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SYNTHESIS OF 6-ARYL-SUBSTITUTED AZOCINO-[5,4-*b*]INDOLES FROM 1-ARYL-SUBSTITUTED 2-ETHYLTETRAHYDRO-β-CARBOLINES

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We optimized the reaction of tetrahydropyridine ring expansion in 1-aryl-substituted tetrahydro-β-carbolines by the action of activated alkynes and achieved higher than 70% yields of the target indoloazocines. The substituents in the 1-aryl ring and at the indole nitrogen atom were shown to affect the rate and selectivity of this transformation.

Keywords: activated alkynes, azocinoindoles, domino reaction, ring expansion.

Indoles fused with medium-sized rings attract the attention of synthetic and medicinal chemists due to their remarkable and diverse biological activity. Azocinoindoles containing two pharmacophore fragments are a part of many alkaloids [1, 2]. However, only few methods for the synthesis of azocinoindoles have been described, with multiple stages and low yields of the target products [3]. We have previously proposed a method for the synthesis of tetrahydroazocino[5,4-*b*]- and tetrahydroazocino[4,5-*b*]indoles based on a domino reaction of the tetrahydropyridine fragment expansion in β- and γ-carbolines, by using activated alkynes [4, 5]. The yields of 6-methyl(isopropyl, benzyl)tetrahydroazocino[5,4-*b*]indoles in acetonitrile were 40-50%. The reaction in methanol was accompanied by cleavage of the carboline tetrahydropyridine ring with the participation of a methanol molecule [5]. The 6-aryl-substituted tetrahydroazocino[5,4-*b*]indoles gave only 6-(2-fluorophenyl)- and 6-(4-fluorophenyl)tetrahydroazocinoindoles in the aforementioned domino reaction.

In the case of 1-(*m*-fluorophenyl)-substituted β-carboline transformation by the action of dimethyl ester of acetylene dicarboxylic acid (DMAD) in the presence of indole or 5-methoxyindole, the initial ammonium zwitterion **A** was shown to undergo cleavage at the C(1)–N bond, giving an "open" cation **B**. The electrophilic substitution of the latter in indole "trap" produced a diindolylarylmethane [6].

Initial biological screening showed that the azocino[5,4-*b*]- and azocino[4,5-*b*]indoles are effective inhibitors of acetyl- and butyrylcholine esterases, and can be further developed as drugs against neurodegeneration [5]. Azocines condensed with 4-aminopyrimidine fragment exhibited high cytotoxic activity during the initial screening. However, no chemical transformations of tetrahydroazocinoindoles have been studied thus far.

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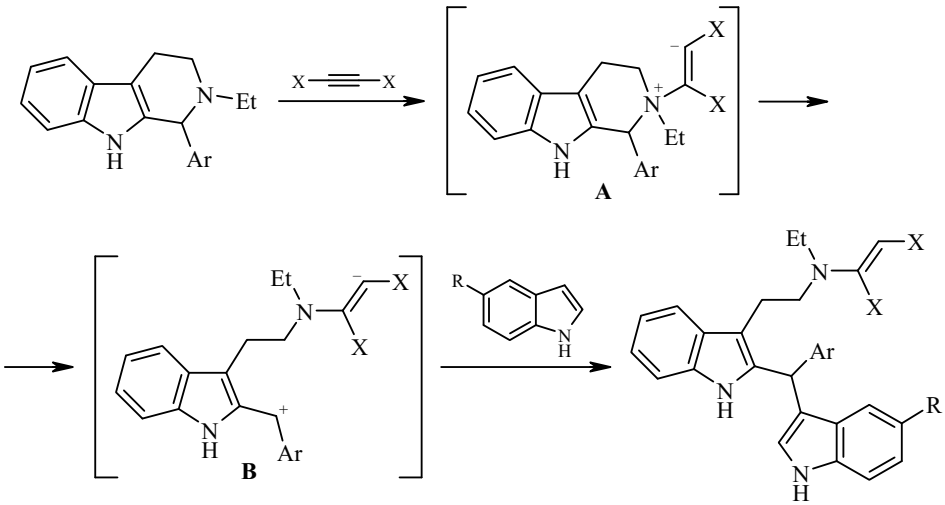
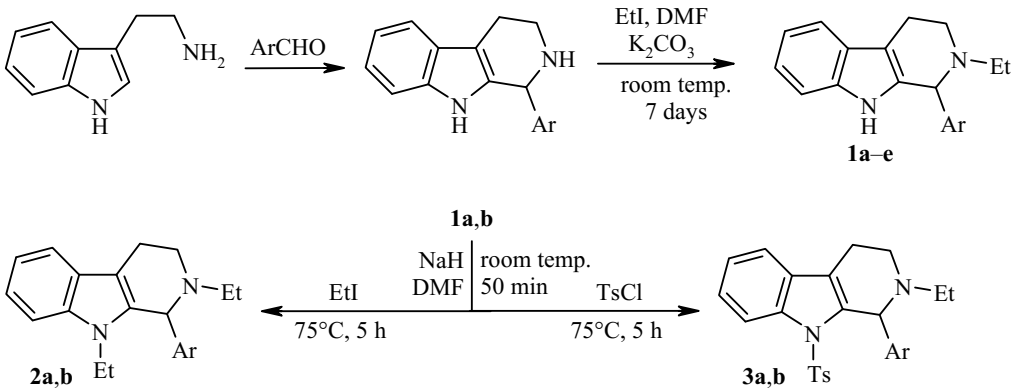


Ar = 3-FC_6H_4; R = H, OMe; X = CO_2Me

Our research interests were focussed on the chemical transformations of 6-aryl-substituted azocino[5,4-*b*]-indoles, the synthesis of which was accomplished by a domino reaction between 1-aryl-substituted tetrahydro-β-carbolines and activated alkynes. This reaction had to be optimized in order to obtain good yields of the 6-aryl-substituted tetrahydroazocinoindoles.

Therefore, we studied the influence of electronic effects due to the substituents at position 1 of the aryl fragment, at the indole nitrogen atom, and alkyne substituents, as well as the type of solvent and catalysts on the tetrahydropyridine ring expansion reaction rate and selectivity in carbolines.

The *N*-ethylcarbolines **1a**,**c**-**e** were obtained from β-carbolines synthesized according to the literature method [5] by treatment with ethyl iodide. Compound **1b** was described in the same work.



a Ar = Ph, **b** Ar = 4-$MeOC_6H_4$, **c** Ar = 3-$MeOC_6H_4$, **d** Ar = 4-FC_6H_4, **e** Ar = 3-FC_6H_4

The 9-ethyl and 9-tosyl derivatives **2a**,**b** and **3a**,**b** were obtained by the action of ethyl iodide or tosyl chloride on sodium derivatives of compounds **1a**,**b**, formed in the reactions of compounds **1a**,**b** with sodium hydride in DMF.

The domino reaction of 1-aryl-substituted carbolines **1a-e** with methyl propiolate, acetylacetylene, and DMAD was studied in dichloromethane, acetonitrile, and trifluoroethanol without catalysts, as well as in the presence of CuI and 1-methylpyrrole. The yields of azocinoindoles depending on the reaction conditions are presented in the Table 1.

TABLE 1. The Yields of Azocinoindoles **4-6 a-e** Depending on the Reaction Conditions*

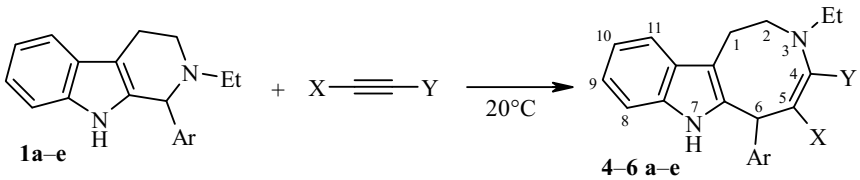
Experiment	Carboline	Alkyne	Solvent	Catalyst*[2]	Reaction time	Azocine (yield, %)
1	**1a**	MP	CH_2Cl_2	—	7 days	**4a** (73)
2			CH_2Cl_2	1-MePyr	10 days	**4a** (61)
3			CH_2Cl_2	CuI	10 days	**4a** (83)
4		AA	CH_2Cl_2	—	2 days	**5a** (34)
5			MeCN	—	2 days	**5a** (65)
6		DMAD*[3]	CH_2Cl_2	—	15 days	**6a** (25)
7	**1b**	MP	CH_2Cl_2	—	8 days	**4b** (75)
8			CH_2Cl_2	1-MePyr	10 days	**4b** (86)
9			CF_3CH_2OH	—	1 h	**4b** (29)
10		AA	CH_2Cl_2	—	2 days	**5b** (92)
11		DMAD	CH_2Cl_2	—	15 days	**6b** (25)
12	**1c**	MP	CH_2Cl_2	—	3 days	**4c** (31)
13			CH_2Cl_2	1-MePyr	5 days	**4c** (72)
14			CH_2Cl_2	CuI	3 days	**4c** (75)
15			MeCN	—	3 days	**4c** (71)
16		AA	CH_2Cl_2	—	2 days	**5c** (76)
17		DMAD	CH_2Cl_2	—	15 days	**6c** (2)
18	**1d**	MP	CH_2Cl_2	—	4 days	**4d** (84)
19		AA	CH_2Cl_2	—	4 days	**5d** (77)
20		DMAD	CH_2Cl_2	—	9 days	**6d** (9)
21	**1e**	MP	CH_2Cl_2	—	2 days	**4e** (56)
22			CH_2Cl_2	1-MePyr	7 days	**4e** (47)
23			CH_2Cl_2	CuI	7 days	**4e** (78)
24			CF_3CH_2OH	—	4.5 h	**4e** (62)
25			MeCN	—	7 days	**4e** (89)
26		AA	CH_2Cl_2	—	3 days	**5e** (45)
27			CF_3CH_2OH	—	1 h	**5e** (60)
28			MeCN	—	7 days	**5e** (44)
29		DMAD	CH_2Cl_2	—	11 days	**6e** (27)

*MP – methyl propiolate, AA – acetylacetylene, 1-MePyr – 1-methylpyrrole.

*[2]1.2 equiv. of 1-methylpyrrole and 30 mol% of CuI were used.

*[3]The reactions with DMAD were performed at 40°C using 5 equiv. of alkyne.

Methyl propiolate and acetylacetylene reacted with the carbolines **1a-c** in dichloromethane at 20°C, forming the respective azocines **4-6 a-c** in 31-92% yields. The interaction of DMAD with carbolines and excess alkyne at 40°C occurred with difficulty, producing multicomponent mixtures, from which only low yields of the azocines **6a-e** could be isolated by chromatography (experiments 6, 11, 17, 20, 29). The yields of azocinoindoles with *para*-substituted phenyl group (experiments 7, 10, 18, 19) were substantially higher than in the case of *meta*-substituted aryl fragments (experiments 12, 16, 21, 26). The obtained results are in good

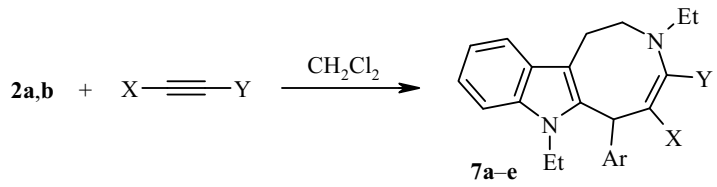


4 X = CO_2Me, Y = H; **5** X = COMe, Y = H; **6** X = Y = CO_2Me; **a** Ar = Ph, **b** Ar = 4-$MeOC_6H_4$, **c** Ar = 3-$MeOC_6H_4$, **d** Ar = 4-FC_6H_4, **e** Ar = 3-FC_6H_4

agreement with our mechanistic interpretation of this process, including the formation of the "open" cation **B**, the generation and stability of which is dictated by the electronic effects of the aryl ring substituents at the C-1 atom in accordance with the values of Hammett constants σ and σ^+ for methoxy groups and fluorine atom [7]. The addition of 30 mol% CuI relative to carboline allowed to increase the yield of azocinoindoles **4a**,**c**,**e** (experiments 3, 14, 23) to 75-83% (i.e., by 22-41%). The presence of 1-methylpyrrole (1.2 equiv.) also increased the yield of azocinoindoles **4b**,**c** to 86 and 72%, respectively (experiments 8, 13). Using acetonitrile as solvent allowed to substantially improve the yields of azocines **4c**,**e** (experiments 15, 25).

Two published examples [8, 9] show that the interaction of *N*-tosylindolizinoindoles with DMAD is accompanied by tetrahydropyridine fragment cleavage and the formation of a polycyclic structure featuring a spiro[indole-3,4'-pyridine] fragment. This observation is explained by the decreased electron density at position 3 of the indole ring due to the electron-withdrawing effect of the tosyl group. In order to establish the effect of substituents at the indole nitrogen atom on the transformation of tetrahydropyridine ring under the action of alkynes, we studied the reactions of *N*-ethyl- and *N*-tosyl-substituted carbolines **2a**,**b** and **3a**,**b** with terminal alkynes.

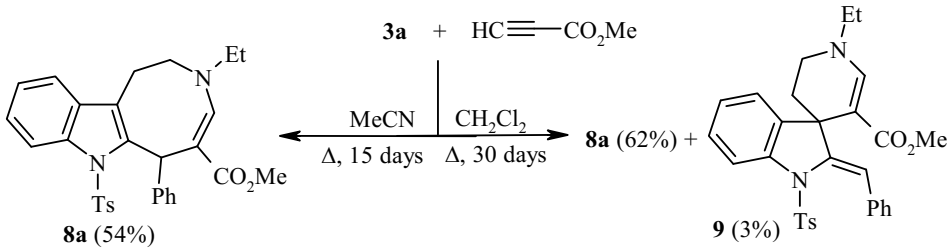
The carboline **2a** reacts with methyl propiolate, acetylacetylene, and DMAD in dichloromethane at 30°C, forming the azocino[5,4-*b*]indoles **7a**-**c**. The reaction of carboline **2b** with methyl propiolate and acetylacetylene occurs at room temperature, giving the azocines **7d**,**e**.



7 a–**c** Ar = Ph, **d**,**e** Ar = 4-MeOC$_6$H$_4$; **a**,**d** X = CO$_2$Me, Y = H; **b**,**e** X = COMe, Y = H; **c** X = Y = CO$_2$Me

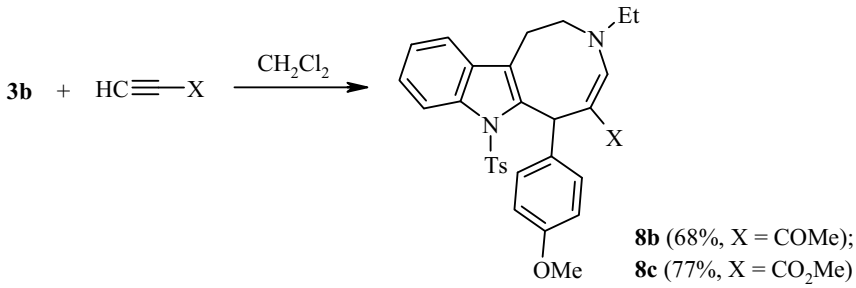
The higher reactivity of *p*-methoxyphenyl derivative **2b** and the superior yields of the azocinoindoles **7d**,**e** (63 and 68%) were apparently caused by the stabilization of the "open" cation **B** by the *para*-methoxyphenyl radical.

The *N*-tosyl-substituted carboline **3a** reacts with methyl propiolate only in refluxing acetonitrile or dichloromethane. Furthermore, the completion of the reaction required a 10-fold excess of alkyne and a considerable time (2-4 weeks). At the same time, the carboline **3a** did not react with DMAD in dichloromethane even after prolonged heating.



The interaction of carboline **3a** with methyl propiolate in acetonitrile resulted only in the isolation of azocinoindole **8a**, while the reaction with methyl propiolate in dichloromethane produced besides the azocinoindole **8a** also the spiro[indole-3,4'-pyridine] **9**.

The *para*-methoxyphenyl-substituted *N*-tosylcarboline **3b** was more reactive towards alkynes in dichloromethane. Thus, interaction with acetylacetylene gave the azocinoindole **8b** in 68% yield even at room temperature. The reaction with methyl propiolate required 10 days at reflux, and the respective azocine **8c** was obtained in 77% yield.



Therefore, we have demonstrated that the electronic effects and the location of substituent in the aryl fragment of 1-aryl-2,3,4,9-tetrahydrocarbolines affects the reaction rate and selectivity of tetrahydropyridine ring expansion in carbolines. The yield of the corresponding azocinoindoles, as a rule, was higher in the series of derivatives with a *para*-substituted aryl group. The use of catalysts (CuI and 1-methylpyrrole), as well as the optimization of solvent was shown to increase the yields of 6-aryl-3-ethyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]-indoles above 70%, enabling the further study of their reactivity. The introduction of electron donating ethyl group at the nitrogen atom of the carboline indole ring essentially did not change the nature of the transformations. The presence of an electron-acceptor (tosyl) substituent at the nitrogen atom of the indole fragment decreased the rate of carboline reaction with alkynes, and led to the formation of mainly azocinoindoles.

EXPERIMENTAL

IR spectra were recorded on an Infralum FT-801 FTIR spectrometer in KBr pellets. ^{1}H NMR spectra were recorded on JEOL JNM-ECS400 (400 MHz, compounds **1a**,**c**-**e**, **2a**, **3b**, **7c**, **8b**) and JEOL JNM-ECA 600 instruments (600 MHz, the rest of compounds). The solvent was DMSO-d_6 (compound **5c**) or $CDCl_3$ (the rest of compounds), internal standard was TMS or the residual solvent protons. The LC/MS data were obtained with a system including Agilent 1100 Series liquid chromatograph, Agilent Technologies LC/MSD VL mass spectrometer (electrospray), and ELSD Sedex 75 detector. Elemental analysis was performed on a EuroEA3000 instrument. Melting points were determined on an SMP 10 apparatus. Thin-layer chromatography was performed on Sorbfil and Alufol plates (development with iodine vapor, $KMnO_4$ and H_2SO_4 solutions), and silica gel from Acros (0.04-0.06 mm), 60 Å was used for column chromatography.

All the solvents used in this work were purified by distillation. Methyl propiolate, acetylacetylene, and DMAD were purchased from Acros Organics and used without additional purification.

Synthesis of the Starting *N*-Ethyl-substituted β-Carbolines 1a,c-e (General Method). Potassium carbonate (4.47 g, 32 mmol) was added to a solution of the corresponding 1-aryl-β-carboline (18 mmol) in DMF (45 ml). Then EtI (2.63 g, 23 mmol) was added dropwise. The reaction mixture was stirred for 7 days at room temperature. The reaction progress was controlled by TLC (Sorbfil, EtOAc). Water (30 ml) was added, and the product was extracted with a 1:1 mixture of EtOAc–Et_2O. The organic layer was dried over $MgSO_4$, the solvent was distilled off under reduced pressure, the residual DMF was removed under vacuum (oil pump). The obtained oil was crystallized from MeOH.

2-Ethyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-β-carboline (1a). Yield 2.73 g (55%), yellow crystals, mp 134-136°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.08 (3H, t, J = 7.6, $NCH_2C\underline{H}_3$); 2.41-2.45 (1H, m, $NC\underline{H}_BCH_3$); 2.66-2.75 (2H, m, 4-CH_B, $NC\underline{H}_ACH_3$); 2.82-2.85 (1H, m) and 3.31 (1H, dt, J = 4.1, J = 11.7, 3-CH_2); 2.93-3.01 (1H, m, 4-CH_A); 4.59 (1H, s, 1-CH); 7.05-7.11 (2H, m, H-6,7); 7.12-7.16 (1H, m, H-5); 7.19 (1H, br. s, NH); 7.27-7.37 (5H, m, H Ph); 7.49-7.53 (1H, m, H-8). Mass spectrum, *m*/*z*: 277 $[M+H]^+$. Found, %: C 82.49; H 7.33; N 10.19. $C_{19}H_{20}N_2$. Calculated, %: C 82.57; H 7.29; N 10.14.

2-Ethyl-1-(3-methoxyphenyl)-2,3,4,9-tetrahydro-β-carboline (1c). Yield 3.03 g (55%), yellow amorphous material, mp 82-84°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.38-2.42 (1H, m, $NC\underline{H}_BCH_3$); 2.64-2.74 (2H, m, 4-CH_B, $NC\underline{H}_ACH_3$); 2.79-2.85 (1H, m, 4-CH_A); 2.92-3.00 (1H, m) and 3.31 (1H, dt, *J* = 3.4, *J* = 11.7, 3-CH_2); 3.74 (3H, s, OCH_3); 4.54 (1H, s, 1-CH); 6.83 (1H, dd, *J* = 2.0, *J* = 8.2, H Ar); 6.91 (1H, br. s, H Ar); 6.94 (1H, d, *J* = 7.6, H Ar); 7.03-7.09 (2H, m, H-6,7); 7.12-7.16 (1H, m, H Ar); 7.21-7.27 (1H, m, H-5); 7.49 (1H, d, *J* = 8.2, H-8); 7.67 (1H, br. s, NH). Mass spectrum, *m*/*z*: 307 $[M+H]^+$. Found, %: C 78.36; H 7.27; N 9.11. $C_{20}H_{22}N_2O$. Calculated, %: C 78.40; H 7.24; N 9.14.

2-Ethyl-1-(4-fluorophenyl)-2,3,4,9-tetrahydro-1*H*-β-carboline (1d). Yield 2.70 g (51%), colorless crystals, mp 120-122°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 (3H, t, *J* = 7.2, $NCH_2C\underline{H}_3$); 2.44-2.51 (1H, m) and 2.69-2.74 (1H, m, 4-CH_2); 2.76-2.82 (1H, m) and 3.37 (1H, dt, *J* = 4.8, *J* = 11.7, 3-CH_2); 2.87-2.91 (1H, m) and 2.96-3.04 (1H, m, $NC\underline{H}_2CH_3$); 4.71 (1H, s, 1-CH); 7.02-7.04 (2H, m, H Ar); 7.07-7.14 (2H, m, H Ar); 7.19 (1H, d, *J* = 7.6, H-5); 7.31 (1H, br. s, NH); 7.32-7.37 (2H, m, H-6,7); 7.52 (1H, d, *J* = 7.6, H-8). Mass spectrum, *m*/*z*: 295 $[M+H]^+$. Found, %: C 77.92; H 6.21; N 9.72. $C_{19}H_{19}FN_2$. Calculated, %: C 77.52; H 6.51; N 9.52.

2-Ethyl-1-(3-fluorophenyl)-2,3,4,9-tetrahydro-β-carboline (1e). Yield 3.97 g (75%), yellow amorphous material, mp 106-108°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.39-2.43 (1H, m, $NC\underline{H}_BCH_3$); 2.64-2.72 (2H, m, 4-CH_B, $NC\underline{H}_ACH_3$); 2.80-2.85 (1H, m, 4-CH_A); 2.89-2.98 (1H, m) and 3.24-3.30 (1H, m, 3-CH_2); 4.58 (1H, s, 1-CH); 6.97 (1H, td, *J* = 2.8, *J* = 11.0, H Ar); 7.04-7.11 (3H, m, H-6,7, H Ar); 7.14 (1H, d, *J* = 7.6, H-5); 7.18 (1H, dd, *J* = 1.4, *J* = 6.9, H Ar); 7.21 (1H, s, NH); 7.26-7.31 (1H, m, H Ar); 7.50 (1H, d, *J* = 7.6, H-8). Mass spectrum, *m*/*z*: 295 $[M+H]^+$. Found, %: C 77.54; H 6.52; N 9.54. $C_{19}H_{19}FN_2$. Calculated, %: C 77.52; H 6.51; N 9.52.

Synthesis of β-Carbolines 2a,b and 3a,b (General Method). A solution of β-carboline **1a**,**b** (8 mmol) in anhydrous DMF (25 ml) at room temperature under argon atmosphere was treated with portions of NaH (0.4 g, 10 mmol, 60% suspension in oil), followed after 50 min by dropwise addition of EtI (1.4 g, 9 mmol) or TsCl (1.4 g, 1.1 mmol). The reaction mixture was stirred for 5 h at 75°C. The reaction progress was controlled by TLC (Sorbfil, 1:5 EtOAc–hexane). The solvent was removed, the residue was purified by chromatography on a silica gel column (1.5×20 cm), eluent 1:20 EtOAc–hexane. Compounds **2a**,**b** were isolated as brown oils, compounds **3a**,**b** were colorless crystals.

2,9-Diethyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-β-carboline (2a). Yield 2.1 g (84%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.95 (3H, t, *J* = 7.3, 2-$CH_2C\underline{H}_3$); 1.22 (3H, t, *J* = 7.2, 9-$CH_2C\underline{H}_3$); 2.61-2.72 (2H, m, 2-$C\underline{H}_2CH_3$); 2.76-2.81 (1H, m, 4-CH_B); 2.88-3.09 (3H, m, 3-CH_2, 4-CH_A); 3.64-3.73 (1H, m) and 3.78-3.87 (1H, m, 9-$C\underline{H}_2CH_3$); 4.91 (1H, s, 1-CH); 7.10-7.14 (1H, m, H Ar); 7.17-7.20 (3H, m, H Ar); 7.23-7.31 (4H, m, H Ar); 7.58 (1H, d, *J* = 7.8, H-5). Mass spectrum, *m*/*z* (I_{rel}, %): 304 $[M]^+$ (28), 303 (7), 248 (16), 247 (80), 246 (92), 232 (14), 230 (14), 228 (19), 227 (100), 218 (18), 217 (38), 216 (10), 197 (8), 172 (6), 152 (6), 143 (7), 128 (5), 115 (10), 104 (4), 91 (6), 77 (9), 56 (10), 42 (16). Found, %: C 82.90; H 7.94; N 9.11. $C_{21}H_{24}N_2$. Calculated, %: C 82.85; H 7.95; N 9.20.

2,9-Diethyl-1-(4-methoxyphenyl)-2,3,4,9-tetrahydro-1*H*-β-carboline (2b). Yield 2.0 g (68%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.98 (3H, t, *J* = 7.2, 2-$CH_2C\underline{H}_3$); 1.22 (3H, t, *J* = 7.2, 9-$CH_2C\underline{H}_3$); 2.60-2.66 (1H, m) and 2.67-2.73 (1H, m, 2-$C\underline{H}_2CH_3$); 2.76-2.80 (1H, m) and 2.94-2.99 (1H, m, 4-CH_2); 2.90 (1H, ddd, *J* = 3.1, *J* = 5.2, *J* = 12.0) and 3.04 (1H, ddd, *J* = 4.6, *J* = 9.4, *J* = 12.0, 3-CH_2); 3.67-2.73 (1H, m) and 3.80-3.87 (1H, m, 9-$C\underline{H}_2CH_3$); 3.78 (3H, s, OCH_3); 4.88 (1H, s, 1-CH); 6.82 (2H, d, *J* = 8.9, H Ar); 7.10-7.13 (3H, m, H Ar); 7.17-7.19 (1H, m, H Ar); 7.26 (1H, d, *J* = 7.6, H-8); 7.58 (1H, d, *J* = 8.3, H-5). Mass spectrum, *m*/*z* (I_{rel}, %): 334 $[M]^+$ (28), 333 (8), 305 (5), 278 (19), 277 (72), 276 (58), 262 (22), 247 (24), 246 (96), 245 (12), 234 (11), 233 (10), 232 (9), 230 (15), 228 (18), 227 (100), 218 (22), 217 (37), 205 (24), 204 (36), 197 (12), 172 (10), 168 (9), 167 (15), 156 (6), 143 (8), 138 (6), 130 (7), 121 (11), 115 (12), 102 (5), 91 (5), 77 (11), 56 (18), 42 (18). Found, %: C 79.28; H 7.60; N 8.56. $C_{22}H_{26}N_2O$. Calculated, %: C 79.01; H 7.84; N 8.38.

2-Ethyl-9-[(4-methylphenyl)sulfonyl]-1-phenyl-2,3,4,9-tetrahydro-1*H*-β-carboline (3a). Yield 2.68 g (78%). Mp 182-184°C. IR spectrum, ν, cm^{-1}: 1168 (S=O), 1364 (S=O). ^{1}H NMR spectrum, δ, ppm (*J*,

Hz): 1.27 (3H, t, J = 6.9, $NCH_2C\underline{H}_3$); 2.28 (3H, s, $ArC\underline{H}_3$); 2.57-2.63 (2H, m, 4-CH_2); 2.67-2.73 (1H, m, $NC\underline{H}_BCH_3$); 2.86-2.92 (2H, m, 3-CH_B, $NC\underline{H}_ACH_3$); 2.95-3.01 (1H, m, 3-CH_A); 5.62 (1H, s, 1-CH); 6.99 (2H, d, J = 8.3, H Ar); 7.10 (2H, d, J = 7.6, H Ar); 7.20-7.24 (3H, m, H Ar); 7.27-7.30 (3H, m, H Ar); 7.33-7.35 (1H, m, H Ar); 7.48 (1H, d, J = 7.6, H Ar); 8.16 (1H, d, J = 8.3, H Ar). Mass spectrum, m/z: 431 $[M+H]^+$. Found, %: C 72.45; H 6.02; N 6.48. $C_{26}H_{26}N_2O_2S$. Calculated, %: C 72.53; H 6.09; N 6.51.

2-Ethyl-1-(4-methoxyphenyl)-9-[(4-methylphenyl)sulfonyl]-2,3,4,9-tetrahydro-1*H*-β-carboline (3b). Yield 1.66 g (45%). Mp 105-107°C (Et_2O–hexane). IR spectrum, ν, cm^{-1}: 1169 (S=O), 1365 (S=O). ^1H NMR spectrum, δ, ppm (J, Hz): 1.27 (3H, t, J = 7.3, $NCH_2C\underline{H}_3$); 2.30 (3H, s, $ArC\underline{H}_3$); 2.56-2.62 (2H, m, 4-CH_2); 2.65-2.72 (1H, m, $NC\underline{H}_BCH_3$); 2.87-2.92 (2H, m, 3-CH_B, $NC\underline{H}_ACH_3$); 2.95-3.00 (1H, m, 3-CH_A); 3.79 (3H, s, OCH_3); 5.58 (1H, s, 1-CH); 6.74 (2H, d, J = 8.9, H Ar); 7.00-7.01 (4H, m, H Ar); 7.28-7.31 (3H, m, H Ar); 7.33-7.36 (1H, m, H Ar); 7.48 (1H, d, J = 7.6, H Ar); 8.17 (1H, d, J = 8.3, H Ar). Mass spectrum, m/z: 461 $[M+H]^+$. Found, %: C 70.78; H 6.00; N 6.30. $C_{27}H_{28}N_2O_3S$. Calculated, %: C 70.41; H 6.13; N 6.08.

The Interaction of Carbolines 1a-e, 2a,b, 3a,b with Alkynes. A solution of β-carboline **1a-e**, **2a**,**b**, **3a**,**b** (1.09 mmol) in CH_2Cl_2, MeCN, or CF_3CH_2OH (10 ml) was treated with methyl propiolate or acetylacetylene (2.18 mmol), or with DMAD (5.45 mmol). The reaction mixture was stirred at 20°C for the duration indicated in Table 1, while controlling the reaction progress by TLC (Sorbfil, 1:3 EtOAc–hexane). The reaction with DMAD was performed at 40°C. The solvent was removed under vacuum, the residue was recrystallized. Azocines **6a**,**b**, **7b**,**c**,**d**, **8b**, **9** were isolated by chromatography on a silica gel column (1.5×20 cm), the eluents are described in the experimental details for each compound. The yields of azocines depending on the reagents and reaction conditions used are given in Table 1.

The Interaction of Tetrahydrocarbolines 1a-c,e with Methyl Propiolate in the Presence of *N*-Methylpyrrole (General Method). A solution of β-carboline **1a-c**,**e** (1.09 mmol) in CH_2Cl_2 (10 ml) was treated with methyl propiolate (0.110 g, 1.20 mmol) and *N*-methylpyrrole (0.105 g, 1.30 mmol). The reaction mixture was stirred at 30°C for the duration indicated in Table 1. The reaction progress was controlled by TLC (Sorbfil, 1:3 EtOAc–hexane). The solvent was removed under vacuum, the residue was crystallized from Et_2O. The yields of azocines **4a-c**,**e** are reported in Table 1.

The Interaction of Tetrahydrocarbolines 1a,c,e with Methyl Propiolate in the Presence of CuI (General Method). A solution of β-carboline **1a**,**c**,**e** (1.09 mmol) in CH_2Cl_2 (10 ml) was treated with methyl propiolate (0.110 g, 1.20 mmol) and CuI (0.062 g, 0.32 mmol). The reaction mixture was stirred at 30°C for the duration indicated in Table 1. The reaction progress was controlled by TLC (Sorbfil, 1:3 EtOAc–hexane). The solvent was removed under vacuum, the residue was crystallized from Et_2O. The yields of azocines **4a**,**c**,**e** are reported in Table 1.

The compounds obtained by using *N*-methylpyrrole or CuI had identical physicochemical and spectral characteristics to the compounds obtained in the absence of catalysts.

Methyl 3-Ethyl-6-phenyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (4a). Colorless crystals, mp 186-188°C (Et_2O). IR spectrum, ν, cm^{-1}: 1644 (C=O). ^1H NMR spectrum, δ, ppm (J, Hz): 1.14 (3H, t, J = 6.9, $NCH_2C\underline{H}_3$); 2.72 (1H, td, J = 2.5, J = 15.8) and 3.65 (1H, td, J = 2.5, J = 15.8, 2-CH_2); 2.96 (1H, dt, J = 4.1, J = 14.4) and 3.09-3.15 (1H, m, 1-CH_2); 3.15-3.26 (2H, m, $NC\underline{H}_2CH_3$); 3.75 (3H, s, OCH_3); 5.94 (1H, s, 6-CH); 7.08-7.14 (3H, m, H Ph); 7.15-7.18 (2H, m, H Ph); 7.24 (2H, t, J = 7.6, H-9,10); 7.33 (1H, d, J = 8.3, H-11); 7.48 (1H, d, J = 7.6, H-8); 7.73 (1H, s, H-4); 8.14 (1H, s, NH). Mass spectrum, m/z: 361 $[M+H]^+$. Found, %: C 76.56; H 6.74; N 7.82. $C_{23}H_{24}N_2O_2$. Calculated, %: C 76.64; H 6.71; N 7.77.

Methyl 3-Ethyl-6-(4-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (4b). Colorless crystals, mp 232-234°C (Et_2O). IR spectrum, ν, cm^{-1}: 1603 (C=O). ^1H NMR spectrum, δ, ppm (J, Hz): 1.19 (3H, t, J = 7.6, $NCH_2C\underline{H}_3$); 2.72 (1H, dt, J = 2.0, J = 13.9) and 3.80 (1H, td, J = 2.0, J = 13.9, 2-CH_2); 2.99 (1H, dt, J = 3.4, J = 15.1) and 3.16 (1H, td, J = 4.1, J = 13.7, 1-CH_2); 3.20-3.31 (2H, m, $NC\underline{H}_2CH_3$); 3.74 (3H, s, $CO_2C\underline{H}_3$); 3.75 (3H, s, $ArOC\underline{H}_3$); 6.25 (1H, s, 6-CH); 6.74 (2H, d, J = 8.3, H Ar); 6.93 (2H, d, J = 8.3, H Ar); 7.10 (1H, t, J = 7.6, H-9); 7.15 (1H, t, J = 7.6, H-10); 7.32 (1H, d, J = 8.3, H-11); 7.47

(1H, d, *J* = 8.3, H-8); 7.49 (1H, s, H-4); 8.33 (1H, s, NH). Mass spectrum, *m*/*z*: 391 $[M+H]^+$. Found, %: C 73.87; H 6.65; N 7.37. $C_{24}H_{26}N_2O_3$. Calculated, %: C 73.82; H 6.71; N 7.17.

Methyl 3-Ethyl-6-(3-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (4c). Light-yellow crystals, mp 184-186°C (Et_2O). IR spectrum, ν, cm^{-1}: 1647 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.09 (3H, t, *J* = 7.6, $NCH_2C\underline{H}_3$); 2.73 (1H, dt, *J* = 2.8, *J* = 15.5) and 2.93 (1H, dt, *J* = 2.8, *J* = 15.5, 1-CH_2); 3.06-3.12 (1H, m) and 3.62-3.66 (1H, m, 2-CH_2); 3.12-3.20 (2H, m, $NC\underline{H}_2CH_3$); 3.67 (3H, s, $ArOC\underline{H}_3$); 3.69 (3H, s, CO_2CH_3); 5.86 (1H, s, 6-CH); 6.62-6.70 (3H, m, H Ar); 7.06 (1H, t, *J* = 7.6, H Ar); 7.08-7.15 (2H, m, H-9,10); 7.28 (1H, d, *J* = 8.2, H-11); 7.42 (1H, d, *J* = 7.6, H-8); 7.66 (1H, s, H-4); 8.15 (1H, s, NH). Mass spectrum, *m*/*z*: 391 $[M+H]^+$. Found, %: C 73.97; H 6.76; N 7.11. $C_{24}H_{26}N_2O_3$. Calculated, %: C 73.82; H 6.71; N 7.17.

Methyl 3-Ethyl-6-(4-fluorophenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (4d). Colorless crystals, mp 161-163°C (Et_2O). IR spectrum, ν, cm^{-1}: 1646 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.17 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.73 (1H, dt, *J* = 2.8, *J* = 16.5) and 3.14-3.19 (1H, m, 1-CH_2); 3.00 (1H, dt, *J* = 4.1, *J* = 15.1) and 3.61-3.67 (1H, m, 2-CH_2); 3.19-3.30 (2H, m, $NC\underline{H}_2CH_3$); 3.76 (3H, s, CO_2CH_3); 5.89 (1H, s, 6-CH); 6.94 (2H, t, *J* = 8.9, H Ar); 7.06-7.11 (2H, m, H Ar); 7.13 (1H, t, *J* = 6.9, H-10); 7.19 (1H, t, *J* = 8.3, H-9); 7.35 (1H, d, *J* = 7.6, H-11); 7.49 (1H, d, *J* = 8.3, H-8); 7.74 (1H, s, H-4); 8.11 (1H, s, NH). Mass spectrum, *m*/*z*: 379 $[M+H]^+$. Found, %: C 72.92; H 6.16; N 7.48. $C_{23}H_{23}FN_2O_2$. Calculated, %: C 73.00; H 6.13; N 7.40.

Methyl 3-Ethyl-6-(3-fluorophenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (4e). Light-gray crystals, mp 208-212°C (Et_2O). IR spectrum, ν, cm^{-1}: 1602 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.16 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.74-2.77 (1H, m, 1-CH_B); 2.99-3.02 (1H, m) and 3.58-3.62 (1H, m, 2-CH_2); 3.15-3.25 (3H, m, $NC\underline{H}_2CH_3$, 1-CH_A); 3.76 (3H, s, CO_2CH_3); 5.93 (1H, s, 6-CH); 6.82-6.85 (2H, m, H Ar); 6.89 (1H, d, *J* = 8.3, H Ar); 7.12 (1H, t, *J* = 7.6, H-10); 7.17-7.20 (2H, m, H-9, H Ar); 7.33 (1H, d, *J* = 8.3, H-11); 7.48 (1H, d, *J* = 7.6, H-8); 7.73 (1H, s, H-4); 8.19 (1H, s, NH). Mass spectrum, *m*/*z*: 379 $[M+H]^+$. Found, %: C 73.11; H 5.88; N 7.47. $C_{23}H_{23}FN_2O_2$. Calculated, %: C 73.00; H 6.13; N 7.40.

1-(3-Ethyl-6-phenyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indol-5-yl)ethanone (5a). Colorless crystals, mp 280-283°C (Et_2O). IR spectrum, ν, cm^{-1}: 1633 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.05 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.28 (3H, s, $COCH_3$); 2.54-2.56 (1H, m, 1-CH_B); 3.00-3.14 (2H, m, 2-CH_B, $NC\underline{H}_BCH_3$); 3.23-3.29 (2H, m, 1-CH_A, $NC\underline{H}_ACH_3$); 3.41-3.54 (1H, m, 2-CH_A); 6.19 (1H, s, 6-CH); 6.85 (2H, d, *J* = 7.8, H-11, H Ph); 6.92 (1H, t, *J* = 7.3, H Ph); 6.94-6.96 (1H, m, H Ph); 7.00 (1H, t, *J* = 7.3, H-10); 7.08 (1H, t, *J* = 7.3, H-9); 7.20 (2H, t, *J* = 7.3, H Ph); 7.36 (1H, d, *J* = 7.9, H-8); 7.64 (1H, s, H-4). Mass spectrum, *m*/*z*: 345 $[M+H]^+$. Found, %: C 80.12; H 7.05; N 8.21. $C_{23}H_{24}N_2O$. Calculated, %: C 80.20; H 7.02; N 8.13.

1-[3-Ethyl-6-(4-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indol-5-yl]ethanone (5b). Colorless crystals, mp 248-250°C (Et_2O). IR spectrum, ν, cm^{-1}: 1555 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.18 (3H, t, *J* = 7.6, $NCH_2C\underline{H}_3$); 2.34 (3H, s, $COCH_3$); 2.75 (1H, dt, *J* = 2.0, *J* = 15.1) and 2.99 (1H, dt, *J* = 3.8, *J* = 15.1, 1-CH_2); 3.16 (1H, td, *J* = 3.8, *J* = 13.0) and 3.80 (1H, td, *J* = 2.0, *J* = 13.0, 2-CH_2); 3.20-3.31 (2H, m, $NC\underline{H}_2CH_3$); 3.74 (3H, s, OCH_3); 6.25 (1H, s, 6-CH); 6.74 (2H, d, *J* = 8.3, H Ar); 6.92 (2H, d, *J* = 8.3, H Ar); 7.10 (1H, t, *J* = 7.5, H-10); 7.15 (1H, t, *J* = 7.5, H-9); 7.32 (1H, d, *J* = 8.0, H-11); 7.47 (1H, d, *J* = 8.3, H-8); 7.49 (1H, s, H-4); 8.33 (1H, s, NH). Mass spectrum, *m*/*z*: 375 $[M+H]^+$. Found, %: C 77.02; H 6.94; N 7.28. $C_{24}H_{26}N_2O_2$. Calculated, %: C 76.98; H 7.00; N 7.48.

1-[3-Ethyl-6-(3-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indol-5-yl]ethanone (5c). Colorless crystals, mp >292°C (decomp., Et_2O). IR spectrum, ν, cm^{-1}: 1650 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.06 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.24 (3H, s, $COCH_3$); 2.54-2.62 (1H, m) and 3.46-3.55 (1H, m, 2-CH_2); 3.03-3.14 (1H, m, 1-CH_B); 3.24-3.36 (3H, m, 1-CH_A, $NC\underline{H}_2CH_3$); 3.60 (3H, s, OCH_3); 6.15 (1H, s, 6-CH); 6.38 (1H, s, H Ar); 6.46 (1H, d, *J* = 7.6, H Ar); 6.74 (1H, d, *J* = 7.6, H Ar); 6.92 (1H, t, *J* = 7.6, H-10); 7.00 (1H, t, H-9); 7.13 (1H, t, *J* = 7.6, H Ar); 7.21 (1H, d, *J* = 7.6, H-11); 7.36 (1H, d, *J* = 7.6, H-8); 7.62 (1H, s, H-4); 10.92 (1H, s, NH). Mass spectrum, *m*/*z*: 375 $[M+H]^+$. Found, %: C 76.92; H 6.97; N 7.55. $C_{24}H_{26}N_2O_2$. Calculated, %: C 76.98; H 7.00; N 7.48.

1-[3-Ethyl-6-(4-fluorophenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indol-5-yl]ethanone (5d). Colorless crystals, mp 193-194°C (Et_2O). IR spectrum, ν, cm^{-1}: 1551 (C=C), 1628 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.18 (3H, t, *J* = 7.6, $NCH_2C\underline{H}_3$); 2.33 (3H, s, $COCH_3$); 2.73 (1H, dt, *J* = 3.4, *J* = 16.5) and 3.00 (1H, dt, *J* = 4.8, *J* = 16.5, 1-CH_2); 3.17 (1H, td, *J* = 4.8, *J* = 13.8) and 3.65-3.68 (1H, m, 2-CH_2); 3.20-3.31 (2H, m, $NC\underline{H}_2CH_3$); 6.28 (1H, s, 6-CH); 6.86 (2H, t, *J* = 8.9, H Ar); 6.90-6.97 (2H, m, H Ar); 7.10 (1H, t, *J* = 7.6, H-9); 7.15 (1H, t, *J* = 7.6, H-10); 7.32 (1H, d, *J* = 7.6, H-8); 7.46 (1H, d, *J* = 8.3, H-11); 7.49 (1H, s, H-4); 7.66 (1H, s, NH). Mass spectrum, *m*/*z*: 363 $[M+H]^+$. Found, %: C 76.14; H 6.43; N 7.78. $C_{23}H_{23}FN_2O$. Calculated, %: C 76.22; H 6.40; N 7.73.

1-[3-Ethyl-6-(3-fluorophenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indol-5-yl]ethanone (5e). Colorless crystals, mp >278°C (decomp., Et_2O). IR spectrum, ν, cm^{-1}: 1609 (C=C), 1633 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.20 (3H, s, $NCH_2C\underline{H}_3$); 2.34 (3H, s, $COCH_3$); 2.78 (1H, dt, *J* = 2.7, *J* = 15.8) and 3.02 (1H, dt, *J* = 2.7, *J* = 15.8, 1-CH_2); 3.16 (1H, dd, *J* = 4.6, *J* = 13.7) and 3.68 (1H, td, *J* = 2.3, *J* = 13.3, 2-CH_2); 3.20-3.34 (2H, m, $NC\underline{H}_2CH_3$); 6.32 (1H, s, 6-CH); 6.70-6.78 (1H, m, H Ar); 6.77-6.84 (2H, m, H-10, H Ar); 7.07 (3H, m, H-9, H Ar); 7.33 (1H, d, *J* = 7.6, H-11); 7.47 (1H, d, *J* = 7.8, H-8); 7.50 (1H, s, H-4); 8.30 (1H, s, NH). Mass spectrum, *m*/*z*: 363 $[M+H]^+$. Found, %: C 76.20; H 6.40; N 7.67. $C_{23}H_{23}FN_2O$. Calculated, %: C 76.22; H 6.40; N 7.73.

Dimethyl 3-Ethyl-6-phenyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-4,5-dicarboxylate (6a). The eluent for column chromatography was 1:1 EtOAc–hexane. Yellow crystals, mp 198-200°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1683, 1727 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.91 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.43 (1H, dd, *J* = 3.7, *J* = 14.4, 1-CH_B); 2.80-2.84 (1H, m, $NC\underline{H}_BCH_3$); 3.04-3.21 (2H, m, 1-CH_A, $NC\underline{H}_ACH_3$); 3.25 (1H, dd, *J* = 5.9, *J* = 15.1) and 3.53 (1H, dd, *J* = 4.1, *J* = 14.4, 2-CH_2); 3.73 (3H, s, CO_2CH_3); 3.79 (3H, s, CO_2CH_3); 5.99 (1H, s, 6-CH); 7.13 (1H, d, *J* = 7.3, H Ph); 7.15-7.20 (4H, m, H Ph); 7.23 (2H, t, *J* = 7.3, H-9,10); 7.36 (1H, d, *J* = 7.8, H-11); 7.49 (1H, d, *J* = 7.8, H-8); 8.19 (1H, s, NH). Mass spectrum, *m*/*z*: 419 $[M+H]^+$. Found, %: C 71.67; H 6.29; N 6.76. $C_{25}H_{26}N_2O_4$. Calculated, %: C 71.75; H 6.26; N 6.69.

Dimethyl 3-Ethyl-6-(4-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-4,5-dicarboxylate (6b). The eluent for column chromatography was 1:5 EtOAc–hexane. Yield 0.12 g (25%), colorless crystals, mp 209-211°C (Et_2O). IR spectrum, ν, cm^{-1}: 1681, 1717 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.91 (3H, t, *J* = 7.2, $NCH_2C\underline{H}_3$); 2.44 (1H, dd, *J* = 3.7, *J* = 16.1, 1-CH_B); 2.78-2.84 (1H, m, $NC\underline{H}_BCH_3$); 3.16-3.25 (2H, m, 1-CH_A, $NC\underline{H}_ACH_3$); 3.25 (1H, dd, *J* = 4.8, *J* = 13.8) and 3.58 (1H, dt, *J* = 4.3, *J* = 13.8, 2-CH_2); 3.72 (3H, s, $ArOC\underline{H}_3$); 3.76 (3H, s, CO_2CH_3); 3.78 (3H, s, CO_2CH_3); 5.92 (1H, s, 6-CH); 6.76 (2H, d, *J* = 8.9, H Ar); 6.98 (2H, d, *J* = 8.9, H Ar); 7.12 (1H, t, *J* = 7.6, H-10); 7.18 (1H, t, *J* = 7.6, H-9); 7.34 (1H, d, *J* = 8.3, H-11); 7.49 (1H, d, *J* = 8.3, H-8); 8.15 (1H, s, NH). Mass spectrum, *m*/*z*: 449 $[M+H]^+$. Found, %: C 69.78; H 6.45; N 6.00. $C_{26}H_{28}N_2O_5$. Calculated, %: C 69.63; H 6.29; N 6.25.

Dimethyl 3-Ethyl-6-(3-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-4,5-dicarboxylate (6c). Colorless crystals, mp 131-132°C (Et_2O). IR spectrum, ν, cm^{-1}: 1669, 1738 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.91 (3H, t, *J* = 7.3, $NCH_2C\underline{H}_3$); 2.49 (1H, dd, *J* = 4.0, *J* = 16.0) and 3.17 (1H, dd, *J* = 5.9, *J* = 16.0, 1-CH_2); 2.79-2.83 (1H, m) and 3.05-3.14 (1H, m, $NC\underline{H}_2CH_3$); 3.26 (1H, dd, *J* = 5.9, *J* = 15.1) and 3.59 (1H, td, *J* = 4.1, *J* = 15.1, 2-CH_2); 3.69 (3H, s, $ArOC\underline{H}_3$); 3.72 (3H, s, CO_2CH_3); 3.77 (3H, s, CO_2CH_3); 5.95 (1H, s, 6-CH); 6.64 (1H, s, H Ar); 6.68-6.71 (2H, m, H-9,10); 7.12 (1H, t, *J* = 7.3, H Ar); 7.13-7.20 (2H, m, H Ar); 7.36 (1H, d, *J* = 7.8, H-11); 7.48 (1H, d, *J* = 7.8, H-8); 8.11 (1H, s, NH). Mass spectrum, *m*/*z*: 449 $[M+H]^+$. Found, %: C 69.49; H 6.25; N 6.37. $C_{26}H_{28}N_2O_5$. Calculated, %: C 69.63; H 6.29; N 6.25.

Dimethyl 3-Ethyl-6-(4-fluorophenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-4,5-dicarboxylate (6d). Yellow crystals, mp 208-210°C (Et_2O). IR spectrum, ν, cm^{-1}: 1686, 1727 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.91 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.43 (1H, dd, *J* = 7.3, *J* = 16.2) and 3.16 (1H, td, *J* = 5.5, *J* = 16.2, 1-CH_2); 2.78-2.83 (1H, m) and 3.06-3.12 (1H, m, $NC\underline{H}_2CH_3$); 3.27 (1H, dd, *J* = 5.5, *J* = 14.4) and 3.49 (1H, td, *J* = 3.4, *J* = 14.4, 2-CH_2); 3.73 (3H, s, CO_2CH_3); 3.78 (3H, s, CO_2CH_3); 5.93 (1H, s, 6-CH); 6.90-6.93 (2H, m, H Ar); 6.29-7.07 (2H, m, H Ar); 7.13 (1H, t, *J* = 7.6, H-10); 7.19 (1H, t, *J* = 7.6, H-9); 7.35 (1H, d, *J* = 7.6, H 11); 7.49 (1H, d, *J* = 7.6, H-8); 8.16 (1H, s, NH). Mass spectrum, *m*/*z*: 437 $[M+H]^+$. Found, %: C 68.71; H 5.80; N 6.47. $C_{25}H_{25}FN_2O_4$. Calculated, %: C 68.79; H 5.77; N 6.42.

Dimethyl 3-Ethyl-6-(3-fluorophenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-4,5-dicarboxylate (6e). Dark-yellow crystals, mp 202-205°C (Et_2O). IR spectrum, ν, cm^{-1}: 1683, 1728 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.89 (3H, t, *J* = 6.9, $NCH_2C\underline{H}_3$); 2.44 (1H, dd, *J* = 2.8, *J* = 14.7) and 3.47 (1H, td, *J* = 4.1, *J* = 14.7, 2-CH_2); 3.04-3.12 (2H, m, $NC\underline{H}_2CH_3$); 3.15 (1H, dd, *J* = 5.5, *J* = 16.5) and 3.26 (1H, dd, *J* = 5.5, *J* = 16.5, 1-CH_2); 3.71 (3H, s, CO_2CH_3); 3.76 (3H, s, CO_2CH_3); 5.95 (1H, s, 6-CH); 6.76 (1H, d, *J* = 10.3, H Ar); 6.83 (2H, t, *J* = 8.3, H-9,10); 7.10 (1H, t, *J* = 6.9, H Ar); 7.13-7.18 (2H, m, H-11, H Ar); 7.32 (1H, d, *J* = 7.6, H Ar); 7.47 (1H, d, *J* = 8.3, H-8); 8.18 (1H, s, NH). Mass spectrum, *m*/*z*: 437 $[M+H]^+$. Found, %: C 68.85; H 5.58; N 6.43. $C_{25}H_{25}FN_2O_4$. Calculated, %: C 68.79; H 5.77; N 6.42.

Methyl 3,7-Diethyl-6-phenyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (7a). The carboline **2a** reacted with methyl propiolate in CH_2Cl_2 at 30°C over 5 days. Yield 0.21 g (50%), colorless crystals, mp 148-150°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1684 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.13 (3H, t, *J* = 7.3, 3-$CH_2C\underline{H}_3$); 1.32 (3H, t, *J* = 7.3, 7-$CH_2C\underline{H}_3$); 2.69-2.74 (1H, m) and 2.95 (1H, ddd, *J* = 2.5, *J* = 4.5, *J* = 14.8, 1-CH_2); 3.16-3.24 (3H, m, 3-$C\underline{H}_2CH_3$, 2-CH_B); 3.60-3.65 (1H, m, 2-CH_A); 3.77 (3H, s, $CO_2C\underline{H}_3$); 4.23-4.29 (1H, m) and 4.36-4.42 (1H, m, 7-$C\underline{H}_2CH_3$); 6.30 (1H, s, 6-CH); 7.10-7.17 (4H, m, H Ph); 7.22 (1H, t, *J* = 7.3, H Ph); 7.25-7.27 (2H, m, H-9,10); 7.35 (1H, d, *J* = 8.3, H-11); 7.50 (1H, d, *J* = 8.3, H-8); 7.74 (1H, s, H-4). Mass spectrum, *m*/*z* (I_{rel}, %): 388 $[M]^+$ (69), 359 (4), 357 (5), 332 (6), 331 (16), 330 (10), 329 (31), 317 (15), 311 (12), 284 (14), 272 (16), 260 (11), 258 (18), 256 (16), 230 (16), 225 (18), 217 (12), 194 (23), 180 (10), 172 (15), 171 (100), 156 (14), 154 (20), 143 (32), 128 (10), 115 (13), 105 (4), 91 (10), 77 (5), 58 (8), 56 (6). Found, %: C 76.90; H 7.50; N 7.05. $C_{25}H_{28}N_2O_2$. Calculated, %: C 77.29; H 7.26; N 7.21.

1-(3,7-Diethyl-6-phenyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indol-5-yl)ethanone (7b). The carboline **2a** reacted with acetylacetylene in CH_2Cl_2 at 30°C over 5 days. The eluent for column chromatography was 1:2 EtOAc–hexane. Yield 0.11 g (28%), colorless crystals, mp 170-172°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1638 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.18 (3H, t, *J* = 7.2, 3-$CH_2C\underline{H}_3$); 1.29 (3H, t, *J* = 6.9, 7-$CH_2C\underline{H}_3$); 2.37 (3H, s, $COCH_3$); 2.74 (1H, dt, *J* = 2.8, *J* = 16.5, 1-CH_B); 2.98 (1H, ddd, *J* = 2.5, *J* = 5.0, *J* = 14.7) and 3.72 (1H, dt, *J* = 2.8, *J* = 14.7, 2-CH_2); 3.19-3.30 (3H, m, 1-CH_A, 3-$C\underline{H}_2CH_3$); 4.20-4.26 (1H, m) and 4.29-4.36 (1H, m, 7-$C\underline{H}_2CH_3$); 6.72 (1H, s, 6-CH); 7.05 (2H, d, *J* = 7.6, H Ph); 7.10-7.15 (2H, m, H Ph); 7.20-7.25 (3H, m, H-9,10, H Ph); 7.34 (1H, d, *J* = 8.3, H-11); 7.50 (1H, d, *J* = 7.6, H-8); 7.52 (1H, s, H-4). Mass spectrum, *m*/*z* (I_{rel}, %): 372 $[M]^+$ (88), 329 (30), 316 (9), 315 (19), 301 (64), 300 (20), 299 (13), 286 (14), 285 (23), 272 (66), 259 (29), 258 (100), 243 (19), 230 (18), 217 (11), 186 (8), 172 (14), 171 (42), 156 (12), 143 (29), 128 (11), 115 (19), 91 (10), 72 (8), 58 (42), 44 (10), 43 (38). Found, %: C 80.25; H 7.70; N 7.32. $C_{25}H_{28}N_2O$. Calculated, %: C 80.61; H 7.58; N 7.52.

Dimethyl 3,7-Diethyl-6-phenyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-4,5-dicarboxylate (7c). The carboline **2a** reacted with DMAD in CH_2Cl_2 at 30°C over 5 days. The eluent for column chromatography was 1:15 EtOAc–hexane. Yield 0.21 g (41%), colorless crystals, mp 180-182°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1678 (C=O), 1730 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.89 (3H, t, *J* = 7.1, 3-$CH_2C\underline{H}_3$); 1.33 (3H, t, *J* = 7.1, 7-$CH_2C\underline{H}_3$); 2.43 (1H, dd, *J* = 3.9, *J* = 16.3) and 3.11-3.20 (1H, m, 1-CH_2); 2.72-2.81 (1H, m) and 2.99-3.08 (1H, m, 3-$C\underline{H}_2CH_3$); 3.23-3.28 (1H, m) and 3.53 (1H, dt, *J* = 4.4, *J* = 14.1, 2-CH_2); 3.77 (3H, s, $CO_2C\underline{H}_3$); 3.78 (3H, s, $CO_2C\underline{H}_3$); 4.24-4.37 (2H, m, 7-$C\underline{H}_2CH_3$); 6.32 (1H, s, 6-CH); 7.11-7.14 (3H, m, H Ph); 7.16-7.19 (1H, m, H Ph); 7.21-7.27 (3H, m, H-9,10, H Ph); 7.37 (1H, d, *J* = 8.2, H-11); 7.51 (1H, d, *J* = 7.8, H-8). Mass spectrum, *m*/*z*: 447 $[M+H]^+$. Found, %: C 72.59; H 6.46; N 6.21. $C_{27}H_{30}N_2O_4$. Calculated, %: C 72.62; H 6.77; N 6.27.

Methyl 3,7-Diethyl-6-(4-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (7d). The carboline **2b** reacted with methyl propiolate in CH_2Cl_2 at room temperature over 4 weeks. The eluent for column chromatography was 1:2 EtOAc–hexane. Yield 0.29 g (63%), yellow crystals, mp 64-67°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1669 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.13 (3H, t, *J* = 6.9, 3-$CH_2C\underline{H}_3$); 1.31 (3H, t, *J* = 7.3, 7-$CH_2C\underline{H}_3$); 2.71 (1H, dt, *J* = 2.8, *J* = 16.5, 1-CH_B); 2.95 (1H, ddd, *J* = 2.6, *J* = 5.0, *J* = 14.5) and 3.69 (1H, dt, *J* = 2.8, *J* = 14.5, 2-CH_2); 3.14-3.25 (3H, m, 3-$C\underline{H}_2CH_3$, 1-CH_A); 3.76 (3H, s, $ArOC\underline{H}_3$); 3.77 (3H, s, CO_2CH_3); 4.22-4.28 (1H, m) and 4.34-4.40 (1H, m, 7-$C\underline{H}_2CH_3$); 6.22 (1H, s, 6-CH);

6.80 (2H, d, J = 8.9, H Ar); 7.02-7.04 (2H, m, H Ar); 7.10-7.12 (1H, m, H-9(10)); 7.19-7.22 (1H, m, H-10(9)); 7.34 (1H, d, J = 8.3, H-11); 7.49 (1H, d, J = 8.3, H-8); 7.73 (1H, s, H-4). Mass spectrum, m/z (I_{rel}, %): 418 $[M]^+$ (100), 417 (34), 400 (12), 363 (34), 361 (28), 360 (22), 359 (20), 343 (22), 333 (14), 315 (15), 302 (65), 301 (25), 300 (30), 288 (30), 273 (26), 253 (13), 252 (22), 251 (16), 250 (14), 230 (18), 225 (30), 223 (17), 207 (32), 195 (19), 181 (30), 172 (38), 171 (29), 169 (24), 156 (34), 143 (32), 133 (28), 127 (19), 126 (39), 114 (26), 102 (25), 80 (9), 78 (17), 71 (40), 64 (13), 62 (19), 55 (31), 53 (30), 42 (12). Found, %: C 74.78; H 7.00; N 6.20. $C_{26}H_{30}N_2O_3$. Calculated, %: C 74.61; H 7.22; N 6.69.

1-[3,7-Diethyl-6-(4-methoxyphenyl)-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indol-5-yl]ethanone (7e). The carboline **2b** reacted with acetylacetylene in CH_2Cl_2 at room temperature for 4 weeks. Yield from CH_2Cl_2 was 0.30 g (68%), colorless crystals, mp 169-172°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1650 (C=O). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.18 (3H, t, J = 7.3, 3-$CH_2C\underline{H}_3$); 1.28 (3H, t, J = 6.9, 7-$CH_2C\underline{H}_3$); 2.35 (3H, s, $COCH_3$); 2.73 (1H, dt, J = 2.8, J = 16.5, 1-CH_B); 2.98 (1H, ddd, J = 2.5, J = 5.2, J = 14.8) and 3.74-3.80 (1H, m, 2-CH_2); 3.19-3.29 (3H, m, 3-$C\underline{H}_2CH_3$ and 1-CH_A); 3.76 (3H, s, $ArOC\underline{H}_3$); 4.19-4.25 (1H, m) and 4.28-4.34 (1H, m, 7-$C\underline{H}_2CH_3$); 6.63 (1H, s, 6-CH); 6.78 (2H, d, J = 8.3, H Ar); 6.94 (2H, d, J = 8.3, H Ar); 7.09-7.12 (1H, m, H-9(10)); 7.19-7.22 (1H, m, H-10(9)); 7.33 (1H, d, J = 8.3, H-11); 7.49 (1H, d, J = 7.6, H-8); 7.50 (1H, s, H-4). Mass spectrum, m/z (I_{rel}, %): 402 $[M]^+$ (100), 359 (32), 345 (24), 344 (12), 332 (20), 331 (67), 330 (13), 316 (12), 315 (21), 314 (13), 303 (18), 302 (72), 301 (11), 289 (27), 288 (99), 171 (21), 143 (13), 58 (16), 43 (11). Found, %: C 77.90; H 7.50; N 7.05. $C_{26}H_{30}N_2O_2$. Calculated, %: C 77.58; H 7.51; N 6.96.

Methyl 3-Ethyl-7-[(4-methylphenyl)sulfonyl]-6-phenyl-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-5-carboxylate (8a). The carboline **3a** was refluxed for 15 days with a 10-fold excess of methyl propiolate in MeCN. Yield 0.30 g (54%), colorless crystals, mp 197-199°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1169 (S=O), 1365 (S=O), 1671 (C=O). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.99 (3H, t, J = 7.2, $NCH_2C\underline{H}_3$); 2.27 (3H, s, $ArC\underline{H}_3$); 2.40 (1H, ddd, J = 2.1, J = 3.4, J = 16.7) and 3.52 (1H, ddd, J = 5.7, J = 13.8, J = 16.7, 1-CH_2); 2.87 (1H, ddd, J = 2.1, J = 5.9, J = 14.8) and 3.47-3.53 (1H, m, 2-CH_2); 3.06-3.12 (1H, m) and 3.14-3.20 (1H, m, $NC\underline{H}_2CH_3$); 3.78 (3H, s, CO_2CH_3); 6.86 (2H, d, J = 7.6, H Ar); 6.97 (1H, s, 6-CH); 7.04 (2H, d, J = 8.3, H Ar); 7.08 (1H, d, J = 6.9, H Ar); 7.09-7.12 (2H, m, H Ar); 7.27-7.30 (1H, m, H-9(10)); 7.34-7.37 (1H, m, H-10(9)); 7.39 (1H, d, J = 7.6, H-11); 7.61 (2H, d, J = 8.3, H Ar); 7.72 (1H, s, H-4); 8.37 (1H, d, J = 8.3, H-8). Mass spectrum, m/z: 515 $[M+H]^+$. Found, %: C 69.93; H 5.86; N 5.41. $C_{30}H_{30}N_2O_4S$. Calculated, %: C 70.02; H 5.88; N 5.44.

Refluxing the carboline **3a** for 30 days with a 10-fold excess of methyl propiolate in CH_2Cl_2 produced besides the azocinoindole **8a** (62% yield) also the spiro[indole-3,4'-pyridine] **9** (3% yield).

1-{3-Ethyl-6-(4-methoxyphenyl)-7-[(4-methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1*H*-azocino[5,4-*b*]-indol-5-yl}ethanone (8b). The carboline **3b** reacts with acetylacetylene in CH_2Cl_2 at room temperature over the course of 4 days. The eluent for column chromatography was 1:1 EtOAc–hexane. Yield 0.37 g (68%), colorless crystals, mp 230-232°C (EtOAc). IR spectrum, ν, cm^{-1}: 1169 (S=O), 1367 (S=O), 1655 (C=O). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.03 (3H, t, J = 7.3, $NCH_2C\underline{H}_3$); 2.26 (3H, s, $ArC\underline{H}_3$); 2.32 (3H, s, $COCH_3$); 2.39 (1H, ddd, J = 1.8, J = 3.8, J = 16.9) and 3.05 (1H, ddd, J = 5.9, J = 13.8, J = 16.9, 1-CH_2); 2.91 (1H, ddd, J = 1.8, J = 5.9, J = 14.8) and 3.56-3.61 (1H, m, 2-CH_2); 3.10-3.16 (1H, m) and 3.17-3.23 (1H, m, $NC\underline{H}_2CH_3$); 3.72 (3H, s, OCH_3); 6.60 (2H, d, J = 8.9, H Ar); 6.62-6.64 (2H, m, H Ar); 6.99 (1H, s, 6-CH); 7.05 (2H, d, J = 8.6, H Ar); 7.27-7.30 (1H, m, H-9(10)); 7.34-7.36 (1H, m, H-10(9)); 7.40 (1H, d, J = 7.6, H-11); 7.50 (1H, s, H-4); 7.69 (2H, d, J = 8.6, H Ar); 8.39 (1H, d, J = 8.3, H-8). Mass spectrum, m/z: 529 $[M+H]^+$. Found, %: C 70.36; H 6.06; N 5.27. $C_{31}H_{32}N_2O_4S$. Calculated, %: C 70.43; H 6.10; N 5.30.

Methyl 3-Ethyl-6-(4-methoxyphenyl)-7-[(4-methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1*H*-azocino-[5,4-*b*]indole-5-carboxylate (8c). The carboline **3b** reacts with methyl propiolate upon refluxing in CH_2Cl_2 over the course of 10 days. Yield 0.36 g (77%), colorless crystals, mp 205-207°C (EtOAc). IR spectrum, ν, cm^{-1}: 1171 (S=O), 1369 (S=O), 1667 (C=O). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.99 (3H, t, J = 7.3, $NCH_2C\underline{H}_3$); 2.28 (3H, s, $ArC\underline{H}_3$); 2.41 (1H, ddd, J = 2.1, J = 3.4, J = 16.7) and 3.02 (1H, ddd, J = 5.7, J = 13.5, J = 16.7, 1-CH_2); 2.88 (1H, ddd, J = 2.1, J = 5.7, J = 14.8) and 3.53-3.58 (1H, m, 2-CH_2); 3.06-3.12 (1H, m) and 3.14-3.20 (1H, m, $NC\underline{H}_2CH_3$); 3.74 (3H, s, $ArOC\underline{H}_3$); 3.77 (3H, s, CO_2CH_3); 6.65 (2H, d, J = 8.9, H Ar); 6.77-6.78 (2H, m, H

Ar); 6.88 (1H, s, 6-CH); 7.05 (2H, d, J = 8.3, H Ar); 7.27-7.29 (1H, m, H-9(10)); 7.33-7.36 (1H, m, H-10(9)); 7.39 (1H, d, J = 7.6, H-11); 7.61 (2H, d, J = 8.3, H Ar); 7.70 (1H, s, H-4); 8.36 (1H, d, J = 8.9, H-8). Mass spectrum, m/z: 545 $[M+H]^+$. Found, %: C 68.12; H 5.90; N 5.42. $C_{31}H_{32}N_2O_5S$. Calculated, %: C 68.36; H 5.92; N 5.14.

Methyl (2*Z*)-2-benzylidene-1'-ethyl-1-[(4-methylphenyl)sulfonyl]-1,2,5',6'-tetrahydro-1'*H*-spiro-[indole-3,4'-pyridine]-3'-carboxylate (9) was obtained as by-product upon refluxing the carboline **3a** with methyl propiolate in CH_2Cl_2, followed by separation of the mixture by column chromatography (eluent 1:5 EtOAc–hexane). Yield 0.02 g (3%), yellow crystals, mp 144-146°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1170 (S=O), 1364 (S=O), 1685 (C=O). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.82 (1H, ddd, J = 3.4, J = 5.2, J = 13.3) and 2.86 (1H, dt, J = 4.5, J = 13.3, 5'-CH_2); 1.14-1.19 (1H, m) and 3.17-3.21 (1H, m, 6'-CH_2); 1.26 (3H, t, J = 7.2, $NCH_2C\underline{H}_3$); 2.34 (3H, s, $ArC\underline{H}_3$); 3.25-3.33 (2H, m, $NC\underline{H}_2CH_3$); 3.31 (3H, s, CO_2CH_3); 6.04 (1H, s, =C<u>H</u>–Ph); 6.89 (1H, d, J = 6.9, H Ar); 7.08-7.11 (3H, m, H Ar); 7.18-7.20 (1H, m, H Ar); 7.25-7.26 (1H, m, H Ar); 7.30-7.32 (2H, m, H Ar); 7.45 (2H, d, J = 8.3, H Ar); 7.56 (2H, d, J = 7.6, H Ar); 7.68 (1H, s, H-2'); 7.78 (1H, d, J = 8.3, H-4). Mass spectrum, m/z: 515 $[M+H]^+$. Found, %: C 69.95; H 5.85; N 5.40. $C_{30}H_{30}N_2O_4S$. Calculated, %: C 70.02; H 5.88; N 5.44.

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