Synthesis and study of the mutagenic activity of di(indeno[2,1-*b*]indolyl)- and di(indeno[2,1-*b*]pyrrolyl)methanes and -dimethylsilanes

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Dihetaryldimethylsilanes and dihetarylmethanes containing indeno[2,1-*b*]indolyl and indeno[2,1-*b*]pyrrolyl fragments were synthesized. Their mutagenic activity was tested according to Ames with standard test strains *Salmonella typhimurium* TA 1537, TA 98, and TA 100.

Key words: indeno[2,1-*b*]indole, indeno[2,1-*b*]pyrrole, Fisher reaction, Ames test.

It is known that polyaromatic fused systems can exhibit mutagenic properties. The basic structural characteristics responsible for the mutagenic activity of such compounds are the planar structure and the polarity of their molecules, which is determined by the type and positions of substituents.[1] The mutual effects of two planar fragments of this type in the same molecule on its total mutagenic activity (synergism) was not studied hitherto.

To answer this question, indeno[2,1-*b*]indoles (**1**), indeno[2,1-*b*]pyrroles (**2**), dihetaryldimethylsilanes **3**—**5**, and dihetarylmethanes **6** and **7** each containing two fragments of the aforesaid types were synthesized and tested for mutagenicity in the present work.

The choice of the model compounds was based on the following reasoning. First, indenoindoles and indenopyrroles are rather easily accessible. Second, when treated with strong bases, these compounds give carbanions, which, in turn, react with various electrophiles to yield CH_2- and $SiMe_2$-bridged bisderivatives. Third, as indenoindole can be regarded as indenopyrrole fused with an additional benzene ring, the comparison of indenoindole and indenopyrrole derivatives makes it possible to study the influence of the additional annelated ring on the total mutagenic activity.

Results and Discussion

At present, the most common and convenient method for the synthesis of indeno[*b*]indoles is the acid-catalyzed cyclization of indanone arylhydrazones (the Fisher reaction).[2] Following this approach, we prepared indenoindoles **1a**—**c** from hydrazones **8a**—**c** (the latter were synthesized by heating the corresponding hydrazines with indan-2-one in ethanol (Scheme 1).

Earlier,[2—4] HCl, PPA, and $ZnCl_2$ were used as cyclization agents. Our choice was H_2SO_4. As both stages of the process occur in the same solvent, and hydrazones **8a**—**c** are formed in virtually quantitative yields, compounds **1a**—**c** may be synthesized by a one-pot procedure.

Methylation of indenoindoles **1a**—**c** under phase-transfer catalysis with *p*-$C_{16}H_{33}NMe_3Br$ as a catalyst (by analogy with indoles[5]) yielded *N*-methylindenoindoles **1d**—**f** (see Scheme 1). Both MeI and more easily available dimethyl sulfate were used as methylating agents, though the latter provides partially resinified products in somewhat lower yields.

Compound **1g** containing trimethylsilyl group at the nitrogen atom was obtained by treating an *N*-lithiumindenoindole **1a** with Me_3SiCl in ether. The smooth silylation of **1a** occurs in the presence of tetramethylethylenediamine, which enhances the nucleophilic properties of the nitrogen atom via complexation with the lithium atom (see Scheme 1).

Compound **1i** (yield 52%) was obtained by treating a lithium derivative of *N*-methyldihydroindenoindole **1d** with Me_3SiCl in ether (see Scheme 1).

N-Phenylindenoindole **1h** was synthesized by the reaction of *N*,*N*-diphenylhydrazine with indan-2-one in ethanol in the presence of H_2SO_4 (see Scheme 1). Using a standard procedure, we failed to isolate diphenylhydrazone **8d**. Apparently, the rate of its cyclization is much higher than that for monophenylhydrazones. Unlike other indenoindoles, compound **1h** crystallizes only slightly and can be isolated in the individual form in low yield (41%) using column chromatography on silica gel.

The initial attempt to synthesize the framework of indeno[2,1-*b*]pyrrole by condensation of indan-2-one

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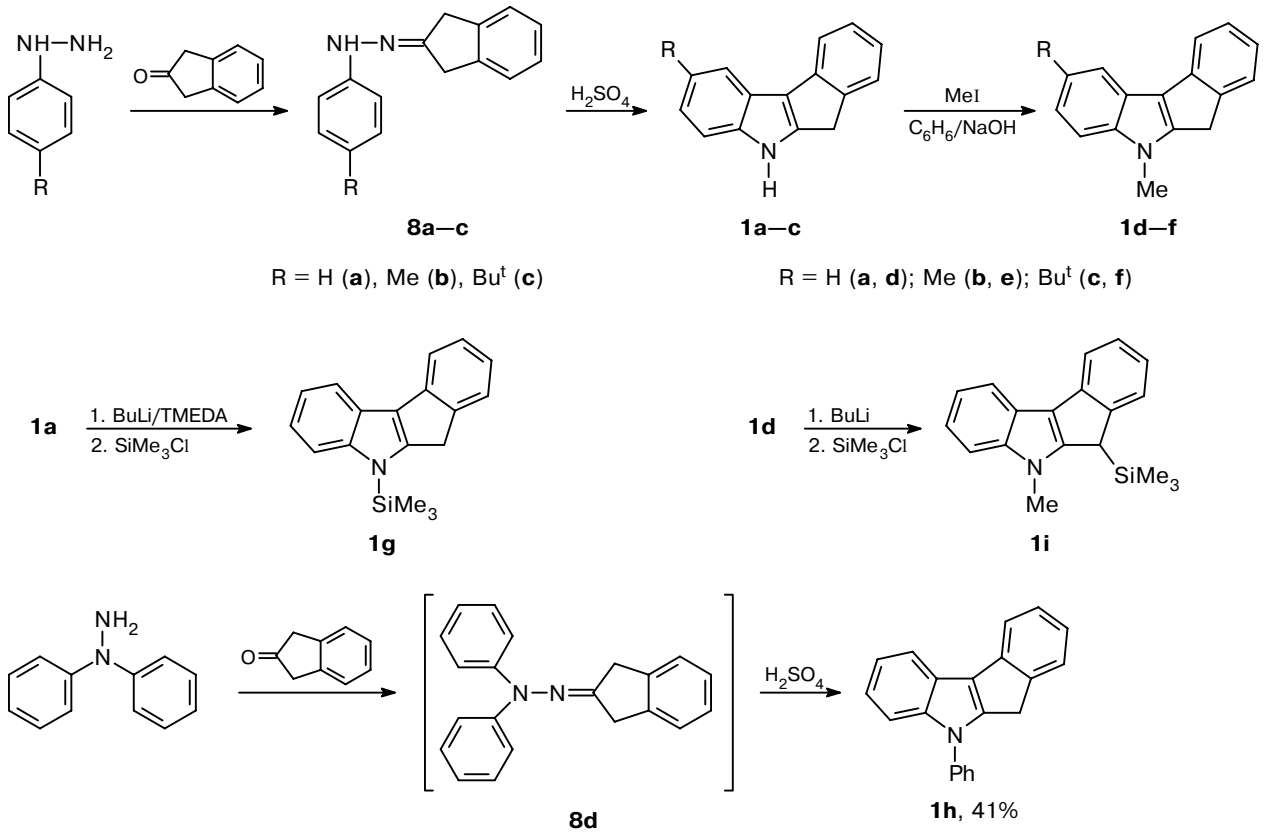
Scheme 1



with oxime **9** (Scheme 2) according to the known procedure[6] gave no target indenopyrrole **2a**. Instead, the condensation of two aminoacetoacetate molecules yielded compound **10**. Because of this, an alternative approach, namely, the condensation of aminoindanone hydrochloride with ethyl acetoacetate was used (*cf.* Ref. 7). As in the case of indenoindoles, indenopyrrole **2b** was methylated at the nitrogen atom under phase-transfer catalysis. Hydrolysis of ester **2c** afforded acid **2d**, which was decarboxylated in diethylene glycol to give indenopyrrole **2e** (see Scheme 2).

Symmetrical dihetarylsilanes were obtained by the action of $SiMe_2Cl_2$ on a lithium salt of indenoindole or indenopyrrole in ether, by analogy with the known procedure[8] (Scheme 3). The yields of products **3** and **4** were 35—60%. Being insoluble in ether, they were easily isolated by filtration as a mixture of racemic and *meso*-forms in the ratio ~1 : 1. The exception is compound **3b**, which is well soluble in ether; its pure racemate was isolated by recrystallization from hexane in 52% yield. The oily *meso*-form of **3b** was not isolated.

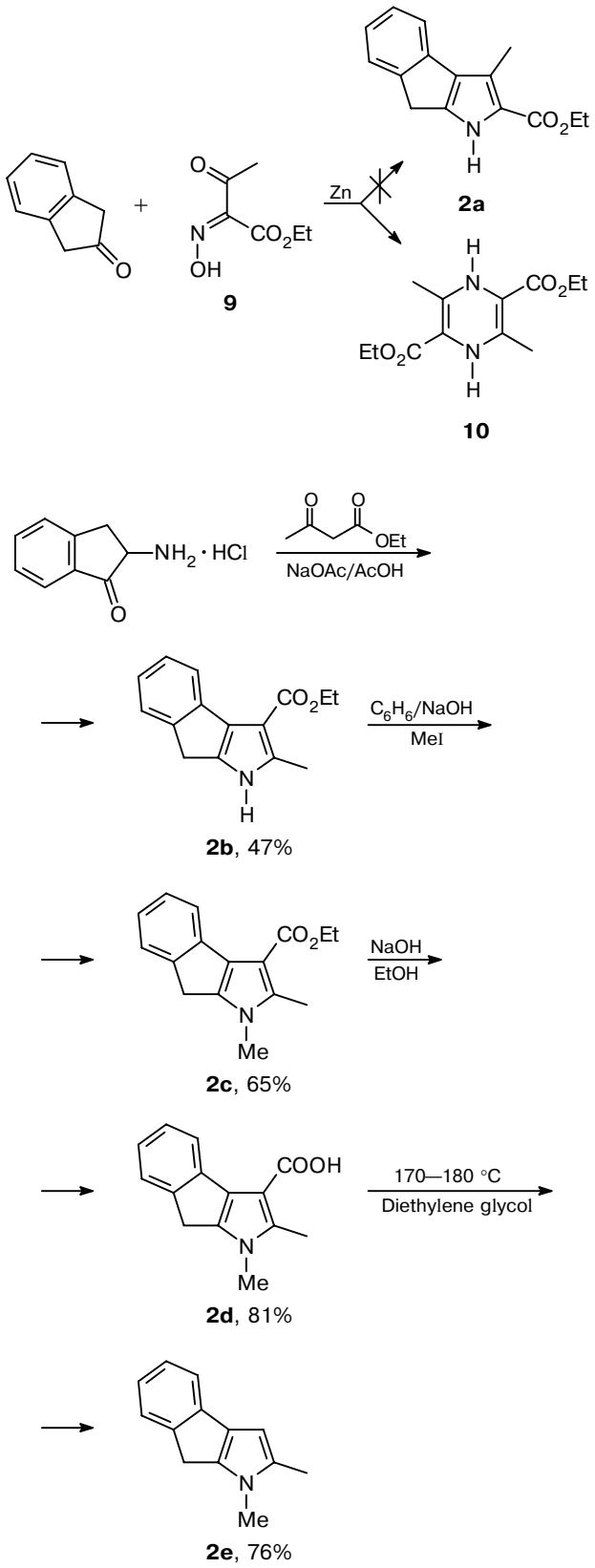
The ratio of stereoisomers was determined by ^{1}H NMR spectroscopy. Thus, the Si-bound methyl groups in the *meso*-forms are diastereotopic giving two singlets in the ^{1}H NMR spectrum. The analogous groups of the racemic form are equivalent, and their ^{1}H NMR spectrum shows one signal (s, 6 H).

Unsymmetrical dihetarylsilanes **5** were synthesized by the action of the corresponding chloro(fluorenyl)dimethylsilanes on the lithium salt of 5-methylindeno[2,1-*b*]indole (**1d**) in ether (see Scheme 3).

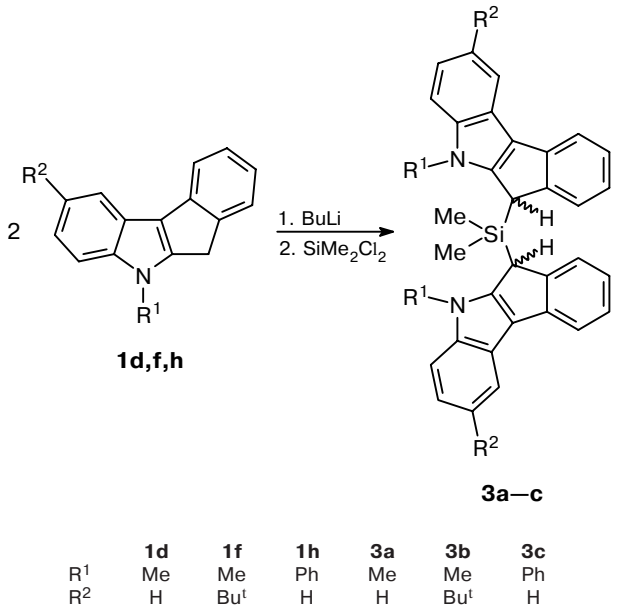
Dihetarylmethanes were obtained by the reactions of indenoindoles and indenopyrroles with CH_2O in DMF in the presence of EtONa according to the known procedure[9] (Scheme 4). Products **6** and **7** are insoluble in DMF and can easily be filtered off. One could assume that derivatives **6** and **7** would also be obtained as mixtures of racemic and *meso*-forms. Unexpectedly, it turned out that only indenopyrrole **7** gives such a mixture in the ratio ~1 : 1, while indenoindole derivatives **6** are formed only as a racemate. To obtain an equimolar mixture of racemic and *meso*-forms of compounds **6**, the racemic form **6** should be treated successively with a solution of BuLi in hexane and with water. It was such a mixture that was tested for mutagenic activity.

The ratio of diastereomers **6** and **7** was determined from the ^{1}H NMR spectra. An ABX_2-type spin system composed of the chemically nonequivalent CH_2 protons of the *meso*-form and the CH protons of the cyclopentadienyl ring gives two different signals (both dt) in the ^{1}H NMR spectrum; the CH protons manifest themselves by a doublet of doublets. The racemate is observed as an AA′XX′ spin system, and the CH_2 protons (like the CH ones) give one signal (dd).

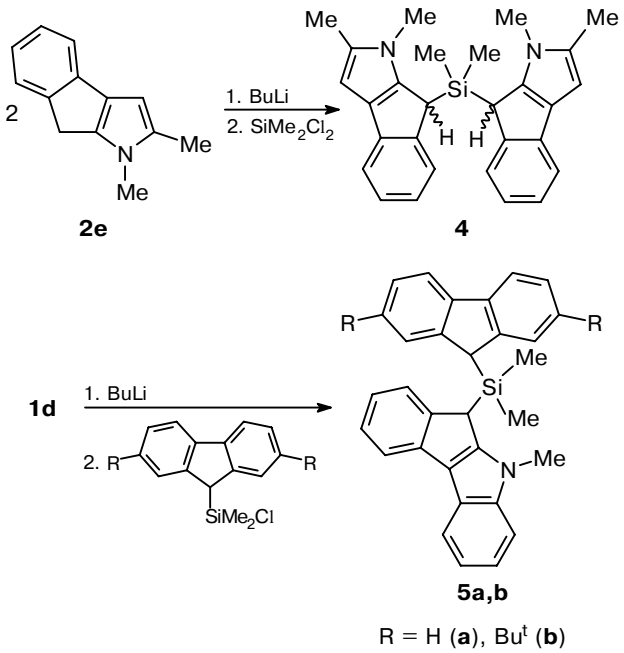
Scheme 2



Scheme 3



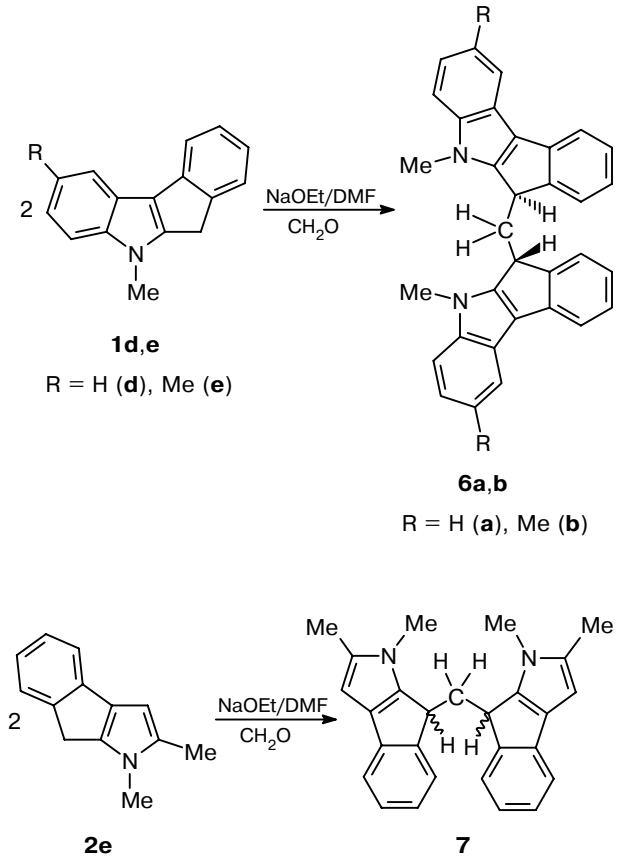
	1d	1f	1h	3a	3b	3c
R^1	Me	Me	Ph	Me	Me	Ph
R^2	H	Bu^t	H	H	Bu^t	H



R = H (**a**), Bu^t (**b**)

The study of mutagenic activity. Mutagenic activity was tested with standard histidine-dependent test strains *Salmonella typhimurium* TA 1537 (hisC3076, rfa, uvrB), TA 98 (hisD3052, rfa, uvrB), and TA 100 (hisG46, rfa, uvrB) as indicators, which are able to revert to the histidine dependence under the action of different-type mutagens.[10] The strains were tested according to the

Scheme 4



standard procedure without metabolic activation of the mammal liver with an S9 fraction.[11]

It was found that the compounds obtained show mutagenic activity only with the strain *Salmonella typhimurium* TA-98, *i.e.*, they cause frameshift mutations of the type −1 (deletion) in the D-gene of the histidine operon. None of the compounds obtained induced frameshift mutations of the type +1 (strain TA 1537), and base mismatch mutations (strain TA 100).

The data on the mutagenicity of the compounds synthesized with strain TA 98 are given in Table 1. Compounds **1a,d**,**g,i**, and **2e**, dihetarylmethanes **6** and **7**, and dihetarylsilanes **3b** and **4** were not found to be mutagens. Compound **6a** in high doses inhibited bacterial growth. The various mutagenic activity was exhibited by compounds **3a**, **3c**, and **5**. (Note that the lowest activity was provided by compound **3a**, which inhibited bacterial growth in high doses, with toxic effect.) Compounds **3c** and **5a** increased the rate of spontaneous mutations ten times and more in the lowest experimental dose (50 μg per plate), but bacterial growth was inhibited only by the latter in high doses. In low doses, compound **5b** is less active than **3c**. Thus, compound **3c** can be regarded as frameshift mutagen possessing high mutagenic activity in a broad range of doses (from low to high), without inhibiting bacterial growth. The latter

Table 1. The number of his$^+$-revertants induced by the compounds under study in *Salmonella typhimurium* TA 98

Compound	Dose*					
	0	50	100	250	500	1000
1a	20	21	23	22	20	25
1d	20	28	27	22	22	31
1g	20	27	30	22	23	30
1i	20	24	38	30	43	29
2e	20	24	31	28	24	29
3a	20	40	50	154	100	t.e.**
3b	31	29	30	31	24	31
3c	20	350	486	726	1097	1572
4	31	30	22	26	27	30
5a	29	461	728	993	799	t.e.**
5b	29	85	129	753	1219	1251
6a	20	19	20	24	17	t.e.**
6b	32	36	36	38	42	45
7	31	28	28	27	29	32

Note. Control: 2-nitrofluorene (5 μg per plate) induced 2313—2876 his$^+$-revertants.
* The dose was measured in micrograms per plate.
** Toxic (bactericidal) effect.

circumstance is very important when the compound is used as an inductor of mutations of microorganisms for the purpose of selecting new lines, *e.g.*, potential producers for microbiological industry.

Thus, the mutagenic synergism was observed only in the case of indenoindole-containing dihetarylsilanes. The only exception is compound **3b**. Apparently, the presence of the bulky *tert*-butyl substituents prevents its intercalation into the DNA molecule. The indenopyrrole derivatives contain fused fragments whose length is insufficient to be firmly retained in DNA and cause mutations. This confirms a significant influence of the number of fused rings in the molecules of the mutagen of this type on its mutagenic properties.

Experimental

^{1}H and ^{13}C NMR were recorded on a Varian VXR-400 instrument. *p*-$C_{16}H_{33}NMe_3Br$ was used as a phase-transfer catalyst. Reactions were carried out in an atmosphere of argon.

Reagents were purchased from Lancaster Co. Diethyl ether was dried according to the known procedure.[12] $SiMe_2Cl_2$ and TMSCl were distilled in an atmosphere of argon immediately before use.

6*H*-Indeno[2,1-*b*]indole (1a)[2]. A mixture of indan-2-one (30 g, 0.23 mol), Pr^{i}OH (300 mL), freshly distilled phenylhydrazine (22.3 mL, 0.23 mol), and TsOH (1 g) was refluxed for 1 h and then cooled. The yellow precipitate that formed was indan-2-one phenylhydrazone. A solution of conc. H_2SO_4 (16 mL) in 50 mL of Pr^{i}OH was added, and the reaction mixture was refluxed for 40 min, cooled, and poured into 800 mL of 2.5% NaOH. The precipitate that formed was filtered off and washed with water and twice with Pr^{i}OH to give compound **1a** (37.8 g, 80%) as colorless crystals, m.p. 205 °C. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 3.70 (s, 2 H, CH_2); 7.10 (t, 1 H, J = 7.8 Hz); 7.21 (m, 2 H); 7.38 (m, 3 H); 7.65 (d, 1 H,

J = 7.8 Hz); 7.87 (dd, 1 H, Ar, J_1 = 5.6 Hz, J_2 = 2.8 Hz); 8.30 (br.s, 1 H, NH).

2-Methyl-6*H*-indeno[2,1-*b*]indole (1b). Compound **1b** was obtained analogously from 1-(4-methylphenyl)hydrazine (12.2 g, 0.1 mol), indan-2-one (13.2 g, 0.1 mol), and TsOH (0.5 g) in 70 mL of Pr^{i}OH. The yield of compound **1b** was 19.3 g (88%), light brown crystals, m.p. 206 °C. Found (%): C, 87.62; H, 5.94; N, 6.44. $C_{16}H_{13}N$. Calculated (%): C, 87.63; H, 5.98; N, 6.39. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 2.54 (s, 3 H, Me); 3.70 (s, 2 H, CH_2); 7.02 (d, 1 H, Ar, J = 7.8 Hz); 7.08 (t, 1 H, Ar, J = 7.8 Hz); 7.23 (d, 1 H, Ar, J = 6.5 Hz); 7.33 (t, 1 H, Ar, J = 7.8 Hz); 7.42 (d, 1 H, Ar, J = 6.5 Hz); 7.64 (m, 2 H, Ar); 8.02 (br.s, 1 H, NH).

2-*tert*-Butyl-6*H*-indeno[2,1-*b*]indole (1c)[2]. Compound **1c** was obtained analogously from 4-*tert*-butylphenylhydrazine (21.5 g, 0.13 mol), indan-2-one (17.2 g, 0.13 mol), and TsOH (0.5 g) in 80 mL of Pr^{i}OH. The yield of compound **1c** was 24.7 g (72%), light brown crystals, m.p. 182—183 °C. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 2.54 (s, 9 H, CMe_3); 3.64 (s, 2 H, CH_2); 7.12 (t, 1 H, Ar, J = 5.9 Hz); 7.25 (d, 1 H, Ar, J = 5.2 Hz); 7.31 (d, 1 H, Ar, J = 5.2 Hz); 7.38 (t, 1 H, Ar, J = 5.9 Hz); 7.45 (d, 1 H, Ar, J = 5.9 Hz); 7.71 (d, 1 H, Ar, J = 5.9 Hz); 7.88 (s, 1 H, Ar); 8.03 (br.s, 1 H, NH).

5-Methyl-6*H*-indeno[2,1-*b*]indole (1d)[13]. Benzene (80 mL), indenoindole **1a** (5 g, 0.022 mol), a phase-transfer catalyst (0.2 g, 0.5 mmol), and MeI (1.6 mL, 0.025 mol) were added to a solution of NaOH (40 g) in 40 mL of water. The reaction mixture was heated with vigorous stirring at 40 °C for 8 h. The organic phase was separated, washed with water, dried with Na_2SO_4, and concentrated. The residue was recrystallized from benzene—hexane (1 : 2) to give compound **1d** (3.4 g, 70%) as colorless crystals, m.p. 172 °C. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 3.66 (s, 2 H, CH_2); 3.78 (s, 3 H, Me); 7.07 (t, 1 H, Ar, J = 6.7 Hz) 7.22 (m, 2 H, Ar); 7.34 (m, 2 H, Ar); 7.42 (d, 1 H, Ar, J = 6.7 Hz); 7.62 (d, 1 H, Ar, J = 6.9 Hz); 7.86 (dd, 1 H, Ar, J_1 = 6.9 Hz, J_2 = 2.1 Hz).

2,5-Dimethyl-6*H*-indeno[2,1-*b*]indole (1e). Benzene (100 mL), indenoindole **1b** (19.3 g, 0.088 mol), a phase-transfer catalyst (0.6 g, 1.6 mmol), and MeI (6.23 mL, 0.01 mol) were added to a solution of NaOH (100 g) in 100 mL of water. The reaction mixture was heated with vigorous stirring at 40 °C for 1 h. After the reaction was completed, the precipitate that formed was filtered off and washed with water and EtOH. The yield of compound **1e** was 18.0 g (88%), colorless crystals, m.p. 199—200 °C. Found (%): C, 87.45; H, 6.44; N, 6.11. $C_{17}H_{15}N$. Calculated (%): C, 87.52; H, 6.48; N, 6.00. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 2.56 (s, 3 H, Me); 3.62 (s, 2 H, CH_2); 3.76 (s, 3 H, N—Me); 7.09 (m, 2 H, Ar) 7.24 (d, 1 H, Ar, J = 6.3 Hz); 7.36 (t, 1 H, Ar, J = 6.3 Hz); 7.43 (d, 1 H, Ar, J = 5.6 Hz); 7.62 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$, 20 °C), δ: 21.6 (Me); 30.0 (CH_2); 31.1 (N—Me); 109.3, 118.2, 119.3, 119.8, 121.9, 122.4, 122.4, 124.6, 127.0, 129.0, 139.7, 140.6, 142.0, 148.5 (all Ar).

2-*tert*-Butyl-5-methyl-6*H*-indeno[2,1-*b*]indole (1f). Compound **1f** was obtained as described for **1e** from indenoindole **1c** (26.0 g, 0.099 mol), a phase-transfer catalyst (0.6 g, 1.6 mmol), and MeI (9.3 mL, 0.15 mol). The yield of compound **1f** was 22.6 g (82%), colorless crystals, m.p. 208—209 °C. Found (%): C, 87.23; H, 7.74; N, 5.03. $C_{20}H_{21}N$. Calculated (%): C, 87.22; H, 7.69; N, 5.09. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 2.54 (s, 9 H, Me); 3.64 (s, 2 H, CH_2); 3.85 (s, 3 H, N—Me); 7.01 (t, 1 H, Ar, J = 6.1 Hz); 7.23 (t, 1 H, Ar, J = 6.1 Hz); 7.32 (m, 2 H, Ar); 7.39 (d, 1 H, Ar, J = 6.1 Hz); 7.64 (d, 1 H, Ar, J = 6.1 Hz); 7.82 (d, 1 H, Ar, J = 1.5 Hz).

5-(Trimethylsilyl)-6*H*-indeno[2,1-*b*]indole (1g). A 2.18 *M* solution of BuLi (22.9 mL) in *n*-hexane was added dropwise with stirring and cooling by water and ice to a suspension of indenoindole **1a** (10.25 g, 0.05 mol) in 100 mL of anhydrous Et_2O. Stirring was continued at ~20 °C for 30 min, and then tetramethylethylenediamine (7.53 mL) was added. The reaction mixture was stirred for an additional 1 h and cooled to −30 °C. A solution of Me_3SiCl (6.3 mL, 0.05 mol) in 10 mL of anhydrous Et_2O was added rapidly, and the reaction mixture was refluxed with stirring for 3 h. After the addition of water (30 mL), the organic phase was separated, washed with water, and dried with Na_2SO_4. The solvent was removed, and the residue was washed twice with light petroleum to give compound **1g** (7.35 g, 53%) as light yellow-green crystals, m.p. 141—143 °C. Found (%): C, 77.90; H, 6.93; N, 5.04. $C_{18}H_{19}NSi$. Calculated (%): C, 77.93; H, 6.90; N, 5.05. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 0.81 (s, 9 H, Si—Me); 3.83 (s, 2 H, CH_2); 7.18 (t, 1 H, Ar, J = 7.7 Hz); 7.28 (t, 1 H, Ar, J = 7.6 Hz); 7.33 (t, 1 H, Ar, J = 7.7 Hz); 7.42 (t, 1 H, Ar, J = 7.6 Hz); 7.49 (d, 1 H, Ar, J = 7.6 Hz); 7.63 (d, 1 H, Ar, J = 7.7 Hz); 7.73 (d, 1 H, Ar, J = 7.6 Hz); 7.96 (d, 1 H, Ar, J = 7.7 Hz).

5-Phenyl-6*H*-indeno[2,1-*b*]indole (1h). A mixture of indan-2-one (2.64 g, 0.02 mol), EtOH (50 mL), 1,1-diphenylhydrazine (3.68 g, 0.02 mol), and conc. H_2SO_4 (1 mL) was refluxed for 1.5 h and then poured into 150 mL of water. The products were extracted with CH_2Cl_2. The organic phases were combined, dried with Na_2SO_4, and concentrated. The residue was chromatographed on SiO_2 in benzene—light petroleum (2 : 1). The yellow oil obtained was dissolved in a minimum amount of boiling hexane. The crystals that formed on cooling were filtered off and washed with cold light petroleum. The yield of compound **1h** was 2.2 g (41%), colorless crystals, m.p. 129—130 °C. Found (%): C, 89.57; H, 5.43; N, 5.00. $C_{21}H_{15}N$. Calculated (%): C, 89.65; H, 5.37; N, 4.98. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 3.80 (s, 2 H, CH_2); 7.14 (t, 1 H, Ar, J = 7.3 Hz); 7.22 (m, 3 H, Ar); 7.42 (m, 3 H, Ar); 7.57 (m, 4 H, Ar); 7.72 (d, 1 H, Ar, J = 7.3 Hz); 7.95 (d, 1 H, Ar, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, 20 °C), δ: 32.0 (CH_2); 110.2, 188.6, 119.4, 120.9, 121.9, 122.4, 122.7, 122.9, 124.5, 124.7, 127.0, 127.1, 129.8, 138.4, 139.6, 141.3, 142.3, 148.8 (all Ar).

5-Methyl-6-(trimethylsilyl)-6*H*-indeno[2,1-*b*]indole (1i). A 1.6 *M* solution of BuLi (6.25 mL, 0.01 mol) in *n*-hexane was added dropwise with stirring and cooling by water and ice to a suspension of indenoindole **1d** (2.19 g, 0.01 mol) in 30 mL of anhydrous Et_2O. After the cooling was completed, the reaction mixture was stirred at ~20 °C for 30 min and then cooled again to −30 °C. A solution of Me_3SiCl (1.27 mL, 0.01 mol) in 10 mL of anhydrous Et_2O was rapidly added, and the resulting mixture was refluxed with stirring for 1 h. The precipitate of LiCl that formed was filtered off, washed with Et_2O, and the filtrate was concentrated. The residue was recrystallized from hexane—benzene to give compound **1i** (1.52 g, 52%) as beige crystals, m.p. 152—154 °C. Found (%): C, 78.24; H, 7.23; N, 4.83. $C_{19}H_{21}NSi$. Calculated (%): C, 78.30; H, 7.26; N, 4.81. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 0.00 (s, 9 H, Si—Me); 3.78 (s, 1 H, CH); 3.84 (s, 3 H, N—Me); 7.10 (t, 1 H, Ar, J = 6.8 Hz); 7.26 (d, 1 H, Ar, J = 6.8 Hz); 7.28 (d, 1 H, Ar, J = 6.8 Hz); 7.36 (m, 2 H, Ar); 7.43 (d, 1 H, Ar, J = 5.9 Hz); 7.73 (d, 1 H, Ar, J = 5.9 Hz); 7.93 (dd, 1 H, Ar, J_1 = 5.9 Hz, J_2 = 2.1 Hz).

Ethyl 2-methyl-8*H*-indeno[2,1-*b*]pyrrole-3-carboxylate (2b).[7] Sodium acetate trihydrate (47.6 g, 0.35 mol) was added in small portions to a mixture of 2-aminoindan-1-one hydrochloride (51.3 g, 0.28 mol) obtained according to the known procedure[14] and ethyl acetoacetate (38 mL, 0.3 mol) in 300 mL of glacial AcOH. The reaction mixture was heated with stirring at 50—60 °C for 5 h and left for 12 h. Then, it was poured into 1.5 L of water, and the precipitate that formed was filtered off and washed with a solution of $NaHCO_3$ and water. The yield of

compound **2b** was 31.8 g (47%), colorless crystals, m.p. 200 °C. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 1.46 (t, 3 H, $OCH_2\underline{Me}$, J = 7.8 Hz); 2.60 (s, 3 H, Me); 3.51 (s, 2 H, CH_2); 4.42 (q, 2 H, $OC\underline{H_2}Me$, J = 7.8 Hz); 7.11, 7.30 (both t, each 1 H, Ar, J = 7.4 Hz); 7.38, 8.02 (both d, each 1 H, Ar, J = 7.4 Hz); 8.40 (br.s, 1 H, NH). ^{13}C NMR (acetone-d_6, 20 °C), δ: 14.0 (Me); 15.1 (Me); 30.9 (CH_2); 59.7 (OCH_2); 107.0, 121.5, 123.6, 125.2, 127.2, 129.3, 137.9, 139.8, 140.9, 144.7 (all Ar); 166.0 (C=O).

Ethyl 1,2-dimethyl-8*H*-indeno[2,1-*b*]pyrrole-3-carboxylate (2c). Compound **2c** was obtained as described for **1e** from indenopyrrole **2b** (15.9 g, 0.066 mol), a phase-transfer catalyst (0.5 g, 1.4 mmol), and MeI (8.1 mL, 0.13 mol). The yield of compound **2c** was 11.0 g (65%), cream-colored crystals, m.p. 152 °C. Found (%): C, 75.35; H, 6.67; N, 5.43. $C_{16}H_{17}NO_2$. Calculated (%): C, 75.26; H, 6.71; N, 5.49. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 1.46 (t, 3 H, $OCH_2\underline{Me}$, J = 7.9 Hz); 2.59 (s, 3 H, Me); 3.46 (s, 3 H, N—Me); 3.51 (s, 2 H, CH_2); 4.42 (q, 2 H, $OC\underline{H_2}Me$, J = 7.9 Hz); 7.08 (t, 1 H, Ar, J = 7.5 Hz); 7.28 (t, 1 H, Ar, J = 7.5 Hz); 7.37 (d, 1 H, Ar, J = 7.5 Hz); 8.00 (d, 1 H, Ar, J = 7.5 Hz).

1,2-Dimethyl-8*H*-indeno[2,1-*b*]pyrrole-3-carboxylic acid (2d). A mixture of ester **2c** (14 g, 0.055 mol), EtOH (150 mL), water (150 mL), and NaOH (130 g) was refluxed with stirring for 6 h and then poured into 200 mL of water. The precipitate of the salt that formed was filtered off and added to a solution of HCl (70 mL) in 200 mL of water. The reaction mixture was stirred for 30 min, and the precipitate that formed was filtered off. The yield of acid **2d** was 10.1 g (81%), m.p. 170—172 °C (decomp.). Found (%): C, 73.92; H, 5.69; N, 6.24. $C_{14}H_{13}NO_2$. Calculated (%): C, 73.99; H, 5.77; N, 6.16. ^{1}H NMR (DMSO-d_6, 20 °C), δ: 2.53 (s, 3 H, Me); 3.52 (s, 3 H, N—Me); 3.56 (s, 2 H, CH_2); 7.03 (t, 1 H, Ar, J = 7.7 Hz); 7.22 (t, 1 H, Ar, J = 7.7 Hz); 7.38 (d, 1 H, Ar, J = 7.7 Hz); 7.92 (d, 1 H, Ar, J = 7.7 Hz). ^{13}C NMR (DMSO-d_6, 20 °C), δ: 11.4 (Me); 29.4 (CH_2); 32.0 (N—CH_2); 105.8, 120.4, 122.6, 124.6, 126.0, 126.4, 138.9, 139.5, 139.9, 143.2 (all Ar); 166.5 (C=O).

1,2-Dimethyl-8*H*-indeno[2,1-*b*]pyrrole (2e). A mixture of acid **2d** (20.7 g, 0.91 mol) and diethylene glycol (230 mL) was heated to 170—200 °C until gas evolution ceased (~50 min). The reaction mixture was cooled with water and ice, and the precipitate that formed was filtered off and washed with EtOH. The yield of compound **2e** was 12.8 g (76%), cream-colored crystals, m.p. 180 °C. Found (%): C, 85.19; H, 7.23; N, 7.58. $C_{13}H_{13}N$. Calculated (%): C, 85.21; H, 7.15; N, 7.64. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 2.14 (s, 3 H, Me); 3.33 (s, 2 H, CH_2); 3.38 (s, 3 H, N—Me); 5.92 (s, 1 H, CH); 6.85 (m, 1 H, Ar) 7.12 (m, 1 H, Ar); 7.19 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$, 20 °C), δ: 29.6 (Me); 29.9 (CH_2); 31.6 (N—Me); 98.4, 117.7, 121.8, 124.5, 126.3, 126.5, 132.2, 139.8, 140.6, 142.9 (all Ar).

Dimethylbis(5-methyl-6*H*-indeno[2,1-*b*]indol-6-yl)silane (3a). A 1.6 *M* solution of BuLi (100 mL, 0.16 mol) in *n*-hexane was added dropwise with stirring and cooling by water and ice to a suspension of indenoindole **1d** (35.0 g, 0.16 mol) in 400 mL of anhydrous Et_2O. After cooling was completed, the reaction mixture was stirred at ~20 °C for 30 min and then cooled to −30 °C. A solution of $SiMe_2Cl_2$ (9.4 mL, 0.08 mol) in 20 mL of anhydrous Et_2O was added rapidly, and the resulting solution was refluxed with stirring for 2 h. Then a solution of NH_4Cl (8.6 g, 0.16 mol) in 100 mL of water was added; the precipitate that formed was filtered off and washed with water and twice with Et_2O to give a colorless crystalline substance. The concentration of the filtrate afforded an additional 4.1 g. The yield of **3a** was 24.6 g (62%), m.p. 226—228 °C. Found (%): C, 82.44; H, 6.19; N, 5.60. $C_{34}H_{30}N_2Si$. Calculated (%): C, 82.55; H, 6.11; N, 5.66. ^{1}H NMR ($CDCl_3$, 20 °C), δ: racemic form: 0.38 (s, 6 H, Si—Me); 3.45 (s, 6 H, N—Me); 4.05 (s, 2 H, CH); 7.79—7.19 (m, 16 H, Ar); *meso*-form: −0.40 (s, 3 H, Si—Me); 0.09 (s, 3 H, Si—Me); 3.75 (s, 6 H, N—Me); 3.80 (s, 2 H, CH); 8.05—7.16 (m, 16 H, Ar).

Bis(2-*tert*-butyl-5-methyl-6*H*-indeno[2,1-*b*]indol-6-yl)-1,1-dimethylsilane (3b). A 2.24 *M* solution of BuLi (18.0 mL, 0.04 mol) in *n*-hexane was added dropwise with stirring and cooling by water and ice to a suspension of indenoindole **1f** (11 g, 0.04 mol) in 200 mL of anhydrous Et_2O. After cooling was completed, the reaction mixture was stirred at ~20 °C for 30 min and then cooled to −30 °C. A solution of $SiMe_2Cl_2$ (2.42 mL, 0.02 mol) in 20 mL of anhydrous Et_2O was added rapidly, and the resulting solution was refluxed for 1 h. Then a solution of NH_4Cl (2.13 g, 0.04 mol) in 40 mL of water was added. The organic layer was separated, washed with water, and concentrated. The residue was dissolved with heating in a minimum amount of hexane and cooled. After ~24 h, the precipitate that formed was filtered off and washed with pentane to give compound **3b** (6.3 g, 52%) as colorless crystals, m.p. 225—227 °C. Found (%): C, 82.99; H, 7.71; N, 5.56. $C_{42}H_{46}N_2Si$. Calculated (%): C, 83.12; H, 7.65; N, 4.62. ^{1}H NMR ($CDCl_3$, 20 °C), δ: racemic form: −0.42 (s, 6 H, Si—Me); 1.45 (s, 18 H, CMe_3); 3.55 (s, 6 H, N—Me); 4.18 (s, 2 H, CH); 7.20 (t, 2 H, Ar, J = 5.8 Hz); 7.27 (d, 2 H, Ar, J = 5.8 Hz); 7.33 (dd, 2 H, Ar, J_1 = 5.5 Hz, J_2 = 1.9 Hz); 7.43 (t, 2 H, Ar, J = 5.8 Hz); 7.70 (d, 2 H, Ar, J = 5.5 Hz); 7.80 (d, 2 H, Ar, J = 5.8 Hz); 7.90 (d, 2 H, Ar, J = 1.9 Hz).

Dimethylbis(5-phenyl-6*H*-indeno[2,1-*b*]indol-6-yl)silane (3c). Compound **3c** was obtained as described for **3a** from indenoindole **1h** (2.81 g, 0.01 mol), a 1.6 *M* solution of BuLi (6.25 mL, 0.01 mol) in *n*-hexane, and $SiMe_2Cl_2$ (0.62 mL, 0.005 mol) in 40 mL of anhydrous Et_2O. The yield of compound **3c** was 1.1 g (35%), light yellow crystals, m.p. 205 °C. Found (%): C, 85.31; H, 5.48; N, 4.49. $C_{44}H_{34}N_2Si$. Calculated (%): C, 85.40; H, 5.54; N, 4.53. ^{1}H NMR ($CDCl_3$, 20 °C), δ: racemic form: −1.01 (s, 6 H, Si—Me); 3.64 (s, 2 H, CH); 7.92—7.09 (m, 26 H, Ar); *meso*-form: −0.98 (s, 3 H, Si—Me); −0.96 (s, 3 H, Si—Me); 3.71 (s, 2 H, CH); 7.72—7.15 (m, 26 H, Ar).

Dimethylbis(1,2-dimethyl-8*H*-indeno[2,1-*b*]pyrrol-8-yl)silane (4). Compound **4** was obtained as described for **3a** from indenopyrrole **2e** (2.75 g, 0.015 mol), a 1.6 *M* solution of BuLi (9.38 mL, 0.015 mol) in *n*-hexane, and $SiMe_2Cl_2$ (0.88 mL, 0.0075 mol) in 50 mL of anhydrous Et_2O. The yield of compound **4** was 1.74 g (55%), light gray crystals, m.p. 153—155 °C. Found (%): C, 79.47; H, 7.08; N, 6.58. $C_{28}H_{30}N_2Si$. Calculated (%): C, 79.57; H, 7.15; N, 6.63. ^{1}H NMR ($CDCl_3$, 20 °C), δ: racemic form: −0.05 (s, 6 H, Si—Me); 2.18 (s, 6 H, Me); 3.21 (s, 2 H, CH); 3.41 (s, 6 H, N—Me); 6.02 (s, 2 H, CH); 7.41—6.79 (m, 8 H, Ar); *meso*-form: −0.51 (s, 3 H, Si—Me); −0.48 (s, 3 H, Si—Me); 2.16 (s, 6 H, Me); 3.12 (s, 2 H, CH); 3.37 (s, 6 H, N—Me); 5.98 (s, 2 H, CH); 7.24—6.64 (m, 8 H, Ar).

6-[9*H*-Fluoren-9-yl(dimethyl)silyl]-5-methyl-6*H*-indeno[2,1-*b*]indole (5a). Compound **5a** was obtained as described for **3a** from indenoindole **1d** (2.19 g, 0.01 mol), a 1.6 *M* solution of BuLi (6.25 mL, 0.01 mol) in *n*-hexane, and chloro(9*H*-fluoren-9-yl)dimethylsilane[15] (2.6 g, 0.01 mol) in 30 mL of anhydrous Et_2O. The yield of compound **5a** was 2.6 g (60%), light yellow crystals, m.p. 206—208 °C. Found (%): C, 84.44; H, 6.19; N, 3.20. $C_{31}H_{27}NSi$. Calculated (%): C, 84.31; H, 6.16; N, 3.17. ^{1}H NMR ($CDCl_3$, 20 °C), δ: −0.41 (s, 3 H, Si—Me); −0.35 (s, 3 H, Si—Me); 3.59 (s, 3 H, N—Me); 3.98 (s, 1 H, CH); 4.30 (s, 1 H, CH); 7.86—7.16 (m, 16 H, Ar).

6-[2,7-Di-*tert*-butyl-9*H*-fluoren-9-yl(dimethyl)silyl]-5-methyl-6*H*-indeno[2,1-*b*]indole (5b). Compound **5b** was obtained as described for **3a** from indenoindole **1d** (0.65 g, 0.003 mol), a 1.6 *M* solution of BuLi (1.9 mL, 0.003 mol) in *n*-hexane, and (2,7-di-*tert*-butyl-9*H*-fluoren-9-yl)chloro(dimethyl)silane[15] (1.1 g, 0.003 mol) in 15 mL of anhydrous Et_2O. The yield of compound **5b** was 1.13 g (68%), light yellow crystals, m.p. 192—194 °C. Found (%): C, 84.47; H, 7.89; N, 2.61. $C_{39}H_{43}NSi$. Calculated (%): C, 84.57; H, 7.83; N, 2.53. ^{1}H NMR ($CDCl_3$, 20 °C), δ: −0.45 (s, 3 H, Si—Me); −0.29 (s, 3 H, Si—Me); 1.25 (s, 9 H, CMe_3); 1.35 (s, 9 H, CMe_3); 3.40 (s, 3 H, N—Me); 3.55 (s, 1 H, CH); 4.01 (s, 1 H, CH); 7.79—6.83 (m, 14 H, Ar).

Bis(5-methyl-6*H*-indeno[2,1-*b*]indol-6-yl)methane (6a). Indenoindole **1d** (21.9 g, 0.1 mol) was heated with stirring in 200 mL of DMF at 60 °C for 5 min. Sodium ethoxide (3.4 g, 0.05 mol) was added, and stirring was continued for 30 min. Then 37% aqueous CH_2O (3.8 mL, 0.05 mol) was added, and the reaction mixture was stirred at 60 °C for 2 h. Ammonium chloride (5.0 g, 0.09 mol) was added, and the precipitate that formed was filtered off and washed with DMF and Et_2O. The yield of compound **6a** was 20.9 g (92%), colorless crystals, m.p. 237 °C. Found (%): C, 87.89; H, 5.86; N, 6.25. $C_{33}H_{26}N_2$. Calculated (%): C, 87.96; H, 5.82; N, 6.22. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 2.27 (dd, 2 H, CH_2, J_1 = 6.2 Hz, J_2 = 8.8 Hz); 3.59 (s, 6 H, N—Me); 4.52 (dd, 2 H, CH, J_1 = 6.2 Hz, J_2 = 8.8 Hz); 7.16 (t, 2 H, Ar, J = 6.5 Hz); 7.24 (m, 6 H, Ar); 7.42 (t, 2 H, Ar, J = 6.2 Hz); 7.68 (d, 2 H, Ar, J = 6.5 Hz); 7.88 (m, 4 H, Ar). ^{13}C NMR ($CDCl_3$, 20 °C), δ: 31.2 (N—Me); 35.1 (CH_2); 40.8 (CH); 109.8, 118.8, 118.9, 119.3, 120.2, 121.2, 121.7, 122.3, 124.8, 127.7, 139.8, 141.5, 146.4, 151.5 (all Ar).

Bis(2,5-dimethyl-6*H*-indeno[2,1-*b*]indol-6-yl)methane (6b). Compound **6b** was obtained analogously from indenoindole **1e** (9.32 g, 0.04 mol), NaOEt (1.36 g, 0.02 mol), 37% aqueous CH_2O (1.52 mL, 0.02 mol), and NH_4Cl (2.5 g, 0.047 mol) in 80 mL of DMF. The yield of compound **6b** was 8.9 g (93%), colorless crystals, m.p. 267 °C. Found (%): C, 87.78; H, 6.29; N, 5.93. $C_{35}H_{30}N_2$. Calculated (%): C, 87.83; H, 6.32; N, 5.85. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 2.34 (dd, 2 H, CH_2, J_1 = 8.1 Hz, J_2 = 6.9 Hz); 2.52 (s, 6 H, Me); 3.59 (s, 6 H, N—Me); 4.48 (dd, 2 H, CH, J_1 = 8.1 Hz, J_2 = 6.9 Hz); 7.05 (d, 2 H, Ar, J = 6.8 Hz); 7.15 (m, 4 H, Ar); 7.42 (t, 2 H, Ar, J = 5.6 Hz); 7.64 (s, 2 H, Ar); 7.69 (d, 2 H, Ar, J = 5.6 Hz); 7.84 (d, 2 H, Ar, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 20 °C), δ: 21.4 (Me); 31.1 (N—Me); 35.2 (CH_2); 40.8 (CH); 109.4, 115.3, 118.4, 118.7, 119.2, 121.9, 122.1, 122.6, 124.9, 128.7, 129.5, 140.1, 146.4, 151.6 (all Ar).

Bis(1,2-dimethyl-8*H*-indeno[2,1-*b*]pyrrol-8-yl)methane (7). Compound **7** was obtained analogously over 5 h from indenopyrrole **2e** (4.3 g, 0.0235 mol), NaOEt (0.80 g, 0.01175 mol), 37% aqueous CH_2O (0.88 mL, 0.01175 mol), and NH_4Cl (1.28 g) in 47 mL of DMF. The yield of compound **7** was 2.6 g (59%), light yellow crystals, m.p. 132—134 °C (decomp.). Found (%): C, 85.59; H, 6.86; N, 7.55. $C_{27}H_{26}N_2$. Calculated (%): C, 85.68; H, 6.92; N, 7.40. ^{1}H NMR ($CDCl_3$, 20 °C), δ: *meso*-form: 2.31 (s, 6 H, Me); 2.89 (dt, 1 H, CH_2, J_1 = 15.9 Hz, J_2 = 6.6 Hz); 2.89 (dt, 1 H, CH_2, J_1 = 15.9 Hz, J_2 = 3.9 Hz); 3.41 (s, 6 H, N—Me); 3.62 (dd, 2 H, CH, J_1 = 6.6 Hz, J_2 = 3.9 Hz); 6.08 (s, 2 H, CH, pyrrole); 7.78—7.08 (m, 8 H, Ar); racemic form: 2.11 (m, 2 H, CH_2); 2.22 (s, 6 H, Me); 3.32 (s, 6 H, N—Me); 4.26 (dd, 2 H, CH, J_1 = 8.3 Hz, J_2 = 6.6 Hz); 6.05 (s, 2 H, CH, pyrrole); 7.78—7.08 (m, 8 H, Ar).

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