Synthesis of indole-containing analogs of (1*R*)-*cis*-chrysanthemic acid and *N*-substituted (1*R*)-*cis*-chrysanthemylamines

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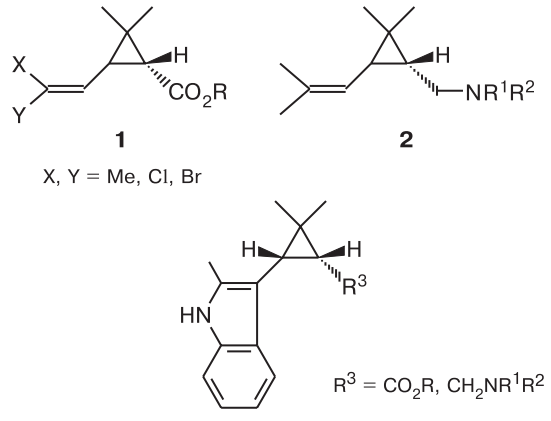
The indolic analogs of (1*R*)-*cis*-chrysanthemic acid and *N*-substituted (1*R*)-*cis*-chrysanthemylamines were obtained by Fischer indole synthesis using the acetonylcyclopropanes derived from (+)-car-3-ene. The cyano- and *N*-cyanamido groups in the starting carbonyl compounds did not hinder indolization. The reduction of the nitrile group bound to the asymmetrical atom of the cyclopropane ring by $LiAlH_4$ in ether can be accompanied by epimerization or racemization.

Key words: (+)-car-3-ene, cyclopropane methyl ketones, Fischer indole synthesis, N-cyanamides, decyanation, nitriles, hydrolysis, reduction, amides, indolic analogs of chrysanthemylamine, epimerization, racemization.

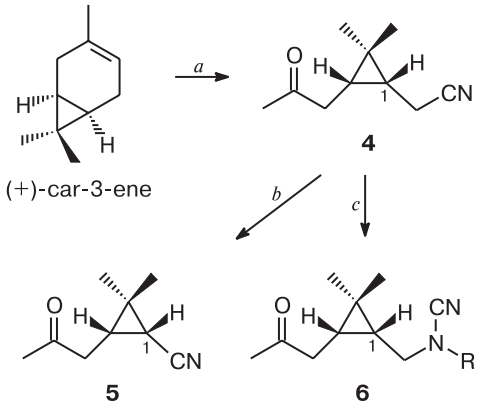
Pyrethroid insecticides represent presently the most efficient chemical facility for combating harmful insects. The modern tendencies in synthesis of new pyrethroids are primarily related to design of acid components, which appears, in particular, as the development of pyrethroid molecules, whose acid components contain heterocyclic fragments. It follows from the review of licensed literature[1] that a set of the known synthetic pyrethroids, whose acid component includes the *N*-heterocyclic fragment, is very scarce[2—12] and mainly presented by compounds of the indole or isoindole series.[3—5,12] However, even this group contains a few substances related to the most efficient pyrethroid insecticides, such as chrysanthemates,[8—13] *viz.*, derivatives of (1*R*)-chrysanthemic acid (**1**, X = Y = Me; R = H) and its halogen-containing analogs (**1**, X,Y = Me, Cl, Br; R = H), as well as *N*-substituted (1*R*)-chrysanthemylamines **2**.[14,15] The purpose of this work is to synthesize indolic analogs of (1*R*)-*cis*-chrysanthemic acid and *N*-substituted (1*R*)-*cis*-chrysanthemylamines (compounds of type **3**) in the enantiomerically pure form.



Results and Discussion

Ketone **4** [16] was used as the key initial compound in synthesis of the indicated indolic analogs (Scheme 1).

Scheme 1



Reagents, conditions, and yields, see Refs.: 16 (*a*), 17 (*b*), 18 (*c*).

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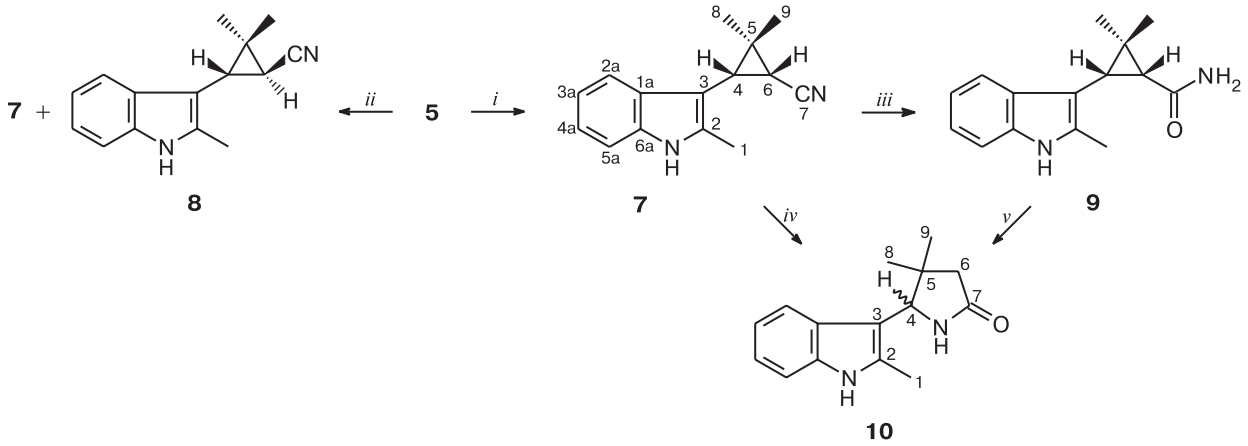
Scheme 2



Reagents, conditions, and yields: *i*. 1) $PhNHNH_2$/MeOH, ~20 °C, 2 h; 2) PPE/CH_2Cl_2, ~20 °C, 20 h; 75% yield. *ii*. 1) $PhNHNH_2$/EtOH, ~20 °C, 2—4 h; 2) PPA, ~50 °C, 8 h; 37% yield, ratio **7** : **8** ≈ 2 : 1. *iii*. H_2O_2/NaOH/MeOH/H_2O, ~20 °C, 2 days; 45% yield. *iv*. KOH/Bu^tOH, Δ, 1 h; 83% yield. *v*. EtOH/H_2O/H_2SO_4, Δ, 2 h, 30% yield.

This compound can readily be prepared in high yield from enantiomerically pure natural (+)-car-3-ene, whose molecule already has the main structural unit of chrysanthemates, *viz.*, 2,2-dimethylcyclopropane fragment. The chemical properties of the CH_2CN group and the absolute configuration of molecule **4** make it possible to synthesize enantiomerically pure ketones **5** [17] and **6** [18] using the minimum number of steps.

Compounds **5** and **6** are the closest precursors of target products **3** because have the (*R*)-configuration of the C(1) atom and the 2-oxopropyl group in position C(3). The latter can be used for the formation of the indole cycle using Fischer method, as shown[19] for ketone **4**. Thus, the problem was a search for conditions under which ketones **5** and **6** would undergo Fischer indole synthesis and other structural fragments of the initial molecules would remain unchanged.

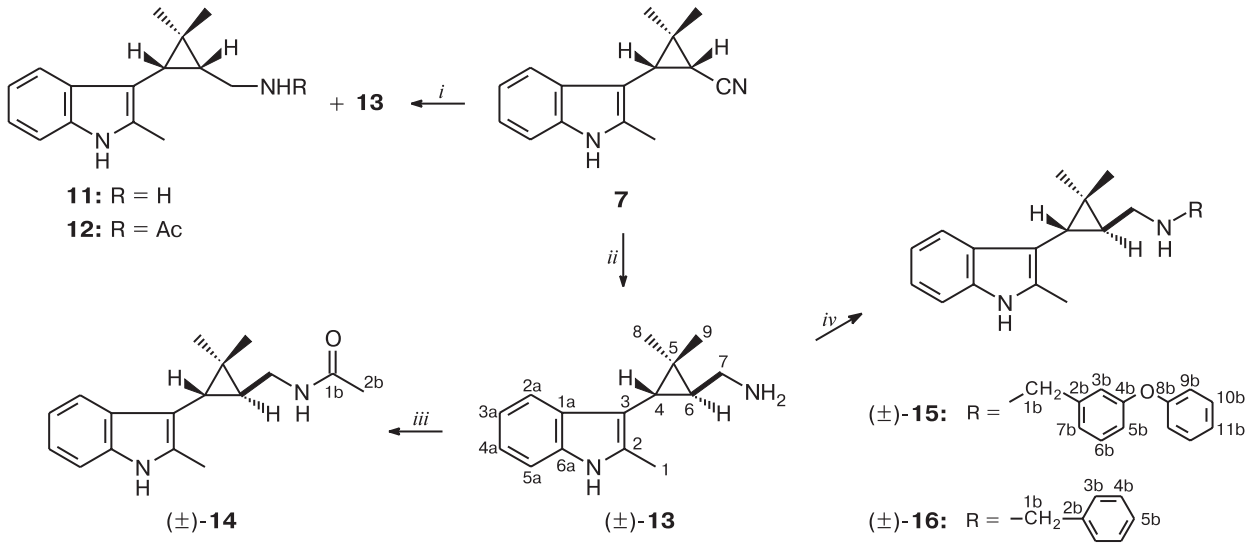
Ketone **5** reacted rapidly with phenylhydrazine in an ethanolic solution without heating to yield the corresponding hydrazone, which underwent Fischer indole synthesis in the presence of polyphosphoric acid (PPA) or its ethyl ester to form indole **7**. However, in the presence of PPA, the yield of indole was only 37% (twofold lower than that in the case of PPE) and the target product was a mixture of *cis*- and *trans*-isomers **7** and **8** in a ratio of 2 : 1 (Scheme 2).* Isomerization **7** ⇌ **8** should be considered as epimerization at one of two asymmetric C(1) or C(3) atoms of the cyclopropane ring. However, it remains yet unclear at which of the atoms it occurs.

Compound **7** is an indolic analog of nitrile of (1*R*)-*cis*-chrysanthemic acid, however, attempts of the transformation of nitrile **7** into the corresponding acid failed. It turned out that the appearance of the 3-indolyl substituent at the C(3) atom of cyclopropane had a substantial effect on hydrolysis of the cyano group. It is known that optically active 2,2-dimethylcyclopropanecarbonitriles close in structure to compound **7**, being heated in an aqueous ethanolic solution[20,21] or in a solution of ethylene glycol[22] and treated with KOH, are easily hydrolyzed to form the corresponding acids, although the inversion of the C(1) atom configuration (epimerization) occurs simultaneously with hydrolysis when ethylene glycol is used. However, hydrolysis of nitrile **7** under these conditions affords lactam **10** due to cyclopropane ring opening. Amide **9** prepared by hydrolysis of compound **7** using the Radziszewski method is more easily transformed into lactam **10**. As shown by ^1H NMR spectroscopy, this process also occurs during prolonged storage without a solvent or when amide **9** is kept in $CHCl_3$ for several days at ~20 °C. Attempts to perform alcoholysis of the amide group in compound **7** to the ester group in an aqueous-ethanolic medium in the presence of H_2SO_4 were also unsuccessful (*cf.* Ref. 21), and lactam **10** was the main product (30% yield) among numerous reaction products. Thus, nitrile **7** and amide **9**, *viz.*, indolic analogs of the corresponding (1*R*)-*cis*-chrysanthemic acid derivatives, are more labile than their nonheterocyclic prototypes, which is also demonstrated in the reduction of the nitrile group by $LiAlH_4$ (Scheme 3).

The cyano group in compound **7** is easily reduced to the aminomethyl group by $LiAlH_4$ in Et_2O (5 h at 20 °C, ~97% yield of amine). However, according to the data of the ^1H NMR spectrum, the product obtained was a mixture of *cis*- and *trans*-isomers in a ratio of 1 : 2 (correspondingly, **11** and **13**). The replacement of diethyl ether by *tert*-butyl methyl ether increased the reaction dura-

* Numeration of atoms in schemes does not correspond to the IUPAC nomenclature and serves only for interpretation of NMR spectra.

Scheme 3



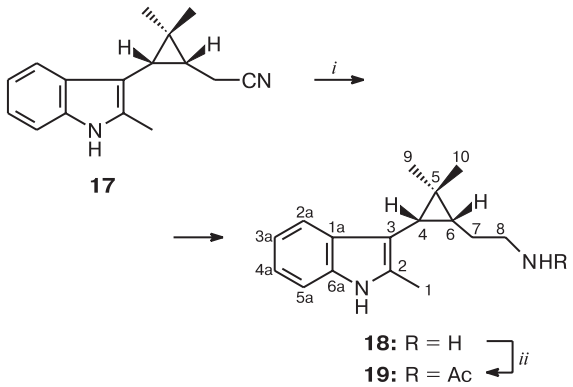
Reagents, conditions, and yields: *i*. $LiAlH_4$/ether, ~20 °C, 5 h, 97% yield, ratio **11** : **13** ~1 : 2; *ii*. $LiAlH_4$/Bu^{t}OMe, ~20 °C, 2 days, 63% yield; *iii*. $AcCl/NEt_3/CH_2Cl_2$, ~20 °C, 15 min, 45% yield; *iv*. 1) $ArCHO/C_6H_6$, Δ, 2 h; 2) $NaBH_4$/MeOH, Δ, 0.5 h, 73% yield (**15**-(±)), 64% yield (**16**-(±)).

tion, decreased the yield of amine, and increased the relative content of *trans*-isomer **13** among the reduction products: the maximum yield of the latter was 63% along with the absence of noticeable amounts of *cis*-amine **11**. As follows from the results of a series of experiments in *tert*-butyl methyl ether, the reduction of nitrile **7** is very sensitive to hydrogenation conditions and quality of the initial reactants, and the yields of amine **13** range within 40—63% (*cf*. Ref. 23). *cis*/*trans*-Isomerization and the complete racemization of the reduction product **13** are observed even at 20 °C. The predominant formation of *trans*-amine **13** in both diethyl and *tert*-butyl methyl ethers is explained by a higher thermodynamic stability of the *trans*-isomer. According to calculations by the molecular mechanics MM2 and quantum-chemical PM3 methods, the heat of formation of *trans*-amine **13** is lower than that of its *cis*-isomer **11** by ~3 kcal mol^{-1}.

The acetylation of amine **13** with acetyl chloride afforded the corresponding acetamide **14**, whose signals in the ^1H and ^{13}C NMR spectra were completely assigned. Taking into account these spectral data, we assigned the signals for *cis*-acetamide **12**, which was obtained only in a mixture with *trans*-acetamide **14** by the acetylation of the product of reduction of nitrile **7** with $LiAlH_4$ in diethyl ether. The condensation of *trans*-amine **13** with *meta*-phenoxybenzaldehyde or benzaldehyde followed by the reduction of Schiff´s bases with $NaBH_4$ easily affords the corresponding arylmethylamines **15** and **16** in high yields.

The absence of optical activity for both acetamide **14** and amines **15** and **16** indicates racemization at the stage of reduction of nitrile **7** with $LiAlH_4$ in *tert*-butyl methyl ether. The racemization of optically active cyclopropane compounds by $LiAlH_4$ is a known process,[23] which occurs, however, only when the reaction center is directly bound to one of the atoms of the cyclopropane ring as, for example, in the initial nitrile **7**. To verify this assumption, we reduced compound **17**,[19] which is a homolog of compound **7**, under similar conditions (Scheme 4).

Scheme 4



Reagents, conditions, and yields: *i*. $LiAlH_4$/ether, ~20 °C, 2 days, 70% yield (**18**). *ii*. $AcCl/NEt_3/CH_2Cl_2$, ~20 °C, 15 min, 86% yield (**19**).

Nitrile **17** is reduced in diethyl ether without epimerization much more slowly and in a lower yield (70%)

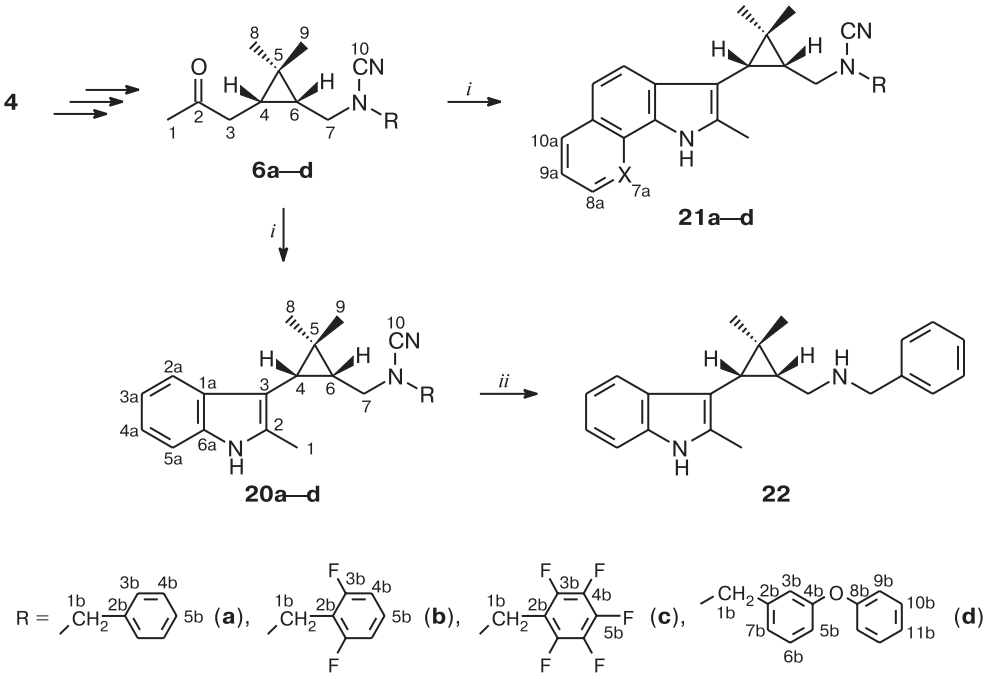
than nitrile **7**. This is indicated by the vicinal spin-spin coupling constant $^3J_{H(4),H(6)}$ = 9.0 Hz, which is characteristic of *cis*-1,2-disubstituted cyclopropanes. In addition, the product of reduction of **17** is not noticeably racemized during the reaction.

Since either a mixture of *cis*- (**11**) and *trans*-isomers (**13**), or racemic *trans*-amine **13** was obtained in the synthesis of the indolic analog of chrysanthemylamine, we applied another sequence of transformations to synthesize analogs of *N*-substituted (1*R*)-*cis*-chrysanthemylamines in the enantiomerically pure form. ω-Ketonitrile **4** has recently been shown[24] to be easily transformed into various *N*-substituted *N*-cyanamides **6a—d** containing the *meta*-phenoxybenzyl and polyfluorobenzyl substituents, which are the most promising from the viewpoint of the insecticidal activity of pyrethroids. Based on ω-keto-*N*-cyanamides **6a—d**, we synthesized a series of heterocyclic compounds **20a—d** and **21a—d** containing the indole fragment (Scheme 5).

Fischer indole synthesis as a method for heterocycle formation turned out to be appropriate for ketocyanamides and allowed the preparation of indole derivatives **20a—d** in high yields (51—95%). In the case of 1-naphthylhydrazine and 8-quinolylhydrazine, the target products were obtained in moderate yields (except for **21a** (69%)). All synthesized indolic analogs of chrysanthemylamines **20** and **21** possessed a considerable optical activity and has the *cis*-arrangement of substituents in the cyclopropane ring, *i.e.*, represented (1*R*)-*cis*-chrysanthemylamine derivatives. Moreover, compounds **20d** and **21d** are heterocyclic aza analogs of the known pyrethroid insecticide cyphenothrin (*cf.* Ref. 18). It is important that the *N*-cyanamide group is retained in the final products because, in particular, *N*-cyanamides exhibit different biological activities.[25—28] In addition, many possibilities of the chemical transformation of the —N(CN)R group are known,[29—33] including those into other pharmacophoric groups.[34—38] It also seems significant that cyanamides can be involved in heterocyclization to form oxazoles,[39] oxazines,[40] oxazolines,[41,42] thiazoles,[43] pyrrolidines,[44] triazines,[45] and pyrimidines.[46] Thus, *N*-cyanamides **20—21** can serve as intermediates in synthesis of other, practically significant compounds.

The *N*-cyano group, which is used as protective for amines, can easily be removed under the action of reducing agents or by hydrolysis.[47—52] In fact, the reduction of *N*-cyanamide **20a** with $LiAlH_4$ in Bu^tOMe affords benzylamine **22**, *viz.*, *cis*-isomer of compound **16** (Scheme 5). A comparison of the chemical shifts of signals and the spin-spin coupling character in the ^1H and ^{13}C NMR spectra of compounds **16** and **22** shows that

Scheme 5



Reagents, conditions, and yields: *i.* 1) $ArNHNH_2$/MeOH, ~20 °C, 2 h; 2) PPE/CH_2Cl_2, ~20 °C, 20 h; 95% (**20a**), 79% (**20b**), 51% (**20c**), 74% (**20d**); 69% (**21a**), 33% (**21b**), 30% (**21c**), 41% (**21d**) yields. *ii.* $LiAlH_4$/Bu^tOMe, ~20 °C, 2 h, 53% yield (**22**).

the NMR spectra of samples **16** and **22** differ significantly despite the structural similarity of these amines. Thus, the NMR spectra allow these compounds and their closest analogs and derivatives to be unambiguously distinguished.

Experimental

Thin layer chromatography was carried out on Silufol plates. To develop spots, plates were sprayed with ethanolic solutions of vanillin (1 g of vanillin + 10 mL of concentrated H_2SO_4 in 100 mL in 95% EtOH) or ninhydrin (0.25 g of ninhydrin and 25 mL of AcOH in 100 mL of 95% EtOH) and heated. Silica gel (KSK trade mark) with a pore size of 0.140—0.315 mm activated at 140 °C for 6—7 h was used for preparative column chromatography.

UV spectra were obtained on a Specord M-40 spectrophotometer in 95% EtOH (c $1 \cdot 10^{-4}$ mol L^{-1}). IR spectra were recorded on a Bruker Vector-22 instrument. Mass spectra were obtained on a Finnigan MAT 8200 spectrometer (50—100 °C, EI, 70 eV). ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (^1H, 200.13 MHz; ^{13}C, 50.32 MHz), Bruker AM-400 (^1H, 400.13 MHz; ^{13}C, 100.61 MHz), and Bruker DRX-500 (^1H, 500.13 MHz; ^{13}C, 125.77 MHz) spectrometers for solutions with a concentration of 70—100 mg mL^{-1} at 25—27 °C. The signal from the solvent was used as internal standard: chloroform-d (δ_C 76.90 ppm, δ_H 7.24), dimethylsulfoxide-d_6 (δ_C 39.50, δ_H 2.50), acetone-d_6 (δ_C 29.80, δ_H 2.04), and C_6F_6 (δ_F 162.90). Angles of optical rotation were measured on a Polamat A polarimeter for solutions in $CHCl_3$. Melting points were determined on a Kofler stage.

(+)-(*1R,3S*)-2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropanecarbonitrile (7). Phenylhydrazine (0.36 g, 3.3 mmol) was added to a solution of ketone **5** [17] (0.45 g, 3.0 mmol) in MeOH (10 mL), the mixture was stored for 2 h at ~20 °C, and the solvent was removed *in vacuo*. The residue (light yellow oil) was dissolved in 10 mL of anhydrous CH_2Cl_2, PPE (2.0 g) was added,[53] and the mixture was left for 12 h at ~20 °C. The solvent was removed *in vacuo*, and the dark brown oil that formed was mixed with 15 mL of an aqueous solution of Na_2CO_3 (0.5 mol L^{-1}) and extracted with Bu^{t}OMe (3×10 mL). The ether extract was dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The residue (0.80 g) was chromatographed on a column packed with SiO_2 (eluent AcOEt—petroleum ether, 1 : 4), and crystalline indole **7** was obtained (0.5 g, 75%) with m.p. 154—157 °C (from EtOAc—hexane). $[\alpha]_{578}^{30}$ +106 (c 2.44). UV (EtOH), λ_{max}/nm (ε): 224 (30500), 282 (6700), 290 (5600). IR (film), ν/cm^{-1}: 3375 (NH_{indole}), 2240 (C≡N), 1455 (C=C_{arom}), 1235, 735 (C—H_{arom}). ^1H NMR ($(CD_3)_2CO$: 1.22 (s, 3 H, $H_3C(8)$); 1.45 (s, 3 H, $H_3C(9)$); 1.97 (d, 1 H, H(6), J = 8.3 Hz); 2.28 (dq, 1 H, H(4), J_1 = 8.3 Hz, J_2 = 1.2 Hz); 2.50 (d, 3 H, $H_3C(1)$, J = 1.2 Hz); 6.99 and 7.03 (both ddd, 1 H, H(3a), H(4a), $J_1 = J_2$ = 7.1 Hz, J_3 = 1.3 Hz); 7.28 (m, 1 H, H(2a)); 7.49 (m, 1 H, H(5a)); 9.98 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($(CD_3)_2CO$), δ: 13.11 (q, C(1)); 16.21 (d, C(6)); 19.27 (q, C(8)); 24.02 (s, C(5)); 26.38 (q, C(9)); 27.87 (d, C(4)); 105.62 (s, C(3)); 111.20 (d, C(5a)); 119.43, 119.66 and 121.36 (all d, C(2a), C(3a), C(4a)); 120.26 (s, C(7)); 129.83 (s, C(1a)); 135.92 and 136.60 (both s, C(2), C(6a)). MS, m/z (I_{rel} (%)): 225 (13), 224 $[M]^+$ (76), 210 (16), 209 (100), 193 (11), 184 (18), 182 (20), 181 (12), 168 (13), 167 (11), 144 (28), 143 (30), 131 (11). Found: m/z 224.1315 $[M]^+$. $C_{15}H_{16}N_2$. Calculated: M = 224.1313.

Synthesis of indolonitriles 7 and 8 in PPA. Phenylhydrazine (0.48 g, 4.4 mmol) was added to a solution of ketone **5** (0.60 g, 4.0 mmol) in MeOH (10 mL). The mixture was stored for 2 h at ~20 °C, the solvent was removed *in vacuo*, and PPA[54] (10.0 g) was added to the residue (light yellow oil). The mixture was stirred to complete dissolution of the hydrazone, and the resulting solution was stored for 8 h at 50 °C. The mixture was diluted with water (30 mL), neutralized by a 25% aqueous solution of NH_3 to pH ~9, and extracted with Bu^{t}OMe (3×10 mL). The ether extract was dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The residue (0.85 g) was chromatographed on a column packed with SiO_2 (eluent AcOEt—petroleum ether, 1 : 4), and a mixture (0.040 g) of *cis*- and *trans*-cyclopropanecarbonitriles **7** and **8** was obtained in a ratio of 2 : 1 according to the ^1H NMR spectral data (overall yield 44%).

***trans*-2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropanecarbonitrile (8).** ^1H NMR ($(CD_3)_2CO$), δ: 0.98 (s, 3 H, $H_3C(8)$); 1.54 (s, 3 H, $H_3C(9)$); 1.78 (d, 1 H, H(6), J = 5.8 Hz); 2.30 (dq, 1 H, H(4), J_1 = 5.8 Hz, J_2 = 1.2 Hz); 2.43 (d, 3 H, $H_3C(1)$, J = 1.2 Hz); 6.99 (m, 2 H, H(3a), H(4a)); 7.26 (m, 1 H, H(2a)); 7.46 (m, 1 H, H(5a)); 10.00 (br.s, 1 H, NH_{indole}).

Amide of (+)-(*1R,3S*)-2,2-dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropanecarboxylic acid (9). NaOH (0.40 g, 10 mmol) was added to a solution of nitrile **7** (0.45 g, 2.0 mmol) in 15 mL of MeOH, and 15 mL of a 33% aqueous solution of H_2O_2 was added dropwise with stirring. The reaction mixture was stored for 2 days at ~20 °C, diluted with water (50 mL), saturated with solid NaCl, and extracted with Bu^{t}OMe (3×10 mL). The ether extract was dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The yellow oil that obtained (0.42 g) was chromatographed on a column packed with SiO_2 (eluent AcOEt—petroleum ether, 1 : 1). Glassy amide **9** was obtained in 45% yield (0.22 g), $[\alpha]_{578}^{28}$ +95 (c 1.98). UV (EtOH), λ_{max}/nm (ε): 226 (33900), 283 (6500), 291 (6000). IR (in $CHCl_3$), ν/cm^{-1}: 3500 (NH_{amide}), 3475 (NH_{indole}), 1670 (C=O_{amide}), 1650 (NH_{amide}), 1455 (C=C_{arom}). ^1H NMR ($CDCl_3$), δ: 1.24 (s, 3 H, $H_3C(8)$); 1.40 (s, 3 H, $H_3C(9)$); 1.74 (d, 1 H, H(6), J = 8.5 Hz); 2.13 (d, 1 H, H(4), J = 8.3 Hz); 2.24 (s, 3 H, $H_3C(1)$); 5.43, 5.63 (both br.s, 1 H + 1 H, NH_2); 6.99—7.05 (m, 2 H, H(3a), H(4a)); 7.15 (m, 1 H, H(2a)); 7.44 (m, 1 H, H(5a)); 8.52 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($CDCl_3$), δ: 12.61 (q, C(1)); 17.39 (q, C(8)); 24.26 (s, C(5)); 28.09 and 31.97 (both d, C(4), C(6)); 29.41 (q, C(9)); 31.97 (d, C(4)); 104.93 (s, C(3)); 110.32 (d, C(5a)); 118.92, 118.97 and 120.80 (all d, C(2a), C(3a), C(4a)); 128.88 (s, C(1a)); 134.96 and 135.37 (both s, C(2), C(6a)); 174.34 (s, C(7)). MS, m/z (I_{rel} (%)): 242 $[M]^+$ (22), 199 (15), 198 (100), 183 (16), 182 (14), 168 (15), 43 (15). Found: m/z 242.1415 $[M]^+$. $C_{15}H_{18}N_2O$. Calculated: M = 242.1419.

(±)-4,4-Dimethyl-5-(2-methyl-1*H*-indol-3-yl)pyrrolidin-2-one (10). Powdered KOH (0.56 g, 10.0 mmol) was added to a solution of nitrile **7** (0.45 g, 2.0 mmol) in 10 mL of Bu^{t}OH, and the mixture was boiled with stirring at 1 h. The reaction mixture was cooled, diluted with water (50 mL), and extracted with Bu^{t}OMe (3×10 mL). The ether extract was dried with anhydrous Na_2SO_4, the solvent was removed *in vacuo*, and

crystalline product **10** was obtained in 83% yield (0.40 g) with m.p. 265—267 °C (from MeOH), $[\alpha]_{578}^{30}$ 0.0 (*c* 2.14). UV (EtOH), λ_{max}/nm (ε): 224 (36600), 282 (7000), 290 (6100). IR (in KBr), ν/cm^{-1}: 3250, 3225 (NH_{indole} and NH_{lactam}); 1670 ($C{=}O_{lactam}$); 1455 ($C{=}C_{arom}$); 755 and 740 ($C{-}H_{arom}$). ^{1}H NMR ($(CD_3)_2SO$), δ: 0.72 (s, 3 H, $H_3C(8)$); 1.20 (s, 3 H, $H_3C(9)$); 2.16 (m, 2 H, $H_2C(6)$); 2.37 (s, 3 H, $H_3C(1)$); 4.64 (s, 1 H, H(4)); 6.92 and 6.99 (both m, 1 H, H(3a), H(4a)); 7.26 (m, 1 H, H(2a)); 7.43 (m, 1 H, H(5a)); 7.83 (br.s, 1 H, NH_{indole}); 10.85 (br.s, 1 H, NH_{amide}). ^{13}C NMR ($(CD_3)_2SO$), δ: 11.95 (q, C(1)); 24.21 (q, C(8)); 28.12 (q, C(9)); 40.52 (s, C(5)); 46.08 (t, C(6)); 61.12 (d, C(4)); 107.48 (s, C(3)); 110.41 (d, C(5a)); 118.30, 118.74 and 119.84 (all d, C(2a), C(3a), C(4a)); 127.47 (s, C(1a)); 132.81 and 135.17 (both s, C(2), C(6a)); 175.60 (s, C(7)). MS, *m*/*z* (I_{rel} (%)): 243 (16), 242 $[M]^+$ (53), 185 (11), 159 (36), 158 (100), 157 (27), 143 (17), 130 (16). Found: *m*/*z* 242.1418 $[M]^+$. $C_{15}H_{18}N_2O$. Calculated: M = 242.1419.

Reaction of amide 9 with EtOH in the presence of H_2SO_4. Water (1.9 mL) and concentrated H_2SO_4 (3.6 mL) were added to a solution of amide **9** (0.48 g, 2.0 mmol) in 16.3 mL of EtOH. The mixture was boiled with a reflux condenser for 10 h. After cooling H_2O (50 mL) was added, and the mixture was extracted with Bu^{t}OMe (3×10 mL). The ether extract was washed with an aqueous solution of Na_2CO_3 (0.5 mol L^{-1}, 15 mL) and a saturated solution of NaCl (15 mL) and dried with anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and a glassy brown mixture (0.34 g) was obtained and chromatographed (SiO_2, eluent AcOEt). Crystalline lactam **10** was obtained in 30% yield (0.15 g).

Reduction of nitriles to amines (general procedure *A*). A solution of nitrile in the corresponding ether (20 mL) was added dropwise to a suspension of $LiAlH_4$ in Et_2O or Bu^{t}OMe. The mixture was stirred at ~20 °C for several hours until the reaction completed (TLC monitoring). Then ether (20 mL) was added, and the reaction mixture was poured into water (50 mL). The organic layer was separated, and the aqueous phase was extracted with ether (3×15 mL). The combined organic phase was treated with a 1 *N* solution of HCl (3×10 mL). The aqueous phase was neutralized with a 25% aqueous solution of NH_3 to pH ~9 and extracted with ether (3×10 mL). The extract was dried with anhydrous Na_2SO_4, the solvent was removed *in vacuo*, and the corresponding amine was obtained.

(±)-*C*-[*trans*-2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropyl]methylamine (13) was prepared by procedure *A* from a suspension of $LiAlH_4$ (0.51 g, 13.5 mmol) in freshly distilled Bu^{t}OMe (10 mL) and a solution of nitrile **7** (1.01 g, 4.5 mmol) in Bu^{t}OMe (20 mL). The reaction was carried out for 2 days at ~20 °C. After standard treatment amine **13** was obtained in 63% yield (0.65 g). ^{1}H NMR ($CDCl_3$—CCl_4), δ: 0.83 (s, 3 H, $H_3C(8)$); 1.32 (m, 1 H, H(6)); 1.34 (s, 3 H, $H_3C(9)$); 1.60 (br.s, 2 H, NH_2); 1.66 (dq, 1 H, H(4), J_1 = 9.0 Hz, J_2 = 1.0 Hz); 2.35 (d, 3 H, $H_3C(1)$, J = 1.0 Hz); 3.05 (m, 2 H, $H_2C(7)$); 6.96 (m, 2 H, H(3a), H(4a)); 7.10 (m, 1 H, H(2a)); 7.42 (m, 1 H, H(5a)); 7.81 (br.s, 1 H, NH_{indole}).

A mixture (0.33 g, 97%) of *cis*- and *trans*-amines **11** and **13** (according to the data of the ^{1}H NMR spectrum, 1 : 2 ratio, respectively) was obtained after standard treatment using procedure *A* from a suspension of $LiAlH_4$ (0.15 g, 4.5 mmol) in anhydrous Et_2O (10 mL) and a solution of nitrile **7** (0.34 g, 1.5 mmol) in Et_2O (20 mL).

***C*-[*cis*-2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropyl]methylamine (11).** ^{1}H NMR ($CDCl_3$—CCl_4), δ: 1.04 (s, 3 H, $H_3C(8)$); 1.34 (m, 1 H, H(6)); 1.35 (s, 3 H, $H_3C(9)$); 1.52 (br.s, 2 H, NH_2); 1.76 (dq, 1 H, H(4); J_1 = 9.0 Hz, J_2 = 1.0 Hz); 2.33 (d, 3 H, $H_3C(1)$, J = 1.0 Hz),); 2.85 (m, 2 H, $H_2C(7)$); 6.96 (m, 2 H, H(3a), H(4a)); 7.10 (m, 1 H, H(2a)); 7.42 (m, 1 H, H(5a)); 7.86 (br.s, 1 H, NH_{indole}).

(±)-*N*-[*trans*-2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]acetamide (14). Et_3N (0.08 g, 0.75 mmol) was added to a solution of amine **13** (0.11 g, 0.50 mmol) in anhydrous CH_2Cl_2, and AcCl (0.06 g, 0.75 mmol) was added dropwise with stirring. After 15 min the solvent was removed *in vacuo*, the residue was stirred with H_2O (10 mL) and Bu^{t}OMe (10 mL), and the organic layer was extracted with Bu^{t}OMe (3×5 mL). The combined organic extracts were washed with a 1 *M* aqueous solution of HCl and a 0.5 *M* solution of Na_2CO_3, and the solvent was removed *in vacuo*. The brown oil that formed (0.12 g) was chromatographed on a column packed with SiO_2 (eluent AcOEt—petroleum ether, 1 : 1, AcOEt, 5% MeOH in AcOEt). Amide **14** was obtained in 45% yield (0.11 g), $[\alpha]_{578}^{15}$ 0.0 (*c* 1.27). UV (EtOH), λ_{max}/nm (ε): 227 (21900), 284 (6000), 292 (5500). IR (in $CHCl_3$), ν/cm^{-1}: 3470 (NH_{indole}), 3315 (NH_{amide}), 1665 ($C{=}O_{amide}$), 1515 (NH_{amide}), 1460 ($C{=}C_{arom}$). ^{1}H NMR ($(CD_3)_2CO$), δ: 0.81 (s, 3 H, $H_3C(8)$); 1.26 (m, 1 H, H(6)); 1.35 (s, 3 H, $H_3C(9)$); 1.48 (dq, 1 H, H(4), J_1 = 6.0 Hz, J_2 = 1.0 Hz); 1.94 (s, 3 H, $H_3C(2b)$); 2.37 (d, 3 H, $H_3C(1)$, J = 1.0 Hz); 3.37 (ddd, 1 H, H(7α), J_1 = 14.0 Hz, J_2 = 8.0 Hz, J_3 = 6.5 Hz); 3.59 (ddd, 1 H, H(7β), J_1 = 14.0 Hz, J_2 = 7.0 Hz, J_3 = 6.0 Hz); 6.94 (m, 2 H, H(3a), H(4a)); 7.22 (m, 1 H, H(2a)); 7.41 (m, 1 H, NH_{amide}); 7.46 (m, 1 H, H(5a)); 9.87 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($(CD_3)_2CO$), δ: 12.29 (q, C(1)); 21.45 (q, C(8)); 21.58 (s, C(5)); 22.97 (q, C(9)); 23.17 (d, C(4)); 26.03 (d, C(6)); 30.56 (q, C(2b)); 40.69 (t, C(7)); 109.66 (s, C(3)); 111.05 (d, C(5a)); 119.17, 119.17 and 120.82 (all d, C(2a), C(3a), C(4a)); 130.86 (s, C(1b)); 134.29 and 136.50 (both s, C(2), C(6a)); 170.10 (s, (1b)). MS, *m*/*z* (I_{rel} (%)): 270 $[M]^+$ (7), 199 (16), 198 (100), 183 (18), 182 (12), 168 (16), 167 (7), 144 (11), 28 (7). Found: *m*/*z* 270.1729 $[M]^+$. $C_{17}H_{22}N_2O$. Calculated: M = 270.1732.

Acetylation of a mixture of amines 11 and 13. A mixture of acetamides **12** and **14** (0.15 g, 56%) was obtained similarly to the previous procedure from a mixture of amines **11** and **13** (0.23 g, 1.0 mmol), Et_3N (0.15 g, 1.5 mmol), and AcCl (0.12 g, 1.5 mmol).

***N*-[*cis*-2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]acetamide (12).** ^{1}H NMR ($CDCl_3$), δ: 1.02 (s, 3 H, $H_3C(8)$); 1.19 (m, 1 H, H(6)); 1.32 (s, 3 H, $H_3C(9)$); 1.72 (dq, 1 H, H(4), J_1 = 9.0 Hz, J_2 = 1.2 Hz); 1.93 (s, 3 H, CH_3CO); 2.26 (d, 3 H, $H_3C(1)$, J = 1.2 Hz); 2.77 (ddd, 1 H, H(7α), J_1 = 14.0 Hz, J_2 = 9.5 Hz, J_3 = 5.0 Hz); 3.70 (ddd, 1 H, H(7β), J_1 = 14.0 Hz, J_2 = J_3 = 6.0 Hz); 5.76 (br.t, 1 H, NH_{amide}, J_1 = 6.0 Hz, J_2 = 5.0 Hz); 7.03 (m, 2 H, H(3a), H(4a)); 7.18 (m, 1 H, H(2a)); 7.46 (m, 1 H, H(5a)); 8.30 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($CDCl_3$), δ: 12.76 (q, C(1)); 16.92 (q, C(8)); 18.22 (s, C(5)); 22.92 (d, C(4)); 23.11 (q, C(2b)); 26.16 (d, C(6)); 28.88 (q, C(9)); 38.28 (t, C(7)); 107.46 (s, C(3)); 110.05 (d, C(5a)); 118.54, 118.84 and 120.55 (all d, C(2a), C(3a), C(4a)); 129.60 (s, C(1a)); 133.86 and 135.38 (both s, C(2), C(6a)); 169.94 (s, C(1b)).

Synthesis of disubstituted amines (general procedure *B*). Aromatic aldehyde (1.1 mmol) was added to a solution of amine **13**

(0.23 g, 1 mmol) in C_6H_6 (15 mL). The mixture was boiled with a Dean-Stark trap for 2 h until the initial amide disappeared (TLC monitoring), after which the solvent was removed *in vacuo*. The resulting imine obtained as a yellowish oil was dissolved in MeOH (10 mL), and $NaBH_4$ (0.19 g, 5 mmol) was added by portions for 10—15 min. The reaction mixture was boiled for 0.5 h, and the solvent was removed *in vacuo*. The residue was mixed with Bu^{t}OMe (10 mL), and 20 mL of water were added. The organic layer was separated, and the aqueous phase was extracted with Bu^{t}OMe (3×10 mL). The combined organic extracts were dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The residue was chromatographed on a column packed with SiO_2 (eluent ethyl acetate—hexane, 2 : 3) to isolate the corresponding amine.

(±)-*N*-[*trans*-2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]-*N*-(3-phenoxybenzyl)amine (15) was prepared using procedure ***B*** from amine **13** (0.23 g) and *m*-$C_6H_5OC_6H_4CHO$ (0.22 g). Chromatography gave amine **15** (0.30 g, 73%), $[\alpha]_{578}^{15}$ 0.0 (*c* 1.62). UV (EtOH), λ_{max}/nm (ε): 228 (23700), 280 (5800), 293 (5600). IR (film), ν/cm^{-1}: 3405 (NH_{indole}), 3290 (NH_{amine}), 1585, 1490, 1460 ($C{=}C_{arom}$), 1250, 1210, 740 and 695 ($C{-}H_{arom}$). ^{1}H NMR ($CDCl_3$—CCl_4), δ: 0.86 (s, 3 H, $H_3C(8)$); 1.30—1.46 (m, 2 H, H(4), H(6)); 1.32 (s, 3 H, $H_3C(9)$); 1.60 (br.s, 1 H, NH_{amine}); 2.36 (s, 3 H, $H_3C(1)$); 2.80 (dd, 1 H, H(7α), J_1 = 12.5 Hz, J_2 = 8.0 Hz); 3.02 (dd, 1 H, H(7β), J_1 = 14.0 Hz, J_2 = 6.5 Hz); 3.89 (m, 2 H, H(1b)); 6.88—7.19 and 7.26—7.33 (both m, 9 H and 3 H, respectively, H(2a), H(3a), H(4a), H(3b), H(5b), H(6b), H(7b) H(9b), H(10b), H(11b)); 7.55 (m, 1 H, H(5a)); 7.73 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 12.33 (q, C(1)); 20.72 (s, C(5)); 21.23 (q, C(8)); 22.97 (q, C(9)); 25.13 (d, C(4)); 30.12 (d, C(6)); 50.25 (t, C(7)); 53.73 (t, C(1b)); 109.90 (d, C(5a)); 109.99 (s, C(3)); 117.33* (d, C(5b)); 118.41, 119.06, 120.70 (all d, C(2a), C(3a), C(4a)); 118.82* (d, 3 C, C(3b), C(9b)); 122.80 and 123.04 (both d, C(7b), C(11b)); 129.56 (d, 2 C, C(10b); 129.61 (d, C(6b)); 129.96 (s, C(1a)); 132.59 and 135.02 (both s, C(2), C(6a)); 142.65 (s, C(2b)); 157.28 and 157.39 (both s, C(6b), C(8b)). MS, *m/z* (I_{rel} (%)): 410 $[M]^+$ (3), 212 (29), 199 (45), 198 (100), 184 (13), 183 (69), 182 (11), 168 (14), 167 (11), 149 (13), 28 (12). Found: *m/z* 410.2359 $[M]^+$. $C_{28}H_{30}N_2O$. Calculated: M = 410.2358.

(±)-*N*-Benzyl-*N*-[*trans*-2,2-dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]amine (16) was prepared according to procedure ***B*** from amine **13** (0.23 g) and C_6H_5CHO (0.12 g). Amine **16** (0.20 g, 64%) was isolated after chromatography, $[\alpha]_{578}^{15}$ 0.0 (*c* 1.62). UV (EtOH), λ_{max}/nm (ε): 227 (22100), 284 (5700), 294 (5400). IR (film), ν/cm^{-1}: 3405 (NH_{indole}), 3285 (NH_{amine}), 1460 ($C{=}C_{arom}$), 740 and 700 ($C{-}H_{arom}$). ^{1}H NMR ($CDCl_3$—CCl_4), δ: 0.87 (s, 3 H, $H_3C(8)$); 1.29—1.44 (m, 2 H, H(4), H(6)); 1.33 (s, 3 H, $H_3C(9)$); 1.70 (br.s, 1 H, NH_{amine}); 2.38 (s, 3 H, $H_3C(1)$); 2.80 (dd, 1 H, H(7α), J_1 = 12.0 Hz, J_2 = 8.0 Hz); 3.06 (dd, 1 H, H(7β), J_1 = 12.0 Hz, J_2 = 6.2 Hz); 3.92 (m, 2 H, $H_2C(1b)$); 7.04—7.09 (m, 2 H, H(3a), H(4a)); 7.15—7.38 (m, 6 H, H(2a), H(3b), H(4b), H(5b)); 7.55 (m, 1 H, H(5a)); 7.75 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 12.31 (q, C(1)); 20.72 (s, C(5)); 21.16 (q, C(8)); 22.94 (q, C(9)); 25.13 (d, C(4)); 30.12 (d, C(6)); 50.31 (t, C(7)); 54.06 (t, C(1b)); 109.89 (s, C(3)); 109.89 (d, C(5a)); 118.81, 119.00 and 120.65 (all d, C(2a), C(3a), C(4a)); 126.81 (d, C(5b)); 128.00 and 128.30 (both d, 2 C, C(3b), C(4b)); 129.98 (s, C(1a)); 132.66 and 135.02 (both s, C(2), C(6a)); 140.41 (s, C(2b)). MS, *m/z* (I_{rel} (%)): 318 $[M]^+$ (3), 254 (13), 199 (33), 198 (100), 183 (10), 168 (11), 120 (45), 91 (72). Found: *m/z* 318.2098 $[M]^+$. $C_{22}H_{26}N_2$. Calculated: M = 318.2096.

(+)-(1*R*,3*S*)-2-[2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropyl]ethylamine (18) was synthesized according to procedure ***A*** from a suspension of $LiAlH_4$ (0.19 g, 5.0 mmol) in anhydrous Et_2O (10 mL) and a solution of nitrile **17** (0.48 g, 2.0 mmol) in 20 mL of Et_2O. The reaction was carried out for 2 days at ~20 °C. Amine **18** was obtained in 70% yield (0.34 g) after standard treatment. ^{1}H NMR ($CDCl_3$—CCl_4), δ: 0.84 (m, 1 H, H(6)); 0.95 (s, 3 H, $H_3C(8)$); 1.28 (s, 3 H, $H_3C(9)$); 1.38 (br.s, 2 H, NH_2); 1.59 (dq, 1 H, H(4), J_1 = 8.6 Hz, J_2 = 1.0 Hz); 1.80 (m, 2 H, $H_2C(7)$); 2.25 (d, 3 H, $H_3C(9)$; J_1 = 1.0 Hz); 2.70 (m, 2 H, $H_2C(8)$); 6.94 (m, 2 H, H(3a), H(4a)); 7.03 (m, 1 H, H(2a)); 7.41 (m, 1 H, H(5a)); 8.12 (br.s, 1 H, NH_{indole}).

(+)-(1*R*,3*S*)-*N*-{2-[2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropyl]ethyl}acetamide (19) was synthesized according to the procedure used for preparation of acetamide **14**. Acetamide **19** was obtained in 86% yield (0.12 g) from amine **18** (0.12 g, 0.5 mmol), Et_3N (0.07 g, 0.7 mmol), and AcCl (0.06 g, 0.7 mmol). $[\alpha]_{578}^{24}$ +84 (*c* 2.35). UV (EtOH), λ_{max}/nm (ε): 227 (23000), 284 (6200), 291 (5700). IR (KBr), ν/cm^{-1}: 3400 (NH_{indole}), 3285 (NH_{amide}), 1655 ($C{=}O_{amide}$), 1555 (NH_{amide}), 1460 ($C{=}C_{arom}$), 740 ($C{-}H_{arom}$). ^{1}H NMR (($CD_3)_2CO$—$CDCl_3$—CCl_4), δ: 0.91 (ddd, 1 H, H(6), J_1 = 13.0 Hz, J_2 = 9.0 Hz, J_3 = 4.5 Hz); 1.05 (m, 1 H, H(7α)); 1.10 (s, 3 H, $H_3C(9)$); 1.28 (s, 3 H, $H_3C(10)$); 1.59 (dq, 1 H, H(4), J_1 = 9.0 Hz, J_2 = 1.0 Hz); 1.81 (s, 3 H, $C\underline{H}_3CO$); 1.89 (m, 1 H, H(7β)); 2.33 (d, 3 H, C(1)Me, J = 1.0 Hz); 3.16 (m, 2 H, $H_2C(8)$); 6.86 (m, 2 H, H(3a), H(4a)); 7.05 (br.s, 1 H, NH_{amide}); 7.14 (m, 1 H, H(2a)); 7.38 (m, 1 H, H(5a)); 9.72 (br.s, 1 H, NH_{indole}). ^{13}C NMR (($CD_3)_2CO$—$CDCl_3$—CCl_4), δ: 13.31 (q, C(1)); 17.45 (q, C(9)); 18.54 (s, C(5)); 22.83 (q, $\underline{C}H_3CO$); 23.55 (t, C(7)); 23.66 (d, C(4)); 27.74 (d, C(6)); 29.70 (q, C(10)); 40.19 (t, C(8)); 108.51 (s, C(3)); 110.62 (d, C(5a)); 118.58, 119.80 and 120.54 (all d, C(2a), C(3a), C(4a)); 130.53 (s, C(1a)); 134.57 and 136.52 (both s, C(2), C(6a)); 169.90 (s, $\underline{C}{=}O$). MS, *m/z* (I_{rel} (%)): 285 $[M^+{+}1]$ (10), 284 $[M]^+$ (50), 225 (19), 224 (12), 212 (34), 210 (37), 199 (17), 198 (100), 183 (20), 182 (32), 170 (19), 169 (15), 168 (36), 167 (13), 154 (11), 144 (41), 131 (63). Found: *m/z* 284.1888 $[M]^+$. $C_{18}H_{24}N_2O$. Calculated: M = 284.1889.

Synthesis of indoles 20a—d and 21a—d (general procedure *C*). Arylhydrazine (or its hydrochloride) (0.55 mmol) and powdered Na_2CO_3 (0.03 g) (only in the case of using arylhydrazine salt) were added to a solution of ketone **6** (0.50 mmol) in 10 mL of MeOH. The mixture was stored for 2 h at ~20 °C, and after filtration the solvent was removed *in vacuo*. The residue (hydrazone in the form of a light yellow oil) was dissolved in 10 mL of anhydrous CH_2Cl_2, and PPE (1.0 g) was added. After stirring the reaction mixture was left for 12 h at ~20 °C, and the solvent was removed *in vacuo*. A 0.5 *M* aqueous solution of Na_2CO_3 (15 mL) was poured to the obtained dark brown oil, and the resulting solution was extracted with Bu^{t}OMe (3×10 mL). The ether extract was dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The corresponding indoles were

* Alternative assignment of signals is possible.

obtained after chromatography on a column packed with SiO_2 (eluent AcOEt—petroleum ether, 1 : 4).

(+)-(*1R,3S*)-*N*-Benzyl-*N*-[2,2-dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]cyanamide (20a) was obtained according to procedure ***C*** from ketone **6a** (0.14 g) and phenylhydrazine (0.06 g). After chromatography cyanamide **20a** was isolated as a light yellow oil (0.16 g, 95%), $[\alpha]_{578}^{20}$ +110 (*c* 3.68). UV (EtOH), λ_{max}/nm (ε): 226 (32700), 283 (7300), 291 (6500). IR (CCl_4), ν/cm^{-1}: 3480 (NH_{indole}), 2210 (C≡N), 1460 (C=C_{arom}), 800, 740 and 700 (C—H_{arom}). ^{1}H NMR ($CDCl_3$—CCl_4), δ: 1.07 (s, 3 H, $H_3C(8)$); 1.32 (ddd, 1 H, H(6), J_1 = 11.0 Hz, J_2 = 9.0 Hz, J_3 = 6.0 Hz); 1.36 (s, 3 H, $H_3C(9)$); 1.81 (dq, 1 H, H(4), J_1 = 9.0 Hz, J_2 = 0.8 Hz); 2.28 (d, 3 H, $H_3C(1)$, J = 0.8 Hz); 2.48 (dd, 1 H, H(7α), J_1 = 12.5, J_2 = 11.0 Hz); 3.42 (dd, 1 H, H(7β), J_1 = 12.5 Hz, J_2 = 6.0 Hz); 4.04 (m, 2 H, $H_2C(1b)$); 6.92—7.00 (m, 2 H, H(3a), H(4a)); 7.10—7.14 (m, 1 H, H(2a); 7.14—7.21 (m, 4 H, H(5a), H(3b), H(4b), H(5b)); 7.81 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 12.95 (q, C(1)); 17.01 (q, C(8)); 19.71 (s, C(5)); 23.67 (d, C(4)); 24.44 (d, C(6)); 28.68 (q, C(9)); 49.47 (t, C(7)); 55.87 (t, C(1b)); 107.37 (s, C(3)); 110.16 (d, C(5a)); 117.54 (s, C(10)); 118.79, 118.92 and 120.87 (all d, C(2a), C(3a), C(4a)); 128.25 (d, C(5b)); 128.25 and 128.66 (both d, 2 C each, C(3b), C(4b)); 129.42 (s, C(1a)); 133.55 (s, C(2b)); 134.80 and 135.49 (both s, C(2), C(6a)). MS, *m/z* (I_{rel} (%)): 344 (2), 343 [M]$^+$ (7), 199 (16), 198 (100), 183 (6), 182 (7), 168 (7), 167 (4), 91 (11). Found: *m/z* 343.2049 [M]$^+$. $C_{23}H_{25}N_3$. Calculated: M = 343.2048.

(+)-(*1R,3S*)-*N*-(2,6-Difluorophenylmethyl)-*N*-[2,2-dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]cyanamide (20b) was prepared according to procedure ***C*** from ketone **6b** (0.15 g) and phenylhydrazine (0.06 g). After chromatography cyanamide **20b** was obtained in 79% yield (0.15 g) as a light yellow viscous oil, $[\alpha]_{578}^{20}$ +107 (*c* 1.18). UV (EtOH), λ_{max}/nm (ε): 226 (30400), 283 (6200), 291 (5600). IR (CCl_4), ν/см$^{-1}$: 3480 (NH_{indole}), 2215 (C≡N), 1475, 1460 (C=C_{arom}), 1235, 1030, 810 (C—H_{arom}). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.07 (s, 3 H, $H_3C(8)$); 1.38 (ddd, 1 H, H(6), J_1 = 11.0 Hz, J_2 = 9.0 Hz, J_3 = 5.0 Hz); 1.40 (s, 3 H, $H_3C(9)$); 1.83 (dq, 1 H, H(4), J_1 = 9.0 Hz, J_2 = 1.0 Hz); 2.36 (d, 3 H, $H_3C(1)$, J = 1.0 Hz); 2.63 (dd, 1 H, H(7α), J_1 = 12.5 Hz, J_2 = 11.0 Hz); 3.72 (dd, 1 H, H(7β), J_1 = 12.5 Hz, J_2 = 5.0 Hz); 4.27 (m, 2 H, $H_2C(1b)$); 6.91—7.06, 7.21—7.26 and 7.33—7.50 (all m, 4 H, 1 H and 2 H, H(2a), H(3a), H(4a), H(5a), H(4b), H(5b)); 9.92 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($(CD_3)_2CO$), δ: 13.14 (q, C(1)); 17.30 (q, C(8)); 20.37 (s, C(5)); 24.91 (d, C(4)); 25.72 (d, C(6)); 28.64 (q, C(9)); 43.61 (t, C(7)); 51.07 (t, C(1b)); 107.84 (s, C(3)); 111.19 (d, C(5a)); 112.35 (dd, $^2J_{C,F}$ = 25.4 Hz, C(4b)); 112.41 (t, $^2J_{C,F}$ = 6.8 Hz, C(2b)); 117.18 (s, C(10)); 119.38, 119.71, 121.33 (all d, C(2a), C(3a), C(4a)); 130.71 (s, C(1a)); 132.30 (dt, $^3J_{C,F}$ = 10.6 Hz, C(5b)); 135.21 and 137.06 (both s, C(2), C(6a)); 162.45 (dd, $^1J_{C,F}$ = 250.4 Hz, $^3J_{C,F}$ = 8.1 Hz, C(3b)). ^{19}F NMR ($CDCl_3$—CCl_4), δ: 48.04 (t, F(3b), J = 7.0 Hz). MS, *m/z* (I_{rel} (%)): 379 [M]$^+$ (6), 199 (16), 198 (100), 183 (7), 182 (10), 170 (5), 168 (10), 127 (17). Found: *m/z* 379.1867 [M]$^+$. $C_{23}H_{23}N_3F_2$. Calculated: M = 379.1860.

(+)-(*1R,3S*)-*N*-[2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]-*N*-(pentafluorophenylmethyl)cyanamide (20c) was prepared using procedure ***C*** from ketone **6c** (0.18 g) and phenylhydrazine (0.06 g). After chromatography compound **20c** was isolated in 51% yield (0.11 g) as colorless crystals with m.p. 160—162 °C (from EtOAc—hexane mixture), $[\alpha]_{578}^{20}$ +102 (*c* 0.92). UV (EtOH), λ_{max}/nm (ε): 226 (49000), 283 (10100), 291 (9100). IR (KBr), ν/cm^{-1}: 3375 (NH_{indole}), 2205 (C≡N), 1510 (C=C_{arom}), 745 (C—H_{arom}). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.10 (s, 3 H, $H_3C(8)$); 1.36 (ddd, 1 H, H(6), J_1 = 11.0 Hz, J_2 = 9.0 Hz, J_3 = 5.0 Hz); 1.38 (s, 3 H, $H_3C(9)$); 1.88 (d, 1 H, H(4), J = 9.0 Hz); 2.39 (s, 3 H, $H_3C(1)$); 2.69 (dd, 1 H, H(7α), J_1 = 12.0 Hz, J_2 = 11.0 Hz); 3.75 (dd, 1 H, H(7β), J_1 = 12.0 Hz, J_2 = 5.0 Hz); 4.40 (s, 2 H, $H_2C(1b)$); 6.94 and 7.00 (both dd, 1 H, H(3a), H(4a), J_1 = J_2 = 8.0 Hz); 7.24 (d, 1 H, H(2a), J = 8.0 Hz); 7.42 (d, 1 H, H(5a), J = 8.0 Hz); 9.87 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($(CD_3)_2CO$), δ*: 13.11 (q, C(1)); 17.24 (q, C(8)); 20.39 (s, C(5)); 24.75 (d, C(4)); 25.39 (d, C(6)); 28.93 (q, C(9)); 43.46 (t, C(7)); 51.04 (t, C(1b)); 107.62 (s, C(3)); 111.13 (d, C(5a)); 116.73 (s, C(10)); 119.29, 119.61 and 121.29 (all d, C(2a), C(3a), C(4a)); 130.52 (s, C(1a)); 135.23 and 136.90 (both s, C(2), C(6a)). ^{19}F NMR ($CDCl_3$—CCl_4), δ: 0.70 (m, F(4b)); 9.04 (m, F(5b)); 21.29 (m, F(3b)). MS, *m/z* (I_{rel} (%)): 433 [M]$^+$ (10), 199 (16), 198 (100), 183 (8), 182 (9), 181 (9), 170 (13), 168 (9), 167 (5). Found: *m/z* 433.1579 [M]$^+$. $C_{23}H_{20}N_3F_5$. Calculated: M = 433.1577.

(+)-(*1R,3S*)-*N*-[2,2-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]-*N*-(3-phenoxybenzyl)cyanamide (20d) was prepared according to procedure ***C*** from ketone **6d** (0.18 g) and phenylhydrazine (0.06 g). After chromatography compound **20d** was obtained in 74% yield (0.16 g) as colorless crystals with m.p. 160—163 °C (from MeCN), $[\alpha]_{578}^{20}$ +89 (*c* 1.65). UV (EtOH), λ_{max}/nm (ε): 226 (44500), 280 (8800), 291 (7100). IR (KBr), ν/cm^{-1}: 3290 (NH_{indole}), 2215 (C≡N), 1585, 1490, 1460 (C=C_{arom}), 780, 735 and 690 (C—H_{arom}). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.07 (s, 3 H, $H_3C(8)$); 1.34 (ddd, 1 H, H(6), J_1 = 11.0 Hz, J_2 = 9.1 Hz, J_3 = 4.7 Hz); 1.36 (s, 3 H, $H_3C(9)$); 1.83 (dq, 1 H, H(4), J_1 = 9.1 Hz, J_2 = 0.9 Hz); 2.34 (d, 3 H, $H_3C(1)$, J = 0.9 Hz); 2.59 (dd, 1 H, H(7α), J_1 = 12.5 Hz, J_2 = 11.0 Hz),); 3.72 (dd, 1 H, H(7β), J_1 = 12.5 Hz, J_2 = 4.7 Hz); 4.19 (s, 2 H, $H_2C(1b)$); 6.90—7.00, 7.09—7.13 and 7.31—7.37 (all m, 6 H, 2 H and 3 H, H(3a), H(4a), H(3b), H(5b), H(6b), H(7b), H(9b), H(10b), H(11b)); 7.22 (d, 1 H, H(2a), J = 8.0 Hz); 7.39 (d, 1 H, H(5a), J = 8.0 Hz); 9.78 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($(CD_3)_2CO$), δ: 13.15 (q, C(1)); 17.50 (q, C(8)); 20.23 (s, C(5)); 24.54 (d, C(4)); 25.60 (d, C(6)); 29.00 (q, C(9)); 50.64 (t, C(7)); 55.99 (t, C(1b)); 107.63 (s, C(3)); 111.12 (d, C(5a)); 118.08 (s, C(10)); 119.18, 119.28, 119.39, 119.64 and 121.23 (all d, C(2a), C(3a), C(4a), C(3b), C(5b)); 119.68 (d, 2 C, C(9b)); 124.18 and 124.33 (both d, C(7b), C(11b)); 130.75 (d, 2 C, C(10b)); 131.01 (d, C(6b)); 130.57 (s, C(1a)); 135.13 and 136.87 (both s, C(2), C(6a)); 138.96 (s, C(2b)); 157.88 and 158.47 (both s, C(4b), C(8b)). MS, *m/z* (I_{rel} (%)): 435 [M]$^+$ (3), 199 (15), 198 (100), 196 (9), 183 (19), 182 (10), 181 (9), 168 (16), 45 (13), 31 (25), 28 (13). Found: *m/z* 435.2309 [M]$^+$. $C_{29}H_{29}N_3O$. Calculated: M = 435.2311.

(+)-(*1R,3S*)-*N*-Benzyl-*N*-[2,2-dimethyl-3-(2-methyl-1*H*-pyrrolo[3,2-h]quinolin-3-yl)cyclopropylmethyl]cyanamide (21a) was prepared according to procedure ***C*** from ketone **6a** (0.14 g) and 8-quinolylhydrazine (0.11 g). After chromatography com-

* In the ^{13}C NMR spectra of compounds **20c** and **21c** chemical shifts of carbon atoms of the pentafluorobenzyl ring were not determined because of their low intensity due to multiple SSC constants $J_{C,F}$.

pound **21a** was isolated (0.14 g, 69%) as a light yellow oil, $[\alpha]_{578}^{20}$ +96 (*c* 1.85). UV (EtOH), λ_{max}/nm (ε): 277 (33100), 354 (3200). IR (CCl_4), ν/cm^{-1}: 3470 (NH_{indole}), 2205 (C≡N), 1375 (C=C_{arom}), 1030, 825 (C—H_{arom}). ^{1}H NMR (($CD_3)_2CO$), δ: 1.14 (s, 3 H, $H_3C(8)$); 1.42 (ddd, 1 H, H(6), J_1 = 10.8 Hz, J_2 = 9.2 Hz, J_3 = 4.9 Hz); 1.42 (s, 3 H, $H_3C(9)$); 1.95 (d, 1 H, H(4), J = 9.2 Hz); 2.50 (s, 3 H, $H_3C(1)$); 2.65 (dd, 1 H, H(7α), J_1 = 12.6 Hz, J_2 = 10.8 Hz); 3.66 (dd, 1 H, H(7β), J_1 = 12.6 Hz, J_2 = 4.9 Hz); 4.21 (s, 2 H, $H_2C(1b)$); 7.28—7.36 (m, 6 H, H(9a), H(3b), H(4b), H(5b)); 7.40 and 7.65 (both d, 1 H, H(2a), H(3a), J = 8.6 Hz); 8.26 (d, 1 H, H(10a), J = 8.1 Hz); 8.74 (d, 1 H, H(8a), J = 4.1 Hz); 11.01 (br.s, 1 H, NH_{indole}). ^{13}C NMR (($CD_3)_2CO$), δ: 13.17 (q, C(1)); 17.45 (q, C(8)); 20.33 (s, C(5)); 24.43 (d, C(4)); 25.67 (d, C(6)); 28.98 (q, C(9)); 50.45 (t, C(7)); 56.40 (t, C(1b)); 110.08 (s, C(3)); 118.16 (s, C(10)); 118.94, 119.49 and 121.49 (all d, C(2a), C(3a), C(9a)); 125.05, 129.06, 129.17 and 130.81 (four s, C(1a), C(4a), C(5a), C(6a)); 128.92 (d, C(5b)); 129.37 (d, C(3b)); 129.42 (d, C(4b)); 135.30 (s, C(2)); 136.84 (d, C(10a)); 138.46 (s, C(2b)); 148.61 (d, C(8a)). MS, *m/z* (I_{rel} (%)): 394 $[M]^+$ (7), 250 (19), 249 (100), 234 (8), 233 (8), 219 (7), 218 (4), 195 (3), 91 (7). Found: *m/z* 394.2163 $[M]^+$. $C_{26}H_{26}N_4$. Calculated: M = 394.2157.

(+)-(*1R,3S*)-*N*-(2,6-Difluorophenylmethyl)-*N*-[2,2-dimethyl-3-(2-methyl-1*H*-pyrrolo[3,2-h]quinolin-3-yl)cyclopropylmethyl]cyanamide (21b) was prepared according to procedure ***C*** from ketone **6b** (0.15 g) and 8-quinolylhydrazine (0.11 g). After chromatography compound **21b** was isolated (0.07 g, 33%) as a light yellow oil, $[\alpha]_{578}^{20}$ +91 (*c* 1.85). UV (EtOH), λ_{max}/nm (ε): 276 (35500), 353 (3600). IR ($CHCl_3$), ν/cm^{-1}: 3460 (NH_{indole}), 2210 (C≡N), 1465, 1375 (C=C_{arom}), 1030, 825 (C—H_{arom}). ^{1}H NMR (($CD_3)_2CO$), δ: 1.10 (s, 3 H, $H_3C(8)$); 1.36 (ddd, 1 H, H(6), J_1 = 11.0 Hz, J_2 = 9.0 Hz, J_3 = 4.8 Hz); 1.40 (s, 3 H, $H_3C(9)$); 1.96 (dq, 1 H, H(4), J_1 = 9.0 Hz, J_2 = 0.8 Hz); 2.53 (d, 3 H, $H_3C(1)$, J = 0.8 Hz); 2.68 (dd, 1 H, H(7α), J_1 = 12.3 Hz, J_2 = 11.0 Hz); 3.77 (dd, 1 H, H(7β), J_1 = 12.3 Hz, J_2 = 4.8 Hz); 4.29 (m, 2 H, $H_2C(1b)$); 6.98—7.06 (m, 2 H, H(4b)); 7.34 (dd, 1 H, H(9a), J_1 = 8.0 Hz, J_2 = 4.3 Hz); 7.40 (m, 1 H, H(5b)); 7.41 and 7.67 (both d, 1 H, H(2a), H(3a), J = 8.5 Hz); 8.26 (dd, 1 H, H(10a), J_1 = 8.0 Hz, J_2 = 2.0 Hz); 8.73 (dd, 1 H, H(8a), J_1 = 4.3 Hz, J_2 = 2.0 Hz); 11.05 (br.s, 1 H, NH_{indole}). ^{13}C NMR (($CD_3)_2CO$), δ: 13.13 (q, C(1)); 17.17 (q, C(8)); 20.39 (s, C(5)); 24.60 (d, C(4)); 25.53 (d, C(6)); 28.93 (q, C(9)); 50.78 (t, C(7)); 43.50 (t, C(1a)); 110.00 (s, C(3)); 112.24 (t, C(2b), $^2J_{C,F}$ = 6.8 Hz); 112.30 (dd, C(4b), $^2J_{C,F}$ = 25.1 Hz); 117.11 (s, C(10)); 118.98, 119.52 and 121.42 (all d, C(2a), C(3a), C(9a)); 125.07, 129.01, 130.96 and 130.81 (all s, C(1a), C(4a), C(5a), C(6a)); 132.09 (dt, C(5b), $^3J_{C,F}$ = 10.5 Hz); 135.20 (s, C(2)); 136.73 (d, C(10a)); 148.74 (d, C(8a)); 162.57 (dd, C(3b), $^1J_{C,F}$ = 248.1 Hz, $^3J_{C,F}$ = 8.4 Hz). ^{19}F NMR ($CDCl_3$—CCl_4), δ: 48.56 (t, F(3b), J = 7.0 Hz). MS, *m/z* (I_{rel} (%)): 430 $[M]^+$ (2), 289 (9), 250 (20), 249 (100), 234 (15), 233 (12), 219 (12), 218 (7), 127 (9), 99 (8). Found: *m/z* 430.1973 $[M]^+$. $C_{26}H_{24}N_4F_2$. Calculated: M = 430.1969.

(+)-(*1R,3S*)-*N*-[2,2-Dimethyl-3-(2-methyl-1*H*-benzo[g]indol-3-yl)cyclopropylmethyl]-*N*-(pentafluorophenylmethyl)cyanamide (21c) was obtained according to procedure ***C*** from ketone **6c** (0.18 g) and 1-naphthylhydrazine (0.11 g). After chromatography compound **21c** was isolated in 30% yield (0.07 g) as colorless crystals with m.p. 210—212 °C (from MeCN), $[\alpha]_{578}^{20}$ +99 (*c* 1.84). UV (EtOH), λ_{max}/nm (ε): 269 (53900), 334 (1600). IR (KBr), ν/cm^{-1}: 3310 (NH_{indole}), 2210 (C≡N), 1525, 1510 (C=C_{arom}), 1140, 810 and 760 (C—H_{arom}). ^{1}H NMR (($CD_3)_2CO$), δ: 1.13 (s, 3 H, $H_3C(8)$); 1.39 (ddd, 1 H, H(6), J_1 = 11.0 Hz, J_2 = 9.0 Hz, J_3 = 4.8 Hz); 1.41 (s, 3 H, $H_3C(9)$); 1.95 (d, 1 H, H(4), J = 9.0 Hz); 2.47 (s, 3 H, $H_3C(1)$); 2.71 (dd, 1 H, H(7α), J_1 = 12.3 Hz, J_2 = 11.0 Hz); 3.77 (dd, 1 H, H(7β), J_1 = 12.3 Hz, J_2 = 4.8 Hz); 4.35 (s, 2 H, $H_2C(1b)$); 7.34 and 7.45 (both dd, 1 H, H(8a), H(9a), J_1 = J_2 = 7.4 Hz); 7.42 and 7.58 (both d, 1 H, H(2a), H(3a), J = 8.7 Hz); 7.87 (d, 1 H, H(7a), J = 7.4 Hz); 8.21 (d, 1 H, H(10a), J = 7.4 Hz); 10.82 (br.s, 1 H, NH_{indole}). ^{13}C NMR (($CD_3)_2CO$), δ*: 13.11 (q, C(1)); 17.20 (q, C(8)); 20.41 (s, C(5)); 24.70 (d, C(4)); 25.38 (d, C(6)); 28.92 (q, C(9)); 43.41 (t, C(7)); 50.97 (t, C(1b)); 109.52 (s, C(3)); 116.74 (s, C(10)); 119.92, 120.52, 120.73, 123.85, 125.85 and 129.20 (all d, C(2a), C(3a), C(7a), C(8a), C(9a), C(10a)); 122.70 and 126.08 (both s, C(4a), C(5a)); 130.82 and 133.42 (both s, 2 C and 1 C, respectively, C(2), C(1a), C(6a)). ^{19}F NMR (($CD_3)_2CO$), δ: 0.65 (m, F(4b)); 8.97 (m, F(5b)); 21.44 (m, F(3b)). MS, *m/z* (I_{rel} (%)): 483 $[M]^+$ (12), 249 (20), 248 (100), 233 (21), 232 (10), 220 (12), 218 (11), 41 (19). Found: *m/z* 483.1730 $[M]^+$. $C_{27}H_{22}N_3F_5$. Calculated: M = 483.1734.

(+)-(*1R,3S*)-*N*-[2,2-Dimethyl-3-(2-methyl-1*H*-pyrrolo[3,2-h]quinolin-3-yl)cyclopropylmethyl]-*N*-(3-phenoxybenzyl)cyanamide (21d) was prepared according to procedure ***C*** from ketone **6d** (0.18 g) and 8-quinolylhydrazine (0.11 g). After chromatography product **21d** was isolated in 41% yield (0.10 g) as a light yellow oil, $[\alpha]_{578}^{20}$ +81 (*c* 3.05). UV (EtOH), λ_{max}/nm (ε): 277 (39000), 354 (3800). IR (CCl_4), ν/cm^{-1}: 3460 (NH_{indole}), 2210 (C≡N), 1490, 1375 (C=C_{arom}), 1255, 830, 685 (C—H_{arom}). ^{1}H NMR (($CD_3)_2CO$), δ: 1.10 (s, 3 H, $H_3C(8)$); 1.34 (ddd, 1 H, H(6), J_1 = 11.0 Hz, J_2 = 9.0 Hz, J_3 = 4.8 Hz); 1.40 (s, 3 H, $H_3C(9)$); 1.91 (dq, 1 H, H(4), J_1 = 9.0 Hz, J_2 = 0.8 Hz); 2.48 (d, 3 H, $H_3C(1)$, J = 0.8 Hz); 2.62 (dd, 1 H, H(7α), J_1 = 12.5 Hz, J_2 = 11.0 Hz); 3.68 (dd, 1 H, H(7β), J_1 = 12.5 Hz, J_2 = 4.8 Hz); 4.19 (s, 2 H, $H_2C(1b)$); 6.91—6.97, 7.02—7.15, 7.26—7.39, 7.61—7.65, 8.21—8.26 and 8.72—8.75 (all m, 4 H, 2 H, 5 H, 1 H, 1 H, 1 H, respectively, H(2a), H(3a), H(8a), H(9a), H(10a), H(3b), H(5b), H(6b), H(7b), H(9b), H(10b), H(11b)); 11.11 (br.s, 1 H, NH_{indole}) ^{13}C NMR (($CD_3)_2CO$), δ: 13.20 (q, C(1)); 17.48 (q, C(8)); 20.35 (s, C(5)); 24.47 (d, C(4)); 25.66 (d, C(6)); 29.04 (q, C(9)); 50.50 (t, C(7)); 56.07 (t, C(1b)); 110.05 (s, C(3)); 117.09 (s, C(10)); 118.96, 119.20, 119.42, 119.52, 121.43, 124.21, 124.29 and 131.01 (all d, C(2a), C(3a), C(9a), C(3b), C(5b), C(6b), C(7b), C(11b)); 119.65 (d, 2 C, C(9b)); 130.72 (d, 2 C, C(10b)); 136.68 (d, C(10a)); 148.77 (d, C(8a)); 119.52 and 124.87 (both s, C(4a), C(5a)); 128.88, 131.01 and 135.18 (all s, C(2), C(1a), C(6a)); 138.91 (s, C(2b)); 157.83 and 158.46 (both s, C(4b), C(8b)). MS, *m/z* (I_{rel} (%)): 486 $[M]^+$ (2), 289 (13), 250 (19), 249 (100), 234 (17), 233 (13), 219 (13), 218 (8), 43 (7). Found: *m/z* 486.2408 $[M]^+$. $C_{32}H_{30}N_4O$. Calculated: M = 486.2419.

(+)-(*1R,3S*)-*N*-Benzyl-*N*-[2,2-dimethyl-3-(2-methyl-1*H*-indol-3-yl)cyclopropylmethyl]amine (22). A solution of indole **20a** (0.34 g, 1 mmol) in 15 mL of Bu^{t}OMe was added dropwise to a suspension of $LiAlH_4$ (0.19 g, 5 mmol) in 5 mL of an-

* In the ^{13}C NMR spectrum of compound **21c** chemical shifts of carbon atoms of the pentafluorobenzyl ring were not determined because of their low intensity due to multiple SSC constants $J_{C,F}$.

hydrous Bu^{t}OMe. The mixture was stirred at ~20 °C for 2 h until initial compound **20a** disappeared (TLC monitoring). The reaction mixture was diluted with 20 mL of Bu^{t}OMe and poured into water (30 mL). The organic layer was separated, and the aqueous phase was extracted with Bu^{t}OMe (3×10 mL). The combined organic extracts were dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The residue (0.31 g) was chromatographed on a column packed with SiO_2 (eluent EtOAc—hexane, 1 : 1), and amine **22** was obtained (0.17 g, 53%), $[\alpha]_{578}^{15}$ +30 (*c* 1.62). UV (EtOH), λ_{max}/nm (ε): 227 (31000), 284 (7000), 292 (6400). IR (CCl_4), ν/cm^{-1}: 3480 (NH_{indole}), 1460 ($C{=}C_{arom}$), 1235, 735 and 700 ($C{-}H_{arom}$). ^{1}H NMR ($CDCl_3$—CCl_4), δ: 0.98 (s, 3 H, $H_3C(8)$); 1.10 (ddd, 1 H, H(6), $J_1 = J_2 = 9.0$ Hz, $J_3 = 5.5$ Hz); 1.31 (s, 3 H, $H_3C(9)$); 1.62 (d, 1 H, H(4), $J = 9.0$ Hz); 2.07 (br.s, 1 H, NH_{amine}); 2.26 (s, 3 H, $H_3C(1)$); 2.29 (dd, 1 H, H(7α), $J_1 = 12.5$ Hz, $J_2 = 9.0$); 2.89 (dd, 1 H, H(7β), $J_1 = 12.5$ Hz, $J_2 = 5.5$ Hz); 3.62 (m, 2 H, $H_2C(1b)$); 6.81—7.02 (m, 2 H, H(3a), H(4a)); 7.08—7.14 (m, 1 H, H(2a)); 7.14—7.21 (m, 5 H, H(3b), H(4b), H(5b)); 7.34—7.40 (m, 1 H, H(5a)); 7.83 (br.s, 1 H, NH_{indole}). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 13.00 (q, C(1)); 17.06 (q, C(8)); 18.32 (s, C(5)); 23.12 (d, C(4)); 27.39 (d, C(6)); 29.29 (q, C(9)); 47.58 (t, C(7)); 54.15 (t, C(1b)); 108.68 (s, C(3)); 109.86 (d, C(5a)); 118.90, 119.42 and 120.82 (all d, C(2a), C(3a), C(4a)); 128.18 and 128.24 (both d, 2 C, C(3b), C(4b)); 126.68 (d, C(5b)); 129.98 (s, C(1a)); 133.20 и 135.50 (both s, C(2), C(6a)); 139.91 (s, C(2b)). MS, *m/z* (I_{rel} (%)): 318 $[M]^+$ (2), 249 (10), 199 (30), 198 (100), 183 (9), 182 (13), 168 (15), 144 (8), 120 (46), 91 (81). Found: *m/z* 318.2095 $[M]^+$. $C_{22}H_{26}N_2$. Calculated: M = 318.2096.

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