_{Ar}), 139.2 (C_{Ar}), 137.0 (C_{Ar}), 134.9 (CH_{Ar}), 133.6 (C_{Ar}), 131.6 (C_{Ar}), 130.2 (CH_{Ar}), 130.0 (CH_{Ar}), 129.8 (CH_{Ar}), 129.6 (CH_{Ar}), 129.1 (CH_{Ar}), 128.0 (CH_{Ar}), 127.7 (CH_{Ar}), 127.2 (C_{Ar}), 127.1 (CH_{Ar}), 126.5 (CH_{Ar}), 125.9 (CH_{Ar}), 125.9 (CH_{Ar}), 125.7 (CH_{Ar}), 125.5 (CH_{Ar}), 124.8 (C_{Ar}), 20.1 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 3017 (w), 2953 (w), 2919 (w), 2858 (w), 1944 (w), 1919 (w), 1834 (w), 1711 (m), 1627 (w), 1581 (w), 1486 (m), 1374 (m), 1358 (m), 1218 (m), 917 (m), 765 (s), 746 (m), 728 (m), 710 (m), 527 (m), 475 (m). MS (EI, 70 eV): *m/z* (%) = 320 (22), 319 ($[M]^+$, 100), 318 (88), 317 (30), 316 (33), 315 (8), 304 (7), 303 (7), 158 (13), 157 (7), 152 (10). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1347.

5-(4-Ethylphenyl)benzo[c]acridine 4e

2-Phenyl-3-(phenylethynyl)quinoline **3e** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4e** as yellow solid (70 mg, 70%), mp. 107 - 109 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.55 (dd, ^{3}J = 8.1 Hz, ^{4}J = 0.9 Hz, 1H, CH_{Ar}), 8.47 (s, 1H, CH_{Ar}), 8.31 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 7.88 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.81 (dd, ^{3}J = 8.1 Hz, ^{4}J = 0.8 Hz, 1H, CH_{Ar}), 7.74 – 7.63 (m, 2H, CH_{Ar}), 7.59 – 7.52 (m, 2H, CH_{Ar}), 7.46 (ddd, ^{3}J = 8.0 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.42 – 7.36 (m, 2H, CH_{Ar}), 7.26 (d, ^{3}J = 8.3 Hz, 2H, CH_{Ar}), 2.68 (q, ^{3}J = 7.6 Hz, 2H, CH_2-CH_3), 1.26 (t, ^{3}J = 7.6 Hz, 3H, CH_2-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.5 (C_{Ar}), 147.3 (C_{Ar}), 143.7 (C_{Ar}), 139.5 (C_{Ar}), 137.4 (C_{Ar}), 134.9 (CH_{Ar}), 133.4 (C_{Ar}), 131.7 (C_{Ar}), 129.8 ($2CH_{Ar}$), 129.7 (CH_{Ar}), 129.6 (CH_{Ar}), 128.9 (CH_{Ar}), 127.9 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 127.2 (C_{Ar}), 127.1 (CH_{Ar}), 126.6 (CH_{Ar}), 125.9 (CH_{Ar}), 125.8 (CH_{Ar}), 125.6 (CH_{Ar}), 124.8 (C_{Ar}), 28.7 (CH_2-CH_3), 15.6 (CH_2-CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3050 (w), 3035 (w), 3019 (w), 2954 (w), 2927 (w), 2864 (w), 1909 (w), 1833 (w), 1687 (w), 1564 (w), 1487 (m), 1412 (m), 1372 (m), 911 (m), 830 (m), 820 (m), 763 (s), 743 (s), 707 (m), 591 (m), 476 (m). MS (EI, 70 eV): *m/z* (%) = 334 (26), 333 ($[M]^+$, 100), 332 (10), 319 (9), 318 (38), 317 (13), 316 (19), 304 (15), 303 (7), 159 (10). HRMS (EI): Calculated for $C_{25}H_{19}N$ 333.1512 found 333.1508.

5-(4-Hydroxyphenyl)benzo[c]acridine 4f'

2-Phenyl-3-(phenylethynyl)quinoline **3f** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4f'** as yellow solid (80 mg, 80%), mp. 234 - 236 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 10.10 (s, 1H, OH), 9.33 (d, ^{3}J = 8.8 Hz, 1H, CH_{Ar}), 8.88 (s, 1H, CH_{Ar}), 8.24 (d, ^{3}J = 8.5 Hz, 1H, CH_{Ar}), 8.11 (d, ^{3}J = 7.9 Hz, 1H, CH_{Ar}), 7.84 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.73 (s, 1H, CH_{Ar}), 7.65 – 7.44 (m, 6H, CH_{Ar}), 7.28 (dd, ^{3}J = 8.8 Hz, ^{4}J = 2.4 Hz, 1H, CH_{Ar}), 7.16 (d, ^{3}J = 2.4 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 158.5 (C_{OH}), 146.8 (C_{Ar}), 146.5 (C_{Ar}), 139.4 (C_{Ar}), 138.1 (C_{Ar}), 135.3 (CH_{Ar}), 134.5 (C_{Ar}), 129.8 (CH_{Ar}), 129.3 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.5 (CH_{Ar}), 126.9 (CH_{Ar}), 126.1 (CH_{Ar}), 126.1 (C_{Ar}), 125.3 (CH_{Ar}), 123.4 (C_{Ar}), 123.1 (C_{Ar}), 116.8 (CH_{Ar}), 110.2 (CH_{Ar}). IR (ATR, cm^{-1}): ṽ = 3045 (w), 2922 (w), 1603 (w), 1487 (m), 1284 (m), 1221 (m), 1207 (m), 870 (m), 764 (m), 749 (s), 701 (s), 539 (m). MS (EI, 70 eV): *m/z* (%) = 322 (24), 321 ([M]$^{+}$, 100), 320 (26), 304 (8), 292 (10), 291 (22), 290 (8), 151 (14), 146 (14). HRMS (ESI): Calculated for $C_{23}H_{15}NO$ $[M+H]^{+}$ 322.123 found 322.124.

5-(4-Fluorophenyl)benzo[c]acridine 4g

2-Phenyl-3-(phenylethynyl)quinoline **3g** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4g** as yellow solid (96 mg, 96%), mp. 143 - 145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.53 – 9.48 (m, 1H, CH_{Ar}), 8.38 (s, 1H, CH_{Ar}), 8.25 (dd, ^{3}J = 8.6 Hz, ^{4}J = 0.7 Hz, 1H, CH_{Ar}), 7.82 (dd, ^{3}J = 8.8 Hz, ^{4}J = 0.6 Hz, 1H, CH_{Ar}), 7.71 – 7.61 (m, 3H, CH_{Ar}), 7.52 (ddd, ^{3}J = 9.0 Hz, ^{3}J = 6.2 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.46 – 7.34 (m, 4H, CH_{Ar}), 7.13 – 7.04 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.6 (d, $^{1}J_{CF}$ = 246.7 Hz, C_{FAr}), 147.9 (C_{Ar}), 147.5 (C_{Ar}), 138.4 (C_{Ar}), 136.2 (d, $^{4}J_{CF}$ = 3.4 Hz, C_{Ar}), 135.0 (CH_{Ar}), 133.3 (C_{Ar}), 131.9 (C_{Ar}), 131.6 (d, $^{3}J_{CF}$ = 8.0 Hz, $2CH_{Ar}$), 129.9 (CH_{Ar}) , 129.8 (CH_{Ar}), 129.1 (CH_{Ar}), 127.8 (CH_{Ar}), 127.4 (C_{Ar}), 127.3 (CH_{Ar}), 126.4 (CH_{Ar}), 126.3 (CH_{Ar}), 126.1 (CH_{Ar}), 125.7 (CH_{Ar}), 124.7 (C_{Ar}), 115.5 (d, $^{2}J_{CF}$ = 21.4 Hz, $2CH_{Ar}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.51 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 3056 (w), 3035 (w), 1827 (w), 1598 (w), 1506 (m), 1486 (m), 1375 (m), 1211 (m), 1161 (m), 914 (m), 845 (m), 818 (m), 767 (s), 749 (m), 709 (m), 520 (m), 472 (m), 405 (m). MS (EI, 70 eV): *m/z* (%) = 324 (24), 323 ([M]$^{+}$, 100), 322 (59), 321 (16), 320 (8), 319 (5), 161 (10), 160 (6), 151 (5). HRMS (EI): Calculated for $C_{23}H_{14}FN$ 323.1105 found 323.1102.

5-(Thiophen-3-yl)benzo[c]acridine 4h

2-Phenyl-3-(phenylethynyl)quinoline **3h** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4h** as yellow solid (30 mg, 30%), mp. 94 - 96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.56 (d, ^{3}J = 7.6 Hz, 1H, CH_{Ar}), 8.52 (s, 1H, CH_{Ar}), 8.33 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 7.93 (dd, ^{3}J = 8.1 Hz, ^{4}J = 0.8 Hz, 2H, CH_{Ar}), 7.78 – 7.67 (m, 2H, CH_{Ar}), 7.67 – 7.58 (m, 2H, CH_{Ar}), 7.50 (ddd, ^{3}J = 6.7 Hz, ^{3}J = 5.2 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.44 – 7.41 (m, 2H, CH_{Ar}), 7.32 – 7.27 (m, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.6 (C_{Ar}), 147.3 (C_{Ar}), 140.5 (C_{Ar}), 135.0 (CH_{Ar}), 134.3 (C_{Ar}), 133.3 (C_{Ar}), 129.9 (C_{Ar}) 129.7 (CH_{Ar}), 129.7 (CH_{Ar}), 129.4 (CH_{Ar}), 129.1 (CH_{Ar}), 127.7 (CH_{Ar}), 127.2 ($2CH_{Ar}$), 126.2 (CH_{Ar}), 126.0 ($2CH_{Ar}$), 125.7 (C_{Ar}) 125.6 (CH_{Ar}), 124.7 (C_{Ar}), 123.9 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3106 (w), 2919 (w), 2850 (w), 1948 (w), 1939 (w), 1903 (w), 1821 (w), 1721 (w), 1579 (w), 1486 (m), 909 (m), 853 (m), 791 (m), 760 (s), 742 (m), 706 (m), 652 (m), 621 (m). MS (EI, 70 eV): *m/z* (%) = 313 (7), 312 (25), 311 ($[M]^+$, 100), 310 (66), 309 (16), 266 (8), 264 (5), 155 (5), 134 (10), 133 (6). HRMS (EI): Calculated for $C_{21}H_{13}NS$ 311.0763 found 311.0756.

3-Methyl-5-phenylbenzo[c]acridine 4i

2-Phenyl-3-(phenylethynyl)quinoline **3i** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4i** as yellow solid (95 mg, 95%), mp. 166 - 167 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.53 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 8.60 (s, 1H, CH_{Ar}), 8.40 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 8.01 (dd, ^{3}J = 8.3 Hz, ^{4}J = 0.5 Hz, 1H, CH_{Ar}), 7.82 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.69 – 7.47 (m, 9H, CH_{Ar}), 2.52 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.9 (C_{Ar}), 147.7 (C_{Ar}), 140.5 (C_{Ar}), 139.5 (C_{Ar}), 139.2 (C_{Ar}), 135.0 (CH_{Ar}), 133.5 (C_{Ar}), 130.0 (C_{Ar}), 130.0 ($2CH_{Ar}$), 129.8 (CH_{Ar}), 129.7 (CH_{Ar}), 128.8 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.7 (CH_{Ar}), 127.3 (C_{Ar}), 126.5 (CH_{Ar}), 126.3 (CH_{Ar}), 125.9 (CH_{Ar}), 125.7 (CH_{Ar}), 124.7 (C_{Ar}), 22.1 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3045 (w), 3024 (w), 2912 (w), 2852 (w), 1609 (m), 1485 (m), 1432 (m), 1365 (m), 915 (m), 792 (m), 766 (m), 744 (s), 705 (s). MS (EI, 70 eV): *m/z* (%) = 321 (4), 320 (27), 319 ($[M]^+$, 100), 318 (23), 317 (8), 316 (11), 315 (6), 305 (6), 304 (27), 303 (12), 302 (6), 160 (6), 158 (7), 157 (6), 152 (18), 151 (8), 51 (4). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1356.

2-Methyl-5-phenylbenzo[c]acridine and 4-Methyl-5-phenylbenzo[c]acridine 4j

2-Phenyl-3-(phenylethynyl)quinoline **3k** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4j** as yellow oil (95 mg, 95%).

Isomer $4j_1$

^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.47 (s, 1H, CH_{Ar}), 8.55 (s, 1H, CH_{Ar}), 8.43 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.97 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 7.86 – 7.81 (m, 1H, CH_{Ar}), 7.81 – 7.77 (m, 1H, CH_{Ar}), 7.62 – 7.44 (m, 8H, CH_{Ar}), 2.71 (s, 3H, CH_3).

Isomer $4j_2$

^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.69 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1H, CH_{Ar}), 8.49 (s, 1H, CH_{Ar}), 8.41 (d, ^3J = 7.1 Hz, 1H, CH_{Ar}), 7.96 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.81 – 7.77 (m, 1H, CH_{Ar}), 7.72 – 7.66 (m, 1H, CH_{Ar}), 7.62 – 7.44 (m, 8H, CH_{Ar}), 2.06 (s, 3H, CH_3).

Isomer $4j_1$ and Isomer $4j_2$

^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.9 (C_{Ar}), 147.8 (C_{Ar}), 147.6 (C_{Ar}), 147.4 (C_{Ar}), 144.8 (C_{Ar}), 140.4 (C_{Ar}), 139.7 (C_{Ar}), 139.5 (C_{Ar}), 137.3 (C_{Ar}), 135.9 (C_{Ar}), 135.0 (CH_{Ar}), 134.5 (CH_{Ar}), 133.4 (CH_{Ar}), 133.1 (C_{Ar}), 132.0 (C_{Ar}), 131.8 (C_{Ar}), 131.2 (C_{Ar}), 130.5 (CH_{Ar}), 130.0 ($2CH_{Ar}$), 129.9 (CH_{Ar}), 129.8 (CH_{Ar}), 129.6 ($2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 127.8 (CH_{Ar}), 127.8 (CH_{Ar}), 127.7 (CH_{Ar}), 127.4 (C_{Ar}), 127.3 (C_{Ar}), 127.2 (CH_{Ar}), 127.0 (CH_{Ar}), 126.6 (CH_{Ar}), 125.9 (CH_{Ar}), 125.9 (CH_{Ar}), 125.5 (CH_{Ar}), 125.1 (CH_{Ar}), 125.1 (C_{Ar}), 124.2 (CH_{Ar}), 124.0 (C_{Ar}), 25.1 (CH_3), 21.9 (CH_3).

IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 3023 (w), 2962 (w), 2919 (w), 2859 (w), 1711 (m), 1620 (w), 1579 (w), 1495 (m), 1484 (m), 1441 (m), 1359 (m), 1218 (m), 911 (m), 824 (m), 768 (m), 745 (s), 700 (s), 530 (m), 475 (m). MS (EI, 70 eV): *m/z* (%) = 320 (26), 319 ($[M]^+$, 100), 318 (32), 317 (11), 316 (11), 315 (7), 304 (10), 303 (9), 158 (13), 152 (14), 151 (6). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1355.

1-Methyl-5-phenylbenzo[c]acridine 4k

2-Phenyl-3-(phenylethynyl)quinoline **3l** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4k** as yellow solid (86 mg, 86%), mp. 120 - 122 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.56 (s, 1H, CH_{Ar}), 8.40 (dd, ^3J = 8.6 Hz, ^4J = 0.8 Hz, 1H, CH_{Ar}), 7.99 (dd, ^3J = 8.3 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.85 – 7.73 (m, 2H, CH_{Ar}), 7.64 (s, 1H, CH_{Ar}), 7.63 – 7.58 (m, 2H,

CH_{Ar}), 7.58 – 7.48 (m, 6H, CH_{Ar}), 3.61 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 150.0 (C_{Ar}), 146.9 (C_{Ar}), 141.2 (C_{Ar}), 140.2 ($2C_{Ar}$), 135.1 (C_{Ar}), 134.1 (CH_{Ar}), 131.8 (CH_{Ar}), 130.2 (C_{Ar}), 130.1 (CH_{Ar}), 130.1 ($2CH_{Ar}$), 129.2 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 126.5 (CH_{Ar}), 126.1 (CH_{Ar}), 126.1 (C_{Ar}), 125.8 (C_{Ar}), 125.5 (CH_{Ar}), 28.1 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3045 (w), 3020 (w), 2965 (w), 2922 (w), 1582 (m), 1563 (m), 1482 (m), 1443 (m), 1426 (m), 1378 (m), 1008 (m), 996 (m), 913 (m), 846 (m), 814 (m), 790 (m), 772 (m), 765 (m), 741 (s), 712 (m), 700 (s), 656 (m). MS (EI, 70 eV): *m/z* (%) = 320 (23), 319 ($[M]^+$, 100), 318 (48), 317 (18), 316 (9), 315 (9), 304 (8), 303 (6), 159 (6), 158 (19), 152 (12). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1350.

3-Methoxy-5-phenylbenzo[c]acridine 4l

2-Phenyl-3-(phenylethynyl)quinoline **3m** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave 4l as yellow oil (10 mg, 10%). ^1H NMR (250 MHz, $CDCl_3$) δ = 9.57 (d, ^3J = 8.9 Hz, 1H, CH_{Ar}), 8.61 (s, 1H, CH_{Ar}), 8.39 (d, ^3J = 8.7 Hz, 1H, CH_{Ar}), 8.01 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 7.81 (ddd, ^3J = 8.5 Hz, ^3J = 6.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.67 (s, 1H, CH_{Ar}), 7.63 – 7.48 (m, 6H, CH_{Ar}), 7.39 (dd, ^3J = 9.0 Hz, ^4J = 2.6 Hz, 1H, CH_{Ar}), 7.31 – 7.27 (m, 1H, CH_{Ar}), 3.85 (s, 3H, CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 2997 (w), 2961 (w), 2922 (w), 2855 (w), 1606 (m), 1487 (m), 1256 (m), 1222 (m), 1094 (m), 1072 (m), 1029 (m), 1015 (m), 915 (m), 833 (m), 802 (m), 787 (s), 764 (m), 744 (m), 697 (m), 586 (m), 530 (m), 448 (m). MS (EI, 70 eV): *m/z* (%) = 336 (29), 335 ($[M]^+$, 100), 320 (16), 304 (9), 292 (10), 291 (36), 290 (17), 160 (10), 146 (24), 144 (9). HRMS (EI): Calculated for $C_{24}H_{17}NO$ 335.1305 found 335.1303.

3-Hydroxy-5-phenylbenzo[c]acridine 4l'

2-Phenyl-3-(phenylethynyl)quinoline **3m** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4l'** as yellow solid (84 mg, 84%), mp. 235 - 237 °C. ^1H NMR (300 MHz, DMSO-d_6) δ = 10.11 (s, 1H, OH), 9.34 (d, ^3J = 8.8 Hz, 1H, CH_{Ar}), 8.90 (s, 1H, CH_{Ar}), 8.25 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.12 (d, ^3J = 7.9 Hz, 1H, CH_{Ar}), 7.86 (ddd, ^3J = 8.5 Hz, ^3J = 6.7 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.74 (s, 1H, CH_{Ar}), 7.65 – 7.49 (m, 6H, CH_{Ar}), 7.30 (dd, ^3J = 8.8 Hz, ^4J = 2.5 Hz, 1H, CH_{Ar}), 7.17 (d, ^3J = 2.4 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 159.1 (C_{OH}), 147.4 (C_{Ar}), 147.1 (C_{Ar}), 140.0 (C_{Ar}), 138.7 (C_{Ar}), 135.8 (CH_{Ar}), 135.0 (C_{Ar}), 130.4 (CH_{Ar}), 129.9 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 128.9 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.1 (CH_{Ar}), 127.4 (CH_{Ar}), 126.7 (CH_{Ar}), 126.7 (C_{Ar}), 125.9 (CH_{Ar}), 124.0 (C_{Ar}), 123.7 (C_{Ar}), 117.3

(CH_{Ar}), 110.7 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3045 (w), 2922 (w), 1603 (w), 1487 (m), 1284 (m), 1221 (m), 1207 (m), 870 (m), 764 (m), 749 (s), 701 (s), 539 (m). MS (EI, 70 eV): *m/z* (%) = 322 (24), 321 ($[M]^+$, 100), 320 (26), 304 (8), 292 (11), 291 (30), 290 (12), 151 (19), 146 (21), 145 (8), 131 (8). HRMS (ESI): Calculated for $C_{23}H_{15}NO$ $[M+H]^+$ 322.1232 found 322.1237.

3-Fluoro-5-phenylbenzo[c]acridine 4m

2-Phenyl-3-(phenylethynyl)quinoline **3n** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4m** as white solid (68 mg, 68%), mp. 130 - 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.63 (dd, ^3J = 8.8 Hz, ^3J = 6.0 Hz, 1H, CH_{Ar}), 8.55 (s, 1H, CH_{Ar}), 8.37 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.97 (ddd, ^3J = 7.8 Hz, ^4J = 4.2 Hz, ^4J = 3.6 Hz, 1H, CH_{Ar}), 7.82 (ddd, ^3J = 8.6 Hz, ^3J = 6.7 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.67 (s, 1H, CH_{Ar}), 7.59 – 7.52 (m, 6H, CH_{Ar}), 7.52 – 7.44 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.4 (d, $^1J_{CF}$ = 248.0 Hz, C_{FAr}), 148.0 (C_{Ar}), 147.0 (C_{Ar}), 139.7 (C_{Ar}), 138.8 (d, $^4J_{CF}$ = 3.3 Hz, C_{Ar}), 135.3 (CH_{Ar}), 135.3 (d, $^3J_{CF}$ = 7.5 Hz, C_{Ar}), 130.0 (CH_{Ar}), 129.9 ($2CH_{Ar}$), 129.8 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.4 (d, $^4J_{CF}$ = 1.5 Hz, C_{Ar}), 128.4 (d, $^3J_{CF}$ = 9.0 Hz, CH_{Ar}), 128.1 (CH_{Ar}), 127.9 (CH_{Ar}), 127.3 (CH_{Ar}), 127.2 (C_{Ar}), 126.1 (CH_{Ar}), 124.3 (C_{Ar}), 115.6 (d, $^2J_{CF}$ = 23.1 Hz, CH_{Ar}), 111.7 (d, $^2J_{CF}$ = 22.9 Hz, CH_{Ar}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.77 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3058 (w), 3029 (w), 2923 (w), 1609 (m), 1485 (m), 1454 (m), 1441 (m), 1362 (m), 1236 (m), 1214 (m), 1191 (m), 1123 (m), 974 (m), 912 (m), 888 (m), 866 (m), 830 (m), 789 (m), 762 (m), 745 (s), 697 (s), 587 (m), 530 (m). MS (EI, 70 eV): *m/z* (%) = 324 (24), 323 ($[M]^+$, 46), 322 (45), 321 (14), 320 (6), 161 (8), 160 (6). HRMS (EI): Calculated for $C_{23}H_{14}FN$ 323.1105 found 323.1105.

3-Fluoro-5-(p-tolyl)benzo[c]acridine 4n

2-Phenyl-3-(phenylethynyl)quinoline **3o** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4n** as yellow solid (60 mg, 60%), mp. 157 - 159 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.63 (dd, ^3J = 8.9 Hz, ^3J = 6.1 Hz, 1H, CH_{Ar}), 8.57 (s, 1H, CH_{Ar}), 8.37 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 7.99 (dd, ^3J = 8.3 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.85 – 7.78 (m, 1H, CH_{Ar}), 7.67 (s, 1H, CH_{Ar}), 7.61 – 7.56 (m, 1H, CH_{Ar}), 7.56 – 7.50 (m, 1H, CH_{Ar}), 7.49 – 7.43 (m, 3H, CH_{Ar}), 7.39 – 7.34 (m, 2H, CH_{Ar}), 2.50 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.4 (d, $^1J_{CF}$ = 247.9 Hz, C_{FAr}), 147.9 (C_{Ar}), 147.0 (C_{Ar}), 138.9 (d, $^4J_{CF}$ = 3.3 Hz, C_{Ar}), 137.9 (C_{Ar}),

136.8 (C_{Ar}), 135.5 (d, $^{3}J_{CF}$ = 8.7 Hz, C_{Ar}), 135.2 (CH_{Ar}), 130.0 (CH_{Ar}), 129.8 (CH_{Ar}), 129.7 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 128.4 (d, $^{4}J_{CF}$ = 1.3 Hz, C_{Ar}), 128.3 (d, $^{3}J_{CF}$ = 9.0 Hz, CH_{Ar}), 127.9 (CH_{Ar}), 127.3 (C_{Ar}), 127.2 (CH_{Ar}), 126.1 (CH_{Ar}), 124.4 (C_{Ar}), 115.6 (d, $^{2}J_{CF}$ = 23.1 Hz, CH_{Ar}), 111.8 (d, $^{2}J_{CF}$ = 22.9 Hz, CH_{Ar}), 21.4 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.88 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 3053 (w), 3022 (w), 2960 (w), 2923 (w), 2868 (w), 1606 (m), 1485 (m), 1453 (m), 1184 (m), 917 (m), 873 (m), 852 (m), 832 (m), 821 (m), 786 (s), 745 (s), 570 (m), 467 (m). MS (EI, 70 eV): *m/z* (%) = 338 (26), 337 ($[M]^+$, 100), 336 (21), 335 (7), 334 (9), 322 (15), 321 (11), 167 (13), 161 (8). HRMS (EI): Calculated for $C_{24}H_{16}FN$ 337.1261 found 337.1258.

5-(4-Fluorophenyl)-3-methylbenzo[c]acridine 4o

2-Phenyl-3-(phenylethynyl)quinoline **3j** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **4o** as white solid (96 mg, 96%), mp. 163 - 165 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.57 (d, ^{3}J = 8.2 Hz, 1H, CH_{Ar}), 8.63 (s, 1H, CH_{Ar}), 8.44 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 8.05 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.87 (ddd, ^{3}J = 8.5 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.70 – 7.54 (m, 6H, CH_{Ar}), 7.33 – 7.27 (m, 2H, CH_{Ar}), 2.57 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.6 (d, $^{1}J_{CF}$ = 246.5 Hz, C_{FAr}), 147.9 (C_{Ar}), 147.7 (C_{Ar}), 139.3 (C_{Ar}), 138.4 (C_{Ar}), 136.4 (d, $^{4}J_{CF}$ = 3.4 Hz, C_{Ar}), 135.1 (CH_{Ar}), 133.5 (C_{Ar}), 131.6 (d, $^{3}J_{CF}$ = 8.0 Hz, $2CH_{Ar}$), 129.8 (CH_{Ar}), 129.8 (CH_{Ar}), 129.7 (C_{Ar}), 128.9 (CH_{Ar}), 127.9 (CH_{Ar}), 127.3 (C_{Ar}), 126.4 (CH_{Ar}), 126.3 (CH_{Ar}), 125.9 (CH_{Ar}), 125.8 (CH_{Ar}), 124.5 (C_{Ar}), 115.5 (d, $^{2}J_{CF}$ = 21.4 Hz, $2CH_{Ar}$), 22.1 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.69 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 3059 (w), 2920 (w), 2854 (w), 1599 (w), 1507 (m), 1486 (m), 1223 (m), 1159 (m), 912 (m), 838 (m), 816 (m), 798 (m), 742 (s), 571 (m). MS (EI, 70 eV): *m/z* (%) = 338 (27), 337 ($[M]^+$, 100), 336 (20), 335 (8), 334 (10), 322 (19), 321 (8), 161 (13). HRMS (EI): Calculated for $C_{24}H_{16}FN$ 337.1261 found 337.1257.

3-Bromo-2-(phenylethynyl)quinoline 5a

3-Bromo-2-iodoquinoline **1** (0.8 mmol), alkyne (1.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 mmol) and CuI (0.08 mmol) in 3.0 ml of triethylamine gave **5a** as yellow solid (173 mg, 94%), mp. 94 - 96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.41 (s, 1H, CH_{Ar}), 8.13 – 8.08 (m, 1H, CH_{Ar}), 7.78 – 7.67 (m, 4H, CH_{Ar}), 7.60 – 7.52 (m, 1H, CH_{Ar}), 7.44 – 7.36 (m, 3H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.8 (C_{Ar}), 143.5 (C_{Ar}), 138.7 (CH_{Ar}), 132.5 ($2CH_{Ar}$), 130.5 (CH_{Ar}),

129.7 (CH_{Ar}), 129.4 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 128.2 (C_{Ar}), 128.2 (CH_{Ar}), 126.7 (CH_{Ar}), 122.0 (C_{Ar}), 119.8 (C_{Ar}), 94.4 (C_{Alkyne}), 88.2 (C_{Alkyne}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 3049 (w), 3032 (w), 2963 (w), 2919 (w), 2850 (w), 2216 (m), 1929 (w), 1892 (w), 1808 (w), 1764 (w), 1613 (w), 1593 (w), 1574 (m), 1488 (m), 1396 (m), 1373 (m), 1125 (m), 987 (m), 905 (m), 855 (m), 776 (m), 760 (s), 747 (s), 692 (m), 619 (m), 526 (m), 473 (m). MS (EI, 70 eV): *m/z* (%) = 310 (17), 309 ($[M]^+$, 99), 308 (22), 307 ($[M]^+$, 100), 228 (39), 227 (62), 226 (14), 201 (16), 200 (26), 127 (42), 101 (40), 100 (23), 99 (11), 98 (10), 87 (10), 77 (10), 76 (11), 75 (42), 74 (18), 63 (13), 51 (23), 50 (14), 39 (11). HRMS (EI): Calculated for $C_{17}H_{10}{}^{79}BrN$ 306.9991 found 306.9989, calculated for $C_{17}H_{10}{}^{81}BrN$ 308.9971 found 308.9971.

3-Bromo-2-((4-(tert-butyl)phenyl)ethynyl)quinoline 5b

3-Bromo-2-iodoquinoline **1** (0.8 mmol), alkyne (1.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 mmol) and CuI (0.08 mmol) in 3.0 ml of triethylamine gave **5b** as yellow solid (195 mg, 89%), mp. 135 - 137 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.40 (s, 1H, CH_{Ar}), 8.10 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.76 – 7.70 (m, 2H, CH_{Ar}), 7.66 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.58 – 7.52 (m, 1H, CH_{Ar}), 7.42 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 1.34 (s, 9H, $3CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 153.2 (C_{Ar}), 146.7 (C_{Ar}), 143.7 (C_{Ar}), 138.6 (CH_{Ar}), 132.3 ($2CH_{Ar}$), 130.4 (CH_{Ar}), 129.3 (CH_{Ar}), 128.2 (C_{Ar}), 128.0 (CH_{Ar}), 126.7 (CH_{Ar}), 125.6 ($2CH_{Ar}$), 119.8 (C_{Ar}), 119.0 (C_{Ar}), 95.0 (C_{Alkyne}), 87.8 (C_{Alkyne}), 35.1 ($C(CH_3)_3$), 31.3 ($3CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3058 (w), 2969 (m), 2956 (m), 2931 (w), 2903 (w), 2864 (w), 2216 (m), 1575 (m), 1504 (m), 1483 (m), 1395 (m), 1365 (m), 1104 (m), 985 (m), 912 (m), 833 (s), 778 (m), 754 (s), 559 (m), 475 (m). MS (EI, 70 eV): *m/z* (%) = 366 (11), 365 ($[M]^+$, 44), 363 ($[M]^+$, 43), 351 (20), 350 (100), 349 (23), 348 (94), 322 (10), 240 (10), 228 (13), 227 (22). 161 (14), 160 (12), 140 (28), 127 (14), 101 (39), 75 (25), 51 (10), 41 (35), 39 (18). HRMS (EI): Calculated for $C_{21}H_{18}{}^{79}BrN$ 363.0617 found 363.0612, calculated for $C_{21}H_{18}{}^{81}BrN$ 365.0597 found 365.0596.

3-Bromo-2-((4-fluorophenyl)ethynyl)quinoline 5c

3-Bromo-2-iodoquinoline **1** (0.8 mmol), alkyne (1.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 mmol) and CuI (0.08 mmol) in 3.0 ml of triethylamine gave **5c** as white solid (175 mg, 90%), mp. 150 - 152 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.41 (s, 1H, CH_{Ar}), 8.09 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.77 – 7.66 (m, 4H, CH_{Ar}), 7.56 (ddd, ^3J = 7.6 Hz, ^3J = 6.2 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.14 – 7.05 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.4 (d, $^1J_{CF}$ = 251.6 Hz, C_{FAr}), 146.8

(C_{Ar}), 143.4 (C_{Ar}), 138.7 (CH_{Ar}), 134.6 (d, $^{3}J_{CF}$ = 8.6 Hz, $2CH_{Ar}$), 130.5 (CH_{Ar}), 129.4 (CH_{Ar}), 128.2 (C_{Ar}), 128.2 (CH_{Ar}), 126.7 (CH_{Ar}), 119.6 (C_{Ar}), 118.2 (d, $^{4}J_{CF}$ = 3.5 Hz, C_{Ar}), 116.0 (d, $^{2}J_{CF}$ = 22.2 Hz, $2CH_{Ar}$), 93.2 (C_{Alkyne}), 88.0 (C_{Alkyne}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -108.58 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 3054 (w), 2984 (w), 2216 (m), 1596 (w), 1578 (w), 1506 (m), 1483 (m), 1226 (m), 1153 (m), 1142 (m), 1124 (m), 987 (m), 832 (s), 777 (m), 747 (s), 701 (m), 526 (m), 460 (m), 456 (m), 399 (m). MS (EI, 70 eV): *m/z* (%) = 328 (17), 327 ($[M]^+$, 97), 326 (21), 325 ($[M]^+$, 100), 246 (30), 245 (56), 219 (11), 218 (22), 145 (51), 123 (13), 101 (39), 99 (13), 75 (45), 74 (16), 63 (10), 51 (20), 50 (13). HRMS (EI): Calculated for $C_{17}H_9{}^{79}BrFN$ 324.9897 found 324.9893, calculated for $C_{17}H_9{}^{81}BrFN$ 326.9877 found 326.9876.

3-Phenyl-2-(phenylethynyl)quinoline 6a

3-Bromo-2-(phenylethynyl)quinoline **5a** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **6a** as yellow oil (108 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.19 (d, ^{3}J = 8.6 Hz, 1H, CH_{Ar}), 8.15 (s, 1H, CH_{Ar}), 7.83 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.78 – 7.70 (m, 3H, CH_{Ar}), 7.60 – 7.47 (m, 4H, CH_{Ar}), 7.44 – 7.39 (m, 2H, CH_{Ar}), 7.35 – 7.27 (m, 3H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.3 (C_{Ar}), 142.6 (C_{Ar}), 138.6 (C_{Ar}), 137.4 (C_{Ar}), 136.0 (CH_{Ar}), 132.2 ($2CH_{Ar}$), 130.1 (CH_{Ar}), 129.8 ($2CH_{Ar}$), 129.2 (CH_{Ar}), 129.1 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 128.2 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.4 (C_{Ar}), 122.4 (C_{Ar}), 93.1 (C_{Alkyne}), 89.3 (C_{Alkyne}). IR (ATR, cm^{-1}): ṽ = 3054 (w), 3033 (w), 2924 (w), 2853 (w), 2213 (m), 1950 (w), 1587 (m), 1489 (m), 1404 (m), 1371 (m), 1150 (m), 908 (m), 789 (m), 751 (s), 726 (m), 697 (s), 687 (s), 598 (m), 534 (m), 496 (m). MS (EI, 70 eV): *m/z* (%) = 306 (14), 305 (66), 304 ($[M]^+$, 100), 303 (12), 302 (17), 301 (6), 152 (12), 151 (15), 150 (6). HRMS (EI): Calculated for $C_{23}H_{14}N$ 304.1121 found 304.1124.

2-(Phenylethynyl)-3-(p-tolyl)quinoline 6b

3-Bromo-2-(phenylethynyl)quinoline **5a** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **6b** as yellow solid (188 mg, 60%), mp. 132 - 134 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (d, ^{3}J = 8.8 Hz, 1H, CH_{Ar}), 8.13 (s, 1H, CH_{Ar}), 7.81 (d, ^{3}J = 8.1 Hz, 1H, CH_{Ar}), 7.72 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.67 – 7.62 (m, 2H, CH_{Ar}), 7.55 (ddd, ^{3}J = 8.1 Hz,

^{3}J = 7.0 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Ar}), 7.48 – 7.43 (m, 2H, CH_{Ar}), 7.36 – 7.28 (m, 5H, CH_{Ar}), 2.47 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.2 (C_{Ar}), 142.7 (C_{Ar}), 138.1 (C_{Ar}), 137.2 (C_{Ar}), 135.9 (CH_{Ar}), 135.6 (C_{Ar}), 132.1 ($2CH_{Ar}$), 129.9 (CH_{Ar}), 129.6 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 129.1 (CH_{Ar}), 129.0 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 127.5 (C_{Ar}), 122.5 (C_{Ar}), 92.9 (C_{Alkyne}), 89.5 (C_{Alkyne}), 21.4 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3019 (w), 2962 (w), 2913 (w), 2856 (w), 2725 (w), 2213 (w), 1585 (w), 1491 (m), 1483 (m), 1399 (m), 1371 (m), 1150 (m), 918 (m), 911 (m), 837 (m), 811 (m), 789 (m), 748 (s), 734 (m), 686 (m), 595 (m), 534 (m), 497 (m). MS (EI, 70 eV): *m/z* (%) = 320 (15), 319 (75), 318 ($[M]^+$, 100), 317 (16), 316 (11), 315 (9), 305 (7), 304 (29), 303 (11), 302 (10), 189 (6), 158 (8), 152 (11), 151 (9), 63 (54). HRMS (EI): Calculated for $C_{24}H_{16}N$ 318.1277 found 318.1276.

2-((4-(tert-Butyl)phenyl)ethynyl)-3-phenylquinoline 6c

3-Bromo-2-(phenylethynyl)quinoline **5b** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **6c** as yellow oil (97 mg, 49%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.19 (d, ^{3}J = 8.8 Hz, 1H, CH_{Ar}), 8.14 (s, 1H, CH_{Ar}), 7.83 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.0 Hz, 1H, CH_{Ar}), 7.77 – 7.69 (m, 3H, CH_{Ar}), 7.59 – 7.46 (m, 4H, CH_{Ar}), 7.39 – 7.31 (m, 4H, CH_{Ar}), 1.31 (s, 9H, $3CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.6 (C_{Ar}), 147.4 (C_{Ar}), 142.9 (C_{Ar}), 138.7 (C_{Ar}), 137.4 (C_{Ar}), 135.9 (CH_{Ar}), 132.0 ($2CH_{Ar}$), 130.0 (CH_{Ar}), 129.8 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 128.2 ($2CH_{Ar}$), 128.2 (CH_{Ar}), 127.7 (CH_{Ar}), 127.5 (CH_{Ar}), 127.3 (C_{Ar}), 125.5 ($2CH_{Ar}$), 119.3 (C_{Ar}), 93.5 (C_{Alkyne}), 88.9 (C_{Alkyne}), 35.0 ($C(CH_3)_3$), 31.2 ($3CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3035 (w), 2960 (w), 2904 (w), 2867 (w), 2213 (w), 1505 (w), 1484 (w), 1404 (m), 1103 (m), 907 (m), 834 (m), 789 (m), 752 (m), 727 (s), 697 (s), 561 (m). MS (EI, 70 eV): *m/z* (%) = 362 (24), 361 ($[M]^+$, 96), 360 (42), 347 (26), 346 (100), 344 (16), 330 (24), 328 (16), 317 (14), 316 (12), 305 (11), 304 (43), 303 (12), 302 (15), 217 (11), 159 (18), 158 (10), 151 (14), 41 (23), 39 (11). HRMS (EI): Calculated for $C_{27}H_{23}N$ 361.1825 found 361.1817.

2-((4-Fluorophenyl)ethynyl)-3-phenylquinoline 6d

3-Bromo-2-(phenylethynyl)quinoline **5c** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(dppf)Cl_2$ (0.06 mmol) and Cs_2CO_3 (1.2 mmol) in 2.0 ml of dry THF gave **6d** as white solid (116 mg, 58%), mp. 121 - 123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (dd, ^{3}J = 8.3 Hz,

^4J = 0.9 Hz, 1H, CH_{Ar}), 8.15 (d, ^4J = 0.8 Hz, 1H, CH_{Ar}), 7.86 – 7.80 (m, 1H, CH_{Ar}), 7.78 – 7.69 (m, 3H, CH_{Ar}), 7.60 – 7.46 (m, 4H, CH_{Ar}), 7.42 – 7.34 (m, 2H, CH_{Ar}), 7.04 – 6.95 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.1 (d, $^1J_{CF}$ = 251.1 Hz, C_{FAr}), 147.3 (C_{Ar}), 142.5 (C_{Ar}), 138.6 (C_{Ar}), 137.3 (C_{Ar}), 136.0 (CH_{Ar}), 134.2 (d, $^3J_{CF}$ = 8.6 Hz, $2CH_{Ar}$), 130.2 (CH_{Ar}), 129.8 ($2CH_{Ar}$), 129.8 (CH_{Ar}), 129.1 ($2CH_{Ar}$), 128.3 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.4 (C_{Ar}), 118.5 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 115.8 (d, $^2J_{CF}$ = 22.1 Hz, $2CH_{Ar}$), 92.0 (C_{Alkyne}), 89.1 (C_{Alkyne}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -109.21 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 3021 (w), 2209 (w), 1903 (w), 1801 (w), 1587 (w), 1504 (m), 1482 (m), 1227 (m), 1215 (m), 1146 (m), 1140 (m), 897 (m), 875 (m), 785 (m), 745 (s), 694 (s), 534 (m), 468 (m), 398 (m). MS (EI, 70 eV): *m/z* (%) = 324 (11), 323 (61), 322 ($[M]^+$, 100), 321 (11), 320 (11), 319 (6), 161 (25), 160 (24), 151 (12), 150 (8), 147 (8), 146 (6). HRMS (EI): Calculated for $C_{23}H_{13}FN$ 322.1027 found 322.1026.

5-Phenylbenzo[a]acridine 7a

3-Phenyl-2-(phenylethynyl)quinoline **6a** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **7a** as white solid (90 mg, 90%), mp. 144 - 146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.46 (s, 1H, CH_{Ar}), 8.85 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 8.30 (d, ^3J = 8.6 Hz, 1H, CH_{Ar}), 8.12 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.03 (s, 1H, CH_{Ar}), 7.95 (dd, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1H, CH_{Ar}), 7.83 (ddd, ^3J = 8.4 Hz, ^3J = 6.7 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.78 – 7.71 (m, 1H, CH_{Ar}), 7.64 – 7.58 (m, 4H, CH_{Ar}), 7.57 – 7.53 (m, 2H, CH_{Ar}), 7.52 – 7.48 (m, 1H, CH_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 148.9 (C_{Ar}), 148.4 (C_{Ar}), 144.7 (C_{Ar}), 140.0 (C_{Ar}), 131.0 (C_{Ar}), 130.6 ($2CH_{Ar}$), 130.6 (C_{Ar}), 130.4 (CH_{Ar}), 129.9 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.0 (CH_{Ar}), 127.8 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 126.7 (C_{Ar}), 126.2 (CH_{Ar}), 124.1 (C_{Ar}), 123.3 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 3024 (w), 2962 (w), 2925 (w), 2853 (w), 1922 (w), 1804 (w), 1601 (m), 1490 (m), 1440 (m), 1411 (m), 1073 (m), 902 (m), 879 (m), 775 (m), 759 (m), 743 (s), 696 (m), 592 (m), 556 (m), 467 (m). MS (EI, 70 eV): *m/z* (%) = 306 (21), 305 ($[M]^+$, 100), 304 (61), 303 (15), 302 (11), 301 (7), 152 (13), 151 (10). HRMS (EI): Calculated for $C_{23}H_{15}N$ 305.1199 found 305.1194.

3-Methyl-5-phenylbenzo[a]acridine 7b

3-Phenyl-2-(phenylethynyl)quinoline **6b** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **7b** as yellow solid (97 mg, 97%), mp. 121 - 123 °C. ^{1}H NMR (250 MHz, $CDCl_3$)

δ = 9.39 (s, 1H, CH_{Ar}), 8.71 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.28 (dd, ^3J = 8.6 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 8.08 (ddd, ^3J = 8.7 Hz, ^4J = 1.3 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 7.98 (s, 1H, CH_{Ar}), 7.84 – 7.77 (m, 1H, CH_{Ar}), 7.71 (dd, ^4J = 1.8 Hz, ^4J = 0.9 Hz, 1H, CH_{Ar}), 7.64 – 7.49 (m, 7H, CH_{Ar}), 2.49 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 148.7 (C_{Ar}), 148.2 (C_{Ar}), 144.5 (C_{Ar}), 140.1 (C_{Ar}), 137.8 (C_{Ar}), 130.9 (C_{Ar}), 130.1 ($2CH_{Ar}$), 129.9 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 128.9 (CH_{Ar}), 128.7 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 128.4 (CH_{Ar}), 128.2 (C_{Ar}), 127.9 (CH_{Ar}), 127.4 (CH_{Ar}), 126.8 (C_{Ar}), 126.1 (CH_{Ar}), 124.1 (C_{Ar}), 123.3 (CH_{Ar}), 21.9 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3043 (w), 2950 (w), 2916 (w), 2849 (w), 2719 (w), 1912 (w), 1613 (m), 1599 (m), 1495 (m), 1374 (m), 900 (m), 876 (m), 809 (m), 773 (m), 765 (m), 741 (s), 712 (m), 701 (s), 589 (m). MS (EI, 70 eV): *m/z* (%) = 321 (40), 319 ($[M]^+$, 100), 318 (30), 317 (11), 316 (11), 315 (7), 305 (7), 304 (34), 303 (13), 152 (31), 151 (9). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1353.

5-(4-(tert-Butyl)phenyl)benzo[a]acridine 7c

3-Phenyl-2-(phenylethynyl)quinoline **6c** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **7c** as yellow solid (95 mg, 95%), mp. 208 - 210 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 9.47 (s, 1H, CH_{Ar}), 8.85 (ddd, ^3J = 8.5 Hz, ^4J = 1.5 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 8.30 (dd, ^3J = 8.9 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.12 (ddt, ^3J = 8.3 Hz, ^4J = 1.2 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 8.05 – 7.99 (m, 2H, CH_{Ar}), 7.83 (ddd, ^3J = 8.7 Hz, ^3J = 6.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.74 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.66 – 7.54 (m, 6H, CH_{Ar}), 1.44 (s, 9H, $3CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.0 (C_{Ar}), 149.0 (C_{Ar}), 148.4 (C_{Ar}), 144.6 (C_{Ar}), 136.9 (C_{Ar}), 131.0 (C_{Ar}), 130.5 (CH_{Ar}), 130.3 (CH_{Ar}), 129.6 ($2CH_{Ar}$), 128.9 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}) 128.4 (C_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 126.6 (C_{Ar}), 126.1 (CH_{Ar}), 125.5 ($2CH_{Ar}$), 124.0 (C_{Ar}), 123.3 (CH_{Ar}), 34.9 ($C(CH_3)_3$), 31.6 ($3CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053 (w), 3025 (w), 2957 (m), 2901 (w), 2864 (w), 1611 (w), 1496 (m), 903 (m), 837 (m), 794 (m), 746 (s), 713 (m), 609 (m), 568 (m), 470 (m). MS (EI, 70 eV): *m/z* (%) = 362 (33), 361 ($[M]^+$, 100), 347 (29), 346 (96), 330 (11), 328 (6), 318 (13), 317 (13), 305 (6), 304 (16), 173 (13), 159 (34). HRMS (EI): Calculated for $C_{27}H_{23}N$ 361.1825 found 361.1824.

5-(4-Fluorophenyl)benzo[a]acridine 7d

3-Phenyl-2-(phenylethynyl)quinoline **6d** (0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **7d** as white solid (92 mg, 92%), mp. 183 - 184 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.42 (s, 1H, CH_{Ar}), 8.82 (ddt, ^{3}J = 8.2 Hz, ^{4}J = 1.2 Hz, ^{4}J = 0.5 Hz, 1H, CH_{Ar}), 8.27 (dd, ^{3}J = 8.7 Hz, ^{4}J = 0.9 Hz, 1H, CH_{Ar}), 8.10 (ddt, ^{3}J = 8.3 Hz, ^{4}J = 1.3 Hz, ^{4}J = 0.6 Hz, 1H, CH_{Ar}), 7.97 (s, 1H, CH_{Ar}), 7.88 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.82 (ddd, ^{3}J = 8.7 Hz, ^{3}J = 6.7 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.73 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.1 Hz, ^{4}J = 1.4 Hz, 1H, CH_{Ar}), 7.64 – 7.53 (m, 4H, CH_{Ar}), 7.31 – 7.16 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.7 (d, $^{1}J_{CF}$ = 247.0 Hz, C_{FAr}), 148.8 (C_{Ar}), 148.6 (C_{Ar}), 143.4 (C_{Ar}), 135.9 (d, $^{4}J_{CF}$ = 3.4 Hz, C_{Ar}), 131.5 (d, $^{3}J_{CF}$ = 8.1 Hz, 2CH_{Ar}), 130.8 (C_{Ar}), 130.6 (C_{Ar}), 130.5 (CH_{Ar}), 130.4 (CH_{Ar}), 129.0 (CH_{Ar}), 128.9 (CH_{Ar}), 128.5 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 127.4 (CH_{Ar}), 126.7 (C_{Ar}), 126.2 (CH_{Ar}), 124.0 (C_{Ar}), 123.4 (CH_{Ar}), 115.6 (d, $^{2}J_{CF}$ = 21.5 Hz, 2CH_{Ar}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.26 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 3041 (w), 1922 (w), 1896 (w), 1806 (w), 1770 (w), 1603 (m), 1508 (m), 1496 (m), 1227 (m), 1158 (m), 904 (m), 834 (m), 826 (m), 761 (m), 744 (s), 616 (m), 552 (m), 524 (m), 410 (m). MS (EI, 70 eV): *m/z* (%) = 324 (31), 323 ($[M]^+$, 100), 322 (75), 321 (15), 320 (9), 319 (6), 161 (18), 160 (9). HRMS (EI): Calculated for $C_{23}H_{14}FN$ 323.1105 found 323.1102.

4-Bromo-3-phenylquinoline 9a

4-Bromo-3-iodoquinoline **8a** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.03 mmol) and Na_2CO_3 (1.2 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **9a** as white solid (111 mg, 65%), mp. 69 - 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.79 (s, 1H, CH_{Ar}), 8.35 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 1.5 Hz, ^{5}J = 0.6 Hz, 1H, CH_{Ar}), 8.18 (ddd, ^{3}J = 8.4 Hz, ^{4}J = 1.3 Hz, ^{5}J = 0.5 Hz, 1H, CH_{Ar}), 7.80 (ddd, ^{3}J = 8.4 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 7.70 (ddd, ^{3}J = 6.9 Hz, ^{3}J = 4.1 Hz, ^{4}J = 1.2 Hz, 1H, CH_{Ar}), 7.54 – 7.47 (m, 5H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.8 (CH_{Ar}), 147.5 (C_{Ar}), 138.3 (C_{Ar}), 136.3 (C_{Ar}), 134.1 (C_{Ar}), 130.4 (CH_{Ar}), 130.0 (2CH_{Ar}), 129.6 (CH_{Ar}), 128.6 (3CH_{Ar}), 128.5 (CH_{Ar}), 128.0 (C_{Ar}), 127.8 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3059 (w), 3026 (w), 2924 (w), 1550 (m), 1480 (m), 1442 (w), 1344 (m), 1307 (w), 1287 (w), 1232 (w), 1209 (w), 1152 (w), 1085 (w), 1032 (w), 966 (w), 938 (w), 918 (w), 869 (w), 809 (m), 781 (w), 756 (vs), 697 (vs), 663 (w), 644 (m), 567 (m), 544 (m), 442 (m), 424 (m). MS (EI, 70 eV): *m/z* (%) = 286 (17), 285 ($[M]^+$, 100), 284 (16), 283 ($[M]^+$, 98), 205 (17), 204 (82), 203 (32), 177 (17), 176 (65), 175 (16), 151 (28), 150 (27), 126 (14), 125 (12), 102 (27). HRMS (EI): Calculated for $C_{15}H_{10}{}^{79}BrN$ 282.99911 found 282.99935, calculated for $C_{15}H_{10}{}^{81}BrN$ 284.9971 found 284.9976.

4-Bromo-3-(4-(tert-butyl)phenyl)quinoline 9b

4-Bromo-3-iodoquinoline **8a** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.03 mmol) and Na_2CO_3 (1.2 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **9b** as off-white solid (210 mg, 69%), mp 119 - 12°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.80 (s, ^3J = 4.1 Hz, 1H, CH_{Ar}), 8.35 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.17 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.78 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.73 – 7.65 (m, 1H, CH_{Ar}), 7.62 – 7.39 (m, 4H, CH_{Ar}), 1.41 (s, 9H, $3CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.6 (C_{Ar}), 151.1 (CH_{Ar}), 147.3 (C_{Ar}), 136.3 (C_{Ar}), 135.2 (C_{Ar}), 134.0 (C_{Ar}), 130.2 ($2CH_{Ar}$), 129.7 (CH_{Ar}), 129.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.1 (C_{Ar}), 127.8 (CH_{Ar}), 125.5 ($2CH_{Ar}$), 34.9 ($C(CH_3)_3$, 31.5 (3 CH_3). IR (ATR, cm^{-1}): ṽ = 2948 (w), 2861 (w), 1550 (w), 1509 (w), 1478 (m), 1458 (w), 1397 (w), 1360 (w), 1338 (m), 1301 (w), 1278 (m), 1266 (w), 1193 (w), 1132 (w), 1109 (m), 1017 (w), 969 (w), 950 (w), 934 (w), 875 (w), 832 (s), 807 (m), 783 (m), 759 (vs), 736 (m), 663 (m), 612 (w), 579 (s), 530 (w). MS (EI, 70 eV): *m/z* (%) = 341 ($[M]^+$, 37), 339 ($[M]^+$, 39), 327 (13), 326 (100), 325 (21), 324 (68), 298 (15), 296 (17), 230 (22), 217 (12), 216 (13), 215 (12), 204 (14), 203 (12), 202 (22), 176 (15), 163 (21). HRMS (EI): Calculated for $C_{19}H_{18}{}^{79}BrN$ 339.0617 found 339.0614, calculated for $C_{19}H_{18}{}^{81}BrN$ 341.0597 found 341.0599.

4-Bromo-3-(4-fluorophenyl)quinoline 9c

4-Bromo-3-iodoquinoline **8a** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.03 mmol) and Na_2CO_3 (1.2 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **9c** as white solid (165 mg, 61%), mp 102 - 103°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.76 (s, 1H, CH_{Ar}), 8.33 (ddd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 8.23 – 8.10 (m, 1H, CH_{Ar}), 7.85 – 7.75 (m, 1H, CH_{Ar}), 7.70 (ddd, ^3J = 8.3 , ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.56 – 7.42 (m, 2H, CH_{Ar}), 7.26 – 7.16 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.9 (d, $^1J_{CF}$ = 248.6 Hz, C_{FAr}), 150.6 (CH_{Ar}), 147.5 (C_{Ar}), 135.4 (C_{Ar}), 134.3 (C_{Ar}), 134.2 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 131.8 (d, $^3J_{CF}$ = 8.3 Hz, $2CH_{Ar}$), 130.5 (CH_{Ar}), 129.6 (CH_{Ar}), 128.7 (CH_{Ar}), 128.0 (C_{Ar}), 127.7 (CH_{Ar}), 115.7 (d, $^2J_{CF}$ = 21.7 Hz, $2CH_{Ar}$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -113.0 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 3038 (w), 1599 (m), 1552 (m), 1511 (m), 1480 (s), 1457 (m), 1338 (m), 1301 (m), 1282 (m), 1272 (w), 1233 (s), 1162 (m), 1146 (m), 1132 (m), 1101 (m), 1076 (m), 1012 (m), 967 (w), 956 (w), 874 (m), 833 (vs), 808 (s), 754 (vs), 723 (m), 682 (s), 627 (m), 554 (vs), 528 (m), 513 (m), 431 (s). MS (EI, 70 eV):

m/z (%) = 304 (20), 303 ([M]$^+$, 99), 302 (20), 301 ([M]$^+$, 100), 223 (21), 222 (77), 221 (24), 195 (16), 194 (53), 175 (18), 174 (11), 169 (18), 168 (26), 149 (10), 144 (15). HRMS (EI): Calculated for $C_{15}H_9N^{79}BrF$ 300.98969 found 300.98984, calculated for $C_{15}H_9N^{81}BrF$ 302.9877 found 302.9881.

4-Bromo-2-methyl-3-phenylquinoline 9d

4-Bromo-3-iodoquinoline **8b** (0.6 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.03 mmol) and Na_2CO_3 (1.2 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **9d** as white solid (108 mg, 63%), mp. 83 - 84 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.23 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 8.08 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 7.76 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.61 (ddd, ^3J = 8.3 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.56 – 7.46 (m, 3H, CH_{Ar}), 7.29 – 7.24 (m, 2H, CH_{Ar}), 2.50 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 158.1 (C_{Ar}), 147.5 (C_{Ar}), 139.8 (C_{Ar}), 136.9 (C_{Ar}), 135.3 (C_{Ar}), 130.3 (CH_{Ar}), 129.2 ($2CH_{Ar}$), 129.0 (CH_{Ar}), 128.9 ($2CH_{Ar}$), 128.2 (CH_{Ar}), 127.6 (CH_{Ar}), 127.4 (CH_{Ar}), 126.8 (C_{Ar}), 25.8 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 3026 (w), 1601 (w), 1577 (w), 1472 (m), 1336 (m), 908 (m), 752 (s), 698 (m), 587 (m). MS (EI, 70 eV): *m/z* (%) = 300 (10), 299 ([M]$^+$, 62), 298 (19), 297 ([M]$^+$, 63), 296 (9), 219 (17), 218 (100), 217 (54), 216 (13), 177 (12), 176 (41), 151 (16), 150 (14), 109 (25), 88 (20), 75 (8). HRMS (EI): Calculated for $C_{16}H_{12}{}^{79}BrN$ 297.01476 found 297.01452, calculated for $C_{16}H_{12}{}^{81}BrN$ 299.0127 found 299.0129.

3-Phenyl-4-(phenylethynyl)quinoline 10a

4-Bromo-3-phenylquinoline **9a** (0.4 mmol), alkyne (0.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.02 mmol) in 3.0 ml of triethylamine gave **10a** as white solid (108 mg, 97%), mp. 115-116 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.03 (s, 1H, CH_{Ar}), 8.51 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 8.22 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.82 – 7.76 (m, 3H, CH_{Ar}), 7.74 – 7.68 (m, 1H, CH_{Ar}), 7.59 – 7.53 (m, 2H, CH_{Ar}), 7.52 – 7.47 (m, 3H, CH_{Ar}), 7.40 – 7.34 (m, 3H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.4 (CH_{Ar}), 146.2 (C_{Ar}), 137.3 (C_{Ar}), 135.9 (C_{Ar}), 131.9 ($2CH_{Ar}$), 130.0 (CH_{Ar}), 129.8 ($2CH_{Ar}$), 129.4 (CH_{Ar}), 129.2 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 128.4 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (C_{Ar}), 127.4 (C_{Ar}), 126.5 (CH_{Ar}), 122.4 (C_{Ar}), 102.3 (C_{Alkyne}), 84.9 (C_{Alkyne}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3050 (w), 3030 (w), 2920 (w), 2204 (w), 1599 (w), 1554 (w), 1495 (m), 1460 (w), 1440 (w), 1384 (w), 1323 (w), 1281 (w), 1262 (w), 1191 (w), 1138 (w), 1095 (w), 1068 (w), 1028 (w), 999 (w), 960 (w), 920 (w),

891 (m), 860 (w), 789 (w), 744 (vs), 714 (w), 699 (m), 685 (vs), 618 (m), 606 (m), 587 (m), 561 (m), 544 (m), 526 (m), 508 (m), 471 (m), 438 (m), 410 (m), 402 (m). MS (EI, 70 eV): *m/z* (%) = 306 (10), 305 (73), 304 ($[M]^+$, 100), 303 (14), 302 (13), 276 (17), 151 (10), 138 (11), 51 (10). HRMS (EI): Calculated for $C_{23}H_{15}N$ 304.1121 found 304.1119.

3-(4-(tert-Butyl)phenyl)-4-(phenylethynyl)quinoline 10b

4-Bromo-3-phenylquinoline **9b** (0.4 mmol), alkyne (0.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.02 mmol) in 3.0 ml of triethylamine gave **10b** as yellow oil (127 mg, 99%). ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.93 (s, 1H, CH_{Ar}), 8.47 – 8.29 (m, 1H, CH_{Ar}), 8.06 (dd, ^3J = 8.1 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.69 – 7.60 (m, 3H, CH_{Ar}), 7.56 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.51 – 7.42 (m, 2H, CH_{Ar}), 7.42 – 7.32 (m, 2H, CH_{Ar}), 7.30 – 7.20 (m, 3H, CH_{Ar}), 1.31 (s, 9H, $3CH_3$). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 151.5 (C_{Ar}), 151.1 (CH_{Ar}), 146.7 (C_{Ar}), 135.8 (C_{Ar}), 134.6 (C_{Ar}), 131.9 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 129.3 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 127.6 (C_{Ar}), 126.7 (C_{Ar}), 126.5 (CH_{Ar}), 125.4 ($2CH_{Ar}$), 122.7 (C_{Ar}), 101.8 (C_{Alkyne}), 85.4 (C_{Alkyne}), 34.8 ($C(CH_3)_3$, 31.5 ($3CH_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2958 (m),2865 (w), 2208 (w), 1569 (m), 1494 (m), 1459 (w), 1443 (w), 1379 (m), 1362 (m), 1268 (m), 1142 (w), 1113 (m), 1020 (w), 892 (w), 833 (s), 754 (vs), 688 (s), 639 (w), 627 (m), 598 (m), 565 (s), 548 (m), 526 (m), 513 (m), 505 (m), 439 (m). MS (EI, 70 eV): *m/z* (%) = 361 ($[M]^+$, 21), 346 (24), 306 (15), 305 (60), 304 (100), 303 (11), 302 (11), 57 (12), 41 (11). HRMS (EI): Calculated for $C_{27}H_{23}N$ 361.1825 found 361.1825.

3-(4-Fluorophenyl)-4-(phenylethynyl)quinoline 10c

4-Bromo-3-phenylquinoline **9c** (0.4 mmol), alkyne (0.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.02 mmol) in 3.0 ml of triethylamine gave **10c** as off-white solid (102 mg, 95%), mp 156-158°C ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.90 (s, 1H, CH_{Ar}), 8.41 (ddd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, ^5J = 0.5 Hz, 1H, CH_{Ar}), 8.12 (dd, ^3J = 8.3 Hz, ^4J = 0.7 Hz, 1H, CH_{Ar}), 7.78 – 7.55 (m, 4H, CH_{Ar}), 7.50 – 7.37 (m, 2H, CH_{Ar}), 7.37 – 7.25 (m, 3H, CH_{Ar}), 7.25 – 7.07 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.1 (d, $^1J_{CF}$ = 248.4 Hz, C_{FAr}), 150.4 (CH_{Ar}), 146.4 (C_{Ar}), 134.9 (C_{Ar}), 133.5 (d, $^4J_{CF}$ = 3.4 Hz, C_{Ar}), 132.0 ($2CH_{Ar}$), 131.7 (d, $^3J_{CF}$ = 8.24 Hz, $2CH_{Ar}$), 130.2 (CH_{Ar}), 129.7 (CH_{Ar}), 129.4 (CH_{Ar}), 128.8 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 127.6 (C_{Ar}), 127.5 (C_{Ar}), 126.6 (CH_{Ar}), 122.3 (C_{Ar}), 115.6 (d, $^2J_{CF}$ = 21.6 Hz, $2CH_{Ar}$), 102.6 (C_{Alkyne}), 84.9 (C_{Alkyne}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -113.2 (CF_{Ar}).

IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 3036 (w), 2208 (w), 1599 (m), 1573 (w), 1558 (w), 1511 (s), 1496 (m), 1486 (m), 1461 (w), 1443 (m), 1387 (w), 1323 (w), 1233 (s), 1173 (w), 1158 (m), 1140 (w), 1101 (w), 1068 (w), 1014 (w), 954 (w), 892 (m), 866 (w), 827 (s), 808 (m), 787 (w), 746 (vs), 721 (m), 699 (m), 684 (s), 645 (w), 633 (w), 596 (m), 544 (m), 519 (s), 509 (s), 491 (m), 437 (m), 431 (m). MS (EI, 70 eV): *m/z* (%) = 324 (20), 323 ($[M]^+$, 92), 322 (100), 321 (18), 320 (12), 294 (15), 161 (13), 147 (10). HRMS (EI): Calculated for $C_{23}H_{14}NF$ 323.1105 found 323.1096.

2-Methyl-3-phenyl-4-(phenylethynyl)quinoline 10d

4-Bromo-3-phenylquinoline **9d** (0.4 mmol), alkyne (0.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.02 mmol) in 3.0 ml of triethylamine gave **10d** as yellow solid (154 mg, 96%), mp. 131 - 133 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.33 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 8.06 (d, ^3J = 8.1 Hz, 1H, CH_{Ar}), 7.70 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.56 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.50 – 7.35 (m, 5H, CH_{Ar}), 7.29 – 7.17 (m, 5H, CH_{Ar}), 2.54 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 157.5 (C_{Ar}), 146.9 (C_{Ar}), 139.0 (C_{Ar}), 137.5 (C_{Ar}), 131.9 ($2CH_{Ar}$), 129.8 ($2CH_{Ar}$), 129.8 (CH_{Ar}), 129.1 (CH_{Ar}), 129.0 (CH_{Ar}), 128.8 (C_{Ar}), 128.5 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 127.9 (CH_{Ar}), 126.7 (CH_{Ar}), 126.3 (CH_{Ar}), 126.2 (C_{Ar}), 122.6 (C_{Ar}), 102.0 (C_{Alkyne}), 85.3 (C_{Alkyne}), 25.2 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 3023 (w), 2955 (w), 2920 (w), 2851 (w), 2208 (w), 1673 (w), 1493 (m), 1442 (m), 1071 (m), 1024 (m), 755 (s), 692 (s). MS (EI, 70 eV): *m/z* (%) = 320 (23), 319 ($[M]^+$, 100), 318 (73), 317 (17), 316 (10), 304 (31), 303 (9), 278 (10), 177 (9), 176 (18), 158 (11), 138 (11). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1348.

12-Phenylbenzo[i]phenanthridine 11a

4-Phenyl-3-(phenylethynyl)quinoline **10a** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **11a** as off-white solid (71 mg, 83%), mp. 220-221°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.28 (s, 1H, CH_{Ar}), 8.99 (d, ^3J = 8.4 Hz, 1H, CH_{Ar}), 8.70 (dd, ^3J = 8.3 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 8.56 (s, 1H, CH_{Ar}), 8.44 (d, ^3J = 8.2 Hz, 1H, CH_{Ar}), 8.07 (dd, ^3J = 8.4 Hz, ^4J = 0.8 Hz, 1H, CH_{Ar}), 7.88 – 7.83 (m, 2H, CH_{Ar}), 7.78 (ddd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.68 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.63 – 7.52 (m, 5H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 146.3 (C_{Ar}), 140.0 (C_{Ar}), 132.5 (C_{Ar}), 131.2 (C_{Ar}), 130.5 (C_{Ar}), 129.9 ($2CH_{Ar}$), 129.8 (C_{Ar}), 129.6 (CH_{Ar}), 128,6 (CH_{Ar}), 128.6 ($2CH_{Ar}$), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 127.8 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5

(CH_{Ar}), 124.4 (C_{Ar}), 122.9 (CH_{Ar}), 122.4 (CH_{Ar}), 121.1 (C_{Ar}), 120.6 (CH_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3059 (w), 2923 (m), 2851 (w), 2210 (w), 1599 (m), 1554 (w), 1505 (vs), 1486 (s), 1441 (m), 1377 (m), 1336 (w), 1228 (vs), 1150 (m), 1125 (m), 1094 (m), 1074 (m), 1033 (w), 1024 (m), 961 (w), 928 (m), 831 (vs), 810 (m), 798 (w), 765 (vs), 752 (s), 701 (vs), 682 (m), 625 (s), 592 (m), 569 (m), 534 (m), 519 (s), 484 (m), 464 (s), 439 (s), 404 (m). MS (EI, 70 eV): *m/z* (%) = 306 (23), 305 ($[M]^+$, 100), 304 (63) 303 (15), 302 (11), 301 (11), 276 (17), 153 (10) 152 (10), 138 (13). HRMS (EI): Calculated for $C_{23}H_{15}N$ 305.1199 found 305.1207.

2-(tert-Butyl)-12-phenylbenzo[i]phenanthridine 11b

4-Phenyl-3-(phenylethynyl)quinoline **10b** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **11b** as yellow solid (101 mg, 80%), mp. 215 - 216 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.24 (d, ^3J = 9.0 Hz, 1H, CH_{Ar}), 8.93 (d, ^3J = 8.8 Hz, 1H, CH_{Ar}), 8.66 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 8.53 (s, ^3J = 6.7 Hz, 1H, CH_{Ar}), 8.32 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 8.05 (d, ^4J = 2.0 Hz, 1H, CH_{Ar}), 7.91 (dd, ^3J = 8.8 Hz, ^4J = 2.1 Hz, 1H, CH_{Ar}), 7.80 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.72 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.67 – 7.53 (m, 5H, CH_{Ar}), 1.38 (s, 9H, $3CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.3(C_{Ar}), 147.4 (CH_{Ar}), 145.0 (C_{Ar}), 144.6 (C_{Ar}), 140.6 (C_{Ar}), 131.6 (C_{Ar}), 131.2 (C_{Ar}), 130.1 ($2CH_{Ar}$), 129.7 (CH_{Ar}), 129.1 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.6 (C_{Ar}), 128.2 (CH_{Ar}), 127.4 (CH_{Ar}), 126.7 (CH_{Ar}), 124.5 (C_{Ar}), 123.1 (CH_{Ar}), 122.8 (CH_{Ar}), 122.3 (CH_{Ar}), 121.3 (C_{Ar}), 120.8 (CH_{Ar}), 35.2 ($C(CH_3)_3$), 31.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2952 (m), 2865 (w), 1610 (w), 1595 (w), 1575 (w), 1492 (w), 1441 (w), 1428 (w), 1375 (m), 1360 (w), 1251 (w), 1239 (w), 1115 (w), 1031 (w), 956 (m), 892 (m), 876 (w), 827 (m), 777 (w), 767 (m), 754 (vs), 699 (s), 668 (w), 596 (m), 583 (m), 573 (m), 435 (m). MS (EI, 70 eV): *m/z* (%) = 362 (15), 361 ($[M]^+$, 47), 347 (29), 346 (100), 304 (12), 303 (10). HRMS (EI): Calculated for $C_{27}H_{23}N$ 361.1825 found 361.1836.

2-Fluoro-12-phenylbenzo[i]phenanthridine 11c

4-Phenyl-3-(phenylethynyl)quinoline **10c** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **11c** as off-white solid (46 mg, 53%), mp 237 - 239°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.11 (s, 1H, CH_{Ar}), 8.95 – 8.79 (m, 1H, CH_{Ar}), 8.63 – 8.52 (m, 1H, CH_{Ar}), 8.49 (s, 1H, CH_{Ar}), 8.24 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.78 – 7.69 (m, 1H, CH_{Ar}), 7.69 – 7.55 (m, 2H, CH_{Ar}), 7.55 – 7.43 (m, 6H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.7 (d,

$^1J_{CF}$ = 247.8 Hz, C_{FAr}), 147.1 (CH_{Ar}), 144.6 (C_{Ar}), 144.1 (C_{Ar}), 139.8 (C_{Ar}), 132.9 (d, $^3J_{CF}$ = 8.6 Hz, C_{Ar}), 131.4 (d, $^4J_{CF}$ = 1.5 Hz, C_{Ar}), 129.9 ($2CH_{Ar}$), 129.8 (CH_{Ar}) 129.3 (CH_{Ar}), 128.9 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 127.7 (CH_{Ar}), 127.3 (d, $^4J_{CF}$ = 1.7 Hz, C_{Ar}), 125.0 (d, $^3J_{CF}$ = 8.9 Hz, CH_{Ar}), 124.3 (C_{Ar}), 122.8 (CH_{Ar}), 122.0 (CH_{Ar}), 121.3 (C_{Ar}), 117.6 (d, $^2J_{CF}$ = 24.3 Hz, CH_{Ar}), 111.9 (d, $^2J_{CF}$ = 22.2 Hz, CH_{Ar}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -112.1 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 3051 (w), 2923 (w), 2851 (w), 1622 (w), 1612 (w), 1599 (w), 1581 (m), 1521 (m), 1511 (m), 1492 (m), 1453 (m), 1418 (m), 1371 (w), 1350 (w), 1257 (m), 1243 (m), 1220 (w), 1204 (m), 1171 (m), 1160 (m), 1140 (w), 1119 (m), 1072 (m), 973 (m), 911 (w), 870 (m), 857 (w), 847 (m), 829 (m), 787 (w), 775 (m), 752 (vs), 713 (m), 701 (s), 678 (m), 666 (m), 647 (w), 594 (m), 583 (m), 554 (m), 528 (m), 507 (m), 441 (m), 429 (m). MS (EI, 70 eV): *m/z* (%) = 324 (23), 323 ($[M]^+$, 100), 322 (51), 321 (13), 320 (7), 294 (14), 161 (7), 147 (10). HRMS (EI): Calculated for $C_{23}H_{14}NF$ 323.1105 found 323.1104.

5-Methyl-12-phenylbenzo[i]phenanthridine 11d

4-Phenyl-3-(phenylethynyl)quinoline **10d** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **11d** as yellow solid (95 mg, 95%), mp. 167 - 169 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.99 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 8.62 – 8.56 (m, 1H, CH_{Ar}), 8.54 (s, 1H, CH_{Ar}), 8.19 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 8.05 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.80 – 7.72 (m, 2H, CH_{Ar}), 7.67 – 7.52 (m, 7H, CH_{Ar}), 3.48 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 157.0 (C_{Ar}), 144.0 (C_{Ar}), 143.8 (C_{Ar}), 140.5 (C_{Ar}), 133.3 (C_{Ar}), 132.3 (C_{Ar}), 131.3 (C_{Ar}), 130.1 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 128.9 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 126.8 (CH_{Ar}), 126.5 (CH_{Ar}), 126.4 (CH_{Ar}), 123.5 (C_{Ar}), 122.8 (C_{Ar}), 122.7 (CH_{Ar}), 121.4 (CH_{Ar}), 31.2 (CH_3). IR (ATR, cm^{-1}): ṽ = 3076 (w), 3043 (w), 2961 (w), 2921 (w), 2852 (w), 1565 (m), 1440 (m), 1367 (m), 1070 (m), 873 (m), 779 (m), 754 (s), 704 (m), 607 (m). MS (EI, 70 eV): *m/z* (%) = 320 (23), 319 ($[M]^+$, 100), 318 (82), 317 (17), 316 (9), 315 (6), 276 (7), 241 (5), 159 (12), 158 (5), 138 (11). HRMS (EI): Calculated for $C_{24}H_{17}N$ 319.1356 found 319.1349.

3-Phenylethynyl-4-bromoquinoline 12a

4-Bromo-3-iodoquinoline **8a** (0.8 mmol), alkyne (1.3 mmol), $Pd(PPh_3)_4$ (0.04 mmol) and CuI (0.04 mmol) in 1.0 ml of triethylamine and 2 ml of acetonitrile gave **12a** as white solid (126 mg, 68%), mp. 104 - 105 °C.^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.91 (s, 1H, CH_{Ar}), 8.34 – 8.19 (m, 1H, CH_{Ar}), 8.19 – 8.04 (m, 1H, CH_{Ar}), 7.87 – 7.55 (m, 4H, CH_{Ar}), 7.50 – 7.34

(m, 3H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 151.3 (CH_{Ar}), 146.6 (C_{Ar}), 137.2 (C_{Ar}), 132.0 ($2CH_{Ar}$), 130.9 (CH_{Ar}), 129.6 (CH_{Ar}), 129.4 (CH_{Ar}), 128.8 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 127.7 (C_{Ar}), 127.6 (CH_{Ar}), 122.4 (C_{Ar}), 120.8 (C_{Ar}), 97.6 (C_{Alkyne}), 86.4 (C_{Alkyne}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 3026 (w), 2922 (w), 2208 (w), 1613 (w), 1548 (m), 1476 (m), 1440 (m), 1346 (m), 1317 (m), 1240 (w), 1136 (w), 1121 (m), 1068 (w), 995 (w), 950 (w), 926 (m), 918 (m), 807 (m), 748 (vs), 683 (s), 673 (s), 630 (m), 563 (m), 530 (m), 504 (m), 491 (m), 430 (m), 400 (m). MS (EI, 70 eV): *m/z* (%) = 310 (18), 309 ($[M]^+$, 100), 308 (25), 307 ($[M]^+$, 93), 228 (36), 227 (46), 201 (24), 200 (50), 199 (12), 175 (14), 174 (18), 150 (12), 122 (15), 114 (18), 100 (28), 99 (12), 98 (13), 87 (17), 75 (14), 74 (14), 73 (14), 63 (18), 62 (10), 52 (10), 50 (20), 39 (29). HRMS (EI): Calculated for $C_{17}H_{10}NBr$ 306.9991 found 306.9997, calculated for $C_{17}H_{10}NBr^{81}$ 308.9971 found 308.9978.

4-Bromo-3-((4-fluorophenyl)ethynyl)quinoline 12b

4-Bromo-3-iodoquinoline **8a** (0.8 mmol), alkyne (1.3 mmol), $Pd(PPh_3)_4$ (0.04 mmol) and CuI (0.04 mmol) in 1.0 ml of triethylamine and 2 ml of acetonitrile gave **12b** as off-white solid (221 mg, 75%), mp 153 - 155°C. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.88 (s, 1H, CH_{Ar}), 8.24 (ddd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, ^5J = 0.5 Hz, 1H, CH_{Ar}), 8.13 (dd, ^3J = 8.3 Hz, ^4J = 0.7 Hz, 1H, CH_{Ar}), 7.77 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.72 – 7.58 (m, 3H, CH_{Ar}), 7.17 – 7.03 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.2 (d, ^1J = 251.2, CF), 151.2 (CH_{Ar}), 146.7 (C_{Ar}), 137.1 (C_{Ar}), 134.0 (d, ^3J = 8.5 Hz, $2CH_{Ar}$), 131.0 (CH_{Ar}), 129.6 (CH_{Ar}), 128.8 (CH_{Ar}), 127.6 (C_{Ar}), 127.4 (CH_{Ar}), 120.6 (C_{Ar}), 118.6 (d, ^4J = 3.6 Hz, C_{Ar}), 116.1 (d, ^2J = 22.2 Hz, $2CH_{Ar}$), 96.4 (C_{Alkyne}), 86.1 (C_{Alkyne}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -109.1. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053 (w), 3042 (w), 2212 (w), 1599 (m), 1589 (w), 1548 (m), 1509 (s), 1476 (s), 1406 (w), 1348 (m), 1319 (m), 1233 (s), 1158 (m), 1121 (m), 1097 (m), 1014 (w), 919 (m), 833 (s), 808 (m), 777 (m), 756 (vs), 658 (s), 641 (w), 608 (w), 563 (m), 532 (s), 505 (m), 464 (m), 420 (m), 404 (m). MS (EI, 70 eV): *m/z* (%) = 328 (18), 327 ($[M]^+$, 95), 326 (16), 325 ($[M]^+$, 100), 246 (39), 245 (41), 219 (17), 218 (41), 193 (10), 192 (14), 168 (17), 123 (12), 122 (11), 110 (10), 51 (10), 39 (11). HRMS (EI): Calculated for $C_{17}H_9N^{79}BrF$ 324.9897 found 324.9894, calculated for $C_{17}H_9N^{81}BrF$ 326.9877 found 326.9877.

4-Bromo-3-(thiophen-3-ylethynyl)quinoline 12c

4-Bromo-3-iodoquinoline **8a** (0.8 mmol), alkyne (1.3 mmol), $Pd(PPh_3)_4$ (0.04 mmol) and CuI (0.04 mmol) in 1.0 ml of triethylamine and 2 ml of acetonitrile gave **12c** as yellow solid (221 mg, 78%), mp 117 - 119°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.81 (s, 1H, CH_{Ar}), 8.23 – 8.11 (m, 1H, CH_{Ar}), 8.03 (dd, ^3J = 8.3 Hz, ^4J = 0.8 Hz, 1H, CH_{Ar}), 7.67 (dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.64 – 7.54 (m, 2H, CH_{Ar}), 7.29 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH_{Ar}), 7.23 (dd, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.3 (CH_{Ar}), 146.7 (C_{Ar}), 136.8 (C_{Ar}), 130.9 (CH_{Ar}), 130.3 (CH_{Ar}), 130.0 (CH_{Ar}), 129.6 (CH_{Ar}), 128.8 (CH_{Ar}), 127.7 (C_{Ar}), 127.4 (CH_{Ar}), 125.9 (CH_{Ar}), 121.5 (C_{Ar}), 120.8 (C_{Ar}), 92.7 (C_{Alkyne}), 86.0 (C_{Alkyne}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3090 (m), 2921 (m), 2853 (m), 2205 (m), 1550 (m), 1476 (s), 1354 (m), 1342 (m), 1334 (m), 1301 (m), 1202 (m), 1119 (m), 864 (m), 808 (m), 787 (s), 759 (vs), 721 (s), 693 (m), 647 (s), 625 (s), 567 (m), 542 (m), 526 (m), 507 (m), 488 (m), 433 (m), 418 (m). MS (EI, 70 eV): *m/z* (%) = 316 (17), 315 ($[M]^+$, 100), 314 (17), 313 ($[M]^+$, 94), 234 (31), 233 (33), 206 (11), 190 (20), 163 (32), 162 (13) 137 (11), 117 (10), 110 (10). HRMS (EI): Calculated for $C_{15}H_8N^{79}BrS$ 312.9555 found 312.9561, calculated for $C_{15}H_8N^{81}BrS$ 314.9535 found 314.9539.

4-Phenyl-3-(phenylethynyl)quinoline 13a

4-Bromo-3-phenylethynylquinoline **12a** (0.4 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.02 mmol) and Na_2CO_3 (0.8 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **13a** as yellow solid (96 mg, 97%), mp 150 - 152°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.01 (s, 1H, CH_{Ar}), 8.11 (dd, ^3J = 8.8 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.70 – 7.58 (m, 2H, CH_{Ar}), 7.54 – 7.40 (m, 6H, CH_{Ar}), 7.25 – 7.14 (m, 5H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.9 (CH_{Ar}), 150.5 (C_{Ar}), 146.9 (C_{Ar}), 136.2 (C_{Ar}), 131.6 ($2CH_{Ar}$), 130.2 ($2CH_{Ar}$), 130.0 (CH_{Ar}), 129.5 (CH_{Ar}), 128.7 (CH_{Ar}), 128.7 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 127.5 (CH_{Ar}), 126.8 (C_{Ar}), 126.5 (CH_{Ar}), 122.8 (C_{Ar}), 116.8 (C_{Ar}), 95.6 (C_{Alkyne}), 86.8 (C_{Alkyne}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 2960 (w), 2923 (w), 1733 (w), 1569 (w), 1556 (w), 1486 (m), 1441 (m), 1377 (m), 1329 (w), 1259 (w), 1068 (m), 1022 (m), 934 (w), 909 (w), 798 (m), 769 (s), 752 (vs), 705 (s), 686 (s), 614 (m), 592 (m), 577 (m), 538 (m), 519 (m), 497 (m), 480 (m), 437 (m), 412 (m). MS (EI, 70 eV): *m/z* (%) = 306 (20), 305 ($[M]^+$, 86), 304 (100), 303 (22), 302 (15), 276 (15). HRMS (EI): Calculated for $C_{23}H_{15}N$ 305.1199 found 305.1192.

4-(4-(tert-Butyl)-phenyl)-3-(phenylethynyl)quinoline 13b

4-Bromo-3-phenylethynylquinoline **12a** (0.4 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.02 mmol) and Na_2CO_3 (0.8 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **13b** as yellow solid (118 mg, 98%), mp 112 - 114°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.99 (s, 1H, CH_{Ar}), 8.12 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 7.73 (dd, ^3J = 8.4 Hz, ^4J = 0.8 Hz, 1H, CH_{Ar}), 7.65 (ddd, ^3J = 8.3 Hz, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.56 – 7.47 (m, 2H, CH_{Ar}), 7.46 – 7.34 (m, 3H, CH_{Ar}), 7.24 – 7.11 (m, 5H, CH_{Ar}), 1.37 (s, 9H, $3CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.8 (CH_{Ar}), 151.2 (C_{Ar}), 146.7 (C_{Ar}), 133.2 (C_{Ar}), 131.6 ($2CH_{Ar}$), 130.1 (CH_{Ar}), 130.0 ($2CH_{Ar}$), 129.5 (CH_{Ar}), 128.7 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 127.4 (CH_{Ar}), 127.0 (C_{Ar}), 126.8 (CH_{Ar}), 125.2 ($2CH_{Ar}$), 123.0 (C_{Ar}), 116.9 (C_{Ar}), 115.1 (C_{Ar}), 95.7 (C_{Alkyne}), 87.1 (C_{Alkyne}), 35.0 (*C*(CH_3), 31.5 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (vw), 2959 (m), 2865 (w), 1562 (w), 1515 (w), 1488 (m), 1442 (w), 1378 (w), 1362 (m), 1266 (w), 1179 (w), 1107 (w), 1024 (w), 926 (w), 913 (w), 832 (m), 767 (s), 752 (vs), 689 (s), 673 (m), 640 (w), 597 (m), 559 (m), 548 (m), 538 (m), 510 (m), 489 (w), 436 (m), 402 (w). MS (EI, 70 eV): *m/z* (%) = 361 ($[M]^+$, 31), 346 (16), 328 (10), 306 (17), 305 (100), 304 (93), 303 (13), 276 (14), 158 (21), 77 (14), 57 (36), 41 (36), 39 (16). HRMS (EI): Calculated for $C_{27}H_{23}N$ 361.1825 found 361.1821.

3-((4-Fluorophenyl)ethynyl)-4-phenylquinoline 13c

4-Bromo-3-phenylethynylquinoline **12b** (0.4 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.02 mmol) and Na_2CO_3 (0.8 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **13c** as yellow oil (94 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.09 (s, 1H, CH_{Ar}), 8.29 – 8.09 (m, 1H, CH_{Ar}), 7.83 – 7.69 (m, 2H, CH_{Ar}), 7.65 – 7.47 (m, 6H, CH_{Ar}), 7.29 – 7.19 (m, 2H, CH_{Ar}), 7.04 – 6.94 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.5 (d, $^1J_{CF}$ = 250.5 Hz, C_{FAr}), 151.7 (CH_{Ar}), 150.6 (C_{Ar}), 146.8 (C_{Ar}), 136.2 (C_{Ar}), 133.6 (d, $^3J_{CF}$ = 8.5 Hz, $2CH_{Ar}$), 130.1 ($2CH_{Ar}$), 130.1 (CH_{Ar}), 129.4 (CH_{Ar}), 128.8 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 127.6 (CH_{Ar}), 126.8 (C_{Ar}), 126.5 (CH_{Ar}), 118.9 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 116.6 (C_{Ar}), 115.8 (d, $^2J_{CF}$ = 22.1 Hz, $2CH_{Ar}$), 94.5 (C_{Alkyne}), 86.5 (C_{Alkyne}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.0 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3059 (w), 2923 (m), 2851 (w), 2210 (w), 1599 (m), 1554 (w), 1505 (vs), 1486 (s), 1441 (m), 1377 (m), 1228 (vs), 1150 (m), 1125 (m), 1094 (m), 1074 (m), 1033 (w), 1024 (m), 961 (w), 928 (m), 831 (vs), 810 (m), 798 (w), 765 (vs), 752 (s), 701 (vs), 682 (m), 625 (s), 592 (m), 569 (m), 534 (m), 519 (s), 484 (m), 464 (s), 439 (s), 404 (m). MS (EI, 70 eV): *m/z* (%) = 324 (23), 323 ($[M]^+$, 100), 322 (96), 321 (20), 320 (11), 294 (15), 207 (11), 161 (13), 141 (12), 44 (12), 32 (41). HRMS (EI): Calculated for $C_{23}H_{14}NF$ 323.1105 found 323.1097.

4-(4-(tert-Butyl)phenyl)-3-((4-fluorophenyl)ethynyl)quinoline 13d

4-Bromo-3-phenylethynylquinoline **12b** (0.4 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.02 mmol) and Na_2CO_3 (0.8 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **13d** as white solid (97 mg, 98%), mp 139 - 141°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.06 (s, 1H, CH_{Ar}), 8.19 (dd, ^3J = 8.4 Hz, ^4J = 0.6 Hz, 1H, CH_{Ar}), 7.80 (ddd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.72 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 , ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.62 – 7.57 (m, 2H, CH_{Ar}), 7.54 – 7.44 (m, 3H, CH_{Ar}), 7.28 – 7.13 (m, 2H, CH_{Ar}), 7.02 – 6.91 (m, 2H, CH_{Ar}), 1.44 (d, ^4J = 2.0 Hz, 9H, $3CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.8 (d, $^1J_{CF}$ = 250.3 Hz, C_{FAr}), 151.8 (C_{Ar}), 151.6 (CH_{Ar}), 151.0 (C_{Ar}), 146.9 (C_{Ar}), 133.5 (d, $^3J_{CF}$ = 8.4 Hz, $2CH_{Ar}$), 133.2 (C_{Ar}), 130.1 ($2CH_{Ar}$), 129.9 (CH_{Ar}), 129.4 (C_{Ar}), 127.4 (CH_{Ar}), 126.7 (CH_{Ar}), 125.2 ($2CH_{Ar}$), 119.1 (d, $^4J_{CF}$ = 3,5 Hz, C_{Ar}), 116.7 (C_{Ar}), 115.7 (d, $^2J_{CF}$ = 22.1 Hz, $2CH_{Ar}$)., 115.1 (CH_{Ar}), 94.5 (C_{Alkyne}), 86.9 (C_{Alkyne}), 35.0 ($C(CH_3)_3$), 31.5 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -110.1 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2947 (m), 2869 (w), 1597 (w), 1505 (s), 1490 (m), 1362 (m), 1266 (w), 1224 (s), 1156 (m), 1121 (m), 1105 (m), 1094 (m), 1022 (m), 1014 (m), 954 (w), 928 (m), 833 (vs), 810 (m), 794 (m), 756 (vs), 684 (m), 658 (m), 620 (m), 592 (m), 561 (m), 548 (m), 536 (m), 521 (m), 507 (m), 464 (m), 435 (m), 408 (m). MS (EI, 70 eV): *m/z* (%) = 380 (9), 379 ($[M]^+$, 34), 364 (18), 348 (11), 324 (22), 323 (84), 322 (100), 321 (14), 294 (12), 57 (17), 41 (12). HRMS (EI): Calculated for $C_{27}H_{22}NF$ 379.1731 found 379.1731.

4-Phenyl-3-(thiophen-3-ylethynyl)quinoline 13e

4-Bromo-3-phenylethynylquinoline **12c** (0.4 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (0.02 mmol) and Na_2CO_3 (0.8 mmol) in 3.0 ml of DMF and 0.3 ml of water gave **13e** as yellow solid (124.8 mg, 84%), mp 134 - 136°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 9.07 (s, 1H, CH_{Ar}), 8.30 – 8.06 (m, 1H, CH_{Ar}), 7.82 – 7.67 (m, 2H, CH_{Ar}), 7.64 – 7.43 (m, 6H, CH_{Ar}), 7.32 (dd, ^4J = 3.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.24 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH_{Ar}), 6.95 (dd, ^3J = 5.0 Hz, ^4J = 1.2, 1H, CH_{Ar}). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 151.4 (CH_{Ar}), 150.8 (C_{Ar}), 146.4 (C_{Ar}), 136.1 (C_{Ar}), 130.2 (CH_{Ar}), 130.1 ($2CH_{Ar}$), 129.7 (CH_{Ar}), 129.4 (CH_{Ar}), 129.1 (CH_{Ar}), 128.8 (CH_{Ar}), 128.4 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 126.9 (C_{Ar}), 126.6 (CH_{Ar}), 125.6 (CH_{Ar}), 121.8 (C_{Ar}), 116.8 (C_{Ar}), 91.0 (C_{Alkyne}), 86.2 (C_{Alkyne}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3102 (w), 3046 (w), 1558 (w), 1486 (m), 1439 (w), 1377 (m), 1348 (w), 1224 (w), 1148 (w), 1115 (w),

1078 (w), 1035 (w), 1004 (w), 934 (m), 857 (m), 820 (w), 798 (w), 767 (vs), 759 (vs), 732 (m), 707 (s), 678 (m), 618 (s), 589 (m), 579 (s), 513 (m), 474 (m), 437 (m), 410 (w). MS (EI, 70 eV): *m/z* (%) = 312 (29), 311 ($[M]^+$, 100), 310 (92), 309 (21), 266 (13), 264 (14), 237 (10), 51 (12), 45 (27). HRMS (EI): Calculated for $C_{21}H_{13}NS$ 311.0763 found 311.0757.

8-Phenylbenzo[k]phenanthridine 14a

3-Phenyl-4-(phenylethynyl)quinoline **13a** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **14a** as yellow solid (75 mg, 92%), mp 116 - 118°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.36 (s, 1H, CH_{Ar}), 9.24 (d, ^3J = 8.5 Hz, 1H, CH_{Ar}), 9.18 – 9.02 (m, 1H, CH_{Ar}), 8.38 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 8.12 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.90 (s, 1H, CH_{Ar}), 7.87 – 7.73 (m, 3H, CH_{Ar}), 7.69 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 7.63 – 7.47 (m, 5H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.4 (CH_{Ar}), 146.2 (C_{Ar}), 140.9 (C_{Ar}), 139.9 (C_{Ar}), 134.2 (C_{Ar}), 131.0 (C_{Ar}), 130.1 (CH_{Ar}), 130.1 ($2CH_{Ar}$), 129.5 (C_{Ar}), 128.7 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 128.5 (CH_{Ar}), 128.2 (CH_{Ar}), 128.0 (CH_{Ar}), 127.3 (CH_{Ar}), 127.2 (CH_{Ar}), 127.1 (CH_{Ar}), 127.0 (CH_{Ar}), 125.6 (CH_{Ar}), 124.7 (C_{Ar}), 124.5 (C_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 3026 (w), 2921 (m), 2853 (w), 1583 (m), 1573 (m), 1498 (m), 1461 (m), 1393 (m), 1371 (m), 1212 (m), 1189 (m), 1119 (m), 1072 (w), 1057 (m), 1031 (w), 965 (m), 952 (m), 878 (w), 868 (w), 785 (m), 763 (vs), 740 (s), 703 (s), 686 (m), 676 (s), 643 (m), 610 (m), 587 (m), 542 (m), 521 (m), 505 (m), 462 (m), 420 (s), 408 (m). MS (EI, 70 eV): *m/z* (%) = 306 (23), 305 ($[M]^+$, 100), 304 (53), 276 (20), 152 (12), 138 (15). HRMS (EI): Calculated for $C_{23}H_{15}N$ 305.1199 found 305.1199.

10-(tert-Butyl)-8-phenylbenzo[k]phenanthridine 14b

3-Phenyl-4-(phenylethynyl)quinoline **13b** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **14b** as white solid (80 mg, 84%), mp 142 - 143°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.36 (s, 1H, CH_{Ar}), 9.20 (d, ^3J = 9.0 Hz, 1H, CH_{Ar}), 9.17 – 9.09 (m, 1H, CH_{Ar}), 8.42 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1H, CH_{Ar}), 8.13 (d, ^4J = 2.1 Hz, 1H, CH_{Ar}), 7.94 – 7.74 (m, 4H, CH_{Ar}), 7.65 – 7.47 (m, 5H, CH_{Ar}), 1.39 (s, 9H, $3CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.8 (CH_{Ar}), 151.6 (C_{Ar}), 141.2 (C_{Ar}), 140.0 (C_{Ar}), 134.4 (C_{Ar}), 131.4 (C_{Ar}), 130.1 (CH_{Ar}), 130.1 ($2CH_{Ar}$), 129.5 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 128.0 (CH_{Ar}), 127.4

(C_{Ar}), 127.4 (CH_{Ar}), 127.2 (CH_{Ar}), 125.7 (CH_{Ar}), 125.6 (CH_{Ar}), 124.6 (C_{Ar}), 124.4 (C_{Ar}), 123.0 (C_{Ar}), 35.3($C(CH_3)_3$), 31.3 (CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2950 (m), 2865 (w), 1618 (w), 1593 (w), 1566 (w), 1496 (w), 1461 (w), 1391 (w), 1371 (w), 1358 (w), 1195 (w), 1020 (w), 925 (w), 897 (w), 866 (m), 845 (m), 796 (w), 777 (m), 752 (vs), 699 (s), 690 (m), 666 (s), 592 (m), 509 (m), 435 (m), 416 (m). MS (EI, 70 eV): *m/z* (%) = 362 (23), 361 ($[M]^+$, 85), 347 (24), 346 (100), 316 (10), 305 (12), (304 (23), (276 (11), (274 (11), 159 (15), 158 (10), 150 (10), 138 (11), 41 (35), 39 (15). HRMS (EI): Calculated for $C_{27}H_{23}N$ 361.1825 found 361.1829.

8-(4-Fluorophenyl)benzo[k]phenanthridine 14c

3-Phenyl-4-(phenylethynyl)quinoline **13c** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **14c** as yellow solid (83 mg, 87%), mp 138 - 140°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.33 (s, 1H, CH_{Ar}), 9.27 – 9.16 (m, 1H, CH_{Ar}), 9.12 – 8.99 (m, 1H, CH_{Ar}), 8.36 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 1H, CH_{Ar}), 8.15 – 7.93 (m, 1H, CH_{Ar}), 7.84 (s, 1H, CH_{Ar}), 7.83 – 7.64 (m, 4H, CH_{Ar}), 7.59 – 7.49 (m, 2H, CH_{Ar}), 7.28 – 7.21 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.5 (d, $^1J_{CF}$ = 247.1 Hz, C_{FAr}), 151.2 (CH_{Ar}), 145.2 (C_{Ar}), 138.5 (C_{Ar}), 134.7 (d, $^4J_{CF}$ = 3.5 Hz, C_{Ar}), 132.9 (C_{Ar}), 130.5 (d, $^3J_{CF}$ = 8.0 2CH_{Ar}), 129.9 (C_{Ar}), 129.1 (CH_{Ar}), 128.4 (C_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 127.0 ($CH_{Ar,}$), 126.1 (CH_{Ar}), 125.9 (CH_{Ar}), 125.9 (2CH_{Ar}), 124.6 (CH_{Ar}), 123.5 (C_{Ar}), 123.2 (C_{Ar}), 114.5 (d, $^2J_{CF}$ = 21.5 Hz, 2CH_{Ar}). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.3 (CF_{Ar}). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 2962 (w), 1604 (w), 1579 (w), 1566 (w), 1507 (m), 1492 (m), 1459 (w), 1420 (w), 1404 (w), 1389 (m), 1261 (w), 1214 (m), 1156 (m), 1092 (m), 1014 (m), 965 (w), 938 (m), 868 (w), 847 (s), 824 (m), 808 (m), 791 (m), 759 (vs), 688 (m), 676 (s), 653 (m), 620 (m), 589 (m), 571 (s), 513 (s), 468 (m), 456 (m), 427 (m), 406 (s). MS (EI, 70 eV): *m/z* (%) = 324 (24), 323 ($[M]^+$, 100), 322 (45), 321 (11), 294 (14), 147 (6). HRMS (EI): Calculated for $C_{23}H_{14}NF$ 323.1105 found 323.1097.

10-(tert-Butyl)-8-(4-fluorophenyl)benzo[k]phenanthridine 14d

3-Phenyl-4-(phenylethynyl)quinoline **13d** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **14d** as yellow solid (43 mg, 70%), mp. 161 - 162 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.33 (s, 1H, CH_{Ar}), 9.19 (d, ^3J = 9.0 Hz, 1H, CH_{Ar}), 9.11 (dd, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1H,

CH_{Ar}), 8.36 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.5 Hz, 1H, CH_{Ar}), 8.05 (d, ^{4}J = 2.1 Hz, 1H, CH_{Ar}), 7.95 – 7.69 (m, 4H, CH_{Ar}), 7.63 – 7.50 (m, 2H, CH_{Ar}), 7.31 – 7.22 (m, 2H, CH_{Ar}), 1.40 (s, 9H, $3CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.5 (d, $^{1}J_{CF}$ = 247.0 Hz, C_{FAr}), 152.3 (CH_{Ar}), 151.2 (C_{Ar}), 146.2 (C_{Ar}), 139.6 (C_{Ar}), 136.0 (d, $^{4}J_{CF}$ = 3.4 Hz, C_{Ar}), 134.0 (C_{Ar}), 131.6 (d, $^{3}J_{CF}$ = 8.0 Hz, $2CH_{Ar}$), 130.8 (C_{Ar}), 130.0 (CH_{Ar}), 128.3 ($2CH_{Ar}$), 127.4 (C_{Ar}), 127.0 (2 CH_{Ar}), 125.7 (CH_{Ar}), 125.4 (CH_{Ar}), 124.4 (C_{Ar}), 124.3 (C_{Ar}), 122.5 (CH_{Ar}), 115.5 (d, $^{2}J_{CF}$ = 21.4 Hz, $2CH_{Ar}$), 35.2 ($C(CH_3)_3$), 31.2 ($3CH_3$). ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.4 (CF_{Ar}). IR (ATR, cm^{-1}): ṽ = 2962 (m), 2867 (w), 1606 (w), 1509 (s), 1494 (m), 1461 (m), 1387 (m), 1369 (m), 1360 (m), 1268 (w), 1255 (w), 1218 (s), 1160 (s), 1097 (m), 1016 (w), 971 (w), 950 (w), 936 (w), 919 (w), 897 (w), 872 (m), 851 (m), 841 (s), 824 (m), 810 (m), 796 (w), 777 (m), 756 (vs), 723 (w), 701 (w), 688 (m), 676 (m), 649 (m), 602 (m), 594 (w), 573 (m), 563 (w), 540 (w), 534 (m), 524 (m), 505 (w), 484 (w), 472 (w), 431 (m), 406 (m). MS (EI, 70 eV): *m/z* (%) = 380 (22), 379 ($[M]^+$, 80), 365 (28), 364 (100), 322 (15), 294 (10). HRMS (EI): Calculated for $C_{27}H_{22}NF$ 379.1731 found 379.1728.

8-(Thiophen-3-yl)benzo[k]phenanthridine 14e

3-Phenyl-4-(phenylethynyl)quinoline **13e** (~0.3 mmol) and methanesulfonic acid (~0.65 ml) gave **14e** as yellow solid (34 mg, 30%), mp. 152 - 153 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.35 (s, 1H, CH_{Ar}), 9.22 (dd, ^{3}J = 8.3 Hz, ^{4}J = 0.8 Hz, 1H, CH_{Ar}), 9.08 (d, ^{3}J = 7.8 Hz, 1H, CH_{Ar}), 8.38 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, 1H, CH_{Ar}), 8.32 – 8.20 (m, 1H, CH_{Ar}), 7.95 (d, ^{4}J = 2.7 Hz, 1H, CH_{Ar}), 7.87 – 7.71 (m, 4H, CH_{Ar}), 7.57 – 7.47 (m, 2H, CH_{Ar}), 7.42 – 7.34 (m, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.1 (CH_{Ar}), 145.9 (C_{Ar}), 140.1 (C_{Ar}), 135.6 (C_{Ar}), 134.2 (C_{Ar}), 131.0 (C_{Ar}), 129.8 (CH_{Ar}), 129.4 (CH_{Ar}), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 128.2 (CH_{Ar}), 127.2 (CH_{Ar}), 127.0 (2 CH_{Ar}), 126.0 (C_{Ar}), 125.9 (CH_{Ar}), 125.8 (C_{Ar}), 125.6 (CH_{Ar}), 124.6 (C_{Ar}), 124.3 (CH_{Ar}), 124.3 (CH_{Ar}). IR (ATR, cm^{-1}): ṽ = 2962 (m), 2867 (w), 1606 (w), 1509 (s), 1494 (m), 1461 (m), 1387 (m), 1369 (m), 1360 (m), 1268 (w), 1255 (w), 1218 (s), 1160 (s), 1097 (m), 1016 (w), 971 (w), 950 (w), 936 (w), 919 (w), 897 (w), 872 (m), 851 (m), 841 (s), 824 (m), 810 (m), 796 (w), 777 (m), 756 (vs), 723 (w), 701 (w), 688 (m), 676 (m), 649 (m), 602 (m), 594 (w), 573 (m), 563 (w), 540 (w), 534 (m), 524 (m), 505 (w), 484 (w), 472 (w), 431 (m), 406 (m). MS (EI, 70 eV): *m/z* (%) = 312 (29), 311 ($[M]^+$, 100), 310 (51), 45 (20). HRMS (EI): Calculated for $C_{21}H_{13}NS$ 311.0763 found 311.0758.

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