New approach to indole alkaloids based on the intramolecular Pauson-Khand reaction¹

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General:

General experimental data and procedures have been previously reported. For purification of crude reaction mixtures flash chromatography was applied in all cases. Silica-gel (230-400 mesh) and basic alumina were used as the stationary phases.

3-Trimethylsilylethynyl-1*H*-indole-2-carbaldehyde, 26. In 50 mL of Et₃N, 4.29 g (15.86 mmol) of indole-2-carbaldehyde were dissolved. Then 0.22 g (0.31 mmol) of Pd(PPh₃)₂Cl₂, 2.68 mL (19.03 mmol) of trimethylsilylacetylene and 0.15 g (0.79 mmol) of Koper (I) iodide were added, and the mixture was stirred at 70°C until completion (t.l.c.). The mixture is then cooled, and the residue is solved in 50 mL of toluene and filtrated through celite. Evaporation of the solvent and purification of the crude by column chromatography (hexane/AcOEt 9:1) gave, 3.44 g (90%) of **26** as a yellow solid. m.p.: 182-183°C (hexane/AcOEt). ¹H-NMR (CDCl₃) 0.32 (s, 9H), 7.22-7.28 (m, 1H), 7.42 (d, 2H, J= 3.4 Hz), 7.84 (d, 1H, J= 8.2 Hz), 9.02 (s, 1H), 10.07 (s, 1H). ¹³C-NMR (CDCl₃) 181.1, 136.7, 128.7, 128.1, 122.2, 121.8, 112.6, 122.5, 109.7, 102.7, 95.1, -0.01. IR (KBr) 3300, 2150, 1650, 1470. Anal. Calcd. for C₁₄H₁₅NOSi: C. 69.67; H. 6.26; N. 5.80. Found: C. 69.53; H. 5.99, N. 5.69.

General Procedure for the reaction of indolecarbaldehydes with Grignard reagents:

Vinylmagnesium bromide or allylmagnesium bromide 1M/THF (1.2 mmol) was added dropwise to a stirred solution of the corresponding aldehyde (1.0 mmol) in dry THF (5 mL) at -78°C. After 3h, saturated aqueous ammonium chloride (5 mL) was added. The organic layer was separated and the aqueous phase extracted with ether (3 x 5 mL). The combination of the organic phases was dried (MgSO₄) and the solvent evaporated under vacuum. The crude was purified by flash chromatography (hexane/EtOAc mixtures) to obtain the corresponding alcohol.

1-[1-(2-Propynyl)-1*H*-indol-2-yl]-2-propen-1-ol, 3. Following the general procedure, from 0.6 g (3.28 mmol) of 1-(2-propynyl)-1*H*-indole-2-carbaldehyde and 3.9 mL (3.94 mmol) of vinylmagnesium bromide, and after purification by flash chromatography (hexane/EtOAc 9:1), 0.7 g (90%) of **3** were obtained as a yellow oil. ¹H-NMR (CDCl₃) 2.04 (d, 1H, J= 5.5 Hz), 2.27 (t, 1H, J= 2.7 Hz), 5.02 (dd,

1H, $J_1 = 18.1$ Hz, $J_2 = 2.7$ Hz), 5.08 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 2.7$ Hz), 5.35-5.52 (m, 3H), 6.21-6.33 (m, 1H), 6.44 (s, 1H), 7.13 (t, 1H, $J = 7.7$ Hz), 7.26 (t, 1H, $J = 8.2$ Hz), 7.42 (d, 1H, $J = 8.2$ Hz), 7.58 (d, 1H, $J = 7.7$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) 139.0, 137.3, 137.2, 127.3, 122.4, 121.0, 120.1, 116.3, 109.4, 101.7, 78.6, 72.3, 68.0, 33.1. IR (neat) 3510, 3280, 3040, 2240, 1640, 1610. Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{NO}$: C. 79.59; H. 6.20; N. 6.63. Found: C. 79.43; H. 5.92, N. 6.74.

1-[1-(2-Propynyl)-1H-indol-2-yl]-3-buten-1-ol, 8. Following the general procedure, from 0.4 g (2.18 mmol) of 1-(2-propynyl)-1H-indole-2-carbaldehyde and 2.62 mL (2.62 mmol) of allylmagnesium bromide, and after purification by flash chromatography (hexane/EtOAc 9:1), 0.5 g (quantitative) of **8** were obtained as a white solid. m.p.: 72-74°C (hexane/EtOAc). $^1\text{H-NMR}$ (CDCl_3) 2.26 (d, 1H, $J = 2.2$ Hz), 2.27 (t, 1H, $J = 2.7$ Hz), 2.72-2.89 (m, 2H), 4.95-5.01 (m, 1H), 5.05 (t, 2H, $J = 2.2$ Hz), 5.19-5.29 (m, 2H), 5.86-6.00 (m, 1H), 6.47 (s, 1H), 7.13 (t, 1H, $J = 7.7$ Hz), 7.25 (t, 1H, $J = 8.2$ Hz), 7.41 (d, 1H, $J = 8.2$ Hz), 7.59 (d, 1H, $J = 7.7$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) 140.0, 137.0, 134.0, 127.3, 122.2, 120.8, 120.0, 118.6, 109.3, 100.4, 78.6, 72.3, 66.2, 40.3, 32.8. IR (KBr) 3510, 3270, 2100, 1640, 1610. Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}$: C. 79.97; H. 6.71; N. 6.22. Found: C. 80.13; H. 5.90, N. 6.44.

1-(1-Allyl-1H-indol-2-yl)-3-trimethylsilyl-2-propyn-1-ol, 4. To a solution of 0.18 mL (1.29 mmol) of trimethylsilylacetylene in 5 mL of dry THF at 0°C, was added dropwise 0.8 mL (1.29 mmol) of BuLi 1.6M/hexane. The mixture was allowed to this temperature during 10 minutes. Then, this solution was added dropwise to a stirred solution of 0.2 g (1.08 mmol) of 1-allyl-1H-indole-2-carbaldehyde in 5 mL of dry THF. After 7h at room temperature saturated aqueous ammonium chloride (5 mL) was added. The organic layers was separated and the aqueous phase extracted with ether (3 x 5 mL). The combination of the organic phases was dried (MgSO_4) and the solvent evaporated under vacuum. The crude was purified by flash chromatography (hexane/EtOAc 9:1) to obtain the 0.2 g (65%) of **4** as a pale yellow oil. $^1\text{H-NMR}$ (CDCl_3) 0.23 (s, 9H), 2.17 (d, 1H, $J = 7.1$ Hz), 4.86-5.01 (m, 3H), 5.14 (d, 1H, $J = 9.3$ Hz), 5.63 (d, 1H, $J = 7.1$ Hz), 5.93-6.05 (m, 1H), 6.70 (s, 1H), 7.11 (t, 1H, $J = 7.7$ Hz), 7.19 (t, 1H, $J = 8.2$ Hz), 7.29 (d, 1H, $J = 8.2$ Hz), 7.61 (d, 1H, $J = 7.7$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) 137.8, 137.5, 133.6, 126.8, 122.3, 121.1, 119.7, 116.2, 109.8, 103.1, 101.8, 91.3, 58.5, 45.9, -0.3. IR (neat) 3380, 3050,

2960, 2170, 1650, 1620. Anal. Calcd. for $C_{17}H_{21}NOSi$: C. 72.04; H. 7.47; N. 4.94. Found: C. 71.89; H. 7.72, N. 4.67.

1-(3-Ethynyl-1*H*-indole-2-yl)-2-propen-1-ol, 27. Following the general procedure, from 4.0 g (16.4 mmol) of **26** and 17.2 mL (17.2 mmol) of vinylmagnesium bromide, and after purification by flash chromatography (hexane/EtOAc 6:1), 3.8 g of the corresponding alcohol were obtained. This compound, solved in 20 mL of THF was treated with 31 mL of TBAF (1M/THF) at room temperature. After completion of the reaction (t.l.c.), a 1:1:1 water/hexane/ether is added (30 mL). The organic layer is separated, dried ($MgSO_4$) and the solvent is eliminated under vacuum. After purification by chromatography (hexane/EtOAc 4:1), 2.26 g (70%) of **27** were obtained as a yellow oil. 1H -NMR ($CDCl_3$) 3.37 (s, 1H), 5.31 (d, 1H, $J = 10.4$ Hz), 5.50 (d, 1H, $J = 18.1$ Hz), 5.74 (d, 1H, $J = 5.5$ Hz), 6.08-6.19 (m, 1H), 7.19-7.24 (m, 2H), 7.35 (d, 1H, $J = 7.1$ Hz), 7.70 (d, 1H, $J = 7.1$ Hz), 8.46 (s, 1H). ^{13}C -NMR ($CDCl_3$) 138.1, 137.3, 136.4, 129.9, 122.2, 121.1, 119.9, 115.1, 111.2, 92.8, 80.7, 77.8, 68.5. IR (neat) 3400, 3300, 2100, 1620. Anal. Calcd. for $C_{13}H_{11}NO$: C. 79.16; H. 5.62; N. 7.10. Found: C. 79.32; H. 7.49, N. 7.44.

1-(3-Ethynyl-1*H*-indole-2-yl)-3-buten-1-ol, 28. Following the general procedure, from 2.8 g (13.8 mmol) of **26** and 14.2 mL (14.2 mmol) of allylmagnesium bromide, and after purification by flash chromatography (hexane/EtOAc 4:1), 3.89 g of the corresponding alcohol were obtained. This compound, solved in 20 mL of THF was treated with 31 mL of TBAF (1M/THF) at room temperature. After completion of the reaction (t.l.c.), a 1:1:1 water/hexane/ether is added (30 mL). The organic layer is separated, dried ($MgSO_4$) and the solvent is eliminated under vacuum. After purification by chromatography (hexane/EtOAc 4:1), 2.6 g (90%) of **28** were obtained as a yellow oil. 1H -NMR ($CDCl_3$) 2.60-2.70 (m, 1H), 2.80-2.88 (m, 1H), 3.36 (s, 1H), 5.21-5.27 (m, 3H), 5.81-5.95 (m, 1H), 7.16-7.22 (m, 2H), 7.35 (d, 1H, $J = 6.1$ Hz), 7.68 (d, 1H, $J = 7.1$ Hz), 8.58 (s, 1H). ^{13}C -NMR ($CDCl_3$) 145.4, 134.3, 133.7, 129.0, 122.5, 120.5, 119.4, 118.6, 111.4, 92.8, 81.4, 78.9, 66.7, 53.2. IR (neat) 3510, 3420, 3300, 2100, 1450. Anal. Calcd. for $C_{14}H_{13}NO$: C. 79.59; H. 6.20; N. 6.63. Found: C. 79.37; H. 6.48, N. 6.54.

2-[1-(*tert*-Butyldimethylsilyloxy)allyl]-1-(2-propynyl)-1*H*-indole, 5. Following the method described for the protection of alcohols as their TBDMS derivatives,²³ from 1.73 g (8.2 mmol) of **3**, 1.39 g (20.5 mmol) of imidazole and 2.47 g (16.4 mmol) of *tert*-butyldimethylsilyl chloride, and after purification by flash chromatography (hexane), 2.03 g (76%) of **5** were obtained as a colorless oil. ¹H-NMR (CDCl₃) -0.04 (s, 3H), 0.11 (s, 3H), 0.91 (s, 9H), 2.24 (t, 1H, J = 2.2 Hz), 4.96 (dd, 1H, J₁ = 18.1 Hz, J₂ = 2.2 Hz), 5.07 (dd, 1H, J₁ = 18.1 Hz, J₂ = 2.2 Hz), 5.23 (dt, 1H, J₁ = 9.9 Hz, J₂ = 1.6 Hz), 5.38 (dt, 1H, J₁ = 17.0 Hz, J₂ = 1.6 Hz), 5.47-5.49 (m, 1H), 6.03-6.13 (m, 1H), 6.37 (s, 1H), 7.12 (t, 1H, J = 7.7 Hz), 7.24 (t, 1H, J = 8.2 Hz), 7.46 (d, 1H, J = 8.2 Hz), 7.57 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 139.2, 139.1, 137.5, 127.6, 121.9, 120.7, 119.9, 114.8, 109.7, 101.3, 78.8, 72.3, 70.2, 33.7, 25.8, 18.2, -4.9, -5.0. IR (neat) 2920, 2840, 1460. Anal. Calcd. for C₂₀H₂₇NOSi: C. 73.79; H. 8.36; N. 4.30. Found: C. 73.62; H. 8.49; N. 4.52.

1-Allyl-2-[1-(*tert*-butyldimethylsilyloxy)-3-trimethylsilyl-2-propynyl]-1*H*-indole, 6. Following the method described for the protection of alcohols as their TBDMS derivatives,²³ from 0.86 g (3.04 mmol) of **4**, 0.52 g (7.6 mmol) of imidazole and 0.92 g (6.1 mmol) of *tert*-butyldimethylsilyl chloride, and after purification by flash chromatography (hexane), 0.96 g (80%) of **6** were obtained as a colorless oil. ¹H-NMR (CDCl₃) 0.14 (s, 3H), 0.16 (s, 3H), 0.19 (s, 9H), 0.91 (s, 9H), 4.98-5.07 (m, 3H), 5.14 (dd, 1H, J₁ = 10.4 Hz, J₂ = 1.1 Hz), 5.67 (s, 1H), 5.94-6.06 (m, 1H), 6.52 (s, 1H), 7.10 (t, 1H, J = 7.7 Hz), 7.20 (t, 1H, J = 7.7 Hz), 7.31 (d, 1H, J = 7.7 Hz), 7.60 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 138.1, 137.8, 133.9, 127.2, 121.9, 121.0, 119.6, 116.2, 110.0, 104.3, 101.1, 91.0, 59.7, 46.5, 25.7, 18.2, -0.3, -4.5, -4.7. IR (neat) 2950, 2920, 2850, 2160. Anal. Calcd. for C₂₃H₃₅NOSi₂: C. 69.46; H. 8.87; N. 3.52. Found: C. 69.23; H. 8.71; N. 3.79.

2-[1-(*tert*-Butyldimethylsilyloxy)-3-butenyl]-1-(2-propynyl)-1*H*-indole, 9. Following the general method described for the protection of alcohols as their TBDMS derivatives, from 0.98 g (4.37 mmol) of **8**, 0.74 g (10.9 mmol) of imidazole and 1.32 g (8.74 mmol) *tert*-butyldimethylsilyl chloride, and after purification by flash chromatography (hexane), 1.17 g (80%) of **9** were obtained as a colorless oil. ¹H-NMR (CDCl₃) -0.12 (s, 3H), 0.06 (s, 3H), 0.88 (s, 9H), 2.29 (t, 1H, J = 2.7 Hz), 2.59-2.79 (m,

2H), 4.89-4.97 (m, 2H), 5.04 (dd, 1H, $J_1 = 12.1$ Hz, $J_2 = 1.6$ Hz), 5.10 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 1.6$ Hz), 5.36 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 2.2$ Hz), 5.68-5.83 (m, 1H), 6.30 (s, 1H), 7.12 (t, 1H, $J = 7.7$ Hz), 7.24 (t, 1H, $J = 8.2$ Hz), 7.44 (d, 1H, $J = 8.2$ Hz), 7.58 (d, 1H, $J = 7.7$ Hz). ^{13}C -NMR (CDCl_3) 140.4, 137.5, 134.6, 127.6, 121.7, 120.7, 119.9, 117.4, 109.5, 101.1, 78.8, 72.5, 70.3, 43.1, 33.6, 25.8, 18.1, -4.8, -5.1. IR (neat) 3300, 2100, 1460. . Anal. Calcd. for $\text{C}_{21}\text{H}_{29}\text{NOSi}$: C. 74.28; H. 8.61; N. 4.13. Found: C. 74.49; H. 8.39, N. 4.29.

1-Allyl-2-[1-(*tert*-butyldimethylsilyloxy)-4-trimethylsilyl-3-butynyl]-1*H*-indole, 11. Following the same procedure used for the synthesis of **4**, from 0.38 mL (2.6 mmol) of 1-propynyltrimethylsilane, 0.39 mL (2.6 mmol) of trimethylethylenediamine, 1.6 mL (2.6 mmol) of BuLi and 0.44 g (2.37 mmol) of 1-allyl-1*H*-indole-2-carbaldehyde, and after purification by flash chromatography (hexane/EtOAc 49:1), 0.41 g (70%) of 1-allyl-2-(3-buten-1-hydroxy-3-trimethylsilyl)-1*H*-indole 1-(1-allyl-1*H*-indol-2-yl)-4-trimethylsilyl-3-buten-1-ol were obtained as a colorless oil. Then, following the general method described for the protection of alcohols as their TBDMS derivatives, from 0.34 g (1.39 mmol) of this alcohol, 0.24 g (3.47 mmol) of imidazole and 0.42 g (2.78 mmol) of *tert*-butyldimethylsilyl chloride, and after purification by flash chromatography (hexane), 0.48 g (96%) of **11** were obtained as a colorless oil. ^1H -NMR (CDCl_3) -0.06 (s, 3H), 0.09 (s, 3H), 0.12 (s, 9H), 0.89 (s, 9H), 2.63 (dd, 1H, $J_1 = 17.0$ Hz, $J_2 = 4.9$ Hz), 2.80 (dd, 1H, $J_1 = 17.0$ Hz, $J_2 = 8.8$ Hz), 4.75-4.87 (m, 2H), 5.03-5.20 (m, 3H), 5.90-6.02 (m, 1H), 6.41 (s, 1H), 7.08 (t, 1H, $J = 7.7$ Hz), 7.18 (t, 1H, $J = 8.2$ Hz), 7.24 (d, 1H, $J = 8.2$ Hz), 7.56 (d, 1H, $J = 7.7$ Hz). ^{13}C -NMR (CDCl_3) 140.9, 137.5, 133.5, 127.5, 121.5, 120.6, 119.5, 116.2, 109.7, 104.0, 100.6, 86.4, 68.9, 46.2, 30.8, 25.8, 18.2, -0.003, -4.7, -5.0. IR (neat) 2160, 1460, 1410.

2-[1-(*tert*-Butyldimethylsilyloxy)allyl]-3-ethynyl-1*H*-indole, 29. Following the general method described for the protection of alcohols as their TBDMS derivatives,²³ from 1.46 g (7.41 mmol) of **27**, 2.02 g of imidazole and 2.8 g of *tert*-butyldimethylsilyl chloride and after purification by flash chromatography (hexane/AcOEt 19:1), 1.2 g (52%) of **29** were obtained as a colorless oil. ^1H -NMR (CDCl_3) 0.03 (s, 3H), 0.15 (s, 3H), 0.92 (s, 9H), 3.35 (s, 1H), 5.17 (dt, 1H, $J_1 = 10.4$ Hz, $J_2 = 1.1$ Hz),

5.43 (dt, 1H, $J_1 = 17.0$ Hz, $J_2 = 1.1$ Hz), 5.65-5.67 (m, 1H), 5.94-6.04 (m, 1H), 7.14-7.25 (m, 2H), 7.35 (dd, 1H, $J_1 = 6.6$ Hz, $J_2 = 1.6$ Hz), 7.69 (dd, 1H, $J_1 = 7.7$ Hz, $J_2 = 1.6$ Hz), 8.33 (s, 1H). ^{13}C -NMR (CDCl_3) 144.1, 138.1, 134.3, 129.1, 122.8, 120.6, 119.7, 114.3, 111.2, 93.5, 81.4, 76.8, 68.5, 25.8, 18.3, -5.0, -5.2. IR (neat) 3460, 3300, 2100, 1440. Anal. Calcd. for $\text{C}_{19}\text{H}_{25}\text{NOSi}$: C. 73.26; H. 8.09; N. 4.50. Found: C. 73.47; H. 8.26, N. 4.41.

2-[1-(*tert*-Butyldimethylsilyloxy)-3-butenyl]-3-ethynyl-1*H*-indole, 30. Following the general method described for the protection of alcohols as their TBDMS derivatives,²³ from 2.91 g (13.8 mmol) of **28**, 3.76 g of imidazole and 5.2 g of *tert*-butyldimethylsilyl chloride and after purification by flash chromatography (hexane/AcOEt 49:1), 2.15 g (50%) of **30** were obtained as a colorless oil. ^1H -NMR (CDCl_3) -0.03 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 2.57-2.63 (m, 2H), 3.34 (s, 1H), 5.04-5.10 (m, 2H), 5.24 (t, 1H, $J = 6.1$ Hz), 5.73-5.88 (m, 1H), 7.15-7.24 (m, 2H), 7.35 (dd, 1H, $J_1 = 6.6$ Hz, $J_2 = 1.6$ Hz), 7.68 (d, 1H, $J = 7.1$ Hz), 8.37 (s, 1H). ^{13}C -NMR (CDCl_3) 145.8, 134.0, 133.5, 129.1, 122.5, 120.6, 119.6, 118.1, 111.1, 92.8, 81.4, 76.9, 67.8, 42.8, 25.7, 18.1, -5.0, -5.1. IR (neat) 3470, 3300, 2100, 1440 Anal. Calcd. for $\text{C}_{20}\text{H}_{27}\text{NOSi}$: C. 73.79; H. 8.36; N. 4.30. Found: C. 73.57; H. 8.20, N. 4.46.

2-[1-Phthalimidoallyl]-1-(2-propynyl)-1*H*-indole, 7. To a cooled solution at 0°C of 0.77 g (3.67mmol) of **3** in 5 mL of dry THF under argon, was added a solution of 0.96 g (3.67 mmol) of triphenylphosphine, 0.58 mL (3.67 mmol) of diethylazodicarboxylate and 0.54 g (3.67 mmol) of potassium phthalimide in 10 mL of dry THF. The reaction was stirred at room temperature for 24h. The solvent was eliminated under vacuum, and the crude was purified by flash chromatography (hexane/EtOAc 9:1) to obtain 0.61 g (50%) of **7** as a yellow solid. m.p.: 140-141°C (hexane/EtOAc). ^1H -NMR (CDCl_3) 1.81 (t, 1H, $J = 2.2$ Hz), 4.84-4.99 (m, 2H), 5.41 (d, 1H, $J = 9.9$ Hz), 5.43 (d, 1H, $J = 17.0$ Hz), 6.20 (d, 1H, $J = 7.1$ Hz), 6.65-6.75 (m, 1H), 6.77 (s, 1H), 7.11 (t, 1H, $J = 7.7$ Hz), 7.22 (t, 1H, $J = 7.7$ Hz), 7.33 (d, 1H, $J = 7.7$ Hz), 7.60 (d, 1H, $J = 7.7$ Hz), 7.68-7.73 (m, 2H), 7.75-7.89 (m, 2H). ^{13}C -NMR (CDCl_3) 167.2, 136.6, 135.0, 133.9, 132.5, 132.5, 131.7, 128.4, 127.3, 127.2, 123.1,

122.3, 121.0, 120.1, 118.8, 109.1, 104.2, 78.1, 72.1, 48.9, 32.6. IR (KBr) 3280, 3030, 1710, 1460.

Anal. Calcd. for $C_{22}H_{16}N_2O_2$: C. 77.63; H. 4.74; N. 8.23. Found: C. 77.49; H. 4.82, N. 8.39.

2-(1-Phthalimido-3-butenyl)-1-(2-propynyl)-1*H*-indole, 10. Following the procedure used for the synthesis of **7**, from 6.2 g (31.47 mmol) of **8**, 8.12 g (31.47 mmol) of triphenylphosphine, 4.95 mL (31.47 mmol) of diethylazodicarboxylate and 4.56 g (31.47 mmol) of potassium phthalimide, and after purification by flash chromatography (hexane/EtOAc 9:1), 6.46 g (60%) of **10** were obtained as a yellow solid. m.p.: 118-119 °C (hexane/EtOAc). 1H -NMR ($CDCl_3$) 1.78 (t, 1H, $J = 2.7$ Hz), 3.09-3.17 (m, 1H), 3.42-3.53 (m, 1H), 4.83-5.00 (m, 2H), 5.06 (d, 1H, $J = 9.9$ Hz), 5.18 (d, 1H, $J = 17.0$ Hz), 5.65 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 4.9$ Hz), 5.77-5.91 (m, 1H), 6.87 (s, 1H), 7.12 (t, 1H, $J = 7.7$ Hz), 7.20 (t, 1H, $J = 8.2$ Hz), 7.32 (d, 1H, $J = 8.2$ Hz), 7.62 (d, 1H, $J = 7.7$ Hz), 7.66-7.71 (m, 2H), 7.76-7.81 (m, 2H). ^{13}C -NMR ($CDCl_3$) 167.7, 136.4, 135.6, 134.1, 133.8, 133.5, 131.5, 127.3, 123.3, 123.0, 122.3, 121.0, 120.1, 119.0, 109.1, 103.5, 78.2, 71.9, 45.7, 35.1, 32.5. IR (KBr) 3460, 2110, 1770, 1710. . Anal. Calcd. for $C_{23}H_{18}N_2O_2$: C. 77.95; H. 5.12; N. 7.90. Found: C. 77.89; H. 4.95, N. 8.02.

2-[1-(*tert*-Butyldimethylsilyloxy)allyl]-3-ethynyl-1-methyl-1*H*-indole, 31. To a solution of 0.7 g (2.25 mmol) of **29** in toluene (10 mL), 0.21 mL of methyl iodide and 0.09 g of tetrabutylammonium iodide were added and this mixture was vigorously stirred jointly with 10 mL of a 30% NaOH solution until completion of the reaction (t.l.c.). After purification by flash chromatography (hexane/EtOAc 49:1), 0.66 g (90%) of **31** were obtained as a colorless oil. 1H -NMR ($CDCl_3$) -0.11 (s, 3H), 0.15 (s, 3H), 0.90 (s, 9H), 3.35 (s, 1H), 3.78 (s, 3H), 5.21 (dt, 1H, $J_1 = 10.4$ Hz, $J_2 = 1.1$ Hz), 5.41 (dt, 1H, $J_1 = 17.0$ Hz, $J_2 = 1.1$ Hz), 5.86-5.89 (m, 1H), 5.97-6.08 (m, 1H), 7.15-7.23 (m, 2H), 7.30 (d, 1H, $J = 7.7$ Hz), 7.69 (d, 1H, $J = 7.7$ Hz). ^{13}C -NMR ($CDCl_3$) 143.7, 138.3, 137.1, 128.1, 122.7, 120.4, 120.0, 114.3, 109.2, 94.9, 81.2, 77.2, 68.0, 31.1, 25.8, 18.1, -5.2, -5.4. IR (neat) 3310, 2100, 1470. Anal. Calcd. for $C_{20}H_{27}NOSi$: C. 73.79; H. 8.36; N. 4.30. Found: C. 73.48; H. 8.52, N. 4.22.

2-[1-(*tert*-Butyldimethylsilyloxy)-3-butenyl]-3-ethynyl-1-methyl-1*H*-indole, 32. To a solution of 1.64 g (5.04 mmol) of **30** in toluene (10 mL), 0.47 mL of methyl iodide and 0.2 g of tetrabutylammonium iodide were added and this mixture was vigorously stirred jointly with 10 mL of

a 30% NaOH solution until completion of the reaction (t.l.c.). After purification by flash chromatography (hexane/EtOAc 49:1), 1.5 g (88%) of **32** were obtained as a colorless oil. ¹H-NMR (CDCl₃) -0.17 (s, 3H), 0.11 (s, 3H), 0.87 (s, 9H), 2.51-2.60 (m, 1H), 2.70-2.79 (m, 1H), 3.34 (s, 1H), 3.93 (s, 3H), 5.02-5.12 (m, 2H), 5.33 (dd, 1H, J₁ = 8.2 Hz, J₂ = 6.6 Hz), 5.71-5.85 (m, 1H), 7.18 (td, 1H, J₁ = 7.7 Hz, J₂ = 1.6 Hz), 7.25 (td, 1H, J₁ = 7.7 Hz, J₂ = 1.6 Hz), 7.32 (d, 1H, J = 7.7 Hz), 7.67 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 145.2, 137.1, 134.1, 128.1, 122.5, 120.4, 119.9, 117.5, 109.2, 94.7, 81.1, 77.3, 68.3, 42.1, 31.4, 25.7, 18.0, -5.2, -5.4. IR (neat) 3310, 2100, 1470. Anal. Calcd. for C₂₁H₂₉NOSi: C. 74.28; H. 8.61; N. 4.13. Found: C. 74.52; H. 8.39, N. 4.49.

3,4-Dihydro-1H-benzo[e]cyclopenta[a]pyrrolizin-2-one, 13. Following method A, from 0.362g of **2**, and after purification by flash chromatography (hexane/EtOAc 9:1), 0.036 g (15%) of **13** were obtained as a brown solid. m.p.: 163-165°C (hexane/EtOAc). ¹H-NMR (CDCl₃) 3.37 (s, 2H), 3.44 (s, 2H), 3.79 (s, 2H), 6.96 (s, 1H), 7.10 (t, 1H, J = 7.7 Hz), 7.24-7.34 (m, 2H), 7.41 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 206.2, 141.2, 134.3, 128.1, 127.5, 126.7, 125.9, 122.9, 114.8, 109.4, 103.4, 39.0, 38.2, 28.5. IR (KBr) 1750, 1600. Anal. Calcd. for C₁₄H₁₁NO: C. 80.36; H. 5.30; N. 6.69. Found: C. 80.48; H. 5.47; N. 6.59.

Synthesis of 14 Following method A, from 0.424 g of **3** a mixture 1:1 of diastereoisomers (**S*****S***) and (**R*****S***) of **14** was obtained. The isomers were separated by flash chromatography (hexane/EtOAc 1:1) to obtain 0.056 g (12%) of diastereoisomer (**S*****S***)-**14α** as a yellow solid. m.p.: 110-111°C (CHCl₃) and 0.063 g (13%) of (**R*****S***)-**14β** as a pale yellow solid. m.p.: >130°C (MeOH). Following method B, 0.070 g (15%) of (**S*****S***)-**14 α** and 0.070 g (15%) of (**R*****S***)-**14 β** were obtained.

(10S*10aS*)-10-Hydroxy-10,10a-dihydro-1H,4H-4a-azacyclopenta[b]fluoren-2-one, 14 α: ¹H-NMR (CDCl₃) 2.17 (sa, 1H), 2.55 (dd, 1H, J₁ = 18.1 Hz, J₂ = 6.6 Hz), 2.72 (dd, 1H, J₁ = 18.1 Hz, J₂ = 2.7 Hz), 3.30-3.40 (m, 1H), 5.03-5.19 (m, 3H), 6.29 (s, 1H), 6.52 (s, 1H), 7.17 (t, 1H, J = 7.7 Hz), 7.25-7.32 (m, 2H), 7.62 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 208.2, 170.4, 136.8, 135.8, 130.8, 127.7,

122.5, 121.2, 120.5, 109.0, 100.6, 63.0, 44.0, 43.8, 36.4. IR (KBr) 3370, 2910, 1710, 1630. Anal. Calcd. for C₁₅H₁₃NO₂: C. 75.30; H. 5.48; N. 5.85. Found: C. 75.40; H. 5.59; N. 5.98.

(10R*10aS*)-10-Hydroxy-10,10a-dihydro-1H,4H-4a-azacyclopenta[b]fluoren-2-one, 14 β : ¹H-NMR (MeOD) 2.53 (d, 1H, J = 19.5 Hz), 2.74 (dd, 1H, J₁ = 19.5 Hz, J₂ = 6.1 Hz), 3.17-3.22 (m, 1H), 4.54 (d, 1H, J = 10.4 Hz), 5.09 (d, 1H, J = 17.7 Hz), 5.19 (d, 1H, J = 17.7 Hz), 6.33 (s, 1H), 6.53 (s, 1H), 7.07 (t, 1H, J = 7.3 Hz), 7.17 (t, 1H, J = 7.9 Hz), 7.35 (d, 1H, J = 7.9 Hz), 7.53 (d, 1H, J = 7.3 Hz). ¹³C-NMR (MeOD) 207.2, 172.8, 141.2, 135.5, 129.7, 128.0, 121.0, 120.1, 119.8, 109.6, 97.4, 69.6, 46.5, 43.9, 38.9. IR (KBr) 3370, 2910, 1710, 1630. Anal. Calcd. for C₁₅H₁₃NO₂: C. 75.30; H. 5.48; N. 5.85. Found: C. 75.42; H. 5.71; N. 5.96.

Synthesis of 15 and 16 Following method A, from 0.564 g of **4**, and after purification by flash chromatography (hexane/EtOAc 9:1), 0.129 g (20%) of **15** was obtained as a colorless oil and 0.048 g (10%) of the diketone **α -16** as a yellow solid m.p.: >130°C (hexane/EtOAc) and 0.048 g (10%) of diketone **β -16** as a yellow oil. Following method B, 0.143 g (23%) of **15**, 0.052 g (11%) of **α -16** and 0.052 g (11%) of **β -16**.

1-Trimethylsilyl-3a,4-dihydro-3H-4a-azacyclopenta[b]fluorene-2,10-dione, 15: ¹H-NMR (CDCl₃) 0.30 (s, 9H), 2.42 (dd, 1H, J₁ = 18.7 Hz, J₂ = 2.7 Hz), 2.89 (dd, 1H, J₁ = 18.7 Hz, J₂ = 6.6 Hz), 3.70-3.89 (m, 2H), 4.83 (dd, 1H, J₁ = 11.0 Hz, J₂ = 5.5 Hz), 7.21 (t, 1H, J = 7.7 Hz), 7.35-7.46 (m, 2H), 7.49 (s, 1H), 7.77 (d, 1H, J = 8.2 Hz). ¹³C-NMR (CDCl₃) 209.8, 178.9, 172.8, 151.2, 137.7, 134.9, 127.3, 126.8, 123.7, 121.6, 110.4, 108.2, 47.0, 41.1, 40.1, -1.0. IR (neat) 2940, 1710, 1610, 1650. Anal. Calcd. for C₁₈H₁₉NO₂Si: C. 69.87; H. 6.19; N. 4.53. Found: C. 70.16; H. 6.36; N. 4.69.

1,3a,4,10a-Tetrahydro-3H-4a-azacyclopenta[b]fluorene-2,10-dione, 16 α : ¹H-NMR (CDCl₃) 2.38 (dd, 1H, J₁ = 17.0 Hz, J₂ = 12.6 Hz), 2.57 (dd, 1H, J₁ = 18.7 Hz, J₂ = 12.1 Hz), 2.73 (d, 1H, J = 7.1 Hz), 2.79 (dd, 1H, J₁ = 7.7 Hz, J₂ = 2.7 Hz), 2.85-2.97 (m, 1H), 3.10-3.21 (m, 1H), 4.07 (t, 1H, J = 11.5 Hz), 4.76 (dd, 1H, J₁ = 11.5 Hz, J₂ = 4.4 Hz), 7.20 (t, 1H, J = 8.2 Hz), 7.34-7.45 (m, 3H), 7.76 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 212.4, 188.4, 137.5, 133.8, 126.9, 126.2, 123.6, 121.4, 110.2, 106.3, 51.0, 47.5,

43.1, 40.0, 37.8. IR (KBr) 2920, 1755, 1690, 1525. Anal. Calcd. for C₁₅H₁₃NO₂: C. 75.30; H. 5.48; N. 5.85. Found: C. 75.45; H. 5.61; N. 5.91.

1,3a,4,10a-Tetrahydro-3H-4a-azacyclopenta[b]fluorene-2,10-dione, 16β: ¹H-NMR (CDCl₃) 2.22 (dd, 1H, J₁ = 18.1 Hz, J₂ = 9.3 Hz), 2.52 (dd, 1H, J₁ = 18.7 Hz, J₂ = 6.6 Hz), 2.64 (dd, 1H, J₁ = 18.7 Hz, J₂ = 9.3 Hz), 2.94 (dd, 1H, J₁ = 18.7 Hz, J₂ = 4.9 Hz), 3.26-3.41 (m, 2H), 4.30 (dd, 1H, J₁ = 13.2 Hz, J₂ = 4.9 Hz), 4.42 (dd, 1H, J₁ = 13.2 Hz, J₂ = 4.9 Hz), 7.20 (t, 1H, J = 8.2 Hz), 7.36-7.46 (m, 3H), 7.75 (d, 1H, J = 8.2 Hz). ¹³C-NMR (CDCl₃) 213.9, 189.5, 137.8, 132.0, 127.2, 126.4, 123.6, 121.6, 110.3, 107.7, 45.5, 41.4, 41.3, 40.6, 35.7. IR (neat) 2920, 1755, 1690, 1525. Anal. Calcd. for C₁₅H₁₃NO₂: C. 75.30; H. 5.48; N. 5.85. Found: C. 75.52; H. 5.63; N. 5.71.

(10S*,10aR*)-10-tert-Butyldimethylsilyloxy-10,10a-dihydro-1H,4H-4a-azacyclopenta[b]fluoren-2-one, 17. Following method A, from 0.410 g of **5**, and after purification by flash chromatography (hexane/EtOAc 10:1), 0.320 g (65%) of **17** were obtained as a yellow solid. m.p.: >150°C (hexane/EtOAc). Following method B, 0.320 g (65%) of **17** were obtained. ¹H-NMR (CDCl₃) 0.20 (s, 3H), 0.28 (s, 3H), 1.02 (s, 9H), 2.45 (d, 1H, J = 20.3 Hz), 2.76 (dd, 1H, J₁ = 19.2 Hz, J₂ = 6.0 Hz), 3.21-3.29 (m, 1H), 4.66 (d, 1H, J = 10.4 Hz), 5.04 (d, 1H, J = 17.6 Hz), 5.16 (d, 1H, J = 17.6 Hz), 6.34 (s, 1H), 6.51 (s, 1H), 7.14-7.29 (m, 3H), 7.63 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 206.5, 171.1, 139.7, 135.7, 130.4, 128.1, 121.6, 120.6, 120.3, 108.7, 98.6, 71.4, 47.1, 43.7, 39.2, 25.7, 18.0, -4.1, -4.2. IR (KBr) 2900, 2840, 1710, 1620. Anal. Calcd. for C₂₁H₂₇NO₂Si: C. 71.34; H. 7.70; N. 3.96. Found: C. 71.23; H. 7.82; N. 4.07.

(10S*,3aS*)-10-tert-Butyldimethylsilyloxy-1-trimethylsilyl-3a,4-dihydro-3H,10H-4a-azacyclopenta[b]fluoren-2-one, 18. Following method A, from 0.800 g of **6**, and after purification by flash chromatography (hexane/EtOAc 5:1), 0.453 g (55%) of **18** were obtained as a white solid. m.p.: 122-123°C (hexane/EtOAc). Following method B, 0.640 g (75%) of **18** were obtained. ¹H-NMR (CDCl₃) -0.01 (s, 3H), 0.19 (s, 3H), 0.27 (s, 9H), 0.82 (s, 9H), 2.21 (dd, 1H, J₁ = 18.7 Hz, J₂ = 2.2 Hz), 2.76 (dd, 1H, J₁ = 18.7 Hz, J₂ = 7.1 Hz), 3.47 (t, 1H, J = 11.0 Hz), 3.93-4.02 (m, 1H), 4.78 (dd, 1H, J₁ = 11.0 Hz, J₂ = 7.7 Hz), 5.96 (s, 1H), 6.50 (s, 1H), 7.14 (t, 1H, J = 8.2 Hz), 7.25 (t, 1H, J = 8.2 Hz), 7.31

(d, 1H, J = 8.2 Hz), 7.61 (d, 1H, J = 8.2 Hz). ¹³C-NMR (CDCl₃) 211.9, 182.4, 138.6, 136.9, 136.5, 128.2, 122.1, 121.0, 120.2, 109.4, 101.2, 62.8, 50.0, 40.6, 34.6, 25.5, 18.0, -0.69, -4.2, -4.4. IR (KBr) 2940, 2840, 1680, 1605, 1470, 1450. Anal. Calcd. for C₂₄H₃₅NO₂Si₂: C. 67.71; H. 8.29; N. 3.29. Found: C. 67.85; H. 8.41; N. 3.36.

(10S*,10aR*)-10-Phthalimido-10,10a-dihydro-1H,4H-4a-azacyclopenta[b]fluoren-2-one, 19.

Following method A, from 0.680 g of **7**, and after purification by flash chromatography (hexane/EtOAc 3:1), 0.566 g (75%) of **19** were obtained as a yellow solid. m.p.: >120°C (hexane/EtOAc). Following method B, 0.570 g (70%) of **19** were obtained. ¹H-NMR (CDCl₃) 2.32 (dd, 1H, J₁ = 18.7 Hz, J₂ = 1.6 Hz), 2.64 (dd, 1H, J₁ = 18.7 Hz, J₂ = 6.6 Hz), 4.32-4.38 (m, 1H), 5.18 (d, 1H, J = 17.0 Hz), 5.27 (d, 1H, J = 17.0 Hz), 5.43 (dd, 1H, J₁ = 11.5 Hz, J₂ = 1.1 Hz), 6.16 (s, 1H), 6.40 (s, 1H), 7.13 (t, 1H, J = 7.7 Hz), 7.25 (t, 1H, J = 8.2 Hz), 7.33 (d, 1H, J = 8.2 Hz), 7.48 (d, 1H, J = 7.7 Hz), 7.76-7.86 (m, 2H), 7.88-7.93 (m, 1H), 7.94-8.04 (m, 1H). ¹³C-NMR (CDCl₃) 205.8, 170.5, 136.1, 134.6, 134.5, 133.3, 130.8, 128.1, 123.9, 123.7, 122.0, 120.7, 120.6, 108.9, 98.1, 51.4, 44.1, 40.6, 38.6. IR (KBr) 1765, 1710, 1630, 1470. Anal. Calcd. for C₂₃H₁₆N₂O₃: C. 74.99; H. 4.38; N. 7.60. Found: C. 75.11; H. 4.49; N. 7.65.

(11S*,12aR*)-11-Hydroxy-4,11,12,12a-tetrahydro-1H-cyclopenta[5,6]azepine[1,2-a]indole-2-one, 20. Following method A, from 0.449 g of **8**, and after purification by flash chromatography (hexane/EtOAc 1:1), 0.090 g (20%) of **20** were obtained as a pale yellow oil. Following method B, 0.046 g (10%) of **20** were obtained. ¹H-NMR (CDCl₃) 1.60 (t, 1H, J = 13.7 Hz), 2.08 (dd, 1H, J₁ = 19.2 Hz, J₂ = 2.2 Hz), 2.65-2.74 (m, 1H), 2.77 (dd, 1H, J₁ = 19.2 Hz, J₂ = 6.6 Hz), 3.64-3.72 (m, 1H), 5.02 (d, 1H, J = 13.7 Hz), 5.26-5.30 (m, 2H), 6.11 (s, 1H), 6.43 (s, 1H); 7.11 (t, 1H, J = 7.7 Hz), 7.27 (t, 1H, J = 8.2 Hz), 7.38 (d, 1H, J = 8.8 Hz), 7.57 (d, 1H, J = 7.7 Hz). ¹³C-NMR (CDCl₃) 208.0, 174.6, 141.0, 136.9, 132.0, 127.0, 122.5, 121.0, 119.9, 108.6, 101.9, 66.4, 44.4, 42.9, 39.7, 38.3. IR (neat) 3250, 2940, 1720. Anal. Calcd. for C₁₆H₁₅NO₂: C. 75.87; H. 5.97; N. 5.53. Found: C. 75.96; H. 6.03; N. 5.43.

(11S*,12aR*)-11-Phthalimido-4,11,12,12a-tetrahydro-1H-cyclopenta[5,6]azepine[1,2-a]indole-2-one, 22: Following method A, from 0.675 g of **10**, and after purification by flash chromatography

(hexane/EtOAc 2:1), 0.070 g (10%) of **22** were obtained as a pale yellow solid. m.p.: >180°C (hexane/EtOAc). Following method B, 0.205 g (30%) of **22** were obtained. ¹H-NMR (CDCl₃) 2.17 (dd, 1H, J₁ = 18.7. Hz, J₂ = 2.2 Hz), 2.49-2.57 (m, 1H) 2.70-2.85 (m, 2H), 3.21-3.29 (m, 1H), 4.83 (d, 1H, J = 14.8 Hz), 5.52 (d, 1H, J = 14.8 Hz), 5.84 (d, 1H, J = 11.0 Hz), 6.11 (d, 1H, J = 3.3 Hz), 7.07 (t, 1H, J = 7.7 Hz), 7.22 (t, 1H, J = 7.7 Hz), 7.38 (d, 1H, J = 8.2 Hz), 7.45 (d, 1H, J = 7.7 Hz), 7.78-7.81 (m, 3H), 7.92-7.94 (m, 2H). ¹³C-NMR (CDCl₃) 206.9, 172.5, 167.5, 138.0, 136.8, 134.4, 132.1, 131.6, 127.1, 123.7, 122.0, 120.7, 120.0, 108.5, 100.3, 48.2, 44.2, 42.8, 38.4, 29.6. IR (KBr) 1780, 1710. Anal. Calcd. for C₂₄H₁₈N₂O₃: C. 75.38; H. 4.74; N. 7.33. Found: C. 75.49; H. 4.86; N. 7.30.

11-(tert-Butyldimethylsilyloxy)-1-trimethylsilyl-3a,4,11,12-tetrahydro-3H-cyclopenta[5,6]azepine[1,2-a]indole-2-one, 23. Following method A, from 0.800 g of **11**, and after purification by flash chromatography (hexane/EtOAc 9:1), 0.120 g (15%) of **23** were obtained as a yellow oil. Following method B, 0.320 g (40%) of **23** were obtained. Following method C, 0.080 g (10%) of **23** were obtained. ¹H-NMR (CDCl₃) 0.07 (s, 3H), 0.16 (s, 3H), 0.27 (s, 9H), 0.97 (s, 9H), 2.14 (dd, 1H, J₁ = 18.1. Hz, J₂ = 3.3 Hz), 2.73 (dd, 1H, J₁ = 18.6. Hz, J₂ = 7.5 Hz), 2.86 (dd, 1H, J₁ = 14.4. Hz, J₂ = 9.3 Hz) 3.15-3.17 (m, 1H), 3.45 (dd, 1H, J₁ = 14.4. Hz, J₂ = 2.1 Hz), 3.77 (dd, 1H, J₁ = 14.4. Hz, J₂ = 10.5 Hz), 4.59 (dd, 1H, J₁ = 13.5. Hz, J₂ = 3.3 Hz), 5.04 (dd, 1H, J₁ = 9.0. Hz, J₂ = 2.1 Hz), 6.50 (s, 1H), 7.11 (t, 1H, J = 7.2 Hz), 7.19 (t, 1H, J = 7.2 Hz), 7.32 (d, 1H, J = 8.1 Hz), 7.61 (d, 1H, J = 8.1 Hz). ¹³C-NMR (CDCl₃) 211.1, 184.1, 143.4, 142.5, 137.0, 127.3, 121.4, 120.7, 119.7, 108.6, 99.9, 67.1, 46.8, 44.9, 42.9, 40.6, 25.7, 18.2, -0.2, -4.5, -5.1. IR (neat) 2960, 2860, 1690. Anal. Calcd. for C₂₅H₃₇NO₂Si₂: C. 68.28; H. 8.48; N. 3.19. Found: C. 68.31; H. 8.53; N. 3.28.

(3aR*,4R*)-4-(tert-Butyldimethylsilyloxy)-3,3a,4,5-tetrahydropentalen[5,4-b]indol-2-one, 33.
Method B: From 0.31 g of **29** a 1:1 mixture of (*S**,*R**) and (*R**,*R**) isomers of **31** were obtained. Upon purification by flash chromatography (hexane/EtOAc 4:1) 0.03 g (15%) of one of the isomers was obtained as a colorless oil. ¹H-NMR (CDCl₃) 0.20 (s, 3H), 0.25 (s, 3H), 0.99 (s, 9H), 2.54 (dd, 1H, J₁ = 16.5 Hz, J₂ = 6.1 Hz), 2.74 (dd, 1H, J₁ = 16.5 Hz, J₂ = 7.1 Hz), 3.83-3.93 (m, 1H), 5.21 (d, 1H, J = 4.4 Hz), 5.91 (d, 1H, J = 1.6 Hz), 7.27-7.46 (m, 2H), 7.70 (d, 1H, J = 6.6 Hz), 8.22 (d, 1H, J = 7.1 Hz), 8.50

(bs, 1H). IR (neat) 2940, 1690, 1610. Anal. Calcd. for $C_{20}H_{25}NO_2Si$: C. 70.75; H. 4.42; N. 4.13. Found: C. 70.41; H. 4.56; N. 4.28.

Synthesis of 34. From 0.32 g of **30**. Method A: a 1:1 mixture of (*S**,*R**) and (*R**,*R**) isomers of **34** were obtained. Upon separation by flash chromatography (hexane/EtOAc 4:1), 0.02 g (20%) of **34 α** and 0.02 g (22%) of **34 β** were obtained, both as colorless oils. Method B: 0.03 g (30%) **34 α** and 0.03 g (35%) of **34 β** .

(3a*S,5*R**)-5-(*tert*-Butyldimethylsilyloxy)-3,3a,4,5-tetrahydro-6*H*-ciclopenta[*c*]carbazol-2-one, 34 α .** 1H -NMR ($CDCl_3$) 0.22 (s, 3H), 0.29 (s, 3H), 1.00 (s, 9H), 1.83 (dd, 1H, $J_1 = 12.6$ Hz, $J_2 = 12.6$ Hz), 2.23 (d 1H, $J = 17.6$ Hz), 2.50-2.60 (m, 1H), 2.69 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 6.6$ Hz), 3.18-3.27 (m, 1H), 5.21-5.26 (m, 1H), 6.30 (s, 1H); 7.27-7.31 (m, 2H), 7.44 (d, 1H, $J = 6.6$ Hz), 7.71 (d, 1H, $J = 6.6$ Hz), 8.51 (bs, 1H). ^{13}C -NMR ($DMSO-d_6$) 206.1, 170.2, 146.7, 137.1, 124.2, 122.7, 121.3, 119.8, 117.1, 112.7, 107.3, 66.4, 40.4, 38.8, 26.0, 25.8, 17.8, 15.1, 14.9, -4.2, -4.8. IR (neat) 3470, 2910, 1690, 1620. Anal. Calcd. For $C_{21}H_{27}NO_2Si$: C. 71.34; H. 7.70; N. 3.96. Found: C. 71.22; H. 7.55; N. 4.10.

(3a*R,5*R**)-5-(*tert*-Butyldimethylsilyloxy)-3,3a,4,5-tetrahydro-6*H*-ciclopenta[*c*]carbazol-2-one, 34 β .** 1H -NMR ($CDCl_3$) 0.20 (s, 3H), 0.23 (s, 3H), 0.91 (s, 9H), 2.00 (dd, 1H, $J_1 = 25.3$ Hz, $J_2 = 11.5$ Hz), 2.19 (dd 1H, $J_1 = 18.1$ Hz, $J_2 = 2.2$ Hz), 2.34 (d, 1H, $J = 11.5$ Hz), 2.71 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 6.6$ Hz), 3.62-3.69 (m, 1H), 5.05 (s, 1H), 6.36 (s, 1H); 7.27-7.31 (m, 2H), 7.45 (d, 1H, $J = 7.7$ Hz), 7.75 (d, 1H, $J = 6.6$ Hz), 8.38 (bs, 1H). ^{13}C -NMR ($DMSO-d_6$) 206.2, 170.2, 147.9, 136.8, 123.9, 123.1, 121.4, 120.1, 118.1, 112.5, 107.7, 62.5, 34.2, 25.9, 17.7, 15.4, 15.0, -4.2, -4.7. IR (neat) 3470, 2910, 1690, 1620. Anal. Calcd. For $C_{21}H_{27}NO_2Si$: C. 71.34; H. 7.70; N. 3.96. Found: C. 71.20; H. 7.53; N. 4.05.

(3a*S,4*R**)-4-(*tert*-Butyldimethylsilyloxy)-5-methyl-3,3a,4,5-tetrahydropentalen[5,4-*b*]indol-2-one, 35.** Method B: From 0.32 g of **31** and after purification by flash chromatography (hexane/EtOAc 4:1), 0.15 g (40%) of **35** as a white solid m.p.: 179-180°C (hexane/AcOEt). 1H -NMR ($CDCl_3$) 0.21 (s, 3H), 0.25 (s, 3H), 0.98 (s, 9H), 2.55 (dd, 1H, $J_1 = 16.5$ Hz, $J_2 = 6.1$ Hz), 2.74 (dd, 1H, $J_1 = 16.5$ Hz, $J_2 = 7.1$ Hz), 3.83 (s, 3H), 3.86-3.92 (m, 1H), 5.28 (d, 1H, $J = 4.4$ Hz), 5.86 (d, 1H, $J = 1.6$ Hz), 7.26-7.38

(m, 3H), 7.69 (d, 1H, $J = 7.7$ Hz). ^{13}C -NMR (CDCl_3) 207.2, 171.9, 155.2, 142.9, 123.5, 122.0, 121.3, 120.6, 155.5, 112.5, 110.5, 73.7, 61.3, 40.7, 30.5, 25.7, 17.8, -3.8, -4.9. IR (KBr) 2940, 2860, 1690, 1610. Anal. Calcd. For $\text{C}_{21}\text{H}_{27}\text{NO}_2\text{Si}$: C. 71.34; H. 7.70; N. 3.96. Found: C. 71.49; H. 7.80; N. 4.87.

References

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