Microwave-assisted four-component, one-pot condensation reaction: an efficient synthesis of annulated pyridines

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A one-pot, effective synthesis of pyridines by a modified Kröhnke procedure is described. Polysubstituted annulated pyridines were synthesized in high yields by four-component, one-pot cyclocondensation reactions of *N*-phenacylpyridinium bromide, aromatic aldehydes, acetophenones or cyclic ketones in the presence of ammonium acetate and acetic acid, assisted by microwave irradiation. In this procedure, cyclic ketones with two α-CH_2 groups yield annulated pyridines with additional α-benzylidene groups, which are derived *in situ* from double aldol condensation of cyclic ketones with two moles of aromatic aldehydes.

Introduction

The pyridyl heterocyclic core is a widespread sub-unit in numerous natural products[1,2] and a versatile ligand in coordination and supramolecular structures,[3,4] which consequently provides a strong incentive for their synthesis. For a number of years polysubstituted pyridines (or Kröhnke pyridines) have been synthesized using an enormous number of preparative approaches such as: [5 + 1]-type Hantzsch synthesis from a 1,5-diketone and a nitrogen derivative;[5,6] [2 + 2 + 2]-type cobalt-catalyzed cyclization of substituted acetylenes and nitriles;[7] [3 + 3]-type cyclization of chalcones and iminophosphoranes[8]; [4 + 2] reactions of unsaturated imines with enolates;[9] and [3 + 2 + 1]-type cyclization of α,β-unsaturated compounds with α-substituted ketones and a nitrogen source.[10] Among these approaches, the [3 + 2 + 1]-type is that most frequently employed.[11] The efficiency of such pyridine ring closures depends on the nature of the α-substituted group in the ketone moiety, which acts as a leaving group in the aromatization process. The two-step Kröhnke synthesis[12–14] *via* condensation of α,β-unsaturated ketones with pyridinium salts in the presence of a mixture of ammonium acetate and acetic acid gives a variety of polysubstituted pyridines and has distinct advantages over the other routes.

Due to the aromatic character of the pyridine heterocycle, its basicity, and the electron-attracting influence of the nitrogen atom, pyridinium cations can behave as nucleophiles and 1,3-dipoles and show a great variety of synthetic uses, such as in the reaction with alkenes substituted with electron-withdrawing groups.[15–18] Pyridinium cations with stronger electron-withdrawing carbonyl, cyano and nitro groups increase the activity of the methylene group and have much more versatile applications. *N*-Phenacylpyridinium bromide in the presence of a base is known to undergo, for example, Knoevenagel condensation with aldehydes,[19,20] Michael addition to α, β-unsaturated carbonyl compounds[21,22] and dipolar cycloaddition with activated alkenes.[23] Therefore, it is worthwhile investigating new types of reactions and synthetic applications of this kind of salt with emphasis on multicomponent reactions (MCRs), which offer significant advantages and are increasingly important in organic and medicinal chemistry. Herein we wish to describe a simple but effective modification of the Kröhnke synthesis of pyridines in one-pot reactions of *N*-phenacylpyridinium bromide with aromatic aldehydes and cyclic ketones under microwave irradiation to give annulated pyridine derivatives.

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Results and discussion

The typical Kröhnke synthesis of pyridines is readily achieved by heating α,β-unsaturated ketones and pyridinium salts in the presences of a mixture of ammonium acetate and acetic acid for several hours.[14,24–26] However, the pyridinium salts and the unsaturated ketones have to be synthesized first, so this method is relatively expensive. It is generally recognized that chalcones are easily formed from the condensation of aromatic aldehydes with acetophenone under mild basic conditions, and in fact there have been several studies[27–30] reporting the aldol condensation under microwave irradiation with little or no solvent in the presence of either an acidic or basic catalyst. Microwave irradiation is very attractive for chemical applications and has become a widely accepted non-conventional energy source for performing organic synthesis.[31,32] Compared with classical heating, microwave-assisted organic synthesis is characterized by spectacular acceleration, higher yields, milder reaction conditions and shorter reaction times as well as allowing syntheses to become environmentally benign, improving many processes.[33–35] We hypothesized that aromatic aldehydes could react with acetophenone to give chalcones *in situ* by the microwave irradiation procedure described above, and then react with pyridinium salts to accomplish the Kröhnke synthesis of 2,4,6-triarylpyridines. So, *N*-phenacylpyridinium bromide **1** was used in the reaction with an equivalent molar ratio of aromatic aldehydes **2** and acetophenones **3** in a mixture of ammonium acetate and acetic acid (Scheme 1).

Under microwave irradiation, the five-component mixture reacted smoothly to give 2,4,6-triarylpyridines **4a–d** in high yield (84–92%).[31] Here, the formation of 2,4,6-triarylpyridine is a typical multicomponent domino reaction. The aromatic aldehyde first reacts with acetophenone to form an α,β-unsaturated ketone, which in turn reacts with *N*-phenacylpyridinium bromide to give a

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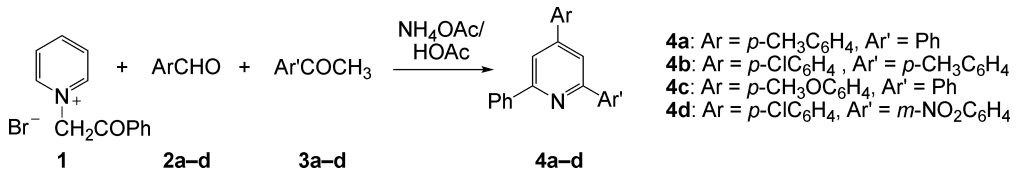
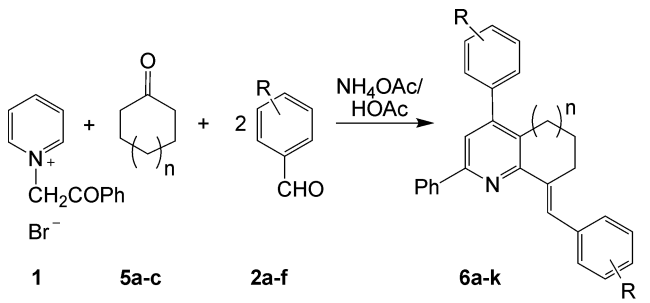


Scheme 1 One-pot synthesis of 2,4,6-triarylpyridines.

1,5-diketone derivative, which is cyclized with ammonia and finally eliminates the pyridinium cation to form the triarylpyridine. So, a two-step Kröhnke synthesis of pyridines can be combined in a one-pot reaction, and this method allows the introduction of various substituted aryl groups into the 2-, 4- and 6-positions of pyridine.

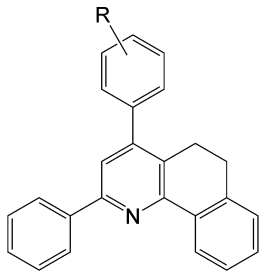
With the initial success of this reaction, we set out to determine the scope and variability of the procedure. A variety of cyclic ketones was used to replace the acetophenone in order to prepare the annulated pyridine derivatives. Under the above-mentioned microwave irradiation conditions, cyclohexanone reacted smoothly and gave the 5,6,7,8-tetrahydroquinolines with an additional 8-benzylidene group as the products **6a–f** (Scheme 2). Compounds **6a–f** clearly result from the reaction of the initially formed 2,6-bis(benzylidene)cyclohexanone, which is derived *in situ* from a double aldol condensation of cyclohexanone with two moles of aromatic aldehyde. Using a 1 : 1 molar ratio of aromatic aldehyde to cyclohexanone still gives these products but in lower yields. Cyclopentanone and cycloheptanone react similarly to give the five- and seven- membered alicyclic fused pyridines with an additional benzylidene group **6g–j** and **6k**, respectively. It is worth mentioning that under microwave irradiation, all aromatic aldehydes, even those bearing electron-donating methyl or methoxy groups, form pyridine derivatives in high yields. 1-Tetralone reacted with one mole of aromatic aldehyde to form 2-benzylidene-1-tetralone. When this compound is used in the above reaction, the expected 5,6-dihydrobenzo[*h*]quinolines **7a–f** (Fig. 1) were formed in 75–90% yield.



6a–f: n = 0, R = H, *p*-CH_3, *p*-Cl, *p*-CH_3O, *m*-NO_2, *m*-CH_3O-*p*-HO
6g–j: n = 1, R = H, *p*-CH_3, *p*-Cl, *p*-CH_3O
6k: n = 2, R = *p*-Cl

Scheme 2 One-pot synthesis of annulated pyridines.

The structures of the polysubstituted and annulated pyridines were characterized by IR, ^{1}H and ^{13}C NMR spectroscopy, and HPLC-MS analysis. It should be mentioned that the reaction under microwave irradiation is very clean, and very small amounts of by-products were detected. Therefore, the work-up procedure involves only a simple filtration of the precipitate followed by crystallization with alcohol. In all instances the products can



7a-f (R = H, *p*-CH_3, *p*-Cl, *p*-CH_3O, *m*-NO_2, *m*-CH_3O-*p*-HO)

Fig. 1 1,2-Diaryl-5,6-dihydrobenzo[*h*]quinolines **7a–f**.

be obtained with high purity, which give very good ^{1}H and ^{13}C NMR spectra. Because there are at least three substituted phenyl groups in each compound and these show very complicated mixed signals in the aromatic region, it is very difficult to elucidate each proton and carbon atom. In order to compare the results of the classical heating with that of microwave heating, we also conducted some reactions using classical heating methods. For example, triarylpyridine **4b** and fused pyridine **6a** were prepared in 78% and 84% yields by heating a mixture of five reaction components at 90 °C for three hours. Similar yields were obtained by the two heating methods, but the microwave heating needs shorter reaction times and is therefore more convenient. The structures of the fused pyridines were further confirmed by X-ray crystal analysis of two representative compounds, **6b** and **7b** (Fig. 2, Fig. 3 and Table 1). In **6b**, the phenyl and 4-methylphenyl groups at the 2- and 4-positions of the pyridine ring are twisted out of the plane of the pyridine ring. In the fused cyclic six-membered ring, which also has a 4-methylbenzyl group attached, there are

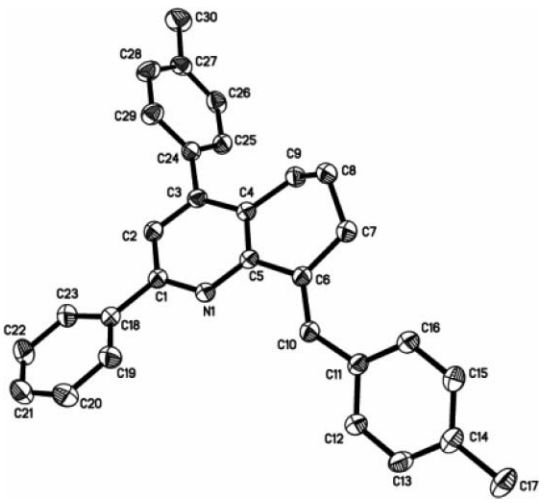


Fig. 2 Molecular structure of compound **6b**. Hydrogen atoms are omitted for clarity.

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Table 1 Crystal data of compounds **6b** and **7b**. CCDC reference numbers 618866 (**6b**) and 628794 (**7b**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617256c

	6b	**7b**
Empirical formula	$C_{30}H_{27}N$	$C_{52}H_{42}N_2$
Formula weight	401.53	694.88
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a/Å	10.0240(17)	10.7313(14)
b/Å	10.7729(18)	10.8332(14)
c/Å	11.1615(19)	17.189(2)
β/°	89.328(2)	101.774(2)
Volume/Å^3	1117.1(3)	1925.0(4)
Z	2	2
Calculated density/g cm^{-3}	1.194	1.199
Absorption coefficient/mm^{-1}	0.068	0.069
F(000)	428	736
Crystal size/mm	0.32 × 0.20 × 0.08	0.40 × 0.20 × 0.20
θ Range for data collection/°	2.02–25.00	2.20 to 25.00
Limiting indices	$-11 \le h \le 11$, $-12 \le k \le 11$, $-13 \le l \le 12$	$-7 \le h \le 12$, $-12 \le k \le 12$, $-20 \le l \le 20$
Reflections collected/unique	5834/3867 [$R_{int} = 0.0183$]	10008/6674 [$R_{int} = 0.0193$]
Completeness (%)	98.4	98.2
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3867/0/282	6674/0/494
Goodness-of-fit on F^2	1.050	1.001
Final R indices [$I > 2\sigma I$]	$R1 = 0.0487$, $wR2 = 0.1207$	$R1 = 0.0619$, $wR2 = 0.1548$
R indices (all data)	$R1 = 0.0761$, $wR2 = 0.1358$	$R1 = 0.1110$, $wR2 = 0.1796$
Largest difference peak and hole/e Å^{-3}	0.181 and −0.177	0.621 and −0.142

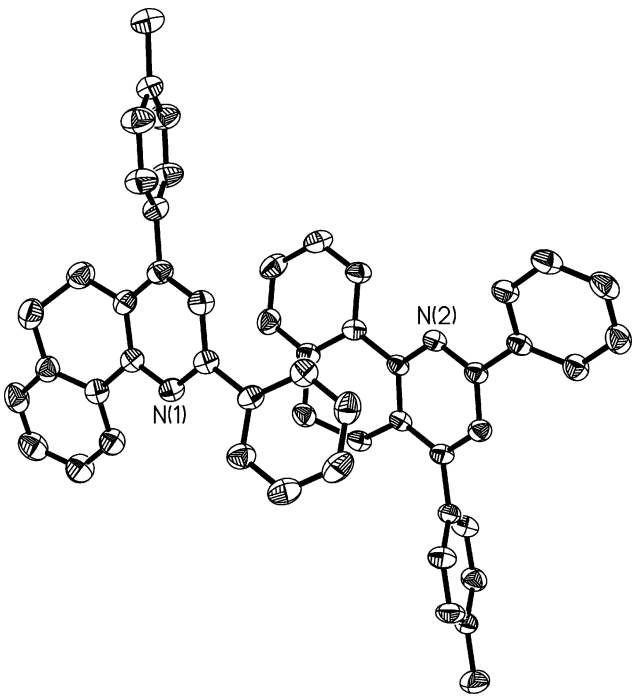
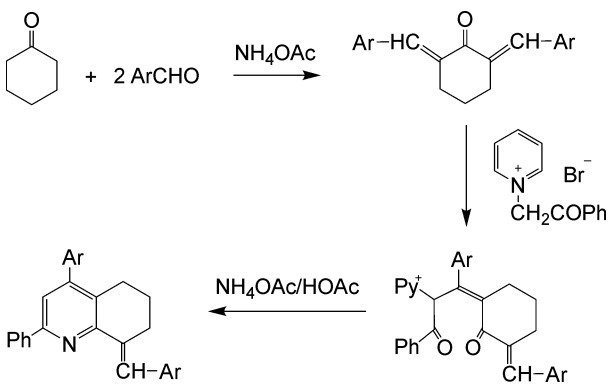


Fig. 3 Molecular structure of compound **7b**.

three carbon atoms with sp^3 hybridization and three carbon atoms having sp^2 hybridization, and so the whole ring is best described as having a screw-boat conformation. The asymmetric unit of compound **7b** contains two independent molecules with slightly different conformations (Fig. 3). In each molecule of **7b**, the 5,6-dihydrobenzo[*h*]quinoline core has a phenyl group at the 2-position, which has come from *N*-phenacylpyridinium chloride, and a 4-methyphenyl group at the 4-position, which has clearly come from 4-methylbenzaldehyde. The central fused cyclic six-membered ring in the 5,6-dihydrobenzo[*h*]quinoline core is also in a screw-boat conformation.

With the assistance of microwave irradiation, a two-step Kröhnke synthesis of pyridines is performed in a one-pot reaction. The reaction proceeds as follows: aromatic aldehydes react firstly with cyclic ketones to form doubly α,β-unsaturated ketones (2-methylcyclohexanone and 1-tetralone could only give mono-α,β-unsaturated ketones), which in turn react with *N*-phenacylpyridinium bromide to give 1,5-diketone derivatives. The latter is then cyclized with ammonia and finally eliminates pyridinium cations to form annulated pyridines (Scheme 3).



Scheme 3 The mechanism of formation of annulated pyridines.

Conclusion

In conclusion, we have described a simple and efficient one-pot procedure for the generation of polysubstituted or annulated pyridines with microwave assistance. The advantages of this approach are as follows: the reaction procedure is convenient, involves simple experimental procedures and product isolation,

and thus dispenses with extensive recrystallization or chromatographic purification steps. Hence it is a useful modification and addition to the existing methods. It is a four-component reaction which allows the construction of relatively complicated nitrogen-containing heterocyclic systems using simple starting materials. The introduction of various substituted alkyl and aryl groups into the 2-, 4- and 6-positions of pyridine is very easy. Further studies aiming to extend the synthetic scope of this reaction, especially using other *N*-substituted pyridinium salts, are currently under way.

Experimental

Material and apparatus

Melting points were recorded on a hot-plate microscope apparatus. IR spectra were obtained on a Bruker Tensor 27 spectrometer (KBr disc). ^{1}H NMR spectra were recorded with a Bruker AV-600 spectrometer with $CDCl_3$ as solvent and TMS as internal standard. HPLC-MS spectra were measured using a Fennigan LCQ Deca XP MAX instrument. Pyridine, aromatic aldehydes, cyclic ketones, 1-tetralone and other reagents are commercial reagents and were used as received. Solvents were purified by standard techniques. *N*-Phenacylpyridinium bromide was prepared according to the published method.[23] The progress of reaction was monitored by TLC.

General procedure for the preparation of 2,4,6-triarylpyridines

To a 50 mL flask was added *N*-phenacylpyridinium bromide (1.2 mmol, 0.280 g), aromatic aldehyde (1.0 mmol), aromatic ketone (1.0 mmol), ammonium acetate (3.0 g) and acetic acid (2.0 mL). The mixture was heated in a microwave for about 3–4 minutes (130 W). After cooling, the reaction mixture was diluted with water (50 mL) and the resulting precipitate was collected by filtration. The crude product was recrystallized from ethanol to give the pure solid sample for analysis.

4a: 2,6-Diphenyl-4-*p*-methylphenylpyridine. 53%. Mp 116–118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, J = 7.2 Hz, 4H, MeC_6H_4), 7.98 (s, 2H, 3,5-PyH), 7.76 (d, J = 8.4 Hz, 2H, ArH), 7.42–7.63 (m, 8H, ArH), 2.54 (s, 3H, CH_3). ^{13}C NMR (600 MHz, $CDCl_3$) δ 157.5, 150.2, 139.6, 139.1, 136.1, 129.8, 129.0, 128.7, 127.2, 127.0, 117.0, 21.2. IR (KBr) υ 3033(w), 2916(w), 1579(s), 1544(s), 1390(m), 1026(w), 814(s), 770(s) cm^{-1}. Anal. calc. for $C_{24}H_{19}N$: C 89.68, H 5.96, N 4.36; found. C 89.50, H 5.62, N 4.28.

4b: 2-Phenyl-4-*p*-chlorophenyl-6-*p*-methylphenylpyridine. 58%. Mp 122–124 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28, 7.76 (d, d, J = 7.8, 4H, *p*-ClC_6H_4), 8.19 (d, J = 7.2 Hz, 2H, MeC_6H_4), 7.90 (s, 2H, 3,5-PyH), 7.54–7.62 (m, 7H, C_6H_5, MeC_6H_4), 2.53 (s, 3H, CH_3). ^{13}C NMR (600 MHz, $CDCl_3$) δ 157.7, 157.6, 148.8, 139.5, 139.2, 137.6, 136.6, 135.1, 129.5, 129.3, 129.1, 128.7, 128.4, 127.1, 127.0, 116.5, 116.4. IR (KBr) υ 3033(w), 1600(s), 1542(s), 1493(s), 1383(m), 1093(m), 1014(m), 816(s), 772(s) cm^{-1}. Anal. calc. for $C_{24}H_{18}ClN$: C 80.00, H 5.10, N 3.94; found. C 79.77, H 5.34, N 4.15.

4c: 2,6-Diphenyl-4-*p*-methoxyphenylpyridine. 82%. Mp 96–98 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31, 7.80 (d, d, J = 7.8 Hz, 4H, $MeOC_6H_4$), 7.96 (s, 2H, 3,5-PyH), 7.81–7.80 (d, J = 7.8 Hz, 2H, $2C_6H_5$), 7.63–7.53 (m, 6H, $2C_6H_5$), 7.16–7.14(d, J = 8.4 Hz, 2H, $2C_6H_5$), 3.98 (s, 3H, CH_3). ^{13}C NMR (600 MHz, $CDCl_3$) δ 160.6, 157.4, 149.8, 139.6, 131.2, 129.0, 128.7, 128.4, 127.2, 116.7, 114.6, 55.4. IR (KBr) υ 3016(w), 2957(w), 2931(w), 1596(s), 1514(s), 1291(s), 1257(s), 1178(s), 1030(s), 840(s) cm^{-1}. Anal. calc. for $C_{24}H_{19}NO$: C 85.43, H 5.68, N 4.15; found. C 85.22, H 5.33, N 3.81.

4d: 2-Phenyl-4-*p*-chlorophenyl-6-*m*-nitrophenylpyridine. 63%. Mp 168–170 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00, 8.55, 8.29 (s, br, s br, 3H, *m*-$NO_2C_6H_4$), 8.17 (d, 2H, J = 7.8 Hz, *p*-ClC_6H_4), 7.90, 7.87 (s, s, 2H, 3,5-PyH), 7.67–7.69 (m, 3H, *m*-$NO_2C_6H_4$, *p*-ClC_6H_4), 7.64–7.55 (m, 5H, C_6H_5). ^{13}C NMR (600 MHz, $CDCl_3$) δ 158.1, 154.9, 149.7, 148.8, 140.8, 140.8, 138.5, 136.8, 135.7, 133.1, 129.9, 129.7, 129.6, 129.5, 129.4, 128.9, 128.5, 127.2, 123.9, 122.0, 118.0, 117.0. IR (KBr) υ 3074(w), 1659(w), 1601(s), 1521(s), 1493(m), 1087(m), 828(m), 770(m) cm^{-1}. Anal. calc. for $C_{23}H_{15}ClN_2O_2$: C 71.41, H 3.91, N 7.24; found. C 71.36, H 4.17, N 7.11.

General procedure for the preparation of annulated pyridines

To a 50 mL flask was added *N*-phenacylpyridinium bromide (1.2 mmol, 0.280 g), aromatic aldehyde (2.0 mmol), cyclic ketone (1.0 mmol), ammonium acetate (3.0 g) and acetic acid (2.0 mL). The mixture was heated in a microwave for about 2–4 minutes (130 W). After cooling, the reaction mixture was diluted with water (50 mL) and the resulting precipitate was collected by filtration. The crude product was recrystallized from ethanol to give the pure solid sample for analysis.

6a. 74%. Mp 140.0–142.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.2 Hz, 1H, PhH), 7.74 (s, 1H, PyH), 7.60 (s, 3H, PhH), 7.56 (d, 2H, J = 7.2 Hz, PhH), 7.50 (s, 3H, PhH), 7.45–7.41 (m, 5H, PhH, CH=), 3.21 (s, 4H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 161.5, 157.2, 146.9, 141.6, 139.8, 138.8, 138.0, 137.9, 136.9, 135.2, 129.2, 129.1, 128.8, 128.6, 128.5, 128.5, 128.4, 128.2, 128.0, 127.1, 126.9, 126.7, 122.8, 122.0, 119.3, 29.4, 29.2, 28.2, 27.73. IR (KBr) υ 3053(w), 2942(w), 1950(w), 1577(m), 1535(m), 1373(m), 1149(w), 920(w), 763(s) cm^{-1}; MS: 359.67. Anal. calc. for $C_{27}H_{21}N$: C 90.22, H 5.89, N 3.89; found. C 89.79, H 5.71, N 3.75.

6b. 75%. Mp 114.5–146.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, 2H, J = 7.8 Hz, PhH), 7.74 (s, 1H, PyH), 7.60 (s, 1H, ArH), 7.53–7.49 (m, 5H, ArH), 7.46–7.43 (t, 1H, PhH), 7.33 (d, 2H, J = 7.8 Hz, PhH), 7.28 (s, 1H, CH=), 7.24 (d, 2H, J = 7.8 Hz, ArH), 3.22 (s, 4H, CH_2), 2.46 (s, 3H, CH_3), 2.41 (s, 3H, CH_3). ^{13}C NMR (600 MHz, $CDCl_3$) δ 139.3, 133.5, 133.2, 132.0, 130.2, 129.7, 129.5, 129.4, 129.2, 129.2, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.2, 127.1, 126.9, 126.1, 29.2, 28.3, 21.3, 21.3. IR (KBr) υ 2926(w), 1628(w), 1528(s), 1435(w), 1349(s), 1092(w), 904(w), 807 (w), 735(w) cm^{-1}; MS: 387.73. Anal. calc. for $C_{29}H_{25}N$: C 89.88, H 6.50, N 3.62; found. C 89.56, H 6.62, N 3.29.

6c. 80%. Mp 160.0–161.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 1H, PhH), 7.68 (s, 1H, ArH), 7.57 (s, 1H, PyH), 7.52–7.47 (m, 7H, ArH), 7.47–7.43 (m, 4H, ArH), 7.38–7.36 (m, 3H, ArH), 7.30 (d, J = 8.4 Hz, 1H, CH=), 3.18 (s, 2H, CH_2); ^{13}C NMR (600 MHz, $CDCl_3$) δ 161.3, 157.4, 145.8, 141.9, 139.4, 137.1, 136.2, 135.0, 134.6, 132.6, 130.3, 130.2, 129.5, 129.0,

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128.8, 128.7, 127.1, 121.7, 119.1, 29.1, 28.1. IR (KBr) υ 2916(w), 1634(m) 1597(m), 1491(s), 1359(w), 1239(w), 1091(m), 896(w), 824(m) cm^{-1}; MS: 428.67. Anal. calc. for $C_{27}H_{19}Cl_2N$: C 75.71, H 4.47, N 3.27; found. C 75.45, H 4.81, N 3.23.

6d. 70%. Mp 167.0–168.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, $J = 7.8$ Hz, 1H, PhH), 7.68 (s, 1H, PyH), 7.63 (s, 1H, ArH), 7.55–7.49 (m, 6H, ArH, PhH), 7.42 (d, $J = 7.2$ Hz, 1H, PhH), 7.30 (d, $J = 7.8$ Hz, 1H, CH=), 7.03–6.98 (m, 2H, ArH), 6.95 (s, 2H, PhH), 3.88–3.84 (m, 6H, OCH_3), 3.18–3.11(m, 4H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 161.7, 161.0, 159.8, 159.2, 158.6, 158.4, 151.0, 146.4, 140.0, 139.4, 136.2, 134.6, 131.2, 131.0, 130.8, 130.5, 129.6, 129.5, 129.4, 128.7, 127.1, 122.2, 121.3, 118.3, 118.7, 114.1, 114.0, 113.9, 55.4, 55.3, 29.3, 29.1, 28.3, 27.8. IR (KBr) υ 3053(w), 2919(w), 1582(w), 1543(w), 1491(w), 1435(w), 1238(w), 1189(w), 1075(w), 1026(w), 917(w), 762(m) cm^{-1}; MS: 419.67. Anal. calc. for $C_{29}H_{25}NO_2$: C 83.03, H 6.01, N 3.34; found. C 83.45, H 5.69, N 3.57.

6e. 71%. Mp 150.0–152.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.46 (s, 2H, ArH), 8.34 (d, $J = 6.6$ Hz, 1H, ArH), 8.16–8.12 (m, 3H, ArH), 7.92–7.88 (m, 2H, ArH), 7.81–7.79 (m, 1H, PhH), 7.74–7.73 (d, $J = 7.2$ Hz, 1H, PhH), 7.67 (s, 1H, PyH), 7.59–7.54 (m, 3H, PhH), 7.48 (d, $J = 6.0$ Hz, 1H, CH=), 3.30–3.27 (d, 4H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 161.1, 161.1, 160.8, 157.9, 148.6, 144.7, 144.1, 143.9, 139.2, 135.3, 134.9, 134.0, 130.0, 129.5, 129.35, 128.9, 127.1, 123.4, 123.1, 123.1, 121.6, 121.0, 119.5, 29.3, 29.1, 28.0, 27.6. IR (KBr) υ 2926(w), 2834(w), 1603(m), 1509(m), 1456(w), 1364(w), 1243(s), 1176(m), 1029(m), 1029(m), 896(w), 823(m), 765(w) cm^{-1}; MS: 449.40. Anal. calc. for $C_{27}H_{19}N_3O_4$: C 72.15, H 4.26, N 9.35; found. C 72.09, H 4.68, N 9.10.

6f. 73%. Mp 175–176 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, $J = 7.2$ Hz, 2H, PhH), 7.68 (s, 1H, PyH), 7.56 (s, 1H, ArH), 7.53–7.51 (m, 2H, PhH), 7.46–7.43 (m, 1H, ArH), 7.18 (d, $J =$ 8.4 Hz, 1H, ArH), 7.13–7.12 (m, 2H, ArH), 7.07–7.06 (m, 2H, ArH), 6.99 (d, $J = 8.4$ Hz, 1H, ArH), 5.79 (s, 1H, OH), 5.71 (s, 1H, OH), 3.98 (d, $J = 6.64$ Hz, 6H, OCH_3), 3.22 (s, 4H, CH_2); ^{13}C NMR (600 MHz, $CDCl_3$) δ 146.7, 146.4, 146.1, 145.0, 130.6, 128.7, 128.7, 127.1, 122.4, 121.5, 118.8, 114.7, 114.5, 112.0, 110.7, 56.1, 55.9, 29.1, 28.4; IR (KBr) υ 2932(w), 2843(w), 1595(w), 1513(s), 1458(w), 1429(w), 1376(w), 1272(m), 1209(m), 1129(w), 901(w), 818(w), 774(w) cm^{-1}; MS: 451.53. Anal. calc. for $C_{29}H_{25}NO_4$: C 77.14, H 5.58, N 3.30. found. C 76.75, H 5.69, N 3.22.

6g. 75%. Mp 137.0–139.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H, ArH), 8.14 (d, $J = 7.8$ Hz, 2H, PhH), 7.53 (s, 1H, PyH), 7.50–7.47 (m, 6H, PhH), 7.43–7.37 (m, 6H, PhH), 7.28–7.24 (m, 1H, CH=), 2.95 (s, 2H, CH_2), 2.76 (t, $J = 6.0$ Hz, 2H, CH_2), 1.78 (t, $J = 5.4$ Hz, 2H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 151.8, 150.6, 148.4, 137.6, 137.5, 136.1, 134.0, 127.7, 126.9, 126.6, 126.6, 126.3, 126.0, 125.8, 125.7, 124.8, 124.6, 117.6, 26.1, 25.9, 21.0. IR (KBr) υ 3053(w), 2942(w), 1577(m), 1535(m), 1373(m), 763(s) cm^{-1}; MS: 373.67. Anal. calc. for $C_{28}H_{23}N$: C 90.04, H 6.21, N 3.75; found. C 89.64, H 5.89, N 3.62.

6h. 78%. Mp 156.5–157.5 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H, PyH), 7.92 (d, $J = 7.8$ Hz, 2H, PhH), 7.30 (s, 1H, PhH), 7.26 (t, $J = 7.8$ Hz, 2H, PhH), 7.19 (d, 3H, $J = 7.8$ Hz, ArH, CH=), 7.06 (s, 4H, ArH), 7.00 (d, 2H, $J = 7.8$ Hz, ArH), 2.73 (s, 2H, CH_2), 2.55 (t, $J = 6.0$ Hz, 2H, CH_2), 2.22 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 1.56 (t, 3H, $J = 6.0$ Hz, CH_2); ^{13}C NMR (600 MHz, $CDCl_3$) δ 153.2, 152.8, 150.5, 138.7, 137.7, 136.8, 136.5, 135.5, 135.4, 132.9, 129.7, 129.1, 128.8, 128.6, 127.7, 126.8, 28.2, 28.0, 23.1, 21.2; IR (KBr) υ 3022(w), 2947(m), 2869(w), 1905(w), 1577(m), 1507(m), 1426(m), 1373(m), 1116(w), 912(w), 817(s), 768(m) cm^{-1}; MS: 401.80. Anal. calc. for $C_{30}H_{27}N$: C 89.73, H 6.78, N 3.49; found. C 89.55, H 6.60, N 3.58.

6i. 70%. Mp 164.0–166.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H, pyH), 8.14 (d, $J = 7.8$ Hz, 2H, ArH), 7.53 (s, 1H, ArH), 7.50–7.47 (m, 5H, ArH), 7.43–7.37 (m, 5H, PhH), 7.28–7.24 (m, 1H, =CH), 2.95 (s, 2H, CH_2), 2.76 (t, $J = 6.0$ Hz, 2H, CH_2), 1.78 (t, $J = 5.4$ Hz, 2H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 153.8, 152.7, 139.6, 138.1, 129.7, 128.8, 128.7, 128.6, 128.4, 127.9, 126.9, 126.7, 119.8, 28.1, 27.9, 23.0. IR (KBr) υ 2946(w), 1636(w), 1582(w), 1532(m), 1485(w), 1372(w), 1181(w), 1088(m), 1010(w), 911(w), 827(m), 769(w) cm^{-1}; MS: 443.67. Anal. calc. for $C_{28}H_{21}Cl_2N$: C 76.02, H 4.78, N 3.17; found. C 76.24, H 5.17, N 3.42.

6j. 75%. Mp 130.0–131.5 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H, ArH), 8.14 (d, $J = 7.2$ Hz, 2H, PhH), 7.50–7.45 (m, 4H, ArH), 7.40 (t, $J = 7.2$ Hz, 1H, PyH), 7.32 (d, $J = 7.8$ Hz, 2H, PhH), 7.04–6.92 (m, 5H, ArH, PhH, CH=), 3.87–3.82 (m, 6H, OCH_3), 2.94 (s, 2H, CH_2), 2.78 (s, 4H, CH_2), 1.78 (s, 2H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 159.4, 158.4, 153.8, 152.9, 150.0, 139.7, 134.6, 132.0, 131.1, 130.8, 130.0, 128.9, 128.6, 127.3, 126.8, 119.5, 113.8, 113.6, 55.4, 55.3, 28.3, 28.0, 23.1. IR (KBr) υ 2930(w), 2930(w), 2833(w), 1607(m), 1508(m), 1438(w), 1381(w), 1381(w), 1291(w), 1347(s), 1174(m), 1111(w), 1032(m), 885(w), 834(w), 766(w) cm^{-1}; MS: 433.53. Anal. calc. for $C_{30}H_{27}NO_2$: C 83.11, H 6.28, N 3.23; found. C 82.87, H 5.91, N 3.02.

6k. 73%. Mp 153.5–155.5 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, 2H, $J = 7.2$ Hz, PhH), 7.47 (s, 1H, PyH), 7.45–7.41 (m, 6H, ArH), 7.37 (t, $J = 7.2$ Hz, 1H, $=CH_2$), 7.32 (d, $J = 8.4$ Hz, 2H, ArH), 7.26 (d, $J = 7.8$ Hz, 2H, ArH), 7.10 (s, 1H, PhH), 2.76–2.67 (m, 4H, CH_2), 1.86–1.75 (m, 4H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 160.6, 153.2, 148.0, 143.2, 138.3, 137.4, 135.2, 133.0, 131.6, 129.8, 129.6, 129.5, 129.2, 129.1, 127.8, 127.7, 127.7, 127.6, 127.0, 125.9, 119.1, 28.6, 26.9, 25.7. IR (KBr) υ 3447(m), 3044(m), 2931(m), 2858(w), 1573(m), 1538(m), 1488(s), 1452(m), 1418(m), 1376(m), 1223(w), 1087(s), 1011(m), 877(m), 764(m) cm^{-1}; MS: 455.80. Anal. calc. for $C_{29}H_{23}Cl_2N$: C 76.32, H 5.08, N 3.07; found. C 76.14, H 5.28, N 3.51.

General procedure for the preparation of 5,6-dihydrobenzo[*h*]quinolines

To a 50 mL flask was added *N*-phenacylpyridinium bromide (1.2 mmol, 0.280 g), aromatic aldehyde (1.0 mmol), 1-tetralone (1.0 mmol), ammonium acetate (3.0 g) and acetic acid (2.0 mL). The mixture was placed in a microwave and heated for about 2–4 minutes (130 W). After cooling, the reaction mixture was diluted with water (50 mL) and the resulting precipitate was collected by filtration. The crude product was recrystallized with ethanol to give the pure solid sample for analysis.

7a. 81%, Mp 123.0–124.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, $J = 7.8$ Hz, 1H, ArH), 8.17 (d, 2H, $J = 7.2$ Hz, PhH), 7.59

(s, 1H, PyH), 7.48 (t, $J = 7.8$ Hz, 4H, ArH), 7.44–7.39 (m, 5H, ArH, PhH), 7.32 (t, $J = 7.2$ Hz, 1H, ArH), 7.21 (d, $J = 7.2$ Hz, 1H, PhH), 2.95 (t, $J = 7.8$ Hz, 2H, CH_2), 2.90 (s, 2H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 154.4, 152.6, 149.3, 139.6, 139.4, 138.2, 135.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.0, 127.5, 127.1, 126.9, 125.8, 112.0, 28.2, 25.3. IR (KBr) υ 3060(w), 3030(w), 2941(w), 2841(w), 1957(w), 1544(m), 1418(m), 1377(m), 1227(m), 1028(w), 834(w), 760(s) cm^{-1}; MS: 333.73. Anal. calc. for $C_{25}H_{19}N$: C 90.06, H 5.74, N 4.20; found. C 89.71, H 5.88, N 4.17.

7b. 85%. Mp 153.8–155.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H, ArH), 8.23 (s, 2H, PhH), 7.64 (br s, 1H, PyH), 7.53 (d, $J = 4.2$ Hz, 2H, PhH), 7.46 (s, 2H, ArH), 7.35 (s, 5H, ArH), 7.28 (s, 1H, PhH), 2.99 (s, 2H, CH_2), 2.90 (s, 2H, CH_2), 2.49 (s, 3H, CH_3). ^{13}C NMR (600 MHz, $CDCl_3$) δ 154.4, 152.3, 149.3, 139.7, 138.3, 137.9, 136.4, 136.3, 129.3, 129.2, 129.1, 128.8, 128.1, 127.5, 127.1, 126.9, 125.8, 120.1, 28.2, 25.4, 21.4. IR (KBr) υ 3032(w), 2928(w), 1906(w), 1581(m), 1542(m), 1506(m), 1419(m), 1376(s), 1225(w), 1029(m), 821(m), 748(vs) cm^{-1}; MS: 347.67. Anal. calc. for $C_{26}H_{21}N$: C 89.88, H 6.09, N 4.03; found. C 89.80, H 6.35, N 3.81.

7c. 82%. Mp 137.2–138.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, $J = 7.2$ Hz, 1H, ArH), 8.16 (d, $J = 7.8$ Hz, PhH), 7.54 (s, 1H, PyH), 7.50–7.45 (m, 4H, ArH), 7.41 (t, $J = 7.2$ Hz, 2H, PhH), 7.34 (d, $J = 7.2$ Hz, 3H, ArH), 7.22 (d, $J = 7.2$ Hz, 1H, ArH), 2.90–2.86 (m, 4H, CH_2) ^{13}C NMR (600 MHz, $CDCl_3$) δ 154.6, 152.8, 148.1, 139.4, 138.1, 137.7, 135.1, 134.2, 130.2, 129.2, 128.9, 128.7 127.8, 127.5, 127.2, 126.8, 125.8, 119.7, 28.1, 25.3. IR (KBr) υ 3032(w), 2936(w), 2846(w), 1906(w), 1597(m), 1542(m), 1488(s), 1419(m), 1376(m), 1272(w), 1088(m), 830(s), 748(vs) cm^{-1}; MS: 367.67. Anal. calc. for $C_{25}H_{18}ClN$: C 81.62, H 4.93, N 3.81; found. C 81.47, H 5.15, N 3.62.

7d. 80%, Mp 104.5–105 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, $J = 7.8$ Hz, 1H, ArH), 8.18 (d, $J = 8.4$ Hz, 2H, PhH), 7.58 (s, 1H, PyH), 7.48 (t, $J = 7.8$ Hz, 2H, PhH), 7.40 (t, $J = 7.8$ Hz, 2H, ArH), 7.34–7.31 (m, 3H, ArH), 7.22 (t, $J = 7.2$ Hz, 1H, ArH), 7.01 (d, $J = 7.8$ Hz, 2H, ArH), 3.87 (s, 3H, OCH_3), 2.95 (t, $J = 7.8$ Hz, 2H, CH_2), 2.90 (s, 2H, CH_2) ^{13}C NMR (600 MHz, $CDCl_3$) δ 159.5, 154.4, 152.6, 149.0, 139.7, 138.2, 136.3, 131.6, 130.1, 129.0, 128.7, 128.0, 127.5, 127.0, 126.8, 125.8, 120.1, 114.0, 55.4, 28.2, 25.4. IR (KBr) υ 3064(w), 3035(w), 2936(w), 2831(w), 1894(w), 1651(m), 1542(m), 1507(vs) 1418(m), 1375(m), 1243(vs), 1030(m), 834(m), 747(s) cm^{-1}; MS: 363.53. Anal. calc. for $C_{26}H_{21}NO$: C 85.92, H 5.82, N 3.85; found. C 85.65, H 5.90, N 3.74.

7e. 82%, Mp 150.1–151.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, 1H, $J = 7.8$ Hz, ArH), 8.30 (s, 2H, ArH), 8.17 (d, $J = 7.8$ Hz, 2H, PhH), 7.74 (d, $J = 7.8$ Hz, 1H, ArH), 7.68 (t, $J = 7.8$ Hz, 1H, ArH), 7.57 (s, 1H, PyH), 7.50 (t, $J = 7.8$ Hz, 2H, PhH), 7.43 (m, 2H, ArH), 7.35 (t, $J = 7.2$ Hz, 1H, ArH), 7.23 (d, 1H, $J = 7.8$ Hz, ArH), 2.89 (s, 4H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 154.9, 153.1, 148.4, 146.7, 141.0, 139.1, 137.9, 134.8, 129.6, 129.4, 129.0, 128.7, 127.5, 127.5, 127.2, 126.8, 125.9, 123.8, 123.0, 119.4, 28.0, 25.2. IR (KBr) υ 3067 (w), 2942(w), 1604(w), 1572(w), 1525(vs), 1432(w), 1416(w), 1383(m), 1347(s), 1282(w), 1090(w), 902(w), 774(m). MS: 378.67. Anal. calc. for $C_{26}H_{21}NO$: C 79.47, H 4.79, N 7.40; found. C 79.21, H 4.91, N 7.11.

7f. 81%. Mp 178.3–178.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, $J = 7.8$ Hz, 1H, ArH), 8.17 (d, $J = 8.4$ Hz, 2H, PhH), 7.58 (s, 1H, PyH), 7.48 (t, $J = 7.8$ Hz, 2H, PhH), 7.40 (d, $J = 7.8$ Hz, 2H, ArH), 7.32 (t, $J = 7.8$ Hz, 1H, ArH), 7.22 (d, $J = 7.8$ Hz, 1H, ArH), 7.03 (d, $J = 7.8$ Hz, 1H, ArH), 6.90 (t, $J = 7.8$ Hz, 2H, ArH), 5.77 (s, 1H, OH), 3.91 (s, 3H, OCH_3), 2.95 (t, $J = 7.2$ Hz, 2H, CH_2), 2.85 (t, $J = 7.2$ Hz, 2H, CH_2). ^{13}C NMR (600 MHz, $CDCl_3$) δ 153.3, 151.5, 148.1, 145.4, 144.6, 138.6, 137.1, 134.2, 130.3, 127.9, 127.6, 127.5, 126.9, 126.32, 126.0, 125.7, 124.7, 121.0, 118.9, 113.3, 110.4, 55.0, 27.1, 24.3. IR (KBr) υ 2931(w), 1601(w), 1538(w), 1513(s), 1466(w), 1416(m), 1384(s), 1267(w), 1242(w), 1197(m), 1121(w), 1079(w), 1030(m), 887(w), 821(w), 745(m) cm^{-1}. MS: 379.67. Anal. calc. for $C_{26}H_{21}NO_2$: C 82.30, H 5.58, N 3.69; found. C 81.89, H 5.75, N 3.47.

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