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THE FIRST CERIUM (IV) AMMONIUM NITRATE (CAN)-CATALYZED FRIEDLÄNDER SYNTHESIS OF QUINOLINES IN IONIC LIQUID

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Abstract - A mild and efficient route for the synthesis of quinolines and polycyclic quinolines utilizing cerium (IV) ammonium nitrate (CAN) as a novel catalyst *via* Friedländer annulation in ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] under mild conditions was described.

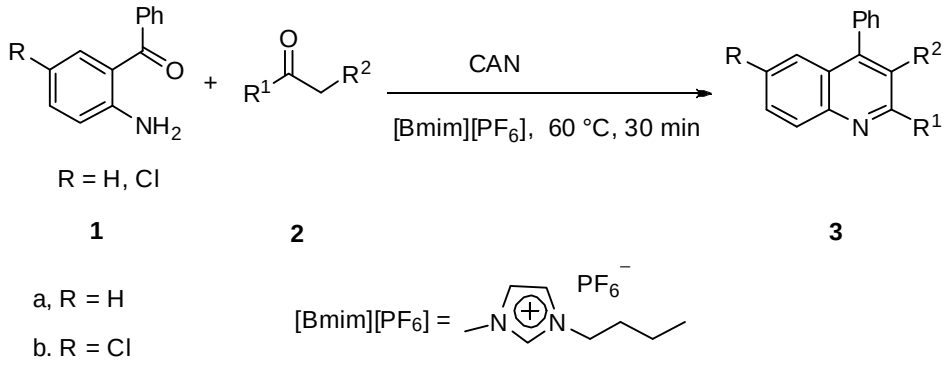
Quinoline derivatives have been well known not only in medicinal chemistry, because of their wide occurrence in natural products[1] and drugs,[2] but also in polymer chemistry, electronics and optoelectronics for their excellent mechanical properties.[3] Versatile methods for the synthesis of the quinoline ring system have been developed.[4]

Friedländer annulation is one of the most simple and straightforward approaches for the synthesis of quinoline derivatives. Friedländer synthesis can be catalysed by strong acids or bases, and may take place without a catalyst at high temperature. Brønsted acids like hydrochloric acid, sulfuric acid, *p*-toluenesulfonic acid and phosphoric acid were widely used as catalysts. However, many of these methods require harsh reaction conditions and lead to several side reactions. Recently, Lewis acids such as $ZnCl_2$, $SnCl_2$, $Bi(OTf)_3$, $Sc(OTf)_3$, silver phosphotungstate, sodium fluoride, $AuCl_3$[5] have been reported to be effective for the synthesis of quinolines. However, many of these procedures suffered from harsh reaction conditions, low yields, difficulties in work up, and the use of stoichiometric and/or relatively expensive reagents. Furthermore, the synthesis of quinolines in general have been carried out in polar solvents such as acetonitrile, THF, DMF and DMSO leading to complex isolation and recovery procedures. Since quinoline derivatives are increasingly useful and important in pharmaceuticals and industry, the development of simple, efficient and eco-benign protocol is still desirable.

Room temperature ionic liquids (RTIL) are liquids that are composed entirely of ions. In fact, ionic liquids can now be produced which remain liquid at room temperature and appear to be undemanding and inexpensive to manufacture.[6] Ionic liquids offer an attractive alterative to conventional organic liquids for clean synthesis, as they are easy to recycle, lack flammability, and possess effectively no vapour pressure. Compared with classical molecular solvents, the ionic liquids are environmentally benign reaction media.[7]

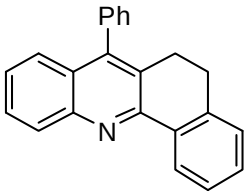
Recently, there has been growing considerable interest in the use of lanthanide reagents, cerium (IV) ammonium nitrate (CAN) is the most notable one electron oxidant and has been utilized extensively for a broad variety of oxidative transformations in organic chemistry.[8] Additionally, many advantages such as inexpensiveness, ecofriendly nature, uncomplicated handling and high reactivity makes CAN a potent catalyst in organic syntheses. More recently, studies have also revealed protocols for mild conditions, fast conversions and convenient work-up procedures using CAN, to make it a powerful tool in chemistry under green and safer approaches. Besides this, CAN is able to catalyze various organic transformations not only based on the Lewis acidic property, but also with electron transfer capability. In this paper, we report the use of CAN as catalyst for the synthesis of quinolines *via* Friedländer annulation in ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]) under mild conditions.

Treatment of 2-aminobenzophenone (**1a**) and ethyl acetoacetate (**2a**) with CAN as catalyst in ionic liquid [Bmim][PF_6] at 60 °C for 30 min caused cyclodehydration to give ethyl 2-methyl-4-phenylquinoline-3-carboxylate (**3a**) in 92% yield (Scheme 1). When the reaction is conducted in a conventional solvent, such as acetonitrile, the preparation of **3a** needs refluxing for 3 h.

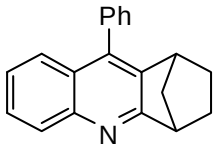


Scheme 1

This method is equally effective for both cyclic and acyclic ketones. Cyclic ketones and various 1,3-diketones such as acetyl acetone and 5,5-dimethylcyclohexanedione reacted efficiently with 2-aminobenzophenones to give the corresponding substituted quinolines. The results are given in Table 1. Interestingly, bicyclic ketone such as α-tetralone (**2g**) and 2-norbornanone (**2h**) also underwent smooth condensation with 2-aminobenzophenones to afford the respective polycyclic quinolines (**3g, 3h**) with good yields (Figure 1). When the reaction is conducted in ionic liquid [Bmim][PF_6], and sulfuric acid as catalyst, the preparation of **3p** needs heating at 80 °C for 5 h.



3g



3h

Figure 1

The products were characterized by ^{1}H, ^{13}C NMR, IR and mass spectroscopic data. This method is clean and free from side reactions such as self-condensation of ketones which are normally observed under basic conditions. Unlike reported methods, the present protocol does not require high temperature or drastic conditions to produce quinoline derivatives. Furthermore, the condensation of 2-aminobenzophenone (**1a**) with ethyl acetoacetate (**2a**) in the presence of concd H_2SO_4 afforded the quinoline product in only 65% yield (entry 1).

In conclusion, we have demonstrated a simple and efficient procedure for the synthesis of quinolines, including polycyclic quinolines, using CAN as catalyst. The significant features of this method include operational simplicity, improved reaction rates, high yields of products and avoidance of the use of hazardous acids or bases.

ACKNOWLEDGEMENT

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EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded on a Shimadzu IR-27 G spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Plus 400 MHz. Chemical shifts (δ) were measured in ppm with respect to TMS. MS were obtained on a JEOL JMS D-300 instrument

General procedure for the preparation quinoline (3)

A mixture of 2-aminobenzophenone (1.0 mmol), ketone (1.3 mmol) and CAN (0.05 mmol) in [Bmim][PF_6] (2 mL) ionic liquid was stirred at 60 °C for 30 min to complete the reaction. Subsequently, the reaction mixture was extracted with EtOAc. The extract was dried ($MgSO_4$) and concentrated under reduced pressure and the residue was purified by chromatography on a silica gel column with hexane-EtOAc (3 : 1) to give quinoline (**3**). The remaining ionic liquid was dried at 80 °C under reduced pressure and reused in subsequent runs.

Table 1. CAN Catalyzed Friedländer Synthesis of Quinolines in [Bmim][PF_6].

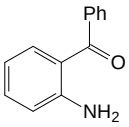
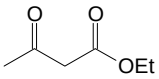
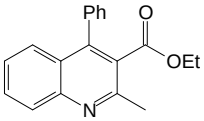
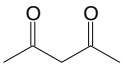
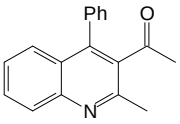
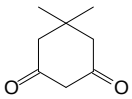
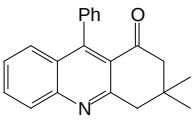
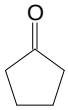
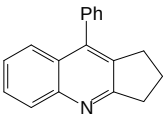
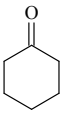
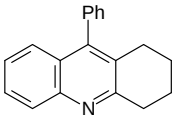
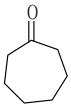
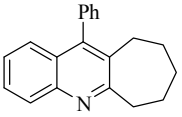
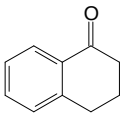
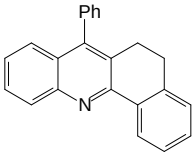
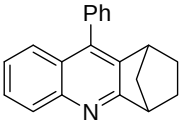
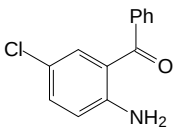
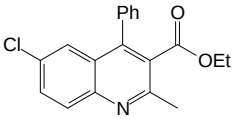
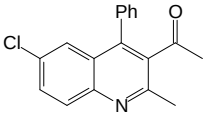
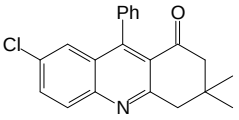
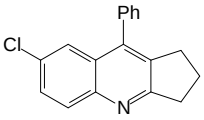
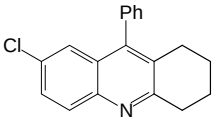
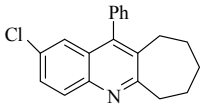
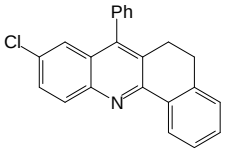
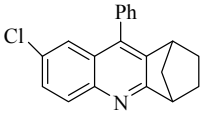
Entry	2-Aminoketone **1**	Ketone **2**	Quinoline **3**	Yield (%)
1	 **1a**	 **2a**	 **3a**	92
2	**1a**	 **2b**	 **3b**	90
3	**1a**	 **2c**	 **3c**	86
4	**1a**	 **2d**	 **3d**	85
5	**1a**	 **2e**	 **3e**	84
6	**1a**	 **2f**	 **3f**	87
7	**1a**	 **2g**	 **3g**	86
8	**1a**	 **2h**	 **3h**	91
9	 **1b**	**2a**	 **3i**	87
10	**1b**	**2b**	 **3j**	88

Table 1 (Continued)

Entry	2-Aminoketone **1**	Ketone **2**	Quinoline **3**	Yield (%)
11	**1b**	**2c**	 **3k**	85
12	**1b**	**2d**	 **3l**	83
13	**1b**	**2e**	 **3m**	85
14	**1b**	**2f**	 **3n**	88
15	**1b**	**2g**	 **3o**	87
16	**1b**	**2h**	 **3p**	90

Ethyl 2-methyl-4-phenylquinoline-3-carboxylate (3a)

Mp 99-100 °C (Lit.,[9] 99-100 °C). IR (KBr) ν : 3060, 2927, 1710 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 0.91 (t, *J* = 7.3 Hz, 3H), 2.76 (s, 3H), 4.00-4.10 (m, 2H), 7.31-7.46 (m, 6H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 13.4, 23.6, 61.1, 124.9, 126.2, 128.0, 128.3, 128.6, 129.2, 130.1, 135.5, 146.1, 147.5, 154.4, 168.2. EI-MS *m/z* : 291 (M^+), 246, 245, 218.

1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (3b)

Mp 114-115 °C (Lit.,[9] 111-112 °C). IR (KBr) ν : 3062, 2907, 1696 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 1.95 (s, 3H), 2.66 (s, 3H), 7.30-7.32 (m, 2H), 7.30-7.39 (m, 1H), 7.44-7.48 (m, 3H), 7.57 (dd, *J* = 0.8, 8.4

Hz, 1H), 7.63-7.68 (m, 1H), 8.03 (d, *J* = 8.4Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 23.7, 31.7, 124.8, 125.9, 126.3, 128.5, 128.6, 128.8, 129.8, 129.9, 134.6, 135.0, 143.7, 147.3, 153.3, 205.5. EI-MS *m/z* : 261 (M^+), 246, 218, 176.

3,3-Dimethyl-9-phenyl-3,4-dihydro-2*H*-acridin-1-one (3c)

Mp 191 °C (Lit.,[9] 195 °C). IR (KBr) ν : 3065, 2868, 1682 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 1.15 (s, 6H), 2.55 (s, 2H), 3.26 (s, 2H), 7.16-7.19 (m, 2H), 7.36-7.39 (m, 1H), 7.44-7.51 (m, 4H), 7.71-7.75 (m, 1H), 8.06 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 28.2, 32.1, 48.2, 54.0, 122.5, 126.3, 127.2, 127.3, 127.9, 128.0, 128.1, 128.3, 131.5, 137.4, 148.8, 150.8, 160.9, 197.7. EI-MS *m/z*: 301 (M^+), 300, 272, 245, 217, 189.

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

Mp 131-132 °C (Lit.,[10] 130 °C). IR (KBr) ν : 3058, 2923, 1569, 1485, 831 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 2.15-2.19 (m, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 3.24 (t, *J* = 7.6 Hz, 2H), 7.35-7.41 (m, 3H), 7.47-7.54 (m, 3H), 7.60-7.64 (m, 2H), 8.06-8.08 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 23.5, 30.3, 35.1, 125.4, 125.6, 126.2, 128.2, 128.4, 129.2, 133.6, 136.7, 142.6, 147.9, 167.4. EI-MS *m/z*: 245 (M^+), 244, 217, 168.

9-Phenyl-1,2,3,4-tetrahydroacridine(3e)

Mp 137 °C (Lit.,[10] 138 °C). IR (KBr) ν : 3061, 2940, 2860, 1570, 1485, 1440, 1220, 765, 705 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 1.75-1.81 (m, 2H), 1.93-1.99 (m, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 7.20-7.35 (m, 4H), 7.46-7.55 (m, 3H), 7.63-7.65 (m, 1H), 8.17 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 22.4, 22.7, 27.8, 33.3, 125.8, 125.8, 126.6, 127.1, 127.9, 128.6, 128.8, 129.0, 136.5, 144.6, 147.9, 158.5. EI-MS *m/z*: 259 (M^+), 244, 230, 217, 202, 189, 121.

11-Phenyl-7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]quinoline (3f)

Mp 109-110 °C (Lit.,[11] 105-107 °C). IR (KBr) ν : 3054, 2927, 2851, 1571, 1485, 1443, 1196, 762, 708 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 1.61 (s, 2H), 1.86 (d, *J* = 2.4 Hz, 4H), 2.72 (t, *J* = 5.6 Hz, 2H), 3.38 (d, *J* = 3.6 Hz, 2H), 7.22-7.23 (m, 2H), 7.23-7.38 (m, 2H), 7.46-7.52 (m, 3H), 7.63 (t, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 26.7, 28.1, 30.5, 31.6, 38.9, 126.0, 126.3, 126.8, 127.2, 128.4, 128.8, 129.1, 134.1, 136.9, 143.9, 146.9, 164.1. EI-MS *m/z*: 273 (M^+), 272, 258, 244, 231, 230.

5,6-Dihydro-7-phenylbenzo[*c*]acridine (3g)

Mp 143-145 °C (Lit.,[12] 148-149 °C). IR (KBr) ν : 3057, 2924, 1574, 14484, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 2.86-2.89 (m, 4H), 7.11-7.72 (m, 11H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.63 (dd, *J* = 1.2, 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 26.4, 28.2, 125.9, 126.0, 126.3, 127.2, 127.4, 127.8, 128.0, 128.4, 128.5, 128.9, 129.5, 129.6, 130.2, 135.0, 136.9, 137.5, 139.2, 147.1, 153.0. EI-MS *m/z*: 307 (M^+), 306, 305, 230, 152.

9-Phenyl-1,2,3,4-tetrahydro-1,4-methano-acridine (3h)

Mp 142 °C (Lit.,[13] 143-143.5 °C). IR (KBr) ν : 3062, 2951, 2869, 1578, 758, 705 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 1.26-1.40 (m, 1H), 1.50-1.58 (m, 1H), 1.67 (td, *J* = 2.0, 12.4 Hz, 1H), 1.92-2.14 (m, 3H), 3.39 (dd, *J* = 1.2, 4.8 Hz, 1H), 3.59 (dd, *J* = 1.6, 4.0 Hz, 1H), 7.33-7.69 (m, 8H), 8.07 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 25.7, 27.4, 40.8, 45.8, 46.5, 125.2, 125.7, 126.4, 127.7, 127.8, 128.3, 128.8, 129.4, 129.8, 135.9, 137.8, 138.1, 146.7, 169.9. EI-MS *m/z*: 272 (M^++1), 271 (M^+), 243, 242, 241.

Ethyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3i)

Mp 102-105 °C (Lit.,[10] 108 °C). IR (KBr) ν : 3075, 2926, 1715 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 0.85 (t, *J* = 7.2 Hz, 3H), 2.69 (s, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 7.25-7.45 (m, 6H), 7.51 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 13.3, 23.4, 61.1, 124.8, 125.5, 128.1, 128.3, 128.4, 129.0, 130.2, 130.7, 132.0, 134.7, 145.0, 145.7, 154.6, 167.7.

EI-MS *m/z*: 327 (M^++2), 325 (M^+), 280, 217, 216.

1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)ethanone (3j)

Mp 155-156 °C (Lit.,[10] 154 °C). IR (KBr) ν : 3049, 2925, 1699 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 1.97 (s, 3H), 2.65 (s, 3H), 7.29-7.31 (m, 2H), 7.48-7.54 (m, 4H), 7.59-7.62 (m, 1H), 7.97 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 23.7, 31.7, 124.8, 125.7, 128.8, 129.1, 129.8, 130.4, 130.8, 132.3, 134.3, 135.4, 142.9, 145.7, 153.8, 205.1. EI-MS *m/z*: 297 (M^++2), 295 (M^+), 280, 217, 176.

7-Chloro-3,3-dimethyl-9-phenyl-3,4-dihydro-2*H*-acridin-1-one (3k)

Mp 209-211 °C (Lit.,[10] 209-211 °C). IR (KBr) ν : 3071, 2946, 1693 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 1.15 (s, 6H), 2.57 (s, 2H), 3.25 (s, 2H), 7.14-7.17 (m, 2H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.42-7.55 (m, 3H), 7.69 (dd, *J* = 2.4, 9.0 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 28.3, 32.2, 48.2, 54.1, 123.2, 126.7, 127.8, 127.9, 128.2, 128.3, 130.1, 132.4, 132.5, 136.7, 147.3, 150.1, 161.4, 197.6. EI-MS *m/z*: 337 (M^++2), 335 (M^+), 334, 306, 279, 216 189.

7-Chloro-2,3-dihydro-9-phenyl-1*H*-cyclopenta[*b*]quinoline (3l)

Mp 103-104 °C (Lit.,[14] 105 °C). IR (KBr) ν : 3038, 2923, 1601, 1483, 828 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 2.17 (m, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 3.22 (t, *J* = 7.6 Hz, 2H), 7.32-7.35 (m, 2H), 7.46-7.58 (m, 5H), 7.99 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 23.4, 30.3, 35.1, 124.5, 127.0, 128.2, 128.7, 128.9, 129.1, 130.3, 131.2, 1134.6, 136.0, 141.8, 146.3, 167.8. EI-MS *m/z*: 281 (M^++2), 279 (M^+), 246, 244.

7-Chloro-9-phenyl-1,2,3,4-tetrahydroacridine (3m)

Mp 163 °C (Lit.,[14] 163 °C). IR (KBr) ν : 3060, 2944, 1604, 1572, 1481, 1215, 703 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 1.78-1.82 (m, 2H), 1.94-1.98 (m, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 3.29 (t, *J* = 6.4 Hz, 2H), 7.22-7.35 (m, 4H), 7.46-7.65 (m, 3H), 7.94 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 22.8, 28.0, 34.1, 124.4, 127.3, 128.0, 128.7, 128.9, 129.1, 129.4, 130.0, 131.0, 136.3, 144.6, 145.6, 129.4. EI-MS *m/z*: 295 (M^++2), 293 (M^+), 278, 258, 230, 189, 120, 89.

2-Chloro-11-phenyl-7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]quinoline (3n)

Mp 190-192 °C (Lit.,[15] 193-195 °C). IR (KBr) ν : 3053, 2925, 2855, 1572, 1479, 1441, 1195, 770, 706 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 1.61 (s, 2H), 1.86 (s, 4H), 2.71 (t, *J* = 4.8 Hz, 2H), 3.36 (s, 2H), 7.21 (d, *J* = 6.4 Hz, 2H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.50-7.68 (m, 4H), 8.15 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 26.6, 28.0, 30.5, 31.6, 38.8, 125.1, 127.6, 128.1, 128.6, 128.9, 129.0, 129.6, 131.9, 135.1, 136.1, 142.4, 146.1. 164.5. EI-MS *m/z*: 309, 307 (M^+), 292, , 278, 253, 241, 216.

9-Chloro-5,6-dihydro-7-phenylbenzo[*c*]acridine (3o)

Mp 134-136 °C (Lit.,[14] 130 °C). IR (KBr) ν : 3052, 2935, 1600, 1479, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 2.81-2.90 (m, 4H), 7.24-7.59 (m, 10H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.59 (dd, *J* = 1.2, 7.6 Hz,1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 26.5, 28.1, 124.8, 126.3, 127.3, 127.7, 127.9, 128.2, 128.7, 129.0, 128.3, 129.4, 129.8, 131.1, 131.6, 134.7, 136.1, 139.2, 144.5, 145.5, 153.3. EI-MS *m/z*: 343 (M^++2), 341 (M^+), 304, 152.

7-Chloro-9-phenyl-1,2,3,4-tetrahydro-1,4-methanoacridine (3p)

Mp 144-145 °C. IR (KBr) ν : 3054, 2965, 2872, 1575, 759, 701 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ : 1.32-1.40 (m, 1H), 1.49-1.58 (m, 1H), 1.69 (td, *J* = 1.2, 12.4 Hz, 1H), 1.92-2.15 (m, 3H), 3.39 (dd, *J* = 1.2, 5.0 Hz, 1H), 3.58 (dd, *J* = 1.2, 4.8 Hz, 1H), 7.34-7.58 (m, 6H), 7.63 (d, *J* = 3.2 Hz, 1H), 7.99 (d, *J* = 12.0

Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 25.7, 27.4, 40.9, 45.8, 46.4, 124.6, 127.3, 128.1, 128.5, 129.3, 129.7, 130.3, 131.0, 135.3, 137.3, 138.6, 145.2, 170.3. EI-MS *m/z*: 307 (M^++2), 306 (M^++1), 305 (M^+), 277, 243, 241. Anal. Calcd for $C_{20}H_{16}ClN$ (305.10): C, 78.55; H, 5.27; N, 4.58. Found: C, 78.75; H, 5.12; N, 4.42.

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