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ORIGINAL PAPER

Synthesis of benzoquinoline derivatives from formyl naphthylamines via Friedländer annulation under metal-free conditions

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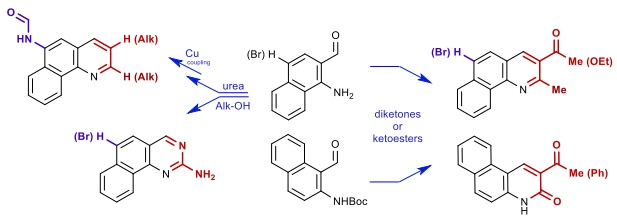
Abstract

The synthesis of benzoquinolines and benzoquinolinones via Friedländer-type condensation of aminonaphthalene carbaldehydes with (1) primary or secondary alcohols mediated by urea/KOH or with (2) diketones or β-ketoesters is described. The behavior of naphthalene derivatives in the Friedländer annulation, resulted in the formation of Friedländer or non-Friedländer products, is also presented.

Graphical abstract



Keywords Benzoquinolines · Benzoquinolinones · Friedländer synthesis · Urea · Formamidation · Copper(II) coupling

Introduction

Functionalized quinolines and quinolinones have aroused strong interest of medicinal and pharmaceutical chemistry, on account of their diverse biological properties [1–5] such as, e.g., anti-inflammatory [6, 7], antimicrobial [8, 9], antioxidant [10], or antitumor [11–14] activity, which qualify them as excellent targets in therapeutic and medicinal research. The classical approaches for the quinoline ring construction involve inter alia Skraup [15] and Doebner–Miller [15, 16] or Pfitzinger [17, 18] methodology. Much attention has been devoted to developing these synthesis methods by using various carbonyl components [19–22].

The aim of the present work is an application of formyl naphthylamines in the construction of alkyl substituted benzo[*h*]- or benzo[*f*]quinolines **B** and quinoline-2(1*H*)-ones **C** via Friedländer condensation (Scheme 1). In this work, we want to shed some light on the mediated by urea/KOH synthesis of quinolines (Friedländer product) and on the specific formation of quinoline-2(1*H*)-ones (non-Friedländer product) from *N*-Boc 2-naphthylamine derivatives under basic conditions.

Results and discussion

We began our studies from the synthesis of carbamates **2**, **7** (Scheme 2) being key compounds in the construction of the benzoquinoline skeleton. Their synthesis involved the

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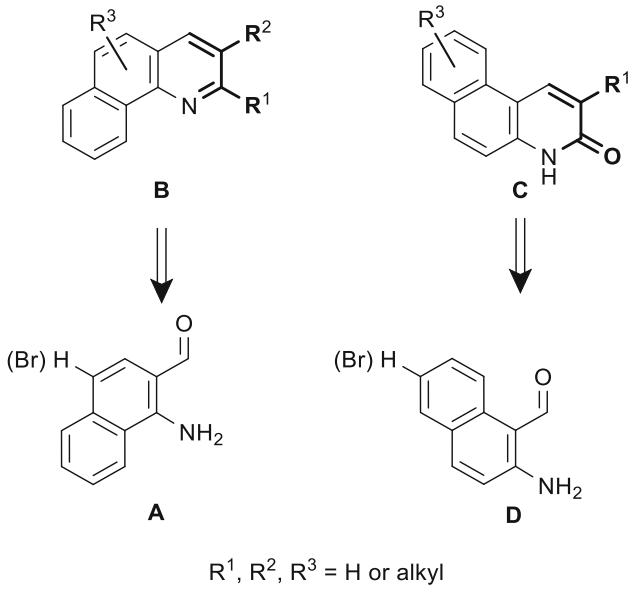
Scheme 1



reactions of the aryllithium species, generated from **2**, **7** and *t*-BuLi or BuLi [23–25], with DMF and provided to corresponding formyl derivatives **2** and **7** with 60 and 50% yields, respectively. Next, derivative **2** subjected to bromination reaction with NBS in acetonitrile used as a solvent led to bromocarbamate **3** (75%). The subsequent cleavage of the Boc protecting group of **3** by treatment with HCl_{aq} afforded desired bromoamine **5** in 92% yield. In turn, the deprotection of *N*-Boc amine **2**, under the same reaction conditions as above, gave aminoaldehyde **4** in good, albeit a bit lower 75% yield (Scheme 2).

On the other hand, attempts to obtain bromocarbamate **8**, bromoamine **10**, or amine **9** ended in failure (Scheme 2). In all cases, difficult to analyze mixtures were obtained, which did not contain target products **8** or **9** (^{1}H NMR).

In the recent years, the indirect variant of Friedländer reaction has become a very popular wherein both electrophilic and/or nucleophilic components are generated in situ from appropriate primary and/or secondary alcohols [26–28]. However, the available in the literature examples often include the use of frequently expensive catalysts, e.g., $RuCl_2$-$(DMSO)_4$ [29–31], $RhCl(PPh_3)_3$ [32], and $IrCl(cod)_2$ [33]. The alternative approach, described in last years, can be the aerial oxidation of alcohols to appropriate carbonyl compounds carried out with air access and without the use of catalyst [34–39].

With the formyl amines **4** and **5** in hand, we focused on the using of primary and secondary alcohols as a source of active carbonyl compounds, able to cyclize with **4** or **5** in the presence of urea and form benzo[*h*]quinolines **11** via Friedländer annulations [40–43]. During our earlier studies on the construction of benzo[*h*]quinazolin-2(1*H*)-ones from 1-naphthylamine derivatives with the use of urea as a condensing agent, we have observed that heating of the 2-formyl-1-naphthylamine with urea/KOH in alcohol solution can led to the formation of benzo[*h*]quinoline skeleton. We began our experiments by investigating the reaction of **5** with ethanol, in the presence of 1 equiv. KOH (Table 1, entry 1). Surprisingly, the cyclization process to **11e** using these conditions did not take place. With the increase of amount of KOH to 7 equiv., the yield of benzoquinoline **11e** was improved but an influence was not

Scheme 2

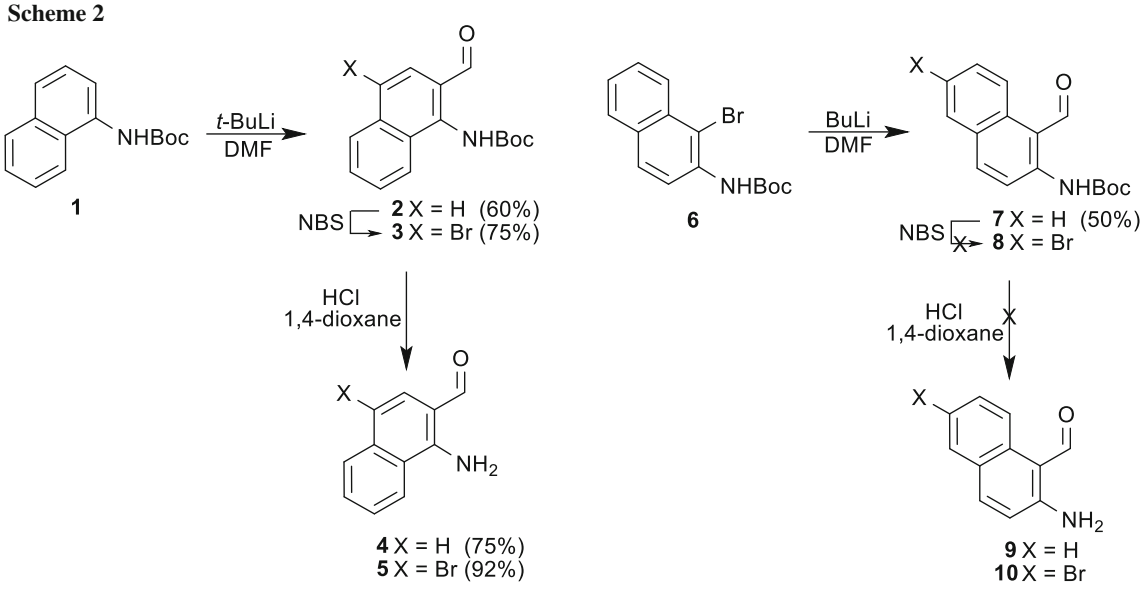
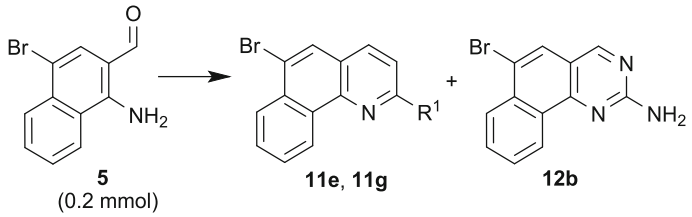


Table 1 Optimization of reaction conditions



Entry	KOH/equiv.	Urea/equiv.	Solv. (5 cm^3)	Temp./°C	Time/h	Yield/%[a]	
						11	**12b**
Product **11e**, R^1 = H							
1[b]	1	–	EtOH	75	20	–[d]	–[d]
2[b]	3	–	EtOH	75	20	Trace[c]	–
3[b]	7	–	EtOH	75	20	6	–
4[b]	7	1	EtOH	75	20	10	–
5[b]	7	2	EtOH	75	20	38	Trace[c]
6[b]	7	3	EtOH	75	20	45	10
Method A							
7	0.20	3	EtOH	75	20	–	–
Product **11g**, R^1 = Me							
8[b]	7	3	*i*-PrOH	75	20	60	25
9[b]	7	1	*i*-PrOH	75	20	30	–
10[b]	1	1	*i*-PrOH	75	20	68	–
Method B							
11[b]	1	–	*i*-PrOH	75	20	6	–
12[e]	1	1	1,4-Dioxane	80	20	–[d]	–[d]
13[f]	1	1	DCM	40	20	–[d]	–[d]
14[b,g]	1	1	*i*-PrOH	75	15	62	6
15[b,g]	1	3	*i*-PrOH	75	15	60	33

[a]Isolated yield

[b]5 cm^3 EtOH or *i*-PrOH

[c]Yield from ^{1}H NMR

[d]No reaction

[e]10 equiv. *i*-PrOH

[f]3 equiv. *i*-PrOH

[g]Inert atmosphere (Ar)

spectacular (6%, Table 1, entries 1–3). These results are in partial contrast with those presented in the literature [34].

It turned out that the addition of urea had a significant impact on the acceleration as well as the yield of the condensation process (Table 1, entries 4–6). The use of urea and base in the molar ratio 3:7 gave **11e** in a satisfactory 45% yield. In this case, a small amount of aminobenzoquinazoline **12b** (10% yield) was also isolated from post-reaction mixture. The formation of **12b** can be an effect of the competing reaction of **5** with urea under basic conditions (similarly to the first stage of the Biginelli reaction) [44–47]. It is notable that the yield of compound **12b** was, to some extent, dependent on an amount of urea (Table 1, entries 4–6). On the other hand, the use of too little amount of KOH (20 mol%, Table 1, entry 7) did not give any reaction product. We found that the reaction worked well not only with EtOH but also with secondary alcohols (*i*-PrOH). The condensation of **5** with *i*-PrOH, using urea and KOH in the molar ratio 3:7, led to benzoquinoline **11g** with a good yield (60%, Table 1, entry 8). Similarly, as in earlier reactions (Table 1, entries 5, 6), the formation of byproduct **12b** (25%) was also observed. The quantity reduction of amount of urea gave better results. The compound **11g** was produced in 68% yield as the sole

reaction product (Table 1, entries 9, 10). Similarly, as in the case of using ethanol (Table 1, entry 3), the condensation of **5** with *i*-PrOH performed in the absence of urea was ineffective (Table 1, entry 11), and resulted in obtaining **11g** in only 6% yield. Also, the application of other solvents, such as 1,4-dioxane or DCM, was inefficient (Table 1, entries 12, 13). Finally, we conducted the reaction between **5** and *i*-PrOH under an argon atmosphere (Table 1, entry 14). To our surprise, the cyclization ran with a similar rate and yield like under air conditions (**11g**, 62% yield, Table 1, entry 14). Increase in the amount of urea led to a little decrease in yield of **11g** (60%), but substantial increase in the formation of **12b** (33%) (Table 1, entry 15).

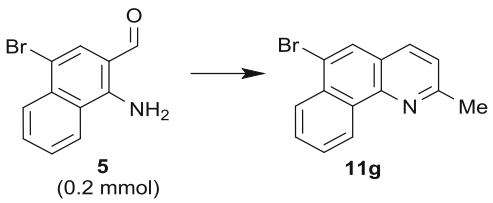
The mechanism of the formation of benzoquinolines **11** in the reaction between **5** and primary/secondary alcohols, in the presence of urea/KOH, is not clear, yet. However, based on the literature reports [48, 49] and results mentioned above (Table 1), we suppose that the first step includes the conversion of alcohols into corresponding carbonyl compounds. To obtain the additional information that may help to understand this type of conversion, some variants of reaction based on the condensation of **5** with acetone were checked (Table 2, entries 1–5).

As can be seen from Table 2, the condensation process of **5** with acetone did not take place only in the presence of urea (Table 2, entries 1, 2). The use of 1 equiv. of urea and 25%mol of KOH (Table 2, entry 4) in comparison to reaction without the use of urea (40%, Table 2, entry 3) gave better result in yield of **11g** (60%). These observations can confirm that urea anion generated by the action of KOH in polar solvents (alcohols) is an active intermediate can mediate the cyclization process (Table 2, entry 4). Information included in Tables 1 and 2 allow to conclude that urea anion can play dual role acting as additional base and nucleophile [50]. Its nucleophilic activity is strongly visible especially during the reaction of amino ketone **5** with alcohols (urea and KOH excess), where amino benzoquinazoline **12b** is produced as side product (Table 1, entries 6, 8, 14, 15).

The probable mechanism for the construction of benzoquinazolines using formylamines and alcohols in the presence of urea was presented below (Scheme 3). We think that the proposed mechanism is not the only one possible for these transformations, and it can operate parallel with, e.g., the classical pathway presented in the literature for Friedländer reaction under basic conditions [51–54].

Despite the fact that our initial experiments performed under air atmosphere were not efficient (Table 1, entries 1–3), it cannot entirely omit the path involved aerial oxidation of **I** (Scheme 3, air [O] path) via the formation of appropriate hydroperoxides, and next elimination of H_2O_2, as it was suggested in the literature [34]. Furthermore, also an alternative oxidation pathways of **I** to **II** by, e.g., H_2O_2 [34, 55–57] or the Oppenauer oxidation of **I** [58–60] [relevant notably under anaerobic conditions (argon)], can have an importance. The observed increase in the reaction yields upon the addition of urea, suggest that, it facilitates the formation of quinolines. Our observations suggest that urea or its anion can participate in the oxidation of **I** to **II** acting as a hydride acceptor and also has an influence on the reaction between formylamine **III** and carbonyl component **II** through, e.g., the hydrogen bonds formation (between urea anion and oxygen atom) activating carbonyl group to nucleophilic attack (Scheme 3, **IV**, **V**) [61]. On the other hand, nitrogen atoms of urea anion can also act on the α hydrogens of **V** or **VII** through the electronegative

Table 2 Confirmation of reaction conditions

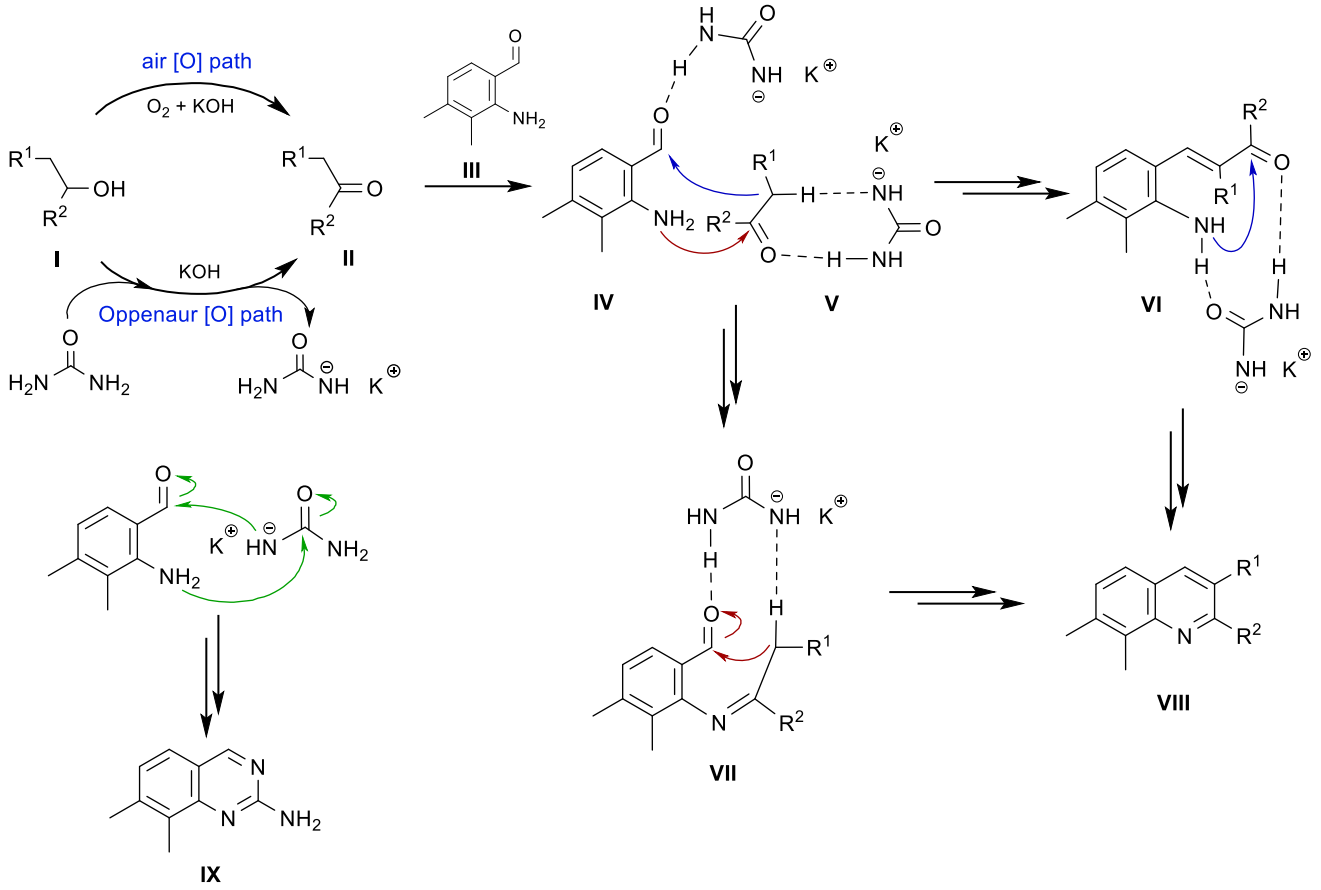


5 (0.2 mmol) → **11g**

Entry	KOH/equiv.	Urea/equiv.	Solv. (8 cm^3)	Temp./°C	Time/h	Yield/%[a] **11g**
1	–	1	Acetone	75	20	–
2	–	3	Acetone	75	20	–
3	0.25	–	Acetone	75	20	40
4	0.25	1	Acetone	75	20	60
5	7	–	Acetone	75	0.5	80

[a]Isolated yield

Scheme 3



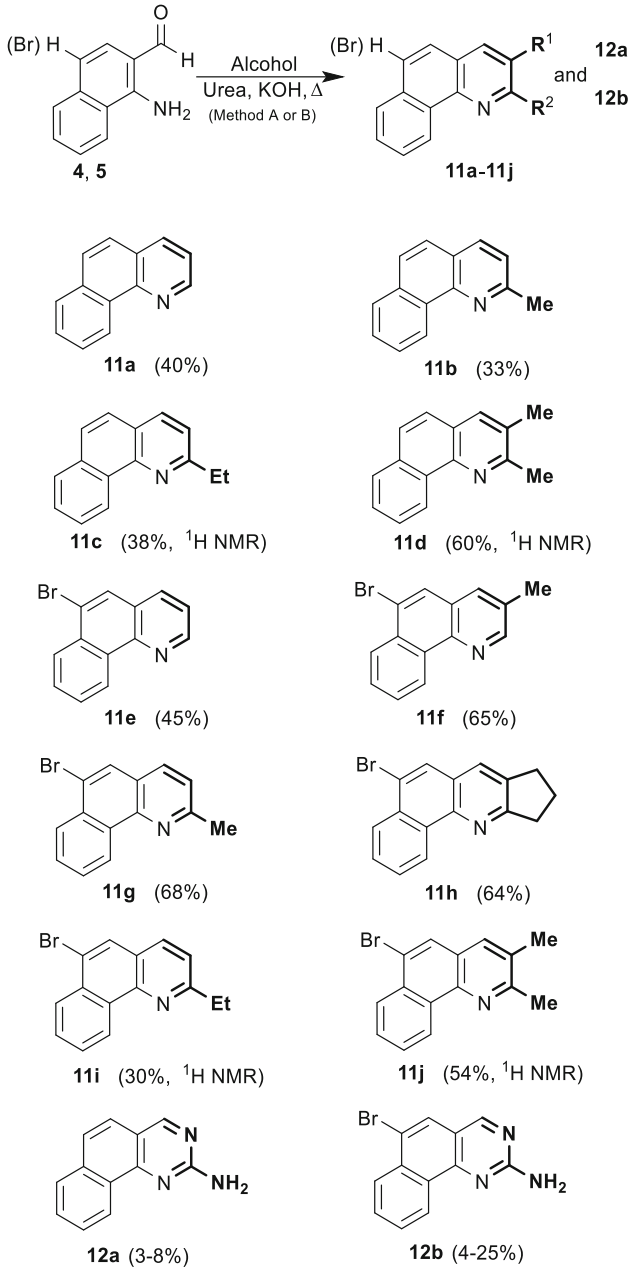
pull and the electron density increase at the carbon atom, making easier nucleophilic attack on the carbonyl carbon atom [62].

With the best conditions in hand (Table 1, entry 6, method A, for primary alcohols; entry 10, method B, for secondary alcohols), next we synthesized series of benzoquinoline derivatives **11** (Scheme 4). The cyclization of non-brominated derivative **4** with EtOH or *i*-PrOH led to the formation of corresponding benzoquinolines **11a** and **11b** in moderate yields, 40 and 33%, respectively (method A). Beyond these target compounds, just like it was described for the reaction of **5** with ethanol, some amounts of amino derivative **12a** (3–8%) and also substrate **4** (10–30%) were achieved. In turn, the reaction of *n*-propyl alcohol (method A) with **5** gave 3-methylbenzoquinoline (**11f**) in much better 65% yield. In this case a small quantity of aminobenzoquinazoline **12b** (about 4%) was also isolated. Good results were achieved for the reaction between **5** and cyclopentanol (method B), and in effect, the tetracyclic derivative **11h** was formed in 64% yield. On the other hand, when unsymmetrical alcohol (*sec*-butanol) was employed to the condensation with **4** or **5**, the reaction proceeded with the formation of mixtures of 2-substituted and 2,3-disubstituted benzoquinolines **11c**, **11d** and **11i**, **11j**, however, with a low regioselectivity. (The molar ratios of **11c/11d** and **11i/11j** were 0.6:1.)

Unexpectedly, condensation reactions of **4** or **5** performed in ethanol, propan-1-ol, or butan-2-ol, provided except **11**, also 2-methylbenzoquinoline or 6-bromo-2-methylbenzoquinoline in 1–7% yields. Both 2-methylquinolines were identified by NMR, HRMS spectroscopy, and by comparison of their NMR spectra with the data recorded for products **11b**, **11g** and also reported in the literature [63, 64]. The formation of unusual products is sometimes observed in Friedländer reaction [65, 66].

In the next step, bromobenzoquinolines **11e**, **11f**, **11h** were subjected to copper(II)-mediated *N*-formamidation reaction [67]. The couplings of **11e**, **11f**, **11h** with formamide were carried out without the use of ligand, in the presence of $CuSO_4{\cdot}5H_2O/K_2CO_3$. (Benzo[*h*]quinolin-6-yl)formamides **13a–13c** were obtained in 62–85% yields (Scheme 5). The spectroscopic analysis of coupling

Scheme 4

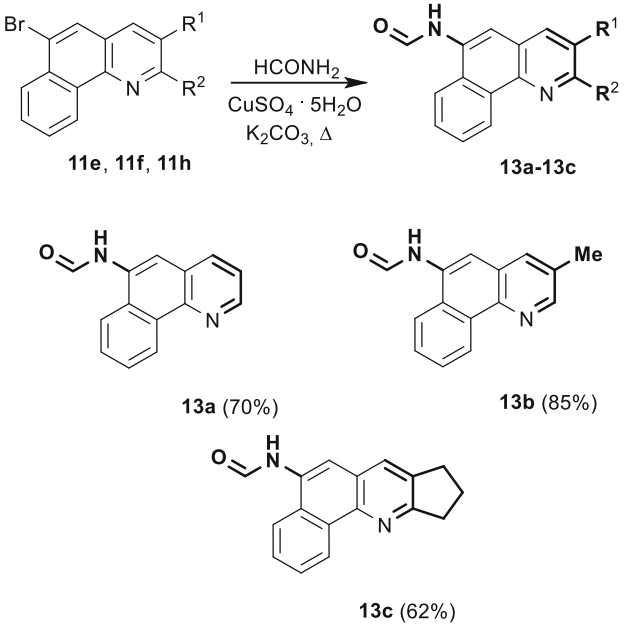


products **13** indicated the occurrence the mixture of rotamers in the ratio 2.2:1 (^{1}H NMR).

Obtained values of proton coupling constant of the NHCHO moiety (e.g., for **13c**: ~ 10.2 Hz for *trans*, ~ 1.2 Hz for *cis*) led to the conclusion that formamide benzoquinolines general exist in the mixture of two rotamers favoring the *Z* form (Scheme 5).

The second part of our work was dedicated to the synthesis of alkyl benzoquinolines via standard Friedländer reaction conditions using dicarbonyl compounds, e.g., ethyl

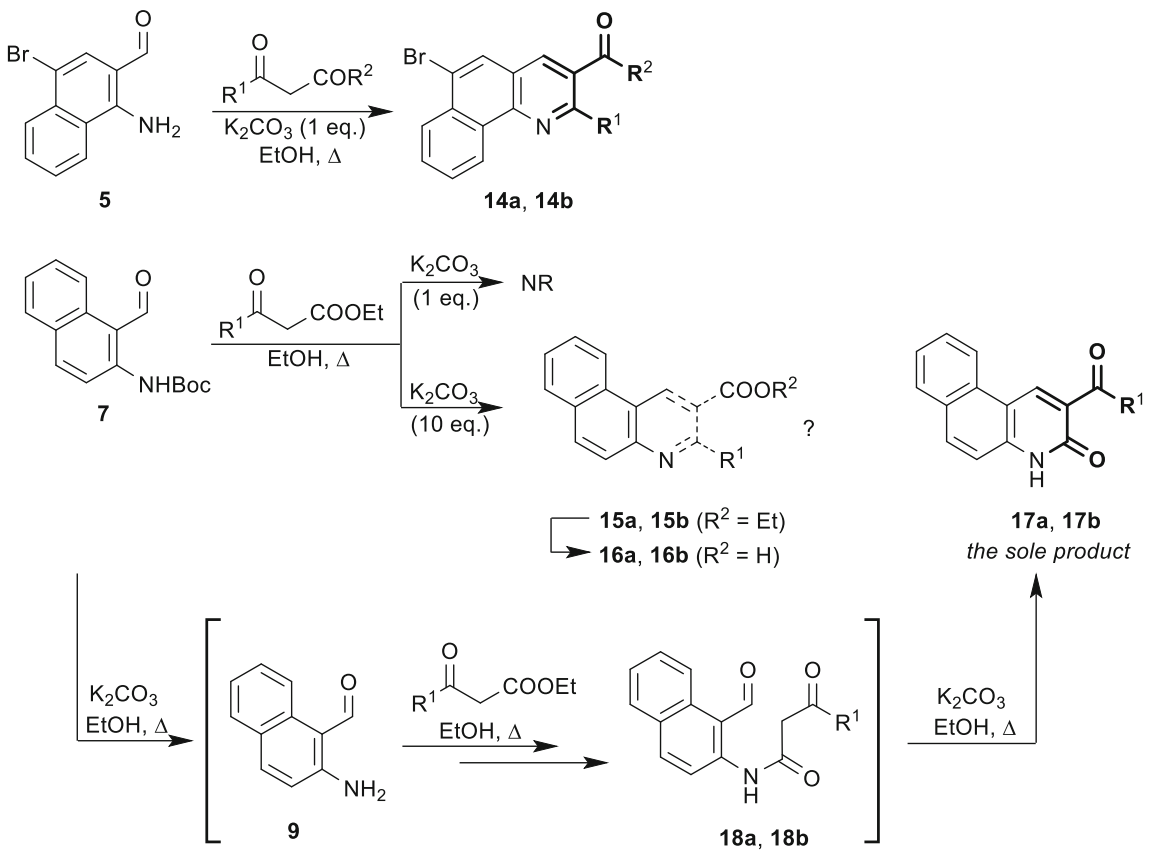
Scheme 5



acetoacetate, acetylacetone, and ethyl benzoylacetate (Scheme 6). Because of using ethanol as a solvent and the possibility of the course of the competitive condensation process, KOH was replaced with weaker base K_2CO_3. When amino aldehyde **5** was treated with 1 equiv. of ethyl acetoacetate and 1 equiv. of base in ethanol as a solvent, the desired product **14a** was received in moderate 25% yield (Scheme 6). In turn, when the amount of ethyl acetoacetate was increased up to 10 equiv. target benzoquinoline **14a** was effectively produced and finally obtained in an excellent 85% yield. Under similar reaction conditions, aminoaldehyde **5** condensed with acetylacetone gave acetylquinoline **14b** in 68% yield. The structures of newly synthesized quinolines **14a**, **14b** were confirmed by NMR spectroscopy analyses. In the ^{13}C NMR spectra of **14a** and **14b** characteristic signals corresponding to carbon atoms of C=O group of COOMe and Ac substituent were observed at 166.5 and 199.9 ppm, respectively and signals of methyl carbon atoms at 2 position were detected at 26.0 ppm. The obtained NMR chemical shift data are in accordance with the literature ones published for 2,3-disubstituted quinolines [68–70] containing ester (166–170 ppm) or acetyl (199–207 ppm) moiety placed at 3 position and methyl group at 2 position (23–26 ppm).

Previously, we have noticed that *N*-Boc-2-naphthylamine derivatives contrary to *N*-Boc-1-naphthylamine are ready for cleavage of the Boc protecting group under basic conditions [23–25]. This fact has prompted us to extend the presented methodology and use the carbamate **7** in the cyclization reaction, without a prior deprotection

Scheme 6



14a, **14b** (R^1= Me, R^2 = Me or OEt); **15a**, **16a**, **17a**, **18a** (R^1 = Me); **15b**, **16b**, **17b**, **18b** (R^1 = Ph)

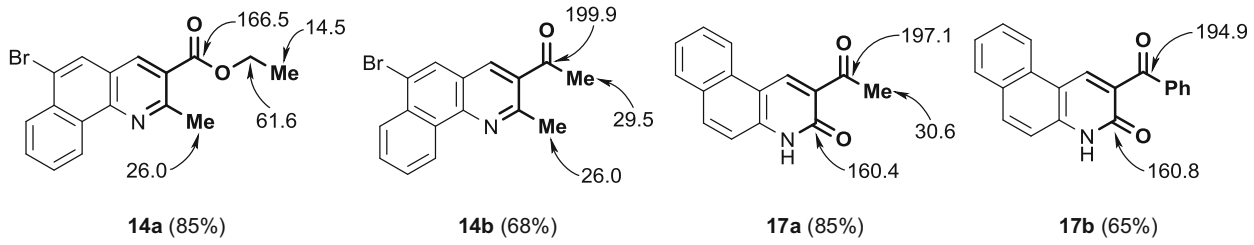
(Scheme 6). As we observed, when compound **7** was treated with ethyl acetoacetate (10 equiv.) in the presence of K_2CO_3 (1 equiv.; Scheme 6, 15 h, 70 °C), similarly as in the case of **5**, the target product was not formed. Furthermore, the formation of amine **9** was also not observed. In ^{1}H NMR spectra of post-reaction mixtures indicated only signals belonging to unreacted carbamate **7**. The increase in an amount of K_2CO_3 from 1 to 5 equiv. led, after 40 h to the mixture of **9** and **7** in the molar ratio 0.84:1 (^{1}H NMR). With evidence to support our ideas in hand, we used 5 equiv. of K_2CO_3 suspended in ethanol to the condensation of **7** with ethyl acetoacetate.

Similarly as for **5** and in accordance with generally accepted course of the Friedländer reaction and commonly available literature reports, from the reaction of **7** with ethyl acetoacetate (Scheme 6), we expected to receive ester **15a**. The analysis of ^{1}H and ^{13}C NMR spectra unexpectedly showed no signals which could be assigned to the ester group. Instead, the ^{1}H NMR spectrum has shown the presence of two characteristic signals at 2.68 ppm and 12.52 ppm, which could indicate the occurrence of methyl group and labile hydrogen atom (–OH or –NH). One may wonder about the possibility of the formation of acid **16a** via hydrolysis of ester **15a** [68]. The formation 2-methylquinoline-3-carboxylic acids under Friedländer reaction conditions is described in literature [71, 72] and their examples were presented in Table 3 (compounds **19** [73], **20** [74]). It is an important to say here, that in each case, it was taken for granted that the formation of compounds **19a**, **19b**, and **20** is a consequence of the hydrolysis of corresponding ethyl esters produced under Friedländer annulations [71–74].

In the ^{13}C NMR spectrum of the reaction product of **7** and ethyl acetoacetate (Scheme 6), our attention was drawn to two carbon atom signals at 197.1 and 160.4 ppm. Very similar ^{13}C NMR peaks were described for compounds **19a** and **19b** (**19a**: 197.3 and 160.4 ppm; **19b**: 203.5 and 159.5 ppm) [73]. In turn, in the ^{13}C NMR spectrum of acid **20** the most downfield carbon signal was situated at 169.0 ppm and was assigned to carbon atom of –COOH group [74], which seems more likely. It is known, that typical range of chemical shifts for carbon of –COOH

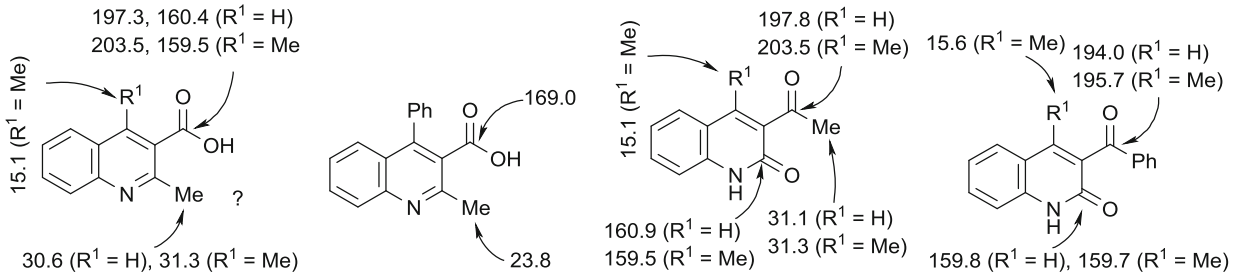
Table 3 ^{13}C NMR data

This work



14a (85%) **14b** (68%) **17a** (85%) **17b** (65%)

Literature [73, 74, 79-81]



19a R^1 = H, **19b** R^1 = Me **20** **21a** R^1 = H, **21b** R^1 = Me **22a** R^1 = H, **22b** R^1 = Me

group in aromatic acids is between 159–170 ppm, while for carbons of –CHO or –COR groups they are usually observed above 190 ppm [75–78]. The comparison of ^{13}C NMR spectroscopic data of the obtained product with compounds **14**, **19**, and **20** and also with signals from spectra of quinolinones **21** [79, 80] and **22** [79–81] (Table 3), led to the conclusion that the reaction of **7** with ethyl acetoacetate (10 equiv.) in the presence of base (5 equiv.) gives benzoquinolinone **17a** (30%). To our delight, increase an amount of base up to 10 equiv. allowed to achieve **17a** in 85% yield. By contrast, the reaction of **7** with ethyl benzoylacetate led to formation of **17b** in 65% yield under the same reaction conditions. In this case, similarly to **17a**, the ^{13}C NMR spectrum showed specific peaks located at 194.9 ppm (keton) and 160.8 ppm (lactam) (Table 3). On the other hand when *N*-Boc derivative **3** (Scheme 2) was treated with ethyl acetoacetate (10 equiv.) in the presence of 10 equiv. K_2CO_3 in ethanol, desired product was not obtained. After reaction unchanged substrates were only isolated, which prove that **3** under these conditions did not undergo cleavage of protecting group and consequently amine **5**, necessary to completion of the reaction is not formed. Besides, the reaction of aminoaldehyde **5** with ethyl acetoacetate (10 equiv.) and K_2CO_3 (10 equiv.) in ethanol leads to ester **14a** as the only product (72%, Scheme 6).

In our opinion, the possible mechanism of the formation of compounds **17** includes 1) in the first step, in situ formation of amine **9** in the presence of base and next 2) the reaction of **9** with ketoester leading to the intermediate **18** [82], which under basic conditions undergoes intramolecular cyclization yielding quinolinones **17** (Scheme 6) [74, 79–81, 83]. This transformation to some extent resembles the Niementowski-type cyclization reaction, described in literature [84].

Conclusion

In summary, we presented the method for the synthesis of alkyl benzoquinolines via KOH/urea-mediated indirect Friedländer reaction of amino naphthalene aldehydes with aliphatic alcohols. We have found that under aerial as well as inert atmosphere the method involving the use of urea may be employed and lead to desired benzoquinolines with good yields. In addition, we have briefly discussed the different behavior of 1- and 2-naphthylamine derivatives during the condensation with dicarbonyl compounds containing active methylene moiety. In result either

benzo[*h*]quinoline or benzo[*f*]quinolinone derivatives were obtained in also good yields as the major products. In copper(II) catalyzed *N*-aryl formamidation reaction, several formamide benzoquinolines have been also synthesized. There is no doubt that new formamide benzoquinolines may constitute excellent starting material to further modifications.

Experimental

Melting points were determined on a Boetius hot stage apparatus. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker Avance III spectrometer at 600 MHz and 150 MHz. The residual $CDCl_3$ or DMSO-d_6 signal was used for reference ($CDCl_3$ at 7.26 ppm or DMSO-d_6 at 2.54 ppm for ^{1}H NMR and $CDCl_3$ at 77.0 ppm or DMSO-d_6 at 39.0 ppm for ^{13}C NMR). IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer. LC/HRMS analyses were performed using an Agilent Technologies HPLC 1290 coupled to an Agilent Technologies 6550 Accurate Mass Q-TOF LC–MS mass spectrometer equipped with a JetStream Technology ion source housed in the Department of Pathophysiology, Medical University of Lublin, Poland. Internal mass calibration was enabled; reference ions of m/z = 121.0509 and 922.0098 were used. The analytical thin layer chromatography tests (TLC) were carried out on Sigma-Aldrich (Supelco) silica gel plates (Kiselgel 60 F_{254}, layer thickness 0.2 mm) and the spots were visualized using UV lamp. The flash column chromatography purifications were performed on Fluka silica gel (Silica gel 60, 0.040–0.063 mm). *t*-Butyllithium or butyllithium solutions (Aldrich) were each time titrated before use [85]. All reactions with organolithium compounds were performed under an argon atmosphere using standard Schlenk technique. Diethyl ether was distilled from sodium benzophenone ketyl prior to use. Commercially available solvents and reagents: *N*,*N*-dimethylformamide (DMF), *N*-bromosuccinimide (NBS), EtOH, PrOH, *i*-PrOH, butan-2-ol, cyclopentanol, urea, acetylacetone, ethyl acetoacetate, ethyl benzoylacetate, $CuSO_4{\cdot}5H_2O$, and formamide were purchased from Sigma-Aldrich and were used without further purification. *N*-Boc-2-naphthylamine (**1**) and *tert*-butyl (1-bromonaphthalen-2-yl)carbamate (**6**) were prepared by a procedure similar to that in the literature [23–25].

General procedure for the preparation of 1-formylnaphthalene and 2-formylnaphthalene carbamates 2 and 7

Under argon, to a solution of *N*-Boc 1-naphthylamine (**1**, 2.1 mmol) or *tert*-butyl (1-bromonaphthalen-2-yl)carbamate (**6**, 1.55 mmol) in 20 cm^3 dry Et_2O at -20 °C, *t*-BuLi solution in pentane or BuLi solution in hexanes (2.2 equiv.) was added dropwise. The reaction mixture was stirred at this temperature for 2 h. Next, a solution of DMF (1 equiv.) at − 20 °C was added dropwise and whole was further stirred for 2 h (− 20 °C). After this time to the reaction mixture 20 cm^3 saturated solution of NH_4Cl was added. The water layer was separated and extracted subsequently with Et_2O (3 × 20 cm^3). The organic phase was dried over $MgSO_4$ and concentrated to dryness. The crude material was separated by flash chromatography.

***tert*-Butyl (2-formylnaphthalen-1-yl)carbamate (2, $C_{16}H_{18}NO_3$)** Beige solid (342 mg, 60% yield); R_f = 0.16 (hex/AcOEt, 10:1); m.p.: 123–125 °C; IR (KBr): $\bar{\nu}$ = 3275, 2999, 2983, 2968, 2870, 1720, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 10.27 (s, 1H, CHO), 8.22–8.05 (m, 2H, NH, Ar–H), 7.87 (d, J = 7.8 Hz, 1H, Ar–H), 7.84–7.78 (m, 2H, Ar–H), 7.66–7.56 (m, 2H, Ar–H), 1.53 (s, 9H, Boc–Me) ppm; ^{13}C NMR ($CDCl_3$): δ = 192.4, 154.5, 138.0, 137.0, 129.3, 128.9, 128.4, 126.9, 126.6, 126.0, 125.7, 125.2, 81.7, 28.4 ppm.

***tert*-Butyl (1-formylnaphthalen-2-yl)carbamate (7, $C_{16}H_{18}NO_3$)** Lemon solid (210 mg, 50% yield); R_f = 0.44 (PE/AcOEt, 10:1); m.p.: 107–109 °C; IR (KBr): $\bar{\nu}$ = 3433, 2983, 2935, 1723, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 11.54 (br s, 1H, NH), 11.01 (br s, 1H, CHO), 8.73 (d, J = 9.3 Hz, 1H, Ar–H), 8.43 (d, J = 8.6 Hz, 1H, Ar–H), 8.02 (d, J = 9.3 Hz, 1H, Ar–H), 7.83 (d, J = 8.0 Hz, 1H, Ar–H), 7.64–7.58 (m, 1H, Ar–H), 7.48–7.42 (m, 1H, Ar–H), 1.57 (s, 9H, Boc–Me) ppm; ^{13}C NMR ($CDCl_3$): δ = 192.2, 153.2, 143.8, 137.5, 134.0, 129.5, 129.0 (2C), 124.9, 119.7, 118.2, 112.0, 81.4, 28.4 ppm.

***tert*-Butyl (4-bromo-2-formylnaphthalen-1-yl)carbamate (3, $C_{16}H_{17}BrNO_3$)** To a solution of the appropriate carbamate **2** (2.5 mmol) in 15 cm^3 acetonitrile at 0 °C, a solution of NBS (3.0 mmol) in 10 cm^3 acetonitrile was added dropwise. Next, the resulting mixture was allowed to warm to ambient temperature. The reaction was continued under these conditions until TLC analysis of the reaction mixture indicated the absence of starting material **2** (4–6 h). After the reaction acetonitrile was removed under reduced pressure and the bromo derivative **3** was separated by flash chromatography. Yellow solid (657 mg, 75% yield); R_f = 0.32 (hex/AcOEt, 5:1); m.p.: 165–168 °C; IR (KBr): $\bar{\nu}$ = 3354, 2969, 2935, 2852, 1701, 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 10.19 (s, 1H, CHO), 8.30–8.26 (m, 1H, Ar–H), 8.16–8.10 (m, 2H, Ar–H), 7.87 (s, 1H, NH), 7.75 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H, Ar–H), 7.66 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H, Ar–H), 1.52 (s, 9H, Boc–Me) ppm; ^{13}C NMR ($CDCl_3$): δ = 190.6, 154.3, 137.5, 135.2, 130.7, 130.3, 129.0, 128.0, 127.7, 126.8, 125.4, 121.1, 82.1, 28.3 ppm.

Procedure for the preparation of amino aldehydes 4, 5

To a mixture of HCl_{aq} (0.5 M) and 1,4-dioxane in the ratio 2:3 (v/v) at room temperature, aldehyde (**2** or **3**, 1.6 mmol) was added. The resulting mixture was then heated at 60 °C (oil bath) for about 3–4 h, until TLC analysis indicated the completion of the reaction. Then all the volatile materials were removed under reduced pressure and 15 cm^3 water was added to residue. The mixture was adjusted to pH 7–8 with saturated $NaHCO_3$ and extracted with chloroform (3 × 20 cm^3). The combined extracts were dried over $MgSO_4$ and then concentrated. A crude residue was subjected to column chromatography to give amines **4** and **5**.

1-Aminonaphthalene-2-carbaldehyde (4) [86] Yellow solid (205 mg, 75% yield); R_f = 0.3 (hex/AcOEt, 5:1); m.p.: 99–101 °C (lit. [86], 97–100 °C).

1-Amino-4-bromonaphthalene-2-carbaldehyde (5, $C_{11}H_9BrNO$) Yellow solid (368 mg, 92% yield); R_f = 0.32 (hex/AcOEt, 5:1); m.p.: 165–168 °C; IR (KBr): $\bar{\nu}$ = 3306, 2751, 1637 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 9.89 (s, 1H, CHO), 8.22–8.19 (m, 1H, Ar–H), 7.93 (d, J = 8.4 Hz, 1H, Ar–H), 7.76 (s, 1H, Ar–H), 7.75–7.71 (m, 1H, Ar–H), 7.60–7.55 (m, 1H, Ar–H), 7.36 (s, 2H, NH_2) ppm; ^{13}C NMR ($CDCl_3$): δ = 192.5, 148.7, 134.9, 132.9, 130.9, 128.3, 126.5, 124.1, 122.3, 113.3, 108.4 ppm.

General procedure for the preparation of benzoquinolines 11

The reaction was carried out in the open air conditions (vessels with air supply). To a mixture of amino aldehyde (**4** or **5**, 0.2 mmol) and KOH (7 equiv. in case of the reaction with primary alcohols or 1 equiv. with secondary alcohols) in 10 cm^3 of appropriate alcohol, urea was added (3 equiv. for reaction with primary alcohols or 1 equiv. with secondary alcohols). The whole mixture was stirred and heated at 75 °C (oil bath) until TLC analysis indicated the absence of substrate **4** or **5**. After the reaction was completed, alcohol was removed under reduced pressure and 15 cm^3 water was added to residue. The mixture was adjusted to pH 7–8 with 0.5 M HCl and then extracted with DCM (3 × 20 cm^3). The combined extracts were dried over $MgSO_4$ and concentrated, and a crude mixture was purified by flash chromatography to give desired benzoquinoline **11**.

Benzo[*h*]quinoline (11a) [87] Light orange solid (14 mg, 40% yield); R_f = 0.54 (hex/AcOEt, 5:1); m.p.: 46–47 °C (lit. [88], 49–51 °C).

2-Methylbenzo[*h*]quinoline (11b) [89, 90] Light orange solid (11 mg, 33% yield); R_f = 0.68 (hex/AcOEt, 5:1); m.p.: 38–39 °C (lit. [90], 47–48 °C).

Mixture of 2-ethylbenzo[*h*]quinoline (11c) [91] and 2,3-dimethylbenzo[*h*]quinoline (11d) [92, 93] Light yellow solid (36 mg, 38% yield (**11c**) and 60% yield (**11d**); R_f = 0.6 (for both compounds; hex/AcOEt, 5:1).

6-Bromobenzo[*h*]quinoline (11e) [94, 95] Beige solid (23 mg, 45% yield); R_f = 0.84 (hex/AcOEt, 1:1); m.p.: 105–107 °C (lit. [95], 109–111.5 °C).

6-Bromo-3-methylbenzo[*h*]quinoline (11f, $C_{14}H_{11}BrN$) Yellow solid (35 mg, 65% yield); R_f = 0.64 (hex/AcOEt, 5:1); m.p.: 114–115 °C; IR (KBr): $\bar{\nu}$ = 2924, 2852, 1595 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 9.31–9.27 (m, 1H, Ar–H), 8.84 (d, J = 2.0 Hz, 1H, Ar–H), 8.34–8.29 (m, 1H, Ar–H), 7.99 (s, 1H, Ar–H), 7.86–7.84 (m, 1H, Ar–H), 7.79–7.75 (m, 2H, Ar–H), 2.56 (s, 3H, Me) ppm; ^{13}C NMR ($CDCl_3$): δ = 150.9, 144.1, 134.3, 132.7, 132.2, 131.7, 128.8, 128.7, 128.0, 127.6, 126.6, 124.6, 122.7, 18.8 ppm.

6-Bromo-2-methylbenzo[*h*]quinoline (11g) [96] Light yellow solid (35 mg, 68% yield); R_f = 0.62 (hex/AcOEt, 5:1); m.p.: 92–94 °C (lit. [96], 101–103 °C).

5-Bromo-9,10-dihydro-8*H*-benzo[*h*]cyclopenta[*b*]quinoline (11h, $C_{16}H_{13}BrN$) Yellow solid (38 mg, 64% yield); R_f = 0.45 (hex/AcOEt, 5:1); m.p.: 105–107 °C; IR (KBr): $\bar{\nu}$ = 3030, 2959, 2920, 2855, 1596 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 9.37–9.31 (m, 1H, Ar–H), 8.32–8.26 (m, 1H, Ar–H), 7.98 (s, 1H, Ar–H), 7.83–7.81 (m, 1H, Ar–H), 7.76–7.72 (m, 2H, Ar–H), 3.26–3.21 (m, 2H, CH_2), 3.15–3.11 (m, 2H, CH_2), 2.30–2.21 (m, 2H, CH_2) ppm; ^{13}C NMR ($CDCl_3$): δ = 167.0, 145.0, 136.9, 132.7, 131.7, 129.9, 129.2, 128.6, 127.6, 127.4, 125.6, 124.7, 121.2, 35.0, 30.8, 23.8 ppm.

Mixture of 6-bromo-2-ethylbenzo[*h*]quinoline (11i, $C_{15}H_{13}BrN$) and 6-bromo-2,3-dimethylbenzo[*h*]quinoline (11j, $C_{15}H_{13}BrN$) Yellow solid (43 mg, 30% yield (**11i**) and 54% yield (**11j**)); R_f = 0.78 (for both compounds; hex/AcOEt, 1:1); ^{1}H NMR ($CDCl_3$): δ = 9.44–9.40 (m, 1H, Ar–H), 9.36–9.32 (m, 1H, Ar–H), 8.34-8.27 (m, 2H, Ar–H, Ar–H), 8.01 (s, 1H, Ar–H), 7.98-7.96 (m, 1H, Ar–H), 7.96 (s, 1H, Ar–H), 7.80–7.72 (m, 5H, 3Ar–H, 2Ar–H), 7.40 (d, J = 8.5 Hz, 1H, Ar–H), 3.09 (q, J = 7.6 Hz, 2H, CH_2), 2.76 (s, 3H, Me), 2.48 (s, 3H, Me), 1.49 (t, J = 7.6 Hz, 3H, CH_2Me) ppm; ^{13}C NMR ($CDCl_3$): δ = 163.2, 158.0, 145.4, 143.6, 135.2, 134.7, 132.7, 132.5, 132.1, 131.7, 131.3, 128.9, 128.8, 128.5, 128.5, 127.7, 127.6, 127.4, 125.6, 125.0, 124.9, 124.6, 124.6, 121.9, 121.4, 121.3, 32.3, 23.9, 19.6, 13.7 ppm.

Benzo[*h*]quinazolin-2-amine (12a, $C_{12}H_{10}N_3$) White solid (1.2–3 mg, 3–8% yield); R_f = 0.07 (hex/AcOEt, 5:1); m.p.: 194–196 °C; IR (KBr): $\bar{\nu}$ = 3336, 3184, 2926, 2854, 1651 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 9.06 (d, J = 8.0 Hz, 1H, Ar–H), 8.97 (s, 1H, Ar–H), 7.86–7.82 (m, 1H, Ar–H), 7.73–7.69 (m, 1H, Ar–H), 7.68–7.63 (m, 1H, Ar–H), 7.55 (s, 2H, Ar–H), 5.28 (s, 2H, NH_2) ppm; ^1H NMR (DMSO-d_6): δ = 9.05 (s, 1H), 8.91 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.77–7.71 (m, 1H), 7.69–7.63 (m, 2H), 7.58–7.54 (m, 1H), 6.93 (s, 2H, NH_2) ppm; ^{13}C NMR ($CDCl_3$): δ = 161.1, 160.7, 152.6, 136.1, 130.0, 129.4, 128.0, 126.8, 124.8, 124.2, 123.6, 117.5 ppm.

6-Bromobenzo[*h*]quinazolin-2-amine (12b, $C_{12}H_9BrN_3$) Light orange solid (2.2–14 mg, 4–25% yield); R_f = 0.5 (hex/AcOEt, 1:1); m.p.: 223–225 °C; IR (KBr): $\bar{\nu}$ = 3479, 3285, 3166, 2925, 2853, 1623, 1606 cm^{-1}; ^1H NMR (DMSO-d_6): δ = 9.06 (s, 1H, Ar–H), 9.00 (d, J = 8.0 Hz, 1H, Ar–H), 8.16 (d, J = 8.2 Hz, 1H, Ar–H), 8.13 (s, 1H, Ar–H), 7.92–7.88 (m, 1H, Ar–H), 7.80–7.75 (m, 1H, Ar–H), 7.13 (s, 2H, NH_2) ppm; ^{13}C NMR (DMSO-d_6): δ = 161.8, 160.4, 151.1, 133.3, 130.9, 129.9, 127.7, 127.3, 126.8, 124.4, 116.5, 114.6 ppm.

General procedure for the preparation of formamide derivatives of benzoquinoline 13 via copper-mediated N-formamidation

Benzoquinoline **11e** or **11f** or **11h** (0.18 mmol), $CuSO_4 \cdot 5H_2O$ (2.5 equiv.) and K_2CO_3 (5 equiv.) suspended in 15 cm^3 formamide was heated with magnetic stirring at 140 °C (oil bath) for about 25 h until TLC analysis indicated the absence of starting benzoquinoline. After cooling to the reaction mixture, 20–30 cm^3 water with ice was added and allowed to stand for 30 min. After this time mixture was extracted with DCM. The combined extracts were dried over $MgSO_4$ and concentrated to give crude product **13** which was next subjected to flash chromatography.

***N*-(Benzo[*h*]quinolin-6-yl)formamide (13a, $C_{14}H_{11}N_2O$)** White solid (27 mg, 70% yield); R_f = 0.42 (hex/AcOEt, 1:2); m.p.: 214–216 °C; IR (KBr): $\bar{\nu}$ = 3434, 3228, 3044, 2928, 2890, 1683, 1658 cm^{-1}; ^1H NMR (DMSO-d_6; mixture of rotamers in the ratio 2.2:1*): δ = 10.61 (d, J = 10.0 Hz, NH*), 10.44 (br s, 1H, NH), 9.33–9.23 (m, 2H, Ar–H, Ar–H*), 8.99–8.90 (m, 2H, Ar–H, Ar–H*), 8.73 (d, J = 10.0 Hz, 1H, CHO*), 8.59 (s, 1H, CHO), 8.42 (s, 1H, Ar–H), 8.40–8.34 (m, 2H, Ar–H, Ar–H*), 8.31–8.23 (m, 2H, Ar–H, Ar–H*), 7.87–7.78 (m, 5H, 2Ar–H, 3Ar–H*), 7.70–7.63 (m, 2H, Ar–H, Ar–H*) ppm; ^{13}C NMR (DMSO-d_6): δ = 163.8, 160.6, 148.5, 148.4, 143.4, 135.6, 135.5, 131.5, 131.4, 131.3, 128.4, 128.4, 127.6, 127.2, 125.8, 124.3, 124.1, 122.9, 122.6, 121.9, 116.8, 115.8 ppm.

***N*-(3-Methylbenzo[*h*]quinolin-6-yl)formamide (13b, $C_{15}H_{13}N_2O$)** White solid (35 mg, 85% yield); R_f = 0.24 (hex/AcOEt, 1:1); m.p.: 221–223 °C; IR (KBr): $\bar{\nu}$ = 3435, 3193, 3101, 2948, 2919, 2876, 1701 cm^{-1}; ^1H NMR (DMSO-d_6; mixture of rotamers in the ratio 2.2:1*): δ = 10.58 (d, J = 10.1 Hz, 1H, NH*), 10.40 (br. s, 1H, NH), 9.27–9.19 (m, 2H, Ar–H, Ar–H*), 8.83–8.77 (m, 2H, Ar–H, Ar–H*), 8.70 (d, J = 10.1 Hz, 1H, CHO*), 8.57 (br. s, 1H, CHO), 8.33 (br. s, 1H, Ar–H), 8.29–8.24 (m, 1H, Ar–H), 8.24–8.19 (m, 1H, Ar–H*), 8.16–8.10 (m, 2H, Ar–H, Ar–H*), 7.83–7.76 (m, 4H, 2Ar–H, 2Ar–H*), 7.70 (br. s, 1H, Ar–H*), 2.51 (s, 6H, Me, Me*) ppm; ^{13}C NMR (DMSO-d_6): δ = 163.9, 160.6, 149.8, 149.7, 142.0, 141.4, 134.7, 134.6, 132.6, 132.0, 131.5, 131.4, 131.3, 128.1, 128.0, 127.9, 127.5, 127.2, 125.7, 125.5, 124.1, 123.9, 122.8, 121.9, 116.7, 115.7, 18.0 ppm.

***N*-(9,10-Dihydro-8*H*-benzo[*h*]cyclopenta[*b*]quinolin-5-yl)formamide (13c, $C_{17}H_{15}N_2O$)** Light yellow solid (28 mg, 62% yield); R_f = 0.32 (hex/AcOEt, 1:1); m.p.: 247–249 °C; IR (KBr): $\bar{\nu}$ = 3433, 3232, 2959, 1687, 1663 cm^{-1}; ^1H NMR (DMSO-d_6; mixture of rotamers in the ratio 2.2:1*): δ = 10.52 (d, J = 10.2 Hz, 1H, NH*), 10.35 (br s, 1H, NH), 9.26–9.20 (m, 2H, Ar–H, Ar–H*), 8.66 (d, J = 10.2 Hz, 1H, CHO*), 8.55 (d, J = 1.2 Hz, 1H, CHO), 8.30 (br. s, 1H, Ar–H), 8.24–8.20 (m, 1H, Ar–H), 8.20–8.16 (m, 1H, Ar–H*), 8.11 (br. s, 2H, Ar–H*, Ar–H), 7.79–7.74 (m, 4H, 2Ar–H, 2Ar–H*), 7.72 (br. s, 1H, Ar–H*), 3.18–3.13 (m, 4H, 2Ar–H, 2Ar–H*), 3.13–3.07 (m, 4H, 2Ar–H, 2Ar–H*), 2.23–2.14 (m, 4H, 2Ar–H, 2Ar–H*) ppm; ^{13}C NMR (DMSO-d_6): δ = 165.5, 165.4, 163.8, 160.5, 141.0, 142.8, 142.3, 136.5, 131.5, 131.4, 131.3, 130.2, 128.1, 127.7, 127.6, 127.2, 127.1, 126.8, 124.4, 124.3, 124.1, 124.0, 122.7, 121.8, 117.7, 116.7, 34.0, 30.0, 23.1 ppm.

General procedure for the preparation of bromobenzoquinolines 14

To a mixture of the amino aldehyde **5** (0.2 mmol) and K_2CO_3 (1 equiv.) in 20 cm^3 ethanol ethyl acetoacetate or acetylacetone (10 equiv.) was added. The whole being then heated at 70 °C (oil bath) until TLC analysis of the reaction mixture indicated the absence of starting material **5** ($\sim$ 25 h). The precipitated crude product **14a** or **14b** was filtered from the solution, washed with 10 cm^3 water, air-dried, and next purified by flash chromatography or crystallization.

Ethyl 6-bromo-2-methylbenzo[*h*]quinoline-3-carboxylate (14a, $C_{17}H_{15}BrNO_2$) White solid (58 mg, 85% yield);

R_f = 0.75 (DCM/PE, 10:1); m.p.: 145–147 °C; IR (KBr): $\bar{\nu}$ = 3004, 2981, 2927, 1726, 1608 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 9.44–9.40 (m, 1H, Ar–H), 8.65 (s, 1H, Ar–H), 8.36–8.31 (m, 1H, Ar–H), 8.08 (s, 1H, Ar–H), 7.85–7.78 (m, 2H, Ar–H), 4.47 (q, J = 7.1 Hz, 2H, CH_2), 3.09 (s, 3H, Me), 1.47 (t, J = 7.1 Hz, 3H, Me) ppm; ^{13}C NMR ($CDCl_3$): δ = 166.5, 158.5, 146.7, 138.3, 133.1, 131.8, 130.1, 128.6, 128.2, 127.7, 125.6, 124.8, 124.3, 122.5, 61.6, 25.9, 14.5 ppm.

1-(6-Bromo-2-methylbenzo[*h*]quinolin-3-yl)ethanone (14b, $C_{16}H_{13}BrNO$) White solid (43 mg, 68% yield); crystallization (PE/DCM, 4:1); m.p.: 188–189 °C; IR (KBr): $\bar{\nu}$ = 2995, 2972, 2927, 1682, 1592 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 9.40–9.37 (m, 1H, Ar–H), 8.38 (s, 1H, Ar–H), 8.35–8.32 (m, 1H, Ar–H), 8.07 (s, 1H, Ar–H), 7.85–7.78 (m, 2H, Ar–H), 3.00 (s, 3H, Me), 2.73 (s, 3H, Me) ppm; ^{13}C NMR ($CDCl_3$): δ = 199.9, 157.4, 146.4, 136.5, 133.0, 131.9, 131.8, 130.1, 128.5, 128.2, 127.7, 125.6, 124.1, 122.6, 29.5, 26.0 ppm.

General procedure for the preparation of benzo[*f*]quinolin-3(4*H*)-ones 17

To a mixture of the carbamate **7** (0.4 mmol) and K_2CO_3 (10 equiv.) in 10 cm^3 ethanol ethyl acetoacetate or ethyl benzoylacetate (10 equiv.) was added. The resulting mixture was then heated at 70 °C (oil bath), until TLC analysis indicated the completion of the condensation process ($\sim$ 15 h). The precipitated solid was filtered from the solution, washed with 10 cm^3 water, air-dried, and next purified by flash chromatography to give product **17**.

2-Acetylbenzo[*f*]quinolin-3(4*H*)-one (17a, $C_{15}H_{12}NO_2$) Light yellow solid (81 mg, 85% yield); R_f = 0.26 (hex/AcOEt, 1:2); decomposition above 300 °C; IR (KBr): $\bar{\nu}$ = 3003, 2928, 2797, 1682, 1628, 1561 cm^{-1}; ^1H NMR (DMSO-d_6): δ = 12.52 (s, 1H, NH), 9.17 (s, 1H, Ar–H), 8.54 (d, J = 8.4 Hz, 1H, Ar–H), 8.15 (d, J = 9.0 Hz, 1H, Ar–H), 7.98 (d, J = 7.8 Hz, 1H, Ar–H), 7.75–7.68 (m, 1H, Ar–H), 7.59–7.55 (m, 1H, Ar–H), 7.52 (d, J = 9.0 Hz, 1H, Ar–H), 2.68 (s, 3H, Me) ppm; ^{13}C NMR (DMSO-d_6): δ = 197.1, 160.4, 140.9, 137.9, 134.6, 129.7, 129.0, 128.8, 128.6, 127.8, 125.5, 121.6, 115.8, 111.7, 30.6 ppm.

2-Benzoylbenzo[*f*]quinolin-3(4*H*)-one (17b, $C_{20}H_{14}NO_2$) Yellow solid (78 mg, 65% yield); R_f = 0.46 (AcOEt); decomposition above 300 °C; IR (KBr): $\bar{\nu}$ = 3010, 2928, 2866, 2797, 1662, 1629 cm^{-1}; ^1H NMR (DMSO-d_6): δ = 8.94 (s, 1H, Ar–H), 8.53 (d, J = 8.4 Hz, 1H, Ar–H), 8.08 (d, J = 8.4 Hz, 1H, Ar–H), 7.96 (d, J = 8.0 Hz, 1H, Ar–H), 7.89–7.85 (m, 2H, Ar–H), 7.67–7.62 (m, 2H, Ar–H), 7.55–7.49 (m, 4H, Ar–H) ppm; ^{13}C NMR (DMSO-d_6): δ = 194.9, 160.8, 141.1, 137.0, 135.6, 133.2, 132.8, 130.6, 129.8, 129.3, 128.8, 128.5, 128.0, 125.0, 121.7, 117.5, 112.1 ppm.

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