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Reactions of *N*-and *C*-Alkenylanilines: VII.* Synthesis of Indole Heterocycles from Products of Reaction between *N*-Mesyl-2-(1-alken-1-yl)anilines and Halogens

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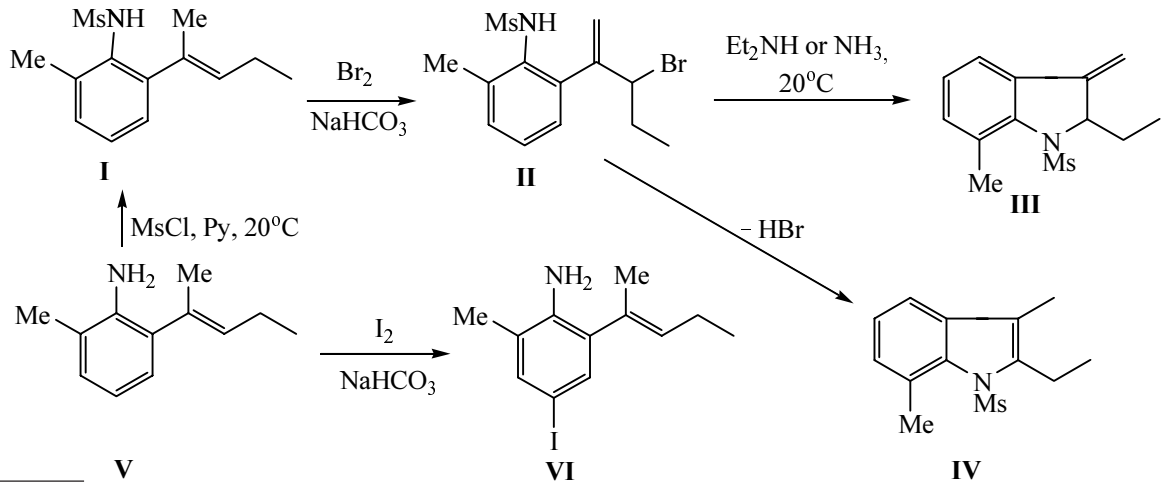
Abstract—*N*-Mesyl-2-(1-methyl-1-butenyl)-6-methylaniline reacted with Br_2 to afford *N*-mesyl-2-(3-bromo-1-penten-2-yl)aniline that under treatment with NH_3 or amines underwent cyclization into *N*-mesyl-7-methyl-3-methylene-2-ethylindoline. The reaction of *N*-mesyl-2-(1-methyl-1-buten-1-yl)-4-methyl- and 2-(1-methyl-1-buten-1-yl)aniline with Br_2 gave rise to the corresponding *N*-mesyl-2-(2-bromo-1-methyl-1-buten-1-yl)anilines. Under the similar conditions *N*-tosyl-2-(1-cyclohexen-1-yl)aniline was converted into *N*-tosyl-2-(6-bromo-1-cyclohexen-1-yl)aniline that under treatment with NH_3 furnished *N*-tosyl-1,2,3,9a-tetrahydrocarbazole. The reaction of *N*-mesyl-1,2,3,9a-tetrahydrocarbazole with $CuBr_2$ in MeOH afforded *N*-mesyl-4-methoxy-1,2,3,4-tetrahydrocarbazole. *N*-Mesyl-6-methyl-2-(1-cyclopenten-1-yl)aniline in reaction with Br_2 in the presence of $NaHCO_3$ was oxidized into the corresponding cyclopentenone, and with NBS it gave *N*-mesyl-2-(2-bromo-1-cyclopenten-1-yl)aniline.

Compounds of 3-methyleneindole structure are used in the synthesis of biologically active substances. However save 2-oxoderivatives [2–5] and a limited number of compounds lacking the 2-oxo group [6–8] these systems are of low stability and suffer isomerization into indole in the course of their preparation due to the influence of various factors. Therefore the development of efficient methods for preparation of indolines with and *exo*-C=C bond is a pressing problem nowadays.

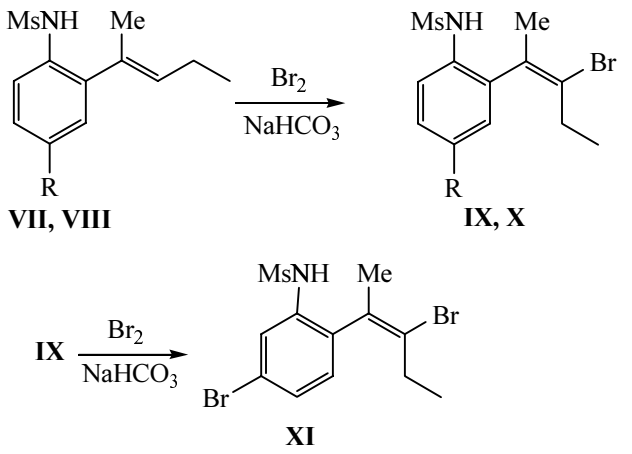
With the goal of synthesizing 3-methyleneindoles we studied the halogenation of *N*-methylsulfonylanilines that were obtained in high yield from the *ortho*-(1-alken-1-yl)anilines. By bromination of compound **I** we prepared a relatively stable allyl halide **II** that in the presence of a base (Et_2NH or NH_3) readily afforded indoline **III** with an *exo*-methylene group. In the absence of amines compound **II** slowly underwent cyclization into indole **IV** in a virtually quantitative yield (Scheme 1).

Scheme 1.



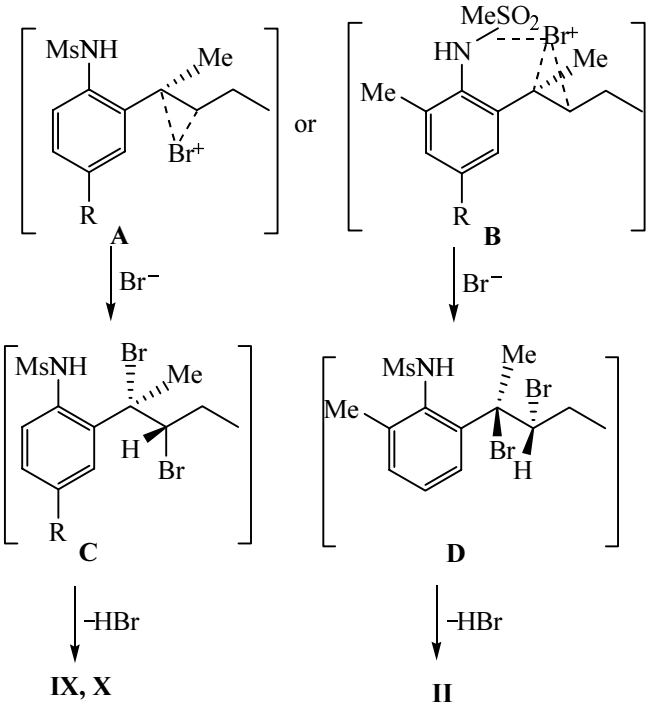
* For communication VI, see [1].

Scheme 2.



R = H (**VII, IX**), Me (**VIII, X**).

Scheme 3.



R = H (**IX**), Me (**X**).

The attempt to prepare indoline with an *exo*-methylene group and a free nitrogen atom by treating with Br_2 amine **V** resulted in tarring of the reaction mixture due to a vigorous reaction. The reaction of I_2 with amine **V** in the presence of $NaHCO_3$ gave rise to iododerivative **VI.**

N-mesyl derivatives **VII** and **VIII** in reaction with Br_2 provided as the principal products exclusively vinyl bromides **IX** or **X** (Scheme 2).

The double bond in compounds **IX** and **X** is deactivated, and at the attack of the next Br_2 molecule on bromide **IX** an electrophilic substitution occurs into the position *5* of the aromatic ring. Apparently the inductive effect of the bromovinyl moiety is stronger than the analogous effect of the methanesulfonyl group, and this governs the substitution direction.

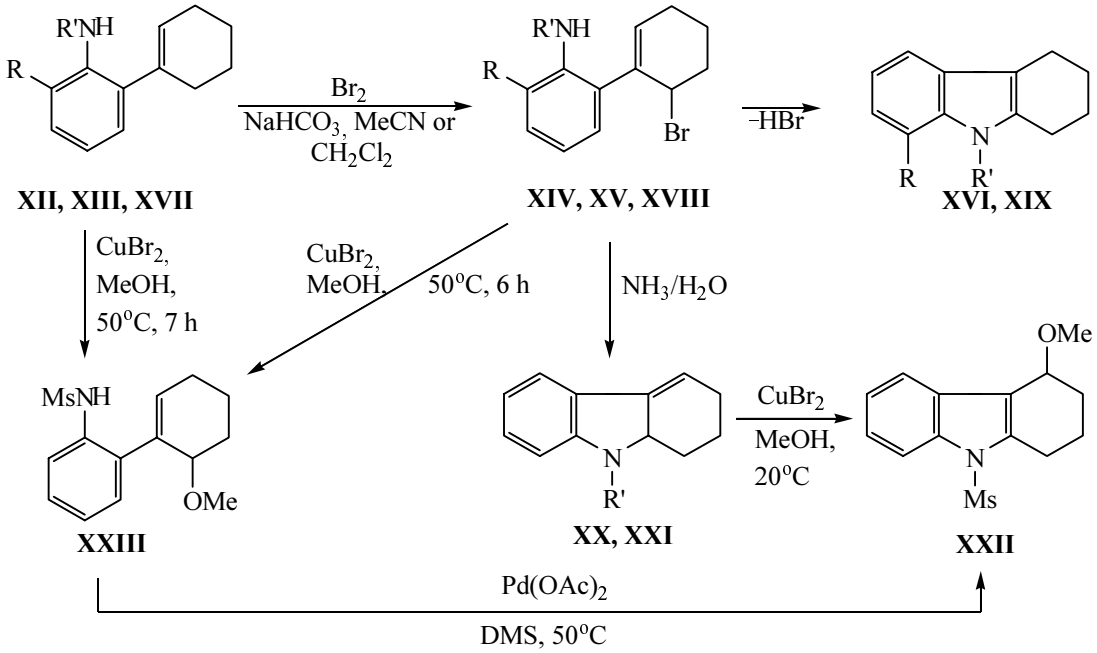
This difference in structure of the reaction products formed from fairly similar alkenylanilines **I, VII,** and **VIII** we understand as follows**.** Pimarily arising bromonium cations coordinated or noncoordinated through the sulonamide group **A** or **B** suffer a *trans*-attack by an anion Br^- and give rise to *trans*-dibromides **C** or **D**. In event of compound **I** presumably due to steric hindrances the elimination is directed to formation of bromoalkene **II** having a terminal double bond. With no methyl substituents in the position *2* of the aromatic ring the methanesulfonyl group does not suffer repulsion in the direction of the alkenyl moiety and does not sterically hamper the free rotation around the $C^{1'}$–$C^{2'}$ bond, and thus dqbromide **C** takes a conformation favorable for the *trans*-elimination of proton $H^{2'}$ and halogen $Br^{1'}$. Therefore in the case of amides **VII** and **VIII** formed bromides **IX** and **X** (Scheme 3).

In the presence of a cyclic fragment the *cis*-elimination is impossible. Thus in reaction with Br_2 mesylate **XII** [9] and tosylate **XIII** of the cyclohexenylaniline also afford relatively stable allyl bromides **XIV** [9] and **XV**. It was demonstrated that bromide **XIV** condensated spontaneously into tetrahydrocarbazole **XVI** [9]. In the presence of a methyl substituent in the position *6* from mesylate **XVII** formed less stable allyl bromide **XVIII**, and in this case the final reaction mixture consisted of **XVIII** and tetrahydrocarbazolea **XIX**. In 24 h bromide **XVIII** disappeared from the mixture, and it contained only **XIX**.

The treatment of allyl bromides **XIV** and **XV** with aqueous ammonia afforded tetrahydrocarbazoles **XX** [9] and **XXI,** valuable intermediates for the synthesis of 4-substituted tetrahydrocarbazoles. For instance, tetrahydrocarbazole **XX** reacted with $CuBr_2$ in MeOH [10] gave 4-methoxycarbazole **XXII** in a high yield. This compound can be also prepared as follows: The reaction of amide **XII** or allyl bromide **XIV** with $CuBr_2$ in MeOH affords methoxyderivative **XXIII**. The latter brought into reaction with $Pd(OAc)_2$ in DMSO also affords heterocycle **XXII** in a 44% yield (Scheme 4).

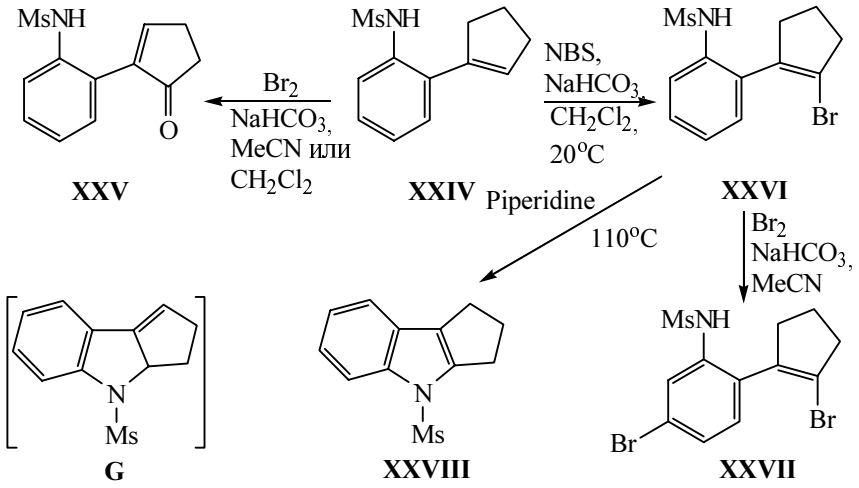
The attempts to use bromine in preparation of a homolog of carbazoles **XX** and **XXI,** tetrahydrocyclopent-

Scheme 4.



R = H, R' = Ms (**XII, XIV, XVI, XX**), Ts (**XIII, XV, XXI**); R = Me, R' = Ms (**XVII, XVIII, XIX**).

Scheme 5.



[*b*]indole **G** starting with *N*-mesylate **XXIV** were unsuccessful (Scheme 5). It was found that in reaction with Br_2 compound **XXIV** [11] furnished as the main reaction product ketone **XXV**. Therewith at the equimolar amount of the halogen initial compound **XXIV** was not completely consumed, and additional bromine amount was required. The analog of compound **XXIV** with a methyl group in the ring under these conditions furnished a similar ketone [12]. The mechanism of these ketones formation is not elucidated. In reaction of amide **XXIV** with NBS vinyl bromide **XXVI** was obtained that treated with bromine underwent halogenation into the aromatic ring providing dibromide **XXVII**. On heating vinyl bromide **XXVI** with piperidine cyclization into indole **XXVIII** occurred in 95% yield.

The composition and structure of compounds synthesized was established by elemental analysis and spectral methods. The signals in the ^1H and ^{13}C NMR spectra were assigned using CH- and HH-correlation methods, double resonance , and JMOD.

Hence the structure of reaction products formed from *N*-mesyl and *N*-tosyl-2-(1-alken-1-yl)anilines depended

on the structure of the alkenyl moiety and on the character of the *ortho*-substituent in the aromatic ring.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM 300 at operating frequency 300 and 75 MHz respectively from solutions in $CDCl_3$, internal reference TMS. The purity of products was checked by GLC on a chromatograph Chrom-5, carrier gas helium (flow rate 50 ml/min), flame-ionization detector, columns 1200×3 mm, stationary phase silicon fluid SE-30 (5%) on Chromaton N-AW DMCS carrier, oven temperature 50–300°C. The column chromatography was carried out on silica gel 0.063 pm (Lancaster). The qualitative TLC was performed on Sorbfil UV-254 plates (ZAO Sorbpolymer, Krasnodar) (eluent C_6H_6–EtOAc, 9:1), spots visualized by UV irradiation (λ 254 nm) and by iodine vapor. Elemental analysis was carried out on C–H–NAnalyzer M-185B.

To a solution of 5.2 mmol of amine in 10 ml of pyridine was added dropwise at stirring 0.86g (7.5 mmol) of MsCl. After 7 h 1 ml of water was added, the mixture was stirred for 1 h, and the solvent was evaporated in a vacuum. To the residue 50 ml of $CHCl_3$ was added, the solution was washed with a saturated water solution of $NaHCO_3$ (20 ml), with water (20 ml), and dried over Na_2SO_4. After evaporating the solvent the reaction products **I** and **XVII** were recrystallized from EtOH.

***N*-Mesyl-2-[(*E*)-1-methyl-1-buten-1-yl]-6-methyl-aniline (I)**. Yield 87%, mp 72–74°C. ^{1}H NMR spectrum, δ, ppm: 1.10 t (3H, CH_3, *J* 7.3 Hz), 2.01 s (3H, $3CH_3$), 2.51 s (3H, $3CH_3$), 3.05 s (3H, $3CH_3$), 2.22 q (2H, CH_2, *J* 7.3 Hz), 5.50 d.t (1H, H$^{2'}$, J_1 1.2, J_2 7.3 Hz), 6.33 br.s (1H, NH), 7.01–7.24 m (3H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 13.5, 19.3, 21.5, 41.6 ($4CH_3$), 17.7 (CH_2), 127.1 (C^4), 127.5 (C$^{2'}$), 129.4 (C^5), 131.0 (C^2), 133.3 (C^3), 133.6 (C^6), 138.0 (C$^{1'}$), 144.5 (C^1). Found, %: C 61.36; H 7.18; N 5.20; S 12.22. $C_{13}H_{19}NO_2S$. Calculated, %: C 61.63; H 7.56; N 5.53; S 12.65.

***N*-Mesyl-2-[1-methyl-1-(*E*)-buten-1-yl]aniline (VII).** Amorphous substance. Yield 82%, R_f 0.4. ^{1}H NMR spectrum, δ, ppm: 1.05 t (3H, CH_3, *J* 7.5 Hz), 1.95–2.25 m (2H, CH_2), 2.15 s (3H, CH_3), 3.10 s (3H, CH_3), 5.55 d.t (1H, H$^{2'}$, J_1 1.2, J_2 7.3 Hz), 6.75 s (1H, NH), 6.90–7.55 m (4H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 13.6, 24.8, 39.2 ($3CH_3$), 22.2 (CH_2), 117.2 (C^6), 123.8 (C^4), 127.9 (C$^{2'}$), 128.7 (C^3), 130.8 (C^2), 133.4 (C^5), 133.6 (C^1), 136.3 (C$^{1'}$). Found, %: C 59.92; H 6.98; N 5.61; S 13.04. $C_{12}H_{17}NO_2S$. Calculated, %: C 60.22; H 7.16; N 5.85; S 13.40.

***N*-Mesyl-2-[(*E*)-1-methyl-1-buten-1-yl]-4-methyl-aniline (VIII)**. Amorphous substance. Yield 84%, R_f 0.4. ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, *J* 7.0 Hz), 1.72–1.86 m (2H, CH_2), 1.97 s (3H, CH_3), 2.10 s (3H, CH_3), 2.98 s (3H, CH_3), 5.68 d.t (1H, H$^{2'}$, J_1 1.2, J_2 7.3 Hz), 6.51 s (1H, NH), 6.89 s (1H, H^3), 7.10 d.d (1H, H^5, J_1 1.6, J_2 8.4 Hz), 7.49 d (1H, H^6, *J* 8.4 Hz). ^{13}C NMR spectrum, δ, ppm: 13.7, 20.5, 22.4, 39.1 ($4CH_3$), 25.0 (CH_2), 118.3 (C^6), 128.5 (C$^{2'}$), 129.2 (C^5), 130.8 (C^4), 131.0 (C^2), 131.8 (C^1), 133.2 (C^3), 133.7 (C$^{1'}$). Found, %: C 61.44; H 7.22; N 5.19; S 12.22. $C_{13}H_{19}NO_2S$. Calculated, %: C 61.63; H 7.56; N 5.53; S 12.65.

***N*-Mesyl-6-methyl-2-(1-cyclohexen-1-yl)aniline (XVII)**. Yield 88%, mp 116°C. ^{1}H NMR spectrum, δ, ppm: 1.64–1.80 m (4H, $2CH_2$), 2.12–2.20 m (2H, CH_2), 2.31 m (2H, CH_2), 2.44 s (3H, CH_3), 3.05 s (3H, CH_3), 5.71 m (1H, H$^{2'}$), 6.54 br.s (1H, NH), 7.03 t (1H, Ar-H, *J* 5.55 Hz), 7.14–7.16 m (2H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 21.8, 22.9, 25.4, 29.9 ($4CH_2$), 19.7, 41.9 ($2CH_3$), 127.1 (C^4), 127.6 (C^3), 128.1 (C$^{2'}$), 129.7 (C^5), 131.3 (C^6), 137.3 (C^2), 138.0 (C^1), 143.2 (C$^{1'}$). Found, %: C 63.49; H 7.08; N 5.30; S 11.98. $C_{14}H_{19}NO_2S$. Calculated, %: C 63.36; H 7.22; N 5.28; S 12.08.

To a reaction mixture containing 2 mmol of sulfonamide and 1.68 g (20 mmol) of $NaHCO_3$ in 15 ml of CH_3CN or $CHCl_3$ was added dropwise 0.32 g (2 mmol) of Br_2 in 5 ml of the same solvent. The solution immediately lost color, On completion of the reaction the solvent was evaporated in a vacuum, the residue was diluted with 50 ml of CH_2Cl_2 and washed with water (2×50 ml). The organic layer was dried over Na_2SO_4. The solvent was removed in a vacuum.

***N*-Mesyl-2-(3-bromo-1-penten-2-yl)-6-methyl-aniline (II)**. Yield of crude allyl bromide **II** was 97%, R_f 0.4. ^{1}H NMR spectrum, δ, ppm: 1.11 t (3H, CH_3, *J* 7.4 Hz), 2.02 m (2H, CH_2), 2.51 s (3H, $2CH_3$), 3.20 s (3H, $2CH_3$), 4.71 d.d (1H, H$^{3'}$, J_1 4.7, J_2 8.8 Hz), 5.41 s (1H, H$^{1'a}$, H$^{1'\alpha}$), 5.83 s (1H, H$^{1'a}$, H$^{1'\alpha}$), 6.32 s (1H, NH), 7.00–7.32 m (3H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 12.1, 19.1, 43.5 ($3CH_3$), 29.7 (CH_2), 59.6 (C$^{3'}$), 119.3 (C$^{1'}$), 127.5 (C^4), 128.6 (C^3), 130.4 (C^5), 133.5 (C^6), 138. (C^2), 139.7 (C^1), 147.7 (C$^{2'}$). Found, %: C 46.59; H 5.23; Br 23.69; N 4.01; S 9.29. $C_{13}H_{18}BrNO_2S$. Calculated, %: C 46.99: H 5.46; Br 24.05; N 4.22; S 9.65.

***N*-Mesyl-2-[(*E*)-2-bromo-1-methyl-1-buten-1-yl]-aniline (IX)**. Yield 81%, mp 103–104°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 1.04 t (3H, CH_3, *J* 7,2 Hz),

2.11 s (3H, CH_3), 2.23 q (2H, CH_2, *J* 7.2 Hz), 3.08 s (3H, CH_3), 6.44 s (1H, NH), 7.07 d.d (1H, H^6, J_1 1.6, J_2 7.5 Hz), 7.15 d.t (1H, H^5, J_1 0.9, J_2 7.2 Hz), 7.31 d.d.d (1H, H^4, J_1 0.9, J_2 1.6, J_3 7.2 Hz), 7.60 d (1H, H^3, *J* 8.3 Hz). ^{13}C NMR spectrum, δ, ppm: 13.4, 24.8, 40.0 ($3CH_3$), 31.7 (CH_2), 118.3 (C^6), 124.3 (C^4), 128.7 (C^3), 128.8 (C^5), 130.5 ($C^{2'}$), 131.2 (C^2), 131.5 (C^1), 133.4 ($C^{1'}$). Found, %: C 45.12; H 4.89; Br 25.80; N 4.23; S 10.44. $C_{12}H_{16}BrNO_2S$. Calculated, %: C 45.29; H 5.07; Br 25.11; N 4.40; S 10.07.

***N*-Mesyl-2-[(*E*)-2-bromo-1-methyl-1-buten-1-yl]-4-methylaniline (X)**. Amorphous substance separated from EtOH as oily compound. Yield 95%, R_f 0.6. ^1H NMR spectrum, δ, ppm: 1.05 t (3H, CH_3, *J* 7.2 Hz), 2.12 s (3H, CH_3), 2.25 q (2H, CH_2, *J* 7.2 Hz), 2.35 s (3H, CH_3), 3.08 s (3H, CH_3), 6.32 s (1H, NH), 6.90 s (1H, H^3), 7.12 d (1H, H^5, *J* 8.3 Hz), 7.48 d (1H, H^6, *J* 8.3 Hz). ^{13}C NMR spectrum, δ, ppm: 13.3, 20.5, 24.9, 39.8 ($4CH_3$), 31.6 (CH_2), 118.9 (C^6), 129.2 (C^3), 129.4 (C^5), 130.6 ($C^{2'}$), 131.9 (C^4), 133.2 (C^2), 133.8 (C^1), 134.3 ($C^{1'}$). Found, %: C 46.72; H 5.21; Br 23.80; N 4.05; S 9.34. $C_{13}H_{18}BrNO_2S$. Calculated, %: C 47.00; H 5.46; Br 24.05; N 4.22; S 9.65.

***N*-Mesyl-5-bromo-2-[(*E*)-2-bromo-1-methyl-1-buten-1-yl]aniline (XI)**. Yield 50%, mp 133–134°C (EtOH). ^1H NMR spectrum, δ, ppm: 1.06 t (3H, CH_3, *J* 7.3 Hz), 2.11 s (3H, CH_3), 2.24 q (2H, CH_2, *J* 7.3 Hz), 3.06 s (3H, CH_3), 6.40 s (1H, NH), 7.23 d (1H, H^6, *J* 2.2 Hz), 7.43 d.d (1H, H^3, J_1 2.2, J_2 8.8 Hz), 7.50 d (1H, H^8, *J* 8.8 Hz). ^{13}C NMR spectrum, δ, ppm: 13.4, 24.7, 40.1 ($3CH_3$), 31.8 (CH_2), 117.1 ($C^{2'}$), 119.9 (C^4), 129.2 (C^5), 131.4 (C^6), 131.6 (C^3), 132.2 (C^2), 132.6 (C^1), 133.4 ($C^{1'}$). Found, %: C 36.32; H 3.54; Br 40.40; N 3.34; S 7.87. $C_{12}H_{15}Br_2NO_2S$. Calculated, %: C 36.29; H 3.81; Br 40.24; N 3.53; S 8.07.

***N*-Mesyl-5-bromo-2-(2-bromo-1-cyclopenten-1-yl)aniline (XXVII)**. On recrystallization from EtOH 0.6 g (51%) of dibromide **XXVII** was obtained, mp 172–174°C. IR spectrum, ν, cm^{-1}: 493, 525, 535 (C–Br), 3265 (NH). ^1H NMR spectrum, δ, ppm: 2.18 quint (2H, CH_2, *J* 7.4 Hz), 2.60–2.70 m (2H, CH_2), 2.85–2.95 m (2H, CH_2), 3.10 s (3H, CH_3), 6.50 s (1H, NH), 7.29 d (1H, H^6, *J* 2.2 Hz), 7.45 d.d (1H, H^4, J_1 2.2, J_2 7.7 Hz), 7.50 d (1H, H^3, *J* 7.7 Hz). ^{13}C NMR spectrum, δ, ppm: 22.1 ($C^{4'}$), 37.5 ($C^{5'}$), 39.6 ($C^{3'}$), 40.9 (SCH_3), 117.5 (C^6), 121.3 (C^4), 123.2 ($C^{2'}$), 130.0 (C^2), 131.6 (C^3), 131.8 (C^5), 133.9 (C^1), 136.3 ($C^{1'}$). Found, %: C 36.05; H 3.01; Br 40.06; N 3.17; S 7.82. $C_{12}H_{13}Br_2NO_2S$. Calculated, %: C 36.48; H 3.32; Br 40.45; N 3.55; S 8.11.

7-Methyl-3-methylene-1-mesyl-2-ethylindoline (III). To a solution of 0.166 g (0.5 mmol) of bromide **II** in 3 ml of MeOH was added 0.2 ml of Et_2NH or 1 ml of 10% solution of NH_3 in MeOH at 20°C. The reaction mixture was left standing for 10 h, MeOH was evaporated in a vacuum, the residue was diluted with 30 ml of CH_2Cl_2, washed with 10% water solution of $NaHCO_3$ and with water. The organic phase was separated and dried with $MgSO_4$. On removing the solvent in a vacuum compound **III** was isolated by column chromatography on silica gel (1 g) (eluent C_6H_6). We obtained 0.11 g (88%) of amorphous compound **III**, R_f 0.6. ^1H NMR spectrum, δ, ppm: 1.01 t (3H, CH_3, *J* 7.3 Hz), 1.31–1.92 m (2H, CH_2), 2.40 s (3H, $2CH_3$), 2.50 s (3H, $2CH_3$), 4.52 d.d (1H, H^2, J_1 4.6, J_2 12.4 Hz), 5.11 d (1H, $H^{1a'}$, *J* 1.5 Hz), 5.63 d (1H, $H^{1b'}$, *J* 1.5 Hz), 7.10–7.31 m (3H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 9.4, 19.3, 34.2 ($3CH_3$), 30.0 (CH_2), 69.9 (C^2), 104.5 (=CH_2), 118.8 (C^5), 126.7 (C^4), 126.9 (C^{3a}), 132.6 (C^6), 133.6 (C^7), 134.4 (C^{7a}), 146.4 (C^3). Mass spectrum, *m/z*: 251 M^+. Found, %: C 61.80; H 6.56; N 5.24; S 12.37. $C_{13}H_{17}NO_2S$. Calculated, %: C 62.12; H 6.83; N 5.57; S 12.76.

***N*-Mesyl-3,7-dimethyl-2-ethylindole (IV)**. After keeping 0.21 g (0.65 mmol) of compound **II** for 100 h at room temperature the substance formed was dissolved in 10 ml of CH_2Cl_2, washed with a saturated water solution of $NaHCO_3$ (10 ml) and water (10 ml). The organic phase was dried over Na_2SO_4. On removing the solvent we obtained 0.16 g (97%) of indole **IV**, R_f 0.7. ^1H NMR spectrum, δ, ppm: 1.00 t (3H, CH_3, *J* 7.0 Hz), 2.61 s (3H, CH_3), 2.75 s (3H, CH_3), 2.85 q (2H, CH_2, *J* 7.0 Hz), 3.50 s (3H, CH_3), 7.30–8.20 m (3H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 9.2, 14.3, 21.7, 36.4 ($4CH_3$), 20.4 (CH_2), 116.1 (C^3), 120.8 (C^5), 125.0 (C^7), 128.3 (C^4), 129.1 (C^6), 135.3 (C^{3a}), 138.7 (C^2), 141.9 (C^{7a}). Found, %: C 61.86; H 6.52; N 5.40; S 12.42. $C_{13}H_{17}NO_2S$. Calculated, %: C 62.12; H 6.82; N 5.57; S 12.76.

6-Methyl-2-[(*E*)-1-methyl-1-buten-1-yl]aniline (V). In the presence of 10 g of KOH 10 g of 2-(1-methylbuten-2-yl-1)-6-methylaniline was heated for 1 h at 300°C, then the reaction mixture was cooled, the products were decanted and distilled in a vacuum. *Cis*- and *trans*-isomers were separated by fractional distillation in a vacuum. The main product, amine **V**, was the first fraction. Yield 5.5 g (55%), bp 116°C (3 mm Hg). IR spectrum, ν, cm^{-1}: 3380, 3460 (NH_2). ^1H NMR spectrum, δ, ppm: 1.00 t (3H, CH_3, *J* 7.4 Hz), 2.00 s (3H, $2CH_3$), 2.32 s (3H, $2CH_3$), 2.31–2.53 m (2H, CH_2), 3.80 s (2H, NH_2), 5.82 t (1H, $H^{2'}$, *J* 7.4 Hz), 6.81–7.31 m (3H, Ar-

H). ^{13}C NMR spectrum, δ, ppm: 14.0, 17.1, 21.5 ($3CH_3$), 17.6 (CH_2), 117.6 (C^4), 122.0 (C^6), 126.4 ($C^{2'}$), 128.5 (C^3), 131.1 (C^5), 132.1 (C^2), 133.1 ($C^{1'}$), 141.0 (C^1). Found, %: C 82.33; H 9.50; N 7.63. $C_{12}H_{17}N$. Calculated, %: C 82.23; H 9.78; N 7.99.

4-Iodo-6-methyl-2-[1-methylbut-2(*Z*)-en-1-yl]aniline (VI). To a solution of 0.7 g (4 mmol) of amine **V** in 20 ml of CCl_4 was added 3.4 g (40 mmol) of $NaHCO_3$, and 2 g (8 mmol) of I_2. On consumption of the initial amine (~6–7 h) the precipitate was filtered off, the reaction mixyure was washed with 10% water solution of $Na_2S_2O_3$ (2×50 ml) and with water (10 ml), then the organic phase was dried over $MgSO_4$. On removing the solvent in a vacuum the product was isolated by column chromatography on silica gel. Yield 0.65 g (54%), R_f 0.4. IR spectrum, ν, cm^{-1}: 3378, 3465 (NH_2). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, *J* 7.4 Hz), 1.82 m (2H, CH_2), 1.90 s (3H, $2CH_3$), 2.20 s (3H, $2CH_3$), 3.82 s (2H, NH_2), 5.63 t (1H, $H^{2'}$, *J* 6.9 Hz), 7.11 s (1H, H^3), 7.33 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 14.3, 17.6, 24.5 ($3CH_3$), 22.7 (CH_2), 79.2 (C^4), 124.7 (C^1), 130.0 (C^2), 132.1 (C^6), 132.2 (C^5), 134.8 ($C^{3'}$), 137.1 (C^2), 140.9 ($C^{2'}$). Found, %: C 47.39; H 5.23; I 41.69; N 4.17. $C_{12}H_{16}IN$. Calculated, %: C 47.86; H 5.35; I 42.14; N 4.65.

***N*-Tosyl-2-(1-cyclohexen-1-yl)aniline (XIII)**. To a solution of 0.86 g (5 mmol) of 2-(1-cyclohexenyl)-aniline in 10 ml of pyridine was added 1.4 g (7.3 mmol) of *p*-toluenesulfonyl chloride [13]. The reaction mixture was left standing for 24 h at room temperature, then it was diluted with 0.5 ml of H_2O, stirred for 30 min, the solvent was evaporated in a vacuum. The residue was diluted with 30 ml of H_2O and 50 ml of CH_2Cl_2. The organic phase was separated, washed with 30 ml of 5% HCl solution, then with water (2×10 ml), and dried over $MgSO_4$. The solvent was evaporated in a vacuum, the residue was recrystallized from EtOH. Yield 1.42 g (87%), mp 120–122°C. ^{1}H NMR spectrum, δ, ppm: 1.53–1.75 m (8H, $4CH_2$), 2.38 s (3H, CH_3), 5.36 d.t (1H, $H^{2'}$, J_1 1.9, J_2 3.5 Hz), 6.92–7.69 m (8H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 21.3 (CH_3), 21.5, 22.6, 25.0, 29.8 ($4CH_2$), 120.9, 124.4, 126.9, 127.4, 128.3, 128.5, 129.4 ($C^{2'}$, C^3, C^4, C^5, C^6, $C^{2''6''}$, $C^{3''5''}$), 132.9, 134.9, 135.8, 136.2, 143.7 (C^1, C^2, $C^{1'}$, $C^{1''}$, $C^{4''}$). Found, %: C 69.58; H 6.27; N 4.09; S 9.64. $C_{19}H_{21}NO_2S$. Calculated, %: C 69.70; H 6.46; N 4.28; S 9.79.

***N*-Mesyl-8-methyl-1,2,3,4-tetrahydrocarbazole (XIX).** To a solution containing 0.53 g (2 mmol) of amide **XVII** and 15 mmol of $NaHCO_3$ in 20 ml of MeCN was added dropwise at vigorous stirring 0.32 g (2 mmol) of a solution of Br_2 in 5 ml of the same solvent. On stirring for 3 h the precipitate was filtered off, and the solvent was evaporated in a vacuum. The residue was dissolved in 30 ml of CH_2Cl_2, and washed with 20 ml of 5% solution of $NaHCO_3$. The organic phase was dried over Na_2SO_4. On evaporating the solvent in a vacuum the residue was subjected to a chromatography on a short column packed with silica gel (1og) to obtain 0.47 g (90%) of amorphous substance **XIX**, R_f 0.75. ^{1}H NMR spectrum, δ, ppm: 1.90–2.00 m (4H, $2CH_2$), 2.55 m (2H, CH_2), 2.60 s (3H, CH_3), 2.75 s (3H, CH_3), 2.90 m (2H, CH_2), 7.05–7.30 m (3H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 21.2 (CH_3), 22.0, 23.2, 23.4, 25.8 ($4CH_2$), 38.0 (CH_3), 115.7 (C^6), 122.4 (C^{4a}), 124.6 (C^7), 127.8 (C^{4b}), 128.4 (C^5), 133.7 (C^{9a}), 137.8 (C^8), 138.5 (C^{8a}). Found, %: C 63.49; H 6.20; N 5.01; S 11.88. $C_{14}H_{17}NO_2S$. Calculated, %: C 63.85; H 6.51; N 5.32; S 12.17. Mass spectrum, *m/z* (I_{rel}, %): 263 (16), M^+, 184 (100) $[M - SO_2CH_3]^+$, 168 (9), 167 (10) $[M - Ms - NH_3]^+$, 157 (12) $[M - Ms - HCN]^+$, 156 (8) $[157 - H]^+$), 154 (6) $[157 - H - H_2]^+$, 141 (5) $[167 - C_2H_2]^+$, 128 (7) $[154 - C_2H_2]^+$, 115 (9) $[167 - 2C_2H_2]^+$, 91 (2), 89 (3) $[167 - 3C_2H_2]^+$, 79 (7) $[SO_2CH_3]^+$, 77 (4), 65 (3), 64 (7) $[SO_2]^+$, 63 (2), 51 (2), 48 (5) $[SO]^+$, 41 (3), 39 (5).

9-Tosyl-1,2,3,9*a*-tetrahydrocarbazole (XXI). To a solution of 0.61 g (1.86 mmol) of amide **XIII** and 1 g of $NaHCO_3$ in 20 ml of CH_2Cl_2 was added dropwise at stirring 0.3 g (1.86 mmol) of Br_2 in 5 ml of CH_2Cl_2. In 2 h the reaction mixture was washed with 50 ml of H_2O and extracted into 50 ml of CH_2Cl_2. The solvent was evaporated in a vacuum to a minimal volume, and 10 ml of 25% aqueous NH_3 was added thereto. The residue was dissolved in 100 ml of CH_2Cl_2 and washed with 50 ml of H_2O. The organic phase was dried over Na_2SO_4. On evaporating the solvent in a vacuum the yield was 0.6 g (99%). ^{1}H NMR spectrum, δ, ppm: 1.45–2.90 m (6H, $3CH_2$), 2.38 s (3H, CH_3), 4.20 d.d (1H, H^{9a}, J_1 3.5, J_2 10.1 Hz), 5.85 q (1H, H^4, *J* 3.6 Hz), 6.90–7.80 m (8H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 20.0, 24.3, 28.9 ($3CH_2$), 21.3 (CH_3), 63.9 (C^{9a}); 115.2, 117.9, 119.9, 123.8, 126.3, 127.5, 129.3 (C^4, C^5, C^6, C^7, C^8, $C^{2'6'}$, $C^{3'5'}$), 128.7, 133.1, 135.4, 143.2, 144.1 (C^{4a}, C^{8a}, $C^{1'}$, C^{4b}, C^4). Found, %: C 70.02; H 5.79; N 4.22; S 9.77. $C_{19}H_{19}NO_2S$. Calculated, %: C 70.13; H 5.88; N 4.30; S 9.85.

4-Methoxy-9-mesyl-1,2,3,4-tetrahydrocarbazole (XXII). *a*. The reaction mixture containing 0.74 g (3.3 mmol) of $CuBr_2$ and 0.41 g (1.65 mmol) of tetrahydrocarbazole **XX** in 20 ml of MeOH was stirred at

20°C for 24 h. On completion of the reaction the mixture was worked up as described for compound **XXIII**. After column chromatograpy on silica gel to remove tar we obtained 0.44 g (96%) of ester **XXII** as a transparent viscous substance, R_f 0.3.

b. The reaction mixture containing 0.23 g (0.82 mmol) of ester **XXIII**, 0.18 g (0.82 mmol) of $Pd(OAc)_2$, and 0.13 g (1.64 mmol) of NaOAc in 9 ml of DMSO was stirred at 50°C for 72 h. Then the reaction mixture was diluted with 50 ml of CH_2Cl_2 and washed with H_2O (2×50 ml). The organic phase was dried over Na_2SO_4. On removing the solvent in a vacuum the residue was subjected to chromatography on a column packed with silica gel (2 g). Yield of compound **XXII** was 0.1 g (44%), R_f 0.3. ^{1}H NMR spectrum, δ, ppm: 1.70–2.20 m (4H, $2CH_2$), 2.80–3.00 m (2H, CH_2), 3.05 s (3H, CH_3), 3.55 s (3H, CH_3), 4.60 d.t (1H, H^4, J_1 1.5, J_2 3.4 Hz), 7.27–7.32 m (2H, Ar-H), 7.60–7.65 m (1H, Ar-H), 7.95–7.99 m (1H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 18.5 (C^2), 24.1 (C^1), 26.3 (C^3), 40.5 (SCH_3), 56.1 (OCH_3), 71.2 (C^4), 113.2 (C^8), 117.9 (C^{4a}), 118.9 (C^5), 123.3 (C^6), 124.0 (C^7), 128.9 (C^{4b}), 135.6 (C^{9a}), 137.5 (C^{8a}). Found, %: C 59.86; H 5.88; N 4.64; S 11.07. $C_{14}H_{17}NO_3S$. Calculated, %: C 60.19; H 6.13; N 5.01; S 11.48.

***N*-Mesyl-2-(6-methoxy-1-cyclohexen-1-yl)aniline (XXIII)**. *a*. The reaction mixture containing 0.45 g (2 mmol) of $CuBr_2$ and 0.25 g (1 mmol) of mesylate **XII** in 20 ml of MeOH was heated at 50–55° C for 7 h. On cooling the mixture to room temperature 25 ml of H_2O was added, the reaction product was extracted into 30 ml of CH_2Cl_2. The organic phase was dried over Na_2SO_4. On removing the solvent in a vacuum the residue was subjected to chromatography on a column (2×40 cm) packed with silica gel (5 g, eluent C_6H_6). We obtained 18 g (65%) of ester **XXIII** as a viscous substance, R_f 0.35.

b. To a solution of 0.45 g (2 mmol) of $CuBr_2$ in 15 ml of MeOH was added dropwise at stirring 0.33 g (1 mmol) of mesylate **XIV** bromide in 5 ml of MeOH. After heating for 6 h at 50–55°C the reaction mixture was cooled to room temperature, and 25 ml of H_2O was added thereto. The reaction product was extracted into 30 ml of CH_2Cl_2. The organic phase was dried over Na_2SO_4. On removing the solvent in a vacuum the residue was subjected to chromatography on a column (2×20 cm) packed with silica gel (0.5 g, eluent C_6H_6). We obtained 0.27 g (96%) of ester **XXIII** as a viscous substance, R_f 0.35. ^{1}H, δ, ppm: 1.45–2.20 m (6H, $3CH_2$), 2.77 s (3H, CH_3), 3.26 s (3H, CH_3), 3.75 d.t (1H, H^6, J_1 0.8, J_2 3.7 Hz), 5.80 d.d (1H, H$^{2'}$, J_1 3.0, J_2 4.4 Hz), 6.80–7.10 m (2H, H^5, H^6), 7.15–7.25 m (1H, H^4), 7.57 d.d (1H, H^3, J_1 1.1, J_2 7.8 Hz). ^{13}C NMR spectrum, δ, ppm: 15.8 (C$^{4'}$), 25.4 (C$^{3'}$), 25.5 (C$^{5'}$), 38.9 (CH_3), 56.1 (OCH_3), 76.9 (C^6), 121.1 (C^6), 124.6 (C^4), 128.1 (C$^{2'}$), 130.4 (C^3), 134.2 (C^5), 135.1 (C^2), 135.6 (C$^{1'}$), 135.9 (C^1). Found, %: C 59.33; H 6.55; N 4.62; S 11.01. $C_{14}H_{19}NO_3S$. Calculated, %: C 59.76; H 6.81; N 4.98; S 11.39.

***N*-Mesyl-2-(5-oxo-1-cyclopenten-1-yl)aniline (XXV)**. To a solution containing 0.47 g (2 mmol) of mesylate **XXIV**, 10 ml of MeCN or CH_2Cl_2, and 1.7 g (20 mmol) of $NaHCO_3$ at vigorous stirring was slowly added dropwise a solution of 0.64 g (4 mmol) of Br_2 in 5 ml of MeCN or CH_2Cl_2. Then the reaction mixture was stirred for 3 h more, the precipitate was filtered off, the solvent was evaporated in a vacuum. The product was isolated by chromatography on silica gel (column 1×30 cm, eluent benzene). Yield 0.186 g (37%), R_f 0.42. ^{1}H NMR spectrum, δ, ppm: 2.55–2.85 m (4H, $2CH_2$), 2.90 s (3H, CH_3), 7.11–7.70 m (4H, Ar-H), 7.85 t (1H, H$^{2'}$, J 2.0 Hz). ^{13}C NMR spectrum, δ, ppm: 27.6 (C$^{3'}$), 35.3 (C$^{4'}$), 39.8 (CH_3), 123.8 (C^6), 125.7 (C^4), 126.1 (C^2), 129.7 (C^3), 130.3 (C^5), 134.4 (C^1), 144.2 (C$^{1'}$), 165.9 (C$^{2'}$), 209.4 (C$^{5'}$). Found, %: C 57.04; H 4.98; N 5.13; S 12.28. $C_{12}H_{13}NO_3S$. Calculated, %: C 57.35; H 5.21; N 5.57; S 12.76.

***N*-Mesyl-2-(2-bromo-1-cyclopenten-1-yl)aniline (XXVI)**. A mixture of 0.71 g (3 mmol) of mesylate **XXIV**, 0.53 g (3 mmol) of NBS, 1 g of $NaHCO_3$, and 20 ml of CH_2Cl_2 was stirred for 4 h. Then to the reaction mixture 10 ml of 12% Na_2SO_3 solution was added, the mixture was stirred for 10 min and extracted with 50 ml of CH_2Cl_2. The organic phase was dried over Na_2SO_4. The solvent was removed in a vacuum, the product was recrystallized from EtOH. Yield of bromide **XXVI** 0.8 g (84%), mp 135–137°C. IR spectrum, ν, cm^{-1}: 490, 526 (C–Br), 3262 (NH). ^{1}H NMR spectrum, δ, ppm: 2.15 quint (2H, CH_2, J 7.4 Hz), 2.65 t.t (2H, CH_2, J_1 2.4, J_2 7.4 Hz), 2.89 t.t (2H, CH_2, J_1 2.4, J_2 7.4 Hz), 3.05 s (3H, CH_3), 6.47 s (1H, NH), 7.15 d.d (1H, H^6, J_1 2.4, J_2 8.4 Hz), 7.18 t.d (1H, H^5, J_1 1.0, J_2 8.4 Hz), 7.35 t.d (1H, H^4, J_1 2.4, J_2 8.4 Hz), 7.62 d.d (1H, H^3, J_1 1.0, J 8.4 Hz). ^{13}C NMR spectrum, δ, ppm: 22.2 (C$^{4'}$), 37.6 (C$^{5'}$), 39.5 (C$^{3'}$), 40.85 (SCH_3), 119.7 (C^6), 122.1 (C$^{2'}$), 124.6 (C^4), 126.1 (C^2), 128.9 (C^3), 129.0 (C^5), 133.6 (C^1), 137.6 (C$^{1'}$). Found, %: C 45.24; H 4.09; Br 24.81; N 3.97; S 9.79. $C_{12}H_{14}BrNO_2S$. Calculated, %: C 45.58; H 4.46; Br 25.27; N 4.43; S 10.14.

***N*-Mesyl-1,2,3,4-tetrahydrocyclopent-[*b*]indole (XXVIII)**. The reaction mixture containing 0.083 g

(0.26 mmol) of bromide **XXVI** and 3 ml of piperidine was heated at reflux. After 4 h the piperidine was evaporated in a vacuum, the residue was dissolved in 15 ml of CH_2Cl_2 and washed with 20 ml of water. The organic phase was dried over Na_2SO_4. The solvent was evaporated in a vacuum. Yield 0.059 g (95%). ^{1}H NMR spectrum, δ, ppm: 2.10–2.80 m (6H, $3CH_2$), 3.00 s (3H, SCH_3), 7.10–7.90 m (4H, Ar-H). ^{13}C NMR spectrum, δ, ppm: 24.0 (C^1), 27.4 (C^2), 27.6 (C^3), 40.3 (CH_3), 113.8 (C^5), 119.2 (C^8), 123.4 (C^7), 123.5 (C^6), 126.3 (C^{8b}), 127.1 (C^{8a}), 140.2 (C^{4a}), 143.7 (C^{3a}). Found, %: C 61.04; H 5.42; N 5.81; S 13.32. $C_{12}H_{13}NO_2S$. Calculated, %: C 61.25; H 5.57; N 5.95; S 13.63.

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