ACID-MEDIATED CYCLOTRANSFORMATIONS OF 4a-SUBSTITUTED 4H-4a,5-DIHYDROINDENO[1,2-*b*]PYRIDINES AS A NEW ROUTE TO 9a-SUBSTITUTED 1H-FLUORENES

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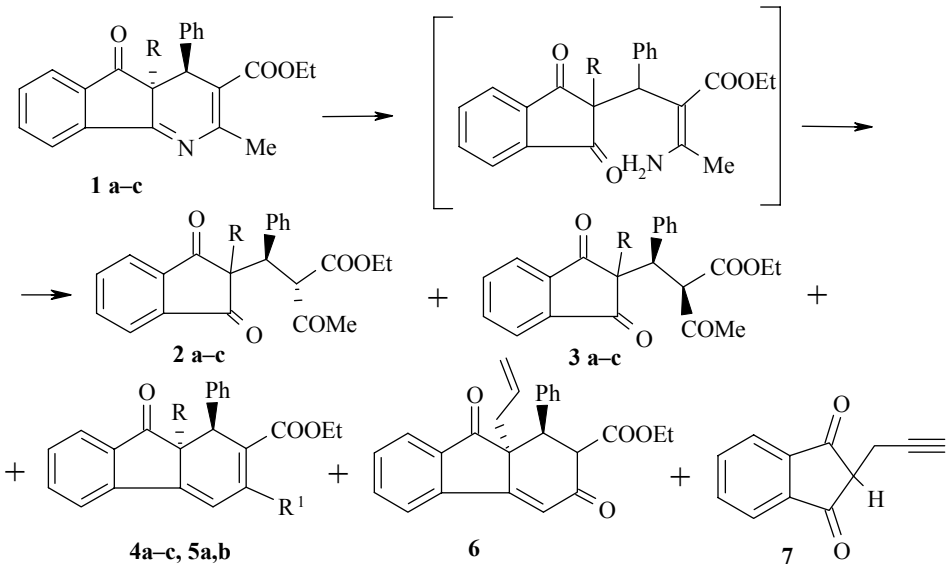
4a-Substituted dihydroindenopyridines undergo cleavage of the $C_{(9b)}$=N bond in water-containing acidic medium, resulting in the formation of diastereomeric ethyl α-acetyl-β-(2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-β-phenylpropionates and 9a-substituted 1,9a-dihydrofluore- none derivatives. The cyclization of α-acetyl-β-(2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-β-phenyl- propionates with benzylammonium acetate affords 3-benzylamino-1,9a-dihydrofluorenones. The methanobenzo[a]azulene compound is also found among cyclization products.

Keywords: 4a-substituted 1H-4a,5-dihydroindenopyridines, 9a-substituted 1H-fluorenes, methanobenzo-[*a*]azulene, cyclotransformation, recyclization.

Naturally occurring and synthetic estrogens have a broad therapeutic utility, including relief of menopausal symptoms, treatment of osteoporosis, and prevention of cardiovascular disease. Due to the fact that estrogen is therapeutically very valuable, great interest has been paid to compounds that mimic the estrogen-like behavior in estrogen-responsive tissues [1, 2]. Tetrahydro-3-oxo-9a-substituted-1H-fluorene derivatives are tried



1–5 a R = Me, **b** R = $CH_2CH=CH_2$; **1c–4c** R = $CH_2C\equiv CH$; **4 a–c** $R^1 = NH_2$, **5 a**,**b** R^1 = OH;

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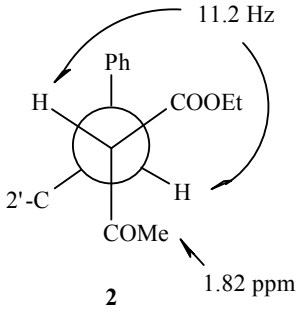
as agents for the treatment of brain edema caused by traumatic head injury [3]. Up to now a significant biological activity is revealed only within a narrow range of structural types of these compounds; therefore synthesis of new 9a-substituted fluorene derivatives is a logical way to establish the structure-activity relationships in this class of compounds. Besides, hydrofluorenones bearing an angular 9a-substituent are versatile building blocks of plant hormones within a gibberellin framework [[4]-6]. The main route to tetrahydrofluorenones is step-by-step ring annulation [3]. We have studied the hydrolysis of easily available 4a-substituted 5-oxo-1H-4a,5-dihydroindeno[1,2-*b*]pyridines as an alternative route to 9a-substituted fluorenes.

In our studies 4a-allyl, propargyl, and ethoxycarbonylmethyl derivatives of dihydroindeno-[1,2-*b*]pyridine have been selected as more suitable candidates for feasible gibbane ring construction. Compounds with *trans*-location of 4,4a-substituents [7] can be prepared by alkylation of the appropriate 5-oxo-1H-4,5-dihydroindenopyridine [8].

Acid hydrolysis of dihydroindenopyridines **1a–c** resulted in the cleavage of the azometine $C_{(9b)}$=N bond, which was followed by hydrolysis of the enamine moiety (main path) and accompanied by recyclization or retro-Michael reaction to a smaller extent. Hydrolysis of the open-chain intermediate afforded 2-alkyl-2-butanoylindandione diastereomers **2** and **3**.

The arrangement of substituents in the side chain of indandiones **2** and **3** was determined by NMR spectroscopy. The singlet corresponding to the isomer **2** acetyl group is shifted upfield under the influence of theindandione carbonyl function in comparison with the same singlet of isomer **3**.



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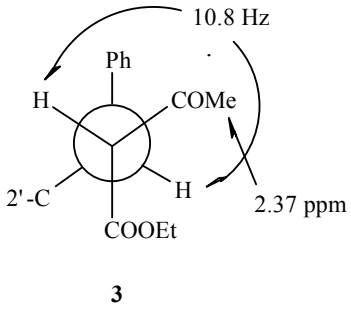

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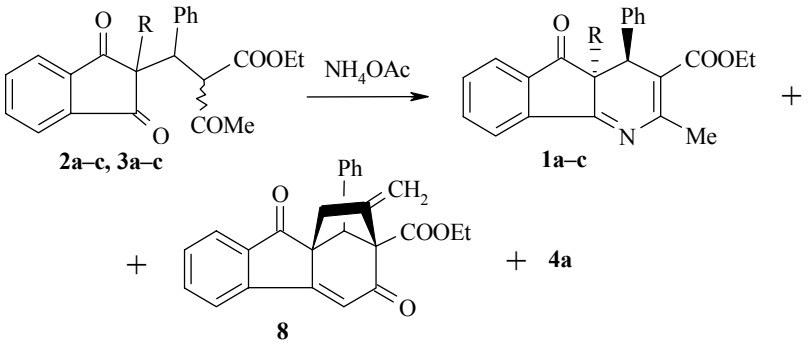
Open-chain enamine hydrolysis proceeds in parallel with intramolecular interaction between the terminal CH_3 and indandione CO groups. The interaction results in the formation of 9a-substituted 3-aminofluorenones **4**, unfortunately in low yield. A similar intramolecular condensation of indandione derivatives **2** or **3** affords fluorenedione **6** or the corresponding enol **5**. Besides the disubstituted indandiones and recyclization products **4-6**, 2-monosubstituted indandione **7** was found among the 4a-propargylindenopyridine **1c** hydrolysis products. 2-(3-Oxobutyl)indandiones **2** and **3** can be converted into fluoren-3-one derivative **6** according to the methods described in [9].

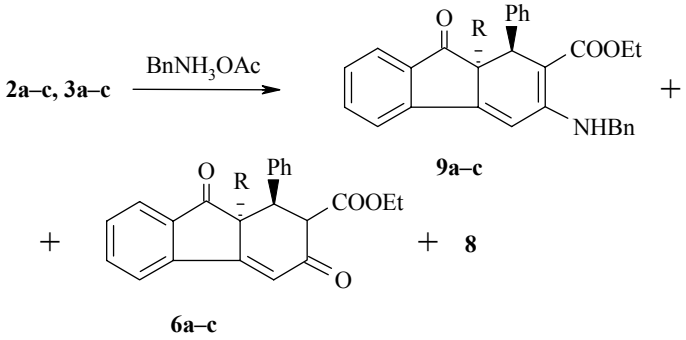
The enolates of ketones **6** are often used to construct the bridge between fluorene $C_{(2)}$ and $C_{(9a)}$ atoms. The electronic features of the mentioned enolates are similar to these of aminofluorenones **4**. Therefore, we tried to improve the outcome of these compounds by cyclization of indandione derivatives **2** and **3** with excess of ammonium acetate in acetic acid medium. 4a-Substituted indeno[1,2-*b*]pyridines **1a-c** were formed as the main reaction products in all the cases studied. However, the formation of 3-amino-9a-methylfluorenone **4a** (yield up to 15%) was also observed.

If propargyl derivatives **2c** and **3c** were used as starting compounds, besides indenopyridine **1c,** a gibbane-type bridged tetracycle, namely, 7,8,9,9a-tetra- hydro-7,9a-methanobenzo[*a*]azulene **8,** was isolated (yield 9%).

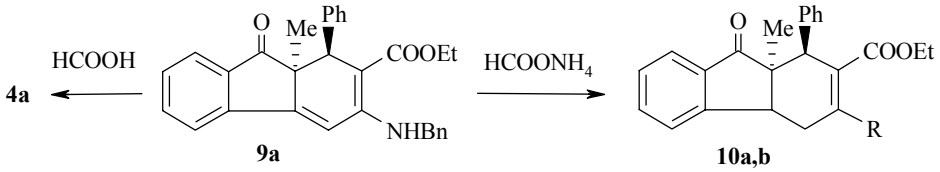
To suppress the pyridine ring formation, ammonium acetate was replaced by benzylammonium acetate. Under such conditions the formation of 3-amino- fluorenone derivative becames predominant and the corresponding benzyl- amino derivatives of 9a-methyl- and 9a-allylfluorenones **9a,b** were isolated in 60% yield.



N-Benzylaminofluorene formation proceeds simultaneously with cyclization, leading to 3-oxofluo-renone derivatives **6**. Transformation of 3-oxo- compounds **6** into aminoderivatives **9** did not proceed under the reaction conditions. Tetracyclic diketone **8** as a minor product was isolated after cyclization of propargylindandione **2c** and **3c**.

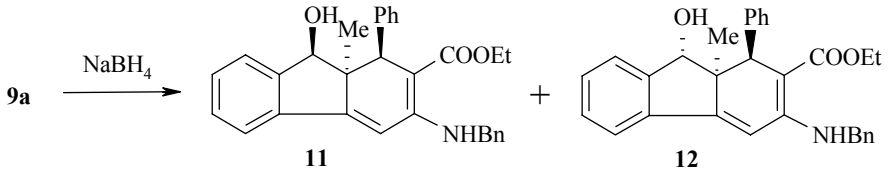


Debenzylation of fluorenes **9a** can be achieved by action of formic acid in the presence of Pd/C catalyst in methanol under reflux. Ammonium formate applied instead of formic acid under similar conditions at room temperature caused the hydrogenation of $C_{(4)}=C_{(4a)}$ bond and afforded benzylamino derivative **10b**. Debenzylation as the second process proceeded under reflux and compound **10a** was formed.

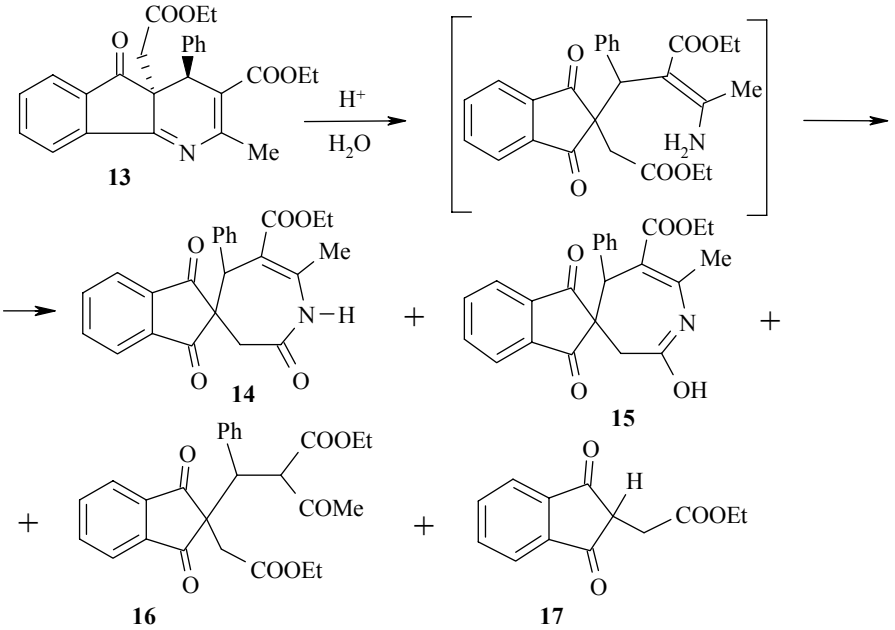


10 a R = NH_2, **b** R = NHBn

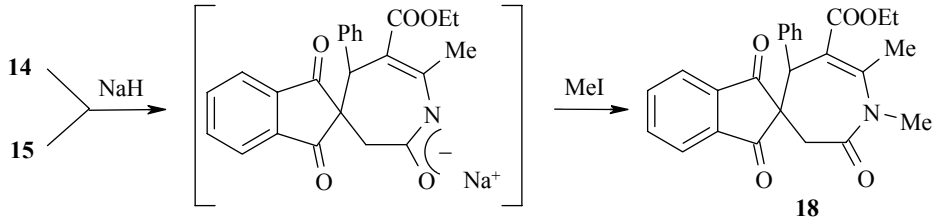
Reduction of 3-(N-benzylamino)fluorenone **9a** with $NaBH_4$ resulted in the formation of 9-hydroxy-diastereomers **11** and **12**. Substituents arrangement of compounds **11** and **12** was determined by NMR studies. In the ^{13}C NMR spectrum the signal corresponding to isomer **12** 9a-methyl group was shifted up-field (20.6 ppm) under the influence of the hydroxyl group in comparison with the same signal of isomer **11** (28.5 ppm), and the 9-H and 9a-CH_3 groups of isomer **11** exhibited a nuclear Overhauser effect. These facts assigned *trans* location of 9-OH and 9a-CH_3 groups in **11** and *cis*-location of these groups in **12**, respectively.



The behavior of 4a-indenopyridine **13** was different under acid hydrolysis conditions. The first act, i.e., hydrolytic breakage of the pyridine ring, was the same, but further transformation of open-chain enamine was different: 2,2-disubstituted indandione **16** as well as retro-Michael product **17** were formed as minors. The main course was an intramolecular interaction between the amino function and the ester carbonyl group, leading to amide formation and azepine ring closure. Spiro(azepine-4,2'-indandione) was isolated as lactam **14** as well as its enol form **15**.



Simultaneous existence of both forms is surprising, but transformation into the N-methyl derivative confirmed that treatment of azepinone derivatives **14** or **15** with NaH followed by interaction with methyl iodide gave the same product, i.e., azepinone **18** in both cases.



The transformation of 4a-allyl- and 4a-propargyl-5-oxo-1H-4a,5-dihydro- indeno[1,2-*b*]pyridines into 9a-substituted 1H-fluorene-9-one derivatives has been achieved *via* the acid-catalyzed pyridine ring opening/recyclization scheme. The cyclotransformation of 4a-ethoxycarbonylmethylindenopyridine did not give the expected gibbane skeleton. Instead, the hydrolytic breakage of the pyridine ring leads to the formation of spiro(azepine-4,2'-indandione) derivatives.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Brucker WH-90 (90 MHz, compounds **2a-c**, **3b,c**, **4b,c**, **5b**, **6a,c**, **7,8,9a,b**, **14-18,** ^{1}H), Varian Mercury-200 (200 and 50 MHz, compounds **14**, ^{1}H and ^{13}C; 200 MHz, compounds **6b**, **9c**, **10a,b,** ^{1}H), and Varian INOVA 600 (600 and 150 MHz, compounds **11**, **12**, ^{1}H and ^{13}C), spectrometers in DMSO-d_6 (compounds **7**, **17**) and $CDCl_3$ (all other compounds) using TMS as internal standard. IR spectra were recorded on a Perkin–Elmer 580 spectrometer as nujol mulls. Exact mass was determined on MS-50 AEI (70 eV) or on Waters-Quattro-Micro (electrospray) instrument.

Hydrolysis of ethyl 4-allyl-2-methyl-5-oxo-4-phenyl-4a,5-dihydro-4H-indeno[1,2-*b*]pyridine-3-carboxylate (**1b**). To a solution of 4a-allylindenopyridine **1b** (4.0 g, 10 mmol) in aqueous ethanol (EtOH/H_2O, 4:1, 250 ml) conc. HCl (5 ml, 52 mmol) was added. After reflux for 7 h the additional amount of conc. HCl (2 ml, 21 mmol) was added and refluxing was continued for 4 h. The reaction mixture, cooled and diluted with water (300 ml), was extracted with CH_2Cl_2 (4×50 ml). The combined organic extracts were dried and evaporated. The oily residue was treated with ether (100 ml) to obtain diastereomer **3b** (0.47 g after crystallization from methanol). The filtrate was evaporated and the residue was chromatographed (ethyl acetate–petroleum ether, 3:20). From the first fraction 3-hydroxyfluorenone **5b** (0.02 g, 0.5%) was obtained, from the second – diastereomer **3b** (0.35 g). The third fraction was an unresolved mixture of diastereomers **2b** and **3b**. From the fourth fraction diastereomer **2b** (0.33 g) was isolated, the fifth one afforded 3-oxofluorenone **6b** (0.02 g, 0.5%), and the sixth gave 3-aminofluorenone **4b** (0.11 g, 3%). Resolution (ethanol-ethyl acetate–petroleum ether, 1:10:150) of diastereomers **2b** and **3b** mixture gave additionally 0.7 g of **3b** (overall yield 38%) and 0.45 g of **2b** (overall yield 23%).

Ethyl *trans*-α-acetyl-β-(2-allyl-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-β-phenylpropionate (**2b**). White solid. Mp 92–94°C (MeOH). IR spectrum, ν, cm^{-1}: 1740 and 1703 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 1.82 (3H, s, $COCH_3$); 2.47 (2H, d, *J* = 6.6, 2-CH_2); 4.00 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.23 (1H, d, *J* = 11.2, H-3); 4.71 (1H, d, *J* = 11.2, H-2); 4.71-5.27 (3H, m, CH_2=CH); 6.89-7.22 (5H, m, Ph); 7.49-8.00 (4H, m, H-4',5',6',7'). Found, %: C 73.80; H 5.95. $C_{25}H_{24}O_5$. Calculated, %: C 74.24; H 5.98.

Ethyl *cis*-α-acetyl-β-(2-allyl-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-β-phenylpropionate (**3b**). White solid. Mp 93-94°C (MeOH). IR spectrum, ν, cm^{-1}: 1742, 1720, 1700 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.73 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.08-2.68 (5H, m, 2-CH_2, $COCH_3$); 3.69 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.29 (1H, d, *J* = 11.2, H-3); 4.58-4.78 (2H, m, $C\underline{H_2}$=CH); 4.91 (1H, d, *J* = 11.2, H-2); 4.91–5.46 (1H, m, CH_2=C$\underline{H}$); 6.87-7.18 (5H, m, C_6H_5); 7.58-8.02 (4H, m, H-4',5',6',7'). Found, %: C 74.14; H 5.94. $C_{25}H_{24}O_5$. Calculated, %: C 74.24; H 5.98.

Ethyl 9a-allyl-3-amino-9-oxo-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**4b**). Dark yellow solid. Mp 187-188°C (*i*-PrOH). IR spectrum, ν, cm^{-1}: 3420, 3300 (NH_2); 1705, 1668 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.17 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.64 (2H, d, *J* = 6.8, 9a-CH_2); 4.08 (2H, m, $O\underline{CH_2}CH_3$); 4.47 (1H, s, H-1); 4.92 (1H, m, $\underline{CH_2}$=CH); 5.02 (1H, m, $\underline{CH_2}$=CH); 5.31-5.87 (1H, m, CH_2=$\underline{CH}$); 6.56 (1H, s, H-4); 6.94-7.93 (11H, m, 4-C_6H_5, H-5,6,7,8, 3-NH_2). Mass spectrum, (ES), *m/z* (*I*, %): calculated – 386 $[M+H]^+$, 408 $[M+Na]^+$; found – 385.9 $[M+H]^+$, 407.9 $[M+Na]^+$.

Ethyl 9a-allyl-3-hydroxy-9-oxo-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**5b**). Yellow solid. Mp 145–147°C (MeOH). IR spectrum, ν, cm^{-1}: 1710 and 1659 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.18 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.62 (2H, d, *J* = 6.8, 9a-CH_2); 4.15 (2H, m, $O\underline{CH_2}CH_3$); 4.33 (1H, s, H-1); 4.92 (1H, m, $\underline{CH_2}$=CH); 5.02 (1H, m, $\underline{CH_2}$=CH); 5.31-5.86 (1H, m, CH_2=$\underline{CH}$); 6.69 (1H, s, H-4); 6.91-7.20 (5H, m, C_6H_5); 7.31-8.00 (4H, m, H-5,6,7,8). Found, %: C 77.42; H 5.75. $C_{25}H_{22}O_4$. Calculated, %: C 77.70; H 5.74.

Ethyl 9a-allyl-3,9-dioxo-1-phenyl-2,3,9,9a-tetrahydro-1H-fluorene-2-carboxylate (**6b**). White solid. Mp 149-150°C (MeOH). IR spectrum, ν, cm^{-1}: 1728, 1658, 1640 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.94 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.70 (1H, dd, *J* = 7.3, *J* = 13.0, 9a-CH_2); 2.76 (1H, dd, *J* = 7.3, *J* = 13.0, 9a-CH_2); 3.90-4.03 (1H, d, *J* = 13.0, H-2 and 2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$,); 4.31 (1H, d, *J* = 13.0, H-1); 4.66-4.94 (2H, m, $\underline{CH_2}$=CH); 5.02-5.25 (1H, m, CH_2=$\underline{CH}$); 6.59 (1H, s, H-4); 7.24-7.44 (5H, m, C_6H_5); 7.58-7.85 (4H, m, H-5,6,7,8). Found, %: C 77.59; H 5.61. $C_{25}H_{22}O_4$. Calculated, %: C 77.70; H 5.74.

Ethyl 2-methyl-5-oxo-4-phenyl-4a-prop-2-ynyl-4a,5-dihydro-4H-indeno[1,2-*b*]pyridine-3-carboxylate (**1c**) was hydrolyzed following the same procedure as described for **1b**, and the 4a-prop-2-ynylindenopyridine (1.90 g, 5 mmol) **1c** was refluxed with conc. HCl for 14 h. Three fractions were obtained after chromatography (ethyl acetate–petroleum ether, 3:20). The first fraction was a mixture of indandione **7** and the starting material, the second one being the mixture of diastereomers **2c** and **3c**. The third fraction afforded 3-aminofluorenone **4c** (0.02 g, 1% after crystallization from methanol). The chromatography of the mixtures mentioned afforded indandione **7** (0.05 g, 5%) and 4a-prop-2-ynylindenopyridine **1c** (0.01 g, 0.5%, elution with petroleum ether–chloroform, 2:1), as well as both diastereomers **2c** (0.36 g, 18%) and **3c** (0.46 g, 23%, elution with ethanol–ethyl acetate–petroleum ether, 1:30:150).

Ethyl *trans*-α-acetyl-β-(2,3-dihydro-1,3-dioxo-2-(prop-2-ynyl)-1H-inden-2-yl)-β-phenylpropionate (**2c**). White solid. Mp 106-110°C (EtOH). IR spectrum, ν, cm^{-1}: 3289 (≡CH); 2105 (C≡C); 1740, 1730, 1703 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.18 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 1.55 (1H, t, *J* = 2.2, ≡CH); 1.81 (3H, s, $COCH_3$); 2.55 (2H, d, *J* = 2.2, $\underline{CH_2}C\equiv$); 3.93 (1H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 3.95 (1H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.20 (1H, d, *J* = 11.2, H-3); 4.63 (1H, d, *J* = 11.2, H-2); 6.95–7.24 (5H, m, C_6H_5); 7.62-8.00 (4H, m, H-4',5',6',7'). Found, %: C 74.26; H 5.48. $C_{25}H_{22}O_5$. Calculated, %: C 74.61; H 5.51.

Ethyl *cis*-α-acetyl-β-(2,3-dihydro-1,3-dioxo-2-(prop-2-ynyl)-1H-inden-2-yl)-β-phenylpropionate (**3c**). White solid. Mp 81-85°C (MeOH/hexane). IR spectrum, ν, cm^{-1}: 3282 (≡CH); 2105 (C≡C); 1748, 1735, 1710 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.81 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 1.62 (1H, t, *J* = 2.6, ≡CH); 2.33 (3H, s, $COCH_3$); 2.46 (1H, dd, *J* = 2.6, *J* = 16.2, $CH_2C\equiv$); 2.72 (1H, dd, *J* = 2.6, *J* = 16.2, $CH_2C\equiv$); 3.74 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.24 (1H, d, *J* = 11.0, H-3); 4.84 (1H, d, *J* = 11.0, H-2); 6.91-7.20 (5H, m, C_6H_5); 7.62-8.00 (4H, m, H-4',5',6',7'). Found, %: C 74.47; H 5.46. $C_{25}H_{22}O_5$. Calculated, %: C 74.61; H 5.51.

Ethyl 3-amino-9-oxo-1-phenyl-9a-(prop-2-ynyl)-9,9a-dihydro-1H-fluorene-2-carboxylate (**4c**). Dark yellow solid. Mp 162-164°C (MeOH/hexane). IR spectrum, ν, cm^{-1}: 3480, 3350 (NH_2); 3260 (C≡H); 1718, 1662 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 1.71 (1H, t, *J* = 2.2, ≡CH); 2.73 (1H, dd, *J* = 2.2, *J* = 15.8, $CH_2C\equiv$); 2.98 (1H, dd, *J* = 2.2, *J* = 15.8, $CH_2C\equiv$); 4.04 (1H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.09 (1H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.44 (1H, s, H-1); 6.29-6.78 (2H, bs, NH_2); 6.55 (1H, s, H-4); 6.93-7.88 (9H, m, 4-C_6H_5, H-5,6,7,8). Mass spectrum (AEI), *m/z* (I_{rel}, %): 383 $[M]^{+\cdot}$ (10), 338 $[M–OEt]^+$ (100), 310 $[M–COOEt]^+$ (46).

2-(Prop-2-ynyl)indan-1,3-dione (**7**). White solid. Mp 109-110°C (MeOH). IR spectrum, ν, cm^{-1}: 3250 (≡CH); 1745, 1710 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.78 (1H, t, *J* = 2.4, ≡CH); 2.78–3.22 (3H, m, H-2, 2-CH_2); 7.73-8.13 (4H, m, H-4,5,6,7). Mass spectrum (AEI), *m/z* (I_{rel}, %): 184 $[M]^{+\cdot}$ (100), 156 (62), 128 (47), 104(97).

Ethyl 4a-ethoxycarbonylmethyl-5-oxo-4-phenyl-4a,5-dihydro-4H-indeno[1,2-*b*]pyridine-3-carboxylate (**13**) (2.15 g, 5 mmol) was hydrolyzed with conc. HCl (2.4 eq) for 5 h as described for compound **1b**. Extraction and evaporation of the reaction mixture followed by treatment with MeOH afforded azepinol **15** (0.70 g). After column chromatography ($CHCl_3$) of filtrate, the evaporated two fractions were collected as a mixture of indandiones **16** and **17,** as well as a mixture of azepines **14** and **15**. Repeated chromatography afforded 0.14 g (14%) of **17** and 0.04 g (2%) of **16** (ethyl acetate–petroleum ether, 3:20) from the first fraction; from the second fraction 0.09 g (4%) of **14** and 0.08 g (overall yield 42%) of **15** (ethyl acetate–petroleum ether, 7:20) were isolated.

Spiro(6-ethoxycarbonyl-7-methyl-2-oxo-5-phenyl-1H-2,3,4,5-tetrahydroazepine-4,2'-indan-1',3'-dione) (**15**). White solid. Mp ~200°C (decomposition), MeOH. IR spectrum, ν, cm^{-1}: 3300 (NH); 1798, 1728 (C=O); 1640 (N–C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.14 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.27 (3H, s, 7-CH_3); 2.33 (1H, d, *J* = 17.0, 3-CH_2); 2.69 (1H, d, *J* = 17.0, 3-CH_2); 4.02 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.71 (1H, s, H-5); 4.86 (1H, bs, NH); 7.07-7.60 (5H, m, C_6H_5); 7.60-7.99 (4H, m, H-4',5',6',7'). Mass spectrum (AEI), *m/z* (I_{rel}, %): 403 $[M]^{+\cdot}$ (20), 374 (24), 348 $[M–OEt]^+$ (36), 330 $[M–COOEt]^+$ (34), 298 (100), 284 (44).

Spiro(6-ethoxycarbonyl-2-hydroxy-7-methyl-5-phenyl-1H-2,3,4,5-tetrahydroazepine-4,2'-indan-1',3'-dione) (**14**). White solid. Mp 200-210°C (decomposition), MeOH. IR spectrum, ν, cm^{-1}: 3233 (OH); 1760, 1730, 1670 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.13 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.51 (3H, s, 7-CH_3); 3.04 (1H, d, *J* = 18.0, 3-CH_2); 3.38 (1H, d, *J* = 18.0, 3-CH_2); 4.06 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.42 (1H, s, H-5); 6.83 (5H, m, C_6H_5); 7.24-7.38 (2H, m, H-5',6'); 7.51-7.80 (2H, m, H-4',7'). ^{13}C NMR spectrum, δ, ppm: 14.1 ($OCH_2\underline{C}H_3$); 20.5 ($H_3\underline{C}C$=); 38.2 (C-3); 44.7 (C-5); 59.1 (C-4); 59.9 ($O\underline{C}H_2CH_3$); 95.5 (C-7); 100.7 (C-6); 122.8; 123.5; 126.8; 127.5; 129.0; 130.7; 135.7; 138.2; 148.5; 151.5 (arom. protons), 167.3 (COOEt); 173.7 (C-2); 202.2 (C=O). Mass spectrum (AEI), *m/z* (I_{rel}, %): 403 $[M]^{+\cdot}$ (19), 358 $[M–OEt]^+$ (23), 330 $[M–COOEt]^+$ (81), 298 (100), 284 (72). Found, %: C 71.34; H 5.22; N 3.34. $C_{24}H_{21}NO_5$. Calculated, %: C 71.45; H 5.25; N 3.47.

Ethyl α-acetyl-β-(2,3-dihydro-1,3-dioxo-2-(ethoxycarbonyl)methyl-1H-inden-2-yl)-β-phenylpropionate (**16**). White solid. Mp 139-142°C (MeOH). IR spectrum, ν, cm^{-1}: 1744, 1723, 1709 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.70 (3H, t, *J* = 7.0, $CH_2COOCH_2\underline{CH_3}$); 1.00 (3H, t, *J* = 7.0, $COOCH_2\underline{CH_3}$); 2.34 (3H, s, $COCH_3$); 2.76 (1H, d, *J* = 17.2, H-3); 3,09 (1H, d, *J* = 17.2, H-2); 3.67 (2H, q, *J* = 7.0, $CH_2COO\underline{CH_2}$); 3.85 (2H, q, *J* = 7.0, $COOCH_2$); 4.13 (1H, d, *J* = 10.4, 2'-CH_2); 4.47 (1H, d, *J* = 10.4, 2'-CH_2); 6.99 (5H, s, C_6H_5); 7.58–7.98 (4H, m, H-4',5',6',7'). Found, %: C 69.03; H 5.87. $C_{26}H_{26}O_7$. Calculated, %: C 69.32; H 5.82.

Ethyl (1,3-dioxoindan-2-yl)acetate (**17**). White solid. Mp 94-96°C (MeOH). IR spectrum, ν, cm^{-1}: 1750, 1710 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.00 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 3.04 (2H, d, *J* = 3.8, 2-CH_2); 3.71 (1H, t, *J* = 3.8, CH); 3.93 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 8.00 (4H, s, H-4',5',6',7'). Found, %: C 66.89; H 5.21. $C_{13}H_{12}O_4$. Calculated, %: C 67.23; H 5.21.

Hydrolysis of ethyl 4a-methyl-5-oxo-4-phenyl-4a,5-dihydro-4H-indeno[1,2-*b*]pyridine-3-carboxylate (**1a**). As described above, 4a-methylindenopyridine **1a** (1.00 g, 3.0 mmol) was refluxed with conc. HCl (2.6 eq) for 5 h. After the usual workup and repeated chromatography (ethyl acetate–petroleum ether, 3:20, and ethanol–ethyl acetate–petroleum ether, 1:7.5:40, for resolution of diastereomers) 3-hydroxyfluorenone **5a** (0.04 g, 4%), diastereomer **2a** (0.48 g, 46%), diastereomer **3a** (0.21 g, 20%), and 3-aminofluorenone **4a** (0.05 g, 5%) were isolated.

Ethyl *cis*-α-acetyl-β-(2,3-dihydro-1,3-dioxo-2-methyl-1H-inden-2-yl)-β-phenylpropionate (**2a**). White solid. Mp 65-66°C (50% aq. MeOH). IR spectrum, ν, cm^{-1}: 1745, 1724, 1705 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.76 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 1.10 (3H, s, 4a-CH_3); 2.34 (3H, s, $COCH_3$); 3.72 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.25 (1H, d, *J* = 11.2, H-3); 4.88 (1H, d, *J* = 11.2, H-2); 6.90-7.28 (5H, m, C_6H_5); 7.61-7.97 (4H, m, H-4',5',6',7'). Found, %: C 73.12; H 6.02. $C_{23}H_{22}O_5$. Calculated, %: C 73.00; H 5.86.

Spiro(6-ethoxycarbonyl-1,7-dimethyl-2-hydroxy-5-phenyl-1H-2,3,4,5-tetrahydroazepine-4,2'-indan-1',3'-dione) (**18**). A (from **15**). A mixture of spirocompound **15** (0.40 g, 1.0 mmol) and NaH (0.05 g, 60% dispersion in mineral oil, 1.2 mmol) was stirred in dry DMF (2 ml) at room temperature for 15 min. MeI (0.12 ml, 2.0 mmol) was introduced into the dark red suspension and stirring was continued for 1 h. Then the water-diluted (20 ml) reaction mixture was extracted with EtOAc (5×10 ml). The combined organic extract was washed with brine (3×15 ml), dried, and evaporated. The residue was treated with EtOH to obtain spirocompound **18** (0.27 g, 65%, crystallyzed from EtOH) as a yellow solid, mp 129–130°C. IR spectrum, ν, cm^{-1}:1742, 1720, 1700 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.17 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.67 (3H, d, ^5J = 1.2, 7-CH_3); 2.95 (2H, s, 3-CH_2); 3.38 (3H, s, N–CH_3); 4.11 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.39 (1H, bs, H-5); 6.75-7.13 (5H, m, C_6H_5); [7.40-7.82 (2H, m) and 8.00-8.20 (1H, m) H-4',5',6',7']. Found, %: C 71.47; H 5.55; N 3.28. $C_{25}H_{23}NO_5$. Calculated, %: C 71.93; H 5.55; N 3.36.

B (from **14**). In a manner similar to Method A, NaH and MeI were sequentially added to the solution of spirocompound **14** in DMF to obtain compound **18** (51%).

Reaction of ethyl *cis*-α-acetyl-β-(2-allyl-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-β-phenylpropionate (**3b**) **with NH_4OAc.** A mixture of compound **3b** (0.40 g, 1 mmol) and NH_4OAc (0.40 g, 5 mmol) in AcOH (1 ml) was heated at 100°C for 4 h, then cooled to room temperature and diluted with water (50 ml). Indenopyridine **1b** (0.32 g, 84%) was filtered off. Mp 150-152°C (149-150°C [8]).

Following the above procedure, 4a-allylindenopyridine **1b** (92%, mp 150-152°C (149-150°C [8])) was prepared from compound **2c,** and **1c** (92%, mp 194-195°C (195-197°C [8])) – from compound **3c**.

Reaction of ethyl *trans*-α-acetyl-β-(2,3-dihydro-1,3-dioxo-2-(prop-2-ynyl)-1H-inden-2-yl)-β-phenylpropionate (**2c**) **with NH_4OAc**. Compound **2c** (0.36 g, 0.9 mmol) and NH_4OAc (0.40 g, 4.9 mmol) were heated for 10 h following the same procedure as in the case of ester **3b**. The solid obtained was treated with petroleum ether (50 ml) and crystallized from ethanol to give 4a-(prop-2-ynyl)indenopyridine **1c** (0.21 g). The filtrate was evaporated and subjected to column chromatography (ethyl acetate–petroleum ether, 3:20) to yield benzoazulene **8** (0.03 g, 9%) and compound **1c** (0.04 g, overall yield 72%).

Ethyl 6,10-dioxo-8-methylene-11-phenyl-7,8,9,9a-tetrahydro-7,9a-methanobenzo[*a*]azulene-7-carboxylate (**8**). White solid. Mp 135-1136°C (MeOH). IR spectrum, ν, cm^{-1}: 1740, 1710, 1665 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.55 (1H, d, *J* = 14.4, 9-CH_2); 3.31 (1H, dt, *J* = 2.2, *J* = 14.4, 9-CH_2); 4.19 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.58 (1H, s, H-11); 5.29 (1H, bs, =CH_2); 5.78 (1H, bs, =CH_2); 6.44 (1H, s, H-5); 7.09 (5H, s, 11-C_6H_5); 7.33-8.00 (4H, m, Ar). Found, %: C 78.12; H 5.08. $C_{25}H_{20}O_4$. Calculated, %: C 78.11; H 5.24.

Reaction of ethyl α-acetyl-β-(2-allyl-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-β-phenylpropionates (**2b and 3b**) **with benzylammonium acetate**. A mixture of ethyl *cis*- and *trans*-(2-allyl-1H-inden-2yl)propionates **2b** and **3b** (2.00 g, 5 mmol) and benzylammonium acetate (3.6 M in AcOH, 12 eq, 16 ml) in glacial AcOH was heated with stirring at 65-70°C for 6.5 h. After cooling to room temperature the red reaction mixture was diluted with water (40 ml) and extracted with CH_2Cl_2 (4×30 ml). The organic phase was dried and evaporated (addition of toluene, 2×50 ml facilitated the evaporation of acetic acid). The red-brown residue was chromatographed (ethyl acetate–petroleum ether–CH_2Cl_2, 1:2:7) to obtain 3-benzylaminofluorenone **9b** (1.45 g, 62%) and 3-oxofluorenone **5b** (0.12 g, 6%).

Ethyl 9a-allyl-3-benzylamino-9-oxo-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**9b**). Yellow solid. Mp 73-74°C (*i*-PrOH). IR spectrum, ν, cm^{-1}: 3300 (NH); 1720, 1665 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.28 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 2.61 (2H, d, *J* = 7.1, CH_2); 4.02 (1H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.04 (1H, q, *J* = 7.0, $O\underline{CH_2}CH_3$); 4.43 (1H, s, H-1); 4.50–4.99 (4H, m, =CH_2, $\underline{CH_2}$Ph); 5.10–5.67 (1H, m, =CH); 6.76 (1H, s, H-4); 6.88–7.09 (5H, m, C_6H_5); 7.09–7.69 (m, 9H, Ar); 9.42 (1H, bs, NH). Found, %: C 80.70; H 6.06; N 2.66. $C_{32}H_{29}NO_3$. Calculated, %: C 80.82; H 6.15; N 2.95.

Reaction of ethyl *trans*-α-acetyl-β-(2,3-dihydro-1,3-dioxo-2-methyl-1H-inden-2-yl)-β-phenylpropionate (**2a**) **with benzyl ammonium acetate** was performed as described above. 3-Benzylaminofluorenone **9a** (1.51 g, 63%) and 3-oxofluorenone **6a** (0.27 g, 14%) were obtained from ethyl-2-methyl-1H-indene-2-propionate **2a** (2.00 g, 5 mmol) and benzyl ammonium acetate (9 ml, 6 eq).

Ethyl 3-benzylamino-9a-methyl-9-oxo-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**9a**). Yellow solid. Mp 124-125°C (MeOH). IR spetrum, ν, cm^{-1}: 3280 (NH); 1725, 1718 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.10 (3H, t, *J* = 7.2, $OCH_2\underline{CH_3}$); 1.35 (3H, s, 9a-CH_3); 4.01 (2H, q, *J* = 7.2, $O\underline{CH_2}CH_3$); 4.34 (1H, s, H-1); 4.63 (2H, d, *J* = 6.9, $\underline{CH_2}$Ph); 6.77 (1H, s, H-4); 6.83-7.74 (14H, m, Ar). Found, %: C 79.85; H 5.96; N 2.88. $C_{30}H_{27}NO_3$. Calculated, %: C 80.15; H 6.05; N 3.12.

Ethyl 9a-methyl-3,9-dioxo-1-phenyl-2,3,9,9a-tetrahydro-1H-fluorene-2-carboxylate (**6a**). White solid. Mp 177-178°C (MeOH). IR spectrum, ν, cm^{-1}: 1730, 1720, 1660 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.92 (3H, t, *J* = 7.2, $OCH_2\underline{CH_3}$); 1.42 (3H, s, 9a-CH_3); [3.90 (1H, d, *J* = 12.4) and 4.19 (1H, d, *J* = 12.4) H-1 and H-2]; 3.94 (2H, q, *J* = 7.2, $O\underline{CH_2}CH_3$); 6.50 (1H, s, H-4); 7.32 (5H, s, C_6H_5); 7.50-7.94 (4H, m, H-5,6,7,8). Found, %: C 76.39; H 5.49. $C_{23}H_{20}O_4$. Calculated, %: C 76.65; H 5.59.

Reaction of ethyl α-acetyl-β-(2,3-dihydro-1,3-dioxo-2-(prop-2-ynyl)-1H-inden-2-yl)-β-phenylpropionates (**2c and 3c**) **with benzyl ammonium acetate** was performed as described above. 3-Benzylaminofluorenone **9c** (0.63 g, 27%), benzoazulene **8** (0.26 g, 13%), and 3-oxofluorenone **6c** (0.09 g, 5%) were obtained from ethyl 2-(prop-2-ynyl)-1H-inden-2-ylpropionates **2c** and **3c** (2.00 g, 5 mmol) and benzyl ammonium acetate (18 eq, 25 ml).

Ethyl 3-benzylamino-9-oxo-1-phenyl-9a-(prop-2-ynyl)-9,9a-dihydro-1H-fluorene-2-carboxylate (**9c**). Yellow solid. Mp 117–119°C (MeOH). IR spectrum, ν, cm^{-1}: 3440 (NH); 3280 (≡CH); 1730 and 1665 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, t, *J* = 7.1, $OCH_2\underline{CH_3}$); 1.70 (1H, t, *J* = 2.6, ≡CH); 2.79 (1H, dd, *J* = 16.3, *J* = 2.6, CH_2–C≡); 2.93 (1H, dd, *J* = 16.3, *J* = 2.6, CH_2–C≡); 4.04 (2H, m, $O\underline{CH_2}CH_3$); 4.45 (1H, s, H-1); 4.70 (2H, m, $\underline{CH_2}Ph$); 6.87 (1H, s, H-4); 6.94-7.79 (14H, m, arom. prot.); 9.47 (1H, bs, NH). Found, %: C 81.15; H 5.69; N 2.73. $C_{32}H_{27}NO_3$. Calculated, %: C 81.16; H 5.75; N 2.96.

Ethyl 3,9-dioxo-1-phenyl-9a-(prop-2-ynyl)-2,3,9,9a-tetrahydro-1H-fluorene-2-carboxylate (**6c**). White solid. Mp 168-169°C (MeOH). IR spectrum, ν, cm^{-1}: 3280 (≡CH); 1750, 1720 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 1.99 (1H, t, *J* = 2.6, ≡CH); 2.48 (1H, dd, *J* = 16.3, *J* = 2.6, CH_2–C≡); 3.45 (1H, dd, *J* = 16.3, *J* = 2.6, CH_2–C≡); 3.94 (2H, q, *J* = 7.02, $O\underline{CH_2}CH_3$); [3.99 (1H, d, *J* = 13.0) and 4.59 (1H, d, *J* = 13.0) H-1 and H-2]; 6.61 (1H, s, H-4); 7.32 (5H, s, C_6H_5); 7.46–7.99 (4H, m, H-5,6,7,8). Found, %: C 78.13; H 5.19. $C_{25}H_{20}O_4$. Calculated, %: C 78.11; H 5.24.

Ethyl 3-amino-9a-methyl-9-oxo-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**4a**) **by reduction of ethyl 3-benzylamino-9a-methyl-9-oxo-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate** (**9a**). A solution of 3-benzylaminofluorenone **9a** (1.00 g, 2 mmol) in methanol (60 ml) was refluxed with Pd/C (0.3 g, three portions of 0.1 g were added after every 10 h) and HCOOH (5.5 ml) for 32 h. The hot reaction mixture was filtered off and filtrate was evaporated. The residue crystallized from MeOH gave 3-aminofluorenone **4a** (0.67 g, 84%). Mp 183-184°C (184-186°C [8]).

Ethyl 3-benzylamino-9a-methyl-9-oxo-1-phenyl-4,4a,9,9a-tetrahydro-1H-fluorene-2-carboxylate (**10b**). To 3-benzylaminofluorenone **9a** (100 mg, 0.22 mmol) dissolved in MeOH (20 ml) Pd/C (26 mg) and $HCOONH_4$ (80 mg, 1.27 mmol) were added. After being stirred for 3.5 h the reaction mixture was filtered off and the filtrate was evaporated. The yellow oil obtained was crystallyzed from MeOH to give fluorenone **10b** (80 mg, 81%) as a white solid, mp 99-100°C. IR spectrum, ν, cm^{-1}: 3280 (NH); 1720, 1650 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.21 (3H, t, *J* = 7.1, $OCH_2\underline{CH_3}$); 1.45 (3H, s, 9a-CH_3); 2.62 (1H, dd, *J* = 15.9, *J* = 8.8, CH_2); 3.05 (1H, t, *J* = 8.8, H-4); 3.25 (1H, dd, *J* = 15.9, *J* = 8.8, CH_2); 4. 09 (2H, m, $O\underline{CH_2}CH_3$); 4.50 (1H, s, H-1); 4.61 (2H, d, *J* = 6.5, $\underline{CH_2}Ph$); 6.87 (5H, s, C_6H_5); 7.14-7.52 (9H, m, H-5,6,7,8, C_6H_5); 9.64 (1H, t, *J* = 6.5, NH). Mass spectrum (ES), *m/z* (*I*, %): calculated – 452 $[M+H]^+$, 474 $[M+Na]^+$; found – 451.9 $[M+H]^+$, 473.9 [M+Na].

Ethyl 3-amino-9a-methyl-9-oxo-1-phenyl-4,4a,9,9a-tetrahydro-1H-fluorene-2-carboxylate (**10a**). 3-Benzylaminofluorenone (200 mg, 0.44 mmol) dissolved in MeOH (20 ml), Pd/C (20 mg) and $HCOONH_4$ (120 mg, 1.90 mmol) were refluxed for 4.5 h. The hot reaction mixture was filtered off and the filtrate was evaporated. The residue crystallyzed from MeOH afforded fluorene **10a** (70 mg, 44%) as a white solid, mp 153-154°C. IR spectrum, ν, cm^{-1}: 3420, 3310 (NH_2), 1700, 1660 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.21 (3H, t, *J* = 7.1, $OCH_2\underline{CH_3}$); 1.48 (3H, s, 9a-CH_3); 2.82 (1H, dd, *J* = 16.2, *J* = 9.4, CH_2); 3.01 (1H, dd, *J* = 16.2, *J* = 9.0, CH_2); 3.31 (1H, dd, *J* = 9.4, *J* = 9.0, H-4a); 4.10 (2H, m, $O\underline{CH_2}CH_3$); 4.44 (1H, s, H-1); 6.46 (2H, bs, NH_2); 6.89 (5H, s, C_6H_5); 7.17-7.59 (4H, m, H-5,6,7,8). Found, %: C 76.45; H 6.41; N 3.72. $C_{23}H_{23}NO_3$. Calculated, %: C 76.43; H 6.41; N 3.88.

Reduction of ethyl 3-benzylamino-9a-methyl-9-oxo-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**9a**) **with $NaBH_4$**. 3-Benzylaminofluorenone **9a** (0.8 g, 1.8 mmol) and $NaBH_4$ (0.68 g, 17.9 mmol) in *i*-PrOH (30 ml) were refluxed for 8.5 h. A fresh portion of $NaBH_4$ (0.34 g, 8.95 mmol) was added and refluxing was continued for additional 9 h. After cooling to room temperature and diluting with water (40 ml) the reaction mixture was extracted with EtOAc (4×30 ml). The combined organic extract was washed with water (2×20 ml), dried and evaporated. Chromatography (CH_2Cl_2) of the yellow oil obtained gave starting material **9a** (0.04 mg, 5%), 9-hydroxyfluorenone **11** (0.30 g, 38%, after drying in vacuo), and 9-hydroxy- fluorenone **12** (0.24 mg, 30%, after drying in vacuo).

Ethyl 3-benzylamino-9-hydroxy-9a-methyl-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**11**). Yellow solid. Mp 98-100°C (*i*-PrOH). IR spectrum, ν, cm^{-1}: 3560 (NH), 3480 (OH), 1655 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.69 (1H, bs, OH); 1.21 (3H, s, 9a-CH_3); 1.23 (3H, t, *J* = 7.3, $OCH_2\underline{CH_3}$); 4.07 (2H, m, $O\underline{CH_2}CH_3$); 4.18 (1H, s, H-1); 4.61 (1H, dd, *J* = 15.6, *J* = 6.3, $\underline{CH_2}$Ph); 4.64 (1H, dd, *J* = 15.6, *J* = 6.3, $\underline{CH_2}$Ph); 4.97 (1H, s, H-9); 6.74 (1H, s, H-4); 7.03-7.10 (3H, m, $\underline{CH}(1\text{-}C_6H_5)_p$, 2 $\underline{CH}(1\text{-}C_6H_5)_m$); 7.26 (1H, m, $CH(\underline{Ph}\text{–}CH_2N)_p$); 7.28-7.32 (2H, m, 2 $\underline{CH}(1\text{-}C_6H_5)_o$); 7.32-7.37 (6H, m, H-6,7, 2 $CH(\underline{Ph}\text{–}CH_2N)_o$; 2 $CH(\underline{Ph}\text{–}CH_2N)_m$); 7.43 (1H, m, H-8); 7.56 (1H, m, H-5); 9.42 (1H, m, NH). ^{13}C NMR spectrum, δ, ppm: 14.3 ($OCH_2\underline{C}H_3$); 28.5 (9a-CH_3); 46.5 (C-1), 46.9 ($\underline{C}H_2$Ph); 48.8 (C-9a); 58.9 ($O\underline{C}H_2CH_3$); 83.9 (C-9); 94.6 (C-2); 108.7 (C-4); 122.0 (C-5); 126.4 ($\underline{C}H(1\text{-}C_6H_5)_p$); 126.5 (C-8); 126.8 ($2\times CH(\underline{Ph}\text{–}CH_2N)_o$); 127.2 ($CH(\underline{Ph}\text{–}CH_2N)_p$); 128.3 ($2\times \underline{C}H(1\text{-}C_6H_5)_m$); 128.7 (2 $\underline{C}H(1\text{-}C_6H_5)_o$); 128.8 (2 $CH(\underline{Ph}\text{–}CH_2N)_m$); 129.2 (C-6); 131.1 (C-7); 136.4 (C-4b); 139.4 ($CH(\underline{Ph}\text{–}CH_2N)_i$); 144.9 ($\underline{C}H(1\text{-}C_6H_5)_i$); 148.9 (C-8a); 153.5 (C-3); 157.3 (C-4a); 170.5 (C=O). Found, %: C 79.40; H 6.71; N 2.70. $C_{30}H_{29}NO_3$. Calculated, %: C 79.80; H 6.47; N 3.10.

Ethyl 3-benzylamino-9-hydroxy-9a-methyl-1-phenyl-9,9a-dihydro-1H-fluorene-2-carboxylate (**12**). Yellow solid. Mp 140-141°C (*i*-PrOH). IR spectrum, ν, cm^{-1}: 3460 (NH), 3420 (OH); 1650 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 (3H, t, *J* = 7.2, $OCH_2\underline{CH_3}$); 1.22 (3H, s, 9a-CH_3); 1.94 (1H, bs, OH); 4.01 (2H, m, $O\underline{CH_2}CH_3$); 4.24 (1H, s, H-1); 4.60-4.67 (3H, m, $\underline{CH_2}$Ph, H-9); 6.60 (1H, s, H-4); 7.07 (1H, m, $\underline{CH}(1\text{-}C_6H_5)_p$); 7.11-7.19 (4H, m, 2 $\underline{CH}(1\text{-}C_6H_5)_o$); $2\times\underline{CH}(1\text{-}C_6H_5)_m$); 7.23-7.32 (4H, m, H-6,7,8 $\underline{CH}(Ph\text{–}CH_2N)_p$); 7.35-7.37 (4H, m, $2\times\underline{CH}(Ph\text{–}CH_2N)_o$); $2\times\underline{CH}(Ph\text{–}CH_2N)_m$); 7.42 (1H, d, *J* = 7.4, H-5); 9.46 (1H, m, NH). ^{13}C NMR spectrum, δ, ppm: 14.3 ($OCH_2\underline{C}H_3$); 20.6 (9a-CH_3); 46.9 ($\underline{C}H_2$Ph); 47.0 (C-1); 50.7 (C-9a); 58.9 ($O\underline{C}H_2CH_3$); 76.0 (C-9); 92.1 (C-2); 107.9 (C-4); 121.9 (C-5); 124.6 (C-8); 126.0 ($\underline{C}H(1\text{-}C_6H_5)_p$); 126.7 ($2\times CH(\underline{Ph}\text{–}CH_2N)_o$); 127.1 ($CH(\underline{Ph}\text{–}CH_2N)_p$); 127.8 ($2\times\underline{C}H(1\text{-}C_6H_5)_m$); 127.9 (C-6); 128.5 ($2\times CH(\underline{Ph}\text{–}CH_2N)_m$); 128.8 ($2\times\underline{C}H(1\text{-}C_6H_5)_o$); 130.4 (C-7), 135.1 (C-4b); 139.5 ($CH(\underline{Ph}\text{–}CH_2N)_i$); 142.3 ($\underline{C}H(1\text{-}C_6H_5)_i$); 148.3 (C-8a); 154.0 (C-3); 155.1 (C-4a); 170.8 (C=O). Found, %: C 79.58; H 6.35; N 2.83. $C_{30}H_{29}NO_3$. Calculated, %: C 79.80; H 6.47; N 3.10.

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