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Friedel-Crafts chemistry. Part 65. A concise synthesis of benzo-and pyrido-annulated *N*-heterocycles via intramolecular Friedel–Crafts reactions

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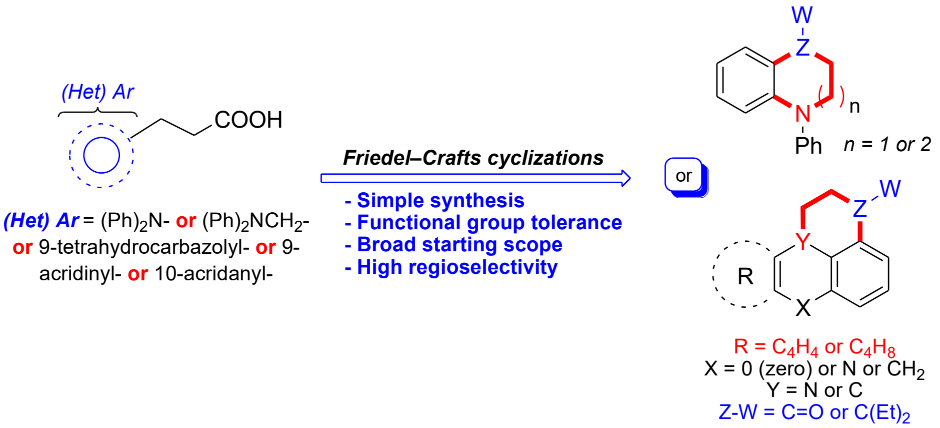
Abstract

An efficient access to substituted tetrahydroquinolines, benzo[*b*]azepines, pyrido[3,2,1-*jk*]carbazoles, benzo[*kl*]acridines and pyrido[3,2,1-*de*]acridines in overall very good yields is described. The process involves Friedel–Crafts cyclizations of homo-and heterocyclic carboxylic acids **1a-e** and alkanols **3a-e** in the presence of $AlCl_3/CH_3NO_2$ or TfOH (trifluoromethanesulfonic acid) or polyphosphoric acid (PPA) under suitable reaction conditions. Starting carboxylic acids **1a-e** were obtained from their literature procedures. Our simple strategy offers easy access to polycyclic-fused systems in short reaction times and in moderate to good yields.



Keywords: Friedel-Crafts cycliacylations; alkanols; pyrido[3,2,1-*jk*]carbazole; Grignard reactions; benzo[*kl*]acridine

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Introduction

Carbazole derivatives are the key structural moieties in several bioactive natural products[1-3] and pharmaceutical[4-6] ingredients (Figure 1). More interestingly studies have discovered that, these classes of compounds exhibit diverse medical functions such as anticancer[7], anticonvulsant[8], anti-inflammatory[9], antiepileptic[10], antioxidative[11], antibacterial[12], antidiarrheal[13], antihistaminic[14] and pancreatic lipase inhibitory activities.[15] Furthermore, carbazole-based compounds are used in many industries (Figure 1) like, dyes[16], optoelectronic devices[17], semiconductors[18], polymers[19], organic light-emitting diodes (OLEDs)[20] and dye-sensitized solar cells (DSCs).[21]

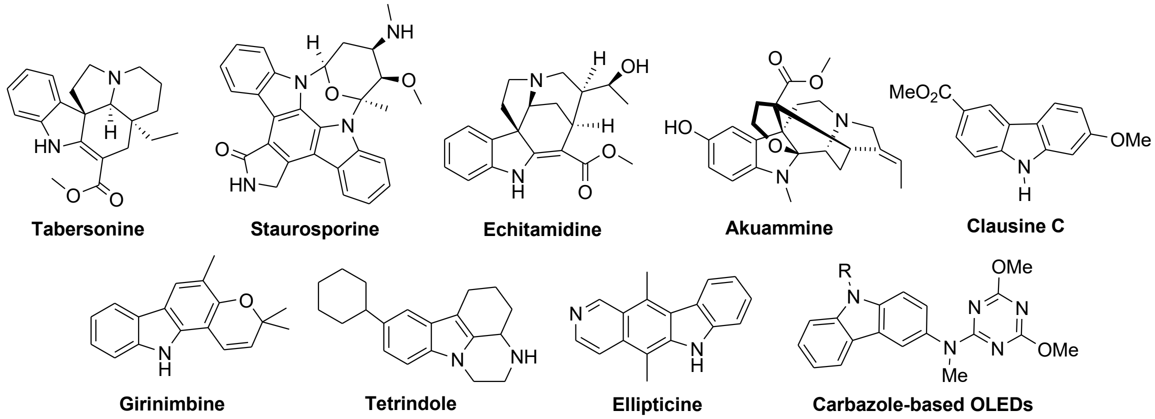


Figure 1. Some of important carbazole-based compounds.

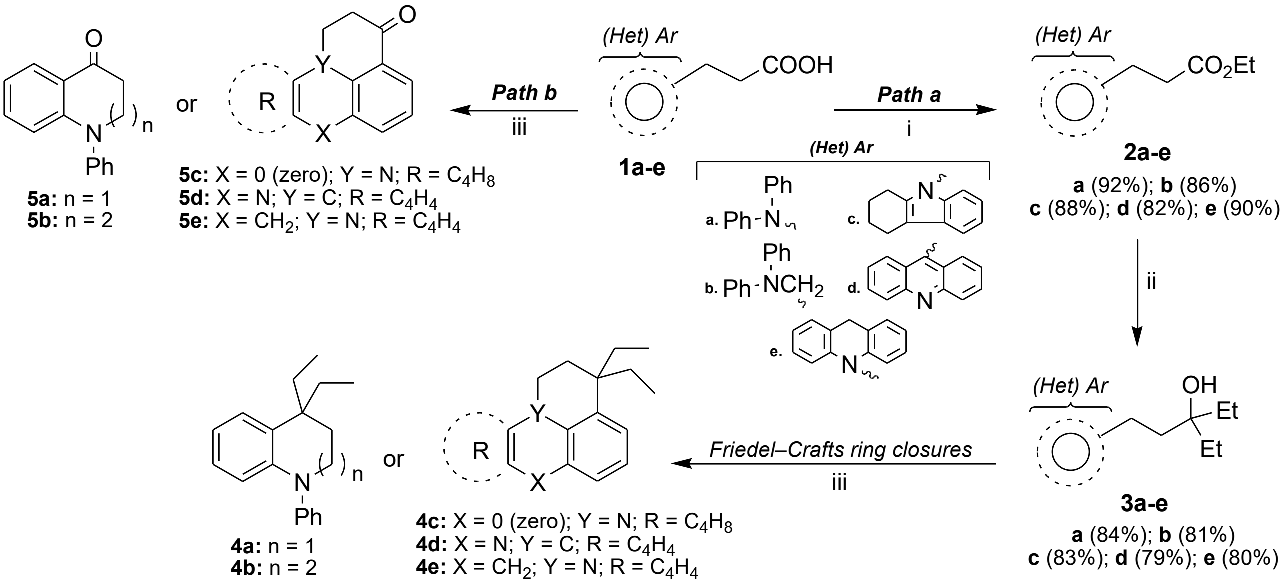
Several classical and newly emerged approaches currently exist in the literature for the synthesis of highly functionalized carbazole molecular scaffolds. Prominent strategies include, Borche-Drechsel cyclization[22], Bucherer synthesis[23], Graebe-Ullmann reaction[24], transition metal-catalyzed C−H functionalization[25], ring-closing metathesis[26], nitrene insertion[27], Fischer indolization[28], Pummerer cyclization[29], Diels-Alder reaction[30], Suzuki-Miyaura coupling[31] and dehydrogenation/cyclization of diarylamines.[32]

In this regard, benzo-and pyrido-annulated carbazoles featuring [6-5-6-(6,7,8)] ring systems have constitute an important class of therapeutic agents in medicinal chemistry. For example, ellipticine is natural pyridocarbazole alkaloids (Figure 1) known to have anticancer activity in many active pharmaceutical.[33-35] There are noteworthy examples in the literature for the constructions of pyridocarbazoles have been reported. Typical approaches to the pyridocarbazoles included, photodehydrogcnation of 1,2-diphenylquinolinium perchlorates and *N*-aryltetrahydroquinolines[36], thermal condensation of carbazoles with diethyl malonates in diphenyl ether at 250-300 °C followed by cyclization[37], intramolecular Diels-Alder reactions of vinylindoles[38], intramolecular Friedel-Crafts acylation of 3-(9-carbazolyl)propanoic acid catalyzed by HF catalyst in a copper pressure vessel or by P_2O_5 in toluene[39], Fischer indole synthesis of tetrahydroquinolines[40], dimerizations of *N*-vinylcarbazoles[41], regioselective intermolecular [4+2] cycloadditions of *N*-carbazolylmethyl-benzotriazoles with both terminal and internal alkenes in the presence of $SnCl_4$ catalyst[42], microwave-assisted domino Fischer indole reaction of 2-(3-oxo-1,3-diarylpropyl)-1-cyclohexanone phenyl hydrazones followed by intramolecular cyclization sequence.[43]

The wide pharmacological potential and multiple applications of carbazole scaffolds have attracted many organic and medicinal chemists to develop efficient routes for their synthesis. In recent communication[44] of this series, we have demonstrated an efficient and simple procedures for the synthesis of various highly valuable medium sized *N*-heteropolycycles via Friedel–Crafts cyclization approach. In connection with our previous studies, herein we describe an extensive efforts to optimize the Friedel–Crafts cyclizations conditions for the synthesis of tetrahydroquinolines, benzo[b]azepines, pyrido[3,2,1-*jk*]carbazoles, benzo[*kl*]acridines and pyrido[3,2,1-*de*]acridines from suitable prepared homo-and heteroaryl carboxylic acids and alcohols (Scheme 1).

Results and Discussion

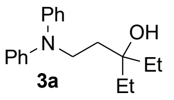
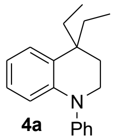
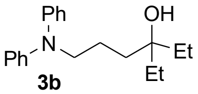
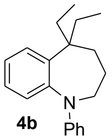
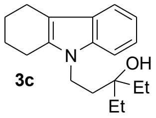
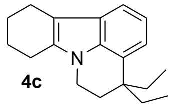
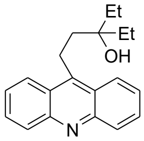
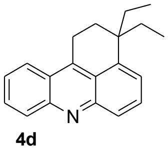
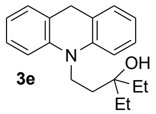
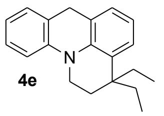
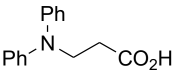
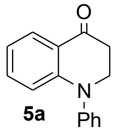
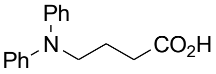
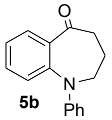
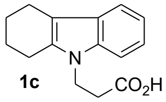
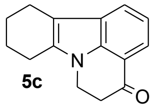
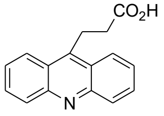
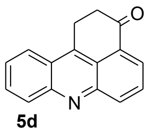
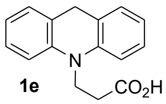
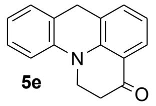
The primary focus of the research is the syntheses of fused *N*-heterocycles **4a-e** & **5a-e** containing medium-sized ring systems which are prominent structural motifs common to both natural products and pharmaceuticals from easily accessible starting materials (Schemes 1 and Table 1). On the other hand, based on the diversity and regioselectivity of Friedel-Crafts reactions, much effort has been dedicated to acyclic precursors **1a-e** synthesis. Several points of emphasis were included such as, the nature, number and relative location of the substituents which are the key parameters to be considered would conceivably benefit before choosing and adaptation a particular cyclization conditions. Therefore, starting heteroaryl carboxylic acids **1a-e** are the proper choice based on its reactivity and polarity. Hence, acids **1a**[45] (Ar = $(Ph)_2N$-), **1b**[46] (Ar = $(Ph)_2N$-CH_2-), **1c**[47] (Het = 9-tetrahydrocarbazolyl) and **1d**[48] (Het = 9-acridinyl) used in this protocol were obtained in good yields using their published procedures.



Schemes 3. Reagents and conditions: (i) $EtOH/H_2SO_4$, 8-10 h, reflux, (ii) EtMgBr, ether/THF, 13-15 h, rt, (iii) $AlCl_3/CH_3NO_2$ or TfOH or PPA-mediated cyclizations under different conditions (Table 1).

Whilst heterocyclic acid **1e** (Het = 10-acridanyl) was obtained by cyanoethylation[49] of acridane in the presence of Triton B (benzyltrimethylammonium hydroxide) followed by hydrolysis of the resulting nitrile by KOH in ethanol. Increasingly, we turned our attention to prepare other cyclization precursors. Alcohols **3a-e** were synthesized via a straightforward two-step reaction sequence in which acids **1a-e** were converted to esters **2a-e** by using $EtOH/H_2SO_4$ followed by addition of ethylmagnesium bromide in ether/THF to furnish the desired precursors **3a-e** in good to excellent yields as depicted in Scheme 1.

Table 1. Optimization of Friedel-Crafts cyclizations of precursors **1a-e** and **3a-e**

Entry	Substrate	Methods	Time, h	Product	Yield (%)
1	 **3a**	I*	8	 **4a**	91
		II*	4		88
		III*	2		79
2	 **3b**	I	6	 **4b**	88
		II	3		86
		III	3		76
3	 **3c**	I	7	 **4c**	92
		II	4		75
		III	2		74
4	 **3d**	I	5	 **4d**	90
		II	4		82
		III	3		80
5	 **3e**	I	8	 **4e**	92
		II	4		85
		III	2		79
6	 **1a**	I	14	 **5a**	88
		II	7		81
		III	10		72
7	 **1b**	I	14	 **5b**	90
		II	6		85
		III	9		75
8	 **1c**	I	14	 **5c**	91
		II	10		80
		III	8		76
9	 **1d**	I	15	 **5d**	86
		II	5		83
		III	8		77
10	 **1e**	I	18	 **5e**	89
		II	8		84
		III	7		78

*Method I: acid **1a-e** or alcohol **3a-e** (2 mmol) in CH_2Cl_2 (15 ml), $AlCl_3$ (10 mmol), CH_3NO_2 (100 mmol), room temperature.

Method II: acid **1a-e or alcohol **3a-e** (3 mmol), TfOH (1 ml, 12 mmol-1,2 ,(DCE (20 ml), reflux .

***Method III: acid **1a-e** or alcohol **3a-e** (3 mmol), PPA (15 g), 140–150 °C.

Efforts were made to optimize intramolecular Friedel-Crafts reactions of precursors **1a-e** & **3a-e**, through the examination of various reaction conditions to achieve the highest yield of the desired heteropolycycles. The variables considered included, screening of several Lewis and Brönsted promoters with different catalyst loadings, solvents of different polarities and temperatures. The intramolecular Friedel-Crafts acylations of acids **1a-e** and alcohols **3a-e** (routes a&b) have been investigated by using $AlCl_3/CH_3NO_2$ or TfOH (trifluoromethanesulfonic acid) or polyphosphoric acid (PPA) under different reaction conditions to furnish highly functionalized polycycles **4a-e** and **5a-e**. The results are compiled in Scheme 1 and Table 1. The constitutions of cyclic products without stereochemical assignment were appropriately characterized by the elemental analysis and spectroscopic analyses.

Notably, the results concerning ring closure of precursor **1a** (Table 1, Entry 6) were consonantly with early pioneered Cookson et al[45] and later Fujii et al[50] studies for cyclizations of several heteroaryl acids and their subsequent reactivity. They successfully adopted the same strategy for the synthesis of quinolinone **5a** via P_2O_5-mediated intramolecular Friedel-Crafts acylations of propanoic acid **1a** in refluxed benzene or xylenes.

Conclusions

In conclusion, the purpose of this research has been the examination of the use of both heteroaryl carboxylic acids and their alcoholic analogues as precursors in Friedel-Crafts intramolecular cyclization reactions. Herein, the present work embodies concise syntheses of a series of tetrahydroquinolines, benzo[*b*]azepines, pyrido[3,2,1-*jk*]carbazoles, benzo[*kl*]acridines and pyrido[3,2,1-*de*]acridines via Friedel-Crafts cyclizations. This synthetic utility offers straightforward access to the structurally diverse N-heterocycles from readily available starting materials.

Experimental Section

General. All chemicals used were of reagent grade and solvents were freshly distilled and dried by standard procedures before use. Melting points were taken on a digital Gallenkamp capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on a on a Mattson 5000 FTIR spectrophotometer using KBr wafer and thin film techniques (ν cm^{-1}). The ^1H- and ^{13}C-NMR measurements were obtained with Jeol-JNM ECA 400 MHz spectrometers in $CDCl_3$ solution, and chemical shifts are expressed in δ (ppm) with reference to TMS as well as coupling constants (*J*) in Hertz. Mass spectra were measured on a Perkin Elmer PE SCIEX-API 2000 mass spectrometer at an ionizing potential of 70 eV using the direct inlet system. Elemental analyses were performed on a GmbH Vario-EL III, 2400, CHNO-elemental analyzer. All reactions were monitored by thin layer chromatography (TLC) using aluminum-backed plates coated with Merck Kieselgel 60 GF254. Plates were visualized under UV light (at 254 and/or 360 nm). Flash column chromatography was performed on silica gel and basic alumina. Acridane was obtained from acridone [*Org. Synth.* **1939**, *19*, 6] by Clemmensen Reduction [E. L. Martin, *Org. React.* **1942**, *1*, 155] with zinc amalgam in hydrochloric acid.

General procedure for the Synthesis of esters 2a-e. A mixture of acid **1a-e** (20 mmol), absolute EtOH (30 mL) and concentrated sulfuric acid (3-5 mL) was refluxed for 8-10 h. The reaction mixture was concentrated under vacuum and the residue was diluted with water (100 mL), basified by addition of solid Na_2CO_3 and extracted with ether (3×40 mL). The organics were washed with water, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude esters **2a-e**. Purifications, yields and spectral data are given in the following:

Ethyl 3-(diphenylamino)propanoate (2a). Yellow oil; 92%, n_D^{25} 1.6103; (Lit[45] b.p. 149-56˚C/0.7mm); IR (Film) ν_{max} 3080, 2965, 1735, 1600, 1580, 1470, 1440, 1385, 1260, 789 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.15 (3H, t, *J* = 7.1 Hz, $\underline{CH_3}CH_2$), 2.70 (2H, t, *J* = 6.7 Hz, $C^{\alpha}H_2$), 3.61 (2H, t, *J* = 6.7 Hz, $C^{\beta}H_2$), 4.11 (2H, q, *J* = 7.1 Hz, $CH_3\underline{CH_2}$), 6.58 (4H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 6.91 (2H, tt, *J* = 8.1, 1.2 Hz), 7.28 (4H, dddd, *J* = 8.2, 8.1, 1.3, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.1 (1C, $-OCH_2\underline{CH_3}$), 32.7 (1C, $-C^{\alpha}H_2$), 52.8 (1C, $-C^{\beta}H_2$), 60.3 (1C, $-O\underline{CH_2}CH_3$), 114.0 (4C, Ar., C-3', C-3", C-5', C-5"), 126.1 (2C, Ar., C-4', C-4"), 129.2 (4C, Ar., C-2', C-2", C-6', C-6"), 148.7 (2C, Ar., C-1', C-1"), 171.7 (1C, C=O, COOEt). Anal. Calcd. for $C_{17}H_{19}NO_2$ (269); C, 75.83; H, 7.06; N, 5.20. Found; C, 76.01; H, 6.92; N, 5.07%.

Ethyl 4-(diphenylamino)butanoate (2b). White needles; 86%, mp 105-7 ºC (ethanol); IR (KBr) ν_{max} 3040, 2975, 1737, 1600, 1590, 1465, 1445, 1370, 1264, 1120, 784 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.18 (3H, t, *J* = 7.1 Hz, $\underline{CH_3}CH_2$), 1.96 (2H, quint, *J* = 7.4 Hz, $C^{\gamma}H_2$), 2.31 (2H, t, *J* = 7.4 Hz $C^{\alpha}H_2$), 3.54 (2H, t, *J* = 7.4 Hz, $C^{\beta}H_2$), 4.16 (2H, q, *J* = 7.1 Hz, $CH_3\underline{CH_2}$), 6.54 (4H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 6.96 (2H, tt, *J* = 8.1, 1.2 Hz), 7.28 (4H, dddd, *J* = 8.2, 8.1, 1.3, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.1 (1C, $-OCH_2\underline{CH_3}$), 24.4 (1C, $-C^{\alpha}H_2$), 33.7 (1C, $-C^{\beta}H_2$), 52.8 (1C, $-C^{\gamma}H_2$), 60.3 (1C, $-O\underline{CH_2}CH_3$), 114.0 (4C, Ar., C-3', C-3", C-5', C-5"), 126.1 (2C, Ar., C-4', C-4"), 129.2 (4C, Ar., C-2', C-2", C-6', C-6"), 148.7 (2C, Ar., C-1', C-1"), 173.1 (1C, C=O, COOEt). Anal. Calcd. for $C_{18}H_{21}NO_2$ (283); C, 76.32; H, 7.42; N, 4.94. Found; C, 76.35; H, 7.52; N, 4.88%.

Ethyl 3-(5,6,7,8-tetrahydrocarbazol-9-yl)propanoate (2c). Pale yellow crystals, 88% (acetone): mp 54-5 ºC (Lit[47] mp 55); IR (KBr) ν_{max} 3050, 2995, 2910, 1725, 1610, 1463, 1440, 1420, 1375, 1180, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.15 (3H, t, *J* = 7.1 Hz, $\underline{CH_3}CH_2$), 1.72 (2H, dtdd, *J* = 13.8, 7.0, 2.9, 1.9 Hz, C^6H_2), 1.83 (2H, dtdd, *J* = 13.7, 6.9, 2.9, 1.9 Hz, C^7H_2), 2.71 (2H, ddd, *J* = 14.2, 7.0, 2.9 Hz, C^5H_2), 2.78 (2H, t, *J* = 6.9 Hz, C^8H_2), 2.97 (2H, ddd, *J* = 14.2, 7.0, 2.9 Hz, $C^{\alpha}H_2$), 4.11 (2H, q, *J* = 7.1 Hz, $CH_3\underline{CH_2}$), 4.33 (2H, t, *J* = 6.9 Hz, $C^{\beta}H_2$), 6.69 (1H, ddd, *J* = 7.7, 1.5, 0.5 Hz), 6.91 (1H, td, *J* = 7.7, 1.7 Hz), 6.99 (1H, ddd, *J* = 7.9, 7.7, 1.5 Hz), 7.01 (1H, ddd, *J* = 7.9, 1.7, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.1 (1C, $-OCH_2\underline{CH_3}$), 22.1 (1C, $-C^6H_2$), 22.6 (1C, $-C^7H_2$), 23.1 (1C, $-C^5H_2$), 23.9 (1C, $-C^8H_2$), 34.6 (1C, $-C^{\alpha}H_2$), 47.6 (1C, $-C^{\beta}H_2$), 60.3 (1C, $-O\underline{CH_2}CH_3$), 109.7 (2C, Ar., C-1, C-4b), 118.2 (1C, Ar., C-4), 121.0 (1C, Ar., C-2), 123.5 (1C, Ar., C-3), 128.3 (1C, Ar., C-4a), 133.6 (1C, Ar., C-8a), 135.6 (1C, Ar., C-9a), 173.0 (1C, C=O, COOEt). Anal. Calcd. for $C_{17}H_{21}NO_2$ (271); C, 75.27; H, 7.74; N, 5.16. Found; C, 75.33; H, 7.68; N, 5.18%.

Ethyl 3-(acridin-9-yl)propanoate (2d). Yellow plates: 82% (ethanol), mp 93-5°C (Lit. mp 95 ºC[48]); IR (KBr) ν_{max} 3040, 2960, 1725, 1595, 1440, 1415, 1365, 1290, 1190, 740, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.15 (3H, t, *J* = 7.1 Hz, $\underline{CH_3}CH_2$), 2.75 (2H, t, *J* = 7.0 Hz $C^{\alpha}H_2$), 3.26 (2H, t, *J* = 7.0 Hz, $C^{\beta}H_2$), 4.11 (2H, q, *J* = 7.1 Hz, $CH_3\underline{CH_2}$), 7.61 (2H, ddd, *J* = 7.9, 7.0, 1.7 Hz), 7.79 (2H, ddd, *J* = 8.1, 7.0, 1.3 Hz), 7.96 (2H, ddd, *J* = 8.1, 1.7, 0.4 Hz), 8.13 (2H, ddd, *J* = 7.9, 1.3, 0.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.1 (1C, $-OCH_2\underline{CH_3}$), 17.6 (1C, $-C^{\alpha}H_2$), 35.9 (1C, $-C^{\beta}H_2$), 60.3 (1C, $-O\underline{CH_2}CH_3$), 124.1 (2C, Ar., C-8a, C-9a), 126.7 (2C, Ar., C-1, C-8), 127.5 (2C, Ar., C-2, C-7), 129.5 (2C, Ar., C-4, C-5), 130.5 (2C, Ar., C-3, C-6), 135.5 (1C, Ar., C-9), 147.7 (2C, Ar., C-4a, C-4c), 172.3 (1C, C=O, COOEt). Anal. Calcd. for $C_{18}H_{17}NO_2$ (279); C, 77.41; H, 6.09; N, 5.01. Found; C, 77.46; H, 6.13; N, 4.92%.

Ethyl 3-(acridin-10(9*H*)-yl)propanoate (2e). Yellow crystals; 90%, mp 138-40 ºC (AcOEt); IR (KBr) ν_{max} 3063, 2955, 1745, 1610, 1590, 1480, 1445, 1372, 1155, 765 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.15 (3H, t, *J* = 7.1 Hz, $\underline{CH_3}CH_2$), 2.71 (2H, t, *J* = 6.7 Hz, $C^{\alpha}H_2$), 3.62-3.80 (4H, 3.69 (2H, d, *J* = 18.2 Hz, $C^{\beta}H_2$), 3.75 (2H, t, *J* = 6.7 Hz, C^9H_2), 4.10 (2H, q, *J* = 7.1 Hz, $CH_3\underline{CH_2}$), 6.26 (2H, ddd, *J* = 8.1, 1.2, 0.5 Hz), 6.68 (2H, ddd, *J* = 7.9, 7.6, 1.2 Hz), 7.04 (2H, ddd, *J* = 8.1, 7.6, 1.2 Hz), 7.18 (2H, ddd, *J* = 7.9, 1.2, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.1,(1C, $-OCH_2\underline{CH_3}$), 32.1 (1C, $-C^{\alpha}H_2$), 33.2 (1C, $-C^9H_2$), 43.5 (1C, $-C^{\beta}H_2$), 60.3 (1C, $-O\underline{CH_2}CH_3$), 116.0 (2C, Ar., C-

2, C-7), 120.6 (2C, Ar., C-4, C-5), 124.3 (2C, Ar., C-3, C-6), 127.5 (2C, Ar., C-1, C-8), 131.9 (2C, Ar., C-8a, C-9a), 141.6 (2C, Ar., C-4a, C-4c), 172.6 (1C, s). (1C, C=O, COOEt). Anal. Calcd. for $C_{18}H_{19}NO_2$ (281); C, 76.86; H, 6.76; N, 4.98. Found; C, 76.91; H, 6.72; N, 5.02%.

General procedure for the Synthesis of alcohols 3a-e. To an ice-cold Grignard reagent prepared from Mg turnings (8 mmol) and alkyl or ethyl bromide (8 mmol) in ether (25 ml) was added ester **2a-e** (3 mmol). The reaction mixture was vigorously stirred for 12-15 h at room temperature and finally decomposed by saturated NH_4Cl soln. The product was extracted with ether (3×30 mL) and the combined organic phases were washed with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated in *vacuo* to afford the crude alcohols **3a-e**. The yields and spectral data are given as the following.

1-(Diphenylamino)-3-ethylpentan-3-ol (3a). White crystals; 84%, m.p. 55-56 ºC (benzene); IR (KBr) ν_{max} 3360, 3255, 3070, 2950, 2850, 1590, 1485, 1450, 1440, 1340, 1145, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 (6H, t, *J* = 7.5 Hz, 2$\underline{CH_3}$), 1.52 (4H, q, *J* = 7.5 Hz, 2CH_2), 1.63 (2H, t, *J* = 7.1 Hz, C^4H_2), 2.41 (1H, *s*, OH exchangeable with D_2O), 3.47 (2H, t, *J* = 7.1 Hz, C^5H_2), 6.51 (4H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 6.92 (2H, tt, *J* = 8.1, 1.2 Hz), 7.22 (4H, dddd, *J* = 8.2, 8.1, 1.3, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 7.7 (2C, 2$\underline{CH_3}$), 30.9 (2C, 2$\underline{CH_2}$), 34.6 (1C, -C^4H_2), 52.8 (1C, N-C^5H_2), 73.7 (1C, C^3-OH), 114.0 (4C, Ar., C-3', C-3", C-5', C-5"), 126.1 (2C, Ar., C-4', C-4"), 129.2 (4C, Ar., C-2', C-2", C-6', C-6"), 148.7 (2C, Ar., C-1', C-1"). MS (EI, 70 eV) *m/z* (%), 284 (M^++1, 11), 283 (M^+, 27), 273 (60), 265 (M^+-H_2O, 36), 236 (14), 208 (16), 168 (100), 139 (7), 89 (4), 77 (48). Anal. Calcd. for $C_{19}H_{25}NO$ (283); C, 80.56; H, 8.83; N, 4.94. Found; C, 80.55; H, 8.75; N, 5.02%.

6-(Diphenylamino)-3-ethylhexan-3-ol (3b). White needles; 81%, mp 115-17 °C (ethanol); IR (KBr) ν_{max} 3380 , 3077, 2960, 1590, 1480, 1460, 1450, 1345, 1294, 1220, 792 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.89-1.01 (6H, 0.95 (6H, t, *J* = 7.5 Hz, 2CH_3), 1.39-1.60 (6H, 1.45 (2H, t, *J* = 7.5 Hz, C^5H_2), 1.54 (4H, q, *J* = 7.5 Hz, 2CH_2), 1.91 (2H, quint, *J* = 7.4 Hz, C^4H_2), 2.74 (1H, *s*, OH exchangeable with D_2O), 3.56 (2H, t, *J* = 7.4 Hz, C^6H_2), 6.51 (4H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 6.92 (2H, tt, *J* = 8.1, 1.2 Hz), 7.22 (4H, dddd, *J* = 8.2, 8.1, 1.3, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 7.7 (2C, 2$\underline{CH_3}$), 24.4 (1C, -C^4H_2), 30.9 (2C, 2$\underline{CH_2}$), 36.3 (1C, -C^5H_2), 52.8 (1C, N-C^6H_2), 73.7 (1C, C^3-OH), 114.0 (4C, Ar., C-3', C-3", C-5', C-5"), 126.1 (2C, Ar., C-4', C-4"), 129.2 (4C, Ar., C-2', C-2", C-6', C-6"), 148.7 (2C, Ar., C-1', C-1"). MS (EI, 70 eV) *m/z* (%), 298 (M^++1, 15), 297 (M^+, 100), 279 (23), 250 (20), 243 (11), 207 (5), 191 (4), 168 (50), 139 (10), 115 (7), 92 (5), 77 (22). Anal. Calcd. for $C_{20}H_{27}NO$ (297); C, 80.80; H, 9.09; N, 4.71. Found; C, 80.84; H, 9.00; N, 4.75%.

3-Ethyl-1-(5,6,7,8-tetrahydrocarbazol-9-yl)pentan-3-ol (3c). Yellow plates, 83%, mp 72-74°C (ethanol); IR (KBr) ν_{max} 3380, 3040, 2970, 1610, 1580, 1480, 1365, 1240, 1145, 740, 680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 (6H, t, *J* = 7.5 Hz, 2CH_3), 1.55 (4H, q, *J* = 7.5 Hz, 2CH_2), 1.69 (2H, dtdd, *J* = 13.8, 7.0, 2.9, 1.9 Hz, C^6H_2), 1.86 (2H, dtdd, *J* = 13.8, 6.9, 2.9, 1.9 Hz, C^7H_2), 1.98 (2H, t, *J* = 7.0 Hz, C^4H_2), 2.78 (2H, ddd, *J* = 14.2, 7.0, 2.9 Hz, C^5H_2), 2.98 (2H, ddd, *J* = 14.2, 7.0, 2.9 Hz, C^8H_2), 3.48 (1H, *s*, OH exchangeable with D_2O), 4.10 (2H, t, *J* = 7.0 Hz, C^5H_2), 6.69 (1H, ddd, *J* = 7.7, 1.5, 0.5 Hz), 6.85-7.06 (2H, 6.91 (td, *J* = 7.7, 1.7 Hz), 6.99 (ddd, *J* = 7.9, 7.7, 1.5 Hz), 7.17 (1H, ddd, *J* = 7.9, 1.7, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 7.7 (2C, 2$\underline{CH_3}$), 22.1 (1C, -C^6H_2), 22.6 (1C, -C^7H_2), 23.1 (1C, -C^8H_2), 23.9 (1C, -C^5H_2), 30.9 (2C, 2$\underline{CH_2}$), 34.6 (1C, -C^4H_2), 47.6 (1C, -C^5H_2), 73.7 (1C, C^3-OH), 109.7 (1C, Ar., C-4b), 109.8 (1C, Ar., C-1), 118.2 (1C, Ar., C-4), 121.0 (1C, Ar., C-2), 123.5 (1C, Ar., C-3), 128.3 (1C, Ar., C-4a), 133.6 (1C, Ar., C-8a), 135.6 (1C, Ar., C-9a). MS (EI, 70 eV) *m/z* (%), 258 (M^+, 19), 257 (M^+-1 100), 240 (29), 237 (17), 210 (30), 194 (6), 165 (9), 134 (27), 118 (18), 91 (6), 78 (14). Anal. Calcd. for $C_{19}H_{27}NO$ (258); C, 88.37; H, 10.46; N, 5.42. Found; C, 88.30; H, 10.50; N, 5.44%.

1-(Acridin-9-yl)-3-ethylpentan-3-ol (3d). Yellow needles; 79%, mp 123-25°C (ethanol); IR (KBr) ν_{max} 3350, 3220, 2980, 1610, 1550, 1515, 1480, 1365, 1370, 1255, 1175, 740, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 (6H, t, *J* = 7.5 Hz, 2CH_3), 1.56 (4H, q, *J* = 7.5 Hz, 2CH_2), 1.84 (2H, t, *J* = 6.8 Hz, C^4H_2), 2.35 (1H, *s*, OH exchangeable with D_2O), 3.07 (2H, t, *J* = 6.8 Hz, C^5H_2), 7.62 (2H, ddd, *J* = 7.9, 7.0, 1.7 Hz), 7.82 (2H, ddd, *J* = 8.1, 7.0, 1.3 Hz), 7.96 (2H, ddd, *J* = 8.1, 1.7, 0.4 Hz), 8.13 (2H, ddd, *J* = 7.9, 1.3, 0.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 7.7 (2C, $2\underline{CH_3}$), 17.6 (1C, $-C^5H_2$), 30.9 (2C, $2\underline{CH_2}$), 34.6 (1C, $-C^4H_2$), 73.7 (1C, C^3-OH), 124.1(2C, Ar., C-9a, C-8a), 126.7 (2C, Ar., C-2, C-7), 127.5 (2C, Ar., C-1, C-8), 129.5 (2C, Ar., C-4, C-5), 130.5 (2C, Ar., C-3, C-6), 135.5 (1C, Ar., C-9), 147.7 (2C, Ar., C-4a, C-10a). MS (EI, 70 eV) *m/z* (%), 294 (M^++1, 20), 293 (M^+, 100), 277 (20), 250 (4), 231 (17), 184 (7), 168 (19), 138 (6), 94 (34), 78 (32). Anal. Calcd. for $C_{20}H_{23}NO$ (293); C, 81.91; H, 7.84; N, 4.77. Found; C, 81.90; H, 7.77; N, 4.84%.

1-(Acridin-10(9*H*)-yl)-3-ethylpentan-3-ol (3e). Brown plates; 80%, mp 70-72°C (benzene); IR (KBr) ν_{max} 3420, 3030, 2985, 1600, 1520, 1465, 1372, 1381, 1250, 1164, 755, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.91 (6H, t, *J* = 7.5 Hz, $2CH_3$), 1.56 (4H, q, *J* = 7.5 Hz, $2CH_2$), 1.63 (2H, t, *J* = 7.3 Hz, C^4H_2), 2.88 (1H, *s*, OH exchangeable with D_2O), 3.50 (2H, t, *J* = 7.3 Hz, C^5H_2), 3.69 (2H, d, *J* = 18.2 Hz, C^9H_2), 6.26 (2H, ddd, *J* = 8.1, 1.2, 0.5 Hz), 6.68 (2H, ddd, *J* = 7.9, 7.6, 1.2 Hz), 7.02 (2H, ddd, *J* = 8.1, 7.6, 1.2 Hz), 7.18 (2H, ddd, *J* = 7.9, 1.2, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 7.7 (2C, $2\underline{CH_3}$), 30.9 (2C, $2\underline{CH_2}$), 33.2 (1C, $-C^5H_2$), 34.6 (1C, $-C^4H_2$), 43.5 (1C, $-N-C^5H_2$), 73.7 (1C, C^3-OH), 116.0 (2C, Ar., C-3, C-7), 120.6 (2C, Ar., C-1, C-9), 124.3 (2C, Ar., C-2, C-8), 127.5 (2C, Ar., C-4, C-6), 131.9 (2C, Ar., C-4a, C-5a), 141.6 (2C, Ar., C-9a, C-9c). MS (EI, 70 eV) *m/z* (%), 296 (M^++1, 5), 295 (M^+, 100), 277 (4), 231 (13), 214 (55), 183 (3), 168 (20), 138 (5), 94 (50), 91 (25), 77 (23). Anal. Calcd. for $C_{20}H_{25}NO$ (295); C, 81.35; H, 8.47; N, 4.74. Found; C, 81.31; H, 8.54; N, 4.71%.

Procedure A. Cyclization using $AlCl_3/CH_3NO_2$ catalyst. To a solution of $AlCl_3$ (10 mmol) in CH_3NO_2 (100 mmol) was added a solution of **1a-e** or alcohol **3a-e** (2 mmol) in DCM (15 mL) dropwise over 10 min at room temperature. The mixture was stirred for a certain time as depicted in Table 1. Afterward, the mixture was poured over ice–cold HCl solution (20 mL, 10%) and extracted with ether (3×30 mL). The organic layer was washed with three portions with H_2O and Na_2CO_3 (20 mL, 10%), followed by saturated brine, and then dried over Na_2SO_4. After filtration, the solution was evaporated under reduced pressure to give the crude cyclic products **4a-e** or **5a-e**.

Procedure B. General procedure for TfOH-mediated cycliacylations. TfOH (12 mmol) was added dropwise to a cooled (0 °C) solution of **1a-e** or alcohol **3a-e** (3 mmol) in DCM (20 mL) and the mixture was stirred at the required temperature for a certain time as shown in Table 1. Thereafter, the mixture was quenched by aqueous $NaHCO_3$ solution (50 ml, 50%) at 0 °C and the product was extracted with EtOAc (3×30 mL). The organic extracts were washed with H_2O, dried over anhydrous Na2SO4 and evaporated in *vacuo* to give the crude products **4a-e** or **5a-e**.

Procedure C. General procedure for PPA-mediated cycliacylations. A mixture of acid **1a-e** or alcohol **3a-e** (3 mmol) and PPA (15 g) was heated on an oil bath at indicated temperature for the required time (Table 1) after which TLC analysis (20% AcOEt/hexane) showed the reaction to be complete. Afterwards, the mixture was cooled to room temperature and made alkaline with by addition of $NaHCO_3$ solution (40 ml, 50%) and then extracted with ether (3×30 mL). The combined organics were washed with saturated brine solution, dried over MgSO, filtered, and concentrated in *vacuo* to afford the crude products **4a-e** or **5a-e**. Further purification and yields of the cyclic products are given in the following.

4,4-Diethyl-1,2,3,4-tetrahydro-1-phenylquinoline (4a). Yield 0.48 g (91%, method I), 0.70 g (88%, method II), 0.63 g (79%, method III); Yellow plates; mp 88-90 °C (benzene); IR (KBr) ν_{max} 3065, 2984, 1610, 1580, 1490, 1445, 1430, 1385, 1270, 1064, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.79 (6H, t, *J* = 6.8 Hz, $2CH_3$), 1.66 (4H, q, *J* = 6.8 Hz, $2CH_2$), 1.73 (2H, ddd, *J* = 13.9, 6.6, 2.5 Hz, C^3H_2), 3.45 (2H, ddd, *J* = 15.1, 6.6, 2.5 Hz, C^2H_2), 6.26 (1H, ddd, *J* = 8.1, 1.2, 0.5 Hz), 6.52 (2H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 6.69 (1H, ddd, *J* = 7.9, 7.6, 1.2 Hz), 6.88 (1H, tt, *J* = 8.1, 1.2 Hz), 7.04 (1H, ddd, *J* = 8.1, 7.6, 1.2 Hz), 7.10 (1H, ddd, *J* = 7.9, 1.2, 0.5 Hz), 7.29 (2H, dddd, *J* = 8.2, 8.1, 1.3, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 9.1 (2C, $2\underline{CH_3}$), 28.1 (2C, $2\underline{CH_2}$), 34.4 (1C, $-C^4(Et)_2$), 44.3 (1C, $-C^3H_2$), 58.2 (1C, $N-C^2H_2$), 126.0 (2C, Ar., C-5, C-7), 126.4 (3C, Ar., C-6, C-2', C-6'), 128.0 (1C, Ar., C-4'), 129.1

(2C, Ar., C-3', C-5'), 131.9 (1C, Ar., C-8), 141.6 (1C, Ar., C-4a), 144.3 (1C, Ar., C-8a), 150.5 (1C, Ar., C-1'). MS (EI, 70 eV) *m/z* (%), 265 (M^+, 100), 263 (M^+-2, 19), 236 (15), 207 (24), 183 (26), 155 (17), 139 (25), 109 (85), 91 (20), 77 (9). Anal. Calcd. for $C_{19}H_{23}N$ (265); C, 86.03; H, 8.67; N, 5.28. Found; C, 86.08; H, 8.71; N, 5.20%.

5,5-Diethyl-2,3,4,5-tetrahydro-1-phenyl-1*H*-benzo[*b*]azepine (4b). Yield 0.49 g (88%, method I), 0.72 g (86%, method II), 0.63 g (76%, method III); Brownish viscous oil; n_D^{25} 1.630; IR (Film) ν_{max} 3050, 2986, 1610, 1590, 1480, 1445, 1330, 1294, 1151, 780 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 0.80 (6H, t, *J* = 8.0 Hz, 2CH$_3$), 1.54 (2H, ddddd, *J* = 14.2, 7.3, 6.6, 3.7, 2.7 Hz, C^{3}H$_2$), 1.67 (2H, ddd, *J* = 13.2, 6.6, 2.8 Hz, C^{4}H$_2$), 1.73 (4H, q, *J* = 8.0 Hz, 2CH$_2$), 3.51 (2H, ddd, *J* = 13.5, 7.3, 3.7 Hz, C^{2}H$_2$), 6.25 (1H, ddd, *J* = 8.1, 1.2, 0.5 Hz), 6.52 (2H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 6.69 (1H, ddd, *J* = 7.8, 7.5, 1.2 Hz), 6.90 (1H, tt, *J* = 8.1, 1.2 Hz), 7.08 (2H, ddd, *J* = 7.8, 1.2, 0.5 Hz), 7.22 (2H, dddd, *J* = 8.2, 8.1, 1.3, 0.5 Hz). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 12.8 (2C, $\underline{2\mathit{CH_3}}$), 27.4 (1C, -C^{3}H$_2$), 28.4 (2C, $\underline{2\mathit{CH_2}}$), 36.5 (1C, -C^5(Et)$_2$), 51.4 (1C, -C^{4}H$_2$), 60.5 (1C, N-C^{2}H$_2$), 122.1 (2C, Ar., C-2', C-6'), 123.5 (1C, Ar., C-4'), 125.3 (1C, Ar., C-7), 127.9 (1C, Ar., C-9), 128.9 (2C, Ar., C-3', C-5'), 129.1 (1C, Ar., C-6), 130.5 (1C, Ar., C-8), 141.2 (1C, Ar., C-5a), 145.6 (1C, Ar., C-9a), 157.4 (1C, Ar., C-1'). MS (EI, 70 eV) *m/z* (%), 279 (M^+, 35), 268 (100), 253 (17), 239 (60), 210 (12), 181 (9), 165 (8), 159 (24), 145 (58), 107 (68), 91 (12), 77 (16). Anal. Calcd. for $C_{20}H_{25}N$ (279); C, 86.02; H, 8.96; N, 5.01. Found; C, 86.07; H, 9.02; N, 4.90%.

4,4-Diethyl-5,6,8,9,10,11-hexahydro-4*H*-pyrido[3,2,1-*jk*]carbazole (4c). Yield 0.47 g (92%, method I), 0.59 g (75%, method II), 0.58 g (74%, method III); Brownish viscous oil: n_D^{25} 1.6480; crystals; mp 127-29 °C (methanol); IR (Film) ν_{max} 3060, 2967, 1610, 1575, 1480, 1322, 1260, 1185, 749 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 0.80 (6H, t, *J* = 6.9 Hz, 2CH$_3$), 1.74 (4H, q, *J* = 6.9 Hz, 2CH$_2$), 1.78 (4H, dtdd, *J* = 13.8, 6.9, 2.9, 1.9 Hz, C^{8}H$_2$-C^{9}H$_2$), 2.23 (2H, ddd, *J* = 13.9, 6.7, 2.9 Hz, C^{10}H$_2$), 2.77 (2H, ddd, *J* = 14.6, 7.0, 2.9 Hz, C^{7}H$_2$), 2.96 (2H, ddd, *J* = 14.1, 6.9, 2.9 Hz, C^{5}H$_2$), 4.35 (2H, ddd, *J* = 16.3, 6.8, 2.8 Hz, C^{6}H$_2$), 6.27 (1H, dd, *J* = 7.7, 2.6 Hz), 6.65 (1H, t, *J* = 7.7 Hz), 6.80 (1H, dd, *J* = 7.6, 2.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 9.1 (2C, $\underline{2\mathit{CH_3}}$), 22.1 (1C, -C^{7}H$_2$), 22.6 (1C, -C^{8}H$_2$), 23.1 (1C, -C^{9}H$_2$), 23.9 (1C, -C^{10}H$_2$), 28.1 (2C, $\underline{2\mathit{CH_2}}$), 34.4 (1C, -C(Et)$_2$), 38.4 (1C, -C^{5}H$_2$), 56.1 (1C, N-C^{6}H$_2$), 113.4 (1C, Ar., C-3b), 118.1 (1C, Ar., C-10a), 120.1 (1C, Ar., C-3), 125.2 (1C, Ar., C-1), 127.0 (1C, Ar., C-2), 130.8 (1C, Ar., C-10b), 133.6 (1C, Ar., C-3a), 150.5 (1C, Ar., C-6a). MS (EI, 70 eV) *m/z* (%), 269 (M^++2, 11), 267 (M^+, 100), 261 (9), 241 (3), 196 (9), 178 (2), 168 (44), 139 (8), 107 (25), 89 (3), 77 (33). Calcd. for $C_{19}H_{25}N$ (267); C, 85.39; H, 9.36; N, 5.24. Found; C, 85.35; H, 9.41; N, 5.23%.

3,3-Diethyl-2,3-dihydro-1*H*-benzo[*kl*]acridine (4d). Yield 0.48 g (90%, method I), 0.66 g (82%, method II), 0.64 g (80%, method III); Reddish viscous oil; n_D^{25} 1.6352; IR (Film) ν_{max} 3090, 2978, 1610, 1585, 1445, 1363, 1230, 1078, 690 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 0.78 (6H, t, *J* = 6.8 Hz, 2CH$_3$), 1.96 (4H, q, *J* = 6.8 Hz, 2CH$_2$), 2.17 (2H, ddd, *J* = 13.8, 6.6, 2.8 Hz, C^{2}H$_2$), 2.95 (2H, ddd, *J* = 13.6, 6.6, 2.8 Hz, C^{1}H$_2$), 7.52 (1H, dd, *J* = 11.5, 2.0 Hz), 7.64 (1H, ddd, *J* = 7.9, 6.9, 1.6 Hz), 7.70 (1H, dd, *J* = 11.5, 6.7 Hz), 7.81 (1H, ddd, *J* = 8.2, 6.9, 1.3 Hz), 8.04 (1H, ddd, *J* = 8.2, 1.6, 0.5 Hz), 8.18 (2H, dddd, *J* = 7.9, 1.3, 1.6, 0.5 Hz). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 9.1 (2C, $\underline{2\mathit{CH_3}}$), 21.1 (1C, -C^{1}H$_2$), 28.1 (2C, $\underline{2\mathit{CH_2}}$), 34.4 (1C, -C^{2}H$_2$), 46.4 (1C, -C^3(Et)$_2$) 121.6 (1C, Ar., C-11a), 124.1 (1C, Ar., C-4), 126.5 (3C, Ar., C-5, C-6, C-11), 126.7 (1C, Ar., C-10), 127.5 (1C, Ar., C-11c), 129.3 (2C, Ar., C-8, C-9), 130.5 (1C, Ar., C-11b), 145.6 (1C, Ar., C-3a), 147.7 (1C, Ar., C-7a), 150.5 (1C, Ar., C-6a). MS (EI, 70 eV) *m/z* (%), 276 (M^++1, 17), 275 (M^+, 100), 249 (48), 237 (64), 214 (40), 197 (42), 183 (47), 165 (21), 152 (14), 108 (37), 91 (10), 78 (18). Anal. Calcd. for $C_{20}H_{21}N$ (275); C, 87.27; H, 7.63; N, 5.09. Found; C, 87.25; H, 7.70; N, 5.04%.

3,3-Diethyl-1,2,3,7-tetrahydropyrido[3,2,1-*de*]acridine (4e). Yield 0.50 g (92%, method I), 0.70 g (85%, method II), 0.65 g (79%, method III); Yellow crystals; mp 115-17 °C (benzene). IR (KBr) ν_{max} 3045, 2980, 1610, 1590, 1487, 1445, 1364, 1273, 1073, 695 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 0.80 (6H, t, *J* = 8.0 Hz, 2CH$_3$), 1.67 (4H, q, *J* = 8.0 Hz, 2CH$_2$), 1.75 (2H, ddd, *J* = 13.9, 6.6, 2.5 Hz, C^{2}H$_2$), 3.72 (2H, ddd, *J* = 14.0, 6.6, 2.5 Hz, C^{1}H$_2$), 3.75 (2H, d, *J* = 18.2 Hz, C^{7}H$_2$), 6.26 (1H, ddd, *J* = 8.1, 1.2, 0.5 Hz), 6.47-6.68 (2H, 6.51 (1H, t, *J* = 7.6 Hz), 6.61 (1H, ddd, *J* = 7.9, 7.6, 1.2 Hz), 6.90 (1H, dd, *J* = 7.6, 1.9 Hz), 7.04 (2H, ddd, *J* = 8.1, 7.6, 1.2 Hz), 7.15 (1H, ddd, *J* = 7.9, 1.2, 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 9.1 (2C, $2\underline{CH_3}$), 28.1 (2C, $2\underline{CH_2}$), 34.4 (1C, -C^7H_2), 35.4 (1C, -$C(Et)_2$), 44.3 (1C, -C^2H_2), 48.1 (1C, N-C^1H_2), 120.6 (1C, Ar., C-11), 122.6 (1C, Ar., C-4), 124.3 (1C, Ar., C-6), 126.5 (2C, Ar., C-5, C-9), 127.5 (1C, Ar., C-10), 128.2 (1C, Ar., C-8), 129.0 (1C, Ar., C-6a), 132.7 (1C, Ar., C-3a), 138.1 (1C, Ar., C-11c), 141.6 (1C, Ar., C-7a), 150.5 (1C, Ar., C-11a). MS (EI, 70 eV) *m/z* (%), 278 (M^++1, 2), 277 (M^+, 14), 276 (100), 260 (4), 246 (33), 220 (16), 200 (18), 184 (67), 171 (26), 152 (15), 139 (32), 108 (8), 76 (27). Anal. Calcd. for $C_{20}H_{23}N$ (277); C, 86.64; H, 8.30; N, 5.05. Found; C, 86.70; H, 8.25; N, 5.04%.

2,3-Dihydro-1-phenylquinolin-4(1*H*)-one (5a). Yield 0.38 g (88%, method I), 0.58 g (81%, method II), 0.51 g (72%, method III); Yellow needles, 89%, mp 81-83 °C (benzene) (Lit[45] mp 83 °C); IR (KBr) ν_{max} 3082, 2954, 1680, 1600, 1577, 1440, 1325, 1244, 1035, 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.68 (2H, ddd, *J* = 15.0, 6.7, 2.8 Hz, C^3H_2), 3.73 (2H, ddd, *J* = 16.1, 6.7, 2.8 Hz, C^2H_2), 6.93 (1H, tt, *J* = 8.1, 1.1 Hz), 7.02 (1H, ddd, *J* = 8.4, 1.3, 0.5 Hz), 7.10 (2H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 7.19 (2H, dddd, *J* = 8.2, 8.1, 1.4, 0.5 Hz), 7.33 (1H, ddd, *J* = 7.9, 7.3, 1.3 Hz), 7.36 (1H, ddd, *J* = 7.9, 1.3, 0.5 Hz), 7.62 (1H, ddd, *J* = 8.4, 7.3, 1.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 36.3 (1C, -C^3H_2), 44.3 (1C, -C^2H_2), 116.0 (1C, s), (1C, Ar., C-6), 126.0 (2C, Ar., C-2', C-6'), 126.5 (2C, Ar., C-3', C-5'), 126.7 (1C, Ar., C-4'), 128.0 (1C, Ar., C-4a), 129.1 (2C, Ar., C-5, C-8), 131.9 (1C, Ar., C-7), 141.6 (1C, Ar., C-8a), 144.3 (1C, Ar., C-1'), 197.8 (1C, C=O, C-4). MS (EI, 70 eV) *m/z* (%), 224 (M^++1, 7), 223 (M^+, 74), 191 (100), 167 (M^+-CO-2CH_2, 36), 163 (80), 135 (44), 99 (38), 87 (23), 77 (5). Anal. Calcd. for $C_{15}H_{13}NO$ (223); C, 80.71; H, 5.82; N, 6.27. Found; C, 80.66; H, 5.84; N, 6.19%.

1,2,3,4-Tetrahydro-1-phenylbenzo[*b*]azepin-5-one (5b). Yield 0.45 g (90%, method I), 0.64 g (85%, method II), 0.57 g (75%, method III); White crystals; 85%; mp 184-186 °C (acetone); IR (KBr) ν_{max} 3060, 2930, 1695, 1610, 1580, 1475, 1440, 1366, 1256, 1192, 1074, 874 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.11 (2H, dtdd, *J* = 13.7, 6.9, 2.3, 2.2 Hz, C^3H_2), 2.53 (2H, ddd, *J* = 16.5, 6.8, 2.3 Hz, C^4H_2), 3.64 (2H, ddd, *J* = 17.2, 6.9, 2.2 Hz, C^2H_2), 6.87 (1H, tt, *J* = 8.1, 1.2 Hz), 7.05 (1H, ddd, *J* = 8.4, 1.2, 0.5 Hz), 7.10 (2H, dtd, *J* = 8.2, 1.2, 0.5 Hz), 7.20 (2H, dddd, *J* = 8.2, 8.1, 1.4, 0.5 Hz), 7.32 (1H, ddd, *J* = 7.9, 7.4, 1.2 Hz), 7.41 (1H, ddd, *J* = 7.9, 1.3, 0.5 Hz), 7.62 (1H, ddd, *J* = 8.4, 7.4, 1.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 27.4 (1C, -C^3H_2), 40.8 (1C, -C^4H_2), 51.4 (1C, -C^2H_2), 120.4 (1C, Ar., C-7), 122.1 (2C, Ar., C-2', C-6'), 123.5 (1C, Ar., C-4'), 127.8 (1C, Ar., C-6), 128.9 (2C, Ar., C-3', C-5'), 129.1 (1C, Ar., C-9), 129.4 (1C, Ar., C-8), 134.5 (1C, Ar., C-8), 141.2 (1C, Ar., C-9a), 145.6 (1C, Ar., C-1'), 205.4 (1C, C=O, C-4). MS (EI, 70 eV) *m/z* (%), 240 (M^++3, 6), 239 (M^++2, 70), 237 (M^+, 100), 214 (63), 209 (M^+-CO, 31), 177 (29), 177 (27), 165 (9), 142 (52), 107 (28), 91 (33), 77 (14). Anal. Calcd. for $C_{16}H_{15}NO$ (237); C, 81.01; H, 6.32; N, 5.90. Found; C, 80.89; H, 6.35; N, 6.05%.

5,6,8,9,10,11-Hexahydropyrido[3,2,1-*jk*]carbazol-4-one (5c). Yield 0.43 g (91%, method I), 0.58 g (80%, method II), 0.55 g (76%, method III); White needles; 90%; mp 142-144 ºC (benzene); IR (KBr) ν_{max} IR (KBr) ν_{max} 3083, 2975, 1690, 1600, 1475, 1460, 1435, 1325, 1256, 1123, 1071, 852 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.74 (2H, dtdd, *J* = 13.7, 7.0, 2.9, 1.9 Hz, C^9H_2), 1.84 (2H, dtdd, *J* = 13.6, 6.9, 2.9, 1.9 Hz, C^8H_2), 2.82 (2H, ddd, *J* = 14.2, 7.0, 2.9 Hz, $C^{10}H_2$), 3.05 (2H, ddd, *J* = 14.0, 6.9, 2.9 Hz, C^7H_2), 3.21 (2H, ddd, *J* = 15.8, 7.0, 3.0 Hz, C^5H_2), 4.38 (2H, ddd, *J* = 15.4, 7.0, 2.9 Hz, C^6H_2), 6.61 (1H, dd, *J* = 8.2, 1.5 Hz), 6.80 (1H, dd, *J* = 8.2, 7.7 Hz), 7.78 (1H, dd, *J* = 7.7, 1.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 22.1 (1C, -C^8H_2), 22.6 (1C, -C^9H_2), 23.1 (1C, -C^7H_2), 23.9 (1C, -$C^{10}H_2$), 34.4 (1C, -C^6H_2), 38.4 (1C, -C^5H_2), 109.7 (1C, Ar., C-10a), 113.4 (1C, Ar.,C-3), 118.1 (1C, Ar., C-2), 120.1 (1C, Ar., C-1), 125.2 (1C, Ar., C-3a), 127.0 (1C, Ar., C-10b), 130.8 (1C, Ar.,C-6b), 133.6 (1C, Ar.,C-3b), 197.1 (1C, C=O, C-4). MS (EI, 70 eV) *m/z* (%), 226 (M^++1, 2), 225 (M^+, 8), 224 (M^+-1, 33), 210 (65), 209 (M^+-CO, 10), 195 (100), 181 (28), 167 (15), 154 (13), 132 (2), 127 (17), 91 (4), 77 (6). Anal. Calcd. for $C_{15}H_{15}NO$ (225); C, 80.00; H, 6.66; N, 6.22. Found; C, 79.92; H, 6.70; N, 6.28%.

1,2-Dihydrobenzo[*kl*]acridin-3-one (5d). Yield 0.43 g (86%, method I), 0.62 g (83%, method II), 0.57 g (77%, method III); Brown crystals; 88%; mp 138-140 ºC (acetone); IR (KBr) ν_{max} 3070, 2930, 1700, 1601, 1572, 1470, 1455, 1319, 1282, 1162, 1070, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.16 (2H, ddd, *J* = 17.5, 6.9, 2.8 Hz,

C^1H_2), 3.41 (2H, ddd, *J* = 15.3, 6.8, 2.9 Hz, C^2H_2), 7.75 (1H, ddd, *J* = 7.9, 7.2, 1.5 Hz), 7.83 (1H, dd, *J* = 11.5, 7.0 Hz), 7.93 (1H, ddd, *J* = 8.5, 7.2, 1.7 Hz), 8.02 (1H, dd, *J* = 7.0, 1.4 Hz), 8.08 (2H, dddd, *J* = 8.5, 7.9, 1.5, 0.4 Hz), 8.25 (1H, dd, *J* = 11.5, 1.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 21.1 (1C, -C^1H_2), 34.4 (1C, -C^2H_2), 120.8 (1C, Ar.,C-11c), 121.6 (1C, Ar.,C-11a), 124.1 (1C, Ar.,C-10), 126.6 (3C, Ar.,C-4, C-8, C-9), 126.7 (1C, Ar.,C-5), 127.5 (1C, Ar.,C-11), 129.3 (2C, Ar.,C-3a, C-1), 130.5 (1C, Ar., C-11b), 145.6 (1C, Ar., C-7a), 147.7 (1C, Ar., C-6a), 197.3 (1C, C=O, C-3). MS (EI, 70 eV) *m/z* (%), 234 (M^++1, 9), 233 (M^+, 24), 207 (8), 205 (M^+-CO, 4), 204 (M^+-CO-H, 4), 193 (11), 182 (24), 165 (45), 152 (100), 134 (30), 91 (9), 77 (12). Anal. Calcd. for $C_{16}H_{11}NO$ (233); C, 82.40; H, 4.72; N, 6.00. Found; C, 82.50; H, 4.68; N, 5.97%.

1,2-Dihydropyrido[3,2,1-*de*]acridin-3(7*H*)-one (5e). Yield 0.44 g (89%, method I), 0.63 g (84%, method II), 0.59 g (78%, method III); Yellow crystals; 86%; mp 182-85 ºC (ethanol); IR (KBr) ν_{max} 3039, 2965, 1700, 1680, 1573, 1480, 1448, 1386, 1278, 1184, 1023, 812 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.73 (2H, ddd, *J* = 15.7, 6.7, 2.8 Hz, C^2H_2), 3.87 (2H, d, *J* = 16.4 Hz, C^1H_2), 3.97 (2H, ddd, *J* = 13.2, 6.7, 2.8 Hz, C^7H_2), 6.29 (1H, ddd, *J* = 8.1, 1.2, 0.5 Hz), 6.92 (1H, ddd, *J* = 7.9, 7.5, 1.2 Hz), 7.09 (2H, ddd, *J* = 8.1, 7.5, 1.4 Hz), 7.17 (1H, dd, *J* = 7.7, 1.2 Hz), 7.25 (1H, dd, *J* = 7.9, 7.7 Hz), 7.61 (1H, dd, *J* = 7.9, 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 35.4 (1C, -C^7H_2), 36.3 (1C, -C^2H_2), 44.3 (1C, -C^1H_2), 120.1 (1C, Ar.,C-5), 120.6 (1C, Ar.,C-9), 121.4 (1C, Ar.,C-11), 122.6 (1C, Ar.,C-3a), 124.3 (1C, Ar.,C-4), 125.8 (1C, Ar.,C-10), 127.5 (1C, Ar.,C-6), 128.2 (1C, Ar.,C-8), 129.0 (1C, Ar.,C-6a), 132.7 (1C, Ar.,C-7a), 138.1 (1C, Ar.,C-11c), 141.6 (1C, Ar.,C-11a), 190.6 (1C, C=O, C-3). MS (EI, 70 eV) *m/z* (%), 235 (M^+, 3), 234 (M^+-1, 23), 233 (M^+-2, 37), 209 (M^+-CO-1, 12), 194 (100), 183 (48), 179 (10), 165 (22), 108 (38), 91 (7), 77 (16). Anal. Calcd. for $C_{16}H_{13}NO$ (235); C, 81.70; H, 5.53; N, 5.95. Found; C, 81.74; H, 5.60; N, 5.87%.

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Supplementary Material

The supplementary material file available online contains copies of ^1H NMR, ^{13}C NMR and mass spectra of compounds **3a-e**, **4a-e**, **5a-e.**

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