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# Regiospecific Three-Component Access to Fluorescent 2,4-Disubstituted Quinolines via One-Pot Coupling-Addition-Cyclocondensation-Sulfur Extrusion Sequence

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*Dedicated to Prof. Dr. Franz Effenberger on the occasion of his 80th birthday*

**Keywords:** Multicomponent reactions / C-C coupling / Fluorescence / Microwave chemistry / Quinolines / Computations

2,4-Di- and 2,4,7-trisubstituted quinolines are readily synthesized in a regioselective fashion from acyl chlorides, terminal alkynes, and 2-aminothiophenols by a consecutive, microwave-assisted one-pot three-component Sonogashira coupling-Michael addition–cyclocondensation sequence and following sulfur extrusion in moderate to good yields. The terminal sulfur extrusion step was studied by DFT computations. The absorption spectra of 2,4-disubstituted quinolines can be rationalized by DFT-ZINDO-CI calculations and all derivatives show intense blue emission upon UV excitation.

## Introduction

Quinolines constitute an important class of bicyclic nitrogen-containing heterocycles. Their framework is an integral part of important natural products,[1] many with considerable biological activity,[2] some of them play an important role as antimalaria drugs.[3] In addition, quinolines are also interesting as ligands for transition-metal complexes[4] and have received attention as important building blocks in organic chemistry.[1d] Furthermore, due to their inherent fluorescent properties quinolines are of general interests as emitting chromophores.[5] As a consequence the quest for new syntheses of quinolines and substituted derivatives is an ongoing theme.[6] Among recent quinoline syntheses are e.g. aromatic annelations by reaction of arylimidoyl radicals with alkynes[7] or the Pd-catalyzed hydroarylation of α-(2-aminoaryl)-α,β-ynones with organoboron derivatives.[8] These innovations prompted us to devise multi-component accesses to quinolines. Alkynones are easily accessible by Sonogashira coupling[9] of acyl chlorides with terminal alkynes.[10] Recently, we could establish particularly favorable conditions for the coupling of acyl chlorides, where only one stoichiometrically necessary equivalent of triethylamine is needed to ensure complete conversion to the desired alkynones.[11] Based upon this facile catalytic access to alkynones under mild conditions we could establish a general diversity-oriented access to many classes of heterocycles based upon multi-component reactions that proceed in the sense of consecutive one-pot coupling–addition–cyclocondensation or coupling–cycloaddition sequences.[12] Upon reaction of dinucleophilic *o*-phenylene diamines with the in situ generated alkynones cryofluorescent 2,4-disubstituted 3*H*-benzo[*b*][1,4]diazepines were obtained in good yields.[13] The analogous reaction with 2-aminothiophenols as dinucleophiles leads to a three-component access to benzo[*b*][1,5]thiazepines.[14] Literature precedence has shown, that at elevated temperatures benzo[*b*][1,5]thiazepines tend to loose elementary sulfur furnishing quinolines.[15] Here we report a regiospecific, microwave-assisted three-component synthesis of 2,4-disubstituted quinolines in the sense of a consecutive coupling-addition–cyclocondensation–sulfur extrusion sequence, mechanistic computations on the sulfur extrusion, and first studies on the electronic properties of the quinoline derivatives by UV/Vis and fluorescence spectroscopy and ZINDO-CI computations.

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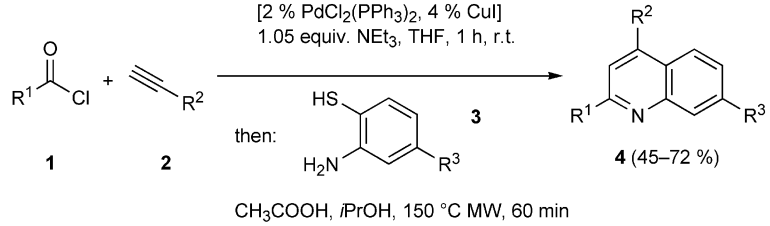
## Results and Discussion

Sulfur extrusion is a well-precedented method for ring contraction,[16] and in particular thiepines undergo aromatization to benzoid arenes upon thermal treatment. Therefore, coupling of acyl chlorides **1** and alkynes **2** under modified Sonogashira conditions in the presence of 2 mol-% of




Scheme 1. One-pot three-component synthesis of 2,4-disubstituted quinolines **4**.

$PdCl_2(PPh_3)_2$ and 4 mol-% of CuI[11] furnished the corresponding alkynones that were reacted in the same reaction vessel with 2-aminothiophenols **3** in the presence of glacial acetic acid and 2-propanol upon microwave irradiation (150 °C, 60 min) to give 2,4-disubstituted quinolines **4** in moderate to good yields (Scheme 1, Table 1). The structures of all quinoline derivatives were unambiguously supported by spectroscopy and combustion analyses or HRMS, and later by X-ray structure analysis for quinoline **4l** (Figure 1).[17]

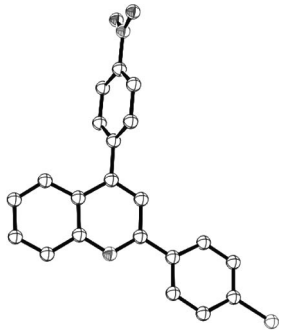


Figure 1. Molecular structure of quinoline **4l** (hydrogen atoms were omitted for clarity).

The quantitative terminal sulfur extrusion represents the crucial point in this sequence. Otherwise mixtures of the desired quinolines and the preceding benzothiazepines are obtained which are very difficult to separate by column chromatography due to similar polarity. Further attempts to trigger the sulfur extrusion, for instance by variation of the pH-conditions (pH 3–8) or by addition of triphenylphosphane[16b] met with failure. Hence, dielectric heating in a microwave cavity at 150 °C for 1 h turned out to be the best solution in most cases for complete conversion. The methodological scope for 2-(hetero)aryl and 4-silyl and 4-aryl substituents is fairly broad and electron-withdrawing, electroneutral, and electron-donating groups are well tolerated. Unfortunately, 2-alkyl substituents (stemming from the alkyne) could not be successfully applied. As a consequence of the mechanism the substitution pattern on the quinoline is regiospecific and the orientation of the substituents is dictated by the Michael addition furnishing benzo[*b*][1,5]thiazepines[14] (vide infra).

Mechanistically intriguing, however, is the sulfur extrusion by which the benzo[*b*][1,5]thiazepines are converted into quinolines. In a DFT-computational study the mechanism of the sulfur extrusion was investigated for the formation of quinoline **4c**. The geometries were optimized using the B3LYP functional and the def-SVP basis set as implemented in the program package Turbomole for DFT calculations.[18] The obtained minima and transition state structures were confirmed by analytical frequency analysis (Figure 2). Hence, the calculations revealed that after the formation of the 2,4-diphenylbenzo[*b*][1,5]thiazepine an 6π-electrocyclic ring closure with a transition state energy of 104.6 kJ/mol furnishes a 1a*H*-1-thia-4-azacyclopropa[*d*]-naphthalene containing a thiirane ring. This isomer is 82.1 kJ/mol less stable than 2,4-diphenylbenzo[*b*][1,5]thiazepine. In the transition state structure the distance of the carbon atoms forming the later thiirane is significantly shortened, while the carbon–sulfur bonds are elongated. The final sulfur extrusion from the thiirane intermediate was not calculated due to substantial computational complexity. But according to experimental and theoretical mechanistic studies on thiepine model systems by Gleiter,[19] Miller,[20] and Kassaee[21] this final step is nucleophile-assisted and proceeds via sulfur–sulfur extraction where the 2,4-diphenylquinoline (**4c**) and $S_8$ are formed.

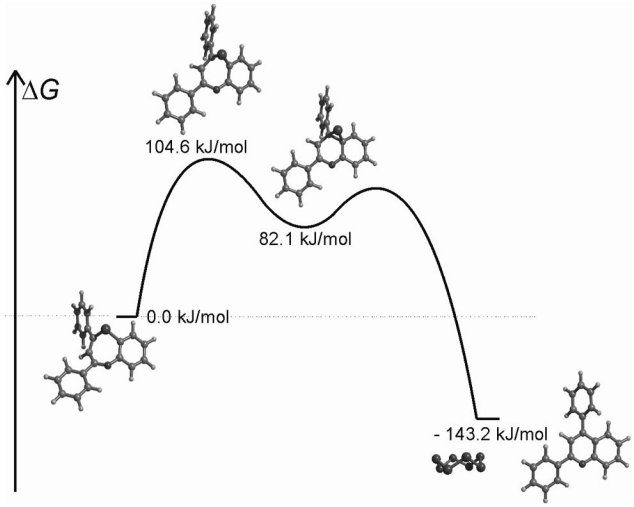



Figure 2. Calculated Gibbs free energies profile of the final sulfur extrusion from 2,4-diphenylbenzo[*b*][1,5]thiazepine to give 2,4-diphenylquinoline (**4c**) and $S_8$.

All 2,4-disubstituted quinolines **4** display long-wavelength absorption bands between 342 and 379 nm with moderate extinction coefficients and intense blue luminescence in a relatively narrow range from 367–393 nm with small Stokes shifts between 700 and 3000 $cm^{-1}$ (Table 2).

Table 1. One-pot three-component synthesis of 2,4-disubstituted quinolines **4**.

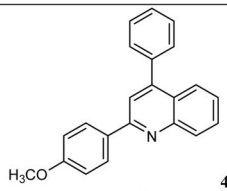
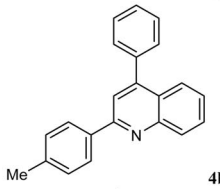
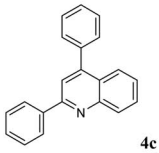
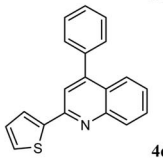
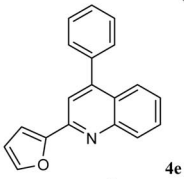
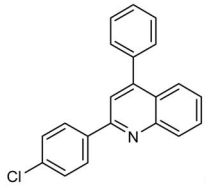
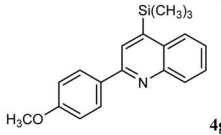
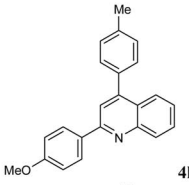
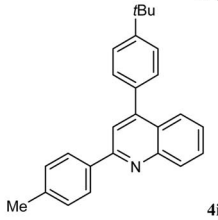
| Entry | Acyl chloride **1** | Alkyne **2** | 2-Aminothiophenol **3** | Quinoline **4** (yield) |
|---|---|---|---|---|
| 1 | $R^1$ = 4-$C_6H_4$OMe (**1a**) | $R^2$ = $C_6H_5$ (**2a**) | $R^3$ = H (**3a**) |  **4a** (58 %) |
| 2 | $R^1$ = 4-$C_6H_4$Me (**1b**) | **2a** | **3a** |  **4b** (57 %) |
| 3 | $R^1$ = $C_6H_5$ (**1c**) | **2a** | **3a** |  **4c** (47 %) |
| 4 | $R^1$ = thiophen-2-yl (**1d**) | **2a** | **3a** |  **4d** (71 %) |
| 5 | $R^1$ = furan-2-yl (**1e**) | **2a** | **3a** |  **4e** (55 %) |
| 6 | $R^1$ = 4-$C_6H_4$Cl (**1f**) | **2a** | **3a** |  **4f** (59 %) |
| 7 | **1a** | $R^2$ = $SiMe_3$ (**2b**) | **3a** |  **4g** (52 %) |
| 8 | **1a** | $R^2$ = 4-$C_6H_4$Me (**2c**) | **3b** |  **4h** (52 %) |
| 9 | **1b** | $R^2$ = 4-$C_6H_4$*t*Bu (**2d**) | **3a** |  **4i** (60 %) |

Table 1. *(Continued)*.

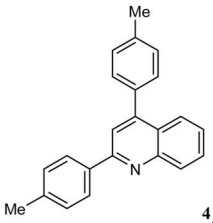
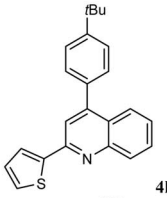
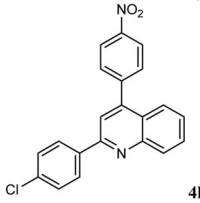
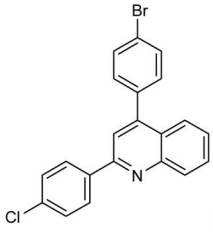
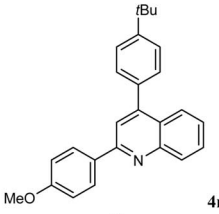
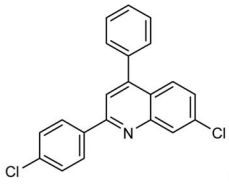
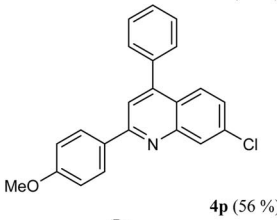
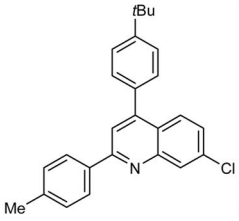
| Entry | Acyl chloride **1** | Alkyne **2** | 2-Aminothiophenol **3** | Quinoline **4** (yield) |
|---|---|---|---|---|
| 10 | **1b** | **2c** | **3a** |  **4j** (48 %) |
| 11 | **1d** | **2d** | **3a** |  **4k** (63 %) |
| 12 | **1f** | $R^2$ = 4- $C_6H_4NO_2$ (**2e**) | **3a** |  **4l** (72 %) |
| 13 | **1f** | $R^2$ = 4-$C_6H_4Br$ (**2f**) | **3a** |  **4m** (45 %) |
| 14 | **1a** | **2d** | **3a** |  **4n** (65 %) |
| 15 | **1f** | **2a** | $R^3$ = Cl (**3b**) |  **4o** (60 %) |
| 16 | **1a** | **2a** | **3b** |  **4p** (56 %) |
| 17 | **1b** | **2d** | **3b** |  **4q** (48 %) |

Table 2. Selected electronic properties (absorption, emission data, and Stokes shifts $\Delta\tilde{\nu}$) of 2,4-disubstituted quinolines **4** (recorded in $CH_2Cl_2$ at 293 K).

| Compound | Absorption $\lambda_{max,abs}$ [nm] ($\varepsilon$)[a] | Emission $\lambda_{max,em}$ [nm][b] | Stokes shift $\Delta\tilde{\nu}$[c] [$cm^{-1}$] |
|---|---|---|---|
| **4a** | 277 (24200), 306 (16800), 374 (4300) | 391 | 1200 |
| **4b** | 270 (42800), 330 (9600), 344 (7400) | 399 | 4000 |
| **4c** | 268 (40200), 327 (9600), 343 (5000) | 373 | 2300 |
| **4d** | 284 (28300), 338 (13100), 353 (11700) | 389 | 2600 |
| **4e** | 270 (25800), 302 (14900), 379 (6000) | 390 | 700 |
| **4f** | 268 (40200), 327 (9600), 343 (5000) | 373 | 2300 |
| **4g** | 260 (9500), 301 (12800), 376 (3400) | 384 | 600 |
| **4h** | 281 (28200), 334 (6500), 347 (5400) | 368 | 3000 |
| **4i** | 268 (17500), 329 (5800), 343 (3500) | 375 | 2500 |
| **4j** | 269 (32100), 330 (13100), 344 (10900) | 381 | 2800 |
| **4k** | 287 (60800), 338 (27400), 352 (24500) | 390 | 2800 |
| **4l** | 265 (7300), 287 (4100), 330 (2900), 343 (2600), 367 (900) | 390 | 1600 |
| **4m** | 269 (93200), 330 (25700), 342 (13500) | 379 | 2900 |
| **4n** | 282 (36700), 335 (25400), 349 (11100) | 389 | 2900 |
| **4o** | 271 (13500), 302 (8600), 315 (9700), 334 (4000) | 388 | 3300 |
| **4p** | 280 (32700), 340 (13900) | 393 | 4000 |
| **4q** | 266 (18300), 334 (4700), 346 (3700) | 377 | 2400 |

[a] Recorded in $CH_2Cl_2$ at $c = 10^{-3}$ M. [b] Recorded in $CH_2Cl_2$ at $c = 10^{-6}$ M. [c] $\Delta\tilde{\nu} = \lambda_{max,abs} - \lambda_{max,em}$ [$cm^{-1}$].

The absorption and emission behavior of 2-substituted quinolines has intensively been studied in the past and have revealed a substantial solvent effect on the efficiency and shift of the bands, particularly by hydrogen bonding in protic solvents.[22] Hence, the electronic properties of 2,4-disubstituted quinolines should display comparable features.

The absorption spectra of the consanguineous series of 4-phenyl-substituted derivatives **4a**–**4f** reveal that 2-substitution on the quinoline core only exerts a bathochromic effect if the donor capacity is sufficiently strong. Both a potent donor such as *p*-anisyl (**4a**) or the sterically less demanding 2-thienyl (**4d**) and 2-furyl (**4e**) donor moieties enhance the ground state coplanarity and thus generate a push-pull system. All other aryl groups with *para*-substituents absorb around 343 nm. Interestingly, in the related series of *p*-anisyl 2-substituted quinolines **4a**, **4g**, **4h**, and **4n**, subtle changes in the electronic properties of the 4-substituent cause substantial hypsochromic shifts of the long-wavelength absorption bands upon altering the substituents phenyl (**4a**) or trimethylsilyl (**4g**) to *p*-tolyl (**4h**) or *p*-*tert*-butylphenyl (**4n**).

The parent derivative of 2,4-diaryl-substituted quinolines, 2,4-diphenylquinoline (**4c**) was chosen as a model for the assignment of the absorption bands in the electronic spectra. First the geometry optimization was computed on the DFT level of theory to obtain a reasonable geometry for the subsequent electronic structure computation.[23] Based upon the DFT structure optimization of **4c** a single-point ZINDO-CI computation was performed as an inexpensive, rapid and relatively accurate calculation[24] for qualitatively assigning the electronic structure of the longest wavelength absorption bands.[25] The three longest wavelength bands of **4c** at 268, 327, and 343 nm are qualitatively reproduced by the computated absorption bands at 263, 288, and 326 nm. The lowest energy band at 343 nm, i.e. the $S_1$ state, displays moderate oscillator strength and a state dipole moment of 2.57 D. This absorption consists to 34% of HOMO-1 to LUMO and 24% of HOMO–LUMO transitions, which are represented by a $\pi$-$\pi^*$ transitions within the quinoline core (Figure 3). In addition a FMO transition from HOMO to LUMO+1 (19%) also contributes to the $S_1$ state. The band at 327 nm possesses higher oscillator strength, a significantly higher state dipole moment (4.18 D) and is based on the $S_3$ singlet state, where substantial contributions of HOMO–LUMO (52%) and HOMO-1-LUMO (13%) are

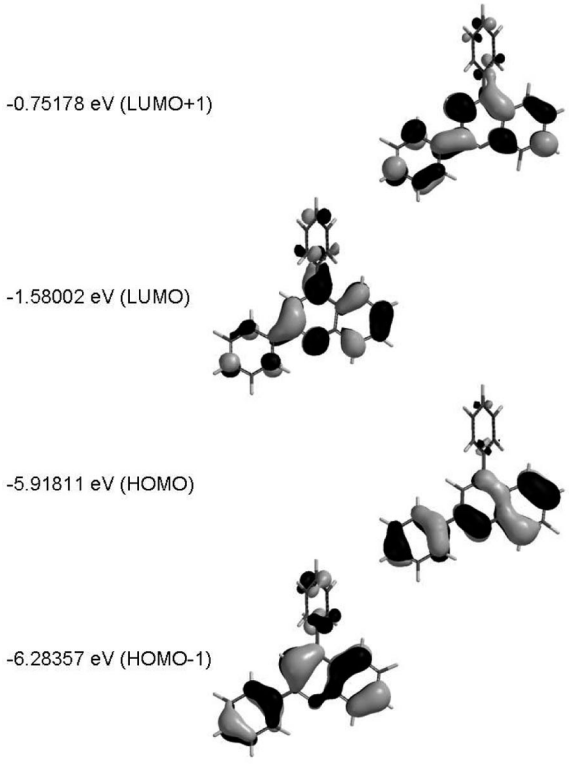



Figure 3. Selected frontier molecular orbitals (FMOs) and orbital energies of **4c**.

found. Finally, the $S_6$ singlet state displays the highest oscillator strength and arises from the absorption band at 268 nm. It predominantly consists of HOMO–LUMO+1 (37%) and HOMO-1-LUMO (34%) transitions. As a consequence of relatively small orbital coefficients in the 4-phenyl moiety in all relevant frontier orbitals only minor substituent effects on the absorption spectra can be expected.

## Conclusions

In conclusion, we have dicovered a versatile and regiospecific one-pot multi-component synthesis of 2,4-di- and 2,4,7-trisubstituted quinolines based upon a microwave-accelerated coupling–addition–cyclocondensation–sulfur extrusion sequence. After addition of 2-aminothiophenols in the addition–cyclocondensation step dielectric heating at 150 °C has proven to effectively assist the terminal sulfur extrusion. The electronic spectra of 2,4-disubstituted quinolines are dominated by the rigid quinoline core structure as shown by rapid DFT-ZINDO-CI calculations, and intense blue fluorescence with moderate Stokes shifts are observed for all derivatives. Studies expanding this novel modular approach to enhance molecular diversity in targets which are of special interest to pharmaceutical or photonic applications and more detailed photophysical investigations are currently underway.

## Experimental Section

**General Considerations:** All reactions involving water-sensitive compounds were carried out in flame-dried glassware under nitrogen atmosphere unless stated otherwise. Reagents and catalysts were purchased reagent grade and used without further purification. Solvents were dried by a solvent purification system. Flash column chromatography: silica gel 60, mesh 230–400. TLC: silica gel plates (60 $F_{254}$). $^1$H-, $^{13}$C-, DEPT-, NOESY-, COSY-, HMQC-, and HMBC spectra were recorded with a 500 MHz NMR spectrometer by using $CDCl_3$ as solvent unless stated otherwise. The assignments of quaternary C, CH, $CH_2$ and $CH_3$ were made on the basis of DEPT spectra. Mass spectra were recorded with a quadruple spectrometer. Absorption spectra were recorded with an HP8452 (Hewlett–Packard, Palo Alto, CA, USA) and a Lambda 19 (Perkin–Elmer, Waltham, MA, USA). Emission spectra were recorded with a LS-55 spectrometer (Perkin–Elmer, Waltham, MA, USA).

Elemental analyses were carried out in the microanalytical laboratory of the Pharmazeutisches Institut of the Heinrich-Heine-Universität, Düsseldorf. Dielectric heating was performed in a single-mode microwave cavity producing continuous irradiation at 2450 MHz.

**General Procedure for the Synthesis of 2,4-Substituted Quinolines 4 (GP):** In a 10 mL microwave tube, $PdCl_2(PPh_3)_2$ (15 mg, 0.02 mmol) and CuI (8 mg, 0.04 mmol) were dissolved in degassed THF (4 mL). Then, (hetero)aroyl chloride **1** (1.00 mmol), alkyne **2** (1.00 mmol), and triethylamine (1.05 mmol) were added to the orange solution. The reaction mixture was stirred at room temperature for 1 h. Finally, the 2-aminothiophenol **3** (1.10 mmol), followed by glacial acetic acid (0.5 mL) and propan-2-ol (0.5 mL), were added to this suspension, and the reaction mixture was heated in the microwave cavity at 150 °C for 60 min. After the system had cooled to room temperature, the solvent was removed under reduced pressure and the crude products were purified by flash chromatography on silica gel (hexane/ethyl acetate) to afford the analytically pure quinolines **4** (for experimental details, see Table 3).

**2-(4-Methoxyphenyl)-4-phenylquinoline (4a):**[8] According to the GP **4a** was obtained as yellow solid; m.p. 76 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 3.87 (s, 3 H, $OCH_3$), 7.04 (d, $^3J$ = 8.9 Hz, 2 H), 7.15 (s, 1 H, C$^3$-H), 7.19–7.22 (m, 1 H), 7.40–7.44 (m, 3 H), 7.51–7.52 (m, 1 H), 7.60–7.61 (m, 1 H), 7.72–7.74 (m, 1 H), 7.95–7.96 (m, 2 H), 8.09–8.11 (m, 2 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 56.8 ($CH_3$), 115.6 (2 CH), 115.8 (CH), 126.4 (CH), 128.0 (CH), 128.1 (CH), 129.3 (2 CH), 130.4 (2 CH), 131.3 (2 CH), 131.4 (CH), 131.5 ($C_{quat}$), 134.4 (CH), 134.6 ($C_{quat}$), 140.6 ($C_{quat}$), 150.4 ($C_{quat}$), 152.3 ($C_{quat}$), 164.0 ($C_{quat}$), 165.9 ($C_{quat}$) ppm. EI MS (70 eV, *m*/*z* (%)): 312 (22), 311 ([M]$^+$, 100), 310 (80), 268 (11), 267 (28), 266 (11), 156 (14), 139 (12), 134 (14), 133 (19), 121 (12). IR (film): $\tilde{\nu}$ = 2935 (w), 1609 (s), 1514 (w), 1481 (w), 1355 (m), 1340 (w), 1321 (w), 1176 (m), 1120 (m), 1072 (s), 1035 (s), 866 (m), 765 (w), 702 (w), 534 (w). $C_{22}H_{17}NO$ (311.4): C 84.86, H 5.50, N 4.50; found C 84.60, H 5.59, N 4.39.

**4-Phenyl-2-(4-tolyl)quinoline (4b):**[6e] According to the GP **4b** was obtained as yellow solid; m.p. 102 °C. $^1$H NMR (500 MHz,

Table 3. Experimental details of the synthesis of 2,4-disubstituted quinolines **4**.

| Entry | Acyl chloride **1** [mg] (mmol) | Alkyne **2** [mg] (mmol) | *ortho*-Aminothiophenol **3** [mg] (mmol) | Quinoline **4** [mg] (yield, %) |
|---|---|---|---|---|
| 1 | 171 (1.00) of **1a** | 102 (1.00) of **2a** | 138 (1.10) of **3a** | 181 (58) of **4a** |
| 2 | 155 (1.00) of **1b** | 102 (1.00) of **2a** | 138 (1.10) of **3a** | 168 (57) of **4b** |
| 3 | 141 (1.00) of **1c** | 102 (1.00) of **2a** | 138 (1.10) of **3a** | 133 (47) of **4c** |
| 4 | 147 (1.00) of **1d** | 102 (1.00) of **2a** | 138 (1.10) of **3a** | 203 (71) of **4d** |
| 5 | 131 (1.00) of **1e** | 102 (1.00) of **2a** | 138 (1.10) of **3a** | 149 (55) of **4e** |
| 6 | 175 (1.00) of **1f** | 102 (1.00) of **2a** | 138 (1.10) of **3a** | 186 (59) of **4f** |
| 7 | 171 (1.00) of **1a** | 98 (1.00) of **2b** | 138 (1.10) of **3a** | 191 (52) of **4g** |
| 8 | 171 (1.00) of **1a** | 116 (1.00) of **2c** | 176 (1.10) of **3b** | 168 (52) of **4h** |
| 9 | 155 (1.00) of **1b** | 158 (1.00) of **2d** | 138 (1.10) of **3a** | 211 (60) of **4i** |
| 10 | 155 (1.00) of **1b** | 116 (1.00) of **2c** | 138 (1.10) of **3a** | 149 (48) of **4j** |
| 11 | 147 (1.00) of **1d** | 158 (1.00) of **2d** | 138 (1.10) of **3a** | 218 (63) of **4k** |
| 12 | 175 (1.00) of **1f** | 147 (1.00) of **2e** | 138 (1.10) of **3a** | 260 (72) of **4l** |
| 13 | 175 (1.00) of **1f** | 181 (1.00) of **2f** | 138 (1.10) of **3a** | 178 (45) of **4m** |
| 14 | 171 (1.00) of **1a** | 158 (1.00) of **2d** | 138 (1.10) of **3a** | 238 (65) of **4n** |
| 15 | 175 (1.00) of **1f** | 102 (1.00) of **2a** | 176 (1.10) of **3b** | 210 (60) of **4o** |
| 16 | 171 (1.00) of **1a** | 102 (1.00) of **2a** | 176 (1.10) of **3b** | 193 (56) of **4p** |
| 17 | 155 (1.00) of **1b** | 158 (1.00) of **2d** | 176 (1.10) of **3b** | 184 (48) of **4q** |

$CDCl_3$): $\delta$ = 2.43 (s, 3 H, $CH_3$), 7.33 (d, $^3J$ = 8.0 Hz, 2 H), 7.44–7.56 (m, 6 H), 7.72 (m, 1 H), 7.80 (s, 1 H, $C^3$-H), 7.89 (d, $^3J$ = 8.4 Hz, 1 H), 8.11 (d, $^3J$ = 8.0 Hz, 2 H), 8.24 (d, $^3J$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.5 ($CH_3$), 119.4 (CH), 125.8 (CH), 125.9 (CH), 126.3 (CH), 127.6 (2 CH), 128.5 (CH), 128.8 (2 CH), 129.6 (CH), 129.8 (2 CH), 130.2 (CH), 137.0 ($C_{quat}$), 138.7 ($C_{quat}$), 139.6 ($C_{quat}$), 149.0 ($C_{quat}$), 149.2 ($C_{quat}$), 157.0 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 3051 (br., m), 2199 (m), 1590 (s), 1542 (m), 1355 (br., m), 1285 (br., w), 822 (m), 774 (s), 704 (m). MALDI-TOF MS (Matrix: 4,5-dihydroxyanthracen-10(9*H*)-one): *m*/*z* (%) = 296 [M + H]$^+$. HRMS (EI): calcd. for $C_{22}H_{16}N$ ([M – H]$^+$) 294.12773, found 294.12771.

**2,4-Diphenylquinoline (4c):**[7b] According to the GP **4c** was obtained as yellow solid; m.p. 109 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.46 (m, 2 H), 7.50–7.56 (m, 7 H), 7.73 (t, $^3J$ = 7.6 Hz, 1 H), 7.82 (s, 1 H, $C^3$-H), 7.90 (m, 1 H), 8.18 (m, 2 H), 8.24 (m, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 119.8 (CH), 125.6 (CH), 125.8 (CH), 126.3 (CH), 127.6 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH), 129.3 (CH), 129.5 (CH), 129.6 (CH), 130.1 (CH), 138.9($C_{quat}$), 140.0 ($C_{quat}$), 149.1 ($C_{quat}$), 149.7 ($C_{quat}$), 157.3 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2924 (m), 1588 (br., m), 1544 (s), 1488 (m), 1356 (m), 1073 (br., m), 766 (m), 702 (m). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 282 [M + H]$^+$.

**4-(Phenyl)-2-(thiophen-2-yl)quinoline (4d):**[6a] According to the GP **4d** was obtained as yellow solid; m.p. 91 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.14 (m, 1 H), 7.42–7.54 (m, 7 H), 7.67–7.73 (m, 3 H), 7.82 (d, $^3J$ = 8.4 Hz, 1 H), 8.20 (d, $^3J$ = 8.4 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 118.3 (CH), 126.1 (CH), 126.3 (CH), 126.6 (CH), 126.6 ($C_{quat}$), 128.5 (CH), 128.9 (CH), 129.0 (CH), 129.0 (2 CH), 129.9 (2 CH), 130.1 (CH), 130.1 (CH), 138.5 ($C_{quat}$), 145.8 ($C_{quat}$), 149.0 ($C_{quat}$), 149.5 ($C_{quat}$), 152.3 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 3062 (br., m), 2362 (br., w), 1723 (br., w), 1590 (m), 1549 (m), 1428 (m), 1356 (br. m), 1228 (br., m), 770 (br., m). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 288 [M + H]$^+$. $C_{19}H_{13}NS$ (287.4): C 79.41, H 4.56, N 4.87; found C 79.37, H 4.49, N 4.90.

**2-(Furan-2-yl)-4-phenylquinoline (4e):**[6e] According to the GP **4e** was obtained as yellow solid; m.p. 109 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.17–7.19 (m, 1 H), 7.27–7.30 (m, 3 H), 7.44–7.47 (m, 3 H), 7.67 (d, $^3J$ = 8.0 Hz, 1 H), 7.78–7.79 (m, 2 H), 7.80–7.82 (m, 1 H), 8.10–8.12 (m, 2 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 124.7 (CH), 126.5 (CH), 127.4 (CH), 128.6 (2 $CH_2$), 129.0 (CH), 129.2 (CH), 129.8 (2 CH), 130.9 (CH), 131.2 (CH), 131.5 (CH), 133.0 ($C_{quat}$), 134.7 (CH), 135.9 ($C_{quat}$), 138.9 ($C_{quat}$), 146.5 ($C_{quat}$), 150.7 ($C_{quat}$), 155.7 ($C_{quat}$) ppm. EI MS [70 eV, *m*/*z* (%)]: 272 (21), 271 ([M]$^{+\cdot}$, 100), 270 (21), 243 (17), 242 (16), 241 (22), 121 (21). IR (KBr): $\tilde{\nu}$ = 1600 (m), 1564 (m), 1558 (s), 1470 (s), 1317 (m), 1202 (w), 1152 (w), 1088 (w), 1065 (w), 1019 (m), 883 (w), 859 (w), 830 (w), 802 (w), 774 (s), 689 (m), 536 (w). $C_{19}H_{13}NO$ (271.3): C 84.11, H 4.83, N 5.16; found C 84.48, H 4.92, N 5.05.

**2-(4-Chlorophenyl)-4-phenylquinoline (4f):**[6g] According to the GP **4f** was obtained as yellow solid; m.p. 103 °C. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.45–7.55 (m, 8 H), 7.68–7.73 (m, 1 H), 7.76 (s, 1 H, $C^3$-H), 7.86–7.91 (m, 1 H), 8.12–8.24 (m, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 119.1 (CH), 125.9 (CH), 126.0 ($C_{quat}$), 126.8 (CH), 128.7 (CH), 128.8 (2 CH), 129.0 (2 CH), 129.2 (2 CH), 129.7 (2 CH), 129.9 (CH), 130.3 (CH), 135.8 ($C_{quat}$), 138.2 ($C_{quat}$), 138.5 ($C_{quat}$), 149.0 ($C_{quat}$), 149.6 ($C_{quat}$), 155.7 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 1719 (w), 1655 (m), 1594 (br. m), 1544 (m), 1489 (br., m), 1356 (br., m), 1094 (m), 1016 (w), 831 (m), 770 (s), 700 (s). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 316 [M + H]$^+$. HRMS (EI): calcd. for $C_{21}H_{13}NCl$ ([M – H]$^+$) 314.07310; found 314.07294.

**2-(4-Methoxyphenyl)-4-(trimethylsilyl)quinoline (4g):**[6f] According to the GP **4g** was obtained as pale yellow solid; m.p. 109 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.25 (s, 9 H, $SiMe_3$), 3.86 (s, 3 H, $OCH_3$), 6.99 (s, 1 H, $C^3$-H), 7.04 (d, $^3J$ = 8.8 Hz, 2 H), 7.15–7.17 (m, 1 H), 7.26–7.31 (m, 2 H), 7.35–7.39 (m, 1 H), 7.95 (d, $^3J$ = 8.8 Hz, 2 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 1.8 (3 $CH_3$), 56.2 ($CH_3$), 115.2 (2 CH), 127.4 (2 CH), 130.4 (CH), 130.4 (2 CH), 131.2 ($C_{quat}$), 132.4 ($C_{quat}$), 133.1 (CH), 138.3 ($C_{quat}$), 152.1 ($C_{quat}$), 155.7 ($C_{quat}$), 158.7 ($C_{quat}$), 166.7 ($C_{quat}$) ppm. EI MS [70 eV, *m*/*z* (%)]: 308 (24), 307 ([M]$^{+\cdot}$, 100), 306 (73), 293 (15), 292 (56), 249 (22), 146 (27), 73 (22). IR (KBr): $\tilde{\nu}$ = 3037 cm$^{-1}$ (w), 2964 (w), 2833 (w), 1594 (s), 1557 (m), 1510 (m), 1424 (m), 1316 (m), 1290 (w), 1256 (s), 1182 (s), 1025 (m), 950 (w), 844 (s), 698 (w), 616 (m), 602 (w), 547 (w), 531 (w). $C_{19}H_{21}NOSi$ (307.5): C 74.22, H 6.88, N 4.56; found C 73.98, H 6.92, N 4.48.

**2-(4-Methoxyphenyl)-4-(4-tolyl)quinoline (4h):**[8] According to the GP **4h** was obtained as yellow solid; m.p. 115–117 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.47 (s, 3 H, $CH_3$), 3.87 (s, 3 H, $OCH_3$), 7.03 (d, $^3J$ = 8.7 Hz, 2 H), 7.34 (d, $^3J$ = 7.9 Hz, 2 H), 7.41 (d, $^3J$ = 8.0 Hz, 1 H), 7.45 (d, $^3J$ = 7.9 Hz, 2 H), 7.69 (m, 1 H), 7.75 (s, 1 H, $C^3$-H), 7.90 (d, $^3J$ = 8.4 Hz, 1 H), 8.16 (d, $^3J$ = 8.7 Hz, 2 H), 8.20 (d, $^3J$ = 8.4 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.5 ($CH_3$), 55.6 ($CH_3$), 114.4 (2 CH), 119.1 (CH), 125.8 ($C_{quat}$), 125.9 (CH), 126.0 (CH), 129.1 (2 CH), 129.5 (2 CH), 129.6 (CH), 129.7 (2 CH), 130.1 (CH), 135.8 ($C_{quat}$), 138.4 ($C_{quat}$), 149.0 ($C_{quat}$), 149.2 ($C_{quat}$), 156.6 ($C_{quat}$), 161 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2934 (br., w), 2345 (w), 1606 (m), 1592 (br., m), 1543 (m), 1497 (m), 1250 (br. m), 1031 (br., m), 822 (m). MALDI-TOF MS [Matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 326 [M + H]$^+$. HRMS (EI): calcd. for $C_{23}H_{19}NO$ ([M – H]$^+$) 325.14612; found 325.14579.

**4-(4-*tert*-Butylphenyl)-2-(4-tolyl)quinoline (4i):** According to the GP **4i** was obtained as yellow solid; m.p. 120 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.43 (s, 9 H, $CMe_3$), 2.43 (s, 3 H, $CH_3$), 7.33 (d, $^3J$ = 7.9 Hz, 2 H), 7.45 (ddd, $^3J$ = 8.2 Hz, $^3J$ = 6.8 Hz, $^4J$ = 1.2 Hz, 1 H), 7.51 (dd, $^3J$ = 8.5 Hz, $^4J$ = 1.1 Hz, 2 H), 7.57 (dd, $^3J$ = 8.5 Hz, $^4J$ = 1.1 Hz, 2 H), 7.72 (ddd, $^3J$ = 8.2 Hz, $^3J$ = 6.8 Hz, $^4J$ = 1.2 Hz, 1 H), 7.82 (s, 1 H, $C^3$-H), 7.97 (dd, $^3J$ = 8.4 Hz, $^4J$ = 0.9 Hz, 1 H), 8.11 (d, $^3J$ = 7.9 Hz, 2 H), 8.25 (dd, $^3J$ = 8.4 Hz, $^4J$ = 0.9 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.5 ($CH_3$), 31.6 (3 × $CH_3$), 34.9 ($C_{quat}$), 119.4 (CH), 125.7 (2 CH), 126.0 (CH), 126.0 ($C_{quat}$), 126.2 (CH), 127.6 (2 CH), 129.5 (2 CH), 129.6 (CH), 129.7 (2 CH), 130.2 (CH), 135.7 ($C_{quat}$), 137.1 ($C_{quat}$), 139.5 ($C_{quat}$), 149.0 ($C_{quat}$), 149.2 ($C_{quat}$), 151.6 ($C_{quat}$), 157.0 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (br., m), 2866 (m), 1592 (s), 1543 (m), 1360 (br., m), 1019 (m), 820 (m), 765 (br., s), 597 (m). MALDI-TOF MS [Matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 352 [M + H]$^+$. $C_{26}H_{25}N$ (351.5): C 88.85, H 7.17, N 3.99; found C 88.64, H 7.28, N 3.79.

**4-(4-Tolyl)-2-(4-tolyl)quinoline (4j):** According to the GP **4j** was obtained as yellow solid; m.p. 88 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.44 (s, 3 H, $CH_3$), 2.49 (s, 3 H, $CH_3$), 7.35 ('t', $^3J$ = 7.9 Hz, 4 H), 7.47 (m, 3 H), 7.72 (m, 1 H), 7.81 (s, 1 H, $C^3$-H), 7.94 (d, $^3J$ = 7.6 Hz, 1 H), 8.13 (d, $^3J$ = 8.2 Hz, 2 H), 8.27 (d, $^3J$ = 8.2 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.5 ($CH_3$), 21.5 ($CH_3$), 119.3 (CH), 125.8 (CH), 125.9 ($C_{quat}$), 126.2 (CH), 127.6 (2 CH), 129.4 (2 CH), 129.5 (CH), 129.6 (2 CH), 129.7 (2 CH), 130.2 (CH), 135.7 ($C_{quat}$), 137.0 ($C_{quat}$), 138.4 ($C_{quat}$), 139.5 ($C_{quat}$), 149.0 ($C_{quat}$), 149.2 ($C_{quat}$), 157.0 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 3027 (m), 2920 (br., m), 1721 (br., w), 1592 (s), 1543 (m), 1497 (m), 1421 (br. m), 1357 (br., m), 114 (br., w), 819 (s), 764 (m). MALDI-TOF MS

[matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 310 [M + H]$^+$. $C_{23}H_{19}N$ (309.4): C 89.23, H 6.19, N 4.53; found C 88.96, H 6.28, N 4.79.

**4-(4-*tert*-Butylphenyl)-2-(thiophen-2-yl)quinoline (4k):** According to the GP **4k** was obtained as yellow solid; m.p. 158 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.41 (s, 9 H, $CMe_3$), 7.14 (dd, $^3J$ = 5.0 Hz, $^3J$ = 5.0 Hz, 1 H), 7.42 (ddd, $^3J$ = 8.2 Hz, $^3J$ = 6.8 Hz, $^4J$ = 1.2 Hz, 1 H), 7.45 (dd, $^3J$ = 5.0 Hz, $^3J$ = 1.1 Hz, 1 H), 7.48 (dd, $^3J$ = 8.5 Hz, $^4J$ = 1.2 Hz, 2 H), 7.56 (dd, $^3J$ = 8.5 Hz, $^4J$ = 1.2 Hz, 2 H), 7.67 (ddd, $^3J$ = 8.2 Hz, $^3J$ = 6.8 Hz, $^4J$ = 1.2 Hz, 1 H), 7.72 (dd, $^3J$ = 5.0 Hz, $^4J$ = 1.1 Hz, 1 H), 7.72 (s, 1 H, C$^3$-H), 7.89 (dd, $^3J$ = 8.4 Hz, $^4J$ = 0.9 Hz, 1 H), 8.13 (dd, $^3J$ = 8.4 Hz, $^4J$ = 0.9 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 31.6 (3 $CH_3$), 35.0 ($C_{quat}$), 118.2 (CH), 125.8 (2 CH), 126.0 (CH), 126.1 (CH), 126.2 ($C_{quat}$), 126.2 (CH), 128.3 (CH), 128.7 (CH), 129.5 (2 CH), 129.8 (CH), 129.9 (CH), 135.4 ($C_{quat}$), 145.7 ($C_{quat}$), 148.6 ($C_{quat}$), 148.9 ($C_{quat}$), 151.8 ($C_{quat}$), 152.0 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2963 (br., m), 2864 (br., w), 3005 (w), 1592 (s), 1499 (m), 1364 (br., s), 1021 (br. w), 840 (m), 769 (m), 713 (m). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 344 [M + H]$^+$. $C_{23}H_{21}NS$ (343.5): C 80.42, H 6.16, N 4.08; found C 80.38, H 6.03, N 4.16.

**2-(4-Chlorophenyl)-4-(4-nitrophenyl)quinoline (4l):**[13] According to the GP **4l** was obtained as yellow solid; m.p. 145 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.41–7.49 (m, 4 H), 7.63–7.74 (m, 5 H), 8.10 (d, $^3J$ = 8.6 Hz, 2 H), 8.36 (d, $^3J$ = 8.8 Hz, 2 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 118.7 (2 CH), 123.9 (2 CH), 124.3 ($C_{quat}$), 124.8 (2 CH), 125.0 ($C_{quat}$), 127.3 (CH), 128.8 (2 CH), 129.1 (2 CH), 130.5 (2 CH), 132.3 ($C_{quat}$), 133.4 ($C_{quat}$), 144.8 ($C_{quat}$), 148.0 ($C_{quat}$), 150.5 ($C_{quat}$), 155.5 ($C_{quat}$) ppm. EI MS [70 eV, *m*/*z* (%)]: 362 (11), 361 ([M]$^{+\cdot}$, 12), 360 (33), 359 (14), 313 (14), 292 (17), 257 (17), 256 (100), 235 (15), 226 (12), 210 (41), 209 (27), 198 (14), 139 (20), 91 (13), 43 (12). IR (KBr): $\tilde{\nu}$ = 1587 cm$^{-1}$ (s), 1544 (m), 1520 (s), 1488 (m), 1422 (w), 1347 (s), 1106 (m), 1090 (m), 1016 (m), 971 (w), 857 (m), 830 (m), 766 (m), 716 (w), 699 (m), 581 (w), 539 (w). $C_{21}H_{13}ClN_2O_2$ (360.8): C 69.91, H 3.63, N 7.76; found C 69.64, H 3.69, N 7.67.

**2-(4-Chlorophenyl)-4-(4-bromophenyl)quinoline (4m):** According to the GP **4m** was obtained as yellow solid; m.p. 149 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.39–7.52 (m, 5 H), 7.65–7.74 (m, 4 H), 7.81 (d, $^3J$ = 8.4 Hz, 1 H), 8.10–8.15 (m, 2 H), 8.20 (d, $^3J$ = 8.5 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 119.2 (CH), 125.6 ($C_{quat}$), 125.7 (CH), 127.3 (CH), 129.3 (2 CH), 130.4 (CH), 130.5 (CH), 131.5 (2 CH), 132.3 (2 CH), 136.0 ($C_{quat}$), 137.3 ($C_{quat}$), 137.9 ($C_{quat}$), 148.5 ($C_{quat}$), 148.8 ($C_{quat}$), 154.3 ($C_{quat}$), 155.7 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 1655 (m), 1594 (br., m), 1484 (br., m), 1421 (m), 1356 (br., w), 1092 (br. s), 1011 (s), 582 (w). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 396 [M + H]$^+$. $C_{21}H_{13}BrClN$ (394.7): C 63.90, H 3.32, N 3.55; found C 63.64, H 3.18, N 3.51.

**4-(4-*tert*-Butylphenyl)-2-(4-methoxyphenyl)quinoline (4n):** According to the GP **4n** was obtained as yellow solid; m.p. 133 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.42 (s, 9 H, $CMe_3$), 3.86 (s, 3 H, OMe), 7.03 (d, $^3J$ = 8.7 Hz, 2 H), 7.43 (m, 1 H), 7.50 (d, $^3J$ = 8.1 Hz, 2 H), 7.56 (d, $^3J$ = 8.1 Hz, 2 H), 7.70 (m, 1 H), 7.77 (s, 1 H, C$^3$-H), 7.94 (d, $^3J$ = 8.3 Hz, 1 H), 8.16 (d, $^3J$ = 8.7 Hz, 2 H), 8.21 (d, $^3J$ = 8.3 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 31.6 (3× $CH_3$), 34.9 ($C_{quat}$), 55.6 ($CH_3$), 114.4 (2 CH), 119.1 (CH), 125.7 (2 CH), 125.8 ($C_{quat}$), 126.0 (CH), 126.0 (CH), 129.1 (2 CH), 129.5 (2 CH), 129.6 (CH), 130.0 (CH), 132.4 ($C_{quat}$), 135.7 ($C_{quat}$), 148.9 ($C_{quat}$), 149.2 ($C_{quat}$), 151.7 ($C_{quat}$), 156.6 ($C_{quat}$), 161.0($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2962 (br., m), 1686 (w), 1607 (br., m), 1459 (w), 1363 (br., w), 1250 (br., m), 1180 (m), 1030 (br., w), 835 (m). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 368 [M + H]$^+$. $C_{26}H_{25}O$ (367.5): C 84.98, H 6.86, N 3.81; found C 84.81, H 6.78, N 3.83.

**7-Chloro-2-(4-chlorophenyl)-4-phenylquinoline (4o):** According to the GP **4o** was obtained as yellow solid; m.p. 124 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.25 (s, 1 H, C$^3$-H), 7.43–7.46 (m, 2 H), 7.53–7.62 (m, 4 H), 7.90 (m, $^3J$ = 8.9 Hz, 1 H), 8.05 (s, 1 H), 8.14 (d, $^3J$ = 8.8 Hz, 2 H), 8.39 (d, $^3J$ = 8.9 Hz, 2 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 120.5 (CH), 126.3 (CH), 129.5 (2 CH), 130.4 (CH), 130.4 (2 CH), 130.6 (CH), 131.2 (2 CH), 131.6 (CH), 131.8 (2 CH), 134.1 (CH), 135.8 ($C_{quat}$), 141.0 ($C_{quat}$), 151.5 ($C_{quat}$), 152.3 ($C_{quat}$), 153.5 ($C_{quat}$), 158.2 ($C_{quat}$), 165.6 ($C_{quat}$) ppm. EI MS [70 eV, *m*/*z* (%)]: 353 (11), 352 (19), 351 (61), 350 (87), 349 (93), 348 (100), 316 (14), 314 (43), 278 (15), 277 (14), 238 (13), 236 (21), 202 (15), 201 (26), 176 (17), 158 (12), 157 (34), 140 (13), 139 (66), 138 (21), 126 (13), 125 (30), 124 (10). IR (KBr): $\tilde{\nu}$ = 1611 (m), 1529 (m), 1451 (s), 1435 (m), 1352 (w), 1301 (s), 1247 (s), 1182 (s), 1110 (w), 1056 (w), 1030 (s), 1011 (m), 835 (s), 783 (m), 705 (m), 672 (w), 609 (m), 527 (w). $C_{21}H_{13}Cl_2N$ (350.2): C 72.01, H 3.74, N 4.00; found C 71.82, H 3.86, N 3.91.

**7-Chloro-2-(4-methoxyphenyl)-4-phenylquinoline (4p):** According to the GP **4p** was obtained as yellow solid; m.p. 106 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 3.87 (s, 3 H, OMe), 7.02 (d, $^3J$ = 8.9 Hz, 2 H), 7.36 (dd, $^3J$ = 8.9 Hz, $^4J$ = 2.1 Hz, 1 H), 7.52 (m, 5 H), 7.74 (s, 1 H, C$^3$-H), 7.78 (d, $^3J$ = 8.9 Hz, 1 H), 8.14 (m, 2 H), 8.18 (s, $^4J$ = 2.1 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 55.6 ($CH_3$), 114.5 (2 CH), 119.1 (CH), 124.2 ($C_{quat}$), 127.0 (CH), 127.2 (CH), 128.8 (CH), 128.9 (2 CH), 129.0 (CH), 129.2 (2 CH), 129.7 (2 CH), 131.9 ($C_{quat}$), 135.6 ($C_{quat}$), 138.3 ($C_{quat}$), 149.3 ($C_{quat}$), 149.5 ($C_{quat}$), 157.6 ($C_{quat}$), 161.3 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2975 (br., m), 1601 (br., s), 1421 (m), 1248 (br., m), 1049 (br., s), 838 (m), 769 (m), 699 (br., m). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 346 [M + H]$^+$. HRMS (EI): calcd. for $C_{22}H_{15}ClNO$ ([M – H]$^+$) 344.08367; found 344.08351.

**4-(4-*tert*-Butylphenyl)-7-chloro-2-(4-tolyl)quinoline (4q):** According to the GP **4q** was obtained as yellow solid; m.p. 42 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.41 (s, 9 H, $CMe_3$), 2.42 (s, 3 H, $CH_3$), 7.31 (d, $^3J$ = 8.2 Hz, 2 H), 7.38 (dd, $^3J$ = 8.9 Hz, $^4J$ = 2.0 Hz, 1 H), 7.46 (d, $^3J$ = 8.2 Hz, 2 H), 7.56 (d, $^3J$ = 8.2 Hz, 2 H), 7.78 (s, 1 H, C$^3$-H), 7.87 (d, $^3J$ = 8.9 Hz, 1 H), 8.07 (d, $^3J$ = 8.2 Hz, 2 H), 8.20 (d, $^4J$ = 2.0 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.6 ($CH_3$), 31.6 (2 $CH_3$), 35.0 ($C_{quat}$), 119.5 (CH), 124.5 ($C_{quat}$), 125.8 (2 CH), 127.0 (CH), 127.4 (CH), 127.7 (2 CH), 129.0 (CH), 129.4 (2 CH), 129.8 (2 CH), 135.3 ($C_{quat}$), 135.5 ($C_{quat}$), 136.6 ($C_{quat}$), 139.9 ($C_{quat}$), 149.3 ($C_{quat}$), 149.6 ($C_{quat}$), 152.0 ($C_{quat}$), 158.0 ($C_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2971 (br., w), 1589 (br., w), 1543 (w), 1491 (w), 1050 (br., w), 909 (w), 826 (br., w). MALDI-TOF MS [matrix: 4,5-dihydroxyanthracen-10(9*H*)-one]: *m*/*z* (%) = 386 [M + H]$^+$. $C_{26}H_{24}ClN$ (385.9): C 80.92, H 6.27, N 3.63; found C 80.26, H 6.97, N 3.43.

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