Green preparation of quinoline derivatives through $FeCl_3 \cdot 6H_2O$ catalyzed Friedlander reaction in ionic liquids

Jianji Wang, Xuesen Fan, Xinying Zhang, and Lijun Han

Abstract: The preparation of substituted quinoline derivatives through a Friedlander condensation reaction utilizing the ionic liquid [bmim][BF_4] as the reaction medium and iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as a catalyst is described. The advantages in using this method include its environmental friendliness, simple operating process in both mild and neutral reaction conditions, and good yields.

Key words: ionic liquid, Friedlander reaction, quinoline derivatives, green chemistry.

Résumé : On décrit l'utilisation du [bmim][BF_4], un liquide ionique, comme milieu réactionnel et de l'hexahydrate du chlorure de fer ($FeCl_3 \cdot 6H_2O$) comme catalyseur pour la préparation de dérivés de quinoléines substituées par la réaction de condensation de Friedlander. Cette méthode présente l'avantage d'être bénigne pour l'environnement, d'impliquer un processus d'opération simple, de se faire dans des conditions douces et neutres et de donner de bons rendements.

Mots clés : liquide ionique, réaction de Friedlander, dérivés de la quinoléine, chimie verte.

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Introduction

For many years, the synthesis of quinoline and its derivatives has been of considerable interest in organic and medicinal chemistry since a large number of natural products and drugs contain this heterocyclic nucleus (1). While versatile methods for the synthesis of the quinoline ring system have been developed (2), many of them suffer from harsh reaction conditions, poor yields, and (or) the use of expensive catalysts. Thus, simple, general, and efficient procedures for the synthesis of this important heterocycle are still in demand.

As one of the most frequently used pathways to prepare quinoline derivatives, Friedlander synthesis involves a condensation of 2-aminobenzaldehyde with an aldehyde, ketone, or polyfunctional carbonyl compound having a reactive α-methylene group (3). This classical process is usually carried out either by refluxing an aqueous or alcoholic solution of the reactants in the presence of a base or by heating a mixture of substrates at temperatures ranging from 150 to 220 °C in the absence of solvent and catalyst to produce the corresponding 2- and 3-substituted quinolines in moderate yields. Unfortunately, attempts to extend this method to the preparation of 4-substituted quinolines from 2-aminoaryl ketones appear to have met with very limited success. Subsequent studies showed that problems resulting from the classical Friedlander procedure can be overcome by using acid catalysis. For example, it has been reported that drops of concentrated sulfuric acid or 6 mol/L hydrochloric acid can be used as efficient catalysts in the Friedlander condensation procedure (4). With this method, various structurally varied substrates, including 2-aminobenzophenone, can give the corresponding quinolines in moderate to high yields. However, this method still has some drawbacks, notably use of very strong acids as the catalyst, use of excessive glacial acetic acid as the solvent, or even requiring the use of a metal bath that can maintain a reaction temperature as high as 200 °C, thus making this method unsuitable for scale up in an environmentally benign and economical way.

Room temperature ionic liquids based on the 1,3-dialkylimidazolium cation are attracting increasing interest as alternative reaction media. The desirable advantages of ionic liquids, include their lack of vapor pressure, wide liquid range, and thermal stability, have made them exceptional reaction media as well as environmentally benign solvents in organic synthesis (5). In line with our research program of using ionic liquids as novel reaction media in organic reactions (6), we wish to report here a novel and efficient procedure for the preparation of quinolines through a Friedlander reaction catalyzed by $FeCl_3 \cdot 6H_2O$ in an ionic liquid (Scheme 1).

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Results and discussion

We set out to examine the Friedlander reaction in one of the most widely used ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), using

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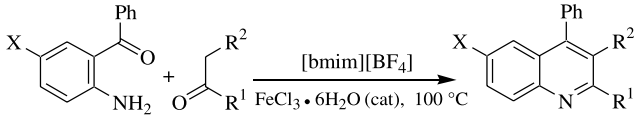
Table 1. Friedlander reaction of 2-aminobenzophenone and acetophenone in different catalytic systems.

Entry	Solvent	Catalyst	Amount of catalyst (mmol)	Reaction temp. (°C)	Reaction time (h)	Isolated yield (%)
1	[bmim][BF_4]	None	0	RT	10	0
2	[bmim][BF_4]	None	0	100	10	9
3	[bmim][BF_4]	$FeCl_3{\cdot}6H_2O$	0.1	100	10	41
4	[bmim][BF_4]	$FeCl_3{\cdot}6H_2O$	0.3	100	10	65
5	[bmim][BF_4]	$FeCl_3{\cdot}6H_2O$	0.5	100	10	78
6	[bmim][BF_4]	$FeCl_3{\cdot}6H_2O$	0.5	100	6	75
7	[bmim][BF_4]	$FeCl_3$	0.5	100	6	74
8	Toluene	$FeCl_3{\cdot}6H_2O$	0.5	100	6	62
9	EtOAc	$FeCl_3{\cdot}6H_2O$	0.5	reflux	6	68
10	THF	$FeCl_3{\cdot}6H_2O$	0.5	reflux	6	8
11	Ethanol	$FeCl_3{\cdot}6H_2O$	0.5	reflux	6	26

Note: Reaction conditions: 1 mL solvent, 1 mmol 2-aminobenzophenone, and 1 mmol acetophenone.

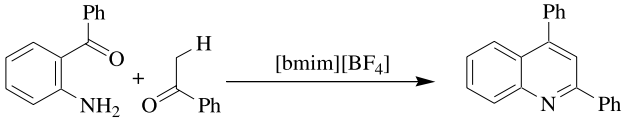
Scheme 1.



1 **2** **3**

(X = H, Cl)

Scheme 2.



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

2-aminobenzophenone (Scheme 2, **1a**) and acetophenone (**2a**) as the starting materials.

Firstly, the mixture of **1a** (1 mmol) and **2a** (1mmol) in 1 mL of [bmim][BF_4] was stirred at room temperature for 10 h, but no reaction took place as indicated by TLC (Table 1, entry 1). Then, the mixture was heated at 100 °C. To our delight, the desired condensation reaction eventually took place but in a rather sluggish way. In fact, after being stirred at 100 °C for more than 10 h, the mixture produced the corresponding quinoline product in less than 10% yield (Table 1, entry 2). This means that while the ionic liquid [bmim][BF_4] itself possesses some catalytic activity for this condensation process, the activity is too low to give the product in a reasonable yield. Bearing in mind that $FeCl_3{\cdot}6H_2O$ has been successfully used as an environmentally benign and efficient Lewis acid catalyst for promoting several kinds of reactions (7), we then added catalytic amounts of $FeCl_3{\cdot}6H_2O$ to the reaction mixture. Fortunately, the expected product was obtained with a much improved yield (Table 1, entry 3). Further studies showed that the yield could be increased to as high as 75% within 6 h when 0.5 mmol of $FeCl_3{\cdot}6H_2O$ was used (Table 1, entry 6). However, any excess use of $FeCl_3{\cdot}6H_2O$ beyond this amount did not show any further increase in yield.

As for the possible mechanism of this catalytic reaction, we believe that the Lewis acidity of Fe(III) ion in $FeCl_3{\cdot}6H_2O$ has played an important role in the promotion of this condensation process. In order to clarify the role of Fe(III) ion and the hydration water of $FeCl_3{\cdot}6H_2O$, anhydrous $FeCl_3$ was also tried as the catalyst for this reaction, and it gave similar results compared with $FeCl_3{\cdot}6H_2O$ (Table 1, entry 7). At this stage, it may be safe to say that it is the Fe(III) ion rather than Fe(III) ion together with the hydration water in $FeCl_3{\cdot}6H_2O$ that acts as the real catalyst in this condensation process. Of the two Fe(III) salts used, although anhydrous $FeCl_3$ exhibited a similar catalytic activity for this reaction when compared with $FeCl_3{\cdot}6H_2O$, the latter is preferred because of its higher solubility in ionic liquid, ease in handling, and lower price.

In addition, the use of several conventional organic solvents, specifically toluene, tetrahydrofuran (THF), ethyl acetate (EtOAc), and ethanol, in this catalytic process were also studied for the sake of comparison with [bmim][BF_4]. The results are also shown in Table 1. It has been shown that of the five solvents used, [bmim][BF_4] gave the highest yield for the desired product under similar reaction conditions. Thus, the use of [bmim][BF_4] as the reaction medium not only avoids the disadvantages of conventional organic solvents, such as volatility, inflammability, and potential pollution hazards, but it also results in greatly enhanced reactivity.

Based on the above results, this process was then extended to other structurally varied substrates to investigate its scope and generality. The results collected are listed in Table 2. It can be seen that under similar conditions, a wide range of ketones containing a reactive α-methylene group can undergo easy condensation with 2-aminobenzophenones to give substituted quinolines with fast reaction times and in reasonably high yields. It is worthwhile noting that both aliphatic and aromatic-aliphatic ketones gave corresponding quinoline products in almost equally fair yields. With unsymmetrical ketone substrates of the type CH_3COCH_2R, from which two different modes of cyclization are theoretically possible, condensation occurred predominantly at the more highly substituted alpha position and thus only one product was obtained (Table 2, entry 13). In addition, higher

Table 2. Preparation of quinoline derivatives through Friedlander reaction catalyzed by $FeCl_3 \cdot 6H_2O$ in ionic liquid.

Entry	X	R^1	R^2	Reaction temp. (°C)	Reaction time (h)	Products	Isolated yield (%)
1	H	C_6H_5	H	100	6	**3a**	75
2	H	4-BrC_6H_4	H	100	6	**3b**	84
3	H	4-$NO_2C_6H_4$	H	100	6	**3c**	89
4	H	CH_3	H	40	8	**3d**	75
5	H	-$(CH_2)_3^-$		100	5	**3e**	74
6	H	-$(CH_2)_4^-$		100	5	**3f**	75
7	Cl	C_6H_5	H	100	6	**3g**	82
8	Cl	4-BrC_6H_4	H	100	6	**3h**	85
9	Cl	4-ClC_6H_4	H	100	6	**3i**	85
10	Cl	4-$CH_3C_6H_4$	H	100	6	**3j**	80
11	Cl	4-$NO_2C_6H_4$	H	100	6	**3k**	92
12	Cl	CH_3	H	40	8	**3l**	78
13	Cl	CH_3	CH_3	60	8	**3m**	73
14	Cl	C_2H_5	CH_3	60	8	**3n**	74
15	Cl	-$(CH_2)_3^-$		100	5	**3o**	70
16	Cl	-$(CH_2)_4^-$		100	5	**3p**	72

yields were obtained using 4-nitroacetophone (Table 2, entries 3 and 11), showing that the yields of quinolines are to some extent affected by the nature of the substituents attached to the aromatic ring of the ketone.

Our attention was then directed toward the possibility of recycling the reaction media since recovery and reuse of the catalyst and solvent are highly preferable for a greener process. At completion, the reaction mixture was diluted with water and extracted with diethyl ether to obtain the desired product. Meanwhile, due to its much higher solubility in water and ionic liquid than in diethyl ether, Fe(III) ion was left and immobilized in [bmim][BF_4]. After removal of water under reduced pressure, [bmim][BF_4] together with the catalyst could be recovered almost quantitatively. Then, their reusability was investigated by using 2-aminobenzophenone and acetophenone as model substrates. It was observed that even in the sixth recycle, reuse of the ionic liquid and the catalyst recovered from the fifth recycle still gave the corresponding product in fairly good yield (Table 3, Recycle no. 6).

In conclusion, [bmim][BF_4] was proved to be a useful and alternative reaction medium, and $FeCl_3 \cdot 6H_2O$ was found to be an efficient catalyst for the preparation of quinolines. The simple experimental and product isolation procedures, combined with ease of recovery and reuse of the catalyst and the reaction media, are expected to contribute to the development of greener and waste free chemical processes for the preparation of quinolines with biological activity. Further studies to develop other new uses for ionic liquid in the preparation of heterocyclic compounds are now in progress in our laboratory.

Experimental

Melting points were measured using a Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded for KBr pellets on a Bruker Vector 22 spectrometer with absorptions given in cm^{-1}. ^1H NMR spectra were obtained with a Bruker AC 400 spectrometer using $CDCl_3$ as the solvent. Chemical shifts (δ) were expressed in ppm downfield from an internal tetramethylsilane standard and coupling constants (*J*) were given in Hz. Mass spectra were recorded on a HP-5989B mass spectrometer. Elemental analyses were performed on an EA-1110 (CE Instruments) instrument.

Table 3. Reusability of both [bmim][BF_4] and catalyst.

Recycle no.	Ionic liquid recovered (%)	Isolated yield of **3a** (%)[a]
1	99	75
2	98	78
3	99	77
4	99	75
5	98	73
6	97	69

[a]Reaction conditions: reaction time 6 h at 100 °C.

The ionic liquid [bmim][BF_4] was prepared and purified according to a literature procedure (8). All other reagents were reagent grade and were used without further purification.

General procedure for the preparation of quinoline derivatives

2-Aminobenzophenone (**1**, 1 mmol), ketone (**2**, 1 mmol) and $FeCl_3 \cdot 6H_2O$ (0.5 mmol) were added to a 10-mL round-bottom flask containing 1 mL of [bmim][BF_4]. The mixture was then stirred at 100 °C for a certain period of time to ensure complete reaction (monitored by TLC). At completion, the reaction mixture was diluted with water (5 mL) and ex-

tracted with ethyl ether (3 × 10 mL). After drying, the combined ether layers were concentrated under reduced pressure and the resulting residue was charged on a silica gel column and eluted with a mixture of ethyl acetate/*n*-hexane (1:8) to obtain product **3**. All products were fully characterized by IR, ^{1}H NMR, MS, and elemental analysis. The aqueous solution of ionic liquid and catalyst was concentrated at reduced pressure to recover the ionic liquid and catalyst for subsequent reuse.

2,4-Diphenylquinoline (3a)

mp 110–111 °C (lit. (9) 112–113 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, 1H, J = 8.4 Hz), 8.19–8.22 (m, 2H), 7.91 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.83 (s, 1H), 7.72–7.76 (m, 1H), and 7.47–7.59 (m, 9H). MS *m/z* (%): 281 (M^+, 70), 280 (M^+ – 1, 100), 202 (9), and 139 (8).

2-(4-Bromophenyl)-4-phenylquinoline (3b)

mp 128–129 °C. IR ν (cm^{-1}) : 3050, 1610, and 1590. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, 1H, J = 8.0 Hz), 8.08–8.11 (m, 2H), 7.90 (d, 1H, J = 8.0 Hz), 7.72–7.78 (m, 2H), 7.64–7.67 (m, 2H), and 7.47–7.59 (m, 6H). MS *m/z* (%): 361 (M^+ +2, 89), 359 (M^+, 100), 278 (40), 202 (17), and 139 (25). Anal. calcd. for $C_{21}H_{14}BrN$: C 70.01, H 3.92, and N 3.89; found: C 69.85, H 3.88, and N 3.73.

2-(4-Nitrophenyl)-4-phenylquinoline (3c)

mp 162–163 °C (lit. (9) 156–161 °C). IR ν (cm^{-1}): 3061, 1620, and 1595. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37–8.42 (m, 4H), 8.31 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 8.0 Hz), 7.87 (s, 1H), 7.80 (t, 1H, J = 8.0 Hz), and 7.54 –7.59 (m, 6H). MS *m/z* (%): 326 (M^+, 100) and 202 (23). Anal. calcd. for $C_{21}H_{14}N_2O_2$: C 77.29, H 4.32, and N 8.58; found: C 77.15, H 4.48, and N 8.63.

2-Methyl-4-phenylquinoline (3d)

mp 93–95 °C (lit. (10) 92–94 °C). IR ν (cm^{-1}): 3057, 2971, 1617, and 1485. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, 1H, J = 8.4 Hz), 7.85 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.8 Hz), 7.66–7.70 (m, 1H), 7.45–7.55 (m, 5H), 7.40–7.45 (m, 1H), 7.22 (s, 1H), and 2.77 (s, 3H). MS *m/z* (%): 219 (M^+, 100), 204 (14), and 176 (10). Anal. calcd. for $C_{16}H_{13}N$: C 87.64, H 5.98, and N 6.39; found: C 87.48, H 6.12, and N 6.46.

2,3-Dihydro-9-phenyl-1H-cyclopenta[b]-quinoline (3e)

mp 104–105.5 °C (lit. (4) 134– 135 °C). IR ν (cm^{-1}) : 3011, 2968, 1610, and 1455. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06–8.08 (m, 1H), 7.60–7.64 (m, 2H), 7.45–7.55 (m, 3H), 7.35–7.40 (m, 3H), 3.24 (t, 2H, J = 8.0 Hz), 2.91 (t, 2H, J = 8.0 Hz), and 2.13–2.21 (m, 2H). MS *m/z* (%): 245 (M^+, 100), 217 (9), and 168 (14). Anal. calcd. for $C_{18}H_{15}N$: C 88.13, H 6.16, and N 5.71; found: C 88.18, H 6.02, and N 5.86.

1,2,3,4-Tetrahydro-9-phenylacridine (3f)

mp 131–133 °C (lit. (4) 142–143 °C). IR ν (cm^{-1}) : 3020, 2978, 1600, and 1495. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, 1H, J = 8.0 Hz), 7.59–7.64 (m, 1H), 7.43–7.55 (m, 3H), 7.28–7.34 (m, 4H), 3.23 (t, 2H, J = 8.0 Hz), 2.59 (t, 2H, J = 8.0 Hz), 1.94–2.00 (m, 2H), and 1.76–1.83 (m, 2H). MS *m/z* (%): 259 (M^+, 100), 230 (12), and 182 (6). Anal. calcd. for $C_{18}H_{17}N$: C 87.99, H 6.61, and N 5.40; found: C 88.07, H 6.52, and N 5.48.

6-Chloro-2,4-diphenylquinoline (3g)

mp 130–132 °C (lit. (11) 130–131 °C). IR ν (cm^{-1}): 3050, 1610, and 1589. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11–8.15 (m, 3H), 7.82 (d, 1H, J = 2.2 Hz), 7.76 (s, 1H), 7.59–7.60 (m, 2H), and 7.45–7.50 (m, 7H). MS *m/z* (%): 317 (M^+ + 2, 33), 315 (M^+, 100), and 280 (32). Anal. calcd. for $C_{21}H_{14}ClN$: C 79.87, H 4.47, and N 4.44; found: C 79.95, H 4.43, and N 4.35.

6-Chloro-2-(4-bromophenyl)-4-phenylquinoline (3h)

mp 174–176 °C (lit. (11) 174–175 °C). IR ν (cm^{-1}): 3061, 1600, and 1590. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, 1H, J = 8.8 Hz), 8.07 (d, 2H, J = 8.8 Hz), 7.85 (d, 1H, J = 2.2 Hz), 7.79 (s, 1H), 7.64–7.68 (m, 3H), and 7.54–7.58 (m, 5H). MS *m/z* (%): 397 (M^+ + 4, 26), 395 (M^+ + 2, 100), 393 (M^+, 79), and 358 (18). Anal. calcd. for $C_{21}H_{13}BrClN$: C 63.90, H 3.32, and N 3.55; found: C 63.85, H 3.21, and N 3.53.

6-Chloro-2-(4-chlorophenyl)-4-phenylquinoline (3i)

mp 164–166 °C (lit.(11) 159–160 °C). IR ν (cm^{-1}): 3058, 1605, and 1587. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, 1H, J = 8.4 Hz), 8.15 (d, 2H, J = 8 Hz), 7.87 (d, 1H, J = 2.2 Hz), 7.80 (s, 1H), 7.68–7.71 (m, 1H), and 7.50–7.59 (m, 7H). MS *m/z* (%): 353 (M^+ + 4, 12), 351 (M^+ + 2, 65), 349 (M^+, 100), and 314 (34). Anal. calcd. for $C_{21}H_{13}Cl_2N$: C 72.02, H 3.74, and N 4.00; found: C 72.07, H 3.71, and N 4.03.

6-Chloro-2-(4-methylphenyl)-4-phenylquinoline (3j)

mp 132–134 °C (lit.[1]1 132–133). IR ν (cm^{-1}): 3048, 1600, and 1580. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, 1H, J = 8.4 Hz), 8.09 (d, 2H, J = 8.0 Hz), 7.85 (d, 1H, J = 3.5 Hz), 7.82 (s, 1H), 7.67–7.64 (m, 1H), 7.57–7.52 (m, 5H), 7.33 (d, 2H, J = 8.0 Hz), and 2.43 (s, 3H). MS *m/z* (%): 331 (M^+ + 2, 34), 329 (M^+, 100), and 294 (23). Anal. calcd. for $C_{22}H_{16}ClN$: C 80.11, H 4.89, and N 4.25; found: C 80.25, H 4.78, and N 4.33.

6-Chloro-2-(4-nitrophenyl)-4-phenylquinoline (3k)

mp 218–220 °C. IR ν (cm^{-1}): 3038, 1610, and 1525. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34–8.38 (m, 4H), 8.20 (d, 1H, J = 8.0 Hz), 7.90 (d, 1H, J = 2.4 Hz), 7.88 (s, 1H), 7.23 (dd, 1H, J_1 = 9.2 Hz, J_2 = 2.4 Hz), and 7.54–7.60 (m, 5H). MS *m/z* (%): 362 (M^+ + 2, 34), 360 (M^+, 100), 314 (40), 278 (32), and 139 (20). Anal. calcd. for $C_{21}H_{13}ClN_2O_2$: C 69.91, H 3.63, and N 7.76; found: C 69.94, H 3.68, and N 7.59.

6-Chloro-2-methyl-4-phenylquinoline (3l)

mp 88–90 °C. IR ν (cm^{-1}): 3050, 2978, 1610, and 1496. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (d, 1H, J = 9.2 Hz), 7.82 (d, 1H, J = 2.4 Hz), 7.62 (dd, 1H, J_1 = 9.2 Hz, J_2 = 2.4 Hz), 7.46–7.57 (m, 5H), 7.24 (s, 1H), and 2.77 (s, 3H). MS *m/z* (%): 255 (M^+ + 2, 32), 253 (M^+, 100), 218 (40), and 176 (11). Anal. calcd. for $C_{16}H_{12}ClN$: C 75.74, H 4.77, and N 5.52; found: C 75.88, H 4.62, and N 5.63.

6-Chloro-2,3-dimethyl-4-phenylquinoline (3m)

mp 121–124 °C. IR ν (cm^{-1}): 3035, 2959, 1610, and 1459. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, 1H, J = 9.2 Hz),

7.47–7.56 (m, 4H), 7.27 (d, 1H, J = 2.4 Hz), 7.20–7.23 (m, 2H), 2.74 (s, 3H), and 2.17 (s, 3H). MS *m/z* (%): 269 (M^+ + 2, 33), 267 (M^+, 100), 232 (32), 217 (15), 189 (18), and 94 (6). Anal. calcd. for $C_{17}H_{14}ClN$: C 76.26, H 5.27, and N 5.23; found: C 76.38, H 5.32, and N 5.16.

6-Chloro-2-ethyl-3-methyl-4-phenylquinoline (3n)

mp 139–141 °C. IR ν (cm^{-1}): 3025, 2950, 1621, and 1493. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, 1H, J = 8.8 Hz), 7.46–7.55 (m, 4H), 7.22–7.26 (m, 3H), 3.05 (q, 2H, J = 7.2 Hz), 2.20 (s, 3H), and 1.41 (t, 3H, J = 7.2 Hz). MS *m/z* (%): 283 (M^+ + 2, 34), 281 (M^+, 100), 217 (9), 189 (7), and 115 (5). Anal. calcd. for $C_{18}H_{16}ClN$: C 76.72, H 5.72, and N 4.97; found: C 76.74, H 5.80, and N 4.88.

6-Chloro-2,3-Dihydro-9-phenyl-1H-cyclopenta[b]-quinoline (3o)

mp 94–96 °C. IR ν (cm^{-1}): 3035, 2970, 1610, and 1486. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, 1H, J = 8.8 Hz), 7.46–7.58 (m, 5H), 7.32–7.35 (m, 2H), 3.20 (t, 2H, J = 8.0 Hz), 2.90 (t, 2H, J = 8.0 Hz), and 2.13–2.20 (m, 2H). MS *m/z* (%): 281 (M^+ + 2, 33), 279 (M^+, 100), 244 (95), 202 (11), and 120 (12). Anal. calcd. for $C_{18}H_{14}ClN$: C 77.28, H 5.04, and N 5.01; found: C 77.40, H 5.02, and N 4.96.

6-Chloro-1,2,3,4-tetrahydro-9-phenylacridine (3p)

mp 163.5–165 °C. IR ν (cm^{-1}): 3038, 2975, 1605, and 1488. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.95 (1H, d, J = 8.8 Hz), 7.48–7.56 (m, 4H), 7.28 (1H, d, J = 2.4 Hz), 7.20–7.22 (m, 2H), 3.18 (t, 2H, J = 6.4 Hz), 2.59 (t, 2H, J = 6.4 Hz), 1.93–1.98 (m, 2H), and 1.77–1.82 (m, 2H). MS *m/z* (%): 295 (M^+ + 2, 35), 293 (M^+, 100), 258 (59), 230 (9), and 121 (8). Anal. calcd. for $C_{19}H_{16}ClN$: C 77.68, H 5.49, and N 4.77; found: C 77.55, H 5.42, and N 4.68.

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