Synthesis of Novel Steroid Alkaloids by Cyclization of Arylimines from Estrone

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Intramolecular Lewis or Brønsted acid-catalyzed cyclization reactions of steroid arylimines **6** yielded either tetrahydroquinolines condensed to the estrane skeleton **9** or *N*-arylamino-D-homosteroids **12–16**, depending on the substituent of the arylimino group.

Introduction

Alkaloids such as solanidine **1**, tomatidine and batrachotoxine are N-containing steroids which are usually found in higher plants and in animals.[1] They show a pronounced biological activity; thus, batrachotoxine is one of the most toxic nonpeptide compounds. The majority of the natural steroid alkaloids are derived from the C-skeleton of cholesterol.

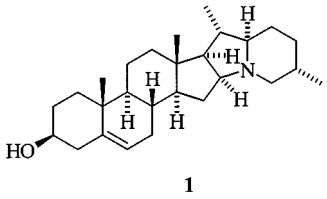

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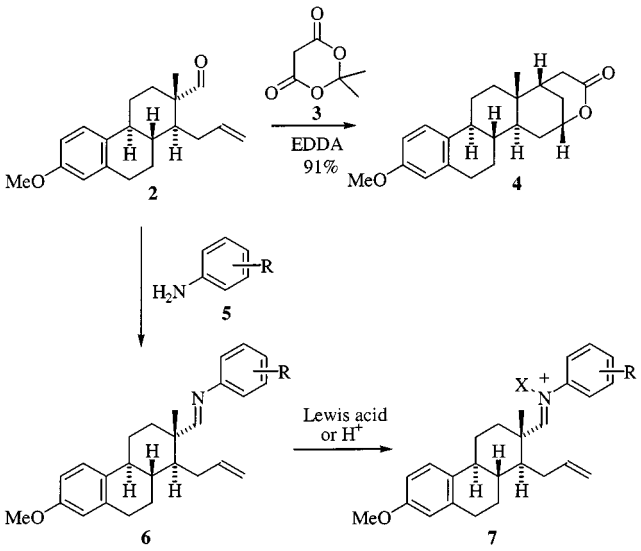
Figure 1. Steroid alkaloid solanidine

It was our goal to synthesize novel analogues of steroid alkaloids using domino reactions. Some time ago we prepared several heterocyclic and D-homosteroids using the cycloaddition of intermediately formed 1,3-buta-1-oxadienes. Thus, the reaction of the estrone derivative **2** with Meldrum′s acid **3** led to **4** in a highly efficient domino reaction[2] with excellent selectivity and yield.[3] For the formation of the steroid alkaloid analogues from the aldehyde **2**,[4] the appropriate imines **6** were expected to undergo a hetero Diels–Alder reaction[5] on treatment with a Lewis or a Brønsted acid via the corresponding iminium ion **7**.

The hetero Diels–Alder reaction of *N*-aryl imines for the synthesis of 1,2,3,4-tetrahydroisoquinoline derivatives is a well-known procedure.[6] A wide variety of electron-rich compounds, such as dihydrofurans,[7] enol ethers,[8] enamines[9] and ketenes[10a] as well as ketene acetals[10b] were used as dienophiles. In addition, several other *N*-heterocyclic compounds, including polycyclic ring systems[5b] and octahydroacridines[11] were synthesized using this approach.



Scheme 1. Synthesis of D-homosteroids and proposed formation of iminium salts from the estrone derivative **2**

However, in contrast to the normal Diels–Alder reaction, the cycloaddition of aryl imines such as 2-aza-1,3-butadienes generally follows a two-step mechanism. First, a carbocation is formed by reaction of the iminium ion with the dienophile moiety;[12] this is succeeded by a Friedel–Crafts alkylation to give the cycloadduct. We anticipated that the Friedel–Crafts alkylation depended on the electron density of the aryl moiety; thus, using anilines with electron-withdrawing groups would decrease the rate of the electrophilic aromatic substitution and consequently new reaction channels for the iminium ion would be opened. This is indeed the case and several new reactions have been observed for the iminium ions **7**. In this manuscript, we describe the reaction of the estrone derivative **2** with different anilines **5a–k**, which led to novel steroid alkaloid analogues with structures depending on the character of the substituent *R* in **5**.[13]

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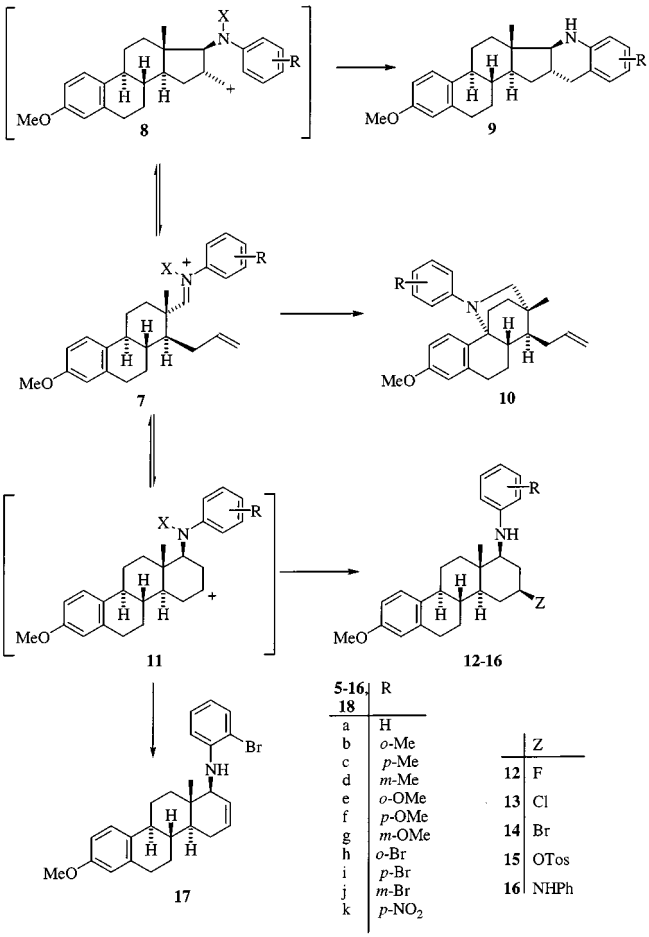
Results and Discussion

Reaction of **2** and **5a** gave the imine **6a** which was identified by NMR spectroscopy but was not isolated due to its instability.[14] Thus, the crude imine was treated with $BF_3{\cdot}OEt_2$ to give the two cyclic products **9a** and **12a** in 38 and 35% isolated yield, respectively; other compounds were not found. Although **9a** is the formal Diels–Alder adduct, we believe that the compound is obtained in a two-step mechanism from the initially formed iminium ion **7a** via the cation **8a** as an intermediate. **8a** can then undergo an electrophilic aromatic substitution to give **9a**. On the other hand, the iminium ion in **7** might also react with the alkene moiety to afford the cation **11** which could be further transformed either by the addition of a nucleophile or by the elimination of a proton. Thus, addition of a fluoride anion to **11a** would explain the formation of **12a** in the reaction of **2** and **5a** in the presence of $BF_3{\cdot}OEt_2$. The formation of an alkene was noticed only in one case, namely in the transformation of **2** and **5h** to give 2% of **17.** An intramolecular electrophilic substitution of **11** to give a bridged compound was not observed, probably due to steric reasons and the instability of the possible products.

It must be assumed that the two intermediately formed cations **8** and **11** are in equilibrium with each other, and that the ratio of the obtained products is determined by the rate of the addition of a nucleophile and the Friedel–Crafts alkylation. This is clearly demonstrated by reaction of **2** with a twofold excess of aniline **5a**; in this transformation, the D-homosteroid **16a** is the only product because of the higher nucleophilicity of aniline compared to the fluoride anion; both, the nucleophilic addition and the Friedel–Crafts alkylation seem to be irreversible under the reaction conditions.

On the other hand, as already mentioned, the rate of the Friedel–Crafts alkylation of **8** should strongly depend on the electron density of the aryl moiety. It would be enhanced by having electron-donating groups such as Me and OMe, and decreased by having electron-withdrawing groups such as Br or NO_2 at the aryl moiety. Thus, in the first case, the reaction channel yielding the steroid alkaloids **9** should dominate, whereas in the second case the D-homosteroids **12–16** should be formed exclusively or as the main products. In addition, the position of the substituent *R* in **8** should also have some influence. This assumption is in complete agreement with the experimental results. Reaction of **2** with **5c** and **5f** gave exclusively **9c** and **9f** in 87% and 95% yield, respectively. In the reaction with **5b**, in addition to **9b** a considerable amount of the corresponding D-homosteroid **12b** was found. Here, it must be assumed that the electrophilic substitution is hampered by the *ortho* substituent due to steric reasons. In the reaction of **2** with the anilines **5d** and **5g** containing a *meta* substituent, two regioisomers could be formed. However, the 5′-substituted compounds **9d** and **9g** were the only products.

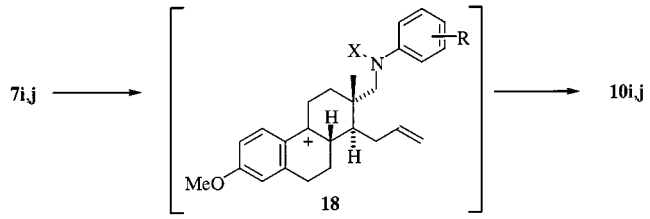
The formation of **9** proceeds in a highly stereoselective manner; in all transformations, only one diastereomer was found. This can be explained by the addition of the alkene moiety to the iminium ion from the *Re*-face *anti* to the angular methyl group in **7** to give in an *anti* fashion the *trans* products.



Scheme 2. Synthesis of steroid alkaloid analogues **9–17** from the estrone derivative **2** and **5**

The reaction of **2** with **5k** containing a *p*-NO_2 group, in the presence of $BF_3{\cdot}OEt_2$ afforded the D-homosteroid **12k** as the only product. Using the anilines **5h–5j** substituted with the weaker electron-withdrawing group Br, the picture changed slightly. With the *o*-bromoaniline **5h**, the D-homosteroid **12h** was formed nearly exclusively, whereas with the other bromoanilines, some of the steroid alkaloids **9** were also obtained. In addition, two novel unusual bridged steroid alkaloid analogues **10i** and **10j** were found in smaller amounts. The formation of these compounds can be explained by a 1,5-hydride shift of the iminium ion **7** to give **18** containing a secondary amine moiety and a carbocation. Subsequent addition of the amine to the carbocation in **18** yields **10**. This transformation can be the main reaction channel if one reduces the double bond in **2**.[15]

The substituent *Z* in **12** could be varied by using different Lewis or Brønsted acids. This has been confirmed for the reaction of **2** with **5k**. In the presence of equimolar amounts of the Lewis acids $SnCl_4$ and $ZnBr_2$, the D-homosteroids **13k** and **14k**, respectively, were the main products, whereas in the presence of *p*-toluenesulfonic acid, **15k** was obtained in 84% yield.



Scheme 3. Formation of **10** from **7**

As was the case for **9**, in the formation of **12−16** only one diastereomer was found in each case. The stereoselective formation of the intermediate cation **11** from **7** can again easily be explained by an addition of the alkene moiety to the iminium ion *anti* to the angular methyl group in **7** as already pointed out for the synthesis of **9**. However, the stereoselective addition of the nucleophile to the cation **11** is quite surprising, since it takes place *syn* to the angular methyl group. Here, it can be postulated that the reaction proceeds in an intramolecular fashion with the formation of the corresponding ammonium salt as an intermediate.

The absolute configuration of the obtained enantiomerically pure compounds **9**, **10** and **12−17** is derived from the initial estrone derivative, of which the stereochemistry was known. The relative configuration of the products was mainly determined by ^{1}H NMR spectroscopy and X-ray analysis. Thus, the X-ray crystal structure analysis of **9f** shows the *trans* annulation of the rings D and E and an α-orientation of the substituent at C-16.[16] Since the NMR spectra of **9f** are in good agreement with the other steroid alkaloids **9**, it can be assumed that they all have the same relative configuration. In the case of **9a** four signals, and in that of **9b−g** three signals for the aromatic protons are found at δ = 6.2−7.1. The hydrogen of the CHN group resonates at δ ≈ 2.7 as a doublet with $J \approx 10.2$ Hz. The structures of **10i**[17] and **12k**[18] were also confirmed by X-ray analysis. In the ^{13}C NMR spectra of **10i** and **10j**, signals at δ ≈ 58 and δ ≈ 61 are found, which is in agreement with a substituted aniline moiety.

The stereochemistry at C-16 and C-17a in ring D of the D-homosteroids **12−16** follows from the coupling constants $J \approx 11.2$ Hz, 10.8 Hz, 5.8 Hz and 5.3 Hz of the signal at δ = 4.6 for 16-H and of $J \approx 11.2$ Hz of the signal for 17a-H at δ = 3.3.

Experimental Section

The melting points were determined on a Kofler block and are uncorrected. − Specific rotation was measured in chloroform (c = 1; $CHCl_3$) at 20°C with Polamat-A and Perkin−Elmer 241 polarimeters. − The IR spectra were recorded in KBr pellets with a Bruker IFS 25 spectrometer. − Mass spectra were obtained on a Varian MAT 311A and a Varian 731 (high resolution) spectrometer. − ^{1}H NMR spectra were obtained at 200 MHz (Varian VXR 200), at 300 MHz (Bruker AMX 300) or at 500 MHz (Varian VXR 500), and the ^{13}C NMR spectra at 50, 75, or 125 MHz on the same instruments. Chemical shifts are reported relative to TMS. ^{13}C NMR spectra are ^{1}H-decoupled. For the determination of the multiplicities, the APT pulse sequence was used. − Elemental analysis was carried out in the analytical laboratory of the University of Szeged. − All solvents were distilled prior to use. The reactions were monitored by TLC on Kieselgel-G (Merck Si 254 F) layers (0.25 mm thickness). The spots were detected by spraying with 5% phosphomolybdic acid in 50% aqueous phosphoric acid. The R_f values were determined for the spots observed by illumination with UV light at 254 and 365 nm.

General Procedure: A solution of **2** (298 mg, 1.00 mmol) and freshly distilled aniline (**5a**) or substituted anilines (**5b−k**, 1.00 mmol) in CH_2Cl_2 (10 mL) in the presence of molecular sieves (4 Å; 150 mg) was heated under a nitrogen atmosphere for 4 h at 40°C. The sieves were removed by filtration and 48% $BF_3{\cdot}OEt_2$ (1.00 mmol) or other Lewis or Brønsted acids ($SnCl_4$; $ZnBr_2$; *p*-toluenesulfonic acid, 1.00 mmol), was added slowly in two portions at room temperature. After adding half of the Lewis acid, the mixture was stirred overnight. After adding the other half of the acid the reaction was carried out until complete conversion (TLC) was achieved. NaOH (1 N, 30 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated in vacuo and the crude product was purified by flash chromatography.

Table 1. Products of the reactions of **2** and **5** in the presence of different Lewis and Brønsted acids[a]

Entry	Substrates	Acid	Overall yield [%]	Product(s)	Ratio
1	**2**+**5a**	$BF_3{\cdot}OEt_2$	73	**9a**+**12a**	38:35
2[b]	**2**+**5a**	$BF_3{\cdot}OEt_2$	72	**16a**	−
3	**2**+**5b**	$BF_3{\cdot}OEt_2$	80	**9b**+**12b**	52:28
4	**2**+**5c**	$BF_3{\cdot}OEt_2$	87	**9c**	−
5	**2**+**5d**	$BF_3{\cdot}OEt_2$	74	**9d**	−
6	**2**+**5e**	$BF_3{\cdot}OEt_2$	68	**9e**	−
7	**2**+**5f**	$BF_3{\cdot}OEt_2$	95	**9f**	−
8	**2**+**5g**	$BF_3{\cdot}OEt_2$	75	**9g**	−
9	**2**+**5h**	$BF_3{\cdot}OEt_2$	67	**12h**+**17**	65:2
10	**2**+**5i**	$BF_3{\cdot}OEt_2$	77	**9i**+**10i**+**12i**	28:14:35
11	**2**+**5i**	$SnCl_4$	65	**13i**	−
12	**2**+**5j**	$BF_3{\cdot}OEt_2$	70	**9j**+**10j**+**12j**	20:8:42
13	**2**+**5k**	$BF_3{\cdot}OEt_2$	93	**12k**	−
14	**2**+**5k**	$SnCl_4$	85	**13k**	−
15	**2**+**5k**	$ZnBr_2$	82	**14k**	−
16	**2**+**5k**	*p*TsOH	84	**15k**	−

[a] A ratio of **2/5** = 1:1 applies in all reactions except entry 2. − [b] A Ratio of **2a/5a** = 1:2.

Cyclization of 2 and Aniline: According to the General Procedure, compound **2** (298 mg, 1.00 mmol), aniline (**5a**, 0.093 mL, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) were allowed to react.

Quinoline Derivative 9a: The crude product was purified by column chromatography (silica gel, $CHCl_3$) to give 142 mg (38%) of pure **9a** as a light brown solid. − M.p. 210−213°C. − $[\alpha]_D$ = +143.8 (c = 1, $CHCl_3$); R_f (benzene) = 0.32. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (s, 3 H, 18-H_3), 1.15−1.97 (m, 15 H), 2.73−2.95 (m, 5 H, 6-H_2, 16a-H_2, 17-H), 3.77 (s, 3 H, 3-OMe), 6.59-6.69 and 6.96−7.03 (m, 3 H and m, 2 H, 4-H and d, 1 H, J = 2.6 Hz, 3′-H, 4′-H, 5′-H and 6′-H), 6.71 (dd, 1 H, J = 8.6 Hz, J = 2.6 Hz, 2-H), 7.21 (d, 1 H, J = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.3 (C-18), 26.2, 27.6, 28.1, 29.8, 35.6, 36.6, 37.3, 38.4, 42.3, 44.5, 51.7, 55.2 (3-OMe), 68.9 (C-17), 111.5 (C-2), 113.8 (C-4), 116.2, 118.1, 123.9 (C-2′), 126.2, 126.6, 130.4, 132.6 (C-10), 138.0 (C-5), 146.5 (C-1′), 157.4 (C-3). − MS (70 eV); m/z (%): 373 (97) [M^+], 298 (28), 257 (23), 144 (100), 130 (22). − $C_{26}H_{31}NO$ (373.54): calcd. C 83.60, H 8.36, N 3.75; found C 83.52, H 8.41, N 3.90.

D-Homosteroid 12a: The crude product was purified by column chromatography (silica gel, $CHCl_3$) to give 138 mg (35%) of pure **12a** as a yellowish solid. − M.p. 124−127°C. − $[\alpha]_D$ = +31.5 (c = 1, $CHCl_3$). − R_f (benzene) = 0.48. − ^{1}H NMR ($CDCl_3$): δ = 0.94 (s, 3 H, 18-H_3), 1.08−2.38 (m, 13 H), 2.86 (m, 2 H, 6-H_2), 3.10 (d, 1 H, J = 11.5 Hz, 17a-H), 3.41 (br. s, 1 H, N−H), 3.78 (s, 3 H, 3-OMe), 4.58 (doublet like multiplet, 1 H, J = 48.2 Hz, 16-H), 6.63 (m, 3 H, 4-H, 2′-H and 6′-H), 6.69 (m, 1 H, 4′-H), 6.72 (dd, 1 H, J = 8.6 Hz, J = 2.8 Hz, 2-H), 7.17 (m, 2 H, 3′-H and 5′-H), 7.20 (d, 1 H, J = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.0 (C-18), 26.0 (C-11), 26.7 (C-7), 30.1 (C-6), 30.3 (d, J = 17.9 Hz, C-15), 35.1 (d, J = 16.8 Hz, C-17), 37.9 (C-12), 38.3 (C-13), 38.6 (C-8), 43.7 (C-9), 45.9 (d, J = 10.5 Hz, C-14), 55.2 (3-OMe), 59.7 (d, J = 13.6 Hz, C-17a), 90.5 (d, J = 173.2 Hz, C-16) 111.7 (C-2), 113.3 (C-4), 113.5 (2 C, C-2′ and C-6′), 117.0 (C-4′), 126.3 (C-1), 129.4 (2 C, C-3′ and C-5′), 132.5 (C-10), 137.7 (C-5), 148.0 (C-1′), 157.6 (C-3). − MS (70 eV); m/z (%): 393 (74) [M^+], 227 (18), 106 (56), 78 (100). − $C_{26}H_{32}FNO$ (393.54): calcd. C 79.35, H 8.20, N 3.56; found C 79.48, H 8.15, N 3.45.

D-Homosteroid 16a: According to the General Procedure, **2** (298 mg, 1.00 mmol), aniline (**5a**, 0.186 mL, 2.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted. Purification of the crude product by column chromatography (silica gel, $CHCl_3$) afforded 336 mg (72%) of pure **16a** as a yellowish oil. − $[\alpha]_D$ = +35.3 (c = 1, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 0.91 (s, 3 H, 18-H_3), 0.92−2.39 (m, 13 H), 2.83 (m, 2 H, 6-H_2), 3.20 (dd, 1 H, J = 11.7 Hz, J = 3.7 Hz, 17a-H), 3.42 (m, 1 H, 16-H), 3.77 (s, 3 H, 3-OMe), 6.57−6.70 (m, 7 H, 2′-H, 2″-H, 4-H, 4′-H, 4″-H, 6′-H and 6″-H), 6.72 (dd, 1 H, J = 8.7 Hz, J = 2.6 Hz, 2-H), 7.10−7.26 (m, 5 H, 1-H, 3′-H, 3″-H, 5′-H and 5″-H). − ^{13}C NMR ($CDCl_3$): δ = 12.3 (C-18), 26.2 (C-11), 26.8 (C-7), 30.2 (C-6), 31.0 (C-15), 35.9, 38.2, 38.9, 39.0, 43.8 (C-9), 48.2 (C-14), 51.4 (C-16), 55.4 (3-OMe), 61.0 (C-17a), 111.8 (C-2), 113.3 (2 C) and 113.4 (2 C, C-2′, C-6′, C-2″ and C-6″), 113.6 (C-4), 117.2 and 117.6 (C-4′ and C-4″), 126.4 (C-1), 129.4 (2 C) and 129.5 (2 C, C-3′, C-5′, C-3″ and C-5″), 133.0 (C-10), 137.9 (C-5), 147.1 and 148.4 (C-1′ and C-1″), 157.7 (C-3). − $C_{32}H_{38}N_2O$ (466.66): calcd. C 82.36, H 8.21, N 6.00; found C 82.15, H 8.14, N 6.10.

Cyclization of 2 and *o*-Methylaniline: According to the General Procedure, **2** (298 mg, 1.00 mmol), *o*-methylaniline (**5b**, 0.107 mL, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted.

Quinoline Derivative 9b: Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) afforded 264 mg (68%) of pure **9b**. The yellowish solid obtained was recrystallized from acetone. − M.p. 176−179°C. − $[\alpha]_D$ = +157.9 (c = 1, $CHCl_3$). − R_f ($CHCl_3$) = 0.81. − ^{1}H NMR ($CDCl_3$): δ = 0.90 (s, 3 H, 18-H_3), 1.30−2.03 (m, 9 H), 2.12 (s, 3 H, 6′-CH_3), 2.18−2.42 (m, 3 H), 2.74−2.92 (m, 5 H, 6-H_2, 16a-H_2 and 17-H), 3.64 (br. s, 1 H, N−H), 3.77 (s, 3 H, 3-OMe), 6.61 (t, 1 H, J = 7.4 Hz, 4′-H), 6.63 (d, 1 H, J = 2.7 Hz, 4-H), 6.71 (dd, 1 H, J = 8.6 Hz, J = 2.7 Hz, 2-H), 6.90 (d, 2 H, J = 7.4 Hz, 3′-H and 5′-H), 7.21 (d, 1 H, J = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.3 (C-18), 17.5 (6′-CH_3), 26.2, 27.7, 28.0, 29.9 (C-6), 35.9, 36.5, 37.1, 38.5, 42.4 (C-13), 44.5 (C-9), 51.9, 55.2 (3-OMe), 69.1 (C-17), 111.5 (C-2), 113.9 (C-4), 117.5 (C-4′), 123.1 and 123.4 (C-2′ and C-6′), 126.2 (C-1), 127.9 and 128.2 (C-3′ and C-5′), 132.7 (C-10), 138.0 (C-5), 144.6 (C-1′), 157.5 (C-3). − MS (70 eV); m/z (%): 387 (84) [M^+], 159 (13), 158 (100), 144 (22). − $C_{27}H_{33}NO$ (387.57): calcd. C 83.68, H 8.58, N 3.61; found C 83.51, H 8.65, N 3.85.

D-Homosteroid 12b: The crude product was purified by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) to give 114 mg (28%) of pure **12b**. The white solid obtained was recrystallized from $CHCl_3$/PE. − M.p. 180−183°C. − $[\alpha]_D$ = +74.8 (c = 1, $CHCl_3$). − R_f ($CHCl_3$) = 0.87. − ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 3 H, 18-H_3), 1.09−2.14 (m, 9 H), 2.15 (s, 3 H, 2′-CH_3), 2.21−2.44 (m, 4 H), 2.88 (m, 2 H, 6-H_2), 3.19 (d, 1 H, J = 11.2 Hz, 17a-H), 3.35 (br. s, 1 H, N−H), 3.77 (s, 3 H, 3-OMe), 4.62 (d-like m, 1 H, J = 48.3 Hz, 16-H), 6.63 (t-like m, 1 H, 4′-H), 6.64 (d, 1 H, J = 2.6 Hz, 4-H), 6.67 (d-like m, 1 H, 6′-H), 6.71 (dd, 1 H, J = 8.6 Hz, J = 2.6 Hz, 2-H), 7.06 (d-like m, 1 H, 3′-H), 7.11 (t-like m, 1 H, 5′-H), 7.18 (d, 1 H, J = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.1 (C-18), 17.6 (2′-CH_3), 26.0 (C-11), 26.6 (C-7), 30.0 (C-6), 30.3 (d, J = 17.9 Hz, C-15), 35.2 (d, J = 16.8 Hz, C-17), 37.8 (C-12), 38.3 (C-13), 38.6 (C-8), 43.6 (C-9), 45.9 (d, J = 10.6 Hz, C-14), 55.2 (3-OMe), 59.2 (d, J = 12.6 Hz, C-17a), 90.5 (d, J = 173.1 Hz, C-16), 110.0 (C-6′), 111.7 (C-2), 113.4 (C-4), 116.6 (C-4′), 121.8 (C-2′), 126.2 (C-1), 127.2 (C-5′), 130.4 (C-3′), 132.4 (C-10), 137.6 (C-5), 145.6 (C-1′), 157.6 (C-3). − MS (70 eV); m/z (%): 407 (100%) [M^+], 227 (12), 120 (86), 118 (32). − $C_{27}H_{34}FNO$ (407.57): calcd. C 79.57, H 8.41, N 3.44; found C 79.65, H 8.52, N 3.25.

Quinoline Derivative 9c: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-methylaniline (**5c**, 107 mg, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted. Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) afforded 337 mg (87%) of **9c**. The yellowish solid obtained was recrystallized from acetone. − M.p. 194−197°C. − $[\alpha]_D$ = +150.2 (c = 1, $CHCl_3$). − R_f ($CHCl_3$) = 0.59. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (s, 3 H, 18-H_3), 1.31−2.06 (m, 9 H), 2.22 (s, 3 H, 4′-CH_3), 2.22−2.43 (m, 3 H), 2.71−2.94 (m, 5 H, 6-H_2, 16a-H_2 and 17-H), 3.77 (s, 3 H, 3-OMe), 6.63 (overlapping m and d, 2 H, J = 2.6 Hz, 6′-H and 4-H), 6.71 (dd, 1 H, J = 8.6 Hz, J = 2.6 Hz, 2-H), 6.82 (m, 2 H, 3′-H and 5′-H), 7.20 (d, 1 H, J = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.4 (C-18), 20.4 (4′-CH_3), 26.2, 27.6, 28.1, 29.8 (C-6), 35.6, 36.6, 37.3, 38.4, 42.3 (C-13), 44.4 (C-9), 51.7, 55.2 (3-OMe), 69.3 (C-17), 111.5 (C-2), 113.8 (C-4), 116.3 (C-6′), 123.9 and 127.3 (C-2′ and C-4′), 126.2 (C-1), 127.2 (C-5′), 130.8 (C-3′), 132.7 (C-10), 138.0 (C-5), 144.1 (C-1′), 157.4 (C-3). − MS (70 eV); m/z (%): 387 (77) [M^+], 159 (13), 158 (100), 144 (23). − $C_{27}H_{33}NO$ (387.57): calcd. C 83.68, H 8.58, N 3.61; found C 83.49, H 8.48, N 3.70.

Quinoline Derivative 9d: According to the General Procedure, **2** (298 mg, 1.00 mmol), *m*-methylaniline (**5d**, 0.108 mL, 1.00 mmol)

and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted. The crude product was purified by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) yielding 287 mg (74%) of pure **9d**. The yellowish solid obtained was recrystallized from acetone. − M.p. 187−190°C. − $[\alpha]_D$ = +115.7 (*c* = 1, $CHCl_3$). − R_f ($CHCl_3$) = 0.68. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (s, 3 H, 18-H_3), 1.20−1.96 (m, 9 H), 2.22 (s, 3 H, 5′-CH_3), 2.24−2.46 (m, 3 H), 2.71−2.92 (m, 5 H, 6-H_2, 16a-H_2 and 17-H), 3.77 (s, 3 H, 3-OMe), 6.45 (br. s, 1 H, 6′-H), 6.50 (d, 1 H, *J* = 7.8 Hz, 4′-H), 6.63 (d, 1 H, *J* = 2.6 Hz, 4-H), 6.71 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.6 Hz, 2-H), 6.89 (d, 1 H, *J* = 7.8 Hz, 3′-H), 7.20 (d, 1 H, *J* = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.3 (C-18), 21.0 (5′-CH_3), 26.2, 27.6, 28.1, 29.8 (C-6), 35.2, 36.6, 37.5, 38.4, 42.2 (C-13), 44.5 (C-9), 51.7, 55.2 (3-OMe), 69.0 (C-17), 111.5 (C-2), 113.7 (C-4), 116.7 (C-6′), 119.1 (C-4′), 120.9 (C-2′), 126.2 (C-1), 130.2 (C-3′), 132.7 (C-10), 136.3 (C-5′), 138.0 (C-5), 146.3 (C-1′), 157.4 (C-3). − MS (70 eV); *m*/*z* (%): 387 (77) [M^+], 159 (12), 158 (100), 144 (20). − $C_{27}H_{33}NO$ (387.57): calcd. C 83.68, H 8.58, N 3.61; found C 83.74, H 8.49, N 3.75.

Quinoline Derivative 9e: According to the General Procedure, **2** (298 mg, 1.00 mmol), *o*-anisidine (**5e**, 0.113 mL, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted. The crude product was chromatographed on column (silica gel, *tert*-butyl methyl ether/PE 5:95) yielding 274 mg (68%) of pure **9e** as a white solid. − M.p. 212−215°C. − $[\alpha]_D$ = +146.3 (*c* = 1, $CHCl_3$). − R_f ($CHCl_3$) = 0.65. − ^{1}H NMR ($CDCl_3$): δ = 0.91 (s, 3 H, 18-H_3), 1.24−2.39 (m, 12 H), 2.71 (d, 1 H, *J* = 10.2 Hz, 17-H), 2.72−2.91 (m, 4 H, 6-H_2 and 16a-H_2), 3.78 (s, 3 H, 3-OMe), 3.84 (s, 3 H, 6′-OMe), 4.29 (br. s, 1 H, N−H), 6.60−6.69 (m, 4 H, 4-H, 3′-H, 4′-H and 5′-H), 6.71 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.7 Hz, 2-H), 7.21 (d, 1 H, *J* = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.4 (C-18), 26.2, 27.7, 28.2, 29.9 (C-6), 35.5, 36.6, 37.2, 38.4, 42.3 (C-13), 44.5 (C-9), 51.8, 55.2 and 55.3 (3-OMe and 6′-OMe), 68.7 (C-17), 107.4 (C-5′), 111.5 (C-2), 113.8 (C-4), 117.1 (C-4′), 122.4 (C-3′), 124.0 (C-2′), 126.2 (C-1), 132.7 (C-10), 136.3 (C-1′), 138.0 (C-5), 147.5 (C-6′), 157.4 (C-3). − MS (70 eV); *m*/*z* (%): 403 (88) [M^+], 174 (100), 160 (30). − $C_{27}H_{33}NO_2$ (403.56): calcd. C 80.36, H 8.24, N 3.47; found C 80.47, H 8.39, N 3.62.

Quinoline Derivative 9f: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-anisidine (**5f**, 123 mg, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted. The crude product was purified by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) yielding 383 mg (95%) of **9f**. The white solid obtained was recrystallized from acetone. − M.p. 223−225°C. − $[\alpha]_D$ = +180.4 (*c* = 1, $CHCl_3$). − R_f ($CHCl_3$) = 0.30. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (s, 3 H, 18-H_3), 1.28−2.38 (m, 12 H), 2.71 (d, 1 H, *J* = 10.2 Hz, 17-H), 2.72−2.94 (m, 4 H, 6-H_2 and 16a-H_2), 3.64 (br. s, 1 H, N−H), 3.73 (s, 3 H, 4′-OMe), 3.78 (s, 3 H, 3-OMe), 6.60 (m, 3 H, 3′-H, 5′-H and 6′-H), 6.64 (d, 1 H, *J* = 2.6 Hz, 4-H), 6.72 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.6 Hz, 2-H), 7.21 (d, 1 H, *J* = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.5 (C-18), 26.4, 27.8, 28.3, 30.0 (C-6), 36.1 (C-16a), 36.8, 37.5, 38.6, 42.5 (C-13), 44.6 (C-9), 51.9, 55.4 and 55.9 (3-OMe and 4′-OMe), 69.7 (C-17), 111.6 (C-2), 113.0, 115.7 and 117.4 (C-3′, C-5′ and C-6′), 114.0 (C-4), 125.4 (C-2′), 126.4 (C-1), 132.9 (C-10), 138.2 (C-5), 140.6 (C-1′), 152.6 (C-4′), 157.6 (C-3). − MS (70 eV); *m*/*z* (%): 403 (100) [M^+], 175 (15), 174 (97), 160 (37). − $C_{27}H_{33}NO_2$ (403.56): calcd. C 80.36, H 8.24, N 3.47, found C 80.27, H 8.39, N 3.61.

Quinoline Derivative 9g: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-anisidine (**5g**, 0.112 mL, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted. Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) afforded 303 mg (75%) of pure **9g**. The white solid obtained was recrystallized from acetone. − M.p. 193−195°C. − $[\alpha]_D$ = 211.8 (*c* = 1, $CHCl_3$). − R_f ($CHCl_3$) = 0.40. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (s, 3 H, 18-H_3), 1.24−2.39 (m, 12 H), 2.66−2.89 (m, 5 H, 6-H_2, 16a-H_2 and 17-H), 3.74 (s, 3 H, 5′-OMe), 3.78 (s, 3 H, 3-OMe), 6.19 (d, 1 H, *J* = 2.3 Hz, 6′-H), 6.28 (dd, 1 H, *J* = 8.4 Hz, *J* = 2.3 Hz, 4′-H), 6.64 (d, 1 H, *J* = 2.6 Hz, 4-H), 6.72 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.6 Hz, 2-H), 6.90 (d, 1 H, *J* = 8.4 Hz, 3′-H), 7.21 (d, 1 H, *J* = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.3 (C-18), 26.2, 27.6, 28.0, 29.8 (C-6), 34.9, 36.6, 37.6, 38.4, 42.3 (C-13), 44.5 (C-9), 51.8, 55.2 (2 C, 3-OMe and 5′-OMe), 68.9 (C-17), 101.2 (C-6′), 104.4 (C-4′), 111.5 (C-2), 113.8 (C-4), 115.5 and 116.5 (C-1′ and C-2′), 126.2 (C-1), 130.9 (C-3′), 132.6 (C-10), 138.0 (C-5), 157.4 (C-3), 158.7 (C-5′). − MS (70 eV); *m*/*z* (%): 403 (100) [M^+], 174 (78), 160 (24). − $C_{27}H_{33}NO_2$ (403.56): calcd. C 80.36, H 8.24, N 3.47; found C 80.12, H 8.37, N 3.61.

Cyclization of 2 and o-Bromoaniline: According to the General Procedure, **2** (298 mg, 1.00 mmol), *o*-bromoaniline (**5h**, 172 mg, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted.

D-Homosteroid 12h: Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5: 95) afforded 307 mg (65%) of pure **12h** as a white solid. − M.p. 142−144°C. − $[\alpha]_D$ = +75.7 (*c* = 1, $CHCl_3$). − R_f (benzene) = 0.63. − ^{1}H NMR ($CDCl_3$): δ = 1.00 (s, 3 H, 18-H_3), 1.05−2.39 (m, 13 H), 2.87 (m, 2 H, 6-H_2), 3.15 (m, 1 H, 17a-H), 3.77 (s, 3 H, 3-OMe), 4.26 (m, 1 H, N−H), 4.58 (doublet like multiplet, 1 H, *J* = 48.4 Hz, 16-H), 6.54 (t like m, 1 H, 4′-H), 6.63 (d, 1 H, *J* = 2.5 Hz, 4-H), 6.69 (d like m, 1 H, 6′-H), 6.72 (dd, 1 H, *J* = 8.7 Hz, *J* = 2.5 Hz, 2-H), 7.16 (t like m, 1 H, 5′-H), 7.18 (d, 1 H, *J* = 8.7 Hz, 1-H), 7.41 (m, 1 H, 3′-H). − ^{13}C NMR ($CDCl_3$): δ = 12.1 (C-18), 26.0 (C-11), 26.6 (C-7), 30.0 (C-6), 30.3 (d, *J* = 17.8 Hz, C-15), 35.0 (d, *J* = 17.9 Hz, C-17), 37.8 (C-12), 38.4 (C-13), 38.6 (C-8), 43.6 (C-9), 46.0 (d, *J* = 10.4 Hz, C-14), 55.2 (3-OMe), 59.8 (d, *J* = 12.9 Hz, C-17a), 90.3 (d, *J* = 174.0 Hz, C-16), 110.2 (C-2′), 111.7 (C-2), 113.4 (C-4), 117.3 and 117.6 (C-4′ and C-6′), 126.2 (C-1), 128.4 (C-5′), 132.3 (C-10), 132.6 (C-3′), 137.6 (C-5), 144.5 (C-1′), 157.6 (C-3). − MS (70 eV); *m*/*z* (%): 473 (100) [M^+], 471 (98), 227 (75), 186 (86), 184 (97), 174 (43), 147 (38), 118 (35), 91 (31). − $C_{26}H_{31}BrFNO$ (472.44): calcd. C 66.10, H 6.61, N 2.96; found C 65.96, H 6.75, N 3.05.

Unsaturated D-Homosteroid 17: Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5: 95) afforded 9 mg (2%) of pure **17** as a white solid. R_f (benzene) = 0.70. − ^{1}H NMR ($CDCl_3$): δ = 0.97 (s, 3 H, 18-H_3, 2.86 (m, 2 H, 6-H_2), 3.77 (s, 3 H, 3-OMe), 3.85 (d, 1 H, *J* = 9.5 Hz, 17a-H), 4.59 (d, 1 H, *J* = 9.5 Hz, NH), 5.44 (d. 1 H, *J* = 10.4 Hz, 17-H), 5.81 (m, 1 H, 16-H), 6.54 (t, 1 H, *J* = 7.7 Hz, 4′-H), 6.63 (d, 1 H, *J* = 2.5 Hz, 4-H), 6.72 (m, 2 H, 2-H and 6′-H), 7.14−7.24 (m, 2 H, 1-H and 5′-H), 7.42 (d, 1 H, *J* = 7.7 Hz, 3′-H). ^{13}C NMR ($CDCl_3$): δ = 12.2 (C-18), 26.2 (2 C), 27.2, 30.2, 37.1 (C-13), 38.3, 40.1, 43.0, 45.3, 55.2 (3-OMe), 61.3 (C-17a), 111.6 (C-2), 112.1 (C-2′), 113.5 (C-4), 115.6, 117.4, 126.3 (C-1), 128.0, 128.3, 128.4 (2 C), 132.6 (C-3′), 137.8 (C-10), 144.9 (C-5), 157.5 (C-3). − MS (70 eV), *m*/*z* (%): 453 (24) and 451 (23): [M^+], 225 (98), 223 (100), 144 (27). − $C_{26}H_{30}BrNO$ (452.44): calcd. C 69.01, H 6.68, N 3.10; found C 69.21, H 6.57, N 3.45.

Cyclization of 2 and *p*-Bromoaniline: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-bromoaniline (**5i**, 172 mg, 1.00

mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted.

Quinoline Derivative 9i: The crude product was purified by column chromatography (silica gel, PE/benzene 25:75) to give 127 mg (28%) of pure **9i** as a white solid. − M.p. 233−235°C. − $[\alpha]_D$ = +125.1 (c = 1, $CHCl_3$). − R_f (benzene) = 0.42. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (s, 3 H, 18-H_3), 1.22−2.48 (m, 14 H), 2.72 (d, 1 H, J = 10.0 Hz, 17-H), 2.86 (m, 2 H, 6-H_2), 3.78 (s, 3 H, 3-OMe), 3.87 (br. s, 1 H, N−H), 6.49 (d, 1 H, J = 8.3 Hz, 5′-H), 6.64 (d, 1 H, J = 2.8 Hz, 4-H), 6.72 (dd, 1 H, J = 8.5 Hz, J = 2.8 Hz, 2-H), 7.06 (dd, 1 H, J = 8.3 Hz, J = 2.3 Hz, 6′-H), 7.11 (d, 1 H, J = 2.3 Hz, 3′-H), 7.21 (d, 1 H, J = 8.5 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.3 (C-18), 26.2, 27.6, 27.9, 29.8, 35.4, 36.5, 37.0, 38.4, 42.2, 44.5, 51.8, 55.2 (3-OMe), 68.8 (C-17), 109.7 (C-4), 111.5 (C-2), 113.8 (C-4), 117.6 (C-6′), 126.0 (C-2′), 126.2 (C-1), 129.3 (C-5′), 132.6 (C-10), 132.8 (C-3′), 138.0 (C-5), 145.7 (C-1′), 157.5 (C-3). − MS (70 eV); *m*/*z* (%): 453 (70) [M^+], 451 (68), 224 (98), 222 (100), 210 (23), 208 (23), 44 (33). − $C_{26}H_{30}BrNO$ (452.43): calcd. C 69.02, H 6.68, N 3.10; found C 69.30, H 6.52, N 3.37.

Bridged Steroid Alkaloid Analogue 10i: The crude product was purified by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) to give 63 mg (14%) of pure **10i**. The yellowish solid obtained was recrystallized from acetone. − M.p. 108−110°C. − $[\alpha]_D$ = +369.0 (c = 1, $CHCl_3$). − R_f (benzene) = 0.82. − ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 3 H, 18-H_3), 1.22−2.53 (m, 10 H), 2.83 (m, 2 H, 6-H_2), 2.87 and 3.48 (dd, 1 H, J = 9.5 Hz, J = 3.0 Hz and d, 1 H, J = 9.5 Hz, N−CH_2), 3.77 (s, 3 H, 3-OMe), 5.00 (d, 1 H, J = 10.0 Hz, 16a-H_2, H_{cis}), 5.07 (d, 1 H, J = 17.0 Hz, 16a-H_2, H_{trans}), 5.91 (m, 1 H, 16-H), 6.13 (d, 2 H, J = 9.0 Hz, 2′-H and 6′-H), 6.54 (dd, 1 H, J = 8.6 Hz, J = 2.7 Hz, 2-H), 6.64 (d, 1 H, J = 2.7 Hz, 4-H), 6.83 (d, 1 H, J = 8.6 Hz, 1-H), 6.92 (d, 2 H, J = 9.0 Hz, 3′-H and 5′-H). − ^{13}C NMR ($CDCl_3$): δ = 23.6 (C-18), 25.7, 28.5, 30.3, 34.4, 35.0, 35.6, 46.4, 47.5, 55.1 (3-OMe), 57.9 (C-9), 61.4 (N−CH_2), 108.9 (C-4′), 112.2 (C-2), 113.4 (C-4), 115.4 (C-16a), 119.2 (2 C, C-2′ and C-6′), 130.1 (C-1), 130.2 (2 C, C-3′ and C-5′), 130.9 (C-10), 138.5 (C-16), 138.8 (C-5), 147.9 (C-1′), 158.3 (C-3). − MS (70 eV); *m*/*z* (%): 453 (49) [M^+], 451 (50), 412 (97), 410 (100), 225 (45), 212 (53), 186 (43), 184 (49), 44 (52). − $C_{26}H_{30}BrNO$ (452.43): calcd. C 69.02, H 6.68, N 3.10; found C 68.95, H 6.71, N 3.25.

D-Homosteroid 12i: Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) afforded 165 mg (35%) of pure **12i** as a white solid. − M.p. 170−171°C. − $[\alpha]_D$ = +1.3 (c = 1, $CHCl_3$). − R_f (benzene) = 0.55. − ^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 3 H, 18-H_3), 1.02−2.38 (m, 13 H), 2.87 (m, 2 H, 6-H_2), 3.04 (d, 1 H, J = 11.5 Hz, 17a-H), 3.45 (br. s, 1 H, N−H), 3.78 (s, 3 H, 3-OMe), 4.57 (doublet like multiplet, 1 H, J = 47.2 Hz, 16-H), 6.51 (d, 2 H, J = 7.8 Hz, 2′-H and 6′-H), 6.64 (d, 1 H, J = 2.7 Hz, 4-H), 6.72 (dd, 1 H, J = 8.5 Hz, J = 2.7 Hz, 2-H), 7.19 (d, 1 H, J = 8.5 Hz, 1-H), 7.23 (d, 2 H, J = 7.8 Hz, 3′-H and 5′-H). − ^{13}C NMR ($CDCl_3$): δ = 12.0 (C-18), 25.9 (C-11), 26.6 (C-7), 30.0 (C-6), 30.2 (d, J = 17.6 Hz, C-15), 35.0 (d, J = 16.8 Hz, C-17), 37.9 (C-12), 38.3 (C-13), 38.6 (C-8), 43.6 (C-9), 45.8 (d, J = 10.9 Hz, C-14), 55.2 (3-OMe), 59.8 (d, J = 13.4 Hz, C-17a), 90.4 (d, J = 174.4 Hz, C-16), 108.6 (C-4′), 111.7 (C-2), 113.4 (C-4), 114.7 (2 C, C-3′ and C-6′), 126.2 (C-1), 132.0 (2 C, C-3′ and C-5′), 132.4 (C-10), 137.6 (C-5), 146.9 (C-1′), 157.6 (C-3). − MS (70 eV); *m*/*z* (%): 473 (100) [M^+], 471 (98), 453 (4) [M^+-HF], 268 (15), 227 (65), 186 (62), 184 (66), 174 (18). − $C_{26}H_{31}BrFNO$ (472.44): calcd. C 66.10, H 6.61, N 2.96; found C 66.23, H 6.85, N 3.05.

D-Homosteroid 13i: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-bromoaniline (**5i**, 172 mg, 1.00 mmol) and $SnCl_4$ (261 mg, 1.00 mmol) was reacted. The crude product was purified by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) to give 318 mg (65%) of **13i** as a white solid. − M.p. 211−214°C. − $[\alpha]_D$ = +75.2 (c = 1, $CHCl_3$). − R_f (benzene) = 0.66. − ^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 3 H, 18-H_3), 1.11−2.40 (m, 13 H), 2.85 (m, 2 H, 6-H_2), 3.03 (dd, 1 H, J = 11.5 Hz, J = 2.6 Hz, 17a-H), 3.55 (br. s, 1 H, N−H), 3.77 (s, 3 H, 3-OMe), 3.92 (m, 1 H, 16-H), 6.50 (d, 2 H, J = 8.6 Hz, 2′-H and 6′-H), 6.63 (d, 1 H, J = 2.6 Hz, 4-H), 6.71 (dd, 1 H, J = 8.6 Hz, J = 2.6 Hz, 2-H), 7.18 (d, 1 H, J = 8.6 Hz, 1-H), 7.22 (d, 2 H, J = 8.6 Hz, 3′-H and 5′-H). − ^{13}C NMR ($CDCl_3$): δ = 12.1 (C-18), 26.0, 26.7, 30.1, 34.7, 37.9, 38.2, 38.7 (C-8), 39.1, 43.6 (C-9), 48.9 (C-14), 55.3 (3-OMe), 57.1 (C-16), 61.6 (C-17a), 108.8 (C-4′), 111.8 (C-2), 113.5 (C-4), 114.9 (2 C, C-2′ and C-6′), 126.3 (C-1), 132.1 (2 C, C-3′ and C-5′), 132.5 (C-10), 137.7 (C-5), 147.0 (C-1′), 157.7 (C-3). − MS (70 eV); *m*/*z* (%): 489 (8) [M^+], 487 (5), 453 (21), 451 (19), 280 (24), 243 (100), 179 (76), 165 (29), 91 (32), 73 (42), 44 (57). − $C_{26}H_{31}BrClNO$ (488.89): calcd. C 63.88, H 6.39, N 2.86; found C 64.02, H 6.27, N 2.95.

Cyclization of 2 and *m*-Bromoaniline: According to the General Procedure, **2** (298 mg, 1.00 mmol), *m*-bromoaniline (**5j**, 0.108 mL, 1.00 mmol) and $BF_3{\cdot}OEt_2$ (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted.

Quinoline Derivative 9j: Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) afforded 90 mg (20%) of pure **9j** as a white solid. − M.p. 198−200°C. − R_f (*tert*-butyl methyl ether/PE 10:90) = 0.51. − ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3 H, 18-H_3), 1.15−2.43 (m, 12 H), 2.62−2.97 (m, 5 H, 6-H_2, 17-H and two others), 3.78 (s, 3 H, 3-OMe), 3.92 (br. s, 1 H, N−H), 6.64 (d, 1 H, J = 2.6 Hz, 4-H), 6.72 (dd, 1 H, J = 8.5 Hz, J = 2.6 Hz, 2-H), 6.74−6.80 (m, 2 H, 4′-H and 6′-H), 6.84 (d, 1 H, J = 8.5 Hz, 3′-H), 7.21 (d, 1 H, J = 8.5 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.3 (C-18), 26.2, 27.6, 27.9, 29.8, 35.1, 36.5, 37.1, 38.4, 42.2 (C-13), 44.5 (C-9), 51.8, 55.2 (3-OMe), 68.5 (C-17), 111.5 (C-2), 113.9 (C-4), 118.5 (C-6′), 119.9, 120.7 (C-4′), 122.7, 126.2 (C-1), 131.6 (C-3′), 132.6 (C-10), 137.9 (C-5), 147.9 (C-1′), 157.5 (C-3). − MS (70 eV); *m*/*z* (%): 453 (83) [M^+], 451 (81), 373 (11), 224 (98), 222 (100), 210 (22), 208 (21). − $C_{26}H_{30}BrNO$ (452.43): calcd. C 69.02, H 6.68, N 3.10; found C 68.95, H 6.72, N 3.31.

Bridged Steroid Alkaloid Analogue 10j: Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) afforded 36 mg (8%) of pure **10j** as a yellow oil. − R_f (*tert*-butyl methyl ether/PE 10:90) = 0.60. − ^{1}H NMR ($CDCl_3$): δ = 0.96 (s, 3 H, 18-H_3), 1.17−2.57 (m, 10 H), 2.85 (m, 2 H, 6-H_2), 2.89 (dd, 1 H, J = 9.5 Hz, J = 2.9 Hz) and 3.48 (d, 1 H, J = 9.5 Hz, N−CH_2), 3.77 (s, 3 H, 3-OMe), 4.99 (d, 1 H, J = 9.9 Hz, 16a-H_2, H_{cis}), 5.07 (d, 1 H, J = 16.7 Hz, 16a-H_2, H_{trans}), 5.90 (m, 1 H, 16-H), 6.02 (m, 1 H), 6.46 (s, 1 H) and 6.62 (m, 2 H, 2′-H, 4′-H, 5′-H and 6′-H), 6.56 (dd, 1 H, J = 8.7 Hz, J = 2.6 Hz, 2-H), 6.65 (d, 1 H, J = 2.6 Hz, 4-H), 6.86 (d, 1 H, J = 8.7 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 23.6 (C-18), 25.8, 28.4, 30.3, 34.4, 35.0, 35.7, 46.4, 47.5, 55.2 (3-OMe), 58.2 (C-9), 61.3 (N−CH_2), 112.2 (C-2), 113.5 (C-4), 115.5 (C-16a), 116.1, 119.3 and 119.8 (C-2′, C-4′ and C-6′), 121.9 (C-3′), 128.4 (C-5′), 130.0 (C-1), 130.8 (C-10), 138.5 (C-16), 138.8 (C-5), 150.2 (C-1′), 158.5 (C-3). − MS (70 eV); *m*/*z* (%): 453 (35) [M^+], 451 (34), 412 (98), 410 (100), 280 (19), 239 (18), 225 (33), 186 (28), 184 (33). − $C_{26}H_{30}BrNO$ (452.43): calcd. C 69.02, H 6.68, N 3.10; found C 69.15, H 6.72, N 3.35.

D-Homosteroid 12j: The crude product was purified by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) to give 198 mg (42%) of pure **12j**. The white solid was recrystallized from

acetone. − M.p. 214−215°C. − $[\alpha]_D$ = +16.2 (*c* = 1, $CHCl_3$). − R_f (*tert*-butyl methyl ether/PE 10:90) = 0.28 − ^{1}H NMR ($CDCl_3$): δ = 0.91 (s, 3 H, 18-H_3), 1.06−2.39 (m, 13 H), 2.87 (m, 2 H, 6-H_2), 3.05 (m, 1 H, 17a-H), 3.51 (m, 1 H, N−H), 3.77 (s, 3 H, 3-OMe), 4.58 (doublet like multiplet, 1 H, *J* = 48.4 Hz, 16-H), 6.52 (dd like m, 1 H, 6′-H), 6.63 (d, 1 H, *J* = 2.7 Hz, 4-H), 6.71 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.7 Hz, 2-H), 6.76 (t like m, 1 H, 2′-H), 6.78 (d like m, 1 H, 4′-H), 7.00 (t like m, 1 H, 5′-H), 7.19 (d, 1 H, *J* = 8.6 Hz, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 12.0 (C-18), 25.9 (C-11), 26.6 (C-7), 30.0 (C-6), 30.2 (d, *J* = 18.4 Hz, C-15), 35.0 (d, *J* = 17.1 Hz, C-17), 37.8 (C-12), 38.3 (C-13), 38.6 (C-8), 43.6 (C-9), 45.8 (d, *J* = 10.7 Hz, C-14), 55.2 (3-OMe), 59.5 (d, *J* = 12.4 Hz, C-17a), 90.3 (d, *J* = 173.4 Hz, C-16), 111.7 (C-2), 111.9 (C-6′), 113.4 (C-4), 115.5 (C-2′), 120.0 (C-4′), 123.4 (C-3′), 126.2 (C-1), 130.6 (C-5′), 132.3 (C-10), 137.6 (C-5), 149.2 (C-1′), 157.6 (C-3). − MS (70 eV); *m*/*z* (%): 473 (100) [M^+], 471 (98), 453 (37) [M^+−HF], 451 (38), 227 (95), 225 (79), 186 (83), 184 (94), 91 (75). − $C_{26}H_{31}BrFNO$ (472.44): calcd. C 66.10, H 6.61, N 2.96; found C 66.25, H 6.51, N 3.05.

D-Homosteroid 12k: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-nitroaniline (**5k**, 138 mg, 1.00 mmol) and $SnCl_4$ (261 mg, 1.00 mmol) was reacted. Purification of the crude product by column chromatography (silica gel, *tert*-butyl methyl ether/PE 5:95) afforded 408 mg (93%) of pure **12k**. The orange solid obtained was recrystallized from acetone. − M.p. 240−243°C. − $[\alpha]_D$ = −91.2 (*c* = 1, $CHCl_3$). − R_f (EtOAc/$CHCl_3$ 3:97) = 0.53 . − ^{1}H NMR ($CDCl_3$): δ = 0.97 (s, 3 H, 18-H_3), 1.10−2.40 (m, 13 H), 2.88 (m, 2 H, 6-H_2), 3.27 (m, 1 H, 17a-H), 3.78 (s, 3 H, 3-OMe), 4.32 (d, 1 H, *J* = 9.7 Hz, N−H), 4.63 (doublet like multiplet, 1 H, *J* = 48.3 Hz, 16-H), 6.58 (d, 2 H, *J* = 9.2 Hz, 2′-H and 6′-H), 6.64 (d, 1 H, *J* = 2.7 Hz, 4-H), 6.72 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.7 Hz, 2-H), 7.18 (d, 1 H, *J* = 8.6 Hz, 1-H), 8.09 (d, 2 H, *J* = 9.2 Hz, 3′-H and 5′-H). − ^{13}C NMR ($CDCl_3$): δ = 12.0 (C-18), 25.8 (C-11), 26.6 (C-7), 30.0 (C-6), 30.1 (d, *J* = 18.0 Hz, C-15), 34.8 (d, *J* = 18.0 Hz, C-17), 37.8 (C-12), 38.5 (C-13), 38.6 (C-8), 43.5 (C-9), 45.7 (d, *J* = 10.5 Hz, C-14), 55.2 (3-OMe), 59.0 (d, *J* = 13.1 Hz, C-17a), 89.9 (d, *J* = 174.0 Hz, C-16), 111.3 (2 C, C-2′ and C-6′), 111.7 (C-2), 113.5 (C-4), 126.2 (C-1), 126.6 (2 C, C-3′ and C-5′), 132.0 (C-10), 137.5 (C-5), 138.0 (C-4′), 152.9 (C-1′), 157.7 (C-3). − MS (70 eV); *m*/*z* (%): 438 (100) [M^+], 418 (44) [M^+-HF], 228 (35), 227 (82), 190 (63), 151 (36), 147 (28), 91 (22). − $C_{26}H_{31}FN_2O_3$ (438.54): calcd. C 71.21, H 7.13, N 6.39; found C 71.05, H 7.27, N 6.51.

D-Homosteroid 13k: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-nitroaniline (**5k**, 138 mg, 1.00 mmol) and BF_3·OEt_2 (48% solution in diethyl ether, 0.29 mL, 1.00 mmol) was reacted. The crude product was purified by column chromatography (silica gel, benzene) to give 387 mg (85%) of pure **13k**. The orange solid obtained was recrystallized from acetone. − M.p. 239−241°C. − $[\alpha]_D$ = +20.7 (*c* = 1, $CHCl_3$). − R_f (EtOAc/$CHCl_3$ 3:97) = 0.57. − ^{1}H NMR ($CDCl_3$): δ = 0.97 (s, 3 H, 18-H_3), 1.16−2.43 (m 13 H), 2.87 (m, 2 H, 6-H_2), 3.27 (m, 1 H, 17a-H), 3.78 (s, 3 H, 3-OMe), 3.97 (m, 1 H, 16-H), 4.32 (d, 1 H, *J* = 9.8 Hz, N−H), 6.57 (d, 2 H, *J* = 9.1 Hz, 2′-H and 6′-H), 6.63 (d, 1 H, *J* = 2.5 Hz, 4-H), 6.71 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.5 Hz, 2-H), 7.17 (d, 1 H, *J* = 8.6 Hz, 1-H), 8.08 (d, 2 H, *J* = 9.1 Hz, 3′-H and 5′-H). − ^{13}C NMR ($CDCl_3$): δ = 12.1 (C-18), 25.8 (C-11), 26.6 (C-7), 29.9 (C-6), 34.5, 37.8, 38.3, 38.6 (C-8), 38.8, 43.4 (C-9), 48.6 (C-14), 55.2 (3-OMe), 56.3 (C-16), 60.7 (C-17a), 111.3 (2 C, C-2′ and C-6′), 111.7 (C-2), 113.5 (C-4), 126.2 (C-1), 126.6 (2 C, C-3′ and C-5′), 132.0 (C-10), 137.5 (C-5), 138.0 (C-4′), 152.8 (C-1′), 157.7 (C-3). − MS (70 eV); *m*/*z* (%): 456 (37), 454 (100), 418 (86), 401 (44), 227 (42), 225 (86), 190 (52), 151 (34). − $C_{26}H_{31}ClN_2O_3$ (455.00): calcd. C 68.63, H 6.87, N 6.16; found C 68.92, H 6.68, N 6.28.

D-Homosteroid 14k: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-nitroaniline (**5k**, 138 mg, 1.00 mmol) and $ZnBr_2$ (225 mg, 1.00 mmol) was reacted. The crude product was purified by column chromatography (silica gel, $CHCl_3$) to give 410 mg (82%) of pure **14k**. The yellow solid obtained was recrystallized from MeOH/$CHCl_3$. − M.p. 206−209°C. − $[\alpha]_D$ = +114.0 (*c* = 1, $CHCl_3$). − R_f (EtOAc/$CHCl_3$ 3:97) = 0.58. − ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 3 H, 18-H_3), 1.17−2.52 (m, 13 H), 2.86 (m, 2 H, 6-H_2), 3.26 (m, 1 H, 17a-H), 3.77 (s, 3 H, 3-OMe), 4.08 (m, 1 H, 16-H), 4.35 (d, 1 H, *J* = 9.7 Hz, N−H), 6.56 (d, 2 H, *J* = 9.2 Hz, 2′-H and 6′-H), 6.63 (d, 1 H, *J* = 2.6 Hz, 4-H), 6.71 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.6 Hz, 2-H), 7.16 (d, 1 H, *J* = 8.6 Hz, 1-H), 8.07 (d, 2 H, *J* = 9.2 Hz, 3′-H and 5′-H). − ^{13}C NMR ($CDCl_3$): δ = 12.1 (C-18), 25.7 (C-11), 26.5 (C-7), 29.9 (C-6), 35.4, 37.8, 38.3, 38.6, 39.6, 43.4 (C-9), 47.3 and 49.7 (C-14 and C-16), 55.2 (3-OMe), 61.3 (C-17a), 111.3 (2 C, C-2′ and C-6′), 111.7 (C-2), 113.4 (C-4), 126.1 (C-1), 126.5 (2 C, C-3′ and C-5′), 132.0 (C-10), 137.5 (C-5), 138.0 (C-4′), 152.9 (C-1′), 157.6 (C-3). − MS (70 eV); *m*/*z* (%): 500 (38) [M^+], 498 (38), 419 (100), 280 (18), 225 (16), 151 (22), 147 (15). − $C_{26}H_{31}BrN_2O_3$ (499.45): calcd. C 62.53, H 6.26, N 5.61; found C 62.71, H 6.15, N 5.79.

D-Homosteroid 15k: According to the General Procedure, **2** (298 mg, 1.00 mmol), *p*-nitroaniline (**5k**, 138 mg, 1.00 mmol) and *p*-TsOH·H_2O (190 mg, 1.00 mmol) was reacted. Purification of the crude product by column chromatography (silica gel, EtOAc/benzene 5:95) afforded 496 mg (84%) of **15k**. The yellow solid obtained was recrystallized from *tert*-butyl methyl ether/PE. − M.p. 170−171°C. − $[\alpha]_D$ = +28.9 (*c* = 1, $CHCl_3$). − R_f (EtOAc/$CHCl_3$ 3:97) = 0.37. − ^{1}H NMR ($CDCl_3$): δ = 0.91 (s, 3 H, 18-H_3), 1.06−2.32 (m, 13 H), 2.45 (s, 3 H, 4′-CH_3), 2.83 (m, 2 H, 6-H_2), 3.22 (m, 1 H, 17a-H), 3.77 (s, 3 H, 3-OMe), 4.31 (d, 1 H, *J* = 9.7 Hz, N−H), 4.55 (m, 1 H, 16-H), 6.49 (d, 2 H, *J* = 9.1 Hz, 2″-H and 6″-H), 6.62 (d, 1 H, *J* = 2.6 Hz, 4-H), 6.70 (dd, 1 H, *J* = 8.6 Hz, *J* = 2.6 Hz, 2-H), 7.14 (d, 1 H, *J* = 8.6 Hz, 1-H), 7.35 (d, 2 H, *J* = 8.1 Hz, 3′-H and 5′-H), 7.81 (d, 2 H, *J* = 8.2 Hz, 2′-H and 6′-H), 8.05 (d, 2 H, *J* = 9.1 Hz, 3″-H and 5″-H). − ^{13}C NMR ($CDCl_3$): δ = 11.9 (C-18), 21.7 (tosyl−CH_3), 25.7, 26.5, 29.9, 30.0, 34.3, 37.6, 38.3, 38.5 (C-8), 43.3 (C-9), 46.3 (C-14), 55.2 (3-OMe), 59.2 (C-17a), 78.9 (C-16), 111.3 (2 C, C-2′′ and C-6″), 111.7 (C-2), 113.4 (C-4), 126.1 (C-1), 126.5 (2 C, C-3″ and C-5″), 127.6 (2 C, C-2′ and C-6′), 129.9 (2 C, C-3′ and C-5′), 131.9 (C-10), 134.2 (C-4′), 137.5 (C-5), 137.9 (C-4″), 144.9 (C-1′), 152.8 (C-1″), 157.7 (C-3). − MS (70 eV); *m*/*z* (%): 418 (100), 228 (33), 190 (100), 151 (22), 91 (22). − $C_{33}H_{38}N_2O_6S$ (590.73): calcd. C 67.10, H 6.48, N 4.74; found C 67.25, H 6.37, N 4.85.

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